Tetrahedron xxx (2017) 1–10

Contents lists available at ScienceDirect

Tetrahedron

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

Copper-catalyzed [1,2]-rearrangements of allylic iodides and aryl α-diazoacetates

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ARTICLE INFO

Article history:
Received 10 October 2016
Received in revised form
10 January 2017
Accepted 20 January 2017
Available online xxx

Keywords:
Rearrangement
Iodonium ylide
Copper catalysis
Ligand control
Iodine
Deuterium labeling

ABSTRACT

The [1,2]- and [2,3]-rearrangements of iodonium ylides are synthetically useful reactions for the generation of functionalized α-iodoesters. Allylic iodides are coupled with α-diazoesters in the presence of a copper catalyst and a ligand to generate iodonium ylides, which undergo metal-mediated rearrangements. By fine-tuning the structure of the ligand, we have reversed the regioselectivity of copper-catalyzed reactions of iodonium ylides from [2,3]- to [1,2]-rearrangements with the use of alternate bipyridine ligands. The preference for [1,2]-rearrangements was further improved by using bulky aryl α-diazoester substrates. Several α-iodoesters with a diverse range of functional groups were generated in good yields (up to 88% yield) and high regioselectivities (up to >95:5 regioisomeric ratio). A deuterium-labeled substrate was utilized to gain insight into the mechanism of the reaction.

1. Introduction

Sigmatropic rearrangements are a broad class of reactions that have revolutionized the synthesis of functionalized molecules.[1] Recent advances in metal catalysis have enhanced the synthetic utility of these rearrangements. Ligands have been designed to fine-tune the reactivity of metal complexes, converting unselective sigmatropic rearrangements into highly selective catalytic processes.

We were intrigued by the [1,2]- and [2,3]-rearrangements of iodonium ylides as efficient methods for generating functionalized α-iodoesters.[2] Despite the potential utility of these reactions, metal-catalyzed regioselective methods have only recently been reported in the literature.[3] In the course of our studies on these rearrangements, we discovered that copper-catalyzed reactions of diazoesters and allylic iodides furnish a mixture of [2,3]- and [1,2]-rearrangement products (Scheme 1a). However, a 6,6′-dibromo-2,2′-bipyridine ligand **L5** can tune the reactivity of the copper catalyst and facilitate the selective formation of the [2,3]-rearrangement product **3** in high yield and diastereoselectivity (Scheme 1b).[3] Based on our observation that other bipyridine ligands yielded different ratios of the two rearrangement products, we hypothesized that we could selectively form the [1,2]-rearrangement product **4** by fine-tuning the steric and electronic properties within the bipyridine class of ligands.[4] Herein, we describe the discovery and application of an alternate bipyridine ligand that favors copper-catalyzed [1,2]-iodonium ylide rearrangements (Scheme 1c). We also present mechanistic data for this switch in regioselectivity.

2. Results and discussion

2.1. Ligand synthesis

To build up a collection of bipyridine ligands with comprehensive electronic and steric properties, we synthesized ligands **L3**, **L4** and **L6** via a homo-coupling of 6-substituted 2-chloropyridines with catalytic amounts of $Ni(PPh_3)Br_2$, zinc powder, and tetrabutylammonium bromide (Scheme 2b).[5] Ligand **L13** was generated from 5-methoxy-2-chloropyridine under slightly modified conditions (Scheme 2c).[6] Ligands **L1**, **L2**, **L5** and **L7-L12** were purchased from Sigma-Aldrich (Scheme 2a).

2.2. Substrate synthesis

We generated a series of α-diazoesters **2a-2f** to assay the effect of the ester functionality on the outcome of the iodonium ylide

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http://dx.doi.org/10.1016/j.tet.2017.01.048
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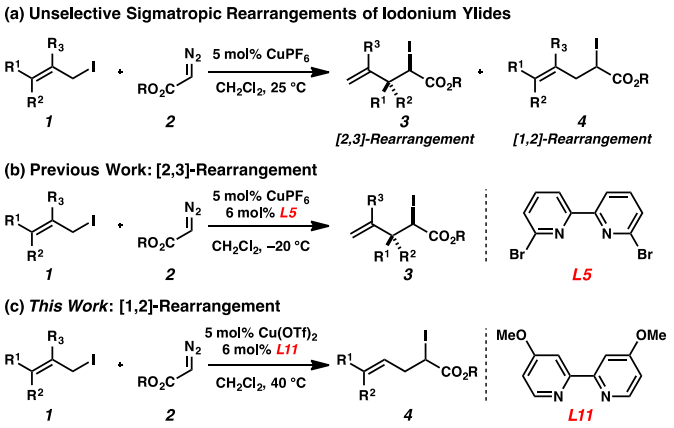
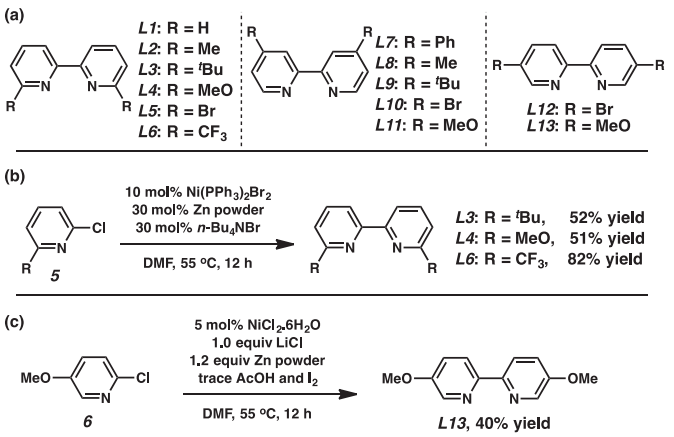
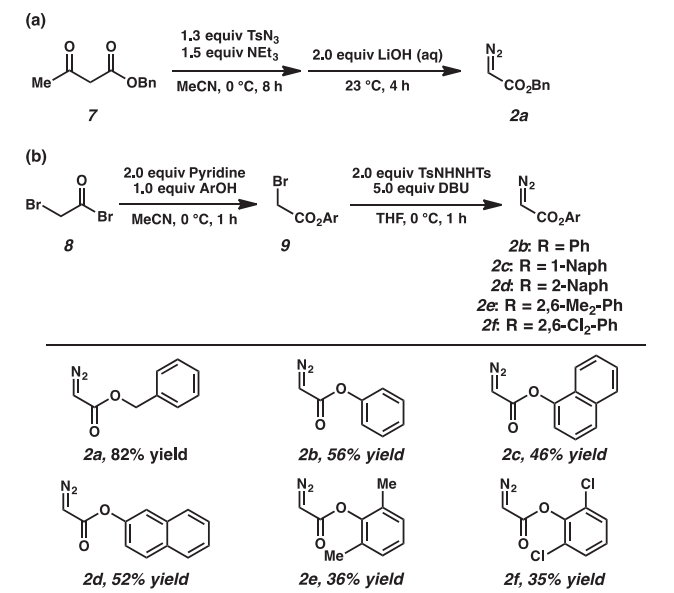


Scheme 1. Regiodivergent [2,3]- and [1,2]-rearrangement of iodonium ylides generated by diazo compounds.



Scheme 2. Synthesis of substituted bipyridines.



Scheme 3. Synthesis of α-diazoesters.

rearrangements (Scheme 3). Benzyl α-diazoester **2a** was generated in two steps from β-ketoester **7** (Scheme 3a).[7] Alternatively, aryl α-diazoesters **2b-2f** were synthesized from bromoacetyl bromide **8** via an esterification with various phenol derivatives followed by a diazotization (Scheme 3b).[8]

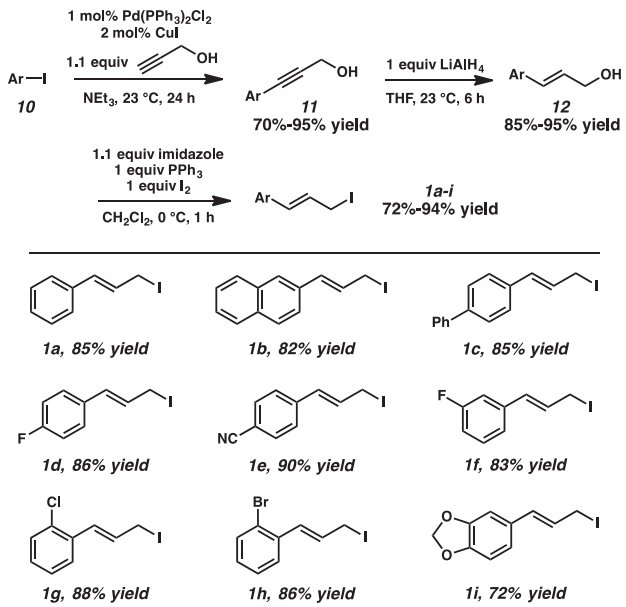
We devised a convergent assembly of aryl-substituted allylic iodides that commenced with a Sonogashira coupling of various aryl iodides **10** and propargyl alcohol (Scheme 4).[9] The resulting internal alkynes **11** were subjected to directed reduction with $LiAlH_4$ to selectively yield (*E*)-cinnamyl alcohols **12**.[10] A subsequent Appel reaction converted these allylic alcohols to the desired (*E*)-allylic iodides **1a-i**.[11]

To access other classes of allylic iodides, we took advantage of the accessibility of the corresponding *E*-allylic alcohols and the ease of iodination (Scheme 5). For example, commercially available prenol **13** and geraniol **14** were directly converted to allylic iodides **1k** and **1m**, respectively. Trisubstituted allylic iodides **1j** and **1l** were synthesized in three steps from acetophenone and cyclohexanone. Horner-Wadsworth-Emmons olefination[12] with triethyl phosphonoacetate furnished α,β-unsaturated esters **16**, which were reduced with DIBAL-H to allylic alcohols **17**. Subsequent iodination resulted in the formation of the desired allylic iodides **1j** and **1l**.

