

Supporting Information

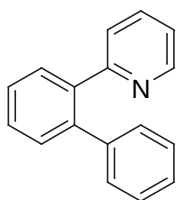
Ruthenium Complex-Catalyzed Direct *ortho* Arylation and Alkenylation of 2-Arylpyridines with Organic Halides

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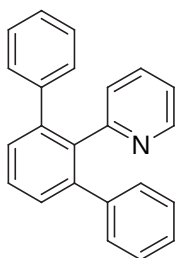
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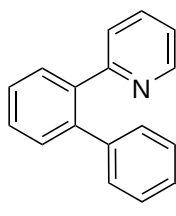
6aa

6aa: mp 86.5-87.5 °C. ^1H NMR (CDCl_3 , 500 MHz): δ 8.63 (ddd, 1H, $J=4.9, 1.8, 1.0$ Hz), 7.72-7.68 (m, 1H), 7.49-7.42 (m, 3H), 7.38 (dt, 1H, $J=7.7, 1.8$ Hz), 7.25-7.20 (m, 3H), 7.18-7.14 (m, 2H), 7.10 (ddd, 1H, $J=7.7, 4.6, 1.1$ Hz), 6.88 (dt, 1H, $J=7.7, 1.0$ Hz). ^{13}C NMR (125 MHz): δ 159.2, 149.4, 141.3, 140.6, 139.5, 135.1, 130.4, 129.7, 128.5, 128.0, 127.6, 126.6, 125.3, 121.2. IR (KBr): 3052, 1587, 1470, 1482, 990, 779, 757, 698, 561 cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{13}\text{N}$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.41; H, 5.84; N, 5.93.



7aa

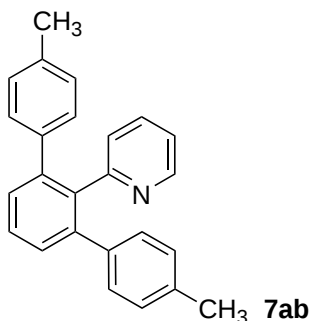
7aa: mp 118-119.5 °C. ^1H NMR (CDCl_3 , 500 MHz): δ 8.31 (ddd, 1H, $J=5.1, 1.6, 1.0$ Hz), 7.52 (dd, 1H, $J=8.3, 7.1$ Hz), 7.45 (d, 1H, $J=7.1$ Hz), 7.30 (dt, 1H, $J=7.7, 1.6$ Hz), 7.17 - 7.08 (m, 10H), 6.91 (dd, 1H, $J=7.7, 5.1$ Hz), 6.88 (d, 1H, $J=7.7$ Hz). ^{13}C NMR (CDCl_3 , 125 MHz): δ 158.9, 148.5, 141.0, 141.6, 138.5, 134.8, 129.6, 129.5, 128.1, 127.6, 126.8, 126.2, 120.8. IR (KBr): 3059, 3022, 1588, 1415, 765, 703 cm^{-1} . Anal Calcd for $\text{C}_{23}\text{H}_{17}\text{N}$: C, 89.87; H, 5.57; N, 4.56. Found: C, 90.10; H, 5.65; N, 4.56.



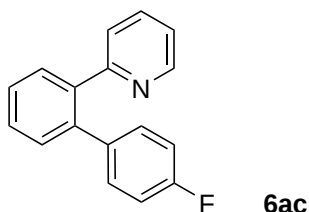
6ab

6ab: ^1H NMR (CDCl_3 , 500 MHz): δ 8.64 (ddd, 1H, $J=4.9, 1.6, 1.1$ Hz), 7.69-7.67 (m, 1H), 7.46-7.41 (m, 3H), 7.39 (dt, 1H, $J=7.8, 1.2$ Hz), 7.10 (ddd, 1H, $J=7.8, 4.9, 1.1$ Hz), 7.04 (s, 4H), 6.90 (dt, 1H, $J=7.8, 1.1$ Hz), 2.32 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 159.4, 149.4, 140.5, 139.4, 138.3, 136.3, 135.2, 130.48, 130.45, 129.5, 128.8, 128.5, 127.4, 125.4, 121.3, 21.1. IR

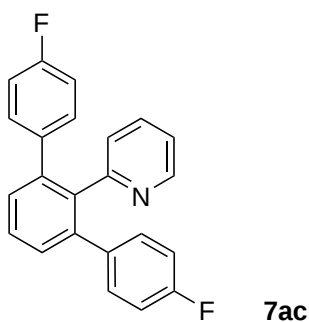
(neat): 3054, 3021, 2920, 1584, 1460, 1423, 822, 756, 479, 459, 447 cm^{-1} . Anal Calcd for $\text{C}_{18}\text{H}_{15}\text{N}$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.11; H, 6.38; N, 5.60.



