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Selective trifluoromethylation and alkynylation of tetrahydroisoquinolines using visible light irradiation by Rose Bengal

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ABSTRACT

A convenient and efficient method for oxidative coupling of tetrahydroisoquinoline derivatives with trimethyl(trifluoromethyl)silane and terminal alkynes to 1-trifluoromethylated or 1-alkynylated tetrahydroisoquinolines via C–H activation was developed using visible light irradiation. The protocol uses Rose Bengal as the catalyst, air as terminal oxidant, and the trifluoromethylation or alkynylation was selectively performed at the α-position of nitrogen under extremely mild conditions.

1. Introduction

Considering the importance of amines containing trifluoromethyl group at the C–α atom and alkaloids in industry as pharmaceutical and agrochemical drugs [1–3], straightforward and eco-friendly preparation of these compounds still represents a challenging task for chemists. The traditional methods for synthesizing such compounds include nucleophilic addition and 1,3-proton shift reactions involving imines of trifluoroacetic aldehyde [4–6], as well as addition reactions of trifluoromethyl carbanion at the C=N bond of azomethine substrates and iminium cations [7–11]. Recently, transition metal-catalyzed C–H bond activation directly to form C–C bond has attracted great attention and a number of excellent results have been obtained because it avoids the preparation of functional groups and makes synthetic schemes shorter and more efficient [12–17]. Among these reactions, oxidation of an sp^3 C–H bond adjacent to a nitrogen atom in a tertiary amine, followed by attack of a carbon nucleophile, is a powerful strategy for C–C bond formation [18–20]. This method resides in the generation of an iminium ion intermediate in the presence of metal catalysts such as Cu^{I}, V^{IV}, Fe^{III}, Fe^{II}, or Ru^{II} and oxidants such as hydrogen peroxide, oxygen, and tert-butylhydroperoxide [21–34]. For example, Li and co-workers developed an efficient copper-catalyzed trifluoromethylation of *N*-aryl-tetrahydroisoquinolines with $TMSCF_3$ via oxidative sp^3 C–H activation at the α-position of nitrogen using DDQ as terminal oxidant [35]. Qing and co-workers reported that benzoyl peroxide (BPO)-promoted oxidative trifluoromethylation of tertiary amines proceeded successfully under transition-metal-free reaction conditions [36]. Despite this extensive progress, the search for an efficient and practical catalytic system for trifluoromethylation of tertiary amines remains a challenge.

With the emergence of the concept of "green chemistry", photoredox catalyzed organic transformations have been attracting much attention in recent years, not only because these transformations exhibit some particular or unexpected reactivities in some cases but also because they are significantly useful for green chemistry [37–40]. Over the past 5 years, a variety of metal-based and organic dyes-based photosensitizers, as photoredox catalysts for organic transformations under visible light irradiation have been developed [41–54]. Among these transformations, the oxidative cross-dehydrogenative coupling (CDC) reaction is an attractive strategy. In this case, generation of iminium ion intermediates by using visible-light photoredox catalysis followed by reactions with carbon pronucleophiles would give α-substituted products [55–60].

α-Trifluoromethylation of tetrahydroisoquinolines is a powerful transformation in organic synthesis because 1-trifluoromethyl-tetrahydroisoquinoline derivatives are highly important bioactive compounds [61,62]. Combining all the above principles and as a continuation of our interest in the design and discovery of new reactions for the synthesis of fluorinated heterocycles [63,64],

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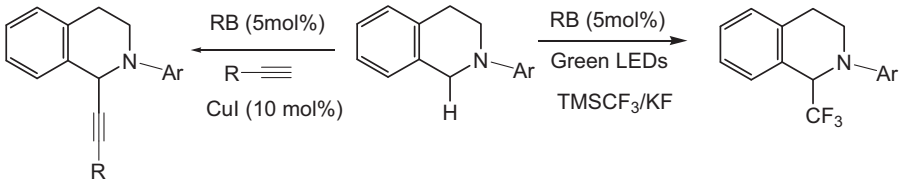


Scheme 1. α-Trifluoromethylation and alkynylation of tetrahydroisoquinolines.

herein, we report a visible-light-induced oxidative α-trifluoromethylation and α-alkynylation of tetrahydroisoquinolines using Rose Bengal as visible light photocatalyst under transition-metal-free reaction conditions (Scheme 1).

2. Results and discussion

Our initial investigation focused on the oxidative trifluoromethylation of 2-phenyl-1,2,3,4-tetrahydroisoquinoline **1a** as an example for the optimization of the reaction conditions. We found that treatment **1a** with Rose Bengal (RB, 5 mol%), $TMSCF_3$ (3.0 equiv.) and KF (3.0 equiv.) in CH_3CN under irradiation by visible light afforded α-trifluoromethylation product **2a** in 45% yield after 48 h (Table 1, entry 1). With this encouraging result, we first examined the influence of organic dyes on the reaction. Amongst the dyes tested, Rose Bengal showed the best reactivity. Other dyes such as Rhodamine B or Eosin Y provided **2a** in 30% and 41% yield, respectively, while tetraphenylporphyrin (TPP) was less efficient (Table 1, entries 2–4). Switching the light source to green LEDs and increasing the amount of $TMCF_3$ from 3 equiv. to 5 equiv., the yield of the desired product **2a** was increased to 67% (Table 1, entries 5 and 6). On using other solvent such as DMF or toluene, the product **2a** could be isolated in lower yield (Table 1, entries 7 and 8). With respect to the catalyst loading, 5 mol% of RB was found to be optimal. When a lower loading of RB (2 mol%), the reaction also proceeded but sluggishly (Table 1, entry 9). However, no significant improvement was observed with 10 mol% of RB (Table 1, entry 10). Importantly, photocatalyst, visible light and air were all critical for this transformation. No reaction was observed in the absence of any of these components (Table 1, entries 11–13).

