SUPPLEMENTARY INFORMATION

A cobalt phosphide catalyst for the hydrogenation of nitriles

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References
1. Recycling experiments

After the reaction, the crude reaction mixture was centrifuged to obtain the reaction solution and the yield was determined by GC analysis. Nano-Co$_2$P/HT was redispersed in 2-propanol (3 mL) and placed in a 50-mL stainless-steel autoclave again with addition of nitrile (0.5 mmol), and NH$_3$ aq. (25%, 1.2 mL) for reuse experiments. The TEM images of the used nano-Co$_2$P/HT catalyst (Fig. S1) showed that the average diameter and size distribution of the nano-Co$_2$P were similar to those of nano-Co$_2$P/HT before use and no aggregation of nano-Co$_2$P occurred, proving high durability of nano-Co$_2$P/HT against aggregation.

2. Characterization

Table S1 The elemental analysis of fresh and used nano-Co$_2$P/HT.

|                  | wt%     |
|------------------|---------|
|                  | Mg      | Al | Co  |
| nano-Co$_2$P/HT_fresh | 19.2    | 7.17 | 1.23 |
| nano-Co$_2$P/HT_after_reaction | 22.3    | 8.04 | 1.16 |

Fig. S1 TEM images of nano-Co$_2$P/HT fresh (left) and after reaction (right).
Fig. S2 TEM images of (a) nano-CoP, (b) nano-Ni$_2$P, (c) nano-Fe$_2$P and (d) nano-Cu$_3$P with SAED pattern (inset) (S1-4).

Fig. S3 XRD patterns of (a) nano-CoP, (b) nano-CoP, (c) nano-Ni$_2$P, (d) nano-Fe$_2$P and (e) nano-Cu$_3$P with PDF reference patterns (S5-8).
Fig. S4 Reuse experiments of nano-Co$_2$P/HT for valeronitrile hydrogenation at 50% conversion. Reaction conditions: nano-Co$_2$P/HT (0.1 g), valeronitrile (0.5 mmol), 2-propanol (3 mL), NH$_3$ aq. (0.8 mL), 130 °C, 40 bar H$_2$, 20 min.

Fig. S5 XPS result of P 2p region of nano-Co$_2$P (S9-10).
3. Comparison of activity between nano-Co$_2$P and reported nonprecious metal catalysts

Table S2 Comparison of activity between nano-Co$_2$P and reported nonprecious metal catalysts for nitrile hydrogenation.

