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ARTICLE

# Group 4 Complexes Bearing Pyrrolide Ligand for Intramolecular Alkene Hydroamination and Activation of C≡N Bond

Zhilei Jiang, Yalan Wang, Wei Liu, and Yahong Li*

**Abstract:** Titanium and zirconium complexes supported by a pyrrolide ligand $HL^1$ [$HL^1$ = 2-cyano-1H-pyrrole], $Ti_2(L^2)_2(NMe_2)_2$ (**1**), $Zr_3(L^2)_3(NMe_2)_6$ (**2**), [$L^2$ = N,N-dimethyl-1H-pyrrol-2-carboximidamide, $NMe_2$-$L^1$] have been synthesized and characterized. The ligand $L^2$ was generated by activation of C≡N bond of $HL^1$ with $HNMe_2$. In complex **1,** two $Ti^{IV}$ atoms are bridged by two nitrogen atoms. There are three characteristic $Zr^{IV}$ ions in **2,** which are six-, seven- and six-coordinated, respectively. They were tested as catalysts for the intramolecular hydroamination of aminoalkenes, and the respectively N-hetero-cycles were afforded in 74% to 99% yields. Moreover, the formation of $L^2$ ligand indicates that the amination of C≡N bond can be considered as a new and rapid way to synthesize other C-N bonds.

## Introduction

Finding efficient synthetic routes to afford small nitrogen-containing molecules is highly desired because of the universal applications of these compounds in biologically active compounds.[1-5] Hydroamination,[6] the direct addition of a N-H bond across an unsaturation carbon-carbon bond, is the most atom economical process to the formation of a new C-N bond. Over the past decades, a plethora of efficient catalysts, including transition metal, [7] main group metal,[8] and rare earth metal complexes,[9] have been reported to promote such transformations. Due to the advantages of commercial availability, low cost, and low toxicity, group 4 metal complexes have been performed as effective catalysts for the intramolecular hydroamination of C-C multiple bonds with amine.[10]

In our previous work,[11-15] we have chosen pyrrole as an ancillary ligand to tune the activity of the complexes in the catalytic studies. Employing pyrrole as an ancillary ligand has always been a hot pot for chemists,[16-20] due to a couple of considerations.[21-22] The first was its expediency; pyrrole can be used to synthesize multidentate ligands. Second, pyrrole has adjustable electron distribution and enough steric hindrance. As a result, it is able to conjugate with unsaturated metal centers in the terms of $\eta^5$ mode,[23-24] thus, enhanceing catalytic activity. Herein, we synthesized the ligand $HL^1$ ($HL^1$ = 2-cyano-1H-pyrrole) and studied its coordination chemistry with titanium and zirconium. Two complexes of compositions $Ti_2(L^2)_2(NMe_2)_2$ (**1**), $Zr_3(L^2)_3(NMe_2)_6$ (**2**) ($L^2$ = $NMe_2$-$L^1$) were prepared and characterized. Their catalytic activities towards intramolecular hydroamination were studied. It is noteworthy that the titanium complex has different structure from that of zirconium complex under the same reaction conditions. To our unforeseen, the generated dimethylamine was readily added to cyano of $HL^1$, forming a new C-N bond *in situ*.

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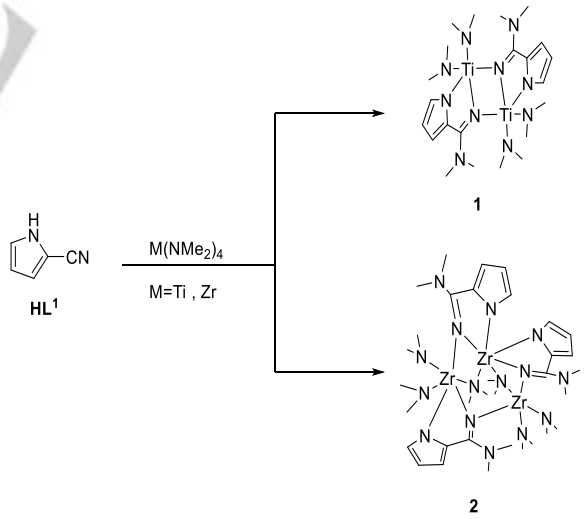
## Results and Discussion

