Supporting Information

Single-Crystal Cobalt Phosphide Nanorods as a High-Performance Catalyst for Reductive Amination of Carbonyl Compounds

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References
1. General experimental details

All the organic reagents were obtained commercially and the purity of each reagent was checked before use.

Co(acac)$_2$ was purchased from Mitsuwa Pure Chemicals. 1-Octadecene (technical grade; 90%) was purchased from Sigma-Aldrich. Co. Hexadecylamine and triphenyl phosphite were purchased from Tokyo Chemical Industry Co., Ltd. SiO$_2$ (Q-9) was procured from Fuji Silysia Chemicals Ltd. Raney Co (about 48%) was purchased from FUJIFILM Wako Pure Chemical. All the substrates were commercially available.

Benzaldehyde (>98%), $p$-anisaldehyde (>99%), 2,3-dimethoxybenzaldehyde (>98%), biphenyl-4-carboxaldehyde (>98%), 4-acetamidobenzaldehyde (>98%), 5-hydroxymethyl-2-furaldehyde (>95%), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (>97%), 5-methylfurfural, cyclohexanecarbaldehyde, heptanal (98%), 4-(methylsulfonyl)acetophenone (>98%), 4-acetylpyridine (>97%), benzophenone (>99%), 1-indanone (>98%), 2-adamantanone (>98%), 2-octanone (>98%), 2-dodecanone (>98%), cyclohexanone (>99%), and estrone (>98%) were obtained from Tokyo Chemical Industry Co., Ltd. $p$-Tolualdehyde (97%), $p$-chlorobenzaldehyde (>98%), acetophenone, 1-(4-methoxyphenyl)ethanone (>98%), $p$-chloroacetophenone (>95%), $p$-bromoacetophenone (98%), 4-(N-acetylamino)acetophenone (96%), and haloperidol (>98%) were obtained from FUJIFILM Wako Pure Chemical.

$^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ESC400 spectrometer. Transmission electron microscopy (TEM) observations were conducted using a JEM-ARM200F instrument operated at 200 kV. Scanning transmission electron microscopy (STEM) images with elemental maps were collected using a FEI Titan Cubed G2 60-300 instrument, operated at 300 kV, and equipped with a Super-X energy-dispersive X-ray spectroscopy (EDX) detector. Elemental mapping based on quantification analysis of EDX spectra was carried out using Esprit.

Co K-edge X-ray absorption spectra were recorded at room temperature using a Si (311) or Si (111) monochromator at the BL01B1 and BL14B2 lines, SPring-8, Japan Synchrotron Radiation Research Institute (JASRI), Harima, Japan. XRD was performed using a Philips X’Pert-MPD diffractometer with Cu-K$_\alpha$ radiation. XPS analysis was performed on an ESCA1700R system equipped with a dual Mg/Al X-ray source and a hemispherical analyzer operating in fixed-analyzer transmission mode. The spectra were obtained using a pass energy of 58.7 eV and an AI-K X-ray source operated at 350 W and 14 kV. Excess charges on the samples were neutralized by argon ion sputtering. The analysis area was 0.8 mm × 2 mm. The working pressure in the analysis chamber was less than 1 × 10$^{-7}$ Pa. Spectra were acquired in the Co 2p, O 1s, C 1s, and Si 2p regions. The C 1s peak at a binding energy (BE) of 285 eV was used as an internal reference.

Fourier-transform infrared (FT-IR) spectra were recorded on a JASCO FT-IR 4100 spectrometer equipped with a mercury cadmium telluride detector.
2. Catalyst preparation and procedure for reaction

Preparation of Co$_2$P NRs

All the reactions were carried out in argon atmosphere using standard Schlenk line techniques. In a typical synthesis, Co(acac)$_2$ (1.0 mmol) and 2.4 g (10.0 mmol) of hexadecylamine were combined with 10.0 mL of 1-octadecene and 2.6 mL (10.0 mmol) of triphenylphosphite in a Schlenk flask. The mixture was heated to 150 °C under argon flow and maintained for 1 h. The temperature was then increased to 300 °C and maintained for 2 h, yielding a black colloidal solution. The mixture was then cooled in air to room temperature. The obtained colloid was isolated by precipitation with acetone, and the redispersion and precipitation cycles were continued using a chloroform-acetone mixed solvent (chloroform:acetone = 1:1) until the supernatant liquid was transparent. The obtained powder was dried overnight in vacuum at room temperature to produce Co$_2$P NRs.

