

**Supplementary Information**

**Copper-Catalyzed Deaminative Alkynylation of Secondary Amines with Alkynes: Selectivity Switch in the Synthesis of Diversified Propargylamines**

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1. General Information

All commercially available reagents were used without purification unless otherwise noted. Visualization of the compounds was accomplished with UV light (254 nm) or iodine. HPLC analysis was performed on an Agilent 1260 infinity II chromatograph with an Eclipse plus C18 column (4.6 mm × 150 mm, 3.5 μm, P/N 959963-902). $^1$H NMR and $^{13}$C NMR spectra were recorded in CDCl$_3$ operating at 400 MHz and 600 MHz. Proton chemical shifts are reported relative to the residual proton signals of the deuterated solvent CDCl$_3$ (7.26 ppm) or TMS. Carbon chemical shifts were internally referenced to the deuterated solvent signals in CDCl$_3$ (77.10 ppm). Chemical shifts are reported in δ (parts per million) values. Coupling constants $J$ are reported in Hz. Proton coupling patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), and multiple (m). High-resolution mass spectra were recorded on a Q-Exactive Spectrometer (Thermo, USA).

2. General Procedure for the Synthesis of Propargylamines 3

\[
\begin{align*}
\text{R}^2 & \quad \downarrow & \quad \text{CuBr}_2 & \quad & \text{TBHP} \\
\text{R}^1 & \quad \text{N} & \quad \text{R}^3 & \quad \text{toluene} & \quad 90 \, ^\circ\text{C}, \quad 2 \, \text{h} \\
1 & & & & 3
\end{align*}
\]

Amines 1 (2.0 mmol), CuBr$_2$ (22.33 mg 20 mol %), 70% TBHP (160 mg, 1.25 mmol), alkynes 2 (0.5 mmol), and toluene (3 mL) were charged into a 25 mL tube along with a magnetic stir bar. The mixture was stirred in an oil bath at 90 °C for 2 hours until alkynes 2 were completely consumed, monitoring with TLC. Subsequently, the mixture was cooled to room temperature and purified by running column chromatography on silica gel using petroleum ether/ethyl acetate. Flash column chromatography was performed on silica gel (100–200 mesh).

3. General Procedure for the Synthesis of Propargylamines 4

\[
\begin{align*}
\text{R}^2 & \quad \downarrow & \quad \text{CuBr}_2 & \quad & \text{TBHP} \\
\text{R}^1 & \quad \text{N} & \quad \text{R}^3 & \quad \text{toluene} & \quad 110 \, ^\circ\text{C}, \quad 20 \, \text{min} \\
1 & & & & 4
\end{align*}
\]

Amines 1 (2.0 mmol), CuBr$_2$ (22.33 mg 20 mol %), 70% TBHP (160 mg, 1.25 mmol), and toluene (1 mL) were charged into a 25 mL tube along with a magnetic stir bar. The mixture was stirred in an oil bath at 110 °C for 20 min; then, alkynes 2 (0.5 mmol) were added into the reaction system,
and the resulting mixture was stirred at 110 °C for another 3 hours. Subsequently, the mixture was cooled to room temperature and purified by running column chromatography on silica gel using petroleum ether/ethyl acetate. Flash column chromatography was performed on silica gel (200–300 mesh).

4. Procedure for the Synthesis of 1-Methyl-2,3-diphenyl-1H-pyrrole 5

Amines 3a (0.5 mmol), KOH (1.2 equiv), and DMSO (2 mL) were charged into a 25 mL tube along with a magnetic stir bar. The mixture was stirred in an oil bath at 120 °C for 1 h. The resulting reaction mixture was diluted with ethyl acetate (10 mL) and water (15 mL) for three times. The layers were separated, and the organic layer was washed with saturated brine solution and dried over NaSO₄. After that, the mixture was purified by running column chromatography on silica gel using petroleum ether/ethyl acetate =40:1. Flash column chromatography was performed on silica gel (100–200 mesh). The product 5a was obtained (37.3 mg, 32%) as colorless oil.