2.3. Reaction optimization

With the substrates and bipyridine ligands in hand, we commenced the optimization of the copper-catalyzed [1,2]-rearrangement of iodonium ylides (Table 1). In the absence of an external ligand, cinnamyl iodide **1a** and α-diazoester **2a** reacted with catalytic $[Cu(MeCN)_4]PF_6$ to furnish a 61:39 mixture of [2,3]- and [1,2]-rearrangement products (entry 1). A survey of bipyridines **L1-L13** revealed a broad range of regioselectivities within this structural class of ligands (entries 2–14). Whereas ligands **L2-L6** favored the formation of the [2,3]-rearrangement product **3** (entries 3–7), bipyridine ligands **L1** and **L7-L13** preferentially formed the [1,2]-rearrangement product **4a** (entries 2 and 8–14). Most notably, ligand **L11** facilitated the formation of the [1,2]-rearrangement product in a regioisomeric ratio of 94:6 (entry 12).

Next, we examined the effect of α-diazoester structure on the regioselectivity of the rearrangement (entries 15–18). Sterically



Scheme 4. Synthesis of aryl allylic iodides.

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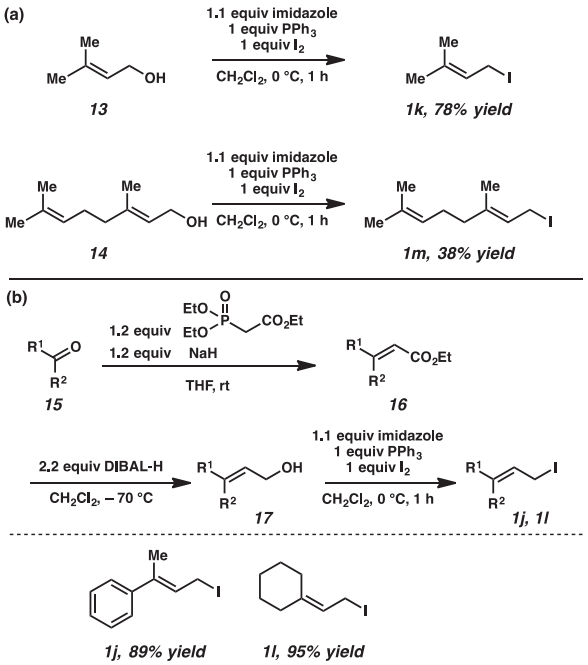
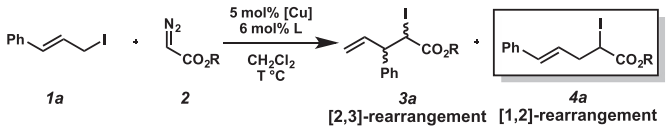


Scheme 5. Synthesis of more complex allylic iodides.

Table 1
Optimization of copper-catalyzed [1,2]-rearrangement of iodonium ylide.[a]



Entry	Ligand	[Cu]	2	T (°C)	Time (h)	Yield (%)	3/4
1	None	$[Cu(MeCN)_4]PF_6$	2a	25	0.5	13	61: 39
2	L1	$[Cu(MeCN)_4]PF_6$	2a	25	2	60	14: 86
3	L2	$[Cu(MeCN)_4]PF_6$	2a	25	2	70	85: 15
4	L3	$[Cu(MeCN)_4]PF_6$	2a	25	8	32	65: 35
5	L4	$[Cu(MeCN)_4]PF_6$	2a	25	2	64	62: 38
6	L5	$[Cu(MeCN)_4]PF_6$	2a	25	0.5	68	>95: 5
7	L6	$[Cu(MeCN)_4]PF_6$	2a	25	0.5	42	91: 9
8	L7	$[Cu(MeCN)_4]PF_6$	2a	25	2	70	10: 90
9	L8	$[Cu(MeCN)_4]PF_6$	2a	25	2	73	9: 91
10	L9	$[Cu(MeCN)_4]PF_6$	2a	25	2	73	10: 90
11	L10	$[Cu(MeCN)_4]PF_6$	2a	25	2	68	33: 67
12	L11	$[Cu(MeCN)_4]PF_6$	2a	25	2	70	6: 94
13	L12	$[Cu(MeCN)_4]PF_6$	2a	25	2	68	33: 67
14	L13	$[Cu(MeCN)_4]PF_6$	2a	25	2	71	17: 83
15	L11	$[Cu(MeCN)_4]PF_6$	2b	25	2	74	20: 80
16	L11	$[Cu(MeCN)_4]PF_6$	2c	25	2	70	6: 94
17	L11	$[Cu(MeCN)_4]PF_6$	2d	25	2	33	<5: 95
18	L11	$[Cu(MeCN)_4]PF_6$	2e	25	2	76	<5: 95
19	L11	CuBr	2e	25	24	24	<5: 95
20	L11	CuOTf	2e	25	2	50	<5: 95
21	L11	$Cu(OTf)_2$	2e	25	8	81	<5: 95
22	L11	$Cu(OTf)_2$	2e	40	2	86	<5: 95
23	L11	$Cu(OTf)_2$	2e	5	48	ND[b]	–

[a] Reaction conditions: allylic iodide **1a** (0.4 mmol), α-diazoester **2** (1.2 equiv), copper catalyst (5 mol%), ligand (6 mol%), CH_2Cl_2 (0.1 M).
[b] ND: No product was detected, and α-diazoester substrate remained.

bulky aryl α-diazoesters **2c-2e** were most effective in facilitating a high preference for the [1,2]-rearrangement product **4a** (entries 16–18). We selected 2,6-dimethyl-phenyl α-diazoester **2e** as the optimal substrate for both yield and regioselectivity of the [1,2]-rearrangement product (entry 18).

A screen of alternative copper(I) and copper(II) sources was conducted to identify the best catalyst precursor for the [1,2]-iodonium ylide rearrangement (entries 19–21). $Cu(OTf)_2$ was most effective for yield while maintaining a high preference for the [1,2]-rearrangement product **4a** (entry 21). After conducting the reaction at several temperatures (entries 21–23), we established the optimal reaction conditions for the copper-catalyzed [1,2]-rearrangement. In the presence of 5 mol% $Cu(OTf)_2$ and 6 mol% dimethoxy-bipyridine ligand **L11**, cinnamyl iodide **1a** and 2,6-dimethyl-phenyl α-diazoester **2e** reacted at 40 °C to furnish the desired product **4a** in 86% yield and >95:5 regioisomeric ratio (entry 22).

2.4. Substrate scope

The copper-catalyzed [1,2]-rearrangement of iodonium ylides in the presence of bipyridine ligand **L11** exhibits a wide substrate scope and functional group tolerance (Table 2). A broad range of aryl-substituted allylic iodides reacted with α-diazoester **2e** to furnish the [1,2]-rearrangement product in high yield and regioselectivity. For example, allylic iodides substituted with aromatic hydrocarbons yielded the rearrangement products in 72–86% yield with >95:5 preference for the [1,2]-rearrangement product (**4a-c**). The reaction is tolerant of phenyl rings with electron-withdrawing groups, such as fluorine (**4d** and **4f**), nitrile (**4e**), chlorine (**4g**), and bromine (**4h**). Substitution at the *ortho* and *para* positions is compatible with the conditions. Gratifyingly, an allylic iodide with an electron-rich aromatic ring was also a suitable substrate for the copper-catalyzed process (**4i**).

We extended the scope of the [1,2]-rearrangement to include trisubstituted allylic iodides (**4j-m**). Products with multiple aliphatic substituents (**4k-4m**) and a mixture of aliphatic and aromatic substituents (**4j**) were generated in high yields and regioisomeric ratios. Interestingly, the configuration of the double bond in the starting material allylic iodide was conserved in the product for all examples except for α-iodoester **4m**, which was obtained as 2:1 mixture of *E:Z* olefins.

We also investigated the scope of aryl α-diazoesters (Table 3). Using various ester groups with different steric (**2c** and **2d**) and electronic (**2f**) properties, the desired products were obtained with exceptional regioselectivities (>95:5) and moderate yields.

2.5. Mechanistic studies

We conducted a deuterium-labeled experiment to gain more insight into the mechanism of the copper-catalyzed [1,2]-rearrangement (Scheme 6). Deuterated allylic iodide **18** reacted with 2,6-dimethyl-phenyl α-diazoester **2e** in the presence of catalytic $Cu(OTf)_2$ and dimethoxy-bipyridine ligand **L11** to yield a mixture of deuterated rearrangement products **19** and **20**. Terminal allylic iodide **18** was utilized in this experiment to avoid any steric bias that may exist for a substituted allylic iodide. The formation of almost equal amounts of isomers **19** and **20** is consistent with a stepwise mechanism that proceeds through an oxidative addition/reductive elimination pathway. We propose that the α-diazoester initially reacts with the copper catalyst to form copper carbenoid ***I***, which then engages with the allylic iodide to yield a copper-coordinated iodonium ylide that can exist as two copper enolate tautomers (***II*** and ***III***).[13] This intermediate can undergo an oxidative addition to generate a copper(III) complex such as ***IV***, ***V***, or ***VI***.[14,15] Reductive elimination of the copper allyl complex would furnish the observed [1,2]-rearrangement product **4** and regenerate the copper catalyst.

