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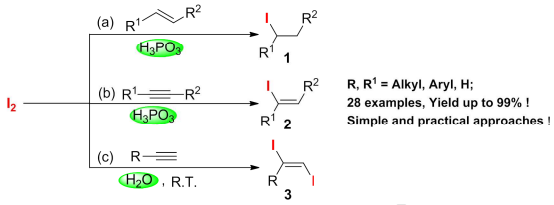

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ABSTRACT

By using I_2 or I_2/ H_3PO_3 system, various alkenes and alkynes were converted to the corresponding alkyl and alkenyl iodides in good yields. In the presence of I_2, alkynes could be di-iodinated using H_2O as the solvent in air at room temperature. This method also features the simple work-up procedure since the pure product could be obtained by extraction. Additionally, for the first time, combining with the non-toxic and cheap phosphonic acid H_3PO_3, alkenes and alkynes were also hydroiodinated successfully, which provides a simple and practical approach for synthesis of organoiodides.

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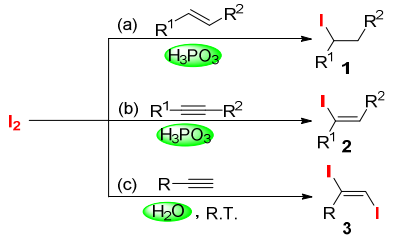
1. Introduction

Organic iodide is one of the most useful chemicals in organic synthesis because of its high reactivity compared to their chloro and bromo counterparts.[1] Herein we report a ready access to these useful compounds, iodoalkanes **1**, iodoalkenes **2** and 1,2-diiodoalkens **3**, by using elemental iodine I_2 via simple and practical hydroiodination and double-iodination of the readily available alkenes and alkynes, respectively (Scheme **1**). Thus, in the presence of phosphonic acid, hydroiodination took place readily with alkenes and alkynes to produce the corresponding iodoalkanes **1** (Scheme 1 (a)) and iodoalkenes 2 (Scheme 1 (b)), respectively, in high yields. On the other hand, in the absence of phosphonic acid, double iodination occurs with alkynes to give the corresponding 1,2-diiodoalkens **3** in high yields (Scheme 1 (c)).

Although there are several methods developed for the synthesis of organic iodides, the direct addition of HI (hydroiodination) to the easily available alkenes and alkynes is apparently is the most straightforward method. However, this method often suffers from drawbacks such as poor yields and side reactions due to the rather difficultly controllable iodine liberation problem of the unstable HI.[2] Therefore, instead of employing hydrogen iodide HI, alter-native reagents that generate HI in situ have been used, such as $H_2/I_2/Rh$,[3] I_2/Al_2O_3,[4] $CuO{\cdot}HBF_4/I_2/Et_3SiH$,[5] TiI_4,[6] Polymethylhydrosiloxane/I_2,[7] I_2/thiol,[8] Me_3SiCl/NaI,[9]



Scheme 1. Selective generation of organic iodides with elemental iodine.

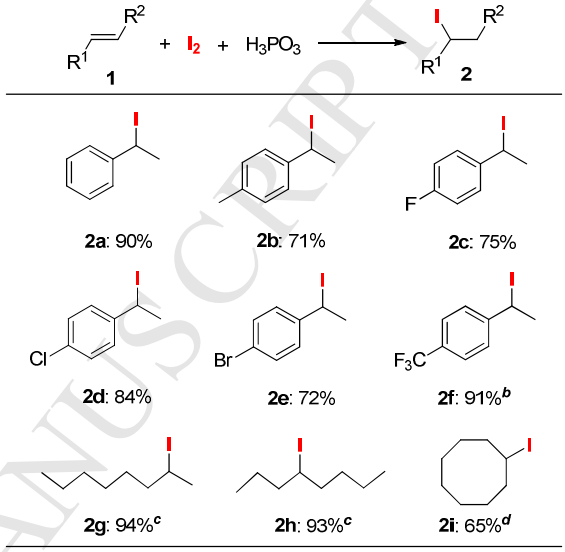
$CeCl_3{\cdot}7H_2O/NaI$.[10] A $Ph_2P(O)H/I_2$ system that may be closely related to the current work was also disclosed by Ogawa et al.[11] However, $Ph_2P(O)H$ is a rather expensive chemical and the preparation of an organoiodide using $Ph_2P(O)H$ is too expensive.

