

Supporting information for the article:

Copper acetate/2-aminobenzethiol complex supported on magnetite/silica nanoparticles as a highly active and recyclable catalyst for 1,2,3-Triazoles Synthesis

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1. Preparation of Fe₃O₄@SiO₂ nano particles:

A micro emulsion was prepared by dissolving sodium dodecylbenzenesulfonate (1.75 g) in xylene (15 mL) by sonication. Then the composed salts solution of FeCl₂·4H₂O, Fe(NO₃)₃·9H₂O ([Fe³⁺]/[Fe²⁺], 1.5/0.75 mmol) and DI water (0.9 mL) was added to the micro emulsion under vigorous stirring, and the solution was kept at room temperature for about 12 h to allow for its stabilization. Next, the reverse-micelle solution was slowly heated to 90°C under continuously flowing argon gas for an hour. After that, hydrazine (1 mL, 34 wt% aqueous solution) was injected into the solution. These particles were aged at 90°C for 3 h, and then cooled down to 40°C within an hour. Finally TEOS (2 mL) was injected into the mixture and stirred for 2 h. The final samples were rigorously washed with aqueous buffer (100 mm sodium phosphate, pH 7.4). The resulting Fe₃O₄@SiO₂ NPs were dried for 12 h at room temperature under vacuum and characterized by XRD, FTIR.¹

2. Atomic absorption diagram of copper

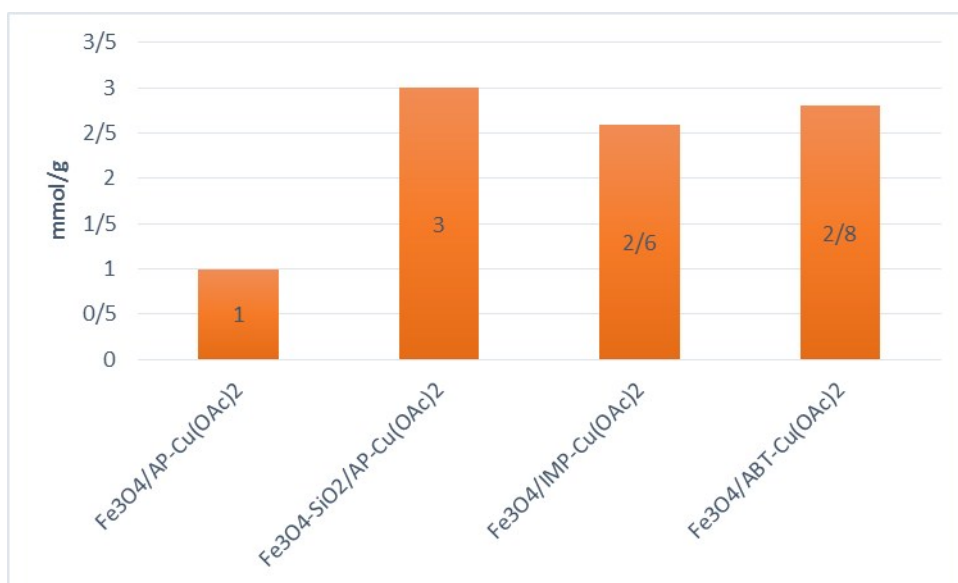


Figure S1. The Atomic absorption diagram of copper acetate complexes with various organic ligands

