

Supplementary Information for

Novel Ligands from Direct Benzylic Functionalisation of Tris(2-pyridylmethyl)amine

Paolo Zardi,^b Justyna Piekos,^a Carlo Bravin,^a Klaus Wurst,^c Federico Droghetti,^d Mirco Natali,^d Giulia Licini,^{a,e} Alfonso Zambon,^{b,*} and Cristiano Zonta^{a,e,*}

^a*Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1, 35131 Padova, Italy*

^b*Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, via Campi 103, 41125, Modena, Italy*

^c*Department of General, Inorganic and Theoretical Chemistry University of Innsbruck A-6020 Innsbruck, Austria*

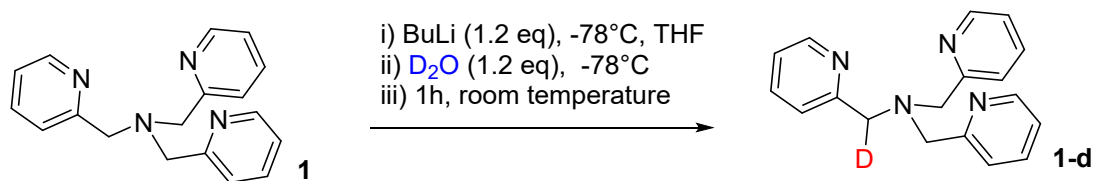
^d*Dipartimento di Scienze Chimiche, Farmaceutiche ed Agrarie, Università di Ferrara, via L. Borsari 46, 44121 Ferrara, Italy*

^e*CIRCC Interuniversity Consortium Chemical Reactivity and Catalysis, Via Celso Ulpiani 27, 70126 Bari, Italy*

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1. H/D exchange experiment



Under argon atmosphere, **1** (100 mg, 0.34 mmol) was dissolved in dry THF (3.5 ml) in a Schlenk flask. After cooling at -78°C, BuLi 2.5 M in hexanes was added (0.165 ml, 0.41 mmol) and the solution was stirred for 30 min. Then, D₂O (7.0 μl, 0.41 mmol) was added and the solution was stirred for 1 h. The reaction was quenched with a saturated NH₄Cl aqueous solution. The solvent was removed under reduced pressure. The resulting brown oil was dissolved in CH₂Cl₂ (10 mL) and the solution washed with a saturated NH₄Cl aqueous solution (3×5 ml). The organic phase was dried over MgSO₄ and evaporated to dryness. The resulting yellow oil was precipitated by crystallization from THF/hexane to give a yellow solid (97.0 mg, 97 %).

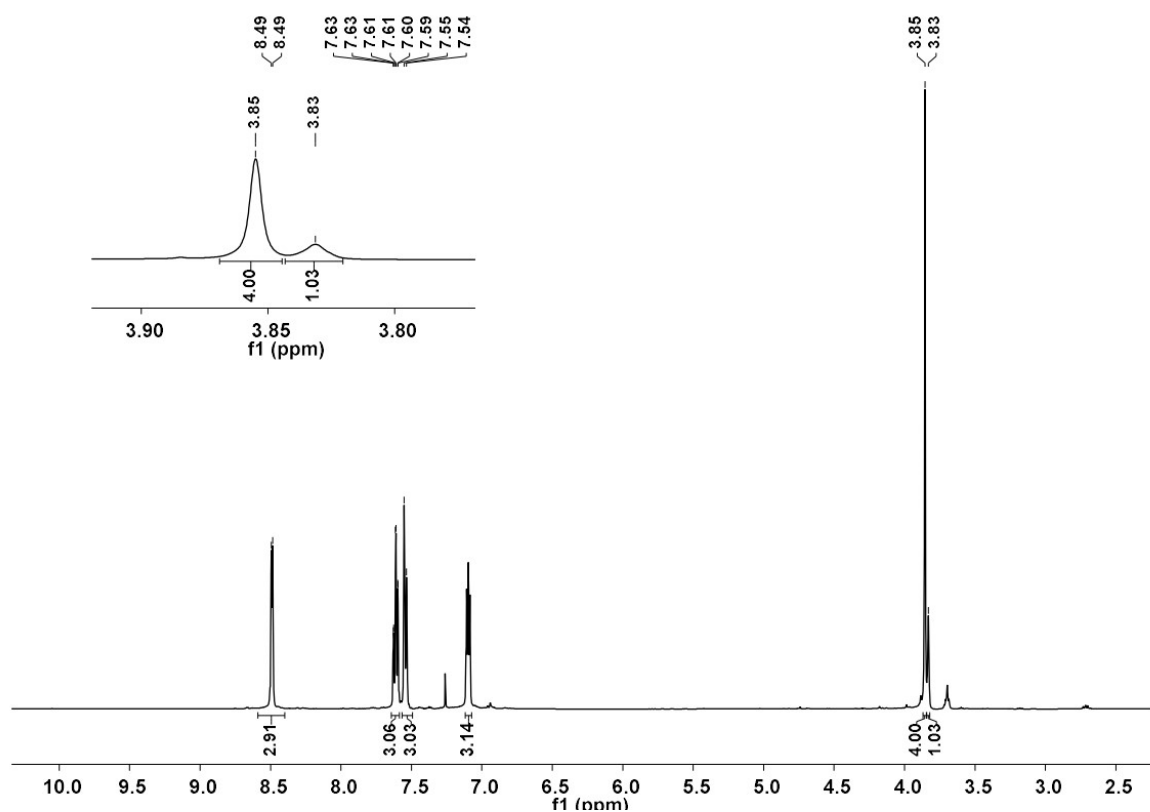


Figure S1. ¹H NMR spectrum of **1-d**.

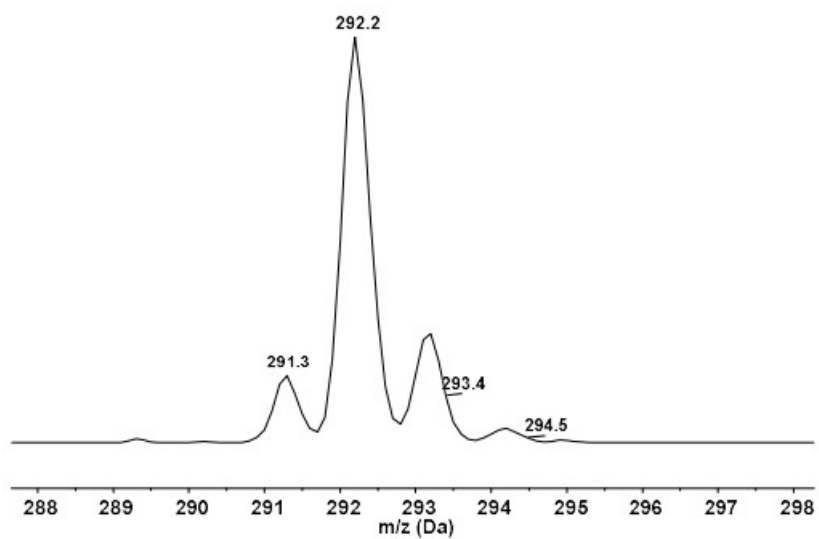
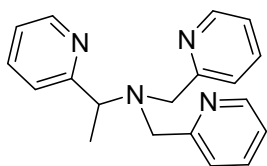


Figure S2. ESI-MS spectrum of 1-d. Calcd for $C_{18}H_{18}N_4D$ [M+1] 292.1667

2. TPMA ligands characterization

2a



^1H NMR (400 MHz, CDCl_3) δ 8.56 (ddd, $J = 4.9, 1.9, 0.9$ Hz, 1H), 8.48 (ddd, $J = 4.9, 1.8, 0.9$ Hz, 2H), 7.63 (m, 3H), 7.55 (d, $J = 7.9$ Hz, 2H), 7.49 (d, $J = 7.9$ Hz, 1H), 7.12 (m, 3H), 4.08 (q, $J = 6.8$ Hz, 1H), 3.99 (d, $J = 15.0$ Hz, 2H), 3.78 (d, $J = 14.9$ Hz, 2H), 1.55 (d, $J = 6.8$ Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 161.97 (C), 160.52 (C), 149.01 (CH), 148.99 (CH), 136.50 (CH), 136.23 (CH), 123.07 (CH), 122.85 (CH), 122.05 (CH), 121.94 (CH), 60.33 (CH), 56.78 (CH_2), 14.57 (CH_3).

HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{21}\text{N}_4$ $[\text{M}+\text{H}]^+$ 305.1761, found 305.1763.

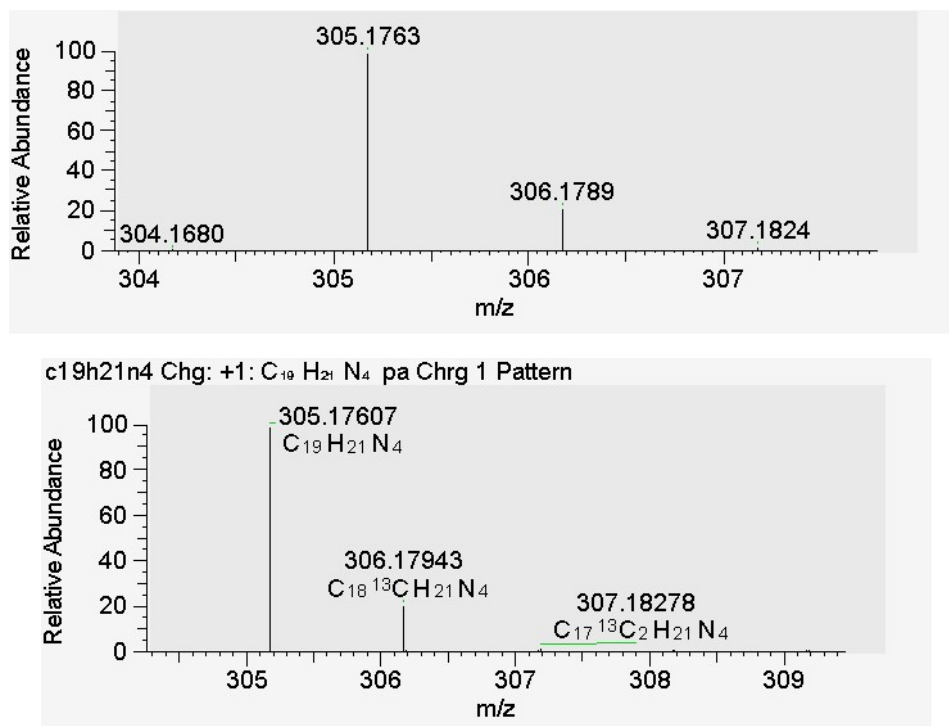
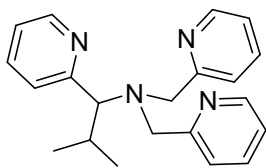


Figure S3. Experimental (top) and simulated (bottom) HR ESI-MS spectrum of 2a.

2b



^1H NMR (600 MHz, CDCl_3) δ 8.67 (d, $J = 4.8$ Hz, 1H), 8.51 (d, $J = 4.8$ Hz, 2H), 7.66 (m, 5H), 7.17 (ddd, $J = 7.6, 4.8, 1.2$ Hz, 1H), 7.13 (m, 3H), 4.11 (d, $J = 15.0$ Hz, 2H), 3.43 (d, $J = 15.0$ Hz, 2H), 3.23 (d, $J = 10.7$ Hz, 1H), 2.69 (m, 1H), 1.23 (d, $J = 6.6$ Hz, 3H), 0.61 (d, $J = 6.5$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 160.63 (C), 157.38 (C), 149.21 (CH), 148.79 (CH), 136.21 (CH), 135.45 (CH), 125.12 (CH), 122.71 (CH), 121.76 (CH), 121.66 (CH), 70.95 (CH), 56.45 (CH_2), 28.00 (CH), 20.62 (CH_3), 20.54 (CH_3).

HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{25}\text{N}_4$ $[\text{M}+\text{H}]^+$ 333.2074, found 333.2071.

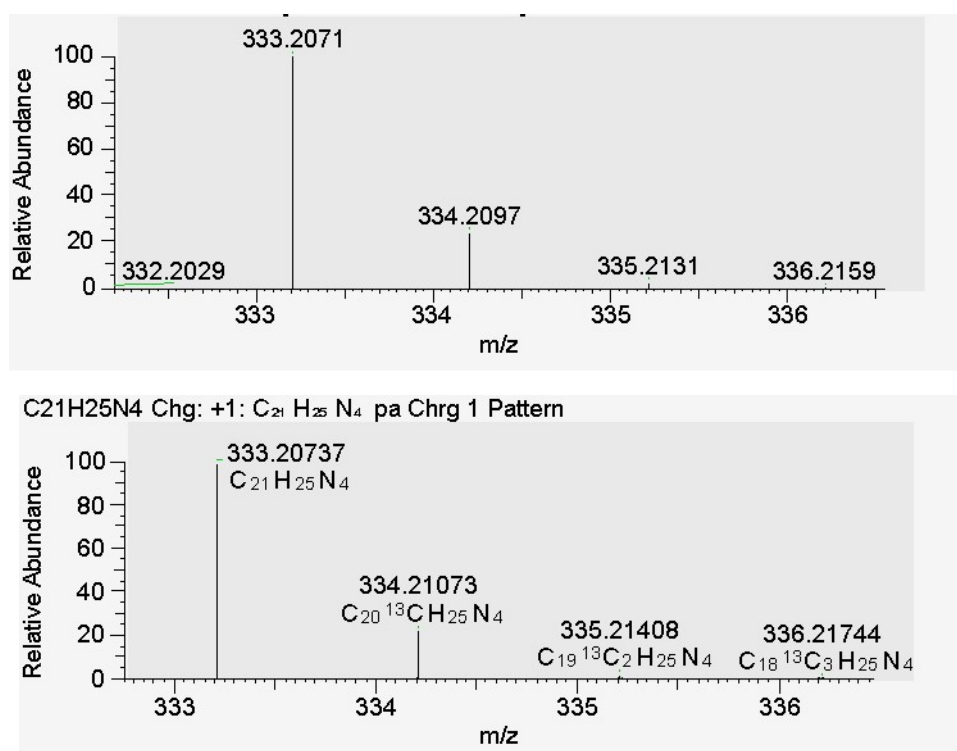
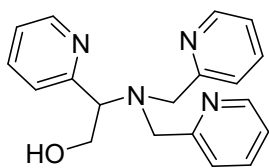


Figure S4. Experimental (top) and simulated (bottom) HR ESI-MS spectrum of 2b.

2c



^1H NMR (600 MHz, CDCl_3) δ 8.59 (d, $J = 4.9$ Hz, 1H), 8.51 (d, $J = 4.9$ Hz, 2H), 7.67 (td, $J = 7.7, 1.8$ Hz, 1H), 7.51 (td, $J = 7.7, 1.6$ Hz, 2H), 7.32 (d, $J = 7.8$ Hz, 1H), 7.27 (d, $J = 7.8$ Hz, 2H), 7.20 (ddd, $J = 7.5, 4.8, 0.9$ Hz, 1H), 7.09 (m, 2H), 4.31 (m, 1H), 4.29 (d, $J = 15.4$ Hz, 2H), 4.16 (dd, $J = 9.2, 4.9$ Hz, 1H), 3.96 (dd, $J = 12.0, 4.9$ Hz, 1H), 3.84 (d, $J = 15.2$ Hz, 2H).

