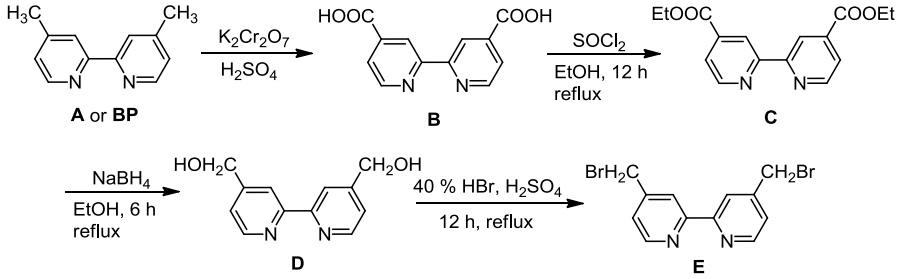
New bi-functional zinc catalysts based on robust and easy-to-handle *N*-chelating ligands for the synthesis of cyclic carbonates from epoxides and CO_2 under mild conditions

Rongchang Luo, Xiantai Zhou, Wuying Zhang, Zhongxiu Liang, Jun Jiang and Hongbing Ji*

Supporting information

1. General Procedure for the Synthesis of 4,4'-dibromomethyl-2,2'-bipyridine

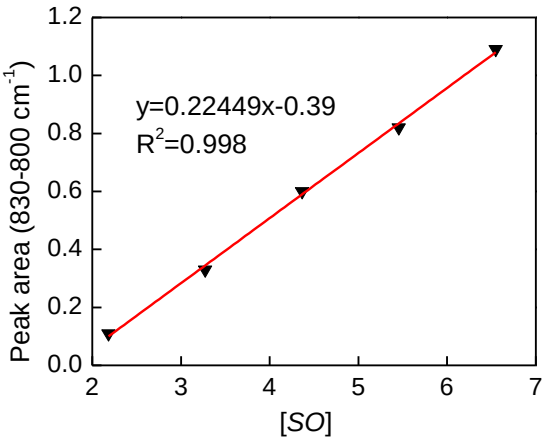


(a) Synthesis of 4,4'-diethoxycarbonyl-2,2'-bipyridine: To a suspension solution of 2,2'-bipyridyl-4,4'-dicarbonyl acid (4.88 g, 20 mmol) in 300 mL ethanol was added thionyl chloride (5 mL) dropwise. The reaction mixture was stirred vigorously under reflux for 12 h. Then the solvent was evaporated and the resulting mixture was portioned between CH_2Cl_2 and water. The organic phase was washed through saturated $NaHCO_3$ for three times. The combined organic layer was dried over $MgSO_4$ and evaporated to give the crude product as a white solid **C**. Yield: 92 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H=8.98 (d, 1H), 8.87-8.89 (d, J=8 Hz, 1H), 7.92-7.94 (d, J=8 Hz, 1H), 4.44-4.50 (q, 2H) 1.43-1.47 (t, J=16 Hz, 3H); ^{13}C NMR (100.4 MHz, CD_3OD) δ_C=165.09, 156.33, 149.99, 139.11, 123.31, 120.66, 83.91, 61.94, 44.41.

