Base-Free Photoredox/Nickel Dual Catalytic Cross-Coupling of Ammonium Alkylsilicates

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General considerations

All reactions were carried out under an inert atmosphere of nitrogen or argon unless otherwise noted. DMF (99.9%, extra dry) was used as received. Triethylamine and disopropylamine were distilled prior to use and stored over activated molecular sieves. Catechol (99%) was sublimed prior to use. [NiCl₂(dme)] was purchased from commercial sources and all other reagents were purchased commercially and used as received, unless otherwise noted. Column chromatography was performed by Combiflash™ using RediSep Rf Gold Normal-Phase Silica™ columns. Photoredox reactions were irradiated with a standard 26 W compact fluorescent light bulb and the temperature was controlled using an external fan. Melting points (°C) are uncorrected. Mass spectra (ESI-TOF) were recorded using CH₂Cl₂, MeCN or MeOH as the solvent. NMR spectra were recorded with Bruker FT spectrometers. ¹H (500.4 MHz) and ¹³C {¹H} (125.8 MHz) NMR chemical shifts are reported relative to internal TMS (δ = 0.00 ppm) or to residual protiated solvent, and ¹⁹F {¹H} NMR (470.8 MHz) chemical shifts were referenced to external CFCl₃ (0.0 ppm). Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad), coupling constant J (Hz) and integration.

Procedure for synthesis of organotrimethoxysilane from organotrichlorosilane

To an oven dried double neck round bottom flask equipped with an inert gas inlet, an addition funnel and a stir bar were successively introduced organotrichlorosilane (1 equiv) and THF (0.3 M). The resulting solution was cooled to –20 °C, then MeOH (4 equiv) and pyridine (4 equiv) were placed into the addition funnel and added dropwise to the trichlorosilane solution under vigorous stirring, resulting in an immediate precipitation of pyridinium chloride salt. After addition, the reaction mixture was allowed to reach rt for 1 h before being diluted with chilled H₂O (same volume as THF) and extracted with Et₂O (3 × THF volume). The combined organic extracts were dried (MgSO₄) and concentrated under vacuum, affording a colorless oil. The latter was finally distilled under reduced pressure to obtain the product in pure form.

Procedure for synthesis of organobis(catechol)silicates

Catechol (1.95 equiv) was introduced into a microwave vial with a stirring bar. The vial was sealed with a Teflon-coated septum cap then purged with N₂ and evacuated four times. THF or 1,4-dioxane (0.5 M) and the corresponding amine (1.2 equiv) were introduced, and the resulting light pink solution was stirred at rt for 15 min before addition of organotrimethoxysilane derivative (1 equiv) (note: no amine base was needed for the synthesis of 14). The reaction mixture was refluxed for 16 h, then an aliquot was taken and analyzed by ¹H NMR. In the case
of an incomplete reaction, the vial was cooled to rt and the reaction mixture concentrated to a glue (to remove MeOH formed during the reaction) before the amine (0.5 equiv) and solvent (1.0 M) were introduced, and the vial was heated at reflux for another 16 h. The vial was finally cooled to rt and the reaction mixture concentrated to a glue before the Et₂O (0.1 M) was introduced. The mixture was then sonicated 15 min to allow the corresponding product to precipitate as a white powder. Note that for some silicates, evaporation under vacuo for a prolonged period of time (16 h) was required before sonication. The vial was finally unsealed and the precipitate was collected by vacuum filtration. The filter cake was washed with Et₂O to afford the desired silicate. In some cases, a trace amount (less than 5%) of tris(catechol)silicate could be detected in the final product, but the latter did not affect the efficiency of the dual photoredox/nickel catalyzed cross coupling. If desired, the product could be purified by dissolving in CH₂Cl₂ followed by precipitation with pentane and filtration.

**Synthesis of photocatalyst [Ru(bpy)₃](PF₆)$_2$**

The synthesis of photocatalyst [Ru(bpy)₃](PF₆)$_2$ has been realized using a modified method of the literature.¹

\[
\text{2,2'}-\text{Bipyridyl (968 mg, 6.20 mmol)} \quad \text{and} \quad \text{RuCl₃•6H₂O (316 mg, 1.00 mmol)} \quad \text{were introduced in a microwave vial with a stirring bar.} \\
\text{The vial was sealed with a Teflon-coated septum cap then purged} \quad \text{with N}_2 \quad \text{and evacuated four times.} \\
\text{The content was solved in degassed EtOH (40 mL)} \quad \text{then stirred at reflux for 16 h.} \\
\text{After cooling to rt, the vial was unsealed and NH}_4\text{PF}_6 \quad \text{(1.63 g, 10 mmol)} \quad \text{was added, resulting in an immediate precipitation of an orange suspension.} \\
\text{The mixture was heated 15 min at 40 °C then cooled to 0 °C in an ice bath.} \\
\text{After 2 h, the precipitate was collected by vacuum filtration} \quad \text{and the cake washed thoroughly with H₂O (~200 mL) then EtOH (~100 mL) and finally Et₂O (~100 mL) to afford the title compound as a brick red solid (710 mg, 83%).} \\
\text{mp >250 °C. Characterization data for this compound matched that reported in the literature.}²
\]

**High Throughput Experimentation Information**

High Throughput Experimentation was performed at the Penn/Merck Center for High Throughput Experimentation at the University of Pennsylvania. The screens were run on a 0.01 mmol scale (relative to ArBr) and analyzed by HPLC with addition of 4,4′-di-tert-butylbiphenyl (0.1 equiv) as internal standard (IS). The graphs depicted hereafter represent product or starting material to internal standard ratios (P/IS or SM/IS, respectively). The ratios calculated are pertinent only to that specific screen; the ratios from one screen should not be quantitatively compared to those from a different screen.

General Procedure for Screens

Reactions were run in glass vials in 24 or 96 well plate reactor blocks having hollowed bottoms, and the vials were equipped with Teflon coated magnetic stir bar (Figure 1). The plate was placed in a glovebox, then the various compounds (silicates, ArBr, ligands, metallic precursors, photoredox catalyst) were added as solutions using micropipettes. If needed, carrying solvents were removed using a centrifugal evaporator. The plate was sealed with a screwed top lid equipped with a PTFE gasket then removed from the glovebox and placed on an LED (white or blue) plate on the top a magnetic stirrer (500 rpm). After 16 h, the plate was unsealed and reaction mixtures were diluted with MeCN (0.50 mL). Aliquots (25 µL) were taken and introduced into an 96 well HPLC plate, diluted with MeCN (0.70 mL) and finally analyzed by HPLC.

Figure S-1. Hollow bottom 96 well plate reactor block equipped with glass vials and blue LED plate.
Screens using HTE Screening Center

**Screen 1.** Optimization of metal catalyzed photoredox cross-coupling using cyclohexylbis(catecholato)silicate•HNEt₃ (2) – Variation of solvents, metal sources and ligands.

![Chemical structure](image)

**Note:** [Ir]PF₆ stands for [Ir(dFCF₃ppy)(bpy)][PF₆] (dFCF₃ppy = 2-(2,4- difluorophenyl)-5-(trifluoromethyl)pyridine; bpy = bipyridine)
Screen 2. Optimization of metal catalyzed photoredox cross-coupling using cyclohexylbis(catecholato)silicate•HNEt$_3$ (2) – Variation of Ni(II) sources and solvents.

![Chemical reaction diagram]

<table>
<thead>
<tr>
<th>Nickel (II) source</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NiCl$_2$(dme)]</td>
<td>THF</td>
</tr>
<tr>
<td>[Ni(NO$_3$)$_2$]$_2$6H$_2$O</td>
<td>MeCN</td>
</tr>
<tr>
<td>2-methylbutan-2-ol</td>
<td>DMA</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
</tr>
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<td></td>
<td>DCE</td>
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<tr>
<td></td>
<td>AcOEt</td>
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<tr>
<td></td>
<td>MeTHF</td>
</tr>
<tr>
<td></td>
<td>DME</td>
</tr>
<tr>
<td></td>
<td>dimethylecarbonate</td>
</tr>
</tbody>
</table>

*Figure S-3.* Optimization of metal catalyzed photoredox cross-coupling using cyclohexylbis(catecholato)silicate•HNEt$_3$, and various Nickel (II) sources and solvents.
Screen 3. Optimization of metal catalyzed photoredox cross-coupling using organobis(catecholato)silicate•HNEt₃ – Variation of photoredox catalysts.

![Chemical structure and reaction scheme]

<table>
<thead>
<tr>
<th>Silicate</th>
<th>Photoredox catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Ir(dFCF₃ppy)₂(bpy)]PF₆</td>
</tr>
<tr>
<td>2</td>
<td>[Ru(bpy)₃]²PF₆</td>
</tr>
<tr>
<td>14</td>
<td>[Ru(phen)₃]²PF₆</td>
</tr>
<tr>
<td>5</td>
<td>[Ru(bpz)₃]²PF₆</td>
</tr>
<tr>
<td></td>
<td>[Ru(bpm)₃]²PF₆</td>
</tr>
<tr>
<td></td>
<td>EosinY</td>
</tr>
</tbody>
</table>

R = benzyl, cyclohexyl, propylammonium, n-hexyl

![Bar graph showing SM/IS values]

Figure S-4. Screening of photoredox catalyst for the cross-coupling of various organobis(catecholato)silicates with bromobenzonitrile. SM/IS graph.
General procedure for photoredox cross-coupling reactions

0.5 mmol scale reaction: To a 2 dram clear glass vial equipped with a Teflon-coated magnetic stir bar was added 4,4’-di-tert-butyl-2,2’-bipyridine (6.7 mg, 0.025 mmol), and [NiCl₂(dme)] (5.5 mg, 0.025 mmol). The vial was capped and purged with nitrogen, then 1.5 mL THF was introduced. The resulting suspension was heated briefly with a heat gun until the nickel and ligand were fully solubilized, yielding a pale green solution. The solution was cooled in an ice bath, resulting in the immediate precipitation of an evergreen solid. Solvents were then evaporated in vacuo to give a fine coating of the ligated nickel complex. Once dry, aryl bromide (0.5 mmol, 1.0 equiv) (liquid aryl bromides were added with solvent), organosilicates (0.6 mmol, 1.2 equiv), and [Ru(bpy)₃]PF₆ (8.6 mg, 0.01 mmol) were added in succession. The vial was then capped and purged four times. Under inert atmosphere, DMF (5 mL) was introduced. The vial containing all the reagents was further sealed with parafilm and stirred approximately 4 cm away from a 26 W fluorescent light bulb. A fan was blown across the reaction setup to suppress the heat generated by the latter (the reaction temperatures were estimated to be ~30 °C). After 16-24 h, an aliquot was taken and analyzed by HPLC to monitor reaction completion.

General work up: The crude reaction mixture was poured in a separatory funnel and diluted with H₂O (20 mL). The resulting suspension was extracted with Et₂O (3 x 30 mL), and the combined organic extracts were washed with a saturated solution of Na₂CO₃ (2 x 20 mL) then H₂O (20 mL), dried (MgSO₄) and concentrated. The residue was purified by column chromatography on silica gel, eluting with EtOAc and hexanes (or with CH₂Cl₂ and 1–PrOH, when needed), to obtain products in pure form.

Special work up for amine-containing compounds: After completion, the crude reaction mixture was diluted with EtOAc (10 mL), filtered through an approximately 6 cm x 4 cm cylindrical plug of Celite, washing with EtOAc (50 mL). The resulting solution was concentrated, retaken in EtOAc (20 mL), poured in a separatory funnel and washed with a saturated solution of Na₂CO₃ (2 x 10 mL) then H₂O (10 mL), dried (MgSO₄) and concentrated. The residue was purified by column chromatography on silica gel, eluting with MeOH and CH₂Cl₂ containing NH₄OH (1 %, v/v), to obtain the product in pure form.
**Gram scale reaction:** To a 100 mL Schlenk flask equipped with a Teflon-coated magnetic stir bar was added $[\text{NiCl}_2(\text{dme})]$ (55 mg, 0.25 mmol) and 4,4'-di-tert-butyl-2,2'-bipyridine (67 mg, 0.25). The flask was capped and purged with nitrogen, then 5.0 mL THF was introduced. The resulting suspension was heated briefly with a heat gun until the nickel and ligand were fully solubilized, yielding a pale green solution. The solution was cooled in an ice bath, resulting in the immediate precipitation of an evergreen solid. Solvents were then evaporated in vacuo to give a fine coating of the ligated nickel complex. Once dry, methyl 4-bromobenzoate (1.075 g, 5.00 mmol), silicate 14 (1.325 g, 6.00 mmol) and $[\text{Ru(bpy)}_3]2\text{PF}_6$ (86 mg, 0.10 mmol) were added in succession. The vial was then capped and purged four times. Under inert atmosphere, DMF (80 mL) was introduced. The vial containing all the reagents was further sealed with parafilm and stirred in the "light chamber" depicted below. Two fans were blown across the reaction setup to suppress the heat generated by the LEDs, reaching 36 °C after 1 h. Reaction completion was monitored by taking aliquots of the reaction mixture and analyzing them by HPLC. After completion (4 h), the crude reaction mixture was diluted with EtOAc (50 mL), filtered through an approximately 6 cm x 4 cm cylindrical plug of Celite, washing with EtOAc (150 mL). The resulting solution was concentrated, retaken in EtOAc (100 mL), poured into a separatory funnel and washed with a saturated solution of Na$_2$CO$_3$ (2 × 50 mL) then H$_2$O (50 mL), dried (MgSO$_4$) and concentrated. The residue was purified by column chromatography on silica gel, eluting with MeOH and CH$_2$Cl$_2$ containing NH$_4$OH (1 %, v/v), to obtain methyl 4-(3-aminopropyl)benzoate in pure form (891 mg, 92%).

