Supporting Information

Synthesis of Easy-modified and Useful Dibenzo-[b,d]azepines by Palladium(II)-Catalyzed Cyclization/Addition with a Green Solvent.

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1. General
All raw reagents were bought from commercial sources and used as received. All reagents were purchased from Sigma Aldrich or Fluorochem and used as received. All reactions apart from where noted were carried out in air. All flash column chromatography was carried out using silica purchased from Fluorochem using the solvent system noted. $^1$H NMR spectra were recorded at 400 MHz using a Bruker Avance III spectrometer. $^{13}$C NMR spectra were recorded at 600 MHz using a Bruker Avance III spectrometer. All coupling constants are reported in Hertz (Hz). In cases where it was required 2D NMR techniques were used to confirm compound identity. Chemical shifts are reported in ppm and are referenced to residual solvent peaks; CHCl$_3$ ($^1$H 7.26 ppm, $^{13}$C 77.0 ppm).

2. General Method for the Synthesis of 1a and 4a

To the solution of $N$-[(2-bromophenyl)acetamide (1 eq) ($N$-[(2-bromophenyl)acetamide was bought from commercial source and $N$-[(2-bromo-5-chlorophenyl)acetamide was prepared according to the procedures reported in the literature Tetrahedron, 2011, 67, 5806-5810)], (2-(2-[(cyanomethyl)phenyl]-4,5,5-trimethyl-1,3,2-dioxaborolan-4-yl)methyl)methylium (1.5 eq) (prepared according to the procedures reported in the patent US 2017/0158704 A1), $K_2$CO$_3$ (2 eq) in the solvent (THF : H$_2$O = 5:1) was added Pd(dppf)Cl$_2$ (0.1 eq). Then the mixture was stirred at 80 °C for 5 h under N$_2$ atmosphere. The reaction was then cooled to room temperature and diluted with H$_2$O, extracted three times with EA, dried by Na$_2$SO$_4$ and evaporated under a vacuum. The crude material was purified by column chromatography to give the desired product.

3. Characterization Data of Products 1a and 4a

Synthesised according to the general method, the crude material was purified by column chromatography (PE : EA = 5:1) to give the desired product as a yellow liquid in 72% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.26 (d, $J = 8.2$ Hz, 1H), 7.64 (d, $J = 7.3$ Hz, 1H), 7.54 – 7.40 (m, 3H), 7.27 (brd, $J = 7.3$ Hz, 1H), 7.22 (t, $J = 7.4$ Hz, 1H), 7.14 (brd, $J = 7.5$ Hz, 1H), 6.68 (s, 1H), 3.50 (d, $J = 18.5$ Hz, 1H), 3.44 (d, $J = 18.5$ Hz, 1H), 1.98 (s, 3H).

HRMS m/z: [M + H]$^+$ calcd for C$_{16}$H$_{14}$N$_2$O, 251.1106; found, 251.1114.
Synthesised according to the general method, the crude material was purified by column chromatography (PE : EA = 5:1) to give the desired product as a yellow liquid in 42% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.43 (s, 1H), 7.64 (d, $J = 7.4$ Hz, 1H), 7.53 (td, $J = 7.6$, 1.6 Hz, 1H), 7.48 (td, $J = 7.5$, 1.3 Hz, 1H), 7.25 (brd, $J = 7.4$ Hz, 1H), 7.19 (dd, $J = 8.2$, 2.1 Hz, 1H), 7.07 (d, $J = 8.2$ Hz, 1H), 6.66 (s, 1H), 3.49 (d, $J = 18.4$ Hz, 1H), 3.42 (d, $J = 18.4$ Hz, 1H), 1.98 (s, 3H).

HRMS m/z: [M + H]$^+$ calcd for C$_{21}$H$_{17}$NCl, 285.0716; found, 285.0720.


To the solution of 1a (100 mg, 0.4 mmol, 1 eq) or 4a (122 mg, 0.4 mmol, 1 eq), arylboronic acid 2 (0.6 mmol, 1.5 eq), KF (47 mg, 0.8 mmol, 2 eq), dtbbpy (11 mg, 0.04 mmol, 0.1 eq) in mix solvent (EtOH : H$_2$O = 1:2, 4 mL) was added TfOH (0.35 mL, 4 mmol, 10 eq) slowly, then the mixture was stirred at Ar at 100 °C for 10 h, and the reaction is a tube sealing reaction. After cooling to room temperature, the reaction was neutralized by saturated NaHCO$_3$, then extracted three times with EA, dried by Na$_2$SO$_4$ and evaporated under a vacuum. The crude material was purified by column chromatography to afford products 3a–3q and 5a–5h.

5. Characterization Data of Products 3a–3q and 5a–5h

3a 6-phenyl-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the 1a (100 mg, 0.4 mmol) and
phenylboronic acid (73 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 91% yield.

\( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta 8.09 \) (dd, \( J = 6.7, 2.9 \) Hz, 2H), \( 7.74 \) (dd, \( J = 7.9, 1.5 \) Hz, 1H), \( 7.71 \) (dq, \( J = 7.0, 2.2 \) Hz, 1H), \( 7.54 \) (dd, \( J = 8.1, 1.5 \) Hz, 1H), \( 7.49 \) (dd, \( J = 7.1, 1.5 \) Hz, 1H), \( 7.46 \) (d, \( J = 3.5 \) Hz, 2H), \( 7.38 \) (d, \( J = 2.6 \) Hz, 3H), \( 7.31 \) (ddd, \( J = 8.2, 7.2, 1.5 \) Hz, 1H), \( 4.35 \) (d, \( J = 12.4 \) Hz, 1H), \( 3.04 \) (d, \( J = 12.5 \) Hz, 1H).

