

Electronic supplementary information for:

Reactivity of different pyrrolyl-functionalized indoles with rare-earth metal(III) amides: Synthesis, structure and catalytic activity of novel trinuclear rare-earth metal amido complexes incorporating μ - η^5 : η^1 bonding indolyl and μ_3 -oxo groups

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1. NMR and MS spectra

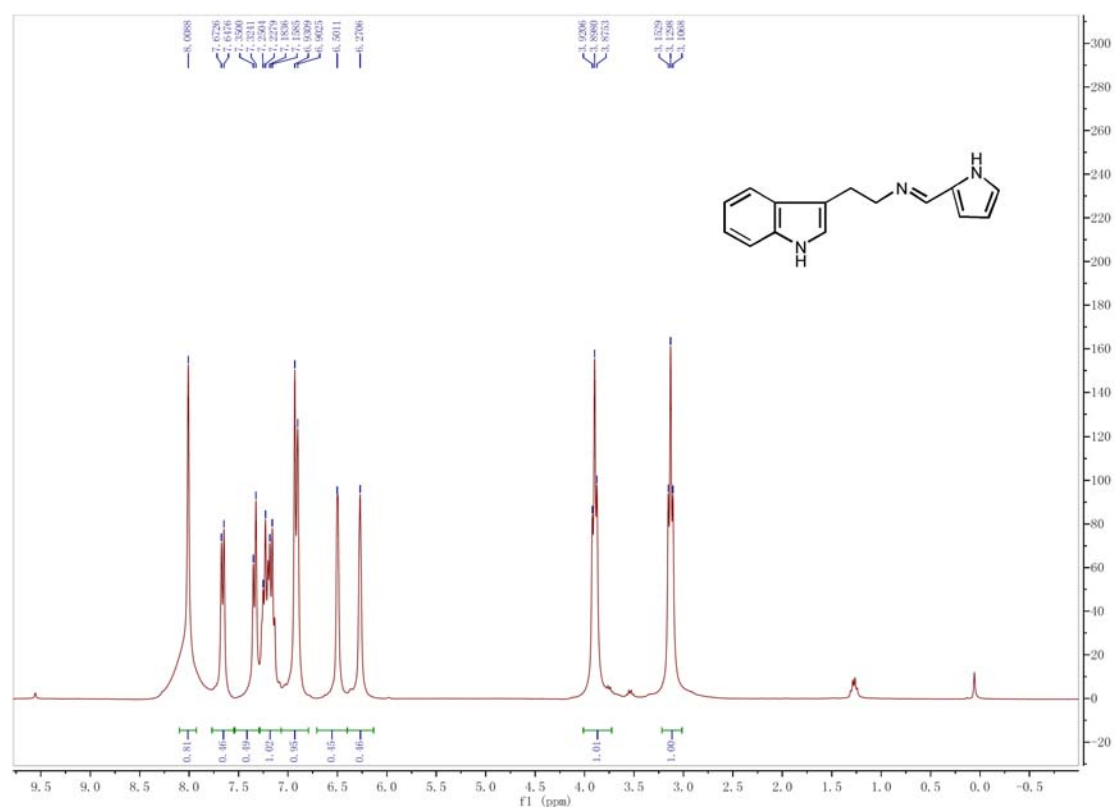


Fig. S1 ¹H NMR of ligand 1

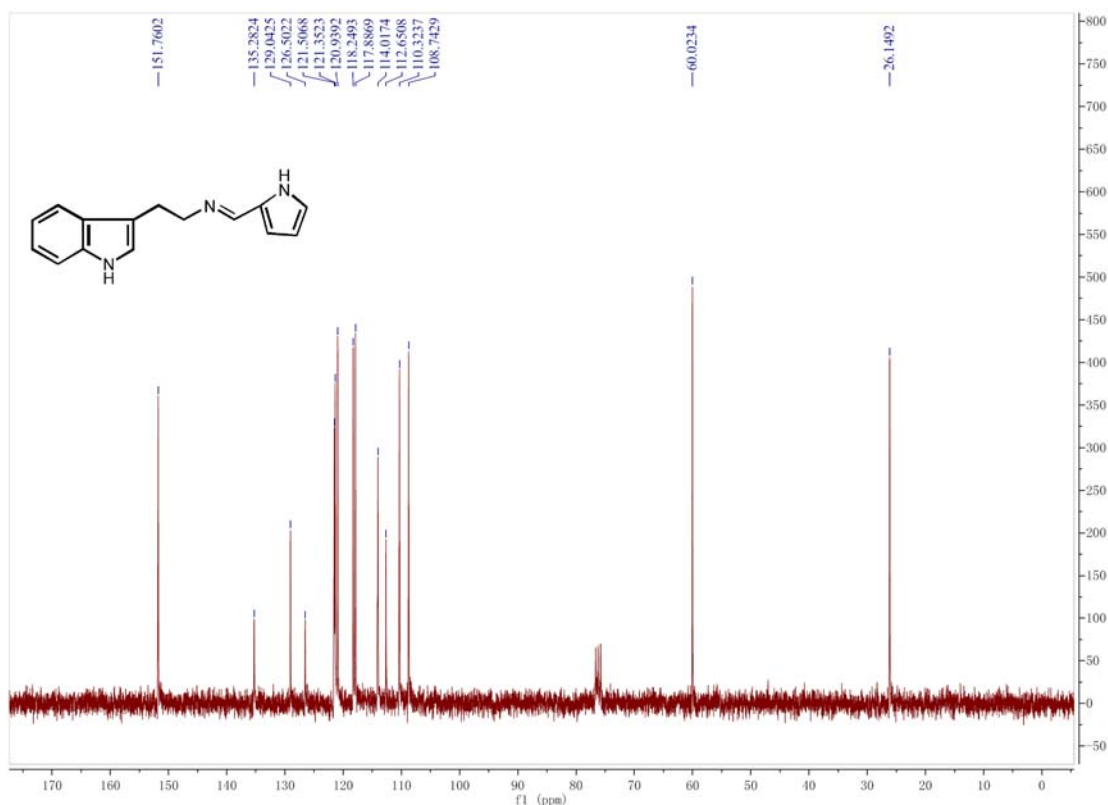


Fig. S2 ¹³C NMR of ligand 1

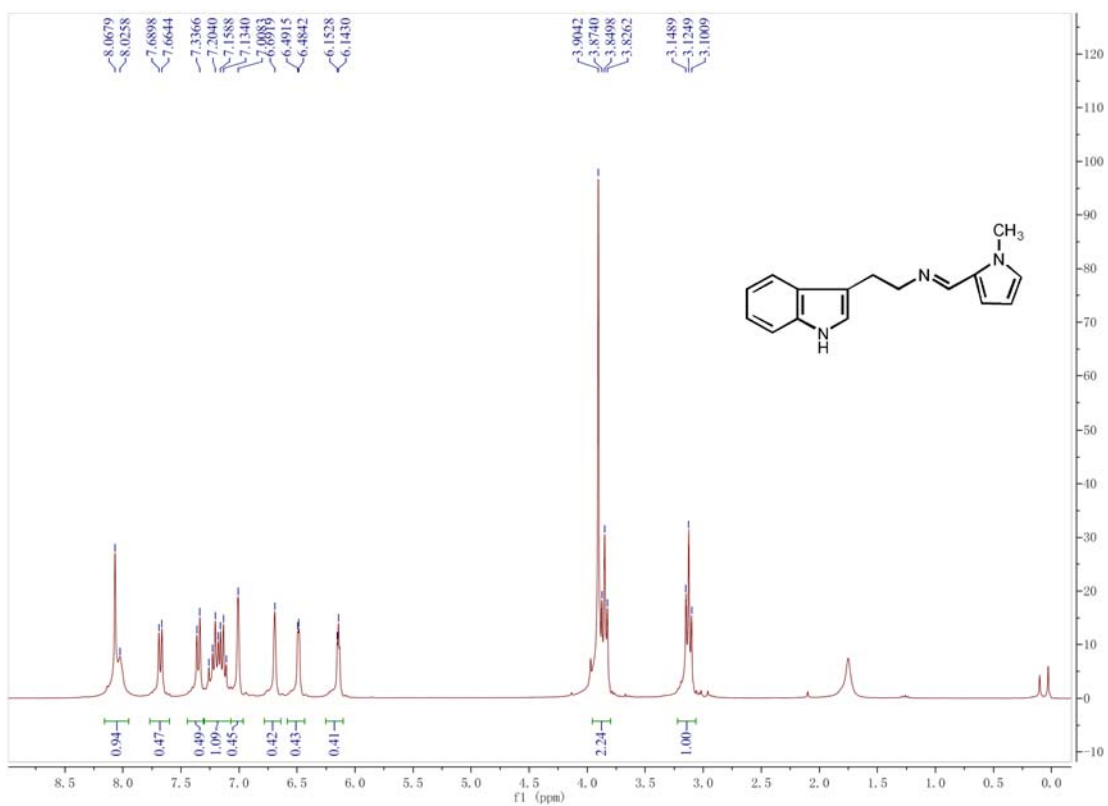


Fig. S3 ¹H NMR of ligand 2

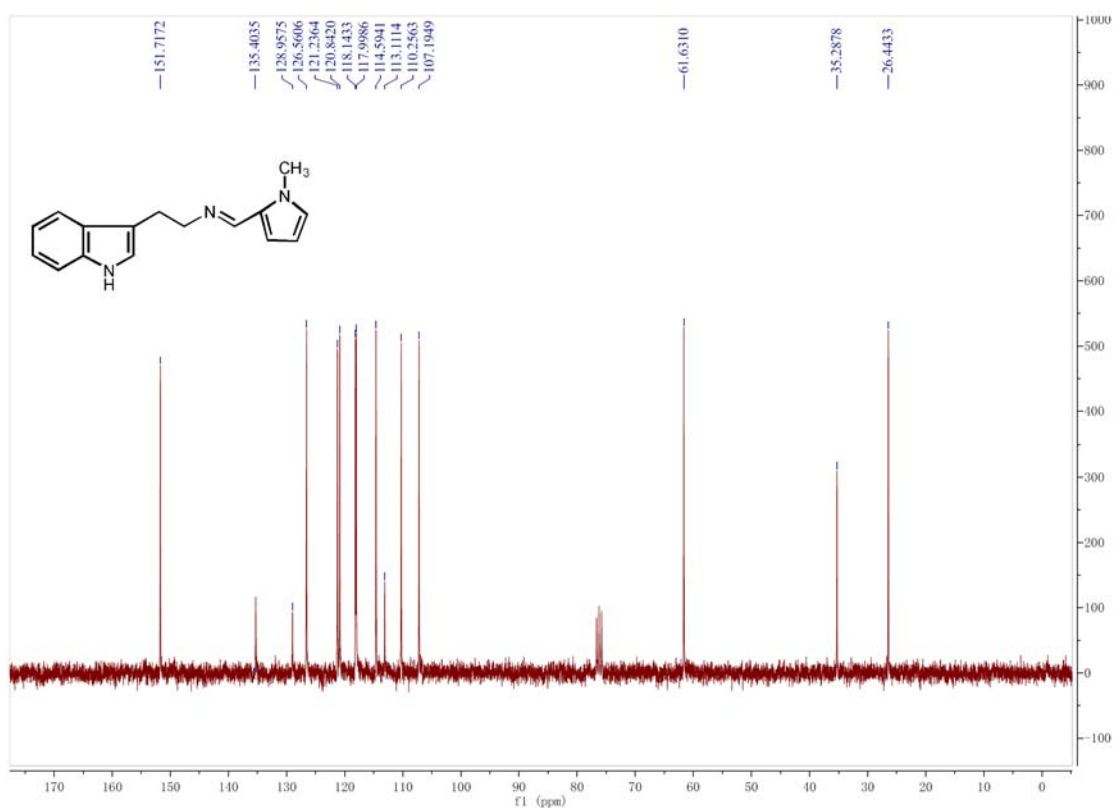


Fig. S4 ¹³C NMR of ligand 2

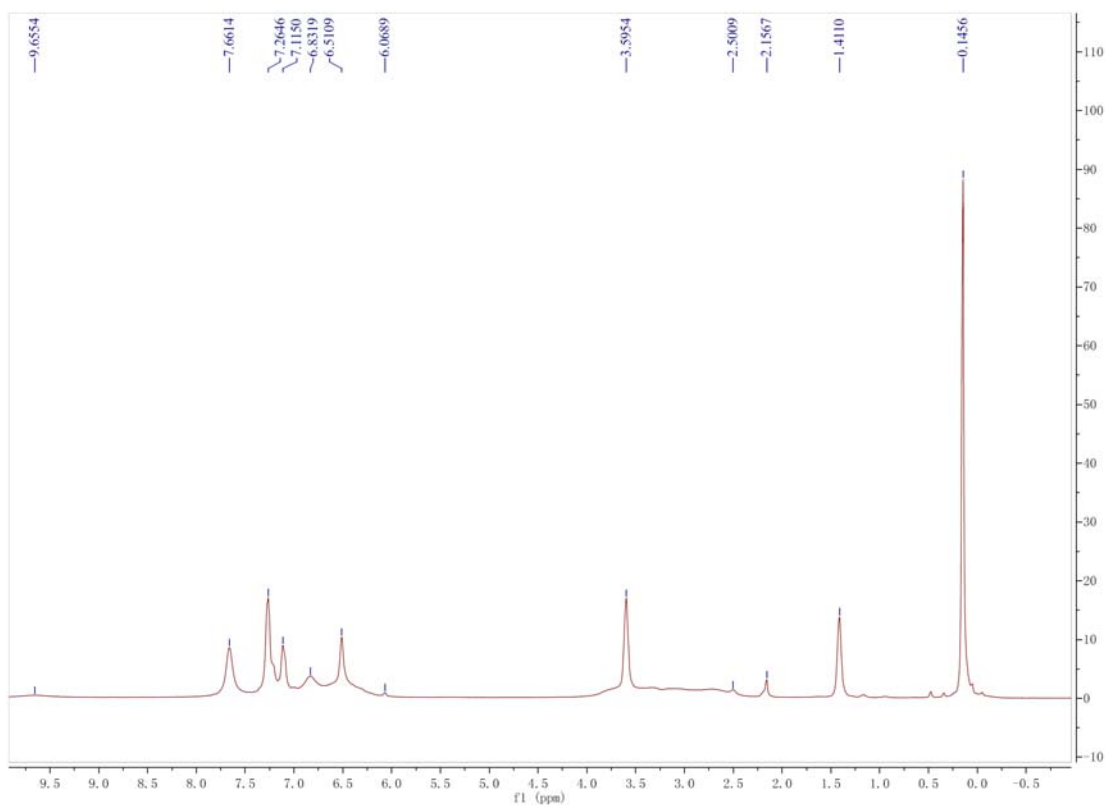


Fig. S5 ¹H NMR of complex 3a

