

Supporting Information

Nano-copper catalyzed three-component tandem cycloaddition and N-alkylation reaction from aminophenylacetylenes, sodium azide and alkyl halides

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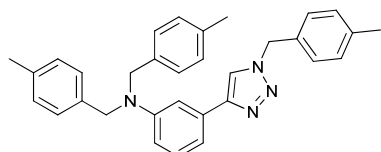
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General Remarks.

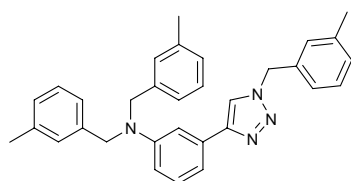
Melting points are uncorrected.

All reagents were from commercial source without any further purification. ¹H NMR spectra were recorded on 400 MHz instruments and recorded relative to the tetramethylsilane signal (0 ppm). ¹³C NMR spectra were obtained at 100 MHz, and chemical shifts were recorded relative to the solvent resonance (CDCl₃, 77.0 ppm).

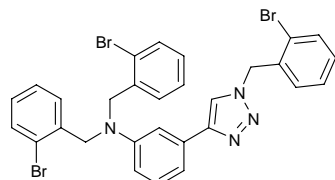
Characterization Data of Products (1a-k)



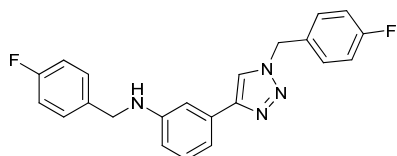
4-(3-(*N,N*-Di(4-methylbenzyl)amino)phenyl)-1-(4-methylbenzyl)-1*H*-1,2,3-triazole (1a): Yield: 87%, yellow solid, mp. 149-150 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 7.9, 1H), 7.66 (d, *J* = 7.5, 1H), 7.49 (s, 1H), 7.30-7.02 (m, 14H), 6.67 (d, *J* = 7.7, 1H), 5.48 (d, *J* = 11.6, 2H), 4.60 (s, 4H), 2.33 (d, *J* = 12.9, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 149.7, 148.7, 138.5, 138.4, 138.2, 131.7, 131.3, 129.7, 129.5, 129.2, 127.9, 126.7, 119.4, 114.2, 109.6, 53.8, 53.5, 29.6. HRMS (ESI, MeOH) *m/z* calcd for C₃₂H₃₂N₄ (M + H)⁺: 473.2627; found 473.3722. IR (KBr, cm⁻¹): 690, 802, 831, 872, 1051, 1180, 1377, 1456, 1491, 1616, 2853, 2923, 3045.



4-(3-(*N,N*-Di(3-methylbenzyl)amino)phenyl)-1-(3-methylbenzyl)-1*H*-1,2,3-triazole (1b): Yield: 85%, yellow solid, mp. 135-137 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.57 (s, 1H), 7.51 (s, 1H), 7.27-7.09 (m, 14H), 6.72 (d, *J* = 7.1, 1H), 5.48 (s, 2H), 4.68 (s, 4H), 2.34 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 149.6, 148.6, 138.7, 138.3, 138.1, 134.6, 131.3, 129.5, 129.2, 128.8, 128.5, 128.4, 127.5, 127.3, 124.9, 123.7, 119.5, 114.2, 112.3, 109.4, 53.9, 53.8, 21.3. HRMS (ESI, MeOH) *m/z* calcd for C₃₂H₃₂N₄ (M + H)⁺: 473.2627; found 473.2700. IR (KBr, cm⁻¹): 690, 806, 889, 1086, 1184, 1380, 1459, 1496, 1608, 2851, 2918, 3020.

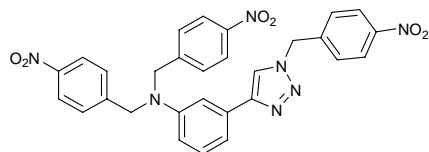


4-(3-(*N,N*-Di(2-bromobenzyl)amino)phenyl)-1-(2-bromobenzyl)-1*H*-1,2,3-triazole (1c): Yield: 74%, yellow solid, mp. 124-127 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.60-7.52 (m, 4H), 7.22-7.07 (m, 12H), 6.47 (s, 1H), 5.60 (s, 2H), 4.65 (s, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 148.1, 147.1, 134.3, 133.1, 131.3, 130.3, 130.1, 129.7, 128.1, 123.2, 120.2, 115.7, 114.9, 112.1, 53.7, 52.1. HRMS (ESI, MeOH) *m/z* calcd for C₂₂H₁₈Br₂N₄ (M + H)⁺: 664.9473; found 664.9890. IR (KBr, cm⁻¹): 654, 690, 743, 782, 872, 1026, 1223, 1469, 1589, 1617, 2850, 3057.

