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Electronic supplementary information

The azide-alkyne cycloaddition catalysed by transition metal oxide nanoparticles

Giorgio Molteni, Anna M. Ferretti, Mario Italo Trioni, Fausto Cargnoni, Alessandro Ponti

Summary

General remarks

Melting points were determined on a Büchi apparatus in open tubes and are uncorrected. FTIR spectra were recorded on a Thermo Nicolet NEXUS 670 FTIR or a Perkin Elmer 1725 X spectrophotometer. Mass spectra were determined on a VG-70EQ apparatus.^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were taken with a Bruker AMX 300 instrument (in $CDCl_3$ solutions at room temperature unless otherwise stated). Chemical shifts are given as parts per million from tetramethylsilane. Coupling constants (*J*) values are given in hertz and are quoted to ±0.1 Hz consistently with NMR equipment accuracy. Transmission electron microscopy (TEM) images were collected using a Zeiss LIBRA 200FE microscope. The TEM specimens were prepared by evaporating in air a drop of diluted NP dispersion on a carbon coated copper grid. The size distribution of the NPs was obtained by analyzing TEM images by the software Pebbles.[1] The M:Fe atomic ratio of MFe_2O_4 NPs (M = Mn, Co) was obtained by analyzing electron energy loss spectra (EELS) by a home-built software based on Egerton's SIGMAL3.[2] The iron concentration of the ferrite nanoparticle dispersions was measured by a spectrophotometric method using tiron as an iron complexing agent.[3] The manganese concentration of the dispersions of MnO and MnS nanoparticles was measured as described below.

All reagents were used as supplied from chemical sources as appropriate. Solvents were dried and stored over 4Å molecular sieves prior to use. Reagent chemicals were purchased from Aldrich Chemical Company Ltd. Concentrated HNO_3 and HCl used for nanoparticle digestion were Aldrich Trace Select reagents.

Compounds **4a**,[4] **5a**,[4] **4b**,[5] **5b**,[5] **4c**[6] and **5c**[7] are known in the literature.

1 S. Mondini, A. M. Ferretti, A. Puglisi, A. Ponti, *Nanoscale*, **2012**, *4*, 5356-5372. Pebbles is freely available from the authors, http://pebbles.istm.cnr.it

2 R. F. Egerton, *Electron Energy-Loss Spectroscopy in the Electron Microscope*, 3rd ed., Springer, Heidelberg, **2011**.

3 S. Mondini, M. Leonzino, C. Drago, A. M. Ferretti, S. Usseglio, D. Maggioni, P. Tornese, B. Chini, A. Ponti, *Langmuir*, **2015**, *31*, 7381-7390.

4 A. M. Ferretti, A. Ponti, G. Molteni, *Tetrahedron Lett.*, **2015**, *56*, 5727-5730.

5 T. Farooq, L. K. Sydnes, K. W. Törnroos, B. E. Haug, Synthesis, **2012**, 2070 – 2078.

6 R. Huisgen, L. Möbius, G. Szeimies, *Chem. Ber*., **1965**, *98*, 4014 – 4021.

7 C. Wentrup, V. V. Ramana Rao, W. Frank, B. E. Fulloon, D. W. Moloney, T. Mosandl, *J. Org. Chem.*, **1999**, *64*, 3608 – 3611.

Wide field TEM images

Figure S1. Wide field TEM images of as-synthesized (a-e) and used (f) nanoparticles. a) Fe_3O_4; b) $CoFe_2O_4$; c) $MnFe_2O_4$; d) MnO; e) α-MnS; f) Fe_3O_4 after 5 runs.

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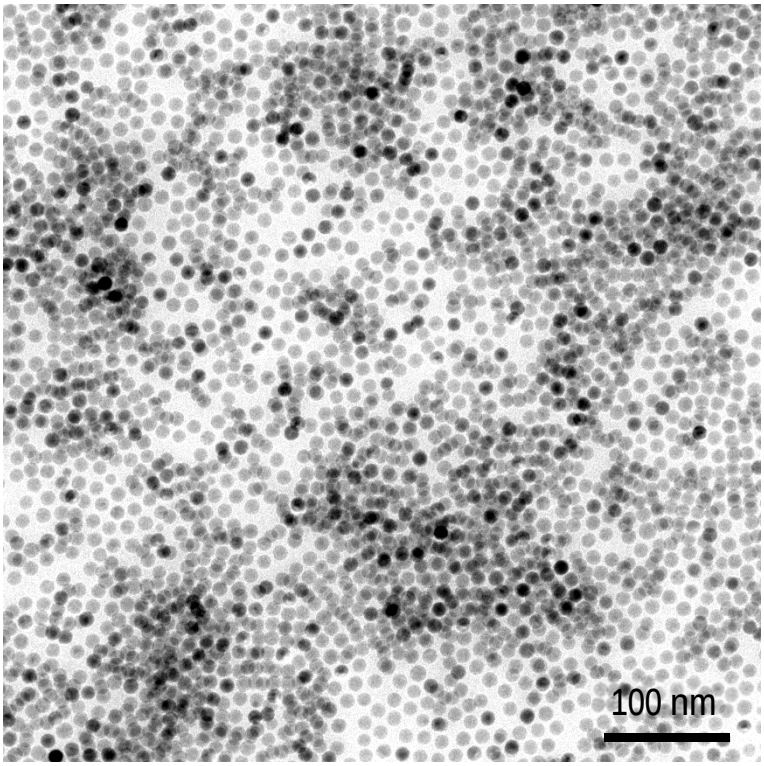

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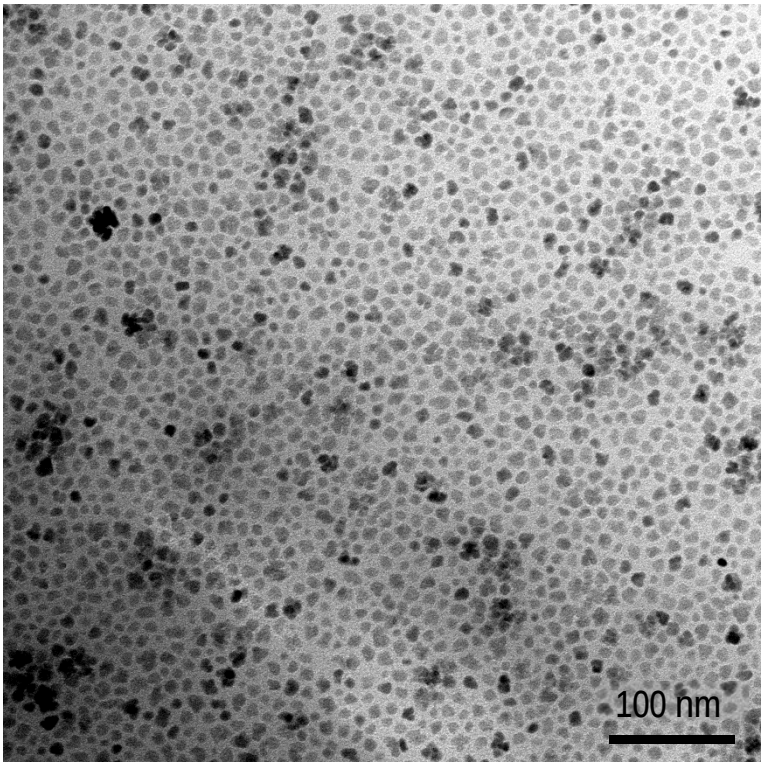

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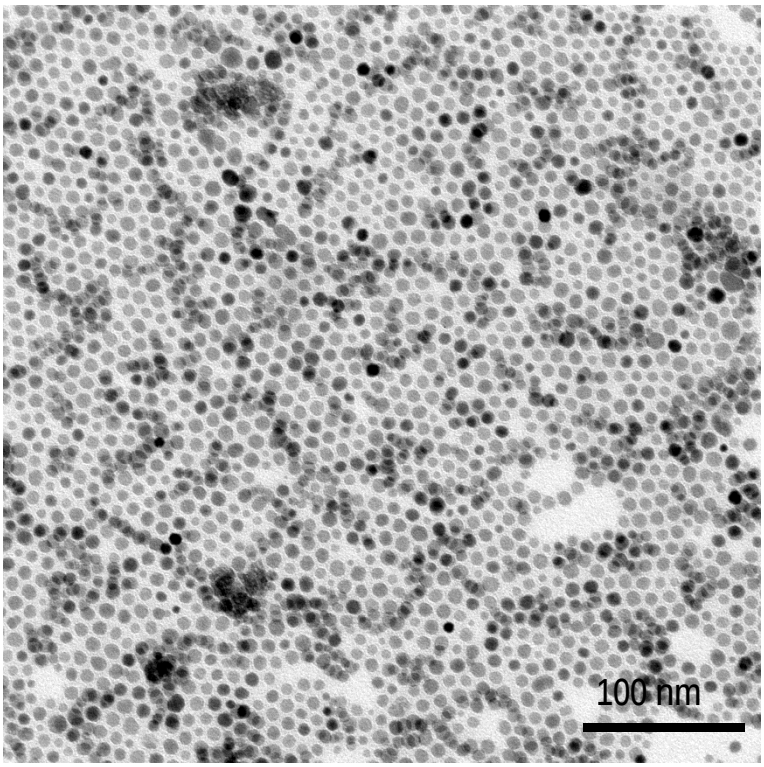

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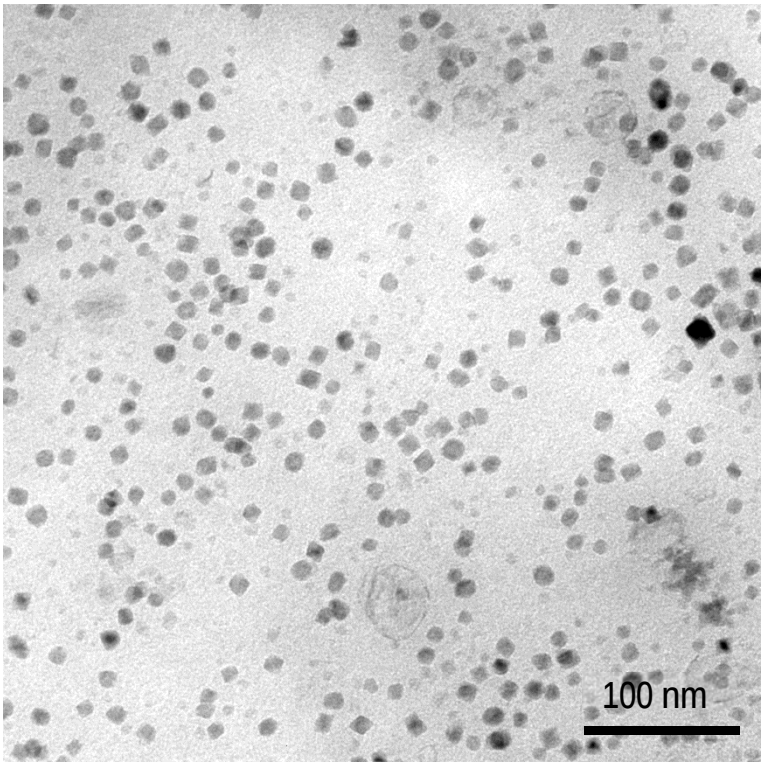

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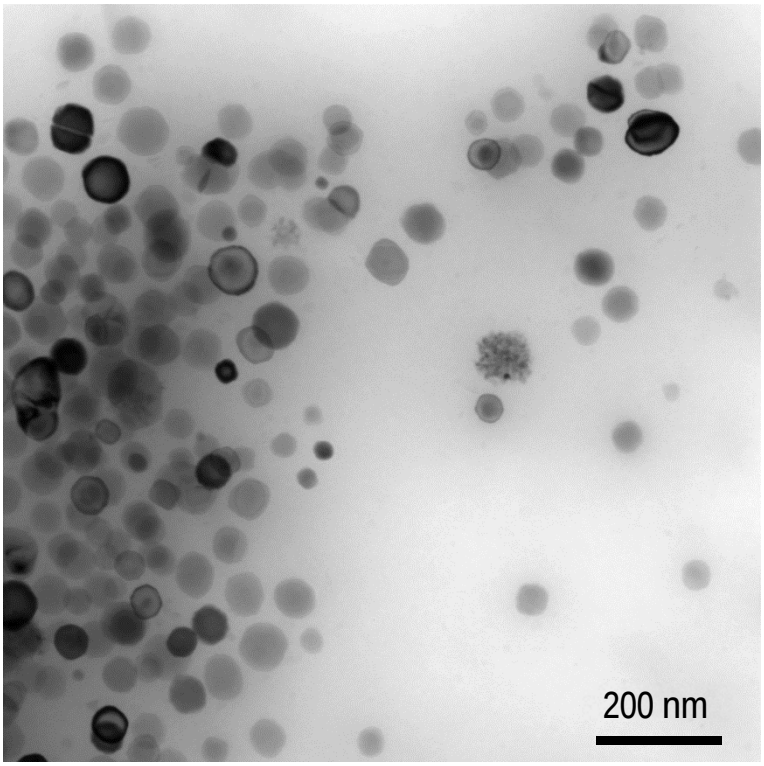

