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# One-step synthesis of (1-iodovinyl) arenes from trimethylsilyl ethynylarene through iodotrimethylsilane-mediated hydroiodation

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## ABSTRACT

One-step access to (1-iodovinyl) arenes from trimethylsilyl ethynylarenes is described. The method is superior to a conventional multi-step approach, and is enhanced by the Sonogashira reaction that provides ready access to a variety of trimethylsilyl ethynylarenes.

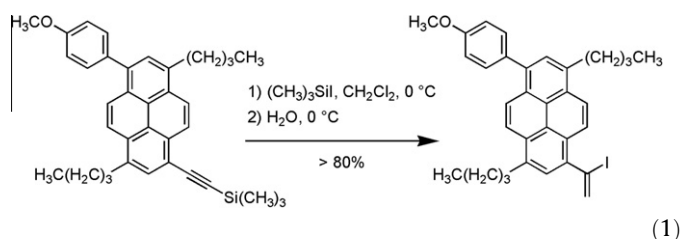
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Vinyl halides are important building blocks in organic synthesis.<sup>1</sup> They are readily converted into various functional groups by halogen–metal exchange and are significant for carbon–carbon bond forming reactions by way of transition-metal catalyzed cross-coupling reactions.<sup>2–4</sup>  $\alpha$ -Vinyl iodides are especially important<sup>5</sup>; the sterically unhindered terminal-olefin and weakly bonded iodine are highly reactive and incredibly useful toward the synthesized complex molecules.<sup>6</sup> Despite the utility of  $\alpha$ -vinyl iodides, their synthetic availability still remains a challenge, because of the inherent difficulty in hydroiodation.<sup>7</sup> The stoichiometric addition of hydrogen iodide (HI) to terminal alkynes is one way to prepare  $\alpha$ -vinyl iodides; however, the generation and transfer of hygroscopic and gaseous HI are inconvenient and difficult to perform.<sup>8–10</sup> As an alternative hydrometalation exists, although it requires several reaction steps.<sup>11</sup>

The pioneering work for synthesis of  $\alpha$ -vinyl iodides from alkynes via addition of HI was reported by Ishii and co-workers: HI was generated in situ from mixing of chlorotrimethylsilane, sodium iodide, and water in acetonitrile.<sup>12</sup> And continuous efforts have aimed to refine this initial method.<sup>13</sup> More recently, Ogawa and co-workers developed a novel hydroiodation of alkynes using an iodine/hydrophosphine binary system.<sup>14</sup> However, there is still room for improvement, especially in terms of its scale;<sup>15</sup> the system worked using 0.2 mmol of starting alkynes.

Recently we have developed the synthesis of unsymmetrically functionalized pyrene derivatives.<sup>16</sup> In the course of our study,

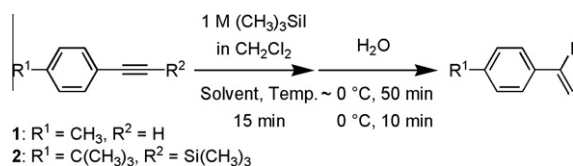
we encountered the unforeseen reaction (Eq. 1). Although we intended the demethylation of the ethereal methyl group, instead  $\alpha$ -vinyl iodide was isolated in high yield. We immediately began exploring the scope and utility of this transformation. Herein we report a simple synthesis of (1-iodovinyl)arenes from both ethynylarenes as well as trimethylsilyl ethynylarenes (Scheme 1). Commercially available TMSI was useful for the direct transformation of both of these functional groups into styrene-type  $\alpha$ -vinyl iodide units in high yield and in one step. Our synthetic protocol does not require operations for desilylation, which is superior to the conventional step-by-step approach.<sup>6,11,14</sup> To the best of our knowledge, so far such a direct synthesis has not been reported. In addition, the protocol is enhanced by Sonogashira reaction that readily makes trimethylsilyl ethynylarenes from aryl halides.<sup>17</sup> Thus, it provides a rapid access to (1-iodovinyl) arenes.



