Supporting Information

Synergistic Combination of Visible-Light Photo-Catalytic Electron and Energy Transfer Facilitating Multicomponent Synthesis of β-Functionalized α,α-Diarylethylamines

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I. Reaction Optimization

Table S1. Optimization of the Reaction Conditions with Diphenylphosphine Oxide

<table>
<thead>
<tr>
<th>entry</th>
<th>ratio (1a:2a:3a)</th>
<th>PC (mol%)</th>
<th>4 Å MS (mg/mmol)</th>
<th>additive (2.0 eq.)</th>
<th>yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.2:2:1</td>
<td>Ir(mppy)&lt;sub&gt;3&lt;/sub&gt; (2.5 mol%)</td>
<td>50</td>
<td>–</td>
<td>34</td>
</tr>
<tr>
<td>2</td>
<td>1.2:2:1</td>
<td>Ir(ppy)&lt;sub&gt;3&lt;/sub&gt; (2.5 mol%)</td>
<td>50</td>
<td>–</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>1.2:2:1</td>
<td>Ir(dF-ppy)&lt;sub&gt;3&lt;/sub&gt; (2.5 mol%)</td>
<td>50</td>
<td>–</td>
<td>50&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>4</td>
<td>1.2:2:1</td>
<td>Ir(dtbby)(ppy)&lt;sub&gt;2&lt;/sub&gt;PF&lt;sub&gt;6&lt;/sub&gt; (2.5 mol%)</td>
<td>50</td>
<td>–</td>
<td>22</td>
</tr>
<tr>
<td>5</td>
<td>1.2:2:1</td>
<td>Ru(bpy)&lt;sub&gt;3&lt;/sub&gt;(PF&lt;sub&gt;6&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; (2.5 mol%)</td>
<td>50</td>
<td>–</td>
<td>N.D.</td>
</tr>
<tr>
<td>6</td>
<td>1.2:2:1</td>
<td>EosinY (2.5 mol%)</td>
<td>50</td>
<td>–</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>2.0:2:1</td>
<td>Ir(dF-ppy)&lt;sub&gt;3&lt;/sub&gt; (2.5 mol%)</td>
<td>50</td>
<td>–</td>
<td>66</td>
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<tr>
<td>8</td>
<td>2.5:2:1</td>
<td>Ir(dF-ppy)&lt;sub&gt;3&lt;/sub&gt; (2.5 mol%)</td>
<td>50</td>
<td>–</td>
<td>72</td>
</tr>
<tr>
<td>9</td>
<td>2.5:2:1</td>
<td>Ir(dF-ppy)&lt;sub&gt;3&lt;/sub&gt; (1.0 mol%)</td>
<td>50</td>
<td>–</td>
<td>72</td>
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<tr>
<td>10</td>
<td>2.5:2:1</td>
<td>Ir(dF-ppy)&lt;sub&gt;3&lt;/sub&gt; (1.0 mol%)</td>
<td>50</td>
<td>NaHCO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>46</td>
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<tr>
<td>11</td>
<td>2.5:2:1</td>
<td>–</td>
<td>50</td>
<td>–</td>
<td>N.D.</td>
</tr>
<tr>
<td>12&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2.5:2:1</td>
<td>Ir(dF-ppy)&lt;sub&gt;3&lt;/sub&gt; (1.0 mol%)</td>
<td>50</td>
<td>–</td>
<td>N.D.</td>
</tr>
</tbody>
</table>

[a] Conditions: 1a (0.12-0.30 mmol), 3a (0.20 mmol), 5a (0.10 mmol), photocatalyst (1.0-2.5 mol%), white light, THF (1.0 mL), nitrogen, rt, 4Å MS, 24h. [b] All yields were assessed by crude 1H NMR spectroscopy using dibromomethane as an internal standard. [c] 44% of the raw materials 1a are left. [d] No light.
II. Experimental Procedures of Mechanistic Studies

1. Triplet Nitrene Trapping

![Graph showing decomposition of azide 1a over time under different conditions]

Series 1 = "Ir(mppy): and blue light"; Series 2 = "Ir(ppy): and blue light"; Series 3 = "Ir(dtbbpy)(ppy):PF6 and blue light"; Series 4 = "No Ir(III)".

**Figure S1-1-1.** Decomposition of azide 1a over time under different conditions
Figure S1-1-2. $^1$H NMR spectrum of crude reaction mixture and the yield was assessed by crude $^1$H NMR spectroscopy using dibromomethane as an internal standard.
Compound **8a**: HRMS (ESI) ([M+H]^+) Calcd. for C_{25}H_{44}N_{3}O_{2}: 418.3434, found: 418.3434

![HRMS Spectrum](image1)

Compound **8a**: HRMS (ESI) ([M+H]^+) Calcd. for C_{25}H_{44}N_{3}O_{2}: 418.3434, m/z: 418.3434 (100.0%), 419.3467 (27.0%), 420.3501 (3.5%), 419.3404 (1.1%)

![HRMS Spectrum](image2)
Figure S1-1-3. The ESI-HRMS and NMR of compound 8a
9H-carbazole (9k): TLC Rf = 0.5 (EA: PE = 1:10); 16.7 mg/0.2 mmol, 50% yield; white solid, mp 245-246 °C; 1H NMR (400 MHz, CDCl3; δ, ppm) 8.09 (d, J = 7.8 Hz, 3H), 7.43 (d, J = 5.6 Hz, 4H), 7.24 (m, 2H); 13C NMR (101 MHz, CDCl3; δ, ppm) 139.4, 125.8, 123.3, 120.3, 119.4, 110.5; IR (neat): 3404, 2921, 1459, 1333, 1217, 747, 728 cm⁻¹; HRMS (ESI) ([M+H]+) Calcd. for C12H10N: 168.0813, found: 168.0807.
Figure S1-1-4. Spectral Copies of $^1$H,$^{13}$C NMR of Compound 9$k$ Obtained in this Study
1,2-di([1,1'-biphenyl]-2-yl)diazene (10k): TLC R<sub>f</sub> = 0.5 (EA: PE = 1:10); 9.3 mg/0.2 mmol, 14% yield; orange solid, mp 133-134 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>; δ, ppm) 7.57 (d, <i>J</i> = 8.0 Hz, 2H), 7.52-7.34 (m, 16H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>; δ, ppm) 149.8, 141.5, 138.9, 130.9, 130.8, 130.7, 128.0, 127.7, 127.3, 116.3; IR (neat): 3048, 1586, 1470, 768, 732, 723 cm<sup>-1</sup>; HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for C<sub>24</sub>H<sub>19</sub>N<sub>2</sub>: 335.1548, found: 335.1551.
Figure S1-1-5. Spectral Copies of $^1$H, $^{13}$C NMR of Compound 10k Obtained in this Study
1a + 2a + 3a $\xrightarrow{\text{Standard condition}}$ 8a

TEMPO• (3.0 equiv) ESI-HMRS

Eq 5

not observed
2. Radical Clock

\[ \text{1a} + \text{2a} + \text{3j} \xrightarrow{\text{Standard condition}} \text{Ts} \]

(2-tosylcyclobutane-1,1-diyldibenzene (11a): TLC \( R_f = 0.5 \) (EA: PE = 1:5); 8.7 mg/0.2 mmol, 12\% yield; white solid, mp 123-124 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\); \( \delta \), ppm) 7.91 (m, 3H), 7.81 (d, \( J = 8.2 \) Hz, 1H), 7.34 (m, 8H), 7.14 (m, 2H), 6.17-6.10 (m, 1H), 3.42 (t, \( J = 6.7 \) Hz, 2H), 2.65 (dt, \( J = 20.7, 6.9 \) Hz, 2H), 2.44-2.39 (m, 3H); \(^13\)C NMR (101 MHz, CDCl\(_3\); \( \delta \), ppm) 144.8, 144.3, 142.7, 141.1, 140.9, 138.5, 130.6, 130.0, 129.9, 129.6, 128.6, 128.4, 127.9, 127.6, 127.5, 127.4, 127.3, 32.6, 32.3, 21.6; IR (neat): 3058, 2923, 2852, 1593, 1318, 1152, 1104, 758, 699 cm\(^{-1}\); HRMS (ESI) ([M+H]\(^+\)) Calcd. for C\(_{23}\)H\(_{23}\)O\(_2\)S: 363.1419, found: 363.1414.
Figure S1-2 Spectral Copies of $^1$H, $^{13}$C NMR of Compound 11a Obtained in this Study
3. Photocatalyst (Standard Condition) vs TBHP (Condition A) Induced Radical Reactions.

\[ 2a + 3a \rightarrow 12a \]

Standard condition 12% 18% Eq 7
Standard condition, air few 20% Eq 8
Condition A few 64% Eq 9

\[ 1a + 2a + 3a \rightarrow 4a + 12a/13a/14a \]

Standard condition 88% trace Eq 12
Condition A no 39%(13a)Eq 13

\[ 1a + 2a \rightarrow Ts - p-Tolyl \]

Standard condition 48% Eq 10
Condition A no Eq 11

\[ \text{Standard Condition: } \text{Ir(mppy)}_3 \]
(2.5 mol%), DMF (1.0 mL), blue light, N\(_2\), rt, 24h.
Condition A: TBHP (2.0 equiv), CH\(_3\)CN, N\(_2\), 80 °C, 24h