| Entry | Catalyst | Active metal | Reaction condition | TON | reference |
|-------|----------|--------------|--------------------|-----|-----------|
| 1     | nano-Co$_2$P/HT | Co | 0.017 mol% catalyst, NH$_3$ aq., 50 bar, 150 °C, 40 h. | 58800 (5000 based on total cobalt atoms) | This work |
| 2     | {Fe(H)(HBH$_3$)(CO)[$(CH_3)N$[(CH$_2$CH$_2$)P(CH(CH$_3$)$_2$)$_2$]$]_2$} | Fe | 0.5−1 mol% catalyst, 30 bar H$_2$, 70−130 °C, 3−6 h. | 174 | Nat. Commun. 54111 (2014) |
| 3     | Fe(PNP)Br$_2$ Complex | Fe | 1−5 mol% catalyst, 1−5 mol% NaHBEt$_3$, 3−15 mol% KHMDS, 60 bar H$_2$, 140°C, 19−48 h. | 100 | Chem. Commun. 52, 1812−1815 (2016) |
| 4     | Fe(PNP$_2^+$) | Fe | 0.5−1 mol% catalyst, 30 bar H$_2$, 40−70 °C, 2−3 h. | 190 | Catal. Sci. Technol. 6, 4768−4772 (2016) |
| 5     | Co PNNH Pincer Complex | Co | 2 mol % catalyst, 2 mol% NaEt$_2$BH, 4.4 mol% KOtBu, 30 bar H$_2$, 135°C, 36−60 h. | 100 | J. Am. Chem. Soc. 137, 8888−8891 (2015) |
| 6     | ($^{13}$MesCCC)-CoCl$_2$py Catalyst Precursor | Co | 4 mol% catalyst, 8 mol % NaHBEt$_3$, 12 mol % KOtBu, 4 bar, 115°C, 8 h. | 25 | J. Am. Chem. Soc. 139, 13554−13561 (2017) |
| 7     | Co(acac)$_3$ + Tetradtentate phosphine | Co | 4 mol% Co(acac)$_3$, 4.4 mol% tetradtentate phosphine, 10 mol% KOtBu, 30 bar H$_2$, 80−120°C, 18 h. | 25 | ChemSusChem 10, 842−846 (2017) |
| 8     | CoBr$_2$ with | Co | 2 mol% CoBr$_2$, 6 mol% | 48 | ACS Catal. 8, |
| catalyst | NaHBEt$_3$ + HN-(CH$_2$CH$_3$PPr$_2$)$_2$(d$_{P}$PNi$_3$P) | NaHBEt$_3$, 20 or 40 bar H$_2$, 110 or 130 °C, 4–24 h. | 9125–9130 (2018) |
|---|---|---|---|
| 9 | Zr$_{12}$-TPDC-Co | Co | 0.5 mol% catalyst, 40 bar H$_2$, 110 °C, 42 h. | 200 J. Am. Chem. Soc. 139, 7004–7011 (2017) |
| 10 | Co(OAc)$_3$/Phen@α-Al$_2$O$_3$ | Co | 4–6 mol% catalyst, 5–40 bar H$_2$, 85–130 °C, 2–24 h. | 25 J. Am. Chem. Soc. 138, 8781–8788 (2016) |
| 11 | Cobalt-terephthalic acid MOF@C-800 | Co | 3.8 mol% catalyst, 25 bar H$_2$, 5 bar NH$_3$, 120 °C, 16 h. | 25 Chem. Sci. 9, 8553–8560 (2018) |
| 12 | Co$_2$O$_3$/NGr@CeO$_2$ | Co | 1.6–5 mol% catalyst, aqueous NH$_3$, 30–50 bar H$_2$, 120 °C, 8–15 h. | 62 Catal. Sci. Technol. 8, 499–507 (2018) |
| 13 | Manganese Pincer Complexes | Mn | 3 mol% catalyst, t-BuONa, 50 bar H$_2$, 120 °C, 24 h. | 33 J. Am. Chem. Soc. 138, 8809–8814 (2016) |
| 14 | Fac-[(CO)$_3$Mn(dippe)(OTf)] | Mn | 3 mol% catalyst, 10 mol% KOBu, 7-35 bar H$_2$, 90 °C, 15–30 min. | 31 ACS Catal. 9, 392–401 (2019) |
| 15 | Bisphosphine Mn(I) Complex | Mn | 2 mol % catalyst, 20 mol % t-BuOK, 100 °C, 50 bar H$_2$, 18 h. | 48 Org. Lett. 20, 7212–7215 (2018) |
| 16 | MC/Ni Catalyst | Ni | 13 mol % MC/Ni catalyst, NH$_3$ aq. (36 wt. %), 2.5 bar H$_2$, 80°C, 6–18 h. | 8 ChemSusChem 12, 1–11 (2019) |
| 17 | Ni nanoparticles embedded in imidazolium based ionic liquids | Ni | 0.7 mol% based on the Ni precursor, 20–30 bar H$_2$, 90°C, 22 h. | 1021 (143 based on total nickel atoms) New J. Chem. 41, 9594–9597 (2017) |
| 18 | Ni/Al$_2$O$_3$-600 | Ni | 20 mg catalyst, 2.5 bar H$_2$, NH$_3$.H$_2$O (36.5 wt%), 60 °C, 6 h. | 8 New J. Chem. 44, 549-555 (2020) |
| 19 | Ni-phen@SiO$_2$ | Ni | 45 mg catalyst (4.5 mol % Ni), 50 bar H$_2$, 100°C, 7 M NH$_3$/MeOH, 20 h. | 22 Sci. Adv. 4, eaat0761, (2018) |
| 20 | Cu/SiO$_2$ with H$_2$ pretreatment | Cu | 6 mol % catalyst, 13–40 bar H$_2$, 110–130°C, 9–20 h. | 12 Applied Catalysis A: General 494, 41–47 (2015) |

4. DFT calculation

Density functional theory (DFT) calculations were performed using the CONQUEST
program (S11). The Perdew, Burke and Ernzerhof (PBE) exchange-correlation functional (S12) was used with a norm-conserving pseudopotential and real-space pseudo atomic orbitals (PAOs) (S13). We used the double-zeta plus polarization (DZP) type PAOs. The ranges of two $s$, two $d$ and a $p$ PAOs for Co were {$(7.8, 6.1), (4.5, 2.1)$ and $(7.8)$} bohr and those of two $s$, two $p$ and a $d$ PAOs for P were {$(5.2, 4.0), (6.5, 4.6)$ and $(6.5)$} bohr.