*Figure S–5.* 0.5 mmol (left) and gram (right) scale photoredox cross-coupling reaction set-up.
General procedure for successive photoredox cross-coupling reactions

To a 4 dram clear glass vial equipped with a Teflon-coated magnetic stir bar was added 4,4’-di-tert-butyl-2,2’-bipyridine (6.7 mg, 0.025 mmol), and [NiCl$_2$(dme)] (5.5 mg, 0.025 mmol). The vial was capped and purged with nitrogen, then 1.5 mL THF was introduced. The resulting suspension was heated briefly with a heat gun until the nickel and ligand were fully solubilized, yielding a pale green solution. The solution was cooled in an ice bath, resulting in the immediate precipitation of an evergreen solid. Solvents were then evaporated in vacuo to give a fine coating of the ligated nickel complex. Once dry, aryl bromide (0.5 mmol, 1.0 equiv) (liquid aryl bromides were added with solvent), organotrifluoroborate (0.51 mmol, 1.05 equiv), and [Ir(dFCF$_3$ppy)$_2$(bpy)]PF$_6$ (10.1 mg, 0.01 mmol) were added in succession. The vial was then capped and purged four times. Under inert atmosphere, dioxane (10 mL) was introduced. The vial containing all the reagents was further sealed with parafilm and stirred approximately 4 cm away from a 26 W fluorescent light bulb. A fan was blown across the reaction setup to suppress the heat generated by the latter (the reaction temperatures were estimated to be ~30 °C). After 48 h, the crude reaction mixture was filtered through an approximately 2 cm x 2 cm cylindrical plug of Celite at air, washing with dioxane (10 mL). The resulting solution was concentrated to approximately 0.5 mL under vacuo, then organosilicate (0.6 mmol, 1.2 equiv) and DMF (5 mL) were added successfully. The resulting solution was then capped and flushed with inert gas. The vial was further sealed with parafilm and stirred approximately 4 cm away from a 26 W fluorescent light bulb for 16 h. Finally, the crude reaction mixture was poured in a separatory funnel and diluted with H$_2$O (20 mL). The resulting suspension was extracted with Et$_2$O (3 × 30 mL), and the combined organic extracts were washed with a saturated solution of Na$_2$CO$_3$ (2 × 20 mL) then H$_2$O (20 mL), dried (MgSO$_4$) and concentrated. The residue was purified by column chromatography on silica gel, eluting with EtOAc and hexanes, to obtain products in pure form.
Compound Characterization Data

Triethylammonium benzylbis(catecholato)silicate (1): obtained as a white powder using THF as solvent (1.89 g, 92%), mp = 118 °C; ¹H NMR (CDCl₃, 500.4 MHz): δ 7.00 (t, J = 7.7 Hz, 2 H), 6.90 (t, J = 7.7 Hz, 1 H), 6.85 (d, J = 7.7 Hz, 2 H), 6.72–6.66 (m, 8 H), 3.07 (q, J = 7.2 Hz, 6 H), 2.25 (s, 2 H), 1.14 (t, J = 7.6 Hz, 9 H) ppm; ¹³C {¹H} NMR (CDCl₃, 125.8 MHz): δ 149.3, 142.0, 129.0, 127.2, 122.9, 118.7, 110.7, 46.1, 26.0, 8.4 ppm; IR: ν = 3031, 2928, 1528, 1482, 1235, 1211, 816, 739, 695 cm⁻¹; HRMS (ESI) m/z calc. for C₁₉H₁₅O₄Si [M – HNEt₃]⁻ 335.0740, found 335.0744; Eₚₐ = + 0.70 V vs SCE.

Triethylammonium cyclohexylbis(catecholato)silicate (2): obtained as a white powder using THF as solvent (1.14 g, 96%), mp 158 °C; ¹H NMR (CDCl₃, 500.4 MHz): δ 6.74–6.68 (m, 4 H), 6.67–6.62 (m, 4 H), 3.24 (q, J = 7.2 Hz, 6 H), 1.63 (d, J = 14.0 Hz, 2 H), 1.54–1.51 (m, 3 H), 1.30 (t, J = 7.6 Hz, 9 H), 1.22–1.12 (m, 2 H), 1.12–1.01 (m, 3 H), 1.09–1.01 (m, 1 H), 0.91 (dt, J = 8.7, 2.6 Hz, 1 H), 0.79–0.74 (m, 1 H) ppm; ¹³C {¹H} NMR (CDCl₃, 125.8 MHz): δ 150.0, 118.4, 110.3, 46.1, 29.4, 28.4, 28.1, 30.0, 8.53 ppm; IR: ν = 3030, 2944, 1486, 1458, 1357, 1262, 1231, 1205, 1101, 1015, 816, 742, 731, 685 cm⁻¹; HRMS (ESI) m/z calc. for C₁₈H₁₉O₄Si [M – i-Pr₂NH₂]⁻ 327.1053, found 327.1055; Eₚₐ = + 0.74 V vs SCE.

Diisopropylammonium exo-2-bicyclo[2.2.1]heptylbis(catecholato)silicate (3): obtained as a white powder using THF as solvent (1.14 g, 81%), mp 188 °C; ¹H NMR (CDCl₃, 500.4 MHz): δ 6.74–6.68 (m, 4 H), 6.67–6.62 (m, 4 H), 3.24 (q, J = 7.2 Hz, 6 H), 2.22 (br s, 1 H), 2.02 (br s, 1 H), 1.65–1.58 (m, 1 H), 1.37–1.31 (m, 2 H), 1.28 (t, J = 7.5 Hz, 9 H), 1.22–1.16 (m, 1 H), 1.09–1.01 (m, 3 H), 0.91 (dt, J = 8.7, 2.6 Hz, 1 H), 0.79–0.74 (m, 1 H) ppm; ¹³C {¹H} NMR (CDCl₃, 125.8 MHz): δ 149.9, 149.7, 118.4, 110.3, 46.1, 29.4, 28.4, 28.1, 30.0, 8.53 ppm; IR: ν = 3035, 2941, 1486, 1458, 1357, 1262, 1231, 1205, 1101, 1017, 816, 732, 704 cm⁻¹; HRMS (ESI) m/z calc. for C₁₉H₁₉O₄Si [M – i-Pr₂NH₂]⁻ 339.1058, found 339.1062.

Triethylammonium methylbis(catecholato)silicate (4): obtained as a gray powder using THF as solvent (1.63 g, 73%), mp 168 °C; ¹H NMR (CDCl₃, 500.4 MHz): δ 6.74–6.71 (m, 4 H), 6.69–6.64 (m, 4 H), 3.23 (q, J = 7.5 Hz, 6 H), 1.29 (t, J = 7.5 Hz, 9 H), 0.14 (s, 3 H) ppm; ¹³C {¹H}
NMR (CDCl₃, 125.8 MHz): δ 149.2, 118.6, 110.7, 46.1, 8.5, –1.1 ppm; IR: ν = 3045, 1598, 1483, 1354, 1240, 1225, 1153, 1098, 1013, 826, 740 cm⁻¹; HRMS (ESI) m/z calc. for C₁₃H₁₁O₄Si [M – HNEt₃]⁻ 259.0432, found 259.0435.

Triethylammonium hexylbis(catecholato)silicate (5): obtained as a white powder using THF as solvent (1.21 g, 88%), mp 116 °C; ¹H NMR (CDCl₃, 500.4 MHz): δ 6.74–6.68 (m, 4 H), 6.67–6.62 (m, 4 H), 3.24 (q, J = 7.2 Hz, 6 H), 1.34–1.25 (m, 11 H), 1.18–1.10 (m, 6 H), 0.78 (t, J = 7.0 Hz, 3 H), 0.69–0.64 (m, 2 H) ppm; ¹³C {¹H} NMR (CDCl₃, 125.8 MHz): δ 149.9, 119.0, 110.8, 46.4, 30.4, 8.5 ppm; IR: ν = 3035, 2924, 1484, 1355, 1239, 1100, 1014, 818, 734 cm⁻¹; HRMS (ESI) m/z calc. for C₁₈H₂₁O₄Si [M – HNEt₃]⁻ 329.1215, found 329.1212; Eₒ = + 0.75 V vs SCE.

Triethylammonium chloromethylbis(catecholato)silicate (6): obtained as a light brown powder using THF as solvent (2.16 g, 93%), mp 108 °C; ¹H NMR (CDCl₃, 500.4 MHz): δ 6.76–6.73 (m, 4 H), 6.72–6.68 (m, 4 H), 3.32 (q, J = 7.1 Hz, 6 H), 2.90 (s, 2 H), 1.37 (t, J = 7.1 Hz, 9 H) ppm; ¹³C {¹H} NMR (CDCl₃, 125.8 MHz): δ 149.0, 119.0, 110.8, 46.4, 30.4, 8.5 ppm; IR: ν = 2963, 1483, 1390, 1351, 1221, 1172, 1153, 1101, 1060, 1012, 829, 783, 771, 739 cm⁻¹; HRMS (ESI) m/z calc. for C₁₃H₁₀ClO₄Si [M – HNEt₃]⁻ 293.0037, found 293.0032.

Triethylammonium 2-(3-cyclohexenyl)ethylbis(catecholato)silicate (7): obtained as a white powder using 1,4-dioxane as solvent (1.70 g, 86%), mp 102 °C; ¹H NMR (CDCl₃, 500.4 MHz): δ 6.75–6.70 (m, 4 H), 6.68–6.64 (m, 4 H), 5.59–5.55 (m, 2 H), 3.27 (q, J = 7.3 Hz, 9 H) ppm; ¹³C {¹H} NMR (CDCl₃, 125.8 MHz): δ 149.6, 149.5, 127.0, 126.8, 118.5, 118.4, 110.6, 46.1, 36.2, 31.6, 31.0, 28.5, 25.4, 13.7, 8.4 ppm; IR: ν = 2913, 1484, 1390, 1356, 1261, 1241, 1227, 1205, 1014, 817, 759, 733, 679 cm⁻¹; HRMS (ESI) m/z calc. for C₂₀H₂₂O₄Si [M – HNEt₃]⁻ 353.1215, found 353.1217.

Diisopropylammonium 2-(3,4-epoxycyclohexyl)ethylbis(catecholato)silicate (8): obtained as a white powder using 1,4-dioxane as solvent (3.29 g, 86%), mp 140 °C; ¹H NMR (DMSO–d₆, 500.4 MHz): δ 6.52–6.47 (m, 4 H), 6.44–6.40 (m, 4 H), 3.33 (sept, J = 6.4 Hz, 2 H), 3.19–3.15 (d, J = 10 Hz, 0.5 H), 3.00–2.93 (m, 1.5 H), 1.91–1.79 (m, 1.5 H), 1.58–1.48 (m, 1 H), 1.37–1.24...
(m, 1 H), 1.18 (d, J = 6.4 Hz, 12 H), 1.14–0.99 (m, 4 H), 0.99–0.88 (m, 0.5 H), 0.82–0.63 (m, 1 H), 0.46–0.40 (m, 2 H) ppm; $^{13}$C $^{1}$H NMR (DMSO–$d_6$, 125.8 MHz): δ 151.1, 151.0, 117.4, 117.3, 109.8, 52.4, 52.0, 51.3, 51.2, 46.7, 35.1, 32.3, 31.8, 31.5, 30.9, 30.7, 26.7, 25.4, 24.4, 23.4, 19.4, 15.6, 15.4 ppm; IR: ν = 2986, 2919, 1485, 1238, 891, 813, 736 cm$^{-1}$; HRMS (ESI) m/z calc. for C$_{20}$H$_{21}$O$_{5}$Si [M – i-Pr$_2$NH$_2$]$^-$ 369.1164, found 369.1169.

Diisopropylammonium N-[5-(bis(catecholato)silicate)-2-aza-1-oxopentyl]caprolactam (9): obtained as a white powder using 1,4-dioxane as solvent (2.74 g, 83%), mp 146 °C; $^1$H NMR (CD$_2$CN, 500.4 MHz): δ 9.10 (br s, 1 H), 6.67–6.62 (m, 4 H), 6.58–6.53 (m, 4 H), 3.89 (t, J = 4.5 Hz, 2 H), 3.53 (t, J = 6.7, 6.7 Hz, 2 H), 3.03 (sept, J = 6.4 Hz, 2 H), 2.67–2.61 (m, 2 H), 1.73–1.65 (m, 4 H), 1.63–1.54 (m, 2 H), 1.46–1.37 (m, 2 H), 1.31 (d, J = 6.4 Hz, 12 H), 0.58–0.50 (m, 2 H) ppm; $^{13}$C $^{1}$H NMR (DMSO–$d_6$, 125.8 MHz): δ 179.3, 154.3, 150.9, 117.5, 109.9, 46.7, 43.4, 43.0, 39.3, 28.6, 28.3, 25.0, 23.3, 19.4, 15.9 ppm; IR: ν = 2928, 1698, 1485, 1239, 813, 738 cm$^{-1}$; HRMS (ESI) m/z calc. for C$_{22}$H$_{25}$N$_2$O$_6$Si [M – i-Pr$_2$NH$_2$]$^-$ 441.1446, found 441.1441.

