

Supporting Information

Tuning Rare-Earth Hydride Reactivity with a Reductive Diazabutadienyl Ligand Beyond Insertion

Xiaoqing Lin^[a], Jie Zhang^{*, [a]} and Xigeng Zhou^{*, [a]}

[a] Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200438, China.

* E-mail: zhangjie@fudan.edu.cn; xgzhou@fudan.edu.cn

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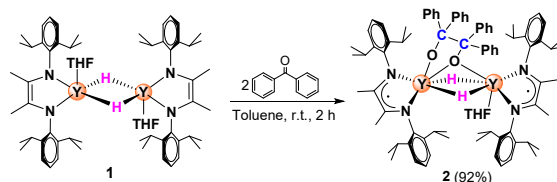
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Experimental Procedures

All reactions were carried out under a dry and oxygen-free nitrogen atmosphere in a Vigor (SG2400/750TS-F) glovebox. Anhydrous tetrahydrofuran, toluene, and *n*-hexane were purified using an MB SPS-800 solvent purification system and dried over fresh sodium chips in the glovebox. C₆D₆, toluene-d₈ and THF-d₈ were purchased from J&K and transferred under vacuum, dried over fresh sodium chips and stored in a glovebox. Organometallic samples for NMR spectroscopic measurements were prepared in a glovebox using J-Young valve NMR tubes. The ¹H spectra were recorded on a Bruker Avance 400 MHz spectrometer at room temperature. The ¹³C NMR spectra were recorded on a Bruker Avance 100 MHz at room temperature. All chemical shifts were reported in δ units and referenced to residual solvent signals of C₆D₆ and TFA-d₁ solvents for ¹H NMR chemical shifts. IR spectra were recorded on a Bruker ALPHA II spectrometer in a glovebox. EPR spectra of solid samples were measured with a Bruker E500-10/12 spectrometer. Low-temperature EPR spectra was acquired on Bruker EMX instrument EMXPLUS-10/12. The gas products were detected using a gas chromatography (GC-2010 Plus) by Barrier Discharge Ionization Detector. Elemental analyses for C, H, and N were carried out on an Elementar Vario Micro Cube elemental analyzer. UV-Vis absorption spectra were collected on an Agilent Cary 60 spectrometer. Rare-earth hydride [(DAD)Y·THF]₂(μ-H)₂ was prepared according to a literature procedure.¹ (Ethyne-*d*)benzene was synthesized from a reaction of PhC≡CLi with D₂O.² (DAD')Li(THF) was prepared by the reaction of lithium and DAD in THF.³

2. Synthesis and characterization of All New Complexes

2.1 Synthesis and characterization of $(\text{DAD}'\text{Y})_2(\mu\text{-H})_2(\mu\text{-}\eta^2\text{:}\eta^1\text{-Ph}_2\text{C}(\text{O})\text{C}(\text{O})\text{Ph}_2)(\text{THF})$ (**2**).



A solution of benzophenone (Ph_2CO) (0.182 g, 1.0 mmol; in 5 mL of toluene) was added slowly to a stirred toluene solution (5 mL) of **1** (0.567 g, 0.5 mmol). After the mixture was stirred at ambient temperature for 2 h, the dark brown solution was evaporated to dryness under vacuum. The residue was washed (5 mL \times 2) with *n*-hexane to give the brown solid powder **2**. Yellow crystals were obtained by a slow solvent evaporation method from a toluene (2 mL) solution of **2**. Yield: 0.656 g (92%). IR (Nujol, cm^{-1}): $\nu = 3055$ (w), 2963 (s), 2865 (m), 1575 (w), 1460 (m), 1433 (m), 1378 (s), 1313 (m), 1251 (w), 1196 (m), 1159 (m), 1099 (m), 1055 (s, $\nu(\text{CO})$), 1028 (s), 971 (m), 932 (w), 852 (s), 784 (s), 745 (s), 708 (s), 694 (m), 651 (m), 598 (w), 536 (m), 448 (w). EPR (293 K): $g = 2.001$. Anal. Calcd for $\text{C}_{86}\text{H}_{110}\text{N}_4\text{O}_3\text{Y}_2$ (1425.59): C, 72.45; H, 7.78; N, 3.93; Found: C, 72.54; H, 7.73; N, 3.99.

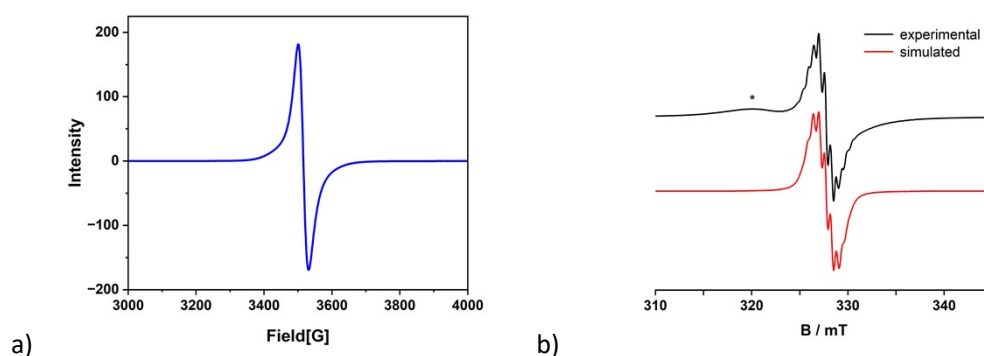


Figure S1. a) EPR spectrum of **2** (293 K) in the solid state, the g -factor is 2.001. b) Experimental (black) and simulated (red) EPR spectra of **2** (210 K) in toluene. The asterisks (*) indicate the signals derived from spin–spin splitting. ($g_{\text{iso}}=2.0018$, $A_{\text{iso}}(^{14}\text{N}, 2\text{N})=5.44\times 10^{-4} \text{ cm}^{-1}$, $A_{\text{iso}}(^{89}\text{Y})=A_{\text{iso}}(^1\text{H}, 2\text{H})=5.60\times 10^{-4} \text{ cm}^{-1}$)

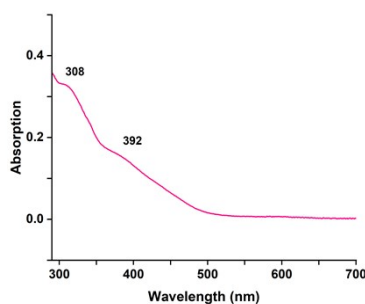
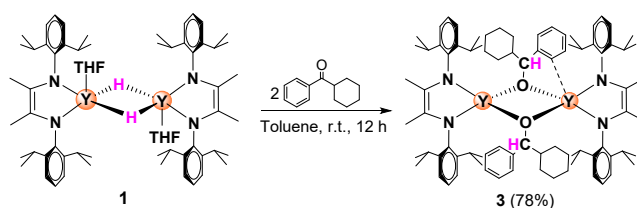


Figure S2. UV/vis spectrum **2** in toluene.

2.2 Synthesis and characterization of $[(\text{DAD})\text{Y}(\mu\text{-OC}(\text{H})\text{PhCy})_2]$ (**3**).



A solution of cyclohexyl phenyl ketone (PhC(O)Cy) (0.188 g, 1.0 mmol; in 5 mL of toluene) was added slowly to a stirred toluene solution (5 mL) of **1** (0.567 g, 0.5 mmol). After the mixture was stirred at ambient temperature for 12 h, the red solution was evaporated to dryness under vacuum. The residue was washed (5 mL \times 2) with *n*-hexane to give the yellow solid powder **3**. Yellow crystals were obtained by a slow solvent evaporation method from a toluene (2 mL) solution of **3**. Yield: 0.533 g (78%). ^1H NMR (400 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ (ppm) = 0.17 (d, J = 6.5 Hz, 6H, CH_3 - ^iPr), 0.22-0.31 (m, 2H, CH_2 -Cy), 0.54-0.68 (m, 4H, CH_2 -Cy), 0.76 (d, J = 6.3 Hz, 6H, CH_3 - ^iPr), 0.80-0.94 (m, 4H, CH_2 -Cy), 1.11-1.17 (m, 2H, CH_2 -Cy), 1.21-1.27 (m, 2H, CH_2 -Cy), 1.32 (d, J = 6.4 Hz, 6H, CH_3 - ^iPr), 1.37-1.43 (m, 18H, N-CCH₃ and CH_3 - ^iPr), 1.46 (d, J = 5.7 Hz, 12H, CH_3 - ^iPr), 1.51-1.59 (m, 4H, CH_2 -Cy), 1.71 (d, J = 6.5 Hz, 6H, CH_3 - ^iPr), 1.75-1.81 (m, 2H, CH_2 -Cy), 1.95 (s, 6H, N-CCH₃), 2.04 (d, J = 10.3 Hz, 2H, CH-Cy), 3.40-3.69 (m, 6H, CH- ^iPr), 4.01-4.09 (m, 2H, CH- ^iPr), 4.94 (d, J = 4.4 Hz, 2H, OCHPhCy), 6.73-6.80 (m, 4H, *H*-Ar), 6.92-6.97 (m, 5H, *H*-Ph), 7.13-7.16 (m, 5H, *H*-Ph), 7.17-7.19 (m, 3H, *H*-Ar), 7.26-7.33 (m, 5H, *H*-Ar). ^{13}C NMR (100 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ (ppm) = 17.0 (s, N-CCH₃), 20.3 (s, N-CCH₃), 24.2 (s, CH_3 - ^iPr), 24.7 (s, CH_3 - ^iPr), 24.8 (s, CH_3 - ^iPr), 24.9 (s, CH_3 - ^iPr), 25.2 (s, CH_3 - ^iPr), 25.4-25.7 (m, CH_2 -Cy), 26.1 (s, CH_2 -Cy), 26.6 (s, CH_2 -Cy), 27.0 (s, CH- ^iPr), 27.3 (s, CH- ^iPr), 27.9 (s, CH_2 -Cy), 30.8 (s, CH_2 -Cy), 31.1 (s, CH_2 -Cy), 45.2 (s, CH-Cy), 82.4 (s, OCHPhCy), 111.0 (s, N-CCH₃), 113.9 (s, N-CCH₃), 122.3 (s, C-Ar), 123.1 (s, C-Ph), 123.4 (s, C-Ph), 123.8 (s, C-Ph), 125.0 (s, C-Ar), 141.3 (s, C-Ph), 144.0 (s, C-Ar), 144.1 (s, C-Ar), 144.5 (s, C-Ph), 145.3 (s, C-Ph), 148.0 (d, J = 3.6 Hz, C-Ph), 149.6 (d, J = 4.2 Hz, C-Ph). Anal. Calcd for $\text{C}_{82}\text{H}_{114}\text{N}_4\text{O}_2\text{Y}_2$ (1365.65): C, 72.12; H, 8.41; N, 4.10; Found: C, 72.19; H, 8.40; N, 4.15.

