Electronic Supplementary Information (ESI) for:

Visible-light-enabled room-temperature dealkylative imidation of secondary and tertiary amine promoted by aerobic ruthenium catalysis

Dong Yang,[†] Jingqi Shi,[†] Jiaming Chen,[†] Xiaoqi Jia,[†] Cuiying Shi,[†] Lifang Ma[†] and Ziyuan Li^{*,†}

† Department of Pharmaceutical and Biological Engineering, School of Chemical Engineering, Sichuan University, No.24 South Section 1, Yihuan Road, Chengdu 610065, China

Table of Contents

General Remarks	S2
Experimental Procedure and Characterization Data	S3-S13
Control Experiments	S14-S18
References	S19
¹ H NMR and ¹³ C NMR Spectra of Products 4a-q , 5a-c	S20–S59

General Remarks

All commercially available compounds were purchased from Sigma-Aldrich, TCI, Acros, J&K Chemicals and Adamas-beta. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. All anhydrous solvents, including ethyl acetate (EtOAc) (99.8%, SafeDry, water < 50 ppm), 1,4-dioxane (99.7%, SafeDry, water < 50 ppm), acetonitrile (MeCN) (99.9%, SafeDry, water < 50 ppm), 1,2-dichloroethane (DCE) (99.5%, SafeDry, water < 50 ppm) and THF (99.8%, SafeDry, water < 50 ppm), were purchased from Adamas-beta. Ru(bpy)₃Cl₂ (98% purity, CAS No. 14323-06-9) were purchased from Adamas-beta. Except for tosyl azide (TsN₃, **3a**, 98%+ purity, in 75% EtOAc solution, CAS No. 941-55-9) that was purchased from Adamas-beta, all other sulfonyl azides 3 were prepared through condensation reactions between sodium azide and corresponding sulfonyl chlorides according to literature reported methods.^[1-3] All visible-light induced reactions were performed on Titan Scientific Lab PR-6 parallel photoreactor purchased from Shanghai Titan Scientific Co., Ltd.^[4] Products were purified by flash chromatography on silica gel using petroleum ether, ethyl acetate and dichloromethane as the eluents. ¹H-NMR spectra were recorded on Bruker AVANCE III-400 and JNM-ECZ400S/L1 spectrometers. Chemical shifts (in ppm) were referenced with TMS in $CDCl_3$ (0 ppm); s = singlet, d = doublet, t = triplet, q = quartet, p = pentad, se = sextet, h = heptet, o = octet. 13 C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl₃ ($\delta = 77.00$ ppm) or DMSO- d_6 ($\delta = 39.50$ ppm). High resolution mass spectra were obtained from an Agilent 6520B Q-TOF mass spectrometer with electron spray ionization (ESI) as the ion source.

Experimental Procedure and Characterization Data

1) Visible-light-enabled imidation of tertiary amines with azides promoted by aerobic ruthenium catalysis (Table 2)



Typical Procedure: To a reaction tube charged with $Ru(bpy)_3Cl_2$ (6.4 mg, 0.01 mmol) was added a solution of sulfonyl azide (**3**, 1.5 mmol) in anhydrous 1,4-dioxane (1 mL) via a syringe under O₂ (1 atm). Then a solution of tertiary amine (**2a-2g**, 0.5 mmol) in anhydrous 1,4-dioxane (1 mL) was added via a syringe upon blue LED (12W) irradiation using Titan Scientific Lab PR-6 parallel photoreactor (460-465 nm blue LED irradiation module from the buttom and side of the reaction mixture in a Shlenk tude with a diameter of 2 cm) with temperature-controlling module as shown in the above images (the distance between the buttom of the raction mixture and the light source is approximately 1.5 cm, and the distance between the side of the reaction mixture and the light source is approximately 1 cm). The reaction mixture was stirred at 25 °C in O₂ under blue LED (12W) irradiation for 6 hours, followed by concentration *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent on silical gel to afford iminated product **4a-4m**. The yields of **4** from tertiary amines were calculated based on the loading of **2a-2g**: acquisition of 0.5 mmol of **4a-4m** from **2a-2g** is equivalent to 100% yield.

2) Visible-light-enabled imidation of secondary amines with azides promoted by aerobic ruthenium catalysis (Table 3)



Typical Procedure: To a reaction tube charged with $Ru(bpy)_3Cl_2$ (6.4 mg, 0.01 mmol) was added a solution of sulfonyl azide (**3**, 1.5 mmol) in anhydrous 1,4-dioxane (1 mL) via a syringe under O₂ (1 atm). Then a solution of secondary amine (**2h-2x**, 0.5 mmol) in anhydrous 1,4-dioxane (1 mL) was added via a syringe upon blue LED (12W) irradiation using Titan Scientific Lab PR-6 parallel photoreactor (460-465 nm blue LED irradiation module from the buttom and side of the reaction mixture in a Shlenk tude with a diameter of 2 cm) with temperature-controlling module as shown in the above images (the distance between the buttom of the raction mixture and the light source is approximately 1.5 cm, and the distance between the side of the reaction mixture and the light source is approximately 1 cm). The reaction mixture was stirred at 25 °C in O₂ under blue LED (12W) irradiation for 6 hours, followed by concentration *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent on silical gel to afford iminated product **4a**, **4i**, **4k** and **4n-4x**. The yields of **4** from secondary amines were calculated based on the loading of **2h-2x**: acquisition of 0.25 mmol of **4a**, **4i**, **4k** and **4n-4x** from **2h-2x** is equivalent to 100% yield.

