Using ruthenium-catalysed propargylic substitutions for the efficient syntheses of rotaxanes

著者	TOKUNAGA Yuji, KAWAI Nobuhiko, SHIMOMURA Youji
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**Using ruthenium-catalysed propargylic substitutions
for the Efficient synthesis syntheses of various rotaxanes via
ruthenium-catalysed propargylic substitution reactions**

Yuji Tokunaga,* Nobuhiko Kawai and Youji Shimomura

*Department of Materials Science and Engineering, Faculty of Engineering, University of Fukui,
Fukui, 910-8507, Japan*

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* Corresponding author. Tel/fax: +81-776-27-8611; e-mail: tokunaga@matse.fukui-u.ac.jp

Abstract—An This paper describes an efficient method—one that takes advantage of hydrogen bond-guided self-assembly and ruthenium-catalysed propargylic substitution—for the preparation of various rotaxanes, involving hydrogen bonding guided self-assembly and ruthenium-catalysed propargylic substitution reaction, is described. The substitution reactions of a pseudorotaxane with a diverse range of heteroatom-centred and carbon atom-centred nucleophiles is were catalysed by the [(Cp*)RuCl(SMe)]₂ complex and to furnish the expected rotaxanes in good yields.

Rotaxanes, are a mechanically interlocked molecules, comprises comprising a dumbbell-like component and a macrocycle.¹ Because To take advantage of rotaxanes' their unique structures and properties, many methods of for synthesissynthesising rotaxanes have been developed in recent years, including clipping synthesis,² end-capping method,³ slipping-of-ring approach,⁴ the method throughmodification of [1]rotaxanes,⁵ end-closing process,⁶ and a shrinking strategy.⁷ strategies. The potential activities of rRotaxanes have encouraged potential applicability as components the design ofwithin molecular machines and devices.¹ The Because the types of selection of functional groups introduced present in to rotaxanes is important considering optimization can affect their physicalof their properties. , it is desirable to devise From a viewpoint of optimization of the properties of rotaxanes, it is desirable to develop a synthetic methods by so thatwhich rotaxanes with possessing a variety of functionalities can can be derived from a common intermediate.

The majority of rotaxane syntheses reported previously have each relied upon the use of one a single type sort of reaction. ThereforeIn addition,, modifications several of rotaxanes, end--capping or and clipping approaches towards rotaxanes along have been performed with subsequent stopper-modification, but these methods have also utilised only one type of reactionhave been reported recently. Stoddart Transformation described the transformation of phosphonium groups as an introducedtemporary stopper part units of the axle end into bulky alkenes by through the Wittig reactions was accomplished by Stoddart.⁸ Leigh developed a new strategy based on the replacement of a mechanically interlocking interlocked auxiliary via through transesterification.⁹ Kihara and Takata also exchanged a stopper part moiety through the use of a Tsuji—Trost allylation reaction.¹⁰ However, these methods have been able to accept only one type of reaction. Therefore, weWe developed developed an efficient method for rotaxane preparation using acetylene—dicobalthexacarbonyl complexation as a primary initial step of an end-capping approach towards rotaxanes and with several the subsequent stopper-modifications, of rotaxane.¹¹ The methodology can accept some reactions, such as Pauson—Khand reaction and Nicholas reactions. HoweverAlthough robust, the this methodology presents has the disadvantages that (a) not every substrate can is be applicable to all each modification reactions, and that (b) the methodit also requires two steps to construct and modify the a rotaxane.

Nishibayashi and co-workers have developed a range of ruthenium-catalysed substitution reactions of propargylic alcohols with various nucleophiles, including alcohols, amines and, amide, sand so on.¹² These reactions might mainly proceed via ruthenium—allenylidene complexes as intermediates formed from the catalyst and the propargylic alcohol, ; subsequently, and the nucleophiles regioselectively regioselectively attack the reactive C₈ atom in the intermediate. Here, we describe a novel method for end-capping method of pseudorotaxanes (prepared using the established¹³ self-assembled secondary ammonium ion/crown ether synthon) based on the ruthenium-catalysed propargylic substitution reactions with different various nucleophiles and a the direct introduction of various functionalities (Figure 1), using established self-assembled synthons, secondary ammonium ion and crown ether.¹³