The hydroiodation of 1-ethynyl-4-methylbenzene (**1**) is examined in Table 1.<sup>18,19</sup> TMSI was employed as a 1 M  $\text{CH}_2\text{Cl}_2$  solution, utilization of neat TMSI was not successful.<sup>20</sup> To the mixture of the alkyne (1 mmol) and TMSI (1.2 equiv) was added  $\text{H}_2\text{O}$  (20 equiv) at

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**Scheme 1.** Synthesis of (1-iodovinyl)arenes from **1** and **2**.

low temperature, the reaction was allowed to warm to 0 °C.<sup>21</sup> Entry 1 illustrates a high yielding transformation when the reaction was carried out at –78 °C. The resulting 1-(1-iodovinyl)-4-methylbenzene was isolated in 88% yield and the Markovnikov addition product's structure was confirmed by <sup>1</sup>H NMR. Over the course of the reaction the starting alkyne completely disappeared in TLC monitoring, additionally the corresponding isomer of β-vinyl iodide was not observed. For entries 2–4, the reaction at –45 °C gave a comparable 87% yield, but decreased at –20 °C and 0 °C.<sup>22</sup> The concentration of the reaction was increased in entries 5 (3.3 mL CH<sub>2</sub>Cl<sub>2</sub>) and 6 (1 mL) and gave comparable yields to entry 1 (8 mL). For entry 7, use of CH<sub>3</sub>OH instead of H<sub>2</sub>O resulted in only 20% yield. For entry 8, addition of H<sub>2</sub>O (20 equiv) to the solvent in advance gave 70% yield. Other solvents were explored in entries 9–13, the hydroiodination in toluene and hexane properly occurred with 81% and 71% yields, respectively. On the other hand, methanol, acetonitrile, and THF were not successful giving multi-spots on TLC monitoring. In marked contrast to the pioneering work,<sup>12,23</sup> it is presumed that the non-polar and non-coordinated solvents are best for this transformation.

Next, we examined the reaction of ((4-*tert*-butylphenyl)ethynyl)trimethylsilane (**2**) with TMSI to give α-vinyl iodides (Table 2). Alkyne **2** was prepared via Sonogashira reaction. For entries 1–5, the equivalent of TMSI was varied, 1.5 equiv proved appropriate to consume all of **2** and to achieve a high yielding transformation (entry 3). For entry 2, unreacted alkyne was recovered in 3% when 1.2 equiv TMSI was used. For entries 6–8, the elevated temperatures to –45, –20, and 0 °C were not successful. Other solvents were explored in entries 9–11, toluene, hexane, and acetonitrile gave 74%, 70%, and 30%, respectively. Thus, the optimum conditions in Table 2 are close to those in Table 1.

Table 3 illustrates different trialkylsilyl patterns tested. Like trimethylsilyl ethynylarene, triethyl-, and triisopropylsilyl substrates

**Table 1**  
Evaluation of the reactivity of **1** conducted via Scheme 1<sup>a</sup>

Entry	Solvent	Temp. (°C)	Yield <sup>b</sup> (%)
1	CH <sub>2</sub> Cl <sub>2</sub>	–78	88
2	CH <sub>2</sub> Cl <sub>2</sub>	–45	87
3	CH <sub>2</sub> Cl <sub>2</sub>	–20	74
4	CH <sub>2</sub> Cl <sub>2</sub>	0	49
5 <sup>c</sup>	CH <sub>2</sub> Cl <sub>2</sub>	–78	82
6 <sup>d</sup>	CH <sub>2</sub> Cl <sub>2</sub>	–78	74
7 <sup>e</sup>	CH <sub>2</sub> Cl <sub>2</sub>	–78	20
8	CH <sub>2</sub> Cl <sub>2</sub> /H <sub>2</sub> O (4% v/v)	–78	70
9	Toluene	–78	81
10	Hexane	–78	71
11	CH <sub>3</sub> CN	–20	24
12	CH <sub>3</sub> OH	–78	0
13	THF	–78	0

<sup>a</sup> Reaction conditions: alkyne **1** (1 mmol), solvent (8 mL), 1 M (CH<sub>3</sub>)<sub>3</sub>SiI in CH<sub>2</sub>Cl<sub>2</sub> (1.2 mmol), H<sub>2</sub>O (20 mmol). All reactions were performed in accordance with the representative procedure in Ref.<sup>21</sup>, unless otherwise stated.

<sup>b</sup> Purified yields after silica gel column chromatography (hexane containing 5% v/v triethylamine).