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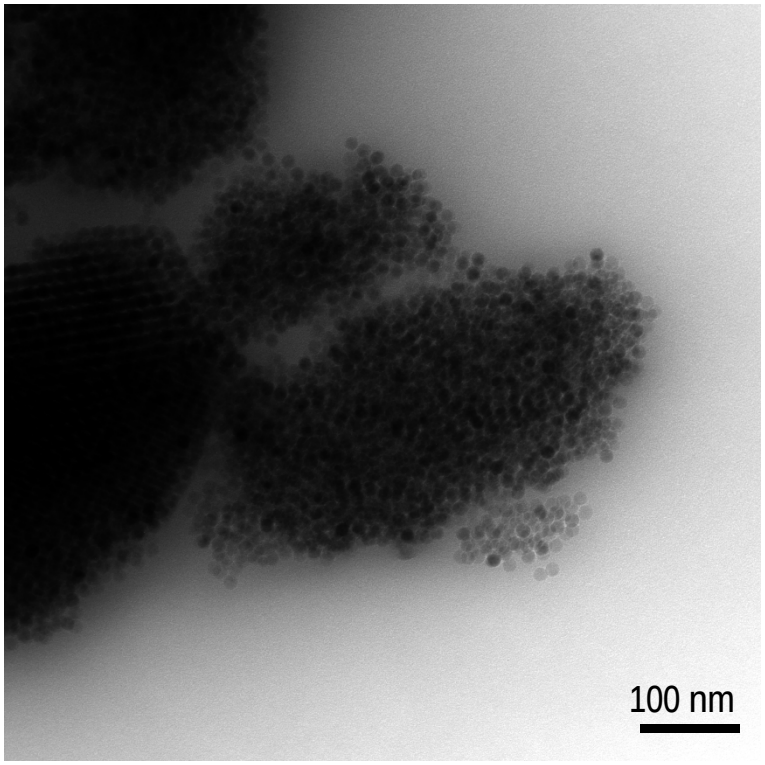


Distribution of the nanoparticle diameters

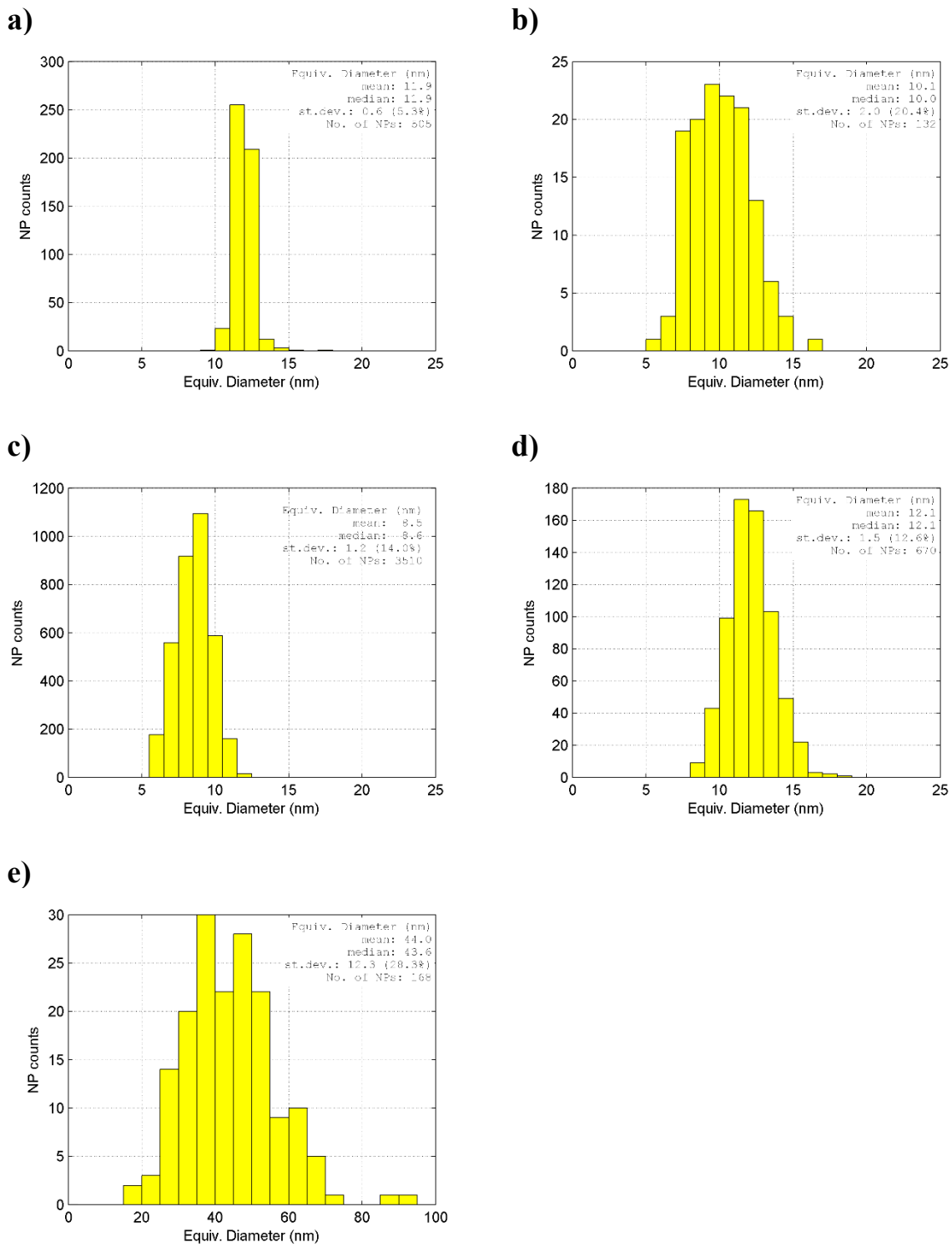


Figure S2. Distribution of the nanoparticle diameter as measured from TEM images using PEBBLES software. a) Fe_3O_4; b) $CoFe_2O_4$; c) $MnFe_2O_4$; d) MnO; e) α-MnS.

Determination of Mn concentration in MnO and α-MnS nanoparticle dispersions

3.0 ml of MnO or α-MnS NPs in *n*-hexane were evaporated under reduced pressure. 37% Hydrochloric acid (0.25 ml, 3 mmol) was added to the black-brown solid residue and the mixture was warmed at 50 °C for 30 min. Water (2 ml) was added and the clear solution was extracted with light petroleum (2 x 3 ml). The aqueous solution was evaporated under reduced pressure (0.05 mmHg) for 1 h at 50 °C giving $MnCl_2 \cdot 4H_2O$ as a pale pink solid (13.0 mg from MnO NPs, 11.4 mg from α-MnS NPs).

Calculation of the ligand density from elemental analysis

The calculation of the ligand density in the NP coating from elemental analysis (CHN) and TEM data relies on the following assumptions:

1. Each NP consists of an inorganic core and an organic coating, the latter comprising a monolayer of ligands
2. The chemical nature of the ligand is known so that its molar weight and percentage elemental composition can be calculated (in our case the ligand is oleate or stearate)
3. The density of the core is equal to the bulk density of the core material
4. The inorganic core does not contain the element(s) upon which the calculation is based (C or H in our case)

We develop the calculation referring to one NP. The calculation can also be developed referring to a macroscopic sample of NPs. No difference in the final result arises.

The density of ligands on the NP surface d = (no. of ligand molecules)/(core surface area)

$$d = \frac{N_{ligand}}{\langle S \rangle} = \frac{N_{ligand}}{\pi \langle D^2 \rangle} = \frac{N_A}{MW_{ligand}} m_{ligand} \frac{1}{\pi \langle D^2 \rangle}$$

where N_A is Avogadro number, MW_{ligand} is the ligand molar weight, m_{ligand} is the mass of ligand in the coating, $\langle S \rangle = \pi \langle D^2 \rangle$ is the mean core surface area, and $\langle D^2 \rangle$ is the mean value of the square of the core diameter, which is calculated from the results of the analysis of the TEM images.

The only unknown quantity in this equation is m_{ligand}. We now show how m_{ligand} is related to the *mass fraction of atom X in the NP* f_X, which is the result of the elemental analysis of a NP sample. To fix the ideas, we chose X = C (carbon) and use f_C from the CHN analysis. The NP mass is $m = m_{ligand} + m_{core}$ and the *ligand mass fraction in the NP* is

$$f_{ligand}^{NP} = \frac{m_{ligand}}{m_{ligand} + m_{core}}$$

The *carbon mass fraction in the NP* is

$$f_C = f_C^{ligand}\, f_{ligand}^{NP} = f_C^{ligand}\, \frac{m_{ligand}}{m_{ligand} + m_{core}}$$

where f_C^{ligand} is the *carbon mass fraction in the pure ligand*, calculated from the ligand chemical formula. By simple algebra we get

$$m_{ligand} = \frac{f_C}{f_C^{ligand} - f_C} m_{core} = \frac{f_C}{f_C^{ligand} - f_C} \rho_{core} \langle V \rangle$$

where ρ_{core} is the core density (approximated as the bulk density of the core material) and $\langle V \rangle$ is the mean core volume. The latter can be written as $(\pi/6)\ \langle D^3 \rangle$, which is calculated from the results of the analysis of the TEM images, and inserted in the preceding equation to give

$$m_{ligand} = \frac{f_C}{f_C^{ligand} - f_C} \rho_{core} \frac{\pi}{6} \langle D^3 \rangle$$

Thus, m_{ligand} is expressed as a combination of known quantities. Inserting this expression in the first equation of this section, we finally get

$$d = \frac{1}{6} \frac{N_A}{MW_{ligand}} \rho_{core} \frac{f_C}{f_C^{ligand} - f_C} \frac{\langle D^3 \rangle}{\langle D^2 \rangle}$$

Loss of nanoparticles during recycle

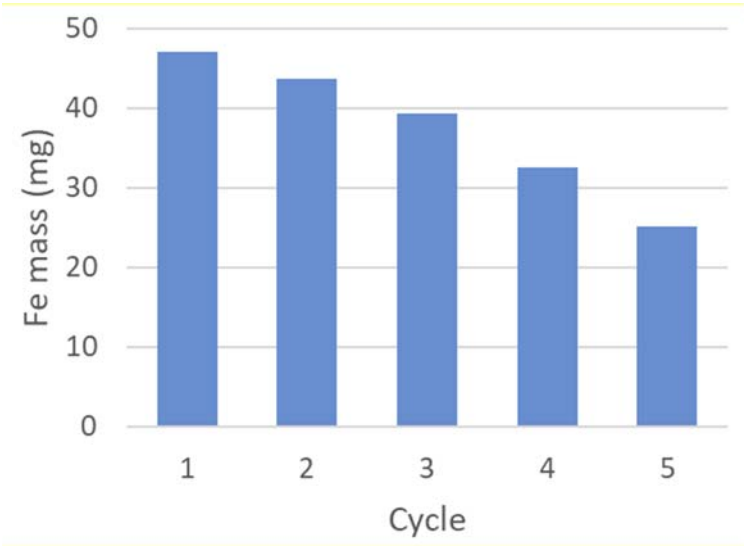


Figure S3. Amount of Fe_3O_4 NPs recovered after each cycle of the cycloaddition of **1c** to **2**.

Physical data of compounds **4a**, **5a**, **4b**, **5b**, **4c**, **5c**, and **6**

1-[2-(2-Iodophenylamino)-2-oxoethyl]-4-methoxycarbonyl-1*H*-1,2,3-triazole **4a** (115 mg, 60%), pale yellow powder, m.p. 180-182°C. IR (nujol): 3290 (N-H), 3125 (triazole C-H), 1723 (ester>C=O), 1670 (amide >C=O). ^{1}H-NMR (δ): 3.98 (3H, s, C<u>H</u>$_3$-), 5.31 (2H, s, -C<u>H</u>$_2$-), 6.90 (1H, dt, *J* = 7.8, 2.0, aromatic), 7.36 (1H, dt, *J* = 7.8, 2.0, aromatic), 7.77 (1H, dd, *J* = 7.9, 1.8, aromatic), 7.84 (1H, br s, N-<u>H</u>), 8.13 (1H, dd, *J* = 7.9, 1.8, aromatic), 8.34 ppm (1H, s, triazole C-<u>H</u>). ^{1}H-NMR (δ, CDCl$_3$-DMSO$_{d6}$): 3.70 (3H, s, C<u>H</u>$_3$-), 5.22 (2H, s, -C<u>H</u>$_2$-), 6.74 (1H, dt, *J* = 7.8, 2.0, aromatic), 7.13 (1H, dt, *J* = 7.8, 2.0, aromatic), 7.37 (1H, dd, *J* = 7.9, 1.8, aromatic), 7.62 (1H, dd, *J* = 7.9, 1.8, aromatic), 8.30 (1H, s, triazole C-<u>H</u>), 9.39 ppm (1H, br s, N-<u>H</u>). ^{13}C-NMR (δ): 50.9 (-<u>C</u>H$_3$), 51.7 (-<u>C</u>H$_2$-), 93.5 (aromatic, <u>C</u>-I), 125.4 (aromatic), 126.9 (aromatic), 127.8 (aromatic), 129.0 (aromatic), 137.3 (≥C-NH-), 138.2 (triazole-<u>C</u>$_5$), 138.4 (triazole-<u>C</u>$_4$), 159.9 (amide ><u>C</u>=O), 162.9 ppm (ester ><u>C</u>=O). MS (*m/z*): 386 (M$^+$).

