Fullerenes

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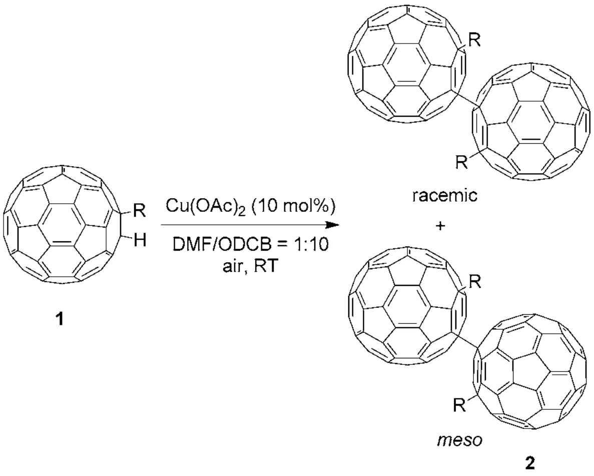
Highly Efficient Cu(OAc)$_2$-Catalyzed Dimerization of Monofunctionalized Hydrofullerenes Leading to Single-Bonded [60]Fullerene Dimers**

Shirong Lu, Tienan Jin, Eunsang Kwon, Ming Bao, and Yoshinori Yamamoto**

The single-bonded fullerene dimer $RC_{60}-C_{60}R$, which has a direct covalent bond between two C_{60} cages, is an interesting and unusual structure that is expected to display interesting optical and electronic properties through the interaction of two adjacent fullerene cages.[1] Since the pioneering work by Krusic and co-workers,[2] studies on ESR and X-ray crystal-structure analysis revealed that singly bonded fullerene dimers consist of racemic and *meso* isomers, which are in equilibrium with the monomer radical ($RC_{60}^{\bullet}$) in solution.[3] Some experimental and theoretical studies on these single-bonded fullerene dimers demonstrated that they were usually formed by dimerization of $RC_{60}^{\bullet}$ radicals, which were generated by various radical reactions;[4] for example, the photoirradiation of C_{60} with perfluoroalkyl iodides in the presence of $(R_3Sn)_2$,[3a] Mn(OAc)$_3$-mediated radical reaction of C_{60} with phosphonate esters[3c] or dialkyl malonates,[5a] and one-electron oxidation of the monoanion RC_{60}^{-} by oxidants.[3b,5b–d] However, their application to the elaborated fullerene dimers is generally limited by low functional-group tolerance, low yield, and the use of large excess amounts of reagents. Functionalization of fullerene by transition-metal catalysis has recently been considered to be a promising and innovative strategy in fullerene chemistry, which offers advantages for high chemical yield, selectivity control, and high functional-group compatibility under mild reaction conditions.[6] However, examples of catalytic dimerization for the synthesis of single-bonded fullerene dimers have never been reported.[6f]

Recently, we developed the cobalt-catalyzed hydroalkylation of C_{60} with active alkyl bromides at ambient temperature to give monoalkylated hydrofullerenes in good to high yields.[7] Our interest in catalytic C–H bond activation led us to consider the possibility of catalytic C–H bond functionalization of the monosubstituted hydrofullerenes toward the construction of fullerene dimers.[8] A study by Komatsu and co-workers revealed that $RC_{60}^{\bullet}$ could be formed from fullerenyl radical cation ($RHC_{60}^{\bullet+}$), which in turn was generated from monofunctionalized hydrofullerene by one-electron oxidation in sulfuric and sulfonic acids.[9] In addition, Yu and co-workers reported the Cu^{II}-catalyzed aryl C–H bond functionalization by using O_2;[10] the reaction was proposed to proceed through the formation of an aryl radical cation ($Ar^{\bullet+}$) species by one electron transfer from the aryl ring to the Cu^{II} catalyst followed by formation of an aryl radical ($Ar^{\bullet}$). Taking these results into consideration, we turned our attention to metal oxidants as catalysts. Herein, we report a novel and efficient Cu(OAc)$_2$-catalyzed homo-dimerization of various monofunctionalized hydrofullerenes that affords the single-bonded fullerene dimers **2** as a mixture of racemic and *meso* isomers in excellent yields in the presence of a small amount of dimethylformamide (DMF) at room temperature under air [Eq. (1); ODCB = 1,2-dichlorobenzene]. Notably, the cross-dimers **3** (see below) were prepared for the first time through cross-dimerization of two different hydrofullerenes.