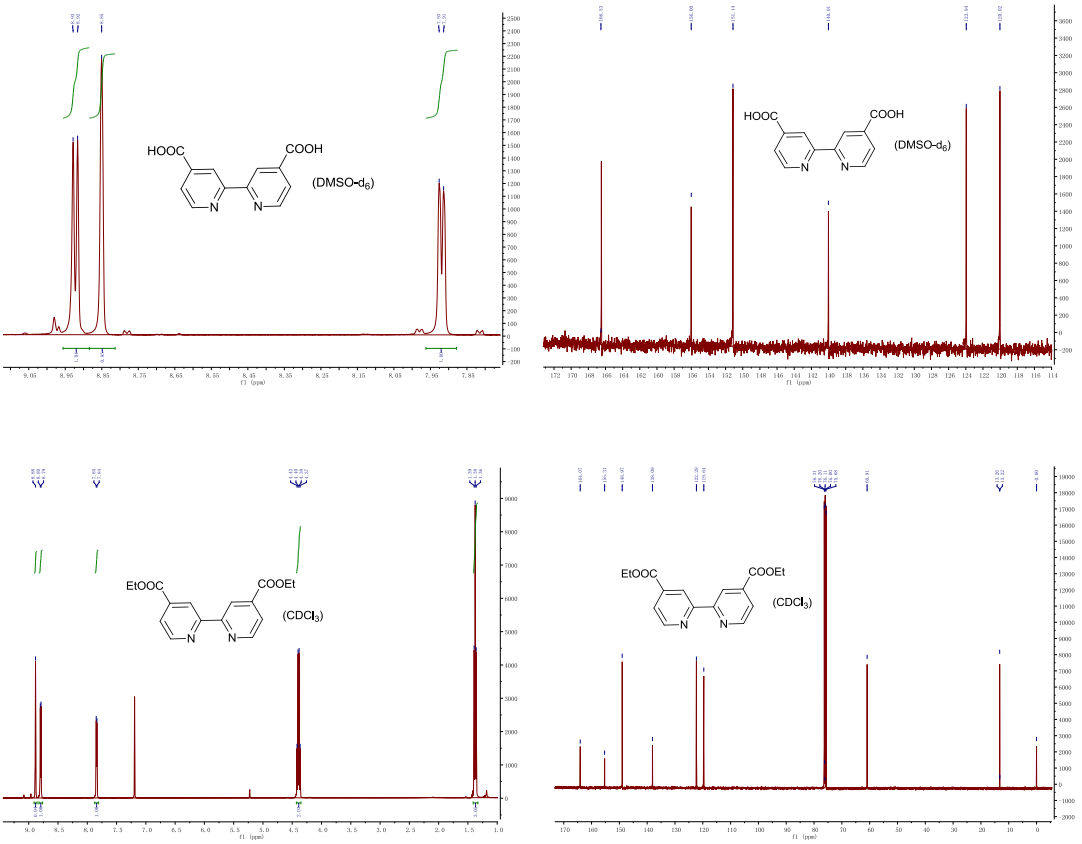
(b) Synthesis of 4,4'-bis(hydroxymethyl)-2,2'-bipyridine: A suspension of 4,4'-diethoxycarbonyl-2,2'-bipyridine (4.5 g, 15 mmol) and sodium borohydride (3.78 g, 0.1 mol) in dry ethanol (300 mL) was stirred at 80 ^{o}C for 12 h. After cooling to room temperature, an ammonium chloride saturated water solution (300 mL) was added to decompose the excess borohydride, and then the solution was stirred at room temperature overnight. The ethanol was removed under vaccum and the resulting mixture was extracted with ethyl acetate (4 × 250 mL). The combined organic layer was dried over $MgSO_4$ and evaporated to give the crude product **D** and was used without further purification. Yield: 80 %. FT-IR (KBr), γ_{max}/cm^{-1}: 3222, 1601, 1556, 1457, 1387, 1197, 1109, 1055, 998, 916, 819, 647, 549, 502; ^{1}H NMR (400 MHz, CD_3OD) δ_H=8.61-8.62 (d, J=4 Hz, 1H), 8.30 (s, 1H), 7.46-7.47 (d, J=4 Hz, 1H), 4.78 (s, 1H); ^{13}C NMR (100.4 MHz, CD_3OD) δ_C=155.74, 152.79, 148.74, 121.30, 118.80, 62.20.

