## COMMUNICATION

# Photo-induced direct alkynylation of methane and other light alkanes by iron catalysis†

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Here we show a practical iron-catalysed photoredox approach for C(sp³)–H alkynylation of methane, ethane, and other light alkanes without pre-functionalisation processes, producing valuable internal alkynes. The protocol has many advantages, including a concise and efficient system, good selectivity, mild conditions, wide application of the synthesised products, and low cost.

## Introduction

Substituted alkynes are fundamental structural motifs and important building blocks in the synthesis of antibiotics,[1] antimycotics,[2] polymers, optical or electronic materials, and liquid crystals.[3] Their synthesis has attracted much attention throughout the history of organic chemistry. One of the most popular and efficient methods to synthesise internal alkynes with C(sp²)–C(sp) bond construction is the transition-metal-catalysed Sonogashira coupling.[4] In the last few decades, C(sp³)–C(sp) coupling of terminal alkynes with unactivated alkyl halides has also been realised with a Sonogashira-type reaction.[5] On the other hand, light alkanes (mainly including C₁–C₆), that are the major constituents of petroleum and natural gas, are widely distributed and abundant in nature. However, their intrinsic inertness and uncontrollable chemo-selectivity lead to a great difficulty in the effective utilization of light alkanes as economical chemical feedstocks.[6] Thus constructing substituted alkynes through direct alkynylation of natural alkanes brings economic and sustainable benefits, as well as great scientific challenges to synthetic chemistry.[7] Early in 1996, the Fuchs group pioneered the alkynylation of simple alkanes with acetylenic triflones and AIBN in a neat reaction

under reflux (Scheme 1a).[7a] Recently, Xu & Feng,[7b] Lei[7c,d] and Tang[7e] groups respectively reported a similar reaction through a radical pathway; equivalent oxidants and high temperature are still essential in these significant systems (Scheme 1a).

Photo-induced hydrogen atom transfer (HAT) catalysis has secured its place as one of the most mild and efficient protocols for the generation of C-centred radicals from unactivated alkanes.[8] With this practical strategy, photoredox alkynylation of C(sp³)–H bonds at the α-position of ethers/amides has been well developed with diarylketone derivatives[9] or decatungstate[10] as photocatalysts (Scheme 1b). However, only a small scope of alkane substrates has been applied in these reactions. Importantly, direct alkynylation of ample gaseous alkanes has rarely been realised to the best of our knowledge due to their low solubility in most solvents.[6,11] In recent years, a chlorine radical generated from a photo-induced ligand-to-metal charge transfer (LMCT) has been proven to be a powerful tool for C(sp³)–H activation of simple alkanes by many groups[12] and us.[13] Meanwhile, iron catalysis has found wide application in the synthesis and utilization of alkynes,[14] and light-driven

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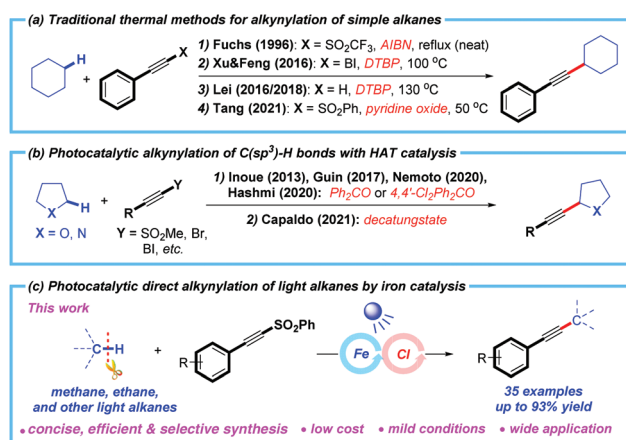


**Scheme 1** Approaches for the alkynylation of C(sp³)–H bonds. AIBN = azodiisobutyronitrile; DTBP = di-*tert*-butyl peroxide; BI = benziodoxole.

organic reactions.[15] With extension of our continuous interest in photo-mediated synthetic reactions,[13,16] we herein report an extremely convenient and highly efficient photocatalytic HAT strategy to realise selective C–H alkynylation of methane and other light alkanes with the only-added cheap iron catalyst (Scheme 1c). This method shows the lowest E-factor and catalyst/oxidant cost among the related reactions mentioned above (for more details see Table S1†). According to the demand for atom-economical and sustainable chemical reactions, this study may have significant implications in high-value-added transformation of natural alkanes and synthetic chemistry of internal alkynes.

