

Heterogeneous gold nanoparticle-based catalysts for the synthesis of click-derived triazoles via the azide-alkyne cycloaddition reaction

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Table S1. Optimization of reaction parameters for the microwave-assisted synthesis of 1,2,3-triazole catalyzed by Au nanoparticles on different supports. ^a

Entry	Catalyst	Catalyst loading, ^b mol %	Weight of catalyst (g)	Temperature, °C	Time, min	Total volume of solvent, mL	Yield, ^c %	TON ^d
1	Au/ZnO	0.13	0.0059	80	15	1.5	25	189
2	Au/Fe ₂ O ₃	0.08	0.0059	80	15	1.5	26	321
3	Au/TiO ₂	0.16	0.0059	80	15	1.5	25	158
4	Au/Al ₂ O ₃	0.07	0.0059	80	15	1.5	29	417
5	Au/TiO ₂ (W)	0.15	0.0059	80	15	1.5	22	145
6	Au/C (W)	0.1	0.0059	80	15	1.5	23	232
7	Blank	-	-	80	15	1.5	0	n/a
8	Au/ZnO	0.13	0.0059	100	15	1.5	24	186
9	Au/Fe ₂ O ₃	0.08	0.0059	100	15	1.5	36	446
10	Au/TiO ₂	0.16	0.0059	100	15	1.5	35	220
11	Au/Al ₂ O ₃	0.07	0.0059	100	15	1.5	28	395
12	Au/TiO ₂ (W)	0.15	0.0059	100	15	1.5	39	261
13	Au/C (W)	0.1	0.0059	100	15	1.5	36	358
14	Au/ZnO	0.13	0.0059	80	15	0.5	30	233
15	Au/Fe ₂ O ₃	0.08	0.0059	80	15	0.5	35	436
16	Au/TiO ₂	0.16	0.0059	80	15	0.5	34	212
17	Au/Al ₂ O ₃	0.07	0.0059	80	15	0.5	37	534
18	Au/TiO ₂ (W)	0.15	0.0059	80	15	0.5	31	207
19	Au/C (W)	0.1	0.0059	80	15	0.5	28	279
20	Au/ZnO	0.1	0.0045	100	15	0.5	28	279
21	Au/Fe ₂ O ₃	0.1	0.0074	100	15	0.5	41	414
22	Au/TiO ₂	0.1	0.0037	100	15	0.5	40	395
23	Au/Al ₂ O ₃	0.1	0.0084	100	15	0.5	43	431
24	Au/TiO ₂ (W)	0.1	0.0037	100	15	0.5	28	291
25	Au/C (W)	0.1	0.0059	100	15	0.5	27	269
26	Au/Fe ₂ O ₃	0.1	0.0074	100	15	0.25	34	344
27	Au/TiO ₂	0.1	0.0037	100	15	0.25	35	351
28	Au/Al ₂ O ₃	0.1	0.0084	100	15	0.25	31	313
29	Au/Fe ₂ O ₃	0.1	0.0074	100	60	0.5	40	401
30	Au/TiO ₂	0.1	0.0037	100	60	0.5	44	438
31	Au/Al ₂ O ₃	0.1	0.0084	100	60	0.5	40	400
32	Au/ZnO	0.1	0.0045	150	15	0.5	63	633
33	Au/Fe ₂ O ₃	0.1	0.0074	150	15	0.5	66	659
34	Au/TiO ₂	0.1	0.0037	150	15	0.5	64	639
35	Au/Al ₂ O ₃	0.1	0.0084	150	15	0.5	67	672
36	Au/TiO ₂ (W)	0.1	0.0037	150	15	0.5	60	602
37	Au/C (W)	0.1	0.0059	150	15	0.5	62	622
38	Blank	-	-	150	15	0.5	28	n/a

39	Au/ZnO	0.5	0.0225	150	15	0.5	67	134
40	Au/Fe ₂ O ₃	0.5	0.037	150	15	0.5	73	146
41	Au/TiO ₂	0.5	0.0185	150	15	0.5	75	150
42	Au/Al ₂ O ₃	0.5	0.0420	150	15	0.5	70	140
43	Au/TiO ₂ (W)	0.5	0.0195	150	15	0.5	69	139
44	Au/C (W)	0.5	0.0295	150	15	0.5	67	134
45	Au/TiO ₂	1.0	0.037	150	15	0.5	79	79
46	Au/TiO ₂	1.5	0.056	150	15	0.5	76	51
47	Au/TiO ₂	0.5	0.0185	150	15	0.5	74	149 ^e
48	Au/TiO ₂	0.5	0.0185	150	15	0.5	73	146 ^f
49	ZnO	10.0	0.0024	150	15	0.5	31	3
50	Fe ₂ O ₃	10.0	0.0048	150	15	0.5	30	3
51	TiO ₂	10.0	0.0024	150	15	0.5	27	3
52	Al ₂ O ₃	10.0	0.0031	150	15	0.5	27	3

^a Reaction conditions: benzyl bromide (0.30 mmol), phenylacetylene (0.33 mmol), NaN₃ (0.33 mmol), H₂O: MeCN (1:1 v/v), MW (30 W). ^b Calculated vs. benzyl bromide. ^c Isolated yield. ^d Turnover number = moles of product per mol of catalyst. ^e NH₄OH (0.66 mmol) was added to the reaction mixture. ^f Trifluoroacetic acid (0.66 mmol) was added to the reaction mixture.

2. N₂ adsorption-desorption isotherms and pore size distributions for the metal oxide supports

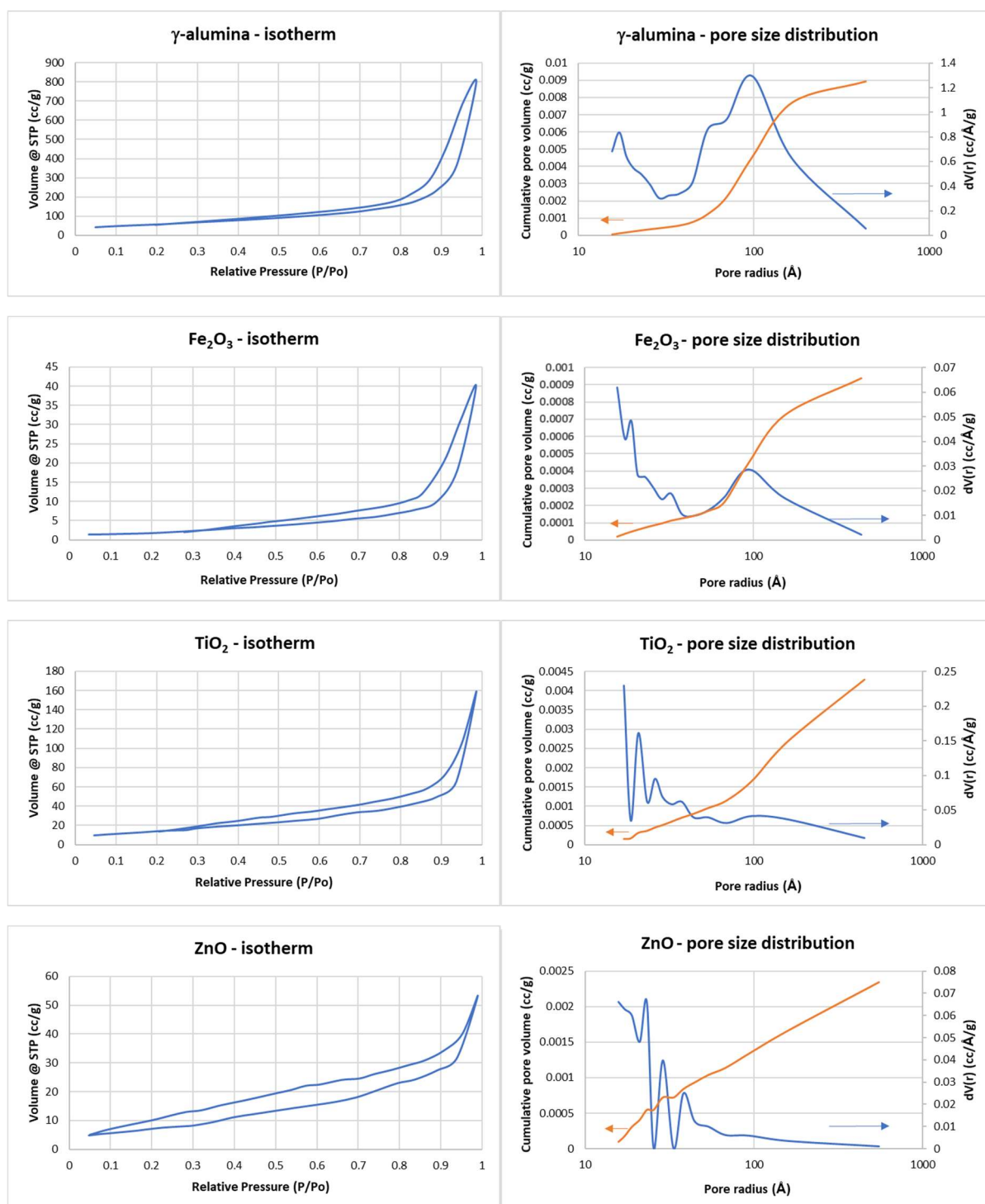


Figure S1. N₂ adsorption-desorption isotherms obtained at -196 °C and respective pore size distributions (BJH desorption) for the metal oxide supports.

