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Transition-metal free synthesis of diaryl vinyl selenides: a simple synthetic approach with high selectivity

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ABSTRACT

A simple, highly efficient synthetic protocol is developed for the synthesis of unsymmetrical diaryl vinyl selenides from diaryldiselenide and β-bromo styrene under transition-metal free conditions in *N*,*N*′-dimethyl propylene urea and 130 °C to afford high yields and excellent selectivities. This method provides a new strategy to fabricate a wide variety of important substituted molecular skeletons and an alternative to conventionally used metal salts, additives, and ligands.

1. Introduction

Introduction of new functionalities into diaryldiselenides (PhSeSePh) is fascinating because of the formation of multipurpose C=C double bonds and a new sp^2 carbon–selenium bond. Diaryl vinyl selenides[1] have unlimited applications, and a simple and facile synthetic procedure is desired by the researchers. Several attempts have been made to carry out effective synthesis of vinyl selenides.[2a] Some of the important techniques involve hydroselenation of alkynes,[2b] Wittig-type reaction,[2c] direct substitution of a halogen atom on the double bond by benzeneselenoate anions,[2d] oxidative zinc insertion of phenylselenyl halides[2e], and direct addition of diphenyldiselenide into alkenyl bromides. However, the abovementioned procedures[2b–2e] are effective but unfavorable in terms of atom economy, because they require the preformation of organometallic reagents and produce a stoichiometric amount of metal waste. To achieve particular isomer, the Raucher and Co., utilized the two-step process of addition of phenylselenyl bromide to monosubstituted alkenes under thermodynamically controlled conditions, followed by dehydrobromination with the strong base and specific substituents on alkenes are important prerequisites.[2f] The synthesis of diphenylvinylselenides from diphenyldiselenide precursors is interesting owing to its moisture stability, low cost and easy of preparation.[2g] The activation of selenium–selenium bond in diphenyldiselenide can be usually accomplished with transition-metal catalysts such as palladium[3] and copper.[4a,b] Such catalysts have been found to be inactive without using indium salts and/or ligands such as PPh_3 and L-proline as additives or Zn dust as a reducing agent. In 1984, Tiecco and colleagues reported that the nucleophilic addition of preformed aryl selenide anions (from diphenyldiselenide) to vinyl halides in good yields, which usually requires high equivalents of strong base to attain a specific stereoisomer[4c,d] with moderate yields.

Nevertheless, much attention has been focused particularly on copper catalysts owing to their cost-effectiveness and commercial availability. The Ranu group used copper nanoparticles[5] as catalyst and Zn dust as a co-catalyst in water under reflux conditions. In this reaction, high loading of copper nanoparticles and zinc dust are essential to achieve good yields with high selectivity. Rao and coworkers also found that copper oxide nanoparticles[6] combined with a base as an additive promotes the coupling of diphenyldiselenide and *trans*-β-iodostyrene in DMSO. As expected, an iodo compound is much more reactive than bromo compound even under mild conditions. Braga et al. reported copper iodide[7] promoted synthesis of vinyl selenides by the cross-coupling of diphenyldiselenide and potassium vinyltrifluoroborates as an alkene source without using any reducing agent.

However, even today, there are very few examples on the preparation of vinyl selenides from diphenyldiselenide without using a transition-metal catalyst. Therefore, transition-metal free synthesis of vinyl selenides should be investigated in order to resolve problems such as the toxicity of transition metals and ligands,

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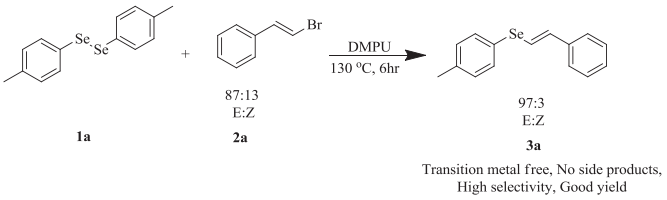
contamination of the products, and the concomitant formation of side products. While looking for the relevant literature references, we were surprised to find a report by Ogawa et al., which states that diphenyldiselenide could be successfully coupled with β-bromo styrene to provide diphenyl vinyl selenide.

