Organic & Biomolecular Chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: T. R. Reddy, D. S. Rao and S. Kashyap, *Org. Biomol. Chem.*, 2018, DOI: 10.1039/C7OB03076B.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/obc

View Article Online
DOI: 10.1039/C7OB03076B

Journal Name

ARTICLE

Chemoselective and Stereospecific Iodination of Alkynes using Sulfonium Iodate(I) Salt

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Dodla S. Rao,[a] Thurpu R. Reddy,[a] and Sudhir Kashyap*[ab]

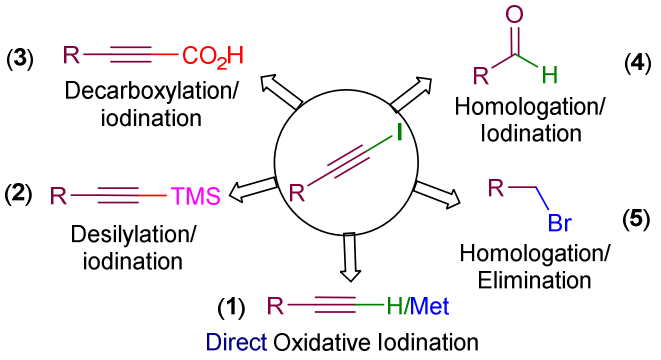
An efficient and highly chemoselective iodination of alkyne using Sulfonium Iodate (I) electrophilc reagent under metal-free conditions has been developed. The reactivity of sulfonium Iodate (I) salt could be significantly diverse in the presence of the water as the solvent, enabling the (*E*)-1,2-diiodoalkenes stereospecifically. This stereodivergent approach is amenable to a wide range of alkyne substrates and demonstrates diverse functional group tolerance resulting synthetically valuable 1-iodoalkyne and (*E*)-vicinal-diiodoalkenes in good to excellent yields (up to 99%) with 100% selectivity at ambient condition.

Introduction

The iodo-functionalized molecules have attracted considerable attention due to their synthetic adaptability as key intermediates and valuable synthons in organic chemistry.[1] In particular, 1-iodoalkynes represent important subclass which have been extensively employed as useful precursors in several fascinating chemical transformations.[2] The presence of iodo moiety in sp-hybridized acetylene led to development of rapid and attractive stereocontrolled techniques viz Cadiot-Chodkiewicz,[3] Nozaki-Takai cross coupling,[4] hetero-functionalization *via* CuAAC "click reactions",[5] total syntheses of active natural products and biologically active molecules.[6] In addition to well appreciated role in material and polymer research,[7] iodoalkyne derivatives exhibit distinctive biological activities hence served as promising chemical probes of outmost pharmaceutical applications such as anti-HIV, anti-microbial, and fungicidal agents.[8]

The conventional procedures for generating synthetically useful 1-iodoalkynes involve direct oxidative iodination of terminal alkyne with iodinating reagents.[9] Most commonly, addition of molecular iodine[9a] or hypervalent iodonium salts on acetylenes applied to access corresponding 1-iodoacetylenes.[9b] Indeed, a combination of hypervalent oxidant such as $PhI(OAc)_2$, with KI as halide source in the presence of metal catalyst and Et_3N as additive also reported for similar transformation.[9c] On the other hand, Bu_4NI as iodo-source with oxone as an oxidizing reagent promoted the iodination of terminal alkynes in aqueous solvent albeit at high temperature with limited substrate scope.[9d]

Alternative classical methods to access desired 1-iodoalkynes in multistep or indirect process (Scheme 1) includes (1) oxidative iodination of metal-acetylides *via* metal-iodo exchange in the presence of a base;[10] (2) NIS/Et_3N-mediated iodo-decarboxylation of propiolic acid intermediate under Hundiesker reaction;[11] (3) desilylation-iodination of trialkylsilylacetylenes using NIS in the presence of metal-salt such as $AgNO_3$;[12] (4) a two-steps Corey-Fuchs homologation-iodination of aldehyde employing strong base such as BuLi or LDA at -78 °C;[13] (5) one-pot homologation-double elimination reaction of benzyl bromide using CHI_3 and NaHMDS under cryogenic reaction conditions.[14]



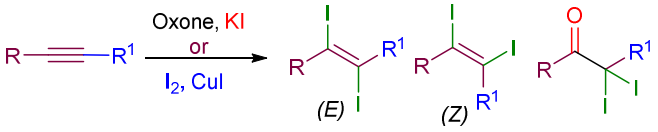
Scheme 1. Previous approaches for the synthesis of 1-iodoalkynes.

Likewise, 1,2-diiodovinyl substrates are considered important synthetic building blocks and have been utilized often as key intermediates in functional group manipulation and valuable precursors in metal-catalyzed coupling reactions.[15] An approach to stereospecific synthesis of 1,2-*trans*-diiodoalkenes is quite elusive and predominantly relies on direct addition of iodine or iodinating reagent on an

[a] *Department of Chemistry, Malaviya National Institute of Technology (MNIT), Jaipur-302 017, INDIA. E-mail: skashyap,chy@mnit.ac.in, skr.kashyap@gmail.com.*
[b] *INSPIRE Faculty, Department of Science and Technology (DST) and Assistant Professor, Academy of Scientific and Innovative Research (AcSIR), INDIA.*

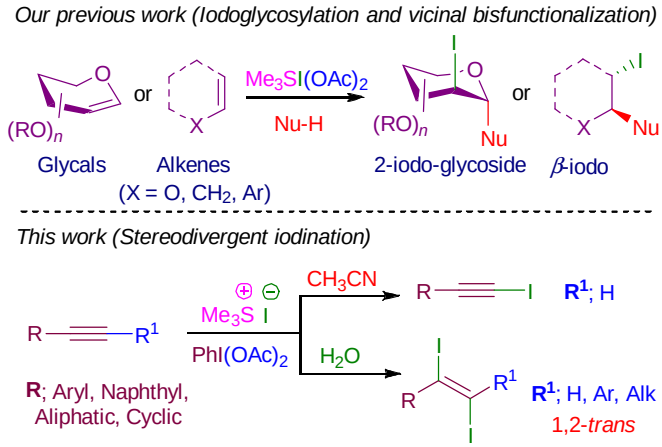
Electronic Supplementary Information (ESI) available: [General synthesis information, procedures, characterization data, spectral charts are provided]. See DOI: 10.1039/x0xx00000x

acetylene triple bond.[16] Though, some of oxidative diiodination methods often require additive such as CuI, H_2O_2, Al_2O_3 and H_2SO_4 to realize stereoselective addition, thereby restricting the substrate scope.[17] Other reported methods utilizing oxone as oxidant and halide salt such as KI and NaI, effectively promoted the oxidative diiodination of a triple bond.[18] However, excessive use of oxidant involving hazardous and toxic iodinating reagent, unconventional processes and stereoselectively indiscriminate *E/Z* isomeric mixture of vicinal diiodoalkenes or oxyhalogenataed α,α'-diidoketones[18a] as by-products are some recognized challenges (Scheme 2).



Scheme 2. Previous approaches towards 1,2-diiodoalkenes.

Owing to the prominence synthetic versatility and short of commercial availability of iodo-functionalized derivatives, development of stereoselective and efficient protocol utilizing preferred reagent system is highly desirable. In this context, we recently demonstrated the utility of sulfonium bis(acetoxy)iodate(I) salt in stereoselective synthesis of 2-deoxy glycoconjugates.[19a] The effectiveness and distinctive adaptability of the present reagent system is further demonstrated for regioselective vicinal bisfunctionalization of a diverse range of olefins[19b] (Scheme 3).



Scheme 3. Selective iodo-functionalization using sulfonium iodate(I) reagent system.

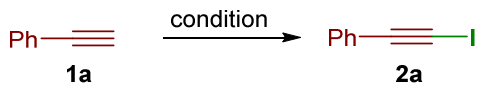
Inspired by the recent success of unprecedented sulfonium iodate reagent, we envisioned that the inherent ability of electrophilc salt would offer facile iodination of an alkyne moiety *via* direct oxidative addition on a triple bond. In continuation of our efforts in search of novel and promising alternative methods involving environmentally benign reagents,[19] herein, we report a solvent controlled stereodivergent process to access 1-iodoalkyne and 1,2-trans-diiodoalkene by employing $Me_3SI/PhI(OAc)_2$ under mild reaction condition (Scheme 3). The present system provides metal-free and molecular iodine free environment, operationally simple and applicable to wide substrate scope. It is pertinent to mention that a combination of Me_3SI and $PhI(OAc)_2$ promoted mono-iodination of alkynes in the presence of acetonitrile as the solvent, whereas, switching to water as sole solvent and altering the amount of iodine source led to the formation of exclusive di-iodination product (*E*)-1,2-diiodoalkene in complete stereospecific manner.