\( ^{13}C \) NMR (151 MHz, CDCl\(_3\)) \( \delta 163.80, 137.85, 136.98, 136.52, 131.46, 130.51, 129.43, 128.55, 128.46, 128.24, 127.99, 127.78, 127.10, 126.93, 126.88, 124.56, 36.43.

HRMS m/z: [M + H]\(^+\) calcd for C\(_{21}\)H\(_{17}\)N, 270.1204; found, 270.1210.

3b 6-(p-tolyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the 1a (100 mg, 0.4 mmol) and p-tolyboronic acid (82 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 89% yield.

\( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta 7.99 \) (d, \( J = 6.0 \) Hz, 2H), \( 7.71 \) (dd, \( J = 10.6, 5.1 \) Hz, 2H), \( 7.49 \) (dd, \( J = 19.8, 7.2 \) Hz, 2H), \( 7.35 \) (d, \( J = 2.8 \) Hz, 3H), \( 7.29 \) (d, \( J = 7.8 \) Hz, 1H), \( 7.25 \) (d, \( J = 4.6 \) Hz, 2H), \( 4.33 \) (dd, \( J = 12.3, 2.2 \) Hz, 1H), \( 3.00 \) (dd, \( J = 12.4, 2.0 \) Hz, 1H), \( 2.39 \) (s, 3H).

\( ^{13}C \) NMR (151 MHz, CDCl\(_3\)) \( \delta 163.51, 146.55, 140.77, 137.03, 136.65, 135.19, 131.42, 129.41, 129.26, 128.40, 128.14, 127.94, 127.72, 126.98, 126.91, 126.85, 124.28, 36.30, 21.38.

HRMS m/z: [M + H]\(^+\) calcd for C\(_{21}\)H\(_{17}\)N, 284.1434; found, 284.1424.

3c 6-(m-tolyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the 1a (100 mg, 0.4 mmol) and m-tolyboronic acid (82 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 90% yield.

\( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta 7.88 \) (d, \( J = 9.0 \) Hz, 2H), \( 7.77 - 7.68 \) (m, 2H), \( 7.54 \) (d, \( J = 7.9 \) Hz, 1H), \( 7.48 \) (dd, \( J = 9.2, 3.6 \) Hz, 1H), \( 7.40 - 7.27 \) (m, 5H), \( 7.26 \) (d, \( J = 2.3 \) Hz, 1H), \( 4.34 \) (dd, \( J = 12.4, 1.9 \) Hz, 1H), \( 3.02 \) (dd, \( J = 12.3, 1.8 \) Hz, 1H), \( 2.42 \) (s, 3H).
C NMR (151 MHz, CDCl₃) δ 164.01, 138.16, 136.97, 136.58, 131.42, 131.32, 129.41, 128.61, 128.41, 128.20, 127.74, 127.05, 126.91, 125.10, 124.47, 36.52, 21.46.

HRMS m/z: [M + H]^+ calcd for C₂₁H₁₇N, 284.1434; found, 284.1427.

3d 6-(o-tolyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the 1a (100 mg, 0.4 mmol) and o-tolylboronic acid (82 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 78% yield.

1H NMR (400 MHz, CDCl₃) δ 7.75 (t, J = 8.4 Hz, 2H), 7.53 – 7.45 (m, 2H), 7.45 – 7.40 (m, 1H), 7.40 – 7.34 (m, 1H), 7.34 – 7.31 (m, 1H), 7.29 (d, J = 7.3 Hz, 2H), 7.19 (dd, J = 15.2, 7.8 Hz, 3H), 3.93 (d, J = 11.9 Hz, 1H), 3.21 (d, J = 11.8 Hz, 1H), 2.23 (s, 3H).

13C NMR (151 MHz, CDCl₃) δ 167.52, 136.64, 136.07, 135.86, 131.15, 130.84, 129.39, 128.91, 128.52, 128.21, 127.99, 127.79, 127.20, 127.15, 126.72, 125.70, 124.70, 41.08, 20.09.

HRMS m/z: [M + H]^+ calcd for C₂₁H₁₇N, 284.1434; found, 284.1421.

3e 6-(4-methoxyphenyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the 1a (100 mg, 0.4 mmol) and 4-methoxyphenylboronic acid (91 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 30:1) to give the desired product as a yellow liquid in 75% yield.

1H NMR (400 MHz, CDCl₃) δ 8.15 – 8.02 (m, 2H), 7.71 (dd, J = 12.0, 5.3 Hz, 2H), 7.56 – 7.42 (m, 2H), 7.35 (s, 3H), 7.31 – 7.23 (m, 1H), 7.02 – 6.92 (m, 2H), 4.32 (d, J = 12.0 Hz, 1H), 3.84 (s, 3H), 2.99 (d, J = 12.3 Hz, 1H).

13C NMR (151 MHz, CDCl₃) δ 161.59, 137.08, 136.61, 131.41, 129.71, 129.41, 128.41, 128.13, 127.74, 126.99, 126.88, 126.81, 124.17, 113.88, 55.38, 36.14.

