Supplementary Information

Perfluoro-tagged phosphine-free palladium nanoparticles supported on silica gel: application to alkynylation of aryl halides, Suzuki–Miyaura cross-coupling, and Heck reactions under aerobic conditions

Roberta Bernini,[a] Sandro Cacchi,*[b] Giancarlo Fabrizi,[b] Giovanni Forte,[c] Francesco Petrucci,[c] Alessandro Prastaro,[a] Sandra Niembro,[d] Alexandr Shafir[d] and Adelina Vallribera*[d]

[a] *Dipartimento A.B.A.C., Università della Tuscia e Consorzio Universitario "La Chimica per l'Ambiente", Via S. Camillo De Lellis, 01100 Viterbo, Italy.*
[b] *Dipartimento di Chimica e Tecnologie del Farmaco, Sapienza,Università di Roma, P.le A. Moro 5, 00185 Rome, Italy.*
[c] *Istituto Superiore di Sanità, Viale Regina Elena 299, 00161 Rome, Italy.*
[d] *Department of Chemistry, Universitat Autònoma de Barcelona, Cerdanyola 08193, Spain.*

Experimental Section

General information

Melting points were determined with a Büchi B-545 apparatus and are uncorrected. All of the reagents and solvents are commercially available and were used as purchased, without further purification. Reaction products were purified on axially compressed columns, packed with SiO_2 25-40 μm (Macherey Nagel), connected to a Gilson solvent delivery system and to a Gilson refractive index detector, and eluting with *n*-hexane/AcOEt mixtures. ^1H NMR (400.13 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded with a Brüker Avance 400 spectrometer. Infrared (IR) spectra were recorded on a JASCO FT/IR-430 spectrophotometer. Mass spectra were determined with a QP2010 Gas Chromatograph Mass spectrometer (EI ion source). Determination of Pd at mass 105 was performed by means of a sector field inductively coupled plasma mass spectrometry technique (SF-ICP-MS, Thermo-Fischer, Bremen, Germany) in medium resolution ($m/\Delta m=3000$) to avoid that interferent signals coming from molecular species, *i.e.*, $^{40}Ar^{65}Cu$, could overlap the signal of Pd at the chosen mass and overestimate the actual Pd value. Quantification of Pd was carried out through the external calibration curve. Rhodium (Rh), selected at mass 103, was used as internal standard to keep under control the instrumental drift. Single element calibrant and internal standard were prepared from 1000 mg/mL stock solutions of Pd in 10% HNO_3 and Rh in 10% HCl (High-Purity Standards, Charleston, USA) by dilution with high purity deionized water. Trasmission electron microscopy (TEM) analyses were performed in the "Servei de Microscòpia" of the Universitat Autònoma de Barcelona, in a JEOL JEM-2010 model at 200 kV. The TEM measurements were made by sonication of the nanoparticulate material in perfluorooctyl bromide for several minutes; then, one drop of the finely divided suspension was placed on a specially produced structure less carbon support film having a thickness of 4-6 nm and dried before observation.

Preparation of phosphine-free perfluoro-tagged palladium nanoparticles Pd*np*-A: a mixture of $PdCl_2$ (0.060 g, 0.34 mmol), NaCl (0.022 g, 0.38 mmol), and 2 mL of MeOH was stirred at room temperature for 24 h. The mixture was filtered through a glass wool plug. Additional MeOH (28 mL) was added to the filtrate. The solution was heated at 60 ºC under stirring and 2,4,6-tris(1H,1H,2H,2H-perfluorodecylthio)-1,3,5-triazine (0.250 g, 0.16 mmol) was added. Then, the mixture was heated under stirring during 24 h. AcONa (0.190 g, 2.32 mmol) was added and stirring was maintained at room temperature for 1 h. The formed black solid was filtered, washed with MeOH, H_2O and Me_2CO; it was then dried to afford 0.270 g of Pd*np*-**A** as a black solid. The size of the nanoparticles was 2.3 ± 0.7 nm, as determined by transmission electron microscopy. Pd analysis (ICP): 13.4 %.

Preparation of (Pd*np*-A)/FSG: 0.020 g of Pd*np*-**A** were added to 10 mL of perfluorooctane and the mixture was heated at 100 °C for 14 h. Then, 1 g of FSG (C_8; 35-70 µm) was added and the mixture was stirred at the same temperature for 1 h. After this time , the solvent was evaporated under vacuum to obtain the desired precatalyst system.

Preparation of Pd*np*-B: a 5 mL round-bottom flask was charged with $PdCl_2$ (17.0 mg, 96 mmol) and NaCl (6.6 mg, 113 µmol). MeOH (1 mL) was subsequently added and the mixture was left stirring at room temperature for 24 h; the mixture was then filtered through a plug of glass wool and the filtrate diluted with additional 9 mL of MeOH. Material **B** (199.9 mg) was added to the flask, and the resulting mixture was heated at 60 °C for 24 h. After this time, NaOAc (56.0 mg, 0.68 mmol) was added, the mixture was removed from the oil bath and was allowed to cool for 90 min. A precipitate formed that was separated by centrifugation, washed successively with MeOH, water and acetone, giving the product as a black solid. Yield: 226.3 mg. Palladium content: 3.47 %. Average particle diameter: 3.2 ± 0.4 nm (based on TEM; measurement of 260 particles).