3. The XRD Spectra of a) Fe₃O₄@SiO₂ and b) Fe₃O₄@SiO₂/ABT-Cu(OAc)₂

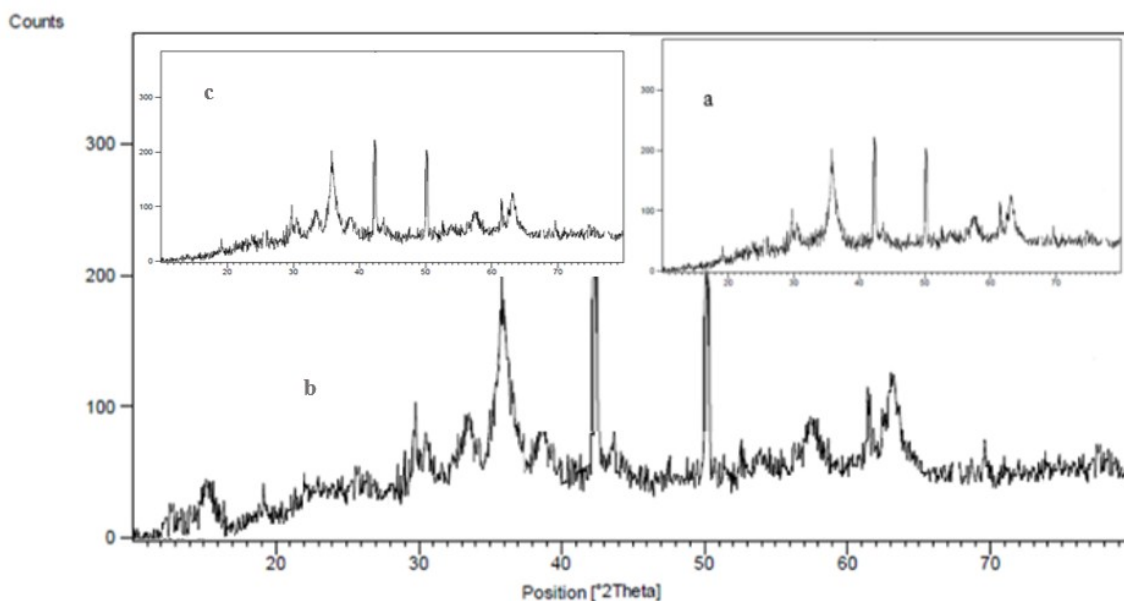


Figure S2. XRD Spectra of a) Fe₃O₄@SiO₂, b) Fe₃O₄@SiO₂/ABT-Cu(OAc)₂ and c) Fe₃O₄@SiO₂/ABT-Cu(OAc)₂ after the 1st run of recycling shows that the copper acetate existence on Fe₃O₄@SiO₂ and the composite structure is preserved.

X-ray diffraction analysis is used to demonstrate the structural order of the Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂/ABT-Cu(OAc)₂ materials. As is seen from figure S2a), the XRD patterns of the Fe₃O₄@SiO₂ are in good agreement with a cubic structure of Fe₃O₄ and a broad band appears in each spectrum is typical for amorphous SiO₂. The XRD patterns in figure S2b showed a little change in the XRD pattern in 2θ = 11.2°, 37.5°, 39° and increases the peak intensities in 2θ = 35°. These observations corroborate the copper acetate existence on Fe₃O₄@SiO₂.²

4. The XRF Table of a) Fe₃O₄@SiO₂ and b) Fe₃O₄@SiO₂/ABT-Cu(OAc)₂

| Table S1. XRF Analysis Results | |
|--------------------------------|----------------------|
| Compound | Concentration (%W/W) |
| Fe ₃ O ₄ | 30.30 |
| SiO ₂ | 28.10 |
| Cu(OAc) ₂ | 6.11 |
| V ₂ O ₅ | 0.073 |
| Al ₂ O ₃ | 0.041 |
| MnO | 0.034 |
| CaO | 0.029 |
| CuO | 0.020 |
| ZnO | 0.009 |
| *LOI* | 35.48 |

| | |
|-----------------------------------|--------|
| Total | 100.26 |
| * Loss on Ignition (1000 °C, 2 h) | |

5. The graphite furnace atomic absorption analysis of various organic ligands in Fe₃O₄@SiO₂/ligand-Cu(OAc)₂

| Table S2. graphite furnace atomic absorption analysis results | | | | | |
|---|-------|-------|-------|-------|-------|
| Copper concentrate (ppm) | | | | | |
| ligand | Run 1 | Run 2 | Run 3 | Run 4 | Run 5 |
| AP | 245 | 48 | 30 | 22 | 10 |
| IMP | 45 | 32 | 25 | 12 | 5 |
| ABT | 8 | 2 | 1 | 0.01 | 0.001 |

