Preparation of CuNi/NH_2-MIL-125(Ti) for the photocatalytic synthesis of 1,4-dihydropyridines and β-acetamido ketones

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Table S1. Comparison studies in the efficiency of CuNi/NH_2-MIL-125 with reported catalytic systems for the synthesis of 1,4-DHP using benzaldehyde, ethyl acetoacetate, and NH_4OAc.

Entry	Catalyst	Conditions	Time (h)	Isolated yield (%) [ref]
1	$H_3PW_{12}O_{40}$@PCN-222 (0.01 g)	Neat, 60 °C	5	90 [1]
2	MIL-101-SO_3H (20 wt.%)	EtOH, 60 °C	8	99 [2]
3	BNPs@$SiO_2(CH_2)_3NHSO_3H$ (0.06 g)	EtOH, 70 °C	0.5	97 [3]
4	-	Ethyl-L-lactate (50 mol%)/H_2O, visible light (W lamp, 150 W)	2.5	90 [4]
5	CuNi/NH_2-MIL-125 (0.02 g)	EtOH, visible light (LED, 100 W)	0.5	96 [this work]

Table S2. Comparison studies in the efficiency of CuNi/NH_2-MIL-125 with reported catalytic systems for the synthesis of β-acetamido ketone using benzaldehyde, acetophenone, acetyl chloride, and acetonitrile.

Entry	Catalyst	Conditions	Time (h)	Isolated yield (%) [ref]
1	$ZrOCl_2 \cdot 8H_2O$ (15 mol%)	r.t.	12	83 [5]
2	$Sc(OTf)_3$ (10 mol%)	r.t.	30	82 [6]
3	$PhB(OH)_2$ (10 mol%)	r.t.	3	75[a] [7]
4	Montmorilonite K-10 (2 g)	70 °C	1	80 [8]
5	$H_7SiV_3W_9O_{40}$ (10 mol%)	80 °C	0.6	90 [9]
6	CuNi/NH_2-MIL-125 (0.02 g)	visible light (LED, 100 W)	2.5	92 [this work]

[a] using 4-methylacetophenone.

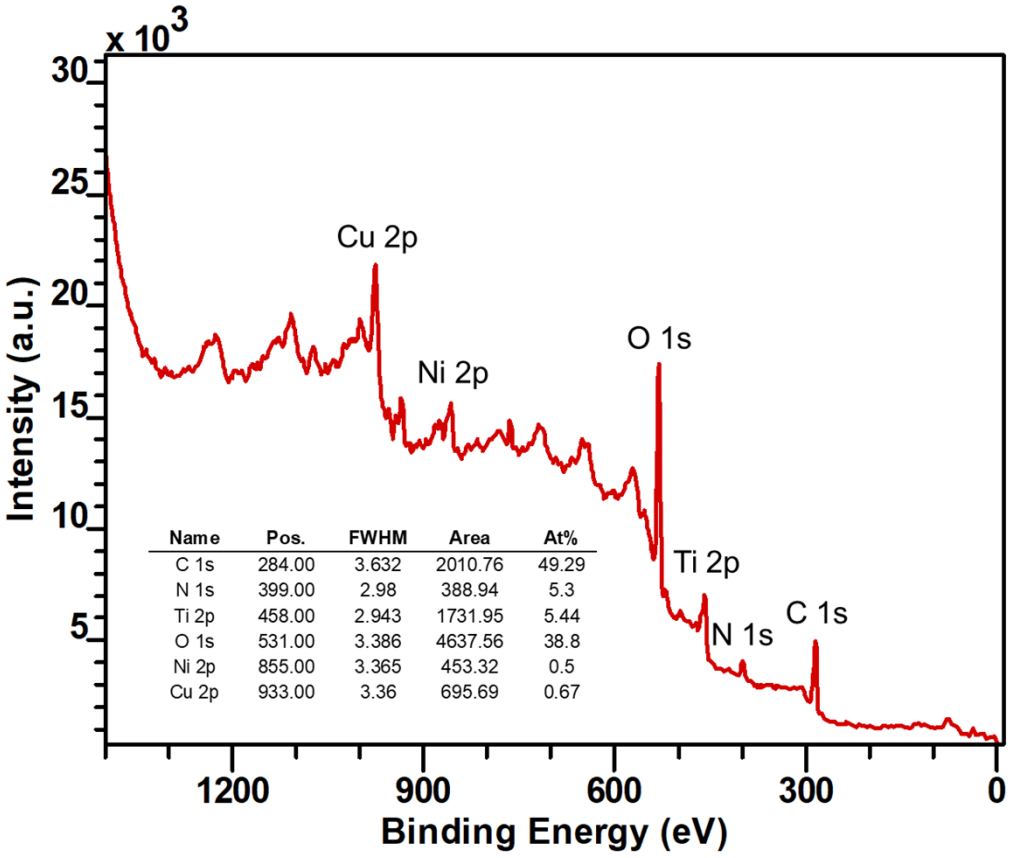


Figure S1. XPS survey of CuNi/NH_2-MIL-125.

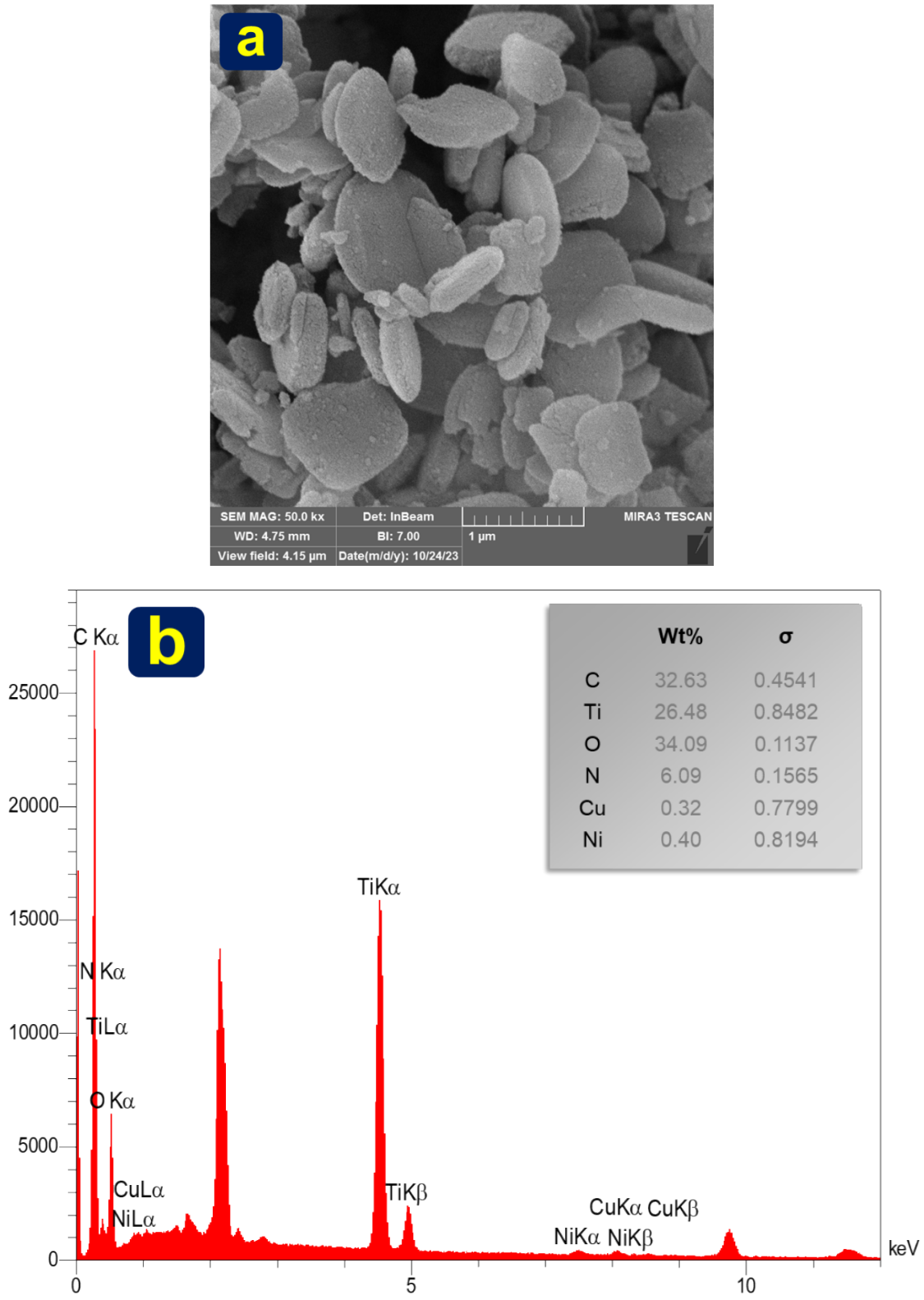


Figure S2. SEM image and EDX spectrum of CuNi/NH_2-MIL-125 after four-time reusing.

