Supporting Information

A catalytic synthesis of selectively substituted biaryls through sequential intermolecular coupling involving arene and ketone C–H bond functionalization

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General

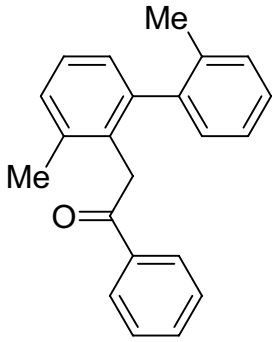
Most chemicals were obtained from commercial suppliers and were used without further purification. 2-*i*-Propyliodobenzene and 4-methoxy-2,3-dimethyliodobenzene were prepared by iodination of the corresponding diazonium salt according to the literature.[1] 4,5-Dimethoxy-2,3-dimethyliodobenzene was prepared as previously described.[2] DMF was dried and stored over 4 Å molecular sieves under nitrogen. 2,3'-Di-*i*-propyl-1,1'-biphenyl[3] was identified by comparison with the data reported in the literature. Reactions were carried out under nitrogen by use of conventional standard Schlenk techniques. Flash column chromatography was performed on Merck Kieselgel 60 and thin layer chromatography on Merck $60F_{254}$ silica plates. Gas chromatography analyses were run with a Carlo Erba HRGC 5300 instrument using a 30 m SE-30 capillary column. ^{1}H and ^{13}C NMR spectra were recorded at 293 K, in $CDCl_3$ on a Bruker AC-300 and AVANCE 300 spectrometers at 300.1 and 75.4 MHz, respectively. ^{1}H and ^{13}C chemical shifts are given in ppm using the solvent as internal reference (7.26 and 77.0 ppm respectively for ^{1}H and ^{13}C). The reported assignments are based on decoupling, COSY, NOESY, C–H, HMBC correlation experiments. MS spectra (EI, 70eV) were performed on a Hewlett Packard HP 6890 GC system equipped with a SE-52 capillary column and a HP5973 Mass Selective Detector mass analyzer and are reported as *m/z* (relative intensity). IR spectra were recorded on a Nicolet FT-IR 5700 spectrophotometer (Thermo Electron Corporation) and are reported in wave numbers (cm^{-1}). Melting points were determined with an Electrothermal apparatus and are uncorrected. Elemental analyses were performed with a Carlo Erba EA 1108-Elemental Analyzer.

General procedure for the reaction of ortho-substituted aryl iodides and ketones

A Schlenk-type flask containing a magnetic stirring bar was charged under nitrogen with the corresponding aryl iodide (1 mmol), palladium acetate (5.6 mg, 0.025 mmol), norbornene (23.5 mg, 0.25 mmol), the desired ketone (1.25 mmol), potassium phenoxide (13.2 mg, 0.10 mmol),

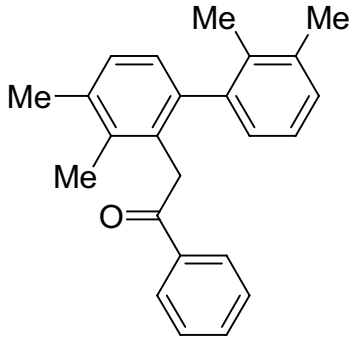
potassium carbonate (152 mg, 1.10 mmol) and DMF (11 mL). The resulting mixture was stirred at 105 °C for 6–48 h. At the end of the reaction the mixture was allowed to cool to room temperature, diluted with EtOAc (30 mL), washed three times with a solution of NaCl (3 × 30 mL) and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude reaction mixture was analyzed by GC and ^{1}H NMR spectroscopy. Products were isolated by flash column chromatography on silica gel using a mixture of hexane-EtOAc 95:5 as eluent.

3,2'-Dimethyl-2-(2-oxo-2-phenylethyl)-1,1'-biphenyl (**3a**)



Yield 28% (42 mg); colorless oil. ^{1}H NMR: δ 7.82 (dt, *J* = 7.2, 1.5 Hz, 2H), 7.54 (tt, *J* = 7.2, 1.5 Hz, 1H), 7.41 (tt, *J* = 7.3, 1.5 Hz, 2H), 7.32–7.06 (m, 7H), 4.27 (d, *J* = 17.7 Hz, 1H), 4.04 (d, *J* = 17.7 Hz, 1H), 2.32 (s, 3H), 2.11 (s, 3H); ^{13}C NMR: δ 197.3, 142.3, 141.3, 137.6, 137.0, 135.8, 132.8, 132.0, 129.9, 129.4, 129.1, 128.4, 127.8, 127.2, 127.1, 126.6, 125.4, 40.3, 20.4, 20.0; IR (film, cm^{-1}): 1687; MS (%): M^+ 300 (20), *m/z* 195 (12), 178 (30), 165 (34), 105 (100), 77 (39), 51 (16). Anal. Calcd. for $C_{22}H_{20}O$: C 87.96; H 6.71. Found: C 87.82; H 6.76.