6. The reusability of various copper salts complexes with ABT

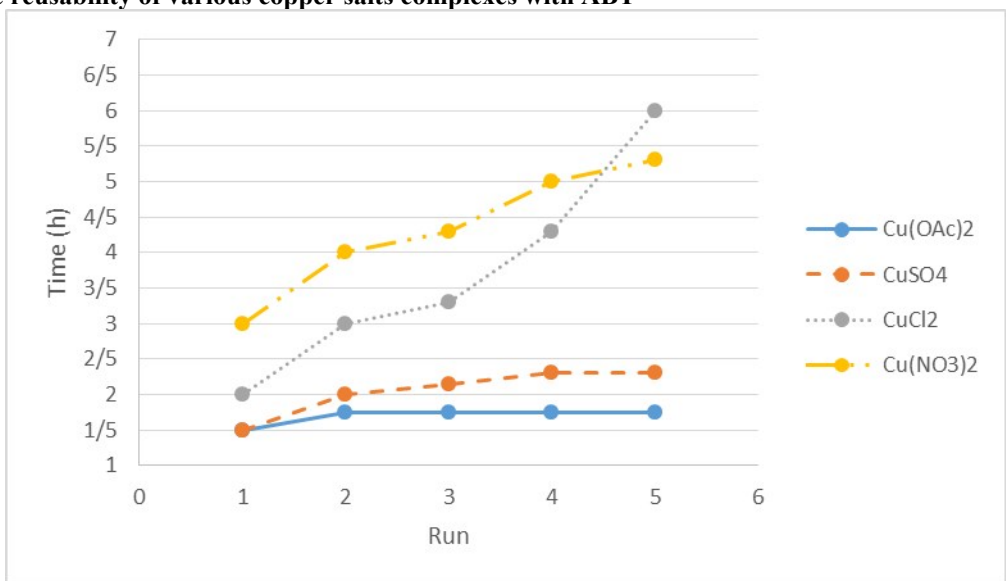
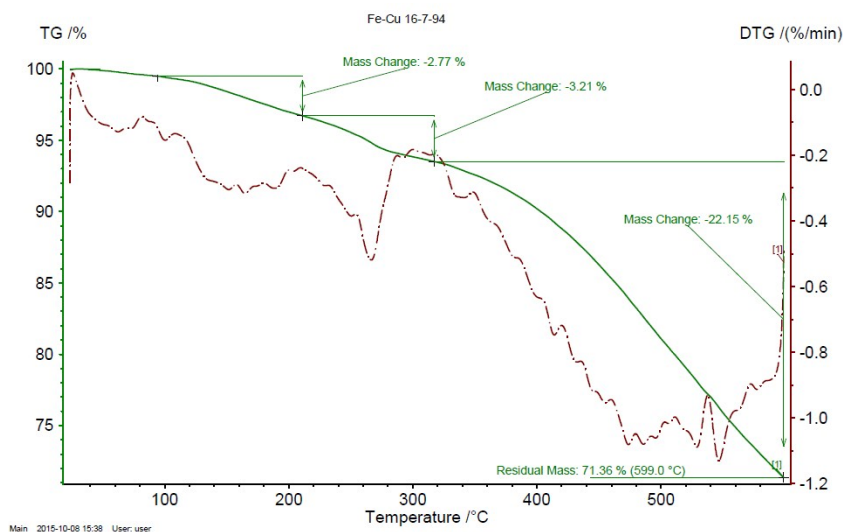
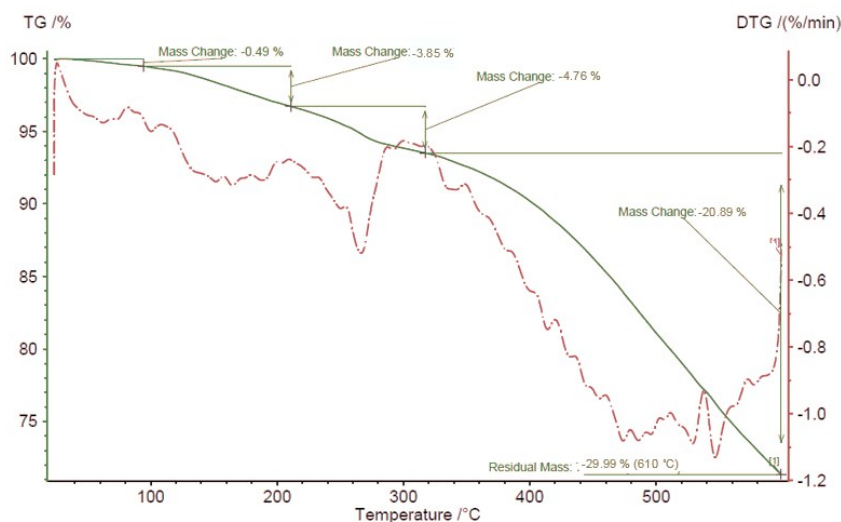


