Supplementary information

C12 aromatic triol-furoin and diol-furil from biobased 5-(hydroxymethyl)furfural: Enhanced selective synthesis, scale-up and mechanistic insight in cyclic catalysis

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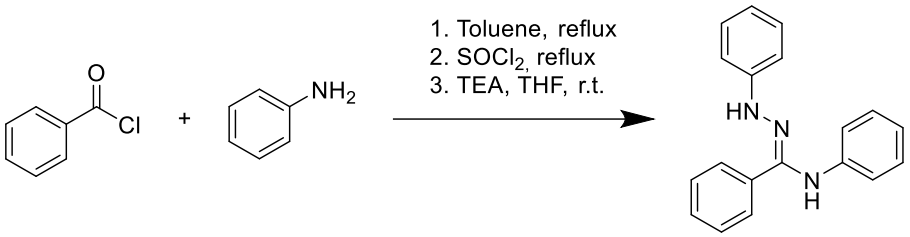
Contents

1. Experiment: Preparation of N-Heterocyclic Carbene (NHC) compound.

The NHC catalyst (TPA-OMe), 5-methoxy-1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazoline, was prepared as almost colorless to cream-colored crystals according to a modified method from a previous report.[1] The chemical structure was elucidated by 1H (400 MHz, Chloroform-d) and 13C NMR (101 MHz, Chloroform-d) (Figure S1).

*Synthesis of N-Phenylbenzamide phenylhydrazone (2)***:**

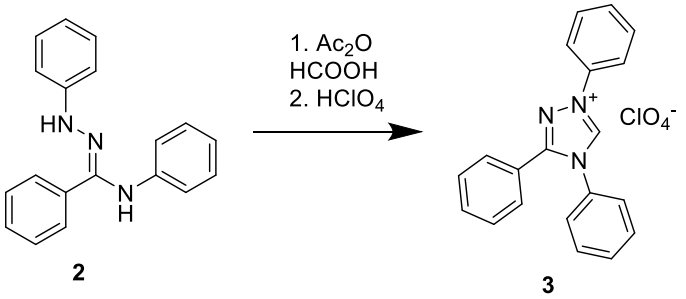


2

A 500 mL round-bottom, three-necked flask was equipped with a magnetic stir bar, thermometer, addition funnel, and a Dimroth reflux condenser. The flask was placed in an ice-water bath, and 35 g of benzoyl chloride followed by 250 mL of toluene were added. To this, 24 g of aniline were added over 30 minutes, keeping the temperature below 15°C. After the addition, the cooling bath was removed, and the reaction mixture was refluxed for 18 hours. During this time, the solids completely dissolved, and the mixture became clear. Next, 55 mL (89 g, density = 1.64 g/mL) of thionyl chloride were added, and refluxing was continued for another 20 hours. The solvent and volatiles were removed using a rotary evaporator under water aspirator vacuum, with the heating bath set to 90°C. The remaining solid was dissolved in 250 mL of tetrahydrofuran, and the solution was cooled in an ice-water bath. A mixture of 52 mL of triethylamine and 25 mL of phenylhydrazine was added dropwise while maintaining the reaction temperature below 30°C. After the addition was complete, the reaction mixture was stirred overnight at room temperature. The volatiles were removed by rotary evaporation (heating bath set to 60°C), and the remaining residue was mixed with 450 mL of 2% acetic

acid solution in water. The mixture was heated to 70-80°C for 1 hour, then cooled to 4°C. The resulting solid was filtered through a glass filter (porosity 3) and washed successively with cold water, ethanol, and MTBE. The product was dried at 40°C to a constant mass, yielding 36 g of a greenish-grey solid.

