Supplementary material

Mesostructured silica-zirconia-tungstophosphoric acid composites as catalyst in calcium channel blocker nifedipine synthesis

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1. Catalysts characterization

Thermal gravimetric analysis (TGA)

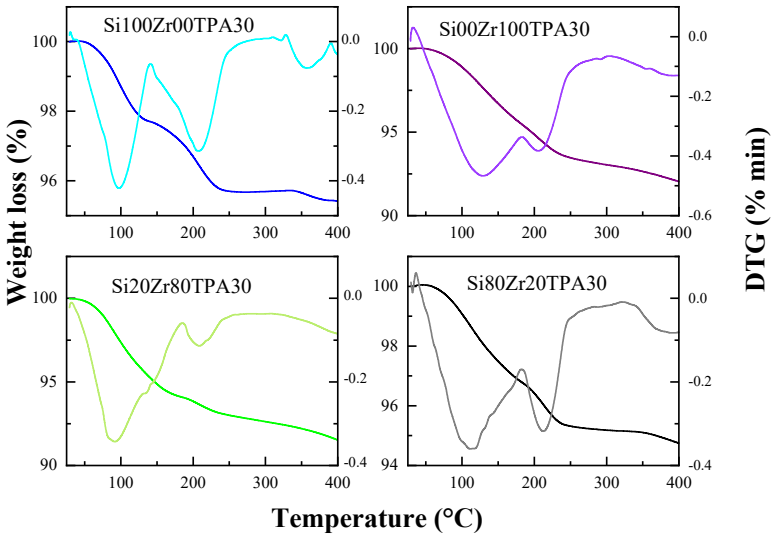

Figure S1. Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG)

Table S1. Weight loss

Material	First loss		Second loss		Total loss (%)
	Weight (%)	Temperature (°C)	Weight (%)	Temperature (°C)	
Si100Zr00TPA30	1.18	97.24	2.38	207.95	3.53
Si80Zr20TPA30	1.45	114.93	2.53	212.79	3.98
Si20Zr80TPA30	2.11	92.12	4.23	207.89	6.34
Si00Zr100TPA30	2.37	129.23	3	205.73	5.37

Potentiometric titration of supports

Table S2. Initial electrode potential (Ei) and total number of acid sites values of supports

Sample	Ei (mV)	Number of acid sites (meq n-butylamine/g)
Si100Zr00TPA00	106	134
Si80Zr20TPA00	117	170
Si20Zr80TPA00	121	97
Si00Zr100TPA00	62	81

Absorption spectrometry

The TPA content in the SiXXZrYYTPA30 materials was estimated as the difference between the amount contained in the tungstophosphoric acid solution originally used for the impregnation and the amount of W that remained in the beaker after removing the dried samples. The content of W present in the final solution was determined by atomic absorption spectrometry using IL457 spectrophotometer (Instrumentation Laboratory Inc). The calibration curve method was used with standards prepared in the laboratory. The analyses were carried out at a wavelength of 255.1 nm, band width 0.3 nm, lamp current 15

mA, phototube amplification 800 V, burner height 4 mm, and acetylene–nitrous oxide flame (11:14). The results obtained revealed that the TPA was fully incorporated in support.

2. Compounds characterization

Mass Spectrum Electronic Impact of substrates, intermediates and product

Compound 1: m/z = 151 (M^+) (1 %), 134 (2 %), 121 (100 %), 104 (22 %), 93 (48 %), 76 (37 %), 65 (64 %), 51 (47 %), 39 (22 %).

Compound 2: m/z = 116 (M^+) (6 %), 85 (9 %), 74 (9 %), 69 (10 %), 59 (11 %), 43 (100 %), 31 (71 %), 15 (13 %).

Compound P1**:** m/z = 115 (M^+) (100 %), 88 (18 %), 84 (45%), 59 (38 %), 55 (51 %), 43 (20 %), 27 (18%).

Compound P2**:** m/z 249 (M^+) (not observed), 207 (1 %), 203 (18 %), 175 (15%), 148 (12 %) 130 (20 %), 120 (62%), 104 (22%), 92 (32%), 43 (100%).

Compound 4 (Nifedipine): 346 (10 %), 329 (100 %), 315 (5%), 298 (6%), 284 (91 %), 268 (50 %), 224 (71 %), 192 (10 %), 77 (12 %).

Compound 6: m/z 344 (<1 %) 298 (100) 312 (20), 281 (25).

Compound 7: 346 (5%), 328 (10), 315 (15), 298 (80), 284 (50), 269 (48), 252 (55), 224 (100), 192 (50). 162 (30).