Preparation of CoP NPs

In a typical synthesis, under a flow of argon, Co(acac)$_2$ (1 mmol), 1-octadecene (5.0 mL, 15.6 mmol) and oleylamine (10 mL, 30.4 mmol) were placed in a Schlenk flask. The mixture was stirred and heated to 120 °C, and this temperature was maintained for 1 h. Then, triphenylphosphine (5.0 mL, 11 mmol) was added to the above solution and heated to 340 °C for 4 h. Afterwards, the mixture was allowed to cool in air to room temperature. To remove as much organics as possible, redispersion and precipitation cycles were continued until the supernatant liquid was transparent using a hexane-ethanol mixed solvent (hexane:ethanol = 1:1). The obtained powder was dried at room temperature in vacuum overnight.

Preparation of Co/SiO$_2$

Co/SiO$_2$ was prepared as follows. SiO$_2$ was soaked in an aqueous solution of Co(NO$_3$)$_2$. After stirring for 10 min, the pH was adjusted to 10.0 with an aqueous NaOH solution and the mixture stirred at room temperature in air for 6 h. The resulting slurry was filtered. The recovered solid was washed with deionized water and then dried at room temperature in vacuo to generate Co/SiO$_2$. Co/SiO$_2$ was then treated under H$_2$ at atmospheric pressure and 250 °C for 2 h to provide Co/SiO$_2$-Red.

Procedure for reaction

A typical reaction procedure for the reductive amination using Co$_2$P NR was as follows. Co$_2$P NR powder (0.004 g) was placed in a 50-mL stainless-steel autoclave with a Teflon inner cylinder, followed by addition of substrate (0.5 mmol), solvent (3 mL). The reaction mixture was stirred vigorously at 100 °C under 5 bar of H$_2$. After the reaction, the reaction solution was analyzed by GC to determine the conversion and the yield using dimethyl sulfone as an internal standard. After reaction, to obtain the hydrochloride salts, the crude reaction mixture was filtered to remove the catalyst and the ammonia was removed under vacuum conditions. The mixture was then added to a hydrogen chloride solution (1.25 M, 1,4-dioxane). The solvent was removed leaving behind the corresponding salt, giving the
pure hydrochloride salts, which were subjected to NMR analysis. The yields of primary and imine are calculated as follows:

\[
\text{Yield (\%) of primary amine} = \frac{\text{the mol of primary amine product}}{\text{the initial mol of substrate}} \times 100\%
\]

\[
\text{Yield (\%) of imine} = \frac{\text{the mol of imine product}}{\text{the initial mol of substrate}} \times 2 \times 100\%
\]

3. Characterization

![Image of SAED pattern and EDX analysis](image)

**Figure S1.** \(d\)-spaces from SAED pattern of Co\(_2\)P NRs.

| Measured \(d\)-space | ICSD\#94379 |
|----------------------|-------------|
| \(d_1=0.218\) nm    | (112)=0.221 nm |
| \(d_2=0.204\) nm    | (103)=0.205 nm |
| \(d_3=0.173\) nm    | (113)=0.177 nm |
|                     | (020)=0.176 nm |
| \(d_4=0.162\) nm    | (302)=0.164 nm |
| \(d_5=0.117\) nm    | (030)=0.117 nm |
| \(d_6=0.104\) nm    | (206)=0.103 nm |
| \(d_7=0.086\) nm    | (040)=0.088 nm |

**Figure S2.** EDX analysis of (a) fresh and (b) used Co\(_2\)P NRs in the yellow squares.
Figure S3. Co 2p XPS spectrum of Co₂P NRs.

Figure S4. TEM image of Co₂P NRs after reaction.

Figure S5. XRD patterns of (a) fresh and (b) used Co₂P NRs.
Figure S6. XANES spectra of (a) fresh and (b) used Co$_2$P NRs.

Figure S7. FT-EXAFS spectra of (a) fresh and (b) used Co$_2$P NRs.