<sup>c</sup> 3.3 mL of CH<sub>2</sub>Cl<sub>2</sub> as a solvent was used.

<sup>d</sup> 1.0 mL of CH<sub>2</sub>Cl<sub>2</sub> as a solvent was used.

<sup>e</sup> CH<sub>3</sub>OH was added instead of H<sub>2</sub>O.

**Table 2**  
Evaluation of the reactivity of **2** via Scheme 1<sup>a</sup>

Entry	Solvent	(CH <sub>3</sub> ) <sub>3</sub> SiI (equiv)	Temp. (°C)	Yield (%)
1	CH <sub>2</sub> Cl <sub>2</sub>	1.0	–78	58
2 <sup>b</sup>	CH <sub>2</sub> Cl <sub>2</sub>	1.2	–78	88
3	CH <sub>2</sub> Cl <sub>2</sub>	1.5	–78	88
4	CH <sub>2</sub> Cl <sub>2</sub>	2.0	–78	64
5	CH <sub>2</sub> Cl <sub>2</sub>	4.0	–78	60
6	CH <sub>2</sub> Cl <sub>2</sub>	1.5	–45	66
7	CH <sub>2</sub> Cl <sub>2</sub>	1.5	–20	63
8	CH <sub>2</sub> Cl <sub>2</sub>	1.5	0	58
9	Toluene	1.5	–78	74
10	Hexane	1.5	–78	70
11	CH <sub>3</sub> CN	1.5	–20	30

<sup>a</sup> Reaction conditions: alkyne **2** (1 mmol), solvent (8 mL), 1 M (CH<sub>3</sub>)<sub>3</sub>SiI in CH<sub>2</sub>Cl<sub>2</sub>, H<sub>2</sub>O (20 mmol).

<sup>b</sup> The starting alkyne was recovered in 3%.

underwent α-vinyl iodation, yet the yields decreased in 80% and 54% (entries 2 and 3); presumably due to the sterically hindered alkyl groups for desilylation process. For entries 2 and 3, unreacted alkynes were recovered in 13% and 45%, and the prolonged reaction time did not increase the yields.

Preliminary mechanistic investigations were performed through deuteration experiments. Deuterioiodination of **1** was carried out with D<sub>2</sub>O, and the deuterium was incorporated under several conditions (Table 4). In each case the major product was (*E*)-adduct<sup>5b</sup> (entries 1–3). For entry 4, when D<sub>2</sub>O was added in advance, a similar selectivity to entry 1 was observed. As a matter of form, deuterium and iodine add to the alkyne with anti-selectivity. Interestingly, this result is the opposite selectivity to Ishii's pioneering work which reported that DI adds to alkynes with complete syn-selectivity.<sup>12</sup> Sub-

**Table 3**  
Effect of the trialkylsilyl groups on the hydroiodation of **2**<sup>a</sup>

Entry	R	Yield (%)	Recovered alkyne (%)
1	CH <sub>3</sub>	88	0
2	CH <sub>2</sub> CH <sub>3</sub>	80	13
3 <sup>b</sup>	CH(CH <sub>3</sub> ) <sub>2</sub>	54	45

<sup>a</sup> Reaction conditions: alkyne (1 mmol), CH<sub>2</sub>Cl<sub>2</sub> (8 mL), 1 M (CH<sub>3</sub>)<sub>3</sub>SiI in CH<sub>2</sub>Cl<sub>2</sub> (1.5 mmol), H<sub>2</sub>O (20 mmol).

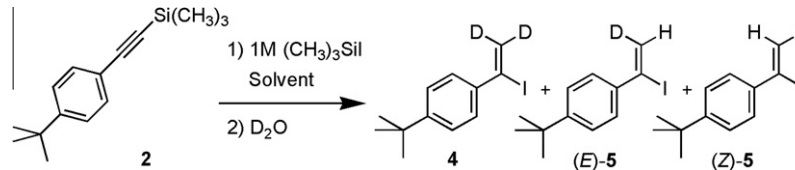
<sup>b</sup> Prolonged reaction time did not increase the yield.

