Rhodium(I)-catalysed intermolecular alkyne insertion into (2-pyridylmethylene)cyclobutenes

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Electronic Supplementary Information

General. All reactions were carried out with standard Schlenk techniques under an argon or nitrogen atmosphere. Column chromatography was carried out on Wakogel® C-200 (75–150 μm). Preparative thin-layer chromatography (TLC) was performed on Wakogel® B-5F. Proton chemical shifts were referenced to residual CHCl₃ signal at 7.26 ppm. Carbon chemical shifts were referenced to CDCl₃ at 77.0 ppm (¹³C NMR signal observed at 88 ppm is considered to be noise and not related to signals of products).

Materials. Cyclobutenones 1¹ and diarylacetylenes 2² were prepared by the literature methods. All other reagents and solvents were obtained from commercial sources and used without further purification.

1. Preparation of Cyclobutenones

\[
\begin{array}{c|c|c}
R^1 & R^2 & \text{R}^1 \text{R}^2 \text{Cl} \\
\hline
\text{Ph} & \text{H} & 64\% \\
4-\text{MeC}_6\text{H}_4 & \text{H} & 57\%
\end{array}
\]

\[
\begin{array}{c|c|c}
R^1 & R^2 & \text{R}^1 \text{R}^2 \text{Cl} \\
\hline
4-\text{MeOC}_6\text{H}_4 & \text{H} & 60\% \\
4-\text{ClC}_6\text{H}_4 & \text{H} & 27\%
\end{array}
\]

\[
\begin{array}{c|c|c}
R^1 & R^2 & \text{R}^1 \text{R}^2 \\
\hline
1-\text{naphthyl} & \text{H} & 9\% \\
\text{Ph} & \text{Pr} & 25\%
\end{array}
\]

2. Preparation of [(2-Pyridyl)methylene]cyclobutenes 1

**Wittig reaction:** To a solution of triphenyl(2-pyridylmethyl)phosphonium chloride (3.0 mmol) in THF (10 mL) was added \(n\)-BuLi (1.6 M hexane solution, 2.8 mL, 4.5 mmol) at 0 °C, and the mixture was further stirred for 2 h at the same temperature. To the resulting ylide solution was added cyclobutenone (2.0 mmol), and the mixture was stirred overnight at 60 °C. After cooling to room temperature, the reaction mixture was filtered (hexane), and the filtrate was concentrated. The residue was purified by column chromatography on silica gel to afford 1. The stereoisomers of cyclobutenes 1a, 1b, 1c, 1h, 1j, 1l and 1n could be separated.

**McMurry coupling:** To a suspension of zinc (20.7 mmol) in THF (40 mL) was added dropwise TiCl\(_4\) (1.0 M CH\(_2\)Cl\(_2\) solution, 8.4 mL, 8.4 mmol) with cooling in an ice-salt bath, and the mixture was further stirred for 20 min at the same temperature and for 2.5 h at 80–90 °C. To the resulting mixture was added a solution of cyclobutenone (3.0 mmol) and 2-pyridyl ketone (9.0 mmol) in THF (60 mL), and the mixture was stirred for 5 h at 80–90 °C.
After cooling to room temperature, 10% K₂CO₃ aqueous solution was added to the reaction mixture, and the mixture was extracted three times with AcOEt. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and the filtrate was concentrated. The residue was purified by column chromatography on silica gel to afford 1.

(E)-1-Phenyl-3-[(2-pyridyl)methylene]cyclobutene ((E)-1a).  

(hexane:AcOEt = 10:1). Brown solid, mp 93–98 °C; ¹H NMR (500 MHz, CDCl₃) δ 3.67 (d, J
= 1.0 Hz, 2H), 6.28 (s, 1H), 6.69 (s, 1H), 7.01–7.05 (m, 1H), 7.30–7.42 (m, 4H), 7.48–7.51 (m, 2H), 7.58 (dt, $J = 2.0$, 7.8 Hz, 1H), 8.52–8.55 (m, 1H); $^{13}$C NMR (75.6 MHz, CDCl$_3$) δ 37.3, 114.8, 120.5, 121.4, 125.7, 128.5, 128.8, 129.0, 133.6, 135.9, 143.7, 149.5, 152.4, 157.0; HRMS (ESI) calcd for C$_{16}$H$_{14}$N [M + H]$^+$ 220.1121, found 220.1125.

(Z)-1-Phenyl-3-[(2-pyridyl)methylene]cyclobutene ((Z)-1a). $R_f$ = 0.29 (hexane:AcOEt = 10:1). Brown solid, mp 76–84 °C; $^1$H NMR (301 MHz, CDCl$_3$) δ 3.32 (s, 2H), 5.99 (s, 1H), 6.96–7.03 (m, 1H), 7.20–7.26 (m, 2H), 7.27–7.39 (m, 3H), 7.45–7.50 (m, 2H), 7.50–7.59 (m, 1H), 8.53–8.57 (m, 1H); $^{13}$C NMR (75.6 MHz, CDCl$_3$) δ 36.7, 114.3, 120.3, 122.1, 125.9, 128.4, 128.7, 128.9, 133.6, 135.9, 141.8, 149.5, 153.8, 157.3; HRMS (ESI) calcd for C$_{16}$H$_{14}$N [M + H]$^+$ 220.1121, found 220.1125.

(E)-3-[(6-Methyl-2-pyridyl)methylene]-1-phenylcyclobutene ((E)-1b). $R_f$ = 0.36 (hexane:AcOEt = 10:1). Yellow solid, mp 97–104 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 2.54 (s, 3H), 3.64 (s, 2H), 6.28 (s, 1H), 6.67 (s, 1H), 6.90 (d, $J = 8.0$ Hz, 1H), 7.18 (d, $J = 8.0$ Hz, 1H), 7.27–7.33 (m, 1H), 7.36–7.41 (m, 2H), 7.46–7.50 (m, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ
24.6, 37.2, 115.1, 118.2, 120.0, 125.6, 128.5, 128.7, 129.1, 133.6, 136.1, 143.4, 152.0, 156.4, 157.9; HRMS (ESI) calcd for C_{17}H_{16}N [M + H]^+ 234.1277, found 234.1279.

\[(Z)-3-[(6\text{-Methyl}-2\text{-pyridyl})\text{methylene}]-1\text{-phenylecyclobutene ((Z)-1b).} \ \ R_f = 0.45 \] (hexane:AcOEt = 10:1). Yellow solid, mp 70–72 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.57 (s, 3H), 3.36 (s, 2H), 6.01 (s, 1H), 6.92 (d, \(J = 7.5\) Hz, 1H), 7.11 (d, \(J = 7.5\) Hz, 1H), 7.29 (s, 1H), 7.30–7.35 (m, 1H), 7.36–7.47 (m, 2H), 7.47–7.54 (m, 3H); \(^{13}\)C NMR (75.6 MHz, CDCl\(_3\)) \(\delta\) 24.8, 36.7, 114.6, 119.2, 120.0, 125.9, 128.5, 128.8, 128.9, 133.7, 136.3, 141.6, 153.7, 156.7, 158.1; HRMS (ESI) calcd for C_{17}H_{16}N [M + H]^+ 234.1277, found 234.1276.

\[(E)-3-[(4,6\text{-Dimethyl}-2\text{-pyridyl})\text{methylene}]-1\text{-phenylecyclobutene ((E)-1c).} \ \ R_f = 0.31 \] (hexane:AcOEt = 10:1). Brown solid, mp 80–84 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.29 (s, 3H), 2.49 (s, 3H), 3.64 (s, 2H), 6.26 (s, 1H), 6.67 (s, 1H), 6.75 (s, 1H), 7.02 (s, 1H), 7.28–7.33 (m, 1H), 7.36–7.40 (m, 2H), 7.47–7.50 (m, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 21.0, 24.3, 37.3, 115.1, 119.2, 121.3, 125.6, 128.5, 128.7, 129.2, 133.7, 143.2, 147.0, 151.8, 156.2, 157.6; HRMS (ESI) calcd for C_{18}H_{18}N [M + H]^+ 248.1434, found 248.1439.
(Z)-3-[(4,6-Dimethyl-2-pyridyl)methylene]-1-phenylcyclobutene ((Z)-1c). \( R_f = 0.37 \) (hexane:AcOEt = 10:1). Brown oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 2.29 (s, 3H), 2.53 (s, 3H), 3.35 (s, 2H), 5.98 (s, 1H), 6.77 (s, 1H), 6.94 (s, 1H), 7.28 (s, 1H), 7.29–7.34 (m, 1H), 7.36–7.42 (m, 2H), 7.50–7.54 (m, 2H); \(^1^3\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 20.9, 24.5, 36.7, 114.6, 120.2, 121.1, 125.9, 128.5, 128.8, 133.8, 141.4, 147.1, 153.5, 156.5, 157.8; HRMS (ESI) calcd for C\(_{18}\)H\(_{18}\)N [M + H]\(^+\) 248.1434, found 248.1434.

(E)- and (Z)-3-[(3-Methyl-2-pyridyl)methylene]-1-phenylcyclobutene (1d). Brown solid; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 2.36 (s, 3H; \( E \)), 2.37 (s, 3H; \( Z \)), 3.39 (s, 2H; \( Z \)), 3.76 (s, 2H; \( E \)), 6.12 (s, 1H; \( Z \)), 6.35 (s, 1H; \( E \)), 6.71 (s, 1H; \( E \)), 6.94–7.00 (m; \( E + Z \)), 7.29–7.42 (m; \( E + Z \)), 7.50–7.56 (m; \( E + Z \)), 8.41–8.45 (m, 1H; \( E \)), 8.46–8.49 (m, 1H; \( Z \)); \(^1^3\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 19.0, 19.1, 36.6, 38.0, 110.1, 110.6, 120.40, 120.45, 125.8, 125.9, 126.5, 128.1, 128.45, 128.47, 128.6, 128.8, 130.09, 130.12, 130.2, 133.9, 137.3, 137.4, 142.4, 145.1, 146.89, 146.95, 153.8, 154.1, 155.4, 155.7; HRMS (ESI) calcd for C\(_{17}\)H\(_{16}\)N [M + H]\(^+\) 234.1277, found 234.1276.
(E)- and (Z)-1-Phenyl-3-[(2-quinolyl)methylene]cyclobutene (1e). Brown solid; $^1$H NMR (500 MHz, CDCl$_3$) δ 3.42 (s, 2H; Z), 3.75 (s, 2H; E), 6.22 (s, 1H; Z), 6.51 (s, 1H; E), 6.73 (s, 1H; E), 7.31–7.57 (m; E + Z), 7.64–7.76 (m; E + Z), 7.98–8.09 (m; E + Z); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 36.9, 37.4, 115.0, 115.8, 119.8, 120.9, 125.5, 125.6, 125.8, 126.0, 126.4, 126.5, 127.31, 127.34, 128.5, 128.6, 128.9, 129.0, 129.1, 129.2, 129.3, 129.4, 133.4, 133.5, 135.6, 135.8, 143.6, 145.3, 148.3, 148.4, 152.8, 154.7, 157.1, 157.4; HRMS (ESI) calcd for C$_{20}$H$_{16}$N [M + H]$^+$ 270.1277, found 270.1277.