As a by-product, a large amount of phosphonic acid (H_3PO_3) was generated from our ongoing project. Phosphonic acid is a low-toxic, common and cheap chemical. However its utility was rather unexploited. For example, it was estimated that million tons of phosphonic acid was generated every year as the by-product from the preparation of RC(O)Cl using PCl_3 and the process of the electroless nickle plating using H_3PO_2. However, most of these phosphonic acid was disposed as waste. Since H_3PO_3 has a potentially reactive P(O)H bond, we expected that this compound might serve as a green H source for reduction. In an effort to develop simple and green synthetic methodologies, we are attracted by the potential using H_3PO_3 as the hydrogen source for hydroiodination of unsaturated bonds, since no examples were reported using H_3PO_3 as a hydrogen source for hydroiodination so far. In addition, as described above, H_3PO_3 was readily available, cheap and low-toxic. The present I_2/H_3PO_3 combination has the advantage that avoiding use metals and expensive materials comparing to the literature methods.[3-11]

2. Results and Discussion

We initiated our research by carrying out the hydroiodination of alkenes. As demonstrated in table 1, in the presence of H_3PO_3/I_2, phenylacetylene **1a** was hydroiodinated smoothly to afford the Markovnikov-type alkyl iodides in 90% yield (**2a**). Similarly, selected examples for hydroiodination of aryl olefins were also given, and indicated that substituents such as Me, F, Cl, Br and CF_3 were well tolerable under the reaction conditions (**2b-2f**). Aliphatic alkenes, terminal alkene **1g** oct-1-ene and internal alkene **1h** (*E*)-oct-4-ene, also gave 94% and 93% yields of the products, respectively (**2g** and **2h**). By slightly tuning the reaction conditions, cyclooctene **1i** also gave a moderate yield of the product (**2i**).

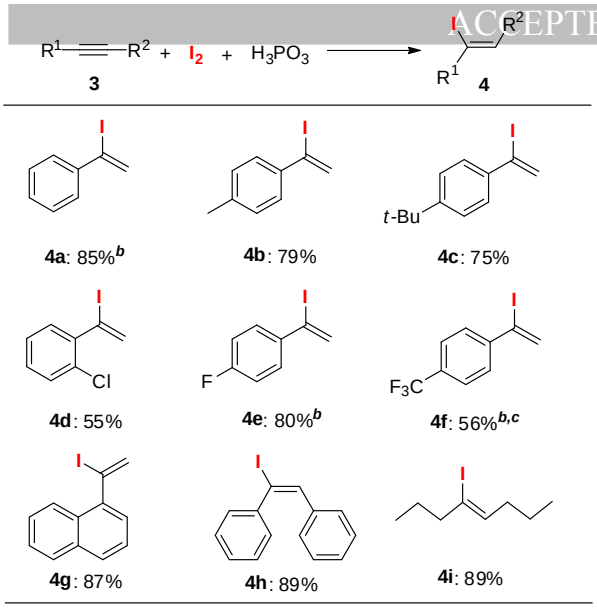
Table 1. Hydroiodination of alkenes with I_2 / H_3PO_3 system.[a]



[a]Reaction conditions: 0.3 mmol **1**, 0.18 mmol I_2, 0.6 mmol H_3PO_3 in 1.5 mL EtOAc at 80 °C for 45 minutes. Isolated yield based on alkynes. [b]Benzene 0.3 mL for 13 minutes. [c]0.225 mmol I_2 and 0.3 mL EtOAc were used, 100 °C, 20 h. [d]0.15 mmol I_2 and 0.9 mmol alkyenes were used in 100 °C for 22 h. Isolated yield based on iodine atom.

The value of this I_2 / H_3PO_3 system lies further on its ability to hydroiodination of alkynes. Thus, a series of hydroiodination reactions were conducted and the results were combined in table 2. Phenylacetylene **3a** underwent this hydroiodination with excellent selectivity to yield the Markovnikov-type adduct **4a** in 85% yields based on iodine atom. When 1.0 equivalent alkynes such as arylethynes bearing methyl and *tert*-bultyl were employed, the iodination also took place to give the corresponding product in good yield (**4b** and **4c**). Worth noting is that arylethynes with electron-withdrawing group such as Cl, F, and CF_3 all could be hyrdroiodinated to the corresponding iodoalknenes in morderate to good yields (**4d-4f**). 1-Ethynylnaphthalene **3g** served as a good substrate in this reaction to produce Markovnikov-type product in 87% yield (**4g**). In the case of internal alkyne 1,2-diphenylethyne **3h**, the iodination proceeded smoothly, producing the (*E*)-olefin product in good yield (**4h**). It should be noted that aliphatic alkyne **3i** could also give high yield of the product under the present reaction conditions (**4i**).

