Supporting Information

General and selective synthesis of primary amines using Ni-based homogeneous catalysts

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S1. Materials and methods

Unless specified, all substrates were obtained commercially from various chemical companies and their purity has been checked before use. Unless otherwise stated, all commercial reagents were used as received without purification. All catalytic reactions were carried out in 300 mL and 100 mL autoclaves (PARR Instrument Company). In order to avoid unspecific reactions, catalytic reactions were carried out either in glass vials, which were placed inside the autoclave, or glass/Teflon vessel fitted autoclaves. GC conversion and yields were determined by GC-FID, HP6890 with FID detector, column HP530 m x 250 mm x 0.25 μm. 1H, 13C NMR data were recorded on a Bruker ARX 300 and Bruker ARX 400 spectrometers using DMSO-d6, CD3OD and CDCl3 solvents. HRMS data were recorded on ESI-HRMS: Mass Spectrometer MAT 95XP (Thermo Electron), 70eV.

X-ray crystal structure analysis of complex A: Data were collected on a Bruker Kappa APEX II Duo diffractometer. The structure was solved by direct methods (SHELXS-97: Sheldrick, G. M. Acta Cryst. 2008, A64, 112.) and refined by full-matrix least-squares procedures on \( F^2 \) (SHELXL-2014: Sheldrick, G. M. Acta Cryst. 2015, C71, 3.). XP (Bruker AXS) was used for graphical representations.
The anhydrous NiCl$_2$ (64.8 mg, 1.0 mmol) in ethanol (6 mL) was stirred at 85 °C under argon to obtain pale yellow solution. To this, triphos ((phenylphosphanediyl) bis(ethane-2,1-diyl)) bis (diphenylphosphate) (535.55 mg, 1. mmol) was added and stirring was continued at 85 °C for 1 h. Upon adding, the ligand pale yellow solution was turned into brown color. After the completion of reaction, the heating and stirring was switched off and allowed to cool for overnight. Dark brown crystals were observed along with a brown solid. The crystals were separated carefully and recrystallized again with ethanol for measuring X-ray diffraction analysis. The remaining reaction mixture was concentrated under reduced pressure to remove ethanol. The brown colored solid was washed with diethyl ether (3 x 10 mL) and dried under high vacuum for 2h to get the [(Ph$_2$PCH$_2$CH$_2$)$_2$PPh]NiCl$_2$ complex as pale brown color solid (600 mg , 90% yield).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.85 – 8.50 (m, 2H), 8.03 – 7.76 (m, 4H), 7.68 – 7.26 (m, 19H), 4.41 – 3.98 (m, 2H), 3.44 – 2.87 (m, 4H), 2.34 – 2.02 (m, 2H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 134.75 (Vd, $J = 10.2$ Hz), 134.10 (Vt, $J = 5.7$ Hz), 133.62 , 132.88 (Vt, $J = 5.7$ Hz), 132.00 (Vd, $J = 15.2$ Hz), 130.16 (Vd, $J = 10.6$ Hz), 129.59 (Vt, $J = 5.1$ Hz), 129.17 (Vt, $J = 5.4$ Hz), 30.90 , 28.47 .

$^{31}$P NMR (162 MHz, Chloroform-d) $\delta$ 111.06 (t, $J = 48.3$ Hz), 48.55 (d, $J = 48.3$ Hz).

ESI-HRMS (m/z pos): Calculated for [C$_{34}$H$_{33}$ClNiP$_3$]: 627.0842; found: 627.0852.

Elemental analysis: Calculated for [C$_{34}$H$_{33}$Cl$_2$NiP$_3$]: C, 61.49; H, 5.01; Cl, 10.68; Ni, 8.84. Found: C, 61.81; H, 4.58; Cl, 10.36; Ni, 7.83.

Crystal data for complex A: C$_{34}$H$_{33}$Cl$_2$NiP$_3$, $M =$ 664.12, monoclinic, space group $P2_1/m$, $a =$ 8.1732(6), $b =$ 20.6167(15), $c =$ 9.3736(7) Å, $\beta =$ 103.6446(11)$^\circ$, $V =$ 1534.92(2) Å$^3$, $T =$ 150(2) K, $Z =$ 2, 26537 reflections measured, 3812 independent reflections ($R_{int} =$ 0.0219), final $R$ values ($I > 2\sigma(I)$): $R_1 =$ 0.0232, $wR_2 =$ 0.0593, final $R$ values (all data): $R_1 =$ 0.0246, $wR_2 =$ 0.0604, GOF on $F^2$: 1.047, 196 parameters.

CCDC 1869414 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.
Figure S1. Molecular structure of complex A in the crystal. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Symmetry transformation used to generate equivalent atoms: x, -y+1/2, z.
S3. General procedure for the synthesis of primary amines

The magnetic stirring bar and Ni(BF₄)₂·6H₂O (4 mol%) and linear triphos ((L₁; phenylphosphanediyli)bis(ethane-2,1-diyl))bis(diphenylphosphane) (4 mol%) were transferred to 8 mL glass vial and then 2 mL degassed (degassed under argon for 15 minutes before adding) trifluoroethanol (TFE) solvent was added. The colorless solution turned in to brown color, which was stirred under argon for 15 minutes. Then, 0.5 mmol of corresponding carbonyl compound was added and the vial was fitted with septum, cap and needle. The reaction vials (8 vials with different substrates at a time) were placed into a 300 mL autoclave. The autoclave was flushed with hydrogen twice at 30 bar pressure and then it was pressurized with 5-7 bar ammonia gas and 40 bar hydrogen.

