Supporting Information

Synthesis of 1,2,3-triazoles in the presence of mixed Mg/Fe oxides and their evaluation as corrosion inhibitors of API 5L X70 steel submerged in HCl

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1. General methods

Commercially available reagents and solvents were used as received. Column chromatography was performed on Kiesel gel silica gel 60 (230-400 mesh). Melting points were determined using a Fisher-Johns apparatus and are uncorrected. The NMR spectra were obtained using Bruker Ascend-400 (400 MHz) spectrometer. Chemical shifts (δ) are given in ppm and coupling constants *J* are given in hertz (Hz). Microwave irradiation experiments were performed on a Discover System (CEM Corporation) single-mode microwave using standard sealed microwave glass vials. Simultaneous air jet cooling (3-4 bar) during microwave irradiation was performed by using a compressor. Powder X-ray diffraction (XRD) was performed using a Philips X'Pert Instrument with Cu-Kα radiation (45kV, 40 mA).

2. Experimental procedures

Synthesis of Mg-Fe (3:1) layered double hydroxide (LDH)

Mg-Fe layer double hydroxide were prepared by a standard co-precipitating procedure using two solutions. The first solution contained 25.6 g of $Mg(NO_3)_2$ and 12.1 g of $Fe(NO_3)_3$ on 45 mL of water. The second solution contained 14g of NaOH and 9.54 g of Na_2CO_3 on 70 mL of water. The firs solution is added to the second solution, while vigorously attiring for 4 hours at room temperature. The brown gel was heated at 60°C for 24 hours, the gel was washed with deionized water to pH 8. The solid was dried in an oven at 120°C for 18 hours.

Preparation of Mg(Fe)O mixed oxides

The calcined material was obtained by heating of as-synthesized LDH at 450°C in a tubular furnace under N_2 flow for 8 hours. 7 g of a black solid is stable in air, which was characterized by XRD, IR, nitrogen physisorption and scanning electron microscopy was obtained.

Characterization of Mg-Fe layered double hydroxide (LDH) and Mg(Fe)O mixed oxides

The as-synthesized LDH exhibited Mg-Fe reflections associated with the layered double hydroxide crystal structure. The maxima correspond to typical diffraction by planes (0 0 3), (0 0 6), (0 1 2), (0 1 5), (0 1 8), (1 1 0) and (1 1 3). These planes are similar to those shown by brucite (Figure S1). Calcining the material yields a

Mg(Fe)O mixed oxide with a periclase-like structure with (104) (018) and (113), plane reflections, which are typical of MgO (Figure S2).

