Electronic Supplementary Information

Visible light-mediated dehydrogenative β-arylsulfonylation of tertiary aliphatic amines with arylsulfonyl chlorides

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1. General methods

Unless specified noted, all reagents were purchased from commercial suppliers without further purification. Column chromatography was performed using 200-300 mesh silica gel (YanTai, China). $^1$H NMR spectra were recorded on BRUKER 400 (400 MHz) spectrophotometer. Chemical shifts (δ) are reported in ppm from TMS as the internal standard (TMS 0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, bs=broad singlet, d = doublet, t = triplet, q =quartlet, m = multiplet), coupling constants (Hz) and integration. $^{13}$C NMR spectra were recorded on BRUKER 400 (100 MHz) with complete proton decoupling spectrophotometer. Mass spectra were measured on Bruker Apex IV FTMS (ESI), infrared spectroscopy was carried out on Nicolet iS460 FT-IR Thermo Fisher Scientific infrared spectrometer.

2. Optimization of the reaction of triethylamine with $p$-toluene sulfonyl chloride

A 25 ml round bottomed flask equipped with a stirring-bar was charged with $p$-tolylsulfonyl chloride (1a, 1 mmol), photocatalyst, and additives in solvent, and then pre-bathed in ice-salt-water mixtures for 5 minutes. Subsequently, triethylamine was added to the system when 23 w fluorescent light turned on with gentle stirring. With TsCl completely consumed, the reaction mixture was diluted with CH$_2$Cl$_2$, silica gel added to, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired product.
**Table S1** Evaluation of various parameters in the photoredox reaction

![Chemical structure diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Photocatalyst</th>
<th>Solvent</th>
<th>Ratio of 2a/1a</th>
<th>Additive</th>
<th>Yield&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
</table>

<sup>a</sup> Reaction conditions: a) Reaction conditions: b) Yield.
<table>
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<tr>
<th></th>
<th>Precursor</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Yield (%)</th>
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* Unless otherwise specified, all reactions were carried out with 2a, 1a (1 mmol), photocatalyst (2.5% mol), under 23 w fluorescent light at -5 to 5 °C open to air with gentle stirring for 5 minutes. $^b$ Isolated yield. $^c$ At temperature of 25 °C. $^d$ At temperature of -30 °C, 8h. $^e$ the mixture was poured into ether and water after concentrated, then organic phase was washed by water and brine, and dried by Na$_2$SO$_4$. $^f$ at the concentration of 1M. $^g$ at the concentration of 0.02M. $^h$ 5 mol % photocatalyst. $^i$ 1 mol % photocatalyst. $^j$ 0.5 mol % photocatalyst. $^k$ fierce stirring. $^l$ most of the product was sulfonamide. $^m$ No light.
3. Synthesis of tertiary amines

According to the reference (J. Org. Chem. 1996, 61, 3849), to an round bottomed flask equipped with a stirring stir bar under Ar atmosphere was added 2 equiv of ethylamine and 1.0 equiv. of 3-phenylpropanal in 1,2- dichloroethane(DCE), and then treated with 1.4 equiv. of sodium triacetoxy borohydride(NaBH(OAc)₃). After the complete consumption of the 3-phenylpropanal, the mixture was quenched by adding saturated aqueous NaHCO₃ solution and extracted with ether. The combined organic layer was washed with 1M HCl and then pH of aqueous phase was to adjust to 10 by 1M NaOH solution. Ether was added to extracted free amine, subsequently dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The product was used without further purification.

According to the reference (J. Org. Chem. 1996, 61, 3849), to an round bottomed flask equipped with a stirring stir bar under Ar atmosphere was added 2 equiv of propanal and 1.0 equiv. dicyclohexylamine in 1,2- dichloroethane(DCE), and then treated with 1.4 equiv. of sodium triacetoxy borohydride(NaBH(OAc)₃). After 24h, the mixture was quenched by adding saturated aqueous NaHCO₃ solution and extracted with ether. The combined organic layer was washed with 1M HCl and then pH of aqueous phase was to adjust to 10 by 1M NaOH solution. Ether was added to extracted free amine, subsequently dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The product was used without further purification.
4. General procedure for β-arylsulfonfylation of tertiary aliphatic amines with arylsulfonyl chlorides

