Synthesis W. Deng et al. Special Topic

Iron-Catalyzed Carboiodination of Alkynes

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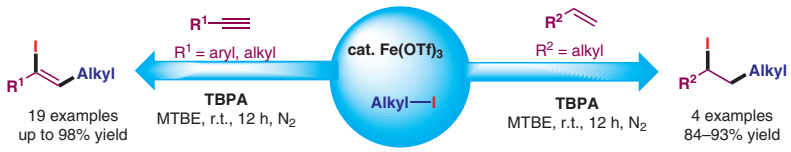
Published as part of the Special Topic *Modern Radical Methods and their Strategic Applications in Synthesis*



Received: 01.02.2018
Accepted after revision: 13.03.2018
Published online: 16.04.2018
DOI: 10.1055/s-0037-1609448; Art ID: ss-2018-c0057-st

Abstract An iron-catalyzed carboiodination of alkynes with alkyl iodides at room temperature was developed. This method could provide synthetically useful vinyl iodides with general alkyl chains, fluoroalkyl group, ester, and cyano group. Conjugated alkynes or unconjugated alkynes were both suitable for this transformation. A radical pathway was proposed for the mechanism and acetyl *tert*-butyl peroxide was selected as the radical initiator. Alkenes could also be applied to this chemistry and produce more complex alkyl iodides.

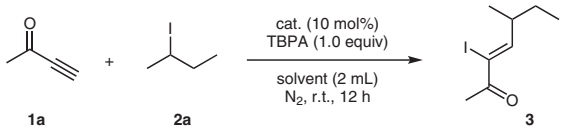
Key words iron catalysis, radical, alkyl iodides, alkynes, carboiodination

Difunctionalization of C≡C bonds is an attractive method to establish functionalized alkenes, which are one of the most broadly existing structural motifs present in organic molecules.[1] Significant progress has been achieved by transition-metal-catalyzed carbon–carbon or carbon–heteroatom (e.g., C–O, C–N, or C–X) bond formation with C≡C bonds. Specially, radical process has particular appeal for performing new transformations because of its widespread application in chemistry and even biology.[2] In this context, carboiodination of alkynes in a radical pathway[3] has attracted considerable attention because vinyl iodide is an important intermediate in organic synthesis.[4] Generally, carboiodination of alkynes with fluoroalkyl iodides as the carbon and iodine sources is the most frequently studied topic, as the easy accessibility of the fluoroalkyl radical initiated by $Na_2S_2O_4$/$NaHCO_3$,[5] AIBN,[6] Et_3B,[7] transition metals,[8] organic peroxides,[9] Zn,[10] or light.[11] The studies on carboiodination of alkynes with simple alkyl halides, however, are less developed with only less research papers being documented. In 1989, Oshima and Utimoto et al. reported an Et_3B-induced radical addition of alkyl iodides to acetylenes in good yields.[12] This methodology was employed by Li's group for the cascade synthesis of γ-lactam derivatives.[13] Later on, Daoust's group further developed this method with ynol ethers as the alkyne substrates[14] and found that water could be used as the reaction medium.[15] Curran's group[16] and Stephenson's group[17] discovered that general alkyl iodides could undergo the carboiodination of alkynes upon irradiation of light. Interestingly, Betrand and coworker found that dialkylzinc showed its ability as an initiator for the sequential radical addition cyclization.[18] Although developments have been achieved, new methods are still highly required. In recent years, we have focused our efforts on the functionalization of unsaturated C–C bonds via radical chemistry.[19] Herein, we present an iron-catalyzed carboiodination of alkynes in a radical mechanism. As far as we are aware, use of the iron catalyst in a radical carboiodination of alkynes with a *simple alkyl group* has not been previously attempted.

The model reaction was initiated with the terminal alkyne but-3-yn-2-one (**1a**) and a general alkyl iodide 2-iodobutane (**2a**) in the presence of an initiator and a metal catalyst (Table 1). Based on our previous studies,[19] $Fe(OTf)_3$ was chosen as the catalyst and TBPA (acetyl *tert*-butyl peroxide) was selected as the initiator.[19c] Because TBPA features the just right reactivity that it can selectively grab the iodine atom from alkyl iodides to activate them rather than react with the terminal alkynes to afford vinyl radicals. An isolated yield of the desired product **3** as high as 72% was obtained when the reaction was performed in DME at room temperature (Table 1, entry 1). The regioselectivity was 9:1 and (*Z*)-**3** was found to be the major product. When $Fe(OTf)_2$ was used as the catalyst, similar result was achieved (entry 2). However, other iron metals, such as $FeBr_3$, $FeCl_3$, and $FeCl_2$, and also other metal triflates, such as $Cu(OTf)_2$, AgOTf, $Zn(OTf)_2$, CuOTf, $Nd(OTf)_3$, $Sc(OTf)_3$, $Y(OTf)_3$, and $La(OTf)_3$ all failed to provide the desired product (entries 3 and 4). In consideration of the reproducibility

of the reaction, $Fe(OTf)_3$ showed a better performance than $Fe(OTf)_2$. Thus, further investigations of this reaction were performed with $Fe(OTf)_3$ as the catalyst. Next, the solvent was screened. Ether solvents such as THF, 1,4-dioxane, and MTBE delivered the desired product **3** and MTBE offered the highest regioselectivity (entries 5–7). Although the solvents, such as MeCN, CH_2Cl_2, DCE, and toluene could be used as the solvent for the reaction, the regioselectivities of the desired product were about 1:2.3 to 1:3.6, which were lower than the ratio provided by MTBE (entries 8–11 vs entry 7). Other solvents, such as DMSO, DMF, and hexane could not be used as the solvent for the reaction (entries 12–14). A lower initiator loading was performed, but both the yield of the product and the regioselectivity dropped (entry 15). Without any metal, only trace amount of the desired product was detected (entry 16). Thus, the reaction conditions as described in entry 7 of Table 1 were selected as the optimal reaction conditions.