^{1}H and ^{13}C NMR Spectrum of compound 7 and 8

Compound 7

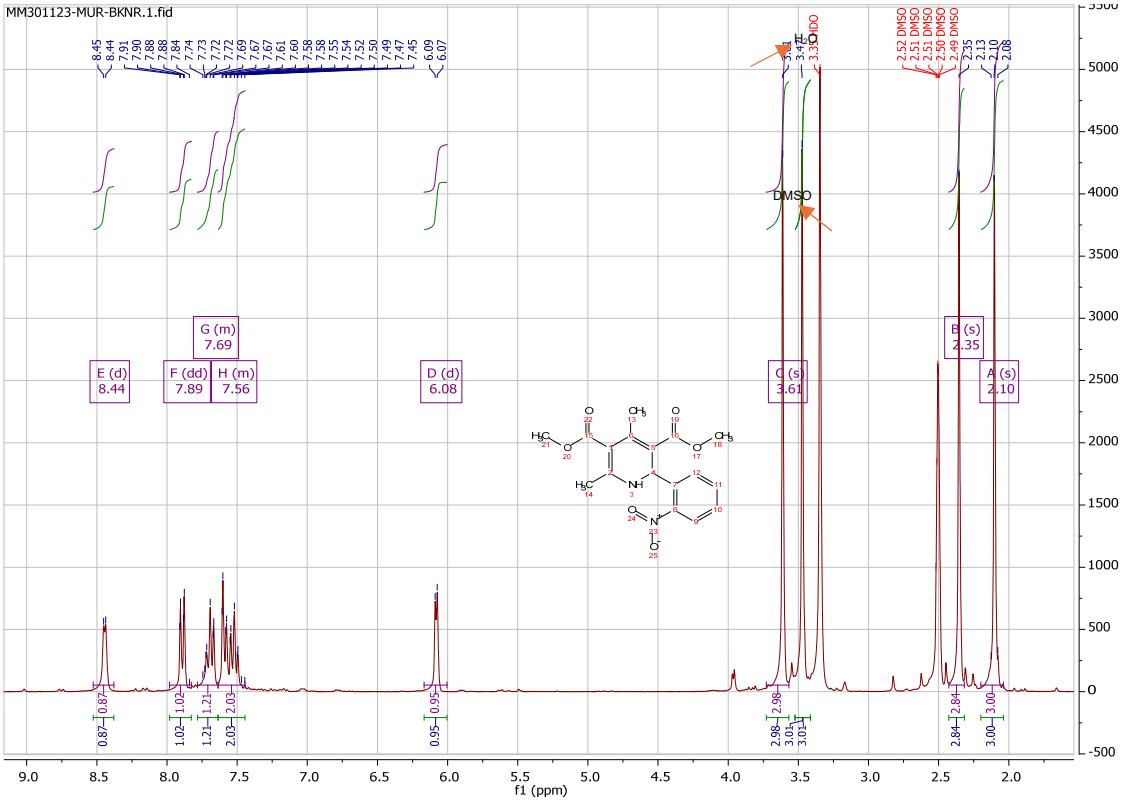

Figure S2. Compound 7: ^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ 8.43 (d, *J* = 4.1 Hz, 1H), 7.89 (d, *J* = 5.9 Hz, 1H), 7.74-7.65 (m, 1H), 7.61-7.54 (m, 2H), 6.08 (d, *J* = 4.3 Hz, 1H), 3.61 (s, 3H), 3.47 (s, 3H), 2.35 (s, 3H), 2.10 (s, 3H).