Figure 1

The preparation of a the key secondary ammonium salt¹¹ **2**•PF₆¹¹ is was initiated by through condensation of the aldehyde **1** and 3,5-dimethylbenzylamine to afford the corresponding imine. Reduction of the imine, followed by salt formation, produces produced the ammonium salt **2**•PF₆, which has possessed a bulky aryl group on one end and a propargyl alcohol moiety at the other. The feasibility of performing ruthenium-catalysed nucleophilic substitution reactions of with the pseudorotaxane consisting formed from of the ammonium ion **2**•PF₆² and dibenzo[24]crown8 (DB24C8) is was validated though an initial experiment using carbazole as a the nucleophile in and dichloroethane as the solvent. The We isolated the corresponding rotaxane **3a** is afforded in good yield, even though the ammonium salt **2**•PF₆ was is insoluble in dichloroethane in the absence of the crown ether. ; i.e., **2**•PF₆ isThe solubility solubilised of the reactant is likely to be improved bythrough complexation of with DB24C8; and the catalyst reacts predominantly to with the soluble solvated pseudorotaxane. Preparation The preparation of **3a** shows suggests that (a) the interaction between the DB24C8 moiety and the secondary ammonium groups is strong under the reaction conditions, and that (b) the carbazole group is sufficiently bulky to prevent unthreading dissociation of the components (Scheme 1). The structure of **3a** was determined from its spectroscopic and analytical data. Especially,The ¹H NMR spectrum of **3a** (Figure 2) suggested that it had a the rotaxane structure of **3a** as shown in Figure 2. The most characteristic evidence for the formation of the rotaxane was is the large downfield shifts of the signals for the benzylic protons signals (δ 4.3 and 4.6 ppm). The shifts are consistent with those reported previously for related the ammonium ion/DB24C8 complexes.^{3,6,8,10,11,13} Moreover, the signals of the methylene protons signals of the crown ether part moiety split were split into more thanseveral two sets of resonances because of the diastereotopicity induced by due to the loss oft planar symmetry and the presence of the chiral

centre at the carbazole terminus; as expected, of DB24C8 and the low rotation rate of DB24C8 around the axle part of rotaxane, and these signals did not merge coalesce at temperatures below 125 °C in DMSO-*d*₆. The FAB mass spectrum of **3a** mass experiments also supported the rotaxane structure, represented by a peak MS (FAB) spectrum of **3a** displayed for the [M – PF₆]⁺ ion peak (at *m/z* 877).¹⁴

Scheme 1

Figure 2

Next, we attempted to optimal optimize the conditions for this transformation were examined. DiminishingDecreasing an the amount of carbazole decreases decreased the rotaxane yield (Table 1, entries 1–3,). Interestingly, decreasing and the amount of DB24C8 for 4 to 2 equiv. has a minor impact on the chemical yields using more than two equivalents relative to the to ammonium salt **2**·PF₆ (cf. entries 1 and 4) had a significant impact, presumably because . Because ammonium ion (NH₄⁺) ions, which we added is generated by ammonium hexafluorophosphate into the reaction mixture as a co-catalyst (see below), seems to competed with the secondary ammonium ion from **2**⁺PF₆ ion for the complexation of with DB24C8, ; i.e., using a greater excess of DB24C8 might ensured complete complexation of **2**·PF₆ and improved the yield. Low A lower temperature (cf. entries 1 and 5) and a longer reaction times (cf. entries 1 and 6) both slightly decreased the yields of the rotaxane slightly (entries 5 and 6). On the other hand,The presence of NH₄PF₆ is was necessary for to achievement achieve an of excellent yield (cf. entry entries 1 and 7). Nishibayashi reported that the addition of ammonium tetrafluoroborate (NH₄BF₄), which might affords a cationic thiolate-bridged diruthenium complex with a vacant site in after exchange of anions between the catalyst and NH₄BF₄, which improved improves the catalytic activity.^{12e} In our case, because we already had hexafluorophosphate anion (PF₆[–]) anions was usedpresent as a counter anions of the ammonium ions **2**. , we suspected Therefore, an anion of the catalyst canthat we might obtain a cationic thiolate-bridged diruthenium complex change from even in the absence of chloride to PF₆[–], and the catalyst can show similar activity without added NH₄PF₆ or NH₄BF₄. HoweverIn practice, however, the absence of NH₄PF₆ decreased the yield. It is likely that ion exchange of the chloride ion, from the ruthenium complex to the NH₂⁺ centre of the **2**⁺ ionwhich prefers an ion-pairing of the ammonium cation,¹⁵ obstructs disrupted the complexation of ammonium ionthe **2**⁺ ion with DB24C8 in the absence of NH₄PF₆.