Table 1 Optimization of the Reaction Conditions[a]



1a + **2a** → **3**

Entry	Catalyst (10 mol%)	Solvent	Yield (%)[b] (*E*/*Z*)
1	$Fe(OTf)_3$	DME	73 (1:9.0)
2	$Fe(OTf)_2$	DME	72 (1:9.4)
3	other irons[c]	DME	trace
4	other triflates[d]	DME	trace
5	$Fe(OTf)_3$	THF	42 (1:2.1)
6	$Fe(OTf)_3$	1,4-dioxane	50 (1:2.2)
7	**$Fe(OTf)_3$**	**MTBE**	**72 (1:12)**
8	$Fe(OTf)_3$	MeCN	66 (1:3.6)
9	$Fe(OTf)_3$	CH_2Cl_2	43 (1:2.3)
10	$Fe(OTf)_3$	DCE	56 (1:2.7)
11	$Fe(OTf)_3$	toluene	49 (1:2.8)
12	$Fe(OTf)_3$	DMSO	trace
13	$Fe(OTf)_3$	DMF	trace
14	$Fe(OTf)_3$	hexane	trace
15[e]	$Fe(OTf)_3$	MTBE	62 (1:3.2)
16[f]	–	MTBE	trace

[a] Reaction conditions: **1a** (1.0 equiv), **2a** (3.0 equiv), catalyst (10 mol%), TBPA (1.0 equiv) in 2 mL of solvent at r.t. for 12 h under N_2 atmosphere. DME: 1,2-dimethoxyethane; MTBE: methyl *tert*-butyl ether.
[b] Yield of the isolated product. *E*/*Z* value was determined by ^{1}H NMR spectroscopy.
[c] Other irons: $FeBr_3$, $FeCl_3$, and $FeCl_2$.
[d] Other triflates: $Cu(OTf)_2$, AgOTf, $Zn(OTf)_2$, CuOTf, $Nd(OTf)_3$, $Sc(OTf)_3$, $Y(OTf)_3$, and $La(OTf)_3$.
[e] TBPA used: 0.5 equiv.
[f] No metal was used.

With the optimal reaction conditions in hand, the substrate scope of alkyl iodides and alkynes were studied (Figure 1). General secondary alkyl iodides, such as 2-iodobutane, cyclohexyl iodide, and cyclopentyl iodide, could undergo the cascade radical relay and atom-transfer radical addition reaction, and provided the corresponding vinyl iodides **3**–**8** with *Z*-selectivities, which were determined by ^{1}H NMR data and the known compound **5**.[20] Conjugated but-3-yn-2-one and ethyl propiolate were good radical acceptors for this reaction. Reaction between general secondary alkyl iodide and substituted phenylacetylenes gave low efficiencies (Figure 1; **7** and **8**).[21] Excellent yields were obtained when activated alkyl iodides were employed. Ethyl 2-iodopropanoate reacted smoothly with substituted phenylacetylenes and afforded the corresponding vinyl iodides **9**–**15** with almost quantitative yields with *E*-selectivities, which were determined by ^{1}H NMR data and the known compounds **16** and **17**.[2j,22] While fluoroalkyl iodides tolerated the reaction conditions and offered the corresponding

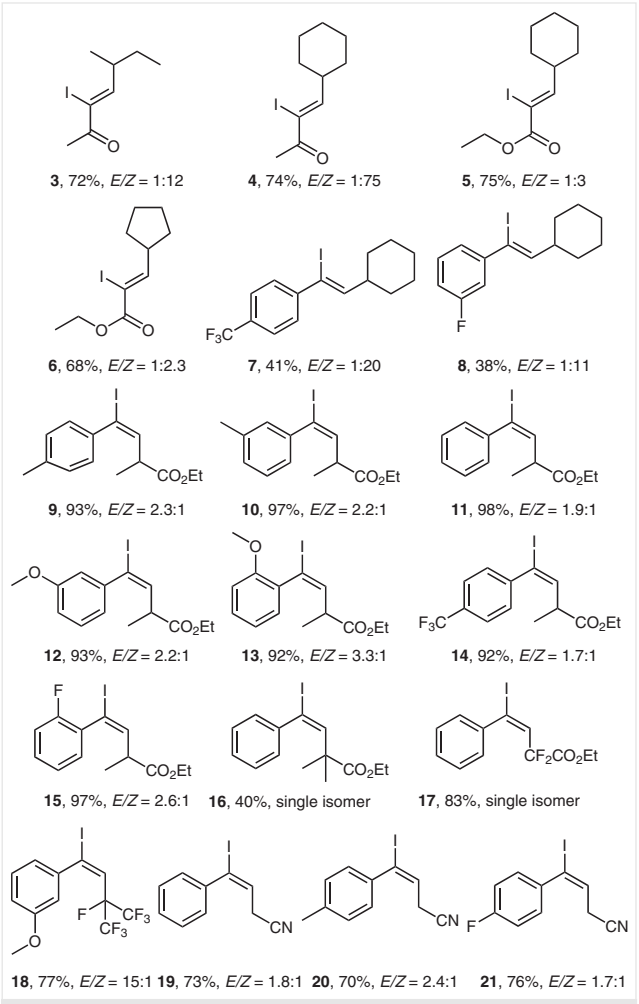


Figure 1 Substrate scope of alkyl iodides and alkynes

vinyl iodides **17** and **18**, iodoacetonitrile reacted with substituted phenylacetylenes and gave the corresponding vinyl iodides **19–21** with a cyano group. Interestingly, when ethyl 2-iodo-2-methylpropionate and ethyl iododifluoroacetate reacted with phenylacetylene, exclusively *E*-selective products **16** and **17** were obtained, respectively.