3) Charaterization of the imidated product 4

(E)-N,N-Diethyl-N'-tosylformimidamide (4a)^[2]

From tertiary amine: The reaction of 0.5 mmol of triethylamine (TEA, 50.6 mg, **2a**) and tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) at 25 °C in O₂ under blue LED (12W) irradiation afforded 115.6 mg of **4a** (91%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (4:1 to 3:1, *v/v*) as the eluent.

From secondary amine: The reaction of 0.5 mmol of diethylamine (DEA, 36.6 mg, 2h) and tosyl azide

(**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) at 25 °C in O₂ under blue LED (12W) irradiation afforded 58.6 mg of **4a** (92%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (4:1 to 3:1, ν/ν) as the eluent.

Colourless oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 8.14$ (s, 1H), 7.76 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 3.47 (q, J = 7.2 Hz, 2H), 3.37 (q, J = 7.2 Hz, 2H), 2.39 (s, 3H), 1.25 (t, J = 7.2 Hz, 3H), 1.14 (t, J = 7.2 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 158.00$, 142.17, 139.74, 129.19, 126.27, 46.96, 40.83, 21.36, 14.41, 11.99 ppm. HRMS *m/z* (ESI) calcd for [C₁₂H₁₈N₂O₂S+H]⁺ 255.1162, found 255.1167.

(E)-N,N-Diethyl-N'-(phenylsulfonyl)formimidamide (4b)^[3]



From tertiary amine: The reaction of 0.5 mmol of triethylamine (TEA, 50.6 mg, **2a**) and benzenesulfonyl azide (**3b**, 274.5 mg, 1.5 mmol) with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) at 25 °C in O₂ under blue LED (12W) irradiation afforded 96.6 mg of **4b** (80%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (4:1 to 3:1, v/v) as the eluent.

Colourless oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 8.16$ (s, 1H), 7.90-7.87 (m, 2H), 7.50-7.46 (m, 3H), 3.48 (q, J = 7.2 Hz, 2H), 3.38 (q, J = 7.2 Hz, 2H), 1.26 (t, J = 7.2 Hz, 3H), 1.15 (t, J = 7.2 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 158.15$, 142.64, 131.67, 128.64, 126.32, 47.07, 40.96, 14.47, 12.05 ppm. HRMS *m*/*z* (ESI) calcd for [C₁₁H₁₆N₂O₂S+H]⁺ 241.1005, found 241.1002; calcd for [C₁₁H₁₆N₂O₂S+Na]⁺ 263.0825, found 263.0827.

(E)-N,N-Diethyl-N'-((4-(tert-butyl)phenyl)sulfonyl)formimidamide (4c)^[3]

From tertiary amine: The reaction of 0.5 mmol of triethylamine (TEA, 50.6 mg, 2a) and 4-(*tert*-butyl)benzenesulfonyl azide (3c, 358.6 mg, 1.5 mmol) with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) at 25 °C in O₂ under blue LED (12W) irradiation afforded 127.2 mg of 4c (86%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (4:1 to 3:1, v/v) as the eluent.

Colourless oil. ¹**H NMR (CDCl₃, 400 MHz)**: δ = 8.16 (s, 1H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 3.48 (q, *J* = 7.2 Hz, 2H), 3.38 (q, *J* = 7.2 Hz, 2H), 1.33 (s, 9H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 2H), 3.48 (q, *J* = 7.2 Hz, 3H), 3.48 (q, J = 7.2 Hz, 3H), 3.48 (

3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 158.11$, 155.24, 139.65, 126.12, 125.60, 46.97, 40.87, 34.96, 31.09, 14.45, 12.06 ppm. HRMS *m/z* (ESI) calcd for [C₁₅H₂₄N₂O₂S+H]⁺ 297.1631, found 297.1634; calcd for [C₁₁H₁₆N₂O₂S+Na]⁺ 319.1451, found 319.1452.

(E)-N,N-Diethyl-N'-((4-methoxyphenyl)sulfonyl)formimidamide (4d)^[3]

From tertiary amine: The reaction of 0.5 mmol of triethylamine (TEA, 50.6 mg, 2a) and 4-methoxybenzenesulfonyl azide (3d, 319.5 mg, 1.5 mmol) with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) at 25 °C in O₂ under blue LED (12W) irradiation afforded 90.5 mg of 4d (67%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (4:1 to 3:1, v/v) as the eluent.

White solid, m.p. 72.5-73.4 °C. ¹H NMR (CDCl₃, 400 MHz): δ = 8.13 (s, 1H), 7.81 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 3.84 (s, 3H), 3.46 (q, *J* = 7.2 Hz, 2H), 3.37 (q, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 162.04, 157.80, 134.52, 128.20, 113.71, 55.40, 46.90, 40.75, 14.37, 11.94 ppm. HRMS *m/z* (ESI) calcd for [C₁₂H₁₈N₂O₃S+H]⁺ 271.1111, found 271.1113.

