Supporting Information

Strategic Design of Gold Nanocatalysts for Effective Photocatalytic Organic Transformation

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1. General information

All reagents were obtained and used as received without further purification. Thin-layer chromatography (TLC) was run on a SiO_2 plate, then visualized under UV light (254 nm), followed by a potassium permanganate staining solution. Irradiation of the reaction mixture was carried out under commercial blue light (425 nm, 18 W) from HepatoChem (EvoluChem™425PF) unless otherwise commented. GC analysis was performed on an Agilent 7890A Gas Chromatograph equipped with an Agilent 5977A Mass Selective Detector. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 AVANCE and 500 AVANCE. All chemical shifts are referenced to residual non-deuterated solvent signals (note: $CDCl_3$ referenced at 7.26 and 77.0 ppm, DMSO-d_6 referenced at 2.50 and 39.5 ppm, CD_3OD referenced at 3.31 and 49.0 ppm, and D_2O referenced at 4.79 ppm, respectively). ^{1}H NMR were presented as following: chemical shifts (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, dd = doublet of doublets, m = multiplet), coupling constant (Hz) and integration. HRMS data was obtained on an Agilent 6890 Gas Chromatograph equipped with JEOL JMS-700 as mass spectrometer. Optical properties for Au-NPs and Au-NCs were characterized using a Shimadzu UV-1800 spectrophotometer operating at a fast-scan rate in a scan range of 300-800 nm. Morphologcial characterization of Au nanocatalysts was performed with FEI Tecnai G2 F20 FE-TEM and JEM-2100 (JEOL Ltd, Japan). Zeta potential was measured by Zeta potential & Particle size analyzer ELSZ-2000 series of Otsuka Electronics.

2. Synthesis of Au nanocatalysts with different sizes and ligands

2.1. Preparation of Au-$NP_{26,GSH}$[1]

(Step 1) Synthesis of citrate-capped Au-NPs (ca. 26 nm): It was prepared using the synthesis procedure reported by Frens et al.[1] Each aqueous stock solution of $HAuCl_4 \cdot 3H_2O$ (25 mM), $AgNO_3$ (0.1 wt%) and citrate (1 wt%) was prepared before Au-NP synthesis. To a completely mixed solution of 25 mM $HAuCl_4 \cdot 3H_2O$ (0.50 mL) and 0.1 wt% $AgNO_3$ (42.50 μL), 1 wt% citrate solution (0.75 mL) was added and mixed. The mixed solution volume was adjusted to 2.5 mL by adding deionized water (approximately 1.20 mL). After incubated at room temperature for 5 min, the $HAuCl_4$/$AgNO_3$/citrate aqueous solution was transferred to a 250 mL of round bottom flask and diluted with deionized water (47.50 mL). The flask was placed in an oil bath and stirred at 60 °C. When the red color emerged to the solution, the reaction solution was naturally cooled down to room temperature.

(Step 2) Ligand exchange for glutathione-capped Au-NPs, Au-$NP_{26,GSH}$: To the prepared aqueous solution of citrate capped Au-NPs (10 mL), L-glutathione (5 mg) was added and ultrasonicated for 30 min. After the solution was centrifuged at the speed of 7,871 g force for 15 min, the supernatant was removed carefully. The precipitated Au-$NP_{26,GSH}$ was re-dispersed in deionized water (1 mL), and the solution was used as a Au-$NP_{26,GSH}$ nanocatalyst stock solution.

2.2. Preparation of Au-$NP_{13,GSH}$[2]

(Step 1) Synthesis of citrate-capped Au-NPs (ca. 13 nm): It was prepared using the synthesis procedure reported by Turkevich et al.[2] In a 250 mL round-bottom flask, $HAuCl_4 \cdot 3H_2O$ (10 mg) was dissolved in 100 mL of deionized water and heated at 100 °C with vigorous stirring. To the aqueous solution, 5 wt% citrate aqueous solution (0.60 mL) was added at once. When the red color emerged to the solution, the reaction solution was naturally cooled down to room temperature.

(Step 2) Ligand exchange for glutathione-capped Au-NPs, Au-$NP_{13,GSH}$: To the prepared aqueous solution of citrate-capped Au-NPs (10 mL), L-glutathione (5 mg) was added and ultrasonicated for 30 min. After the solution was centrifuged at the speed of 7,871 g force for 15 min, the supernatant was removed carefully. The precipitated Au-$NP_{13,GSH}$ was re-dispersed in deionized water (1 mL), and the solution was used as a Au-$NP_{13,GSH}$ nanocatalyst stock solution.

2.3. Preparation of Au-NC_{GSH}[3]

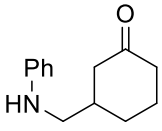
Au-NC_{GSH} was synthesized by following the procedure reported by Chen et al.[3] In a 250 mL round-bottom flask equipped with a condenser, $HAuCl_4 \cdot 3H_2O$ (120 mg) and L-glutathione (138 mg) were dissolved in deionized water (150 mL) and heated at 75 °C for 24 h with vigorous stirring. After then, the reaction solution was cooled down to room temperature. To purify Au-NC_{GSH}, the resulted aqueous solution (10 mL) was transferred to a 50 mL conical tube and mixed with acetonitrile (30 mL). The mixed solution was stored in a refrigerator for 3 h approximately. Once Au-NC_{GSH} was precipitated, the supernatant was removed carefully. The yellowish precipitates were dispersed in 30 mL of mixed solution (acetonitrile:deionized water=3:1 v/v) and then subjected to another cycle of cooling and removal of the supernatant. Finally, a stock solution of Au-NC_{GSH} was prepared by dispersing the precipitates in deionized water (1 mL).

2.4. Preparation of Au-NC_{MHA} and Au-NC_{MUA}[4]

Each aqueous solution of $HAuCl_4 \cdot 3H_2O$ (20 mM) and 6-mercaptohexanoic acid (MHA, 5 mM) or mercaptoundecanoic acid (MUA, 5 mM) was prepared. For the synthesis of Au-NC_{MHA}, in a 20 mL vial, deionized water (2.35 mL) was added to a mixture of $HAuCl_4$ stock solution (20 mM, 0.25 mL) and aqueous MHA stock solution (5 mM, 2.00 mL). The reaction mixture was first treated with 1 M of aqueous NaOH solution (0.30 mL), and then freshly prepared $NaBH_4$ (43 mg) solution containing 0.2 M of aqueous NaOH solution (0.10 mL) was rapidly added to the mixture. The reaction mixture was maintained for 24 h at room temperature under stirring. After the reaction was completed, Au-NC_{MHA} was collected by centrifugation at the speed of 7,871 g force for 30 min with a centrifugal filter (Amicon ®Ultra-4). The obtained Au-NC_{MHA} was dispersed in deionized in water (1 mL) as a Au-NC_{MHA} stock solution. Au-NC_{MUA} was synthesized by following the same procedure for Au-NC_{MHA} except for MUA stock solution preparation, 5 mM ethanolic solution was used instead of aqueous solution due to its poor solubility in deionized water.

3. General procedure for Giese reaction between 1 and 2

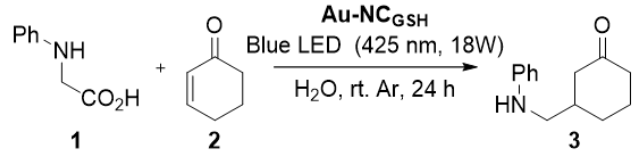
All Au-nanocatalyst solutions were prepared by adjusting its absorbance at 425 nm to 1. After the catalyst solution preparation, *N*-phenylglycine (**1**, 0.2 mmol, 30 mg, 1.0 equiv.) and 2-cyclohexen-1-one (**2**, 4.0 mmol, 384 mg, 20.0 equiv.) were charged in a 8 mL-glass vial. Au-nanocatalyst solution (2 mL) was added and the reaction mixture was degassed with Ar gas for 15 min. The reaction mixture was stirred at room temperature under blue light (425 nm, 18 W). After the reaction, the aqueous layer was extracted with $CHCl_3$ and concentrated under reduced pressure. The resulted mixture was diluted with $CHCl_3$ (6 mL) and 1 mL of the solution was obtained. The internal standard dodecane (0.1 mmol, 17 mg) was added before GC/MS analysis.

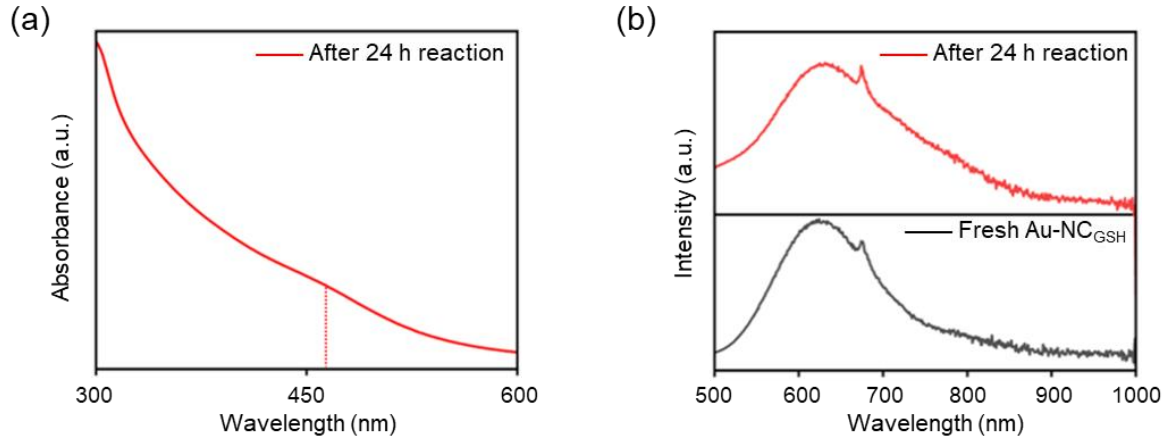


3

Clear film (85%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.12 (m, 2H), 6.75 – 6.66 (m, 1H), 6.65 – 6.55 (m, 2H), 3.80 (br s, 1H), 3.21 – 3.03 (m, 2H), 2.57 – 2.46 (m, 1H), 2.44 – 2.36 (m, 1H), 2.34 – 2.24 (m, 1H), 2.18 – 2.06 (m, 3H), 2.06 – 1.99 (m, 1H), 1.76 – 1.63 (m, 1H), 1.49 – 1.40 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.08, 148.06, 129.45, 117.61, 112.81, 49.53, 46.11, 41.59, 39.03, 29.39, 25.11; HRMS (ESI) *m/z* calcd for $C_{13}H_{17}NO$ [$(M+H)^+$] 203.1310, found 203.1316. ^{1}HNMR data was consistent with previous report.[5]