A 25ml round bottomed flask equipped with a stirring-bar was charged with arylsulfonyl chloride (1 mmol), photocatalyst (1 mol%), in acetone, and then pre-bathed in ice-salt-water mixtures for 5 minutes. Subsequently, tertiary amine was added to the system when 23 w fluorescent light turned on with gentle stirring. With arylsulfonyl chloride completely consumed, the reaction mixture was diluted with CH$_2$Cl$_2$, silica gel added to, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired product.
5. Experimental data for the described substances

\[
\begin{align*}
\text{N, N-diethyl-3-phenylpropan-1-amine} \\
\text{Yielding the title compound as light yellow oil in 70% yield.} \ \ &\text{^1H NMR (400 MHz, CDCl}_3\text{): } \delta \\
&7.27 (t, J = 7.5 \text{ Hz, 2H}), 7.15-7.20 (m, 3H), 2.61 (t, J = 7.8 \text{ Hz, 2H}), 2.52 (q, J = 7.1 \text{ Hz, 4H}), \\
&2.46 (t, J = 7.6 \text{ Hz, 2H}), 1.74-1.82 (m, 2H), 1.00 (t, J = 7.1 \text{ Hz, 6H}); \text{^13C NMR (100 MHz, CDCl}_3\text{): } \delta \\
&142.6, 128.6, 128.5, 125.9, 52.7, 47.1, 34.1, 28.9, 11.9. \text{ IR (film, cm}^{-1}\text{): } \nu 2928, 2853, 2809, 1450. \text{ HRMS (ESI): Calcd for C}_{13}\text{H}_{22}\text{N}[\text{MH}]^+: m/z 192.1747; \text{ found: 192.1744.}
\end{align*}
\]

\[
\begin{align*}
\text{N-cyclohexyl-N-propylcyclohexanamine} \\
\text{Yielding the title compound as light yellow oil in quantitative yield.} \ \ &\text{^1H NMR (CDCl}_3, 400 \text{ MHz): } \delta \\
&2.49-2.54 (m, 2H), 2.40-2.44 (m, 2H), 1.70-1.75 (m, 7H), 1.57-1.61 (m, 3H), 1.37 (q, \\
&J = 7.5 \text{ Hz, 2H}), 1.17-1.24 (m, 8H), 1.05-1.08 (m, 2H), 0.82 (q, J = 7.4 \text{ Hz, 3H}); \text{^13C NMR (CDCl}_3, 100 \text{ MHz): } \delta \\
&58.3, 48.8, 31.9, 26.7, 26.6, 25.0, 11.9. \text{ IR (film, cm}^{-1}\text{): } \nu 2968, 2935, 2870, 2799. \text{ HRMS (ESI): Calcd for C}_{15}\text{H}_{30}\text{N}[\text{MH}]^+: m/z 224.2373; \text{ found: 224.2368.}
\end{align*}
\]

\[
\begin{align*}
\text{(E)-N, N-diethyl-2-tosylethenamine} \\
\text{Prepared according to the general procedure from 1a (1 mmol), 2a (4 mmol), Ru(bpy)_3(PF}_6)_2 \\
&(0.01 \text{ mmol) and acetone (5 mL) under visible light irradiation for 3 minutes to provide the}
\end{align*}
\]
title compound as a white solid (47% yield). M.p.: 80-81°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.73 (d, $J = 8.0$ Hz, 2H), 7.30 (d, $J = 12.8$ Hz, 1H), 7.25 (d, $J = 8.0$ Hz, 2H), 4.90 (d, $J = 12.8$ Hz, 1H), 3.16(bs, 4H), 2.39 (s, 3H), 1.14 (bs, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$148.8, 142.6, 142.1, 129.5, 126.2, 91.8, 50.1(bs), 42.8(bs), 21.5, 14.8(bs), 11.3(bs), $^{13}$C NMR (125 MHz, DMSO, 100°C): 149.5, 144.2, 142.0, 129.9, 126.2, 92.8, 46.2, 21.3, 13.2. IR (film, cm$^{-1}$): $\nu$ 3076, 2977, 2935, 2876, 1617(vs), 1493, 1450. HRMS (ESI): Calcd for C$_{13}$H$_{20}$O$_2$NS [MH]$^+$: m/z 254.1209; found: 254.1206.

