**Well-Defined, Air-Stable (NHC)Pd(allyl)Cl (NHC= N-Heterocyclic Carbene)
Catalysts for the Arylation of Ketone**

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Supporting Information

- **General Considerations:** All aryl halides and ketones were used distilled over MgSO_4 (Aldrich). THF (Aldrich) was dried and distilled over Na/benzophenone. NaO^tBu (Aldrich) was sublimed in a cold finger apparatus and was stored in a MBraun glovebox. Palladium chloride was purchased from Strem Chemical Company. Allyl chloride (Aldrich) was used as received. Flash chromatography was performed on silica gel 60 (320-400 mesh) with hexanes/ethyl acetate or hexanes/THF.
- The imidazolium salts: IPrHCl , SIPrHCl , I^tBuHCl and IMesHCl and corresponding carbenes were synthesized according to literature procedures.¹
- ^1H and ^{13}C NMR spectra were recorded on Varian-300 or Varian-400 MHz spectrometer at room temperature. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and dried with appropriate drying agents prior to use.
- Elemental analysis was performed by Desert Analysis, Tucson, AZ.
- Reactions were performed in oven dried, screw cap vials with magnetic stirring, under argon atmosphere. The septa were used to prevent solvent evaporation.
- All reported yields are isolated yields and are the average of two runs.

(SIPr)Pd(Cl)allyl (2): SIPr carbene (2 mmol, 780 mg) and $[\text{Pd}(\text{allyl})\text{Cl}]_2$ (1 mmol, 365.8 mg) were mixed together in a Schlenk tube in the drybox. Dry THF (20 ml) was added by cannula and stirred at room temperature for 30 min. THF was removed in vacuum and 40

ml of anhydrous hexane was added to precipitate the product. The product was filtered in air and washed with hexane. Yield 96% (1.10 g)

¹H-NMR(400MHz CDCl₃): 7.35(t, 2H), 7.26 (d., 2H), 7.20(overlapped with solvent, 2H), 4.75 (m, 1H), 4.0-4.07(m, 4H), 3.88 (dd, 1H), 3.39-3.54 (m, 4H), 3.01 (d, 1H), 2.73 (d, 1H), 1.55 (s, 1H), 1.46(d, 6H), 1.36(d, 6H), 1.28(d, 6H), 1.24(d, 6H).

¹³C-NMR (400MHz C₆D₆): 24.21, 24.39, 26.95, 29.03, 29.14, 50.02, 54.32, 72.74, 109.90, 114.55, 124.87, 129.74, 137.26, 147.89, 148.14, 215.38.

Elemental analysis:

Anal. Calcd.: C, 62.80, H, 7.51, N, 4.89.

Found: C, 62.61; H, 7.51; N, 5.13.

Reaction Procedure for α -Arylation of Ketone: In a typical procedure, a reaction vial containing a magnetic stirring bar was loaded inside the drybox with 4 ml dry THF, 100 mg NaO^tBu and 5.6mg (SIPr)Pd(allyl)Cl. The ketone (1.0 mmol) and aryl halide (1.0 mmol) were added outside of dry box, through the septum fitted cap using a syringe. When one or both substrates were solids they were loaded in the drybox. The reaction was carried out at the indicated temperature. All reactions were conducted under inert atmosphere and monitored by GC. After consumption of reactants, the reactions were quenched with water and extracted in diethyl ether. The organic layer was dried over Na₂SO₄, mixed with silica gel and evaporated. The product/silica gel mixture was placed at the top of a flash chromatography column and eluted using an ethyl acetate/hexane (1:10) mixtures.

1-phenyl-2-[4-(trifluoromethyl)phenyl]-1-propanone² (Table 2 Entry 1) The general procedure afforded 225 mg (81%) of the title compound.

2-(p-methoxyphenyl)-acetophenone³ (Table 2 Entry 2) The general procedure afforded 176 mg (78%) of the title compound.

2-(phenyl)-acetophenone³ (Table 2 Entry 3) The general procedure afforded 182 mg (93%) of the title compound.

2-Phenyl-1-tetralone⁴ (Table 2 Entry 4) The general procedure afforded 111 mg (50%) of the title compound.

2,4-diphenyl- 3-pentanone⁵ (Table 2 Entry 5). The general procedure using 2 mmol of base and 2 mmol of aryl halide afforded 209 mg (88%) of the desired product.

1-phenyl-2-[3-(methoxy)phenyl]-1-propanone⁷ (Table 2 Entry 6) The general procedure afforded 197 mg (88%) of the title compound.

1-phenyl-2-(phenyl)- 1-propanone⁷ (Table 2 Entry 7) The general procedure afforded 191 mg (91%) of the title compound.

1-(1-naphthyl)-2-phenylethanone⁶ (Table 2 Entry 8) The general procedure afforded 86 mg (35%) of the title compound.