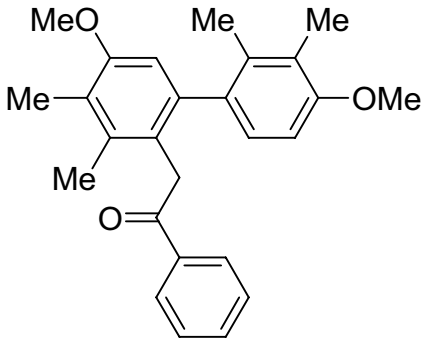
3,4,2',3'-Tetramethyl-2-(2-oxo-2-phenylethyl)-1,1'-biphenyl (**3b**)



Yield 73% (120 mg); colorless oil. ^{1}H NMR: δ 7.84–7.79 (m, 2H), 7.54 (tt, *J* = 7.3, 1.5 Hz, 1H), 7.44–7.38 (m, 2H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.09 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.97 (br d, *J* = 7.6 Hz, 2H), 4.31 (d, *J* = 17.7 Hz, 1H), 4.06 (d, *J* = 17.7 Hz, 1H), 2.40 (s, 3H), 2.27 (s, 3H), 2.20 (s, 3H), 1.98 (s, 3H); ^{13}C NMR: δ 197.5, 141.8, 140.8, 137.0, 136.9, 136.0, 135.5, 134.6, 132.7, 131.9, 128.6, 128.3, 127.8, 127.4, 126.8, 125.0, 40.7, 20.8, 20.4, 16.7, 16.4; IR (film,

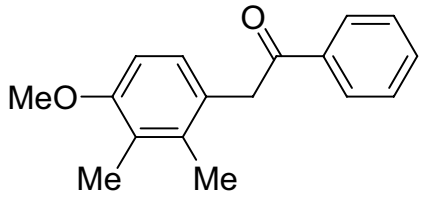
cm^{-1}): 1689; MS (%): M^+ 328 (20), *m/z*; 223 (24), 208 (23), 193 (41), 105 (100), 77 (42). Anal. Calcd. for $C_{24}H_{24}O$: C 87.76; H 7.37. Found: C 87.67; H 7.41.

3,4,2',3'-Tetramethyl-5,4'-dimethoxy-2-(2-oxo-2-phenylethyl)-1,1'-biphenyl (**3c**)



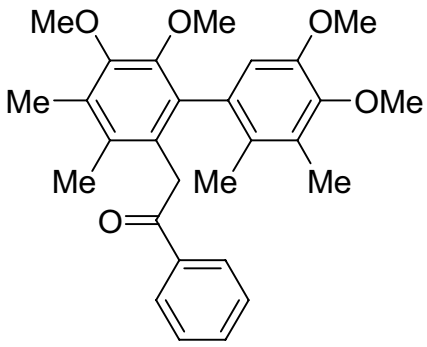
Yield 71% (138 mg); white solid; m.p. (*n*-hexane): 158–159 °C. ^{1}H NMR: δ 7.81–7.76 (m, 2H), 7.50 (t, *J* = 7.3 Hz, further split, 1H), 7.41–7.35 (m, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 6.55 (s, 1H), 4.20 (d, *J* = 17.8 Hz, 1H), 3.95 (d, *J* = 17.8 Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 2.24 (s, 3H), 2.14, 2.13 (2s, 6H), 1.97 (s, 3H); ^{13}C NMR: δ 198.1, 156.5, 155.9, 140.8, 137.1, 137.0, 135.9, 134.7, 132.7, 128.3, 127.9, 127.2, 125.0, 124.6, 124.0, 109.8, 107.3, 55.5, 55.4, 40.5, 17.2, 16.9, 12.2, 12.0; IR (KBr, cm^{-1}): 1688; MS (%): M^+ 388 (25), *m/z* 283 (100), 268 (53), 253 (40), 237 (21), 105 (59), 77 (54), 51 (19). Anal. Calcd. for $C_{26}H_{28}O_3$: C 80.38; H 7.26. Found: C 80.28; H 7.33.

