

Supporting Information

A new approach to large scale production of dimethyl sulfone: A promising and strong recyclable solvent for ligand-free Cu-catalyzed C-C cross-coupling reactions

Shen Cheng,^a Wei Wei,^a Xingyu Zhang,^a Hewei Yu,^a Mingming Huang,^{*b}, Milad Kazemnejadi^c

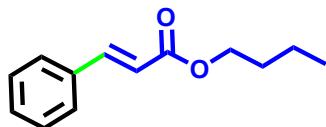
^a School of Energy and Power Engineering, Qilu University of Technology, Jinan 250353, China.

^b School of Mechanical and Automotive Engineering, Qilu University of Technology, Jinan 250353, China.

^c Department of Chemistry, College of Science, Shiraz University, Shiraz 7194684795, Iran.

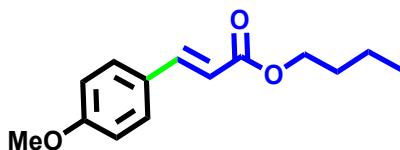
*Corresponding author. E-mail address: miladkazemnejadi@yahoo.com (Milad Kazemnejadi), dahuangby@sina.com (Mingming Huang)

Characterization of some selected compounds:



3a

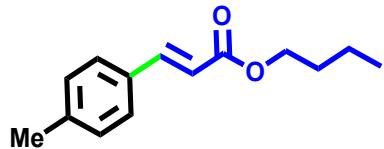
¹H-NMR (250 MHz, CDCl₃) δ: 0.90 (t, 3H, *J*= 7.5 Hz), 1.37 (m, 2H), 1.65 (m, 2H), 4.17 (t, 2H, *J*= 6.7 Hz), 6.53 (d, 1H, *J*= 16 Hz), 7.60 (d, 2H, *J*= 8.7 Hz), 7.63 (d, 1H, *J*= 16.2 Hz), 8.18 (d, 2H, *J*= 8.7 Hz) ppm; ¹³C NMR (62.9 MHz, CDCl₃) δ: 13.7, 19.1, 30.6, 64.8, 122.5, 124.1, 128.5, 140.5, 141.5, 166.0 ppm.



3b

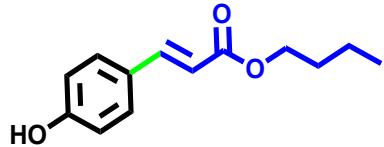
¹H NMR (250 MHz, CDCl₃) δ: 0.89 (t, 3H, *J*= 7.5 Hz), 1.35 (m, 2H, *J*= 7.5 Hz), 1.61 (quint, 2H, *J*= 5.0 Hz), 3.76 (s, 3H), 4.13 (t, 2H, *J*= 6.7 Hz), 6.24 (d, 1H, *J*= 16.0 Hz), 6.83 (d, 2H, *J*= 5.0 Hz),

7.40 (d, 2H, $J= 5.0$ Hz), 7.56 (d, 1H, $J= 16.0$ Hz) ppm; ^{13}C NMR (62.9 MHz, CDCl_3) δ : 13.8, 19.2, 30.8, 55.36, 64.3, 114.3, 115.8, 129.7, 144.2, 161.3 ppm.



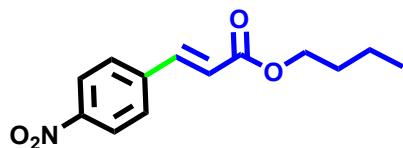
3c

^1H -NMR (250 MHz, CDCl_3) δ : 0.85 (t, 3H, $J= 4.7$ Hz), 1.32 (m, 2H), 1.56 (m, 2H), 2.24 (s, 3H), 4.09 (t, 2H, $J= 5.0$ Hz), 6.30 (dd, 1H, $J= 16.0$ Hz, $J'= 5.9$ Hz), 7.06 (m, 2H), 7.29 (m, 2H), 7.52 (dd, 1H, $J= 18.2$ Hz, $J'= 5.5$ Hz) ppm; ^{13}C NMR (62.9 MHz, CDCl_3) δ : 13.7, 19.2, 21.4, 30.8, 64.2, 117.1, 128.3, 129.5, 131.7, 140.5, 144.5, 167.2 ppm.