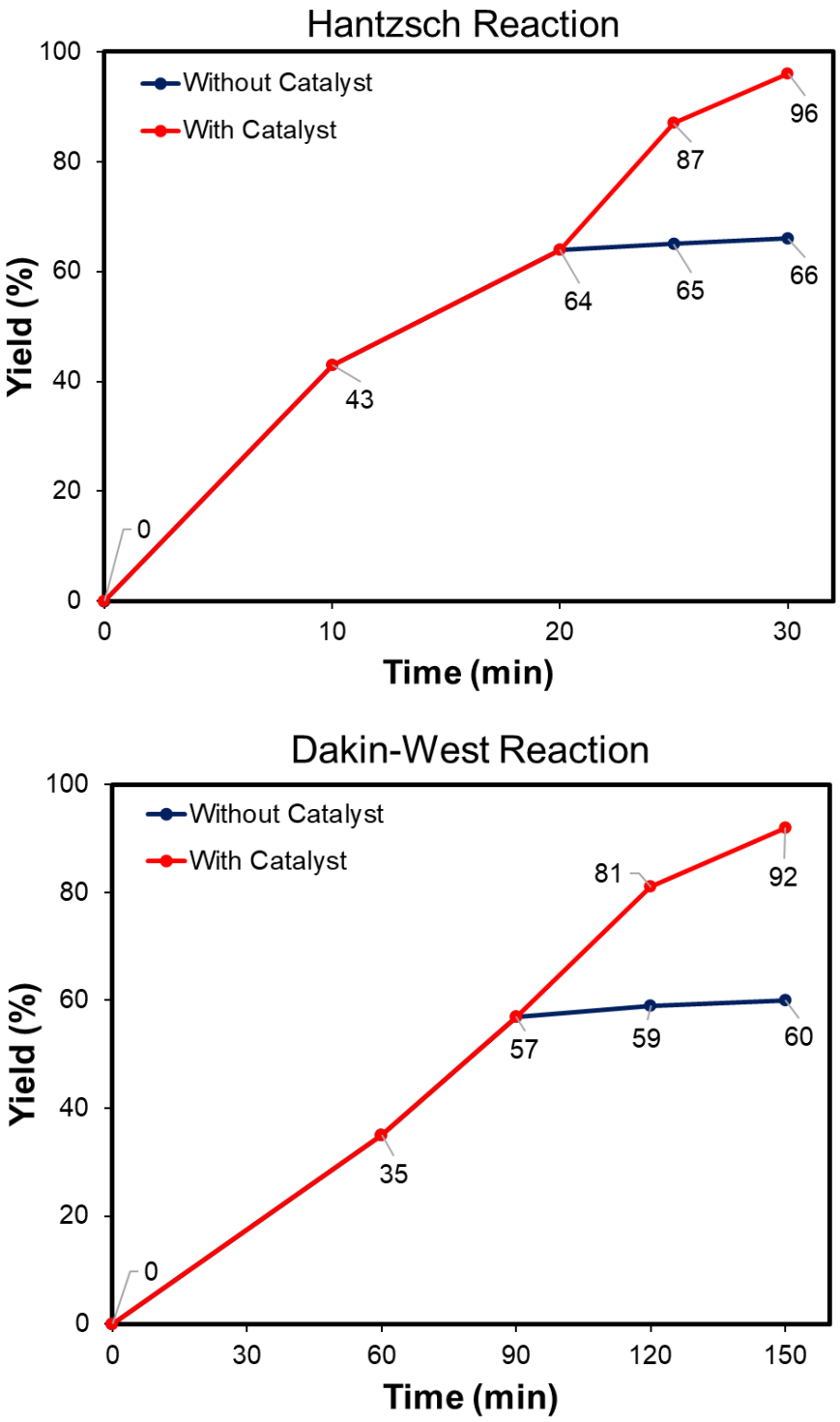
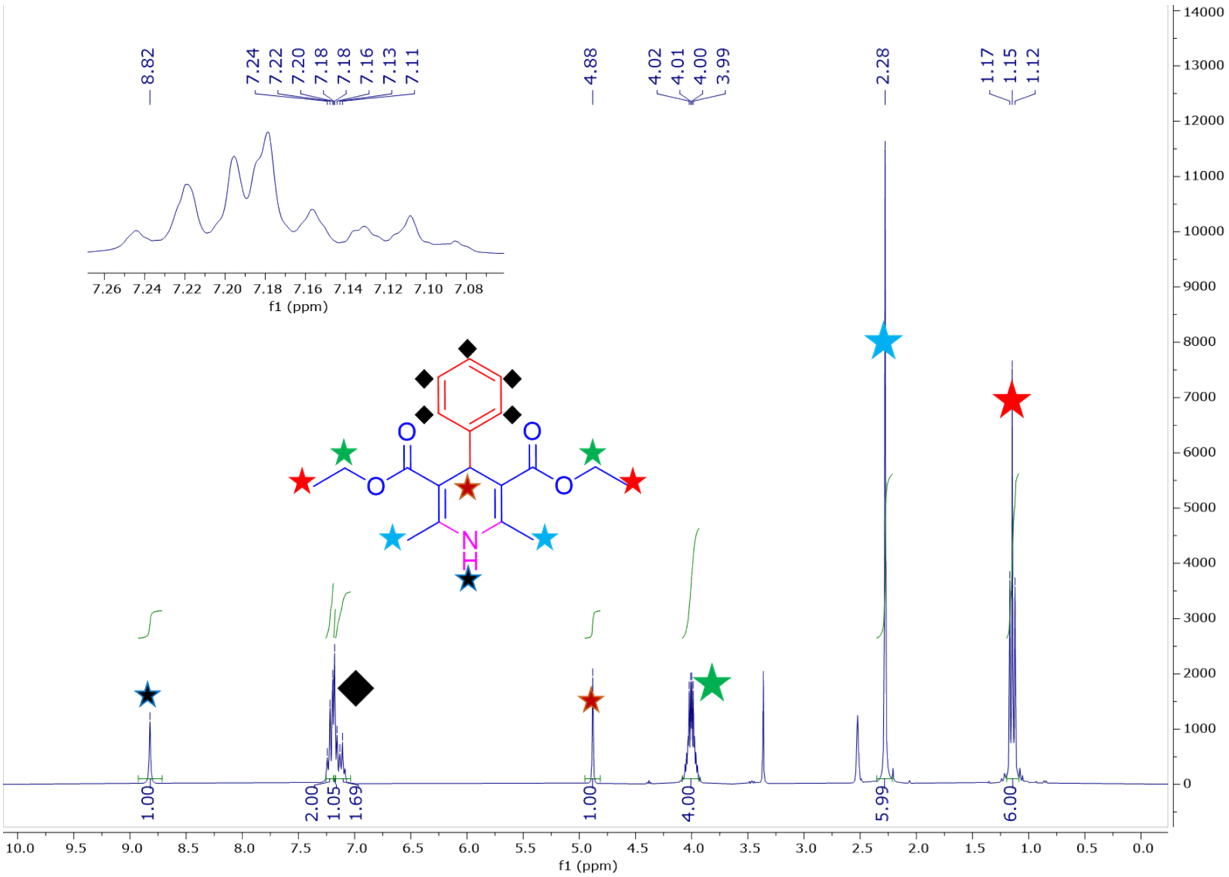
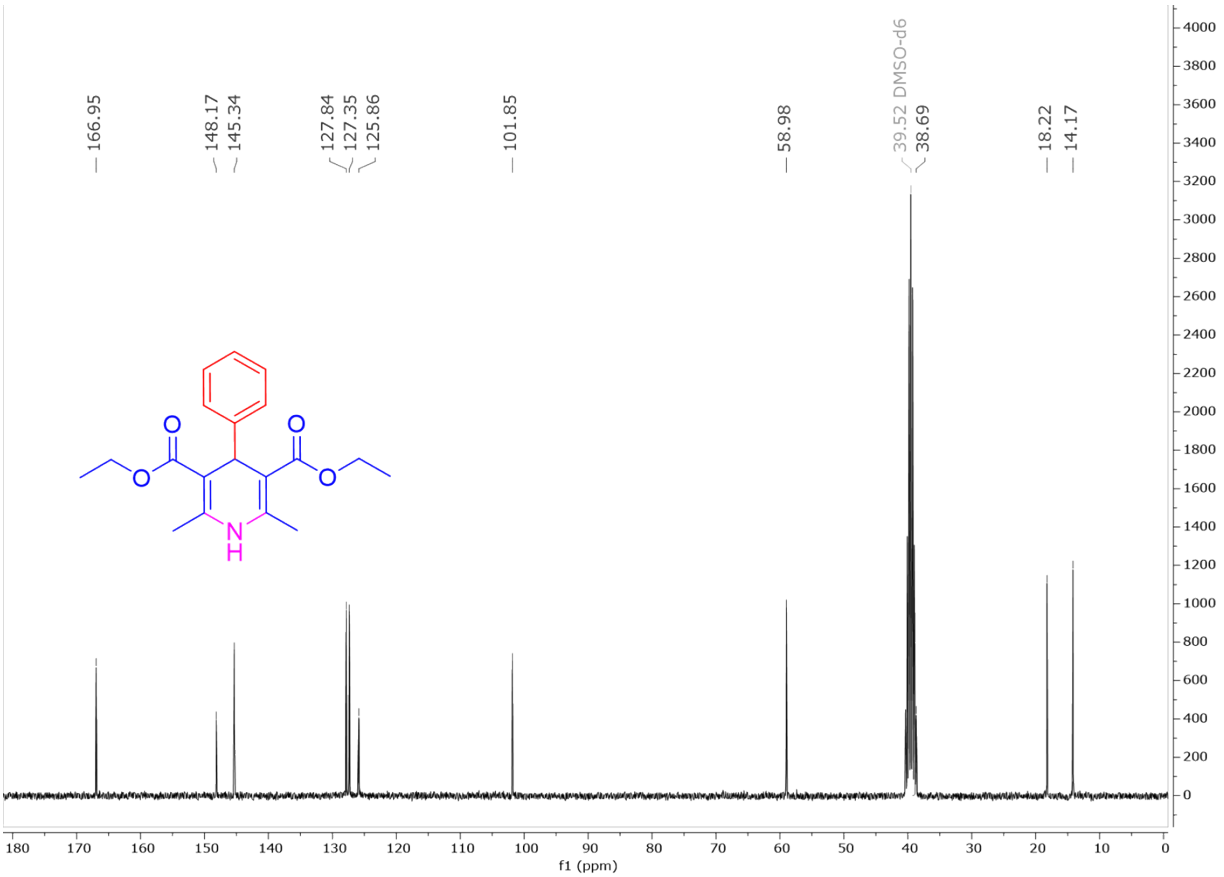


Figure S3. Hot filtration test of the photocatalyst for the Hantzsch and Dakin-West reactions.