(2-tosylethane-1,1-diyl)dibenzenes (12a): TLC \( R_f = 0.5 \) (EA: PE = 1:5); Colorless solid, mp 121-123°C; \(^1\)H NMR (400 MHz, CDCl\(_3\); \( \delta \), ppm) 7.87 (m, 4H), 7.44 (d, \( J = 8.4 \) Hz, 2H), 7.35-7.32 (m, 4H), 7.30 (s, 1H), 7.26 (s, 1H), 7.24 (s, 1H), 5.56 (s, 1H), 5.50 (s, 1H), 2.41 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\); \( \delta \), ppm) 148.6, 146.3, 144.1, 140.3, 129.9, 128.9, 128.4, 128.2, 128.1, 127.8, 127.5, 116.6, 21.6; IR (neat): 3048, 1586, 1470, 768, 732, 723 cm\(^{-1}\); HRMS (ESI) ([M+H]\(^+\)) Calcd. for C\(_{21}\)H\(_{20}\)O\(_2\)S: 337.1259, found: 337.1257.
Figure S1-3.1. Spectral Copies of $^1$H, $^{13}$C NMR of Compound 12a Obtained in this Study
(2-tosylethene-1,1-diyl)dibenzene (13a): TLC $R_f = 0.5$ (EA: PE = 1:5); white solid, mp 92-93 ºC; 
$^1$H NMR (400 MHz, CDCl$_3$; $\delta$, ppm) 7.47 (d, $J = 8.1$ Hz, 2H), 7.40-7.35 (m, 2H), 7.30 (m, 4H), 7.20 (d, $J = 7.9$ Hz, 2H), 7.15 (d, $J = 8.1$ Hz, 2H), 7.10 (d, $J = 7.7$ Hz, 2H), 6.99 (s, 1H), 2.38 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$; $\delta$, ppm) 154.7, 143.7, 139.2, 135.5, 130.2, 129.7, 129.3, 128.9, 128.8, 128.6, 128.2, 127.8, 127.7, 21.6; IR (neat): 3056, 2917, 2849, 1594, 1568, 1489, 1444, 1314, 1301, 1149, 1137, 1084, 1030; cm$^{-1}$; HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{21}$H$_{21}$O$_2$S: 357.0926, found: 357.0930.
Figure S1-3-2. Spectral Copies of $^1$H, $^{13}$C NMR of Compound 13a Obtained in this Study
4-methyl-N-(p-tolyl)benzenesulfonamide (14a): TLC R_f = 0.5 (EA: PE = 1:10); 25.0 mg/0.2 mmol, 48% yield; white solid, mp 114-116 °C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) 7.62 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 7.9 Hz, 2H), 7.03 (d, J = 7.9 Hz, 2H), 6.94 (d, J = 8.3 Hz, 2H), 6.55 (s, 1H), 2.37 (s, 3H), 2.27 (s, 3H); ¹³C NMR (101 MHz, CDCl₃; δ, ppm) 143.7, 136.1, 135.4, 133.7, 129.8, 129.6, 127.3, 122.4, 21.6, 20.9; IR (neat): 3251, 2923, 2853, 1509, 1331, 1159, 1091, 812, 667, 551 cm⁻¹; HRMS (ESI) ([M+Na]⁺) Calcd. for C₁₄H₁₆NO₂S: 284.0721, found: 284.0723.
Figure S1-3-3. Spectral Copies of $^1$H, $^{13}$C NMR of Compound 14a Obtained in this Study
4. Luminescence Quenching Experiment

The luminescence quenching experiment was taken using a Cary Eclipse fluorescence spectrophotometer (Varian, USA). The emission intensity was collected at 520 nm. The samples were prepared by mixing Ir(mppy)$_3$ (2.5×10$^{-4}$ mol/L) and different amount of quenchers (p-methylphenyl azide 1a and 1,1-diphenylethylene 3a) in DMF (total volume = 1.0 mL) in a light path quartzfluorescence cuvette. The concentration of 1a and 3a stock solution both are 1.0 mol/mL in DMF. For each quenching experiment, different volumes of quenchers (1a and 3a) stock solution was titrated to a mixed solution of Ir(mppy)$_3$ (5, 10, 10, 10, 20, 20, 40, 80×10$^{-3}$ mL, in a total volume = 1.0 mL). Then the emission intensity was collected and the results were presented in Figure S2-1.

![Figure S2-1](image1.png)

**Figure S2-1.** Quenching of Ir(mppy)$_3$ fluorescence emission in the presence of quenchers (p-methylphenyl azide 1a and 1,1-diphenylethylene 3a)
An indeed fluorescence quenching phenomenon of $\text{Ir(mppy)}_3$ under various concentrations of quenchers ($p$-methylphenyl azide $\text{1a}$ and 1,1-diphenylethylene $\text{3a}$) was demonstrated in a curve of $[I_0/I]$ vs $C$, as shown in Figure S2-2 (Stern-Volmer plots).

![Luminescence quenching of $\text{Ir(mppy)}_3$ by quenchers (p-methylphenyl azide $\text{1a}$ and 1,1-diphenylethylene $\text{3a}$)](image)

**Figure S2-2.** Luminescence quenching of $\text{Ir(mppy)}_3$ by quenchers (p-methylphenyl azide $\text{1a}$ and 1,1-diphenylethylene $\text{3a}$)

The luminescence quenching experiment was taken using a Cary Eclipse fluorescence spectrophotometer (Varian, USA). The emission intensity was collected at 520 nm. The samples were prepared by mixing by $\text{Ir(mppy)}_3$ ($2.5 \times 10^{-4}$ mol/L) and different amount of 4-methylenesulfinic acid $\text{2a}$ in DMF (total volume = 1.0 mL) in a light path quartzfluorescence cuvette. The concentration of $\text{2a}$ stock solution are $7.6 \times 10^{-3}$ mol/mL in DMF. For each quenching experiment, different volumes of $\text{2a}$ stock solution was titrated to a mixed solution of $\text{Ir(mppy)}_3$ (5, 5, 5, 5, 5, 5*10$^{-3}$ mL, in a total volume = 1.0 mL). Then the emission intensity was collected and the results were presented in Figure S2-3. An fluorescence quenching phenomenon of $\text{Ir(mppy)}_3$ under various concentrations of $\text{1a}$ was shown in Figure S2-4 (Stern-Volmer plots).
Figure S2-3. Quenching of Ir(mppy)$_3$ fluorescence emission in the presence of 4-methybenzenesulfonic acid 2a

Figure S2-4. Luminescence quenching of Ir(mppy)$_3$ by 4-methybenzenesulfonic acid 2a
III. General Information

Thin layer chromatography (TLC) was performed on pre-coated silica gel GF254 plates. Visualization of TLC was achieved by the use of UV light (254 nm). Column chromatography was performed on silica gel (300-400 mesh) using a proper eluent. $^1$H NMR was recorded on FT AM 400 (400 MHz). Chemical shifts were reported in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane or chloroform-d (CDCl$_3$) at 7.26 ppm. The following abbreviations were used to describe peak splitting patterns: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, m = multiplet. Coupling constants, $J$, were reported in hertz (Hz). The fully decoupled $^{13}$C NMR was recorded on FT AM 400 (100 MHz). Chemical shifts were reported in ppm referenced to the center of a triplet at 77.0 ppm of chloroform-d. Infrared (IR) spectra were recorded neat in KBr cell. Frequencies are given in centimeter inverse (cm$^{-1}$) and only selected absorbance is reported. High resolution mass spectra were obtained by using the UHD Accurate-Mass Q-TOF. Melting points (mp) were determined with a digital electrothermal apparatus without further correction. Stern-Volmer fluorescence quenching experiments were taken at ambient temperature using Edinburgh FS5 spectrofluorometer. The LED strips (2 meter, 12W) were directly got from the supermarket. Wavelength of the blue LEDs is at 470 nm. Unless otherwise mentioned, all commercial reagents and solvents were used without further purification. Various azide$^{[1-4]}$, arylsulfinic acid$^{[5]}$ and 1,1-diarylethylene$^{[6]}$ were prepared according to the literature procedures.
IV. General Procedures for the Preparation of Starting Materials

1. Preparation of Various Azides

1.1. Preparation of $p$-aryl azide, $m$-aryl azide and heteroaryl azide (1a-1h, 1l, 1j, 1n and 1o)$^{[1]}$

In a two-neck round-bottom flask were charged with AcOH (10.0 mL), H$_2$O (10.0 mL) and aniline (10.0 mmol), then the mixture was cooled in an ice-bath. NaNO$_2$ (1.2 eq.) was added slowly below 10°C. The orange solution was left to stir for 1 h at 0°C. Then NaN$_3$ (1.4 eq.) was added (maximum temperature 0°C), the color disappeared and evolution of gases was observed. The reaction was left at 0°C for 10 minutes and then 2h at rt. The solution was diluted with water and CH$_2$Cl$_2$. The phases were separated and the aqueous phase was extracted twice with CH$_2$Cl$_2$ (50 mL). The organic layer was washed with saturated aqueous NaHCO$_3$ (3 x 25 mL), brine (25 mL), treated with anhydrous Na$_2$SO$_4$, filtered and the solvents were concentrated under reduced pressure. Purification by flash column chromatography on silica gel (petroleum ether / ethyl acetate = 1:45) afforded the corresponding product.

1.2. Preparation of $o$-aryl azide (1k-1m and 1p)$^{[2]}$

The corresponding aniline derivative (1.0 eq.) was dissolved in MeCN (0.2 M) and cooled to 0 °C. $t$-Butyl nitrite (4.0 eq.) and trimethylsilyl azide (3.0 eq.) were added slowly and the resulting mixture was warmed to room temperature. After 1 h, the solution was diluted with water and CH$_2$Cl$_2$. The phases were separated and the aqueous phase was extracted twice with CH$_2$Cl$_2$ (50 mL). The organic layer was washed with saturated aqueous NaHCO$_3$ (3 x 25 mL), brine (25 mL), treated with anhydrous Na$_2$SO$_4$, filtered and the solvents were concentrated under reduced pressure. Purification by flash column chromatography on silica gel (petroleum ether / ethyl acetate = 1:45) afforded the corresponding product.
1.3. Preparation of azidocyclohexane (1c')\textsuperscript{[3]}

To a 10 mL reaction tube containing the alcohol (2.0 mmol) in benzene (4 mL) was added trimethylsilyl azide (1.2 eq.), followed by BF\textsubscript{3} · OEt\textsubscript{2} (1.2 eq.). The mixture allowed to stir for 24 h at 23\textdegree C under nitrogen atmosphere. The reaction system was extracted with Et\textsubscript{2}O (3 x 25 mL), washed with water (2 x 25 mL), dried over Na\textsubscript{2}SO\textsubscript{4}, and the organic phase was concentrated under reduced pressure (bath temperature 35 \textdegree C). The residue was purified by flash chromatography (hexane) to afford the white solid (203.8 mg, 58\% yield).

1.4. Preparation of p-tosyl azide (1d')\textsuperscript{[4]}

To a 100 mL flask, a solution of sodium azide (2.86 g, 44 mmol) in water (12 mL) and acetone (20 mL) was rapidly added a solution of p-toluenesulfonyl chloride (1.0 eq.) in acetone (20 mL). The mixture warmed slightly and two phases were formed. After stirring at room temperature for 4 h, acetone was evaporated under reduced pressure (bath temperature 35 \textdegree C), the residue was extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 x 25 mL), washed with water (2 x 25 mL), dried over Na\textsubscript{2}SO\textsubscript{4}, and the organic phase was concentrated under reduced pressure (bath temperature 35 \textdegree C) to give the compound as a colorless oil (7.78 g, 98\% yield).

2. Preparation of sulfinic acids (2a and 2q-2t)\textsuperscript{[5]}

To a 50 mL flask containing Na\textsubscript{2}SO\textsubscript{3} (3.0 eq.) was added, and the solid was completely dissolved in pure water. Then substituted sulfonyl chloride (10.0 mmol) was added into reaction system. The mixture was stirred at 75 \textdegree C for 5 h. Then, this aqueous solution was washed with chloroform twice, acidified with excess concentrated HCl solution, cooled and filtered. The white precipitate was recrystallized from water, affording the substituted sulfinic acids.

