

# **K-bis(2-ethylhexyl) phosphate (BEHPK): a novel additive for C-H arylation**

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***Supporting Information***

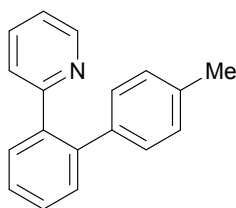
## Experimental

**General:** Melting points are uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (400 and 100 MHz, respectively) were recorded with tetramethylsilane used as an internal standard. Silica gel column chromatography was performed using Kieselgel 60 (E. Merck). Thin-layer chromatography (TLC) was carried out on E. Merck 0.25 mm pre-coated glass-backed plates (60 F<sub>254</sub>). Development was accomplished using 5% phosphomolybdic acid in ethanol-heat or visualized by UV light where feasible. All solvents and reagents were used as received.

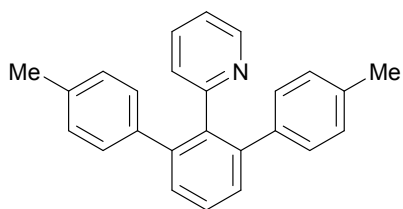
**A typical procedure for C-H arylation using BEHPK: synthesis of {2'-[1-benzyl-1*H*-tetrazol-5-yl]biphenyl-4-yl}methyl acetate **3** and [{3'-(4-acetoxymethylphenyl)-2'-[1-benzyl-1*H*-tetrazol-5-yl]biphenyl-4-yl}methyl acetate **4**.**

Into 50 mL two neck flask were sequentially added 1-benzyl-5-phenyl-1*H*-tetrazole (**1**) (2.0 g, 8.46 mmol), 4-bromobenzyl acetate (**2**) (2.13 g, 9.31 mmol), PPh<sub>3</sub> (44 mg, 0.168 mmol), K<sub>2</sub>CO<sub>3</sub> (1.17 g, 8.46 mmol), 2.5% NMP solution of BEHPK (0.0608 g/2.44 mL, 0.168 mmol) and NMP (10 mL) at 25 °C under N<sub>2</sub> atmosphere. Reaction mixture was heated to 138°C and [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (26 g, 0.0423 mmol) was added in one portion under stirring. Reaction was continued at 138°C for 6 h. Reaction mixture was cooled to 25°C prior to the addition of MTBE (20 mL) and stirred for 10 minutes. Filtered reaction mixture through sintered funnel and residue washed with MTBE (20 mL). Combined the organic layers, submitted sample for HPLC assay analysis. The organic layers were combined and washed with water (2 x 10 mL). Separated aqueous

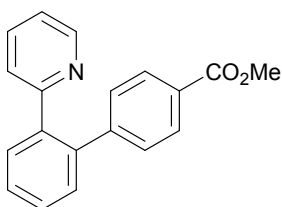
layer was extracted with MTBE (2 x 10 mL). Combined organic layers were washed with water (2 x 20 mL), brine (1 x 20 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The filtrate was submitted to HPLC analysis (**3**: 2.83 g, 87%; **4**: 206 mg, 4.68%) and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/AcOEt = 4:1) to provide monoarylation product **3** (2.67 g, 82%) and diarylation product **4** (45.1 mg, 1%). HPLC conditions: Cadenza CD-C-18 (4.6X 150) mm, 3 μ; M.P.A – buffer (0.03M KH<sub>2</sub>PO<sub>4</sub>) : acetonitrile (95:5), M.P.B – Buffer (0.03M KH<sub>2</sub>PO<sub>4</sub>) : acetonitrile (40:60), isocratic, A/B = 10:90; 1.0 mL/min; 225 nm, Inj vol - 10μL, column oven temp: 40 °C, sample conc.: 1000 ppm in diluent (acetonitrile). Compound **3**: mp: 73.4°C. IR (neat): 1741, 1603 cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 7.63 (td, *J* = 7.6, 1.4 Hz, 1H), 7.57 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.44 (td, *J* = 7.6, 1.4 Hz), 7.34 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.22 (t, *J* = 8.6 Hz, 1H), 7.16 (t, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 7.2 Hz, 2H), 6.76 (d, *J* = 7.2 Hz, 2H), 5.09 (s, 2H), 4.82 (s, 2H), 2.11 (s, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ = 170.7, 154.5, 141.2, 138.6, 135.9, 133.0, 131.6, 131.3, 130.3, 129.2, 129.1, 128.6, 128.0, 122.6, 65.5, 51.3, 21.0. Mass: 385 [M + H]<sup>+</sup>. HRMS: Calcd for C<sub>23</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>: 407.1484 [M + Na]<sup>+</sup>. Found: 407.1482 [M + Na]<sup>+</sup>. Compound **4**: mp: 155.3 °C; IR (KBr): *v*<sub>max</sub> = 1740, 1730, 1252, 1226 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.70 (t, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.26-7.22 (m, 1H), 7.17-7.12 (m, 6H), 6.96 (d, *J* = 8.0 Hz, 4H), 6.68 (d, *J* = 7.2 Hz, 2H), 5.03 (s, 4H), 4.73 (s, 2H), 2.10 (s, 6H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ = 170.8, 152.9, 143.1, 138.8, 135.6, 132.6, 131.4, 129.7, 129.1, 128.8, 128.7, 128.2, 128.1, 121.3, 65.7, 50.8, 21.0; HRMS: [M + Na]<sup>+</sup> calcd for C<sub>32</sub>H<sub>28</sub>N<sub>4</sub>O<sub>4</sub>Na 555.2008, found 555.2009; Mass: [M + Na]<sup>+</sup>: 555.2.