## Results and discussion

Initially, the coupling of cyclohexane (1a) and (4-methylphenyl)-ethynyl phenyl sulfone (2a) was examined as the model reaction to optimise reaction conditions (Table 1). After considerable efforts, we found that the reaction gave the best result with $FeCl_3 \cdot 6H_2O$ (0.05 equiv.) as the catalyst and $CH_3CN$ as the solvent under a $N_2$ atmosphere and irradiation of a 30 W 395 nm LED for 3 hours (entry 1, for more details see Tables S2–5†). Control experiments showed that both ferric and chloride ions were crucial for the photo-induced coupling reaction, in which TEAC was used as a soluble source of chloride ions (entries 2–4). The water in $FeCl_3 \cdot 6H_2O$ exhibited little effect on the efficiency of the reaction (entry 5). Solvent effects were also investigated, and other solvents, such as DMSO and $CH_2Cl_2$, afforded lower yields of 3aa than $CH_3CN$ (entries 6 and 7). Next, the effect of the reaction time was surveyed. Either reducing or prolonging the reaction time would

decrease the coupling yield (entries 8 and 9). The decreased yield with an extended reaction time might be due to the partial decomposition of 3aa to some unknown byproducts under the model conditions. Finally, the reaction did not work without light (entry 10) or under air (entry 11).

With the optimised reaction conditions established, the scope of alkanes was investigated first (Table 2). A variety of liquid alkanes including cyclic (3aa–3ea) and linear (3fa–3ia) ones reacted with 2a smoothly, giving the desired internal alkynes in good efficiency. Moreover, three components of liquid petroleum gas (LPG), n-butane, isobutane and propane, were respectively used as alkane substrates in this strategy. Impressively, the reactions generated the target alkynylation products in good yields at ambient temperature and pressure (3ja–3la). Fixing and functionalising natural gaseous alkanes, especially methane and ethane, is a fundamentally intriguing challenge in organic synthesis.[17] Fortunately, both ethane (3mr) and methane (3nr) were effective substrates for our photocatalytic protocol with moderate yields obtained, applying 2r as the alkynylation reagent instead of 2a due to volatility

**Table 2** Scope of alkane substrates[a]



3 (yield, regiomeric ratio and time)[b]

*liquid alkanes*

3aa (92%, 3 h)    3ba (85%, 3 h)    3ca (85%, 7 h)

3da (86%, 7 h)    3ea (84%, 3 h)    3fa (75%, 1:1.3:1.2 r.r., 8 h)

3ga (78%, 1:2.9(2+3) r.r., 8 h)    3ha (85%, 7.9:1:3.0 r.r., 3 h)    3ia (62%, >99:<1 r.r., 7 h)[c]

*gaseous alkanes*

from *n-butane*
3ja (70%, 1:1.9 r.r., 3 h)[c,d]

from *iso-butane*
3ka (75%, >99:<1 r.r., 3 h)[c,d]

from *propane*
3la (65%, 1.26:1 r.r., 3 h)[c,d]

from *ethane*
3mr (52%, 5 h)[c,d]

from *methane*
3nr (50%, 12 h)[c,d,e]

[a] Reaction conditions: a $N_2$ atmosphere and irradiation with a 30 W 395 nm LED, alkanes (1) (2 mmol, 10 equiv.), a radical trap (2a or 2r) (0.2 mmol, 1 equiv.), $FeCl_3 \cdot 6H_2O$ (10 μmol, 0.05 equiv.), $CH_3CN$ (2 mL), rt (~25 °C), 3–12 h. [b] Yields of 3 refers to isolated yields; the regiomeric ratios (rr) of 3 were determined by GC and GC-MS analysis. [c] The reaction mixture was irradiated with a 30 W 365 nm LED. [d] The reaction was performed with 0.1 equiv. of catalyst and 5 mL of $CH_3CN$. [e] The reaction was performed in methane (5 MPa) under the irradiation of a 70 W 365 nm LED.