Results and discussion

At the outset, phenyl acetylene (**1a**) was used as the model substrate to examine oxidative iodination reaction by employing sulfonium bis(acetoxy)iodate(I) $Me_3SI(OAc)_2$, active electrophilic reagent system. Accordingly, a preformed solution of Me_3SI (1.1 equiv) and $PhI(OAc)_2$ (1.1 equiv) in CH_2Cl_2, assumingly generate $Me_3SI(OAc)_2$ *in situ*, was treated with **1a** (1.0 equiv) at room temperature. Although, reaction proceeded smoothly to afford the desired 1-(iodoethynyl)benzene (**2a**) in moderate yield (88%) after 6 h (Table 1, entry 1). To our delight, there was a significant improvement in the yield (98%) as well rate of iodination reaction when the reaction was performed in acetonitrile as the solvent (Table 1, entry 2).

Noteworthy, direct oxidative iodination of **1a** employing $Me_3SI(OAc)_2$ (1.1 equiv.) in acetonitrile works well to furnish **2a** in acceptable yield in 1 h (Table 1, entry 3). Further optimization by using other organic solvents such as 1,2-dichloroethane, toluene, AcOH, THF or DMF resulted no improvement (Entries 4-8). Nevertheless, these results highlighted the advantages of advanced protocol over conventional oxidizing reagent systems.

Table 1. Synthesis of 1-iodoalkyne and comparative studies.



1a **2a**

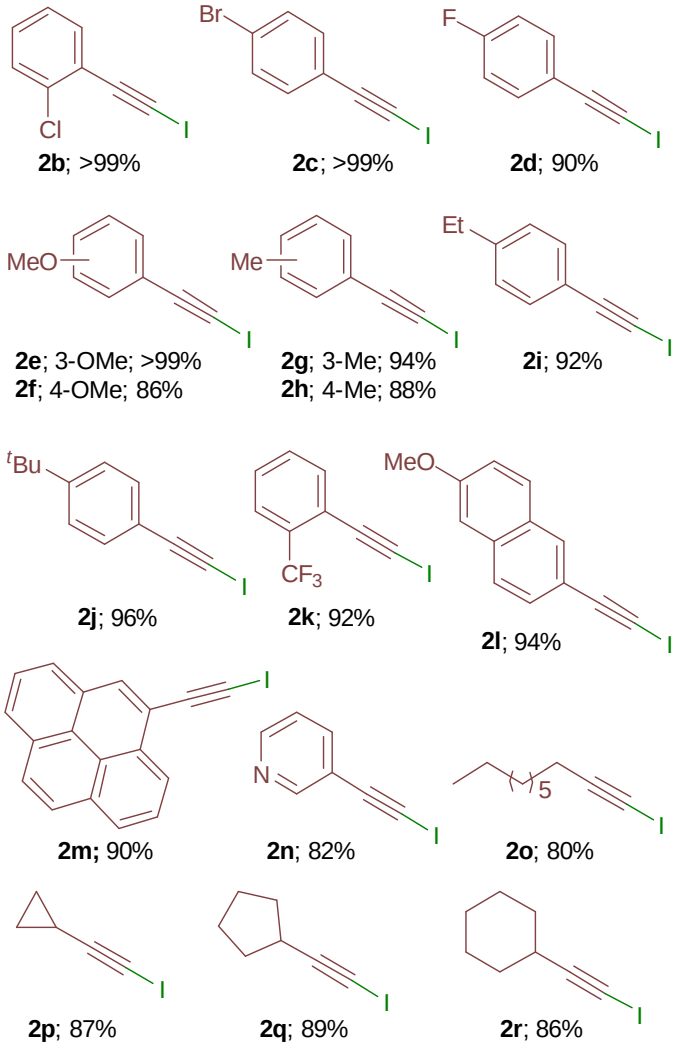
Entry	Iodo source	Oxidant	Solvent	*t*[h]	Yield of **2a**
1	Me_3SI	$PhI(OAc)_2$	CH_2Cl_2	6.0	88%
2	Me_3SI	$PhI(OAc)_2$	CH_3CN	0.5	**98%**
3	$Me_3SI(OAc)_2$	-	CH_3CN	1.0	92%
4	Me_3SI	$PhI(OAc)_2$	DCE	2.0	86%
5	Me_3SI	$PhI(OAc)_2$	Toluene	6.0	NR
6	Me_3SI	$PhI(OAc)_2$	AcOH	3.0	85%
7	Me_3SI	$PhI(OAc)_2$	THF	6.0	NR
8	Me_3SI	$PhI(OAc)_2$	DMF	12	78%

[a]Reaction conditions: **1a** (1.0 equiv.), Me_3SI /$PhI(OAc)_2$ (1.1 equiv. each) or $Me_3SI(OAc)_2$ (1.1 equiv.), solvent (2 mL), rt., NR = No reaction.

DOI: 10.1039/C7OB03076B

Having optimized protocol in hand, we next investigated the scope and generality of high yielding and selective iodination for a wide range of electronically diverse alkynes (Table 2). The aryl alkynes containing different substituted halogens for instance 2-chloro (**1b**), 3-bromo (**1c**) and 4-flouro-phenylacetylene (**1d**) efficiently afforded the desired 1-iodoalkynes in excellent yields (**2b-2d**).

Table 2. Scope of $Me_3SI(OAc)_2$-mediated iodination[a]



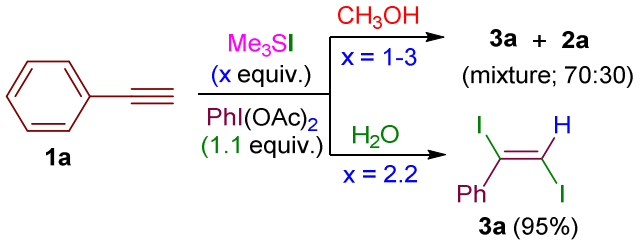
[a]Reaction conditions: Substrate **1** (1.0 equiv), Me_3SI (1.1 equiv.), $PhI(OAc)_2$ (1.1 equiv.), acetonitrile (2 mL), rt, 30 min.

As summarized in Table 2, we next probed the feasibility of electron-donating substituent such as methoxy (**1e-1f**), methyl (**1g-1h**), ethyl (**1i**) and *tert*-butyl (**1j**) on phenyl ring. Of note, all the reactions proceeded smoothly, affording the corresponding iodinated products **2e-2j** in 86-99% yields. Indeed, trifluoromethyl substrate **1k** found to be compatible under present conditions, underwent oxidative iodination reaction resulting the desired product **2k** in 92% yield. Subsequently, the selective iodination of polycyclic aryls such as naphthyl **1l** and pyrene **1m** containing acetylene moiety are accomplished successfully to obtain the venerable iodoacetylene derivatives **2l-2m** in 94% and 90% yield respectively. Notably, a heterocyclic bearing alkyne such as 3-ethynylpyridine (**1n**), performed well under "oxidative-iodination" process to generate synthetically useful **2n** in 82% yield.

Encouraged by these findings, we next examined the scope of unactivated acetylenes such as aliphatic and alicyclic alkyne substrates. For this purpose, dec-1-yne (**1o**), a ten carbon chain containing acetylene, was allowed to react under optimized reaction condition to realize the selective iodination furnishing 1-iododec-1-yne (**2o**) in 80% yield at ambient temperature. Subsequently, acetylenes comprising alicyclic moiety such as cyclopropyl (**1p**), cyclopentyl (**1q**) and cyclohexyl (**1r**) were iodinated successfully by using sulfonium iodate(I) reagent to obtain the corresponding products in good yields (**2p-2r**). On the other hand, the previous reported method using Bu_4NI/oxone for the oxidative iodination of substrates comprising heterocyclic, aliphatic, naphthyl or aryl acetylenes with methoxy substituent failed to deliver desired product,[9d] further confirming the prominence of sulfonium iodate(I) reagent system.

Next, it was of interest to explore the possibility of sulfonium iodate(I) reagent system for di-iodination of sp-hybridized alkyne moiety to generate synthetically useful vicinal diiodoalkenes. Initially, treatment of a preformed solution of Me_3SI and $PhI(OAc)_2$ (1.1 equiv each) in CH_3OH with phenylacetylene **1a** (1.0 equiv) at room temperature resulted the mixture of di-iodo product **3a** along with mono-iodo **2a** in a ratio 70:30, as observed by ^1H NMR spectrum of crude reaction mixture (Scheme 4). We anticipated that the activation of alkyne by $Me_3SI(OAc)_2$ electrophilic salt generated *in situ* from $Me_3SI/PhI(OAc)_2$ following addition of Me_3SI as a second iodine source (nucleophilic iodide) would provide effective and selective di-iodination. However, increasing the relative molar amount of Me_3SI (2-3 equiv) with $PhI(OAc)_2$ (1.1 equiv) did not offer the requisite selectivity even after prolonged reaction time or by varying the temperature.