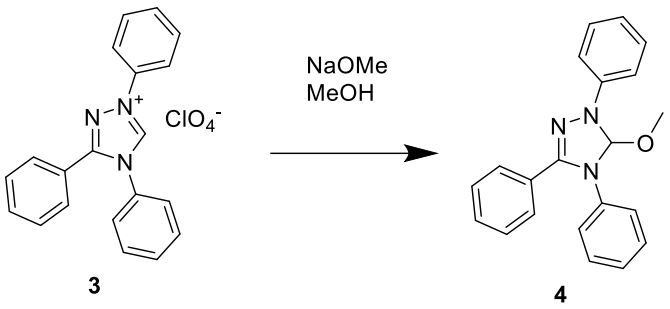
Synthesis of 1,3,4-Triphenyl-1,2,4-triazol-1-ium perchlorate (3):



2 3

A 1000 mL single-neck round-bottom flask was charged with 210 mL of acetic anhydride and 105 mL of 85% formic acid. The mixture was heated in a 60°C bath for 1 hour. Then, 36 g of compound 2 was added over 15 minutes, and the reaction mixture was stirred at room temperature for 24 hours. Volatiles were removed using a rotary evaporator with an 80°C heating bath. The water aspirator was then switched to an oil pump for more efficient removal of the remaining volatiles. Remaining brown oil (58 g) was treated with 250 ml 35% $HClO_4$. Formed solids were crushed with spatula, filtered and washed with water and cold methanol. Solid was recrystallized from methanol, filtered and dried in air. Yield: 37 g colorless solid. Melting point 208-218°C (literature m.p. 220°C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.38 (s, 1H), 8.11 (d, J = 7.9 Hz, 2H), 7.80 (t, *J* = 7.7 Hz, 2H), 7.71 (m, 6H), 7.64 (m, 1H), 7.55 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ 153.71, 143.64, 135.31, 132.78, 132.52, 131.99, 131.33, 130.88, 130.67, 129.76, 129.69, 127.03, 122.83, 121.09.

Synthesis of 5-Methoxy-1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazoline (4):



Compound 3 (200 g) was ground into a fine powder using a pestle and mortar and transferred into a 4000 mL round-bottom flask equipped with a mechanical stirrer and 3000 mL of methanol (MeOH). To this slurry, at room temperature, 200 mL of freshly prepared 30% sodium methoxide (NaOMe) in MeOH was added. The mixture was stirred at room temperature for 22 hours. It was then cooled to 4°C, filtered, and washed with cold MeOH. The resulting solid was recrystallized in 80 g portions using 700 mL of MeOH at 100°C in a pressurized bottle. The solution was chilled to 4°C, filtered, and washed with a small amount of cold MeOH. After air drying, 133 g of a cream/white solid was obtained. Melting point: 115-120°C.

2. ^{1}H- and ^{13}C-NMR spectrum of 5-methoxy-1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazoline

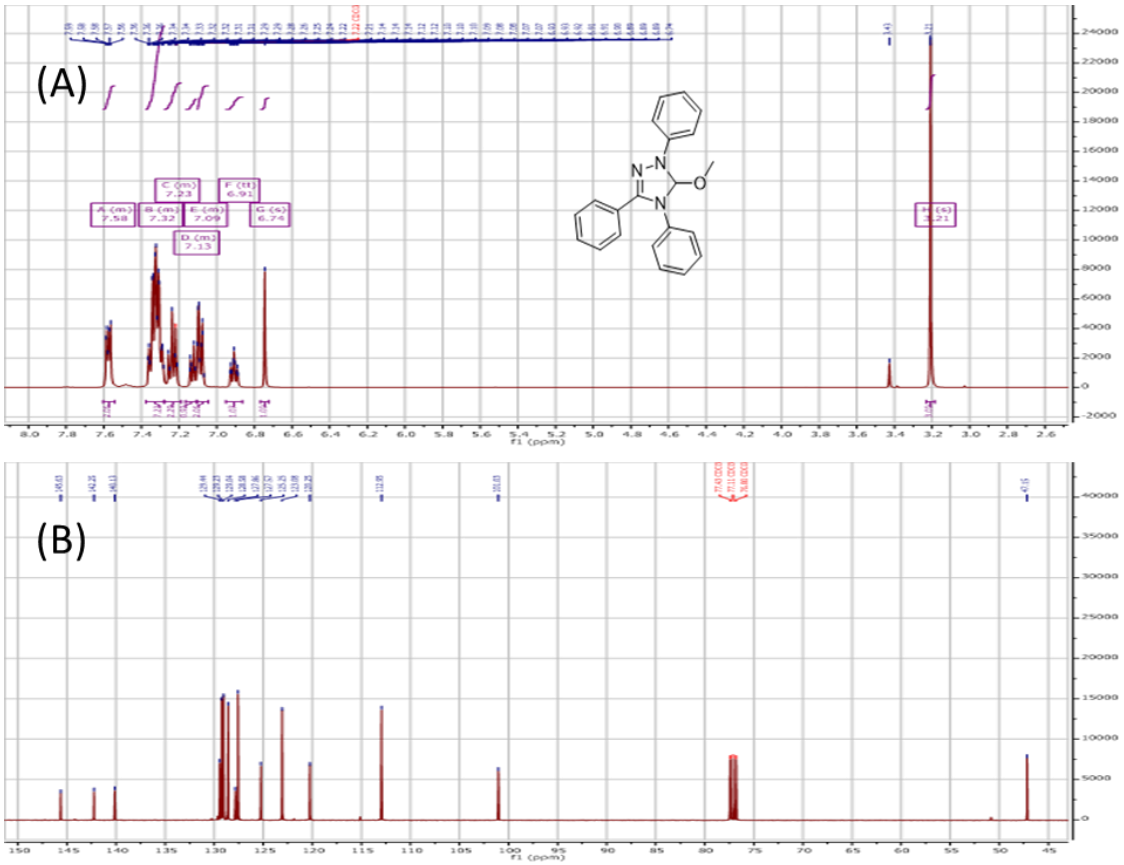


Figure S1. ^{1}H- and ^{13}C-NMR spectra of 5-methoxy-1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazoline. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.54 (m, 2H), 7.38 – 7.28 (m, 7H), 7.28 – 7.19 (m, 2H), 7.17 – 7.11 (m, 1H), 7.10 – 7.05 (m, 2H), 6.91 (tt, *J* = 6.9, 1.5 Hz, 1H), 6.74 (s, 1H), 3.21 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.63, 142.25, 140.13, 129.44, 129.23, 129.04, 128.58, 127.86, 127.57, 125.25, 123.08, 120.25, 112.95, 101.03, 47.15.