5. ¹H NMR and ¹³C NMR Date of Products 3–5

N-benzyl-N-methyl-3-phenylprop-2-yn-1-amine (3a)

(98.7 mg, 84%) as light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.47-7.26 (m, 9H), 3.64 (s, 2H), 3.51 (s, 2H), 2.40 (s, 3H). ¹³C NMR (400 MHz, CDCl₃) δ 137.9, 131.3, 132.7, 128.8, 127.9, 127.8, 127.6, 126.8, 122.8, 85.3, 83.9, 59.8, 45.3, 41.5. LC-MS m/z (ESI⁺): Calculated for C₁₇H₁₇N ([M+H]+): 236.1, found: 236.1. Known compound[¹].

N-benzyl-3-(4-methoxyphenyl)-N-methylprop-2-yn-1-amine (3b)
N-benzyl-3-(4-ethylphenyl)-N-methylprop-2-yn-1-amine (3c)

(107.8 mg, 82%) as light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40-7.13 (m, 9H), 3.63 (s, 3H), 3.50 (s, 2H), 2.66 (q, $J = 22.8$ Hz, 2H), 2.39 (s, 3H), 1.24 (t, $J = 15.2$ Hz 3H). $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ 144.0, 138.0, 131.3, 128.8, 127.9, 127.4, 126.8, 120.0, 85.4, 83.1, 59.8, 45.3, 41.5, 28.3, 15.0. HRMS m/z (ESI$^+$): Calculated for C$_{19}$H$_{21}$N ([M+H]$^+$): 264.1747, found: 264.1746.

N-benzyl-3-(4-(tert-butyl)phenyl)-N-methylprop-2-yn-1-amine (3d)

(122.3 mg, 84%) as light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43-7.36 (m, 9H), 3.64 (s, 2H) 3.51 (s, 2H), 2.40 (s, 3H), 1.32 (s, 9H). $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ 150.8, 138.0, 131.0, 128.8, 127.9, 126.8, 124.8, 119.8, 85.4, 83.1, 59.8, 45.3, 41.5, 34.3, 30.7. LC-MS m/z (ESI$^+$): Calculated for C$_{21}$H$_{25}$N ([M+H]$^+$): 292.2, found: 292.2. Known compound$^{[3]}$

N-benzyl-N-methyl-3-(p-tolyl)prop-2-yn-1-amine (3e)

(100.8 mg, 81%) as light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37-7.10 (m, 9H), 3.63 (s, 2H) 3.50 (s, 2H), 2.39 (s, 3H), 2.34 (s, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ 138.0, 137.6, 131.2, 128.8,
128.6, 127.9, 126.7, 119.8, 85.3, 83.2, 59.8, 45.3, 41.5, 21.0. LC-MS m/z (ESI⁺): Calculated for C_{18}H_{19}N ([M+H]⁺): 250.2, found: 250.1. Known compound [4]

**N-benzyl-N-methyl-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-amine (3f)**

![Image of N-benzyl-N-methyl-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-amine (3f)]

(106.1 mg, 70%) as light yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.58-7.27 (m, 9H), 3.64 (s, 2H) 3.53 (s, 2H), 2.41 (s, 3H). \(^{13}\)C NMR (400 MHz, CDCl\(_3\)) \(\delta\) 137.8, 131.5, 128.7, 127.9, 126.9, 124.8, 124.7, 86.8, 84.0, 59.9, 45.2, 41.6. \(^{19}\)F NMR (400 MHz, CDCl\(_3\)) \(\delta\) -62.8 (s). LC-MS m/z (ESI⁺): Calculated for C_{18}H_{16}F_{3}N ([M+H]⁺): 304.1, found: 304.1. Known compound [2]