![Diisopropylammonium N-[5-(bis(catecholato)silicate)-2-aza-1-oxopentyl]caprolactam (9)](image)

Diisopropylammonium 3-(phenylamino)propylbis(catecholato)silicate (10): obtained as a white powder using 1,4-dioxane and a trace amount of Et$_2$O, mp 154 °C; $^1$H NMR (DMSO–$d_6$, 500.4 MHz): δ 8.01 (br s, 2 H), 6.99 (t, J = 7.3 Hz, 2 H), 6.54–6.51 (m, 4 H), 6.45–6.41 (m, 7 H), 5.32 (t, J = 5.1 Hz, 1 H), 3.34 (sept, J = 6.4 Hz, 2 H), 2.79 (td, J = 7.9, 5.1 Hz, 2 H), 1.46 (tt, J = 7.9, 7.9 Hz, 2 H), 1.19 (d, J = 6.4 Hz, 12 H), 0.54 (t, J = 7.9 Hz, 2 H) ppm; $^{13}$C $^{1}$H NMR (DMSO–$d_6$, 125.8 MHz): δ 151.0, 145.5, 129.1, 117.5, 115.2, 112.1, 109.9, 66.7, 16.8, 46.6, 24.7, 19.2, 16.2 ppm; IR: ν = 2859, 1601, 1484, 1239, 1149, 813, 739 cm$^{-1}$; HRMS (ESI) m/z calc. for C$_{21}$H$_{20}$NO$_4$Si [M – i-Pr$_2$NH$_2$]$^-$ 378.1167, found 378.1167.

![Diisopropylammonium 3-(phenylamino)propylbis(catecholato)silicate (10)](image)

Triethylammonium 2-(pyridin-2-yl)ethylbis(catecholato)silicate (11): obtained as a white powder using THF as solvent (3.54 g, 91%), together with 8% of SM, mp = 168 °C; $^1$H NMR (CDCl$_3$, 500.4 MHz): δ 9.53 (br s, 1 H), 8.34 (d, J = 5.4 Hz, 1 H), 7.48 (dd, J = 7.9, J = 6.3 Hz, 1 H), 7.10 (d, J = 7.9 Hz, 1 H), 6.98 (dd, J = 6.3, J = 5.3 Hz, 1 H), 6.71–6.67 (m, 4 H), 6.65–6.60 (m, 4 H), 3.12 (q, J = 6.5 Hz, 6 H), 2.84 (m, 2 H), 1.22 (t, J = 6.5 Hz, 9 H), 1.12–1.07 (m, 2 H) ppm; $^{13}$C $^{1}$H NMR (CDCl$_3$, 125.8 MHz): δ 149.6, 147.6, 136.7, 125.5, 120.6, 118.4, 114.8, 110.7, 46.0, 32.6, 16.7, 9.2 ppm; IR: ν = 2859, 1601, 1484, 1239, 813, 739, 692 cm$^{-1}$; HRMS (ESI) m/z calc. for C$_{19}$H$_{16}$NO$_4$Si [M – HNEt$_3$]$^-$ 350.0854, found 350.0851.

![Triethylammonium 2-(pyridin-2-yl)ethylbis(catecholato)silicate (11)](image)
Diisopropylammonium 3,3,4,4,5,5,6,6,6-nonafluorohexyl(bcatecholato)silicate (12): obtained as a white powder using THF as solvent (1.48 g, 92%), mp 65 °C; \(^1\)H NMR (CDCl\(_3\), 500.4 MHz): \(\delta\) 6.76–6.73 (m, 4 H), 6.69–6.66 (m, 4 H), 3.34 (sept, \(J = 6.6\) Hz, 2 H), 2.16–2.02 (m, 2 H), 1.41 (d, \(J = 6.6\) Hz, 12 H), 0.95–0.88 (m, 2 H) ppm; \(^{13}\)C \(\{^1\)H\}\} NMR (CDCl\(_3\), 125.8 MHz): \(\delta\) 149.3, 119.2, 111.0, 46.4, 26.4 (t, \(J = 22\) Hz), 8.6, 5.9 ppm; \(^{19}\)F \(\{^1\)H\}\} NMR (CDCl\(_3\), 470.8 MHz): \(\delta\) –81.1, –116.4, –124.4, –126.1 ppm; IR: \(\nu\) = 3049, 1599, 1484, 1352, 1238, 121, 1129, 1101, 1059, 1013, 877, 822, 792, 737, 690 cm\(^{-1}\); HRMS (ESI) m/z calc. for C\(_{18}\)H\(_{12}\)F\(_9\)O\(_4\)Si \([\text{M} – \text{i-Pr}_2\text{NH}_2]\)^— 491.0361, found 491.0361.

Triethylammonium 3-acetoxypropyl(bcatecholato)silicate (13): obtained as a white powder using THF as solvent (1.92 g, 95%), mp 88 °C; \(^1\)H NMR (CDCl\(_3\), 500.4 MHz): \(\delta\) 6.75–6.73 (m, 4 H), 6.68–6.65 (m, 4 H), 3.89 (t, \(J = 7.2\) Hz, 2 H), 3.28 (q, \(J = 6.6\) Hz, 6 H), 1.94 (s, 3 H), 1.69–1.66 (m, 2 H), 1.32 (t, \(J = 6.6\) Hz, 9 H), 0.71–0.66 (m, 2 H) ppm; \(^{13}\)C \(\{^1\)H\}\} NMR (CDCl\(_3\), 125.8 MHz): \(\delta\) 171.2, 149.4, 118.6, 110.7, 67.3, 46.1, 23.6, 21.0, 12.4, 8.4 ppm; IR: \(\nu\) = 3038, 1725, 1483, 1238, 1197, 1030, 1016, 815, 735, 701, 664 cm\(^{-1}\); HRMS (ESI) m/z calc. for C\(_{17}\)H\(_{17}\)O\(_6\)Si \([\text{M} – \text{HNEt}_3]\)^— 345.0794, found 345.0796.

3-Ammoniumpropyl(bcatecholato)silicate (14): obtained as a white powder using THF as solvent (1.97 g, 94%), crystallized with 0.75 equiv THF, mp >250 °C; \(^1\)H NMR (DMSO-\(d_6\), 500.4 MHz): \(\delta\) 7.43 (br s, 3 H), 6.55–6.51 (m, 4 H), 6.47–6.42 (m, 4 H), 2.59 (t, \(J = 7.6\) Hz, 2 H), 1.48 (td, \(J = 7.6, 7.6\) Hz, 2 H), 0.53–0.48 (m, 2 H) ppm; \(^{13}\)C \(\{^1\)H\}\} NMR (DMSO-\(d_6\), 125.8 MHz): \(\delta\) 150.8, 117.6, 110.0, 42.3, 23.3, 15.3 ppm; IR: \(\nu\) = 3048, 2930, 1601, 1483, 1355, 1242, 1101, 1048, 1013, 889, 826, 733, 705 cm\(^{-1}\); HRMS (ESI) m/z calc. for C\(_{15}\)H\(_{16}\)NO\(_4\)Si \([\text{M} – \text{H}]^+\) 302.0854, found 302.0859.

1-Benzyl-4-methoxybenzene (15): obtained as a colorless oil (76 mg, 77%); \(^1\)H NMR (CDCl\(_3\), 500.4 MHz): \(\delta\) 7.28 (t, \(J = 7.5\) Hz, 2 H), 7.20–7.16 (m, 3 H), 7.10 (d, \(J = 9.0\) Hz, 2 H), 6.83 (d, \(J = 9.0\) Hz, 2 H), 3.92 (s, 2 H), 3.78 (s, 3 H) ppm; \(^{13}\)C \(\{^1\)H\}\} NMR (CDCl\(_3\), 125.8 MHz): 158.1, 141.7, 133.4, 130.0, 129.0, 128.6, 126.1, 114.0, 55.4, 41.2 ppm; HRMS (ESI) m/z calc. for C\(_{14}\)H\(_{14}\)O \([\text{M}]^+\) 198.1045, found 198.1048.

1-Cyclohexyl-4-methoxybenzene (16): obtained as a colorless oil (89 mg, 94%); $^1$H NMR (CDCl$_3$, 500.4 MHz): δ 7.13 (d, $J$ = 7.6 Hz, 2 H), 6.84 (d, $J$ = 7.6 Hz, 2 H), 3.78 (s, 3 H), 2.47–2.41 (m, 1 H), 1.86–1.71 (m, 4 H), 1.73 (dd, $J$ = 13.0, 4.7 Hz, 1 H), 1.44–1.32 (m, 4 H), 1.29–1.19 (m, 1 H) ppm; $^{13}$C NMR (CDCl$_3$, 125.8 MHz): 157.8, 140.5, 127.8, 113.8, 55.4, 43.9, 34.9, 27.1, 26.3 ppm; HRMS (ESI) m/z calc. for C$_{13}$H$_{18}$O [M]$^+$ 190.1358, found 190.1359.

exo-2-(4-Methoxyphenyl)bicyclo[2.2.1]heptane (17): obtained as a colorless oil (92 mg, 91%); $^1$H NMR (CDCl$_3$, 500.4 MHz): δ 7.16 (d, $J$ = 8.6 Hz, 2 H), 6.86 (d, $J$ = 8.6 Hz, 2 H), 3.81 (s, 3 H), 2.71 (dd, $J$ = 6.3, 8.8 Hz, 1 H), 2.37 (d, $J$ = 5.8 Hz, 2 H), 1.77 (ddd, $J$ = 2.4, 9.9, 9.9 Hz, 1 H), 1.69–1.52 (m, 4 H), 1.41–1.34 (m, 1 H), 1.31–1.26 (m, 1 H), 1.19 (d, $J$ = 4.5 Hz, 1 H) ppm; $^{13}$C {$^1$H} NMR (CDCl$_3$, 125.8 MHz): 157.6, 139.9, 128.1, 113.7, 55.4, 46.7, 43.3, 39.3, 37.0, 36.1, 30.7, 29.1 ppm; IR: ν = 2948, 2848, 2833, 1611, 1510, 1463, 1454, 1441, 1294, 1277, 1245, 1208, 1178, 1139, 1107, 1035, 822, 763, 600, 532 cm$^{-1}$; HRMS (ESI) m/z calc. for C$_{14}$H$_{18}$O [M]$^+$ 202.1358, found 202.1356.

1-Hexyl-4-methoxybenzene (19): obtained as a colorless oil (82 mg, 85%); $^1$H NMR (CDCl$_3$, 500.4 MHz): δ 7.09 (d, $J$ = 8.7 Hz, 2 H), 6.82 (d, $J$ = 8.7 Hz, 2 H), 3.78 (s, 3 H), 2.54 (t, $J$ = 7.4 Hz, 2 H), 1.57 (q, $J$ = 7.2 Hz, 2 H), 1.35–1.26 (m, 6 H), 0.88 (t, $J$ = 6.9 Hz, 3 H) ppm; $^{13}$C {$^1$H} NMR (CDCl$_3$, 125.8 MHz): 157.7, 146.1, 129.4, 113.8, 55.4, 35.2, 31.9, 29.1, 22.8, 14.7 ppm; HRMS (ESI) m/z calc. for C$_{13}$H$_{19}$O [M–H]$^-$ 191.1436, found 191.1426.

1-(2-(Cyclohex-3-en-1-yl)ethyl)-4-methoxybenzene (21): obtained as a colorless oil (100 mg, 93%); $^1$H NMR (CDCl$_3$, 500.4 MHz): δ 7.12 (d, $J$ = 8.0 Hz, 2 H), 6.84 (d, $J$ = 8.0 Hz, 2 H), 5.67 (br s, 2 H), 3.80 (s, 3 H), 2.61 (t, $J$ = 7.3 Hz, 2 H), 2.16 (dd, $J$ = 17.3, 4.0 Hz, 1 H), 2.09–2.02 (m, 2 H), 1.83–1.77 (m, 1 H), 1.76–1.68 (m, 1 H), 1.63–1.55 (m, 3 H), 1.33–1.22 (m, 1 H) ppm; $^{13}$C {$^1$H} NMR (CDCl$_3$, 125.8 MHz): 157.5, 134.9, 129.1, 126.9, 126.4, 113.6, 55.2, 38.7, 32.9, 32.2, 31.7, 28.8, 25.1 ppm; IR: ν = 3021, 2910, 2834, 1612, 1511, 1489, 1454, 1440, 1300, 1242, 1176, 1141, 1109, 1037, 820, 727, 653, 562, 521 cm$^{-1}$; HRMS (ESI) m/z calc. for C$_{15}$H$_{20}$O [M]$^+$ 216.1514, found 216.1511.