![3b](image)

(E)-$N,N$-diethyl-2-(o-tolylsulfonyl)ethenamine

Prepared according to the general procedure from 2-methylbenzene-1-sulfonfyl chloride (1 mmol), 2a (4 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 5 minutes to provide the title compound as a white solid (47% yield). M.p.: 51-52°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.01 (d, $J = 8.0$ Hz, 1H), 7.36-7.40 (m, 1H), 7.23-7.30 (m, 3H), 4.92 (d, $J = 12.8$ Hz, 1H), 3.17(q, $J = 8$ Hz, 4H), 2.62 (s, 3H), 1.14 (bs, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.6, 142.8, 136.4, 132.2, 131.8, 127.6, 126.1, 90.6, 50.1(bs), 42.8(bs), 20.2, 14.8(bs), 11.3(bs). IR (film, cm$^{-1}$): $\nu$ 3066, 2976, 2922, 2871, 1613(vs), 1493, 1468. HRMS (ESI): Calcd for C$_{13}$H$_{20}$O$_2$NS [MH]$^+$: m/z 254.1209; found: 254.1205.

![3c](image)

(E)-$N,N$-diethyl-2-(m-tolylsulfonyl)ethenamine

Prepared according to the general procedure from 3-methylbenzene-1-sulfonfyl chloride (1
mmol), 2a (4 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 5 minutes to provide the title compound as a white solid (45% yield). M.p.: 72-73°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.63-7.67 (m, 2H), 7.28-7.30 (m, 3H), 4.90 (d, $J$ = 12.8 Hz, 1H), 3.17(broad doublet, 4H), 2.40 (s, 3H), 1.15 (bs, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$148.9, 145.2, 138.9, 132.3, 128.7, 126.4, 123.2, 91.3, 50.0(bs), 42.7(bs), 21.4, 14.2(bs), 11.2(bs) , IR (film, cm$^{-1}$): $\nu$ 3063, 2976, 2935, 2872, 1614(vs), 1469. HRMS (ESI): Calcd for C$_{13}$H$_{20}$O$_2$NS [MH]$^+$: m/z 254.1209; found: 254.1205.

\[ \text{(E)}-N,N\text{-diethyl-2-} (\text{m-tolylsulfonyl})\text{ethenamine} \]

Prepared according to the general procedure from benzenesulfonyl chloride (1 mmol), 2a (4 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 5 minutes to provide the title compound as a white solid (40% yield). M.p.: 45-46°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.84-7.86 (m, 2H), 7.43-7.48 (m, 3H), 7.31 (d, $J$ = 12.8 Hz, 1H), 4.91 (d, $J$ = 12.8 Hz, 1H), 3.17(broad doublet, 4H), 1.14 (bs, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$149.1, 145.4, 131.5, 128.8, 126.0, 91.1, 50.1(bs), 42.7(bs), 14.7(bs), 11.2(bs) , IR (film, cm$^{-1}$): $\nu$ 3069, 2977, 2936, 2875, 1614(vs), 1452, 1468. HRMS (ESI): Calcd for C$_{12}$H$_{18}$O$_2$NS [MH]$^+$: m/z 240.1053; found: 254.1050.

\[ \text{(E)}-N,N\text{-diethyl-2-} (\text{4-methoxyphenylsulfonyl})\text{ethenamine} \]

Prepared according to the general procedure from 4-methoxybenzene-1-sulfonyl chloride (1 mmol), 2a (4 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.01 mmol) and acetone (5 mL) under visible light
irradiation for 5 minutes to provide the title compound as a white solid (41% yield). M.p.: 74-75°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.78 (d, $J = 8.4$ Hz, 1H), 7.28 (d, $J = 12.8$ Hz, 1H), 6.93 (d, $J = 8.4$ Hz, 1H), 4.90 (d, $J = 12.8$ Hz, 1H), 3.84 (s, 3H), 3.16 (bs, 4H), 1.14 (bs, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$162.1, 148.6, 137.4, 128.3, 114.1, 92.3, 55.7, 50.0(bs), 42.4(bs), 14.8(bs), 11.4(bs), IR (film, cm$^{-1}$): ν 3069, 2975, 2934, 2872, 1612(vs), 1495, 1460. HRMS (ESI): Calcd for C$_{13}$H$_{20}$O$_3$NS [MH]$^+$: m/z 270.1158; found: 270.1155.