### *Syntheses and Structures of Complexes*

The $HL^1$ ligand ( $HL^1$ = 2-cyano-1H-pyrrole ) was prepared by modifying the literature method.[25] Reaction of the $HL^1$ ligand with one equivalent of $Ti(NMe_2)_4$ and $Zr(NMe_2)_4$ in THF, respectively, gave complexes $Ti_2(L^2)_2(NMe_2)_2$ (**1**), $Zr_3(L^2)_3(NMe_2)_6$ (**2**) (Scheme 1). The crystals of **1**, and **2** were readily afforded by standing in toluene/hexane solution of the complexes at 0 °C for two weeks. The molecular structures of **1**, and **2** have been determined by single-crystal X-ray diffraction measurements. The crystal data of complexes are listed in **Table 1** and the selected bond lengths and angles are summarized in **Table 2**.




**Scheme 1.** Synthesis of complexes **1** and **2** based on $HL^1$ ligand.

Single crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the monoclinic space group $P2_1/n$. The structure of **1** is depicted in Figure 1. The dinuclear complex **1** is symmetrical and each part consists of one $Ti^{IV}$ ion, one pyrrolyl ligand, and two aminomethyl groups. The central $Ti^{IV}$ ion is five-coordinate, and possesses distorted pentahedral geometry. The deprotonated $L^2$

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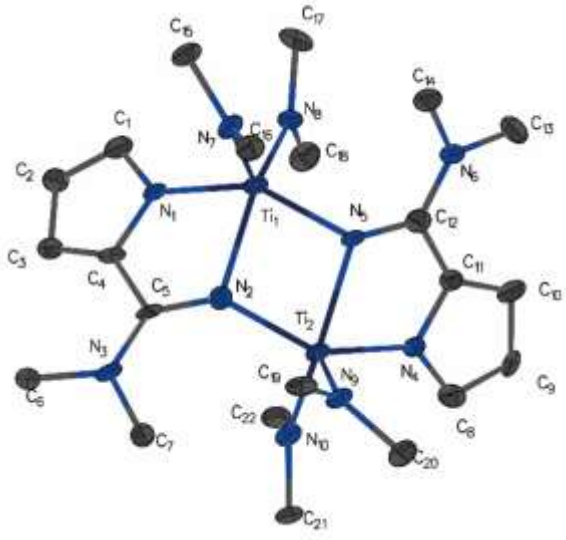


**Figure 1.** ORTEP drawing of **1**. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity.

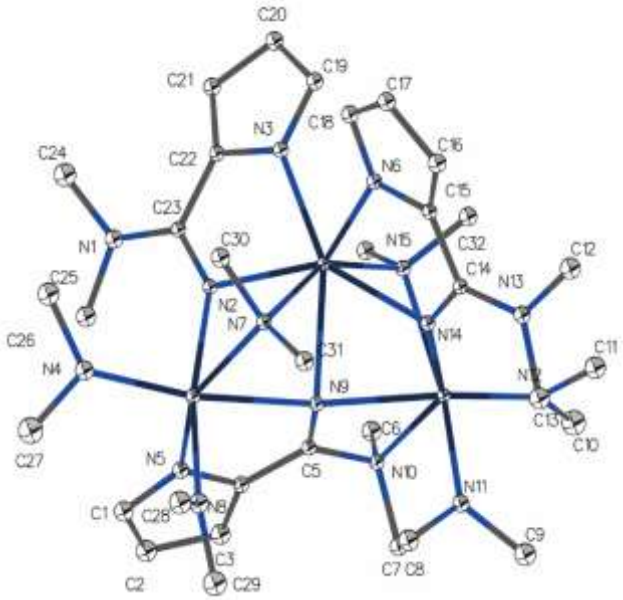


**Figure 2.** ORTEP drawing of **2**. Thermal ellipsoids are drawn at the 30 % probability level, and hydrogen atoms are omitted for clarity.

ligand chelates to titanium ion through two nitrogen atoms. The averaged Ti-N(dimethylamide) bond length is 1.913(8) Å, whereas the average Ti-N(pyrrolyl) and Ti-N(cyano) distances are 2.102(8) Å and 2.109(8) Å, respectively.