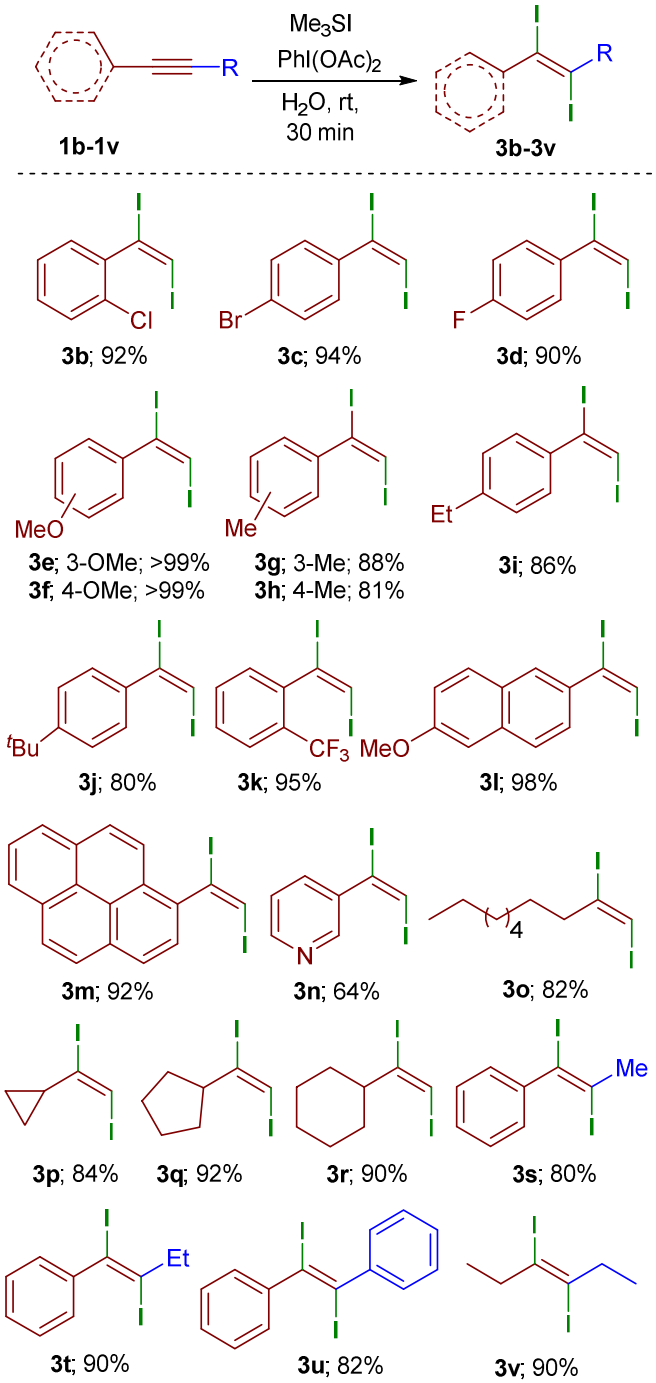
Interestingly, by switching the solvent system to water and altering the equivalents of Me_3SI (2.2 equiv), di-iodination reaction proceeded efficiently and complete conversion of **1a** was realized in at most 30 min affording the exclusive *(E)*-(1,2-diiodovinyl)benzene (**3a**) in 95% yield (Scheme 4). The stereochemistry of compound **3a** was precisely correlated by proton and proton-decoupled carbon spectrum, also found consistent and with conformity that of literature data.[9d]



Scheme 4. Stereospecific vicinal di-iodination of alkyne.

Gratifying, changing to water "green" solvent system could led to entirely different product with absolute stereo chemistry. Noteworthy, the divergent synthesis of a choice of product from same substrate by employing equivalent reagent under solvent controlled conditions is quite attractive with a purpose of expanding the utility. With the optimized reaction conditions, we investigated the scope and generality of the stereospecific *trans*-diiodination protocol, results are summarized in Table 3.

Table 3. Substrate scope for $Me_3SI/PhI(OAc)_2$-mediated di-iodination of alkynes[a]

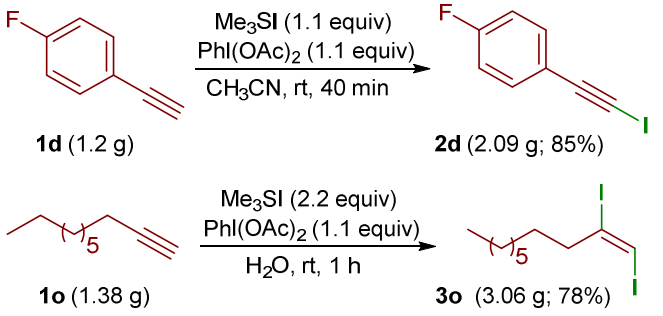


[a]Reaction conditions: Substrate **1** (1.0 equiv), Me_3SI (2.2 equiv.), $PhI(OAc)_2$ (1.1 equiv.), water (2 mL), rt, 30 min.

Aromatic alkynes with halogen at different position including 2-chloro, 4-bromo, 4-flouro (**1b-1d**) and electron rich substituents for instance 3-methoxy, 4-methoxy, 3-methyl, 4-methyl, 4-ethyl, 4-tert-butyl (**1e-1j**) were evaluating under stabilized conditions to obtain the desired di-iodinated products **3b-3h** in good to excellent yields. Also, the aryl acetylene containing CF_3 moiety **1k**, a naphthyl **1l** or a pyrene **1m** were all performed well affording the desired 1,2-diiodovinyl compounds **3k-3n** in good yields. In contrast, **1n** apparently gave a mixture of diiodo/iodo product **3n/2n** under standard conditions in 91% overall yield; **3n** (64%) and **2n** (27%), approximately 3:1 ratio, determine by relative integration of separable proton in ^1H NMR spectrum.

We further extended the scope for unactivated substrates, aliphatic and alicyclic acetylenes under eco-friendly protocol (Table 3). We observed that dec-1-yne (**1o**), and cyclic acetylenes **1p-1r** effectively participated in present oxidative-diiodination resulting the desired products **3o-3r** in 100% stereospecific manner. Given this success, validity of $Me_3SI/PhI(OAc)_2/H_2O$ system is further investigated for the stereoselective transformation of internal acetylenes into 1,2-*trans*-diiodoalkenes. Thus, 1-phenyl-1-propyne (**1s**) reacted well and afforded the (E)-1,2-diiodo-1-phenylpropene **3s** in 80% yield, confirming the *anti*-addition. Subsequently, 1-phenyl-1-butyne (**1t**) and 1,2-diphenylethyne (**1u**) were iodinated in good yields leading to (*E*)-1,2-diiodoolefins (**3t-3u**) with controlled stereoselectivity. Nevertheless, the oxidative di-iodination reaction was applicable to an aliphatic internal acetylene for instance 3-hexyne (**1v**), affording (E)-3,4-diiodohex-3-ene (**3v**) in 90% yield.

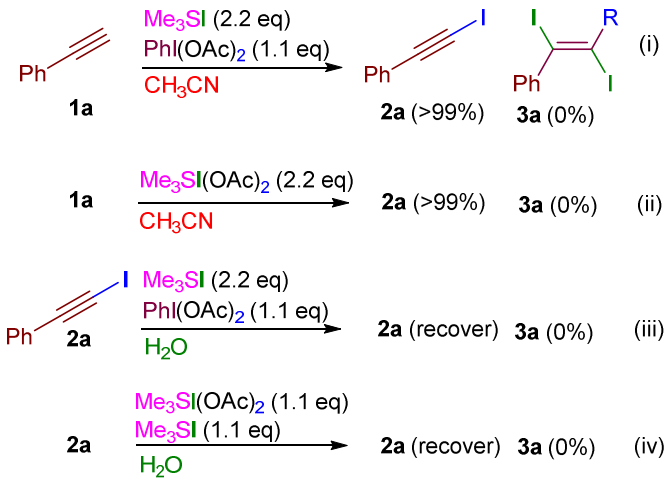
To further established the synthetic potential of representative protocol, the gram-scale selective iodination of acetylene was successfully conducted. (Scheme 5). Employing Me_3SI and $PhI(OAc)_2$ (1.1 equiv each) in a large scale iodination of 1-fluoro-4-ethynylbenzene **1d** (1.2 g, 10 mmol) in acetonitrile at room temperature afforded the product **2d** (2.09 g) in 85% yield, slightly lower as compared to 1.0 mmol scale (90%). In addition, 1-decyne **1o** (1.38 g) under standard di-iodination conditions resulted the corresponding (E)-1,2-diiododec-1-ene **3o** (3.06 g) in 78% isolated yield albeit in a longer reaction time. Nevertheless, the results are consistent in support with aforementioned selective iodination, highlighting the efficiency and feasibility on large scale.