**N-benzyl-3-(4-chlorophenyl)-N-methylprop-2-yn-1-amine (3g)**

![Image of N-benzyl-3-(4-chlorophenyl)-N-methylprop-2-yn-1-amine (3g)]

(100.8 mg, 75%) as light yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.43-7.31 (m, 9H), 3.67 (s, 2H) 3.54 (s, 2H), 2.44 (s, 3H). \(^{13}\)C NMR (400 MHz, CDCl\(_3\)) \(\delta\) 137.9, 133.6, 132.5, 128.7, 128.1, 127.9, 126.8, 85.1, 84.1, 59.9, 45.3, 41.6. LC-MS m/z (ESI⁺): Calculated for C_{17}H_{16}ClN ([M+H]⁺): 270.1, found: 270.1. Known compound [5]

**N-benzyl-3-(3-fluorophenyl)-N-methylprop-2-yn-1-amine (3h)**

![Image of N-benzyl-3-(3-fluorophenyl)-N-methylprop-2-yn-1-amine (3h)]

(89.8 mg, 71%) as light yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.38-6.99 (m, 9H), 3.63 (s, 2H), 3.51 (s, 2H), 2.40 (s, 3H). \(^{13}\)C NMR (400 MHz, CDCl\(_3\)) \(\delta\) 163.1, 160.7, 137.9, 128.7, 127.9, 127.2, 127.1, 126.8, 118.2, 118.0, 115.0, 114.8, 85.1, 84.1, 59.8, 45.2, 41.5. \(^{19}\)F NMR (400 MHz, CDCl\(_3\)) \(\delta\) -113.0 (s). HRMS m/z (ESI⁺): Calculated for C_{17}H_{16}FN ([M+H]⁺): 254.1340, found: 254.1340.

**N-benzyl-3-(2-fluorophenyl)-N-methylprop-2-yn-1-amine (3i)**
N-benzyl-3-cyclopropyl-N-methylprop-2-yn-1-amine(3j)

(31.8 mg, 32%) as light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36-7.56 (m, 5H), 3.57 (s, 2H), 3.27 (d, $J = 2.0$ Hz 2H), 2.32 (s, 2H), 1.33-1.28 (m, 1H), 0.82-0.69 (m, 4H). $^{13}$C NMR (600 MHz, CDCl$_3$) δ 138.6, 129.2, 128.2, 127.1, 88.8, 70.0, 60.2, 45.5, 41.8, 8.31, -0.44. LC-MS m/z (ESI$^+$): Calculated for C$_{14}$H$_{17}$N ([M+H]$^+$): 200.1, found: 200.1. Known compound.$^5$

N-(4-chlorobenzyl)-N-methyl-3-phenylprop-2-yn-1-amine(3k)

(98.2 mg, 73%) as light yellow oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.50-7.49 (m, 2H), 7.35-7.34 (m, 7H), 3.64 (s, 2H), 3.54 (s, 2H), 2.42 (s, 3H). $^{13}$C NMR (600 MHz, CDCl$_3$) δ 137.0, 131.7, 130.5, 128.5, 128.3, 128.1, 123.2, 85.8, 84.1, 59.4, 45.7, 41.9. LC-MS m/z (ESI$^+$): Calculated for C$_{17}$H$_{16}$ClN ([M+H]$^+$): 270.1, found: 270.1. Known compound.$^6$

N-methyl-3-phenyl-N-(4-(trifluoromethyl)benzyl)prop-2-yn-1-amine(3l)