**Table 4**  
Deuterioiodination of **1**<sup>a</sup>

Entry	Solvent	Yield <sup>b</sup> (%)		% D <sup>b</sup>
		( <i>E</i> )-3	( <i>Z</i> )-3	
1	CH <sub>2</sub> Cl <sub>2</sub>	59	23	87
2	Toluene	62	16	80
3	Hexane	71	2	89
4	CH <sub>2</sub> Cl <sub>2</sub> /H <sub>2</sub> O (4% v/v)	53	12	86

<sup>a</sup> Reaction conditions: alkyne **1** (1 mmol), CH<sub>2</sub>Cl<sub>2</sub> as a solvent (8 mL), 1 M (CH<sub>3</sub>)<sub>3</sub>SiI in CH<sub>2</sub>Cl<sub>2</sub> (1.2 mmol), D<sub>2</sub>O (20 mmol).

<sup>b</sup> Determined by <sup>1</sup>H NMR in Ref.<sup>12,5b</sup>

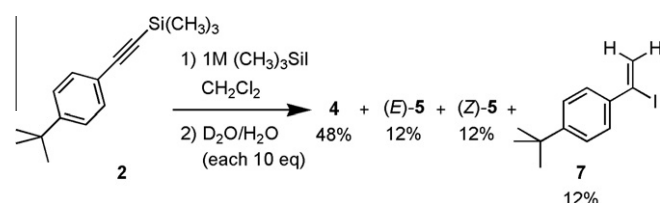
**Table 5**Deuteration experiments of **2**<sup>a</sup>


Entry	Solvent	Yield <sup>b</sup> (%)		
		<b>4</b>	( <i>E</i> )- <b>5</b>	( <i>Z</i> )- <b>5</b>
1	CH <sub>2</sub> Cl <sub>2</sub>	83	2	2
2	Toluene	71	3	3
3	Hexane	61	3	3

<sup>a</sup> Reaction conditions: alkyne **2** (1 mmol), CH<sub>2</sub>Cl<sub>2</sub> as a solvent (8 mL), 1 M (CH<sub>3</sub>)<sub>3</sub>SiI in CH<sub>2</sub>Cl<sub>2</sub> (1.5 mmol), D<sub>2</sub>O (20 mmol). The deuterium was incorporated better than 95%.<sup>b</sup> Determined by <sup>1</sup>H NMR in Ref.<sup>12,5b</sup>

sequently, deuteration experiments of **2** were carried out, and the results are summarized in Table 5. For entries 1–3, **4** was formed along with the same and small amounts of (*E*)-**5** and (*Z*)-**5**. The proportions of (*E*) to (*Z*) between Tables 4 and 5 make a sharp contrast: thus  $\alpha$ -vinyl iodations of **1** and **2** were treated with the blends of D<sub>2</sub>O and H<sub>2</sub>O (each 10 equiv) (Schemes 2 and 3). There is clearly a difference between **1** and **2**: the (*E*) isomer was preferred to (*Z*) in **1**,<sup>24</sup> while an equal mixture of (*E*) and (*Z*) was observed in **2**. In addition, protonation preferentially occurred in **1**, while deuteration in **2**. Although it is difficult to give the details of the mechanism in **2** at the present moment, these outcomes indicate that **2** considerably differs from **1** in the reaction pathway to  $\alpha$ -vinyl iodation. As for the plausible pathway in Scheme 3, initial addition of HI to **2** would give hydroiodinated iodotrimethylsilylalkene with 1:1 (*E*)/(*Z*) ratio. This intermediate could then undergo desilylation reaction with another HI, finally giving the desired compound.<sup>25–27</sup>