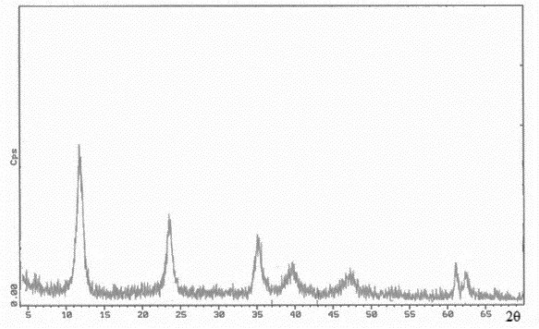


Figure S1. X-ray diffraction patterns of as-synthesized LDH

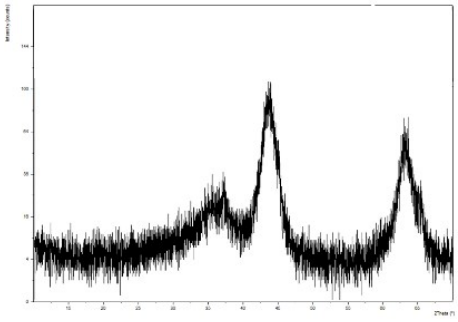


Figure S2. X-ray diffraction patterns of Mg(Fe)O mixed oxide

General procedure for the synthesis of 1,2,3-triazole 1a

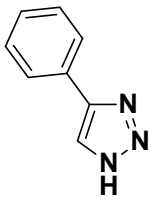
A mixture of catalyst (50 mg) and DMF (3 mL) was placed in a microwave tube having a magnetic stirrer. Subsequently, β-nitroestirene (1 mmol), NaN_3 (1.2 mmol), and sodium ascorbate (50 mg), were added to the mixture, which was heated under microwave irradiation (30 W, 80 °C) during 30 minutes. Then, the material was removed by centrifugation and washed with CH_2Cl_2 (5x5mL). The combined organic extracts were evaporated, giving the corresponding 1,2,3-triazole, which was purified by column chromatography (Hexanes-EtOAc 1:1) and/or recrystallization (CH_2Cl_2-hexanes, 1:2).

General procedure for the synthesis of 1,2,3-triazoles 1b-1h

A mixture of catalyst (50 mg) and EtOH-H_2O (2 mL, 3:1 *v/v*) was placed in a microwave tube having a magnetic stirrer. Subsequently, alkynes **2b**-**2h** (1 mmol), benzyl chloride **3** (1.2 mmol), NaN_3 (1.2 mmol), and sodium ascorbate (50 mg), were added to the mixture, which was heated under microwave irradiation (30 W, 80 °C) during 30 minutes. Then, the material was removed by centrifugation and washed with CH_2Cl_2 (5x5mL). The combined organic extracts were evaporated, giving the corresponding 1,2,3-triazole, which was purified by column chromatography (CH_2Cl_2 or hexanes-EtOAc 1:1) and/or recrystallization (CH_2Cl_2-hexanes, 1:2).

3. Characterization data

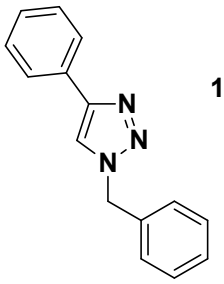
4-phenyl-1H-1,2,3-triazole (1a).



1a

White solid, yield 60%, mp = 149-151 °C [Lit.[1] mp = 147-148 °C].
NMR ^{1}H (DMSO-*d6*, 400 MHz): δ = 7.37 (s, 1 H), 7.47 (s, 2 H), 7.88 (d, *J* = 5.0 Hz, 2 H), 8.06-8.67 (m, 1 H), 15.16 (s, 1 H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ = 126.04 (2xArCH), 127.73 (ArCH), 128.59 (2xArCH), 129.39 (C_{ipso}), 130.99 (ArCH, triazole), 162.79 (C_{ipso}, triazole).[2]

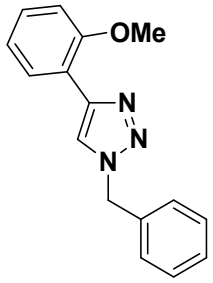
1-Benzyl-4-phenyl-1*H*-1,2,3-triazole (1b).



1b

White solid, yield 65%, mp = 129-131 °C [Lit.[3] mp = 127-130 °C].
NMR ^{1}H ($CDCl_3$, 400 MHz): δ = 5.56 (s, 2H, NCH_2), 7.28-7.32 (m, 3H, ArH), 7.35-7.41 (m, 5H, ArH), 7.65 (s, 1H, ArH, triazole), 7.77-7.80 (m, 2H, ArH); NMR ^{13}C ($CDCl_3$, 100 MHz): δ = 54.2 (NCH_2), 119.5 (ArCH, triazole), 125.7 (2xArCH), 128.1 (2xArCH), 128.2 (ArCH), 128.78 (ArCH), 128.8 (2xArCH), 129.1 (2xArCH), 130.6 (C_{ipso}), 134.7 (C_{ipso}), 148.2 (C_{ipso}, triazole).[4]

1-benzyl-4-(2-methoxyphenyl)-1H-1,2,3-triazole (1c).

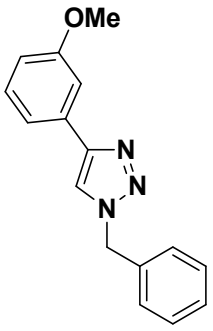


1c

White solid, yield 55%, mp = 165-167 °C [Lit.[5] mp = 167-169 °C].

