Supporting Information

A Mechanistic Study on Multifunctional Fei-Phos Ligand-controlled Asymmetric Palladium -Catalyzed Allylic Substitutions

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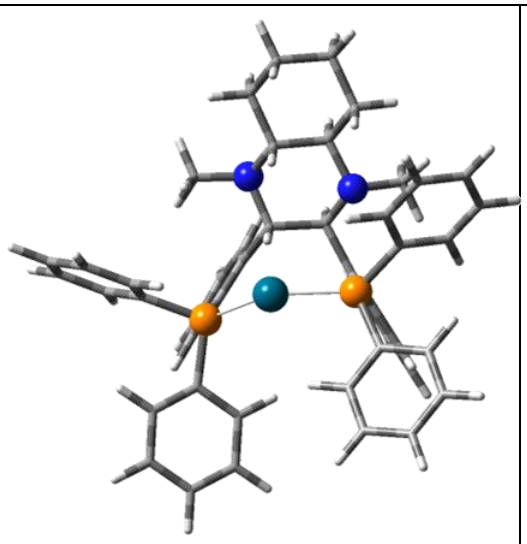
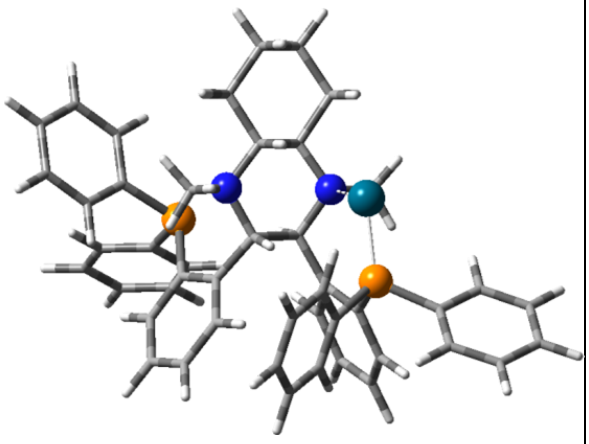
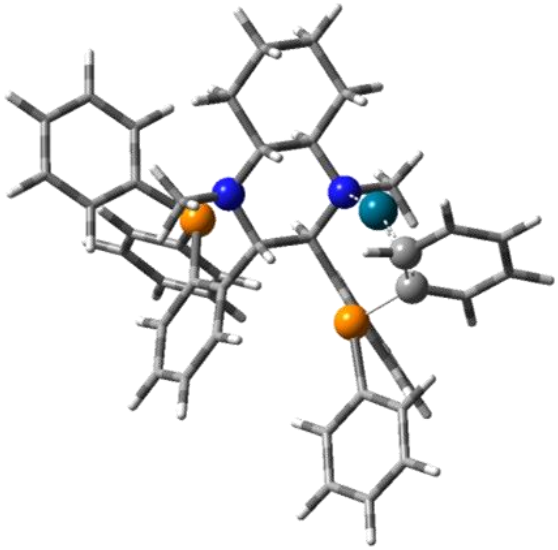
Figure S1. Potential energy for coordination of Fei-Phos with palladium center calculated at B3LYP/6-31G(d,p) level of theory (B3LYP/6-31G(d,p) for C, H, P, N of Fei-Phos; LanL2DZ for Pd).

<table>
<tr><td>  </td><td>  </td></tr>
<tr><td>I (ΔE = 0.0 kcal/mol)
Pd-P1 = 2.310 Å
Pd-P2 = 2.328 Å</td><td>II (ΔE = 17.1 kcal/mol)
Pd-P = 2.219 Å
Pd-N = 2.380 Å</td></tr>
<tr><td colspan="2">  </td></tr>
<tr><td colspan="2">III (ΔE = 21.9 kcal/mol), Pd-N = 2.249 Å, Pd-C1 = 2.201 Å, Pd-C2 = 2.225 Å</td></tr>
</table>

I) Pd center coordinates to two phosphine

II) Pd center coordinates to one phosphine and one nitrogen

III) Pd center coordinates to one nitrogen and one C=C bond of the phenyl ring.

Figure S2. Plot of conversion versus time (min) showing the different reaction rate in the AAA reaction of MeOH and MeOD under the optimized reaction conditions: a) MeOH (♦); b) deuterium-modified methanol (MeOD, ■).

