

Proceedings

Green Synthesis of Symmetric Dimaleamic Acids from Dianilines and Maleic Anhydride: Behind New Bidentate Ligands for MOFs [†]

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Abstract: We herein report the synthesis and characterization of six α,β -unsaturated dicarboxylic acid ligands with different phenyl spacers and two ligands with a biphenyl and anthraquinone spacers. All these dimaleamic acids were synthesized in 16 to 99% yields via a base-catalyzed maleimide ring opening in water (ligand **2**) or by a di-*N*-acylation from the corresponding diamines and maleic anhydride in acetic acid (ligands **4**, **6**, **8**, **10**, **12**, **14** and **16**). These reactions were performed using green solvents, while requiring minimal work up procedures, and making them suitable alternatives to access quickly to these types of bidentate ligands, which can be used to fabricate new MOFs.

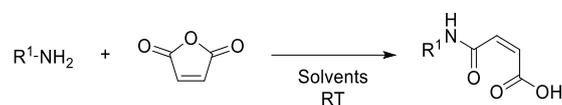
Keywords: MOFs; bidentate ligands; dicarboxylates; maleic anhydride; dimaleimides; dimaleamic acids; green chemistry

1. Introduction

Metal-Organic Frameworks (MOFs) are hybrid structures composed by the union, via coordination bonds, of metal ions or metal clusters to organic ligands with donor atoms, producing crystalline and often highly porous materials through a repetitive network that propagates into one, two or three dimensions [1]. Given that the amount of ligands and metal salts that can be combined for MOF synthesis is practically unlimited, MOFs can be tailored according to its intended use, and have therefore been used in several applications of economic, technological and environmental importance such as luminescence and sensing [2], electrochemistry [3], catalysis [4], gas capture, storage and separation [5] and biomedicine [6]. Most of the ligands used to construct MOFs are neutral or anionic. The drawback of using neutral ligands is the requirement of counter ions due to the positive charge generated by the formation of the coordination bond, while anionic ligands do not have this disadvantage because they bind metal atoms via a charge compensation [7]. Pyridine

and pyrazine are among the most common donor groups present on neutral ligands, while for the anionic ligands, carboxylates are the most common ones [8]. The carboxylate group can bind to the metal atom in a monodentate or bidentate manner, the latter of which produces the strongest binding. When bidentate binding occurs, it causes the in-situ formation of inorganic clusters called secondary building units (SBUs), which confer great rigidity to the framework being constructed and facilitates its self-assembly [9]. The spacers used in the ligand's backbone also play a key role in MOF synthesis; due to this, most ligands have bound or fused aromatic rings as central or extending units because their rigidity can benefit the crystal packing and arrangement, for instance, via π - π Stacking-type interactions [10].

The maleamic acid is a nitrogen-containing analog of maleic acid. The *N*-substituted maleamic acids are highly conjugated, and their use as polydentate ligands has been well documented with lanthanide ions such as La^{3+} [11], Eu^{3+} , Tb^{3+} and Yb^{3+} [12], and transition metals such as Cu^{2+} [13,14]. The most common method for the maleamic acid synthesis involves the reaction between a primary amine and maleic anhydride under mild reaction conditions (Scheme 1), in a wide variety of solvents, for instance, dichloromethane [15], diethyl ether [16], toluene [17], tetrahydrofuran [18] or xylene [19], which may pose health and environmental hazards.



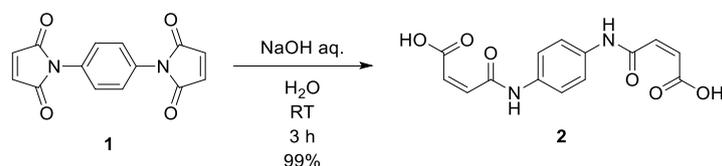
Scheme 1. General reaction scheme for the synthesis of maleamic acids.

The main objective of this work is to provide environmentally benign procedures for the synthesis of ligands that can be used to construct novel MOF structures. To do this, we present the synthesis and spectroscopic characterization of eight *bis*-maleamic acid ligands, the first of which (ligand **2**) was synthesized in water as solvent from a *bis*-maleimide, and the rest in acetic acid from the corresponding diamines and maleic anhydride. Also, ligands **12** and **16** have not been previously reported and their structure show that this procedure can be applicable to fabricate ligands with a more complex backbone.

2. Results and Discussion

2.1. Synthesis of (2*E*,2'*E*)-4,4'-(1,4-phenylenebis(azanediyl))bis(4-oxobut-2-enoic acid) (**2**)

For the synthesis of the ligand **2**, the *N,N'*-(1,4-phenylene)dimalimide **1** was reacted in an aqueous solution [0.1 M] of sodium hydroxide for 3 h to afford the target molecule (2*E*,2'*E*)-4,4'-(1,4-phenylenebis(azanediyl))bis(4-oxobut-2-enoic acid) in almost quantitative yield (99%) via a base-catalyzed maleimide ring opening reaction (Scheme 2). This methodology has been utilized to obtain maleamic acids [20–22], but, to the best of our knowledge, the hydrolysis of a *bis*-maleimide such as **1** to produce a *bis*-maleamic acid has not been reported yet.



Scheme 2. Synthesis of the ligand **2**.

The *bis*-carboxylic acid **2** was characterized by its physicochemical properties, as well as by spectroscopic techniques. The Figure 1 shows the ^1H spectrum of compound **2**. There is a broad singlet at 13.24 ppm, which is characteristic of the acidic protons from the carboxylic acid moiety, as well as a key singlet at 10.46 ppm, which corresponds to NH protons. There is also a singlet at 7.60

ppm corresponding to the four H atoms from the aromatic ring, and a couple of doublets at 6.47 and 6.31 ppm, respectively, which correspond to the alkene moiety.