![3f](image)

$(E)$-$N,N$-diethyl-2-(4-methoxyphenylsulfonyl)ethenamine

Prepared according to the general procedure from 4-fluorobenzene-1-sulfonyl chloride (1 mmol), 2a (4 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 10 minutes to provide the title compound as a white solid (33% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.84-7.87(m, 2H), 7.31 (d, $J = 12.7$ Hz, 1H), 7.12 (t, $J = 8.6$ Hz, 2H), 4.89 (d, $J = 12.7$ Hz, 1H), 3.18 (broad doublet, 4H), 1.15 (bs, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$165.6, 163.1, 149.2, 141.65, 141.62, 128.8, 128.7, 116.0, 115.8, 91.1, 50.2(bs), 42.7(bs), 14.7(bs), 11.1(bs), IR (film, cm$^{-1}$): ν 3073, 2979, 2934, 2881, 1615(vs), 1493, 1469. HRMS (ESI): Calcd for C$_{12}$H$_{17}$O$_2$NS [MH]$^+$: m/z 258.0959; found: 258.0956.

![3g](image)

$(E)$-2-(4-chlorophenylsulfonyl)-$N,N$-diethylethenamine
Prepared according to the general procedure from 4-chlorobenzene-1-sulfonyl chloride (1 mmol), 2a (4 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 3 minutes to provide the title compound as a white solid (42% yield). M.p.: 42-43°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.79 (d, $J$ = 8.4 Hz, 2H), 7.42 (t, $J$ = 8.4 Hz, 2H), 7.29 (d, $J$ = 12.8 Hz, 1H), 4.87 (d, $J$ = 12.8 Hz, 1H), 3.18 (broad doublet, 4H), 1.15 (bs, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.4, 144.1, 137.8, 129.1, 127.7, 124.9, 90.9, 50.2(bs), 42.8(bs), 14.8(bs), 11.2(bs), IR (film, cm$^{-1}$): $\nu$ 3077, 2976, 2934, 2872, 1613(vs), 1507. HRMS (ESI): Calcd for C$_{12}$H$_{17}$O$_2$N$_3$S$^+$ [MH]$^+$: m/z 274.0663; found: 274.0659.

![3h](image)

(E)-2-(4-bromophenylsulfonyl)-N,N-diethylethenamine

Prepared according to the general procedure from 4-bromobenzene-1-sulfonyl chloride (1 mmol), 2a (4 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 5 minutes to provide the title compound as a white solid (45% yield). M.p.: 94-95°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.71 (d, $J$ = 8.0 Hz, 2H), 7.59 (t, $J$ = 8.0 Hz, 2H), 7.30 (d, $J$ = 12.8 Hz, 1H), 4.87 (d, $J$ = 12.8 Hz, 1H), 3.18 (broad doublet, 4H), 1.15 (bs, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.4, 144.6, 132.1, 127.9, 126.2, 90.8, 50.2(bs), 42.8(bs), 14.8(bs), 11.2(bs), IR (film, cm$^{-1}$): $\nu$ 3069, 2969, 2920, 2850, 1610(vs), 1569. HRMS (ESI): Calcd for C$_{12}$H$_{17}$O$_2$N$_7$S$^+$BrS [MH]$^+$: m/z 318.0158; found: 318.0155.

![3i](image)

(E)-N,N-diethyl-2-(thiophen-2-ylsulfonyl)ethenamine
Prepared according to the general procedure from thiophene-2-sulfonyl chloride (1 mmol), 2a (4 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 5 minutes to provide the title compound as a white solid (47% yield). M.p.: 75-77°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.48-7.52 (m, 2H), 7.33 (t, $J$ = 12.8 Hz, 2H), 7.00-7.03 (m, 1H), 4.87 (d, $J$ = 12.8 Hz, 1H), 3.18 (m, 4H), 1.17 (bs, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.2, 148.2, 130.5, 130.0, 127.2, 92.1, 50.2(bs), 42.8(bs), 14.8(bs), 11.2(bs), IR (film, cm$^{-1}$): $\nu$ 3078, 2976, 2934, 2875, 1613(vs), 1507. HRMS (ESI): Calcd for C$_{10}$H$_{16}$O$_2$NS $[MH]^+$: m/z 246.0617; found: 246.0614.