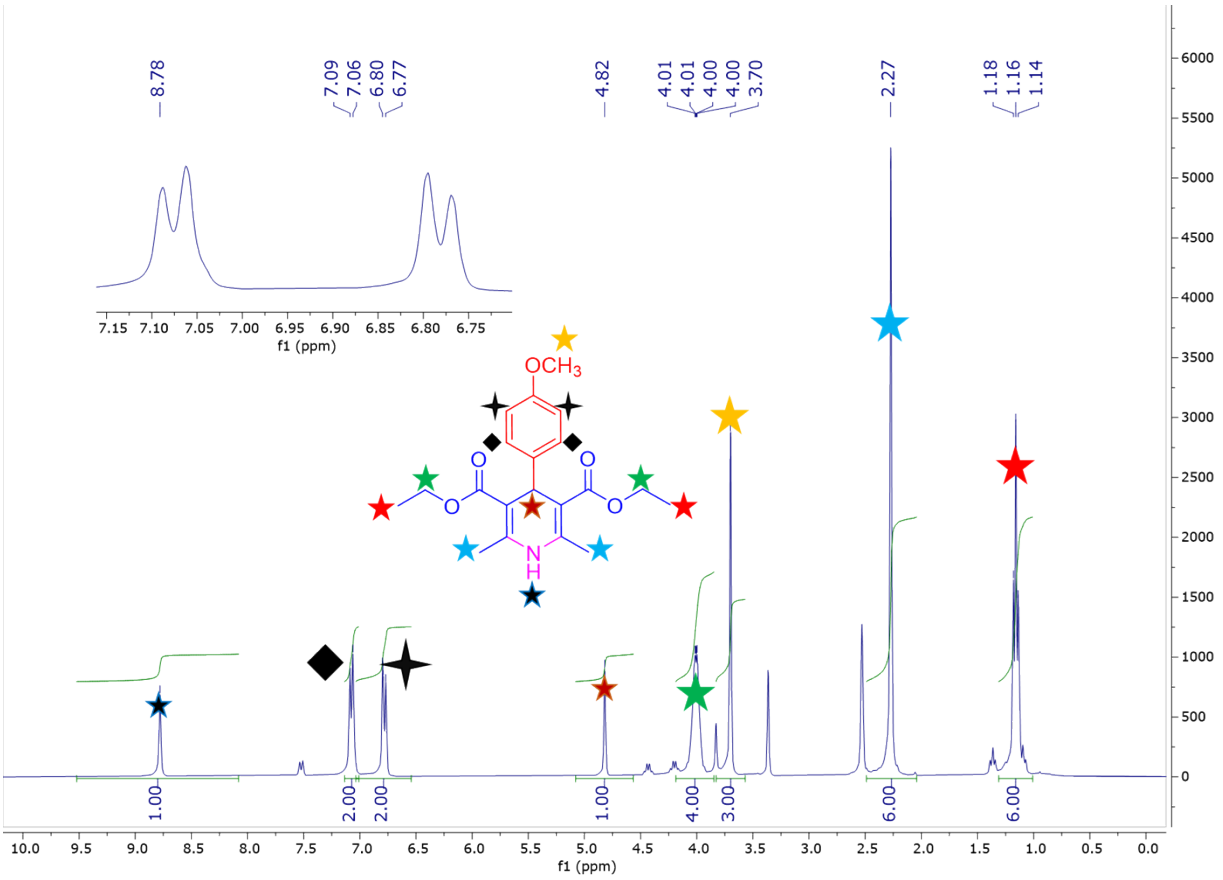


^{1}H NMR (300 MHz, DMSO-d_6), δ: 8.82 (s, 1H), 7.23 (t, J = 7.3 Hz, 2H), 7.21–715 (m, 1H), 7.16 (d, J = 6.9 Hz, 2H), 4.88 (s, 1H), 4.00 (q, J = 4.1 Hz, 4H), 2.28 (s, 6H), 1.15 (t, J = 7.1 Hz, 6H).

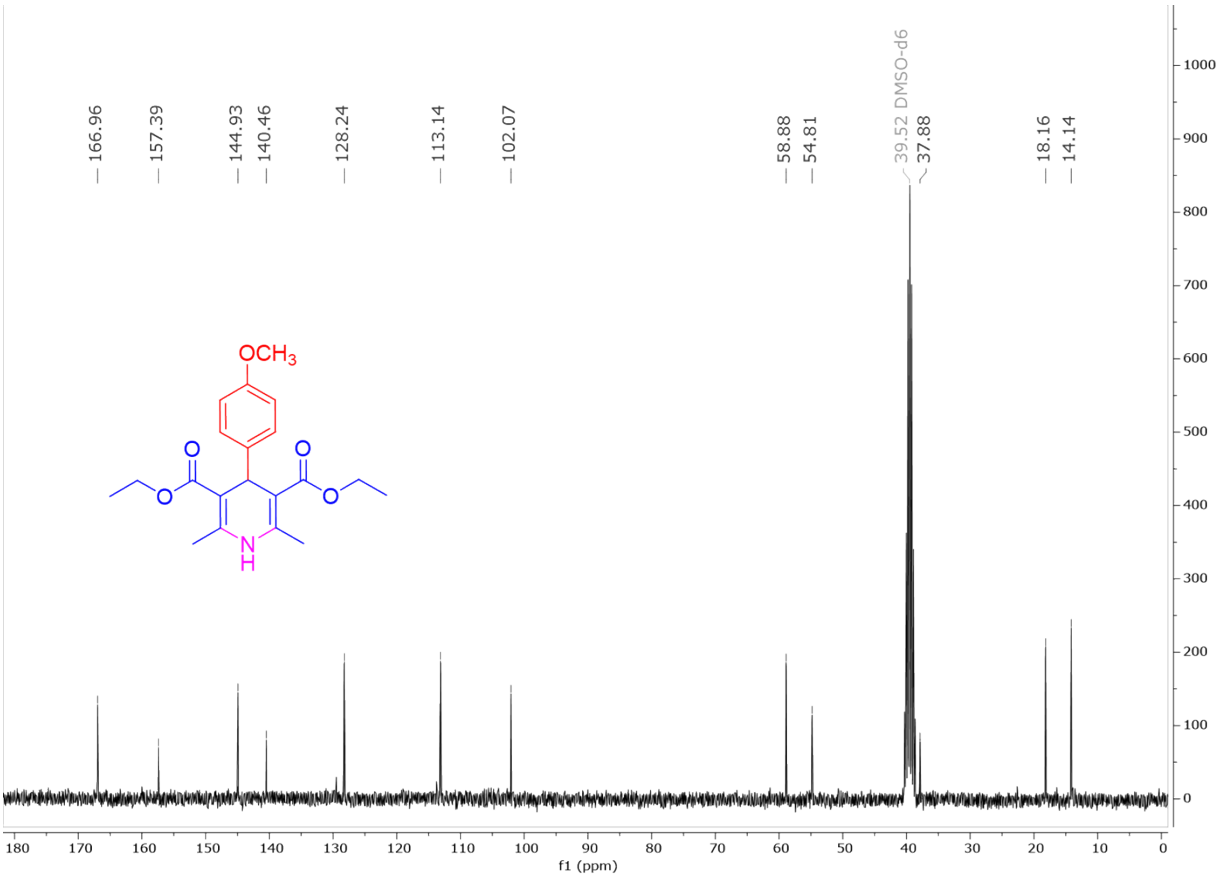


^{13}C NMR (75 MHz, DMSO-d_6), δ: 166.95, 148.17, 145.34, 127.84, 127.35, 125.86, 101.85, 58.98, 38.69, 18.22, 14.17.

Figure S4. ^{1}H and ^{13}C NMR of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (Table 3, entry 1).

