Highly chemo- and diastereo-selective synthesis of 2,6-diazabicyclo[3.2.0]heptan-7-ones, pyrrolidines and perhydroazirino[2,3-c]pyrroles

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1. General Information S2

2. General procedure for synthesis of compound 4-halo-3,6-diaryl-2,6-diaza-bicyclo[3.2.0]heptan-7-one 2 S2

3. General procedure for synthesis of compound 4-halo-2-alkyl-3,6-diaryl-2,6-diazabicyclo[3.2.0]heptan-7-one 6 S7

4. Typical procedure for the preparation of Alkyl 4-iodo-5-aryl-3-(arylamino)pyrrolidine-2-carboxylate S9

5. Typical procedure for the preparation of 4,6-diaryl-3,6-diazabicyclo[3.1.0] hexane-2-carboxylic acid S13

6. Copies of 1H, 13C NMR spectra S15
1. General Information

Materials and methods

Oxygen- and moisture-sensitive reactions were carried out under nitrogen atmosphere. Solvents were purified and dried by standard methods prior to use. All commercially available reagents and solvents (purchased from Aldrich, Merck, Spectrochem, Acros) were used without further purification unless otherwise noted. Analytical thin layer chromatography (TLC) was conducted on Merck Kieselgel 60 F254. Compounds were visualized with both short- and long-wavelength UV light. Column chromatography was performed on silica gel (100-200 mesh). Melting points were determined in capillary tubes using a Mel-Temp apparatus and are not corrected. Infrared spectra were obtained as films on KBr salt plates except where otherwise specified, using a Perkin Elmer FT-IR spectrometer. $^1$H NMR spectra were obtained with CDCl$_3$ at 300 & 500 MHz, using Bruker spectrometers (residual chloroform referenced to 7.26 ppm) or DMSO-d$_6$ (residual DMSO referenced to 2.50 ppm and residual water in DMSO-d$_6$ appearing at 3.33 ppm). Chemical shift values are expressed as parts per million downfield from TMS and $J$ values are in hertz. Splitting patterns are indicated as s: singlet, d: doublet, t: triplet, m: multiplet, dd: double doublet, ddd: doublet of a doublet of a doublet, and br: broad peak. $^{13}$C NMR spectra were recorded with CDCl$_3$ at 75 MHz, using Bruker spectrometers (residual chloroform referenced to 77.0 ppm) or DMSO-d$_6$ (residual DMSO referenced to 39.5 ppm). Infrared spectra were recorded on a Perkin Elmer FT-IR spectrometer. HRMS were recorded on Bruker high resolution spectrometer (BrukermicrOTOF QII).

2. General procedure for synthesis of compound 4-halo-3,6-diaryl-2,6-diaza-bicyclo[3.2.0]heptan-7-one 2.

To a solution of compounds 1 (0.1 g, 1 equiv) in DCM (10 ml) was added bromine/iodine (1.2 equiv). The reaction was stirred for 10 minutes. This was followed by addition of K$_2$CO$_3$ at 0 ºC. The solution was stirred at 0 ºC for 1–2 h. The progress of the reaction was monitored with the help of tlc. After completion of the reaction, reaction mixture was diluted with DCM and washed with Na$_2$S$_2$O$_3$/water solution followed by brine solution. The dichloromethane solution was dried over anhydrous Na$_2$SO$_4$ and solvent was evaporated. Crude residue was purified by flash column chromatography using silica gel (100:200 mesh) in EtOAc/cyclohexane (2:8) as an elutent system to get compounds 2.

4-Iodo-3,6-diphenyl-2,6-diaza-bicyclo[3.2.0]heptan-7-one (2a). Yield: 90%; White solid, Mp: 118–119 ºC; $^1$H NMR (300 MHz, CDCl$_3$) 7.36 (d, $J$ = 7.2 Hz, 2H), 7.10-7.19 (m 5H), 6.97-7.04 (t, $J$ = 7.5 Hz, 1H), 6.90 (d, $J$ = 7.5 Hz, 2H), 5.02 (d, $J$ = 3.9 Hz, 2H), 4.94 (bs, 1H), 4.91 (d,
$J = 3.6$ Hz, 1H). $\delta^1$C NMR (75 MHz, CDCl$_3$) $\delta 164.2, 139.6, 136.1, 129.0, 128.2, 127.2, 125.3, 124.4, 116.8, 74.7, 71.8, 67.8, 30.7. MS (EI) $m/z$ 391 (M+1)$^+$, $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 1755, HRMS calculated for C$_{17}$H$_{15}$I$_2$N$_2$O (M+H)$^+$ 391.0307, found 391.0314.

X-Ray crystal data and structure refinement. CCDC 972460 contains the supplementary crystallographic data. C$_{17}$H$_{15}$I$_2$N$_2$O, $V = 2958.9(2)$ Å$^3$ Mr = 390.21, $Z = 8$, orthorhombic, $a = 9.8710(5)$ Å, $m = 2.165$ mm$^{-1}$, $b = 16.0822(8)$ Å, $T = 100(2)$ K, $c = 18.6387(8)$ Å, $a = 90$, $b = 90$, $g = 90$; $b = 104.719(2)$, $T_{\text{min}} = 0.655$, $T_{\text{max}} = 0.677$, $R_{\text{int}} = 0.0252$, 3047 measured reflections, $wR(F2) = 0.0759$, $S = 1.155$

**4-Iodo-3-phenyl-6-(p-tolyl)-2,6-diazabicyclo[3.2.0]heptan-7-one (2b).** Yield: 82%; White solid, Mp: 129–131 °C; $\delta^1$H NMR (300 MHz, CDCl$_3$) 7.37 (dd, $J = 6.9$, 0.9 Hz, 2H), 7.11-7.21 (m, 3H), 6.96 (d, $J = 8.1$ Hz, 1H ), 6.78 (dd, $J = 6.6$, 1.8 Hz, 2H), 5.01 (d, $J = 3.6$ Hz, 2H ), 4.91 (bs, 2H), 2.24 (s, 3H). $\delta^1$C NMR (75 MHz, CDCl$_3$) $\delta$ 163.9, 139.7, 134.2, 133.6, 129.5, 128.2, 127.1, 125.4, 116.8, 74.8, 71.8, 67.8, 30.8, 20.9. MS (EI) $m/z$ 405 (M+1)$^+$, $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 1755, HRMS calculated for C$_{18}$H$_{17}$I$_2$N$_2$O (M+H)$^+$ 405.0464, found 405.0488.