**Table 1** Optimization of the reaction conditions[a]



| Entry | Variation from the standard conditions | Yield[b]/% |
|---|---|---|
| 1 | None | 92 |
| 2 | $Fe(NO_3)_3 \cdot 9H_2O$ instead of $FeCl_3 \cdot 6H_2O$ | ND |
| 3 | $Fe(NO_3)_3 \cdot 9H_2O$ + TEAC (0.15 equiv.) instead of $FeCl_3 \cdot 6H_2O$ | 52 |
| 4 | TEAC (0.15 equiv.) instead of $FeCl_3 \cdot 6H_2O$ | Trace |
| 5 | Anhydrous $FeCl_3$ instead of $FeCl_3 \cdot 6H_2O$ | 91 |
| 6 | DMSO instead of $CH_3CN$ | 32 |
| 7 | $CH_2Cl_2$ instead of $CH_3CN$ | 25 |
| 8 | Time reduced to 2 h | 75 |
| 9 | Time prolonged to 5 h | 46 |
| 10 | No light | ND |
| 11 | Air | ND |

[a] Standard conditions: a $N_2$ atmosphere and irradiation with a 30 W 395 nm LED, cyclohexane (1a) (2 mmol, 10 equiv.), (4 methylphenyl) ethynyl phenyl sulfone (2a) (0.2 mmol, 1 equiv.), $FeCl_3 \cdot 6H_2O$ (10 μmol, 0.05 equiv.), $CH_3CN$ (2 mL), rt (~25 °C), 3 h. [b] Isolated yield. TEAC = tetraethylammonium chloride. ND = not detected. DMSO = dimethyl sulfoxide.

problems of the products. The slight loss of efficiency should be due to their low solubility and the low stability of the 1° carbon radical. The regiomeric ratios (rr) towards different sites of alkanes were also studied. To our surprise, the results suggested that the regioselectivities with **2** as a radical trap were quite different from those reported previously.[7,13,18] Besides the stabilities of the resulting carbon radicals (3°/2°/1°) and quantities of hydrogens with the same chemical environment, the stereo-hindrance effects around the corresponding alkyl radicals also played a vital role in deciding the regiomeric ratios. As a consequence, the regiomeric ratios between 1° and 2° carbons (see **3fa**, **3ja**, and **3la**) partly increased compared to those reported for other functionalisations (such as **3la**: 1.26 : 1 for alkynylation *vs.* 1 : 1 for alkylation[13]). Importantly, a scarcely little alkynylation product from 3° C–H activation was observed in this system (see **3ha**, **3ia**, and **3ka**).

Subsequently, diverse 1-(2-(arylsulfonyl)ethynyl)benzenes (**2**) with substituents on the phenyl rings were attempted to extend the application scope (Table 3). To our delight, various examples proceeded well with cyclohexane and afforded the corresponding aliphatic internal alkynes in good to excellent yields (see **3ab–3as**). Many functional groups, such as alkyl (**3ab**, **3ad**), phenyl (**3ao**), naphthyl (**3ap**), methoxyl (**3ae–3ag**), fluoro (**3an**), chloro (**3ah–3aj**), bromo (**3ak–3am**), and ester groups (**3aq–3as**), were introduced into the produced internal alkynes at different substituted positions, demonstrating the excellent functional group tolerance of this reaction.

Furthermore, three complicated sulfone substrates were prepared from glycylglycine, geraniol, and (+)-dehydroabietylamine, respectively. It was gratifying to find that the method showed moderate reactivity towards these naturally-sourced examples, showing the potential utility for late-stage modification of complex molecules.

To further demonstrate the practicability of this method, a series of transformations have been performed for versatile alkyne functionalisation (Scheme 2). Notably, a gram-scale synthesis with **2a** (3.9 mmol, 1.00 g) and **1a** was carried out in a batch reaction, obtaining 0.71 g of **3aa** in 90.8% yield without obvious loss of efficiency. To further increase the light utilization efficiency,[19] a well-designed continuous-flow photocatalytic micro-reactor was used, capable to afford similar results to those of the batch reaction with a reduced time and attenuated light irradiation. From the alkylated internal alkyne **3aa**, diverse transformations have been achieved.[20] For instance, Fe-catalysed radical addition of the Cl–S σ-bond in sulfenyl chloride to a C–C triple bond gave a useful chlorothiolation adduct **4a** regio- and stereoselectively.[20a] Coupled with another cerium-catalysed process, the hydroiodination product **4b** was isolated in good yield and *Z/E* selectivity.[20b] Multi-functional α,α-diazidoketone **4c**[20c] and benzoin bis-ethers **4d**[20d] were successfully delivered under mild conditions. Finally, direct iron-catalysed hydrolysis of the alkynyl moiety produced aryl ketone **4e** with high yield and regioselectivity.[20e]