3. Preparation of olefins (3u-3z, 3a', 3b' and 3c')\textsuperscript{[6]}

S25
To a solution of carbonyl compounds (0.5 mmol) in THF (3 mL) was added Grignard reagents in THF (0.5 M, 2.2 mL, 2.2 eq.) at room temperature, and the mixture was stirred for 30 min, then the diethyl phosphite (1.2 eq.) was added to this mixture at room temperature. After 5 h, the solution was diluted with water and CH$_2$Cl$_2$. The phases were separated and the aqueous phase was extracted twice with CH$_2$Cl$_2$ (50 mL). The organic layer was washed with saturated aqueous NaHCO$_3$ (3 x 25 mL), brine (25 mL), treated with anhydrous Na$_2$SO$_4$, filtered and the solvents were concentrated under reduced pressure. Purification by flash column chromatography on silica gel (petroleum ether / ethyl acetate = 1:45) afforded the corresponding product.
V. Experimental Procedure for Products 4 and 6

1. Synthesis Procedure of Products 4

\[ \text{Ar-N}_3 + \text{Ar-SO}_2\text{H} \xrightarrow{\text{Blue light}} \text{Ar-SO}_2\text{Ar} \]

Under the protection of \( \text{N}_2 \), corresponding sulfinic acid (0.2 mmol), olefins (2.0 eq.), azide (1.2 eq.), \( \text{Ir(mppy)}_3 \) (2.5 mol\%) and anhydrous \( N,N \)-dimethylformamide (degassed) (2.0 mL) were added to a 10 mL glass vial equipped with a stirring bar. The solution was stirred at a distance of 1.5 cm from a 24 W blue LED lamp at room temperature (a fan was equipped to control the temperature to 28~32 ℃) for 24 hours. The reaction system was extracted with ethyl acetate (3 x 10 mL), washed with \( \text{NaCl} \) aqueous (10 mL), dried over \( \text{Na}_2\text{SO}_4 \), and concentrated the organic layer under reduced pressure. The product was purified by flash chromatography on silicagel using petroleum ether / ethyl acetate (15:1).

2. Spectroscopic Data of Products 4

\( N-(1,1\text{-diphenyl-2-tosylethyl})-4\text{-methylaniline} \) (4a): TLC \( R_f = 0.5 \) (EA: PE = 1:5); 77.6 mg, 88% yield; white solid, mp 165-166 ℃; \( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\); \( \delta \), ppm) 7.38-7.33 (m, 4H), 7.23 (d, \( J = 9.0 \text{ Hz} \), 3H), 7.16 (d, \( J = 6.0 \text{ Hz} \), 5H), 7.01 (d, \( J = 8.1 \text{ Hz} \), 2H), 6.77 (d, \( J = 8.3 \text{ Hz} \), 2H), 6.26 (d, \( J = 8.3 \text{ Hz} \), 2H), 6.01 (s, 1H), 4.29 (s, 2H), 2.34 (s, 3H), 2.16 (s, 3H); \( ^{13}\text{C NMR} \) (101 MHz, CDCl\(_3\); \( \delta \), ppm) 143.8, 142.8, 142.2, 137.8, 129.5, 129.2, 128.4, 128.0, 127.3, 117.6, 64.7, 63.9, 21.5, 20.4; IR (neat): 3390, 3055, 2922, 2864, 1615, 1515, 1316, 1137, 811, 700 cm\(^{-1}\); HRMS (ESI) ([M+H]\(^+\)) Calcd. for \( \text{C}_{28}\text{H}_{28}\text{NO}_2\text{S} \): 442.1840, found: 442.1841.

\( N-(1,1\text{-diphenyl-2-tosylethyl})-4\text{-methoxyaniline} \) (4b): TLC \( R_f = 0.5 \) (EA: PE = 1:3); 76.8 mg, 84% yield; white solid, mp 174-175 ℃; \( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\); \( \delta \), ppm) 7.38-7.33 (m, 4H), 7.23 (d, \( J = 9.0 \text{ Hz} \), 3H), 7.16 (d, \( J = 6.0 \text{ Hz} \), 5H), 7.01 (d, \( J = 8.1 \text{ Hz} \), 2H), 6.77 (d, \( J = 8.3 \text{ Hz} \), 2H), 6.26 (d,
$J = 8.3 \text{ Hz, } 2\text{H}$, $6.01 \text{ (s, } 1\text{H})$, $4.29 \text{ (s, } 2\text{H})$, $2.34 \text{ (s, } 3\text{H})$, $2.16 \text{ (s, } 3\text{H})$; $^{13}\text{C NMR (101 MHz, CDCl}_3; \delta \text{, ppm) } 143.8, 142.8, 142.2, 137.8, 129.5, 129.2, 128.4, 128.0, 127.3, 117.6, 64.7, 63.9, 21.5, 20.4$; IR (neat): 3381, 3059, 2936, 2835, 1600, 1505, 1455, 1317, 743, 701 cm$^{-1}$; HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{28}$H$_{27}$NNaO$_3$S: 480.1610, found: 480.1612.

4-(tert-buty)-N-(1,1-diphenyl-2-tosylethyl)aniline (4c): TLC $R_f = 0.5$ (EA: PE = 1:5); 79.2 mg, 82% yield; white solid, mp 168-169 °C; $^1\text{H NMR (400 MHz, CDCl}_3; \delta \text{, ppm) } 7.39 \text{ (m, } 4\text{H}), 7.23-7.18 \text{ (m, } 5\text{H}), 7.16 \text{ (m, } 3\text{H}), 7.02-6.96 \text{ (m, } 4\text{H}), 6.30 \text{ (d, } J = 8.7 \text{ Hz, } 2\text{H}), 5.91 \text{ (s, } 1\text{H}), 4.37 \text{ (s, } 2\text{H}), 2.33 \text{ (s, } 3\text{H}), 1.21 \text{ (s, } 9\text{H})$; $^{13}\text{C NMR (101 MHz, CDCl}_3; \delta \text{, ppm) } 143.8, 142.8, 141.6, 138.1, 129.4, 128.5, 127.3, 127.2, 127.0, 125.5, 117.1, 64.7, 62.5, 33.8, 31.5, 21.5$; IR (neat): 3387, 3058, 2961, 2865, 1596, 1516, 1316, 1140, 737, 702 cm$^{-1}$; HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{31}$H$_{33}$NNaO$_2$S: 506.2130, found: 506.2131.

N-(1,1-diphenyl-2-tosylethyl)-4-ethylaniline (4d): TLC $R_f = 0.5$ (EA: PE = 1:5); 81.9 mg, 90% yield; white solid, mp 166-167 °C; $^1\text{H NMR (400 MHz, CDCl}_3; \delta \text{, ppm) } 7.39-7.35 \text{ (m, } 4\text{H}), 7.21 \text{ (m, } 3\text{H}), 7.18 \text{ (d, } J = 7.2 \text{ Hz, } 5\text{H}), 7.02 \text{ (d, } J = 8.1 \text{ Hz, } 2\text{H}), 6.80 \text{ (d, } J = 8.3 \text{ Hz, } 2\text{H}), 6.29 \text{ (d, } J = 8.4 \text{ Hz, } 2\text{H}), 5.98 \text{ (s, } 1\text{H}), 4.32 \text{ (s, } 2\text{H}), 2.47 \text{ (q, } J = 7.6 \text{ Hz, } 2\text{H}), 2.34 \text{ (s, } 3\text{H}), 1.13 \text{ (t, } J = 7.6 \text{ Hz, } 3\text{H})$; $^{13}\text{C NMR (101 MHz, CDCl}_3; \delta \text{, ppm) } 143.8, 143.0, 142.5, 129.4, 138.1, 128.4, 128.0, 127.4, 127.3, 127.2, 117.6, 64.7, 63.4, 27.8, 21.5, 15.7$; IR (neat): 3386, 3061, 2918, 2850, 1515, 1447, 1316, 1219, 820, 772 cm$^{-1}$; HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{29}$H$_{29}$NNaO$_2$S: 478.1817, found: 478.1818.
N-(1,1-diphenyl-2-tosylethyl)-4-fluoroaniline (4e): TLC $R_f = 0.5$ (EA: PE = 1:5); 69.4 mg, 78% yield; white solid, mp 183-184 °C; $^1$H NMR (400 MHz, CDCl$_3$; $\delta$, ppm) 7.32-7.30 (m, 4H), 7.24-7.22 (m, 3H), 7.18-7.16 (m, 5H), 7.03 (d, $J = 8.1$ Hz, 2H), 6.67 (m, 2H), 6.32-6.29 (m, 2H), 6.04 (s, 1H), 4.26 (s, 2H), 2.34 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$; $\delta$, ppm) 156.8 (d, $J = 238.4$ Hz), 144.0, 142.0, 141.4, 137.7, 129.5, 128.4, 127.4 (t, $J = 3.0$ Hz), 119.1 (d, $J = 8.1$ Hz), 115.1 (d, $J = 22.2$ Hz), 64.9, 63.7, 21.5; $^{19}$F NMR (376 MHz, CDCl$_3$; $\delta$, ppm) -125.6; IR (neat): 3388, 3060, 3029, 2925, 1597, 1507, 1316, 1138, 761, 701 cm$^{-1}$; HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{27}$H$_{24}$FNNaO$_2$: 468.1410, found: 468.1408.

4-chloro-N-(1,1-diphenyl-2-tosylethyl)aniline (4f): TLC $R_f = 0.5$ (EA: PE = 1:5); 66.4 mg, 72% yield; white solid, mp 177-178 °C; $^1$H NMR (400 MHz, CDCl$_3$; $\delta$, ppm) 7.35-7.30 (m, 4H), 7.24 (s, 2H), 7.18 (d, $J = 3.9$ Hz, 6H), 7.03 (d, $J = 7.9$ Hz, 2H), 6.89 (d, $J = 8.6$ Hz, 2H), 6.29 (s, 1H), 6.24 (d, $J = 8.7$ Hz, 2H), 4.24 (s, 2H), 2.35 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$; $\delta$, ppm) 144.1, 140.9, 131.4, 129.6, 128.5, 127.5, 118.1, 64.82, 64.78, 21.5; IR (neat): 3385, 3059, 3030, 2926, 1597, 1493, 1317, 1138, 817, 703 cm$^{-1}$; HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{27}$H$_{24}$ClNNaO$_2$: 484.1114, found: 484.1124.