After having established the optimized conditions for the present reaction, various tetrahydroisoquinoline derivatives **1a–n** were subjected to the above conditions, and the results are summarized in Table 2. As indicated, the oxidative trifluoromethylation of all the substrates proceeded smoothly to provide the corresponding products **2a–n** in 52–74% yields. The reaction could tolerate various substituents on the aromatic groups. Generally, electron-withdrawing aryl groups including fluoro, chloro, bromo and trifluoromethyl (Table 2, entries 2–5) allowed the reaction to be completed in a longer time. On the other hand, electron-donating substitutent on the benzene ring such as methyl (Table 2, entry 6) and methoxy (Table 2, entries 7 and 8) proceeded well. In addition, *N*-naphthyl, *N*-allyl and *N*-benzyl tetrahydroisoquinolines also underwent facile CDC reactions with $TMSCF_3$ to afford the desired coupled products **2i–k** in 65, 58, 60% yields, respectively (Table 2, entries 9–11). However, *N*-alkyl-substituted tetrahydroisoquinoline proved less reactive and gave 1-trifluoromethylated tetrahydroisoquinoline in 52% yield (Table 2, entry 12). Interestingly, the substrates incorporation of a bromo group at the C7-position in the dihydroisoquinoline or two methoxy substituents at the C6- and C7-positions also reacted smoothly with $TMSCF_3$ to give the products **2k** or **2l** in 65% and 60% yield, respectively (Table 2, entries 13 and 14). When *N*-H and *N*-Boc tetrahydroisoquinolines were used, the CDC reactions did not occur at all under visible light irradiation (Table 2, entries 15 and 16).

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

Entry	Organic dye	Solvent	$TMSCF_3$ (equiv.)	LED color	Time (h)	Yield (%)[b]
1	RB (5 mol%)	CH_3CN	3	White light	48	45
2	Rhodamine B (5 mol%)	CH_3CN	3	White light	48	30
3	TPP (5 mol%)	CH_3CN	3	White light	48	Trace
4	Eosin Y (5 mol%)	CH_3CN	3	White light	48	41
5	RB (5 mol%)	CH_3CN	3	Green	36	56
6	RB (5 mol%)	CH_3CN	5	Green	36	67
7	RB (5 mol%)	DMF	5	Green	48	43
8	RB (5 mol%)	Toluene	5	Green	48	37
9	RB (2 mol%)	CH_3CN	5	Green	48	43
10	RB (10 mol%)	CH_3CN	5	Green	36	68
11[c]	RB (5 mol%)	CH_3CN	5	–	48	0
12[d]	RB (5 mol%)	CH_3CN	5	Green	48	Trace
13[e]	–	CH_3CN	5	Green	48	0

[a] Reaction conditions: **1a** (0.3 mmol), $TMSCF_3$/KF and solvent (3.0 mL).
[b] Isolated yield.
[c] Reaction was carried out in the dark.
[d] Reaction was carried out under an N_2 atmosphere.
[e] Reaction was carried out without catalyst.

Table 2
Visible-light-induced α-trifluoromethylation of tetrahydroisoquinolines.[a]