HRMS m/z: [M + H]^+ calcd for C₂₁H₁₇NO, 300.1383; found, 300.1366.
Synthesised according to the general method, after addition of the 1a (100 mg, 0.4 mmol) and 3-methoxyphenylboronic acid (91 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 30:1) to give the desired product as a yellow liquid in 80% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.77 – 7.65 (m, 3H), 7.63 (s, 1H), 7.52 (d, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 7.2$ Hz, 1H), 7.37 (t, $J = 5.2$ Hz, 4H), 7.30 (t, $J = 7.4$ Hz, 1H), 7.00 (d, $J = 6.5$ Hz, 1H), 4.32 (d, $J = 12.4$ Hz, 1H), 3.86 (s, 3H), 3.02 (d, $J = 12.4$ Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 163.37, 159.79, 146.36, 139.39, 136.95, 136.58, 131.42, 129.44, 128.42, 128.23, 127.74, 127.05, 126.94, 126.87, 124.49, 120.42, 116.67, 112.87, 55.37, 36.50.

HRMS m/z: [M + H]$^+$ calcd for C$_{21}$H$_{17}$NO, 300.1383; found, 300.1379.

Synthesised according to the general method, after addition of the 1a (100 mg, 0.4 mmol) and 4-tert-butylbenzeneboronic acid (107 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 91% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, $J = 6.9$ Hz, 2H), 7.77 – 7.67 (m, 2H), 7.56 – 7.43 (m, 4H), 7.36 (s, 3H), 7.32 – 7.26 (m, 1H), 4.35 (d, $J = 12.3$ Hz, 1H), 3.01 (d, $J = 12.4$ Hz, 1H), 1.33 (s, 9H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 162.78, 153.27, 146.02, 136.46, 136.09, 134.55, 130.82, 128.82, 127.80, 127.53, 127.15, 127.12, 126.38, 126.35, 126.30, 124.93, 123.68, 35.63, 34.22, 30.56.

HRMS m/z: [M + H]$^+$ calcd for C$_{24}$H$_{23}$N, 326.1903; found, 326.1899.
3h 6-(naphthalen-2-yl)-7H-dibenzo[bd]azepine

Synthesised according to the general method, after addition of the 1a (100 mg, 0.4 mmol) and naphthalen-2-ylboronic acid (103 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 74% yield. 

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.55 (s, 1H), 8.25 (d, \(J = 8.6\) Hz, 1H), 7.98 (dd, \(J = 8.2, 4.7\) Hz, 1H), 7.87 (dd, \(J = 12.8, 7.3\) Hz, 2H), 7.79 – 7.71 (m, 2H), 7.59 – 7.48 (m, 4H), 7.46 – 7.42 (m, 1H), 7.38 (dd, \(J = 5.1, 3.9\) Hz, 2H), 7.32 (t, \(J = 7.5\) Hz, 1H), 4.53 (d, \(J = 12.5\) Hz, 1H), 3.11 (d, \(J = 12.4\) Hz, 1H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 163.36, 146.63, 137.05, 136.63, 135.31, 134.32, 132.98, 131.41, 129.46, 128.97, 128.47, 128.30, 128.25, 128.15, 128.1, 127.66, 127.26, 127.07, 127.02, 126.91, 126.42, 125.04, 124.49, 36.30.

HRMS m/z: \([M + H]^+\) calcd for C\(_{24}\)H\(_{17}\)N, 320.1434; found, 320.1433.

3i 6-(4-(trifluoromethyl)phenyl)-7H-dibenzo[bd]azepine

Synthesised according to the general method, after addition of the 1a (100 mg, 0.4 mmol) and 4-(trifluoromethyl)phenylboronic acid (114 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 45% yield. 

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.18 (d, \(J = 6.1\) Hz, 2H), 7.78 – 7.67 (m, 4H), 7.54 – 7.46 (m, 2H), 7.36 (dd, \(J = 18.7, 5.0\) Hz, 4H), 4.31 (d, \(J = 12.3\) Hz, 1H), 3.06 (d, \(J = 12.7\) Hz, 1H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 162.03, 146.07, 141.28, 136.91, 136.19, 131.38, 129.50, 128.62, 128.42, 128.20, 127.91, 127.30, 126.99, 126.76, 125.50, 125.48, 124.96, 36.40.

HRMS m/z: \([M + H]^+\) calcd for C\(_{21}\)H\(_{14}\)F\(_3\)N, 338.1151; found, 338.1144.
3j 6-(3-(trifluoromethyl)phenyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the 1a (100 mg, 0.4 mmol) and 3-(trifluoromethyl)phenylboronic acid (114 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 40% yield.

$\text{H NMR (400 MHz, CDCl}_3 \delta 8.36 (s, 1H), 8.26 (d, \ J = 7.6 \ Hz, 1H), 7.81 - 7.66 (m, 3H), 7.63 - 7.46 (m, 3H), 7.45 - 7.29 (m, 4H), 4.32 (d, \ J = 12.2 \ Hz, 1H), 3.06 (d, \ J = 12.5 \ Hz, 1H).}$

$\text{C NMR (151 MHz, CDCl}_3 \delta 161.81, 146.08, 138.76, 136.94, 131.38, 131.17, 131.00, 129.50, 129.07, 128.62, 128.43, 127.91, 127.30, 126.99, 126.86, 126.84, 126.76, 124.90, 124.76, 124.74, 123.08, 36.25.}$

$\text{HRMS m/z: [M + H]+ calcd for C}_{21}\text{H}_{14}\text{F}_{3}\text{N}, 338.1151; found, 338.1144.}$

3k 6-(3-chlorophenyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the 1a (100 mg, 0.4 mmol) and 3-chlorophenylboronic acid (94 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 66% yield.