4-bromo-N-(1,1-diphenyl-2-tosylethyl)aniline (4g): TLC $R_f = 0.5$ (EA: PE = 1:5); 77.8 mg, 77% yield; white solid, mp 172-173 °C; $^1$H NMR (400 MHz, CDCl$_3$; $\delta$, ppm) 7.32 (m, 4H), 7.24 (s, 2H), 7.21-7.16 (m, 6H), 7.03 (m, 4H), 6.33 (s, 1H), 6.19 (d, $J = 8.8$ Hz, 2H), 4.23 (s, 2H), 2.36 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$; $\delta$, ppm) 144.5, 140.9, 131.4, 129.6, 128.5, 127.5, 127.4, 118.4, 100.0, 65.0, 21.6; IR (neat): 3378, 2925, 2851, 1592, 1489, 1317, 1136, 745, 701 cm$^{-1}$; HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{27}$H$_{24}$BrNNaO$_2$: 528.0609, found: 528.0607.
\[ \text{N}-\text{(1,1-diphenyl-2-tosylethyl)-4-(trifluoromethyl)aniline (4h): } \text{TLC } R_f = 0.5 \text{ (EA: PE = 1:5); 80.2 mg, 81\% yield; white solid, mp 174-175 ^\circ C; } \text{^1H NMR (400 MHz, CDCl}_3; \delta, \text{ ppm) 7.33 (m, 4H), 7.26 (m, 3H), 7.21-7.18 (m, 5H), 7.17 (s, 1H), 7.15 (s, 1H), 7.02 (d, } J = 8.1 \text{ Hz, 2H), 6.69 (s, 1H), 6.32 (d, } J = 8.5 \text{ Hz, 2H), 4.25 (s, 2H), 2.34 (s, 3H); } \text{^13C NMR (101 MHz, CDCl}_3; \delta, \text{ ppm) 148.3, 144.2, 138.7 (d, } J = 318.2 \text{ Hz), 128.6 (t, } J = 97.0 \text{ Hz), 127.4 (d, } J = 2.0 \text{ Hz), 125.8 (q, } J = 3.0 \text{ Hz), 119.6 (d, } J = 32.3 \text{ Hz), 115.4, 65.6, 64.9, 21.5; } \text{^19F NMR (376 MHz, CDCl}_3; \delta, \text{ ppm) -61.2; IR (neat): 3381, 3061, 3033, 2928, 1615, 1526, 1324, 1137, 755, 701 \text{ cm}^{-1}; HRMS (ESI) ([M+H]^+) Calcd. for C\text{\textsubscript{28}H\textsubscript{25}F\textsubscript{3}NO\textsubscript{2}S: 496.1558, found: 496.1560.} \]

\[ \text{N}-\text{(1,1-diphenyl-2-tosylethyl)-3-methylaniline (4i): } \text{TLC } R_f = 0.5 \text{ (EA: PE = 1:5); 64.4 mg, 73\% yield; white solid, mp 154-155 ^\circ C; } \text{^1H NMR (400 MHz, CDCl}_3; \delta, \text{ ppm) 7.36 (m, 4H), 7.26 (s, 1H), 7.24 (s, 1H), 7.20-7.15 (m, 6H), 7.02 (d, } J = 8.1 \text{ Hz, 2H), 6.79 (m, 1H), 6.48 (d, } J = 7.4 \text{ Hz, 1H), 6.28 (s, 1H), 6.12 (s, 1H), 6.01 (d, } J = 8.1 \text{ Hz, 1H), 4.29 (s, 2H), 2.34 (s, 3H), 2.11 (s, 3H); } \text{^13C NMR (101 MHz, CDCl}_3; \delta, \text{ ppm) 145.3, 143.9, 141.9, 138.3, 137.7, 129.5, 128.4, 127.4, 127.3, 119.5, 118.2, 113.9, 64.7, 64.3, 21.5; IR (neat): 3389, 3056, 3033, 2928, 1606, 1490, 1316, 1138, 770, 701 \text{ cm}^{-1}; HRMS (ESI) ([M+Na]^+) Calcd. for C\text{\textsubscript{28}H\textsubscript{27}NNaO\textsubscript{2}S: 464.1660, found: 464.1659.} \]

\[ \text{3-chloro-N-(1,1-diphenyl-2-tosylethyl)aniline (4j): } \text{TLC } R_f = 0.5 \text{ (EA: PE = 1:5); 46.1 mg, 50\% yield; yellow oily liquid; } \text{^1H NMR (400 MHz, CDCl}_3; \delta, \text{ ppm) 7.33 (m, 4H), 7.28 (d, } J = 9.0 \text{ Hz, 2H), 7.19 (m, 6H), 7.03 (d, } J = 8.1 \text{ Hz, 2H), 6.82 (m, 1H), 6.60 (d, } J = 7.2 \text{ Hz, 1H), 6.37 (s, 1H), 6.29 (s, 1H), 6.16 (m, 1H), 4.25 (s, 2H), 2.35 (s, 3H); } \text{^13C NMR (101 MHz, CDCl}_3; \delta, \text{ ppm) 146.7, 144.1, 140.9, 137.3, 134.2, 129.6, 129.5, 128.5, 127.6, 127.5, 118.3, 116.5, 114.7, 65.0, 64.8, 21.5; } \]
IR (neat): 3384, 3059, 3031, 2926, 1596, 1481, 1317, 1138, 739, 701 cm⁻¹; HRMS (ESI) ([M+Na]⁺)
Calcd. for C₂₇H₂₄ClNNaO₂S: 484.1114, found: 484.1111.

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N-(1,1'-diphenyl-2-tosylethyl)-[1,1'-biphenyl]-2-amine (4k): \text{TLC } R_f = 0.5 \text{ (EA: PE = 1:5); 55.3 mg, 55% yield; white solid, mp 188-189 °C; } ^1\text{H NMR (400 MHz, CDCl}_3; \delta, \text{ ppm) 7.67 (d, } J = 7.3 \text{ Hz, 2H}, 7.59 \text{ (m, 2H), 7.47 (d, } J = 7.4 \text{ Hz, 1H), 7.32 (d, } J = 6.7 \text{ Hz, 4H), 7.19-7.11 \text{ (m, 9H), 6.98 (d, } J = 8.1 \text{ Hz, 2H), 6.76-6.64 \text{ (m, 2H), 6.17 (s, 1H), 5.87 (d, } J = 7.8 \text{ Hz, 1H), 4.23 (s, 2H), 2.31 (s, 3H); } ^{13}\text{C NMR (101 MHz, CDCl}_3; \delta, \text{ ppm) 143.8, 142.1, 141.4, 139.7, 137.7, 130.3, 130.0, 129.9, 129.4, 128.9, 128.7, 128.5, 127.6, 127.51, 127.47, 127.32, 127.29, 127.26, 117.4, 114.7, 64.9, 64.5, 21.5; } \text{IR (neat): 3377, 3058, 2926, 1596, 1513, 1319, 1144, 740, 702 cm}^{-1}; \text{ HRMS (ESI) ([M+Na]⁺) Calcd. for C}_{33}\text{H}_{29}\text{BrNNaO}_2\text{S: 526.1817, found: 526.1818.} \]

2-bromo-N-(1,1'-diphenyl-2-tosylethyl)aniline (4l): TLC R_f = 0.5 (EA: PE = 1:5); 56.6 mg, 56% yield; yellow oily liquid; \(^1\text{H NMR (400 MHz, CDCl}_3; \delta, \text{ ppm) 7.44 (d, } J = 1.4 \text{ Hz, 0.5H), 7.42 (d, } J = 1.4 \text{ Hz, 0.5H), 7.35 \text{ (m, 6H), 7.20 \text{ (m, 6H), 7.01 (d, } J = 8.1 \text{ Hz, 2H), 6.82 (s, 1H), 6.64-6.58 \text{ (m, 1H), 6.44 \text{ (m, 1H), 5.77 \text{ (m, 1H), 4.33 \text{ (s, 2H), 2.33 (s, 3H); } ^{13}\text{C NMR (101 MHz, CDCl}_3; \delta, \text{ ppm) 143.9, 142.2, 140.5, 137.2, 132.6, 129.5, 128.5, 127.6, 127.5, 118.3, 115.5, 65.7, 21.5; } \text{IR (neat): 3358, 3060, 3027, 2926, 1595, 1494, 1321, 1139, 743, 701 cm}^{-1}; \text{ HRMS (ESI) ([M+Na]⁺) Calcd. for C}_{27}\text{H}_{23}\text{BrNNaO}_2\text{S: 528.0609, found: 528.0606.} \]

N-(1,1'-diphenyl-2-tosylethyl)-2-methylaniline (4m): TLC R_f = 0.5 (EA: PE = 1:5); 58.2 mg, 66% yield; yellow oily liquid; \(^1\text{H NMR (400 MHz, CDCl}_3; \delta, \text{ ppm) 7.39-7.35 \text{ (m, 4H), 7.25-7.22 \text{ (m, 2H), 7.20-7.14 \text{ (m, 6H), 7.11-7.08 \text{ (m, 1H), 7.03-6.99 \text{ (m, 2H), 6.59-6.52 \text{ (m, 2H), 6.29 (s, 1H),} \]
5.75-5.69 (m, 1H), 4.30 (s, 2H), 2.48 (s, 3H), 2.34 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$; $\delta$, ppm) 143.9, 143.4, 140.9, 137.4, 130.2, 129.5, 128.4, 127.7, 127.5, 127.3, 124.1, 117.3, 114.3, 66.1, 64.7, 21.5, 18.5; IR (neat): 3400, 3058, 2926, 2858, 1591, 1484, 1317, 1136, 747, 701 cm$^{-1}$; HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{28}$H$_{27}$NNaO$_2$: 464.1660, found: 464.1663.

$\text{N-}(1,1$-$\text{diphenyl-2-tosylethyl})\text{aniline (4n)}$: TLC $R_f = 0.5$ (EA: PE = 1:5); 64.9 mg, 76% yield; white solid, mp 168-169 °C; $^1$H NMR (400 MHz, CDCl$_3$; $\delta$, ppm) 7.40-7.33 (m, 4H), 7.23 (d, $J = 6.8$ Hz, 3H), 7.17 (d, $J = 6.6$ Hz, 5H), 7.01 (d, $J = 8.1$ Hz, 2H), 6.95 (m, 2H), 6.66 (m, 1H), 6.34 (d, $J = 7.9$ Hz, 2H), 6.18 (s, 1H), 4.29 (s, 2H), 2.33 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$; $\delta$, ppm) 145.4, 143.9, 141.8, 137.7, 129.5, 128.6, 128.4, 127.4, 127.3, 118.6, 117.1, 64.8, 64.2, 21.5; IR (neat): 3389, 3056, 3028, 2925, 1600, 1496, 1317, 1138, 750, 701 cm$^{-1}$; HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{27}$H$_{25}$NNaO$_2$: 450.1504, found: 450.1508.