4. Stability of Au-NC$_{GSH}$ during photocatalysis





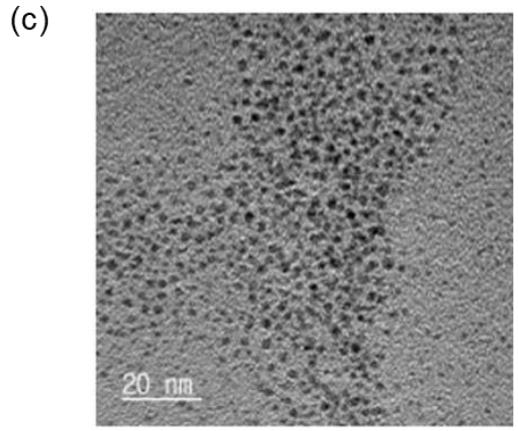


Figure S1. Stability of Au-NC$_{GSH}$ during photocatalysis with blue LED (425 nm, 18 W): (a) UV-Vis spectra before (black) and after 24 h photocatalytic Giese reaction between **1** and **2**. The recovered catalyst was collected by centrifugation at 2000 g for 20 min with a centrifugal filter (Amicon ®Ultra-4); (b) Photoluminiscence (PL) spectra of the recovered (red) and fresh Au-NC$_{GSH}$ (black); (c) TEM image of the recovered Au-NC$_{GSH}$.

5. Stability of Au-NP$_{GSH}$ during photocatalysis

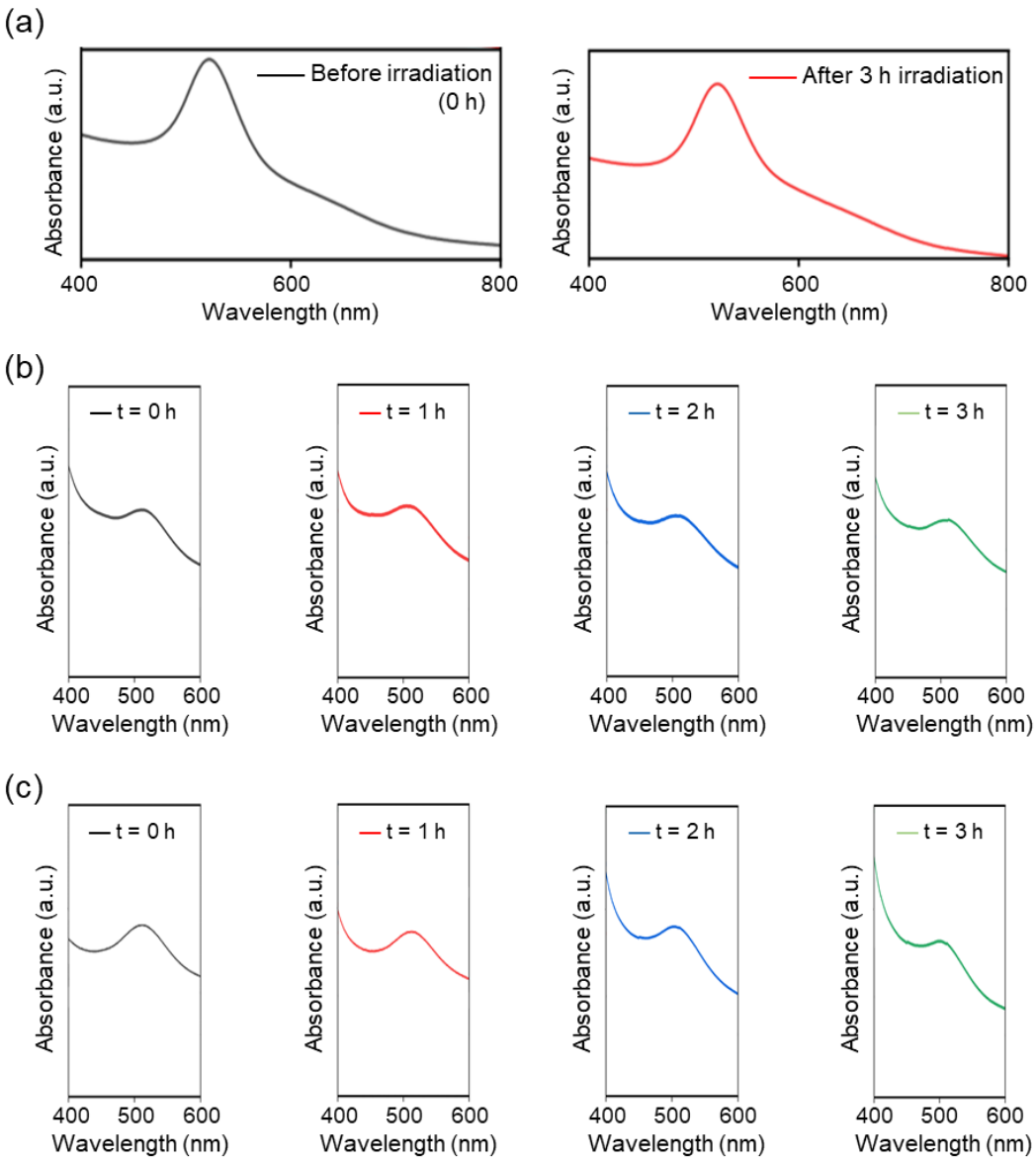
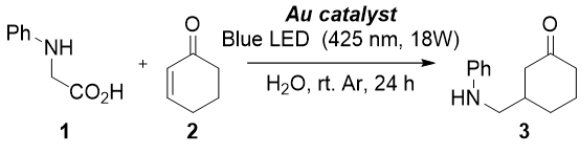
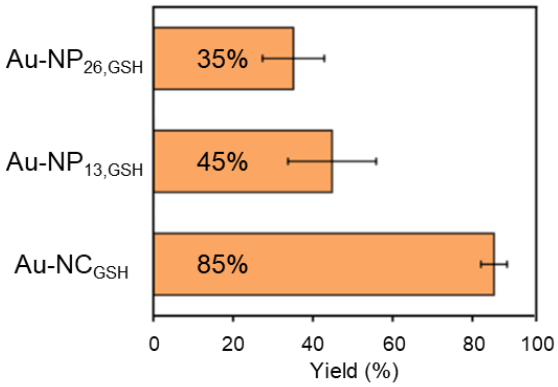


Figure S2. Stability of Au-NP$_{GSH}$ during photocatalysis with blue LED (425 nm, 18 W): (a) UV-Vis spectra of before (black) and after 3 h irradiation (red) of the Au-NP$_{26,GSH}$ aqueous catalyst solution; (b) UV-Vis spectra during photocatalytic Giese reaction between **1** and **2** with 13 nm Au-NP$_{GSH}$ (Au-NP$_{13,GSH}$); (c) UV-Vis spectra of the model reaction with 26 nm Au-NP$_{GSH}$ (Au-NP$_{26,GSH}$). Aliquot of the reaction mixture (200 µL) was monitored in different reaction times (0 h, 1 h, 2 h and 3 h) after diluting the aliquot with water (1.8 mL)

6. Photocatalytic reactions of Au nanocatalysts



(a)



(b)

Au catalyst	Wavelength	Yield
$Au\text{-}NP_{26,GSH}$	425 nm	6%
	525 nm	8%
$Au\text{-}NP_{13,GSH}$	425 nm	8%
	525 nm	7%
$Au\text{-}NC_{GSH}$	425 nm	32%
	525 nm	trace

(c)

Au catalyst	Intensity	Yield	Intensity	Yield	Intensity	Yield
$Au\text{-}NC_{GSH}$	18 W	32%	30 W	47%	40 W	69%

Figure S3. Giese reaction with Au nanocatalysts. (a) Yield of 24 h reactions with each catalyst; (b) Wavelength effect after 3-hour reactions. The intensities of 425 nm and 525 nm are 18 W and 20 W, respectively; (c) Intensity effects after 3-hour reactions. The wavelengths of 18 W, 30 W, and 40 W are 425 nm, 427 nm, and 427 nm. The yields were measured by gas chromatography.

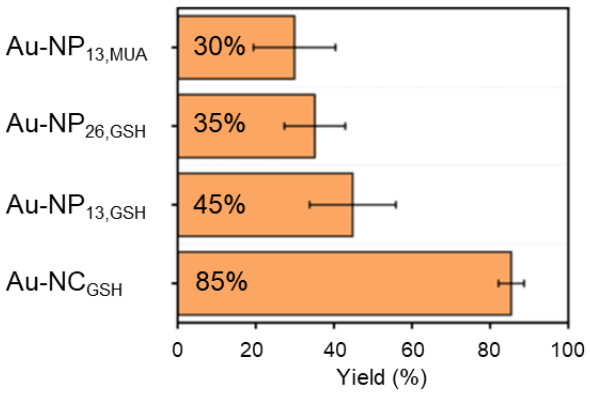
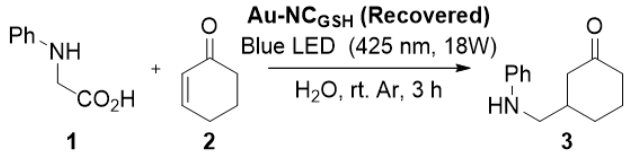


Figure S4. Results of the photocatalysis with Au catalysts under blue LED (425 nm, 18 W) after 24 h reaction.