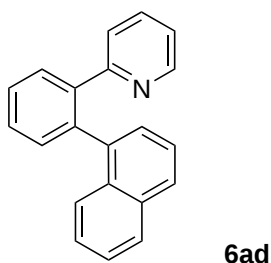
7ab: mp 148.5-149.5 $^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 500 MHz): δ 8.33 (ddd, 1H, $J=4.9, 1.8, 1.1$ Hz), 7.48 (dd, 1H, $J=8.4, 6.8$ Hz), 7.41 (d, 1H, $J=6.8$ Hz), 7.41 (d, 1H, 8.4 Hz), 7.31 (dt, 1H, $J=7.7, 1.8$ Hz), 6.99-6.94 (m, 8H), 6.92 (ddd, 1H, $J=7.7, 4.9, 1.1$ Hz), 6.88 (dt, 1H, $J=7.7, 1.1$ Hz), 2.26 (s, 6H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 159.2, 148.5, 141.7, 138.7, 138.4, 135.8, 134.9, 129.5, 129.3, 128.3, 128.1, 126.8, 120.8, 21.0. IR (KBr): 3022, 2920, 1583, 1560, 1512, 1452, 1419, 1021, 818, 799, 745, 522 cm^{-1} . Anal Calcd for $\text{C}_{25}\text{H}_{21}\text{N}$: C, 89.51; H, 6.31; N, 4.18. Found: C, 89.60; H, 6.42; N, 4.14.



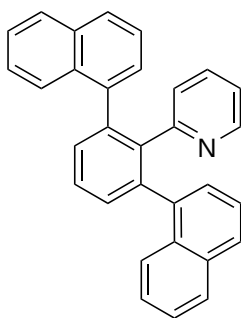
6ac: mp 83.0-84.5 $^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 500 MHz): δ 8.35 (ddd, 1H, $J=4.8, 1.6, 0.9$ Hz), 7.69-7.67 (m, 1H), 7.47-7.39 (m, 3H), 7.42 (dt, 1H, $J=7.7, 1.8$ Hz), 7.13-7.09 (m, 3H), 6.95-6.89 (m, 2H), 6.90 (d, 1H, $J=8.4$ Hz). ^{13}C NMR (CDCl_3 , 125 MHz): δ 161.9 (d, $J_{\text{C-F}}=244.5$ Hz), 159.1, 149.5, 139.5, 137.3, 135.3, 131.2 (d, $J_{\text{C-F}}=7.9$ Hz), 130.5, 130.4, 128.5, 127.7, 125.2, 121.4, 115.0 (d, $J_{\text{C-F}}=21.4$ Hz). IR (KBr): 3064, 1586, 1512, 1471, 1220, 1159, 839, 798, 758, 555 cm^{-1} . Anal Calcd for $\text{C}_{17}\text{H}_{12}\text{FN}$: C, 81.91; H, 4.85; N, 5.62; F, 7.62. Found: C, 81.88; H, 5.11; N, 5.57.



7ac: mp 100.0-101.0 °C. ^1H NMR (CDCl_3 , 500 MHz): δ 8.34 (ddd, 1H, $J=4.9, 1.8, 1.0$ Hz), 7.51 (dd, 1H, $J=8.2, 7.2$ Hz), 7.417 (d, 1H, $J=7.2$ Hz), 7.416 (d, 1H, $J=8.2$ Hz), 7.33 (dt, 1H, $J=7.6, 1.8$ Hz), 7.07-7.03 (m, 4H), 6.95 (ddd, $J=7.6, 4.9, 1.1$ Hz), 6.86-6.82 (m, 5H, H-3, -Ph). ^{13}C NMR (CDCl_3 , 125 MHz): δ 161.6 (d, $J_{\text{C-F}}=224.6$ Hz), 158.6, 148.7, 140.9, 138.6, 137.39, 137.37, 135.1, 131.1 (d, $J_{\text{C-F}}=8.0$ Hz), 129.5, 128.3, 126.7, 121.1, 114.6 (d, $J_{\text{C-F}}=21.3$ Hz). IR (KBr): 3048, 1603, 1510, 1455, 1423, 1220, 1161, 837, 807, 795, 751, 554, 523 cm^{-1} . Anal Calcd for $\text{C}_{23}\text{H}_{15}\text{F}_2\text{N}$: C, 80.45; H, 4.40; N, 4.08; F, 11.07. Found: C, 80.63; H, 4.38; N, 4.12.