Typical procedure for alkynylation of aryl halides using 0.1 mol% of Pd*np*-A/FSG or Pd*np*-B: 3-(trifluoromethyl)iodobenzene (272 mg, 1 mmol), Pd*np*-**A**/FSG (40 mg) or Pd*np*-**B** (3mg), pyrrolidine (142 mg, 2 mmol), and phenylacetylene (102 mg, 1 mmol.) in water (2 mL) were orbitally stirred for 3 h at 100 °C with a Heidolph Synthesis System. Then, after cooling, the reaction mixture was centrifuged. The liquid phase was decanted, extracted with AcOEt, the organic layer was washed with deionized water and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by chromatography (SiO_2, 35 g, *n*-hexane/AcOEt 96/4 v/v) to give 233.7 mg (95% yield) of: **3a** m.p.: 105-106 °C; IR (KBr) 2919, 1710, 1681, 1639 cm^{-1}; ^1H NMR (CDCl3) δ 7.99-7.97 (d, *J = 3.18 Hz*, 2 H), 7.74-7.70 (d, *J =16 Hz*, 1H), 7.63-7.61 (d, *J =8.2 Hz*, 2H), 6.56-6.52 (d, *J =16 Hz*, 1H), 3.84 (s, 3H), 2.63 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 197.2, 166.8, 143.2, 138.6, 138.0, 128.8, 128.1, 120.3, 51.8, 26.6; MS *m/z* (relative intensity) 204 (M+, 34), 189 (100), 161 (15), 102 (12); Anal calcd for $C_{12}H_{12}O_4$ C, 65.45; H, 5.49; found C, 65.39; H, 5.43. (Known compound, see: Rocaboy, C.; Gladysz, J. A. *Org. Lett.* 2002, **4**, 1993).

Typical procedure for the preparation of 2,3-disubstituted indoles in the presence of Pd*np*-B: 2,2,2-trifluoro-N-(2-(phenylethynyl)phenyl)acetamide (289 mg, 1 mmol), Pd*np*-**B** (3mg), K_2CO_3 (276 mg, 2 mmol) and 1-iodo-3-(trifluoromethyl)benzene (272 mg, 1 mmol.) in CH_3CN (2 mL) were orbitally stirred for 3 h at 100 °C with a Heidolph Synthesis System. Then, after cooling, the reaction mixture was centrifuged. The liquid phase was decanted, diluted with AcOEt, washed with deionized water and the organic layer was dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by chromatography (SiO_2, 35 g, *n*-hexane/AcOEt 96/4 v/v) to give 307 mg (91% yield) of **5b** mp: 70 °C; IR (KBr) 3383, 1456, 1324 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.28 (s, 1 H), 7.82 (s, 1 H), 7.75-7.73 (d, *J = 8.0 Hz*, 1H), 7.64, 7.60 (t, *J = 8.0 Hz*, 2H), 7.53-7.32 (m, 8 H), 7.28-7.25 (t, *J = 8.0 Hz*, 1H); ^{13}C NMR ($CDCl_3$) δ 136.1, 135.9, 134.9, 133.5 (q, *J = 1.2 Hz*) , 132.2, 131.2, 130.8, 129.0, 128.9, 128.4, 128.2, 126.8, 126.7, 124.3 (q, *J = 272.5 Hz*), 123.1, 122.9 (q, *J = 3.9 Hz*), 120.9, 119.3, 113.5, 111.2; Anal Calcd for $C_{21}H_{14}F_3N$ C, 74.77; H, 4.18; found C, 74.70; H, 4.14. (Known compound, see: S. Cacchi, et al., *Synthesis,* 2003, ***5***, 728).

Typical procedure for the preparation of Suzuki-Miyaura cross-coupling product using 0.1 mol% of Pd*np*-A/FSG or Pd*np*-B: 4-iodobenzoic acid (248 mg, 1 mmol), Pd*np*-**A** /FSG (40 mg) or Pd*np*-**B** (3 mg), K_2CO_3 (276 mg, 2 mmol), KF (116.2, 2mmol), and *o*-tolylboronic acid (136 mg, 1 mmol.) in water (2 mL) were orbitally stirred for 5 h (for Pd*np*-**A** /FSG) or 1h (for Pd*np*-**B**) at 100 °C with a Heidolph Synthesis System. Then, after cooling, the reaction mixture was centrifuged. The liquid phase was decanted, extarcted with AcOEt, the organic layer was washed with deionized water and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by chromatography (SiO_2, 35 g, *n*-Hexane/AcOEt 96/4 v/v) to give 210 mg (99% yield) of **7a** mp: 187.5-188.8 °C; IR (KBr) 2949, 2905, 1673, 1608, 1427, 1321, 1291 cm^{-1}; ^1H NMR (DMSO) δ 8.02−7.99 (d, *J = 8.6 Hz*, 2H), (H), 7.44-7.43(d, *J = 8.0 Hz*, 2H), 7.33-7.21 (m, 4 H), 2.24(s, 3H);