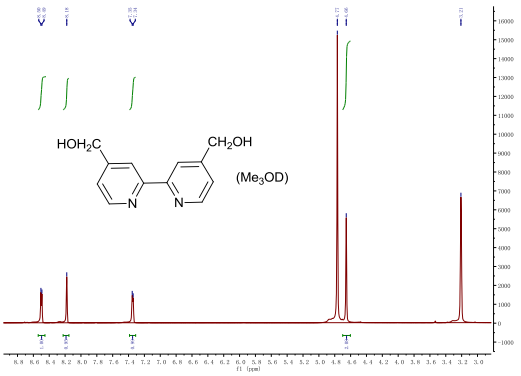
(c) Synthesis of 4,4'-dibromomethyl-2,2'-bipyridine: To a stirred mixture of 4,4'-dihydroxymethyl-2,2'-bipyridine (2.16 g, 10 mmol) and 40% hydrobromic acid (20 mL), 8 mL concentrated sulfuric acid was added dropwise slowly. The resulting solution was refluxed for 12 h, followed by being cooled to the room temperature and addition of 100 mL ice water. The pH was adjusted to 7 by addition of sodium hydroxide. The produced precipitate was filtered, washed with cold water and dried to offer 1.45 g grey powder **E** (85 %). FT-IR (KBr), γ_{max}/cm^{-1}: 3018, 1592, 1553, 1455, 1375, 1250, 1215, 1113, 1060, 988, 902, 850, 829, 741, 667, 638, 558; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H=8.68-8.70 (d, J=8 Hz, 1H), 8.49 (s, 1H), 7.39-7.40 (d, J=4 Hz, 1H), 4.50 (s, 1H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ_C=155.89, 149.42, 148.64, 123.88, 121.09, 29.77.