^{13}C NMR (150 MHz, CDCl_3) δ 160.07 (C), 159.06 (C), 149.33 (CH), 148.91 (CH), 136.64 (CH), 136.43 (CH), 123.71 (CH), 123.20 (CH), 122.55 (CH), 122.07 (CH), 67.04 (CH), 61.84 (CH_2), 57.02 (CH_2).

HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{21}\text{N}_4\text{O}$ $[\text{M}+\text{H}]^+$ 321.1710, found 321.1706.

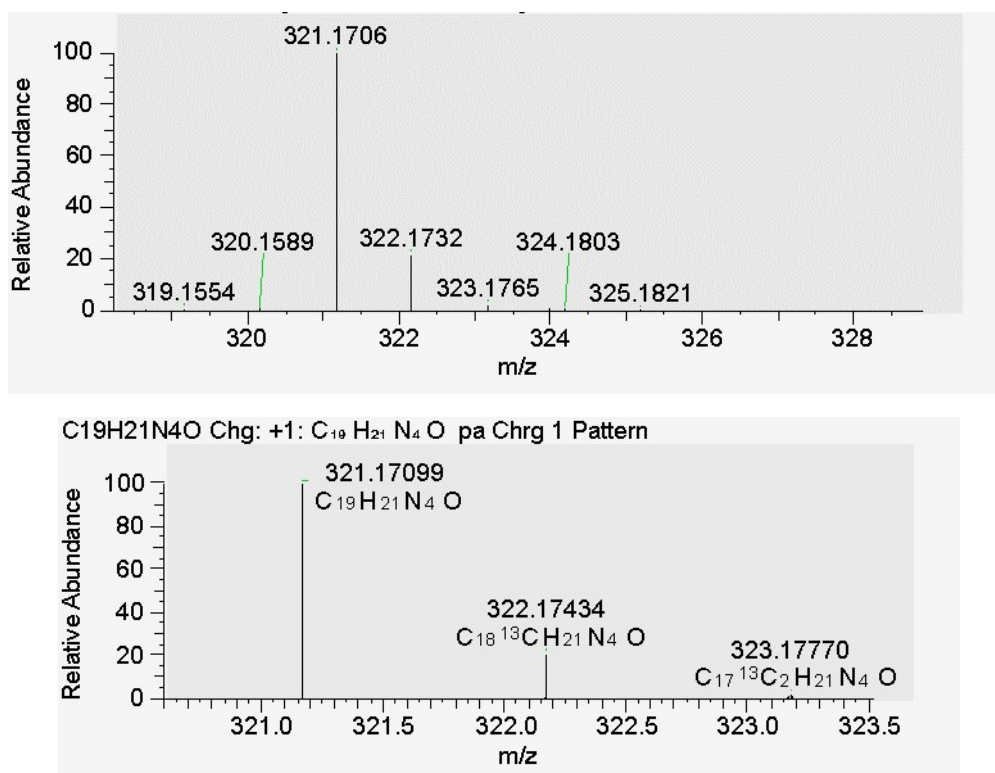
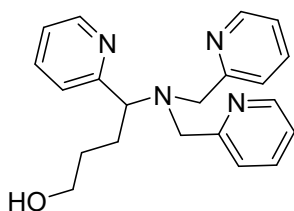


Figure S5. Experimental (top) and simulated (bottom) HR ESI-MS spectrum of 2c.

2e



¹H NMR (400 MHz, CDCl₃) δ 8.59 (d, *J* = 4.9 Hz, 1H), 8.49 (d, *J* = 4.9 Hz, 2H), 7.66 (td, *J* = 7.7, 1.9 Hz, 1H), 7.60 (td, *J* = 7.6, 1.8 Hz, 2H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.17 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H), 7.12 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 2H), 4.06 (d, *J* = 14.6 Hz, 2H), 3.92 (t, *J* = 7.0 Hz, 1H), 3.66 (d, *J* = 15.0 Hz, 2H), 3.65 (m, 1H), 3.55 (m, 1H), 2.34 (m, 1H), 2.11 (m, 1H), 1.61 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 159.85 (C), 159.55 (C), 149.10 (CH), 148.90 (CH), 136.64 (CH), 136.24 (CH), 124.50 (CH), 123.46 (CH), 122.37 (CH), 122.13 (CH), 64.42 (CH₂), 61.73 (CH), 56.71 (CH₂), 30.06 (CH₂), 25.56 (CH₂).

HRMS (ESI): calcd for C₂₁H₂₅N₄O [M+H]⁺ 349.2023, found 349.2014.

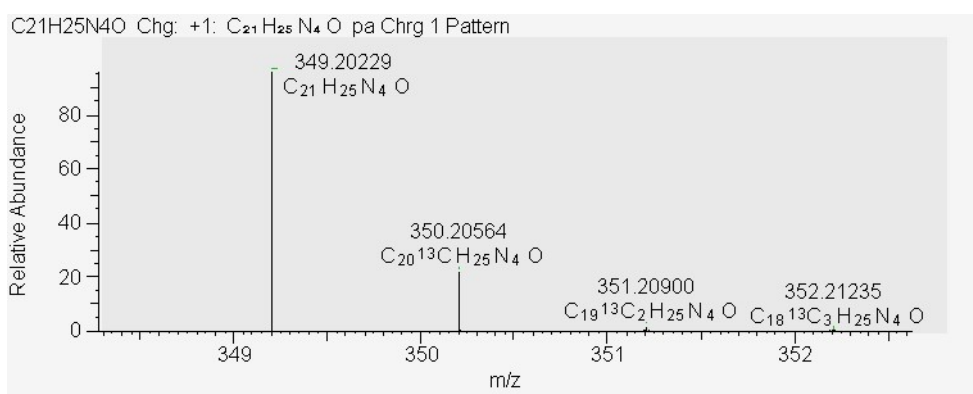
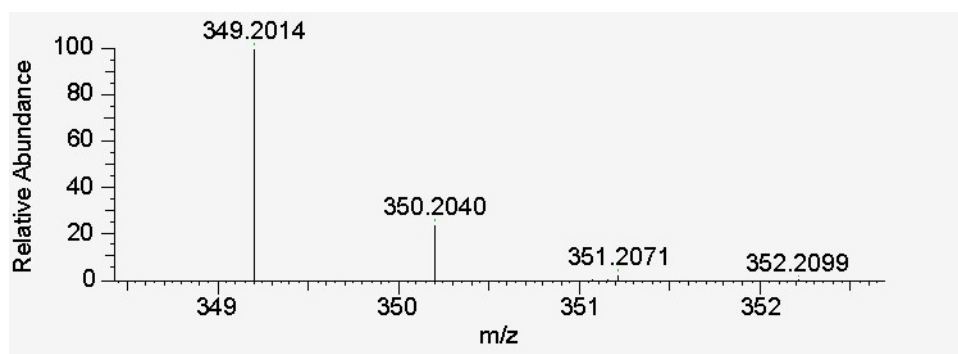
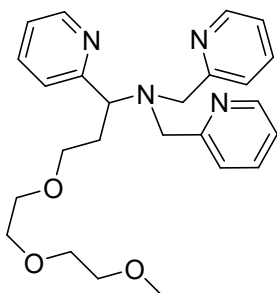


Figure S7. Experimental (top) and simulated (bottom) HR ESI-MS spectrum of 2e.

2f



^1H NMR (400 MHz, CDCl_3) δ 8.60 (d, $J = 4.9$ Hz, 1H), 8.48 (d, $J = 4.9$ Hz, 2H), 7.64 (m, 3H), 7.55 (d, $J = 7.8$ Hz, 2H), 7.25 (d, $J = 7.5$ Hz, 1H), 7.16 (ddd, $J = 7.6, 4.8, 1.2$ Hz, 1H), 7.11 (ddd, $J = 7.4, 4.9, 1.3$ Hz, 2H), 4.07 (d, $J = 15.0$ Hz, 2H), 3.97 (t, $J = 7.3$ Hz, 1H), 3.59 (d, $J = 15.2$ Hz, 2H), 3.57 – 3.40 (m, 10H), 3.35 (s, 3H), 2.37 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 160.63 (C), 158.50 (C), 149.22 (CH), 148.93 (CH), 136.50 (CH), 135.99 (CH), 124.73 (CH), 122.95 (CH), 122.27 (CH), 121.92 (CH), 72.05 (CH_3), 70.66 (CH_2), 70.63 (CH_2), 70.07 (CH_2), 68.82 (CH_2), 61.05 (CH), 59.15 (CH_2), 56.78 (CH_2), 30.60 (CH_2).

HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{33}\text{N}_4\text{O}_3$ $[\text{M}+\text{H}]^+$ 437.2547, found 437.2547.

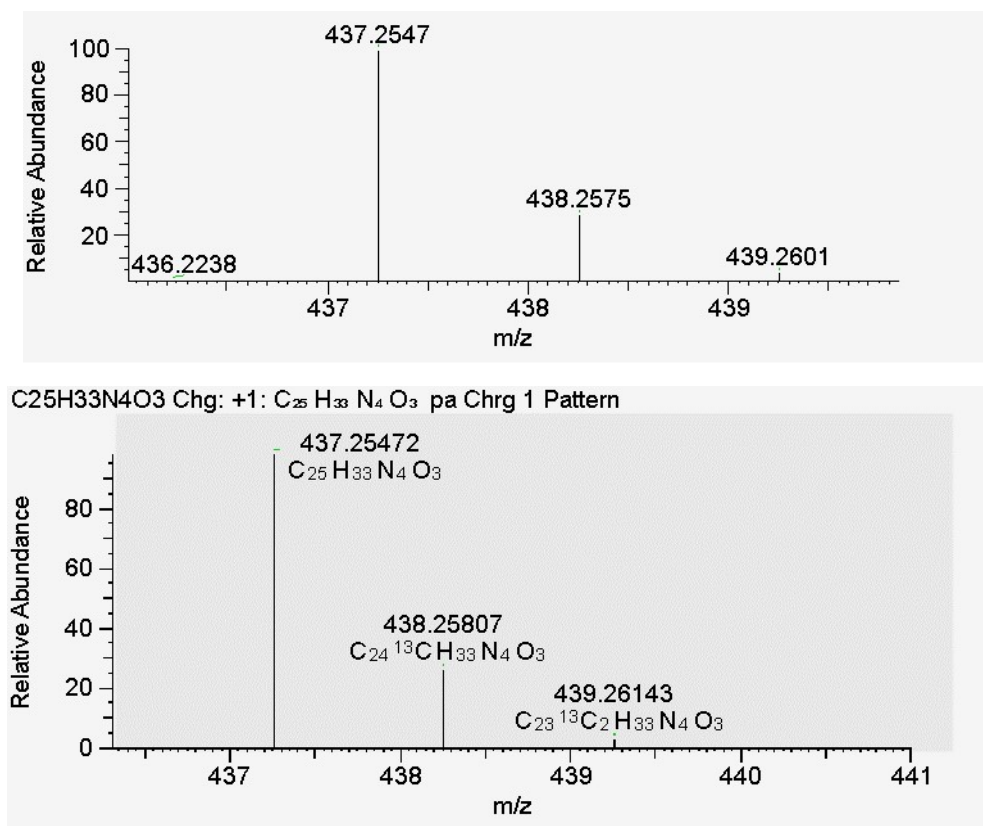
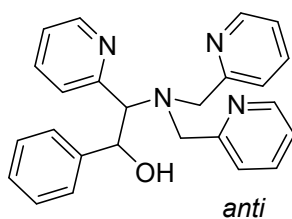


Figure S8. Experimental (top) and simulated (bottom) HR ESI-MS spectrum of 2f.

2g



^1H NMR (600 MHz, CDCl_3) δ 8.63 (d, $J = 4.8$ Hz, 1H), 8.54 (d, $J = 4.9$ Hz, 2H), 7.54 (td, $J = 7.6, 1.8$ Hz, 2H), 7.44 (td, $J = 7.6, 1.9$ Hz, 1H), 7.33 (d, $J = 7.8$ Hz, 2H), 7.17 – 7.04 (m, 8H), 6.77 (d, $J = 7.8$ Hz, 1H), 5.55 (d, $J = 9.6$ Hz, 1H), 4.45 (d, $J = 15.0$ Hz, 2H), 3.85 (d, $J = 9.6$ Hz, 1H), 3.65 (d, $J = 15.0$ Hz, 2H).

^{13}C NMR (150 MHz, CDCl_3) δ 160.03 (C), 157.11 (C), 149.17 (CH), 148.98 (CH), 148.96 (CH), 142.11 (C), 136.60 (CH), 135.84 (CH), 127.83 (CH), 127.41 (CH), 127.09 (CH), 125.40 (CH), 123.34 (CH), 122.38 (CH), 122.07 (CH), 72.58 (CH), 72.25 (CH), 57.11 (CH_2).

HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{25}\text{N}_4\text{O}_3$ $[\text{M}+\text{H}]^+$ 397.2023, found 397.2014.

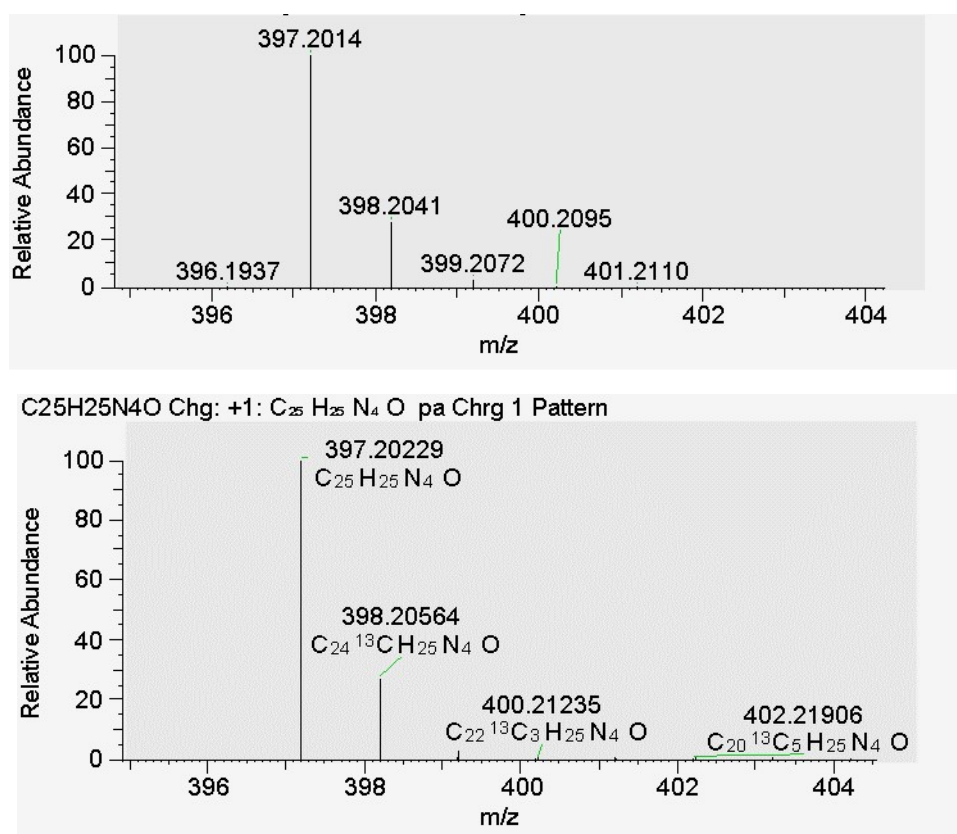
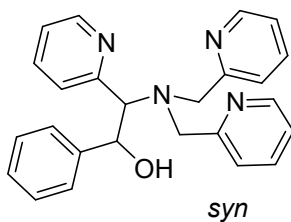


Figure S9. Experimental (top) and simulated (bottom) HR ESI-MS spectrum of 2g.