NMR ^{1}H ($CDCl_3$, 400 MHz): δ = 3.89 (s, 3H, OCH_3), 5.61 (s, 2H, NCH_2), 6.97 (dd, *J* = 1.0, 8.3 Hz, 1H, ArH), 7.09 (td, *J* = 1.0, 7.6 Hz, 1H, ArH), 7.30-7.41 (m, 6H, ArH), 8.00 (s, 1H, ArH, triazole), 8.39 (dd, *J* = 1.7, 7.7 Hz, 1H, ArH); NMR ^{13}C ($CDCl_3$, 100 MHz): δ = 53.9 (NCH_2), 55.3 (OCH_3), 110.7 (ArCH, triazole), 119.4 (C_{ipso}), 121.0 (ArCH), 123.0 (ArCH), 127.7 (ArCH), 127.8 (2xArCH), 128.5 (ArCH), 128.9 (ArCH), 129.0 (2xArCH), 135.2 (C_{ipso}), 143.6 (C_{ipso}, triazole), 155.6 (C_{ipso}).[5]

1-benzyl-4-(3-methoxyphenyl)-1H-1,2,3-triazole (1d).

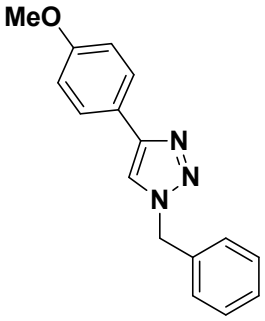


1d

White solid, yield 55%, mp = 158-160 °C

NMR ^{1}H ($CDCl_3$, 400 MHz): δ = 3.87 (s, 3H, OCH_3), 5.58 (s, 2H, NCH_2), 6.88 (ddd, *J* = 1.6, 2.6, 7.7 Hz, 1H, ArH), 7.29-7.35 (m, 4H, ArH), 7.38-7.43 (m, 3H, ArH), 7.45 (ddd, *J* = 0.4, 1.3, 2.6 Hz, 1H, ArH), 7.67 (s, 1H, ArH, triazole); NMR ^{13}C ($CDCl_3$, 100 MHz): δ = 54.2 (NCH_2), 55.3 (OCH_3), 110.7 (ArCH, triazole), 114.3 (ArCH), 118.1 (ArCH), 119.7 (ArCH), 128.0 (2xArCH), 128.7 (ArCH), 129.1 (2xArCH), 129.8 (ArCH), 131.8 (C_{ipso}), 134.6 (C_{ipso}), 148.1 (C_{ipso}, triazole), 160.0 (C_{ipso}).[6]

1-benzyl-4-(4-methoxyphenyl)-1H-1,2,3-triazole (1e).

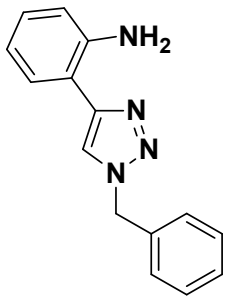


1e

White solid, yield 60%, mp = 144-145 °C [Lit.[7] mp = 143-144 °C].

NMR ^{1}H ($CDCl_3$, 400 MHz): δ = 3.84 (s, 3H, OCH_3), 5.57 (s, 2H, NCH_2), 6.95 (d, *J* = 8.9 Hz, 2H, ArH), 7.31-7.42 (m, 5H, ArH), 7.60 (s, 1H, ArH, triazole), 7.74 (d, *J* = 8.9 Hz, 2H, ArH); NMR ^{13}C ($CDCl_3$, 100 MHz): δ = 54.2 (NCH_2), 55.3 (OCH_3), 114.2 (ArCH, triazole), 118.7 (ArCH), 123.3 (C_{ipso}), 127.0 (2xArCH), 128.0 (2xArCH), 128.7 (2xArCH), 129.1 (2xArCH), 134.8 (C_{ipso}), 148.1 (C_{ipso}, triazole), 159.6 (C_{ipso}).[7]

2-(1-benzyl-1H-1,2,3-triazol-4-yl)aniline (3e).