Figure S8. EXAFS fitting curves in $k$-space (upper panel) and $R$-space (lower panel) of (a) Co foil, (b) bulk Co$_2$P, (c) Co$_2$P NRs, and (d) used Co$_2$P NRs.
Table S1. Curve-fitting of Co K-edge EXAFS for Co foil, Co$_2$P bulk, Co$_2$P NRs, and used Co$_2$P NRs

| Sample          | Shell | CN$^a$  | r (Å)$^b$ | D.W.$^c$ | R factor (%) |
|-----------------|-------|---------|-----------|-----------|--------------|
| Co foil         | Co–Co | 10.6 ± 0.2 | 2.49 ± 0.01 | 0.007 ± 0.002 | 2.6          |
| Bulk Co$_2$P    | Co–P  | 2.0 ± 0.1  | 2.24 ± 0.03 | 0.005 ± 0.002 | 9.4          |
|                 | Co–Co | 4.0 ± 0.2  | 2.56 ± 0.02 | 0.010 ± 0.003 |              |
| Co$_2$P NRs     | Co–P  | 1.8 ± 0.2  | 2.22 ± 0.04 | 0.007 ± 0.004 | 7.4          |
|                 | Co–Co | 2.8 ± 0.2  | 2.60 ± 0.03 | 0.009 ± 0.004 |              |
| Used Co$_2$P NRs| Co–P  | 1.8 ± 0.2  | 2.14 ± 0.05 | 0.009 ± 0.006 | 11.3         |
|                 | Co–Co | 2.5 ± 0.3  | 2.60 ± 0.04 | 0.011 ± 0.006 |              |

$^a$Coordination number. $^b$Bond distance. $^c$Debye–Waller factor.

4. Comparison of activity between Co$_2$P NRs and reported non-noble-metal-based catalysts

Table S2. Comparison of activity between Co$_2$P NRs and reported non-noble-metal-based catalysts for reductive amination.

| Catalyst        | Metal   | Reaction Conditions                | NH$_3$ Source | Carbonyl Compound | TON  | Ref.                                |
|-----------------|---------|-----------------------------------|---------------|-------------------|------|-------------------------------------|
| Co$_2$P NRs     | Co      | 1–10 bar H$_2$, aq. NH$_3$ or ethanol, 100–120 °C (Scale-up condition: 40 bar H$_2$, 130 °C) | aq. NH$_3$ or NH$_2$OAc | aldehyde, ketone | 10 (1000) | This work                          |
| Co-DABCO-TPA@C-800 | Co   | 40 bar H$_2$, 5–7 bar NH$_3$, t-BuOH or THF, 120 °C | NH$_3$ gas | aldehyde, ketone | 29  | Jagadeesh, R. V. et al. Science 2017, 358, 326–332 |
| Co@NC-800       | Co      | 10 bar H$_2$, aq. NH$_3$, ethanol, 130 °C | aq. NH$_3$ | aldehyde          | 147 | Yuan, Z. et al. J. Catal. 2019, 370, 347–356 |
| Raney Co        | Co      | 10 bar H$_2$, 1 bar NH$_3$, CH$_3$OH, 120 °C | NH$_3$ gas | furfural          | 6   | Wei, J. et al. ChemCatChem 2019, 11, 5562–5569 |
The catalytic activity of Co$_2$P NR was tested under the same reaction conditions as that mentioned in supplementary Table 5 of reference S1, i.e., 80 °C, 8.6 mol% metal loading, 1 bar H$_2$, 48 h. The comparison of yields is shown in Scheme S1. The yield of benzylamine with Ni/Al$_2$O$_3$ (used in S1) was low (6%). In contrast, the yield of benzylamine with Co$_2$P NR was 79%, clearly demonstrating the superior activity of Co$_2$P NR.

![Scheme S1](image_url)
5. Typical reaction procedure

The synthesis of primary amine from aldehyde and aq. NH₃

The Co₂P NRs (4.0 mg) were placed in a 50-mL stainless-steel autoclave with a Teflon inner cylinder, followed by addition of benzaldehyde (1a) (0.5 mmol) and aq. NH₃ (3.0 mL). The reaction mixture was stirred vigorously at 100 °C under 5 bar of H₂. The reaction solution was then analyzed by GC–MS to determine the conversion and yield using an internal standard method.

The synthesis of primary amine from ketone and NH₄OAc

The Co₂P NRs (4.0 mg) were placed in a 50-mL stainless-steel autoclave with a Teflon inner cylinder, followed by adding acetophenone (5a), ethanol (3 mL) and NH₄OAc (0.20 g). The reaction mixture was stirred vigorously at 100 °C under 10 bar of H₂. The reaction solution was then analyzed by GC–MS to determine the conversion and yield using an internal standard method.

