Three-component carboarylation of unactivated imines with arynes and carbon nucleophiles

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General information

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AC-400 FT spectrometer (400 MHz and 100 MHz, respectively) using tetramethylsilane as an internal reference. NMR multiplicities were abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass). Electrospray ionization (ESI) mass spectrometry data were acquired using a Thermo LTQ Orbitrap XL instrument equipped with an ESI source and controlled by Xcalibur software. Matrix assisted laser desorption ionization (MALDI) mass spectra were recorded on a MALDI-TOF spectrometer equipped with a MALDI source.

The preparation of imines 1a, 1b, 1h, 1i, 1n, and 1u was shown below, and the rest of imines 1 and 2-(trimethylsilyl)aryl triflates 2b-g were prepared according to literature procedures. The rest of chemicals were purchased from the Sinopharm Chemical Reagent Co., Meryer, Acros, Alfa Aesar, and TCI.

Unless otherwise noted, all the reactions were performed in oven-dried glassware under a nitrogen atmosphere with freshly distilled solvents. Toluene, 1,2-dichloroethane, chloroform, and acetonitrile were dried and distilled from calcium hydride. Tetrahydrofuran was dried and distilled from metal sodium and benzophenone. CsF was dried in vacuum at 130 °C for 2 h before use.

Abbreviations: TBAF = tetrabutylammonium fluoride, Tf = trifluoromethanesulfonyl, THF = tetrahydrofuran, TMS = trimethylsilyl.

Preparation of imines

(1) Preparation of imines 1a, 1b, 1h, and 1u

\[ \text{R}^1\text{CHO} + \text{MeNH}_2 \xrightarrow{\text{water, rt}} \text{R}^1\text{NMe} \]

A flask containing an aldehyde (3.0 mmol) and aqueous solution of methylamine (0.19 mol, 40 wt.%, 15 mL) was stirred at room temperature for 10 h. The mixture was extracted with dichloromethane (10 mL × 3), washed with brine, and dried over potassium hydroxide. After filtration, all volatiles were removed under reduced pressure to give crude imines, which were used in the following three-component reaction without further purification.

(E)-1-Cyclohexyl-N-methylmethanimine (1a). Colorless oil (0.353 g, 94% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.52 (d, J = 3.7 Hz, 1H), 3.24 (s, 3H), 2.19-2.07 (m, 1H), 1.85-1.62 (m, 5H), 1.34-1.13 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.3, 48.0, 43.5, 29.6, 26.1, 25.6; IR (film): ν 2927, 2848, 1676, 1453, 1401 cm$^{-1}$; HRMS (ESI) calcd for C$_9$H$_{16}$N$^+$ (M+H)$^+$ 126.1277, found 126.1273.
(E)-1-Cyclopropyl-N-methylmethanimine (1b). Colorless oil (0.127 g, 51% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.99 (d, $J$ = 7.5 Hz, 1H), 3.22 (s, 3H), 1.71-1.59 (m, 1H), 0.90-0.81 (m, 2H), 0.71-0.62 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.7, 47.6, 16.3, 5.8; IR (film): $\nu$ 2973, 2921, 2848, 1670, 1394 cm$^{-1}$; HRMS (ESI) calcd for C$_5$H$_{10}$N$^+$ (M+H)$^+$ 84.0808, found 84.0803.

(1b)

(E)-1-Ferrocenyl-N-methylmethanimine (1h). Red oil (0.627 g, 92% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (s, 1H), 4.61 (s, 2H), 4.35 (s, 2H), 4.18 (s, 5H), 3.34 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.2, 80.8, 70.3, 69.1, 68.3, 48.5; IR (film): $\nu$ 3097, 2927, 2881, 2770, 1683, 1650, 1460, 1401 cm$^{-1}$; MS (MALDI) calcd for C$_{12}$H$_{13}$FeN$^+$ (M)+ 227.04, found 227.01.

(1h)

(E)-N-Methyl-1-(4-(methylsulfonyl)phenyl)methanimine (1u). Yellow solid (0.533 g, 90% yield); m.p. 170-171 ºC; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.36 (d, $J$ = 1.6 Hz, 1H), 7.99 (d, $J$ = 8.4 Hz, 2H), 7.90 (d, $J$ = 8.4 Hz, 2H), 3.58 (d, $J$ = 1.6 Hz, 3H), 3.07 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.6, 141.9, 141.1, 128.7, 127.9, 48.6, 44.6; IR (film): $\nu$ 2960, 2926, 2861, 1643, 1453, 1401 cm$^{-1}$; HRMS (ESI) calcd for C$_9$H$_{12}$NO$_2$S$^+$ (M+H)$^+$ 198.0583, found 198.0575.

(1u)

(2) Preparation of imines 1i and 1n

A flask containing cyclohexanecarbaldehyde (0.337 g, 3.0 mmol), an amine (6.0 mmol), dichloromethane (20 mL), and magnesium sulfate (1.20 g) was stirred at room temperature for 10 h. After filtration, all volatiles were removed under reduced pressure to give crude imines, which were used in the following three-component reaction without further purification.
(E)-N-Butyl-1-cyclohexylmethanimine (1i). Colorless oil (0.462 g, 92% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 (d, $J = 5.1$ Hz, 1H), 3.33 (t, $J = 7.0$ Hz, 2H), 2.23-2.09 (m, 1H), 1.83-1.71 (m, 4H), 1.69-1.63 (m, 1H), 1.61-1.51 (m, 2H), 1.36-1.16 (m, 7H), 0.91 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.8, 61.2, 43.6, 33.0, 29.9, 26.1, 25.6, 20.4, 14.0; IR (film): $\nu$ 2926, 2855, 1670, 1453, 1381 cm$^{-1}$; HRMS (ESI) calcd for C$_{11}$H$_{22}$N$^+$ (M+H)$^+$ 168.1747, found 168.1742.

