Supporting Information

Carbamoylation of Azomethine Imines via Visible-Light Photoredox Catalysis

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General Considerations

Unless otherwise stated, all reagents were purchased from commercial sources and used without additional purification. THF was freshly distilled under argon from the sodium anion of benzophenone. All other anhydrous solvents were purchased or obtained from in house solvent purification towers. HPLC grade solvents were used in the photocatalyzed reactions.

All air or moisture-sensitive reactions were conducted in flame dried glassware under nitrogen atmosphere.

All reactions were monitored by thin layer chromatography using Merck silica gel aluminum sheets 60 F254, using hexane/acetone, hexane/EtOAc or DCM/MeOH as mobile phase and visualized by UV lamp, permanganate and vanillin stains.

Flash column chromatography was accomplished using silica gel 60 (230-400 mesh) and hexane/acetone, hexane/EtOAc or DCM/MeOH as eluent systems.

^{1}H and ^{13}C spectra were recorded on Brucker NMR spectrometers at 298 K. ^{1}H (400 MHz) and ^{13}C (126 MHz) NMR chemical shifts are reported relative to internal TMS (δ = 0.00 ppm; $CDCl_3$: 7.26 ppm for ^{1}H nuclei and 77.16 for ^{13}C nuclei); (δ = 0.00 ppm; DMSO-*d6*: 2.50 ppm for ^{1}H nuclei and 40.00 for ^{13}C nuclei); (δ = 0.00 ppm; CD_3OD: 3.31 ppm for ^{1}H nuclei and 49.0 for ^{13}C nuclei). Chemical shifts are given in ppm. Coupling constant values *J* are given in Hertz. The multiplicities are described as: brs = broad signal, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, ddd = doublet of doublet of doublets, dddd = doublet of doublet of doublet of doublets and m = multiplet.

Mass spectra data were recorded at Waters Technologies of Brazil. The samples were solubilized in acetonitrile/water 90:10 and analyzed by ASAP probe in the Xevo G2-XS QTOF spectrometer. Spectra were acquired in MS mode.

The diastereoisomeric ratios were determined by NMR analysis of crude reactions.

Photoreactions

A 34 W Kessil H150 blue LED (emission: 456 nm) was used as the visible light source. All chemicals and photocatalysts were purchased and used as received from suppliers unless otherwise noted. The photocatalyst 2,4,5,6-Tetra(carbazol-9-yl)isophthalonitrile 4CzIPN was prepared following the reported experimental procedure.[1] HPLC grade solvents were used in the photocatalyzed reactions.

[1] J. Luo and J. Zhang, *ACS Catal.*, **2016**, *6*, 873 - 877.

Experimental Set-Up

Photoredox reactions were kept under blue LED irradiation using Schlenk tubes as reaction vessels (up to 3 Schlenk tubes per reactor). They were placed at approximately 7 cm from the irradiation source and the temperature (~30 °C) was controlled using a desk fan placed above the photoreactor.

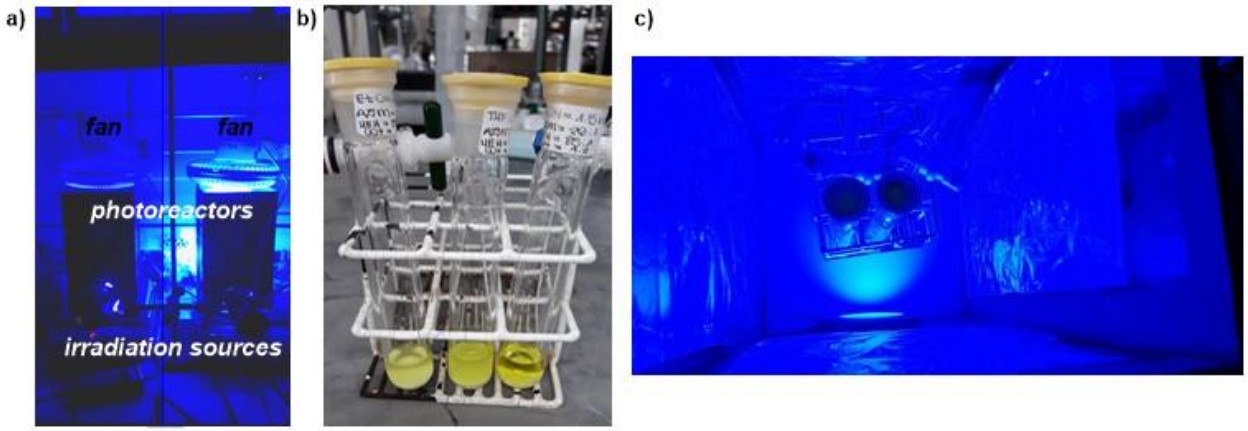
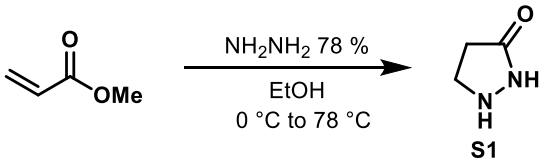


Figure S1. Experimental set-up for the photocatalyzed reactions. a) Photoreactors with the irradiation source and the external fan. b) The Schlenk tubes filled with the reaction mixture. c) Schlenk's distance from the irradiation source inside the photoreactor.

Starting Materials Preparation

Azomethine Imine Synthesis (3' – 16')

<u>Pyrazolidin-3-one (S1):</u>

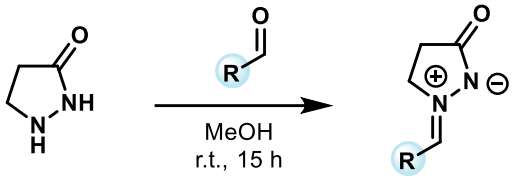


Scheme S1. Preparation of pyrazolidin-3-one S1.

Pyrazolidin-3-one **S1** was prepared following the reported experimental procedure:[2] in a flame-dried round bottom flask a solution of hydrazine monohydrate 78 % (1.0 equiv) in absolute ethanol (4 M) was cooled to 0 °C using an ice bath. Methyl acrylate (1.0 equiv) was slowly added, and the solution was stirred at 0 °C for 30 min and then was heated to reflux using an oil bath and stirred until the reaction be completed judging by TLC analysis. The solution was concentrated under vacuum to yield the crude pyrazolidin-3-one as a clear or yellow oil. The pyrazolidin-3-one was used immediately in the next step without purification.

[2] S. E. Winterton and J. M. Ready, *Org. Lett*., **2016**, *18*, 2608–2611.

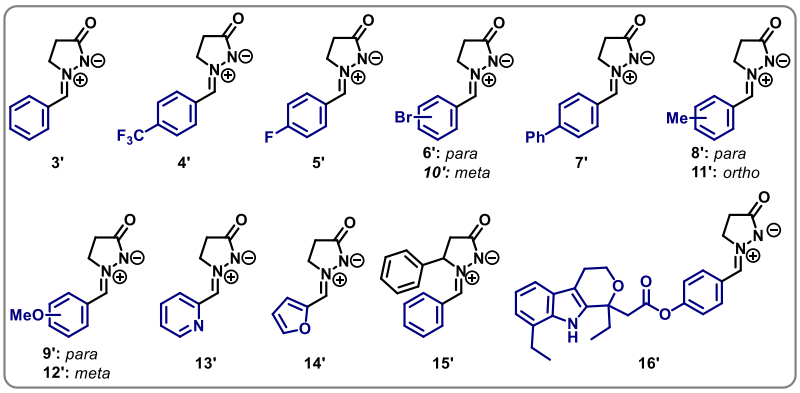
Azomethine Imines:



Scheme S2. Preparation of azomethine imines.

Azomethine imines were prepared following the reported experimental procedure:[2] The crude pyrazolidinone **S1** (1.0 equiv) obtained in the previous step and the corresponding aldehydes (1.2 equiv) were dissolved in anhydrous MeOH (1 M). The mixture was stirred at room temperature overnight and then concentrated under vacuum to remove the solvent. Et_2O was added to precipitate the product (if the precipitation does not occur, it can be promoted by the addition of few drops of hexane followed by cooling in the freezer). The resulting solid was collected by filtration, washed with Et_2O and dried to yield the final product. For substrates that do not precipitate, the reaction crudes were purified by column chromatography using DCM/ MeOH (20:1) as eluent.

The following **azomethine imines** were used as starting materials for the scope evaluation. The reported compounds were prepared and characterized according to literature[2-6]. The compound **16'** was prepared using the same experimental procedure[2] and its spectroscopic data is reported in the appropriated session in the SI.

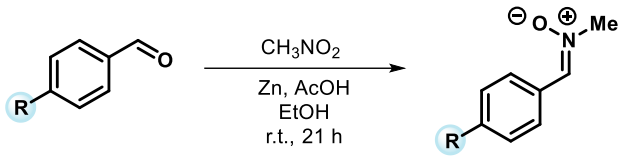


Scheme S3. Azomethine imines used as starting material during the scope study.

Spectroscopic data of *C,N*-Cyclic Azomethine Imines:

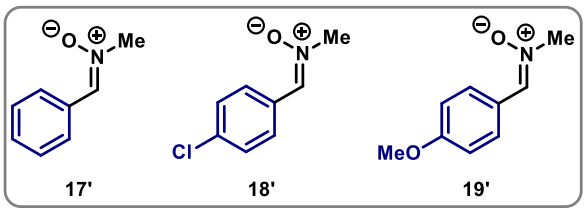
3’, 4’, 6’, 9’, 13’, 15’[2]; 5’, 8’, 12’, 14’ [3]; 7’ [4]; 10’ [5] and 11’ [6].

_N_-Methyl-Nitrone Synthesis (17’ – 19’)



Scheme S4. Preparation of N-Methyl-Nitrones.

N-methyl-nitrones were prepared following the reported experimental procedure:[7,8] To a solution of aromatic aldehyde (1.0 equiv), nitromethane (4.0 equiv) and zinc powder (6 equiv) in 95% ethanol (0.19 M) at 0 °C was added glacial acetic acid (7 equiv) dropwise over a period of 1 h. Next, the mixture was allowed to stir for 20 h at room temperature. The suspension was filtered; the filtrate concentrated under vacuum, and the crude mixture was purified by flash column chromatography using AcOEt/ MeOH (50:1) as eluent to give the corresponding nitrone.



Scheme S5. N-Methyl-nitrones used as starting material during the scope study.

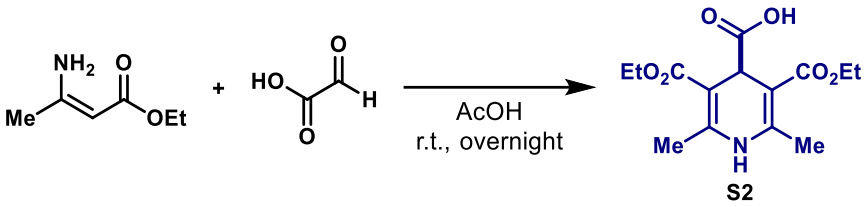
Spectroscopic data of _N_-Methyl Nitrones:

17’, 18’ [7] and 19’[8].

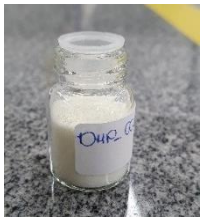
Carbamoyl-1,4-Dihydropyridines Synthesis (20’ – 52’)

<u>Synthesis of 3,5-diethoxycarbonyl-2,6-dimethyl-1,4-dihydropyridine-4-carboxylic acid (S2)</u>

[3] Q. Du, J.-M. Neudörfl and H.-G. Schmalz, *Chem. Eur. J.*, **2018**, *24*, 2379-2383.
[4] C. Li, C. -S. Wang, T.-Z. Li, G.-J. Mei and F. Shi, *Org. Lett.*, **2019**, *21*, 598–602.
[5] R. Shintani and G. C. Fu, *J. Am. Chem. Soc.,* **2003**, *125*, 10778–10779.
[6] R. Shintani and T. Hayashi, *J. Am. Chem. Soc.,* **2006**, *128*, 6330–6331.
[7] S. Pagoti, D. Dutta and J. Dash, *Adv. Synth. Catal.,* **2013**, *355*, 3532–3538.
[8] M. M. Andrade, M. T. Barros and R. C. Pinto, *Tetrahedron,* **2008**, *64*, 10521–10530.



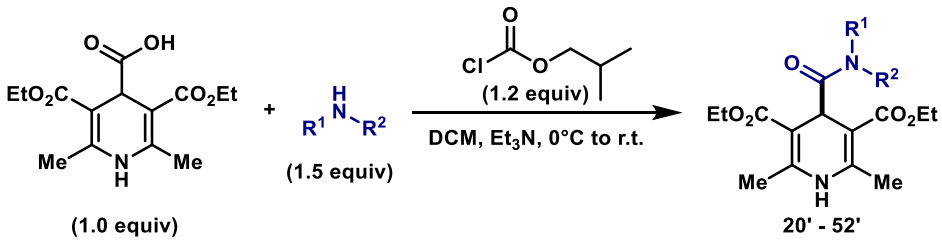
Scheme S6. Preparation of 1,4-dihydropyridine-4-carboxylic acid.



The 1,4-dihydropyridine-4-carboxylic acid was prepared following the reported experimental procedure:[9] A solution of glyoxylic acid 50 % wt in H_2O (1 equiv) was slowly added to a solution of ethyl-3-aminocrotonate (2.0 equiv) in glacial acetic acid (2.7 M) at 0 °C. A yellow precipitate is formed (**Figure S2**), and the resulting mixture was left stirring overnight at room temperature. The solid was filtered, washed with acetic acid and water, and dried under reduced pressure to give the 1,4-dihydropyridine-4-carboxylic acid as a white solid (image on the left) (yield = 35 %)

Figure S2. General aspect of the reaction mixture after the glyoxylic acid addition.

4-Carbamoyl-1,4-Dihydropyridines 20' - 52'



Scheme S7. Preparation of 4-carbamoyl-1,4-dihydropyridines 20' – 52'.

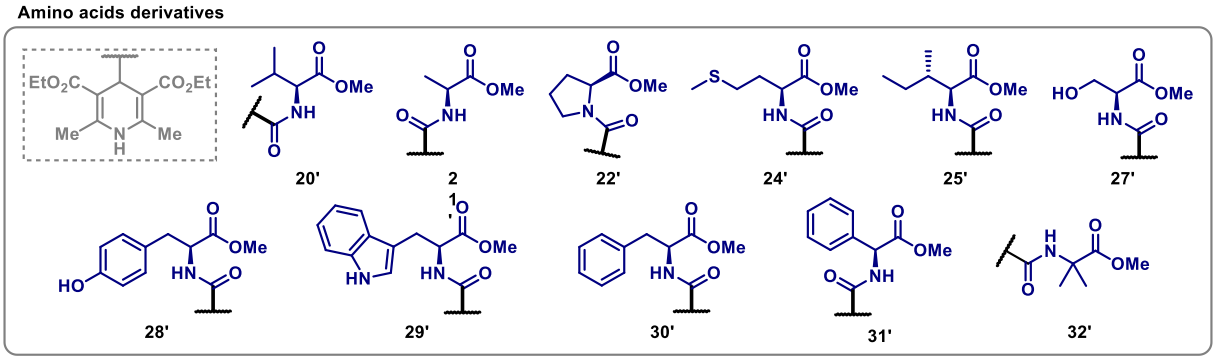
[9] G. Ya. Dubur and Ya. R. Uldrikis, *Chem. Heterocycl. Compd*., **1972**, *5*, 762–763.

The 1,4-DHPs were prepared following the reported experimental procedure:[10] In a 50 mL round bottom flask under N_2 atmosphere, 1,4-dihydropyridine-4-carboxylic acid **S2** (1.5 mmol) was suspended in DCM (0.2 M), followed by addition of Et_3N (1.1 equiv or 2.2 equiv when using the amine hydrochloride salt). Then isobutyl chloroformate (1.2 equiv) was added dropwise at 0 °C. The resulting mixture was left to stir at 0 °C for 10 min and additional 20 min at room temperature. Next, the amine (1.5 equiv) was added, and the reaction was stirred at room temperature until completion, judging by TLC analysis. The solution was diluted with DCM, washed with saturated $NaHCO_3$ and water. The combined organic layers were dried with Na_2SO_4, concentrated, and precipitated with hexane and filtered or purified by flash chromatography (*n*-hexane/acetone 7:3) to afford the corresponding 4-carbamoyl-1,4-dihydropyridine.

The following **4-carbamoyl-1,4-dihydropyridines** were used as starting materials for the scope evaluation. The reported compounds were prepared and characterized according to literature.[10] The new compounds were prepared using the same experimental procedure and their spectroscopic data are reported in the appropriated session in the SI (compounds 22', 25', 31', 32', 33', 35', 36', 37', 38', 39', 40', 41', 43', 44', 45', 47', 48', 49' and 50').

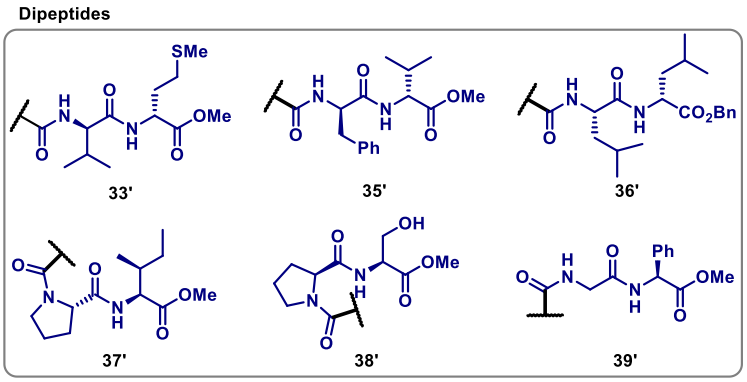
Spectroscopic data of 4-carbamoyl-1,4-dihydropyridines:

20', 21', 24', 27', 28', 29', 30', 42', 46', 51', 52' [10]

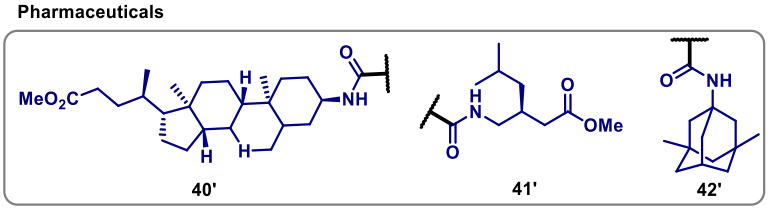


Scheme S8. 4-carbamoyl-1,4-dihydropyridines derived from amino acids.

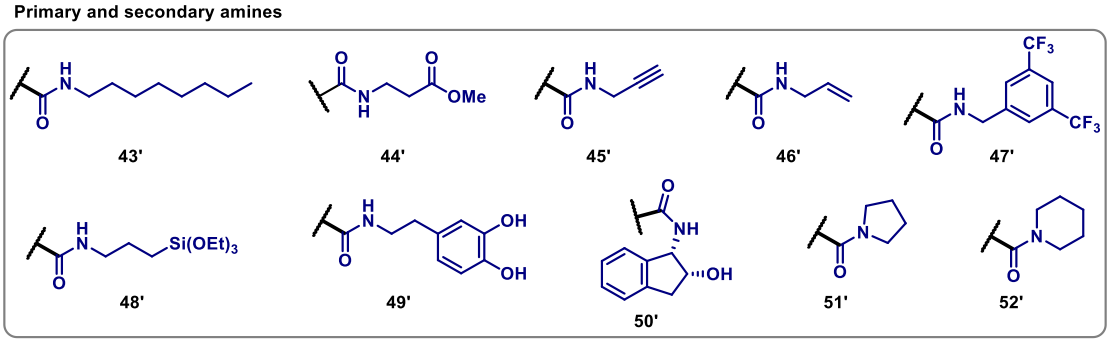
[10] N. Alandini, L. Buzzetti, G. Favi, T. Schulte, L. Candish, K. D. Collins and P. Melchiorre, *Angew. Chem. Int. Ed.,* **2020**, *59*, 5248-5253.



Scheme S9. 4-carbamoyl-1,4-dihydropyridines derived from dipeptides.



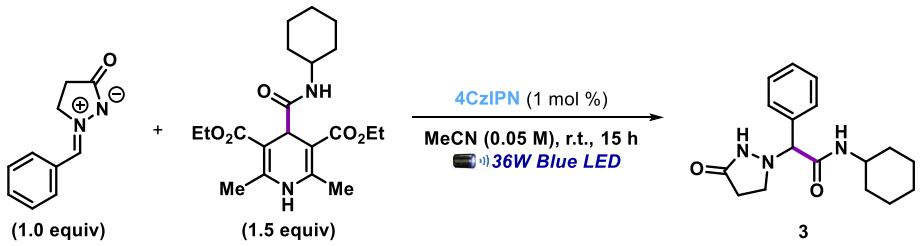
Scheme S10. 4-carbamoyl-1,4-dihydropyridines derived from pharmaceutical compounds.



Scheme S11. 4-carbamoyl-1,4-dihydropyridines derived from primary and secondary amines.

Optimization Studies

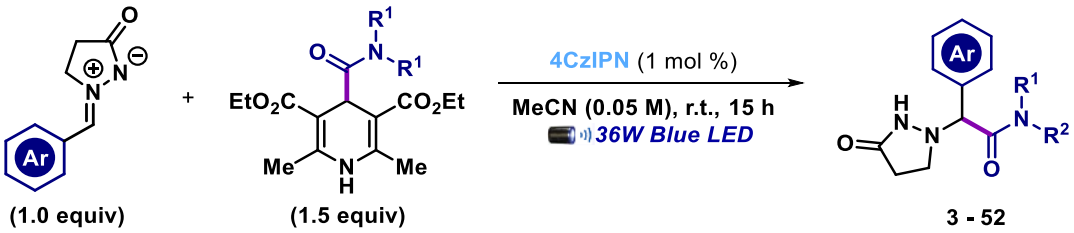
Table 1. Evaluation of reaction parameters [a]



entry	deviation from standard conditions	3 (%)[b]
1	**none**	**70**
2	**THF** instead of MeCN	68
3	**EtOAc** instead of MeCN	43
4	**DCM** instead of MeCN	54
5	**[ ] = 0.1 M**	63
6	**K_2CO_3** (2 equiv)	64
7	**2.5 mol%** of 4-CzIPN	54
8	**5 mol%** of 4-CzIPN	15
9	**reverse stoichiometry**	52
10	**$PhCO_2H$** (10 mol %)	65
11	**KH_2PO_4** (10 mol %)	40
12	**CSA** (10 mol %)	61

*[a] Reaction conditions: **1a** (0.15 mmol), **2a** (1.5 equiv, 0.225 mmol), **4-CzIPN** (1 mol %) in MeCN (3.0 mL). [b] Isolated yields after column chromatography.*

General Procedure for Carbamoylation of Azomethine Imines (GP1)



A dried Schlenk tube of borosilicate glass equipped with a stir bar was charged with the azomethine imine (0.15 mmol, 1.0 equiv), the 4-carbamoyl-1,4-dihydropyridine (1.5 equiv) and the photocatalyst 4CzIPN (1 mol %). Acetonitrile (3 mL) was added and the Schlenk tube was sealed with PTFE/silicon septum and connected to a vacuum line. The solution was degassed 3 times *via* a freeze-pump-thaw procedure and stirred under irradiation by a 34 W Kessil H150 blue LED (emission: 456 nm) with the temperature controlled by a fan (~ 30 °C). Upon completion, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography using DCM/ MeOH (20:1) as solvent mixture to afford the title compound.

Gram-Scale Reaction

A dried Schlenk tube of borosilicate glass equipped with a stir bar was charged with the azomethine imine (1.0 mmol, 1.0 equiv), the carbamoyl-1,4-dihydropyridine (1.5 equiv) and the photocatalyst 4CzIPN (1 mol %). Acetonitrile (20 mL) was added and the Schlenk tube was sealed with PTFE/silicon septum and connected to a vacuum line. The solution was degassed 3 times *via* a freeze-pump-thaw procedure and stirred under irradiation by 2 x 34 W Kessil H150 blue LED (emission: 456 nm) with the temperature controlled by a fan (~ 30 °C). Upon completion, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography using DCM/ MeOH (20:1) as solvent mixture to afford the title compound.

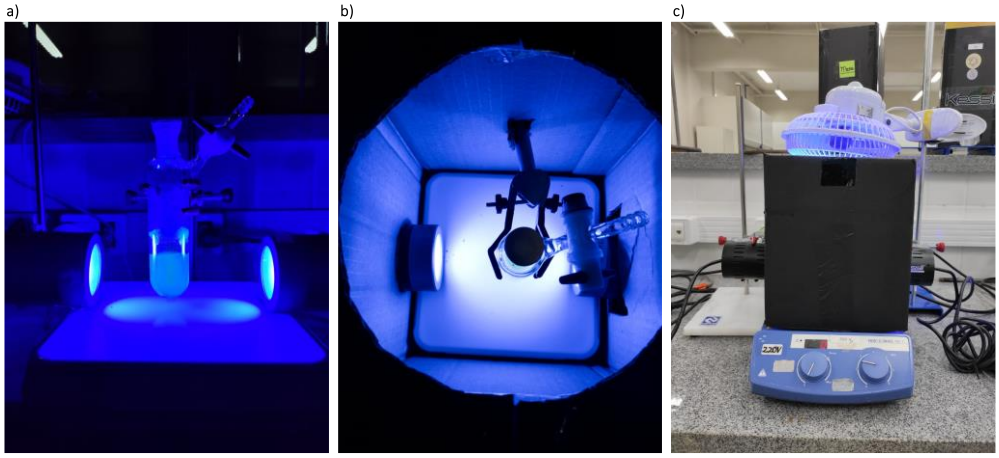
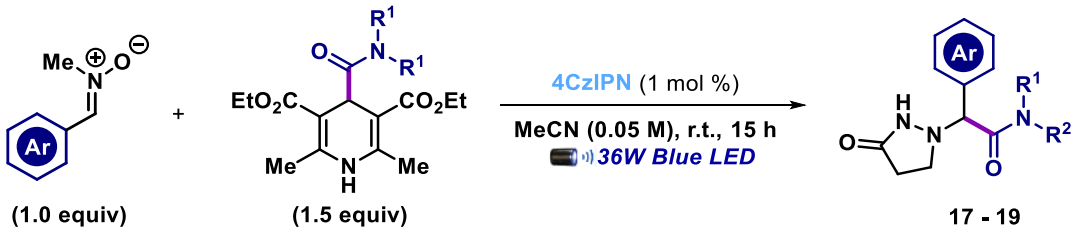


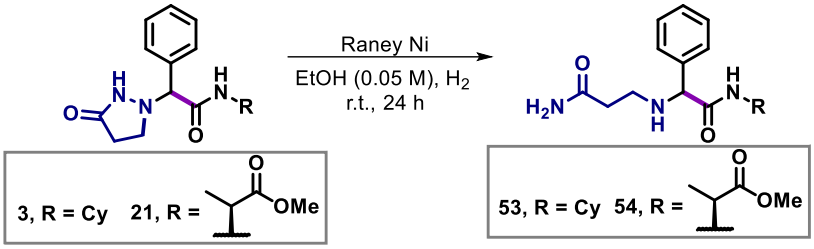
Figure S3. Experimental set-up for the gram-scale experiment. a) Reaction vessel irradiated by two external 34 W Kessil H150 blue LED lamps. b) Schlenk tube disposal inside the photoreactor. c) Photoreactor equipped with two irradiation sources and the external fan.

General Procedure for Carbamoylation of Nitrones (GP2)



A dried Schlenk tube of borosilicate glass equipped with a stir bar was charged with the nitrone (0.15 mmol, 1.0 equiv), the 4-carbamoyl-1,4-dihydropyridine (1.5 equiv) and the photocatalyst 4CzIPN (1 mol %). Acetonitrile (3 mL) was added and the Schlenk tube was sealed with PTFE/silicon septum and connected to a vacuum line. The solution was degassed 3 times *via* a freeze-pump-thaw procedure and stirred under irradiation by a 34 W Kessil H150 blue LED (emission: 456 nm) with the temperature controlled by a fan (~ 30 °C). Upon completion, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography using DCM/ MeOH (20:1) as solvent mixture to afford the title compound.

General Procedure for the Pyrazolidinone Reductive Cleavage (GP3)

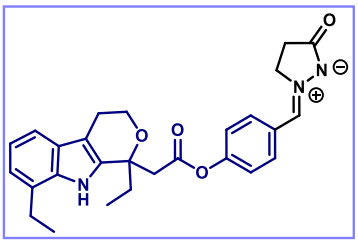


700 mg of Raney®-Nickel 2800 (slurry in H_2O) was added to a small vial and the catalyst was washed 3 times with EtOH. Then, a solution of **3** or **21** (0.2 mmol) in EtOH (4 mL) was added to the vial containing the activated catalyst, which was sealed with a septum. The reaction mixture was placed under H_2 atmosphere using balloons containing H_2 and kept under vigorous agitation for 24 h at room temperature. The reaction crude was filtered through celite, concentrated under reduced pressure, and purified by column chromatography (DCM/ MeOH 9:1) to furnish the corresponding primary amides **53** or **54**.

Compound Characterization

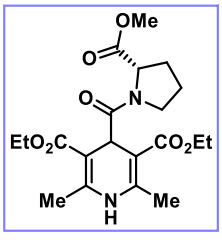
Starting Materials

2-(4-(2-(1,8-diethyl-1,3,4,9-tetrahydropyrano[3,4-*b*]indol-1-yl)acetoxy)benzylidene)-5-oxopyrazolidin-2-ium-1-ide (16')



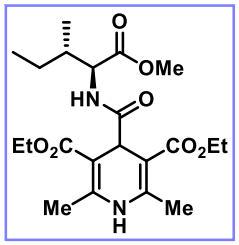
The compound **16'** was obtained as a yellow solid (39.5 mg, 43 %) following the general procedure for the synthesis of 4-carbamoyl-1,4-dihydropyridines (2.0 mmol scale). The crude material was purified by flash column chromatography (DCM/ MeOH 20:1). **^{1}H NMR (DMSO-d_6, 400 MHz):** δ 10.64 (s, 1H), 8.32 – 8.28 (m, 2H), 7.64 (s, 1H), 7.26 (d, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.95 – 6.89 (m, 2H), 4.54 (t, *J* = 8.0 Hz, 2H), 4.05 – 3.99 (m, 2H), 3.32 (d, *J* = 13.4 Hz, 1H), 3.09 (d, *J* = 13.3 Hz, 1H), 2.85 (q, *J* = 7.4 Hz, 2H), 2.74 – 2.66 (m, 2H), 2.58 – 2.53 (m, 2H), 2.16 (dt, *J* = 14.6, 7.2 Hz, 1H), 2.11 – 2.04 (m, 1H), 1.25 (t, *J* = 7.5 Hz, 3H), 0.72 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (DMSO-d_6, 101 MHz):** δ 184.4, 168.1, 151.9, 135.6, 134.6, 132.3, 131.0, 127.6, 126.6, 126.0, 122.1, 119.8, 118.8, 115.5, 107.5, 79.2, 75.7, 60.2, 57.3, 42.8, 30.9, 29.2, 23.8, 21.9, 14.5, 7.9. **HRMS (ESI):** m/z calc. for $C_{27}H_{29}N_3O_4$ $[M+H]^+$ 460.2231, found 460.2228.

(*S*)-diethyl-4-(2-(methoxycarbonyl)pyrrolidine-1-carbonyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (22')



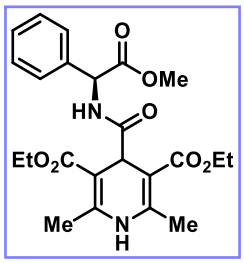
The compound **22'** was obtained as a yellow solid (312.2 mg, 51 %) following the general procedure for the synthesis of 4-carbamoyl-1,4-dihydropyridines (1.5 mmol scale). The crude material was purified by flash column chromatography (*n*-hexane/acetone 7:3). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.58 (s, 1H), 4.85 (s, 1H), 4.40 (dd, *J* = 8.6, 4.8 Hz, 1H), 4.26 – 4.20 (m, 1H), 4.17 – 4.12 (m, 4H), 3.58 (s, 3H), 2.23 (dt, *J* = 13.0, 7.3 Hz, 2H), 2.16 (s, 3H), 2.10 (s, 3H), 2.06 – 2.01 (m, 1H),), 1.96 – 1.89 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.26 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.5, 172.9, 167.9, 167.6, 148.5, 147.8, 98.5, 97.8, 59.9, 59.5, 51.9, 47.5, 39.5, 29.4, 25.4, 19.4, 18.8, 14.7. **HRMS (ESI):** m/z calc. for $C_{20}H_{28}N_2O_7$ $[M+H]^+$ 409.1969, found 409.1968.

Diethyl-4-(((2*S*,3*S*)-1-methoxy-3-methyl-1-oxopentan-2-yl)carbamoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (25')



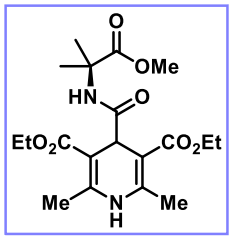
The compound **25'** was obtained as a yellow solid (381.8 mg, 60%) following the general procedure for the synthesis of 4-carbamoyl-1,4-dihydropyridines (1.5 mmol scale). The crude material was purified by flash column chromatography (*n*-hexane/acetone 7:3). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.63 (brs, 1H), 7.12 (d, *J* = 9.0 Hz, zH), 4.66 (s, 1H), 4.25 – 4.11 (m, 4H), 3.68 (s, 3H), 2.21 (s, 3H), 2.16 (s, 3H), 1.90 – 1.83 (m, 1H), 1.47 – 1.37 (m, 1H), 1.29 (td, *J* = 7.0, 3.1 Hz, 6H), 1.25 – 1.10 (m, 1H), 0.92 – 0.87 (m, 6H).**^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.5, 172.3, 167.8, 147.6, 97.8, 60.4, 60.2, 56.7, 52.01, 41.6, 37.9, 25.1, 19.1, 19.1, 15.6, 14.5, 14.4, 11.7. **HRMS (ESI):** m/z calc. for $C_{21}H_{33}N_2O_7$ $[M+H]^+$ 425.2282, found 425.2298.

Diethyl-(*S*)-4-((2-methoxy-2-oxo-1-phenylethyl)carbamoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (31')



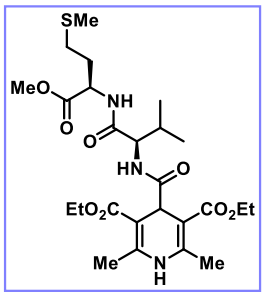
The compound **31'** was obtained as a white solid (313.1 mg, 47 %) following the general procedure for the synthesis of 4-carbamoyl-1,4-dihydropyridines (1.5 mmol scale). The crude material was purified by flash column chromatography (*n*-hexane/acetone 7:3). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.70 (d, *J* = 7.5 Hz, 1H), 7.32 – 7.30 (m, 5H), 5.46 (d, *J* = 7.4 Hz, 1H), 4.68 (s, 1H), 4.25 – 4.20 (m, 2H), 4.15 – 4.10 (m, 2H), 3.68 (s, 3H), 2.19 (s, 3H), 1.83 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.0, 171.1, 167.9, 167.7, 147.9, 147.6, 137.0, 129.0, 128.9, 128.4, 127.3, 127.2, 97.8, 97.3, 60.4, 60.2, 56.7, 52.8, 41.6, 19.1, 18.6, 14.5, 14.4. **HRMS (ESI):** m/z calc. for $C_{23}H_{28}N_2O_7$ $[M+H]^+$ 445.1969, found 445.1995.

Diethyl 4-((1-methoxy-2-methyl-1-oxopropan-2-yl)carbamoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (32')



The compound **32'** was obtained as a white solid (445.7 mg, 75 %) following the general procedure for the synthesis of 4-carbamoyl-1,4-dihydropyridines (1.5 mmol scale). The crude material was purified by flash column chromatography (*n*-hexane/acetone 7:3). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.63 (brs, 1H), 6.97 (brs, 1H), 4.53 (s, 1H), 4.18 (q, *J* = 6.8 Hz, 4H), 3.64 (s, 3H), 2.19 (s, 6H), 1.49 (s, 6H), 1.29 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 175.0, 173.8, 167.8, 147.4, 98.0, 60.2, 56.2, 52.5, 42.3, 25.1, 19.1, 14.6. **HRMS (ESI):** m/z calc. for $C_{19}H_{29}N_2O_7$ $[M+H]^+$ 397.1969, found 397.1956.

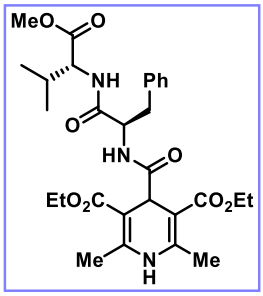
Diethyl-4-(((*R*)-1-(((*R*)-1-methoxy-4-(methylthio)-1-oxobutan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)carbamoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (33')



The compound **33'** was obtained as a yellow solid (405.9 mg, 50 %) following the general procedure for the synthesis of 4-carbamoyl-1,4-dihydropyridines (1.5 mmol scale). The crude material was purified by flash column chromatography (*n*-hexane/acetone 7:3). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.18 (brs, 1H), 7.10 (d, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 8.9 Hz, 1H), 4.58 (q, *J* = 6.5, 6.0 Hz, 1H), 4.52 (s, 1H), 4.30 – 4.27 (m, 1H), 4.23 – 4.06 (m, 4H), 3.66 (s, 3H), 2.35 (ddd, *J* = 17.1, 8.3, 4.8 Hz, 2H), 2.12 (s, 3H), 2.10 (s, 3H), 2.04 (s, 3H), 2.02 – 1.97 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 6H), 0.88 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 175.2, 172.2, 171.4, 168.8, 167.9, 147.5, 98.2, 97.9, 60.6, 60.4, 58.5, 52.4, 51.6, 42.8, 31.4, 30.1, 29.8,

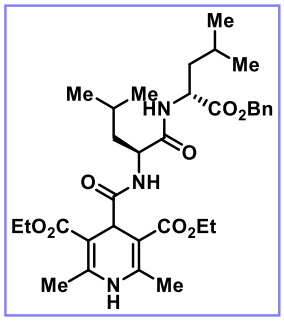
19.4, 19.2, 19.1, 17.1, 15.5, 14.6, 14.5. **HRMS (ESI):** m/z calc. for $C_{25}H_{40}N_3O_8S^+$ $[M+H]^+$ 542.2531, found 542.2567.

Diethyl-4-(((*R*)-1-(((*R*)-1-methoxy-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)carbamoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (35')



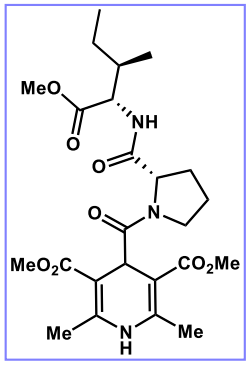
The compound **35'** was obtained as a yellow solid (367.8 mg, 44 %) following the general procedure for the synthesis of 4-carbamoyl-1,4-dihydropyridines (1.5 mmol scale). The crude material was purified by flash column chromatography (*n*-hexane/acetone 7:3). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.74 (s, 1H), 7.30 – 7.21 (m, 5H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 4.67 (q, *J* = 7.7 Hz, 1H), 4.54 (s, 1H), 4.44 (dd, *J* = 8.4, 5.5 Hz, 1H), 4.11 (dddd, *J* = 24.7, 13.7, 11.1, 7.0 Hz, 4H), 3.69 (s, 3H), 3.18 (dd, *J* = 14.3, 5.6 Hz, 1H), 3.08 (dd, *J* = 14.3, 7.6 Hz, 1H), 2.18 (s, 3H), 2.10 (s, 3H), 2.14 – 2.06 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 6H), 0.87 – 0.84 (m, 6H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 175.0, 171.9, 171.0, 168.2, 167.7, 147.5, 136.9, 129.3, 128.6, 126.9, 97.9, 97.7, 60.3, 60.2, 57.5, 54.6, 52.0, 42.1, 37.6, 31.2, 19.1, 19.0, 18.9, 18.1, 14.5, 14.4. **HRMS (ESI):** m/z calc. for $C_{29}H_{40}N_3O_8^+$ $[M+H]^+$ 558.2810, found 558.2823.

Diethyl-4-(((*S*)-1-(((*R*)-1-(benzyloxy)-4-methyl-1-oxopentan-2-yl)amino)-4-methyl-1-oxopentan-2-yl)carbamoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (36')



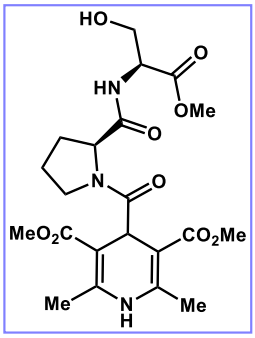
The compound **36'** was obtained as a yellow solid (570.4 mg, 62 %) following the general procedure for the synthesis of 4-carbamoyl-1,4-dihydropyridines (1.5 mmol scale). The crude material was purified by flash column chromatography (*n*-hexane/acetone 7:3). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.34 (s, 1H), 7.35 – 7.29 (m, 5H), 7.03 (d, *J* = 8.5 Hz, 1H), 6.69 (d, *J* = 7.9 Hz, 1H), 5.14 (q, *J* = 12.3 Hz, 2H), 4.65 (td, *J* = 8.8, 5.2 Hz, 1H), 4.50 (s, 1H), 4.38 (ddd, *J* = 11.4, 7.9, 3.8 Hz, 1H), 4.26 – 4.05 (m, 4H), 2.14 (s, 3H), 2.08 (s, 3H), 1.80 (ddd, *J* = 13.9, 9.9, 3.8 Hz, 1H), 1.66 – 1.58 (m, 2H), 1.57 – 1.48 (m, 3H), 1.25 (dtd, *J* = 14.2, 7.2, 1.7 Hz, 6H), 0.93 – 0.81 (m, 12H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 175.6, 172.7, 172.2, 168.5, 167.9, 147.7, 147.1, 135.7, 128.6, 128.4, 128.2, 98.5, 97.4, 66.9, 60.3, 52.2, 50.7, 43.3, 40.9, 40.4, 24.6, 23.4, 22.9, 21.8, 20.9, 18.9, 14.6, 14.5. **HRMS (ESI):** m/z calc. for $C_{33}H_{48}N_3O_8^+$ $[M+H]^+$ 614.3436, found 614.3447.

Diethyl-4-((*S*)-2-(((2*S*,3*R*)-1-methoxy-3-methyl-1-oxopentan-2-yl)carbamoyl)pyrrolidine-1-carbonyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (37')



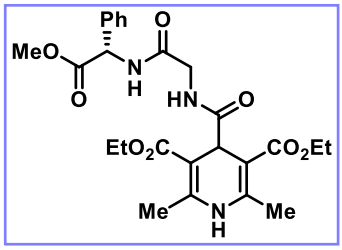
The compound **37'** was obtained as a yellow solid (148.5 mg, 19 %) following the general procedure for the synthesis of 4-carbamoyl-1,4-dihydropyridines (1.5 mmol scale). The crude material was purified by flash column chromatography (*n*-hexane/acetone 7:3). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.44 (s, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 4.69 (s, 1H), 4.56 (d, *J* = 7.6 Hz, 1H), 4.50 (dd, *J* = 8.6, 4.8 Hz, 1H), 4.27 – 4.20 (m, 2H), 4.15 (q, *J* = 7.1 Hz, 4H), 3.68 (s, 3H), 2.14 (s, 1H), 2.13 (s, 3H), 2.07 (s, 3H), 2.03 – 1.94 (m, 3H), 1.25 (td, *J* = 7.1, 3.3 Hz, 7H), 0.89 (dd, *J* = 7.1, 3.3 Hz, 2H), 0.81 (t, *J* = 8.0 Hz, 6H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 175.5, 172.1, 172.0, 168.4, 167.7, 147.9, 147.4, 98.6, 61.0, 60.1, 59.9, 56.5, 51.8, 47.4, 40.0, 37.4, 29.6, 24.9, 24.3, 19.3, 19.3, 15.2, 14.5, 14.3, 11.4. **HRMS (ESI):** m/z calc. for $C_{26}H_{39}N_3O_8$ $[M+H]^+$ 522.2810, found 522.2811.

