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Supporting Information

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Catalytic Arylation Reactions via C–H Bond Activation with Aryl Tosylates

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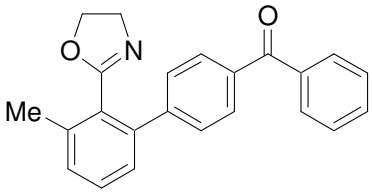
General remarks

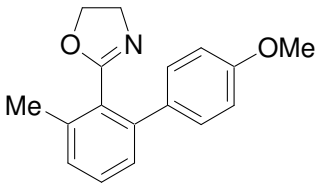
Catalytic reactions were carried out on a 1 mmol scale under a N_2 atmosphere using pre-dried glassware. Chemicals were obtained from commercial sources, and were used without further purification. NMP was freshly distilled from CaH_2 under N_2. Yields refer to isolated compounds, estimated to be > 95% pure as determined by ^{1}H-NMR and GC. Flash chromatography: Macherey-Nagel silica gel 60 (70–230 mesh). NMR: Spectra were recorded on a Bruker ARX 300 instrument in the solvent indicated; chemical shifts (δ) are given in ppm.

Representative procedure for ruthenium-catalyzed cross-coupling reactions of aryl tosylates (Table 2, entry 10): A solution of [($RuCl_2$(*p*-cymene)]$_2$ (15 mg, 0.025 mmol, 2.5 mol%), **8** (43 mg, 0.10 mmol, 10 mol%), K_2CO_3 (207 mg, 1.50 mmol), **1** (163 mg, 1.01 mmol) and **2j** (424 mg, 1.20 mmol) in dry NMP (2.0 mL) was stirred for 23 h at 120 °C under N_2. Et_2O (75 mL) and H_2O (75 mL) were added to the reaction mixture. The separated aqueous phase was extracted with Et_2O (2 × 75 mL). The combined organic layers were washed with H_2O and brine, dried over $MgSO_4$ and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (*n*-pentane/Et_2O, 1/1 → 1/3) to yield **3j** as a pale brown solid (320 mg, 94 %).



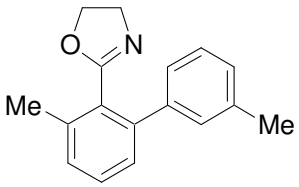
3j

[2`-(4,5-Dihydro-oxazol-2-yl)-3`-methyl-biphenyl-4-yl]-phenyl-methanone (**3j**): ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.87-7.78 (m, 4H), 7.63-7.45 (m, 5H), 7.43-7.21 (m, 3H), 4.18 (t, *J* = 9.3 Hz, 2H), 3.88 (t, *J* = 9.3 Hz, 2H), 2.44 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 196.4, 164.2, 145.6, 140.9, 137.9, 137.8, 136.1, 132.3, 130.0, 130.0, 129.7, 129.6, 128.4, 128.3, 128.1, 127.1, 67.3, 55.2, 19.8. IR (KBr): 3063, 3031, 2879, 1943, 1655, 1605, 1461, 1447, 1349, 1314, 1148, 1048, 976 cm^{-1}. MS (EI) *m/z* (relative intensity) 341 (25) [M^+], 340 (100), 296 (3), 191 (1), 165 (3), 105 (9), 77 (11). HR-MS (EI) *m/z* calcd for $C_{23}H_{19}NO_2$ 341.1416, found 341.1391.



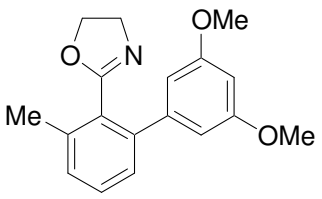
3a

2-(4`-Methoxy-3-methyl-biphenyl-2-yl)-4,5-dihydro-oxazole (3a) (Table 2, entry 1): The representative procedure was followed, using oxazoline **1** (164 mg, 1.02 mmol) and aryl tosylate **2a** (334 mg, 1.20 mmol). After 23 h, purification by chromatography (*n*-pentane/Et_2O, 1/1 → 1/2) yielded **3a** (194 mg, 71 %) as a light brown oil. The spectral data were in accordance with those reported in the literature.[1] ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.37-7.28 (m, 3H), 7.18 (md, *J* = 8.1 Hz, 2H), 6.90 (md, *J* = 8.8 Hz, 2H), 4.15 (t, *J* = 9.3 Hz, 2H), 3.91-3.81 (m, 5H), 2.40 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.6, 158.8, 141.5, 137.4, 133.6, 129.5, 129.4, 128.5, 128.1, 127.1, 113.4, 67.1, 55.2, 55.0, 19.7. IR (KBr): 3062, 2933, 1884, 1666, 1610, 1514, 1461, 1346, 1291, 1248, 1180, 937 cm^{-1}. MS (EI) *m/z* (relative intensity) 267 (17) [M^+], 266 (100), 222 (4), 152 (2). HR-MS (EI) *m/z* calcd for $C_{17}H_{17}NO_2$ 267.1225, found 267.1259.