**6-(4-Chlorophenyl)-4-iodo-3-phenyl-2,6-diazabicyclo[3.2.0]heptan-7-one (2c).** Yield: 65%; Pale yellow solid, Mp: 143–144; $\delta^1$H NMR (300 MHz, CDCl$_3$) 7.35 (dd, $J = 8.1$, 1.2 Hz, 2H), 7.10-7.20 (m, 5H), 6.83 (d, $J = 6.6$ Hz, 2H), 5.01 (d, $J = 3.6$ Hz, 2H), 4.92 (bs, 2H). $\delta^1$C NMR (75 MHz, CDCl$_3$) $\delta$ 164.1, 139.5, 134.6, 129.1, 128.9, 128.3, 127.2, 125.3, 118.0, 74.5, 72.2, 67.9, 30.3. MS (EI) $m/z$ 425 (M+1)$^+$, $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 1755, HRMS calculated for C$_{17}$H$_{14}$ClIN$_2$O (M+H)$^+$ 424.9918, found 424.9915.
**4-ido-6-(4-methoxyphenyl)-3-phenyl-2,6-diazabicyclo[3.2.0]heptan-7-one (2d).** Yield: 66%; White solid, Mp: 137-139; δ H NMR (300 MHz, CDCl3) 7.37 (d, J = 7.2 Hz, 2H), 7.10-7.19 (m, 5H), 6.80 (dd, J = 6.6, 1.8 Hz, 2H), 5.01 (d, J = 3.6 Hz, 2H), 4.91 (bs, 2H). δ C NMR (75 MHz, CDCl3) δ 164.0, 139.7, 134.2, 133.7, 129.5, 128.2, 127.1, 125.3, 116.8, 74.8, 71.7, 67.8, 55.9, 30.8. MS (EI) m/z 421 (M+1), νmax (KBr)/cm⁻¹ 1755, HRMS calculated for C_{18}H_{17}IN_{2}O (M+H)⁺ 421.0413, found 421.0411.

![Diagram of 4-ido-6-(4-methoxyphenyl)-3-phenyl-2,6-diazabicyclo[3.2.0]heptan-7-one (2d).](image)

**6-(4-fluorophenyl)-4-ido-3-phenyl-2,6-diazabicyclo[3.2.0]heptan-7-one (2e).** Yield: 62%; Pale yellow solid, Mp: 124-127; δ H NMR (300 MHz, CDCl3) 7.34-7.37 (m, 2H, ArH), 7.10-7.26 (m, 5H, ArH), 5.00 (d, J = 3.6 Hz, 2H, H₂ & H₄), 4.92 (m, 2H, H₁ & H₃). δ C NMR (75 MHz, CDCl₃) δ 163.9, 139.7, 134.2, 133.7, 129.6, 128.3, 128.0, 127.2, 125.4, 116.9, 74.8, 71.8, 67.9, 30.8. MS (EI) m/z 409 (M+1)⁺, νmax (KBr)/cm⁻¹ 1750, HRMS calculated (M+H)⁺ 409.0213, found 409.0207, Anal. Calc. for C_{17}H_{14}FIN_{2}O: C, 50.02; H, 3.46; N, 6.86; found: C, 50.06; H, 3.51; N, 6.81.

![Diagram of 6-(4-fluorophenyl)-4-ido-3-phenyl-2,6-diazabicyclo[3.2.0]heptan-7-one (2e).](image)

**6-cyclohexyl-4-ido-3-phenyl-2,6-diazabicyclo[3.2.0]heptan-7-one (2f).** Yield: 75%; Pale yellow solid, Mp: 110-111; δ H NMR (500 MHz, CDCl₃) 7.18-7.39 (m, 5H, ArH), 5.07 (d, J = 4.0 Hz, 2H, H₃ & H₄), 5.02 (s, 1H, H₁), 5.00 (d, J = 3.5 Hz, 1H, H₂), 3.57-3.62 (m, 1H, cyclohexyl-H), 0.85-1.95 (m, 10H, cyclohexyl-H). δ C NMR (75 MHz, CDCl₃) δ 164.5, 128.8, 128.7, 126.7 123.6, 74.7, 71.8, 67.9, 52.7, 31.8, 30.6, 29.7, 25.0. MS (EI) m/z 397 (M+1)⁺, νmax (KBr)/cm⁻¹ 1755, HRMS calculated (M+H)⁺ 397.0777, found 397.0773, Anal. Calc. for C_{17}H_{21}IN_{2}O: C, 51.53; H, 5.34; N, 7.07; found: C, 51.60; H, 5.39; N, 7.04.

![Diagram of 6-cyclohexyl-4-ido-3-phenyl-2,6-diazabicyclo[3.2.0]heptan-7-one (2f).](image)
6-benzyl-4-iodo-3-phenyl-2,6-diazabicyclo[3.2.0]heptan-7-one (2g). Yield: 60%; Yellow solid, Mp: 125–126; δ\textsubscript{H} \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) 7.21-7.36 (m, 10H, ArH), 5.04 (d, J = 3.5 Hz, 2H, H\textsubscript{3} & H\textsubscript{4}), 4.94 (s, 1H, H\textsubscript{1}) 4.92 (d, J = 3.5 Hz, 1H, H\textsubscript{3}), 4.09-4.14 (m, 2H, CH\textsubscript{2}). δ\textsubscript{C} NMR (75 MHz, CDCl\textsubscript{3}) δ 170.1, 143.4, 128.8, 128.7, 128.5, 127.9, 127.2, 126.6, 123.5, 74.4, 70.3, 65.8, 47.26, 29.7. MS (El) m/z 405 (M+1)\textsuperscript{+}, \nu\textsubscript{max} (KBr)/cm\textsuperscript{-1} 1752, HRMS calculated (M+H)* 405.0464, found 405.0462, Anal. Calc. for C\textsubscript{19}H\textsubscript{17}BrN\textsubscript{2}O: C, 53.48; H, 4.24; N, 6.93; found: C, 53.52; H, 4.29; N, 6.89.