Dimethyl 4-((*S*)-2-(((*S*)-3-hydroxy-1-methoxy-1-oxopropan-2-yl)carbamoyl)pyrrolidine-1-carbonyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (38')



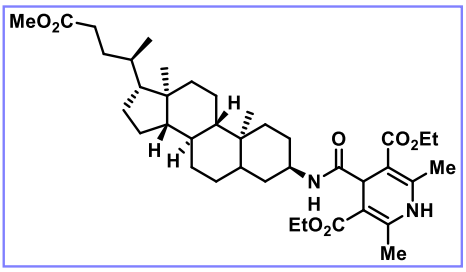
The compound **38'** was obtained as a yellow oil (147.2 mg, 21%) following the general procedure for the synthesis of 4-carbamoyl-1,4-dihydropyridines (1.5 mmol scale). The crude material was purified by flash column chromatography (*n*-hexane/acetone 7:3). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.57 (s, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 4.65 (s, 1H), 4.66 – 4.62 (m, 1H), 4.43 (dd, *J* = 8.1, 4.1 Hz, 1H), 4.28 (td, *J* = 11.7, 5.8 Hz, 1H), 4.23 – 4.10 (m, 4H), 3.85 (dd, *J* = 11.6, 2.9 Hz, 1H), 3.73 (s, 3H), 3.67 (dd, *J* = 11.6, 4.1 Hz, 1H), 2.26 – 2.19 (m, 1H), 2.17 (s, 3H), 2.11 (s, 3H), 2.14 – 2.07 (m, 1H), 1.97 (dd, *J* = 13.1, 7.4 Hz, 1H), 1.31 – 1.24 (m, 6H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 174.0, 171.1, 167.9, 167.7, 147.9, 147.6, 137.0, 129.0, 128.9, 128.5, 127.3, 127.2, 97.8, 97.3, 60.4, 60.2, 56.8, 52.8, 41.6, 19.0, 18.6, 14.5, 14.43. **HRMS (ESI)** m/z calc. for $C_{23}H_{34}N_3O_9$ $[M+H]^+$ 496.2290, found 496.2295.

Diethyl (*S*)-4-((2-((2-methoxy-2-oxo-1-phenylethyl)amino)-2-oxoethyl)carbamoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (39')



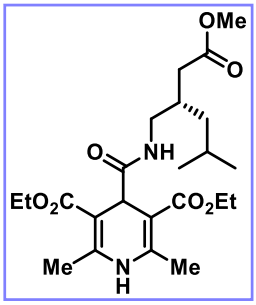
The compound **39'** was obtained as a yellow oil (293.2 mg, 39%) following the general procedure for the synthesis of 4-carbamoyl-1,4-dihydropyridines (1.5 mmol scale). The crude material was purified by flash column chromatography (*n*-hexane/acetone 7:3). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.42 – 7.30 (m, 5H), 7.10 (t, *J* = 5.7 Hz, 1H), 5.59 (d, *J* = 7.5 Hz, 1H), 4.54 (s, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 4.09 – 3.99 (m, 2H), 3.97 (d, *J* = 5.9 Hz, 2H), 3.70 (s, 3H), 2.19 (d, *J* = 3.4 Hz, 6H), 1.27 – 1.22 (m, 6H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 175.5, 171.1, 168.9, 168.2, 168.0, 147.5, 147.2, 136.3, 129.0, 128.6, 127.5, 98.3, 98.0, 60.5, 60.4, 56.3, 52.8, 43.5, 42.6, 19.4, 19.3, 14.5. **HRMS (ESI):** m/z calc. for $C_{25}H_{32}N_3O_8^+$ $[M+H]^+$ 502.2184, found 502.2214.

Diethyl-4-(((3*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-((*R*)-5-methoxy-5-oxopentan-2-yl)-10,13 dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)carbamoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (40')



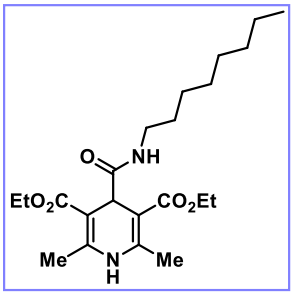
The compound **40'** was obtained as a white solid (651.7 mg, 65%) following the general procedure for the synthesis of 4-carbamoyl-1,4-dihydropyridines (1.5 mmol scale). The crude material was purified by flash column chromatography (*n*-hexane/acetone 7:3). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.14 (s, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 4.60 (s, 1H), 4.24 – 4.12 (m, 4H), 4.06 – 4.04 (m, 1H), 3.65 (s, 3H), 2.34 (ddd, *J* = 15.3, 10.1, 5.1 Hz, 1H), 2.24 – 2.20 (m, 1H), 2.19 (s, 3H), 2.18 (s, 3H), 1.98 – 1.93 (m, 2H), 1.88 – 1.76 (m, 3H), 1.55 (t, *J* = 11.4 Hz, 3H), 1.49 – 1.29 (m, 9H), 1.28 – 1.24 (m, 8H), 1.17 – 1.03 (m, 6H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.64 (s, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 174.9, 173.9, 168.35, 168.3, 147.5, 98.0, 76.8, 60.2, 60.2, 56.6, 56.1, 51.6, 45.4, 42.9, 41.8, 40.3, 39.9, 37.8, 35.8, 35.5, 35.2, 31.2, 31.1, 30.9, 28.3, 26.9, 26.3, 25.1, 24.3, 24.1, 21.1, 19.1, 19.1, 18.4, 14.6, 14.6, 12.2. **HRMS (ESI):** m/z calc. for $C_{39}H_{61}N_2O_7^+$ $[M+H]^+$ 669.4473, found 669.4481.

Diethyl (*S*)-4-((2-(2-methoxy-2-oxoethyl)-4-methylpentyl)carbamoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (41')



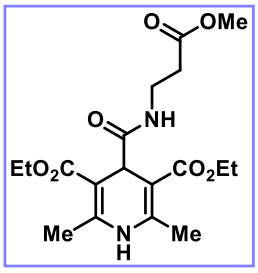
The compound **41'** was obtained as a white solid (447.7 mg, 66%) following the general procedure for the synthesis of 4-carbamoyl-1,4-dihydropyridines (1.5 mmol scale). The crude material was purified by flash column chromatography (*n*-hexane/acetone 7:3). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.70 (s, 1H), 6.78 (t, *J* = 6.1 Hz, 1H), 4.56 (s, 1H), 4.18 (dt, *J* = 7.0, 5.5 Hz, 4H), 3.66 (s, 3H), 3.28 – 3.22 (m, 2H, 3.15 – 3.09 (m, 1H), 2.21 (s, 6H), 2.07 (dd, *J* = 12.7, 6.5 Hz, 1H), 1.64 – 1.56 (m, 1H), 1.45 (t, *J* = 7.1 Hz, 1H), 1.28 (td, *J* = 7.1, 0.9 Hz, 6H), 1.19 – 1.05 (m, 2H), 0.86 (dd, *J* = 9.6, 6.6 Hz, 6H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 174.9, 173.4, 168.1, 147.4, 98.2, 60.3, 51.6, 42.6, 41.8, 41.4, 37.1, 33.5, 25.3, 22.8, 19.3, 14.5. δ. **HRMS (ESI):** m/z calc. for $C_{23}H_{37}N_2O_7^+$ $[M+H]^+$ 453.2595, found 453.2593.

Diethyl 2,6-dimethyl-4-(octylcarbamoyl)-1,4-dihydropyridine-3,5-dicarboxylate (43')



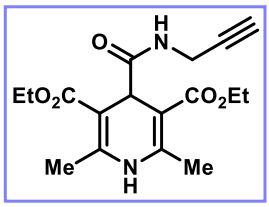
The product **43'** was obtained as a yellow solid (355.2 mg, 58%) following the general procedure for the synthesis of 4-carbamoyl-1,4-dihydropyridines (1.5 mmol scale). The crude material was purified by flash column chromatography (*n*-hexane/acetone 7:3). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.34 (s, 1H), 6.72 (t, *J* = 5.6 Hz, 1H), 4.55 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 4H), 3.17 (q, *J* = 6.7 Hz, 2H), 2.18 (s, 6H), 1.46 – 1.43 (m, 2H), 1.29 – 1.25 (m, 16H), 0.87 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.9, 168.2, 147.7, 97.8, 60.1, 41.8, 39.6, 31.9, 29.7, 29.4, 29.4, 26.9, 22.8, 18.9, 14.5, 14.2. **HRMS (ESI):** m/z calc. for $C_{22}H_{36}N_2O_5$ $[M+H]^+$ 409.2697, found 409.2695.

Diethyl 4-((3-methoxy-3-oxopropyl)carbamoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (44')



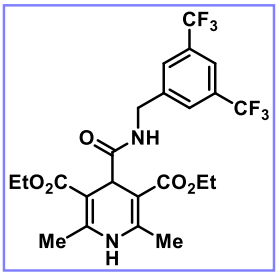
The product **44'** was obtained as a yellow solid (412.7 mg, 72%) following the general procedure for the synthesis of 4-carbamoyl-1,4-dihydropyridines (1.5 mmol scale). The crude material was purified by flash column chromatography (*n*-hexane/acetone 7:3). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.99 (s, 1H), 7.01 (t, *J* = 6.0 Hz, 1H), 4.53 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 4H), 3.68 (s, 3H), 3.47 (q, *J* = 6.3 Hz, 2H), 2.48 (t, *J* = 6.3 Hz, 2H), 2.19 (s, 6H), 1.27 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 175.0, 172.5, 167.9, 147.6, 97.9, 60.2, 51.8, 41.8, 35.1, 34.2, 19.0, 14.5. **HRMS (ESI):** m/z calc. for $C_{18}H_{27}N_2O_7$ $[M+Na]^+$ 405.1632, found 405.1632.

Diethyl 2,6-dimethyl-4-(prop-2-yn-1-ylcarbamoyl)-1,4-dihydropyridine-3,5-dicarboxylate (45')



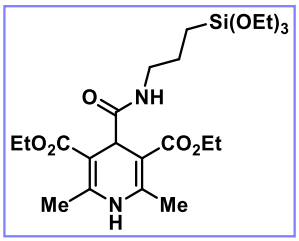
The product **45'** was obtained as a yellow solid (350.8 mg, 70%) following the general procedure for the synthesis of 4-carbamoyl-1,4-dihydropyridines (1.5 mmol scale). The crude material was purified by flash column chromatography (*n*-hexane/acetone 7:3). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.64 (brs, 1H), 6.98 (t, *J* = 5.1 Hz, 1H), 4.58 (s, 1H), 4.19 (q, *J* = 6.9 Hz, 5H), 3.98 (dd, *J* = 4.9, 2.0 Hz, 2H), 2.21 (s, 6H), 2.16 (s, 1H), 1.29 (t, *J* = 6.8 Hz, 6H).**^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.5, 167.9, 147.5, 97.6, 79.7, 71.2, 60.2, 41.5, 29.2, 19.1, 14.4. **HRMS (ESI):** m/z calc. for $C_{17}H_{22}N_2O_5$ $[M+H]^+$ 335.1601, found 335.1606.

Diethyl-4-((3,5-bis(trifluoromethyl)benzyl)carbamoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (47')



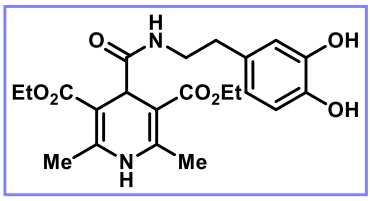
The product **47'** was obtained as a yellow solid (650 mg, 83%) following the general procedure for the synthesis of 4-carbamoyl-1,4-dihydropyridines (1.5 mmol scale). The crude material was purified by flash column chromatography (*n*-hexane/acetone 7:3). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.67 (s, 1H), 7.57 (s, 2H), 7.33 (t, *J* = 6.3 Hz, 1H), 7.19 (s, 1H), 4.56 (s, 1H), 4.46 (d, *J* = 6.2 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 4H), 2.07 (s, 6H), 1.19 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 175.1, 168.2, 147.4, 142.0, 131.8 (q, *J* = 33.4 Hz), 127.1, 123.4 (q, *J* = 272.8 Hz), 121.2 – 121.1 (m), 98.0, 60.5, 42.5, 42.0, 19.2, 14.4. **HRMS (ESI):** m/z calc. for $C_{23}H_{24}F_6N_2O_5$ $[M+Na]^+$ 545.1482, found 545.1494.

Diethyl-2,6-dimethyl-4-((3-(triethoxysilyl)propyl)carbamoyl)-1,4-dihydropyridine-3,5-dicarboxylate (48')



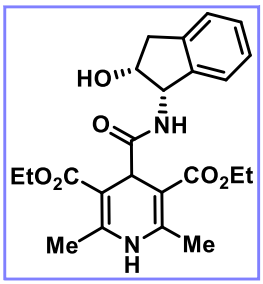
The product **48'** was obtained as a yellow solid (502.7 mg, 67%) following the general procedure for the synthesis of 4-carbamoyl-1,4-dihydropyridines (1.5 mmol scale). The crude material was purified by flash column chromatography (*n*-hexane/acetone 7:3). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.95 (s, 1H), 6.72 (t, *J* = 5.9 Hz, 1H), 4.54 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 4H), 3.80 (q, *J* = 7.0 Hz, 6H), 3.18 (q, *J* = 6.7 Hz, 2H), 2.19 (s, 6H), 1.60 – 1.53 (m, 2H), 1.27 (t, *J* = 7.4 Hz, 6H), 1.23 – 1.19 (m, 9H), 0.61 – 0.57 (m, 2H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.7, 168.1, 147.5, 98.1, 60.2, 58.5, 42.2, 41.8, 23.3, 19.1, 18.4, 14.6, 7.8. **HRMS (ESI):** m/z calc. for $C_{23}H_{41}N_2O_8Si$ $[M+H]^+$ 501.2627, found 501.2631.

Diethyl 4-((3,4-dihydroxyphenethyl)carbamoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (49')



The compound **49'** was obtained as a white solid (181.5 mg, 28%) following the general procedure for the synthesis of 4-carbamoyl-1,4-dihydropyridines (1.5 mmol scale). The crude material was purified by flash column chromatography (*n*-hexane/acetone 7:3). **^{1}H NMR (Metanol-*d*4, 400 MHz):** δ 6.69 (d, *J* = 7.9 Hz, 1H), 6.62 (d, *J* = 1.2 Hz, 1H), 6.49 (dd, *J* = 8.0, 2.1 Hz, 1H), 4.50 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 4H), 3.38 – 3.33 (m, 2H), 2.62 (t, *J* = 7.0 Hz, 2H), 2.30 (s, 6H), 1.26 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (Metanol-*d*4, 126 MHz):** δ 176.4, 169.4, 149.3, 146.3, 144.8, 131.8, 120.9, 116.7, 116.3, 98.8, 61.2, 42.5, 41.8, 35.7, 18.9, 14.7. **HRMS (ESI):** m/z calc. for $C_{22}H_{28}N_2O_7$ $[M+H]^+$ 433.1969, found 433.1988.

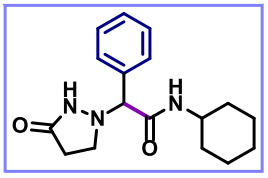
Diethyl 4-(((1*S*,2*R*)-2-hydroxy-2,3-dihydro-1H-inden-1-yl)carbamoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (50')



The product **50'** was obtained as a yellow solid (327.6 mg, 51%) following the general procedure for the synthesis of 4-carbamoyl-1,4-dihydropyridines (1.5 mmol scale). The crude material was purified by flash column chromatography (*n*-hexane/acetone 7:3). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.00 (s, 1H), 7.33 – 7.19 (m, 4H), 6.96 (d, *J* = 8.4 Hz, 1H), 5.33 (dd, *J* = 8.4, 4.8 Hz, 1H), 4.64 – 4.61 (m, 2H), 4.28 – 4.12 (m, 4H), 3.14 (dd, *J* = 16.5, 5.1 Hz, 1H), 3.00 (brs, 1H), 2.28 (s, 3H), 2.24 (s, 3H), 1.26 (q, *J* = 7.0 Hz, 6H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 175.6, 168.5, 167.7, 147.5, 140.5, 128.3, 127.1, 125.5, 124.2, 98.6, 98.2, 73.4, 60.6, 60.3, 58.4, 43.1, 39.6, 19.3, 19.2, 14.6, 14.5. **HRMS (ESI):** m/z calc. for $C_{23}H_{29}N_2O_6$ $[M+H]^+$ 429.2020, found 429.2016.

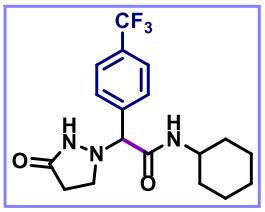
Scope for the carbamoylation of azomethine imines

N-cyclohexyl-2-(3-oxopyrazolidin-1-yl)acetamide (3)



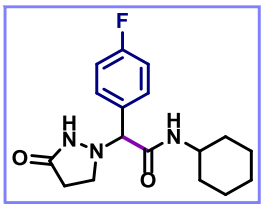
The product **3** was obtained as a colorless oil (31.6 mg, 70%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.39-7.34 (m, 5H), 6.20 (brs, 1H), 4.23 (s, 1H), 3.72 (qt, *J* = 8.5, 4.0 Hz, 1H), 3.24 (dt, *J* = 10.7, 7.5 Hz, 2H), 2.38 (t, *J* = 7.4 Hz, 2H), 1.82 (td, *J* = 12.4, 4.1 Hz, 2H), 1.68-1.55 (m, 3H), 1.37 – 1.26 (m, 2H), 1.10 (pd, *J* = 11.8, 3.4 Hz, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 174.4, 168.6, 135.1, 129.2, 129.2, 128.5, 76.1, 50.1, 48.4, 32.9, 32.8, 29.6, 25.5, 24.8. **HRMS (ESI):** m/z calc. for $C_{17}H_{24}N_3O_2$ $[M+H]^+$ 302.1863, found 302.1861.

N-cyclohexyl-2-(3-oxopyrazolidin-1-yl)-2-(4-(trifluoromethyl)phenyl)acetamide (4)



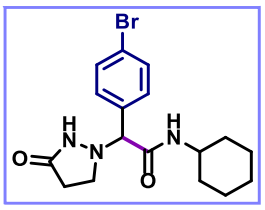
The product **4** was obtained as a colorless oil (40.4 mg, 73%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 6.30 (brs, 1H), 4.35 (s, 1H), 3.76 – 3.68 (m, 1H), 3.31 (q, *J* = 8.9 Hz, 2H), 2.44 (dq, *J* = 16.8, 9.0 Hz, 2H), 1.84 (t, *J* = 16.6 Hz, 2H), 1.69 – 1.57 (m, 3H), 1.38 – 1.27 (m, 2H), 1.19 – 1.07 (m, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 174.7, 167.7, 139.1, 131.6 (q, *J* = 32.2 Hz), 128.9, 126.2 (q, *J* = 3.9 Hz), 123.9(q, *J* = 271.9 Hz), 75.7, 50.7, 48.5, 32.9, 32.9, 29.5, 25.5, 24.8. **HRMS (ESI):** m/z calc. for $C_{18}H_{23}F_3N_3O_2$ $[M+H]^+$ 370.1737, found 370.1733.

N-cyclohexyl-2-(4-fluorophenyl)-2-(3-oxopyrazolidin-1-yl)acetamide (5)



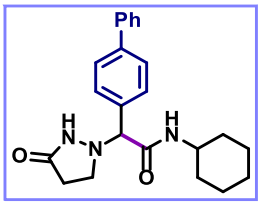
The product **5** was obtained as a colorless oil (36.8 mg, 77%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.42 (dd, *J* = 8.4, 5.3 Hz, 2H), 7.08 (t, *J* = 8.3 Hz, 2H), 6.27 (brs, 1H), 4.38 (s, 1H), 3.75 (dtt, *J* = 11.1, 8.0, 3.8 Hz, 1H), 3.34 (q, *J* = 8.2 Hz, 2H), 2.51 – 2.37 (m, 2H), 1.84 (dd, *J* = 12.2, 4.1 Hz, 2H), 1.69 – 1.65 (m, 2H), 1.60 (dt, *J* = 12.2, 3.8 Hz, 1H), 1.34 (qt, *J* = 12.3, 3.7 Hz, 2H), 1.13 (dddd, *J* = 15.7, 11.8, 7.9, 3.8 Hz, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 174.7, 168.5, 163.1 (d, *J* = 248.7 Hz), 131.1, 130.3 (d, *J* = 8.3 Hz), 116.2 (d, *J* = 21.7 Hz), 75.3, 50.6, 48.3, 32.9, 29.6, 25.5, 24.8. **HRMS (ESI):** m/z calc. for $C_{17}H_{23}FN_3O_2$ $[M+H]^+$ 320.1769, found 320.1765.

2-(4-bromophenyl)-*N*-cyclohexyl-2-(3-oxopyrazolidin-1-yl)acetamide (6)



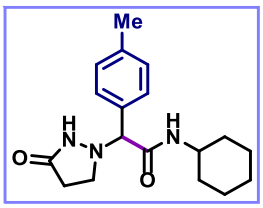
The product **6** was obtained as a colorless oil (31.3 mg, 55%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.16 (brs, 1H), 4.16 (s, 1H), 3.65 (dtt, *J* = 10.9, 8.8, 3.9 Hz, 1H), 3.21 (q, *J* = 9.0, 8.5 Hz, 2H), 2.40 – 2.30 (m, 2H), 1.81 – 1.73 (m, 2H), 1.63 – 1.58 (m, 2H), 1.56 – 1.51 (m, 1H), 1.33 – 1.19 (m, 2H), 1.13 – 0.99 (m, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 174.6, 168.1, 134.2, 132.4, 130.1, 123.4, 75.4, 50.6, 48.4, 32.9, 29.5, 25.5, 24.8. **HRMS (ESI):** m/z calc. for $C_{17}H_{23}BrN_3O_2$ $[M+H]^+$ 380.0968, found 380.0975.

2-([1,1'-biphenyl]-4-yl)-*N*-cyclohexyl-2-(3-oxopyrazolidin-1-yl)acetamide (7)



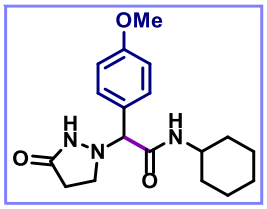
The product **7** was obtained as a colorless oil (30.5 mg, 54%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.54 – 7.49 (m, 4H), 7.40 – 7.36 (m, 4H), 7.32 – 7.28 (m, 1H), 6.10 (brs, 1H), 4.19 (s, 1H), 3.74 – 3.63 (m, 1H), 3.25 – 3.19 (m, 2H), 2.37 (t, *J* = 8.9 Hz, 2H), 1.82 – 1.76 (m, 2H), 1.60 (dt, *J* = 13.5, 3.8 Hz, 2H), 1.55 – 1.50 (m, 1H), 1.33 – 1.21 (m, 2H), 1.12 – 1.02 (m, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 174.4, 168.7, 142.2, 140.2, 134.1, 129.0, 128.9, 128.0, 127.8, 127.2, 75.9, 50.7, 48.3, 33.0, 32.9, 29.6, 25.5, 24.8. **HRMS (ESI):** m/z calc. for $C_{23}H_{28}N_3O_2$ $[M+H]^+$ 378.2176, found 378.2170.

_N_-cyclohexyl-2-(3-oxopyrazolidin-1-yl)-2-(p-tolyl)acetamide (8)



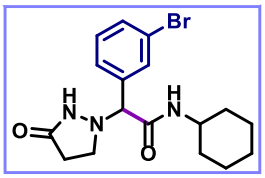
The product **8** was obtained as a colorless oil (25.1 mg, 53%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.19 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.01 (brs, 1H), 4.11 (s, 1H), 3.71 – 3.62 (m, 1H), 3.17 (dt, *J* = 10.8, 7.4 Hz, 2H), 2.33 (t, *J* = 8.2 Hz, 2H), 2.28 (s, 3H), 1.75 (t, *J* = 12.0 Hz, 2H), 1.59 (dt, *J* = 14.5, 4.6 Hz, 2H), 1.52 (dt, *J* = 7.7, 4.0 Hz, 1H), 1.32 – 1.18 (m, 2H), 1.11 – 0.98 (m, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 174.3, 168.9, 139.2, 132.0, 130.0, 128.4, 75.8, 50.6, 48.2, 33.0, 32.9, 29.7, 25.5, 24.8, 21.3. **HRMS (ESI):** m/z calc. for $C_{18}H_{26}N_3O_2$ $[M+H]^+$ 316.2020, found 316.2015.

_N_-cyclohexyl-2-(4-methoxyphenyl)-2-(3-oxopyrazolidin-1-yl)acetamide (9)



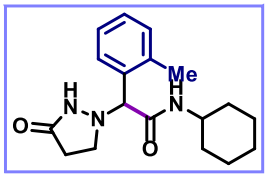
The product **9** was obtained as a colorless oil (29.8 mg, 60%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.29 (d, *J* = 8.3 Hz, 2H), 6.89 (d, *J* = 8.3 Hz, 2H), 6.14 (brs, 1H), 4.15 (s, 1H), 3.81 (s, 3H), 3.78 – 3.70 (m, 1H), 3.22 (dt, *J* = 10.9, 7.4 Hz, 2H), 2.38 (t, *J* = 8.2 Hz, 1H), 1.87 – 1.81 (m, 2H), 1.69 – 1.57 (m, 3H), 1.38 – 1.24 (m, 2H), 1.18 – 1.06 (m, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 174.5, 169.1, 160.2, 129.8, 127.1, 114.6, 75.4, 55.4, 50.5, 48.2, 32.9, 29.7, 25.5, 24.8. **HRMS (ESI):** m/z calc. for $C_{18}H_{26}N_3O_3$ $[M+H]^+$ 332.1969, found 332.1973.

2-(3-bromophenyl)-_N_-cyclohexyl-2-(3-oxopyrazolidin-1-yl)acetamide (10)



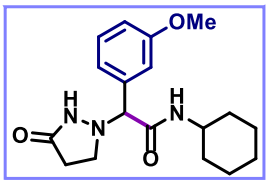
The product **10** was obtained as a colorless oil (29.6 mg, 52%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.51 (s, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.21 – 7.17 (m, 1H), 6.25 (brs, 1H), 4.22 (s, 1H), 3.67 (q, *J* = 11.5, 10.6 Hz, 1H), 3.26 (dd, *J* = 17.6, 8.6 Hz, 2H), 2.47 – 2.35 (m, 2H), 1.78 (t, *J* = 10.2 Hz, 2H), 1.61 (dt, *J* = 13.2, 3.9 Hz, 2H), 1.56 – 1.51 (m, 1H), 1.32 – 1.22 (m, 2H), 1.08 (tt, *J* = 12.9, 6.1 Hz, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 174.5, 167.8, 137.1, 132.5, 131.5, 130.8, 127.2, 123.3, 75.3, 50.6, 48.4, 32.9, 32.9, 29.5, 25.5, 24.8. **HRMS (ESI):** m/z calc. for $C_{17}H_{23}BrN_3O_2$ $[M+H]^+$ 380.0968, found 380.0961.

_N_-cyclohexyl-2-(3-oxopyrazolidin-1-yl)-2-(o-tolyl)acetamide (11)



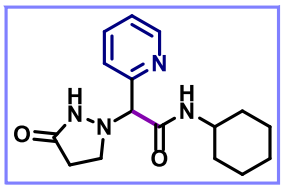
The product **11** was obtained as a colorless oil (26.0 mg, 55%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.33 (d, *J* = 7.3 Hz, 1H), 7.21 – 7.10 (m, 3H), 5.98 (brs, 1H), 4.53 (s, 1H), 3.69 – 3.62 (m, 1H), 3.22 – 3.13 (m, 1H), 2.42 – 2.29 (m, 2H), 2.41 (s, 3H), 1.81 – 1.69 (m, 2H), 1.55 (t, *J* = 18.6 Hz, 3H), 1.29 – 1.18 (m, 2H), 1.10 – 0.95 (m, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 174.0, 168.8, 138.0, 137.9, 131.7, 131.0, 129.1, 126.9, 77.5, 50.7, 48.3, 32.9, 32.8, 29.8, 25.5, 24.8, 20.3. **HRMS (ESI):** m/z calc. for $C_{18}H_{26}N_3O_2$ $[M+H]^+$ 316.2020, found 316.2016.

***N*-cyclohexyl-2-(3-methoxyphenyl)-2-(3-oxopyrazolidin-1-yl)acetamide (12)**



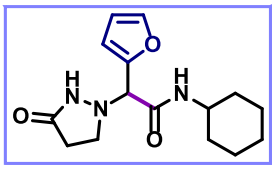
The product **12** was obtained as a colorless oil (24.8 mg, 50%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.21 (t, *J* = 7.9 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.86 (s, 1H), 6.82 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.08 (brs, 1H), 4.11 (s, 1H), 3.74 (s, 3H), 3.71 – 3.62 (m, 1H), 3.18 (dt, *J* = 10.6, 7.9 Hz, 1H), 2.36 (t, *J* = 8.1 Hz, 2H), 1.96 (brs, 1H), 1.77 (td, *J* = 11.5, 10.8, 3.2 Hz, 2H), 1.62 – 1.57 (m, 2H), 1.55 – 1.50 (m, 1H), 1.32 – 1.16 (m, 2H), 1.11 – 0.99 (m, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 174.4, 168.6, 160.1, 136.7, 130.3, 120.6, 114.8, 113.8, 76.1, 55.4, 50.6, 48.2, 32.9, 32.9, 29.6, 25.5, 24.8. **HRMS (ESI):** m/z calc. for $C_{18}H_{26}N_3O_3$ $[M+H]^+$ 332.1969, found 332.1982.

***N*-cyclohexyl-2-(3-oxopyrazolidin-1-yl)-2-(pyridin-2-yl)acetamide (13)**



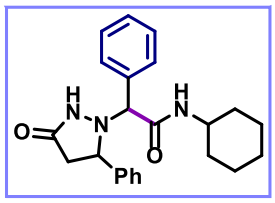
The product **13** was obtained as a colorless oil (21.3 mg, 47%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.56 (d, *J* = 4.5 Hz, 1H), 7.73 (tt, *J* = 7.7, 1.5 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.31 – 7.27 (m, 1H), 6.69 (d, *J* = 8.4 Hz, 1H), 4.50 (s, 1H), 3.68 (tq, *J* = 10.9, 3.9 Hz, 1H), 3.45 (brs, 1H), 3.41 – 3.34 (m, 1H), 2.49 (tt, *J* = 13.5, 6.8 Hz, 2H), 1.77 (dd, *J* = 22.6, 12.8 Hz, 2H), 1.64 (dt, *J* = 12.4, 3.8 Hz, 2H), 1.58 – 1.54 (m, 1H), 1.30 (dddd, *J* = 21.5, 12.6, 9.1, 4.5 Hz, 2H), 1.11 (tdd, *J* = 15.3, 11.8, 7.3 Hz, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 174.5, 167.4, 155.2, 149.6, 137.6, 123.9, 123.8, 77.3, 50.7, 48.4, 32.8, 32.7, 29.6, 25.5, 24.8. **HRMS (ESI):** m/z calc. for $C_{16}H_{23}N_4O_2$ $[M+H]^+$ 303.1816, found 303.1809.

***N*-cyclohexyl-2-(furan-2-yl)-2-(3-oxopyrazolidin-1-yl)acetamide (14)**



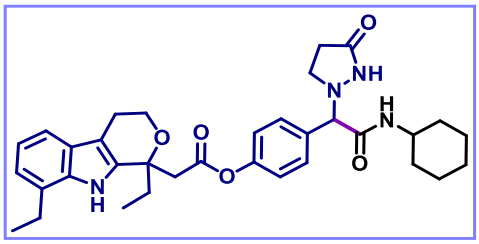
The product **14** was obtained as a colorless oil (22.7 mg, 52%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.44 (s, 1H), 6.45 (d, *J* = 3.5 Hz, 1H), 6.42 (brs, 1H), 6.39 (dt, *J* = 3.1, 1.3 Hz, 1H), 4.47 (s, 1H), 3.78 (dtt, *J* = 10.6, 7.1, 4.0 Hz, 1H), 3.46 (brs, 1H), 3.34 (dt, *J* = 11.5, 7.5 Hz, 1H), 2.25 (td, *J* = 8.4, 2.3 Hz, 2H), 1.88 (dt, *J* = 12.3, 4.1 Hz, 2H), 1.69 (dt, *J* = 13.2, 3.9 Hz, 2H), 1.60 (dt, *J* = 12.7, 4.0 Hz, 1H), 1.35 (td, *J* = 14.6, 14.2, 7.6 Hz, 2H), 1.21 – 1.10 (m, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 174.9, 166.3, 147.6, 143.7, 111.9, 111.3, 68.6, 50.4, 48.5, 32.9, 29.4, 25.5, 24.8. **HRMS (ESI):** m/z calc. for $C_{15}H_{22}N_3O_3$ $[M+H]^+$ 292.1656, found 292.1652.

(2S)-*N*-cyclohexyl-2-(3-oxo-5-phenylpyrazolidin-1-yl)-2-phenylacetamide (15)



The product **15** was obtained as a colorless oil (33.0 mg, 58 %) following the general procedure **GP1**. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). Reported spectra of one diastereoisomer. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.34 – 7.32 (m, 2H), 7.25 – 7.17 (m, 6H), 7.13 – 7.11 (m, 2H), 5.94 (s, 1H), 4.50 (s, 1H), 4.38 (d, *J* = 6.5 Hz, 1H), 3.70 – 3.63 (m, 1H), 2.87 (dd, *J* = 16.5, 8.1 Hz, 1H), 2.30 (d, *J* = 16.8 Hz, 1H), 1.72 (dd, *J* = 12.4, 9.5 Hz, 2H), 1.52 (t, *J* = 16.2 Hz, 2H), 1.28 – 1.18 (m, 3H), 1.07 – 0.92 (m, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 173.5, 168.3, 129.5, 129.2, 128.8, 128.0, 126.7, 76.2, 63.2, 48.5, 36.8, 32.9, 32.8, 25.5, 24.8. **HRMS (ESI)** m/z calc. for $C_{23}H_{28}N_3O_2$ $[M+H]^+$ 378.2176 found 378.2182.

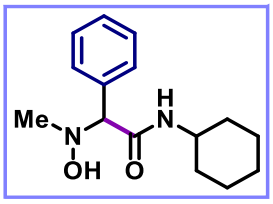
4-(2-(cyclohexylamino)-2-oxo-1-(3-oxopyrazolidin-1-yl)ethyl)phenyl 2-(1,8-diethyl-1,3,4,9-tetrahydropyrano[3,4-b]indol-1-yl)acetate (16)



The product **16** was obtained as a white solid (73.8 mg, 84%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.72 (s, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.09 – 7.00 (m, 4H), 6.14 (brs, 1H), 4.22 (s, 1H), 4.09 (dt, *J* = 10.1, 4.8 Hz, 1H), 4.01 (ddd, *J* = 11.5, 7.5, 4.4 Hz, 1H), 3.78 – 370 (m, 1H), 3.29 – 3.23 (m, 2H), 3.17 (d, *J* = 16.3 Hz, 1H), 2.90 – 2.45 (m, 5H), 2.53 – 2.36 (m, 2H), 2.14 (ddt, *J* = 34.1, 14.5, 7.3 Hz, 2H), 1.94 – 1.59 (m, 10H), 1.31 (td, *J* = 7.5, 3.2 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 174.4, 171.1, 168.3, 150.9, 135.4, 134.7, 133.2, 129.6, 126.7, 126.3, 122.4, 120.7, 119.9, 116.1, 109.0, 75.6, 74.9, 60.9, 50.8, 48.3, 43.4, 33.0, 32.9, 31.0, 29.5, 25.5, 24.8, 24.2, 22.5, 13.9, 7.8. **HRMS (ESI):** m/z calc. for $C_{34}H_{43}N_4O_5$ $[M+H]^+$ 587.3228, found 587.3235.

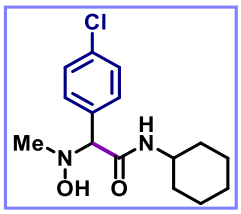
Scope for the carbamoylation of nitrones

_N_-cyclohexyl-2-(hydroxy(methyl)amino)-2-phenylacetamide (17)



The product **17** was obtained as a yellow oil (19.5 mg, 50%) following the general procedure GP2. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.39 – 7.32 (m, 5H), 6.30 (d, *J* = 8.1 Hz, 1H), 4.08 (s, 1H), 3.81-7.72 (m, 1H), 2.53 (s, 3H), 1.86 (d, *J* = 11.1 Hz, 2H), 1.62 (m, 3H), 1.38-1.28 (m, 2H), 1.17 – 1.10 (m, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 170.0, 160.4, 136.0, 128.9, 128.7, 78.9, 48.1, 45.7, 33.0, 25.6, 24.9. **HRMS (ESI):** m/z calc. for $C_{15}H_{23}N_2O_2$ $[M+H]^+$ 263.1754, found 263.1763.

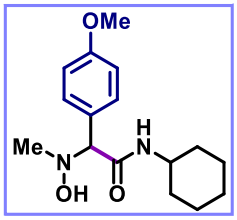
2-(4-chlorophenyl)-_N_-cyclohexyl-2-(hydroxy(methyl)amino)acetamide (18)



The product **18** was obtained as a colorless oil (21.8 mg, 49%) following the general procedure **GP2**. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 6.9 Hz, 1H), 4.44 (s, 1H), 3.79 – 3.69 (m, 1H), 2.65 (s, 3H), 1.90 – 1.82 (m, 2H), 1.68 (ddd, *J* = 16.2, 7.9, 3.9 Hz, 2H), 1.62 – 1.57 (m, 1H), 1.32 (td, *J* = 13.2, 1.7 Hz, 2H), 1.25 (s, 1H), 1.22 – 1.08 (m, 3H). **^{13}C NMR ($CDCl_3$, 126**

MHz): δ 169.5, 134.6, 134.4, 130.1, 129.8, 129.1, 128.2, 78.1, 48.2, 45.8, 33.0, 33.0, 25.6, 24.9. **HRMS (ESI)** m/z calc. for $C_{15}H_{22}ClN_2O_2$ $[M+H]^+$ 297.1364, found 297.1378.

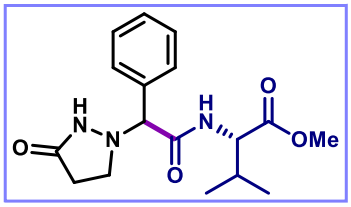
_N_-cyclohexyl-2-(hydroxy(methyl)amino)-2-(4-methoxyphenyl)acetamide (19)



The product **19** was obtained as a white solid (22 mg, 50 %) following the general procedure GP2. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.29 (d, *J* = 7.9 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.13 (d, *J* = 7.7 Hz, 1H), 4.01 (s, 1H), 3.80 (s, 3H), 3.78 – 3.74 (m, 1H), 2.51 (s, 3H), 1.87 (d, *J* = 11.6 Hz, 2H), 1.68 – 1.58 (m, 3H), 1.39 – 1.29 (m, 2H), 1.13 (ddd, *J* = 14.7, 11.6, 2.5 Hz, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 170.3, 159.9, 129.9, 114.3, 78.1, 55.4, 48.1, 45.5, 33.1, 25.6, 24.9. **HRMS (ESI):** m/z calc. for $C_{16}H_{25}N_2O_3$ $[M+H]^+$ 293.1860, found 293.1866.

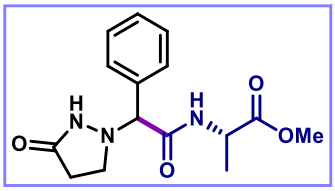
Scope for the 4-carbamoyl-1,4-dihydropyridines

Methyl-(2-(3-oxopyrazolidin-1-yl)-2-phenylacetyl)-*L*-valinate (20)



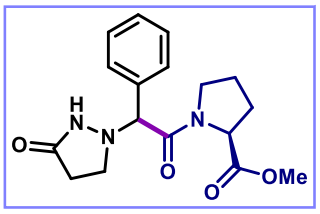
The product **20** was obtained as a yellow oil (30.5 mg, 61%, 1:1 dr) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.47 – 7.45 (m, 2H), 7.42 – 7.35 (m, 3H), 7.03 (d, *J* = 9.6 Hz, 1H), 4.55 (dd, *J* = 9.6, 4.3 Hz, 1H), 4.41 (brs, 1H), 3.77 (s, 3H), 7.48 – 7.40 (m, 1H), 3.22 (brs, 1H), 2.64 – 2.53 (m, 1H), 2.44 (dd, *J* = 25.2, 14.8 Hz, 1H), 2.26 (tt, *J* = 14.0, 6.9 Hz, 1H), 0.90 (d, *J* = 6.9 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.8, 174.5, 173.0, 169.9, 135.1, 129.3, 129.3, 129.2, 129.1, 128.8, 128.0, 75.6, 56.8, 56.6, 52.9, 52.6, 50.3, 31.3, 30.6, 29.8, 29.6, 19.3, 19.1, 17.7, 17.6. **HRMS (ESI):** m/z calc. for $C_{17}H_{24}N_3O_4$ $[M+H]^+$ 334.1761, found 334.1752.

Methyl-(2-(3-oxopyrazolidin-1-yl)-2-phenylacetyl)-*L*-alaninate (21)



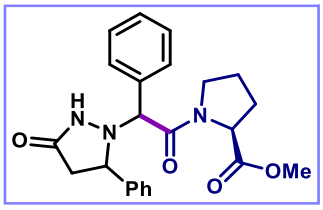
The product **21** was obtained as a yellow oil (13.7 mg, 30%, 1:1 dr) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.45 – 7.37 (m, 10H), 7.12 (d, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.7 Hz, 1H), 4.65 – 4.54 (m, 2H), 4.30 (s, 1H), 4.27 (s, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.54 – 3.52 (m, 1H), 3.47 (t, *J* = 6.6 Hz, 1H), 3.39 – 3.25 (m, 2H), 2.60 – 2.50 (m, 1H), 2.44 – 2.38 (m, 2H), 2.36 – 2.29 (m, 1H), 1.41 (d, *J* = 7.4 Hz, 3H), 1.38 (d, *J* = 7.1 Hz, 3H).**^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.7, 174.5, 174.4, 173.7, 169.9, 169.4, 129.3, 129.2, 128.9, 128.1, 77.4, 75.8, 53.1, 52.8, 48.0, 47.7, 29.8, 29.8, 18.22, 17.7. **HRMS (ESI):** m/z calc. for $C_{15}H_{20}N_3O_4$ $[M+H]^+$ 306.1448, found 306.1458.

Methyl-2-(3-oxopyrazolidin-1-yl)-2-phenylacetyl)-*L*-prolinate (22)



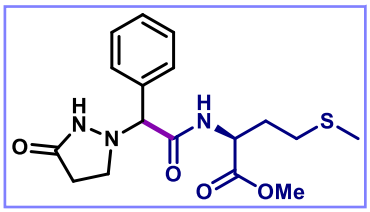
The product **22** was obtained as a white solid (36.4 mg, 73%, 1:1 dr) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.87 (brs, 1H), 7.68 (brs, 1H), 7.42 – 7.37 (m, 10H), 4.51 (dd, *J* = 8.2, 4.1 Hz, 1H), 4.45 (s, 1H), 4.44 – 4.41 (m, 1H), 4.23 – 4.11 (m, 1H), 3.75 (s, 3H), 3.71 (dd, *J* = 7.2, 4.3 Hz, 1H), 3.67 (s, 3H), 3.46 – 3.41 (m, 1H), 3.25 – 3.18 (m, 2H), 3.16 – 3.11 (m, 1H), 3.05 – 2.99 (m, 1H), 2.36 – 2.25 (m, 2H), 2.17 – 2.09 (m, 3H), 2.07 – 1.99 (m, 2H), 1.96 – 1.88 (m, 2H), 1.86 – 1.77 (m, 4H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 187.9, 174.7, 174.5, 172.5, 172.1, 169.2, 168.8, 168.7, 130.1, 129.7, 129.4, 129.2, 129.0, 106.7, 73.5, 73.5, 59.5, 59.4, 52.6, 52.3, 49.8, 49.4, 46.9, 46.7, 30.2, 30.0, 28.7, 28.6, 25.1, 24.8. **HRMS (ESI):** m/z calc. for $C_{17}H_{22}N_3O_4$ $[M+H]^+$ 332.1605, found 332.1601.