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\[ N-[(3-(4-Methoxyphenyl)propyl)-2-aza-1-oxopentyl]caprolactam \ (23): \obtained as a colorless oil (81 mg, 53\%); \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500.4 MHz): \delta 9.30 (br s, 1 H), 7.10 (d, \textit{J} = 8.3 Hz, 2 H), 6.82 (d, \textit{J} = 8.3 Hz, 2 H), 3.98 (d, \textit{J} = 2.1 Hz, 2 H), 3.77 (s, 3 H), 3.29 (q, \textit{J} = 6.4 Hz, 2 H), 2.71–2.68 (m, 2 H), 2.61 (t, \textit{J} = 8.3 Hz, 2 H), 1.85 (q, \textit{J} = 7.7 Hz, 2 H), 1.80–1.68 (m, 6 H) ppm; \textsuperscript{13}C \{\textsuperscript{1}H\} NMR (CDCl\textsubscript{3}, 125.8 MHz): 179.6, 157.9, 155.0, 133.7, 129.4, 113.9, 55.4, 43.9, 40.1, 39.9, 32.4, 31.4, 29.3, 28.5, 23.7 ppm; IR: \nu = 2930, 1695, 1610, 1529, 1510, 1462, 1454, 1437, 1317, 1350, 1332, 1242, 1213, 1175, 1164, 969, 809 cm\textsuperscript{-1}; HRMS (ESI) m/z calc. for C\textsubscript{17}H\textsubscript{25}N\textsubscript{2}O\textsubscript{3} \[M + H\]^+ 305.1865, found 305.1861.

\[ N-(3-(4-Methoxyphenyl)propyl)aniline \ (24): \obtained as a yellow crystalline solid (77 mg, 64\%); \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500.4 MHz): \delta 7.18 (td, \textit{J} = 7.4, 1.1 Hz, 2 H), 7.13 (d, \textit{J} = 8.2 Hz, 2 H), 6.86 (d, \textit{J} = 8.9 Hz, 2 H), 6.71 (tt, \textit{J} = 7.3, 1.1 Hz, 1 H), 6.60 (dd, \textit{J} = 8.6, 1.1 Hz, 2 H), 3.81 (s, 3 H), 3.38–3.92 (br s, 1 H), 3.16 (t, \textit{J} = 7.5 Hz, 2 H), 2.70 (t, \textit{J} = 7.5 Hz, 2 H), 1.94 (tt, \textit{J} = 7.5, 7.5 Hz, 2 H) ppm; \textsuperscript{13}C \{\textsuperscript{1}H\} NMR (CDCl\textsubscript{3}, 125.8 MHz): 157.8, 148.3, 133.6, 129.8, 129.1, 117.2, 113.8, 112.7, 55.2, 43.4, 32.4, 31.2 ppm; IR: \nu = 3388, 2911, 2851, 1603, 1507, 1472, 1320, 1255, 1237, 1176, 1095, 1057, 991, 811, 768, 748, 557, 511 cm\textsuperscript{-1}; HRMS (ESI) m/z calc. for C\textsubscript{16}H\textsubscript{20}NO \[M + H\]^+ 242.1545, found 242.1550.

\[ 2-(4-Methoxyphenethyl)pyridine \ (25): \obtained as a colorless oil (53 mg, 50\%); \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500.4 MHz): \delta 8.55 (dd, \textit{J} = 4.5, 2.3 Hz, 1 H), 7.55 (ddd, \textit{J} = 7.5, 7.5, 2.1 Hz, 1 H), 7.12–7.08 (m, 3 H), 7.06 (d, \textit{J} = 7.7 Hz, 1 H), 6.81 (d, \textit{J} = 8.6 Hz, 2 H), 3.77 (s, 3 H), 3.09–3.03 (m, 2 H), 3.02–2.96 (m, 2 H) ppm; \textsuperscript{13}C \{\textsuperscript{1}H\} NMR (CDCl\textsubscript{3}, 125.8 MHz): 161.3, 157.8, 149.2, 136.2, 133.6, 129.3, 122.9, 121.0, 113.7, 55.15, 40.42, 35.1 ppm; IR: \nu = 3006, 2932, 1610, 1588, 1568, 1510, 1473, 1454, 1434, 1300, 1242, 1177, 1149, 1034, 822, 749 cm\textsuperscript{-1}; HRMS (ESI) m/z calc. for C\textsubscript{14}H\textsubscript{16}NO \[M + H\]^+ 214.1232, found 214.1236.

\[ 4-(3,3,4,4,5,6,6,6-Nonafluorohexyl)-1,1'-biphenyl \ (26): \obtained as a colorless solid (177 mg, 88\%); mp 55 \degree C; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500.4 MHz): \delta 7.57 (d, \textit{J} = 7.8 Hz, 2 H), 7.54 (d, \textit{J} = 7.8 Hz, 2 H), 7.43 (dd, \textit{J} = 7.7, 7.4 Hz, 2 H), 7.33 (t, \textit{J} = 7.4 Hz, 1 H), 7.27 (d, \textit{J} = 7.7 Hz, 2 H), 2.98–2.84 (m, 2 H), 2.47–2.34 (m, 2 H) ppm; \textsuperscript{13}C \{\textsuperscript{1}H\} NMR (CDCl\textsubscript{3}, 125.8 MHz): 140.7, 139.7, 138.1, 128.7, 128.6, 127.4, 127.2, 126.9, 32.8 (t, \textit{J} = 22.3 Hz), 26.0 ppm; \textsuperscript{19}F \{\textsuperscript{1}H\} NMR (CDCl\textsubscript{3}, 242.1545, found 242.1550.

S16
470.8 MHz: –81.1, –114.2, –124.4, –125.9 ppm; IR: ν = 1488, 1357, 1301, 1215, 1167, 1130, 1089, 1049, 1007, 983, 881, 838, 760, 750, 734, 693 cm⁻¹; HRMS (ESI) m/z calc. for C₁₈H₁₃F₉ [M⁺] 400.0874, found 400.0875.

3-(4-Methoxyphenyl)propyl acetate (27): obtained as a colorless oil (82 mg, 79%); ¹H NMR (CDCl₃, 500.4 MHz): δ 7.10 (d, J = 8.4 Hz, 2 H), 6.83 (d, J = 8.4 Hz, 2 H), 4.07 (t, J = 6.5 Hz, 2 H), 3.79 (s, 3 H), 2.63 (t, J = 7.9 Hz, 2 H), 2.06 (s, 3 H), 1.92 (tt, J = 6.5, 7.9 Hz, 2 H) ppm; ¹³C {¹H} NMR (CDCl₃, 125.8 MHz): 171.3, 158.0, 133.4, 129.4, 114.0, 64.0, 55.4, 31.4, 30.6, 21.2 ppm; IR: ν = 2953, 1735, 1612, 1511, 1464, 1386, 1365, 1300, 1235, 1177, 1113, 1033, 951, 810, 700, 532 cm⁻¹; HRMS (ESI) m/z calc. for C₁₂H₁₆O₃ [M⁺] 208.1299, found 208.1297.

3-(4-Methoxyphenyl)propan-1-amine (28): obtained as a yellow oil (56 mg, 68%); ¹H NMR (CDCl₃, 500.4 MHz): δ 7.09 (d, J = 7.0 Hz, 2 H), 6.82 (d, J = 7.0 Hz, 2 H), 3.78 (s, 3 H), 2.71 (t, J = 6.8 Hz, 2 H), 2.59 (t, J = 7.8 Hz, 2 H), 1.78 (tt, J = 6.8, 7.8 Hz 2 H) 1.39 (br s, 2 H) ppm; ¹³C {¹H} NMR (CDCl₃, 125.8 MHz): 157.7, 134.1, 129.2, 113.7, 55.1, 41.6, 35.5, 32.2 ppm; IR: ν = 3320, 2925, 2854, 1663, 1611, 1584, 1512, 1464, 1300, 1245, 1177, 1093, 1035, 907, 648, 530 cm⁻¹; HRMS (ESI) m/z calc. for C₁₀H₁₆NO [M + H]⁺ 166.1231, found 166.1232.

4-(3-Aminopropyl)benzonitrile (29): obtained as a light brown oil (69 mg, 86%); ¹H NMR (CDCl₃, 500.4 MHz): δ 7.57 (d, J = 8.0 Hz, 2 H), 7.29 (d, J = 8.0 Hz, 2 H), 2.88–2.80 (br s, 2 H), 2.80–2.70 (m, 4 H), 1.81 (tt, J = 7.7, 7.5 Hz, 2 H) ppm; ¹³C {¹H} NMR (CDCl₃, 125.8 MHz): 147.5, 132.1, 129.1, 119.0, 109.7, 41.0, 33.8, 33.2 ppm; IR: ν = 3124, 3110, 2869, 2270, 1710, 1661, 1599, 1573, 1448, 1364, 1314, 1179, 850, 698 cm⁻¹; HRMS (ESI) m/z calc. for C₁₀H₁₃N₂ [M + H]⁺ 161.1079, found 161.1082.

2-(3-Aminopropyl)benzonitrile (30): obtained as a dark yellow oil (67 mg, 84%); ¹H NMR (CDCl₃, 500.4 MHz): δ 7.58 (d, J = 8.0 Hz, 1 H), 7.49 (d, J = 8.0 Hz, 1 H), 7.31 (d, J = 7.5 Hz, 1 H), 7.29–7.24 (m, 4 H), 2.87 (t, J = 6.6 Hz, 2 H), 2.76 (t, J = 5.7 Hz, 2 H), 2.24 (br s, 2 H), 1.87–1.77 (m, 2 H) ppm; ¹³C {¹H} NMR (CDCl₃, 125.8 MHz): 146.2, 133.0, 132.9, 129.7, 126.7, 118.2, 112.4, 41.5, 34.4, 32.0 ppm; IR: ν = 3364, 2933, 2867, 2223, 1710, 1661, 1599, 1573, 1448, 1364, 1314, 1164, 1035, 844, 759, 665, 539, 508 cm⁻¹; HRMS (ESI) m/z calc. for C₁₀H₁₂N₂Na [M + Na]⁺ 183.0898, found 183.0901.
3-(4-(Trifluoromethyl)phenyl)propan-1-amine (31): obtained as a brown oil (82 mg, 81%); \(^1\)H NMR (CDCl\(_3\), 500.4 MHz): 7.54 (d, \(J = 7.5\) Hz, 2 H), 7.31 (d, \(J = 7.5\) Hz, 2 H), 2.78–2.71 (m, 4 H), 1.80 (tt, \(J = 7.3, 7.2\) Hz, 2 H), 1.36 (br s, 2 H) ppm; \(^{13}\)C \(^1\)H NMR (CDCl\(_3\), 125.8 MHz): 146.9, 128.6, 128.1, 125.2 (q, \(J = 3.4\) Hz), 123.2, 41.5, 34.9, 33.0 ppm; \(^{19}\)F \(^1\)H NMR (CDCl\(_3\), 470.8 MHz): –62.3 ppm; IR: \(\nu = 2934, 2862, 1617, 1585, 1454, 1418, 1322, 1160, 1112, 1065, 1018, 953, 840, 815, 730, 630\) cm\(^{-1}\); HRMS (ESI) m/z calc. for C\(_{10}\)H\(_{13}\)NF\(_3\) [M + H]\(^+\) 204.1002, found 204.1000.

Methyl 4-(3-aminopropyl)benzoate (32): obtained as a colorless solid (91 mg, 94%), mp 104 °C; \(^1\)H NMR (CDCl\(_3\), 500.4 MHz): 7.94 (d, \(J = 7.7\) Hz, 2 H), 7.24 (d, \(J = 7.7\) Hz, 2 H), 3.89 (s, 3 H), 2.75–2.66 (m, 4 H), 2.43–2.00 (m, 2 H), 1.78 (tt, \(J = 7.2, 7.4\) Hz, 2 H) ppm; \(^{13}\)C \(^1\)H NMR (CDCl\(_3\), 125.8 MHz): 166.9, 147.5, 129.6, 128.3, 127.7, 51.8, 41.5, 34.7, 33.2 ppm; IR: \(\nu = 2922, 2857, 1717, 1608, 1574, 1435, 1416, 1392, 1310, 1271, 1210, 1177, 110, 1020, 763, 701\) cm\(^{-1}\); HRMS (ESI) m/z calc. for C\(_{11}\)H\(_{16}\)NO \([\text{M + H}]^+\) 194.1181, found 194.1183.

\(N\)-(4-(3-Aminopropyl)phenyl)acetamide (33): obtained as an off white powder (72 mg, 75%), mp 94 °C; \(^1\)H NMR (DMSO-\(d_6\), 500.4 MHz): \(\delta = 9.91\) (s, 1 H), 7.49 (d, \(J = 8.9\) Hz, 2 H), 7.10 (d, \(J = 8.9\) Hz, 2 H), 4.21 (br s, 2 H), 2.61 (br s, 1 H), 2.55 (t, \(J = 6.6\) Hz, 2 H), 2.52–2.49 (m, 1 H), 2.02 (s, 3 H), 1.77–1.66 (m, 2 H) ppm; \(^{13}\)C \(^1\)H NMR (DMSO-\(d_6\), 125.8 MHz): 168.4, 137.6, 136.6, 128.7, 119.4, 33.1, 32.8, 32.1, 24.3 ppm; IR: \(\nu = 3244, 3180, 3112, 3030, 2930, 1662, 1601, 1536, 1813, 1410, 1370, 1316, 1264, 828, 790, 745\) cm\(^{-1}\); HRMS (ESI) m/z calc. for C\(_{11}\)H\(_{16}\)N\(_2\)ONa [M + Na]\(^+\) 215.1166, found 215.1160.

