Supplementary Information

A rapid metal free synthesis of 5-substituted-1H-tetrazoles using cuttlebone as a natural high effective and low cost heterogeneous catalyst

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Experimental

General

The purity determinations of the products were accomplished by TLC on silica gel polygram STL G/UV 254 plates. The melting points of products were determined with an Electrothermal Type 9100 melting point apparatus. The FT-IR spectra were recorded on an Avatar 370 FT-IR Therma Nicolet spectrometer. The NMR spectra were provided on Brucker Avance 100 and 400 MHz instruments in acetone-\(d_6\), DMSO-\(d_6\) and CD\(_3\)CN. Elemental analyses were performed using a Thermo Finnegan Flash EA 1112 Series instrument. Mass spectra were recorded with Agilent Technologies (HP) 5973 Network Mass Selective Detector, Shimadzu GC-MS-QP5050 and a CH7A Varianmat Bremem instruments at 70 eV. Elemental compositions were determined with a Leo 1450 VP scanning electron microscope equipped with an SC7620 energy dispersive spectrometer (SEM-EDS) presenting a 133 eV resolution at 20 kV. All of the products were known compounds and characterized by the FT-IR spectroscopy and comparison of their melting points with known compounds. The structure of selected products was further confirmed by \(^1\)H NMR, \(^{13}\)C NMR spectroscopy, and mass spectrometry. Cuttlebone was taken out from cuttlefish \((\textit{Sepia esculenta})\), which is commonly found in the seaboard of Persian Gulf in Iran.
Figure 1: FT-IR spectrum of cuttlebone (*Sepia esculenta*).

Figure 2: FT-IR spectrum of extracted β-chitin from cuttlebone.
Figure 3: FT-IR spectrum of 6th recovered cuttlebone.

Figure 4: SEM image of cuttlebone.
Figure 5: SEM image of finely powdered cuttlebone.

Figure 6: EDS of finely powdered cuttlebone
Figure 7: $^1$H NMR (400 MHz, DMSO-$d_6$) of 5-Phenyl-$1H$-tetrazole (Table 2, entry 1).

Figure 8: $^{13}$C NMR (100 MHz, DMSO-$d_6$) of 5-Phenyl-$1H$-tetrazole (Table 2, entry 1).
9: $^{13}$C NMR (100 MHz, DMSO-$d_6$) of 5-Phenyl-$1H$-tetrazole (Table 2, entry 1) expanded.

Figure 10: FT-IR (KBr) of 5-Phenyl-$1H$-tetrazole (Table 2, entry 1).
Figure 11: $^1$H NMR (100 MHz, DMSO-$d_6$) of 5-(4-Boromophenyl)-1H-tetrazole (Table 2, entry 2).

Figure 12: FT-IR (KBr) of 5-(4-Boromophenyl)-1H-tetrazole (Table 2, entry 2).
Figure 13: Mass spectrum of 5-(4-Boromophenyl)-1H-tetrazole (Table 2, entry 2).

Figure 14: $^1$H NMR (400 MHz, DMSO-$d_6$) of 5-(4-Chlorophenyl)-1H-tetrazole (Table 2, entry 3).
Figure 15: $^{13}$C NMR (100 MHz, DMSO-$d_6$) of 5-(4-Chlorophenyl)-1H-tetrazole (Table 2, entry 3).

Figure 16: FT-IR (KBr) of 5-(4-Chlorophenyl)-1H-tetrazole (Table 2, entry 3).
Figure 17: $^1$H NMR (100 MHz, CD$_3$CN) of 4-(1$H$-tetrazol-5-yl)benzonitrile (Table 2, entry 4).

Figure 18: $^{13}$C NMR (100 MHz, DMSO-$d_6$) of 4-(1$H$-tetrazol-5-yl)benzonitrile (Table 2, entry 4).
Figure 19: FT-IR (KBr) of 4-(1H-tetrazol-5-yl)benzonitrile (Table 2, entry 4).

Figure 20: Mass spectrum of 4-(1H-tetrazol-5-yl)benzonitrile (Table 2, entry 4).
Figure 21: $^1$H NMR (400 MHz, DMSO-$d_6$) of 5-(4-Nitrophenyl)-1$H$-tetrazole (Table 2, entry 5).

Figure 22: $^1$H NMR (400 MHz, DMSO-$d_6$) of 5-(4-Nitrophenyl)-1$H$-tetrazole (Table 2, entry 5) expanded.
Figure 23: $^{13}$C NMR (100 MHz, DMSO-$d_6$) of 5-(4-Nitrophenyl)-1H-tetrazole (Table 2, entry 5).

Figure 24: FT-IR (KBr) of 5-(4-Nitrophenyl)-1H-tetrazole (Table 2, entry 5).
Figure 25: $^1$H NMR (400 MHz, DMSO-$d_6$) of 4-Nitro-2-(1H-tetrazol-5-yl)benzenamine (Table 2, entry 6).