(E)-1-Cyclohexyl-N-(prop-2-yn-1-yl)methanimine (1n). Colorless oil (0.394 g, 88% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83-7.79 (m, 1H), 4.27-4.23 (m, 2H), 2.43 (t, $J = 2.5$ Hz, 1H), 2.28-2.17 (m, 1H), 1.87-1.73 (m, 4H), 1.72-1.64 (m, 1H), 1.37-1.17 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.7, 79.5, 75.0, 47.2, 43.6, 29.6, 26.1, 25.6; IR (film): $\nu$ 3313, 2927, 2849, 1670, 1447, 1375 cm$^{-1}$; HRMS (ESI) calcd for C$_{10}$H$_{16}$N$^+$ (M+H)$^+$ 150.1277, found 150.1273.

Optimization of the reaction conditions$^a$

For the procedure, see below. The results were summarized in the following table.

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* Reaction conditions: 1a (0.20 mmol), 2a (0.24 mmol), chloroform (0.5 mL), F\(^-\) source (0.48 mmol), solvent (0.5 mL), 50 °C, 10 h.  
  b Isolated yields.  
  c 1 M in THF.  
  d 2a (0.30 mmol), F\(^-\) source (0.60 mmol).  
  e Chloroform (0.3 mL), MeCN (0.3 mL).

**General procedure for the three-component reaction of imines, arynes, and chloroform (Schemes 2 and 3)**

A flask containing dry CsF (91.1 mg, 0.60 mmol) was evacuated and purged with nitrogen gas three times. To the flask were added 2-(trimethylsilyl)aryl triflate 2 (0.30 mmol), imine 1 (0.20 mmol), acetonitrile (0.3 mL), and chloroform (0.3 mL). The mixture was stirred at 65 °C for 10 h, cooled to room temperature, and purified directly by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:20 to 0:1 v/v), to give amine 3 or enamine 4.

**Analytical data for the products (Schemes 2 and 3)**

\[ \text{N-Methyl-N-(2,2,2-trichloro-1-cyclohexylethyl)aniline (3a). Colorless oil (52.0 mg, 81\% yield); } \]
\[ ^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.29-7.21 (m, 2H), 6.84-6.72 (m, 3H), 4.40 (d, } J = 9.2 \text{ Hz, 1H), 2.97 } \text{s, 3H), 2.38-2.15 (m, 2H), 1.87-1.79 (m, 1H), 1.76-1.61 (m, 3H), 1.39-0.97 (m, 5H); } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 150.7, 129.3, 117.7, 112.9, 104.8, 77.0, 40.3, 31.9, 31.5, 31.4, 26.5, 26.2; \text{IR (film): } \nu 3060, 3031, 2930, 2850, 1605, 1501, 1450, 1371, 816, 747, 687 \text{ cm}^{-1}; \text{HRMS (ESI) calcd for } \text{C}_{15}\text{H}_{21}\text{NCl}_3^{+} (\text{M+H})^{+} 320.0734, \text{found 320.0728.} \]

\[ \text{N-Methyl-N-(2,2,2-trichloro-1-cyclohexylethyl)aniline (3b). Colorless oil (52.0 mg, 81\% yield); } \]
N-Methyl-N-(2,2,2-trichloro-1-cyclopropylethyl)aniline (3b). Colorless oil (40.7 mg, 73% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.27-7.21 (m, 2H), 6.89 (d, \(J = 8.2\) Hz, 2H), 6.78 (t, \(J = 7.2\) Hz, 1H), 3.84 (d, \(J = 8.7\) Hz, 1H), 3.17 (s, 3H), 1.58-1.46 (m, 1H), 0.83-0.73 (m, 1H), 0.72-0.60 (m, 1H), 0.29-0.17 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 150.6, 129.1, 118.1, 113.4, 104.9, 78.5, 33.7, 11.5, 10.1, 2.6; IR (film): \(\nu\) 3071, 3018, 2927, 2822, 1604, 1505, 1362, 817, 746, 687 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{12}\)H\(_{15}\)NCl\(_3\)+ (M+H)+ 278.0265, found 278.0259.

N-Methyl-N-(1,1,1-trichlorotridecan-2-yl)aniline (3c). Colorless oil (59.7 mg, 76% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.30-7.22 (m, 2H), 6.90 (d, \(J = 8.3\) Hz, 2H), 6.79 (t, \(J = 7.3\) Hz, 1H), 4.59 (dd, \(J = 10.3, 3.4\) Hz, 1H), 3.01 (s, 3H), 2.21-2.02 (m, 2H), 1.44-1.13 (m, 18H), 0.88 (t, \(J = 6.9\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 150.9, 129.2, 118.1, 113.7, 105.0, 73.1, 32.1, 31.5, 29.7, 29.5, 28.0, 26.5, 22.8, 14.3; IR (film): \(\nu\) 3031, 2920, 2855, 1597, 1505, 1460, 1381, 785, 752, 693 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{20}\)H\(_{33}\)NCl\(_3\)+ (M+H)+ 392.1673, found 392.1663.

N-Methyl-N-(2,2,2-trichloro-1-(4-methoxyphenyl)ethyl)aniline (3d). Yellow oil (49.6 mg, 72% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.58-7.47 (m, 2H), 7.35-7.26 (m, 2H), 7.07 (d, \(J = 8.2\) Hz, 2H), 5.86 (s, 1H), 3.81 (s, 3H), 2.90 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 159.4, 150.5, 130.3, 129.4, 127.1, 118.9, 114.2, 113.8, 102.8, 76.3, 55.4, 34.7; IR (film): \(\nu\) 3064, 3038, 2953, 2926, 2842, 1597, 1512, 1460, 1348, 798, 746, 693 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{16}\)H\(_{17}\)NOCl\(_3\)+ (M+H)+ 344.0370, found 344.0367.