Table S3. Reductive amination of acetophenone under various reaction conditions using the Co₂P NRs catalyst.

| Entry | NH₃ Source | Solvent | Yield (%)<sup>b</sup> | 6a | 7a |
|-------|------------|---------|-----------------------|----|----|
| 1     | 3 mL aq. NH₃ | -       | 49                    | 47 |    |
| 2     | 2.5 bar NH₃ gas | ethanol | 0                     | 0  |    |
| 3     | 0.2 g NH₄OAc | ethanol | 83                    | 0  |    |
| 4     | 0.1 g NH₄OAc | ethanol | 81                    | 0  |    |
| 5     | 0.05 g NH₄OAc | ethanol | 74                    | 0  |    |

<sup>a</sup>Reaction conditions: Co₂P NRs (4.0 mg), acetophenone (0.5 mmol), solvent (3 mL), 10 bar H₂, 12 h. <sup>b</sup>Determined by GS-MS using an internal standard method.

6. Recycling experiment

After the reaction, Co₂P NRs were recovered by filtration. The catalyst was washed with water and dried at room temperature in vacuo without further purification or reactivation before reuse.
7. Control experiments

(1) Control experiments using N-benzylidenebenzylamine (3a) as starting material in the (1) presence or (2) absence of ammonia. Reaction conditions: Co₂P NRs (4.0 mg), N-benzylidenebenzylamine (0.5 mmol), 5 bar H₂, 100 °C, aq. NH₃, 0.5 h. (1): aq. NH₃ 25% (3 mL); (2): water (3 mL).

Figure S9. Control experiments using N-benzylidenebenzylamine (3a) as starting material in the (1) presence or (2) absence of ammonia. Reaction conditions: Co₂P NRs (4.0 mg), N-benzylidenebenzylamine (0.5 mmol), 5 bar H₂, 100 °C, 0.5 h. (1): aq. NH₃ 25% (3 mL); (2): water (3 mL).
8. Product identification

NMR data

2a (S1)

\[
\begin{align*}
\text{benzylamine hydrochloride} \\
^1H\text{ NMR (400 MHz, DMSO-}\text{d}_6\text{): } \delta = 8.49 (s, 3H), 7.50 (d, J = 6.8 \text{ Hz}, 2H), 7.43–7.35 (m, 3H), 4.00 (s, 2H) \text{ ppm}. \\
^13C\text{ NMR (100 MHz, DMSO-}\text{d}_6\text{): } \delta = 134.07, 128.88, 128.51, 128.35, 42.12 \text{ ppm}.
\end{align*}
\]

2b (S1)

\[
\begin{align*}
p-\text{tolylmethanaminium hydrochloride} \\
^1H\text{ NMR (400 MHz, DMSO-}\text{d}_6\text{): } \delta = 8.26 (s, 3H), 7.37 (d, J = 8.40 \text{ Hz}, 2H), 7.11 (d, J = 8.40 \text{ Hz}, 2H), 3.93 (s, 2H), 2.30 (s, 3H) \text{ ppm}. \\
^13C\text{ NMR (100 MHz, DMSO-}\text{d}_6\text{): } \delta = 137.59, 131.43, 129.01, 128.82, 41.99, 20.72 \text{ ppm}.
\end{align*}
\]

2c (S2)

\[
\begin{align*}
(4\text{-methoxyphenyl})\text{methanaminium hydrochloride} \\
^1H\text{ NMR (400 MHz, DMSO-}\text{d}_6\text{): } \delta = 8.18 (s, 3H), 7.39 (d, J = 8.40 \text{ Hz}, 2H), 6.97 (d, J = 8.40 \text{ Hz}, 2H), 3.97–3.93 (m, 2H), 3.76 (s, 3H) \text{ ppm}. \\
^13C\text{ NMR (100 MHz, DMSO-}\text{d}_6\text{): } \delta = 159.25, 130.52, 126.13, 113.82, 55.18, 41.62 \text{ ppm}.
\end{align*}
\]

2d (S2)

\[
\begin{align*}
2,3\text{-dimethoxybenzylamine hydrochloride} \\
^1H\text{ NMR (400 MHz, DMSO-}\text{d}_6\text{): } \delta = 8.61 (s, 3H), 7.14–7.10 (m, 3H), 3.99 (s, 2H), 3.84 (s, 3H), 3.82 (s, 3H) \text{ ppm}. \\
^13C\text{ NMR (100 MHz, DMSO-}\text{d}_6\text{): } \delta = 152.26, 146.70, 127.44, 124.07, 121.43, 113.44, 60.49, 55.91, 36.71 \text{ ppm}.
\end{align*}
\]