1-[2-(2-Iodophenylamino)-2-oxoethyl]-5-methoxycarbonyl-1*H*-1,2,3-triazole **5a** (42 mg, 22%), pale yellow powder, m.p. 170-173°C (from diisopropyl ether). IR (nujol): 3220 (N-H), 3070 (triazole C-H), 1740 (ester >C=O), 1670 (amide >C=O). ^{1}H-NMR (δ): 3.95 (3H, s, C<u>H</u>$_3$-), 5.64 (2H, s, -C<u>H</u>$_2$-), 6.88 (1H, dt, *J* = 7.8, 2.0, aromatic), 7.34 (1H, dt, *J* = 7.8, 2.0, aromatic), 7.54 (1H, br s, N-<u>H</u>), 7.76 (1H, dd, *J* = 7.9, 1.8, aromatic), 7.84 (1H, br s, N-<u>H</u>), 8.15 (1H, dd, *J* = 7.9, 1.8, aromatic), 8.24 ppm (1H, s, triazole C-<u>H</u>). ^{13}C-NMR (δ): 52.9 (-<u>C</u>H$_3$), 53.4 (-<u>C</u>H$_2$-), 122.2 (aromatic), 126.8 (aromatic), 128.8 (aromatic), 129.4 (aromatic), 137.1 (triazole-<u>C</u>$_4$), 138.0 (aromatic), 138.9 (triazole-<u>C</u>$_5$), 158.7 (amide ><u>C</u>=O), 162.9 (ester ><u>C</u>=O). MS (*m/z*): 386 (M$^+$).

In the case of the reaction carried out at 45°C (Table 3, entry 2), unchanged **1a** was eluted first (60 mg, 40%), followed by **5a** (47 mg, 25%) and **4a** (63 mg, 32%).

1-Benzyl-4-methoxycarbonyl-1*H*-1,2,3-triazole **4b** (73 mg, 67%), white powder, m.p. 116-118°C, *lit.* 115-116.[21] IR (nujol): 3128 (triazole C-H), 1728 (ester >C=O). ^{1}H-NMR (δ): 3.94 (3H, s, C<u>H</u>$_3$-), 5.60 (2H, s, -C<u>H</u>$_2$-), 7.3-7.4 (5H, m, aromatics), 7.99 ppm (1H, s, triazole C-<u>H</u>). ^{13}C-NMR (δ): 52.1 (-<u>C</u>H$_3$), 54.5 (-<u>C</u>H$_2$-), 127.3 (triazole-<u>C</u>$_5$), 128.3 (aromatic), 129.1 (aromatic), 129.3 (aromatic), 133.7 (aromatic), 140.3 (triazole-<u>C</u>$_4$), 161.1 ppm (ester ><u>C</u>=O). MS (*m/z*): 217 (M$^+$).

1-Benzyl-5-methoxycarbonyl-1*H*-1,2,3-triazole **5b** (25 mg, 23%), colourless oil. IR (nujol): 3137 (triazole C-H), 1727 (ester >C=O). ^{1}H-NMR (δ): 3.89 (3H, s, C<u>H</u>$_3$-), 5.92 (2H, s, -C<u>H</u>$_2$-), 7.3-7.4 (5H, m, aromatics), 8.13 ppm (1H, s, triazole C-<u>H</u>). ^{13}C-NMR (δ, ppm): 52.4 (-<u>C</u>H$_3$), 53.4 (-<u>C</u>H$_2$-), 127.4 (aromatic), 128.0 (aromatic), 128.7 (aromatic), 129.3 (aromatic), 134.9 (triazole-<u>C</u>$_5$), 138.2 (triazole-<u>C</u>$_4$), 158.8 ppm (ester ><u>C</u>=O). MS (*m/z*): 217 (M^+).

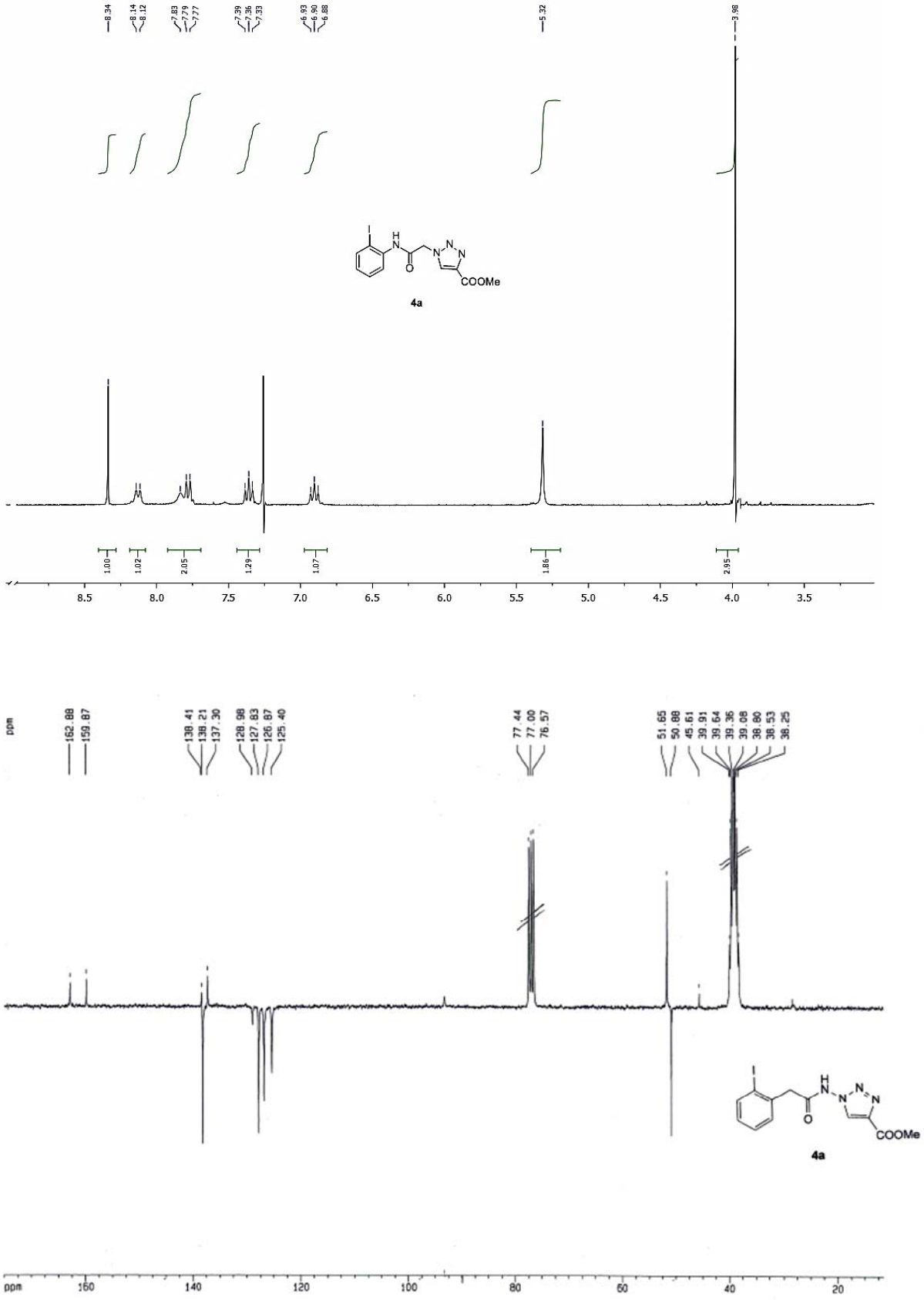
1-Phenyl-4-methoxycarbonyl-1*H*-1,2,3-triazole **4c** (72 mg, 70%), white powder, m.p. 120-122°C, *lit*. 120-121.5.[22] IR (nujol): 3125 (triazole C-H), 1725 (ester >C=O). ^{1}H-NMR (δ): 4.00 (3H, s, C<u>H</u>$_3$-), 7.4-7.7 (5H, m, aromatics), 8.51 ppm (1H, s, triazole C-<u>H</u>). ^{13}C-NMR (δ): 52.3 (-<u>C</u>H$_3$), 120.8 (aromatic), 125.6 (aromatic), 128.9 (triazole-C$_5$), 129.5 (aromatic), 136.3 (aromatic), 140.5 (triazole-<u>C</u>$_5$), 161.0 ppm (ester ><u>C</u>=O). MS (*m/z*): 203 (M^+).

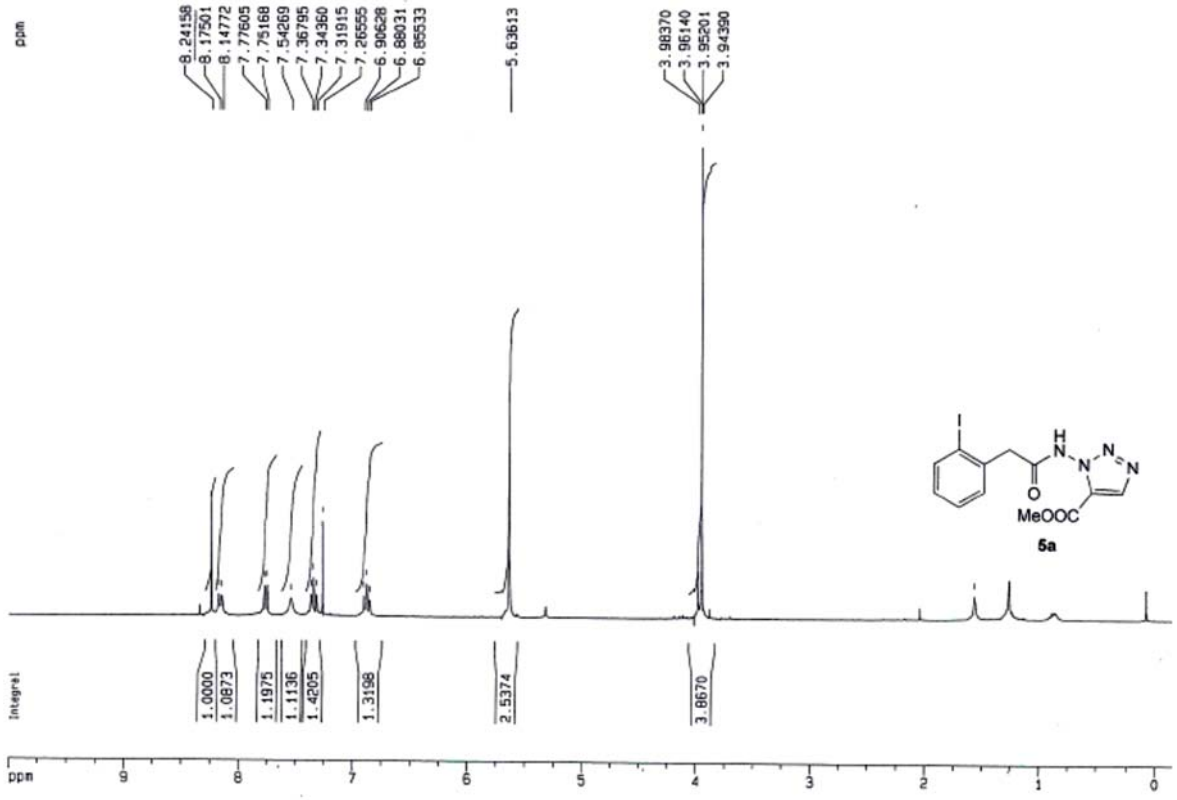
1-Phenyl-5-methoxycarbonyl-1*H*-1,2,3-triazole **5c** (25 mg, 25%), white powder, m.p. 98-100°C (from diisopropyl ether), *lit*. 99-100.5.[22] IR (nujol): 3120 (triazole C-H), 1730 (ester >C=O). ^{1}H-NMR (δ): 3.85 (3H, s, C<u>H</u>$_3$-), 7.4-7.7 (5H, m, aromatics), 8.26 ppm (1H, s, triazole C-<u>H</u>). ^{13}C-NMR (δ): 53.3 (-<u>C</u>H$_3$), 120.8 (aromatic), 125.8 (aromatic), 129.9 (aromatic), 130.1 (triazole-<u>C</u>$_4$), 137.1 (aromatic), 140.8 (triazole-<u>C</u>$_5$), 161.6 ppm (ester ><u>C</u>=O). MS (*m/z*): 203 (M^+).

1-[2-(2-Iodophenylamino)-2-oxoethyl]-4,5-dimethoxycarbonyl-1*H*-1,2,3-triazole **6**, pale yellow powder, m.p. 171-172°C (from diisopropyl ether). IR (nujol): 3210 (amide N-H), 1759 (ester >C=O), 1733 (ester >C=O). ^{1}H-NMR (δ): 3.98 (3H, s, C<u>H</u>$_3$-), 3.99 (3H, s, C<u>H</u>$_3$-), 5.54 (2H, s, -C<u>H</u>$_2$-), 6.88 (1H, dt, *J* = 7.6, 2.0, aromatic), 7.34 (1H, dt, *J* = 7.6, 2.0, aromatic), 7.55 (1H, br s, N-<u>H</u>), 7.77 (1H, dd, *J* = 7.8, 1.8, aromatic), 8.09 ppm (1H, dd, *J* = 7.8, 1.8, aromatic). ^{13}C-NMR (δ): 52.7 (-<u>C</u>H$_3$), 52.9 (t, -<u>C</u>H$_2$-), 53.7 (-<u>C</u>H$_3$), 122.9 (aromatic), 127.2 (aromatic), 129.3 (aromatic), 130.6 (aromatic), 137.1 (triazole <u>C</u>), 139.0 (aromatic), 140.0 (triazole <u>C</u>), 158.6 (amide ><u>C</u>=O), 160.2 (ester ><u>C</u>=O), 162.5 (ester >C=O). We were not able to assign the two ester <u>C</u>H$_3$ peaks to the two ester groups in the molecule. MS (*m/z*): 444 (M^+).