3. Proposed mechanism of 5-HMF carboligation

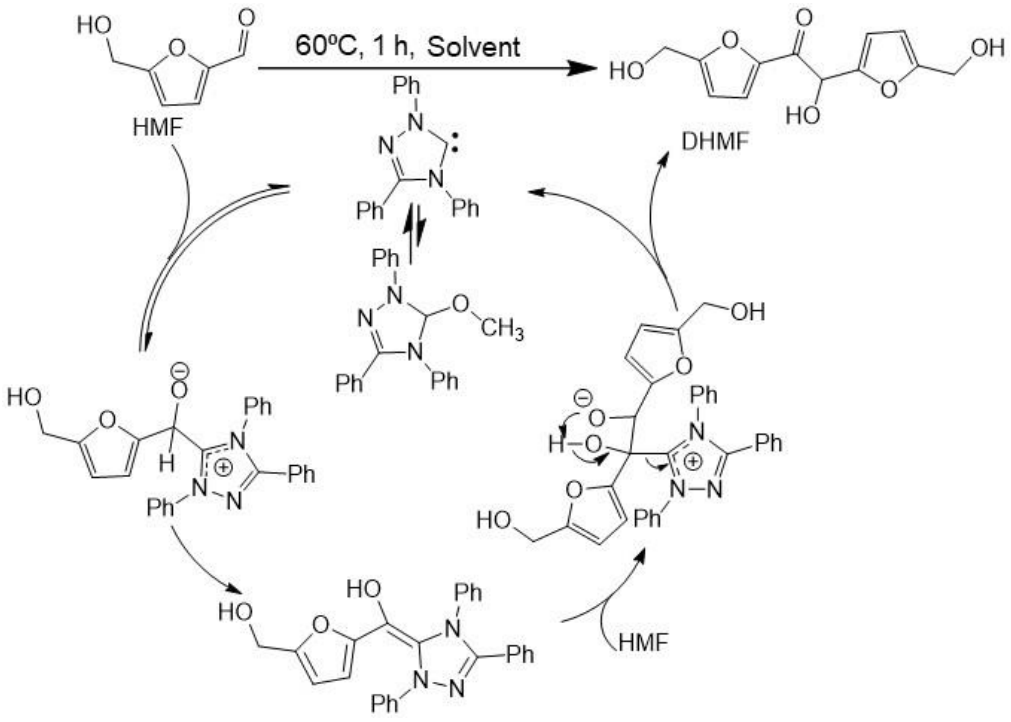


Figure S2. Possible mechanism of carboligation of 5-HMF to DHMF in THF by NHC catalyst (TPA-OMe). The mechanism was redrawn, considering the equilibrium between TPA-OMe and TPA, and reaction in solvent, from previous report based on the solvent free NHC-catalyzed self-condensation of HMF to DHMF and depicted umpolung catalytic cycle.[2]

4. ^{1}H-NMR spectrum of DHMF and BHMF

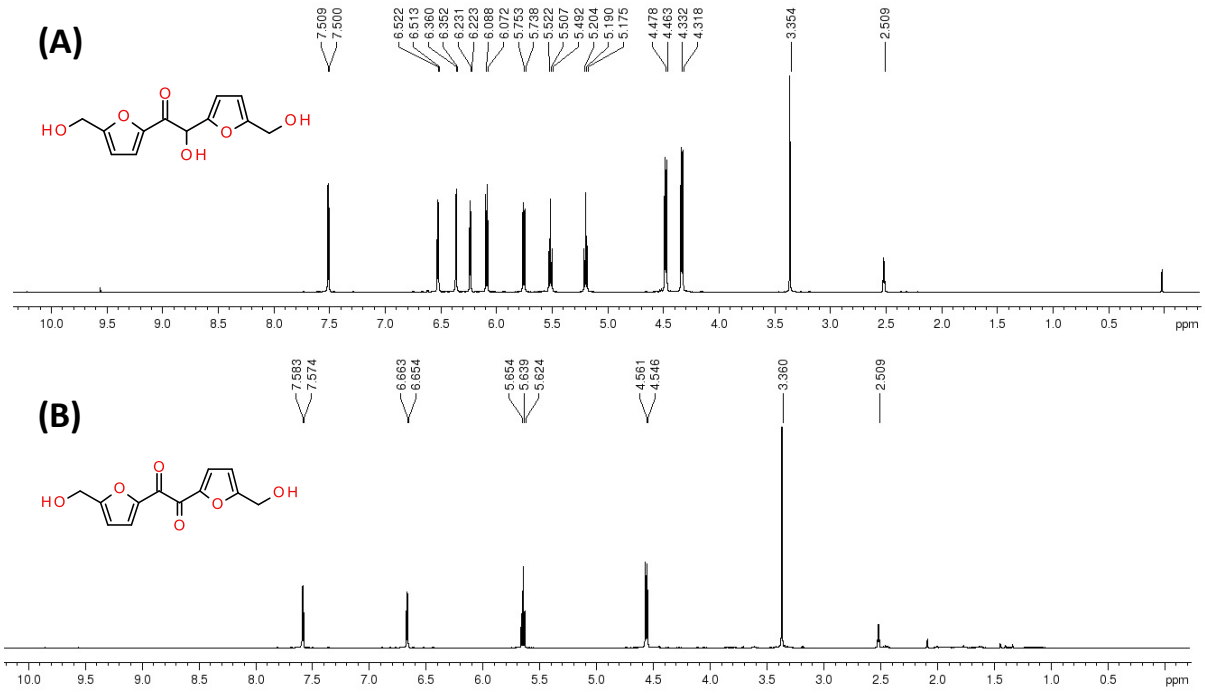


Figure S3. TLC results separated in ethyl acetate as a mobile phase on the selective oxidation of DHMF to BHMF at reaction time course by DBU.

References

1. Dieter Enders, Klaus Breuer, Ulrike Kallfass, Tim Balensiefer, "Preparation and Application of 1,3,4-Triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene, A Stable Carbene", Synthesis 2003(8): 1292-1295.
2. Zang, H. and Chen, E.Y., 2015. Organocatalytic upgrading of furfural and 5-hydroxymethyl furfural to C10 and C12 furoins with quantitative yield and atom-efficiency. *International Journal of Molecular Sciences*, *16*(4), pp.7143-7158.