4-bromo-3,6-diphenyl-2,6-diazabicyclo[3.2.0]heptan-7-one (2h). Yield: 61%; Brown solid, Mp: 131–132; δ\textsubscript{H} \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) 7.38 (m, 2H, ArH), 7.10-7.22 (m, 5H, ArH), 6.97-7.04 (m, 1H, ArH), 6.93 (m, 2H, ArH), 5.02 (bs, 1H, H\textsubscript{3}), 4.92 (d, J = 3.6 Hz, 1H, H\textsubscript{4}), 4.91 (bs, 1H, H\textsubscript{4}), 4.83 (d, J = 3.6 Hz, 1H, H\textsubscript{5}). δ\textsubscript{C} NMR 75 MHz, CDCl\textsubscript{3} δ 164.1, 139.0, 136.1, 129, 128.2, 127.2, 125.4, 124.5, 116.7, 73.1, 71.7, 66.1, 52.7. MS (El) m/z 343 (M+1)\textsuperscript{+}, Anal. Calc. for C\textsubscript{17}H\textsubscript{15}BrN\textsubscript{2}O: C, 59.49; H, 4.41; N, 8.16; found: C, 59.41; H, 4.38; N, 8.20.

4-bromo-3-phenyl-6-(p-tolyl)-2,6-diazabicyclo[3.2.0]heptan-7-one (2i). Yield: 55%; Brown solid; δ\textsubscript{H} \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) 7.39 (m, 2H, ArH), 7.10-7.23 (m, 3H, ArH), 6.97 (m, 2H, ArH), 6.80 (m, 2H, ArH), 5.02 (s, 1H, H\textsubscript{3}), 4.91 (d, J = 3.6 Hz, 1H, H\textsubscript{4}), 4.90 (bs, 1H, H\textsubscript{1}), 4.81 (d, J = 3.6 Hz, 1H, H\textsubscript{3}), 2.24 (s, 3H, CH\textsubscript{3}). δ\textsubscript{C} NMR (75 MHz, CDCl\textsubscript{3}) δ 163.8, 139.0, 134.2, 133.6, 129.5, 128.2, 127.2, 125.4, 116.8, 73.1, 71.6, 66.2, 52.7, 20.9. MS (El) m/z 357 (M+1)\textsuperscript{+}, Anal. Calc. for C\textsubscript{18}H\textsubscript{17}BrN\textsubscript{2}O: C, 60.52; H, 4.80; N, 7.84; found: C, 60.49; H, 4.75; N, 7.87.
**4-bromo-6-(4-chlorophenyl)-3-phenyl-2,6-diazabicyclo[3.2.0]heptan-7-one (2j).** Yield: 50%; Light brown solid, δ<sub>H</sub> 1H NMR (300 MHz, CDCl<sub>3</sub>) 7.30-7.40 (m, 3H, ArH), 7.16-7.22 (m, 2H), 7.13 (m, 2H, ArH), 6.86 (m, 2H, ArH), 5.02 (s, 1H, ArH), 4.93 (d, J = 3.6 Hz, 1H, H<sub>3</sub>), 4.89 (s, 1H, H<sub>1</sub>), 4.81 (d, J = 3.6 Hz, 1H, H<sub>3</sub>). δ<sub>C</sub> 13C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.5, 134.5, 129.6, 129.1, 128.8, 128.3, 127.5, 125.5, 117.9, 73.0, 71.5, 66.0, 51.6. MS (EI) m/z 377 (M+1)<sup>+</sup>, Anal. Calc. for C<sub>17</sub>H<sub>14</sub>BrClN<sub>2</sub>O: C, 54.06; H, 3.74; N, 7.42; found: C, 54.03; H, 3.68; N, 7.45.

**4-bromo-6-(4-methoxyphenyl)-3-phenyl-2,6-diazabicyclo[3.2.0]heptan-7-one (2k).** Yield: 55%; Brown solid, δ<sub>H</sub> 1H NMR (300 MHz, CDCl<sub>3</sub>) 7.37-7.51 (m, 4H, ArH), 7.10-7.18 (m, 2H, ArH), 7.06 (m, 2H, ArH), 6.86 (m, 2H, ArH), 6.01 (s, 1H, H<sub>3</sub>), 4.92 (d, J = 3.6 Hz, 1H, H<sub>4</sub>), 4.91 (s, 1H, H<sub>1</sub>), 4.83 (d, J = 3.6 Hz, 1H, H<sub>3</sub>), 3.18 (s, 3H, OCH<sub>3</sub>). δ<sub>C</sub> 13C NMR (75 MHz, CDCl<sub>3</sub>) δ 164.0, 134.3, 129.7, 129.2, 128.8, 128.3, 127.5, 125.4, 116.8, 73.1, 71.6, 66.2, 57.8, 52.7. MS (EI) m/z 373 (M+1)<sup>+</sup>, Anal. Calc. for C<sub>19</sub>H<sub>17</sub>BrN<sub>2</sub>O<sub>2</sub>: C, 57.92; H, 4.59; N, 7.51; found: C, 57.91; H, 4.55; N, 7.57.