7. Recyclability of Au-NC$_{GSH}$



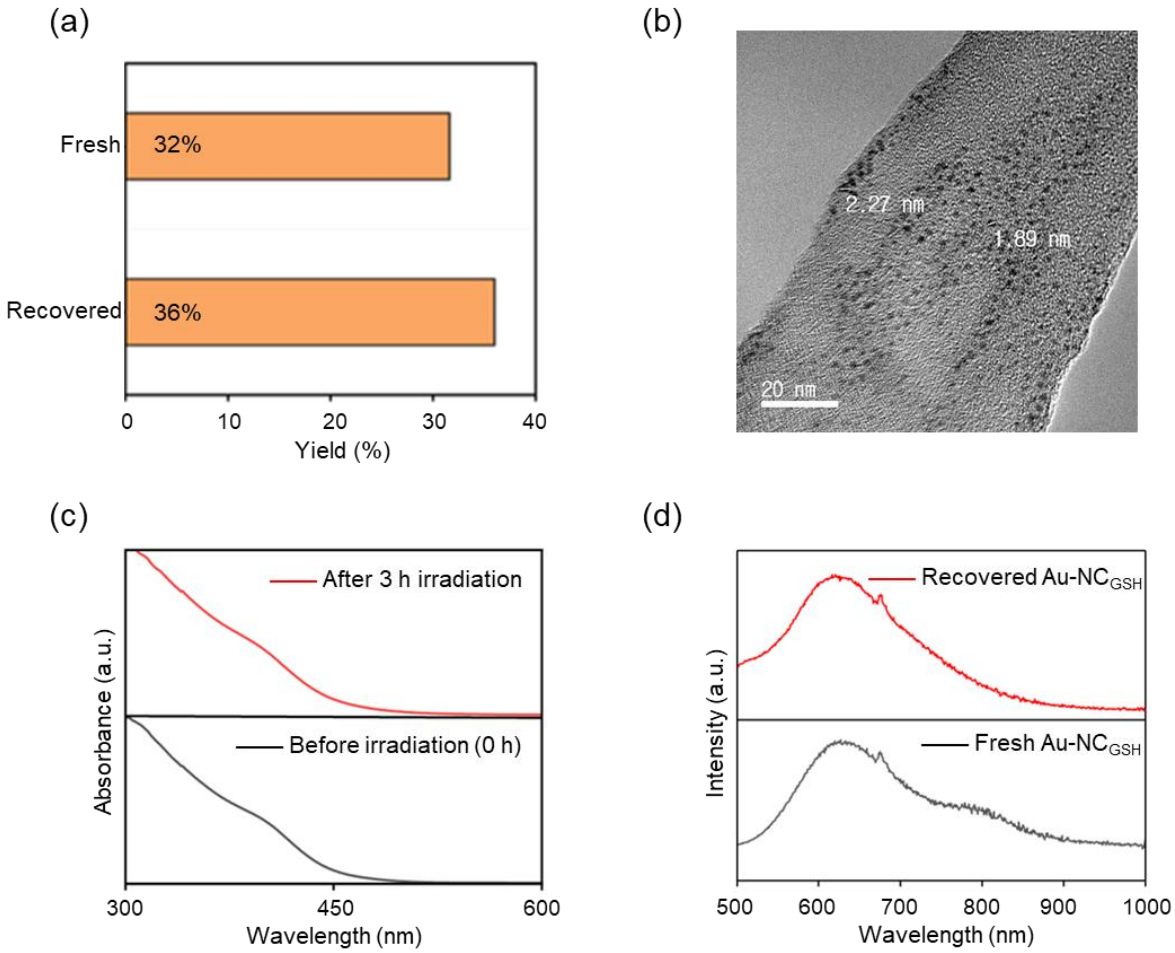
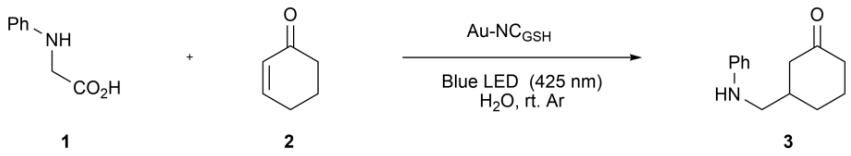


Figure S5. Recyclability of Au-NC$_{GSH}$ after photocatalysis with blue LED (425 nm, 18 W): (a) Yield after 3 h reaction with recovered Au-NC$_{GSH}$; (b) TEM image; (c) UV-Vis spectra; and (d) Photoluminiscence (PL) spectra of of the recovered Au-NC$_{GSH}$ from 3 h reaction (red) and fresh Au-NC$_{GSH}$ (black).

8. Control experiments on model Giese reaction



1 **2** **3**

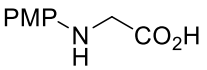
Entry	Conditions	**3**[a]
1	No Au-NC_{GSH}	n.d.
2	No light	n.d.
3	With a hole scavenger (EtOH, 2 mL)	trace
4	With an electron scavenger (NaS_2O_8, 3.0 equiv.)	n.d.
5	With a radical scavenger (TEMPO, 3.0 equiv.)	n.d.

Table S1. Control experiments on model Giese reaction [a]Yield was determined by gas chromatography. n.d.: not detected

9. Synthesis of (±)-pregabalin·HCl

9.1. Preparation of (4-methoxyphenyl)glycine (4)

(4-Methoxyphenyl)glycine was synthesized according to the previous report with slight modification.[6]

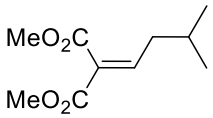


4

^{1}H NMR (500 MHz, DMSO-d_6) δ 6.71 (d, J = 8.9 Hz, 2H), 6.51 (d, J = 8.9 Hz, 2H), 3.72 (s, 2H), 3.63 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 172.94, 150.99, 142.41, 114.54, 113.15, 55.31, 45.51; HRMS (ESI) *m/z* calcd for $C_9H_{11}NO_3$ [(M+H)$^+$] 181.0739, found 181.0735. The ^{1}HNMR data was consistent with the previous report.[7]

9.2. Preparation of dimethyl 2-(3-methylbutylidene)malonate (5)

Dimethyl 2-(3-methylbutylidene)malonate was synthesized according to the reported method.[8]

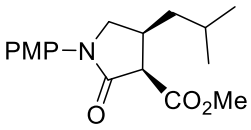


5

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.97 (t, J = 7.9 Hz, 1H), 3.74 (s, 3H), 3.70 (s, 3H), 2.11 (dd, J = 7.9, 6.8 Hz, 2H), 1.87 – 1.67 (m, 1H), 0.86 (d, J = 6.7 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.92, 164.27, 149.23, 128.55, 52.22, 52.10, 38.60, 28.09, 22.32; HRMS (ESI) *m/z* calcd for $C_{10}H_{17}O_4$ [(M+H)$^+$] 201.1127, found 201.1124. ^{1}HNMR was consistent with previous report.[8]

9.3. Preparation of (±)-pregabalin·HCl

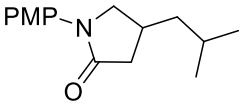
Compound **6** was synthesized according to the general procedure using Au-NC_{GSH} solution. After **4** (0.2 mmol, 36 mg, 1.0 equiv.) and **5** (2 mmol, 400 mg, 10.0 equiv.) were charged in glass vial (8 mL), 2 mL of Au-NC_{GSH} solution was added. The reaction mixture was degassed with Ar gas for 15 min. The reaction mixture was stirred at room temperature under blue light (425 nm, 18 W) for 48 h. The crude was purified by column chromatography. The product was afforded as white crystal (49 mg, 80% yield). Purification conditions: *n*-hexane:EtOAc= 2:1), R_f=0.5 in *n*-hexane/EtOAc=2:1).



(±) **6**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, J = 9.1 Hz, 2H), 6.89 (d, J = 9.1 Hz, 2H), 3.95 (dd, J = 9.4, 8.0 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.44 (dd, J = 9.4, 7.5 Hz, 1H), 3.32 (d, J = 8.6 Hz, 1H), 3.01 – 2.89 (m, 1H), 1.68 – 1.60 (m, 1H), 1.54 – 1.39 (m, 2H), 0.94 (d, J = 6.7 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.51, 168.44, 157.01, 132.19, 121.99, 114.20, 56.67, 55.62, 53.51, 52.87, 43.26, 34.24, 26.10, 22.73, 22.66; HRMS (ESI) *m/z* calcd for $C_{17}H_{23}NO_4$ [(M+H)$^+$] 305.1627, found 305.1626.

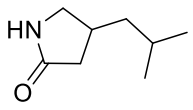
Compound **6** (0.14 mmol, 43 mg, 1.0 equiv.) was dissolved in THF (0.5 mL) and 2.5 M aqueous solution of NaOH (0.5 mL) was added. The reaction mixture was stirred at room temperature overnight. After the reaction, the aqueous layer was acidified with 1N HCl and extracted with EtOAc (5 mL x 2). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure to afford carboxylic acid intermediate. The carboxylic acid intermediate was dissolved in a mixture of H_2O (1.5 mL) and 1,4-dioxane (0.3 mL). To the reaction mixture, conc. HCl (0.5 mL) was added and refluxed for 48 h. After the reaction was completed, the aqueous layer was extracted with EtOAc (5 mL x 2). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude was purified by column chromatography. Purification conditions: *n*-hexane/EtOAc=2:1), R_f=0.4 in *n*-hexane/EtOAc=2:1). The product was afforded as white crystalline (30 mg, 86% yield).



7

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 9.1 Hz, 1H), 6.89 (d, *J* = 9.1 Hz, 1H), 3.85 (dd, *J* = 9.4, 7.8 Hz, 1H), 3.79 (s, 3H), 3.44 (dd, *J* = 9.4, 7.3 Hz, 1H), 2.69 (dd, *J* = 16.7, 8.4 Hz, 1H), 2.61 – 2.43 (m, 1H), 2.25 (dd, *J* = 16.7, 8.5 Hz, 1H), 1.71 – 1.58 (m, 1H), 1.41 (t, *J* = 7.3 Hz, 2H), 0.93 (dd, *J* = 6.6, 5.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.58, 156.63, 132.76, 121.88, 114.13, 55.58, 55.19, 43.84, 39.45, 29.87, 26.29, 22.82, 22.68; HRMS (ESI) *m/z* calcd for $C_{15}H_{21}NO_2$ [$(M+H)^+$] 247.1572, found 247.1573.