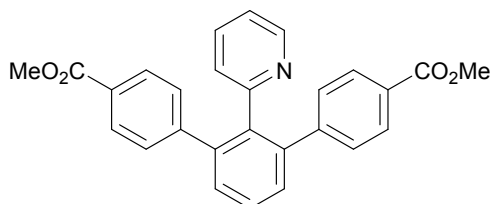
IR (KBr):  $\nu_{\max}$  = 3054, 3021, 2922, 2858, 1584, 1556, 1486, 1460, 1424, 1150, 795, 740  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  = 8.63 (d,  $J$  = 4.0 Hz, 1H), 7.69-7.67 (m, 1H), 7.46-7.37 (m, 4H), 7.11-7.04 (m, 5H), 6.89 (d,  $J$  = 7.6 Hz, 1H), 2.31 (s, 3H);  $^{13}\text{C}$ -NMR: (DMSO- $d_6$ )  $\delta$  = 159.3, 149.3, 140.5, 139.3, 138.3, 136.3, 135.1, 130.4, 129.5, 128.7, 128.4, 127.3, 125.3, 121.2, 21.1; Mass:  $[\text{M} + \text{H}]^+$ : 246.<sup>1</sup>



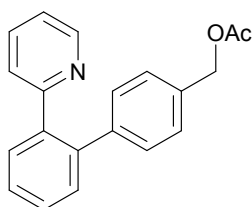
mp: 154.2 °C; IR (KBr):  $\nu_{\max}$  = 3023, 2993, 2918, 1583, 1560, 1512, 1451, 1419, 817, 799, 744  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  = 8.33 (d,  $J$  = 4.4 Hz, 1H), 7.50-7.46 (m, 1H), 7.41 (d,  $J$  = 7.2 Hz, 2H), 7.33-7.25 (m, 1H), 7.04-6.87 (m, 10H), 2.26 (s, 6H);  $^{13}\text{C}$ -NMR (DMSO- $d_6$ ):  $\delta$  = 159.2, 148.4, 141.7, 138.6, 138.4, 135.7, 134.8, 133.4, 129.3, 128.3, 128.0, 126.7, 120.7, 21.0; Mass:  $[\text{M} + \text{H}]^+$ : 336.<sup>1</sup>



mp: 130.9 °C; IR (KBr):  $\nu_{\max}$  = 2951, 2924, 1723, 1707, 1275, 1110, 760, 704  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ):  $\delta$  = 8.52 (d,  $J$  = 4.0 Hz, 1H), 7.83 (d,  $J$  = 8.4 Hz, 2H), 7.63-7.60 (m, 2H), 7.55 (t,  $J$  = 3.6 Hz, 2H), 7.48 (d,  $J$  = 3.2 Hz, 1H), 7.24 (t,  $J$  = 8.4 Hz, 3H), 7.04 (d,  $J$  = 8.0 Hz, 1H), 3.84 (s, 3H);  $^{13}\text{C}$ -NMR ( $\text{DMSO-}d_6$ ):  $\delta$  = 166.0, 158.2, 149.2, 145.2, 139.4, 139.1, 135.9, 130.5, 130.2, 129.6, 128.9, 128.6, 128.1, 127.8, 124.7, 121.9, 52.1; Mass:  $[\text{M} + \text{H}]^+$ : 290.<sup>1</sup>