The autoclave was placed into an aluminum block preheated at 120 °C-130 (placed 30 minutes before counting the reaction time in ordered to attain reaction temperature) and the reactions were stirred for required time. During the reaction, the inside temperature of the autoclave was measured to be 100-120 °C (10 °C less than temperature set at aluminum block) and this temperature was used as the reaction temperature. After the completion of the reactions, the autoclave was cooled to room temperature. The remaining ammonia and hydrogen were discharged and the vials containing reaction products were removed from the autoclave. The reaction mixture was filtered off and washed thoroughly with ethyl acetate. The reaction products were analyzed by GC-MS. The corresponding primary amines were converted to their respective hydrochloride salt and characterized by NMR and GC-MS analysis. For converting into hydrochloride salt of amine, 1-2 mL methanolic HCl (0.5M HCl in methanol) was added to the ether solution of respective amine and stirred at room temperature for 4-5 h. Then, solvent was removed, and the resulted hydrochloride salt of amine is dried under high vacuum. The yields were determined by GC for the selected amines: After completion of the reaction, n-hexadecane (100µL) as standard was added to the reaction vials and the reaction products were diluted with ethyl acetate followed by filtration using plug of silica and then analyzed by GC.
S4. General procedure for the hydrogenation of nitroarenes to aromatic primary amines

The magnetic stirring bar and Ni(BF₄)₂·6H₂O (4 mol%) and linear triphos ((phenylphosphanediyl)bis(ethane-2,1-diyli))bis(diphenylphosphane) (4 mol%) were transferred to 8 mL glass vial and then 2 mL degassed (degassed under argon for 15 minutes before adding) trifluoroethanol (TFE) solvent was added. The colorless solution turned in to brown color, which was stirred under argon for 15 minutes. Then, 0.5 mmol corresponding nitro compounds was added and the vial was fitted with septum, cap and needle. The reaction vials (8 vials with different substrates at a time) were placed into a 300 mL autoclave. The autoclave was flushed with hydrogen twice at 30 bar pressure and then it was pressurized 40 bar hydrogen. The autoclave was placed into an aluminum block preheated at 130 °C (placed 30 minutes before counting the reaction time in ordered to attain reaction temperature) and the reactions were stirred for required time. During the reaction the inside temperature of the autoclave was measured to be 120 °C and this temperature was used as the reaction temperature. After the completion of the reactions, the autoclave was cooled to room temperature. The remaining hydrogen was discharged and the vials containing reaction products were removed from the autoclave. The reaction mixture was filtered off and washed thoroughly with ethyl acetate. The reaction products were analyzed by GC-MS. The corresponding anilines were isolated by column chromatography to their respective amines, which were characterized by NMR and GC-MS analysis. The yields were determined by GC for the selected amines: After completion of the reaction, n-hexadecane (100µL) as standard was added to the reaction vials and the reaction products were diluted with ethyl acetate followed by filtration using plug of silica and then analyzed by GC.
S5. Solvent screening

Table S1. Influence of solvents on Ni-tripos catalyzed reductive amination of veratraldehyde

![Chemical structure](image)

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<th>Entry</th>
<th>Solvent</th>
<th>Conv. (%)</th>
<th>Yield of 2 (%)</th>
<th>Yield of 3 (%)</th>
<th>Yield of 4 (%)</th>
<th>Yield of 5 (%)</th>
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<td>-</td>
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Reaction conditions: 0.5 mmol veratraldehyde, 4 mol% Ni(BF$_4$)$_2$.6H$_2$O, 4 mol% triphos (L1), 5-7 bar NH$_3$, 40 bar H$_2$, 2 mL solvent, 100 °C, 15 h, GC yields using n-hexadecane as standard.

Table S2. Influence of solvents on Ni-tripos catalyzed hydrogenation of nitrobenzene

![Chemical structure](image)

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<td>4</td>
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<td>8$^c$</td>
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<td>97</td>
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Reaction conditions: 0.5 mmol nitrobenzene, 4 mol% Ni(BF$_4$)$_2$.6H$_2$O, 4 mol% triphos (L1), 40 bar H$_2$, 2 mL solvent, 100 °C, 15 h, GC yields using n-hexadecane as standard. $^a$Same as for 24h. $^b$Same as ‘a’ at 120 °C for 24h.
S6. Catalytic poison test

Table S3.

<table>
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<tr>
<th>Entry</th>
<th>Catalytic poison</th>
<th>Conv. (%)</th>
<th>Yield of 2 (%)</th>
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<th>Yield of 4 (%)</th>
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<tr>
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<td>92</td>
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Reaction conditions: 0.5 mmol veratraldehyde, 4 mol% Ni(BF₄)₂·6H₂O, 4 mol% triphos (L1), 5-7 bar NH₃, 40 bar H₂, 2 mL trifluoroethanol (TFE), 100 °C, 15 h, GC yields using n-hexadecane as standard.

S7. Computational details

DFT calculation

All calculations were carried out with Gaussian 16 program.⁵¹ Geometry optimization was carried out in gas phase at the B3PW91⁵² level with the TZVP⁵³ basis set. All optimized structures were further characterized either as energy minimums without imaginary frequencies or transition states with only one imaginary frequency by frequency calculations, which provided zero-point vibrational energies and thermodynamic corrections to enthalpy and Gibbs free energy at 298.15 K under 1 atmosphere. On the basis of B3PW91/TZVP geometries in gas phase, single-point energies including solvation effect of 2,2,2-trifluoroethanol (TFE) as solvent (dielectric constant ε = 26.69) based on solute electron density (SMD⁵⁴) and van der Waals dispersion (D3⁵) with the gas phase optimized geometries were computed (B3PW91-SMD-D3). The Gibbs free energies at 298.15 K were further corrected to standard state in solution with a standard concentration of 1 mol/L (p = 24.5 atm) from standard state in gas phase (p = 1 atm).

Table S4. Energetic data from B3PW91 full optimization (B3PW91/FOpt) as well as from single-point calculations with the B3PW91 optimized geometries including solvation effect and van der Waals dispersion correction (B3PW91-SCRF-D3//SP)

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<th>Compound</th>
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### Table S5. B3PW91 optimized Cartesian Coordinates

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#### Ph-CH2NH

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</tr>
<tr>
<td>C</td>
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</table>
S8. NMR Data

(4-methoxyphenyl)methanamine hydrochloride

\[ \text{O} \quad \text{NH}_3^+ \text{Cl}^- \]

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.56 (br s, 3H), 7.45 (d, $J$ = 9.0 Hz, 2H), 6.95 (d, $J$ = 8.7 Hz, 2H), 3.92 (s, 2H), 3.75 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 159.74, 131.03, 126.47, 114.31, 55.65, 42.04. White solid.

(3,4,5-trimethoxyphenyl)methanamine hydrochloride

\[ \text{O} \quad \text{O} \quad \text{O} \quad \text{NH}_3^+ \text{Cl}^- \]

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.67 (br s, 3H), 6.97 (s, 2H), 3.94 (s, 2H), 3.78 (s, 6H), 3.64 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 153.22, 137.70, 130.08, 107.03, 60.46, 56.47, 42.83. Off white solid.

p-tolylmethanamine hydrochloride

\[ \text{NH}_3^+ \text{Cl}^- \]

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.63 (br s, 3H), 7.40 (d, $J$ = 8.0 Hz, 2H), 7.20 (d, $J$ = 7.8 Hz, 2H), 3.94 (s, 2H), 2.30 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 138.10, 131.54, 129.46, 129.44, 42.30, 21.22. White solid.