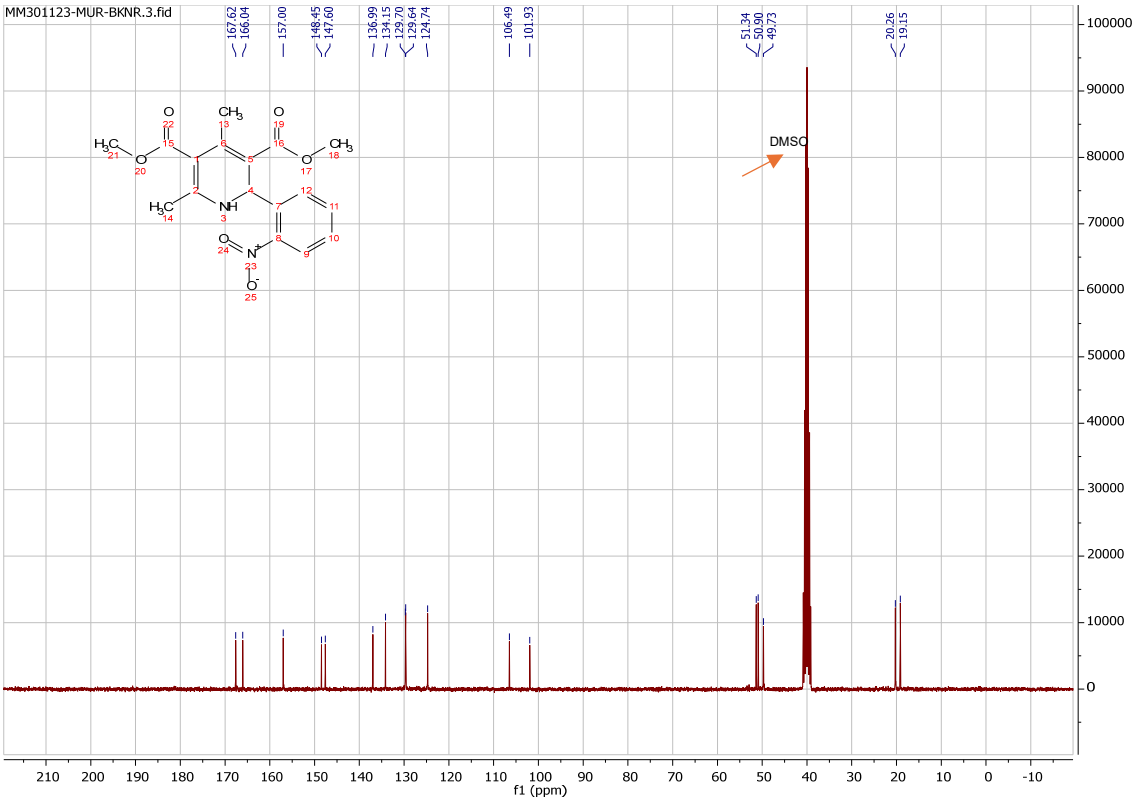

Figure S3. Compound 7: ^{13}C NMR (75 MHz, DMSO) δ 167.62, 166.04, 157.07, 148.45, 147.60, 136.99, 134.15, 129.70, 129.64, 124.74, 106.49, 101.93, 50.90, 49.73, 20.26, 19.15.

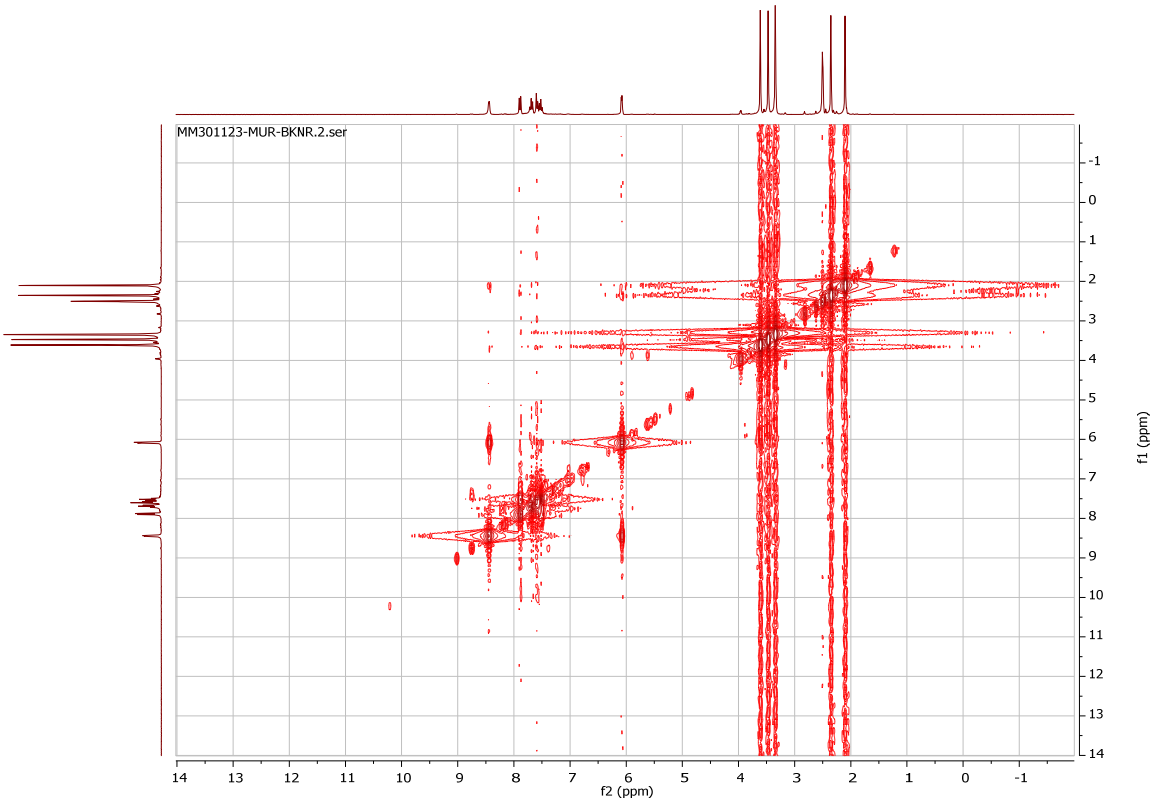

Figure S4. Compound 7: ^{1}H-^{1}H COSY NMR (300 MHz, DMSO-*d*6), δ_H/δ_H: 8.45/8.68, 7.65/7.93, 7.51/7.29, 6.08/5.84, 3.61/3.85, 3.47/3.24, 2.35/2.28, 2.10/1.87.