2e (S1)

\[
\begin{align*}
(4\text{-bromophenyl})\text{methanaminium hydrochloride} \\
^1H\text{ NMR (400 MHz, DMSO-}\text{d}_6\text{): } \delta = 8.71 (s, 3H), 7.60 (d, J = 8.00 \text{ Hz}, 2H), 7.48 (d, J = 8.00 \text{ Hz}, 2H), 3.98 (d, J = 5.20 \text{ Hz}, 2H) \text{ ppm}. \\
^13C\text{ NMR (100 MHz, DMSO-}\text{d}_6\text{): } \delta = 133.47, 131.29, 131.25, 121.58, 41.35 \text{ ppm}.
\end{align*}
\]

S12
2f (S3)

(4-chlorophenyl)methanaminium hydrochloride
$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 8.71$ (s, 3H), 7.57 (d, $J = 8.00$ Hz, 2H), 7.47 (d, $J = 8.00$ Hz, 2H), 4.01 (s, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 133.10$, 133.04, 130.99, 128.40, 41.34 ppm.

2g (S1)

(1,1'-biphenyl)-4-methanaminium hydrochloride
$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 8.26$ (s, 3H), 7.70 (m, 4H), 7.56 (m, 2H), 7.48 (m, 2H), 7.39 (m, 1H), 4.08 (s, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 140.20$, 139.45, 133.17, 129.50, 128.93, 127.63, 126.73, 126.63, 41.82 ppm.

2h (S1)

(4-acetamidophenyl)methanaminium hydrochloride
$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 10.29$ (s, 1H), 8.48 (s, 3H), 7.64 (d, $J = 8.40$ Hz, 2H), 7.42 (d, $J = 8.80$ Hz, 2H), 3.93 (s, 2H), 2.07 (s, 3H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 168.49$, 139.48, 130.27, 129.41, 118.80, 41.75, 23.93 ppm.

2i (S1)

(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanaminium hydrochloride
$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 8.62$ (s, 3H), 7.69 (d, $J = 7.60$ Hz, 2H), 7.52 (d, $J = 7.20$ Hz, 2H), 4.03 (s, 2H), 1.31 (s, 12H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 137.21$, 134.41, 128.20, 83.66, 41.96, 24.57 ppm.

2j (S6)

(5-methylthien-2-yl)methylamine hydrochloride
$^1$H NMR (400 MHz, methanol-$d_4$): $\delta = 8.64$ (s, 3H), 7.06 (d, $J = 3.20$ Hz, 1H), 6.73 (d, $J = 2.80$ Hz, 1H), 4.10 (s, 2H), 2.43 (s, 3H) ppm. $^{13}$C NMR (100 MHz, methanol-$d_4$): $\delta = 140.50$, 132.80, 129.06, 125.32, 36.75, 14.87 ppm.

S13
2k

(4-(methylsulfinyl)phenyl)methanamine hydrochloride

$^1$H NMR (400 MHz, methanol-$d_4$): $\delta = 7.85$ (d, $J = 8.00$ Hz, 2H), 7.77 (d, $J = 8.40$, 2H), 4.29 (s, 2H), 2.87 (s, 3H) ppm. $^{13}$C NMR (100 MHz, methanol-$d_4$): $\delta = 147.26, 137.93, 132.29, 125.65, 43.76, 43.61$ ppm.

2l (S7)

Benzo[b]thiophen-2-yl methanamine hydrochloride

$^1$H NMR (400 MHz, methanol-$d_4$): $\delta = 7.80$–7.78 (m, 1H), 7.75–7.72 (m, 1H), 7.42 (s, 1H), 7.33–7.26 (m, 2H), 4.35 (s, 2H) ppm. $^{13}$C NMR (100 MHz, methanol-$d_4$): $\delta = 141.73, 140.74, 136.33, 127.09, 126.38, 125.94, 125.08, 123.37, 39.44$ ppm.

2m (S8)

Furan-2-ylmethanamine hydrochloride

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 8.46$ (sbr, 3H), 7.73 (m 1H), 6.56–6.54 (m, 1H), 6.48–5.51 (m, 1H), 4.06 (m, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 147.78, 143.99, 111.04, 110.42, 35.01$ ppm.