(113.6 mg, 75%) as light yellow oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.64-7.62 (m, 2H), 7.54-7.50 (m, 4H), 7.37-7.35 (m, 3H), 3.74 (s, 2H), 3.57 (s, 2H), 2.45 (s, 3H). $^{13}$C NMR (600 MHz, CDCl$_3$) δ 142.7, 131.7, 129.3, 128.3, 128.1, 125.3, 125.2, 123.1, 85.9, 84.0, 59.7, 45.9, 42.0. HRMS m/z (ESI$^+$): Calculated for C$_{17}$H$_{16}$F$_3$N ([M+H]$^+$): 304.1308, found: 304.1304.
(88.6 mg, 70%) as light yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.51-7.49 (m, 2H), 7.39-7.34 (m, 5H), 7.07-7.03 (m, 2H), 3.64 (s, 2H), 3.54 (s, 2H), 2.43 (s, 3H). \(^1^3\)C NMR (600 MHz, CDCl\(_3\)) \(\delta\) 162.9, 161.3, 134.2, 131.7, 130.7, 128.3, 128.1, 123.2, 115.2, 115.0, 85.8, 84.2, 59.4, 45.6, 41.9. HRMS m/z (ESI\(^+\)): Calculated for C\(_{17}\)H\(_{16}\)FN ([M+H]\(^+\)): 254.1340, found: 254.1340.

\(N\)-methyl-\(N\)-(4-methylbenzyl)-3-phenylprop-2-yn-1-amine(3n)

(98.3 mg, 70%) as light yellow oil. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.52-7.51 (m, 2H), 7.37-7.18 (m, 7H), 3.66 (s, 2H), 3.55 (s, 2H), 2.45 (s, 3H), 2.39 (s, 3H). \(^1^3\)C NMR (600 MHz, CDCl\(_3\)) \(\delta\) 136.8, 135.3, 131.7, 129.2, 129.0, 128.3, 128.0, 123.3, 85.7, 84.5, 60.0, 45.6, 42.0, 21.1. HRMS m/z (ESI\(^+\)): Calculated for C\(_{18}\)H\(_{19}\)N ([M+H]\(^+\)): 250.1590, found: 250.1593.

\(N\)-(4-methoxybenzyl)-\(N\)-methyl-3-phenylprop-2-yn-1-amine(3o)

(107.3 mg, 81%) as light yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.51-7.31 (m, 7H), 6.92-6.89 (m, 2H), 3.83 (s, 3H), 3.62 (s, 2H), 3.53 (s, 2H), 2.43 (s, 3H). \(^1^3\)C NMR (600 MHz, CDCl\(_3\)) \(\delta\) 158.4, 131.3, 130.0, 129.9, 127.8, 127.5, 122.9, 113.2, 85.2, 84.0, 59.1, 54.8, 45.0, 41.4. LC-MS m/z (ESI\(^+\)): Calculated for C\(_{18}\)H\(_{19}\)ON ([M+H]\(^+\)): 266.2, found: 266.1. Known compound\(^{[6]}\)

\(N\)-methyl-\(N\)-phenethyl-3-phenylprop-2-yn-1-amine(3p)
(94.7 mg, 76%) as yellow oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.49-7.47 (m, 2H), 7.35-7.24 (m, 7H), 3.67 (s, 2H), 2.89-2.86 (m, 2H), 2.82-2.80 (m, 2H), 2.49 (s, 3H). $^{13}$C NMR (600 MHz, CDCl$_3$) $\delta$140.2, 131.7, 128.7, 128.4, 128.3, 128.0, 126.1, 123.2, 85.5, 84.3, 57.7, 46.5, 42.1, 34.4. HRMS m/z (ESI$^+$): Calculated for C$_{18}$H$_{19}$ON ([M+H]$^+$): 250.1590, found: 250.1594.