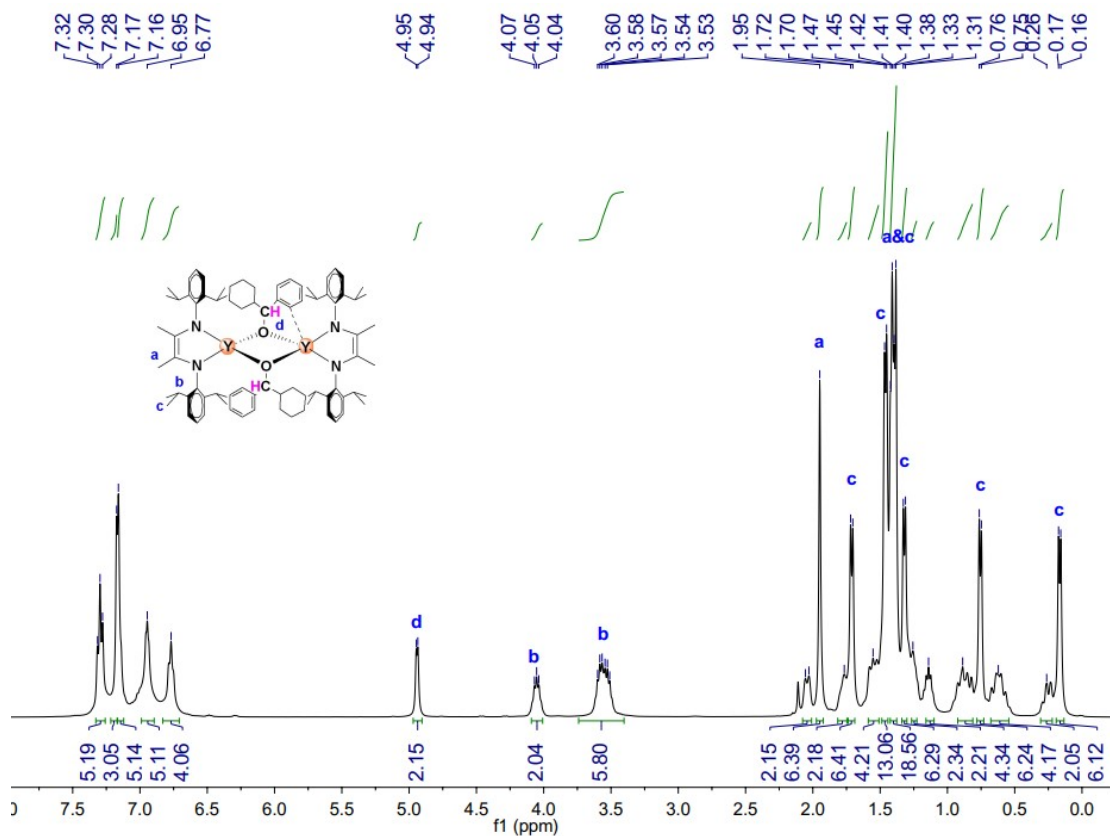


Figure S3. ^1H NMR spectrum of complex **3** in C_6D_6 at room temperature.

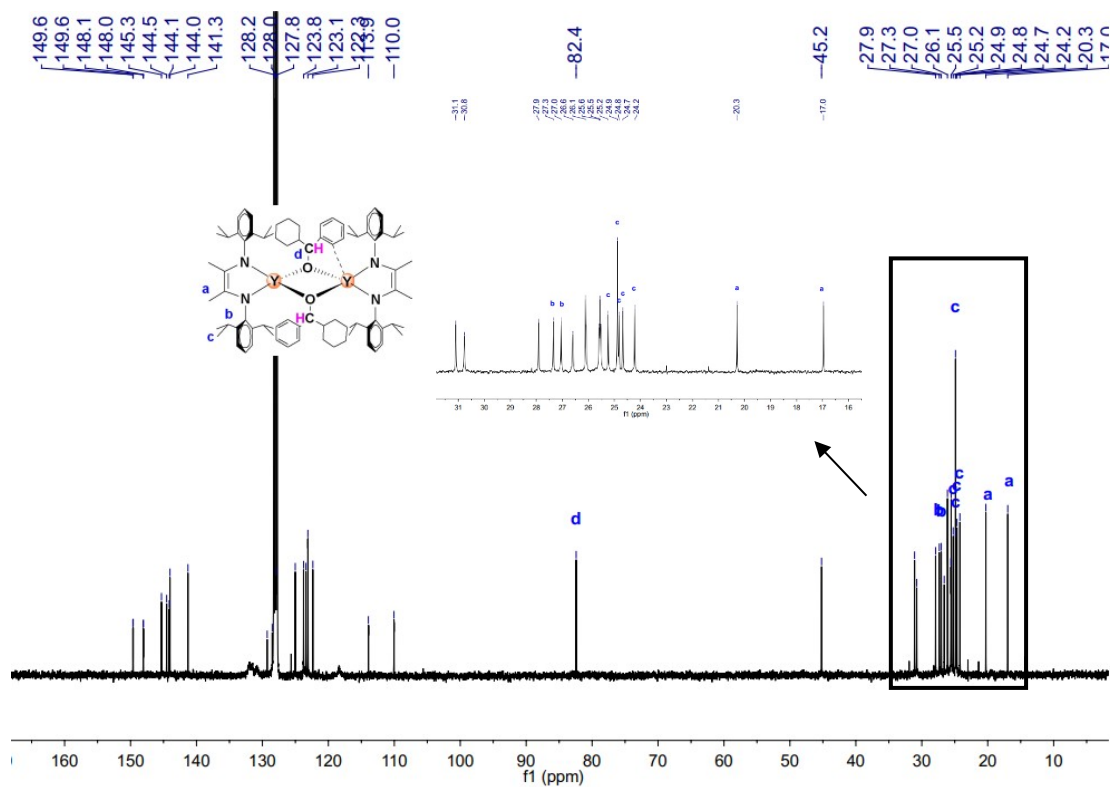


Figure S4. ^{13}C NMR spectrum of complex **3** in C_6D_6 at room temperature.

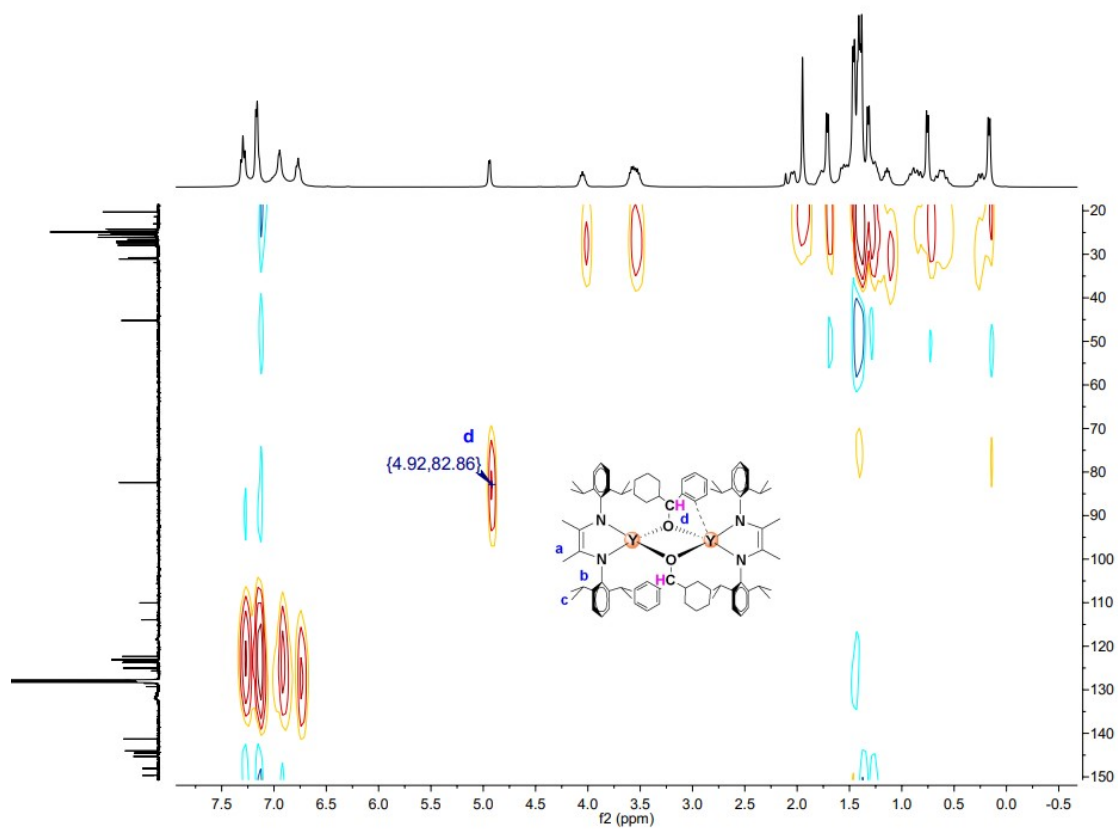


Figure S5. ^{13}C - ^1H HSQC spectrum of complex **3** in C_6D_6 at room temperature.