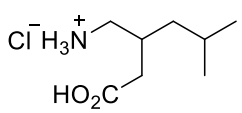
Compound **7** (0.15 mmol, 38 mg, 1.0 equiv.) was dissolved in a mixture of MeCN (1.5 mL) and H_2O (0.3 mL). To the reaction mixture, CAN (0.45 mmol, 247 mg, 3.0 equiv.) was added and stirred at room temperature for 3 h. After the reaction was completed, the reaction mixture was diluted with EtOAc (2 mL) and extracted with EtOAc (5 mL x 3). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude was purified by column chromatography to afford pale white film (21 mg, 97% yield). Purification conditions: *n*-hexane/EtOAc=1:4), R_f=0.2 in *n*-hexane/EtOAc=1:4).



8

^{1}H NMR (500 MHz, CD_3OD) δ 3.49 (dd, *J* = 9.8, 7.9 Hz, 1H), 3.00 (dd, *J* = 9.8, 7.2 Hz, 1H), 2.64 – 2.51 (m, 1H), 2.40 (dd, *J* = 16.7, 8.6 Hz, 1H), 1.99 (dd, *J* = 16.6, 8.4 Hz, 1H), 1.67 – 1.55 (m, 1H), 1.37 (d, *J* = 7.3 Hz, 2H), 0.93 (dd, *J* = 6.6, 5.1 Hz, 6H); ^{13}C NMR (126 MHz, CD_3OD) δ 180.82, 49.55, 44.94, 38.13, 34.21, 27.37, 23.07, 22.89; HRMS (ESI) *m/z* calcd for $C_8H_{15}NO$ [$(M+H)^+$] 141.1154, found 141.1154.

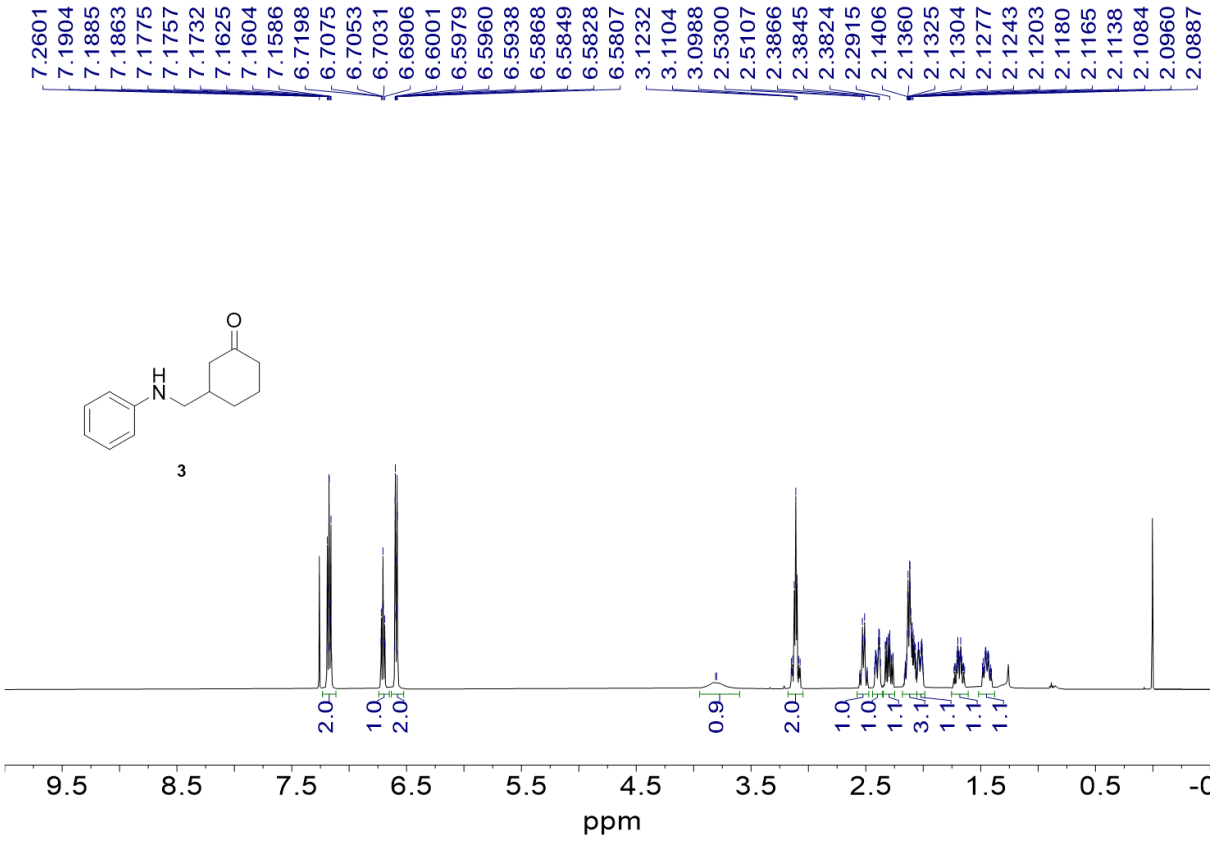
Compound **8** (0.15 mmol, 21 mg, 1.0 equiv.) was dissolved in conc. HCl solution (2.5 mL), and the reaction mixture was refluxed overnight. After the reaction was completed, the resulting mixture was concentrated under reduced pressure and dried under vacuum. The product was afforded as pale brown crystalline (28 mg, 96% yield).



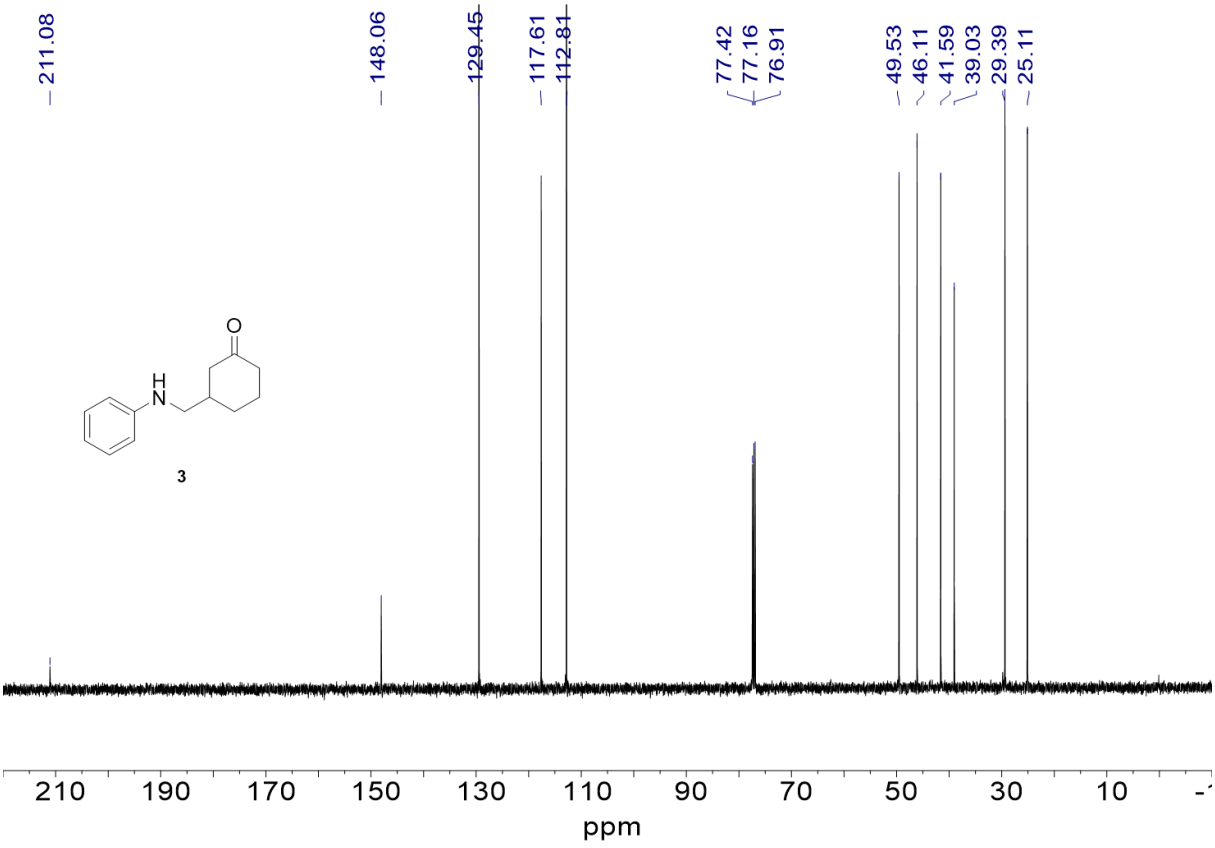
9

^{1}H NMR (400 MHz, D_2O) δ 2.95 (d, *J* = 6.4 Hz, 2H), 2.50 – 2.32 (m, 2H), 2.23 – 2.12 (m, 1H), 1.65 – 1.50 (m, 1H), 1.18 (dd, *J* = 7.2, 7.2 Hz, 2H), 0.81 (dd, *J* = 9.1, 6.5 Hz, 6H); ^{13}C NMR (101 MHz, D_2O) δ 176.69, 42.96, 40.10, 36.12, 30.81, 24.31, 21.90, 21.25; HRMS (ESI) *m/z* calcd for $C_8H_{18}NO_2$ [$(M+H)^+$] 160.1338, found 160.1343.