(4-(tert-butyl)phenyl)methanamine hydrochloride

\[ \text{NH}_3^+ \text{Cl}^- \]

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.60 (br s, 3H), 7.54 – 7.14 (m, 4H), 3.95 (s, 2H), 1.27 (s, 9H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 151.33, 131.63, 129.25, 125.72, 42.23, 34.79, 31.54. White solid.
(4-chlorophenyl)methanamine hydrochloride

\[\text{NH}_3\cdot\text{Cl}^-\]

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.70 (br s, 3H), 7.57 (d, $J = 8.5$ Hz, 2H), 7.47 (d, $J = 8.4$ Hz, 2H), 4.00 (s, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 133.59 , 133.51 , 131.48 , 128.90 , 41.81 . White solid.

(4-(trifluoromethyl)phenyl)methanamine hydrochloride

\[\text{F}_3\text{C} \quad \text{NH}_3\cdot\text{Cl}^-\]

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.81 (br s, 3H), 7.95 – 7.53 (m, 4H), 4.12 (s, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 139.30 , 130.27 , 129.26 (q, $J = 31.8$ Hz), 125.74 (q, $J = 3.7$ Hz), 124.58 (q, $J = 272.2$ Hz), 41.99. White solid.

(4-(trifluoromethoxy)phenyl)methanamine hydrochloride

\[\text{O} \quad \text{F}_3\text{C} \quad \text{NH}_3\cdot\text{Cl}^-\]

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.70 (br s, 3H), 7.69 (d, $J = 8.7$ Hz, 2H), 7.41 (d, $J = 7.8$ Hz, 2H), 4.07 (s, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 148.70 , 134.06 , 131.67 , 121.52 , 120.48 (q, $J = 256.3$ Hz), 41.77 . Off white solid.

(3-hydroxy-4-methoxyphenyl)methanamine hydrochloride

\[\text{O} \quad \text{O} \quad \text{NH}_3\cdot\text{Cl}^-\]

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.49 (br s, 3H), 7.22 – 6.82 (m, 3H), 3.90 (s, 2H), 3.81 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 148.27 , 146.87 , 126.82 , 120.45 , 116.84 , 112.51 , 56.15 , 42.32 . Brown solid.

(4-(methylthio)phenyl)methanamine hydrochloride

\[\text{S} \quad \text{NH}_3\cdot\text{Cl}^-\]

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.99 (br s, 3H), 7.46 (d, $J = 8.3$ Hz, 2H), 7.26 (d, $J = 8.3$ Hz, 2H), 3.95 (s, 2H), 2.46 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 138.95 , 131.05 , 130.18 , 126.22 , 42.10 , 15.14 . Brown solid.
**benzo[d][1,3]dioxol-5-ylmethanamine hydrochloride**

![Chemical Structure of benzo[d][1,3]dioxol-5-ylmethanamine hydrochloride]

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.58 (br s, 3H), 7.16 (d, $J = 1.7$ Hz, 1H), 6.98 (dd, $J = 8.0$, 1.7 Hz, 1H), 6.93 (dd, $J = 7.9$, 0.4 Hz, 1H), 6.03 (s, 2H), 3.90 (s, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 147.69, 147.67, 128.17, 123.35, 109.99, 108.65, 101.63, 42.37. *Off white solid.*

**(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)methanamine hydrochloride**

![Chemical Structure of (2,3-dihydrobenzo[b][1,4]dioxin-6-yl)methanamine hydrochloride]

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.29 (br s, 3H), 7.07 (d, $J = 2.1$ Hz, 1H), 6.96 (dd, $J = 8.3$, 2.1 Hz, 1H), 6.85 (d, $J = 8.3$ Hz, 1H), 4.23 (s, 4H), 3.86 (s, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 143.91, 143.57, 127.44, 122.54, 118.40, 117.45, 64.56, 64.52, 42.05. *Off white solid.*

**(benzo[d][1,3]dioxol-5-yl)-2-methylpropan-1-amine hydrochloride**

![Chemical Structure of (benzo[d][1,3]dioxol-5-yl)-2-methylpropan-1-amine hydrochloride]

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.30 (br s, 3H), 6.81 – 6.78 (m, 2H), 6.63 (dd, $J = 8.0$, 1.6 Hz, 1H), 5.95 (s, 2H), 2.73 – 2.63 (m, 2H), 2.63 – 2.54 (m, 1H), 2.28 (dd, $J = 13.5$, 8.3 Hz, 1H), 2.08 – 1.96 (m, 1H), 0.85 (d, $J = 6.6$ Hz, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 147.58, 145.86, 133.85, 122.38, 109.74, 108.43, 101.13, 44.25, 33.72, 17.30. *Pale brown solid.*

**(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanamine hydrochloride**

![Chemical Structure of (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanamine hydrochloride]

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.61 (br s, 3H), 7.69 (d, $J = 8.0$ Hz, 2H), 7.52 (d, $J = 8.1$ Hz, 2H), 4.02 (s, 2H), 1.30 (s, 12H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 137.85, 134.96, 129.42, 128.77, 84.22, 42.50, 25.13. *Off white solid.*

**(E)-(4-styrylphenyl)methanamine hydrochloride**

![Chemical Structure of (E)-(4-styrylphenyl)methanamine hydrochloride]

$^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.61 (br s, 3H), 7.69 – 7.56 (m, 4H), 7.52 (d, $J = 8.0$ Hz, 2H), 7.45 – 7.32 (m, 3H), 7.32 – 7.20 (m, 2H), 4.02 (s, 2H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ 137.59, 137.32, 133.76, 129.86, 129.46, 129.40, 129.20, 128.26, 128.22, 127.00, 42.37. *Yellow solid.*
(4-(benzyloxy)phenyl)methanamine hydrochloride

\[
\text{Ph} \quad \overset{\text{O}}{\text{O}} \quad \overset{\text{NH}_3^+\text{Cl}^-}{\text{H}}
\]

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.59 (br s, 3H), 7.49 – 7.25 (m, 7H), 7.02 (d, $J = 8.7$ Hz, 2H), 5.12 (s, 2H), 3.91 (s, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 158.74, 137.41, 131.06, 128.90, 128.28, 128.08, 126.70, 115.23, 69.61, 42.03. **Off white solid.**