(E)- and (Z)-1-Phenyl-3-[(2-pyrazyl)methylene]cyclobutene (1f). Brown solid; $^1$H NMR (500 MHz, CDCl$_3$) δ 3.39 (s, 2H; Z), 3.68 (s, 2H; E), 5.99 (s, 1H; Z), 6.23 (s, 1H; E), 6.67 (s, 1H; E), 7.27 (s, 1H; Z), 7.31–7.43 (m; E + Z), 7.48–7.55 (m; E + Z), 8.25 (d, J = 2.0 Hz, 1H; E), 8.28 (d, J = 3.0 Hz, 1H; Z), 8.45 (t, J = 2.0 Hz, 1H; E), 8.50 (t, J = 2.0 Hz, 1H; Z), 8.52 (d, J = 1.0 Hz, 1H; Z), 8.57 (d, J = 1.0 Hz, 1H; E); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 36.8, 37.6, 110.4, 111.1, 126.0, 126.2, 128.56, 128.60, 128.8, 129.3, 129.4, 133.27, 133.3, 140.7, 140.8, 143.4, 143.8, 144.2, 144.7, 146.4, 153.1, 153.3, 154.0, 155.2; HRMS (ESI) calcd for C$_{15}$H$_{13}$N$_2$ [M + H]$^+$ 221.1073, found 221.1073.
(E)- and (Z)-3-Benzylidene-1-phenylcyclobutene (1g). Yellow solid; $^1$H NMR (500 MHz, CDCl$_3$) δ 3.42 (s, 2H; minor), 3.69 (s, 2H; major), 6.02 (s, 1H; minor), 6.23 (s, 1H; major), 6.74 (s, 1H; major), 7.16 (s, 1H; minor), 7.23–7.60 (m, 10H; major + minor); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 36.8, 36.9, 114.7, 115.0, 125.4, 125.6, 126.06, 126.11, 126.9, 127.20, 127.24, 128.4, 128.51, 128.53, 128.7, 129.4, 133.8, 137.5, 138.1, 139.6, 150.1; HRMS (ESI) calcd for C$_{17}$H$_{14}$Na [M + Na]$^+$ 241.0988, found 241.0985.

(E)-1-(4-Methylphenyl)-3-[(2-pyridyl)methylene]cyclobutene ((E)-1h). $R_f$ = 0.21 (hexane:AcOEt = 10:1). Brown solid, mp 68–72 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 2.38 (s, 3H), 3.64 (s, 2H), 6.25 (s, 1H), 6.62 (s, 1H), 6.99–7.03 (m, 1H), 7.19 (d, $J = 7.5$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 1H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.56 (dt, $J = 2.0$, 7.8 Hz, 1H), 8.51–8.54 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 21.5, 37.3, 114.3, 120.3, 121.3, 125.7, 128.0, 129.3, 130.9, 135.9, 139.1, 144.0, 149.4, 152.4, 157.2; HRMS (ESI) calcd for C$_{17}$H$_{16}$N [M + H]$^+$ 234.1277, found 234.1277.
(Z)-1-(4-Methylphenyl)-3-[(2-pyridyl)methylene]cyclobutene ((Z)-1h). \( R_f = 0.30 \) (hexane:AcOEt = 10:1). Brown oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 2.38 (s, 3H), 3.35 (s, 2H), 6.00 (s, 1H), 7.01–7.06 (m, 1H), 7.18–7.24 (m, 3H), 7.25–7.30 (m, 1H), 7.40–7.44 (m, 2H), 7.57–7.63 (m, 1H), 8.56–8.59 (m, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 21.5, 36.8, 113.9, 120.3, 122.1, 126.0, 127.7, 129.3, 131.0, 136.0, 139.3, 142.1, 149.5, 154.1, 157.5; HRMS (ESI) calcd for C\(_{17}\)H\(_{16}\)N [M + H]\(^+\) 234.1277, found 234.1277.

(E)- and (Z)-1-(4-Methylphenyl)-3-[(3-methyl-2-pyridyl)methylene]cyclobutene (1i). Yellow solid; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 2.355 (s, 3H; \( E \)), 2.361 (s, 3H; \( Z \)), 2.39 (s, 3H + 3H; \( E + Z \)), 3.36 (s, 2H; \( Z \)), 3.73 (s, 2H; \( E \)), 6.09 (s, 1H; \( Z \)), 6.32 (s, 1H; \( E \)), 6.64 (s, 1H; \( E \)), 6.92–7.00 (m, 1H + 1H; \( E + Z \)), 7.18–7.22 (m, 2H + 2H; \( E + Z \)), 7.34 (s, 1H; \( Z \)), 7.36–7.46 (m, 3H + 3H; \( E + Z \)), 8.40–8.43 (m, 1H; \( E \)), 8.45–8.49 (m, 1H; \( Z \)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 19.0, 19.1, 21.5, 36.6, 38.0, 109.6, 110.1, 120.28, 120.31, 125.8, 126.0, 127.5, 129.1, 129.2,
130.0, 130.1, 131.2, 137.3, 137.4, 138.8, 139.0, 142.7, 145.4, 146.88, 146.94, 154.0, 154.2, 155.5, 155.8; HRMS (ESI) calcd for C_{18}H_{18}N [M + H]^+ 248.1434, found 248.1434.

(E)-1-(4-Methoxyphenyl)-3-[(2-pyridyl)methylene]cyclobutene ((E)-1j). \( R_f = 0.13 \) (hexane:AcOEt = 10:1). Brown solid, mp 115–119 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 3.63 (s, 2H), 3.83 (s, 3H), 6.22 (s, 1H), 6.53 (s, 1H), 6.88–6.93 (m, 2H), 6.98–7.02 (m, 1H), 7.32 (d, \( J = 8.0 \) Hz, 1H), 7.40–7.45 (m, 2H), 7.55 (dt, \( J = 1.5, 7.7 \) Hz, 1H), 8.50–8.53 (m, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 37.4, 55.3, 113.7, 114.0, 114.0, 120.2, 121.2, 126.6, 126.7, 127.3, 135.9, 144.1, 149.4, 152.1, 157.3, 160.2; HRMS (ESI) calcd for C\(_{17}\)H\(_{16}\)NO [M + H]^+ 250.1226, found 250.1226.

(Z)-1-(4-Methoxyphenyl)-3-[(2-pyridyl)methylene]cyclobutene ((Z)-1j). \( R_f = 0.20 \) (hexane:AcOEt = 10:1). Brown solid, mp 103–106 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 3.32 (s, 2H), 3.81 (s, 3H), 5.96 (s, 1H), 6.88–6.93 (m, 2H), 6.98–7.03 (m, 1H), 7.14 (s, 1H), 7.26 (d, \( J \)
= 8.0 Hz, 1H), 7.42–7.47 (m, 2H), 7.57 (dt, $J = 1.7, 7.7$ Hz, 1H), 8.56 (d, $J = 4.0$ Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 36.8, 55.2, 113.2, 114.0, 120.1, 121.9, 126.4, 126.7, 127.5, 135.9, 142.1, 149.4, 153.7, 157.5, 160.3; HRMS (ESI) calcd for C$_{17}$H$_{16}$NO [M + H]$^+$ 250.1226, found 250.1226.

(E)- and (Z)-1-(4-Methoxyphenyl)-3-[(3-methyl-2-pyridyl)methylene]cyclobutene (1k). Yellow solid; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 2.34 (s, 3H; $E$), 2.35 (s, 3H; $Z$), 3.34 (s, 2H, Z), 3.70 (s, 2H; $E$), 3.83 (s, 3H + 3H; $E + Z$), 6.05 (s, 1H; $Z$), 6.28 (s, 1H; $E$), 6.55 (s, 1H; $E$), 6.89–6.98 (m, 3H + 3H; $E + Z$), 7.24 (s, 1H; $Z$), 7.34–7.40 (m, 1H +1H; $E + Z$), 7.42–7.50 (m, 2H + 2H; $E + Z$), 8.40 (d, $J = 5.0$ Hz, 1H; $E$), 8.45 (d, $J = 4.5$ Hz, 1H; $Z$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 19.1, 19.2, 36.7, 38.1, 55.3, 109.0, 109.5, 114.0, 120.19, 120.22, 126.2, 127.0, 127.4, 127.6, 127.9, 129.9, 130.0, 137.3, 137.4, 142.8, 145.5, 146.87, 146.95, 153.8, 153.9, 155.6, 155.9, 160.1, 160.3; HRMS (ESI) calcd for C$_{18}$H$_{18}$NO [M + H]$^+$ 264.1383, found 264.1383.
(E)-1-(4-Chlorophenyl)-3-[(2-pyridyl)methylene|cyclobutene ((E)-II). \( R_f = 0.21 \) (hexane:AcOEt = 10:1). Brown solid, mp 108–114 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 3.65 (s, 2H), 6.28 (s, 1H), 6.66 (s, 1H), 7.01–7.06 (m, 1H), 7.30–7.43 (m, 5H), 7.58 (dt, \( J = 1.3, 7.8 \) Hz, 1H), 8.53 (d, \( J = 4.0 \) Hz, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 37.4, 115.3, 120.6, 121.6, 127.0, 128.8, 129.5, 132.1, 134.6, 136.0, 143.3, 149.6, 151.1, 156.9; HRMS (ESI) calcd for \( \text{C}_{16}\text{H}_{13}\text{ClN} [M + H]^+ \) 254.0731, found 254.0731.