We hypothesize that this remarkable switch in regioselectivity by the two bipyridine ligands **L5** and **L11** can be rationalized by

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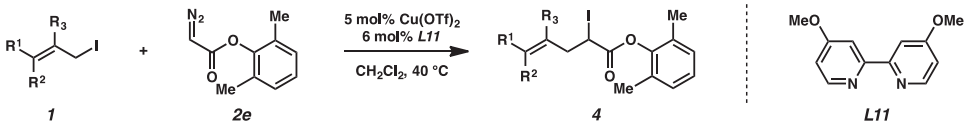
Table 2
Substrate scope of copper-catalyzed [1,2]-rearrangement of iodonium ylides.



1 2e 4 L11

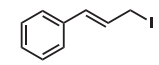
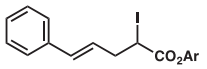
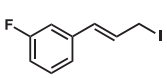
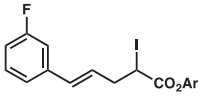
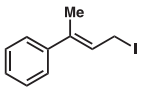
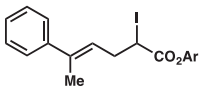
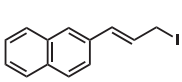
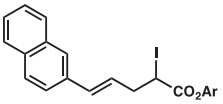
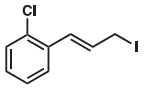
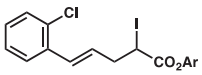
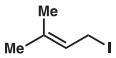
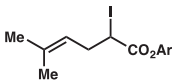
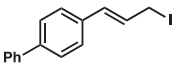
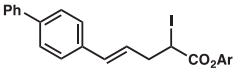
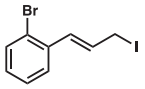
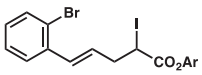
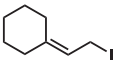
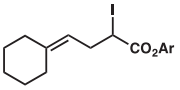
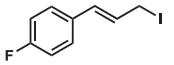
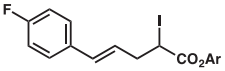
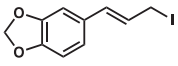
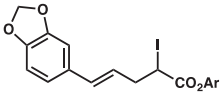
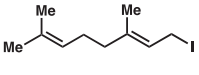
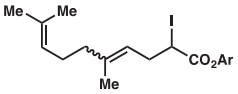
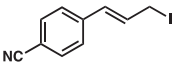
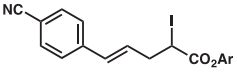
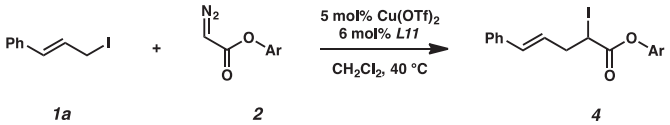
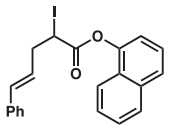
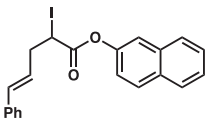
Allylic Iodide	Product	Allylic Iodide	Product	Allylic Iodide	Product
 1a	 4a 86% yield, >95:5 rr	 1f	 4f 78% yield, 93:7 rr	 1j	 4j 82% yield, >95:5 rr
 1b	 4b 82% yield, >95:5 rr	 1g	 4g 88% yield, >95:5 rr	 1k	 4k 74% yield, >95:5 rr
 1c	 4c 78% yield, >95:5 rr	 1h	 4h 78% yield, >95:5 rr	 1l	 4l 42% yield, 94:6 rr
 1d	 4d 84% yield, >95:5 rr	 1i	 4i 45% yield, >95:5 rr	 1m	 4m 74% yield, >95:5 rr E:Z = 2:1
 1e	 4e 66% yield, >95:5 rr				

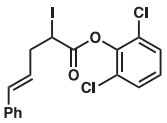
Table 3
Aryl α-diazoesters scope of copper-catalyzed [1,2]-rearrangement of iodonium ylides.



1a 2 4

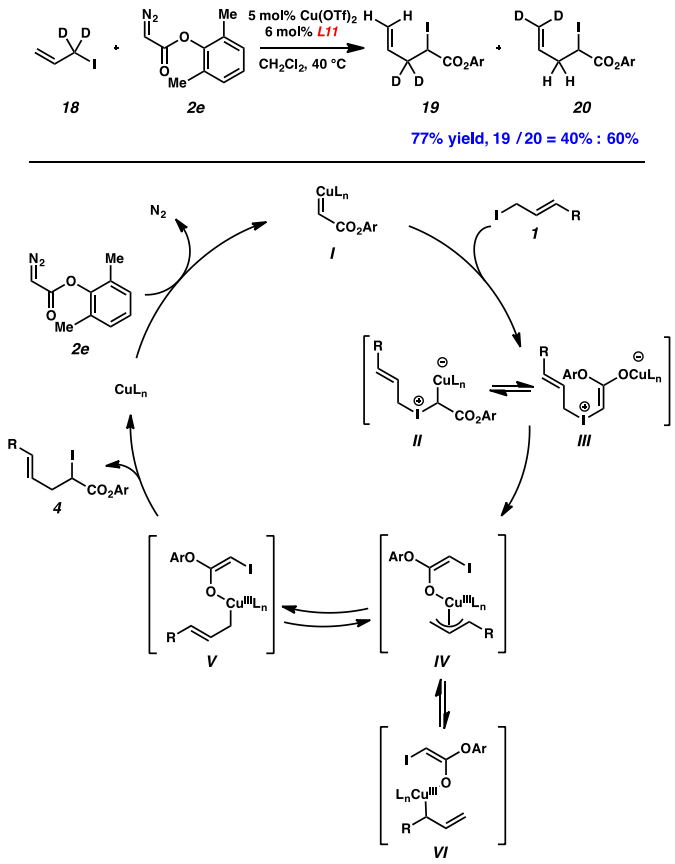

4n 76% yield, >95:5 rr


4o 70% yield, >95:5 rr


4p 61% yield, 95:5 rr

examining the steric and electronic properties of these structurally similar yet unique ligands. In the presence of dibromo-bipyridine ligand **L5**, we propose the selective formation of [2,3]-rearrangement product **3** via a concerted rearrangement mechanism. We hypothesize that this reaction pathway is preferred for ligands such as **L5** that are poor σ-donors. Electron-deficient ligands decrease the reactivity of copper-coordinated iodonium ylide ***II***-***III*** toward oxidative addition,[16] thus favoring the formation of the [2,3]-rearrangement product through a concerted mechanism. On the other hand, an electron-rich ligand such as dimethoxy-bipyridine **L11** would facilitate oxidative addition of copper-coordinated iodonium ylide ***II***-***III*** to form a copper(III) complex such as ***IV***-***VI***. In addition, the sterically unhindered dimethoxy-bipyridine ligand **L11** may favor oxidative addition more than the

Please cite this article in press as: Xu B, et al., Copper-catalyzed [1,2]-rearrangements of allylic iodides and aryl α-diazoacetates, Tetrahedron (2017), http://dx.doi.org/10.1016/j.tet.2017.01.048



Scheme 6. Mechanistic studies.

electronically similar yet sterically more bulky dimethoxybipyridine ligands **L4** and **L13**, due to a more congested coordination sphere of the oxidative addition product.[15] The ligand's steric bulk can therefore impact the relative rates of oxidative addition, which accounts for the lower regioisomeric ratio observed with the less bulky ligands **L4** and **L13** (Table 1, entries 5 and 14).

The ester functionality of α-diazoesters **2a-2e** also impacts the regioselectivity of the copper-catalyzed rearrangement. Although the structures of these esters most likely do not have a drastic effect on the preference for a concerted rearrangement or a stepwise oxidative addition/reductive elimination mechanism, we surmise that the steric bulk of the ester group can effect the stability of the competing isomers of copper(III) complexes such as ***IV-VI***.[17] A sterically bulky ester such as 2,6-dimethyl-phenyl α-diazoester **2e** may favor σ-complex **V** over the more congested σ-complex **VI**, which would lead to the formation of [1,2]-rearrangement product **4** after reductive elimination.

3. Conclusion

We have developed a highly selective copper-catalyzed [1,2]-rearrangement of iodonium ylides, in which the regioselectivity is dictated by the steric and electronic properties of the bipyridine ligand and the steric properties of the α-diazoester. Remarkably, we have been able to reverse the regioselectivity of iodonium ylide rearrangements with the use of alternate bipyridine ligands. Originally selective for a [2,3]-rearrangement with **L5**, the outcome of the reaction can be altered to selectively form the [1,2]-rearrangement product with the use of bipyridine **L11**. This drastic change in product distribution upon fine-tuning of ligand structure represents a powerful approach to control other classes of sigmatropic rearrangements. In addition, the combination of copper-catalyzed diazo decomposition and copper(I)-(III) chemistry may represent a new direction in copper catalysis that could lead to the discovery of many new transformations.