Methyl (2-(3-oxo-5-phenylpyrazolidin-1-yl)-2-phenylacetyl)-*L*-prolinate (23)



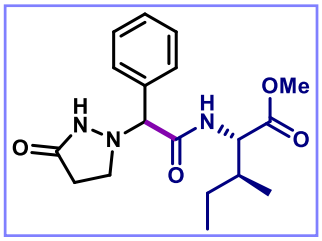
The product **23** was obtained as a colorless oil (30 mg, 50 %, 1:1 dr) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.85 (s, 1H), 7.79 (s, 1H), 7.41 (dd, *J* = 7.1, 4.2 Hz, 4H), 7.30 (d, *J* = 5.2 Hz, 3H), 7.23 (d, *J* = 4.8 Hz, 3H), 7.19 – 7.12 (m, 10H), 4.70 (s, 1H), 4.64 (s, 1H), 4.53 – 4.47 (m, 1H), 4.46 – 4.41 (m, 2H), 4.34 (dd, *J* = 8.9, 3.8 Hz, 1H), 3.76 (s, 3H), 3.63 (s, 3H), 3.53 – 3.45 (m, 2H), 3.30 (dd, *J* = 16.1, 7.0 Hz, 1H), 3.21 – 3.13 (m, 2H), 3.05 (dd, *J* = 16.9, 8.9 Hz, 1H), 2.47 – 2.43 (m, 1H), 2.39 (dd, *J* = 17.6, 3.5 Hz, 1H), 2.08 – 1.92 (m, 5H), 1.88 – 1.82 (m, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 173.3, 172.8, 172.5, 172.23, 168.4, 168.1, 141.4, 141.3, 133.5, 132.9, 129.8, 129.5, 129.2, 128.8, 128.4, 128.3, 127.3, 127.3, 126.6, 126.5, 73.9, 73.5, 62.6, 61.7, 59.7, 59.6, 52.6, 52.3, 47.0, 46.6, 37.6, 37.0, 28.7, 28.5, 25.1, 24.9. **HRMS (ESI):** m/z calc. for $C_{23}H_{26}N_3O_4$ $[M+H]^+$ 408.1918, found 408.1916.

Methyl-(3-oxopyrazolidin-1-yl)(phenyl)methyl)-*L*-methioninate (24)



The product **24** was obtained as a yellow oil (40.5 mg, 74%, 1:1 dr) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.41 – 7.36 (m, 4H), 7.34 – 7.29 (m, 6H), 4.65 (dtd, *J* = 16.1, 8.4, 4.7 Hz, 2H), 4.27 (s, 1H), 4.24 (s, 1H), 3.71 (s, 3H), 3.68 (s, 3H), 3.28 (dq, *J* = 26.1, 8.8 Hz, 2H), 2.41 – 2.22 (m, 6H), 2.06 (dtd, *J* = 16.3, 13.0, 11.9, 6.7 Hz, 2H), 1.95 (s, 3H), 1.92 (s, 3H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.8, 174.5, 172.7, 169.9, 134.9, 129.3, 129.2, 128.8, 128.0, 75.8, 53.1, 52.9, 51.5, 51.2, 50.3, 31.2, 30.8, 30.3, 30.1, 29.8, 29.7, 15.6, 15.6. **HRMS (ESI):** m/z calc. for $C_{17}H_{24}N_3O_4S$ $[M+H]^+$ 366.1482, found 366.1474.

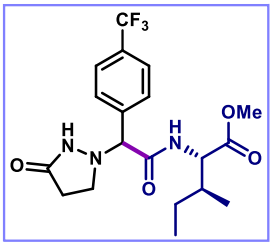
Methyl-(2-(3-oxopyrazolidin-1-yl)-2-phenylacetyl)-*L*-isoleucinate (25)



The product **25** was obtained as a colorless oil (25.5 mg, 49%, 1:1 dr) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.47 – 7.29 (m, 10H), 7.13 (d, *J* = 8.9 Hz, 1H), 7.01 (d, *J* = 9.4 Hz, 1H), 4.58 (dd, *J* = 9.4, 4.4 Hz, 2H), 4.35 (s, 1H), 4.29 (s, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 3.34 (dq, *J* = 18.7, 8.6, 8.1 Hz, 2H), 2.60 – 2.30 (m, 4H), 1.99 – 1.93 (m, 1H), 1.89 – 1.80 (m, 1H), 1.40 – 1.21 (m, 4H), 0.93 – 0.87 (m, 6H), 0.85 – 0.77

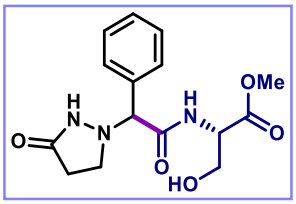
(m, 6H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 174.8, 174.6, 173.1, 172.8, 170.1, 169.7, 135.0, 129.3, 129.2, 129.1, 128.9, 128.1, 128.0, 75.7, 56.3, 52.8, 52.5, 37.8, 37.2, 29.8, 29.7, 25.1, 15.9, 15.6, 11.8, 11.6. **HRMS (ESI):** m/z calc. for $C_{18}H_{26}N_3O_4$ $[M+H]^+$ 348.1918, found 348.1938.

Methyl (2-(3-oxopyrazolidin-1-yl)-2-(4-(trifluoromethyl)phenyl)acetyl)-*L*-isoleucinate (26)



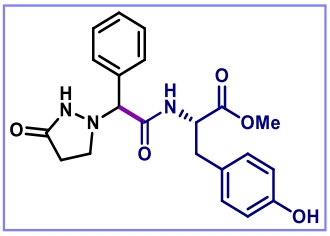
The product **26** was obtained as a colorless oil (34.9 mg, 56%, 1:1 dr) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.70 – 7.56 (m, 8H), 7.08 (d, *J* = 9.6 Hz, 1H), 4.60 – 4.55 (m, 2H), 4.54 (s, 1H), 4.38 (s, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.41 (dtt, *J* = 11.7, 8.5, 3.5 Hz, 2H), 2.64 – 2.50 (m, 2H), 2.39 (dt, *J* = 16.4, 8.0 Hz, 2H), 2.00 – 1.90 (m, 1H), 1.79 (brs, 1H), 1.39 – 1.23 (m, 2H), 1.20 – 1.00 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H), 0.80 (d, *J* = 6.9 Hz, 6H), 0.78 – 0.72 (m, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 175.2, 174.6, 173.5, 169.2, 169.1, 139.4, 139.1, 131.23 (q, *J* = 29.9 Hz), 129.1, 128.4, 126.2 (d, *J* = 3.4 Hz), 125.9 (d, *J* = 3.3 Hz), 123.9 (dd, *J* = 272.4, 15.8 Hz), 76.5, 75.0, 56.3, 56.1, 52.9, 52.7, 50.3, 50.1, 37.9, 37.2, 29.8, 29.5, 25.1, 25.0, 15.9, 15.6, 11.7, 11.6. **HRMS (ESI):** m/z calc. for $C_{19}H_{25}F_3N_3O_4$ $[M+H]^+$ 416.1800, found 416.1804.

Methyl-(2-(3-oxopyrazolidin-1-yl)-2-phenylacetyl)-*L*-serinate (27)



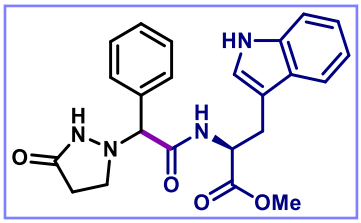
The product **27** was obtained as a colorless oil (15.8 mg, 33%, 1:1 dr) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.71 (d, *J* = 7.2 Hz, 2H), 7.47 – 7.44 (m, 2H), 7.38 – 7.34 (m, 8H), 4.63 (d, *J* = 7.5 Hz, 1H), 4.55 (dd, *J* = 6.6, 3.5 Hz, 1H), 4.39 (s, 1H), 4.33 (s, 1H), 4.03 – 3.93 (m, 4H), 3.78 (s, 6H), 3.36 (dt, *J* = 12.0, 8.3 Hz, 3H), 3.06 – 3.01 (m, 1H), 2.66 (dt, *J* = 17.4, 9.0 Hz, 1H), 2.53 (t, *J* = 7.1 Hz, 1H), 2.33 (ddt, *J* = 17.3, 13.9, 6.9 Hz, 2H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 176.7, 171.0, 169.6, 135.2, 129.3, 129.2, 128.2, 62.8, 62.6, 55.5, 54.8, 53.2, 52.9, 50.4, 49.7, 30.0, 29.9. **HRMS (ESI):** m/z calc. for $C_{15}H_{20}N_3O_5$ $[M+H]^+$ 322.1397, found 322.1410.

Methyl ((3-oxopyrazolidin-1-yl)(phenyl)methyl)-*L*-tyrosinate (28)



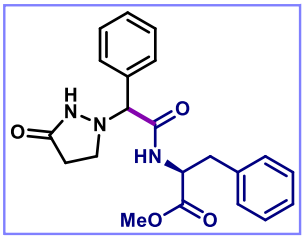
The product **28** was obtained as a colorless oil (29.5 mg, 49%, 1:1 dr) following the general procedure GP1. Reported spectra of the major diastereoisomer. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR (Methanol-*d*4, 400 MHz):** δ 7.90 (s, 1H), 7.41 – 7.32 (m, 5H), 6.76 (d, *J* = 8.1 Hz, 2H), 6.54 (d, *J* = 8.3 Hz, 2H), 4.63 (dd, *J* = 8.5, 5.2 Hz, 1H), 4.42 (s, 1H), 3.69 (s, 3H), 3.22 – 3.19 (m, 2H), 3.01 (dd, *J* = 13.9, 5.1 Hz, 1H), 2.86 (dd, *J* = 14.0, 8.7 Hz, 1H), 2.41 – 2.34 (m, 2H). **^{13}C NMR (Methanol-*d*4, 126 MHz):** δ 177.4, 173.3, 172.0, 157.3, 136.5, 131.3, 131.1, 130.1, 129.9, 129.8, 128.3, 116.2, 75.8, 55.0, 52.7, 37.1, 30.3. **HRMS (ESI):** m/z calc. for $C_{21}H_{23}N_3O_5$ $[M]^+$ 397.1638, found 398.1656.

Methyl-(3-oxopyrazolidin-1-yl)(phenyl)methyl)-*L*-tryptophanate (29)



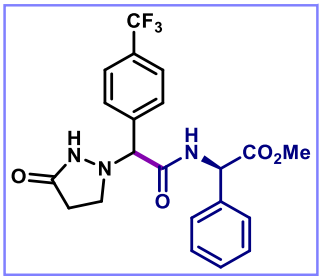
The product **29** was obtained as a yellow oil (42.2 mg, 67%,1:1 dr) following the general procedure GP1. Reported spectra of the major diastereoisomer. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.43 (brs, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.29 (m, 6H), 7.25 – 7.13 (m, 3H), 6.91 (brs, 1H), 4.95 – 4.90 (m, 1H), 4.36 (s, 1H), 3.75 (s, 3H), 3.30 (d, *J* = 5.6 Hz, 2H), 2.43 – 2.32 (m, 2H), 2.30 – 2.17 (m, 2H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.4, 173.3, 136.2, 134.4, 129.1, 128.2, 127.5, 123.0, 122.5, 119.9, 118.5, 111.6, 109.4, 76.5, 53.0, 52.6, 49.9, 29.6, 26.9. **HRMS (ESI):** m/z calc. for $C_{23}H_{25}N_4O_4$ $[M+H]^+$ 421.1870, found 421.1863.

Methyl (2-(3-oxopyrazolidin-1-yl)-2-phenylacetyl)-*L*-phenylalaninate (30)



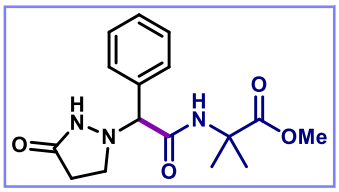
The product **30** was obtained as a yellow oil (37.2 mg, 65%,1:1 dr) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR (Methanol-*d*4, 400 MHz):** δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.36 – 7.32 (m, 8H), 7.24 – 7.18 (m, 5H), 7.14 – 7.12 (m, 5H), 6.98 – 6.95 (m, 2H), 4.72 (ddd, *J* = 11.5, 9.2, 5.1 Hz, 2H), 4.42 (s, 1H), 4.35 (s, 1H), 3.70 (s, 6H), 3.23 (dd, *J* = 13.9, 5.0 Hz, 2H), 3.19 – 3.15 (m, 2H), 3.13 (dd, *J* = 13.9, 5.1 Hz, 2H), 2.99 (ddd, *J* = 22.2, 13.9, 9.3 Hz, 2H), 2.42 – 2.33 (m, 4H). **^{13}C NMR (Methanol-*d*4, 101 MHz):** δ 177.5, 173.4, 173.2, 172.1, 172.0, 138.1, 137.8, 136.6, 136.4, 133.9, 130.7, 130.3, 130.1, 130.1, 129.9, 129.85, 129.8, 129.6, 129.5, 127.9, 127.8, 76.6, 75.9, 54.9, 54.8, 52.9, 52.8, 51.3, 51.1, 37.8, 37.7, 30.3. **HRMS (ESI):** m/z calc. for $C_{21}H_{24}N_3O_4$ $[M+H]^+$ 382.1761, found 382.1757.

Methyl (2*R*)-2-(2-(3-oxopyrazolidin-1-yl)-2-(4-(trifluoromethyl)phenyl)acetamido)-2-phenylacetate (31)



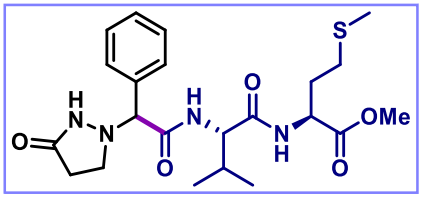
The product **31** was obtained as a white solid (78 mg, 45 %, 1:1 d.r) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR (Methanol-*d*4, 400 MHz):** δ 7.71– 7.61 (m, 8H), 7.32 – 7.25 (m, 10H), 5.46 (s, 1H), 5.40 (s, 1H), 4.67 (s, 1H), 4.63 (s, 1H), 3.69 (s, 3H), 3.59 (s, 3H), 3.40 – 3.28 (m, 4H), 2.43 (brs, 4H). **^{13}C NMR (Methanol-*d*4, 101 MHz):** δ 177.7, 172.4, 172.3, 171.1, 170.9, 141.1, 136.9, 136.7, 132.0, 131.7, 130.7, 130.6, 129.9, 129.9, 129.7, 128.8, 128.7, 126.6, 126.5, 126.5, 75.3, 74.9, 58.3, 58.1, 53.1, 53.1, 51.5, 51.3, 30.3. **HRMS (ESI):** m/z calc. for $C_{21}H_{21}F_3N_3O_4$ $[M+H]^+$ 436.1479, found 436.1507.

Methyl 2-methyl-2-(2-(3-oxopyrazolidin-1-yl)-2-phenylacetamido)propanoate (32)



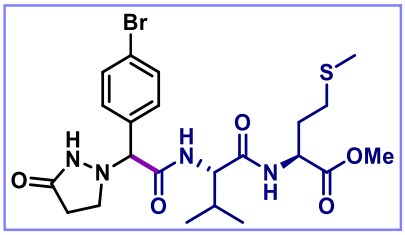
The product **32** was obtained as a yellow oil (33.5 mg, 70%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.39 – 7.35 (m, 5H), 6.89 (brs, 1H), 4.20 (s, 1H), 3.71 (s, 3H), 3.30 (dt, *J* = 10.8, 7.6 Hz, 1H), 2.41 (tt, *J* = 16.6, 9.2 Hz, 2H), 1.52 (s, 3H), 1.49 (s, 3H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 175.4, 174.5, 169.6, 134.7, 129.3, 128.6, 76.6, 56.9, 53.1, 50.5, 29.8, 25.5, 24.5. **HRMS (ESI):** m/z calc. for $C_{16}H_{22}N_3O_4$ $[M+H]^+$ 320.1605, found 320.1607.

Methyl (2-(3-oxopyrazolidin-1-yl)-2-phenylacetyl)-*L*-valyl-*L*-methioninate (33)



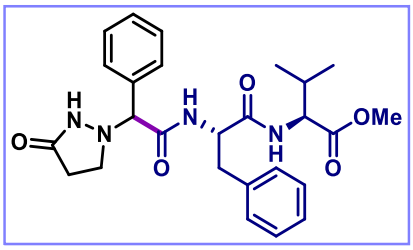
The product **33** was obtained as a yellow oil (51.5 mg, 74%, 1:1 dr) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.34 – 7.08 (m, 20H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 2H), 4.86 – 4.71 (m, 2H), 4.48 – 4.36 (m, 2H), 4.22 (s, 1H), 4.21 (s, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 3.13 – 2.95 (m, 4H), 2.53 – 2.46 (m, 1H), 2.42 – 2.25 (m, 3H), 2.20 – 1.95 (m, 4H), 1.40 (dt, *J* = 11.0, 6.8 Hz, 2H), 0.89 – 0.80 (m, 8H), 0.68 (t, *J* = 7.2 Hz, 4H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.9, 174.6, 172.2, 172.2, 171.9, 171.0, 170.7, 170.1, 135.2, 134.9, 129.4, 129.3, 128.9, 128.0, 75.6, 58.4, 58.1, 52.7, 52.7, 52.0, 51.7, 31.4, 31.2, 31.1, 30.9, 30.0, 29.8, 29.7, 19.5, 19.2, 18.1, 17.9, 15.6, 15.5. **HRMS (ESI):** m/z calc. for $C_{22}H_{33}N_4O_5S$ $[M+H]^+$ 465.2166, found 465.2163.

Methyl (2-(4-bromophenyl)-2-(3-oxopyrazolidin-1-yl)acetyl)-*L*-valyl-*L*-methioninate (34)



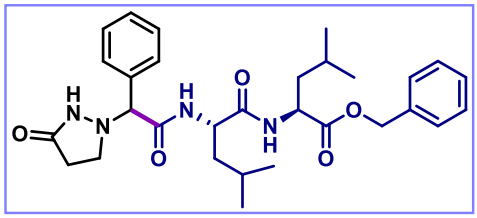
The product **34** was obtained as a yellow oil (78.1 mg, 96%, 1:1 dr) following the general procedure GP1. Reported spectra of the major diastereoisomer. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.51 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 8.9 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 4.70 (q, *J* = 7.3 Hz, 1H), 4.35 – 4.27 (m, 1H), 4.26 (s, 1H), 3.75 (s, 3H), 3.33 (dq, *J* = 18.9, 9.3 Hz, 2H), 2.50 (t, *J* = 7.2 Hz, 2H), 2.46 – 2.31 (m, 2H), 2.20 – 2.12 (m, 1H), 2.09 (s, 3H), 2.00 (tt, *J* = 13.9, 7.0 Hz, 2H), 0.90 (t, *J* = 7.6 Hz, 3H).**^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.7, 172.2, 171.8, 170.2, 134.2, 132.4, 129.6, 123.3, 76.3, 58.1, 52.7, 52.0, 50.0, 31.1, 30.9, 30.0, 29.6, 19.5, 18.0, 15.6. **HRMS (ESI):** m/z calc. for $C_{22}H_{32}BrN_4O_5S$ $[M+H]^+$ 543.1271, found 543.1294.

Methyl (2-(3-oxopyrazolidin-1-yl)-2-phenylacetyl)-*L*-phenylalanyl-*L*-valinate (35)



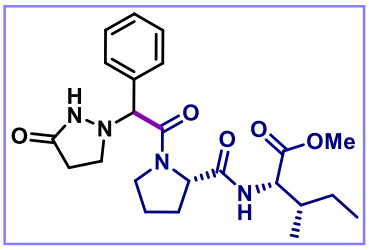
The product **35** was obtained as a yellow oil (56.9 mg, 79%, 1:1 dr) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.36 – 7.06 (m, 6H), 7.01 (d, *J* = 7.9 Hz, 0H), 6.77 (d, *J* = 8.7 Hz, 1H), 4.87 – 4.68 (m, 1H), 4.50 – 4.34 (m, 1H), 4.22 (s, 1H), 4.21 (s, 1H), 3.72 (s, 1H), 3.69 (s, 1H), 3.16 – 2.93 (m, 1H), 2.55 – 2.39 (m, 0H), 2.31 (dp, *J* = 15.9, 7.8 Hz, 1H), 2.04 (ddq, *J* = 26.4, 12.8, 6.6 Hz, 1H), 1.40 (dt, *J* = 11.0, 6.8 Hz, 1H), 0.91 – 0.78 (m, 2H), 0.68 (t, *J* = 7.2 Hz, 1H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.6, 172.0, 171.9, 170.7, 170.3, 170.0, 136.3, 136.1, 134.7, 129.4, 129.2, 129.2, 129.1, 129.1, 128.9, 128.8, 128.7, 128.5, 128.2, 127.3, 127.2, 76.6, 76.0, 57.7, 57.5, 54.0, 53.9, 52.2, 52.2, 50.4, 50.1, 37.9, 37.3, 31.0, 30.9, 29.7, 29.5, 18.9, 18.8, 17.8, 17.6. **HRMS (ESI):** m/z calc. for $C_{26}H_{33}N_4O_5$ $[M+H]^+$ 481.2445, found 481.2446.

Benzyl (2-(3-oxopyrazolidin-1-yl)-2-phenylacetyl)-*L*-leucyl-*L*-leucinate (36)



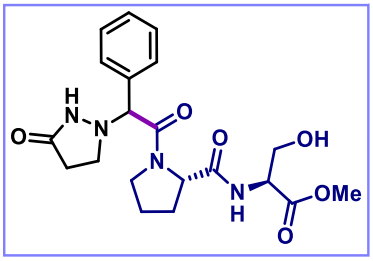
The product **36** was obtained as a yellow oil (78.8 mg, 98%, 1:1 dr) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.41 – 7.32 (m, 17H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 1H), 6.63 (d, *J* = 7.4 Hz, 1H), 5.24 – 5.12 (m, 4H), 4.58 (td, *J* = 8.9, 4.1 Hz, 1H), 4.48 (p, *J* = 7.8 Hz, 2H), 4.33 (s, 1H), 4.31 (s, 1H), 3.36 – 3.29 (m, 2H), 2.63 – 2.46 (m, 2H), 2.37 – 2.21 (m, 2H), 1.66 – 1.47 (m, 12H), 0.90 – 0.85 (m, 16H), 0.79 – 0.75 (m, 8H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.7, 174.4, 173.6, 173.1, 172.4, 171.9, 170.5, 169.9, 135.3, 135.0, 129.2, 129.0, 128.6, 128.6, 128.4, 128.4, 127.9, 75.3, 67.5, 67.4, 51.1, 50.9, 50.8, 50.7, 41.2, 40.9, 40.7, 40.0, 29.7, 29.6, 24.9, 24.9, 24.8, 24.7, 22.9, 22.9, 21.9, 21.7. **HRMS (ESI):** m/z calc. for $C_{30}H_{41}N_4O_5$ $[M+H]^+$ 537.3071, found 537.3077.

Methyl (-2-(3-oxopyrazolidin-1-yl)-2-phenylacetyl)-*L*-prolyl-*L*-isoleucinate (37)



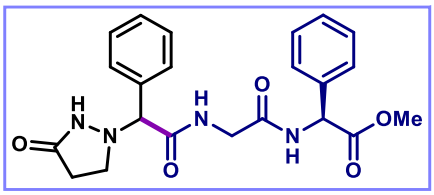
The product **37** was obtained as a yellow oil (49.9 mg, 75%, 1:1 dr) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.33 (s, 1H), 8.17 (d, *J* = 9.0 Hz, 1H), 7.48 (ddd, *J* = 7.1, 3.9, 2.0 Hz, 3H), 7.45 – 7.42 (m, 1H), 7.41 – 7.37 (m, 5H), 4.57 (ddd, *J* = 9.6, 5.9, 2.8 Hz, 2H), 4.49 (dd, *J* = 8.5, 4.7 Hz, 1H), 4.44 (dd, *J* = 8.6, 5.0 Hz, 1H), 4.40 (s, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 3.71 – 3.66 (m, 2H), 3.61 – 3.55 (m, 2H), 3.27 – 3.13 (m, 2H), 3.10 – 3.01 (m, 2H), 2.48 – 2.23 (m, 4H), 2.10 – 1.80 (m, 10H), 1.50 – 1.33 (m, 4H), 0.93 – 0.87 (m, 12H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.9, 173.4, 172.3, 170.5, 170.4, 170.3, 170.1, 132.8, 129.9, 129.6, 129.5, 129.4, 129.3, 74.6, 60.0, 57.8, 57.0, 56.7, 52.8, 52.1, 49.5, 49.4, 47.2, 47.0, 38.1, 37.6, 30.1, 27.2, 26.2, 25.1, 25.1, 25.0, 24.2, 15.8, 15.7, 11.7, 11.7. **HRMS (ESI):** m/z calc. for $C_{23}H_{33}N_4O_5$ $[M+H]^+$ 445.2445, found 445.2475.

Methyl (2-(3-oxopyrazolidin-1-yl)-2-phenylacetyl)-*L*-prolyl-*L*-serinate (38)



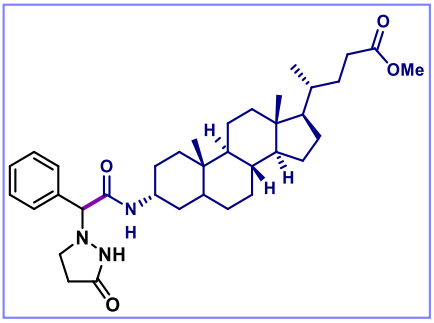
The product **38** was obtained as a yellow oil (31 mg, 51 %, 1:1 dr) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.37 (brs, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.46 – 7.40 (m, 5H), 4.62 (dd, *J* = 16.4, 7.3 Hz, 2H), 4.51 (s, 1H), 4.05 (dd, *J* = 11.1, 2.5 Hz, 1H), 3.90 (d, *J* = 10.6 Hz, 1H), 3.78 (s, 3H), 3.71 – 3.64 (dd, m, 1H), 3.29 – 3.22 (m, 1H), 3.16 – 3.05 (m, 2H), 2.55 – 2.49 (m, 1H), 2.29 – 2.24 (m, 2H), 2.12 – 2.08 (m, 1H), 1.85 – 1.75 (m, 2H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 175.3, 171.3, 169.8, 132.6, 129.6, 129.3, 74.03, 62.5, 60.6, 54.7, 52.9, 49.1, 47.0, 30.0, 27.4, 24.8. **HRMS (ESI):** m/z calc. for $C_{20}H_{27}N_4O_6$ $[M+H]^+$ 419.1925, found 419.1924.

Methyl (2*S*)-2-(2-(2-(3-oxopyrazolidin-1-yl)-2-phenylacetamido)acetamido)-2-phenylacetate (39)



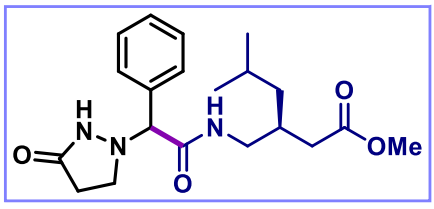
The product **39** was obtained as a yellow oil (39.4 mg, 62%, 1:1 dr) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.37 – 7.29 (m, 10H), 7.15 (d, *J* = 6.6 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 5.57 (d, *J* = 7.1 Hz, 1H), 4.29 (dd, *J* = 6.5 Hz, 1H), 4.24 (d, *J* = 16.5, 7.3 Hz, 1H), 4.09 (dd, *J* = 17.9, 7.4 Hz, 1H), 3.72 (s, 3H), 3.32 (p, *J* = 8.9 Hz, 1H), 3.13 (brs, 1H), 2.52 (brs, 1H), 2.31 (dt, *J* = 16.1, 7.9 Hz, 1H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.8, 174.8, 171.5, 171.3, 170.9, 170.8, 169.0, 168.9, 136.0, 135.7, 134.8, 129.2, 129.2, 128.9, 128.8, 128.4, 128.3, 127.5, 127.4, 76.4, 56.7, 56.7, 53.2, 53.1, 50.1, 50.1, 42.4, 42.3, 29.8, 29.8. **HRMS (ESI):** m/z calc. for $C_{22}H_{25}N_4O_5$ $[M+H]^+$ 425.1819, found 425.1844.

Methyl-(4*R*)-4-((3*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3-(2-(3-oxopyrazolidin-1-yl)-2-phenylacetamido)hexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)pentanoate (40)



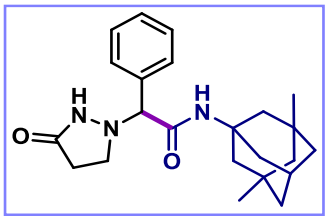
The product **40** was obtained as a yellow oil (42.6 mg, 48%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.37 – 7.24 (m, 5H), 6.46 (brs, 1H), 4.24 (s, 1H), 4.08 – 4.03 (m, 1H), 3.59 (s, 1H), 3.25 (dd, *J* = 17.0, 8.5 Hz, 1H), 2.45 – 2.20 (m, 3H), 2.14 (ddd, *J* = 15.6, 9.7, 6.4 Hz, 1H), 1.95 – 1.85 (m, 2H), 1.82 – 1.67 (m, 3H), 1.51 – 1.42 (m, 3H), 1.34 – 0.90 (m, 17H), 0.83 (d, *J* = 5.9 Hz, 6H), 0.76 – 0.68 (m, 2H), 0.56 (s, 3H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.9, 174.3, 168.7, 135.1, 129.4, 128.5, 128.5, 76.0, 56.5, 56.0, 51.6, 50.7, 45.5, 42.8, 40.2, 39.8, 38.2, 35.7, 35.4, 35.1, 31.4, 31.4, 31.1, 31.1, 30.5, 30.3, 29.6, 28.3, 26.8, 26.8, 26.2, 24.7, 24.5, 24.3, 21.1, 18.3, 12.1. **HRMS (ESI):** m/z calc. for $C_{36}H_{54}N_3O_4$ $[M+H]^+$ 592.4109, found 592.4105.

Methyl 4-methyl-3-((2-(3-oxopyrazolidin-1-yl)-2-phenylacetamido)methyl)hexanoate (41)



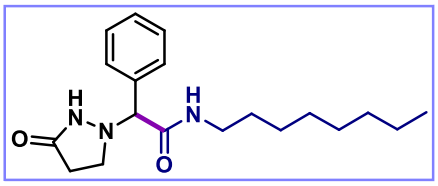
The product **41** was obtained as a yellow oil (30.9 mg, 55%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.74 (brs, 1H), 7.42 – 7.34 (m, 5H), 6.61 – 6.54 (m, 1H), 4.22 (s, 1H), 3.65 (d, *J* = 5.7 Hz, 3H), 3.30 – 3.21 (m, 3H), 3.14 (ddt, *J* = 13.7, 10.2, 6.8 Hz, 1H), 2.41 – 2.32 (m, 2H), 2.27 – 2.20 (m, 1H), 2.14 (dt, *J* = 15.2, 7.7 Hz, 1H), 2.09 – 2.02 (m, 1H), 1.55 (dp, *J* = 13.2, 6.6 Hz, 1H), 1.03 (td, *J* = 7.1, 3.9 Hz, 2H), 0.83 (dd, *J* = 6.6, 1.4 Hz, 3H), 0.79 (dd, *J* = 12.9, 6.5 Hz, 3H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.5, 174.5, 174.1, 174.0, 170.0, 135.4, 135.3, 129.4, 129.3, 128.4, 128.4, 76.4, 76.4, 52.0, 52.0, 50.7, 50.6, 43.4, 43.3, 41.8, 37.5, 37.4, 33.2, 29.7, 25.2, 22.8, 22.8, 22.6, 22.5. **HRMS (ESI):** m/z calc. for $C_{20}H_{30}N_3O_4$ $[M+H]^+$ 376.2231, found 376.2225.

***N*-((1*r*,3*R*,5*S*,7*r*)-3,5-dimethyladamantan-1-yl)-2-(3-oxopyrazolidin-1-yl)-2-phenylacetamide (42)**



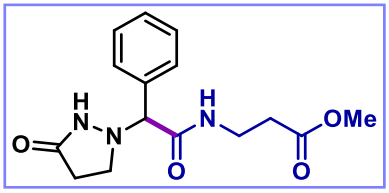
The product **42** was obtained as a yellow oil (44.6 mg, 78%) following the general procedure **GP1**. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.41 – 7.36 (m, 5H), 6.00 (s, 1H), 4.21 (s, 1H), 3.29 (dd, *J* = 16.2, 8.3 Hz, 2H), 2.43 - 2.38 (m, 2H), 2.13 – 2.11 (m, 1H), 1.77 (s, 2H), 1.57 (dd, *J* = 26.2, 11.7 Hz, 4H), 1.30 – 1.25 (m, 4H), 1.12 (s, 2H), 0.82 (s, 6H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.1, 168.3, 134.9, 129.4, 128.5, 76.4, 53.9, 50.6, 47.5, 42.6, 40.0, 32.5, 30.1, 29.6. **HRMS (ESI)** m/z calc. for $C_{23}H_{32}N_3O_2$ $[M+H]^+$ 382.2489, found 382.2483.

_N_-octyl-2-(3-oxopyrazolidin-1-yl)-2-phenylacetamide (43)



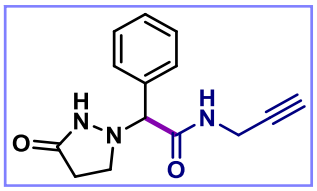
The product **43** was obtained as a yellow oil (22.0 mg, 44%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.38 – 7.34 (m, 5H), 6.32 (brs, 1H), 4.22 (s, 1H), 3.21 (tq, *J* = 13.7, 7.0 Hz, 2H), 2.39 (t, *J* = 8.0 Hz, 2H), 1.46 – 1.38 (m, 12H), 1.30 – 1.21 (m, 12H), 0.86 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.7, 169.7, 135.2, 129.2, 129.2, 128.5, 76.2, 50.6, 39.5, 31.8, 29.6, 29.5, 29.2, 26.9, 22.7, 14.2. **HRMS (ESI):** m/z calc. for $C_{19}H_{30}N_3O_2$ $[M+H]^+$ 332.2333, found 332.2358.

Methyl 3-(2-(3-oxopyrazolidin-1-yl)-2-phenylacetamido)propanoate (44)



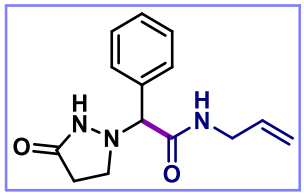
The product **44** was obtained as a white solid (26.3 mg, 57%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.38 – 7.33 (m, 5H), 4.24 (s, 1H), 3.65 (s, 3H), 3.55 – 3.39 (m, 2H), 3.29 – 3.23 (m, 2H), 2.58 – 2.43 (m, 3H), 2.34 (dd, *J* = 16.6, 8.3 Hz, 1H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.8, 173.3, 169.8, 135.2, 129.2, 129.1, 128.4, 76.2, 52.1, 50.4, 35.0, 33.4, 29.6. **HRMS (ESI):** m/z calc. for $C_{15}H_{20}N_3O_4$ $[M+H]^+$ 306.1448, found 306.1444.

2-(3-oxopyrazolidin-1-yl)-2-phenyl-_N_-(prop-2-yn-1-yl)acetamide (45)



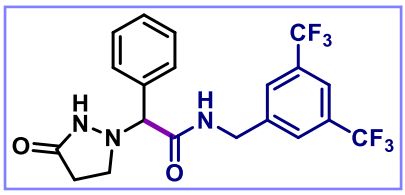
The product **45** was obtained as a white solid (22.7 mg, 59%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.40 – 7.36 (m, 5H), 6.71 (brs, 1H), 4.29 (s, 1H), 4.02 (d, *J* = 3.1 Hz, 2H), 3.26 (dd, *J* = 16.3, 8.1 Hz, 2H), 2.47 – 2.31 (m, 2H), 2.22 (t, *J* = 2.5 Hz, 1H).**^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.7, 169.5, 134.7, 131.7, 129.3, 128.6, 79.2, 75.9, 72.1, 50.5, 29.6, 29.3.**HRMS (ESI):** m/z calc. for $C_{14}H_{16}N_3O_2$ $[M+H]^+$ 258.1237, found 258.1235.

_N_-allyl-2-(3-oxopyrazolidin-1-yl)-2-phenylacetamide (46)



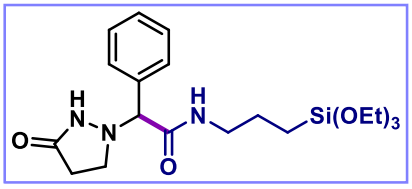
The product **46** was obtained as a white solid (19.8 mg, 51%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.42 – 7.35 (m, 5H), 6.41 (brs, 1H), 5.76 (ddt, *J* = 17.1, 10.4, 5.6 Hz, 1H), 5.09 – 5.02 (m, 2H), 4.27 (s, 1H), 3.91 – 3.79 (m, 2H), 3.26 (dt, *J* = 10.8, 4.1 Hz, 2H), 2.42 – 2.37 (m, 2H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 174.7, 169.7, 135.2, 133.7, 129.3, 129.3, 128.5, 116.8, 76.2, 50.6, 41.8, 29.7. **HRMS (ESI):** m/z calc. for $C_{14}H_{18}N_3O_2$ $[M+H]^+$ 260.1394, found 260.1382.

_N_-(3,5-bis(trifluoromethyl)benzyl)-2-(3-oxopyrazolidin-1-yl)-2-phenylacetamide (47)



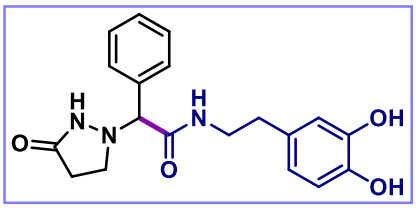
The product **47** was obtained as a colorless oil (25.4 mg, 38%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.73 (s, 1H), 7.52 (s, 1H), 7.42 – 7.38 (m, 5H), 7.01 (brs, 1H), 4.61 (dd, *J* = 15.7, 6.4 Hz, 1H), 4.49 (dd, *J* = 15.9, 5.6 Hz, 1H), 4.44 (s, 1H), 3.33 (q, *J* = 8.4 Hz, 1H), 3.24 (brs, 1H), 2.49 – 2.34 (m, 2H).**^{13}C NMR ($CDCl_3$, 126 MHz):** δ 175.0, 170.1, 140.8, 134.5, 132.0 (q, *J* = 33.5 Hz), 129.7, 129.6, 128.3, 127.5, 123.22 (d, *J* = 272.8 Hz), 121.5 (hept, *J* = 3.8 Hz), 76.0, 50.5, 42.4, 29.6. **HRMS (ESI):** m/z calc. for $C_{20}H_{18}F_6N_3O_2$ $[M+H]^+$ 446.1298, found 446.1292.

2-(3-oxopyrazolidin-1-yl)-2-phenyl-_N_-(3-(triethoxysilyl)propyl)acetamide (48)



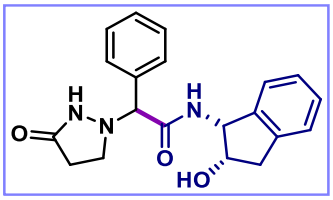
The product **48** was obtained as a white solid (46.3 mg, 73%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.31 – 7.25 (m, 3H), 6.40 (t, *J* = 5.5 Hz, 1H), 4.13 (s, 1H), 3.69 (q, *J* = 7.0 Hz, 6H), 3.14 (h, *J* = 7.6 Hz, 4H), 2.37 – 2.22 (m, 2H), 1.49 (p, *J* = 7.1 Hz, 2H), 1.11 (t, *J* = 7.0 Hz, 9H), 0.46 – 0.42 (m, 2H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 174.6, 169.8, 135.4, 129.3, 129.2, 128.5, 76.3, 58.6, 50.6, 41.7, 29.7, 22.8, 18.4, 7.7. **HRMS (ESI):** m/z calc. for $C_{20}H_{34}N_3O_5Si$ $[M+H]^+$ 424.2262, found 424.2259.

_N_-(3,4-dihydroxyphenethyl)-2-(3-oxopyrazolidin-1-yl)-2-phenylacetamide (49)



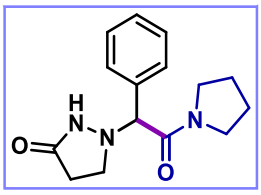
The product **49** was obtained as a white solid (39.7 mg, 74%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR (Methanol-*d*4, 400 MHz):** δ 7.42 – 7.35 (m, 5H), 6.65 (s, 1H), 6.63 – 6.62 (m, 1H), 6.42 (dd, *J* = 8.0, 1.7 Hz, 1H), 4.33 (s, 1H), 3.38 (dt, *J* = 6.8, 5.1 Hz, 1H), 3.21 (t, *J* = 7.8 Hz, 1H), 2.68 – 2.60 (m, 1H), 2.38 (t, *J* = 7.6 Hz, 1H).**^{13}C NMR (Methanol-*d*4, 101 MHz):** δ 177.6, 172.1, 163.7, 146.3, 144.8, 136.9, 131.8, 129.9, 129.8, 129.8, 121.2, 116.9, 116.4, 76.6, 51.2, 41.9, 35.5, 30.3. **HRMS (ESI):** m/z calc. for $C_{19}H_{22}N_3O_4$ $[M+H]^+$ 356.1605, found 356.1600

_N_-((1_R_,2_S_)-2-hydroxy-2,3-dihydro-1_H_-inden-1-yl)-2-(3-oxopyrazolidin-1-yl)-2-phenylacetamide (50)



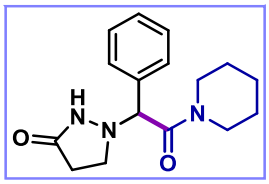
The product **50** was obtained as a white solid (15.8 mg, 30%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 9.47 (brs, 1H), 7.50 (dd, *J* = 7.2, 2.1 Hz, 2H), 7.43 – 7.39 (m, 3H), 7.28 – 7.21 (m, 5H), 6.98 (d, *J* = 7.5 Hz, 1H), 5.37 (dd, *J* = 9.4, 5.2 Hz, 1H), 4.72 – 4.70 (m, 1H), 4.40 (s, 1H), 3.34 (dt, *J* = 11.8, 8.9 Hz, 1H), 3.14 (d, *J* = 5.7 Hz, 1H), 2.96 (dd, *J* = 17.0, 8.2 Hz, 1H), 2.63 (dt, *J* = 17.3, 8.8 Hz, 1H), 2.30 (ddd, *J* = 17.0, 9.0, 5.8 Hz, 1H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 175.8, 170.6, 140.7, 140.4, 135.6, 129.3, 129.2, 128.4, 128.1, 127.2, 125.4, 124.3, 77.2, 73.0, 57.3, 49.7, 40.1, 29.9. **HRMS (ESI):** m/z calc. for $C_{20}H_{22}N_3O_4$ $[M+H]^+$ 352.1656, found 352.1649.

1-(2-oxo-1-phenyl-2-(pyrrolidin-1-yl)ethyl)pyrazolidin-3-one (51)



The product **51** was obtained as a colorless oil (27.4 mg, 67%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.48 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.41 – 7.35 (m, 3H), 4.71 (s, 1H), 3.62 (dt, *J* = 10.0, 6.2 Hz, 1H), 3.49 (dt, *J* = 12.8, 6.8 Hz, 1H), 3.35 – 3.21 (m, 4H), 3.04 (dt, *J* = 10.1, 6.7 Hz, 1H), 2.33 (dt, *J* = 16.0, 8.0 Hz, 1H), 1.84 – 1.67 (m, 4H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 177.3, 170.1, 134.9, 130.8, 130.2, 130.0, 73.6, 47.5, 30.6, 26.9, 24.8. **HRMS (ESI):** m/z calc. for $C_{15}H_{20}N_3O_2$ $[M+H]^+$ 274.1550, found 274.1571.

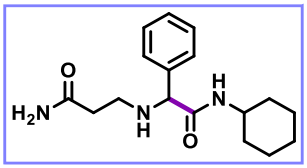
1-(2-oxo-1-phenyl-2-(piperidin-1-yl)ethyl)pyrazolidin-3-one (52)



The product **52** was obtained as a colorless oil (22.8 mg, 53%) following the general procedure GP1. The crude material was purified by flash column chromatography (DCM/MeOH 20:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.39 – 3.35 (m, 5H), 4.70 (s, 1H), 3.72 (dd, *J* = 13.2, 6.4 Hz, 1H), 3.39 – 3.29 (m, 3H), 3.21 (t, *J* = 5.4 Hz, 2H), 3.31 – 3.21 (m, 1H), 2.08 (brs, 1H), 1.58 – 1.46 (m, 4H), 1.40 – 1.27 (m, 2H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 174.4, 167.7, 132.7, 129.7, 129.4, 129.3, 72.2, 49.4, 46.6, 43.4, 30.0, 25.5, 25.4, 24.3. **HRMS (ESI):** m/z calc. for $C_{16}H_{22}N_3O_2$ $[M+H]^+$ 288.1707, found 288.1703.