$N$-methyl-$N$-(3-phenylprop-2-yn-1-yl)cyclohexanamine (3q)

![Diagram](image)

(65.8 mg, 58%) as light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46-7.42 (m, 2H), 7.32-7.29 (m, 3H), 3.66 (s, 2H), 2.48-2.45 (m, 4H), 2.00-1.97 (m, 2H), 1.83-1.80 (m, 2H), 1.66-1.62 (m, 1H), 1.32-1.17 (m, 5H). $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ 131.2, 127.7, 127.4, 122.9, 85.0, 84.4, 60.6, 43.2, 29.3, 25.6, 25.1. LC-MS m/z (ESI$^+$): Calculated for C$_{16}$H$_{21}$N ([M+H]$^+$): 228.2, found: 288.2. Known compound[1]

$N$-methyl-$N$-(3-phenylprop-2-yn-1-yl)tetrahydro-2$H$-pyran-4-amine (3r)

![Diagram](image)

(61.8 mg, 54%) as light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45-7.43 (m, 2H), 7.32-7.30 (m, 3H), 4.05-4.01 (m, 4H), 3.67 (s, 2H), 3.45-3.38 (m, 2H), 2.63-2.60 (m, 1H), 2.44 (s, 3H), 1.90-1.86 (m, 2H) 1.59-1.55 (m, 2H). $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ 131.2, 127.8, 127.6, 122.7, 84.9, 84.1, 66.6, 57.7, 42.9, 38.0, 30.1. HRMS m/z (ESI$^+$): Calculated for C$_{16}$H$_{21}$N ([M+H]$^+$): 230.1539, found: 230.1535.

$N$-methyl-3-phenyl-$N$-propylprop-2-yn-1-amine(3s')

![Diagram](image)

(32.7 mg, 35%) as light yellow oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.47-7.45 (m, 2H), 7.31-7.30 (m, 3H), 3.56 (s, 2H), 2.47-2.45 (m, 2H), 2.39 (s, 3H), 1.56-1.53 (m, 2H), 0.97 (t, $J$ = 15.0 Hz 3H). $^{13}$C
NMR (600 MHz, CDCl₃) δ 131.7, 128.2, 127.9, 123.3, 85.2, 84.6, 58.0, 46.4, 41.9, 20.8, 11.9. HRMS m/z (ESI⁺): Calculated for C₁₃H₁₇N ([M+H⁺]): 188.1434, found: 188.1434.

N-methyl-1-phenyl-N-propylpent-1-yn-3-amine(3s)

(54.9 mg, 51%) as light yellow oil. ¹H NMR (600 MHz, CDCl₃) δ 7.47-7.45 (m, 2H), 7.32-7.31 (m, 3H), 3.54-3.51 (m, 1H), 2.52-2.42 (m, 2H), 2.32 (s, 3H), 1.77-1.73 (m, 2H), 1.56-1.53 (m, 2H), 1.10 (t, J = 14.4 Hz 3H), 0.96 (t, J = 15.0 Hz 3H). ¹³C NMR (600 MHz, CDCl₃) δ 131.7, 128.2, 127.7, 123.6, 87.7, 85.5, 58.6, 56.7, 38.0, 27.1, 21.1, 11.9, 11.4. HRMS m/z (ESI⁺): Calculated for C₁₅H₂₁N ([M+H⁺]): 216.1747, found: 216.1736.

N,N-diethyl-4-phenylbut-3-yn-2-amine (3t)

(62.3 mg, 62%) as light yellow oil. ¹H NMR (600 MHz, CDCl₃) δ 7.44-7.43 (m, 2H), 7.31-7.30 (m, 3H), 3.95-3.93 (m, 1H), 2.80-2.74 (m, 2H), 2.56-2.53 (m, 2H), 1.45 (d, J = 6.6 Hz 3H), 1.15 (d, J = 14.4 Hz 6H), 1.90-1.86 (m, 2H) 1.59-1.55 (m, 2H). ¹³C NMR (600 MHz, CDCl₃) δ 131.6, 128.2, 127.7, 123.5, 89.5, 84.0, 48.3, 44.6, 20.1, 13.6. LC-MS m/z (ESI⁺): Calculated for C₁₄H₁₉N ([M+H⁺]): 202.2, found: 202.1. Known compound [⁷]

1-phenyl-N,N-dipropylpent-1-yn-3-amine(3u)