\(4\)-(3-Aminopropyl)phenyl)methanol (34): obtained as a brown oil (69 mg, 85%); \(^1\)H NMR (CDCl\(_3\), 500.4 MHz): \(\delta = 7.30\) (d, \(J = 8.2\) Hz, 2 H), 7.19 (d, \(J = 8.9\) Hz, 2 H), 4.67 (s, 2 H), 2.74 (t, \(J = 7.1\) Hz, 2 H), 2.67 (t, \(J = 7.9\) Hz, 2 H), 1.78 (tt, \(J = 7.1, 7.9\) Hz, 2 H), 1.51 (br s, 3 H) ppm; \(^{13}\)C \(^1\)H NMR (CDCl\(_3\), 125.8 MHz): 141.4, 138.5, 128.5, 127.1, 65.0, 41.6, 35.2, 32.9 ppm; IR: \(\nu = 3338, 2970, 2933, 2883, 1466, 1407, 1378, 1341, 1306, 1160, 1128, 1108, 951, 817, 644, 487\) cm\(^{-1}\); HRMS (ESI) m/z calc. for C\(_{10}\)H\(_{16}\)NO \([\text{M + H}]^+\) 166.1236, found 166.1232.

3-(3-(1H-Pyrazol-5-yl)phenyl)propan-1-amine (35): obtained as a dark yellow oil (71 mg, 71%); \(^1\)H NMR (CDCl\(_3\), 500.4 MHz): \(\delta = 7.58\)–7.52 (m, 3 H), 7.26 (dd, \(J = 7.5, 7.5\) Hz, 1 H), 7.08
(d, J = 7.5 Hz, 1 H), 6.55 (s, 1 H), 5.15–4.81 (br s, 3 H), 2.70 (tt, J = 7.0, 7.0 Hz, 2 H), 2.61 (t, J = 7.0 Hz, 2 H), 1.76 (t, J = 7.0 Hz, 2 H) ppm; \(^1\)C \{\(^1\)H\} NMR (CDCl\(_3\), 125.8 MHz): 148.7, 142.6, 133.7, 128.9, 128.2, 125.8, 123.5, 102.6, 41.5, 34.8, 30.7 ppm; IR: \(\nu = \) 3158, 3049, 2924, 2855, 1661, 1607, 1587, 1471, 1434, 1352, 1248, 1097, 1041, 923, 907, 794, 759, 699, 609 cm\(^{-1}\); HRMS (ESI) m/z calc. for C\(_{12}\)H\(_{16}\)N\(_3\) [M + H]\(^+\) 202.1343, found 202.1344.

3-(1-Methyl-1H-indazol-5-yl)propan-1-amine (36): obtained as a light brown oil (91 mg, 96%); \(^1\)H NMR (CDCl\(_3\), 500.4 MHz): \(\delta = 7.98\) (s, 1 H), 7.27 (dd, J = 6.8, 7.4 Hz, 1 H), 7.20 (d, J = 7.4 Hz, 1 H), 6.89 (d, J = 6.8 Hz, 1 H), 4.03 (s, 3 H), 2.91 (t, J = 6.9 Hz, 2 H), 2.85–2.59 (m, 2 H), 1.92 (t, J = 8.2 Hz, 2 H), 1.27 (br s, 1 H), 0.97 (br s, 1 H) ppm; \(^13\)C \{\(^1\)H\} NMR (CDCl\(_3\), 125.8 MHz): 140.1, 135.2, 131.4, 126.6, 123.9, 119.7, 107.0, 41.4, 35.7, 32.6, 30.7 ppm; IR: \(\nu = \) 2928, 2848, 2727, 1611, 1463, 1449, 1440, 1432, 1392, 1230, 1152, 987, 970, 954, 817, 783, 744, 730 cm\(^{-1}\); HRMS (ESI) m/z calc. for C\(_{11}\)H\(_{16}\)N\(_3\) [M + H]\(^+\) 190.1344, found 190.1346.

3-(1H-Indol-5-yl)propan-1-amine (37): obtained as a light yellow oil (76 mg, 87%); \(^1\)H NMR (CDCl\(_3\), 500.4 MHz): \(\delta = 8.54\) (br s, 1 H), 7.45 (s, 1 H), 7.29 (d, J = 5.1 Hz, 1 H), 7.15 (s, 1 H), 7.02 (d, J = 5.1 Hz, 1 H), 6.49 (s, 1 H), 2.92–2.71 (m, 4 H), 1.87 (br s, 2 H), 1.34–1.21 (m, 2 H) ppm; \(^13\)C \{\(^1\)H\} NMR (CDCl\(_3\), 125.8 MHz): \(\delta = 134.39\), 133.0, 126.0, 124.4, 122.7, 119.0, 110.8, 101.9, 33.4, 33.2, 29.6 ppm; IR: \(\nu = \) 3229, 2922, 1615, 1512, 1476, 1422, 1343, 1046, 1022, 999, 820, 767 cm\(^{-1}\); HRMS (ESI) m/z calc. for C\(_{11}\)H\(_{15}\)N\(_2\) [M + H]\(^+\) 175.1235, found 175.1239.

tert-Butyl 4-(5-(3-aminopropyl)pyrimidin-2-yl)piperazine-1-carboxylate (38): obtained as an off white powder (86 mg, 53%), mp 126 °C; \(^1\)H NMR (CDCl\(_3\), 500.4 MHz): \(\delta = 8.16\) (s, 2 H), 4.60–4.07 (m, 2 H), 3.74 (br s, 4 H), 3.47 (br s, 4 H), 2.90–2.70 (m, 2 H), 2.48 (br s, 2 H), 1.86–1.69 (m, 2 H), 1.47 (s, 9 H) ppm; \(^13\)C \{\(^1\)H\} NMR (CDCl\(_3\), 125.8 MHz): \(\delta = 180.7\), 157.4, 154.7, 122.3, 79.8, 43.7, 44.4–42.8 (m, 2 C) 43.1, 28.35, 26.6 ppm; IR: \(\nu = \) 2922, 2858, 1683, 1603, 1537, 1487, 1450, 1417, 1365, 1243, 1166, 1126, 1085, 997, 949 cm\(^{-1}\); HRMS (ESI) m/z calc. for C\(_{16}\)H\(_{28}\)N\(_3\)O\(_2\) [M + H]\(^+\) 322.2243, found 322.2238.

5-(exo-Bicyclo[2.2.1]heptan-2-yl)pyrimidine (39): reaction carried out starting from 0.368 mmol of ArBr, obtained as a colorless oil (63 mg, 98%); \(^1\)H NMR (CDCl\(_3\), 500.4 MHz): \(\delta = 9.02\)
(s, 1 H), 8.58 (s, 2 H), 2.72 (dd, \( J = 5.6, 9.3 \) Hz, 1 H), 2.42 (t, \( J = 4.6 \) Hz, 1 H), 2.38 (d, \( J = 3.3 \) Hz, 1 H), 1.83 (ddd, \( J = 2.4, 9.4, 11.2 \) Hz, 1 H), 1.71–1.57 (m, 3 H), 1.48 (dt, \( J = 2.0, 2.0, 10.0 \) Hz, 1 H), 1.42–1.36 (m, 1 H), 1.32–1.23 (m, 2 H) ppm; \(^{13}\)C \{\(^{1}\)H\} NMR (CDCl\(_3\), 125.8 MHz): 156.1, 155.6, 139.8, 42.9, 42.3, 38.4, 36.8, 36.0, 30.2, 28.5 ppm; IR: \( \nu = 3041, 2950, 2870, 1557, 1454, 1411, 1330, 1312, 1298, 1273, 1236, 1208, 1190, 1166, 1138, 1036, 728 \) cm\(^{-1}\); HRMS (ESI) m/z calc. for C\(_{11}\)H\(_{15}\)N\(_2\) [M + H]\(^{+}\) 175.1235, found 175.1238.

2-(4-(exo-Bicyclo[2.2.1]heptan-2-yl)phenyl)-1,3,4-oxadiazole (40): obtained as a colorless solid (113 mg, 94\%), mp 101 °C; \(^{1}\)H NMR (CDCl\(_3\), 500.4 MHz): \( \delta = 8.44 \) (s, 1 H), 7.99 (d, \( J = 7.7 \) Hz, 2 H), 7.37 (d, \( J = 7.7 \) Hz, 2 H), 2.82 (dd, \( J = 5.7, 8.9 \) Hz, 1 H), 2.38–2.34 (m, 2 H), 1.78 (ddd, \( J = 2.2, 9.5, 11.9 \) Hz, 1 H), 1.71–1.57 (m, 3 H), 1.53 (dd, \( J = 2.8, 9.4 \) Hz, 1 H), 1.39 (t, \( J = 9.2 \) Hz, 1 H), 1.34–1.27 (m, 1 H), 1.24 (dd, \( J = 2.8, 9.3 \) Hz, 1 H) ppm; \(^{13}\)C \{\(^{1}\)H\} NMR (CDCl\(_3\), 125.8 MHz): 164.8, 152.3, 152.1, 127.7, 126.9, 120.5, 47.4, 42.6, 39.0, 36.8, 36.1, 30.5, 28.7 ppm; IR: \( \nu = 3110, 2955, 2867, 1611, 1578, 1504, 1493, 1453, 1413, 1097, 1066, 1015, 954, 895, 847, 831, 713 \) cm\(^{-1}\); HRMS (ESI) m/z calc. for C\(_{15}\)H\(_{16}\)N\(_2\)Na [M + Na]\(^{+}\) 263.1160, found 263.1163.

3-(exo-Bicyclo[2.2.1]heptan-2-yl)-5-methoxypyridine (41): obtained as a light brown oil (77 mg, 76\%); \(^{1}\)H NMR (CDCl\(_3\), 500.4 MHz): \( \delta = 8.09 \) (br s, 2 H), 7.02 (s, 1 H), 3.83 (s, 3 H), 2.72 (dd, \( J = 5.6, 9.0 \) Hz, 1 H), 2.38–2.34 (m, 2 H), 1.78 (ddd, \( J = 2.0, 10.0, 11.0 \) Hz, 1 H), 1.65–1.52 (m, 3 H), 1.49 (dd, \( J = 2.5, 9.7 \) Hz, 1 H), 1.36 (t, \( J = 9.0 \) Hz, 1 H), 1.30–1.24 (m, 1 H), 1.21 (dd, \( J = 2.8, 9.3 \) Hz, 1 H) ppm; \(^{13}\)C \{\(^{1}\)H\} NMR (CDCl\(_3\), 125.8 MHz): 155.5, 143.4, 141.6, 133.7, 119.5, 55.40, 44.7, 42.6, 38.7, 36.7, 36.1, 30.4, 28.6 ppm; IR: \( \nu = 2949, 2869, 1585, 1456, 1242, 1283, 1264, 1178, 1158, 1039, 866, 716 \) cm\(^{-1}\); HRMS (ESI) m/z calc. for C\(_{13}\)H\(_{18}\)NO [M + H]\(^{+}\) 204.1388, found 204.1392.

5-(exo-Bicyclo[2.2.1]heptan-2-yl)thiophene-2-sulfonamide (42): obtained as a colorless oil (91 mg, 71\%); \(^{1}\)H NMR (CDCl\(_3\), 500.4 MHz): \( \delta = 7.48 \) (d, \( J = 4.1 \) Hz, 1 H), 6.74 (d, \( J = 4.1 \) Hz, 1 H), 5.13 (br s, 2 H), 2.95 (dd, \( J = 5.5, 8.8 \) Hz, 1 H), 2.40–2.35 (m, 2 H), 1.87 (ddd, \( J = 3.4, 9.8, 10.9 \) Hz, 1 H), 1.71–1.57 (m, 3 H), 1.53 (dt, \( J = 2.0, 2.0, 10.0 \) Hz, 1 H), 1.40–1.34 (m, 1 H), 1.29–1.24 (m, 2 H) ppm; \(^{13}\)C \{\(^{1}\)H\} NMR (CDCl\(_3\), 125.8 MHz): 160.4, 138.9, 131.8, 122.7, 44.8, 43.5, 40.5, 36.5, 36.2, 29.7, 28.4 ppm; IR: \( \nu = 3264, 2950, 2870, 1593, 1545, 1440, 1330, 1154, 1083, 1013, 892, 810, 804, 729, 671 \) cm\(^{-1}\); HRMS (ESI) m/z calc. for C\(_{11}\)H\(_{14}\)NO\(_2\)S\(_2\) [M – H]\(^{-}\) 256.0466, found 256.0464.
5-(exo-Bicyclo[2.2.1]heptan-2-yl)pyridin-2-amine (43): obtained as a light brown solid (60 mg, 64%); 1H NMR (CDCl3, 500.4 MHz): δ 7.93 (d, J = 1.9 Hz, 1 H), 7.29 (dd, J = 1.9, 8.3 Hz, 1 H), 6.44 (d, J = 8.3 Hz, 1 H), 6.31 (br s, 2 H), 6.20 (dd, J = 5.9, 8.9 Hz, 1 H), 2.34 (br s, 1 H), 2.26 (br s, 1 H), 1.72 (ddd, J = 3.3, 9.1, 10.0 Hz, 1 H), 1.60–1.55 (m, 3 H), 1.47 (dt, J = 1.9, 1.9, 10.1 Hz, 1 H), 1.36–1.20 (m, 2 H), 1.17 (d, J = 8.3 Hz, 1 H) ppm; 13C {1H} NMR (CDCl3, 125.8 MHz): 156.2, 146.4, 136.7, 132.8, 108.2, 44.2, 42.9, 38.8, 36.7, 35.9, 30.4, 28.7 ppm; IR: ν = 3352, 3186, 2948, 2868, 1621, 1499, 1454, 1392, 1257, 1204, 1147, 823, 766, 742 cm⁻¹; HRMS (ESI) m/z calc. for C13H17N2 [M + H]⁺ 189.1392, found 189.1394.