$\text{N-}(1,1$-$\text{diphenyl-2-tosylethyl})\text{pyridin-3-amine (4o)}$: TLC $R_f = 0.5$ (EA: PE = 1:5); 30.0 mg, 35% yield; yellow oily liquid; $^1$H NMR (400 MHz, CDCl$_3$; $\delta$, ppm) 7.90 (d, $J = 4.6$ Hz, 1H), 7.86 (d, $J = 2.4$ Hz, 1H), 7.34-7.30 (m, 4H), 7.28 (s, 2H), 7.19 (d, $J = 3.4$ Hz, 6H), 7.04 (d, $J = 8.0$ Hz, 2H), 6.80 (m, 1H), 6.45 (s, 1H), 6.42 (s, 1H), 4.24 (s, 2H), 2.35 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$; $\delta$, ppm) 142.2, 129.6, 128.7, 127.8, 127.5, 123.7, 65.3, 64.9, 21.5; IR (neat): 3371, 3056, 2923, 2850, 1581, 1478, 1316, 1139, 763, 702 cm$^{-1}$; HRMS (ESI) ([M+H]$^+$) Calcd. for C$_{26}$H$_{25}$N$_2$O$_2$: 429.1636, found: 429.1638.
2-(tert-butyl)-N-(1,1,3,3-tetraphenyl-4-tosylbutyl)aniline (4p): TLC $R_f = 0.5$ (EA: PE = 1:5); 62.3 mg, 47% yield; white solid, mp 168-169 °C; $^1$H NMR (400 MHz, CDCl$_3$; δ, ppm) 7.34 (d, $J = 3.7$ Hz, 4H), 7.27 (s, 1H), 7.14 (m, 8H), 7.11 (s, 9H), 7.07-7.02 (m, 3H), 6.42 (s, 1H), 6.31 (d, $J = 8.6$ Hz, 1H), 5.68 (d, $J = 8.7$ Hz, 1H), 4.56 (s, 2H), 4.22 (s, 2H), 2.35 (s, 3H), 1.53 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$; δ, ppm) 144.8, 143.9, 143.3, 140.9, 140.1, 137.4, 143.3, 132.9, 129.5, 129.3, 128.3, 128.2, 127.50, 127.45, 127.37, 127.2, 126.1, 116.9, 67.6, 66.0, 55.9, 34.7, 30.1, 21.6; IR (neat): 3435, 3058, 2960, 2871, 1597, 1494, 1318, 1134, 737, 701 cm$^{-1}$; HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{45}$H$_{45}$NNaO$_2$S: 686.3069, found: 686.3056.

N-(1,1-diphenyl-2-(phenylsulfonyl)ethyl)-4-methylaniline (4q): TLC $R_f = 0.5$ (EA: PE = 1:5); 66.6 mg, 78% yield; white solid, mp 165-166 °C; $^1$H NMR (400 MHz, CDCl$_3$; δ, ppm) 7.42 (m, 1H), 7.34 (d, $J = 7.3$ Hz, 6H), 7.22 (s, 1H), 7.21-7.13 (m, 7H), 6.78 (d, $J = 8.2$ Hz, 2H), 6.28 (d, $J = 8.2$ Hz, 2H), 6.00 (s, 1H), 4.32 (s, 2H), 2.16 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$; δ, ppm) 142.8, 142.2, 140.8, 132.9, 129.2, 128.9, 128.4, 128.2, 127.4, 127.3, 117.8, 64.7, 63.7, 20.4; IR (neat): 3389, 3058, 3024, 2920, 1615, 1514, 1447, 1307, 738, 700 cm$^{-1}$; HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{27}$H$_{25}$NNaO$_2$S: 450.1504, found: 450.1505.

N-(2-((4-chlorophenyl)sulfonyl)-1,1-diphenylethyl)-4-methylaniline (4r): TLC $R_f = 0.5$ (EA: PE = 1:5); 63.6 mg, 69% yield; white solid, mp 175-176 °C; $^1$H NMR (400 MHz, CDCl$_3$; δ, ppm) 7.33 (m, 5H), 7.24 (s, 1H), 7.17 (m, 8H), 6.77 (d, $J = 8.2$ Hz, 2H), 6.25 (d, $J = 8.2$ Hz, 2H), 5.92 (s, 1H), 4.33 (s, 2H), 2.16 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$; δ, ppm) 142.6, 142.1, 139.7, 139.0, 129.3,
129.1, 128.9, 128.5, 128.3, 127.4, 127.3, 127.4, 127.3, 126.5, 117.7, 64.6, 63.8; IR (neat): 3394, 3058, 3024, 2921, 1615, 1582, 1447, 1317, 737, 701 cm⁻¹; HRMS (ESI) ([M+Na]^+) Calcd. for C₂₇H₂₄ClNNaO₂S: 484.1114, found: 484.1113.

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\text{N-}\left(\text{2-}\left(\text{4-bromophenylsulfonyl}\right)\text{-1,1-diphenylethyl}\right)\text{-4-methylaniline (4s)}: \text{TLC } R_f = 0.5 \text{ (EA: PE = 1:5); 70.7 mg, 70\% yield; white solid, mp 172-173 °C; } ^1\text{H NMR (400 MHz, CDCl}_3; \delta, ppm) 7.36-7.30 \text{ (m, 6H), 7.26 \text{ (s, 2H), 7.20-7.16 \text{ (m, 6H), 7.16 \text{ (s, 1H), 6.78 \text{ (d, } J = 8.3 \text{ Hz, 2H), 6.25 \text{ (d, } J = 8.4 \text{ Hz, 2H), 4.33 \text{ (s, 2H), 2.16 \text{ (s, 3H); } } ^{13}\text{C NMR (101 MHz, CDCl}_3; \delta, ppm) 142.6, 142.1, 139.5, 132.1, 131.9, 130.6, 129.8, 129.3, 129.1, 128.9, 128.5, 128.2, 127.9, 127.4, 127.3, 117.7, 64.6, 63.8, 20.4; } \text{IR (neat)}: 3391, 3084, 3022, 2919, 1615, 1514, 1317, 1157, 761, 700 \text{ cm}^{-1}; \text{HRMS (ESI) ([M+Na]^+) Calcd. for C}_{27}\text{H}_{24}\text{BrNNaO}_2\text{S: 528.0609, found: 528.0607.}
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\text{N-}\left(\text{1,1-diphenyl-2-(o-tolylsulfonyl)ethyl}\right)\text{-4-methylaniline (4t): TLC } R_f = 0.5 \text{ (EA: PE = 1:5); 60.9 mg, 69\% yield; yellow oily liquid; } ^1\text{H NMR (400 MHz, CDCl}_3; \delta, ppm) 7.35 \text{ (s, 2H), 7.34-7.32 \text{ (m, 2H), 7.30 \text{ (s, 1H), 7.28 \text{ (m, 1H), 7.18-7.16 \text{ (m, 1H), 7.15 \text{ (s, 2H), 7.13 \text{ (d, } J = 5.7 \text{ Hz, 3H), 7.09 \text{ (d, } J = 7.3 \text{ Hz, 1H), 6.98 \text{ (m, 1H), 6.74 \text{ (d, } J = 8.2 \text{ Hz, 2H), 6.24 \text{ (d, } J = 8.4 \text{ Hz, 2H), 6.08 \text{ (s, 1H), 4.29 \text{ (s, 2H), 2.51 \text{ (s, 2H), 2.13 \text{ (s, 3H); } } ^{13}\text{C NMR (101 MHz, CDCl}_3; \delta, ppm) 142.8, 141.8, 138.6, 136.9, 133.1, 132.2, 129.7, 129.2, 127.9, 127.4, 126.5, 117.4, 64.7, 63.4, 20.4, 20.3; } \text{IR (neat)}: 3391, 3058, 3023, 2921, 1615, 1515, 1310, 1153, 787, 701 \text{ cm}^{-1}; \text{HRMS (ESI) ([M+Na]^+) Calcd. for C}_{28}\text{H}_{27}\text{NNaO}_2\text{S: 464.1660, found: 464.1659.}
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S34
**N-(1,1-bis(4-chlorophenyl)-2-tosylethyl)-4-methylaniline (4u):** TLC Rf = 0.5 (EA: PE = 1:5); 78.4 mg, 77% yield; white solid, mp 168-169 °C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) 7.22 (m, 6H), 7.08 (m, 6H), 6.79 (d, J = 8.2 Hz, 2H), 6.24 (d, J = 8.3 Hz, 2H), 6.04 (s, 1H), 4.16 (s, 2H), 2.40 (s, 3H), 2.16 (s, 3H); ¹³C NMR (101 MHz, CDCl₃; δ, ppm) 144.4, 142.2, 139.9, 137.1, 133.6, 129.6, 129.3, 129.0, 128.5, 127.4, 117.8, 64.5, 64.1, 21.6, 20.4; IR (neat): 3390, 3025, 2921, 2854, 1614, 1515, 1317, 1138, 813, 717 cm⁻¹; HRMS (ESI) ([M+Na⁺]) Calcd. for C₂₈H₂₅Cl₂NO₂S: 532.0881, found: 532.0878.

**N-(1-(4-bromophenyl)-1-(4-chlorophenyl)-2-tosylethyl)-4-methylaniline (4v):** TLC Rf = 0.5 (EA: PE = 1:5); 84.1 mg, 76% yield; white solid, mp 163-164 °C; ¹H NMR (400 MHz, CDCl₃; δ, ppm) 7.23 (m, 6H), 7.17-7.06 (m, 6H), 6.79 (d, J = 8.2 Hz, 2H), 6.24 (d, J = 8.4 Hz, 2H), 6.04 (s, 1H), 4.16 (s, 2H), 2.41 (s, 3H), 2.17 (s, 3H); ¹³C NMR (101 MHz, CDCl₃; δ, ppm) 144.4, 142.1, 140.4, 140.0, 137.1, 133.6, 131.5, 129.6, 129.4, 129.0, 128.59, 128.56, 127.4, 121.9, 117.8, 64.4, 64.2, 21.6, 20.4; IR (neat): 3390, 3025, 2921, 2854, 1614, 1514, 1317, 1138, 812, 758 cm⁻¹; HRMS (ESI) ([M+Na⁺]) Calcd. for C₂₈H₂₂BrClINaO₂S: 576.0376, found: 576.0377.
N-(1-(4-chlorophenyl)-1-(4-fluorophenyl)-2-tosylethyl)-4-methylaniline (4w): TLC Rf = 0.5 (EA: PE = 1:5); 84.8 mg, 86% yield; white solid, mp 171-172 °C; 1H NMR (400 MHz, CDCl3; δ, ppm) 7.28 (m, 3H), 7.23-7.19 (m, 3H), 7.08 (m, 4H), 6.86 (m, 2H), 6.79 (d, J = 8.3 Hz, 2H), 6.24 (d, J = 8.4 Hz, 2H), 6.03 (s, 1H), 4.18 (s, 2H), 2.39 (s, 3H), 2.16 (s, 3H); 13C NMR (101 MHz, CDCl3; δ, ppm) 161.9 (d, J = 248.5 Hz), 144.4, 142.3, 140.0, 137.5 (d, J = 3.0 Hz), 137.3, 133.5, 129.3 (d, J = 9.1 Hz), 128.5, 128.4, 127.4, 117.8, 115.3 (d, J = 21.2 Hz), 64.4 (d, J = 47.0 Hz), 21.5, 20.4; 19F NMR (376 MHz, CDCl3; δ, ppm) -114.52; IR (neat): 3390, 3027, 2921, 2853, 1598, 1510, 1317, 1137, 813, 712 cm⁻¹; HRMS (ESI) ([M+Na⁺]⁺ Calcd. for C29H25ClFNNaO2S: 516.1177, found: 516.1179.