(85.1 mg, 70%) as light yellow oil. ¹H NMR (600 MHz, CDCl₃) δ 7.46-7.45 (m, 2H), 7.32-7.31 (m, 3H), 3.57 (t, J = 15.6 Hz 1H), 2.57-2.52 (m, 2H), 2.47-2.43 (m, 2H), 1.74-1.71 (m, 2H), 1.55-1.47 (m, 4H), 1.08 (t, J = 15.0 Hz 3H), 0.95 (t, J = 15.0 Hz 6H). ¹³C NMR (600 MHz, CDCl₃) δ 131.7,
128.2, 127.6, 123.7, 89.2, 84.4, 56.0, 53.6, 27.4, 21.7, 12.0, 11.4. LC-MS m/z (ESI^+): Calculated for C_{17}H_{25}N ([M+H]^+): 244.2, found: 244.2. Known compound[^7]

_N-benzyl-N-methyl-1,3-diphenylprop-2-yn-1-amine (4a)_

![N-benzyl-N-methyl-1,3-diphenylprop-2-yn-1-amine](image)

(124.4 mg, 80%) as yellow oil. ^1H NMR (600 MHz, CDCl$_3$) δ 7.68-7.67 (d, $J$ = 7.8 Hz 2H), 7.57-7.56 (m, 2H), 7.42-7.40 (d, $J$ = 7.8 Hz 2H), 7.36-7.22 (m, 9H), 4.91 (s, 1H), 3.73-3.62 (m, 2H), 2.24 (s, 3H).

^13C NMR (600 MHz, CDCl$_3$) δ 139.3, 139.1, 131.9, 129.1, 128.4, 128.2, 127.6, 127.1, 123.3, 88.7, 84.8 59.6, 59.0, 38.1. LC-MS m/z (ESI^+): Calculated for C$_{23}$H$_{21}$N ([M+H]^+): 312.2, found: 312.2. Known compound[^5]

_N-(4-chlorobenzyl)-1-(4-chlorophenyl)-N-methyl-3-phenylprop-2-yn-1-amine (4b)_

![N-(4-chlorobenzyl)-1-(4-chlorophenyl)-N-methyl-3-phenylprop-2-yn-1-amine](image)

(142.1 mg, 75%) as yellow oil. ^1H NMR (400 MHz, CDCl$_3$) δ 7.64-7.58 (m, 4H), 7.41-7.34 (m, 9H), 4.48 (s, 1H), 3.70-3.60 (m, 2H), 2.24 (s, 3H). ^13C NMR (400 MHz, CDCl$_3$) δ 137.1, 137.0, 132.9, 132.4, 131.4, 129.8, 129.2, 128.0, 127.9, 127.8, 122.4, 88.6, 83.3, 58.6, 57.6, 37.5. HRMS m/z (ESI^+): Calculated for C$_{23}$H$_{19}$Cl$_2$N ([M+H]^+): 380.0967, found: 380.0949.

_N-(4-fluorobenzyl)-1-(4-fluorophenyl)-N-methyl-3-phenylprop-2-yn-1-amine (4c)_

![N-(4-fluorobenzyl)-1-(4-fluorophenyl)-N-methyl-3-phenylprop-2-yn-1-amine](image)

[^5]: Reference number.
[^7]: Reference number.
(119.7 mg, 75%) as yellow oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.69-7.61 (m, 4H), 7.42-7.40 (m, 5H), 7.12-7.06 (m, 4H), 4.91 (s, 1H), 3.73-3.63 (m, 2H), 2.26 (s, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$) δ 163.0, 162.8, 160.6, 160.4, 134.4, 134.3, 134.2, 131.4, 130.0, 129.9, 129.5, 129.4, 127.9, 122.5, 114.8, 114.6, 114.4, 88.5, 83.7, 58.4, 57.6, 37.4. HRMS m/z (ESI$^+$): Calculated for C$_{23}$H$_{19}$F$_2$N ([M+H$^+$]): 348.1558, found: 348.1547.