Scheme 5. Scale-up reactions for selective iodination.

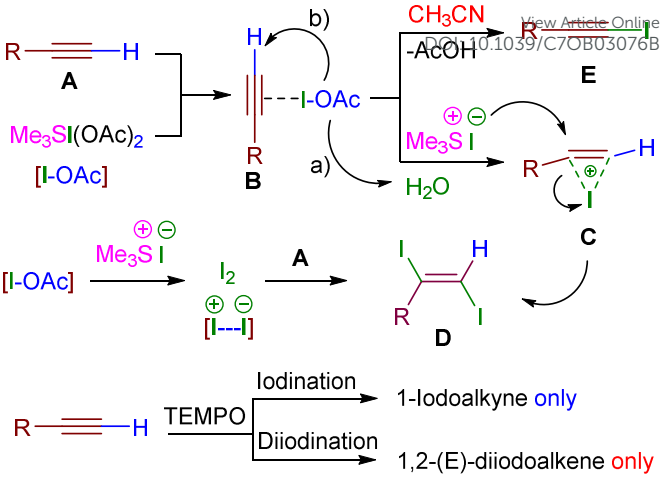
DOI: 10.1039/C7OB03076B

To gain the insight into the mechanism of di-iodination reaction, a series of control experiments were performed (Scheme 6). The reaction of **1a** with excess of Me_3SI (2.2 equiv) and oxidant $PhI(OAc)_2$ (1.1 equiv) in acetonitrile failed to produced any di-iodinated product **3a**, instead **2a** was obtained as a sole product in quantitative yield (Scheme 6, eq. i). Similar results were obtained when **1a** was activated with 2.2 equivalence of electrophilic salt, $Me_3SI(OAc)_2$ in acetonitrile (Eq. ii). Next, submitting 1-iodoalkyne **2a** to our standard di-iodination conditions also found to be ineffective, resulting complete recovery of starting material (Eq. iii). The reaction was re-examined by iodate reagent $Me_3SI(OAc)_2$ in the presence of 1.1 equivalence Me_3SI as iodosource in water, providing un-reacted **2a** (Eq. iv). These experiments indicate distinct activation of acetylene moiety by electrophilic salt in the presence of H_2O and possibility of enhanced nucleophilicity of iodide salt in more polar solvent. Illustrating the crucial role of water for the oxidative di-iodination, these results also ruled out the involvement of **2a** as an intermediate in this transformation.



Scheme 6. Control experiments and effect of solvent on selective iodination of alkyne.

Although a detailed mechanism for sulfonium iodate mediated di-iodination remains unclear at this moment, we proposed a plausible pathway based on literature analogy and supported by aforementioned control experiments. As shown in scheme 7, it is hypothesized that the electrophilic iodate (I^+) salt $Me_3SI(OAc)_2$ (an equivalent to IOAC) generated via oxidative transfer of acetyl groups from $PhI(OAc)_2$ to Me_3SI would trap an alkyne (**A**) to form the π-coordinated species **B**. Thereafter, generation of iodonium species **C** and AcO^- ion, which could trapped under present solvent system (pathway a). Subsequent attack of nucleophilic iodide (I^-) on iodonium ion intermediate **C** from opposite side finally leading to di-iodination adduct 1,2-*trans*-diiodoalkene **D** with absolute *anti*-addition selectivity. Alternatively, molecular iodine could be generated by the combination of an iodide ion ($Me_3S^+I^-$) and electrophilc iodate (I) salt (acetyl hypoiodite, AcO^-I^+), which then undergoes electrophilic addition on a triple bond to produce 1,2-(*E*)-diiodoalkene stereospecifically.



Scheme 7. A plausible mechanism for $Me_3SI(OAc)_2$-mediated selective iodination of alkynes.

In case of acetonitrile solvent, the reactive π-coordinated complex **B** could produce mono-iodo product **E** *via* intramolecular deprotonation of terminal alkyne by acetate ion to release acetic acid (pathway b). To further support the mechanism, a positive starch solution test observing by a colour changes from red to intense blue, confirming the existence of the electrophilc iodate (I) species and formation of molecular iodine intermediate. Moreover, the presence of TEMPO, a radical scavenger under the standard oxidative iodination processes, does not influences the outcome of the reactions, supporting the postulated ionic mechanistic scenario and consistent with the experimental results and literature precedent.

Conclusions

In conclusion, we have developed a metal-free, molecular iodine free protocol for stereodivergent iodination of alkynes under solvent-controlled process. The intrinsic reactivity of sulfonium iodate(I) salt in two different solvents resulting in selective iodination to access 1-iodoalkynes and vicinal (*E*)-diiodoalkenes. This protocol successfully applied to a wide range of substrates affording diverse functionalized and synthetically useful iodinated molecules at ambient temperature. This new system not only provide an efficient and operationally simple process, but also utilizing readily available and environmentally benign reagents. The present results open new dimensions of sulfonium iodate reagent for other nucleophilic version to introduce nitrogen, carbon, oxygen, and sulphur functionality on C-C multiple bond. Mechanistic studies and further investigating synthetic application of sulfonium iodate(I) salt in modern organic chemistry are currently ongoing in our laboratory.

Experimental

General Synthesis Information: Unless otherwise noted, materials were obtained from commercial suppliers and used without purification. Anhydrous solvents were purchased for

the reactions and used without further desiccation. All reactions were performed in flame-dried round bottom flasks, fitted with rubber septa or glass gas adapters, under a positive pressure of nitrogen or argon. Analytical thin-layer chromatography (TLC) was performed using aluminum backed UV F254 pre-coated silica gel flexible plates. Removal of solvent under reduced pressure refers to distillation with a rotary evaporator attached to a vacuum pump (~3 mmHg). Melting points were obtained in open capillary tubes using a micro melting point apparatus and were uncorrected. Optical rotations were recorded with a digital polarimeter at 589 nm (sodium D-line). NMR were recorded on 300, 400 or 500 MHz nuclear magnetic resonance spectrometers. The proton resonances are annotated as: chemical shift (δ) relative to tetramethylsilane (δ 0.0) using the residual solvent signal as an internal standard or tetramethylsilane itself: chloroform-d (δ 7.26, singlet), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), coupling constant (*J*, Hz), and number of protons for a given resonance is indicated by nH. The chemical shifts of ^{13}C NMR are reported in ppm relative to the central line of the triplet at 77.0 ppm for $CDCl_3$. IR spectra were recorded on an FT-IR spectrometer and wave numbers of maximum absorption peaks are presented in cm^{-1}. High resolution mass analyses (HRMS) were performed on a mass spectrometer using ESI-TOF techniques.

Representative procedure for the synthesis of 1-iodoalkyne (A); A preformed solution of Me_3SI (242 mg, 1.1 mmol, 1.1 equiv.) and $PhI(OAc)_2$ (354 mg, 1.1 mmol, 1.1 equiv.) in acetonitrile (2 mL) was treated with alkyne **1** (**1a**, 102 mg, 110 uL, 1.0 mmol, 1.0 equiv.) at room temperature. After the completion of reaction, the reaction was diluted with EtOAc (10 mL), quenched with saturated $NaHCO_3$ (5 mL), saturated aqueous sodium thiosulfate (2 mL) and extracted with EtOAc (3 X 30 mL). The combined organic layers were washed with brine solution, dried over anhydrous Na_2SO_4, concentrated in vacuo and purified by silica gel column chromatography to obtain the desired 1-iodoalkynes (**2a-2r**). All the products were fully characterised by ^1H and ^{13}C spectroscopy and MS spectrometry and were in complete agreement with the assigned structure and correlated with literature data.