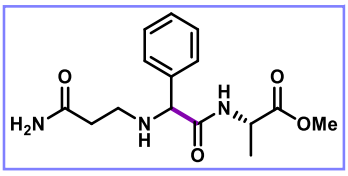
Derivatization

3-((2-(cyclohexylamino)-2-oxo-1-phenylethyl)amino)propanamide (53)



The product **53** was obtained as a white solid (44.0 mg, 73%) following the general procedure GP3. The crude material was purified by flash column chromatography (DCM/MeOH 9:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.37 – 7.29 (m, 5H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.45 (brs, 1H), 5.58 (brs, 1H), 4.22 (s, 1H), 3.72 (ddt, *J* = 14.5, 10.9, 5.5 Hz, 1H), 2.95 – 2.84 (m, 2H), 2.43 (qt, *J* = 9.7, 5.3 Hz, 2H), 1.87 – 1.82 (m, 2H), 1.67 (d, *J* = 13.7 Hz, 2H), 1.61 – 1.57 (m, 1H), 1.37 – 1.27 (m, 2H), 1.25 – 1.09 (m, 3H). **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 174.6, 171.0, 139.3, 128.9, 128.3, 127.5, 67.3, 48.1, 44.0, 35.3, 32.9, 25.5, 24.9. **HRMS (ESI):** m/z calc. for $C_{17}H_{26}N_3O_2$ $[M+H]^+$ 304.2020, found 304.2040.

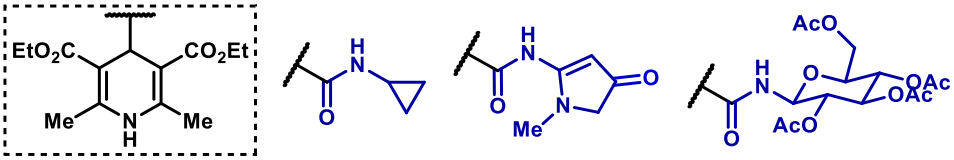
2S)-methyl 2-(2-((3-amino-3-oxopropyl)amino)-2-phenylacetamido)propanoate (54)



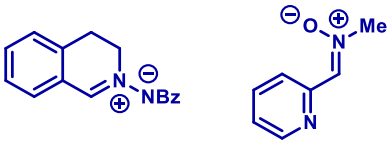
The product **54** was obtained as a yellow oil (13.5 mg, 32%) following the general procedure GP3. Reported signals of the major diastereoisomer (3:1) (* for overlapped signals). The crude material was purified by flash column chromatography (DCM/MeOH 9:1). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.41 – 7.31 (m, 7H)*, 6.34 (s, 1H), 5.53 (s, 1H), 4.61 – 4.54 (m, 2H)*, 4.21 (d, *J* = 8.3 Hz, 1H), 3.73 (s, 3H), 3.00 – 2.90 (m, 2H), 2.55 – 2.29 (m, 3H)*, 1.40 (dd, *J* = 11.7, 5.0 Hz, 4H)*. **^{13}C NMR ($CDCl_3$, 126 MHz):** δ 174.5, 174.3, 173.9, 173.4, 171.9, 169.3, 138.7, 129.3, 129.2, 128.9, 128.4, 127.6, 127.2, 67.6, 67.1, 52.7, 52.5, 47.9, 47.7, 44.3, 43.8, 29.7, 18.1. **HRMS (ESI):** m/z calc. for $C_{15}H_{21}N_3O_4$ $[M+H]^+$ 308.1605, found 308.1612.

Unsuccessful Substrates

4-carbamoyl-1,4-dihydropyridines:



1.3-Dipoles:



Mechanistic Evidences

Cyclic voltammetry

The measurement was performed using a glassy carbon working electrode, a Pt wire auxiliary electrode, and Ag/AgCl (satd. KCl) reference electrode. The ferrocene was considered as the external standard. The analysis was performed under N_2 atmosphere and using a degasified solution of the compound in MeCN (0.5 mM) containing a 0.1 M $TBAPF_6$ solution in MeCN. The potential range scanned was typically -2.5 V – 2.5 V at a 100 mV/s.

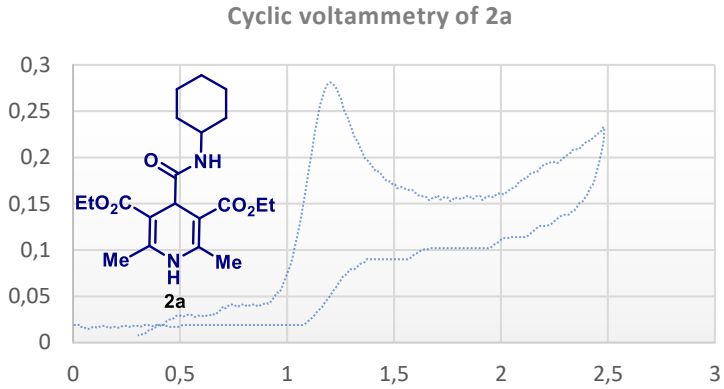
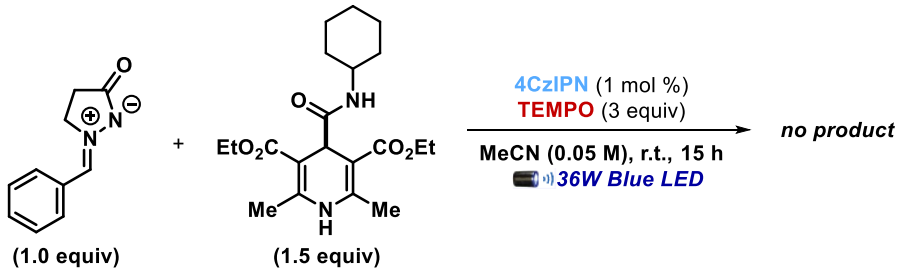


Figure S4. Cyclic voltammogram of **2a** [0.5 mM] in [0.1 M] $TBAPF_6$ in ACN. Scan rate 100 $mV.s^{-1}$. Eox ($1a^{\cdot+}$/1a) = +1.21 V.

Trapping experiment

Experimental Procedure: The radical-trapping experiment was carried out using TEMPO (2,2,6,6-Tetramethyl-1-piperidinyloxy) as radical scavenger. The starting material **1a** (0.15 mmol, 1.0 equiv), **2a** (0.22 mmol, 1.5 equiv), the photocatalyst 4CzIPN (1 mol %) and TEMPO (3.0 equiv) were dissolved in 3.0 mL of MeCN in a dried Schlenk tube equipped with a stir bar. The Schlenk tube was sealed with PTFE/silicon septum and connected to a vacuum line and the solution was degassed 3 times via a freeze-pump-thaw procedure. The resulting solution was stirred for 15 h at ~5 cm from the irradiation source (a 34 W Kessil H150 blue LED lamp).



Results: After the reaction time, the product **3** could not be noticed on the TLC plate. An aliquot was removed from the crude reaction and a sample was prepared in 1 % HCOOH/ MeOH and analyzed by mass spectrometry using an ACQUITY UPC^2-MS apparatus through direct infusion.

The MS full scan experiment indicated the presence of the radical scavenger and the starting material **1a** as showed in ***Figure S5***. Additionally, the peak at *m/z* 283.1702 could be an evidence of the trapping of the carbamoyl radical by **TEMPO**. The peak at *m/z* 332.1838 is associated with the direct addition of the radical scavenger to the azomethine imine, since the mismatch of the redox potentials of the iminium ion and the photocatalyst do not supports the formation of the reduced azomethine imine, as discussed for the mechanism proposals. Besides these peaks, other intermediates were evidenced as showed in the ***Figure S5***.

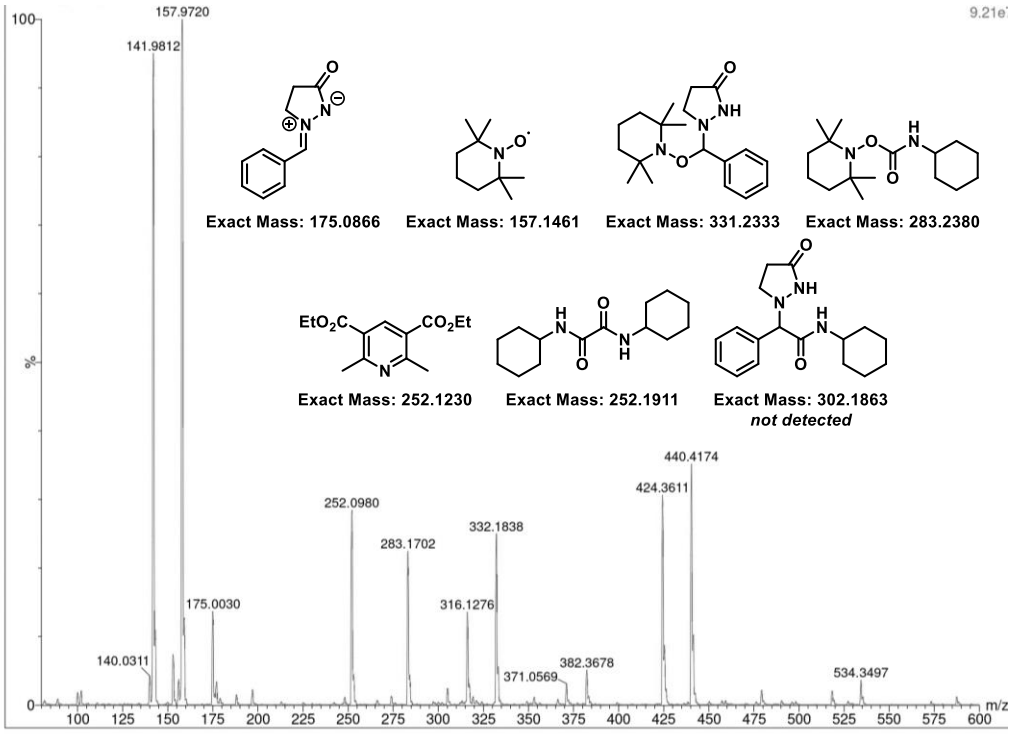


Figure S5. MS full scan experiment via direct infusion of the reaction crude. The exact mass of compounds are reported as the $[M+H]^+$ adduct.

UV-Vis Spectra

The UV/Vis absorption spectroscopy was recorded at room temperature with a 10 mm quartz cuvette.

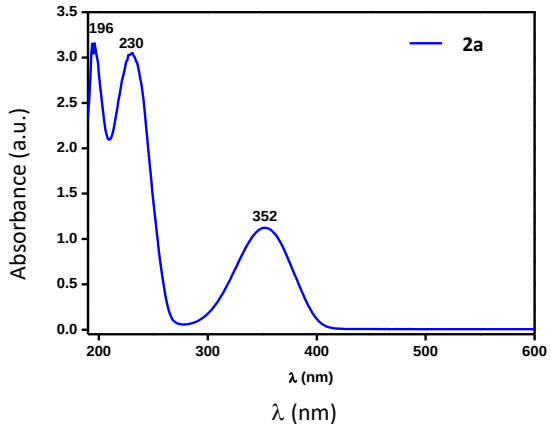


*Figure S6. Absorption spectra of a solution of **2a** (MeCN, 0.9 uM).*

The UV-Vis spectra of the cyclohexyl amine-derived dihydropyridine **2a** showed the absorption maximum at 352 nm. This value ruled out the possibility of occurring a direct excitation under the blue LED

irradiation source (λ = 456 nm) employed in this study. At its wavelength, the only active specie is the photocatalyst, which exhibits absorption at 507 nm.[11]

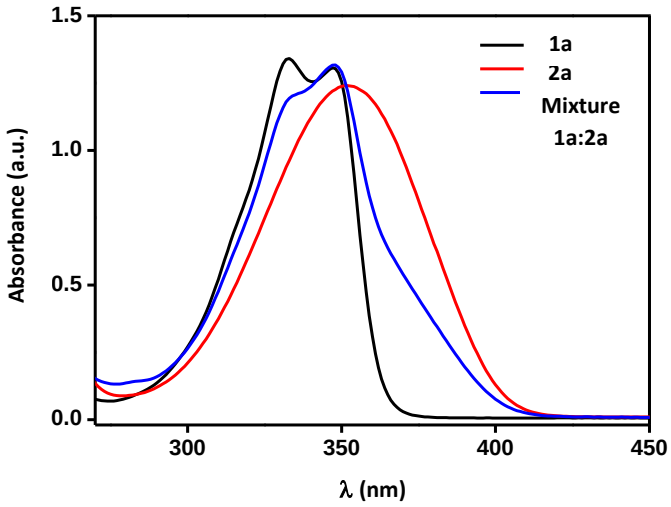


*Figure S7. UV-Vis spectra of azomethine **1a** (black line, 0.050 M in MeCN), 4-carbamoyl-1,4-dihydropyridines **2a** (red line, 0.050 M in MeCN), and an equimolar mixture of **1a** and **2a** (blue line, 0.050 M in MeCN).*

The UV-Vis spectra of 1a, 2a, and of their equimolar combination ruled out a possible formation of an electron donor-acceptor (EDA) complex since no bathochromic shift could be noticed when the spectra of the equimolar mixture was recorded.

Fluorescence quenching experiments

Fluorescence measurements were acquired at room temperature using a RF-5301 PC Fluorescence Spectrophotometer with excitation slits open at 1.5 nm and emission slit open at 3 nm. Emission quenching was done using quartz cuvettes with argon-purged solvent (MeCN). All the prepared solutions were degassed and successively added to the cuvette using 2.5 mL gas tight syringe through a rubber septum fitted with an argon balloon.

[11] H. Uoyama, K. Goushi, K. Shizu, H. Nomura and C. Adachi, *Nature*, **2012**, *492*, 234 – 240.

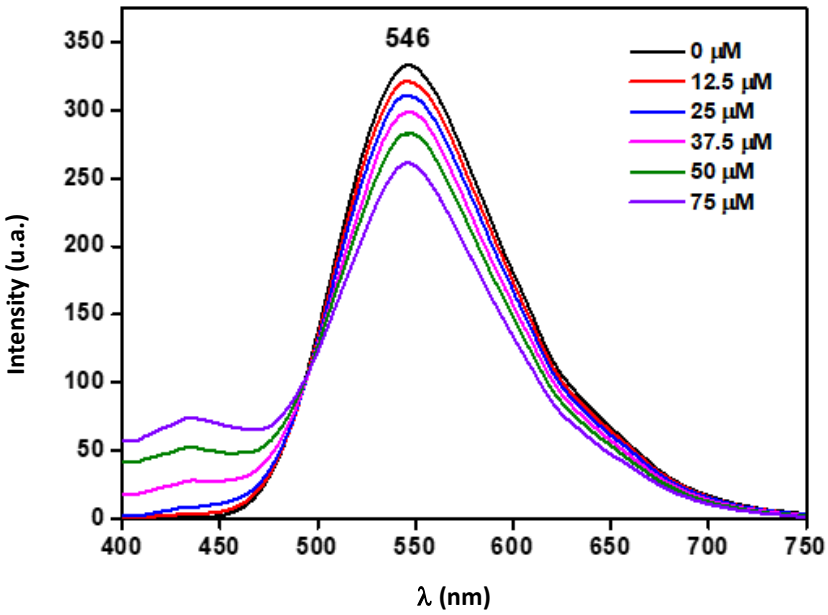


*Figure S8. Emission of the 4CZIPN solution (black line, MeCN) recorded in presence of increasing amounts of HEH **2a** as quencher with a λex = 410 nm.*

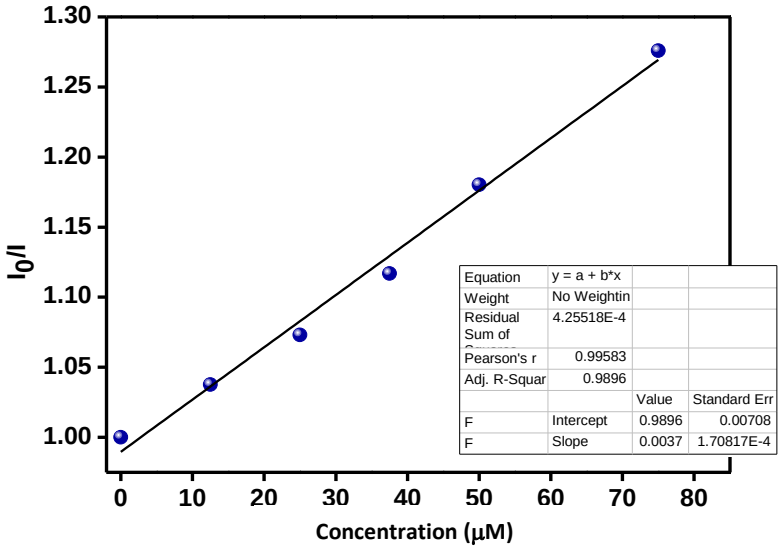


Figure S9. Stern-Volmer plot analysis derived from the data extracted from Figure S8.

The Stern–Volmer relationship

The data obtained from the Stern-Volmer analysis allowed the determination of the kinetic of the photophysical intermolecular deactivation process, following the Stern–Volmer relationship:

$$\frac{I0}{I} = 1 + KSV \text{ x } [Q]$$

$$\mathbf{KSV = K_q \times t_0} \qquad \text{[Eq. 1]}$$

Considering:

I_0 = intensity, or rate of catalyst fluorescence, without the quencher

I = = intensity, or rate of catalyst fluorescence, with the quencher

K_{sv} = Stern-Volmer constant

[Q] = concentration of the quencher

k_q= quencher rate coefficient

t_0= lifetime of the emissive excited state of the catalyst without the quencher

The quencher rate coefficient was determined from the Stern-Volmer equation (1) and using a lifetime of t_0 = 5.1 us for 4CZIPN.

$$\mathbf{K_q} = 7.2 \times 10^8 \text{ L.mol}^{-1}.\text{s}^{-1}$$

Control reactions

Control experiments were carried out in order to investigate the reactivity of the reaction components under photolytic conditions. Thus, the reactions were conducted under the optimized condition **a)** in the absence of the carbamoyl radical source and **b)** in the absence of azomethine imine as the trapper of the generated radical. The reaction crudes were analyzed by HRMS (ESI-QTOF).

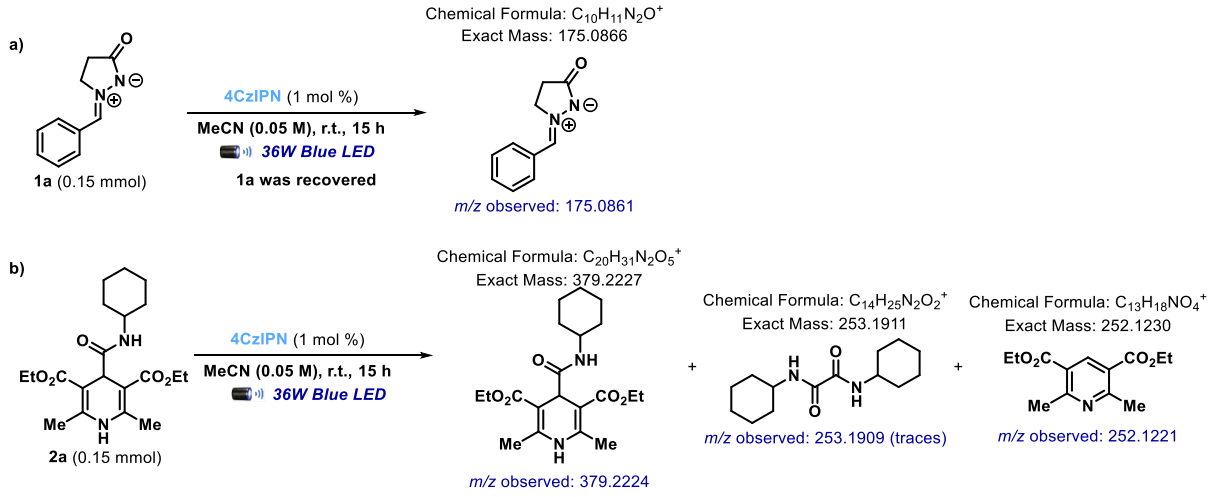
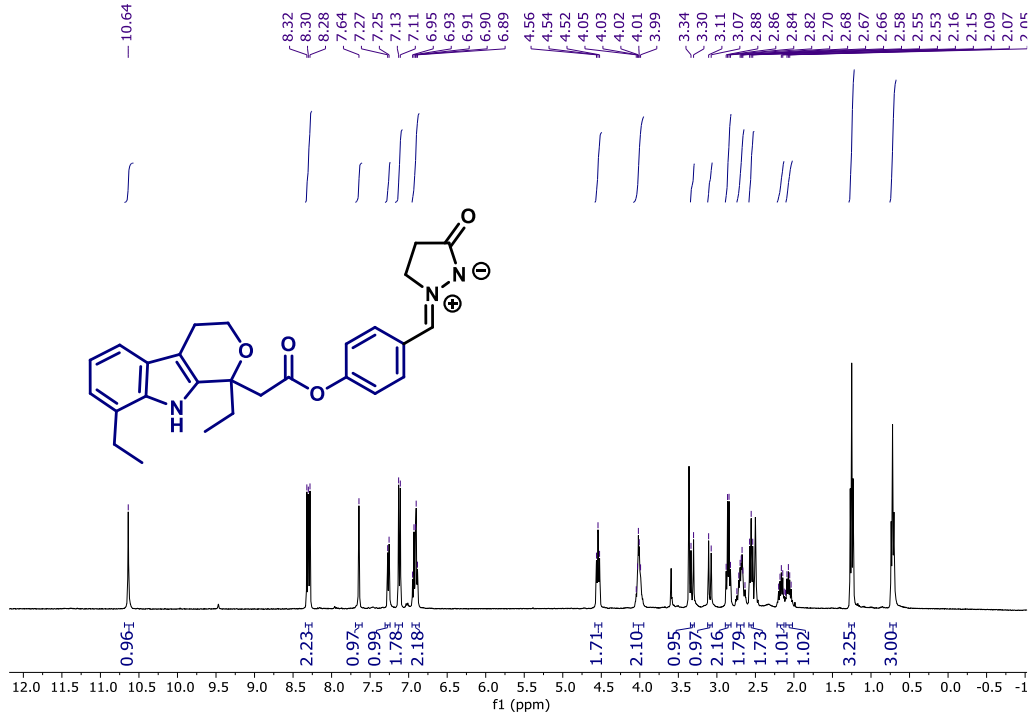
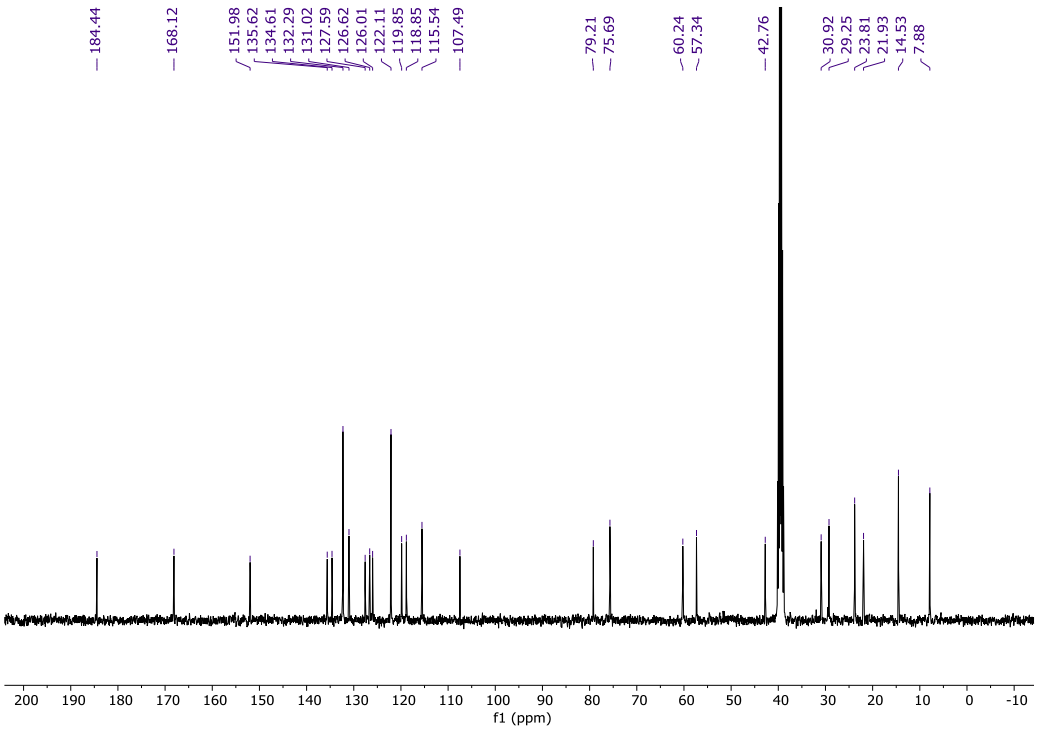


Figure S10. Control experiments to evaluate the reactivity of the isolated components under the optimized reaction condition.

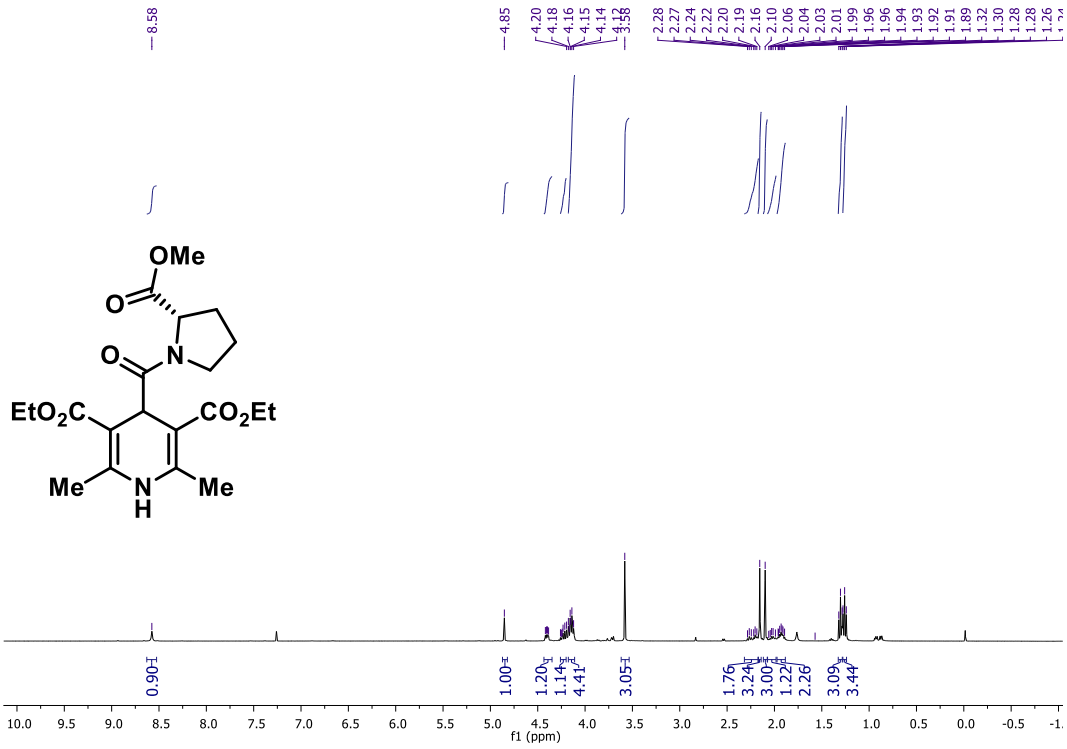
NMR Spectra



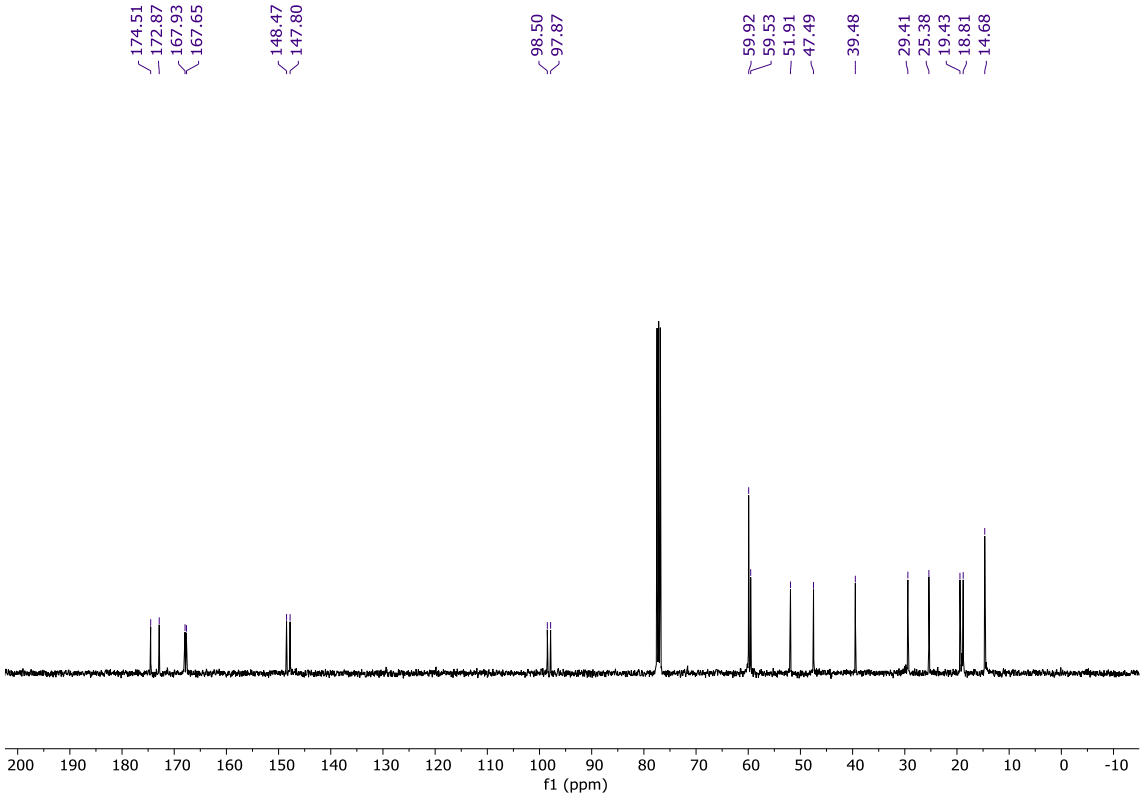
^{1}H NMR (DMSO-d6, 400 MHz) of 16'.



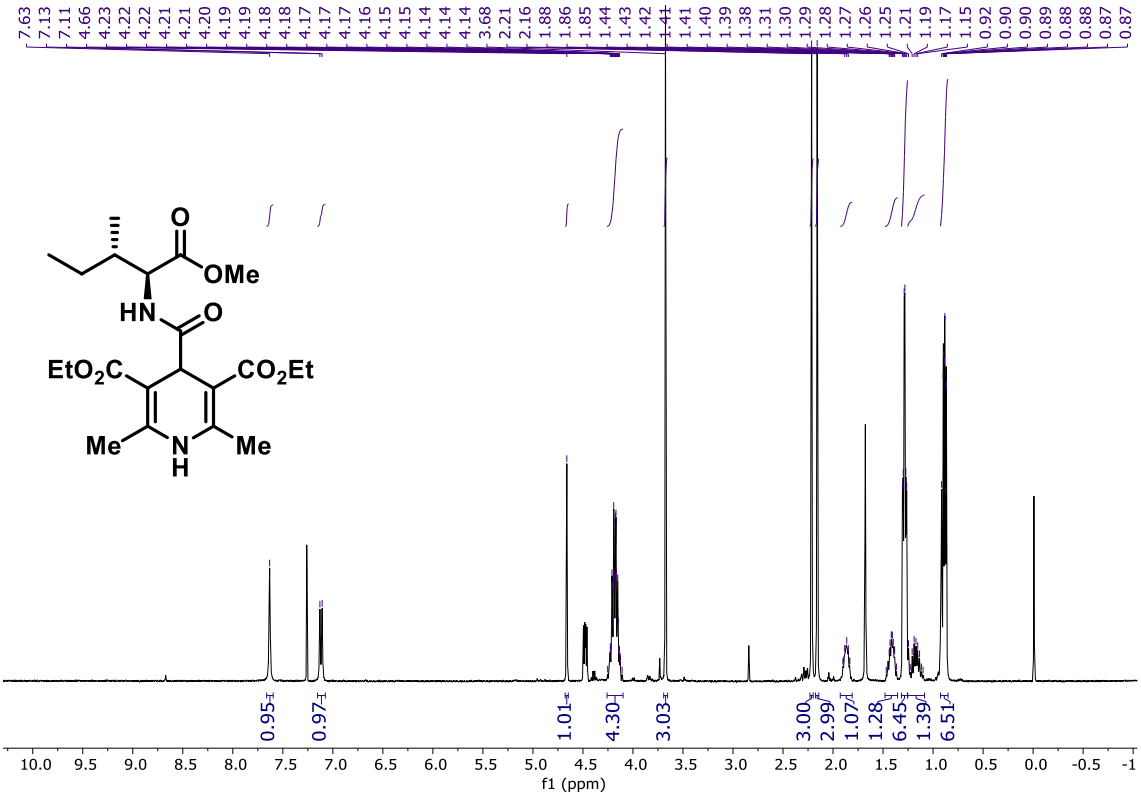
^{13}C NMR (DMSO-d6, 126 MHz) of 16'.



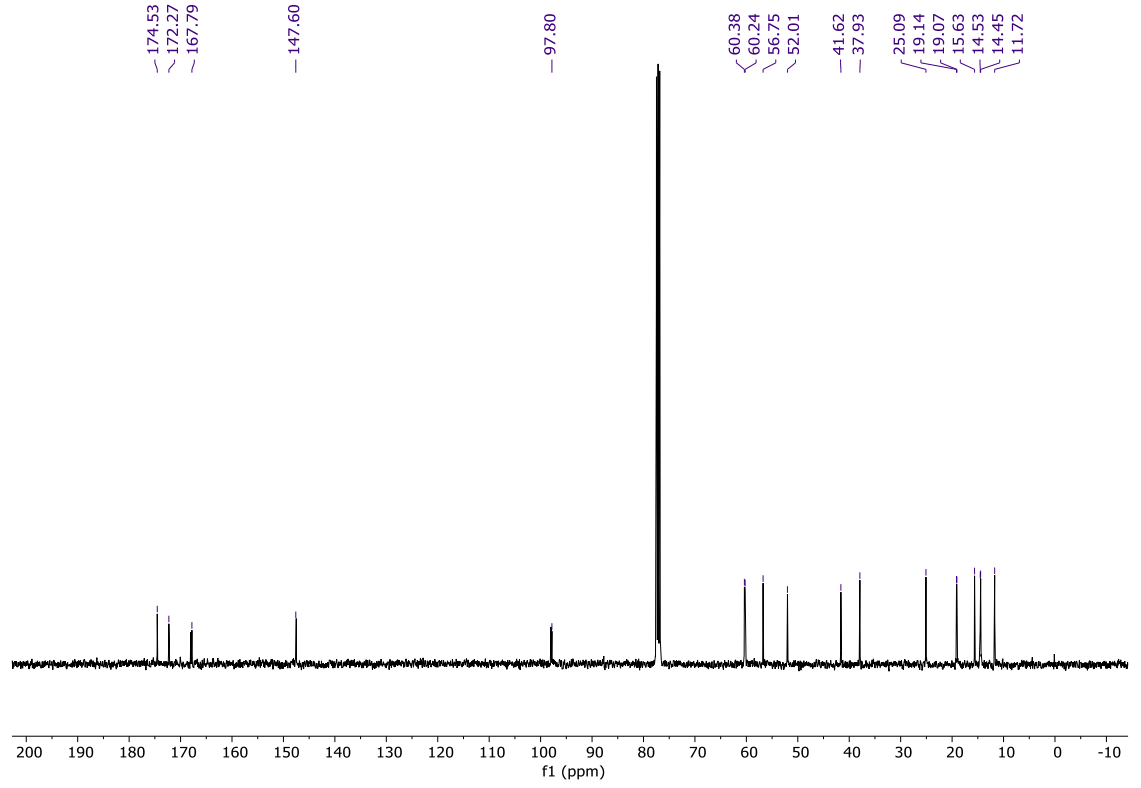
^{1}H NMR ($CDCl_3$, 400 MHz) of 22'.



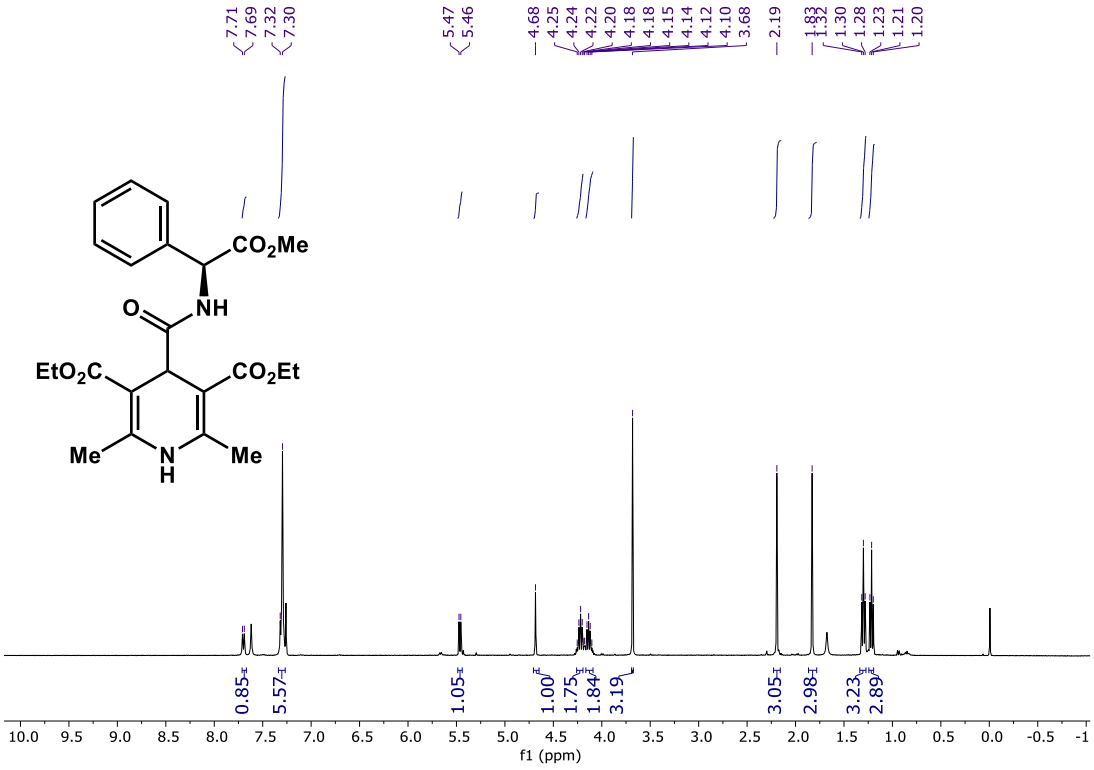
^{13}C NMR ($CDCl_3$, 126 MHz) of 22'.



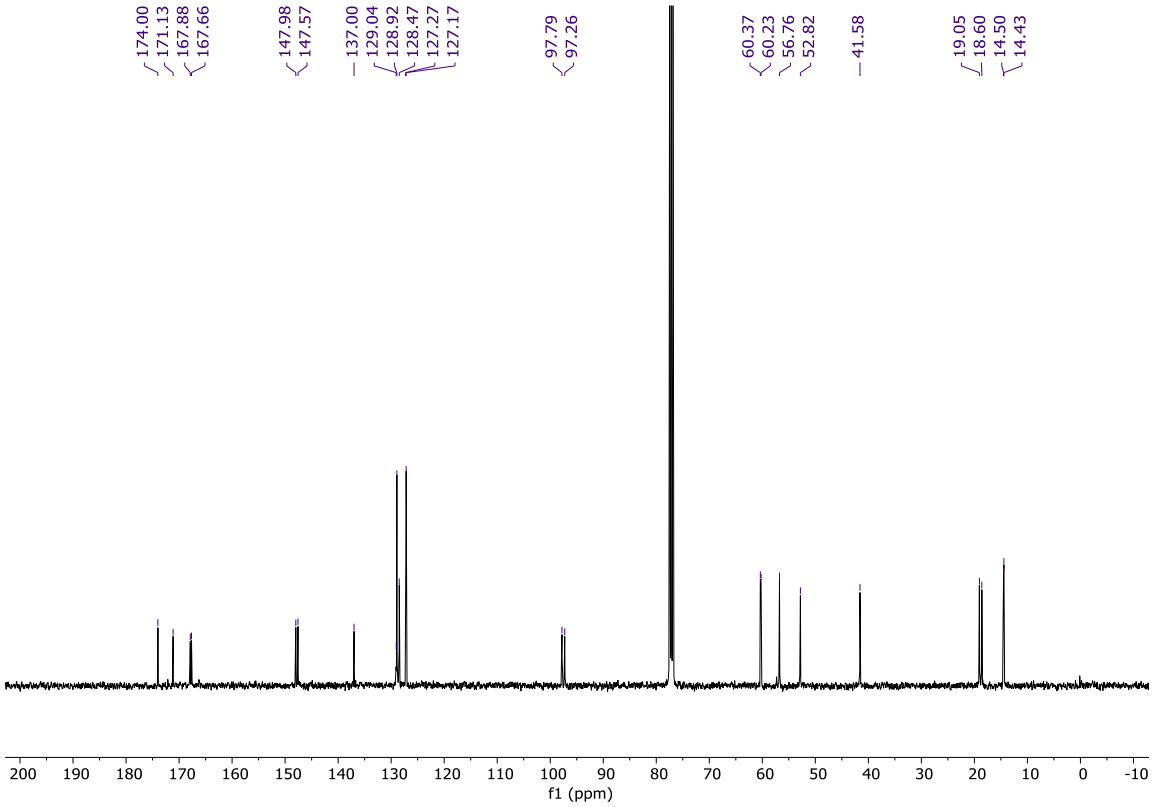
[1]H NMR (CDCl3, 400 MHz) of 25'.



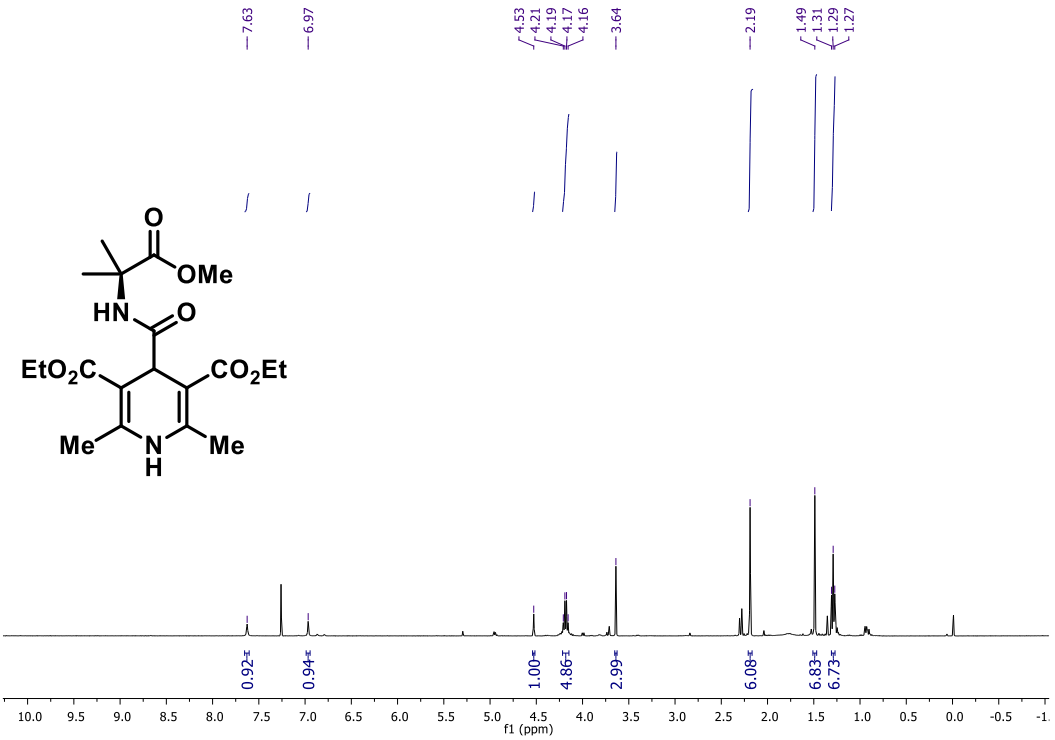
[13]C NMR (CDCl3, 126 MHz) of 25'.