2. Standard curve for *in situ* IR spectra: five different concentrations of styrene oxide in propylene carbonate.



3. NMR of various intermediates and catalysts IL-BPZ

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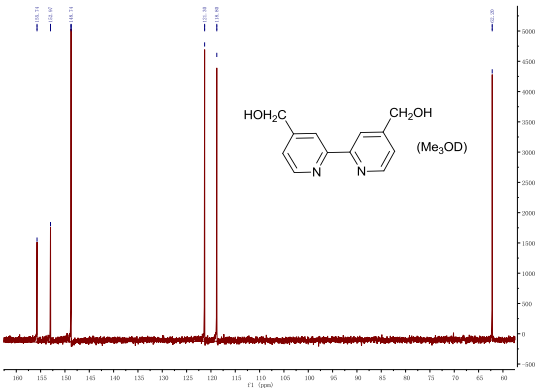
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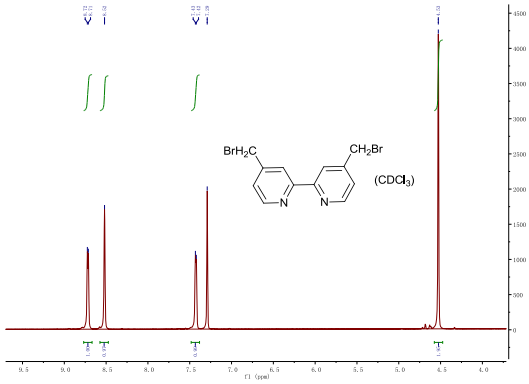
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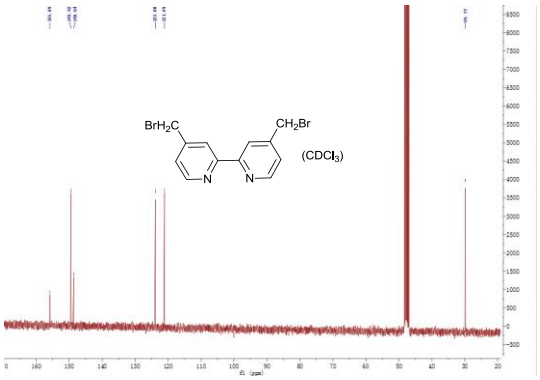
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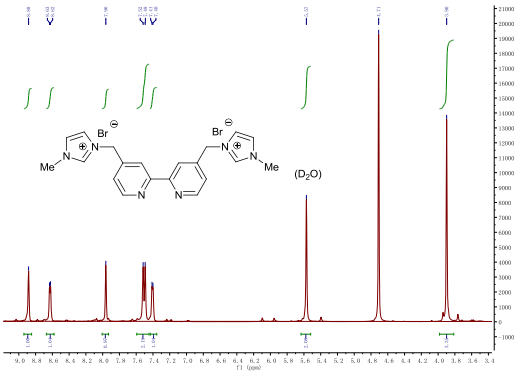
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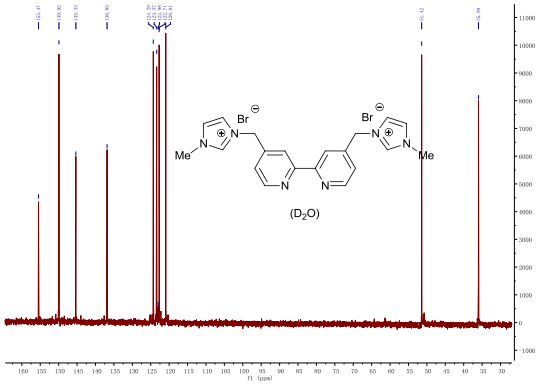