As shown in Scheme 3, several control experiments were executed to explore the reaction mechanism. To prove the

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**Table 3**  Scope of ethynyl phenyl sulfones[a]



3 (yield, time)[b]

**3ab** (90%, 3 h)  **3ac** (91%, 3 h)  **3ad** (93%, 3 h)  **3ae** (91%, 3 h)  **3af** (89%, 3 h)  **3ag** (90%, 3 h)

**3ah** (90%, 3 h)  **3ai** (91%, 3 h)  **3aj** (90%, 3 h)  **3ak** (89%, 3 h)  **3al** (90%, 3 h)  **3am**(88%, 3 h)

**3an** (85%, 5 h)  **3ao** (83%, 3 h)  from *Glycylglycine* **3at** (45%, 12 h)  from *(+)-dehydroabietylamine* **3av** (43%, 12 h)

**3ap** (84%, 3 h)  **3aq** (85%, 3 h)  from *Geraniol* **3au** (41%, 12 h)

**3ar** (89%, 3 h)  **3as** (85%, 3 h)

[a] Reaction conditions: a $N_2$ atmosphere and irradiation with a 30 W 395 nm LED, cyclohexane (**1a**) (2 mmol, 10 equiv.), a radical trap (**2**) (0.2 mmol, 1 equiv.), FeCl$_3$·6H$_2$O (10 μmol, 0.05 equiv.), CH$_3$CN (2 mL), rt (~25 °C), 3–12 h. [b] Isolated yield.
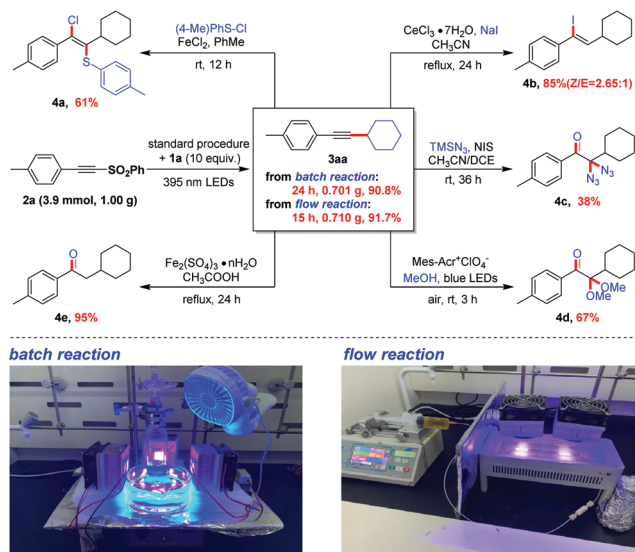
Scheme 2 Scale-up and application studies of the synthesised products. TMS = trimethylsilyl; NIS = *N*-iodosuccinimide; Mes-Acr⁺ = 9-mesityl-10-methylacridinium ion.
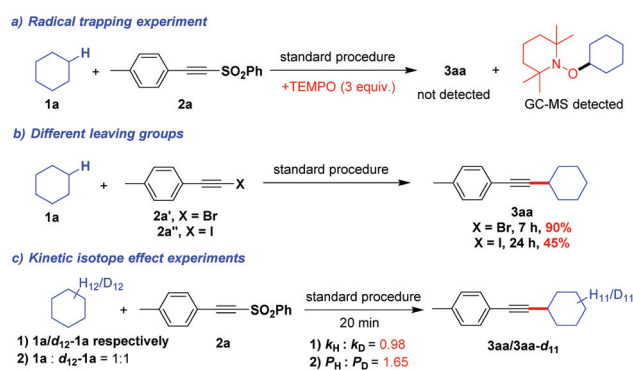