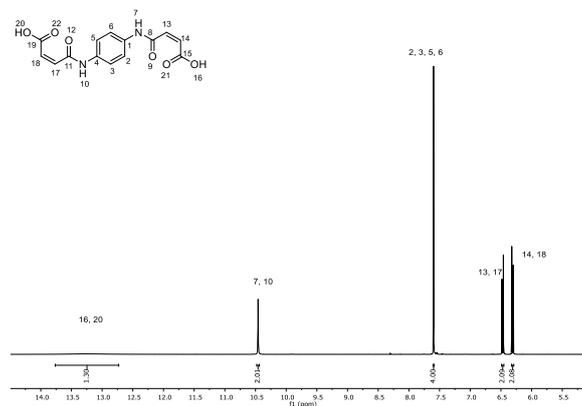
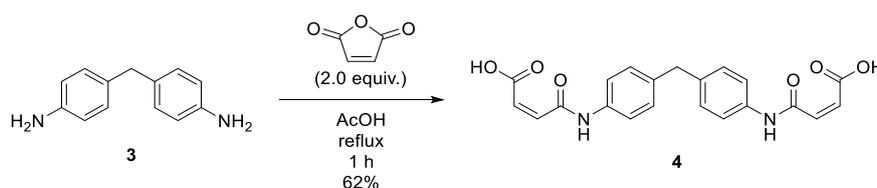


Figure 1. ¹H NMR spectrum of compound 2.

2.2. Synthesis of (2Z,2'Z)-4,4'-((methylenebis(4,1-phenylene))bis(azanediyl))bis(4-oxobut-2-enoic acid) (4)

4,4'-methylenedianiline (3) was reacted with a slight excess of maleic anhydride for one hour in acetic acid as solvent to generate the desired compound (2Z,2'Z)-4,4'-((methylenebis(4,1-phenylene))bis(azanediyl))bis(4-oxobut-2-enoic acid) (4) in 62% yield (Scheme 3).



Scheme 3. Synthesis of ligand 4.

Compound 4 was characterized by its spectroscopic properties. Figure 2a shows the ¹H NMR spectra of compound 4. The broad singlet corresponding to the carboxylic acid protons can be found at 13.07 ppm followed by the singlet attributed to the NH protons at 10.43 ppm. Next, there are two doublets at 7.54 and 7.17 ppm corresponding to the A²B² system of the aromatic rings, and finally another set of two doublets which correspond to the alkene protons. Figure 2b shows the ¹³C NMR spectrum. There are two key peaks at 166.7 and 163.1 ppm, respectively which correspond to both carbonyl carbons, as well as another peak at 40 ppm belonging to the methylene carbon.

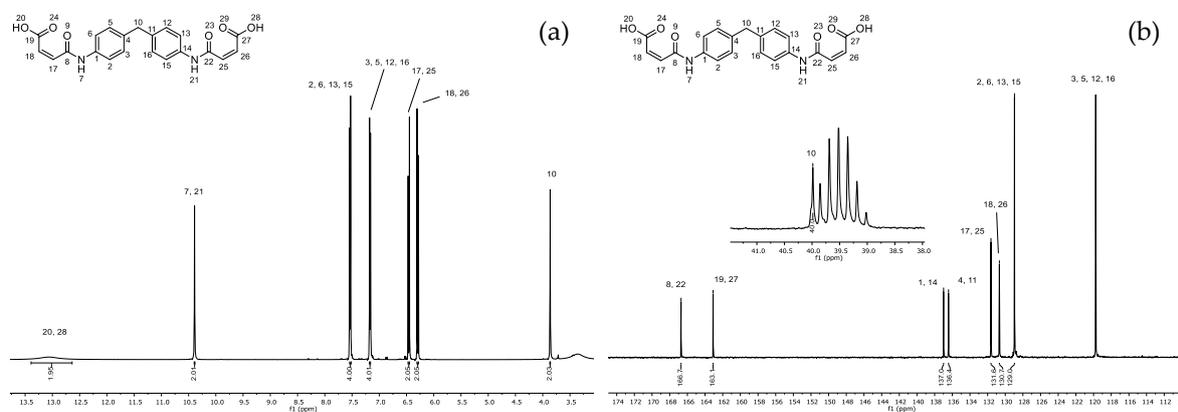
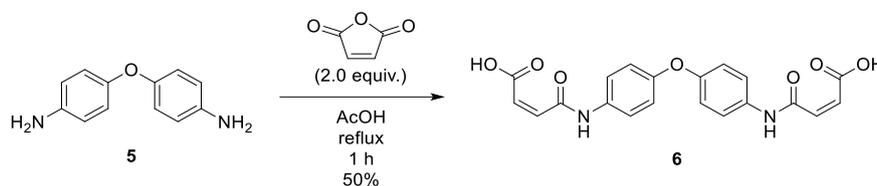


Figure 2. (a) ¹H NMR spectrum of ligand 4. (b) ¹³C NMR spectrum of ligand 4.

2.3. Synthesis of (2Z,2'Z)-4,4'-((oxybis(4,1-phenylene))bis(azanediyl))bis(4-oxobut-2-enoic acid) (6)

4,4'-oxydianiline (**5**) was reacted with 2 equivalents of maleic anhydride for one hour in acetic acid as solvent to generate the desired compound (2Z,2'Z)-4,4'-((oxybis(4,1-phenylene))bis(azanediyl))bis(4-oxobut-2-enoic acid) (**6**) via an *N*-acylation reaction, in 50% yield (Scheme 4).



Scheme 4. Synthesis of ligand **6**.

Table 6 was characterized by its spectroscopic properties. Figure 3a shows a the ¹H NMR spectra of compound **6**. There is a key broad singlet corresponding to the carboxylic acid protons at 13.12 ppm followed by the singlet attributed to the NH protons at 10.43 ppm. The set of two doublets at 7.62 and 6.98 ppm corresponding to the A²B² system of the aromatic rings, and finally another set of two doublets corresponding to the vinylic protons. The ¹³C NMR spectrum shows the expected 8 signals, with the key peaks at 166.6 and 163.0 ppm corresponding to both pairs of carbonyl carbons (Figure 3b).