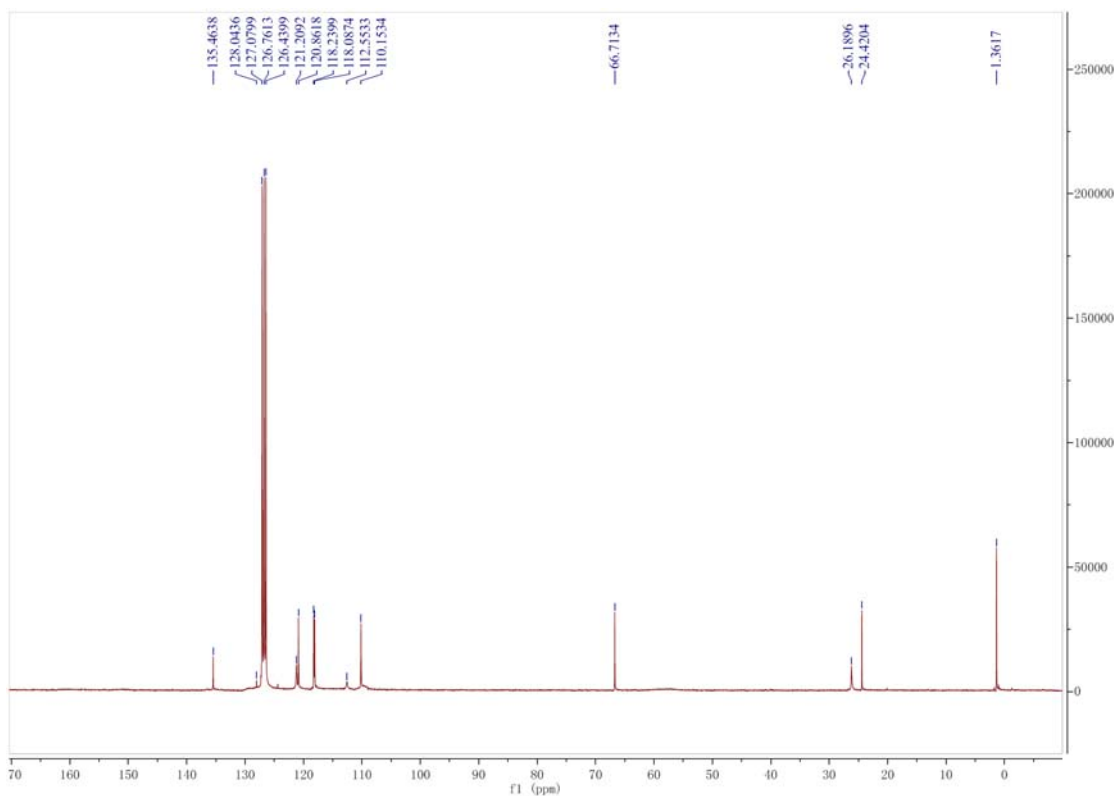


Fig. S6 ¹³C NMR of complex 3a

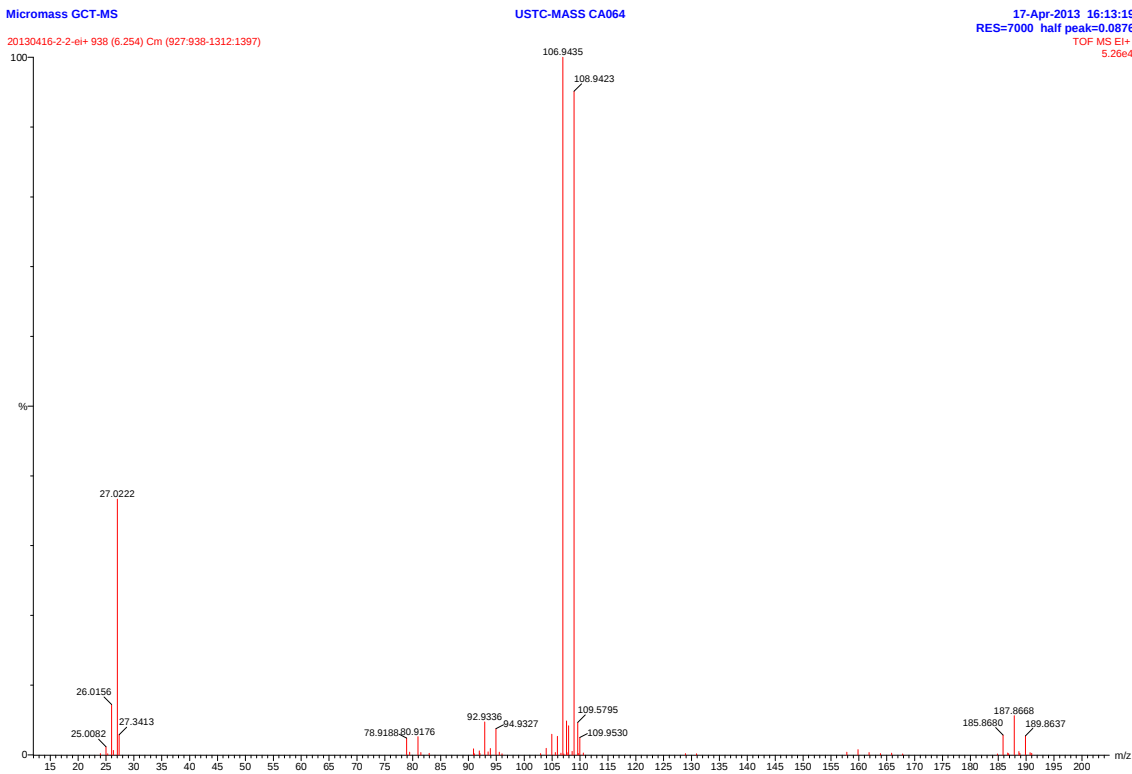
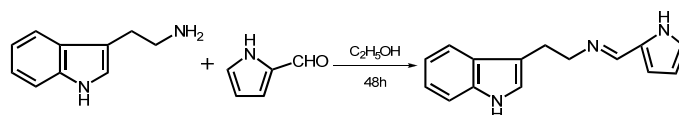


Fig. S7 MS for probing the excluded ethylene gas absorbed by Br₂/CCl₄

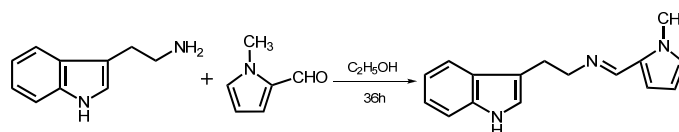
Table S1 Selected MS Data for probing the excluded ethylene gas absorbed by Br₂/CCl₄

SPECTRUM – MS TOF MS EI+ 5.26e4					
Tolerance = 4.0 mDa / DBE: min = 0.0, max = 50.0					
Monoisotopic Mass, Odd and Even Electron Ions					
81 formula(e) evaluated with 12 results within limits (up to 50 closest results for each mass)					
Minimum:	1.00			0.0	
Maximum:	100.00	4.0	5.0	50.0	
Mass	Relative Abundance	Calc. Mass	mDa	PPM	Formula
25.0082	1.14	25.0078	0.4	15.0	C ₂ H ⁺