Table 2. Hydroiodination of alkynes with I_2 / H_3PO_3 system.[a]

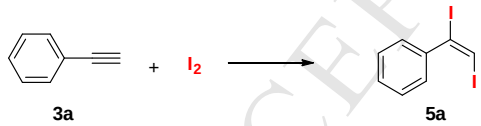


[a]Reaction conditions: 0.3 mmol **3**, 0.15 mmol I_2, 0.9 mmol H_3PO_3 in 1.5 mL CH_3CN at 80 °C for 15 minutes. Isolated yield based on alkynes. [b]0.15 mmol I_2, 0.9 mmol alkynes were used. Isolated yield based on iodine atom. [c]3 h.

During the above-mentioned studies of HI addition with alkyne, we found that interestingly, when the reaction was conducted in the absence of H_3PO_3, selective double-iodination took place to produce the corresponding 1,2-diioalkens in high yields. 1,2-diiodoalkenes are key intermediates in cross coupling reactions for constructing complex molecules since they possess two highly reactive sites.[2] Literature searches revealed that several procedures toward 1,2-diiodoalkenes including CuI/I_2,[12] PhI(OAc)$_2$/ I^- ,[13] I_2/Al_2O_3,[14] ICl/I^-,[15] H_2O_2/I_2 etc. Although a few examples were found with this double-iodination by using iodine only,[17] a simpler, greener, and more practical method for their preparation are clearly desirable.

As shown in table 3, under N_2, phenylacetylene **3a** was mixed with 1.0 equivalent I_2 and stirred in benzene at 60 °C for 1 hour gave 92% yield of (*E*)-(1,2-diiodovinyl)benzene **5a** (entry 1).

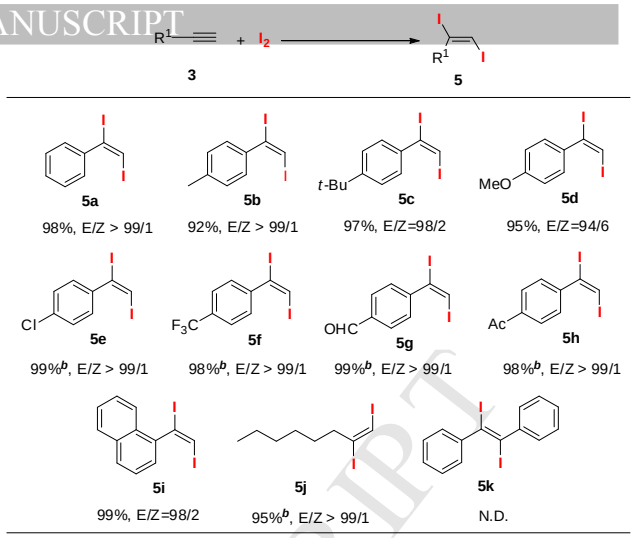
Table 3. Optimization of the reaction conditions.[a]



entry	solvent	temp.	I_2 (equiv.)	time	yield[b]
1	benzene	60 °C	1.0	1 h	92%
2	benzene	R.T.	1.0	1 h	83%
3	benzene	R.T.	1.0	3 h	88%
4	benzene	R.T.	1.25	3 h	97%
5	CH_2Cl_2	R.T.	1.25	3 h	82%
6	CH_3CN	R.T.	1.25	3 h	96%
7	EtOAc	R.T.	1.25	3 h	81%
8	H_2O	R.T.	1.25	3 h	98%
9[c]	H_2O	R.T.	1.25	3 h	98%

[a]Reaction conditions: **3a** (0.3 mmol) and I_2 stirred in a solvent (1.0 mL) under N_2. [b]GC yield based on **3a** using n-decane as an internal standard. [c]Under air.

