Supporting Information

Palladium-Catalyzed Primary Amine-Directed Regioselective Mono- and Di-Alkynylation of Biaryl-2-Amines

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A. General Information

All purchased reagents and solvents were used without further purification unless otherwise noted. Melting points were measured with a melting point instrument and were uncorrected. $^1$H and $^{13}$C NMR spectra were recorded using a Bruker DRX-400 spectrometer using CDCl$_3$ or DMSO-$d_6$ as solvent. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. GC-MS was obtained using electron ionization. TLC was performed by using commercially prepared 100-400 mesh silica gel plates and visualization was effected at 254 nm. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker TENSOR 27 spectrometer.
B. Optimization of Reaction Conditions

Table S1. Optimization of Reaction Conditions for Monoalkynylation

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>additive</th>
<th>solvent</th>
<th>yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Cu(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>toluene</td>
<td>n.d.</td>
</tr>
<tr>
<td>2</td>
<td>Pd(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>AgOAc</td>
<td>toluene</td>
<td>76</td>
</tr>
<tr>
<td>3</td>
<td>PdCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>AgOAc</td>
<td>toluene</td>
<td>54</td>
</tr>
<tr>
<td>4</td>
<td>Pd(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>AgOAc</td>
<td>toluene</td>
<td>62</td>
</tr>
<tr>
<td>5</td>
<td>Pd(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>AgOAc</td>
<td>DCE</td>
<td>53</td>
</tr>
<tr>
<td>6</td>
<td>Pd(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>AgOAc</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>AgOAc</td>
<td>toluene</td>
<td>n.d.</td>
</tr>
<tr>
<td>8</td>
<td>Pd(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-</td>
<td>toluene</td>
<td>n.d.</td>
</tr>
<tr>
<td>9&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Pd(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>AgOAc</td>
<td>toluene</td>
<td>84(80)</td>
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<td>10&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Pd(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>AgOAc</td>
<td>toluene</td>
<td>69(63)</td>
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<td>11&lt;sup&gt;e&lt;/sup&gt;</td>
<td>Pd(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>AgOAc</td>
<td>toluene</td>
<td>37(31)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: a mixture of 1a (0.2 mmol), 2a (0.2 mmol), additive (0.4 mmol, 2 equiv), catalyst (0.01 mmol, 5 mol %) and solvent (1.5 mL) was sealed in a 25 mL Schlenk tube at 100 °C for 12 h under N<sub>2</sub>. <sup>b</sup> Determined by GC using dodecane as an internal standard. Numbers in parentheses are yields of isolated products. n.d. = not detected. <sup>c</sup> 1a (0.2 mmol), 2a (0.14 mmol), AgOAc (0.28 mmol, 2 equiv) and catalyst (0.007 mmol, 5 mol %) were used. <sup>d</sup> Using the corresponding alkynyl chloride (2b). <sup>e</sup> Using the corresponding alkynyl iodide (2c).
Table S2. Optimization of Reaction Conditions for Dialkynylation

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>entry</th>
<th>1a (mmol)</th>
<th>2a (mmol)</th>
<th>AgOAc (mmol)</th>
<th>solvent</th>
<th>yieldb (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>0.14</td>
<td>0.56</td>
<td>toluene</td>
<td>&lt; 5</td>
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<tr>
<td>2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.8</td>
<td>toluene</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
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<td>0.25</td>
<td>0.8</td>
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<tr>
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<td>0.3</td>
<td>0.8</td>
<td>toluene</td>
<td>31</td>
</tr>
<tr>
<td>5</td>
<td>0.2</td>
<td>0.35</td>
<td>0.8</td>
<td>toluene</td>
<td>52</td>
</tr>
<tr>
<td>6</td>
<td>0.2</td>
<td>0.4</td>
<td>0.8</td>
<td>toluene</td>
<td>64</td>
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<td>7</td>
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<td>0.45</td>
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<td>72</td>
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<td>8</td>
<td>0.2</td>
<td>0.5</td>
<td>0.8</td>
<td>toluene</td>
<td><strong>82</strong></td>
</tr>
<tr>
<td>9</td>
<td>0.2</td>
<td>0.55</td>
<td>0.8</td>
<td>toluene</td>
<td>81</td>
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</table>

*Reaction conditions: a mixture of 1a (0.2 mmol), 2a (0.14-0.55 mmol), AgOAc (4 equiv), Pd(OAc)$_2$ (5 mol %) and toluene (1.5 mL) were sealed in a 25 mL Schlenk tube at 100 °C for 12 h under N$_2$. bisolated yield.

<table>
<thead>
<tr>
<th>entry</th>
<th>1a (mmol)</th>
<th>2a (mmol)</th>
<th>AgOAc (mmol)</th>
<th>solvent</th>
<th>yieldb (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>0.5</td>
<td>0.4</td>
<td>toluene</td>
<td>&lt; 21</td>
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<tr>
<td>2</td>
<td>0.2</td>
<td>0.5</td>
<td>0.5</td>
<td>toluene</td>
<td>36</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>0.5</td>
<td>0.6</td>
<td>toluene</td>
<td>53</td>
</tr>
<tr>
<td>4</td>
<td>0.2</td>
<td>0.5</td>
<td>0.7</td>
<td>toluene</td>
<td>67</td>
</tr>
<tr>
<td>5</td>
<td><strong>0.2</strong></td>
<td><strong>0.5</strong></td>
<td><strong>0.8</strong></td>
<td>toluene</td>
<td><strong>82</strong></td>
</tr>
<tr>
<td>6</td>
<td>0.2</td>
<td>0.5</td>
<td>0.9</td>
<td>toluene</td>
<td>81</td>
</tr>
</tbody>
</table>

*Reaction conditions: a mixture of 1a (0.2 mmol), 2a (0.5 mmol), AgOAc (2-4.5 equiv), Pd(OAc)$_2$ (5 mol %) and toluene (1.5 mL) were sealed in a 25 mL Schlenk tube at 100 °C for 12 h under N$_2$. bisolated yield.
C. General Procedure for the Synthesis of 3 and 4

1. Monoalkynylation of Biaryl-2-amines

\[
\begin{align*}
\text{Biaryl-2-amines } 1 \text{ (0.2 mmol), (bromoethynyl)triisopropylsilane } 2a \text{ (0.14 mmol), Pd(OAc)}_2 \text{ (0.007 mmol, 5 mol %), AgOAc (0.28 mmol, 2 equiv) and toluene (1.5 mL) were sealed in a Schlenk tube under N}_2 \text{ atmosphere. After this, the mixture was stirred at 100 °C (oil bath temperature) for 12 h. After the reaction was completed (monitored by TLC), the resulting mixture were cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired products } 3 \text{ were obtained in the corresponding yields after purified by column chromatography on silica gel with mixture of petroleum ether and ethyl acetate.}
\end{align*}
\]

2. Dialkynylation of Biaryl-2-amines

\[
\begin{align*}
\text{Biaryl-2-amines } 1 \text{ (0.2 mmol), (bromoethynyl)triisopropylsilane } 2a \text{ (0.5 mmol), Pd(OAc)}_2 \text{ (0.01 mmol, 5 mol %), AgOAc (0.8 mmol, 4 equiv) and toluene (1.5 mL) were sealed in a Schlenk tube under N}_2 \text{ atmosphere. After this, the mixture was stirred at 100 °C (oil bath temperature) for 12 h. After the reaction was completed (monitored by TLC), the resulting mixture were cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired products } 4 \text{ were obtained in the corresponding yields after purified by column chromatography on silica gel with mixture of petroleum ether and ethyl acetate.}
\end{align*}
\]
D. Intermolecular Kinetic Isotope Effect Experiment

[1,1′-biphenyl]-2-amine 1a (0.2 mmol), [1,1′-biphenyl]-2’,3’,4’,5’,6’-d5-2-amine 1a-d5 (0.2 mmol), (bromoethyl)triisopropylsilane 2a (0.14 mmol), Pd(OAc)2 (0.007 mmol, 5 mol %), AgOAc (0.28 mmol, 2 equiv) and toluene (1.5 mL) were sealed in a Schlenk tube under N2 atmosphere. After this, the mixture was stirred at 100 °C (oil bath temperature) for 1.5 h, the resulting mixture were cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. Then the resulting residue was purified by column chromatography on silica gel with petroleum ether/EtOAc (40/1) as eluent to afford a mixture of 3a and 3a-d4 in 25% isolated yield (12.2 mg). The KIE value (K_H/K_D = 2) was determined on the basis of 1H NMR analysis. Data for compounds 3a/3a-d4: 1H NMR (400 MHz, CDCl3) δ 7.61 (d, J = 7.8 Hz, 0.7H), 7.35 (m, J = 14.8, 7.4, 6.0 Hz, 2H), 7.15-7.09 (m, 2H), 6.78 (m, J = 7.6, 0.8 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 3.44 (s, 2H), 0.97 (s, 21H).