N-Methyl-N-(2,2,2-trichloro-1-(3-methoxyphenyl)ethyl)aniline (3e). Yellow oil (43.4 mg, 63% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.35-7.22 (m, 3H), 7.21-7.12 (m, 2H), 7.07 (d, \(J = 8.2\) Hz, 2H), 6.89-6.83 (m, 2H), 5.88 (s, 1H), 3.78 (s, 3H), 2.91 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 159.5, 150.4, 136.5, 129.5, 129.4, 121.4, 118.9, 115.4, 114.1, 113.1, 102.4, 76.3, 55.4, 34.8; IR (film): \(\nu\) 3029, 2931, 2832, 1599, 1507, 1488, 1460, 806, 748, 689 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{16}\)H\(_{17}\)NOCl\(_3\)+ (M+H)+ 344.0370, found 344.0367.
**N-Methyl-N-(2,2,2-trichloro-1-(2-methoxyphenyl)ethyl)aniline (3f).** Yellow oil (45.5 mg, 66% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.08 (dd, $J$ = 7.9, 1.5 Hz, 1H), 7.38-7.26 (m, 3H), 7.14 (d, $J$ = 8.1 Hz, 2H), 7.03-6.98 (m, 1H), 6.88 (dd, $J$ = 8.2, 0.7 Hz, 1H), 6.81 (t, $J$ = 7.2 Hz, 1H), 6.40 (s, 1H), 3.57 (s, 3H), 2.92 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.9, 150.6, 129.5, 129.1, 128.7, 123.8, 111.9, 118.3, 114.4, 111.1, 103.4, 69.2, 55.6, 34.9; IR (film): $\nu$ 3063, 2923, 2858, 1606, 1505, 1464, 1379, 800, 753, 688 cm$^{-1}$; HRMS (ESI) calcd for C$_{16}$H$_{17}$NOCl$_3$+ (M+H)$^+$ 344.0370, found 344.0365.

**N-Methyl-N-(2,2,2-trichloro-1-mesitylethyl)aniline (3g).** Yellow oil (50.7 mg, 71% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.23-7.17 (m, 2H), 7.14-7.08 (m, 2H), 6.96-6.89 (m, 1H), 6.84 (s, 1H), 6.78 (s, 1H), 6.03 (s, 1H), 3.04 (s, 3H), 2.61 (s, 3H), 2.49 (s, 3H), 2.22 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 151.6, 139.0, 138.0, 137.7, 132.1, 131.9, 129.9, 128.8, 122.0, 120.8, 104.1, 78.9, 41.6, 23.9, 23.2, 20.8; IR (film): $\nu$ 3062, 3020, 2957, 2919, 2865, 1599, 1494, 1449, 1377, 815, 748, 695, 651 cm$^{-1}$; HRMS (ESI) calcd for C$_{18}$H$_{21}$NCl$_3$+ (M+H)$^+$ 356.0734, found 356.0725.

**N-Methyl-N-(2,2,2-trichloro-1-ferrocenylethyl)aniline (3h).** Red oil (57.3 mg, 68% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40-7.30 (m, 2H), 7.00 (d, $J$ = 8.2 Hz, 2H), 6.85 (t, $J$ = 7.3 Hz, 1H), 5.94 (s, 1H), 4.70 (s, 1H), 4.38 (s, 1H), 4.26 (s, 1H), 4.21 (s, 1H), 4.13 (s, 5H), 3.01 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 150.3, 129.5, 118.3, 113.5, 103.2, 83.2, 73.9, 71.3, 69.6, 69.2, 68.1, 67.8, 34.1; IR (film): $\nu$ 3088, 2954, 2924, 2859, 1594, 1502, 1458, 814, 752, 693 cm$^{-1}$; MS (MALDI) calcd for C$_{19}$H$_{18}$FeNCl$_3$+ (M)$^+$ 420.98, found 420.99.

**N-Butyl-N-(2,2,2-trichloro-1-cyclohexylethyl)aniline (3i).** Colorless oil (55.9 mg, 77% yield);
**1H NMR (400 MHz, CDCl3)** δ 7.24 (t, J = 7.8 Hz, 2H), 6.82 (d, J = 8.2 Hz, 2H), 6.76 (t, J = 7.2 Hz, 1H), 4.33 (d, J = 9.3 Hz, 1H), 3.46 (t, J = 8.0 Hz, 2H), 2.33-2.27 (m, 1H), 2.23-2.13 (m, 1H), 1.88-1.80 (m, 2H), 1.76-1.48 (m, 4H), 1.41-1.00 (m, 7H), 0.95 (t, J = 7.3 Hz, 3H); **13C NMR (100 MHz, CDCl3)** δ 149.3, 129.2, 117.9, 114.7, 105.1, 79.0, 43.5, 41.1, 32.1, 32.0, 29.0, 26.6, 26.5, 26.3, 20.7, 14.1; IR (film): ν 3064, 3031, 2960, 2927, 2855, 1601, 1500, 1446, 1368, 811, 746, 693 cm⁻¹; HRMS (ESI) calcd for C18H27NCl3⁺ (M+H)⁺ 362.1204, found 362.1197.