^{1}H- and ^{13}C-NMR spectra of compounds **4a**, **5a, 4b, 5b, 4c, 5c,** and **6**

Figure S3. ^{1}H- and ^{13}C-NMR spectra of compounds **4a**, **5a, 4b, 5b, 4c, 5c,** and **6**.

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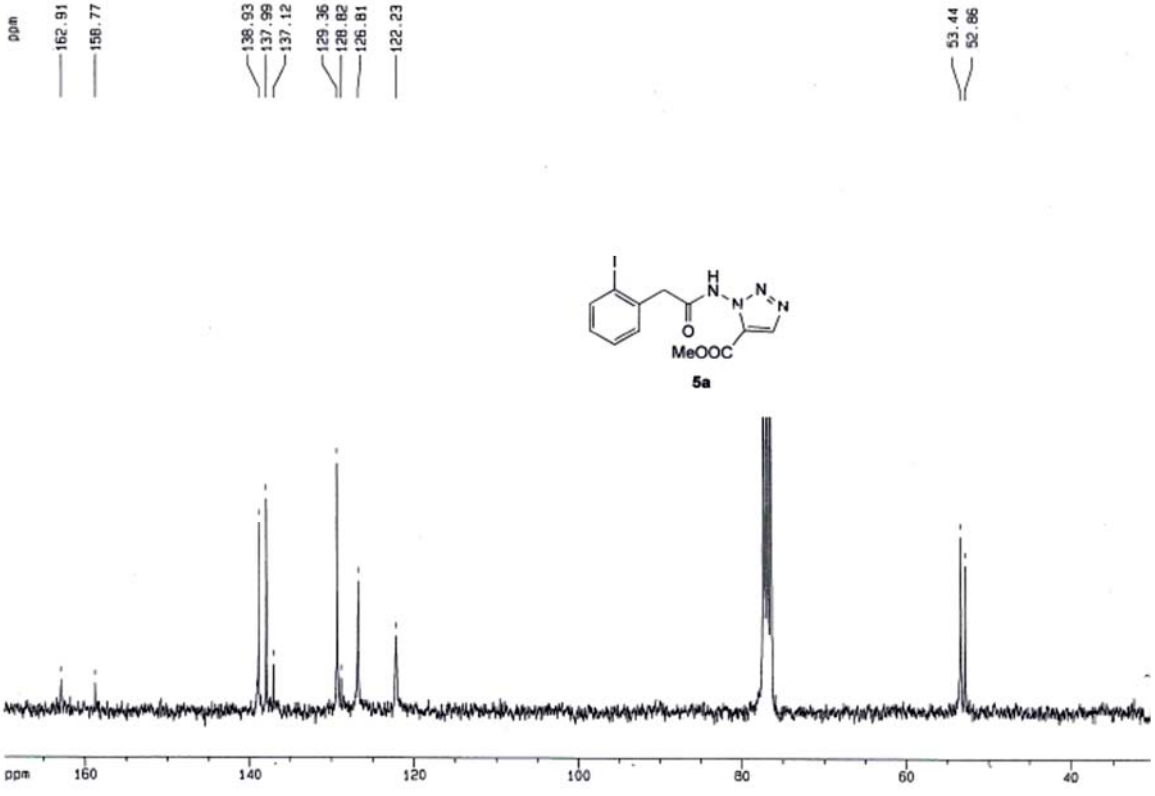
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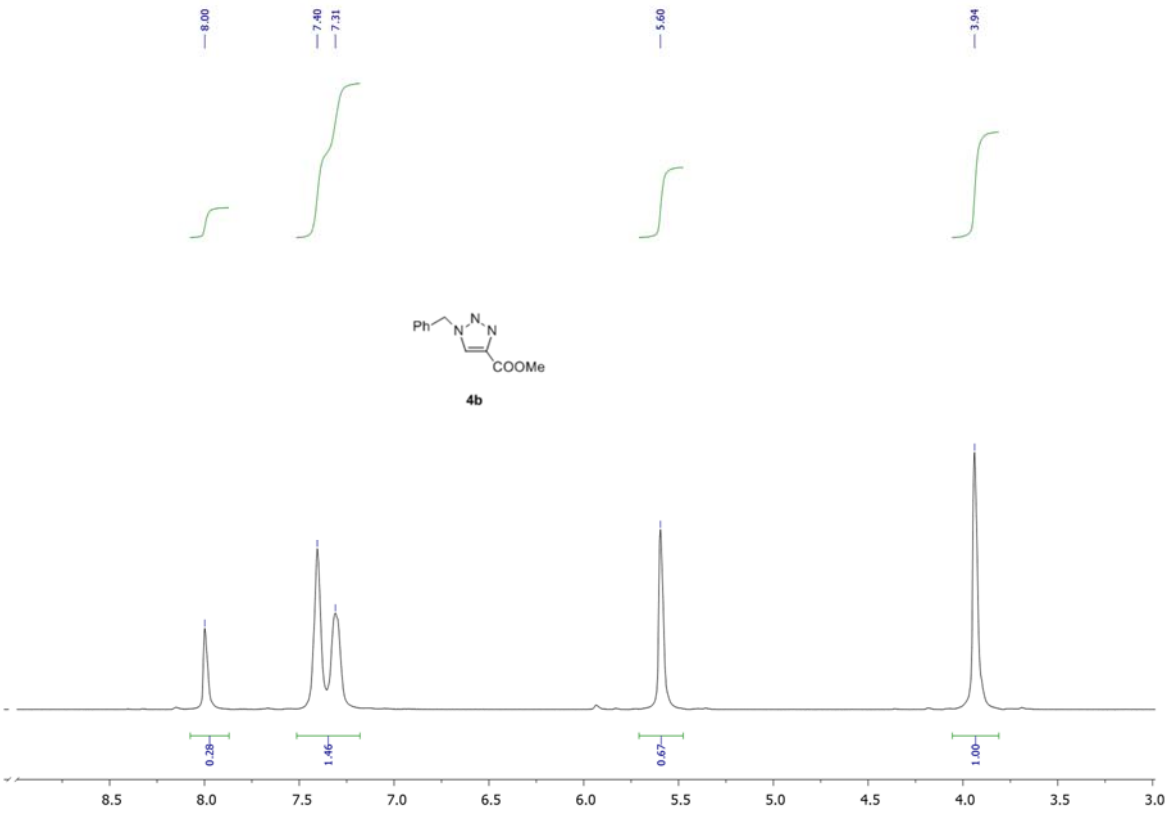
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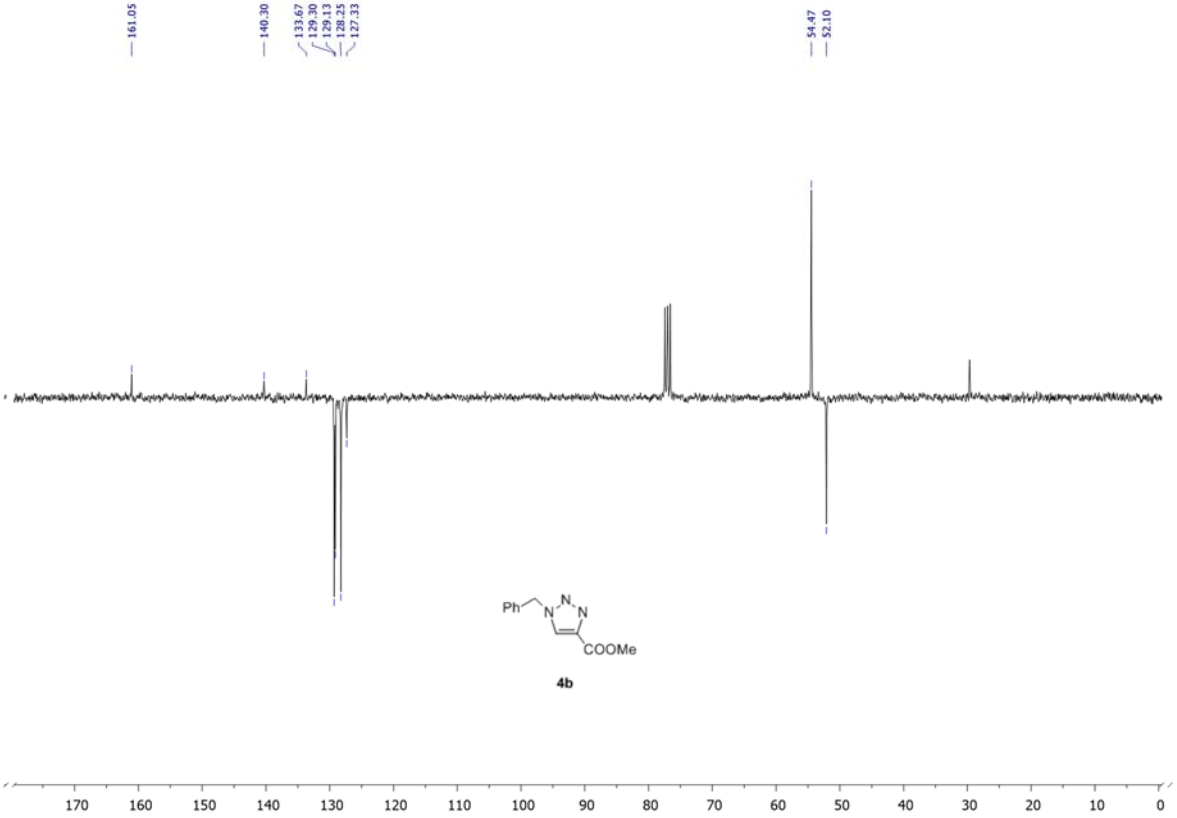
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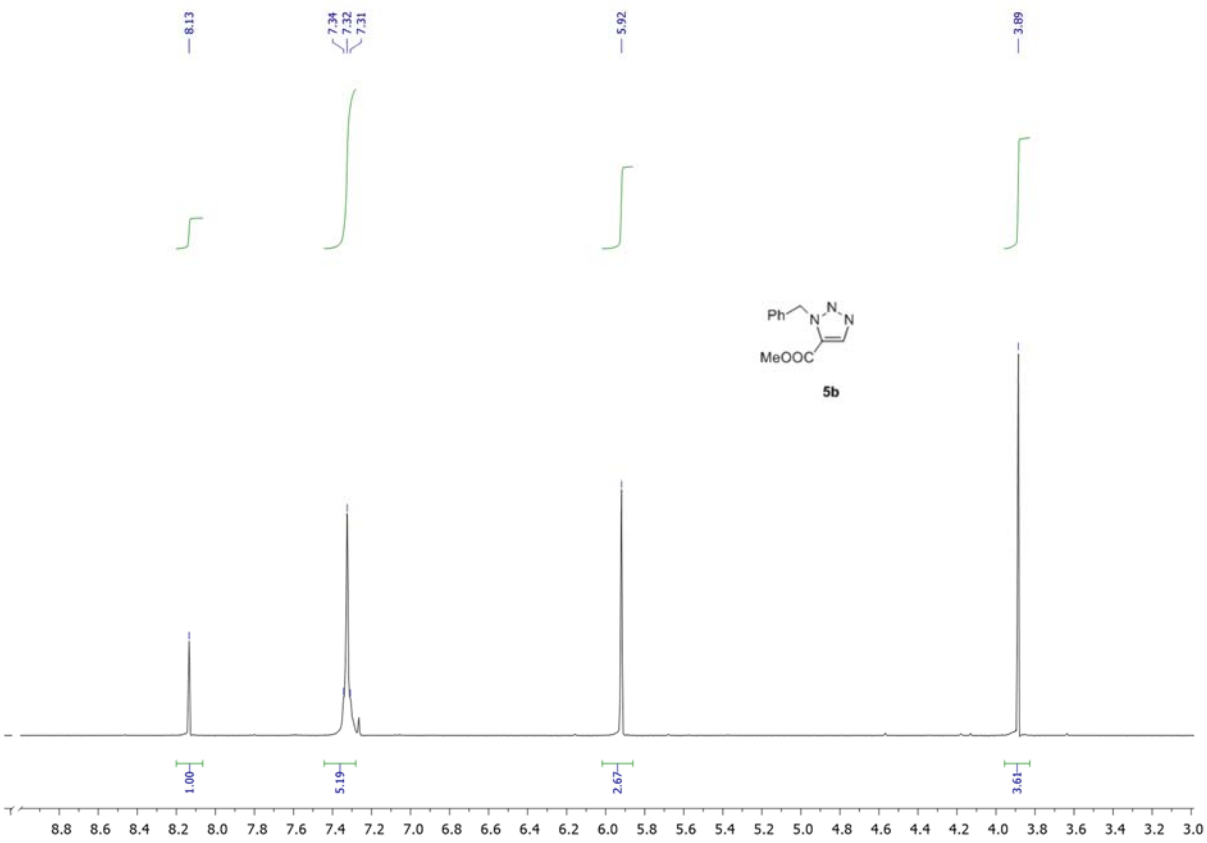
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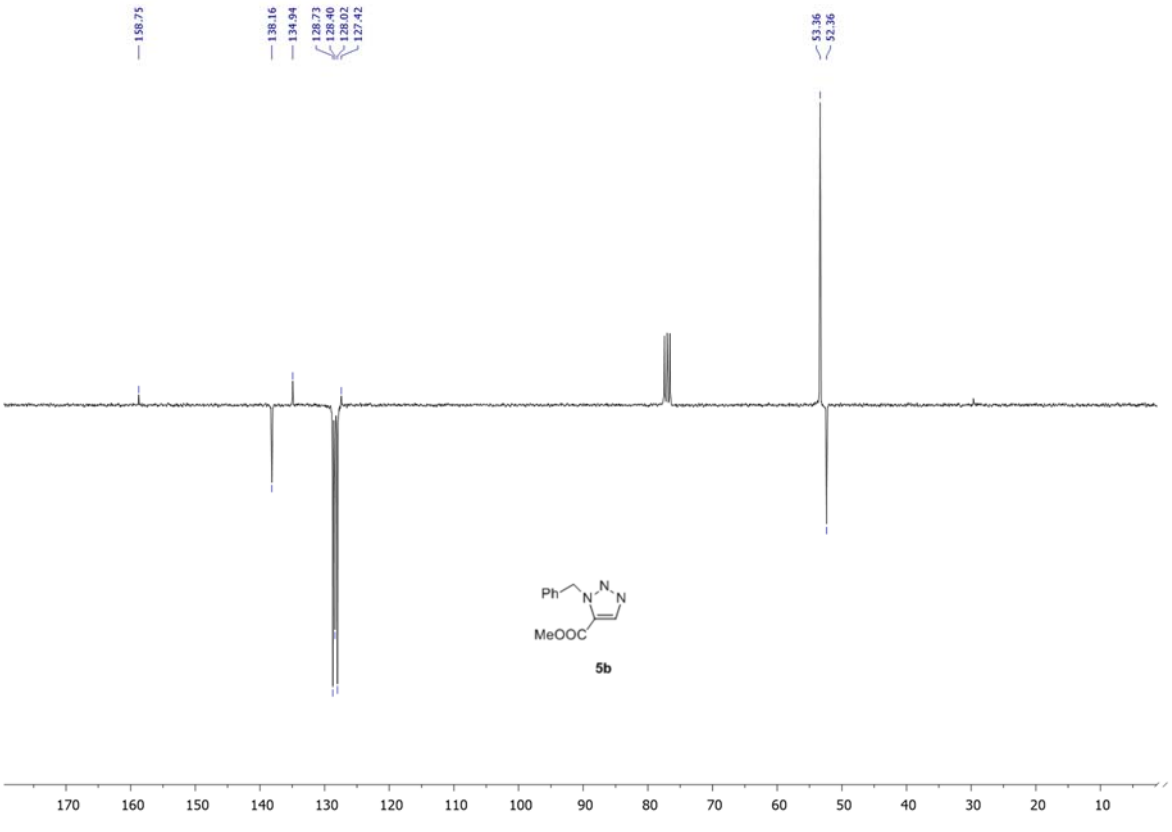
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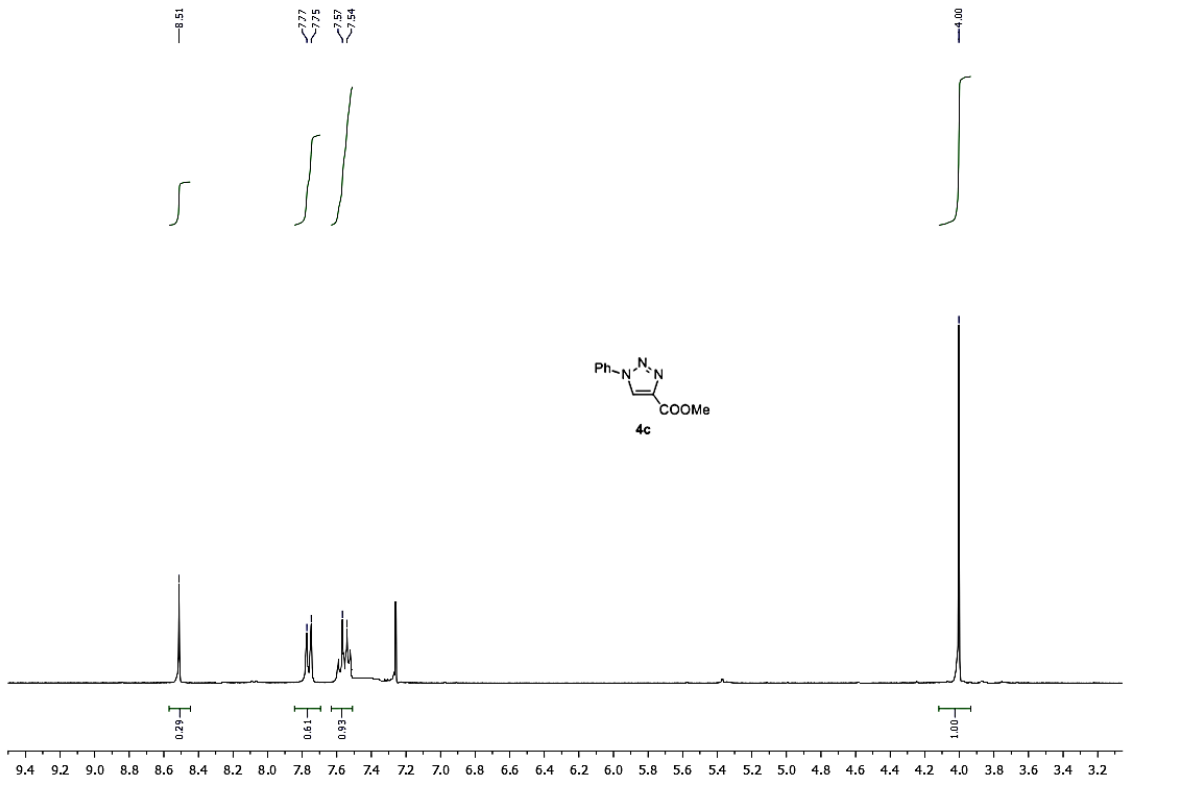
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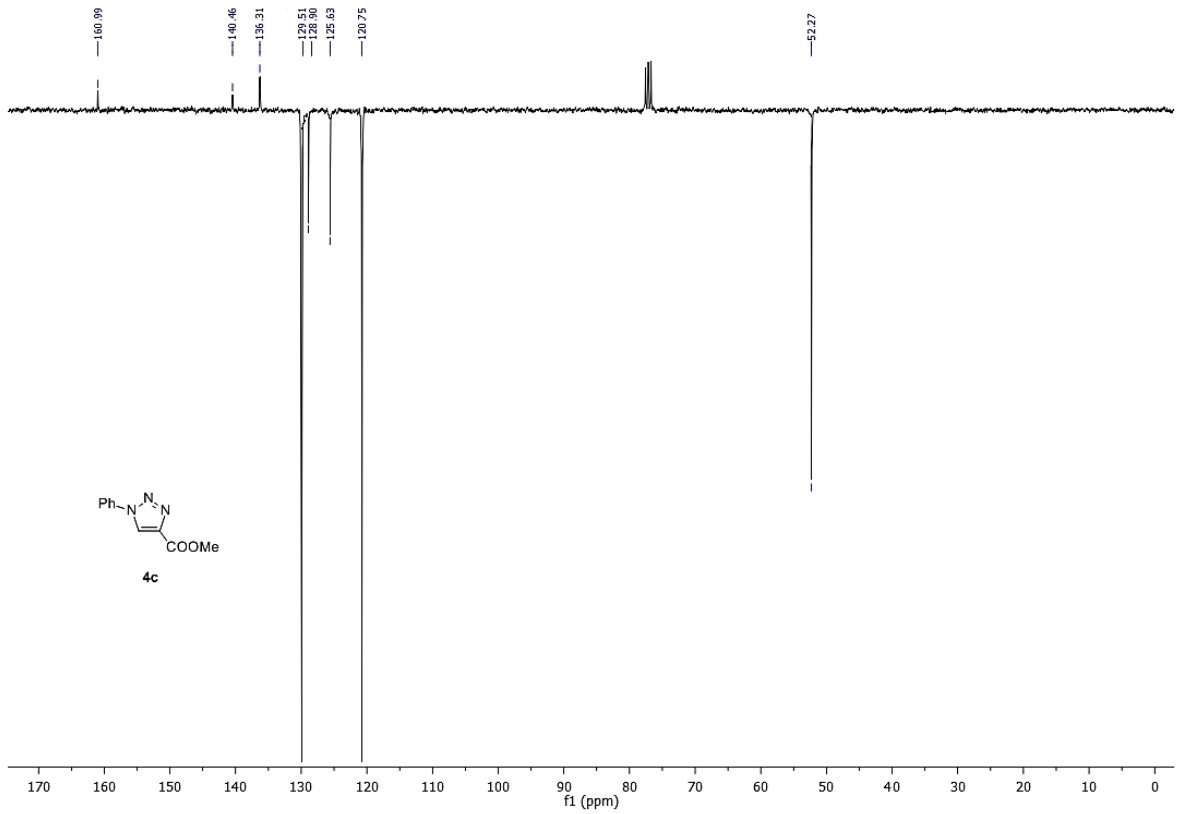
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125.63
120.75
52.27
Ph