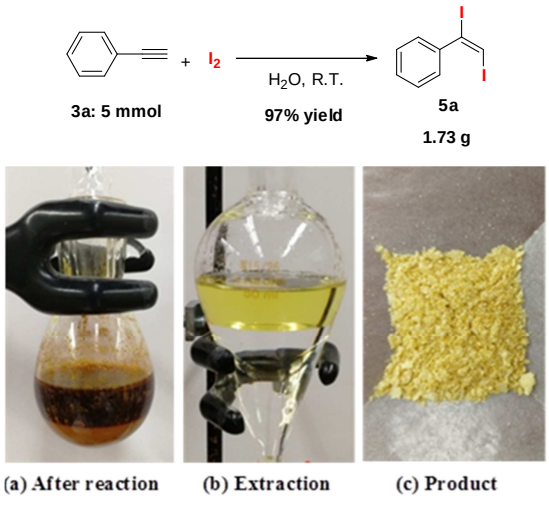
Table 4. Double-iodination of alkynes with I_2.[a]



[a]Reaction conditions: 0.3 mmol **3**, 0.375 mmol I_2, 1.0 mL H_2O, R.T., 3 h. Isolated yield based on alkynes. *E*/*Z* ratio was determined by GC-MS. [b]22 h.

Decreasing the temperature from 60 °C to room temperature, product **5a** could also be obtained in good yield (entry 2). By further prolonging the reaction time and increase the amount of I_2 good results (entry 3 and 4) were obtained. During screening the solvents, we are delighted to find that H_2O performed the best among other solvents such as CH_2Cl_2, CH_3CN, and EtOAc (entry 5-8). Encouraged by the above results, we next examined the reaction under air, and found that phenylacetylene **3a** could be readily di-iodinated by I_2 in excellent yield (entry 9).

Having optimized the reaction conditions, we next explored the substrate scope of this iodination reaction. As summarized in Table 4, various functionalized alkynes having diverse groups on the aromatic ring were well tolerated in this system. The electron-donating arylethynes bearing methyl, *tert*-bultyl and OMe groups in the *para*-position of benzene ring were compatible under this reaction conditions, generating the corresponding (*E*)-diiodoalkenes in high yields with excellent stereoselectively (**5b**–**5d**). By prolonging the reaction time, substrates with electron-withdrawing groups such as Cl, CF_3, CHO and C(O)Me on the benzene ring were also double-iodinated successfully, furnishing the products in excellent yields (**5e**–**5h**). 1-Ethynylnaphthalene was also applicable to this iodination reaction, giving the desired



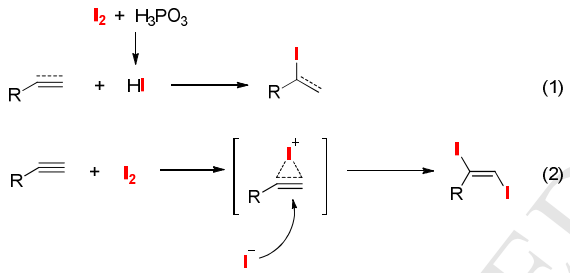
Scheme 2. Scale-up reaction.

product **5i** in a nearly quantitative yield. It is worth noting that ali-phatic alkynes also work efficiently under the current

conditions, producing the expected product in 95% yield (**5j**). However, when 1,2-diphenylethyne was used as the substrate, no addition took place as confirmed by GC-MS and the 1,2-diphenylethyne was recovered (**5k**).

To probe the scalability of this iodination reaction, a gram-scale reaction was conducted. Thus, phenylacetylene **3a** and powder I_2 were charged in the bottle, and 10 mL H_2O was added then. Because of the relatively poor solubility of I_2 and phenylacetylene in H_2O, 1mL CH_3CN was added into the reaction mixture. The mixture was vigorously stirred for 46 hours at room temperature. As illustrated in scheme 2, the product was precipitated on the bottom after the reaction (scheme 2, pic a). To remove excess I_2, 5.0 wt% $Na_2S_2O_3$ aqueous solutions was poured into the solution, and then the mixture was extracted with EtOAc three times (scheme 2, pic b). The supernatant was combined and dried with Mg_2SO_4. Removing the solvent under vacuum affords analytically pure product **5a** in 97% yield (scheme 2, pic c). This reaction clearly shows the potential in practical organic synthesis since because of its green and mild reaction conditions as well as the simple process operation.

Although the detailed mechanism was not clear, a plausible reaction path has been depicted based on literatures. As shown in scheme 3, H_3PO_3 may react with I_2 to form HI that then, follows the Markovnikov rule, adds to alkenes or alkyne leads to the corresponding organoiodides (eq. 1). For the double-iodination of alkynes, it is assumed that molecule iodine undergoes electronic *anti*-addition to alkynes via a cyclic iodonium ion to afford the 1,2-diioalkens (eq. 2).[20,21]



Scheme 3. A possible mechanism.