(E)-N,N-Diethyl-N'-((4-fluorophenyl)sulfonyl)formimidamide (4e)^[3]

From tertiary amine: The reaction of 0.5 mmol of triethylamine (TEA, 50.6 mg, 2a) and 4-fluorobenzenesulfonyl azide (3e, 301.5 mg, 1.5 mmol) with $Ru(bpy)_3Cl_2$ (6.4 mg, 0.01 mmol) at 25 °C in O₂ under blue LED (12W) irradiation afforded 124.9 mg of 4e (97%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (4:1 to 3:1, v/v) as the eluent.

Colourless oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 8.15$ (s, 1H), 7.88 (dd, J = 8.8 Hz, 3.6 Hz, 2H), 7.16-7.11 (m, 2H), 3.48 (q, J = 7.2 Hz, 2H), 3.40 (q, J = 7.2 Hz, 2H), 1.27 (t, J = 7.2 Hz, 3H), 1.14 (t, J = 7.2 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 164.47$ (d, J = 251.4 Hz), 158.06, 138.68 (d, J = 3.1 Hz), 128.87 (d, J = 9.0 Hz), 115.73 (d, J = 22.2 Hz), 47.12, 40.97, 14.38, 11.98 ppm. HRMS *m*/*z* (ESI) calcd for [C₁₁H₁₅FN₂O₂S+H]⁺ 259.0911, found 259.0910; calcd for [C₁₁H₁₅FN₂O₂S+Na]⁺ 281.0731, found 281.0731.

(E)-N,N-Diethyl-N'-((4-chlorophenyl)sulfonyl)formimidamide (4f)



From tertiary amine: The reaction of 0.5 mmol of triethylamine (TEA, 50.6 mg, 2a) and 4-chlorobenzenesulfonyl azide (3f, 325.5 mg, 1.5 mmol) with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) at 25 °C in O₂ under blue LED (12W) irradiation afforded 112.6 mg of 4f (82%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (4:1 to 3:1, v/v) as the eluent.

Colourless oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 8.14$ (s, 1H), 7.82 (d, J = 8.7 Hz, 2H), 7.43 (d, J = 8.7 Hz, 2H), 3.48 (q, J = 7.2 Hz, 2H), 3.40 (q, J = 7.2 Hz, 2H), 1.27 (t, J = 7.2 Hz, 3H), 1.14 (t, J = 7.2 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 158.08$, 141.19, 137.93, 128.85, 127.80, 47.12, 40.99, 14.39, 11.99 ppm. HRMS *m*/z (ESI) calcd for [C₁₁H₁₅ClN₂O₂S+H]⁺ 275.0616, found 275.0619.

(E)-N,N-Diethyl-N'-((4-(trifluoromethyl)phenyl)sulfonyl)formimidamide (4g)



From tertiary amine: The reaction of 0.5 mmol of triethylamine (TEA, 50.6 mg, **2a**) and 4-(trifluoromethyl)benzenesulfonyl azide (**3g**, 376.5 mg, 1.5 mmol) with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) at 25 °C in O₂ under blue LED (12W) irradiation afforded 138.4 mg of **4g** (90%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (4:1 to 3:1, ν/ν) as the eluent. Colourless oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 8.16$ (s, 1H), 8.01 (d, J = 8.3 Hz, 2H), 7.73 (d, J = 8.3 Hz,

2H), 3.50 (q, J = 7.2 Hz, 2H), 3.41 (q, J = 7.2 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H), 1.16 (t, J = 7.2 Hz, 3H) ppm. ¹³C **NMR (CDCl₃, 100 MHz)**: $\delta = 158.27$, 146.12, 133.41 (q, J = 32.6 Hz), 126.87, 125.80 (q, J = 3.7 Hz), 123.40 (q, J = 271.2 Hz), 47.25, 41.13, 14.40, 12.02 ppm. **HRMS** *m*/*z* (**ESI**) calcd for [C₁₂H₁₅F₃N₂O₂S+H]⁺ 309.0879, found 309.0879; calcd for [C₁₂H₁₅F₃N₂O₂S+Na]⁺ 331.0699, found 331.0705.

(E)-N,N-Diisopropyl-N'-tosylformimidamide (4h)^[3]



From tertiary amine: The reaction of 0.5 mmol of diisopropyl ethanamine (DIPEA, 64.6 mg, **2b**) and tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) at 25 °C in O₂ under blue LED (12W) irradiation afforded 125.9 mg of **4h** (89%) after flash chromatography on

silica gel using petroleum ether and ethyl acetate (6:1, v/v) as the eluent.

White solid, m.p. 82.5-84.0 °C. ¹H NMR (CDCl₃, 400 MHz): δ = 8.25 (s, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 1H), 4.52 (p, *J* = 6.8 Hz, 1H), 3.68 (p, *J* = 6.8 Hz, 1H), 2.39 (s, 3H), 1.31 (d, *J* = 6.8 Hz, 6H), 1.21 (d, *J* = 6.8 Hz, 6H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 156.26, 142.01, 139.91, 129.16, 126.17, 48.46, 47.83, 23.49, 21.34, 19.51 ppm. HRMS *m/z* (ESI) calcd for [C₁₄H₂₂N₂O₂S+H]⁺ 283.1475, found 283.1477.

(E)-N,N-Dipropyl-N'-tosylformimidamide (4i)^[3]



From tertiary amine: The reaction of 0.5 mmol of tripropylamine (71.6 mg, **2c**) and tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) at 25 °C in O₂ under blue LED (12W) irradiation afforded 120.4 mg of **4i** (85%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (4:1 to 3:1, *v*/*v*) as the eluent.