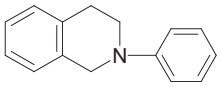
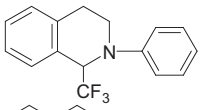
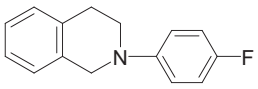
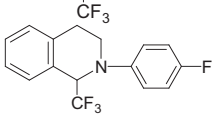
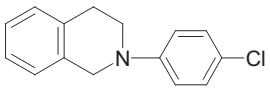
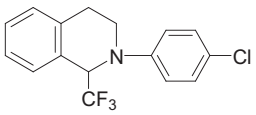
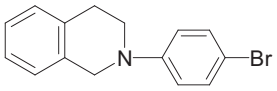
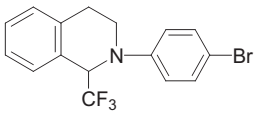
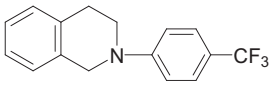
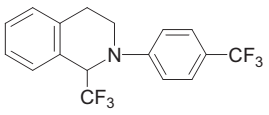
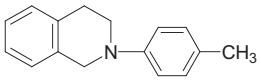
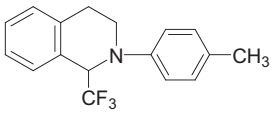
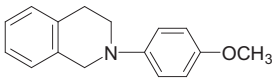
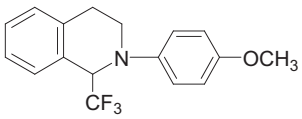
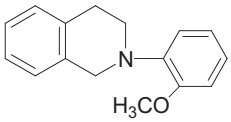
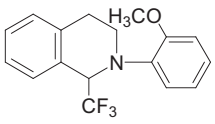
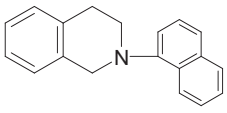
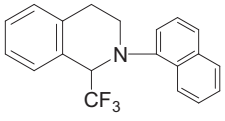
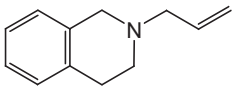
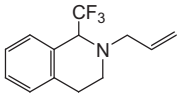
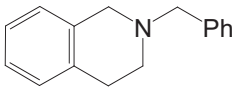
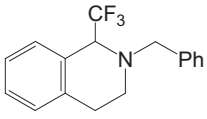
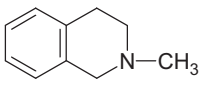
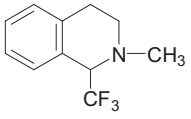
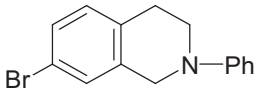
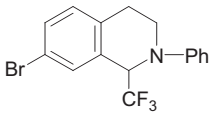
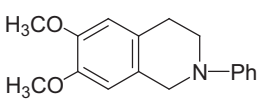
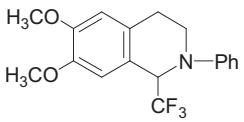
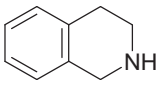
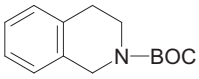
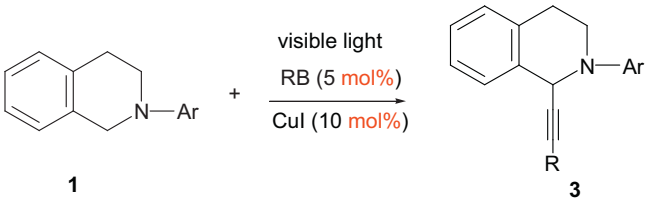
Entry	Substrate	Product	Time (h)	Yield (%)[b]
1			36	**2a**, 67
2			48	**2b**, 69
3			48	**2c**, 73
4			48	**2d**, 71
5			72	**2e**, 56
6			30	**2f**, 74
7			30	**2g**, 69
8			30	**2h**, 63
9			40	**2i**, 65
10			48	**2j**, 58
11			48	**2k**, 60
12			72	**2l**, 52
13			48	**2m**, 65
14			48	**2n**, 60

Table 2 (*Continued*)

Entry	Substrate	Product	Time (h)	Yield (%)[b]
15			72	0
16			72	0

[a] Reaction conditions: **1a** (0.3 mmol), $TMSCF_3$ (1.5 mmol), KF (1.5 mmol), RB (5 mol%) in CH_3CN (3.0 mL).
[b] Isolated yield.

Table 3
Visible-light-induced α-alkynylation of tetrahydroisoquinolines.[a] .

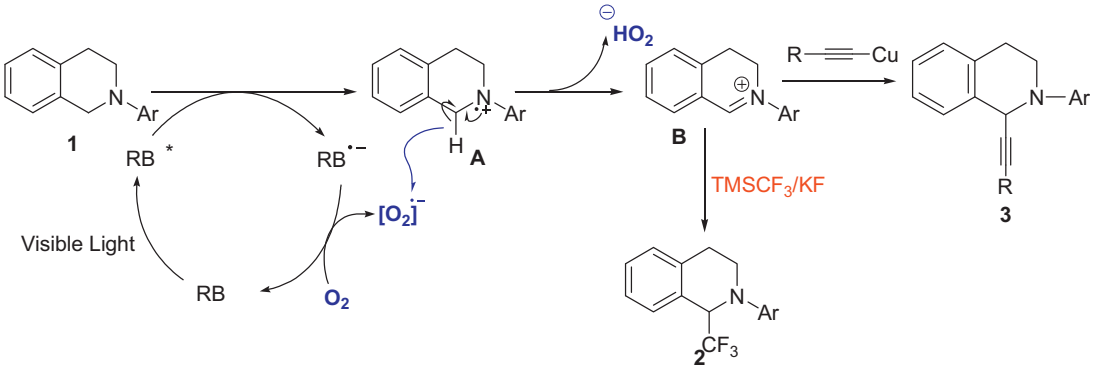


Entry	Ar	R	Time (h)	Yield (%)[b]
1	Ph	Ph	36	**3a**, 73
2	Ph	4-$CH_3C_6H_4$	48	**3b**, 69
3	Ph	4-$CH_3OC_6H_4$	48	**3c**, 65
4	Ph	4-F C_6H_4	40	**3d**, 82
5	Ph	4-Br C_6H_4	40	**3e**, 80
6	Ph	Bu	48	**3f**, 53
7	4-$CH_3C_6H_4$	Ph	30	**3g**, 69
8	4-$CH_3OC_6H_4$	Ph	30	**3h**, 63
9	4-ClC_6H_4	Ph	40	**3i**, 65
10	2-Naphthy	Ph	48	**3j**, 75

[a] Reaction conditions: **1a** (0.3 mmol), alkynes (0.45 mmol), CuI (10 mol%), RB (5 mol%) in CH_3CN (3.0 mL).
[b] Isolated yield.