2‘-(Triisopropylsilyl)ethynyl-[1,1′-biphenyl]-2-amine 3a (0.2 mmol), 2′-(triisopropylsilyl)ethynyl-[1,1′-biphenyl]-3’,4’,5’,6’-d4-2-amine 3a-d4 (0.2 mmol), (bromoethyl)triisopropylsilane 2a (0.5 mmol), Pd(OAc)2 (0.01 mmol, 5 mol %), AgOAc (0.8 mmol, 4 equiv) and toluene (1.5 mL) were sealed in a Schlenk tube under N2 atmosphere. After this, the mixture was stirred at 100 °C (oil bath temperature) for 1.5 h, the resulting mixture were cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. Then the resulting residue was purified by column chromatography on silica gel with petroleum ether/EtOAc (40/1) as eluent to afford a mixture of 4a and 4a-d3 in 21% isolated yield (15.6 mg). The KIE value (K_H/K_D = 5) was determined on the basis of 1H NMR analysis. Data for compounds 4a/4a-d3: 1H NMR (400 MHz, CDCl3) δ 7.58 (d, J = 7.8 Hz, 1.7H), 7.29 (d, J = 6.5
Hz, 0.8H), 7.08 (m, J = 7.6, 7.2, 2.2 Hz, 2H), 6.76 (t, J = 7.6 Hz, 1H), 6.70 (d, J = 7.8 Hz, 1H), 3.43 (s, 2H), 0.97 (s, 42H).

\[ n(H) = 0.68 \]
\[ n(D) = (1 - 0.68) = 0.32 \]
\[ KIE = n(H)/n(D) = 2 \]
\[ n(H) = 1.67 \]
\[ n(D) = (2 - 1.67) = 0.33 \]
\[ KIE = \frac{n(H)}{n(D)} = 5 \]
E. X-ray Crystallographic Analysis

1. X-ray Crystallographic Analysis for Product 3o

The X-ray crystallographic structures for 3o. ORTEP representation with 50% probability thermal ellipsoids. Solvent and hydrogen are omitted for clarity. Crystal data have been deposited to CCDC, number 1560805.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{33}H_{35}NSi</td>
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<tr>
<td>Formula weight</td>
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<td>Temperature</td>
<td>373(10) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Triclinic, ( P_{\alpha} )</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>( a )</td>
<td>9.0089(6) Å</td>
</tr>
<tr>
<td>( b )</td>
<td>13.9567(6) Å</td>
</tr>
<tr>
<td>( c )</td>
<td>22.3783(10) Å</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>98.702(4) deg.</td>
</tr>
<tr>
<td>( \beta )</td>
<td>99.193(4) deg.</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>99.700(4) deg.</td>
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<tr>
<td>Volume</td>
<td>2691.6(2) Å( ^3 )</td>
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<td>( Z ), Calculated density</td>
<td>4, 1.169 Mg/( m^3 )</td>
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<tr>
<td>Absorption coefficient</td>
<td>0.109 mm(^{-1})</td>
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<tr>
<td>( F(000) )</td>
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<td>Crystal size</td>
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<tr>
<td>Theta range for data collection</td>
<td>3.315 to 29.544 deg.</td>
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</tbody>
</table>
Limiting indices

-11 ≤ h ≤ 12, -17 ≤ k ≤ 17, -28 ≤ l ≤ 30

Reflections collected / unique

25384 / 12544 [R(int) = 0.1029]

Completeness to theta = 25.00

99.8%

Refinement method

Full-matrix least-squares on F^2

Data / restraints / parameters

25385 / 15 / 651

Goodness-of-fit on F^2

1.033

Final R indices [I>2sigma(I)]

R_f = 0.0728, wR_f = 0.1708

R indices (all data)

R_f = 0.1029, wR_f = 0.1909

2. X-ray Crystallographic Analysis for Product 4b

The X-ray crystallographic structures for 4b. ORTEP representation with 50% probability thermal ellipsoids. Solvent and hydrogen are omitted for clarity. Crystal data have been deposited to CCDC, number 1560853.

Empirical formula

C_{40}H_{55}N_{2}Si_{2}

Formula weight

606.03

Temperature

378(10) K

Wavelength

0.71073 Å

Crystal system, space group

Monoclinic, P_1
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
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<tr>
<td>Unit cell dimensions</td>
<td>$a = 15.3730 \text{ (8) } \AA$ $\alpha = 90.000 \text{ (4) }^\circ$, $b = 7.7388 \text{ (4) } \AA$ $\beta = 101.174 \text{ (4) }^\circ$, $c = 32.2857 \text{ (16) } \AA$ $\gamma = 90.000 \text{ (4) }^\circ$.</td>
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<td>Z, Calculated density</td>
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<td>Absorption coefficient</td>
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<td>F(000)</td>
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<td>Crystal size</td>
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<td>Theta range for data collection</td>
<td>3.264 to 24.999 deg.</td>
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<tr>
<td>Limiting indices</td>
<td>$-17 \leq h \leq 18$, $-9 \leq k \leq 8$, $-38 \leq l \leq 38$</td>
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<tr>
<td>Reflections collected / unique</td>
<td>16703 / 6618 [R(int) = 0.1200]</td>
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<tr>
<td>Completeness to theta = 25.00</td>
<td>99.6%</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
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<tr>
<td>Data / restraints / parameters</td>
<td>16703 / 0 / 400</td>
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<td>Goodness-of-fit on F$^2$</td>
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</tr>
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<td>Final R indices [$I&gt;2\sigma(I)$]</td>
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<tr>
<td>R indices (all data)</td>
<td>$R_I = 0.1200$, $wR_2 = 0.2730$</td>
</tr>
</tbody>
</table>
F. Characterization Date for All Products

2′-((Triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3a)

3a as a brown oil (39.1 mg, 80% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 35/1, v/v); 1H NMR (400 MHz, CDCl_3) δ 7.61 (d, J = 7.8 Hz, 1H), 7.40-7.28 (m, 3H), 7.15-7.08 (m, 2H), 6.78 (m, J = 7.4, 3.8 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 3.11 (s, 2H), 0.96 (s, 21H); 13C NMR (100 MHz, CDCl_3) δ 143.6, 142.3, 133.2, 130.6, 130.2, 128.7, 128.6, 127.2, 127.0, 123.3, 118.4, 115.7, 105.4, 94.0, 18.5, 11.2; ν_{max} (KBr)/cm^{-1} 3470, 3059, 2939, 2863, 2154, 1616, 1464, 1263, 752, 666, 454; HRMS (ESI) m/z: calcd for C_{23}H_{32}NSi [M+H]^+ 350.2299; found 350.2304.

2′-((Triisopropylsilyl)ethynyl)-[1,1′-4′,1″-terphenyl]-2-amine (3b)

3b as a brown oil (47.0 mg, 79% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 35/1, v/v); 1H NMR (400 MHz, CDCl_3) δ 7.83 (d, J = 2.0 Hz, 1H), 7.66-7.60 (m, 3H), 7.49-7.37 (m, 4H), 7.14 (dd, J = 12.2, 4.5 Hz, 2H), 6.81 (t, J = 7.8 Hz, 1H), 6.75 (d, J = 7.8 Hz, 1H), 6.70 (d, J = 7.8 Hz, 1H), 3.60 (s, 2H), 0.99 (s, 21H); 13C NMR (100 MHz, CDCl_3) δ 143.8, 141.2, 140.3, 140.1, 140.0, 131.7, 130.6, 128.8, 128.7, 127.6, 127.1, 126.6, 123.7, 118.4, 115.6, 105.4, 94.1, 18.5, 11.2; ν_{max} (KBr)/cm^{-1} 3472, 3306, 3029, 2933, 2863, 2152, 1674, 1546, 1383, 1304, 1257, 748, 667, 458; HRMS (ESI) m/z: calcd for C_{29}H_{36}NSi [M+H]^+ 426.2621; found 426.2618.

4′-Ethyl-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3c)

3c as a brown oil (39.6 mg, 75% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 35/1, v/v); 1H NMR (400 MHz, CDCl_3) δ 7.43 (s, 1H), 7.25-7.19 (m, 2H), 7.10 (dd, J = 11.9, 4.5 Hz, 2H), 6.75 (t, J = 7.4 Hz, 1H), 6.70 (d, J = 7.8 Hz, 1H), 6.63 (d, J = 7.8 Hz, 1H), 6.61 (d, J = 7.8 Hz, 1H), 3.11 (s, 2H), 0.96 (s, 21H); 13C NMR (100 MHz, CDCl_3) δ 143.6, 142.3, 133.2, 130.6, 130.2, 128.7, 128.6, 127.2, 127.0, 123.3, 118.4, 115.7, 105.4, 94.0, 18.5, 11.2; ν_{max} (KBr)/cm^{-1} 3470, 3059, 2939, 2863, 2154, 1616, 1464, 1263, 752, 666, 454; HRMS (ESI) m/z: calcd for C_{23}H_{32}NSi [M+H]^+ 350.2299; found 350.2304.
Hz, 1H), 3.38 (s, 2H), 2.66 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H), 0.96 (s, 21H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.9, 143.3, 139.6, 132.4, 130.7, 130.1, 128.5, 128.4, 127.0, 123.1, 118.3, 115.5, 105.8, 93.3, 28.4, 18.5, 15.4, 11.2; \(\nu_{\text{max}}\) (KBr)/cm\(^{-1}\) 3487, 3396, 2944, 2865, 2152, 1456, 1254, 1178, 980, 916, 881, 670, 459; HRMS (ESI) m/z: calcd for C\(_{25}\)H\(_{36}\)NSi [M+H]\(^+\) 378.2621; found 378.2616.

**4'-Fluoro-2'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (3d)**

\(\text{3d as a brown oil (42.1 mg, 82% yield); } R_f = 0.2\) (petroleum ether/ethyl acetate = 35/1, v/v); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.33-7.27 (m, 2H), 7.10 (m, J = 10.5, 9.9, 7.2 Hz, 3H), 6.77 (t, J = 7.4 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 3.20 (s, 2H), 0.96 (s, 21H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.8, 160.3, 143.8, 138.4, 131.8 (d, J = 8.6 Hz), 130.7, 128.7, 125.9, 125.1 (d, J = 9.6 Hz), 119.5 (d, J = 22.6 Hz), 117.0 (d, J = 227.8 Hz), 116.1 (d, J = 22.0 Hz), 104.2, 95.4, 18.4, 11.1; \(\nu_{\text{max}}\) (KBr)/cm\(^{-1}\) 3475, 3387, 2940, 2863, 2152, 1612, 1470, 1381, 1260, 1151, 999, 957, 751, 667, 460; HRMS (ESI) m/z: calcd for C\(_{23}\)H\(_{31}\)FNSi [M+H]\(^+\) 368.2204; found 368.2210.