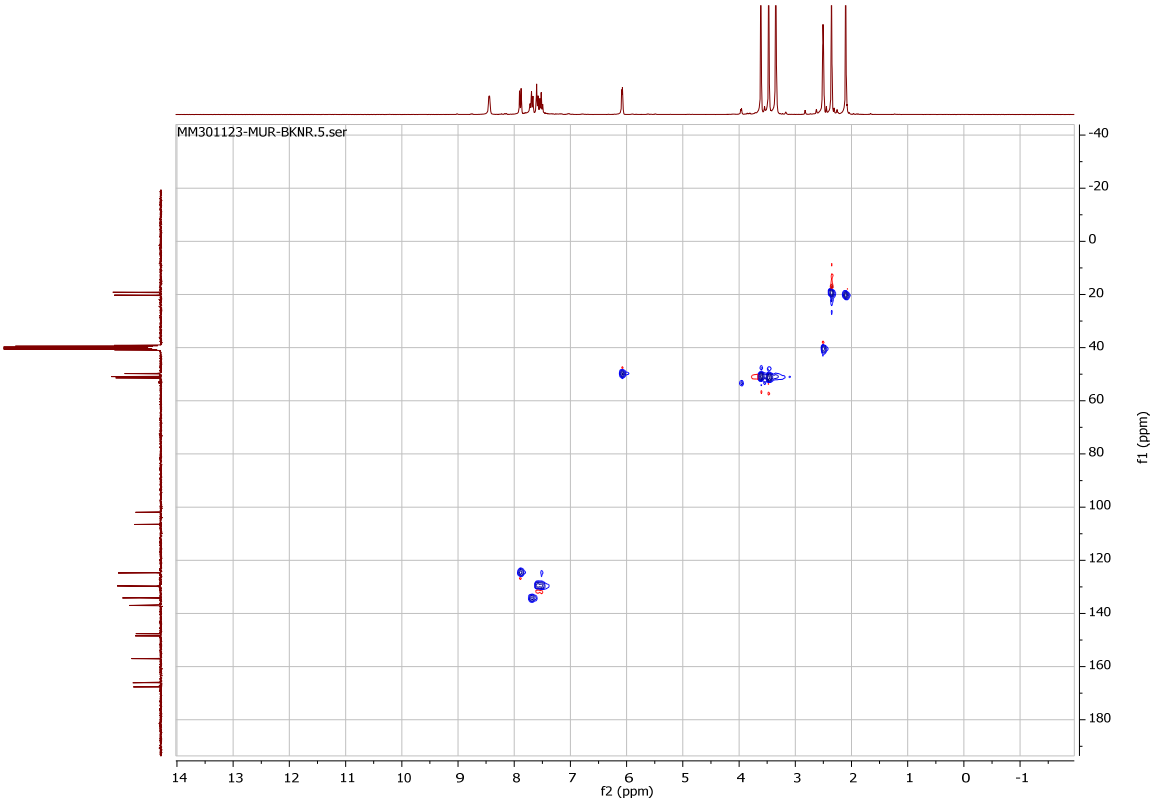

Figure S5. Compound 7: ^{1}H-^{13}C HSQC NMR (300 MHz, DMSO-*d*6), δ_H/δ_C: 7.89/124.62, 7.68/134.25, 7.58/129.47, 6.08/49.79, 3.61/50.86, 3.47/51.29, 2.35/19.37, 2.10/17.17.