After successful oxidative trifluoromethylation of tetrahydroisoquinolines, we turned our attention to apply this methodology for the alkynylation of *N*-aryl tetrahydroisoquinolines and the results are summarized in Table 3. In general, aromatic alkynes electron-donating substituents on the benzene ring gave slightly lower yields of desired products, whereas the electron-inductive substituent afforded the best yields among all results for being apt to form an alkynylcopper intermediate. We also investigated the influence of the substituents attached to the isoquinoline. A variety of different *N*-arylated isoquinolines were subjected to the general reaction conditions and the desired alkynylation products were obtained in good isolated yields.

Based on the above results and related literature [59,60], a plausible reaction mechanism is depicted in Scheme 2. The reductive quenching of RB*, the excited state of RB, generated under visible light irradiation, by *N*-aryl tetrahydroisoquinolines **1** would form radical cation **A** and RB radical anion. Subsequent electron transfer from RB radical anion to molecular oxygen regenerates RB and at the same time generates dioxygen radical anion, which could then abstract a hydrogen atom from the



Scheme 2. Proposed mechanism for the trifluoromethylation and alkynylation of tetrahydroisoquinolines.

α-position of the radical cation **A** to give an iminium intermediate **B** and release HO_2^-. The iminium intermediate **B** undergoes addition with $TMSCF_3$/KF and alkynylcopper to afford the final product **2** or **3**.

3. Conclusion

In conclusion, we have developed a simple and effective aerobic, metal-free catalytic reaction for the direct oxidative α-trifluoromethylation and α-alkynylation of *N*-aryl tetrahydroisoquinolines by means of visible-light irradiation. The process showed considerable synthetic advantages in terms of product diversity and the operational simplicity, practicability as well as the mild reaction conditions using visible light as the energy source.

4. Experimental

4.1. General

Chemicals used were obtained from commercial suppliers and used without further purifications. ^{1}H NMR spectra and ^{13}C NMR spectra were measured in $CDCl_3$ and recorded on Bruker Avance-400 spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) with TMS as an internal standard. EIMS were determined with a HP5989B mass spectrometer. Elemental analyses were performed on an EA-1110 instrument.

4.2. Typical procedure for trifluoromethylation of tetrahydroisoquinolines

RB (0.015 mmol, 5 mol%) was added to a mixture of 2-phenyl-1,2,3,4-tetrahydroisoquinoline **1a** (0.3 mmol), potassium fluoride (1.5 mmol) and trifluoromethyltrimethylsilane (1.5 mmol) in CH_3CN (3 mL). The resulting mixture was stirred at room temperature under green LEDs irradiation. After **1a** was completely consumed (monitored by TLC), the solvent was removed in vacuo. The crude product was directly purified by SiO_2 gel column chromatography to give the corresponding product **2a**.

4.2.1. 1-(Trifluoromethyl)-1,2,3,4-tetrahydro-2-phenylisoquinoline (2a)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.22 (m, 6H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.86 (t, *J* = 7.6 Hz, 1H), 5.17 (q, *J* = 7.6 Hz, 1H), 3.82–3.77 (m, 1H), 3.54–3.48 (m, 1H), 3.02–3.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 137.1, 129.4, 129.0 (d, *J* = 2.0 Hz), 128.9, 128.6, 126.5, 126.2 (q, *J* = 285.0 Hz), 119.2, 114.6, 114.5, 61.2 (q, *J* = 29.6 Hz), 43.6, 27.5; MS (EI) *m*/*z* 277 (M^+); Anal. Calcd. for $C_{16}H_{14}F_3N$: (%) C, 69.30; H, 5.09; N, 5.05. Found: C, 69.42; H, 5.24; N, 4.98.

4.2.2. 1-(Trifluoromethyl)-2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (2b)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.20 (m, 4H), 7.03–6.90 (m, 4H), 5.07 (q, *J* = 8.4 Hz, 1H), 3.77–3.69 (m, 1H), 3.48–3.39 (m, 1H), 2.94–3.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9 (d, *J* = 238.0 Hz), 146.2 (d, *J* = 2.5 Hz), 136.8, 128.9 (q, *J* = 1.5 Hz), 128.8 (q, *J* = 1.5 Hz), 128.7, 128.6 (q, *J* = 0.8 Hz), 126.5, 126.1 (q, *J* = 285.2 Hz), 116.7 (d, *J* = 1.0 Hz), 116.5 (d, *J* = 0.8 Hz), 115.8, 115.7, 61.6 (q, *J* = 29.5 Hz), 44.5 (d, *J* = 1.0 Hz), 27.3 (d, *J* = 1.2 Hz); MS (EI) *m*/*z* 295 (M^+); Anal. Calcd. for $C_{16}H_{13}F_4N$: (%) C, 65.08; H, 4.44; N, 4.74. Found: C, 65.23; H, 4.19; N, 4.55.