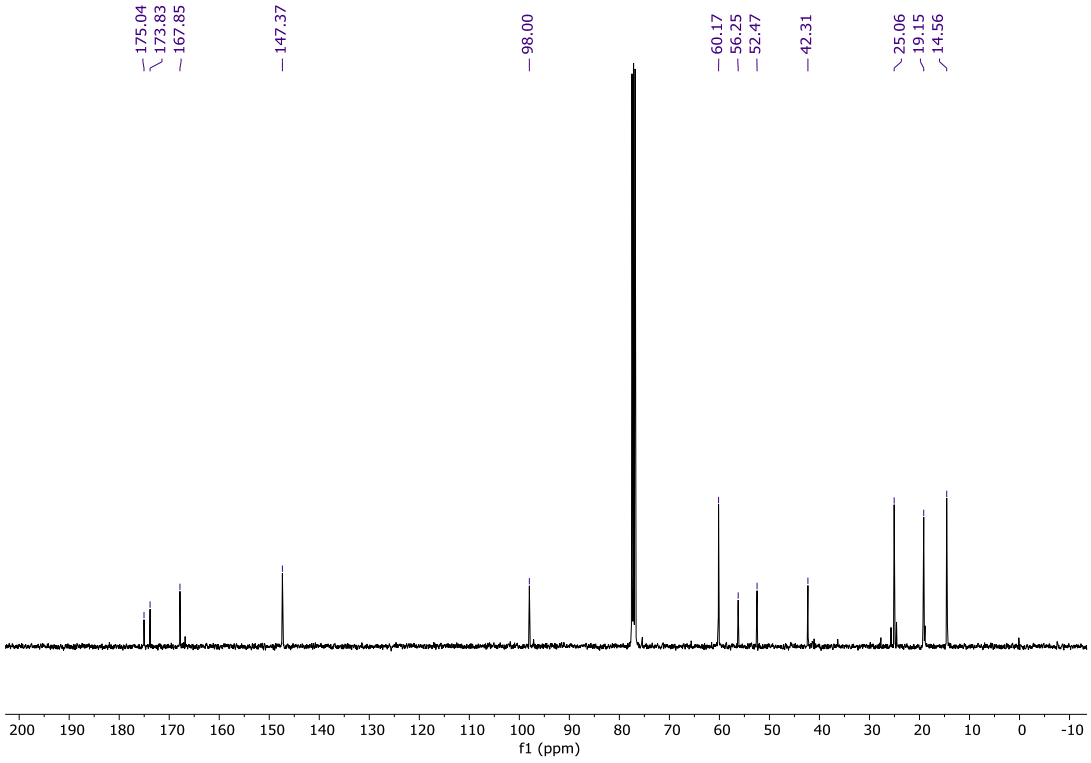
^{1}H NMR (CDCl3, 400 MHz) of 31'.



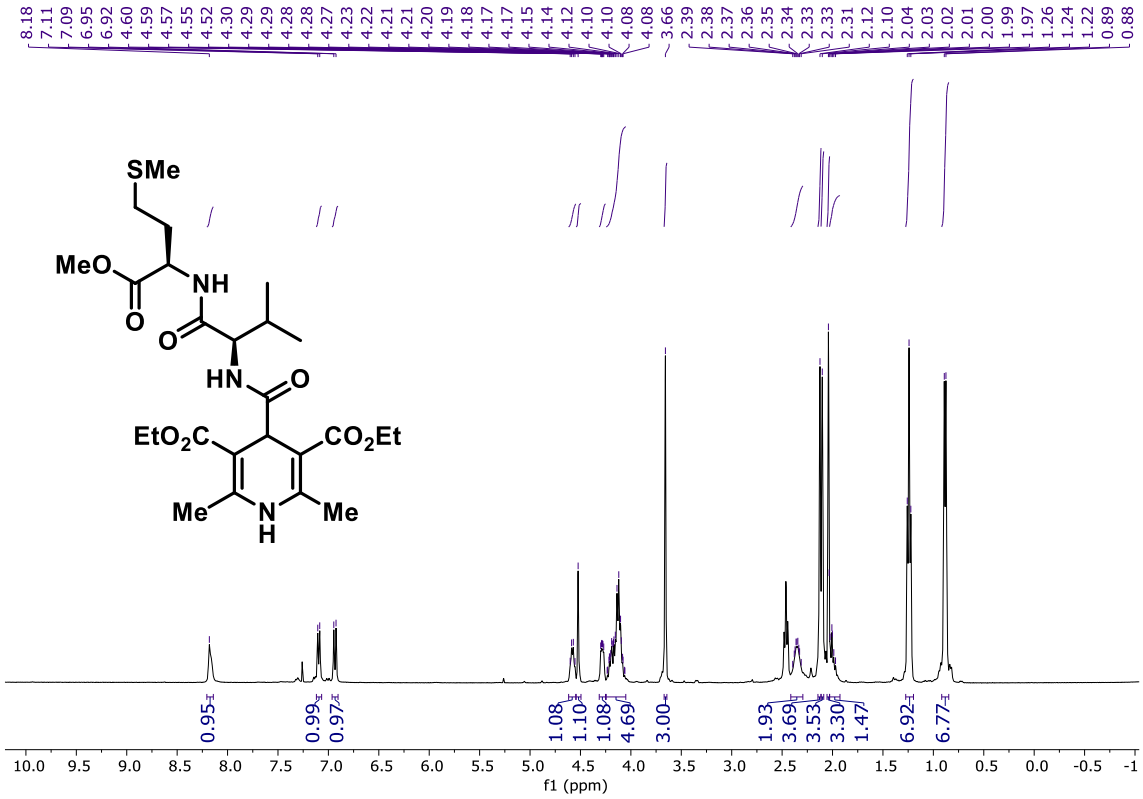
^{13}C NMR (CDCl3, 126 MHz) of 31'.



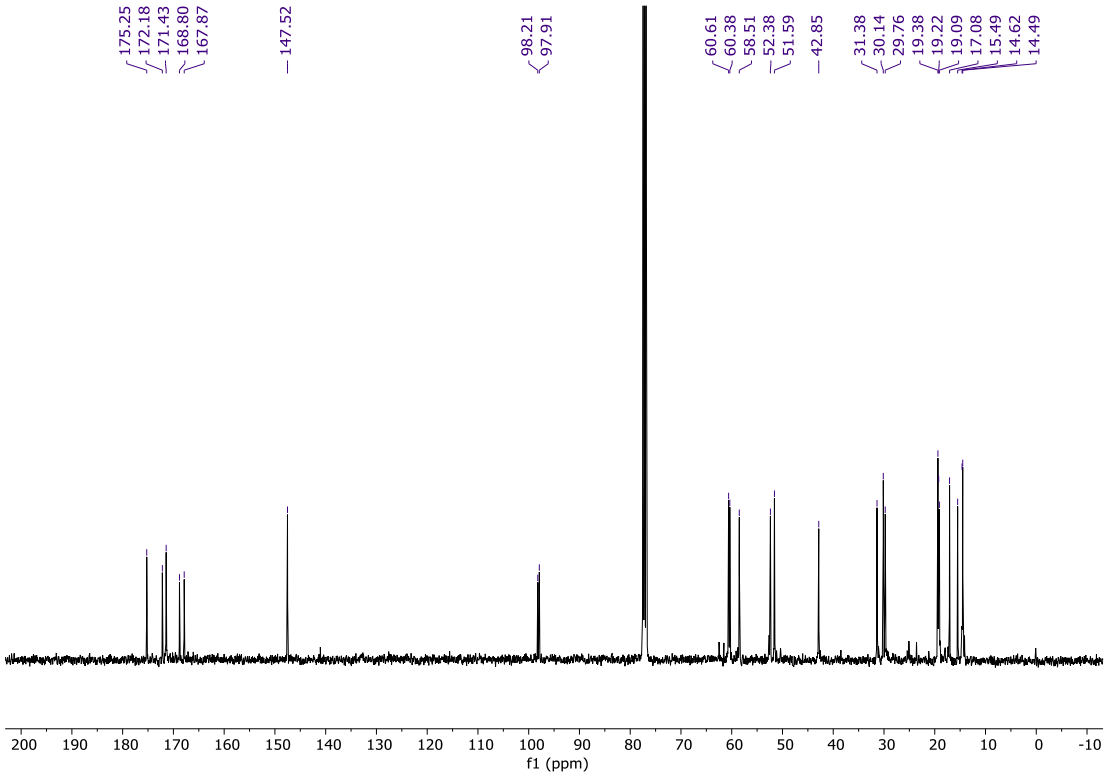
^{1}H NMR (CDCl3, 400 MHz) of 32'.



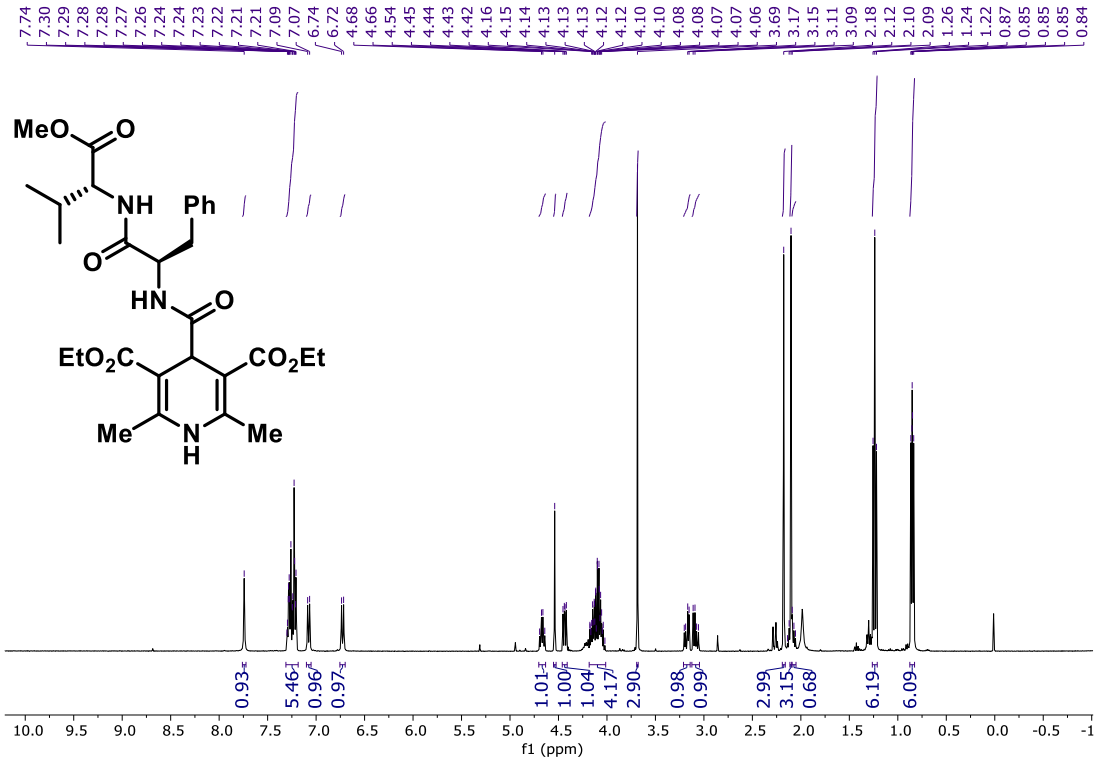
^{13}C NMR (CDCl3, 126 MHz) of 32'.



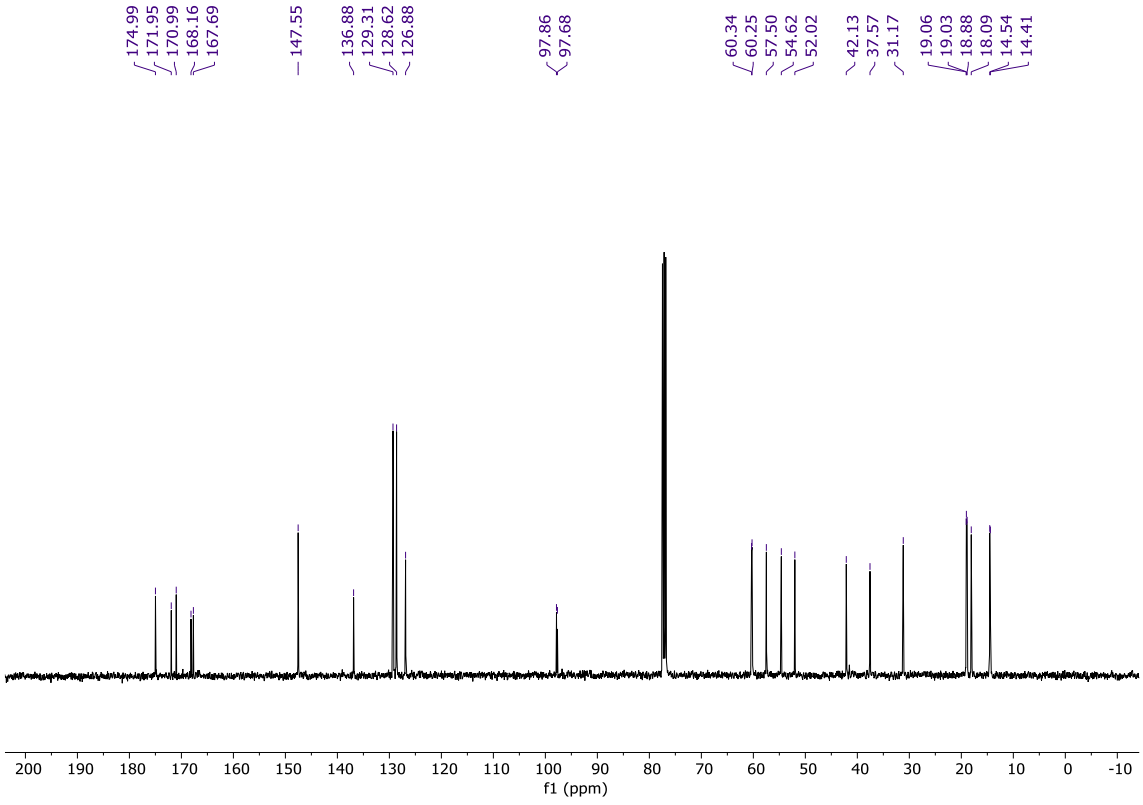
^{1}H NMR (CDCl3, 400 MHz) of 33'.



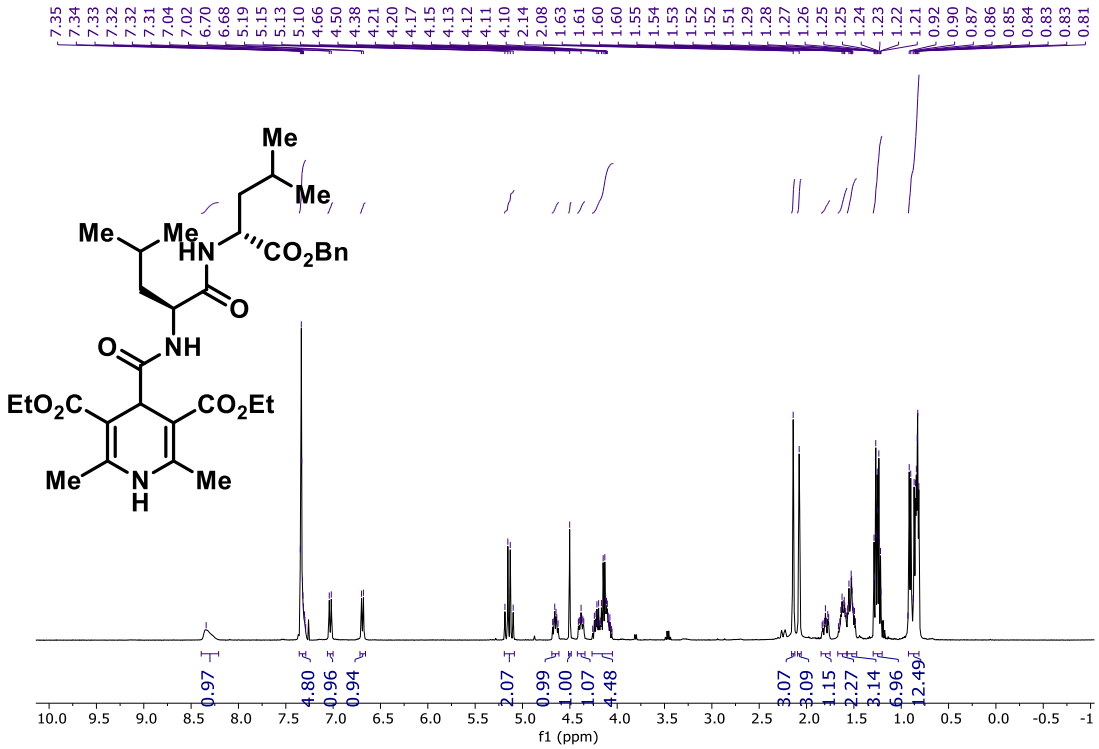
^{13}C NMR (CDCl3, 126 MHz) of 33'.



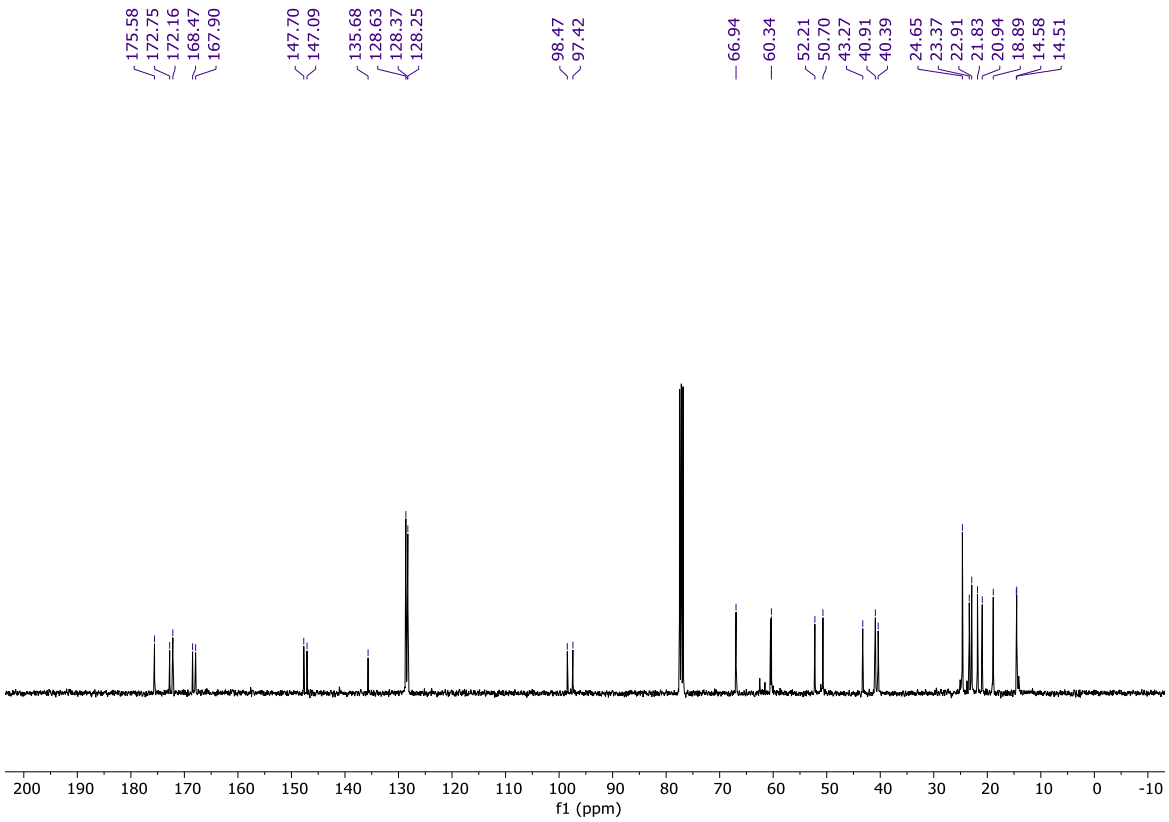
^{1}H NMR (CDCl3, 400 MHz) of 35'.



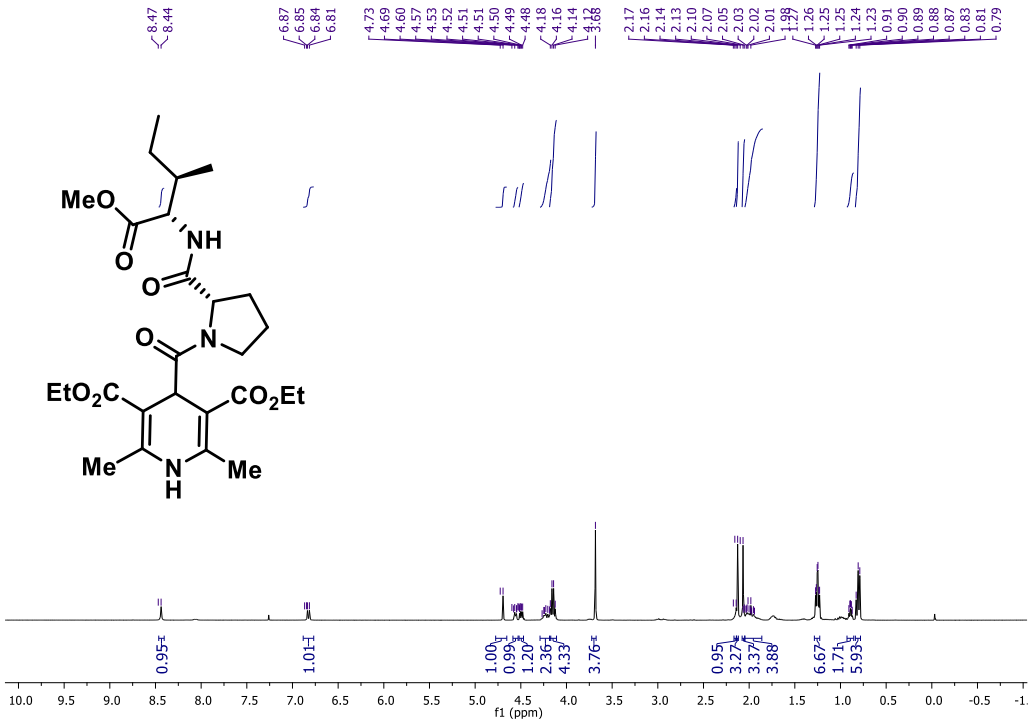
^{13}C NMR (CDCl3, 126 MHz) of 35'.



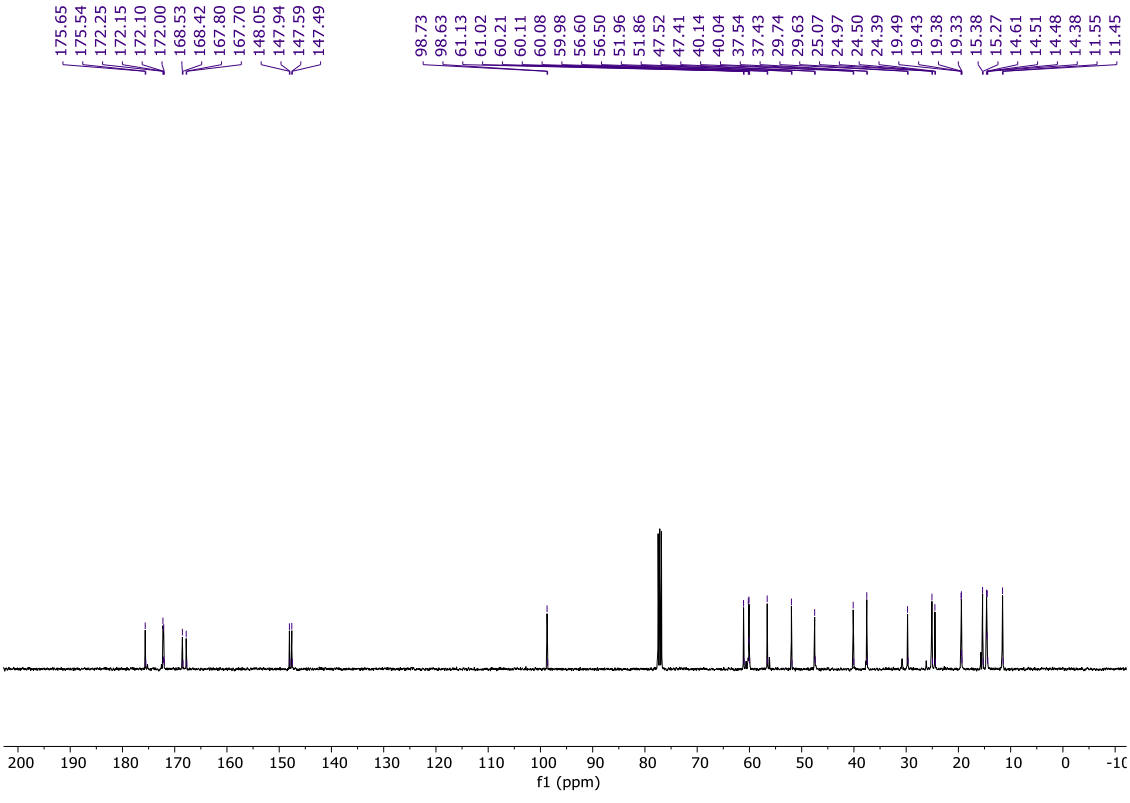
^{1}H NMR (CDCl3, 400 MHz) of 36'.



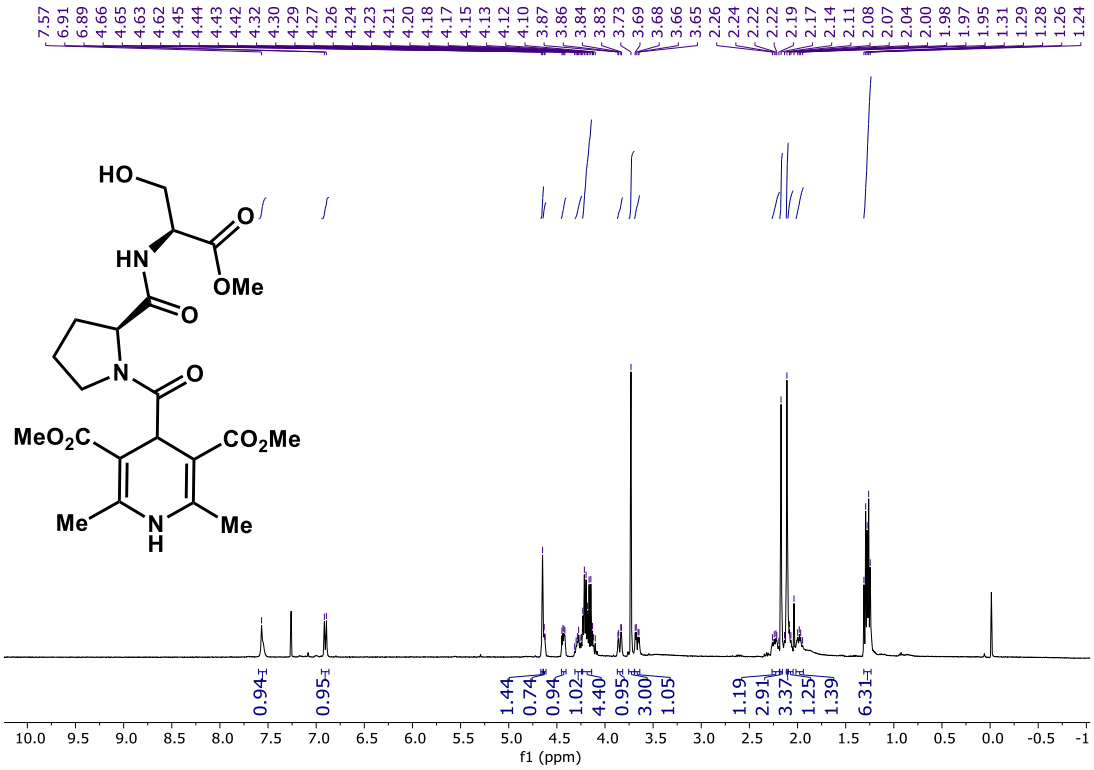
^{13}C NMR (CDCl3, 126 MHz) of 36'.



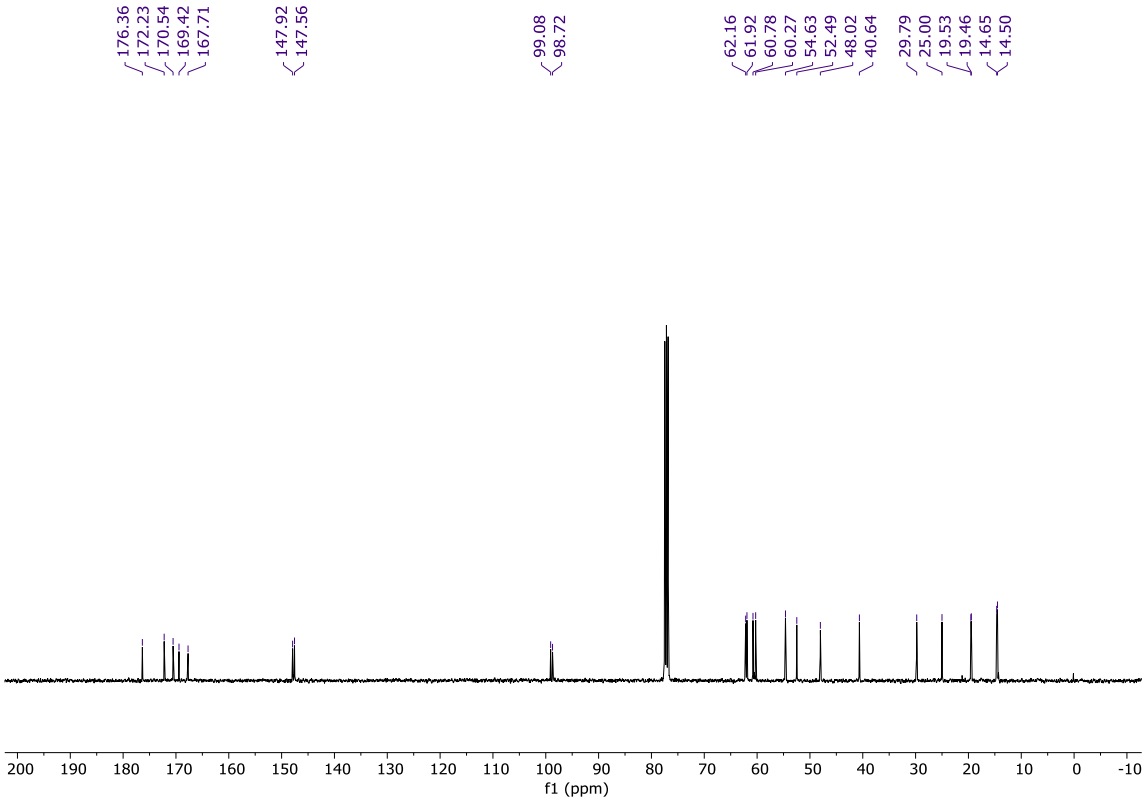
^{1}H NMR (CDCl3, 400 MHz) of 37'.



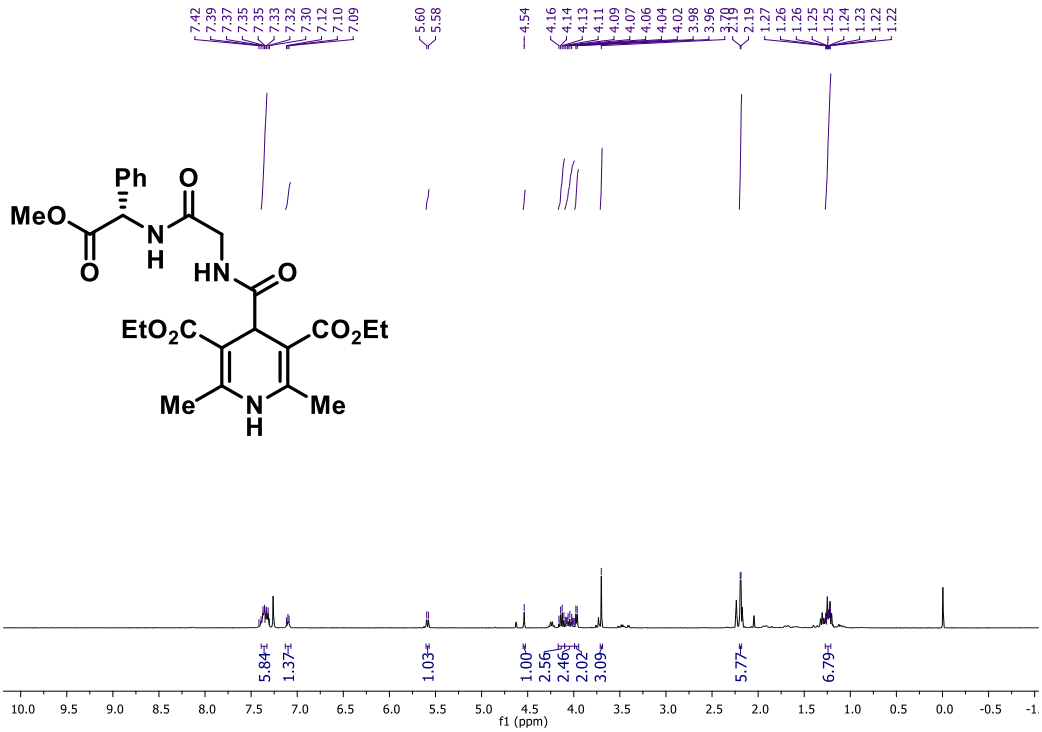
^{13}C NMR (CDCl3, 126 MHz) of 37'.



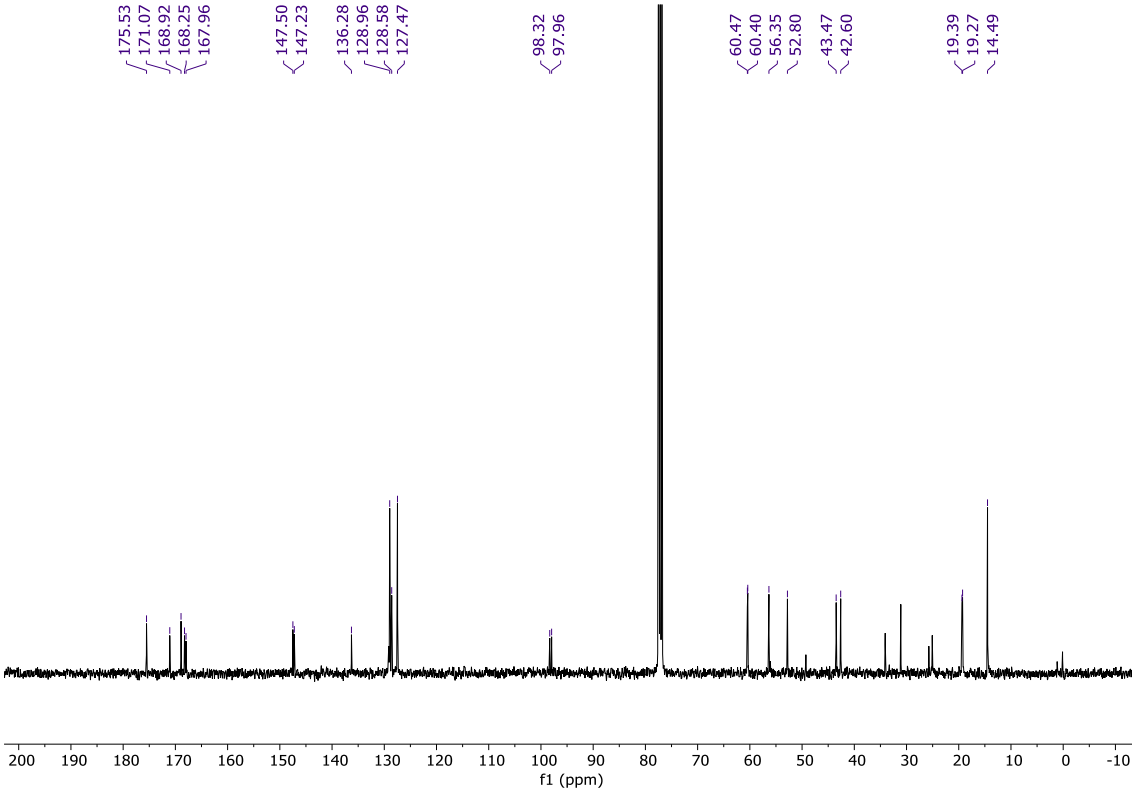
[1]H NMR (CDCl3, 400 MHz) of 38'.



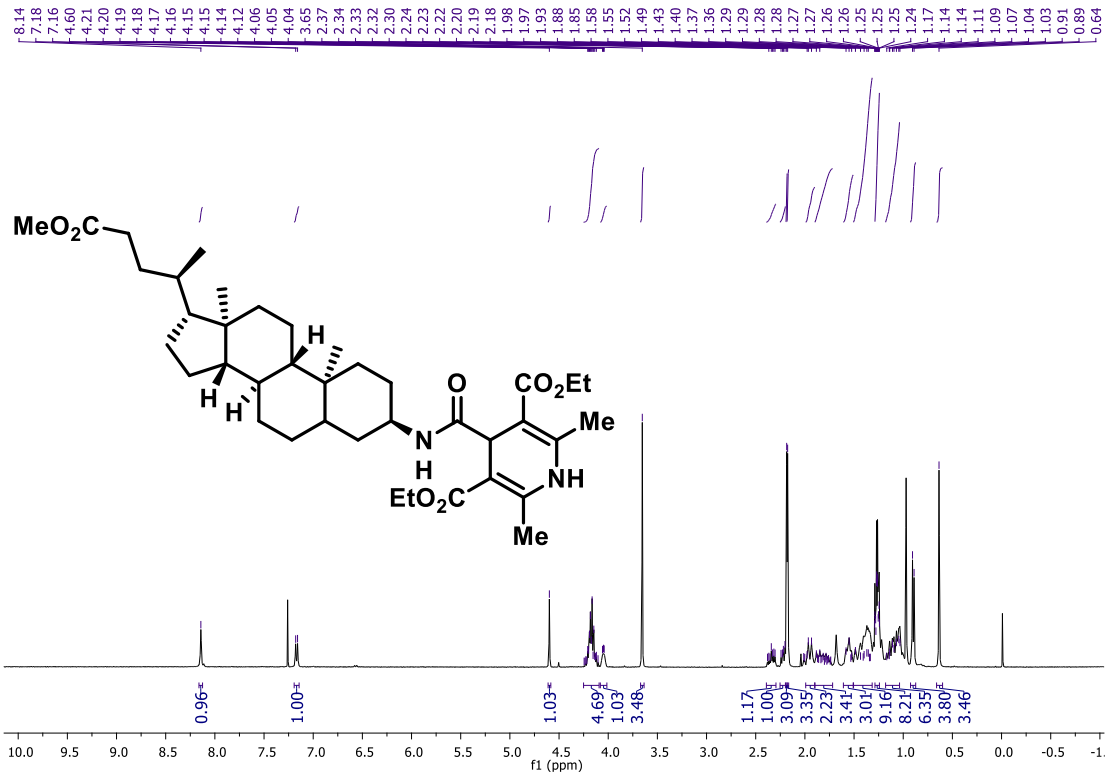
[13]C NMR (CDCl3, 126 MHz) of 38'.



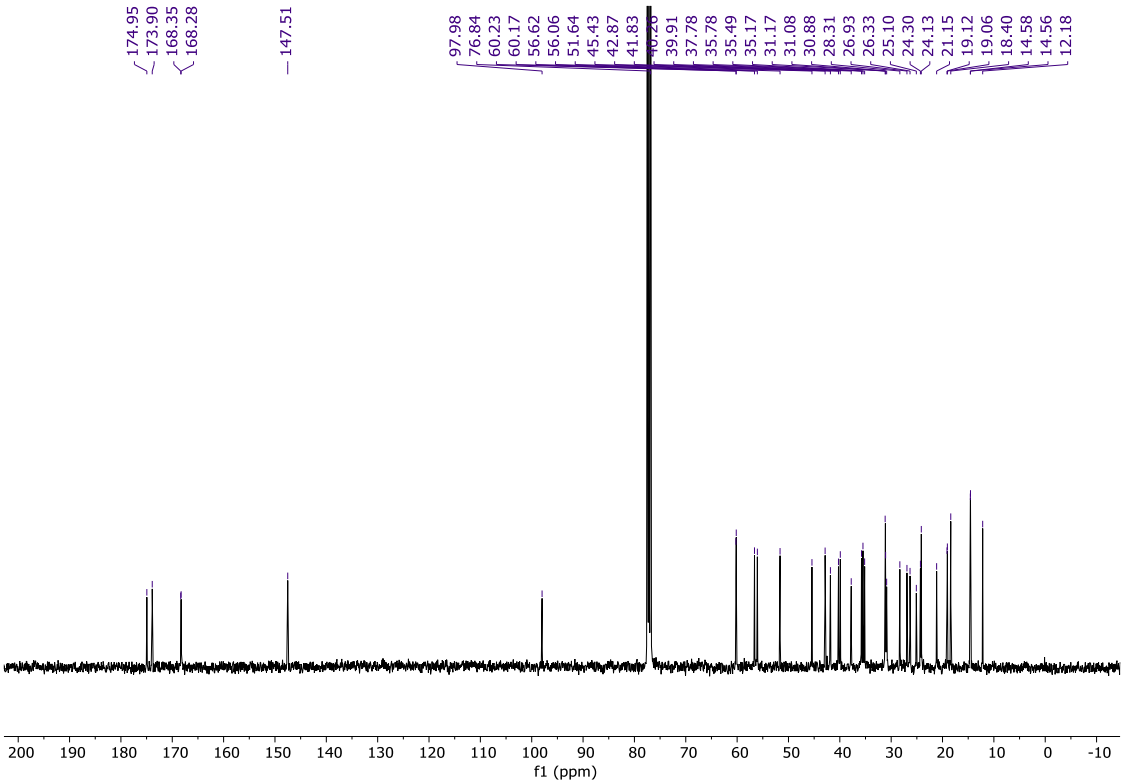
[1]H NMR (CDCl3, 400 MHz) of 39'.



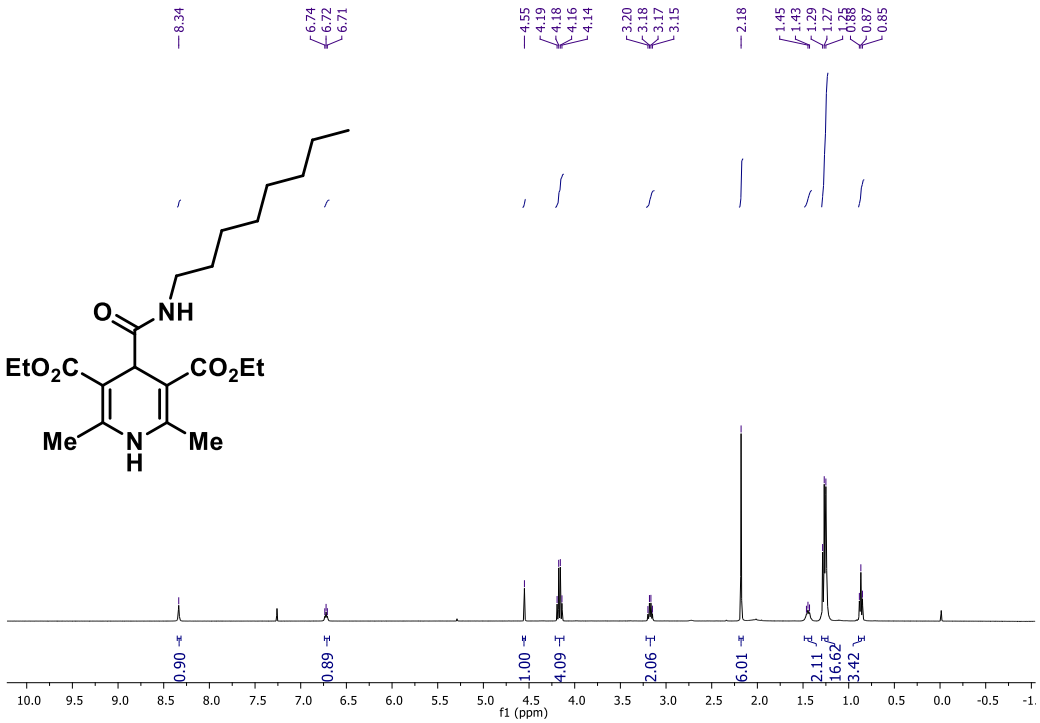
[13]C NMR (CDCl3, 126 MHz) of 39'.