Table 1

Table 2 portrays presents the results for the ruthenium-catalysed substitution reactions of we performed using different various nucleophiles in the presence to of the ammonium salt **2**·PF₆ in the presence of and DB24C8 crown ether. The reaction shows displayed good substrate generality. The A 2-substituted aniline derivative is was converted to the corresponding rotaxane **3b** in excellent yield (entry 2).), whereas However, thethe reaction of a 3,5-disubstituted aniline derivative affords afforded the its corresponding rotaxane **3c** in only moderate yield (entry 3). These results agree well with previous finings that Reportedly, thethe existence of electron-donating groups to on the aniline aromatic ring of aniline decreasedd the reaction rate on for the propargylic amination, whereas, and the introduction presence of the electron-withdrawing groups on the 2 and 4 positions of aniline improved improves the substitution reaction.^{12e} Good agreement exists between their previous results and ours. Sulphonamide A sulphonamide and an amide both reacted efficiently with the pseudorotaxane, and with the corresponding products rotaxanes **3d** and **3e** , respectively, are being isolated obtained, respectively, in 60% and 64% isolated yields, respectively (entries 4 and 5). We also investigated Propargylic the propargylic substitution reactions of the pseudorotaxane with carbon-- centred, sulphur--centred, and phosphorus-atom-centred nucleophiles were also investigated:, obtaining the rotaxanes **3f–3h** , respectively, are obtained in good or to moderate yields (entries 6–8, respectively). For the phosphine oxide, we performed the reaction carried out at low temperature, because to avoid the double phosphinylation reaction that proceeded proceeds at high temperature.¹² In contrast, whenWhen we used 2-methylfuran and benzyl mercaptan are used as nucleophiles, although the corresponding carbon—carbon and sulphur—carbon bond formation reactions proceeded. , However, the introduced stopper groups are were insufficiently large to prevent dethreading of the DB24C8 moiety; i.e., we did not isolate rotaxanes from these reactions.

Table 2

Recently, mMany efficient and convenient transformations methods of organic compounds have beenare mediated achieved by using a transition metal catalyst. s; some of these reactions In fact, some effectivehave been applied effectively to rotaxane syntheses and modifications of rotaxane were achieved using a transition metal catalyst.^{10,16} It Because it is important that the interactions between the axle and wheel be maintained under the reaction conditions, when using pseudorotaxane systems based on ammonium ions and crown ethers, used for these processes. Therefore, theonly catalysts, that are which are unaffected byactive under acidic and/or neutral conditions, are applicable to this such types of rotaxane consisting ofsyntheses ammonium and crown ether. Furthermore, selection of the nucleophile is also crucialcritical to

avoid deprotonation of the secondary ammonium ion, at the recognition part site of the axle moiety, in these kinds of nucleophilic substitution reactions.

In summary, this effort has facilitated the construction of various a number of rotaxanes featuring various functionalities through the application of using ruthenium-catalysed propargylic substitution reactions. We are exploring the scope of this new technique for rotaxane synthesis is being explored in our ongoing studies in this area.