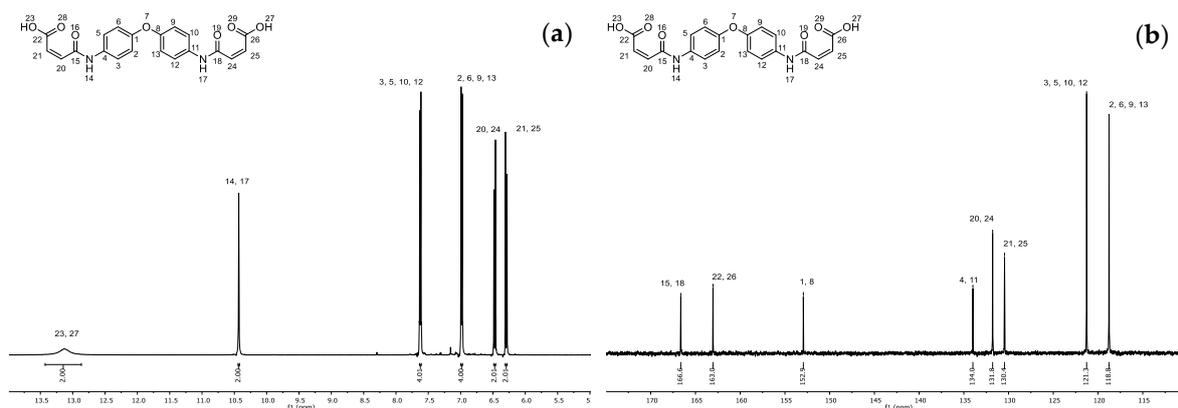
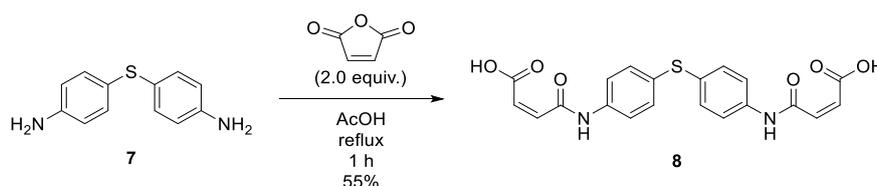


Figure 3. (a) ¹H NMR spectrum of ligand **6**. (b) ¹³C NMR spectrum of ligand **6**.

2.4. Synthesis of (2Z,2'Z)-4,4'-((thiobis(4,1-phenylene))bis(azanediyl))bis(4-oxobut-2-enoic acid) (8)

4,4'-thiodianiline (**7**) reacted with 2 equivalents of maleic anhydride for one hour in acetic acid as solvent furnishing the desired compound (2Z,2'Z)-4,4'-((thiobis(4,1-phenylene))bis(azanediyl))bis(4-oxobut-2-enoic acid) (**8**) via an *N*-acylation reaction, in 55% yield (Scheme 5).



Scheme 5. Synthesis of ligand **8**.

The ligand **8** was characterized by spectroscopic techniques. Figure 4a shows the ¹H NMR spectrum, which shows the key broad singlet at 12.97 ppm that belongs to the carboxylic acid protons

and another singlet for the NH protons at 10.47 ppm. There are two sets of two doublets, the first at 7.63 and 7.29 ppm corresponding to the A²B² system of the aromatic rings, and the following set belongs to the alkene protons. Figure 4b shows the ¹³C NMR spectrum, which shows the expected 8 signals, the two key peaks being at 166.8 and 163.3 ppm and correspond to the carbonyl carbons.

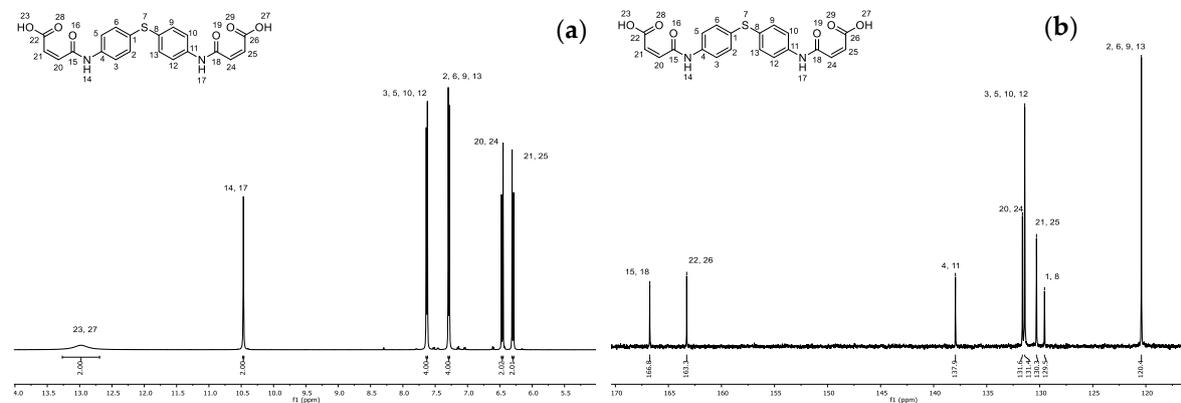
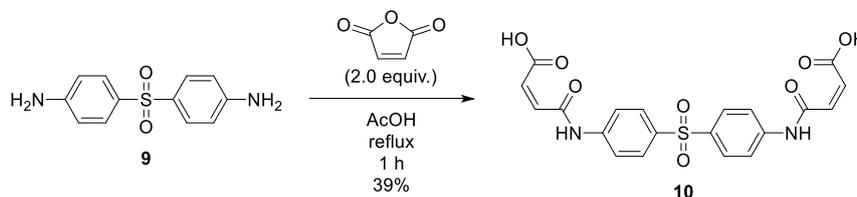


Figure 4. (a) ¹H NMR spectrum of ligand 6. (b) ¹³C NMR spectrum of ligand 8.