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[*] Prof. Dr. T. Jin, Prof. Dr. Y. Yamamoto
WPI Advanced Institute for Materials Research (WPI-AIMR)
Tohoku University, Sendai 980-8577 (Japan)
E-mail: tjin@m.tohoku.ac.jp
yoshi@m.tohoku.ac.jp
Homepage: http://www.wpi-aimr.tohoku.ac.jp/~yamamoto/
S. Lu
Department of Chemistry, Graduate School of Science
Tohoku University (Japan)
and
State Key Laboratory of Fine Chemicals
Dalian University of Technology (China)
Dr. E. Kwon
Research and Analytical Center for Giant Molecules
Graduate School of Science, Tohoku University (Japan)
Prof. Dr. M. Bao
State Key Laboratory of Fine Chemicals
Dalian University of Technology (China)

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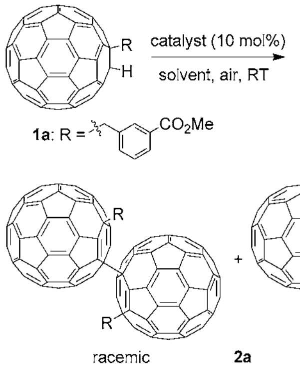
We initiated this unprecedented but highly promising catalytic dimerization by examining solvents and catalysts at room temperature under air. The yields in Table 1 were determined by HPLC analysis using C_{60} as an internal standard. Homo-dimerization of the monofunctionalized hydrofullerene **1a**[7] in the presence of $Cu(OAc)_2$ (10 mol%) by using ODCB as a sole solvent afforded only trace amounts of the corresponding dimer **2a**, and **1a** was recovered almost quantitatively (Table 1, entry 1). The remarkable enhancement of efficiency on addition of organometal reagents to C_{60} by adding pyridine or DMF reported by the Nakamura group[11] led us to examine polar solvents mixed with ODCB. The addition of 1,4-dioxane did not affect the yield of **2a**, whereas the use of tetrahydrofuran afforded **2a** in 20% yield (Table 1, entries 2 and 3). We further examined more-polar additives. To our delight, the addition of CH_3CN or DMF improved the yields of **2a** to 92% and 94%, respectively, within 4 h (Table 1, entries 4 and 5). A decrease of the amount of DMF resulted in slightly increased yield (Table 1, entry 6).

Table 1: Screening of catalysts and solvents for the homo-dimerization of monofunctionalized [60]hydrofullerenes.[a]



Entry	Catalyst	Solvent (1:3)	*t* [h]	**2a** [%][b]	**1a** [%][b]
1	$Cu(OAc)_2$	ODCB	24	trace	97
2	$Cu(OAc)_2$	1,4-dioxane/ODCB	24	trace	96
3	$Cu(OAc)_2$	THF/ODCB	24	20	78
4	$Cu(OAc)_2$	CH_3CN/ODCB	4	92	4
5	$Cu(OAc)_2$	DMF/ODCB	4	94	4
6	$Cu(OAc)_2$	DMF/ODCB (1:10)	4	97 (92)	2
7[c]	$Cu(OAc)_2$	DMF/ODCB	4	14	84
8[c,d]	$Cu(OAc)_2$	DMF/ODCB	2	93	2
9	$Cu(OCH_3)_2$	CH_3CN/ODCB	48	66	25
10	AgOAc	CH_3CN/ODCB	48	81	13
11	$CuCl_2$	CH_3CN/ODCB	48	trace	96
12	$Cu(OTf)_2$	CH_3CN/ODCB	48	0	94
13	$Au(OAc)_3$	CH_3CN/ODCB	48	86	11
14	$Pd(OAc)_2$	CH_3CN/ODCB	48	12	85
15	$Ni(OAc)_2$	CH_3CN/ODCB	48	20	78
16	$Zn(OAc)_2$	CH_3CN/ODCB	24	0	98
17	$Mn(OAc)_3$	CH_3CN/ODCB	24	14	82
18	none	CH_3CN/ODCB	24	0	99

[a] Conditions: The catalyst (10 mol%) was added to a solution (10 mL) of **1a** (0.1 mmol) and additives in ODCB under air. The resulting mixture was stirred at room temperature for the times shown. [b] Yields determined by HPLC by using C_{60} as an internal standard. Yield of product isolated by silica-gel chromatography is shown in parentheses. [c] Reaction was conducted under argon atmosphere. [d] 1.0 equivalent of $Cu(OAc)_2$ was used.

