Supporting Information

C-H Activation and Palladium Migration within Biaryls under Heck Reaction Conditions

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General comments. $^1$H and $^{13}$C assignments were made using $^1$H-$^1$H and $^1$H-$^{13}$C 2D correlation spectroscopy and DEPT experiments. Where unambiguous assignments are not possible, this is indicated. The same numbering system has been employed throughout and corresponds to the following diagram, with similar systems applying to the 2- and 4-bromo derivatives.

![Diagram]

Part A. Preparation of biaryl substrates.

1. For procedures used to prepare 4-aryl-3-bromopyridines 1a-c and 3-aryl-2-bromopyridines 5 – see Karig, G.; Spencer, J. A.; Gallagher, T. Organic Lett. 2001, 3, 835-838.

Preparation of 1a has been described (see above)

3-Bromo-4-phenylpyridine 1b
Isolated in 43% yield as colorless crystals; Rf 0.58 (hexane-EtOAc, 1:1); mp 47-49°C (hexanes); $\delta_H$ (300 MHz, CDCl$_3$) 8.82 (1 H, d, $J$ 0.6, H-2), 8.55 (1 H, d, $J$ 4.8, H-6), 7.40-7.53 (5 H, m, C-2’, C-3’, C-4’), 7.28 (1 H, dd, $J$ 4.8, 0.6, H-5); $\delta_C$ (75.4 MHz,
CDCl₃) 152.5 (C-2), 150.4 (C-4), 148.3 (C-6), 138.2 (C-1’), 128.8 (C-4’ and either C-2’ or C-3’), 128.4 (C-2’ or C-3’), 125.6 (C-5), 120.9 (C-3). All data were consistent with those reported in the literature (Comins, D. L.; Mantlo, N.B. *J. Heterocycl. Chem.* 1983, **20**, 1239; Shiao, M. J.; Chia, W. L.; Shing, T. L.; Chow, T. J. *J. Chem. Res.*-S 1992, 247).

3-Bromo-4-(4’-methoxyphenyl)pyridine 1c
Isolated in 33% yield as off-white crystals; Rf 0.35 (hexane-EtOAc, 1:1); mp 77-79°C (hexane); δH (300 MHz, CDCl₃) 8.79 (1 H, s, H-2), 8.52 (1 H, d, J 5, H-6), 7.41 (2 H, AA’BB’, J 8.9, H-2’), 7.00 (2 H, AA’BB’, J 8.9, H-3’), 7.26 (1 H, d, J 5, H-5), 3.88 (3 H, s); δC (75.4 MHz, CDCl₃) 160.0 (C-4’), 152.6 (C-2), 149.3 (C-4), 148.3 (C-6), 130.6 (C-1’), 130.3 (C-2’), 125.7 (C-5), 121.0 (C-3), 113.8 (C-3’), 55.4 (C-5’); m/z (CI) 266 (81M+H+, 100 %); HRMS: Found: M⁺, 262.9941. C₁₂H₁₀⁷⁹BrNO requires 262.9946. ¹H NMR data and mp were consistent with those reported in the literature (Comins, D. L.; Mantlo, N.B. *J. Heterocycl. Chem.* 1983, **20**, 1239).

2. Preparation of 3-aryl –4-bromopyridines 10a and 10b has been described: see Karig, G.; Thasana, N.; Gallagher, T. *Synlett* 2002, 808-810.

3. Preparation of other biaryls 12a-c, 18a-c, 19.

*Suzuki Reaction; General Procedure.*
To a solution of requisite haloarene (see below) (0.38 mmol, 1.0 eq) in toluene (5 mL) and EtOH (1 mL) was added the appropriate boronic acid (see below) (0.57 mmol, 1.5 eq), Pd(PPh₃)₄ (0.019 mmol, 0.05 eq) and 2 M sodium carbonate solution (2 mL) and the mixture stirred vigorously and heated at reflux for 1-6 hours and the reaction was monitored by TLC. (Reactions involving 3- and 4-pyridine boronic acids were generally slower). When reaction was complete, the mixture was allowed to cool to room temperature then diluted with water. The mixture was extracted with Et₂O (3x10 mL), washed (with aq. NaHCO₃), dried (MgSO₄), and the solvent evaporated in vacuo. The crude product was purified by column chromatography eluting with EtOAc/hexanes.