4. Experimental section

4.1. General information

All reactions were carried out in capped reaction vials or flasks with magnetic stirring unless otherwise indicated. Commercially obtained reagents were used as received. Solvents were dried by passage through an activated alumina column under argon. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Silica gel (particle size 0.032–0.063 mm) purchased from SiliCycle was used for flash chromatography. ^{1}H NMR spectra were recorded on Varian Inova-400 or Varian Inova-500 spectrometers. ^{13}C NMR spectra were recorded on Varian Inova-400 spectrometers. Data for ^{1}H NMR spectra are reported relative to chloroform as an internal standard (7.26 ppm) and are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are reported relative to chloroform as an internal standard (77.0 ppm) and are reported in terms of chemical shift (δ ppm). Melting points were measured on a Fisher ScientificTM melting point apparatus (12–144). APCI-LRMS data were measured using an AB Sciex QTRAP-4500 LC/MS.

4.2. Synthesis of substituted bipyridines

4.2.1. 6,6'-di-tert-Butyl-2,2'-bipyridine (*L3*)[18]

A 100 mL oven-dried flask was charged with $Ni(PPh_3)_2Br_2$ (520 mg, 0.7 mmol), zinc dust (137 mg, 2.1 mmol), tetrabutylammonium bromide (676 mg, 2.1 mmol) and 6-*tert*-butyl-2-chloro-pyridine (**5a**, 1.2 g, 7 mmol). After the flask was evacuated and refilled with argon, dry DMF (20 mL) was added and the suspension was stirred at 55 °C. After the reaction was complete (monitored by TLC), the mixture was filtered through Celite and washed with Et_2O (200 mL). The combined solution was then washed with water (100 mL x 3) and brine (100 mL), dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography on silica gel (Hexane/EtOAc = 30:1, v/v) to afford desired 6,6'-*di-tert*-Butyl-2,2'-bipyridine as a white solid, 488 mg, 52% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32 (d, J = 7.5 Hz, 2H, ArH), 7.72 (t, J = 7.5 Hz, 2H, ArH), 7.32 (d, J = 7.5 Hz, 2H, ArH), 1.42 (s, 18H, 2^{t}Bu).

4.2.2. 6,6′-Dimethoxy-2,2'-bipyridine (*L4*)[4]

Following the same procedure for the synthesis of **L3**, 6,6'-dimethoxy-2,2'-bipyridine was obtained as a white solid, 550 mg (starting from 10 mmol **5b**), 51% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, J = 7.5 Hz, 2H, ArH), 7.69 (t, J = 8.0 Hz, 2H, ArH), 6.76 (d, J = 8.0 Hz, 2H, ArH), 4.04 (s, 6H, 2OCH_3).

4.2.3. 6,6′-Bis(trifluoromethyl)-2,2'-bipyridine (*L6*)[19]

Following the same procedure for the synthesis of **L3**, 6,6′-Bis(trifluoromethyl)-2,2'-bipyridine was obtained as a white solid, 360 mg (starting from 3 mmol **5c**), 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.73 (d, J = 8.0 Hz, 2H, ArH), 8.03 (t, J = 8.0 Hz, 2H, ArH), 7.74 (d, J = 7.5 Hz, 2H, ArH).

4.2.4. 5,5′-Dimethoxy-2,2'-bipyridine (*L13*)[5]

A 100 mL round-bottom flask was charged with $NiCl_2 \cdot 6H_2O$

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(40 mg, 0.15 mmol) and DMF (10 mL). The resulting solution was stirred and heated to 40 °C. Then, 2-chloro-5-methoxypyridine (**6**, 3 mmol), anhydrous LiCl (130 mg, 3 mmol), and zinc dust (230 mg, 3.6 mmol) were added. When the temperature rose to 50 °C, a grain of iodine crystal and two drops of acetic acid were added to the mixture. The mixture was stirred at 55–60 °C until complete conversion of 2-halopyridine (monitored by TLC). To the cooled reaction mixture was added 1 N HCl aqueous solution (5 mL) to consume the remaining zinc dust. The resulting mixture was made alkaline with aqueous ammonia (25%) and diluted with CH_2Cl_2. The organic layers were collected, dried over anhydrous Na_2SO_4, concentrated, and purified by column chromatography on silica gel (Hexane/EtOAc = 10:1, v/v) to afford desired 5,5'-dimethoxy-2,2'-bipyridine as a light yellow solid, 130 mg, 40% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.33 (d, J = 3.0 Hz, 2H, ArH), 8.24 (d, J = 9.0 Hz, 2H, ArH), 7.30 (dd, J_1 = 9.0 Hz and J_2 = 3.0 Hz, 2H, ArH), 3.91 (s, 6H, $2OCH_3$).

4.3. Synthesis of α-diazoesters

NB: For safety considerations, during the synthesis of a-diazo-compounds, TsN_3 or NaN_3 should not be in contact with metals. Special precautions should also be taken when diazo- or azide-compounds are subjected to heat or high pressure.

4.3.1. Benzyl 2-diazoacetate (**2a**)[6]

A 250 mL oven-dried flask was charged with benzyl 3-oxobutanoate (**7**, 5.8 g, 30 mmol), triethylamine (4.5 g, 45 mmol) and dry acetonitrile (80 mL), followed by slow addition of 4-methylbenzenesulfonyl azide (7.7 g, 39 mmol). The mixture was stirred at room temperature until the reaction was complete (monitored by TLC). An aqueous solution of LiOH (100 mmol in 60 mL H_2O) was slowly added. The suspension was stirred at room temperature for 6 h and extracted by Et_2O (100 mL x 3). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography on silica gel (Hexane/EtOAc = 15:1, v/v) to afford **2a** as an orange oil, 4.3 g, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.30 (m, 5H, ArH), 5.21 (s, 2H, CH_2), 4.80 (brs, 1H, CHN_2).

4.3.2. Phenyl 2-diazoacetate (**2b**)[7]

Phenol (940 mg, 10 mmol) and pyridine (1.58 g, 20 mmol) were dissolved in acetonitrile (20 mL) and bromoacetyl bromide (3.03 g, 15 mmol) was slowly added at 0 °C. After stirring for 10 min at this temperature, the reaction was quenched with H_2O. The solution was extracted with CH_2Cl_2 (50 mL x 3). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4 and concentrated to afford a residue, which was dissolved with *N,N'*-ditosylhydrazine (6.8 g, 20 mmol) in THF (50 mL). The mixture was cooled to 0 °C, followed by a slow addition of DBU (7.6 g, 50 mmol). The mixture was stirred at 0 °C until the reaction was complete (monitored by TLC). The reaction was quenched by saturated $NaHCO_3$ solution, and extracted with Et_2O (100 mL x 3). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4, concentrated and purified by flash column chromatography on silica gel (Hexane/EtOAc = 15:1, v/v) to afford **2b** as a yellow semi-oil, 0.9 g, 56% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42–7.35 (m, 2H, ArH), 7.26–7.21 (m, 1H, ArH), 7.16–7.11 (m, 2H, ArH), 4.97 (brs, 1H, CHN_2).

4.3.3. Naphthalen-1-yl 2-diazoacetate (**2c**)

Following the same procedure for the synthesis of **2b**, **2c** was obtained as a yellow solid, mp: 76–77 °C, 975 mg, 46% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95–7.86 (m, 2H, ArH), 7.77 (d, J = 8.4 Hz, 1H, ArH), 7.58–7.51 (m, 2H, ArH), 7.49 (t, J = 8.0 Hz, 1H, ArH), 7.33 (d, J = 7.2 Hz, 1H, ArH), 5.15 (brs, 1H, CHN_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2, 134.6, 128.0, 127.0, 126.5, 126.4, 126.1, 125.3, 121.1, 118.2, 46.8. IR (neat, cm^{-1}): 3122, 2127, 1684, 1336, 1210, 1080, 924, 783. APCI-MS calcd for $[C_{12}H_9N_2O_2, M + H]^+$: 213.07, Found 213.11.

4.3.4. Naphthalen-2-yl 2-diazoacetate (**2d**)

Following the same procedure for the synthesis of **2b**, **2d** was obtained as a yellow solid, mp: 55–56 °C, 1.1 g, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.79 (m, 3H, ArH), 7.62 (d, J = 2.0 Hz, 1H, ArH), 7.53–7.44 (m, 2H, ArH), 7.28 (dd, J_1 = 8.8 Hz and J_1 = 2.0 Hz, 1H, ArH), 5.03 (brs, 1H, CHN_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 133.7, 131.4, 129.4, 127.7, 127.6, 126.6, 125.7, 121.1, 118.6, 46.9. IR (neat, cm^{-1}): 3114, 2112, 1697, 1362, 1207, 1145, 970, 724. $[C_{12}H_9N_2O_2, M + H]^+$: 213.07, Found 213.12.

4.3.5. 2,6-Dimethylphenyl 2-diazoacetate (**2e**)

Following the same procedure for the synthesis of **2b**, **2e** was obtained as a yellow solid, mp: 80–81 °C, 684 mg, 36% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08–7.05 (m, 3H, ArH), 5.02 (brs, 1H, CHN_2), 2.20 (s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 130.6, 128.5, 126.0, 46.2, 16.3. IR (neat, cm^{-1}): 3124, 2133, 1693, 1371, 1182, 1148, 970, 729. APCI-MS calcd for $[C_{10}H_{11}N_2O_2, M + H]^+$: 191.08, Found 191.13.