3. ^1H NMR spectra of 1,2,3-triazoles obtained by AuNPs catalyzed AAC

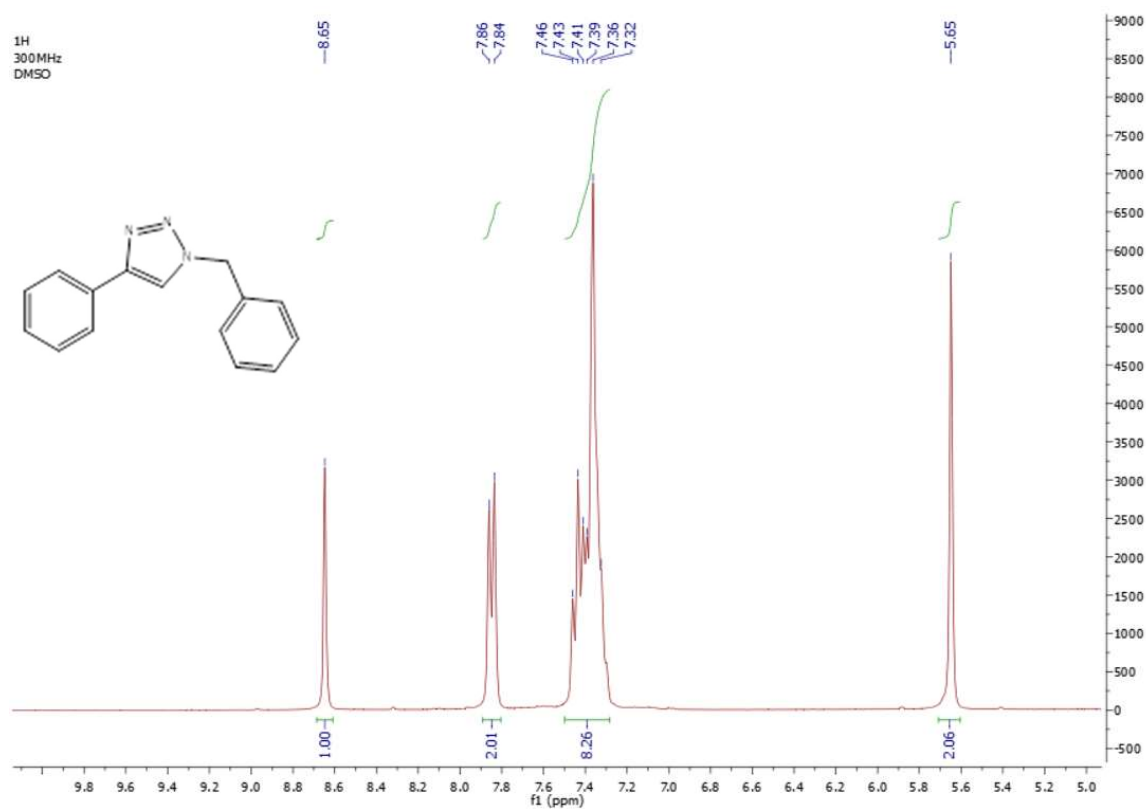


Figure S2. ^1H NMR spectrum of 1-benzyl-4-phenyl-1H-1,2,3-triazole obtained by AAC catalysed by Au/TiO₂ NPs at 150 °C.

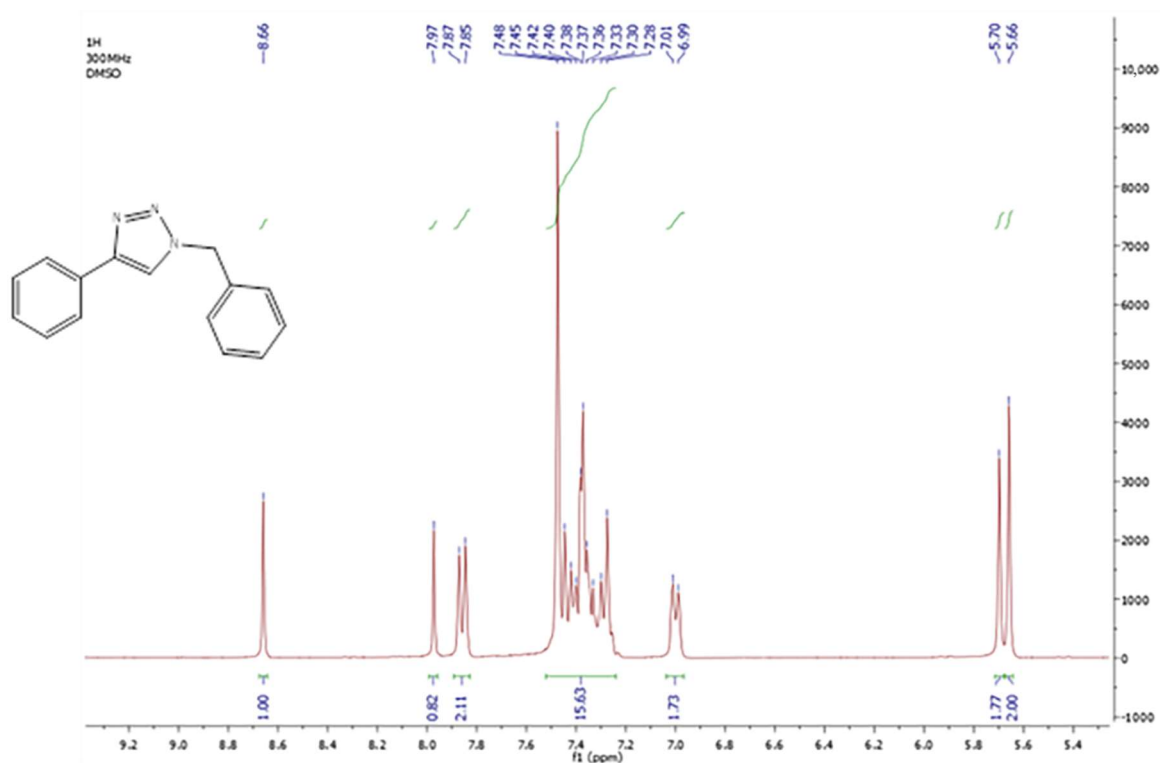


Figure S3. ^1H NMR spectrum of a blank sample at 150 °C.

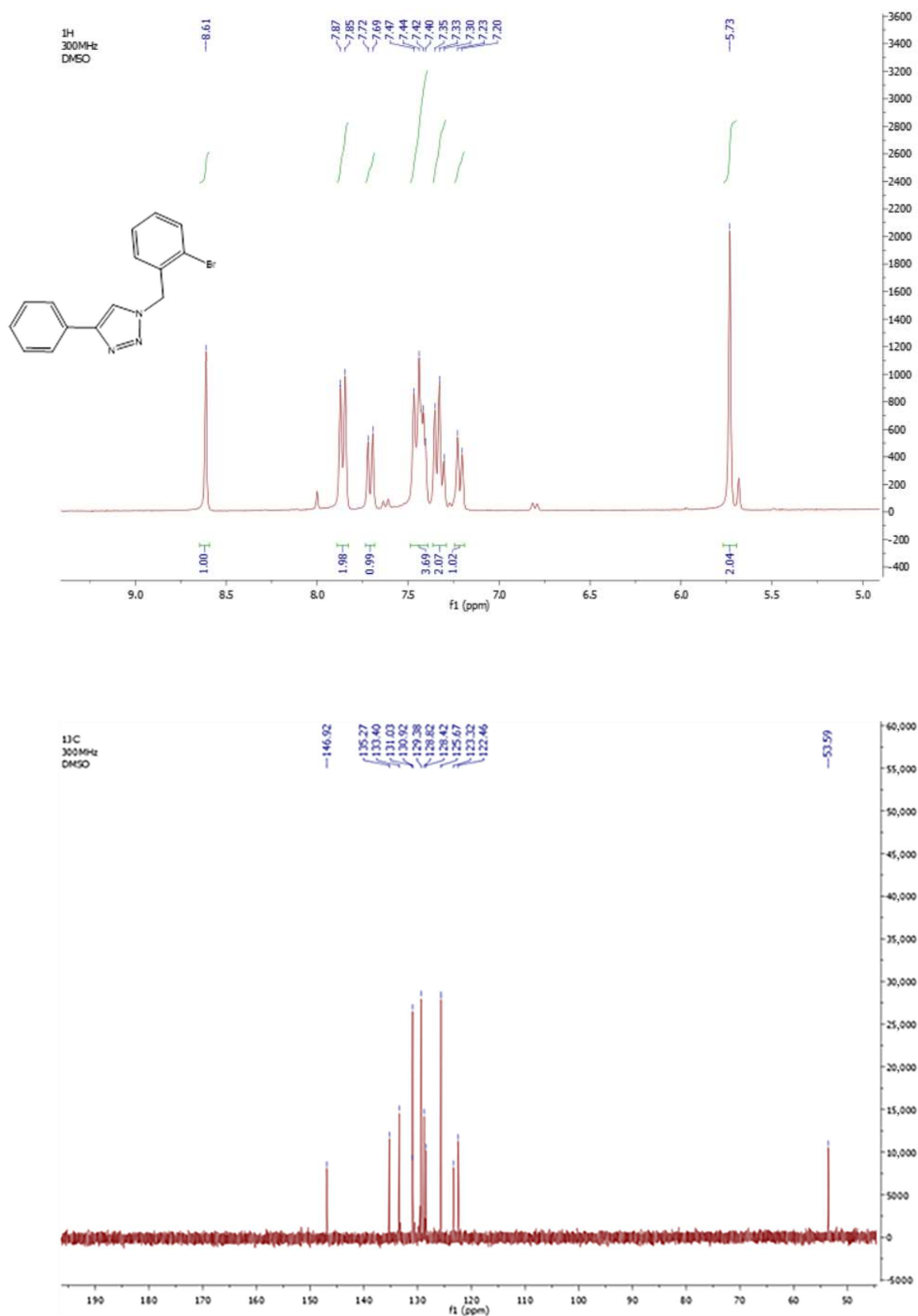


Figure S4. ¹H and ¹³C NMR spectra of 1-(2-bromobenzyl)-4-phenyl-1H-1,2,3-triazole.