Scheme 3 Control experiments for mechanism study.

existence of radical intermediates, a radical trapping experiment was performed by addition of (2,2,6,6-tetramethyl-piperidin-1-yl)oxy (TEMPO) as a radical-trapping reagent (Scheme 3a). No **3aa** was observed in this reaction, and GC-MS analysis revealed the existence of cyclohexyl radicals trapped by TEMPO, suggesting that the reaction undergoes a radical pathway (for more details see Fig. S3–4†). Different leaving groups were attempted next (Scheme 3b). Coupling of **1a** with 1-(bromoethynyl)-4-methylbenzene (**2a′**) or 1-(iodoethynyl)-4-methylbenzene (**2a″**) provided **3aa** in reasonable yields with an extended time. Kinetic isotopic effect (KIE) studies with separate kinetic experiments were carried out to gain insights into the C(sp³)–H cleavage step for this alkynylation reaction (Scheme 3c). The KIE values given by $k_H/k_D$[21] and $P_H/P_D$[21] were measured as 0.98 and 1.65 using (a) **1a**/$d_{12}$-**1a** respectively as substrates or (b) a 1 : 1 mixture of **1a** and $d_{12}$-**1a** as substrates to produce **3aa** (for more details see Scheme S2†). These values indicated the radical-intermediated HAT process to be a
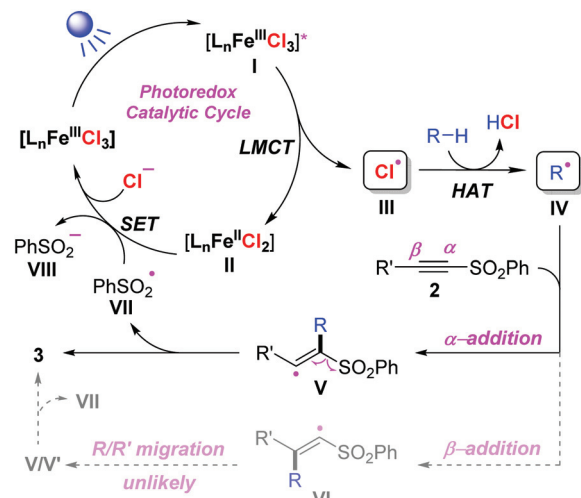


Scheme 4 Proposed reaction pathway.

"product-determining step", but not a "rate-determining step" in this catalytic system.[21] Finally, the quantum yield of the model reaction was calculated to be 0.074 (for more details see Scheme S3†), indicating that radical chain processes made little contribution in the alkynylation strategy.[22]

On the basis of the results above and previous reports,[23] we proposed the reaction mechanism (Scheme 4). First, irradiation of the Fe(III)–Cl complex gives the excited state **I**, and a subsequent LMCT generates an intermediate Fe(II) complex **II** and a highly active chlorine radical **III**. A following HAT from alkane to **III** results in an alkyl radical **IV** and hydrogen chloride. Next, the radical addition between **IV** and **2** may occur at two possible positions. The β-addition followed by an exclusive R/R′ group migration was unlikely, while an α-addition followed by a sulphonyl radical **VII** elimination and the target product **3** formation was suggested. The density functional theory (DFT) calculation results also proved that the conversion of **V** to **3** could take place spontaneously according to the thermodynamic law (for more details see chapter 4.5 in the ESI†). Then a single electron transfer (SET) from **II** to **VII** provides a sulphinic acid ion **VIII** with regeneration of the catalyst.

## Conclusions

In summary, an iron-catalysed aliphatic C–H alkynylation with photo-induced LMCT/HAT processes under mild conditions has been developed. Various liquid alkanes and more challenging gaseous alkanes, including methane and ethane, are suitable for the transformation. The use of an expensive photocatalyst or additional reductant is avoided in this protocol. Furthermore, the method presents remarkable regioselectivities towards 1° and 2° C(sp³)–H. The tolerance for diverse functional groups, as well as natural product fragments, could make this approach attractive for complex mole-

cule modification or late-stage functionalisation. Scale-up synthesis with flow chemistry and wide application of the synthesised internal alkynes emphasise a broad prospect for this strategy.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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