![](image)

**N-Isopropyl-N-(2,2,2-trichloro-1-cyclohexylethyl)aniline (3j).** Colorless oil (42.5 mg, 61% yield); **1H NMR (400 MHz, CDCl3)** δ 7.24-7.18 (m, 2H), 7.02 (d, J = 8.1 Hz, 2H), 6.80 (t, J = 7.2 Hz, 1H), 4.27 (d, J = 9.5 Hz, 1H), 4.24-4.13 (m, 1H), 2.36-2.30 (m, 1H), 2.17-2.07 (m, 1H), 2.05-1.99 (m, 1H), 1.87-1.81 (m, 1H), 1.75-1.64 (m, 2H), 1.45 (d, J = 6.8 Hz, 3H), 1.38 (d, J = 6.9 Hz, 3H), 1.35-1.15 (m, 4H), 1.12-0.98 (m, 1H); **13C NMR (100 MHz, CDCl3)** δ 148.3, 128.7, 119.0, 105.6, 80.4, 41.3, 32.8, 32.4, 26.9, 26.4, 22.5, 21.5; IR (film): ν 3058, 2932, 2851, 1600, 1505, 1450, 1368, 801, 752, 699 cm⁻¹; HRMS (ESI) calcd for C17H25NCl3⁺ (M+H)⁺ 348.1047, found 348.1041.

![](image)

**N-(tert-Butyl)-N-(2,2,2-trichloro-1-cyclohexylethyl)aniline (3k).** Colorless oil (37.0 mg, 51% yield); **1H NMR (400 MHz, CDCl3)** δ 7.40-7.34 (m, 2H), 7.30-7.22 (m, 3H), 4.04 (d, J = 8.3 Hz, 1H), 2.49-2.40 (m, 1H), 2.14-2.05 (m, 1H), 1.90-1.82 (m, 1H), 1.79-1.63 (m, 3H), 1.36-1.06 (m, 14H); **13C NMR (100 MHz, CDCl3)** δ 141.4, 135.5, 127.4, 126.5, 106.7, 77.1, 56.9, 41.9, 34.2, 32.5, 30.3, 27.3, 27.0, 26.6; IR (film): ν 3051, 2927, 2848, 1597, 1453, 1492, 1401, 1362, 804, 752, 707 cm⁻¹; HRMS (ESI) calcd for C18H27NCl3⁺ (M+H)⁺ 362.1204, found 362.1196.

![](image)

**N-Benzyl-N-(2,2,2-trichloro-1-cyclohexylethyl)aniline (3l).** Colorless oil (50.8 mg, 64% yield); **1H NMR (400 MHz, CDCl3)** δ 7.29-7.19 (m, 4H), 7.18-7.10 (m, 3H), 6.85 (d, J = 8.4 Hz, 2H), 6.74 (t, J = 7.2 Hz, 1H), 4.87 (s, 2H), 4.54 (d, J = 7.7 Hz, 1H), 2.32-2.14 (m, 3H), 1.89-1.81 (m, 1H), 1.76-1.63 (m, 2H), 1.55-1.43 (m, 1H), 1.35-1.16 (m, 4H); **13C NMR (100 MHz, CDCl3)** δ 150.0, 138.4, 128.9, 128.4, 127.4, 126.5, 119.1, 116.7, 104.7, 80.6, 48.6, 41.5, 32.6, 31.9, 26.9, 26.6, 26.3;
IR (film): $\nu$ 3057, 3031, 2930, 2855, 1604, 1499, 1453, 1322, 811, 753, 698 cm$^{-1}$; HRMS (ESI) calcd for C$_{21}$H$_{25}$NCl$_3^+$ (M+H)$^+$ 396.1047, found 396.1040.

![3m](image)

$N$-Allyl-$N$(2,2,2-trichloro-1-cyclohexylethyl)aniline (3m). Colorless oil (45.1 mg, 65% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29-7.18 (m, 2H), 6.85 (d, $J$ = 8.2 Hz, 2H), 6.77 (t, $J$ = 7.2 Hz, 1H), 5.94-5.78 (m, 1H), 5.29-5.13 (m, 2H), 4.41 (d, $J$ = 9.1 Hz, 1H), 4.20 (d, $J$ = 5.7 Hz, 2H), 2.33-2.27 (m, 1H), 2.25-2.12 (m, 1H), 1.96-1.78 (m, 2H), 1.75-1.63 (m, 2H), 1.39-1.04 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.4, 135.6, 129.1, 118.3, 117.2, 115.2, 104.9, 78.8, 46.8, 41.1, 32.1, 31.8, 26.6, 26.4, 26.2; IR (film): $\nu$ 3071, 2926, 2855, 1603, 1500, 1450, 817, 752, 687 cm$^{-1}$;

![3n](image)

$N$-(Prop-2-yn-1-yl)-$N$(2,2,2-trichloro-1-cyclohexylethyl)aniline (3n). Colorless oil (37.2 mg, 54% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35-7.26 (m, 2H), 6.97 (d, $J$ = 8.2 Hz, 2H), 6.83 (t, $J$ = 7.3 Hz, 1H), 4.50 (dd, $J$ = 18.5, 2.4 Hz, 1H), 4.44 (d, $J$ = 9.4 Hz, 1H), 4.08 (dd, $J$ = 18.5, 2.4 Hz, 1H), 2.40-2.17 (m, 3H), 2.14-2.05 (m, 1H), 1.90-1.80 (m, 1H), 1.74-1.64 (m, 2H), 1.40-1.14 (m, 4H), 1.10-0.98 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.7, 129.3, 118.7, 113.8, 104.2, 80.0, 77.2, 77.0, 72.3, 41.1, 34.3, 32.1, 31.9, 26.6, 26.2, 26.1; IR (film): $\nu$ 3310, 3044, 2926, 2855, 1597, 1504, 1453, 1388, 814, 746, 686 cm$^{-1}$; HRMS (ESI) calcd for C$_{17}$H$_{23}$NCl$_3^+$ (M+H)$^+$ 346.0891, found 346.0883.