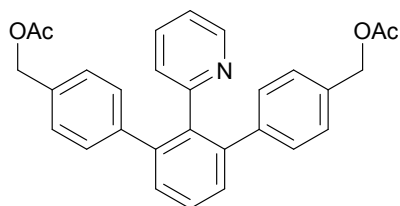


mp: 196.5 °C; IR (KBr):  $\nu_{\max}$  = 2948, 1715, 1285, 1102, 768, 706  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ):  $\delta$  = 8.35 (d,  $J$  = 4.0 Hz, 1H), 7.75 (d,  $J$  = 8.4 Hz, 4H), 7.66 (t,  $J$  = 7.6 Hz, 1H), 7.53 (d,  $J$  = 7.6 Hz, 2H), 7.45 (t,  $J$  = 7.6 Hz, 1H), 7.18 (d,  $J$  = 8.0 Hz, 4H), 7.07 (t,  $J$  = 7.6 Hz, 1H), 6.94 (d,  $J$  = 7.6 Hz, 1H), 3.81 (s, 6H);  $^{13}\text{C}$ -NMR ( $\text{DMSO-}d_6$ ):  $\delta$  = 166.0, 157.4, 148.5, 145.9, 140.4, 138.4, 135.4, 129.7, 128.6, 128.5, 127.6, 126.6, 121.7, 52.1; Mass:  $[\text{M} + \text{H}]^+$ : 424.<sup>1</sup>

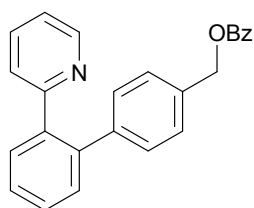


IR (KBr):  $\nu_{\max}$  = 1738, 1585, 1462, 1231  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 8.63 (dt,  $J$  = 4.8, 0.8 Hz, 1H), 7.70-7.66 (m, 1H), 7.49-7.45 (m, 2H), 7.44-7.38 (m, 2H), 7.25 (d,  $J$  = 8.0 Hz, 2H), 7.16 (d,  $J$  = 6.8 Hz, 2H), 7.14-7.09 (m, 1H), 6.90 (d,  $J$  = 7.6 Hz, 1H), 5.08 (s,

2H), 2.10 (s, 3H);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta = 170.7, 159.0, 149.3, 141.1, 139.9, 139.3, 135.2, 134.2, 130.3, 129.7, 128.4, 127.7, 127.6, 125.2, 121.3, 65.8, 20.8$ ; HRMS:  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{20}\text{H}_{17}\text{NO}_2\text{Na}$  326.1157, found 326.1152; Mass:  $[\text{M} + \text{H}]^+$ : 304.

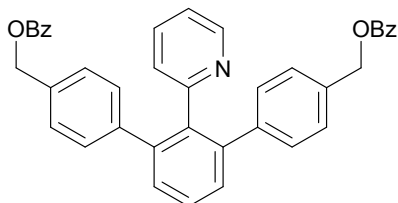


mp: 192 °C; IR (KBr):  $\nu_{\text{max}} = 1729, 1241 \text{ cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 8.33\text{-}8.32$  (m, 1H), 7.55-7.50 (m, 1H), 7.43 (d,  $J = 8.0 \text{ Hz}$ , 2H), 7.32 (dt,  $J = 7.2, 0.8 \text{ Hz}$ , 1H), 7.14 (d,  $J = 8.0 \text{ Hz}$ , 4H), 7.09 (d,  $J = 8.0 \text{ Hz}$ , 4H), 6.96-6.92 (m, 1H), 6.88 (d,  $J = 7.6 \text{ Hz}$ , 1H), 5.03 (s, 4H), 2.08 (s, 6H);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta = 170.8, 158.7, 148.6, 141.5, 141.4, 138.4, 135.0, 133.9, 129.8, 129.6, 128.3, 127.5, 126.7, 121.1, 66.0, 21.0$ ; HRMS:  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{29}\text{H}_{26}\text{NO}_4$  452.1862, found 452.1865; Mass:  $[\text{M} + \text{H}]^+$ : 452.0.