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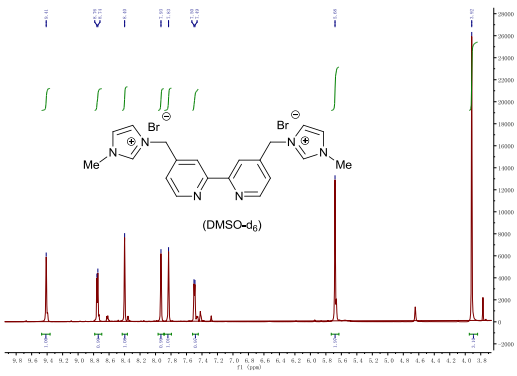
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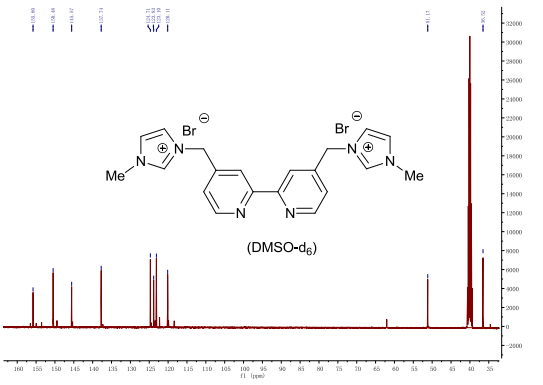
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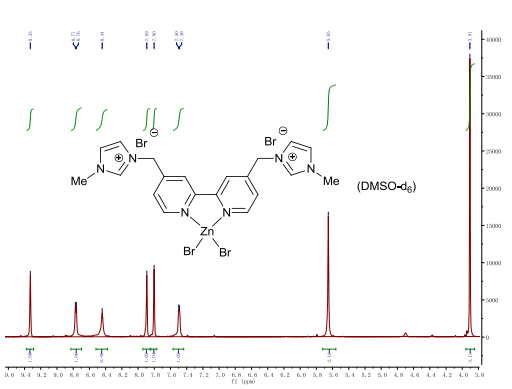
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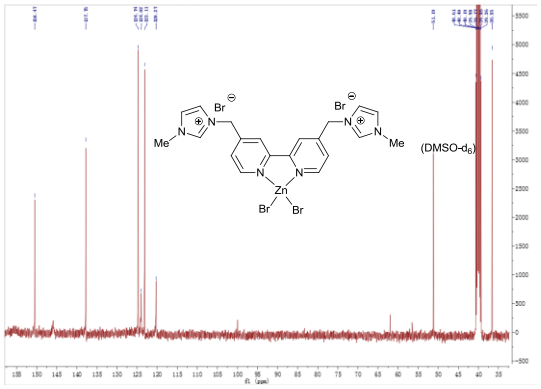
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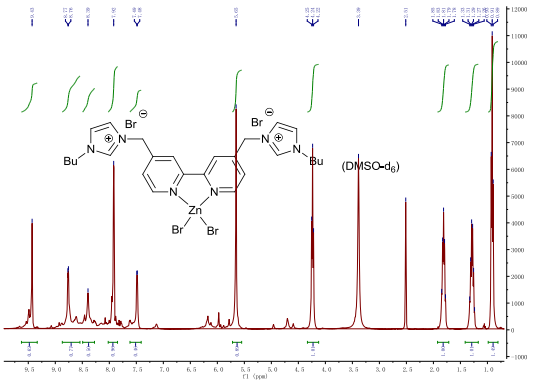
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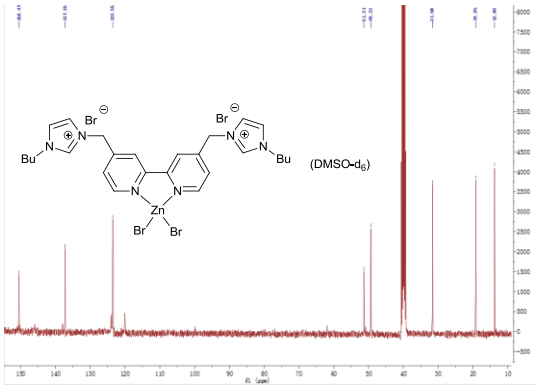