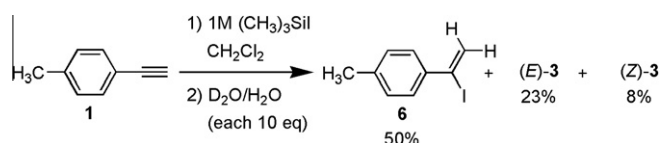
Table 6 represents outcomes of this method for several alkynes listed in Figure 1. For entries 1–6, the commercially available ethynylarenes were employed,<sup>14,28</sup> and converted into the corresponding  $\alpha$ -vinyl iodides in moderate to good yields. Generally,  $\alpha$ -vinyl iodides are not stable;<sup>5a,11a</sup> 1-(1-iodovinyl)-4-methoxybenzene in entry 5 immediately decomposed at ambient temperature in ca. 15 min.<sup>14</sup> We made attempts to evaluate this method for other alkynes, however, unfortunately, other alkynes gave unstable products (these are described in Supplementary data).<sup>29</sup> For entries 6 and 7, different starting alkynes gave the identical products, and interestingly the former resulted in 45% yield and the latter in 92%. These would reflect the individual mechanism of  $\alpha$ -vinyl iodation which was implied in deuterium experiments in Schemes 2 and 3, and it is a great advantage to approach  $\alpha$ -vinyl iodides from another synthetic route. For entry 8, **15** was successfully prepared in 93% yield. For entry 9, the reaction at 1 mmol scale gave the product in 71% isolated yield, and entry 10 was conducted at 5 mmol scale (1.02 g) of alkyne **16** giving 68% yield: this is a valuable process because the product of 1-(1-iodovinyl)-3-methoxybenzene cannot be prepared through hydroiodation.<sup>5a,10e,11a,12</sup> For entry 11, pyrene **17** leads to **18** in 82% yield, in which TMSI easily cleaved trimethylsilyl group at R<sup>1</sup> substituent. For entry 12, pyrene **19** bearing trimethylsilyl ethynyl groups at 3,8-positions gave the corresponding vinyl

**Scheme 3.**  $\alpha$ -Vinyl iodination of **2** with a mixture of D<sub>2</sub>O (10 equiv) and H<sub>2</sub>O (10 equiv).

**20** in 70% yield. Both vinyl compounds **18** and **20** are solid materials, and likely to be more stable than liquids. For entry 13, the desired 2-(1-iodovinyl)biphenyl was observed in 57% yield, however the corresponding isomers that are 3-(1-iodovinyl)biphenyl and 4-(1-iodovinyl)biphenyl were too unstable to isolate. For entry 14, the reaction did not proceed<sup>29</sup> and the starting **22** was recovered in >90%. The influence of representative functional groups was also checked, however, 1-ethynyl-4-(trifluoromethyl)benzene, 1-chloro-4-ethynylbenzene, 1-bromo-4-ethynylbenzene, and 2,5-bis((trimethylsilyl)ethynyl)pyridine were not successful for the

**Table 6**Evaluation of the reactivity of several alkynes for the  $\alpha$ -vinyl iodation<sup>a</sup>

Entry	Alkyne	Product	Yield <sup>b</sup> (%)
1	<b>8</b>	(1-Iodovinyl)benzene	78
2	<b>9</b>	1-(1-Iodovinyl)-4-pentylbenzene	72
3	<b>10</b>	1-(1-Iodovinyl)-2-methoxybenzene	71
4	<b>11</b>	1-(1-Iodovinyl)-3-methoxybenzene	60
5	<b>12</b>	1-(1-Iodovinyl)-4-methoxybenzene	78
6	<b>13</b>	1,4-Bis(1-iodovinyl)benzene	45
7 <sup>c, d</sup>	<b>14</b>	1,4-Bis(1-iodovinyl)benzene	92
8 <sup>c, d</sup>	<b>15</b>	1,3-Bis(1-iodovinyl)benzene	93
9	<b>16</b>	1-(1-Iodovinyl)-3-methoxybenzene	71
10 <sup>e</sup>	<b>16</b>	1-(1-Iodovinyl)-3-methoxybenzene	68
11 <sup>f</sup>	<b>17</b>	<b>18</b>	82
12 <sup>d, g</sup>	<b>19</b>	<b>20</b>	70
13 <sup>h</sup>	<b>21</b>	2-(1-Iodovinyl)biphenyl	57 <sup>i</sup>
14 <sup>j</sup>	<b>22</b>	3-(1-Iodovinyl)benzenamine	0

<sup>a</sup> Reaction conditions: alkyne **1** (1 mmol), CH<sub>2</sub>Cl<sub>2</sub> (8 mL), 1 M (CH<sub>3</sub>)<sub>3</sub>SiI in CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL), H<sub>2</sub>O (20 mmol).<sup>b</sup> Isolated yields, unless otherwise noted.<sup>c</sup> The reactions were conducted at –20 °C.<sup>d</sup> 3 mL of 1 M (CH<sub>3</sub>)<sub>3</sub>SiI in CH<sub>2</sub>Cl<sub>2</sub> was used.<sup>e</sup> 5 mmol (1.02 g) of the starting alkyne was used.<sup>f</sup> The reactions were conducted at 0 °C.<sup>g</sup> The reactions were conducted at room temperature.<sup>h</sup> The starting alkyne was recovered in 39%.<sup>i</sup> Determined by <sup>1</sup>H NMR.<sup>j</sup> The starting alkyne was recovered in >90%.**Scheme 2.**  $\alpha$ -Vinyl iodination of **1** with a mixture of D<sub>2</sub>O (10 equiv) and H<sub>2</sub>O (10 equiv).