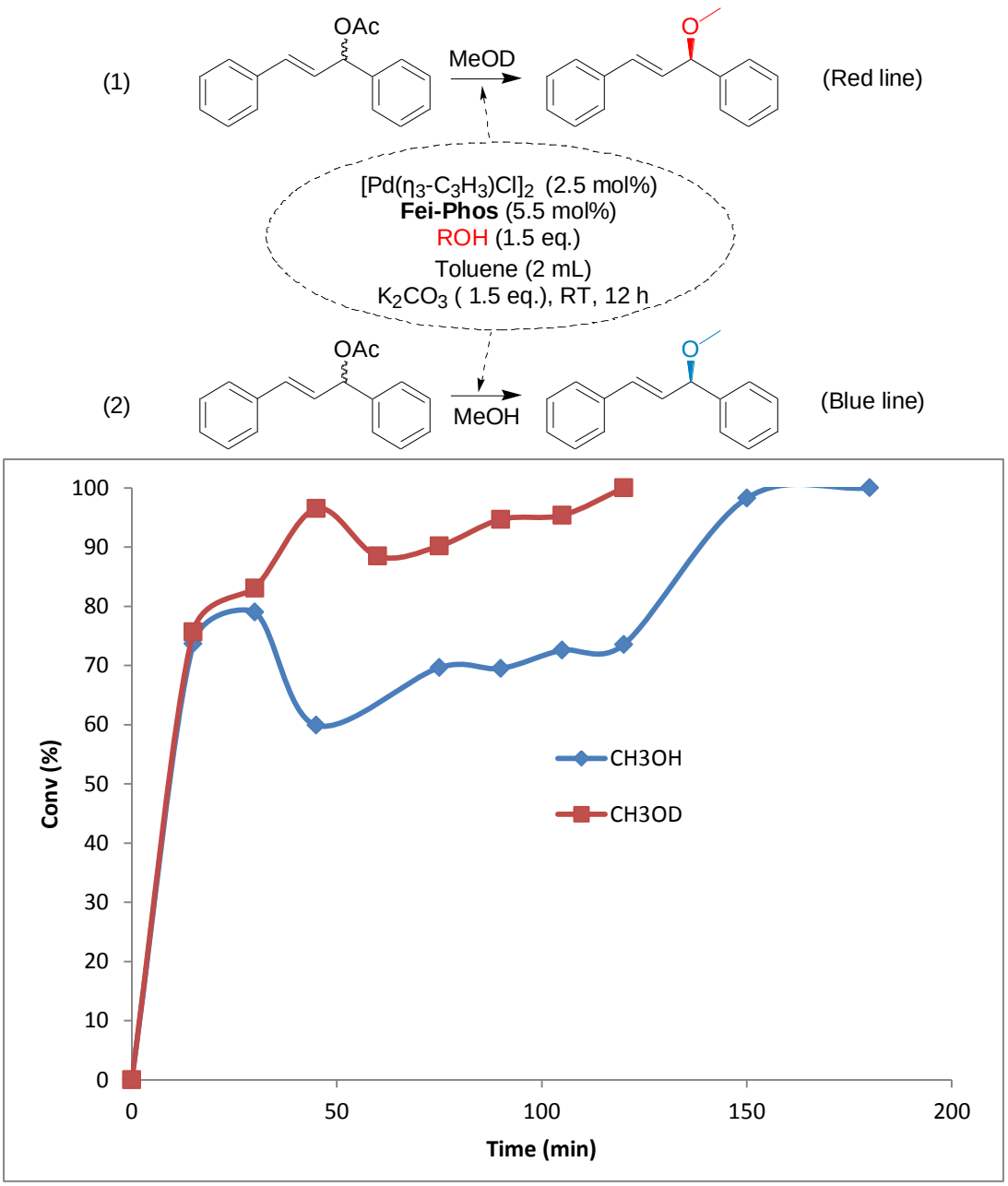


Figure S3. Plot of conversion versus time (min) showing the reaction rate in the AAA reaction of benzyl alcohol under the optimized reaction conditions.

