Synthesis of New Pro-PYE Ligands as Co-Catalysts toward Pd-Catalyzed Heck-Mizoroki Cross Coupling Reactions

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Figure S1: $^1$H, $^{13}$CNMR, IR spectra of [H$_2$L]$^1$][OTf]$_2$
Figure S2: $^1$H, $^{13}$CNMR, IR spectra and HOMO-LUMO of [H$_2$L$^2$][OTf]$_2$
### Bond angles

| Concerned Atoms | Experimental | Calculated | Concerned Atoms | Experimental | Calculated |
|-----------------|--------------|------------|-----------------|--------------|------------|
| C1-N1-C2        | 123.0        | 124.9      | O1-S1-O3        | 114.8        | 113.2      |
| N1-C2-C3        | 123.6        | 122.9      | O2-S1-O1        | 114.3        | 113.8      |
| C2-C3-C4        | 120.6        | 121.4      | O3-S1-O2        | 115.3        | 105.1      |
| C3-C4-C5        | 119.8        | 119.5      | O1-S1-C8        | 103.7        | 106.2      |
| C4-C5-C6        | 119.0        | 118.7      | O3-S1-C8        | 103.8        | 106.5      |
| C5-C6-N2        | 121.7        | 122.0      | O2-S1-C8        | 102.7        | 106.4      |
| C6-N2-C7        | 119.4        | 117.2      | F3-C8-F1        | 107.1        | 110.1      |
| C6-N2-C2        | 120.8        | 121.5      | F2-C8-F3        | 106.0        | 111.3      |
| N2-C2-C3        | 118.0        | 117.0      | F1-C8-F2        | 105.1        | 109.5      |
| C7-N2-C2        | 119.7        | 121.2      | F2-C8-S1        | 112.0        | 106.0      |
| N2-C2-N1        | 118.4        | 120.1      | F3-C8-S1        | 111.8        | 108.5      |

**Figure S3:** $^1$H, $^{13}$CNMR, IR spectra, HOMO-LUMO and bond angles of [H$_2$L$_3$][OTf]$_2$
HOMO (Gaussian)                    LUMO (Gaussian)

Bond angles

| Atom no's | Experimental | Calculated | Atom no's | Experimental | Calculated |
|-----------|--------------|------------|-----------|--------------|-----------|
| C1-N1     | 1.46         | 1.49       | O1-S1     | 1.43         | 1.47      |
| N1-C2     | 1.34         | 1.39       | O2-S1     | 1.43         | 1.39      |
| C2-C3     | 1.40         | 1.41       | S1-C8     | 1.82         | 1.82      |
| C3-C4     | 1.36         | 1.39       | F3-C8     | 1.31         | 1.37      |
| C4-C5     | 1.39         | 1.38       | F1-C8     | 1.33         | 1.36      |
| C5-C6     | 1.34         | 1.38       | F2-C8     | 1.32         | 1.36      |
| C6-N2     | 1.36         | 1.35       | C1-C1     | 1.51         | 2.19      |
| N2-C7     | 1.46         | 1.48       | N2-C2     | 1.36         | 1.38      |
| N2-C2     | 1.36         | 1.38       | O3-S1     | 1.42         | 1.47      |
| O3-S1     | 1.42         | 1.47       | O1-S1     | 1.43         | 1.47      |

Figure S4: $^1$H, $^{13}$CNMR, IR spectra, HOMO-LUMO & bond angles of [H$_2$L$_4$][OTf]$_2$
**Bond angles**

| Concerned Atoms | Experimental | Calculated |
|-----------------|--------------|------------|
| C1-N1-C2        | 123.7        | 122.9      |
| N1-C2-C3        | 123.5        | 121.7      |
| C2-C3-C4        | 121.2        | 121.4      |
| C3-C4-C5        | 119.6        | 119.3      |
| C4-C5-C6        | 119.0        | 118.8      |
| C5-C6-N2        | 122.7        | 122.1      |
| C6-N2-C2        | 120.0        | 121.2      |
| N2-C2-C3        | 117.4        | 117.3      |
| N2-C2-N1        | 119.1        | 121.0      |
| C6-N2-C7        | 120.1        | 116.9      |
| N2-C7-C8        | 110.0        | 109.5      |