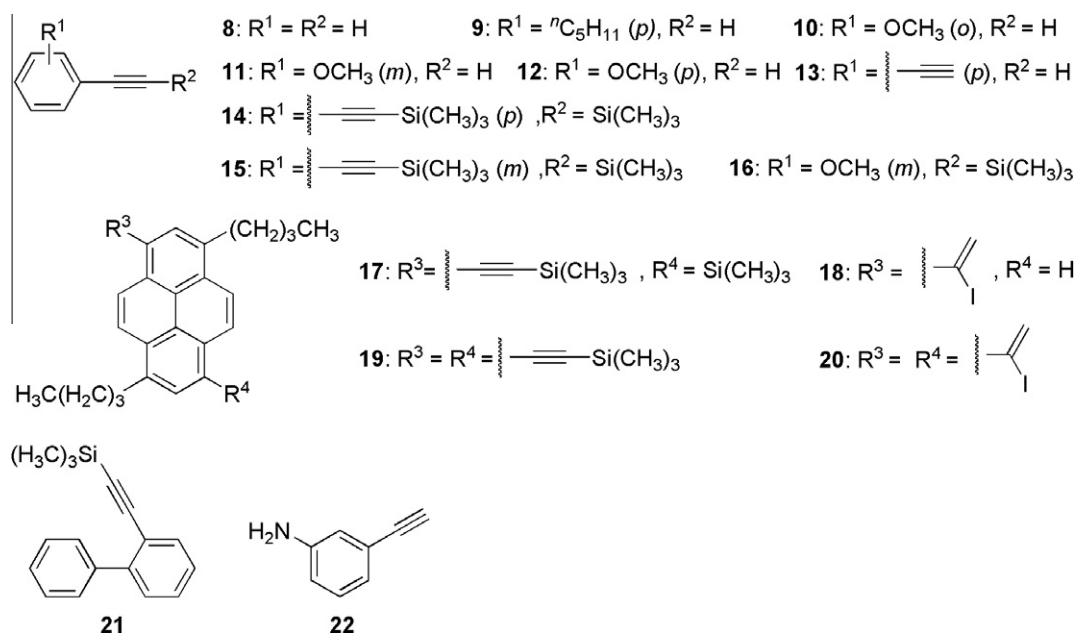


Figure 1. Compounds 8–22.

hydroiodination. In addition, unfortunately, several attempts to transform alkyl-substituted terminal and internal alkynes did not give the corresponding  $\alpha$ -vinyl iodides.<sup>30</sup>

In summary, commercially available TMSI was found to convert trimethylsilyl ethynylarenes into (1-iodovinyl)arenes in one-step. Under the optimized reaction conditions, the reaction occurred quickly under routine conditions, and was readily amenable to scale up. Deuteration experiments suggest that the reaction pathway of  $\alpha$ -vinyl iodation is different between **1** and **2**. This approach afforded a wide variety of new and potentially useful (1-iodovinyl)arenes. The synthetic utility of (1-iodovinyl)arenes is clear and we hope that our straightforward and versatile methodology finds widespread use in organic synthesis. Application and complete mechanistic elucidation are ongoing for further development of this reaction and will be reported in due course.

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2012.05.004>.