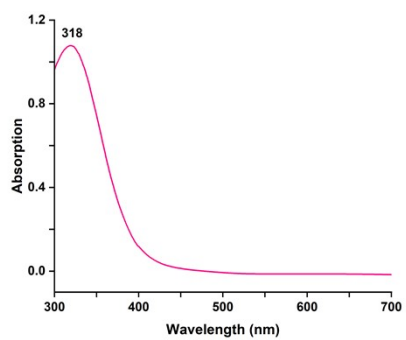
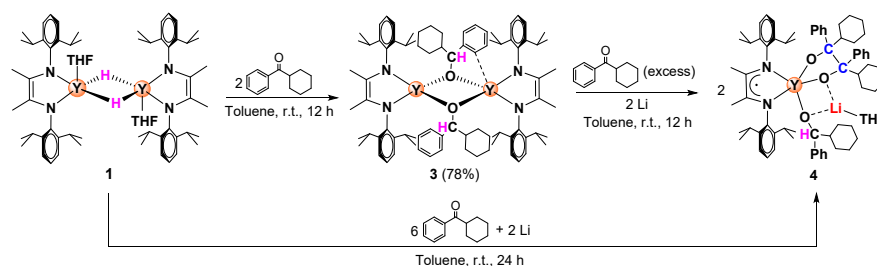


Figure S6. UV/vis spectrum of **3** in toluene.

2.3 Synthesis and characterization of (DAD')Y(PhCyC(O)C(O)PhCy)(OC(H)PhCy)Li(THF) (**4**).



Path A: A solution of excess cyclohexyl phenyl ketone (PhC(O)Cy) (0.282 g, 1.5 mmol; in 10 mL of toluene) was added slowly to a stirred toluene solution (10 mL) of **3** (0.410 g, 0.3 mmol), and then 2 equivalents of Li (0.004 g, 0.6 mmol) was added to the mixture at ambient temperature. Keeping stirring for 12 h, the mixture was filtered and the red filtrate was evaporated to dryness under vacuum. The residue was washed (5 mL \times 2) with *n*-hexane to give the yellow solid powder **4**. Yellow crystals were obtained by a slow solvent evaporation method from a toluene (2 mL) solution of **4**. Yield: 0.417 g (61%).

Path B: A solution of cyclohexyl phenyl ketone (PhC(O)Cy) (0.565 g, 3.0 mmol; in 10 mL of toluene) was added slowly to a stirred toluene solution (10 mL) of **1** (0.567 g, 0.5 mmol), and then 2 equivalents of Li (0.007 g, 1.0 mmol) was added to the mixture at ambient temperature. Keeping stirring for 24 h, the mixture was filtered and the red filtrate was evaporated to dryness under vacuum. The residue was washed (5 mL \times 2) with *n*-hexane to give the yellow solid powder **4**. Yellow crystals were obtained by a slow solvent evaporation method from a toluene (2 mL) solution of **4**. Yield: 0.603 g (53%).

IR (Nujol, cm^{-1}): $\nu = 3053$ (w), 2960 (s), 2918 (s), 2854 (m), 1575 (w), 1435 (m), 1378 (m), 1315 (w), 1253 (w), 1231 (w), 1198 (w), 1089 (s), 1067 (s, $\nu(\text{CO})$), 1038 (m), 1005 (m), 915 (w), 889 (w), 864 (w), 778 (m), 762 (w), 713 (s), 645 (w), 573 (w), 508 (w), 438 (w). EPR (293 K): $g = 2.001$. Anal. Calcd for $\text{C}_{71}\text{H}_{97}\text{N}_2\text{O}_4\text{YLi}$ (1138.36): C, 74.91; H, 8.59; N, 2.46; Found: C, 74.83; H, 8.64; N, 2.45.

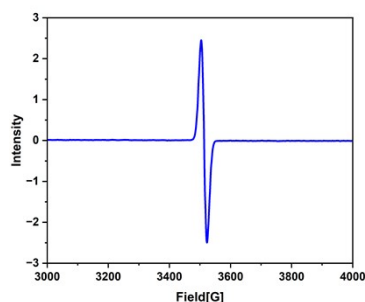


Figure S7. EPR spectrum of complex **4** (293 K) in the solid state, the g -factor is 2.001.

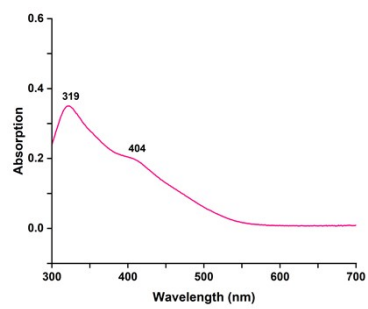
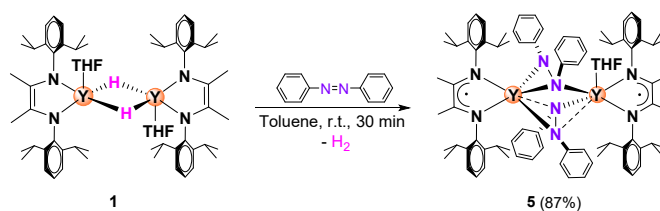


Figure S8. UV/vis spectrum of **4** in toluene.

2.4 Synthesis and characterization of (DAD'Y)₂(μ-N(Ph)NPh)₂(THF) (5).



A solution of azobenzene (PhN=NPh) (0.182 g, 1.0 mmol; in 5 mL of toluene) was added slowly to a stirred toluene solution (10 mL) of **1** (0.567 g, 0.5 mmol). After the mixture was stirred at ambient temperature for 30 min, the dark red solution was evaporated to dryness under vacuum. The residue was washed (5 mL × 2) with *n*-hexane to give the brown solid powder **5**. Yellow crystals were obtained by a slow solvent evaporation method from a toluene (2 mL) solution of **5**. Yield: 0.619 g (87%). IR (Nujol, cm⁻¹): $\nu = 3055$ (w), 2960 (s), 2868 (m), 1588 (s), 1478 (s), 1431 (m), 1370 (s), 1308 (s), 1255 (m), 1237 (m), 1192 (m), 1170 (m), 1069 (w), 991 (w), 971 (w), 852 (m), 784 (s), 747 (s), 698 (w), 616 (w), 539 (w). EPR (293 K): $g = 2.000$. Anal. Calcd for C₈₄H₁₀₈N₈OY₂ (1423.60): C, 70.87; H, 7.65; N, 7.87; Found: C, 70.40; H, 7.80; N, 7.76.

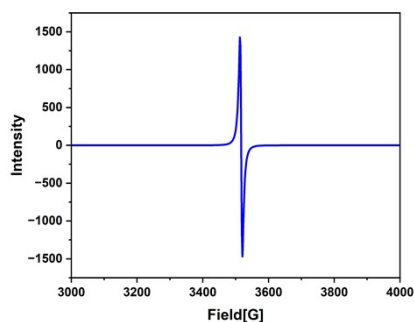


Figure S9. EPR spectrum of complex **5** (293 K) in the solid state, the g -factor is 2.000.

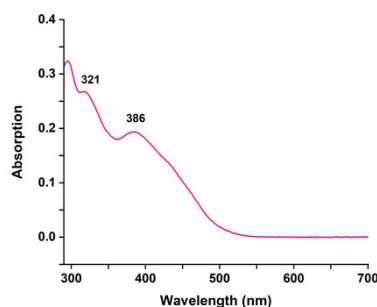
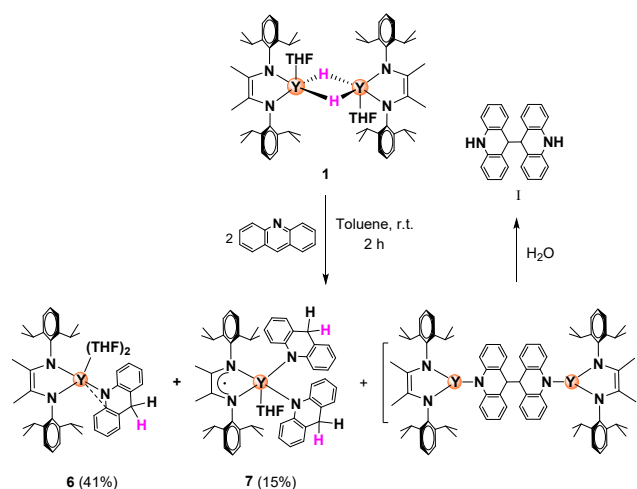


Figure S10. UV/vis spectrum of **5** in toluene.