It should be noted that, in the absence of air, the present reaction produced the corresponding dimer **2a** in only 14% yield under a catalytic amount of $Cu(OAc)_2$ (Table 1, entry 7). This result indicates that air has an important role, which is indispensable for achieving high catalytic activity. Moreover, recent studies on the formation of the single-bonded fullerene dimers show that the fullerene radical ($R^1C_{60}^{\bullet}$) is almost certainly a key intermediate, which can be formed from the corresponding fullerene anion ($R^1C_{60}^{-}$) by O_2 or I_2 oxidant.[3b,5b–d] If this is the case, the fact that a stoichiometric amount of $Cu(OAc)_2$ affords **2a** in 93% yield in the absence of air means that $Cu(OAc)_2$ can generate $R^1C_{60}^{\bullet}$ under the present solvent systems (Table 1, entry 8). To gain further insight into the role of the metal oxidant, we examined various metal catalysts. Other coinage-metal catalysts with lower acidity than $Cu(OAc)_2$, such as $Cu(OMe)_2$ and AgOAc, are also active, but the yields are lower than that with $Cu(OAc)_2$ and longer reaction times are needed (Table 1, entries 9 and 10). Lewis acidic metal catalysts, such as $CuCl_2$ and $Cu(OTf)_2$, are totally inactive, although $Au(OAc)_3$ showed good catalytic activity notwithstanding its higher acidity (Table 1, entries 11–13). In contrast, several other transition-metal acetates, such as $Pd(OAc)_2$, $Ni(OAc)_2$, $Zn(OAc)_2$, and $Mn(OAc)_3$, are less active or completely ineffective (Table 1, entries 14–17). It is clear that the reaction did not proceed without metal catalysts (Table 1, entry 18). In addition, under optimized conditions (10 mol% of $Cu(OAc)_2$ in a 1:10 mixture of DMF and ODCB at room temperature under air for 4 h), the reaction proceeded with similar efficiency on a one-gram scale, giving **2a** in 90% yield.

The structure for the *meso* isomer of **2a** was unambiguously confirmed by single-crystal X-ray diffraction analysis (Figure 1).[12] A crystal of the *meso* isomer was grown as the predominant component in $CHCl_3/CS_2$ at −15 °C from a mixture of *meso* and racemic products. The fullerene–fullerene C−C bond (1.53(2) Å) is slightly shorter than the reported one.[3b,c] The UV/Vis spectrum of **2a** in chloroform showed a broad absorption band at 445 nm, which is red-shifted relative to that of the corresponding hydrofullerene **1a** (433 nm). The cyclic voltammogram (CV) of **2a** in ODCB

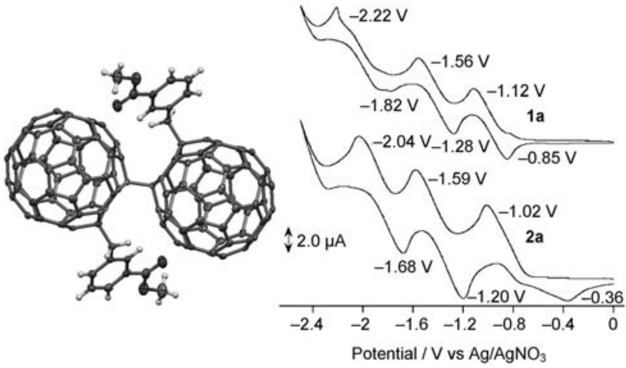


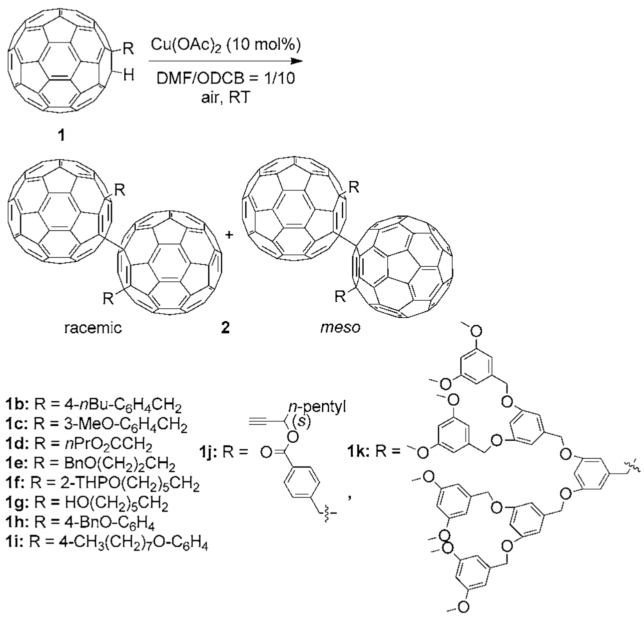
Figure 1. ORTEP of the *meso* isomer of **2a** and CVs of **1a** and **2a** in ODCB.

