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Experimental Section

General

Solvents were dried by standard procedures. IR spectra were recorded on a Bio-Rad FTS-40 spectrophotometer. The NMR spectra were recorded on Bruker AC-E200, Bruker ACE-300, or a Varian Unity 400 plus spectrometer. For the ^{31}P NMR spectra, the spectrometer frequency at 81.015, 121.496, or 161.897 MHz was employed, respectively, and chemical shifts are given in ppm (δ) relative to 85% H_3PO_4 in $CDCl_3$. Values upfield of the standard are defined as negative. Mass spectrometric analyses were collected on a JEOL SX-102A spectrometer. Elemental analyses were done on a Perkin-Elmer 2400 CHN analyzer.

Synthesis and Characterization

{Pt(PPh$_3$)$_2$[η^3-CH$_2$C(2-pyrrolyl)CH$_2$]}(BF$_4$) (2a). A two-necked round-bottomed flask was charged with [Pt(PPh$_3$)$_2$(η^3-C$_3$H$_3$)](BF$_4$) (51 mg, 0.059 mmol) and dry $CDCl_3$ (1 mL). Pyrrole (4 μL, 0.6 mmol) was injected into solution at 25 °C. The reaction solution was stirred in nitrogen atmosphere for 20 h. The conversion to **2a** was over 90% based on the NMR data. ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ 18.1 ($J_{P\text{-}Pt}$ = 3757 Hz); ^1H NMR ($CDCl_3$, 300 MHz) δ 2.68 (2H, dd, $J_{H\text{-}H}$ = 3.0 Hz, $J_{H\text{-}P}$ = 7.0 Hz, $J_{H\text{-}Pt}$ = 45 Hz, anti-H), 3.74 (2H, br, syn-H), 6.0 (1H, br, 3-H$_{py}$), 6.2 (1H, br, 4-H$_{py}$), 7.1-7.7 (31H, m, phenyl H & 5-H$_{py}$), 9.95 (1H, br, N<u>H</u>); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 58.6 (dd, $J_{C\text{-}P}$ = 3.8, 35.9 Hz, $J_{C\text{-}Pt}$ = 106 Hz, C_t), 110.5 ($J_{C\text{-}Pt}$ = 12.1 Hz, 4-C$_{py}$), 112.2 ($J_{C\text{-}Pt}$ = 23.8 Hz, 3-C$_{py}$), 125.6 (s, $J_{C\text{-}Pt}$ = 16 Hz, 5-C$_{py}$), 126.0 ($J_{C\text{-}Pt}$ = 38 Hz, C_c), 128.2 (s, 2-C$_{py}$), 128.6-133.6 (phenyl C).

{Pt(PPh$_3$)$_2$[η^3-CH$_2$C(2-N-methylpyrrolyl)CH$_2$]}(BF$_4$) (2b).

[Pt-(PPh$_3$)$_2$(η^3-C$_3$H$_3$)](BF$_4$) was prepared in situ with equimolar amount of *trans*-Pt(Br)(PPh$_3$)$_2$(η^1-CHCCH$_2$) (302 mg, 0.358 mmol) and AgBF$_4$ (70 mg, 0.358 mmol) in CH_2Cl_2 at -20 °C. After filtering off AgBr precipitate,