3-(Naphthalen-1-yl)propyl acetate (44): obtained as a colorless oil (108 mg, 95%); 1H NMR (CDCl3, 500.4 MHz): δ 8.06 (d, J = 8.4 Hz, 1 H), 7.89 (d, J = 7.9 Hz, 1 H), 7.76 (d, J = 7.9 Hz, 1 H), 7.57–7.49 (m, 2 H), 7.43 (t, J = 7.8 Hz, 1 H), 7.36 (d, J = 6.7 Hz, 1 H), 4.20 (t, J = 6.7 Hz, 2 H), 3.19 (t, J = 8.0 Hz, 2 H), 1.92 (tt, J = 6.7, 8.0 Hz, 2 H), 2.11 (s, 3 H) ppm; 13C NMR (CDCl3, 125.8 MHz): 171.1, 137.2, 133.9, 131.7, 128.8, 126.8, 126.0, 125.8, 125.4, 125.3, 123.5, 64.0, 29.4, 29.2, 20.9 ppm; IR: ν = 2954, 1733, 1596, 1510, 1464, 1434, 1386, 1232, 1166, 1038, 976, 950, 876, 791, 776, 734 cm⁻¹; HRMS (ESI) m/z calc. for C15H16O2Na [M + Na]⁺ 251.1048, found 251.1049.

3-(3-(1H-Pyrazol-5-yl)phenyl)propyl acetate (45): obtained as a pale yellow oil (88 mg, 72%); 1H NMR (CDCl3, 500.4 MHz): δ 12.8–10.2 (br s, 1 H), 7.61-7.59 (m, 3 H), 7.32 (dd, J = 8.0, 7.5 Hz, 1 H), 7.15 (d, J = 7.5 Hz, 1 H), 6.61 (s, 1 H), 4.10 (t, J = 6.5 Hz, 2 H), 2.71 (t, J = 7.5 Hz, 2 H), 2.05 (s, 3 H), 1.92 (tt, J = 6.5, 7.5 Hz, 2 H) ppm; 13C NMR (CDCl3, 125.8 MHz): 171.5, 149.1, 141.9, 133.5, 132.3, 129.1, 128.3, 125.9, 123.7, 102.8, 64.0, 32.3, 30.3, 21.2 ppm; IR: ν = 3173, 3055, 2954, 1733, 1610, 1470, 1450, 1366, 1095, 1037, 972, 933, 898, 764, 699, 605 cm⁻¹; HRMS (ESI) m/z calc. for C14H16N2O2Na [M + Na]⁺ 267.1109, found 267.1121.

3-(4-Hydroxyphenyl)propyl acetate (46): obtained as a light brown oil (66 mg, 68%); 1H NMR (CDCl3, 500.4 MHz): δ 7.04 (dd, J = 8.0, 2.0 Hz, 2 H), 6.79 (dd, J = 8.0, 2.0 Hz, 2 H), 5.29 (s br, 1 H), 4.08 (m, 2 H), 2.61 (t, J = 7.5 Hz, 2 H), 2.06 (s, 3 H), 1.93 (m, 2 H) ppm; 13C NMR (CDCl3, 125.8 MHz): 171.8, 154.1, 133.3, 129.6, 115.4, 64.1, 31.3, 30.5, 21.2 ppm; IR: ν = 3385, 3090, 2905, 1734, 1707, 1614, 1596, 1390, 1229, 1172, 1035, 846, 822, 746, 555 cm⁻¹; HRMS (ESI) m/z calc. for C11H13O3 [M - H]⁻ 193.0865, found 193.0864.
3-(Benzofuran-5-yl)propyl acetate (47): obtained as a colorless oil (95 mg, 87%); $^1$H NMR (CDCl$_3$, 500.4 MHz): $\delta$ 7.60 (d, $J = 2.0$ Hz, 1 H), 7.43-7.40 (m, 2 H), 7.12 (d, $J = 8.5$, 1.5 Hz, 1 H), 6.71 (dd, $J = 1.5$, 2.0 Hz, 1 H), 4.10 (t, $J = 7.0$ Hz, 2 H), 2.78 (t, $J = 7.5$ Hz, 2 H), 2.06 (s, 3 H), 1.99 (tt, $J = 7.0$, 7.5 Hz, 2 H) ppm; $^{13}$C NMR (CDCl$_3$, 125.8 MHz): 171.3, 153.8, 145.3, 135.8, 127.7, 125.0, 120.6, 111.3, 106.5, 64.0, 32.3, 30.9, 21.1 ppm; IR: $\nu = 2953$, 1734, 1468, 1445, 1387, 1365, 1197, 1126, 1110, 1031, 978, 884, 813, 691, 631, 606 cm$^{-1}$; HRMS (ESI) m/z calc. for C$_{13}$H$_{14}$O$_3$Na [M + Na]$^+$ 241.0841, found 251.0844.

3-(1H-Indol-5-yl)propyl acetate (48): obtained as a white crystalline solid (81 mg, 75%); mp 121 °C; $^1$H NMR (CDCl$_3$, 500.4 MHz): $\delta$ 8.10 (s br, 1 H), 7.46 (s, 1 H), 7.31 (d, $J = 8.0$ Hz, 1 H), 7.18 (s, 1 H), 7.04 (d, $J = 8.0$ Hz, 1 H), 6.51 (s, 1 H), 4.13 (t, $J = 6.5$ Hz, 2 H), 2.80 (t, $J = 7.5$ Hz, 2 H), 2.09 (s, 3 H), 1.93 (tt, $J = 6.5$, 7.5 Hz, 2 H) ppm; $^{13}$C NMR (CDCl$_3$, 125.8 MHz): 171.6, 134.6, 132.6, 128.3, 124.6, 123.0, 120.1, 111.1, 102.3, 64.3, 32.4, 31.1, 21.2 ppm; IR: $\nu = 3281$, 2852, 1702, 1368, 1238, 1142, 1070, 896, 868, 809, 760, 731, 631, 573 cm$^{-1}$; HRMS (ESI) m/z calc. for C$_{13}$H$_{16}$NO$_2$ [M + H]$^+$ 218.1181, found 218.1186.

$N$-(3-(4-Fluorophenyl)propyl)aniline (49): obtained as a pale yellow oil (102 mg, 89%); $^1$H NMR (CDCl$_3$, 500.4 MHz): $\delta$ 7.18–7.09 (m, 4 H), 6.79 (t, $J = 8.5$ Hz, 2 H), 6.68 (t, $J = 7.3$ Hz, 1 H), 6.56 (t, $J = 7.8$ Hz, 2 H), 3.57 (br s, 1 H), 3.11 (t, $J = 7.3$ Hz, 2 H), 2.68 (t, $J = 7.3$ Hz, 2 H), 1.90 (q, $J = 7.3$ Hz, 2 H) ppm; $^{13}$C ($^1$H) NMR (CDCl$_3$, 125.8 MHz): 161.5 (d, $J = 240.9$ Hz), 148.5, 137.5 (d, $J = 3.9$ Hz), 129.9 (d, $J = 9.0$ Hz), 129.4, 117.4, 115.2 (d, $J = 21.1$ Hz), 112.9, 43.4, 32.7, 31.4 ppm; $^{19}$F ($^1$H) NMR (CDCl$_3$, 470.8 MHz): $–117.5$ ppm; IR: $\nu = 2932$, 2860, 1601, 1505, 1476, 1454, 1430, 1318, 1256, 1218, 1179, 1156, 1095, 869, 848, 820, 747, 691, 542, 500 cm$^{-1}$; HRMS (ESI) m/z calc. for C$_{15}$H$_{16}$NF [M]$^+$ 229.1267, found 229.1260.

Methyl (S)-2-((tert-butoxycarbonyl)amino)-3-(4-(3-(phenylamino)propyl)phenyl)propanoate (50): obtained as a colorless oil (158 mg, 76%); $[\alpha]_D^{20} = -89.5$ (CHCl$_3$, $c = 1.0$); $^1$H NMR (CDCl$_3$, 500.4 MHz): $\delta$ 7.18 (t, $J = 7.4$ Hz, 2 H), 7.14 (d, $J = 8.2$ Hz, 2 H), 7.07 (d, $J = 7.4$ Hz, 2 H), 6.71 (t, $J = 7.5$ Hz, 1 H), 6.60 (d, $J = 8.5$ Hz, 2 H), 5.04 (d, $J = 9.4$ Hz, 1 H), 4.60 (dd, $J = 9.4$, ...
4.7 Hz, 1 H), 3.88–3.45 (br s, 1 H), 3.71 (s, 3 H), 3.15 (t, \( J = 6.9 \) Hz, 2 H), 3.13–3.01 (m, 2 H), 2.72 (t, \( J = 7.8 \) Hz, 2 H), 1.92 (tt, \( J = 6.9, 7.8 \) Hz, 2 H), 1.44 (s, 9 H) ppm; \(^{13}\)C \(^{1}\)H NMR (CDCl\(_3\), 125.8 MHz): 172.3, 155.1, 148.3, 140.3, 133.5, 129.3, 129.2, 128.5, 117.2, 112.7, 79.8, 54.4, 52.1, 43.4, 37.9, 32.9, 30.9, 28.3 ppm; IR: \( \nu = 3352, 2976, 1742, 1704, 1602, 1503, 1435, 1365, 1320, 1252, 1171, 1161, 1155, 1058, 1020, 991, 910, 748, 732, 692 \) cm\(^{-1}\); HRMS (ESI) m/z calc. for C\(_{24}\)H\(_{32}\)N\(_2\)O\(_4\)Na [M + Na]\(^+\) 435.2260, found 435.2263.

N-(3-(2-Chlorophenyl)propyl)aniline (51): obtained as a yellow oil (108 mg, 88%); \(^1\)H NMR (CDCl\(_3\), 500.4 MHz): \( \delta = 7.33 \) (d, \( J = 7.4 \) Hz, 1 H), 7.22–7.09 (m, 5 H), 6.68 (t, \( J = 7.4 \) Hz, 1 H), 6.58 (d, \( J = 8.1 \) Hz, 2 H), 3.62 (br s, 1 H), 3.15 (t, \( J = 6.8 \) Hz, 2 H), 2.83 (t, \( J = 7.6 \) Hz, 2 H), 1.92 (tt, \( J = 6.8, 7.6 \) Hz, 2 H) ppm; \(^{13}\)C \(^{1}\)H NMR (CDCl\(_3\), 125.8 MHz): 148.5, 139.4, 134.1, 130.6, 129.7, 129.4, 127.7, 127.1, 117.4, 112.9, 43.6, 31.3, 29.7 ppm; IR: \( \nu = 3310, 2930, 2862, 1601, 1504, 1473, 1256, 1153, 1131, 1051, 992, 744, 691, 680, 508 \) cm\(^{-1}\); HRMS (ESI) m/z calc. for C\(_{15}\)H\(_{17}\)NCl [M + H]\(^+\) 246.1050, found 246.1048.