26.0156	7.19	26.0157	-0.1	-1.9	C ₂ H ₂ ⁺
27.0222	36.64	27.0235	-1.3	-47.2	C ₂ H ₃ ⁺
78.9188	2.38	78.9183	0.5	5.9	⁷⁹ Br ⁺
80.9176	2.60	80.9163	1.3	16.2	⁸¹ Br ⁺
92.9336	4.71	92.9340	-0.4	-4.2	CH ₂ ⁷⁹ Br ⁺
94.9327	3.73	94.9319	0.8	8.0	CH ₂ ⁸¹ Br ⁺
104.9346	2.93	104.9340	0.6	5.8	C ₂ H ₂ ⁷⁹ Br ⁺
106.9435	100.00	106.9496	-6.1		C ₂ H ₄ ⁷⁹ Br ⁺
108.9423	94.95	108.9476	-5.3		C ₂ H ₄ ⁸¹ Br ⁺
109.9530	2.45	109.9554	-2.4	-22.0	C ₂ H ₅ ⁸¹ Br ⁺
185.8680	2.79	185.8680	0.0	0.1	C ₂ H ₄ ⁷⁹ Br ₂ ⁺
187.8668	5.60	187.8659	0.9	4.7	C ₂ H ₄ ⁷⁹ Br ⁸¹ Br ⁺
189.8637	2.70	189.8639	-0.2	-0.9	C ₂ H ₄ ⁸¹ Br ₂ ⁺

2. Preparation of ligands



Scheme S1 Preparation of *N*-((1*H*-pyrrol-2-yl)methylene)-2-(1*H*-indol-3-yl)ethanamine