N-methylpyrrole (30 μL) was charged and the reaction was allowed to last for 3 h at 25 °C. Adding diethyl ether to the concentrated reaction solution gave the product in 81% yield. ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ 18.2 ($J_{P\text{-}Pt}$ = 3823 Hz); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.18 (2H, d, $J_{H\text{-}P}$ = 9.0 Hz, $J_{H\text{-}Pt}$ = 41.5 Hz, anti-H), 3.42 (3H, s, $NC\underline{H}_3$), 3.55 (2H, br, syn-H), 6.07 (1H, dd, $J_{H\text{-}H}$ = 2.0, 3.9 Hz, $J_{H\text{-}Pt}$ = 11 Hz, 4-H_{py}), 6.19 (1H, dd, $J_{H\text{-}H}$ = 2.6, 3.9 Hz, 3-H_{py}), 6.78 (1H, dd, $J_{H\text{-}H}$ = 2.0, 2.6 Hz, $J_{H\text{-}Pt}$ = 10.3 Hz, 5-H_{py}), 7.1-7.7 (30H, m, phenyl H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 36.3 (s, $N\underline{C}H_3$), 63.1 (dd, $J_{C\text{-}P}$ = 3.3, 34.5 Hz, $J_{C\text{-}Pt}$ = 100.4 Hz, C_t), 109.0 ($J_{C\text{-}Pt}$ = 10.1 Hz, 4-C_{py}), 113.8 ($J_{C\text{-}Pt}$ = 28 Hz, 3-C_{py}), 127.5-133.8 (phenyl C, C_c, and 2-C_{py}). Anal. Calcd for $PtC_{44}H_{40}NP_2BF_4$: C, 57.03; H, 4.35; N, 1.51. Found : C, 56.30; H, 4.21; N, 1.19.

{Pt(PPh$_3$)$_2$[η^3-CH$_2$C(3-indolyl)CH$_2$]}(BF$_4$) (3a). Refer to the preparation of **2b.** Complex **1** was prepared from *trans*-Pt(Br)(PPh$_3$)$_2$(η^1-CHCCH$_2$) (300 mg, 0.358 mmol) and $AgBF_4$ (78 mg, 0.401 mmol) and was allowed to react with indole (420 mg, 3.59 mmol) in CH_2Cl_2 at 25 °C for 7 h. The isolated yield was 286 mg (83%). ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ 18.8 ($J_{P\text{-}Pt}$ = 3803 Hz); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.85 (2H, dd, $J_{H\text{-}H}$ = 1.2 Hz, $J_{H\text{-}P}$ = 9.4 Hz, $J_{H\text{-}Pt}$ = 44.2 Hz, anti-H), 3.89 (2H, br, syn-H), 6.84-7.71 (35H, phenyl & indolyl H), 10.50 (1H, s, N$\underline{H}$); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 61.1 (d, $J_{C\text{-}P}$ = 31.9 Hz, C_t), 110.7, 113.5, 119.0, 121.1, 122.8, 124.2, 129.0, 137.4 ($C_{indolyl}$), 132 (C_c), 128-134 (phenyl C); MS (FAB, m/z): 876 (M^+-BF_4). Anal. Calcd for $PtC_{47}H_{40}NP_2BF_4$: C, 58.56; H, 4.19; N, 1.45. Found : C, 57.70; H, 4.28; N, 1.45.

{Pt(PPh$_3$)$_2$[η^3-CH$_2$C(2-(3-methylindolyl))CH$_2$]}(BF$_4$) (3b). Refer to the preparation of **3a**. Complex **1** prepared from *trans*-Pt(Br)(PPh$_3$)$_2$(η^1-CHCCH$_2$) (300 mg, 0.358 mmol) and $AgBF_4$ (78 mg, 0.401 mmol) reacted with 3-methylindole (920 mg, 7.02 mmol) in CH_2Cl_2 (15 mL) at 5 °C for 12 h gave **3b** in 78% yield (273 mg). ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ 17.9 ($J_{P\text{-}Pt}$

= 3835 Hz); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.08 (3H, Me)), 3.94 (2H, br, syn-H), 3.17 (2H, d, J_{H-H} unresolved, J_{H-P} = 9.0 Hz, J_{H-Pt} = 40.8 Hz, anti-H), 7.0-7.5 (34H, m, phenyl & indolyl H), 8.58 (1H, s, NH); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 10.4 (s, $\underline{C}H_3$), 63.6 (d, J_{C-P} = 29.5 Hz, C_t), 112.3, 115.5, 119.4, 119.8, 120.1, 136.6 (indole-C), 127.1 (*ipso*-C), 129-133 (phenyl C). MS (FAB, m/z): 890 (M^+-BF_4).