(Z)-1-(4-Chlorophenyl)-3-[(2-pyridyl)methylene|cyclobutene ((Z)-II). \( R_f = 0.30 \) (hexane:AcOEt = 10:1). Brown solid, mp 82–86 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 3.32 (s, 2H), 6.01 (s, 1H), 7.04 (dd, \( J = 7.5, 5.0 \) Hz, 1H), 7.24 (d, \( J = 8.0 \) Hz, 1H), 7.28 (s, 1H), 7.31–7.36 (m, 2H), 7.39–7.43 (m, 2H), 7.58 (dt, \( J = 1.7, 7.6 \) Hz, 1H), 8.57 (d, \( J = 5.0 \) Hz, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 36.7, 114.8, 120.5, 122.3, 127.1, 128.8, 129.5, 132.1, 134.7, 136.0, 141.3, 149.5, 152.4, 157.1; HRMS (ESI) calcd for \( \text{C}_{16}\text{H}_{13}\text{ClN} [M + H]^+ \) 254.0731, found 254.0731.
\((E)\)- and \((Z)\)-1-(4-Chlorophenyl)-3-[(3-methyl-2-pyridyl)methylene]cyclobutene (1m). Brown solid; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.345 (s, 3H), 2.352 (s, 3H), 3.34 (s, 2H), 3.71 (s, 2H), 6.12 (s, 1H; \(Z\)), 6.35 (s, 1H; \(E\)), 6.67 (s, 1H; \(E\)), 6.93–7.00 (m, 1H + 1H; \(E + Z\)), 7.31–7.45 (m, 5H + 6H; \(E + Z\)), 8.38–8.42 (m, 1H; \(E\)), 8.43–8.47 (m, 1H; \(Z\)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 19.0, 19.1, 36.6, 38.0, 110.6, 111.1, 120.55, 120.60, 127.0, 127.1, 128.7, 129.0, 130.3, 130.7, 132.4, 134.3, 134.5, 137.4, 137.5, 142.0, 144.7, 146.9, 147.0, 152.4, 152.7, 155.2; HRMS (ESI) calcd for C\(_{17}\)H\(_{15}\)ClN [M + H]\(^+\) 268.0888, found 268.0887.

\[(E)\]-1-(1-Naphthyl)-3-[(2-pyridyl)methylene]cyclobutene \((E)\)-1n. \(R_f\) = 0.15 (hexane:AcOEt = 10:1). Brown oil; \(^1\)H NMR (301 MHz, CDCl\(_3\)) \(\delta\) 3.91 (s, 2H), 6.36 (s, 1H), 6.98 (s, 1H), 7.01–7.08 (m, 1H), 7.39 (d, \(J = 8.1\) Hz, 1H), 7.44–7.66 (m, 5H), 7.79–7.92 (m, 2H), 8.40 (d, \(J = 8.1\) Hz, 1H), 8.55–8.60 (m, 1H); \(^{13}\)C NMR (75.6 MHz, CDCl\(_3\)) \(\delta\) 39.6, 114.8, 120.5, 121.5, 124.9, 125.3, 126.0, 126.6, 126.9, 128.8, 129.8, 130.3, 131.1, 132.4, 133.8, 136.0, 144.4, 149.5, 151.2, 157.0; HRMS (ESI) calcd for C\(_{20}\)H\(_{16}\)N [M + H]\(^+\) 270.1277, found 270.1277.
(Z)-1-(1-Naphthyl)-3-[(2-pyridyl)methylene]cyclobutene ((Z)-1n). $R_f = 0.21$ (hexane:AcOEt = 10:1). Brown oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 3.62 (s, 2H), 6.07 (s, 1H), 7.05–7.10 (m, 1H), 7.32 (d, $J = 8.0$ Hz, 1H), 7.47–7.66 (m, 6H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 8.5$ Hz, 1H), 8.51 (d, $J = 8.5$ Hz, 1H), 8.62–8.65 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 39.2, 114.4, 120.5, 122.3, 125.2, 125.3, 126.0, 126.8, 127.0, 128.8, 130.0, 130.5, 131.3, 132.1, 133.8, 136.1, 142.5, 149.6, 152.8, 157.4; HRMS (ESI) calcd for $C_{20}H_{16}N$ [M + H]$^+$ 270.1277, found 270.1277.

(E)- and (Z)-1-Phenyl-3-[1-(2-pyridyl)ethylidene]cyclobutene (1o). Brown solid; $^1$H NMR (301 MHz, CDCl$_3$) $\delta$ 2.16 (s, 3H; major), 2.25 (s, 3H; minor), 3.36 (s, 2H; major), 3.57 (s, 2H; minor), 6.86 (s, 1H; minor), 7.03–7.12 (m, 1H + 1H; major + minor), 7.13 (s, 1H; major), 7.27–7.52 (m, 6H + 6H; major + minor), 7.56–7.68 (m, 1H + 1H; major + minor), 8.57–8.65 (m, 1H + 1H; major + minor); $^{13}$C NMR (75.6 MHz, CDCl$_3$) $\delta$ 15.5, 15.9, 35.7, 37.5, 119.7, 120.1, 120.5, 120.6, 121.0, 121.1, 125.4, 125.5, 127.9, 128.36, 128.40, 128.44,
128.5, 128.8, 133.8, 134.0, 135.6, 135.8, 138.4, 139.0, 148.96, 149.03, 149.4, 150.6, 158.8, 159.2; HRMS (ESI) calcd for C_{17}H_{16}N [M + H]^+ 234.1277, found 234.1277.

(E)- and (Z)-3-Phenyl-3-[phenyl(2-pyridyl)methylene]cyclobutene (1p). Yellow oil; 

$^1$H NMR (500 MHz, CDCl$_3$) δ 3.28 (s, 2H; major), 3.54 (s, 2H; minor), 6.63 (s, 1H; minor), 6.97–7.50 (m, 14H + 13H; major + minor), 8.51–8.55 (m, 1H; minor), 8.56–8.60 (m, 1H; major); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 36.5, 37.3, 120.8, 120.9, 123.5, 123.7, 125.59, 125.63, 126.2, 126.7, 126.8, 128.1, 128.18, 128.24, 128.4, 128.5, 128.6, 129.5, 129.7, 129.9, 133.7, 133.8, 135.7, 135.8, 139.2, 139.6, 139.8, 140.5, 149.2, 149.3, 153.1, 153.5, 158.9, 159.2; HRMS (ESI) calcd for C$_{22}$H$_{18}$N [M + H]$^+$ 296.1434, found 296.1434.

(E)-3-[(3-Methyl-2-pyridyl)methylene]-1-phenyl-2-propylcyclobutene (1q). Brown solid; 37–41 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 1.02–1.10 (m, 3H), 1.68–1.78 (m, 2H), 2.37 (s, 3H), 2.54 (t, $J = 7.2$ Hz, 2H), 3.63 (s, 2H), 6.32 (s, 1H), 6.92–6.98 (m, 1H), 7.25–7.31 (m, 1H), 7.35–7.43 (m, 3H), 7.47–7.53 (m, 2H), 8.39–8.43 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 14.4, 19.2, 21.2, 28.2, 37.0, 107.7, 120.4, 126.8, 127.8, 128.5, 130.2, 135.2, 137.4, 143.9,
146.93, 146.95, 147.2, 155.5; HRMS (ESI) calcd for C_{20}H_{22}N [M + H]^{+} 276.1747, found 276.1747.

**General Procedure for Rhodium(I)-Catalysed Insertion of Alkynes 2 into [(2-Pyridyl)methylene]cyclobutens 1.** A Schlenk tube was charged with RhCl(PPh$_3$)$_3$ (5.0 µmol), cyclobutene 1 (0.100 mmol), and alkyne 2 (0.120 mmol), and the tube was evacuated and backfilled with nitrogen (liquid substrates were added via syringe after mesitylene). Mesitylene (0.50 mL) was added via a syringe through the septum, and the mixture was heated at 170 °C with stirring for the indicated period of time. The reaction mixture was cooled to room temperature and then filtered through a plug of Florisil® washing with hexane–AcOEt (3:1), and the filtrate was concentrated. The residue was purified by preparative TLC on silica gel to afford cycloadduct 3.

![1,2,5-Triphenyl-3-[(2-pyridyl)methyl]benzene (3aa).](image)

1,2,5-Triphenyl-3-[(2-pyridyl)methyl]benzene (3aa). The general procedure was followed using 1a (11.0 mg, 0.050 mmol) and 2a (10.8 mg, 0.061 mmol) for 7 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3aa (13.5 mg, 0.034 mmol, 68%) as a white solid. Mp 111–115 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 4.18 (s, 2H), 6.87 (d, $J = 8.0$ Hz, 1H), 7.03–7.10 (m, 3H), 7.11–7.23 (m, 8H), 7.33–7.39 (m, 1H), 7.42–7.52 (m, 3H), 7.58–7.64 (m, 2H), 7.65–7.70 (m, 2H), 8.49–8.54 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 42.6, 120.9, 123.3, 126.2, 126.5, 127.2, 127.27, 127.34, 127.4, 127.7, 128.1, 128.7, 129.8,
3-[(6-Methyl-2-pyridyl)methyl]-1,2,5-triphenylbenzene (3ba). The general procedure was followed using 1b (23.3 mg, 0.100 mmol) and 2a (21.4 mg, 0.120 mmol) for 6 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3ba (31.6 mg, 0.077 mmol, 77%) as a yellow solid. Mp 121–126 °C; ^1H NMR (500 MHz, CDCl₃) δ 2.51 (s, 3H), 4.14 (s, 2H), 6.72 (d, J = 7.5 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 7.03–7.08 (m, 2H), 7.11–7.21 (m, 8H), 7.33–7.47 (m, 4H), 7.57–7.61 (m, 2H), 7.64–7.68 (m, 2H); ^13C NMR (126 MHz, CDCl₃) δ 24.4, 42.5, 120.1, 120.5, 126.2, 126.5, 127.1, 127.2, 127.3, 127.4, 127.6, 128.0, 128.7, 129.8, 130.6, 136.5, 138.5, 139.3, 139.8, 140.1, 140.6, 141.9, 142.4, 157.5, 160.3; HRMS (ESI) calcd for C₃₁H₂₆N [M + H]^+ 412.2060, found 412.2060.

3-[(3,5-Dimethyl-2-pyridyl)methyl]-1,2,5-triphenylbenzene (3ca). The general procedure was followed using 1c (24.7 mg, 0.100 mmol) and 2a (21.4 mg, 0.120 mmol) for 5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3ca (35.2 mg, 0.083 mmol, 83%) as a yellow solid. Mp 108–111 °C; ^1H NMR (500 MHz, CDCl₃) δ 2.19 (s,
3H), 2.47 (s, 3H), 4.10 (s, 2H), 6.50 (s, 1H), 6.77 (s, 1H), 7.04–7.08 (m, 2H), 7.11–7.21 (m, 8H), 7.33–7.38 (m, 1H), 7.42–7.47 (m, 2H), 7.57–7.61 (m, 2H), 7.66 (d, J = 8.0 Hz, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 20.9, 24.2, 42.3, 121.1, 121.6, 126.2, 126.4, 127.1 [overlapping], 127.3, 127.4, 127.6, 128.0, 128.7, 129.8, 130.7, 138.6, 139.4, 139.8, 140.0, 140.6, 141.9, 142.3, 147.5, 157.2, 160.0; HRMS (ESI) calcd for C$_{32}$H$_{28}$N [M + H]$^+$ 426.2216, found 426.2218.