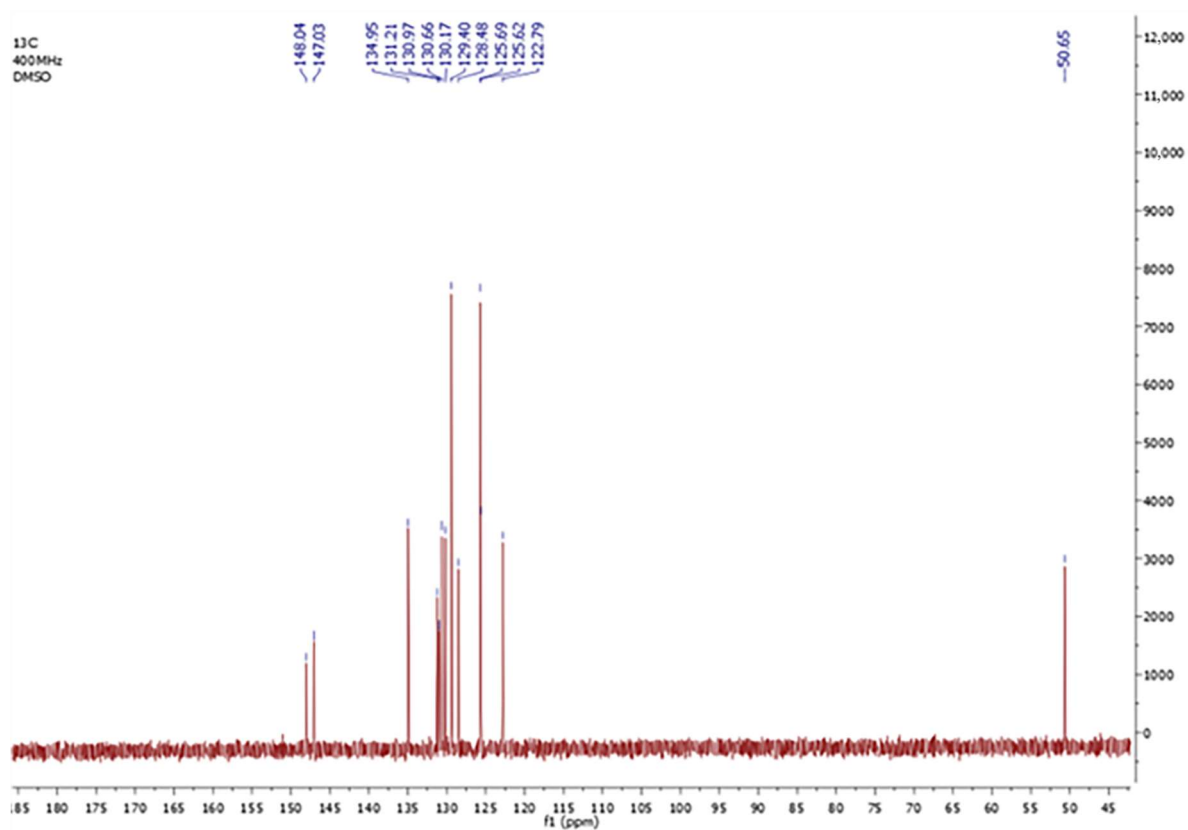
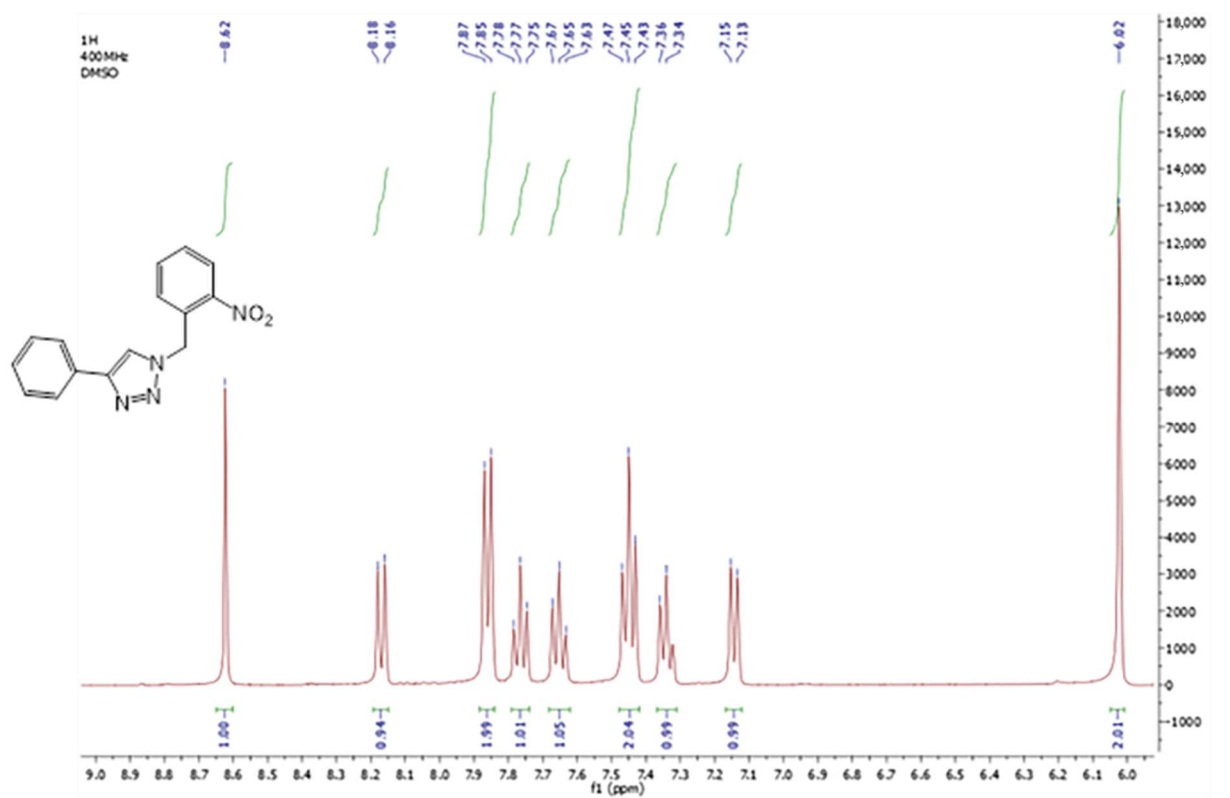


Figure S5. ¹H and ¹³C NMR spectra of 1-(2-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole.

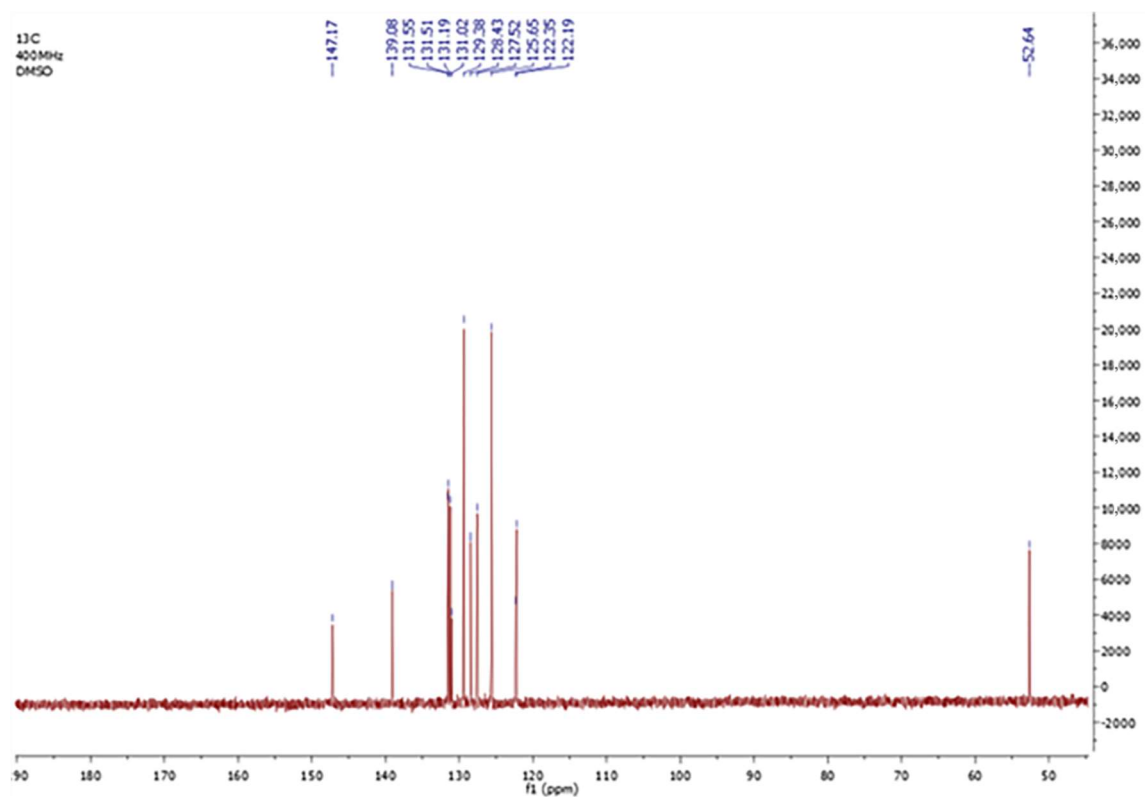
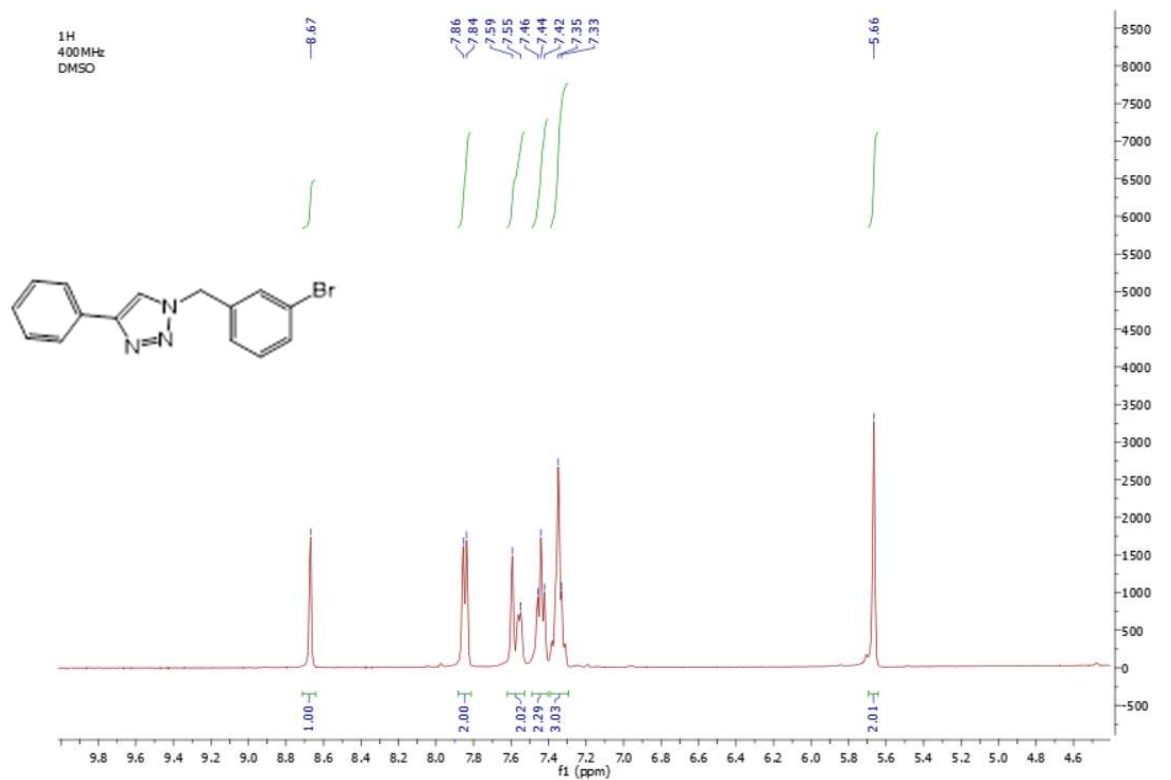


