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Insertion Homo- and Copolymerization of Diallyl Ether

*Zhongbao Jian and Stefan Mecking**

Abstract: *The previously unresolved issue of polymerization of allyl monomers $CH_2{=}CHCH_2X$ is overcome by a palladium-catalyzed insertion polymerization of diallyl ether as a monomer. An enhanced 2,1-insertion of diallyl ether as compared to mono-allyl ether retards the formation of an unreactive five-membered cyclic O-chelate (after 1,2-insertion) that otherwise hinders further polymerization, and also enhances incorporation in ethylene polymers (20.4 mol %). Cyclic ether repeat units are formed selectively (96 %–99 %) by an intramolecular insertion of the second allyl moiety of the monomer. These features even enable a homopolymerization to yield polymers (poly-diallyl ether) with degrees of polymerization of $DP_n \approx 44$.*

Vinyl polymers are employed on a vast scale for a myriad of applications. Prominent examples are acrylate and methacrylate polymers, poly(vinyl chloride), or vinyl acetate homo- and copolymers. By contrast, a (co)polymerization of polar allyl monomers $CH_2{=}CHCH_2X$ has remained largely elusive.

A free-radical[1,2] or cationic[3] polymerization of allyl monomers is suppressed presumably by the formation of stable π-allyl radicals or cations, respectively, that retard or terminate the chain growth reaction. Recently, a coordination–insertion copolymerization of polar allyl monomer with ethylene has been found to be possible.[4] Various allyl monomers (for example X = OAc, OH, NR_2, Cl, acrylate) were copolymerized with ethylene using nickel or palladium catalysts.[5–7] Despite these significant achievements, the catalytic activities are limited and the allyl monomer incorporation is relatively low (0.1–7.9 mol %). The origin of these limitations remains unclear to date. We now report studies of diallyl ether insertion and polymerization reactivity that illuminate these issues and reveal an approach to overcome them, even allowing for an insertion homopolymerization.

Copolymerizations of allyl ethyl ether (AEE) and ethylene (E) were performed using the dianisyl phosphinesulfonato palladium catalyst precursor **1**, which is well-established for polar vinyl monomer insertion polymerizations.[8–10] Under pressure-reactor conditions, exposure of **1** to 5 bar of E and 0.1 M of AEE at 80 °C resulted in the formation of a copolymer with a low AEE incorporation of 0.8 mol % (Table 1, entry 1).[11] Increasing the concentration of AEE led to an increase of AEE incorporation in the copolymers along with a decrease in catalytic activity and molecular weight (Table 1, entries 2–5). However, the AEE incorporations were limited to only 4.0 mol %. These low incorporations agree with the polymerization behavior of other polar allyl monomers reported previously.[5c] With the aim of enhancing the co-monomer incorporation, a further allyl monomer acrolein diethyl acetal (ADEA)[12] was also tested in the copolymerization reaction (Table 1, entries 6 versus 3). However, the co-monomer incorporation almost remains unaltered.

Surprisingly, for diallyl ether (DAE) as a monomer under otherwise identical reaction conditions (0.1 M), catalytic activity and co-monomer incorporation in the reaction with E are enhanced versus AEE (Table 2, entry 1 versus Table 1, entry 1). As expected, at a given E pressure, the incorporation of DAE in the copolymers increases with increasing concentration of the co-monomer in the reaction mixture to reach 20.4 mol % at an initial concentration $[\mathrm{DAE}] = 1.2\ \mathrm{mol\,L^{-1}}$ (Table 2, entries 2–7). This high incorporation of electron-rich allyl monomer DAE matches with the most favorable electron-poor vinyl monomers such as acrylate reported to date.[9f,13,14] A lower temperature results in a decreased incorporation of DAE (Table 2, entries 8 and 9 vs. 3). Consistently throughout these copolymerization studies (Tables 1 and 2), not only catalytic activity (TOF_E and TOF_{DAE}) but also co-monomer incorporation of DAE are higher compared to the mono-allyl analogue AEE. Note that incorporations are given on the basis of molecules of DAE incorporated, that is, the amount of allyl moieties incorporated (see below) is twice as high owing to the difunctional character of DAE.