**4-bromo-6-(4-fluorophenyl)-3-phenyl-2,6-diazabicyclo[3.2.0]heptan-7-one (2l).** Yield: 60%; Brown solid, δ<sub>H</sub> 1H NMR (300 MHz, CDCl<sub>3</sub>) 7.02-7.29 (m, 7H, ArH), 6.78-6.81 (m, 2H, ArH), 4.76-4.96 (m, 2H, H<sub>3</sub>& H<sub>4</sub>), 4.66 (t, J = 3.3 Hz, 1H, H<sub>3</sub>), 4.66 (s, 1H, H<sub>1</sub>). δ<sub>C</sub> 13C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.5, 134.5, 129.6, 129.1, 128.8, 128.3, 127.5, 125.5, 117.9, 73.0, 71.5, 66.0, 51.6. MS (EI) m/z 361 (M+1)<sup>+</sup>, Anal. Calc. for C<sub>19</sub>H<sub>14</sub>FBrN<sub>2</sub>O: C, 56.53; H, 3.91; N, 7.76; found: C, 56.55; H, 3.96; N, 7.73.
6-benzyl-4-bromo-3-phenyl-2,6-diazabicyclo[3.2.0]heptan-7-one (2m). Yield: 45%; Yellow solid, \( \delta^1_H \text{NMR (500 MHz, CDCl}_3 \) 7.23-7.37 (m, 10H, ArH), 5.01 (s, 1H, H\(_5\)), 4.93 (d, \( J = 3.5 \text{ Hz, 1H, H}_4 \)), 4.81 (s, 1H, H\(_1\)), 4.68 (d, \( J = 3.5 \text{ Hz, 1H, H}_5 \)), 4.10-4.15 (m, 2H, CH\(_2\)). \( \delta^1_C \text{ NMR (75 MHz, CDCl}_3 \) \( \delta \) 169.1, 143.4, 128.8, 128.7, 128.6, 127.8, 127.2, 126.7, 123.5, 73.0, 69.9, 65.8, 50.6, 47.2. MS (EI) \( m/z \) 357 (M+1)\(^+\). Anal. Calc. for C\(_{18}\)H\(_{13}\)BrN\(_2\): C, 60.52; H, 4.80; N, 7.84; found: C, 60.54; H, 4.85; N, 7.80.

3. General procedure for synthesis of compound 4-halo-2-alkyl-3,6-diaryl-2,6-diazabicyclo[3.2.0]heptan-7-one 6. To a solution of compounds 5 (0.1 g, 1 equiv) in DCM (10 ml) was added bromine/iodine (1.2 equiv). The reaction was stirred for 10 minutes. This was followed by addition of K\(_2\)CO\(_3\) at 0 °C. The solution was stirred at 0 °C. The progress of the reaction was monitored with the help of tlc. After completion of the reaction, reaction mixture was diluted with DCM and washed with Na\(_2\)S\(_2\)O\(_4\)/water solution followed by brine solution. The dichloromethane solution was dried over anhydrous Na\(_2\)SO\(_4\) and solvent was evaporated. Crude residue was purified by flash column chromatography using silica gel (100:200 mesh) in EtOAc/cyclohexane (2:8) as an eluent system to get compounds 6.

3-(methylamino)-1-phenyl-4-((E)-styryl)azetidin-2-one (5a). White solid, \( \delta^1_H \text{NMR (500 MHz, CDCl}_3 \) 7.48 (m, 2H, ArH), 7.43-7.45 (m, 2H, ArH), 7.28-7.38 (m, 5H, ArH), 7.10 (m, 1H, ArH), 6.85 (d, \( J = 16.5 \text{ Hz, 1H, H}_5 \)), 6.53 (dd, \( J = 16.0, 8.0 \text{ Hz, 1H, H}_5 \)), 4.86 (t, \( J = 6.5 \text{ Hz, 1H, H}_5 \)), 4.46 (d, \( J = 5.5 \text{ Hz, 1H, H}_5 \)), 2.90 (s, 3H, NCH\(_3\)). \( \delta^1_C \text{ NMR (75 MHz, CDCl}_3 \) \( \delta \) 165.9, 138.3, 136.0, 135.3, 129.1, 128.3, 128.1, 126.6, 124.3, 116.7, 57.5, 56.1, 32.4. MS (EI) \( m/z \) 279 (M+1)\(^+\). Anal. Calc. for C\(_{18}\)H\(_{13}\)N\(_2\): C, 77.67; H, 6.52; N, 10.06; found: C, 77.71; H, 6.54; N, 10.02.
3-(dimethylamino)-1-phenyl-4-((E)-styryl)azetidin-2-one (5b). White solid, $\delta_{1}^1$H NMR (500 MHz, CDCl$_3$) 7.46-7.51 (m, 4H, ArH), 7.28-7.40 (m, 5H, ArH), 7.07 (m, 1H, ArH), 6.75 (d, $J = 16.0$ Hz, 1H, H$_6$), 6.30 (dd, $J = 15.5$, 9.0 Hz, 1H, H$_3$), 4.88 (t, $J = 6.5$ Hz, 1H, H$_3$), 4.45 (d, $J = 6.0$ Hz, 1H, H$_3$), 2.92 (s, 6H, N(CH$_3$)$_2$). $\delta_{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 165.9, 138.7, 136.6, 135.6, 130.1, 128.7, 128.1, 126.6, 124.6, 124.3, 57.5, 56.8, 38.3. MS (El) $m/z$ 293 (M+1)$^+$, Anal. Calc. for C$_{19}$H$_{20}$N$_2$O: C, 78.05; H, 6.89; N, 9.58; found: C, 78.11; H, 6.93; N, 9.54.

4-methyl-N-(2-oxo-1-phenyl-4-((E)-styryl)azetidin-3-yl)benzenesulfonamide (5c). White solid, $\delta_{1}^1$H NMR (500 MHz, CDCl$_3$) 7.74-7.77 (m, 2H, ArH), 7.06-7.31 (m, 12H, ArH), 6.45 (d, $J = 15.5$ Hz, 1H, H$_6$), 5.93 (dd, $J = 16.0$, 9.0 Hz, 1H, H$_3$), 5.06 (t, $J = 6.5$ Hz, 1H, H$_3$), 4.78 (d, $J = 6.5$ Hz, 1H, H$_3$), 2.71 (s, 3H, CH$_3$). $\delta_{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 166.2, 139.4, 137.0, 136.3, 136.0, 135.3, 131.5, 130.1, 129.4, 128.7, 128.1, 126.6, 124.6, 124.3, 117.1, 57.5, 56.1, 16.2. MS (El) $m/z$ 419 (M+1)$^+$, Anal. Calc. for C$_{24}$H$_{22}$N$_2$O$_2$: C, 68.88; H, 5.30; N, 6.69; found: C, 68.95; H, 5.33; N, 6.65.