2-(4-Methoxy-2,3-dimethylphenyl)-1-phenylethanone



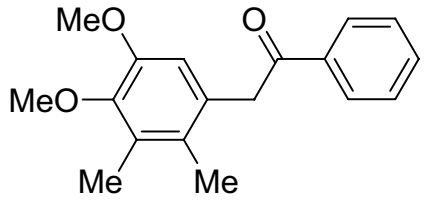
Yield 15% (38 mg); white solid; m.p. (*n*-hexane): 116–117 °C. ^{1}H NMR: δ 7.86 (d, *J* = 7.0 Hz, further split, 2H), 7.59 (t, *J* = 7.3 Hz, further split, 1H), 7.49 (m, 2H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 4.31 (s, 2H), 3.82 (s, 3H), 2.21 (s, 3H), 2.15 (s, 3H); ^{13}C NMR: δ 197.9, 156.6, 136.8, 136.6, 133.0, 128.6, 128.2, 128.0, 125.5, 125.4, 107.7, 55.4, 43.7, 16.2, 12.1; IR (KBr, cm^{-1}): 1677; MS (%): M^+ 254 (21), *m/z* 149 (100), 105 (18), 91 (14), 77 (18). Anal. Calcd. for $C_{17}H_{18}O_2$: C 80.28; H 7.13. Found: C 80.14; H 7.19.

3,4,2',3'-Tetramethyl-5,6,4',5'-tetramethoxy-2-(2-oxo-2-phenylethyl)-1,1'-biphenyl (**3d**)



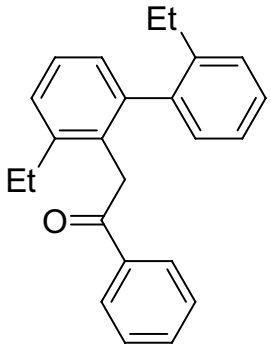
Yield 79% (175 mg); white solid; m.p. (*n*-hexane): 166–167 °C. ^{1}H NMR: δ 7.75–7.71 (m, 2H), 7.51 (tt, *J* = 7.4, 1.5 Hz, 1H), 7.40–7.34 (m, 2H), 6.52 (s, 1H), 4.09 (d, *J* = 17.8 Hz, 1H), 3.86 (d, *J* = 17.8 Hz, 1H), 3.85 (s, 3H), 3.70 (s, 3H), 3.60, 3.59 (2s, 6H), 2.31 (s, 3H), 2.15 (s, 3H), 2.13 (s, 3H), 1.87 (s, 3H); ^{13}C NMR: δ 197.9, 150.0, 149.9, 148.2, 146.1, 136.9, 134.6, 132.9, 132.7, 132.4, 130.6, 130.2, 128.4, 127.7, 111.1, 60.4, 60.2, 60.1, 55.3, 40.5, 16.6 , 12.8, 12.6; IR (KBr, cm^{-1}): 1684; MS (%): M^+ 448 (31), *m/z*; 343 (50), 328 (19), 312 (64), 297 (26), 281 (21), 105 (100), 77 (71). Anal. Calcd. for $C_{28}H_{32}O_5$: C 74.97; H 7.19. Found: C 75.08; H 7.23.

2-(4,5-Dimethoxy-2,3-dimethylphenyl)-1-phenylethanone



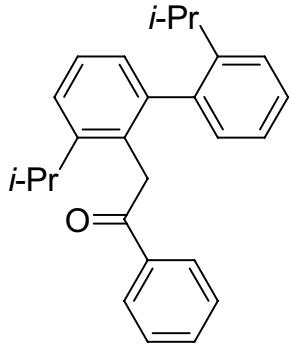
Yield 13% (37 mg); white solid; m.p. (*n*-hexane): 143–144 °C. ^{1}H NMR: δ 8.05 (d, *J* = 7.3 Hz, further split, 2H), 7.59 (t, *J* = 7.3 Hz, further split, 1H), 7.48 (t, *J* = 7.2 Hz, further split, 2H), 6.59 (s, 1H), 4.31 (s, 2H), 3.80, 3.79 (2s, 6H), 2.24 (s, 3H), 2.07 (s, 3H); ^{13}C NMR: δ 197.4, 150.1, 146.0, 136.6, 133.0, 130.9, 128.5, 128.3, 128.2, 128.0, 111.9, 60.1, 55.4, 43.9, 15.5, 12.6; IR (KBr, cm^{-1}): 1683; MS (%): M^+ 284 (24), *m/z* 179 (100), 105 (19), 91 (10), 77 (22). Anal. Calcd. for $C_{18}H_{20}O_3$: C 76.03; H 7.09. Found: C 75.93; H 7.13.