Scheme S2 Preparation of *N*-((1-methyl-1*H*-pyrrol-2-yl)methylene)-2-(1*H*-indol-3-yl)ethanamine

3. Representation of complexes and selected bond distances and bond angles

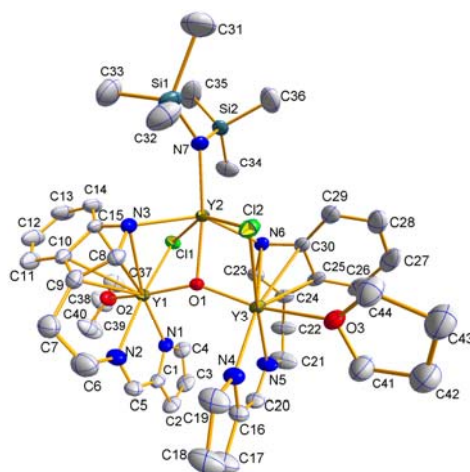


Fig. S8. Structure of complex **3a**. Hydrogen atoms were omitted for clarity, ellipsoids set at the 30% probability level. Selected bond distances (Å) and angles (°): Y(1)-O(1) 2.091(3), Y(1)-N(1) 2.366(4), Y(1)-N(2) 2.401(4), Y(1)-O(2) 2.420(3), Y(1)-N(3) 2.646(4), Y(1)-C(8) 2.660(4), Y(1)-Cl(1) 2.7954(12), Y(1)-C(15) 2.816(5), Y(1)-C(9) 2.817(5), Y(1)-C(10) 2.919(5), Y(2)-N(7) 2.268(3), Y(2)-O(1) 2.269(3), Y(2)-N(3) 2.446(4), Y(2)-N(6) 2.467(4), Y(2)-Cl(2) 2.6990(12), Y(2)-Cl(1) 2.7316(13), Y(3)-O(1) 2.111(3), Y(3)-N(4) 2.351(3), Y(3)-O(3) 2.397(3), Y(3)-N(5) 2.427(4), Y(3)-C(23) 2.659(4), Y(3)-N(6) 2.678(3), Y(3)-Cl(2) 2.7717(11), Y(3)-C(24) 2.815(4), Y(3)-C(30) 2.862(4), Y(3)-C(25) 2.948(4), O(1)-Y(1)-N(1) 92.84(12), O(1)-Y(1)-N(2) 100.35(13), O(1)-Y(1)-O(2) 155.40(11), N(1)-Y(1)-O(2) 78.79(13), N(2)-Y(1)-O(2) 98.56(14), O(1)-Y(1)-N(3) 73.45(11), N(1)-Y(1)-N(3) 166.21(13), O(2)-Y(1)-N(3) 114.33(12), O(1)-Y(1)-Cl(1) 77.15(8), O(2)-Y(1)-Cl(1) 82.34(9), N(7)-Y(2)-O(1) 164.42(12), N(7)-Y(2)-N(3) 94.16(13), O(1)-Y(2)-N(3) 74.81(11), N(7)-Y(2)-N(6) 116.47(13), O(1)-Y(2)-N(6) 74.94(11), N(3)-Y(2)-N(6) 149.35(12), N(7)-Y(2)-Cl(2) 95.94(10), O(1)-Y(2)-Cl(2) 74.94(7), N(7)-Y(2)-Cl(1) 113.53(10), O(1)-Y(2)-Cl(1) 75.88(7), Cl(2)-Y(2)-Cl(1) 150.47(4), O(1)-Y(3)-N(4) 94.78(12), O(1)-Y(3)-O(3) 152.86(11), N(4)-Y(3)-O(3) 81.47(12), O(1)-Y(3)-N(5) 110.09(13), O(3)-Y(3)-N(5) 93.98(13), O(1)-Y(3)-N(6) 73.01(11), O(3)-Y(3)-N(6) 110.33(11), O(1)-Y(3)-Cl(2) 75.70(8), O(3)-Y(3)-Cl(2) 79.22(8), Y(2)-Cl(1)-Y(1) 77.29(3), Y(2)-Cl(2)-Y(3) 78.98(3), Y(1)-O(1)-Y(3) 149.87(14), Y(1)-O(1)-Y(2) 104.64(11), Y(3)-O(1)-Y(2) 105.13(11), Y(2)-N(3)-Y(1) 85.28(11), Y(2)-N(6)-Y(3) 85.02(10).

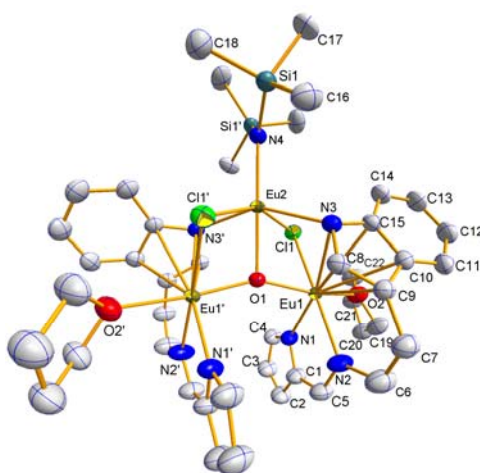


Fig. S9. Structure of complex **3b**. Hydrogen atoms were omitted for clarity, ellipsoids set at the 30% probability level. Selected bond distances (Å) and angles (°): Eu(1)-O(1) 2.0676(12), Eu(1)-N(1) 2.312(5), Eu(1)-N(2) 2.364(5), Eu(1)-O(2) 2.378(5), Eu(1)-C(8) 2.610(5), Eu(1)-N(3) 2.631(4), Eu(1)-Cl(1) 2.7560(14), Eu(1)-C(9)

2.775(6), Eu(1)-C(15) 2.842(5), Eu(1)-C(10) 2.933(6), Eu(2)-N(4) 2.195(6), Eu(2)-O(1) 2.261(5), Eu(2)-N(3) 2.416(5), Eu(2)-Cl(1) 2.6559(15), O(1)-Eu(1)-N(1) 91.52(18), O(1)-Eu(1)-N(2) 106.9(2), O(1)-Eu(1)-O(2) 155.26(13), N(1)-Eu(1)-O(2) 80.60(19), N(2)-Eu(1)-O(2) 92.8(2), O(1)-Eu(1)-N(3) 73.44(15), O(2)-Eu(1)-N(3) 113.26(17), O(1)-Eu(1)-Cl(1) 77.65(11), O(2)-Eu(1)-Cl(1) 81.00(12), N(4)-Eu(2)-O(1) 180.000(1), N(4)-Eu(2)-N(3) 105.14(11), O(1)-Eu(2)-N(3) 74.86(11), N(3)#1-Eu(2)-N(3) 149.7(2), N(4)-Eu(2)-Cl(1) 103.15(3), O(1)-Eu(2)-Cl(1) 76.85(3), Cl(1)-Eu(2)-Cl(1)#1 153.70(6), Eu(2)-Cl(1)-Eu(1) 77.58(4), Eu(1)#1-O(1)-Eu(1) 153.9(3), Eu(1)-O(1)-Eu(2) 103.07(14).