**Bulk Co, Co$_2$P and Co$_2$P surface**

8×8×8 Monkhorst–Pack grid (S14) was used for the bulk Co and Co$_2$P in the present calculations. The unit cells of the bulk Co and Co$_2$P were rectangular in the present calculations. The $c/a$ ratios of the unit cells were fixed to the experimental ratios, 1.623 (S15) and 0.602 (S16) for bulk Co and Co$_2$P, and the $b/a$ ratio was $\sqrt{3}$ . As shown in Fig. 6c, the unit cell of Co$_2$P consists of two layers, six Co atoms in the pyramidal site (P-site) and two P atoms in the first layer and six Co atoms in the tetrahedral site (T-site) and four P atoms in the second layer. For the calculation of the Co$_2$P (0001) surface, we used a supercell slab consisting of eight layers (about 12 Å thickness) with a vacuum gap (about 15 Å). 8×8×1 grid was used for the surface system. All atoms were relaxed in the geometry optimizations of bulk Co (hcp), bulk Co$_2$P (hexagonal) and the Co$_2$P surface systems. The lattice constants of bulk Co$_2$P calculated with the PAOs were very close to those with the plane-wave functions (S17), as shown in Table S3.

| Table S3 Lattice constants of hexagonal Co$_2$P (Å). |
|---------------------------------|-----------------|-----------------|
| Nonmagnetic | Ferromagnetic |
| a | c | a | c |
| PAOs | 5.754 | 3.452 | 5.767 | 3.460 |
| Plane waves$^a$ | 5.723 | 3.406 |
| Exptl.$^b$ | 5.742 | 3.457 |

$^a$Reference S16, $^b$Reference S17

Projected density of states (PDOS) of bulk Co, Co$_2$P and the Co$_2$P surface system are shown in Fig. S7, which were calculated based on the PAOs, i.e., the projection weights were determined using the PAO-based band coefficients. Since it was found experimentally that the nano-Co$_2$P doesn’t have magnetism, the magnetism was not considered in the present calculations. In Fig. S7, the increase of $d$-electrons around Fermi level is found both for P-site and T-site Co atoms in the Co$_2$P surfaces. The comparison of the Co-$d$ PDOS is given in Fig. 6 for T-site Co.
The dissociation of a H$_2$ molecule on Co$_2$P surfaces was simulated. We first put a H$_2$ molecules on the Co$_2$P surface with the distance of 1.2 Å and then relaxed the geometry. Only the geometries of the H$_2$ molecule and the first and second layers of Co$_2$P were relaxed, while the Co$_2$P consisted of 8 layers. Several H$_2$ positions were investigated as shown in Fig. S8. The increases of the Co d-electrons around Fermi level are found both for P- and T-sites Co atoms. The comparison of the Co-d PDOS is given in Fig. 6 for T-site Co. The distances of the two H atoms ($r_{HH}$) and the adsorption energies are presented in Fig. S8. The stabilization energy $\Delta E$ was calculated as

$$\Delta E = E(\text{Co}_2\text{P-H}_2) - E(\text{Co}_2\text{P}) - E(\text{H}_2).$$

The dispersion energies were considered by using the DFT-D2 method (S18). The basis set superposition errors (BSSEs) were corrected by the counterpoise method (S19). The H$_2$ molecules are dissociated largely when adsorbing to the bridge and hollow sites in Fig. S8. When a H$_2$ molecule adsorbs to the on-top site, the two H atoms are bonded to the nearest Co atom, while the distance between two H atoms is longer than an isolated H$_2$ molecule (0.79 Å). In the optimized geometry of “bridge 2” of T-site layer, the H atoms are located at the different hollow sites.

**Fig. S7** PDOS of Co atoms in bulk Co, bulk Co$_2$P and Co$_2$P surface (green: s orbital, blue: p orbital, red: d orbital, black: total). Fermi level is set to be zero.