Figure S6. ¹H and ¹³C NMR spectra of 1-(3-bromobenzyl)-4-phenyl-1H-1,2,3-triazole.

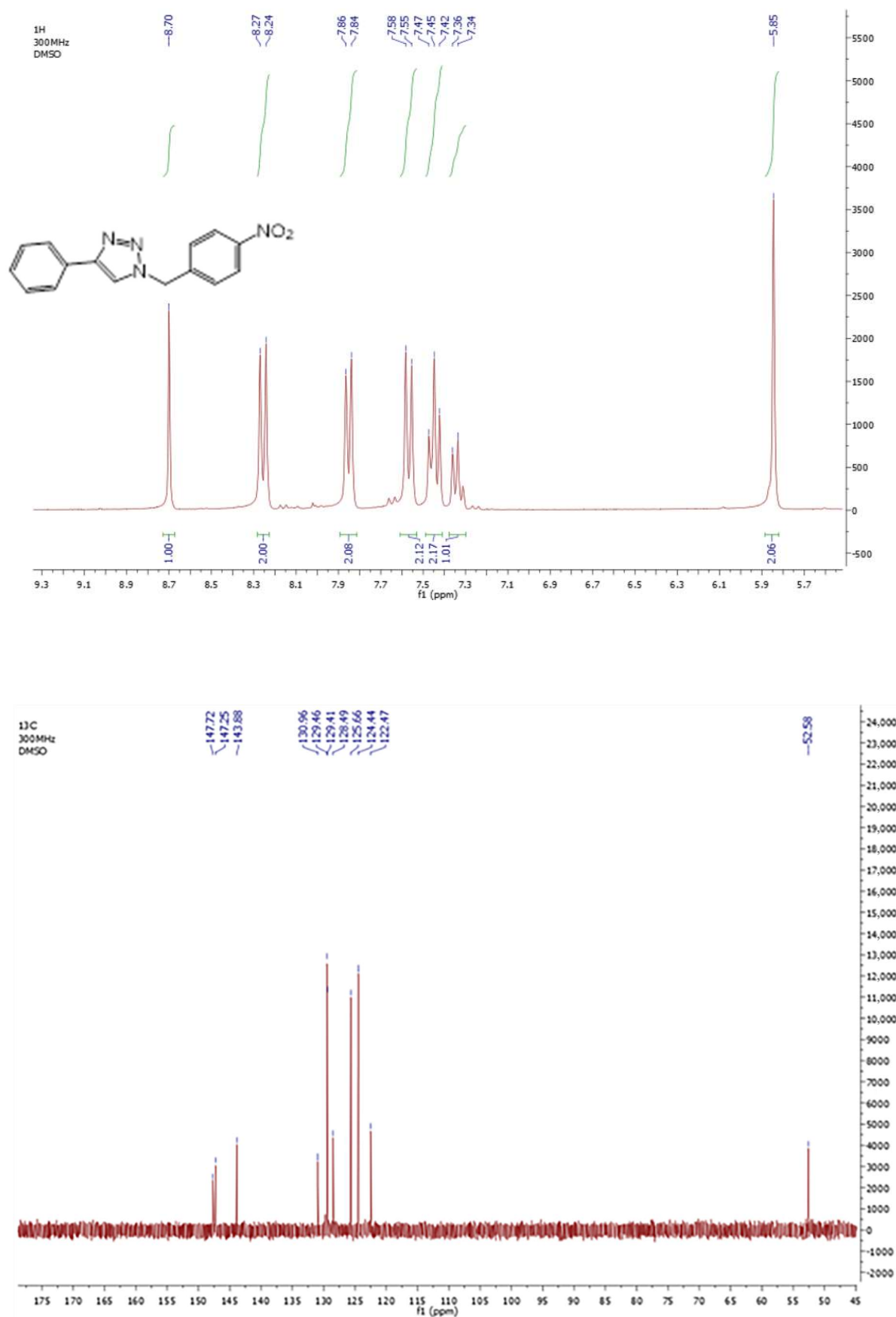


Figure S7. ¹H and ¹³C NMR spectra of 1-(4-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole.

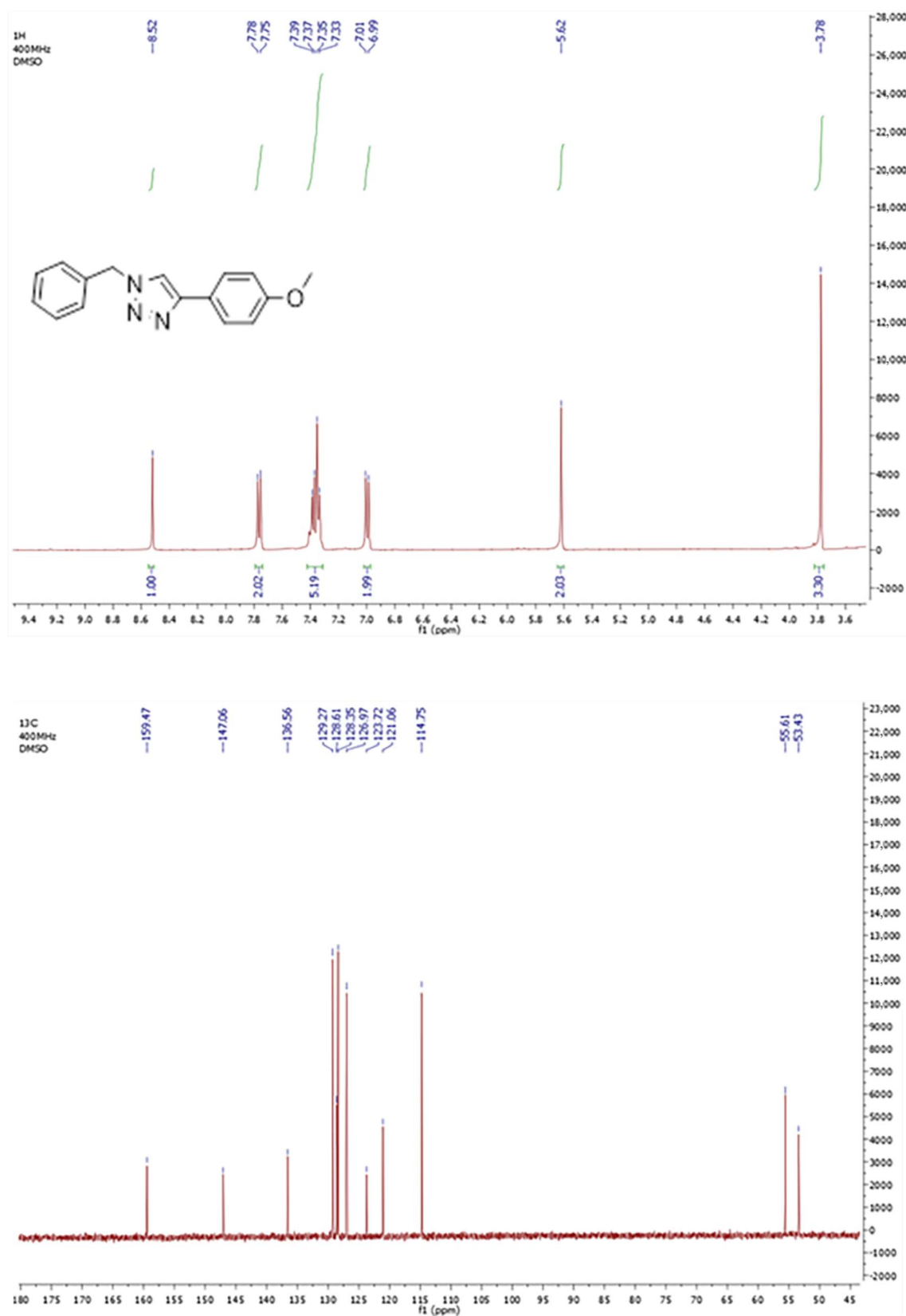


Figure S8. ¹H and ¹³C NMR spectra of 1-benzyl-4-(4-methoxyphenyl)-1H-1,2,3-triazole.