With *E*/*Z* ratio of 80:20 under transition-metal free conditions using toxic hexamethylphosphoramide as a solvent at elevated temperatures. A key problem associated with the transition-metal free reaction is the loss of trans-selectivity. Therefore, it is highly desirable to develop an efficient, atom economic, and environmentally friendly synthetic method to attain high stereoselectivity with good yields.

2. Results and discussion

Our extensive reinvestigation of Ogawa's findings[8] led to some serendipitous results, which we describe here in detail. In this paper, we disclose that the cross-coupling of diphenyldiselenide with β-bromo styrene (87:13, *E*/*Z*) using DMPU (*N*,*N*′-dimethyl propylene urea) as a solvent in the absence of catalysts, ligands, additives, and bases affords diphenylvinylselenides in high yield (97:3, *E*/*Z*) enriched with trans-isomer. To the best of our knowledge, there has been no report on the synthesis of diphenylvinylselenides from diphenyldiselenide precursor with high trans-selectivity in the absence of metal catalysts.

The reaction is very easy to perform, because no catalysts, co-catalysts, ligands, or bases are required. Bis(4-methyl-phenyl) diselenide and β-bromo styrene were used as model substrates to explore the reaction-optimization conditions (Scheme 1, Table 1).



Scheme 1.

Table 1
Reaction optimizations

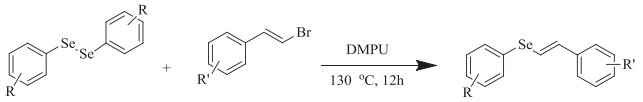
Entry	Solvent	Catalyst	Temp	*E*/*Z*[a]	Yield[a]
1	DMSO		130	Traces	
2	DMPU		130	97:3	91
3	DMF		130	94:6	76
4	DMA		130	97:3	81
5	NMP		130	97:3	83
6	1,4-Dioxane		Reflux		NR
7	1,2-Dimethoxyethane		Reflux		NR
8	Acetonitrile		Reflux		NR
9	THF		Reflux		NR
10	Toluene		Reflux		NR
11	DMPU	CuO (5 mol %)[d]	130	97:3	89
12	DMPU	CuO/Zn dust (5 mol %/2 equiv)	130	97:3	80[b]
13	DMPU		130	99.24:0.76	91[c]
14	—		130		Traces
15	DMPU		130		NR[e]

[a] Determined by GC–MS.
[b] Di(4-methyl-phenyl) selenide as side product (20%).
[c] β-Bromo styrene (98:2).
[d] CuO nanopowder (purchase from Aldrich, Cat. No. 544868), 6 h.
[e] 1-Bromo-1-propene was used (an experiment with 1-bromo-1-propene with diphenyldiselenide didn't proceed well under the present conditions).

The cross-coupling reaction of bis(4-methyl-phenyl) diselenide(1 mmol) and β-bromo styrene(2.2 mmol) in 4 mL DMPU at 130 °C (Scheme 1) provided (*E*)-and (*Z*)-1-methyl-4-(2-phenyl selenylvinyl)-benzene with the highest selectivity for trans-stereoisomer (97%). As shown in Table 1, among the solvents examined, DMPU showed excellent yields, whereas DMF, DMA, and NMP were less successful. No reaction took place in other solvents such as dioxane, dimethoxyethane, acetonitrile, THF, and toluene.

The addition of CuO nanopowder failed to improve the selectivity (entry 11, Table 1), which shows no value of added transition-metal catalysts under the present conditions. In the case of entry 12, a combination of CuO nanopowder and zinc dust greatly enhances the formation of di(4-methyl-phenyl) selenideside product and as a consequence the yield is poorer. A reaction with β-bromo styrene[9] enriched with trans-product (98%) (entry13, Table 1) led to the corresponding cross-coupled product with excellent improvement of trans-selectivity (99.24%). Traces of products were detected when the reactions were performed under DMSO or solvent free conditions (entries 1 and 14). Indeed, only starting materials were recovered when we place 1-bromo-1-propene instead of β-bromo styrene (entry 15, Table 1).