2n

5-methyl-2-furanylmethanamine hydrochloride

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 8.62$ (s, 3H), 6.43 (d, $J = 3.60$ Hz, 1H), 6.10 (d, $J = 3.20$ Hz, 1H), 3.97 (s, 2H), 2.27 (s, 3H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 152.08, 145.89, 111.08, 106.86, 34.93, 13.21$ ppm.

2o

5-aminomethylfurfuryl alcohol hydrochloride

$^1$H NMR (400 MHz, methanol-$d_4$): $\delta = 6.12$ (d, $J = 3.20$ Hz, 1H), 6.06 (d, $J = 3.20$ Hz, 1H), 4.38 (s, 2H), 3.66 (s, 2H) ppm. $^{13}$C NMR (100 MHz, methanol-$d_4$): $\delta = 156.67, 155.21, 109.17, 107.43, 57.45, 39.38$ ppm.
2p (S9)

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

DL-2-amino-1-propanol hydrochloride

$^1$H NMR (400 MHz, methanol-\textit{d}_4): $\delta = 3.79$ (dd, $J = 16.0$, 7.2 Hz, 1H), 3.59 (dd, $J = 18.4$, 2.8 Hz, 1H), 3.45–3.36 (m, 1H), 1.25 (d, $J = 6.8$ Hz, 3H) ppm. $^{13}$C NMR (100 MHz, methanol-\textit{d}_4): $\delta = 64.79$, 51.02, 15.99 ppm.

2q (S1)

\[
\begin{align*}
\text{NH}_2\text{HCl} \\
\end{align*}
\]

pentan-1-aminium hydrochloride

$^1$H NMR (400 MHz, DMSO-\textit{d}_6): $\delta = 7.93$ (s, 3H), 2.73 (t, $J = 7.32$ Hz, 2H), 1.54 (m, 2H), 1.33–1.26 (m, 4H), 0.88 (t, $J = 6.84$ Hz, 3H) ppm. $^{13}$C NMR (100 MHz, DMSO-\textit{d}_6): $\delta = 38.76$, 27.86, 26.62, 21.63, 13.74 ppm.

2r (S10)

\[
\begin{align*}
\text{NH}_2\text{HCl} \\
\end{align*}
\]

cyclohexanemethanamine hydrochloride

$^1$H NMR (400 MHz, DMSO-\textit{d}_6): $\delta = 7.85$ (s, 3H), 2.62 (d, $J = 6.45$ Hz, 2H), 1.69–1.51 (m, 6H), 1.18–1.15 (m, 3H), 0.93–0.88 (m, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-\textit{d}_6): $\delta = 44.40$, 35.38, 29.65, 25.57, 25.00 ppm.

2s (S1)

\[
\begin{align*}
\text{NH}_2\text{HCl} \\
\end{align*}
\]

hexylamine hydrochloride

$^1$H NMR (400 MHz, DMSO-\textit{d}_6): $\delta = 7.75$(s, 3H), 2.78–2.71 (m, 2H), 1.57–1.47 (m, 8H), 0.90–0.84 (m, 3H) ppm. $^{13}$C NMR (100 MHz, DMSO-\textit{d}_6): $\delta = 38.62$, 30.99, 28.14, 26.85, 25.78, 21.91, 13.85 ppm.

2t (S1)

\[
\begin{align*}
\text{NH}_2\text{HCl} \\
\end{align*}
\]

1-decylamine hydrochloride

$^1$H NMR (400 MHz, DMSO-\textit{d}_6): $\delta = 7.75$ (s, 3H), 2.77–2.73 (m, 2H), 1.56–1.49 (m, 2H), 1.30–1.22 (m, 14H), 0.88–0.84 (m, 3H) ppm. $^{13}$C NMR (100 MHz, DMSO-\textit{d}_6): $\delta = 38.78$, 31.23, 28.82, 28.77, 28.63, 28.46, 26.91, 25.74, 22.03, 13.91 ppm.
6a (S2)

\[
\text{H} \quad \begin{array}{c}
\text{H} \\
\text{NH}_{2}\text{HCl}
\end{array}
\]