![Image 1](image1.png)

3-[(3-methyl-2-pyridyl)methyl]-1,2,5-triphenylbenzene (3da). The general procedure was followed using 1d (23.3 mg, 0.100 mmol) and 2a (21.4 mg, 0.120 mmol) for 4 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3da (38.2 mg, 0.093 mmol, 93%) as a yellow solid. Mp 148–150 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 2.00 (s, 3H), 4.09 (s, 2H), 7.04–7.26 (m, 12H), 7.28–7.34 (m, 1H), 7.35–7.42 (m, 3H), 7.51–7.58 (m, 3H), 8.40–8.44 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 18.8, 40.3, 121.5, 126.2, 126.5, 126.7, 127.0, 127.1, 127.2, 127.4, 127.7, 128.6, 129.8, 130.5, 131.9, 137.8, 138.2, 139.5, 139.6, 140.0, 140.8, 141.9, 142.1, 146.6, 159.0; HRMS (ESI) calcd for C$_{31}$H$_{26}$N [M + H]$^+$ 412.2060, found 412.2060.

![Image 2](image2.png)
1,2,5-Triphenyl-3-[(2-quinolyl)methyl]benzene (3ea). The general procedure was followed using 1e (26.8 mg, 0.100 mmol) and 2a (21.4 mg, 0.120 mmol) for 3 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3ea (38.5 mg, 0.086 mmol, 86%) as a brown solid. Mp 143–148 °C; 1H NMR (500 MHz, CDCl3) δ 4.35 (s, 2H), 7.04–7.08 (m, 1H), 7.09–7.12 (m, 2H), 7.13–7.21 (m, 8H), 7.30–7.36 (m, 1H), 7.41 (d, J = 7.5 Hz, 2H), 7.46–7.50 (m, 1H), 7.58–7.65 (m, 4H), 7.66–7.71 (m, 1H), 7.75 (d, J = 8.5 Hz, 1H), 7.98 (d, J = 8.5 Hz, 1H), 8.04 (d, J = 8.5 Hz, 1H); 13C NMR (126 MHz, CDCl3) δ 43.2, 121.6, 125.8, 126.2, 126.6, 127.1, 127.32, 127.34, 127.4, 127.5, 127.8, 128.0, 128.7, 128.9, 129.3, 129.8, 130.7, 136.3, 138.2, 139.3, 139.8, 140.2, 140.5, 141.8, 142.5, 147.7, 161.3; HRMS (ESI) calcd for C34H26N [M + H]+ 448.2060, found 448.2061.

1,2,5-Triphenyl-3-[(2-pyrazyl)methyl]benzene (3fa). The general procedure was followed using 1f (22.0 mg, 0.100 mmol) and 2a (21.4 mg, 0.120 mmol) for 5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 5:1) yielded 3fa (10.6 mg, 0.027 mmol, 27%) as a brown solid. Mp 119–121 °C; 1H NMR (500 MHz, CDCl3) δ 4.17 (s, 2H), 6.97–7.02 (m, 2H), 7.04–7.19 (m, 8H), 7.33–7.38 (m, 1H), 7.42–7.47 (m, 2H), 7.57–7.60 (m, 1H), 7.61–7.63 (m, 1H), 7.66 (d, J = 7.5 Hz, 2H), 8.00 (s, 1H), 8.29–8.32 (m, 1H), 8.40–8.43 (m, 1H); 13C NMR (126 MHz, CDCl3) δ 40.2, 126.3, 126.8 [overlapping], 127.2, 127.48, 127.50, 127.7, 127.9, 128.2, 128.8, 129.8, 130.5, 137.2, 139.2, 139.6, 140.4, 141.5, 141.9, 142.7, 143.9, 144.8, 156.6; HRMS (ESI) calcd for C29H23N2 [M + H]+ 399.1856, found 399.1857.
1,2-Bis(4-methylphenyl)-5-phenyl-3-[(2-pyridyl)methyl]benzene (3ab). The general procedure was followed using 1a (21.9 mg, 0.100 mmol) and 2b (24.9 mg, 0.121 mmol) for 10 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1, twice) yielded 3ab (24.3 mg, 0.057 mmol, 57%) as a brown oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 2.27 (s, 3H), 2.29 (s, 3H), 4.14 (s, 2H), 6.87 (d, $J$ = 8.0 Hz, 1H), 6.91–7.08 (m, 9H), 7.30–7.36 (m, 1H), 7.39–7.45 (m, 2H), 7.49 (dt, $J$ = 1.8, 7.5 Hz, 1H), 7.53–7.55 (m, 2H), 7.61–7.65 (m, 2H), 8.47–8.51 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 21.1, 21.2, 42.5, 120.9, 123.3, 127.1, 127.2, 127.4, 127.8, 128.2, 128.5, 129.7, 130.4, 135.7, 135.9, 136.3, 136.4, 138.5, 139.0, 139.7, 140.0, 140.7, 142.4, 149.0, 161.1; HRMS (ESI) calcd for C$_{32}$H$_{28}$N [M + H]$^+$ 426.2216, found 426.2218.

1,2-Bis(4-methylphenyl)-3-[(3-methyl-2-pyridyl)methyl]-5-phenylbenzene (3db). The general procedure was followed using 1a (23.3 mg, 0.100 mmol) and 2b (24.8 mg, 0.120 mmol) for 4 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3db (32.4 mg, 0.074 mmol, 74%) as a white solid. Mp 173–178 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 2.01 (s, 3H), 2.28 (s, 3H), 2.32 (s, 3H), 4.08 (s, 2H), 6.95–7.09 (m, 9H), 7.16–7.20
(m, 1H), 7.27–7.33 (m, 1H), 7.34–7.42 (m, 3H), 7.48–7.57 (m, 3H), 8.41–8.45 (m, 1H); $^{13}\text{C}$ NMR (126 MHz, CDCl$_3$) δ 18.8, 21.1, 21.2, 40.4, 121.5, 126.3, 127.1, 128.2, 128.5, 128.6, 129.7, 130.4, 131.9, 135.6, 135.9, 136.7, 137.8, 138.3, 139.1, 139.4, 139.7, 140.9, 142.0, 146.6, 159.2; HRMS (ESI) calcd for C$_{33}$H$_{30}$N $[\text{M} + \text{H}]^+$ 440.2373, found 440.2373.

![Structural diagram of 1,2-Bis(4-methoxyphenyl)-5-phenyl-3-[(2-pyridyl)methyl]benzene (3ac).](image)

1,2-Bis(4-methoxyphenyl)-5-phenyl-3-[(2-pyridyl)methyl]benzene (3ac). The general procedure was followed using 1a (22.0 mg, 0.100 mmol) and 2c (28.6 mg, 0.120 mmol) for 9 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3ac (19.3 mg, 0.042 mmol, 42%) as a yellow solid. Mp 138–140 °C; $^{1}$H NMR (500 MHz, CDCl$_3$) δ 3.75 (s, 3H), 3.77 (s, 3H), 4.17 (s, 2H), 6.68–6.75 (m, 4H), 6.87 (d, $J = 8.0$ Hz, 1H), 6.91–6.95 (m, 2H), 7.02–7.09 (m, 3H), 7.30–7.36 (m, 1H), 7.42 (t, $J = 7.7$ Hz, 2H), 7.48–7.55 (m, 3H), 7.62–7.65 (m, 2H), 8.48–8.51 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 42.4, 55.09, 55.11, 113.0, 113.3, 121.0, 123.4, 127.1, 127.3, 127.4, 127.8, 128.7, 130.8, 131.6, 131.8, 134.4, 136.5, 138.5, 139.4, 140.0, 140.7, 142.3, 148.7, 157.9, 158.1, 161.0; HRMS (ESI) calcd for C$_{32}$H$_{28}$NNaO$_2$ [M + Na]$^+$ 480.1934, found 480.1935.
1,2-Bis(4-methoxylphenyl)-3-[(3-methyl-2-pyridyl)methyl]-5-phenylbenzene (3dc).
The general procedure was followed using 1d (23.3 mg, 0.100 mmol) and 2c (28.6 mg, 0.120 mmol) for 5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3dc (28.8 mg, 0.061 mmol, 61%) as a yellow solid. Mp 147–151 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.01 (s, 3H), 3.76 (s, 3H), 3.78 (s, 3H), 4.09 (s, 2H), 6.69–6.74 (m, 2H), 6.75–6.79 (m, 2H), 7.00–7.04 (m, 2H), 7.04–7.08 (m, 3H), 7.19 (s, 1H), 7.27–7.32 (m, 1H), 7.35–7.41 (m, 3H), 7.50 (s, 1H), 7.54 (d, \(J = 8.5\) Hz, 2H), 8.42 (d, \(J = 4.0\) Hz, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 18.8, 40.4, 55.08, 55.12, 113.0, 113.3, 121.5, 126.3, 127.0, 127.09, 127.11, 128.6, 130.9, 131.6, 131.9, 132.0, 134.5, 137.8, 138.5, 139.1, 139.8, 140.9, 141.8, 146.6, 157.9, 158.1, 159.2; HRMS (ESI) calcd for C\(_{35}\)H\(_{30}\)NO\(_2\) [M + H]\(^+\) 472.2271, found 472.2270.

\[\text{Ph} \quad \text{Cl} \quad \text{Cl} \]

1,2-Bis(4-chlorophenyl)-5-phenyl-3-[(2-pyridyl)methyl]benzene (3ad). The general procedure was followed using 1a (22.0 mg, 0.100 mmol) and 2d (29.7 mg, 0.120 mmol) for 9 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1, four times) yielded 3ad (22.0 mg, 0.047 mmol, 47%) as a yellow solid. Mp 137–139 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 4.13 (s, 2H), 6.86 (d, \(J = 8.0\) Hz, 1H), 6.94 (d, \(J = 8.5\) Hz, 2H), 7.02 (d, \(J = 8.5\) Hz, 2H), 7.06–7.19 (m, 5H), 7.36 (t, \(J = 7.5\) Hz, 1H), 7.44 (t, \(J = 7.7\) Hz, 2H), 7.49–7.55 (m, 2H), 7.59 (d, \(J = 2.5\) Hz, 1H), 7.63 (d, \(J = 7.0\) Hz, 2H), 8.49 (d, \(J = 4.5\) Hz, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 42.6, 121.1, 123.1, 127.1, 127.2, 127.6, 127.9, 128.1, 128.6, 128.8, 131.0,
131.8, 132.5, 132.7, 136.2, 138.3, 138.6, 140.0, 140.3, 140.6, 141.2, 149.3, 160.5; HRMS (ESI) calcd for C_{30}H_{22}Cl_2N \ [M + H]^+ 466.1124, found 466.1126.