4.2.3. 2-(4-Chlorophenyl)-1-(trifluoromethyl)-1,2,3,4-tetrahydroisoquinoline (2c)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.21 (m, 6H), 6.89 (d, *J* = 9.2 Hz, 2H), 5.09 (q, *J* = 8.0 Hz, 1H), 3.78–3.70 (m, 1H), 3.48–3.40 (m, 1H), 2.96–3.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 136.7, 129.3, 129.1, 128.9, 128.8 (q, *J* = 1.6 Hz), 128.6 (d, *J* = 1.2 Hz), 128.5, 126.4, 126.0 (q, *J* = 285.5 Hz), 123.9, 115.7 (d, *J* = 0.7 Hz), 61.3 (q, *J* = 29.8 Hz), 43.8, 27.4 (d, *J* = 1.3 Hz); MS (EI) *m*/*z* 311 (M^+); Anal. Calcd. for $C_{16}H_{13}F_3NCl$: (%) C, 61.65; H, 4.20; N, 4.49. Found: C, 61.81; H, 4.12; N, 4.63.

4.2.4. 2-(4-Bromophenyl)-1-(trifluoromethyl)-1,2,3,4-tetrahydroisoquinoline (2d)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.21 (m, 6H), 6.85 (d, *J* = 9.2 Hz, 2H), 5.08 (q, *J* = 8.4 Hz, 1H), 3.78–3.71 (m, 1H), 3.49–3.41 (m, 1H), 3.00–3.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 136.7,132.1, 128.9 (q, *J* = 1.8 Hz), 128.5, 126.5 (q, *J* = 285.0 Hz), 116.1, 111.2, 61.3 (q, *J* = 30.1 Hz), 43.7, 27.4; MS (EI) *m*/*z* 355 (M^+); Anal. Calcd. for $C_{16}H_{13}BrF_3N$: (%) C, 53.95; H, 3.68; N, 3.93. Found: C, 54.13; H, 3.79; N, 3.80.

4.2.5. 1-(Trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline (2e)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.8 Hz, 2H), 7.36–7.25 (m, 4H), 7.01 (d, *J* = 8.8 Hz, 2H), 5.23 (q, *J* = 8.0 Hz, 1H), 3.86–3.79 (m, 1H), 3.54–3.48 (m, 1H), 3.00–3.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4 (d, *J* = 0.8 Hz), 136.4,129.1, 128.8 (dd, *J* = 1.6 Hz, *J* = 2.8 Hz), 128.5, 128.4 (q, *J* = 235.6 Hz), 127.21 (d, *J* = 286.0 Hz), 126.7, 126.6 (q, *J* = 4.0 Hz), 113.2 (d, *J* = 1.2 Hz), 60.7 (q, *J* = 30.6 Hz), 43.6, 27.3 (q, *J* = 2.1 Hz); MS (EI) *m*/*z* 345 (M^+); Anal. Calcd. for $C_{17}H_{13}F_6N$: (%) C, 59.13; H, 3.79; N, 4.06. Found: C, 59.28; H, 3.97; N, 3.98.

4.2.6. 1-(Trifluoromethyl)-1,2,3,4-tetrahydro-2-p-tolylisoquinoline (2f)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.27 (m, 2H), 7.24–7.19 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 5.11 (q, *J* = 8.0 Hz, 1H), 3.78–3.72 (m, 1H), 3.49–3.43 (m, 1H), 3.00–3.06 (br s, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 137.1, 129.9, 129.0, 128.9 (d, *J* = 1.3 Hz), 128.7, 128.6, 126.4, 126.2 (q, *J* = 284.9 Hz), 115.0, 61.4 (q, *J* = 29.6 Hz), 43.9, 27.4, 20.4; MS (EI) *m*/*z* 291 (M^+); Anal. Calcd. for $C_{17}H_{16}F_3N$: (%) C, 70.09; H, 5.54; N, 4.81. Found: C, 70.21; H, 5.30; N, 4.93.

4.2.7. 1-(Trifluoromethyl)-1,2,3,4-tetrahydro-2-(4-methoxyphenyl)isoquinoline (2g)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.21 (m, 4H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.01 (q, *J* = 8.0 Hz, 1H), 3.77 (s, 3H), 3.75–3.72 (m, 1H), 3.46–3.40 (m, 1H), 2.96–3.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6, 144.2, 137.1, 129.0, 128.8, 128.7, 126.4, 126.0 (q, *J* = 284.7 Hz), 117.6, 114.7, 62.0 (q, *J* = 29.5 Hz), 55.8, 44.8, 27.3; MS (EI) *m*/*z* 307 (M^+); Anal. Calcd. for $C_{17}H_{16}F_3NO$: (%) C, 66.44; H, 5.25; N, 4.56. Found: C, 66.18; H, 5.09; N, 4.70.

4.2.8. 1-(Trifluoromethyl)-1,2,3,4-tetrahydro-2-(2-methoxyphenyl)isoquinoline (2h)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.20 (m, 4H), 6.99 (t, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 5.15 (q, *J* = 8.4 Hz, 1H), 3.80 (s, 3H), 3.74–3.69 (m, 1H), 3.52–3.45 (m, 1H), 2.90–3.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 139.9, 136.7, 129.3, 128.9, 128.7, 128.1, 126.4 (q, *J* = 287.3 Hz), 125.9, 124.2, 123.9, 121.2, 121.1, 60.6 (q, *J* = 27.0 Hz), 55.6, 45.3, 28.1; MS (EI) *m*/*z* 307 (M^+); Anal. Calcd. for $C_{17}H_{16}F_3NO$: (%) C, 66.44; H, 5.25; N, 4.56. Found: C, 66.31; H, 5.41; N, 4.63.