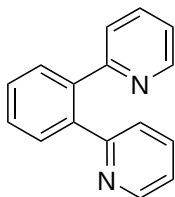


6ad: mp 84.2-85.0 °C. ^1H NMR (CDCl_3 , 500 MHz): δ 8.53 (ddd, 1H, $J=4.9, 1.8, 0.9$ Hz), 7.87 (dd, 1H, $J=7.6, 1.3$ Hz), 7.80 (d, 1H, $J=8.2$ Hz), 7.76 (d, 1H, $J=8.2$ Hz), 7.66 (d, 1H, $J=8.2$ Hz), 7.57 (dt, 1H, $J=7.6, 1.4$ Hz), 7.51 (dt, 1H, $J=7.6, 1.4$ Hz), 7.44 (dd, 1H, $J=7.6, 1.3$ Hz), 7.40-7.36 (m, 2H), 7.32-7.27 (m, 2H), 7.07 (dt, 1H, $J=7.7, 1.8$ Hz), 6.90 (ddd, 1H, $J=7.7, 4.9, 0.9$ Hz), 6.68 (dt, 1H, $J=7.7, 0.9$ Hz). ^{13}C NMR (CDCl_3 , 125 MHz): δ 158.6, 149.3, 140.6, 139.2, 138.7, 134.9, 133.4, 131.9, 131.6, 130.2, 128.2, 128.0, 128.0, 127.5, 126.1, 126.0, 125.6, 125.2, 124.2, 121.2. IR (KBr): 3055, 1584, 1459, 1424, 1392, 1021, 802, 779, 617, 577, 516 cm^{-1} . Anal Calcd for $\text{C}_{21}\text{H}_{15}\text{N}$: C, 89.65; H, 5.37; N, 4.98. Found: C, 89.76; H, 5.49; N, 4.92.



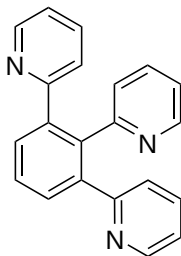
7ad

7ad: mp 219.3-220.2 °C. ^1H NMR (CDCl_3 , 500 MHz): δ 8.06 (d, 1H, $J=4.3$ H), 7.84-6.44 (m, 20H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 158.6, 15.3, 148.3, 147.9, 147.6, 141.6, 140.3, 140.2, 140.0, 139.9, 139.2, 139.2, 139.0, 134.6, 134.1, 134.0, 133.2, 132.2, 132.1, 132.1, 131.9, 130.6, 130.6, 130.4, 130.1, 128.5, 128.2, 128.2, 128.0, 127.9, 127.4, 127.1, 127.1, 126.9, 126.6, 126.3, 125.8, 125.8, 125.7, 125.7, 125.4, 125.4, 125.3, 124.8, 124.7, 120.6, 120.4, 120.3. IR (KBr): 3047, 1588, 1417, 1389, 802, 780, 761 cm^{-1} . Anal Calcd for $\text{C}_{31}\text{H}_{21}\text{N}$: C, 91.37; H, 5.19; N, 3.44. Found: C, 91.45; H, 5.13; N, 3.16.



6ae

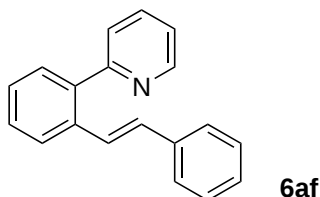
6ae: mp 126.8-128.2 °C. ^1H NMR (CDCl_3 , 500 MHz): δ 8.59 (ddd, 2H, $J=4.9$, 1.7, 0.9 Hz), 7.68 (dd, 2H, $J=5.7$, 3.3 Hz), 7.51 (dd, 2H, $J=5.7$, 3.3 Hz), 7.44 (dt, 2H, $J=7.7$, 1.7 Hz), 7.12 (ddd, 2H, $J=7.7$, 4.9, 1.1 Hz), 6.99 (dt, 2H, $J=7.7$, 0.5 Hz). ^{13}C NMR (CDCl_3 , 125 MHz): δ 159.2, 149.4, 139.7, 135.4, 130.3, 128.6, 125.0, 121.4. IR (KBr): 3049, 1585, 1561, 1461, 1431, 1419, 1143, 989, 797, 753, 622 cm^{-1} . Anal Calcd for $\text{C}_{16}\text{H}_{12}\text{N}_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.93; H, 5.21; N, 11.86.