**Figure S5:** $^1$H, $^{13}$CNMR, IR spectra, HOMO-LUMO and bond angles of [H$_2$L$_5$][I]$_2$
### Bond angles

| Concerned Atoms | Experimental | Calculated | Concerned Atoms | Experimental | Calculated |
|-----------------|--------------|------------|----------------|--------------|------------|
| Cl₁-C₁-N₁      | 117.5        | 117.4      | H6B-C₆-H₆C     | 109.5        | 109.5      |
| C₆-N₁-C₅       | 118.7        | 118.8      | H6B-C₆-H₆A     | 109.5        | 109.5      |
| C₁-N₁-C₆       | 119.3        | 120.3      | H₆A-C₆-H₆C     | 109.5        | 109.5      |
| C₆-C₅-N₁       | 121.9        | 120.6      | H₆C-C₆-N₁      | 109.5        | 109.5      |
| N₁-C₁-C₂       | 121.2        | 119.6      | H₆A-C₆-N₁      | 109.5        | 109.5      |
| C₅-C₄-C₃       | 119.4        | 119.0      | F₁-C₇-S₁       | 112.0        | 111.9      |
| C₄-C₃-C₂       | 119.7        | 119.5      | F₃-C₇-S₁       | 111.4        | 111.6      |
| C₃-C₂-C₁       | 119.0        | 119.0      | O₂-S₁-O₁       | 114.0        | 113.9      |

![Infrared spectra](image_url)
| Concerned Atoms | Experimental | Calculated |
|----------------|--------------|------------|
| Cl1-C1-C2      | 121.3        | 118.1      |
| C7-S1-O2       | 103.3        | 106.4      |
| C7-S1-O3       | 103.4        | 106.5      |
| C7-S1-O1       | 103.1        | 106.4      |
| F1-C7-F3       | 108.4        | 112.5      |
| F3-C7-F2       | 109.6        | 113.4      |
| F1-C7-F2       | 106.5        | 105.7      |
| F2-C7-S1       | 112.6        | 107.6      |
| O2-S1-O3       | 115.6        | 114.5      |

**Bond lengths**

**Figure S6:** ¹H, ¹³C NMR, IR, bond lengths and bond angles of [P₂Me₂][CF₃SO₃]
### Bond angles

| Concerned Atoms | Experimental | Calculated | Concerned Atoms | Experimental | Calculated |
|-----------------|--------------|------------|-----------------|--------------|------------|
| C5-C4-C3        | 114.5        | 119.2      | C4-C5-H5        | 114.2        | 114.1      |
| C4-C3-C2        | 113.7        | 119.2      | N1-C6-H6A       | 110.0        | 109.1      |
| C3-C2-C1        | 130.6        | 120.3      | N1-C6-H6B       | 109.9        | 108.7      |
| I1-C1-N1        | 117.7        | 125.5      | N1-C6-C7        | 109.1        | 108.3      |
| N1-C5-C4        | 131.5        | 121.6      | H6A-C6-H6B      | 108.2        | 107.8      |
| I1-C1-C2        | 127.7        | 115.1      | H6A-C6-C7       | 109.9        | 108.9      |
| N1-C6-C7        | 109.1        | 109.8      | H6B-C6-C7       | 109.8        | 108.9      |
| C1-N1-C6        | 114.7        | 115.4      | C6-C7-H7A       | 109.5        | 108.7      |
| C5-N1-C6        | 130.1        | 131.0      | C6-C7-H7B       | 109.5        | 108.7      |
| Concerned Atoms | Experimental values | Computed values | Concerned Atoms | Experimental values | Computed values |
|----------------|---------------------|----------------|----------------|---------------------|----------------|
| C1-I1-I2       | 177.5               | 178.4          | C6-C7-H7C      | 109.5              | 108.7          |
| C1-C2-H2       | 114.6               | 114.5          | H7A-C7-H7B     | 109.5              | 108.7          |
| H2-C2-C3       | 114.8               | 113.9          | N1-C1-C2       | 114.6              | 114.4          |
| C2-C3-H3       | 123.1               | 122.4          | H7A-C7-H7C     | 109.5              | 108.9          |
| H3-C3-C4       | 123.2               | 122.5          | H7B-C7-H7C     | 109.4              | 108.9          |