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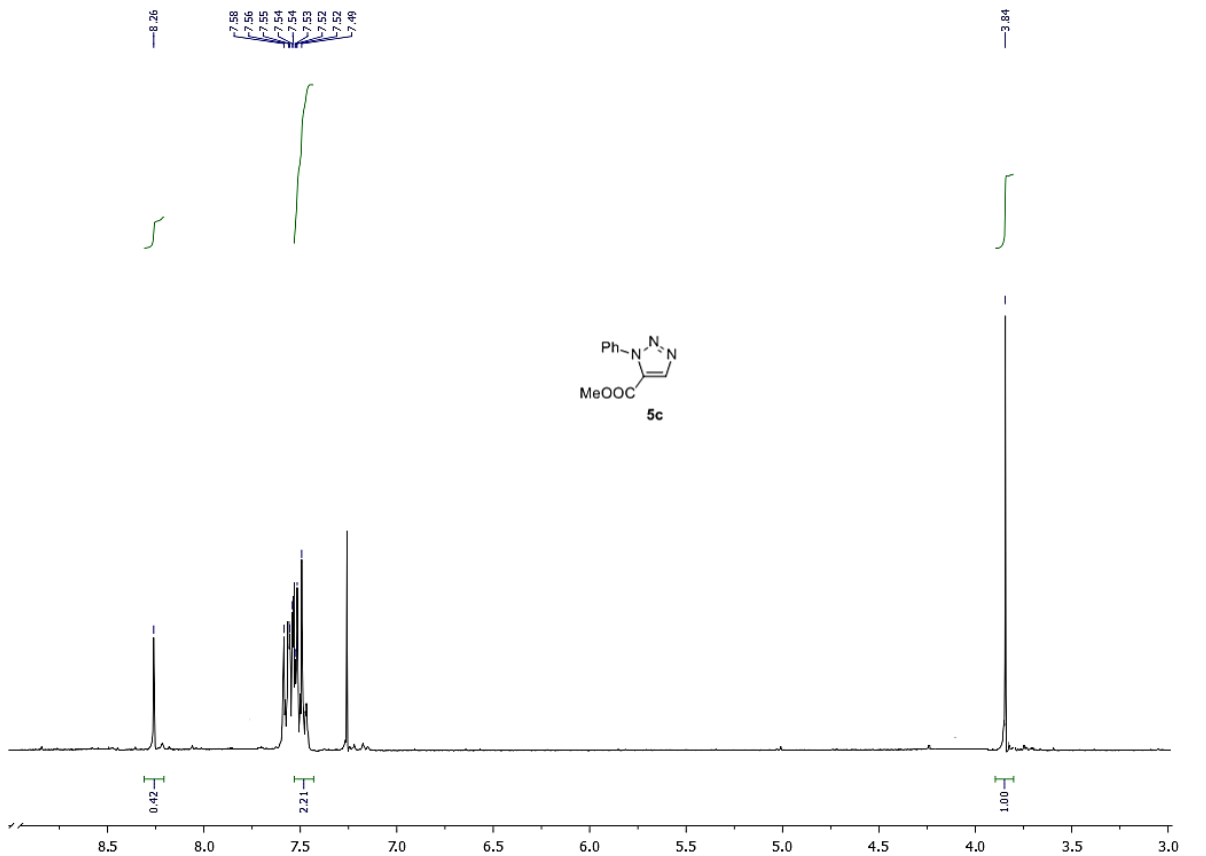
N
N
COOMe
4c
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.26
7.58
7.56
7.55
7.54
7.54
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7.52
7.52
7.49
3.84
Ph
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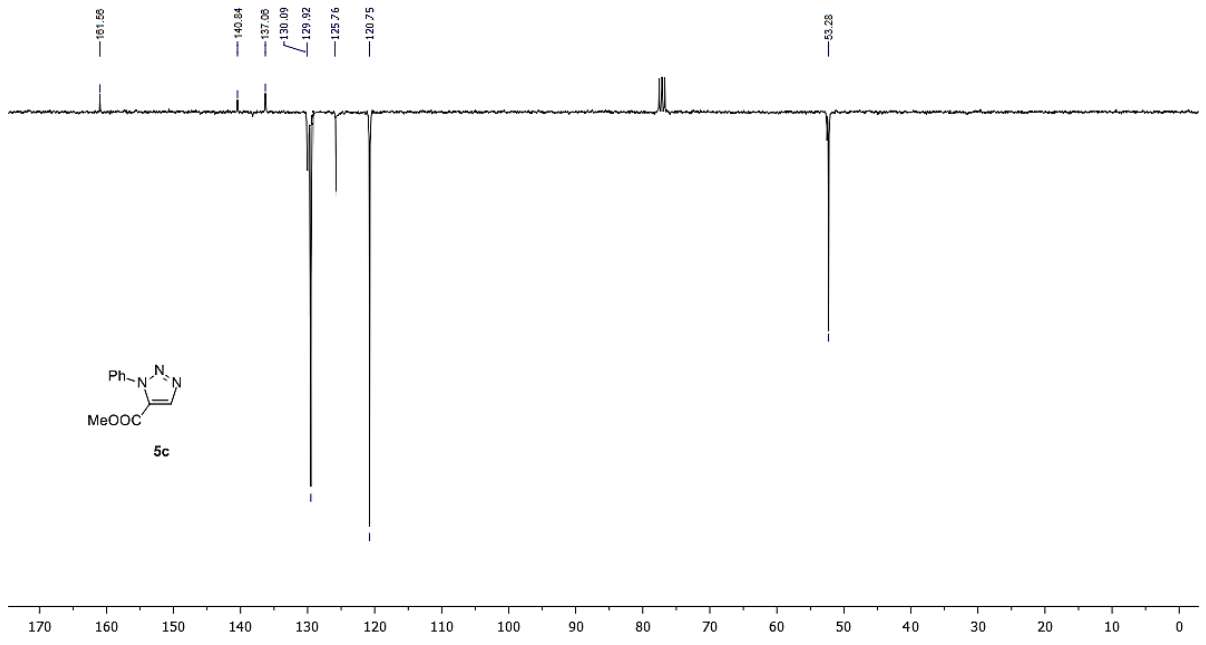
N
N
MeOOC
5c
0.42
2.21
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0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140.84
137.06
130.09
129.92
125.76
120.75
53.28
Ph
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N
N
MeOOC
5c
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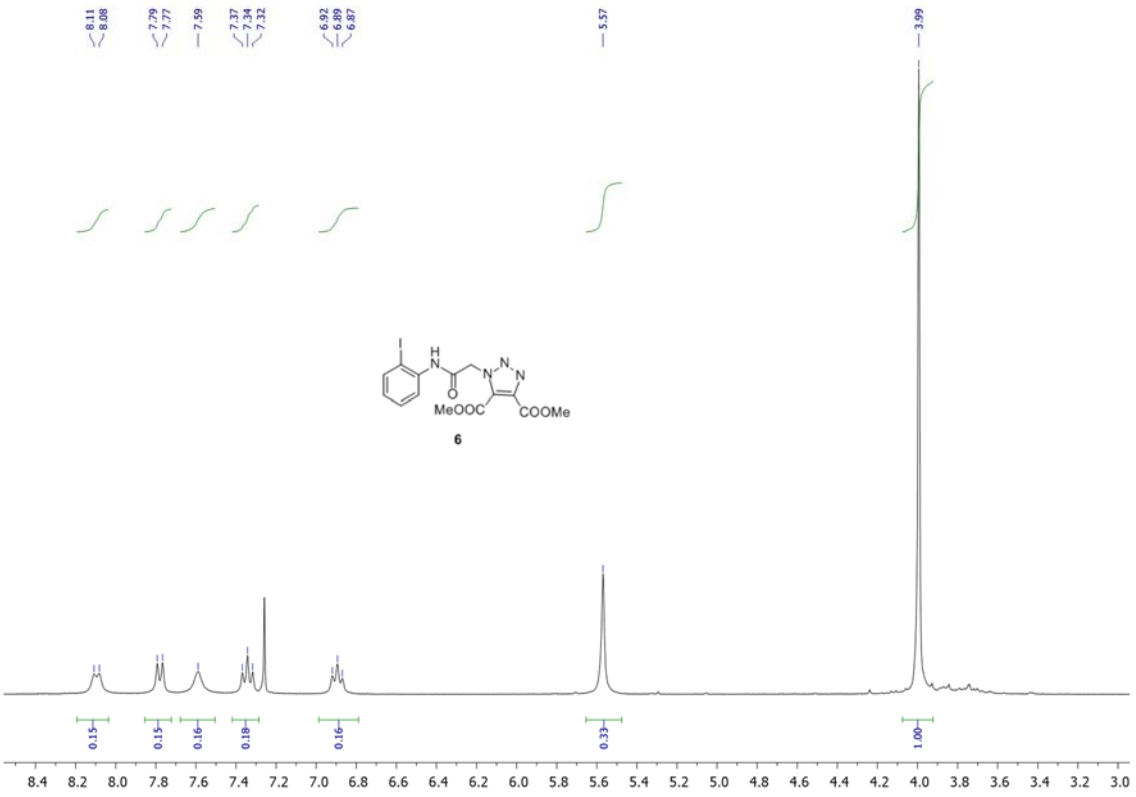
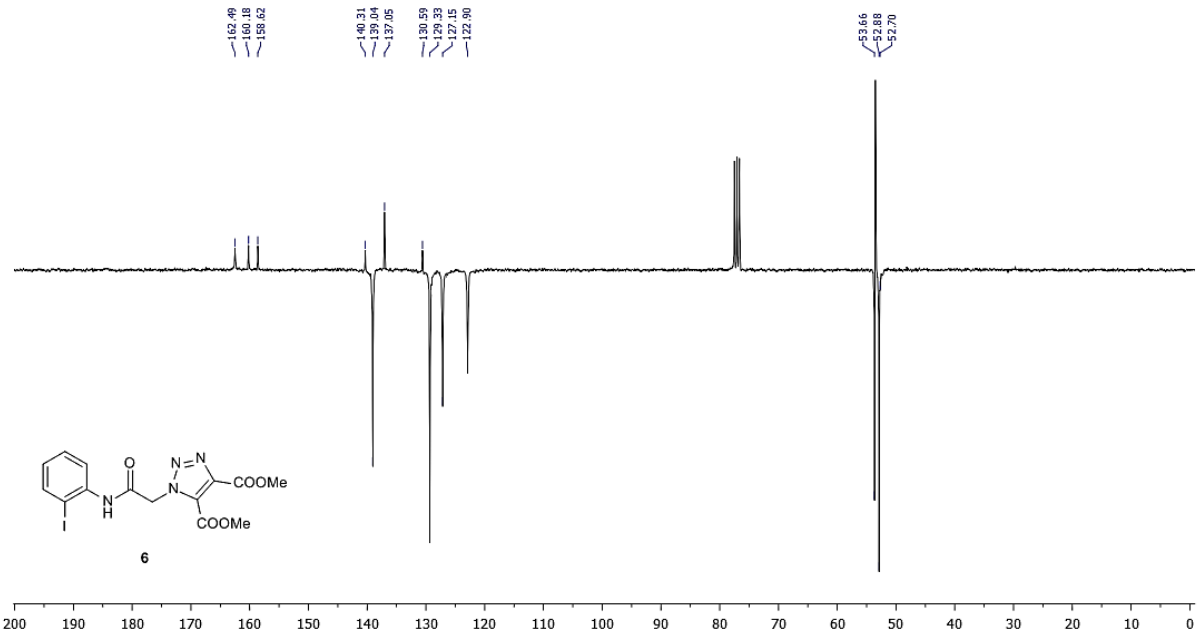
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.11
8.08
7.79
7.77
7.59
7.37
7.34
7.32
6.92
6.89
6.87
5.57
3.99
MeOOC
COOMe
6
0.15
0.15
0.16
0.18
0.16
0.33
1.00
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0