**H$_2$ on Co$_2$P surface**

The dissociation of a H$_2$ molecule on Co$_2$P surfaces was simulated. We first put a H$_2$ molecules on the Co$_2$P surface with the distance of 1.2 Å and then relaxed the geometry. Only the geometries of the H$_2$ molecule and the first and second layers of Co$_2$P were relaxed, while the Co$_2$P consisted of 8 layers. Several H$_2$ positions were investigated as shown in Fig. S8. The increases of the Co d-electrons around Fermi level are found both for P- and T-sites Co atoms. The comparison of the Co-d PDOS is given in Fig. 6 for T-site Co. The distances of the two H atoms ($r_{HH}$) and the adsorption energies are presented in Fig. S8. The stabilization energy $\Delta E$ was calculated as

$$\Delta E = E(\text{Co}_2\text{P-H}_2) - E(\text{Co}_2\text{P}) - E(\text{H}_2).$$

The dispersion energies were considered by using the DFT-D2 method (S18). The basis set superposition errors (BSSEs) were corrected by the counterpoise method (S19). The H$_2$ molecules are dissociated largely when adsorbing to the bridge and hollow sites in Fig. S8. When a H$_2$ molecule adsorbs to the on-top site, the two H atoms are bonded to the nearest Co atom, while the distance between two H atoms is longer than an isolated H$_2$ molecule (0.79 Å). In the optimized geometry of “bridge 2” of T-site layer, the H atoms are located at the different hollow sites.
**Fig. S8.** Initial and optimized structures of the H₂ molecules on Co₂P (0001) surface. Co, P, and H atoms are coloured in blue, pink and red. H–H distances in the initial structures are 0.79 Å. H–H distances and the adsorption energies in the optimized structures are written in the figure.
5. Product identification

Table 1, 1b

\textit{n-Pentylamine hydrochloride (S20)}

\begin{center}
\includegraphics[width=\textwidth]{n-pentylamine_hydrochloride.png}
\end{center}

CAS registry No. [142-65-4]. $^1$H NMR (DMSO, 400 MHz): $\delta = 7.95$ (s, 3H), 2.73 (t, $J = 7.3$, 2H), 1.56 (m, 2H), 1.33-1.26 (m, 4H), 0.88 (t, $J = 6.8$, 3H). $^{13}$C NMR (DMSO, 100 MHz): 38.7, 27.9, 26.5, 21.5, 13.6.
Table 1, 2b

1-Cyclohexylmethanamine hydrochloride (S20)

\[
\text{NH}_2\cdot\text{HCl}
\]

CAS registry No. [50877-01-5]. \(^1\)H NMR (DMSO, 400 MHz): \(\delta = 7.84\) (s, 3H), 2.62 (d, \(J = 6.4\), 2H), 1.69 (m, 4H), 1.53 (m, 2H), 1.16 (m, 3H), 0.91 (m, 2H). \(^1\)C NMR (DMSO, 100 MHz): 44.3, 35.3, 29.6, 25.5, 25.0.
Table 1, 3b

Decylamine hydrochloride (S22)

\[
\text{C}_{9}\text{H}_{19}\overset{\text{NH}_2}\text{HCl}
\]

CAS registry No. [143-09-9]. \(^1\)H NMR (DMSO, 400 MHz): \(\delta = 7.75\) (s, 3H), 2.75 (t, \(J = 8.5\), 2H), 1.51 (m, 2H), 1.25 (m, 14H), 0.86 (t, \(J = 7.6\), 3H). \(^{13}\)C NMR (100 MHz, DMSO): 38.7, 31.2, 28.8, 28.7, 28.6, 28.4, 26.9, 25.7, 22.0, 13.9.
Table 1, 4b

1-Adamantylmethylamine hydrochloride (S2I)

\[ \text{NH}_2\cdot\text{HCl} \]

CAS registry No. [1501-98-0]. \(^1\)H NMR (DMSO, 400 MHz): \( \delta = 7.76 \) (s, 3H), 2.48 (s, 2H), 1.96 (s, 3H), 1.68 (d, \( J = 11.9 \), 3H), 1.59 (d, \( J = 11.4 \), 3H), 1.50 (s, 6H). \(^1\)C NMR (DMSO, 100 MHz): 49.9, 38.7, 36.0, 30.5, 27.4.
Table 1, 5b

**Benzylamine hydrochloride (S21)**

\[
\text{\ce{\text{NH}_2\cdot\text{HCl}}}
\]

CAS registry No. [3287-99-8]. \(^1\)H NMR (DMSO, 400 MHz): \(\delta = 8.05\) (s, 3H), 7.30 (m, 5H), 3.01 (s, 2H). \(^{13}\)C NMR (DMSO, 100 MHz): 134.0, 128.9, 128.5, 128.3, 42.1.
Table 1. 6b