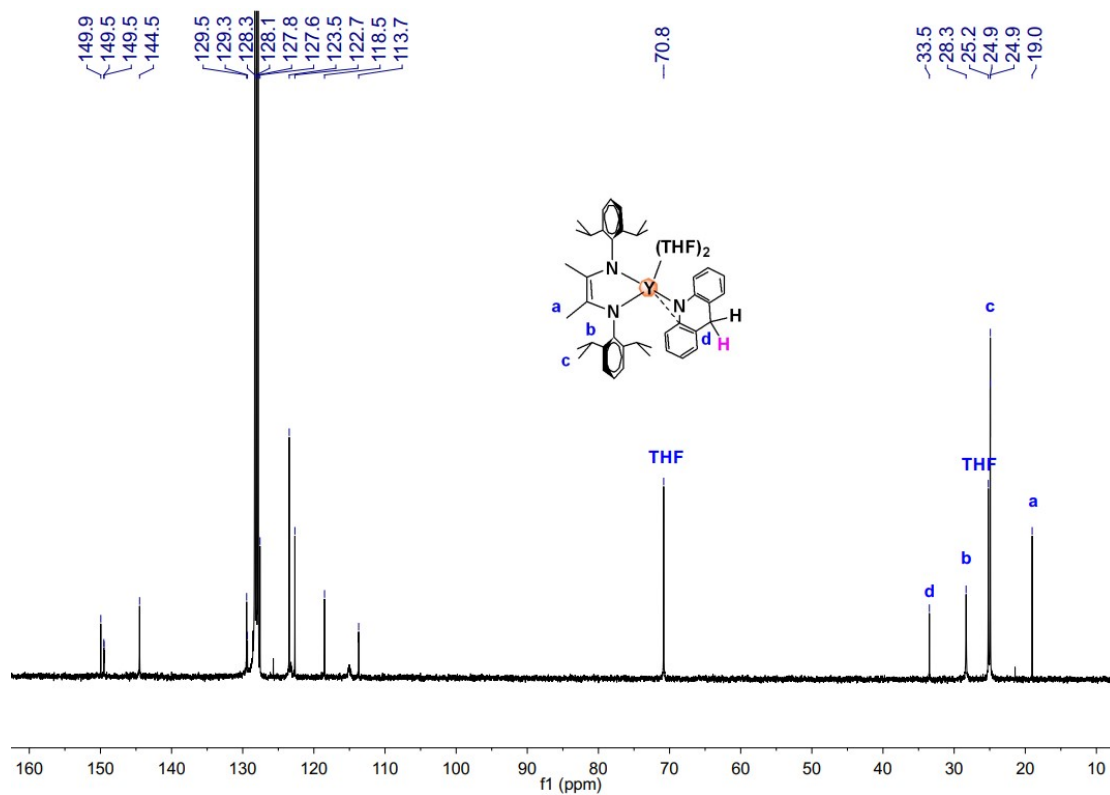
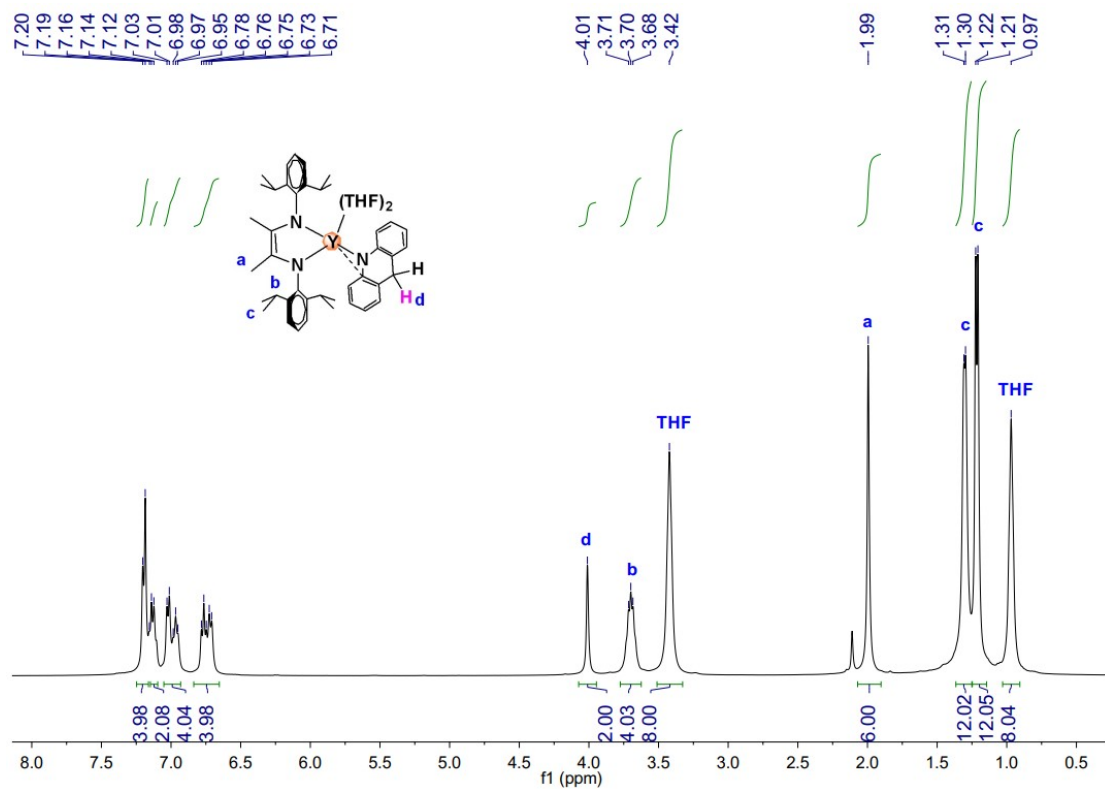
2.5 Synthesis and characterization of (DAD)Y(NC₁₃H₁₀)(THF)₂ (**6**) and (DAD')Y(NC₁₃H₁₀)₂(THF) (**7**).



A solution of acridine (0.179 g, 1.0 mmol; in 5 mL of toluene) was added slowly to a stirred toluene solution (5 mL) of **1** (0.567 g, 0.5 mmol). After the mixture was stirred at ambient temperature for 2 h, the dark red solution was evaporated to dryness under vacuum. The residue was washed (5 mL \times 2) with *n*-hexane to give the yellow solid powder complexes. The yellow powder complexes were then extracted with toluene to give crude product **6**, accompanied by a slow solvent evaporation method for extracting solution to give pale-yellow single crystals of **6**, while insoluble residue was redissolved in THF, accompanied by a slow solvent evaporation method to give yellow single crystals of **7**, which are all suitable for X-ray diffraction analysis. Then the mother liquor was hydrolyzed with water (2 mL) and extracted with DCM (3 \times 10 mL). The organic phases were combined, dried with anhydrous Na₂SO₄, and evaporated under vacuum. A yellow solid was obtained and identified to contain the acridine dimer (**1**), analyzed by ¹H NMR spectroscopy. The spectral data of acridine dimer are matched with the previously reported data.⁴

For **6**, Yield: 0.335 g (41%). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ (ppm) = 0.97 (s, 8H, THF), 1.22 (d, *J* = 6.4 Hz, 12H, CH₃-^{*i*}Pr), 1.30 (d, *J* = 4.5 Hz, 12H, CH₃-^{*i*}Pr), 1.99 (s, 6H, N-CCH₃), 3.42 (s, 8H, THF), 3.62-3.77 (m, 4H, CH-^{*i*}Pr), 4.01 (s, 2H, CH₂-NC₁₃H₁₀), 6.65-6.84 (m, 4H, *H*-Ph), 6.93-7.05 (m, 4H, *H*-Ph), 7.08-7.15 (m, 2H, *H*-Ar), 7.16-7.21 (m, 4H, *H*-Ar). ¹³C NMR (100 MHz, C₆D₆, 25 °C): δ (ppm) = 19.0 (s, N-CCH₃), 25.0 (d, *J* = 2.5 Hz, CH₃-^{*i*}Pr), 25.2 (s, THF), 28.3 (s, CH-^{*i*}Pr), 33.5 (s, CH₂-NC₁₃H₁₀), 70.8 (s, THF), 113.7 (s, N-CCH₃), 118.5 (s, C-Ph), 122.7 (s, C-Ar), 123.5 (s, C-Ar), 127.6 (s, C-Ph), 129.5 (s, C-Ph), 144.5 (s, C-Ar), 149.5 (d, *J* = 3.7 Hz, C-Ph), 149.9 (s, C-Ph). Anal. Calcd for C₄₉H₆₆N₃O₂Y (817.95): C, 71.95; H, 8.13; N, 5.14; Found: C, 71.68; H, 8.20; N, 5.21.

For **7**, Yield: 0.139 g (15%). IR (Nujol, cm⁻¹): ν = 3055 (w), 2959 (m), 2864 (w), 1589 (m), 1450 (s), 1431 (s), 1375 (s), 1310 (m), 1278 (m), 1255 (s), 1214 (m), 1194 (s), 1150 (m), 1120(m), 1069 (w), 1034 (w), 991 (w), 971 (w), 886 (s), 852 (w), 839 (w), 764 (s), 747 (m), 722(m), 618 (w), 440 (w). EPR (293 K): *g* = 2.002. Anal. Calcd for C₅₈H₆₈N₄OY (926.07): C, 75.22; H, 7.40; N, 6.05; Found: C, 75.33; H, 7.36; N, 6.01.



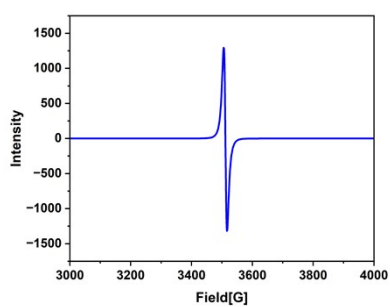


Figure S13. EPR spectrum of complex **7** (293 K) in the solid state, the g -factor is 2.002.

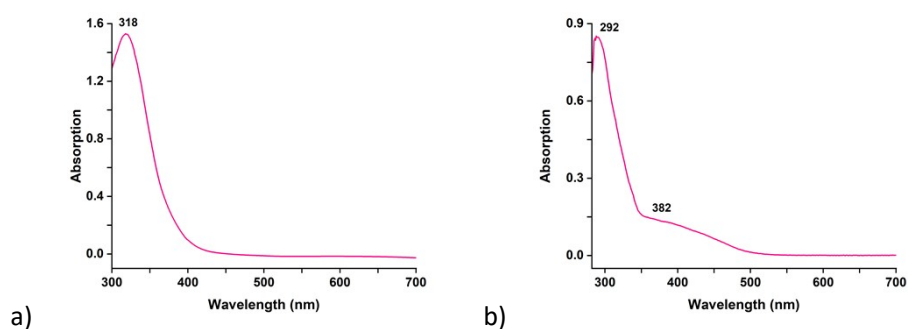


Figure S14. a) UV/vis spectrum of **6** in toluene; b) UV/vis spectrum of **7** in toluene.