{Pt(PPh$_3$)$_2$[η^3-CH$_2$C(4-Me$_2$NC$_6$H$_4$)CH$_2$]}(BF$_4$) (4). Refer to the preparation of **3a**. Complex **1** prepared from *trans*-Pt(Br)(PPh$_3$)$_2$(η^1-CHCCH$_2$) (300 mg, 0.358 mmol) and $AgBF_4$ (78 mg, 0.401 mmol) reacted with $PhNMe_2$ (866 mg, 7.16 mmol) in CH_2Cl_2 (15 mL) at 5 °C for 24 h gave **4** in 50% yield (173 mg). ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ 18.5 (J_{P-Pt} = 3799 Hz); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.94 (2H, dd, J_{H-H} = 3.8 Hz, J_{H-P} = 9.2 Hz, J_{H-Pt} = 37.1 Hz, anti-H), 3.10 (6H, s, $C\underline{H}_3$), 3.73 (2H, br, syn-H), 6.64 (2H, d, J_{H-H} = 8.8 Hz, *o*-phenyl), 7.0-7.4 (32H, m, phenyl & *o*-aryl H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 40.1 (s, $\underline{C}H_3$), 61.6 (d, J_{C-P} = 30.4 Hz, C_t), 111.6 (*o*-aryl C), 120.7 (*ipso*-C), 128-134 (phenyl C), 152.5 (N$\underline{C}$); MS (FAB, m/z) 854 (M^+-BF_4). Anal. Calcd for $PtC_{47}H_{44}NP_2BF_4 \cdot 0.5CH_2Cl_2$: C, 56.46; H, 4.46; N, 1.39. Found : C, 56.87; H, 4.44; N, 1.23.

{Pt(PPh$_3$)$_2$[η^3-CH$_2$C(2,4-(MeO)$_2$C$_6$H$_3$)CH$_2$]}(BF$_4$) (5). Refer to the preparation of **3a**. Complex **1** prepared from *trans*-Pt(Br)(PPh$_3$)$_2$(η^1-CHCCH$_2$) (300 mg, 0.358 mmol) and $AgBF_4$ (78 mg, 0.401 mmol) reacted with 1,3-$(MeO)_2C_6H_4$ (1 mL, 7.25 mmol) in CH_2Cl_2 (15 mL) at 5 °C for 3 days gave **5** in 83% yield (292 mg). ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ 19.2 (J_{P-Pt} = 3875 Hz); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.07 (2H, d, J_{H-P} = 8.3 Hz, J_{H-Pt} = 39.3 Hz, anti-H), 3.49 (3H, s, $OC\underline{H}_3$), 3.91 (3H, s, $OC\underline{H}_3$), 4.03 (2H, br, syn-H), 6.45 (1H, dd, J_{H-H} = 1.9, 8.7 Hz, *m*-C$\underline{H}$), 6.54 (1H, d, J_{H-H} = 1.9 Hz, *m*-C$\underline{H}$), 7.0-7.4 (31H, m, phenyl & *o*-aryl H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 55.6, 55.9 (s, s, $OC\underline{H}_3$), 66.8 (dd, J_{C-P} = 3.8, 32.6 Hz, J_{C-Pt} = 85.0 Hz, C_t), 98.8, 105.8 (s, s, *m*-$\underline{C}$H), 115.6 (s, *ipso*-C), 133.9 (s, C_c), 129-134

(phosphino phenyl C), 159.3 ($J_{C\text{-}Pt}$ = 16.7 Hz, *o*-C), 163.3 ($J_{C\text{-}Pt}$ = 9.1 Hz, *p*-C). MS (FAB, m/z): 896 (M^+-BF_4).