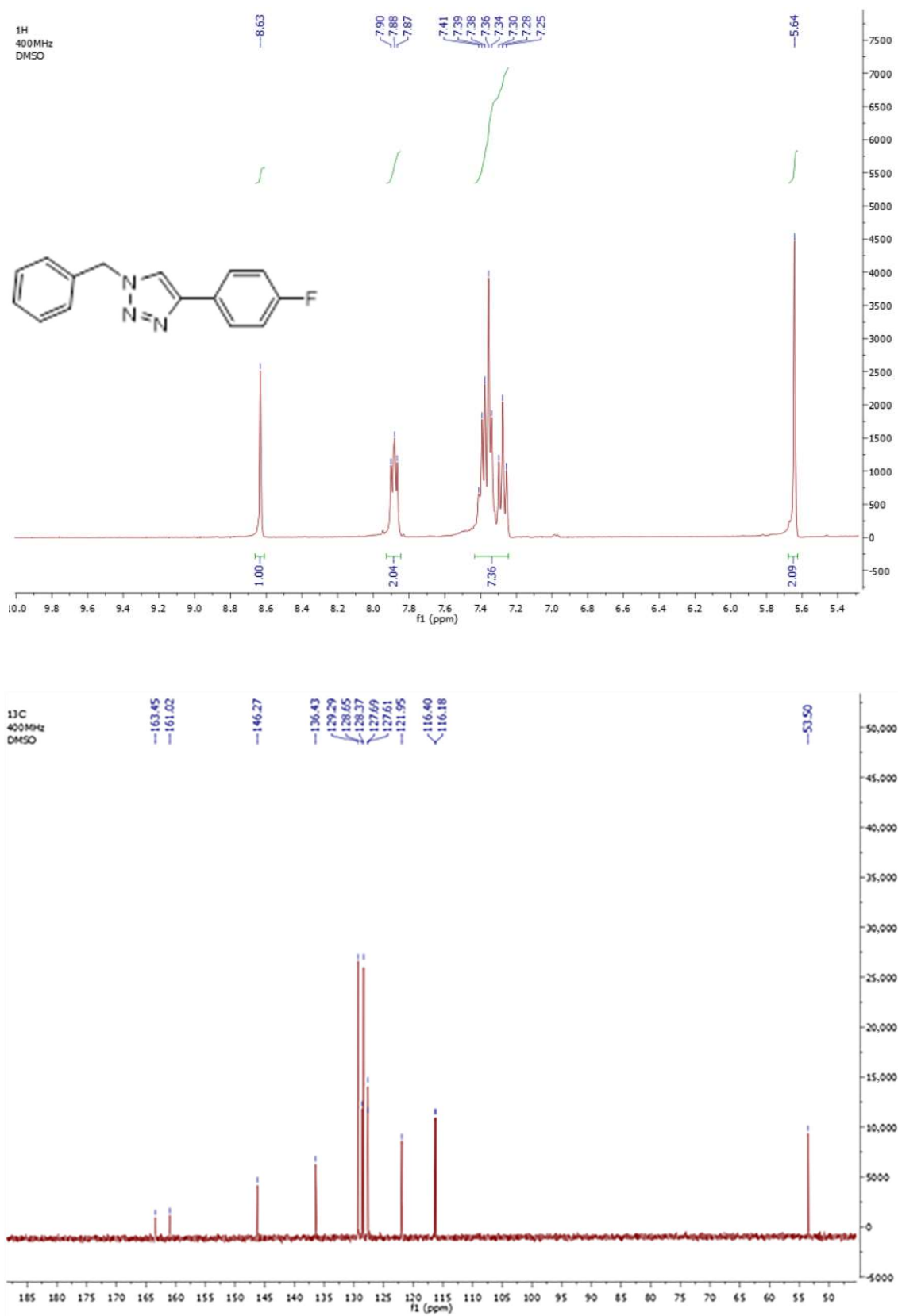


Figure S9. ¹H and ¹³C NMR spectra of 1-benzyl-4-(4-fluorophenyl)-1H-1,2,3-triazole.

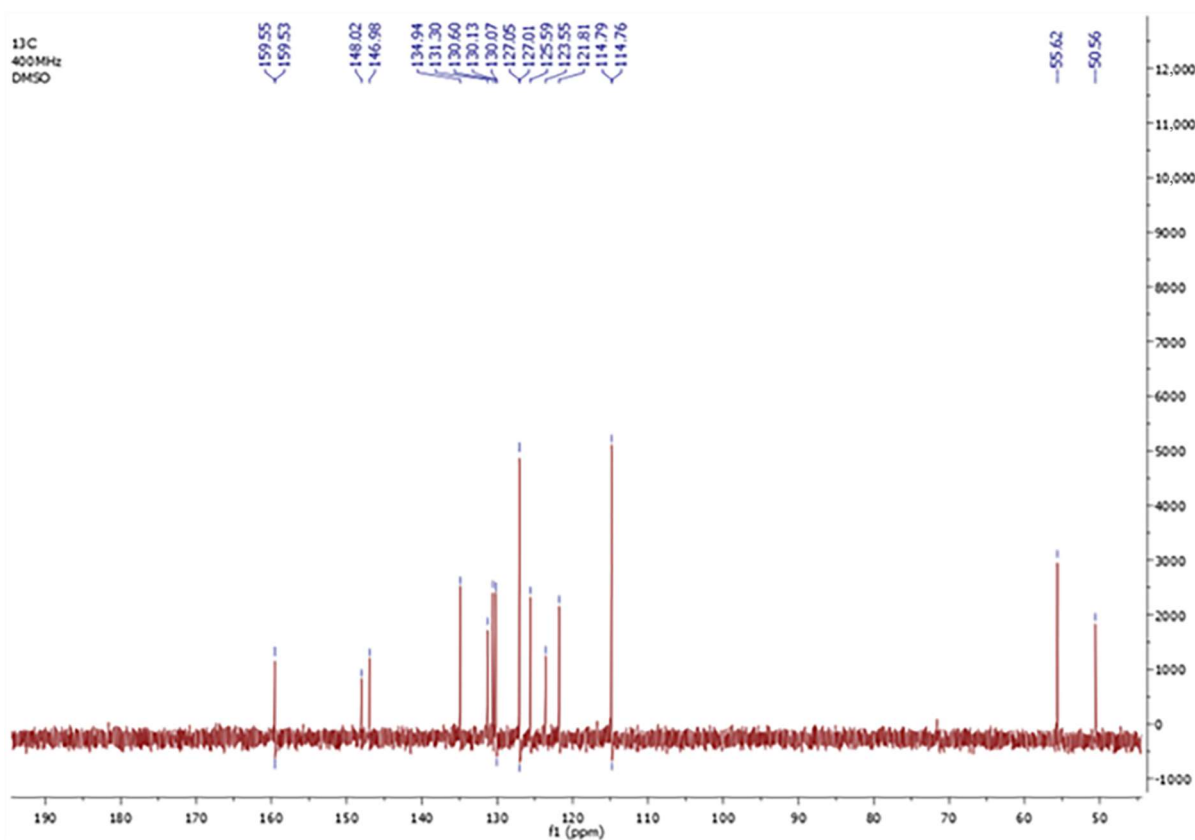
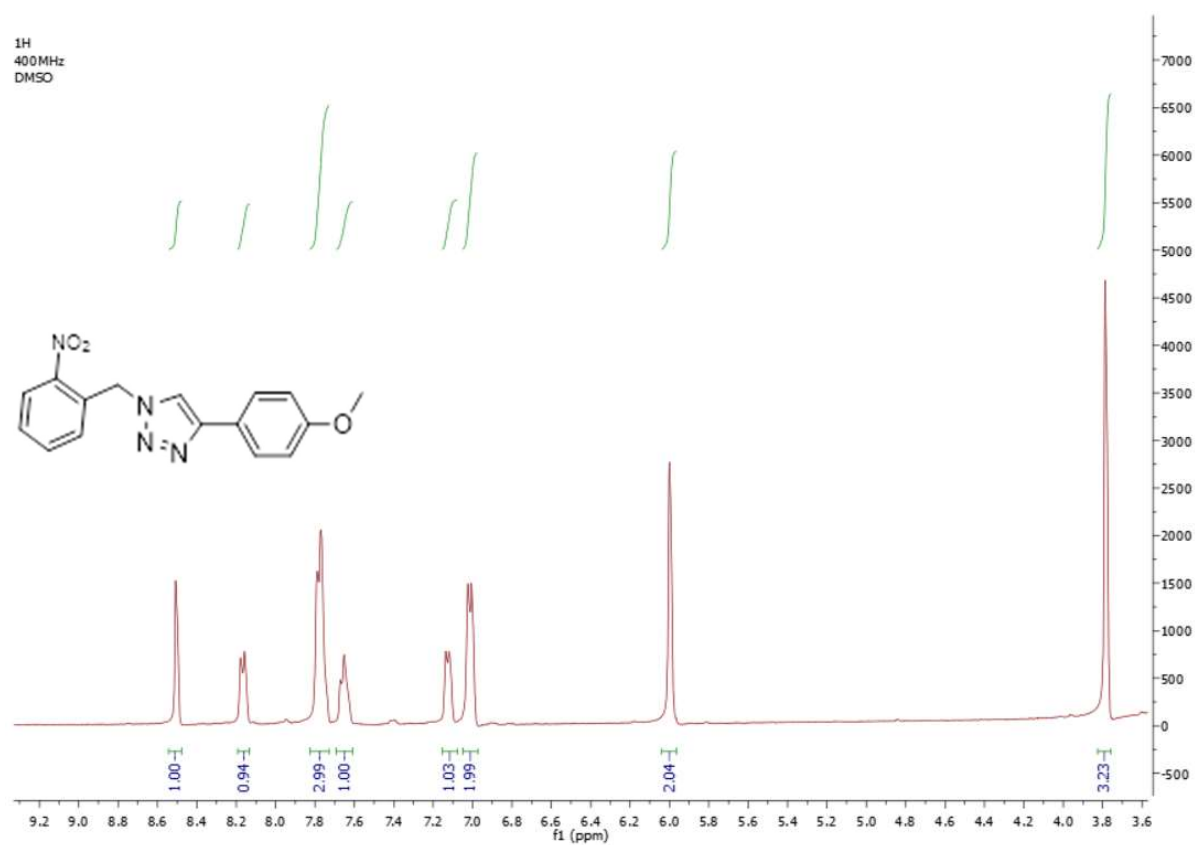


Figure S10. ¹H and ¹³C NMR spectra of 4-(4-methoxyphenyl)-1-(2-nitrobenzyl)-1H-1,2,3-triazole.