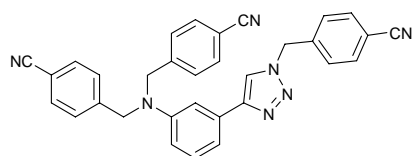


4-(3-(*N*-(4-Fluorobenzyl)amino)phenyl)-1-(4-fluorobenzyl)-1*H*-1,2,3-triazole (1d): Yield: 77%, yellow solid, mp. 138-140 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.56 (s, 1H), 7.23- 6.94(m, 11H), 6.50 (d, *J* = 7.2 Hz, 1H), 5.46 (s, 2H), 4.53 (s, 1H), 4.27 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 148.4, 148.1, 129.8, 129.8, 129.6, 129.1, 128.9, 119.4, 116.1, 115.9, 115.4, 112.9, 110.1, 53.3,

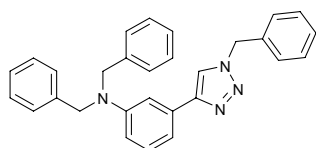
47.5. HRMS (ESI, MeOH) m/z calcd for $C_{22}H_{18}F_2N_4$ ($M + H$)⁺: 377.1500; found 377.2520. IR (KBr, cm^{-1}): 767, 817, 895, 1054, 1228, 1464, 1618, 1637, 2917, 3062, 3415.



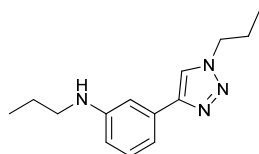
4-(3-(*N,N*-Di(4-nitrophenyl)amino)phenyl)-1-(4-nitrobenzyl)-1*H*-1,2,3-triazole (1e): Yield: 72%, yellow solid, mp. 156-158 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.16-8.11 (m, 5H), 7.64 (s, 1H), 7.60 (s, 1H), 7.45 (s, 1H), 7.35 (t, $J = 9.1$ Hz, 5H), 7.19-7.14 (m, 2H), 6.99 (d, $J = 7.6$ Hz, 1H), 6.56 (s, 1H), 5.59 (s, 2H), 4.72 (s, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 148.3, 147.6, 146.9, 141.7, 130.8, 129.6, 128.3, 123.9, 120.1, 115.6, 114.9, 111.9, 52.8. HRMS (ESI, MeOH) m/z calcd for $C_{29}H_{23}O_6N_7$ ($M + Me$)⁺: 579.1866; found 579.1894. IR (KBr, cm^{-1}): 690, 783, 857, 908, 1108, 1223, 1344, 1469, 1518, 1609, 2918, 3079.



4-(3-(*N,N*-Di(4-cyanophenyl)amino)phenyl)-1-(4-cyanobenzyl)-1*H*-1,2,3-triazole (1f): Yield: 75%, yellow solid, mp. 136-137°C. ¹H NMR (400 MHz, CDCl₃): δ 7.69 (d, $J = 3.2$ Hz, 1H), 7.66-7.59 (m, 5H), 7.52 (d, $J = 3.3$ Hz, 1H), 7.38-7.34 (m, 6H), 7.25 (s, 1H), 7.19 (t, $J = 7.9$ Hz, 1H), 7.03 (d, $J = 7.5$ Hz, 1H), 6.60 (d, $J = 7.7$ Hz, 1H), 5.60 (s, 2H), 4.71 (s, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 148.4, 147.9, 145.1, 139.8, 132.6, 132.2, 131.0, 129.7, 128.2, 127.6, 119.9, 118.0, 115.6, 115.2, 112.6, 109.9, 53.2, 47.3. HRMS (ESI, MeOH) m/z calcd for $C_{32}H_{23}N_7$ ($M + H$)⁺: 506.2015; found 506.3146. IR (KBr, cm^{-1}): 692, 782, 815, 866, 1078, 1175, 1459, 1609, 2227, 2922, 3055.