3d

^1H -NMR (250 MHz, CDCl_3) δ : 0.87 (t, 3H, $J= 7.5$ Hz), 1.33 (m, 2H), 1.52 (m, 2H), 4.13 (t, 2H, $J= 7.5$ Hz), 6.20 (d, 1H, $J= 12.5$ Hz), 6.80 (d, 3H, $J= 7.5$ Hz), 7.32 (d, 2H, $J= 10$ Hz), 7.55 (d, 1H, $J= 15$ Hz) ppm; ^{13}C NMR (62.9 MHz, CDCl_3) δ : 13.7, 19.1, 30.7, 64.7, 116.0 (2C), 126.5, 130.0 (2C), 145.1, 158.6, 168.4 ppm.



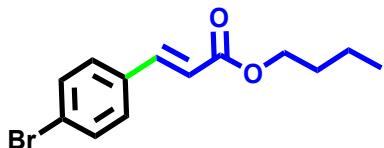
3e

^1H -NMR (250 MHz, CDCl_3) δ : 0.97 (t, 3H, $J= 7.2$ Hz), 1.45 (m, 2H), 1.67 (m, 2H), 4.23 (t, 2H, $J= 7.5$ Hz), 6.54 (dd, 1H, $J= 16.0$ Hz, $J'= 6.2$ Hz), 7.67 (m, 3H), 8.24 (m, 2H) ppm; ^{13}C NMR (62.9 MHz, CDCl_3) δ : 13.7, 19.1, 30.6, 64.9, 122.5, 124.1, 128.6, 140.5, 141.5 ppm.

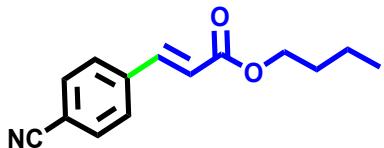


3f

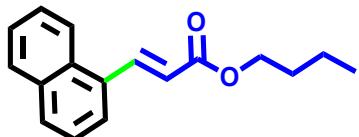
¹H-NMR (250 MHz, CDCl₃) δ: 0.88 (t, 3H, *J*= 7.5 Hz), 1.35 (m, 2H), 1.62 (m, 2H), 4.14 (t, 2H, *J*= 7.5 Hz), 6.29 (d, 1H, *J*= 17.5 Hz), 7.42-7.57 (m, 2H), 7.94-7.97 (m, 2H), 8.02 (d, 1H, *J*= 17.5 Hz) ppm; ¹³C NMR (62.9 MHz, CDCl₃) δ: 13.9, 19.1, 30.6, 64.7, 123.3, 124.6, 129.2, 130.2, 130.3, 133.5, 139.7, 148.2, 165.9 ppm.

**3g**

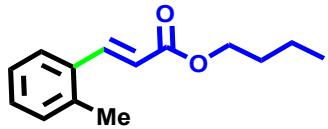
¹H-NMR (250 MHz, CDCl₃) δ: 0.87 (t, 3H, *J*= 7.5 Hz), 1.34 (m, 2H), 1.60 (m, 2H), 4.12 (t, 2H, *J*= 7.5 Hz), 6.33 (d, 1H, *J*= 17.5 Hz), 7.19-7.30 (m, 2H), 7.40-7.43 (m, 2H), 7.51 (d, 1H, *J*= 17.5 Hz) ppm; ¹³C NMR (62.9 MHz, CDCl₃) δ: 13.7, 19.1, 30.7, 64.5, 111.9, 124.4, 129.3 (2C), 132.0 (2C), 133.3, 143.1, 166.7 ppm.

**3h**

¹H-NMR (250 MHz, CDCl₃) δ: 0.89 (t, 3H, *J*= 7.2 Hz), 1.35 (m, 2H), 1.64 (m, 2H), 4.16 (t, 2H, *J*= 6.5 Hz), 6.48 (d, 1H, *J*= 16 Hz), 7.59, (m, 5H) ppm; ¹³C NMR (62.9 MHz, CDCl₃) δ: 13.6, 19.1, 27.8, 30.6, 64.7, 113.2, 118.3, 121.8, 128.3, 132.5, 138.5, 142.0, 166.1 ppm.