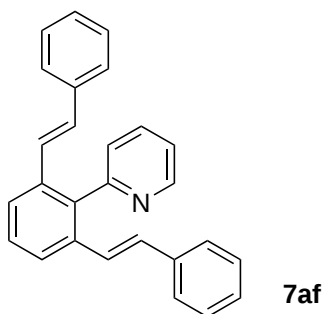
7ae

7ae: mp 197.4-198.2 °C. ^1H NMR (CDCl_3 , 500 MHz): δ 8.52 (d, 2H, $J=4.9$ Hz), 8.30 (dd, 1H,

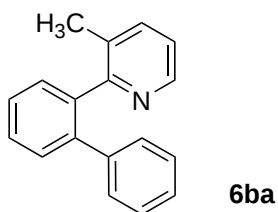
$J=4.9, 0.7$ Hz), 7.74 (d, 2H, $J=7.6$ Hz), 7.62 (t, 1H, $J=7.6$ Hz), 7.38 (t, 2H, $J=7.7$ Hz), 7.34 (t, 1H, $J=7.5$ Hz), 7.05 (dd, 2H, $J=7.7, 4.9$ Hz), 6.97 (t, 1H, $J=7.5$ Hz), 6.95 (d, 1H, $J=7.5$ Hz), 6.92 (dd, 2H, $J=7.7, 0.5$ Hz). ^{13}C NMR (CDCl_3 , 125 MHz): δ 159.2, 158.7, 149.1, 148.5, 140.8, 138.4, 135.2, 135.1, 130.3, 128.5, 126.8, 124.9, 121.1, 121.0. IR (KBr): 3049, 1583, 1562, 1474, 1445, 1413, 989, 793, 777, 757, 626 cm^{-1} . Anal Calcd for $\text{C}_{21}\text{H}_{15}\text{N}_3$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.32, H, 5.19; N, 13.30.



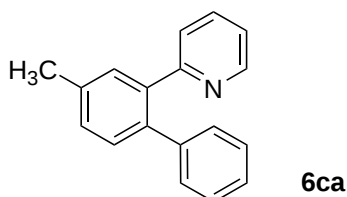
6af: ^1H NMR (CDCl_3 , 500 MHz): δ 8.73 (ddd, 1H, $J=4.9, 1.8, 1.0$ Hz), 7.74 (dd, 1H, $J=7.8, 1.6$ Hz), 7.67 (dt, 1H, $J=7.5, 1.8$ Hz), 7.54 (dd, 1H, $J=7.5, 1.5$ Hz), 7.45-7.33 (m, 5H), 7.29-7.21 (m, 3H), 7.23 (d, 1H, $J=16.2$ Hz), 7.19 (dt, 1H, $J=7.5, 1.0$ Hz), 7.04 (d, 1H, $J=16.2$ Hz). ^{13}C NMR (CDCl_3 , 125 MHz): δ 159.0, 149.6, 149.6, 139.7, 137.7, 136.1, 135.8, 130.0, 130.2, 128.8, 128.7, 127.8, 127.7, 126.7, 126.4, 125.1, 122.0. IR (neat): 3057, 3023, 1583, 1494, 1459, 1424, 962, 795, 729, 691 cm^{-1} . Anal Calcd for $\text{C}_{19}\text{H}_{15}\text{N}$: C, 88.68; H, 5.88; N, 5.44. Found: C, 87.97, H, 6.02; N, 5.31.