**Bond lengths**

**Figure S7:** $^1$H, $^{13}$CNMR, IR spectra, HOMO LUMO, bond lengths and bond angles of $[P_{3}^{3}E_{3}][I]$.

**Table 1: Crystal structure Data of S3**

Table 1: Crystal data and structure refinement for a.

- **Identification code**: 8A
- **Empirical formula**: C10 H13 F3 N2 O3 S
- **Formula weight**: 298.28
- **Temperature**: 100(2) K
- **Wavelength**: 1.54178 Å
Crystal system  Orthorhombic

Space group  Pbcn

Unit cell dimensions  
\[ a = 15.5634(3) \text{ Å} \quad \alpha = 90^\circ. \]
\[ b = 12.4382(2) \text{ Å} \quad \beta = 90^\circ. \]
\[ c = 12.8282(3) \text{ Å} \quad \gamma = 90^\circ. \]

Volume  2483.29(9) Å³

Z  8

Density (calculated)  1.596 Mg/m³

Absorption coefficient  2.780 mm⁻¹

F(000)  1232

Crystal size  0.170 x 0.050 x 0.040 mm³

Theta range for data collection  4.551 to 68.305°.

Index ranges  
\[-18 \leq h \leq 18, \quad -14 \leq k \leq 14, \quad -15 \leq l \leq 15 \]

Reflections collected  36806

Independent reflections  2282 [R(int) = 0.0771]

Completeness to theta = 67.679°  100.0 %

Refinement method  Full-matrix least-squares on F²

Data / restraints / parameters  2282 / 0 / 177

Goodness-of-fit on F²  1.049

Final R indices [I>2sigma(I)]  
R1 = 0.0580, wR2 = 0.1377

R indices (all data)  
R1 = 0.0684, wR2 = 0.1446

Extinction coefficient  n/a

Largest diff. peak and hole  1.159 and -0.746 e.Å⁻³

Atomic coordinates ( x 10⁴) and equivalent isotropic displacement parameters (Å² x 10⁴)

for a. U(eq) is defined as one third of the trace of the orthogonalized Uᵢⱼ tensor.
|     | x      | y      | z      | U(eq) |
|-----|--------|--------|--------|-------|
| S(1)| 2443(1)| 6040(1)| 5767(1)| 17(1) |
| F(1)| 894(2) | 5291(2)| 5554(4)| 104(2)|
| F(2)| 1788(1)| 4081(2)| 5875(2)| 32(1) |
| F(3)| 1746(3)| 4798(3)| 4369(2)| 99(2) |
| O(1)| 2345(2)| 6101(2)| 6870(2)| 50(1) |
| O(2)| 3253(2)| 5576(2)| 5474(3)| 46(1) |
| O(3)| 2196(2)| 6945(2)| 5156(2)| 32(1) |
| N(1)| 4128(2)| 4665(2)| 2998(2)| 14(1) |
| N(2)| 3768(2)| 6459(2)| 3240(2)| 16(1) |
| C(1)| 3932(2)| 7474(3)| 3596(3)| 23(1) |
| C(2)| 4672(2)| 7707(3)| 4100(3)| 27(1) |
| C(3)| 5262(2)| 6879(3)| 4275(2)| 21(1) |
| C(4)| 5089(2)| 5857(3)| 3949(2)| 16(1) |
| C(5)| 4325(2)| 5635(2)| 3398(2)| 13(1) |
| C(6)| 2971(2)| 6281(3)| 2649(3)| 22(1) |
| C(7)| 4699(2)| 3727(2)| 2979(2)| 13(1) |
| C(8)| 4142(2)| 2714(2)| 2962(3)| 17(1) |
| C(9)| 4689(2)| 1693(3)| 2960(3)| 21(1) |
| C(10)|1688(2)| 4992(3)| 5367(3)| 28(1)|

Bond lengths [Å] and angles [Å°] for a.