1-phenylethanaminium hydrochloride

\(^1\text{H} \text{NMR} (400 \text{ MHz, DMSO-}d_6): \delta = 8.65 \text{ (s, 3H), 7.54–7.51 (m, 2H), 7.44–7.34 (m, 3H), 4.37–4.32 (m, 1H), 1.51 (d, } J = 6.40 \text{ Hz, 3H)} \text{ ppm. } ^{13}\text{C} \text{NMR (100 MHz, DMSO-}d_6): \delta = 139.44, 128.57, 128.23, 126.79, 49.96, 20.77 \text{ ppm.}

6b (S2)

\[
\text{MeO} \quad \begin{array}{c}
\text{H} \\
\text{NH}_{2}\text{HCl}
\end{array}
\]

1-(4-methoxyphenyl)ethanaminium hydrochloride

\(^1\text{H} \text{NMR} (400 \text{ MHz, DMSO-}d_6): \delta = 8.56 \text{ (s, 3H), 7.48 (d, } J = 8.40 \text{ Hz, 2H), 6.96 (d, } J = 8.40 \text{ Hz, 2H), 4.35–4.30 (m, 1H), 3.76 (s, 3H), 1.52 (d, } J = 6.80 \text{ Hz, 3H)} \text{ ppm. } ^{13}\text{C} \text{NMR (100 MHz, DMSO-}d_6): \delta = 159.14, 131.19, 128.37, 114.01, 55.42, 49.64, 20.70 \text{ ppm.}

6c (S2)

\[
\text{Cl} \quad \begin{array}{c}
\text{H} \\
\text{NH}_{2}\text{HCl}
\end{array}
\]

1-(4-chlorophenyl)ethanaminium hydrochloride

\(^1\text{H} \text{NMR} (400 \text{ MHz, DMSO-}d_6): \delta = 7.63 \text{ (d, } J = 8.40 \text{ Hz, 2H), 7.48 (d, } J = 8.40 \text{ Hz, 2H), 4.43–4.39 (m, 1H), 1.54 (d, } J = 6.80 \text{ Hz, 3H)} \text{ ppm. } ^{13}\text{C} \text{NMR (100 MHz, DMSO-}d_6): \delta = 138.50, 132.76, 129.05, 128.53, 49.37, 20.86 \text{ ppm.}

6d(S4)

\[
\text{Br} \quad \begin{array}{c}
\text{H} \\
\text{NH}_{2}\text{HCl}
\end{array}
\]

1-(4-bromophenyl)ethanamine hydrochloride

\(^1\text{H} \text{NMR} (400 \text{ MHz, DMSO-}d_6): \delta = 8.71 \text{ (s, 3H), 7.62 (d, } J = 8.00 \text{ Hz, 2H), 7.51 (d, } J = 8.00 \text{ Hz, 2H), 4.39–4.38 (m, 1H), 1.50 (d, } J = 6.40 \text{ Hz, 3H)} \text{ ppm. } ^{13}\text{C} \text{NMR (100 MHz, DMSO-}d_6): \delta = 138.76, 131.45, 129.17, 121.46, 49.32, 20.49 \text{ ppm.}

6e(S1)

\[
\text{O} \quad \begin{array}{c}
\text{H} \\
\text{NH}_{2}\text{HCl}
\end{array}
\]

1-(4-acetamidophenyl)ethanaminium hydrochloride

\(^1\text{H} \text{NMR} (400 \text{ MHz, DMSO-}d_6): \delta = 10.20 \text{ (s, 1H), 8.52 (s, 3H), 7.61 (d, } J = 8.80 \text{ Hz, 2H), 7.42 (d, } J = 8.00 \text{ Hz, 2H), 4.31–4.26 (m, 1H), 2.06 (s, 3H), 1.49 (d, } J = 6.80 \text{ Hz, 3H)} \text{ ppm. } ^{13}\text{C} \text{NMR (100 MHz, DMSO-}d_6): \delta = 168.46, 139.40, 133.60, 127.23, 118.96, 49.58, 23.92, 20.53 \text{ ppm.}
6f(S2)

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

1-((4-(methylsulfonyl)phenyl)ethanuminium hydrochloride

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 8.96$ (s, 3H), 8.00 (d, $J = 8.40$ Hz, 2H), 7.90 (d, $J = 8.40$ Hz, 2H), 4.60–4.57 (m, 1H), 3.28 (s, 3H), 1.60 (d, $J = 6.80$ Hz, 3H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 145.15$, 140.65, 128.21, 127.42, 49.82, 43.66, 20.85 ppm.