2.5. Synthesis of (2Z,2'Z)-4,4'-((sulfonylbis(4,1-phenylene))bis(azanediy))bis(4-oxobut-2-enoic acid) (10)

The 4,4'-sulfonyldianiline (9) reacted with 2 equivalents of maleic anhydride for one hour in acetic acid as solvent furnishing the target compound (2Z,2'Z)-4,4'-((sulfonylbis(4,1-phenylene))bis(azanediy))bis(4-oxobut-2-enoic acid) (10) via an *N*-acylation reaction, in 39% yield (Scheme 6).



Scheme 6. Synthesis of compound 10.

Thus, the ligand 10 was characterized by spectroscopic techniques. Figure 5a shows the ¹H NMR spectrum, which shows the key broad singlet at 12.86 ppm that corresponds to the carboxylic acid protons and another singlet for the NH protons at 10.68 ppm. Two sets of two doublets, the first at 7.88 and 7.82 ppm corresponds to the A²B² system of the aromatic rings, and the following set belongs to the alkene protons. Figure 5b shows the ¹³C NMR spectrum which shows the expected 8 signals, the two key peaks being at 166.8 and 163.8 ppm, and correspond to the carbonyl carbons.

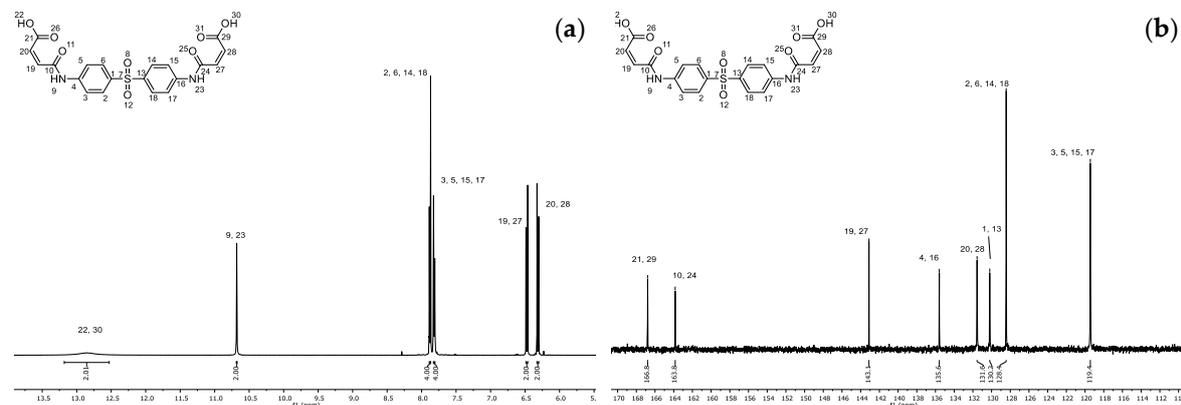
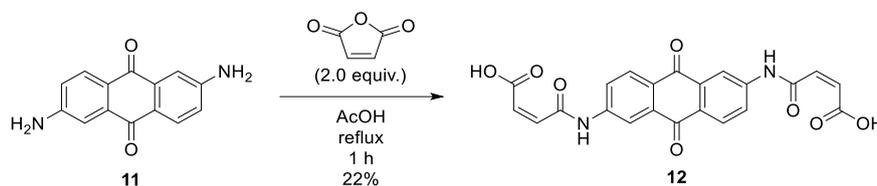


Figure 5. (a) ¹H NMR spectrum of ligand 10. (b) ¹³C NMR spectrum of ligand 10.

2.6. Synthesis of (2Z,2'Z)-4,4'-((9,10-dioxo-9,10-dihydroanthracene-2,6-diyl)bis(azanediyl))bis(4-oxobut-2-enoic acid) (12)

2,6-diaminoanthracene-9,10-dione (**11**) reacted with 2 equivalents of maleic anhydride for one hour in acetic acid as solvent furnishing the target compound (2Z,2'Z)-4,4'-((9,10-dioxo-9,10-dihydroanthracene-2,6-diyl)bis(azanediyl))bis(4-oxobut-2-enoic acid) (**12**) via an *N*-acylation reaction, in 22% yield (Scheme 7).



Scheme 7. Synthesis of ligand **12**.

The ligand **12** was characterized by spectroscopic techniques. Figure 6a shows the ^1H NMR spectrum, which shows the key broad singlet at 12.88 ppm that corresponds to the carboxylic acid protons, and another singlet for the NH protons at 10.93 ppm. Three doublets at 8.47, 8.17 and 8.07 ppm correspond to the trisubstituted phenyl rings and two doublets of the alkene protons. Figure 6b shows the ^{13}C NMR spectrum, which shows the expected 11 signals, the two key peaks being at 166.9 and 164.0 ppm correspond to the carbonyl from the amide and carboxylic acid, and another peak at 181.2 ppm, which accounts for both carbonyls of the anthraquinone core.