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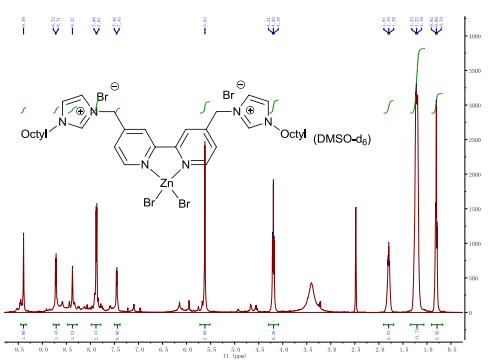
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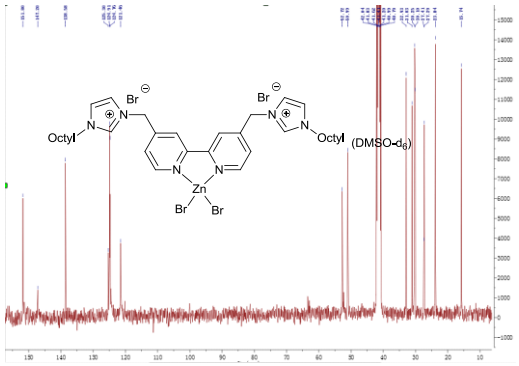
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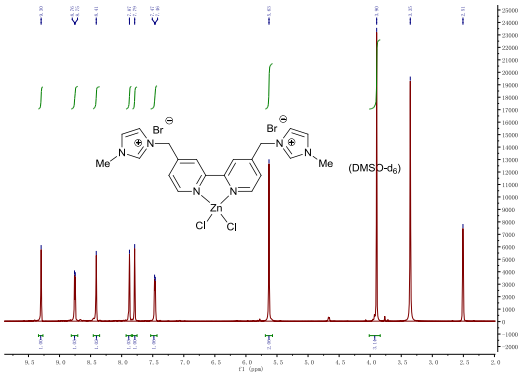
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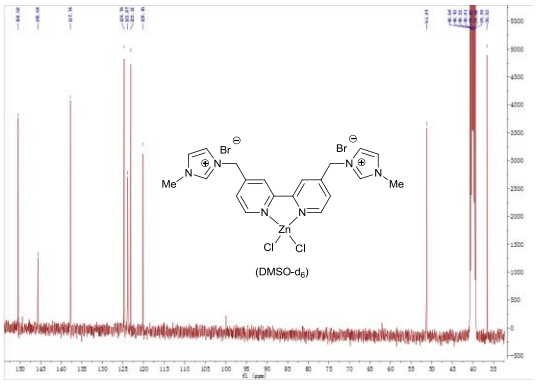
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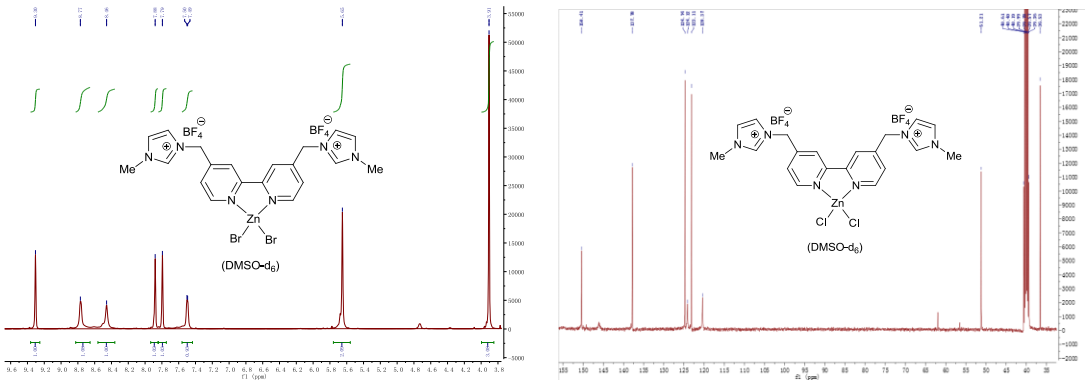
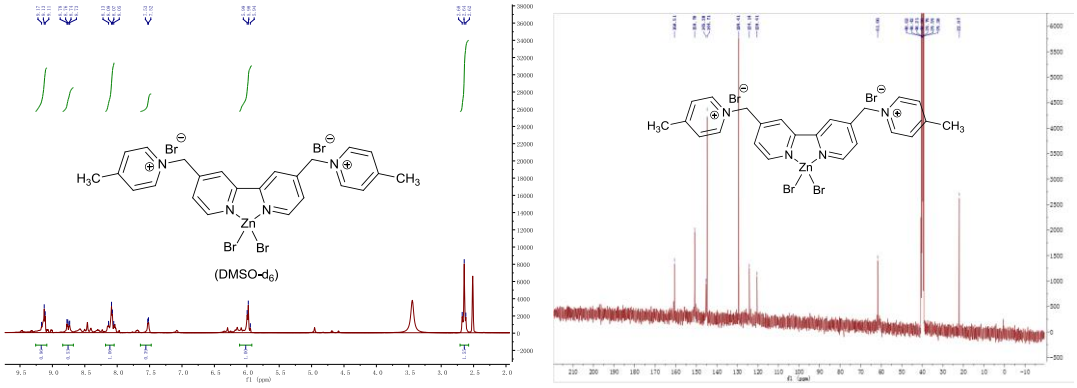
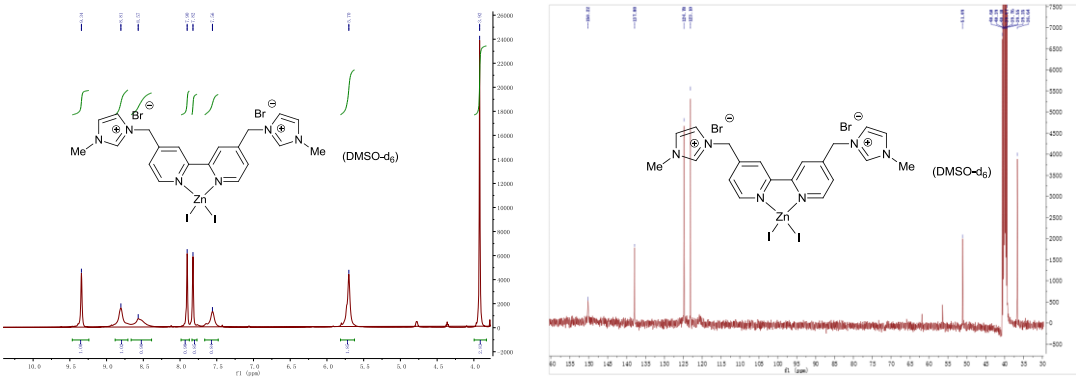
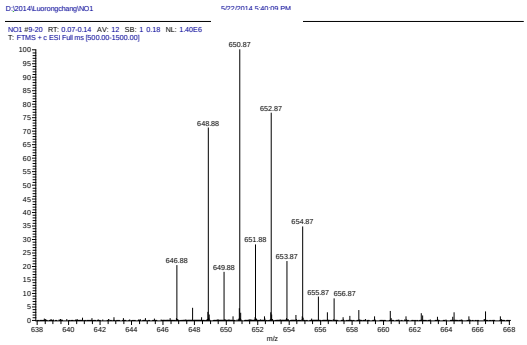
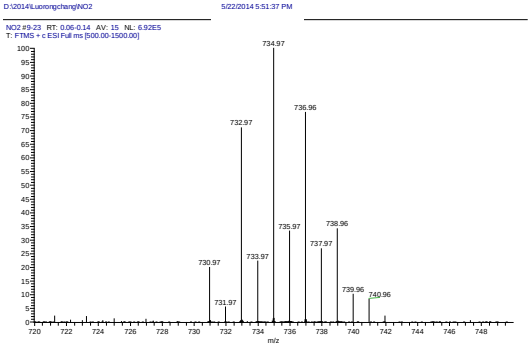