162.49
160.18
158.62
140.31
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137.05
130.59
129.33
127.15
122.90
53.66
52.88
52.70
COOMe
COOMe
6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

Electron density corresponding to relevant molecular orbitals of **1c** and **2** from periodic DFT calculations

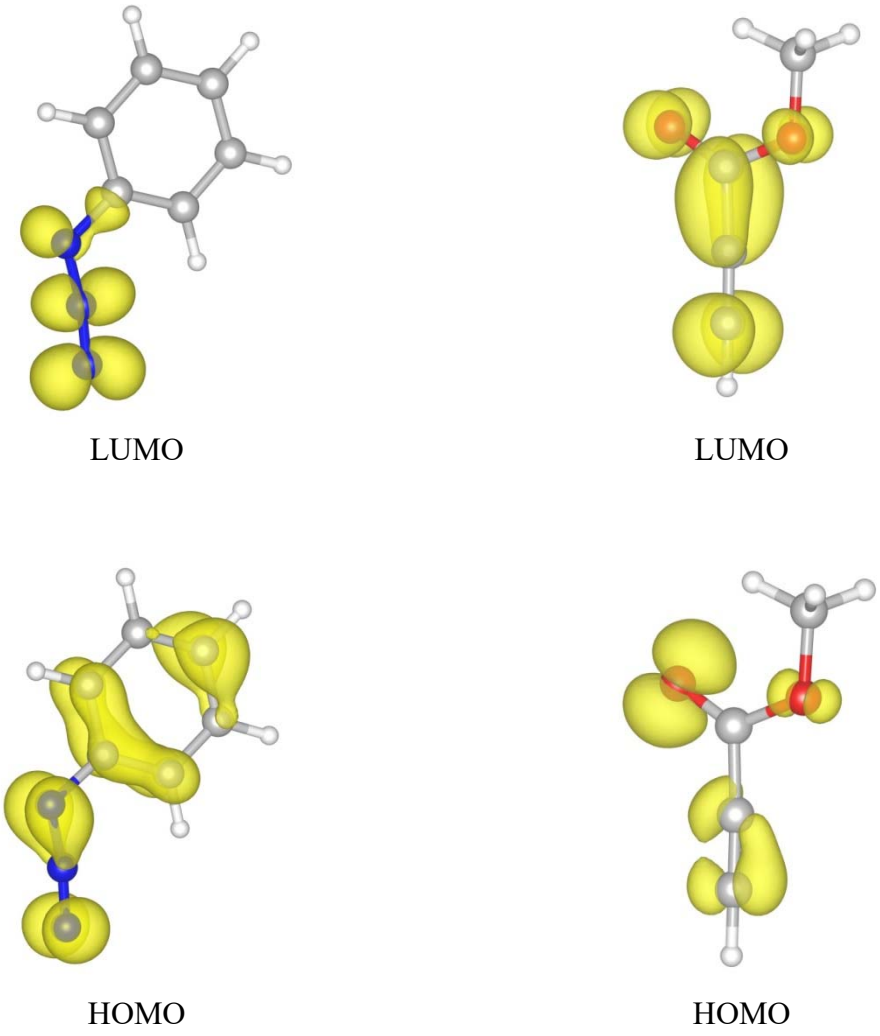
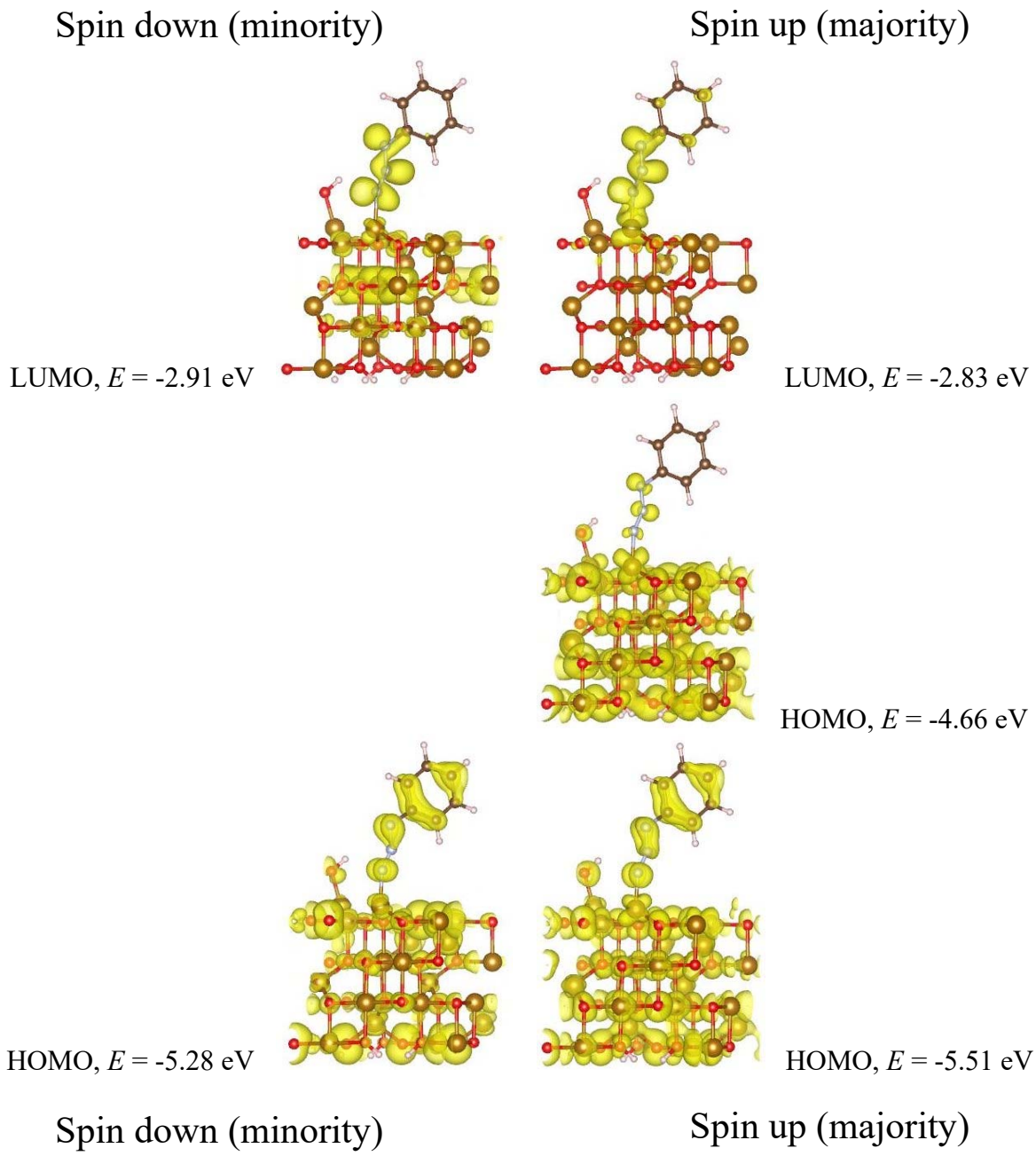


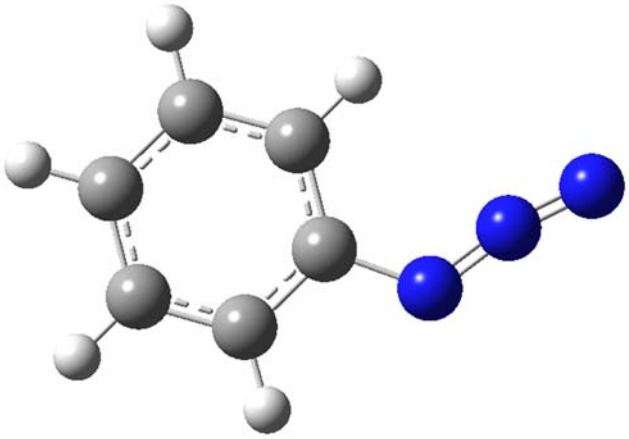
Figure S4. Electron density corresponding to relevant molecular orbitals of **1c** and **2** from periodic DFT calculations.