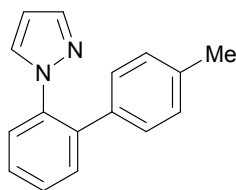


IR (KBr):  $\nu_{\text{max}} = 3419, 3059, 3030, 3008, 2954, 1918, 1718, 1584, 1461, 1269, 1107, 757 \text{ cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ):  $\delta = 8.55$  (d,  $J = 4.0 \text{ Hz}$ , 1H), 7.99 (d,  $J = 7.6 \text{ Hz}$ , 2H), 7.67 (t,  $J = 7.2 \text{ Hz}$ , 1H), 7.60-7.43 (m, 7H), 7.35 (d,  $J = 7.6 \text{ Hz}$ , 2H), 7.23 (t,  $J = 5.6 \text{ Hz}$ , 1H), 7.12 (d,  $J = 8.0 \text{ Hz}$ , 2H), 7.0 (d,  $J = 8.0 \text{ Hz}$ , 1H), 5.33 (s, 2H);  $^{13}\text{C}$ -NMR ( $\text{DMSO-}d_6$ ):  $\delta = 165.5, 158.6, 149.2, 140.7, 139.6, 139.3, 135.7, 134.5, 133.4, 130.4, 130.3,$

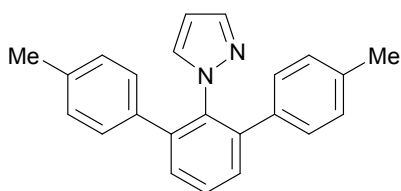
129.5, 129.4, 129.2, 128.8, 128.5, 127.6, 127.5, 124.7, 121.7, 65.8; HRMS:  $[M + H]^+$  calcd for  $C_{25}H_{20}O_2N$  366.1494, found 366.1491; Mass:  $[M + H]^+$ : 366.



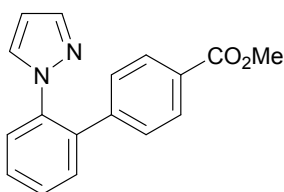
mp: 159.4 °C; IR (KBr):  $\nu_{\max} = 3059, 3027, 2932, 1723, 1449, 1267, 1109, 709 \text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta = 8.31$  (d,  $J = 4.0$  Hz, 1H), 7.98 (d,  $J = 7.6$  Hz, 4H), 7.68-7.65 (m, 1H), 7.61-7.51 (m, 6H), 7.45-7.42 (m, 3H), 7.27 (d,  $J = 7.6$  Hz, 4H), 7.10-7.02 (m, 5H), 6.96 (d,  $J = 7.6$  Hz, 1 H), 5.23 (s, 4H);  $^{13}\text{C}$ -NMR (DMSO- $d_6$ ):  $\delta = 165.5, 158.1, 148.3, 140.9, 138.4, 135.2, 134.1, 133.4, 129.5, 129.4, 129.3, 129.2, 128.8, 128.3, 127.2, 126.5, 121.4, 65.8$ ; HRMS:  $[M + H]^+$  calcd for  $C_{39}H_{30}O_4N$  576.2175, found 576.2170; Mass:  $[M + H]^+$ : 576.



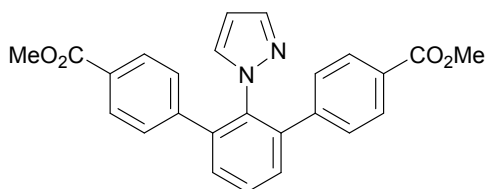
IR (KBr):  $\nu_{\max} = 3025, 2921, 1517, 1393, 1044, 937, 820, 703 \text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta = 7.70$  (s, 1H), 7.60 - 7.48 (m, 4H), 7.44 (d,  $J = 2.0$  Hz, 1H), 7.09 (d,  $J = 7.6$  Hz, 2 H), 6.93 (d,  $J = 8.0$  Hz, 2H), 6.29 (s, 1H), 2.27 (s, 3H);  $^{13}\text{C}$ -NMR (DMSO- $d_6$ ):  $\delta = 139.9, 138.2, 136.6, 136.5, 135.3, 131.6, 130.8, 128.9, 128.5, 128.1, 128.0, 126.7, 106.5, 20.6$ ; Mass:  $[M + H]^+$ : 235.<sup>2</sup>



mp: 110.4 °C; IR (KBr):  $\nu_{\max}$  = 1517, 1456, 1048  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.53 (t,  $J$  = 6.8 Hz, 1H), 7.47 - 7.40 (m, 3H), 7.09 (d,  $J$  = 4.0 Hz, 1H), 7.05-6.98 (m, 8 H) 6.08 (t,  $J$  = 2.0 Hz, 1H), 2.305 (s, 6H);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  = 140.3, 139.2, 136.8, 136.3, 135.8, 132.4, 129.8, 129.0, 128.7, 128.0, 105.9, 21.1; HRMS:  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{20}\text{N}_2\text{Na}$  347.1524, found 347.1521; Mass:  $[\text{M} + \text{H}]^+$  : 325.