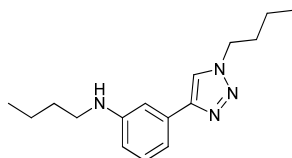


4-(3-(*N,N*-Dibenzylamino)phenyl)-1-benzyl-1*H*-1,2,3-triazole (1g): Yield: 81%, yellow solid, mp. 132-134°C. ¹H NMR (400 MHz, CDCl₃): δ 7.46 (s, 2H), 7.27 (s, 2H), 7.17 (d, $J = 3.2$ Hz, 2H), 7.10 (d, $J = 6.8$ Hz, 5H), 6.97 (t, $J = 8.5$ Hz, 3H), 6.89 (t, $J = 8.5$ Hz, 4H), 6.59 (d, $J = 6.3$ Hz, 2H), 5.41 (s, 2H), 4.51 (s, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 148.1, 146.7, 134.6, 129.6, 129.0, 128.6, 127.9, 119.5, 115.9, 114.9, 112.1, 54.1, 29.6. HRMS (ESI, MeOH) m/z calcd for $C_{29}H_{26}N_4$ ($M + H$)⁺: 431.2157; found 431.2218. IR (KBr, cm^{-1}): 694, 765, 860, 1068, 1178, 1451, 1620, 2850, 3031.

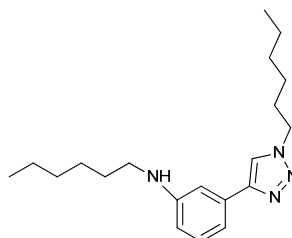


4-(3-(*N-n*-Propylamino)phenyl)-1-*n*-propyl-1*H*-1,2,3-triazole (1h): Yield: 80%, yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.68 (s, 1H), 7.28 (s, 2H), 7.20-7.16 (m, 2H), 6.65 (s, 1H), 4.32 (s, 2H),

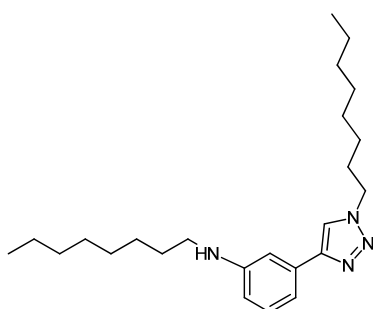
3.85 (s, 2H), 1.94 (d, $J=6.4$, 2H), 1.63 (s, 2H), 1.25 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 147.4, 146.8, 131.2, 129.4, 119.5, 115.4, 114.6, 111.8, 51.6, 29.4, 23.3, 10.7. HRMS (ESI, MeOH) m/z calcd for $\text{C}_{17}\text{H}_{26}\text{N}_4$ ($\text{M} + \text{H}$) $^+$: 245.1688; found 245.1447. IR (KBr, cm^{-1}): 691, 784, 871, 1049, 1167, 1363, 1464, 1487, 1614, 2851, 2920, 3131, 3351.



4-(3-(*N*-n-Butylamino)phenyl)-1-n-butyl-1H-1,2,3-triazole (1i): Yield: 72%, yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 7.60 (s, 1H), 7.11-7.08 (m, 2H), 6.96 (d, $J = 7.6$ Hz, 1H), 6.50-6.46 (m, 1H), 4.26 (t, $J = 7.2$ Hz, 2H), 3.63 (s, 1H), 3.07 (t, $J = 7.1$ Hz, 2H), 1.82-1.77 (m, 2H), 1.54-1.51 (m, 2H), 1.34-1.30 (m, 4H), 0.86 (dd, $J = 7.3, 6.2$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 148.9, 148.0, 131.5, 129.5, 119.5, 114.4, 112.5, 109.6, 50.0, 43.6, 32.2, 31.6, 20.2, 19.6, 13.8. HRMS (ESI, MeOH) m/z calcd for $\text{C}_{17}\text{H}_{26}\text{N}_4$ ($\text{M} + \text{H}$) $^+$: 273.2001; found 273.2043. IR (KBr, cm^{-1}): 691, 775, 880, 1048, 1162, 1346, 1469, 1589, 1617, 2923, 3035, 3416.