3,2'-Diethyl-2-(2-oxo-2-phenylethyl)-1,1'-biphenyl (**3e**)



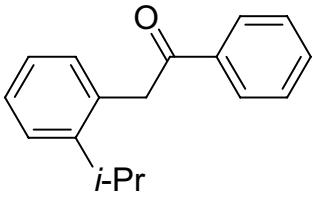
Yield 74% (121 mg); colorless oil. ^{1}H NMR: δ 7.77 (d, *J* = 7.2 Hz, further split, 2H), 7.52 (tt, *J* = 7.2, 1.6 Hz, 1H), 7.39 (tt, *J* = 7.2, 1.6 Hz, 2H), 7.36–7.18 (m, 4H), 7.12–7.06 (m, 3H), 4.28 (d, *J* = 17.7 Hz, 1H), 4.01 (d, *J* = 17.7 Hz, 1H), 2.61 (q, *J* = 7.2 Hz, 2H), 2.41 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR: δ 197.6, 143.1, 142.2, 141.8, 140.9, 137.0, 132.8, 131.4, 129.6, 128.4, 128.1, 127.8, 127.4, 127.3, 127.0, 126.6, 125.3, 39.8, 26.3, 26.0, 15.1, 14.6; IR (film, cm^{-1}): 1690; MS (%): M^{+} 328 (16), *m/z*; 178 (18), 165 (20), 105 (100), 77 (33). Anal. Calcd. for $C_{24}H_{24}O$: C 87.76; H 7.37. Found: C 87.64; H 7.43.

3,2'-Di-i-propyl-2-(2-oxo-2-phenylethyl)-1,1'-biphenyl (**3f**)



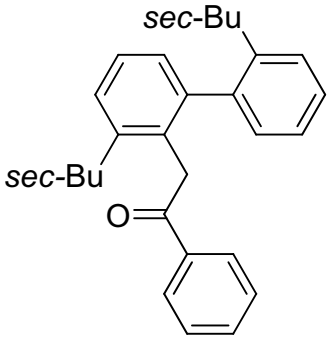
Yield 84% (150 mg); colorless oil. ^{1}H NMR: δ 7.83–7.77 (m, 2H), 7.58–7.50 (m, 1H), 7.46–7.24 (m, 6H), 7.12–7.06 (m, 3H), 4.32 (d, *J* = 18.0 Hz, 1H), 4.11 (d, *J* = 18.0 Hz, 1H), 2.89, 2.82 (2hept, *J* = 6.8 Hz, 2H), 1.31, 129 (2d, *J* = 6.8 Hz, 6H), 1.15 (d, *J* = 6.8 Hz, 3H), 1.10 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR: δ 197.2, 148.1, 146.6, 142.2, 140.5, 137.0, 132.8, 130.5, 129.6, 128.4, 127.8, 127.6, 127.2, 126.6, 125.4, 125.2, 124.3, 39.8, 30.2, 29.7, 24.8, 24.0, 23.9, 23.3; IR (film, cm^{-1}): 1690; MS (%): M^{+} 356 (42), *m/z* 313 (17), 237 (15), 207 (22), 191 (11), 178 (13), 167 (20), 105 (100), 77 (28), 43 (12). Anal. Calcd. for $C_{26}H_{28}O$: C 87.60; H 7.92. Found: C 87.48; H 7.97.