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References and notes

1. For selected reviews on rotaxanes, see: (a) In *Molecular Catenanes, Rotaxanes and Knots*; Sauvage, J.-P.; Dietrich-Buchecker, C., Eds.; Wiley-VCH: Weinheim, 1999; (b) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348–3391; (c) Ballardini, R.; Balzani, V.; Credi, A.; Gandolfi, M. T.; Venturi, M. *Acc. Chem. Res.* **2001**, *34*, 445–455; (d) Harada, A.; *Acc. Chem. Res.* **2001**, *34*, 456–465; Schalley, C. A.; Beizai, K.; Vögtle, F. *Acc. Chem. Res.* **2001**, *34*, 465–476; (e) Collin, J.-P.; Dietrich-Buchecker, C.; Gavina, P.; Jimenez-Molero, M. C.; Sauvage, J.-P. *Acc. Chem. Res.* **2001**, *34*, 477–487; (f) Yui, N.; Ooya, T. *Chem. Eur. J.* **2006**, *12*, 6730–6737; (g) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72–191.
2. For examples, see: (a) Asakawa, M.; Brancato, G.; Fanti, M.; Leigh, D. A.; Shimizu, T.; Slawin, A. M. Z.; Wong, J. K. Y.; Zerbetto, F.; Zhang, S. *J. Am. Chem. Soc.* **2002**, *124*, 2939–2950; (b) Wisner, J. A.; Beer, P. D.; Drew, M. G. B.; Sambrook, M. R. *J. Am. Chem. Soc.* **2002**, *124*, 12469–12476; (c) Glink, P. T.; Oliva, A. I.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1870–1875.
3. For examples, see: (a) Cao, J.; Fyfe, M. C. T.; Stoddart, J. F.; Cousins, G. R. L.; Glink, P. T. *J. Org. Chem.* **2000**, *65*, 1937–1946; (b) Watanabe, N.; Yagi, T.; Kihara, N.; Takata, T. *Chem. Commun.* **2002**, 2720–2721; (c) Cantrill, S. J.; Fulton, D. A.; Heiss, A. M.; Pease, A. R.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **2000**, *6*, 2274–2287;

- (d) Kolchinski, A. G.; Alcock, N. W.; Roesner, R. A.; Busch, D. H. *Chem. Commun.* **1998**, 1437–1438; (e) Tokunaga, Y.; Kakuchi, S.; Akasaka, K.; Nishikawa, N.; Shimomura, Y.; Isa, K.; Seo, T. *Chem. Lett.* **2002**, 810–811; (f) Zehnder II, D. W., II; Smithrud, D. B. *Org. Lett.* **2001**, 3, 2485–2487; (Gg) Hung, W.-C.; Liao, K.-S.; Liu, Y.-H.; Peng, S.-M.; Chiu, S.-H. *Org. Lett.* **2004**, 6, 4183–4186.
4. For examples, see; : (a) Cantrill, S. J.; Preece, J. A.; Stoddart, J. F.; Wang, Z.-H.; White, A. J. P.; Williams, D. J. *Tetrahedron* **2000**, 56, 6675–6681; (b) Händel, M.; Plevoets, M.; Gestermann, S.; Vögtle, F. *Angew. Chem., Int. Ed.* **1997**, 36, 1199–1201.
 5. For examples, see; : (a) Kameta, N.; Hiratani, K.; Nagawa, Y. *Chem. Commun.* **2004**, 466–467; (b) Kawai, H.; Umehara, T.; Fujiwara, K.; Tsuji, T.; Suzuki, T. *Angew. Chem., Int. Ed.* **2006**, 45, 4281–4286.
 6. Tokunaga, Y.; Akasaka, K.; Hisada, K.; Shimomura, Y.; Kakuchi, S. *Chem. Commun.* **2003**, 2250–2251.
 7. Yoon, I.; Narita, M.; Shimizu, T.; Asakawa, M. *J. Am. Chem. Soc.* **2004**, 126, 16740–16741.
 8. (a) Rowan, S. J.; Stoddart, J. F. *J. Am. Chem. Soc.* **2000**, 122, 164–165; (b) Chiu, S.-H.; Rowan, S. J.; Cantrill, S. J.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **2002**, 8, 5170–5183.
 9. Hannam, J. S.; Lacy, S. M.; Leigh, D. A.; Saiz, C. G.; Slawin, A. M. Z.; Stitchell, S. G. *Angew. Chem., Int. Ed.* **2004**, 43, 3260–3264.
 10. Kihara, N.; Motoda, S.; Yokozawa, T.; Takata, T. *Org. Lett.* **2005**, 7, 1199–1202.
 11. Tokunaga, Y.; Ohta, G.; Yamauchi, Y.; Goda, T.; Kawai, N.; Sugihara, T.; Shimomura, Y. *Chem. Lett.* **2006**, 35, 766–767.
 12. (a) Nishibayashi, Y.; Wakiji, I.; Hidai, M. *J. Am. Chem. Soc.* **2000**, 122, 11019–11020; (b) Inada, Y.; Nishibayashi, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc.* **2002**, 124, 15172–15173; (c) Nishibayashi, Y.; Wakiji, I.; Ishii, Y.; Uemura, S.; Hidai, M. *J. Am. Chem. Soc.* **2001**, 123, 3393–3394; (d) Nishibayashi, Y.; Onodera, G.; Inada, Y.; Hidai, M.; Uemura, S. *Organometallics*, **2003**, 22, 873–876; (de) Nishibayashi, Y.; Wakiji, I.; Hidai, M.; *J. Am. Chem. Soc.* **2000**, 122, 11019–11020; (ef) Nishibayashi, Y.; Milton, M. D.; Inada, Y.; Yoshikawa, M.; Wakiji, I.; Hidai, M.; Uemura, S. *Chem. Eur. J.* **2005**, 11, 1433–1451.
 13. Ashton, P. R.; Campbell, P. J.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Philp, D.; Spencer, N.; Stoddart, J. F.; Tasker, P. A.; Williams, D. J. *Angew. Chem., Int. Ed.* **1995**, 34, 1865–1869.
 14. A solution of **2·PF₆** (100 mg, 0.235 mmol) and DB24C8 (422 mg, 0.94 mmol) in dichloroethane (5 ml)((*how much?*))) were added to a suspension of Met-DIRUX (7.5 mg, 12 μmol) and ammonium hexafluorophosphate (3.8 mg, 23.5 μmol) in