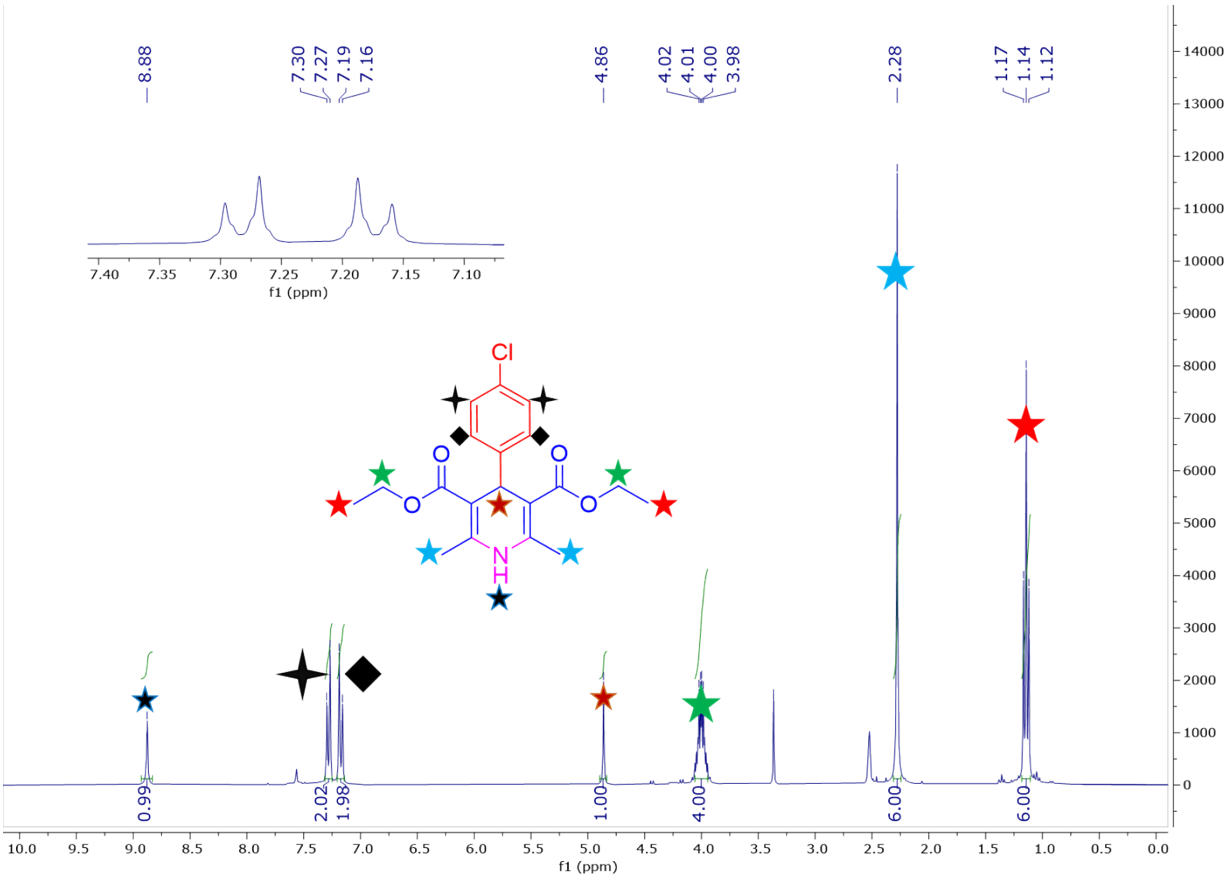


^{1}H NMR (300 MHz, DMSO-d_6), δ: 8.78 (s, 1H), 7.09–7.06 (d, J = 7.3 Hz, 2H), 6.80–6.76 (d, J = 8.4 Hz, 2H), 4.82 (s, 1H), 4.01 (q, J = 3.6, 1.3 Hz, 4H), 3.70 (s, 3H), 2.27 (s, 6H), 1.16 (t, J = 6.5 Hz, 6H).

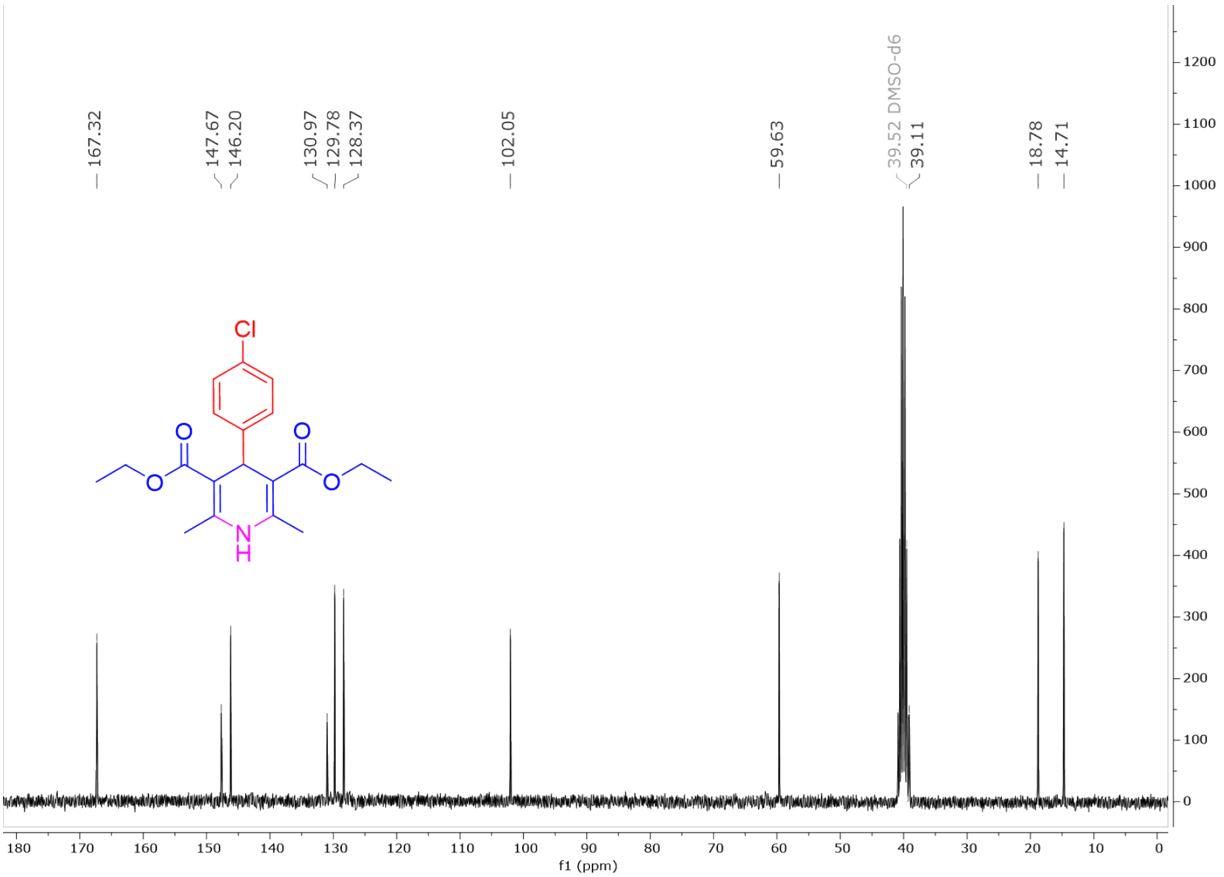


^{13}C NMR (75 MHz, DMSO-d_6), δ: 166.96, 157.39, 144.93, 140.46, 128.24, 113.14, 102.07, 58.88, 54.81, 37.88, 18.16, 14.14.

Figure S5. ^{1}H and ^{13}C NMR of diethyl 4-(4-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (Table 3, entry 3).

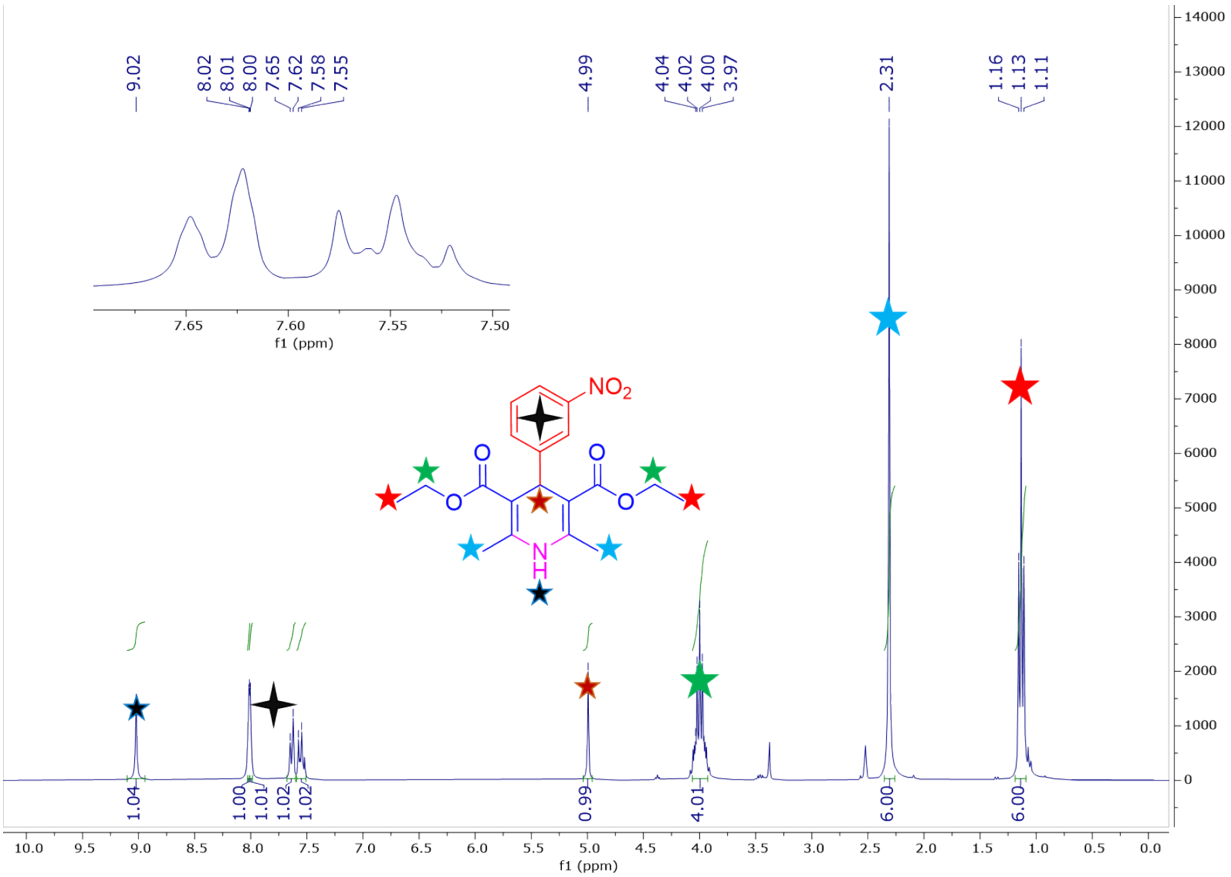


^{1}H NMR (300 MHz, DMSO-d_6), δ: 8.88 (s, 1H), 7.30–7.27 (d, J = 8.4 Hz, 2H), 7.19–7.16 (d, J = 8.5 Hz, 2H), 4.86 (s, 1H), 4.02–3.98 (q, J = 4.3 Hz, 4H), 2.28 (s, 6H), 1.14 (t, J = 7.1 Hz, 6H).