2-Bromo-4’-methoxybiphenyl 12a
From 4-methoxyphenyl boronic acid and 2-bromo-1-iodobenzene and isolated in 68% yield as a pale yellow oil; Rf 0.38 (hexane-EtOAc, 6:1); δH (300 MHz, CDCl₃) 7.66 (1
H, dd, J 8.6, 0.7, H-3), 7.35 (2 H, AA′BB′, J 8.8, H-2), 7.30-7.35 (3 H, m, H-4, H-5, H-6), 6.96 (2 H, AA′BB′, J 8.8, H-3′), 3.86 (3 H, s, OMe); δC (75.4 MHz, CDCl₃) 159.0 (C-4), 142.2 (C-1), 137.1 (C-1′), 133.1, 131.4, 128.4, 127.4 (C-3, C-4, C-5, C-6), 130.6 (C-2′), 122.9 (C-2), 113.3 (C-3′), 55.3 (OMe); m/z (EI+) 277 (100 %);


2-Bromo-4'-methoxy-4-nitrobiphenyl 12b

From 4-methoxyphenyl boronic acid and 2-bromo-1-iodo-4-nitrobenzene isolated in 32 % yield as a yellow gum; Rf 0.40 (hexane-EtOAc, 1:1); δH (300 MHz, CDCl₃) 8.53 (1 H, d, J 2.4, H-3), 8.18 (1 H, dd, J 8.4, 2.4, H-5), 7.48 (1 H, d, J 8.4, H-6), 7.37 (2 H, AA′BB′, J 8.9, H-2), 6.99 (2 H, AA′BB′, J 8.9, H-3′), 3.87 (3 H, s, OMe); δC (75.4 MHz, CDCl₃) 160.0 (C-4), 148.7 (C-1), 146.9 (C-4), 131.6 (C-6), 131.3 (C-1′), 130.4 (C-2′), 128.4 (C-3), 123.0 (C-2′), 122.3 (C-5), 113.8 (C-3′), 55.4 (OMe); m/z (EI+) 310 (⁷⁵M+H⁺, 60 %), 309 (⁷⁵M⁺, 100), 308 (⁷⁹M+H⁺, 60), 307 (⁷⁹M⁺, 100); HRMS: Found: M⁺H⁺, 307.9902. C₁₁H₁₁⁺⁷⁹BrNO₂ requires 307.9922.

2-Bromo-4-nitrobiphenyl 12c

From phenyl boronic acid and 2-bromo-1-iodo-4-nitrobenzene isolated in 66 % yield as a pale orange solid; Rf 0.25 (hexane-DCM; 3:1); mp 84-86 °C (ethanol/petrol) (lit. (see below) mp 86 °C); δH (300 MHz, CDCl₃) 8.56 (1 H, d, J 2.2, H-3), 8.22 (1 H, dd, J 8.5, 2.2, H-5), 7.50 (1 H, d, J 8.5, H-6), 7.38-7.53 (5 H, m, H-2′, H-3′, H-4′); δC (75.4 MHz, CDCl₃) 149.0 (C-1), 147.3 (C-4), 139.1 (C-1′), 131.7 (C-6), 129.0 (C-2′), 128.8 (C-4′), 128.4 (C-3′), 128.3 (C-3), 123.0 (C-2), 122.3 (C-5); m/z (EI+) 279 (⁷⁵M⁺, 100 %), 277 (⁷⁹M⁺, 100); HRMS: Found: M⁺, 276.9744. C₁₀H₇⁺⁷⁵BrNO₂ requires 276.9738. This compound has been reported previously in the literature (Byron, D. J; Gray, G. W.; Ibbotson, G. A.; Worrall, B. M. J. Chem. Soc. 1963, 2246) but no spectroscopic data have been described.

Preparation of 18a-c was carried out using the general Suzuki procedure (described above) with pyridine 4-boronic acid and the requisite iodoarene.