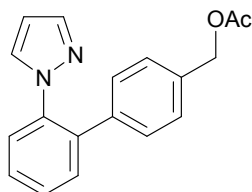
mp: 113.0 °C; IR (KBr):  $\nu_{\max}$  = 1723, 1281, 1116, 760, 706  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ):  $\delta$  = 7.85 (d,  $J$  = 8.4 Hz, 2H), 7.58 (t,  $J$  = 4.4, 6H), 7.17 (d,  $J$  = 8.0 Hz, 2H), 6.32 (s, 1H), 3.84 (s, 3H);  $^{13}\text{C}$ -NMR ( $\text{DMSO}-d_6$ ):  $\delta$  = 165.9, 134.2, 140.2, 138.3, 135.6, 130.8, 129.2, 129.05, 128.73, 128.5, 128.4, 126.7, 106.7, 52.11; Mass:  $[\text{M} + \text{H}]^+$ : 279.<sup>1</sup>



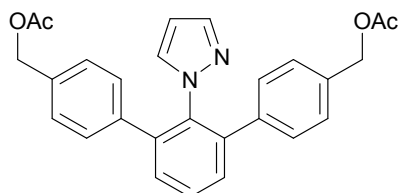
mp: 199.6 °C; IR (KBr):  $\nu_{\max}$  = 1717, 1275, 1102, 768, 706  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ):  $\delta$  = .81 (d,  $J$  = 8.0 Hz, 4H), 7.75 (t,  $J$  = 8.0 Hz, 1H), 7.65 (d,  $J$  = 7.6 Hz, 2H), 7.49 (s, 1H), 7.37 (s, 1H), 7.21 (d,  $J$  = 8.0, 4H), 6.13 (s, 1H), 3.83 (s, 6H);  $^{13}\text{C}$ -NMR ( $\text{DMSO}-$



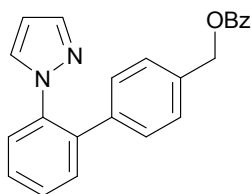
*d*<sub>6</sub>):  $\delta = 165.9, 142.9, 139.5, 138.9, 136.1, 133.4, 130.5, 129.7, 128.8, 128.4, 128.3, 106.4, 52.1$ ; Mass:  $[M + H]^+$  : 413.<sup>1</sup>



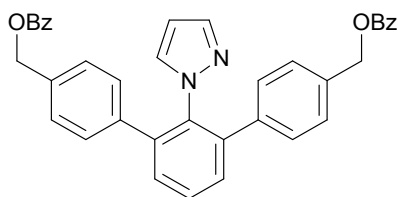
IR (KBr):  $\nu_{\max} = 1918, 1734, 1249 \text{ cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 7.63$  (d,  $J = 1.6 \text{ Hz}$ , 1H), 7.60 (dt,  $J = 8.4, 4.1, 1.2 \text{ Hz}$ , 1H), 7.48 - 7.45 (m, 3H), 7.27 (d,  $J = 7.2 \text{ Hz}$ , 2H), 7.10 (dd,  $J = 5.6, 2.4 \text{ Hz}$ , 3H), 6.21 (t,  $J = 2.4 \text{ Hz}$ , 1H), 5.09 (s, 2H), 2.11 (s, 3H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 170.7, 140.2, 138.4, 138.3, 136.1, 135.0, 131.2, 130.9, 128.6, 128.4, 128.2, 128.1, 127.7, 126.6, 106.4, 65.7, 20.9$ ; HRMS:  $[M + \text{Na}]^+$  calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_2\text{N}_2\text{Na}$  315.1109, found 315.1114; Mass:  $[M + \text{Na}]^+$  : 314.