![3o](image)

2-Phenyl-1-(trichloromethyl)-1,2,3,4-tetrahydroisoquinoline (3o). White solid (52.3 mg, 80% yield); m.p. 100-101 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.65 (d, $J$ = 7.7 Hz, 1H), 7.34-7.17 (m, 5H), 7.03 (d, $J$ = 8.1 Hz, 2H), 6.84 (t, $J$ = 7.3 Hz, 1H), 5.64 (s, 1H), 4.13-4.05 (m, 1H), 3.67-3.59 (m, 1H), 3.23-3.15 (m, 1H), 3.12-3.02 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 150.0, 136.5, 131.8, 129.9, 129.3, 128.9, 128.8, 125.8, 119.4, 116.0, 106.4, 74.3, 43.0, 27.5; IR (film): $\nu$ 3064, 3031, 2923, 2855, 1597, 1499, 1401, 803, 746, 687 cm$^{-1}$; HRMS (ESI) calcd for C$_{16}$H$_{15}$NCl$_3^+$ (M+H)$^+$ 326.0265, found 326.0260.
1'-Phenyl-2'(trichloromethyl)spiro[cyclohexane-1,3'-indoline] (3p). Yellow oil (54.8 mg, 72% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 (d, $J = 7.9$ Hz, 2H), 7.36-7.26 (m, 3H), 7.21-7.12 (m, 2H), 7.02 (t, $J = 7.3$ Hz, 1H), 6.98-6.90 (m, 1H), 4.57 (s, 1H), 2.50-2.40 (m, 1H), 2.30-2.20 (m, 1H), 2.08-1.87 (m, 2H), 1.73-1.37 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.9, 145.8, 141.0, 129.3, 127.2, 123.0, 122.4, 121.9, 118.8, 114.6, 102.2, 85.8, 51.8, 41.3, 28.3, 25.8, 23.8, 22.6; IR (film): $\nu$ 3038, 2926, 2858, 1597, 1492, 1473, 1460, 1355, 820, 746, 699 cm$^{-1}$; HRMS (ESI) calcd for C$_{20}$H$_{21}$NCl$_3$ (M+H)$^+$ 380.0734, found 380.0726.

4-Methoxy-N-phenyl-N-(1,1,1-trichloro-3-methylbutan-2-yl)aniline (3q). Yellow oil (44.7 mg, 60% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 (d, $J = 8.2$ Hz, 2H), 7.20-7.13 (m, 2H), 6.92-6.86 (m, 2H), 6.85-6.67 (m, 3H), 4.69 (d, $J = 9.8$ Hz, 1H), 3.82 (s, 3H), 2.43-2.31 (m, 1H), 1.33 (d, $J = 6.7$ Hz, 3H), 1.23 (d, $J = 6.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 131.5, 129.0, 117.7, 114.4, 105.0, 78.5, 55.5, 31.6, 23.1, 21.9; IR (film): $\nu$ 3005, 2960, 2933, 2842, 1612, 1501, 1459, 792, 746, 693 cm$^{-1}$; HRMS (ESI) calcd for C$_{18}$H$_{21}$OCl$_3$ (M+H)$^+$ 372.0683, found 372.0678.

4-Methoxy-N-phenyl-N-(2,2,2-trichloro-1-(4-methoxyphenyl)ethyl)aniline (3r). Yellow oil (45.4 mg, 52% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29-7.24 (m, 2H), 7.21-7.15 (m, 2H), 6.89 -6.74 (m, 9H), 6.13 (s, 1H), 3.80 (s, 3H), 3.79 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.8, 158.2, 150.5, 135.7, 133.4, 132.0, 129.0, 127.4, 119.7, 117.3, 114.0, 113.3, 103.7, 76.0, 55.5, 55.3; IR (film): $\nu$ 3011, 2933, 2842, 1612, 1501, 1459, 792, 746, 693 cm$^{-1}$; HRMS (ESI) calcd for C$_{22}$H$_{21}$O$_2$NCl$_3$ (M+H)$^+$ 436.0632, found 436.0624.
A 40:60 mixture of N,4-dimethyl-N-(2,2,2-trichloro-1-cyclohexylethyl)aniline (3s) and N,3-dimethyl-N-(2,2,2-trichloro-1-cyclohexylethyl)aniline (3s') was obtained as a colorless oil (49.5 mg, 74% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) for amine 3s: \(\delta\) 7.06 (d, \(J = 8.2\) Hz, 2H), 6.72 (d, \(J = 8.2\) Hz, 2H), 4.35 (d, \(J = 9.3\) Hz, 1H), 2.96 (s, 3H), 2.27-2.17 (m, 5H), 1.86-1.80 (m, 1H), 1.76-1.62 (m, 3H), 1.39-0.96 (m, 5H); \(^1\)H NMR (400 MHz, CDCl\(_3\)) for amine 3s': \(\delta\) 7.14 (t, \(J = 7.9\) Hz, 1H), 6.65-6.56 (m, 3H), 4.38 (d, \(J = 9.3\) Hz, 1H), 2.96 (s, 3H), 2.39-2.28 (m, 5H), 1.86-1.80 (m, 1H), 1.76-1.62 (m, 3H), 1.39-0.96 (m, 5H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 150.6, 148.4, 138.9, 129.7, 129.0, 126.6, 118.5, 113.4, 112.8, 110.1, 104.9, 104.7, 77.2, 76.9, 40.2, 31.8, 31.4, 31.3, 31.2, 26.4, 26.3, 26.1, 20.2; IR (film): \(\nu\) 2926, 2849, 1604, 1519, 1492, 1302, 804, 759 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{16}\)H\(_{24}\)NCl\(_3\)\(^+\) (M+H)\(^+\) 334.0891, found 334.0888.