This methodology could also be used for carboiodination of unactivated alkynes and unactivated alkenes, providing the unconjugated vinyl iodides and secondary alkyl iodides, respectively (Figure 2). Unconjugated vinyl iodides **22**[23] and **23** were synthesized from the aliphatic alkynes and fluoroalkyl iodides in high yields. The reaction between aliphatic alkenes and fluoroalkyl iodides provided the secondary alkyl iodides with excellent performance.

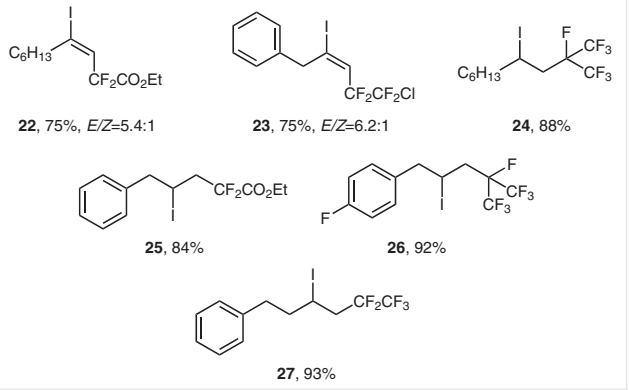
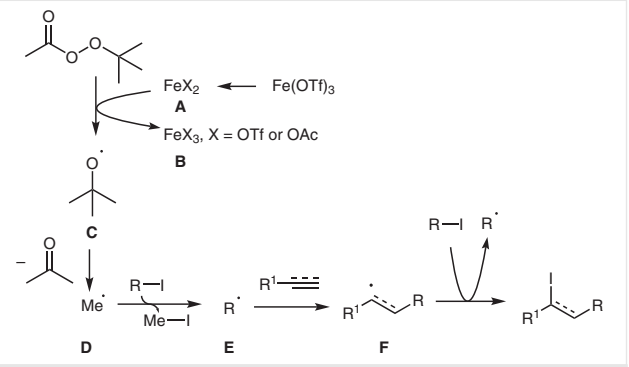


Figure 2 Substrate scope of the unactivated alkynes and alkenes

Based on the understanding of this chemistry, a radical mechanism is proposed (Scheme 1). Initially, $Fe(OTf)_3$ is reduced to the active catalyst Fe(II) **A**.[19] Then Fe(II) **A** can be oxidized by acetyl *tert*-butyl peroxide through a single-electron transfer affording complex Fe(III) **B** and *tert*-butoxyl radical **C**, which would decompose to generate an acetone and a methyl radical **D**. Iodine atom exchange with alkyl iodide generates the alkyl radical **E**. The resulting alkyl radical reacts directly with the alkyne to form a vinyl radical intermediate **F**, which then undergoes atom transfer radical addition with alkyl iodide substrate to afford the final product.



Scheme 1 Proposed reaction mechanism

In conclusion, we have developed the first iron-catalyzed carboiodination of alkynes with simple alkyl iodides as both the carbon source and the iodine source, providing synthetically useful vinyl iodides under mild reaction conditions. The alkyl iodides with general alkyl chains, fluoroalkyl group, ester, and cyano group could be applied as the substrates, while conjugated alkynes or unconjugated alkynes are both suitable for this transformation. Alkenes could also be used in this chemistry and produce more complex alkyl iodides. Acetyl *tert*-butyl peroxide was selected as the radical initiator. A cascade radical relay and atom transfer radical addition was supposed to be the reaction mechanism.

All reactions were carried out under an atmosphere of N_2 in a flame-dried glassware with magnetic stirring, unless otherwise indicated. Commercially obtained reagents were used directly as received. Solvents were dried by Innovative Technology Solvent Purification System. Liquids and solutions were transferred via syringe. All reactions were monitored by TLC. GC-MS data were recorded on Thermo ISQ QD. ^1H and ^{13}C NMR spectra were recorded on Bruker BioSpin Avance III HD spectrometer. Data for ^1H NMR spectra are reported relative to $CHCl_3$ as an internal standard (7.26 ppm) and are reported as follows: chemical shift (ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are reported relative to $CHCl_3$ as an internal standard (77.23 ppm) and are reported in terms of chemical shift (ppm). HRMS data were recorded on Waters Micromass GCT Premier or Thermo Fisher Scientific LTQ FT Ultra mass spectrometer.