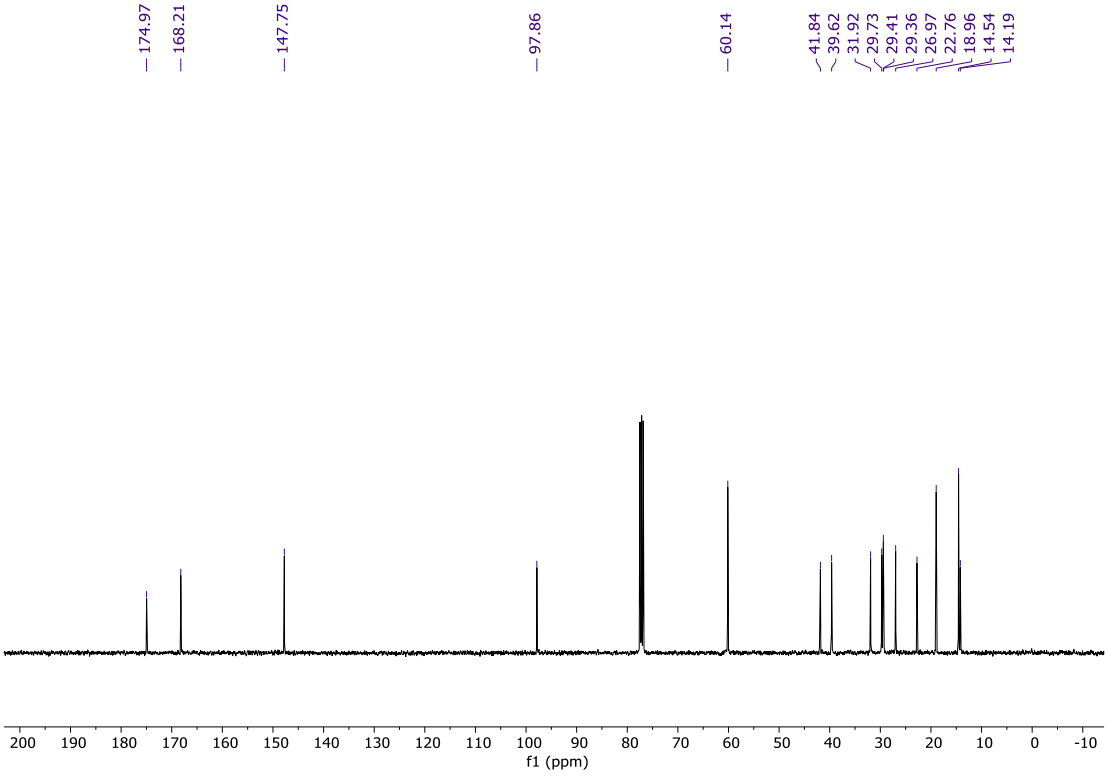
^{1}H NMR (CDCl3, 400 MHz) of 40'.



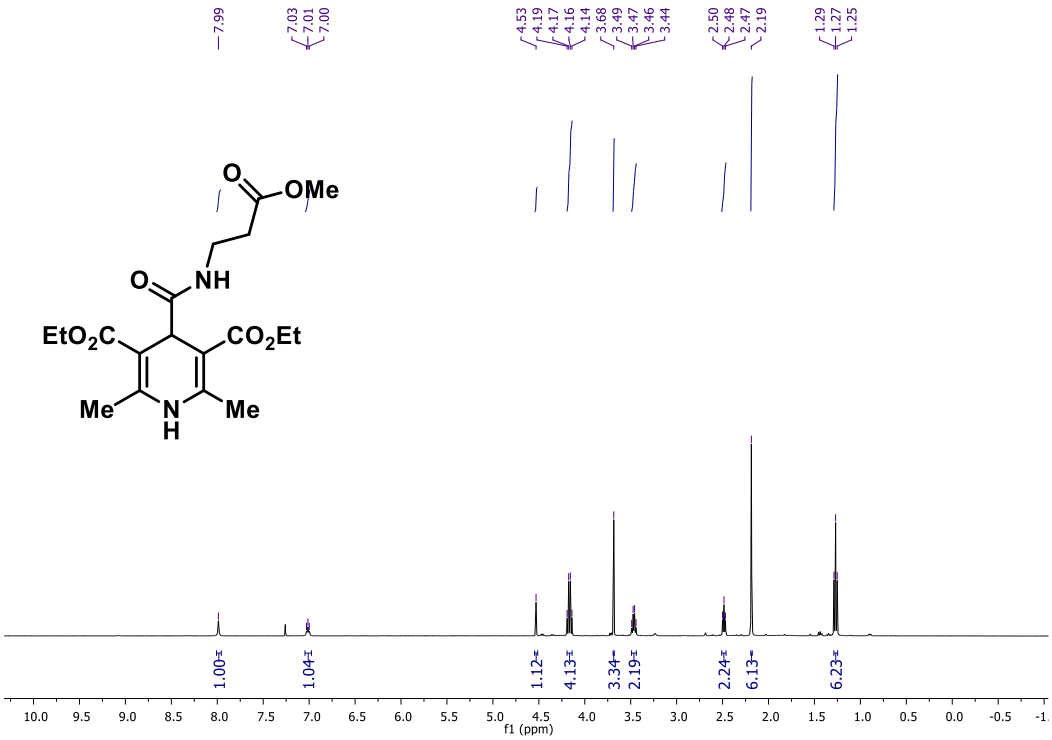
^{13}C NMR (CDCl3, 126 MHz) of 40'.



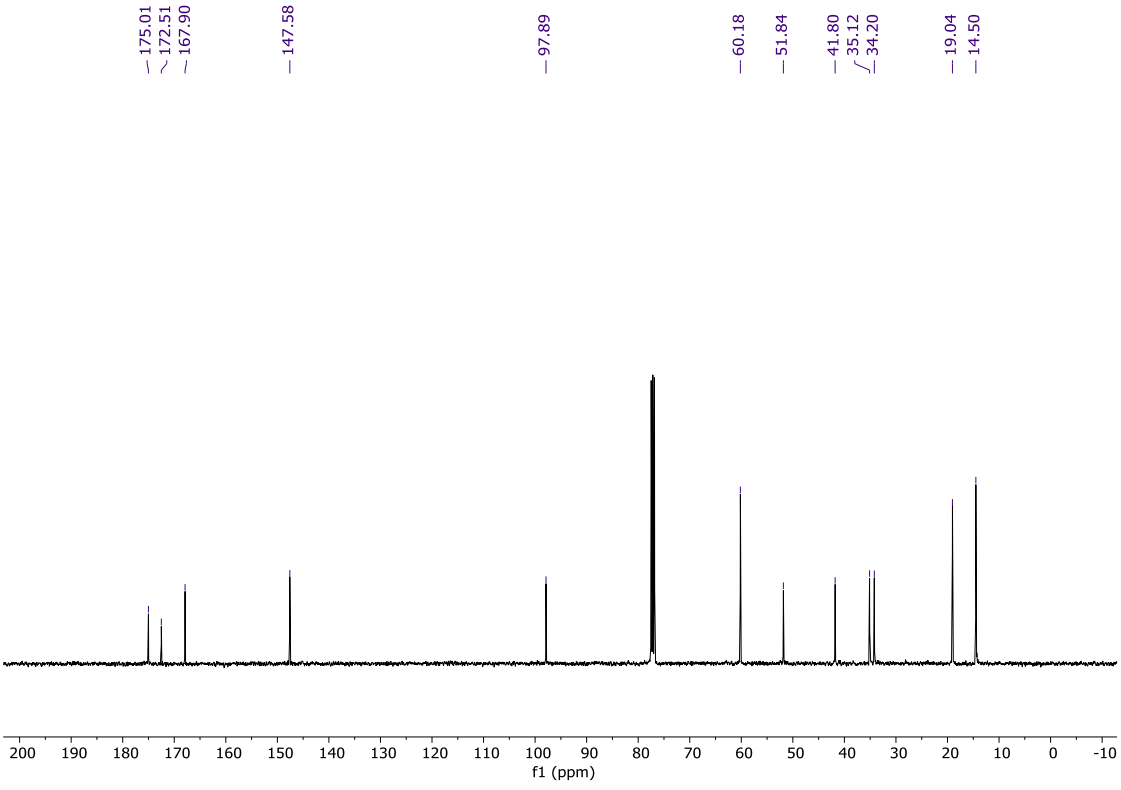
^{1}H NMR (CDCl3, 400 MHz) of 43'.



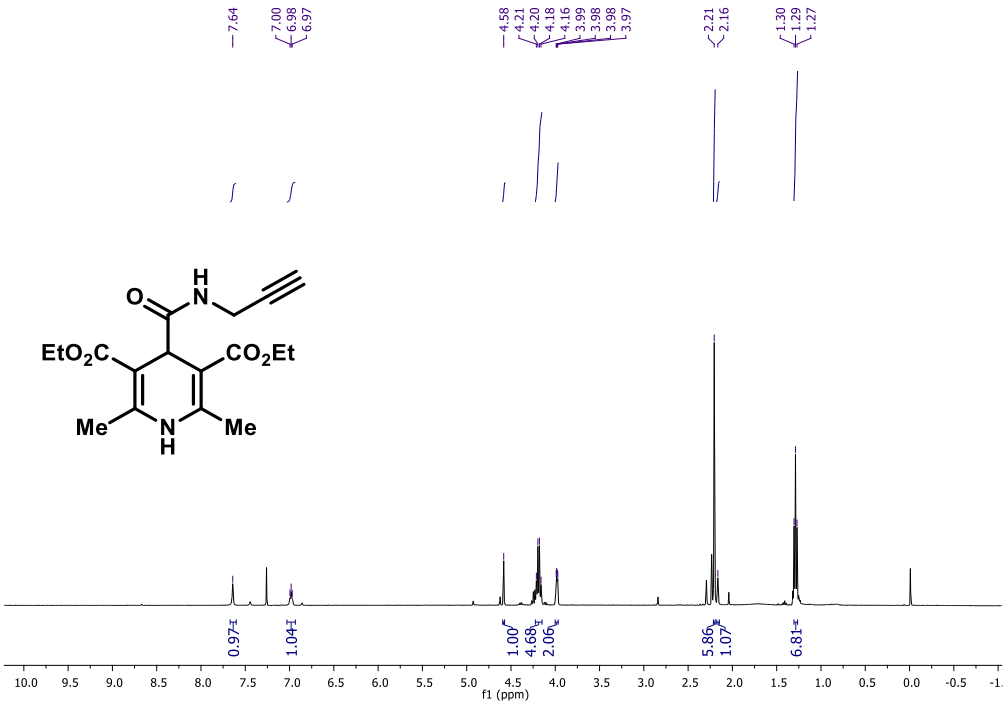
^{13}C NMR (CDCl3, 126 MHz) of 43'.



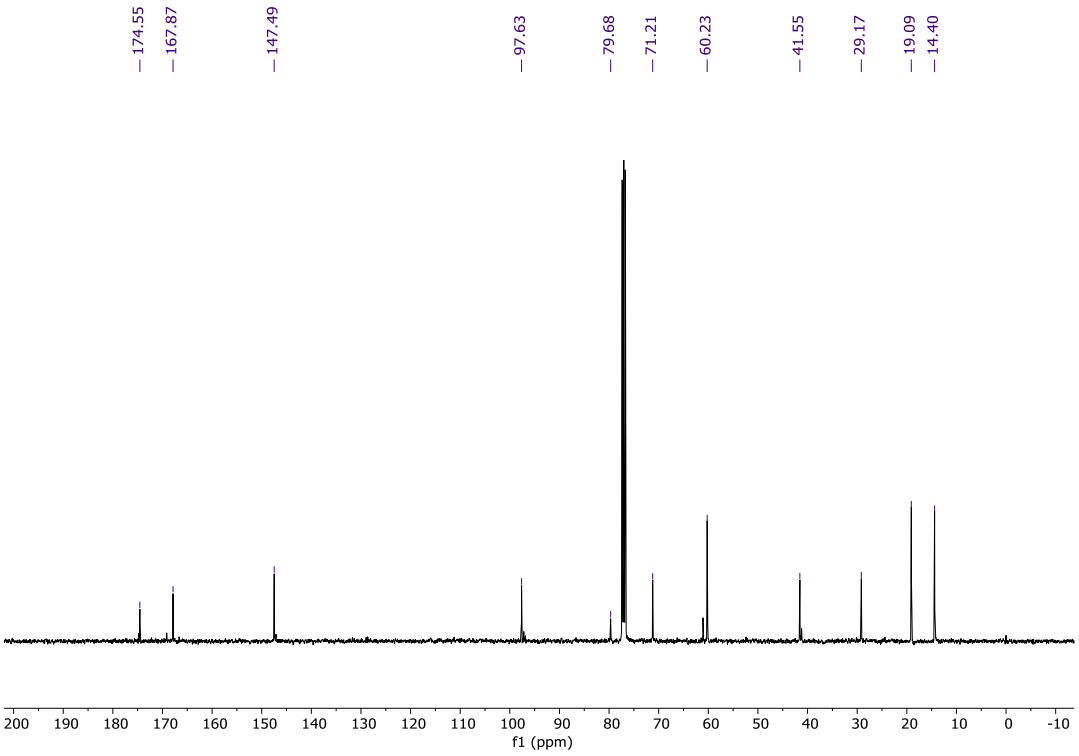
^{1}H NMR (CDCl3, 400 MHz) of 44'.



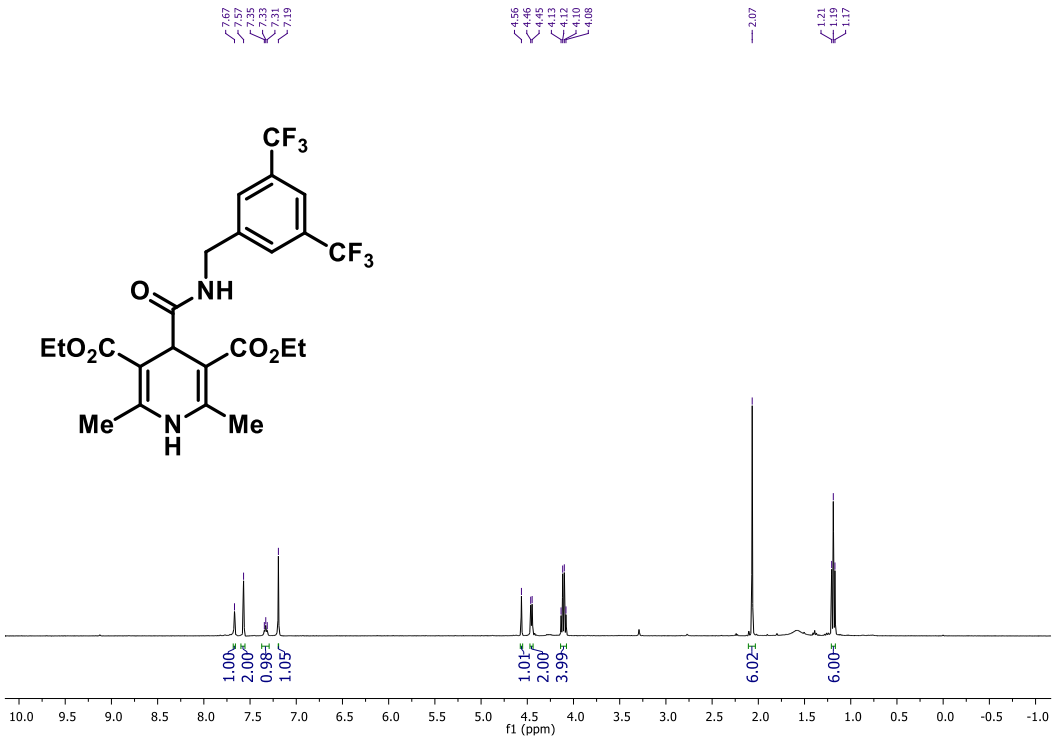
^{13}C NMR (CDCl3, 126 MHz) of 44'.



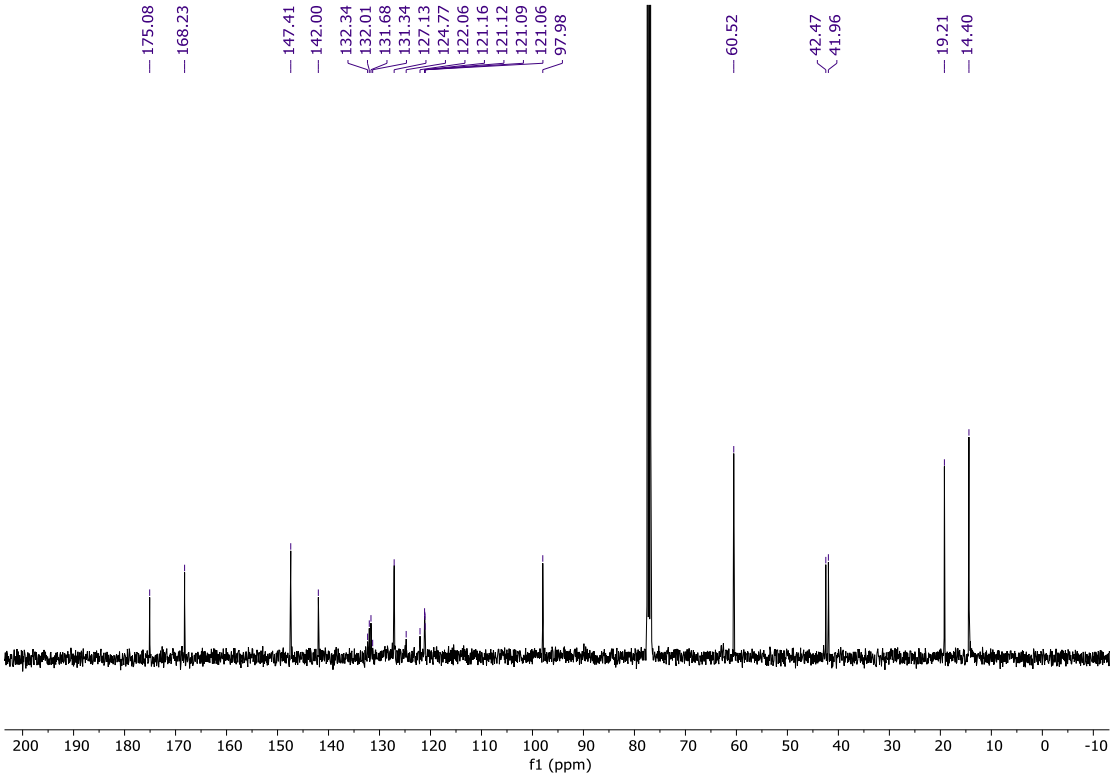
^{1}H NMR (CDCl3, 400 MHz) of 45'.



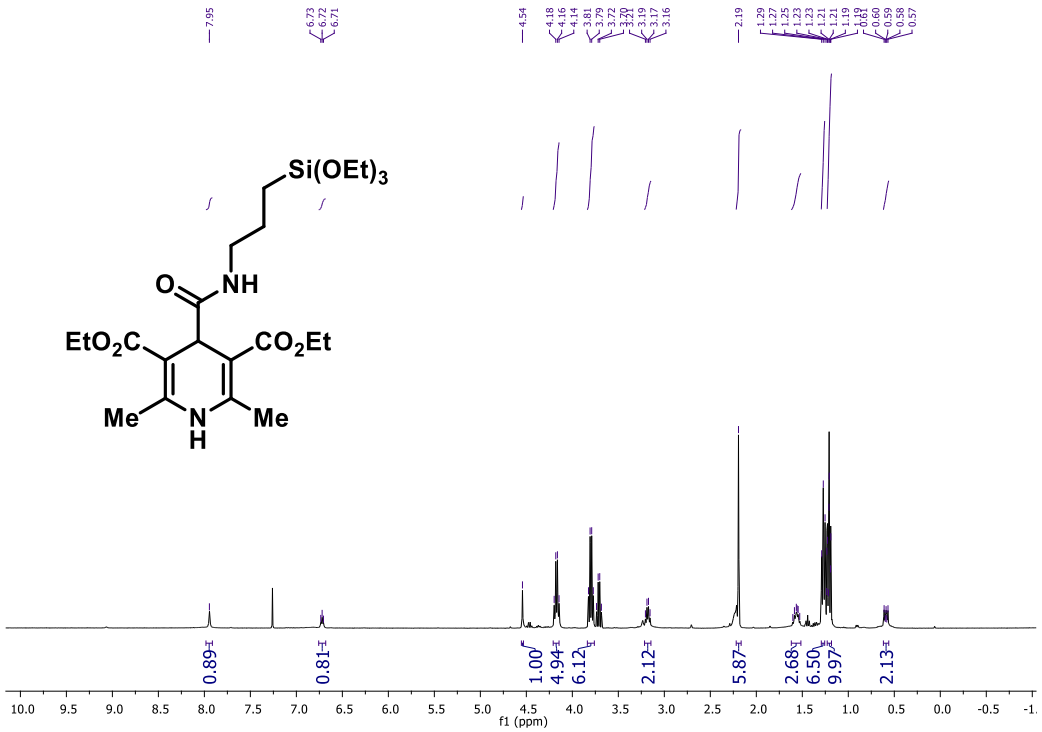
^{13}C NMR (CDCl3, 126 MHz) of 45'.



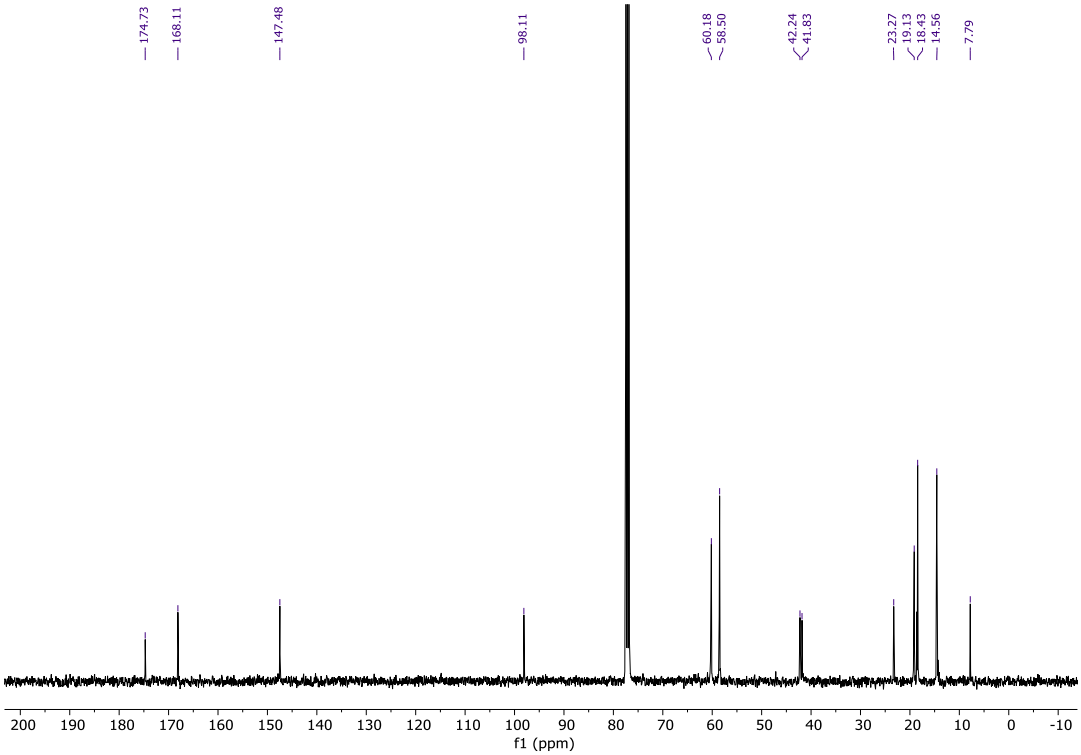
^{1}H NMR (CDCl3, 400 MHz) of 47'.



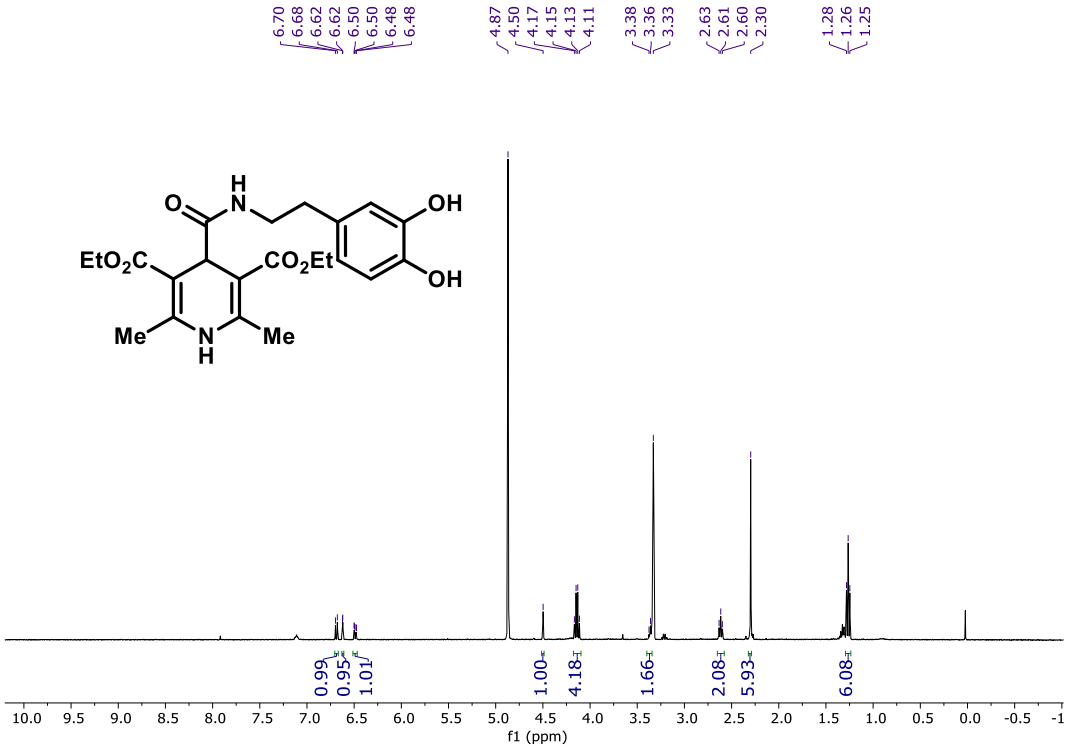
^{13}C NMR (CDCl3, 126 MHz) of 47'.



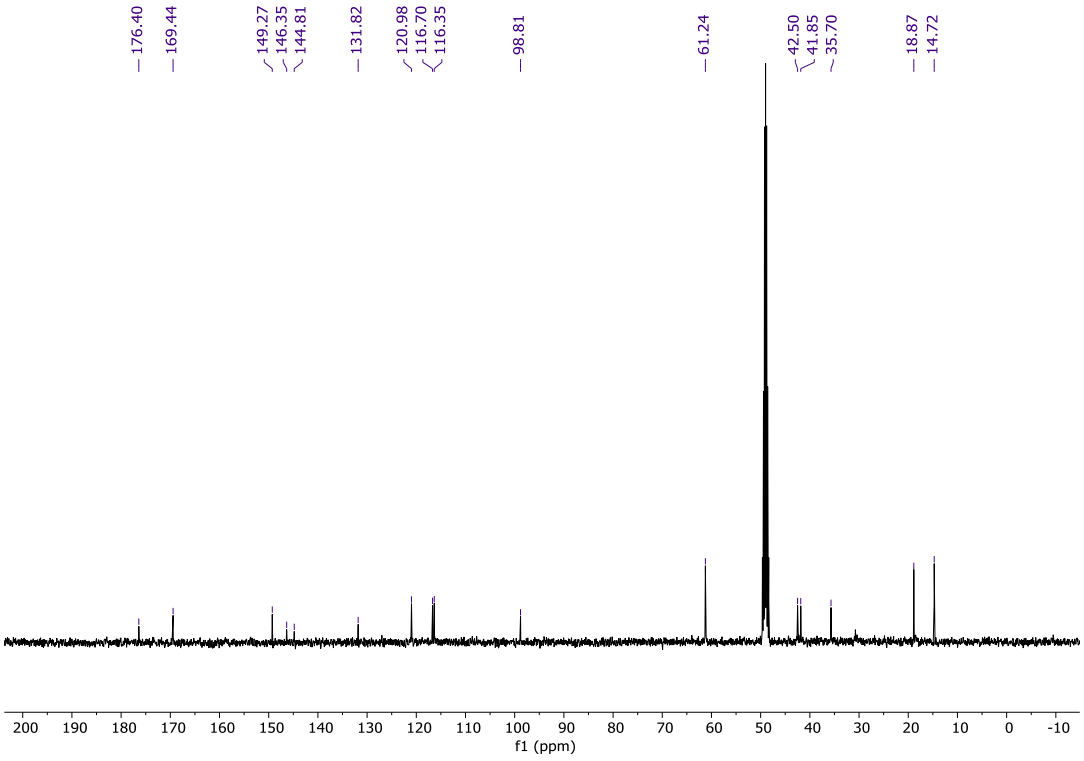
^{1}H NMR (CDCl3, 400 MHz) of 48'.



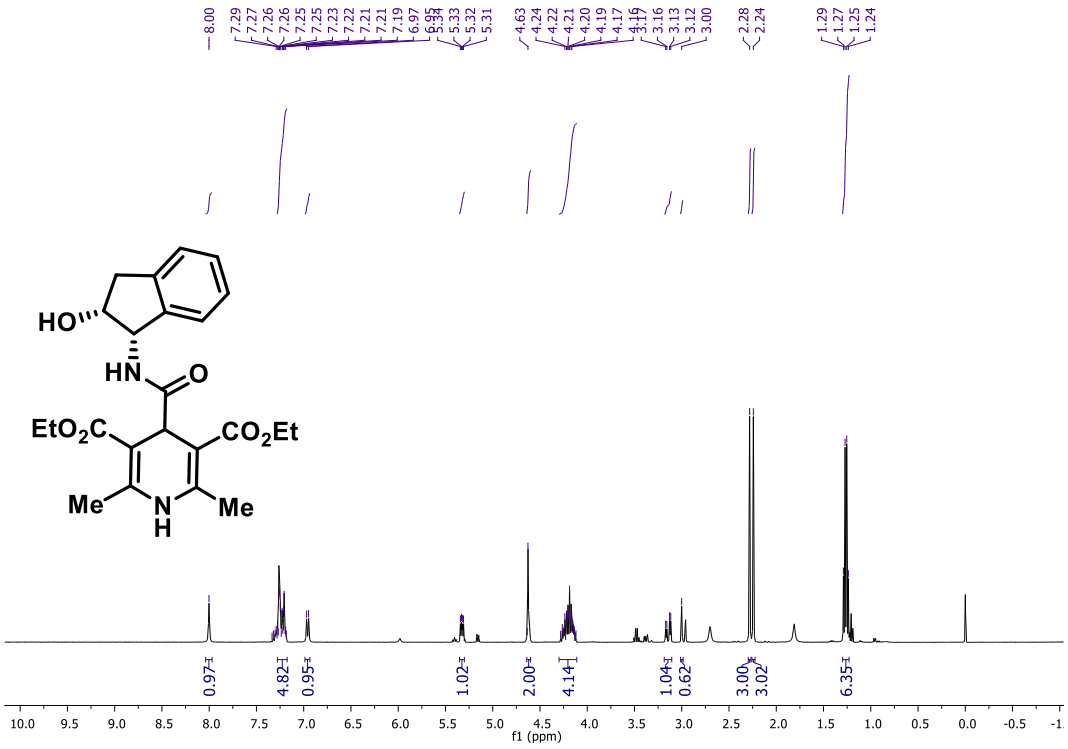
^{13}C NMR (CDCl3, 126 MHz) of 48'.



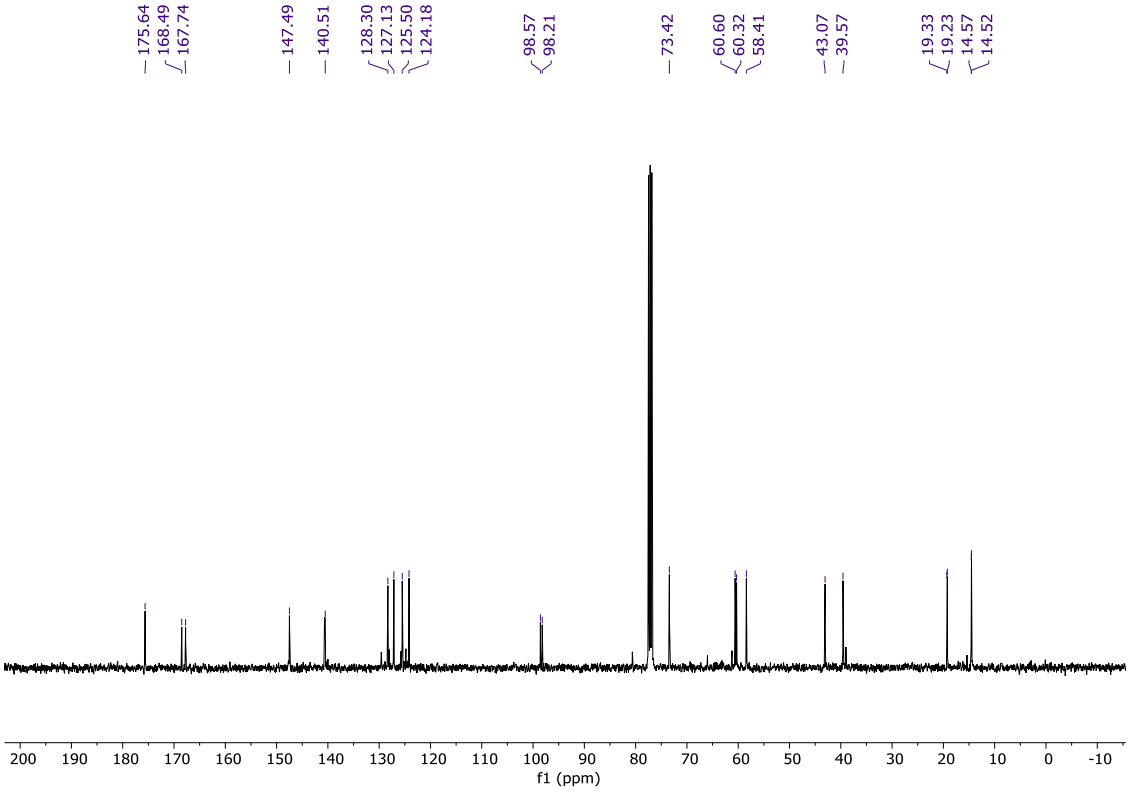
^{1}H NMR (CD_3OD, 400 MHz) of 49'.



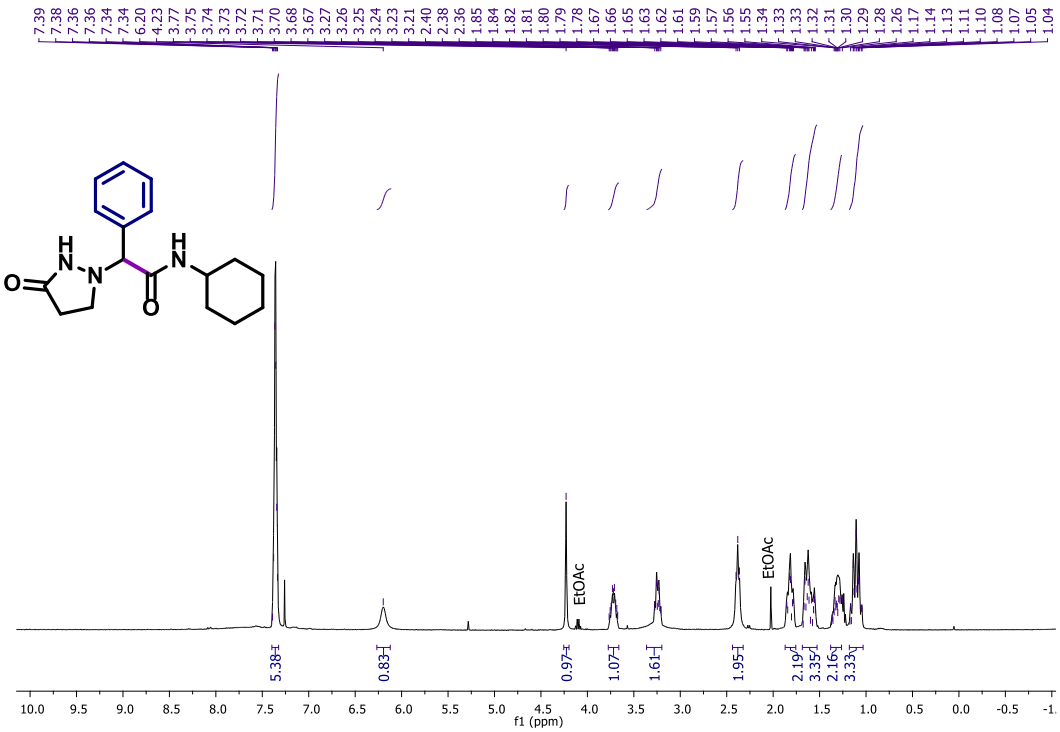
^{13}C NMR (CD_3OD, 126 MHz) of 49'.



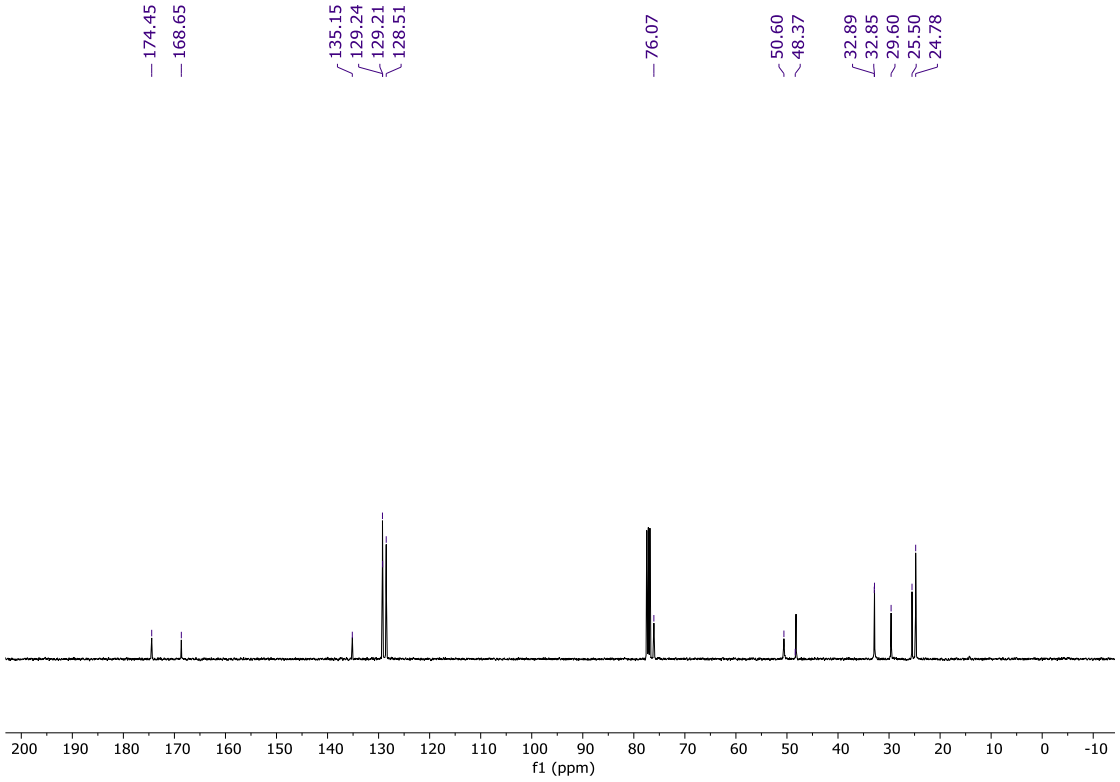
[1]H NMR (CDCl3, 400 MHz) of 50'.



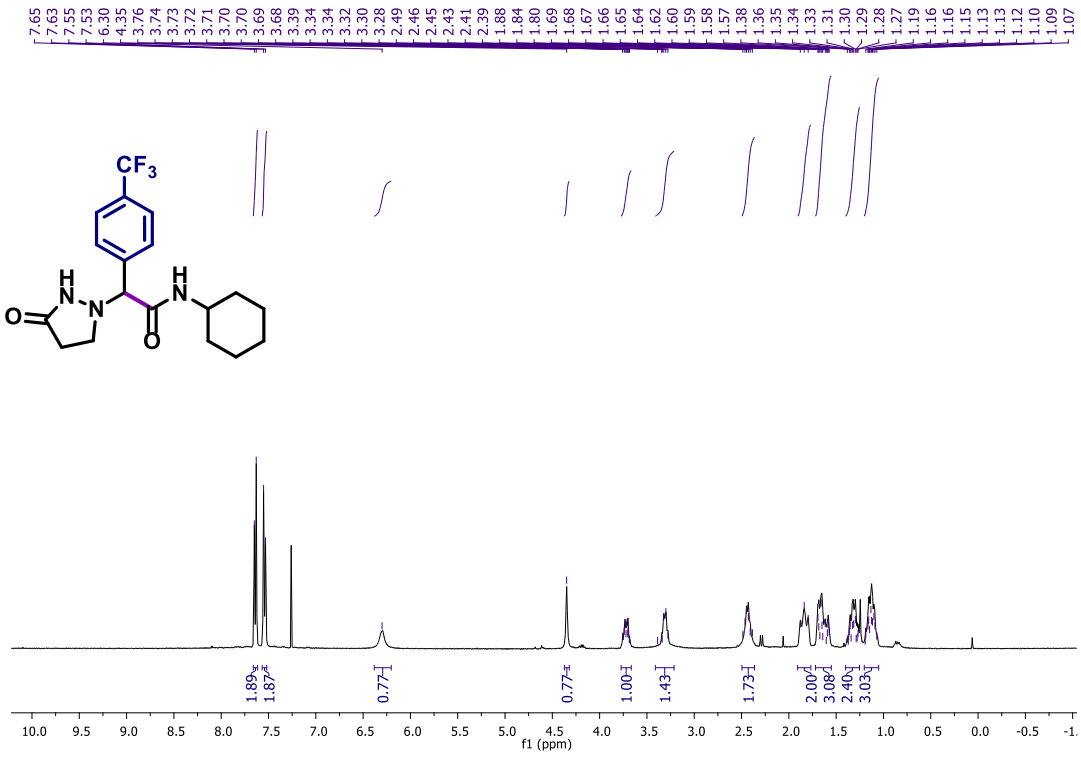
[13]C NMR (CDCl3, 126 MHz) of 50'.