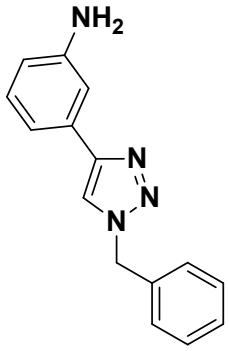


1f

Yelow solid, yield 50%, mp = 94-96 °C. [Lit.[8] mp = 97-98 °C].

NMR ^{1}H ($CDCl_3$, 400 MHz): δ = 5.50 (br s, 2H, NH_2), 5.55 (s, 2H, NCH_2), 6.62-6.76 (m, 2H, ArH), 7.08 (dd, *J* = 1.55, 8.04 Hz, 1H, ArH), 7.24-7.40 (m, 6H, ArH), 7.65 (s, 1H, ArH, triazole); NMR ^{13}C ($CDCl_3$, 100 MHz): δ = 54.3 (NCH_2), 113.5 (ArCH, triazole), 116.7 (ArCH), 117.2 (ArCH), 119.7 (ArCH), 127.6 (2xArCH), 128.0 (ArCH), 128.7 (2xArCH), 129.0 (ArCH), 129.1(C_{ipso}), 134.5 (C_{ipso}), 145.1 (C_{ipso}, triazole), 148.8 (C_{ipso}, NH_2).[8]

3-(1-benzyl-1H-1,2,3-triazol-4-yl)aniline (1g).

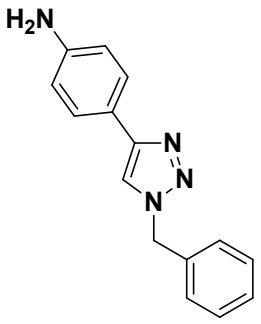


1g

Yelow solid, yield 50%, mp = 149.151 °C. [Lit.[8] mp = 145-147 °C].

NMR ^{1}H ($CDCl_3$, 400 MHz): δ = 3.74 (bs, 2H, NH_2), 5.55 (s, 2H, NCH_2), 6.62 (d, *J* = 6.0 Hz, 1H, ArH), 7.01-7.16 (m, 2H, ArH), 7.26-7.30 (m, 3H, ArH), 7.34 -7.38 (m, 3H, ArH), 7.60 (s, 1H, ArH, triazole); NMR ^{13}C ($CDCl_3$, 100 MHz): δ = 54.1 (NCH_2), 112.1 (ArCH, triazole), 114.8 (ArCH), 115.9 (ArCH), 119.5 (ArCH), 128.0 (2xArCH), 128.7 (ArCH), 128.9 (2xArCH), 129.7 (ArCH), 131.4 (C_{ipso}), 134.7 (C_{ipso}), 146.8 (C_{ipso}, triazole), 148.3(C_{ipso}, NH_2).[9]

4-(1-benzyl-1H-1,2,3-triazol-4-yl)aniline (1h).



1h

Yelow solid, yield 55%, mp = 161-163 °C. [Lit.[8] mp = 160-161 °C].

NMR ^{1}H ($CDCl_3$, 400 MHz): δ = 3.74 (bs, 2H, NH_2), 5.55 (s, 2H, NCH_2), 6.68-6.73 (m, 2H, ArH), 7.27-7.41 (m, 5H, ArH), 7.52 (s, 1H, ArH, triazole), 7.56-7.62 (m, 2H, ArH); NMR ^{13}C ($CDCl_3$, 100 MHz): δ = 54.1 (NCH_2), 115.2 (ArCH, triazole), 118.1 (2xArCH), 121.1 (ArCH), 126.1 (C_{ipso}), 126.9 (2xArCH), 128.0 (2xArCH), 128.7 (2xArCH), 129.1 (C_{ipso}), 134.9 (C_{ipso}, triazole), 146.5(C_{ipso}, NH_2).[10]

4. References

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