4.2.9. 1-(Trifluoromethyl)-1,2,3,4-tetrahydro-2-(naphthalen-1-yl)isoquinoline (2i)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34–8.30 (m, 1H), 7.90–7.86 (m, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.55–7.46 (m, 3H), 7.41–7.24 (m, 4H), 7.01 (br, 1H), 5.01 (q, *J* = 8.4 Hz, 1H), 3.87–3.76 (m, 1H), 3.43–3.38 (m, 1H), 3.00–2.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4,

137.3, 134.9, 129.2, 128.8 (q, J = 2.3 Hz), 128.5, 126.2, 126.1, 126.0, 125.8, 125.1, 123.8, 119.9, 113.1, 62.3 (q, J = 28.9 Hz), 47.2, 26.4; MS (EI) m/z 327 (M^+); Anal. Calcd. for $C_{20}H_{16}F_3N$: (%) C, 73.38; H, 4.93; N, 4.28. Found: C, 73.30; H, 4.92; N, 4.40.

*4.2.10. 2-Allyl-1,2,3,4-tetrahydroisoquinoline (**2j**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.32 (m, 4H), 6.11–6.01 (m, 1H), 5.35–5.28 (m, 2H), 4.34 (q, J = 8.4 Hz, 1H), 3.55 (d, J = 7.2 Hz, 2H), 3.46–3.40 (m, 1H), 2.98–2.87 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 134.9, 129.5 (dd, J = 1.8 Hz, J = 3.2 Hz), 128.5, 128.3 (dd, J = 1.0 Hz, J = 1.2 Hz), 128.0, 127.2 (q, J = 284.0 Hz), 126.0, 118.3, 61.3 (q, J = 28.2 Hz), 59.0, 46.1, 28.9; MS (EI) m/z 241 (M^+); Anal. Calcd. for $C_{13}H_{14}F_3N$: (%) C, 64.72; H, 5.85; N, 5.81. Found: C, 64.60; H, 5.68; N, 5.92.

*4.2.11. 2-Benzyl-1-(trifluoromethyl)-1,2,3,4-tetrahydroisoquinoline (**2k**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.10 (m, 9H), 4.20 (q, J = 8.0 Hz, 1H), 3.89 (dd, J = 13.6 Hz, J = 40.8 Hz, 2H), 3.25–3.140 (m, 1H), 2.73–2.65 (m, 2H), 2.61–2.54 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 136.3, 128.6 (d, J = 1.7 Hz), 127.6, 127.5, 127.4, 127.1, 126.3, 125.1 (d, J = 283.1 Hz), 61.5 (q, J = 27.5 Hz), 59.6, 44.3, 26.4; MS (EI) m/z 291 (M^+); Anal. Calcd. for $C_{17}H_{16}F_3N$: (%) C, 70.09; H, 5.54; N, 4.81. Found: C, 70.22; H, 5.76; N, 4.70.

*4.2.12. 1-(Trifluoromethyl)-1,2,3,4-tetrahydro-2-methylisoquinoline (**2l**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.10 (m, 4H), 3.99 (q, J = 8.0 Hz, 1H), 3.21–3.14 (m, 1H), 2.87–2.80 (m, 1H), 2.76–2.69 (m, 1H), 2.61 (s, 3H), 2.57–2.53 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 129.4 (q, J = 1.8 Hz), 128.3, 128.2 (q, J = 1.5 Hz), 128.1, 126.1 (q, J = 282.1 Hz), 126.1, 64.9 (q, J = 29.7 Hz), 49.9, 45.5 (t, J = 1.6 Hz), 28.1; MS (EI) m/z 215 (M^+); Anal. Calcd. for $C_{11}H_{12}F_3N$: (%) C, 61.39; H, 5.62; N, 6.51. Found: C, 61.54; H, 5.50; N, 6.63.

*4.2.13. 7-bromo-1-(trifluoromethyl)-1,2,3,4-tetrahydro-2-phenylisoquinoline (**2m**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (s, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.30–7.21 (m, 2H), 7.06 (d, J = 8.0 Hz, 1H), 6.92 (d, J = 8.0 Hz, 2H), 6.87 (t, J = 7.6 Hz, 1H), 5.12 (q, J = 8.0 Hz, 1H), 3.77–3.70 (m, 1H), 3.57–3.18 (m, 1H), 2.97–2.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 135.8, 131.8, 131.5 (q, J = 2.1 Hz), 130.8 (q, J = 1.6 Hz), 130.2, 129.5, 125.9 (q, J = 286.0 Hz), 119.7, 119.6, 114.9 (d, J = 1.2 Hz), 60.7 (d, J = 29.9 Hz), 43.2 (d, J = 0.8 Hz), 26.7 (d, J = 1.6 Hz); MS (EI) m/z 355 (M^+); Anal. Calcd. for $C_{16}H_{13}BrF_3N$: (%) C, 53.95; H, 3.68; N, 3.93. Found: C, 53.87; H, 3.79; N, 3.80.