4-ido-2-methyl-3,6-diphenyl-2,6-diazabicyclo[3.2.0]heptan-7-one (6a). Yield: 75%; White solid, $\delta_{1}^1$H NMR (500 MHz, CDCl$_3$) 7.43-7.45 (m, 2H, ArH), 7.28-7.38 (m, 5H, ArH), 7.10 (m, 1H, ArH), 6.92 (m, 1H, ArH), 5.03 (d, $J = 4.0$ Hz, 2H, H$_3$ & H$_8$), 4.95 (s, 1H, H$_3$), 4.92 (d, $J = 3.0$ Hz, 1H, H$_3$), 2.40 (s, 3H, CH$_3$). $\delta_{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 163.9, 139.4, 136.3, 129.4, 128.3, 127.4, 125.3, 124.6, 116.3, 74.7, 71.6, 67.5, 43.7, 30.7. MS (El) $m/z$ 405 (M+1)$^+$, HRMS calculated (M+H)$^+$ 405.0464, found 405.0655, Anal. Calc. for C$_{18}$H$_{17}$I$_3$O: C, 53.48; H, 4.24; N, 6.93; found: C, 53.54; H, 4.30; N, 6.89.
4-bromo-2-methyl-3,6-diphenyl-2,6-diazabicyclo[3.2.0]heptan-7-one (6b). Yield: 40%; Brown solid; δ_1^H NMR (500 MHz, CDCl₃) 7.43-7.49 (m, 4H, ArH), 7.28-7.37 (m, 5H, ArH), 7.10 (m, 1H, ArH), 5.00 (s, 1H, H₃), 4.81-4.89 (m, 2H, H₂ & H₄), 4.82 (d, J = 3.5 Hz, 1H, H₅), 2.44 (s, 3H, CH₃). δ C NMR (75 MHz, CDCl₃) δ 165.3, 138.0, 135.6, 129.1, 128.7, 128.4, 126.7, 124.3, 117.0, 73.8, 71.9, 66.2, 52.7, 45.8. (EI) m/z 357 (M+1)^+, Anal. Calc. for C₁₈H₁₂BrN₂O: C, 60.52; H, 4.80; N, 7.84; found: C, 60.50; H, 4.71; N, 7.78.

4. Typical procedure for the preparation of Alkyl 4-iodo-5-aryl-3-(arylamino)pyrrolidine-2-carboxylate 7. To a solution of compounds 2 (30mg, 1 eq) in methanol/ethanol (5 ml), NaOMe/NaOEt (3 eq) was added and the reaction mixture was stirred at 0 °C for 1.5 h. The progress of the reaction was monitored with the help of TLC. After completion of the reaction, the mixture was quenched with ice and pH adjust to 6-7 extracted with ethyl acetate (3 times). The combined organic layers were washed with water and brine, dried over anhydrous Na₂SO₄ and the solvent was evaporated to get compound (7) as a pure product as solid.

Methyl 4-iodo-5-phenyl-3-(phenylamino)pyrrolidine-2-carboxylate (7a). Yield: 85%; White solid; δ_1^H NMR (500 MHz, CDCl₃) 7.52 (m, 2H, ArH), 7.31-7.39 (m, 3H, ArH), 7.19 (t, J = 7.5 Hz, 2H, ArH), 6.76 (t, J = 7.5 Hz, 1H, ArH), 6.63 (d, J = 7.8 Hz, 2H, ArH), 4.70 (d, J = 7.5 Hz, 1H, H₃), 4.46 (bs, 2H, H₂ & H₄), 4.11 (d, J = 7.2 Hz, 1H, H₅), 3.64 (s, 3H, COOCH₃). δ C NMR (75 MHz, CDCl₃) δ 172.1, 145.8, 139.3, 129.3, 128.9, 128.4, 127, 118.7, 113.9, 71.0, 66.0, 61.7, 52.3, 29.3. MS (EI) m/z 423 (M+1)^+, HRMS calculated (M+H)^+ 423.0569, found 423.0561, Anal. Calc. for C₁₉H₁₉N₂O₂: C, 51.20; H, 4.54; N, 6.63; found: C, 51.12; H, 4.49; N, 6.69.

Methyl 4-iodo-5-phenyl-3-(p-tolylamino)pyrrolidine-2-carboxylate (7b). Yield: 88%; White solid; δ_1^H NMR (300 MHz, CDCl₃) 7.51 (m, 2H, ArH), 7.31-7.38 (m, 3H, ArH), 6.99 (m, 2H, ArH), 6.53 (d, J = 8.4 Hz, 2H, ArH), 4.69 (d, J = 7.2 Hz, 1H, H₂), 4.43 (bs, 2H, H₃ & H₄), 4.06-4.10 (m, 1H, H₅), 3.66
Methyl 3-((4-chlorophenyl)amino)-4-iodo-5-phenylpyrrolidine-2-carboxylate (7c). Yield: 75%; White solid; δ^1^H NMR (500 MHz, CDCl₃) 7.43-7.45 (m, 2H, ArH), 7.28-7.39 (m, 3H, ArH), 7.12 (d, J = 8.0 Hz, 2H, ArH), 6.81-6.89 (m, 2H, ArH), 6.49 (d, J = 6.0 Hz, 1H, H₂), 4.48 (bs, 2H, H₃ & H₄), 4.12 (d, J = 7.0 Hz, 1H, H₅), 3.63 (s, 3H, CH₃). δ^13^C NMR (75 MHz, CDCl₃) δ 171.4, 146.6, 139.4, 129.1, 128.5, 128.4, 127.1, 117.3, 114.2, 71.2, 65.8, 61.8, 52.6, 29.7. MS (EI) m/z 457 (M+1)^+ , HRMS calculated (M+H)^+ 457.0180, found 457.0177, Anal. Calc. for C₁₈H₁₈ClN₂O₂: C, 47.34; H, 3.97; N, 6.13; found: C, 47.31; H, 3.92; N, 6.17.

Methyl 4-iodo-3-((4-methoxyphenyl)amino)-5-phenylpyrrolidine-2-carboxylate (7d). Yield: 79%; White solid; δ^1^H NMR (500 MHz, CDCl₃) 7.32-7.38 (m, 4H, ArH), 7.10-7.25 (m, 3H, ArH), 6.83-6.87 (m, 2H, ArH), 4.69 (d, J = 6.5 Hz, 1H, H₂), 4.49 (bs, 2H, H₃ & H₄), 4.15 (d, J = 7.5 Hz, 1H, H₅), 3.77 (s, 3H, OCH₃), 3.60 (s, 3H, COOCH₃). δ^13^C NMR (75 MHz, CDCl₃) δ 169.0, 145.6, 137.7, 129.1, 128.7, 128.3, 127.0, 117.0, 113.6, 71.2, 66.5, 61.3, 55.8, 52.0, 29.6. MS (EI) m/z 453 (M+1)^+ , HRMS calculated (M+H) 453.0675, found 453.0669, Anal. Calc. for C₁₉H₁₈N₂O₃: C, 50.46; H, 4.68; N, 6.19; found: C, 50.39; H, 4.63; N, 6.21.