\(\begin{align*}
\text{N,3,4-Trimethyl-N-(2,2,2-trichloro-1-cyclohexylethyl)aniline (3t). Colorless oil (53.7 mg, 77\% yield);} \\
\text{\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.01 (d, \(J = 8.2\) Hz, 1H), 6.63-6.53 (m, 2H), 4.35 (d, \(J = 9.3\) Hz, 1H), 2.95 (s, 3H), 2.38-2.14 (m, 8H), 1.87-1.79 (m, 1H), 1.77-1.56 (m, 3H), 1.37-0.96 (m, 5H);} \\
\text{\(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 149.0, 137.4, 130.4, 125.6, 114.3, 110.4, 105.1, 77.1, 40.4, 32.0, 31.5, 31.4, 26.5, 26.2, 20.6, 18.7; IR (film): \(\nu\) 2923, 2860, 1617, 1505, 1450, 1381, 804, 752, 704 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{17}\)H\(_{25}\)NCl\(_3\)\(^+\) (M+H)\(^+\) 348.1047, found 348.1040.}
\end{align*}\)

\(\begin{align*}
\text{3,4-Dimethoxy-N-methyl-N-(2,2,2-trichloro-1-cyclohexylethyl)aniline (3u). Colorless oil (57.1 mg, 75\% yield);} \\
\text{\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.80 (d, \(J = 8.8\) Hz, 1H), 6.40 (d, \(J = 2.9\) Hz, 1H), 6.33 (dd, \(J = 8.8, 2.9\) Hz, 1H), 4.25 (d, \(J = 9.1\) Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 2.97 (s, 3H), 2.34-2.17 (m, 2H), 1.88-1.64 (m, 4H), 1.38-0.98 (m, 5H);} \\
\text{\(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 149.7, 146.1, 141.6,}
\end{align*}\)
112.9, 105.1, 99.1, 78.2, 56.6, 56.1, 40.4, 32.0, 31.9, 31.5, 26.5, 26.2; IR (film): ν 2920, 2855, 1600, 1512, 1450, 804, 759 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{17}\)H\(_{25}\)NO\(_2\)Cl\(_3\)\(^+\) (M+H\(^+\))\(^+\) 380.0945, found 380.0944.

3,4-Difluoro-\(N\)-methyl-\(N\)-(2,2,2-trichloro-1-cyclohexylethyl)aniline (3v). Colorless oil (27.8 mg, 39% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(δ\) 7.07-6.97 (m, 1H), 6.63-6.51 (m, 1H), 6.50-6.40 (m, 1H), 4.21 (d, \(J = 9.2\) Hz, 1H), 2.94 (s, 3H), 2.37-2.14 (m, 2H), 1.88-1.79 (m, 1H), 1.78-1.62 (m, 3H), 1.37-0.96 (m, 5H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(δ\) 150.8 (dd, \(J = 243.0, 13.2\) Hz), 148.0 (d, \(J = 8.2\) Hz), 143.1 (dd, \(J = 236.8, 13.1\) Hz), 117.4 (dd, \(J = 17.6, 1.8\) Hz), 108.1 (dd, \(J = 5.4, 2.9\) Hz), 104.3, 102.1 (d, \(J = 21.5\) Hz), 77.7, 40.3, 31.9, 31.4, 26.4, 26.1; IR (film): ν 2926, 2855, 1604, 1520, 1446, 811, 759, 703 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{15}\)H\(_{19}\)NCl\(_3\)F\(_2\)\(^+\) (M+H\(^+\))\(^+\) 356.0546, found 356.0538.

3-Methoxy-\(N\)-methyl-\(N\)-(2,2,2-trichloro-1-cyclohexylethyl)aniline (3w). Colorless oil (59.6 mg, 85% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(δ\) 7.16 (t, \(J = 8.3\) Hz, 1H), 6.47-6.40 (m, 1H), 6.36-6.30 (m, 2H), 4.37 (d, \(J = 9.3\) Hz, 1H), 3.79 (s, 3H), 2.95 (s, 3H), 2.35-2.15 (m, 2H), 1.88-1.78 (m, 1H), 1.75-1.61 (m, 3H), 1.37-0.97 (m, 5H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(δ\) 160.8, 152.1, 130.0, 106.1, 104.6, 101.9, 100.0, 77.01, 55.3, 40.3, 31.9, 31.6, 31.3, 26.4, 26.1; IR (film): ν 2926, 2848, 1610, 1578, 1447, 1302, 799, 765 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{16}\)H\(_{23}\)NOCl\(_3\)\(^+\) (M+H\(^+\))\(^+\) 350.0840, found 350.0835.

\(N\)-Methyl-\(N\)-(2,2,2-trichloro-1-cyclohexylethyl)naphthalen-2-amine (3x). Colorless oil (53.4 mg,
72% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.76-7.64 (m, 3H), 7.38 (t, \(J = 7.5\) Hz, 1H), 7.26-7.16 (m, 2H), 7.01 (s, 1H), 4.54 (d, \(J = 9.1\) Hz, 1H), 3.09 (s, 3H), 2.42-2.22 (m, 2H), 1.88-1.82 (m, 3H), 1.79-1.64 (m, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.5, 135.0, 129.0, 127.6, 127.3, 126.6, 126.5, 122.7, 115.9, 107.2, 104.8, 76.8, 40.4, 31.9, 31.4, 26.5, 26.2; IR (film): \(\nu\) 3054, 2926, 2855, 1636, 1603, 1512, 1482, 1388, 804, 759, 706 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{19}\)H\(_{23}\)NCl\(_3\)\(^+(M+H)\)\(^+\) 370.0891, found 370.0885.

\(4a\)  

\(N\)-(2,2-Dichloro-1-(4-(trifluoromethyl)phenyl)vinyl)-N-methylaniline (4a). Yellow oil (35.3 mg, 51% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.65-7.62 (m, 4H), 7.28-7.21 (m, 2H), 6.83 (t, \(J = 7.3\) Hz, 1H), 6.81-6.75 (m, 2H), 3.1 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 146.4, 140.6, 139.0, 131.1, 130.8, 130.1, 129.4, 125.4 (q, \(J = 3.8\) Hz), 121.0, 119.2, 114.0, 37.6; IR (film): \(\nu\) 2966, 2926, 2861, 1604, 1518, 1459, 1381, 746 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{16}\)H\(_{13}\)NF\(_2\)Cl\(_2\)\(^+(M+H)\)\(^+\) 346.0372, found 346.0361.