S(1)-O(3) 1.425(3)
| Bond                    | Length  |
|------------------------|---------|
| S(1)-O(1)              | 1.426(3) |
| S(1)-O(2)              | 1.437(3) |
| S(1)-C(10)             | 1.828(4) |
| F(1)-C(10)             | 1.313(5) |
| F(2)-C(10)             | 1.315(4) |
| F(3)-C(10)             | 1.306(5) |
| N(1)-C(5)              | 1.346(4) |
| N(1)-C(7)              | 1.468(4) |
| N(1)-H(5)              | 0.84(4)  |
| N(2)-C(5)              | 1.358(4) |
| N(2)-C(1)              | 1.367(4) |
| N(2)-C(6)              | 1.470(4) |
| C(1)-C(2)              | 1.352(5) |
| C(1)-H(1)              | 0.9500   |
| C(2)-C(3)              | 1.398(5) |
| C(2)-H(2)              | 0.9500   |
| C(3)-C(4)              | 1.366(5) |
| C(3)-H(3)              | 0.9500   |
| C(4)-C(5)              | 1.412(4) |
| C(4)-H(4)              | 0.9500   |
| C(6)-H(6A)             | 0.9800   |
| C(6)-H(6B)             | 0.9800   |
| C(6)-H(6C)             | 0.9800   |
| C(7)-C(8)              | 1.529(4) |
| C(7)-C(7)#1            | 1.546(6) |
| Bond/Angle                                      | Distance/Value |
|------------------------------------------------|----------------|
| C(7)-H(7)                                      | 1.0000         |
| C(8)-C(9)                                      | 1.528(4)       |
| C(8)-H(8A)                                     | 0.9900         |
| C(8)-H(8B)                                     | 0.9900         |
| C(9)-C(9)#1                                    | 1.526(7)       |
| C(9)-H(9A)                                     | 0.9900         |
| C(9)-H(9B)                                     | 0.9900         |
| O(3)-S(1)-O(1)                                 | 118.35(19)     |
| O(3)-S(1)-O(2)                                 | 114.25(18)     |
| O(1)-S(1)-O(2)                                 | 112.0(2)       |
| O(3)-S(1)-C(10)                                | 103.68(16)     |
| O(1)-S(1)-C(10)                                | 104.37(18)     |
| O(2)-S(1)-C(10)                                | 101.78(18)     |
| C(5)-N(1)-C(7)                                 | 125.5(3)       |
| C(5)-N(1)-H(5)                                 | 121(3)         |
| C(7)-N(1)-H(5)                                 | 113(3)         |
| C(5)-N(2)-C(1)                                 | 121.9(3)       |
| C(5)-N(2)-C(6)                                 | 120.1(3)       |
| C(1)-N(2)-C(6)                                 | 118.0(3)       |
| C(2)-C(1)-N(2)                                 | 121.2(3)       |
| C(2)-C(1)-H(1)                                 | 119.4          |
| N(2)-C(1)-H(1)                                 | 119.4          |
| C(1)-C(2)-C(3)                                 | 118.6(3)       |
| C(1)-C(2)-H(2)                                 | 120.7          |
C(3)-C(2)-H(2) 120.7
C(4)-C(3)-C(2) 120.5(3)
C(4)-C(3)-H(3) 119.8
C(2)-C(3)-H(3) 119.8
C(3)-C(4)-C(5) 120.1(3)
C(3)-C(4)-H(4) 119.9
C(5)-C(4)-H(4) 119.9
N(1)-C(5)-N(2) 118.3(3)
N(1)-C(5)-C(4) 123.9(3)
N(2)-C(5)-C(4) 117.7(3)
N(2)-C(6)-H(6A) 109.5
N(2)-C(6)-H(6B) 109.5
H(6A)-C(6)-H(6B) 109.5
N(2)-C(6)-H(6C) 109.5
H(6A)-C(6)-H(6C) 109.5
H(6B)-C(6)-H(6C) 109.5
N(1)-C(7)-C(8) 108.2(2)
N(1)-C(7)-C(7)#1 112.4(2)
C(8)-C(7)-C(7)#1 109.4(2)
N(1)-C(7)-H(7) 109.0
C(8)-C(7)-H(7) 109.0
C(7)#1-C(7)-H(7) 109.0
C(9)-C(8)-C(7) 111.7(3)
C(9)-C(8)-H(8A) 109.3
C(7)-C(8)-H(8A) 109.3
C(9)-C(8)-H(8B) 109.3
C(7)-C(8)-H(8B) 109.3
H(8A)-C(8)-H(8B) 107.9
C(9)#1-C(9)-C(8) 110.8(2)
C(9)#1-C(9)-H(9A) 109.5
C(8)-C(9)-H(9A) 109.5
C(9)#1-C(9)-H(9B) 109.5
C(8)-C(9)-H(9B) 109.5
H(9A)-C(9)-H(9B) 108.1
F(3)-C(10)-F(1) 107.2(4)
F(3)-C(10)-F(2) 108.6(3)
F(1)-C(10)-F(2) 105.4(3)
F(3)-C(10)-S(1) 111.3(3)
F(1)-C(10)-S(1) 110.6(3)
F(2)-C(10)-S(1) 113.5(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2