6g(S2)

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

1-(pyridin-4-yl)ethanuminium hydrochloride

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 9.30$ (s, 3 H), 8.97 (s, 2H), 8.24–8.22 (m, 2H), 4.70 (s, 1H), 1.57 (d, $J = 6.80$ Hz, 3H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 157.17$, 142.82, 125.01, 49.06, 20.11 ppm.

6h(S1)

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

diphenylmethanaminium hydrochloride

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 8.99$ (s, 3H), 7.50–7.33 (m, 10H), 5.62 (s, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 138.19$, 128.87, 128.42, 127.26, 57.06 ppm.

6i(S1)

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

2,3-dihydro-1H-inden-1-aminium hydrochloride

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 8.71$ (s, 3H), 7.71–7.67 (m, 1H), 7.33–7.22 (m, 3H), 4.70–4.61 (m, 1H), 3.12–3.01 (m, 1H), 2.91–2.80 (m, 1H), 2.49–2.39 (m, 1H), 2.08–1.95 (m, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 143.98$, 139.48, 128.93, 126.60, 125.21, 124.87, 54.63, 30.33, 29.90 ppm.

6j(S1)

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

adamantan-2-aminium hydrochloride

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 8.25$ (s, 3H), 3.29–3.27 (m, 1H), 2.09–1.48 (m, 14H) ppm.
$^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 54.66, 36.80, 36.13, 29.96, 29.46, 26.39, 26.29$ ppm.

6k(S1)

\[ \text{heptan-2-amine hydrochloride} \]

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 8.00$ (s, 3H), 3.15–3.05 (m, 1H), 1.65–1.35 (m, 2H), 1.35–1.20 (m, 6H), 1.17 (d, $J = 7.23$ Hz, 3H), 0.90–0.84 (m, 3H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 46.71, 33.99, 30.89, 24.35, 21.82, 18.05, 13.77$ ppm.

6l(S1)

\[ \text{2-dodecylamine hydrochloride} \]

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 7.96$ (s, 3H), 3.12–3.09 (m, 1H), 1.57–1.17 (m, 18H), 1.07 (d, $J = 6.44$ Hz, 3H), 0.88–0.83 (m, 3H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 47.06, 34.42, 31.58, 29.32, 29.27, 29.18, 29.10, 29.04, 25.08, 22.39, 18.44, 14.29$ ppm.

6m(S1)

\[ \text{cyclohexylamine hydrochloride} \]

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 8.21$ (s, 3H), 2.98–2.87 (m, 1H), 1.95–1.92 (m, 2H), 1.73–1.70 (m, 2H), 1.59–1.56 (m, 1H), 1.37–1.20 (m, 4H), 1.13–1.07 (m, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 49.77, 30.52, 24.84, 24.07$ ppm.

6n

\[ \text{4-(4-(4-chlorophenyl)-4-hydroxypiperidin-1-yl)-1-(4-fluorophenyl)butan-1-amine hydrochloride} \]

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 10.65$ (s, 1H), 8.66 (s, 3H), 7.63–7.54 (m, 2H), 7.44 (d, $J = 8.40$ Hz, 2H), 7.38 (d, $J = 8.42$ Hz, 2H), 7.28–7.19 (m, 2H), 5.56 (s, 1H), 4.29–4.25 (m, 1H), 3.18–3.01 (m, 6H), 2.41–2.28 (m, 2H), 2.06–1.47 (m, 6H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 161.04, 147.03, 133.87$ (d, $J = 3.02$ Hz), 131.64, 129.95 (d, $J = 5.04$ Hz), 128.18, 126.77, 115.85, 115.65, 68.05, 54.89, 53.14, 48.20, 34.87, 31.48, 19.85 ppm.

6o
(5S,8R,9R,10S,13S,14S,17S)-17-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-amine hydrochloride

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 8.08$ (s, 3H), 4.23–4.00 (s, 1H), 3.47–3.39 (m, 1H), 3.34 (s, 1H), 1.87–0.71 (m, 22H), 0.75 (s, 3H), 0.62 (s, 3H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 79.93$, 53.15, 50.66, 46.13, 42.46, 37.89, 36.56, 35.44, 34.93, 31.05, 30.71, 30.44, 29.75, 27.66, 23.74, 22.94, 19.83, 11.23, 10.99 ppm.
NMR spectra
Cl
\[\text{NH}_2\cdot\text{HCl}\]
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