4.3.6. 2,6-Dichlorophenyl 2-diazoacetate (**2f**)

Following the same procedure for the synthesis of **2b**, **2f** was obtained as a light yellow oil, 808 mg, 35% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.0 Hz, 2H, ArH), 7.15 (t, J = 8.0 Hz, 2H, ArH), 5.12 (brs, 1H, CHN_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 129.4, 128.6, 127.3, 46.8. IR (neat, cm^{-1}): 3123, 2115, 1700, 1443, 1361, 1338, 1196, 1127, 768. APCI-MS calcd for $[C_8H_5Cl_2N_2O_2, M + H]^+$: 230.97, Found 230.99.

4.4. Synthesis of allylic iodides

4.4.1. (E)-(3-Iodoprop-1-en-1-yl)benzene (**1a**)[3]

A 100 mL flask was charged with $Pd(PPh_3)Cl_2$ (70 mg, 0.1 mmol) and CuI (38 mg, 0.2 mmol). After the flask was evacuated and refilled with argon, NEt_3 (20 mL) was added and the suspension was stirred at room temperature. A solution of iodobenzene (**10a**, 2.04 g, 10 mmol) and propargyl alcohol (616 mg, 11 mmol) in NEt_3 (10 mL) was added to the suspension. After the reaction was complete (monitored by TLC), the mixture was filtered through a plug of Celite and washed with EtOAc (20 mL x 3). The combined solution was concentrated and purified by column chromatography on silica gel (Hexane/EtOAc = 3:1, v/v) to afford 3-phenylprop-2-yn-1-ol (**11a**, 1.24 g, 94% yield) as a yellow oil.

A 50 mL oven-dried flask was charged with $LiAlH_4$ (190 mg, 5 mmol) and dry THF (15 mL). The mixture was cooled to 0 °C, followed by a slow addition of **11a** (660 mg, 5 mmol, in 5 mL THF). The mixture was stirred at room temperature until the reaction was complete (monitored by ^{1}H NMR). The mixture was then cooled to 0 °C and carefully quenched by H_2O (1.2 mL), 15% NaOH (1.2 mL) and H_2O (1.2 mL) to afford a suspension, which was filtered through Celite and washed with EtOAc (30 mL x 3). The combined solution was concentrated and purified by column chromatography on silica gel (Hexane/EtOAc = 3:1, v/v) to afford (*E*)-3-phenylprop-2-en-1-ol (**12a**, 636 mg, 95% yield) as a colorless oil.

A 50 mL flask was charged with PPh_3 (786 mg, 3 mmol), imidazole (224 mg, 3.3 mmol) and CH_2Cl_2 (10 mL). To the stirring solution was added iodine (750 g, 3 mmol) in portions. After 30 min, the flask was wrapped with aluminum foil and cooled by ice bath, followed by slow addition of **12a** (402 mg, 3 mmol, in 5 mL CH_2Cl_2). After the reaction was complete (monitored by ^{1}H NMR), the mixture was filtered through a plug of silica gel, which was then

Please cite this article in press as: Xu B, et al., Copper-catalyzed [1,2]-rearrangements of allylic iodides and aryl α-diazoacetates, Tetrahedron (2017), http://dx.doi.org/10.1016/j.tet.2017.01.048

washed with Hexane/EtOAc (v/v = 10:1, 20 mL x 2). The combined solution was concentrated and purified by flash column chromatography on silica gel (Hexane/EtOAc = 30:1, v/v) to afford **1a** as a bright yellow solid, 622 mg, 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39–7.35 (m, 2H, ArH), 7.34–7.30 (m, 2H, ArH), 7.28–7.23 (m, 1H, ArH), 6.60 (d, J = 15.5 Hz, 1H, ArCH =), 6.44 (dt, J_1 = 15.5 Hz and J_2 = 8.5 Hz, 1H, =C<u>H</u>CH$_2$), 4.12 (d, J = 8.5 Hz, 2H, CH_2I).

*4.4.2. (E)-2-(3-Iodoprop-1-en-1-yl)naphthalene (**1b**)*[3]

Following the same procedure for the synthesis of **1a**, **1b** was obtained as a yellow solid, 723 mg, 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82–7.76 (m, 3H, ArH), 7.73 (s, 1H, ArH), 7.59–7.55 (m, 1H, ArH), 7.50–7.42 (m, 2H, ArH), 6.76 (d, J = 15.5 Hz, 1H, ArCH =), 6.57 (dt, J_1 = 15.5 Hz and J_2 = 8.0 Hz, 1H, =C<u>H</u>CH$_2$), 4.18 (d, J = 8.0 Hz, 2H, CH_2I).

*4.4.3. (E)-4-(3-Iodoprop-1-en-1-yl)-1,1'-biphenyl (**1c**)*[3]

Following the same procedure for the synthesis of **1a**, **1c** was obtained as a yellow solid, 816 mg, 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62–7.54 (m, 4H, ArH), 7.47–7.41 (m, 4H, ArH), 7.37–7.32 (m, 1H, ArH), 6.64 (d, J = 15.5 Hz, 1H, ArCH =), 6.49 (dt, J_1 = 15.5 Hz and J_2 = 8.0 Hz, 1H, =C<u>H</u>CH$_2$), 4.15 (dd, J_1 = 8.5 Hz and J_2 = 1.0 Hz, 2H, CH_2I).

*4.4.4. (E)-1-Fluoro-4-(3-iodoprop-1-en-1-yl)benzene (**1d**)*[3]

Following the same procedure for the synthesis of **1a**, **1d** was obtained as a yellow solid, 676 mg, 86% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37–7.30 (m, 2H, ArH), 7.05–6.97 (m, 2H, ArH), 6.56 (d, J = 15.5 Hz, 1H, ArCH =), 6.36 (dt, J_1 = 15.5 Hz and J_2 = 8.0 Hz, 1H, =C<u>H</u>CH$_2$), 4.10 (dd, J_1 = 8.0 Hz and J_2 = 1.0 Hz, 2H, CH_2I).

*4.4.5. (E)-4-(3-Iodoprop-1-en-1-yl)benzonitrile (**1e**)*[3]

Following the same procedure for the synthesis of **1a**, **1e** was obtained as a yellow solid, 726 mg, 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J = 8.5 Hz, 2H, ArH), 7.44 (d, J = 8.5 Hz, 2H, ArH), 6.62–6.51 (m, 2H, CH=CH), 4.09 (d, J = 7.0 Hz, 2H, CH_2I).

*4.4.6. (E)-1-Fluoro-3-(3-iodoprop-1-en-1-yl)benzene (**1f**)*[3]

Following the same procedure for the synthesis of **1a**, **1f** was obtained as a yellow solid, 652 mg, 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30–7.23 (m, 1H, ArH), 7.15–7.09 (m, 1H, ArH), 7.08–7.01 (m, 1H, ArH), 6.97–6.90 (m, 1H, ArH), 6.55 (d, J = 15.5 Hz, 1H, ArCH =), 6.43 (dt, J_1 = 15.5 Hz and J_2 = 8.0 Hz, 1H, =C<u>H</u>CH$_2$), 4.08 (d, J = 8.0 Hz, 2H, CH_2I).

*4.4.7. (E)-1-Chloro-2-(3-iodoprop-1-en-1-yl)benzene (**1g**)*

Following the same procedure for the synthesis of **1a**, **1g** was obtained as a yellow solid, mp: 28–29 °C, 734 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (dd, J_1 = 7.6 Hz and J_2 = 2.0 Hz, 1H, ArH), 7.35 (dd, J_1 = 7.6 Hz and J_2 = 2.0 Hz, 1H, ArH), 7.25–7.17 (m, 2H, ArH), 6.99 (d, J = 15.6 Hz, 1H, ArCH =), 6.44 (dt, J_1 = 15.6 Hz and J_2 = 8.0 Hz, 1H, =C<u>H</u>CH$_2$), 4.13 (dd, J_1 = 8.0 Hz and J_2 = 1.5 Hz, 2H, CH_2I); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.9, 133.1, 129.7, 129.5, 129.1, 128.8, 126.9, 126.8, 6.1. IR (neat, cm^{-1}): 3040, 1468, 1440, 1146, 1035, 959, 749. APCI-MS calcd for [C_9H_9ClI, M + H]$^+$: 278.94, Found 278.96.

*4.4.8. (E)-1-Bromo-2-(3-iodoprop-1-en-1-yl)benzene (**1h**)*

Following the same procedure for the synthesis of **1a**, **1h** was obtained as a yellow solid, mp: 31–32 °C, 833 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–7.49 (m, 2H, ArH), 7.30–7.24 (m, 1H, ArH), 7.14–7.08 (m, 1H, ArH), 6.94 (d, J = 15.2 Hz, 1H, ArCH =), 6.40 (dt, J_1 = 15.6 Hz and J_2 = 8.0 Hz, 1H, =C<u>H</u>CH$_2$), 4.13 (dd, J_1 = 8.0 Hz and J_2 = 1.5 Hz, 2H, CH_2I); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.6, 133.0, 131.4, 129.6, 129.3, 127.5, 127.0, 123.7, 5.9. IR (neat, cm^{-1}): 3038, 1464, 1435, 1145, 1021, 957, 747. APCI-MS calcd for [C_9H_9BrI, M + H]$^+$: 322.89, Found 322.90.