3b

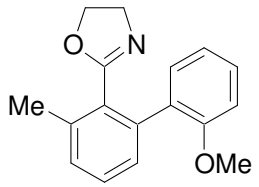
2-(3,3`-Dimethyl-biphenyl-2-yl)-4,5-dihydro-oxazole (3b) (Table 2, entry 2): The representative procedure was followed, using oxazoline **1** (163 mg, 1.01 mmol) and aryl tosylate **2b** (316 mg, 1.20 mmol). After 23 h, purification by chromatography (*n*-pentane/Et_2O, 3/1 → 1/1) yielded biphenyl **3b** (206 mg, 81 %) as a brown oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.36-7.07 (m, 7H), 4.13 (t, J = 9.4 Hz, 2H), 3.84 (t, J = 9.3 Hz, 2H), 2.40 (s, 3H), 2.37 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.5, 142.1, 141.1, 137.5, 137.4, 129.5, 129.2, 128.8, 128.1, 127.8, 127.2, 125.4, 67.1, 58.3, 55.1, 21.4, 19.8. IR (KBr): 2922, 1660, 1458, 1250, 1234, 1041, 971, 936, 985, 776 cm^{-1}. MS (EI) *m/z* (relative intensity) 251 (16) [M^+], 250 (100), 206 (6), 165 (3), 152 (1). HR-MS (EI) *m/z* calcd for $C_{17}H_{17}NO$ 251.1310, found 251.1275.



3c

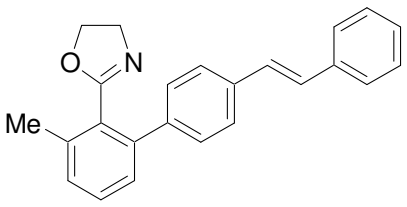
2-(3`,5`-Dimethoxy-3-methyl-biphenyl-2-yl)-4,5-dihydro-oxazole (3c)

(Table 2, entry 3): The representative procedure was followed, using oxazoline **1** (161 mg, 1.00 mmol) and aryl tosylate **2c** (370 mg, 1.20 mmol). After 23 h, purification by chromatography (*n*-pentane/Et_2O, 3/1 → 0/1) yielded **3c** (151 mg, 51 %) as a brown oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.34 (t, J = 7.6 Hz, 1H), 7.25-7.19 (m, 2H), 6.60 (d, J = 2.2 Hz, 2H), 6.43 (t, J = 2.2 Hz, 1H), 4.18 (t, J = 9.4 Hz, 2H), 3.90 (t, J = 9.4 Hz, 2H), 3.79 (s, 6H), 2.41 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.5, 160.3, 143.5, 141.8, 137.5, 129.4, 129.1, 128.0, 127.0, 106.5, 99.8, 67.3, 55.3, 55.2, 19.7. IR (KBr): 3064, 2936, 1664, 1597, 1462, 1418, 1351, 1236, 1204, 1155, 1064, 1046, 972, 939, 845 cm^{-1}. MS (EI) *m/z* (relative intensity) 297 (26) [M^+], 296 (100), 282 (10), 252 (7), 181 (2), 153 (3), 115 (2). HR-MS (EI) *m/z* calcd for $C_{18}H_{19}NO_3$ 297.1365, found 297.1354.



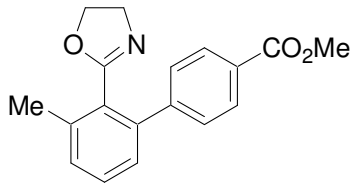
3d

2-(2`-Methoxy-3-methyl-biphenyl-2-yl)-4,5-dihydro-oxazole (3d) (Table 2, entry 4): The representative procedure was followed, using oxazoline **1** (162 mg, 1.00 mmol) and aryl tosylate **2d** (334 mg, 1.20 mmol). After 23 h, purification by chromatography (*n*-pentane/Et_2O, 3/1 → 0/1) yielded product **3d** (134 mg, 50 %) as a grey solid. The spectral data were in accordance with those reported in the literature.[1] ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.37-7.17 (m, 5H), 6.99-6.89 (m, 2H), 4.05 (t, J = 9.3 Hz, 2H), 3.84-3.73 (m, 5H), 2.43 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.5, 156.5, 138.7, 137.2, 130.7, 130.2, 129.0, 128.9, 128.8, 128.5, 128.2, 120.1, 110.6, 66.9, 55.5, 55.1, 20.1. IR (KBr): 3063, 2891, 1667, 1496, 1432, 1340, 1234, 1078, 1035, 1020, 935 cm^{-1}. MS (EI) *m/z* (relative intensity) 266 (1) [M-H$^+$], 237 (15), 236 (100), 192 (13), 165 (5). HR-MS (EI) *m/z* calcd for $C_{17}H_{17}NO_2$ 267.1259, found 267.1252.