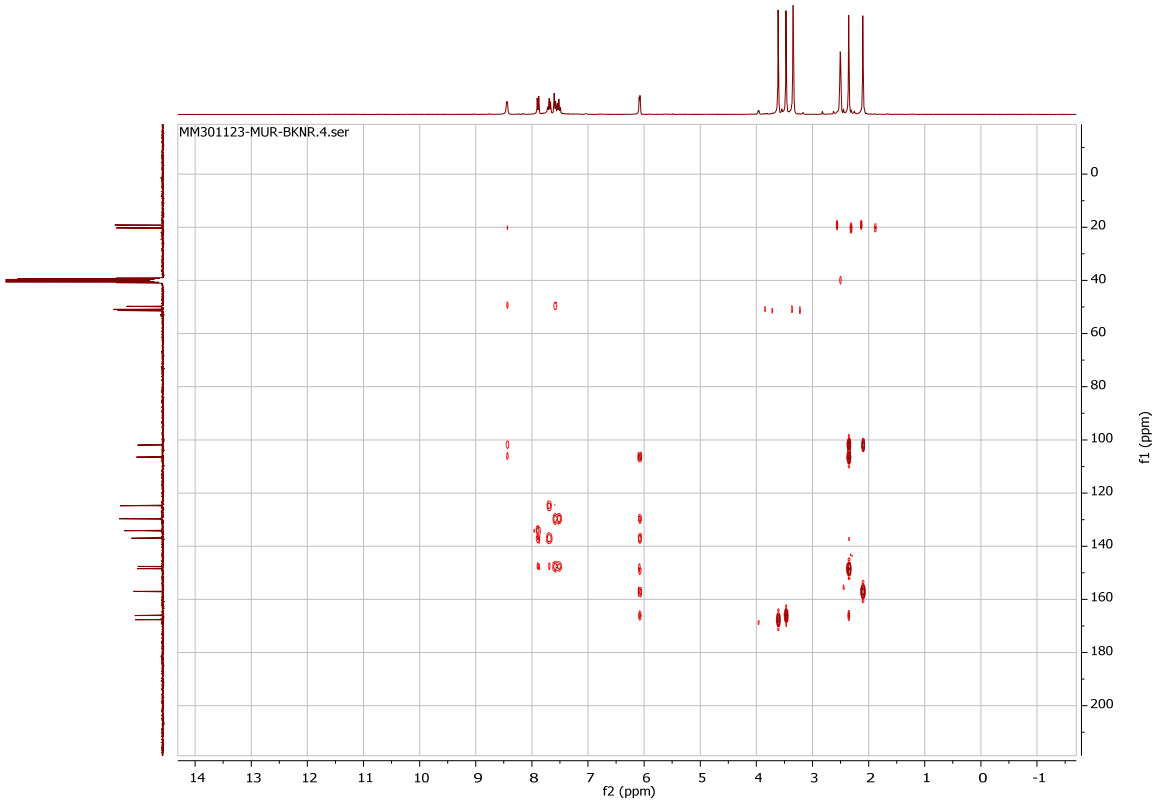

Figure S6. Compound 7: ^{1}H-^{13}C HMBC NMR (300 MHz, DMSO-*d*6), δ_H/δ_C: 7.90/137.04, 7.59/129.78, 7.58/147.70, 6.06/106.44, 3.61/167.67, 3.47/166.11, 2.14/20.25, 1.88/19.20.