1-(4-(3-((Phenylamino)propyl)phenyl)ethan-1-one (52): obtained as a colorless crystalline solid (120 mg, 95%); mp 104–105 °C, \(^1\)H NMR (CDCl\(_3\), 500.4 MHz): \( \delta = 7.90 \) (d, \( J = 7.6 \) Hz, 2 H), 7.30 (d, \( J = 7.6 \) Hz, 2 H), 7.18 (t, \( J = 7.6 \) Hz, 2 H), 6.71 (t, \( J = 7.6 \) Hz, 1 H), 6.58 (d, \( J = 7.6 \) Hz, 2 H), 3.64 (br s, 1 H), 3.11 (t, \( J = 7.5 \) Hz, 2 H), 2.68 (t, \( J = 7.5 \) Hz, 2 H), 2.59 (s, 3 H), 1.98 (q, \( J = 7.5 \) Hz, 2 H) ppm; \(^{13}\)C \(^{1}\)H NMR (CDCl\(_3\), 125.8 MHz): 197.9, 148.3, 147.7, 135.4, 129.4, 128.8 \([\times 2]\), 117.5, 112.9, 43.4, 33.6, 30.9, 26.8 ppm; IR: \( \nu = 3358, 2118, 1642, 1604, 1503, 1413, 1361, 1258, 1236, 1188, 1082, 891, 870, 748, 693, 614, 539 \) cm\(^{-1}\); HRMS (ESI) m/z calc. for C\(_{17}\)H\(_{20}\)NO [M + H]\(^+\) 254.1545, found 254.1549.

tert-Butyl 5-(3-((phenylamino)propyl)-1H-indazole-1-carboxylate (53): obtained as a yellow oil (165 mg, 94%); \(^1\)H NMR (CDCl\(_3\), 500.4 MHz): \( \delta = 8.12 \) (s, 1 H), 8.08 (s, 1 H), 7.64 (d, \( J = 8.3 \) Hz, 1 H), 7.20–7.14 (m, 3 H), 6.70 (t, \( J = 7.5 \) Hz, 1 H), 6.59 (d, \( J = 8.1 \) Hz, 2 H), 3.65 (br s, 1 H), 3.18 (t, \( J = 6.8 \) Hz, 2 H), 2.91 (t, \( J = 8.0 \) Hz, 2 H), 2.03 (m, 2 H), 1.72 (s, 9 H) ppm; \(^{13}\)C \(^{1}\)H NMR (CDCl\(_3\), 125.8 MHz): 149.6, 148.4, 143.6, 140.5, 139.6, 129.4, 125.0, 124.5, 121.1, 117.4, 114.1, 112.9, 85.0, 43.5, 34.2, 31.4, 28.4 ppm; IR: \( \nu = 3342, 2980, 2854, 1735, 1712, 1602, 1480, 1345, 1291, 1251, 1150, 1028, 938, 764, 748, 730, 692 \) cm\(^{-1}\); HRMS (ESI) m/z calc. for C\(_{21}\)H\(_{26}\)N\(_3\)O\(_2\) [M + H]\(^+\) 352.2025, found 352.2023.
3-(2-(Tetrahydro-2H-pyran-4-yl)phenyl)propyl acetate (55): obtained as a crystalline powder (127 mg, 97%), mp 46 °C; $^1$H NMR (CDCl$_3$, 500.4 MHz): $\delta$ 7.28–7.25 (m, 1 H), 7.24–7.20 (m, 1 H), 7.18–7.14 (m, 2 H), 4.16–4.09 (m, 4 H), 3.56 (t, $J$ = 11.2 Hz, 2 H), 2.99 (tt, $J$ = 11.9, 3.0 Hz, 1 H), 2.75 (t, $J$ = 8.1 Hz, 2 H), 2.09 (s, 3 H), 1.96–1.94 (m, 4 H), 1.69–1.64 (m, 2 H) ppm; $^{13}$C {$^1$H} NMR (CDCl$_3$, 125.8 MHz): 171.0, 143.3, 138.8, 129.5, 126.6, 126.2, 126.1, 68.6, 63.9, 36.8, 34.0, 30.5, 29.0, 20.9 ppm; IR: $\nu$ = 2923, 2848, 1734, 1493, 1465, 1385, 1365, 1236, 1126, 1087, 1034, 1019, 980, 901, 838, 764 cm$^{-1}$; HRMS (ESI) m/z calc. for C$_{16}$H$_{23}$O$_3$ [M + H]$^+$ 263.1647, found 263.1653.

2-Benzyl-6-(tetrahydro-2H-pyran-4-yl)pyridine (57): obtained as a light yellow oil (91 mg, 72%); $^1$H NMR (CDCl$_3$, 500.4 MHz): $\delta$ 7.52 (d, $J$ = 7.9 Hz, 1 H), 7.4–7.27 (m, 4 H), 7.25–7.20 (m, 1 H), 7.00 (d, $J$ = 7.7 Hz, 1 H), 6.92 (d, $J$ = 7.7 Hz, 1 H), 4.15 (s, 2 H), 4.11 (dt, $J$ = 10.9, 2.7 Hz, 2 H), 3.61–3.53 (m, 2 H), 2.98 (q, $J$ = 7.8 Hz, 1 H), 1.95–1.87 (m, 4 H) ppm; $^{13}$C {$^1$H} NMR (CDCl$_3$, 125.8 MHz): 163.8, 160.3, 139.6, 136.9, 129.0, 128.4, 126.2, 120.6, 117.8, 68.1, 44.7, 43.4, 32.5 ppm; IR: $\nu$ = 2949, 2917, 2841, 1588, 1575, 1494, 1451, 1386, 1237, 1128, 1086, 1029, 980, 866, 823, 774 cm$^{-1}$; HRMS (ESI) m/z calc. for C$_{17}$H$_{20}$NO [M + H]$^+$ 254.1545, found 254.1548.

2,6-Dibenzylpyridine (58): obtained as a light yellow oil (24 mg, 19%); $^1$H NMR (CDCl$_3$, 500.4 MHz): $\delta$ 7.46 (t, $J$ = 7.9 Hz, 1 H), 7.34–7.26 (m, 8 H), 7.26–7.21 (m, 2 H), 6.90 (d, $J$ = 7.2 Hz, 2 H), 4.18 (s, 4 H) ppm; $^{13}$C {$^1$H} NMR (CDCl$_3$, 125.8 MHz): 160.4, 139.5, 136.9, 129.1, 128.4, 126.2, 120.5, 44.5 ppm; IR: $\nu$ = 3026, 2919, 1588, 1573, 1494, 1451, 1386, 1237, 1128, 1086, 1029, 769, 737, 696 cm$^{-1}$; HRMS (ESI) m/z calc. for C$_{19}$H$_{18}$N [M + H]$^+$ 260.1439, found 260.1445.

Triethylammonium phenylbis(catecholato)silicate (59): obtained as a white powder using THF as solvent (3.28 g, 93%), mp = 203 °C; $^1$H NMR (DMSO-d$_6$, 500.4 MHz): $\delta$ 8.79 (br. s, 1 H), 7.51 (d, $J$ = 7.0 Hz, 2 H), 7.16–7.10 (m, 3 H), 6.63–6.58 (m, 4 H), 6.51–6.48 (m, 4 H), 3.06 (q, $J$ = 7.5 Hz, 6 H), 1.14 (t, $J$ = 7.5 Hz, 9 H) ppm; $^{13}$C {$^1$H} NMR (DMSO-d$_6$, 125.8 MHz): $\delta$ 150.8, 142.3, 135.1, 128.2, 127.1, 117.9, 110.2, 46.2, 9.0 ppm; IR: $\nu$ = 1483, 1439, 1388, 1351, 1240, 1227, 1157, 1113, 1101, 1012, 889, 819, 761, 737, 723, 700 cm$^{-1}$; HRMS (ESI) m/z calc. for C$_{18}$H$_{13}$O$_3$Si [M – HNEt$_3$]$^-$ 321.0582, found 321.0588; $E_{pa}$ = + 0.76 V vs SCE.

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Triethylammonium benzylbis(methyl-2-hydroxyisobutyro)silicate (60): Alpha-hydroxyisobutyric acid (477 mg, 4.89 mmol, 1.95 equiv) was introduced into a microwave vial with a stirring bar. The vial was sealed with a Teflon-coated septum cap then purged with N₂ and evacuated four times. 1,4-Dioxane (5 mL) and triethylamine (0.39 mL, 287 mg, 2.88 mmol, 1.2 equiv) were introduced, and the resulting slurry was stirred at rt for 15 min before addition of benzyltrimethoxysilane (500 mg, 2.35 mmol, 1 equiv). The reaction mixture was refluxed for 16 h, then the vial was cooled to rt and the reaction mixture concentrated to a glue before the Et₂O (25 mL) was introduced. The mixture was then sonicated 15 min to allow the corresponding product to precipitate as a white powder. The filter cake was finally washed with Et₂O to afford 60 as a white powder (810 mg, 81%), mp = 96 °C; ¹H NMR (DMSO-d₆, 500.4 MHz): δ 8.89 (br. s, 1 H), 7.09 (t, J = 7.1 Hz, 2 H), 6.99 (t, J = 7.1 Hz, 2 H), 6.93 (d, J = 7.1 Hz, 1 H), 3.85 (q, J = 7.3 Hz, 6 H), 2.04–1.93 (m, 2 H), 1.16 (t, J = 7.3 Hz, 9 H), 1.10 (s, 6 H), 0.84 (s, 6 H) ppm; ¹³C {¹H} NMR (DMSO-d₆, 125.8 MHz): δ 179.2, 141.8, 129.1, 127.8, 123.5, 73.5, 46.2, 28.9, 28.3, 26.7, 9.1 ppm; IR: ν = 1707, 1668, 1470, 1378, 1357, 1325, 1204, 1187, 1164, 1012, 861, 810, 796, 778, 694 cm⁻¹; HRMS (ESI) m/z calc. for C₁₅H₁₉O₇Si [M – HNEt₃]⁻ 323.0950, found 323.0945; E_{pa} > + 2.00 V vs SCE.
Spectral data

$^1$H NMR (CDCl$_3$, 500.4 MHz) of triethylammonium benzylbis(catecholato)silicate (I)

$^{13}$C $\{^1$H$\}$ NMR (CDCl$_3$, 125.8 MHz) of triethylammonium benzylbis(catecholato)silicate (I)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of triethylammonium benzylbis(catecholato)silicate (1) after 3 months on benchtop.
$^1$H NMR (CDCl$_3$, 500.4 MHz) of triethylammonium cyclohexylbis(catecholato)silicate (2)

$^{13}$C \{\textsuperscript{1}H\} NMR (CDCl$_3$, 125.8 MHz) of triethylammonium cyclohexylbis(catecholato)silicate (2)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of triethylammonium cyclohexylbis(catecholato)silicate (2) after 3 months on benchtop.
$^1$H NMR (CDCl$_3$, 500.4 MHz) of triethylammonium exo-2-bicyclo[2.2.1]heptylbis(catecholato)silicate (3)

$^{13}$C NMR {^1$H$} (CDCl$_3$, 125.8 MHz) of triethylammonium exo-2-bicyclo[2.2.1]heptylbis(catecholato)silicate (3)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of triethylammonium exo-2-bicyclo[2.2.1]heptylbis(catecholato)silicate (3) after 3 months on benchtop.
$^1$H NMR (CDCl$_3$, 500.4 MHz) of triethylammonium methylbis(catecholato)silicate (4)

$^{13}$C NMR $^1$H (CDCl$_3$, 125.8 MHz) of triethylammonium methylbis(catecholato)silicate (4)
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$\text{H NMR (CDCl}_3, 500.4 \text{ MHz)}$ of triethylammonium hexylbis(catecholato)silicate ($5$)

$\text{^{13}C NMR \{} ^{1}\text{H} \text{ (CDCl}_3, 125.8 \text{ MHz)}$ of triethylammonium hexylbis(catecholato)silicate ($5$)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of triethylammonium chloromethylbis(catecholato) silicate (6)

$^{13}$C NMR $^1$H (CDCl$_3$, 125.8 MHz) of triethylammonium chloromethylbis(catecholato) silicate (6)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of triethylammonium 2-(3-cyclohexenyl)ethylbis(catecholato)silicate (7).

$^{13}$C NMR {$^1$H} (CDCl$_3$, 125.8 MHz) of triethylammonium 2-(3-cyclohexenyl)ethylbis(catecholato)silicate (7).
$^1$H NMR (DMSO–d$_6$, 500.4 MHz) of diisopropylammonium 2-(3,4-epoxycyclohexyl)ethylbis(catecholato)silicate (8)

$^{13}$C NMR ($^1$H) (DMSO–d$_6$, 125.8 MHz) of diisopropylammonium 2-(3,4-epoxycyclohexyl)ethylbis(catecholato)silicate (8)
$^1$H NMR (CD$_3$CN, 500.4 MHz) of diisopropylammonium $N$-[5-(bis(catecholato)silicate)-2-aza-1-oxopentyl]caprolactam (9)

$^{13}$C NMR {${^1}$H} (DMSO-$d_6$, 125.8 MHz) of diisopropylammonium $N$-[5-(bis(catecholato)silicate)-2-aza-1-oxopentyl]caprolactam (9)
$^1$H NMR (DMSO-$d_6$, 500.4 MHz) of diisopropylammonium 3-(phenylamino)propylbis(catecholato)silicate (10)

$^{13}$C NMR {$^1$H} (DMSO-$d_6$, 125.8 MHz) of diisopropylammonium 3-(phenylamino)propylbis(catecholato) silicate (10)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of triethylammonium 2-(pyridin-2-yl)ethylbis(catecholato)silicate (11)

$^{13}$C NMR {$^1$H} (CDCl$_3$, 125.8 MHz) of triethylammonium 2-(pyridin-2-yl)ethylbis(catecholato)silicate (11)

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$^1$H NMR (CDCl$_3$, 500.4 MHz) of diisopropylammonium 3,3,4,4,5,5,6,6,6-nonafluorohexylbis(catecholato)silicate (12)

$^{13}$C NMR {$^1$H} (CDCl$_3$, 125.8 MHz) of diisopropylammonium 3,3,4,4,5,5,6,6,6-nonafluorohexylbis(catecholato)silicate (12)
$^{19}$F NMR $^{1}H$ (CDCl$_3$, 470.8 MHz) of diisopropylammonium 3,3,4,4,5,5,6,6,6-nonanfloroxybis(catecholato)silicate (12)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of triethylammonium 3-acetoxypropylbis(catecholato)silicate (13)