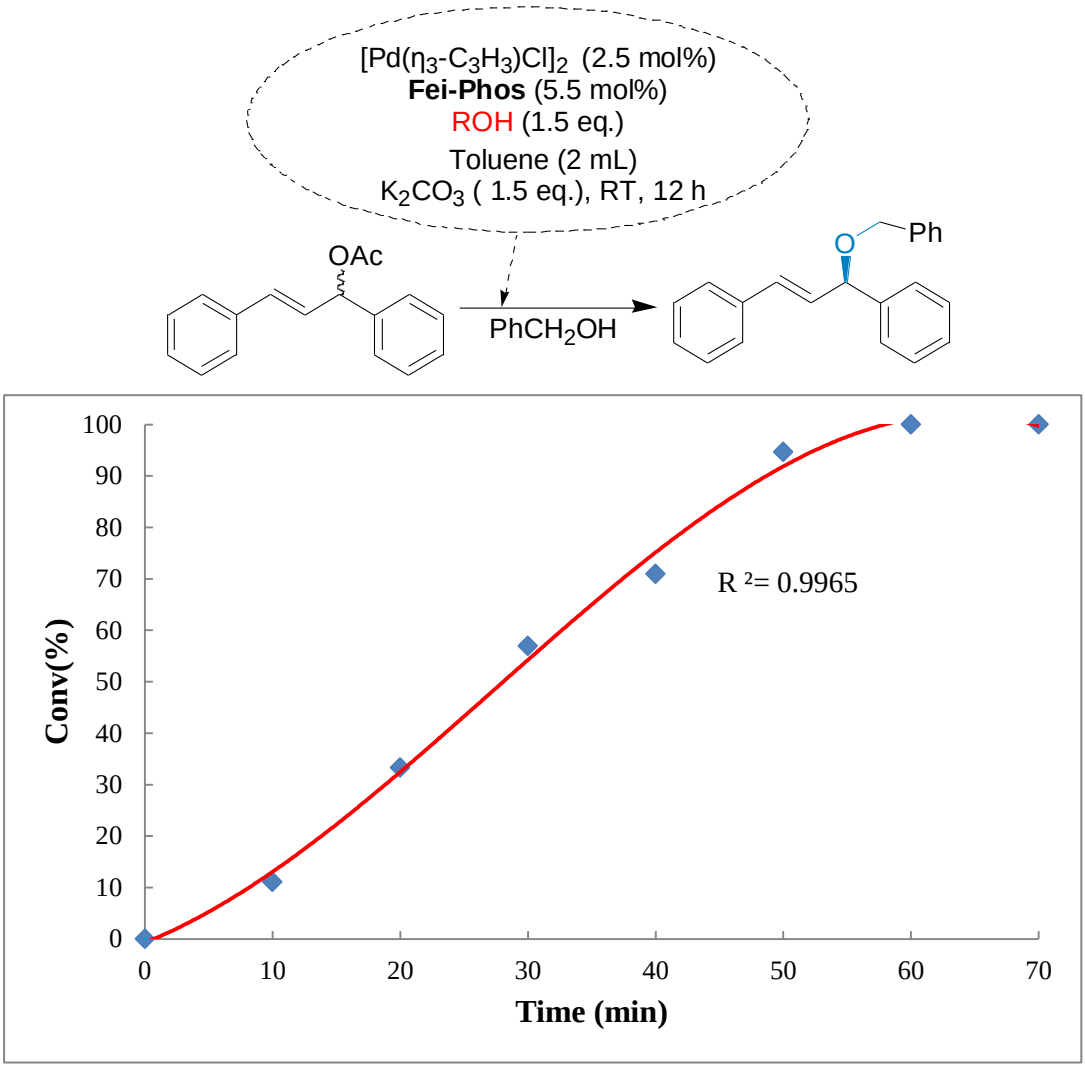
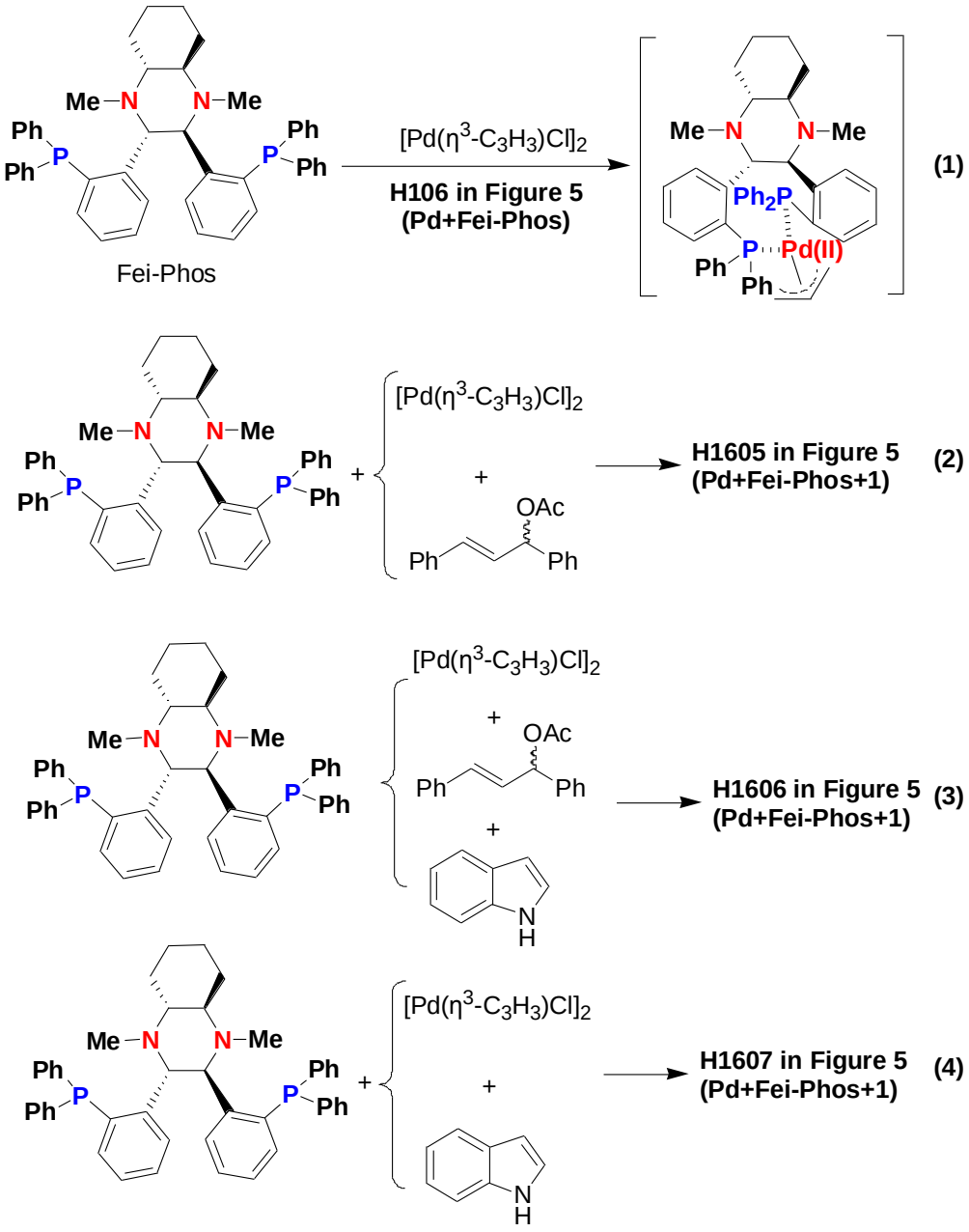