From secondary amine: The reaction of 0.5 mmol of dipropylamine (50.6 mg, **2i**) and tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) at 25 °C in O₂ under blue LED (12W) irradiation afforded 60.9 mg of **4i** (86%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (4:1 to 3:1, *v*/*v*) as the eluent.

Colourless oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 8.15$ (s, 1H), 7.75 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.2 Hz, 1H), 3.36 (t, J = 7.6 Hz, 2H), 3.26 (t, J = 7.4 Hz, 2H), 2.39 (s, 3H), 1.65-1.54 (m, 4H), 0.90 (t, J = 7.4 Hz, 3H), 0.85 (t, J = 7.4 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 158.85$, 142.14, 139.79, 129.20, 126.27, 54.20, 47.80, 21.84, 21.39, 19.90, 11.13, 10.78 ppm. HRMS *m*/*z* (ESI) calcd for $[C_{14}H_{22}N_2O_2S+H]^+$ 283.1475, found 283.1475.

(E)-N,N-Dipentyl-N'-tosylformimidamide (4j)

From tertiary amine: The reaction of 0.5 mmol of tripentylamine (113.7 mg, **2d**) and tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) at 25 °C in O₂ under blue LED (12W) irradiation afforded 138.7 mg of **4j** (82%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (4:1 to 3:1, ν/ν) as the eluent.

Colourless oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 8.13$ (s, 1H), 7.75 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.2 Hz, 1H), 3.39 (t, J = 7.6 Hz, 2H), 3.28 (t, J = 7.4 Hz, 2H), 2.39 (s, 3H), 1.71-1.49 (m, 4H), 1.36-1.15 (m, 8H), 0.90 (t, J = 7.3 Hz, 3H), 0.82 (t, J = 7.2 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 158.77$, 142.17, 139.91, 129.22, 126.31, 52.53, 46.15, 28.81, 28.50, 28.31, 26.30, 22.25, 22.20, 21.43, 13.88, 13.82 ppm. HRMS *m*/*z* (ESI) calcd for [C₁₈H₃₀N₂O₂S+Na]⁺ 361.1920, found 361.1919.

(E)-N-Ethyl-N-phenyl-N'-tosylformimidamide (4k)^[2]



From tertiary amine: The reaction of 0.5 mmol of *N*,*N*-diethylaniline (74.6 mg, **2e**) and tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) at 25 °C in O₂ under blue LED (12W) irradiation afforded 72.8 mg of **4k** (48%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1 to 6:1, *v*/*v*) as the eluent.

From secondary amine: The reaction of 0.5 mmol of *N*-ethylaniline (60.5 mg, **2k**) and tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) at 25 °C in O₂ under blue LED (12W) irradiation afforded 41.1 mg of **4k** (54%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1 to 6:1, *v*/*v*) as the eluent.

Yellow oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 8.45$ (s, 1H), 7.81 (d, J = 8.2 Hz, 2H), 7.45-7.41 (m, 2H), 7.36-7.34 (m, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.20-7.18 (m, 2H), 3.96 (q, J = 7.2 Hz, 2H), 2.41 (s, 3H), 1.17 (t, J = 7.2 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 158.05$, 142.63, 141.88, 139.11, 129.82, 129.34, 127.65, 126.56, 123.54, 44.05, 21.44, 12.32 ppm. HRMS *m*/*z* (ESI) calcd for [C₁₆H₁₈N₂O₂S+H]⁺ 303.1162, found 303.1160.

(E)-N-Ethyl-N-cyclohexyl-N'-tosylformimidamide (4l)

From tertiary amine: The reaction of 0.5 mmol of *N*,*N*-diethylcyclohexanamine (77.6 mg, **2f**) and tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) at 25 °C in O₂ under blue LED (12W) irradiation afforded 103.6 mg of **4l** (67%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1 to 6:1, *v*/*v*) as the eluent.

From secondary amine: The reaction of 0.5 mmol of *N*-ethylcyclohexanamine (63.6 mg, **2n**) and tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) at 25 °C in O₂ under blue LED (12W) irradiation for 24 hours afforded 55.6 mg of **4l** (72%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1 to 6:1, *v/v*) as the eluent.

White solid, m.p. 94.4-95.5 °C. ¹H NMR (CDCl₃, 400 MHz): δ = 8.21 (s, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 3.43 (q, *J* = 7.2 Hz, 2H), 3.25-3.17 (m, 1H), 2.39 (s, 3H), 1.88-1.68 (m, 6H), 1.54-1.44 (m, 2H), 1.36-1.24 (m, 2H), 1.15 (t, *J* = 7.2 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 157.22, 142.07, 139.94, 129.19, 126.26, 62.97, 40.54, 32.52, 25.56, 24.96, 21.40, 13.27 ppm. HRMS *m*/z (ESI) calcd for [C₁₆H₂₄N₂O₂S+H]⁺ 309.1631, found 309.1631.

(E)-4-Methyl-N-(piperidin-1-ylmethylene)benzenesulfonimide (4m)^[2]



From tertiary amine: The reaction of 0.5 mmol of *N*-ethylpiperidine (56.6, **2g**) and tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) at 25 °C in O₂ under blue LED (12W) irradiation afforded 93.5 mg of **4m** (70%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (4:1 to 3:1, ν/ν) as the eluent.