Iodoethynylbenzene (2a): Following general procedure **A** using ethynylbenzene (**1a,** 93 mg, 0.912 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (204 mg, 0.893 mmol, 98%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 1.9 Hz, 1H), 7.43- 7.42 (m, 1H), 7.33-7.30 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.30, 128.78, 128.21, 123.36, 94.11, 6.10; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[9d]

1-Chloro-2-(iodoethynyl)benzene (2b): Following general procedure **A** using 1-chloro-2-ethynylbenzene (**1b,** 125 mg, 0.919 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow solid (238 mg, 0.909 mmol, 99%). Mp. 101-102 °C; (literature: 100-102 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 7.49-7.45 (m, 1H), 7.38 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.28-7.24 (m, 1H), 7.23 (dd, *J* = 4.7, 1.8 Hz, 1H), 7.21-7.18 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.64, 134.12, 129.71, 129.16, 126.31, 123.17, 90.83, 12.27; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[14]

1-Bromo-4-(iodoethynyl)benzene (2c): Following general procedure **A** using 4-bromo-2-ethynylbenzene (**1c,** 100 mg, 0.552 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow solid (168 mg, 0.546 mmol, 99%). Mp. 88-89 °C; (literature: 89-91 °C). ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.29(d, *J* = 8.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.68, 131.48, 123.13, 122.25, 93.01, 8.02; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[9d]

1-Fluoro-4-(iodoethynyl)benzene (2d): Following general procedure **A** using 4-fluoro-2-ethynylbenzene (**1d,** 105 mg, 0.873 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (193 mg, 0.786 mmol, 90%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.37 (m, 2H), 7.03-6.97 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.99, 161.51, 134.28, 134.20, 115.64, 115.42, 92.97, 5.94; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[9d]

1-(iodoethynyl)-3-methoxybenzene (2e): Following general procedure **A** using 1-ethynyl-3-methoxybenzene (**1e,** 104 mg, 0.787 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow solid (201 mg, 0.780 mmol, 99%). Mp. 43-44 °C; (literature: 41-42 °C). ^1H NMR (500 MHz, $CDCl_3$) δ 7.24-7.17 (m, 1H), 7.06-6.99 (m, 1H), 6.96 (dd, *J* = 2.5, 1.4 Hz, 1H), 6.91-6.84 (m, 1H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.04, 129.21, 124.74, 124.18, 116.98, 115.44, 93.98, 55.17, 6.48; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[14]

1-(iodoethynyl)-4-methoxybenzene (2f): Following general procedure **A** using 1-ethynyl-4-methoxybenzene (**1f,** 102 mg, 0.771 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow solid (171 mg, 0.663 mmol, 86%). Mp. 63-64 °C; (literature 61-62 °C). ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.78, 133.65, 115.37, 113.73, 93.90, 55.16, 4.23; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[9d]

1-(iodoethynyl)-3-methylbenzene (2g): Following general procedure **A** using 1-ethynyl-3-methylbenzene (**1g,** 90 mg, 0.775 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow solid (176 mg, 0.729 mmol, 94%). Mp. 47-49 °C; (literature 49-51 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 7.27-7.19 (m, 3H), 7.15 (d, *J* = 6.9 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.84, 132.79, 129.65, 129.29, 128.05, 123.05, 94.24, 21.15, 5.81; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[9e]

Journal Name ARTICLE

View Article Online
DOI: 10.1039/C7OB03076B

1-(iodoethynyl)-4-methylbenzene (2h): Following general procedure **A** using 1-ethynyl-4-methylbenzene (**1h,** 92 mg, 0.789 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow solid (168 mg, 0.694 mmol, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.3 Hz, 2H), 7.11 (d, *J* = 7.5 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.98, 132.16, 128.95, 120.32, 94.21, 21.50, 4.90; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[14]

1-ethyl-4-(iodoethynyl)benzene (2i): Following general procedure **A** using 1-ethynyl-4-ethylbenzene (**1i,** 93 mg, 0.715 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (169 mg, 0.658 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.0 Hz,2H), 2.64 (q, *J* = 7.6 Hz, 1H), 1.22 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.26, 132.26, 127.76, 120.56, 94.25, 28.80, 15.26, 4.84; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[9c]

1-(tert-butyl)-4-(iodoethynyl)benzene (2j): Following general procedure **A** using 1-(tert-butyl)-4-ethynylbenzene (**1j,** 88 mg, 0.555 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow solid (151 mg, 0.532 mmol, 96%). Mp. 90-92 °C; (literature 88-90 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 1.30 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.99, 131.97, 125.15, 120.32, 94.17, 42.35, 34.71, 31.08, 30.92, 13.18; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[14]

1-(iodoethynyl)-2-(trifluoromethyl)benzene (2k): Following general procedure **A** using 1-ethynyl-2-(trifluoromethyl)benzene (**1k,** 122 mg, 0.718 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow solid (195 mg, 0.661 mmol, 92%). Mp. 62-63 °C; (literature 64-65 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 9.1 Hz, 1H), 8.20 (d, *J* = 7.6 Hz, 1H), 8.17 (d, *J* = 7.6 Hz, 1H), 8.13 (d, *J* = 9.1 Hz, 1H), 8.09 - 8.04 (m, 3H), 8.00 (dd, *J* = 12.2, 4.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.90, 131.50, 131.11, 130.92, 130.32, 128.60, 128.42, 127.09, 126.24, 125.74, 125.69, 125.15, 124.24, 124.20, 124.14, 117.72, 93.44, 10.94; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[14]

2-(iodoethynyl)-6-methoxynaphthalene (2l): Following general procedure **A** using 2-ethynyl-6-methoxynaphthalene (**1l,** 100 mg, 0.549 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow solid (159 mg, 0.516 mmol, 94%). Mp. 94-96 °C; (literature 95-96 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.69-7.63 (m, 2H), 7.43 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.15 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.08 (d, *J* = 2.3 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.52, 134.35, 132.34, 129.34, 129.26, 128.17, 126.74, 119.49, 118.25, 105.75, 94.61, 55.34, 5.20; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[12a]

4-(iodoethynyl)pyrene (2m): Following general procedure **A** using 4-ethynylpyrene (**1m,** 100 mg, 0.438 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow solid (139 mg, 0.394 mmol, 90%). Mp. 125-127 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 9.1 Hz, 1H), 8.20 (d, *J* = 7.6 Hz, 1H), 8.17 (d, *J* = 7.6 Hz, 1H), 8.13 (d, *J* = 9.1 Hz, 1H), 8.09 -8.04 (m, 3H), 8.00 (dd, *J* = 12.2, 4.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.90, 131.50, 131.11, 130.92, 130.32, 128.60, 128.42, 127.09, 126.24, 125.74, 125.69, 125.15, 124.24, 124.20, 124.14, 117.72, 93.44, 10.94; IR ($CHCl_3$, cm^{-1}): 3050, 2125, 1690, 1500, 980, 750, 550; HRMS (ESI-TOF) m/z $[M + NH_4]^+$ calcd. for $C_{18}H_{13}IN^+$: 370.00927; found: 370.00985.

3-(iodoethynyl)pyridine (2n): Following general procedure **A** using 3-ethynylpyridine (**1n,** 100 mg, 0.970 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow solid (182 mg, 0.80 mmol, 82%). Mp. 104-106 °C; ^{1}H NMR (400 MHz,) δ 8.68 (s, 1H), 8.55 (d, *J* = 4.9 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 6.9 Hz, 1H); ^{13}C NMR (101 MHz,) δ 152.66, 148.58, 139.55, 123.07, 120.74, 90.52, 11.66; IR ($CHCl_3$, cm^{-1}): 3057, 2880, 2100, 1630, 1450, 720, 570; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd. for $C_7H_5IN^+$: 229.94667; found: 229.94498.

1-iododec-1-yne (2o): Following general procedure **A** using dec-1-yne (**1o,** 76.6 mg, 0.555 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (117 mg, 0.444 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (t, *J* = 7.1 Hz, 2H), 1.50 (dt, *J* = 7.5, 7.0 Hz, 2H), 1.40-1.26 (m, 10H), 0.88 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 94.83, 31.80, 29.69, 29.13, 29.02, 28.77, 28.47, 22.64, 20.80, 14.10, -7.65; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[9g]

(iodoethynyl)cyclopropane (2p): Following general procedure **A** using ethynylcyclopropane (**1p,** 80 mg, 1.207 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (186 mg, 1.050 mmol, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.49 (tdd, *J* = 6.4, 5.5, 3.2 Hz, 1H), 1.02-0.95 (m, 2H), 0.90-0.84 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 124.35, 28.74, 16.95, 12.80; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[12]

(iodoethynyl)cyclopentane (2q): Following general procedure **A** using ethynylcyclopentane (**1q,** 81 mg, 0.863 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (169 mg, 0.768 mmol, 89%). ^{1}H NMR (400 MHz,) δ 2.52 (ddd, *J* = 12.7, 8.9, 3.5 Hz, 1H), 1.77 (dd, *J* = 8.4, 5.6 Hz, 2H), 1.68 (ddd, *J* = 8.8, 8.1, 4.9 Hz, 2H), 1.54-1.38 (m, 2H), 1.33-1.18 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.06, 56.48, 34.36, 29.69, 25.28; IR ($CHCl_3$, cm^{-1}): 3250, 2810, 2150, 1700, 620, 520; HRMS (ESI-TOF) m/z $[M + NH_4]^+$ calcd. for $C_7H_{13}IN^+$: 238.00927; found: 238.00959.