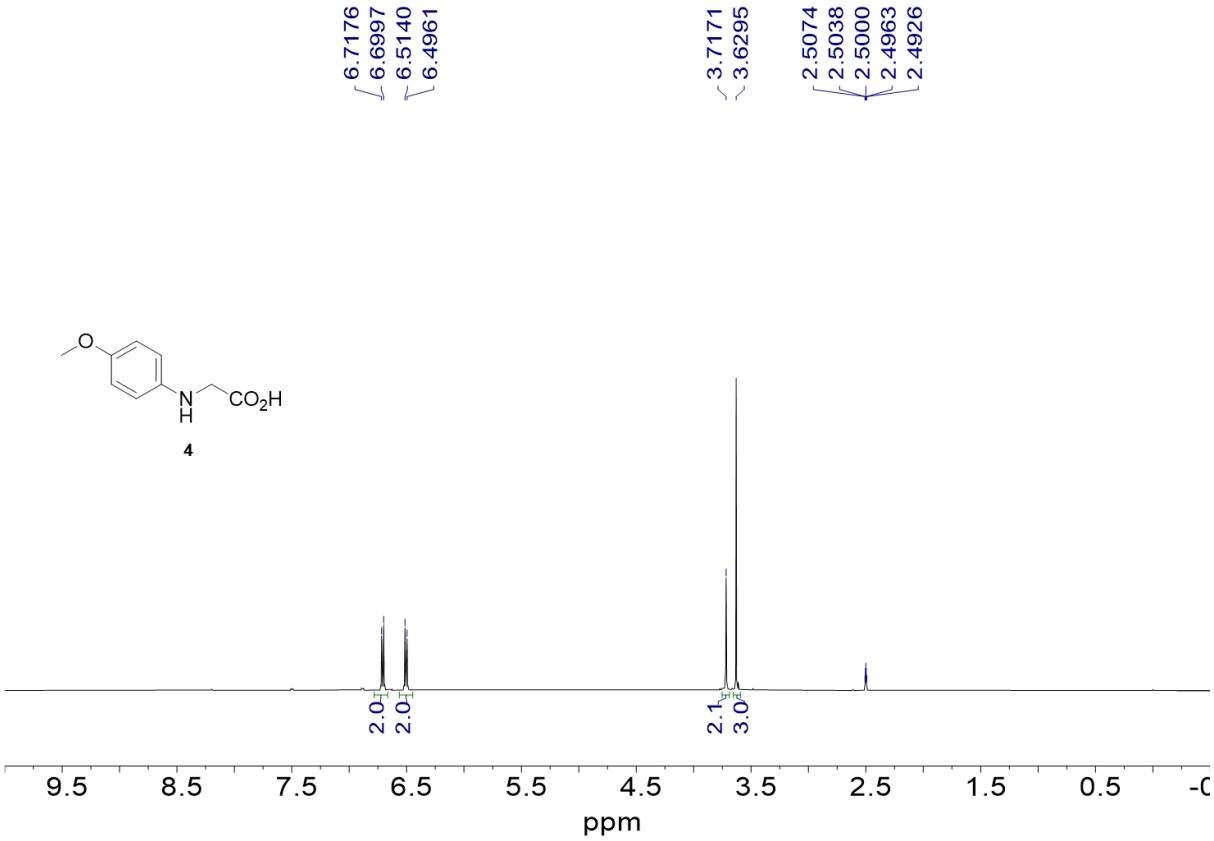
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

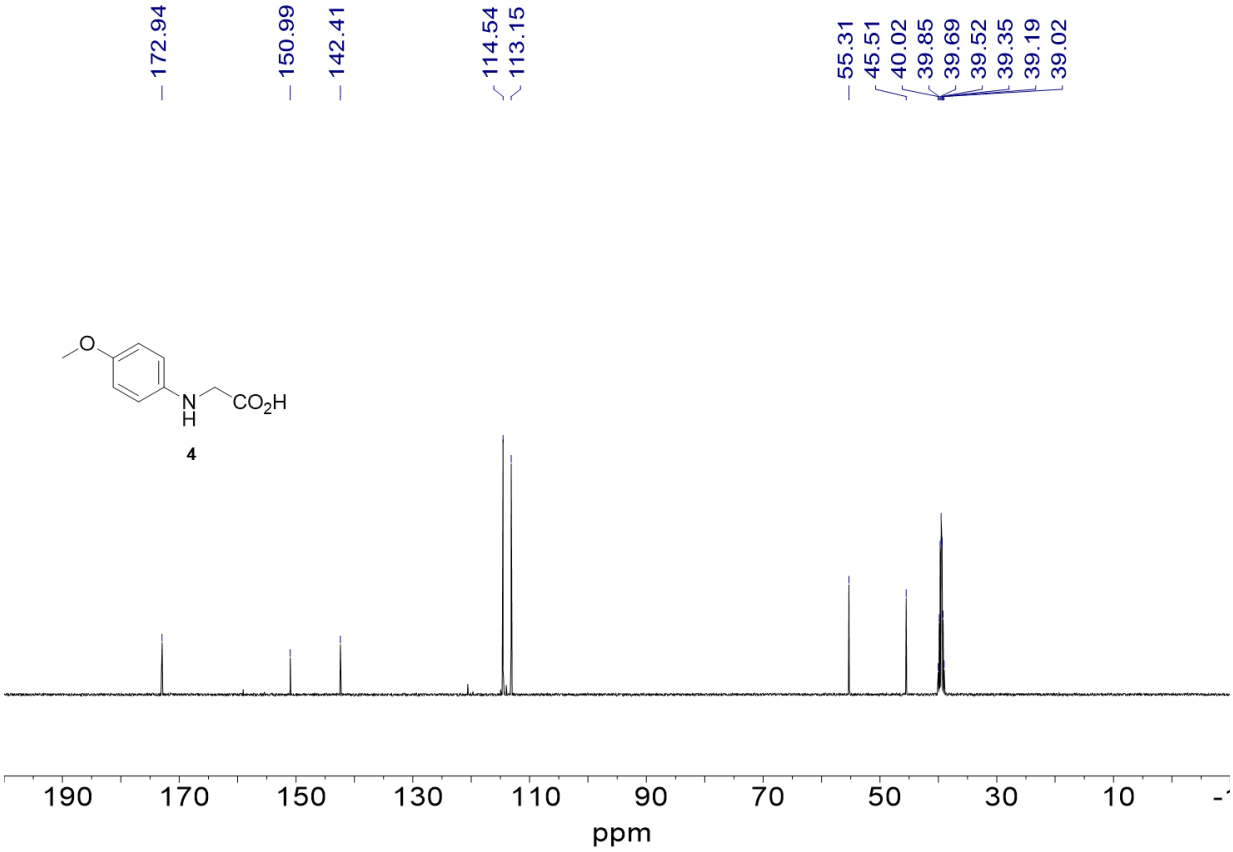


^{1}H NMR (500 MHz, DMSO-d_6)



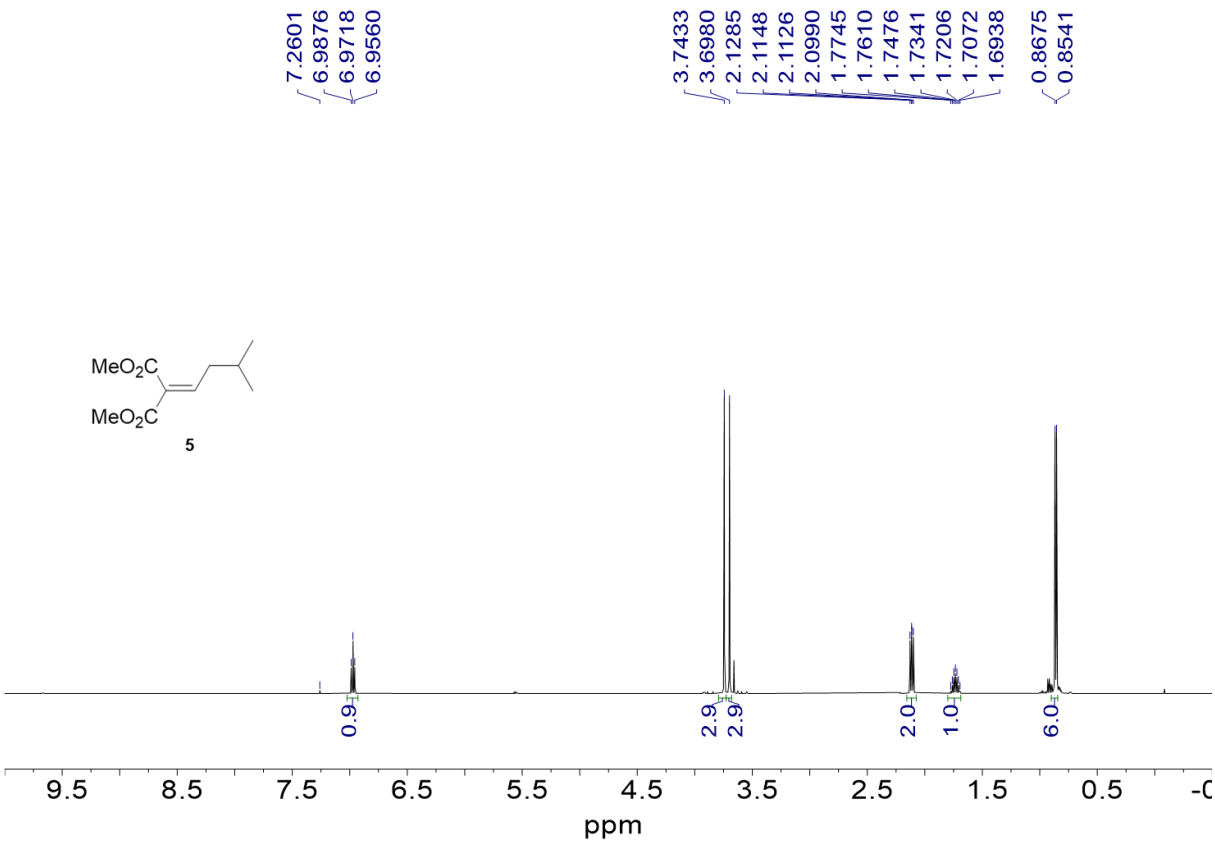
4

^{13}C NMR (126 MHz, DMSO-d_6)