Colourless oil. ¹H NMR (CDCl₃, 400 MHz): δ = 8.12 (s, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.59 (t, *J* = 5.6 Hz, 2H), 3.41 (t, *J* = 5.6 Hz, 2H), 2.39 (s, 3H), 1.67-1.57 (m, 6H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 157.23, 142.27, 139.65, 129.23, 126.40, 51.82, 44.58, 26.36, 24.79, 23.90, 21.40 ppm. HRMS *m/z* (ESI) calcd for [C₁₃H₁₈N₂O₂S+H]⁺ 267.1162, found 267.1164.

(E)-N,N-Dibutyl-N'-tosylformimidamide (4n)^[2]



From secondary amine: The reaction of 0.5 mmol of dibutylamine (71.6 mg, **2j**) and tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) at 25 °C in O₂ under blue LED (12W) irradiation afforded 69.6 mg of **4n** (90%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (4:1 to 3:1, *v*/*v*) as the eluent.

Colourless oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 8.13$ (s, 1H), 7.75 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.0 Hz,

1H), 3.39 (t, J = 7.6 Hz, 2H), 3.28 (t, J = 7.4 Hz, 2H), 2.39 (s, 3H), 1.59-1.47 (m, 4H), 1.33-1.23 (m, 4H), 0.94 (t, J = 7.3 Hz, 3H), 0.87 (t, J = 7.3 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 158.70$, 142.14, 139.84, 129.18, 126.29, 52.26, 45.93, 30.66, 28.65, 21.41, 19.90, 19.59, 13.63, 13.53 ppm. HRMS *m*/*z* (ESI) calcd for [C₁₆H₂₆N₂O₂S+Na]⁺ 333.1607, found 333.1611.

(E/Z)-N-Butyl-N-phenyl-N'-tosylformimidamide $(E:Z \approx 97:3)$ (40)



From secondary amine: The reaction of 0.5 mmol of *N*-butylaniline (74.6 mg, **2l**) and tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) at 25 °C in O₂ under blue LED (12W) irradiation afforded 39.8 mg of **4o** (48%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1 to 6:1, *v*/*v*) as the eluent.

Yellow oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 8.46$ (s, 1H), 7.80 (d, J = 8.3 Hz, 2H), 7.45-7.41 (m, 2H), 7.36-7.32 (m, 1H), 7.30-7.27 (m, 2H), 7.20-7.18 (m, 2H), 3.92 (t, J = 7.6 Hz, 2H), 2.42 (s, 3H), 1.53 (p, J = 7.6 Hz, 2H), 1.31-1.21 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 158.53$, 142.64, 142.06, 139.09, 129.84, 129.35, 127.65, 126.54, 123.59, 48.53, 28.91, 21.50, 19.79, 13.59 ppm. HRMS *m*/z (ESI) calcd for [C₁₈H₂₂N₂O₂S+Na]⁺ 353.1294, found 353.1285.

(E)-N-Ethyl-N-(m-tolyl)-N'-tosylformimidamide (4p)



From secondary amine: The reaction of 0.5 mmol of *N*-ethyl-3-methylaniline (67.6 mg, **2m**) and tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) at 25 °C in O₂ under blue LED (12W) irradiation for 24 hours afforded 43.4 mg of **4p** (55%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1 to 6:1, *v/v*) as the eluent.

Yellow oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 8.44$ (s, 1H), 7.81 (d, J = 8.0 Hz, 2H), 7.32-7.26 (m, 3H), 7.15 (d, J = 7.6 Hz, 1H), 6.99-6.98 (m, 2H), 3.95 (q, J = 7.2 Hz, 2H), 2.41 (s, 3H), 2.39 (s, 3H), 1.17 (t, J = 7.2 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 158.06$, 142.62, 141.83, 140.06, 139.16, 129.59, 129.36, 128.43, 126.56, 124.22, 120.53, 44.05, 21.49, 21.33, 12.37 ppm. HRMS *m*/*z* (ESI) calcd for [C₁₇H₂₀N₂O₂S+H]⁺ 317.1318, found 317.1322.

4) Gram-scale reactions of visible-light-enabled imidation with azides promoted by aerobic

ruthenium catalysis (Scheme 2)



Typical Procedure: To a three-necked flask charged with Ru(bpy)₃Cl₂ (128.1 mg, 0.2 mmol) was added a solution of tosyl azide (**3a**, 8.76 mL of 75% solution in EtOAc, 30 mmol) in anhydrous 1,4-dioxane (15 mL) via a syringe under O₂ (1 atm). Then a solution of triethylamine (**2a**, 1.01 g, 10 mmol) in anhydrous 1,4-dioxane (10 mL) was added via a syringe upon blue LED irradiation of a coiled 12W blue LED band (2 meters long, coiled as a four-layer ring with a diameter of 16 cm, and the flask is located in the center of this LED ring, as shown in the above picture). The reaction mixture was stirred at 25 °C in O₂ under blue LED (12W) irradiation for 24 hours, followed by concentration *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (4:1 to 3:1, v/v) as the eluent on silical gel to afford 2.09 g of the iminated product **4a** (82%). The yield of **4a** from this tertiary amine was calculated based on the loading of **2a**: acquisition of 10 mmol of **4a** from **2a** is equivalent to 100% yield.