$\text{H NMR (400 MHz, CDCl}_3 \delta 8.07 (s, 1H), 7.96 (d, \ J = 7.1 \ Hz, 1H), 7.77 - 7.67 (m, 2H), 7.57 - 7.45 (m, 2H), 7.45 - 7.28 (m, 6H), 4.32 - 4.21 (m, 1H), 3.03 (d, \ J = 12.5 \ Hz, 1H).}$

$\text{C NMR (151 MHz, CDCl}_3 \delta 161.96, 146.08, 139.75, 136.88, 136.22, 134.71, 131.35, 130.31, 129.71, 129.44, 128.51, 128.34, 128.05, 127.83, 127.20, 126.94, 126.77, 125.94, 124.76, 36.27.}$

$\text{HRMS m/z: [M + H]^+ calcd for C}_{20}\text{H}_{14}\text{ClN}, 304.0888; found, 304.0860.}$

3l 6-(4-chlorophenyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the 1a (100 mg, 0.4 mmol) and 3-chlorophenylboronic acid (94 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 66% yield.

$\text{H NMR (400 MHz, CDCl}_3 \delta 8.36 (s, 1H), 8.26 (d, \ J = 7.6 \ Hz, 1H), 7.81 - 7.66 (m, 3H), 7.63 - 7.46 (m, 3H), 7.45 - 7.29 (m, 4H), 4.32 (d, \ J = 12.2 \ Hz, 1H), 3.06 (d, \ J = 12.5 \ Hz, 1H).}$

$\text{C NMR (151 MHz, CDCl}_3 \delta 161.81, 146.08, 138.76, 136.94, 131.38, 131.17, 131.00, 129.50, 129.07, 128.62, 128.43, 127.91, 127.30, 126.99, 126.86, 126.84, 126.76, 124.90, 124.76, 124.74, 123.08, 36.25.}$

$\text{HRMS m/z: [M + H]^+ calcd for C}_{21}\text{H}_{14}\text{ClN}, 338.1151; found, 338.1144.}$
Synthesised according to the general method, after addition of the 1a (100 mg, 0.4 mmol) and 4-chlorophenylboronic acid (94 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 85% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.07 – 8.00 (m, 2H), 7.77 – 7.68 (m, 2H), 7.49 (d, $J$ = 8.2 Hz, 2H), 7.45 – 7.28 (m, 6H), 4.28 (d, $J$ = 12.5 Hz, 1H), 3.02 (d, $J$ = 12.5 Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 163.16, 143.15, 140.29, 137.04, 136.77, 136.58, 131.45, 129.46, 128.86, 128.45, 128.25, 127.79, 127.23, 127.13, 127.09, 126.98, 126.88, 124.48, 36.33.

HRMS m/z: [M + H]$^+$ calcd for C$_{20}$H$_{14}$ClN, 304.0888; found, 304.0883.

3m 6-(3,4-dichlorophenyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the 1a (100 mg, 0.4 mmol) and 3,4-dichlorophenylboronic acid (114 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 68% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.19 (s, 1H), 7.94 (d, $J$ = 8.7 Hz, 1H), 7.80 – 7.68 (m, 2H), 7.52 (dd, $J$ = 10.7, 7.0 Hz, 3H), 7.40 (dd, $J$ = 12.6, 8.8 Hz, 4H), 4.29 – 4.21 (m, 1H), 3.04 (d, $J$ = 12.5 Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 166.29, 145.59, 139.45, 136.61, 131.97, 131.11, 130.39, 130.30, 129.79, 129.32, 128.52, 128.16, 127.86, 127.36, 127.27, 126.95, 126.87, 125.04, 40.63.

HRMS m/z: [M + H]$^+$ calcd for C$_{20}$H$_{13}$Cl$_2$N, 338.0498; found, 338.0480.

3n 6-(4-bromophenyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the 1a (100 mg, 0.4 mmol) and 4-bromophenylboronic acid (120 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 89% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.96 (d, $J$ = 8.4 Hz, 2H), 7.73 (dd, $J$ = 11.9, 6.4 Hz, 2H), 7.58 (d, $J$ = 8.4 Hz, 2H), 7.50 (dd, $J$ = 8.3, 7.0 Hz, 2H), 7.36 (ddd, $J$ = 19.6, 10.6, 5.9 Hz, 4H), 4.27 (d, $J$ = 12.5 Hz, 1H), 3.02 (d, $J$ = 12.4 Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 162.19, 146.26, 136.95, 136.58, 136.40, 136.32, 131.36, 129.46,
129.25, 128.74, 128.53, 128.29, 127.83, 127.17, 126.91, 126.74, 124.63, 36.21.

HRMS m/z: [M + H]⁺ calcd for C₂₀H₁₄BrN, 348.0382; found, 348.0374.

3o 6-(3,4-dimethylphenyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the 1a (100 mg, 0.4 mmol) and 3,4-dimethylphenylboronic acid (90 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 84% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.78 (m, 2H), 7.72 (dd, J = 9.9, 5.1 Hz, 2H), 7.55 – 7.43 (m, 2H), 7.35 (d, J = 2.9 Hz, 3H), 7.21 (d, J = 4.9 Hz, 1H), 4.34 (dd, J = 12.3, 2.8 Hz, 1H), 2.99 (dd, J = 12.3, 2.8 Hz, 1H), 2.31 (s, 6H).

¹³C NMR (151 MHz, CDCl₃) δ 163.76, 146.62, 139.55, 137.02, 136.86, 136.70, 135.56, 131.40, 129.74, 129.40, 129.11, 128.36, 128.13, 127.70, 126.95, 126.91, 126.87, 125.47, 124.23, 36.33, 19.87, 19.74.

HRMS m/z: [M + H]⁺ calcd for C₂₂H₁₉N, 298.1590; found, 298.1585.

3p 6-(3,4-dimethoxyphenyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the 1a (100 mg, 0.4 mmol) and 3,4-dimethoxyphenylboronic acid (109 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 25:1) to give the desired product as a yellow liquid in 80% yield.

