Supporting Information for

One-Pot Synthesis of Carbazoles from Cyclohexanones and Aryl hydrazine Chlorides under Metal-Free Conditions

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General information:

All experiments were carried out under an atmosphere of oxygen. Flash column chromatography was performed over silica gel 48-75 μm. \(^1\)H NMR and \(^{13}\)C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to SiMe\(_4\) or chloroform signals. MS analyses were performed on an Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra were recorded at the Center for Mass Spectrometry, Peking University. The structures of known compounds were further corroborated by comparing their \(^1\)H NMR data and MS data with those of literature. All reagents were used as received from commercial sources without further purification.

General procedure: (3a):

A 25 mL oven-dried reaction vessel was charged with cyclohexanone (1a, 20.7 μL, 0.2 mmol), phenylhydrazine hydrochloride (2a, 43.4 mg, 0.3 mmol) and reflushed with oxygen (1 atm). \(N\)-methyl-2-pyrrolidone (0.4 mL) was added to the sealed reaction vessel by syringe. The resulting solution was stirred at 140 °C for 24 h. After cooling to room temperature the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give 3a as pale yellow solid; yield: 24.4 mg (73%).

Carbazole (3a, CAS: 86-74-8) \(^{[1]}\)

\[
\text{\includegraphics[width=0.2\textwidth]{carbazole.png}}
\]

\(^1\)H NMR (CDCl\(_3\), 400 MHz, ppm): \(\delta 8.09-8.06 (m, 3H), 7.43-7.40 (m, 4H), 7.26-7.23 (m, 2H); \]
\(^{13}\)C NMR (CDCl\(_3\), 100 MHz, ppm): \(\delta 139.6, 125.8, 123.4, 120.3, 119.5, 110.6; \) MS (EI) m/z (%): 167 (100), 139, 113, 83, 75.

3-Methyl-carbazole (3b, CAS: 4630-20-0) \(^{[1]}\)

\[
\text{\includegraphics[width=0.2\textwidth]{3-methyl-carbazole.png}}
\]

The reaction was conducted with 4-methylcyclohexanone (1b, 24.4 μL, 0.2 mmol), phenylhydrazine hydrochloride (2a, 43.4 mg, 0.3 mmol). The residue was purified by column
chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give 3b as pale yellow solid; yield: 27.2 mg (75%).

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 8.04 (d, $J = 7.6$ Hz, 1H), 7.95 (s, 1H), 7.88 (s, 1H), 7.41-7.20 (m, 5H), 2.53 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 139.9, 137.8, 128.8, 127.2, 125.7, 123.6, 123.3, 120.3, 120.2, 119.3, 110.6, 110.3, 21.4; MS (EI) m/z (%): 181 (100), 152, 127, 90, 77.

3-Ethyl-carbazole (3c, CAS: 5599-49-5) [1]

The reaction was conducted with 4-ethylcyclohexanone (1c, 28.2 $\mu$L, 0.2 mmol), phenylhydrazine hydrochloride (2a, 43.4 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give 3c as pale yellow solid; yield: 28.5 mg (73%).

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 8.06 (d, $J = 7.8$ Hz, 1H), 7.96-7.90 (m, 2H), 7.40-7.34 (m, 3 H), 7.28-7.20 (m, 2H), 2.83 (q, $J = 7.5$ Hz, 2H), 1.34 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 139.6, 138.0, 135.6, 126.2, 125.6, 123.6, 123.4, 120.2, 119.3, 119.0, 110.6, 110.4, 29.0, 16.4; MS (EI) m/z (%): 195, 180 (100), 167, 152, 139, 90.

3-Pentyl-carbazole (3d)

The reaction was conducted with 4-pentylcyclohexanone (1d, 37.8 $\mu$L, 0.2 mmol), phenylhydrazine hydrochloride (2a, 43.4 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give 3d as pale yellow solid; yield: 35.1 mg (74%).

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 8.05 (d, $J = 7.6$ Hz, 1H), 7.95-7.87 (m, 2H), 7.40-7.33 (m, 3 H), 7.26-7.20 (m, 2H), 2.78 (q, $J = 7.6$ Hz, 2H), 1.72-7.70 (m, 2H), 1.37 (m, 4H), 0.91 (m, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 139.9, 138.0, 134.2, 126.6, 125.6, 123.6, 123.4, 120.2,
119.6, 119.2, 110.5, 110.2, 36.0, 32.0, 31.6, 22.6, 14.0; MS (EI) m/z (%): 237, 217, 204, 191, 180 (100), 152; HRMS calcd. for : C_{17}H_{19}N [M]+ 237.1512, found 237.1511.

3-(*tert*-Pentyl)- carbazole (3e)

The reaction was conducted with 4-(*tert*-pentyl)cyclohexanone (1e, 36.6 μL, 0.2 mmol), phenylhydrazine hydrochloride (2a, 43.4 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give 3e as pale yellow solid; yield: 36.5 mg (74%).