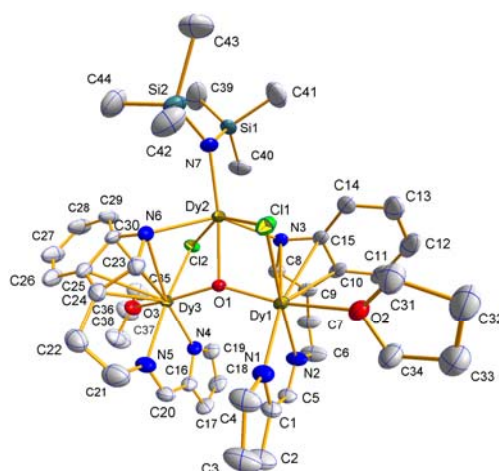


Fig. S10. Structure of complex **3c**. Hydrogen atoms were omitted for clarity, ellipsoids set at the 30% probability level. Selected bond distances (Å) and angles (°): Dy(1)-O(1) 2.123(3), Dy(1)-N(1) 2.361(4), Dy(1)-O(2) 2.403(3), Dy(1)-N(2) 2.433(4), Dy(1)-C(8) 2.668(5), Dy(1)-N(3) 2.682(4), Dy(1)-Cl(1) 2.7801(11), Dy(1)-C(9) 2.814(5), Dy(1)-C(15) 2.847(4), Dy(1)-C(10) 2.938(5), Dy(2)-N(7) 2.260(4), Dy(2)-O(1) 2.281(3), Dy(2)-N(6) 2.462(4), Dy(2)-N(3) 2.490(4), Dy(2)-Cl(1) 2.7084(11), Dy(2)-Cl(2) 2.7463(12), Dy(3)-O(1) 2.097(3), Dy(3)-N(4) 2.379(4), Dy(3)-N(5) 2.406(4), Dy(3)-O(3) 2.433(3), Dy(3)-N(6) 2.654(4), Dy(3)-C(23) 2.672(5), Dy(3)-Cl(2) 2.7989(12), Dy(3)-C(24) 2.814(5), Dy(3)-C(30) 2.821(5), Dy(3)-C(25) 2.916(5), O(1)-Dy(1)-N(1) 94.74(13), O(1)-Dy(1)-O(2) 152.79(11), N(1)-Dy(1)-O(2) 81.23(13), O(1)-Dy(1)-N(2) 110.31(14), O(2)-Dy(1)-N(2) 93.66(14), O(1)-Dy(1)-N(3) 72.82(11), O(2)-Dy(1)-N(3) 110.94(12), O(1)-Dy(1)-Cl(1) 75.55(8), O(2)-Dy(1)-Cl(1) 79.41(8), N(7)-Dy(2)-O(1) 164.18(13), N(7)-Dy(2)-N(6) 94.24(14), O(1)-Dy(2)-N(6) 74.50(12), N(7)-Dy(2)-N(3) 117.28(14), O(1)-Dy(2)-N(3) 74.34(11), N(7)-Dy(2)-Cl(1) 95.99(11), O(1)-Dy(2)-Cl(1) 74.76(7), N(7)-Dy(2)-Cl(2) 114.05(11), O(1)-Dy(2)-Cl(2) 75.46(7), Cl(1)-Dy(2)-Cl(2) 149.88(4), O(1)-Dy(3)-N(4) 92.40(13), O(1)-Dy(3)-N(5) 100.40(15), O(1)-Dy(3)-O(3) 155.37(12), N(4)-Dy(3)-O(3) 78.90(14), N(5)-Dy(3)-O(3) 98.24(16), O(1)-Dy(3)-N(6) 73.40(11), O(3)-Dy(3)-N(6) 114.89(13), O(1)-Dy(3)-Cl(2) 77.04(8), O(3)-Dy(3)-Cl(2) 82.63(10), Dy(2)-Cl(1)-Dy(1) 79.31(3), Dy(2)-Cl(2)-Dy(3) 77.50(3), Dy(3)-O(1)-Dy(1) 149.55(15), Dy(3)-O(1)-Dy(2) 104.81(12), Dy(1)-O(1)-Dy(2) 105.32(12).

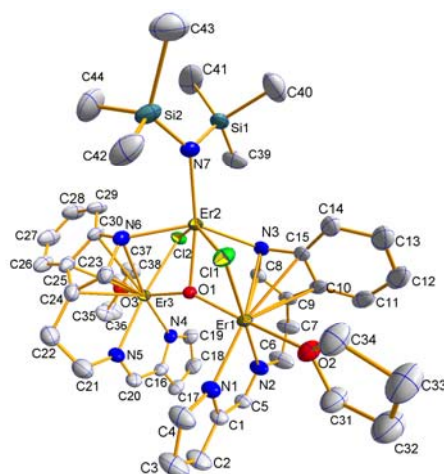


Fig. S11. Structure of complex **3d**. Hydrogen atoms were omitted for clarity, ellipsoids set at the 30% probability level. Selected bond distances (Å) and angles (°): Er(1)-O(1) 2.105(3), Er(1)-N(1) 2.334(4), Er(1)-O(2) 2.388(4), Er(1)-N(2) 2.400(4), Er(1)-C(8) 2.647(5), Er(1)-N(3) 2.669(4), Er(1)-Cl(1) 2.7625(12), Er(1)-C(9) 2.796(5), Er(1)-C(15) 2.844(5), Er(1)-C(10) 2.930(5), Er(1)-Er(2) 3.4612(3), Er(2)-N(7) 2.252(4), Er(2)-O(1) 2.267(3), Er(2)-N(6) 2.426(4), Er(2)-N(3) 2.450(4), Er(2)-Cl(1) 2.6788(13), Er(2)-Cl(2) 2.7132(14), Er(2)-Si(1) 3.3517(16), Er(2)-Er(3) 3.4328(3), Er(3)-O(1) 2.080(3), Er(3)-N(4) 2.355(4), Er(3)-N(5) 2.373(4), Er(3)-O(3) 2.417(4), Er(3)-N(6) 2.627(4), Er(3)-C(23) 2.643(5), Er(3)-Cl(2) 2.7819(13), Er(3)-C(30) 2.792(5), Er(3)-C(24) 2.797(5), Er(3)-C(25) 2.902(6), O(1)-Er(1)-N(1) 94.22(14), O(1)-Er(1)-O(2) 152.44(12), N(1)-Er(1)-O(2) 81.34(15), O(1)-Er(1)-N(2) 109.36(15), O(2)-Er(1)-N(2) 94.85(15), O(1)-Er(1)-N(3) 73.15(12), O(2)-Er(1)-N(3) 110.47(13), O(1)-Er(1)-Cl(1) 75.61(9), O(2)-Er(1)-Cl(1) 78.98(9), N(7)-Er(2)-O(1) 165.18(14), N(7)-Er(2)-N(6) 94.41(15), O(1)-Er(2)-N(6) 75.00(13), N(7)-Er(2)-N(3) 115.89(15), O(1)-Er(2)-N(3) 75.15(12), N(6)-Er(2)-N(3) 149.71(13), N(7)-Er(2)-Cl(1) 96.40(11), O(1)-Er(2)-Cl(1) 75.00(8), N(7)-Er(2)-Cl(2) 113.03(11), O(1)-Er(2)-Cl(2) 75.80(8), Cl(1)-Er(2)-Cl(2) 150.50(4), O(1)-Er(3)-N(4) 92.27(14), O(1)-Er(3)-N(5) 100.46(16), O(1)-Er(3)-O(3) 154.85(13), N(4)-Er(3)-O(3) 78.83(15), N(5)-Er(3)-O(3) 98.71(16), O(1)-Er(3)-N(6) 73.79(13), O(3)-Er(3)-N(6) 114.18(14), O(1)-Er(3)-Cl(2) 77.12(9), O(3)-Er(3)-Cl(2) 81.97(10), Er(2)-Cl(1)-Er(1) 78.98(3), Er(2)-Cl(2)-Er(3) 77.31(4), Er(3)-O(1)-Er(1) 150.84(16), Er(3)-O(1)-Er(2) 104.23(13), Er(1)-O(1)-Er(2) 104.60(13), Er(2)-N(3)-Er(1) 84.97(12), Er(2)-N(6)-Er(3) 85.49(13).