Compound 8

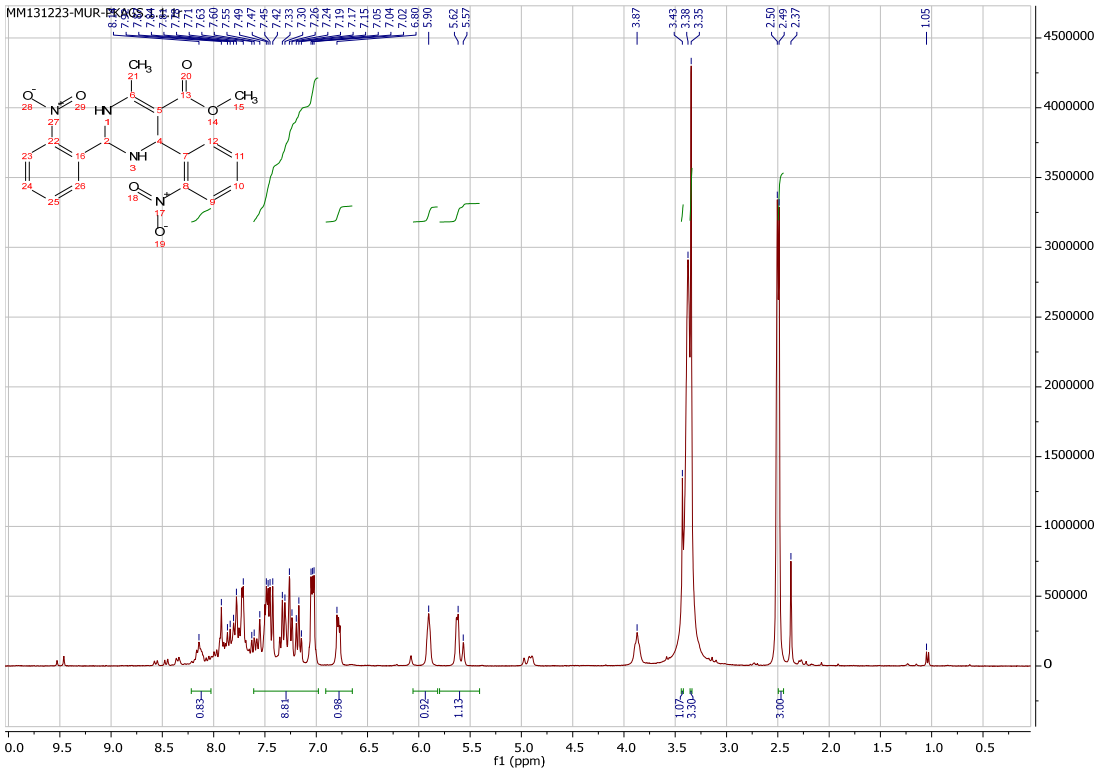

Figure S7. Compound 8: ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.41 (d, *J* = 4.1 Hz, 1H), 7.89-7.01 (m, 8H), 6.75 (t, *J* = 3.3 Hz, 1H), 5.58 (d, *J* = 5.9 Hz, 1H), 5.60 (d, *J* = 4.7 Hz, 1H), 3.43 (s, 1H), 3.38 (s, 3H), 2.49 (s, 3H).

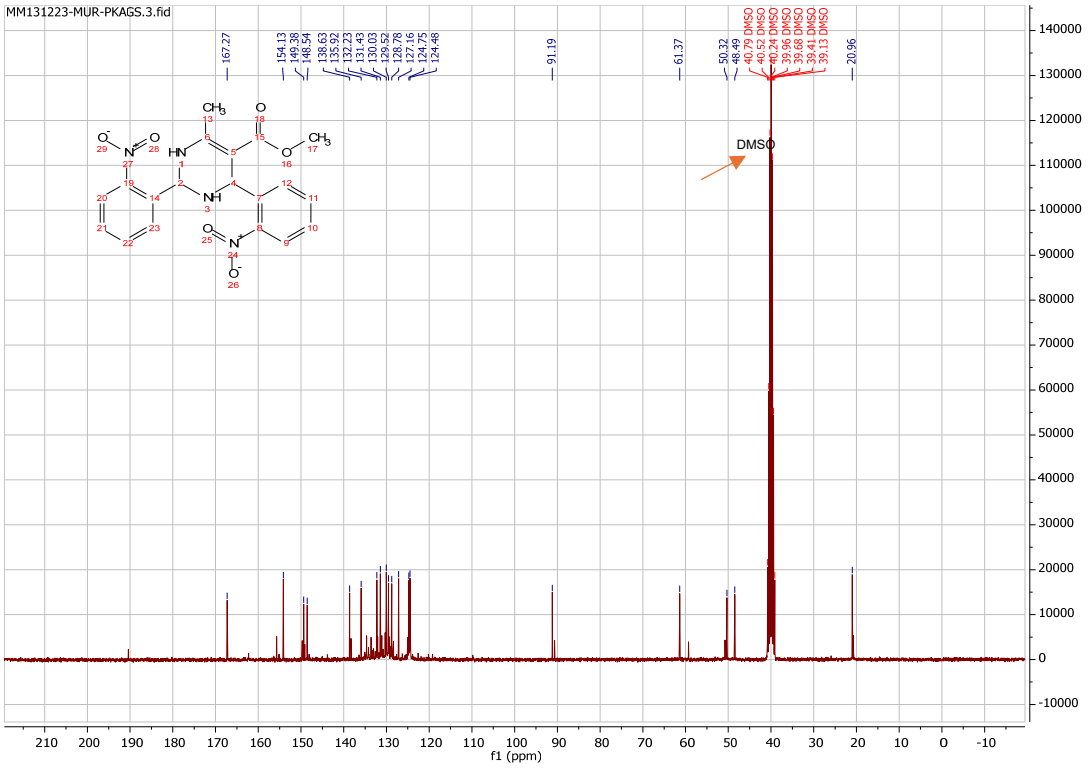

Figure S8. Compound 8: ^{13}C NMR (75 MHz, DMSO) δ 167.27, 154.13, 149.38, 148.54, 138.63, 135.92, 132.23, 131.43, 130.03, 129.52, 128.78, 127.16, 124.75, 124.48, 91.19, 61.37, 50.32, 48.49, 20.96.