3. Conclusion

In summary, we have successfully demonstrated the double-iodination of terminal alkynes using iodine under mild conditions. This approach has advantages such as using H_2O as solvent, easy scale-up and simple work-up. What's more, by using the combination of iodine and the cheap and low-toxic hydrogen source H_3PO_3, for the first time, the selective hydroiodination of various alkynes and alkenes, were achieved, that selectively generate the corresponding Markovnikov-type products in good yields. This reaction provided a simple and practical protocol to synthesize a wide range of alkyl and alkenyl iodides, which are important building blocks in organic synthesis.

4. Experimental section

4.1 General information

Unless otherwise noted, all reactions were carried out in oven-dried Schlenk tubes under argon. Reagents and solvents were obtained from TCI or Wako Pure Chemical Industries, Ltd, and purified according to standard methods. Flash column chromatography was performed using 200-300 mesh silica gel. Visualization on TLC was achieved by the use of UV light (254 nm). Shimadzu GC-2010 equipped with FID detector was used to analysis the reaction mixture. ^{1}H NMR and ^{13}C NMR spectroscopy were recorded on a JEOL JNM-ECS400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) in $CDCl_3$. The coupling constants *J* are given in Hz. Chemical shifts for ^{1}H NMR are referred to internal Me_4Si (0 ppm). GC-MS were conducted on a Shimadzu GCMS-QP2010 plus equipped with EI ion source.

4.2 Typical procedure for preparation of targeted molecules

Under argon, alkenes or alkynes, I_2 and H_3PO_3 were added into a 10 mL dried Schlenk tube equipped with a magnetic stir bar, then solvent was charged. The tube was stirred at indicated temperature and time. After reaction, the mixture was quenched by 5.0 wt% $Na_2S_2O_3$ aqueous solution and was extracted with EtOAc three times. Then the combined the organic layer was dried over Mg_2SO_4 and filtrated. The filtrate was concentrated and the residue was further purified by column chromatography on silica gel (or GPC) to give the product.

Under air, ethynylbenzene **3** and I_2 were added into a 10 mL dried Schlenk tube equipped with a magnetic stir bar, then 1.0 mL H_2O was charged. The tube was stirred at room temperature for indicated time. After reaction, the mixture was quenched by 5.0 wt % $Na_2S_2O_3$ aqueous solution and was extracted with EtOAc three times. Then the combined the organic layer was dried over Mg_2SO_4 and filtrated. After evaporation of the solvent under reduced pressure, the analytically pure product was obtained.

*4.2.1 (1-Iodoethyl)benzene (**2a**)*[3]

Colorless oil, yield 90%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.45–7.42 (m, 2H), 7.32–7.22 (m, 3H), 5.40 (q, *J* = 7.1 Hz, 1H), 2.21 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 145.45, 128.78, 128.02, 126.63, 29.05, 26.21. GC-MS (EI, 70 eV) m/z = 232 (M^+).

*4.2.2 1-(1-Iodoethyl)-4-methylbenzene (**2b**)*[18]

Light brown oil, yield 71%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.24–7.23 (m, 2H), 7.01–6.99 (m, 2H), 5.31 (q, *J* = 7.0 Hz, 1H), 2.20 (s, 3H), 2.09 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 142.54, 137.86, 129.42, 126.47, 29.09, 26.87, 21.29. GC-MS (EI, 70 eV) m/z = 246 (M^+).

*4.2.3 1-Fluoro-4-(1-iodoethyl)benzene (**2c**)*[3]

Colorless oil, yield 75%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.46–7.43 (m, 2H), 7.04–7.00 (m, 2H), 5.42 (q, *J* = 7.0 Hz, 1H), 2.23 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 161.94 (d, *J* = 246 Hz), 141.34 (d, *J* = 3.4 Hz), 128.28 (d, *J* = 8.1 Hz), 115.60 (d, *J* = 21.5 Hz), 29.19, 24.97. GC-MS (EI, 70 eV) m/z = 250 (M^+).

*4.2.4 1-Chloro-4-(1-iodoethyl)benzene (**2d**)*[3]

Light brown oil, yield 84%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.39–7.36 (m, 2H), 7.28–7.24 (m, 2H), 5.35 (t, *J* = 7.2 Hz, 1H), 2.18 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 144.03, 133.51, 128.95, 127.99, 28.97, 24.45. GC-MS (EI, 70 eV) m/z = 266 (M^+).