Anisotropic displacement parameters (Å² x 10⁹) for a. The anisotropic displacement factor exponent takes the form: -2π²[ h²a*²U¹¹ + ... + 2 h k a* b* U¹² ]

|       | U¹¹  | U²²  | U³³  | U¹²  | U¹³  | U¹²  |
|-------|------|------|------|------|------|------|
| S(1)  | 16(1)| 15(1)| 21(1)| 0(1) | -3(1)| -1(1)|
| F(1)  | 19(1)| 34(2)| 257(6)| 23(2)| -33(2)| -4(1)|
| Atom | x   | y   | z   | U(eq) |
|------|-----|-----|-----|-------|
| F(2) | 33(1) | 20(1) | 42(1) | 9(1) | -14(1) | -6(1) |
| F(3) | 32(2) | 30(2) | 27(2) | 2(1) | -28(2) | -83(3) |
| O(1) | 11(1) | 11(2) | 11(1) | 11(2) | -22(2) |
| O(2) | 11(1) | 11(2) | 11(1) | 11(2) | -22(2) |
| O(3) | 11(1) | 11(2) | 11(1) | 11(2) | -22(2) |
| N(1) | 11(1) | 11(2) | 11(1) | 11(2) | -22(2) |
| N(2) | 11(1) | 11(2) | 11(1) | 11(2) | -22(2) |
| C(1) | 11(1) | 11(2) | 11(1) | 11(2) | -22(2) |
| C(2) | 11(1) | 11(2) | 11(1) | 11(2) | -22(2) |
| C(3) | 11(1) | 11(2) | 11(1) | 11(2) | -22(2) |
| C(4) | 11(1) | 11(2) | 11(1) | 11(2) | -22(2) |
| C(5) | 11(1) | 11(2) | 11(1) | 11(2) | -22(2) |
| C(6) | 11(1) | 11(2) | 11(1) | 11(2) | -22(2) |
| C(7) | 11(1) | 11(2) | 11(1) | 11(2) | -22(2) |
| C(8) | 11(1) | 11(2) | 11(1) | 11(2) | -22(2) |
| C(9) | 11(1) | 11(2) | 11(1) | 11(2) | -22(2) |
| C(10) | 11(1) | 11(2) | 11(1) | 11(2) | -22(2) |