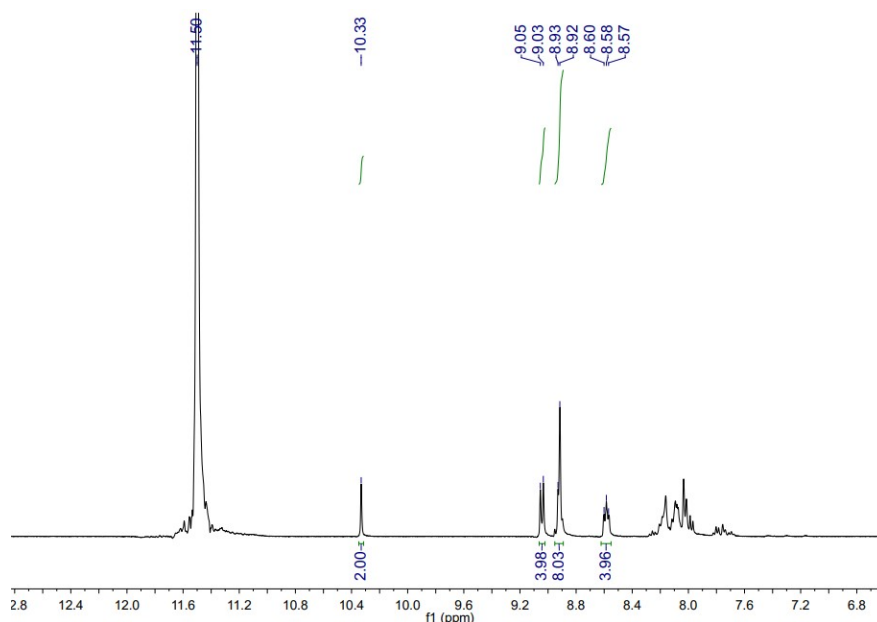
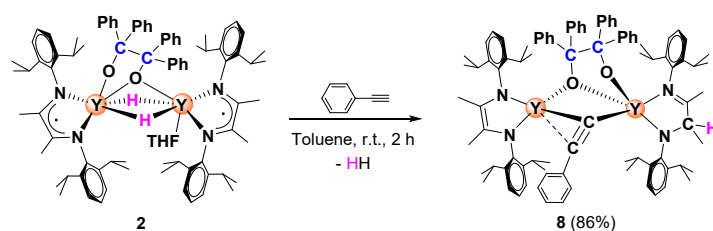


Figure S15. ^1H NMR spectrum of the crude organic compound **I** formed by the reaction of **1** with acridine after hydrolysis in TFA-d_1 .

2.6 Synthesis and characterization of (DAD)Y(μ -Ph₂C(O)C(O)Ph₂)(μ - η^2 : η^1 -C \equiv CPh)Y(HDAD) (**8**).



A solution of phenylacetylene (PhC \equiv CH) (0.031g, 0.3 mmol; in 5 mL of toluene) was added slowly to a stirred toluene solution (5 mL) of **2** (0.410 g, 0.3 mmol). After the mixture was stirred at ambient temperature for 2 h, the light red solution was evaporated to dryness under vacuum. The residue was washed (5 mL \times 2) with *n*-hexane to give the pale-yellow solid powder **8**. Yellow crystals were obtained by a slow solvent evaporation method from a toluene (2 mL) solution of **8**. Yield: 0.375 g (86%). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ (ppm) = 0.32 (d, *J* = 6.5 Hz, 3H, CH₃-^{*i*}Pr), 0.47 (d, *J* = 6.8 Hz, 3H, CH₃-^{*i*}Pr), 0.91 (s, 3H, N-CHCH₃), 0.96 (d, *J* = 6.7 Hz, 3H, CH₃-^{*i*}Pr), 1.01 (t, *J* = 7.3 Hz, 6H, CH₃-^{*i*}Pr), 1.06 (d, *J* = 6.7 Hz, 3H, CH₃-^{*i*}Pr), 1.11 (d, *J* = 2.4 Hz, 3H, CH₃-^{*i*}Pr), 1.13 (overlap s, 3H, N=CCH₃), 1.17 (d, *J* = 6.6 Hz, 3H, CH₃-^{*i*}Pr), 1.21 (d, *J* = 6.6 Hz, 3H, CH₃-^{*i*}Pr), 1.28 (d, *J* = 6.5 Hz, 6H, CH₃-^{*i*}Pr), 1.34 (t, *J* = 7.3 Hz, 6H, CH₃-^{*i*}Pr), 1.41 (s, 3H, N-CCH₃), 1.45 (d, *J* = 6.5 Hz, 3H, CH₃-^{*i*}Pr), 1.56 (s, 3H, N-CCH₃), 1.84 (d, *J* = 6.5 Hz, 3H, CH₃-^{*i*}Pr), 2.07 (d, *J* = 6.7 Hz, 3H, CH₃-^{*i*}Pr), 2.65–2.75 (m, 1H, CH-^{*i*}Pr), 3.02–3.11 (m, 1H, CH-^{*i*}Pr), 3.11–3.21 (m, 1H, CH-^{*i*}Pr), 3.53–3.65 (m, 2H, CH-^{*i*}Pr and N-CHCH₃), 3.71–3.89 (m, 4H, CH-^{*i*}Pr), 6.12–6.33 (m, 3H, *H*-Ph), 6.48 (br s, 2H, *H*-Ph), 6.61 (t, *J* = 7.3 Hz, 2H, *H*-Ph), 6.70 (t, *J* = 7.2 Hz, 2H, *H*-Ph), 6.76 (br s, 2H, *H*-Ph), 6.85–6.89 (m, 2H, *H*-Ph), 6.91–6.99 (m, 4H, *H*-Ph and *H*-Ar), 7.00–7.05 (m, 2H, *H*-Ph), 7.08–7.14 (m, 3H, *H*-Ar), 7.20–7.26 (m, 5H, *H*-Ar), 7.35 (d, *J* = 7.6 Hz, 2H, *H*-Ph), 7.43 (d, *J* = 7.5 Hz, 4H, *H*-Ph), 8.04 (d, *J* = 6.4 Hz, 2H, *H*-Ph). ¹³C NMR (100 MHz, C₆D₆, 25 °C): δ (ppm) = 16.3 (s, N-CCH₃), 16.9 (s, N-CHCH₃), 22.4 (s, N=CCH₃), 23.3 (s, CH₃-^{*i*}Pr), 24.7 (s, CH₃-^{*i*}Pr), 24.8 (s, CH₃-^{*i*}Pr), 25.4–25.6 (m, CH₃-^{*i*}Pr), 26.0 (s, CH₃-^{*i*}Pr), 26.2 (s, CH₃-^{*i*}Pr), 26.4 (s, CH₃-^{*i*}Pr), 26.6–27.2 (m, CH₃-^{*i*}Pr), 27.3 (s, CH-^{*i*}Pr), 27.7 (s, CH-^{*i*}Pr), 28.6 (s, CH-^{*i*}Pr), 28.7 (s, CH-^{*i*}Pr), 28.8 (s, CH-^{*i*}Pr), 29.1 (s, CH₃-^{*i*}Pr), 29.2 (s, CH₃-^{*i*}Pr), 29.5 (s, CH-^{*i*}Pr), 71.6 (s, N-CHCH₃), 111.0 (s, N-CCH₃), 113.0 (s, N-CCH₃), 122.2 (s, C-Ph), 122.7 (s, C-Ph), 122.9 (s, YC \equiv C), 123.6 (s, C-Ar), 123.7 (s, C-Ar), 124.0 (d, ²*J*_{YC} = 5.1 Hz, YC \equiv C), 124.3 (s, C-Ph), 125.7 (s, C-Ph), 126.0 (s, C-Ar), 126.6 (s, C-Ar), 127.3 (s, C-Ar), 129.8 (s, C-Ar), 133.5 (s, C-Ph), 140.5 (s, C-Ph), 141.8 (s, C-Ph), 143.0 (s, C-Ph), 143.7 (s, C-Ph), 143.8 (s, C-Ar), 145.3 (s, C-Ph), 145.6 (s, C-Ph), 146.0 (s, C-Ph), 146.5 (s, C-Ph), 146.9 (s, C-Ph), 148.5 (d, ¹*J*_{YC} = 65.6 Hz, YC \equiv C), 149.1 (s, C-Ph), 150.1 (s, C-Ph), 151.8 (s, YC \equiv C), 154.1 (d, C-Ph), 200.2 (s, C-Ph). Calcd for C₉₀H₁₀₆N₄O₂Y₂ (1453.67): C, 74.36; H, 7.35; N, 3.85; Found: C, 74.35; H, 7.53; N, 3.64.

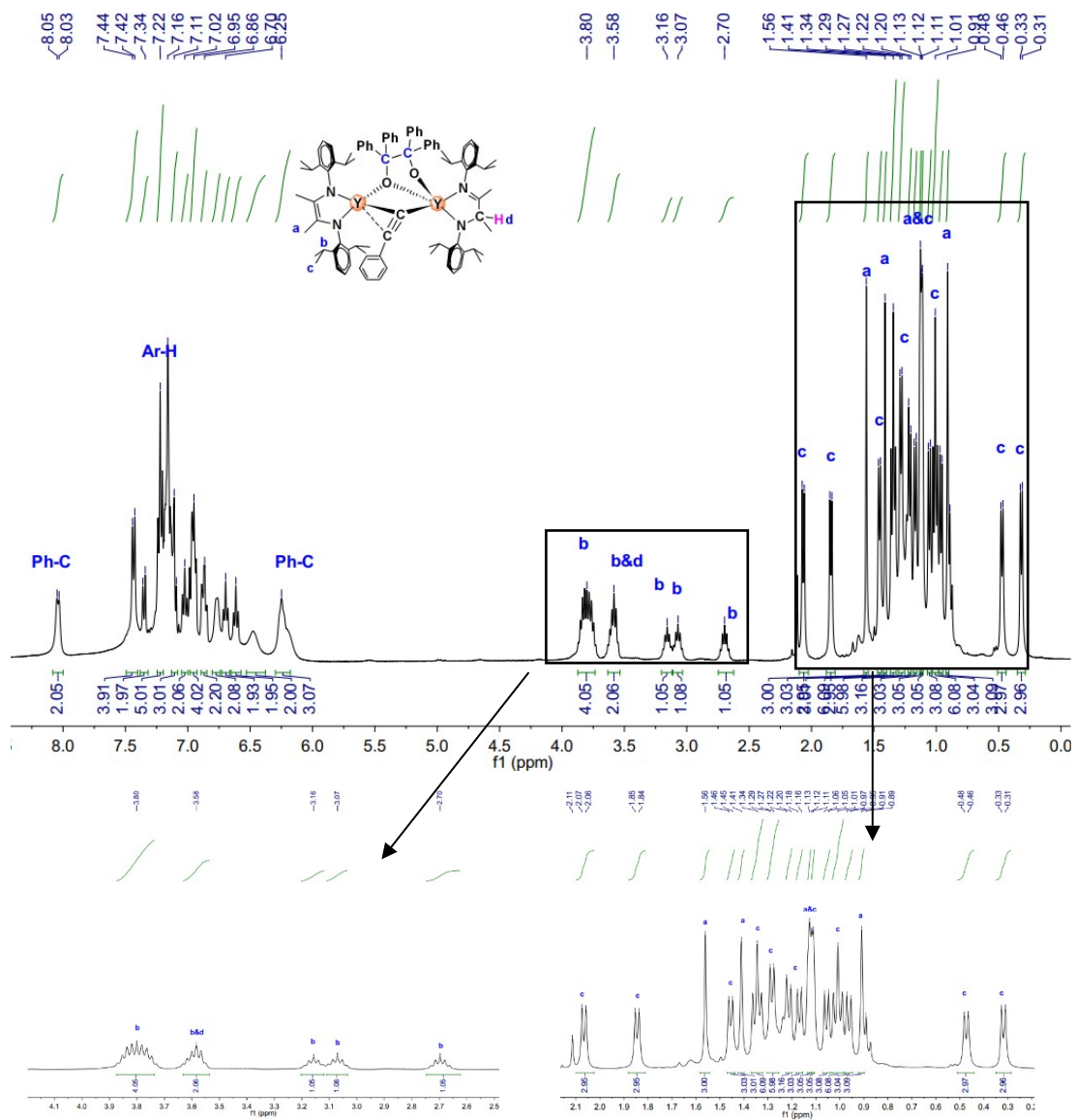


Figure S16. ^1H NMR spectrum of complex **8** in C_6D_6 at room temperature.