2-(2-i-Propylphenyl)-1-phenylethanone



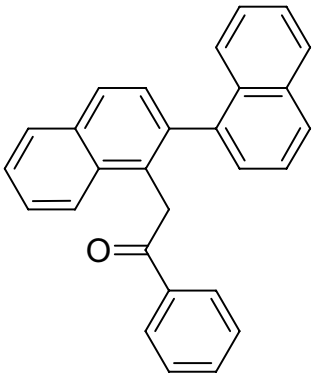
Yield 4% (10 mg); colorless oil. ^{1}H NMR: δ 8.09 (d, *J* = 7.2 Hz, further split, 2H), 7.62 (t, *J* = 7.3 Hz, further split, 1H), 7.58–7.29 (m, 4H), 7.24–7.12 (m, 2H), 4.42 (s, 2H), 3.02 (hept, *J* = 6.8 Hz, 1H), 1.28 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR: δ 197.7, 147.3, 136.8, 133.0, 131.7, 130.6, 128.6, 128.2, 127.5, 125.7, 125.4, 42.9, 29.5, 23.6; IR (film, cm^{-1}): 1691; MS (%): M^{+} 238 (15), *m/z* 105 (100), 77 (33). Calcd. for $C_{17}H_{18}O$: C 85.67; H 7.61. Found: C 85.58; H 7.66.

3,2'-Di-sec-butyl-2-(2-oxo-2-phenylethyl)-1,1'-biphenyl (**3g**)



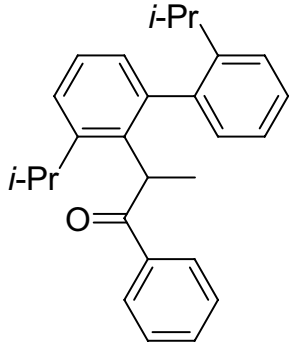
Yield 82% (157 mg); pale yellow oil. A 1:1:1:1 mixture of four stereoisomers. ^{1}H NMR: δ 7.82–7.73 (m, 2H), 7.56–7.48 (m, 1H), 7.43–7.21 (m, 6H), 7.09–6.98 (m, 3H), 4.26, 4.22, 4.21 (3d, *J* = 18.0 Hz, 1H), 4.04, 4.03, 3.99 (3d, *J* = 18.0 Hz, 1H), 2.60–2.42 (m, 2H), 1.78–1.42 (m, 4H), 1.28–1.16 (m, 3H), 1.11, 1.10, 1.08, 0.99 (4d, *J* = 6.9 Hz, 3H), 0.85–0.68 (m, 6H); ^{13}C NMR: δ 197.5, 197.4, 197.3, 197.2, 147.2, 147.0, 146.9, 145.3, 145.1, 145.0, 142.2, 142.1, 141.9, 141.8, 141.4, 141.3, 141.2, 137.1, 137.0, 136.9, 132.7, 131.3, 131.2, 131.1, 130.9, 129.7, 129.5, 128.4, 127.7, 127.6, 127.5, 127.47, 127.44, 127.2, 127.1, 126.6, 126.44, 126.39, 125.62, 125.58, 125.53, 125.50, 125.2, 125.1, 124.6, 124.5, 124.4, 40.4, 40.13, 40.08, 39.9, 37.44, 37.4, 37.22, 37.2, 36.9, 36.8, 36.3, 36.1, 31.9, 31.7, 31.5, 31.3, 30.8, 30.4, 30.3, 30.1, 23.0, 22.8, 22.1, 21.9, 21.7, 21.64, 21.59, 21.57, 12.6, 12.4, 12.37, 12.24, 12.2; IR (film, cm^{-1}): 1691; MS (%): M^{+} 384 (9), *m/z* 265 (7), 221 (8), 193 (13), 178 (20), 167 (20), 105 (100), 77 (39), 57 (17), 43 (19). Anal. Calcd. for $C_{28}H_{32}O$: C 87.45; H 8.39. Found: C 87.37; H 8.45.

1-(2-oxo-2-phenylethyl)-2,1'-binaphthyl (**3h**)



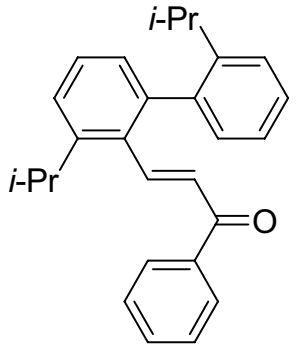
Yield 75% (139 mg); white solid; m.p. (*n*-hexane): 174–174.5 ºC. ^{1}H NMR: δ 8.00–7.66 (m, 7H), 7.59–7.34 (m, 11H), 4.76 (d, *J* = 17.7 Hz, 1H), 4.33 (d, *J* = 17.7 Hz, 1H); ^{13}C NMR: δ 197.5, 139.3, 138.6, 136.6, 133.5, 133.2, 132.9, 132.7, 132.1, 130.0, 128.7, 128.6, 128.4, 128.1, 127.9, 127.7, 127.2, 127.1, 126.6, 126.2, 126.1, 125.8, 125.6, 125.2, 124.4, 40.1; IR (KBr, cm^{-1}): 1684; MS (%): M^{+} 372 (31), *m/z* 265 (73), 252 (26), 105 (100), 77 (43), 51 (12). Anal. Calcd. for $C_{28}H_{20}O$: C 90.29; H 5.41. Found: C 90.14; H 5.44.