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for a.
|       |       |       |       |     |
|-------|-------|-------|-------|-----|
| H(3)  | 5787  | 7029  | 4623  | 25  |
| H(4)  | 5484  | 5294  | 4094  | 19  |
| H(6A) | 3111  | 6002  | 1955  | 32  |
| H(6B) | 2660  | 6962  | 2580  | 32  |
| H(6C) | 2611  | 5759  | 3019  | 32  |
| H(7)  | 5056  | 3725  | 3628  | 15  |
| H(8A) | 3762  | 2710  | 3581  | 20  |
| H(8B) | 3774  | 2723  | 2333  | 20  |
| H(9A) | 5016  | 1646  | 3620  | 25  |
| H(9B) | 4309  | 1056  | 2915  | 25  |
| H(5)  | 3670  | 4570  | 2660  | 24(10) |

Torsion angles [Å°] for a.

| Torsion Angle                  | Value   |
|--------------------------------|---------|
| C(5)-N(2)-C(1)-C(2)           | 1.8(5)  |
| C(6)-N(2)-C(1)-C(2)           | -176.7(3) |
| N(2)-C(1)-C(2)-C(3)           | -1.6(5)  |
| C(1)-C(2)-C(3)-C(4)           | -0.5(5)  |
| C(2)-C(3)-C(4)-C(5)           | 2.3(5)   |
| C(7)-N(1)-C(5)-N(2)           | 171.9(3) |
| C(7)-N(1)-C(5)-C(4)           | -6.3(5)  |
| C(1)-N(2)-C(5)-N(1)           | -178.2(3) |
| C(6)-N(2)-C(5)-N(1)           | 0.3(4)   |
| C(1)-N(2)-C(5)-C(4)           | 0.0(4)   |
| C(6)-N(2)-C(5)-C(4)           | 178.6(3) |
| C(3)-C(4)-C(5)-N(1)           | 176.1(3) |
C(3)-C(4)-C(5)-N(2)  -2.1(4)  
C(5)-N(1)-C(7)-C(8)  153.4(3)  
C(5)-N(1)-C(7)-C(7)#1  85.7(4)  
N(1)-C(7)-C(8)-C(9)  -179.1(3)  
C(7)#1-C(7)-C(8)-C(9)  58.3(4)  
C(7)-C(8)-C(9)-C(9)#1  -56.5(4)  
O(3)-S(1)-C(10)-F(3)  59.4(4)  
O(1)-S(1)-C(10)-F(3)  -176.1(3)  
O(2)-S(1)-C(10)-F(3)  -59.5(4)  
O(3)-S(1)-C(10)-F(1)  -59.6(4)  
O(1)-S(1)-C(10)-F(1)  64.9(4)  
O(2)-S(1)-C(10)-F(1)  -178.4(3)  
O(3)-S(1)-C(10)-F(2)  -177.8(3)  
O(1)-S(1)-C(10)-F(2)  -53.2(3)  
O(2)-S(1)-C(10)-F(2)  63.4(3)  

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2

Hydrogen bonds for a [Å and °].

| D-H...A   | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|-----------|--------|----------|----------|--------|
| C(1)-H(1)...F(3)#2 | 0.95   | 2.51     | 3.233(4) | 132.7  |
| C(2)-H(2)...F(1)#3 | 0.95   | 2.36     | 3.165(5) | 142.4  |
| C(4)-H(4)...O(2)#4 | 0.95   | 2.31     | 3.221(4) | 160.4  |
|                  | d   | r   | D(μm)     | ϕ   |
|------------------|-----|-----|-----------|-----|
| C(6)-H(6B)...O(1) | 0.98| 2.58| 3.442(5)  | 147.4 |
| C(6)-H(6C)...F(3) | 0.98| 2.50| 3.450(5)  | 163.9 |
| N(1)-H(5)...O(1) | 0.84(4)| 2.45(4)| 3.271(5) | 167(4) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2
#2 -x+1/2,y+1/2,z
#3 x+1/2,-y+3/2,-z+1
#4 -x+1,-y+1,-z+1
#5 -x+1/2,-y+3/2,z-1/2
#6 x,-y+1,z-1/2