**4'-(Trifluoromethyl)-2'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (3e)**

\(\text{3e as a brown oil (49.6 mg, 85% yield); } R_f = 0.3\) (petroleum ether/ethyl acetate = 35/1, v/v); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 (s, 1H), 7.62 (d, J = 8.6 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.16 (t, J = 7.8 Hz, 1H), 7.16 (t, J = 7.8 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 6.80 (t, J = 7.6 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 3.20 (s, 2H), 0.97 (s, 21H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 145.9, 143.5, 130.8, 130.3, 129.9 (q, J = 4.5 Hz), 129.6, 129.2, 127.8, 125.6, 125.1 (q, J = 3.5 Hz), 124.3, 122.4, 117.2 (d, J = 268.6 Hz), 103.8, 96.3, 18.4, 11.1; \(\nu_{\text{max}}\)
HRMS (ESI) m/z: calcd for C_{24}H_{31}F_{3}NSi [M+H]^+ 418.2172; found 418.2177.

1-(2'-Amino-2-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-4-yl)ethan-1-one (3f)

3f as a brown oil (41.6 mg, 76% yield); R_f = 0.2 (petroleum ether/ethyl acetate = 35/1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, J = 1.8 Hz, 1H), 7.94 (dd, J = 8.0, 2.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.14 (m, J = 7.8, 1.5 Hz, 1H), 7.09 (dd, J = 7.6, 1.5 Hz, 1H), 6.79 (m, J = 7.6, 1.0 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 3.42 (s, 2H), 2.64 (s, 3H), 0.97 (s, 21H); ^13C NMR (100 MHz, CDCl_3) δ 197.1, 147.0, 143.4, 136.1, 133.1, 130.6, 130.2, 129.1, 128.2, 125.9, 124.0, 118.5, 115.9, 104.4, 95.5, 26.7, 18.5, 11.1; ν_max (KBr)/cm^{-1} 3473, 3372, 2932, 2863, 2153, 1617, 1459, 1358, 998, 885, 744, 673, 451; HRMS (ESI) m/z: calcd for C_{25}H_{34}NOSi [M+H]^+ 392.2404; found 392.2406.

2'-((Triisopropylsilyl)ethynyl)-4'-vinyl-[1,1'-biphenyl]-2-amine (3g)

3g as a brown oil (43.6 mg, 83% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, J = 1.8 Hz, 1H), 7.43 (dd, J = 8.0, 1.8 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.16-7.06 (m, 2H), 6.74 (m, J = 17.4, 8.6 Hz, 3H), 5.81 (d, J = 17.6 Hz, 1H), 5.31 (d, J = 11.1 Hz, 1H), 3.53 (s, 2H), 0.97 (s, 21H); ^13C NMR (100 MHz, CDCl_3) δ 143.8, 141.6, 136.7, 135.7, 130.9, 130.6, 130.4, 128.6, 126.6, 126.4, 123.5, 118.3, 115.6, 114.7, 105.3, 94.0, 18.5, 11.2; ν_max (KBr)/cm^{-1} 3473, 3385, 2936, 2863, 2150, 1616, 1459, 1382, 1296, 1155, 1069, 992, 749, 669, 458; HRMS (ESI) m/z: calcd for C_{25}H_{34}NSi [M+H]^+ 376.2455; found 376.2452.
3',5'-Dichloro-2'-(triisopropylsilyl)ethynyl]-[1,1'-biphenyl]-2-amine (3h)

3h as a brown oil (44.4 mg, 76% yield); R$_f$ = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 (d, $J$ = 2.2 Hz, 1H), 7.26 (s, 1H), 7.15 (m, $J$ = 8.0, 1.4 Hz, 1H), 7.06 (dd, $J$ = 7.6, 1.3 Hz, 1H), 6.78 (t, $J$ = 7.4 Hz, 1H), 6.73 (d, $J$ = 8.0 Hz, 1H), 3.30 (s, 2H), 0.97 (s, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 145.3, 143.4, 137.8, 134.2, 130.2, 129.3, 128.7, 128.2, 125.2, 122.1, 118.6, 115.9, 102.0, 100.5, 18.4, 11.1; $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3474, 3382, 2939, 2864, 2158, 1673, 1619, 1498, 1429, 1256, 881, 742, 672, 472; HRMS (ESI) m/z: calcd for C$_{23}$H$_{30}$Cl$_2$NSi [M+H]$^+$ 418.1519; found 418.1523.

3',5'-Dimethyl-2'-(triisopropylsilyl)ethynyl]-[1,1'-biphenyl]-2-amine (3i)

3i as a brown oil (41.2 mg, 78% yield); R$_f$ = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.13-7.07 (m, 2H), 7.05 (s, 1H), 6.99 (s, 1H), 6.77 (t, $J$ = 7.4 Hz, 1H), 6.72 (d, $J$ = 8.0 Hz, 1H), 3.35 (s, 2H), 2.51 (s, 3H), 2.35 (s, 3H), 0.97 (s, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.7, 142.5, 141.2, 138.3, 130.4, 129.3, 128.3, 128.1, 127.7, 120.23, 118.3, 115.6, 104.1, 97.5, 21.3, 18.5, 11.2; $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3472, 3382, 2939, 2864, 2158, 1673, 1619, 1498, 1429, 1256, 881, 742, 672, 472; HRMS (ESI) m/z: calcd for C$_{25}$H$_{36}$NSi [M+H]$^+$ 378.2621; found 378.2616.

2'-Methoxy-4'-methyl-6'-(triisopropylsilyl)ethynyl]-[1,1'-biphenyl]-2-amine (3j)

3j as a yellow solid (40.2 mg, 73% yield); mp 82-83 ºC; R$_f$ = 0.2 (petroleum ether/ethyl acetate = 35/1, v/v); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.18 (d, $J$ = 8.4 Hz, 1H), 7.11 (m, $J$ = 7.8, 1.6 Hz, 1H), 7.05 (dd, $J$ = 7.6, 1.5 Hz, 1H), 6.88 (d, $J$ = 8.4 Hz, 1H), 6.79 (m, $J$ = 7.4, 1.0 Hz, 1H), 6.74 (dd, $J$ = 8.0, 0.8 Hz, 1H), 3.72 (s, 3H), 3.51 (s, 2H), 2.46 (s, 3H), 0.95 (s, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 155.2, 144.1, 133.3, 131.0, 130.7,
129.3, 128.4, 125.0, 123.7, 118.5, 115.6, 111.6, 103.8, 98.5, 56.1, 20.6, 18.5, 11.1; $\nu_{\text{max}}$ (KBr)/cm$^{-1}$
3470, 3379, 2941, 2864, 2149, 1677, 1616, 1499, 1384, 1164, 1108, 923, 742, 670, 476; HRMS (ESI) m/z: calcd for C$_{23}$H$_{36}$NO$_2$Si [M+H]$^+$ 394.2561; found 394.2568.

2'-Fluoro-6'-(triisopropylsilyl)ethynyl-[1,1'-biphenyl]-2-amine (3k)

3k as a brown oil (44.7 mg, 87% yield); $R_f = 0.3$ (petroleum ether/ethyl acetate = 35/1, v/v); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 (d, $J = 8.4$ Hz, 1H), 7.27 (m, $J = 5.6$ Hz, 1H), 7.16-7.07 (m, 3H), 6.79 (m, $J = 7.6$, 0.9 Hz, 1H), 6.74 (d, $J = 8.0$ Hz, 1H), 3.38 (s, 2H), 0.94 (s, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.3, 158.9, 144.2, 131.0, 129.4, 129.3, 129.0, 128.9 (d, $J = 2.8$ Hz), 126.1 (d, $J = 4.5$ Hz), 120.0, 117.1 (d, $J = 270.3$ Hz), 116.2 (d, $J = 22.9$ Hz), 104.1 (d, $J = 4.2$ Hz), 95.3, 18.5, 11.1; $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3477, 3390, 3066, 2941, 2864, 2152, 1618, 1564, 1456, 1264, 987, 795, 745, 461; HRMS (ESI) m/z: calcd for C$_{23}$H$_{36}$NO$_2$Si [M+H]$^+$ 368.2204; found 368.2208.

2-(2-((Triisopropylsilyl)ethynyl)naphthalen-1-yl)aniline (3l)

3l as a brown oil (46.4 mg, 83% yield); $R_f = 0.3$ (petroleum ether/ethyl acetate = 35/1, v/v); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (dd, $J = 17.4$, 8.3 Hz, 2H), 7.67 (d, $J = 8.6$ Hz, 1H), 7.57 (d, $J = 8.4$ Hz, 1H), 7.51-7.46 (m, 1H), 7.44-7.38 (m, 1H), 7.23 (m, $J = 8.0$, 1.5 Hz, 1H), 7.12 (dd, $J = 7.6$, 1.4 Hz, 1H), 6.88 (m, $J = 7.4$, 0.8 Hz, 1H), 6.82 (d, $J = 8.0$ Hz, 1H), 3.27 (s, 2H), 1.00 (s, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.3, 140.4, 133.3, 132.1, 131.2, 129.2, 128.8, 128.0, 127.6, 126.8, 126.6, 126.5, 124.5, 121.2, 118.5, 115.6, 106.1, 94.6, 18.5, 11.2; $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3474, 3383, 3057, 2943, 2864, 2147, 1615, 1497, 1458, 1070, 989, 926, 819, 747, 459; HRMS (ESI) m/z: calcd for C$_{27}$H$_{34}$NSi [M+H]$^+$ 400.2455; found 400.2461.
2-(Methoxy-2-((triisopropylsilyl)ethynyl)naphthalen-1-yl)aniline (3m)

3m as a yellow solid (31.8 mg, 53% yield); mp 108-109 °C; R_f = 0.2 (petroleum ether/ethyl acetate = 35/1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 8.05 (s, 1H), 7.72-7.68 (m, 2H), 7.18-7.12 (m, 5H), 6.80 (m, J = 7.4, 0.8 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 3.93 (s, 3H), 3.50 (s, 2H), 0.99 (s, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 158.2, 144.1, 136.5, 133.4, 132.0, 130.9, 129.3, 128.8, 128.7, 128.5, 126.9, 121.9, 119.9, 118.3, 115.54, 105.8, 105.2, 93.9, 55.3, 18.5, 11.2; ν_max (KBr)/cm⁻¹ 3462, 3372, 3056, 2932, 2862, 2146, 1617, 1494, 1457, 881, 807, 748, 671, 463; HRMS (ESI) m/z: calcd for C₂₈H₃₆NOSi [M+H]⁺ 430.2561; found 430.2563.