As shown by X-ray analysis, complex **2** crystallizes in the monoclinic space group $P2_1/c$. The structure of **2** (Figure 2) is trinuclear. Three zirconium atoms are connected via one nitrogen atom of cyano. Zr2 connects to Zr1 and Zr3 via nitrogen atoms of cyano and aminomethyl group. The averaged Zr-N(dimethylamide) bond lengths is 2.075(3) Å, which is close to those of reported in the literatures.[26-28]

**Table 1.** Crystal data and structure refinements for **1** and **2**.

| | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{22}H_{42}N_{10}Ti_2$ | $C_{33}H_{63}N_{15}Zr_3$ |
| Formula weight (g·mol$^{-1}$) | 542.45 | 939.3 |
| Temperature (K) | 223(2) | 119.99 |
| Wavelength | 0.604 | 0.753 |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/n$ | $P2_1/c$ |
| *a*/Å | 11.328(2) | 8.9093(6) |
| *b*/Å | 14.832(3) | 23.0154(14) |
| *c*/Å | 16.702(3) | 21.2812(13) |
| *α*/° | 90 | 90 |
| *β*/° | 98.39(3) | 96.582(2) |
| *γ*/° | 90 | 90 |
| Volume/Å$^3$ | 2776.2(9) | 4335.0(5) |
| *Z* | 4 | 2 |
| $\rho_{calc}$(g/cm$^3$) | 1.298 | 1.514 |
| *F*(000) | 1152 | 2038.0 |
| Crystal size(mm$^3$) | 0.40 × 0.20 × 0.20 | 0.40 × 0.20 × 0.10 |
| Radiation | MoKα (*λ* = 0.71073) | MoKα (λ = 0.71073) |
| Theta range for data collection(°) | 4.68 to 50.096 | 3.54 to 54.956 |
| Limiting indices | -8 ≤ h ≤ 13<br>-16 ≤ k ≤ 17<br>-19 ≤ l ≤ 19 | -11 ≤ h ≤ 11<br>-29 ≤ k ≤ 29<br>-27 ≤ l ≤ 27 |
| Reflections collected/unique | 12328/4874 | 79738/9940 |
| Data/restraints/parameters | 4874/0/319 | 9940/0/520 |
| *GOF* | 1.255 | 1.159 |
| $R_1$,$wR_2$[I › 2σ(I)] | $R_1$ = 0.1552<br>$wR_2$ = 0.2974 | $R_1$ = 0.0400<br>$wR_2$ = 0.0953 |
| Final R indexes [all data] | $R_1$ = 0.1932<br>$wR_2$ = 0.3197 | $R_1$ = 0.0599<br>$wR_2$ = 0.1155 |
| Largest diff. peak/hole [e Å$^{-3}$] | 0.73/-0.62 | 0.71/-1.14 |