1,2-Bis(4-chlorophenyl)-3-[(3-methyl-2-pyridyl)methyl]-5-phenylbenzene (3dd).
The general procedure was followed using 1d (23.3 mg, 0.100 mmol) and 2d (30.0 mg, 0.121 mmol) for 4 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3dd (39.6 mg, 0.082 mmol, 83%) as a white solid. Mp 153–155 °C; ¹H NMR (500 MHz, CDCl₃) δ 2.02 (s, 3H), 4.05 (s, 2H), 6.99–7.09 (m, 5H), 7.16 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.28 (s, 1H), 7.30–7.35 (m, 1H), 7.35–7.48 (m, 3H), 7.48 (s, 1H), 7.55 (d, J = 7.5 Hz, 2H), 8.41 (d, J = 4.0 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 18.8, 40.1, 121.6, 127.0, 127.1, 127.3, 127.4, 127.9, 128.1, 128.7, 131.0, 131.7, 131.8, 132.5, 132.7, 137.79, 137.83, 138.1, 138.4, 140.1, 140.4, 140.5, 140.8, 146.7, 158.6; HRMS (ESI) calcd for C_{31}H_{24}Cl_2N \ [M + H]^+ 480.1280, found 480.1280.

5-Phenyl-3-[(2-pyridyl)methyl]-1,2-bis[4-(trifluoromethyl)phenyl]benzene (3ae).
The general procedure was followed using 1a (22.0 mg, 0.100 mmol) and 2e (37.7 mg, 0.120
mmol) for 9 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3ae (32.9 mg, 0.062 mmol, 61%) as a yellow solid. Mp 163–167 °C; ¹H NMR (500 MHz, CDCl₃) δ 4.12 (s, 2H), 6.83 (d, J = 7.5 Hz, 1H), 7.07 (dd, J = 7.0, 5.5 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.35–7.40 (m, 1H), 7.40–7.52 (m, 7H), 7.53–7.56 (m, 1H), 7.62–7.67 (m, 3H), 8.48 (d, J = 4.0 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 42.6, 121.2, 123.1, 124.0 (q, J = 272.3 Hz), 124.1 (q, J = 272.3 Hz), 124.7 (q, J = 3.6 Hz), 124.8 (q, J = 3.5 Hz), 127.2, 127.3, 127.7, 128.7 (q, J = 31.2 Hz), 128.9, 129.06 (q, J = 32.3 Hz), 129.09, 130.0, 130.9, 136.3, 138.1, 138.6, 140.1, 140.9, 141.1, 142.9, 145.0, 149.3, 160.3; HRMS (ESI) calcd for C₃₂H₂₂F₆N [M + H]⁺ 534.1651, found 534.1655.

3-[(3-Methyl-2-pyridyl)methyl]-5-phenyl-1,2-bis[4-(trifluoromethyl)phenyl]benzene (3de). The general procedure was followed using 1d (23.3 mg, 0.100 mmol) and 2e (37.7 mg, 0.120 mmol) for 4 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3de (47.1 mg, 0.086 mmol, 86%) as a brown solid. Mp 154–157 °C; ¹H NMR (500 MHz, CDCl₃) δ 2.02 (s, 3H), 4.04 (s, 2H), 7.06 (dd, J = 7.5, 5.0 Hz, 1H), 7.18–7.25 (m, 4H), 7.33–7.38 (m, 3H), 7.40–7.50 (m, 6H), 7.52 (s, 1H), 7.55–7.60 (m, 2H), 8.40 (d, J = 4.5 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 18.8, 40.1, 121.6, 124.05 (q, J = 271.0 Hz), 124.10 (q, J = 271.2 Hz), 124.7 (q, J = 4.0 Hz), 124.8 (q, J = 3.6 Hz), 127.08, 127.13, 127.6, 128.0, 128.7 (q, J = 32.4 Hz), 128.8, 129.1 (q, J = 32.3 Hz), 130.0,
130.8, 131.6, 137.8, 137.9, 138.5, 140.2, 140.6, 140.9, 143.1, 145.1, 146.8, 158.4; HRMS (ESI) calcd for C_{33}H_{24}F_6N [M + H]^+ 548.1807, found 548.1808.

1,2-Bis(4-dimethylphenyl)-5-phenyl-3-[(2-pyridyl)methyl]benzene (3af). The general procedure was followed using 1a (21.8 mg, 0.099 mmol) and 2f (28.1 mg, 0.120 mmol) for 11 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3af (26.4 mg, 0.058 mmol, 59%) as a yellow solid. Mp 91–94 °C; \(^1^H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.16 (s, 6H), 2.17 (s, 6H), 4.13 (s, 2H), 6.62 (s, 2H), 6.74–6.79 (m, 4H), 6.87 (d, \(J = 7.5\) Hz, 1H), 7.05–7.09 (m, 1H), 7.31–7.36 (m, 1H), 7.40–7.45 (m, 2H), 7.50 (dt, \(J = 2.0, 7.8\) Hz, 1H), 7.54 (s, 2H), 7.65 (d, \(J = 8.0\) Hz, 2H), 8.48–8.52 (m, 1H); \(^1^3^C\) NMR (126 MHz, CDCl\(_3\)) \(\delta\) 21.15, 21.18, 42.7, 120.9, 123.4, 127.08, 127.14, 127.2, 127.67, 127.73 [overlapping], 127.9, 128.4, 128.7, 136.1, 136.5, 136.7, 138.2, 139.2, 139.7, 140.1, 140.8, 141.7, 142.5, 148.9, 161.3; HRMS (ESI) calcd for C_{34}H_{32}N [M + H]^+ 454.2529, found 454.2530.
1,2-Bis(4-dimethylphenyl)-3-[(3-methyl-2-pyridyl)methyl]-5-phenylbenzene (3df).

The general procedure was followed using 1d (23.3 mg, 0.100 mmol) and 2f (28.1 mg, 0.120 mmol) for 6 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3df (39.0 mg, 0.083 mmol, 84%) as a brown oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 2.00 (s, 3H), 2.18 (s, 6H), 2.19 (s, 6H), 4.07 (s, 2H), 6.69 (s, 2H), 6.75–6.82 (m, 4H), 7.06 (dd, $J = 7.5$, 5.0 Hz, 1H), 7.19 (s, 1H), 7.28–7.33 (m, 1H), 7.35–7.42 (m, 3H), 7.51 (s, 1H), 7.54–7.59 (m, 2H), 8.43 (d, $J = 4.5$ Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 18.7, 21.15, 21.19, 40.5, 121.4, 126.2, 126.8, 127.0, 127.1, 127.6, 127.76, 127.84, 128.2, 128.6, 132.0, 136.5, 136.7, 137.7, 138.1, 139.47, 139.52, 139.8, 141.0, 141.7, 142.1, 146.5, 159.3; HRMS (ESI) calcd for C$_{35}$H$_{34}$N [M + H]$^+$ 468.2686, found 468.2685.

![Chemical Structure of 1,2-Bis(4-dimethylphenyl)-3-[(3-methyl-2-pyridyl)methyl]-5-phenylbenzene (3df).](image)

1,2-Bis(2-methylphenyl)-3-[(3-methyl-2-pyridyl)methyl]-5-phenylbenzene (3dg).

The general procedure was followed using 1d (23.3 mg, 0.100 mmol) and 2g (24.9 mg, 0.121 mmol) for 7 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3dg (26.8 mg, 0.061 mmol, 61%) as a yellow solid. Mp 99–103 °C; $^1$H NMR (500 MHz, CDCl$_3$, mixture of rotational isomers) δ 1.90–2.33 (m, 9H; major + minor), 3.87–3.99 (m, 2H; major), 4.58–4.71 (m, 2H; minor), 6.88–7.58 (m, 17H; major + minor), 8.42 (s, 1H; major), 8.49–8.52 (m, 1H; minor); $^{13}$C NMR (126 MHz, CDCl$_3$, mixture of rotational isomers) δ 18.7, 18.9, 19.5, 20.0, 20.1, 20.3, 20.4, 20.6, 40.1, 40.3, 40.9, 121.5, 121.6, 121.9, 122.0, 123.3, 124.3, 124.6, 124.7, 125.1, 125.37, 125.44, 125.8, 125.9, 126.1, 126.6, 126.7, 126.8, 126.9,
127.00, 127.04, 127.1, 127.3, 127.47, 127.51, 128.1, 128.6, 128.68, 128.70, 128.77, 129.3, 129.4, 129.5, 129.6, 129.7, 129.78, 129.84, 131.48, 131.53, 131.8, 131.9, 132.0, 132.3, 135.3, 135.4, 136.2, 136.3, 137.6, 137.7, 138.0, 138.3, 138.4, 138.7, 139.1, 139.15, 139.17, 139.3, 139.4, 139.9, 140.26, 140.27, 140.5, 140.7, 140.8, 141.2, 141.3, 141.45, 141.50, 141.55, 145.2, 146.7, 146.9, 158.6, 158.75, 158.76; HRMS (ESI) calcd for C\text{33}H\text{30}N [M + H]^+ 440.2373, found 440.2372.

![Structure](image-url)

3-[(3-Methyl-2-pyridyl)methyl]-1,2-bis(1-naphthyl)-5-phenylbenzene (3dh). The general procedure was followed using 1d (23.3 mg, 0.100 mmol) and 2h (35.4 mg, 0.127 mmol) for 16 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 5:1) yielded 3dh (38.1 mg, 0.074 mmol, 75%) as a brown oil. $^1$H NMR (500 MHz, CDCl$_3$, mixture of rotational isomers) $\delta$ 1.80–1.88 (m, 3H), 3.81–4.00 (m, 2H), 6.87–7.90 (m, 23H), 8.37–8.43 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 18.5, 18.6, 40.2, 40.4, 121.4, 121.5, 124.2, 124.4, 124.5, 124.96, 125.04, 125.25, 125.28, 125.4, 125.6, 126.0, 126.1, 126.2, 126.4, 126.5, 126.6, 126.7, 126.9, 127.09, 127.12, 127.14, 127.16, 127.26, 127.6, 127.75, 127.78, 127.9, 128.1, 128.2, 128.4, 128.66, 128.69, 128.8, 131.8, 132.0, 132.6, 133.0, 133.10, 133.14, 136.7, 137.3, 137.55, 137.61, 138.70, 138.73, 139.2, 139.57, 139.65, 140.6, 141.1, 141.2, 146.7, 158.55, 158.65; HRMS (ESI) calcd for C$_{39}$H$_{30}$N [M + H]$^+$ 512.2373, found 512.2372.
5-Phenyl-3-[(2-pyridyl)methyl]-1,2-bis(2-thienyl)benzene (3ai). The general procedure was followed using 1a (21.9 mg, 0.100 mmol) and 2i (22.7 mg, 0.119 mmol) for 9 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 8:1, twice) yielded 3ai (18.9 mg, 0.046 mmol, 46%) as a yellow solid. Mp 117–120 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 4.22 (s, 2H), 6.82–6.85 (m, 1H), 6.87–6.91 (m, 2H), 6.94 (d, $J = 8.0$ Hz, 1H), 6.99 (dd, $J = 5.2$, 3.3 Hz, 1H), 7.07–7.12 (m, 1H), 7.20 (dd, $J = 5.0$, 1.5 Hz, 1H), 7.31 (dd, $J = 5.0$, 1.0 Hz, 1H), 7.34–7.39 (m, 1H), 7.42–7.48 (m, 2H), 7.51–7.56 (m, 2H), 7.63 (dd, $J = 8.3$, 1.2 Hz, 2H), 7.73 (d, $J = 2.5$ Hz, 2H), 8.51 (d, $J = 4.5$ Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 42.6, 121.2, 123.3, 126.1, 126.6, 126.7, 126.8, 127.18, 127.24, 127.7, 128.5, 128.8, 129.0, 131.7, 136.5, 136.7, 139.7, 140.2, 140.8, 141.5, 143.1, 149.0, 160.7; HRMS (ESI) calcd for C$_{26}$H$_{20}$NS$_2$ [M + H]$^+$ 410.1032, found 410.1032.