¹H NMR (400 MHz, Chloroform-d) δ 7.71 (q, J = 7.2, 6.4 Hz, 4H), 7.56 – 7.41 (m, 2H), 7.39 – 7.27 (m, 4H), 6.92 (d, J = 8.3 Hz, 1H), 4.34 (d, J = 12.3 Hz, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 2.99 (d, J = 12.4 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 162.75, 151.41, 149.15, 146.57, 137.04, 136.62, 131.38, 130.60, 129.42, 128.40, 128.16, 127.75, 127.00, 126.88, 126.79, 124.21, 121.34, 110.59, 110.17, 55.95, 35.94.

HRMS m/z: [M + H]⁺ calcd for C₂₂H₁₈NO₂, 330.1489; found, 330.1489.
5a 3-chloro-6-phenyl-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the 4a (122 mg, 0.4 mmol) and phenylboronic acid (73 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 89% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.01 (s, 2H), 7.58 (d, $J = 11.3$ Hz, 2H), 7.46 (s, 1H), 7.38 (s, 3H), 7.30 (s, 3H), 7.18 (d, $J = 8.6$ Hz, 1H), 4.29 (d, $J = 12.4$ Hz, 1H), 2.90 (s, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 164.40, 147.32, 137.55, 136.21, 136.10, 133.15, 130.69, 130.55, 129.87, 128.56, 128.50, 128.22, 127.96, 127.19, 127.04, 126.46, 124.53, 36.37.

HRMS m/z: [M + H]$^+$ calcd for C$_{21}$H$_{17}$NCl, 304.0815; found, 304.0814.

5b 3-chloro-6-(p-tolyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the 4a (122 mg, 0.4 mmol) and p-tolylboronic acid (82 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 90% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.89 (s, 2H), 7.53 (d, $J = 11.2$ Hz, 2H), 7.45 (d, $J = 9.8$ Hz, 1H), 7.28 (s, 3H), 7.16 (d, $J = 17.7$ Hz, 3H), 4.23 (d, $J = 11.1$ Hz, 1H), 2.83 (d, $J = 11.0$ Hz, 1H), 2.31 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 164.23, 147.46, 141.10, 136.26, 136.11, 134.73, 133.09, 130.50, 129.86, 129.28, 128.42, 128.16, 127.97, 127.10, 127.01, 126.43, 124.32, 36.21, 21.36.

HRMS m/z: [M + H]$^+$ calcd for C$_{21}$H$_{15}$ClN, 318.0971; found, 318.0982.

5c 6-(m-tolyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the 4a (122 mg, 0.4 mmol) and m-
tolylboronic acid (82 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 87% yield.

**1H NMR (400 MHz, CDCl₃)**
δ 7.72 (p, J = 8.3, 7.6 Hz, 2H), 7.50 (d, J = 21.9 Hz, 2H), 7.41 (s, 1H), 7.21 (d, J = 8.3 Hz, 4H), 7.10 (d, J = 23.6 Hz, 2H), 4.22 (d, J = 13.3 Hz, 1H), 2.80 (s, 1H), 2.25 (s, 3H).

**13C NMR (151 MHz, CDCl₃)**
δ 165.09, 149.53, 139.16, 137.52, 136.27, 136.10, 133.15, 131.57, 130.55, 129.87, 128.61, 128.49, 128.42, 128.20, 127.18, 127.08, 126.46, 125.13, 124.50, 36.50, 21.45.

HRMS m/z: [M + H]+ calcd for C₂₁H₁₇ClN, 318.0971; found, 318.0990.

![5d 3-chloro-6-(o-tolyl)-7H-dibenzo[bd]azepine](image)

5d 3-chloro-6-(o-tolyl)-7H-dibenzo[bd]azepine

Synthesised according to the general method, after addition of the 4a (122 mg, 0.4 mmol) and o-tolylboronic acid (82 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 80% yield.

**1H NMR (400 MHz, CDCl₃)**
δ 7.70 (d, J = 8.5 Hz, 2H), 7.53 (s, 1H), 7.40 (d, J = 5.5 Hz, 2H), 7.31 (d, J = 9.7 Hz, 3H), 7.23 (d, J = 6.1 Hz, 3H), 3.98 (dd, J = 12.5, 4.3 Hz, 1H), 3.18 (dd, J = 12.0, 4.3 Hz, 1H), 2.39 (s, 3H).

**13C NMR (151 MHz, CDCl₃)**
δ 168.55, 146.75, 139.86, 135.97, 135.84, 135.78, 133.17, 130.94, 130.55, 129.55, 129.07, 128.49, 128.27, 127.96, 127.32, 126.29, 125.71, 124.73, 40.93, 20.58.

HRMS m/z: [M + H]+ calcd for C₂₁H₁₇ClN, 318.0971; found, 318.0972.

![5e 3-chloro-6-(4-methoxyphenyl)-7H-dibenzo[bd]azepine](image)

5e 3-chloro-6-(4-methoxyphenyl)-7H-dibenzo[bd]azepine

Synthesised according to the general method, after addition of the 4a (122 mg, 0.4 mmol) and 4-methoxyphenylboronic acid (91 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 30:1) to give the desired product as a yellow liquid in 79% yield.