Employing the same apparatus via the above procedure, the reaction of 10 mmol of diethylamine (**2h**, g, 10 mmol) and tosyl azide (**3a**, 8.76 mL of 75% solution in EtOAc, 30 mmol) with Ru(bpy)₃Cl₂ (128.1 mg, 0.2

mmol) at 25 °C in O_2 under blue LED (12W) irradiation for 24 hours afforded 1.01 g of the iminated product **4a** (79%). The yield of **4a** from this secondary amine was calculated based on the loading of **2h**: acquisition of 5 mmol of **4a** from **2h** is equivalent to 100% yield.

2 (0.5 n	a = 3a $(3 eq)$	Ru cat. (2 mol%) 12W Blue LED 1,4-dioxane (2 mL) O ₂ (1 atm), r. t., 6 h	N N Ts 4a
Entry	Ru c	at.	Yield (%) ^a
1	Ru(Ph ₃ P) ₂ (CO) ₂ C	l ₂ (14564-35-3)	7%
2	Ru(COD)Cl ₂ (50982-13-3)	12%
3	$Ru(Ph_3P)_3Cl_2$ (15529-49-4)	14%
4	RuCl ₃ (100	49-08-8)	21%

5) Reactions with other commonly used ruthenium catalysts

^a Reaction conditions: TEA **2a** (0.5 mmol), TsN₃ (1.5 mmol), Ru catalyst (0.01 mmol) in 1,4-dioxane (2 mL) at room temperature in O₂ (1 atm) under 12W bule LED irradiation for 6 hours. ^b Isolated yields of **4a** based on **2a**.

Control Experiments

1) Control experiments on tertiary amine 2a (Table 4)



Typical Procedures:

Entry 1: To a reaction tube charged with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) was added a solution of tosyl azide (**3a**, 438 µL of 75% solution in EtOAc, 1.5 mmol) in anhydrous 1,4-dioxane (1 mL) via a syringe under O₂ (1 atm). Then a solution of triethylamine (TEA, **2a**, 50.6 mg, 0.5 mmol) in anhydrous 1,4-dioxane (1 mL) was added via a syringe upon blue LED (12W) irradiation. The reaction mixture was stirred at 25 °C in O₂ under blue LED (12W) irradiation for 6 hours, followed by concentration *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (3:1 to 2:1 to 1:1, v/v) as the eluent on silical gel to afford 109.8 mg of **4a** (86%), 76.4 mg of **5a** (89%), 8.1 mg of **5b** (7%) and 7.0 mg of **5c** (6%).

<u>Entry 2:</u> To a reaction tube charged with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) was added a solution of tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) in anhydrous 1,4-dioxane (1 mL) via a syringe under argon (1 atm). Then a solution of triethylamine (TEA, **2a**, 50.6 mg, 0.5 mmol) in anhydrous 1,4-dioxane (1 mL) was added via a syringe upon blue LED (12W) irradiation. The reaction mixture was stirred at 25 °C in argon under blue LED (12W) irradiation for 6 hours, followed by concentration *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (3:1 to 2:1 to 1:1, *v/v*) as the eluent on silical gel to afford 66.4 mg of **4a** (52%), 76.8 mg of **5a** (90%), 5.7 mg of **5b** (5%) and 8.8 mg of **5c** (8%).

<u>Entry 3:</u> To a reaction tube was added a solution of tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) in anhydrous 1,4-dioxane (1 mL) via a syringe under O₂ (1 atm). Then a solution of triethylamine (TEA, **2a**, 50.6 mg, 0.5 mmol) in anhydrous 1,4-dioxane (1 mL) was added via a syringe upon blue LED (12W) irradiation. The reaction mixture was stirred at 25 °C in O₂ under blue LED (12W) irradiation for 6 hours, followed by concentration *in vacuo* to give dark residue, which was then purified by flash

chromatography using petroleum ether and ethyl acetate (3:1 to 2:1 to 1:1, v/v) as the eluent on silical gel to afford 32.3 mg of **4a** (25%), 38.2 mg of **5a** (45%) and 7.0 mg of **5b** (6%). None of **5c** could be observe on GC-MS.

<u>Entry 4:</u> To a reaction tube was added a solution of tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) in anhydrous 1,4-dioxane (1 mL) via a syringe under argon (1 atm). Then a solution of triethylamine (TEA, **2a**, 50.6 mg, 0.5 mmol) in anhydrous 1,4-dioxane (1 mL) was added via a syringe upon blue LED (12W) irradiation. The reaction mixture was stirred at 25 °C in argon under blue LED (12W) irradiation for 6 hours, followed by concentration *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (3:1 to 2:1 to 1:1, *v/v*) as the eluent on silical gel to afford 33.1 mg of **4a** (26%), 42.2 mg of **5a** (49%) and 5.4 mg of **5b** (5%). None of **5c** could be observe on GC-MS.

<u>Entry 5:</u> To a reaction tube tightly wrapped with tinfoil and charged with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) was added a solution of tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) in anhydrous 1,4-dioxane (1 mL) via a syringe under O₂ (1 atm). Then a solution of triethylamine (TEA, **2a**, 50.6 mg, 0.5 mmol) in anhydrous 1,4-dioxane (1 mL) was added via a syringe. The reaction mixture was stirred at 25 °C in dark for 6 hours, and none of **4a** or **5a-c** could be observed on GC-MS.