dichloroethane (2 ml); after the addition of carbazole (197 mg, 1.18 mmol), was added a solution of ammonium salt **2PF₆** (100 mg, 0.235 mmol) and DB24C8 (422 mg, 0.94 mmol) in dichloroethane and carbazole (197 mg, 1.18 mmol), and the reaction mixture was heated at 60 °C for 1 hr. After cooling down to room temperature, the reaction mixture was concentrated evaporated to dryness to give a solid, which was washed with a mixture of hexane– and toluene (2:1). Chloroform was added To to the solid; was added chloroform, the resulting heterogeneous mixture was filtered though celite, and the filtrate was concentrated. Purification of the residue by through column chromatography on silica gel with (chloroformCHCl₃–/ethyl acetateEtOAc, (1:1) as eluent gave a solid, which which was then dissolved in acetone-/water (60 ml, 2:1). Ammonium hexafluorophosphate (0.156 g, 940 mmol) was added to the reaction mixturesolution and the mixture stirred for 2 h at room temperature. After removal evaporation of the acetone, the precipitate was filtered off and washed with water to afford the rotaxane **3a** (200 mg, 83 %): %). IR (KBr) $\nu_{\max}$ (cm⁻¹): 1057, 1106, 1252, 1325, 1453, 1596, 1624, 2128, 2923, 3161. ¹H NMR (500 MHz, CDCl₃) δ : 2.13 (s, 6H), 2.77 (d, *J* = 2.5 Hz, 1H), 3.24–3.46 (m, 8H), 3.50–3.63 (m, 4H), 3.70–3.78 (m, 4H), 3.80–3.97 (m, 4H), 4.02–4.16 (m, 4H), 4.32–4.43 (m, 2H), 4.49–4.62 (m, 2H), 6.53–6.62 (m, 2H), 6.70–6.90 (m, 10H), 7.21–7.35 (m, 4H), 7.36–7.45 (m, 2H), 7.45–7.64 (m, 4H), 8.05–8.13 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ : 21.06, 48.42, 51.90, 52.52, 67.88, 68.18, 69.80, 70.05, 70.37, 70.51, 76.37, 78.13, 110.10, 112.48, 112.64, 119.73, 120.24, 121.55, 121.57, 123.41, 125.73, 126.51, 126.80, 129.78, 130.58, 131.19, 131.88, 137.54, 138.22, 139.23, 147.26. FAB-MS *m/z*: 877 ([M – PF₆)⁺]⁺.