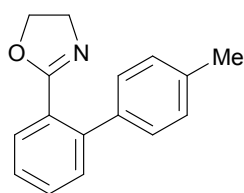
mp: 162.8 °C; IR (KBr):  $\nu_{\max} = 1729, 1243 \text{ cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 7.57$  (t,  $J = 6.8 \text{ Hz}$ , 1H), 7.48 (d,  $J = 7.2 \text{ Hz}$ , 2H), 7.39 (d,  $J = 1.6 \text{ Hz}$ , 1H), 7.22 (d,  $J = 8.0 \text{ Hz}$ , 4H), 7.11-7.07 (m, 5H), 6.08 (t,  $J = 2.0$ , 1H), 5.07 (s, 4H), 2.10 (s, 6H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 170.7, 140.2, 139.8, 139.4, 138.4, 136.2, 134.8, 132.3, 130.1, 129.1, 128.5, 128.2, 128.3, 127.7, 106.1, 65.7, 20.8$ ; HRMS:  $[M + \text{Na}]^+$  calcd for  $\text{C}_{27}\text{H}_{24}\text{O}_4\text{N}_2\text{Na}$  463.1634, found 463.1636; Mass:  $[M + H]^+$ : 441.2.



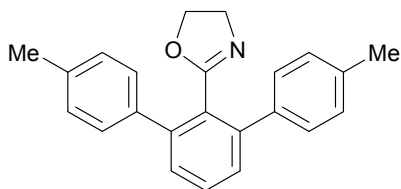
mp = 103.4 °C; IR (KBr):  $\nu_{\max}$  = 3114, 1713, 1275, 1106, 706  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  = 8.01 (d,  $J$  = 7.2 Hz, 2H), 7.68 (t,  $J$  = 7.2 Hz, 1H), 7.60 - 7.55 (m, 8H), 7.39 (d,  $J$  = 7.6 Hz, 2H), 7.08 (d,  $J$  = 8.0 Hz, 2H), 6.31 (s, 1H), 5.34 (s, 2H);  $^{13}\text{C}$ -NMR (DMSO- $d_6$ ):  $\delta$  = 165.6, 140.1, 138.2, 138.0, 136.2, 135.2, 133.4, 131.7, 131.0, 129.5, 129.2, 128.8, 128.7, 128.5, 128.3, 127.8, 126.8, 106.6, 65.8; HRMS:  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{18}\text{O}_2\text{N}_2\text{Na}$  377.1266, found 377.1271; Mass:  $[\text{M} + \text{H}]^+$ : 355.



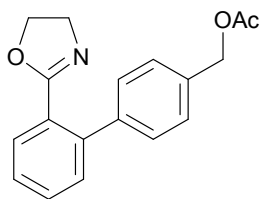
mp: 122.4 °C; IR (KBr):  $\nu_{\max}$  = 2933, 1721, 1267, 1177, 706  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  = 8.01 (d,  $J$  = 7.6 Hz, 4H), 7.68 (t,  $J$  = 6.8 Hz, 3H), 7.56-7.51 (m, 7H), 7.38-7.33 (m, 5H), 7.12 (d,  $J$  = 8.0 Hz, 4H), 6.12 (s, 1H), 5.32 (s, 4H);  $^{13}\text{C}$ -NMR (DMSO- $d_6$ ):  $\delta$  = 165.6, 139.6, 139.3, 138.1, 136.1, 135.0, 133.4, 130.2, 129.5, 129.2, 128.8, 128.2, 127.5, 106.2, 65.8; HRMS:  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{37}\text{H}_{28}\text{O}_4\text{N}_2\text{Na}$  587.1947, found 587.1948; Mass:  $[\text{M} + \text{H}]^+$ : 565.



IR (KBr):  $\nu_{\max}$  = 3057, 2967, 2877, 1649, 1478, 1236, 1078, 1038, 940, 759  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  = 7.66 (d,  $J$  = 7.2 Hz, 1H), 7.55 (d,  $J$  = 7.6 Hz, 1H), 7.44-7.39 (m, 2H), 7.21 (s, 4H), 4.09 (t,  $J$  = 9.6 Hz, 2H), 3.78 (t,  $J$  = 9.6 Hz, 2H), 2.36 (s, 3H);  $^{13}\text{C}$ -NMR (DMSO- $d_6$ ):  $\delta$  = 164.5, 140.9, 137.6, 136.4, 130.6, 130.1, 129.9, 128.7, 127.9, 127.4, 126.9, 67.3, 54.6, 20.7; HRMS:  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{16}\text{H}_{16}\text{ON}$  238.1232, found 238.1233; Mass:  $[\text{M} + \text{H}]^+$ : 238.