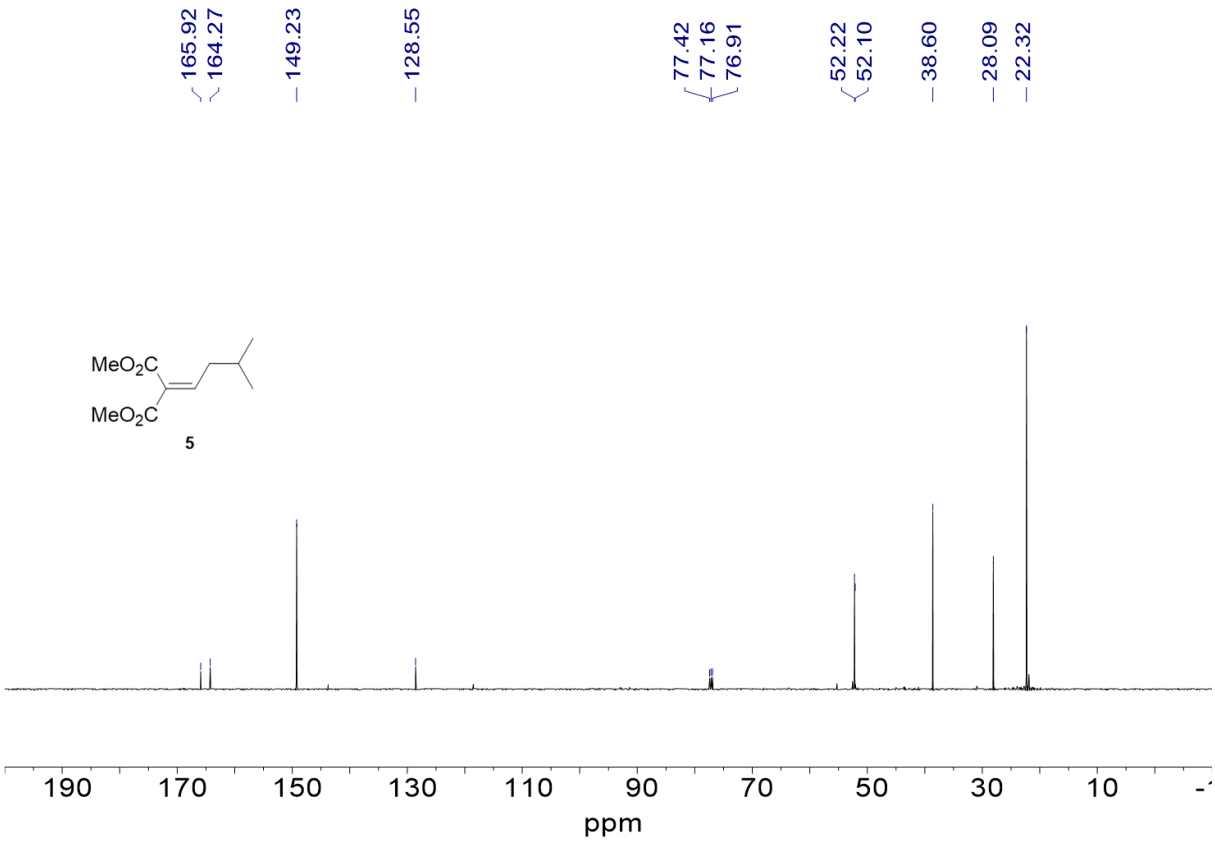


4

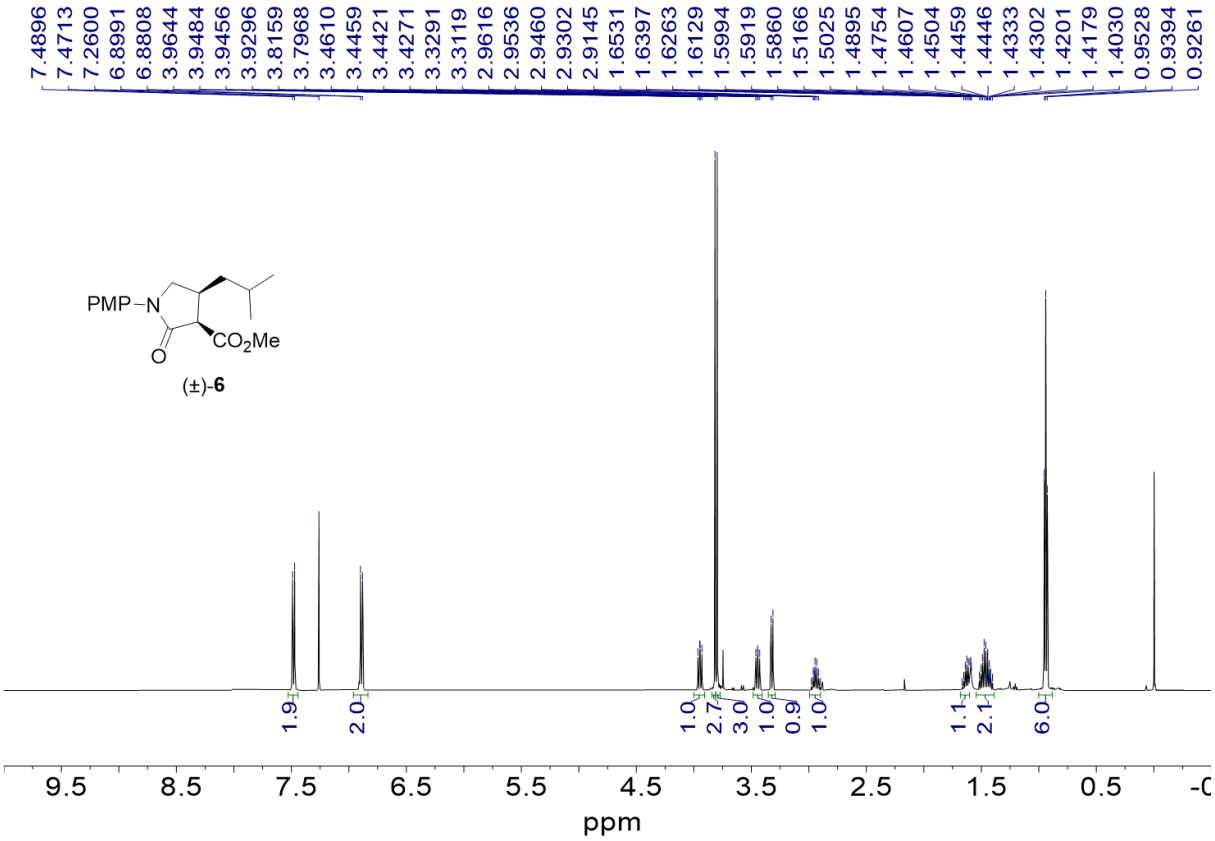
^{1}H NMR (500 MHz, $CDCl_3$)



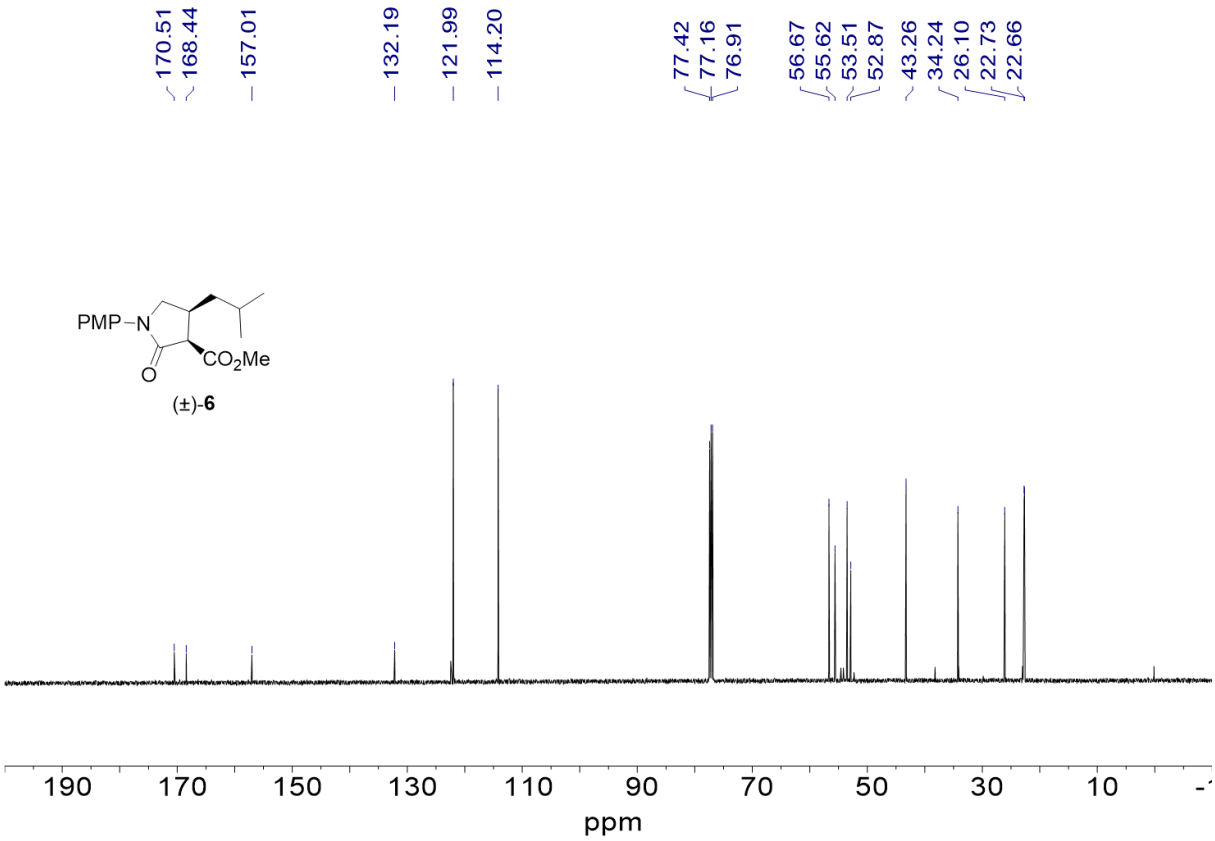
^{13}C NMR (126 MHz, $CDCl_3$)