Methyl 4-bromo-5-phenyl-3-(phenylamino)pyrrolidine-2-carboxylate (7e). Yield: 87%; White solid; δ^1^H NMR (300 MHz, CDCl₃) 7.50 (m, 2H, ArH), 7.29-7.38 (m, 3H, ArH), 7.17 (t, J = 6.6 Hz, 2H, ArH), 6.75 (t, J = 7.5 Hz, 1H, ArH), 6.61 (d, J = 7.8 Hz, 2H, ArH), 4.60 (d, J = 6.0 Hz, 1H, H₂), 4.48
(d, J = 6 Hz, 1H, H₂), 4.40 (bs, 1H, H₃), 4.07 (dd, J = 3.9, 2.1 Hz, 1H, H₄), 3.68 (s, 3H, COOCH₃). δ NMR (75 MHz, CDCl₃) δ 171.6, 145.6, 139.4, 129.4, 128.8, 126.9, 118.7, 113.9, 69.8, 64.5, 61.8, 56.3, 52.3, 33.8. MS (EI) m/z 375 (M+H)⁺, HRMS calculated (M+H)⁺ 375.0704, found 375.0704.

**Anal. Calc. for C₁₃H₁₂BrN₂O₂: C, 57.61; H, 5.10; N, 7.47; found: C, 57.59; H, 5.04; N, 7.50.**

**Methyl 4-bromo-5-phenyl-3-(p-tolylamino)pyrrolidine-2-carboxylate (7f).** Yield: 90%; White solid; δᵣ¹H NMR (300 MHz, CDCl₃) 7.5 (m, 2H, ArH), 7.28-7.38 (m, 3H, ArH), 6.98 (d, J = 7.8 Hz, 2H, ArH), 6.51 (d, J = 7.8 Hz, 2H, ArH), 4.60 (d, J = 5.7 Hz, 1H, H₂), 4.47 (d, J = 5.7 Hz, 1H, H₃), 4.36 (bs, 1H, H₄), 4.06 (dd, J = 6, 3.6 Hz, 1H, H₅), 3.68 (s, 3H, COOCH₃), 2.22 (s, 3H, CH₃). δ NMR (75 MHz, CDCl₃) δ 171.8, 143.3, 139.9, 129.8, 128.2, 128.0, 126.8, 114.1, 70.0, 64.9, 61.9, 56, 52.2, 29.7, 20.4. MS (EI) m/z 389 (M+1)⁺, HRMS calculated (M+H)⁺ 389.0865, found 389.0852.

**Anal. Calc. for C₁₃H₁₂BrN₂O₂: C, 58.62; H, 5.44; N, 7.20; found: C, 58.60; H, 5.41; N, 7.28.**

**Methyl 4-bromo-3-(4-chlorophenylamino)-5-phenylpyrrolidine-2-carboxylate (7g).** Yield: 80%; Brown solid; δᵣ¹H NMR (500 MHz, CDCl₃) 7.42-7.45 (m, 2H, ArH), 7.28-7.38 (m, 3H, ArH), 7.11 (t, J = 6.5 Hz, 2H, ArH), 6.81-6.87 (m, 2H, ArH), 4.62 (d, J = 5.5 Hz, 1H, H₂), 4.46 (d, J = 5.5 Hz, 1H, H₃), 4.37 (bs, 1H, H₄), 4.08 (dd, J = 6.0 & 3.0 Hz, 1H, H₅), 3.65 (s, 3H, COOCH₃). δ NMR (75 MHz, CDCl₃) δ 169.7, 145.2, 139.0, 129.6, 129.1, 128.7, 125.1, 116.7, 114.3, 70.9, 64.7, 60.9, 56.1, 53.0. MS (EI) m/z 409(M+1)⁺, HRMS calculated (M+H)⁺ 409.0318, found 409.0313. Anal. Calc. for C₁₈H₁₇BrClN₂O₂: C, 52.77; H, 4.43; N, 6.84; found: C, 52.73; H, 4.39; N, 6.87.

**Methyl 4-bromo-3-(4-methoxyphenylamino)-5-phenylpyrrolidine-2-carboxylate (7h).** Yield: 82%; Brown solid; δᵣ¹H NMR (500 MHz, CDCl₃) 7.47-7.49 (m, 2H, ArH), 7.28-7.42 (m, 3H, ArH), 7.22-7.23 (m, 2H, ArH), 7.04-7.06 (m, 2H, ArH), 4.61 (d, J = 6.0 Hz, 1H, H₂), 4.46 (d, J = 5.5 Hz, 1H,
C NMR (75 MHz, CDCl₃) δ 171.8, 146.0, 139.0, 129.1, 128.7, 128.1, 126.6, 118.4, 114.3, 70.9, 64.7, 61.3, 57.5, 56.1, 52.7. MS (El) m/z 405 (M+1)⁺, HRMS calculated (M+H)⁺ 405.0814, found 405.0806, Anal. Calc. for C₂₅H₂₁BrN₂O₃: C, 56.31; H, 5.22; N, 6.91; found: C, 56.29; H, 5.17; N, 6.96.

**Ethyl 4-iodo-5-phenyl-3-(phenylamino)pyrrolidine-2-carboxylate (7i).** Yield: 86%; White solid; δ¹H NMR (500 MHz, CDCl₃) 7.28-40 (m, 5H, ArH), 7.06-7.12 (m, 2H, ArH), 6.76 (t, J = 7.5 Hz, 1H, ArH), 6.62 (d, J = 7.5 Hz, 2H, ArH), 4.70 (d, J = 6.0 Hz, 1H, H₂), 4.17 (m, 2H, CH₂), 3.78 (d, J = 7.0 Hz, 1H, H₃), 1.27 (t, J = 7.5 Hz, 3H, CH₂CH₃). δ¹C NMR (75 MHz, CDCl₃) δ 170.7, 145.6, 139.4, 129.4, 128.7, 128.3, 127.0, 118.7, 113.6, 71.2, 66.1, 61.3, 60.3, 29.3, 14.5. MS (El) m/z 437 (M+1)⁺, HRMS calculated (M+H)⁺ 437.0726, found 437.0720, Anal. Calc. for C₂₅H₂₁N₂O₂: C, 52.31; H, 4.85; N, 6.42; found: C, 52.27; H, 4.79; N, 6.47.