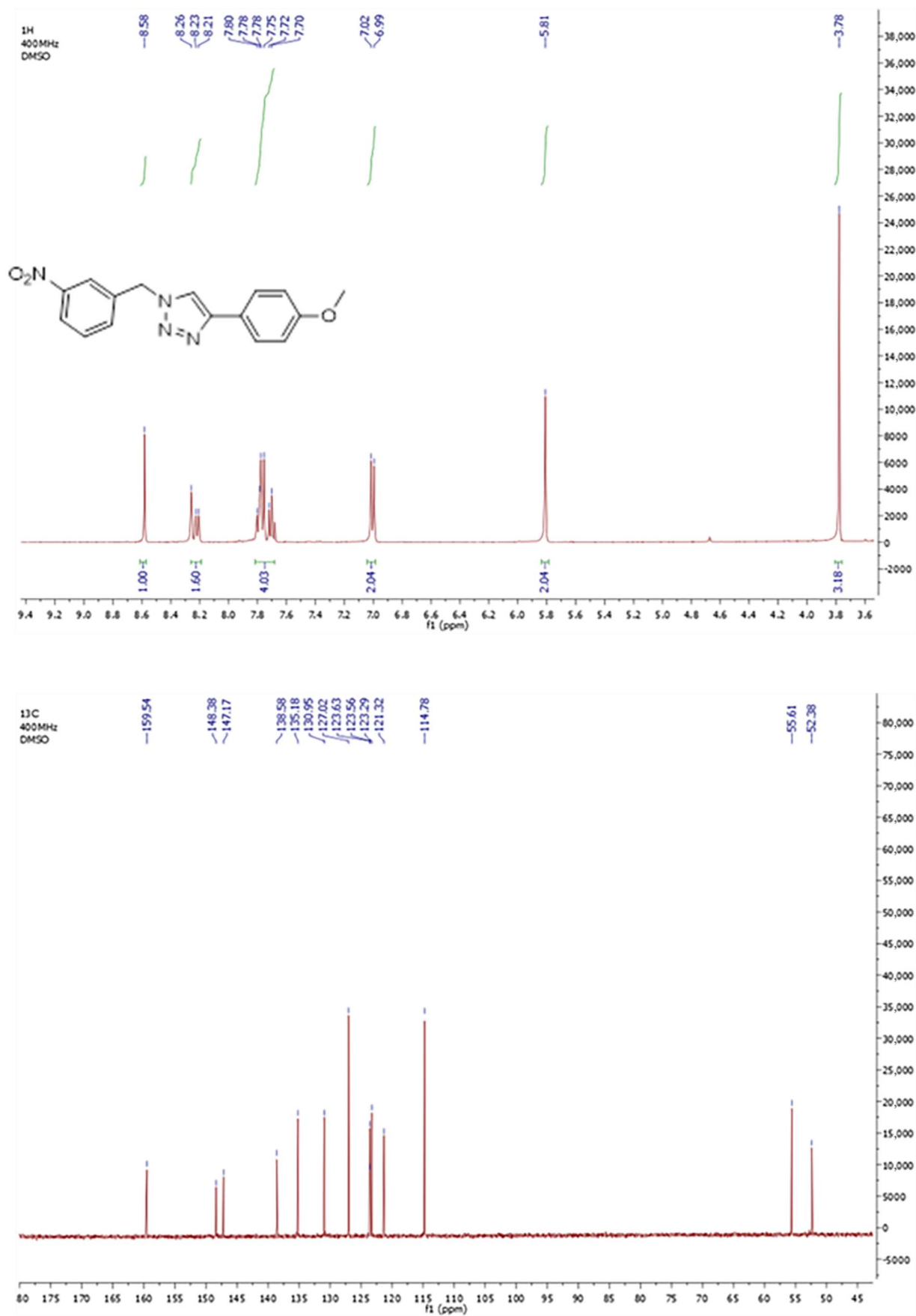


Figure S11. ¹H and ¹³C NMR spectra of 4-(4-methoxyphenyl)-1-(3-nitrobenzyl)-1H-1,2,3-triazole.

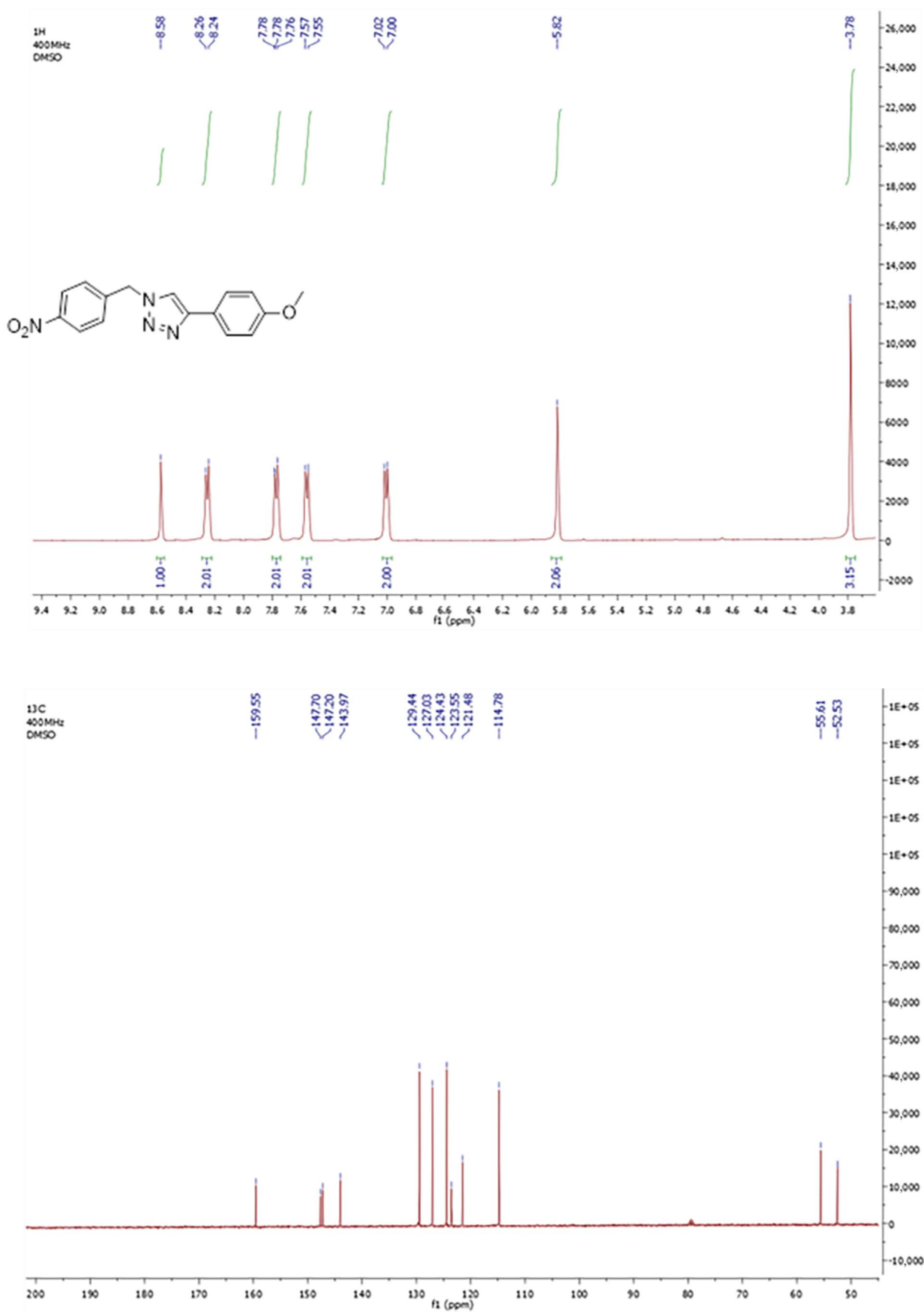


Figure S12. ¹H and ¹³C NMR spectra of 4-(4-methoxyphenyl)-1-(4-nitrobenzyl)-1H-1,2,3-triazole.