Iron-Catalyzed Carboiodination of But-3-yn-2-one (1a); (*Z*)-3-Iodo-5-methylhept-3-en-2-one (3, *E*/*Z* = 1:12); Typical Procedure

To a flame-dried Schlenk tube was added $Fe(OTf)_3$ (25 mg, 0.05 mmol, 10 mol%), followed by the addition of MTBE (2 mL) under N_2 atmosphere. Then but-3-yn-2-one (**1a**; 34 mg, 0.5 mmol, 1 equiv), 2-iodobutane (**2a**; 276 mg, 1.5 mmol, 3 equiv), and *tert*-butyl peroxyacetate (66 mg, 0.5 mmol, 1 equiv) were added sequentially. The mixture was stirred at r.t. for 12 h. Afterwards, the reaction solution was diluted with EtOAc and filtered through a plug of diatomite. The filtrate was concentrated by rotary evaporation under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc/PE 100:1) to afford product **3** as a pale yellow liquid; yield: 90.7 mg (0.36 mmol, 72%).

^1H NMR (400 MHz, $CDCl_3$): δ = 6.69 (d, *J* = 9.1 Hz, 0.92 H), 6.24 (d, *J* = 10.6 Hz, 0.07 H), 2.72–2.51 (m, 1 H), 2.47 (s, 2.72 H), 2.45 (s, 0.25 H), 1.48 (pent, *J* = 7.2 Hz, 2 H), 1.06 (d, *J* = 6.7 Hz, 2.91 H), 0.97 (d, *J* = 6.6 Hz, 0.32 H), 0.90 (t, *J* = 7.5 Hz, 3.03 H), 0.82 (t, *J* = 7.4 Hz, 0.44 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.85, 192.76, 158.21, 154.76, 110.89, 99.99, 44.11, 39.45, 29.58, 29.16, 28.80, 25.47, 19.90, 18.39, 11.79.

HRMS (ESI): *m*/*z* calcd for $[C_8H_{13}IONa]^+$ ([M + Na]$^+$): 274.9903; found: 274.9901.

(*Z*)-4-Cyclohexyl-3-iodobut-3-en-2-one (4, *E*/*Z* = 1:75)

Pale yellow liquid; yield: 102.9 mg (74%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.74 (d, *J* = 8.7 Hz, 1 H), 2.59–2.43 (m, 4 H), 1.81–1.65 (m, 5 H), 1.41–1.28 (m, 2 H), 1.27–1.15 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.80, 157.38, 110.05, 46.84, 30.67, 25.68, 25.36, 25.25.

HRMS (ESI): *m*/*z* calcd for $[C_{10}H_{15}IONa]^+$ ([M + Na]$^+$): 301.0060; found: 301.0058.

Ethyl (*Z*)-3-Cyclohexyl-2-iodoacrylate[20] (5, *E*/*Z* = 1:3)

Pale yellow liquid; yield: 115.5 mg (75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.96 (d, *J* = 9.0 Hz, 0.75 H), 6.69 (d, *J* = 10.0 Hz, 0.25 H), 4.27–4.19 (m, 2 H), 2.82 (qt, *J* = 11.2, 3.5 Hz, 0.25 H), 2.48–2.35 (m, 0.78 H), 1.79–1.59 (m, 6 H), 1.33–1.28 (m, 4 H), 1.26–1.16 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.98, 163.13, 160.50, 157.11, 92.70, 83.21, 62.61, 62.14, 45.93, 42.50, 32.10, 30.55, 25.73, 25.70, 25.42, 25.28, 14.21, 14.08.

Ethyl (*Z*)-3-Cyclopentyl-2-iodoacrylate (6, *E*/*Z* = 1:2.3)

Pale yellow liquid; yield: 100.0 mg (68%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (d, *J* = 9.1 Hz, 0.69 H), 6.76 (d, *J* = 10.0 Hz, 0.30 H), 4.32–4.12 (m, 2 H), 3.22 (sext, *J* = 8.5 Hz, 0.33 H), 2.81 (sext, *J* = 8.3 Hz, 0.69 H), 2.00–1.82 (m, 2 H), 1.78–1.52 (m, 4 H), 1.43–1.25 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.08, 163.11, 160.52, 157.80, 93.15, 82.92, 62.59, 62.14, 47.54, 43.92, 33.00, 31.96, 25.63, 25.28, 14.23, 14.10.

HRMS (ESI): *m*/*z* calcd for $[C_{10}H_{15}IO_2Na]^+$ ([M + Na]$^+$): 317.0009; found: 317.0010.

(*Z*)-1-(2-Cyclohexyl-1-iodovinyl)-4-(trifluoromethyl)benzene (7, *E*/*Z* = 1:20)

Pale yellow liquid; yield: 77.9 mg (41%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61–7.37 (m, 4 H), 6.38 (d, *J* = 10.3 Hz, 0.10 H), 5.79 (d, *J* = 8.4 Hz, 0.90 H), 2.48–2.36 (m, 0.92 H), 2.02–1.96 (m, 0.11 H), 1.91–1.63 (m, 5 H), 1.44–1.12 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.21, 146.56, 145.82, 129.91 (q, *J* = 32.6 Hz), 128.94, 125.11 (q, *J* = 3.8 Hz), 123.94 (q, *J* = 270.3 Hz), 100.08, 46.73, 41.37, 32.57, 31.43, 25.88, 25.57.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.51 (s, 0.1 × 3 F), –62.61 (s, 0.9 × 3 F).

HRMS (EI$^+$): *m*/*z* calcd for $[C_{15}H_{16}F_3I]^+$ ([M]$^+$): 380.0249; found: 380.0239.