^{13}CNMR(DMSO) δ 167.7, 146.24, 140.84, 135.17, 130.99, 129.86, 129.75, 129.73, 128.35, 126.56, 20.58. Anal Calcd for $C_{14}H_{12}O_{22}$ C, 79.22; H,5.70; found C, 79.20; H,5.68.

Typical procedure for the preparation of methylcinnamate esters using 0.1 mol% of Pd*np*-A /FSG or Pd*np*-B: *p*-acetil iodobenzene (246.05 mg, 1 mmol), Pd*np*-**A** /FSG (40 mg), Et_3N (303 mg, 3 mmol), and methyl acrylate (172 mg, 2 mmol.) in MeCN (2 mL) were orbitally stirred for 24 h at 100 °C with a Heidolph Synthesis System. Then, after cooling, the reaction mixture was centrifuged. The liquid phase was decanted, diluted with AcOEt, the organic layer was washed with deionized water and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by chromatography (SiO_2, 35 g, *n*-Hexane/AcOEt 96/4 v/v) to give 182 mg (89% yield) of **8b** m.p.: 105-106 °C; IR (KBr) 2919, 1710, 1681, 1639 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.99-7.97 (d, *J = 3.18 Hz*, 2H), 7.74-7.70 (d, *J = 16.0 Hz*, 1H), 7.63-7.61 (d, *J = 8.2 Hz*, 2H), 6.56-6.52 (d, *J =16.0 Hz*, 1 H), 3.84 (s, 3 H), 2.63 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 197.2, 166.8, 143.2, 138.6, 138.0, 128.8, 128.1, 120.3, 51.8, 26.6; MS *m/z* (relative intensity) 204 (M+, 34), 189 (100), 161 (15), 102 (12); Anal calcd for $C_{12}H_{12}O_4$ C, 65.45; H, 5.49;found C, 65.39; H, 5.43. (Known compound, see: C. Rocaboy, J. A Gladysz, *Org. Lett.* 2002, **4**, 1993).

Recycling procedure: The mixture was cooled at room temperature, centrifuged (3000 rpm × 20 min.) and the solution was pipetted. Then, the solid supported palladium was washed with methanol (4 × 3 mL), the resulting suspension was centrifuged and the solvent was decanted each time. The recovered solid material was dried under high vacuum at 60 °C for 2 h and reused.

3f: mp: 110.2-111.4 °C; IR (KBr): 3000, 2918, 2219, 1679, 1265 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.68-7.61 (m, 4H), 7.58-7.55 (m, 2H), 7.44-7.40 (m, 3H); ^{13}CNMR ($CDCl_3$) δ 132.1, 131.9, 129.2, 128.5, 128.3, 122.4, 118.7, 111.4, 93.6, 87.6. MS m/z (relative intensity): 203 (M$^+$, 100), 177 (6), 151 (9), 99 (7), 88 (13), 75 (19), 63 (21)50 (44); Anal Calcd for $C_{15}H_9N$, 88.64; H, 4.46; found C, 88.67; H, 4.48. (Known compound, see: K. Yoshida, T. Fueno, *J. Org. Chem.* 1973, **38**, 1045).

3g: 88.5-89.7 °C; IR (KBr): 3122, 1500, 1485, 685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.58-7.53 (m, 4H), 7.35-7.29 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 131.7, 128.5, 128.3, 123.2, 89.5. MS m/z (relative intensity): 178 (M$^+$, 100), 152 (15), 126 (8), 89 (10), 76 (6), 63 (12), 50 (8); Anal Calcd for $C_{14}H_{10}$, 94.36; H, 5.66; found C, 94.38; H, 5.68. (Known compound, see: L. A. Carpino, H.-W. Chen, *J. Am. Chem. Soc.* 1979, **101**, 390).

3h: mp: 106-107 °C; IR (KBr) 2995, 2214, 1525, 1350, 826, 761, 690cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.15 (s, 1H), 7.65–7.63 (dd, *J_1 =7.6 Hz, J_2 =1.2 Hz*, 1H), 7.56 (m, 2H), 7.40 (m, *J = 3.2 Hz* 3H), 7.35 (d, *J = 8.0 Hz*, 1H), 2.64 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 148.6, 135.0, 133.0, 132.4, 131.2, 128.4, 128.0, 127.0, 122.1, 121.9, 90.8, 86.4, 19.9 MS m/z (relative intensity) 237 (M$^+$, 100), 223 (48), 179 (15). Anal Calcd for $C_{15}H_{11}NO_2$ C, 75.94, H, 4.67; found C, 75.97; H, 4.69. (Known compound, see: Roger Soler et al., *Synthesis,* 2007, ***19***, 3068).