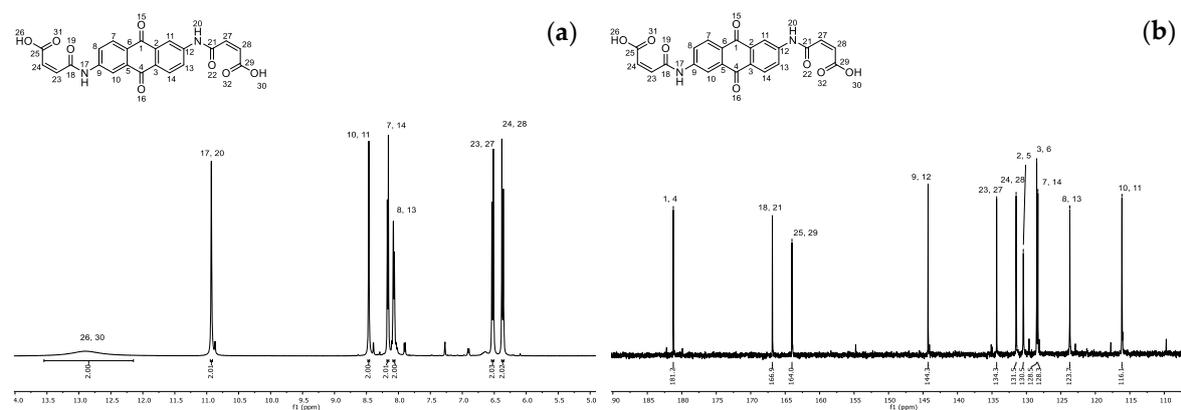
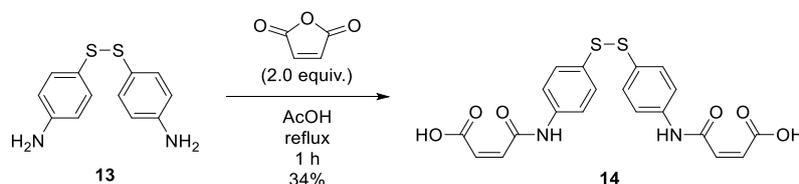


Figure 6. (a) ^1H NMR spectrum of ligand **12**. (b) ^{13}C NMR spectrum of ligand **12**.

2.7. Synthesis of (2Z,2'Z)-4,4'-((disulfanediyldis(4,1-phenylene))bis(azanediyl))bis(4-oxobut-2-enoic acid) (14)

For the synthesis of ligand **14**, 4,4'-disulfanediyldianiline (**13**) was reacted with 2 equivalents of maleic anhydride for one hour in acetic acid as solvent furnishing the target compound (2Z,2'Z)-4,4'-((disulfanediyldis(4,1-phenylene))bis(azanediyl))bis(4-oxobut-2-enoic acid) (**14**) via an *N*-acylation reaction, in 34% yield (Scheme 8).



Scheme 8. Synthesis of ligand disulfane bridged **14**.

The ligand **14** was characterized by spectroscopic techniques. Figure 7a shows the ^1H NMR spectrum which shows the key broad singlet at 12.94 ppm that corresponds to the carboxylic acid protons and another singlet for the NH protons at 10.50 ppm. The two doublets corresponding to the A^2B^2 system of the phenyl rings are present at 7.64 and 7.47 ppm followed by the two doublets of the alkene protons at 6.46 and 6.30 ppm. Figure 7b shows the ^{13}C NMR spectrum which shows the expected 7 signals, the two key peaks being at 166.8 and 163.3 ppm corresponding to the carbonyl carbons.

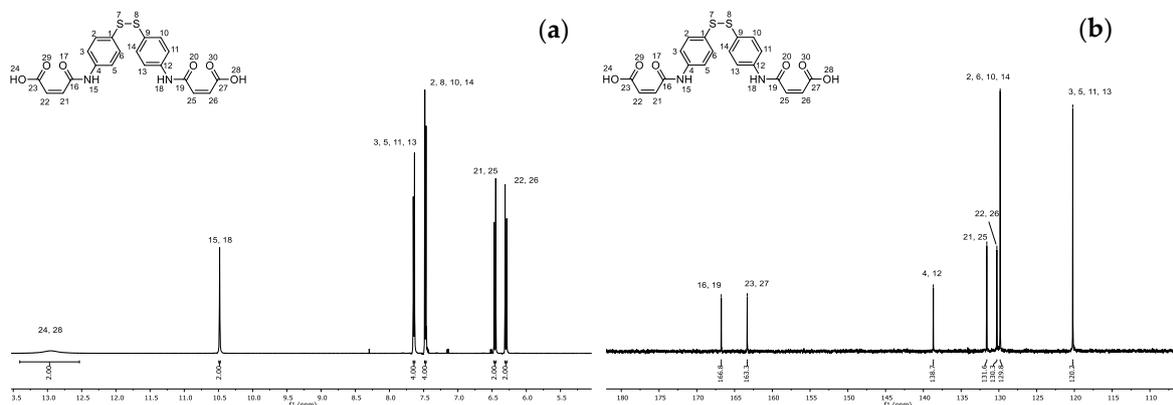
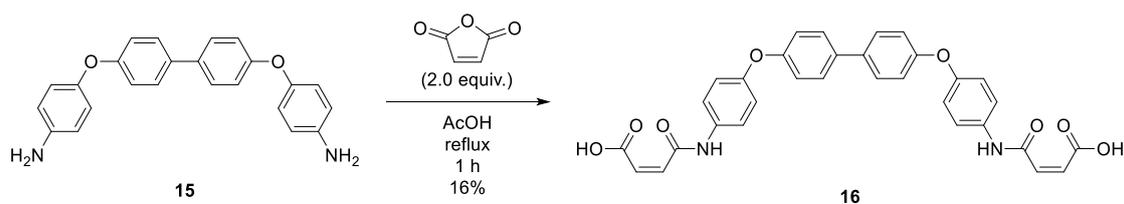


Figure 7. (a) ^1H NMR spectrum of disulfane bridged ligand **14**. (b) ^{13}C NMR spectrum of disulfane bridged ligand **14**.

2.8. Synthesis of (2Z,2'Z)-4,4'-(((1,1'-biphenyl]-4,4'-diylbis(oxy))bis(4,1-phenylene))bis(azanediyl))bis(4-oxobut-2-enoic acid) (**16**)

For the synthesis of ligand **16**, 4,4'-([1,1'-biphenyl]-4,4'-diylbis(oxy))dianiline (**15**) was reacted with 2 equivalents of maleic anhydride for one hour in acetic acid as solvent furnishing the target compound (2Z,2'Z)-4,4'-(((1,1'-biphenyl]-4,4'-diylbis(oxy))bis(4,1-phenylene))bis(azanediyl))bis(4-oxobut-2-enoic acid) via an *N*-acylation reaction, in 16% yield (Scheme 9)



Scheme 9. Synthesis of ligand **16**.