To account for these observations, polymer microstructures were analyzed. According to the quantitative ^{13}C NMR spectrum (Supporting Information, Figure S30), the E-AEE copolymer possesses a highly linear polyethylene backbone. AEE is incorporated primarily into the polymer main chain. Chain-end analysis indicates that AEE is incorporated into saturated initiating chain ends, but it is not detected in unsaturated terminating chain ends.[15] For the E-DAE copolymers, a richer variety of microstructure motifs results from the possible reaction pathways of the two allylic double bonds of the monomer. In principle, an incorporation of DAE can occur in a non-cyclic fashion (repeat unit **I**, arising from insertion into alkyls **2**, **5**, and **6** in Scheme 1) or yield cyclic structures (**II** from **4**; **III** from **3**, **7**; or **IV** from **8**). To illuminate the regio- and stereochemistry of the polymers, ethylene-d_4 and DAE were copolymerized with **1**.

The resulting copolymers feature ^1H NMR resonances at $\delta = 3.97$ and 3.42 (CH_2O), 1.80 (CH), 1.55 and 1.33 ppm (CH_2) with an integral ratio of ca. 2:1:2, arising from *trans*-**II** units (Figure 1). COSY and TOCSY2D experiments further confirm that these resonances at $\delta = 3.91$ and 3.50, 2.16, 1.45

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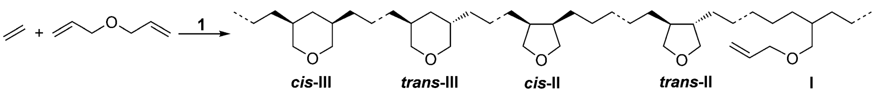
Table 1: Copolymerization of ethylene with allyl ether and acrolein diethyl acetal.[a]

Entry	Monomer	Conc. [mol L^{-1}]	t [h]	Yield [mg]	TOF[b] E	TOF[b] AEE	Incorp.[c] [mol%]	M_n[d] [g mol^{-1}]	M_w/M_n[d]	T_m[e] [°C]
1	AEE	0.1	2	160	140	1.1	0.8	3800	1.9	123
2	AEE	0.2	5	150	51	0.7	1.4	3700	1.8	120
3	AEE	0.3	7	180	43	1.0	2.3	3300	1.8	114
4	AEE	0.4	12	220	30	0.9	2.9	3000	1.8	109
5	AEE	0.6	17	180	17	0.7	4.0	2500	1.7	104
6	ADEA	0.3	4	120	49	1.0	2.1	3100	2.3	115

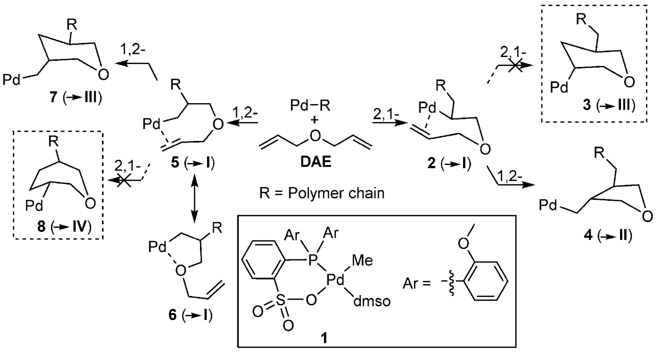
[a] Reaction conditions: toluene + monomer, 50 mL; 80 °C; catalyst precursor **1**, 20 µmol; ethylene, 5 bar; 1000 rpm; unless noted otherwise. [b] Units: mol mol_{Pd}^{-1} h^{-1}. [c] Determined by ^{1}H NMR spectroscopy in $C_2D_2Cl_4$ at 130 °C. [d] Determined by GPC in 1,2,4-trichlorobenzene at 160 °C versus linear polyethylene. [e] Determined by DSC.