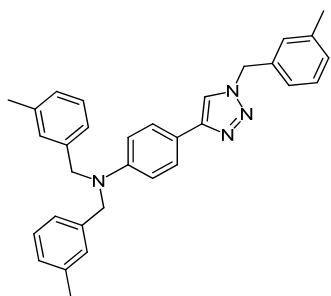


4-(3-(*N*-n-Hexylamino)phenyl)-1-n-hexyl-1H-1,2,3-triazole (1j): Yield: 66%, yellow oil. ^1H NMR (400 MHz, CDCl_3): 7.61 (s, 1H), 7.12-7.10 (m, 2H), 6.97 (d, $J = 7.6$ Hz, 1H), 6.50 (dd, $J = 8.1, 1.5$ Hz, 1H), 4.29 (t, $J = 7.2$ Hz, 2H), 3.64 (s, 1H), 3.08 (t, $J = 7.1$ Hz, 2H), 1.86-1.83 (m, 2H), 1.61-1.50 (m, 2H), 1.30-1.18 (m, 12H), 0.84-0.81 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 148.9, 148.0, 131.5, 129.5, 119.3, 114.5, 112.6, 109.7, 50.3, 44.0, 31.1, 30.3, 29.4, 26.8, 26.1, 22.4, 13.9. HRMS (ESI, MeOH) m/z calcd for $\text{C}_{17}\text{H}_{26}\text{N}_4$ ($\text{M} + \text{H}$) $^+$: 329.2627; found 329.2737. IR (KBr, cm^{-1}): 696, 790, 880, 1046, 1354, 1462, 1566, 1622, 2851, 3045, 3338.

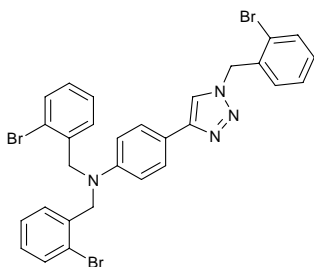


4-(3-(*N*-n-Octylamino)phenyl)-1-n-octyl-1H-1,2,3-triazole (1k): Yield: 61%, yellow oil. ^1H NMR (400 MHz, CDCl_3): 7.59 (s, 1H), 7.16 (s, 1H), 7.11-7.05 (m, 2H), 6.55 (d, $J = 7.7$ Hz, 1H), 4.25 (t, $J = 6.4$ Hz, 2H), 3.62 (s, 2H), 1.82-1.77 (m, 2H), 1.65-1.61 (m, 2H), 1.26-1.12 (m, 20H), 0.78 (t, $J = 6.8$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 147.7, 146.8, 131.6, 129.6, 119.4, 115.9, 114.8, 112.2, 50.3, 31.9, 31.6, 30.3, 29.6, 29.3, 29.0, 28.9, 26.4, 22.5, 14.0. HRMS (ESI, MeOH) m/z calcd for $\text{C}_{17}\text{H}_{26}\text{N}_4$ ($\text{M} + \text{H}$) $^+$: 385.3253; found 385.3718. IR (KBr, cm^{-1}): 692, 802, 900, 1045, 1355, 1454, 1589, 1623, 2850, 3040, 3444.

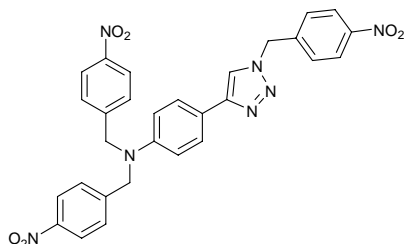
Spectral Data of Products 2a-g and 3a



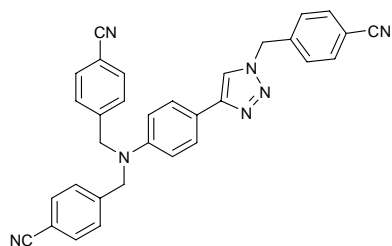
4-(4-(*N,N*-Di(3-methylbenzyl)amino)phenyl)-1-(3-methylbenzyl)-1*H*-1,2,3-triazole (2a): Yield: 86%, yellow solid, mp. 133-134 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.49 (s, 1H), 7.31 (s, 1H), 7.25 (s, 1H), 7.17-7.09 (m, 12H), 7.05(s, 1H), 6.68 (s, 1H), 5.47 (s, 2H), 4.61 (s, 4H), 2.35 (s, 3H), 2.31 (s, 5H). ¹³C NMR (100 MHz, CDCl₃): δ 149.6, 148.7, 138.5, 136.4, 135.3, 131.7, 131.4, 129.7, 129.6, 129.2, 128.0, 126.7, 119.4, 114.2, 53.9, 53.5, 21.0. HRMS (ESI, MeOH) *m/z* calcd for C₂₉H₂₃Br₃N₄ (M + H)⁺: 473.2627; found 473.2962. IR (KBr, cm⁻¹): 690, 749, 804, 1048, 1218, 1348, 1452, 1491, 1581, 2851, 2918, 3042.