3i: mp: 89-91 °C; IR (KBr): 3460, 3366, 3064, 3029, 2205 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.59-7.55 (m, 2H), 7.43-7.37 (m, 4H), 7.21-7.15 (m, 1H), 6.79-6.75 (m, 2H), 4.29 (bs, 2H); ^{13}CNMR (100.6 MHz) ($CDCl_3$) δ 148.1, 132.6, 131.9, 130.2, 128.8, 128.6, 123.7, 118.5, 114.8, 108.4, 95.1, 86.3. MS m/z (relative intensity): 193 (M$^+$, 100), 165 (48). Anal Calcd for $C_{14}H_{11}N$ C, 87.01; H, 5.74; found C, 87.07; H, 5.80

3p: OIl; IR (KBr) 2212, 1597, 1509, 1292, 1253, 835 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.64–7.57 (dd, *J_1 = 8.0 Hz, J_2 = 8.0 Hz*, 4H), 7.51-7.49 (d, *J_1 = 8.0 Hz*, 2H), 6.92-6.90 (d, *J = 8.0 Hz*, 2H), 3.85 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 160.4, 133.4, 132.0, 1319, 128.7, 118.7, 114.2, 111.1, 94.2, 86.8, 55.4, MS m/z (relative intensity) 178 (M$^+$, 100), 152 (15), 126 (8), 89 (9), 77 (6). Anal Calcd for $C_{16}H_{11}NO$ C, 82.38; H, 4.75; found C, 82.38; H, 4.75. (Known compound, see: R. Soler et al., *Synthesis,* 2007, ***19***, 3068).

3m: Oil; IR (neat) 2211, 1596, 1509, 1292, 1253, 835 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.64-7.48 (d, 4H), 7.51-7.49 (d, *J = 8.0 Hz*, 2H), 6.92-6.90 (d, *J = 8.0 Hz*, 2H), 3.85 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 160.4, 133.4, 132.1, 131.9, 128.7, 118.7, 114.2, 111.1, 94.2, 86.8, 55.5, MS m/z (relative intensity) 233 (M$^+$,100), 218 (38), 190 (44), 175 (13). Anal Calcd for $C_{16}H_{14}O$, C, 86.45; H, 6.35; found C, 86.46; H, 6.36. (Known compound, see: H. Bühl, B. Seitz, H. Meier, *Synthesis,* 1977, **33**, 449).

3r: mp: 77–78 °C; IR (KBr): 3427, 3015, 2928, 2858, 1602 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.32 (d, *J = 9.0 Hz*, 2H), 6.75 (d, *J = 9.0 Hz*, 2H), 4.43 (s, 2H), 3.76 (s, 3H), 2.60 (s, 1H); ^{13}CNMR ($CDCl_3$) δ 159.6, 133.1, 114.7, 113.8, 86.0, 55.2, 51.4. MS m/z (relative intensity) 162 (M$^+$,100), 91 (50), 131 (39), 145 (38) Anal Calcd for $C_{10}H_{10}O_2$ C, 74.06; H,6.21; found C, 74.10; H, 6.14. (Known compound, see: A. S. Paraskar and A. Sudalai, *Tetrahedron* 2006, **62**, 5756).

3t: Oil; IR (KBr) 2977, 2225, 1926, 1600, 1261 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.59–7.57 (d, *J = 8.0 Hz*, 2H), 7.49-7.47 (d, *J = 8.0 Hz*, 2H), 2.19 (s, 1H), 1.63 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 132.09, 131.89, 127.73, 118.37, 111.48, 98.28, 80.51, 65.49, 31.20. Anal Calcd for $C_{12}H_{11}NO$ C, 77.81; H, 5.99; found C, 77.82; H, 5.60. (Known compound, see: R. Soler et al., *Synthesis,* 2007, ***19***, 3068).

3u: Oil; IR (neat) 3424, 2973, 2933, 1681, 1600, 1267 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.86–7.84 (d, J = 8.0 Hz, 2H), 7.46-7.44 (d, *J = 8.0 Hz*, 2H), 2.72 (s, 1H), 2.59 (s, 3H), 1.79 (m, 2H), 1.57 (s, 3H), 1.09 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 197.6, 136.1, 131.8, 128.2, 127.9, 96.4, 82.5, 69.1, 36.6, 29.2, 26.6, 9.1. Anal Calcd for $C_{14}H_{16}O_2$ C, 77.75; H, 7.46; found C, 77.70; H, 7.48.