**Table 2.** Selected bond lengths /Å and angles /° for **1** and **2**.

| **1** | | | |
|---|---|---|---|
| Ti(1)-N(1) | 2.090(8) | Ti(1)-N(2) | 2.109(8) |
| Ti(1)-N(5) | 2.013(8) | Ti(1)-N(7) | 1.894(8) |
| Ti(1)-N(8) | 1.926(8) | Ti(2)-N(2) | 1.989(8) |
| Ti(2)-N(4) | 2.114(8) | Ti(2)-N(5) | 2.108(7) |
| Ti(2)-N(9) | 1.900(8) | Ti(2)-N(10) | 1.930(8) |
| N(1)-Ti(1)-N(2) | 75.8(3) | N(7)-Ti(1)-N(1) | 101.7(3) |
| N(7)-Ti(1)-N(8) | 109.3(4) | N(8)-Ti(1)-N(5) | 97.0(3) |
| N(5)-Ti(2)-N(4) | 74.9(3) | N(10)-Ti(2)-N(2) | 99.2(3) |
| N(9)-Ti(2)-N(4) | 109.8(3) | N(9)-Ti(2)-N(10) | 104.4(3) |
| **2** | | | |
| Zr(1)-N(11) | 2.083(2) | Zr(1)-N(12) | 2.046(3) |
| Zr(2)-N(15) | 2.203(3) | Zr(1)-N(15) | 2.419(3) |
| Zr(3)-N(4) | 2.082(3) | Zr(2)-N(7) | 2.285(3) |
| Zr(3)-N(7) | 2.264(3) | Zr(3)-N(8) | 2.088(3) |
| N(9)-Zr(1)-N(10) | 59.62(10) | N(15)-Zr(2)-N(7) | 150.53(10) |
| N(11)-Zr(1)-N(15) | 168.96(10) | N(7)-Zr(3)-N(9) | 78.66(10) |
| N(12)-Zr(1)-N(11) | 95.63(11) | N(3)-Zr(2)-N(9) | 134.21(10) |
| N(12)-Zr(1)-N(15) | 95.38(10) | N(4)-Zr(3)-N(7) | 105.55(11) |
| N(8)-Zr(3)-N(7) | 99.41(11) | N(4)-Zr(3)-N(8) | 96.05(12) |
| N(2)-Zr(2)-N(7) | 76.07(10) | N(4)-Zr(3)-N(9) | 164.50(10) |

### *Intramolecular Hydroamination of Aminoalkenes Catalyzed by 1 and 2*

To evaluate the catalytic activities of **1** and **2**, intramolecular hydroamination reaction of 2,2-diphenylpent-4-enyl-amine (**3a**) was first investigated to compare the catalytic activities of **1** and **2**. (**Table 3**). Firstly, the reaction conditions were optimized. 10 mol% of complexes **1** and **2** were employed to catalyze this reaction, and the cyclized products **4a** were afforded in 74%, 99%

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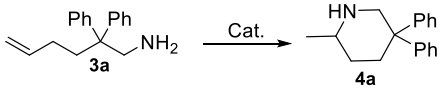
yields, respectively (entries 1, 2). Then, different concentrations of complexes **2** were compared (entries 3, 4).

**Table 3.** Intramolecular hydroamination of amionalkene[a]

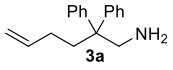
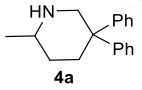
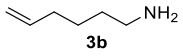
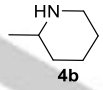
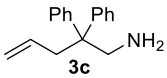
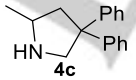
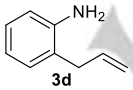
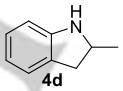
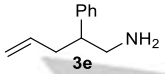
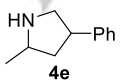
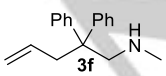
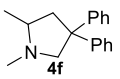



| Entry | Cat. | Conc.( %) | Yield[b](**3a**) |
|---|---|---|---|
| 1 | **1** | 10 | 74 |
| 2 | **2** | 10 | 99 |
| 3 | **2** | 5 | 99 |
| 4 | **2** | 2 | 91 |

[a] Conditons: reaction in PhCl (2 mL), [substrate] = 0.5 mmol, 12 h, 110 °C. [b] isolated yield.