3,2'-Di-i-propyl-2-(1-methyl-2-oxo-2-phenylethyl)-1,1'-biphenyl (**3i**)



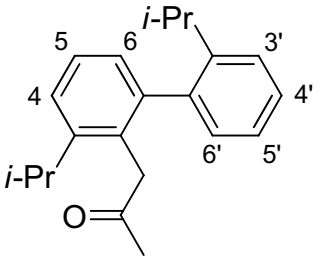
Yield 29% (54 mg); colorless oil. A 1:1 mixture of two stereoisomers. ^{1}H NMR: δ 7.58, 7.53 (2d further split, *J* = 8.3 Hz, 2H), 7.46–7.12 (m, 9H), 7.07-6.99 (m, 1H), 4.27 (br q, *J* = 7.0 Hz, 1H), 2.92, 2.71 (2 hept, *J* = 6.8 Hz, 1H), 2.90, 2.84 (2 hept, *J* = 6.9 Hz, 1H), 1.57, 1.44 (2d, *J* = 7.0 Hz, 3H), 1.24, 1.22 (2d, *J* = 6.7 Hz, 3H), 1.21, 1.18 (2d, *J* = 6.7 Hz, 3H), 1.09, 0.89 (2d, *J* = 6.7 Hz, 3H), 1.01, 0.96 (2d, *J* = 6.8 Hz, 3H); ^{13}C NMR: δ 203.1, 202.7, 148.5, 148.3, 147.3, 146.9, 141.2, 141.0, 140.6, 140.2, 137.7, 137.6, 137.3, 137.0, 132.0, 130.1, 129.3, 128.63, 128.56, 128.3, 128.1, 128.01, 127.96, 127.89, 126.7, 126.6, 126.4, 126.3, 126.1, 125.6, 125.3, 125.0, 47.40, 47.37, 30.2, 29.97, 29.95, 29.7, 25.8, 25.70, 25.67, 25.5, 23.6, 23.5, 23.4, 22.8, 19.2, 17.7; IR (film, cm^{-1}): 1675; MS (%): M^{+} 370 (18), *m/z* 237 (12), 181 (100), 179 (28), 165 (21), 105 (73), 77 (38), 43 (46). Anal. Calcd. for $C_{27}H_{30}O$: C 87.52; H 8.16. Found: C 87.45; H 8.22.

3,2'-Di-i-propyl-2-(3-oxo-3-phenylpropenyl)-1,1'-biphenyl



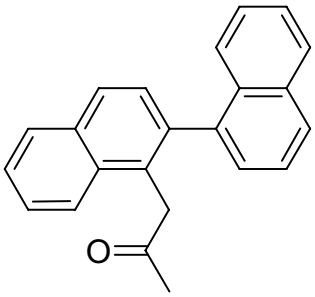
Yield 30% (55 mg); yellow oil. ^{1}H NMR: δ 7.85 (d, *J* = 16.0 Hz, 1H), 7.53–7.25 (m, 10H), 7.19 (d, *J* = 7.4 Hz, further split, 1H), 7.11 (dd, *J* = 5.9, 2.8 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 3.38 (hept, *J* = 6.8 Hz, 1H), 2.74 (hept, *J* = 6.8 Hz, 1H), 1.34 (d, *J* = 6.8 Hz, 3H), 1.28 (d, *J* = 6.8 Hz, 3H), 1.09 (d, *J* = 6.8 Hz, 3H), 1.06 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR: δ 190.6, 148.1, 146.2, 142.0, 141.1, 140.7, 137.8, 132.6, 132.5, 130.2, 129.2, 128.44, 128.41, 128.28, 128.26, 127.8, 125.8, 125.6, 124.4, 30.0, 29.9, 25.0, 24.1, 23.7, 22.8; IR (film, cm^{-1}): 1665, 1610; MS (%): M^{+} 368 (5), *m/z* 325 (43), 263 (25), 262 (24), 205 (23), 179 (85), 105 (100), 77 (58). Anal. Calcd. for $C_{27}H_{28}O$: C 88.00; H 7.66. Found: C 88.19; H 7.72.