(4-((2-chloro-6-fluorobenzyl)oxy)-3-methoxyphenyl)methanamine hydrochloride

\[
\text{O} \quad \overset{\text{F}}{\text{O}} \quad \overset{\text{Cl}}{\text{Cl}} \quad \overset{\text{NH}_3^+\text{Cl}^-}{\text{H}}
\]

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.55 (br s, 3H), 7.56 – 7.46 (m, 1H), 7.45 – 7.38 (m, 1H), 7.36 – 7.26 (m, 2H), 7.13 (d, $J = 8.2$ Hz, 1H), 7.03 (dd, $J = 8.2$, 2.0 Hz, 1H), 5.12 (s, 2H), 3.95 (s, 2H), 3.75 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 161.94 (d, $J = 249.9$ Hz), 149.52, 148.10, 136.00 (d, $J = 5.1$ Hz), 132.29 (d, $J = 9.9$ Hz), 127.91, 126.18 (d, $J = 3.2$ Hz), 122.49 (d, $J = 17.9$ Hz), 121.85, 115.23 (d, $J = 22.4$ Hz), 114.14, 113.80, 62.12, 56.07, 42.47. **Off white solid.**

[1,1'-biphenyl]-4-ylmethanamine hydrochloride

\[
\text{NH}_3^+\text{Cl}^-\quad \overset{\text{NH}_3^+\text{Cl}^-}{\text{H}}
\]

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.75 (br s, 3H), 7.77 – 7.58 (m, 6H), 7.50 – 7.44 (m, 2H), 7.41 – 7.34 (m, 1H), 4.06 (s, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 140.59, 139.99, 133.74, 130.12, 129.45, 128.12, 127.19, 127.14, 42.25. **Off white solid.**

KM24-108 2,2-diphenylethan-1-amine hydrochloride

\[
\text{NH}_3^+\text{Cl}^-\quad \overset{\text{NH}_3^+\text{Cl}^-}{\text{H}}
\]

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.20 (br s, 3H), 7.41 – 7.30 (m, 8H), 7.27 – 7.20 (m, 2H), 4.41 (t, $J = 7.9$ Hz, 1H), 3.53 (d, $J = 7.9$ Hz, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 141.56, 129.22, 128.29, 127.45, 48.97, 42.82. **Pale brown solid.**

S24
3-(4-(tert-butyl)phenyl)-2-methylpropan-1-amine hydrochloride

\[ \text{NH}_3^+ \text{Cl}^- \]

$^1$H NMR (400 MHz, DMSO-\(d_6\)) $\delta$ 8.36 (br s, 3H), 7.34 (d, \(J = 8.2\) Hz, 2H), 7.17 (d, \(J = 8.3\) Hz, 2H), 2.81 – 2.71 (m, 2H), 2.71 – 2.62 (m, 1H), 2.39 (dd, \(J = 13.5\), 8.3 Hz, 1H), 2.19 – 2.06 (m, 1H), 1.29 (s, 9H), 0.92 (d, \(J = 6.6\) Hz, 3H). $^{13}$C NMR (101 MHz, DMSO-\(d_6\)) $\delta$ 148.65, 136.95, 129.15, 125.39, 44.37, 39.67, 34.50, 33.54, 31.65, 17.46. Pale brown solid.

1-(3-methoxyphenyl)ethan-1-amine hydrochloride

\[ \text{NH}_3^+ \text{Cl}^- \]

$^1$H NMR (300 MHz, DMSO-\(d_6\)) $\delta$ 8.57 (br s, 3H), 7.31 (dd, \(J = 8.2\), 7.6 Hz, 1H), 7.27 – 7.19 (m, 1H), 7.14 – 7.04 (m, 1H), 6.91 (ddd, \(J = 8.3\), 2.6, 0.9 Hz, 1H), 4.33 (q, \(J = 6.8\) Hz, 1H), 3.77 (s, 3H), 1.52 (d, \(J = 6.7\) Hz, 3H). $^{13}$C NMR (75 MHz, DMSO-\(d_6\)) $\delta$ 159.85, 141.54, 130.18, 119.34, 114.19, 113.05, 55.70, 50.48, 21.37. White solid.

1-(4-fluorophenyl)ethan-1-amine hydrochloride

\[ \text{NH}_3^+ \text{Cl}^- \]

$^1$H NMR (300 MHz, DMSO-\(d_6\)) $\delta$ 8.76 (br s, 3H), 7.78 – 7.48 (m, 2H), 7.35 – 7.10 (m, 2H), 4.50 – 4.24 (m, 1H), 1.52 (d, \(J = 6.8\) Hz, 3H). $^{13}$C NMR (75 MHz, DMSO-\(d_6\)) $\delta$ 162.34 (d, \(J = 244.4\) Hz), 136.19 (d, \(J = 3.1\) Hz), 129.71 (d, \(J = 8.4\) Hz), 115.85 (d, \(J = 21.4\) Hz), 49.80, 21.25. Brown solid.

1-(2-methoxy-4-(trifluoromethoxy)phenyl)ethan-1-amine hydrochloride

\[ \text{NH}_3^+ \text{Cl}^- \]

$^1$H NMR (300 MHz, DMSO-\(d_6\)) $\delta$ 8.58 (br s, 3H), 7.68 (d, \(J = 8.4\) Hz, 1H), 7.26 – 6.84 (m, 2H), 4.79 – 4.40 (m, 1H), 3.94 (s, 3H), 1.55 (d, \(J = 6.7\) Hz, 3H). $^{13}$C NMR (75 MHz, DMSO-\(d_6\)) $\delta$ 157.82, 149.65, 128.81, 126.76, 120.49 (q, \(J = 256.5\) Hz), 112.91, 105.51, 56.76, 44.66, 19.56. Off white solid.
KM24-154 2-methyl-1-phenylpropan-1-amine hydrochloride

\[
\text{\textbf{1H NMR (300 MHz, DMSO-}d_6\text{)}} \delta 8.08 \text{ (br s, 3H), 7.53 – 7.44 (m, 2H), 7.42 – 7.28 (m, 3H), 4.06 – } \\
\text{3.70 (m, 1H), 2.30 – 2.06 (m, 1H), 0.99 (d, } J = 6.2 \text{ Hz, 3H), 0.67 (d, } J = 6.3 \text{ Hz, 3H). } \text{\textbf{13C NMR (75 MHz, DMSO-}d_6\text{)}} \delta 137.93, 128.82, 128.65, 128.33, 60.57, 32.60, 20.03, 18.96. \text{ Off white solid.}
\]