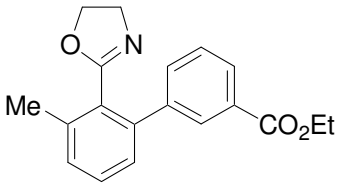
3e

2-(3-Methyl-4′-styryl-biphenyl-2-yl)-4,5-dihydro-oxazole (3e) (Table 2, entry 5): The representative procedure was followed, using oxazoline **1** (163 mg, 1.01 mmol) and aryl tosylate **2e** (421 mg, 1.20 mmol). After 23 h, purification by chromatography (*n*-pentane/Et_2O, 10/1 → 4/1) yielded **3e** (285 mg, 85 %) as a colorless solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.55-7.48 (m, 4H), 7.44-7.32 (m, 5H), 7.29-7.20 (m, 3H), 7.14 (s, 2H), 4.16 (t, *J* = 8.7 Hz, 2H), 3.89 (t, *J* = 8.9 Hz, 2H), 2.43 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.4, 141.6, 140.6, 137.6, 137.3, 136.1, 129.5, 129.0, 128.7, 128.6, 128.3, 128.1, 127.6, 127.1, 126.5, 126.2, 67.2, 55.2, 19.8. IR (KBr): 3060, 2968, 2902, 2882, 1659, 1594, 1465, 1344, 1251, 1108, 1043, 970, 896 cm^{-1}. MS (EI) *m/z* (relative intensity) 340 (4), 339 (25) [M^+], 338 (100), 265 (3), 195 (2), 126 (2). HR-MS (EI) *m/z* calcd for $C_{24}H_{21}NO$ 339.1623, found 339.1582.



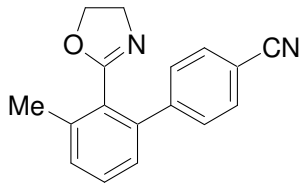
3f

2`-(4,5-Dihydro-oxazol-2-yl)-3`-methyl-biphenyl-4-carboxylic acid methyl ester (3f) (Table 2, entry 6): The representative procedure was followed, using oxazoline **1** (161 mg, 1.00 mmol) and aryl tosylate **2f** (369 mg, 1.20 mmol). After 23 h, purification by chromatography (*n*-pentane/Et_2O, 1/1 → 1/2) yielded **3f** (275 mg, 93 %) as a pale yellow solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.96 (md, J = 8.6 Hz, 2H), 7.50 (md, J = 8.6 Hz, 2H), 7.41-7.33 (m, 1H), 7.29-7.17 (m, 2H), 4.15 (t, J = 9.4 Hz, 2H), 3.85 (t, J = 9.4 Hz, 2H), 2.62 (s, 3H), 2.42 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 167.0, 164.1, 146.2, 140.8, 137.8, 135.7, 129.7, 129.6, 129.4, 128.6, 128.1, 127.0, 67.2, 55.1, 29.6, 19.8. IR (KBr): 3064, 2878, 1726, 1666, 1610, 1460, 1436, 1314, 1280, 1196, 1042, 932, 856 cm^{-1}. MS (EI) *m/z* (relative intensity) 295 (17) [M^+], 294 (100), 264 (3), 250 (4), 191 (2), 165 (3). HR-MS (EI) *m/z* calcd for $C_{18}H_{17}NO_3$ 295.1208, found 295.1182.



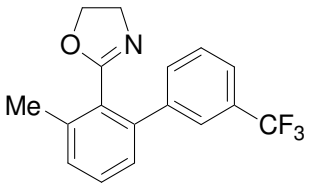
3g

2`-(4,5-Dihydro-oxazol-2-yl)-3`-methyl-biphenyl-3-carboxylic acid ethyl ester (3g) (Table 2, entry 7): The representative procedure was followed, using oxazoline **1** (165 mg, 1.02 mmol) and aryl tosylate **2g** (390 mg, 1.20 mmol). After 23 h, purification by chromatography (*n*-pentane/Et_2O, 3/1 → 1/1) yielded biphenyl **3g** (231 mg, 73 %) as a brown oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.18–8.09 (m, 1H), 8.04–7.97 (m, 1H), 7.65–7.57 (m, 1H), 7.50–7.34 (m, 2H), 7.28–7.19 (m, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.17 (t, *J* = 9.4 Hz, 2H), 3.85 (t, *J* = 9.4 Hz, 2H), 2.43 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.5, 164.2, 141.3, 140.9, 137.7, 132.8, 130.4, 129.6, 129.5, 129.4, 128.3, 128.2, 127.1, 127.0, 67.2, 60.9, 55.2, 19.8, 14.3. IR (KBr): 3064, 2979, 2902, 1715, 1666, 1582, 1463, 1367, 1308, 1249, 1122, 937, 896 cm^{-1}. MS (EI) *m/z* (relative intensity) 309 (23) [M^+], 308 (100), 280 (18), 264 (5), 165 (4), 152 (2). HR-MS (EI) *m/z* calcd for $C_{19}H_{19}NO_3$ 309.1365, found 309.1321.