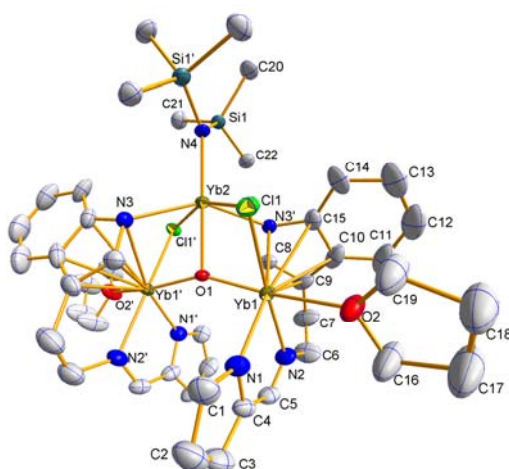


Fig. S12. Structure of complex **3e**. Hydrogen atoms were omitted for clarity, ellipsoids set at the 30% probability level. Selected bond distances (Å) and angles (°): Yb(1)-O(1) 2.0742(10), Yb(1)-N(1) 2.284(5), Yb(1)-N(2)

2.371(5), Yb(1)-O(2) 2.376(4), Yb(1)-C(8) 2.613(6), Yb(1)-N(3)#1 2.656(4), Yb(1)-Cl(1) 2.7342(12), Yb(1)-C(9) 2.793(6), Yb(1)-C(15) 2.906(6), Yb(1)-C(10) 2.963(6), Yb(2)-N(4) 2.211(5), Yb(2)-O(1) 2.231(4), Yb(2)-N(3)#1 2.419(4), Yb(2)-Cl(1) 2.6755(13), N(3)-Yb(1)#1 2.656(4), O(1)-Yb(1)-N(1) 91.13(16), O(1)-Yb(1)-N(2) 108.08(16), O(1)-Yb(1)-O(2) 157.67(13), N(1)-Yb(1)-O(2) 81.36(19), N(2)-Yb(1)-O(2) 89.68(17), O(1)-Yb(1)-N(3)#1 71.84(12), O(2)-Yb(1)-N(3)#1 114.67(17), O(1)-Yb(1)-Cl(1) 78.98(9), O(2)-Yb(1)-Cl(1) 81.89(11), N(4)-Yb(2)-O(1) 180.000(1), N(4)-Yb(2)-N(3) 105.61(10), O(1)-Yb(2)-N(3) 74.39(10), N(3)#1-Yb(2)-N(3) 148.8(2), N(4)-Yb(2)-Cl(1) 102.22(3), O(1)-Yb(2)-Cl(1) 77.78(3), Cl(1)-Yb(2)-Cl(1)#1 155.56(6), Yb(2)-Cl(1)-Yb(1) 77.37(3), Yb(1)-O(1)-Yb(1)#1 153.1(2), Yb(1)-O(1)-Yb(2) 103.45(11), Yb(2)-N(3)-Yb(1)#1 83.42(12).

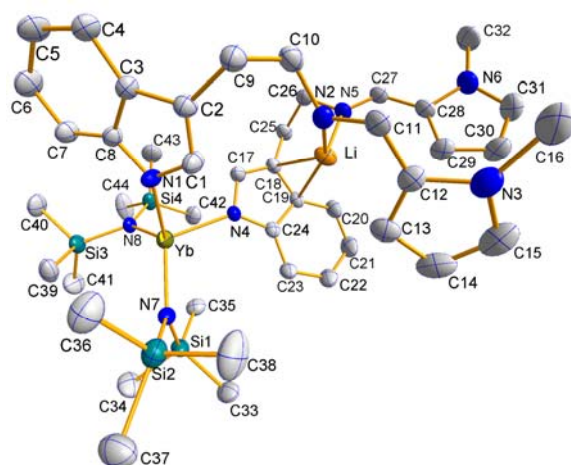


Fig. S13. Structure of complex **4a**. Hydrogen atoms were omitted for clarity, ellipsoids set at the 30% probability level. Selected bond distances (Å) and angles (°): Yb-N(7) 2.202(3), Yb-N(8) 2.207(3), Yb-N(1) 2.247(3), Yb-N(4) 2.268(3), Li-N(2) 2.005(9), Li-N(5) 2.024(8), Li-C(18) 2.524(9), Li-C(19) 2.415(8), N(7)-Yb-N(8) 120.82(11), N(7)-Yb-N(1) 114.30(12), N(8)-Yb-N(1) 108.95(12), N(7)-Yb-N(4) 108.10(12), N(8)-Yb-N(4) 112.25(12), N(1)-Yb-N(4) 87.53(13), N(2)-Li-N(5) 106.6(4)

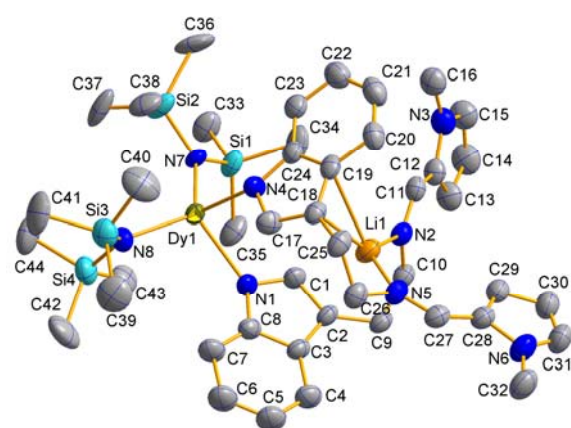


Fig. S14. Molecular Structure of complex **4b**. Hydrogen atoms were omitted for clarity, ellipsoids set at the 30% probability level. Selected bond distances (Å) and angles (°): Dy(1)-N(7) 2.245(6), Dy(1)-N(8) 2.259(7), Dy(1)-N(1) 2.339(7), Dy(1)-N(4) 2.291(7), Li(1)-N(2) 2.027(19), Li(1)-N(5) 1.999(19), Li(1)-C(18) 2.467(19), Li(1)-C(19) 2.711(19), N(7)-Dy(1)-N(8) 122.3(3), N(7)-Dy(1)-N(1) 115.9(2), N(8)-Dy(1)-N(1) 108.1(3), N(7)-Dy(1)-N(4) 106.5(3), N(8)-Dy(1)-N(4) 112.8(3), N(1)-Dy(1)-N(4) 85.3(3), N(2)-Li(1)-N(5) 127.0(9)

4. General Procedures for Hydrophosphonylation of Aldehydes

A mixture of the rare-earth metal complex (0.01 mmol) and diethyl phosphite (10 mmol) was stirred for 5 min. Aldehyde (10 mmol) was then added and the resulting mixture was stirred under solvent-free conditions for 10 min. After 10 min, the temperature of the exothermic reaction returned to room temperature. Water was added, and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous Na₂SO₄. After filtration, the solvent was evaporated under reduced pressure. Recrystallization of the crude product from hexane and diethyl ether gave the desired product.

Diethyl(hydroxy(phenyl)methyl)phosphonate (5a). Melting point (mp) 82–83 °C (lit.¹ mp 83 °C); ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.49–7.47 (d, 2H, *J* = 5.8 Hz, ArH), 7.30–7.28 (d, 3H, *J* = 8.1 Hz, ArH), 5.01 (d, *J* = 9.8 Hz, 1H, CH), 4.07–3.96 (m, 4H, CH₂), 3.73 (s, 1H, OH), 1.29–1.19 (m, 6H, CH₃). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 136.8, 128.2, 128.0, 127.1 (d, *J* = 5.6 Hz), 70.7 (d, *J* = 159.7 Hz), 63.4 (d, *J* = 7.0 Hz), 63.0 (d, *J* = 7.4 Hz), 16.3. HRMS (ESI) *m/z*: calcd for C₁₁H₁₇O₄P [M+H]⁺: 245.0943; Found: 245.0945.

Diethyl hydroxy(4-methoxyphenyl)methylphosphonate (5b). mp 121–123 °C (lit.² mp 121–124 °C); ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.41 (dd, *J* = 8.8, 2.2 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 4.95 (dd, *J* = 9.9, 4.9 Hz, 1H), 4.13–3.87 (m, 4H), 3.81 (s, 3H), 1.25 (m, 6H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 159.4, 128.8, 128.5 (d, *J* = 6.0 Hz), 113.6, 70.3 (d, *J* = 161.3 Hz), 63.2 (d, *J* = 6.8 Hz), 62.9 (d, *J* = 7.2 Hz), 55.0, 16.4 (d, *J* = 4.5 Hz). HRMS (ESI) *m/z*: calcd for C₁₂H₁₉O₅P [M+H]⁺: 275.1048; Found: 275.1044.