(iodoethynyl)cyclohexane (2r): Following general procedure **A** using ethynylcyclohexane (**1r,** 83 mg, 0.766 mmol) and purified

by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (154 mg, 0.659 mmol, 86%). ^{1}H NMR (400 MHz,) δ 2.52 (ddd, *J* = 12.7, 8.9, 3.5 Hz, 1H), 1.77 (ddd, *J* = 8.4, 8.1, 5.6 Hz, 2H), 1.68 (ddd, *J* = 8.8, 8.1, 4.9 Hz, 2H), 1.54-1.36 (m, 3H), 1.35-1.17 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 98.92, 32.39, 31.14, 25.71, 25.69, 24.70, -7.13; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[9g]

Representative procedure for the synthesis of *(E)*-1,2-diiodoalkenes (B); A preformed solution of Me_3SI (484 mg, 2.2 mmol, 2.2 equiv.) and $PhI(OAc)_2$ (354 mg, 1.1 mmol, 1.1 equiv.) in water (2 mL) was treated with alkyne **1** (**1a**, 102 mg, 110 uL, 1.0 mmol, 1.0 equiv.) at room temperature. After the completion of reaction, the reaction was diluted with EtOAc (10 mL), quenched with saturated $NaHCO_3$ (5 mL), saturated aqueous sodium thiosulfate (2 mL) and extracted with EtOAc (3 X 30 mL). The combined organic layers were washed with brine solution, dried over anhydrous Na_2SO_4, concentrated in vacuo and purified by silica gel column chromatography to obtain the desired *(E)*-1,2-diiodoalkenes (**3a-3v**). All the products were fully characterised by ^{1}H and ^{13}C spectroscopy and MS spectrometry and were in complete agreement with the assigned structure and correlated with literature data.

(E)-(1,2-diiodovinyl)benzene (3a): Following general procedure **B** using ethynylbenzene (**1a,** 93 mg, 0.912 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow solid (308 mg, 0.866 mmol, 95%). Mp. 71-73 °C; (literature 72-74 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.32 (m, 5H), 7.26 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.97, 128.89, 128.44, 128.36, 96.19, 80.83; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[18b]

(E)-1-chloro-2-(1,2-diiodovinyl)benzene (3b): Following general procedure **B** using 1-chloro-2-ethynylbenzene (**1b,** 125 mg, 0.919 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as light brown oil (329 mg, 0.845 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.35 (m, 1H), 7.33 (s, 1H), 7.31-7.25 (m, 2H), 7.21-7.17 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.76, 131.41, 130.06, 130.04, 129.37, 127.12, 92.24, 84.93; IR ($CHCl_3$, cm^{-1}): 3016, 1435, 1215, 744; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd. for $C_8H_6ClI_2^+$: 390.82417; found: 390.82559.

(E)-1-bromo-4-(1,2-diiodovinyl)benzene (3c): Following general procedure **B** using 4-bromo-2-ethynylbenzene (**1c,** 100 mg, 0.552 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow solid (225 mg, 0.52 mmol, 94%). Mp. 63-64 °C; (literature 63-64 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.7 Hz, 1H), 7.28 (s, 1H), 7.22 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.79, 131.60, 130.09, 123.03, 94.57, 81.78; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[18b]

(E)-1-(1,2-diiodovinyl)-4-fluorobenzene (3d): Following general procedure **B** using 4-fluoro-2-ethynylbenzene (**1d,** 105 mg, 0.873 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale orange oil (293 mg, 0.786 mmol 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 8.2, 5.5 Hz, 1H), 7.25 (s, 1H), 7.04 (dd, *J* = 8.2, 0.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.58, 161.09, 138.94, 138.91, 130.55, 130.46, 115.56, 115.34, 94.91, 81.61; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[18b]

(E)-1-(1,2-diiodovinyl)-3-methoxybenzene (3e): Following general procedure **B** using 1-ethynyl-3-methoxybenzene (**1e,** 104 mg, 0.787 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (301 mg, 0.78 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 7.25 (s, 1H), 6.97-6.92 (m, 1H), 6.89-6.85 (m, 2H), 3.83 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.14, 144.15, 129.45, 120.76, 114.74, 113.75, 95.84, 80.83, 55.33; IR ($CHCl_3$, cm^{-1}): 2932, 1576, 1260, 758; HRMS (ESI-TOF) m/z $[M + NH_4]^+$ calcd. for $C_9H_{12}I_2NO^+$: 403.90028; found: 403.90212.

(E)-1-(1,2-diiodovinyl)-4-methoxybenzene (3f): Following general procedure **B** using 1-ethynyl-4-methoxybenzene (**1f,** 102 mg, 0.771 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (295 mg, 0.764 mmol, 99%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.9 Hz, 1H), 7.19 (s, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 3.83 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.70, 135.14, 130.17, 113.60, 96.59, 79.87, 55.29; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[18b]

(E)-1-(1,2-diiodovinyl)-3-methylbenzene (3g): Following general procedure **B** using 1-ethynyl-3-methylbenzene (**1g,** 90 mg, 0.775 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (252 mg, 0.682 mmol, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.3 Hz, 1H), 7.22 (s, 1H), 7.16 -7.10 (m, 1H), 2.36 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.84, 138.07, 129.68, 128.91, 128.21, 125.44, 96.47, 80.55, 21.36; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[18b]

(E)-1-(1,2-diiodovinyl)-4-methylbenzene (3h): Following general procedure **B** using 1-ethynyl-4-methylbenzene (**1h,** 92 mg, 0.79 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (236 mg, 0.639 mmol, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.2 Hz, 1H), 7.22 (s, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 2.36 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.13, 139.05, 129.05, 128.44, 96.57, 80.17, 77.25, 77.00, 77.00, 76.75, 21.42; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[18b]

(E)-1-(1,2-diiodovinyl)-4-ethylbenzene (3i): Following general procedure **A** using 1-ethynyl-4-ethylbenzene (**1i,** 93 mg, 0.715 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale orange oil (236 mg, 0.615 mmol, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.2 Hz, 1H), 7.22 (s, 1H), 7.19 (d, *J* = 8.4 Hz,

DOI: 10.1039/C7OB02076B

1H), 2.66 (q, *J* = 7.6 Hz, 1H), 1.26 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.25, 140.24, 128.54, 127.82, 96.66, 80.05, 28.68, 15.12; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[18b]

(E)-1-(tert-butyl)-4-(1,2-diiodovinyl)benzene (3j): Following general procedure **B** using 1-(tert-butyl)-4-ethynylbenzene (**1j,** 88 mg, 0.555 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow solid (187 mg, 0.455 mmol, 82%). Mp. 63-64 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.22 (s, 1H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.07, 131.83, 128.35, 125.23, 96.76, 79.82, 34.78, 31.19; IR ($CHCl_3$, cm^{-1}): 3066, 2954, 2926, 2858, 1607, 1498, 1458, 1150, 829, 777, 597; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd. for $C_{12}H_{14}I_2Na^+$: 434.90826; found: 434.90542.

(E)-1-(1,2-diiodovinyl)-2-(trifluoromethyl)benzene (3k): Following general procedure **B** using 1-ethynyl-2-(trifluoromethyl)benzene (**1k,** 122 mg, 0.718 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as light brown oil (289 mg, 0.68 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.37 (s, 1H), 7.24 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.26, 132.44, 129.78, 129.01, 126.84, 126.79, 90.40, 85.57; IR ($CHCl_3$, cm^{-1}): 3052, 3002, 2941, 2843, 2165, 1626, 1598, 1480, 1388, 1228, 1172, 1161, 1026, 900, 550, 750; HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd. for $C_9H_9I_2N^+$: 441.87764; found: 441.87903.

(E)-2-(1,2-diiodovinyl)-6-methoxynaphthalene (3l): Following general procedure **B** using 2-ethynyl-6-methoxynaphthalene (**1l,** 100 mg, 0.549 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (234 mg, 0.538 mmol, 98%). Mp. 117-119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 1.5 Hz, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.41 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.30 (s, 1H), 7.17 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.13 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.60, 137.99, 134.51, 129.80, 128.09, 127.92, 126.95, 126.51, 119.53, 105.82, 96.78, 80.40, 55.38; IR ($CHCl_3$, cm^{-1}): 3075, 2835, 2300, 2024, 1595, 1490, 1462, 1433, 1254, 1114, 1047, 1023, 751, 550; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd. for $C_{13}H_{10}I_2Na^+$: 458.87178; found: 458.87929.

(E)-1-(1,2-diiodovinyl)pyrene (3m): Following general procedure **B** using 4-ethynylpyrene (**1m,** 100 mg, 0.438 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (194 mg, 0.403 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29-8.22 (m, 3H), 8.18 (d, *J* = 7.9 Hz, 2H), 8.14 (d, *J* = 9.3 Hz, 1H), 8.06 (d, *J* = 9.3 Hz, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.66 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.88, 131.62, 131.30, 131.10, 129.45, 128.20, 128.20, 127.38, 126.47, 125.52, 125.37, 125.09, 124.90, 124.70, 124.37, 95.14, 84.70; IR ($CHCl_3$, cm^{-1}): 3050, 2250, 1690, 1500, 980, 750, 550 HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd. for $C_{18}H_{14}I_2N^+$: 497.92156; found: 497.92092.