![Chemical Structure](image)

N-(1-(4-bromophenyl)-1-(4-fluorophenyl)-2-tosylethyl)-4-methylaniline (4x): TLC Rf = 0.5 (EA: PE = 1:5); 87.0 mg, 81% yield; white solid, mp 158-159 °C; 1H NMR (400 MHz, CDCl3; δ, ppm) 7.30-7.26 (m, 2H), 7.25-7.20 (m, 4H), 7.16-7.12 (m, 2H), 7.07 (d, J = 8.2 Hz, 2H), 6.89-6.83 (m, 2H), 6.79 (d, J = 8.3 Hz, 2H), 6.24 (d, J = 8.4 Hz, 2H), 6.04 (s, 1H), 4.17 (s, 2H), 2.40 (s, 3H), 2.18 (s, 3H); 13C NMR (101 MHz, CDCl3; δ, ppm) 161.9 (d, JCF = 248.5 Hz), 144.4, 142.2, 140.4, 137.5 (d, JCF = 3.0 Hz), 137.2, 131.3, 129.4 (d, JCF = 9.1 Hz), 128.5, 127.4, 121.8, 117.8, 115.4 (d, JCF = 21.2 Hz), 64.3 (d, JCF = 41.0 Hz), 21.5, 20.4; 19F NMR (376 MHz, CDCl3; δ, ppm) -114.41; IR (neat): 3394, 3022, 2920, 2857, 1599, 1486, 1317, 1137, 814, 757 cm⁻¹; HRMS (ESI) ([M+Na⁺]⁺ Calcd. for C28H23BrFNNaO2S: 560.0671, found: 560.0674.

![Chemical Structure](image)

4-methyl-N-(1-(m-tolyl)-1-(p-tolyl)-2-tosylethyl)aniline (4y): TLC Rf = 0.5 (EA: PE = 1:5); 42.2 mg, 45% yield; white solid, mp 138-139 °C; 1H NMR (400 MHz, CDCl3; δ, ppm) 7.29 (s, 1H), 7.24 (s, 3H), 7.22 (s, 2H), 7.04 (d, J = 8.1 Hz, 2H), 6.98 (d, J = 8.1 Hz, 4H), 6.80 (d, J = 8.3 Hz, 2H), 6.30 (d, J = 8.4 Hz, 2H), 6.05 (s, 1H), 4.27 (s, 2H), 2.39 (s, 3H), 2.29 (s, 6H), 2.19 (s, 3H); 13C NMR (101 MHz, CDCl3; δ, ppm) 143.6, 143.0, 139.3, 137.8, 136.9, 129.8, 129.3, 129.1, 129.0, 128.4, 128.3, 127.7, 127.5, 127.3, 117.5, 64.5, 64.2, 21.5, 20.9, 20.4; IR (neat): 3390, 3024, 2921, 2853,

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\begin{align*}
N\text{-}(1\text{-}(3\text{-chlorophenyl})\text{-}1\text{-}(4\text{-fluorophenyl})\text{-}2\text{-tosylethyl})\text{-}4\text{-methylaniline} (4z): TLC \text{ } R_f = 0.5 \text{ (EA: PE = 1:5); 69.1 mg, 70\% yield; yellow oily liquid; } ^1\text{H NMR} (400 MHz, CDCl$_3$; $\delta$, ppm) 7.29 (m, 4H), 7.24 (s, 1H), 7.18-7.11 (m, 3H), 7.07 (d, $J = 8.1$ Hz, 2H), 6.87 (m, 2H), 6.80 (d, $J = 8.3$ Hz, 2H), 6.25 (d, $J = 8.4$ Hz, 2H), 5.97 (s, 1H), 4.20 (s, 2H), 2.39 (s, 3H), 2.17 (s, 3H); ^{13}\text{C NMR} (101 MHz, CDCl$_3$; $\delta$, ppm) 161.9 (d, $J = 248.5$ Hz), 144.4, 144.1, 142.2, 137.4 (d, $J = 3.0$ Hz), 137.3, 134.4, 129.8, 129.6, 129.3 (d, $J = 8.1$ Hz), 128.7, 127.8, 127.6, 127.4, 125.6, 118.0, 115.4 (d, $J = 21.2$ Hz), 64.3 (d, $J = 41.0$ Hz), 21.5, 20.4; ^{19}\text{F NMR} (376 MHz, CDCl$_3$; $\delta$, ppm) -114.52; IR (neat): 3389, 3024, 2923, 2857, 1596, 1510, 1302, 1139, 813, 759 cm$^{-1}$; HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{28}$H$_{25}$ClFNNaO$_2$S: 516.1177, found: 516.1179.
\end{align*}
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N-((1-(2-chlorophenyl))-1-(4-chlorophenyl))-2-tosylethyl)-4-methylaniline (4a*): TLC R_f = 0.5 (EA: PE = 1:5); 76.4 mg, 75% yield; yellow oily liquid; ^1H NMR (400 MHz, CDCl_3; δ, ppm) 7.93 (s, 1H), 7.30 - 7.14 (m, 3H), 7.06 (m, 4H), 6.90 (d, J = 7.8 Hz, 1H), 6.78 (m, 2H), 6.26 (m, 2H), 6.00 (s, 1H), 4.99 (m, 1H), 4.14 (m, 1H), 2.36 (d, J = 4.1 Hz, 3H), 2.16 (d, J = 5.1 Hz, 3H); ^13C NMR (101 MHz, CDCl_3; δ, ppm) 144.1, 141.5, 137.8, 136.6, 133.6, 133.3, 131.6, 130.9, 130.2, 129.3, 129.1, 128.1, 127.7, 127.0, 120.5, 64.8, 60.0, 21.6, 20.5; IR (neat): 3396, 3005, 2914, 2849, 1513, 1490, 1275, 1141, 765, 750 cm\(^{-1}\); HRMS (ESI) ([M+Na]^+) Calcd. for C_{28}H_{25}Cl_2N_3NaO_2S: 532.0881, 532.0879, found: 307.1812.

4-methyl-N-((1-(naphthalen-1-yl))-1-phenyl)-2-tosylethyl)aniline (4b*): TLC R_f = 0.5 (EA: PE = 1:5); 49.1 mg, 50% yield; white solid, mp 193-194 °C; ^1H NMR (400 MHz, CDCl_3; δ, ppm) 7.78 (s, 1H), 7.72-7.67 (m, 2H), 7.51 (d, J = 8.7 Hz, 1H), 7.44 (m, 2H), 7.41-7.38 (m, 2H), 7.32 (m, 1H), 7.17 (m, 5H), 6.80-6.75 (m, 4H), 6.33 (d, J = 8.3 Hz, 2H), 6.11 (s, 1H), 4.38 (s, 2H), 2.18 (s, 3H), 2.15 (s, 3H); ^13C NMR (101 MHz, CDCl_3; δ, ppm) 143.8, 142.8, 142.4, 139.2, 137.4, 132.8, 132.4, 129.24, 129.20, 128.5, 128.4, 128.1, 127.6, 127.40, 127.35, 127.26, 126.3, 126.1, 125.8, 118.1, 64.8, 63.7, 21.4, 20.4; IR (neat): 3391, 3055, 2922, 2864, 1615, 1515, 1316, 1136, 748, 700 cm\(^{-1}\); HRMS (ESI) ([M+Na]^+) Calcd. for C_{32}H_{29}N_3NaO_2S: 514.1817, found: 514.1821.

3. Substrates Failing to Undergo Efficient Reaction

Azide:

![Azide](image1)

4c* giving 6% yield

Sulfinic acid:

![Sulfinic acid](image2)

4d* N.D.

2e* N.D.

2f* N.D.

4. Synthesis Procedure of Products 6
Under the protection of N₂, corresponding diphenylphosphine oxide (0.2 mmol), olefins (2.0 eq.), azide (2.5 eq.), Ir(df-ppy)₃ (1.0 mol%), 4Å MS (100.0 mg) and anhydrous THF (degassed) (2.0 mL) were added to a 10 mL glass vial equipped with a stirring bar. The solution was stirred at a distance of 1.5 cm from a 24 White LED lamp at room temperature (a fan was equipped to control the temperature to 28~32 ℃) for 24h. The reaction system was concentrated under reduced pressure and the product was purified by flash chromatography on silicagel using petroleum ether / ethyl acetate (9:1).

5. Spectroscopic Data of Products 6

(2,2-diphenyl-2-(p-tolylamino)ethyl)diphenylphosphine oxide (6a): TLC R_f = 0.5 (EA: PE = 1:3); 70.1 mg, 72% yield; white solid, mp 196-197 ℃; ¹H NMR (400 MHz, CDCl₃; δ, ppm) 7.44-7.33 (m, 10H), 7.25 (m, 4H), 7.06 (m, 6H), 6.93 (s, 1H), 6.72 (d, J = 7.5 Hz, 2H), 6.29 (d, J = 7.3 Hz, 2H), 3.43 (d, J = 9.8 Hz, 2H), 2.12 (s, 3H); ¹³C NMR (101 MHz, CDCl₃; δ, ppm) 143.8 (d, J = 23.2 Hz), 134.1, 131.1, 130.4 (d, J = 9.1 Hz), 128.9, 128. (d, J = 12.1 Hz), 128.0 (d, J = 6.1 Hz), 126.9 (d, J = 20.2 Hz), 117.5, 65.5, 41.8 (d, J = 70.7 Hz), 20.4; ³¹P NMR (121.5 MHz, CDCl₃; δ, ppm) 29.29; HRMS (ESI) ([M+H]^+) Calcd. for C₃₃H₃₁NOP: 488.2143, found: 488.2124.

(2,2-bis(4-fluorophenyl)-2-(p-tolylamino)ethyl)diphenylphosphine oxide (6b): TLC R_f = 0.5 (EA: PE = 1:3); 66.9 mg, 64% yield; white solid, mp 237-238 ℃; ¹H NMR (400 MHz, CDCl₃; δ, ppm) 7.45-7.39 (m, 6H), 7.35-7.27 (m, 9H), 6.78-6.71 (m, 6H), 6.27 (d, J = 8.4 Hz, 2H), 3.35 (d, J = 9.9 Hz, 2H), 2.14 (s, 3H); ¹³C NMR (101 MHz, CDCl₃; δ, ppm) 161.6 (d, J = 247.4 Hz), 143.4,
139.1 (d, $J = 3.0$ Hz), 133.2 (d, $J = 101.0$ Hz), 131.3 (d, $J = 3.0$ Hz), 130.3 (d, $J = 9.1$ Hz), 129.8 (d, $J = 8.1$ Hz), 129.0, 128.4 (d, $J = 11.1$ Hz), 127.6, 117.8, 114.7 (d, $J = 21.1$ Hz), 64.8 (d, $J = 4.0$ Hz), 42.6 (d, $J = 68.0$ Hz), 20.4; $^{19}$F NMR (376 MHz, CDCl$_3$; $\delta$, ppm) 115.88; $^{31}$P NMR (121.5 MHz, CDCl$_3$; $\delta$, ppm) 29.08; IR (neat): 3307, 3055, 2922, 2853, 1602, 1507, 1229, 1160, 747, 715 cm$^{-1}$; HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{33}$H$_{28}$F$_2$NNaOP: 546.1775, found: 546.1778.