(*Z*)-1-(2-Cyclohexyl-1-iodovinyl)-3-fluorobenzene (8, *E*/*Z* = 1:11)

Pale yellow liquid; yield: 62.7 mg (38%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24–7.12 (m, 2 H), 7.08 (d, *J* = 10.1 Hz, 0.91 H), 6.97 (d, *J* = 7.8 Hz, 0.13 H), 6.93–6.81 (m, 1 H), 6.24 (d, *J* = 10.3 Hz, 0.10 H), 5.67 (d, *J* = 8.4 Hz, 0.90 H), 2.42–2.24 (m, 0.93 H), 1.96–1.88 (m, 0.14 H), 1.82–1.53 (m, 5 H), 1.35–1.06 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.28 (d, *J* = 246.1 Hz), 145.33 (d, *J* = 7.8 Hz), 144.89, 129.48 (d, *J* = 8.4 Hz), 124.29 (d, *J* = 2.8 Hz), 115.78 (d, *J* = 22.8 Hz), 114.82 (d, *J* = 21.2 Hz), 100.33 (d, *J* = 2.6 Hz), 46.63, 41.32, 32.57, 31.47, 25.91, 25.68, 25.60, 25.38.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –112.70 (s, 0.1 F), –113.52 (s, 0.9 F).

HRMS (EI$^+$): *m*/*z* calcd for $[C_{14}H_{16}FI]^+$ ([M]$^+$): 330.0281; found: 330.0275.

Ethyl (*E*)-4-Iodo-2-methyl-4-(*p*-tolyl)but-3-enoate (9, *E*/*Z* = 2.3:1)

Pale yellow liquid; yield: 160.0 mg (93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 8.2 Hz, 0.54 H), 7.21 (d, *J* = 8.1 Hz, 1.53 H), 7.16–7.08 (m, 2 H), 6.49 (d, *J* = 10.3 Hz, 0.75 H), 6.01 (d, *J* = 8.8 Hz, 0.26 H), 4.23–4.09 (m, 2 H), 3.60–3.50 (m, 0.27 H), 3.20–3.09 (m, 0.77 H), 2.34 (s, 3 H), 1.37 (d, *J* = 7.1 Hz, 0.87 H), 1.32–1.24 (m, 3 H), 1.20 (d, *J* = 7.0 Hz, 2.44 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.84, 173.19, 140.70, 139.94, 138.53, 138.51, 138.34, 136.39, 129.01, 128.87, 128.52, 128.32, 106.40, 97.60, 60.94, 60.89, 48.49, 42.51, 21.29, 21.11, 17.79, 17.27, 14.26, 14.19.

HRMS (ESI): *m*/*z* calcd for $[C_{14}H_{17}IO_2Na]^+$ ([M + Na]$^+$): 367.0165; found: 367.0165.

Ethyl (*E*)-4-Iodo-2-methyl-4-(*m*-tolyl)but-3-enoate (10, *E*/*Z* = 2.2:1)

Pale yellow liquid; yield: 166.8 mg (97%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21–6.96 (m, 4 H), 6.40 (d, *J* = 10.3 Hz, 0.73 H), 5.95 (d, *J* = 8.8 Hz, 0.26 H), 4.13–4.01 (m, 2 H), 3.52–3.41 (m, 0.27 H), 2.93–2.76 (m, 0.75 H), 2.25 (s, 3 H), 1.32–1.06 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.61, 173.19, 142.64, 141.23, 140.75, 138.02, 136.96, 129.35, 129.22, 129.01, 128.23, 128.14, 125.89, 125.46, 97.53, 60.98, 60.91, 48.47, 42.53, 21.44, 21.36, 17.83, 17.30, 14.30, 14.23.

HRMS (ESI): *m*/*z* calcd for $[C_{14}H_{17}IO_2Na]^+$ ([M + Na]$^+$): 367.0165; found: 367.0169.

Ethyl (*E*)-4-Iodo-2-methyl-4-phenylbut-3-enoate (11, *E*/*Z* = 1.9:1)

Pale yellow liquid; yield: 161.7 mg (98%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 6.7 Hz, 0.73 H), 7.29–7.14 (m, 4.51 H), 6.43 (d, *J* = 10.3 Hz, 0.65 H), 5.97 (d, *J* = 8.8 Hz, 0.35 H), 4.15–4.00 (m, 2 H), 3.52–3.42 (m, 0.35 H), 3.05 (dq, *J* = 10.3, 7.0 Hz, 0.66 H), 1.28 (d, *J* = 7.2 Hz, 1.12 H), 1.22–1.14 (m, 3 H), 1.11 (d, *J* = 7.0 Hz, 2.04 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.76, 173.12, 142.65, 141.31, 140.97, 137.21, 128.66, 128.58, 128.41, 128.38, 128.25, 106.23, 97.22, 61.00, 60.95, 48.49, 42.51, 17.81, 17.28, 14.30, 14.22.

HRMS (ESI): *m*/*z* calcd for $[C_{13}H_{15}IO_2Na]^+$ ([M + Na]$^+$): 353.0009; found: 353.0009.

Ethyl (*E*)-4-Iodo-4-(3-methoxyphenyl)-2-methylbut-3-enoate (12, *E*/*Z* = 2.2:1)

Pale yellow liquid; yield: 167.4 mg (93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.17 (m, 1 H), 7.05 (d, *J* = 8.1 Hz, 0.35 H), 7.02–6.98 (m, 0.33 H), 6.89 (d, *J* = 7.7 Hz, 0.69 H), 6.86–6.78 (m, 1.66 H), 6.49 (d, *J* = 10.3 Hz, 0.66 H), 6.07 (d, *J* = 8.8 Hz, 0.33 H), 4.21–4.09 (m, 2 H), 3.87–3.74 (m, 3 H), 3.59–3.49 (m, 0.33 H), 3.17 (dq, *J* = 10.2, 7.0 Hz, 0.67 H), 1.36 (d, *J* = 7.1 Hz, 1.07 H), 1.31–1.24 (m, 3 H), 1.20 (d, *J* = 7.0 Hz, 2.04 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.71, 173.12, 159.23, 159.18, 144.03, 142.47, 140.97, 137.30, 129.40, 129.18, 121.01, 120.76, 114.45, 114.22, 114.12, 113.81, 105.83, 96.88, 60.99, 60.94, 55.36, 55.29, 48.42, 42.58, 17.80, 17.24, 14.28, 14.22.