Our final optimized conditions were proved to be compatible with a wide array of substituted diselenides and β-bromo styrenes (Scheme 2, Table 2). The model substrates **1a** and **2a** afforded **3a**[†] in 91% yield in 6 h (Scheme 1). However, other substrates (except for entry 1, Table 2, 6 h) required extended reaction times (12 h). It is clear that there is no substantial substituent effect with diaryldiselenides containing *p*-methoxy, *p*-chloro, or *m*-trifluoro methyl groups (entries 2,4, and 5); however, the trans-selectivity slightly decreased to 96% for *o*-methyldiphenyldiselenide (entry 3). When comparing the yields, all functionalities were well tolerated and provided vinylated products in excellent yields. The reactions of β-bromo styrenes with different substituents were also investigated, and a variety of substituted β-bromo styrenes were proved to be reactive under the studied reaction conditions and led to good to excellent yields. In general, styrenes containing *o*-methyl, *o*-methoxy, or *p*-chloro substituents were readily coupled, and afforded the corresponding coupled products (entries 6, 8, and 9), while a methoxy group at the *para* position (entry 7) makes the reaction slightly sluggish, which led to a high selectivity and yield. Excellent *trans*-selectivity[10] has been reported for the products obtained from substituted β-bromo styrenes (entries 6, 8, and 9). Unfortunately, no reaction takes place when phenyl vinylboronic acid and potassium *trans*-styryl trifluoroborate were used as coupling partners instead of β-bromo styrene (entries 10 and 11). Unfortunately, this methodology is failed to provide good yield in the case of diphenylsulfides and tellurides (Scheme 3) while stereoselectivity seems excellent[‡].

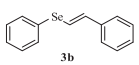
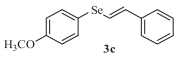
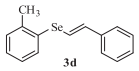
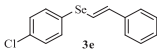
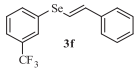
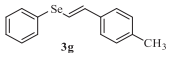
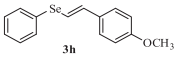
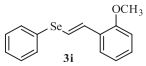
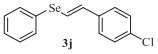
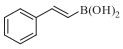
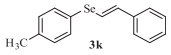
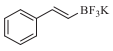
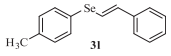


Scheme 2.

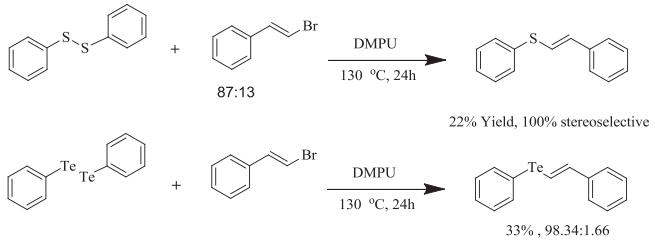
We prefer GC–MS to measure accurate percentage of stereoisomers present in the product. We synthesized diphenylvinylselenide using Ogawa's procedure to compare with our report and measured GC–MS (Figs. 1 and 2). We found that our report shows high trans-isomer present in the product. In addition, ^{1}H NMR

[†] Compounds numbers corrected as bold.
[‡] Experiments with diphenyl disulfides and ditellurides proceeded slowly with β-bromo styrene in DMPU solvent at 130 °C for 24 h afforded yields 22 and 33%, respectively, with stereoselectivity 100 and 98.34% of trans-isomers.