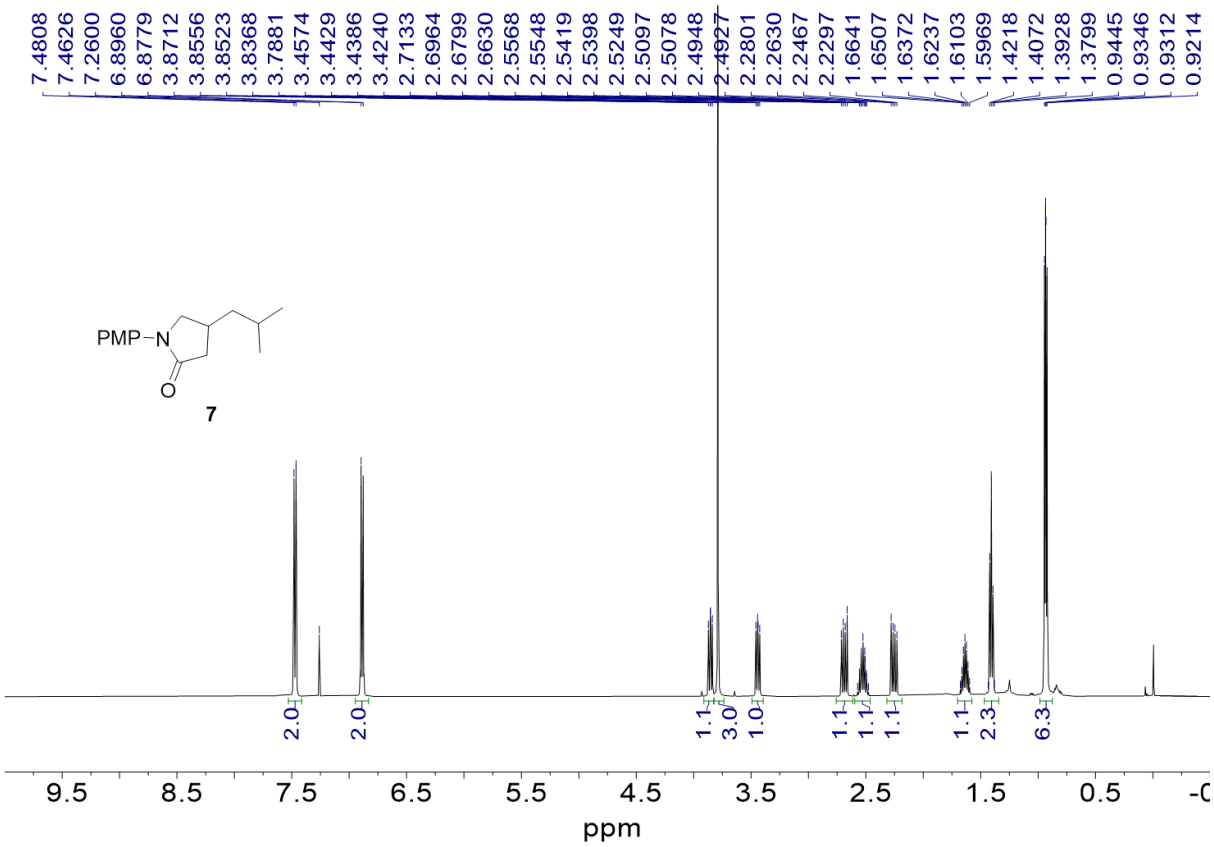
^{1}H NMR (500 MHz, $CDCl_3$)



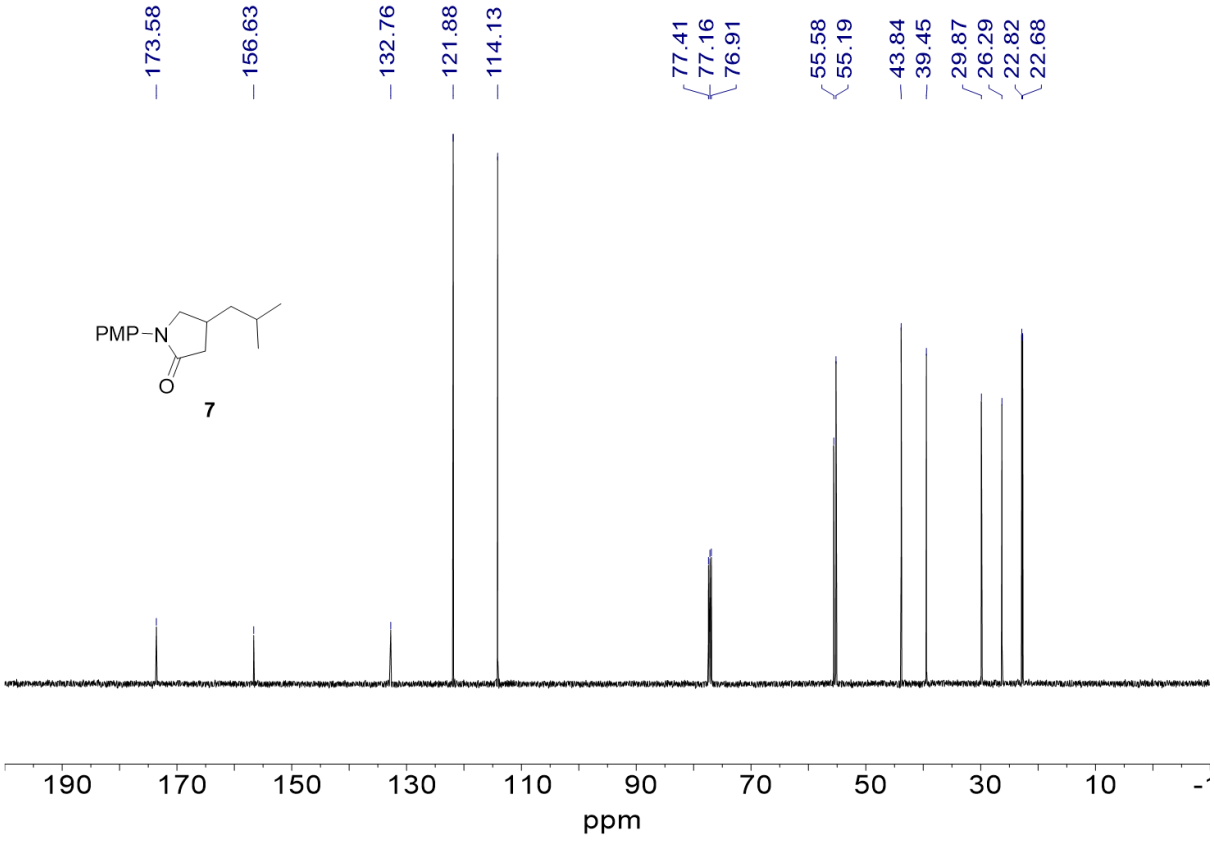
^{13}C NMR (126 MHz, $CDCl_3$)



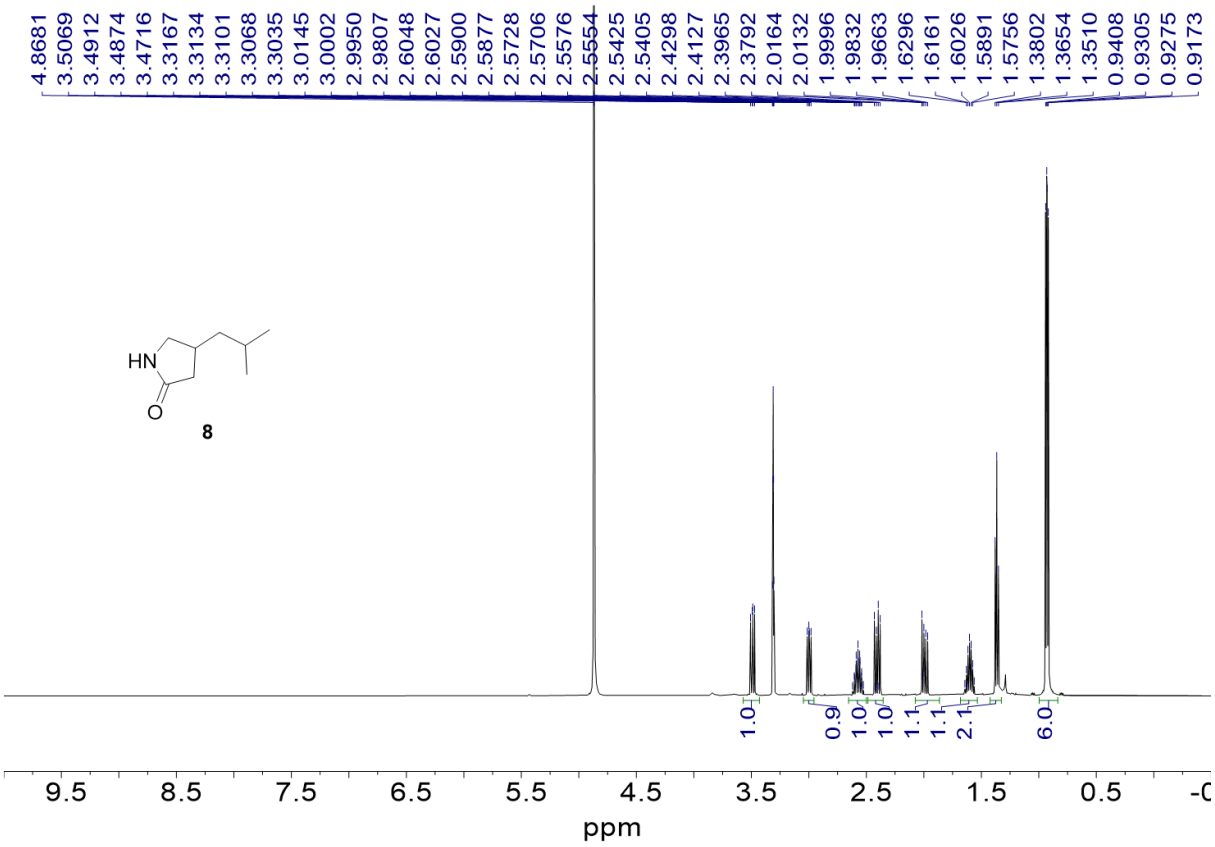
^{1}H NMR (500 MHz, $CDCl_3$)