**Ethyl 4-iodo-5-phenyl-3-(p-tolylamino)pyrrolidine-2-carboxylate (7j).** Yield: 82%; White solid; δ¹H NMR (500 MHz, CDCl₃) 7.35-7.49 (m, 4H, ArH), 7.22-7.28 (m, 3H, ArH), 7.05 (d, J = 8.5 Hz, 2H, ArH), 4.68 (d, J = 7.0 Hz, 1H, H₂), 4.39-4.50 (m, 2H, H₂ & H₃), 4.10-4.18 (m, 3H, CH₂ & H₃), 2.27 (s, 3H, CH₃), 1.28 (t, J = 7.5 Hz, 3H, CH₂CH₃). δ¹C NMR (75 MHz, CDCl₃) δ 171.4, 143.5, 139.4, 129.4, 128.7, 128.1, 126.3, 120.8, 114.3, 71.2, 66.5, 62.0, 60.3, 33.8, 20.7, 13.8. MS (El) m/z 451 (M+1)⁺, HRMS calculated (M+H)⁺ 451.0882, found 451.0879, Anal. Calc. for C₂₆H₂₃N₂O₂: C, 53.34; H, 5.15; N, 6.22; found: C, 53.31; H, 5.10; N, 6.27.

**Ethyl 4-bromo-5-phenyl-3-(phenylamino)pyrrolidine-2-carboxylate (7k).** Yield: 73%; Brown solid; δ¹H NMR (500 MHz, CDCl₃) 7.50 (m, 2H, ArH), 7.32-7.48 (m, 5H, ArH), 7.23-7.28 (m, 2H, ArH), 7.02 (t, J = 7.5 Hz, 1H, ArH), 4.61 (d, J = 5.5 Hz, 1H, H₂), 4.46 (d, J = 5.5 Hz, 1H, H₃), 4.39 (bs,
1H, H3), 4.06-4.13 (m, 3H, CH2 & H4), 1.19 (t, J = 7.5 Hz, 3H, CH2CH3). δH NMR (75 MHz, CDCl3) δ 171.1, 145.2, 139.4, 129.4, 129.1, 127.8, 126.3, 118.7, 114.0, 69.9, 64.4, 61.6, 60.6, 56.9, 14.5. MS (EI) m/z 390 (M+1)+, HRMS calculated (M+H)+ 389.0865, found 389.0855, Anal. Calc. for C19H21BrN2O2: C, 58.62; H, 5.44; N, 7.20; found: C, 58.59; H, 5.36; N, 7.24.

**Ethyl 4-bromo-5-phenyl-3-(p-tolylamino)pyrrolidine-2-carboxylate (7l)**. Yield: 81%; Brown solid; δH 1H NMR (500 MHz, CDCl3) 7.28-7.49 (m, 5H, ArH), 7.22 (m, 2H, ArH), 7.05 (m, 2H, ArH), 1.21 (t, J = 7.5 Hz, 3H, CH2CH3). δC NMR (75 MHz, CDCl3) δ 170.1, 143.4, 139.8, 129.7, 129.4, 128.7, 128.1, 126.6, 114.3, 70.3, 64.7, 62.0, 60.6, 56.1, 29.7, 21.5, 13.7. MS (EI) m/z 404 (M+1)+, HRMS calculated (M+H)+ 403.1021, found 403.1014, Anal. Calc. for C26H23BrN2O2: C, 59.56; H, 5.75; N, 6.95; found: C, 59.51; H, 5.73; N, 6.98.

5. **Typical procedure for the preparation of 4,6-diaryl-3,6-diazabicyclo[3.1.0]hexane-2-carboxylic acid 8**. To a solution of compound 2 (30mg, 1 eq) in methanol/ethanol (5 ml), NaOMe/NaOEt (6.5 eq) was added and the reaction mixture was stirred at room temperature for 1 hr. Then the reaction mixture was heated up to 50°C for 30 minutes. The progress of the reaction was monitored with the help of TLC. After completion of the reaction, the mixture was quenched with ice and pH adjust to 6-7. Now, the reaction mixture was concentrated under reduced pressure and purified via flash column chromatography using silica gel (100:200 mesh) in MeOH/DCM (1:9) as an eluent system to get compound 6 as a pure product.

**4,6-diphenyl-3,6-diazabicyclo[3.1.0]hexane-2-carboxylic acid (8a)**. Yield: 90%; Brown solid; δH 1H NMR (300 MHz, MeOD) 7.68 (dd, dJ = 8.4 & 1.5 Hz, 2H, ArH), 7.31-7.42 (m, 3H, ArH), 7.12 (t, J = 7.8 Hz, 2H, ArH), 6.58 (d, dJ = 7.8 Hz, 3H, ArH), 4.10 (d, dJ = 1.8 Hz, 1H, H2), 3.68 (d, dJ = 1.8 Hz, 1H, H3), 3.23 (dd, dJ = 4.5, 2.1 Hz, 1H, H3), 3.08 (dd, dJ = 4.5, 2.1 Hz, 1H, H4). δC NMR (75 MHz, DMSOD) δ 173.8, 154.1, 141.8, 129.07, 128.6, 127.8, 127.5, 121.7, 120.9, 64.3, 63.6, 49.7, 49.0. MS (EI) m/z 281 (M+1)+, HRMS calculated (M+H)+ 281.1290, found 281.1289, Anal. Calc. for C17H16N2O2: C, 72.84; H, 5.75; N, 9.99; found: C, 72.78; H, 5.71; N, 10.02.
4-phenyl-6-(p-tolyl)-3,6-diazabicyclo[3.1.0]hexane-2-carboxylic acid (8b). Yield: 88%; Brown solid; \( \delta \) \textsuperscript{1}H NMR (500 MHz, MeOD) 7.51 (m, 2H, ArH), 7.25-7.48 (m, 3H, ArH), 7.03 (m, 2H, ArH), 6.70 (d, \( J = 7.5 \) Hz, 2H, ArH), 4.09 (d, \( J = 2.0 \) Hz, 1H, H\_2), 3.65 (d, \( J = 2.0 \) Hz, 1H, H\_3), 3.19 (dd, \( J = 4.0, 2.0 \) Hz, 1H, H\_4), 3.08 (dd, \( J = 4.5, 2.0 \) Hz, 1H, H\_5). MS (EI) \textit{m/z} 295 (M\( +\)H\(^+\), HRMS calculated (M\( +\)H\(^+\)) 295.1447, found 295.1440, Anal. Calc. for C\(_{18}\)H\(_{16}\)N\(_2\)O\(_2\): C, 73.45; H, 6.16; N, 9.52; found: C, 73.38; H, 6.10; N, 9.54.