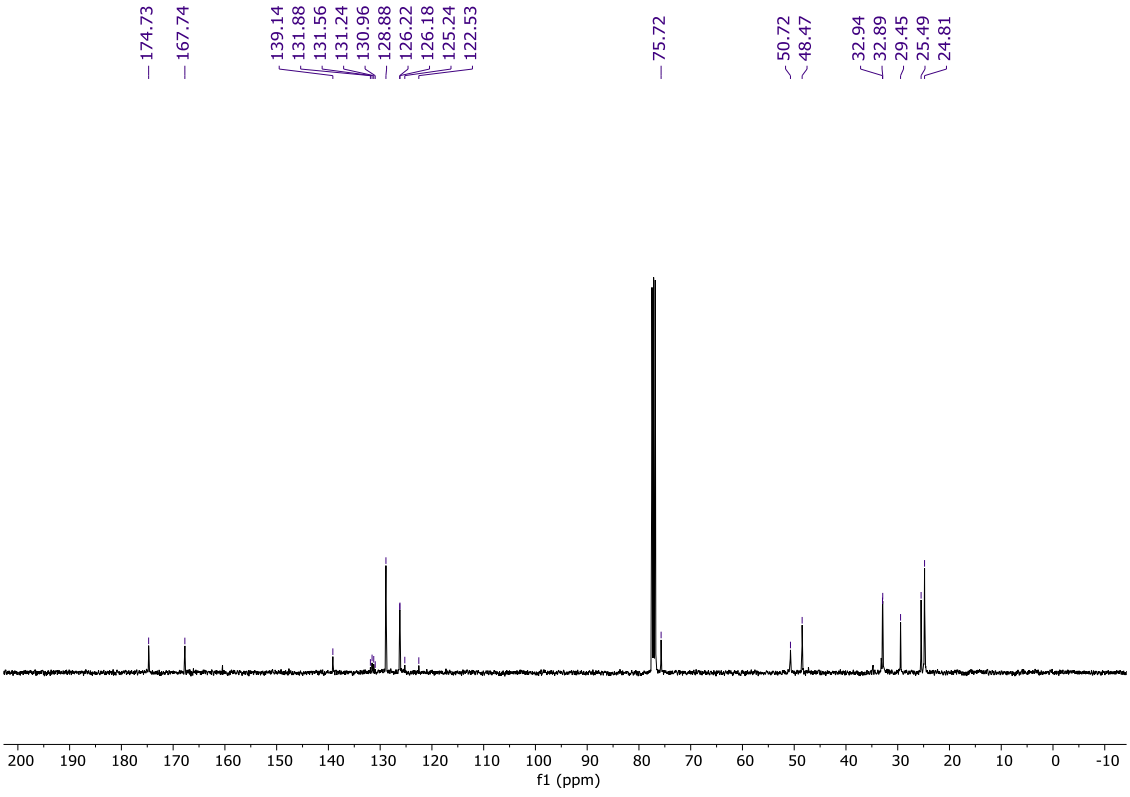
^{1}H NMR ($CDCl_3$, 400 MHz) of 3.



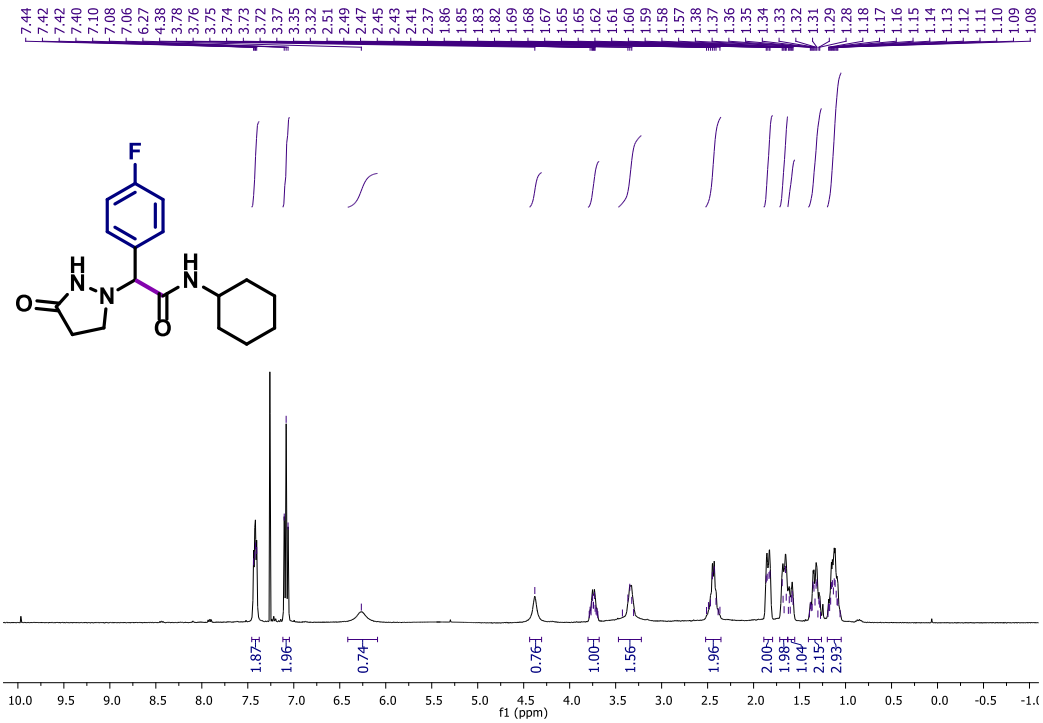
^{13}C NMR ($CDCl_3$, 126 MHz) of 3.



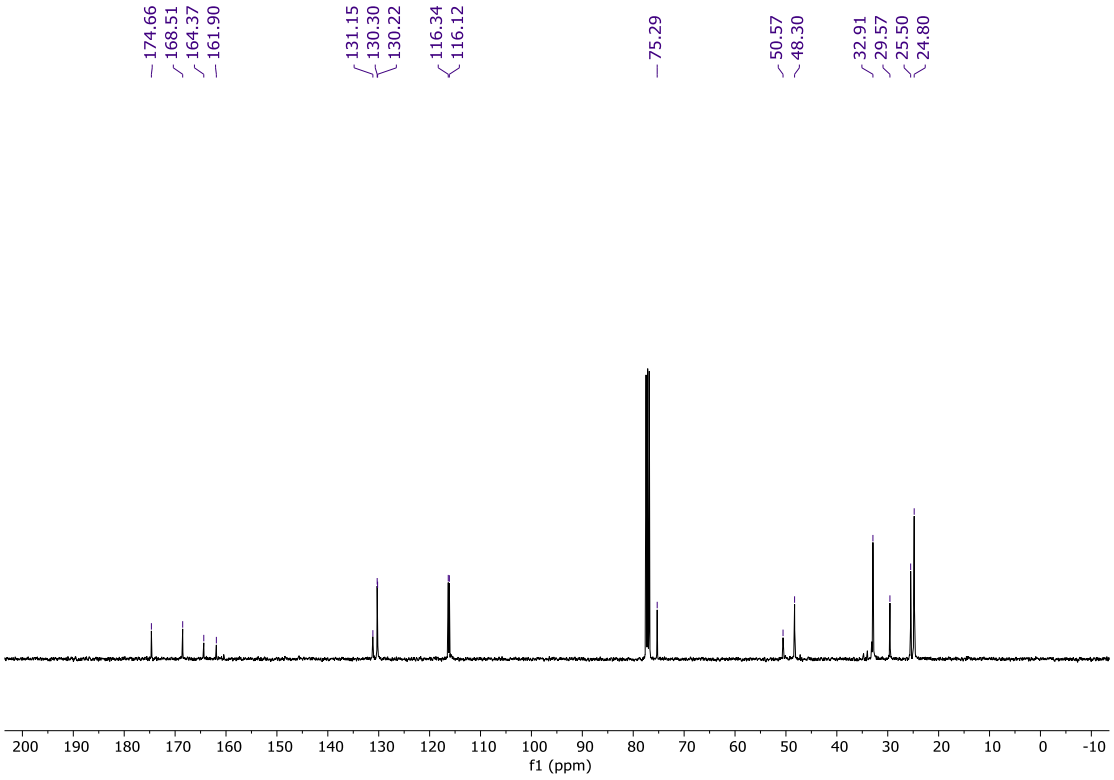
^{1}H NMR ($CDCl_3$, 400 MHz) of 4.



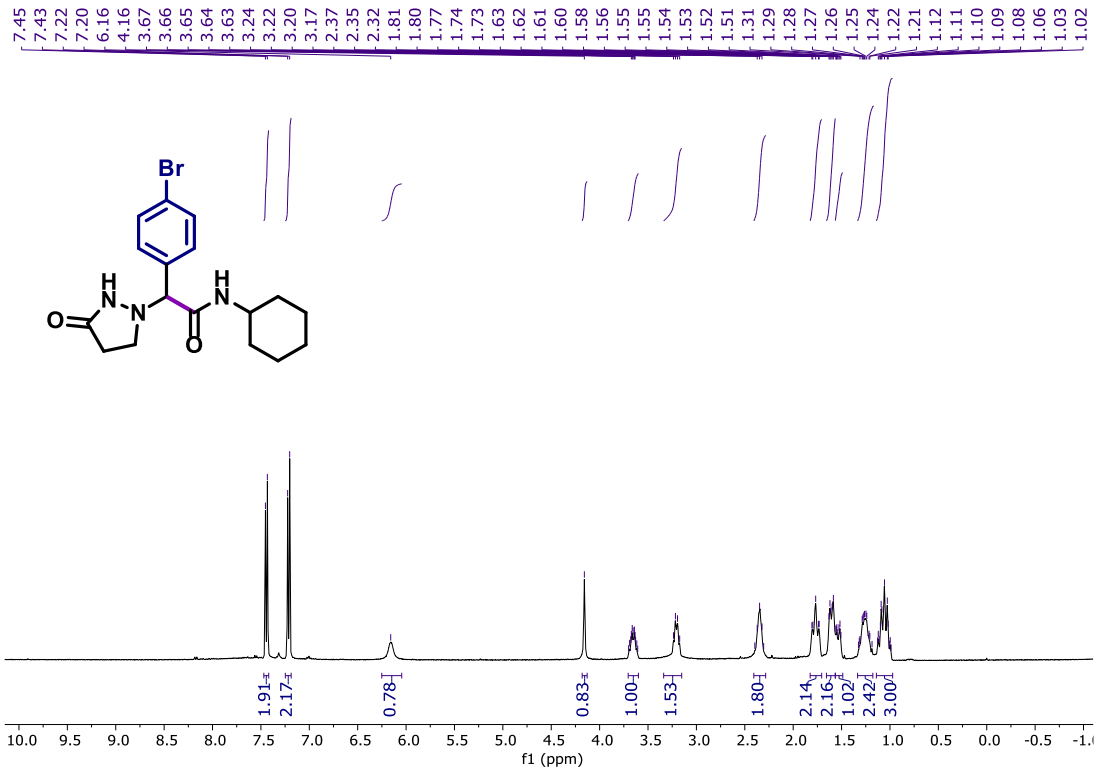
^{13}C NMR ($CDCl_3$, 126 MHz) of 4.



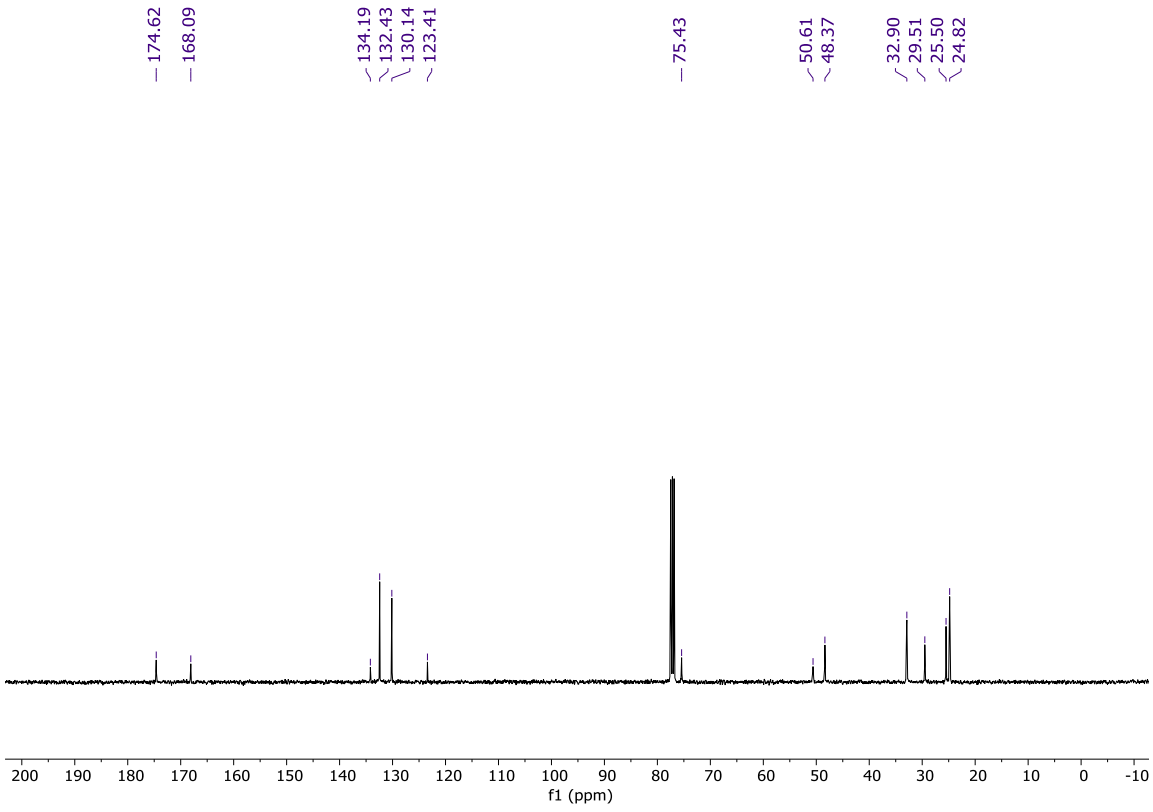
^{1}H NMR ($CDCl_3$, 400 MHz) of 5.



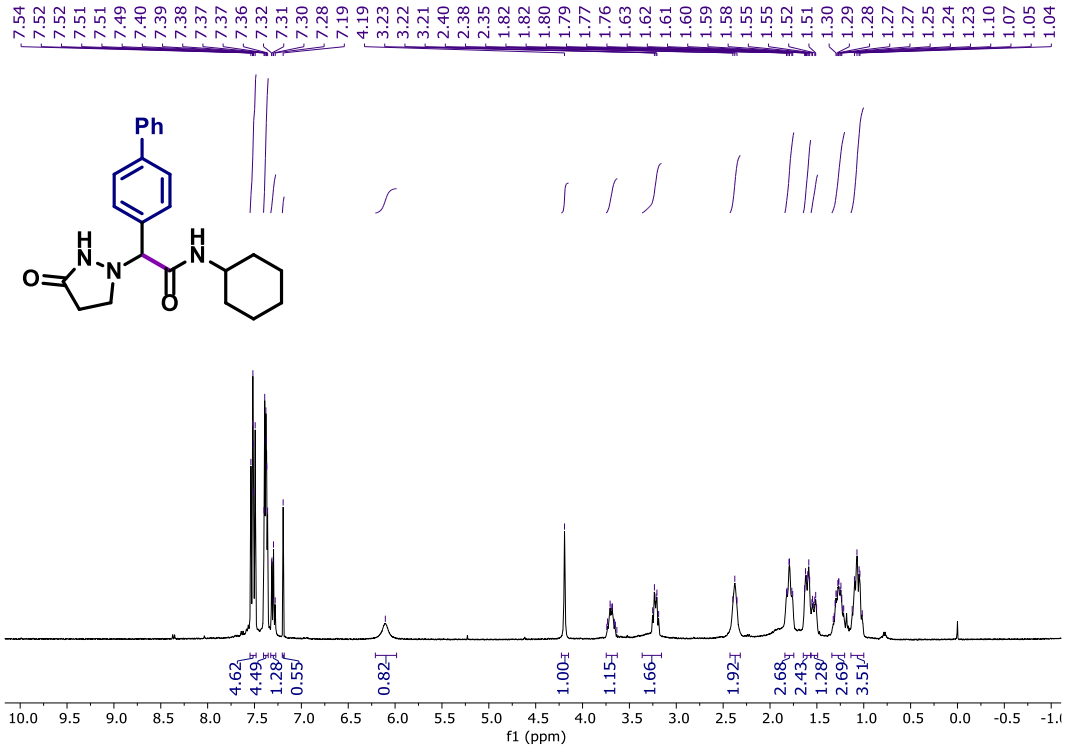
^{13}C NMR ($CDCl_3$, 126 MHz) of 5.



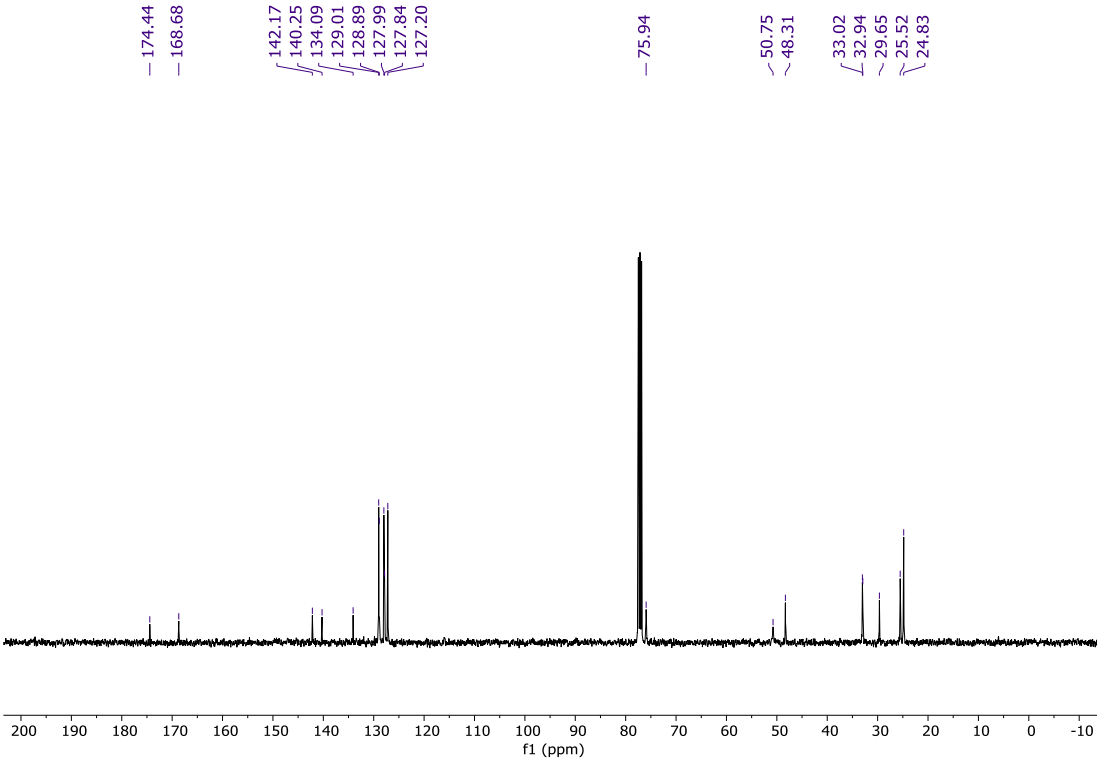
^{1}H NMR ($CDCl_3$, 400 MHz) of 6.



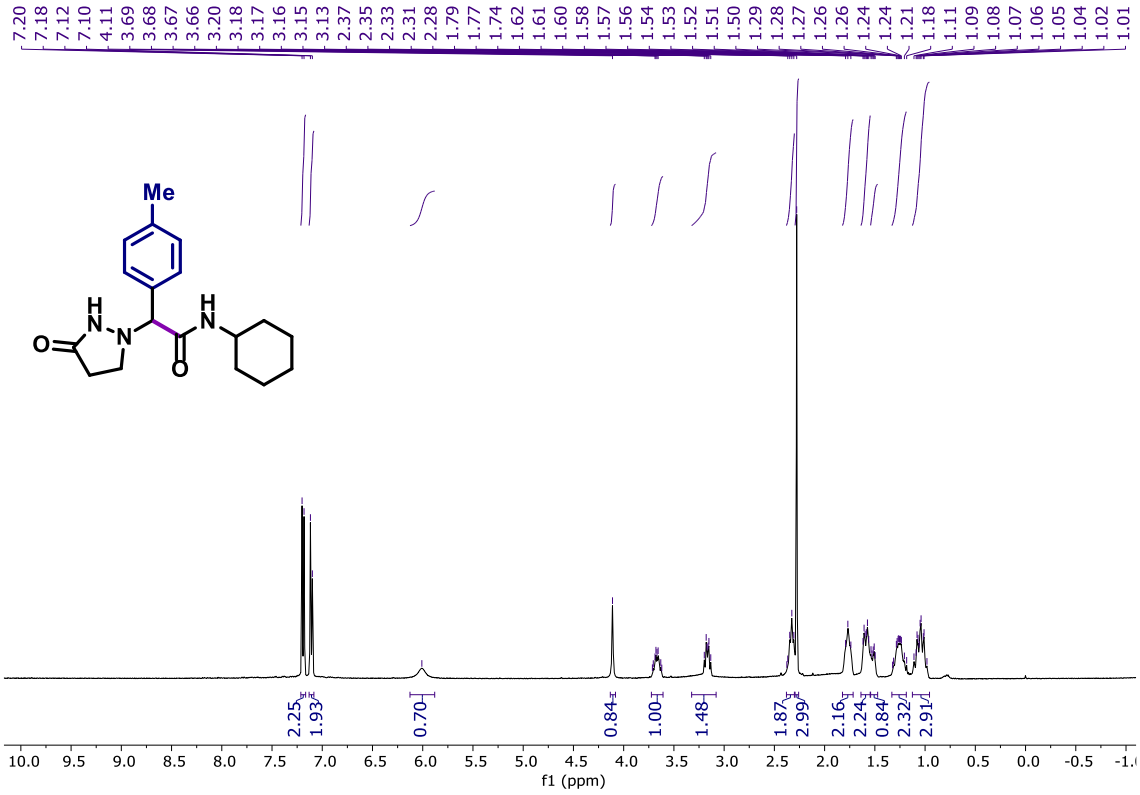
^{13}C NMR ($CDCl_3$, 126 MHz) of 6.



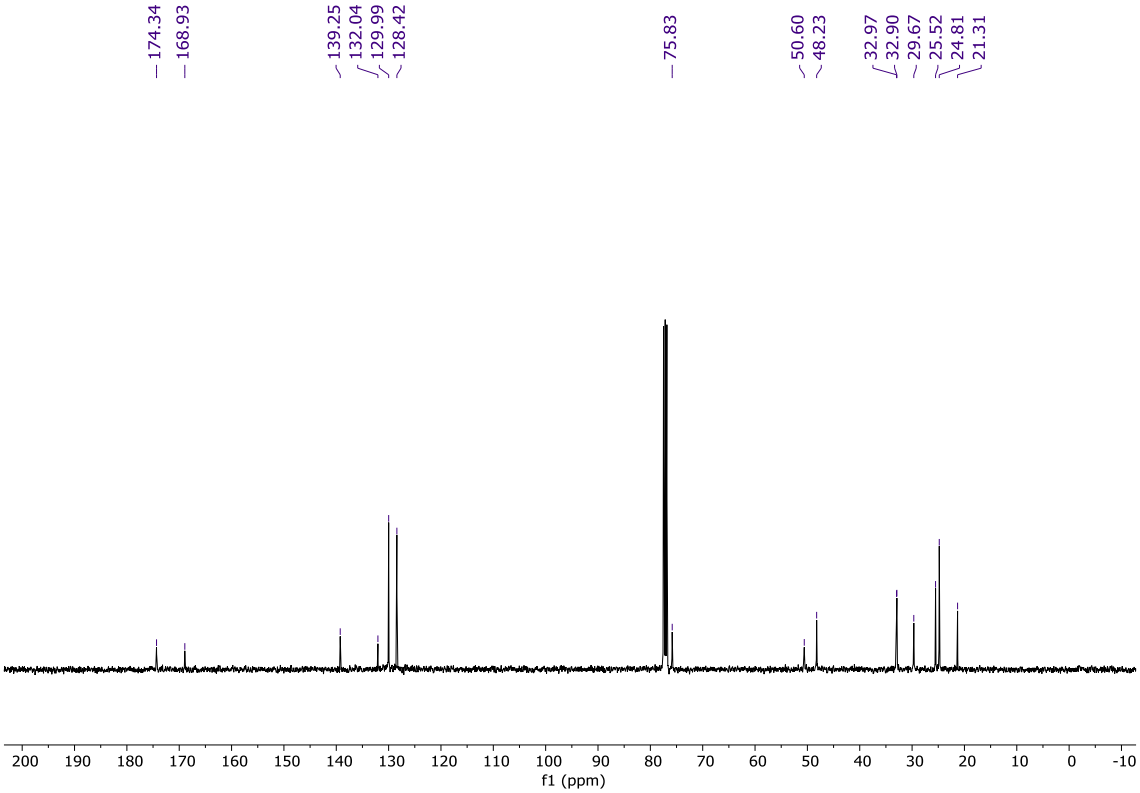
^{1}H NMR ($CDCl_3$, 400 MHz) of 7.



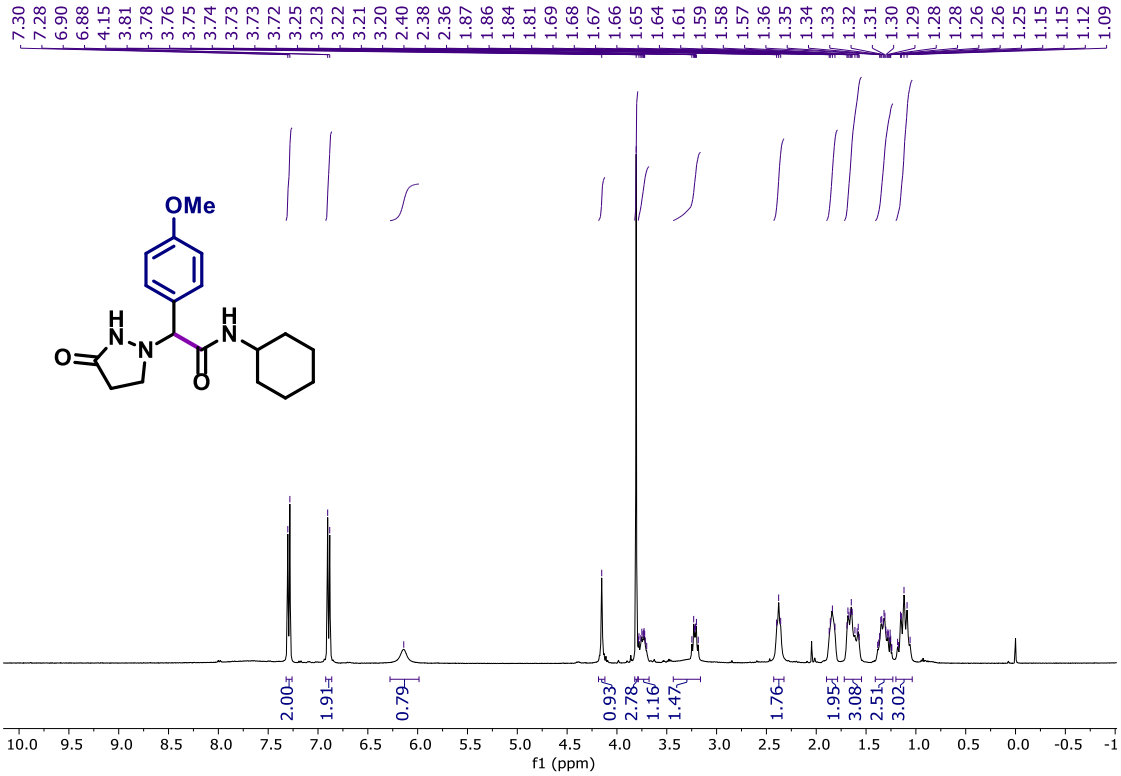
^{13}C NMR ($CDCl_3$, 126 MHz) of 7.



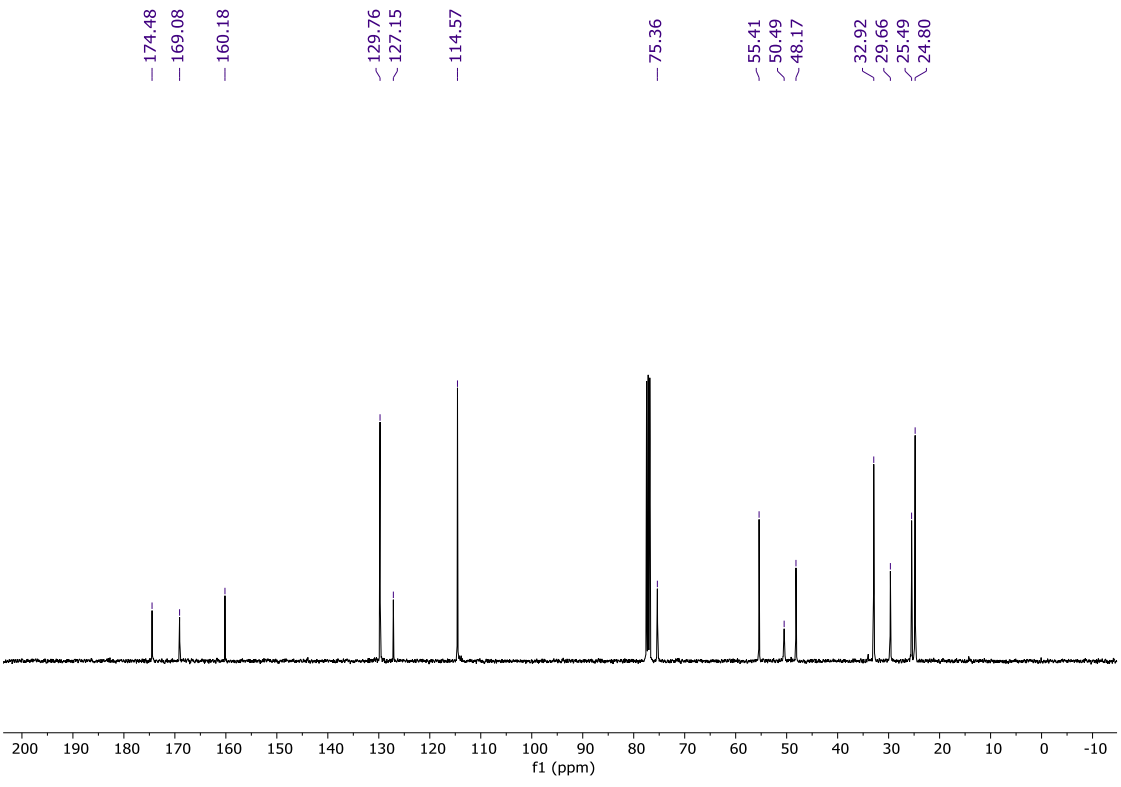
^{1}H NMR ($CDCl_3$, 400 MHz) of 8.



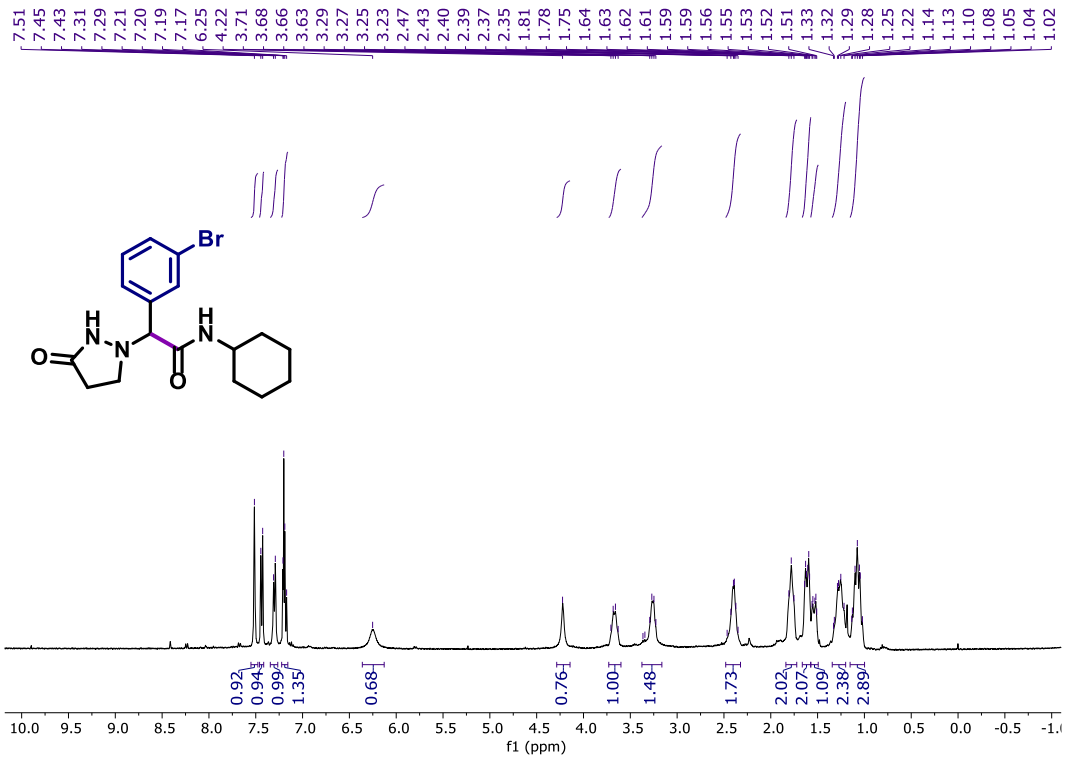
^{13}C NMR ($CDCl_3$, 126 MHz) of 8.



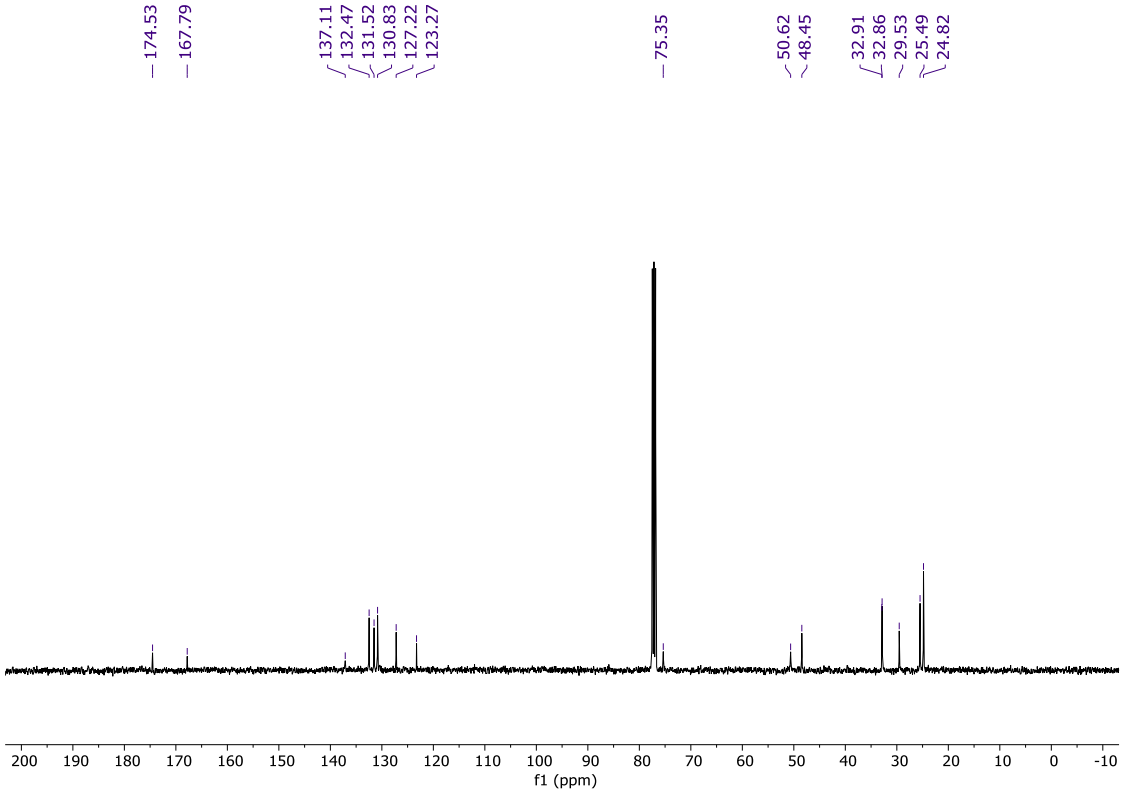
^{1}H NMR ($CDCl_3$, 400 MHz) of 9.



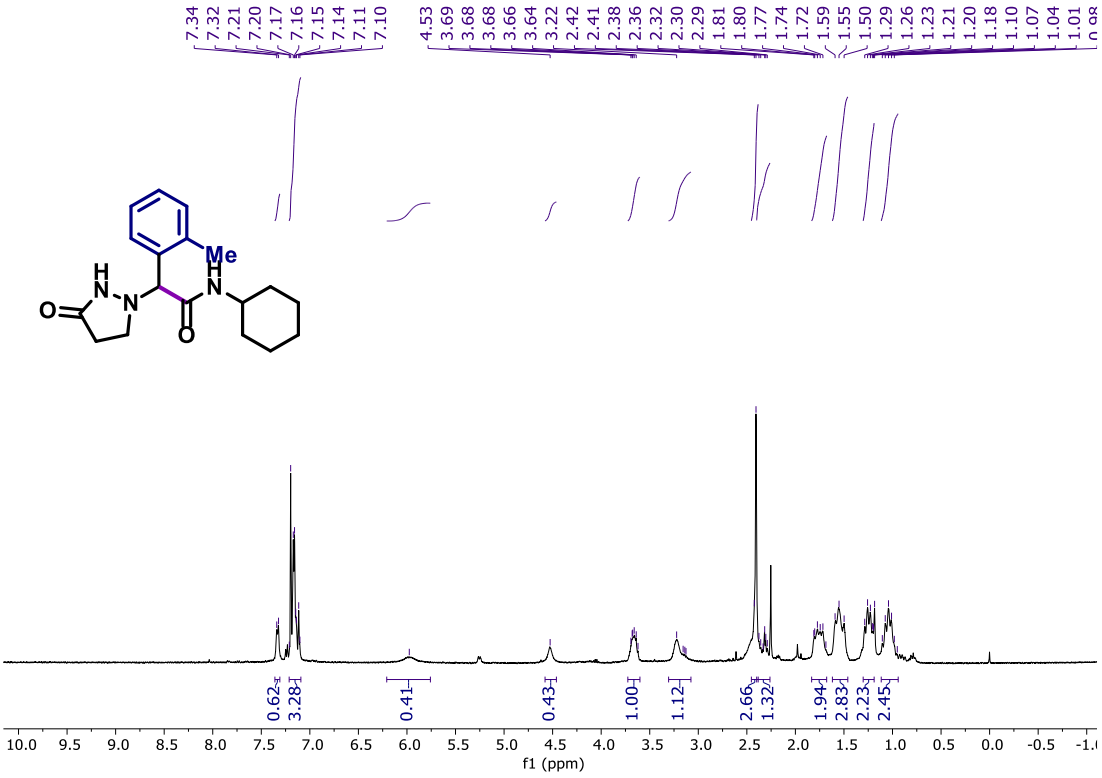
^{13}C NMR ($CDCl_3$, 126 MHz) of 9.



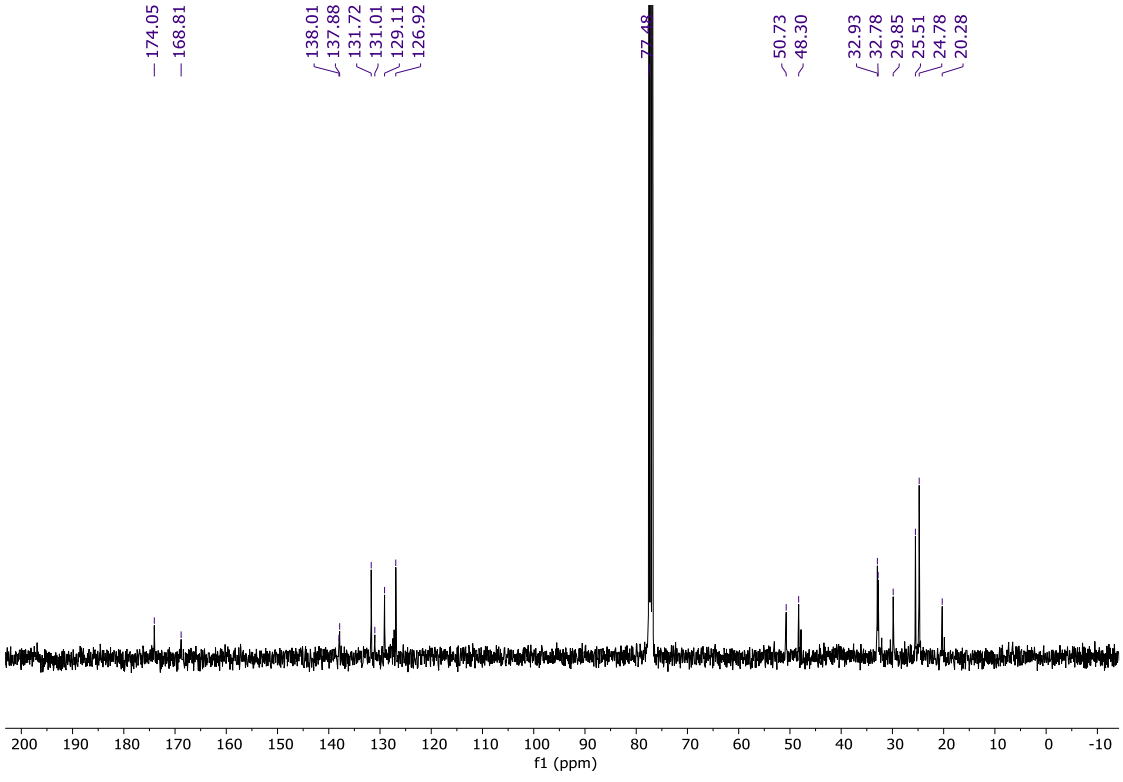
^{1}H NMR ($CDCl_3$, 400 MHz) of 10.



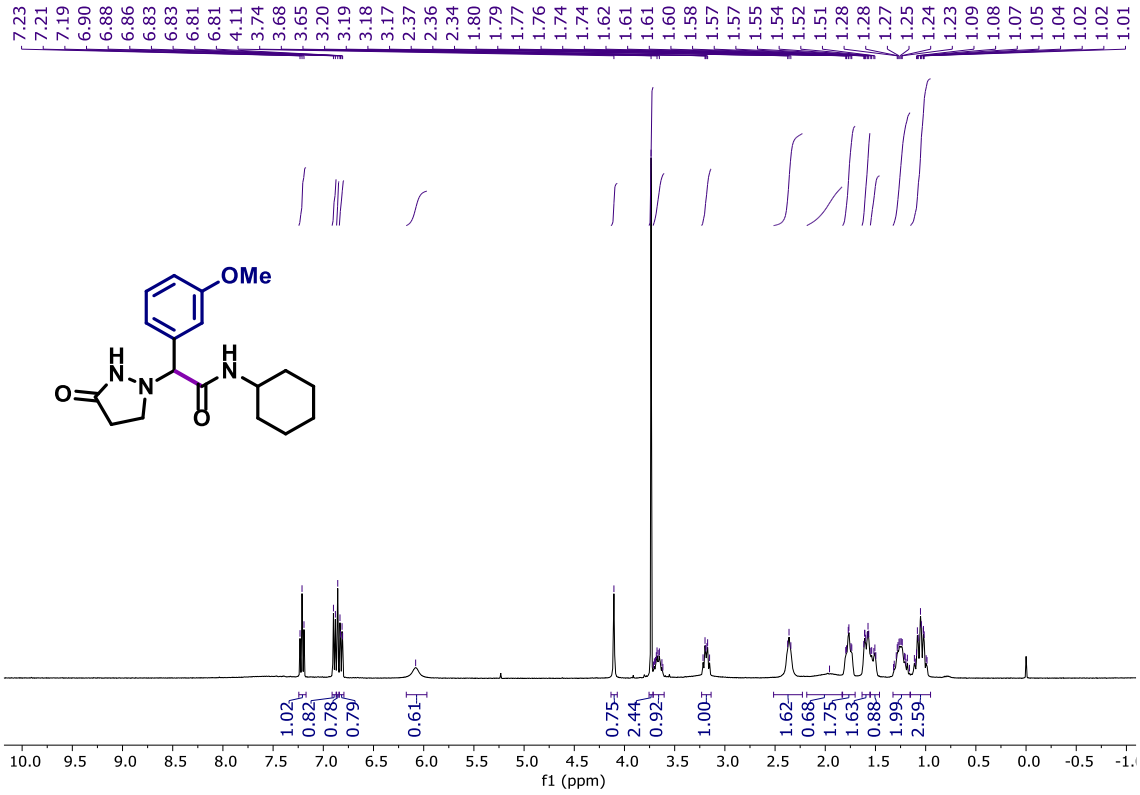
^{13}C NMR ($CDCl_3$, 126 MHz) of 10.