1-phenyl-2-(3-pyridinyl)- 1-propanone⁷(Table 2 Entry 9) The general procedure afforded 126.5 mg (60%) of the title compound.

2-(4-benzoylphenyl)-1-phenyl-1-propanone⁷ (Table 2 Entry 10) The general procedure afforded 223 mg (71%) of the title compound.

1-phenyl-2-(2,4,6-trimethylphenyl)- 1-propanone⁸ (Table 3 Entry 1) The general procedure afforded 181.5 mg (72%) of the title compound.

2-(2-methoxyphenyl)-1-phenyl-1-propanone⁹ (Table 3 Entry 2) The general procedure afforded 192 mg (80%) of the title compound.

2-(2-methylphenyl)-1-phenyl- 1-propanone¹⁰ (Table 3 Entry 3) The general procedure afforded 195 mg (87%) of the title compound.

2-(2-methylphenyl)-1-phenyl- ethanone⁷ (Table 3 Entry 4) The general procedure afforded 189 mg (90%) of the title compound.

-(2-methylphenyl)-tetralone⁷ (Table 3 Entry 5) The general procedure afforded 212 mg (90%) of the title compound. ¹H-NMR (400 MHz): 8.1 (d, 1H), 7.5 (1 H), 7.4-7.2 (m, 6H), 3.92 (t,1H), 3.0-3.1 (m, 2H), 2.42 (t, 2H);2.39(s, 3H).

2-(2-methoxyphenyl)-1-phenyl- ethanone⁹ (Table 3 Entry 6) The general procedure afforded 181 mg (80%) of the title compound.

1-(2-methoxyphenyl)-3,3-dimethyl-2-butanone¹¹(Table 3 Entry 7) The general procedure afforded 175 mg (91%) of the title compound.

2-(2,4,6-trimethylphenyl)- 3-pentanone¹² (Table 3 Entry 8) The general procedure afforded 139 mg (68%) of the title compound.

1-phenyl-2-(phenyl)- 1-propanone⁷ (Table 4 Entry 1) The general procedure afforded 191 mg (91%) of the title compound.

2-phenyl-3-pentanone¹³ (Table 4 Entry 2) The general procedure afforded 87% of the title compound by NMR. Yield was determined by NMR in view of the volatility of the product.

2-(4-methylphenyl)-1-phenyl-1-propanone¹⁰ (Table 4 Entry 3) The general procedure afforded 208 mg (93%) of the title compound.

2-(4-methylphenyl)-1-phenyl-ethanone¹⁴ (Table 4 Entry 4) The general procedure afforded 185 mg (88%) of the title compound.

2-(4-methoxyphenyl)-1-phenyl-1-propanone⁷ (Table 4 Entry 5) The general procedure afforded 216 mg (90%) of the title compound.

2-(p-methoxyphenyl)-acetophenone³ (Table 4 Entry 6) The general procedure afforded 196.5 mg (87%) of the title compound.

1) (a) Arduengo, A. J. III. US patent **5 077 414**, 1991; (b) Kelly, R.A.; Sommer, W.; Nolan, S. P. manuscript in preparation.

2) Nicolaou, K. C.; Montagnon, T.; Baran, P. S.; Zhong, Y.-L. *J. Am. Chem. Soc.*, **2002**, *124*, 2245-2258.

3) Hamann, B.C.; Hartwig, J.F. *J. Am. Chem. Soc.*, **1997**, *119*, 12382-12383.

4) Wang, D.Z.; Kim, Y.-J.; Streitwieser, A. *J. Am. Chem. Soc.*, **2000**, *122*, 10754-10760.

5) Dolhem, E.; Ocafrain, M.; Nedelec, J. Y.; Troupel, M. *Tetrahedron*, **1997**, *53*, 17089-17096.

6) Baumgartner, M.T.; Gallego, M.H.; Pierini, A.B. *J. Org. Chem.*, **1998**, *63*, 6394-6397.

7) Kawatsura, M.; Hartwig, J.F. *J. Am. Chem. Soc.*, **1999**, *121*, 1473-1478.

8) Wagner, P.J.; Zhou, B. *J. Am. Chem. Soc.*, **1988**, *110*, 611-612.

9) Bell, H. C.; Pinhey, J.T.; Sternhell, S. *Aust. J. Chem.*, **1982**, *35*, 2237-2245.

10) Culkin, D.A.; Hartwig, J.F. *J. Am. Chem. Soc.*, **2001**, *123*, 5816-5817.

11) Beugelmans, R.; Ginsburg, H. *J. Chem. Soc., Chem. Commun.*, **1980**, *11*, 508-509.

12) Bunnett, J.F.; Sundberg, J.E. *J. Org. Chem.*, **1976**, *41*, 1702-1706.

13) Rathke, M.W.; Vogiazoglou, D. *J. Org. Chem.*, **1987**, *52*, 3697-3698.

14) Angle, S.R.; Neitzel, M.L. *J. Org. Chem.*, **2000**, *65*, 6458-6461.