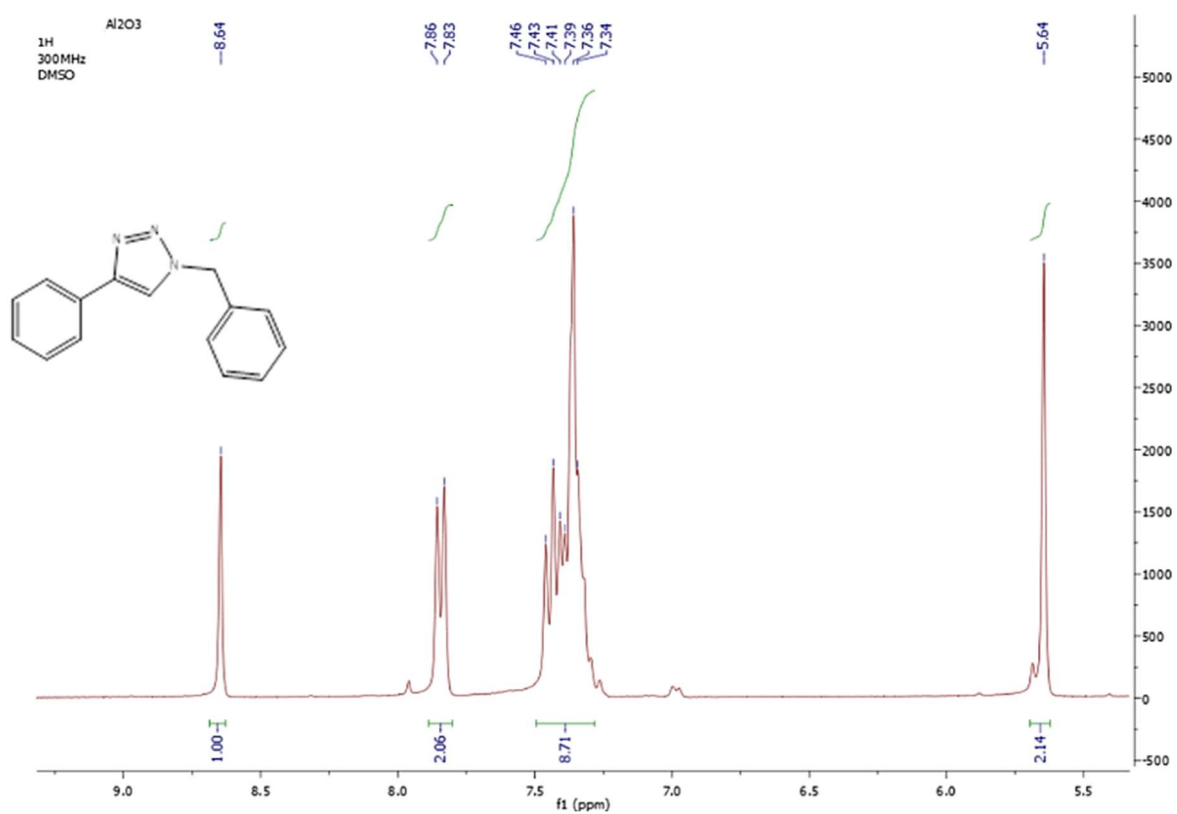


Figure S13. ¹H NMR spectrum of 1-benzyl-4-phenyl-1H-1,2,3-triazole from reaction catalysed by Al₂O₃ at 150 °C.

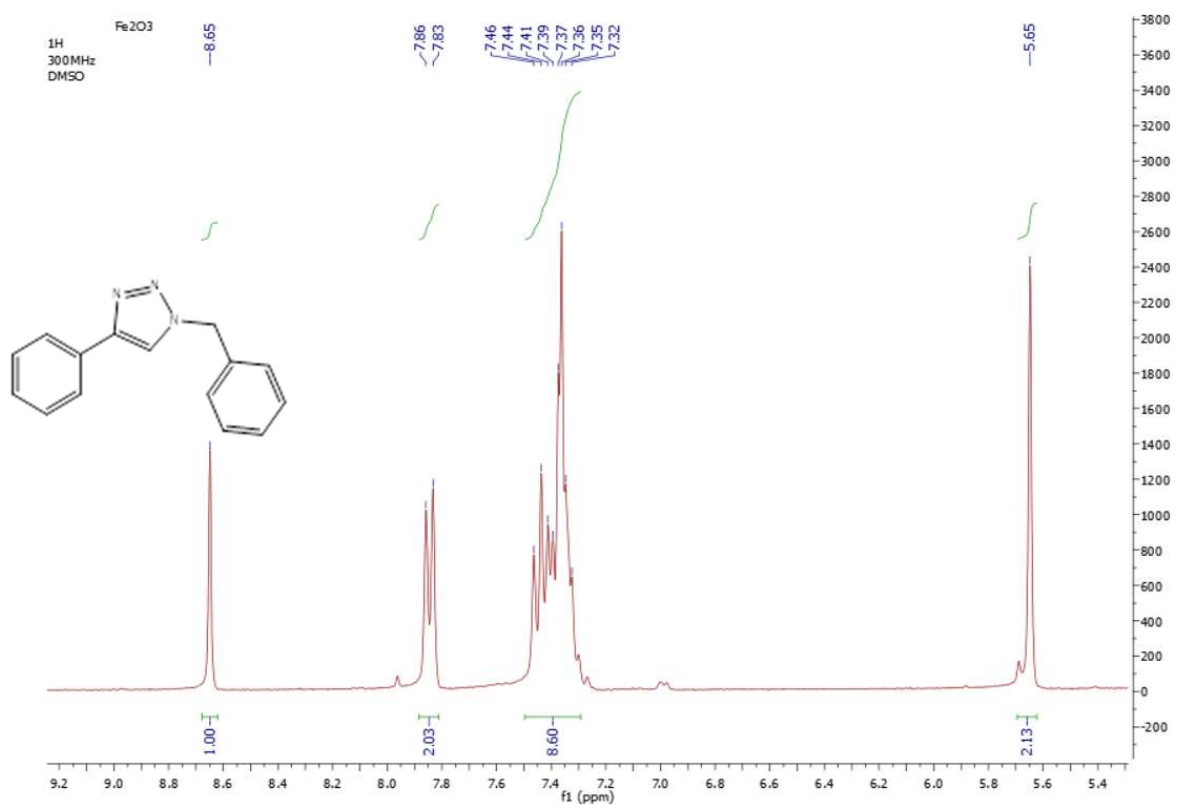


Figure S14. ¹H NMR spectrum of 1-benzyl-4-phenyl-1H-1,2,3-triazole from reaction catalysed by Fe₂O₃ at 150 °C.

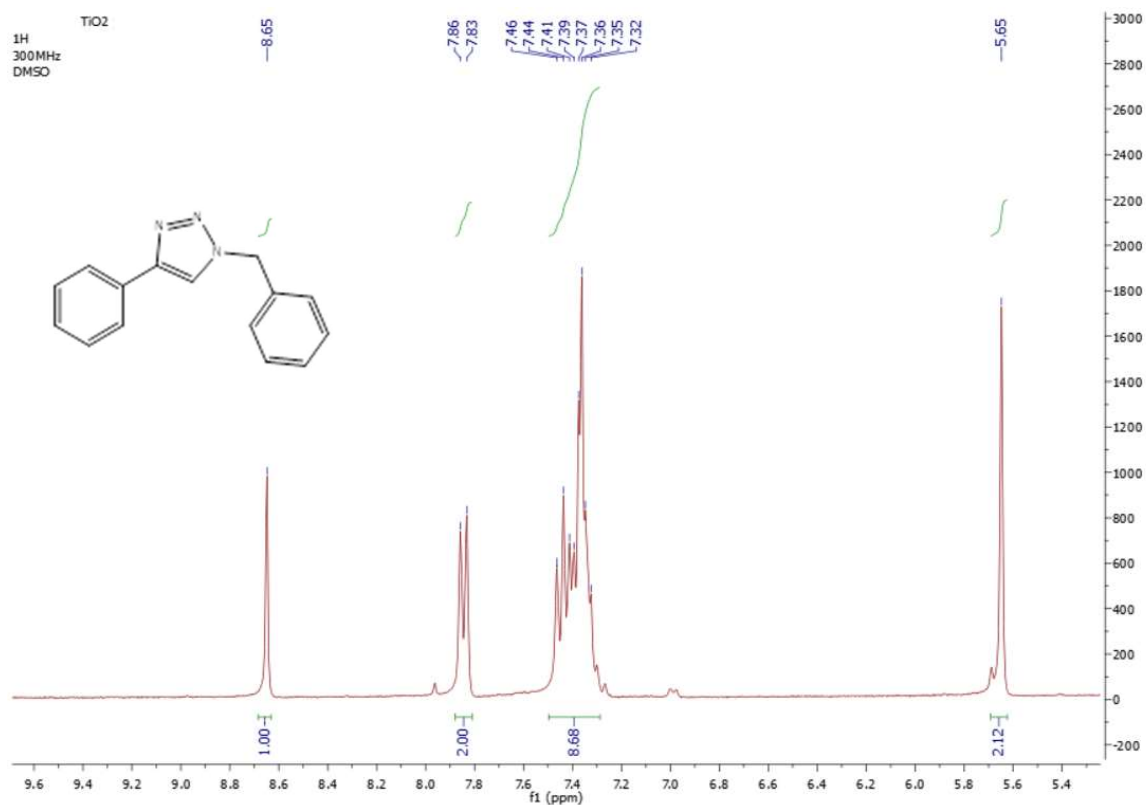


Figure S15. ¹H NMR spectrum of 1-benzyl-4-phenyl-1H-1,2,3-triazole from reaction catalysed by TiO₂ at 150 °C.