2-Phenylethylamine hydrochloride (S21)

\[
\text{\begin{center}
\begin{tabular}{c}
\textbf{NH}_2\cdot\text{HCl} \\
\end{tabular}
\end{center}}
\]

CAS registry No. [156-28-5]. $^1$H NMR (DMSO, 400 MHz): $\delta = 8.07$ (s, 3H), 7.36-7.23 (m, 5H), 3.10-2.82 (m, 4H). $^{13}$C NMR (DMSO, 100 MHz): 137.4, 128.53, 128.52, 126.6, 39.8, 32.9.
Table 1, 7b
3-Picolylamine hydrochloride (S23)

NH₂·HCl

CAS registry No. [84359-15-9]. ¹H NMR (DMSO, 400 MHz): δ = 8.78 (s, 1H), 8.72-8.43 (m, 4 H), 8.10 (d, J = 5.7, 1H), 7.60 (t, J = 8.0, 1H), 4.21 (s, 2H). ¹³C NMR (DMSO, 100 MHz): 66.3, 38.6, 28.6, 28.4, 26.8, 25.7.
Table 1. 8b

4-Picolyamine hydrochloride (S24)

\[
\text{NH}_2\cdot\text{HCl}
\]

CAS registry No. [64460-41-9]. $^1$H NMR (DMSO, 400 MHz): $\delta = 8.61$ (s, 2H), 7.52 (d, 2H, $J = 4.4$), 4.19 (s, 2H). $^{13}$C NMR (DMSO, 100 MHz): 149.6, 143.8, 123.2, 41.2.
Table 1, 9b

Furan-2-ylmethanamine hydrochloride (S25)

\[
\text{NH}_2\cdot\text{HCl}
\]

CAS registry No. [4753-68-8]. $^1$H NMR (DMSO, 400 MHz): $\delta = 8.50$ (sbr, 3H), 7.73 (m 1H), 6.54–6.56 (m, 1H), 6.48–5.51 (m, 1H), 4.06 (m, 2H). $^{13}$C NMR (DMSO, 100 MHz): 147.6, 143.8, 110.9, 110.2, 34.8.
Table 1, 10b

(1H-indol-5-yl) methanamine monohydrochloride (S26)

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

CAS registry No. [865878-77-9]. \(^1\)H NMR (DMSO, 400 MHz) : \(\delta = 10.88\) (s, 1H), 8.82 (s, 3H), 7.95 (s, 1H), 7.37 (t, \(J = 2.8\), 1H), 7.31 (dd, \(J = 8.4, 1.7\), 1H), 7.32–7.16 (m, 2H), 4.08 (s, 2H). \(^{13}\)C NMR (DMSO, 100 MHz): 135.6, 127.4, 126.1, 121.9, 120.8, 111.3, 100.8.
Table 1, 11b

4-Methoxybenzylamine hydrochloride (S21)

\[
\text{MeO} \quad \text{NH}_2 \cdot \text{HCl}
\]

CAS registry No. [17061-61-9]. \(^1\)H NMR (DMSO, 400 MHz): \(\delta = 8.18 \ (s, 3\text{H}), 7.47-7.30 \ (m, 2\text{H}), 7.04-6.89 \ (m, 2\text{H}), 3.93 \ (s, 2\text{H}), 3.75 \ (s, 3\text{H})\). \(^{13}\)C NMR (DMSO, 100 MHz): 157.8, 129.4, 128.7, 113.5, 55.0, 44.0.
Table 1, 12b

4-Bromobenzylamine hydrochloride (S2I)

\[
\begin{align*}
\text{Br} & \quad \text{NH}_2\cdot\text{HCl} \\
\text{C} & \quad \text{C} & \quad \text{C}
\end{align*}
\]

CAS registry No. [26177-44-6]. $^1$H NMR (DMSO, 400 MHz): $\delta = 8.49$ (s, 3H), 7.61 (d, $J = 7.9$, 2H), 7.48 (d, $J = 7.8$, 2H), 3.98 (s, 2H). $^{13}$C NMR (DMSO, 100 MHz): 133.4, 131.3, 131.2, 121.6, 41.3.
Table 1, 13b

4-Trifluoromethylbenzylamine hydrochloride (S21)

\[
\begin{align*}
\text{CF}_3 & \quad \text{NH}_2 \cdot \text{HCl} \\
\end{align*}
\]