*4.2.14. 1-(Trifluoromethyl)-1,2,3,4-tetrahydro-6,7-dimethoxy-2-phenylisoquinoline (**2n**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (t, J = 8.4 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 6.91–6.86 (m, 2H), 6.73 (s, 1H), 5.13 (q, J = 7.6 Hz, 1H), 3.90 (s, 6H), 3.82–3.75 (m, 1H), 3.61–3.53 (m, 1H), 2.97–2.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 129.2, 147.4, 129.3, 126.2 (q, J = 285.7 Hz), 120.4, 120.3, 119.2, 114.8, 111.5 (q, J = 2.2 Hz), 111.2, 60.8 (q, J = 29.6 Hz), 56.0, 55.9, 43.4, 26.7 (q, J = 1.2 Hz); MS (EI) m/z 337 (M^+); Anal. Calcd. for $C_{18}H_{18}F_3NO_2$: (%) C, 64.09; H, 5.38; N, 4.15. Found: C, 64.24; H, 5.57; N, 4.02.

4.3. Typical procedure for alkynylation of tetrahydroisoquinolines

RB (5 mol%) was added to a mixture of 2-phenyl-1,2,3,4-tetrahydroisoquinoline **1a** (0.3 mmol), CuI (10 mol%) and alkyne (0.45 mmol, 1.5 equiv.) in CH_3CN (3 mL). The resulting mixture was stirred at room temperature under green LEDs irradiation for the time indicated. After **1a** was completely consumed (monitored by TLC), the solvent was removed in vacuo. The crude product was directly purified by SiO_2 gel column chromatography to give the corresponding product **3a**.

*4.3.1. 1,2,3,4-Tetrahydro-2-phenyl-1-(2-phenylethynyl)isoquinoline (**3a**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.30 (m, 5H), 7.26–7.20 (m, 6H), 7.15 (d, J = 7.9 Hz, 2H), 6.93 (t, J = 7.2 Hz, 1H), 5.68 (s, 1H), 3.81–3.74 (m, 1H), 3.72–3.65 (m, 1H), 3.27–3.12 (m, 1H), 2.99 (dt, J = 16.2 Hz, J = 4.0 Hz, 1); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 135.2, 134.3, 131.7, 129.2, 128.9, 128.1, 128.0, 127.5, 127.3, 126.2, 122.9, 119.8, 116.7, 88.5, 84.7, 52.3, 43.4, 28.7; MS (EI) m/z 309 (M^+).

*4.3.2. 1,2,3,4-Tetrahydro-2-phenyl-1-(2-p-tolylethynyl)isoquinoline (**3b**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.30 (m, 3H), 7.25–7.13 (m, 7H), 7.01 (d, J = 8.0 Hz, 2H), 6.90 (t, J = 7.2 Hz, 1H), 5.65 (s, 1H), 3.80–3.65 (m, 2H), 3.25–3.12 (m, 1H), 3.01 (dt, J = 16.0 Hz, J = 3.6 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 138.1, 135.4, 134.3, 131.5, 129.2, 128.8, 128.7, 127.5, 127.1, 126.1, 119.7, 119.6, 116.8, 87.6, 84.9, 52.3, 43.5, 28.8, 21.3; MS (EI) m/z 323 (M^+).

*4.3.3. 1,2,3,4-Tetrahydro-1-(2-(4-methoxyphenyl)ethynyl)-2-phenylisoquinoline (**3c**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.32 (m, 1H), 7.31–7.26 (m, 2H), 7.21–7.15 (m, 4H), 7.15–7.10 (m, 1H), 7.08 (d, J = 8.0 Hz, 2H), 6.84 (dd, J = 7.6, 7.6 Hz, 1H), 6.69 (dt, J = 8.8, 2.4 Hz, 2H), 5.59 (s, 1H), 3.75–3.61 (m, 2H), 3.66 (s, 3H), 3.10 (ddd, J = 16.0, 9.6, 6.2 Hz, 1H), 2.92 (dt, J = 16.0, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 149.3, 135.4, 134.2, 132.9, 128.9, 128.7, 127.3, 126.9, 126.0, 119.3, 116.4, 114.9, 113.5, 87.0, 84.5, 55.2, 52.2, 43.4, 28.9; MS (EI) m/z 339 (M^+).

*4.3.4. 1-(2-(4-Fluorophenyl)ethynyl)-1,2,3,4-tetrahydro-2-phenylisoquinoline (**3d**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.18 (m, 8H), 7.12 (d, J = 8.0 Hz, 2H), 6.94–6.85 (m, 3H), 5.62 (s, 1H), 3.82–3.71 (m, 1H), 3.70–3.60 (m, 1H), 3.15 (ddd, J = 16.0, 10.4, 6.0 Hz, 1H), 2.98 (ddd, J = 16.0, 3.8, 3.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6 (d, J = 247.3 Hz), 149.4, 135.1, 134.0, 133.4 (d, J = 8.5 Hz), 129.0, 128.9, 127.1, 127.0, 126.1, 119.6, 118.9 (d, J = 3.2 Hz), 116.5, 115.2 (d, J = 22.3 Hz), 88.4, 83.5, 52.4, 43.5, 29.1; MS (EI) m/z 327 (M^+).