(E)-N, N-diethyl-2-tosylethenamine

Prepared according to the general procedure from N-ethyldiisopropylamine (4 mmol), 1a (1 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 3 minutes to provide the title compound as a white solid (41% yield). M.p.: 133-134°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.72 (d, $J$ = 7.2 Hz, 2H), 7.39 (d, $J$ = 12.8 Hz, 1H), 7.25 (d, $J$ = 7.2 Hz, 2H), 4.96 (d, $J$ = 12.8 Hz, 1H), 3.56(bs, 4H), 2.39 (s, 3H), 1.20 (bs, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 145.1, 142.8, 142.0, 129.5, 126.3, 91.9, 49.4(bs), 47.7(bs), 21.7, 21.6(bs), 19.7(bs) IR (film, cm$^{-1}$): $\nu$ 3074, 2976, 2934, 2875, 1613(vs), 1507. HRMS (ESI): Calcd for C$_{15}$H$_{24}$O$_2$NS $[MH]^+$: m/z 282.1522; found: 282.1519.

(E)-N,N-dipropyl-2-tosylprop-1-en-1-amine
Prepared according to the general procedure from **tri-n-propylamine** (4 mmol), **1a** (1 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 10 minutes to provide the title compound as a white solid (41% yield). M.p.: 86-87°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.68 (d, $J = 8.0$ Hz, 2H), 7.31 (s, 1H), 7.25 (d, $J = 8$ Hz, 2H), 3.15 (t, $J = 7.6$ Hz, 4H), 2.40(s, 3H), 1.87 (s, 3H), 1.56-1.61 (m, 4H), 0.89 (t, $J = 7.2$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 145.6, 142.3, 139.8, 129.5, 127.2, 97.1, 54.8, 22.8, 21.6, 11.1, 11.0. IR (film, cm$^{-1}$): v 2964, 2933, 2874, 1628 (vs), 1495, 1457. HRMS (ESI): Calcd for C$_{16}$H$_{26}$O$_2$NS [MH]$^+$: m/z 296.1679; found: 296.1678.

![4c](image)

**(E)-N,N-dibutyl-2-tosylbut-1-en-1-amine**

Prepared according to the general procedure from **tri-n-butylamine** (4 mmol), **1a** (1 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 40 minutes in room temperature to provide the crude product with little amine. Then it was dissolved in ether and washed with 1M HCl. Subsequently organic phase was washed by brine, dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure, providing a white solid (36% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.70 (d, $J = 8$ Hz, 2H), 7.31 (s, 1H), 7.25 (d, $J = 8$ Hz, 2H), 3.17 (t, $J = 7.6$ Hz, 4H), 2.21 (q, $J = 8$ Hz, 2H), 1.52-1.56(m, 4H), 1.28-1.33(m, 4H), 0.93 (t, $J = 7.4$ Hz, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 145.4, 142.2, 140.8, 129.4, 127.2, 104.2, 52.8, 31.4, 21.6, 19.9, 18.8, 16.0, 13.9. IR (film, cm$^{-1}$): v 2959, 2929, 2872, 1620 (vs), 1460. HRMS (ESI): Calcd for C$_{19}$H$_{32}$O$_2$NS [MH]$^+$: m/z 338.2148; found: 338.2141.
Prepared according to the general procedure from 1-ethylpiperidine (4 mmol), 1a (1 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 10 minutes to provide the title compound as a white solid with two regioisomers (41% yield), and then the major isomer was separated from the other by semi-HPLC. Major isomer M.p.: 105-108°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.70 (d, $J$ = 8 Hz, 2H), 7.31 (s, 1H), 7.25 (d, $J$ = 8 Hz, 2H), 3.19 (q, $J$ = 7.2 Hz, 2H), 3.04 (q, $J$ = 5.6 Hz, 2H), 2.40(s, 3H), 2.15 (q, $J$ = 6.0 Hz, 2H), 1.80 (m, 2H), 1.16 (q, $J$ = 7.2 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.7, 142.3, 140.2, 129.6, 127.0, 100.1, 50.6, 45.0, 21.7, 21.3, 19.9, 14.0. IR (film, cm$^{-1}$): ν 3048, 2963, 2923, 2852, 1616(vs), 1491, 1468. HRMS (ESI): Calcd for C$_{14}$H$_{20}$O$_2$NS [MH]$^+$: m/z 266.1209; found: 266.1206. Minor isomer $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.74 (d, $J$ = 8 Hz, 2H), 7.23-7.26 (m, 3H), 4.95 (d, $J$ = 12.8 Hz, 1H), 3.15 (bs, 3H), 2.40 (s, 3H), 1.60(bs, 7H).$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.7, 142.5, 142.2, 129.5, 126.3, 92.5, 60.5, 23.9, 21.2, 14.3 . HRMS (ESI): Calcd for C$_{14}$H$_{20}$O$_2$NS [MH]$^+$: m/z 266.1209; found: 266.1206.