2h



^1H NMR (400 MHz, CDCl_3) δ 8.58 (d, $J = 4.9$ Hz, 1H), 8.50 (d, $J = 4.8$ Hz, 2H), 7.66 (td, $J = 7.7, 1.8$ Hz, 1H), 7.54 (td, $J = 7.7, 1.8$ Hz, 2H), 7.38 (d, $J = 7.9$ Hz, 1H), 7.22 (m, 6H), 7.13 (m, 4H), 5.62 (d, $J = 6.2$ Hz, 1H), 4.17 (d, $J = 15.1$ Hz, 2H), 4.07 (d, $J = 6.3$ Hz, 1H), 3.66 (d, $J = 15.1$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 159.76 (C), 157.84 (C), 148.69 (CH), 148.56 (CH), 142.98 (C), 136.77 (CH), 136.69 (CH), 128.04 (CH), 127.28 (CH), 127.15 (CH), 126.41 (CH), 123.21 (CH), 122.69 (CH), 122.15 (CH), 74.28 (CH), 68.89 (CH), 57.42 (CH_2).

HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{25}\text{N}_4\text{O}_3$ $[\text{M}+\text{H}]^+$ 397.2023, found 397.2019.

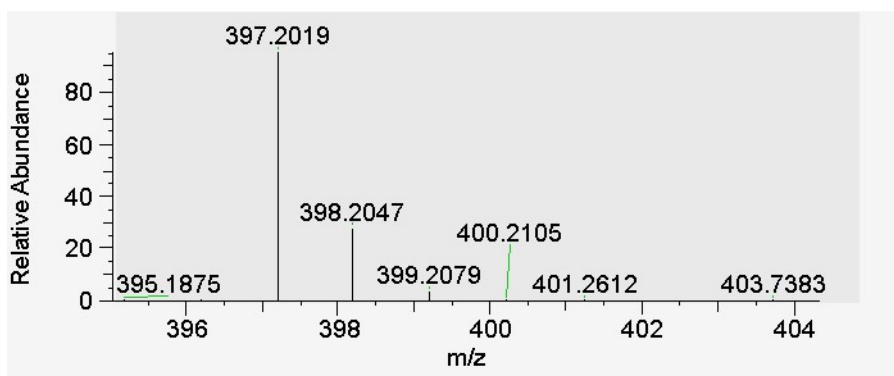
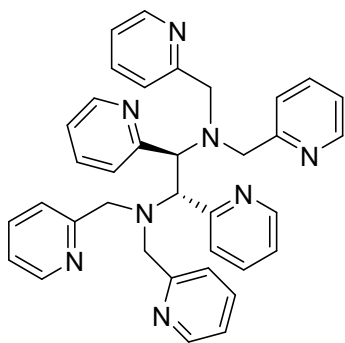


Figure S10. Experimental (top) and simulated (bottom) HR ESI-MS spectrum of **2h**.

21



^1H NMR (400 MHz, CDCl_3) δ 8.68 (d, $J = 4.6$ Hz, m, 2H), 8.39 (d, $J = 4.8$ Hz, m, 4H), 7.61 (td, $J = 7.6, 1.9$ Hz, 2H), 7.44 (td, $J = 7.7, 1.8$ Hz, 4H), 7.26 (m, 2H), 7.12 (d, $J = 7.6$ Hz, 2H), 7.05 (dd, $J = 6.6, 5.1$ Hz, 4H), 6.79 (d, $J = 7.9$ Hz, 4H), 4.89 (s, 2H), 3.95 (d, $J = 15.2$ Hz, 4H), 3.45 (d, $J = 15.2$ Hz, 4H).

^{13}C NMR (101 MHz, CDCl_3) δ 160.12 (C), 157.07 (C), 149.17 (CH), 148.47 (CH), 136.31 (CH), 135.60 (CH), 125.77 (CH), 123.09 (CH), 122.14 (CH), 121.87 (CH), 64.81 (CH), 57.28 (CH_2).

HRMS (ESI): calcd for $\text{C}_{36}\text{H}_{35}\text{N}_8$ $[\text{M}+\text{H}]^+$ 579.2979, found 579.2969. Calcd for $\text{C}_{36}\text{H}_{36}\text{N}_8$ $[\text{M}+2\text{H}]^{2+}$ 290.1526, found 290.1520.

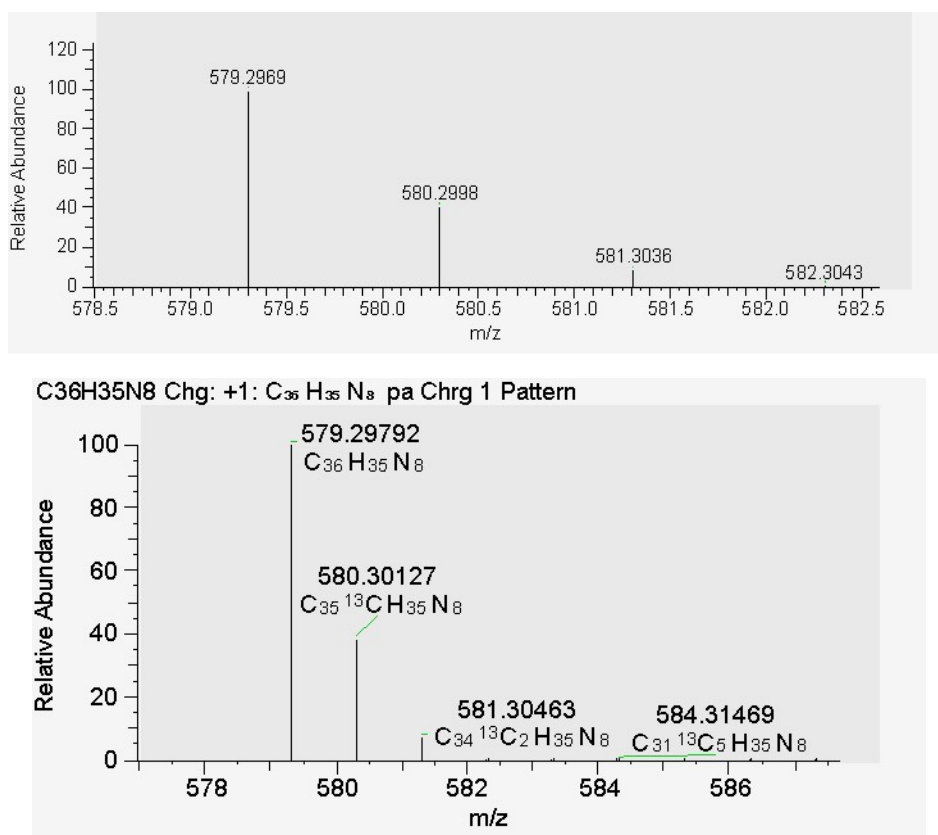
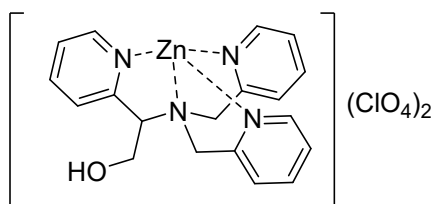


Figure S11. Experimental (top) and simulated (bottom) HR ESI-MS spectrum of 21.