(E)-3-(1,2-diiodovinyl)pyridine (3n): Following general procedure **B** using 3-ethynylpyridine (**1n,** 100 mg, 0.970 mmol) and purified by silica gel column chromatography, eluting with 50:1 hexanes/EtOAc afforded the inseparable mixture of title compound as pale yellow solid (221 mg, 0.621 mmol, 64%) along with **2n**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.55-8.53 (m, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.37 (s, 1H), 7.35-7.27 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.32, 148.06, 136.17, 134.93, 123.27, 107.85, 83.23; IR ($CHCl_3$, cm^{-1}): 3057, 2880, 2100, 1630, 1450, 720, 570; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd. for $C_7H_6I_2N^+$: 357.85841; found: 357.85508.

(E)-1,2-diiododec-1-ene (3o): Following general procedure **B** using dec-1-yne (**1o,** 77 mg, 0.555 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (178 mg, 0.455 mmol, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.80 (s, 1H), 2.53-2.47 (m, 2H), 1.58-1.49 (m, 4H), 1.36-1.24 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 104.47, 78.95, 44.61, 31.81, 29.36, 29.15, 28.14, 28.12, 22.65, 14.15; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[16f]

(E)-(1,2-diiodovinyl)cyclopropane (3p): Following general procedure **B** using ethynylcyclopropane (**1p,** 80 mg, 1.207 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (324 mg, 1.014 mmol, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 1H), 1.50 (ttd, *J* = 7.5, 5.2, 0.8 Hz, 1H), 0.82 (dqd, *J* = 3.9, 2.0, 0.7 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 109.78, 23.07, 9.51; IR ($CHCl_3$, cm^{-1}): 2953, 1216, 749; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd. for $C_5H_6I_2Na^+$: 342.84566; found: 342.84417.

(E)-(1,2-diiodovinyl)cyclopentane (3q): Following general procedure **B** using ethynylcyclopentane (**1q,** 81 mg, 0.863 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (276 mg, 0.794 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (s, 1H), 2.62-2.45 (m, 1H), 1.82-1.71 (m, 4H), 1.69-1.57 (m, 2H), 1.48-1.38 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 115.46, 77.32, 50.34, 33.11, 25.53; IR ($CHCl_3$, cm^{-1}): 3075, 1421, 951, 748; HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd. for $C_7H_{14}I_2N^+$: 365.92156; found: 365.92247.

(E)-(1,2-diiodovinyl)cyclohexane (3r): Following general procedure **B** using ethynylcyclohexane (**1r,** 83 mg, 0.767 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (249 mg, 0.69 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (s, 1H), 2.08 (tt, *J* = 10.8, 3.5 Hz, 1H), 1.80 (ddd, *J* = 10.0, 4.8, 2.0 Hz, 1H), 1.74-1.66 (m, 1H), 1.62-1.52 (m, 1H), 1.50-1.11 (m, 7H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 114.37, 76.42, 48.78, 32.29, 25.46, 25.20; IR ($CHCl_3$, cm^{-1}): 2925, 1729, 772; HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd. for $C_8H_{16}I_2N^+$: 379.93721; found: 379.93624; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[16f]

(E)-(1,2-diiodoprop-1-en-1-yl)benzene (3s): Following general procedure **B** using prop-1-yn-1-ylbenzene (**1s,** 93 mg, 0.80 mmol) and purified by silica gel column chromatography,

eluting with hexanes afforded the title compound as pale yellow oil (236 mg, 0.640 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.32 (m, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.26 (s, 1H), 7.22 (dd, *J* = 8.2, 1.4 Hz, 1H), 2.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.09, 128.43, 128.38, 128.22, 96.30, 95.47, 40.18; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[18b]

(E)-(1,2-diiodobut-1-en-1-yl)benzene (3t): Following general procedure **B** using but-1-yn-1-ylbenzene (**1t,** 92 mg, 0.704 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (243 mg, 0.634 mmol, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 10.2, 4.6 Hz, 2H), 7.30-7.26 (m, 1H), 7.22-7.18 (m, 1H), 2.88 (q, *J* = 7.4 Hz, 2H), 1.18 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.96, 128.43, 128.34, 128.13, 106.49, 93.66, 44.83, 12.92; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[18b]

(E)-1,2-diiodo-1,2-diphenylethene (3u): Following general procedure **B** using 1,2-diphenylethyne (**1u,** 100 mg, 0.561 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (204 mg, 0.472 mmol, 84%). Mp. 149-151 °C; (literature 148-150 °C). ^{1}H NMR (400 MHz,) δ 7.56 -.751 (m, 3H), 7.40-7.31 (m, 7H); ^{13}C NMR (101 MHz,) δ 147.60, 131.59, 128.54, 128.40, 128.33, 128.24, 123.24, 89.34; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[18b]

(E)-3,4-diiodohex-3-ene (3v): Following general procedure **B** using hex-3-yne (**1v,** 72 mg, 0.881 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (266 mg, 0.793 mmol, 90%). Mp. 149-151 °C; (literature 148-150 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.70 (q, *J* = 7.3 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 102.46, 77.32, 77.00, 77.00, 76.68, 45.05, 12.69; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.[16b]

Acknowledgements

SK gratefully acknowledge the Department of Science and Technology, India for the INSPIRE Faculty award (IFA12-CH-54) and Start-up Research Grant for Young Scientists (SB/FT/CS-024/2014).

Notes and references

1 (a) X. Yang, A. Althammer, P. Knochel, *Org. Lett.,* 2004, **6**, 1665-1667; (b) F. Diederich, P. J. Stang, *Metal-Catalysed Cross-Coupling Reactions*, Wiley-VCH, Weinheim, Germany, 1998; (c) Y. Sasson, 'Formation of Carbon-Halogen Bonds (Cl, Br, I), in *The Chemistry of Functional Groups, Supplement D2: The Chemistry of Halides, Pseudo Halides and Azides, Part 2*, S. Patai and Z. Rappoport, eds., Wiley, Chichester, 1995, pp. 535-620; (d) A. Gómez-Herrera, F. Nahra, M. Brill, S. P. Nolan C. S. J. Cazin, ChemCatChem 2016, **8**, 3381-3388.

2 For recent examples, see: (a) W. Wu, H. Jiang, *Acc. Chem. Res.,* 2014, **47**, 2483-2504; (b) J. Panteleev, K. Geyer, A. Aguilar, L. Wang, M. Lautens, *Org. Lett.,* 2010, **12**, 5092-5095; (c) J. A. Crossley, D. L. Browne, *J. Org. Chem.,* 2010, **75**, 5414-5416; (d) C. Wang, C. J. Forsyth, *Org. Lett.,* 2006, **8**, 2997-3000, (e) X. Zeng, S. Liu, Z. Shi, B. Xu, *Org. Lett.*, 2016, **18**, 4770-4773, (f) C. R. Reddy, Sujatarani A. Panda, A. Ramaraju, *J. Org. Chem.*, 2017, **82**, 944-949.

3 (a) For insights of the Cadiot-Chodkiewicz reaction, see: Tsuji, J. In *Palladium Reagents and Catalysis: New Perspectives for the 21st Century*, 2nd ed.; Wiley: Chichester, 2004; Chapter 3, pp 22-228 and references cited therein; (b) M. Alami, F. Ferri, *Tetrahedron Lett*., 1996, **37**, 2763-2766; (c) W.-Q. Yang, T. Kitahara, *Tetrahedron,* 2000, **56**, 1451-1461; (d) M. D. Shair, T. Y. Yoon, K. K. Mosny, T. C. Chou, S. J. Danishefsky, J. *Am. Chem. Soc.,* 1996, **118**, 9509;-9525 (e) T. R. Hoye, P. R. Hanson, *Tetrahedron Lett.,* 1993, **32**, 5043-5046.

4 (a) D. L. Usanov, H. Yamamoto, *J. Am. Chem. Soc.,* 2011, **133**, 1286-1289; (b) S. Inuki, A. Iwata, S. Oishi, N. Fujii, H. Ohno, *J. Org. Chem.,* 2011, **76**, 2072-2083; (c) H. Liu, C. Chen, L. Wang, X. Tong, *Org. Lett.,* 2011, **13**, 5072-5075; (d) J. B. Nerenberg, D. T. Hung, P. K. Somers, S. L. Schreiber, *J. Am. Chem. Soc.,* 1993, **113**, 12621-2622; (e) T. D. Aicher, Y. Kishi, *Tetrahedron Lett.,* 1987, **28**, 3463-3466; (f) K. Takai, T. Kuroda, S. Nakatsukasa, K. Oshima, H. Nozaki, *Tetrahedron Lett.,* 1985, **26**, 5585-5588.