Table 2
Substrate scope of vinylation of diphenyldiselenides

Entry	R	R′ [*E*/*Z*][a]	Product	*E*/*Z*[a]	Yield[a]
1	H	H	 3b	98:2	93
2	OCH_3	H	 3c	97:3	94
3	CH_3	H	 3d	96:4	98
4	Cl	H	 3e	97:3	96
5	CF_3	H	 3f	98:2	91
6	H	CH_3 [99.8:0.2]	 3g	99.6:0.4	94
7	H	OCH_3 [100:0]	 3h	98:2	81
8	H	OCH_3 [100:0]	 3i	99.6:0.4	93
9	H	Cl [100:0]	 3j	99.6:0.4	95
10	CH_3		 3k	—	NR
11	CH_3		 3l	—	NR

[a] Determined by GC–MS, yield (refer to diphenyldiselenide), and stereoselectivity based on average of two independent runs, 12 h.



Scheme 3.

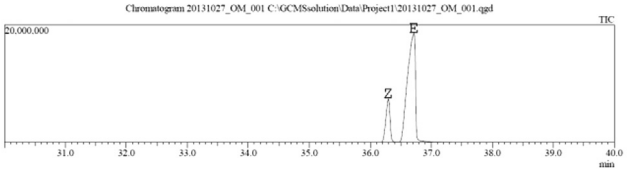
analysis of **3a** based on integration of distinct CH_3 signals shows 4.76% of *Z*-isomer, which is slightly higher than GC–MS report, 2.36% (see ESI).

3. Conclusion

In summary, we successfully achieved the transition-metal free synthesis of diaryl vinyl selenides by employing a suitable temperature (130 °C) and DMPU as a solvent. This simple synthetic approach provides good functional-group tolerance and high yields. In addition, we found that the *E*/*Z* ratio of the conversion of β-bromo styrenes to coupled products can be greatly enhanced or reproduced without metal catalysts, ligands, bases, or additives.

GC-MS analysis of stereoselectivity:

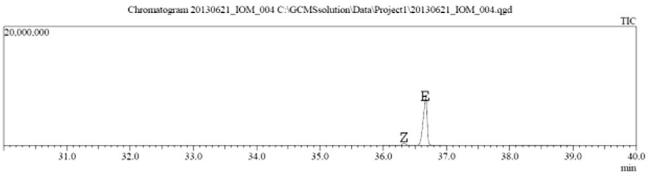
Ogawa's work:



RT	Area	Area%	Mw.
36.295	34383653	17.08 (Z)	260
36.715	166513962	82.92 (E)	260

Fig. 1. GC–MS analysis of Ogawa's report.

This work:



RT	Area	Area%	Mw.
36.353	24371	1.39 (Z)	260
36.652	1734041	98.61 (E)	260

Fig. 2. GC–MS analysis of our report.

4. Experimental section

4.1. General

Reagents were purchased from Aldrich Chemical Co., TCI and Strem Chemical Co. and used as received. Reaction products were analyzed by GC–MS (Shimadzu-QP2010 SE), IR (Shimadzu-Prestige 21), ^{1}H NMR, and ^{13}C NMR (Varian Mercury Plus, 300 MHz). Chemical shift values were recorded as parts per million relative to tetramethylsilane as an internal standard, unless otherwise indicated, and coupling constants in Hertz. High-resolution mass carried out at Korea Basic Science Institute (Daegu). Starting materials were synthesized from previously reported procedure (see Supplementary data).

4.2. General procedure for the synthesis of diaryl vinyl selenides[§]

To a 10 mL sealed aluminum capped glass vial with septum, charged diphenyldiselenide (50 mg, 0.1602 mmol), β-bromo styrene (64 mg, 0.3526 mmol), and DMPU (4 mL). The mixture was

[§] We included detailed experimental procedure in the experimental section of the manuscript. The products obtained are identified by using GC–MS. The product diphenyl vinyl selenide retention time and molecular weight vary with starting materials diphenyldiselenide and β-bromo styrene. We used diphenyldiselenide as limiting reagent while β-bromo styrene in 2.2 equiv. The yield was calculated on comparison with retention time and molecular weight of diphenyldiselenide and diphenyl vinyl selenide, which includes presence of any side products. For example, entry 12, Table 1 shows 80% yield, which corresponds to presence of side product 20%. In this case, no starting material was detected in GC–MS. So, we mentioned 80% as yield.

heated at 130 °C under vigorous magnetic stirring for the indicated time. After stirring for appropriate time, mixture was cooled to rt, diluted with water, extracted with ether five times. The combined ether layer was washed with water, dried with anhydrous sodium sulfate, and concentrated in a rotary evaporator. The residue was analyzed by GC–MS. After the GC–MS analysis, the crude product was chromatographed on silica gel afforded the desired product.