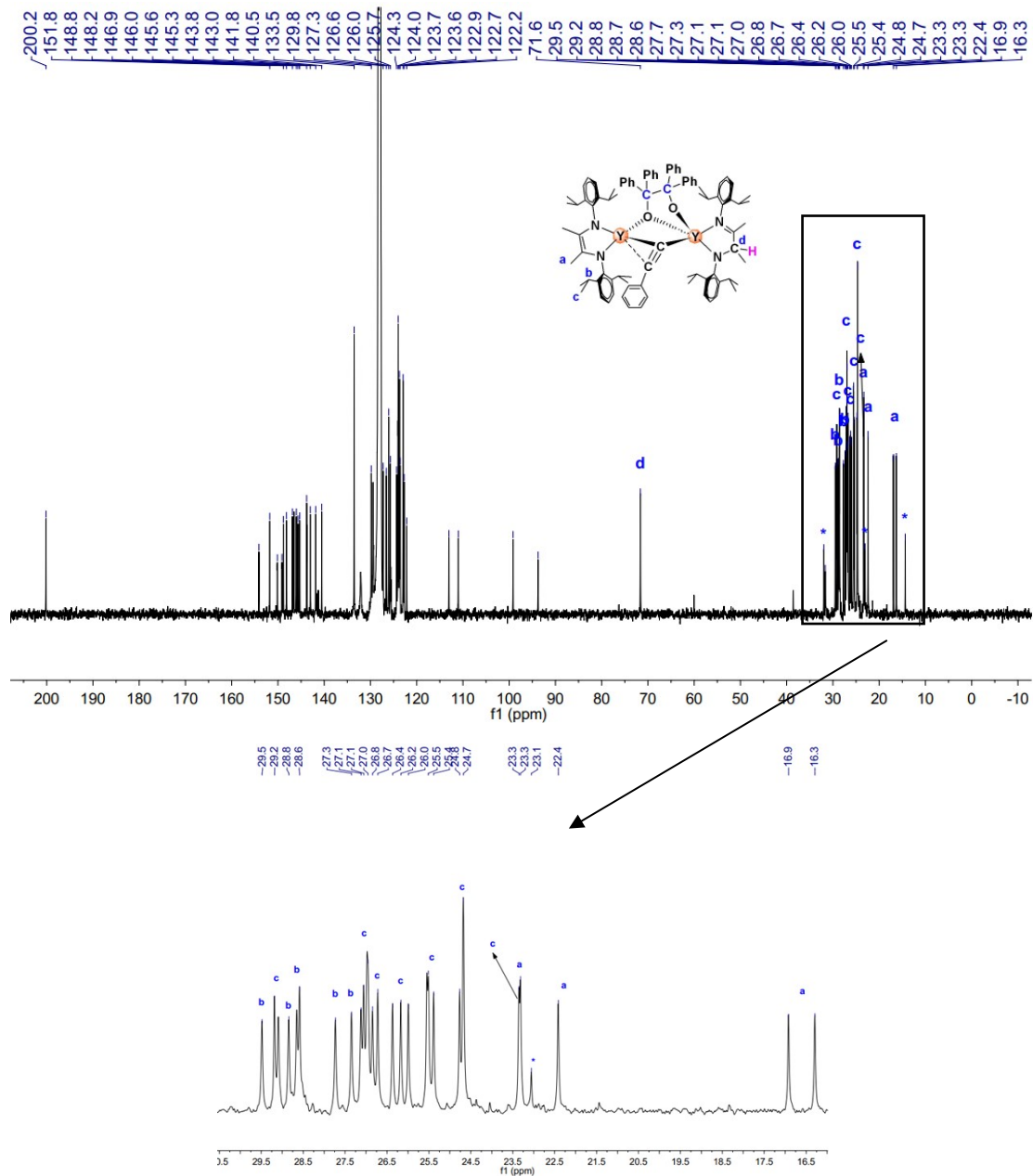


Figure S17. ^{13}C NMR spectrum of complex **8** in C_6D_6 at room temperature.

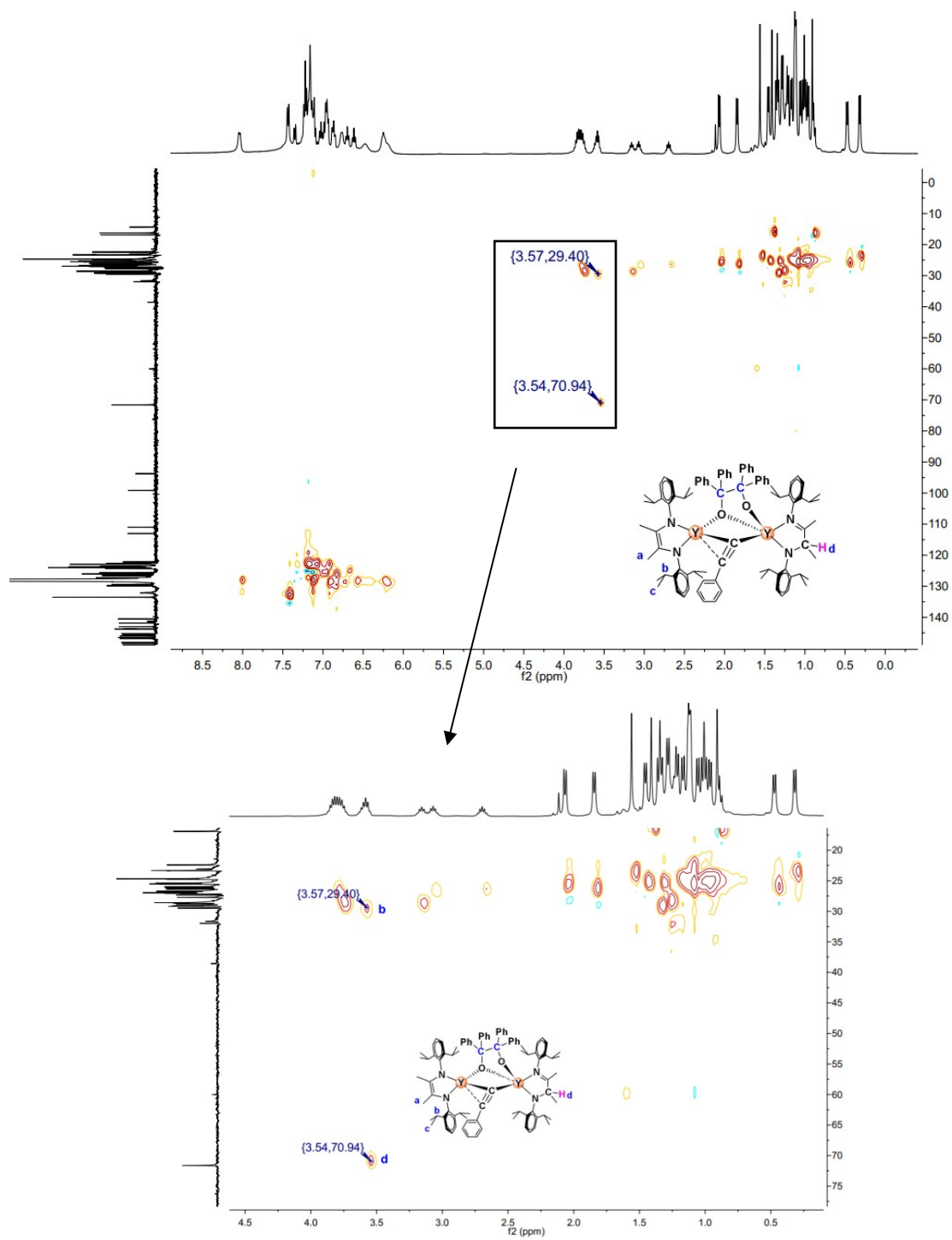


Figure S18. ^{13}C - ^1H HSQC spectrum of complex **8** in C_6D_6 at room temperature.

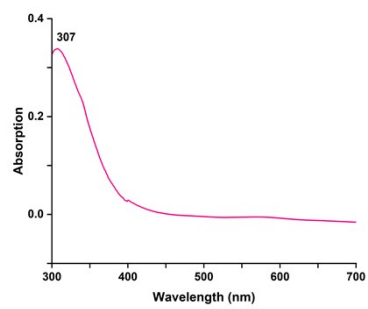
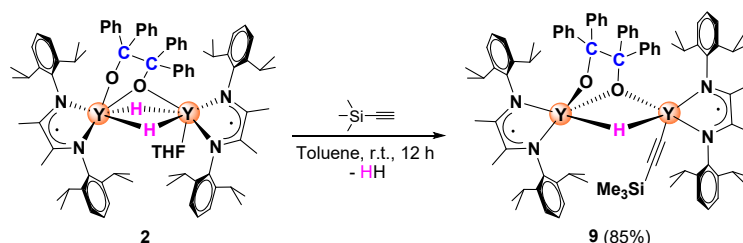


Figure S19. UV/vis spectrum of **8** in toluene.