$N$-methyl-$N$-(4-methylbenzyl)-3-phenyl-1-(p-tolyl)prop-2-yn-1-amine(4d)

$N$-(4-methoxybenzyl)-1-(4-methoxyphenyl)-$N$-methyl-3-phenylprop-2-yn-1-amine(4e)

(146.5 mg, 79%) as yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.66-7.39 (m, 9H), 6.98-6.94 (m, 4H), 4.94 (s, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.75-3.62(m, 2H), 2.29(s, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$) δ 158.6, 158.3, 131.4, 130.9, 130.8, 129.7, 129.0, 127.9, 127.7, 122.9, 113.3, 113.0, 88.0, 84.7, 58.3, 57.7, 37.3. HRMS m/z (ESI$^+$): Calculated for C$_{25}$H$_{25}$N$O_2$ ([M+H$^+$]): 372.1958, found: 372.1937.

$N$-benzyl-$N$-ethyl-1,3-diphenylprop-2-yn-1-amine(4f)
N-methyl-N-phenethyl-1,4-diphenylbut-3-yn-2-amine (4g)

(110.2 mg, 65%) as light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44-7.26 (m, 15H), 3.97 (t, $J$ = 14.8 Hz 1H), 3.08-3.05 (m, 2H), 2.92-2.83 (m, 4H), 2.52 (s, 3H).

$^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ 140.1, 138.4, 131.2, 129.0, 128.4, 127.9, 127.8, 127.5, 126.0, 125.6, 125.3, 86.4, 84.3, 58.7, 56.4, 40.0, 37.8, 34.3. HRMS m/z (ESI$^+$): Calculated for C$_{25}$H$_{25}$N ([M+H]$^+$): 340.2060, found: 340.2061.

N-benzyl-N-methyl-1-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-amine (4h)

(130.8 mg, 69%) as light yellow oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.73-7.67 (m, 6H), 7.49-7.33 (m, 8H) 5.01 (s, 1H) 3.82-3.69 (m, 2H) 2.32 (s, 3H).

$^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ 139.1, 138.6, 132.2, 130.1, 129.9, 129.0, 128.4, 128.3, 127.7, 127.2, 127.0, 125.3, 124.9, 123.1, 87.7, 87.4, 59.6, 59.0, 38.1. LC-MS m/z (ESI$^+$): Calculated for C$_{24}$H$_{20}$F$_3$N ([M+H]$^+$): 380.2, found: 380.2. Known compound$^8$
**N-benzyl-3-(4-methoxyphenyl)-N-methyl-1-phenylprop-2-yn-1-amine (4i)**

![Chemical structure of 4i](image)

(138.2 mg, 81%) as colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J = 7.8$ Hz, 2H), 7.58-7.56 (m, 2H), 7.49-7.28 (m, 8H), 6.95-6.94 (m, 2H) 4.97 (s, 1H), 3.88 (s, 3H), 3.79-3.69 (m, 2H), 2.30 (s, 3H). $^{13}$C NMR (600 MHz, CDCl$_3$) $\delta$ 159.6, 139.4, 139.3, 133.3, 129.1, 128.4, 128.3, 128.2, 127.5, 127.1, 88.5, 83.2, 59.7, 59.0, 55.4, 38.1. LC-MS m/z (ESI$^+$): Calculated for C$_{24}$H$_{23}$NO ([M+H]$^+$): 342.2, found: 342.2. Known compound[8]

**N-benzyl-3-cyclopropyl-N-methyl-1-phenylprop-2-yn-1-amine (4j)**

![Chemical structure of 4j](image)