3. Zinc complexes characterization

3c



^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 8.69 (d, $J = 5.3$ Hz, 1H), 8.61 (d, $J = 5.3$ Hz, 1H), 8.59 (d, $J = 5.3$ Hz, 1H), 8.15 (td, $J = 7.8, 1.7$ Hz, 1H), 8.03 (dt, $J = 7.8, 4.7$ Hz, 1H), 7.91 (t, $J = 7.3$ Hz, 1H), 7.81 (d, $J = 8.0$ Hz, 1H), 7.65 (t, $J = 6.4$ Hz, 1H), 7.57 (d, $J = 7.5$ Hz, 2H), 7.48 (t, $J = 6.4$ Hz, 1H), 7.38 (d, $J = 7.9$ Hz, 1H), 5.70 (s, 1H), 4.60 (d, $J = 16.8$ Hz, 1H), 4.48 (d, $J = 16.9$ Hz, 1H), 4.40 (m, 2H), 4.34 (d, $J = 17.5$ Hz, 1H), 4.25 (m, 1H), 4.20 (d, $J = 17.6$ Hz, 1H).

^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 155.54 (C), 154.81 (C), 154.54 (C), 147.69 (CH), 147.25 (2 CH), 140.93 (CH), 140.73 (CH), 140.33 (CH), 124.98 (CH), 124.89 (CH), 124.63 (CH), 124.50 (CH), 124.38 (CH), 123.83 (CH), 66.78 (CH), 59.43 (CH₂), 58.92 (CH₂), 54.71 (CH₂).

HRMS (ESI): calcd for $\text{C}_{20}\text{H}_{21}\text{N}_4\text{O}_3\text{Zn}$ [$\text{M} - 2 \text{ClO}_4 + \text{HCOO}$] $^+$ 429.0900, found 429.0897

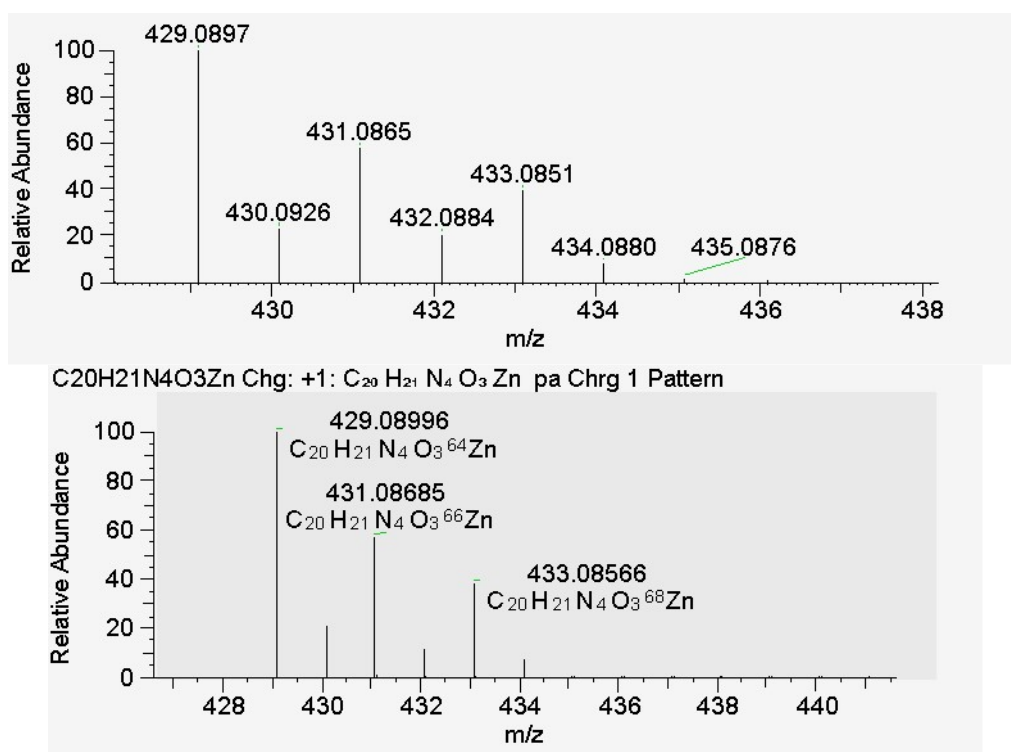
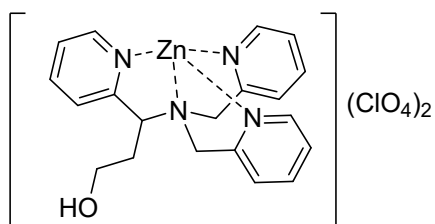


Figure S12. Experimental (top) and simulated (bottom) HR ESI-MS spectrum of 3c.

3d



^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 8.70 (d, $J = 5.2$ Hz, 1H), 8.60 (br, 1H), 8.14 (td, $J = 7.8, 1.7$ Hz, 1H), 8.04 (td, $J = 7.7, 1.6$ Hz, 1H), 7.89 (t, $J = 7.6$ Hz, 1H), 7.80 (d, $J = 8.1$ Hz, 1H), 7.63 (t, $J = 6.5$ Hz, 1H), 7.56 (m, 2H), 7.46 (t, $J = 6.5$ Hz, 1H), 7.33 (d, $J = 7.9$ Hz, 1H), 5.19 (br, 1H), 4.46 (m, 3H), 4.16 (m, 2H), 3.80 (m, 1H), 3.67 (m, 1H), 2.44 (m, 1H), 2.35 (m, 1H).

^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 156.78 (C), 154.64 (C), 154.31 (C), 147.99 (CH), 147.21 (2CH), 141.09 (CH), 140.75 (CH), 140.22 (CH), 124.94 (CH), 124.91 (CH), 124.57 (CH), 124.30 (CH), 123.96 (CH), 123.70 (CH), 63.44 (CH), 58.73 (CH₂), 58.31 (CH₂), 54.18 (CH₂), 30.42 (CH₂).

HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{23}\text{N}_4\text{O}_3\text{Zn}$ [$\text{M} - 2 \text{ClO}_4 + \text{HCOO}$] $^+$ 443.1056, found 443.1053.

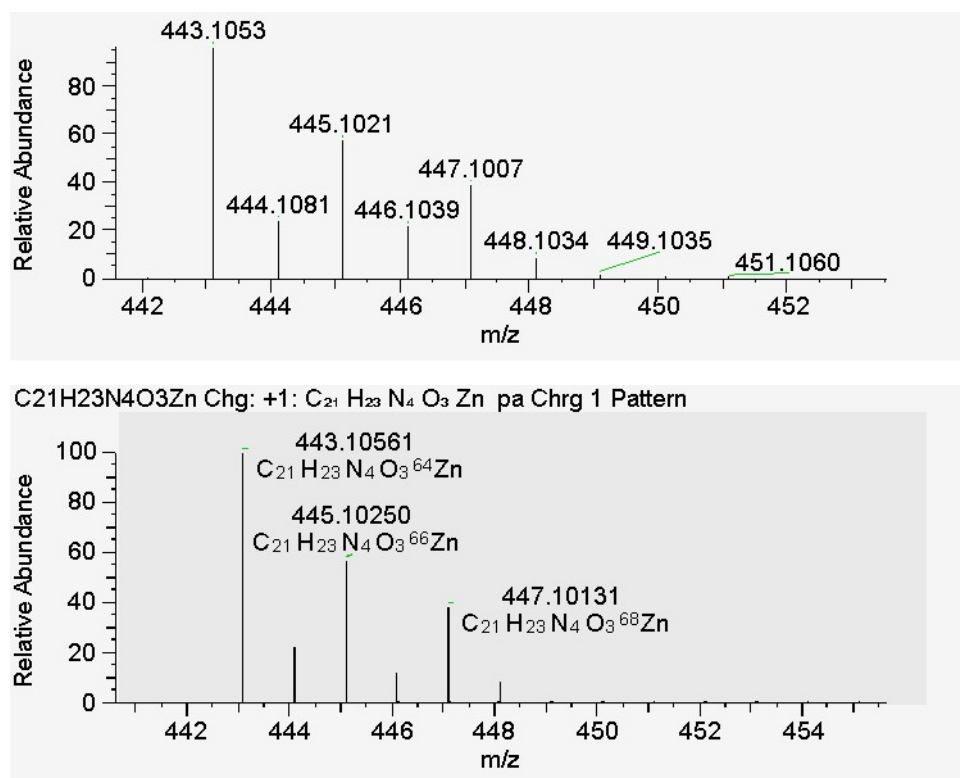
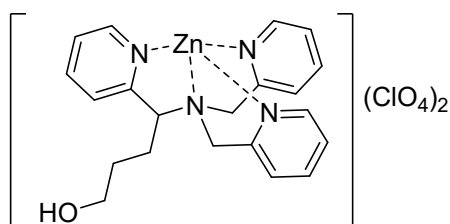