The ligand **16** was characterized by spectroscopic techniques. Figure 8a shows the ^1H NMR spectrum which shows the key broad singlet at 13.13 ppm that corresponds to the carboxylic acid protons and another singlet for the NH protons at 10.46 ppm. In this case, there are two sets of two doublets that correspond to both non-equivalent (anisochrone) A^2B^2 system of the four *p*-substituted phenyl rings at 7.66, 7.63, 7.06 and 7.05 ppm followed by the two doublets of the alkene protons at 6.48 and 6.31 ppm. Figure 8b shows the ^{13}C NMR spectrum, which shows 11 signals, the two key peaks being at 166.7 and 163.1 ppm correspond to carbonyl carbons.

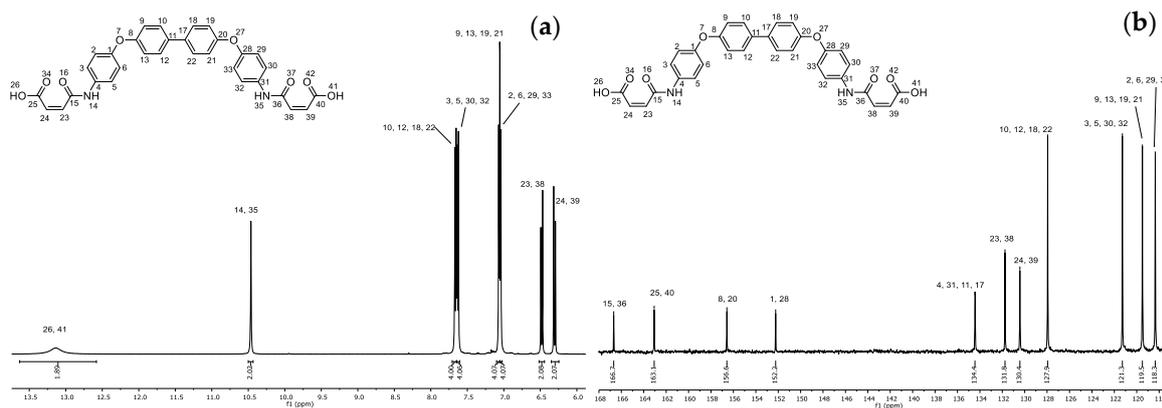


Figure 8. (a) ¹H NMR spectrum of ligand 16. (b) ¹³C NMR spectrum of ligand 16.

3. Conclusions

The ligand **2** was synthesized via a base catalyzed *bis*-maleimide ring opening in water in near quantitative yield (>99%). Ligands **4**, **6**, **8**, **10**, **12**, **14** and **16** were synthesized via a reaction between the corresponding diamines and maleic anhydride in acetic acid as solvent in good to moderate yields (16–62%). Furthermore, ligands **12** and **16** have not been previously reported. The described processes use green solvents, mild reaction conditions, and a minimal work-up procedure, which makes them attractive alternatives for the synthesis of ligands with potential application for fabricating new MOFs.

4. Experimental Section

4.1. General Information, Instrumentation and Chemicals

¹H and ¹³C NMR spectra were acquired on a Bruker Advance III (500 MHz) spectrometer. The solvent was deuterated dimethyl sulfoxide (*d*⁶-DMSO). Chemical shifts are reported in parts per million (/ppm). The internal reference for NMR spectra is with respect to tetramethyl silane (TMS) at 0.0 ppm. Coupling constants are reported in Hertz (J/Hz). Multiplicities of the signals are reported using the standard abbreviations: singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). NMR data were treated using the MestReNova software (12.0.0–20080). Reaction progress was monitored by thin layer chromatography (TLC) on precoated kieselgel 60 F254 plates and the spots were visualized under UV light (254 or 365 nm). Structural drawings were created using the ChemDraw professional software (15.0.0.106). All starting materials were purchased from Sigma-Aldrich and were used without further purification nor dehydration. The solvents were distilled and dried according to standard procedures.

4.2. Synthesis of (2*E*,2'*E*)-4,4'-(1,4-phenylenebis(azanediyl))bis(4-oxobut-2-enoic acid) (**2**)

In a 50 mL round-bottomed flask were added 0.27 g (1.0 equiv.) of 1,1'-(1,4-phenylene)bis(1*H*-pyrrole-2,5-dione) (**1**) into 20 mL of distilled water to obtain a turbid solution. Then, an aqueous solution of sodium hydroxide (10 mL, 0.5 M) was poured slowly into the mixture avoiding surpassing a pH of 12, at room temperature. After 3 h of stirring, a yellow solution was obtained. It was acidified with [3 M] HCl until a pH of 2 was reached. This prompted a yellow precipitate to appear which was collected by filtration, washed with distilled water, and dried at room temperature to afford 0.30 g of a yellow powder in 99% yield. ¹H NMR (500 MHz, *d*⁶-DMSO): δ 13.24 (s, 2H, H-16, H-20), 10.46 (s, 2H, H-7, H-10), 7.60 (s, 4H, H-2, H-3, H-5, H-6), 6.47 (d, *J* = 12.1 Hz, 2H, H-13, H-17), 6.31 (d, *J* = 12.1 Hz, 2H, H-14, H-18).