{Pt(PPh$_3$)$_2$[η^3-CH$_2$C(2,4,6-(MeO)$_3$C$_6$H$_2$)CH$_2$]}(BF$_4$) (6). Refer to the preparation of **3a**. Complex **1** prepared from *trans*-Pt(Br)(PPh$_3$)$_2$(η^1-CHCCH$_2$) (300 mg, 0.358 mmol) and $AgBF_4$ (78 mg, 0.401 mmol) reacted with 1,3,5-$(MeO)_3C_6H_3$ (1.2 g, 7.15 mmol) in CH_2Cl_2 (15 mL) at 5 °C for 24 h gave **6** in 84% yield (305 mg). ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ 19.1 ($J_{P\text{-}Pt}$ = 3912 Hz); ^1H NMR ($CDCl_3$, 300 MHz) δ 3.12 (2H, d, $J_{H\text{-}P}$ = 8.3 Hz, $J_{H\text{-}Pt}$ = 40.7 Hz, anti-H), 3.47 (6H, s, *o*-OC<u>H</u>$_3$), 3.92 (3H, s, *p*-OC<u>H</u>$_3$), 4.08 (2H, br, syn-H), 6.19 (2H, s, *m*-C<u>H</u>), 7.1-7.3 (30H, m, phenyl H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 55.8, 56.0 (s, s, O<u>C</u>H$_3$), 69.7 (d, $J_{C\text{-}P}$ = 29.6 Hz, $J_{C\text{-}Pt}$ = 89.5 Hz, C_t), 91.1 (s, *m*-C), 104.1 ($J_{C\text{-}Pt}$ = 17.5 Hz, *ipso*-C), 133 (s, C_c), 129-134 (phosphino phenyl C), 160.1 ($J_{C\text{-}Pt}$ = 19.0 Hz, *o*-C), 163.0 (s, *p*-C). MS (FAB, m/z): 927 (M^+-BF_4).

2-(2',4',6'-trimethoxyphenyl)propene

CH$_2$=C[2',4',6'-(MeO)$_3$C$_6$H$_2$]CH$_3$ (7a).

Compound **7a** was resulted from the reaction of **6** (30 mg, 0.03 mmol) and Bu_4NBH_4 (15 mg, 0.06 mmol) in $CDCl_3$ for 1 day. The yield was 60% based on the NMR data. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.99 (3H, dd, $J_{H\text{-}H}$ = 0.7, 1.4 Hz, C<u>H</u>$_3$), 3.81 (3H, s, OC<u>H</u>$_3$), 3.87 (6H, s, OC<u>H</u>$_3$), 4.84 (1H, dt, $J_{H\text{-}H}$ = 0.7, 2.5 Hz, =C<u>H</u>$_2$), 5.30 (1H, dt, $J_{H\text{-}H}$ = 1.4, 2.5 Hz, =C<u>H</u>$_2$), 6.15 (2H, *m*-C<u>H</u>); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 23.7 (<u>C</u>H$_3$), 55.3, 55.9 (O<u>C</u>H$_3$), 90.8 (*m*-C), 116.0 (=<u>C</u>H$_2$), 139.1 (Ar-<u>C</u>), 157.8 (*o*-C), 160.0 (*p*-C); HRMS: calcd for $C_{12}H_{16}O_3S$ (M^+) 208.1099, found 208.1090.

(3-phenylthio)-2-(2',4',6'-trimethoxyphenyl)-propene

CH$_2$=C[2',4',6'-(MeO)$_3$C$_6$H$_2$]CH$_2$(SPh) (7b).

Compound **7c** was resulted from the reaction of **6** (30 mg, 0.03 mmol) and NaSPh (12 mg, 0.09 mmol) in $CDCl_3$ for 3 days. The yield was 58% based on the NMR data. ^1H NMR ($CDCl_3$, 300 MHz) δ 3.73 (6H, s, OC<u>H</u>$_3$), 3.80 (3H,

s, OC$\underline{H}_3$), 3.83 (2H, dd, J_{H-H} = 0.9, 1.4 Hz, C$\underline{H}_2$), 5.05 (1H, dt, J_{H-H} = 0.9, 1.7 Hz, =C$\underline{H}_2$), 5.57 (1H, dt, J_{H-H} = 1.4, 1.7 Hz, =C$\underline{H}_2$), 6.12 (2H, *m*-C$\underline{H}$); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 39.6 ($\underline{C}H_2$), 55.3, 55.7 (O$\underline{C}H_3$), 90.7 (*m*-C), 118.2 (=$\underline{C}H_2$), 137.7 (Ar-$\underline{C}$), 158.4 (*o*-C), 160.5 (*p*-C); HRMS: calcd for $C_{18}H_{20}O_3S$ (M^+) 316.1133, found 316.1136.