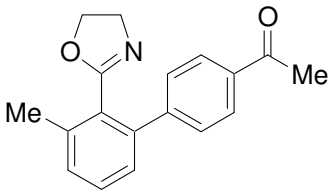
3h

2`-(4,5-Dihydro-ozazol-2-yl)-3`-methyl-biphenyl-4-carbonitrile (3h) (Table 2, entry 8): The representative procedure was followed, using oxazoline **1** (162 mg, 1.00 mmol) and aryl tosylate **2h** (329 mg, 1.20 mmol). After 23 h, purification by chromatography (*n*-pentane/Et_2O, 3/1 → 0/1) yielded product **3h** (155 mg, 59 %) as a red solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.66 (md, *J* = 8.6 Hz, 2H), 7.51 (md, *J* = 8.6 Hz, 2H), 7.44-7.34 (m, 1H), 7.32-7.25 (m, 1H), 7.21-7.14 (m, 1H), 4.17 (t, *J* = 9.5 Hz, 2H), 3.87 (t, *J* = 9.4 Hz, 2H), 2.43 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 163.9, 146.0, 140.1, 138.0, 131.8, 130.1, 129.7, 129.2, 128.0, 126.9, 118.9, 110.0, 67.3, 55.1, 19.8. IR (KBr): 2885, 2231, 1651, 1459, 1346, 1255, 1047, 969, 932, 848, 790, 758 cm^{-1}. MS (EI) *m/z* (relative intensity) 262 (18) [M^+], 261 (100), 217 (13), 190 (11), 177 (3), 151 (2). HR-MS (EI) *m/z* calcd for $C_{17}H_{14}N_2O$ 262.1106, found 262.1059.



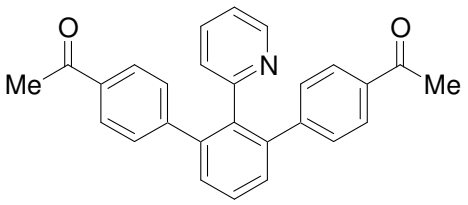
3i

2-(3-Methyl-3′-trifluoromethyl-biphenyl-2-yl)-4,5-dihydro-oxazole (3i) (Table 2, entry 9): The representative procedure was followed, using oxazoline **1** (161 mg, 1.00 mmol) and aryl tosylate **2i** (380 mg, 1.20 mmol). After 23 h, purification by chromatography (*n*-pentane/Et_2O, 4/1 → 3/2) yielded biphenyl **3i** (293 mg, 96 %) as pale brown crystals. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.73 (s, 1H), 7.60 (t, J = 7.5 Hz, 2H), 7.50-7.39 (m, 2H), 7.30-7.21 (m, 2H), 4.17 (t, J = 9.1 Hz, 2H), 3.86 (t, J = 9.3 Hz, 2H), 2.43 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.1, 141.9, 140.4, 137.9, 131.8, 130.3 (J = 32 Hz), 129.7, 129.6, 128.6, 128.3, 127.0, 125.2 (J = 4 Hz), 124.2 (J = 272 Hz), 123.8 (J = 4 Hz), 67.2, 55.1, 19.8. ^{19}F-NMR (375 MHz, $CDCl_3$): δ = -61.47. IR (KBr): 2881, 1664, 1456, 1334, 1236, 1160, 1119, 1067, 1041, 970, 934, 897 cm^{-1}. MS (EI) *m/z* (relative intensity) 305 (18) [M^+], 304 (100), 260 (11), 247 (4), 165 (6). HR-MS (EI) *m/z* calcd for $C_{17}H_{14}F_3NO$ 305.1027, found 305.1026.



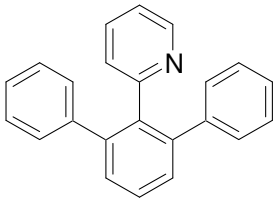
3k

1-[2′-(4,5-Dihydro-oxazol-2-yl)-3′-methyl-biphenyl-4-yl]-ethanone (3k) (Table 2, entry 11): The representative procedure was followed, using oxazoline **1** (162 mg, 1.00 mmol) and aryl tosylate **2k** (350 mg, 1.20 mmol). After 23 h, purification by chromatography (*n*-pentane/Et_2O, 3/1 → 1/4) yielded product **3k** (261 mg, 93 %) as a light brown solid. The spectral data were in accordance with those reported in the literature.[1] ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.96 (md, *J* = 8.6 Hz, 2H), 7.50 (md, *J* = 8.6 Hz, 2H), 7.42-7.33 (m, 1H), 7.30-7.18 (m, 2H), 4.15 (t, *J* = 8.6 Hz, 2H), 3.85 (t, *J* = 8.7 Hz, 2H), 2.62 (s, 3H), 2.42 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 197.8, 164.1, 146.2, 140.8, 137.8, 135.8, 129.7, 129.6, 128.6, 128.1, 128.0, 127.0, 67.2, 55.1, 25.6, 19.8. IR (KBr): 3064, 2878, 1679, 1606, 1402, 1357, 1269, 1253, 1186, 1045, 932, 844 cm^{-1}. MS (EI) *m/z* (relative intensity) 279 (17) [M^+], 278 (100), 234 (3), 165 (3). HR-MS (EI) *m/z* calcd for $C_{18}H_{17}NO_2$ 279.1259, found 279.1197.



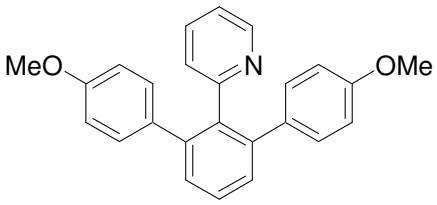
11a

1-(4-Acetyl-2′-pyridin-2-yl-1,1′:3′,1′′-terphenyl-4′′-yl)-ethanone (11a) (Table 4, entry 1): The representative procedure was followed, using 2-phenylpyridine (**9a**) (153 mg, 0.986 mmol) and aryl chloride **10a** (332 mg, 2.14 mmol). After 24 h at 120 °C, purification by chromatography (*n*-pentane/Et_2O, 1/1 → 1/3 → 1/4 → 0/1) yielded **11a** (334 mg, 87 %) as a light brown solid. The spectral data were in accordance with those reported in the literature.[2] ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.30 (d, J = 5.0 Hz, 1H), 7.75 (d, J = 8.1, 4H), 7.56 (dd, J = 8.6, 6.4 Hz, 1H), 7.50-7.45 (m, 2H), 7.31 (dt, J = 7.7, 1.8 Hz, 1H), 7.18 (d, J = 8.1 Hz, 4H), 6.94 (ddd, J = 7.5, 4.8, 0.9 Hz, 1H), 6.86 (d, J = 7.7 Hz, 1H), 2.56 (s, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 197.7, 157.9, 148.7, 146.3, 140.9, 138.3, 135.3, 135.1, 129.8, 129.7, 128.5, 127.8, 126.6, 121.4, 26.5. IR (KBr): 3053, 2919, 1680, 1605, 1268, 958, 809 cm^{-1}. MS (EI) *m/z* (relative intensity) 391 (68) [M^+], 390 (100), 348 (13). HR-MS (EI) *m/z* calcd for $C_{27}H_{21}NO_2$ 391.1572, found 391.1550.



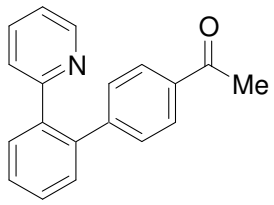
11b

2-(1,1′:3′,1′′-Terphenyl)-2′-yl-pyridine (11b) (Table 4, entry 2): The representative procedure was followed, using 2-phenylpyridine (**9a**) (155 mg, 1.00 mmol) and aryl chloride **10b** (258 mg, 2.29 mmol). After 8 h at 120 °C, purification by chromatography (*n*-pentane/Et_2O, 6/1 → 4/1 → 3/1 → 1/1) yielded **11b** (304 mg, 99 %) as a light brown solid. The spectral data were in accordance with those reported in the literature.[2] ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.32 (ddd, J = 4.9, 1.6, 1.0 Hz, 1H), 7.53 (dd, J = 9.0, 6.0 Hz, 1H), 7.45 (d, J = 6.3 Hz, 2H), 7.30 (dt, J = 7.6, 1.7 Hz, 1H), 7.20–7.10 (m, 10H) 6.90–6.80 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 158.9, 148.4, 141.8, 141.5, 138.4, 134.8, 129.6, 129.4, 128.1, 127.6, 126.7, 126.2, 120.8. IR (KBr): 3058, 3024, 1590, 1416, 1024, 760, 703 cm^{-1}. MS (EI) *m/z* (relative intensity) 307 (51) [M^+], 306 (100), 304 (14), 291 (4). HR-MS (EI) *m/z* calcd for $C_{23}H_{16}N$ 306.1283, found 306.1257.



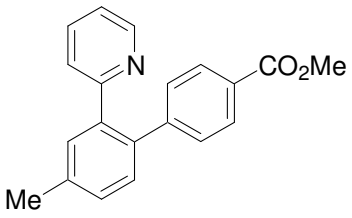
11c

2-(4,4′′-Dimethoxy-1,1′:3′,1′′-terphenyl-2′yl)pyridine (11c) (Table 4, entry 3): The representative procedure was followed, using 2-phenylpyridine (**9a**) (153 mg, 0.986 mmol) and aryl chloride **10c** (314 mg, 2.20 mmol). After 24 h at 120 °C, purification by chromatography (*n*-pentane/Et_2O, 3/1 → 1/1) yielded **11c** (330 mg, 91 %) as light brown solid. The spectral data were in accordance with those reported in the literature.[2] ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.36 (d, J = 4.5 Hz, 1H), 7.48 (dd, J = 8.9, 6.2 Hz, 1H), 7.45-7.35 (m, 2H), 7.33 (dt, J = 7.8, 1.6 Hz, 1H), 7.01 (d, J = 8.5 Hz, 4H), 6.92 (dd, J = 7.6, 5.1 Hz, 1H), 6.88 (d, J = 7.9 Hz, 1H), 6.70 (d, J = 8.5 Hz, 4H), 3.74 (s, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 159.2, 158.2, 148.5, 141.4, 138.4, 135.0, 134.0, 130.6, 129.1, 128.1, 126.7, 120.7, 113.1, 55.1. IR (KBr): 3037, 1609, 1582, 1513, 1233, 1183, 1040, 806 cm^{-1}. MS (EI) *m/z* (relative intensity) 367 (95) [M^+], 366 (100), 353 (21), 352 (92). HR-MS (EI) *m/z* calcd for $C_{25}H_{21}NO_2$ 367.1572, found 367.1552.



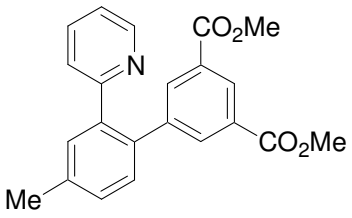
12a

1-(2′-Pyridin-2-yl-biphenyl-4-yl)-ethanone (12a) (Table 3, entry 6): The representative procedure was followed, using 2-phenylpyridine (**9a**) (156 mg, 1.01 mmol) and aryl tosylate **2k** (640 mg, 2.20 mmol). After 24 h, purification by chromatography (*n*-pentane/Et_2O, 2/1 → 1/1 → 1/2) yielded **12a** (179 mg, 65 %) as a brown oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.62 (md, J = 4.9 Hz, 1H), 7.84 (md, J = 8.4 Hz, 2H), 7.72-7.68 (m, 1H), 7.53-7.42 (m, 4H), 7.26 (dt, J = 8.4, 1.9 Hz, 2H), 7.14 (ddd, J = 7.6, 4.9, 1.2 Hz, 1H), 6.95 (dt, J = 7.9, 1.1 Hz, 1H), 2.58 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 197.8, 158.8, 149.4, 146.4, 139.5, 139.4, 135.7, 135.3, 130.6, 130.3, 129.8, 128.7, 128.3, 128.1, 125.2, 121.6, 26.6. IR (KBr): 3044, 1673, 1606, 1586, 1429, 1404, 1357, 1270, 839, 752, 600 cm^{-1}. MS (EI) *m/z* (relative intensity) 273 (33) [M^+], 272 (100), 230 (16), 202 (8), 128 (3), 114 (5), 43 (3). HR-MS (EI) *m/z* calcd for $C_{19}H_{15}NO$ 273.1154, found 273.1134.



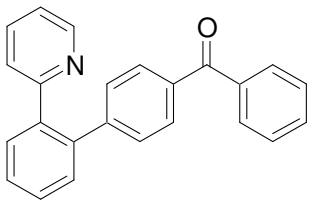
12b

4-Methyl-2-pyridin-2-yl-biphenyl-4′-carboxylic acid methyl ester (12b) (Table 4, entry 4): The representative procedure was followed, using 2-(3-methylphenyl)-pyridine (**9b**) (167 mg, 0.987 mmol) and aryl tosylate **2f** (338 mg, 1.10 mmol). After 24 h, purification by chromatography (*n*-pentane/Et_2O, 5/1 → 3/1 → 2/1, CH_2Cl_2/Et_2O, 1/0 → 50/1) yielded **12b** (168 mg, 56 %) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.62 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.88 (dt, *J* = 8.4, 1.9 Hz, 2H), 7.53-7.52 (m, 1H), 7.39 (dt, *J* = 7.7, 1.9 Hz, 1H), 7.35-7.28 (m, 2H), 7.20 (dt, *J* = 8.4, 1.9 Hz, 2H), 7.11 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 6.87 (dt, *J* = 7.9, 1.1 Hz, 1H), 3.89 (s, 3H), 2.45 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 167.0, 158.9, 149.4, 146.2, 139.3, 138.2, 136.8, 135.5, 131.2, 130.3, 129.7, 129.4, 129.3, 128.2, 125.3, 121.5, 52.0, 21.1. IR (KBr): 1717, 1607, 1586, 1433, 1273, 1178, 1112, 1101, 774, 746, 706 cm^{-1}. MS (EI) *m/z* (relative intensity) 302 (100) [$(M-H)^+$], 272 (4), 242 (13), 228 (5), 135 (3), 120 (3), 114 (3). HR-MS (EI) *m/z* calcd for $C_{20}H_{17}NO_2$ 303.1259, found 303.1231.



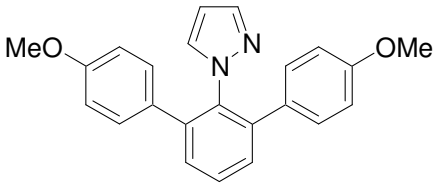
12c

4-Methyl-2-pyridin-2-yl-biphenyl-3′,5′-dicarboxylic acid methyl ester (12c) (Table 4, entry 5): The representative procedure was followed, using 2-(3-methylphenyl)-pyridine (**9b**) (165 mg, 0.975 mmol) and aryl tosylate **2l** (401 mg, 1.10 mmol). After 24 h, purification by chromatography (*n*-pentane/Et_2O, 3/1 → 2/1 → 1/1) yielded **12c** (196 mg, 56 %) as a white solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.58 (ddd, J = 4.9, 1.8, 1.0 Hz, 1H), 8.51 (t, J = 1.6 Hz, 1H), 7.99 (d, J = 1.6 Hz, 2H), 7.51-7.50 (m, 1H), 7.47-7.40 (m, 1H), 7.36-7.28 (m, 2H), 7.10 (ddd, J = 7.5, 4.9, 1.1 Hz, 1H), 6.93 (dt, J = 8.0, 1.1 Hz, 1H), 3.86 (s, 6H), 2.45 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.0, 158.7, 149.4, 142.1, 139.3, 138.3, 135.7, 135.7, 134.8, 131.1, 130.4, 130.3, 129.5, 128.7, 125.1, 121.6, 52.2, 21.1. IR (KBr): 2953, 1725, 1587, 1436, 1341, 1244, 1000, 795, 764, 755 cm^{-1}. MS (EI) *m/z* (relative intensity) 360 (70) [$(M-H)^+$], 346 (77), 328 (100), 302 (25), 242 (23), 120 (8). HR-MS (EI) *m/z* calcd for $C_{22}H_{19}NO_4$ 361.1314, found 361.1290.



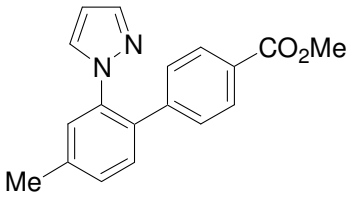
12d

Phenyl-(2'-pyridin-2-yl-biphenyl-4-yl)-methanone (12d) (Table 4, entry 6): The representative procedure was followed, using 2-phenylpyridine (**9a**) (153 mg, 0.986 mmol) and aryl tosylate **2j** (388 mg, 1.10 mmol). After 24 h, purification by chromatography (*n*-pentane/Et_2O, 5/1 → 3/1 → 2/1) yielded **12d** (179 mg, 54 %) as a brown oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.62 (ddd, J = 5.0, 1.8, 1.0 Hz, 1H), 7.79–7.67 (m, 5H), 7.61–7.43 (m, 7H), 7.27 (dt, J = 8.4, 1.8 Hz, 2H), 7.14 (ddd, J = 7.5, 5.0, 1.1 Hz, 1H), 6.97 (dt, J = 7.9, 1.1 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 196.4, 158.7, 149.3, 145.8, 139.6, 139.3, 137.7, 135.8, 135.7, 132.3, 130.7, 130.4, 130.0, 129.9, 129.6, 128.8, 128.3, 128.2, 125.4, 121.7. IR (KBr): 1657, 1603, 1586, 1462, 1425, 1315, 1277, 938, 925, 797, 752, 702 cm^{-1}. MS (EI) *m/z* (relative intensity) 334 (100) [$(M-H)^+$], 228 (9), 202 (4), 105 (5), 77 (5). HR-MS (EI) *m/z* calcd for $C_{24}H_{17}NO$ 335.1310, found 335.1288.



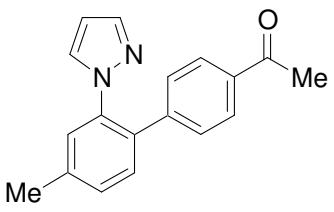
14a

1-(4,4′′-Dimethoxy-1,1′:3′,1′′-terphenyl-2′-yl)-1*H*-pyrazole (14a) (Table 4, entry 7): The representative procedure was followed, using 1-phenyl-1-*H*-pyrazole (**13a**) (141 mg, 0.978 mmol) and aryl chloride **10c** (348 mg, 2.20 mmol). After 24 h, purification by chromatography (*n*-pentane/Et_2O, 5/1 → 3/1 → 1/1) yielded **14a** (289 mg, 81 %) as a white solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.55-7.50 (m, 1H), 7.45-7.42 (m, 3H), 7.09 (dd, *J* = 2.4, 0.6 Hz, 1H), 7.03 (dt, *J* = 9.6, 2.5 Hz, 4H), 6.76 (dt, *J* = 9.6, 2.5 Hz, 4H), 6.10-6.09 (m, 1H), 3.77 (s, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 158.8, 140.1, 139.2, 136.2, 132.4, 131.1, 129.6, 129.3, 129.0, 113.5, 106.0, 55.1. IR (KBr): 1608, 1515, 1462, 1280, 1241, 1183, 1039, 1030, 843, 835, 800, 762 cm^{-1}. MS (EI) *m/z* (relative intensity) 355 (100) [$(M-H)^+$], 341 (6), 311 (4), 297 (2), 269 (2). HR-MS (EI) *m/z* calcd for $C_{23}H_{20}N_2O_2$ 356.1525, found 356.1502.



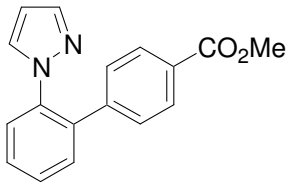
15a

4-Methyl-2-pyrazole-1-yl-biphenyl-4′-carboxylic acid methyl ester (15a) (Table 4, entry 8): The representative procedure was followed, using 1-(3-methylphenyl)-1-*H*-pyrazole (**13b**) (157 mg, 0.992 mmol) and aryl tosylate **2f** (368 mg, 1.20 mmol). After 24 h, purification by chromatography (CH_2Cl_2) yielded **15a** (177 mg, 61 %) as a brown liquid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.93 (dt, *J* = 8.4, 1.9 Hz, 2H), 7.62 (dd, *J* = 1.9, 0.6 Hz, 1H), 7.44-7.43 (m, 1H), 7.38-7.35 (m, 1H), 7.31-7.27(m, 1H), 7.14 (dt, *J* = 8.5, 1.9 Hz, 2H), 7.06 (dd, *J* = 2.4, 0.6 Hz, 1H), 6.18l (dd, *J* = 1.9, 2.3 Hz, 1H), 3.90 (s, 3H), 2.45 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.8, 143.3, 140.3, 139.4, 138.2, 132.8, 131.2, 130.6, 129.6, 129.2, 128.8, 128.5, 127.2, 106.6, 52.1, 20.9. IR (KBr): 2952, 1716, 1608, 1526, 1433, 1314, 1281, 1192, 1120, 1108, 832, 778, 766, 708, 625 cm^{-1}. MS (EI) *m/z* (relative intensity) 291 (100) [$(M-H)^+$], 261 (5), 231 (7), 204 (4), 191 (3), 165 (4), 130 (5). HR-MS (EI) *m/z* calcd for $C_{18}H_{16}N_2O_2$ 292.1212, found 292.1180.



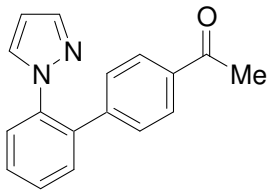
15b

4-Acetyl-4′-methyl-2′-pyrazole-1-yl-biphenyl (15b) (Table 4, entry 9): The representative procedure was followed, using 1-(3-methylphenyl)-1-*H*-pyrazole (**13b**) (158 mg, 1.00 mmol) and aryl tosylate **2k** (348 mg, 1.20 mmol). After 24 h, purification by chromatography (Et_2O/CH_2Cl_2, 1/0 → 20/1) yielded **15b** (141 mg, 51 %) as a white solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.85 (dt, *J* = 8.5, 1.9 Hz, 2H), 7.62 (dd, *J* = 1.8, 0.6 Hz, 1H), 7.44-7.43 (m, 1H), 7.38-7.35 (m, 1H), 7.31-7.28 (m, 1H), 7.16 (dt, *J* = 8.5, 1.9 Hz, 2H), 7.09 (dd, *J* = 2.3, 0.6 Hz, 1H), 6.20 (dd, *J* = 2.3, 1.9 Hz, 1H), 2.57 (s, 3H), 2.45 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 197.7, 143.4, 140.4, 139.4, 138.3, 135.7, 132.7, 131.2, 130.6, 129.3, 128.7, 128.4, 127.3, 106.6, 26.5, 20.9. IR (KBr): 1679, 1603, 1525, 1517, 1401, 1356, 1268, 954, 826, 764, 621 cm^{-1}. MS (EI) *m/z* (relative intensity) 275 (100) [$(M-H)^+$], 261 (10), 233 (9), 218 (4), 191 (3). HR-MS (EI) *m/z* calcd for $C_{18}H_{16}N_2O$ 276.1263, found 276.1238.



15c

2-Pyrazole-1-yl-biphenyl-4′-carboxylic acid methyl ester (15c) (Table 4, entry 10): The representative procedure was followed, using 1-phenyl-1-*H*-pyrazole (**13a**) (144 mg, 1.00 mmol) and aryl tosylate **2f** (348 mg, 1.14 mmol). After 24 h, purification by chromatography (*n*-pentane/Et_2O, 7/1 → 5/1 → 2/1) yielded **15c** (154 mg, 55 %) as a white solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.95 (dt, *J* = 8.5, 1.9 Hz, 2H), 7.64-7.59 (m, 2H), 7.54-7.47 (m, 3H), 7.17 (dt, *J* = 8.5, 1.9 Hz, 2H), 7.09 (dd, *J* = 2.4, 0.6 Hz, 1H), 6.20 (dd, *J* = 2.4, 1.9 Hz, 1H), 3.91 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.8, 143.2, 140.5, 138.6, 135.8, 131.2, 130.8, 129.7, 129.1, 129.0, 128.5, 128.5, 126.7, 106.7, 52.1. IR (KBr): 2951, 1722, 1611, 1520, 1436, 1394, 1281, 1184, 1114, 756, 744 cm^{-1}. MS (EI) *m/z* (relative intensity) 277 (100) [$(M-H)^+$], 247 (4), 218 (6), 191 (3), 123 (5), 96 (3). HR-MS (EI) *m/z* calcd for $C_{17}H_{14}N_2O_2$ 278.1055, found 278.1031.



15d

4-Acetyl-2′-pyrazole-1-yl-biphenyl (15d) (Table 4, entry 11): The representative procedure was followed, using 1-phenyl-1-*H*-pyrazole (**13a**) (144 mg, 1.00 mmol) and aryl tosylate **2k** (290 mg, 1.00 mmol). After 24 h, purification by chromatography (*n*-pentane/Et_2O, 3/1 → 2/1 → 1/1, CH_2Cl_2/Et_2O, 100/1 → 50/1) yielded **15d** (149 mg, 57 %) as a light brown solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.87 (md, *J* = 8.5 Hz, 2H), 7.63-7.58 (m, 2H), 7.54-7.47 (m, 3H), 7.19 (md, *J* = 8.5 Hz, 2H), 7.12 (dd, *J* = 2.4, 0.6 Hz, 1H), 6.22 (dd, *J* = 2.3, 1.9 Hz, 1H), 2.58 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 197.6, 143.4, 140.5, 138.5, 135.9, 135.8, 131.2, 130.8, 129.1, 128.7, 128.5, 128.4, 126.8, 106.7, 26.6. IR (KBr): 1683, 1606, 1520, 1485, 1462, 1396, 1358, 1267, 940, 850, 842, 761, 601 cm^{-1}. MS (EI) *m/z* (relative intensity) 261 (100) [$(M-H)^+$], 247 (9), 219 (10), 191 (3), 123 (4). HR-MS (EI) *m/z* calcd for $C_{17}H_{14}N_2O$ 262.1106, found 262.1082.

[1] S. Oi, E. Aizawa, Y. Ogino, Y. Inoue, *J. Org. Chem.* **2005**, *70*, 3113-3119.

[2] L. Ackermann, *Org. Lett.* **2005**, 7, 3123-3125.