*4.2.5 1-Bromo-4-(1-iodoethyl)benzene (**2e**)*[3]

White solid, yield 72%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.36–7.33 (m, 2H), 7.25–7.22 (m, 2H), 5.26 (t, *J* = 7.0 Hz, 1H), 2.11 (d, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 144.46, 131.84, 128.22, 121.56, 28.80, 24.31. GC-MS (EI, 70 eV) m/z = 311 (M^+).

*4.2.6 1-(1-Iodoethyl)-4-(trifluoromethyl)benzene (**2f**)*

Colorless oil, yield 91%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.57–7.52 (m, 4H), 5.36 (q, *J* = 7.1 Hz, 1H), 2.21 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz $CDCl_3$): δ 149.27, 130.48 (q, J = 32 Hz), 127.02, 125.81 (q, J = 36 Hz), 124.01 (q, J = 271 Hz), 28.62, 23.21. GC-MS (EI, 70 eV) m/z = 300 (M^+).

*4.2.7 2-Iodooctane (**2g**)*[3]

Colorless oil, yield 94%; ^{1}H NMR (400 MHz $CDCl_3$): δ 4.22–4.14 (m, 1H), 1.91–1.50 (d, J = 6.8 Hz, 3H), 1.84–1.79 (m, 1H), 1.64–1.55 (m, 1H), 1.38–1.28 (m, 8H), 0.89–0.86 (m, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 43.03, 31.76, 30.96, 29.76, 29.02, 28.51, 22.68, 14.15. GC-MS (EI, 70 eV) m/z = 240 (M^+).

*4.2.8 4-Iodooctane (**2h**)*[3]

Colorless oil, yield 93%; ^{1}H NMR (400 MHz $CDCl_3$): δ 4.15–4.09 (m, 1H), 1.90–1.80 (m, 2H), 1.72–1.29 (m, 8H), 0.93–0.89 (m, 6H). ^{13}C NMR (100 MHz $CDCl_3$): δ 42.82, 40.51, 40.36, 31.77, 22.88, 22.07, 14.08, 13.36. GC-MS (EI, 70 eV) m/z = 204 (M^+).

*4.2.9 Iodocyclooctane (**2i**)*[3]

Colorless oil, yield 65%; ^{1}H NMR (400 MHz $CDCl_3$): δ 4.62–4.55 (m, 1H), 2.25–2.19 (m, 4H), 1.69–1.41 (m, 10H). ^{13}C NMR (100 MHz $CDCl_3$): δ 38.40, 38.02, 27.53, 26.74, 25.23. GC-MS (EI, 70 eV) m/z = 238 (M^+).

*4.2.10 (1-Iodovinyl)benzene (**4a**)*[11a]

Colorless oil, yield 85%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.53–7.49 (m, 2H), 7.33–7.27 (m, 3H), 6.47 (d, J = 1.8 Hz, 1H), 6.08 (d, J = 1.8 Hz, 1H). ^{13}C NMR (100 MHz $CDCl_3$): δ 141.77, 128.95, 128.33, 128.17, 127.39, 107.52. GC-MS (EI, 70 eV) m/z = 230 (M^+).

*4.2.11 1-(1-Iodovinyl)-4-methylbenzene (**4b**)*[19]

Colorless oil, yield 79%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.43–7.40 (m, 2H), 7.11 (d, d, J = 8.0 Hz, 2H), 6.43 (d, J = 1.7 Hz, 1H), 6.04 (d, J = 1.7 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 139.02, 128.97, 128.09, 126.56, 107.78, 21.22. GC-MS (EI, 70 eV) m/z = 244 (M^+).

*4.2.12 1-(Tert-butyl)-4-(1-iodovinyl)benzene (**4c**)*[19]

Colorless oil, yield 75%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.49–7.45 (m, 2H), 7.35–7.32 (m, 2H), 6.45 (d, J = 1.6 Hz, 1H), 6.04 (d, J = 1.7 Hz, 1H), 1.32 (m, 9H). ^{13}C NMR (100 MHz $CDCl_3$): δ 152.19, 138.85, 127.92, 126.60, 125.25, 107.72, 34.72, 31.33. GC-MS (EI, 70 eV) m/z = 286 (M^+).