*4.4.9. (E)-5-(3-Iodoprop-1-en-1-yl)benzo[d][1,3]dioxole (**1i**)*

Following the same procedure for the synthesis of **1a**, **1i** was obtained as a yellow solid, mp: 49–50 °C, 622 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.91 (d, J = 2.0 Hz, 1H, ArH), 6.80 (dd, J_1 = 8.0 Hz and J_2 = 1.6 Hz, 1H, ArH), 6.75 (d, J = 8.0 Hz, 1H, ArH), 6.52 (d, J = 15.6 Hz, 1H, ArCH =), 6.26 (dt, J_1 = 15.6 Hz and J_2 = 8.0 Hz, 1H, =C<u>H</u>CH$_2$), 5.96 (s, 2H, OCH_2O), 4.10 (dd, J_1 = 8.0 Hz and J_2 = 1.5 Hz, 2H, CH_2I); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 147.7, 132.9, 130.3, 125.1, 121.6, 108.3, 105.7, 101.2, 7.4. IR (neat, cm^{-1}): 2893, 1500, 1486, 1443, 1248, 1038, 928. APCI-MS calcd for [$C_{10}H_{10}IO_2$, M + H]$^+$: 288.97, Found 288.97.

*4.4.10. (E)-(4-Iodobut-2-en-2-yl)benzene (**1j**)*[20]

Neat triethyl phosphonoacetate (2.24 g, 10 mmol) was added to a suspension of NaH (60%, 400 mg, 10 mmol) in dry THF (50 mL). After 30 min, a solution of acetophenone (960 mg, 8 mmol) in dry THF (10 mL) was added, and the resulting mixture was stirred overnight. The reaction was quenched by the addition of water (50 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 × 50 mL). The combined organic solutions were dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography on silica gel (Hexane/EtOAc = 10:1, v/v) to afford ethyl (*E*)-3-phenylbut-2-enoate (**16a**) as a colorless oil, 1.25 g, 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50–7.45 (m, 2H, ArH), 7.40–7.33 (m, 3H, ArH), 6.15–6.11 (m, 1H, CH =), 4.22 (q, J = 7.0 Hz, 2H, OCH_2), 2.58 (d, J = 1.0 Hz, 3H, CH_3), 1.32 (t, J = 7.0 Hz, 3H, CH2C<u>H</u>$_3$).

To a cooled (−78 °C) solution of **16a** (950 mg, 5 mmol) in CH_2Cl_2 (30 mL) was added DIBAL-H (1.2 M in toluene, 9 mL, 11 mmol). When the reduction was complete, the reaction was quenched by $Na_2SO_4 \cdot 10H_2O$ (4.8 g, 15 mmol). When a precipitate appeared, the mixture was diluted with Et_2O (50 mL) and stirred for 1 h. Solids were filtered off and washed with Et_2O (50 mL x 3). After drying over anhydrous Na_2SO_4, the solution was concentrated to afford (*E*)-3-phenylbut-2-en-1-ol (**17a)** as a crude oil, which underwent an iodination to afford desired **1j** as a yellow oil, 460 mg (2 mmol scale), 89% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50–7.30 (m, 5H, ArH), 6.17 (t, J = 9.0 Hz, 1H, CH), 4.19 (d, J = 9.0 Hz, 2H, CH_2I), 2.12 (s, 3H, CH_3).

*4.4.11. 1-Iodo-3-methylbut-2-ene (**1k**)*[3]

Following the same iodination procedure for the synthesis of **1a**, **1k** was obtained from commercially available 3-methylbut-2-en-1-ol (**13**) as a light yellow oil, 764 mg (5 mmol scale), 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.56–5.49 (m, 1H, CH), 3.93 (d, J = 9.0 Hz, 1H, ArH), 1.73 (s, 3H, CH_3), 1.65 (s, 3H, CH_3).

*4.4.12. (2-Iodoethylidene)cyclohexane (**1l**)*[3]

Following the same procedure for the synthesis of **1j**, **1l** was obtained as light yellow oil, 448 mg (2 mmol scale), 95% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.48 (t, J = 8.5 Hz, 1H, CH =), 3.95 (d, J = 8.0 Hz, 2H, CH_2I), 2.19–2.14 (m, 2H, CH_2), 2.10–2.06 (m, 2H, CH_2), 1.58–1.50 (m, 6H, 3CH_2).

*4.4.13. (E)-1-Iodo-3,7-dimethylocta-2,6-diene (**1m**)*[10]

Following the same iodination procedure for the synthesis of **1a**, **1m** was obtained from commercially available geraniol (**14**) as a light yellow oil, 502 mg (5 mmol scale), 38% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.51 (t, J = 8.4 Hz, 1H, CH =), 5.04 (t, J = 6.8 Hz, 1H, CH =), 3.91 (d, J = 8.8 Hz, 2H, CH_2I), 2.12–1.94 (m, 4H, 2CH_2), 1.66 (s, 3H, CH_3), 1.62 (s, 3H, CH_3), 1.58 (s, 3H, CH_3).

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4.5. Copper-catalyzed [1,2]-rearrangement of iodonium ylide

Typical procedure: A 8 mL reaction vial was charged with $Cu(OTf)_2$ (7.2 mg, 0.02 mmol) and 4,4'-dimethoxy-2,2'-bipyridine (5.2 mg, 0.024 mmol). The vial was degassed and refilled with argon. After CH_2Cl_2 (4 mL) was added, the mixture was stirred at room temperature for 2 h. Then the mixture was stirred in a 40 °C oil bath, followed by addition of allylic iodides **1** (0.4 mmol) and α-diazoester **2** (0.48 mmol) in sequence. The mixture was stirred at 40 °C until the reaction was complete (monitored by TLC). The mixture was then concentrated and purified by flash column chromatography on silica gel (PE/EtOAc = 30:1) to afford [1,2]-rearrangement products **4**.

4.5.1. 2,6-Dimethylphenyl (E)-2-iodo-5-phenylpent-4-enoate (**4a**)

White solid, mp: 58–59 °C, 86% yield, >95:5 rr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.29 (m, 4H, ArH), 7.28–7.23 (m, 1H, ArH), 7.09–7.00 (m, 3H, ArH), 6.59 (d, J = 16.0 Hz, 1H, ArCH =), 6.19 (dt, J_1 = 16.0 Hz and J_2 = 7.2 Hz, 1H, =C<u>H</u>CH$_2$), 4.68 (dd, J_1 = 9.2 Hz and J_2 = 6.4 Hz, 1H, CHI), 3.24–2.94 (m, 2H, CH_2), 2.17 (brs, 6H, 2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 147.6, 136.6, 134.4, 130.4, 128.8, 128.6, 127.8, 126.3, 126.2, 125.8, 39.6, 17.5, 16.5. IR (neat, cm^{-1}): 3026, 2923, 1747, 1162, 1108, 965, 769, 744, 691. APCI-MS calcd for $[C_{19}H_{20}IO_2, M + H]^+$: 407.05, Found 407.05.

4.5.2. 2,6-Dimethylphenyl (E)-2-iodo-5-(naphthalen-2-yl)pent-4-enoate (**4b**)

White solid, mp: 110–112 °C, 82% yield, >95:5 rr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–7.76 (m, 3H, ArH), 7.72 (s, 1H, ArH), 7.57 (dd, J_1 = 8.8 Hz and J_2 = 1.6 Hz, 1H, ArH), 7.50–7.42 (m, 2H, ArH), 7.07–7.00 (m, 3H, ArH), 6.75 (d, J = 16.0 Hz, 1H, ArCH =), 6.32 (dt, J_1 = 16.0 Hz and J_2 = 7.2 Hz, 1H, =C<u>H</u>CH$_2$), 4.71 (dd, J_1 = 9.2 Hz and J_2 = 6.4 Hz, 1H, CHI), 3.29–3.00 (m, 2H, CH_2), 2.16 (brs, 6H, 2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 147.6, 134.5, 134.0, 133.5, 133.0, 130.4, 128.8, 128.3, 128.0, 127.7, 126.4, 126.3, 126.2, 126.1, 126.0, 123.2, 39.8, 17.4, 16.5. IR (neat, cm^{-1}): 3053, 2922, 1747, 1472, 1161, 1108, 964, 809, 770, 744. APCI-MS calcd for $[C_{23}H_{22}IO_2, M + H]^+$: 457.07, Found 457.06.

4.5.3. 2,6-Dimethylphenyl (E)-5-([1,1'-biphenyl]-4-yl)-2-iodopent-4-enoate (**4c**)

White solid, mp: 138–140 °C, 78% yield, >95:5 rr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.54 (m, 4H, ArH), 7.47–7.41 (m, 4H, ArH), 7.38–7.32 (m, 1H, ArH), 7.08–7.00 (m, 3H, ArH), 6.63 (d, J = 16.0 Hz, 1H, ArCH =), 6.24 (dt, J_1 = 16.0 Hz and J_2 = 7.2 Hz, 1H, =C<u>H</u>CH$_2$), 4.69 (dd, J_1 = 9.2 Hz and J_2 = 6.4 Hz, 1H, CHI), 3.25–2.96 (m, 2H, CH_2), 2.18 (brs, 6H, 2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 147.6, 140.6, 140.5, 135.6, 133.9, 130.4, 128.8, 128.7, 127.4, 127.3, 126.9, 126.7, 126.2, 125.9, 39.7, 17.5, 16.6. IR (neat, cm^{-1}): 3027, 1747, 1484, 1161, 1109, 968, 758, 697. APCI-MS calcd for $[C_{25}H_{24}IO_2, M + H]^+$: 483.08, Found 483.08.