Figure 26: $^1$H NMR (400 MHz, DMSO-$d_6$) of 4-Nitro-2-(1H-tetrazol-5-yl)benzenamine (Table 2, entry 6) expanded.
Figure 27: $^{13}$C NMR (100 MHz, DMSO-$d_6$) of 4-Nitro-2-(1H-tetrazol-5-yl)benzenamine (Table 2, entry 6).

Figure 28: $^{13}$C NMR (100 MHz, DMSO-$d_6$) of 4-Nitro-2-(1H-tetrazol-5-yl)benzenamine (Table 2, entry 6) expanded.
Figure 29: FT-IR (KBr) of 4-Nitro-2-(1H-tetrazol-5-yl)benzenamine (Table 2, entry 6).

Figure 30: $^1$H NMR (100 MHz, acetone-$d_6$) of 5-(4-Ethoxyphenyl)-1H-tetrazole (Table 2, entry 7).
Figure 31: FT-IR (KBr) of 5-(4-Ethoxyphenyl)-1H-tetrazole (Table 2, entry 7).

Figure 32: $^1$H NMR (400 MHz, DMSO-$d_6$) of 5-(3, 5-Dimethoxyphenyl)-1H-tetrazole (Table 2, entry 8).
Figure 33: $^{13}$C NMR (100 MHz, DMSO-$d_6$) of 5-(3,5-Dimethoxyphenyl)-1H-tetrazole (Table 2, entry 8).

Figure 34: FT-IR (KBr) of 5-(3,5-Dimethoxyphenyl)-1H-tetrazole (Table 2, entry 8).
Figure 35: Mass spectrum of 5-(3, 5-Dimethoxyphenyl)-1H-tetrazole (Table 2, entry 8).

Figure 36: $^1$H NMR (100 MHz, CD$_3$CN) of 5-$m$-Tolyl-1H-tetrazole (Table 2, entry 9).
Figure 37: FT-IR (KBr) of 5-\textit{m}-Tolyl-1\textit{H}-tetrazole (Table 2, entry 9).

Figure 38: $^1$H NMR (400 MHz, DMSO-$d_6$) of 4-(1\textit{H}-tetrazol-5-yl) phenol (Table 2, entry 10).
Figure 39: $^1$H NMR (400 MHz, DMSO-$d_6$) of 4-(1H-tetrazol-5-yl)phenol (Table 2, entry 10) expanded.

Figure 40: $^{13}$C NMR (100 MHz, DMSO-$d_6$) of 4-(1H-tetrazol-5-yl) phenol (Table 2, entry 10).
Figure 41: FT-IR (KBr) of 4-(1H-tetrazol-5-yl) phenol (Table 2, entry 10).

Figure 42: FT-IR (KBr) of 2-(1H-tetrazol-5-yl)phenol (Table 2, entry 11).
**Figure 43:** Mass spectrum of 2-(1H-tetrazol-5-yl)phenol (Table 2, entry 11).

**Figure 44:** $^1$H NMR (100 MHz, DMSO-$d_6$) of 5-(Phenanthren-9-yl)-1H-tetrazole (Table 2, entry 12).
Figure 45: FT-IR (KBr) of 5-(Phenanthren-9-yl)-1H-tetrazole (Table 2, entry 12).

Figure 46: Mass spectrum of 5-(Phenanthren-9-yl)-1H-tetrazole (Table 2, entry 12).
Figure 47: $^1$H NMR (100 MHz, CD$_3$CN) of 5-(Thiophen-2-yl)-1$H$-tetrazole (Table 2, entry 13).

Figure 48: FT-IR (KBr) of 5-(Thiophen-2-yl)-1$H$-tetrazole (Table 2, entry 13).
Figure 49: Mass spectrum of 5-(Thiophen-2-yl)-1H-tetrazole (Table 2, entry 13).

Figure 50: FT-IR (KBr) of 4-(1H-tetrazol-5-yl) pyridine (Table 2, entry 14).
Figure 51: $^1$H NMR (400 MHz, DMSO-$d_6$) of 2-(1H-tetrazol-5-yl)pyridine (Table 2, entry 15).

Figure 52: $^{13}$C NMR (100 MHz, DMSO-$d_6$) of 2-(1H-tetrazol-5-yl) pyridine (Table 2, entry 15).
Figure 53: FT-IR of 2-(1H-tetrazol-5-yl) pyridine (Table 2, entry 15).

Figure 54: FT-IR of 5-Isobutyl-1H-tetrazole (Table 2, entry 16).
Figure 55: $^1$H NMR (100 MHz, CDCl$_3$) of 5-Isopentyl-1$H$-tetrazole (Table 2, entry 17).

Figure 56: FT-IR of 5-Isopentyl-1$H$-tetrazole (Table 2, entry 17).
**Figure 57:** $^1$H NMR (100 MHz, CD$_3$CN) of 5-Benzyl-1H-tetrazole (Table 2, entry 18).

**Figure 58:** FT-IR of 5-Benzyl-1H-tetrazole (Table 2, entry 18).