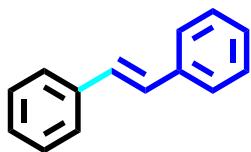
**3i**

¹H-NMR (250 MHz, CDCl₃) δ: 0.87 (t, 3H, *J*= 7.2 Hz), 1.37 (m, 2H), 1.65 (m, 2H), 4.17 (t, 2H, *J*= 7.0 Hz), 6.40 (d, 1H, *J*= 14.0 Hz), 7.31-7.42 (m, 3H), 7.58-7.74 (m, 3H), 8.05 (d, 1H, *J*= 8.2 Hz), 8.40 (d, 1H, *J*= 15.7 Hz) ppm; ¹³C NMR (62.9 MHz, CDCl₃) δ: 13.8, 19.2, 30.8, 64.5, 120.9, 123.3, 124.4, 124.9, 125.4, 125.8, 126.2, 126.4, 126.6, 126.8, 128.7, 129.1, 130.4, 131.4, 131.8, 133.6, 141.5, 166.9 ppm.



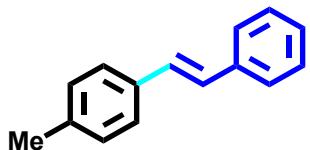
3j

¹H-NMR (250 MHz, CDCl₃) δ: 0.85 (t, 3H, *J*= 2.5 Hz), 1.32 (m, 2H), 1.57 (m, 2H), 2.30 (s, 3H), 4.11 (t, 2H), 6.27 (dd, 1H, *J*= 15.9 Hz, *J'*= 4.8 Hz), 7.11 (m, 3H), 7.41 (m, 1H), 7.84 (dd, 1H, *J*= 13.7 Hz, *J'*= 4.3 Hz) ppm; ¹³C NMR (62.9 MHz, CDCl₃) δ: 13.7, 18.9, 19.7, 30.7, 64.3, 119.2, 126.3, 129.9, 130.7, 133.4, 137.5, 142.2, 167.0 ppm.



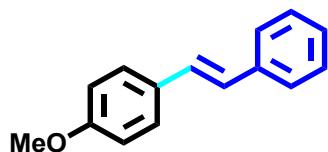
3l

¹H-NMR (250 MHz, CDCl₃) δ: 7.13 (d, 2H), 7.31 (m, 6H), 7.52 (m, 4H) ppm.



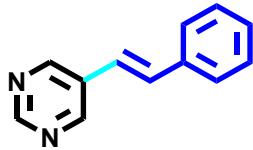
3m

¹H-NMR (250 MHz, CDCl₃) δ: 2.26 (s, 3H), 6.91-7.64 (m, 9H) ppm; ¹³C NMR (62.9 MHz, CDCl₃) δ: 21.3, 126.4, 126.4, 127.4, 127.7, 128.6, 129.4, 134.5, 137.5 ppm.



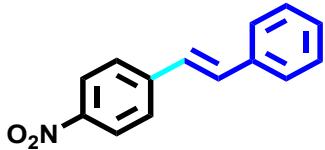
3n

¹H NMR (250 MHz, CDCl₃) δ: 3.77 (s, 3H), 6.80 (d, 2H, *J*= 8.5 Hz), 6.89 (d, 1H, *J*= 16.5 Hz), 6.99 (d, 1H, *J*= 16.0 Hz), 7.18 (t, 1H, *J*= 6.5 Hz), 7.28 (t, 2H, *J*= 7.5 Hz), 7.37 (d, 2H, *J*= 8.5 Hz), 7.42 (d, 2H, *J*= 7.5 Hz) ppm; ¹³C NMR (62.9 MHz, CDCl₃) δ: 57.5, 116.5, 126.0, 126.5, 127.0, 127.5, 128.0, 129.5, 130.9, 138.8, 160.5 ppm.



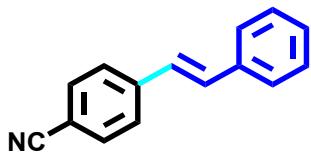
3o

¹H-NMR (250 MHz, CDCl₃) δ: 6.89 (d, 1H, *J*= 16.5 Hz), 7.15 (d, 1H, *J*= 16.5 Hz), 7.25-7.47 (m, 5H), 8.77 (s, 2H), 9.12 (s, 1H) ppm; ¹³C NMR (62.9 MHz, CDCl₃) δ: 121.0, 126.8, 128.8, 128.8, 130.9, 132.8, 135.9, 154.2, 157.1 ppm.