Figure S3. The reusability of various copper salts complexes with ABT

7. The TGA analysis of Fe₃O₄@SiO₂/ABT-Cu(OAc)₂



a



b

Figure S4. TGA analysis of a) $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{ABT}-\text{Cu}(\text{OAc})_2$ b) $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{ABT}-\text{Cu}(\text{OAc})_2$ after the 1st run of recycling

8. Optimization table of the 1-aryl 1,2,3-triazole synthesis

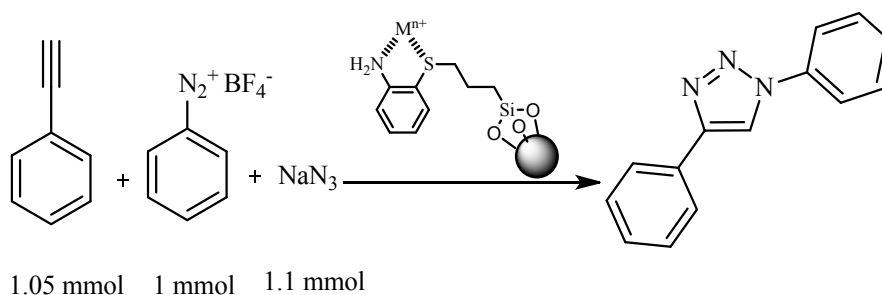


Table S3. Optimized condition for 1-phenyl 1, 2, 3-triazole synthesis

| Entry | M ^a | Solvent ^b | Tem. (°C) | Time (h) | Yield (%) |
|-----------|-----------------------------------|-----------------------|-----------|----------|-----------|
| 1 | - | H ₂ O | 25 | 8 | 5 |
| 2 | CuI ^c | H ₂ O | 25 | 8 | 50 |
| 3 | CuCl ^c | H ₂ O | 25 | 8 | 30 |
| 4 | AgI ^c | H ₂ O | 25 | 8 | 30 |
| 5 | Ni(OAc) ₂ ^f | H ₂ O | 25 | 8 | 10 |
| 6 | Co(OAc) ₂ ^f | H ₂ O | 25 | 8 | 10 |
| 7 | ZnCl ₂ ^f | H ₂ O | 25 | 8 | 10 |
| 8 | Cu(OAc) ₂ | H ₂ O | 25 | 8 | 50 |
| 9 | Cu(OAc) ₂ | H ₂ O | 50 | 6 | 93 |
| 10 | Cu(OAc)₂ | H₂O | 70 | 1 | 95 |
| 11 | Cu(OAc) ₂ | H ₂ O | 100 | 0.5 | 95 |

| | | | | | |
|----|-----------------------------------|-------------------------------|----|------|----|
| 12 | Cu(OAc) ₂ | EtOH | 70 | 1.5 | 92 |
| 13 | Cu(OAc) ₂ | PEG | 70 | 2 | 94 |
| 14 | Cu(OAc) ₂ | PEG/H ₂ O (1:1) | 70 | 1.25 | 95 |
| 15 | Cu(OAc) ₂ | PEG/EtOH (9:1) | 70 | 1.25 | 92 |
| 16 | Cu(OAc) ₂ | Glycerol | 70 | 1.5 | 95 |
| 17 | Cu(OAc) ₂ | EtOAc | 70 | 8 | 30 |
| 18 | Cu(OAc) ₂ | CH ₃ CN | 70 | 8 | 30 |
| 19 | Cu(OAc) ₂ | n-Hexane | 70 | 8 | 5 |
| 20 | Cu(OAc) ₂ | - | 70 | 8 | 20 |
| 21 | Cu(OAc) ₂ ^d | H ₂ O | 70 | 4 | 96 |
| 22 | Cu(OAc) ₂ ^e | H ₂ O | 70 | 0.75 | 95 |

^a Catalyst (2 mol%), ^b solvent (1 mL), ^c under N₂, ^d catalyst (1 mol%),
^e catalyst (4 mol%), ^f by-product observed

According to table 3 data, when the reaction is proceed in room temperature, none desired completion reaction time were detected (entries 1-8). With respect to less energy consumption, 70 °C was the best chose to produce the product (entry 10).