1-(benzo[d][1,3]dioxol-5-yl)ethan-1-amine hydrochloride

\[
\text{\textbf{1H NMR (300 MHz, DMSO-}d_6\text{)}} \delta 8.66 \text{ (br s, 3H), 7.21 (d, } J = 1.7 \text{ Hz, 1H), 6.99 (dd, } J = 8.1, 1.7 \text{ Hz, 1H), 6.91 (d, } J = 8.0 \text{ Hz, 1H), 6.02 (s, 2H), 4.40 – 4.12 (m, 1H), 1.49 (d, } J = 6.7 \text{ Hz, 3H). } \text{\textbf{13C NMR (75 MHz, DMSO-}d_6\text{)}} \delta 147.81, 147.52, 133.69, 121.10, 108.65, 107.85, 101.64, 50.34, 21.30. \text{ Off white solid.}
\]

4-(1H-indol-3-yl)butan-2-amine hydrochloride

\[
\text{\textbf{1H NMR (300 MHz, DMSO-}d_6\text{)}} \delta 11.01 \text{ (s, 1H), 8.32 (br s, 3H), 7.57 (d, } J = 7.7 \text{ Hz, 1H), 7.39 (d, } J = 8.0 \text{ Hz, 1H), 7.18 (d, } J = 2.1 \text{ Hz, 1H), 7.14 – 7.02 (m, 1H), 7.03 – 6.94 (m, 1H), 3.31 – 3.02 (m, 1H), 2.88 – 2.65 (m, 2H), 2.20 – 1.98 (m, 1H), 1.91 – 1.68 (m, 1H), 1.30 (d, } J = 6.5 \text{ Hz, 3H). } \text{\textbf{13C NMR (75 MHz, DMSO-}d_6\text{)}} \delta 136.81, 127.40, 122.81, 121.40, 118.85, 118.64, 113.59, 111.95, 47.13, 35.17, 21.26, 18.54. \text{ Brown solid.}
\]

1-(4-(methylthio)phenyl)ethan-1-amine hydrochloride

\[
\text{\textbf{1H NMR (300 MHz, DMSO-}d_6\text{)}} \delta 8.31 \text{ (br s, 3H), 7.48 (d, } J = 7.9 \text{ Hz, 2H), 7.29 (d, } J = 8.0 \text{ Hz, 2H), 4.53 – 4.08 (m, 1H), 2.47 (s, 3H), 1.51 (d, } J = 6.4 \text{ Hz, 3H). } \text{\textbf{13C NMR (75 MHz, DMSO-}d_6\text{)}} \delta 138.88, 136.38, 128.07, 126.44, 50.09, 21.27, 15.29. \text{ Brown solid.}
\]
1-(4-(methylsulfonyl)phenyl)ethan-1-amine hydrochloride

\[
\text{NH}_3\text{Cl}^-
\]

\(^1\text{H} \text{ NMR (300 MHz, DMSO-}^d_6\text{)} \delta 8.87 \text{ (br s, 3H), 7.98 (d, } J = 8.4 \text{ Hz, 2H), 7.84 (d, } J = 8.4 \text{ Hz, 2H), 4.66 – 4.42 \text{ (m, 1H), 3.24 (s, 3H), 1.55 (d, } J = 6.8 \text{ Hz, 3H).} \quad \text{^13C NMR (75 MHz, DMSO-}^d_6\text{)} \delta 145.49 , 141.06 , 128.44 , 127.74 , 50.03 , 43.85 , 21.12 . \ \text{Pale brown solid.}
\]

4-(3-aminobutyl)phenol

\[
\text{NH}_2
\]

\(^1\text{H} \text{ NMR (300 MHz, DMSO-}^d_6\text{)} \delta 6.98 \text{ (d, } J = 8.4 \text{ Hz, 2H), 6.68 (d, } J = 8.4 \text{ Hz, 2H), 6.28 (br s, 2H), 3.02 – 2.78 \text{ (m, 1H), 2.66 – 2.33 \text{ (m, 2H), 1.82 – 1.48 \text{ (m, 2H), 1.10 (d, } J = 6.4 \text{ Hz, 3H).} \quad \text{^13C NMR (75 MHz, DMSO-}^d_6\text{)} \delta 155.88 , 132.03 , 129.44 , 115.57 , 46.57 , 39.49 , 31.06 , 21.37 . \ \text{Brown solid.}
\]

4-(4-hydroxy-3-methoxyphenyl)butan-2-amine hydrochloride

\[
\text{NH}_3\text{Cl}^-
\]

\(^1\text{H} \text{ NMR (300 MHz, DMSO-}^d_6\text{)} \delta 8.27 \text{ (br s, 3H), 6.84 (d, } J = 1.9 \text{ Hz, 1H), 6.78 (d, } J = 7.9 \text{ Hz, 1H), 6.64 (dd, } J = 8.0 , 1.9 \text{ Hz, 1H), 3.79 (s, 3H), 3.27 – 2.98 \text{ (m, 1H), 2.71 – 2.55 \text{ (m, 2H), 2.10 – 1.85 \text{ (m, 1H), 1.88 – 1.62 \text{ (m, 1H), 1.28 (d, } J = 6.5 \text{ Hz, 3H).} \quad \text{^13C NMR (75 MHz, DMSO-}^d_6\text{)} \delta 147.90 , 145.10 , 132.10 , 120.70 , 115.82 , 112.91 , 56.02 , 46.86 , 36.50 , 30.86 , 18.46 . \ \text{Pale yellow solid.}
\]

(1-hydroxycyclohexyl)(phenyl)methanamine hydrochloride

\[
\text{NH}_3\text{Cl}^-
\]

\(^1\text{H} \text{ NMR (300 MHz, DMSO-}^d_6\text{)} \delta 8.45 \text{ (br s, 3H), 7.57 – 7.42 \text{ (m, 2H), 7.45 – 7.24 \text{ (m, 3H), 5.04 (s, 1H), 4.11 (s, 1H), 1.89 – 0.90 \text{ (m, 10H).} \quad \text{^13C NMR (75 MHz, DMSO-}^d_6\text{)} \delta 135.87 , 129.40 , 128.62 , 128.38 , 71.20 , 63.23 , 34.87 , 33.02 , 25.48 , 21.47 , 21.12 . \ \text{Off white solid.}
\]
1-phenylpentan-1- amine hydrochloride

\[
\text{NH}_3^+ \text{Cl}^-
\]

\(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 8.59 (br s, 3H), 7.56 – 7.46 (m, 2H), 7.46 – 7.34 (m, 3H), 4.15 (dd, \(J = 9.5, 5.4\) Hz, 1H), 2.05 – 1.91 (m, 1H), 1.89 – 1.70 (m, 1H), 1.30 – 0.93 (m, 4H), 0.80 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) 138.41 , 129.15 , 128.94 , 127.91 , 54.94 , 34.36 , 27.65 , 22.10 , 14.18 . Pale brown solid.