3-[(3-Methyl-2-pyridyl)methyl]-5-phenyl-1,2-bis(2-thienyl)benzene (3di). The general procedure was followed using 1d (23.3 mg, 0.100 mmol) and 2i (22.8 mg, 0.120 mmol) for 4 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1, twice) yielded 3di (36.7 mg, 0.087 mmol, 87%) as a yellow solid. Mp 125–128 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 2.11 (s, 3H), 4.19 (s, 2H), 6.90–6.94 (m, 3H), 7.02–7.06 (m, 1H), 7.09 (dd, $J$
= 7.5, 4.5 Hz, 1H), 7.20–7.23 (m, 2H), 7.32–7.38 (m, 2H), 7.39–7.45 (m, 3H), 7.54–7.59 (m, 2H), 7.73 (s, 1H), 8.45 (d, J = 4.5 Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 18.8, 40.2, 121.6, 126.0, 126.5, 126.7, 126.8, 126.9, 127.0, 127.1, 127.5, 128.7, 128.8, 131.4, 131.9, 136.3, 137.8, 139.9, 140.3, 140.7, 141.2, 143.1, 146.6, 158.6; HRMS (ESI) calcd for C$_{27}$H$_{22}$NS$_2$ [M + H]$^+$ 424.1188, found 424.1188.

![Structure](image1.png)

**1,2-Dibutyl-5-phenyl-3-[(2-pyridyl)methyl]benzene (3aj).** The general procedure was followed using 1a (21.8 mg, 0.099 mmol) and 2j (16.8 mg, 0.122 mmol) for 9 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3aj (20.1 mg, 0.056 mmol, 57%) as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 0.91 (t, J = 7.3 Hz, 3H), 0.98 (t, J = 7.5 Hz, 3H), 1.31–1.50 (m, 6H), 1.59–1.68 (m, 2H), 2.60–2.71 (m, 4H), 4.30 (m, 2H), 7.00 (d, J = 8.0 Hz, 1H), 7.08–7.13 (m, 1H), 7.26 (s, 1H), 7.28–7.35 (m, 2H), 7.38–7.43 (m, 2H), 7.52–7.59 (m, 3H), 8.55–8.59 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 13.9, 14.0, 23.0, 23.3, 28.8, 32.9, 33.0, 34.0, 42.5, 121.0, 122.8, 126.8, 126.9, 127.0, 127.2, 128.6, 136.4, 137.7, 138.4, 138.7, 141.2, 141.9, 149.2, 161.5; HRMS (ESI) calcd for C$_{26}$H$_{32}$N [M + H]$^+$ 358.2529, found 358.2529.

![Structure](image2.png)
1,2-Dibutyl-3-[(3-methyl-2-pyridyl)methyl]-5-phenylbenzene (3dj). The general procedure was followed using 1d (23.3 mg, 0.100 mmol) and 2j (16.7 mg, 0.121 mmol) for 4 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3dj (30.3 mg, 0.082 mmol, 82%) as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 0.96–1.02 (m, 6H), 1.42–1.53 (m, 6H), 1.61–1.69 (m, 2H), 2.25 (s, 3H), 2.68–2.79 (m, 4H), 4.30 (s, 2H), 6.80 (s, 1H), 7.12 (dd, $J = 7.7$, 4.8 Hz, 1H), 7.23–7.28 (m, 2H), 7.32–7.38 (m, 2H), 7.41–7.49 (m, 3H), 8.46 (d, $J = 5.0$ Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 13.9, 14.0, 19.0, 23.0, 23.4, 28.7, 32.5, 33.0, 33.9, 39.7, 121.6, 125.1, 126.3, 126.6, 126.9, 128.5, 132.2, 137.4, 138.0, 138.16, 138.24, 141.3, 141.5, 146.8, 159.0; HRMS (ESI) calcd for C$_{27}$H$_{34}$N [M + H]$^+$ 372.2686, found 372.2687.

![Chemical structure of 1,2-Dibutyl-3-[(3-methyl-2-pyridyl)methyl]-5-phenylbenzene (3dj).](image)

2-[(3-methyl-2-pyridyl)methyl]-1,4-diphenylbenzene (3dk). The general procedure was followed using 1d (23.3 mg, 0.100 mmol) and 2k (30.8 mg, 0.302 mmol) for 7 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 5:1) yielded 3dk (26.8 mg, 0.080 mmol, 80%) as a brown oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 1.96 (s, 3H), 4.22 (s, 2H), 7.06 (dd, $J = 7.8$, 4.8 Hz, 1H), 7.29–7.33 (m, 1H), 7.34–7.45 (m, 10H), 7.48–7.54 (m, 3H), 8.39–8.43 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 18.7, 39.6, 121.6, 124.9, 127.0, 127.09, 127.12, 127.9, 128.2, 128.6, 129.3, 130.3, 131.9, 136.9, 138.0, 140.2, 140.9, 141.0, 141.3, 146.4, 159.0; HRMS (ESI) calcd for C$_{25}$H$_{22}$N [M + H]$^+$ 336.1747, found 336.1748.
2-[(3-methyl-2-pyridyl)methyl]-1-octyl-4-phenylbenzene (3dl) and 1-[(3-methyl-2-pyridyl)methyl]-3-octyl-5-phenylbenzene (3’dl). The general procedure was followed using 1d (23.3 mg, 0.100 mmol) and 2l (20.7 mg, 0.150 mmol) for 6 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1, twice) yielded 3dl (14.5 mg, 0.039 mmol, 39%) and 3’dl (4.5 mg, 0.012 mmol, 12%).

3dl: Brown oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 0.89 (t, \(J = 6.8\) Hz, 3H), 1.23–1.44 (m, 10H), 1.55–1.64 (m, 2H), 2.24 (s, 3H), 2.69–2.74 (m, 2H), 4.28 (s, 2H), 6.99 (s, 1H), 7.12 (dd, \(J = 7.8, 4.8\) Hz, 1H), 7.24–7.29 (m, 2H), 7.33–7.40 (m, 3H), 7.42–7.49 (m, 3H), 8.43–8.46 (m, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 14.1, 19.0, 22.7, 29.3, 29.5, 29.8, 30.6, 31.9, 33.0, 39.1, 121.8, 125.0, 126.8, 126.9, 127.4, 128.5, 129.6, 132.2, 137.0, 138.2, 138.6, 140.3, 141.2, 146.6, 158.6; HRMS (ESI) calcd for C\(_{27}\)H\(_{34}\)N [M + H]\(^+\) 372.2686, found 372.2683.

3’dl: Brown oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 0.88 (t, \(J = 6.5\) Hz, 3H), 1.20–1.36 (m, 10H), 1.56–1.66 (m, 2H), 2.28 (s, 3H), 2.57–2.63 (m, 2H), 4.23 (s, 2H), 7.01 (s, 1H), 7.06–7.11 (m, 1H), 7.23 (s, 2H), 7.28–7.34 (m, 1H), 7.37–7.44 (m, 3H), 7.54 (d, \(J = 7.5\) Hz, 2H), 8.44 (d, \(J = 4.0\) Hz, 1H); \(^{13}\)C NMR (75.6 MHz, CDCl\(_3\)) \(\delta\) 14.1, 19.1, 22.7, 29.2, 29.4, 29.5, 31.5, 31.9, 36.0, 42.4, 121.7, 124.9, 125.3, 127.0, 127.2, 127.9, 128.6, 131.8, 138.1, 139.3, 141.2, 141.4, 143.5, 146.8, 158.8; HRMS (ESI) calcd for C\(_{27}\)H\(_{34}\)N [M + H]\(^+\) 372.2686, found 372.2686.
1-Methyl-3-[(3-methyl-2-pyridyl)methyl]-2,5-diphenylbenzene (3dm) and 2-methyl-1-[(3-methyl-2-pyridyl)methyl]-3,5-diphenylbenzene (3’dm). The general procedure was followed using 1d (23.3 mg, 0.100 mmol) and 2m (14.0 mg, 0.121 mmol) for 7 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1, twice) yielded 3dm (12.1 mg, 0.035 mmol, 35%) and 3’dm (5.4 mg, 0.015 mmol, 15%).

3dm: Brown oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.99 (s, 3H), 2.12 (s, 3H), 3.97 (s, 2H), 7.02 (s, 1H), 7.06 (dd, $J$ = 7.5, 4.5 Hz, 1H), 7.17–7.21 (m, 2H), 7.27–7.44 (m, 8H), 7.50–7.54 (m, 2H), 8.38 (d, $J$ = 4.5 Hz, 1H); $^{13}$C NMR (75.6 MHz, CDCl$_3$) $\delta$ 18.8, 21.1, 40.3, 121.4, 125.0, 126.7, 126.8, 127.0, 127.1, 128.4, 128.5, 129.2, 131.8, 136.5, 137.6, 137.8, 139.9, 140.4, 140.7, 141.2, 146.7, 159.0; HRMS (ESI) calcd for C$_{26}$H$_{24}$N [M + H]$^+$ 350.1903, found 350.1902.