2-(3-((triisopropylsilyl)ethynyl)benzo[b]thiophen-2-yl)aniline (3n)

3n as a brown oil (28.9 mg, 51% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 35/1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.39 (dd, J = 6.8, 5.6 Hz, 2H), 7.20 (t, J = 7.8 Hz, 1H), 6.79 (dd, J = 17.6, 8.0 Hz, 2H), 3.58 (s, 2H), 1.07 (s, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 145.7, 144.7, 140.2, 138.5, 131.8, 130.1, 125.0, 124.9, 123.1, 122.1, 118.7, 118.2, 116.8, 116.0, 99.7, 97.0, 18.6, 11.3; ν_max (KBr)/cm⁻¹ 3488, 3374, 2944, 2864, 2155, 1702, 1620, 1466, 1368, 1306, 1109, 833, 670; HRMS (ESI) m/z: calcd for C₂₅H₂₅N₃Si [M+H]⁺ 406.2019; found 406.2021.

2-(2-((Triisopropylsilyl)ethynyl)pyren-1-yl)aniline (3o)

3o as a brown solid (47.7 mg, 72% yield); mp 113-114 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 35/1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 8.40 (s, 1H), 8.11 (dd, J = 10.8, 7.6 Hz, 2H), 8.06-8.00 (m, 2H), 7.98-7.93 (m,
2H), 7.76 (d, J = 9.2 Hz, 1H), 7.25 (m, J = 7.8, 1.5 Hz, 1H), 7.21-7.18 (m, 1H), 6.90 (t, J = 7.4 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 3.40 (s, 2H), 1.01 (s, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.5, 136.7, 131.6, 131.4, 131.1, 130.5, 129.8, 128.9, 128.9, 128.1, 128.0, 126.7, 126.4, 125.5, 125.4, 125.3, 124.8, 124.6, 124.5, 121.7, 118.6, 115.6, 106.2, 94.3, 18.6, 11.2; ν$_{\text{max}}$ (KBr)/cm$^{-1}$ 3473, 3382, 3043, 2942, 2863, 2149, 1613, 1500, 1293, 1072, 993, 746, 683, 464; HRMS (ESI) m/z: calcd for C$_{33}$H$_{36}$NSi [M+H]$^+$ 474.2612; found 474.2615.

5'-Chloro-2'-(triisopropylsilyl)ethynyl-[1,1'-biphenyl]-2-amine (3p)

\[ \begin{align*} \text{3p} & \text{ as a brown oil (32.7 mg, 61% yield); } R_f = 0.4 \text{ (petroleum ether/ethyl} \\
& \text{acetate = 35/1, v/v); } ^1H \text{ NMR (400 MHz, CDCl}_3) \delta 7.53 \text{ (d, } J = 8.4 \text{ Hz, 1H),} \\
& 7.35 \text{ (d, } J = 2.2 \text{ Hz, 1H),} 7.29 \text{ (dd, } J = 8.4, 2.2 \text{ Hz, 1H),} 7.13 \text{ (m, } J = 8.0, 1.6 \text{ Hz, 1H),} 7.07 \text{ (dd, } J = 7.6, 1.4 \text{ Hz, 1H),} 6.78 \text{ (m, } J = 7.5, 0.8 \text{ Hz, 1H),} 6.72 \text{ (d, } J = 8.0 \text{ Hz, 1H),} 3.32 \text{ (s, 2H),} 0.96 \text{ (s,} \\
& 22H); ^{13}C \text{ NMR (100 MHz, CDCl}_3) \delta 143.9, 143.6, 134.4, 134.2, 130.4, 130.3, 129.0, 127.5, 125.6, \\
& 121.9, 118.4, 115.8, 104.3, 95.2, 18.5, 11.1; ν_{\text{max}} (KBr)/cm^{-1} 3475, 3386, 3027, 2944, 2864, 2155, \\
& 1616, 1583, 1230, 1206, 1012, 921, 883, 823, 747, 675, 466; \text{ HRMS (ESI) m/z: calcd for} \\
& C_{23}H_{31}NClSi [M+H]^+ 384.1909; \text{ found 384.1915.} \end{align*} \]

4-Methyl-2'-(triisopropylsilyl)ethynyl-[1,1'-biphenyl]-2-amine (3q)

\[ \begin{align*} \text{3q} & \text{ as a brown oil (38.6 mg, 76% yield); } R_f = 0.3 \text{ (petroleum ether/ethyl} \\
& \text{acetate} = 35/1, v/v); ^1H \text{ NMR (400 MHz, CDCl}_3) \delta 7.60 \text{ (dd, } J = 7.6, 0.6 \text{ Hz, 1H),} \\
& 7.39-7.27 \text{ (m, 3H),} 7.00 \text{ (d, } J = 7.6 \text{ Hz, 1H),} 6.61 \text{ (d, } J = 7.8 \text{ Hz, 1H),} 6.56 \text{ (s, 1H),} 3.53 \text{ (s, 2H),} \\
& 2.29 \text{ (s, 3H),} 0.98 \text{ (s, 21H); } ^{13}C \text{ NMR (100 MHz, CDCl}_3) \delta 143.5, 142.4, 138.3, 133.1, 130.4, \\
& 130.2, 128.6, 127.1, 124.3, 123.5, 119.3, 116.3, 105.6, 93.8, 21.2, 18.4, 11.2; ν_{\text{max}} (KBr)/cm^{-1} 3473,
3383, 2941, 2864, 2154, 1618, 1466, 1381, 1300, 1071, 998, 801, 700, 454; HRMS (ESI) m/z: calcd for C_{24}H_{34}NSi [M+H]^+ 364.2455; found 364.2460.

**5-Methyl-2'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (3r)**

![Structural formula of 3r](image)

3r as a brown oil (37.1 mg, 73% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 35/1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 7.58 (t, J = 6.0 Hz, 1H), 7.36-7.23 (m, 3H), 6.91 (t, J = 6.0 Hz, 2H), 6.67-6.57 (m, 1H), 3.18 (s, 2H), 2.21 (s, 3H), 0.96 (s, 21H); ^13C NMR (100 MHz, CDCl_3) δ 142.4, 141.1, 133.1, 131.0, 130.1, 129.1, 128.6, 127.4, 127.1, 123.3, 115.9, 105.6, 93.8, 20.4, 18.5, 11.2; ν_max (KBr)/cm^{-1} 3468, 3380, 2940, 2863, 2154, 1621, 1504, 918, 882, 825, 757, 669, 460; HRMS (ESI) m/z: calcd for C_{24}H_{34}NSi [M+H]^+ 364.2455; found 364.2462.

**Ethyl 2-amino-2'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-4-carboxylate (3s)**

![Structural formula of 3s](image)

3s as a brown oil (48.3 mg, 82% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 20/1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, J = 7.8 Hz, 1H), 7.45 (dd, J = 7.8, 1.6 Hz, 1H), 7.42-7.37 (m, 2H), 7.32 (dd, J = 12.4, 7.5, 1.2 Hz, 2H), 7.16 (d, J = 7.8 Hz, 1H), 4.37 (q, J = 7.2 Hz, 2H), 3.49 (s, 2H), 1.39 (t, J = 7.2 Hz, 3H), 0.94 (s, 21H); ^13C NMR (100 MHz, CDCl_3) δ 166.7, 143.9, 141.3, 133.2, 131.2, 130.7, 130.6, 129.6, 128.8, 127.7, 123.1, 119.3, 116.3, 104.9, 94.6, 60.7, 18.4, 14.3, 11.1; ν_max (KBr)/cm^{-1} 3479, 3380, 2943, 2865, 2154, 1716, 1622, 1466, 1426, 1296, 1233, 1106, 831, 722, 461; HRMS (ESI) m/z: calcd for C_{26}H_{36}NO_2Si [M+H]^+ 422.2510; found 422.2515.

**Ethyl 6-amino-2'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-3-carboxylate (3t)**

![Structural formula of 3t](image)

3t as a brown oil (49.5 mg, 84% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 20/1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 7.86-7.80 (m, 2H), 7.62
(d, $J = 7.6$ Hz, 1H), 7.39 (t, $J = 7.4$ Hz, 1H), 7.32 (dd, $J = 9.0$, 7.8 Hz, 2H), 6.69 (d, $J = 8.4$ Hz, 1H), 4.29 (dd, $J = 7.1$, 4.6 Hz, 2H), 3.98 (s, 2H), 1.33 (t, $J = 7.1$ Hz, 3H), 0.94 (s, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.7, 148.2, 141.0, 133.2, 132.6, 130.1, 128.8, 127.7, 125.5, 123.5, 119.8, 114.3, 105.0, 94.5, 60.2, 18.4, 14.4, 11.1; $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3487, 3374, 2944, 2865, 2155, 1703, 1620, 1465, 1369, 1237, 1151, 1109, 833, 670, 460; HRMS (ESI) m/z: calcd for C$_{26}$H$_{36}$NO$_2$Si [M+H]$^+$ 422.2510; found 422.2513.