exhibited three reversible waves on reduction, which would correspond to the formation of monoanion, dianon, and trianion of its monomer (Figure 1).[3b] The different values between dimer **2a** and monomer **1a** on half-wave potentials ($E_{1/2}^{\mathrm{red}}$) clearly indicate the electronic interaction between the two C_{60} cages of **2a**.

The present $Cu(OAc)_2$-catalyzed dimerization of monosubstituted hydrofullerenes **1** showed high compatibility with a variety of functional groups, producing the corresponding single-bonded dimers **2** in very high yields (Table 2; THP = tetrahydropyranyl). All of the reactions were monitored by TLC and HPLC analysis, and the corresponding dimers **2** were isolated by silica gel column chromatography as a mixture of *meso* and racemic isomers. In each case, a very small amount of recovered **1** and unidentified products was observed, but these impurities could be removed by silica gel column chromatography. An *n*-Butyl (**1b**) or a methoxy group (**1c**) on the benzene ring of monobenzyl-substituted hydrofullerenes was tolerated, affording the corresponding dimers **2b,c** in excellent yields (Table 2, entries 1 and 2).[7] It is noteworthy that hydrofullerene **1j** with a propargyl ester group on the benzyl moiety produced the desired dimer **2j** in 91% yield without the formation of any conjugated diynes generated from the Glaser reaction (Table 2, entry 9).[13] Alkyl-substituted hydrofullerenes with an ester group (**1d**)[7] as well as benzyl- and THP-protected alcohols (**1e** and **1f**) are also active substrates, producing the corresponding dimers **2d–f** in high yields, whereas hydrofullerene **1g** with an unprotected hydroxy group showed a lower activity, giving **2g** in 70% yield in the presence of 30 mol% of $Cu(OAc)_2$ catalyst under longer reaction times (24 h) (Table 2, entries 3–6). The reaction also proceeded well with hydrofullerenes with a benzene ring substituted directly to the C_{60} moiety, giving **2h** and **2i** in 81% and 84% yield, respectively (Table 2, entries 7 and 8). The present copper catalysis was applied to the construction of a fullerene-bound macromolecule, which may be useful for versatile electronic materials. For example, under the standard conditions, the fullerene-bound dendrimer **1k** afforded the corresponding dendritic dimer **2k** in 79% yield (Table 2, entry 10).[7] It should be mentioned that the prepared dimers, except for **2d** and **2h**, showed good solubility in toluene and ODCB. In particular, the dendritic dimer **2k** exhibited dramatically improved solubility in various organic solvents.

This method also provides an interesting opportunity for the synthesis of novel cross-dimers containing two different functionalized C_{60} units (Table 3). Under the standard conditions, cross-dimerization of two different hydrofullerenes **1a** and **1f** proceeded smoothly to produce the desired cross-dimer **3a** in 31% yield together with the two homodimers **2a** and **2f** in 26% and 30% yield, respectively (Table 3, entry 1). Cross-dimer **3a** was speculated to consist of four isomers according to the four possible kinds of monoradicals (Figure 2),[3b,c] although the individual isomers cannot be completely identified from ^1H NMR spectra and HPLC analysis. Similarly, cross-dimerizations of **1a** and **1e**, as well as **1e** and **1f**, afforded the cross-dimers **3b** and **3c**, respectively, in similar yields together with the corresponding homodimers (Table 3, entries 2 and 3). All products were isolated by silica gel chromatography. Interestingly, the cross-dimers **3** are in equilibrium with homodimers **2** in solution. For example, monitoring by ^1H NMR spectroscopy showed that the pure

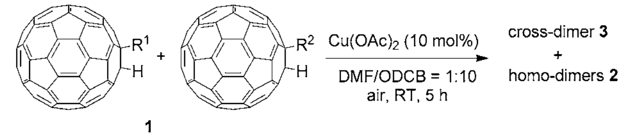
Table 2: $Cu(OAc)_2$-catalyzed homo-dimerization of monosubstituted hydrofullerenes.[a]



