## Supporting Information for *cis*-to-*trans* Isomerization Promoted by Pyridine as a Crucial Step for the Selective Preparation of *trans* Pt(SAr)(Cl)(PAr'<sub>3</sub>)<sub>2</sub>

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Contents of Supporting Information.  $^{1}$ H and  $^{31}$ P NMR spectrum of *trans*-1e (pS2, S3), *trans*-1i (pS4, S5) and *trans*-1l (pS6, S7). The  $^{31}$ P NMR spectra of crude reaction mixtures of run 5 in Table 4, run 7 in Table 4, and run 2 in Table 5 were shown in the following S8-S10. The peak at  $\delta$  23.1 in S8 was assigned as *trans*-Pt(SC<sub>6</sub>H<sub>4</sub>-2-Cl)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. The ratio of *trans*-1f/*trans*-4f was 98/2. The peaks at  $\delta$  15.7 and  $\delta$  22.5 in S9 were assigned as *cis*-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and *trans*-Pt(SC<sub>6</sub>H<sub>4</sub>-2-Cl)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, respectively. The ratio of *trans*-1h/*cis*-2a/*trans*-4h was 92/4/4. The peaks at  $\delta$  12.7 and  $\delta$  20.8 in S10 were assigned as *cis*-PtCl<sub>2</sub>[P(C<sub>6</sub>H<sub>4</sub>-4-OMe)<sub>3</sub>]<sub>2</sub> and *trans*-Pt(SC<sub>6</sub>H<sub>4</sub>-4-OMe)<sub>3</sub>]<sub>2</sub>, respectively. The ratio of *trans*-1l/*cis*-2c/*trans*-4l was 87/4/9.

