5-Fluoro-2'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (3u)

3u as a brown oil (37.5 mg, 73% yield); $R_f = 0.3$ (petroleum ether/ethyl acetate = 35/1, v/v); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62 (dd, $J = 6.6$, 2.4 Hz, 1H), 7.41-7.37 (m, 1H), 7.33 (t, $J = 6.8$ Hz, 2H), 6.86 (m, $J = 11.2$, 4.3 Hz, 2H), 6.66 (dd, $J = 8.3$, 4.8 Hz, 1H), 3.25 (s, 2H), 0.98 (s, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.3, 154.9, 141.1, 139.9, 133.2, 128.8, 128.7 (d, $J = 222.5$ Hz), 127.9 (d, $J = 7.5$ Hz), 123.2, 117.0 (d, $J = 22.5$ Hz), 116.5 (d, $J = 7.7$ Hz), 115.0 (d, $J = 22.2$ Hz), 105.0, 94.5, 18.4, 11.2; $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3469, 3382, 3061, 2942, 2864, 2154, 1614, 1501, 1471, 1264, 1177, 995, 879, 827, 704, 459; HRMS (ESI) m/z: calcd for C$_{23}$H$_{31}$FNSi [M+H]$^+$ 368.2204; found 368.2211.

5-(Trifluoromethyl)-2'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (3v)

3v as a brown oil (37.4 mg, 64% yield); $R_f = 0.3$ (petroleum ether/ethyl acetate = 35/1, v/v); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 (dd, $J = 7.5$, 1.2 Hz, 1H), 7.43-7.29 (m, 5H), 6.75 (d, $J = 8.2$ Hz, 1H), 3.75 (s, 2H), 0.96 (s, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.9, 140.6, 133.3, 128.8 (d, $J = 207$ Hz), 128.9, 127.7 (q, $J = 3.8$ Hz), 126.2, 125.9 (q, $J = 3.7$ Hz), 123.5, 123.4, 120.8, 119.9 (q, $J = 32.4$ Hz), 114.7, 104.7, 94.7, 18.4, 11.1; $\nu_{\text{max}}$
(KBr)/cm⁻¹ 3494, 3401, 2946, 2866, 2156, 1625, 1464, 1332, 1244, 1151, 1115, 880, 760, 670, 459; HRMS (ESI) m/z: calcd for C_{24}H_{31}F_{3}NSi [M+H]⁺ 418.2172; found 418.2177.

3,5-Dichloro-2'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (3w)

3w as a brown oil (40.9 mg, 70% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 7.62 (dd, J = 7.6, 1.4 Hz, 1H), 7.38 (dd, J = 12.8, 7.4, 1.6 Hz, 2H), 7.29-7.25 (m, 2H), 7.01 (d, J = 2.4 Hz, 1H), 3.97 (s, 2H), 0.98 (s, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 140.2, 139.6, 133.2, 129.7, 128.9, 128.8, 128.7, 128.2, 128.1, 123.3, 122.1, 119.7, 104.5, 95.3, 18.4, 11.1; ν_max (KBr)/cm⁻¹ 3489, 3394, 3063, 2944, 2864, 2155, 1612, 1459, 1107, 920, 880, 759, 718, 467; HRMS (ESI) m/z: calcd for C_{23}H_{29}Cl_{2}NSi [M+H]⁺ 418.1519; found 418.1523.

2',6'-Bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (4a)

4a as a brown oil (86.7 mg, 82% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, J = 7.8 Hz, 2H), 7.24 (d, J = 6.4 Hz, 1H), 7.06-6.99 (m, 2H), 6.71 (t, J = 7.4 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 3.42 (s, 2H), 0.93 (s, 42H); ¹³C NMR (100 MHz, CDCl₃) δ 144.9, 143.7, 132.8, 130.3, 128.6, 127.1, 125.8, 124.5, 118.5, 115.7, 104.8, 94.4, 18.5, 11.1; ν_max (KBr)/cm⁻¹ 3478, 3390, 2942, 2864, 2151, 1617, 1458, 1069, 978, 922, 881, 744, 709, 671, 459; HRMS (ESI) m/z: calcd for C_{34}H_{52}NSi₂ [M+H]⁺ 530.3633; found 530.3639.

2',6'-Bis((triisopropylsilyl)ethynyl)-[1,1':4',1''-terphenyl]-2-amine (4b)

4b as a yellow solid (89.5 mg, 74% yield); mp 128-129 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 7.75 (s, 2H), 7.64-7.61 (m, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.39 (dd, J = 8.3,
6.3 Hz, 1H), 7.07 (dd, J = 10.2, 4.1 Hz, 2H), 6.77-6.73 (m, 1H), 6.69 (dd, J = 8.4, 0.8 Hz, 1H), 3.45 (s, 2H), 0.95 (s, 51H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.8, 143.7, 140.5, 139.5, 131.5, 130.4, 128.9, 128.6, 127.8, 127.1, 125.5, 124.9, 118.5, 115.8, 104.9, 94.5, 18.5, 11.2; \(\nu_{max}\) (KBr)/cm\(^{-1}\) 3479, 3389, 3029, 2941, 2863, 2152, 1615, 1501, 1460, 1251, 1070, 1003, 920, 745, 672, 461; HRMS (ESI) m/z: calcd for C\(_{40}\)H\(_{56}\)NSi\(_2\) [M+H\(^+\)] 606.3946; found 606.3950.

4'-Ethyl-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (4c)

4c as a brown oil (88.1 mg, 79% yield); \(R_f\) = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.38 (s, 2H), 7.05-6.99 (m, 2H), 6.71 (t, \(J = 7.2\) Hz, 1H), 6.65 (d, \(J = 8.0\) Hz, 1H), 3.17 (s, 2H), 2.63 (t, \(J = 7.6\) Hz, 2H), 1.28 (t, \(J = 7.6\) Hz, 3H), 0.94 (s, 42H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.9, 143.2, 142.3, 132.4, 130.5, 128.4, 125.8, 124.2, 118.5, 115.7, 105.2, 93.7, 28.2, 18.5, 15.3, 11.2; \(\nu_{max}\) (KBr)/cm\(^{-1}\) 3478, 3389, 2940, 2864, 2153, 1616, 1501, 1461, 1068, 997, 881, 743, 718, 458; HRMS (ESI) m/z: calcd for C\(_{36}\)H\(_{56}\)NSi\(_2\) [M+H\(^+\)] 558.4102; found 558.3952.

4'-Isopropyl-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (4d)

4d as a brown oil (82.2 mg, 72% yield); \(R_f\) = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.39 (s, 2H), 7.05-7.00 (m, 2H), 6.71 (t, \(J = 7.2\) Hz, 1H), 6.66 (d, \(J = 7.8\) Hz, 1H), 3.17 (s, 2H), 1.29 (d, \(J = 6.8\) Hz, 6H), 1.06 (d, \(J = 5.6\) Hz, 1H), 0.93 (s, 42H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 147.8, 143.8, 142.5, 131.1, 130.5, 128.4, 125.9, 124.2, 118.5, 115.7, 105.3, 93.7, 33.7, 23.7, 18.5, 11.2; \(\nu_{max}\) (KBr)/cm\(^{-1}\) 3477, 3389, 2949, 2865, 2151, 1616, 1502, 1461, 1298, 1073, 1000, 882, 744, 672, 461; HRMS (ESI) m/z: calcd for C\(_{37}\)H\(_{58}\)NSi\(_2\) [M+H\(^+\)] 572.4102; found 572.4104.

4'-Methoxy-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (4e)
4e as a brown solid (63.7 mg, 57% yield); mp 83-84 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 20/1, v/v); ^1H NMR (400 MHz, CDCl_3)  δ 7.08 (s, 2H), 7.04-6.99 (m, 2H), 6.71-6.67 (m, 1H), 6.64 (d, J = 8.0 Hz, 1H), 3.84 (s, 3H), 3.31 (s, 2H), 0.93 (s, 42H); ^13C NMR (100 MHz, CDCl_3) δ 158.1, 144.1, 137.6, 130.8, 128.4, 125.5, 125.3, 118.5, 118.4, 115.6, 104.8, 94.2, 55.6, 18.5, 11.1; ν_{max}(KBr)/cm\(^{-1}\) 3476, 3387, 2941, 2863, 2150, 1615, 1501, 1461, 1194, 1153, 1061, 1003, 921, 743, 671, 463; HRMS (ESI) m/z: calcd for C_{35}H_{54}NSi_2 [M+H]^+ 560.3738; found 560.3743.

4'-Fluoro-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (4f)

4f as a brown oil (72.2 mg, 66% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 35/1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 7.29 (d, J = 2.6 Hz, 2H), 7.10-7.05 (m, 1H), 7.02 (d, J = 7.6 Hz, 1H), 6.74 (t, J = 7.4 Hz, 1H), 6.68 (d, J = 8.0 Hz, 1H), 3.42 (s, 2H), 0.96 (s, 42H); ^13C NMR (100 MHz, CDCl_3) δ 162.2, 159.7, 143.9, 141.1, 130.5, 128.8, 126.1 (d, J = 10.2 Hz), 124.8, 119.6 (d, J = 22.5 Hz), 117.1 (d, J = 279.1 Hz), 103.7 (d, J = 3.1 Hz), 95.8, 18.4, 17.7, 11.1; ν_{max}(KBr)/cm\(^{-1}\) 3478, 3392, 2942, 2864, 2159, 1617, 1579, 1312, 1131, 1070, 1000, 744, 670, 460; HRMS (ESI) m/z: calcd for C_{34}H_{51}FNSi_2 [M+H]^+ 548.3539; found 548.3533.

4'-(Trifluoromethyl)-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (4g)

4g as a brown oil (95.5 mg, 80% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 7.74 (s, 2H), 7.10-7.05 (m, 1H), 6.99 (dd, J = 7.6, 1.3 Hz, 1H), 6.74 (t, J = 7.4 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 2.87 (s, 2H), 0.94 (s, 42H); ^13C NMR (100 MHz, CDCl_3) δ 148.2, 143.5, 130.0 (q, J = 32.9 Hz), 129.9, 129.0, 129.0 (q, J = 3.7 Hz), 125.5, 124.6, 123.4 (q, J = 271.0 Hz), 118.6,
115.9, 103.3, 96.7, 18.4, 11.1; \nu_{\text{max}} (\text{KBr})/\text{cm}^{-1} 3479, 3392, 2946, 2865, 2155, 1618, 1502, 1462, 1233, 1169, 1136, 889, 739, 672, 464; HRMS (ESI) m/z: calcd for C_{35}H_{51}F_3NSi_2 [M+H]^+ 598.3507; found 598.3515.