*4.2.1. 1(E) and (Z)-(Styryl)(4-methyl-phenyl)selenide (**3aa**): [E/Z, 97:3].* ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.35 (s, 3H), 6.83 (d, J=15.9 Hz; 1H), 7.06–7.15 (m, 3H), 7.18–7.34 (m, 5H), 7.39–7.50 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 120.4, 124.7, 126.2, 127.6, 128.8, 130.3, 133.3, 134.3, 137.3, 137.8. IR (neat), ν 3022, 2366, 1600, 1482, 1432, 1028, 952, 800, 725, 674. HRMS (EI) calcd for $C_{15}H_{14}Se$ 274.0263, found 274.0261[¶].

*4.2.2. (E) and (Z)-(Styryl)(phenyl)selenide (**3b**): [E/Z, 98:2].* ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.85 (d, J=15.9 Hz; 1H), 7.15–7.42 (m, 9H), 7.54–7.63 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 119.6, 126.2, 127.6, 127.8, 127.9, 128.5, 128.6, 128.8, 129.3, 129.5, 130.3, 131.7, 132.7, 132.9, 135.4, 137.2. IR (neat), ν 3056, 2357, 1583, 1482, 1440, 1028, 952, 733, 683. HRMS (EI) calcd for $C_{14}H_{12}Se$ 260.0106, found 260.0104.

*4.2.3. (E) and (Z)-(Styryl)(4-methoxy-phenyl)selenide (**3c**): [E/Z, 97:3].* ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.82 (s, 3H), 6.74 (d, J=15.6 Hz; 1H), 6.90 (d, J=8.7 Hz; 1H), 7.13 (d, J=15.6 Hz; 1H), 7.20–7.42 (m, 10H), 7.50–7.57 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.6, 115.2, 119.4, 121.3, 126.1, 127.5, 128.4, 128.8, 133.1, 135.3, 135.8, 137.4, 159.9. IR (neat), ν 3006, 2374, 1718, 1591, 1482, 1289, 1255, 1171, 1028, 952, 834, 725, 691. HRMS (EI) calcd for $C_{15}H_{14}OSe$ 290.0208, found 290.0210.

*4.2.4. (E) and (Z)-(Styryl)(2-methyl-phenyl)selenide (**3d**): [E/Z, 96:4].* ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.45 (s, 3H), 6.85 (d, J=15.6 Hz; 1H), 7.12 (d, J=15.6 Hz; 1H), 7.24–7.36 (m, 5H), 7.53 (d, J=7.2 Hz; 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.5, 119.0, 126.2, 127.0, 127.8, 127.9, 128.2, 128.6, 128.8, 130.1, 130.4, 130.6, 131.0, 133.0, 135.3, 137.3, 139.9. IR (neat), ν 3014, 2366, 1768, 1457, 1272, 1171, 1087, 750. HRMS (EI) calcd for $C_{15}H_{14}Se$ 274.0263, found 274.0261.

*4.2.5. (E) and (Z)-Styryl(4-chloro-phenyl)selenide (**3e**): [E/Z, 97:3].* ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.69 (d, J=9 Hz; 1H), 6.85 (d, J=15 Hz; 1H), 6.98 (d, J=10.2 Hz; 1H), 7.09 (d, J=15.9 Hz; 1H), 7.25–7.52 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 118.8, 126.3, 128.1, 128.5, 128.6, 128.7, 128.9, 129.7, 133.9, 134.0, 134.2, 136.2, 137.0. IR (neat), ν 3022, 2349, 1474, 1103, 1011, 943, 809, 725, 683. HRMS (EI) calcd for $C_{14}H_{11}ClSe$ 293.9716, found 293.9714.