3z: Oil; IR (neat) 3428, 3060, 2985, 2229, 1602, 1500, 1448 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.73–7.70 (m, 2 H), 7.60-7.53 (q, J_1 = *8.0 Hz*, J_2 = *12.0 Hz*, 4H), 7.41 (m, 2H), 7.32 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 145.11, 132.3, 132.1, 128.5, 128.0, 127.6, 124.9, 118.4, 111.8, 97.2, 83.2, 70.4, 33.1 Anal Calcd for $C_{18}H_{16}O_2$ C, 81.79; H, 6.10; found C, 81.77; H, 6.16. (Known compound, see: S. B. Park and H. Alper, *Chem. Comm.,* 2004, 1306).

3za: Oil: IR (neat) 3415, 2965, 2873, 2223, 1681, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.87–7.85 (d, *J = 8.0 Hz*, 2H) 7.46–7.44 (d, *J = 8.0 Hz*, 2H), 2.57 (s, 4H), 2.07-2.04 (m, 4 H), 1.90-1.76 (m, 4H); ^{13}CNMR($CDCl_3$) δ 197.0, 136.13, 131.74, 128.21, 128.01, 96.65, 82.31, 74.81, 42.51, 26.63, 23.58. Anal Calcd for $C_{15}H_{16}O_2$ C, 78.92; H, 7.06; found C, 78.93; H, 7.08.

3zb: Oil: IR (neat) 3399, 2958, 2223, 1606, 1454, 1247 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38–7.36 (d, *J =8.0 Hz*, 2H), 6.85–6.83 (d, *J =8.0 Hz*, 2H), 3.82 (s, 3H), 2.08-1.27 (m, 12 H); ^{13}CNMR($CDCl_3$) δ 159.55, 133.09, 115.07, 113.92, 91.53, 83.01, 75.02, 55.31, 42.65, 23.58; Anal Calcd for $C_{14}H_{16}O_2$ C, 77.75; H, 7.46; found C, 77.76; H, 7.47. (Known compound, see: M. Csékei, Z. Novák and A. Kotschy, *Tetrahedron* 2008, **64**, 975).

5a: mp: 120-121 °C; IR (KBr) 3387, 1454 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.2 (s, 1H), 7.78-7.62 (m, 1H), 7.11-7.58 (m, 13H); ^{13}C NMR ($CDCl_3$) δ 136.0, 135.2, 134.2, 132.8, 130.3, 128.9, 128.7, 128.6, 128.3, 127.8, 126.3, 122.8, 120.5, 119.8, 115.1, 111.0; Anal Calcd for $C_{20}H_{15}N$ C, 89.19; H, 5.61; found C, 89.10; H, 5.59.(Known compound, see: S. Cacchi, et al., *Synthesis,* 2003, **5**, 728).

5c: mp: 211-212 °C; IR (KBr) 3325, 2227 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 11.81 (s, 1H), 7.80 (d, *J = 8.2 Hz*, 2 H), 7.67-7.28 (m, 9 H), 7.22 (t, *J = 6.4 Hz*, 1 H), 7.1(t, *J = 6.4 Hz*, 1 H); ^{13}C NMR (DMSO-d_6) δ 140.7, 136.2, 135.7, 13.5, 131.9, 130.3, 128.8, 128.6, 128.1, 127.1, 122.4, 120.3, 119.1, 118.3, 111.8, 111.5, 108.1; Anal Calcd for $C_{21}H_{14}N_2$ C, 85.69; H, 4.79; found C, 85.61; H, 4.77. (Known compound, see: S. Cacchi, et al., *Synthesis,* 2003, **5**, 728).

5d: mp: 203-204 °C; IR (KBr) 3264, 2923, 1658, 1599 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 11.77 (s, 1H), 7.99 (d, *J = 8.3 Hz*, 2H), 7.00-7.68 (m, 11H), 2.61 (s, 3H); ^{13}C NMR (CDCl$_3$) 197.4, 140.6, 136.3, 135.3, 134.3, 132.2, 129.6, 128.7, 128.6, 128.5, 128.0, 127.4, 122.3, 120.2, 118.5, 112.1, 111.7, 26.6; Anal Calcd for $C_{22}H_{17}NO$ C, 86.86; H, 5.50; found C, 84.61; H, 5.50. (Known compound, see: S. Cacchi, et al., *Synthesis,* 2003, **5**, 728).

5e: Oil; IR (KBr) 3401, 1455, 1328 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.22(s, 1H), 7.76-7.74 (d, *J = 8.0 Hz* 1H), 7.49-7.45 (m, 3H), 7.40-7.17 (m, 9H), 2.42 (s, 3H); ^{13}C NMR (CDCl$_3$) δ138.9, 136.4, 136.2, 135.5, 134.2, 133.0, 129.3, 129.0, 128.8, 128.3, 127.5, 124.4, 122.2, 120.1, 118.7, 111.4, 25.7; Anal Calcd for $C_{21}H_{17}N$ C, 89.01; H, 6.05; found C, 88.94; H, 6.01. (Known compound, see: S. Cacchi, et al., *Synthesis,* 2003, **5**, 728).