Electron density of relevant states of **1c** adsorbed on the (001) face of magnetite from periodic DFT calculations

Figure S5. Electron density of relevant states of **1c** adsorbed on the (001) face of magnetite from periodic DFT calculations.Each electron density plot refers to a peak in the density of states (DOS) of the **1c**-magnetite system. (See Figure 6 in the main text). All electronic states contained in an energy window centered on the peak maximum *E* and with width equal to the full-width-at-half-height of the peak were considered when calculating the electron density corresponding to the peak.

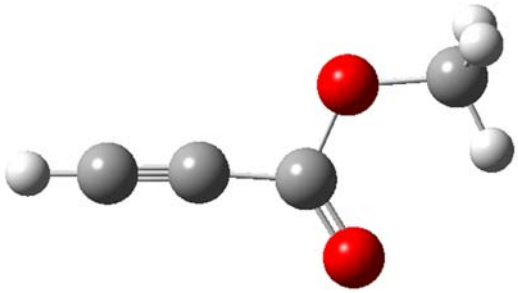


Geometrical parameters and minimum energy structure of **1c** and **2** (OPBE/LANLDZ)



1c

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.681671	0.129814	-0.008713
2	7	0	-0.220808	0.890663	-0.007186
3	7	0	-1.012020	1.863639	-0.005746
4	6	0	-2.429257	1.699520	-0.003633
5	6	0	-3.086608	0.447051	-0.002947
6	6	0	-4.490325	0.405552	-0.000846
7	6	0	-5.244651	1.593902	0.000575
8	6	0	-4.581473	2.836440	-0.000126
9	6	0	-3.180037	2.895202	-0.002218
10	1	0	-2.514626	-0.481462	-0.004028
11	1	0	-4.995137	-0.561356	-0.000316
12	1	0	-6.333891	1.551702	0.002197
13	1	0	-5.156130	3.763099	0.000960
14	1	0	-2.655406	3.849432	-0.002772

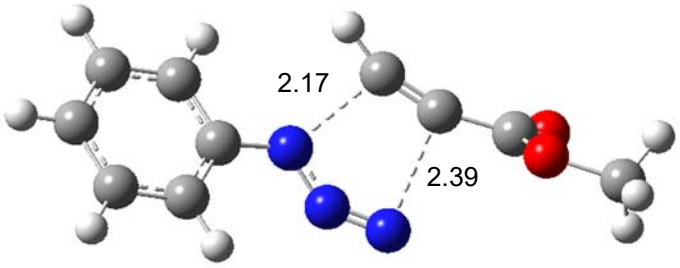


2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.233360	0.041355	0.000000
2	6	0	-1.006473	-0.031943	0.000000
3	6	0	0.426527	-0.220150	0.000000
4	8	0	0.999295	-1.328290	0.000000
5	8	0	1.067587	1.011762	0.000000
6	6	0	2.540177	1.019261	0.000000
7	1	0	-3.303682	0.113058	0.000000
8	1	0	2.941130	-0.001005	0.000000
9	1	0	2.856734	1.560743	-0.899398
10	1	0	2.856734	1.560743	0.899398

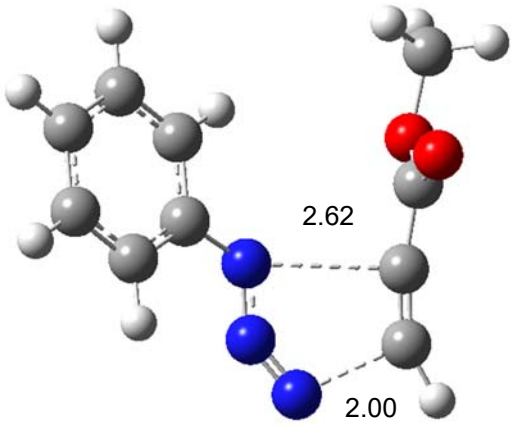
Geometrical parameters and structure of the regioisomeric transition states of the **1c** + **2** reaction leading the **4** and **5** cycloadducts (OPBE /LANLDZ)

Figure S6. Geometrical parameters and structure of the regioisomeric transition states of the **1c** + **2** reaction leading the **4** and **5** cycloadducts (OPBE /LANLDZ)



1c + **2** → **4**

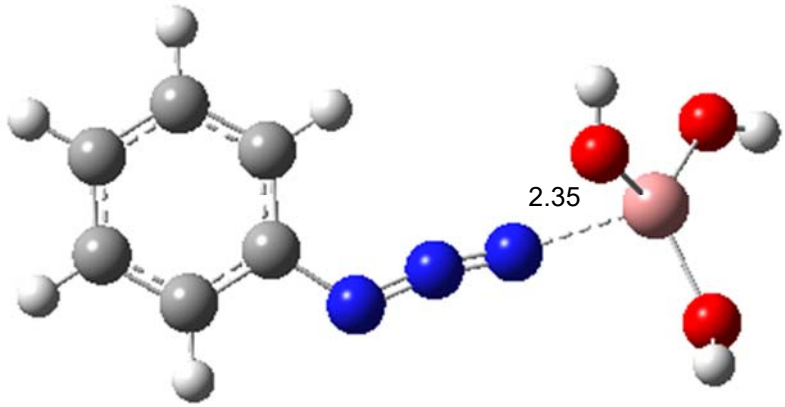
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.784246	1.321192	-0.414563
2	6	0	-1.868091	0.752217	-0.143716
3	7	0	-1.088327	-1.128329	1.112642
4	7	0	0.048164	-0.784315	0.979983
5	7	0	0.782775	0.165752	0.549947
6	6	0	2.156109	0.018989	0.217401
7	6	0	2.772221	-1.235438	-0.003725
8	6	0	4.127668	-1.287603	-0.362022
9	6	0	4.874774	-0.104479	-0.521146
10	6	0	4.254968	1.140436	-0.303473
11	6	0	2.904474	1.208244	0.072123
12	1	0	-0.098748	2.034903	-0.832954
13	1	0	2.197263	-2.154184	0.110871
14	1	0	4.599764	-2.257483	-0.523164
15	1	0	5.925937	-0.152947	-0.805383
16	1	0	4.826406	2.062551	-0.413575
17	1	0	2.431948	2.169171	0.271548
18	6	0	-3.276646	0.472187	0.031419
19	8	0	-4.005384	0.969199	0.914502
20	8	0	-3.719123	-0.427317	-0.931276
21	6	0	-5.138643	-0.802878	-0.847507
22	1	0	-5.352769	-1.279821	0.117920
23	1	0	-5.780546	0.080146	-0.965661
24	1	0	-5.287015	-1.506346	-1.672165



1c + 2 → 5

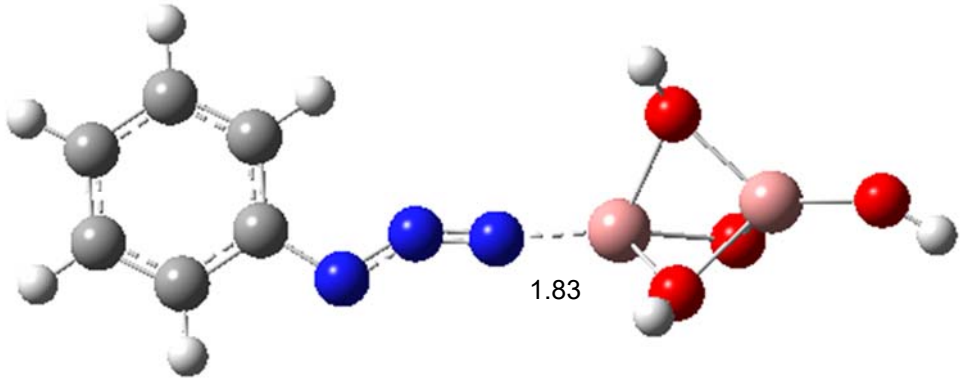
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.260650	0.923880	0.235478
2	6	0	-2.395611	2.170259	0.158980
3	7	0	-0.705647	3.086680	-0.392461
4	7	0	0.116453	2.209718	-0.495491
5	7	0	0.254865	0.947921	-0.506034
6	6	0	1.484827	0.288905	-0.253369
7	6	0	2.604123	0.919217	0.342263
8	6	0	3.770057	0.176832	0.580217
9	6	0	3.831773	-1.190157	0.246201
10	6	0	2.713701	-1.812057	-0.341650
11	6	0	1.545068	-1.079881	-0.598105
12	1	0	-2.968097	3.080435	0.223082
13	1	0	2.559391	1.975748	0.606384
14	1	0	4.632740	0.667545	1.032582
15	1	0	4.740056	-1.761187	0.439293
16	1	0	2.753876	-2.868511	-0.608679
17	1	0	0.680938	-1.546770	-1.067331
18	6	0	-2.336564	-0.488292	0.509828
19	8	0	-2.217827	-1.004755	1.642471
20	8	0	-2.606024	-1.211669	-0.648517
21	6	0	-2.785335	-2.660069	-0.464965
22	1	0	-1.890153	-3.109992	-0.015731
23	1	0	-3.650012	-2.860859	0.181368
24	1	0	-2.955962	-3.047073	-1.473962

Geometrical parameters and minimum energy structure of **1c**-$Fe(OH)_3$ and **1c**-$Fe_2(OH)_4$ (OPBE/LANL2/LANLDZ)



1c-$Fe(OH)_3$

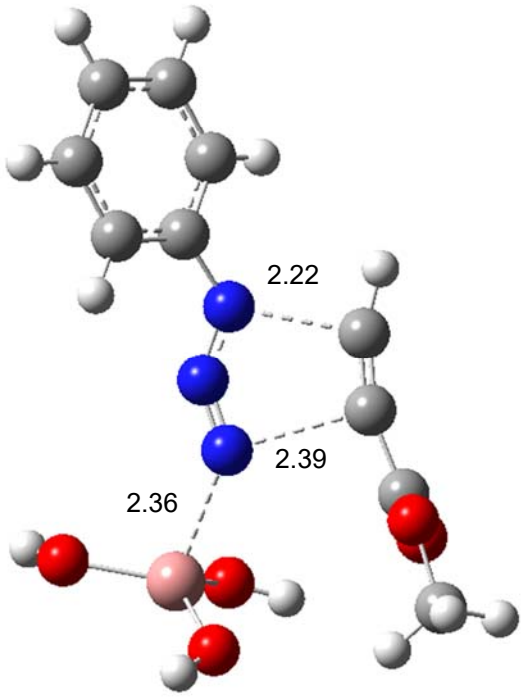
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.889690	-0.527083	-0.922247
2	7	0	-0.225350	-0.770412	-0.617628
3	7	0	-1.327740	-1.260216	-0.317994
4	6	0	-2.522383	-0.493877	-0.156115
5	6	0	-2.579482	0.912571	-0.284701
6	6	0	-3.808927	1.565334	-0.104401
7	6	0	-4.972110	0.833562	0.202320
8	6	0	-4.901692	-0.566936	0.330404
9	6	0	-3.681459	-1.235810	0.152648
10	1	0	-1.683676	1.488981	-0.517038
11	1	0	-3.855969	2.650291	-0.202370
12	1	0	-5.921865	1.349980	0.341247
13	1	0	-5.797354	-1.140575	0.569004
14	1	0	-3.611147	-2.318060	0.248583
15	26	0	2.884920	0.134152	0.131550
16	8	0	2.104572	0.870673	1.624388
17	8	0	3.676818	-1.508281	0.318720
18	8	0	3.618085	1.312567	-1.062706
19	1	0	2.057159	1.815141	1.868904
20	1	0	3.710880	-2.093663	1.099472
21	1	0	4.338371	1.175196	-1.707175