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- Hydrohalogenation of 1-ethynyl-4-methylbenzene was attempted with TMSBr and TMSI, however, TMS-Br gave only trace amounts of  $\alpha$ -vinyl bromide and TMS-Cl did not serve at all as a source of hydrochlorination. In both experiments, most of the starting alkyne remained.
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- We purchased the seal-tubed TMSI (5 g) in neat form from Tokyo Chemical Industry Co., LTD, and it included a portion of Al metal inside the tube for inhibiting the decomposition of TMSI. 5 g of TMSI was added to 24 mL of dried  $\text{CH}_2\text{Cl}_2$  along with the Al metal as a solid, thus providing colorless 1 M  $\text{CH}_2\text{Cl}_2$  solution of TMSI for our experimental usage. The Al metal would not have a crucial role for the reactivity of the TMSI solution: actually, the reactivity of the freshly prepared TMSI solution was not influenced by with or without the metal. The stock solution in the presence of the Al metal was stable for at least two weeks, although it turned to slightly red colored solution.

21. *The representative procedure for the  $\alpha$ -vinyl iodation:* To a solution of alkyne (1 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (8 mL) at  $-78^\circ\text{C}$  was added appropriate amount of TMSI (1 M in  $\text{CH}_2\text{Cl}_2$ ) dropwise over 8 min. After 15 min stirring,  $\text{H}_2\text{O}$  was added, and the mixture was allowed to warm to  $0^\circ\text{C}$  over 50 min, and followed by additional stirring for 10 min. The reaction was quenched at  $0^\circ\text{C}$  with saturated aqueous sodium thiosulfate, stirred for 30 min, and allowed to warm to ambient temperature. To the mixture was added  $\text{CH}_2\text{Cl}_2$  and organic phases were washed with brine, and then dried over  $\text{Na}_2\text{SO}_4$ , and concentrated to give a crude product. Purification by silica gel column chromatography (Hexane containing 5 % v/v triethylamine) gave a desired (1-iodovinyl)arene. Analytical Data for **10** in Table 6, entry 11;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.41 (d,  $J = 9.5$  Hz, 1H), 8.34 (d,  $J = 9.5$  Hz, 1H), 8.18 (d,  $J = 9.2$  Hz, 1H), 8.12 (d,  $J = 7.7$  Hz, 1H), 8.06 (d,  $J = 9.2$  Hz, 1H), 7.85 (d,  $J = 7.7$  Hz, 1H), 7.82 (s, 1H), 6.49 (s, 1H), 6.41 (s, 1H), 3.34–3.29 (m, 4H), 1.86–1.80 (m, 4H), 1.53–1.47 (m, 4H), 1.02–0.98 (m, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 138.3, 137.8, 136.9, 131.7, 130.0, 129.6, 129.1, 128.1, 128.0, 127.3, 125.9, 125.82, 125.80, 125.2, 124.8, 123.2, 122.8, 104.0, 34.4, 34.2, 33.8, 33.7, 23.3, 23.2, 14.4. MS (FAB)  $m/z = 339$   $[\text{M}-\text{I}]^+$ . Anal. Calcd for  $\text{C}_{26}\text{H}_{27}\text{I}$ : C, 66.96; H, 5.84. Found: C, 67.02; H, 5.65.
22. The reaction at  $-20$  and  $0^\circ\text{C}$  consumed the starting alkyne, and the crude products contained unclear byproducts.
23. In Ishii's system, acetonitrile was reported as an essential solvent for the  $\alpha$ -vinyl iodation.
24. No isomerization between (*E*)-**3** and (*Z*)-**3** was observed under the condition in Scheme 2.
25. (a) Alzeer, J.; Vasella, A. *Helv. Chim. Acta* **1995**, 78, 177–193; (b) Corey, E. J.; Kirst, H. A. *Tetrahedron Lett.* **1968**, 9, 5041–5043.
26. We consider the result in Scheme 3 would not be ascribed to isotope effect. If this is the case of isotope effect, then **4** should be a minor product.
27. The result in Scheme 3 was reproducible: the second experiment gave yields of 46% for **4**, each 11% for (*E*)-**5**, (*Z*)-**5**, and **7**.
28. (a) Takács, A.; Farkas, R.; Kollár, L. *Tetrahedron* **2008**, 64, 61–66; (b) Bartoli, G.; Cipolletti, R.; Antonio, D. G.; Giovannini, R.; Lanari, S.; Marcolini, M.; Marcantoni, E. *Org. Biomol. Chem.* **2010**, 8, 3509–3517.
29. A lot of other (1-iodovinyl)arenes proved not to isolate due to the unstable compounds: see [Supplementary data](#).
30. These are summarized in [Supplementary data](#).