5f: mp: 184-185 °C; IR (KBr) 3418, 1602, 1510 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8. 22 (s, 1H), 7.71-7.69 (d, *J = 8.0 Hz* 1H), 7.51-7.15 (m, 11H), 6.99-6.97 (d, *J = 8.0 Hz* 1H), 3.86 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 159.8, 143.4, 143.0, 139.4, 135.6, 132.3, 128.9, 128.7, 127.9, 127.4, 126.5, 126.2, 125.7,1, 14.2, 55.8; Anal Calcd for $C_{22}H_{18}NO$ C, 85.56; H, 6.08; found C, 85.50; H, 6.02. (Known compound, see: S. Cacchi, et al., *Synthesis,* 2003, **5**, 728).

5g: Oil; IR (KBr) 3374, 1591, 1500 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.23 (s, 1H), 7.72-7.70 (d, *J = 8.0 Hz*, 1 H), 7.46-7.22 (m, 12 H); ^{13}C NMR (CDCl$_3$) δ 135.9, 134.5, 133.7, 132.4, 132.1, 131.5, 128.9, 128.8, 128.5, 128.3, 128.1, 122.9, 120.7, 119.5, 113.1, 111.1; Anal Calcd for $C_{20}H_{14}ClN$ C, 79.07; H, 4.65; found C, 79.00; H, 4.59.

5h: mp: 227-228 °C; IR (KBr) 3374, 1591, 1500, 1336 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 11.88 (s, 1 H), 8.22 (d, *J = 8.8 Hz* 2H), 7.68-7.35 (m, 9H), 7.23 (dt, *J_1 = 7.5 Hz, J_2 = 1.2 Hz* 1 H), 7.11(dt, *J_1 = 7.5 Hz, J_2 = 1.1 Hz* 1H); ^{13}C NMR (CDCl$_3$) δ 145.0, 143.0, 136.3, 136.1, 131.7, 130.2, 128.8, 128.7, 128.3, 127.0, 123.9, 122.5, 120.5, 118.3, 111.9, 111.1 Anal Calcd for $C_{20}H_{14}N_2O_2$ C, 76.42; H, 4.49; found C, 76.35; H, 4.48. (Known compound, see: S. Cacchi, et al., *Synthesis,* 2003, **5**, 728).

7b: mp: 235.0-235.4 °C; IR (KBr) 2925, 1685, 1605, 1560, 1356, 1322, 1262 cm^{-1}; ^1H NMR (DMSO) δ 12.9 (s, 1H), 8.0-7.9 (d, *J = 8.0 Hz*, 2H), 7.77-7.75 (d, *J = 8.0 Hz*, 2H),7.68-7.66 (d, *J = 8.0 Hz*, 2H), 7.57 (s, 1H), 7.25 (t, 1H); ^{13}C NMR (DMSO) δ 167.62, 143.90, 135.65, 130.83, 130.42, 130.01, 127.17, 126.73, 125.34, 116.12, 115.90, 14.74. Anal Calcd for $C_{14}H_{11}FO_2$ C, 73.03, H, 4.82; found C, 73.05, H, 4.83.

7c: mp: 97.8-98.6 °C; IR (KBr) 2923, 2853, 1607, 1586, 1500, 1287, 1245, 806 cm^{-1}; ^1H NMR($CDCl_3$) δ 7.25-7.21 (m, 6H), 6.95 (d, *J = 8.8 Hz*, 2H), 3.85 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (DMSO) δ 158.5, 141.5, 135.5, 134.4, 130.3, 130.2, 129.9, 126.9, 125.7, 113.5, 55.3, 20.5 ,. Anal Calcd for; found. $C_{14}H_{14}O$ C, 84.81; H, 7.12; found C, 84.75; H, 7.07. (Known compound, see: Tao, Bin; *J. Org. Chem*, 2004, **69**, 4330).

7d: mp: 153.3-154.5 °C; IR (KBr) 1673, 1600, 1294, 1818 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.03–8.01 (d, *J = 8.0 Hz*, 2 H), 7.67-7.65 (d, *J = 8.0 Hz*, 2 H), 7.61-7.58 (d, *J = 8.0 Hz,* 2 H), 7.03-7.01 (d, *J = 8.0 Hz* 2H), 3.88 (s, 3H), 2.64 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 197.7, 159.9, 145.4, 135.4, 132.3, 129.0, 128.4, 126.6, 114.4, 55.4, 26.6; Anal Calcd for $C_{11}H_{10}OS$ C, 69.44; H, 5.30; found C, 69.50; H, 5.35. (Known compound, see: C. C. Tzschucke et al, *Angew.Chem. Int. Ed.*. 2002, **41**, 4500).

7e: mp: 120.0-121.1 °C; IR (KBr) 2846, 2673, 2551, 1689, 1609, 1500, 1428, 1398, 1125 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.07–8.05 (d, *J =8.0 Hz*, 2H), 7.93-7.91 (d, *J = 8.0 Hz*, 2H), 7.84-7.80 (m, 4 H); ^{13}C NMR (DMSO-d_6) δ 167.5, 143.5, 143.1, 131.1, 130.5, 128.3, 127.7, 126.4, 126.4. Anal Calcd for $C_{14}H_9F_3O_2$ C, 63.16; H, 3.41; found C, 63.17; H, 3.42.

7f: mp: 218.0-219.4 °C; IR (KBr) 2949, 2668, 2548, 1680, 1607, 1422, 1318, 1288 cm^{-1}; ^1H NMR (DMSO-d_6) δ 12.9 (s, 1H), 8.04-8.02 (d, *J = 8.0 Hz*, 2H), 7.81-7.79 (d, *J = 8.0 Hz*, 2H), 7.74-7.72 (d, *J = 8.0 Hz*, 2H), 7.75-7.48 (t, 2 H), 7.44-7.42 (d, *J = 8.0 Hz*, 2H); ^{13}C NMR (DMSO-d_6) δ 167.5, 144.7, 139.5, 130.4, 130.0, 129.5, 128.7, 127.4, 127.2. Anal Calcd for $C_{13}H_{10}O_2$ C, 78.77; H, 5.09 found C, 78.78; H, 5.10. (Known compound, see: K. M. Dawood, A. Kirschning *Tetrahedron* 2005, **61**, 12121).

7g: mp: 250.0-251.7 °C; IR (KBr) 2953, 2834, 2547, 1678, 1601, 1430, 1313, 1289 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.00–7.98 (d, *J = 7.7 Hz*, 2H), 7.76-7.68 (m, 4H), 7.07-7.05 (d, *J = 6.4 Hz*, 2H), 3.81 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 167.7, 160.07, 144.46, 131.76, 130.46, 129.37, 128.64, 126.62, 115.02, 55.73. Anal Calcd for $C_{14}H_{12}O_3$ C, 73.67; H,5.30; found C, 73.65; H,5.28.

7h: Oil; IR (neat) 2949, 2668, 2548, 1680; ^1H NMR (DMSO-d_6) δ 8.00–7.98 (d, *J = 7.7 Hz*, 2H), 7.76-7.68 (m, 4H), 7.07-7.05 (d, *J = 6.4 Hz*, 2H), 2.36 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 167.7, 160.07, 144.46, 131.76, 130.46, 129.37, 128.64, 126.62, 115.02, 20.58; Anal Calcd for $C_{14}H_{12}O_2$ C, 79.22; H, 5.70; found C, 79.17; H, 5.66

7i: mp: 73.5-73.6 °C; IR (KBr) 2923, 2853, 1607, 1586, 1500, 1287, 1245, 806 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.68 (s, 4H), 7.58-7.56 (d, *J = 8.0 Hz*, 2H), 7.04-7.01 (d, *J = 8.0 Hz*, 2H); ^{13}C NMR ($CDCl_3$) δ 159.9, 144.35, 132.2, 128.4, 126.9, 125.77, 125.73, 125.7, 125.6, 123.1, 114.5, 55.4. Anal Calcd for $C_{14}H_{11}F_3O$ C, 66.6; H, 4.4; found C, 66.7; H, 4.5.

7l: mp: 65.5-66.8 °C; IR (KBr) 3079, 2931, 2109, 1926 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.72 (s, 4H), 7.64-7.62 (d, *J = 8.0 Hz*, 2H), 7.52-7.48 (t, J_1= *8.0 Hz*, J_2= *4.0 Hz*, 2H); 7.45-7.43 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 144.6, 139.7, 129.0, 128.7, 128.2, 127.4, 127.3, 126.1, 125.7. Anal Calcd for $C_{13}H_9F_3$ C, 70.27; H, 4.08 found C, 70.28; H, 4.09. (Known compound, see: O. Navarro et al, *J. Org. Chem.* 2004, **69**, 3173).

7m: Oil; IR (neat) 3058, 2360, 1681, 1477, 748 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.51–7.48 (m, 2H), 7.44-7.40 (m, 3H), 7.35-7.32 (m, 4H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 142.1, 135.4, 130.4, 129.9, 129.3, 128.2, 127.3, 126.9, 125.9, 29.8, 20.6; Anal Calcd for $C_{13}H_{12}$ C, 92.81; H, 7.19; found C, 92.87; H, 7.23. (Known compound, see: N. E. Leadbeater et al, *Org. Lett.* 2002, **4**, 2973).

7n: mp: 120.6-121.4 °C; IR (KBr) 1685, 1605, 1396, 1356, 1322, 823 cm^{-1}; ^1H NMR ($CDCl_3$) 8.09-8.07 (d, *J = 8.0 Hz* 2H), 7.75-7.70 (m, 6H), 2.67 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 197.6, 144.2, 143.4, 136.6, 129.1, 127.6, 127.5, 125.9, 26.73. Anal Calcd for $C_{15}H_{11}F_3O$ C, 68.19; H, 4.20 found. C, 68.20; H, 4.21. (Known compound, see: B. H. Lipshutz et al. *Org. Lett.*, 2008, **10**, 4279).

7o: Oil; IR (neat) 3349, 3054, 2360, 1683, 1265 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.05–8.03 (d, *J = 8.0 Hz*, 2H), 7.71-7.69 (d, *J = 8.0* Hz, 1H),7.54-7.52 (d, *J = 8.0* Hz, 2H), 7.42-7.38 (m, 1H), 7.34-7.32

(m, 1 H), 7.28-7.24 (m, 1 H) 2.67 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 197.7, 145.8, 141.5, 136.2, 133.3, 131.1, 129.8, 129.4, 128.1, 127.6, 122.3, 26.7; Anal Calcd for $C_{14}H_{11}BrO$ C, 61.11; H, 4.03; found C, 61.05; H, 3.98.

7p: mp: 151.7-152.2 °C; IR (KBr) 3099, 1674, 1600, 1273, 785 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.01–7.99 (d, *J = 8.0 Hz*, 2H), 7.71-7.69 (d, *J = 8.0 Hz*, 2H), 7.60-7.59 (m, 1H), 7.46-7.43 (m, 2H), 2.60 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 197.6, 141.1, 140.2, 135.7, 129.1, 126.8, 126.4, 126.2, 122.1, 26.6; Anal Calcd for $C_{12}H_{10}OS$ C, 71.25; H, 4.98; found C, 71.20; H, 4.92. (Known compound, see: K. M. Dawood, A. Kirschning Tetrahedron 2005, **61**, 12121).

7q: Oil; IR (KBr) 2928, 2850, 1600, 1589 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.34–7.27 (m, 6H), 7.24-7.12 (m, 2H), 2.30 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 197.6, 141.1, 140.2, 135.7, 129.1, 126.8, 126.4, 126.2, 122.1, 26.6; Anal Calcd for $C_{13}H_{11}F$ C, 83.84; H, 5.95; found C, 83.89; H, 5.90.

7r: mp: 117 °C; IR (KBr) 2227, 1685, 1604, 1523, 1268 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.10–8.08 (d, *J = 8.0 Hz*, 2H), 7.80-7.70 (m, 6H), 2.67 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 197.5, 144.3, 143.5, 136.9, 132.8, 129.2, 127.9, 127.5, 118.6, 111.9, 26.7; Anal Calcd for $C_{15}H_{11}NO$ C, 81.43; H, 5.01; found C, 81.49; H, 5.07.

7s: mp: 126.2-127.4 °C; IR (KBr) 3097, 1606, 1535, 1502, 1245, 781 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.58–7.5 6 (d, *J = 8.0 Hz*, 2H), 7.41-7.39 (m, 3H), 6.98-6.96 (d, *J = 8.0 Hz,* 2H), 3.87 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 158.9, 142.1, 128.8, 127.6, 126.3, 126.1, 118.9, 114.3, 55.39; Anal Calcd for $C_{11}H_{10}OS$ C, 69.44; H, 5.30; found C, 69.50; H, 5.35.

7t: Oil °C; IR (KBr) 3345, 3060, 1681, 1604, 1267 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.05–8.03 (d, *J = 8.0 Hz*, 2H), 7.47-7.45 (d, *J = 8.0 Hz*, 2H), 7.33-7.26 (m, 4H), 2.68 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 198.1, 147.7, 140.7, 135.6, 135.2, 130.6, 129.5, 128.3, 127.9, 127.5, 125.9, 26.7, 20.4 ; Anal Calcd for $C_{15}H_{14}O$, C, 85.68; H, 6.71; found C, 85.40; H, 6.76.

7u: Oil °C; IR (KBr) 3475, 1683, 1402, 1344, 1263 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 13.23 (s, 1H), 8.04–8.02 (d, *J = 8.0 Hz*, 1H), 7.99-7.92 (m, 3H), 7.73-7.71 (m, 1H), 7.50-7.25 (s, 1H), 7.23-7.21 (s, 1H) 2.60 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 198.6, 168.6, 140.9, 137.4, 134.7, 134.0, 132.8, 130.5, 128.6, 127.6, 127.4, 94.5, 27.3; Anal Calcd for $C_{15}H_{12}O_3$, C, 74.99; H, 5.03; found C, 74.97; H, 5.06.

7v: m.p.: 110.6-111.3 °C; IR (KBr) 1687, 1348, 821 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.22–8.21 (d, *J = 4.0 Hz*, 1H), 8.06-8.04 (d, *J = 8.0 Hz*, 2H), 7.77-7.67 (m, 3H), 7.45-7.43 (d, *J = 8.0 Hz*, 1H) 2.65 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 197.7, 149.6, 142.8, 135.6, 141.8, 138.8, 136.5, 134.3, 133.5, 133.4, 133.2, 133.1, 131.4, 129.2, 129.0, 127.4, 127.0, 123.1, 26.7, 20.2; Anal Calcd for $C_{15}H_{13}NO_3$, C, 70.58; H, 5.13; found C, 70.60; H, 5.17.