*4.3.5. 1-(2-(4-Bromophenyl)ethynyl)-1,2,3,4-tetrahydro-2-phenylisoquinoline (**3e**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.28 (m, 4H), 7.25–7.15 (m, 4H), 7.13–7.05 (m, 4H), 6.89 (dt, J = 7.6, 1.2 Hz, 1H), 5.61 (s, 1H), 3.77–3.58 (m, 2H), 3.13 (ddd, J = 15.6, 9.6, 5.6 Hz, 1H), 2.95 (dt, J = 16.0, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 134.9, 134.3, 133.0, 131.2, 129.0, 128.8, 127.3, 127.2, 126.3, 122.1, 121.8, 119.6, 116.5, 89.7, 83.6, 52.3, 43.5, 28.9; MS (EI) m/z 387 (M^+).

*4.3.6. 1-(Hex-1-ynyl)-1,2,3,4-tetrahydro-2-phenylisoquinoline (**3f**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.19 (m, 3H), 7.15–7.06 (m, 3H), 6.98 (d, J = 8.2 Hz, 2H), 6.81 (t, J = 7.2 Hz, 1H), 5.36 (s, 1H), 3.62 (m, 1H), 3.52 (ddd, J = 12.4 Hz, J = 10.4 Hz, J = 4.4 Hz, 1H), 3.04 (ddd, J = 16.2 Hz, J = 10.2 Hz, J = 6.0 Hz, 1H), 2.86 (dt, J = 16.0 Hz, J = 3.6 Hz, 1H), 2.02 (m, 2H), 1.32–1.23 (m, 2H), 1.22–1.11 (m, 2H), 0.75 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.2, 134.1, 129.2, 128.9, 127.3, 127.1, 126.1, 119.6, 116.8, 52.0, 43.4, 30.8, 28.8, 21.7, 18.5, 13.4; MS (EI) m/z 289 (M^+).

*4.3.7. 1,2,3,4-Tetrahydro-1-(2-phenylethynyl)-2-p-tolylisoquinoline (**3g**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.35 (m, 1H), 7.35–7.27 (m, 1H), 7.25–7.16 (m, 2H), 7.13 (d, J = 8.4 Hz, 1H), 7.04 (d, J = 8.4 Hz, 1H), 5.61 (s, 1H), 3.71–3.60 (m, 1H), 3.18 (ddd, J = 16.6 Hz,

J = 9.4 Hz, J = 7.4 Hz, 1H), 2.96 (dt, J = 16.0 Hz, J = 3.5 Hz, 1H), 2.31 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.2, 131.7, 129.7, 128.9, 128.2, 128.1, 127.4, 127.3, 126.2, 117.5, 53.1, 43.9, 28.8, 20.6; MS (EI) m/z 323 (M^+).

*4.3.8. 1,2,3,4-Tetrahydro-2-(4-methoxyphenyl)-1-(2-phenylethynyl)isoquinoline (**3h**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (s, 1H), 7.26–7.06 (m, 10H), 6.89 (d, J = 8.0 Hz, 2H), 5.52 (s, 1H), 3.81 (s, 3H), 3.71–3.46 (m, 2H), 3.15 (ddd, J = 16.0, 10.8, 6.8 Hz, 1H), 2.95 (d, J = 16.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.4, 144.3, 135.8, 134.2, 131.9, 129.4, 128.2, 128.1, 127.6, 127.3, 126.4, 123.3, 120.3, 114.8, 89.1, 85.8, 55.9, 54.7, 44.9, 29.6. MS (EI) m/z 339 (M^+).

*4.3.9. 2-(4-Chlorophenyl)-1,2,3,4-tetrahydro-1-(2-phenylethynyl)isoquinoline (**3i**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.35 (m, 1H), 7.34–7.20 (m, 10H), 7.06 (d, J = 8.8 Hz, 2H), 5.65 (s, 1H), 3.76–3.70 (m, 2H), 3.20 (ddd, J = 16.0 Hz, J = 9.6 Hz, J = 7.2 Hz, 1H), 3.05 (dt, J = 16.0 Hz, J = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 135.2, 134.0, 131.9, 129.1, 128.9, 128.3, 128.2, 127.5, 127.3, 126.4, 124.5, 122.8, 117.9, 88.3, 85.2, 52.3, 43.6, 28.8; MS (EI) m/z 343 (M^+).

*4.3.10. 1,2,3,4-Tetrahydro-2-(naphthalen-3-yl)-1-(2-phenylethynyl)isoquinoline (**3j**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.71 (m, 3H), 7.44–7.39 (m, 4H), 7.35–7.20 (m, 9H), 5.81 (s, 1H), 3.91 (m, 1H), 3.58 (ddd, J = 12.4 Hz, J = 10.4 Hz, J = 4.4 Hz, 1H), 3.12 (ddd, J = 16.0 Hz, J = 10.4 Hz, J = 6.2 Hz, 1H), 2.94 (dt, J = 16.0 Hz, J = 4.0 Hz, 1H), 2.34–2.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 135.4, 134.7, 134.3, 131.7, 129.1, 128.9, 128.5, 128.1, 127.6, 127.5, 127.4, 126.9, 126.3, 126.2, 123.5, 122.9, 119.3, 111.5, 88.3, 85.1, 52.5, 43.6, 28.9; MS (EI) m/z 359 (M^+).

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