Prepared according to the general procedure from 1-methylpiperidine (4 mmol), 1a (1 mmol),...
Ru(bpy)$_3$(PF$_6$)$_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 10 minutes to provide the title compound as a white solid with two regioisomers (36% yield), and then the major isomer was separated from the other by semi-HPLC. Major isomer M.p.: 87-88°C. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.72 (d, $J$ = 8 Hz, 2H), 7.27 (d, $J$ = 8 Hz, 2H), 7.00 (s, 1H), 3.46 (q, $J$ = 6 Hz, 2H), 3.07 (q, $J$ = 7.2 Hz, 2H), 2.68 (q, $J$ = 6 Hz, 2H), 2.41(s, 3H), 1.15 (q, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.5, 142.6, 139.9, 129.6, 126.7, 106.1, 52.2, 44.8, 27.7, 21.6, 13.6. IR (film, cm$^{-1}$): $\nu$ 3062, 2973, 2930, 2855, 1577(vs), 1493, HRMS (ESI): Calcd for C$_{13}$H$_{18}$O$_2$NS [MH]$^+$: m/z 252.1053; found: 266.1050. Minor isomer M.p.: 123-125°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.75 (d, $J$ = 8 Hz, 2H), 7.12-7.29 (m, 8H), 4.82 (d, $J$ = 12.8 Hz, 1H), 4.92 (bs, 2H), 3.13 (bs, 4H), 3.03 (bs, 2H), 2.40(s, 3H), 1.92 (bs, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.7, 142.7, 142.2, 129.6, 126.4, 93.1, 25.5, 21.6, 14.4. IR (film, cm$^{-1}$): $\nu$ 3062, 2955, 2921, 2852, 1612(vs), 1458, HRMS (ESI): Calcd for C$_{13}$H$_{18}$O$_2$NS [MH]$^+$: m/z 2652.1051; found: 252.1053.

![4f](image-url)

*(E)-N-ethyl-3-phenyl-N-(2-tosylvinyl)propan-1-amine*

Prepared according to the general procedure from *N-ethyl-3-phenyl-N-propylpropan-1-amine* (4 mmol), 1a (4 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 40 minutes to provide the crude product with little amine. Then it was dissolved in ether and washed with 1M HCl. Subsequently organic phase was washed by brine, dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure, providing a white solid (25% yield). M.p.: 58-59°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.72 (d, $J$ = 8.0 Hz, 2H), 7.12-7.29 (m, 8H), 4.90(bs, 1H), 3.13 (bs, 4H), 2.58 (d, $J$ = 7.2 Hz, 2H), 2.39(s, 3H),

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1.87 (d, J = 7.2 Hz, 2H), 1.11 (bs, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.2, 142.6, 142.2, 140.8, 129.5, 128.7, 128.4, 126.4, 126.3, 92.2, 32.9(bs), 21.6. IR (film, cm$^{-1}$): v 3060, 3024, 2971, 2931, 2870, 1613(vs), 1495. HRMS (ESI): Calcd for C$_{20}$H$_{26}$O$_2$NS [MH]$^+$: m/z 344.1679; found: 344.1674.