Diethyl hydroxy(4-chlorophenyl)methylphosphonate (5c). mp 71–73 °C (lit.³ mp 72–73 °C); ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.37 (d, *J* = 7.3 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 4.94 (d, *J* = 10.8 Hz, 1H), 4.03–3.96 (m, 4H), 1.24–1.16 (m, 6H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 135.8, 133.6 (d, *J* = 3.8 Hz), 128.5 (d, *J* = 5.7 Hz), 128.2 (d, *J* = 2.4 Hz), 69.8 (d, *J* = 161.9 Hz), 63.4 (d, *J* = 7.1 Hz), 63.1 (d, *J* = 7.4 Hz), 16.3 (d, *J* = 5.5 Hz). HRMS (ESI) *m/z*: calcd for C₁₁H₁₆ClO₄P [M+H]⁺: 279.0553; Found: 279.0554.

Diethyl hydroxy(2,4-dichlorophenyl)methylphosphonate (5d).⁴ mp 70–71 °C; ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.66 (d, *J* = 8.3 Hz, 1H), 7.37 (m, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 5.48 (d, *J* = 11.4 Hz, 1H), 4.13–3.99 (m, 4H), 3.22 (s, 1H), 1.32–1.19 (m, 6H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 134.1 (s), 133.4 (d, *J* = 7.9 Hz), 130.4 (d, *J* = 4.0 Hz), 128.7 (s), 127.2 (d, *J* = 2.9 Hz), 66.4 (d, *J* = 164.0 Hz), 63.7 (d, *J* = 7.3 Hz), 63.2 (d, *J* = 7.4 Hz), 16.3 (s). HRMS (ESI) *m/z*: calcd for C₁₁H₁₅Cl₂O₄P [M+H]⁺: 313.0163; Found: 313.0164.

Diethyl hydroxy(2-nitrophenyl)methylphosphonate (5e).⁵ mp 123–125 °C; ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.98 (t, *J* = 7.8 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 7.4 Hz, 1H), 6.25 (d, *J* = 14.2 Hz, 1H), 4.10 (d, *J* = 6.3 Hz, 4H), 3.62 (s, 1H), 1.29–1.16 (m, 6H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 147.5, 133.3 (d, *J* = 3.0 Hz), 132.9, 129.0 (d, *J* = 4.5 Hz), 128.3 (d, *J* = 3.2 Hz), 124.6 (d, *J* = 2.3 Hz), 65.4 (d, *J* = 161.1 Hz), 64.2 (d, *J* = 7.3 Hz), 63.3 (d, *J* = 7.5 Hz), 16.2. HRMS (ESI) *m/z*: calcd for C₁₁H₁₆NO₆P [M+H]⁺: 290.0793; Found: 290.0793.

Diethyl hydroxy(3-nitrophenyl)methylphosphonate (5f). mp 93–94 °C (lit.⁶ mp 93–95 °C); ¹H NMR (300 MHz, CDCl₃, ppm): δ 8.38 (s, 1H), 8.17 (d, *J* = 7.4 Hz, 1H), 7.81 (d, *J* = 6.7 Hz, 1H), 7.56–7.51 (m, 1H), 5.16 (d, *J* = 10.8 Hz, 1H), 4.13–4.10 (m, 4H), 2.75 (s, 1H), 1.29–1.24 (m, 6H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 148.0, 139.5, 133.1 (d, *J* = 5.3 Hz), 128.9, 122.7 (d, *J* = 2.9 Hz), 122.0 (d, *J* = 5.3 Hz), 69.7 (d, *J* = 160.7 Hz), 64.0 (d, *J* = 7.2 Hz), 63.3 (d, *J* = 7.6 Hz), 16.3. HRMS (ESI) *m/z*: calcd for C₁₁H₁₆NO₆P [M+H]⁺: 290.0793; Found: 290.0792.

Diethyl hydroxy(4-nitrophenyl)methylphosphonate (5g). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 8.23 (s, 1H), 8.20 (s, 1H), 7.67 (d, $J = 2.2$ Hz, 1H), 7.65 (d, $J = 2.1$ Hz, 1H), 7.26 (s, 1H), 5.16 (d, $J = 12.3$ Hz, 1H), 4.16-4.06 (m, 5H), 1.37-1.23 (m, 8H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 147.4 (d, $J = 3.7$ Hz), 144.7, 127.8 (d, $J = 5.2$ Hz), 123.2 (d, $J = 2.5$ Hz), 69.9 (d, $J = 160.4$ Hz), 63.9 (d, $J = 7.1$ Hz), 63.3 (d, $J = 7.6$ Hz), 62.0, 16.3 (dd, $J = 5.4, 3.3$ Hz). HRMS (ESI) m/z : calcd for $\text{C}_{11}\text{H}_{16}\text{NO}_6\text{P}$ $[\text{M}+\text{H}]^+$: 290.0793; Found: 290.0791.

Diethyl hydroxy(furan-2-yl)methylphosphonate (5h). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.40 (d, $J = 11.0$ Hz, 1H), 6.49 (d, $J = 10.3$ Hz, 1H), 6.36 (s, 1H), 4.97 (d, $J = 15.6$ Hz, 1H), 4.17-4.06 (m, 4H), 1.31-1.22 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 150.5, 142.5, 110.6, 109.7, 109.0, 64.3 (d, $J = 168.2$ Hz), 16.2. HRMS (ESI) m/z : calcd for $\text{C}_{11}\text{H}_{15}\text{Cl}_2\text{O}_4\text{P}$ $[\text{M}+\text{H}]^+$: 313.0163; Found: 313.0163.

Diethyl 1-hydroxypropylphosphonate (5i). (lit.²) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 4.19-4.14 (m, 4H), 3.78 (s, 1H), 3.02 (s, 1H), 1.85 (s, 2H), 1.36-1.31 (m, 6H), 1.09-1.05 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 68.2 (d, $J = 162.4$ Hz), 61.6 (dd, $J = 25.2, 17.8$ Hz), 24.2, 15.9 (d, $J = 5.3$ Hz), 9.8 (d, $J = 14.0$ Hz). HRMS (ESI) m/z : calcd for $\text{C}_7\text{H}_{17}\text{O}_4\text{P}$ $[\text{M}+\text{H}]^+$: 197.0943; Found: 197.0938.

Diethyl 1-hydroxybutylphosphonate (5j). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 4.13-4.08 (m, 4H), 3.81 (s, 1H), 2.36 (s, 1H), 1.61 (s, 4H), 1.30-1.26 (m, 6H), 0.91-0.86 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 66.9 (d, $J = 161.8$ Hz), 62.1 (d, $J = 7.1$ Hz), 33.1, 18.6 (d, $J = 13.9$ Hz), 16.2 (d, $J = 5.3$ Hz), 13.4. HRMS (ESI) m/z : calcd for $\text{C}_8\text{H}_{19}\text{O}_4\text{P}$ $[\text{M}+\text{H}]^+$: 211.1099; Found: 211.1101.

Diethyl 1-hydroxy-2-methyl-propylphosphonate (5k). (lit.²) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 4.13-4.08 (m, 4H), 3.60-3.56 (m, 1H), 2.05-2.00 (m, 1H), 1.70 (s, 1H), 1.30-1.26 (m, 6H), 1.01-0.99 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 72.7 (d, $J = 157.6$ Hz), 62.2 (d, $J = 7.2$ Hz), 30.1 (d, $J = 2.7$ Hz), 19.8 (d, $J = 9.5$ Hz), 17.8 (d, $J = 7.7$ Hz), 16.4 (d, $J = 5.6$ Hz). HRMS (ESI) m/z : calcd for $\text{C}_8\text{H}_{19}\text{O}_4\text{P}$ $[\text{M}+\text{H}]^+$: 211.1099; Found: 211.1095.