**1H NMR (400 MHz, CDCl₃)**
δ 7.95 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 14.5 Hz, 2H), 7.41 (s, 1H), 7.23 (s, 3H), 7.11 (d, J = 8.6 Hz, 1H), 6.84 (d, J = 18.7 Hz, 2H), 4.21 (d, J = 12.5 Hz, 1H), 3.72 (s, 3H), 2.82 (d, J = 12.4 Hz, 1H).
\[ ^{13}C \text{ NMR (151 MHz, CDCl}_3 \] \( \delta \) 163.13, 161.75, 147.56, 136.27, 136.17, 133.09, 130.51, 130.00, 129.84, 129.74, 128.40, 128.17, 127.65, 127.09, 126.97, 126.40, 124.16, 55.31, 36.06.

HRMS m/z: [M + H]^+ calcd for C\(_{21}\)H\(_{17}\)ClNO, 334.0920; found, 334.0930.

5f 3-chloro-6-(4-chlorophenyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the 4a (122 mg, 0.4 mmol) and 4-chlorophenylboronic acid (94 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 89% yield.

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \] \( \delta \) 7.90 (d, \( J = 27.6 \text{ Hz, 2H} \)), 7.54 (d, \( J = 27.4 \text{ Hz, 2H} \)), 7.38 (s, 2H), 7.28 (s, 3H), 7.13 (s, 1H), 4.16 (d, \( J = 32.6 \text{ Hz, 1H} \)), 2.87 (d, \( J = 32.8 \text{ Hz, 1H} \)).

\[ ^{13}C \text{ NMR (151 MHz, CDCl}_3 \] \( \delta \) 163.50, 146.24, 136.24, 135.89, 133.27, 130.58, 129.31, 128.80, 128.62, 128.33, 127.35, 126.95, 126.46, 124.76, 36.21.

HRMS m/z: [M + H]^+ calcd for C\(_{20}\)H\(_{13}\)Cl\(_2\)N, 338.0425; found, 338.0430.

\[ \begin{array}{c}
\text{Cl} \\
\text{N} \\
\text{Cl}
\end{array} \]

5g 6-(4-bromophenyl)-3-chloro-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the 4a (122 mg, 0.4 mmol) and 4-bromophenylboronic acid (120 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 88% yield.

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \] \( \delta \) 7.81 (t, \( J = 9.2 \text{ Hz, 2H} \)), 7.53 (s, 2H), 7.42 (s, 2H), 7.24 (s, 3H), 7.14 (s, 1H), 4.15 (d, \( J = 23.0 \text{ Hz, 1H} \)), 2.85 (d, \( J = 15.2 \text{ Hz, 1H} \)).

\[ ^{13}C \text{ NMR (151 MHz, CDCl}_3 \] \( \delta \) 163.18, 147.90, 146.33, 136.19, 135.92, 133.27, 132.16, 130.59, 129.51, 128.63, 128.33, 127.36, 127.07, 126.64, 125.49, 124.79, 36.81.

HRMS m/z: [M + H]^+ calcd for C\(_{20}\)H\(_{13}\)BrClN, 381.9920; found, 381.9921.
**5h 3-chloro-6-(3-(trifluoromethyl)phenyl)-7H-dibenzo[b,d]azepine**

Synthesised according to the general method, after addition of the 4a (122 mg, 0.4 mmol) and 3-(trifluoromethyl)phenylboronic acid (114 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 43% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.22 (d, $J = 34.9$ Hz, 2H), 7.62 (s, 3H), 7.52 (s, 1H), 7.35 (d, $J = 6.3$ Hz, 3H), 7.19 (s, 1H), 4.30 (dd, $J = 30.3$, 12.8 Hz, 1H), 2.88 (s, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 162.73, 146.85, 137.98, 136.08, 135.80, 133.40, 131.06, 130.64, 129.88, 129.16, 128.79, 128.44, 127.50, 127.20, 126.98, 126.55, 125.07, 124.82, 36.85.

HRMS m/z: [M + H]$^+$ calcld for C$_{21}$H$_{14}$F$_3$ClN, 372.0689; found, 372.0690.

### 6. Large-Scale Experiment

Synthesised according to the general method, and the amount of material is magnified tenfold. After addition of the 1a (1.0 g, 4 mmol) and phenylboronic acid (0.7 g, 6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using an oil bath. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow solid in 85% yield. The product are shown below.

![Fig. S1 The product of large-scale experiment](image)
7. General Method for the Synthesis of 6a and 7a

To the solution of A (0.3 mmol, 1 eq) and 2a (0.45 mmol, 1.5 eq) in the THF/H₂O (THF : H₂O = 5:1, 4.8 mL) was added Pd(PPh₃)₄ (0.03 mmol, 0.1 eq) and Na₂CO₃ (0.6 mmol, 2 eq), heated to 68 °C, then stirred at N₂ atmosphere for about 5 h. The reaction was then cooled to room temperature and diluted with H₂O, extracted three times with EA, dried by Na₂SO₄ and evaporated under a vacuum. The crude material was purified by column chromatography to give the desired product.

8. Characterization Data of Products 6a and 7a

Synthesised according to the general method. The crude material was purified by column chromatography (PE : EA = 60:1) to give the desired product as a yellow liquid in 86% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, J = 4.9 Hz, 2H), 7.80 – 7.68 (m, 4H), 7.67 – 7.56 (m, 3H), 7.48 (dd, J = 6.9, 2.8 Hz, 3H), 7.40 (t, J = 4.6 Hz, 4H), 7.34 (d, J = 5.9 Hz, 1H), 4.41 (d, J = 12.3 Hz, 1H), 3.08 (d, J = 12.2 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 162.36, 146.21, 136.94, 136.83, 136.31, 131.71, 131.36, 129.48, 128.54, 128.31, 127.84, 127.19, 126.90, 126.75, 125.09, 124.68, 36.20.

HRMS m/z: [M + H]⁺ calcd for C₂₆H₁₉N, 346.1590; found, 346.1587.