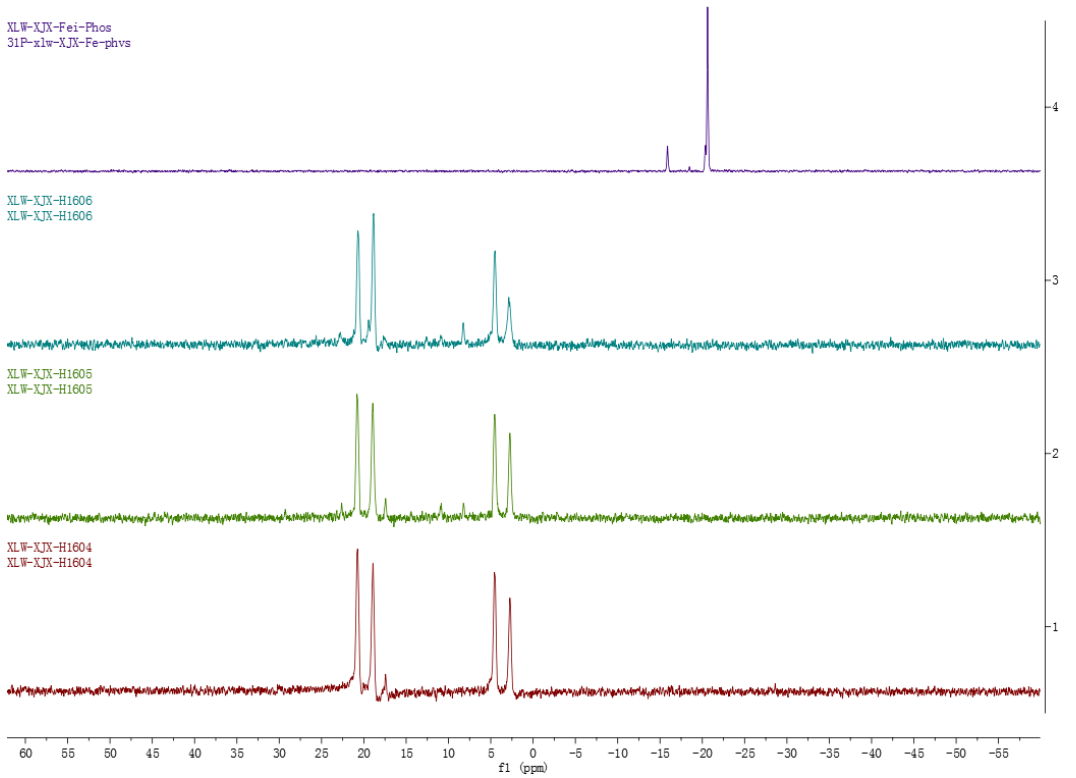