1,3-diphenylpropan-2- amine hydrochloride

\[
\text{NH}_3^+ \text{Cl}^-
\]

\(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 8.26 (br s, 3H), 7.44 – 7.08 (m, 10H), 3.76 – 3.56 (m, 1H), 3.03 (dd, \(J = 13.9, 6.2\) Hz, 2H), 2.80 (dd, \(J = 13.9, 6.9\) Hz, 2H). \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) 136.96 , 129.84 , 129.07 , 127.25 , 53.61 , 38.17 . Brown solid.

1-phenyl-2-(p-tolyl)ethan-1-amine hydrochloride

\[
\text{NH}_3^+ \text{Cl}^-
\]

\(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 8.87 (br s, 3H), 7.50 – 7.37 (m, 2H), 7.36 – 7.25 (m, 3H), 7.06 – 6.84 (m, 4H), 4.53 – 4.29 (m, 1H), 3.42 (dd, \(J = 13.4, 5.0\) Hz, 1H), 3.08 (dd, \(J = 13.3, 10.2\) Hz, 1H), 2.18 (s, 3H). \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) 137.56 , 135.97 , 133.58 , 129.56 , 129.29 , 128.86 , 128.38 , 56.43 , 40.25 , 21.07 . White solid.

1-(4-hydroxy-3-methoxyphenyl)propan-2- amine hydrochloride

\[
\text{NH}_3^+ \text{Cl}^-
\]

\(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 8.19 (br s, 3H), 6.80 (d, \(J = 1.9\) Hz, 1H), 6.74 (d, \(J = 8.0\) Hz, 1H), 6.60 (dd, \(J = 8.0, 1.9\) Hz, 1H), 3.75 (s, 3H), 3.39 – 3.23 (m, 1H), 2.93 (dd, \(J = 13.4, 5.2\) Hz, 1H), 2.58 (dd, \(J = 9.0, 4.4\) Hz, 1H), 1.12 (d, \(J = 6.7\) Hz, 3H). \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) 147.98 , 145.80 , 127.84 , 121.92 , 115.94 , 113.73 , 56.00 , 48.66 , 31.76 , 18.04 . Brown solid.
4-(6-methoxynaphthalen-2-yl)butan-2-amine hydrochloride

\[
\text{\text{O}}\quad \text{\text{NH}_3^+\text{Cl}^-}
\]

\(^1\text{H} \text{ NMR (300 MHz, DMSO-}\text{d}_6) \delta 8.33 \ (\text{br s, 3H}), 7.74 \ (\text{dd, } J = 8.7, 2.7 \text{ Hz, 2H}), 7.65 – 7.60 \ (\text{m, 1H}), 7.34 \ (\text{dd, } J = 8.4, 1.7 \text{ Hz, 1H}), 7.26 \ (\text{d, } J = 2.5 \text{ Hz, 1H}), 7.12 \ (\text{dd, } J = 8.9, 2.5 \text{ Hz, 1H}), 3.83 \ (\text{s, 3H}), 3.32 – 3.09 \ (\text{m, 1H}), 2.93 – 2.66 \ (\text{m, 2H}), 2.18 – 1.93 \ (\text{m, 1H}), 1.93 – 1.70 \ (\text{m, 1H}), 1.28 \ (\text{d, } J = 6.5 \text{ Hz, 3H}). \ ^{13}\text{C} \text{ NMR (75 MHz, DMSO-}\text{d}_6) \delta 157.26 , 136.54 , 133.26 , 129.25 , 129.02 , 128.02 , 127.31 , 126.40 , 119.00 , 106.23 , 55.60 , 46.97 , 36.21 , 31.28 , 18.51 . \text{ Off white solid.}

6-(3,7-dimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1H-purin-1-yl)hexan-2-amine hydrochloride

\[
\text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{O} \quad \text{NH}_3^+\text{Cl}^-\]

\(^1\text{H} \text{ NMR (300 MHz, Methanol-}\text{d}_4) \delta 7.91 \ (\text{s, 1H}), 4.83 \ (\text{br s, 3H}), 3.89 \ (\text{s, 3H}), 3.87 – 3.81 \ (\text{m, 2H}), 3.40 \ (\text{s, 3H}), 3.29 – 3.15 \ (\text{m, 1H}), 1.71 – 1.47 \ (\text{m, 4H}), 1.44 – 1.30 \ (\text{m, 2H}), 1.24 \ (\text{d, } J = 6.5 \text{ Hz, 3H}). \ ^{13}\text{C} \text{ NMR (75 MHz, Methanol-}\text{d}_4) \delta 154.88 , 151.35 , 147.73 , 142.34 , 107.26 , 47.55 , 40.46 , 33.88 , 32.92 , 28.96 , 27.13 , 22.29 , 17.33 . \text{ White solid.}

1-(4-fluorophenyl)-4-(4-(pyridin-2-yl)piperazin-1-yl)butan-1-amine

\[
\text{NH}_2 \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{F}
\]

\(^1\text{H} \text{ NMR (300 MHz, Chloroform-}\text{d} ) \delta 8.14 – 8.04 \ (\text{m, 1H}), 7.45 – 7.33 \ (\text{m, 1H}), 7.29 – 7.21 \ (\text{m, 2H}), 6.98 – 6.89 \ (\text{m, 2H}), 6.58 – 6.47 \ (\text{m, 2H}), 3.87 \ (\text{t, } J = 6.9 \text{ Hz, 1H}), 3.65 \ (\text{br s, 2H}), 3.49 – 3.38 \ (\text{m, 4H}), 2.49 – 2.37 \ (\text{m, 4H}), 2.34 – 2.25 \ (\text{m, 2H}), 1.93 – 1.27 \ (\text{m, 4H}). \ ^{13}\text{C} \text{ NMR (75 MHz, Chloroform-}\text{d} ) \delta 161.96 \ (\text{d, } J = 245.2 \text{ Hz}), 159.46 , 147.91 , 140.36 , 137.44 , 128.11 \ (\text{d, } J = 7.9 \text{ Hz}), 115.36 \ (\text{d, } J = 21.2 \text{ Hz}), 113.31 , 107.07 , 58.33 , 55.45 , 52.96 , 45.09 , 36.85 , 23.69 . \text{ Brown solid.}
(8R,9S,13S,14S)-3-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-amine hydrochloride (diastereomeric mixture)