Table 2: Copolymerization of ethylene with diallyl ether.[a]



Entry	Conc. [mol L^{-1}]	t [h]	Yield [mg]	TOF[b] E	TOF[b] DAE	Incorp.[c] [mol%]	Microstructure[c] [%] I	cis-II	trans-II	cis-III	trans-III	M_n[d] [g mol^{-1}]	M_w/M_n[d]	T_m[e] [°C]
1	0.1	1	290	479	11.3	2.3	1.2	3.9	68.9	11.3	14.7	5900	2.1	118
2	0.2	2.5	300	185	8.3	4.3	1.6	3.1	62.5	12.5	20.3	5500	2.1	111
3	0.3	4	300	108	7.5	6.5	1.8	3.4	60.4	13.2	21.2	4100	2.4	100
4	0.4	5.5	240	60	5.1	7.9	2.2	3.6	60.0	13.5	20.7	4000	2.1	95
5	0.6	7	180	32	4.1	11.4	2.4	3.9	59.7	13.5	20.5	3200	1.8	82
6	0.8	13	160	14	2.2	13.5	3.2	4.0	59.4	13.8	19.6	3100	1.8	76
7	1.2	16	190	11	2.8	20.4	3.6	5.5	56.5	12.6	21.8	2300	1.7	52
8[f]	0.3	16	55	6	0.1	2.3	0.9	5.8	82.6	4.4	6.3	3700	2.4	119
9[g]	0.3	7	130	28	1.6	5.5	0.8	3.6	66.6	12.0	17.0	4000	2.5	101
10[h]	0.6	7	840	207	2.7[i]	1.3[i]	–	–[17]	–	–	–	1800	1.8	121

[a] Reaction conditions: toluene + diallyl ether, 50 mL; 80 °C; catalyst precursor **1**, 20 µmol; ethylene, 5 bar; 1000 rpm; unless noted otherwise. [b] Units: mol mol_{Pd}^{-1} h^{-1}. [c] Determined by ^{1}H NMR spectroscopy in $C_2D_2Cl_4$ at 130 °C. [d] Determined by GPC in 1,2,4-trichlorobenzene at 160 °C versus linear polyethylene. [e] Determined by DSC. [f] Polymerization temperature: 30 °C. [g] Polymerization temperature: 60 °C. [h] Monomer: 2,5-dihydrofuran. [i] TOF and incorporation of 2,5-dihydrofuran, respectively.



Scheme 1. Possible microstructures after insertion of DAE into Pd–R.

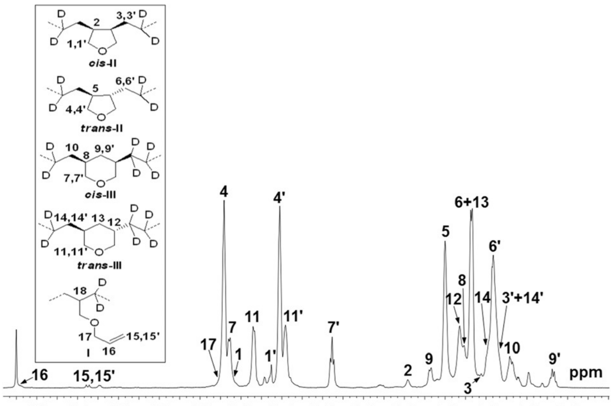
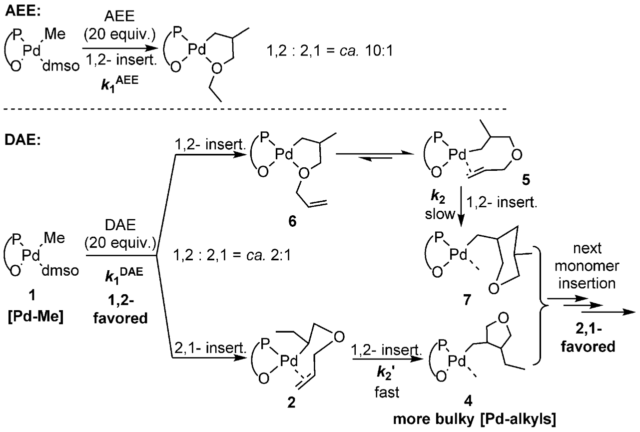


Figure 1. ^{1}H NMR spectrum (600 MHz, 120 °C, $C_2D_2Cl_4$) of an ethylene-d_4–DAE copolymer obtained with **1**.

and 1.28 ppm; 3.92 and 2.92, 1.62, 1.95 and 0.75, 1.17 ppm; 3.68 and 3.36, 1.66, 1.55, 1.39 and 1.29 ppm originate from *cis*-**II**, *cis*-**III**, and *trans*-**III**, respectively (Supporting Information, Figures S31–S37). The non-cyclic motif **I** gives rise to four identifiable multiplets at $\delta = 5.96$, 5.30 and 5.19, 3.99 ppm, respectively. Seven-membered cycles (**IV**) were not found.