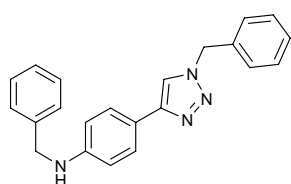
4-(4-(*N,N*-Di(2-bromobenzyl)amino)phenyl)-1-(2-bromobenzyl)-1*H*-1,2,3-triazole (2b): Yield: 70%, yellow solid, mp. 133-136 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.54 (t, *J*=4.0, 3H), 7.24-7.12 (m, *J*=6.5, 6H), 6.96-6.78 (m, 6H), 6.64 (s, 1H), 6.54 (d, *J*=8.5, 1H), 5.68 (s, 1H), 5.60 (s, 1H), 4.91 (s, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 148.4, 147.0, 133.0, 132.8, 132.6, 130.2, 129.9, 129.8, 127.6, 127.1, 126.8, 123.2, 119.3, 118.7, 115.1, 114.9, 53.6, 51.9. HRMS (ESI, MeOH) *m/z* calcd for C₂₉H₂₃Br₃N₄ (M + H)⁺: 664.9473; found 664.9865. IR (KBr, cm⁻¹): 517, 743, 828, 1026, 1176, 1481, 1611, 2917, 3069.



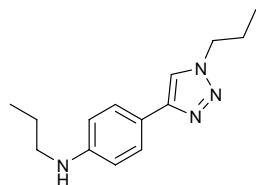
4-(4-(*N,N*-Di(4-nitrophenyl)amino)phenyl)-1-(4-nitrobenzyl)-1*H*-1,2,3-triazole (2c): Yield: 71%, yellow solid, mp. 153-154 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.24-8.00 (m, 6H), 7.63–7.19 (m, 9H), 6.87 (dd, *J* = 8.0, 8.1 Hz, 2H), 5.61 (s, 2H), 4.70 (s, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 148.8, 147.5, 146.8, 145.0, 140.1, 127.6, 126.9, 126.9, 118.3, 115.1, 112.9, 53.3, 47.5. HRMS (ESI, MeOH) *m/z* calcd for C₂₉H₂₃O₆N₇ (M + Me)⁺: 579.1866; found 579.2087. IR (KBr, cm⁻¹): 825, 1045, 1181, 1343, 1454, 1620, 2850, 3042.



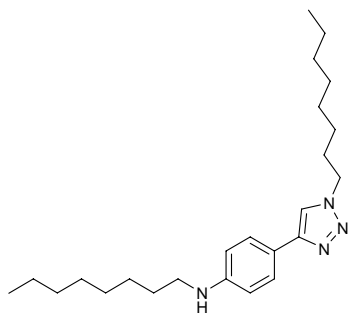
4-(4-(*N,N*-Di(4-cyanophenyl)amino)phenyl)-1-(4-cyanobenzyl)-1*H*-1,2,3-triazole (2d): Yield: 74%, yellow solid, mp. 149-151 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.64-7.46 (m, 9H), 7.28-7.19 (m, 6H), 6.61 (d, *J* = 7.9 Hz, 2H), 5.54 (s, 2H), 4.65 (s, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 147.2, 145.6, 142.0, 141.9, 127.6, 127.3, 126.9, 124.1, 124.0, 123.7, 118.7, 118.5, 113.0, 112.9, 112.6, 54.3, 53.0. HRMS (ESI, MeOH) *m/z* calcd for C₃₂H₂₃N₇ (M + H)⁺ : 506.2015; found 506.3598. IR (KBr, cm⁻¹): 817, 1045, 1200, 1456, 1609, 2227, 2851, 3077.