9. The FT-IR, ¹H- and ¹³C-NMR spectrums of products

1- Benzyl- 4- phenyl- 1H- 1, 2, 3- triazole (Table 2. Entry 1)

Yield: 95%, white solid, m.p. 129-131 °C.

FT-IR: ν_{\max} (neat) = 2920, 1522, 1486, 1438, 1383, 1087, 839, 759 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 5.53 (s, 2H), 7.50 (m, 5H), 7.50 (s, 1H), 7.60 (s, 2H), 7.70 (s, 1H), 7.82 (s, 2H), 7.83 ppm.

¹³CNMR (125 MHz, CDCl₃): δ = 56.5, 126.0, 127.3, 127.9, 128.1, 128.7, 129.9, 131.2, 131.7, 134.1, 150.0 ppm.

1-(4- nitrobenzyl)- 1H-1, 2, 3- triazole (Table 2. Entry 2)

Yield: 90%, white solid, m.p. 156-158 °C.

FT-IR: ν_{\max} (neat) = 3014, 1605, 1517, 1346, 1216, 810, 764, 729, 659 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 5.75 (s, 2H), 7.28-7.48 (m, 5H), 7.77 (s, 1H), 7.84 (d, J = 7.6 Hz, 2H), 8.26 (d, J = 8.4 Hz, 2H) ppm.

¹³CNMR (125 MHz, CDCl₃): δ = 57.8, 123.0, 127.0, 127.9, 128.9, 129.7, 130.9, 131.0, 141.7, 144.1, 150.2 ppm.

1- phenyl- 2-(4- phenyl- 1H- 1,2,3- triazol- 1- yl) ethanone (Table 2. Entry 3)

Yield: 85%, white solid, m.p. 160-162 °C.

FT-IR: ν_{\max} (neat) = 3008, 2930, 1607, 1520, 1443, 1407, 1325, 1301, 974, 751 cm⁻¹.

^1H NMR (400 MHz, CDCl_3): δ = 5.00 (s, 2H), 7.48-7.55 (m, 6H), 7.70 (s, 1H), 7.84 (s, 2H), 8.20 (s, 2H) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ = 56.8, 121.0, 127.8, 128.6, 128.9, 130.7, 132.9, 133.0, 133.8, 147.1, 188.2 ppm.

1-(naphthalen-1-yl methyl)-4-phenyl-1H-1,2,3-triazole (Table 2. Entry 4)

Yield: 92%, white solid, m.p. 128-130 °C.

FT-IR: ν_{max} (neat) = 3120, 2920, 1522, 1486, 1401, 1321, 1087, 839, 759 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 5.88 (s, 2H), 6.00 (d, J = 7.5 Hz, 1H), 7.30-7.31 (m, 1H), 7.50-7.51 (m, 5H), 7.64-7.65 (m, 1H), 7.89-7.90 (m, 2H), 7.82 (d, J = 6.8 Hz, 2H), 7.99-8.01 (m, 1H) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ = 55.8, 124.0, 125.8, 125.9, 126.0, 126.7, 126.9, 127.0, 128.8, 129.1, 130.2, 132.2, 133.8, 134.5, 150.0 ppm.

1-(2-chlorobenzyl)-4-phenyl-1H-1,2,3-triazole (Table 2. Entry 5)

Yield: 90%, white solid, m.p. 90-92 °C.

FT-IR: ν_{max} (neat) = 3110, 2919, 1594, 1580, 1483, 1396, 1094, 750, 692 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 5.36 (s, 2H), 7.20-7.21 (m, 3H), 7.50-7.51 (m, 4H), 7.80 (d, J = 7.6 Hz, 2H) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ = 51.0, 126.9, 127.1, 129.0, 127.8, 131.1, 131.2, 135.1, 138.8, 151.2 ppm.