1-(2'-Amino-2,6-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-4-yl)ethan-1-one (4h)

4h as a yellow solid (87.9 mg, 77% yield); mp 99-100 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 15/1, v/v); \(^1\)H NMR (400 MHz, CDCl_3) \(\delta\) 8.07 (s, 3H), 7.06 (dd, \(J = 10.9, 4.5\) Hz, 1H), 7.00 (dd, \(J = 7.6, 1.3\) Hz, 1H), 6.73 (t, \(J = 7.6\) Hz, 1H), 6.67 (d, \(J = 8.0\) Hz, 1H), 3.25 (s, 2H), 2.64 (s, 3H), 0.94 (s, 42H); \(^{13}\)C NMR (100 MHz, CDCl_3) \(\delta\) 196.7, 149.3, 143.4, 136.1, 132.2, 129.9, 129.0, 125.2, 124.9, 118.6, 115.9, 103.85, 95.9, 26.7, 18.5, 11.1; \nu_{\text{max}} (\text{KBr})/\text{cm}^{-1} 3475, 3381, 2939, 2864, 2152, 1691, 1619, 1461, 1306, 1070, 1006, 884, 744, 714, 672, 464; HRMS (ESI) m/z: calcd for C_{36}H_{54}NOSi_2 [M+H]^+ 572.3788; found 572.3741.

2',6'-Bis((triisopropylsilyl)ethynyl)-4'-vinyl-[1,1'-biphenyl]-2-amine (4i)

4i as a brown oil (93.2 mg, 84% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); \(^1\)H NMR (400 MHz, CDCl_3) \(\delta\) 7.57 (s, 2H), 7.06-7.00 (m, 2H), 6.74-6.64 (m, 3H), 5.82 (d, \(J = 17.6\) Hz, 1H), 5.33 (d, \(J = 10.8\) Hz, 1H), 3.43 (s, 2H), 0.94 (s, 42H); \(^{13}\)C NMR (100 MHz, CDCl_3) \(\delta\) 143.1, 142.8, 135.8, 134.1, 129.4, 129.3, 127.6, 124.5, 123.7, 117.4, 114.7, 114.4, 103.8, 93.3, 17.5, 10.1; \nu_{\text{max}} (\text{KBr})/\text{cm}^{-1} 3477, 3389, 2943, 2864, 2152, 1616, 1500, 1461, 1298, 1068, 916, 802, 671, 460; HRMS (ESI) m/z: calcd for C_{36}H_{54}NSi_2 [M+H]^+ 556.3789; found 556.3794.

3',5'-Dichloro-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (4j)

S24
4j as a brown solid (85.9 mg, 72% yield); mp 103-104 °C; Rf = 0.5 (petroleum ether/ethyl acetate = 35/1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 7.51 (s, 1H), 7.08-7.04 (m, 1H), 6.98 (dd, J = 7.6, 1.4 Hz, 1H), 6.73 (t, J = 7.2 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 2.91 (s, 2H), 0.94 (s, 42H); ¹³C NMR (100 MHz, CDCl₃) δ 147.9, 143.3, 136.6, 129.9, 129.1, 128.8, 125.1, 123.0, 123.0, 118.8, 116.0, 102.1, 100.2, 18.4, 11.1; v_max (KBr)/cm⁻¹ 3463, 3383, 2940, 2862, 2160, 1618, 1497, 1459, 1148, 1067, 919, 790, 751, 672, 470; HRMS (ESI) m/z: calcd for C₃₄H₅₀Cl₂NSi₂ [M+H]+ 530.3633; found 530.3639.

3',5'-Dimethyl-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (4k)

4k as a brown solid (76.9 mg, 69% yield); mp 137-138 °C; Rf = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 7.09 (s, 3H), 7.09 (s, 1H), 7.04-6.99 (m, 2H), 6.71 (t, J = 7.4 Hz, 1H), 6.76-6.61 (m, 2H), 6.66 (d, J = 8.0 Hz, 1H), 2.87 (s, 2H), 2.47 (s, 6H), 0.93 (s, 42H); ¹³C NMR (100 MHz, CDCl₃) δ 145.1, 143.5, 141.0, 130.3, 129.8, 128.3, 127.0, 121.6, 118.6, 115.8, 103.6, 97.9, 21.4, 18.5, 11.2; v_max (KBr)/cm⁻¹ 3374, 2940, 2864, 2150, 1615, 1459, 1378, 1074, 995, 883, 743, 672, 603, 463; HRMS (ESI) m/z: calcd for C₃₆H₅₆NSi₂ [M+H]+ 558.3946; found 558.3940.

3'-Chloro-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (4l)

4l as a yellow solid (38.3 mg, 34% yield); mp 79-80 °C; Rf = 0.5 (petroleum ether/ethyl acetate = 35/1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, J = 8.4 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.07 (m, 1H), 6.99 (dd, J = 7.6, 1.3 Hz, 1H), 6.72 (t, J = 7.6 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 2.80 (s, 2H), 0.93 (d, J = 9.4 Hz, 42H); ¹³C NMR (100 MHz, CDCl₃) δ 146.7, 143.5, 136.9, 132.8, 130.1, 128.9, 128.2, 125.4, 124.4, 122.9, 118.6, 115.9, 103.9, 101.3, 101.0, 95.4, 18.5, 11.1; v_max (KBr)/cm⁻¹ 3479,
HRMS (ESI) m/z: calcd for C$_{34}$H$_{51}$ClNSi$_2$ [M+H]$^+$ 564.3243; found 564.3239.

2-(6-Methoxy-1,3-bis((triisopropylsilyl)ethynyl)naphthalen-2-yl)aniline (4m)

4m as a brown solid (57.2 mg, 47% yield); mp 111-112 °C; R$_f$ = 0.3 (petroleum ether/ethyl acetate = 20/1, v/v); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$

8.30 (d, $J$ = 9.2 Hz, 1H), 7.99 (s, 1H), 7.25-7.21 (m, 1H), 7.11-7.04 (m, 3H), 6.74 (t, $J$ = 7.4 Hz, 1H), 6.68 (d, $J$ = 8.0 Hz, 1H), 3.93 (s, 3H), 3.43 (s, 2H), 0.99 (s, 21H), 0.95 (s, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.4, 144.0, 140.5, 133.4, 132.0, 130.7, 128.9, 128.5, 128.2, 126.3, 122.4, 121.5, 120.3, 118.5, 115.7, 105.7, 105.3, 102.8, 99.9, 94.1, 55.4, 18.6, 18.5, 11.2, 11.2; $\nu_{max}$ (KBr)/cm$^{-1}$ 376, 3383, 2939, 2864, 2150, 1686, 1496, 1459, 1230, 1164, 1000, 882, 822, 671, 462; HRMS (ESI) m/z: calcd for C$_{39}$H$_{56}$NOSi$_2$ [M+H]$^+$ 610.3895; found 610.3890.

5-Chloro-3-fluoro-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (4n)

4n as a brown oil (87.2 mg, 75% yield); R$_f$ = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 (d, $J$ = 7.8 Hz, 2H), 7.30 (t, $J$ = 7.8 Hz, 1H), 6.96 (dd, $J$ = 10.8, 2.3 Hz, 1H), 6.89-6.88 (m, 1H), 3.47 (s, 2H), 0.97 (s, 42H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.8, 150.4, 141.9 (d, $J$ = 3.1 Hz), 132.7, 131.6 (d, $J$ = 12.8 Hz), 128.4 (d, $J$ = 4.4 Hz), 126.1 (d, $J$ = 374.7 Hz), 125.6 (d, $J$ = 3.0 Hz), 121.8 (d, $J$ = 10.6 Hz), 114.8 (d, $J$ = 22.4 Hz), 104.0, 95.5, 18.4, 11.1; $\nu_{max}$ (KBr)/cm$^{-1}$ 3488, 3396, 2945, 2865, 2152, 1573, 1456, 1255, 1178, 1074, 980, 916, 881, 803, 670, 461; HRMS (ESI) m/z: calcd for C$_{39}$H$_{56}$ClFNSi$_2$ [M+H]$^+$ 582.3149; found 582.3154.

5-Methyl-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (4o)
4o as a yellow solid (82.5 mg, 76% yield); mp 60-61 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); 1H NMR (400 MHz, CDCl_3) δ 7.52 (d, J = 7.8 Hz, 2H), 7.25 (d, J = 4.0 Hz, 1H), 6.84 (d, J = 9.8 Hz, 2H), 6.57 (d, J = 8.0 Hz, 1H), 3.24 (s, 2H), 2.18 (s, 3H), 0.93 (s, 42H); 13C NMR (100 MHz, CDCl_3) δ 145.2, 141.2, 138.1, 132.7, 130.5, 129.1, 127.4, 127.0, 126.1, 124.4, 116.1, 104.9, 94.3, 20.3, 18.4, 11.2; ν_max (KBr)/cm⁻¹ 3471, 3384, 2941, 2864, 2151, 1620, 1505, 1458, 1318, 979, 920, 882, 804, 741, 671, 459; HRMS (ESI) m/z: calcd for C_{35}H_{54}NSi_{2}[M+H]^+ 544.3789; found 544.3785.