\(4b\)  

4-(2,2-Dichloro-1-(methyl(phenyl)amino)vinyl)benzonitrile (4b). Yellow oil (38.8 mg, 64% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.65-7.62 (m, 4H), 7.28-7.21 (m, 2H), 6.84 (t, \(J = 7.3\) Hz, 1H), 6.79-6.73 (m, 2H), 3.11 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 146.1, 140.4, 140.1, 132.2, 130.4, 129.5, 121.8, 119.4, 118.5, 114.1, 112.6, 37.7; IR (film): \(\nu\) 2928, 2859, 2226, 1593, 1490, 748, 694 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{16}\)H\(_{13}\)N\(_2\)Cl\(_2\)\(^+(M+H)\)\(^+\) 303.0450, found 303.0451.

\(4c\)  

\(N\)-(2,2-Dichloro-1-(4-(methylsulfonyl)phenyl)vinyl)-N-methylaniline (4c). Yellow solid (28.5 mg, 40% yield); m.p. 189-190 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.91 (d, \(J = 8.3\) Hz, 2H), 7.25 (d, \(J = 8.3\) Hz, 2H), 6.84 (t, \(J = 7.3\) Hz, 1H), 6.78 (d, \(J = 8.1\) Hz, 2H), 3.11 (s, 3H), 3.06 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 146.1, 141.1, 140.7, 140.3, 130.6, 129.5, 127.5, 121.9, 119.4, 114.1, 44.5, 37.7; IR (film): \(\nu\) 3019, 2921, 2846, 1593, 1498, 1395, 1313, 1150, 748, 686 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{16}\)H\(_{13}\)NO\(_2\)SCl\(_2\)\(^+(M+H)\)\(^+\) 356.0273, found 356.0271.
$N$-(2,2-Dichloro-1-(4-nitrophenyl)vinyl)-$N$-methylaniline (4d). Yellow oil (31.7 mg, 49% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.19 (d, $J = 8.8$ Hz, 2H), 7.70 (d, $J = 8.8$ Hz, 2H), 7.25 (t, $J = 7.9$ Hz, 2H), 6.84 (t, $J = 7.3$ Hz, 1H), 6.77 (d, $J = 8.1$ Hz, 2H), 3.13 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 147.8, 146.1, 142.0, 140.2, 130.7, 129.5, 123.7, 122.2, 119.5, 114.2, 37.8; IR (film): $\nu$ 2960, 2921, 2853, 1600, 1511, 1340, 748, 693 cm$^{-1}$; HRMS (ESI) calcd for C$_{15}$H$_{13}$N$_2$O$_2$Cl$_2$ $^{+}$ (M+H)$^{+}$ 323.0349, found 323.0344.

$N$-(2,2-Dichloro-1-(3-nitrophenyl)vinyl)-$N$-methylaniline (4e). Yellow oil (31.0 mg, 48% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.41 (t, $J = 2.0$ Hz, 1H), 8.17 (ddd, $J = 8.2$, 2.3, 1.0 Hz, 1H), 7.83 (ddd, $J = 7.8$, 1.7, 1.1 Hz, 1H), 7.52 (t, $J = 8.0$ Hz, 1H), 7.29-7.21 (m, 2H), 6.87-6.76 (m, 3H), 3.16 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.3, 146.1, 140.0, 137.3, 135.5, 129.5, 124.7, 124.0, 121.4, 119.5, 114.3, 37.8; IR (film): $\nu$ 3084, 2928, 2819, 1600, 1532, 1497, 1348, 816, 749, 693 cm$^{-1}$; HRMS (ESI) calcd for C$_{15}$H$_{13}$N$_2$O$_2$Cl$_2$ $^{+}$ (M+H)$^{+}$ 323.0349, found 323.0346.

**Reaction of imine 1a, benzyne precursor 2a, and deuterated chloroform (Equation 2)**

A flask containing dry CsF (91.1 mg, 0.60 mmol) was evacuated and purged with nitrogen gas three times. To the flask were added 2-(trimethylsilyl)phenyl triflate (2a) (89.5 mg, 0.30 mmol), imine 1a (25.0 mg, 0.20 mmol), acetonitrile (0.30 mL), and deuterated chloroform (0.30 mL). The mixture was stirred at 65 °C for 10 h, cooled to room temperature, and purified directly by silica gel chromatography, eluting with petroleum ether, to give $N$-methyl-$N$-(2,2,2-trichloro-1-cyclohexyl-ethyl)aniline-2-d (3a-D1) as a colorless oil (47.0 mg, 73% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29-7.22 (m, 2H), 6.84-6.73 (m, 2H), 4.39 (d, $J = 9.2$ Hz, 1H), 2.97 (s, 3H), 2.38-2.16 (m, 2H), 1.88-1.79 (m, 1H), 1.77-1.60 (m, 3H), 1.38-0.96 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 150.6, 129.3, 129.2, 117.7, 112.9, 104.8, 77.0, 40.3, 31.9, 31.5, 31.4, 26.5, 26.2; IR (film): $\nu$ 2921, 2848, 1591, 1479, 1450, 1375, 818, 752 cm$^{-1}$; HRMS (ESI) calcd for C$_{15}$H$_{20}$DNCl$_3$ $^{+}$ (M+H)$^{+}$ 321.0797, found 321.0791.
Elimination of HCl from 2,2,2-trichloroethanamine 3d (Equation 3)