(2,2-bis(4-chlorophenyl)-2-(p-tolylamino)ethyl)diphenylphosphine oxide (6c): TLC $R_f$ = 0.5 (EA: PE = 1:3); 68.8 mg, 62% yield; white solid, mp 226-227 °C; $^1$H NMR (400 MHz, CDCl$_3$; $\delta$, ppm) 7.45-7.38 (m, 6H), 7.32-7.26 (m, 8H), 7.01 (d, $J = 8.6$ Hz, 4H), 6.93 (s, 1H), 6.75 (d, $J = 8.2$ Hz, 2H), 6.28 (d, $J = 8.4$ Hz, 2H), 3.31 (d, $J = 9.9$ Hz, 2H), 2.14 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$; $\delta$, ppm) 143.2, 141.7 (d, $J = 8.1$ Hz), 141.66, 133.0 (t, $J = 49.5$ Hz), 131.3 (d, $J = 3.0$ Hz), 130.3 (d, $J = 10.1$ Hz), 129.3 (d, $J = 42.4$ Hz), 128.4 (d, $J = 12.1$ Hz), 128.1, 117.8, 64.9, 42.4 (d, $J = 67.7$ Hz), 20.4; $^{31}$P NMR (121.5 MHz, CDCl$_3$; $\delta$, ppm) 29.03; IR (neat): 3320, 3053, 2927, 2859, 1600, 1497, 1275, 1176, 815, 747 cm$^{-1}$; HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{33}$H$_{28}$Cl$_2$NNaOP: 578.1184, found: 578.1185.

(2-(4-bromophenyl)-2-(4-chlorophenyl)-2-(p-tolylamino)ethyl)diphenylphosphine oxide (6d): TLC $R_f$ = 0.5 (EA: PE = 1:3); 80.3 mg, 67% yield; white solid, mp 222-223 °C; $^1$H NMR (400 MHz, CDCl$_3$; $\delta$, ppm) 7.45-7.37 (m, 6H), 7.32-7.27 (m, 6H), 7.22 (d, $J = 8.8$ Hz, 2H), 7.16 (d, $J = 8.7$ Hz, 2H), 7.02 (d, $J = 8.7$ Hz, 2H), 6.93 (s, 1H), 6.75 (d, $J = 8.2$ Hz, 2H), 6.28 (d, $J = 8.4$ Hz, 2H), 3.31 (d, $J = 9.9$ Hz, 2H), 2.14 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$; $\delta$, ppm) 143.2, 142.1 (d, $J = 8.1$ Hz), 141.7 (d, $J = 8.1$ Hz), 133.5 (d, $J = 15.1$ Hz), 132.5 (d, $J = 15$ Hz), 131.3 (q, $J = 2.0$ Hz), 131.0, 130.3 (d, $J = 15$ Hz), 129.5 (t, $J = 40.0$ Hz), 128.4 (d, $J = 12.1$ Hz), 127.9 (d, $J = 42.4$ Hz), 121.3, 117.7, 65.0, 64.9, 42.5 (d, $J = 68.7$ Hz), 20.4; $^{31}$P NMR (121.5 MHz, CDCl$_3$; $\delta$, ppm) 29.01; IR (neat): 3307, 3055, 2922, 2853, 1614, 1512, 1486, 1178, 747, 694 cm$^{-1}$; HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{33}$H$_{28}$BrClNNaOP: 622.0678, found: 622.0680.
(2-(4-chlorophenyl)-2-(4-fluorophenyl)-2-(p-tolylamino)ethyl)diphenylphosphine oxide (6e): TLC $R_f = 0.5$ (EA: PE = 1:3); 70.1 mg, 65% yield; white solid, mp 231-232 °C; $^1$H NMR (400 MHz, CDCl$_3$; $\delta$, ppm) 7.42-7.36 (m, 7H), 7.35-7.25 (m, 8H), 7.02-6.97 (m, 2H), 6.92 (s, 1H), 6.78-6.75 (m, 3H), 6.27 (d, $J = 8.4$ Hz, 2H), 3.33 (m, 2H), 2.14 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$; $\delta$, ppm) 161.7 (d, $J = 247.4$ Hz), 143.4, 141.8 (d, $J = 7.1$ Hz), 139.1 (dd, $J = 6.0$, 3.0 Hz), 133.6 (d, $J = 39.4$ Hz), 132.9, 132.6 (d, $J = 40.4$ Hz), 131.4 (d, $J = 3.0$ Hz), 131.2 (d, $J = 3.0$ Hz), 130.3 (dd, $J = 6.0$, 3.0 Hz), 129.8 (d, $J = 8.1$ Hz), 129.6, 129.1, 128.4 (dd, $J = 7.0$, 5.0 Hz), 128.0, 127.7, 117.8, 114.8 (d, $J = 22.1$ Hz), 64.9 (d, $J = 4.0$ Hz), 42.5 (d, $J = 68.7$ Hz), 20.4; $^{19}$F NMR (376 MHz, CDCl$_3$; $\delta$, ppm) 115.64; $^{31}$P NMR (121.5 MHz, CDCl$_3$; $\delta$, ppm) 29.03; IR (neat): 3310, 3055, 2921, 2855, 1603, 1508, 1437, 1178, 771, 748 cm$^{-1}$; HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{33}$H$_{28}$ClFNaOP: 562.1479, found: 562.1477.

(2-(4-bromophenyl)-2-(4-fluorophenyl)-2-(p-tolylamino)ethyl)diphenylphosphine oxide (6f): TLC $R_f = 0.5$ (EA: PE = 1:3); 82.8 mg, 71% yield; white solid, mp 229-230 °C; $^1$H NMR (400 MHz, CDCl$_3$; $\delta$, ppm) 7.49-7.37 (m, 6H), 7.33 (m, 5H), 7.28 (d, $J = 3.2$ Hz, 1H), 7.24-7.18 (m, 2H), 7.13 (d, $J = 8.7$ Hz, 2H), 6.92 (s, 1H), 6.83-6.71 (m, 4H), 6.27 (d, $J = 8.4$ Hz, 2H), 3.32 (m, 2H), 2.14 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$; $\delta$, ppm) 161.6 (d, $J = 247.4$ Hz), 143.3, 141.8 (d, $J = 7.1$ Hz), 139.1 (dd, $J = 6.0$, 3.0 Hz), 133.6 (d, $J = 54.5$ Hz), 132.6 (d, $J = 55.5$ Hz), 131.4 (d, $J = 3.0$ Hz), 131.2 (d, $J = 3.0$ Hz), 131.1, 130.3 (dd, $J = 5.0$, 4.0 Hz), 129.9, 129.8 (d, $J = 8.1$ Hz), 129.0, 128.4 (dd, $J = 8.0$, 3.0 Hz), 127.7, 121.2, 117.8, 114.8 (d, $J = 21.12$ Hz), 64.9 (d, $J = 4.0$ Hz), 42.4 (d, $J = 68.7$ Hz), 20.4; $^{19}$F NMR (376 MHz, CDCl$_3$; $\delta$, ppm) 115.59; $^{31}$P NMR (121.5 MHz, CDCl$_3$; $\delta$, ppm) 29.03; IR (neat): 3312, 3056, 2921, 2855, 1603, 1485, 1437, 1178, 819, 714 cm$^{-1}$; HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{33}$H$_{28}$BrFNaOP: 606.0974, found: 606.0977.
diphenyl(2-(m-tolyl)-2-(p-tolyl)-2-(p-tolylamino)ethyl)phosphine oxide (6g): TLC Rf = 0.5 (EA: PE = 1:3); 64.9 mg, 63% yield; white solid, mp 205-206 °C; 1H NMR (400 MHz, CDCl3; δ, ppm) 7.69-7.64 (m, 1H), 7.51-7.46 (m, 1H), 7.42-7.39 (m, 2H), 7.38-7.36 (m, 2H), 7.34-7.31 (m, 2H), 7.27 (s, 2H), 7.24-7.21 (m, 4H), 7.13-7.08 (m, 0.80H), 6.97-6.95 (d, J = 8.0 Hz, 0.55H), 6.85 (m, 4H), 6.71 (d, J = 8.3 Hz, 1.5Hz), 6.66 (d, J = 9.3 Hz, 0.20H), 6.60 (d, J = 8.2 Hz, 0.48H), 6.30 (d, J = 8.4 Hz, 1.45H), 3.38-3.34 (m, 2H), 2.35 (s, 0.5H), 2.23 (d, J = 4.7 Hz, 1H), 2.20 (s, 5H), 2.12 (s, 2.5H); 13C NMR (101 MHz, CDCl3; δ, ppm) 144.1, 140.7 (d, J = 8.5 Hz), 136.2, 133.6 (d, J = 10.4 Hz), 131.4 (d, J = 3.0 Hz), 130.9, 130.8 (d, J = 3.0 Hz), 130.4 (d, J = 3.0 Hz), 129.7, 129.0, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 128.2 (d, J = 90.9 Hz), 117.3, 115.3, 65.1 (d, J = 4.0 Hz), 42.9 (d, J = 70.7 Hz), 20.9, 20.4; 31P NMR (121.5 MHz, CDC13; δ, ppm) 29.27; IR (neat): 3307, 3053, 2928, 2851, 1563, 1472, 1397, 1183, 824, 696 cm⁻¹; HRMS (ESI) ([M+Na]+) Calcd. for C38H34NaOP: 538.2276, found: 538.2273.