3,2'-Di-i-propyl-2-(2-oxopropyl)-1,1'-biphenyl (**3j**)



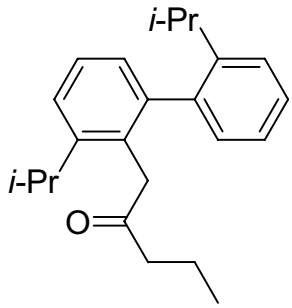
Yield 70% (103 mg) ; white solid; m.p. (*n*-hexane): 91.5–92 ºC. ^{1}H NMR: δ 7.41–7.33 (m, 3H, H3', H4, H4'), 7.30 (t, *J* = 7.8 Hz, 1H, H5), 7.17 (td, *J* = 6.8, 1.8 Hz, 1H, H5'), 7.04–7.01 (m, 2H, H6', H6), 3.72 (d, *J* = 17.7 Hz, 1H, CH(H)), 3.50 (d, *J* = 17.7 Hz, 1H, CH(H)), 2.87 (hept, *J* = 6.8 Hz, 1H, $CH(CH_3)_2$), 2.68 (hept, *J* = 6.8 Hz, 1H, $CH(CH_3)_2$), 1.94 (s, 3H, $COCH_3$), 1.27, 1.26 (2d, *J* = 6.8 Hz, 6H, $2CH_3$), 1.12, 1.10 (2d, *J* = 6.8 Hz, 6H, $2CH_3$); ^{13}C NMR: δ 206.2 (CO), 147.9 (C3), 146.5 (C2'), 141.9 (C1), 140.5 (C1'), 130.3 (C2), 129.6 (C6'), 127.8 (C4'), 127.3 (C6), 126.7 (C5), 125.4 (C3'), 125.2 (C5'), 124.4 (C4), 45.0 (CH_2), 30.0 ($CH(CH_3)_2$), 29.7 ($CH(CH_3)_2$), 29.6 ($COCH_3$), 24.8 (CH_3), 24.1 (CH_3), 23.7 (CH_3), 23.1 (CH_3); IR (KBr, cm^{-1}): 1716; MS (%): M^{+} 294 (18), *m/z* 251 (19), 237 (24), 209 (52), 178 (30), 167 (100), 43 (43). Anal. Calcd. for $C_{21}H_{26}O$: C 85.67; H 8.90. Found: C 85.54; H 9.00.

1-(2-Oxopropyl)-2,1'-binaphthyl (**3k**)



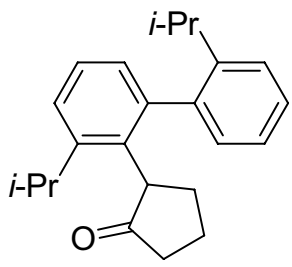
Yield 54% (84 mg); pale yellow oil. ^{1}H NMR: δ 7.99–7.82 (m, 5H), 7.62–7.33 (m, 8H), 4.08 (d, *J* = 17.2 Hz, 1H), 3.77 (d, *J* = 17.2 Hz, 1H), 1.90 (s, 3H); ^{13}C NMR: δ 206.7, 139.3, 138.5, 133.6, 133.2, 132.6, 132.0, 129.7, 128.8, 128.7, 128.3, 128.0, 127.4, 127.2, 126.9, 126.3, 126.1, 126.0, 125.9, 125.3, 124.3, 45.7, 29.4; IR (film, cm^{-1}): 1716; MS (%): M^{+} 310 (30), *m/z*; 265 (100), 252 (35), 43 (79). Anal. Calcd. for $C_{23}H_{18}O$: C 89.00; H 5.85. Found: C 88.87; H 5.89.

3,2'-Di-i-propyl-2-(2-oxo-2-penthyl)-1,1'-biphenyl (**3l**)