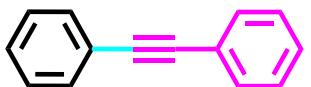


3p

¹H NMR (250 MHz, CDCl₃) δ: 7.23 (d, 1H, *J*= 16.5 Hz), 7.37 (d, 1H, *J*= 16 Hz), 7.45-7.55 (m, 3H), 7.71 (d, 2H, *J*= 7.3 Hz), 7.80 (d, 2H, *J*= 9.3 Hz), 8.40 (d, 2H, *J*= 9.3 Hz) ppm; ¹³C NMR (60 MHz, CDCl₃) δ: 125.5, 127.0, 128.0, 128.5, 129.0, 130.1, 135.5, 140.5, 149.9, 152.2 ppm.

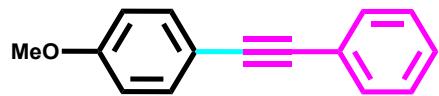


¹H NMR (250 MHz, CDCl₃) δ: 7.02 (d, 1H, *J*= 16.5 Hz), 7.45-7.60 (m, 6H), 7.49 (t, 2H, *J*= 7.5 Hz), 7.40 (t, 1H, *J*= 7.45 Hz), 7.20 (d, 1H, *J*= 16.5 Hz) ppm.



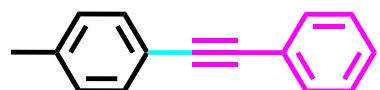
5a

¹H-NMR (250 MHz, CDCl₃) δ: 7.23-7.28 (m, 6H), 7.43-7.47 (m, 4H) ppm; ¹³C-NMR (62.9 MHz, CDCl₃) δ: 89.5, 123.3, 128.3, 129.2, 131.6 ppm; MS (m/e)= 178 [M⁺]; Elemental Analysis: Calcd. C: 94.33, H: 5.67%, Found. C: 94.11, H: 5.89%.



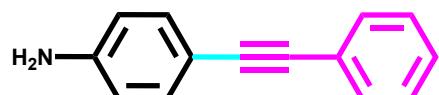
5b

¹H-NMR (250 MHz, CDCl₃) δ: 3.76 (s, 3H, CH₃), 6.79 (d, 2H, *J*= 8.2 Hz, Ar-H), 7.21-7.25 (m, 3H, Ar-H), 7.37-7.44 (m, 4H, Ar-H) ppm; ¹³C-NMR (62.9 MHz, CDCl₃) δ: 55.2, 88.0, 89.4, 114.0, 115.3, 123.6, 127.9, 128.3, 131.4, 133.0, 159.6 ppm; MS (m/e)= 208 [M⁺]; Elemental Analysis: Calcd. C: 86.50, H: 5.82%, Found. C: 86.64, H: 5.71%.



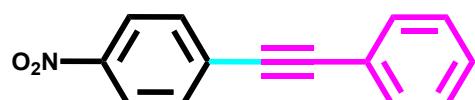
5c

¹H-NMR (CDCl₃, 250 MHz) δ: 2.22 (s, 3H, CH₃), 7.14 (d, 2H, *J*= 8.4 Hz, Ar-H), 7.19-7.42 (m, 7H, Ar-H) ppm; ¹³C-NMR (62.9 MHz, CDCl₃) δ: 21.5, 88.7, 89.6, 120.2, 123.5, 128.1, 128.3, 129.1, 131.5, 131.7, 138.4 ppm; MS (m/e)= 192 [M⁺]; Elemental Analysis: Calcd. C: 93.77, H: 6.30%, Found. C: 93.57, H: 6.23%.



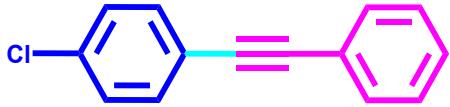
5d

¹H-NMR (250 MHz, CDCl₃) δ: 3.62 (s, 2H, NH₂), 6.52 (s, 2H, Ar-H), 7.22-7.40 (m, 7H, Ar-H) ppm; ¹³C-NMR (62.9 MHz, CDCl₃) δ: 87.3, 90.2, 112.5, 114.7, 123.9, 127.7, 128.3, 131.3, 132.9, 146.7 ppm.