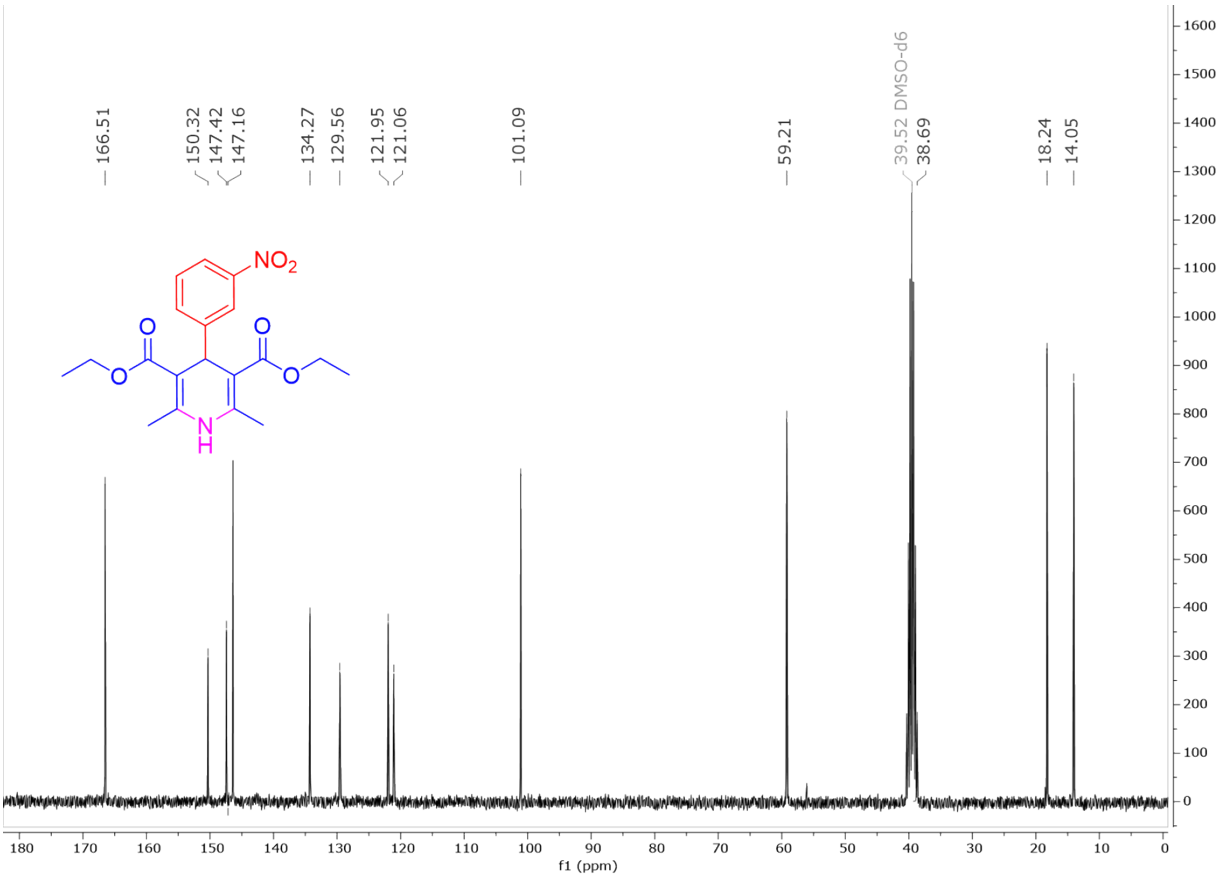


^{13}C NMR (75 MHz, DMSO-d_6), δ: 167.32, 147.67, 146.20, 130.97, 129.78, 128.37, 102.05, 59.63, 39.11, 18.78, 14.71.

Figure S6. ^{1}H and ^{13}C NMR of diethyl 4-(4-chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (Table 3, entry 5).

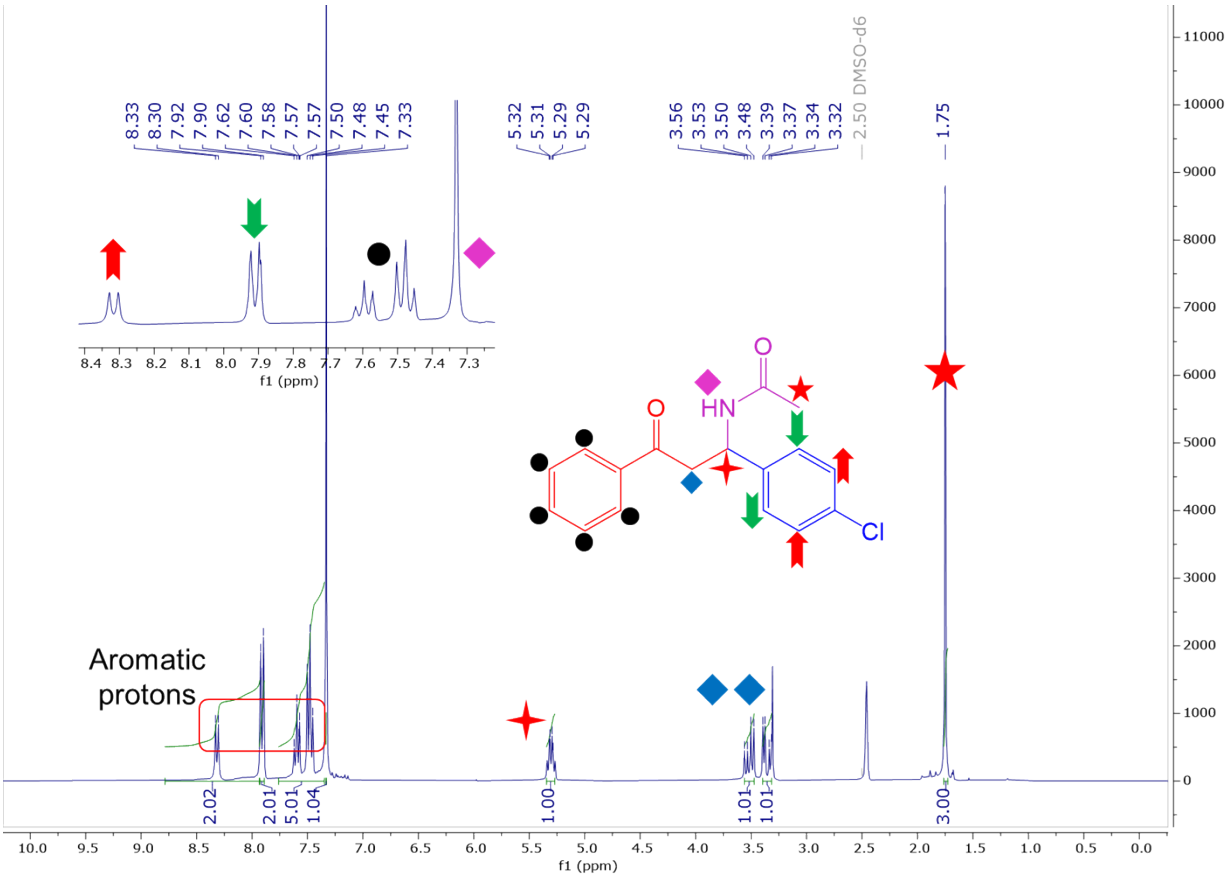


^{1}H NMR (300 MHz, DMSO-d_6), δ: 9.02 (s, 1H), 8.02–8.00 (d, 1H), 8.00 (s, 1H), 7.65–7.62 (d, J = 7.9 Hz, 1H), 7.58–7.55 (d, J = 8.5 Hz, 1H), 4.99 (s, 1H), 4.04–3.97 (q, J = 7.2 Hz, 4H), 2.31 (s, 6H), 1.13 (t, J = 7.1 Hz, 6H).