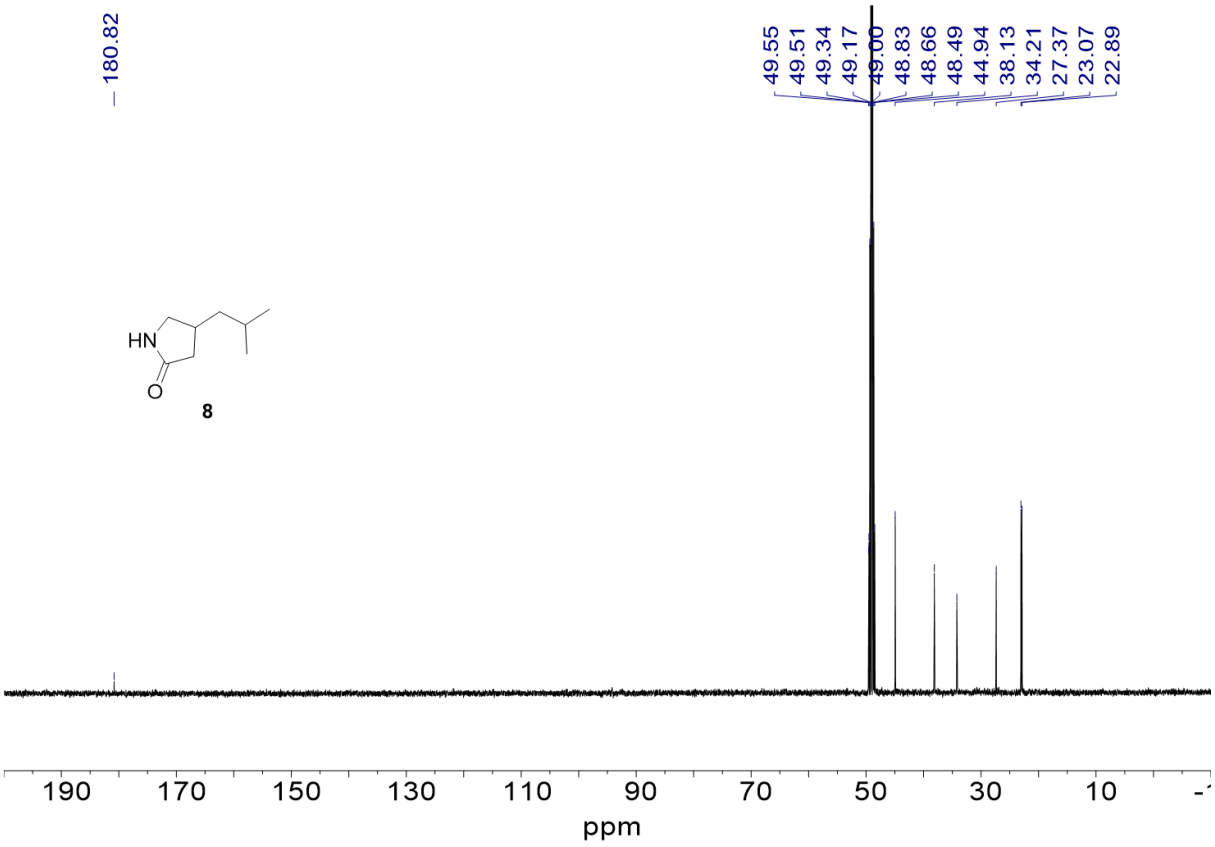
^{13}C NMR (126 MHz, $CDCl_3$)



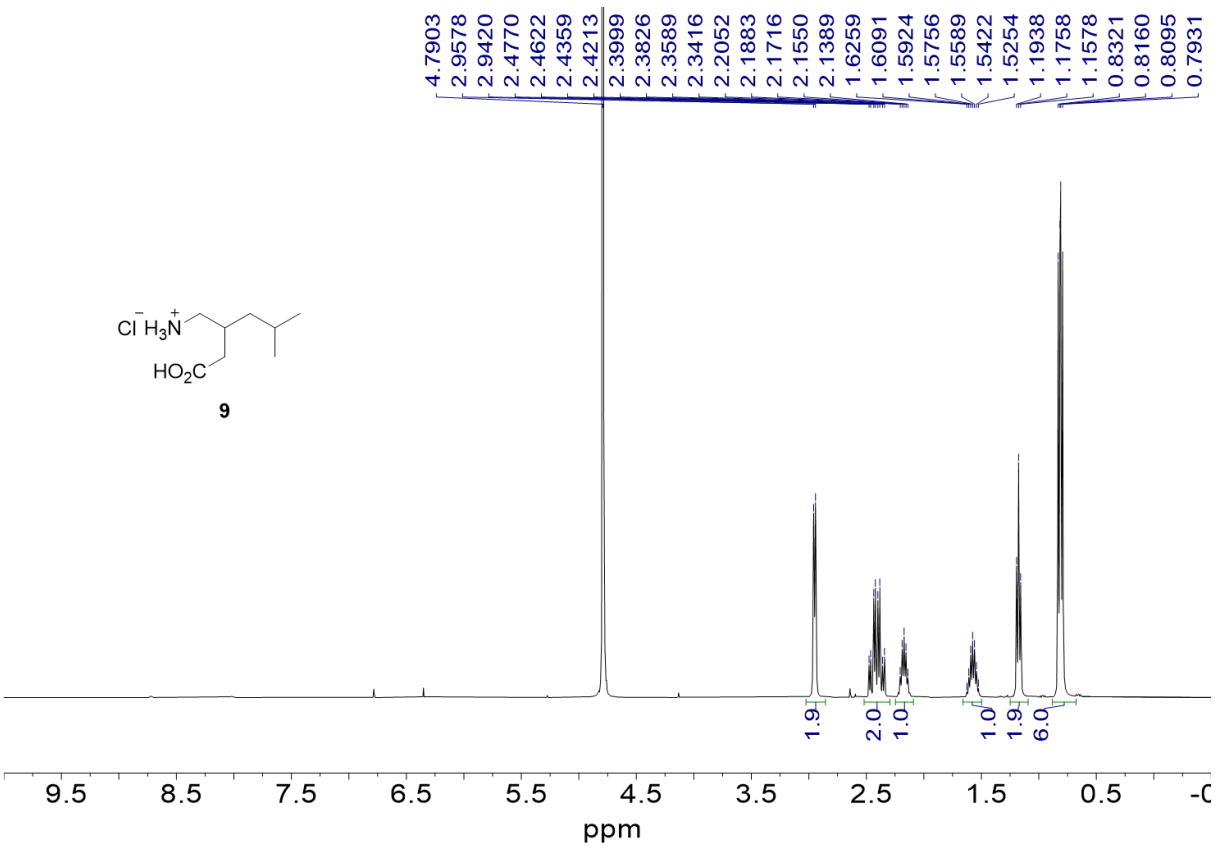
^{1}H NMR (500 MHz, CD_3OD)



^{13}C NMR (126 MHz, CD_3OD)



^{1}H NMR (400 MHz, D_2O)



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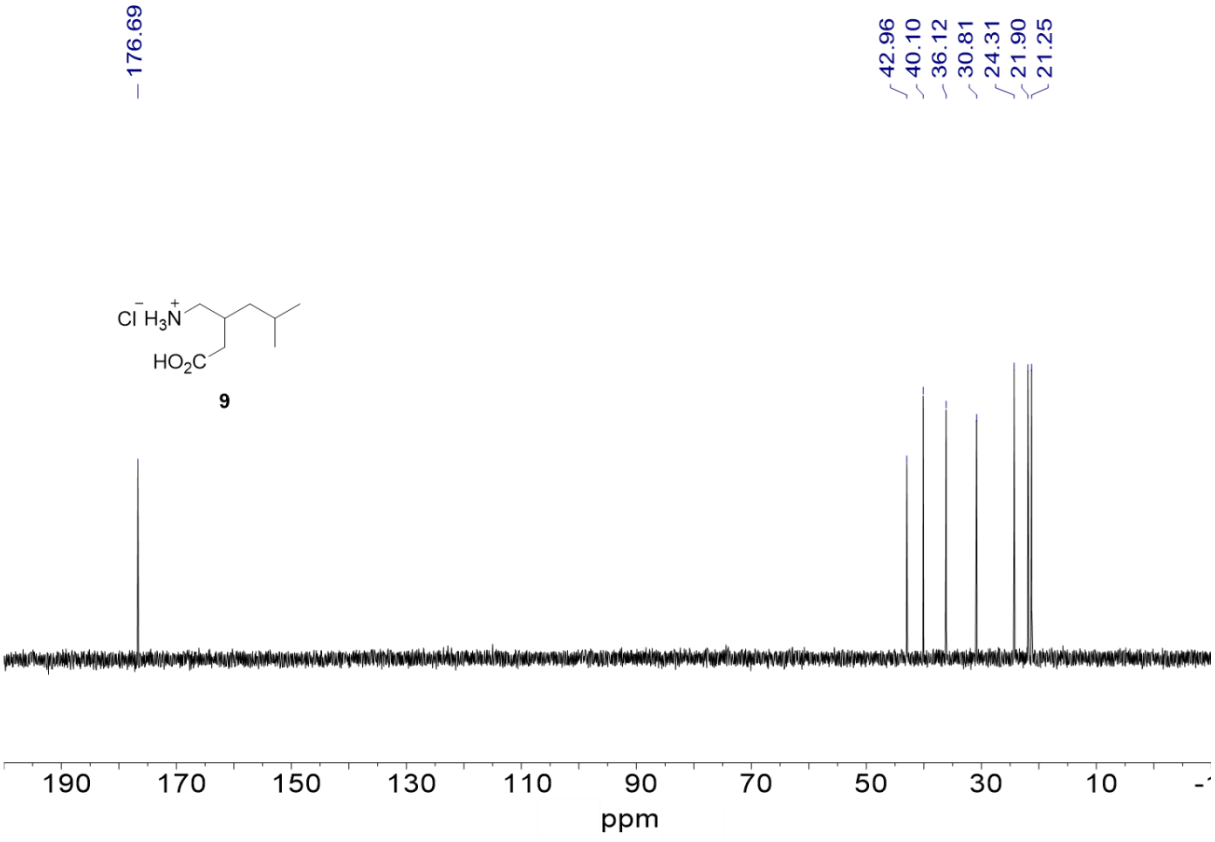
^{13}C NMR (101 MHz, D_2O)



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