1D and 2D NMR analyses of all E-DAE copolymers reveal a highly linear microstructure (ca. 1–2 methyl branches/1000 C) with cyclic and non-cyclic structures incorporated in the main chain (Supporting Information, Figures S38–S46). Notably, E-DAE copolymers with virtually exclusively cyclic units are accessible (96 %–99 %). That is, an initial insertion of DAE into the growing polymer chain is succeeded by an insertion of the second allylic double bond of the monomer (Scheme 1), rather than by an insertion of E. A similar scenario has been observed recently in the established acrylate copolymerization with **1**, using a di-vinyl monomer.[13]

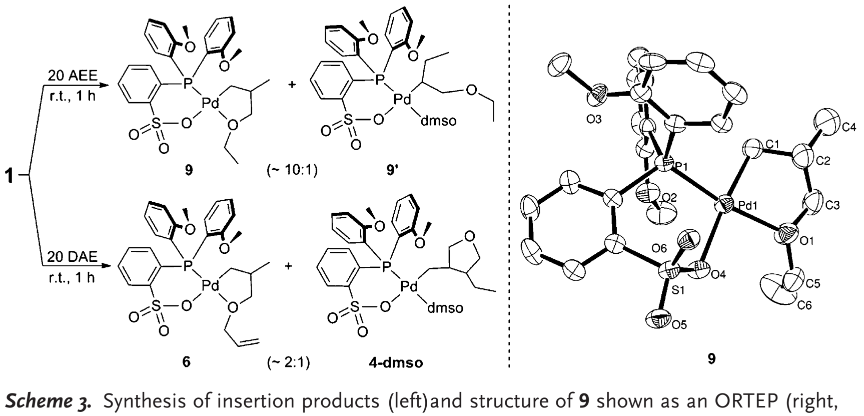
Within the cyclic motifs of E-DAE copolymers, the content of five-membered cyclic structure **II**, in which *trans*-**II** predominates, is circa twofold higher than that of the six-membered cyclic structure **III**.[16] Additionally, ATR-IR spectra of E-DAE copolymers feature characteristic bands at 1096 and 1047 cm^{-1}, 925 cm^{-1}, assigned to ν(C-O-C) of **III** and **II**, respectively (Supporting Information, Figure S53). The predominant cyclic repeat units **II** in the E-DAE copolymers resemble a copolymer of ethylene and 2,5-dihydrofuran. Probing such a copolymerization for comparison (entry 10 vs. entry 5 in Table 2), the incorporation of 2,5-dihydrofuran is low (1.3 mol %),[17] however, compared to 11.4 mol % for DAE (7.3 mol % for tetrahydrofuran structure **II**).



Scheme 2. Stoichiometric insertion studies.