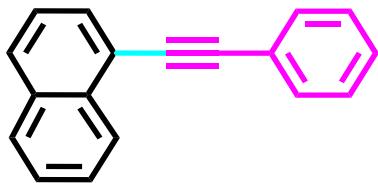
5e

¹H-NMR (250 MHz, CDCl₃) δ: 7.37-7.41 (m, 3H, Ar-H), 7.54-7.57 (m, 2H, Ar-H), 7.68 (d, 2H, *J*= 12.5 Hz, Ar-H), 8.22 (d, 2H, *J*= 7.5 Hz, Ar-H) ppm; ¹³C-NMR (62.9 MHz, CDCl₃) δ: 87.5, 94.7, 122.0, 123.6, 128.5, 129.2, 130.2, 131.8, 132.2, 146.9 ppm; MS (m/e)= 224 [M⁺]; Elemental Analysis: Calcd. C: 75.32, H: 4.07, N: 6.27%, Found. C: 75.42, H: 4.21, N: 6.15%.



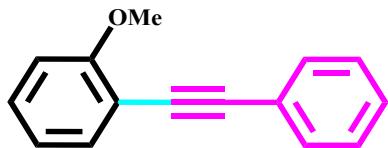
5f

¹H NMR (250 MHz, CDCl₃) δ: 7.13-7.43 (m, 9H, Ar-H) ppm; ¹³C NMR (62.9 MHz, CDCl₃) δ: 88.2, 90.3, 121.8, 122.9, 128.4, 128.5, 128.7, 131.6, 132.8, 134.2 ppm.



5g

¹H-NMR (250 MHz, CDCl₃) δ: 7.26-7.74 (m, 11H, Ar-H), 8.36 (d, 1H, *J*= 8.2 Hz, Ar-H); ¹³C-NMR (62.9 MHz, CDCl₃) δ: 87.5, 94.3, 120.9, 123.4, 125.3, 125.6, 126.2, 126.4, 126.8, 128.3, 128.42, 128.47, 128.8, 130.4, 131.7, 133.2, 133.3, 141.1 ppm; MS (m/e) = 228 [M⁺]; Elemental Analysis: Calcd. C: 94.69, H: 5.31%, Found. C: 94.41, H: 5.59%.



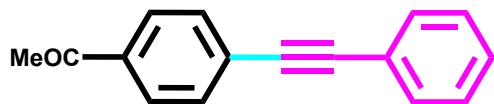
5h

¹H NMR (250 MHz, CDCl₃) δ: 3.82 (s, 3H, CH₃), 6.87 (d, 2H, *J*= 7.25 Hz, Ar-H), 7.31-7.33 (m, 3H, Ar-H), 7.45-7.53 (m, 4H, Ar-H) ppm; ¹³C NMR (CDCl₃, 62.9 MHz): δ: 55.8, 85.6, 93.3, 110.6, 112.4, 120.4, 123.5, 128.0, 128.1, 129.7, 131.6, 133.5, 159.8 ppm.



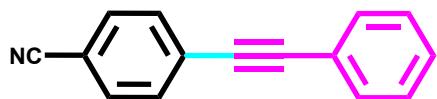
2i

¹H NMR (250 MHz, CDCl₃) δ: 2.44 (s, 3H, CH₃), 7.14-7.46 (m, 9H, Ar-H) ppm; ¹³C NMR (CDCl₃, 62.9 MHz) δ: 20.7, 86.01, 94.2, 123.0, 125.5, 128.1, 128.30, 128.35, 129.4, 131.5, 131.8, 140.1 ppm; MS (m/e)= 192 [M⁺]; Elemental Analysis: Calcd. C: 93.70, H: 6.30%, Found. C: 93.82, H: 6.18%.

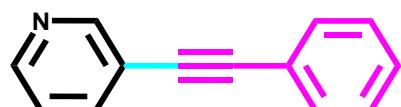


5j

¹H-NMR (250 MHz, CDCl₃) δ: 2.51 (s, 3H, CH₃), 7.16-7.33 (m, 3H, Ar-H), 7.45-7.54 (m, 4H, Ar-H), 7.86 (d, 2H, J=7.5 Hz, Ar-H) ppm; ¹³C-NMR (62.9 MHz, CDCl₃) δ: 27.0, 88.9, 92.9, 123.0, 128.2, 128.3, 128.8, 129.5, 132.0, 132.2, 136.5, 197.6 ppm.

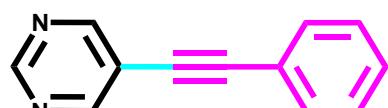


¹H-NMR (250 MHz, CDCl₃) δ: 7.28-7.31 (m, 3H, Ar-H), 7.44-7.53 (m, 6H, Ar-H) ppm; ¹³C-NMR (62.9 MHz, CDCl₃) δ: 87.7, 93.7, 111.4, 118.5, 122.2, 128.2, 128.5, 129.1, 131.7, 132.03, 132.06 ppm; MS (m/e)= 203 [M⁺]; Elemental Analysis: Calcd. C: 88.64, H: 4.47, N: 6.89%, Found. C: 88.77, H: 4.57, N: 6.66%.