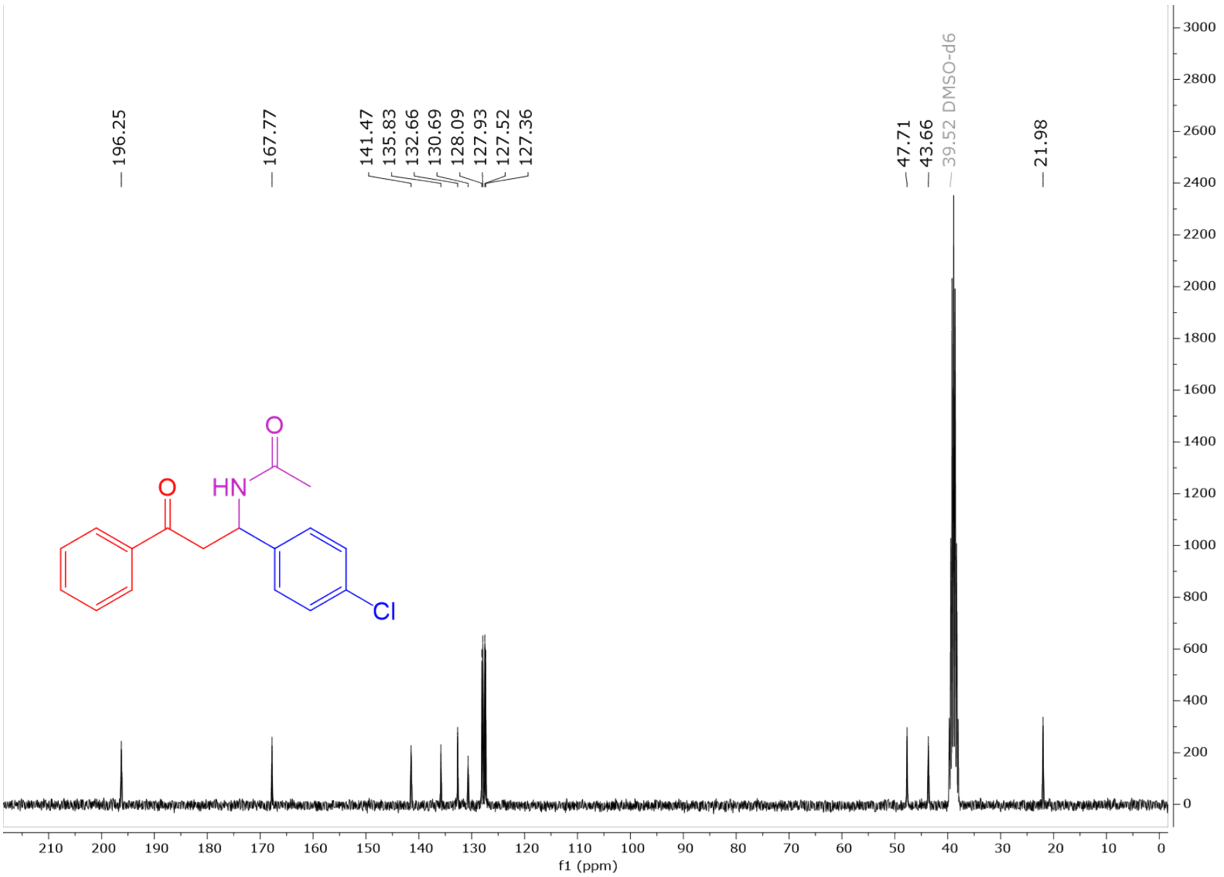


^{13}C NMR (75 MHz, DMSO-d_6), δ: 166.51, 150.32, 147.42, 147.16, 134.27, 129.56, 121.95, 121.06, 101.09, 59.21, 38.69, 18.24, 14.05.

Figure S7. ^{1}H and ^{13}C NMR of diethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (Table 3, entry 6).

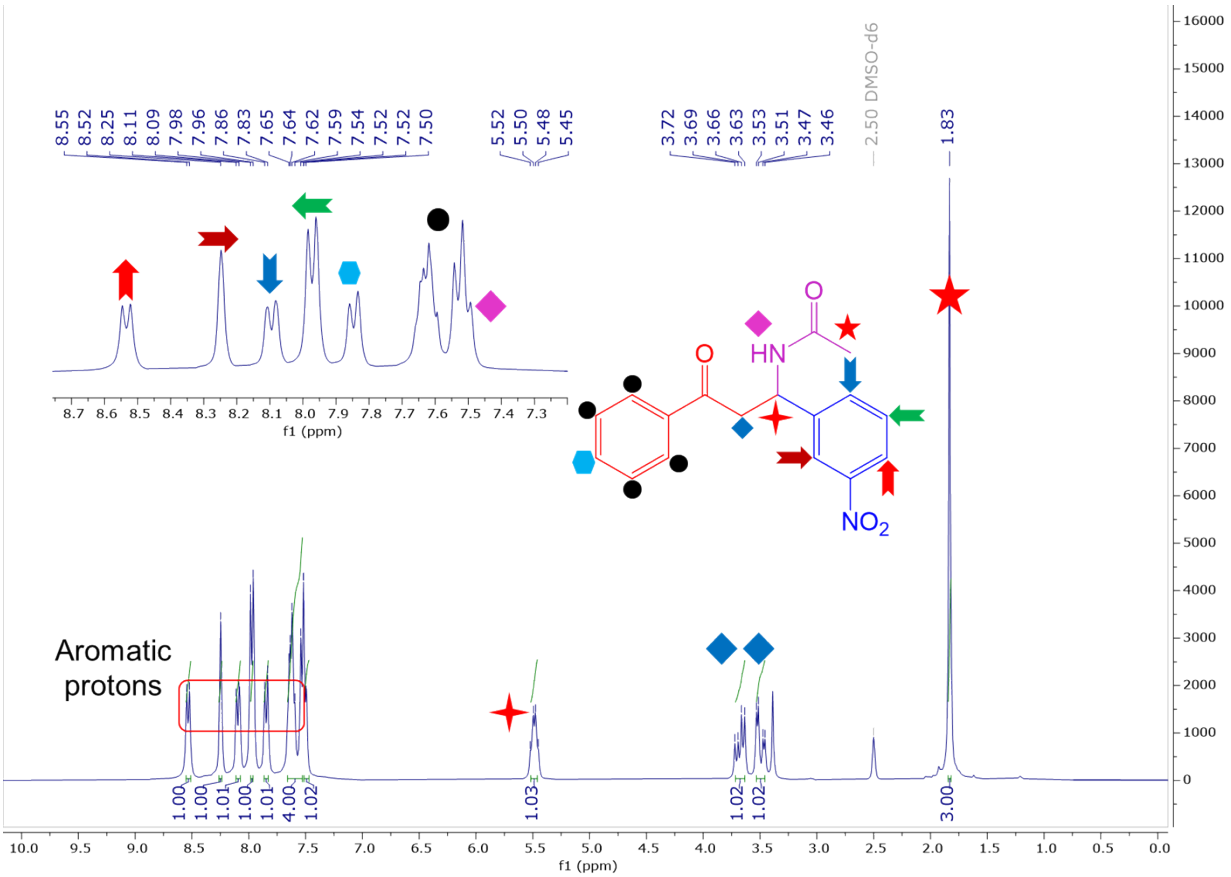


^{1}H NMR (300 MHz, DMSO-d_6), δ: 8.34–8.30 (d, J = 7.8 Hz, 2H), 7.94–7.88 (d, J = 7.0 Hz, 2H), 7.63–7.44 (m, 5H), 7.33 (s, 1H), 5.34–5.28 (dd, J = 7.4, 7.4 Hz, 1H), 3.57–3.46 (dd, J = 17.2, 8.3 Hz, 1H), 3.41–3.31 (dd, J = 17.3, 5.9 Hz, 1H), 1.75 (s, 3H).

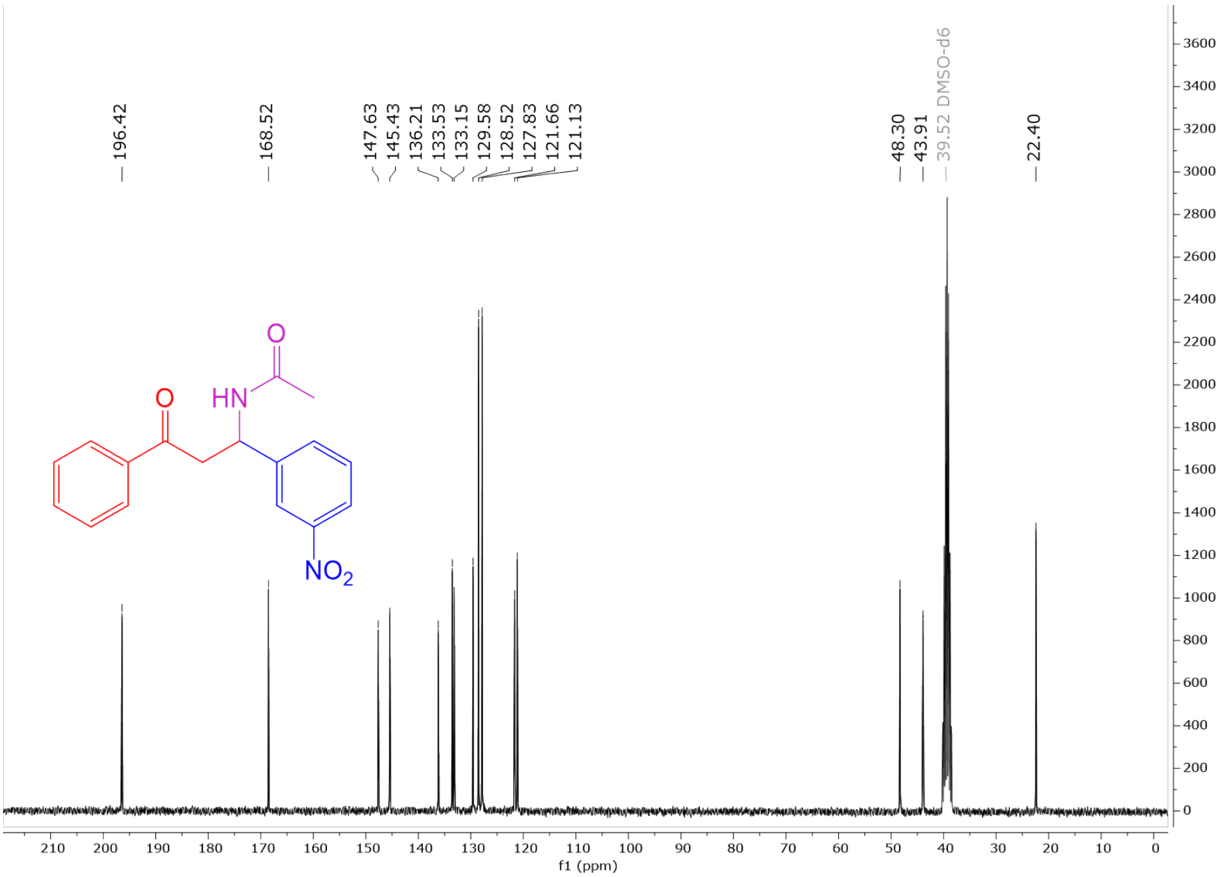


^{13}C NMR (75 MHz, DMSO-d_6), δ: 196.25, 167.77, 141.47, 135.83, 132.66, 130.69, 128.09, 127.93, 127.52, 127.36, 47.71, 43.66, 21.98.