4.5.4. 2,6-Dimethylphenyl (E)-5-(4-fluorophenyl)-2-iodopent-4-enoate (**4d**)

White solid, mp: 77–78 °C, 84% yield, >95:5 rr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.29 (m, 2H, ArH), 7.08–6.97 (m, 5H, ArH), 6.55 (d, J = 16.0 Hz, 1H, ArCH =), 6.10 (dt, J_1 = 16.0 Hz and J_2 = 7.2 Hz, 1H, =C<u>H</u>CH$_2$), 4.66 (dd, J_1 = 9.2 Hz and J_2 = 6.4 Hz, 1H, CHI), 3.21–293 (m, 2H, CH_2), 2.15 (brs, 6H, 2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 162.4 (d, J = 246.0 Hz), 147.6, 133.2, 132.8 (d, J = 3.4 Hz), 130.3, 128.8, 127.8 (d, J = 8.0 Hz), 126.2, 125.5 (d, J = 2.3 Hz), 115.5 (d, J = 21.6 Hz), 39.5, 17.4, 16.5. IR (neat, cm^{-1}): 3039, 2922, 1747, 1600, 1508, 1473, 1229, 1159, 1109, 967, 771. APCI-MS calcd for $[C_{19}H_{19}FIO_2, M + H]^+$: 425.04, Found 425.04.

4.5.5. 2,6-Dimethylphenyl (E)-5-(4-cyanophenyl)-2-iodopent-4-enoate (**4e**)

Colorless semi-oil, 66% yield, >95:5 rr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8.4 Hz, 2H, ArH), 7.44 (d, J = 8.4 Hz, 2H, ArH), 7.07–7.01 (m, 3H, ArH), 6.60 (d, J = 16.0 Hz, 1H, ArCH =), 6.33 (dt, J_1 = 16.0 Hz and J_2 = 7.2 Hz, 1H, =C<u>H</u>CH$_2$), 4.70 (dd, J_1 = 8.8 Hz and J_2 = 6.8 Hz, 1H, CHI), 3.25–2.98 (m, 2H, CH_2), 2.15 (brs, 6H, 2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 147.5, 141.0, 132.7, 132.5, 130.2, 130.0, 128.8, 126.7, 126.3, 118.8, 111.0, 39.4, 16.6, 16.5. IR (neat, cm^{-1}): 3036, 2922, 2224, 1746, 1604, 1473, 1161, 1110, 969, 772, 731. APCI-MS calcd for $[C_{20}H_{19}INO_2, M + H]^+$: 432.05, Found 432.06.

4.5.6. 2,6-Dimethylphenyl (E)-5-(3-fluorophenyl)-2-iodopent-4-enoate (**4f**)

Colorless semi-oil, 78% yield, 93:7 rr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.24 (m, 1H, ArH), 7.12 (d, J = 7.6 Hz, 1H, ArH), 7.09–7.01 (m, 4H, ArH), 6.96 (td, J_1 = 8.4 Hz and J_2 = 2.0 Hz, 1H, ArH), 6.56 (d, J = 16.0 Hz, 1H, ArCH =), 6.20 (dt, J_1 = 16.0 Hz and J_2 = 7.2 Hz, 1H, =C<u>H</u>CH$_2$), 4.68 (dd, J_1 = 8.8 Hz and J_2 = 6.4 Hz, 1H, CHI), 3.23–295 (m, 2H, CH_2), 2.16 (brs, 6H, 2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 163.1 (d, J = 244.2 Hz), 147.5, 138.9 (d, J = 7.7 Hz), 133.3 (d, J = 2.6 Hz), 130.3, 130.1 (d, J = 8.4 Hz), 128.8, 127.3, 126.2, 122.2 (d, J = 2.7 Hz), 114.7 (d, J = 21.2 Hz), 112.6 (d, J = 21.5 Hz), 39.4, 17.1, 16.5. IR (neat, cm^{-1}): 2923, 1747, 1609, 1582, 1473, 1446, 1248, 1162, 1109, 967, 770. APCI-MS calcd for $[C_{19}H_{19}FIO_2, M + H]^+$: 425.04, Found 425.04.

4.5.7. 2,6-Dimethylphenyl (E)-5-(2-chlorophenyl)-2-iodopent-4-enoate (**4g**)

Colorless semi-oil, 88% yield, >95:5 rr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.48 (m, 1H, ArH), 7.38–7.33 (m, 1H, ArH), 7.25–7.17 (m, 2H, ArH), 7.07–7.03 (m, 3H, ArH), 6.98 (d, J = 16.0 Hz, 1H, ArCH =), 6.20 (dt, J_1 = 16.0 Hz and J_2 = 7.2 Hz, 1H, =C<u>H</u>CH$_2$), 4.70 (dd, J_1 = 8.4 Hz and J_2 = 6.8 Hz, 1H, CHI), 3.25–3.01 (m, 2H, CH_2), 2.18 (brs, 6H, 2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 147.6, 134.7, 133.0, 130.4, 130.3, 129.8, 128.9, 128.8, 128.7, 126.9, 126.7, 126.2, 39.5, 17.5, 16.6. IR (neat, cm^{-1}): 3041, 2921, 1746, 1470, 1162, 1107, 965, 768, 748. APCI-MS calcd for $[C_{19}H_{19}ClIO_2, M + H]^+$: 441.01, Found 441.01.

4.5.8. 2,6-Dimethylphenyl (E)-5-(2-bromophenyl)-2-iodopent-4-enoate (**4h**)

White solid, mp: 52–53 °C, 78% yield, >95:5 rr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (dd, J_1 = 8.0 Hz and J_2 = 0.8 Hz, 1H, ArH), 7.49 (dd, J_1 = 8.0 Hz and J_2 = 1.6 Hz, 1H, ArH), 7.30–7.24 (m, 1H, ArH), 7.16–7.10 (m, 1H, ArH), 7.08–7.01 (m, 3H, ArH), 6.94 (d, J = 16.0 Hz, 1H, ArCH =), 6.16 (dt, J_1 = 16.0 Hz and J_2 = 7.2 Hz, 1H, =C<u>H</u>CH$_2$), 4.70 (dd, J_1 = 8.4 Hz and J_2 = 6.8 Hz, 1H, CHI), 3.25–3.01 (m, 2H, CH_2), 2.19 (brs, 6H, 2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 147.6, 136.5, 133.0, 130.3, 129.0, 128.9, 128.8, 127.5, 126.9, 126.2, 123.5, 110.0, 39.4, 17.5, 16.6. IR (neat, cm^{-1}): 3042, 2922, 1746, 1466, 1163, 1107, 1022, 964, 769, 749. APCI-MS calcd for $[C_{19}H_{19}BrIO_2, M + H]^+$: 484.96, Found 484.97.

4.5.9. 2,6-Dimethylphenyl (E)-5-(benzo[d][1,3]dioxol-5-yl)-2-iodopent-4-enoate (**4i**)

White solid, mp: 94–96 °C, 45% yield, >95:5 rr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07–7.00 (m, 3H, ArH), 6.90 (d, J = 1.2 Hz, 1H, ArH), 6.79 (dd, J_1 = 8.0 Hz and J_2 = 1.2 Hz, 1H, ArH), 6.75 (d, J = 8.0 Hz, 1H, ArH), 6.49 (d, J = 15.6 Hz, 1H, ArCH =), 6.01 (dt, J_1 = 16.0 Hz and J_2 = 7.2 Hz, 1H, =C<u>H</u>CH$_2$), 5.96 (s, 2H, OCH_2O), 4.64 (dd, J_1 = 8.8 Hz and J_2 = 6.4 Hz, 1H, CHI), 3.19–2.91 (m, 2H, CH_2), 2.16 (brs, 6H, 2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 148.0, 147.6, 147.3, 134.0, 131.1, 130.4, 128.8, 126.2, 124.0, 121.1, 108.3, 105.4, 101.1, 39.5, 17.7, 16.5. IR (neat, cm^{-1}): 2920, 1746, 1503, 1488, 1445,

Please cite this article in press as: Xu B, et al., Copper-catalyzed [1,2]-rearrangements of allylic iodides and aryl α-diazoacetates, Tetrahedron (2017), http://dx.doi.org/10.1016/j.tet.2017.01.048

1249, 1162, 1037, 963, 929, 770. APCI-MS calcd for $[C_{20}H_{20}IO_4, M + H]^+$: 451.04, Found 451.05.

*4.5.10. 2,6-Dimethylphenyl (E)-2-iodo-5-phenylhex-4-enoate (**4j**)*

Colorless semi-oil, 82% yield, >95:5 rr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.36 (m, 2H, ArH), 7.35–7.30 (m, 2H, ArH), 7.29–7.26 (m, 1H, ArH), 7.06–7.01 (m, 3H, ArH), 5.75 (td, J_1 = 7.2 Hz and J_2 = 1.2 Hz, 1H, =CH), 4.67 (dd, J_1 = 8.8 Hz and J_2 = 6.8 Hz, 1H, CHI), 3.27–2.96 (m, 2H, CH_2), 2.16 (brs, 6H, $2CH_3$), 2.10 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 147.6, 143.0, 139.2, 130.4, 128.8, 128.3, 127.2, 126.2, 125.7, 124.1, 35.8, 17.7, 16.5, 16.4. IR (neat, cm^{-1}): 2920, 1747, 1473, 1157, 1108, 768, 756, 696. APCI-MS calcd for $[C_{20}H_{22}IO_2, M + H]^+$: 421.07, Found 421.09.