4-Methyl-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4p)

4p as a brown oil (79.3 mg, 73% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); 1H NMR (400 MHz, CDCl_3) δ 7.58 (d, J = 7.8 Hz, 2H), 7.32-7.27 (m, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.59 (d, J = 7.8 Hz, 1H), 6.54 (s, 1H), 3.42 (s, 2H), 2.28 (s, 3H), 0.99 (s, 42H); 13C NMR (100 MHz, CDCl_3) δ 145.2, 143.5, 138.1, 132.7, 130.2, 127.0, 124.6, 123.2, 119.5, 116.4, 105.0, 94.2, 21.1, 18.4, 11.2; ν_max (KBr)/cm⁻¹ 3478, 3389, 2943, 2865, 2151, 1620, 1515, 1459, 1318, 979, 922, 882, 755, 671, 457; HRMS (ESI) m/z: calcd for C_{35}H_{54}NSi_{2}[M+H]^+ 544.3789; found 544.3779.

4-Chloro-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4q)

4q as a brown oil (79.9 mg, 71% yield); R_f = 0.5 (petroleum ether/ethyl acetate = 35/1, v/v); 1H NMR (400 MHz, CDCl_3) δ 7.46 (d, J = 7.8 Hz, 2H), 7.19 (d, J = 8.0 Hz, 1H), 6.87 (d, J = 8.2 Hz, 1H), 6.63 (dd, J = 8.2, 2.0 Hz, 1H), 6.59 (d, J = 1.8 Hz, 1H), 3.42 (s, 2H), 0.87 (s, 42H); 13C NMR (100 MHz, CDCl_3) δ 145.1, 143.6, 134.1, 132.7, 131.5, 127.5, 124.5, 124.2, 118.3, 115.2, 104.4, 94.9, 18.4, 11.2; ν_max
(KBr)/cm$^{-1}$ 3483, 3393, 2944, 2865, 2151, 1615, 1567, 1497, 1238, 1070, 980, 883, 843, 754, 671, 460; HRMS (ESI) m/z: calcd for C$_{34}$H$_{51}$CINSi$_2$ [M+H]$^+$ 564.3243; found 564.3243.

**Ethyl 6-amino-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-3-carboxylate (4r)**

4r as a yellow solid (96.2 mg, 80% yield); mp 108-109 °C; $R_f = 0.3$

(petroleum ether/ethyl acetate = 10/1, v/v); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$

7.84-7.76 (m, 2H), 7.55 (d, $J = 7.8$ Hz, 2H), 7.28 (t, $J = 7.6$ Hz, 1H), 6.65 (d, $J = 8.4$ Hz, 1H), 4.27 (q, $J = 7.2$ Hz, 2H), 3.71 (s, 2H), 1.32 (t, $J = 7.2$ Hz, 4H), 0.91 (s, 42H);

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.8, 148.3, 143.4, 132.8, 132.7, 130.9, 127.6, 124.6, 124.4, 120.0, 114.4, 104.4, 95.0, 60.0, 18.4, 14.4, 11.1; $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3490, 3375, 2944, 2865, 2151, 1705, 1620, 1573, 1459, 1368, 1298, 1150, 1109, 981, 917, 465; HRMS (ESI) m/z: calcd for C$_{37}$H$_{56}$NO$_2$Si$_2$ [M+H]$^+$ 602.3844; found 602.3850.

**Ethyl 2-amino-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-4-carboxylate (4s)**

4s as a yellow solid (99.7 mg, 83% yield); mp 85-86 °C; $R_f = 0.3$

(petroleum ether/ethyl acetate = 10/1, v/v); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$

7.55 (d, $J = 7.8$ Hz, 2H), 7.43 (dd, $J = 8.0$, 1.6 Hz, 1H), 7.38 (d, $J = 1.4$

Hz, 1H), 7.28 (t, $J = 6.2$ Hz, 1H), 7.11 (d, $J = 8.0$ Hz, 1H), 4.37 (q, $J = 7.2$ Hz, 2H), 3.21 (s, 2H), 1.38 (t, $J = 7.2$ Hz, 3H), 0.92 (s, 42H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.9, 144.0, 143.8, 132.7, 130.7, 130.5, 130.3, 127.6, 124.1, 119.6, 116.5, 104.3, 95.1, 60.5, 18.4, 14.4, 11.1; $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3480, 3381, 2943, 2865, 2151, 1719, 1622, 1569, 1460, 1431, 1369, 1297, 1232, 979, 714, 463;

HRMS (ESI) m/z: calcd for C$_{37}$H$_{55}$NNaO$_2$Si$_2$ [M+Na]$^+$ 624.3664; found 624.3674.
5-(Trifluoromethyl)-2’,6’-bis((triisopropylsilyl)ethynyl)-[1,1’-biphenyl]-2-amine (4t)

4t as a yellow solid (80.0 mg, 67% yield); mp 78-79 °C; Rf = 0.4 (petroleum ether/ethyl acetate = 35/1, v/v); 1H NMR (400 MHz, CDCl3) δ 7.56 (d, J = 7.8 Hz, 2H), 7.34-7.27 (m, 3H), 6.71 (d, J = 8.2 Hz, 1H), 3.72 (s, 2H), 0.92 (s, 42H); 13C NMR (100 MHz, CDCl3) δ 147.0, 142.9, 132.9, 127.9, 127.6 (q, J = 4.1 Hz), 126.0 (q, J = 3.6 Hz), 125.0, 124.9 (q, J = 269.0 Hz), 124.6, 120.1 (q, J = 32.3 Hz), 114.8, 104.1, 95.2, 18.4, 11.1; νmax (KBr)/cm⁻¹ 3494, 3402, 2945, 2865, 2151, 1513, 1460, 1381, 1150, 1116, 980, 883, 670, 457; HRMS (ESI) m/z: calcd for C35H51F3NSi2 [M+H]+ 598.3507; found 598.3512.

2’-Ethynyl-[1,1’-biphenyl]-2-amine (5a)

5a as a yellow oil (35.1 mg, 91% yield); Rf = 0.3 (petroleum ether/ethyl acetate = 20/1, v/v); 1H NMR (400 MHz, CDCl3) δ 7.62 (d, J = 7.8 Hz, 1H), 7.41 (m, J = 7.6, 1.3 Hz, 1H), 7.36-7.30 (m, 2H), 7.18 (m, J = 7.8, 1.5 Hz, 1H), 7.12 (dd, J = 7.5, 1.6 Hz, 1H), 2.99 (s, 1H); 13C NMR (100 MHz, CDCl3) δ 143.6, 142.2, 133.5, 130.6, 130.3, 129.2, 128.8, 127.4, 126.4, 121.9, 118.3, 115.6, 82.3, 80.2; νmax (KBr)/cm⁻¹ 3474, 3383, 3301, 3060, 2939, 2864, 2150, 1676, 1617, 1500, 1462, 1381, 1253, 1077, 1000, 802, 670, 458; HRMS (ESI) m/z: calcd for C14H12N [M+H]+ 194.0964; found 194.0968.

6-Methylphenanthridine (6a)

6a as a yellow solid (30.2 mg, 78% yield); mp 85-86 °C; Rf = 0.3 (petroleum ether/ethyl acetate = 5/1, v/v); 1H NMR (400 MHz, CDCl3) δ 8.64 (d, J = 8.4 Hz, 1H), 8.55 (d, J = 8.2 Hz, 1H), 8.23 (d, J = 8.2 Hz, 1H), 8.12 (d, J = 8.2 Hz, 1H), 7.90-7.82 (m, 1H),
7.76-7.67 (m, 2H), 7.66-7.60 (m, 1H), 3.06 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.9, 143.6, 132.6, 130.6, 129.3, 128.7, 127.3, 126.6, 126.4, 125.9, 123.8, 122.3, 122.0, 23.3; $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3307, 2926, 2859, 2312, 1675, 1636, 1599, 1544, 1308, 1253, 1087, 806, 753, 654, 576, 455; HRMS (ESI) m/z: calcd for C$_{14}$H$_{12}$N [M+H]$^+$ 194.0964; found 194.0968.

5-Thiocyanato-2'-(triisopropylsilyl)ethynyl-[1,1'-biphenyl]-2-amine (7a)

7a as a yellow oil (108.1 mg, 89% yield); $R_f$ = 0.4 (petroleum ether/ethyl acetate = 20/1, v/v); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62 (dd, $J = 7.4$, 1.2 Hz, 1H), 7.41 (m, $J = 7.5$, 1.4 Hz, 1H), 7.38-7.33 (m, 2H), 7.32-7.27 (m, 2H), 6.74 (d, $J = 8.4$ Hz, 1H), 3.88 (s, 2H), 0.96 (s, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.4, 140.0, 135.01, 133.3, 129.8, 128.9, 128.1, 123.4, 116.6, 112.1, 109.3, 104.7, 94.9, 18.5, 11.1; $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3484, 3383, 2941, 2863, 2154, 1615, 1495, 1468, 1402, 1306, 919, 882, 670; HRMS (ESI) m/z: calcd for C$_{24}$H$_{30}$N$_2$NaSSi [M+Na]$^+$ 429.1791; found 429.1794.