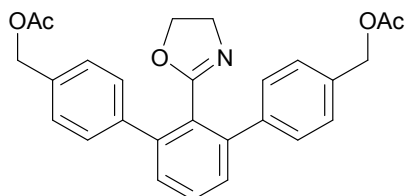


mp: 151.1°C; IR (KBr):  $\nu_{\max}$  = 3052, 2899, 2873, 1668, 1243, 1099, 1038, 820, 795, 760, 704  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  = 7.59 (t,  $J$  = 7.6 Hz, 1H), 7.38 (d,  $J$  = 7.6 Hz, 2H), 7.29 (d,  $J$  = 7.6 Hz, 4H), 7.22 (d,  $J$  = 8.0 Hz, 4H), 3.91 (t,  $J$  = 9.2 Hz, 2H), 3.50 (t,  $J$  = 9.2 Hz, 2H), 2.33 (s, 6H);  $^{13}\text{C}$ -NMR (DMSO- $d_6$ ):  $\delta$  = 162.7, 141.5, 137.4, 136.5, 129.9, 128.7, 128.6, 128.1, 127.0, 66.8, 54.6, 20.7; HRMS:  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{23}\text{H}_{22}\text{ON}$  328.1701, found 328.1700; Mass:  $[\text{M} + \text{H}]^+$ : 328.

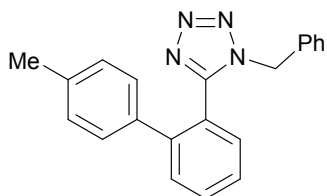


IR (KBr):  $\nu_{\max}$  = 1735, 1648, 1226  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.77 (dd,  $J$  = 7.8, 1.2 Hz, 1H), 7.50 (dt,  $J$  = 7.6, 6.4 Hz, 1H), 7.41-7.36 (m, 6H), 5.15 (s, 2H), 4.14 (t,  $J$  = 9.2 Hz, 2H), 3.92 (t,  $J$  = 9.2 Hz, 2H), 2.13 (s, 3H);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  = 170.8, 165.8, 141.2,

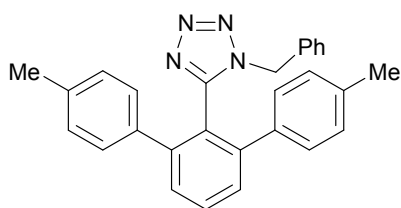
141.1, 134.7, 130.5, 130.3, 130.1, 128.4, 127.8, 127.4, 127.2, 67.7, 65.9, 54.9, 20.9;  
HRMS:  $[M+H]^+$  calcd for  $C_{18}H_{18}NO_3$  296.1286, found 296.1285 ; Mass:  $[M + H]^+$ : 296.



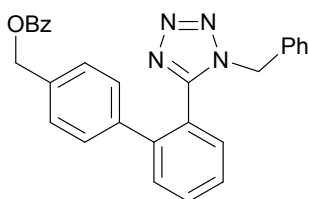
mp: 152.5°C; IR (KBr):  $\nu_{\max} = 1725, 1665, 1246 \text{ cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 7.53$  (t,  $J = 7.2 \text{ Hz}$ , 1H), 7.45 (d,  $J = 6.4 \text{ Hz}$ , 4H), 7.38 (dd,  $J = 8.0, 3.2 \text{ Hz}$ , 6H), 5.15 (s, 4H), 3.91 (t,  $J = 9.6 \text{ Hz}$ , 2H), 3.61 (t,  $J = 9.6 \text{ Hz}$ , 2H), 2.13 (s, 6H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 170.8, 163.7, 141.8, 140.7, 134.9, 129.6, 128.9, 128.7, 127.8, 127.4, 67.3, 65.9, 55.01, 20.97$ ; HRMS:  $[M + H]^+$  calcd for  $C_{27}H_{26}O_5N$  444.1811, found 444.1810; Mass:  $[M + H]^+$  : 444.