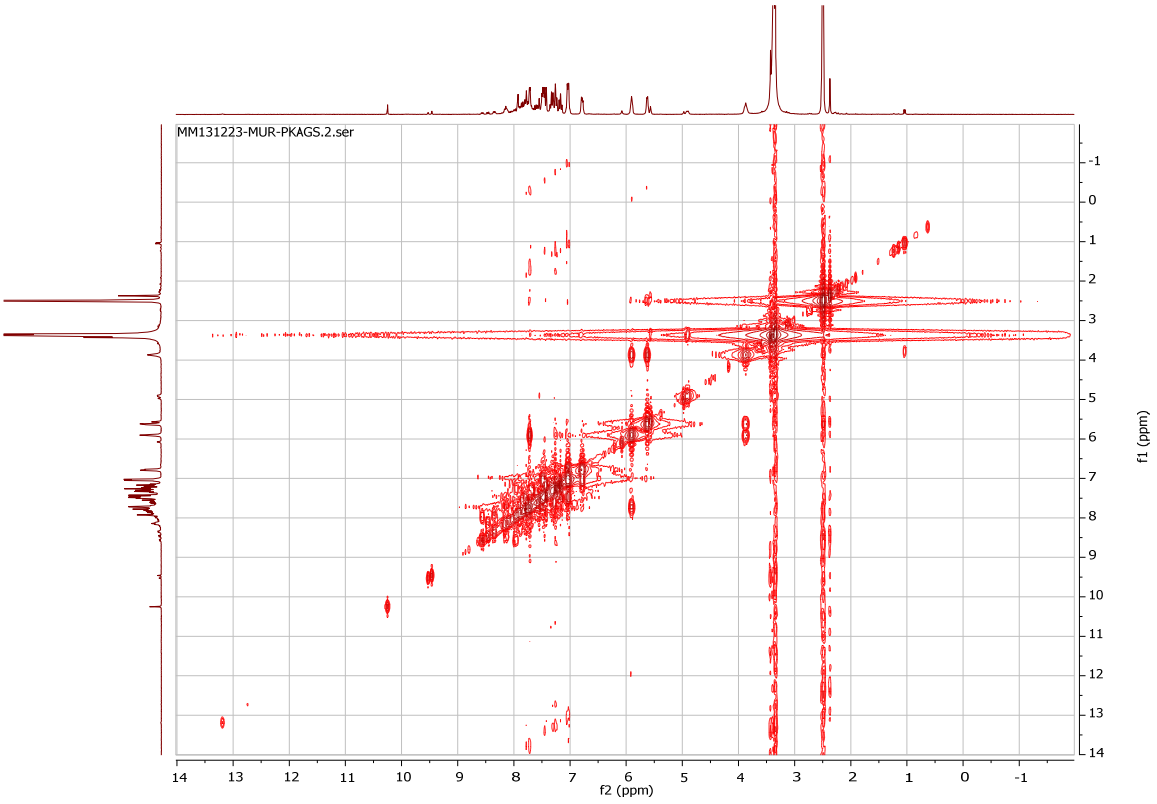

Figure S9. Compound 8: ^{1}H-^{1}H COSY NMR (300 MHz, DMSO-*d*6), δ_H/δ_H: 8.00/8.56, 7.94/8.17, 7.45/7.81, 7.20/7.45, 7.04/7.27, 6.79/7.03, 5.89/5.66, 5.61/5.26, 3.38/3.61, 2.37/2.60.