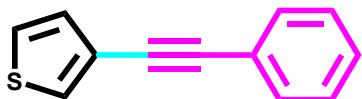
5k

¹H-NMR (250 MHz, CDCl₃) δ: 7.26-7.29 (m, 4H, Ar-H), 7.44-7.47 (m, 2H, Ar-H), 7.70 (m, 1H, Ar-H), 8.45 (m, 1H, Ar-H), 8.68 (s, 1H, Ar-H) ppm; ¹³C-NMR (62.9 MHz, CDCl₃) δ: 85.9, 92.7, 120.5, 122.4, 123.0, 128.4, 128.8, 131.6, 138.4, 148.4, 152.1 ppm; MS (m/e)= 179 [M⁺]; Elemental Analysis: Calcd. C: 87.12, H: 5.07, N: 7.81%, Found. C: 87.27, H: 4.91, N: 7.82%.



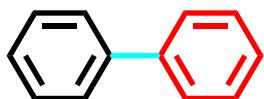
5l

¹H-NMR (250 MHz, CDCl₃) δ: 7.29-7.48 (m, 5H, Ar-H), 8.77 (s, 2H, Ar-H), 9.06 (s, 1H, Ar-H) ppm; ¹³C-NMR (62.9 MHz, CDCl₃) δ: 82.3, 96.3, 119.9, 121.7, 128.5, 128.7, 129.1, 129.3, 131.7, 139.3, 156.6, 158.5 ppm; MS (m/e)= 180 [M⁺]; Elemental Analysis: Calcd. C: 79.98, H: 4.48, N: 15.54%, Found. C: 79.81, H: 4.62, N: 15.57%.



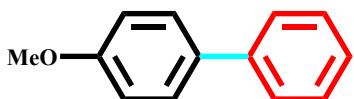
5m

¹H-NMR (250 MHz, CDCl₃) δ: 7.31-7.42 (m, 5H, Ar-H), 7.59-7.64 (m, 3H, Ar-H) ppm; ¹³C-NMR (62.9 MHz, CDCl₃) δ: 84.7, 89.1, 123.3, 125.5, 127.2, 128.5, 128.7, 129.3, 129.9, 131.7, 132.6 ppm; MS (m/e)= 184 [M⁺]; Elemental Analysis: Calcd. C: 78.22, H: 4.39%, Found. C: 78.10, H: 4.46%.



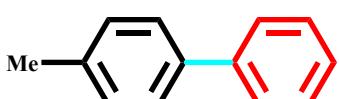
7a

¹H NMR (250 MHz, CDCl₃) δ: 7.26-7.71 (m, 10H) ppm; ¹³C-NMR (62.9 MHz, CDCl₃) δ: 127.2, 127.4, 130.3, 145.5 ppm.



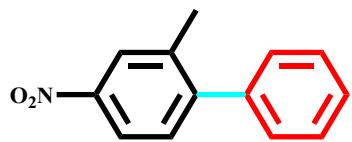
7b

¹H NMR (250 MHz, CDCl₃) δ: 3.85 (s, 3H), 6.98 (d, *J*= 7.5 Hz, 2H), 7.28 (t, *J*= 7.2 Hz, 2H), 7.41 (t, *J*= 7.2 Hz, 2H), 7.51-7.57 (m, 3H) ppm; ¹³CNMR (62.9 MHz, CDCl₃) δ: 55.3, 114.3, 127.1, 128.2, 128.4, 128.8, 133.8, 140.9, 159.2 ppm.



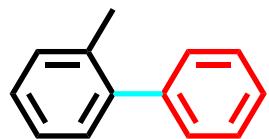
7c

¹H NMR (250 MHz, CDCl₃) δ: 2.53 (s, 3H), 7.37-7.55 (m, 7H), 7.62-7.74 (m, 2H) ppm; ¹³C NMR (62.9 MHz, CDCl₃) δ: 21.6, 127.5, 127.8, 128.8, 129.4, 130.1, 131.4, 132.1, 138.1 ppm.