Diethyl 1-hydroxy-3-methyl-butylphosphonate (5l). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 4.10-4.06 (m, 4H), 3.87 (s, 1H), 1.83 (s, 2H), 1.60 (d, $J = 10.8$ Hz, 1H), 1.27-1.23 (m, 6H), 0.89-0.82 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 65.5 (d, $J = 161.8$ Hz), 62.3, 39.8, 23.8 (d, $J = 14.1$ Hz), 23.4, 20.9, 16.3 (d, $J = 5.4$ Hz). HRMS (ESI) m/z : calcd for $\text{C}_9\text{H}_{21}\text{O}_4\text{P}$ $[\text{M}+\text{H}]^+$: 225.1256; Found: 225.1253.

Diethyl 1-hydroxy-2,2-dimethyl-propylphosphonate (5m). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 4.17 (s, 4H), 3.57 (s, 1H), 2.41 (s, 1H), 1.36-1.32 (m, 6H), 1.09 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 75.8 (d, $J = 155.1$ Hz), 62.2, 34.5, 26.6 (d, $J = 6.3$ Hz), 16.3. HRMS (ESI) m/z : calcd for $\text{C}_9\text{H}_{21}\text{O}_4\text{P}$ $[\text{M}+\text{H}]^+$: 225.1256; Found: 225.1256.

5. General Procedures for Hydrophosphonylation of Ketones

A mixture of the rare-earth metal complex (0.01 mmol) and diethyl phosphite (12 mmol) was stirred for 5 min, then acetophenone (10 mmol) was added to the mixture. The resulting mixture was stirred at room temperature under solvent-free conditions for 1 h. After the reaction was completed, water was added, and the mixture was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , and filtered. Then the solvent was evaporated under reduced pressure. The final products were further purified by washing with hexane.

Diethyl 1-hydroxy-1-phenyl-ethylphosphonate (6a).⁹ ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.42 (s, 5H), 4.07 - 3.89 (m, 4H), 3.66 (d, *J* = 3.9 Hz, 1H), 1.74 (d, *J* = 15.6 Hz, 3H), 1.23-1.15 (m, 6H). ¹³C NMR (300 MHz, CDCl₃, ppm): δ 141.2, 127.9, 127.3, 125.9 (d, *J* = 4.3 Hz), 73.3 (d, *J* = 149.3 Hz), 63.4 (d, *J* = 7.4 Hz), 63.2 (d, *J* = 7.6 Hz), 25.8, 16.4 (d, *J* = 4.8 Hz). HRMS (ESI) Calcd. for C₁₂H₁₉O₄P [M+H]⁺: 259.1099, Found 259.1096.

Diethyl 1-hydroxy-1-(4-nitro)phenyl-ethylphosphonate (6b).¹⁰ ¹H NMR (300 MHz, CDCl₃, ppm): δ 8.13 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 6.9 Hz, 2H), 5.11 (d, *J* = 12.9 Hz, 1H), 4.10-4.01 (m, 4H), 1.79 (d, *J* = 15.6 Hz, 3H), 1.24 - 1.15 (m, 6H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 148.9, 147.1, 127.0 (d, *J* = 4.0 Hz), 123.0, 73.5 (d, *J* = 159.5 Hz), 64.0 (d, *J* = 7.5 Hz), 63.4 (d, *J* = 7.9 Hz), 25.9, 16.4 (d, *J* = 5.3 Hz). HRMS (ESI) Calcd. for C₁₂H₁₈NO₆P [M+H]⁺: 304.0950, Found 304.0954.

Diethyl 1-hydroxy-1-(4-chloro)phenyl-ethylphosphonate (6c).¹¹ ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.48 (d, *J* = 7.3 Hz, 2H), 7.25 (d, *J* = 7.5 Hz, 2H), 4.47 (br, 1H), 4.06-3.92 (m, 4H), 1.73 (d, *J* = 15.4 Hz, 3H), 1.18 (s, 6H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 139.9, 133.2 (d, *J* = 3.5 Hz), 128.0, 127.5 (d, *J* = 4.3 Hz), 73.1 (d, *J* = 160.2 Hz), 63.6 (d, *J* = 7.5 Hz), 63.2 (d, *J* = 7.9 Hz), 25.8 (d, *J* = 3.9 Hz), 16.4 (d, *J* = 4.0 Hz). HRMS (ESI) Calcd. for C₁₂H₁₈ClO₄P [M+H]⁺: 293.0709, Found 293.0708.

Diethyl 1-hydroxy-1-(4-trifluoromethyl)phenyl-ethylphosphonate (6d). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.68 (d, *J* = 7.7 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 5.12 (br, 1H), 4.10-3.94 (m, 4H), 1.76 (d, *J* = 15.6 Hz, 3H), 1.21-1.15 (m, 6H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 145.8, 129.6 (d, *J* = 3.0 Hz), 129.1 (d, *J* = 3.0 Hz), 126.4 (d, *J* = 4.1 Hz), 124.7, 122.4, 73.2 (d, *J* = 160.2 Hz), 63.8 (d, *J* = 7.4 Hz), 63.2 (d, *J* = 7.9 Hz), 25.7 (d, *J* = 3.4 Hz), 16.3 (d, *J* = 3.4 Hz). HRMS (ESI) Calcd. for C₁₃H₁₈F₃O₄P [M+H]⁺: 327.0973, found 327.0973.

Diethyl 1-hydroxy-1-(2-methyl)phenyl-ethylphosphonate (6e). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.52 (m, 1H), 7.10 (m, 3H), 4.03-3.82 (m, 4H), 2.93 (d, *J* = 7.2 Hz, 1H), 2.59 (s, 3H), 1.85 (d, *J* = 15.3 Hz, 3H), 1.23-1.13 (m, 6H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 138.1, 137.1 (d, *J* = 5.5 Hz), 132.8, 127.8, 127.7 (d, *J* = 4.7 Hz), 125.5, 75.8 (d, *J* = 157.0 Hz), 63.4 (d, *J* = 7.6 Hz), 63.0 (d, *J* = 7.5 Hz), 26.6, 22.9, 16.4 (d, *J* = 4.7 Hz). HRMS (ESI) Calcd. for C₁₃H₂₁O₄P [M+H]⁺: 273.1255, Found 273.1252.

Diethyl 1-hydroxy-1-(4-methyl)phenyl-ethylphosphonate (6f). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.43 (d, *J* = 7.0 Hz, 2H), 7.10 (d, *J* = 7.3 Hz, 2H), 4.05-3.79 (m, 4H), 2.28 (s, 3H), 1.74 (d, *J* = 15.4 Hz, 3H), 1.22-1.13 (m, 6H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 138.0, 136.9 (d, *J* = 3.7 Hz), 128.7, 125.8 (d, *J* = 4.3 Hz), 73.4 (d, *J* = 158.7 Hz), 63.4, 63.2, 25.9, 21.0, 16.4 (d, *J* = 5.0 Hz). HRMS (ESI) Calcd. for C₁₃H₂₁O₄P [M+H]⁺: 273.1255, Found 273.1256.

Diethyl 1-hydroxy-1-methyl-ethylphosphonate (6g).² ¹H NMR (300 MHz, CDCl₃, ppm): δ 4.21-4.11 (m, 4H), 3.35 (br, 1H), 1.44 (s, 3H), 1.39 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 69.2 (d, *J* = 163.1 Hz), 62.7 (d, *J* = 7.5 Hz), 24.9 (d, *J* = 5.2 Hz), 16.4 (d, *J* = 5.5 Hz). HRMS (ESI) Calcd. for C₇H₁₇O₄P [M+H]⁺: 197.0943, Found 197.0945.

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Copies of ^1H and ^{13}C NMR Spectra of phosphonate