2.7 Synthesis and characterization of (DAD'Y)₂(μ-Ph₂C(O)C(O)Ph₂)(μ-H)(CCMe₃Si) (9).



A solution of trimethylsilylacetylene (Me₃SiC≡CH) (0.029 g, 0.3 mmol; in 5 mL of toluene) was added slowly to a stirred toluene solution (5 mL) of **2** (0.410 g, 0.3 mmol). After the mixture was stirred at ambient temperature for 12 h, the reddish brown solution was evaporated to dryness under vacuum. The residue was washed (5 mL × 2) with *n*-hexane to give the yellow solid powder **9**. Yellow crystals were obtained by a slow solvent evaporation method from a toluene (2 mL) solution of **9**. Yield: 0.370 g (85%). IR (Nujol, cm⁻¹): ν = 3055 (w), 2961 (s), 2867 (w), 2276 (m, ν(C≡C)), 1580 (w), 1460 (m), 1435 (s), 1378 (s), 1315 (m), 1249 (m), 1200 (m), 1057 (w), 975 (w), 854 (m), 786 (s), 764 (w), 700 (w), 671 (w), 653 (w), 596 (w), 498 (m), 448(w). EPR (293 K): g = 2.000. Anal. Calcd for C₈₇H₁₁₀N₄O₂SiY₂ (1449.71): C, 72.08; H, 7.65; N, 3.87; Found: C, 72.14; H, 7.59; N, 3.92.

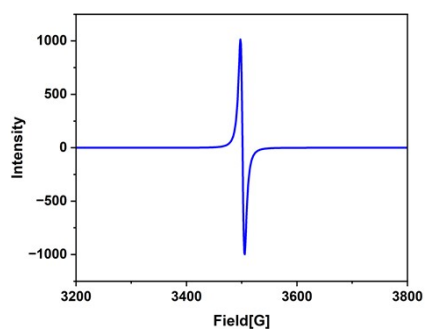


Figure S20. EPR spectrum of complex **9** (293 K) in the solid state, the g-factor is 2.000.

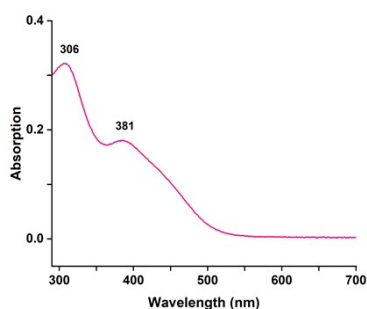


Figure S21. UV/vis spectra of **9** in toluene.

3. X-ray Crystallographic Analysis of All New Complexes

Suitable crystals were collected and wrapped in dried immersion oil. Data collections were performed on Bruker D8 VENTURE system diffractometers (Ga K α radiation, ω -scan technique, λ = 1.34138 Å) at a low temperature. The structures were solved by using the SHELXS-97 program⁵ and refined on F^2 by full-matrix least-squares techniques using the SHELXL-2014 program⁶ for all the non-hydrogen atoms. Except for the hydrogen atoms on yttrium atoms, hydrogen atoms were placed at the calculated positions and included in the structure calculation without further refinement of the parameters. The hydrogen atoms attached to yttrium atoms were located by difference Fourier syntheses and their coordinates and isotropic parameters were refined. The residual electron densities were of no chemical significance. Details of SQUEEZE⁷ are given in the cif files. CCDC 2329822 (**2**), 2329827 (**3**), 2329829 (**4**), 2329828 (**5**), 2329826 (**6**), 2329824 (**7**), 2329825 (**8**) and 2329823 (**9**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html.

Table S1. Crystal data and structure refinement for complexes **2**, **3** and **4**

	2	3·2C₇H₈	4·C₆H₁₄
Formula	C ₈₆ H ₁₁₀ N ₄ O ₃ Y ₂	C ₉₆ H ₁₃₀ N ₄ O ₂ Y ₂	C ₇₇ H ₁₁₁ LiN ₂ O ₄ Y
Formula weight	1425.59	1549.87	1224.52
Temperature/K	173	173	173
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a/Å	13.2897(6)	13.7315(8)	12.6063(4)
b/Å	14.2776(7)	14.1106(8)	13.0301(5)
c/Å	22.7523(11)	25.3879(14)	23.8401(8)
α/°	97.017(2)	94.876(2)	98.8010(10)
β/°	92.226(2)	101.634(2)	91.8920(10)
γ/°	107.071(2)	112.234(2)	113.6200(10)
Volume/Å ³	4083.3(3)	4388.7(4)	3526.4(2)
Z	2	2	2
ρ _{calc} /cm ³	1.159	1.229	1.153
μ/mm ⁻¹	1.503	1.431	1.01
F(000)	1512	1736	1322
Crystal size/mm ³	0.32 × 0.22 × 0.12	0.21 × 0.13 × 0.09	0.27 × 0.18 × 0.11
Radiation	GaKα (λ = 1.34139)	GaKα (λ = 1.34139)	GaKα (λ = 1.34139)
2θ range for data collection/°	9.65 to 107.996	6.244 to 105.964	6.55 to 112.068
Index ranges	-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -27 ≤ l ≤ 27	-16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -30 ≤ l ≤ 30	-14 ≤ h ≤ 15, -16 ≤ k ≤ 16, -29 ≤ l ≤ 29
Reflections collected	28588	124763	57541
Independent reflections	14813 [R _{int} = 0.0271, R _{sigma} = 0.0496]	15019 [R _{int} = 0.0388, R _{sigma} = 0.0206]	13877 [R _{int} = 0.0562, R _{sigma} = 0.0414]
Data/restraints/parameter s	14813/0/884	15019/4/947	13877/186/856
Goodness-of-fit on F ²	1.076	1.17	1.053
Final R indexes [I > 2σ (I)]	R ₁ = 0.0375, wR ₂ = 0.0993	R ₁ = 0.0653, wR ₂ = 0.1744	R ₁ = 0.0560, wR ₂ = 0.1524
Final R indexes [all data]	R ₁ = 0.0440, wR ₂ = 0.1034	R ₁ = 0.0674, wR ₂ = 0.1753	R ₁ = 0.0640, wR ₂ = 0.1591
Largest diff. peak and hole / e Å ⁻³	0.84/-1.04	2.02/-1.92	1.01/-0.95

Table S2. Crystal data and structure refinement for complexes **5**, **6** and **7**

	5	6	7
Formula	C ₈₄ H ₁₀₈ N ₈ OY ₂	C ₄₉ H ₆₆ N ₃ O ₂ Y	C ₅₈ H ₆₈ N ₄ OY
Formula weight	1423.60	817.95	926.07
Temperature/K	173	173	173
Crystal system	monoclinic	monoclinic	monoclinic
Space group	C2/c	P2 ₁ /c	I2/a
a/Å	49.6846(11)	27.1862(19)	24.1554(9)
b/Å	13.9903(3)	15.7900(11)	14.3209(6)
c/Å	28.2437(6)	23.2063(16)	32.5426(12)
α/°	90	90	90
β/°	123.5810(10)	108.635(2)	96.000(2)
γ/°	90	90	90
Volume/Å ³	16355.7(6)	9439.5(11)	11195.7(8)
Z	8	8	8
ρ _{calc} /cm ³	1.156	1.151	1.296
μ/mm ⁻¹	1.498	1.348	1.219
F(000)	6032	3488	4648
Crystal size/mm ³	0.65 × 0.39 × 0.12	0.28 × 0.15 × 0.08	0.35 × 0.26 × 0.11
Radiation	GaKα (λ = 1.34139)	GaKα (λ = 1.34139)	GaKα (λ = 1.34139)
2θ range for data collection/°	7.83 to 106.118	5.994 to 110.164	5.872 to 111.938
Index ranges	-59 ≤ h ≤ 59, -16 ≤ k ≤ 16, -33 ≤ l ≤ 33	-33 ≤ h ≤ 33, -19 ≤ k ≤ 19, -28 ≤ l ≤ 27	-29 ≤ h ≤ 29, -17 ≤ k ≤ 17, -40 ≤ l ≤ 40
Reflections collected	169384	134160	81260
Independent reflections	14474 [R _{int} = 0.0427, R _{sigma} = 0.0194]	17788 [R _{int} = 0.0412, R _{sigma} = 0.0231]	11044 [R _{int} = 0.0410, R _{sigma} = 0.0230]
Data/restraints/parameter s	14474/0/876	17788/0/1011	11044/0/587
Goodness-of-fit on F ²	0.996	1.042	1.082
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0377, wR ₂ = 0.1201	R ₁ = 0.0368, wR ₂ = 0.0909	R ₁ = 0.0325, wR ₂ = 0.0966
Final R indexes [all data]	R ₁ = 0.0447, wR ₂ = 0.1265	R ₁ = 0.0489, wR ₂ = 0.1014	R ₁ = 0.0373, wR ₂ = 0.1035
Largest diff. peak and hole / e Å ⁻³	0.64/-0.67	0.73/-0.81	0.44/-0.67

Table S3. Crystal data and structure refinement for complexes **8** and **9**

	8·C₇H₈	9·C₆H₁₄
Formula	C ₉₇ H ₁₁₄ N ₄ O ₂ Y ₂	C ₉₃ H ₁₂₄ N ₄ O ₂ SiY ₂
Formula weight	1545.75	1535.88
Temperature/K	231	170
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /n
a/Å	21.750(2)	18.0326(18)
b/Å	16.8112(15)	23.290(2)
c/Å	25.488(2)	21.669(2)
α/°	90	90
β/°	95.778(4)	96.420(4)
γ/°	90	90
Volume/Å ³	9272.1(15)	9043.3(15)
Z	4	4
ρ _{calc} /cm ³	1.226	1.196
μ/mm ⁻¹	1.374	1.471
F(000)	3632	3472
Crystal size/mm ³	0.35 × 0.21 × 0.15	0.26 × 0.18 × 0.07
Radiation	GaKα (λ = 1.34139)	GaKα (λ = 1.34139)
2θ range for data collection/°	6.37 to 110.17	5.414 to 108.694
Index ranges	-26 ≤ h ≤ 26, -20 ≤ k ≤ 20, -29 ≤ l ≤ 31	-21 ≤ h ≤ 21, -28 ≤ k ≤ 27, -23 ≤ l ≤ 26
Reflections collected	150036	153139
Independent reflections	17498 [R _{int} = 0.0926, R _{sigma} = 0.0450]	16663 [R _{int} = 0.0778, R _{sigma} = 0.0368]
Data/restraints/parameters	17498/1/955	16663/133/1005
Goodness-of-fit on F ²	1.026	1.041
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0556, wR ₂ = 0.1348	R ₁ = 0.0487, wR ₂ = 0.1334
Final R indexes [all data]	R ₁ = 0.0856, wR ₂ = 0.1630	R ₁ = 0.0566, wR ₂ = 0.1400
Largest diff. peak and hole / e Å ⁻³	1.07/-1.37	0.93/-1.09