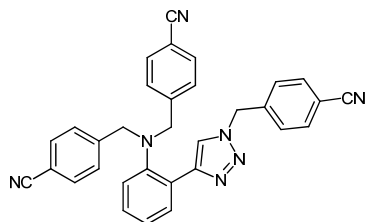
4-(4-(*N*-benzylamino)phenyl)-1-benzyl-1*H*-1,2,3-triazole (2e): Yield: 82%, yellow solid, mp. 126-127 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.65 (s, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.30-7.19 (m, 7H), 6.64 (d, *J* = 7.9 Hz, 2H), 5.48 (s, 2H), 4.24 (t, *J* = 6.5 Hz, 2H), 3.71 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 148.4, 148.0, 134.7, 133.1, 132.8, 128.9, 128.5, 128.3, 128.1, 127.8, 127.0, 127.2, 126.8, 123.9, 118.2, 115.2, 54.0, 52.4. HRMS (ESI, MeOH) *m/z* calcd for C₂₉H₂₆N₄ (M + H)⁺ : 341.1688; found 341.1695. IR (KBr, cm⁻¹): 777, 863, 1047, 1276, 1454, 1589, 1620, 2849, 2918, 3031, 3450.



4-(4-(*N-n*-Propylamino)phenyl)-1-*n*-propyl-1*H*-1,2,3-triazole (2f): Yield: 76%, yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.53 (s, 2H), 7.26 (d, *J* = 7.8 Hz, 1H), 6.65 – 6.51 (m, 2H), 4.27 (t, *J* = 6.6 Hz, 2H), 3.78 (s, 2H), 3.65 (s, 2H), 1.83 (s, 2H), 1.47(s, 2H), 1.23 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 147.9, 127.2, 126.8, 118.1, 115.1, 50.2, 48.8, 22.3, 13.9. HRMS (ESI, MeOH) *m/z* calcd for C₁₇H₂₆N₄ (M + H)⁺ : 245.1688; found 245.1692. IR (KBr, cm⁻¹): 831, 1049, 1179, 1357, 1461, 1500, 1625, 2855, 2924, 3027, 3462.



4-(4-(*N-n*-Octylamino)phenyl)-1-*n*-octyl-1*H*-1,2,3-triazole (2g): Yield: 65%, yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 8.00 (d, *J*=8.0, 1H), 7.34 (t, *J*=7.1, 2H), 6.76-6.59 (m, 2H), 4.43 (s, 2H), 3.86 (s, 2H), 1.99 (s, 2H), 1.56 (s, 2H), 1.26 (s, 15H), 1.09 (s, 5H), 0.89 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 147.5, 147.1, 132.9, 127.2, 115.2, 114.6, 48.8, 31.6, 31.6, 29.6, 28.8, 28.7, 26.4, 26.4, 22.5, 13.9. HRMS (ESI, MeOH) *m/z* calcd for C₈H₆N₄ (M + H)⁺: 385.3253; found 385.3433. IR (KBr, cm⁻¹): 720, 830, 1178, 1370, 1457, 1459, 1558, 1622, 2850, 2919, 3085, 3458.



4-(2-(*N,N*-Di(4-cyanophenyl)amino)phenyl)-1-(4-cyanobenzyl)-1*H*-1,2,3-triazole (3a): Yield: 55%, yellow solid, mp. 155-157 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.89 – 7.85 (m, 2H), 7.61 – 7.59 (m, 2H), 7.42 (d, *J* = 8.2 Hz, 4H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.19 (s, 1H), 7.12 (d, *J* = 8.1 Hz, 5H), 6.75 (d, *J* = 7.6 Hz, 1H), 5.60 (s, 2H), 3.87 (s, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 146.80, 146.31, 142.34, 139.96, 132.89, 132.07, 129.39, 129.05, 128.24, 124.70, 122.85, 122.11, 118.52, 117.93, 112.93, 111.34, 56.67, 53.41. HRMS (ESI, MeOH) *m/z* calcd for C₃₂H₂₃N₇ (M + H)⁺ : 506.2015; found 506.2548. IR (KBr, cm⁻¹): 760, 1045, 1201, 1455, 1606, 2225, 2851, 3055.

^1H and ^{13}C NMR Spectra