$^{13}$C NMR ($^1$H) (CDCl$_3$, 125.8 MHz) of triethylammonium 3-acetoxypropylbis(catecholato)silicate (13)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of triethylammonium 3-ace-toxypropylbis(catecholato)silicate (13) after 3 months on benchtop.
$^1$H NMR (DMSO-$d_6$, 500.4 MHz) of 3-ammoniumpropylbis(catecholato)silicate (14)

$^{13}$C NMR {$^1$H} (DMSO-$d_6$, 125.8 MHz) of 3-ammoniumpropylbis(catecholato)silicate (14)
$^1$H NMR (DMSO-$d_6$, 500.4 MHz) of 3-ammoniumpropylbis(catecholato)silicate (14) after 3 months on benchtop.
$^\text{1}H$ NMR (CDCl$_3$, 500.4 MHz) of 1-benzyl-4-methoxybenzene (15)

$^{13}$C NMR (CDCl$_3$, 125.8 MHz) of 1-benzyl-4-methoxybenzene (15)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of 1-cyclohexyl-4-methoxybenzene (16)

$^{13}$C NMR {$^1$H} (CDCl$_3$, 125.8 MHz) of 1-cyclohexyl-4-methoxybenzene (16)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of exo-2-(4-methoxyphenyl)bicyclo[2.2.1]heptane (17)

$^{13}$C NMR {$^1$H} (CDCl$_3$, 125.8 MHz) of exo-2-(4-methoxyphenyl)bicyclo[2.2.1]heptane (17)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of 1-hexyl-4-methoxybenzene (19)

$^{13}$C NMR {$^1$H} (CDCl$_3$, 125.8 MHz) of 1-hexyl-4-methoxybenzene (19)
$^{1}$H NMR (CDCl$_3$, 500.4 MHz) of 1-(2-(cyclohex-3-en-1-yl)ethyl)-4-methoxybenzene (21)

$^{13}$C NMR {$^1$H} (CDCl$_3$, 125.8 MHz) of 1-(2-(cyclohex-3-en-1-yl)ethyl)-4-methoxybenzene (21)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of $N$-[(3-(4-methoxyphenyl)propyl)-2-aza-1-oxopentyl]caprolactam (23)

$^{13}$C NMR ($^1$H) (CDCl$_3$, 125.8 MHz) of $N$-[(3-(4-methoxyphenyl)propyl)-2-aza-1-oxopentyl]caprolactam (23)

S51
$^1$H NMR (CDCl$_3$, 500.4 MHz) of N-(3-(4-methoxyphenyl)propyl)aniline (24)

$^{13}$C NMR ($^1$H) (CDCl$_3$, 125.8 MHz) of N-(3-(4-methoxyphenyl)propyl)aniline (24)
$^{1}H$ NMR (CDCl₃, 500.4 MHz) of 2-(4-methoxyphenethyl)pyridine (25)

$^{13}C$ NMR {$^{1}H$} (CDCl₃, 125.8 MHz) of 2-(4-methoxyphenethyl)pyridine (25)
S54

$^1$H NMR (CDCl$_3$, 500.4 MHz) of 4-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-1,1'-biphenyl (26)

$^{13}$C NMR ($^1$H} (CDCl$_3$, 125.8 MHz) of 4-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-1,1'-biphenyl (26)
$^{19}$F NMR \{H\} (CDCl$_3$, 470.8 MHz) of 4-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-1,1'-biphenyl (26)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of 3-(4-methoxyphenyl)propyl acetate (27)

$^{13}$C NMR ($^1$H) (CDCl$_3$, 125.8 MHz) of 3-(4-methoxyphenyl)propyl acetate (27)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of 3-(4-methoxyphenyl)propan-1-amine (28)

$^{13}$C NMR {$^1$H} (CDCl$_3$, 125.8 MHz) of 3-(4-methoxyphenyl)propan-1-amine (28)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of 4-(3-aminopropyl)benzonitrile (29)

$^{13}$C NMR ($^1$H) (CDCl$_3$, 125.8 MHz) of 4-(3-aminopropyl)benzonitrile (29)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of 2-(3-aminopropyl)benzonitrile (30)

$^{13}$C NMR {$^1$H} (CDCl$_3$, 125.8 MHz) of 2-(3-aminopropyl)benzonitrile (30)
$^{1}$H NMR (CDCl$_3$, 500.4 MHz) of 3-(4-(trifluoromethyl)phenyl)propan-1-amine (31)

$^{13}$C NMR ($^1$H, CDCl$_3$, 125.8 MHz) of 3-(4-(trifluoromethyl)phenyl)propan-1-amine (31)
$^{19}$F NMR $^{1}H$ (CDCl$_3$, 470.8 MHz) of 3-(4-(trifluoromethyl)phenyl)propan-1-amine (31)
$\text{H NMR (CDCl}_3, 500.4 \text{ MHz) of methyl 4-(3-aminopropyl)benzoate (32)}$

$\text{C NMR} \{^1\text{H}\} (\text{CDCl}_3, 125.8 \text{ MHz})$ of methyl 4-(3-aminopropyl)benzoate (32)
\textsuperscript{1}H NMR (DMSO-\textit{d}_6, 500.4 MHz) of \(N-(4-(3\text{-}aminopropyl)phenyl)acetamide\) (33)

\textsuperscript{13}C NMR \{\textsuperscript{1}H\} (DMSO-\textit{d}_6, 125.8 MHz) of \(N-(4-(3\text{-}aminopropyl)phenyl)acetamide\) (33)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of (4-(3-aminopropyl)phenyl)methanol (34)

$^{13}$C NMR {^1$H$} (CDCl$_3$, 125.8 MHz) of (4-(3-aminopropyl)phenyl)methanol (34)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of 3-(3-(1H-pyrazol-5-yl)phenyl)propan-1-amine (35)

$^{13}$C NMR {$^1$H} (CDCl$_3$, 125.8 MHz) of 3-(3-(1H-pyrazol-5-yl)phenyl)propan-1-amine (35)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of 3-(1-methyl-1H-indazol-5-yl)propan-1-amine (36)

$^{13}$C NMR ($^1$H) (CDCl$_3$, 125.8 MHz) of 3-(1-methyl-1H-indazol-5-yl)propan-1-amine (36)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of 3-(1H-indol-5-yl)propan-1-amine (37)

$^{13}$C NMR {$^1$H} (CDCl$_3$, 125.8 MHz) of 3-(1H-indol-5-yl)propan-1-amine (37)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of tert-butyl 4-(5-(3-aminopropyl)pyrimidin-2-yl)piperazine-1-carboxylate (38)

$^{13}$C NMR ($^1$H) (CDCl$_3$, 125.8 MHz) of tert-butyl 4-(5-(3-aminopropyl)pyrimidin-2-yl)piperazine-1-carboxylate (38)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of 5-(exo-bicyclo[2.2.1]heptan-2-yl)pyrimidine (39)

$^{13}$C NMR ($^1$H) (CDCl$_3$, 125.8 MHz) of 5-(exo-bicyclo[2.2.1]heptan-2-yl)pyrimidine (39)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of 2-(4-(exo-bicyclo[2.2.1]heptan-2-yl)phenyl)-1,3,4-oxadiazole (40)

$^{13}$C NMR {$^1$H} (CDCl$_3$, 125.8 MHz) of 2-(4-(exo-bicyclo[2.2.1]heptan-2-yl)phenyl)-1,3,4-oxadiazole (40)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of 3-(exo-bicyclo[2.2.1]heptan-2-yl)-5-methoxypyridine (41)

$^{13}$C NMR {^1}H} (CDCl$_3$, 125.8 MHz) of 3-(exo-bicyclo[2.2.1]heptan-2-yl)-5-methoxypyridine (41)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of 5-($exo$-bicyclo[2.2.1]heptan-2-yl)thiophene-2-sulfonamide (42)

$^{13}$C NMR {$^1$H} (CDCl$_3$, 125.8 MHz) of 5-($exo$-bicyclo[2.2.1]heptan-2-yl)thiophene-2-sulfonamide (42)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of 5-($exo$-bicyclo[2.2.1]heptan-2-yl)pyridin-2-amine (43)

$^{13}$C NMR (CDCl$_3$, 125.8 MHz) of 5-($exo$-bicyclo[2.2.1]heptan-2-yl)pyridin-2-amine (43)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of 3-(naphthalen-1-yl)propyl acetate (44)

$^{13}$C NMR {${^1}$H} (CDCl$_3$, 125.8 MHz) of 3-(naphthalen-1-yl)propyl acetate (44)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of 3-(3-(1H-pyrazol-5-yl)phenyl)propyl acetate (45)

$^{13}$C NMR ($^1$H) (CDCl$_3$, 125.8 MHz) of 3-(3-(1H-pyrazol-5-yl)phenyl)propyl acetate (45)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of 3-(4-hydroxyphenyl)propyl acetate (46)

$^{13}$C NMR {${^1}$H} (CDCl$_3$, 125.8 MHz) of 3-(4-hydroxyphenyl)propyl acetate (46)
\(^1\)H NMR (CDCl\(_3\), 500.4 MHz) of 3-(benzofuran-5-yl)propyl acetate (47)

\(^{13}\)C NMR \({^1}\)H (CDCl\(_3\), 125.8 MHz) of 3-(benzofuran-5-yl)propyl acetate (47)
1H NMR (CDCl₃, 500.4 MHz) of 3-(1H-indol-5-yl)propyl acetate (48)

13C NMR {1H} (CDCl₃, 125.8 MHz) of 3-(1H-indol-5-yl)propyl acetate (48)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of N-(3-(4-fluorophenyl)propyl)aniline (49)

$^{13}$C NMR {$^1$H} (CDCl$_3$, 125.8 MHz) of N-(3-(4-fluorophenyl)propyl)aniline (49)
\(^{19}\)F NMR \(^{1}\)H (CDCl\(_3\), 470.8 MHz) of \(N\)-(3-(4-fluorophenyl)propyl)aniline (49)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of methyl (S)-2-((tert-butoxycarbonyl)amino)-3-(4-(3-(phenylamino)propyl)phenyl)propanoate (50).

$^{13}$C NMR ($^1$H) (CDCl$_3$, 125.8 MHz) of methyl (S)-2-((tert-butoxycarbonyl)amino)-3-(4-(3-(phenylamino)propyl)phenyl)propanoate (50).
$^1$H NMR (CDCl$_3$, 500.4 MHz) of N-(3-(2-chlorophenyl)propyl)aniline (51)

$^{13}$C NMR {$^1$H} (CDCl$_3$, 125.8 MHz) of N-(3-(2-chlorophenyl)propyl)aniline (51)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of 1-(4-(3-(phenylamino)propyl)phenyl)ethan-1-one (52)

$^{13}$C NMR {^1$H$} (CDCl$_3$, 125.8 MHz) of 1-(4-(3-(phenylamino)propyl)phenyl)ethan-1-one (52)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of tert-butyl 5-(3-(phenylamino)propyl)-1$H$-indazole-1-carboxylate (53)

$^{13}$C NMR ($^1$H) (CDCl$_3$, 125.8 MHz) of tert-butyl 5-(3-(phenylamino)propyl)-1$H$-indazole-1-carboxylate (53)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of 3-(2-(tetrahydro-2H-pyran-4-yl)phenyl)propyl acetate (55)

$^{13}$C NMR ($^1$H) (CDCl$_3$, 125.8 MHz) of 3-(2-(tetrahydro-2H-pyran-4-yl)phenyl)propyl acetate (55)
\(^1\)H NMR (CDCl\(_3\), 500.4 MHz) of 2-benzyl-6-(tetrahydro-2\(H\)-pyran-4-yl)pyridine (57)

\(^{13}\)C NMR \({}^1\text{H}\) (CDCl\(_3\), 125.8 MHz) of 2-benzyl-6-(tetrahydro-2\(H\)-pyran-4-yl)pyridine (57)
$^1$H NMR (CDCl$_3$, 500.4 MHz) of 2,6-dibenzylpyridine (58)

$^{13}$C NMR $^1$H} (CDCl$_3$, 125.8 MHz) of 2,6-dibenzylpyridine (58)
$^1$H NMR (DMSO-$d_6$, 500.4 MHz) of triethylammonium phenylbis(catecholato)silicate (59)

$^{13}$C NMR $^1$H (DMSO-$d_6$, 125.8 MHz) of triethylammonium phenylbis(catecholato)silicate (59)
$^{1}\text{H NMR} \ (\text{DMSO}-d_6, \ 500.4 \ \text{MHz}) \ of \ triethylammonium \ benzylbis(\text{methyl-2-hydroxyisobutyro})\text{silicate} \ (60)$

$^{13}\text{C NMR} \ \{^{1}\text{H}\} \ (\text{DMSO}-d_6, \ 125.8 \ \text{MHz}) \ of \ triethylammonium \ benzylbis(\text{methyl-2-hydroxyisobutyro})\text{silicate} \ (60)$
**Cyclic voltammetry**

Voltammetric measurements were recorded on a CH Instruments: Model 600E Series Electrochemical Analyzer using a standard three electrodes setup in dry and degassed MeCN (10 mL), with ferrocene as internal reference ($E^{0}_{1/2} = + 0.40 \, V \, vs \, SCE$) and tetrabutylammonium hexafluorophosphate as electrolyte (0.10 mmol). Cyclic voltammograms were recorded with a step potential of 0.002 V at a scan rate of 0.1 V/s.