Under optimal conditions, the substrate scope of **3** for intramolecular alkene hydroamination was further explored, and the results were summarized in **Table 4**. Both aliphatic and aromatic pimary amines were cyclized to generate six- and five-membered N-heterocycles in 84-99% yields (**Table 4**, entries 1-5). In all cases, no evidence of hydroaminoalkylation side reactivity is observed. Contrary to results with other group 4 metal systems,[29-31] complex **2** is completely chemoselective for hydro-amination. The related substrate containing a secondary amine **3f** was prepared and was tested for intramolecular hydroamination with complex **2** (entry 6). Unsuccessfully, despite prolonged reaction times and evevated reaction temperature, the secondary aminoalkene **3f** is resistant to cyclization. It's similar to the results of Schafer[32]and Livinghouse.[33] It suggests that alkene hydroam-ination is mediated by zirconium imido complex, which undergoes a [2+2] cycloaddition reaction with alkene through a chairlike transition state. This imido-based mechanism is established for hydroamination catalyzed by group 4 metals.[34-41]

**Table 4.** Intramolecular alkene hydroamination with complexes 2[a]

| Entry | Substrate | Cond. | Product | Yeild (%) |
|---|---|---|---|---|
| 1 |  **3a** | 12h 110 °C |  **4a** | 99 |
| 2 |  **3b** | 24h 120 °C |  **4b** | 84 |
| 3 |  **3c** | 12h 110 °C |  **4c** | 94 |
| 4 |  **3d** | 48h 140 °C |  **4d** | 93 |
| 5 |  **3e** | 24h 120 °C |  **4e** | 92 |
| 6 |  **3f** | 72h 145 °C |  **4f** | 0 |

[a] Conditions: **3**(0.5 mmol), **2** (0.025 mmol), PhCl (2 mL). [b] Isolated yield.

## Conclusions

In summary, Ti and Zr complexes based on pyrrolide ligand have been prepared, and complex **2** showed good activities in catalyzing intramolecular hydroamination reaction. Various amin-oalkenes with different functional groups were transformed into respectively N-heterocycle in 84% to 99% yields. It is noteworthy that generated dimethylamine was readily added to cyano, which is a rapid way to form C-N bond. Further studies on development of application of transforation of dimethylamine are ongoing in our group.

## Experimental Section

**General Considerations:** All manipulations of air-sensitive compounds were carried out in a Mikrouna glovebox in a purified nitrogen atmosphere. $Ti(NMe_2)_4$, and $Zr(NMe_2)_4$ were purchased from Acros and used without further purification. Toluene, THF, and hexane were freshly distilled from purple sodium benzophenone ketyl before use. PhCl was dried over $CaH_2$. $CDCl_3$ was distilled under argon from phosphorus pentoxide. Elemental analyses for carbon, hydrogen, and nitrogen were performed with Carlo-Erba EA1110 CHNO-S microanalyzer. NMR spectra were recorded with an Agilent-400 spectrometer at ambient temperature by using TMS as an internal standard, and chemical shifts are reported in ppm.

**X-ray Crystallography:** Data were collected at 173(2) K on Bruker APEXII diffractometer for **1** and **2** utilizing Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å); the $\omega$ and $\varphi$ scan technique was applied. The structures were solved by direct methods using SHELXS-97 and refined on $F^2$ using full-matrix least-squares with SHELXL-97. CCDC-1827525 (**1**) and CCDC-1827759 (**2**) contain the supplementary crystallographic data for this paper.

**Synthesis of the Ligand:** Hydroxylamine hydrochloride (6.95 g, 100.00 mmol), sodium acetate (8.20 g, 100.00 mmol), and pyrrole-2-aldehyde (9.50 g 100.00 mmol) were combined with $H_2O$ (40 mL). The mixture was stirred at room temperature for 3 h and afforded white precipitate. The residue was washed with 3 x 10 mL water and dried under vacuum to get a white solid. $Ac_2O$ (72 mL) was carefully added to the resulting solid, then the solution was refluxed at 110 °C for 1 h. After the mixture was cooled, quenched it with 200 mL $H_2O$, added 1M aqueous $Na_2CO_3$ until the evolution of gas ceased. The aqueous phase was extracted with 3 x 100 mL dichloromethane. The combined organic phase was dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by column chromatography to give a yellow liquid. Yield: 6.6 g (72%). **$^1$H NMR** (600 MHz, $CDCl_3$): δ 9.84 (s, 1H), 6.94 (s, 1H), 6.87 (s, 1H), 6.24 (s, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 124.2, 120.4, 115.1, 110.0, 100.3.

**Synthesis of $Ti_2(L_2)_2(NMe_2)_2$ (1):** A solution of ligand $HL^1$ (0.092 g, 1.0 mmol) in THF (2 mL) was added to $Ti(NMe_2)_4$ solution (0.2 242 g, 1.0 mmol) in THF (2 mL) carefully at -35 °C. The reaction mixture was stirred at room temperature overnight after which time volatiles were removed under reduced pressure to get a yellow solid. Yield: 0.225 g (83%). The yellow crystals were obtained by recrystallizing in toluene. **$^1$H NMR** (600 MHz, $C_6D_6$): δ 6.96 (s, 1H), 6.41 (s, 1H), 6.21 (s, 1H), 3.34 (s, 6H), 3.09 (s, 12H). **$^{13}$C NMR** (150 MHz, $C_6D_6$): δ 134.9, 132.4, 127.9, 113.02, 110.8, 45.0, 39.1. Elemental analysis calcd (%): C 48.72; H 7.81; N 25.82 %; found: C 48.72; H 7.52; N 25.48 %.

**Synthesis of $Zr_3(L^2)_3(NMe_2)_6$ (2):** A solution of ligand $HL^1$ (0.092 g, 1.0 mmol) in THF (2 mL) was added to $Zr(NMe_2)_4$ solution (0.267 g, 1.0 mmol) in THF (2 mL) carefully at -35 °C. The reaction mixture was stirred at room temperature overnight after which time volatiles were removed under reduced pressure to get a yellow solid. Yield: 0.244 g (78%). The yellow crystals were obtained by recrystallizing in toluene. **$^1$H NMR** (600 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.24 (s, 1H), 7.00-6.96 (d, *J* = 28.2 Hz, 2H), 6.54-6.50 (dd, *J* = 19.8, 3.6 Hz, 2H), 6.41 (d, *J* = 3.6 Hz, 1H), 6.24-6.21 (d, *J* = 18.6 Hz, 2H), 3.50-3.43 (m, 6H), 3.38 (s, 6H), 3.33 (s, 9H), 3.25 (s, 9H), 3.09 (s, 12H), 3.00 (s, 6H), 2.62 (s, 3H), 2.39 (s, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$): δ 169.3, 168.7, 164.8, 136.8, 135.4, 135.1, 132.9, 131.9, 114.8, 111.7, 110.9, 110.5, 109.6, 48.3, 45.4, 45.1, 44.9, 43.8, 43.3, 41.0, 39.8, 38.7. Elemental analysis calcd (%): C 42.00; H 6.73; N 22.27 %; found: C 42.65; H 6.69; N 22.12 %.

**General procedure for hydroamination reactions**

The reactions were carried out in a glovebox filled with nitrogen. A solution of complex **2** (24 mg, 0.025 mmol) in PhCl (2 mL) and **3** was added subsequently. The resulting solution was stirred at the desired temperature for the desired time. After reaction, the solvent was removed under vacuo. Column chromatography of the residue on silica gel gave a pure product.

**2-Methyl-5,5-diphenylpiperidine (4a)**

**4a** was afforded from **3a** (126 mg, 0.5 mmol) as a colourless oil in 99% yield (125 mg). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.33-7.31 (d, *J* = 10.8 Hz, 2H), 7.26-7.22 (t, *J* = 11.1 Hz, 2H), 7.12-6.99 (m, 6H), 3.84-3.80 (d, *J* = 20.4 Hz, 1H), 3.03-3.00 (d, *J* = 20.4 Hz, 1H), 2.68-2.60 (m, 2 H), 2.15-2.08 (t, *J* =19.8 Hz, 1H), 1.56-1.52 (d, *J* = 20.4 Hz, 2H), 1.08-1.05(m, 1H), 0.92-0.90 (d, *J* = 9.6 Hz, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 148.6, 144.5, 128.4, 128.0, 126.1, 125.5, 55.5, 52.0, 45.0, 35.2, 31.1, 22.2.

**2-Methyl-piperidine (4b)**

**4b** was afforded from **3b** (50 mg, 0.5 mmol) as a colourless oil in 84% yield (42 mg). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 3.05-3.03 (d, *J* = 9.0 Hz, 1H), 2. 66-2.62 (t, *J* = 17.1 Hz, 2H), 2.62-2.57 (m, 1H), 1.77-1.75 (d, *J* = 17.1 Hz, 1H), 1.62-1.60 (d, *J* = 18.9 Hz, 1H), 1.57-1.56 (d, *J* = 17 .1 Hz, 1H), 2.15-2.08 (t, *J* = 29.7 Hz, 1H), 1.56-1.52 (d, *J* = 30.6 Hz, 2H), 1.38-1.33 (dd, *J* = 30.6, 18.0 Hz, 2H), 1.09-1.07 (m, 1H), 1.04-1.03 (d, *J* = 9.9 Hz, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 52.2, 47.1, 34.6, 26.1, 24.8, 23.0.

**2-Methyl-4,4-diphenyl-pyrrolidine (4c)**

**4c** was afforded from **3c** (119 mg, 0.5 mmol) as a colourless oil in 94% yield (112 mg). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.21-7.14 (m, 8H), 7.10-7.07 (t, *J* = 13.5 Hz, 2H), 3.61-3.58 (d, *J* = 17.4 Hz, 1H), 3.40-3.37 (d, *J* = 16.8 Hz, 1H), 3.30-3.28 (m, 1H), 2.69-2.64 (q, *J* = 9.6 Hz, 1H), 2.27 (s, 1H), 1.98-1.93 (dd, *J* = 19.2, 13.8 Hz, 1H), 1.13-1.18 (d, *J* = 9.6 Hz, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 147.8, 147.0, 128.3, 127.0, 126.0, 57.8, 57.3, 53.1, 47.1, 22.3.

**2-Methyl-indoline (4d)**

**4d** was afforded from **3d** (67 mg, 0.5 mmol) as a light yellow oil in 93% yield (62 mg). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.05-7.03 (d, *J* =9.0 Hz, 1H), 7.00-6.96 (t, *J* =9.5 Hz, 1H), 6.68-6.64 (t, *J* = 9.3 Hz, 1H), 6.56-6.54 (d, *J* = 10.0 Hz, 1H), 3.97-3.89 (m, 1H), 3.66 (s, 1H), 3.13-3.07 (dd, *J* = 19.0, 10.5 Hz, 1H), 2.62-2.56 (q, *J* = 9.8 Hz, 1H), 1.25-1.23 (d, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 151.1, 129.0, 127.3, 124.8, 118.6, 109.2, 55.3, 37.9, 22.4.

**2-Methyl-4-phenyl-pyrrolidine (4e)**

**4e** was afforded from **3e** (81 mg, 0.5 mmol) as a light yellow oil in 92% yield (75 mg). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.29-7.27 (d, *J* =7.2 Hz, 2H), 7.24-7.19 (m, 3H), 4.33(s, 1H), 3.53-3.45 (m, 2H), 3.40-3.33 (t, *J* = 8.2 Hz, 1H), 2.91-2.87 (t, *J* = 5.8 Hz, 1H), 2.08-2.01 (m, 1H), 1.87-1.80 (m, 1H), 1.26-1.25(d, *J* = 6.4 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 147.9, 147.2, 128.5, 127.2, 126.2, 58.1, 57.4, 53.3, 47.2, 22.5.

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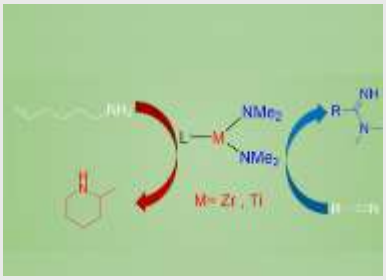


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