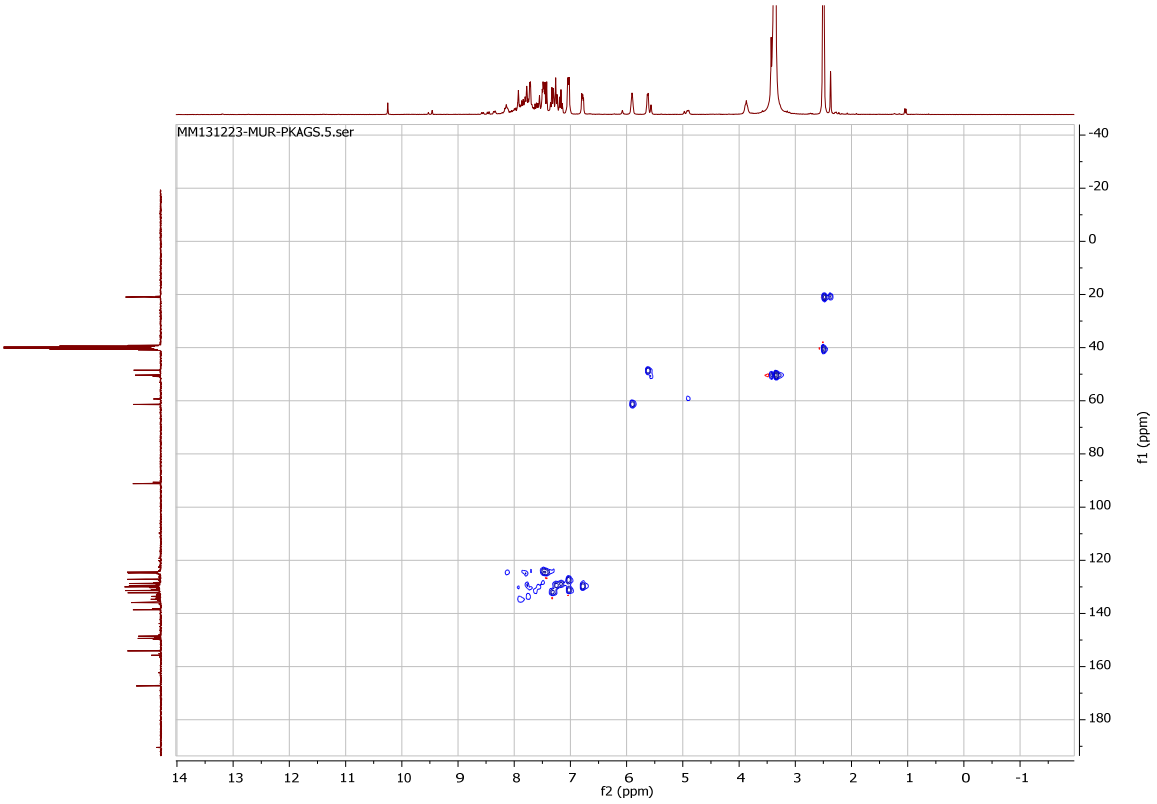

Figure S10. Compound 8: ^{1}H-^{13}C HSQC NMR (300 MHz, DMSO-*d*6), δ_H/δ_C: 7.80/124.94, 7.46/124.46, 7.32/132.10, 7.17/128.86, 7.04/127.35, 5.89/61.28, 5.62/48.61, 3.42/50.40, 3.35/50.32, 2.48/20.98.

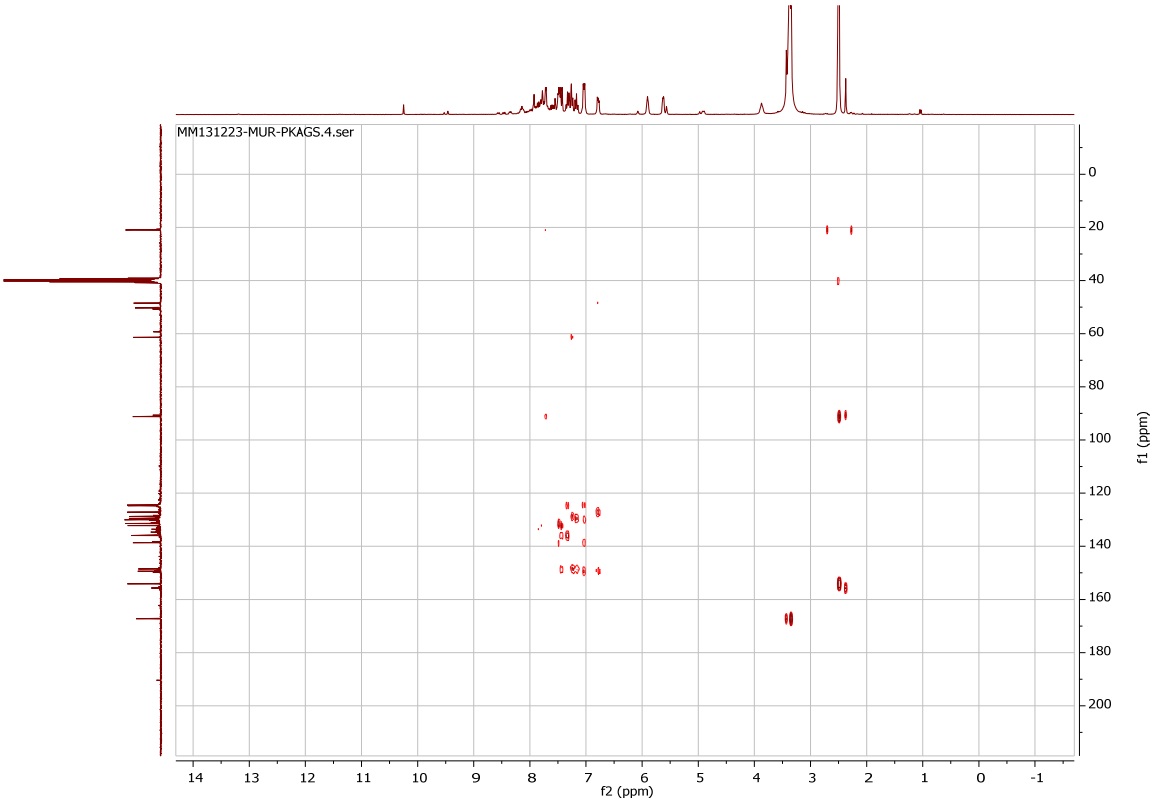

Figure S11. Compound 8: ^{1}H-^{13}C HMBC NMR (300 MHz, DMSO-*d*6), δ_H/δ_C: 7.49/131.48, 7.44/132.26, 7.04/149.34, 7.03/138.66, 6.79/127.21, 6.78/49.34, 3.35/167.30, 2.49/90.61, 2.70/20.93, 2.27/21.04.