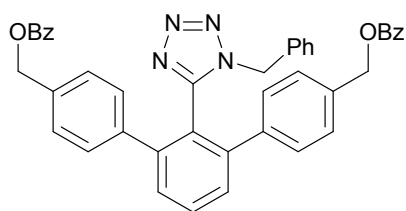
mp: 140 °C; IR (KBr):  $\nu_{\max} = 1455, 1093 \text{ cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 7.61$  (dt,  $J = 8.0, 1.6 \text{ Hz}$ , 1H), 7.56 (dd,  $J = 7.8, 0.8 \text{ Hz}$ , 1H), 7.39 (dt,  $J = 7.8, 1.2 \text{ Hz}$ , 1H), 7.33 (dd,  $J = 7.8, 1.2 \text{ Hz}$ , 1H), 7.22-7.08 (m, 5H), 7.03 (d,  $J = 8.4 \text{ Hz}$ , 2H), 6.75 (d,  $J = 7.2 \text{ Hz}$ , 2H), 4.76 (s, 2H), 2.34 (s, 3H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 154.5, 141.4, 137.7, 135.6, 132.9, 131.3, 130.9, 129.9, 129.4, 128.4, 128.2, 127.6, 127.3, 122.3, 50.5, 20.8$ ; HRMS:  $[M + \text{Na}]^+$  calcd for  $C_{21}H_{18}N_4\text{Na}$  349.1429, found 349.1425; Mass:  $[M + H]^+$ : 327.



mp 183.5 °C; IR (KBr):  $\nu_{\max}$  = 3061, 3033, 2917, 2858, 1736, 1513, 1457, 1439, 1404, 1104, 798;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.65 (t,  $J$  = 7.6 Hz, 1H), 7.45 (d,  $J$  = 8.0 Hz, 2H), 7.28-7.20 (m, 1H), 7.13 (t,  $J$  = 8.0 Hz, 2H), 6.96 (d,  $J$  = 8.0 Hz, 4H), 6.84 (d,  $J$  = 8.0 Hz, 4H), 6.70 (d,  $J$  = 7.2 Hz, 2H), 4.71 (s, 2H), 2.24 (s, 6H);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  = 153.1, 143.5, 137.4, 136.1, 132.7, 131.1, 129.2, 128.9, 128.7, 128.6, 128.5, 128.2, 121.2, 50.6, 21.0; HRMS:  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{28}\text{H}_{24}\text{N}_4$  417.2079, found 417.2080; Mass:  $[\text{M} + \text{H}]^+$ : 417.



Mp: 105.6 °C; IR (KBr):  $\nu_{\max}$  = 3055, 3033, 2934, 2884, 1719, 1598, 1461, 1449, 1403, 1263, 1117, 1102, 775, 697  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 8.10 (d,  $J$  = 7.2 Hz, 2H), 7.66 - 7.56 (m, 3H), 7.48-7.35 (m, 6H), 7.26-7.12 (m, 5H), 6.76 (d,  $J$  = 7.2 Hz, 2H), 5.35 (s, 2H), 4.83 (s, 2H);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  = 166.3, 154.5, 141.2, 138.6, 136.0, 133.1, 132.9, 131.6, 131.2, 130.3, 129.7, 128.8, 128.7, 128.5, 128.4, 127.9, 127.7, 122.6, 65.9, 50.8; HRMS:  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{28}\text{H}_{22}\text{N}_4\text{O}_2\text{Na}$  469.1640, found 467.1640; Mass:  $[\text{M} + \text{Na}]^+$ : 469.



mp: 118.2 °C ; IR (KBr):  $\nu_{\text{max}}$  = 3061, 3034, 1717, 1451, 1378, 1315, 1271, 1109, 1102, 1070, ,1023, 800, 713, 689  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 8.07 (d,  $J$  = 7.6 Hz, 4H), 7.71 (t,  $J$  = 8 Hz, 5H), 7.57 (t,  $J$  = 7.2 Hz, 2H), 7.50 (d,  $J$  = 7.6 Hz, 2H), 7.45 (t,  $J$  = 7.6 Hz, 4H), 7.26 – 7.18 (m, 1H), 7.12 (t,  $J$  = 7.6 Hz, 2H), 7.00 (d,  $J$  = 8.0 Hz, 4H), 6.68 (d,  $J$  = 7.6 Hz, 2H), 5.30 (s, 4H), 4.74 (s, 2H);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  = 166.2, 152.8, 143.0, 138.7, 135.6, 133.2, 133.0, 132.5, 131.7, 131.3, 129.9, 129.6, 129.1, 128.7, 128.6, 128.3, 128.0, 127.8, 123.9, 121.2, 65.93, 50.7; HRMS:  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{42}\text{H}_{32}\text{N}_4\text{O}_4\text{Na}$  679.2321, found 679.2321; Mass:  $[\text{M} + \text{H}]^+$ : 657.

## Reference

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