Figure S13. Experimental (top) and simulated (bottom) HR ESI-MS spectrum of 3d

3e



^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.72 (d, $J = 5.2$ Hz, 1H), 8.61 (br, 2H), 8.15 (td, $J = 7.8, 1.8$ Hz, 1H), 8.05 (td, $J = 7.7, 1.7$ Hz, 1H), 7.88 (td, $J = 7.7, 1.7$ Hz, 1H), 7.77 (d, $J = 8.0$ Hz, 1H), 7.64 (dd, $J = 7.6, 5.2$ Hz, 1H), 7.58 (m, 2H), 7.46 (m, 1H), 7.32 (d, $J = 8.0$ Hz, 1H), 4.72 (t, $J = 4.7$ Hz, 1H), 4.55 (d, $J = 16.5$ Hz, 1H), 4.45 (d, $J = 16.7$ Hz, 1H), 4.26 (dd, $J = 8.8, 3.7$ Hz, 1H), 3.59 (m, 2H), 2.25 (m, 2H), 1.76 (p, $J = 6.3$ Hz, 2H).

^{13}C NMR (101 MHz, $\text{DMSO-}d_6\text{O}$) δ 156.85 (C), 154.74 (C), 154.36 (C), 148.11 (CH), 147.31 (CH), 147.25 (CH), 141.13 (CH), 140.79 (CH), 140.24 (CH), 124.99 (CH), 124.91 (CH), 124.67 (CH), 124.28 (CH), 124.05 (CH), 123.66 (CH), 66.40 (CH), 60.57 (CH_2), 58.73 (CH_2), 53.79 (CH_2), 30.35 (CH_2), 24.32 (CH_2).

HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{25}\text{N}_4\text{O}_3\text{Zn}$ [$\text{M} - 2 \text{ClO}_4 + \text{HCOO}$] $^+$ 457.1213, found 457.1206.

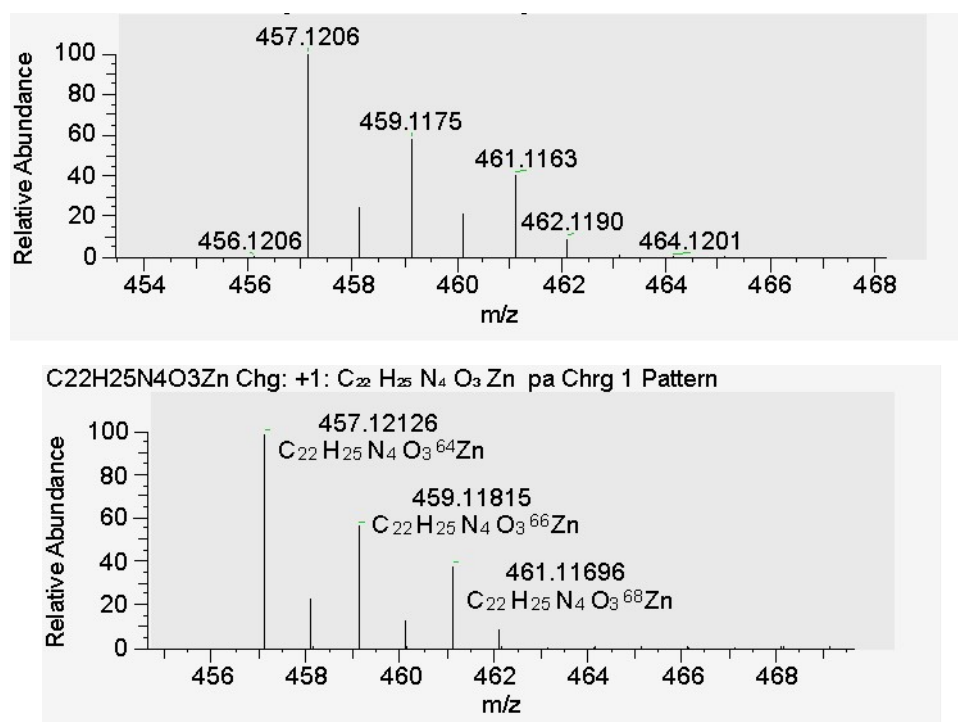
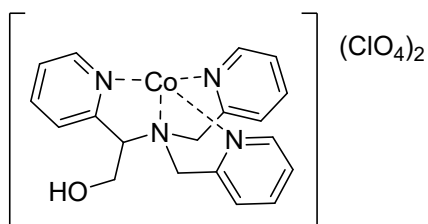


Figure S14. Experimental (top) and simulated (bottom) HR ESI-MS spectrum of 3e

4. Cobalt complexes characterization

4c



Elemental analysis: calcd. for $\text{C}_{19}\text{H}_{20}\text{N}_4\text{O}_9\text{Cl}_2\text{Co}\cdot\text{H}_2\text{O}\cdot 0.5 \text{CH}_3\text{CN}$: C, 38.95; H, 3.84; N, 10.22. Found: C, 39.10; H, 3.81; N, 10.03.

HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{20}\text{N}_4\text{O}_5\text{ClCo}$ $[\text{M} - \text{ClO}_4]^+$ 478.0449, found 478.0447.

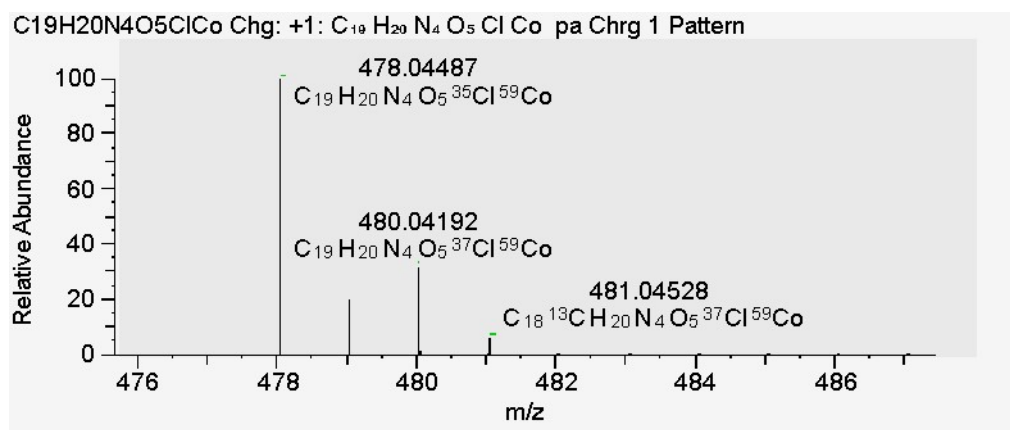
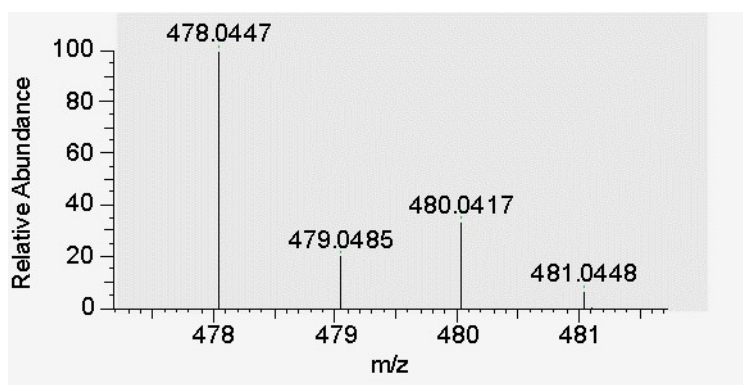
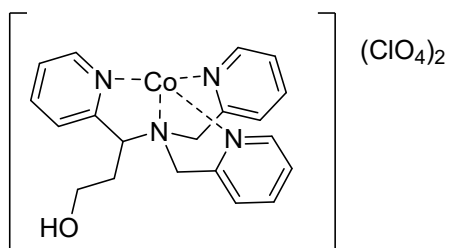


Figure S15. Experimental (top) and simulated (bottom) HR ESI-MS spectrum of 4c

4d



Elemental analysis (%) calcd. for $\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_9\text{Cl}_2\text{Co}\cdot 0.33\text{ CH}_3\text{CN}\cdot 1.67\text{ H}_2\text{O}$: C, 39.03; H, 4.17; N, 9.54. Found: C, 38.60; H, 3.95; N, 9.71.