(2-(3-chlorophenyl)-2-(4-fluorophenyl)-2-(p-tolylamino)ethyl)diphenylphosphine oxide (6h): TLC Rf = 0.5 (EA: PE = 1:3); 57.1 mg, 53% yield; Yellow oily liquid; 1H NMR (400 MHz, CDCl3; δ, ppm) 7.48-7.37 (m, 7H), 7.32 (m, 7H), 7.04 (d, J = 8.0 Hz, 2H), 6.87 (s, 1H), 6.75 (m, 4H), 6.29 (d, J = 8.4 Hz, 2H), 3.34 (d, J = 10.0 Hz, 2H), 2.14 (s, 3H); 13C NMR (101 MHz, CDCl3; δ, ppm) 161.6 (d, J = 248.4 Hz), 146.0 (d, J = 7.1 Hz), 143.3, 138.8 (dd, J = 6.0, 3.0 Hz), 134.0, 133.6 (d, J = 54.5 Hz), 132.6 (d, J = 55.5 Hz), 131.5 (d, J = 3.0 Hz), 131.4 (d, J = 3.0 Hz), 130.3 (q, J = 5.0 Hz), 129.7 (d, J = 8.1 Hz), 129.4, 129.1, 128.4 (d, J = 12.1 Hz), 128.2, 127.8, 127.2, 126.1, 117.9, 114.8 (d, J = 21.2 Hz), 65.0 (d, J = 4.0 Hz), 41.5 (d, J = 69.7 Hz), 20.4; 19F NMR (376 MHz, CDCl3; δ, ppm) 115.71; 31P NMR (121.5 MHz, CDC13; δ, ppm) 28.94; IR (neat): 3311, 3051, 2928, 2853, 1507, 1437, 1220, 1178, 825, 747 cm⁻¹; HRMS (ESI) ([M+H]+) Calcd. for C35H29ClFNOP: 540.1659, found: 540.1661.
diphenyl(2-\(o\)-tolyl)-2-(p-tolyl)-2-(p-tolylamino)ethyl)phosphine oxide (6i): TLC R{sub f} = 0.5 (EA: PE = 1:3); 69.1 mg, 67% yield; Yellow oily liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\); \(\delta\), ppm) 7.55 (d, \(J = 7.4\) Hz, 1H), 7.46-7.26 (m, 9H), 7.21-7.07 (m, 6H), 6.90 (d, \(J = 6.8\) Hz, 1H), 6.77 (d, \(J = 8.2\) Hz, 2H), 6.68 (d, \(J = 8.0\) Hz, 2H), 6.43 (d, \(J = 8.4\) Hz, 2H), 3.54 (m, 1H), 3.27 (m, 1H), 2.15 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\); \(\delta\), ppm) 144.1, 143.4 (d, \(J = 9.1\) Hz), 140.1 (d, \(J = 7.1\) Hz), 138.4, 135.9, 134.7 (d, \(J = 100.0\) Hz), 132.8, 132.5 (d, \(J = 101.0\) Hz), 131.2 (d, \(J = 3.0\) Hz), 130.6 (d, \(J = 9.1\) Hz), 130.3 (d, \(J = 3.0\) Hz), 130.1 (d, \(J = 10.1\) Hz), 129.7, 129.0, 128.8, 128.3 J = 12.1 Hz), 128.0, 127.9, 127.8, 127.7, 127.6, 127.1, 125.3, 120.3, 115.3, 65.8 (d, \(J = 3.0\) Hz), 39.0 (d, \(J = 73.7\) Hz), 21.8, 20.8, 20.5; \(^{31}\)P NMR (121.5 MHz, CDCl\(_3\); \(\delta\), ppm) 29.32; IR (neat): 3322, 3055, 2922, 2855, 1514, 1437, 1186, 1116, 803, 696 cm\(^{-1}\); HRMS (ESI) ([M+Na\(^+\]) Calcd. for C\(_{35}\)H\(_{34}\)N\(_2\)NaOP: 538.2276, found: 538.2279.

(2-(2-chlorophenyl)-2-(4-chlorophenyl)-2-(p-tolylamino)ethyl)diphenylphosphine oxide (6j):

TLC R{sub f} = 0.5 (EA: PE = 1:3); 66.6 mg, 60% yield; Yellow oily liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\); \(\delta\), ppm) 7.90 (d, \(J = 7.7\) Hz, 1H), 7.71-7.63 (m, 2H), 7.50-7.29 (m, 7H), 7.24-7.12 (m, 7H), 6.93 (m, 1H), 6.72 (m, 3H), 6.29 (d, \(J = 8.4\) Hz, 2H), 4.05 (m, 1H), 3.37 (m, 1H), 2.13 (d, \(J = 6.0\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\); \(\delta\), ppm) 142.7, 141.26, 139.23, 133.1 (d, \(J = 18.15\) Hz), 131.6 (d, \(J = 30.0\) Hz), 130.9 (d, \(J = 3.0\) Hz), 130.4 (d, \(J = 10.1\) Hz), 130.1 (d, \(J = 9.1\) Hz), 129.0 (d, \(J = 16.1\) Hz), 128.7 (d, \(J = 12.1\) Hz), 127.9, 127.8 (d, \(J = 4.0\) Hz), 126.6, 119.9, 65.8 (d, \(J = 3.0\) Hz), 20.4; \(^{31}\)P NMR (121.5 MHz, CDCl\(_3\); \(\delta\), ppm) 28.80; IR (neat): 3306, 3051, 2923, 2854, 1511, 1436, 1219, 1116, 772, 749 cm\(^{-1}\); HRMS (ESI) ([M+H\(^+\]) Calcd. for C\(_{35}\)H\(_{29}\)Cl\(_2\)NOP: 556.1364, found: 556.1367.
(2,2-di-o-toly-2-(p-tolylamino)ethyl)diphenylphosphine oxide (6k): TLC Rf = 0.5 (EA: PE = 1:3); 51.5 mg, 50% yield; Yellow oily liquid; 1H NMR (400 MHz, CDCl3; δ, ppm) 7.48 (m, 3H), 7.43-7.39 (m, 4H), 7.22 (d, J = 7.5 Hz, 2H), 7.11-7.03 (m, 8H), 6.95 (m, 2H), 6.68 (d, J = 8.2 Hz, 2H), 6.21 (d, J = 8.4 Hz, 2H), 3.54 (d, J = 10.3 Hz, 2H), 2.10 (s, 3H), 2.05 (s, 6H); 13C NMR (101 MHz, CDCl3; δ, ppm) 144.0, 142.9 (d, J = 7.1 Hz), 141. (d, J = 9.1 Hz), 132.0 (d, J = 36.4 Hz), 131.7 (d, J = 4.1 Hz), 131.4 (d, J = 43.4 Hz), 131.3 (d, J = 3.0 Hz), 128.8, 128.2, 127.9, 126.9, 126.0, 125.4, 125.3, 116.4, 65.8 (d, J = 4.0 Hz), 41.8 (d, J = 67.7 Hz), 21.06, 21.02, 20.3; 31P NMR (121.5 MHz, CDCl3; δ, ppm) 29.39; IR (neat): 3306, 3055, 2923, 2854, 1615, 1515, 1447, 1171, 751, 699 cm⁻¹; HRMS (ESI) ([M+H]+) Calcd. for C35H33NOP: 516.2456, found: 516.2457.
VI. References

VII. Spectral Copies of $^1$H, $^{13}$C NMR of Products 4 and 6

$N$-(1,1-diphenyl-2-tosylethyl)-4-methylaniline (4a)
$N$-$(1,1$-$diphenyl$-2$-tosylethyl)$-4$-methoxyaniline (4b)
4-(tert-butyl)-N-(1,1-diphenyl-2-tosylethyl)aniline (4c)
$N$-(1,1-diphenyl-2-tosylethyl)-4-ethylaniline (4d)
$N$-(1,1-diphenyl-2-tosylethyl)-4-fluoroaniline (4e)
4-chloro-N-(1,1-diphenyl-2-tosylethyl)aniline (4f)
4-bromo-N-(1,1-diphenyl-2-tosylethyl)aniline (4g)
$N$-(1,1-diphenyl-2-tosylethyl)-4-(trifluoromethyl)aniline (4h)
$N$-(1,1-diphenyl-2-tosylethyl)-3-methylaniline (4i)
3-chloro-\(N\)-(1,1-diphenyl-2-tosylethyl)aniline (4j)
$N$-(1,1-diphenyl-2-tosylethyl)-[1,1'-biphenyl]-2-amine (4k)
2-bromo-N-(1,1-diphenyl-2-tosylethyl)aniline (4l)
$N(1,1\text{-diphenyl}-2\text{-tosylethyl})$-2-methylaniline (4m)
*N*(1,1-diphenyl-2-tosylethyl)aniline (4n)
N-(1,1-diphenyl-2-tosylethyl)pyridin-3-amine (4o)
2-(tert-butyl)-N-(1,1,3,3-tetraphenyl-4-tosylbutyl)aniline (4p)
$N$-(1,1-diphenyl-2-(phenylsulfonyl)ethyl)-4-methylaniline (4q)
$N$-(2-((4-chlorophenyl)sulfonyl)-1,1-diphenylethyl)-4-methylaniline (4r)
N-(2-((4-bromophenyl)sulfonyl)-1,1-diphenylethyl)-4-methylaniline (4s)
N-(1,1-diphenyl-2-(o-tolylsulfonyl)ethyl)-4-methylaniline (4t)
$N$-(1,1-bis(4-chlorophenyl)-2-tosylethyl)-4-methylaniline (4u)
$N$-(1-(4-bromophenyl)-1-(4-chlorophenyl)-2-tosylethyl)-4-methylaniline (4v)
N-(1-(4-chlorophenyl)-1-(4-fluorophenyl)-2-tosylethyl)-4-methylaniline (4w)
N-(1-(4-bromophenyl)-1-(4-fluorophenyl)-2-tosylethyl)-4-methylaniline (4x)
4-methyl-N-(1-(m-tolyl)-1-(p-tolyl)-2-tosylethyl)aniline (4y)
N-(1-(3-chlorophenyl)-1-(4-fluorophenyl)-2-tosylethyl)-4-methylaniline (4z)
$N$-(1-(2-chlorophenyl)-1-(4-chlorophenyl)-2-tosylethyl)-4-methylaniline (4a')
4-methyl-N-(1-(naphthalen-1-yl)-1-phenyl-2-tosylethyl)aniline (4b’)

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\text{structure image}
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(2,2-diphenyl-2-(p-tolylamino)ethyl)diphenylphosphine oxide (6a)
(2,2-bis(4-fluorophenyl)-2-(p-tolylamino)ethyl)diphenylphosphine oxide (6b)
(2,2-bis(4-chlorophenyl)-2-(p-tolylamino)ethyl)diphenylphosphine oxide (6c)
(2-(4-bromophenyl)-2-(4-chlorophenyl)-2-(p-tolylamino)ethyl)diphenylphosphine oxide (6d)
(2-(4-chlorophenyl)-2-(4-fluorophenyl)-2-(p-tolylamino)ethyl)diphenylphosphine oxide (6e)
(2-(4-bromophenyl)-2-(4-fluorophenyl)-2-(p-tolylamino)ethyl)diphenylphosphine oxide (6f)
diphenyl(2-(m-tolyl)-2-(p-tolyl)-2-(p-tolylamino)ethyl)phosphine oxide (6g)
(2-(3-chlorophenyl)-2-(4-fluorophenyl)-2-(p-tolylamino)ethyl)diphenylphosphine oxide (6h)
diphenyl(2-(o-tolyl)-2-(p-tolyl)-2-(p-tolylamino)ethyl)phosphine oxide (6i)
(2-(2-chlorophenyl)-2-(4-chlorophenyl)-2-(p-tolylamino)ethyl)diphenylphosphine oxide (6j)
(2,2-di-o-tolyl-2-(p-tolylamino)ethyl)diphenylphosphine oxide (6k)