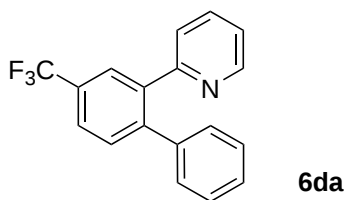
7af: mp 148.0-149.5 $^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 500 MHz): δ 8.80 (ddd, 1H, $J=4.9, 1.8, 1.0$ Hz), 7.76 (dt, 1H, $J=7.7, 1.8$ Hz), 7.69 (d, 1H, $J=7.8$ Hz), 7.43 (t, 1H, $J=7.8$ Hz), 7.35-7.17 (m, 13H), 6.98 (d, 2H, $J=16.2$ Hz), 6.76 (d, 2H, $J=16.2$ Hz). ^{13}C NMR (CDCl_3 , 125 MHz): δ 158.3, 149.7, 138.8, 137.5, 136.7, 136.1, 130.2, 128.62, 128.60, 127.6, 127.2, 126.6, 126.5, 124.9, 122.2. IR (KBr): 3055, 3028, 1581, 1493, 1469, 1446, 1416, 1071, 1023, 961, 795, 777, 751, 731, 692 cm^{-1} . Anal Calcd for $\text{C}_{27}\text{H}_{21}\text{N}_3$: C, 90.21; H, 5.89; N, 3.90. Found: C, 89.34, H, 6.05; N, 3.83.



6ba: ^1H NMR (CDCl_3 , 500 MHz): δ 8.49 (d, 1H, $J=4.8$ Hz), 7.50-7.39 (m, 4H), 7.29 (d, 1H, $J=7.7$ Hz), 7.18-7.11 (m, 5H), 7.10 (dd, 1H, $J=7.7$, 4.8 Hz), 1.75 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 141.1, 140.6, 139.4, 137.4, 131.6, 129.9, 129.7, 129.2, 128.3, 127.8, 127.4, 126.6, 122.1, 18.8. IR (neat): 3056, 1567, 1452, 1419, 1023, 743, 701 cm^{-1} . Anal Calcd for $\text{C}_{18}\text{H}_{15}\text{N}$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.04; H, 6.37; N, 5.70.

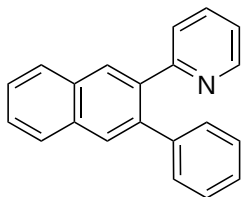


6ca: mp 76.5-77.5 $^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 500 MHz): δ 8.64 (ddd, 1H, $J=4.9$, 1.8, 1.1 Hz), 7.53 (d, 1H, $J=1.6$ Hz), 7.36 (dt, 1H, $J=7.7$, 1.8 Hz), 7.33 (d, 1H, $J=7.7$ Hz), 7.28 (dd, 1H, $J=7.7$, 1.6 Hz), 7.24-7.19 (m, 3H), 7.15-7.13 (m, 2H), 7.09 (ddd, 1H, $J=7.7$, 4.9, 1.1 Hz), 6.85 (dt, 1H, $J=7.7$, 1.1 Hz), 2.45 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 159.4, 149.4, 141.3, 139.3, 137.8, 137.4, 135.1, 131.1, 130.5, 129.7, 129.3, 128.0, 126.5, 125.5, 121.3, 21.1. IR (KBr): 3024, 1584, 1560, 1482, 1461, 1430, 827, 792, 771, 746, 701, 575. Anal Calcd for $\text{C}_{18}\text{H}_{15}\text{N}$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.12; H, 6.21; N, 5.44.



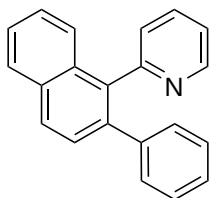
6da: ^1H NMR (CDCl_3 , 500 MHz): δ 8.66 (ddd, 1H, $J=4.9$, 1.8, 1.0 Hz), 7.99 (d, 1H, $J=1.4$ Hz), 7.71 (dd, 1H, $J=8.0$, 1.4 Hz), 7.55 (d, 1H, $J=8.0$ Hz), 7.40 (dt, 1H, $J=7.7$, 1.8 Hz), 7.28 - 7.24 (m, 3H), 7.14 (ddd, 1H, $J=7.7$, 4.9, 1.0 Hz), 7.18-7.11 (m, 2H), 6.88 (dt, 1H, $J=7.7$, 1.0 Hz). ^{13}C NMR (CDCl_3 , 125 MHz): δ 157.8, 149.7, 144.0, 140.0, 140.0, 135.4, 131.0, 129.9 (q, $J_{\text{C-F}}=32.4$ Hz), 129.7, 128.3, 127.6 (q, $J_{\text{C-F}}=3.5$ Hz), 127.5, 125.3, 125.1 (q, $J_{\text{C-F}}=3.8$ Hz), 124.1 (q, $J_{\text{C-F}}=270.6$ Hz), 121.9. IR (neat): 3059, 1616, 1587, 1567, 1467, 1404, 1336, 1275, 1126, 1083,

841, 794, 773, 746, 701, 462 cm^{-1} . Anal Calcd for $\text{C}_{18}\text{H}_{12}\text{F}_3\text{N}$: C, 72.24; H, 4.04; N, 4.68. Found: C, 72.39; H, 4.21; N, 4.56.