4,4-bis(phenylsulfonyl)-2-(2',4',6'-trimethoxyphenyl)-1-butene CH_2=C[2',4',6'-(MeO)$_3C_6H_2$]$CH_2CH(SO_2Ph)_2$ (7c).

Refer to the preparation of **7b**. The yield was 34% based on the NMR data. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.20 (2H, d, J_{H-H} = 4.5 Hz, C$\underline{H}_2$), 3.67 (6H, s, OC$\underline{H}_3$), 3.79 (3H, s, OC$\underline{H}_3$), 4.53 (1H, t, J_{H-H} = 4.5 Hz, C$\underline{H}$), 4.86, 5.20 (1H, 1H, d, d, J_{H-H} = 1.2 Hz, =C$\underline{H}_2$), 5.98 (2H, *m*-C$\underline{H}$); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 29.7 ($\underline{C}H_2$), 55.3, 55.7 (O$\underline{C}H_3$), 80.0 ($\underline{C}$H), 90.7 (*m*-C), 113.5 (=$\underline{C}H_2$), 120.3 (*ipso*-C), 138.6 (Ar-$\underline{C}$), 158.2 (*o*-C), 160.8 (*p*-C); HRMS: calcd for $C_{25}H_{26}O_7S_2$ (M^+) 502.1120, found 502.1087.

Crossover Labeling Experiment.

Comlpex **1** prepared from the reaction of *trans*-Pt(PPh_3)$_2$(η^1-C_3H_3)(Br) (100 mg, 0.119 mmol) and $AgBF_4$ (26 mg, 0.13 mmol) in CH_2Cl_2 at -20 °C, reacted with a mixture of 1,3,5-(MeO)$_3C_6H_3$ (200 mg, 1.19 mmol) and 1,3,5-(MeO)$_3C_6D_3$/-1,3,5-(MeO)$_3C_6D_2H$ (d_3:d_2 = 78:22, 204 mg, 1.19 mmol) at 5 °C for 1 day. The deuterium-labeled complex **6'** was precipitated by adding diethylether to the concentrated reaction solution. The integrations of the ^{1}H NMR resonances for **6'** are: δ 3.12 (2H, 7.05), δ 3.47 (6H, 23.8), δ 3.92 (3H, 10.8), δ 4.08 (2H, 6.92), δ 6.19 (2H, 4.01).

The reaction of **6'** (50 mg, 0.05 mmol) and NaSPh (20 mg, 0.15 mmol) was stirred in $CDCl_3$ at 25 °C for 3 days to gave deuterated products of **7b**. In the ^{1}H NMR spectra, the deuterium was found at δ 3.83, 5.05, 5.57, and

6.12. The HRMS showed the relative intensities for M(316.1141):M+1-(317.1196):M+2(318.1264):M+3(319.1307) = 24:31:34:12. **7b** contains 18 carbon atoms. The data is then calibrated with the ^{13}C abundance. The ratio of M:M+1:M+2:M+3 becomes 28:31:34:7. The starting labeling ratio for 1,3,5-trimethoxybenzene is d_0:d_2:d_3 = 50:11:39. The labeling ratio would be exactly the same, if the reaction of **1** and arene underwent an intramolecular process. Without considering the primary isotope effect, the data with full deuterium scrambling could be calculated.

$d_0 = (50)(11/3 + 50) = 26.8$

$d_1 = (50)(11x2/3 + 39) + (11x/3 + 50)(11x2/3) = 27.1$

$d_2 = (39+11x2/3)(11x2/3) + (11/3 + 50)(11/3 + 39) = 26.3$

$d_3 = (39+11/3)(11x2/3 + 39) = 19.8$

These experimental data match with an intermolecular process.