*4.5.11. 2,6-Dimethylphenyl 2-iodo-5-methylhex-4-enoate (**4k**)*

Colorless oil, 74% yield, >95:5 rr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08–7.02 (m, 3H, ArH), 5.20–5.12 (m, 1H, =CH), 4.53 (dd, J_1 = 9.6 Hz and J_2 = 6.0 Hz, 1H, CHI), 3.06–2.73 (m, 2H, CH_2), 2.19 (brs, 6H, $2CH_3$), 1.71 (s, 3H, CH_3), 1.67 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 147.6, 136.7, 130.4, 128.7, 126.1, 121.0, 35.4, 25.8, 18.2, 18.1, 16.4. IR (neat, cm^{-1}): 2967, 2923, 1750, 1473, 1342, 1164, 1139, 1107, 768. APCI-MS calcd for $[C_{15}H_{20}IO_2, M + H]^+$: 359.05, Found 359.05.

*4.5.12. 2,6-Dimethylphenyl 4-cyclohexylidene-2-iodobutanoate (**4l**)*

Colorless oil, 42% yield, 94:6 rr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07–7.01 (m, 3H, ArH), 5.12 (t, J = 7.2 Hz, 1H, =CH), 4.50 (dd, J_1 = 9.2 Hz and J_2 = 6.4 Hz, 1H, CHI), 3.01–2.75 (m, 2H, CH_2), 2.19 (brs, 6H, $2CH_3$), 2.26–2.00 (m, 4H, $2CH_2$), 1.60–1.48 (m, 6H, $3CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 147.6, 144.7, 130.4, 128.7, 126.1, 117.6, 37.1, 34.4, 29.1, 28.3, 27.6, 26.7, 18.7, 16.5. IR (neat, cm^{-1}): 2925, 2852, 1751, 1473, 1445, 1342, 1164, 1148, 1103, 768. APCI-MS calcd for $[C_{18}H_{24}IO_2, M + H]^+$: 399.08, Found 399.08.

*4.5.13. 2,6-Dimethylphenyl 2-iodo-5,9-dimethyldeca-4,8-dienoate (**4m, E/Z = 2:1**)*

Colorless oil, 74% yield, >95:5 rr, E/Z = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08–7.03 (m, 3H, ArH), 5.18 (t, J = 7.2 Hz, 1H, =CH), 5.14–5.06 (m, 1H, =CH), 4.56–4.48 (m, 1H, CHI), 3.05–2.75 (m, 2H, CH_2), 2.19 (brs, 6H, $2CH_3$), 2.14–1.97 (m, 4H, $2CH_2$), 1.72–1.66 (m, 6H, $2CH_3$), 1.63–1.59 (m, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 147.6, 140.2, 131.7, 130.4, 128.7, 126.1, 123.8, 120.7, 39.7 (35.0), 35.2 (32.2), 26.4 (26.2), 25.7 (23.4), 18.3 (18.4), 17.7 (17.6), 16.6 (16.4), 16.5. IR (neat, cm^{-1}): 2965, 2921, 1751, 1163, 1137, 1105, 768. APCI-MS calcd for $[C_{20}H_{28}IO_2, M + H]^+$: 427.11, Found 427.11.

*4.5.14. Naphthalen-1-yl (E)-2-iodo-5-phenylpent-4-enoate (**4n**)*

Colorless semi-oil, 76% yield, >95:5 rr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.4 Hz, 1H, ArH), 7.87 (d, J = 8.0 Hz, 1H, ArH), 7.76 (d, J = 8.4 Hz, 1H, ArH), 7.52–7.45 (m, 2H, ArH), 7.44–7.40 (m, 2H, ArH), 7.39–7.32 (m, 3H, ArH), 7.32–7.27 (m, 1H, ArH), 7.23 (dd, J_1 = 7.6 Hz and J_2 = 0.8 Hz, 1H, ArH), 6.65 (d, J = 15.6 Hz, 1H, ArCH =), 6.27 (dt, J_1 = 15.6 Hz and J_2 = 7.2 Hz, 1H, =C<u>H</u>CH$_2$), 4.78 (dd, J_1 = 9.2 Hz and J_2 = 6.4 Hz, 1H, CHI), 3.30–3.02 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 146.2, 136.6, 134.6, 134.5, 128.7, 127.9, 127.8, 126.8, 126.6, 126.5, 126.4, 126.3, 125.7, 125.2, 121.1, 117.5, 39.6, 18.1. IR (neat, cm^{-1}): 3055, 3025, 1752, 1598, 1389, 1219, 1144, 1106, 966, 794, 770, 744, 692. APCI-MS calcd for $[C_{21}H_{18}IO_2, M + H]^+$: 429.03, Found 429.03.

*4.5.15. Naphthalen-2-yl (E)-2-iodo-5-phenylpent-4-enoate (**4o**)*

Colorless semi-oil, 70% yield, >95:5 rr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.83 (m, 2H, ArH), 7.81–7.76 (m, 1H, ArH), 7.56 (d, J = 2.0 Hz, 1H, ArH), 7.53–7.45 (m, 2H, ArH), 7.43–7.38 (m, 2H, ArH), 7.37–7.31 (m, 2H, ArH), 7.30–7.26 (m, 1H, ArH), 7.23 (dd, J_1 = 8.8 Hz and J_2 = 2.4 Hz, 1H, ArH), 6.62 (d, J = 15.6 Hz, 1H, ArCH =), 6.22 (dt, J_1 = 16.0 Hz and J_2 = 7.2 Hz, 1H, =C<u>H</u>CH$_2$), 4.66 (dd, J_1 = 8.8 Hz and J_2 = 6.8 Hz, 1H, CHI), 3.22–2.96 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 148.1, 136.7, 134.2, 133.6, 131.6, 129.5, 128.7, 127.8, 127.7, 127.6, 126.7, 126.3, 125.9, 125.8, 120.2, 118.1, 39.4, 18.7. IR (neat, cm^{-1}): 3024, 1747, 1628, 1508, 1207, 1155, 1100, 964, 740. APCI-MS calcd for $[C_{21}H_{18}IO_2, M + H]^+$: 429.03, Found 429.03.

*4.5.16. 2,6-Dichlorophenyl (E)-2-iodo-5-phenylpent-4-enoate (**4p**)*

Colorless oil, 61% yield, 95:5 rr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.31 (m, 6H, ArH), 7.30–7.26 (m, 1H, ArH), 7.16 (t, J = 8.0 Hz, 1H, ArH), 6.59 (d, J = 15.6 Hz, 1H, ArCH =), 6.22 (dt, J_1 = 16.0 Hz and J_2 = 7.2 Hz, 1H, =C<u>H</u>CH$_2$), 4.70 (dd, J_1 = 8.8 Hz and J_2 = 6.8 Hz, 1H, CHI), 3.25–2.95 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.5, 143.3, 136.7, 134.4, 129.1, 128.8, 128.6, 127.7, 127.5, 126.3, 125.7, 39.5, 16.4. IR (neat, cm^{-1}): 3025, 2921, 1762, 1576, 1445, 1226, 1138, 1090, 964, 795, 770, 741, 692. APCI-MS calcd for $[C_{17}H_{14}Cl_2IO_2, M + H]^+$: 446.94, Found 446.95.

4.6. Deuterium study

A 8 mL reaction vial was charged with $Cu(OTf)_2$ (7.2 mg, 0.02 mmol) and 4,4'-dimethoxy-2,2'-bipyridine (5.2 mg, 0.024 mmol). The vial was degassed and refilled with argon. After CH_2Cl_2 (3 mL) was added, the mixture was stirred at room temperature for 1 h. Then the mixture was stirred in a 40 °C oil bath, followed by addition of **18**[3] (0.4 mmol) and **2e** (0.48 mmol) as a mixed solution in CH_2Cl_2 (1 mL). The mixture was stirred at 40 °C until the reaction was complete (monitored by TLC). The mixture was then concentrated and purified by flash column chromatography on silica gel (PE/EtOAc = 30:1) to afford a colorless semi-oil as a mixture of **19** and **20**, 77% yield, **19**: **20** = 40%: 60% (monitored by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08–7.03 (m, 3H, ArH), 5.86–5.76 (m, 1H, CH =), 5.29–5.21 (m, 2(H/D), =C(H/D)$_2$), 4.64–4.57 (m, 1H, CHI), 3.06–2.80 (m, 2(H/D), C(H/D)$_2$), 2.20 (s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 147.6, 134.4 (134.5), 130.4, 128.8, 126.2, 119.3, 40.2, 17.4 (17.2), 16.6. APCI-MS calcd for $[C_{13}H_{14}D_2IO_2, M + H]^+$: 333.03, Found 333.03.

Acknowledgments

Financial support was provided by W. W. Caruth, Jr. Endowed Scholarship, Welch Foundation (I-1748), National Institutes of Health (R01GM102604), National Science Foundation (1150875), and Sloan Research Fellowship.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2017.01.048.

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