$\text{NH}_3^+\text{Cl}^-$

$^1$H NMR (300 MHz, DMSO-$d_6$) (diastereomeric mixture) $\delta$ 9.09 (br s, 1H), 8.24 (br s, 3H), 7.03 (d, $J = 8.1$ Hz, 1H), 6.53 (dd, $J = 8.4$, 2.5 Hz, 1H), 6.46 (d, $J = 2.6$ Hz, 1H), 3.22 – 2.91 (m, 1H), 2.86 – 2.61 (m, 2H), 2.30 – 2.00 (m, 4H), 1.85 – 1.51 (m, 4H), 1.35 – 1.20 (m, 5H), 0.75 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) (diastereomeric mixture) $\delta$ 155.52, 155.41, 137.44, 137.41, 130.82, 130.36, 126.53, 126.42, 115.43, 115.40, 113.26, 113.21, 59.95, 59.24, 51.27, 49.98, 47.93, 43.99, 43.86, 43.56, 43.27, 39.16, 38.66, 36.23, 29.64, 29.53, 28.38, 28.26, 27.50, 27.44, 26.71, 26.18, 26.09, 23.55, 18.33, 12.15. (traces of ethylacetate solvent peak was observed in the NMR spectra).


4-(tert-butyl)cyclohexan-1- amine hydrochloride (diastereomeric mixture)

$\text{NH}_3^+\text{Cl}^-$

$^1$H NMR (300 MHz, DMSO-$d_6$) (diastereomeric mixture) $\delta$ 7.43 (br s, 3H), 3.32 – 2.56 (m, 1H), 2.19 – 1.23 (m, 7H), 1.06 – 0.87 (m, 2H), 0.78 (s, 9H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) (diastereomeric mixture) $\delta$ 49.94, 47.50, 46.72, 46.01, 32.72, 32.47, 30.89, 28.93, 27.94, 27.81, 25.37, 20.71. Off white solid.

Nonan-5-amine hydrochloride

$\text{NH}_3^+\text{Cl}^-$

$^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 8.10 (br s, 3H), 3.11 – 2.84 (m, 1H), 1.57 – 1.47 (m, 4H), 1.33 – 1.20 (m, 8H), 0.90 – 0.81 (m, 6H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 51.09, 31.92, 27.01, 22.44, 14.20. White solid.
Octan-2-amine hydrochloride

\[ \text{NH}_3^+ \text{Cl}^- \]

\(^1\text{H NMR (300 MHz, DMSO-}d_6\text{)} \delta 8.09 (br s, 3H), 3.29 – 3.04 (m, 1H), 1.73 – 1.59 (m, 1H), 1.58 – 1.42 (m, 1H), 1.40 – 1.27 (m, 8H), 1.23 (d, \(J = 6.5\text{ Hz, }3\text{H}), 0.96 – 0.89 (m, 3H). \(^{13}\text{C NMR (75 MHz, DMSO-}d_6\text{)} \delta 47.23 , 34.52 , 31.51 , 28.88 , 25.18 , 22.44 , 18.53 , 14.40\). White solid.

4-(2,6,6-trimethylcyclohex-1-en-1-yl)butan-2-amine hydrochloride

\[ \text{NH}_3^+ \text{Cl}^- \]

\(^1\text{H NMR (300 MHz, DMSO-}d_6\text{)} \delta 8.14 (br s, 3H), 3.20 – 3.05 (m, 1H), 2.07 – 1.92 (m, 2H), 1.87 (t, \(J = 6.2\text{ Hz, }2\text{H}), 1.75 – 1.59 (m, 1H), 1.56 (s, 3H), 1.54 – 1.44 (m, 3H), 1.42 – 1.33 (m, 2H), 1.22 (d, \(J = 6.5\text{ Hz, }3\text{H}), 0.97 (s, 3H), 0.97 (s, 3H). \(^{13}\text{C NMR (75 MHz, DMSO-}d_6\text{)} \delta 136.49 , 127.31 , 47.71 , 39.78 , 35.18 , 35.05 , 32.69 , 28.84 , 24.60 , 20.07 , 19.48 , 18.43\). Brown solid.

(5S,8R,9R,10S,13S,14S,17S)-17-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-amine hydrochloride (diastereomeric mixture)

\[ \text{NH}_3^+ \text{Cl}^- \]

\(^1\text{H NMR (300 MHz, DMSO-}d_6\text{) (diastereomeric mixture)} \delta 8.07 (br s, 3H), 4.44 (s, 1H), 3.57 – 3.33 (m, 1H), 1.99 – 0.81 (m, 23H), 0.75 (s, 3H), 0.63 (s, 3H). \(^{13}\text{C NMR (75 MHz, DMSO-}d_6\text{) (diastereomeric mixture)} \delta 80.52, 80.48 , 54.07 , 53.68 , 52.92 , 52.71 , 51.21 , 51.01 , 49.90 , 46.68 , 44.57 , 44.02, 42.18, 43.02 , 38.42 , 37.11 , 37.05 , 36.49 , 36.00 , 35.56 , 35.48 , 32.76 , 31.61 , 31.26 , 30.98 , 30.30 , 28.44 , 28.21 , 26.32 , 26.27 , 24.29 , 23.51 , 20.79 , 20.72 , 20.41 , 12.28 , 11.80 , 11.55 \). HRMS (EI): Calcd for C19H33NO [M]+ 291.2556; found 291.2549. White solid.
(3R,8R,9S,10S,13S,14S)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-amine hydrochloride (diastereomeric mixture)

\[
\text{HO}^+\text{NH}_3^+\text{Cl}^-
\]

\(^1\)H NMR (300 MHz, DMSO-\(d_6\)) (diastereomeric mixture) \(\delta\) 7.98 (br s, 3H), 3.90 – 3.71 (m, 1H), 3.14 – 2.96 (m, 1H), 2.29 – 1.89 (m, 1H), 1.79 – 0.86 (m, 21H), 0.83 – 0.56 (m, 6H). \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) 64.62, 64.47, 59.92, 59.09, 54.22, 53.80, 53.69, 52.40, 49.01, 48.93, 43.57, 42.22, 38.97, 36.26, 36.15, 36.11, 35.70, 35.26, 32.58, 32.47, 32.41, 32.36, 31.91, 29.07, 28.64, 28.58, 28.23, 26.57, 24.96, 23.80, 20.24, 20.16, 18.26, 18.07, 12.12, 12.08, 11.57, 11.53.