CAS registry No. [3047-99-2]. \(^1\)H NMR (DMSO, 400 MHz): \(\delta = 8.71 \text{ (s, 3H)}, 7.85-7.60 \text{ (m, 4H)}, 4.12 \text{ (s, 2H)}\). \(^{13}\)C NMR (DMSO, 100 MHz): 138.8, 129.7, 128.6, 125.2, 122.7, 41.5.
Table 1, 14b

1-[4-(Aminomethyl)phenyl]ethan-1-one hydrochloride(S20)

![Chemical Structure](image)

CAS registry No. [66522-66-5]. $^1$H NMR (DMSO, 400 MHz): $\delta = 8.51$ (s, 3H), 7.97 (d, $J = 8.5$, 2H), 7.66 (d, $J = 8$, 2H), 4.09 (s, 2H), 2.58 (s, 3H). $^{13}$C NMR (DMSO, 100 MHz): 197.6, 139.1, 136.5, 129.0, 128.2, 41.6, 26.8.
Table 1, 15b

4-(Aminomethyl)benzoic acid methyl ester hydrochloride (S20)

![Structure of 4-(Aminomethyl)benzoic acid methyl ester hydrochloride (S20)]

CAS registry No. [6232-11-7]. $^1$H NMR (DMSO, 400 MHz): $\delta = 8.46$ (s, 3H), 8.00 (d, $J = 8.4$, 2H), 7.63 (d, $J = 8.0$, 2H), 4.11 (s, 2H), 3.86 (s, 3H). $^{13}$C NMR (DMSO, 100 MHz): 165.8, 129.3, 129.1, 129.0, 128.2, 52.2, 41.7.
Scheme 2, 16b

1,6-Diaminohexane dihydrochloride (S2I)

\[
\text{Cl} - \text{H}_2\text{N} - \text{NH}_2 \cdot \text{HCl}
\]

CAS registry No. [6055-52-3]. \(^1\)H NMR (DMSO, 400 MHz): \(\delta = 7.82\) (s, 6H), 2.83-2.58 (m, 4H), 1.67-1.46 (m, 4H), 1.37-1.22 (m, 4H). \(^13\)C NMR (DMSO, 100 MHz): 38.4, 26.6, 25.2.
Scheme 2, 17b

1,10-diaminododecane dihydrochloride (S20)

CAS registry No. [7408-92-6]. $^1$H NMR (DMSO, 400 MHz): $\delta = 8.08$ (s, 6H), 2.71 (m, 4H), 1.55 (m, 4H), 1.26 (m, 12H). $^{13}$C NMR (DMSO, 100 MHz): 38.6, 28.6, 28.4, 26.8, 25.7.
Scheme 2, 18b

1,4-Bis(aminomethyl)benzene dihydrochloride (S28)

\[
\text{Cl-H-H_2N} \quad \begin{array}{c}
\text{NH}_2\text{HCl}
\end{array}
\]

CAS registry No. [3057-45-2]. \(^1\)H NMR (DMSO, 400 MHz): \(\delta = 8.48 \text{ (s, 6H)}, 7.50 \text{ (s, 4H)}, 4.01 \text{ (s, 4H)}. \(^13\)C NMR (DMSO, 100 MHz): 134.2, 128.6, 41.8.
Scheme 2, 19b

m-Xylylenediamine dihydrochloride (S28)

\[
\begin{align*}
\text{Cl} & \equiv \text{H} \cdot \text{H}_2\text{N} \\
& \begin{array}{c}
\text{NH}_2 \cdot \text{HCl}
\end{array}
\end{align*}
\]

CAS registry No. [51964-30-8]. $^1$H NMR (DMSO, 400 MHz): $\delta = 8.66$ (s, 6H), 7.61 (d, $J = 1.9$ Hz, 1H), 7.55 (dd, $J = 7.4$, 1.8 Hz, 2H), 7.45 (dd, $J = 8.4$, 6.9 Hz, 1H), 3.99 (s, 4H). $^{13}$C NMR (DMSO, 100 MHz): 134.3, 129.6, 128.8, 128.6, 41.9.
Scheme 2, 20b

**N,N,N',N'-Tetrakis(3-aminopropyl)-1,4-butanediamine (S27)**

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

CAS registry No. [120239-63-6]. 1H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta = 2.83\) (t, 8H), 2.62 (t, 8H), 2.41 (m, 4H), 1.78(t, 8H), 1.60(m, 4H), 1.48(m, 8H). \(^{13}\)C NMR (CDCl\textsubscript{3}, 100 MHz): 53.6, 51.4, 40.3, 31.4, 24.5.
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