1c-$Fe_2(OH)_4$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.455562	-0.395643	0.192934
2	7	0	1.663510	-0.357145	0.108726
3	7	0	2.737218	-1.057868	-0.013437
4	6	0	3.983251	-0.366084	-0.050068
5	6	0	4.140552	1.038749	0.038685
6	6	0	5.425217	1.599945	-0.009535
7	6	0	6.562710	0.779515	-0.145719
8	6	0	6.403215	-0.617131	-0.233664
9	6	0	5.123887	-1.191009	-0.186660
10	1	0	3.264189	1.678741	0.144395
11	1	0	5.539857	2.682701	0.059394
12	1	0	7.558003	1.222977	-0.182741
13	1	0	7.276702	-1.261527	-0.338833
14	1	0	4.987997	-2.269873	-0.253123
15	26	0	-1.358046	-0.224541	0.413295
16	8	0	-2.243865	1.504104	-0.295490
17	1	0	-1.946642	2.176238	-0.933252
18	8	0	-2.943696	-0.275090	1.579708
19	1	0	-3.100853	0.207649	2.411207
20	8	0	-2.501482	-1.194598	-0.892696
21	1	0	-2.326830	-1.595865	-1.760697
22	26	0	-3.759914	0.230573	-0.222027
23	8	0	-5.519350	0.270780	-0.650683
24	1	0	-6.345347	-0.228762	-0.541825

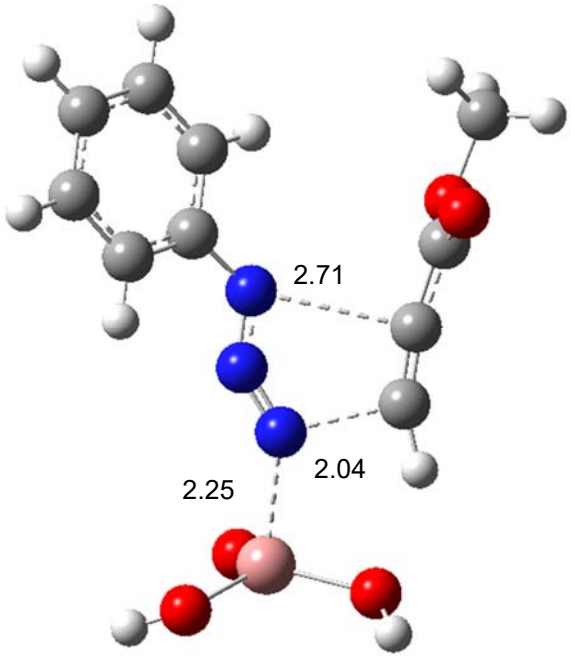
Geometrical parameters and structure of the regioisomeric transition states of the **1c**-$Fe(OH)_3$ + **2** reaction leading the **4** and **5** cycloadducts (OPBE/LANL2/LANLDZ)



1c-$Fe(OH)_3$ + **2** → **4**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.749241	2.325395	-0.624066
2	6	0	0.453629	2.094545	-0.364560
3	7	0	0.371965	-0.242209	0.113304
4	7	0	-0.809477	-0.306800	-0.073952
5	7	0	-1.797207	0.377592	-0.474584
6	6	0	-3.151050	0.112816	-0.126827
7	6	0	-3.521182	-0.696603	0.972491
8	6	0	-4.880918	-0.879909	1.263742
9	6	0	-5.872615	-0.252519	0.484619
10	6	0	-5.495246	0.554220	-0.605396

11	6	0	-4.139551	0.734337	-0.920223
12	1	0	-1.652044	2.847451	-0.880234
13	1	0	-2.756481	-1.181849	1.578790
14	1	0	-5.165776	-1.512295	2.105070
15	1	0	-6.926805	-0.396366	0.721260
16	1	0	-6.256605	1.034748	-1.220045
17	1	0	-3.842877	1.333164	-1.780267
18	6	0	1.894262	2.226024	-0.227742
19	8	0	2.711502	2.080409	-1.159972
20	8	0	2.226975	2.541240	1.074236
21	6	0	3.669938	2.607633	1.376556
22	1	0	4.113220	1.612381	1.256370
23	1	0	4.169118	3.329098	0.717074
24	1	0	3.714486	2.934172	2.419556
25	26	0	2.173185	-1.751709	-0.141600
26	8	0	1.308313	-3.349804	0.134659
27	8	0	2.579240	-1.325880	-1.871720
28	8	0	3.292204	-1.193759	1.213805
29	1	0	1.025622	-3.992750	-0.544494
30	1	0	3.112111	-0.580500	-2.211042
31	1	0	3.412211	-1.656184	2.066558

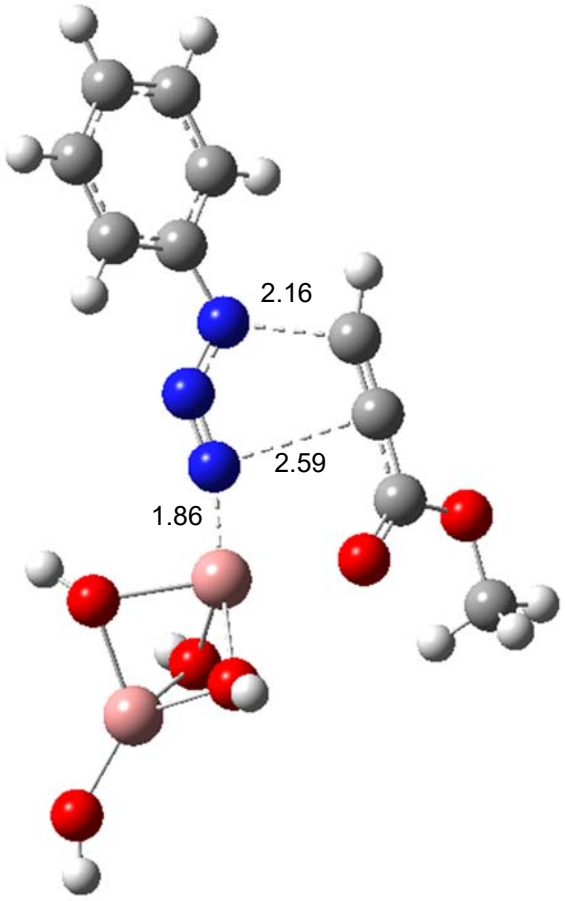


1c-$Fe(OH)_3$ + **2** → **5**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.351317	-2.029017	0.446880
2	6	0	-0.882482	-1.805393	0.549512
3	7	0	-1.319792	0.107589	0.163308
4	7	0	-0.284871	0.685800	-0.099097
5	7	0	0.938312	0.421265	-0.280986
6	6	0	1.989555	1.362930	-0.148280
7	6	0	1.863291	2.571954	0.577698
8	6	0	2.968401	3.428210	0.682520
9	6	0	4.199487	3.086642	0.088119
10	6	0	4.318406	1.879117	-0.626193
11	6	0	3.218915	1.017446	-0.751907
12	1	0	-1.931149	-2.045968	0.719819
13	1	0	0.912884	2.835262	1.041690
14	1	0	2.869314	4.363477	1.234312
15	1	0	5.054893	3.756072	0.179690
16	1	0	5.266577	1.611561	-1.092937
17	1	0	3.291892	0.088972	-1.315146
18	6	0	1.695365	-2.548584	0.530875
19	8	0	2.338658	-2.688996	1.593230
20	8	0	2.173503	-2.913011	-0.722470
21	6	0	3.506299	-3.537819	-0.738292
22	1	0	4.255225	-2.868640	-0.294753
23	1	0	3.491867	-4.482366	-0.178825

24	1	0	3.714677	-3.716617	-1.797197
25	26	0	-3.526286	0.310368	-0.126946
26	8	0	-3.738951	0.381864	-1.945018
27	8	0	-3.911760	-1.307390	0.708800
28	8	0	-4.015482	1.827068	0.777821
29	1	0	-3.955523	-0.325361	-2.582149
30	1	0	-4.422330	-1.406759	1.535922
31	1	0	-4.339509	2.669023	0.403105

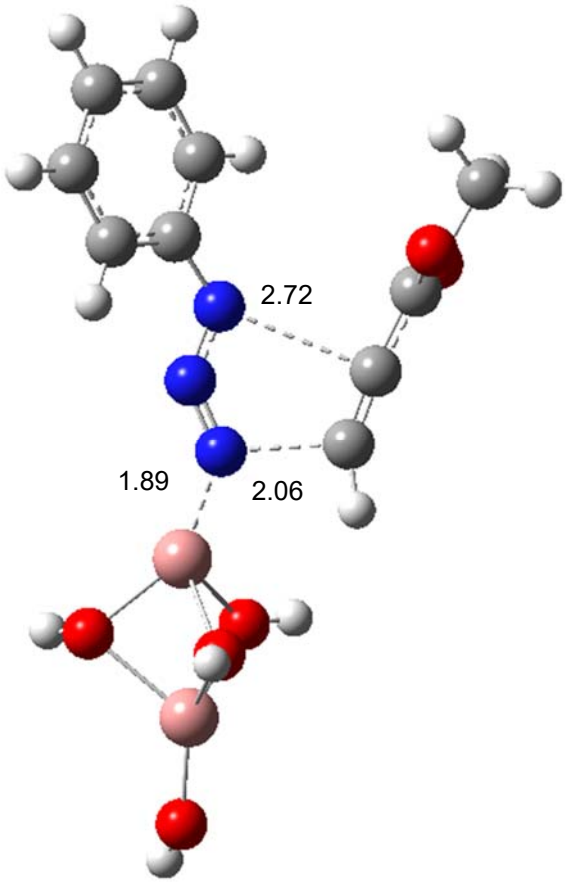
Geometrical parameters and structure of the regioisomeric transition states of the **1c**-$Fe_2(OH)_4$ + **2** reaction leading the **4** and **5** cycloadducts (OPBE/LANL2/LANLDZ)



TS **1c**-$Fe_2(OH)_4$ + **2** → **4**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.333665	2.283858	0.252216
2	6	0	-1.105160	2.505200	0.160102
3	7	0	-0.466475	0.075864	-0.327533
4	7	0	-1.630125	-0.317056	-0.339442
5	7	0	-2.771255	0.297500	-0.465077
6	6	0	-3.972948	-0.421441	-0.210230
7	6	0	-4.026903	-1.666036	0.463701
8	6	0	-5.266676	-2.279049	0.695963
9	6	0	-6.462807	-1.663287	0.276916
10	6	0	-6.407057	-0.424856	-0.390302
11	6	0	-5.172010	0.194026	-0.639419
12	1	0	-3.363244	2.456462	0.511625

13	1	0	-3.103905	-2.142064	0.793584
14	1	0	-5.300425	-3.240075	1.211159
15	1	0	-7.423031	-2.144289	0.464338
16	1	0	-7.325625	0.056333	-0.727969
17	1	0	-5.123008	1.137269	-1.182861
18	6	0	0.188717	3.091699	-0.007182
19	8	0	0.429375	4.159415	-0.607023
20	8	0	1.210906	2.324804	0.601813
21	6	0	2.538909	2.980978	0.652849
22	1	0	2.896632	3.185545	-0.362336
23	1	0	2.459105	3.917302	1.218758
24	1	0	3.179969	2.254766	1.155664
25	26	0	1.327872	-0.111799	0.139478
26	8	0	1.653653	-2.217494	0.095905
27	8	0	2.909838	-0.268213	1.388172
28	8	0	2.719076	-0.035128	-1.314723
29	1	0	1.143294	-2.894450	-0.384352
30	1	0	2.842803	-0.619989	2.295968
31	1	0	2.600942	-0.017825	-2.280896
32	26	0	3.464190	-1.493043	-0.129417
33	8	0	5.086959	-2.236281	-0.427277
34	1	0	6.037030	-2.040629	-0.472531



TS **1c**-$Fe_2(OH)_4$ + **2** → **5**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.456304	2.054431	0.611269
2	6	0	-0.254576	1.745232	0.789500
3	7	0	0.181735	-0.171406	0.179919
4	7	0	-0.882962	-0.788588	-0.022975
5	7	0	-2.071004	-0.413963	-0.358419
6	6	0	-3.142244	-1.338602	-0.207627
7	6	0	-3.069827	-2.540309	0.539456
8	6	0	-4.197628	-3.367346	0.636061
9	6	0	-5.405817	-3.009698	0.004383
10	6	0	-5.476838	-1.812147	-0.733114
11	6	0	-4.353525	-0.979420	-0.842633
12	1	0	0.741796	1.950662	1.143501
13	1	0	-2.138107	-2.814954	1.033483
14	1	0	-4.136872	-4.292519	1.210902
15	1	0	-6.279971	-3.655948	0.088450
16	1	0	-6.407545	-1.528181	-1.225374
17	1	0	-4.392130	-0.055429	-1.417636
18	6	0	-2.808533	2.528863	0.560316
19	8	0	-3.634439	2.464502	1.499098
20	8	0	-3.086283	3.116512	-0.675572
21	6	0	-4.429899	3.696375	-0.810925
22	1	0	-5.203059	2.939814	-0.622472

23	1	0	-4.563745	4.527201	-0.105061
24	1	0	-4.474584	4.054345	-1.844074
25	26	0	2.030351	-0.468461	-0.105799
26	8	0	3.476443	-1.702356	-0.599510
27	8	0	3.125928	0.922662	-1.043375
28	8	0	3.262299	-0.027930	1.492734
29	1	0	3.638199	-2.159666	-1.445789
30	1	0	2.994246	1.811179	-1.414989
31	1	0	3.269050	-0.356845	2.407648
32	26	0	4.551447	-0.011816	0.020759
33	8	0	6.327434	0.184788	-0.242962
34	1	0	7.031702	0.155540	-0.910636