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): δ 8.08 (d, $J$ = 7.6 Hz, 1H), 8.02 (s, 1H), 7.95 (s, 1H), 7.44-7.35 (m, 4H), 7.26-7.20 (m, 1H), 1.76 (q, $J$ = 7.2 Hz, 2H), 1.41 (s, 6H), 0.72 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): δ 140.8, 140.0, 137.7, 125.5, 124.4, 123.7, 123.2, 120.1, 119.2, 117.3, 110.6, 110.0, 37.9, 37.4, 29.1, 9.3; MS (EI) m/z (%): 237, 222, 208 (100), 191, 180, 167; HRMS calcd. for : C_{17}H_{20}N [M+1]$^+$ 238.1590, found 238.1589.

3-Phenyl-carbazole (3f, CAS: 103012-26-6)$^{[2]}$

The reaction was conducted with 4-phenylcyclohexanone (1f, 34.8 mg, 0.2 mmol), phenylhydrazine hydrochloride (2a, 43.4 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give 3f as pale yellow solid; yield: 33.0 mg (68%).

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): δ 8.29 (s, 1H), 8.14-8.08 (m, 2H), 7.73-7.67 (m, 3H), 7.50-7.42 (m, 5H), 7.36-7.33 (m, 1H), 7.26 (s, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): δ 142.2, 140.1, 139.1, 133.2, 128.7, 127.3, 126.5, 126.1, 125.5, 124.0, 123.6, 120.4, 119.6, 118.9, 110.8, 110.7 MS (EI) m/z (%): 243 (100), 227, 213, 139, 120.
Ethyl carbazole-3-carboxylate (3g, CAS: 51035-14-4) \[^{[3]}\]

The reaction was conducted with ethyl 4-oxocyclohexanecarboxylate (1g, 31.9 μL, 0.2 mmol), phenylhydrazine hydrochloride (2a, 43.4 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give 3g as pale yellow solid; yield: 33.9 mg (71%).

\(^1\)H NMR (CDCl\(_3\), 400 MHz, ppm): \(\delta\) 8.82 (s, 1H), 8.29 (s, 1H), 8.15-8.14 (m, 2H), 7.47-7.43 (m, 3H), 7.32-7.26 (m, 1H), 4.44 (q, \(J\) = 7.2 Hz, 2H), 1.46 (t, \(J\) = 7.0 Hz, 3H);

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz, ppm): \(\delta\) 167.5, 142.3, 127.5, 126.5, 123.4, 123.2, 122.8, 121.0, 120.7, 120.3, 110.9, 110.1, 60.7, 14.5; MS (EI) m/z (%): 239, 224, 211, 194 (100), 166, 139.

1,2-Benzocarbazole (3j, CAS: 239-01-0) \[^{[2]}\]

The reaction was conducted with 3,4-dihydronaphthalen-1-one (1j, 26.7 μL, 0.2 mmol), phenylhydrazine hydrochloride (2a, 43.4 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give 3j as pale yellow solid; yield: 34.7 mg (80%).

\(^1\)H NMR (CDCl\(_3\), 400 MHz, ppm): \(\delta\) 8.76 (s, 1H), 8.14-7.99 (m, 4H), 7.66-7.50 (m, 4H), 7.44-7.41 (m, 1H), 7.32-7.24 (m, 1H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz, ppm): \(\delta\) 138.6, 134.9, 132.5, 129.1, 125.6, 125.2, 124.9, 124.3, 121.2, 120.5, 120.3, 120.0, 119.9, 119.3, 118.6, 111.1; MS (EI) m/z (%): 217 (100), 189, 163, 108, 94.

3-Methyl-carbazole (3k, CAS: 4630-20-0) \[^{[1]}\]
The reaction was conducted with cyclohexanone (1a, 20.7 μL, 0.2 mmol), \(\rho\)-tolylhydrazine hydrochloride (2b, 47.4 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give 3k as pale yellow solid; yield: 21.7 mg (63%).

\(^1\)H NMR (CDCl\(_3\), 400 MHz, ppm): 8.04 (d, \(J = 7.6\) Hz, 1H), 7.95 (s, 1H), 7.88 (s, 1H), 7.20 (m, 5H), 2.53 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz, ppm): 139.9, 137.8, 128.8, 127.2, 125.7, 123.6, 123.3, 120.3, 120.2, 119.3, 110.6, 110.3, 21.4; MS (EI) m/z (%): 181 (100), 152, 127, 90, 77.

3-Methoxy-carbazole (3l, CAS: 18992-85-3) [1]

The reaction was conducted with cyclohexanone (1a, 20.7 μL, 0.2 mmol), (4-methoxyphenyl)hydrazine hydrochloride (2c, 52.4 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 4:1) to give 3l as pale yellow solid; yield: 24.0 mg (61%).