Figure S4. ^{31}P-NMR and ^{1}H-NMR analysis of the mixture of Pd/Fei-Phos with two substrates respectively.





^{31}P NMR analysis of Pd/Fei-Phos complex

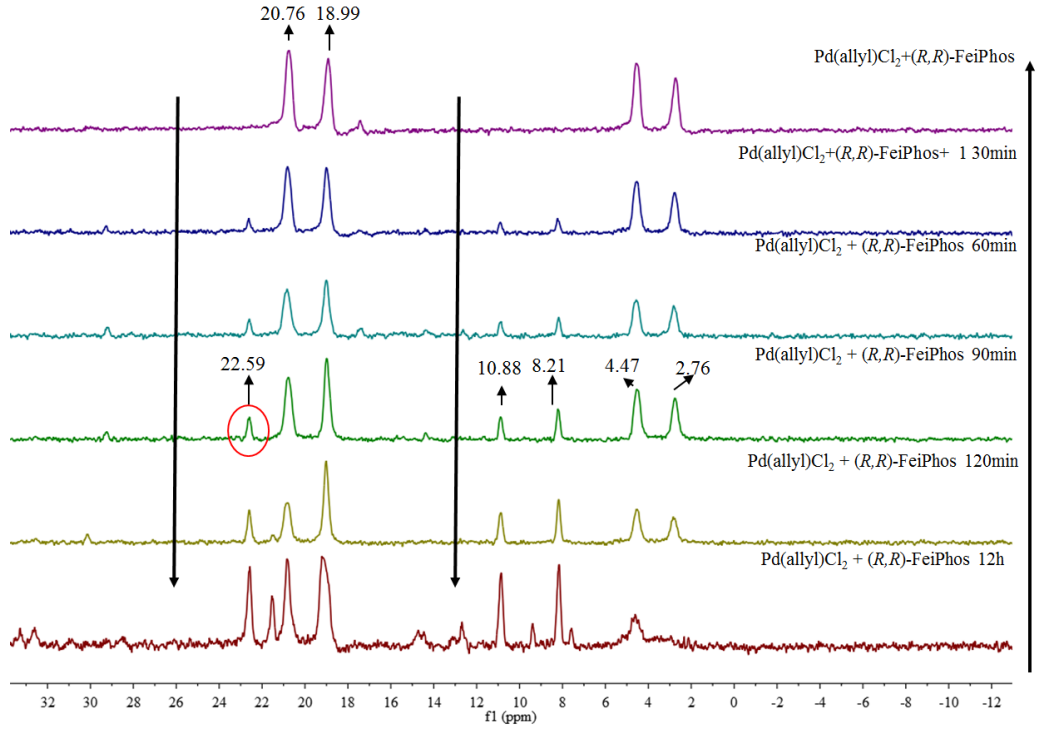


Figure S4-1. ^{31}P-NMR analysis

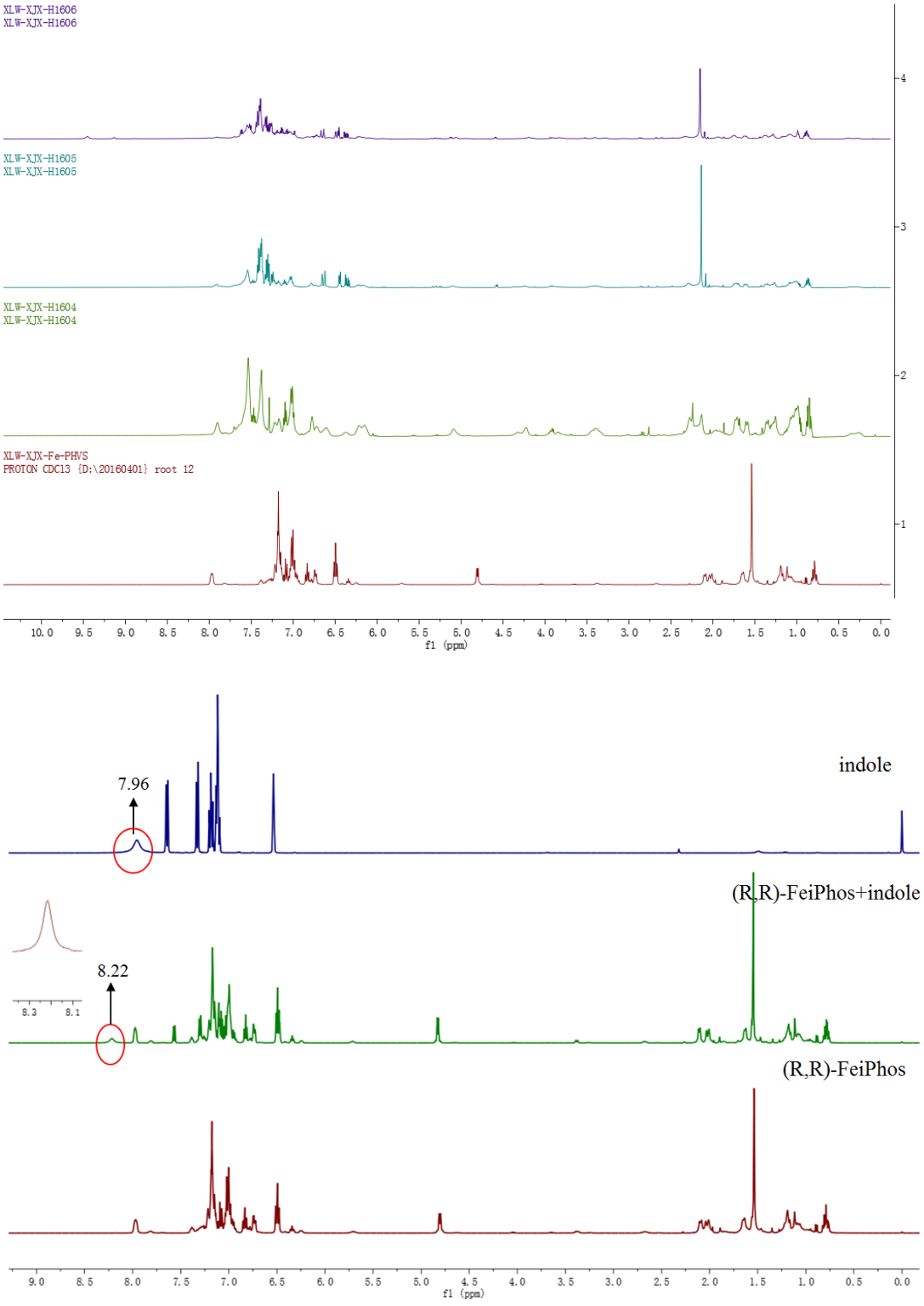


Figure S4-2. ^{1}H-NMR analysis