3’dm: Brown solid, mp 130–135 °C; $^1$H NMR (301 MHz, CDCl$_3$) $\delta$ 2.25 (s, 3H), 2.31 (s, 3H), 4.27 (s, 2H), 6.99–7.02 (m, 1H), 7.12 (dd, $J$ = 7.7, 5.3 Hz, 1H), 7.23–7.52 (m, 12H), 8.44–8.48 (m, 1H); $^{13}$C NMR (75.6 MHz, CDCl$_3$) $\delta$ 16.8, 19.0, 40.2, 121.7, 126.2, 126.7, 126.88, 126.90, 127.0, 128.0, 128.6, 129.5, 133.2, 137.9, 138.1, 138.5, 141.0, 142.6, 142.9, 147.0, 158.5; HRMS (ESI) calcd for C$_{26}$H$_{23}$NNa [M + Na]$^+$ 372.1723, found 372.1724.
1-Ethyl-2-isopropenyl-3-[(3-methyl-2-pyridyl)methyl]-5-phenylbenzene (3dn) and 2-ethyl-1-isopropenyl-3-[(3-methyl-2-pyridyl)methyl]-5-phenylbenzene (3′dn).

The general procedure was followed using 1d (23.3 mg, 0.100 mmol) and 2n (27.8 mg, 0.295 mmol) for 6 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1, twice) yielded an inseparable mixture of 3dn and 3′dn (25.6 mg, 0.078 mmol, 78%) as a brown oil.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.21 (t, $J = 7.5$ Hz, 3H; minor), 1.27 (t, $J = 7.5$ Hz, 3H; major), 2.05 (s, 3H; major), 2.12 (s, 3H; minor), 2.21 (s, 3H; major), 2.27 (s, 3H; minor), 2.70 (q, $J = 7.5$ Hz, 2H; major), 2.82 (q, $J = 7.0$ Hz, 2H; minor), 4.19 (d, $J = 16.0$ Hz, 1H; major), 4.31 (d, $J = 16.0$ Hz, 1H; major), 4.31 (s, 2H; minor), 4.92 (s, 1H + 1H; major + minor), 5.23 (s, 1H; minor), 5.37 (s, 1H; major), 6.84 (s, 1H; major), 6.86 (s, 1H; minor), 7.08–7.49 (m, 8H + 8H; major + minor), 8.42–8.48 (m, 1H + 1H; major + minor); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 15.4, 16.3, 18.98, 19.01, 22.8, 24.5, 25.8, 26.2, 39.4, 114.7, 115.8, 121.6, 121.7, 124.5, 125.1, 125.9, 126.8, 126.9, 127.1, 128.5, 132.2, 136.3, 137.98, 138.04, 139.5, 141.1, 141.3, 141.4, 141.5, 144.0, 146.6, 159.0; HRMS (ESI) calcd for C$_{24}$H$_{25}$Na [M + Na]$^+$ 350.1879, found 350.1877.
**5-(4-Methylphenyl)-1,2-diphenyl-3-[(2-pyridyl)methyl]benzene (3ha).** The general procedure was followed using **1h** (35.0 mg, 0.150 mmol) and **2a** (32.1 mg, 0.180 mmol) for 10 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded **3ha** (42.5 mg, 0.103 mmol, 69%) as a yellow solid. Mp 100–102 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 2.41 (s, 3H), 4.17 (s, 2H), 6.86 (d, $J = 8.0$ Hz, 1H), 7.03–7.08 (m, 3H), 7.10–7.21 (m, 8H), 7.23–7.28 (m, 2H), 7.49 (dt, $J = 2.0$, 7.7 Hz, 1H), 7.54–7.60 (m, 4H), 8.49–8.53 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 21.1, 42.6, 120.9, 123.3, 126.1, 126.5, 127.0, 127.1, 127.4, 127.7, 127.9, 129.4, 129.8, 130.6, 136.1, 137.1, 137.7, 138.3, 139.46, 139.48, 140.1, 141.9, 142.4, 149.1, 161.0; HRMS (ESI) calcd for C$_{31}$H$_{26}$N [M + H]$^+$ 412.2060, found 412.2056.

**5-(4-Methylphenyl)-3-[(3-methyl-2-pyridyl)methyl]-1,2-diphenylbenzene (3ia).** The general procedure was followed using **1i** (24.8 mg, 0.100 mmol) and **2a** (21.4 mg, 0.120 mmol) for 7 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded **3ia** (37.0 mg, 0.087 mmol, 87%) as a white solid. Mp 127–129 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 2.01 (s, 3H), 2.38 (s, 3H), 4.09 (s, 2H), 7.06 (dd, $J = 7.5$, 4.5 Hz, 1H), 7.09–7.26 (m, 13H), 7.36 (d, $J = 7.5$ Hz, 1H), 7.47 (d, $J = 7.0$ Hz, 2H), 7.53 (s, 1H), 8.43 (d, $J = 4.0$ Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 18.8, 21.0, 40.3, 121.5, 126.1, 126.4, 126.5, 126.8, 126.9, 127.4, 127.7, 129.4, 129.8, 130.6, 131.8, 137.0, 137.7, 137.9, 138.1, 139.2, 139.7, 139.9, 142.0, 146.7, 159.1; HRMS (ESI) calcd for C$_{32}$H$_{28}$N [M + H]$^+$ 426.2216, found 426.2213.
5-(4-Methoxylphenyl)-1,2-diphenyl-3-[(2-pyridyl)methyl]benzene (3ja). The general procedure was followed using 1j (37.4 mg, 0.150 mmol) and 2a (32.1 mg, 0.180 mmol) for 24 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3ja (37.4 mg, 0.087 mmol, 58%) as a brown solid. Mp 135–137 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 3.85 (s, 3H), 4.16 (s, 2H), 6.85 (d, $J$ = 8.0 Hz, 1H), 6.98 (d, $J$ = 8.5 Hz, 2H), 7.01–7.08 (m, 3H), 7.10–7.20 (m, 8H), 7.46–7.52 (m, 1H), 7.52–7.62 (m, 4H), 8.48–8.52 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 42.5, 55.3, 114.1, 121.0, 123.3, 126.1, 126.4, 126.8, 127.4, 127.6, 127.7, 128.1, 129.8, 130.6, 133.1, 136.3, 138.2, 139.1, 139.4, 139.7, 141.9, 142.4, 149.0, 159.2, 160.9; HRMS (ESI) calcd for C$_{31}$H$_{26}$NO [M + H]$^+$ 428.2009, found 428.2009.

5-(4-Methoxylphenyl)-3-[(3-methyl-2-pyridyl)methyl]-1,2-diphenylbenzene (3ka). The general procedure was followed using 1k (26.3 mg, 0.100 mmol) and 2a (21.4 mg, 0.120 mmol) for 5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3ka (37.5 mg, 0.085 mmol, 85%) as a white solid. Mp 121–124 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 1.99 (s, 3H), 3.83 (s, 3H), 4.08 (s, 2H), 6.93 (d, $J$ = 8.5 Hz, 2H), 7.04–7.23 (m, 12H), 7.36 (d, $J$ = 7.5 Hz, 1H), 7.46–7.52 (m, 3H), 8.40–8.45 (m, 1H); $^{13}$C NMR (75.6 MHz,
CDCl$_3$ $\delta$ 18.8, 40.4, 55.3, 114.1, 121.4, 126.1, 126.2, 126.4, 126.5, 127.4, 127.7, 128.1, 129.8, 130.6, 131.8, 133.3, 137.6, 138.1, 138.9, 139.5, 139.7, 141.99, 142.03, 146.7, 159.1, 159.2; HRMS (ESI) calcd for C$_{32}$H$_{28}$NO [M + H]$^+$ 442.2165, found 442.2166.

![Structural diagram](image)

5-(4-Chlorophenyl)-1,2-diphenyl-3-[(2-pyridyl)methyl]benzene (3la). The general procedure was followed using 1I (25.4 mg, 0.100 mmol) and 2a (21.4 mg, 0.120 mmol) for 24 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3la (22.6 mg, 0.052 mmol, 52%) as a yellow solid. Mp 126–128 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 4.14 (s, 2H), 6.81 (d, $J$ = 8.0 Hz, 1H), 7.00–7.08 (m, 3H), 7.09–7.20 (m, 8H), 7.37–7.42 (m, 2H), 7.47 (dt, $J$ = 1.8, 7.5 Hz, 1H), 7.50–7.60 (m, 4H), 8.48–8.51 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 42.5, 121.0, 123.3, 126.3, 126.6, 127.0, 127.5, 127.7, 127.9, 128.4, 128.9, 129.8, 130.5, 133.4, 136.2, 138.6, 138.9, 139.0, 139.3, 140.1, 141.7, 142.6, 149.2, 160.8; HRMS (ESI) calcd for C$_{30}$H$_{23}$ClN [M + H]$^+$ 432.1514, found 432.1517.

![Structural diagram](image)

5-(4-Chlorophenyl)-3-[(3-methyl-2-pyridyl)methyl]-1,2-diphenylbenzene (3ma). The general procedure was followed using 1m (26.8 mg, 0.100 mmol) and 2a (21.4 mg, 0.120 mmol) for 24 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3ma (22.4 mg, 0.052 mmol, 52%) as a yellow solid. Mp 126–128 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 4.14 (s, 2H), 6.81 (d, $J$ = 8.0 Hz, 1H), 7.00–7.08 (m, 3H), 7.09–7.20 (m, 8H), 7.37–7.42 (m, 2H), 7.47 (dt, $J$ = 1.8, 7.5 Hz, 1H), 7.50–7.60 (m, 4H), 8.48–8.51 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 42.5, 121.0, 123.3, 126.3, 126.6, 127.0, 127.5, 127.7, 127.9, 128.4, 128.9, 129.8, 130.5, 133.4, 136.2, 138.6, 138.9, 139.0, 139.3, 140.1, 141.7, 142.6, 149.2, 160.8; HRMS (ESI) calcd for C$_{30}$H$_{23}$ClN [M + H]$^+$ 432.1514, found 432.1517.
mmol) for 5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3ma (38.4 mg, 0.086 mmol, 86%) as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 2.01 (s, 3H), 4.10 (s, 2H), 7.05–7.29 (m, 12H), 7.35–7.41 (m, 3H), 7.48–7.53 (m, 3H), 8.45 (d, $J = 4.5$ Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 18.7, 40.2, 121.5, 126.2, 126.55, 126.61, 126.8, 27.5, 127.7, 128.3, 128.8, 129.8, 130.5, 131.8, 133.3, 137.7, 138.4, 138.7, 139.2, 139.4, 139.8, 141.7, 142.2, 146.7, 158.9; HRMS (ESI) calcd for C$_{31}$H$_{25}$ClN [M + H]$^+$ 446.1670, found 446.1671.