5 (a) J. E. Hein, J. C. Tripp, L. B. Krasnova, K. B. Sharpless, V. V. Fokin, *Angew. Chem. Int. Ed.,* 2009, **48**, 8018-8021; (b) B. Wang, J. Zhang, X. Wang, N. Liu, W. Chen, Y. Hu, *J. Org. Chem*., 2013, **78**, 10519-10523.

6 (a) K. C. Nicolaou, *Angew. Chem. Int. Ed. Engl.,* 1993, **32**, 1377-1385; (b) J. M. Tedder, A. Nechvatal, A. W. Murray, J. Carnduff in *Basic Organic Chemistry, Vol. 4*, John Wiley & Sons, London, 1971.

7 (a) E. Schwartz, K. Breitenkamp, V. V. Folkin, Macromolecules, 2011, **44**, 4735-4741; (b) L. Luo, C. Wilhelm, A. Sun, C. P. Grey, J. W. Lauher, N. S. Goroff, *J. Am. Chem. Soc.,* 2008, **130**, 7702-7709; (c) A. Sun, J. W. Lauher, N. S. Goroff, *Science,* 2006, **312**, 1030-1034.

8 (a) N. Joubert, F. Amblard, K. L. Rapp, R. F. Schinazi, L. A. Agrofoglio, *Tetrahedron,* 2008, **64**, 4444-4452; (b) G. W. Kabalka, T. M. Shoup, M. M. Goodman, *Nucl. Med. Biol.* 2000, **27**, 279-287; (c) T. Jeffery, *J. Chem. Soc. Chem. Commun.,* 1988, 909-910; and references cited therein.

9 (a) L.-G. Meng, P.-J. Cai, Q.-X. Guo, S. Xue, *Synth. Commun.* 2008, **38**, 225-231; (b) H. Monenschein, G. Sourkouni-Argirusi, K. M. Schubothe, T. O'Hare, A. Kirschning, *Org. Lett.* 1999, **1**, 2101-2104; (c) J. Yan, J. Li, D. Cheng, *Synlett,* 2007, 2442-2444; (d) K. Srujana, P. Swamy, M. Naresh, C. Durgaiah, B. Rammurthy, G. K. Sai, T. Sony, N. Narender *Chemistry Select,* 2017, **2**, 748-752; (e) K. R. Reddy, M. Venkateshwar, C. U. Maheswari, S. P. Kumar, *Tetrahedron Lett.,* 2010, **51**, 2170-2173; (f) Y. Brunel, G. Rousseau, T*etrahedron Lett.*, 1995, **36**, 2619-2622; (g) S.-N. Chen, T.-T. Hung, *J. Chin. Chem. Soc.,* 2009, **56**, 1078-1081; (h) Y. Liu, D. Huang, J. Huang, K. Maruoka, *J. Org. Chem.,* 2017, **82**, 11865-11871.

10 For selected examples, see: (a) G. W. Kabalka, A. R. Mereddy, *Tetrahedron Lett.,* 2004, **45**, 1417-1419; (b) J. E. Luithle, J. Pietruszka, *Eur. J. Org. Chem.,* 2000, 2557-2562; (c) I. J. Blackmore, A. N. Boa, E. J. Murray, M. Dennis, S. Woodward, *Tetrahedron Lett.,* 1999, **40**, 6671-6672; (d) T. Mandai, T. Matsumoto, M. Kawada, J. Tsuji, *J. Org. Chem.,* 1992, **57**, 6090-6094.

11 (a) J. P. Das, S. Roy, *J. Org. Chem.,* 2002, **67**, 7861-7864; (b) D. Naskar, S. Roy, *J. Org. Chem.,* 1999, **64**, 6896-6897.

12 (a) P. Starkov, F. Rota, J. M. D'Oyley, T. D. Sheppard, *Adv. Synth. Catal.,* 2012, **354**, 3217-3224; (b) T. Nishikawa, S. Shibuya, S. Hosokawa, M. Isobe, *Synlett,* 1994, 485-486.

13 (a) E. J. Corey, P. L. Fuchs, *Tetrahedron Lett*., 1972, **13**, 3769-3772; (b) Z. Wang, S. Campagna, K. Yang, G. Xu, M. E. Pierce,

View Article Online
DOI: 10.1039/C7OB03076B

J. M. Fortunak, P. N. Confalone, *J. Org. Chem.,* 2000, **65**, 1889-1891; (c) G. J. Hollingworth, A. M. E. Richecoeur, J. Sweeney, *J. Chem. Soc. Perkin Trans., 1* 1996, 2833-2836; (d) G. J. Hollingworth, J. Sweeney, *Synlett,* 1993, 463-465; (e) P. Michel, A. Rassat, *Tetrahedron Lett.,* 1999, **40**, 8579-8581; (f) B. Bonnet, Y. Le Gallic, G. Ple, L. Duhamel, *Synthesis,* 1993, 1071-1073.

14 G. Pelletier, S. Lie, J. J. Mousseau, A. B. Charette, *Org. Lett.,* 2012, **14**, 5464-5467.

15 (a) J. Barluenga, J. M. Montserrat, J. Flórez, *J. Org. Chem.,* 1993, **58**, 5976-5980; (b) C. Huynh, G. Linstrumelle, *Tetrahedron,* 1988, **44**, 6337-6344; (c) M. E. Wright, C. K. Lowe-Ma, *Organometallics,* 1990, **9**, 347-352; (d) N. Hénaff, A. Whiting, *J. Chem. Soc., Perkin Trans., 1* 2000, 395-400; and references therein.

16 or some selected examples, see: (a) J.-H. Li, Y.-X. Xie, D.-L. Yin, *Green Chem.,* 2002, **4**, 505-506; (b) A. O. Terent'ev, D. A. Borisov, I. B. Krylov, G. I. Nikishin, *Synth. Commun.* 2007, **37**, 3151-3164; (c) G. Raffa, S. Belot, G. Balme, N. Monteiro, *Org. Biomol. Chem.,* 2011, **9**, 1474-1478; (d) R. A. Hollins, M. P. A. Campos, *J. Org. Chem.,* 1979, **44**, 3931-3934; (e) V. L. D. Heasley, F. Shellhamer, L. E. Heasley, D. B. Yaeger, *J. Org. Chem.,* 1980, **45**, 4649-4652; (f) J.-A. Chen, C.-S. Lin, L. K. Liu, *J. Chin. Chem. Soc.,* 1996, **43**, 95-99.

17 (a) J. Duan, W. R. Jr. Dolbier, Q.-Y. Chen, *J. Org. Chem.,* 1998, **63**, 9486-9489; (b) M. Jereb, M. Zupan, S. Stavber, *Chem. Commun.,* 2004, 2614-2615; (c) Larson, S.; Luidhardt, T.; Kabalka, G. W.; Pagni, R. M. *Tetrahedron Lett.,* 1988, **29**, 35-36; (d) G. Stavber, J. Iskra, M. Zupan, S. Stavber, *Adv. Synth. Catal.,* 2008, **350**, 2921-2929.

18 (a) S. Madabhushi, R. Jillella, K. K. R. Mallu, K. R. Godala, V. S. Vangipuram, *Tetrahedron Lett.,* 2013, **54**, 3993-3996; (b) Q. Jiang J.-Y. Wang, C.-C. Guo, *Synthesis,* 2015, **47**, 2081-2087.

19 (a) T. R. Reddy, D. S. Rao, K. Babachary, S. Kashyap, *Eur. J. Org. Chem.,* 2016, 291-311; (b) D. S. Rao, T. R. Reddy, K. Babachary, S. Kashyap, *Org. Biomol. Chem.,* 2016, **14**, 7529-7543; (c) G. Kundoor, D. S. Rao, S. Kashyap, *Asian J. Org. Chem.,* 2016, **5**, 264-270; (d) S. K. Battina, S. Kashyap, *Tetrahedron Lett.,* 2016, **57**, 811-814; (e) S. Chittela, T. R. Reddy, P. R. Krishna, S. Kashyap, *J. Org. Chem.,* 2015, **80**, 7108-7116; (f) T. R. Reddy, D. S. Rao, S. Kashyap, *RSC Adv.,* 2015, **5**, 28338-28343; (g) B. Srinivas, T. R. Reddy, S. Kashyap, *Carbohydr. Res.,* 2015, **406**, 86-92; (h) T. R. Reddy, S. Chittela, S. Kashyap, *Tetrahedron,* 2014, **70**, 9224-9229; (i) S. Chittela, T. R. Reddy, P. R. Krishna, S. Kashyap, *RSC Adv.,* 2014, **4**, 46327-46331.