A reaction tube containing dry CsF (30.4 mg, 0.20 mmol) was evacuated and purged with nitrogen gas three times. A solution of 2,2,2-trichloroethanamine 3d (34.5 mg, 0.10 mmol) in acetonitrile (0.5 mL) was added via syringes. The mixture was stirred at 65 °C for 10 h, cooled to room temperature, and purified directly by silica gel chromatography, eluting with petroleum ether, to give N-(2,2-dichloro-1-(4-methoxyphenyl)vinyl)-N-methylaniline (4g) as a colorless oil (25.0 mg, 81% yield); ¹H NMR (400 MHz, CDCl₃) for the major tautomer: δ 7.46 (dd, J = 9.3, 2.4 Hz, 2H), 7.27-7.20 (m, 2H), 6.88-6.83 (m, 2H), 3.80 (s, 3H), 3.06 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) for the major tautomer: δ 160.1, 146.8, 141.5, 132.4, 131.2, 129.3, 127.2, 118.6, 113.9, 113.8, 55.4, 37.5; IR (film): ν 2934, 2835, 1600, 1498, 1348, 843, 749, 693 cm⁻¹; HRMS (ESI) calcd for C₁₆H₁₄ONCl₂⁺ (M+H)⁺ 308.0604, found 308.0606.

Reaction of imine 1a, benzyne precursor 2a, and acetoniitride (Scheme 5)

A flask containing dry CsF (91.1 mg, 0.60 mmol) was evacuated and purged with nitrogen gas three times. To the flask were added 2-(trimethylsilyl)phenyl triflate (2a) (89.5 mg, 0.30 mmol), imine 1a (25.0 mg, 0.20 mmol), acetonitrile (0.60 mL). The mixture was stirred at 65 °C for 10 h, cooled to room temperature, and purified directly by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:5 v/v), to give 3-cyclohexyl-3-(methyl(phenyl)amino)propanenitrile (8) as a colorless oil (28.6 mg, 59% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.19 (m, 2H), 6.84-6.70 (m, 3H), 3.83-3.74 (m, 1H), 2.85 (s, 3H), 2.62-2.56 (m, 2H), 1.88-1.59 (m, 6H), 1.37-0.82 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 150.1, 129.4, 118.4, 117.6, 117.6, 113.5, 60.6, 40.1, 31.2, 30.7, 30.5, 26.2, 26.1, 25.9, 18.9; IR (film): ν 2928, 2853, 2242, 1629, 1498, 1348, 1243, 1154 cm⁻¹; HRMS (ESI) calcd for C₁₆H₂₃N₂⁺ (M+H)⁺ 243.1856, found 243.1854.

Reaction of imine 1a, benzyne precursor 2a, and methyl propiolate (Scheme 5)

A reaction tube containing dry KF (34.9 mg, 0.60 mmol) and 18-crown-6 (0.159 g, 0.60 mmol)
was evacuated and purged with nitrogen gas three times. To the flask were added 2-(trimethylsilyl)phenyl triflate (2a) (89.5 mg, 0.30 mmol), imine 1a (25.0 mg, 0.20 mmol), tetrahydrofuran (0.5 mL) via syringes. The mixture was stirred at room temperature for 10 h. The mixture was purified directly by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:5 v/v), to give methyl 4-cyclohexyl-4-(methyl(phenyl)amino)but-2-ynoate (9) as a colorless oil (30.8 mg, 54% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29-7.20 (m, 2H), 6.91-6.74 (m, 3H), 4.21 (d, $J$ = 9.9 Hz, 1H), 3.74 (s, 3H), 2.85 (s, 3H), 2.10-2.03 (m, 1H), 1.94-1.61 (m, 5H), 1.35-0.85 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.1, 150.3, 129.3, 118.7, 114.9, 86.5, 77.1, 58.5, 52.8, 40.7, 33.6, 30.7, 30.1, 26.4, 26.0, 25.9; IR (film): $\nu$ 2928, 2853, 2226, 1716, 1600, 1504, 1436 cm$^{-1}$; HRMS (ESI) calcd for C$_{18}$H$_{24}$NO$_2$+ (M+H)$^+$ 286.1802, found 286.1799.

References


$^{1}$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}$H NMR (400 MHz, CDCl$_3$)
13C NMR (100 MHz, CDCl₃)
1i

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$1n$

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}\text{H NMR (400 MHz, CDCl}_3)$
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

3a
$^{13}$H NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^\text{13C NMR (100 MHz, CDCl}_3\text{)}$
Figure 3d

$^1$H NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl₃)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

3i
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^13$C NMR (100 MHz, CDCl$_3$)
$^{1}\text{H NMR (400 MHz, CDCl}_3\text{)}$

3n
$^{13}$C NMR (100 MHz, CDCl$_3$)
$3\sigma$

$^1\text{H NMR (400 MHz, CDCl}_3\text{)}$
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^13$C NMR (100 MHz, CDCl$_3$)
3s/3s', R = 4-Me/3-Me, 40:60
$^1$H NMR (400 MHz, CDCl$_3$)
$3s/3s'$, $R = 4$-Me/3-Me, 40:60
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)

S-70
$^1$H NMR (400 MHz, CDCl$_3$)
$\text{OMe}$

$\text{Me}$

$\text{CCl}_3$

3w

$^1\text{H NMR (CDCl}_3, 400 \text{ MHz)}$
$^{13}$C NMR (CDCl$_3$, 100 MHz)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl₃)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
\(^1\)H NMR (400 MHz, CDCl\(_3\))
\[ 4d \]

\(^1\)H NMR (400 MHz, CDCl\(_3\))
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}$H NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^13$C NMR (100 MHz, CDCl$_3$)
\[ \text{Ph}_2N \quad \text{Me} \]

\[ \text{CO}_2\text{Me} \]

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