4. Molecular Structures of Complex 3 and 6

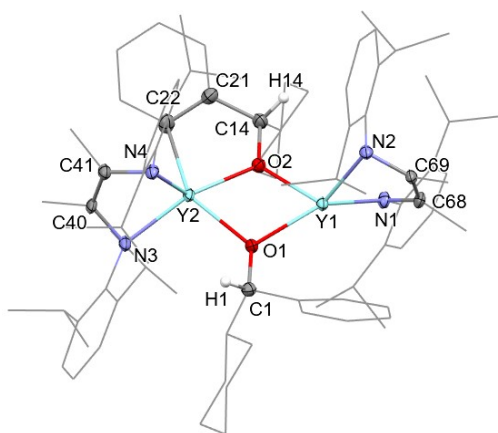


Figure S22. Molecular structure of **3** with 30% thermal ellipsoids. Hydrogen atoms (except for H1 and H14) are omitted for clarity. Selected bond lengths [Å] and angles (°): Y1-O1 2.297(3), Y1-O2 2.225(4), Y2-O1 2.244(3), Y2-O2 2.307(3), C40-C41 1.370(8), C68-C69 1.381(8), C1-O1 1.425(6), C14-O2 1.428(6); Y1-O1-Y2 105.54(14), Y1-O2-Y2 105.84(14), Y2-O2-C14 124.1(3).

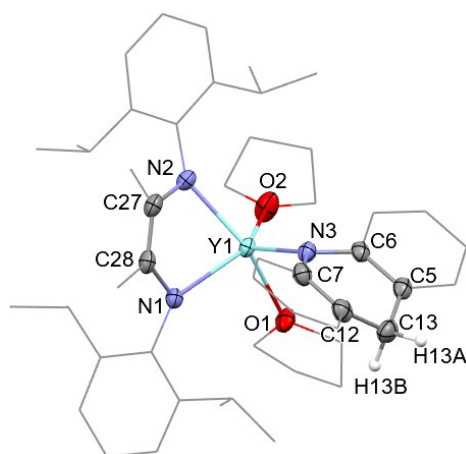


Figure S23. Molecular structure of **6** with 30% thermal ellipsoids. Hydrogen atoms (except for H13A and H13B) are omitted for clarity. Selected bond lengths [Å] and angles (°): Y1-N3 2.2855(19), Y1-C6 2.995(2), N3-C6 1.394(3), C6-C5 1.409(4), C5-C13 1.499(4), C13-C12 1.507(4), C12-C7 1.405(4), C7-N3 1.400(3); Y1-N3-C6 106.42(15), Y1-N3-C7 132.90(15), C6-N3-C7 115.7(2), C7-C12-C13 118.2(2), C12-C13-C5 111.2(2), C13-C5-C6 117.4(2).

5. The spectra of in situ ^1H NMR tracking experiments

In a glovebox, **2** (0.028 g, 0.02 mmol) was weighed into an NMR tube equipped with a Teflon valve (J-Young). Then, a mixture of (ethynyl-*d*)benzene (0.0022 g, 0.021 mmol) in C_6D_6 (0.3 mL) was added via syringe. The subsequent reaction was monitored by ^1H NMR spectroscopy. The monitoring reaction was completed after 2 hours at room temperature.

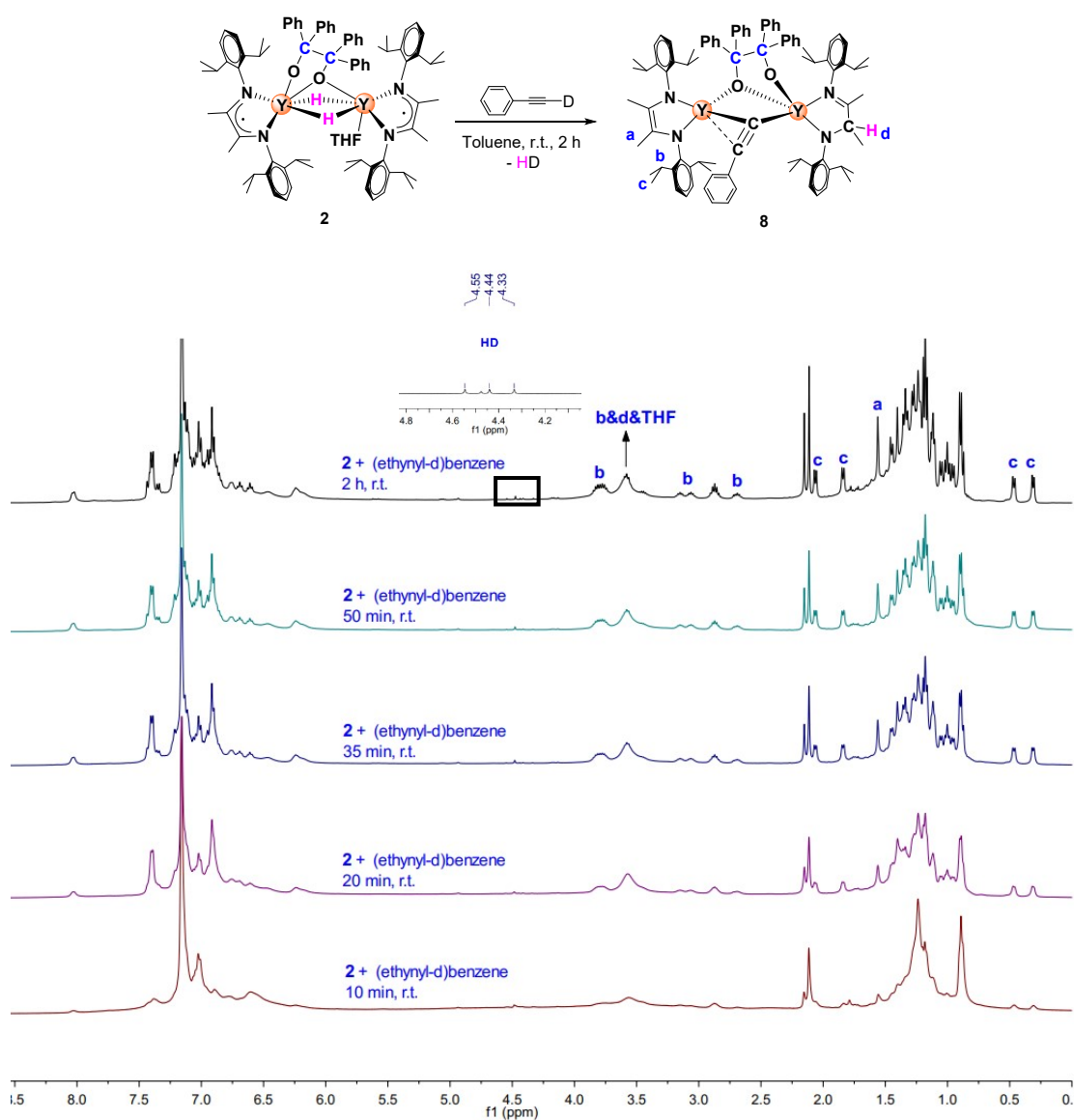


Figure S24. The in situ ^1H NMR spectra of **2** with (ethynyl-*d*)benzene in C_6D_6 at room temperature.

6. Detection of H₂ generated in the reaction by GC

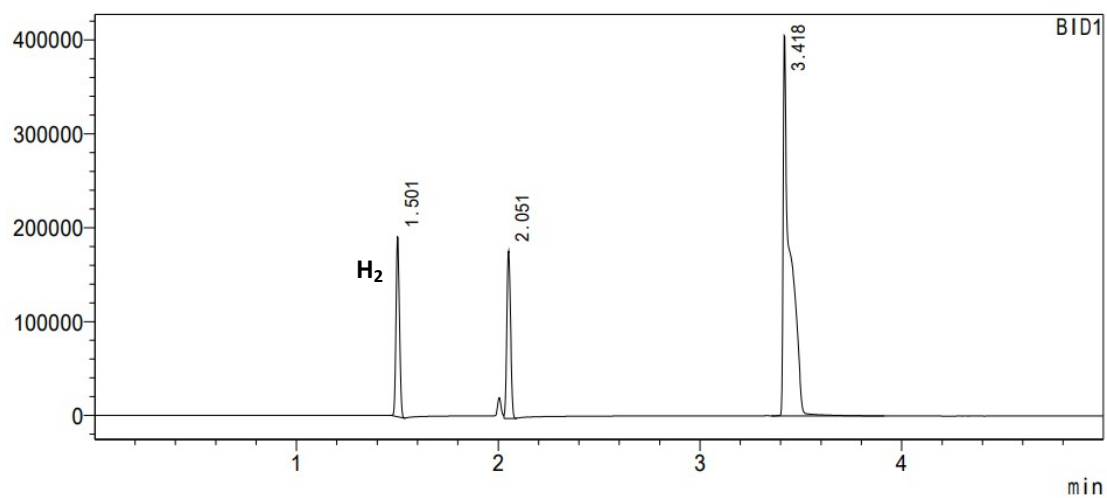


Figure S25. GC analysis data of the crude reaction mixture formed by the reaction of **1** with azobenzene. The peak area of hydrogen is 232624 appearing at 1.501 min of the retention time.

7. References

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