HRMS (ESI): calcd for $\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_5\text{ClCo}$ $[\text{M} - \text{ClO}_4]^+$ 492.0605, found 492.0608.

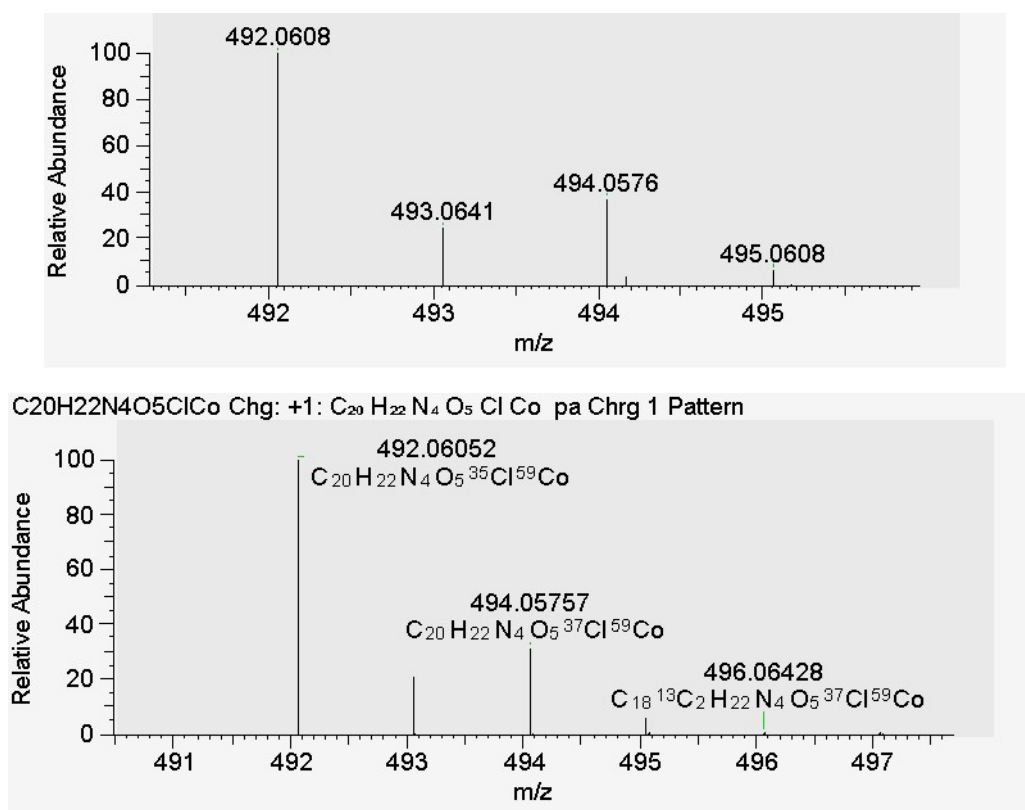
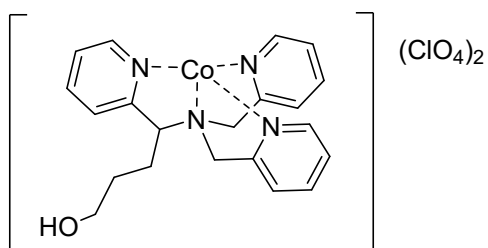


Figure S16. Experimental (top) and simulated (bottom) HR ESI-MS spectrum of 4d

4e



Elemental analysis (%) calcd. for C₂₁H₂₅N₄O₅Cl₂Co·0.67 CH₃CN: C, 42.33; H, 4.14; N, 10.32. Found: C, 42.72; H, 4.25; N, 9.81.

HRMS (ESI): calcd for C₂₁H₂₅N₄O₅ClCo [M - ClO₄]⁺ 506.0762, found 506.0759.

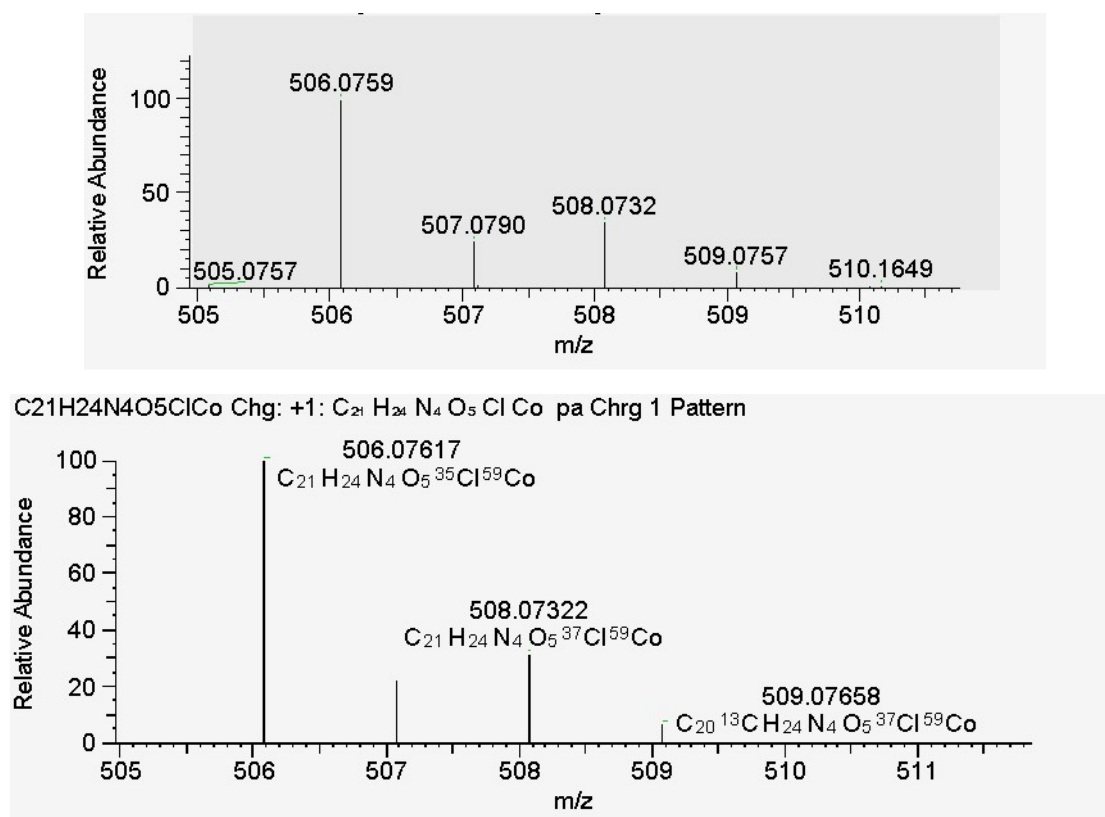


Figure S17. Experimental (top) and simulated (bottom) HR ESI-MS spectrum of 4e

5. NMR spectra