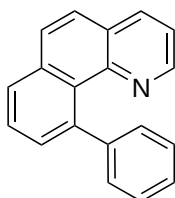
6ea

6ea: mp 103.5-106.0 $^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 500 MHz): δ 8.67 (ddd, 1H, J = 4.9, 1.8, 1.0 Hz), 8.20 (s, 1H), 7.94 (dd, 1H, J = 7.0, 2.2 Hz), 7.91 (s, 1H), 7.90 (dd, 1H, J = 7.0, 2.2 Hz), 7.54-7.50 (m, 2H), 7.42, (dt, 1H, J = 7.7, 1.8 Hz), 7.31-7.23 (m, 5H), 7.13 (ddd, 1H, J = 7.7, 4.9, 1.0 Hz), 6.96 (d, 1H, J = 7.7 Hz). ^{13}C NMR (CDCl_3 , 125 MHz): δ 159.1, 149.4, 141.3, 138.6, 137.8, 135.2, 133.2, 132.6, 130.1, 129.8, 129.6, 128.2, 128.1, 127.7, 126.8, 126.7, 126.3, 125.5, 121.4. IR (KBr): 3054, 1585, 1423, 896, 752, 698, 568, 477 cm^{-1} . Anal Calcd for $\text{C}_{21}\text{H}_{15}\text{N}$: C, 89.65; H, 5.37; N, 4.98. Found: C, 88.93; H, 5.54; N, 4.93.



6fa

6fa: mp 106.0-107.0 $^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 500 MHz): δ 8.74 (d, 1H, J = 4.0 Hz), 7.98 (d, 1H, J = 8.5 Hz), 7.92 (d, 1H, J = 8.1 Hz), 7.59 (d, 1H, J = 8.5 Hz), 7.57 (d, 1H, J = 8.4 Hz), 7.52 (dt, 1H, J = 7.6, 1.8 Hz), 7.49 (ddd, 1H, J = 8.1, 7.6, 1.2 Hz), 7.42 (ddd, 1H, J = 8.4, 7.6, 1.3 Hz), 7.20-7.15 (m, 6H), 7.03 (d, 1H, J = 7.6 Hz). ^{13}C NMR (CDCl_3 , 125 MHz): δ 158.7, 149.0, 141.6, 138.5, 136.4, 135.8, 132.8, 132.3, 130.0, 128.5, 128.0, 127.9, 127.7, 126.7, 126.6, 126.4, 126.2, 125.8, 121.6. IR (KBr): 3048, 1587, 1562, 1472, 1428, 823, 764, 704, 592, 577 cm^{-1} . Anal Calcd for $\text{C}_{21}\text{H}_{15}\text{N}$: C, 89.65; H, 5.37; N, 4.98. Found: C, 89.66; H, 5.58; N, 4.93.



6ga

6ga: ^1H NMR (CDCl_3 , 500 MHz): δ 8.41 (dd, 1H, J = 4.3, 1.8 Hz), 8.07 (dd, 1H, J = 7.9, 1.8

Hz), 7.92 (dd, 1H, J = 7.7, 1.3 Hz), 7.85 (d, 1H, J = 8.6 Hz), 7.68 (d, 1H, J = 8.6 Hz), 7.67 (t, 1H, J = 7.7 Hz), 7.54 (dd, 1H, J = 7.7, 1.3 Hz), 7.42 - 7.33 (m, 5H), 7.30 (dd, 1H, J = 7.9, 4.3 Hz). ^{13}C NMR (CDCl_3 , 125 MHz): δ 146.90, 146.88, 146.5, 141.8, 135.2, 135.0, 131.5, 129.1, 128.8, 128.3, 128.0, 127.4, 127.3, 127.1, 126.0, 125.7, 121.1. IR (neat): 3048, 1588, 1509, 1443, 1417, 836, 757, 731, 699 cm^{-1} . Anal Calcd for $\text{C}_{19}\text{H}_{13}\text{N}$: C, 89.38; H, 5.13; N, 5.49. Found: C, 89.12; H, 5.16; N, 5.42.