2'-(1-Benzyl-1H-1,2,3-triazol-4-yl)-[1,1'-biphenyl]-2-amine (8a)

8a as a yellow oil (56.7 mg, 87% yield); $R_f$ = 0.3 (petroleum ether/ethyl acetate = 20/1, v/v); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.28 (dd, $J = 7.8$, 1.1 Hz, 1H), 7.48 (m, $J = 7.6$, 1.4 Hz, 1H), 7.41 (m, $J = 7.6$, 1.4 Hz, 1H), 7.30 (ddd, $J = 9.0$, 6.6, 1.8 Hz, 4H), 7.09 (ddd, $J = 9.2$, 7.8, 2.8 Hz, 3H), 6.95 (dd, $J = 7.6$, 1.4 Hz, 1H), 6.71 (t, $J = 7.4$ Hz, 1H), 6.56 (d, $J = 8.0$ Hz, 1H), 6.46 (s, 1H), 5.32 (s, 2H), 3.13 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.0, 143.5, 136.4, 134.6, 130.5, 130.1, 130.0, 128.9, 128.8, 128.5, 128.4, 128.3, 128.2, 127.8, 126.7, 121.9, 118.5, 115.1, 53.8; $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3464, 3363, 3058, 2927, 2861, 2151, 1615, 1452, 1348, 1299, 1223, 1073, 1044, 809, 753, 507; HRMS (ESI) m/z: calcd for C$_{21}$H$_{18}$N$_2$Na [M+Na]$^+$ 349.1424; found 349.1434.
1-(2'-Amino-[1,1'-biphenyl]-2-yl)ethan-1-one (9a) as a yellow oil (31.7 mg, 75% yield); R$_f$ = 0.2 (petroleum ether/ethyl acetate = 10/1, v/v); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.62 (d, $J$ = 8.4 Hz, 1H), 8.53 (d, $J$ = 8.2 Hz, 1H), 8.21 (d, $J$ = 8.2 Hz, 1H), 8.12 (d, $J$ = 8.2 Hz, 1H), 7.87-7.81 (m, 1H), 7.70 (m, $J$ = 8.2, 1.2 Hz, 2H), 7.65-7.58 (m, 1H), 3.05 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.9, 143.6, 132.6, 130.5, 129.3, 128.6, 127.3, 126.5, 126.3, 125.9, 123.8, 122.3, 121.9, 23.3; $\nu_{max}$ (KBr)/cm$^{-1}$ 3462, 3068, 2922, 2853, 2309, 1614, 1580, 1444, 1375, 1316, 860, 753, 720, 614, 436; HRMS (ESI) m/z: calcd for C$_{14}$H$_{13}$NNaO [M+Na]$^+$ 234.0889; found 234.0891.
G. The Preparation of Palladacycle Intermediate A

\[
\begin{align*}
\text{Palladacycle Intermediate A: } & [1,1^{14}\text{-biphenyl}]-2\text{-amine } \text{1a} \text{ (0.6 mmol), PdCl}_2 \text{ (0.6 mmol), and } \\
& \text{MeOH (4 mL) were sealed in a Schlenk tube under N}_2 \text{ atmosphere. After this, the mixture was} \\
& \text{stirred at room temperature for 24 h. The precipitate was filtered, washed with 10 mL } \text{MeOH, 10} \\
& \text{mL diethylether and dried under vacuum. Palladacycle A as a brown solid (119.3 mg, 68% yield);} \\
& \text{ }^1\text{H NMR (400 MHz, DMSO)} \delta 7.70-7.37 \text{ (m, 10H), 7.30-7.14 \text{ (m, 4H), 6.26 \text{ (s, 2H)};} \\
& \text{ }^{13}\text{C NMR (100 MHz, CDCl}_3) \delta 138.6, 138.3, 138.2, 135.0, 130.3, 129.8, 129.4, 128.6, 127.6, 127.4, 125.2, \\
& 124.8; \nu_{\text{max}} \text{(KBr)/cm}^{-1} 3241, 3183, 3096, 1567, 1480, 1453, 1314, 1287, 1129, 1178, 826, 760, \\
& 701, 520. \text{HRMS (ESI) Calcd for C}_{24}\text{H}_{20}\text{N}_2\text{ClPd}_2 \text{[M-Cl]}^+ 584.9388; \text{Found, 584.9382.}
\end{align*}
\]
H. Further Synthetic Applications

(a) 2'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine 3a (0.2 mmol), TBFA (1 M in THF, 0.4 ML) and THF (1.0 mL) were sealed in a Schlenk tube under N\textsubscript{2} atmosphere. After this, the mixture was stirred at room temperature for 3 h. After the reaction was completed (monitored by TLC), the resulting mixture was extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired products 5a were obtained after purified by column chromatography on silica gel with mixture of petroleum ether and ethyl acetate.

(b) i) 2'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine 3a was hydrolyzed to 5a. ii) 5a (0.1 mmol), PdCl\textsubscript{2} (5 mol %) and CH\textsubscript{3}CN (1 mL) were sealed in a Schlenk tube under N\textsubscript{2} atmosphere. After this, the mixture was stirred at 100 °C for 12 h. After the reaction was completed (monitored by TLC), the resulting mixture were cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired products 6a were obtained in the corresponding yields after purified by column chromatography on silica gel with mixture of petroleum ether and ethyl acetate.
(c) 2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine 3a (0.3 mmol), KSCN (2 equiv), Cu(OTf)₂ (20 mol%), TMEDA (20 mol%) and BF₃·Et₂O were mixed in DMSO to stir under an O₂ balloon at 80 °C. After the reaction was completed (monitored by TLC), the resulting mixture were cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired products 7a were obtained in the corresponding yields after purified by column chromatography on silica gel with mixture of petroleum ether and ethyl acetate.

(d) i) 2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine 3a was hydrolyzed to 5a. ii) 5a (0.2 mmol), Benzylazide (0.2 mmol), CuI (10 mol %) and DMF (1 mL) were sealed in a Schlenk tube under N₂ atmosphere. After this, the mixture was stirred at 80 °C for 12 h. After the reaction was completed (monitored by TLC), the resulting mixture were cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired products 8a were obtained in the corresponding yields after purified by column chromatography on silica gel with mixture of petroleum ether and ethyl acetate.
(e) 2′-(triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine 3a (0.2 mmol) and KOH (3 equiv) were sealed in a Schlenk tube under N₂ atmosphere. After this, the mixture was stirred at 100 °C for 12 h. After the reaction was completed (monitored by TLC), the resulting mixture were cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired products 9a were obtained in the corresponding yields after purified by column chromatography on silica gel with mixture of petroleum ether and ethyl acetate.
I. Copies of $^1$H and $^{13}$C NMR Spectra

2'-((Triisopropylsilyl)ethynyl)-1,1'-biphenyl-2-amine (3a)
2-(Trisopropylsilyl)ethyl)-[1,1'-4,1'-terphenyl]-2-amine (3b)
4'-Ethyl-2'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (3c)
4′-Fluoro-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3d)
$4'-(\text{Trifluoromethyl})-2'-(\text{triisopropylsilyl})\text{ethyl}n)-[1,1'\text{-biphenyl}]-2\text{-amine (3e)}$
1-(2'-Amino-2-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-4-yl)ethan-1-one (3f)
2'-(Triisopropylsilyl)ethynyl)-4'-vinyl-[1,1'-biphenyl]-2-amine (3g)
3′,5′-Dichloro-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3h)
3',5'-Dimethyl-2'-(triisopropylsilyl)ethynyl-[1,1'-biphenyl]-2-amine (3i)
2'-Methoxy-4'-methyl-6'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (3j)
2′-Fluoro-6′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3k)
2-(2-((Triisopropylsilyl)ethynyl)naphthalen-1-yl)aniline (3l)
2-((Methoxy-2-(triisopropylsilyl)ethynyl)naphthalen-1-yl)aniline (3m)
2-(3-((triisopropylsilyl)ethynyl)benzo[b]thiophen-2-yl)aniline (3n)

H NMR (400 MHz, CDCl₃)

13C NMR (100 MHz, CDCl₃)
2-(2-((Triisopropylsilyl)ethynyl)pyren-1-yl)aniline (3o)

$\text{H NMR (400 MHz, CDCl}_3\text{)}$

$\text{^1}C\text{ NMR (100 MHz, CDCl}_3\text{)}$
$5'$-Chloro-2'-(triisopropylsilyl)ethynyl-[1,1'$-biphenyl]-2-amine (3p)
4-Methyl-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3q)
5-Methyl-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3r)
Ethyl 2-amino-2'-(triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-4-carboxylate (3s)
Ethyl 6-amino-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-3-carboxylate (3t)
5-Fluoro-2′-((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (3u)
$\text{S59}$

5-(Trifluoromethyl)-2'-(triisopropylsilyl)ethynyl]-[1,1'-biphenyl]-2-amine (3v)
3,5-Dichloro-2'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (3w)
2',6'-Bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (4a)
2',6'-Bis((triisopropylsilyl)ethynyl)-[1,1':4',1''-terphenyl]-2-amine (4b)
4′-Ethyl-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4c)

$^1$H NMR (400 MHz, CDCl$_3$)

$^1$C NMR (100 MHz, CDCl$_3$)
4'-Isopropyl-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (4d)
4′-Methoxy-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4e)
4'-Fluoro-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (4f)

**H NMR (400 MHz, CDCl₃)

13C NMR (100 MHz, CDCl₃)
4′-(Trifluoromethyl)-2′,6′-bis((triisopropylsilyl)ethynyl)-[1,1′-biphenyl]-2-amine (4g)
1-(2'-Amino-2,6-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-4-yl)ethan-1-one (4h)
2',6'-Bis((triisopropylsilyl)ethynyl)-4'-vinyl-[1,1'-biphenyl]-2-amine (4i)
3',5'-Dichloro-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (4j)
3',5'-Dimethyl-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (4k)
3'-Chloro-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (4l)
2-(6-Methoxy-1,3-bis((triisopropylsilyl)ethynyl)naphthalen-2-yl)aniline (4m)
5-Chloro-3-fluoro-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (4n)
5-Methyl-2',6'-bis((trisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (4o)
4-Methyl-2',6'-bis(triisopropylsilyl)ethynyl]-[1,1'-biphenyl]-2-amine (4p)
4-Chloro-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (4q)
Ethyl 6-amino-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-3-carboxylate (4r)
Ethyl 2-amino-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-4-carboxylate (4s)
5-(Trifluoromethyl)-2',6'-bis((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (4t)
2'-Ethynyl-[1,1'-biphenyl]-2-amine (5a)
6-Methylphenanthridine (6a)
5-Thiocyanato-2'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-amine (7a)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2′-(1-Benzyl-1H-1,2,3-triazol-4-yl)-[1,1′-biphenyl]-2-amine (8a)

\[ \text{1H NMR (400 MHz, CDCl}_3\text{)} \]

\[ \text{13C NMR (100 MHz, CDCl}_3\text{)} \]

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1-(2'-Amino-[1,1'-biphenyl]-2-yl)ethan-1-one (9a)