The underlying insertion events were elucidated by stoichiometric NMR studies (Supporting Information, Figures S1–S4). Under pseudo first-order conditions (excess monomer, ca. 20 equiv), the insertion of AEE into the Pd–Me bond of **1** at 25 °C overwhelmingly yields the 1,2-insertion product (1,2:2,1 = ca. 10:1 within 1 h) with an observed rate constant (k_1^{AEE}) of 18.5×10^{-4} s^{-1} (Scheme 2). Note that, even over prolonged reaction times, no second insertion is detected, indicating that the first AEE 1.2-insertion product is very stable, which is due to chelating coordination of the ether oxygen atom (see below). Under otherwise identical conditions, the observed rate constant ($k_1^{DAE}=23.0\times10^{-4}$ s^{-1}) for the insertion of DAE into the Pd–Me bond of **1** is higher. However, unexpectedly, the preference for 1,2- over 2,1-insertion (Scheme 2, **6** vs. **2**) is strongly decreased to only ca. 2:1 as observed after ca. 1 h of reaction time. Owing to the presence of a stable five-membered *O*-chelate in the 1,2-product, the rate of intramolecular insertion of the remaining second double bond in **6** (to form **7**) is much slower than for the 2,1-insertion product **2** (to form **4**) ($k_2 \ll k_2'$; Supporting Information, Figures S3 and S23). Accordingly, over a prolonged time of ca. 17 h, the intensity of signals from 2,1-insertion products containing tetrahydrofuran structures (such as the tetrahydrofuran ring in **4**) increases gradually, and is higher than those from 1,2-insertion product (**6**) by a factor of ca 1.5 (Supporting Information, Figure S3). In a short conclusion based on kinetic experiments: 1) 1,2-insertion of DAE into the Pd-Me bond of **1** is preferred, but this preference is not very pronounced (1,2:2,1 = ca. 2:1) and much lower than that observed for AEE (1,2:2,1 = ca. 10:1); 2) after insertions, with the increase of bulk of Pd-alkyl bonds, 1,2-favored insertion of DAE gradually converts into 2,1-favored insertion; 3) therefore it appears reasonable that, for insertion of DAE into more bulky palladium–alkyl bonds (such as analogues of **4** and **7** in Scheme 2) during chain growth, 2,1-insertion can actually be favored. This mechanistic consideration based on kinetic experiments of DAE is consistent with the observed E-DAE copolymer microstructures, where the amount of tetrahydrofuran structures derived from 2,1-insertion of DAE into palladium–polyethylene growing chains (more bulky palladium–alkyl bonds) is higher than that of tetrahydropyran structures derived from 1,2-insertion of DAE (columns *cis*-II/*trans*-II versus *cis*-III/*trans*-III, Table 2).[18] The altered regioselectivity from 1,2- to 2,1- is crucial in the DAE polymerization, as it reduces the formation of chelated 1,2-product that seriously retards chain growth.

The key 1,2-insertion product **9** from the reaction of AEE with **1** (Scheme 3) could be isolated and fully characterized by NMR spectroscopy (**9**:**9′** = 10:1; Supporting Information, Figures S5–S9). The solid-state structure of **9**, as determined by single-crystal X-ray diffraction, unambiguously confirms the presence of a five-membered cyclic chelate (Scheme 3). As outlined, under otherwise identical conditions, the reaction of DAE with **1** gave products **6** (1,2-) and **4**-dmso (2,1-1,2-) in the ratio of ca. 2:1. To confirm their structures, the pyridine adducts **6**-pyridine and **4**-pyridine that are more easily analyzed owing to well-separated proton signals in the ^{1}H NMR spectrum were also generated. As shown in the

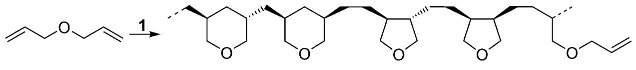


Scheme 3. Synthesis of insertion products (left)and structure of **9** shown as an ORTEP (right, ellipsoids set at 50 % probability with hydrogen atoms omitted for clarity).[19]

Supporting Information, Figures S10–S22, signals in 1D and 2D NMR spectra could be assigned to the different products.

These findings also suggested the possibility of a homopolymerization of allyl monomers. In a control experiment without added catalyst precursor or other initiators, DAE was found to be unreactive (Table 3, entry 1). In the presence of **1**, DAE homopolymers were formed with moderate activities (Table 3, entries 2–5).[20,21] Their microstructures essentially resemble those of the DAE repeat units in the aforementioned E-DAE copolymers (Supporting Information, Figure S25). Degrees of polymerization amounted to up to DP$_n$ ≈ 44 ($M_n = 4350\,\mathrm{g\,mol^{-1}}$) (Supporting Information, Figures S26–S29). Further control experiments essentially rule out a free-radical or cationic mechanism of chain growth (Table 3, entries 6 and 7). Such polymerizations occurred with much lower productivities to give lower molecular weight products ($M_n < 500\,\mathrm{g\,mol^{-1}}$) with a completely different microstructure (Supporting Information, Figure S25). By contrast to this insertion homopolymerization of diallyl ether monomer DAE, exposure of mono-allyl ether monomer AEE to **1** resulted in the formation of a much lower molecular weight product with DP$_n \approx 2$ with a low productivity (Table 3, entries 8 versus 2).