4-(2'-Bromo-4'-nitrophenyl)pyridine 18a

From pyridine 4-boronic acid and 2-bromo-1-iodo-4-nitrobenzene and isolated in 55 % yield as a off-white crystalline solid; Rf 0.14 (hexane-EtOAc, 1:1); δH (300
4-(2'-Bromophenyl)pyridine 18b
From pyridine 4-boronic acid and 2-bromo-1-iodobenzene and isolated in 32 % yield as off-white crystalline solid; Rf 0.22 (hexane-EtOAc, 1:1); δH (300 MHz, CDCl3) 8.68 (2 H, AA′BB′, J 6.2, H-2), 7.69 (1 H, dd, J 7.9, 1.2, H-3′), 7.40 (1 H, ddd, J 7.7, 7.3, 1.2, H-5′), 7.35 (2 H, AA′BB′, J 6.2, H-3), 7.29 (1 H, dd d, J 7.9, 7.7, 1.9, H-4′), 7.26 (1 H, dd, J 7.3, 1.9, H-6′); δC (75.4 MHz, CDCl3) 149.6 (C-2), 148.6 (C-4), 139.8 (C-1′), 133.4 (C-3′), 130.7, (C-4′), 129.8 (C-6′), 127.6 (C-5′), 124.2 (C-3), 121.7 (C-2′); m/z (EI+) 235 (81M+, 100 %), 233 (79M+, 100); HRMS: Found: M+, 232.9842. C11H879BrN requires 232.9840.

4-(2'-Bromo-4'-methoxyphenyl)pyridine 18c
From pyridine 4-boronic acid and 2-bromo-1-iodo-4-methoxybenzene and isolated in 38 % yield as creamy white crystals Rf 0.17 (hexane-EtOAc, 3:1); mp 92-93 ºC; δH (300 MHz, CDCl3) 8.65 (2 H, AA′BB′, J 6, H-2), 7.34 (2 H, AA′BB′, J 6, H-3), 7.24 (1 H, d, J 2.5, H-3′), 7.23 (1 H, d, J 8.6, H-6′), 6.95 (1 H, dd, J 8.6, 2.5, H-5′), 3.85 (3 H, s, OMe); δC (75.4 MHz, CDCl3) 160.1 (C-4′), 149.5 (C-2), 148.4 (C-4), 132. (C-1′), 131.4 (C-6′), 124.5 (C-3), 122.1 (C-2′), 118.6 (C-3′), 113.9 (C-5′), 55.7 (OMe); m/z (EI+) 265 (81M+, 35 %), 263 (79M+, 35); HRMS: Found: M+, 264.9925. C12H1079BrNO requires 264.9925.

3-(2'-Bromo-4'-nitrophenyl)pyridine 19
Prepared from pyridine-3-boronic acid and 2-bromo-1-iodo-4-nitrobenzene and isolated in 40% yield as cream crystals; Rf 0.14 (hexane–EtOAc, 1:1); δH (300 MHz, CDCl3) 8.72 (1 H, dd, J 3.5, H-6), 8.68 (1 H, d, J 1.6, H-2), 8.59 (1 H, d, J 2.0, H-3′), 8.28 (1 H, dd, J 8.4, 2.4, H-5′), 7.81-7.76 (1 H, m, H-4), 7.53 (1 H, d, J 8.4, H-6′), 7.46-7.41 (1 H, m, H-5); δC (75.4 MHz, CDCl3) 150.0 and 149.4 (C-6 or C-2), 145.3/134.9/123.2 (C-1′, C-2′, C-4′ or C-3 – these could not be assigned and one quaternary signal was not seen), 136.5/128.5/123.0/122.6 (C-4, C-5, C-3′ or C-6′ –
these could not be assigned), 131.7 (C-5'); m/z (EI+) 280 (81M+, 100%), 278 (79M+, 100%); HRMS: Found: M+, 277.9704. C_{17}H_{2}N_{2}O_{2}Br requires 277.9691.

**Part B. Heck Reactions**

**General Procedure** We wish to make it clear that this procedure was followed for all of the Heck reactions described in this paper. It is important to appreciate that the Heck conditions employed may have a significant effect on the distribution of products, and in order to maintain consistency we have used the same conditions throughout.