1-(4-bromobenzyl)-4-phenyl-1H-1,2,3-triazole (Table 2. Entry 6)

Yield: 90%, white solid, m.p. 150-154 °C.

FT-IR: ν_{max} (neat) = 3134, 2916, 1595, 1410, 809, 778, 758 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 5.57 (s, 2H), 7.21 (d, J = 7.3 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.43 (d, J = 7.7 Hz, 2H), 7.54 (d, J = 5.0 Hz, 2H), 7.72 (s, 1H), 7.84 (d, J = 7.3 Hz, 2H) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ = 57.7, 121.2, 128.1, 128.9, 129.0, 130.5, 131.2, 131.6, 135.0, 148.6 ppm.

2-(1-(4-bromobenzyl)-1H-1,2,3-triazol-4-yl) propan-2-ol (Table 2. Entry 7)

Yield: 95%, white solid, m.p. 111-112 °C.

FT-IR: ν_{max} (neat) = 3390, 3121, 2932, 2100, 1604, 1481, 1457, 1074, 765, 693 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.63 (s, 6H), 2.52 (s, OH), 5.47 (s, 2H), 7.17 (d, J = 8.4 Hz, 2H), 7.36 (s, 1H), 7.52 (d, J = 8.4 Hz, 2H) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ = 32.6, 58.0, 78.8, 120.9, 122.3, 130.5, 131.9, 132.0, 138.5 ppm.

2-(1-benzyl-1H-1,2,3-triazol-4-yl) propan-2-ol (Table 2. Entry 8)

Yield: 90%, white solid, m.p. 190-193 °C.

FT-IR: ν_{max} (neat) = 3286, 3121, 2981, 1666, 1454, 1389, 1177, 856, 716 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.42 (s, 6H), 5.45 (s, 2H), 5.63 (s, 1H), 7.22 (d, J = 7.2 Hz, 2H), 7.67 (s, 1H), 7.82 (d, J = 7.2 Hz, 2H) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ = 30.8, 58.2, 75.6, 121.2, 122.8, 131.1, 131.8, 131.9, 134.9 ppm.

4-Phenyl-1-(p-tolyl)-1H-1,2,3-triazole (Table 3. Entry 1)

Yield: 95%, white solid, m.p. 158-160 °C.

FT-IR: ν_{\max} (neat) = 3134, 2924, 1515, 1463, 1302, 1249, 1038, 826 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 2.32 (s, 3H), 7.50-7.62 (m, 7H), 7.80 (d, 2H), 8.10 (s, 1H) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ = 21.7, 127.7, 128.9, 129.0, 130.8, 131.8, 133.9, 134.0, 138.7, 151.2 ppm.

1-(4-Methoxyphenyl)-4-phenyl-1H-1, 2, 3-triazole (Table 3. Entry 2)

Yield: 85%, white solid, m.p. 159-160 $^{\circ}\text{C}$.

FT-IR: ν_{\max} (neat) = 3000, 2930, 1607, 1520, 1443, 1407, 1325, 1301, 974, 751 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 3.88 (s, 3H), 6.00 (d, J = 6.4 Hz, 2H), 7.15 (d, J = 6.4 Hz, 2H), 7.59-7.60 (m, 3H), 7.80 (d, J = 7.2 Hz, 2H), 8.12 (s, 1H) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ = 53.5, 115.2, 124.1, 128.3, 128.9, 129.4, 129.7, 130.6, 132.1, 150.0, 168.1 ppm.

2-(1-(4-Methoxyphenyl)-1H-1, 2, 3-triazol-4-yl)propan-2-ol (Table 3. Entry 3)

Yield: 90%, white solid, m.p. 97-99 $^{\circ}\text{C}$.

FT-IR: ν_{\max} (neat) = 3312, 2976, 1661, 1607, 1513, 1444, 1375, 1250, 1214, 1178, 1063, 962, 823 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.71 (s, 6H), 2.76 (s, OH), 3.86 (s, 3H), 6.98-7.01 (m, 2H), 7.62 (m, 2H), 7.83 (s, 1H) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ = 30.5, 55.6, 68.6, 114.7, 117.7, 122.2, 130.6, 156.1, 159.9 ppm.