$\text{(E)-N-cyclohexyl-N-(2-tosylprop-1-enyl)cyclohexanamine}$

Prepared according to the general procedure from $\text{N-cyclohexyl-N-propylcyclohexanamine}$ (4 mmol), 1a (4 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 10 minutes to provide the crude product with little amine. Then it was dissolved in ether and washed with 1M HCl. Subsequently organic phase was washed by brine, dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure, providing a white solid (36% yield). M.p.: 138-140°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.68 (d, J = 8.0 Hz, 2H), 7.45 (s, 1H), 7.26 (d, J = 8.0 Hz, 2H), 3.34(bs, 2H), 2.40 (s, 3H), 1.89 (s, 3H), 1.80-1.83(m, 4H), 1.70-1.76(m, 4H), 1.63-1.66(m, 2H), 1.45-1.55(m, 4H), 1.22-1.32(m, 4H), 1.08-1.17(m, 2H), $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 142.1, 142.0, 140.1, 129.5, 127.2, 96.2, 57.0, 33.3, 26.1, 25.4, 21.6, 12.3. IR (film, cm$^{-1}$): v 2930, 2855, 1618(vs), 1492. HRMS (ESI): Calcd for C$_{20}$H$_{26}$O$_2$NS [MH]$^+$: m/z 376.2305; found: 376.2299.
(E)-N-cyclohexyl-N-(2-tosylprop-1-enyl)cyclohexanamine

A 25 ml Schlenk tube equipped with stir-bar was charged with 1a (1 mmol), photocatalyst Ru(bpy)_3(PF_6)_2 (1 mol %), the system was evacuated 3 times and backfilled with Ar, then solvent 5 ml CH_3CN and triethylamine (4 mmol) were added by syringe. After 3h under 23 w fluorescent light, the reaction mixture was diluted with CH_2Cl_2 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired product. M.p.: 85-86°C. ^1H NMR (400 MHz, CDCl_3): δ 8.12 (s, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.92 (s, 4H), 3.58 (bs, 2H), 3.33 (bs, 2H), 2.31 (s, 3H), 2.30 (s, 3H), 1.24 (bs, 3H), 1.08 (m, 3H); ^13C NMR (100 MHz, CDCl_3): δ 151.7, 142.4, 139.4, 135.3, 134.8, 129.5, 129.1, 127.9, 125.1, 91.8, 21.5, 21.0. IR (film, cm⁻¹): ν 2975, 2930, 2868, 1599 (vs), 1491. HRMS (ESI): Calcd for C_{20}H_{26}O_2NS_2 [MH]^+: m/z 376.1390; found: 376.1395.
6. Copies of $^1$H, $^{13}$C NMR spectra and HRMS spectra

$N, N$-diethyl-3-phenylpropan-1-amine
$N$-cyclohexyl-$N$-propylcyclohexanamine
(E)-N, N-diethyl-2-tosylethenamine
373K(DMSO)
(E)-N, N-diethyl-2-(o-tolylsulfonyl)ethenamine
(E)-N,N-diethyl-2-(m-tolylsulfonyl)ethenamine
(E)-N,N-diethyl-2-(m-tolylsulfonyl)ethenamine
(E)-N,N-diethyl-2-(4-methoxyphenylsulfonyl)ethenamine
(E)-\(N,N\)-diethyl-2-(4-fluorophenylsulfonyl)ethenamine
(E)-2-(4-chlorophenylsulfonyl)-N,N-diethylethenamine
(E)-2-(4-bromophenylsulfonyl)-N,N-diethylethenamine
(E)-N,N-dieethyl-2-(thiophen-2-ylsulfonyl)ethenamine
(E)-N-isopropyl-N-(2-tosylvinyl)propan-2-amine
(E)-N,N-dipropyl-2-tosylprop-1-en-1-amine
2D-NOESY (600 MHz, CDCl$_3$)
(E)-N,N-dibutyl-2-tosylbut-1-en-1-amine
2D-NOESY (600 MHz, CDCl₃)
Ethyl-5-tosyl-1,2,3,4-tetrahydropyridine
(E)-1-(2-tosylvinyl)piperidine
Ethyl-4-tosyl-2,3-dihydro-1H-pyrrole
\((E)-1-(2\text{-}tosylvinyl)\text{pyrrolidine}\)
(E)-N-ethyl-3-phenyl-N-(2-tosylvinyl)propan-1-amine
(E)-N-cyclohexyl-N-(2-tosylprop-1-enyl)cyclohexanamine
(Z)-N,N-diethyl-1-(p-tolylthio)-2-tosylethenamine