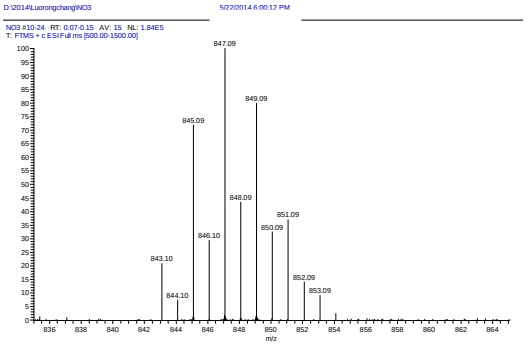




4. High Resolution Mass Spectrometry of catalysts **IL-BPZ**



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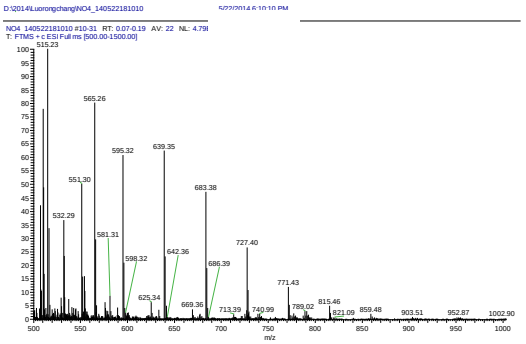
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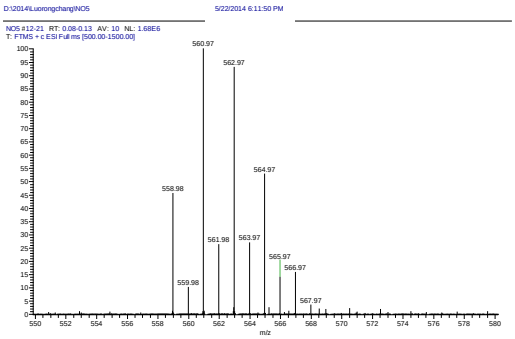
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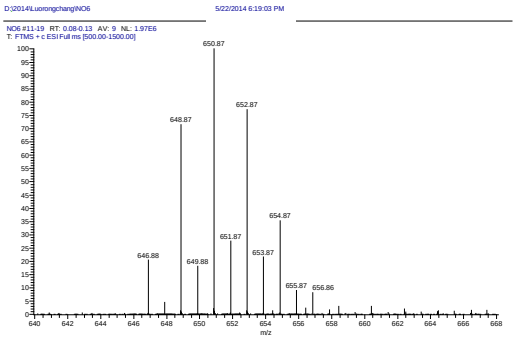
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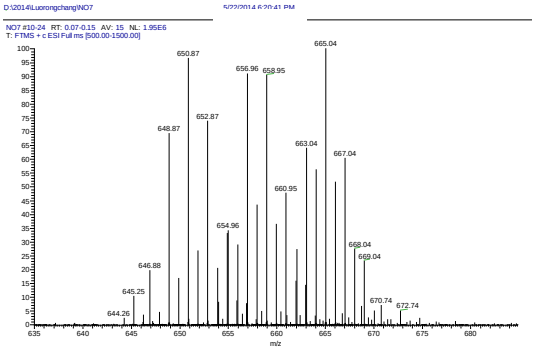
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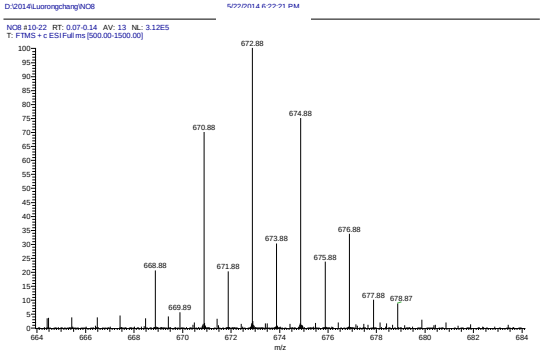
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