Synthesised according to the general method. The crude material was purified by column chromatography (PE : EA = 60:1) to give the desired product as a yellow liquid in 63% yield.
1H NMR (400 MHz, CDCl₃) δ 8.09 (t, J = 7.8 Hz, 2H), 7.58 (d, J = 22.7 Hz, 6H), 7.47 (d, J = 10.1 Hz, 1H), 7.40 (s, 2H), 7.32 (s, 4H), 7.19 (d, J = 15.5 Hz, 1H), 4.34 (dt, J = 12.6, 6.8 Hz, 1H), 2.94 (dt, J = 12.6, 6.6 Hz, 1H).

13C NMR (151 MHz, CDCl₃) δ 162.88, 146.63, 143.45, 139.14, 136.34, 136.25, 133.22, 130.59, 129.92, 128.88, 128.56, 128.51, 128.29, 127.86, 127.27, 127.13, 127.08, 126.53, 124.56, 36.32.

HRMS m/z: [M + H]^+ calcd for C_{26}H_{19}N, 380.1128; found, 380.1187.

9. Synthesis Method and Characterization Data of Products 8a, 8b and 8c

To a solution of 5a (42.5 mg, 0.14 mmol, 1 eq) in toluene was added Dave-Phos (4.4 mg, 0.011 mmol, 0.08 eq), Pd₂(dba)_3 (6.4 mg, 0.007 mmol, 0.05 eq), t-BuONa (19.4 mg, 0.2 mmol, 1.4 eq), cyclohexylamine (16.9 mg, 0.17 mmol, 1.2 eq) and the mixture was stirred overnight at 100 °C under nitrogen atmosphere. The reaction mixture was then cooled to room temperature and quenched with water, extracted three times with EA, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography (PE : EA = 30:1 ) to give the desired product as a yellow oil in 54% yield.

1H NMR (400 MHz, CD₃OD) δ 8.04 – 7.95 (m, 2H), 7.58 (dd, J = 7.5, 1.1 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.45 (dd, J = 6.4, 3.7 Hz, 1H), 7.35 (dd, J = 7.2, 1.3 Hz, 1H), 7.32 – 7.23 (m, 2H), 6.66 (dd, J = 6.1, 2.4 Hz, 2H), 4.32 (d, J = 12.3 Hz, 1H), 3.31 (s, 1H), 2.98 (d, J = 12.2 Hz, 1H), 2.09 (t, J = 14.4 Hz, 2H), 1.79 (d, J = 13.3 Hz, 2H), 1.67 (d, J = 12.7 Hz, 1H), 1.49 – 1.35 (m, 2H), 1.30 – 1.17 (m, 3H).

13C NMR (151 MHz, CD₃OD) δ 166.19, 149.24, 148.28, 139.52, 138.72, 136.60, 131.52, 131.15, 129.61, 129.07, 128.37, 128.16, 128.10, 127.94, 122.04, 113.32, 109.65, 52.92, 38.04, 34.31, 34.19, 27.13, 26.26.

HRMS m/z: [M + H]^+ calcd for C_{26}H_{26}N₂, 367.2169; found, 367.2171.

To a solution of 5a (42.5 mg, 0.14 mmol, 1 eq) in toluene was added S-Phos (2.9 mg, 0.007 mmol, 0.05 eq), Pd₂(dba)_3 (7.7 mg, 0.008 mmol, 0.06 eq), t-BuOK (31.4 mg, 0.28 mmol, 2 eq), piperidine (17.9 mg, 0.21 mmol, 1.5 eq) and the mixture was stirred overnight at 100 °C under nitrogen atmosphere. The reaction mixture was then cooled to room temperature and quenched with water, extracted three times with EA, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography (PE : EA = 30:1 ) to give the desired product as a yellow oil in 86% yield.

1H NMR (400 MHz, CD₃OD) δ 8.03 (d, J = 2.9 Hz, 2H), 7.61 (d, J = 5.5 Hz, 2H), 7.45 (s, 3H), 7.38 (s,
17

1H), 7.32 (d, J = 3.0 Hz, 2H), 6.99 (d, J = 14.2 Hz, 2H), 4.36 (d, J = 12.5 Hz, 1H), 3.26 (s, 4H), 2.96 (d, J = 12.2 Hz, 1H), 1.73 (s, 4H), 1.63 (s, 2H).

$^{13}$C NMR (151 MHz, CD$_3$OD) $\delta$ 166.32, 152.99, 148.07, 139.39, 138.24, 137.04, 131.60, 131.03, 129.63, 129.10, 128.64, 128.61, 128.23, 128.04, 124.43, 115.72, 113.68, 51.55, 37.82, 26.80, 25.43.

HRMS m/z: [M + H]$^+$ calcd for C$_{25}$H$_{24}$N$_2$, 353.2012; found, 353.2010.

N

N

Cl

toluene, 100 °C, overnight

25a

8c

Synthesised according to the general method same as 8a. The crude material was purified by column chromatography (PE : EA = 30:1) to give the desired product as a yellow oil in 47% yield.

$^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 8.01 (ddd, J = 4.0, 2.2, 0.6 Hz, 2H), 7.61 (dd, J = 7.2, 1.4 Hz, 1H), 7.52 (d, J = 8.6 Hz, 1H), 7.48 – 7.43 (m, 3H), 7.37 (dd, J = 7.0, 1.6 Hz, 1H), 7.34 – 7.26 (m, 2H), 6.92 (d, J = 2.4 Hz, 1H), 6.84 (ddd, J = 8.4, 2.4, 0.6 Hz, 1H), 4.35 (d, J = 12.3 Hz, 1H), 2.99 (d, J = 12.3 Hz, 1H), 1.39 (s, 9H).