HRMS (ESI): *m*/*z* calcd for $[C_{14}H_{17}IO_3Na]^+$ ([M + Na]$^+$): 383.0115; found: 383.0115.

Ethyl (*E*)-4-Iodo-4-(2-methoxyphenyl)-2-methylbut-3-enoate (13, *E*/*Z* = 3.3:1)

Pale yellow liquid; yield: 165.6 mg (92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.15 (m, 1 H), 7.14–7.04 (m, 1 H), 6.89–6.75 (m, 2 H), 6.47 (d, *J* = 8.8 Hz, 0.76 H), 5.78 (d, *J* = 8.8 Hz, 0.23 H), 4.10 (q, *J* = 7.1 Hz, 0.59 H), 4.03 (q, *J* = 7.1 Hz, 1.67 H), 3.77 (d, *J* = 3.1 Hz, 3 H), 3.50–3.40 (m, 0.23 H), 2.93–2.77 (m, 0.79 H), 1.29 (d, *J* = 7.1 Hz, 0.79 H), 1.23–1.14 (m, 3 H), 1.10 (d, *J* = 7.1 Hz, 2.55 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.90, 173.31, 156.26, 155.64, 141.99, 138.58, 132.62, 130.31, 130.00, 129.92, 129.80, 129.79, 120.45, 120.22, 111.34, 111.26, 99.99, 99.28, 60.87, 60.75, 55.61, 55.50, 47.84, 42.88, 17.30, 16.86, 14.27, 14.19.

HRMS (ESI): *m*/*z* calcd for $[C_{14}H_{17}IO_3Na]^+$ ([M + Na]$^+$): 383.0115; found: 383.0110.

Ethyl (*E*)-4-Iodo-2-methyl-4-[4-(trifluoromethyl)phenyl]but-3-enoate (14, *E*/*Z* = 1.7:1)

Pale yellow liquid; yield: 183.1 mg (92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62–7.53 (m, 2.84 H), 7.42 (d, *J* = 8.0 Hz, 1.26 H), 6.56 (d, *J* = 10.5 Hz, 0.62 H), 6.15 (d, *J* = 8.8 Hz, 0.38 H), 4.23–4.09 (m, 2 H), 3.59–3.49 (m, 0.38 H), 3.06 (dq, *J* = 10.5, 7.0 Hz, 0.64 H), 1.38 (d, *J* = 7.1 Hz, 1.17 H), 1.31–1.24 (m, 3 H), 1.20 (d, *J* = 7.0 Hz, 1.98 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.45, 172.70, 145.99, 144.78, 142.17, 139.20, 130.40 (q, *J* = 32.4 Hz), 130.35 (q, *J* = 32.4 Hz), 128.96, 128.84, 125.44 (q, *J* = 3.7 Hz), 125.22 (q, *J* = 3.8 Hz), 103.77, 94.48, 61.12, 61.10, 48.45, 42.61, 17.60, 17.14, 14.21, 14.14.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.61, –62.75.

HRMS (EI$^+$): *m*/*z* calcd for $[C_{14}H_{14}F_3IO_2]^+$ ([M]$^+$): 397.9991; found: 397.9983.

Ethyl (*E*)-4-(2-Fluorophenyl)-4-iodo-2-methylbut-3-enoate (15, *E*/*Z* = 2.6:1)

Pale yellow liquid; yield: 168.8 mg (97%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.12 (m, 2.18 H), 7.10–6.91 (m, 2.11 H), 6.56 (d, *J* = 10.3 Hz, 0.73 H), 5.93 (d, *J* = 8.8 Hz, 0.28 H), 4.15–3.99 (m, 2 H), 3.45 (pent, *J* = 7.2 Hz, 0.29 H), 2.88 (dq, *J* = 9.7, 7.1 Hz, 0.75 H), 1.30 (d, *J* = 7.1 Hz, 0.89 H), 1.24–1.12 (m, 5.63 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.50, 172.84, 158.71 (d, *J* = 247.9 Hz), 158.30 (d, *J* = 248.75 Hz), 143.73, 140.86 (d, *J* = 2.5 Hz), 131.44 (d, *J* = 2.0 Hz), 131.24 (d, *J* = 13.3 Hz), 130.49, 130.45 (d, *J* = 8.3 Hz), 130.04 (d, *J* = 8.3 Hz), 128.86 (d, *J* = 15.6 Hz), 124.20 (d, *J* = 3.7 Hz), 123.86 (d, *J* = 3.7 Hz), 94.85, 87.21, 61.02, 60.94, 48.16, 43.00, 17.39, 17.09, 14.23, 14.13.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –112.64, –113.71.

HRMS (ESI): *m*/*z* calcd for $[C_{13}H_{14}FIO_2Na]^+$ ([M + Na]$^+$): 370.9915; found: 370.9916.