<u>Entry 6:</u> To a reaction tube charged with $Ru(bpy)_3Cl_2$ (6.4 mg, 0.01 mmol) was added a solution of tosyl azide (**3a**, 438 µL of 75% solution in EtOAc, 1.5 mmol) in anhydrous 1,4-dioxane (1 mL) via a syringe under O₂ (1 atm). Then a solution of triethylamine (TEA, **2a**, 50.6 mg, 0.5 mmol) and TEMPO (390.6 mg, 2.5 mmol) in anhydrous 1,4-dioxane (1 mL) was added via a syringe upon blue LED (12W) irradiation. The reaction mixture was stirred at 25 °C in O₂ under blue LED (12W) irradiation for 6 hours, and none of **4a** or **5a-c** could be observed on GC-MS.

<u>Entry 7:</u> To a reaction tube charged with $Ru(bpy)_3Cl_2$ (6.4 mg, 0.01 mmol) was added a solution of tosyl azide (**3a**, 438 µL of 75% solution in EtOAc, 1.5 mmol) in anhydrous 1,4-dioxane (2 mL) via a syringe under O₂ (1 atm). Then the reaction mixture was stirred at 25 °C in O₂ under blue LED (12W) irradiation for 6 hours, and none of **4a** or **5a-c** could be observed on GC-MS.

4-Methylbenzenesulfonamide (5a)^[5]

White solid, m.p. 114.0-114.6 °C. ¹H NMR (DMSO-d₆, 400 MHz): δ = 7.71 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.26 (s, 2H), 2.37 (s, 3H) ppm. ¹³C NMR (DMSO-d₆, 100 MHz): δ = 141.82, 141.42, 129.26, 125.59, 20.87 ppm. GC-MS *m*/z (EI) calcd for [C₇H₉NO₂S] 171.04, found 171.0.

(E/Z)-N-Ethyl-N'-tosylformimidamide $(E:Z \approx 4:1)$ (5b)

White solid, m.p. 80.2-80.7 °C. ¹H NMR (CDCl₃, 400 MHz): δ = 8.26 (d, *J* = 5.1 Hz, 1.00H), 8.12 (d, *J* = 13.5 Hz, 0.28H), 7.75-7.71 (m, 2.56H), 7.28-7.25 (m, 2.54H), 6.67 (s, 1.00H), 3.42-3.34 (m, 2.47H), 2.40 (s, 3.78 H), 1.24 (t, *J* = 7.2 Hz, 0.75H), 1.16 (t, *J* = 7.3 Hz, 3.01H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 157.64, 142.87, 142.57, 139.20, 138.86, 129.48, 129.34, 126.35, 126.33, 41.30, 36.74, 21.44, 18.99, 15.91, 13.68 ppm. HRMS *m*/z (ESI) calcd for [C₁₀H₁₄N₂O₂S+H]⁺ 227.0849, found 227.0857.

(E)-N,N-Dimethyl-N'-tosylformimidamide (5c)^[2]

Light-yellow solid, m.p. 93.2-93.8 °C. ¹H NMR (CDCl₃, 400 MHz): $\delta = 8.13$ (s, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 3.31 (s, 3H), 3.01 (s, 3H), 2.40 (s, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 159.03$, 142.44, 139.46, 129.29, 126.45, 41.43, 35.46, 21.45 ppm. HRMS *m*/z (ESI) calcd for [C₁₀H₁₄N₂O₂S+H]⁺ 227.0849, found 227.0852.

2) Control experiments on N-substituted enamine 1b (Table 5)



Typical Procedures:

Entry 1: To a reaction tube charged with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) was added a solution of tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) in anhydrous 1,4-dioxane (1 mL) via a syringe under O₂ (1 atm). Then a solution of 1-vinylpyrrolidin-2-one (**1b**, 55.5 mg, 0.5 mmol) in anhydrous 1,4-dioxane (1 mL) was added via a syringe upon blue LED (12W) irradiation. The reaction mixture was stirred at 25 °C in O₂ under blue LED (12W) irradiation for 24 hours, followed by concentration *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (4:1 to 3:1, *v/v*) as the eluent on silical gel to afford 41.5 mg of **4x** (31%).

<u>Entry 2:</u> To a reaction tube charged with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) was added a solution of tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) in anhydrous 1,4-dioxane (1 mL) via a syringe under argon (1 atm). Then a solution of 1-vinylpyrrolidin-2-one (**1b**, 55.5 mg, 0.5 mmol) in anhydrous 1,4-dioxane (1 mL) was added via a syringe upon blue LED (12W) irradiation. The reaction mixture was stirred at 25 °C in argon under blue LED (12W) irradiation for 24 hours, followed by concentration *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (4:1 to 3:1, v/v) as the eluent on silical gel to afford 14.9 mg of **4x** (11%).

<u>Entry 3:</u> To a reaction tube was added a solution of tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) in anhydrous 1,4-dioxane (1 mL) via a syringe under O₂ (1 atm). Then a solution of 1-vinylpyrrolidin-2-one (**1b**, 55.5 mg, 0.5 mmol) in anhydrous 1,4-dioxane (1 mL) was added via a syringe upon blue LED (12W) irradiation. The reaction mixture was stirred at 25 °C in O₂ under blue LED (12W) irradiation for 24 hours, and only trace amount of amidine **4q** could be observed on TLC.