Entry	1	*t* [h]	2	Yield 2 [%][b]	Yield 1 [%][b]
1	**1b**	4	**2b**	90	2
2	**1c**	4	**2c**	96	trace
3	**1d**	4	**2d**	88	2
4	**1e**	4	**2e**	90	trace
5	**1f**	4	**2f**	94	3
6[c]	**1g**	24	**2g**	70	3
7	**1h**	5	**2h**	81	trace
8	**1i**	5.5	**2i**	84	2
9	**1j**	4.5	**2j**	91	trace
10	**1k**	5	**2k**	79	trace

[a] Conditions: $Cu(OAc)_2$ (10 mol%) was added to a solution of **1** (0.1 mmol) and DMF (1 mL) in ODCB (10 mL) under air. The resulting mixture was stirred at room temperature for the times shown. [b] Yields of isolated product. [c] 30 mol% of $Cu(OAc)_2$ was used.

Table 3: $Cu(OAc)_2$-catalyzed cross-dimerization.[a]



Entry	1 (R¹)	1 (R²)	Homo-dimer 2 [%][b]	Cross-dimer 3 [%][b]
1	**1a**	**1f**	26 (**2a**); 30 (**2f**)	31 (**3a**)
2	**1a**	**1e**	25 (**2a**); 31 (**2e**)	32 (**3b**)
3	**1e**	**1f**	29 (**2e**); 31 (**2f**)	33 (**3c**)

[a] Conditions: To a solution of two different hydrofullerenes **1** (0.1 mmol) and DMF (1 mL) in 1,2-dichlorobenzene (ODCB, 10 mL) under an air atmosphere was added $Cu(OAc)_2$ (10 mol%). The resulting mixture was stirred at room temperature for 5 h. [b] Dimers **2** and **3** were isolated by silica-gel chromatography.

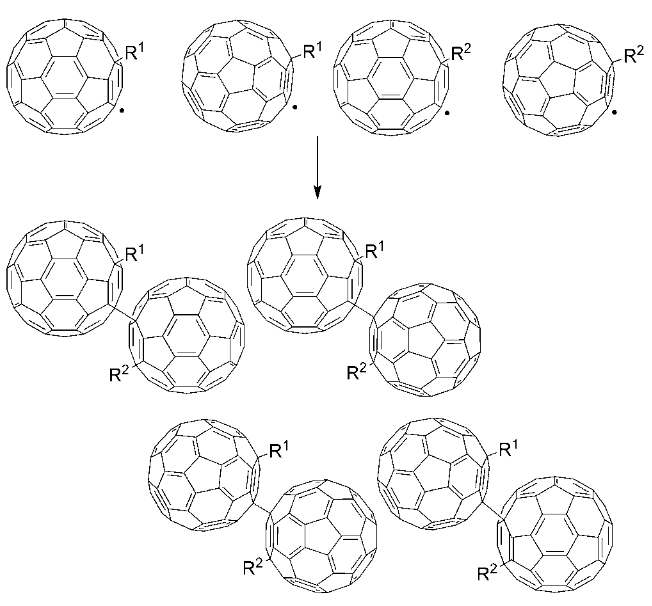
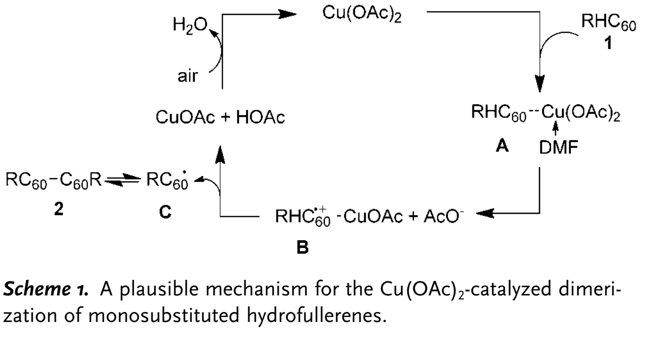


Figure 2. Four plausible isomers of cross-dimers **3** speculated from their four different radical monomers.

dimer **3a** was gradually converted into **2a** and **2f** in $CDCl_3$/CS_2 at ambient temperature and reached equilibrium after 12 h, although this interconversion rate between the cross-dimer and homodimers was slow enough to identify its ^1H and ^{13}C NMR spectra. Furthermore, **3a** was obtained by mixing of the two homodimers **2a** and **2f** in $CDCl_3$/CS_2 at ambient temperature through similar interconversion. In sharp contrast, **3a** is very stable in the solid state; it can be stored for several months at ambient temperature without any structural changes. The single-bonded dimers dissociate to the stable monoradicals in solution, followed by recombination of the resulting monoradicals to form various dimers, which was in good agreement with the previous studies reported by the groups of Komatsu and Wang.[3b,c] This interconversion provides an alternative approach for the construction of cross-dimers from various homodimers in solution.