Figure S8. ^{1}H and ^{13}C NMR of *N*-(1-(4-chlorophenyl)-3-oxo-3-phenylpropyl)acetamide (Table 5, entry 3).

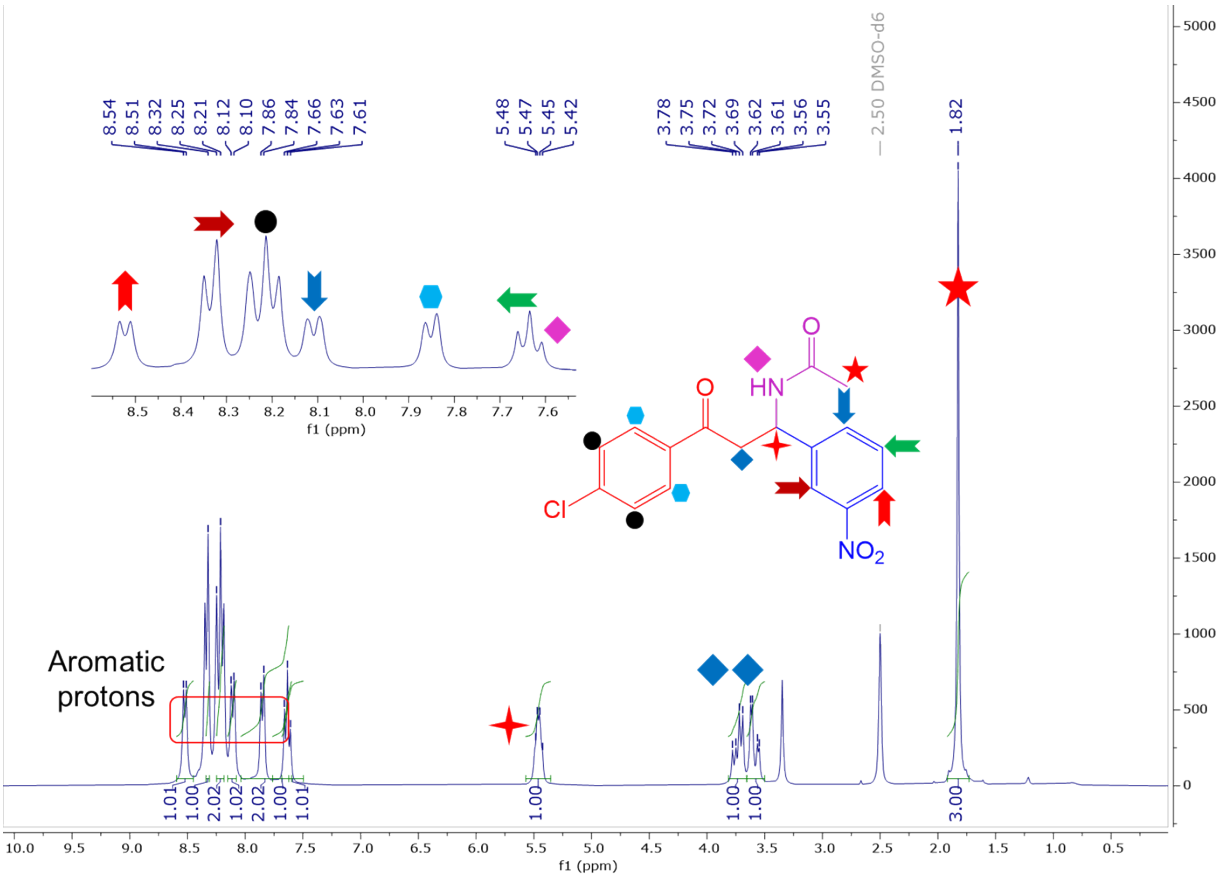


^{1}H NMR (300 MHz, DMSO-d_6), δ: 8.55–8.52 (d, J = 7.5 Hz, 1H), 8.25 (s, 1H), 8.11–8.09 (d, J = 7.7 Hz, 1H), 7.98–7.96 (d, J = 7.1 Hz, 1H), 7.85 (d, J = 7.7 Hz, 1H), 7.69–7.51 (m, 4H), 7.50 (s, 1H), 5.55–5.43 (dd, J = 7.6, 7.6 Hz, 1H), 3.72–3.63 (dd, J = 17.6, 8.4 Hz, 1H), 3.55–3.45 (dd, J = 17.5, 5.4 Hz, 1H), 1.83 (s, 3H).

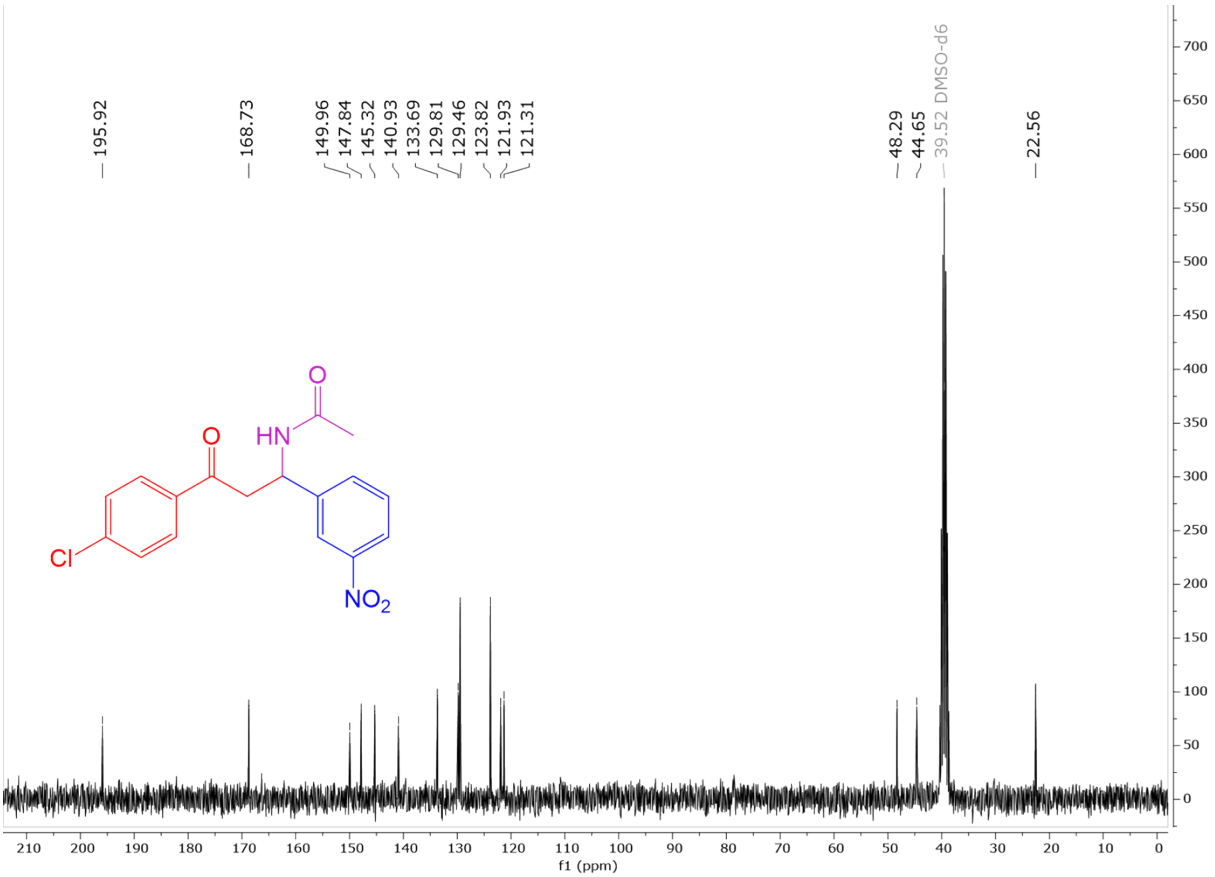


^{13}C NMR (75 MHz, DMSO-d_6), δ: 196.42, 168.52, 147.63, 145.43, 136.21, 133.53, 133.15, 129.58, 128.52, 127.83, 121.66, 121.13, 48.30, 43.91, 22.40.