(20.6 mg, 15%) as light yellow oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.66-7.65 (m, 2H), 7.45-7.30 (m, 8H), 7.49-7.28 (m, 8H), 4.71 (s, 1H) 3.69-3.57 (m, 2H), 2.20 (s, 3H), 1.49-1.46 (m, 1H), 0.93-0.84 (m, 4H). $^{13}$C NMR (600 MHz, CDCl$_3$) $\delta$ 139.7, 139.6, 129.0, 128.4, 128.3, 128.0, 127.3, 127.0, 92.1, 70.1, 59.2, 58.8, 37.9, 8.7, -0.3. LC-MS m/z (ESI$^+$): Calculated for C$_{20}$H$_{21}$N ([M+H]$^+$): 276.2, found: 276.2. Known compound[8]

**1-Methyl-2,3-diphenyl-1H-pyrrole (5)**

![Chemical structure of 5](image)

(37.3 mg, 32%) as colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42-7.31 (m, 5H), 7.24-7.19 (m, 4H), 7.13-7.10 (m, 1H), 6.78 (d, $J = 3.0$ Hz, 1H), 6.45 (d, $J = 3.0$ Hz, 1H), 3.55 (s, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ 136.2, 132.4, 130.6, 130.2, 128.0, 127.6, 127.3, 127.1, 124.6, 122.4, 121.8,
107.4, 34.3. LC-MS m/z (ESI⁺): Calculated for C₂₀H₂₁N ([M+H]⁺): 234.1, found: 234.1. Known compound[⁹]
6. $^1$H NMR and $^{13}$C NMR Spectra

(3a)

$^1$H NMR and $^{13}$C NMR Spectra

Sample Name: H047-9-F
Solvent: CDCl$_3$

NMR data and spectrum images are shown in the diagram.
(3o)

20201211002
No. : 20201211002
Solvent: CDCl3
Sample Name: H047-34-A
D:\600MHz\2020data\20201211002

20210226149
No. : 20210226149
Solvent: CDCl3
Sample Name: H047-66-B
D:\400MHz\2021data\20210226149

$\text{C}_8\text{H}_5\text{O}$

$\text{C}_8\text{H}_5\text{O}$
Sample Name: H047-73-D
Solvent: CDCl3
D:\600MHz\2021data\20210318002

Sample Name: H047-10-F
Solvent: CDCl3
D:\400MHz\2020data\20201105024

(3q)

Sample Name: H047-73-D
Solvent: CDCl3
D:\600MHz\2021data\20210318002

Sample Name: H047-10-F
Solvent: CDCl3
D:\400MHz\2020data\20201105024

S32 / S49
(4b)
Sample Name: H047-1-B
Solvent: CDCl3

(4i)

Sample Name: H047-1-A
Solvent: CDCl3

Chemical shifts (ppm):
- H047-1-B:
  - 3.00, 2.01, 2.97, 0.99, 1.98, 8.00, 1.98, 1.98, 2.30, 3.69, 3.71, 3.77, 3.79, 3.88, 4.97, 6.94, 6.94, 6.95, 6.95, 7.28, 7.31, 7.32, 7.34, 7.35, 7.37, 7.39, 7.40, 7.41, 7.42, 7.43, 7.47, 7.48, 7.56, 7.56, 7.57, 7.57, 7.73, 7.75
- H047-1-A:
  - 3.02, 2.01, 2.02, 2.97, 0.99, 1.98, 8.00, 1.98, 1.98, 2.30, 3.69, 3.71, 3.77, 3.79, 3.88, 4.97, 6.94, 6.94, 6.95, 6.95, 7.28, 7.31, 7.32, 7.34, 7.35, 7.37, 7.39, 7.40, 7.41, 7.42, 7.43, 7.47, 7.48, 7.56, 7.56, 7.57, 7.57, 7.73, 7.75
Sample Name: H047-1-C
Solvent: CDCl3

Chemical shifts:

- C6: 128.29 ppm
- C7: 128.36 ppm
- C8: 129.02 ppm
- C9: 139.55 ppm
- C10: 139.68 ppm

Structures:

1. Benzene ring with methyl group
2. Compound with cyclohexane ring and methyl group
3. Compound with nitrogen atom and methyl group
References