<u>Entry 4</u>: To a reaction tube was added a solution of tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) in anhydrous 1,4-dioxane (1 mL) via a syringe under argon (1 atm). Then a solution of 1-vinylpyrrolidin-2-one (**1b**, 55.5 mg, 0.5 mmol) in anhydrous 1,4-dioxane (1 mL) was added via a syringe upon blue LED (12W) irradiation. The reaction mixture was stirred at 25 °C in argon under blue LED (12W) irradiation for 24 hours, and only trace amount of amidine **4q** could be observed on TLC.

<u>Entry 5:</u> To a reaction tube tightly wrapped with tinfoil and charged with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) was added a solution of tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) in anhydrous 1,4-dioxane (1 mL) via a syringe under O₂ (1 atm). Then a solution of 1-vinylpyrrolidin-2-one (**1b**, 55.5 mg, 0.5 mmol) in anhydrous 1,4-dioxane (1 mL) was added via a syringe. The reaction mixture was stirred in dark at 25 °C in O₂ for 24 hours, and only trace amount of amidine **4q** could be observed on TLC.

<u>Entry 6:</u> To a reaction tube tightly wrapped with tinfoil and charged with Ru(bpy)₃Cl₂ (6.4 mg, 0.01 mmol) was added a solution of tosyl azide (**3a**, 438 μ L of 75% solution in EtOAc, 1.5 mmol) in anhydrous 1,4-dioxane (1 mL) via a syringe under argon (1 atm). Then a solution of 1-vinylpyrrolidin-2-one (**1b**, 55.5 mg, 0.5 mmol) in anhydrous 1,4-dioxane (1 mL) was added via a syringe. The reaction mixture was stirred in dark at 25 °C in argon for 24 hours, and only trace amount of amidine **4q** could be observed on TLC.

(E)-4-Methyl-N-((2-oxopyrrolidin-1-yl)methylene)benzenesulfonamide (4q)

White solid, m.p. 137.2-137.7 °C. ¹H NMR (CDCl₃, 400 MHz): δ = 9.00 (s, 1H), 7.81 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 3.77 (t, *J* = 7.3 Hz, 2H), 3.62 (t, *J* = 8.1 Hz, 2H), 2.43 (s, 3H), 2.16 (p, *J* = 7.7 Hz, 2H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 175.80, 153.32, 144.10, 136.46, 129.67, 127.50, 44.15, 31.42, 21.59, 17.76 ppm. HRMS *m/z* (ESI) calcd for [C₁₂H₁₄N₂O₃S+H]⁺ 267.0798, found 267.0800.

3) Control experiments on secondary amine 2h (Scheme 3)



Typical Procedure for Scheme 3a: To a reaction tube charged with $Ru(bpy)_3Cl_2$ (6.4 mg, 0.01 mmol) was added a solution of tosyl azide (**3a**, 438 µL of 75% solution in EtOAc, 1.5 mmol) in anhydrous 1,4-dioxane (1 mL) via a syringe under O₂ (1 atm). Then a solution of diethylamine (DEA, **2h**, 36.6 mg) in anhydrous 1,4-dioxane (1 mL) was added via a syringe upon blue LED (12W) irradiation. The reaction mixture was stirred at 25 °C in O₂ under blue LED (12W) irradiation for 6 hours, followed by concentration *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (4:1 to 3:1, *v/v*) as the eluent on silical gel to afford 58.2 mg of **4a** (92%) and 84.0 mg of **5a** (98%).

Typical Procedure for Scheme 3b: To a reaction tube charged with $Ru(bpy)_3Cl_2$ (6.4 mg, 0.01 mmol) was added a solution of tosyl azide (**3a**, 438 µL of 75% solution in EtOAc, 1.5 mmol) in anhydrous 1,4-dioxane (1 mL) via a syringe under argon (1 atm). Then a solution of diethylamine (DEA, **2h**, 36.6 mg) in anhydrous 1,4-dioxane (1 mL) was added via a syringe upon blue LED (12W) irradiation. The reaction mixture was stirred at 25 °C in argon under blue LED (12W) irradiation for 6 hours, followed by concentration *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (4:1 to 3:1, *v/v*) as the eluent on silical gel to afford 89.8 mg of **4a** (71%) and 76.6 mg of **5a** (90%).

References

- [1] T. Jiang, Z. Y. Gu, L. Yin, S. Y. Wang and S. J. Ji, J. Org. Chem., 2017, 82, 7913-7919.
- [2] J. Gui, H. Xie, H. Jiang and W. Zeng, Org. Lett., 2019, 21, 2804-2807.
- [3] R. Ding, H. Chen, Y.-L. Xu, H.-T. Tang, Y.-Y. Chen and Y.-M. Pan, Adv. Synth. Catal., 2019, 361, 3656-3660.
- [4] Pleas visit https://www.tansoole.com/upload/detail/05/YC93_WGLV_05039134.html for purchasing the Titan Scientific Lab PR-6 parallel photoreactor (May 19th, 2021).
- [5] E. Hayashi, Y. Yamaguchi, Y. Kita and M. Hara, Chem. Commun., 2020, 56, 2095-2098.

¹H and ¹³C NMR spectra of 4a-q and 5a-c



































A A A A A A A A A A A A A A A A A A A
4i Ts Ts 4i Ts 4i Ts 4i Ts 4i Ts 4i Ts 4i Ts 4i Ts 4i Ts 4i Ts 5i 10 10 10 10 10 10 10 10 10 10







S40



































S57