15. Huang, F.; Jones, J. W.; Slebodnick, C.; Gibson, H. W. *J. Am. Chem. Soc.* **2003**, *125*, 7001–7004.
16. For eExamples of transition- metal-catalysed rotaxane syntheses. Ru-catalysed hydrosilylation: ; (a) by Ru-catalysed hydrosilylation: Sasabe, H.; Kihara, N.; Mizuno, K.; Ogawa, A.; Takata, T. *Tetrahedron Lett.* **2005**, *46*, 3851–3853; Suzuki coupling: (b) by Suzuki coupling reaction: Terao, J.; Tang, A.; Michels, J. J.; Krivokapic, A.; Anderson, H. L. *Chem. Commun.* **2004**, 56–57; (c) Michels, J. J.; O’Connell, M. J.; Taylor, P. N.; Wilson, J. S.; Cacialli, F.; Anderson, H. L. *Chem. Eur. J.* **2003**, *9*, 6167–6176; olefin metathesis: (cd) by olefin metathesis: Coumans, R. G. E.; Elemans, J. A. A. W.; Thordarson, P.; Nolte, R. J. M.; Rowan, A. E. *Angew. Chem., Int. Ed.* **2003**, *42*, 650–654; (e) Hannam, J. S.; Kidd, T. J.; Leigh, D. A.; Wilson, A. J. *Org. Lett.* **2003**, *5*, 1907–1910; (f) Badjic, J. D.; Cantrill, S. J.; Grubbs, R. H.; Guidry, E. N.; Orenes, R.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2004**, *43*, 3273–3278; (g) Fuller, A.-M.; Leigh, D. A.; Lusby, P. J.; Oswald, I. D. H.; Parsons, S.; Walker, D. B. *Angew. Chem., Int. Ed.* **2004**,

43, , 3914–3918; (h) Vignon, S. A.; Jarrosson, T.; Iijima, T.; Tseng, H.-R.; Sanders, J. K. M.; Stoddart, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 9884–9885.

Figure 1. A model forCartoon representation of the use of nucleophilic substitution for the efficient synthesis of various rotaxanes though from the same pseudorotaxane intermediate.

Scheme 1. Reagents and conditions: (a) 3,5-dimethylbenzylammonium chloride, Et_3N , MgSO_4 ; (b) NaBH_4 ; (c) HPF_6 (60% for three steps).

Figure 2. Partial ^1H NMR spectrum of rotaxane **3a**.

Table 1. Synthesis of rotaxane **3a** by through ruthenium-catalysed propargylic substitution reaction.^a

Entry	Carbazole (equiv)	DB24C8 (equiv)	NH ₄ PF ₆ (equiv)	Temperature (°C)	Time (h)	Yield ^b (%)
1	5	4	0.05	60	1	97
2	3	4	0.05	60	1	90
3	2	4	0.05	60	1	76
4	5	2	0.05	60	1	86
5	5	4	0.05	40	1	90
6	5	4	0.05	60	2	84
7	5	4	0	60	1	81

^a 5% mol of Amount of %mol of the ruthenium catalyst was used (mol%). ^b NMR spectroscopic yield.

Table 2. Synthesis Syntheses of rotaxanes **3** by through ruthenium- catalysed propargylic substitutions reaction.^a

Entry	Nu-H	Product	Yield ^b
1		3a	97 (83)
2		3b	95 (75)
3		3c	79 (54)
4		3d	87 (60)
5		3e	87 (64)
6		3f	88 (72)
7		3g	60 (44)

^a Reaction conditions: The A mixture of ammonium salt **2**•**PF**₆ (0.235 mmol), DB24C8 (4 equiv), the nucleophile (5 equiv), the catalyst (0.05 equiv), and NH₄PF₆ (0.1 equiv) in dichloroethane was heated at 60 ° °C for 1 h, except for entry 8. ^b NMR spectroscopic yield, ; the values in parentheses are (): isolated yields. ^c The This reaction was carried outperformed at 40 ° °C.