*4.2.13 1-Chloro-2-(1-iodovinyl)benzene (**4d**)*

Colorless oil, yield 55%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.36–7.28 (m, 2H), 7.25–7.21 (m, 2H), 6.23–6.21 (m, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 142.21, 131.91, 131.52, 130.07, 130.04, 129.72, 126.81, 99.92. GC-MS (EI, 70 eV) m/z = 264 (M^+).

*4.2.14 1-Fluoro-4-(1-iodovinyl)benzene (**4e**)*[1g]

Colorless oil, yield 80%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.51–7.46 (m, 2H), 7.02–6.96 (m, 2H), 6.39 (d, J = 1.8 Hz, 1H), 6.05 (d, J = 1.8 Hz, 1H). ^{13}C NMR (100 MHz $CDCl_3$): δ 162.98 (d, J = 247 Hz), 138.02 (d, J = 3.0 Hz), 129.88 (d, J = 8.0 Hz), 127.46, 115.14 (d, J = 22 Hz), 105.79. GC-MS (EI, 70 eV) m/z = 248 (M^+).

*4.2.15 1-(1-Iodovinyl)-4-(trifluoromethyl)benzene (**4f**)*[11a]

Colorless oil, yield 56%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.62–7.55 (m, 4H), 6.53 (d, J = 1.7 Hz, 1H), 6.18 (d, J = 1.7 Hz, 1H). ^{13}C NMR (100 MHz $CDCl_3$): δ 145.16, 130.98 (q, J = 148 Hz), 129.31, 128.46, 126.78, 125.34 (q, J = 14 Hz), 104.98. GC-MS (EI, 70 eV) m/z = 298 (M^+).

*4.2.16 1-(1-Iodovinyl)naphthalene (**4g**)*[20]

Light yellow oil, yield 87%; ^{1}H NMR (400 MHz $CDCl_3$): δ 8.23–8.20 (m, 1H), 7.90–7.82 (m, 2H), 7.63–7.58 (m, 1H), 7.54–7.48 (m, 2H), 7.44–7.40 (m, 1H), 6.38 (d, J = 1.1 Hz, 1H), 6.34 (d, J = 1.0 Hz, 1H). ^{13}C NMR (100 MHz $CDCl_3$): δ 141.63, 133.78, 131.23, 129.88, 128.98, 128.33, 126.40, 126.24, 125.82, 125.43, 125.26, 102.42. GC-MS (EI, 70 eV) m/z = 280 (M^+).

*4.2.17 (E)-(1-Iodoethene-1,2-diyl)dibenzene (**4h**)*[1f]

Brown oil, yield 89%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.46 (s, 1H), 7.37–7.28 (m, 5H), 7.16–7.11 (m, 3H), 6.97–6.94 (m, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 143.11, 141.45, 137.28, 128.87, 128.82, 128.52, 128.28, 127.67, 98.57. GC-MS (EI, 70 eV) m/z = 306 (M^+).

*4.2.18 (Z)-4-Iodooct-4-ene (**4i**)*[11b]

Colorless oil, yield 89%; ^{1}H NMR (400 MHz $CDCl_3$): δ 5.46 (t, J = 8.0 Hz, 1H), 2.42 (t, J = 7.2 Hz, 2H), 2.08 (m, 2H), 1.56–1.39 (m, 4H), 0.94–0.85 (m, 6H). ^{13}C NMR (100 MHz $CDCl_3$): δ 134.87, 109.70, 47.19, 38.44, 22.57, 21.81, 13.79, 12.71. GC-MS (EI, 70 eV) m/z = 238 (M+).

*4.2.19 (E)-(1,2-Diiodovinyl)benzene (**5a**)*[13b]

Light yellow solid, yield 98%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.37–7.34 (m, 5H), 7.26 (s, 1H). ^{13}C NMR (100 MHz $CDCl_3$): δ 143.18, 129.07, 128.60, 128.53, 96.28, 80.92. GC-MS (EI, 70 eV) m/z = 356 (M^+).

*4.2.20 (E)-1-(1,2-Diiodovinyl)-4-methylbenzene (**5b**)*[23]

Light yellow oil, yield 92%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.29–7.25 (m, 2H), 7.22 (s, 1H), 7.18–7.16 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 140.26, 139.18, 129.19, 128.58, 96.73, 80.35, 21.57. GC-MS (EI, 70 eV) m/z = 370 (M^+).