4.3. Synthesis of (2Z,2'Z)-4,4'-((methylenebis(4,1-phenylene))bis(azanediyl))bis(4-oxobut-2-enoic acid) (4)

In a 50 mL two-neck round-bottomed flask, a mixture of 0.20 g (2.0 equiv.) of maleic anhydride and 5 mL of acetic acid were heated until reflux. To this mixture, a solution of 0.20 g (1.0 equiv.) of 4,4'-methylenedianiline in 5 mL of acetic acid was added dropwise. After the addition was completed, the mixture was kept at reflux until a precipitate was formed. The solution was let to cool at RT and 30 mL of water were added, the product was filtered and washed with a 8:2 water:ethanol mixture and was let to dry affording 0.24 g of a white powder in 62% yield. ¹H NMR (500 MHz, *d*⁶-DMSO): δ 13.07 (s, 2H, H-20, H-28), 10.39 (s, 2H, H-7, H-21), 7.54 (d, *J* = 8.6 Hz, 4H, H-2, H-6, H-13, H-15), 7.17 (d, *J* = 8.5 Hz, 4H, H-3, H-5, H-12, H-16), 6.46 (d, *J* = 12.1 Hz, 2H, H-17, H-25), 6.29 (d, *J* = 12.1 Hz, 2H, H-18, H-26), 3.86 (s, 1H, H-10); ¹³C NMR (126 MHz, *d*⁶-DMSO): δ 166.7 (C-8, C-22), 163.1 (C-19, C-27), 137.0 (C-1, C-14), 136.4 (C-4, C-11), 131.6 (C-17, C-25), 130.7 (C-18, C-26), 129.0 (C-2, C-6, C-13, C-15), 119.8 (C-3, C-5, C-12, C-16), 40.0 (C-10).

4.4. Synthesis of (2Z,2'Z)-4,4'-((oxybis(4,1-phenylene))bis(azanediyl))bis(4-oxobut-2-enoic acid) (6)

In a 50 mL two-neck round-bottomed flask, a mixture of 0.20 g (2.0 equiv.) of maleic anhydride and 5 mL of acetic acid were heated until reflux. To this mixture, a solution of 0.20 g (1.0 equiv.) of 4,4'-oxydianiline in 5 mL of acetic acid was added dropwise. After the addition was completed, the mixture was kept at reflux until a precipitate was formed. The solution was let to cool at RT and 30 mL of water were added, the product was filtered and washed with a 8:2 water:ethanol mixture and was let to dry affording 0.20 g of a white powder in 50% yield. ¹H NMR (500 MHz, *d*⁶-DMSO): δ 13.12 (s, 2H, H-23, H-27), 10.43 (s, 2H, H-14, H-17), 7.62 (d, *J* = 9.0 Hz, 4H, H-3, H-5, H-10, H-12), 6.98 (d, *J* = 9.0 Hz, 4H, H-2, H-6, H-9, H-13), 6.47 (d, *J* = 12.1 Hz, 2H, H-20, H-24), 6.29 (d, *J* = 12.1 Hz, 2H, H-21, H-25); ¹³C NMR (126 MHz, *d*⁶-DMSO) δ 166.6 (C-15, C-18), 163.0 (C-22, C-26), 152.9 (C-1, C-8), 134.0 (C-4, C-11), 131.8 (C-20, C-24), 130.5 (C-21, C-25), 121.3 (C-3, C-5, C-10, C-12), 118.8 (C-2, C-6, C-9, C-13).

4.5. Synthesis of (2Z,2'Z)-4,4'-((thiobis(4,1-phenylene))bis(azanediyl))bis(4-oxobut-2-enoic acid) (8)

In a 50 mL two-neck round-bottomed flask, a mixture of 0.20 g (2.0 equiv.) of maleic anhydride and 5 mL of acetic acid were heated until reflux. To this mixture, a solution of 0.22 g (1.0 equiv.) of 4,4'-thiodianiline in 5 mL of acetic acid was added dropwise. After the addition was completed, the mixture was kept at reflux until a precipitate was formed. The solution was let to cool at RT and 30 mL of water were added, the product was filtered and washed with a 8:2 water:ethanol mixture and was let to dry affording 0.23 g of a grey powder in 55% yield. ¹H NMR (500 MHz, *d*⁶-DMSO): δ 12.97 (s, 2H, H-23, H-27), 10.47 (2H, H-14, H-17), 7.63 (d, *J* = 8.7 Hz, 4H, H-3, H-5, H-10, H-12), 7.29 (d, *J* = 8.7 Hz, 4H, H-2, H-6, H-9, H-13), 6.46 (d, *J* = 12.0 Hz, 2H, H-20, H-24), 6.30 (d, *J* = 12.0 Hz, 2H, H-21, H-25); ¹³C NMR (126 MHz, *d*⁶-DMSO): δ 166.8 (C-15, C-18), 163.3 (C-22, C-26), 138.0 (C-4, C-11), 131.6 (C-20, C-24), 131.4 (C-3, C-5, C-10, C-12), 130.3 (C-21, C-25), 129.6 (C-1, C-8), 120.4 (C-2, C-6, C-9, C-13).

4.6. Synthesis of (2Z,2'Z)-4,4'-((sulfonylbis(4,1-phenylene))bis(azanediyl))bis(4-oxobut-2-enoic acid) (10)

In a 50 mL two-neck round-bottomed flask, a mixture of 0.20 g (2.0 equiv.) of maleic anhydride and 5 mL of acetic acid were heated until reflux. To this mixture, a solution of 0.25 g (1.0 equiv.) of 4,4'-sulfonyldianiline in 5 mL of acetic acid was added dropwise. After the addition was completed, the mixture was kept at reflux until a precipitate was formed. The solution was let to cool at RT and 30 mL of water were added, the product was filtered and washed with a 8:2 water:ethanol mixture and was let to dry affording 0.17 g of a white powder in 39% yield. ¹H NMR (500 MHz, *d*⁶-DMSO): δ 12.86 (s, 2H, H-22, H-30), 10.68 (s, 2H, H-9, H-23), 7.88 (d, *J* = 9.0 Hz, 4H, H-2, H-6, H-14, H-18), 7.82 (d, *J* = 9.0 Hz, 4H, H-3, H-5, H-15, H-17), 6.47 (d, *J* = 12.0 Hz, 2H, H-19, H-27), 6.31 (d, *J* = 12.0 Hz, 2H, H-20, H-28); ¹³C NMR (126 MHz, *d*⁶-DMSO): δ 166.8 (C-21, C-29), 163.8 (C-10, C-24), 143.1 (C-19, C-27), 135.6 (C-4, C-16), 131.6 (C-20, C-28), 130.2 (C-1, C-13), 128.4 (C-2, C-6, C-14, C-18), 119.4 (C-3, C-5, C-15, C-17).