1-(4-Chlorophenyl)-4-hexyl-1H-1, 2, 3-triazole (Table 3. Entry 4)

Yield: 95%, white solid, m.p. 224-227 $^{\circ}\text{C}$.

FT-IR: ν_{\max} (neat) = 3064, 2922, 1555, 1497, 1095, 1049, 823, 724 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 0.86 (d, J = 5.8 Hz, 3H), 1.53 (m, 6H), 1.78 (m, 2H), 2.80 (t, J = 3.4 Hz, 5H), 7.45 (d, J = 6.1 Hz, 2H), 7.80 (d, J = 5.7 Hz, 2H), 8.32 (s, 1H) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ = 14.6, 21.1, 27.7, 28.2, 30.8, 31.1, 114.5, 121.3, 127.2, 135.7, 135.9, 136.4 ppm.

1-(4-Bromophenyl)-4-hexyl-1H-1, 2, 3-triazole (Table 3. Entry 5)

Yield: 92%, white solid, m.p. 229-231 $^{\circ}\text{C}$.

FT-IR: ν_{\max} (neat) = 3110, 2921, 2852, 1493, 1221, 1045, 986, 819, 721 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 0.95 (d, J = 5.2 Hz, 3H), 1.45-1.46 (m, 6H), 1.73-1.74 (m, 2H), 2.65 (t, J = 4.4 Hz, 5H), 7.50 (d, J = 5.5 Hz, 2H), 7.63 (d, J = 5.5 Hz, 2H), 8.40 (s, 1H) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ = 13.5, 22.3, 28.0, 28.6, 31.0, 31.5, 115.2, 120.5, 129.1, 133.1, 134.6, 135.0 ppm.

1-(2-Nitrophenyl)-4-phenyl-1H-1, 2, 3-triazole (Table 3. Entry 6)

Yield: 90%, white solid, m.p. 142-145 $^{\circ}\text{C}$.

FT-IR: ν_{\max} (neat) = 3143, 1602, 1518, 1354, 1232, 1029, 755, 693 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.50-7.51 (m, 3H), 7.75-7.76 (m, 1H), 7.95-7.96 (m, 2H), 8.01-8.02 (m, 2H), 8.24 (s, 1H), 8.50 (d, J = 5.75 Hz, 1H) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ = 123.1, 128.5, 128.6, 129.1, 129.5, 130.6, 131.9, 135.2, 145.8, 149.5 ppm.

1-(3-Nitrophenyl)-4-phenyl-1H-1, 2, 3-triazole (Table 3. Entry 7)

Yield: 90%, white solid, m.p. 197-199 °C.

FT-IR: ν_{max} (neat) = 3138, 1603, 1528, 1411, 1344, 1256, 1233, 1074, 1037, 879, 755, 689 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.28 (s, 1H), 7.41 (t, J = 7.2 Hz, 1H), 7.51 (dd, J_1 = 8.4, J_2 = 6.4 Hz, 2H), 7.81 (t, J = 8.4 Hz, 3H), 7.94 (d, J = 8.4 Hz, 2H), 8.33 (m, 3H), 8.67 (t, J = 2.2 Hz, 1H), ppm.

^{13}C NMR (125 MHz, CDCl_3): δ = 106.5, 124.2, 126.9, 128.8, 129.0, 129.5, 130.9, 134.7, 138.5, 149.1 ppm.

4-Hexyl-1-(3-nitrophenyl)-1H-1, 2, 3-triazole (Table 3. Entry 8)

Yield: 92%, white solid, m.p. 96-97 °C.

FT-IR: ν_{max} (neat) = 3155, 2921, 1528, 1455, 1345, 1224, 1044, 1000, 886, 804, 735, 665 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 0.92 (s, 3H), 1.38-1.42 (m, 6H), 1.77-1.80 (m, 2H), 2.84-2.91 (m, 2H), 7.75-7.79 (m, 1H), 8.21-8.23 (m, 1H), 8.30-8.32 (m, 2H), 8.59 (s, 1H) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ = 13.5, 21.6, 28.2, 28.6, 32.2, 32.5, 105.3, 118.8, 124.5, 128.6, 128.8, 134.8, 135.9, 138.1 ppm.

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