Ethyl (*E*)-4-Iodo-2,2-dimethyl-4-phenylbut-3-enoate[22] (16, *E* Only)

Pale yellow liquid; yield: 68.8 mg (40%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24–7.12 (m, 5 H), 6.46 (s, 1 H), 3.65 (q, *J* = 7.2 Hz, 2 H), 1.13 (s, 6 H), 1.07 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.00, 146.20, 142.51, 128.25, 128.07, 127.96, 96.31, 60.73, 47.26, 26.92, 13.94.

Ethyl (*E*)-2,2-Difluoro-4-iodo-4-phenylbut-3-enoate[2j] (17, *E* Only)

Pale yellow liquid; yield: 146.1 mg (83%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.27 (m, 5 H), 6.72 (t, *J* = 10.9 Hz, 1 H), 3.95 (q, *J* = 7.2 Hz, 2 H), 1.18 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.53 (t, *J* = 33.2 Hz), 140.66, 133.04 (t, *J* = 28.5 Hz), 129.48, 128.08, 127.84 (t, *J* = 1.9 Hz), 110.87 (t, *J* = 248.5 Hz), 108.77 (t, *J* = 10.2 Hz), 63.17, 13.72.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –93.76.

(*E*)-1-Methoxy-3-[3,4,4,4-tetrafluoro-1-iodo-3-(trifluoromethyl)but-1-en-1-yl]benzene (18, *E*/*Z* = 15:1)

Pale yellow liquid; yield: 164.8 mg (77%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (t, *J* = 7.9 Hz, 1 H), 6.91–6.71 (m, 3 H), 6.41 (d, *J* = 24.0 Hz, 1 H), 3.79 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.74, 142.85, 129.03, 123.26 (d, *J* = 14.0 Hz), 119.57 (dq, *J* = 27.6 Hz), 118.91, 114.56, 112.07 (d, *J* = 2.8 Hz), 109.01, 93.64–90.55 (m), 55.23.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –76.55 (d, *J* = 8.9 Hz), –76.74 (d, *J* = 8.0 Hz), –184.96 (hept, *J* = 8.0 Hz), –188.41 (hept, *J* = 8.9 Hz).

HRMS (EI$^+$): *m*/*z* calcd for $[C_{12}H_8F_7IO]^+$ ([M]$^+$): 427.9508; found: 427.9514.

(*E*)-4-Iodo-4-phenylbut-3-enenitrile (19, *E*/*Z* = 1.8:1)

Pale yellow liquid; yield: 98.2 mg (73%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.24 (m, 5 H), 6.45 (t, *J* = 7.5 Hz, 0.64 H), 6.00 (t, *J* = 6.6 Hz, 0.36 H), 3.38 (d, *J* = 6.5 Hz, 0.74 H), 2.97 (d, *J* = 7.5 Hz, 1.35 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.68, 139.99, 129.34, 129.22, 128.85, 128.66, 128.53, 128.45, 128.05, 125.83, 116.74, 116.41, 111.66, 101.80, 26.54, 19.99.

HRMS (ESI): *m*/*z* calcd for $[C_{10}H_8INNa]^+$ ([M + Na]$^+$): 291.9594; found: 291.9592.

(*E*)-4-Iodo-4-(*p*-tolyl)but-3-enenitrile (20, *E*/*Z* = 2.4:1)

Pale yellow liquid; yield: 99.1 mg (70%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 8.2 Hz, 0.64 H), 7.22–7.12 (m, 3.51 H), 6.43 (t, *J* = 7.5 Hz, 0.71 H), 5.97 (t, *J* = 6.5 Hz, 0.30 H), 3.38 (d, *J* = 6.6 Hz, 0.61 H), 2.99 (d, *J* = 7.4 Hz, 1.49 H), 2.36 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.49, 139.35, 138.92, 137.13, 129.48, 129.17, 128.35, 128.31, 128.01, 124.95, 116.85, 116.53, 111.93, 102.24, 26.55, 21.37, 21.21, 19.98.

HRMS (ESI): *m*/*z* calcd for $[C_{11}H_{10}INNa]^+$ ([M + Na]$^+$): 305.9750; found: 305.9747.

(*E*)-4-(4-Fluorophenyl)-4-iodobut-3-enenitrile (21, *E*/*Z* = 1.7:1)

Pale yellow liquid; yield: 109.1 mg (76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.41 (m, 0.75 H), 7.31–7.24 (m, 1.48 H), 7.12–7.00 (m, 2 H), 6.47 (t, *J* = 7.5 Hz, 0.63 H), 5.97 (t, *J* = 6.5 Hz, 0.37 H), 3.39 (d, *J* = 6.5 Hz, 0.76 H), 2.98 (d, *J* = 7.5 Hz, 1.33 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.11 (d, *J* = 250.1 Hz), 162.67 (d, *J* = 250.4 Hz), 136.07 (d, *J* = 3.5 Hz), 130.17 (d, *J* = 8.4 Hz), 130.03 (d, *J* = 8.5 Hz), 129.14, 125.97, 116.38 (d, *J* = 40.8 Hz), 115.97 (d, *J* = 22.0 Hz), 115.44 (d, *J* = 21.8 Hz), 110.01, 100.40, 26.50, 19.94.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –110.89, –111.81.

HRMS (EI$^+$): *m*/*z* calcd for $[C_{10}H_7FIN]^+$ ([M]$^+$): 286.9607; found: 286.9610.