*4.2.6. (E) and (Z)-Styryl(3-trifluoromethyl-phenyl)selenide (**3f**): [E/Z, 98:2].* ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.01 (d, J=15.6 Hz; 1H), 7.14 (d, J=15.9 Hz; 1H), 7.25–7.43 (m, 7H), 7.53 (d, J=8.1 Hz; 1H), 7.69 (d, J=8.4 Hz; 1H), 7.78 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 117.6, 124.1, 124.3, 126.5, 128.3, 128.9, 129.8, 132.0, 135.3, 136.8, 137.6. IR (neat), ν 2997, 2366, 1322, 1272, 1137, 750. HRMS (EI) calcd for $C_{15}H_{11}F_3Se$ 327.9977, found 327.9978.

*4.2.7. (E) and (Z)-(4-Methylstyryl)(phenyl)selenide (**3g**): [E/Z, 99.6:0.4].* ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.35 (s, 3H), 6.93 (d, J=15.6 Hz; 1H), 7.11–7.18 (m, 3H), 7.25–7.36 (m, 5H), 7.54–7.58 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) 118.0, 126.2, 127.5, 129.5, 129.6, 130.7, 134.5, 135.9, 137.8. IR (neat), ν 3014, 2358, 1483, 1281, 759. HRMS (EI) calcd for $C_{15}H_{14}Se$ 274.0263, found 274.0261.

*4.2.8. (E) and (Z)-(4-Methoxystyryl)(phenyl)selenide (**3h**): [E/Z, 98:2].* ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.81 (s, 3H) 6.84–6.91 (m, 3H), 6.99 (d, J=15.9 Hz; 1H), 7.25–7.30 (m, 4H), 7.52–7.58 (m, 2H); ^{13}**C** NMR ($CDCl_3$, 75 MHz) 55.5, 114.0, 114.3, 116.1, 127.3, 127.6, 129.5, 130.1, 131.0, 132.2, 136.1, 159.6. IR (neat), ν 3014, 2349, 1617, 1507, 1246, 1036, 1171, 758. HRMS (EI) calcd for $C_{15}H_{14}OSe$ 290.0208, found 290.0210.

*4.2.9. (E) and (Z)-(2-methoxystyryl)(phenyl)selenide (**3i**): [E/Z, 98:2].* ^{1}H NMR ($CDCl_3$, 300 MHz) δ3.85 (s, 3H), 6.87–6.96 (m, 2H), 7.22–7.47 (m, 8H), 7.55–7.58 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) 111.2, 120.1, 120.9, 126.3, 127.3, 129.0, 129.4, 131.1, 131.3, 132.3, 156.7. IR (neat), ν 3022, 2349, 1280, 1642, 761. HRMS (EI) calcd for $C_{15}H_{14}OSe$ 290.0213, found 290.0210.

*4.2.10. (E) and (Z)-(4-Chlorostyryl)(phenyl)selenide(**3j**): [E/Z, 99.6:0.4].* ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.81 (d, J=15.6 Hz; 1H), 7.15 (d, J=15.6 Hz; 1H), 7.25–7.34 (m, 7H), 7.54–7.64 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 120.9, 127.4, 127.4, 127.9, 129.0, 129.4, 129.6, 129.9, 131.7, 133.1, 133.4, 135.7. IR (neat), ν 3022, 2357, 1591, 1491, 1272, 960, 750, 683. HRMS (EI) calcd for $C_{14}H_{11}ClSe$ 293.9718, found 293.9714.

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Supplementary data

Copies of ^{1}H, ^{13}C NMR spectra, and GC–MS splitting pattern for all compounds. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.03.011.

References and notes

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10. At present, we do not know the exact mechanism but assumed the reaction is following $S_N2$pathway. Our investigation is currently underway.

¶ According to Tetrahedron format, we included general procedure, ^{1}H, ^{13}C, IR, and HRMS data in the manuscript.