Figure S9. ^{1}H and ^{13}C NMR of *N*-(1-(3-nitrophenyl)-3-oxo-3-phenylpropyl)acetamide (Table 5, entry 6).

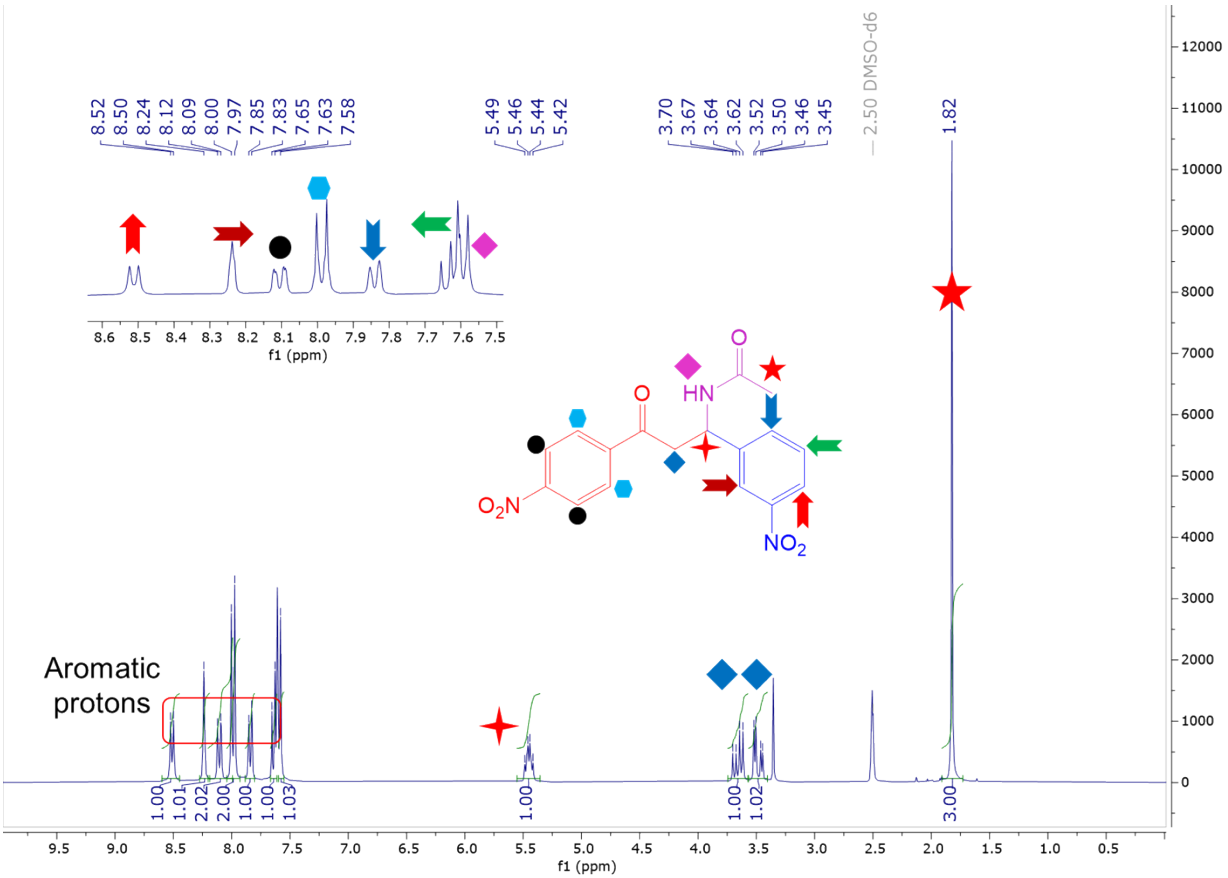


^{1}H NMR (300 MHz, DMSO-d_6), δ: 8.54–8.51 (d, J = 7.4 Hz, 1H), 8.32 (s, 1H), 8.26–8.20 (d, J = 10.7 Hz, 2H), 8.14–8.08 (d, J = 7.4 Hz, 1H), 7.88–7.82 (d, J = 7.6 Hz, 2H), 7.68–7.62 (d, J = 8.0 Hz, 1H), 7.61 (s, 1H), 5.50–5.42 (dd, J = 7.7, 7.7 Hz, 1H), 3.80–3.68 (dd, J = 17.9, 8.8 Hz, 1H), 3.64–3.54 (dd, J = 17.9, 5.1 Hz, 1H), 1.82 (s, 3H).

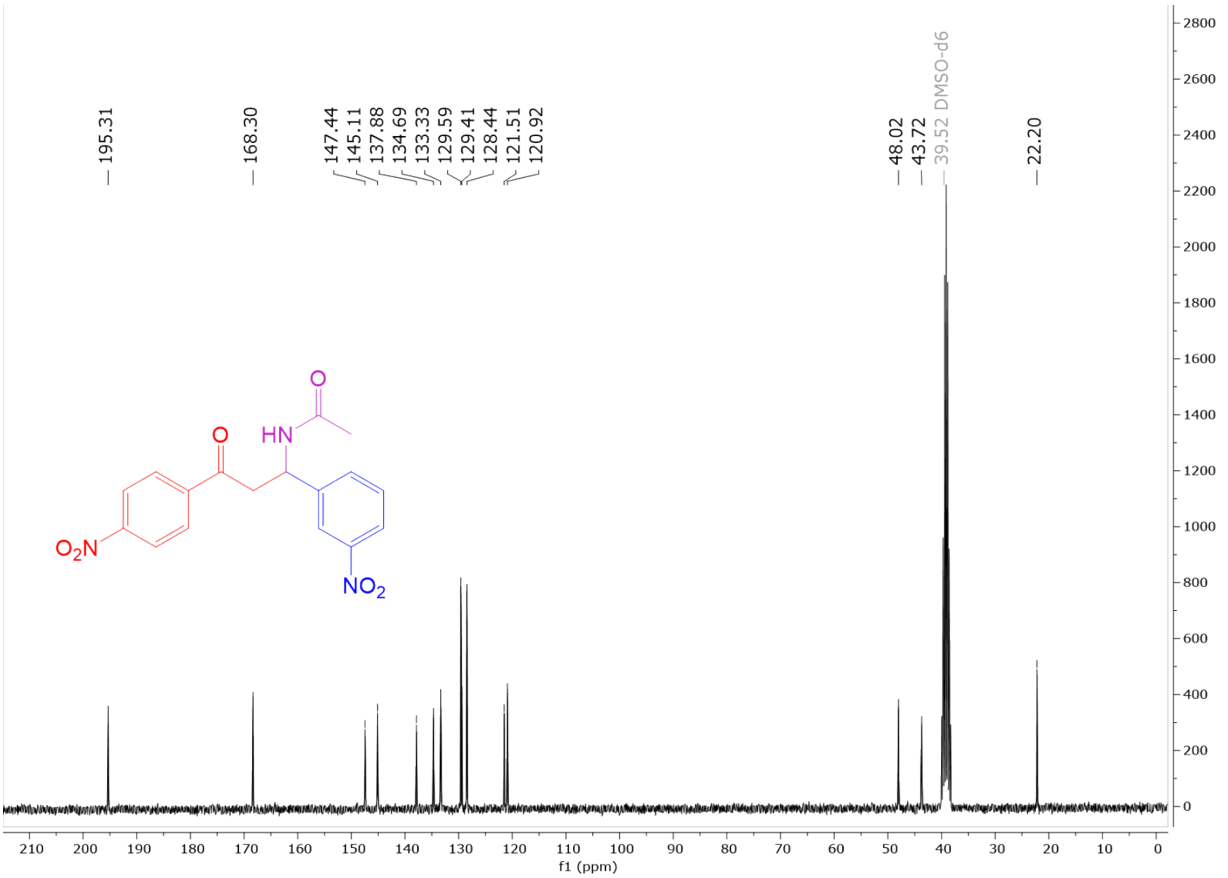


^{13}C NMR (75 MHz, DMSO-d_6), δ: 195.92, 168.73, 149.96, 147.84, 145.32, 140.93, 133.69, 129.81, 129.46, 123.82, 121.93, 121.31, 48.29, 44.65, 22.56.

Figure S10. ^{1}H and ^{13}C NMR of *N*-(3-(4-chlorophenyl)-1-(3-nitrophenyl)-3-oxopropyl)acetamide **(Table 5, entry 7).**



^{1}H NMR (300 MHz, DMSO-d_6), δ: 8.52–8.50 (d, J = 7.5 Hz, 1H), 8.24 (s, 1H), 8.13–8.09 (d, J = 8.2 Hz, 2H), 8.00–7.97 (d, J = 8.6 Hz, 2H), 7.86–7.82 (d, J = 7.5 Hz, 1H), 7.66–7.62 (d, J = 8.0 Hz, 1H), 7.58 (s, 1H), 5.48–5.42 (dd, J = 7.8, 7.8 Hz, 1H), 3.72–3.60 (dd, J = 17.6, 8.6 Hz, 1H), 3.54–3.44 (dd, J = 17.6, 5.3 Hz, 1H), 1.82 (s, 3H).



^{13}C NMR (75 MHz, DMSO-d_6), δ: 195.31, 168.30, 147.44, 145.11, 137.88, 134.69, 133.33, 129.59, 129.41, 128.44, 121.51, 120.92, 48.02, 43.72, 22.20.

Figure S11. ^{1}H and ^{13}C NMR of *N*-(1-(3-nitrophenyl)-3-(4-nitrophenyl)-3-oxopropyl)acetamide **(Table 5, entry 8).**

References

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