![Chemical Structure](image)

5-(1-Naphthyl)-1,2-diphenyl-3-[(2-pyridyl)methyl]benzene (3na). The general procedure was followed using 1n (26.8 mg, 0.100 mmol) and 2a (21.4 mg, 0.120 mmol) for 10 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3na (30.7 mg, 0.069 mmol, 69%) as a brown oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 4.19 (s, 2H), 6.93 (d, $J = 8.0$ Hz, 1H), 7.03–7.08 (m, 1H), 7.09–7.25 (m, 10H), 7.43–7.55 (m, 7H), 7.84–7.88 (m, 1H), 7.89–7.93 (m, 1H), 8.11 (d, $J = 8.5$ Hz, 1H), 8.47–8.50 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 42.4, 121.0, 123.3, 125.4, 125.7, 126.0, 126.07, 126.14, 126.54, 127.1, 127.4, 127.68, 127.74, 128.3, 129.9, 130.1, 130.7, 131.0, 131.5, 133.8, 136.2, 137.9, 139.5, 139.6, 139.67, 139.70, 141.7, 141.9, 149.1, 161.0; HRMS (ESI) calcd for C$_{34}$H$_{26}$N [M + H]$^+$ 448.2060, found 448.2062.
1,2,5-Triphenyl-3-[1-(2-pyridyl)ethyl]benzene (3oa). The general procedure was followed using 1o (23.3 mg, 0.100 mmol) and 2a (21.4 mg, 0.120 mmol) for 6 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3oa (30.7 mg, 0.075 mmol, 75%) as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.69 (d, $J = 6.5$ Hz, 3H), 4.40 (q, $J = 7.0$ Hz, 1H), 6.92 (d, $J = 8.0$ Hz, 1H), 6.98 (d, $J = 7.0$ Hz, 1H), 7.04–7.09 (m, 1H), 7.10–7.24 (m, 9H), 7.29 (t, $J = 7.0$ Hz, 1H), 7.35 (t, $J = 7.0$ Hz, 1H), 7.44 (t, $J = 7.5$ Hz, 1H), 7.50 (t, $J = 7.7$ Hz, 1H), 7.53 (s, 1H), 7.65 (d, $J = 8.0$ Hz, 2H), 7.73 (s, 1H), 8.56 (d, $J = 4.5$ Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 21.5, 43.1, 121.0, 122.9, 125.5, 126.1, 126.5, 126.9, 127.2, 127.3, 127.4, 127.6, 127.8, 128.7, 129.8, 130.5, 130.9, 136.1, 139.1, 139.5, 140.2, 140.8, 142.0, 142.2, 144.4, 148.9, 164.7; HRMS (ESI) calcd for C$_{31}$H$_{26}$N [M + H]$^+$ 412.2060, found 412.2059.

1,2,5-Triphenyl-3-[phenyl(2-pyridyl)methyl]benzene (3pa). The general procedure was followed using 1p (29.4 mg, 0.100 mmol) and 2a (21.4 mg, 0.120 mmol) for 6 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) yielded 3pa (29.6 mg, 0.062 mmol, 63%) as a yellow solid. Mp 69–76 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.75 (s, 1H), 6.89 (d, $J = 7.5$ Hz, 1H), 6.97 (d, $J = 7.5$ Hz, 1H), 6.97–7.03 (m, 1H), 7.05–7.17 (m, 11H), 7.18–7.24 (m, 1H), 7.24–7.30 (m, 2H), 7.30–7.36 (m, 1H), 7.42 (t, $J = 7.5$ Hz, 2H),
7.52–7.60 (m, 5H), 8.58–8.62 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 55.9, 121.2, 124.1, 126.1, 126.3, 126.5, 127.1, 127.21, 127.24, 127.4, 127.5, 127.6, 127.7, 128.2, 128.7, 129.5, 129.8, 130.6, 130.7, 136.2, 139.3, 139.7, 140.1, 140.8, 141.8, 141.9, 142.4, 143.1, 149.4, 163.2; HRMS (ESI) calcd for C$_{36}$H$_{27}$NNa [M + Na]$^+$ 496.2036, found 496.2039.

3qa: Mp 139–142 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 0.66 (t, $J = 7.0$ Hz, 3H), 1.32–1.43 (m, 2H), 1.99 (s, 3H), 2.50–2.58 (m, 2H), 4.04 (s, 2H), 6.94–7.11 (m, 11H), 7.22 (s, 1H), 7.26–7.50 (m, 6H), 8.39 (d, $J = 4.5$ Hz, 1H); $^{13}$C NMR (75.6 MHz, CDCl$_3$) δ 14.7, 18.9, 23.9, 33.0, 36.3, 120.6, 125.7, 126.0, 126.6, 127.17, 127.19, 127.8, 129.5, 129.9, 130.4, 130.6, 130.8, 136.4, 136.7, 138.8, 139.2, 140.7, 141.0, 141.6, 142.1, 142.8, 146.7, 159.6; HRMS (ESI) calcd for C$_{34}$H$_{32}$N [M + H]$^+$ 454.2529, found 454.2529.

3’qa: $^1$H NMR (500 MHz, CDCl$_3$) δ 0.40 (t, $J = 7.0$ Hz, 3H), 1.05–1.16 (m, 2H), 2.01 (s, 3H), 2.25–2.37 (m, 2H), 3.92 (s, 2H), 6.78 (s, 1H), 6.95–7.40 (m, 17H), 8.35 (d, $J = 4.5$ Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 14.3, 18.9, 24.0, 32.7, 40.0, 121.4, 125.8, 125.9, 126.5,
127.0, 127.3, 127.8, 129.3, 129.4, 130.1, 130.4, 131.9, 134.1, 136.5, 137.7, 140.5, 140.76, 140.81, 141.4, 141.7, 142.7, 146.6, 158.9; HRMS (ESI) calcd for C$_{34}$H$_{32}$N [M + H]$^+$ 454.2529, found 454.2532.

**Oxidation of 1.** The methylene group of 1 was oxidised according to the procedure developed by Maes.$^3$

![Diagram of 1-(3-Methylpicolinoyl)-2,3,5-triphenylbenzene (4a).]

**1-(3-Methylpicolinoyl)-2,3,5-triphenylbenzene (4a).** 95% Yield; White solid, mp 129–132 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 2.32 (s, 3H), 6.84–6.98 (m, 5H), 6.99 (dd, $J = 8.0$, 5.0 Hz, 1H), 7.08–7.19 (m, 5H), 7.24 (d, $J = 7.5$ Hz, 1H), 7.38 (t, $J = 7.2$ Hz, 1H), 7.47 (t, $J = 7.5$ Hz, 2H), 7.71–7.77 (m, 2H), 7.81 (s, 1H), 7.97 (s, 1H), 8.23 (d, $J = 4.5$ Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 19.2, 124.8, 126.4, 126.5, 126.7, 127.1, 127.3, 127.6, 128.8, 129.8, 130.2, 131.4, 133.9, 138.3, 138.8, 138.9, 139.9, 140.4, 140.6, 141.8, 142.0, 145.4, 154.1, 200.0; HRMS (ESI) calcd for C$_{31}$H$_{23}$NNaO [M + Na]$^+$ 448.1672, found 448.1675; IR (ν/cm$^{-1}$): 1674, 1450, 1335, 1281, 964, 756, 702.

![Diagram of 1-(3-Methylpicolinoyl)-2,3,5-triphenylbenzene (4a).]

1,2-Dibutyl-3-(3-methylpicolinoyl)-5-phenylbenzene (4b). 66% Yield; Yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) δ 0.92 (t, $J$ = 7.3 Hz, 3H), 1.00 (t, $J$ = 7.3 Hz, 3H), 1.39 (sextet, $J$ = 7.5 Hz, 2H), 1.48 (sextet, $J$ = 7.5 Hz, 2H), 1.54–1.63 (m, 2H), 1.64–1.72 (m, 2H), 2.60 (s, 3H), 2.73–2.82 (m, 4H), 7.26–7.33 (m, 3H), 7.36–7.41 (m, 2H), 7.48–7.54 (m, 3H), 7.65 (d, $J$ = 7.5 Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 13.8, 14.0, 19.2, 22.9, 23.3, 29.1, 32.5, 33.66, 33.72, 125.0, 125.1, 125.2, 126.7, 126.8, 126.9, 127.0, 128.6, 131.0, 134.0, 137.9, 139.4, 139.5, 139.9, 140.6, 142.5, 146.2, 146.36, 146.42, 155.1, 199.5; HRMS (ESI) calcd for C$_{27}$H$_{31}$NNaO$^+$ [M + Na]$^+$ 408.2298, found 408.2298; IR (ν/cm$^{-1}$): 1674, 1458, 1327, 756.

Removal of Picolinoyl Group. The picolinoyl of 4 was removed according to the procedure developed by Swan.$^4$

1,2,4-Triphenylbenzene (5a). 93% Yield; white solid, 100–101 ºC; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.22–7.32 (m, 10H), 7.40–7.45 (m, 1H), 7.52 (t, $J$ = 7.2 Hz, 2H), 7.57 (d, $J$ = 8.0 Hz, 1H), 7.69–7.76 (m, 4H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 126.1, 126.5, 126.6, 127.1, 127.4, 127.89, 127.92, 128.8, 129.4, 129.85, 129.89, 131.1, 139.5, 140.4, 140.6, 141.0, 141.1, 141.5. The spectral data matched those reported in the literature.$^5$

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**1,2-Dibutyl-4-phenylbenzene (5b).** 52% Yield; Colorless oil; $^1$H NMR (301 MHz, CDCl$_3$) δ 0.80–0.90 (m, 6H), 1.25–1.40 (m, 4H), 1.43–1.57 (m, 4H), 2.49–2.60 (m, 4H), 7.07–7.14 (m, 1H), 7.16–7.34 (m, 5H), 7.44–7.50 (m, 2H); $^{13}$C NMR (75.6 MHz, CDCl$_3$) δ 14.0 [overlapping], 22.9 [overlapping], 32.1, 32.6, 33.5, 33.6, 124.4, 126.8, 127.0, 127.9, 128.6, 129.6, 138.6, 139.7, 140.9, 141.4; HRMS (ESI) calcd for C$_{20}$H$_{26}$Na [M + Na]$^+$ 289.1927, found 289.1925.
(E)-1b

\[
\begin{array}{c}
\text{Ph} \\
\text{Me}
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(Z)-1h

![NMR Spectrum](image)
(Z)-1j

![NMR spectrum and structural diagram](image)
(E)-1n
(Z)-1n
3ba

[Chemical structure image]

[Graphical representation of NMR spectrum]
3ca

![Chemical structure of 3ca](image)

- Ph: Phenyl group
- Me: Methyl group
3fa
3dd
3ae

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\[ \text{N} \]

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\[ \text{CF}_3 \]
3de

![Chemical Structure](image)

![NMR Spectrum](image)
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3ai
3dk
3'dl
3dm

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![Chemical Structure Image]

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![NMR Spectrum Image]
3dn and 3'dn

3dn

3’dn
3ma
3na
3pa

![Graphical representation of chemical structure](image_url)
3qa

[Chemical structure diagram]

[1D NMR spectrum]

[13C NMR spectrum]