Some modified Heck reaction conditions were examined and these are reported in the text, but for all the results shown in Schemes 2, 3 and 5, this general procedure was used.

Bromoarene (0.11 mmol, 1.0 eq) was dissolved in dry, distilled acetonitrile (2 mL) in a sealed tube. Pd(OAc)$_2$ (2.4 mg, 0.01 mmol, 0.1 eq), P(o-Tol)$_3$ (6.5 mg, 0.02 mmol, 0.2 eq), triethylamine (76 µl, 0.54 mmol, 5 eq) and ethyl acrylate (35 µl, 0.32 mmol, 3 eq) were added, the tube was flushed with nitrogen, sealed and heated to 125 °C for 20 hours. The mixture was cooled to room temperature, diluted with water, extracted with CH$_2$Cl$_2$ (2x10 mL) and dried (MgSO$_4$). Filtration followed by evaporation *in vacuo* gave an orange oil. The crude product was assayed by $^1$H NMR prior to purification by column chromatography and/or HPLC, but yields and product ratios are based on isolated compounds, homogeneous by TLC and $^1$H NMR.

Numbering system used is shown below.
Products resulting from Heck reaction of 1a

Retention product 3a: Rf 0.18 (hexane–EtOAc, 1:1); mp 112-113 °C (hexane); δH (300 MHz, CDCl3) 8.95 (1 H, s, H-2), 8.70 (1 H, d, J 5.0, H-6), 8.37 (2 H, AA’BB’, J 8.9, H-2'), 7.55 (1 H, d, J 15.9, H-1”), 7.54 (2 H, AA’BB’, J 8.9, H-3’), 7.31 (1 H, dd, J 4.9, 0.6, H-5), 6.52 (1 H, d, J 15.9, H-2”), 4.24 (2 H, q, J 7.2), 1.32 (3 H, t, J 7.2); δC (75.4 MHz, CDCl3) 166.7 (C=O), 151.4 (C-6), 149.6 (C-2), 149.0/ 147.6/ 144.5 (C-4’, C-4, C-1’), 139.9 (C-1”), 131.1 (C-3’), 129.0 (C-3), 124.8, 124.7 (C-2’, C-5), 123.1 (C-2”), 61.8, 15.1; m/z (EI+) 298 (M+, 100%); HRMS: Found: M+, 298.0941. C16H14N2O4 requires 298.0954.

Crossover product 4a: Rf 0.13 (hexane–EtOAc; 1:1); mp 155-157 °C (hexane); δH (300 MHz; CDCl3) 8.77 (2 H, AA’BB’, J 6.1, H-2), 8.58 (1 H, d, J 2.2, H-6’), 8.31 (1 H, dd, J 8.6, 2.2, H-4’), 7.0 (1 H, d, J 15.9, H-2”), 7.55 (1 H, d, J 8.6, H-3’), 7.28 (2 H, AA’BB’, J 6.1, H-3), 6.57 (1 H, d, J 15.9, H-2”), 4.25 (2 H, q, J 7.2), 1.32 (3 H, t, J 7.2); δC (75.4 MHz, CDCl3) 165.7 (C=O), 150.3 (C-2), 148.2 (C-4), 145.7/ 145.4 (C-5’, C-2’), 139.9 (C-1”), 134.4 (C-1’), 131.3 (C-3’), 124.0 (C-3), 124.2/ 123.4/ 122.2 (C-4’, C-6’, C-2”), 61.0, 14.2; m/z (CI) 299 (M+H+, 100%); HRMS: Found: M+H+, 299.1028. C16H15N2O4 requires 299.1032.

Reduction product 2: Rf 0.16 (hexane–EtOAc, 1:1); δH (270 MHz, CDCl3) 8.75 (2 H, AA’BB’, J 6.1, H-2), 8.36 (2 H, AA’BB’, J 8.9, H-3’), 7.80 (2 H, AA’BB’, J 8.9, H-2’), 7.53 (2 H, AA’BB’, J 6.1, H-3); δC (100.6 MHz, CDCl3) 150.9 (C-2), 148.1/ 146.2/ 144.7 (C-4, C-1’, C-4’), 128.2/ 124.6/ 121.9 (C-2’, C-3’, C-3). These data are consistent with those described in the literature for this compound (Ishikura, M.; Ohta, T.; Tershima, M. Chem. Pharm. Bull. 1985, 33, 4755).

Products resulting from Heck reaction of 1b

3b: Rf 0.23 (hexane–EtOAc, 1:1); mp 98-100 °C (hexane); δH (300 MHz, CDCl3) 8.89 (1 H, s, H-2), 8.63 (1 H, d, J 4.4, H-6), 7.69 (1 H, J 16.1, H-1”), 7.44-7.52 (3 H, m, H-2’, H-1”), 7.29-7.57 (3 H, m, H-3’, H-5), 6.49 (1 H, d, J 16.1, H-2”), 4.23 (2 H, q, J 7.2), 1.30 (3 H, t, J 7.2); δC (75.4 MHz, CDCl3) 166.3 (C=O), 150.3 (C-6), 149.3 (C-4), 148.5 (C-2), 140.6 (C-1”), 137.2 (C-1’), 129.3 (C-2’), 128.9 (C-4’), 128.9/ 128.8 (C-3’, C-3), 124.4 (C-5), 120.9 (C-2”), 60.7, 14.3; m/z (CI) 254 (M+H+, 100%); HRMS: Found: M+H+, 254.1177. C16H16NO2 requires 254.1181.
4b: Rf 0.17 (hexane–EtOAc, 1:1); mp 76-77 °C (hexane); δ_H (300 MHz, CDCl₃) 8.69 (2 H, AA'BB'; J 5.7, H-2), 7.73 (1 H, m, ArH'), 7.64 (1 H, d, J 15.9, H-1"), 7.44-7.50 (2 H, m, ArH'), 7.35 (1 H, m, H-6), 7.27 (2 H, AA'BB'; J 7.7, H-3), 6.42 (1 H, d, J 15.9, H-2"), 4.22 (2 H, q, J 7.1), 1.29 (3 H, t, J 7.1); δ_C (75.4 MHz, CDCl₃) 156.5 (C=O), 149.8 (C-2), 147.8 (C-4), 142.4 (C-1"), 139.8 (C-2'), 132.6 (C-1'), 130.1/130.0/128.9/127.1 (C-3', C-4', C-5', C-6'), 124.6 (C-3), 120.4 (C-2"), 60.6, 14.3; m/z (CI) 254 (M+H⁺, 100 %); HRMS: Found: M+H⁺, 254.1182. C₁₆H₁₆NO₂ requires 254.1181.

Products resulting from Heck reaction of 1c

Retention product 3c: Rf 0.25 (hexane-EtOAc, 1:1); mp 76-78 °C (hexane); δ_H (270 MHz, CDCl₃) 8.85 (1 H, s, H-2), 8.59 (1 H, d, J 4.9, H-6), 7.72 (1 H, d, J 16.1, H-1"), 7.29 (2 H, AA'BB'; J 8.9, H-2"), 7.27 (1 H, d, J 4.9, H-5), 7.01 (2 H, AA'BB'; J 8.9, H-3'), 6.48 (1 H, d, J 16.1, H-2"), 4.24 (2 H, q, J 7.2, H-7), 3.86 (3 H, s, OMe), 1.31 (3 H, t, J 7.2, H-8); δ_C (67.9 MHz, CDCl₃) 166.4 (C=O), 160.3, 150.2, 149.0, 148.7, 141.0, 130.7, 129.6, 128.7, 124.2, 120.7, 114.3, 60.6 (OMe), 55.4, 14.3; m/z (EI+) 283 (M⁺, 38 %); HRMS: Found: M⁺, 283.1208. C₁₇H₁₇NO₃ requires 283.1208.

Crossover product 4c: Rf 0.17 (hexane-EtOAc, 1:1); mp 54-56 °C (hexane); δ_H (300 MHz, CDCl₃) 8.66 (2 H, AA'BB'; J 6.2, H-2), 7.63 (1 H, d, J 15.8, H-1"), 7.29 (1 H, d, J 8.5, H-3'), 7.23 (2 H, AA'BB'; J 6.2, H-3), 7.19 (1 H, d, J 2.6, H-6'), 7.03 (1 H, dd, J 8.5, 2.6, H-4'), 6.41 (1 H, d, J 15.8, H-2"), 4.24 (2 H, q, J 7.2), 3.87 (3 H, s, OMe), 1.31 (3 H, t, J 7.2); δ_C (75.4 MHz, CDCl₃) 167.1 (C=O), 159.9 (C-5'), 149.7 (C-2), 147.3 (C-4), 142.6 (C-1"), 133.8, 132.6 (C-2', C-1'), 131.4 (C-3'), 124.7 (C-3), 120.5 (C-2"), 116.3 (C-4'), 111.7 (C-6'), 60.6, 55.5 (OMe), 14.2; m/z (EI+) 283 (M⁺, 45%); HRMS: Found: M⁺, 283.1208. C₁₇H₁₇NO₃ requires 283.1208.

Products resulting from Heck reaction of 5 and 19 (for yields, see text of paper)

6: Isolated as colorless crystals; Rf 0.40 (hexane–EtOAc, 1:1); mp 134-135 °C (EtOAc/Hexanes); δ_H (300 MHz, CDCl₃) 8.72 (1 H, dd, J 4.6, 1.6, H-6), 8.36 (2 H, AA'BB'; J 8.8, H-3'), 7.67 (1 H, dd, J 7.8, 1.6, H-4), 7.59 (1 H, d, J 15.2, H-1"), 7.53 (2 H, AA'BB'; J 8.8, H-2"), 7.40 (1 H, dd, J 7.8, 4.6, H-5), 7.12 (1 H, d, J 15.2, H-2"), 4.23 (2 H, q, J 7.1, H-4"), 1.29 (3 H, t, J 7.1, H-5"); δ_C (75.4 MHz, CDCl₃) 165.8 (C-
7: Isolated as colorless crystals; R_f 0.13 (hexane–EtOAc, 1:1); mp 119-120 °C (hexane); τH (300 MHz, CDCl₃) 8.74 (1 H, br s, H-6), 8.64 (1 H, br s, H-2), 8.58 (1 H, d, J 2.2, H-6'), 8.32 (1 H, dd, J 8.4, 2.4, H-4'), 7.70-7.66 (1 H, m, H-4), 7.58 (1 H, d, J 15.9, H-1''), 7.56 (1 H, d, J 8.4, H-5), 7.49-7.44 (1 H, m, H-5), 6.69 (1 H, d, J 15.9, H-2''), 4.24 (2 H, q, J 7.1), 1.31 (3 H, t, J 7.1); τC (75.4 MHz, CDCl₃) 165.8 (C-3''), 150.1 (C-6), 149.7 (C-2), 148.0/144.6/134.7 (C-3, C-1' or C-2' or C-5' – two signals overlap), 140.2 (C-1''), 136.8 (C-4), 131.7 (C-3'), 124.2 (C-4'), 123.4 (C-5'), 123.2 (C-2''), 122.2 (C-6'), 61.0, 14.2; m/z (EI+) 298 (M+, 2%); HRMS: Found: M+, 298.0950. C₁₆H₁₄N₂O₄ requires 298.0954.

8: Isolated as a pale yellow oil; R_f 0.23 (hexane–EtOAc, 1:1); τH (300 MHz, CDCl₃) 8.60 (1 H, dd, J 4.7, 1.7, H-6), 8.33 (2 H, AA'BB', J 8.8, H-3'), 7.55 (2 H, AA'BB', J 8.8, H-2'), 7.51 (1 H, dd, J 7.7, 1.7, H-4), 7.24 (1 H, dd, J 7.7, 1.7, H-5), 4.08 (2 H, q, J 7.2), 3.03 (2 H, t, J 7.2, H-1''), 2.81 (2 H, t, J 7.2, H-2''), 1.20 (3 H, t, J 7.2); τC (75.4 MHz, CDCl₃) 173.1 (C-3''), 156.7 (C-2), 149.1 (C-6), 146.3 (C-3 or C-1' or C-4'), 137.0 (C-4), 134.9 (C-3 or C-1' or C-4'), 130.2 (C-2'), 125.6 (C-3 or C-1' or C-4'), 123.8 (C-3'), 121.3 (C-5), 60.4, 32.4 (C-2''), 30.0 (C-1''), 14.2; m/z (EI+) 300 (M+, 23%); HRMS: Found: M+, 300.1105. C₁₆H₁₆N₂O₄ requires 300.1110.

9: Isolated as cream crystals; R_f 0.09 (hexane–EtOAc, 1:1); mp 138-140 °C (hexane); τH (300 MHz, CDCl₃) 8.90 (1 H, d, J 1.8, H-2), 8.70 (1 H, dd, J 4.8, 1.3, H-6), 8.36 (2 H, AA'BB', J 9.0, H-3'), 7.97-7.92 (1 H, m, H-4), 7.77 (2 H, AA'BB', J 9.0, H-2'), 7.48-7.43 (1 H, m, H-5); τC (75.4 MHz, CDCl₃) 171.2 (C-3), 150.0 (C-6), 148.3 (C-2), 147.7/144.3 (C-4' and C-1''), 134.7 (C-4), 128.0 (C-2''), 124.4 (C-3'), 123.9 (C-5); m/z (EI+) 200 (M+, 71%). These data are consistent with those described in the literature for this compound (Klemm, L. H.; Dorsey, J. J. Heterocycl. Chem. 1991, 28, 1153).
Product resulting from Heck reaction of 10a

11a: Isolated as a colorless solid; Rf = 0.26 (1:1 EtOAc:hexane); mp 154-155 °C (EtOAc:hexane); 1H NMR (300 MHz, C6D6) δ 8.44 (1 H, s, H-2), 7.84 (1 H, d, J 8.8, H-6), 7.73 (2 H, AA'BB', J 8.8, H-3'), 7.46 (d, J 15.9, H-1''), 6.88 (1 H, d, J 8.8 Hz, H-5), 6.69 (2 H, AA'BB', J 8.8, H-2'), 6.33 (1 H, d, J 15.9, H-2''), 4.01 (2 H, q, J 7.1), 0.99 (3 H, t, J 7.1); 13C NMR (75 MHz, C6D6) δ 166.1, 142.9, 140.3, 134.7, 131.1, 128.3, 125.1, 124.7, 124.3, 61.6, 14.8; MS (EI+) m/z 298 (M+, 48%); HRMS: Found: 298.0953. C16H14N2O4 requires 298.0936.

Product resulting from Heck reaction of 10b

11b: Isolated as a colorless solid; Rf = 0.34 (1:1 EtOAc:hexane); mp 68-69 °C (EtOAc:hexane); 1H NMR (300 MHz, CDCl3) δ 8.63 (1 H, s, H-2), 8.59 (1 H, d, J 8.8, H-6) 7.68 (1 H, d, J 16.0, H-1''), 7.48 (1 H, d, J 5.2, H-5), 7.28 (2 H, AA'BB', J 8.8, H-2'), 7.08 (2 H, AA'BB', J 8.8, H-3'), 6.54 (1 H, d, J 16.0, H-2''), 4.19 (2 H, q, J 7.2), 3.87 (3 H, s, OMe), 1.31 (3 H, t, J 7.2); 13C NMR (75 MHz, CDCl3) δ 166.1, 159.8, 151.3, 148.3, 141.1, 139.7, 136.7, 131.1, 128.4, 123.0, 120.2, 114.2, 60.8, 55.4, 14.2; MS (EI+) m/z 283 (M+, 40%); HRMS: Found: 283.1208. C17H17NO3 requires 283.1211.

Products resulting from Heck reaction of 12a-c

13a: Isolated as colorless crystals; mp 63-65 °C (hexane); δH (300 MHz, CDCl3) 7.76 (1 H, d, J 15.9, H-1''), 7.70-7.66 (1 H, m, H-3'), 7.45-7.32 (3 H, m, H-6, H-4 and H-5), 7.24 (2 H, AA'BB', J 8.8, H-2'), 7.18 (2 H, AA'BB', J 8.8, H-3'), 6.39 (1 H, d, J 15.9, H-2''), 4.22 (2 H, q, J 7.2), 3.86 (3 H, s, OMe), 1.29 (3 H, t, J 7.2); δC (75.4 MHz, CDCl3) 167.0 (C-3''), 159.2 (C-4'), 144.0 (C-1''), 142.6 (C-2), 132 and 132.2 (C-1 and C-1'), 131.0 (C-2'), 130.5 (C-6), 129.8 (C-5), 127.3 (C-4), 126.8 (C-3), 118.9 (C-2''), 113.8 (C-3'), 60.4, 55.4 (OMe), 14.3; m/z (EI+) 282 (M+, 50%); HRMS: Found: M+, 282.1263. C18H18O3 requires 282.1256.

13b: Isolated as colorless crystals; Rf 0.21 (hexane–EtOAc, 4:1); mp 122-125 °C (hexane); δH (300 MHz, CDCl3) 8.53 (1 H, d, J 2.4, H-6), 8.24 (1 H, dd, J 8.6, 2.4, H-
4), 7.72 (1 H, d, J 16.0, H-1'”), 7.53 (1 H, d, J 8.6, H-3), 7.27 (2 H, AABB', J 8.8, H-2''), 7.02 (2 H, AABB', J 8.8, H-3'), 6.55 (1 H, d, J 16.0, H-2''), 4.25 (2 H, q, J 7.1), 3.88 (3 H, s, OMe), 1.32 (3 H, t, J 7.1); δC (75.4 MHz, CDCl3) 166.2 (C-3''), 160.2 (C-4''), 148.4 and 147.1 (C-2 and C-1), 141.8 (C-1'”), 13.0 (C-1), 131.4 (C-3), 130.9 (C-2''), 130.0 (C-5), 124.0 (C-4), 122.1 (C-6), 121.7 (C-2''), 114.2 (C-3), 60.8, 55.4 (OMe), 14.3; m/z (EI+) 327 (M+, 100%); HRMS: Found: M+, 327.1107. C18H17NO5 requires 327.1107.

13c: Isolated as colorless crystals; Rf 0.28 (hexane–EtOAc, 4:1); mp 107-110 °C (hexane); δH (300 MHz, CDCl3) 8.56 (1 H, d, J 2.4, H-6), 8.26 (1 H, dd, J 8.5, 2.4, H-4), 7.69 (1 H, d, J 16, H-1'”), 7.55 (1 H, d, J 8.5, H-3), 7.52-7.43 (3 H, m, H-2' and H-4'), 7.35-7.31 (2 H, m, H-3'), 6.56 (1 H, d, J 16.0, H-2''), 4.23 (2 H, q, J 7.2), 1.31 (1 H, t, J 7.2); δC (75.4 MHz, CDCl3) 166.1 (C-3''), 148.6 and 147.4 (C-2 and C-5), 141.4 (C-1'”), 137.8 and 134.1 (C-1 and C-1'), 131.6 (C-3), 129.5 (C-3'), 128.9 (C-4'), 128.7 (C-2''), 124.0 (C-4), 122.0 (C-2''), 60.8, 14.2; m/z (EI+) 297 (M+, 45%); HRMS: Found: M+, 297.1002. C17H15NO4 requires 297.1001.

14c: Isolated as colorless crystals; Rf 0.27 (hexane–EtOAc, 4:1); mp 79-83 °C δH (300 MHz, CDCl3) 8.32 (2 H, AABB', J 8.9, H-3'), 7.75-7.71 (1 H, m, Ph-H), 7.60 (1 H, d, J 16.0, H-1'”), 7.54-7.46 (2 H, m, Ph-H), 7.50 (2 H, AABB', J 8.9, H-2''), 7.39-7.31 (1 H, m, Ph-H), 6.43 (1 H, d, J 16.0, H-2''), 4.22 (2 H, q, J 7.2), 1.29 (3 H, t, J 7.2); m/z (EI+) 297 (M+, 50%); HRMS: Found: M+, 297.1017. C17H15NO4 requires 297.1001. We were unable to obtain 13C NMR data for 14c due to a lack of material.

**Products resulting from Heck reaction of 18a-c**

The products of these Heck reactions correspond to 3a-c and 4a-c and spectroscopic data for these compounds are described above.