Ethyl (*E*)-2,2-Difluoro-4-iododec-3-enoate[23] (22, *E*/*Z* = 5.4:1)

Pale yellow liquid; yield: 135.1 mg (75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.40 (t, *J* = 13.2 Hz, 1 H), 4.33 (q, *J* = 7.1 Hz, 2 H), 2.60 (t, *J* = 7.5 Hz, 2 H), 1.54 (pent, *J* = 7.1 Hz, 2 H), 1.40–1.28 (m, 9 H), 0.89 (t, *J* = 6.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.20 (t, *J* = 34.4 Hz), 131.22 (t, *J* = 27.1 Hz), 119.67 (t, *J* = 7.6 Hz), 111.54 (t, *J* = 252.3 Hz), 63.32, 40.74, 31.53, 29.86, 28.05, 22.51, 14.03, 13.90.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –97.74.

(*E*)-(5-Chloro-4,4,5,5-tetrafluoro-2-iodopent-2-en-1-yl)benzene (23, *E*/*Z* = 6.2:1)

Pale yellow liquid; yield: 141.8 mg (75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.31 (m, 3 H), 7.26–7.20 (m, 2 H), 6.55 (t, *J* = 13.8 Hz, 1 H), 4.08 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.78, 129.00, 128.74, 127.55 (t, *J* = 23.6 Hz), 127.42, 122.86 (tt, *J* =38.7 Hz), 120.01 (t, *J* = 5.3 Hz), 113.46 (tt, *J* = 33.9 Hz), 46.65 (t, *J* = 2.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –71.33 to –71.42 (m), –104.25 (t, *J* = 5.8 Hz).

HRMS (EI$^+$): *m*/*z* calcd for $[C_{11}H_8ClF_4I]^+$ ([M]$^+$): 377.9295; found: 377.9282.

1,1,1,2-Tetrafluoro-4-iodo-2-(trifluoromethyl)decane (24)

Pale yellow liquid; yield: 179.1 mg (88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.38–4.28 (m, 1 H), 3.00–2.76 (m, 2 H), 1.87–1.68 (m, 2 H), 1.60–1.47 (m, 1 H), 1.44–1.26 (m, 7 H), 0.90 (t, *J* = 6.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.60 (m), 91.99 (m), 40.84 (d, *J* = 2.9 Hz), 39.67 (d, *J* = 18.2 Hz), 31.56, 29.66, 28.13, 22.97, 22.55, 14.01.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –76.76 (d, *J* = 523.7 Hz), –185.57.

HRMS (EI$^+$): *m*/*z* calcd for $[C_{11}H_{15}F_7I]^+$ ([M]$^+$): 407.0107; found: 407.0104.

Ethyl 2,2-Difluoro-4-iodo-5-phenylpentanoate[24] (25)

Pale yellow liquid; yield: 154.6 mg (84%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.25 (m, 3 H), 7.22–7.15 (m, 2 H), 4.40–4.28 (m, 3 H), 3.30–3.15 (m, 2 H), 2.99–2.70 (m, 2 H), 1.35 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.42 (t, *J* = 32.3 Hz), 138.83, 129.03, 128.62, 127.23, 115.22 (t, *J* = 253.4 Hz), 63.31, 47.22 (d, *J* = 1.4 Hz), 44.36 (t, *J* = 23.4 Hz), 21.94 (t, *J* = 3.8 Hz), 13.92.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –100.74 to –107.24 (m).

1-Fluoro-4-[4,5,5,5-tetrafluoro-2-iodo-4-(trifluoromethyl)pentyl]benzene (26)

Pale yellow liquid; yield: 198.7 mg (92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18–7.11 (m, 2 H), 7.05–6.97 (m, 2 H), 4.46–4.35 (m, 1 H), 3.29–3.04 (m, 2 H), 3.03–2.82 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.06 (d, *J* = 246.0 Hz), 134.41 (d, *J* = 3.3 Hz), 130.49 (d, *J* = 8.1 Hz), 120.61 (qt, *J* = 286.5, 28.5 Hz), 115.47 (d, *J* = 21.3 Hz), 93.81–90.20 (m), 46.41 (d, *J* = 3.1 Hz), 38.98 (d, *J* = 18.3 Hz), 22.03.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –75.90 to –77.65 (m), –115.07, –185.08 to –185.30 (m).

HRMS (EI$^+$): *m*/*z* calcd for $[C_{12}H_9F_8I]^+$ ([M]$^+$): 431.9621; found: 431.9615.

(5,5,6,6,6-Pentafluoro-3-iodohexyl)benzene (27)

Pale yellow liquid; yield: 175.8 mg (93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.26 (m, 2 H), 7.25–7.18 (m, 3 H), 4.29–4.19 (m, 1 H), 2.98–2.66 (m, 4 H), 2.15–2.06 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.89, 128.63, 128.51, 126.41, 118.56 (qt, *J* = 284.0 Hz, *J* = 35.4 Hz), 115.14 (tq, *J* = 255.5 Hz, *J* = 37.7 Hz), 41.71 (t, *J* = 2.2 Hz), 41.55 (t, *J* = 20.7 Hz), 35.68, 20.05.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –85.85, –114.71 to –119.73 (m).

HRMS (EI$^+$): *m*/*z* calcd for $[C_{12}H_{12}F_5I]^+$ ([M]$^+$): 377.9904; found: 377.9894.

Funding Information

We thank NSFC (Grant Nos. 21502191 and 21672213), Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB20000000), The 100 Talents Program, 'The 1000 Youth Talents Program', and Haixi Institute of CAS (CXZX-2017-P01) for financial support.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1609448.

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