Table 3: Homopolymerization of diallyl ether.[a]



Entry	Cat.	Yield [mg]	TOF[b]	M_n[c] [g mol^{-1}]	M_w/M_n[c]
1	–	–	–	–	–
2	**1**	110	4.7	3660	1.3
3[d]	**1**	200	4.3	3970	1.4
4[e]	**1**	140	5.9	3970	1.4
5[f]	**1**	190	8.1	4350	1.7
6	AIBN	35	1.1	–	–
7	$[Ph_3C][B(C_6F_5)_4]$	50	3.2	–	–
8[g]	**1**	15	0.7	–	–

[a] Reaction conditions: toluene + monomer, 5 mL; 80 °C; 4 h; diallyl ether, 225 equiv; $[Ph_3C][B(C_6F_5)_4]$, 40 μmol or AIBN, 80 μmol or catalyst precursor **1**, 60 μmol; unless noted otherwise. [b] Units: mol mol$_{Pd}^{-1}$ h^{-1}. [c] Determined by GPC in THF at 40 °C versus linear polystyrene. [d] 8 h. [e] diallyl ether, 450 equiv [f] 95 °C. [g] Allyl ethyl ether: 225 equiv.

In summary, the utilization of diallyl ether as a monomer allows for a much enhanced incorporation of an allyl monomer in insertion copolymerizations. This overcomes the thus far relatively low incorporation of allyl co-monomers (and of electron-rich co-monomers in general). Even homopolymerizations are possible, which thus far are difficult for allyl monomers by any polymerization mechanism. This particular reactivity can be accounted for by an altered or even inverted regioselectivity of insertion for the $CH_2{=}CHCH_2OR$ allylic double bond of diallyl ether ($R = CH_2CH{=}CH_2$) versus other allyl ethers (such as R = Et). This disfavors the otherwise predominant 1,2-insertion pathway that leads to a stable and unreactive five-membered cyclic *O*-chelate with the ether oxygen atom of the inserted monomer unit binding to the metal center. A consecutive intramolecular insertion of the second allyl moiety of the monomer very selectively forms cyclic ether repeat units, with a clear preference for five-membered cyclic tetrahydrofuran motifs.

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[15] In the ethylene–vinyl ether copolymer, vinyl ether is also not detected at terminating chain ends. See Ref. [9b].

[16] *Trans* selectivity is preferred owing to the steric repulsion of two substituents on the rings (3,4 in a five-membered cyclic structure **II** and 3,5 in a six-membered cyclic structure **III**). Generally, the steric repulsion of 3,4-di-substituents is larger than that of 3,5-di-substituents. In reported ethylene–acrylic anhydride copolymers (see Ref. [13]), a preferred *trans* selectivity of 3,4-di-substituents in a five-membered cyclic structure was also observed and confirmed by a crystal structure of an analogue.

[17] The microstructure of the copolymer from the reaction of ethylene and 2,5-dihydrofuran is complex in that it contains 3,4-disubstituted (analogous to the five-membered cyclic structure **II**) as well as 2,3-disubstituted tetrahydrofuran motifs, and further unidentifiable structures.

[18] In the kinetic experiments, 1,2-insertion of DAE into the Pd−Me bond is preferred, but 2,1-insertion of DAE into more bulky palladium–alkyl bonds appears to be favored. In the copolymerization experiments, the insertion of DAE into the Pd−Me bond to form chain ends is only an initiating step, and the 2,1-insertion of DAE into palladium–polyethylene growing chains (more bulky palladium alkyls) to form in-chain five-membered cyclic structure **II** is the favored step.

[19] CCDC 1060855 (**9**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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[21] For cyclopolymerizations of nonfunctionalized dienes, see: a) G. W. Coates, R. M. Waymouth, *J. Am. Chem. Soc.* **1991**, *113*, 6270; b) X. Shi, Y. Wang, J. Liu, D. Cui, Y. Men, Y. Li, *Macromolecules* **2011**, *44*, 1062; c) K. E. Crawford, L. R. Sita, *J. Am. Chem. Soc.* **2013**, *135*, 8778; for reactions of functionalized 1,6-dienes catalyzed by α-diimine Pd^{II} catalysts, see: d) T. Okada, S. Park, D. Takeuchi, K. Osakada, *Angew. Chem. Int. Ed.* **2007**, *46*, 6141; *Angew. Chem.* **2007**, *119*, 6253; e) S. Park, D. Takeuchi, K. Osakada, *J. Am. Chem. Soc.* **2006**, *128*, 3510.

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