4.7. Synthesis of (2Z,2'Z)-4,4'-((9,10-dioxo-9,10-dihydroanthracene-2,6-diyl)bis(azanediyl))bis(4-oxobut-2-enoic acid) (12)

In a 50 mL two-neck round-bottomed flask, a mixture of 0.20 g (2.0 equiv.) of maleic anhydride and 5 mL of acetic acid were heated until reflux. To this mixture, a solution of 0.24 g (1.0 equiv.) of 2,6-diaminoanthracene-9,10-dione in 5 mL of acetic acid was added dropwise. After the addition was completed, the mixture was kept at reflux until a precipitate was formed. The solution was let to cool at RT and 30 mL of water were added, the product was filtered and washed with a 8:2 water:ethanol mixture and was let to dry affording 0.01 g of a red powder in 22% yield. ¹H NMR (500 MHz, *d*⁶-DMSO): δ 12.88 (s, 2H, H-26, H-30), 10.93 (s, 2H, H-17, H-20), 8.47 (d, *J* = 2.4 Hz, 2H, H-10, H-11) 8.17 (d, *J* = 8.5 Hz, 2H, H-7, H-14), 8.07 (dd, *J* = 8.6, 2.3 Hz, 2H, H-8, H-13), 6.53 (d, *J* = 12.0 Hz, 2H, H-23, H-27), 6.37 (d, *J* = 11.9 Hz, 2H, H-24, H-28); ¹³C NMR (126 MHz, *d*⁶-DMSO): δ 181.2 (C-1, C-4), 166.9 (C-18, C-21), 164.0 (C-25, C-29), 144.3 (C-9, C-12), 134.3 (C-23, C-27), 131.5 (C-24, C-28), 130.5 (C-2, C-5), 128.5 (C-3, C-6), 128.3 (C-7, C-14), 123.7 (C-8, C-13), 116.1 (C-10, C-11).

4.8. Synthesis of (2Z,2'Z)-4,4'-((disulfanediylbis(4,1-phenylene))bis(azanediyl))bis(4-oxobut-2-enoic acid) (14)

In a 50 mL two-neck round-bottomed flask, a mixture of 0.20 g (2.0 equiv.) of maleic anhydride and 5 mL of acetic acid were heated until reflux. To this mixture, a solution of 0.25 g (1.0 equiv.) of 4,4'-disulfanediyl dianiline in 5 mL of acetic acid was added dropwise. After the addition was completed, the mixture was kept at reflux until a precipitate was formed. The solution was let to cool at RT and 30 mL of water were added, the product was filtered and washed with a 8:2 water:ethanol mixture and was let to dry affording 0.15 g of a grey powder in 34% yield. ¹H NMR (500 MHz, *d*⁶-DMSO): δ 12.94 (s, 2H, H-24, H-28), 10.48 (s, 2H, H-15, H-18), 7.64 (d, *J* = 8.8 Hz, 4H, H-3, H-5, H-11, H-13), 7.47 (d, *J* = 8.9 Hz, 4H, H-2, H-8, H-10, H-14), 6.46 (d, *J* = 12.1 Hz, 2H, H-21, H-25), 6.30 (d, *J* = 12.0 Hz, 2H, H-22, H-26); ¹³C NMR (126 MHz, *d*⁶-DMSO): δ 166.8 (C-16, C-19), 163.3 (C-23, C-27), 138.7 (C-4, C-12), 131.6 (C-21, C-25), 130.3 (C-22, C-26), 129.8 (C-2, C-6, C-10, C-14), 120.2 (C-3, C-5, C-11, C-13).

4.9. Synthesis of (2Z,2'Z)-4,4'-(((1,1'-biphenyl)-4,4'-diylbis(oxy))bis(4,1-phenylene))bis(azanediyl))bis(4-oxobut-2-enoic acid) (16)

In a 50 mL two-neck round-bottomed flask, a mixture of 0.20 g (2.0 equiv.) of maleic anhydride and 5 mL of acetic acid were heated until reflux. To this mixture, a solution of 0.37 g (1.0 equiv.) of 4,4'-((1,1'-biphenyl)-4,4'-diylbis(oxy))dianiline in 5 mL of acetic acid was added dropwise. After the addition was completed, the mixture was kept at reflux until a precipitate was formed. The solution was let to cool at RT and 30 mL of water were added, the product was filtered and washed with a 8:2 water:ethanol mixture and was let to dry affording 0.09 g of a white powder in 16% yield. ¹H NMR (500 MHz, *d*⁶-DMSO): δ 13.13 (s, 2H, H-26, H-41), 10.46 (s, 2H, H-14, H-35), 7.66 (d, *J* = 9.0 Hz, 4H, H-10, H-12, H-18, H-22), 7.63 (d, *J* = 8.7 Hz, 4H, H-3, H-5, H-30, H-32), 7.06 (d, *J* = 7.3 Hz, 4H, H-9, H-13, H-19, H-21), 7.05 (d, *J* = 6.9 Hz, 4H, H-2, H-6, H-29, H-33), 6.48 (d, *J* = 12.1 Hz, 2H, H-23, H-38), 6.31 (d, *J* = 12.0 Hz, 2H, H-24, H-39); ¹³C NMR (126 MHz, *d*⁶-DMSO) δ 166.7 (C-15, C-36), 163.1 (C-25, C-40), 156.6 (C-8, C-20), 152.2 (C-1, C-28), 134.4 (C-4, C-31, C-11, C-17), 131.8 (C-23, C-38), 130.4 (C-24, C-39), 128.0 (C-10, C-12, C-18, C-22), 121.3 (C-3, C-5, C-30, C-32), 119.5 (C-9, C-13, C-19, C-21), 118.4 (C-2, C-6, C-29, C-33).

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