6-(4-chlorophenyl)-4-phenyl-3,6-diazabicyclo[3.1.0]hexane-2-carboxylic acid (8c). Yield: 82%; Brown solid; \( \delta \) \textsuperscript{1}H NMR (500 MHz, MeOD) 7.25-7.51 (m, 5H, ArH), 6.99-7.02 (m, 2H, ArH), 6.71-6.76 (m, 2H, ArH), 4.10 (d, \( J = 2.0 \) Hz, 1H, H\_2), 3.64 (d, \( J = 2.0 \) Hz, 1H, H\_3), 3.20 (dd, \( J = 4.5, 2.0 \) Hz, 1H, H\_4), 3.08 (m, 1H, H\_5). MS (EI) \textit{m/z} 315 (M\( +\)H\(^+\), HRMS calculated (M\( +\)H\(^+\)) 315.0900, found 315.0891, Anal. Calc. for C\(_{17}\)H\(_{15}\)ClN\(_2\)O\(_2\): C, 64.87; H, 4.80; N, 8.90; found: C, 64.85; H, 4.85; N, 8.96.

6-(4-methoxyphenyl)-4-phenyl-3,6-diazabicyclo[3.1.0]hexane-2-carboxylic acid (8d). Yield: 85%; Brown solid; \( \delta \) \textsuperscript{1}H NMR (500 MHz, MeOD) 7.23-7.53 (m, 5H, ArH), 6.74-7.02 (m, 4H, ArH), 4.10 (d, \( J = 1.5 \) Hz, 1H, H\_2), 3.66 (d, \( J = 1.5 \) Hz, 1H, H\_3), 3.23 (dd, \( J = 4.5, 2.0 \) Hz, 1H, H\_4), 3.19 (s, 3H, OCH\(_3\)) 3.07 (dd, \( J = 4.5 & 2.0 \) Hz, 1H, H\_5). MS (EI) \textit{m/z} 311 (M\( +\)H\(^+\), HRMS calculated (M\( +\)H\(^+\)) 311.1396, found 310.1388, Anal. Calc. for C\(_{18}\)H\(_{18}\)N\(_2\)O\(_3\): C, 69.66; H, 5.85; N, 9.03; found: C, 69.63; H, 5.78; N, 9.08.
6. Copies of $^1$H, $^{13}$C NMR spectra
$^1$H NMR spectrum of 2a:

$^{13}$C NMR spectrum of 2a:
Mass spectrum of 2a:
$^1$H NMR spectrum of 2b:

$^{13}$C NMR spectrum of 2b:
HRMS spectrum of 2b:
$^1$H NMR spectrum of $2c$:

$^{13}$C NMR spectrum of $2c$: 
$^1$H NMR spectrum of 2d:

$^{13}$C NMR spectrum of 2d:
$^1$H NMR spectrum of 2e:

$^{13}$C NMR spectrum of 2e:
$^1$H NMR spectrum of 2f:

$^{13}$C NMR spectrum of 2f:
$^1$H NMR spectrum of $2g$:

$^{13}$C NMR spectrum of $2g$: 
$^1$H NMR spectrum of 2h:

$^{13}$C NMR spectrum of 2h:
$^1$H NMR spectrum of 2i:

$^{13}$C NMR spectrum of 2i:
\(^1\)H NMR spectrum of 2j:

\(^{13}\)C NMR spectrum of 2j:
$^1$H NMR spectrum of 2l:

$^{13}$C NMR spectrum of 2l:
$^1$H NMR spectrum of 2m:

$^{13}$C NMR spectrum of 2m:
$^1$H NMR spectrum of 5a:

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

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

$^{13}$C NMR spectrum of 5c:
$^1$H NMR spectrum of 6a:

$^{13}$C NMR spectrum of 6a:
$^1$H NMR spectrum of 6b:

$^{13}$C NMR spectrum of 6b:
$^1$H NMR spectrum of 7a:

$^{13}$C NMR spectrum of 7a:
$^1$H NMR spectrum of 7b:

$^{13}$C NMR spectrum of 7b:
$^1$H NMR spectrum of 7c:

$^{13}$C NMR spectrum of 7c:
$^1$H NMR spectrum of 7d:

$^{13}$C NMR spectrum of 7d:
$^1$H NMR spectrum of 7e:

$^{13}$C NMR spectrum of 7e:
$^1$H NMR spectrum of 7f:

$^{13}$C NMR spectrum of 7f:
$^1$H NMR spectrum of $7g$:

$^{13}$C NMR spectrum of $7g$: 
$^1$H NMR spectrum of 7h:

$^{13}$C NMR spectrum of 7h:
$^1$H NMR spectrum of 7i:

$^{13}$C NMR spectrum of 7i:
$^1$H NMR spectrum of 7j:

$^{13}$C NMR spectrum of 7j:
$^1$H NMR spectrum of 7k:

$^{13}$C NMR spectrum of 7k:
$^1$H NMR spectrum of 7l:

$^{13}$C NMR spectrum of 7l:
$^1$H NMR spectrum of 8a:

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

$^{13}$C NMR spectrum of 8b:
$^1$H NMR spectrum of $^8$c:

$^{13}$C NMR spectrum of $^8$c:
$^1$H NMR spectrum of 8d:

$^{13}$C NMR spectrum of 8d: