Supporting Information

Palladium-catalyzed unsymmetrical aryl couplings in sequence leading to *o*-teraryls: dramatic olefin effect on selectivity

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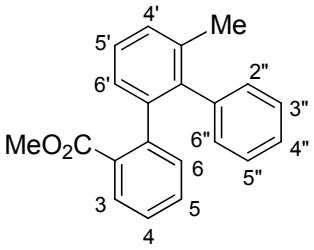
General

Reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Most chemicals were commercially available and used as received. Methyl bromobenzoates were prepared by esterification from the corresponding bromobenzoic acids. 2-*i*-Propyliodobenzene was prepared by iodination of the corresponding diazonium salt according to the literature.[1] Identification of the previously reported 2,3'-dimethyl-1,1';2',1"-terphenyl, 2,3'-di-*i*-propyl-1,1';2',1"-terphenyl and 2,3'-dimethoxycarbonyl-1,1';2',1"-terphenyl (compounds **5**; R^1 = Me, *i*-Pr, CO_2Me) was obtained by comparison with the data reported in the literature.[2] DMF was dried and stored over 4 Å molecular sieves under nitrogen. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 293 K using Bruker AC300, AVANCE300 and AVANCE400 spectrometers. Chemical shifts are given in ppm and are referenced to the solvent (7.26 and 77.0 ppm for ^1H and ^{13}C, respectively). The reported assignments are based on COSY, NOESY, direct C–H correlation and HMBC experiments; one or more asterisks (*) indicate interchangeable assignments. Mass spectra (EI) were performed using a Finnigan Mat SSQ 710 mass spectrometer working at 70 eV ionization energy. IR were recorded on a Perkin-Elmer 298 FT-IR spectrophotometer. Gas chromatography analyses were carried out with a Carlo Erba GC8000TOP instrument using a 30 m long SE-30 gas capillary column. Flash column chromatography was performed on Merck Kieselgel 60 and analytical TLC on Merck 60 F254 plates. Elemental analyses were carried out with a Carlo Erba EA 1108-Elemental Analyzer. Melting points were determined with an Electrothermal apparatus and are uncorrected.

General procedure for the synthesis of o-teraryls

A mixture of $Pd(OAc)_2$ (5 mg, 0.022 mmol), K_2CO_3 (608 mg, 4.4 mmol), the desired *ortho*-substituted aryl iodide (1.1 mmol), aryl bromide (1.1 mmol), norbornene (52 mg, 0.55 mmol), the arylboronic acid (1.3 mmol) and diethyl maleate, if used, (303 mg, 1.76 mmol) in DMF (20 mL) was heated at 105 °C with stirring under nitrogen for 24 h. After cooling to room temperature, the mixture was diluted with EtOAc (20 ml), treated with water (3 × 50 ml) and the resulting organic layer was dried over anhydrous Na_2SO_4. The product was isolated by flash column chromatography using mixtures of hexane-EtOAc-CH_2Cl_2 as eluent.

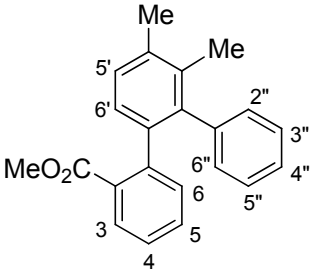
*2-Methoxycarbonyl-3'-methyl-1,1';2',1''-terphenyl (**3**; R^1 = Me, R^2 = CO_2Me)*



M.p. (hexane): 84 °C. ^{1}H NMR: δ 7.69 (1H, dd, *J* = 7.7, 1.5 Hz, H3), 7.31–7.23 (3H, m, H4', H5', H5 centred at 7.26), 7.21–6.97 (8H, m, H4, H2''–H6'', H6, H6'), 3.66 (3H, s, CO_2CH_3), 2.18 (3H, s, CH_3); ^{13}C NMR: δ 167.8 (CO_2CH_3), 143.2 (C1), 141.2 (C1'), 140.0 (C1''), 139.9 (C3'), 135.9 (C2'), 131.8 (C6), 130.6 (C5), 130.5 (C2), 130.1, 129.9 (broad, C2'', C6''), 129.4 (C3), 129.1 (C4'), 127.5, 127.3 (broad, C3'', C5''), 126.6 (C5'), 126.5 (C6'), 126.4 (C4), 126.2 (C4''), 51.6 (CO_2CH_3), 21.0 (CH_3); IR (KBr, cm^{-1}): ν 1720; MS: M^+ 302 (55), *m/z* 270 (30), 243 (61), 242 (100), 239 (44), 228 (83), 165 (39), 119 (78), 113 (61).

Anal. Calc. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.37; H, 6.06.

*3',4'-Dimethyl-2-methoxycarbonyl-1,1';2',1''-terphenyl (**3**; R^1 = Me +4'-Me, R^2 = CO_2Me)*

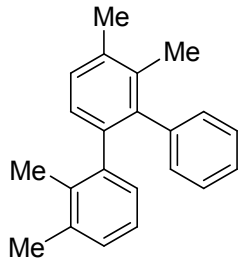


M.p. (hexane): 99 °C. ^{1}H NMR: δ 7.83–7.77 (2H, m, H3, H5), 7.49–7.40 (1H, br d, H5'), 7.26–7.15 (4H, m, H6', H3'', H4'', H5''), 7.15–7.09 (2H, m, H4, H6), 7.08–7.02 (2H, m, H2'', H6''), 3.87 (3H, s, CO_2CH_3), 2.93, 2.91 (6H, 2s, CH_3); ^{13}C NMR: δ 167.0 (CO_2CH_3), 147.9 (C4'), 147.5 (C3'), 147.3 (C1), 144.7 (C2), 140.6 (C1'), 139.6 (C1''), 139.4 (C2'), 130.5 (C2'', C6''), 129.8 (C6), 128.7 (C3, C5), 127.7 (C4), 127.6 (C3'', C5'', C5'), 127.1 (C6'), 126.5 (C4''), 51.9 (CO_2CH_3), 29.8, 29.1

(CH_3); IR (KBr, cm^{-1}): ν 1714; MS: M^+ 316 (55), *m/z* 283 (50), 241 (47), 179 (22), 178 (24), 165 (22), 142 (72), 126 (39), 119 (100), 113 (44), 59 (69).

Anal. Calc. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.45; H, 6.41.

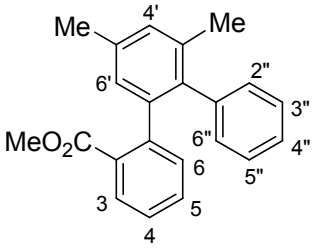
*2,3,3',4'-Tetramethyl-1,1';2',1''-terphenyl (**5**; Table 1, entry 2)*



M.p. (CH_2Cl_2): 88 °C. ^{1}H NMR: δ 7.22 (1H, br d, *J* = 7.7 Hz), 7.19–7.10 (3H, m), 7.05–6.96 (3H, m), 6.95–6.91 (1H, m), 6.87 (1H, d, *J* = 7.3 Hz), 6.83 (1H, dd, *J* = 7.4, 1.6 Hz), 2.41 (3H, s), 2.16 (3H, s), 2.08 (3H, s), 1.93 (3H, s); ^{13}C NMR: δ 141.9, 141.1, 140.8, 139.7, 136.1, 135.6, 134.6, 134.2, 130.5, 129.3, 128.4, 128.3, 127.9, 127.3, 127.2, 127.0, 126.0, 124.1, 20.7, 20.4, 17.5, 17.2; MS: M^+ 286 (100), *m/z* 271 (50), 256 (35), 193 (32), 165 (15), 73 (42).

Anal. Calc. for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.21; H, 7.79.

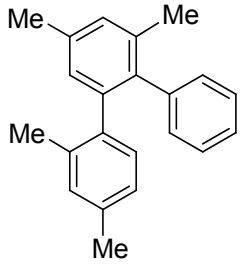
*3',5'-Dimethyl-2-methoxycarbonyl-1,1';2',1''-terphenyl (**3**; R^1 = Me + 5'-Me, R^2 = CO_2Me)*



M.p. (hexane): 131 °C. ^{1}H NMR: δ 7.65 (1H, dd, *J* = 7.9, 1.6 Hz, H3), 7.27 (1H, td, *J* = 7.5, 1.5 Hz, H5), 7.16 (1H, td, *J* = 7.7, 1.5 Hz, H4), 7.13–7.02 (6H, m, H4, H2", H6", H4', H4", H6, H3"*), 6.94 (1H, br s, H5"*), 6.92 (1H, s further split, H6'), 3.66 (3H, s, CO_2CH_3), 2.38 (3H, s, CH_3(C5')), 2.13 (3H, s, CH_3(C3')); ^{13}C NMR: δ 167.8 (CO_2CH_3), 143.3 (C1), 141.1 (C1"), 140.0 (C1'), 137.1 (C2'), 136.1 (C5'), 136.7 (C3'), 131.9 (C6), 130.7 (C5), 130.5 (C2), 130.3, 130.2 (C3", C5"), 130.1 (C4'), 129.3 (C3), 127.5, 127.3 (C2", C6"), 127.2 (C6'), 126.3 (C4), 126.1 (C4"), 51.8 (CO_2CH_3), 21.1 (CH_3(C5')), 21.0 (CH_3(C3')); IR (KBr, cm^{-1}): ν 1719; MS: M^+ 316 (96), *m/z* 285 (22), 284 (30), 283 (25), 269 (48), 257 (41), 256 (51), 242 (68), 241 (100), 238 (80), 226 (22), 215 (25), 202 (14), 165 (16), 120 (19).

Anal. Calc. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.44; H, 6.40.

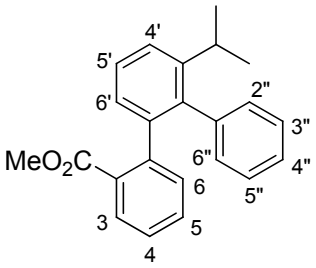
*2,4,3',5'-Tetramethyl-1,1';2',1"-terphenyl (**5**; Table 1, entry 3)*



M.p. (CH_2Cl_2): 128–129 °C. ^{1}H NMR: δ 7.22–7.13 (4H, m), 7.03 (2H br s), 6.95 (1H, br s), 6.89–6.85 (2H, m), 6.82–6.79 (1H, br d, *J* = 7.9 Hz), 2.41 (3H, s), 2.24 (3H, s), 2.16 (3H, s), 2.02 (3H, s); ^{13}C NMR: δ 141.2, 140.3, 138.8, 138.3, 136.2, 136.1, 135.9, 135.2, 130.7, 130.4, 130.1, 129.7, 129.4, 128.5, 127.4, 127.3, 126.0, 125.4, 21.12, 21.08, 21.04, 20.3; MS: M^+ 286 (100), *m/z* 271 (54), 256 (37), 239 (18), 193 (11), 178 (12), 165 (10).

Anal. Calc. for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.23; H, 7.77.

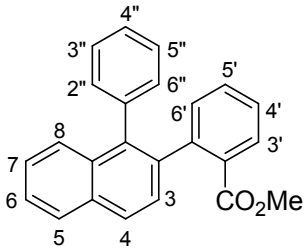
*2-Methoxycarbonyl-3'-i-propyl-1,1';2',1"-terphenyl (**3**; R^1 = i-Pr, R^2 = CO_2Me)*



M.p. (hexane): 59–60 °C. ^{1}H NMR: δ 7.71 (1H, dd, *J* = 7.7, 1.5 Hz, H3), 7.45 (1H, dd, *J* = 7.8, 1.7 Hz, H4'), 7.39 (1H, dd, *J* = 7.8, 7.1 Hz, H5'), 7.27 (1H, td, *J* = 7.5, 1.5 Hz, H5), 7.22–7.01 (8H, m, H4, H2"–H6", H6, H6'), 3.66 (3H, s, CO_2CH_3), 2.91 (1H, hept., *J* = 6.8 Hz, $(CH_3)_2CH$), 1.19 (6H, d, *J* = 6.8 Hz, $(CH_3)_2CH$); ^{13}C NMR: δ 167.8 (CO_2CH_3), 146.7 (C3'), 143.4 (C1), 141.2 (C1'), 139.8 (C1"), 138.9 (C2'), 131.8 (C6), 130.5 (C2), 130.5 (C5), 130.3, 130.0 (broad, C2", C6"), 129.4 (C3), 127.4, 127.1 (broad, C3", C5"), 126.9 (C5'), 126.3 (C4), 126.2 (C4"), 126.1 (C6'), 124.3 (C4'), 51.6 (CO_2CH_3), 29.8 ($(CH_3)_2CH$), 24.2, 24.1 ($(CH_3)_2CH$); IR (KBr, cm^{-1}): ν 1719; MS: M^+ 330 (26), *m/z* 284 (21), 283 (100), 240 (24), 239 (58), 134 (28), 126 (29), 119 (70), 113 (18).

Anal. Calc. for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.52; H, 6.77.

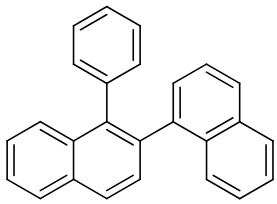
*2-(2'-Methoxycarbonylphenyl)-1-phenylnaphthalene (**3**; Table 1, entry 5*)



M.p. (hexane): 126 °C. ^{1}H NMR: δ 7.97–7.90 (2H, m, H5, H4), 7.81 (1H, dd, *J* = 7.6, 1.6 Hz, H3'), 7.69 (1H, br d further split, H8), 7.54–7.48 (1H, m, H6), 7.46–7.39 (2H, m with a d centered at 7.44, *J* = 8.4 Hz, H3, H7), 7.36–7.20 (7H, m, H5', H2"–H6" and H4'), 7.13 (1H, dd further split, H6'), 3.63 (3H, s, CH_3); ^{13}C NMR: δ 167.8 (CO_2CH_3), 143.1 (C1'), 138.7 (C1"), 138.3 (C2), 136.9 (C1), 132.8 (C4a), 132.5 (C8a), 132.2 (C6'), 131.1 (C3"*), 130.8 (C5', C5"*), 130.6 (C2'), 129.7 (C3'), 128.0 (C5), 127.7 (C2"**), 127.4 (C3), 127.3 (C6"**), 126.9 (C4), 126.7 (C8, C4"), 126.6 (C4'), 126.1 (C7), 125.5 (C6), 51.8 (CH_3); IR (KBr, cm^{-1}): ν 1721; MS: M^+ 338 (100), *m/z* 305 (22), 278 (78), 277 (73), 276 (73), 153 (22), 138 (89), 125 (28).

Anal. Calc. for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.20; H, 5.39.

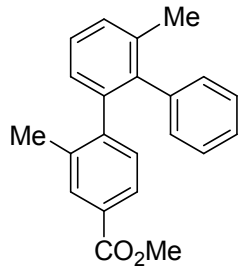
*1-Phenyl-2,1',binaphthyl (**5**, Table 1, entry 5)*



M.p. (hexane): 155 °C. ^{1}H NMR: δ 8.01–7.92 (2H, m), 7.80 (1H, br d, *J* = 7.9 Hz), 7.72–7.64 (2H, m), 7.58–7.22 (9H, m), 7.16 (1H, dd, *J* = 7.0, 1.3 Hz), 7.09 (1H, m), 6.98–6.87 (2H, m); ^{13}C NMR: δ 139.5, 139.1, 138.8, 137.0, 133.3, 133.0, 132.8, 132.5, 131.1, 129.9, 128.9, 128.2, 128.0, 127.9, 127.6, 127.1, 127.0, 126.9, 126.8, 126.5, 126.4, 126.2, 125.8, 125.6, 125.4, 124.7; MS: M^+ 330 (100), *m/z* 313 (10), 302 (10), 253 (21), 252 (30), 202 (12), 156 (10).

Anal. Calc. for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 94.48; H, 5.52.

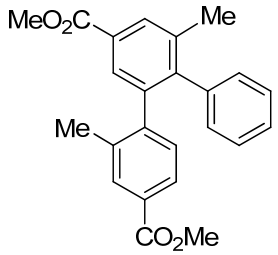
*2,3'-Dimethyl-4-methoxycarbonyl-1,1';2',1"-terphenyl (**3**; R^1 = Me, R^2 = Me + 4-CO_2Me)*



M.p. (hexane): 101 °C. ^{1}H NMR: δ 7.98 (1H, d, *J* = 1.2 Hz), 7.81 (1H, dd, *J* = 7.6, 1.2 Hz), 7.21–7.11 (4H, m), 7.08–6.93 (5H, m), 3.92 (3H, s), 2.20 (3H, s), 2.01 (3H, s); ^{13}C NMR: δ 167.1, 145.6, 141.5, 140.5, 139.1, 136.8, 135.3, 130.6, 130.3, 129.9, 129.4, 138.6, 127.6, 127.4, 126.9, 126.7, 124.7, 52.0, 21.1, 20.3; IR (KBr, cm^{-1}): ν 1714; MS: M$^+$ 316 (100), *m/z* 285 (13), 257 (44), 242 (71), 215 (14), 165 (11).

Anal. Calc. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.45; H, 6.43.

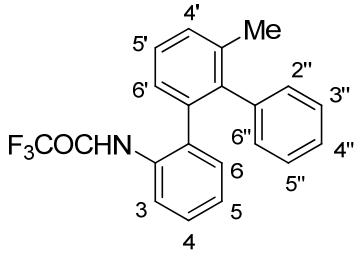
*2,3'-Dimethyl-4, 5'-dimethoxycarbonyl-1,1';2',1''-terphenyl (**6**; Table 1, entry 6)*



M.p. ($CHCl_3$): 133 °C. ^{1}H NMR: δ 8.01 (1H, br s), 7.78 (1H, s), 7.73 (1H, s), 7.67 (1H, d, *J* = 7.8 Hz), 7.21–7.11 (3H, m), 7.09–6.93 (3H, m), 3.95 (3H, s), 3.88 (3H, s), 2.23 (3H, s), 2.07 (3H, s); ^{13}C NMR: δ 167.1, 167.0, 145.6, 145.3, 140.6, 138.7, 137.1, 135.9, 130.7, 130.6, 130.5, 129.8, 128.6, 128.5, 128.1, 127.8, 127.7, 127.0, 126.0, 52.1, 51.9, 21.1, 20.2; IR (KBr, cm^{-1}): ν 1714, 1712; MS: M$^+$ 374 (100), *m/z* 343 (40), 256 (58), 239 (65), 226 (18), 59 (20).

Anal. Calc. for $C_{24}H_{22}O_4$: C, 76.99; H, 5.92. Found: C, 77.00; H, 5.97.

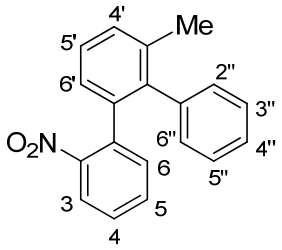
*2-Trifluoroacetamido-3'-methyl-1,1';2',1''-terphenyl (**3**; R^1 = Me, R^2 = NHCOCF$_3$)*



M.p. (hexane): 83° C. ^{1}H NMR: δ 8.01 (1H, d, *J* = 7.9, H3), 7.67 (1H, br s, NH), 7.45–7.36 (2H, m, H2", H6"), 7.29–7.14 (7H, m, H4, H3", H5", H4', H5', H5, H6'); 7.01 (1H, br d, *J* = 7.7 Hz, H6), 6.93 (1H, m, H4"); ^{13}C NMR: δ 154.0 (quart, J_{CF} = 37.3 Hz, CO), 141.4 (C2'), 138.6 (C2), 137.3 (C1"), 135.7 (C3'), 133.0 (C1), 132.2 (C1'), 131.1 (C5'), 131.0 (C4'), 130.2, 128.7 (C3", C5"), 128.2 (C6'), 128.01 (C2"*), 127.98 (C4), 127.79 (C6"*), 127.76 (C4"), 127.1 (C6), 125.3 (C5), 120.4 (C3), 119.4 (quart, J_{CF} = 288.3 Hz, CF_3), 21.1 (CH_3); MS: M$^+$ 355 (100), *m/z* 268(20), 258(28), 242 (54), 228 (20), 165 (17), 152 (14), 69 (19).

Anal. Calc. for $C_{21}H_{16}F_3NO$: C, 70.98; H, 4.54. Found: C, 71.01; H, 4.55.

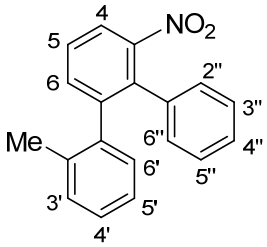
*3'-Methyl-2-nitro-1,1';2',1''-terphenyl (**3**; R^1 = Me, R^2 = NO_2)*



M.p. (hexane): 141–142 °C. ^{1}H NMR: δ 7.47 (1H, dd, *J* = 8.0, 1.2 Hz, H3), 7.38 (1H, td, *J* = 7.5, 1.1 Hz, H5'), 7.35–7.31 (2H, m, H4, H5), 7.27–7.25 (1H, m, H4'), 7.18–7.08 (6H, m, H6', H2'', H6'', H3'', H5'', H6), 6.95 (1H, br d, H4''), 2.17 (3H, s, CH_3); ^{13}C NMR: δ 148.8 (C2'), 140.0 (C2), 139.2 (C1''), 137.6 (C1), 137.1(C1'), 136.6 (C3), 133.0 (C6'), 131.8 (C5'), 130.0 (C4), 129.8 (C4''), 129.7 (C6), 128.2 (C3''*), 127.5 (C4'), 127.4 (C5''*), 127.2 (C5), 126.6, 126.0 (C2'', C6''), 123.8 (C3'), 20.9 (CH_3); IR (KBr, cm^{-1}): ν 1572, 1383; MS: M^+ 289 (100), *m/z* 272 (67), 244 (96), 239 (87), 228 (99), 226 (83), 215 (64), 202 (42), 189 (28), 113 (26).

Anal. Calc. for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23. Found: C, 78.82; H, 5.29.

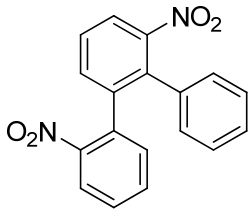
*2'-Methyl-3-nitro-1,1';2,1''-terphenyl (**4**; R^1 = Me, R^2 = NO_2)*



M.p. (hexane): 137 °C. ^{1}H NMR: δ 7.79 (1H, dd, *J* = 6.8, 2.4 Hz, H4), 7.54–7.48 (2H, m, H6, H5'), 7.21–7.07 (4H, m, H3'', H5'', H4', H4''), 7.05–6.98 (4H, m, H3', H2'', H6'', H5'), 6.94 (1H, br d, *J* = 6.9 Hz, H6'), 1.96 (3H, s, CH_3); ^{13}C NMR: δ 150.9 (C3), 143.7 (C1), 138.8 (C1''), 135.4 (C2'), 135.1 (C1'), 134.7 (C2), 133.8 (C6), 130.2 (C6'), 129.8 (C3'), 127.8 (C4'', C2'', C6''), 127.7 (C5) , 127.6 (C5', C3'', C5''), 125.1 (C3'), 122.5 (C4), 20.1 (CH_3); IR (KBr, cm^{-1}): ν 1570, 1369; MS: M^+ 289 (100), *m/z* 272 (51), 254 (60), 239 (67), 228 (41), 226 (70), 215 (61), 202 (33), 189 (22), 165 (58), 113 (21).

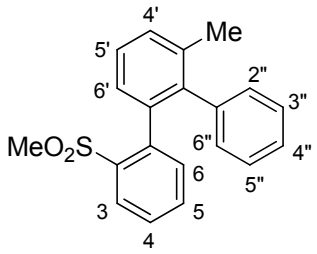
Anal. Calc. for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23. Found: C, 78.94; H, 5.22.

*2,3'-Dinitro-1,1';2',1''-terphenyl (**6**; R^1, R^2 = NO_2)*



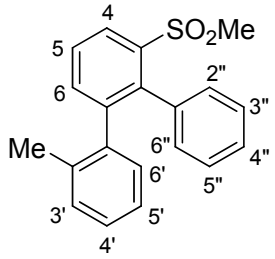
M.p. (hexane/CH_2Cl_2 9:1): 164–165 °C. ^{1}H NMR: δ 7.87 (1H, dd, *J* = 7.8, 1.6Hz), 7.84 (1H, dd, *J* = 7.3, 1.3 Hz), 7.57 (1H, t, *J* = 7.8 Hz), 7.54–7.46 (2H, m), 7.38 (1H, td, *J* = 8.1, 1.6 Hz), 7.21–7.13 (4H, m), 7.10 (1H, br signal), 6.93 (1H, br signal); ^{13}C NMR: δ 150.4, 148.2, 140.4, 134.6, 134.4, 134.3, 132.7, 132.6, 132.3, 128.9, 128.8, 128.5, 128.3, 127.9, 127.7, 124.4, 123.4; IR (KBr, cm^{-1}): ν 1564, 1491, 1362; MS: 320 (20), 226 (92), 189 (35), 113 (30), 112 (30), 77 (40), 44 (100).
Anal. Calc. for $C_{18}H_{12}N_2O_4$: C, 67.50; H, 3.78. Found: C, 67.39; H, 3.81.

*3'-Methyl-2-methylsulphonyl-1,1';2',1''-terphenyl (**3**; R^1 = Me, R^2 = SO_2Me)*



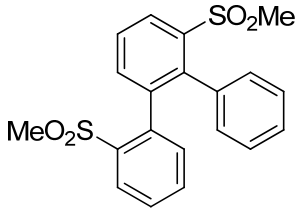
M.p. (CH_2Cl_2): 87 °C. ^{1}H NMR: δ 8.22 (1H, dd, *J* = 7.8, 1.5 Hz, H3), 8.00 (1H, m, H5), 7.80 (1H, d further split, *J* = 7.9 Hz, H6), 7.57–7.47 (2H, m, H4, H5'), 7.42–7.27 (3H, m, H4', H3'', H5''), 7.22–7.20 (1H, m, H4''), 7.19 (1H, br signal, H2''*), 7.12 (1H, m, H6'), 7.09 (1H, br signal, H6''*), 2. 96 (3H, s, SO_2CH_3), 2.16 (3H, s, CH_3); ^{13}C NMR: δ 141.07 (C2), 141.03 (C3'), 139.5 (C1'), 139.0 (C1), 137.9 (C1''), 136.9 (C2'), 135.4 (C3), 134.7 (C5), 133.6 (C5'), 132.0 (C6'), 131.1 (C4), 130.2 (C4'), 128.6 (C3''*), 128.0 (C6), 127.6 (C5''*), 126.7 (C4''), 126.5, 126.2 (C2'', C6''), 45.3 (SO_2CH_3), 21.1 (CH_3); IR (KBr, cm^{-1}): ν 1356, 1167; MS: M^+ 322 (18), *m/z* 243 (100), 228 (98), 215 (20), 165 (10), 119 (13).
Anal. Calc. for $C_{20}H_{18}SO_2$: C, 74.50; H, 5.63. Found: C, 74.52; H, 5.67.

*2'-Methyl-3-methylsulphonyl-1,1';2,1''-terphenyl (**4**; R^1 = Me, R^2 = SO_2Me)*



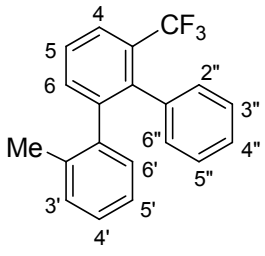
M.p. (hexane): 111–112 °C. ^{1}H NMR: δ 8.32 (1H, d, *J* = 7.9, 1.4 Hz, H4), 7.62 (1H, t, *J* = 7.9 Hz, H5), 7.59 (1H, dd, *J* = 7.8, 1.4 Hz, H6), 7.24–7.18 (5H, m, H6', H3", H5", H2", H6"), 7.10–7.06 (2H, m, H4", H5'), 7.00 (1H, m, H4'), 6.92 (1H, d, *J* = 8.0 Hz, H3'), 2.60 (3H, s, SO_2CH_3), 2.05 (3H, s, CH_3); ^{13}C NMR: δ 144.1 (C3), 140.5 (C1), 139.8 (C2), 139.3 (C2'), 135.8 (C1"), 135.3 (C1'), 135.1 (C6), 131.7 (C5), 130.3, 130.1 (C3", C5"), 129.7 (C3'), 128.0 (C4'), 127.6, 127.5 (C2", C6"), 127.4 (C4), 127.3 (C5'), 127.0 (C4"), 124.9 (C6'), 43.5 (SO_2CH_3), 20.4 (CH_3); IR (KBr, cm^{-1}): ν 1362, 1170; MS: M^+ 322 (100), *m/z* 241 (81), 228 (39), 226 (36), 215 (25), 165 (32).
Anal. Calc. for $C_{20}H_{18}SO_2$: C, 74.50; H, 5.63. Found: C, 74.52; H, 5.67.

*2,3'-Disulphonyl-1,1';2',1"-terphenyl (**6**; R^1, R^2 = SO_2Me)*



M.p. (CH_2Cl_2): 139 °C. ^{1}H NMR: δ 8.33 (1H, d, *J* = 7.6 Hz), 8.14 (1H, d, *J* = 6.8 Hz), 7.93 (1H, br s), 7.73 (1H, m), 7.65–7.62 (2H, m), 7.42–7.31 (4H, m), 7.22 (1H, m), 7.09 (1H, br s), 3.01 (3H, s), 2.64 (3H, s); ^{13}C NMR: δ 140.5, 139.0, 138.8, 135.2, 134.1, 133.8, 133.2, 132.1, 130.4, 130.2, 129.1, 128.6, 128.4, 128.1, 127.6, 127.1, 126.9, 123.9, 50.8, 43.8; IR (KBr, cm^{-1}): ν 1357, 1352, 1171, 1168; MS: M^+ 386 (10), *m/z* 307 (16), 228 (100), 226 (53), 215 (17).
Anal. Calc. for $C_{20}H_{18}S_2O_4$: C, 62.15; H, 4.69. Found: C, 62.19; H, 4.74.

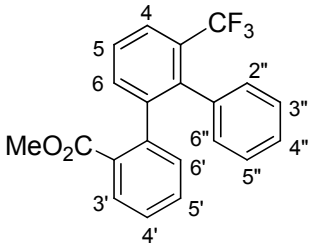
*2'-Methyl-3-trifluoromethyl-1,1';2,1"-terphenyl (**4**; R^1 = Me, R^2 = CF_3)*



M.p. ($CHCl_3$): 56 °C. ^{1}H NMR: δ 7.78 (1H, dd, J = 7.7, 1.7 Hz, H4), 7.50 (1H, m, H5), 7.44 (1H, dd, J = 7.8, 1.7 Hz, H6), 7.16–7.05 (4H, m, H2", H6", H3", H5"), 7.04–6.96 (4H, m, H3', H4", H4', H5'), 6.87 (1H, br d, H6'), 2.02 (3H, s, CH_3); ^{13}C NMR: δ 143.4 (C1), 140.0 (C2), 139.8 (C1'), 137.2 (C1"), 135.3 (C2'), 133.2 (C6), 130.8 (C2"*), 130.3 (C6'), 129.5 (C3'), 129.2 (quart, $J_{C,F}$ = 26.2 Hz, C3), 128.8 (C4"), 127.1 (C4'), 127.0 (C3", C5"), 126.9 (C5), 126.7 (C6"*), 125.0 (quart, $J_{C,F}$ = 5.7 Hz, C4), 124.7 (C5'), 124.1 (quart, $J_{C,F}$ = 274.2 Hz, CF_3), 20.3 (CH_3); MS (EI, 70 eV): M^+ 312 (100), *m/z* 297 (57), 257 (21), 228 (36),165 (18), 135 (19). MS: M^+ 312 (100), *m/z* 297 (57), 257 (21), 228 (36), 165 (18), 135 (19).

Anal. Calc. for $C_{20}H_{15}F_3$: C, 76.91; H, 4.84. Found: C, 76.93; H, 4.90.

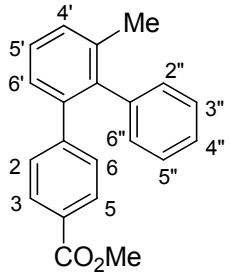
*2'-Methoxycarbonyl-3-trifluoromethyl-1,1';2,1"-terphenyl (**3**; $R^1 = CF_3$, $R^2 = CO_2Me$)*



M.p. (hexane): 91–92 °C. ^{1}H NMR: δ 7.82 (1H, dd, J = 7.8, 1.4 Hz, H4), 7.77 (1H, dd, J = 7.8, 1.4 Hz, H3'), 7.52 (1H, dd, J = 7.7, 0.8 Hz, H5), 7.45 (1H, dd, J = 7.8, 1.3 Hz, H6), 7.32 (1H, td, J = 7.5, 1.5 Hz, H5'), 7.22 (1H, td, J = 7.5, 1.4 Hz, H4'), 7.17–7.11 (4H, m, H2"*, H3", H5", H4"), 7.11–7.00 (2H, m, H6', H6"*), 3.70 (3H, s, CO_2CH_3); ^{13}C NMR: δ 167.2 (CO_2CH_3), 143.6 (C1), 141.6 (C1'), 138.9 (quart, $J_{C,F}$ = 1.8 Hz, C2), 137.1 (C1"), 132.1 (C6), 131.6 (C6'), 130.9 (C5'), 130.1 (C2"*), 129.9 (C2'), 129.8 (C3'), 129.6 (C6"*), 128.9 (quart, $J_{C,F}$ = 29.2 Hz, C3), 127.04 (C4'), 127.01 (C3"**), 126.9 (C4"), 126.8 (C5), 126.7 (C5"**), 124.9 (quart, $J_{C,F}$ = 5.5 Hz, C4), 124.2 (quart, $J_{C,F}$ = 274.2 Hz, CF_3), 51.8 (CO_2CH_3); IR (KBr, cm^{-1}): ν 1725; MS: M^+ 356 (33), *m/z* 297 (41), 296 (47), 257 (48), 228 (78), 227 (30), 226 (47), 138 (33), 128 (100), 113 (44), 77 (25).

Anal. Calc. for $C_{21}H_{15}F_3O_2$: C, 70.78; H, 4.24. Found: C, 70.67; H, 4.31.

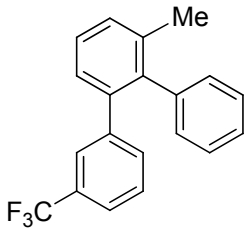
*4-Methoxycarbonyl-3'-methyl-1,1';2',1"-terphenyl (**14**; R^1 = Me, R^2 = 4-CO_2Me, R^3 = H, X = CH)*



M.p. (hexane): 113–114 °C. ^{1}H NMR: δ 7.84–7.78 (2H, m, H3, H5), 7.37–7.32 (2H, m, H4', H5'), 7.30–7.16 (4H, m, H6', H4", H3", H5"), 7.16–7.11 (2H, m, H2, H6), 7.06–7.01 (2H, m, H2", H6"), 3.87 (3H, s, CO_2CH_3), 2.19 (3H, s, CH_3); ^{13}C NMR: δ 167.0 (CO_2CH_3), 146.9 (C1), 140.5 (C1'), 140.4 (C2'), 139.8 (C1"), 136.7 (C3'), 130.2 (C2", C6"), 129.8 (C2, C6), 129.7 (C4'), 128.7 (C3, C5), 127.8 (C3", C5"), 127.7 (C4), 127.4 (C6'), 127.3 (C5'), 126.5 (C4"), 51.9 (CO_2CH_3), 21.1 (CH_3); IR (KBr, cm^{-1}): ν 1716; MS: M^+ 302 (84), *m/z* 271 (28), 243 (62), 242 (22), 228 (100), 227 (33), 226 (32), 202 (22), 165 (27), 135 (48), 119 (50), 113 (44), 101 (22).

Anal. Calc. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.44; H, 5.94.

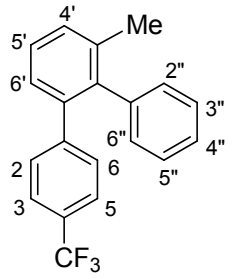
*3'-Methyl-3-trifluoromethyl-1,1';2',1"-terphenyl (**14**; R^1 = Me, R^2 = 3-CF_3, R^3 = H, X = CH)*



^{1}H NMR: δ 7.38–7.31 (4H, m), 7.29–7.17 (6H, m), 7.05–7.01 (2H, m), 2.20 (3H, s); ^{13}C NMR: δ 142.6, 140.5, 140.0, 139.6, 136.8, 133.0, 130.2, 129.8, 128.8 (quart, $J_{C,F}$ = 27.1 Hz), 127.9, 127.8, 127.42, 127.38, 126.64 (quart, $J_{C,F}$ = 3.8 Hz), 126.57, 124.0 (quart, $J_{C,F}$ = 272.0 Hz), 122.8 (quart, $J_{C,F}$ = 3.6 Hz), 21.1; MS: M^+ 312 (100), *m/z* 297 (32), 243 (24), 228 (35), 165 (26).

Anal. Calc. for $C_{20}H_{15}F_3$: C, 76.91; H, 4.84. Found: C, 76.95; H, 4.87.

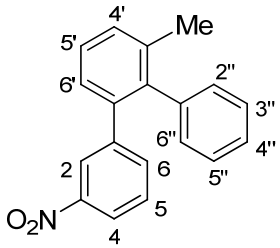
*3'-Methyl-4-trifluoromethyl-1,1';2',1"-terphenyl (**14**; R^1 = Me, R^2 = 4-CF_3, R^3 = H, X = CH)*



^{1}H NMR: δ 7.47–7.41 (2H, m, H3, H5), 7.41–7.37 (2H, m, H5', H4'), 7.33–7.20 (6H, m, H6', H3", H5", H4", H2, H6), 7.12–7.06 (2H, m, H2", H6"), 2.25 (3H, s, CH_3); ^{13}C NMR: δ 145.7, 140.4, 140.1, 139.7 (C3'), 136.8 (C2'), 130.3 (C2", C6"), 130.0 (C2, C6), 129.9 (C4'), 128.6 (quart, $J_{C,F}$ = 32.2 Hz, C4), 127.9 (C3", C5"), 127.5 (C6'), 127.4 (C5'), 126.6 (C4"), 124.4 (quart, $J_{C,F}$ = 3.9 Hz, C3, C5), 124.3 (quart, $J_{C,F}$ = 272.4 Hz, CF_3), 21.1 (CH_3); MS: M^+ 312 (100), *m/z* 297 (22), 243 (19), 228 (24), 165 (19).

Anal. Calc. for $C_{20}H_{15}F_3$: C, 76.91; H, 4.84. Found: C, 76.97; H, 4.86.

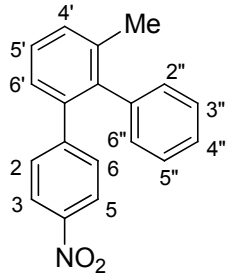
*3'-Methyl-3-nitro-1,1';2',1''-terphenyl (**14**; R^1 = Me, R^2 = 3-NO_2, R^3 = H, X = CH)*



^{1}H NMR: δ 7.99–7.93 (2H, m), 7.39–7.32 (3H, m), 7.30–7.16 (5H, m), 7.07–7.01 (2H, m); ^{13}C NMR: δ 147.6, 143.6, 140.5, 139.3, 139.0, 137.0, 135.8, 130.2 (3C), 128.2, 128.1 (2C), 127.5, 127.1, 126.8, 124.6, 121.1, 21.1; IR (KBr, cm^{-1}): ν 1563, 1368; MS: M^+ 289 (100), *m/z* 242 (46), 241 (50), 228 (55), 226 (55), 215 (32), 202 (25), 165 (19), 113 (11).

Anal. Calc. for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23. Found: C, 78.92; H, 5.19.

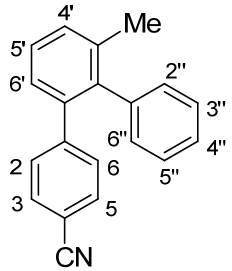
*3'-Methyl-4-nitro-1,1';2',1''-terphenyl (**14**; R^1 = Me, R^2 = 4-NO_2, R^3 = H, X = CH)*



M.p. (hexane:CH_2Cl_2 = 9:1): 144 °C. ^{1}H NMR: δ 8.00–7.97 (2H, m, H3, H5), 7.38–7.35 (2H, m, H4', H5'), 7.28–7.19 (6H, m, H3'', H5'', H6', H4'', H2, H6), 7.05–7.00 (2H, m, H2'', H6''), 2.20 (3H, s, CH_3); ^{13}C NMR: δ 149.1 (C1), 146.1 (C4), 140.3 (C2'), 139.3 (C1''), 139.3 (C1'), 137.0 (C3'), 130.5 (C2, C6), 130.4 (C4'), 130.2 (C2'', C6''), 128.1 (C3'', C5''), 127.5 (C5'), 127.3 (C6'), 126.9 (C4''), 122.7 (C3, C5), 21.0 (CH_3); IR (KBr, cm^{-1}): ν 1572, 1368; MS: M^+ 289 (100), *m/z* 242 (38), 228 (65), 226 (41), 215 (30), 202 (22), 165 (19), 113 (26), 101 (15).

Anal. Calc. for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23. Found: C, 78.81; H, 5.24.

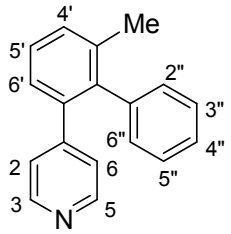
*4-Cyano-3'-methyl-1,1';2',1''-terphenyl (**14**; R^1 = Me, R^2 = 4-CN, R^3 = H, X = CH)*



M.p. (hexane): 113 °C. ^{1}H NMR: δ 7.43–7.39 (2H, m, H3, H5), 7.37–7.35 (2H, m, H5', H4'), 7.27–7.20 (4H, m, H6', H3", H5", H4"), 7.17–7.13 (2H, m, H2, H6), 7.03–6.99 (2H, m, H2", H6"), 2.19 (3H, s, CH_3); ^{13}C NMR: δ 146.9, 140.3, 139.7, 139.4, 136.9, 131.3 (C3, C5), 130.4 (C2, C6), 130.2 (C4'*, C2", C6"), 128.0 (C3", C5"), 127.4 (C5'*), 127.3 (C6'**), 126.8 (C4"**), 119.0 (C4), 109.8 (CN), 21.0 (CH_3); IR (KBr, cm^{-1}): ν 2232; MS: M^+ 269 (100), *m/z* 254 (52), 268 (35), 227 (17), 165 (17).

Anal. Calc. for $C_{20}H_{15}N$: C, 89.19; H, 5.61. Found: C, 89.19; H, 5.64.

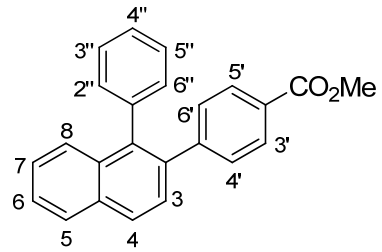
*4-[(3'-Methyl-2'-phenyl)phenyl]pyridine (**14**; R^1 = Me, R^2, R^3 = H, X = N)*



M.p. (hexane): 122 °C. ^{1}H: δ 8.38–8.34 (2H, m, H2, H6), 7.38–7.34 (2H, m, H4', H5'), 7.28–7.20 (4H, m, H3", H4", H5", H6'), 7.06–7.00 (2H, m, H2", H6"), 6.99–6.95 (2H, m, H3, H5), 2.18 (3H, CH_3); ^{13}C NMR: δ 149.9, 148.9, 140.2, 139.3, 138.7, 136.9, 130.3, 130.1, 128.0, 127.4, 127.2, 126.8, 124.7, 21.0; MS: M^+ 245 (100), *m/z* 244 (47), 230 (29), 202 (18).

Anal. Calc. for $C_{18}H_{15}N$: C, 88.13; H, 5.71. Found: C, 88.11; H, 5.80.

*2-(4'-Methoxycarbonylphenyl)-1-phenylnaphthalene (**14**; R^1 = –(CH)$_4$–, R^2 = 4-CO_2Me, R^3 = H, X = CH)*

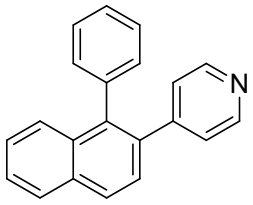


M.p. (hexane): 161 °C. ^{1}H NMR: δ 7.95, 7.94 (overlapping d and dd, *J* = 8.3 Hz, H4; *J* = 8.6, 1.3 Hz, H5), 7.90–7.85 (2H, m, H3', H5'), 7.69 (1H, dd, *J* = 8.5, 1.0 Hz, H8), 7.57 (1H, *J* = 8.4 Hz, H3), 7.52 (1H, ddd, *J* = 8.1, 6.8, 1.3 Hz, H6), 7.43 (1H, ddd, *J* = 8.4, 6.8, 1.4 Hz, H7), 7.33–7.27 (3H, m, H3", H5", H4"), 7.26–7.17 (4H, m, H2', H6', H2", H6"), 3.89 (CH_3); ^{13}C NMR: δ 167.0 (CO_2CH_3), 146.9 (C1'), 138.5 (C1"), 137.8 (C1), 137.2 (C2), 133.0 (C4a), 132.5 (C8a), 131.3 (C2", C6"), 130.1 (C2', C6'), 128.9 (C3', C5'), 127.9 (C3", C5"), 127.9 (C5), 127.8 (C4', C4), 127.7 (C3), 127.0 (C4"), 126.9 (C8), 126.4 (C7), 126.0 (C6), 52.0 (CH_3); IR (KBr, cm^{-1}): ν 1716; MS: M^+

338 (100), *m/z* 307 (15), 279 (45), 278 (50), 277 (46), 276 (49), 263 (14), 252 (25), 203 (18), 138 (19).

Anal. Calc. for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.15; H, 5.42.

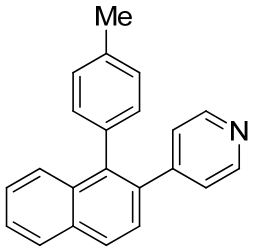
*4-(1'-phenylnaphthalen-2'-yl)pyridine (**14**; R^1 = –(CH)$_4$–, R^2, R^3 = H, X = N)*



M.p. (hexane): 131–132 °C. ^{1}H NMR: δ 8.44–8.40 (2H, m, H2, H6), 7.98–7.92 (2H, 2 overlapping br d, H4', H5'), 7.69 (1H, br d, *J* = 8.4 Hz, H8'), 7.57–7.50 [2H, 2 overlapping signals, H6', H3' (d centred at 7.54, *J* = 8.5 Hz)], 7.47–7.39 (1H, m, H7'), 7.36–7.30 (3H, m, H3", H5", H4"), 7.21–7.17 (2H, m, H2", H6"), 7.08–7.05 (2H, m, H3, H5); ^{13}C NMR: δ 149.9 (C4), 149.0 (C2, C6), 138.0 (C1', C1"), 135.3 (C2'), 133.2 (C4'a), 132.5 (C8'a), 131.2 (C2", C6"), 128.0 (C3", C5", C4'), 127.9 (C5'), 127.2 (C4"), 127.0 (C3'), 126.9 (C8'), 126.5 (C7'), 126.3 (C6'), 124.9 (C3, C5); MS: M^+ 281 (100), *m/z* 252 (17), 226 (11), 203 (22), 139 (12), 125 (9), 113 (10).

Anal. Calc. for $C_{21}H_{15}N$: C, 89.65; H, 5.37. Found: C, 89.67; H, 5.34.

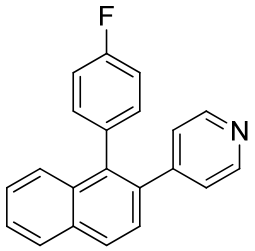
*4-[1'-(4"-Methylphenyl)naphthalen-2'-yl]pyridine (**14**; R^1 = –(CH)$_4$–, R^2 = H, R^3 = 4-Me, X = N)*



M.p. (hexane): 138 °C. ^{1}H NMR: δ 8.43–8.40 (2H, m), 7.97–7.91 (2H, 2 overlapping br d), 7.71 (1H, d further split, *J* = 8.7 Hz), 7.56–7.49 (2H, 2 overlapping signals with a d centred at 7.52, *J* = 8.5 Hz), 7.46–7.40 (1H, m), 7.15–7.11 (2H, m), 7.09–7.04 (4H, m), 2.38 (3H, s); ^{13}C NMR: δ 150.3, 149.0, 138.2, 136.9, 135.4, 134.9, 133.3, 132.7, 131.1, 128.8, 127.92, 127.90, 127.06, 127.04, 126.5, 126.3, 125.0, 21.2; MS: M^+ 295 (100), *m/z* 280 (35), 140 (16).

Anal. Calc. for $C_{22}H_{17}N$: C, 89.46; H, 5.80. Found: C, 89.47; H, 5.84.

*4-[1'-(4"-Fluorophenyl)naphthalen-2'-yl]pyridine (**14**; R^1 = –(CH)$_4$–, R^2 = H, R^3 = 4-F, X = N)*



M.p. (hexane): 117–118 °C. ^{1}H NMR: δ 8.46–8.42 (2H, m), 7.99–7.93 (2H, m), 7.63 (1H, d further split, J = 8.8 Hz), 7.58–7.41 (3H, m), 7.17–7.12 (2H, m), 7.08–7.00 (4H, m); ^{13}C NMR: δ 161.7 (d, $J_{C,F}$ = 245.0 Hz), 150.1, 148.8, 137.0, 135.5, 133.9, 133.3, 132.8 (d, $J_{C,F}$ = 12.0 Hz), 132.7, 128.4, 128.0, 127.0, 126.8, 126.7, 126.5, 125.1, 115.26 (d, $J_{C,F}$ = 21.1 Hz); MS: M^{+} 299 (100), *m/z* 270 (17), 221 (21).

Anal. Calc. for $C_{21}H_{14}FN$: C, 84.26; H, 4.71. Found: C, 84.27; H, 4.80.

References

1 M. S. Lesslie and U. J. H. Mayer, *J. Chem. Soc*., 1961, 611–618.

2 E. Motti, A. Mignozzi and M. Catellani, *J. Mol. Catal. A: Chemical* 2003, **204-205**, 115–124.