\(^1\)H NMR (CDCl\(_3\), 400 MHz, ppm): 8.04 (d, \(J = 7.6\) Hz, 1H), 7.92 (s, 1H), 7.56 (s, 1H); 7.41-7.20 (m, 5H), 2.53 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz, ppm): 154.0, 140.4, 134.5, 125.8, 123.9, 123.4, 120.3, 119.1, 115.1, 111.3, 110.8, 103.4, 56.2; MS (EI) m/z (%): 197, 182 (100), 154, 139, 127, 98.

3-Fluoro-carbazole (3m, CAS: 391-45-7) [1]

The reaction was conducted with cyclohexanone (1a, 20.7 μL, 0.2 mmol), (4-fluorophenyl)hydrazine hydrochloride (2d, 48.6 mg, 0.3 mmol). The residue was purified by
column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give 3m as pale yellow solid; yield: 29.6 mg (80%).

$^{1}$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 8.03-8.01 (m, 2H), 7.73 (d, $J = 7.6$ Hz, 1H), 7.43 (s, 2H), 7.36-7.33 (m, 1H), 7.26-7.23 (m, 1H), 7.18-7.14 (m, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 157.6 ($J = 235.0$ Hz), 140.6, 135.8, 126.4, 124.0 ($J = 9.7$ Hz), 123.2 ($J = 3.8$ Hz), 120.6, 119.5, 113.6 ($J = 25.5$ Hz), 111.1 ($J = 9.0$ Hz), 110.9, 106.0 ($J = 23.7$ Hz); MS (EI) m/z (%): 185 (100), 164, 157, 131, 92.

3-Chloro-carbazole (3n, CAS: 2732-25-4) $^{[1]}$

![3-Chloro-carbazole](image)

The reaction was conducted with cyclohexanone (1a, 20.7 μL, 0.2 mmol), (4-chlorophenyl)hydrazine hydrochloride (2e, 53.4 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give 3n as pale yellow solid; yield: 30.2 mg (75%).

$^{1}$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 8.07-8.02 (m, 3H), 7.44 (s, 2H), 7.38-7.33 (m, 2H), 7.26 (s, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 140.1, 137.8, 126.6, 125.9, 125.0, 124.7, 122.6, 120.5, 120.1, 119.9, 111.5, 110.8; MS (EI) m/z (%): 201 (100), 174, 166, 139, 113, 82.

3-Bromo-carbazole (3o, CAS: 1592-95-6) $^{[4]}$

![3-Bromo-carbazole](image)

The reaction was conducted with cyclohexanone (1a, 20.7 μL, 0.2 mmol), (4-bromophenyl)hydrazine hydrochloride (2f, 66.6 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give 3o as pale yellow solid; yield: 33.3 mg (68%).

$^{1}$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 8.19 (s, 1H), 8.08-8.02 (m, 2H), 7.51-7.44 (m, 3H), 7.32-7.26 (m, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): $\delta$ 139.9, 138.1, 128.6, 126.6, 125.3, 123.1,
122.5, 120.5, 119.9, 112.3, 112.0, 110.8; MS (EI) m/z (%): 247 (100), 166, 139, 123, 113, 82.

4-Methyl-carbazole (3p, CAS: 6510-65-2) [1]

The reaction was conducted with cyclohexanone (1a, 20.7 μL, 0.2 mmol), o-tolylhydrazine hydrochloride (2g, 47.4 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give 3p as pale yellow solid; yield: 15.2 mg (42%).

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): δ 8.07 (d, $J = 7.6$ Hz, 1H), 7.98-7.93 (m, 2H), 7.48-7.40 (m, 2H), 7.26-7.23 (m, 2H), 7.19-7.15 (m, 1H), 2.58 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): δ 139.5, 138.9, 126.4, 125.8, 125.7, 124.0, 123.0, 120.5, 119.6, 119.5, 118.0, 110.7, 16.8; MS (EI) m/z (%): MS (EI) m/z (%): 197, 182 (100), 154, 139, 127, 98.

3-Methyl-carbazole (3r, CAS: 4630-20-0) [1]

The reaction was conducted with cyclohexanone (1a, 20.7 μL, 0.2 mmol), phenylhydrazine sulfate (2i, 61.8 mg, 0.3 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give 3r as pale yellow solid; yield: 26.1 mg (72%).

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): δ 8.04 (d, $J = 7.6$ Hz, 1H), 7.95 (s, 1H), 7.88 (s, 1H), 7.41-7.20 (m, 5H), 2.53 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm): δ 139.9, 137.8, 128.8, 127.2, 125.7, 123.6, 123.3, 120.3, 120.2, 119.3, 110.6, 110.3, 21.4; MS (EI) m/z (%): 181 (100), 152, 127, 90, 77.

References:


$^1$H NMR and $^{13}$C NMR spectra for all compounds