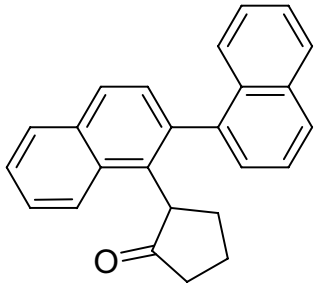
Yield 61% (91 mg); colorless oil. ^{1}H NMR: δ 7.41–7.24 (m, 4H), 7.18–7.12 (m, 1H), 7.00 (d, *J* = 7.3 Hz, further split, 2H), 3.68 (d, *J* = 17.6 Hz, 1H), 3.46 (d, *J* = 17.6 Hz, 1H), 2.85 (hept, *J* = 6.8 Hz, 1H), 2.67 (hept, *J* = 6.8 Hz, 1H), 2.18–2.08 (m, 2H), 1.52–1.37 (m, 2H), 1.25, 1.24 (2d, *J* = 6.8 Hz, 6H), 1.11, 1.09 (2d, *J* = 7.0 Hz, 6H), 0.80 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR: δ 208.2, 147.9, 146.5, 141.9, 140.5, 130.4, 129.7, 127.7, 127.2, 126.6, 125.4, 125.2, 124.3, 44.3, 44.2, 30.0, 29.7, 24.8, 24.1, 23.7, 23.1, 17.2, 13.6; IR (film, cm^{-1}): 1719; MS (%): M^{+} 322 (15), *m/z* 237 (30), 209 (42), 195 (22), 178 (28), 167 (100), 71 (74), 43 (88). Anal. Calcd for $C_{23}H_{30}O$: C 85.66; H 9.38. Found: C 85.58;H 9.43.

3,2'-Di-i-propyl-2-(2-oxocyclopentyl)-1,1'-biphenyl (**3m**)



Yield 67% (107 mg); colorless oil. ^{1}H NMR: δ 7.40–7.28 (m, 3H), 7.25 (t, *J* = 6.9 Hz, 1H), 7.17 (td, *J* = 6.9, 2.2 Hz, 1H), 7.05 (br d, *J* = 7.5 Hz, 1H), 6.96 (dd, *J* = 7.5, 1.7 Hz, 1H), 3.10 (m, 1H), 2.86 (m, 1H), 2.48–2.17 (m, 4H), 2.15–1.91 (m, 2H), 1.76–1.60 (m, 1H), 1.27 (d, *J* = 6.7 Hz, 3H), 1.22 (d, *J* = 6.7 Hz, 3H), 1.09 (d, *J* = 6.7 Hz, 3H), 1.04 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR: δ 217.5, 147.2, 147.1, 143.2, 140.9, 134.7, 129.3, 127.7, 127.1, 126.5, 125.9, 125.5, 124.9, 54.0, 37.3, 32.1, 31.7, 29.5, 25.0, 24.5, 23.3, 23.0, 20.8; IR (film, cm^{-1}): 1739; MS (%): M^{+} 320 (63), *m/z*; 287 (21), 235 (23), 217 (22), 207 (35), 191 (36), 179 (100), 165 (30), 43 (52). Anal. Calcd. for $C_{23}H_{28}O$: C 86.20; H 8.81. Found: C 86.09; H 8.86.

1-(2-Oxocyclopentyl)-2,1'-binaphthyl (**3n**)



Yield 71% (119 mg); white solid; m.p. (*n*-hexane): 129–130.5 °C. A 10:3 mixture of two stereoisomers. ^{1}H NMR: δ 7.98–7.88 (m, 3H), 7.83, 7.82 (2d, *J* = 8.4 Hz, 1H), 7.66 (br d, *J* = 7.8 Hz, 1H), 7.57–7.45 (m, 5H), 7.42–7.32 (m, 3H), 3.68, 3.61–3.42 (dd and m, *J* = 12.0, 9.6 Hz, 1H), 2.69–2.02 (m, 4H), 1.81–1.49 (m, 2H); ^{13}C NMR: δ 218.4, 139.76, 139.72, 134.1, 133.8, 133.6, 133.4, 132.5, 132.3, 129.6, 129.5, 129.4, 128.56, 128.53, 128.2, 127.9, 127.8, 127.5, 127.3, 126.8, 126.6, 126.5, 126.3, 126.2, 126.0, 125.9, 125.49, 125.44, 125.40, 125.1, 54.1, 37.8, 31.3, 29.0; IR (KBr, cm^{-1}): 1737; MS (%): M^{+} 336 (83), *m/z* 279 (100), 265 (59), 252 (22), 138 (25), 133 (27). Anal. Calcd. for $C_{25}H_{20}O$: C 89.25; H 5.99. Found: C 89.17; H 6.04.

References

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

2 N. Della Ca', G. Sassi and M. Catellani, *Adv. Synth. Catal.*, 2008, **350**, 2179–2182.

3 S. Deledda, E. Motti and M. Catellani, *Can. J. Chem.*, 2005, **83**, 741–747.