A plausible mechanism for the present catalytic dimerization based on our experimental observations, as well as works on the generation of radical cation species by the groups of Komatsu[9] and Yu,[10] is shown in Scheme 1. Initially, the one-electron oxidation of hydrofullerene **1** takes place through the single-electron transfer from the C_{60} moiety to $Cu(OAc)_2$, leading to radical cation **B**. We assume that coordination of $Cu(OAc)_2$ to the C_{60} moiety to form intermediate **A** may accelerate the one-electron oxidation, wherein polar solvents such as DMF and CH_3CN stabilize **A**. Elimination of a proton on the radical cation **B** by the acetate anion forms the monoradical **C**, which produces the corresponding single-bonded dimers. Dimerization of two monoradicals with *R* and *S* configuration gives the *meso* isomer (*R*–*S*), whereas dimerization of two monoradicals with the same configuration affords a racemic mixture of *R*–*R* and *S*–*S* isomers.[3c] We also speculate that polar solvents stabilize the radical cation **B** to assist the subsequent release of the proton. Finally, the $Cu(OAc)_2$ catalyst is regenerated by oxidation of CuOAc under an air atmosphere and in the presence of acetic acid.



Scheme 1. A plausible mechanism for the $Cu(OAc)_2$-catalyzed dimerization of monosubstituted hydrofullerenes.

In conclusion, we have demonstrated for the first time that single-bonded fullerene dimers can be synthesized in excellent yields through the catalytic dimerization of monosubstituted hydrofullerenes. A wide range of functional groups are tolerated. In contrast to the previously reported methods, the present catalytic reaction can be carried out under very mild conditions with remarkably higher yields. Fullerene-bound dendritic homodimers and various cross-dimers, which are otherwise difficult to obtain, were synthesized in good to high yields for the first time. The present catalytic dimerization of monosubstituted hydrofullerenes seems to proceed through $Cu(OAc)_2$-catalyzed generation of a fullerenyl radical cation species followed by formation of a fullerenyl radical. The $Cu(OAc)_2$ catalyst combined with a small amount of DMF under air is crucial for the efficient formation of the corresponding single-bonded fullerene dimers. Investigation on further catalytic functionalization of fullerenes and application to materials science are in progress.

Experimental Section

2a: To a solution of **1a** (87 mg, 0.1 mmol) in DMF and ODCB (1:10, 11 mL) was added $Cu(OAc)_2$ (1.8 mg, 0.01 mmol) at room temperature under air. The reaction mixture was stirred at room temperature for 4 h. The reaction was monitored by HPLC analysis (elution with toluene at 0.6 $mL\,min^{-1}$ flow rate, detection at 320 nm). The mixture was subjected directly with silica gel chromatography (toluene/hexane = 1:1). A solution of **2a** in toluene and hexane was evaporated at below 60 °C, and the residue was washed with acetone to afford **2a** in 92 % yield (80 mg).

3a: To a solution of **1a** (44 mg, 0.05 mmol) and **1f** (46 mg, 0.05 mmol) in DMF and ODCB (1:10, 11 mL) was added $Cu(OAc)_2$ (1.8 mg, 0.01 mmol) at room temperature under air. The reaction mixture was stirred at room temperature for 5 h. The reaction was monitored by HPLC analysis (elution with toluene at 0.6 $mL\,min^{-1}$ flow rate, detection at 320 nm). The mixture was subjected directly with silica gel chromatography using toluene as an eluent. Product **2a** was isolated as the first fragment, followed by **3a** and **2f**. A solution of **3a** in toluene was evaporated at below 60 °C, and the residue was washed with acetone to remove the remaining toluene, affording **3a** in 31 % yield (28 mg). Similarly, **2a** and **2f** were obtained in 26 % (23 mg) and 30 % (26 mg) yield, respectively, after evaporation of toluene and washing with acetone.

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[12] CCDC 846755 (*meso* isomer of **2a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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