2,4,6-trimethylaniline

\[
\begin{array}{c}
\text{NH}_2
\end{array}
\]

\(^1\)H NMR (300 MHz, Chloroform-\(d\)) \(\delta\) 6.82 – 6.52 (m, 2H), 3.42 (br s, 2H), 2.12 (s, 3H), 2.07 (s, 6H). \(^{13}\)C NMR (75 MHz, Chloroform-\(d\)) \(\delta\) 140.00, 128.91, 127.32, 122.03, 20.44, 17.66. Brown oil.

N1,N1-dimethylbenzene-1,3-diamine

\[
\begin{array}{c}
\text{N} \\
\text{NH}_2
\end{array}
\]

\(^1\)H NMR (300 MHz, Chloroform-\(d\)) \(\delta\) 7.02 – 6.88 (m, 1H), 6.18 – 6.07 (m, 1H), 6.07 – 5.93 (m, 2H), 3.37 (br s, 2H), 2.83 (s, 6H). \(^{13}\)C NMR (75 MHz, Chloroform-\(d\)) \(\delta\) 151.85, 147.30, 129.87, 104.30, 103.82, 99.63, 40.62. Brown gum.

methyl 4-aminobenzoate

\[
\begin{array}{c}
\text{O} \\
\text{NH}_2
\end{array}
\]

\(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 7.67 (d, \(J = 8.7\) Hz, 2H), 6.60 (d, \(J = 8.7\) Hz, 2H), 5.95 (br s, 2H), 3.73 (s, 3H). \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) 166.90, 153.89, 131.55, 116.31, 113.17, 51.58. Brown solid.
4-aminobenzamide

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{NH}_2 \\
\text{O} & \\
\end{align*}
\]

\(^{1}\text{H} \text{NMR (300 MHz, DMSO-\text{d}_6)} \delta 7.63 (d, J = 8.6 \text{ Hz, 2H}), 6.94 (s, 1\text{H}), 6.57 (d, J = 8.6 \text{ Hz, 2H}), 5.62 (s, 1\text{H}), 3.63 (br s, 2\text{H}). \quad ^{13}\text{C NMR (75 MHz, DMSO-\text{d}_6)} \delta 168.85, 152.17, 129.65, 121.29, 113.04. \quad \text{Pale brown solid.}

2,6-dichlorobenzene-1,4-diamine

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{NH}_2 \\
\text{Cl} & \quad \text{Cl} \\
\end{align*}
\]

\(^{1}\text{H} \text{NMR (300 MHz, Chloroform-\text{d})} \delta 6.53 (s, 2\text{H}), 3.79 (br s, 2\text{H}), 3.41 (br s, 2\text{H}). \quad ^{13}\text{C NMR (75 MHz, Chloroform-\text{d})} \delta 138.36, 132.53, 120.81, 115.41. \quad \text{Brown solid.}

4-phenoxyaniline

\[
\begin{align*}
\text{NH}_2 & \quad \text{O} \quad \text{Ph} \\
\end{align*}
\]

\(^{1}\text{H} \text{NMR (300 MHz, DMSO-\text{d}_6)} \delta 7.34 – 7.24 (m, 2\text{H}), 7.04 – 6.95 (m, 1\text{H}), 6.89 – 6.83 (m, 2\text{H}), 6.77 (d, J = 8.8 \text{ Hz, 2H}), 6.62 (d, J = 8.8 \text{ Hz, 2H}), 5.02 (br s, 2\text{H}). \quad ^{13}\text{C NMR (75 MHz, DMSO-\text{d}_6)} \delta 159.44, 145.98, 145.88, 130.11, 122.17, 121.39, 116.87, 115.39. \quad \text{Pale brown solid.}

[1,1'-biphenyl]-2-amine

\[
\begin{align*}
\text{Ph} & \quad \text{NH}_2 \\
\end{align*}
\]

\(^{1}\text{H} \text{NMR (300 MHz, Chloroform-\text{d})} \delta 7.61 – 7.49 (m, 4\text{H}), 7.48 – 7.37 (m, 1\text{H}), 7.31 – 7.19 (m, 2\text{H}), 6.99 – 6.89 (m, 1\text{H}), 6.84 (dd, J = 8.1, 1.3 \text{ Hz, 1H}), 3.85 (br s, 2\text{H}). \quad ^{13}\text{C NMR (75 MHz, Chloroform-\text{d})} \delta 143.48, 139.60, 130.54, 129.19, 128.90, 128.59, 127.77, 127.26, 118.80, 115.76. \quad \text{Off white Solid.}
Quinolin-6-amine

![Quinolin-6-amine structure]

\(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 8.47 (dd, \(J = 4.2, 1.7\) Hz, 1H), 7.98 – 7.88 (m, 1H), 7.70 (d, \(J = 9.0\) Hz, 1H), 7.27 (dd, \(J = 8.3, 4.2\) Hz, 1H), 7.17 (dd, \(J = 9.0, 2.5\) Hz, 1H), 6.79 (d, \(J = 2.5\) Hz, 1H), 5.66 (br s, 2H). \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) 147.52, 145.39, 142.33, 133.43, 130.30, 129.91, 122.14, 121.66, 105.19. Brown solid.

N-(4-amino-3-(trifluoromethyl)phenyl)isobutyramide

![N-(4-amino-3-(trifluoromethyl)phenyl)isobutyramide structure]

\(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 9.63 (s, 1H), 7.73 (d, \(J = 2.4\) Hz, 1H), 7.48 – 7.37 (m, 1H), 6.79 (dd, \(J = 8.8, 0.9\) Hz, 1H), 5.32 (br s, 2H), 2.57 – 2.48 (m, 1H), 1.08 (d, \(J = 6.8\) Hz, 6H). \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) 175.11, 142.48, 128.79, 126.44 (q, \(J = 272.0\) Hz), 125.44, 117.61, 117.39 (q, \(J = 5.6\) Hz), 110.72 (q, \(J = 29.5\) Hz), 35.21, 19.97. Yellow Solid.
S9. NMR and HRMS spectra
190128.408.10
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190128.408.11
Kathir ILM24-66
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S37
190128.410.11.5d
Kathir (LM24-75)
Au1H DMSO (C:\Bruker\TopSpin3.5\pl6) 1901 10

190128.410.11.5d
Kathir (LM24-75)
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PROTON DMSO (C:\Bruker\TopSpin3.6.0) 1901 45
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S91