$^{13}$C NMR (151 MHz, CD$_3$OD) $\delta$ 166.32, 148.27, 147.84, 139.44, 138.46, 136.84, 131.57, 130.75, 129.62, 129.09, 128.54, 128.42, 128.20, 127.99, 117.37, 114.77, 52.56, 37.94, 30.14.

HRMS m/z: [M + H]$^+$ calcd for C$_{24}$H$_{24}$N, 341.2012; found, 341.2014.

10. Characterization Data of Controlled Experiment Intermediate C

Synthesised according to the general method for the synthesis of dibenzo-[b,d]azepines products, after addition of the 1a (100 mg, 0.4 mmol) and phenylboronic acid (73 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate only for 1 hour in order to capture the intermediate C. The crude material was purified by column chromatography (PE : EA = 2:1) to give the desired product as a yellow oil in 18% yield.

$^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 7.79 (d, J = 7.4 Hz, 2H), 7.66 (d, J = 8.1 Hz, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.41 – 7.34 (m, 4H), 7.31 (dd, J = 7.2, 1.4 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.21 – 7.17 (m, 1H), 7.16 – 7.09 (m, 2H), 4.21 (dd, J = 107.0, 17.5 Hz, 2H), 1.93 (s, 3H).

$^{13}$C NMR (151 MHz, CD$_3$OD) $\delta$ 200.72, 171.83, 140.15, 137.90, 136.46, 136.23, 135.27, 134.43, 132.30, 131.48, 131.31, 129.63, 129.22, 129.20, 129.18, 128.18, 126.19, 49.43, 49.28, 49.14, 49.00, 48.86, 48.72, 48.57, 43.94, 23.33.

HRMS m/z: [M + H]$^+$ calcd for C$_{26}$H$_{19}$N, 330.1489; found, 330.1488.
11. NMR Spectra for Compounds of this paper:

$^1$H NMR Spectra of Compound 1a:

$^1$H NMR Spectra of Compound 3a:
$^{13}$C NMR Spectra of Compound 3a:

$^1$H NMR Spectra of Compound 3b:
$^{13}$C NMR Spectra of Compound 3b:

$^1$H NMR Spectra of Compound 3c:
$^{13}$C NMR Spectra of Compound 3c:

$^1$H NMR Spectra of Compound 3d:
$^{13}\text{C}$ NMR Spectra of Compound 3d:

$^1\text{H}$ NMR Spectra of Compound 3e:
$^{13}$C NMR Spectra of Compound 3e:

$^1$H NMR Spectra of Compound 3f:
$^{13}$C NMR Spectra of Compound 3f:

$^1$H NMR Spectra of Compound 3g:
$^{13}$C NMR Spectra of Compound 3g:

$^1$H NMR Spectra of Compound 3h:
$^{13}$C NMR Spectra of Compound 3h:

$^1$H NMR Spectra of Compound 3i:
$^{13}$C NMR Spectra of Compound 3i:

$^1$H NMR Spectra of Compound 3j:
$^{13}$C NMR Spectra of Compound 3j:

$^1$H NMR Spectra of Compound 3k:
$^{13}$C NMR Spectra of Compound 3k:

![13C NMR Spectra of Compound 3k](image)

$^1$H NMR Spectra of Compound 3l:

![1H NMR Spectra of Compound 3l](image)
$^{13}$C NMR Spectra of Compound 3l:

$^1$H NMR Spectra of Compound 3m:
\(^{13}\)C NMR Spectra of Compound 3m:

\(^{1}\)H NMR Spectra of Compound 3n:
$^{13}$C NMR Spectra of Compound 3n:

$^1$H NMR Spectra of Compound 3o:
$^{13}$C NMR Spectra of Compound 3o:

$^1$H NMR Spectra of Compound 3p:
$^{13}$C NMR Spectra of Compound 3p:

$^1$H NMR Spectra of Compound 4a:
$^1$H NMR Spectra of Compound 5a:

$^{13}$C NMR Spectra of Compound 5a:
$^1$H NMR Spectra of Compound 5b:

$^{13}$C NMR Spectra of Compound 5b:
$^1$H NMR Spectra of Compound 5c:

$^{13}$C NMR Spectra of Compound 5c:
$^1$H NMR Spectra of Compound 5d:

$^{13}$C NMR Spectra of Compound 5d:
$^1$H NMR Spectra of Compound 5e:

$^{13}$C NMR Spectra of Compound 5e:
$^1$H NMR Spectra of Compound $5f$:

$^{13}$C NMR Spectra of Compound $5f$: 
$^1$H NMR Spectra of Compound 5g:

$^{13}$C NMR Spectra of Compound 5g:
$^1$H NMR Spectra of Compound 5h:

$^{13}$C NMR Spectra of Compound 5h:
$^1$H NMR Spectra of Compound 6a:

$^{13}$C NMR Spectra of Compound 6a:
$^1$H NMR Spectra of Compound 7a:

$^{13}$C NMR Spectra of Compound 7a:
$^1$H NMR Spectra of Compound 8a:

$^{13}$C NMR Spectra of Compound 8a:
$^1$H NMR Spectra of Compound 8b:

$^{13}$C NMR Spectra of Compound 8b:
**$^1$H NMR Spectra of Compound 8c:**

![H NMR Spectra of Compound 8c]

**$^{13}$C NMR Spectra of Compound 8c:**

![C NMR Spectra of Compound 8c]
$^1$H NMR Spectra of intermediate C:

$^{13}$C NMR Spectra of intermediate C: