

## Electronic Supporting Information

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### Metal-exchangeable Macrocycles: From *Bismetallo-Ru<sub>2</sub>/Zn* Triangle to Ru<sub>2</sub>/Fe Triangular Assembly

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#### Materials and Methods:

NMR spectra were recorded on a Bruker ADVANCE 400 or 500 NMR Spectrometer. <sup>1</sup>H NMR chemical shifts were reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard.

Mass spectra were determined on Waters Xevo Q-ToF Mass Spectrometer.

Absorption spectra were measured with Hitachi (model U-3010) UV-Vis spectrophotometer in a 1-cm quartz cell. Emission spectra were measured with Hitachi (F-7000) fluorescence spectrophotometer in a 1-cm quartz cell.

Cyclic voltammetry (CV) were performed with a Zahner IM6 electrochemical workstation using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Hg/Hg<sub>2</sub>Cl<sub>2</sub> electrode as the reference electrode. 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) dissolved in CH<sub>3</sub>CN was employed as the supporting electrolyte. The plot includes the signal of the ferrocene as an internal potential marker.

The activation energies (E<sub>a</sub>) from P3 to T5 were determined by variable temperature NMR and from T4 to T5 by variable temperature UV spectra measurements according to the Arrhenius equation:

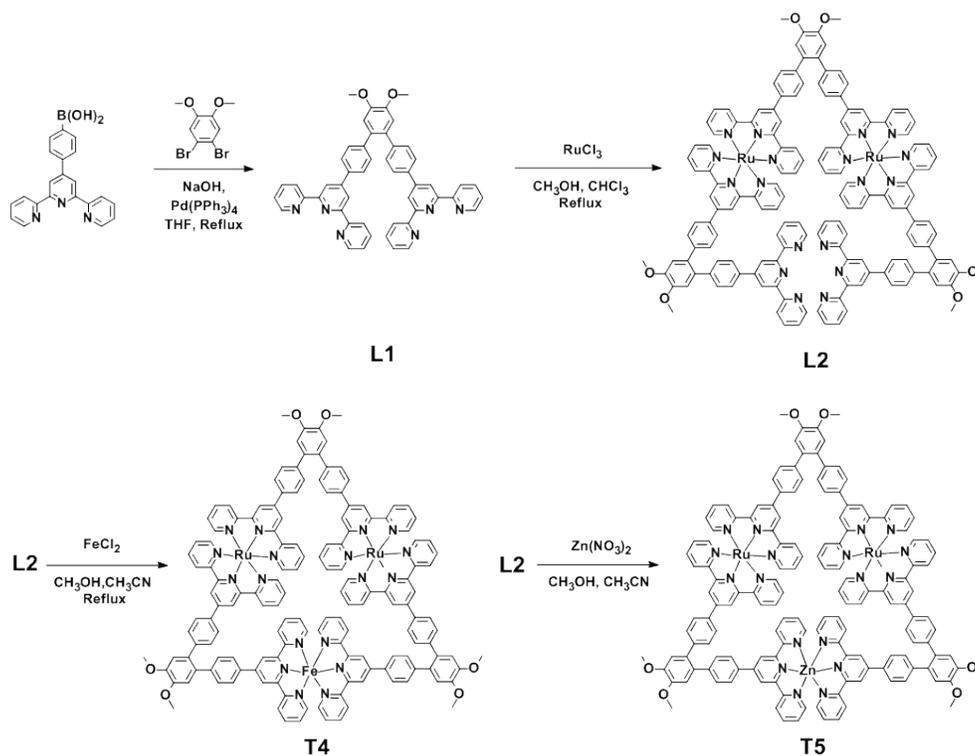
$$\ln(k_2/k_1) = -E_a/R(1/T_2 - 1/T_1),$$

$$\text{So, } E_a = -R \ln(k_2/k_1) / (1/T_2 - 1/T_1), R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified.

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## Synthesis and characterizations of L1, L2, T4 and T5.



Scheme S1. Synthetic Route of ligand of **L1** and complexes of **L2**, **T4** and **T5**

The compound **L1** was synthesized according to literature procedures.<sup>S1</sup>

**L2:** **L1** (209 mg, 0.27 mmol) and RuCl<sub>3</sub> (31 mg, 0.12 mmol) were added into a 250 mL flask, then 100 mL CH<sub>3</sub>OH and 100 mL CHCl<sub>3</sub> were added as solvent. The suspension was stirred at 75 °C for 24 hours. After cooled to ambient temperature, 20 mL CH<sub>3</sub>OH was added to the solution, followed by precipitation with NH<sub>4</sub>PF<sub>6</sub> to afford as a red solid, which was washed with copious amounts of MeOH to give a mixture containing complex **L2**, then purified by Al<sub>2</sub>O<sub>3</sub> chromatographic column to give **L2** as a pale-red solid (97 mg, 35%). M.P. > 200 °C; <sup>1</sup>H NMR (500 MHz, 298 K, MeOD, ppm) δ= 9.30 (s, 4H), 9.27 (s, 4H), 8.88 (d, 4H), 8.85 (d, 4H), 8.72 (s, 4H), 8.70 (d, 4H), 8.68 (d, 4H), 8.29 (d, 4H), 8.23 (d, 4H), 8.03 (t, 4H), 8.00 (t, 4H), 7.97 (t, 4H), 7.92 (d, 4H), 7.69 (d, 4H), 7.61 (d, 4H), 7.54 (d, 4H), 7.52 (d, 4H), 7.50 (d, 4H), 7.48 (t, 4H), 7.24 (t, 8H), 7.23 (s, 2H), 7.21 (s, 2H), 7.20 (s, 2H); ESI/MS (m/z): 615.1 [**L2**-4PF<sub>6</sub><sup>-</sup>]<sup>4+</sup> (calculated 615.2), 868.4 [**L2**-3PF<sub>6</sub><sup>-</sup>]<sup>3+</sup> (calculated 868.5), 1375.1 [**L2**-2PF<sub>6</sub><sup>-</sup>]<sup>2+</sup> (calculated 1375.3).

**T4:** **L2** (7.6 mg, 0.0025 mmol) and FeCl<sub>2</sub> (0.4 mg, 0.0025 mmol) were added to a 50 mL flask with a mixed solvents of CH<sub>3</sub>OH and CH<sub>3</sub>CN. The suspension was stirred at 85 °C for 10 hours. Followed by counterion exchange with PF<sub>6</sub><sup>-</sup> and washed with copious amounts of MeOH to give complex **T4** (7.5 mg, 92%) as a dark-red solid. M.P. > 200 °C; <sup>1</sup>H NMR (500 MHz, 298 K, CD<sub>3</sub>CN, ppm) δ= 9.20(s,

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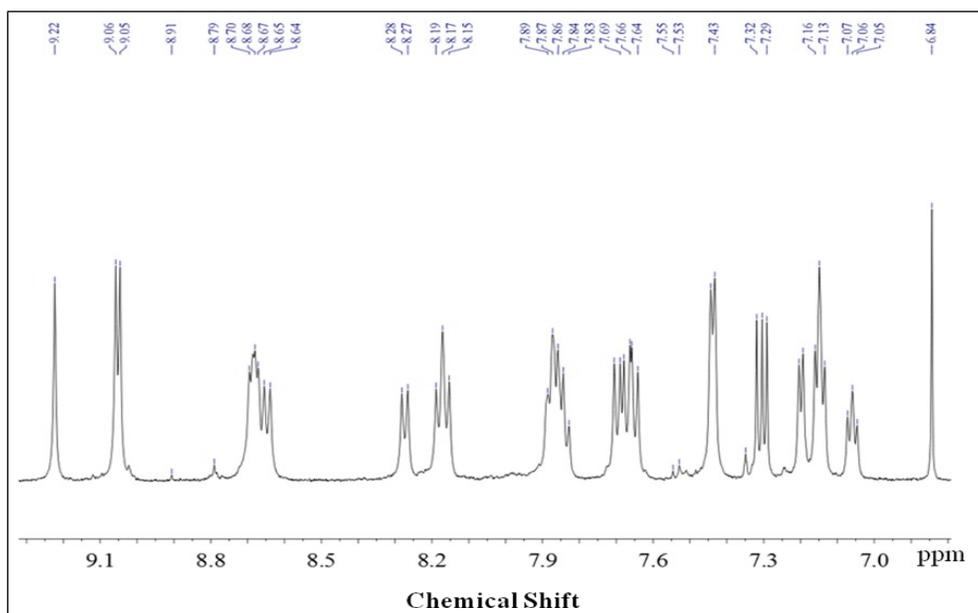
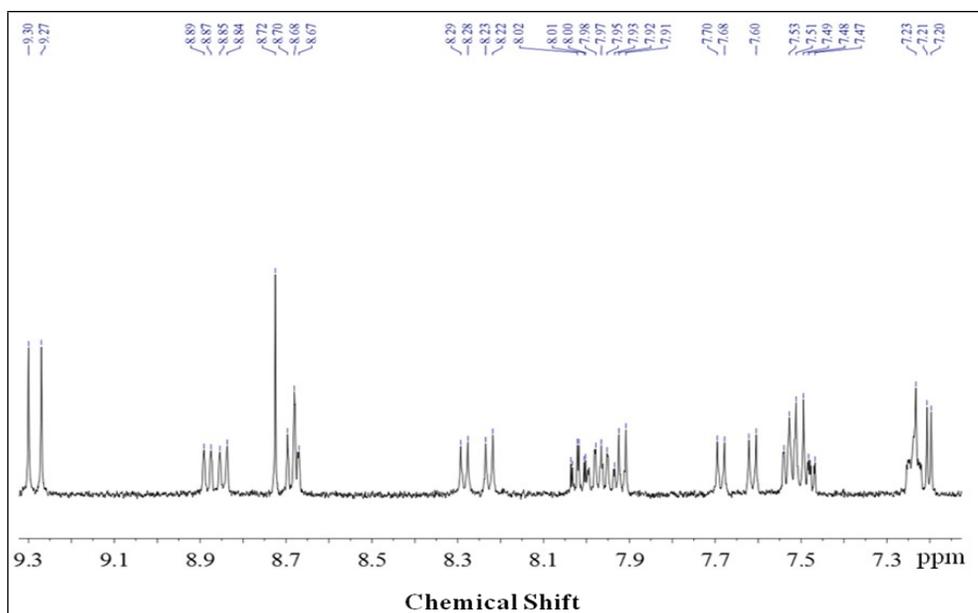
4H), 9.03(s, 4H), 9.02(s, 4H), 8.65(m, 8H), 8.62(d, 4H), 8.25(d, 4H), 8.15(m, 8H), 7.84(t, 4H), 7.83(m, 8H), 7.67(d, 4H), 7.63(m, 8H), 7.41(m, 8H), 7.29(s, 2H), 7.28(s, 2H), 7.26(s, 2H), 7.18(d, 4H), 7.12(m, 8H), 7.03(t, 4H).  $^{13}\text{C}$  NMR (500 MHz, 298K,  $\text{CD}_3\text{CN}$ , ppm): 160.98, 158.28, 158.12, 155.65, 155.03, 152.68, 149.97, 149.42, 148.62, 144.00, 138.82, 138.33, 136.06, 133.86, 131.68, 131.40, 128.60, 127.52, 127.36, 125.14, 124.01, 122.18, 120.76, 117.32, 114.86, 56.03, 46.34; ESI/MS (m/z): 419.43 [ $\text{T4-6PF}_6^-$ ] $^{6+}$  (calculated 419.44), 532.30 [ $\text{T4-5PF}_6^-$ ] $^{5+}$  (calculated 532.32), 701.62 [ $\text{T4-4PF}_6^-$ ] $^{4+}$  (calculated 701.64), 983.84 [ $\text{T4-3PF}_6^-$ ] $^{3+}$  (calculated 983.84).

**T5:** **L2** (6.3 mg, 0.002 mmol) and  $\text{Zn}(\text{NO}_3)_2$  (0.6 mg, 0.002 mmol) were used to prepare **T5** according to the similar method above to give **T5** as a red solid (5.8 mg, 91%). M.P. > 200°C;  $^1\text{H}$  NMR (500 MHz, 298 K,  $\text{CD}_3\text{CN}$ , ppm):  $\delta$ = 9.04(s, 4H), 9.03(s, 4H), 9.00(s,4H), 8.73(d, 4H), 8.68(d, 4H), 8.66(d, 4H), 8.15(d, 4H), 8.13(m, 8H), 8.07(t, 4H), 7.85(m, 8H), 7.84(d, 4H), 7.61(m, 12H), 7.42(m, 8H), 7.34(t, 4H), 7.26(s, 2H), 7.25(s, 2H), 7.23(s, 2H), 7.12(m, 8H).  $^{13}\text{C}$  NMR (500 MHz, 298K,  $\text{CD}_3\text{CN}$ , ppm): 158.19, 155.41, 152.37, 149.78, 149.31, 147.96, 147.88, 147.69, 141.18, 137.97, 131.35, 127.74, 127.49, 127.42, 127.37, 124.56, 121.44, 121.35, 117.29, 55.81; ESI/MS (m/z): 534.32 [ $\text{T5-5PF}_6^-$ ] $^{5+}$  (calculated 534.31), 704.14 [ $\text{T5-4PF}_6^-$ ] $^{4+}$  (calculated 704.14), 987.17 [ $\text{T5-3PF}_6^-$ ] $^{3+}$  (calculated 987.17), 1552.63 [ $\text{T5-2PF}_6^-$ ] $^{2+}$  (calculated 1552.63).

## Reference:

S1. A. Schultz, Y. Cao, M. Huang, S. Z. D. Cheng, X. Li, C. N. Moorefield, C. Wesdemiotis and G. R. Newkome, *Dalton Trans.*, **2012**, *41*, 11573.

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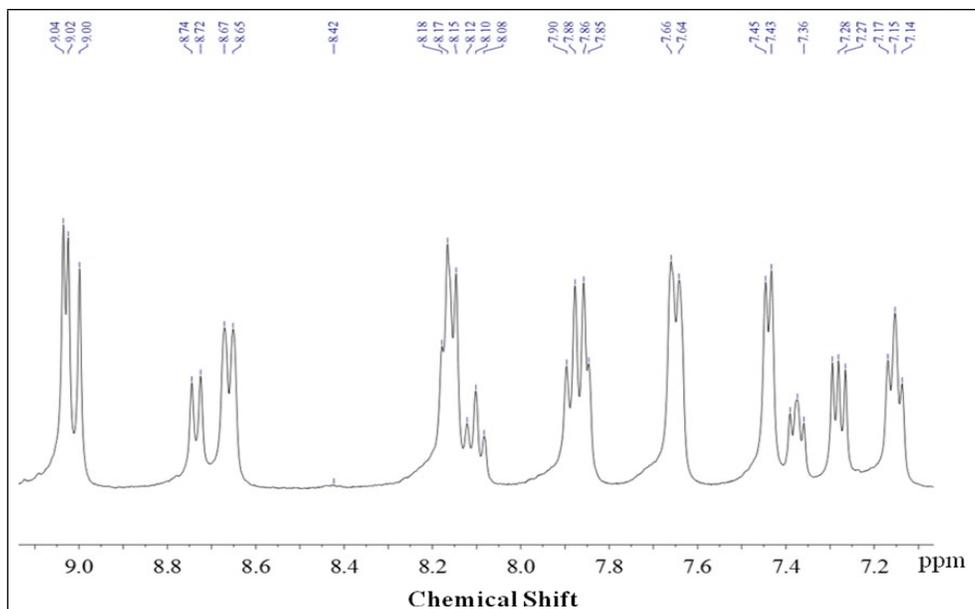


Figure S3.  $^1\text{H}$  NMR spectrum of complex **T5** in  $\text{CD}_3\text{CN}$

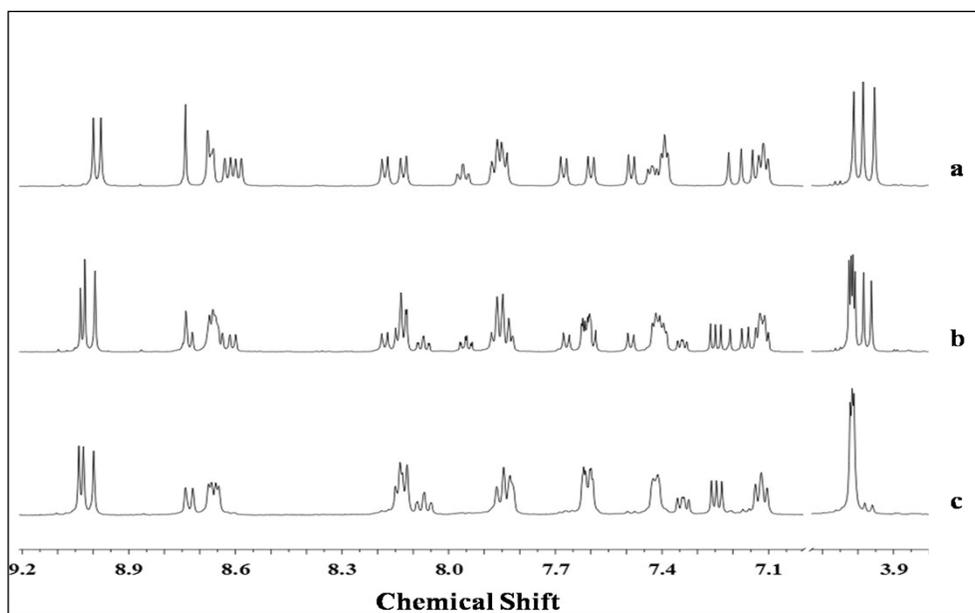


Figure S4.  $^1\text{H}$  NMR spectrum of (a) **L2**, (b) **L2** treated with 0.25eq  $\text{Zn}(\text{NO}_3)_2$  (c) **L2** treated with 1.0 eq  $\text{Zn}(\text{NO}_3)_2$  in  $\text{CD}_3\text{CN}$  at 298 K.

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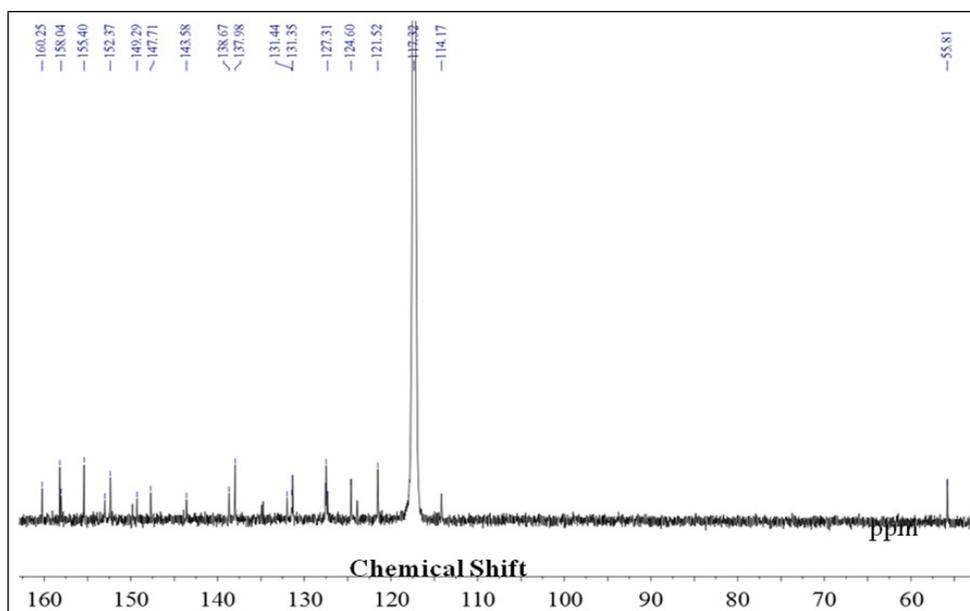


Figure S5.  $^{13}\text{C}$  NMR spectrum of complex **T4** in  $\text{CD}_3\text{CN}$

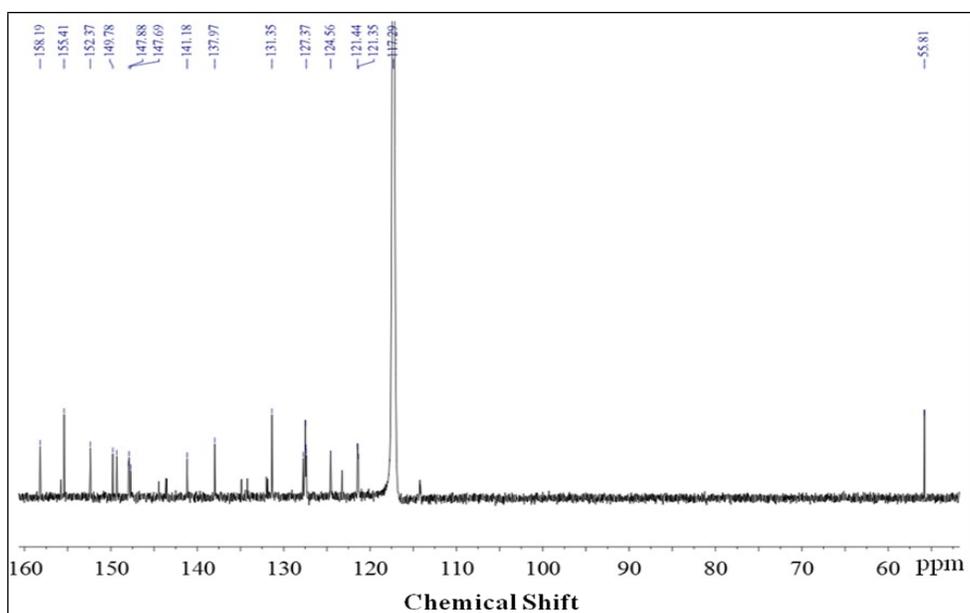


Figure S6.  $^{13}\text{C}$  NMR spectrum of complex **T5** in  $\text{CD}_3\text{CN}$

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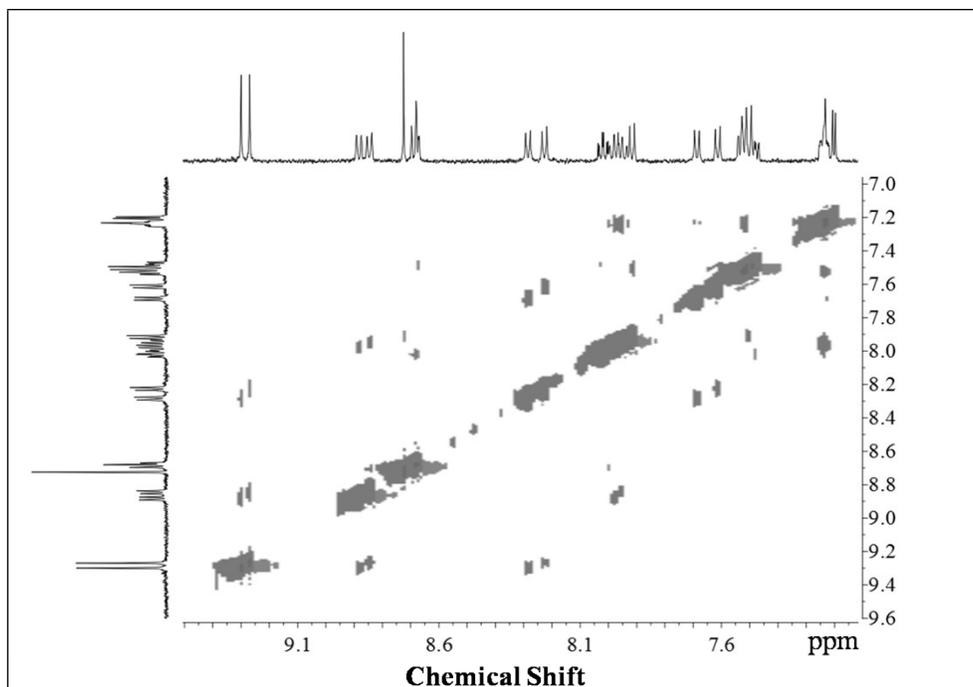


Figure S7. Nosey spectrum of complex **L2** in CD<sub>3</sub>OD

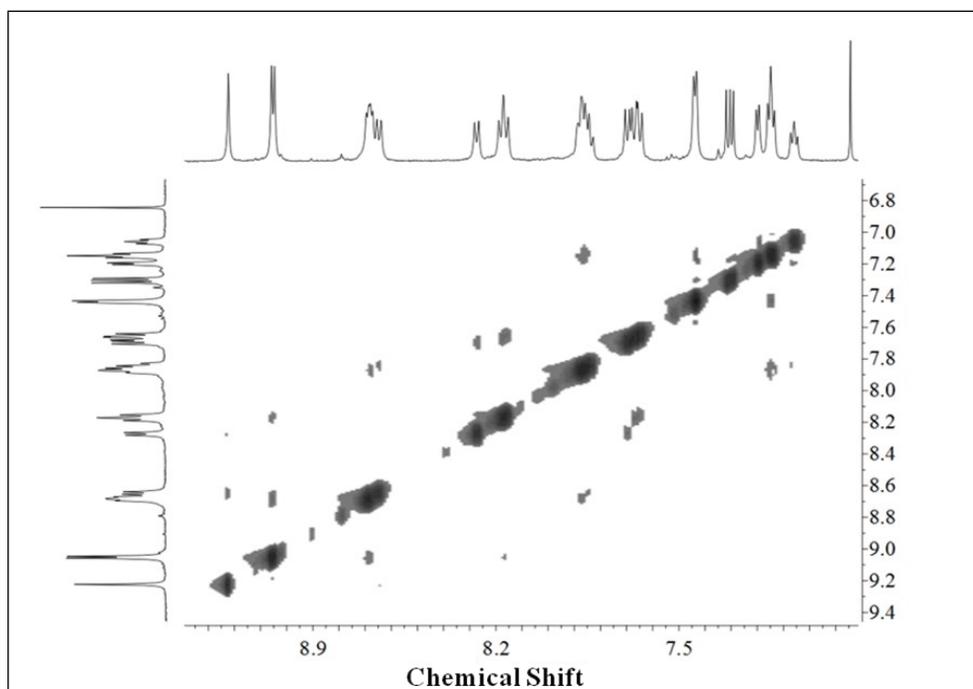


Figure S8. Nosey spectrum of triangle **T4** in CD<sub>3</sub>CN

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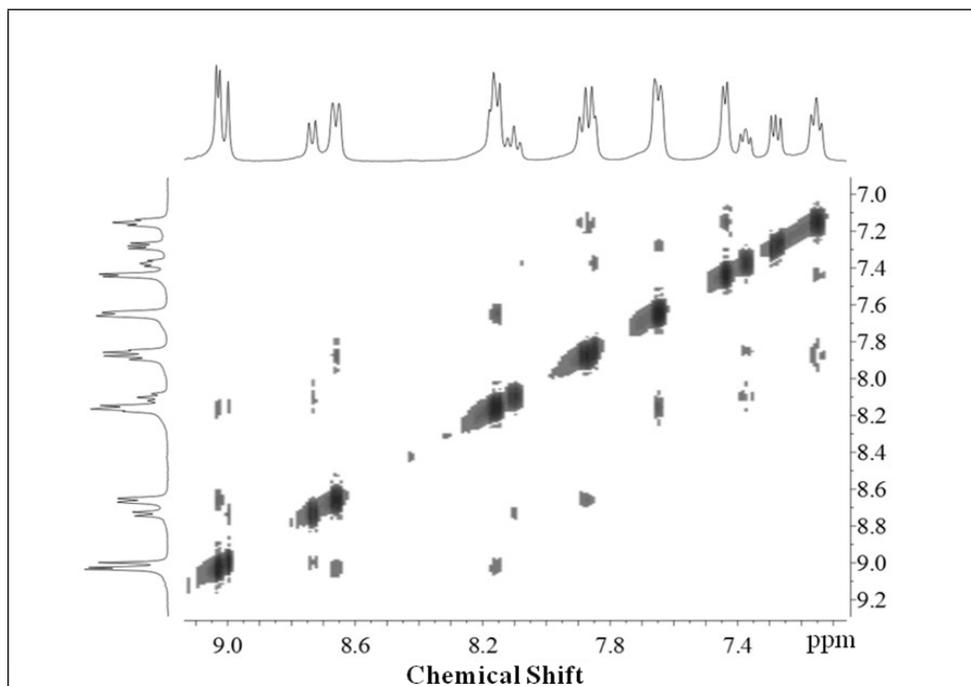


Figure S9. Nosey spectrum of triangle **T5** in CD<sub>3</sub>CN

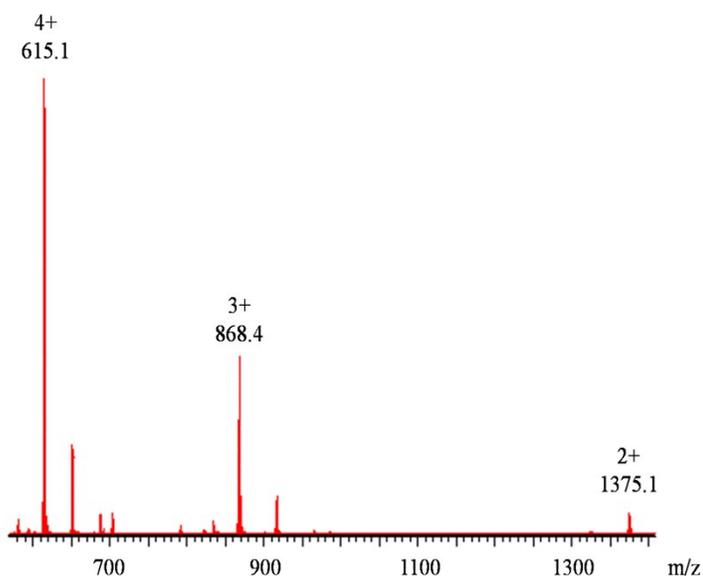


Figure S10. ESI-MS spectrum of metallo-organic ligand **L2**.

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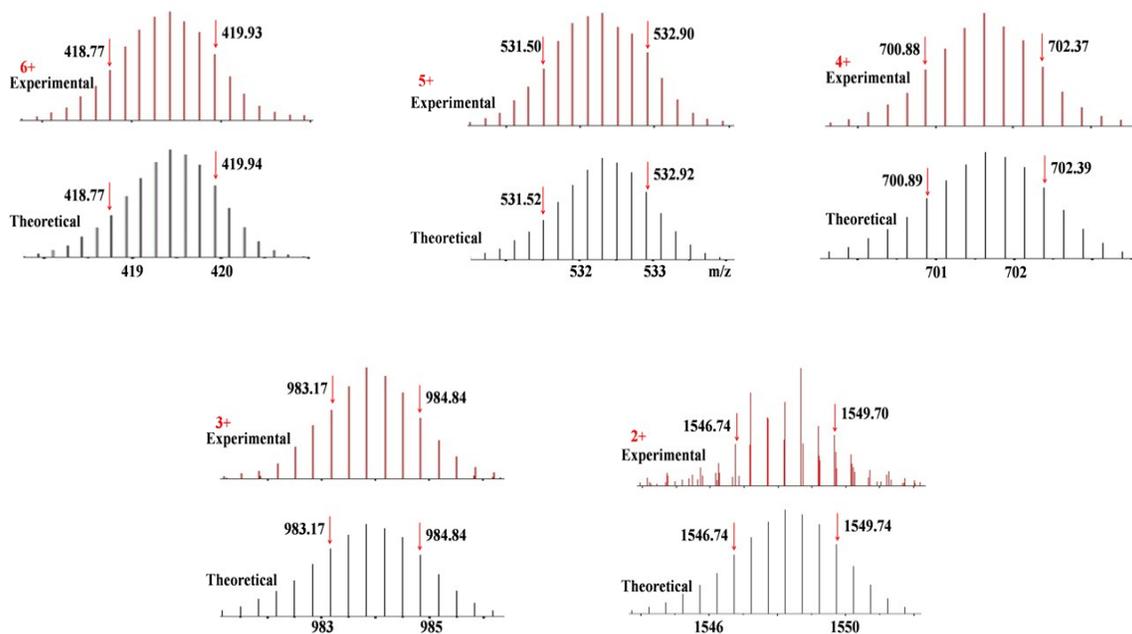


Figure S11. Measured and calculated isotope patterns for the different charge states (2+ to 6+) observed from T4 (PF<sub>6</sub><sup>-</sup> as counterion).

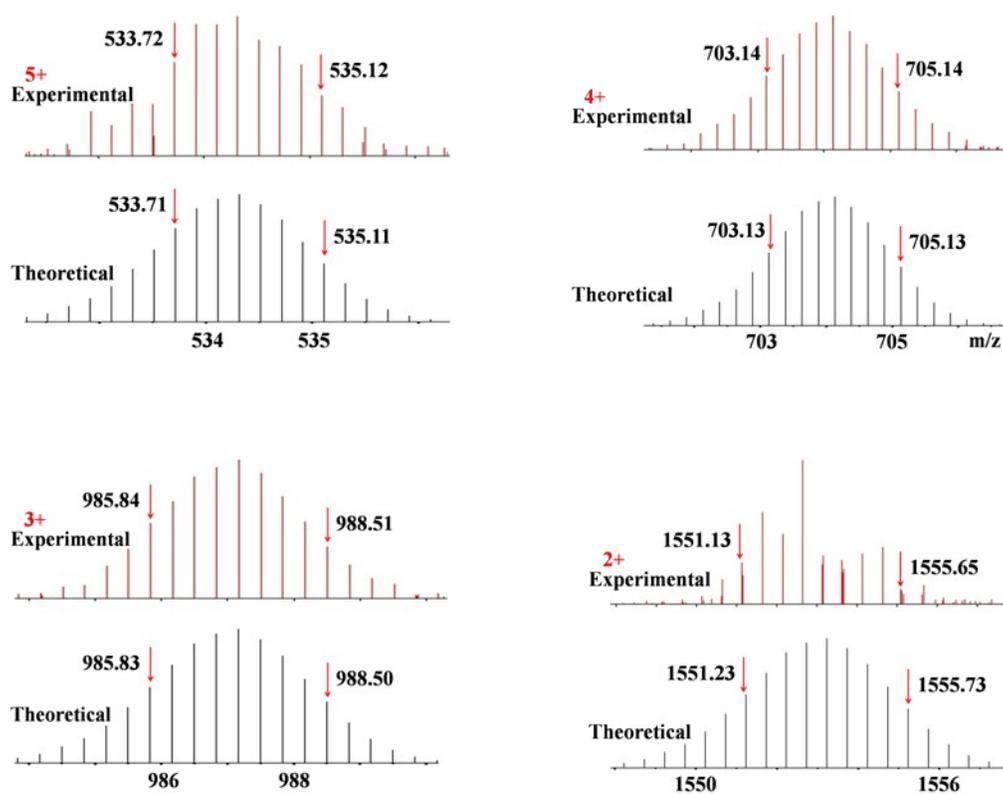


Figure S12. Measured and calculated isotope patterns for different charge states (2+ to 5+) observed from T5 (PF<sub>6</sub><sup>-</sup> as counterion).

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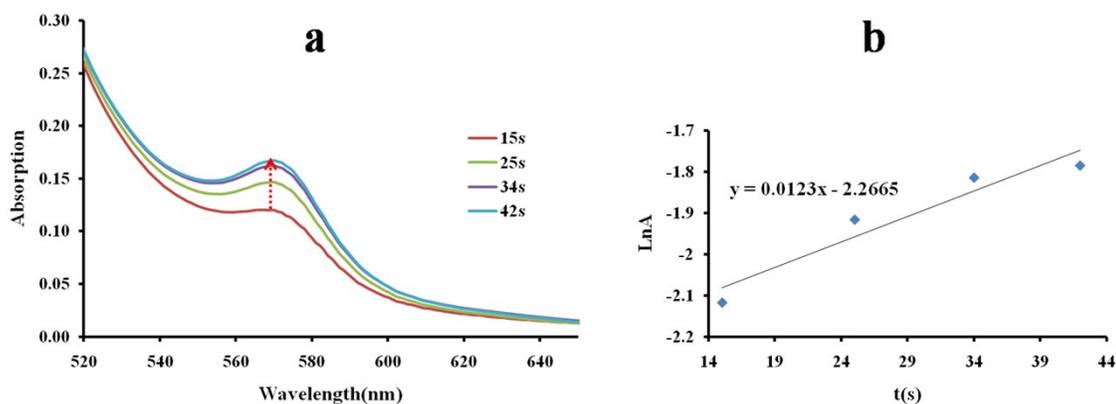


Figure S13. (a) UV-vis absorption/time dependent changes of **T5** in the presence of Fe<sup>2+</sup> in V<sub>1/1</sub> CH<sub>3</sub>CN and CH<sub>3</sub>OH at **311.15 K**. (b) Plot of LnA (A is the absorption intensity at 567 nm) versus time and corresponding fitting line.

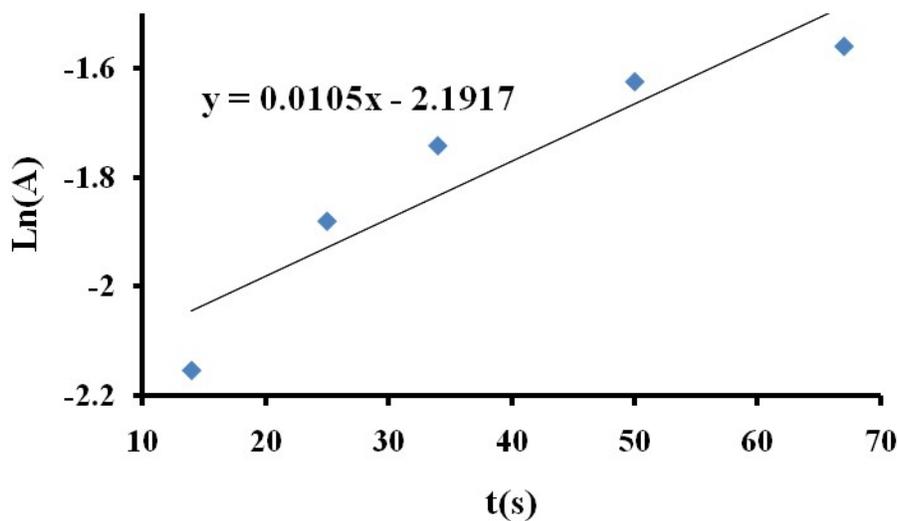


Figure S14. Plot of LnA (A is the absorption intensity at 567 nm) versus time and corresponding fitting line and equation (according to UV-vis absorption/time dependent changes of **T5** in the presence of Fe<sup>2+</sup> in CH<sub>3</sub>CN at **298.15 K**).

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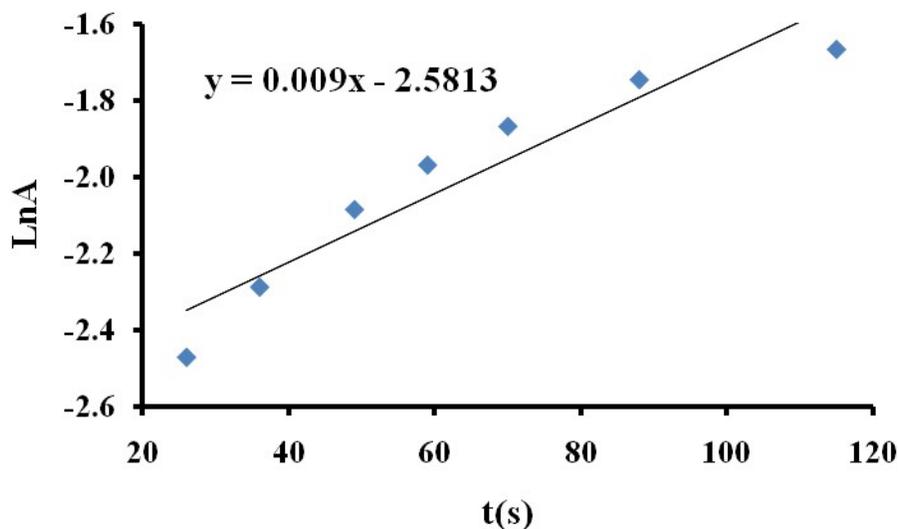


Figure S15. Plot of  $\text{Ln}A$  ( $A$  is the absorption intensity at 567 nm) versus time and corresponding fitting line and equation (according to UV-vis absorption/time dependent changes of **T5** in the presence of  $\text{Fe}^{2+}$  in  $\text{CH}_3\text{CN}$  at **286.15 K**).

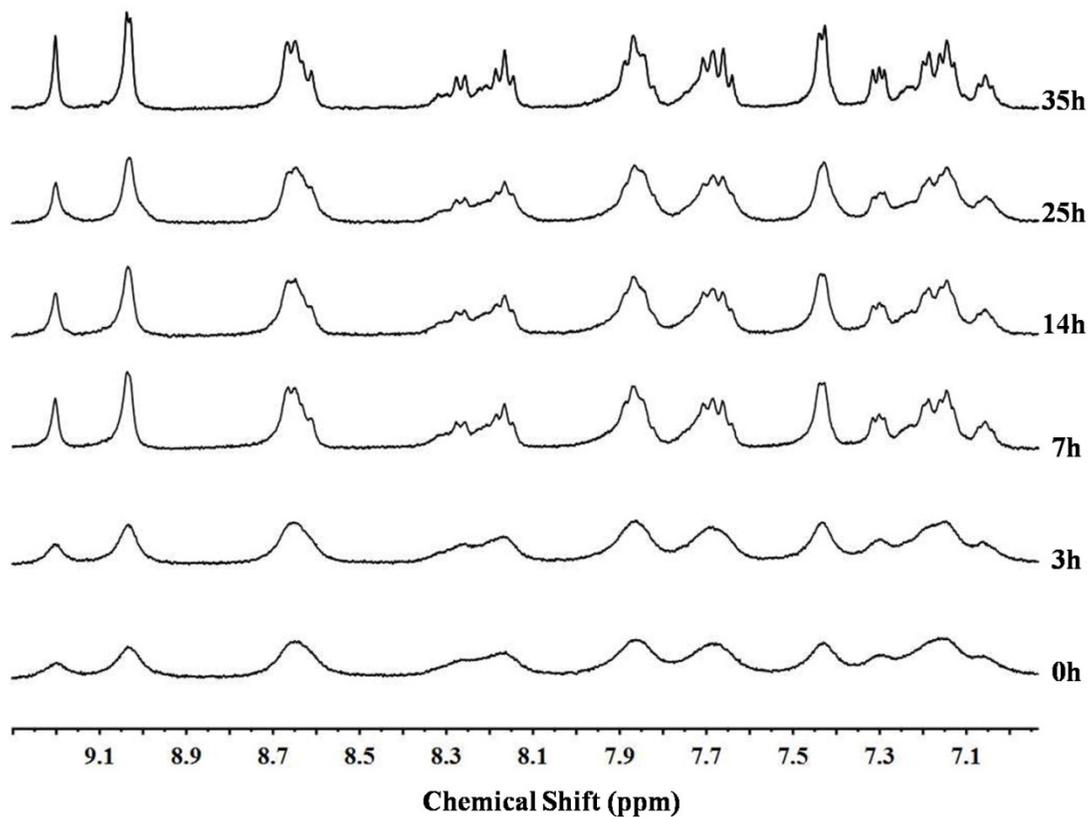


Figure S16.  $^1\text{H}$  NMR spectrum of transformation process from **P3** to **T5** at different time at 333 K in  $\text{CD}_3\text{CN}$ .

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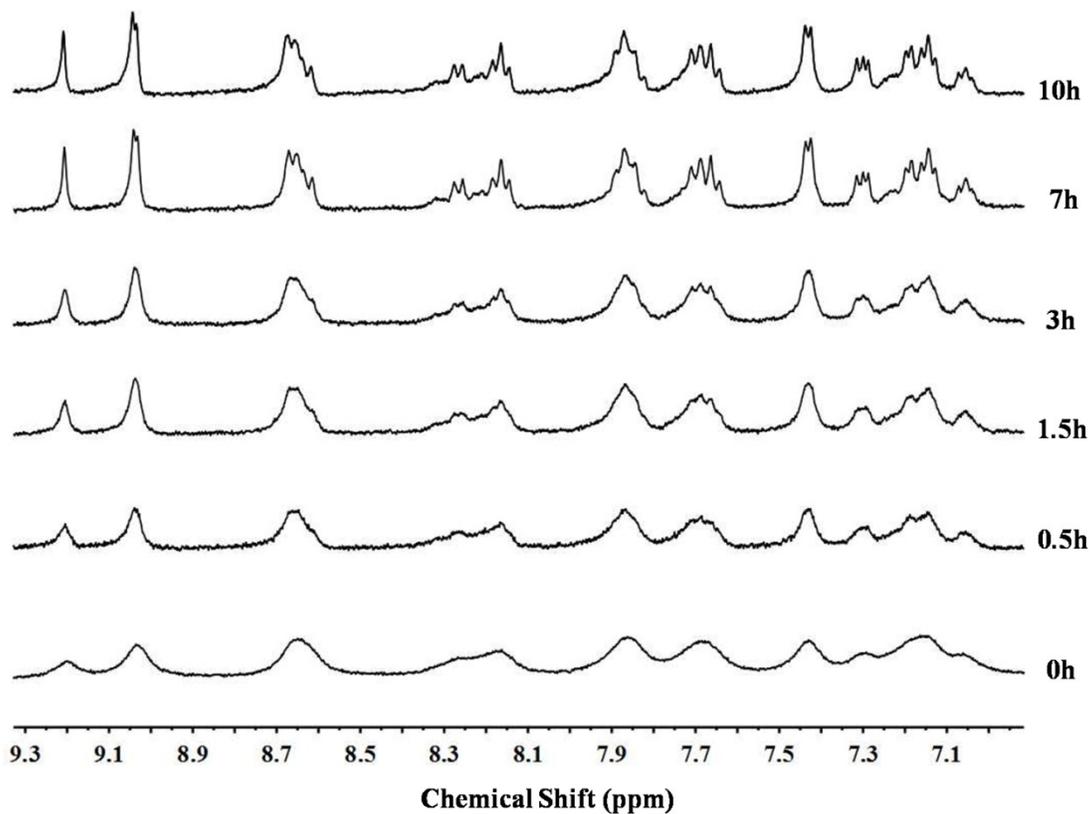


Figure S17. <sup>1</sup>H NMR spectrum of transformation process from **P3** to **T5** at different time at 353 K in CD<sub>3</sub>CN.