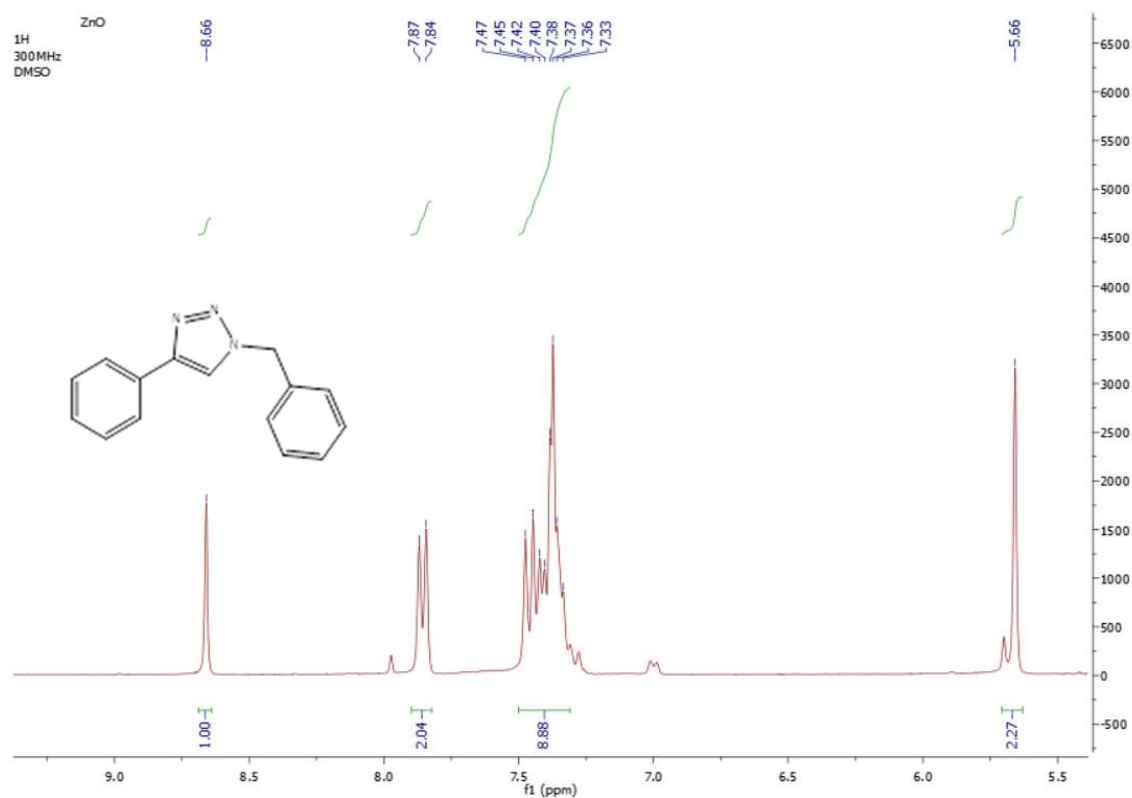


Figure S16. ¹H NMR spectrum of 1-benzyl-4-phenyl-1H-1,2,3-triazole from reaction catalysed by ZnO at 150 °C.

4. TEM images of Au/ TiO₂ after recycling (the darker spots correspond to Au NPs).

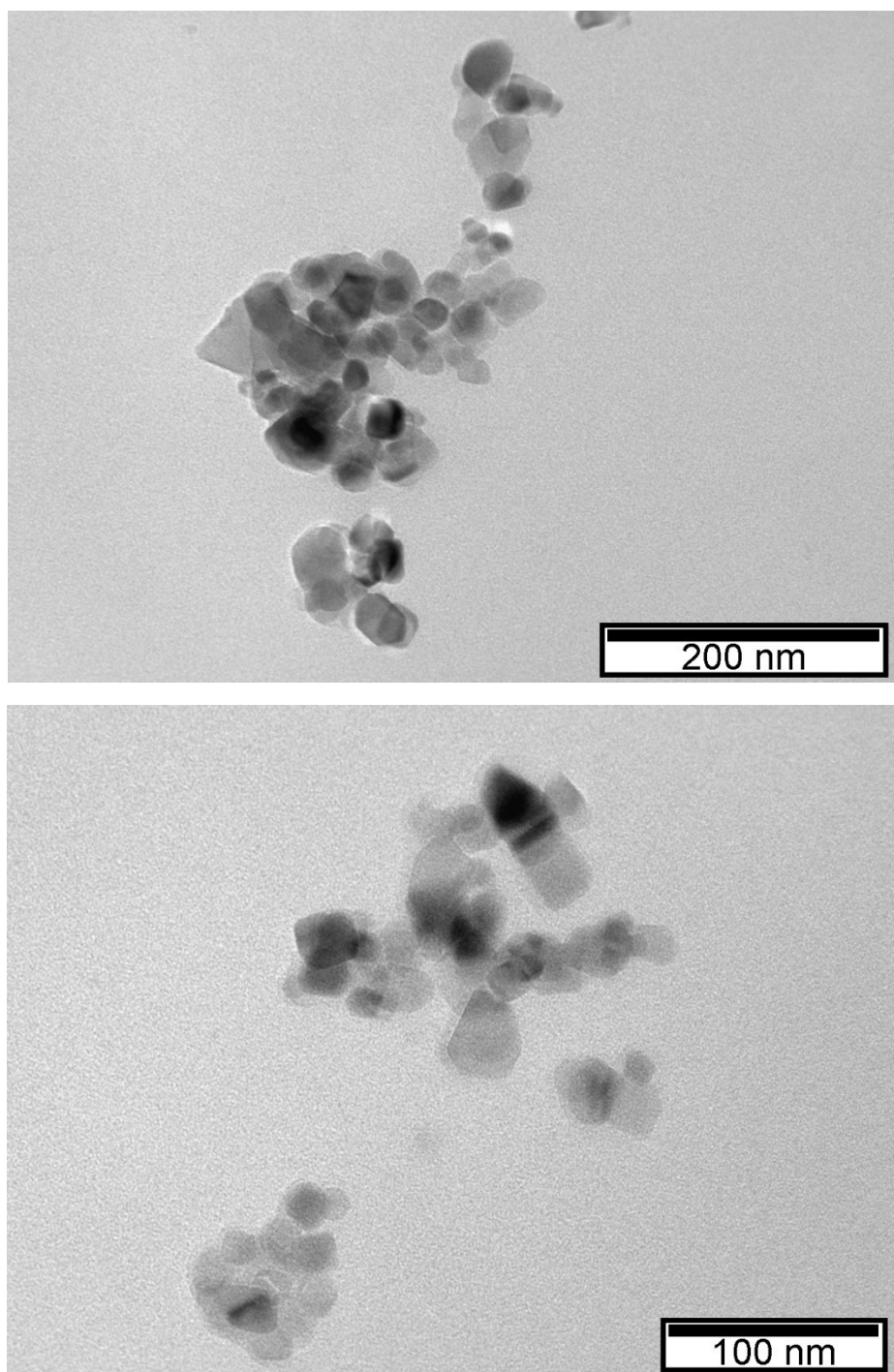


Figure S17. TEM images of Au/TiO₂ after 5 cycle runs.

5. The O 1s XPS spectra of the metal oxide supports and the Au-based materials.

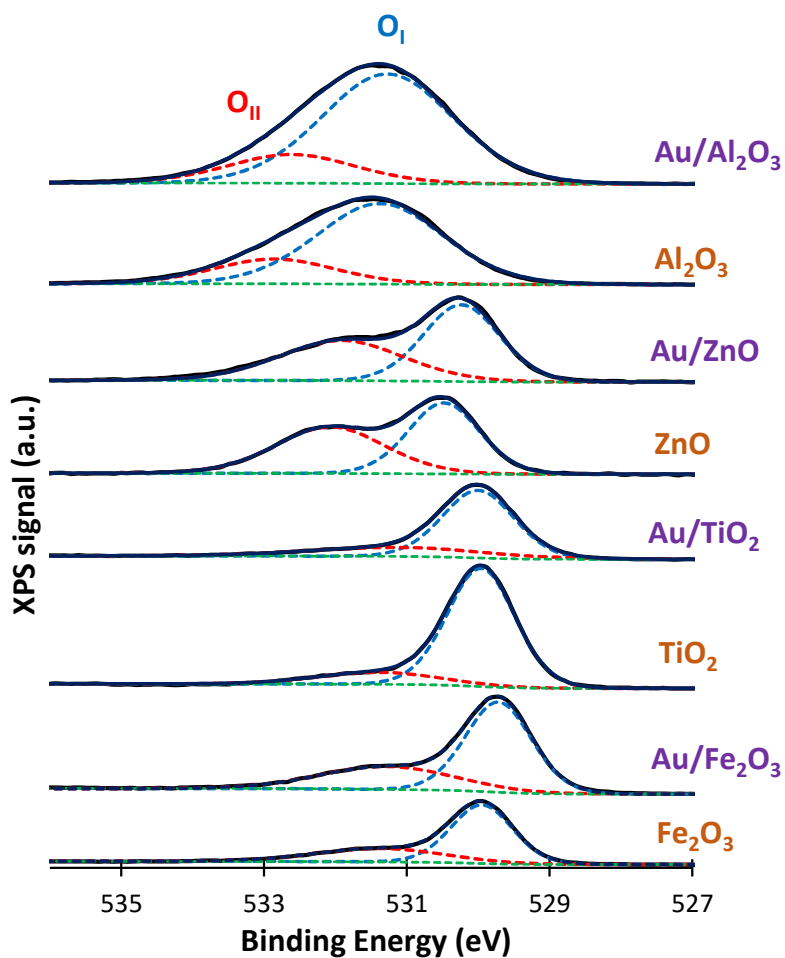


Figure S18. O 1s XPS spectrum of metal oxides and supported Au NP-based catalysts (adapted from Martins, L.M.D.R.S.; Carabineiro, S.A.C.; Wang, J.; Rocha, B.G.M.; Maldonado-Hódar, F.J.; Pombeiro, A.J.L. Supported Gold Nanoparticles as Reusable Catalysts for Oxidation Reactions of Industrial Significance. *ChemCatChem* **2017**, *9*, 1211–1221, doi:10.1002/cctc.201601442 with permission from Wiley).