*4.2.21 (E)-1-(Tert-butyl)-4-(1,2-diiodovinyl)benzene (**5c**)*[21]

Light yellow oil, yield 97%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.38–7.31 (m, 4H), 7.23 (s, 1H), 1.34 (s, 9H). ^{13}C NMR (100 MHz $CDCl_3$): δ 152.20, 139.89, 128.51, 125.39, 96.96, 80.04, 34.93, 31.36. GC-MS (EI, 70 eV) m/z = 412 (M^+).

*4.2.22 (E)-1-(1,2-Diiodovinyl)-4-methoxybenzene (**5d**)*[13b]

Light yellow oil, yield 95%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.35–7.32 (m, 2H), 7.19 (s, 1H), 6.89–6.85 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 159.89, 135.33, 130.36, 113.78, 96.77, 80.06, 55.48. GC-MS (EI, 70 eV) m/z = 386 (M+).

*4.2.23 (E)-1-Chloro-4-(1,2-diiodovinyl)benzene (**5e**)*[22]

White solid, yield 99%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.35–7.28 (m, 5H). ^{13}C NMR (100 MHz $CDCl_3$): δ 141.59, 134.93, 130.04, 128.83, 94.62, 81.73. GC-MS (EI, 70 eV) m/z = 390 (M^+).

*4.2.24 (E)-1-(1,2-Diiodovinyl)-4-(trifluoromethyl)benzene (**5f**)*[21]

Light yellow oil, yield 98%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.65–7.63 (d, J = 8.0 Hz, 2H), 7.48–7.46 (d, J = 8.0 Hz, 2H), 7.36 (s, 1H). ^{13}C NMR (100 MHz $CDCl_3$): δ 146.66, 130.89 (q, J = 32 Hz), 129.06, 125.68 (q, J = 3.0 Hz), 123.86 (q, J = 271 Hz), 93.88, 82.58. GC-MS (EI, 70 eV) m/z = 424 (M^+).

*4.2.25 (E)-4-(1,2-Diiodovinyl)benzaldehyde (**5g**)*

Light yellow oil, yield 99%; ^{1}H NMR (400 MHz $CDCl_3$): δ 10.02 (s, 1H), 7.89–7.86 (m, 2H), 7.50–7.48 (m, 2H), 7.35 (s, 1H). ^{13}C NMR (100 MHz $CDCl_3$): δ 191.40, 148.92, 136.25, 129.94, 129.30, 93.97, 82.52. GC-MS (EI, 70 eV) m/z = 384 (M^+).

*4.2.26 (E)-1-(4-(1,2-Diiodovinyl)phenyl)ethanone (**5h**)*

Light yellow oil, yield 98%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.95–7.92 (m, 2H), 7.43–7.40 (m, 2H), 7.32 (s, 1H), 2.59 (s, 3H). 13C NMR (100 MHz $CDCl_3$): δ 197.24, 147.60, 137.08, 128.91, 128.62, 94.44, 82.27, 26.84. GC-MS (EI, 70 eV) m/z = 398 (M^+).

*4.2.27 (E)-1-(1,2-Diiodovinyl)naphthalene (**5i**)*[23]

Light yellow solid, yield 99%; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.94–7.87 (m, 3H), 7.63–7.58 (m, 1H), 7.55–7.40 (m, 4H). ^{13}C NMR (100 MHz $CDCl_3$): δ 141.01, 133.91, 129.38, 128.62, 126.69, 125.76, 125.65, 125.14, 94.38, 84.53. GC-MS (EI, 70 eV) m/z = 406 (M^+).

*4.2.28 (E)-1,2-Diiodooct-1-ene (**5j**)*[21]

Colorless oil, yield 95%; ^{1}H NMR (400 MHz $CDCl_3$): δ 6.79 (s, 1H), 2.49 (t, J = 8.0 Hz, 2H), 1.55–1.49 (m, 2H), 1.35–1.31 (m, 6H), 0.91–0.88 (m, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 104.56, 78.99, 44.77, 31.70, 28.23, 27.95, 22.64, 14.17. GC-MS (EI, 70 eV) m/z = 364 (M^+).

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- For the first time, using I_2/ H_3PO_3 system, alkenes and alkynes were hydroiodinated successfully in high selectivity.
- In the presence of I_2, alkynes could be double-iodinated under green and mild conditions.
- A green and practical protocol and the work-up procedure is simple.