7d

¹H NMR (250 MHz, CDCl₃) δ: 2.53 (s, 3H), 7.39-7.49 (m, 5H), 7.91-7.87 (m, 3H) ppm;
¹³C NMR (62.9 MHz, CDCl₃) δ: 20.6, 120.8, 125.1, 127.9, 128.4, 128.6, 130.6, 137.2, 139.7, 148.5 ppm.



7d

¹H NMR (250 MHz, CDCl₃) δ: 2.43 (s, 3H), 7.39-7.59 (m, 7H), 7.73 (m, 2H) ppm; ¹³C NMR (62.9 MHz, CDCl₃) δ: 20.6, 125.9, 126.4, 127.6, 128.2, 128.9, 129.3, 129.9, 130.4, 135.0, 141.3, 142.0 ppm.



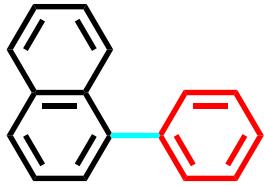
7e

¹H NMR (250 MHz, CDCl₃) δ: 7.41-7.48 (m, 3H), 7.58-7.76 (m, 6H) ppm; ¹³C NMR (62.9 MHz, CDCl₃) δ: 110.8, 118.6, 127.3, 128.7, 129.3, 129.9, 132.1, 139.8, 146.2 ppm.



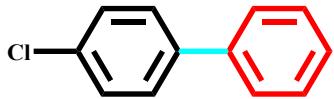
7f

¹H NMR (250 MHz, CDCl₃) δ: 7.45-7.76 (m, 7H), 8.31 (d, *J*= 9.0 Hz, 2H) ppm; ¹³C NMR (62.9 MHz, CDCl₃) δ: 124.9, 127.6, 127.9, 128.9, 129.5, 129.7, 141.1, 147.8 ppm.



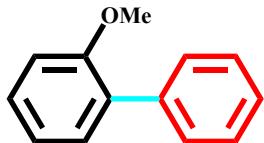
7g

¹H NMR (250 MHz, CDCl₃) δ: 7.29-7.53 (m, 8H), 7.84-7.93 (m, 3H) ppm; ¹³CNMR (62.9 MHz, CDCl₃) δ: 125.3, 125.7, 125.9, 126.1, 126.8, 127.4, 128.2, 129.0, 129.9, 131.7, 133.7, 136.9, 137.8, 140.3 ppm; Elemental Analysis: Calcd. C: 93.54, H: 6.46%, Found. C: 93.40, H: 6.60%.



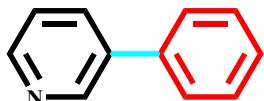
7h

¹H NMR (250 MHz, CDCl₃) δ: 7.29-7.50 (m, 9H) ppm; ¹³CNMR (62.9 MHz, CDCl₃) δ: 126.9, 127.5, 128.3, 128.7, 129.0, 133.7, 138.4, 139.1 ppm.



7i

¹H NMR (250 MHz, CDCl₃) δ: 3.79 (s, 3H), 6.97-7.04 (m, 2H), 7.29-7.42 (m, 5H), 7.54 (d, *J*=8.1 Hz, 2H) ppm; ¹³C NMR (62.9 MHz, CDCl₃) δ: 55.6, 111.5, 121.1, 127.0, 128.1, 128.9, 129.6, 131.2, 138.9, 157.0 ppm.



7j

¹H NMR (250 MHz, CDCl₃) δ: 7.33-7.59 (m, 6H), 7.86-7.88 (m, 1H), 8.59 (d, *J*=4.0 Hz, 1H), 8.86 (s, 1H) ppm; ¹³C NMR (62.9 MHz, CDCl₃) δ: 123.4, 127.1, 128.3, 129.1, 134.5, 136.8, 137.8, 149.3, 149.4; Elemental Analysis: Calcd. C: 85.12, H: 5.85, N: 9.03%, Found. C: 85.28, H: 5.65, N: 9.07%.



7k

¹H NMR (250 MHz, CDCl₃) δ: 7.23 (d, *J*= 9.0 Hz, 1H) 7.43-7.99 (m, 7H), 8.71 (s, 1H) ppm; ¹³C NMR (62.9 MHz, CDCl₃) δ: 120.3, 122.4, 126.3, 127.7, 137.0, 139.5, 149.3, 157.1 ppm;
Elemental Analysis: Calcd. C: 85.13, H: 5.85, N: 9.03%, Found. C: 85.29, H: 5.60, N: 9.11%.