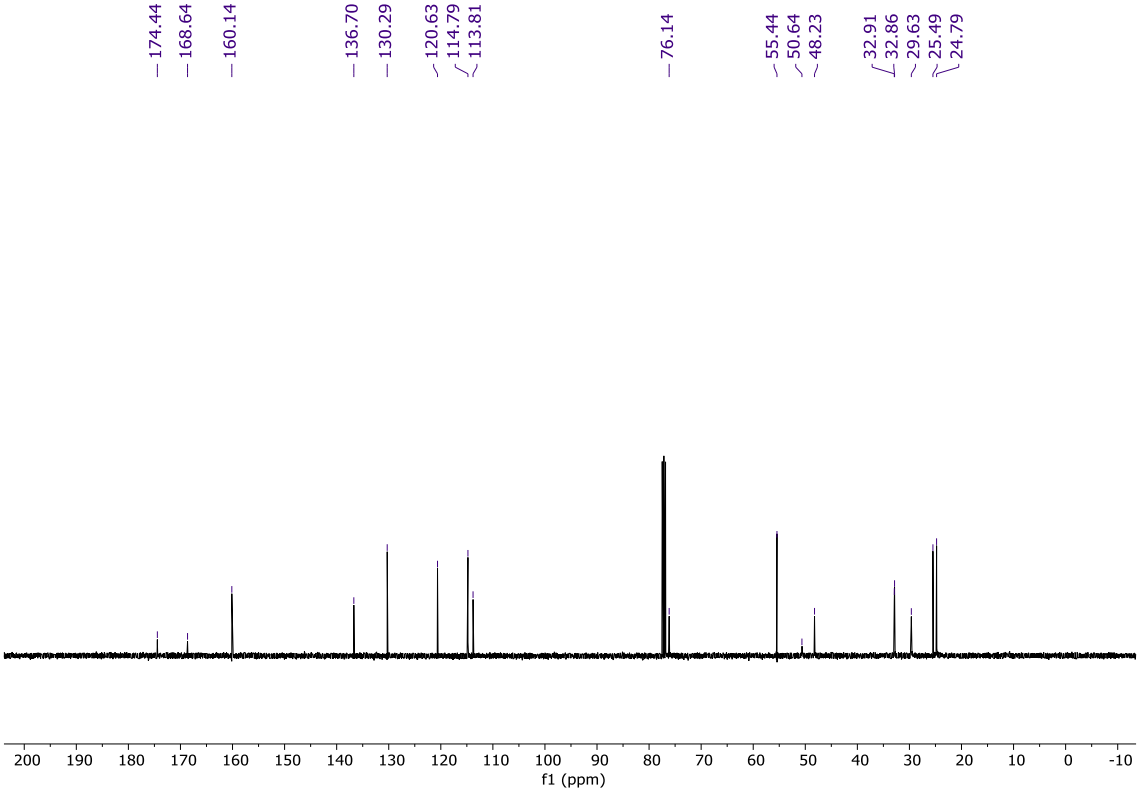
^{1}H NMR ($CDCl_3$, 400 MHz) of 11.



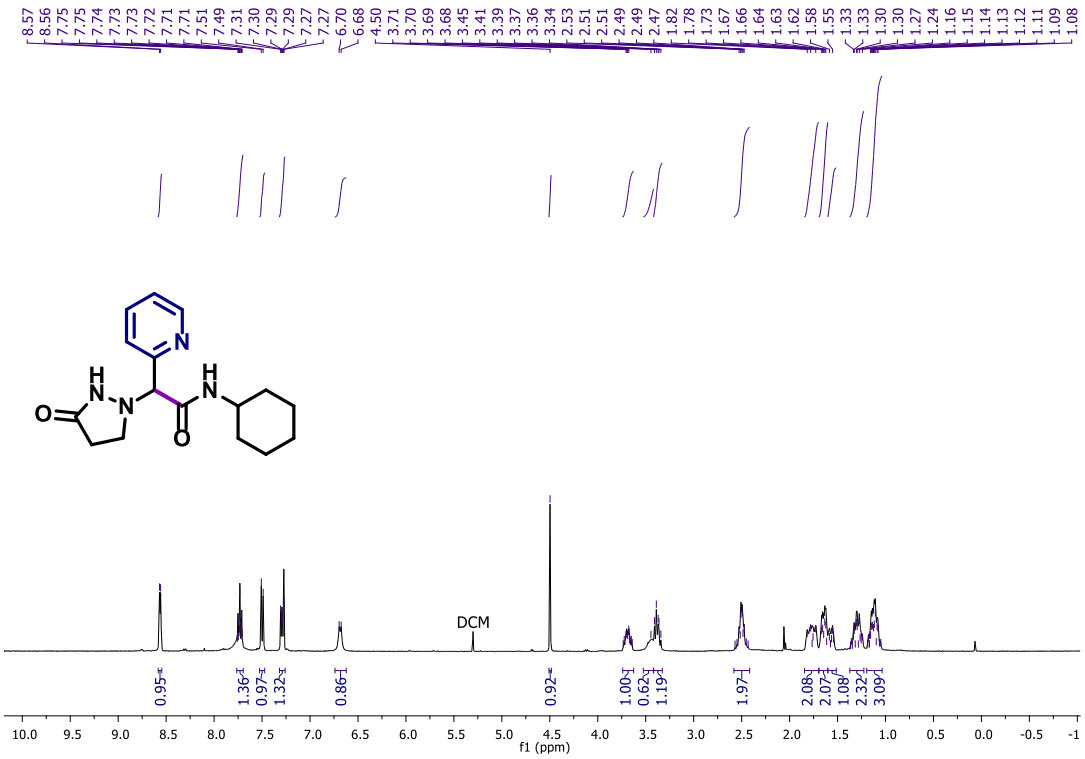
^{13}C NMR ($CDCl_3$, 126 MHz) of 11.



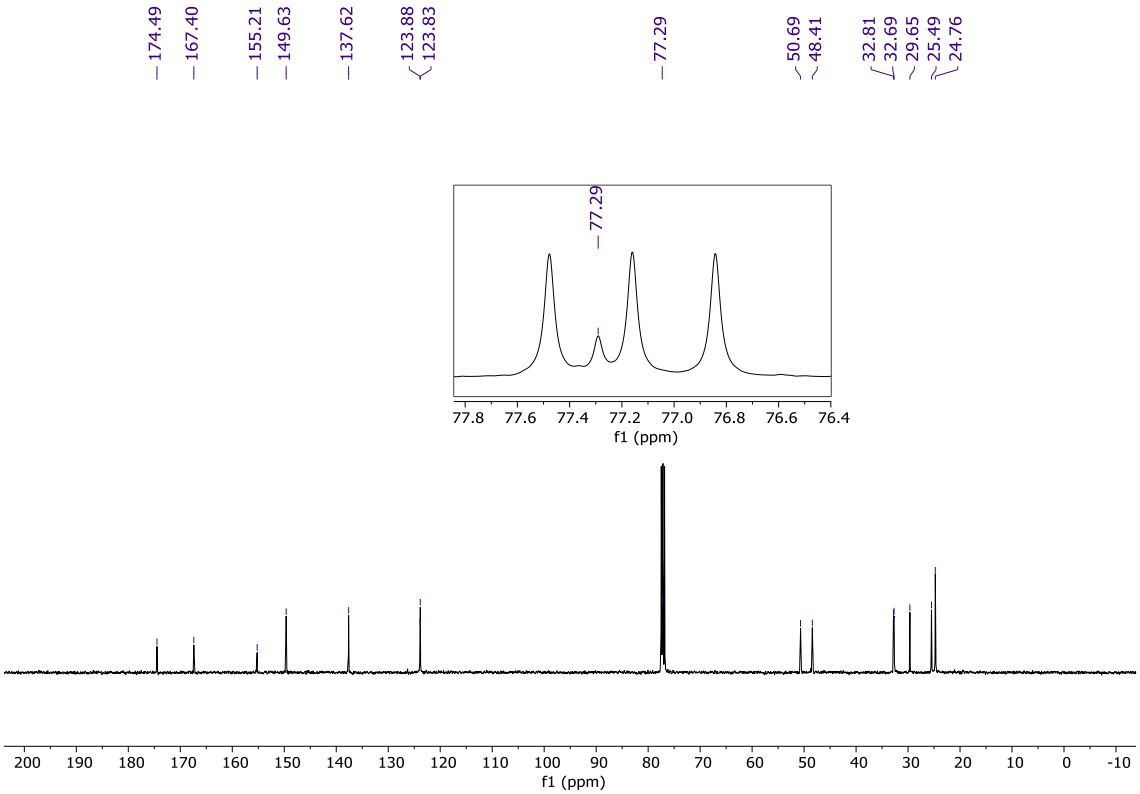
^{1}H NMR ($CDCl_3$, 400 MHz) of 12.



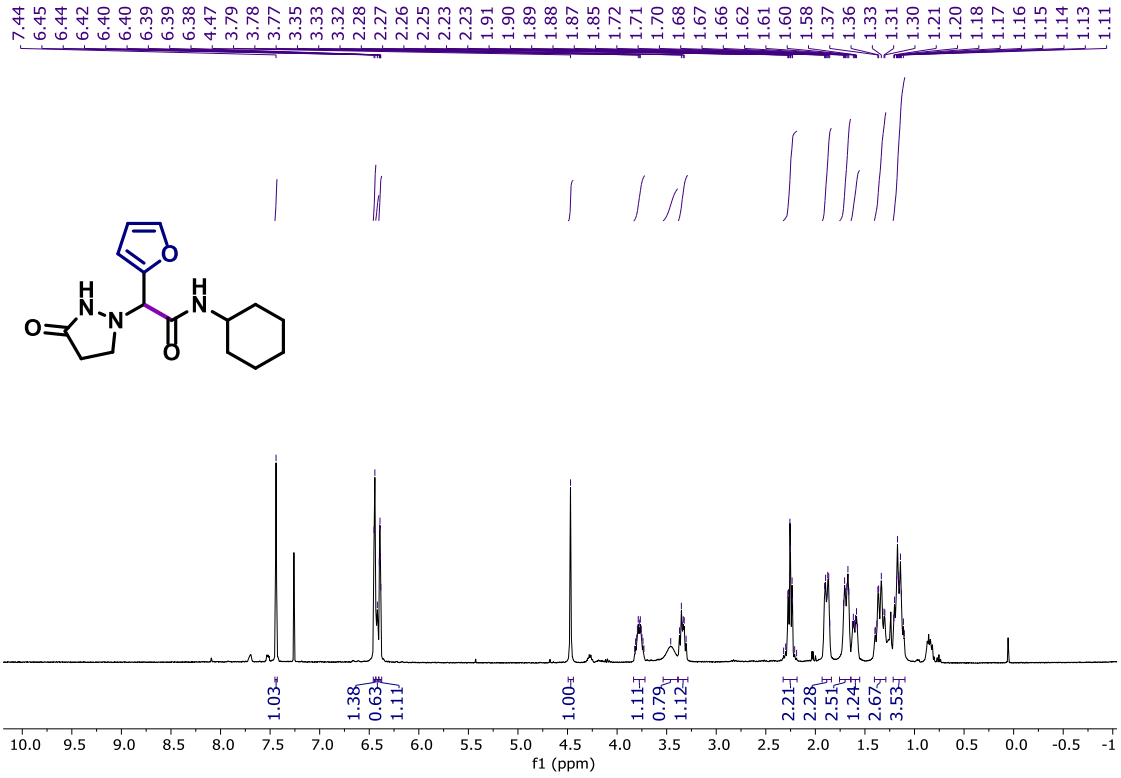
^{13}C NMR ($CDCl_3$, 126 MHz) of 12.



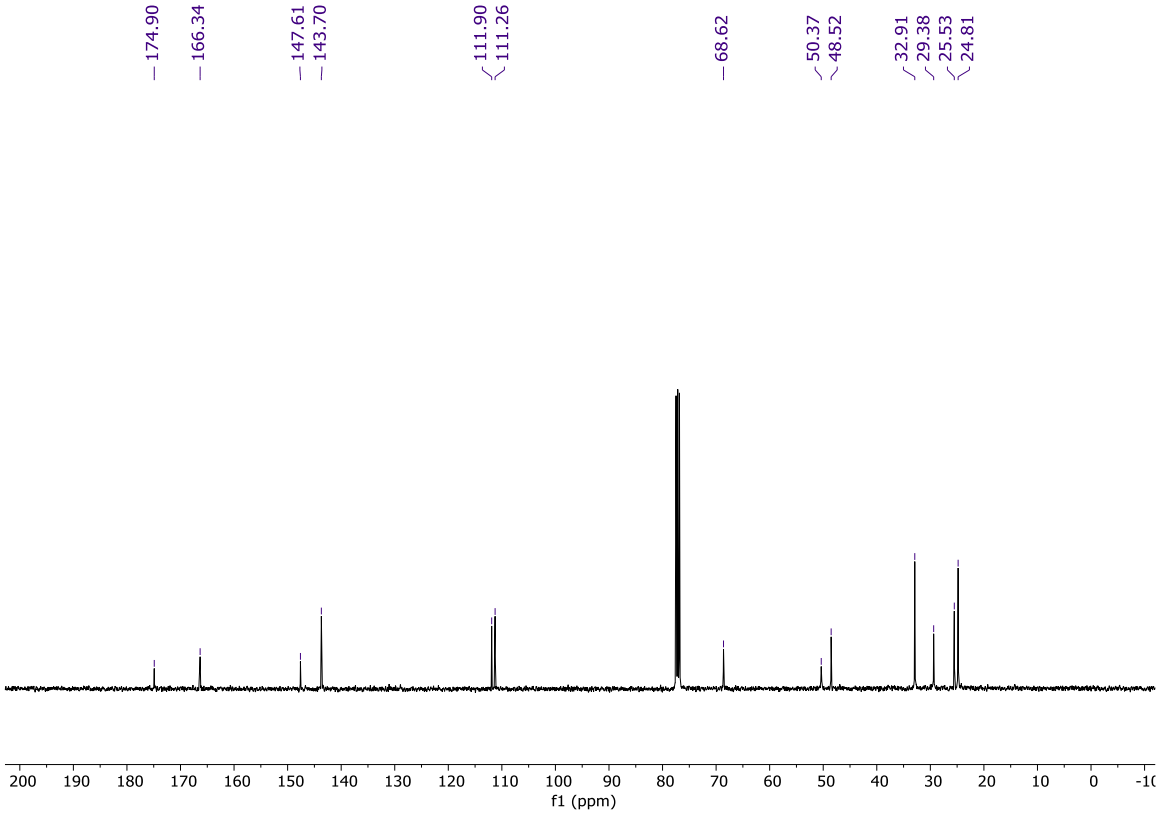
^{1}H NMR ($CDCl_3$, 400 MHz) of 13.



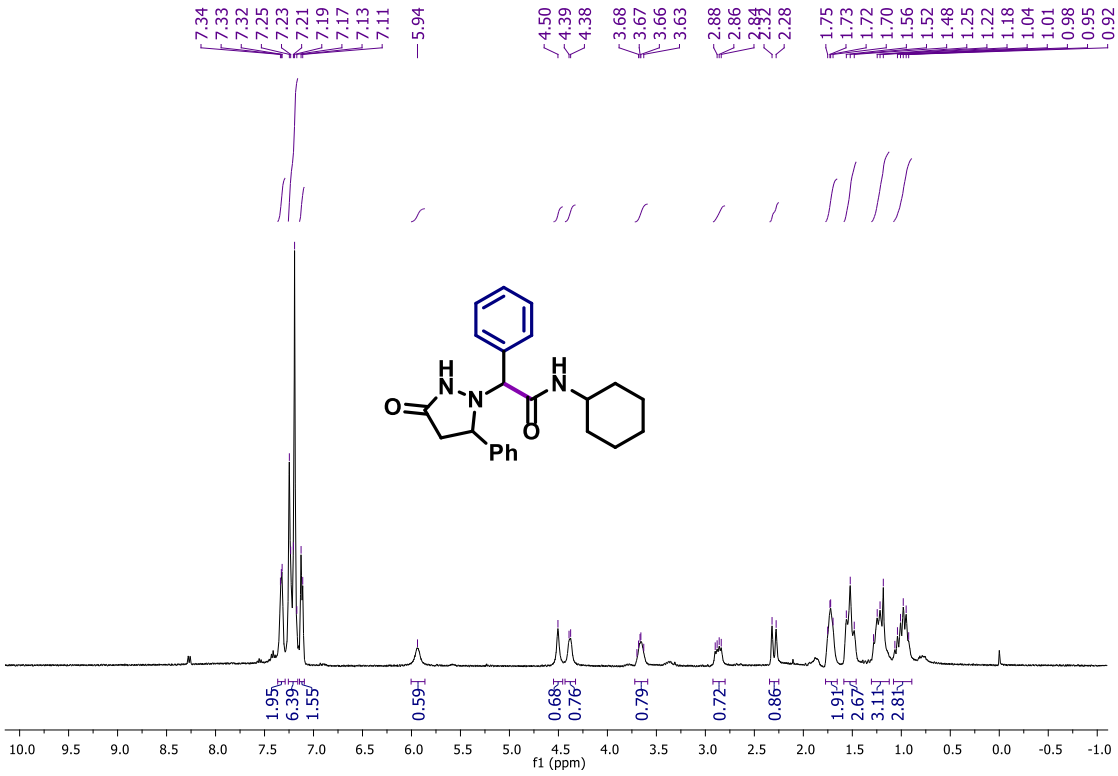
^{13}C NMR ($CDCl_3$, 126 MHz) of 13.



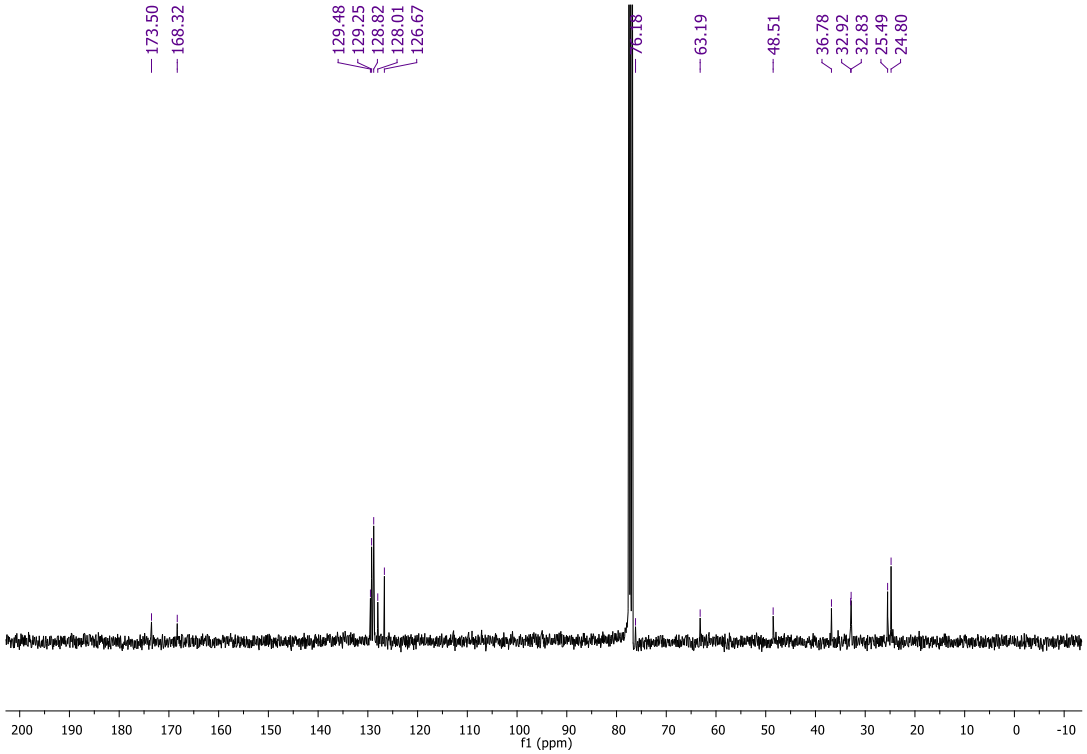
^{1}H NMR ($CDCl_3$, 400 MHz) of 14.



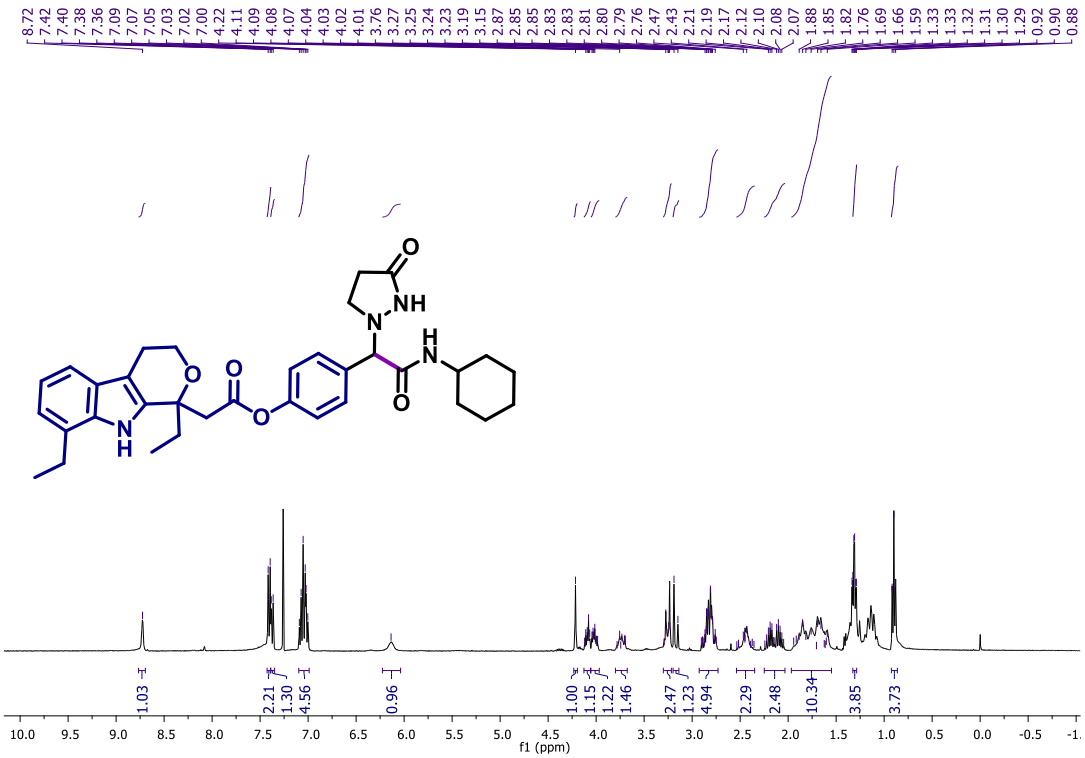
^{13}C NMR ($CDCl_3$, 126 MHz) of 14.



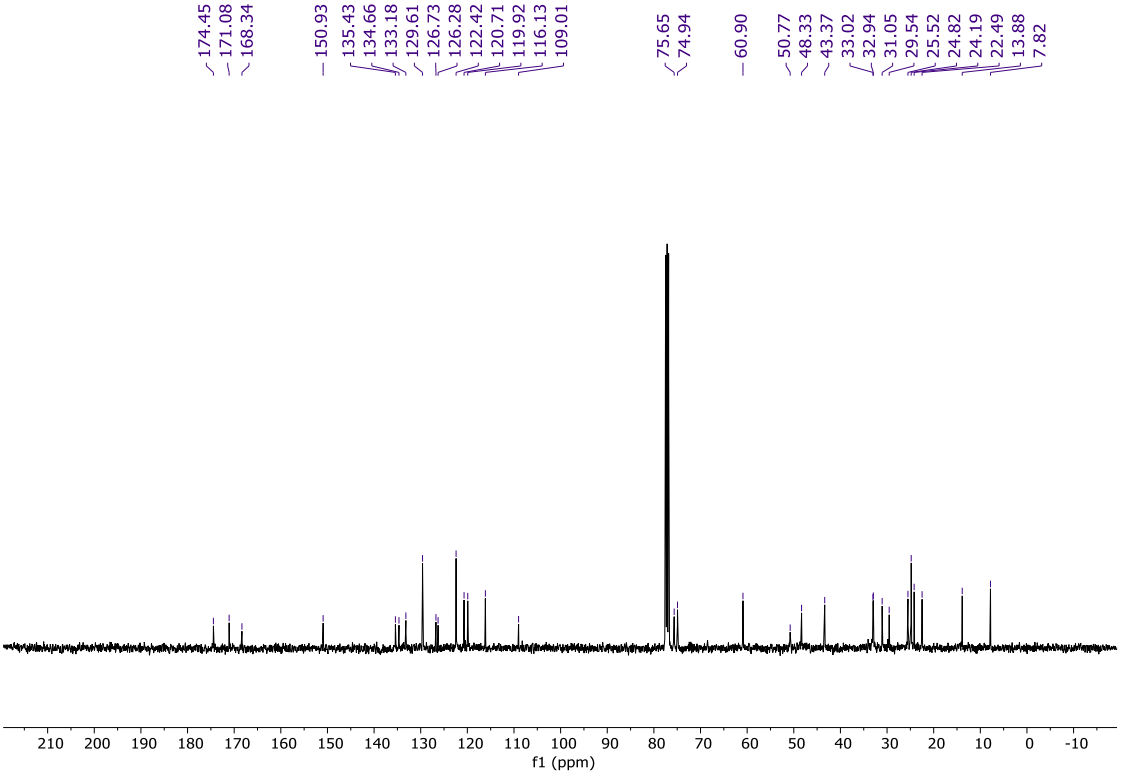
^{1}H NMR ($CDCl_3$, 400 MHz) of 15.



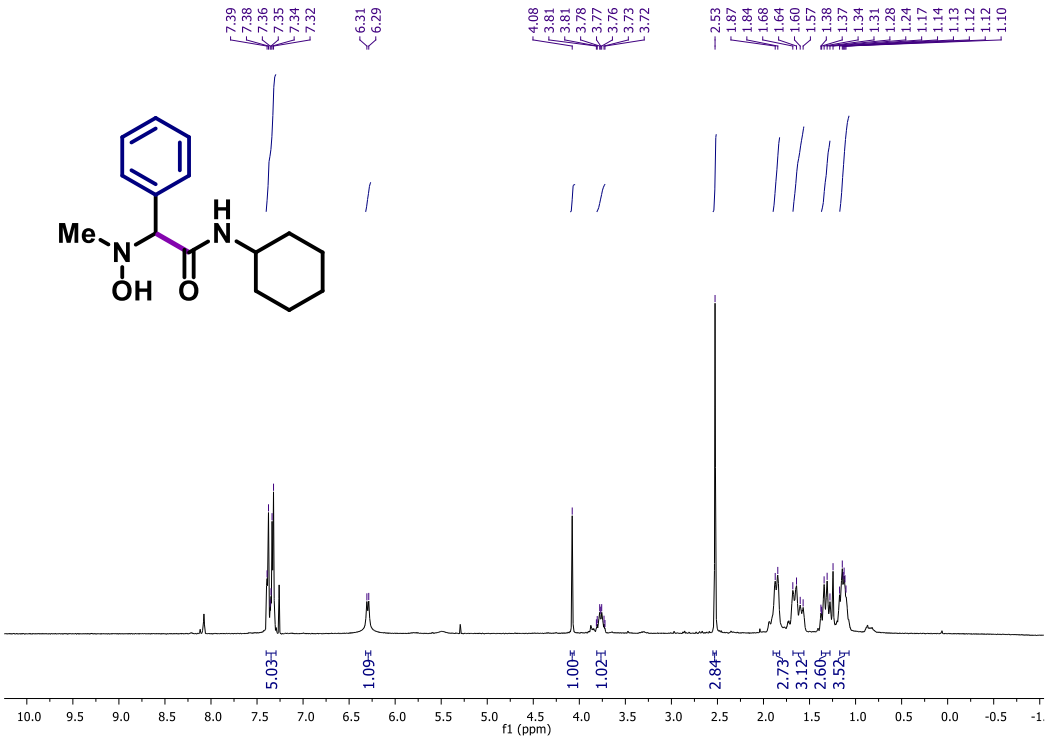
^{13}C NMR ($CDCl_3$, 126 MHz) of 15.



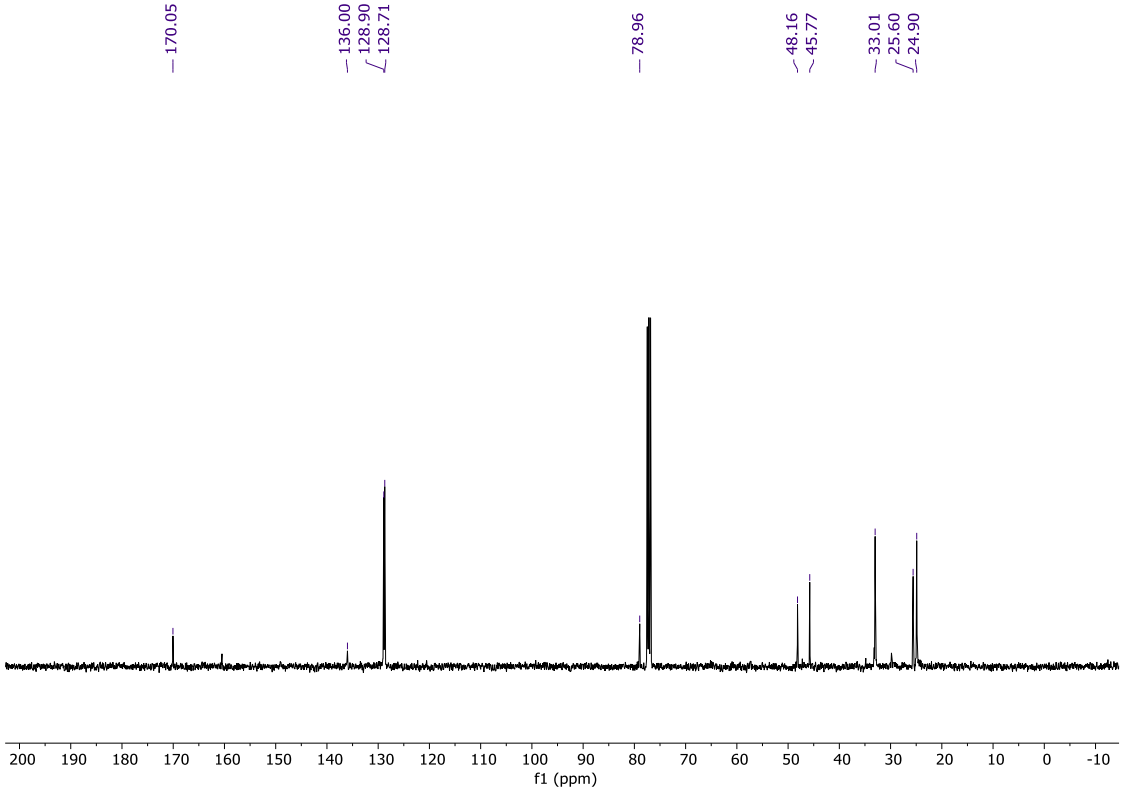
^{1}H NMR ($CDCl_3$, 400 MHz) of 16.



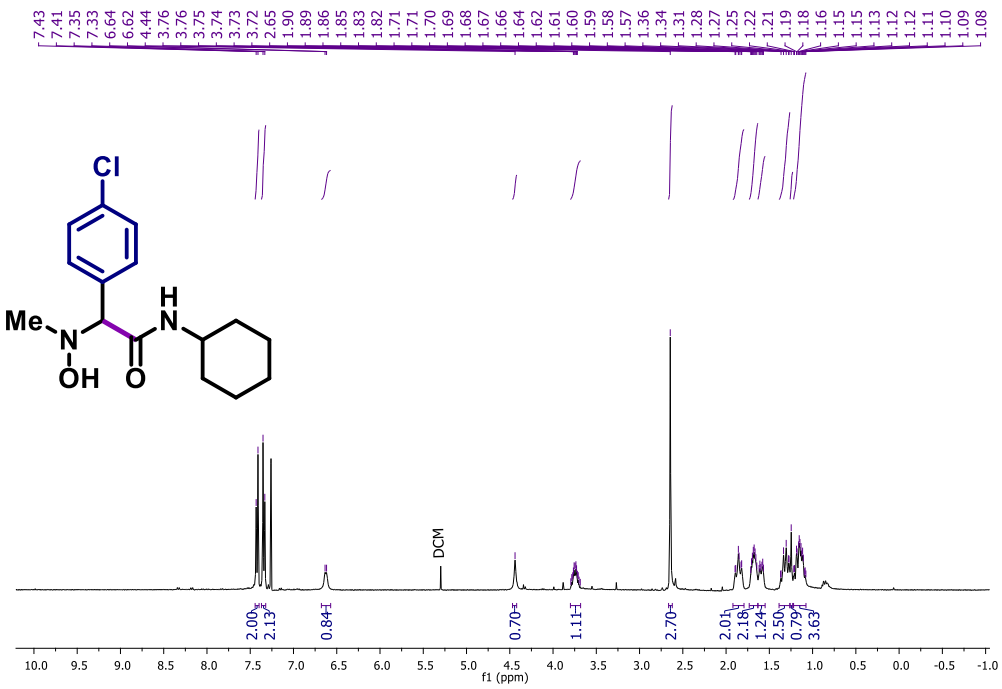
^{13}C NMR ($CDCl_3$, 126 MHz) of 16.



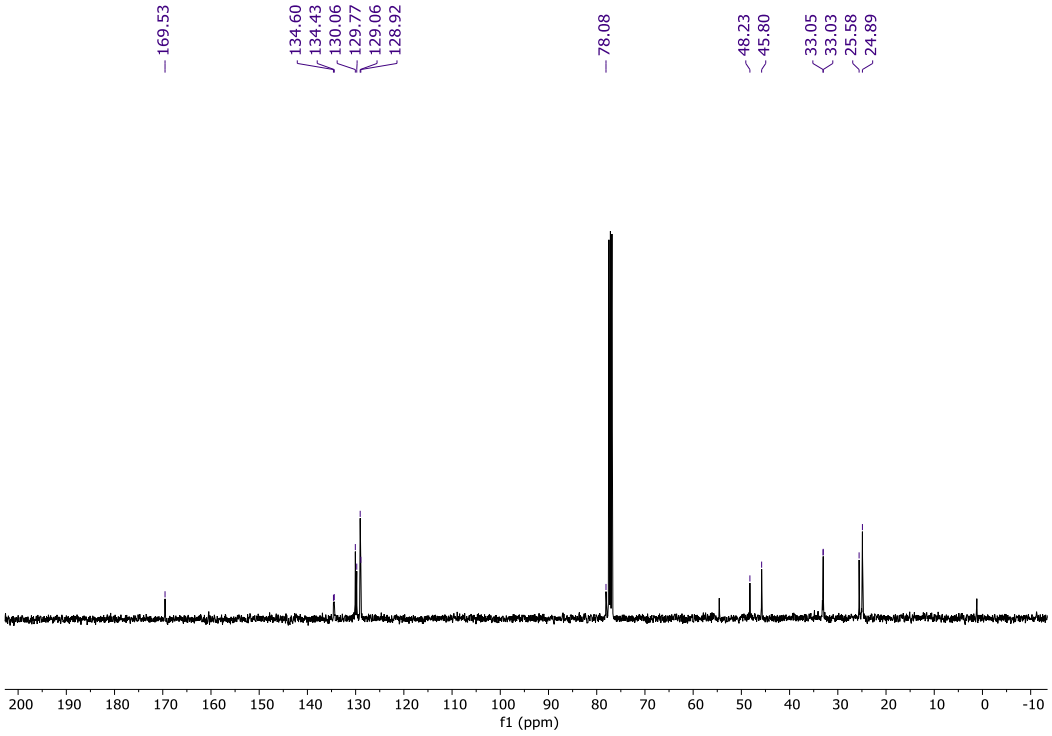
^{1}H NMR ($CDCl_3$, 400 MHz) of 17.



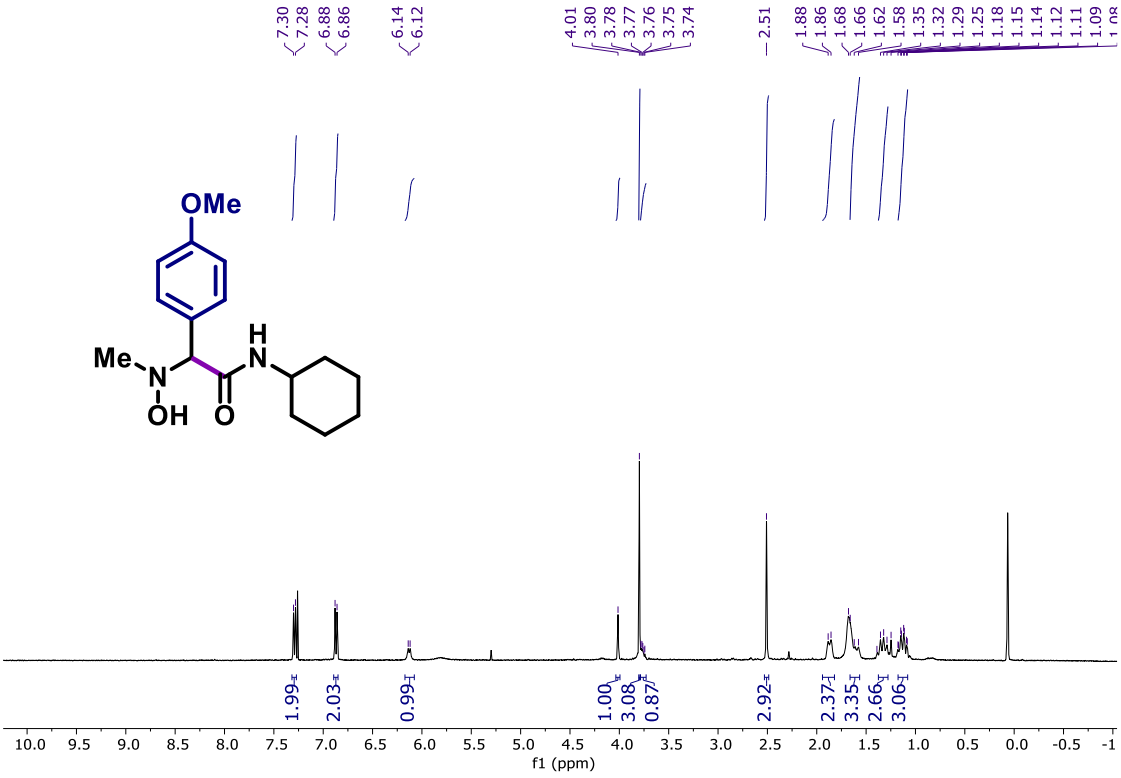
^{13}C NMR ($CDCl_3$, 126 MHz) of 17.



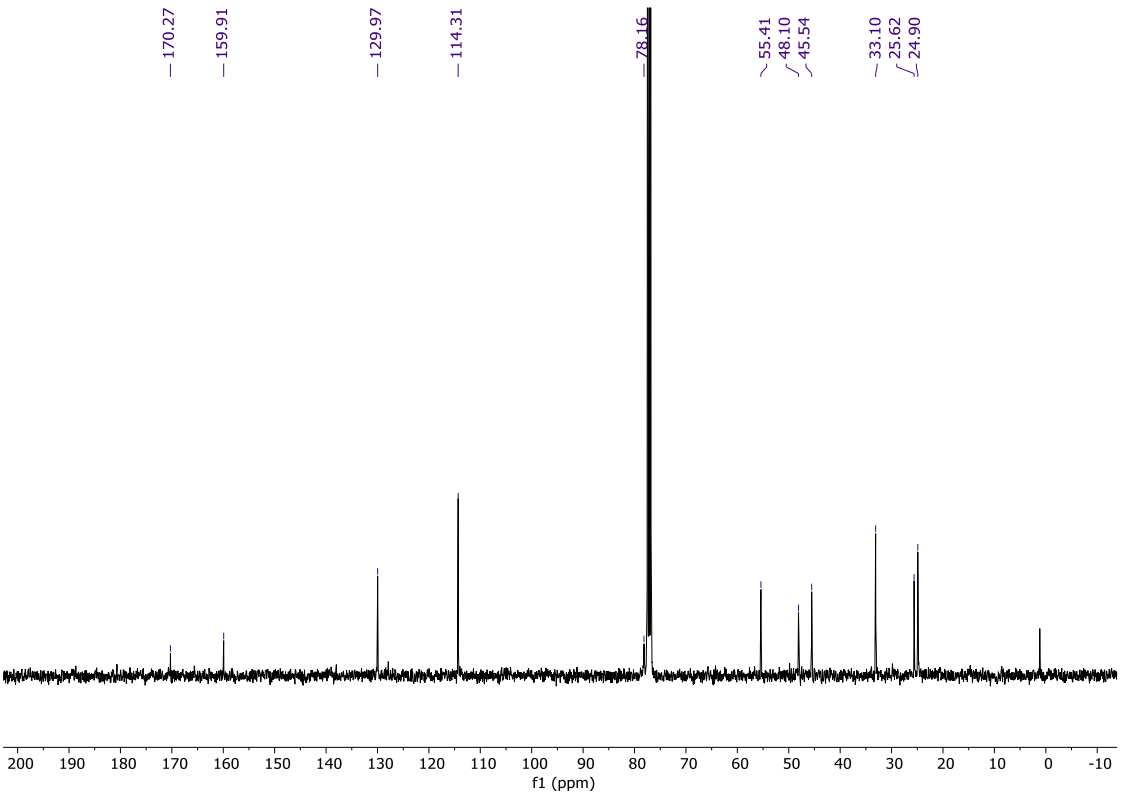
^{1}H NMR ($CDCl_3$, 400 MHz) of 18.



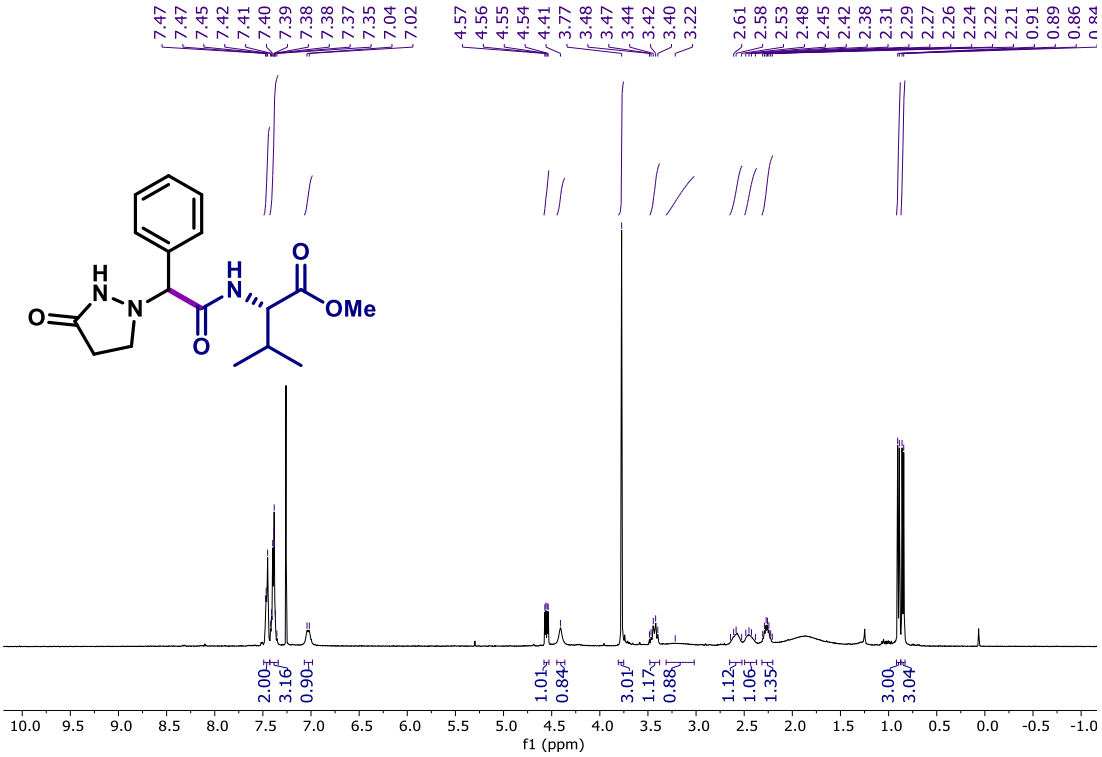
^{13}C NMR ($CDCl_3$, 126 MHz) of 18.



^{1}H NMR ($CDCl_3$, 400 MHz) of 19.



^{13}C NMR ($CDCl_3$, 126 MHz) of 19.



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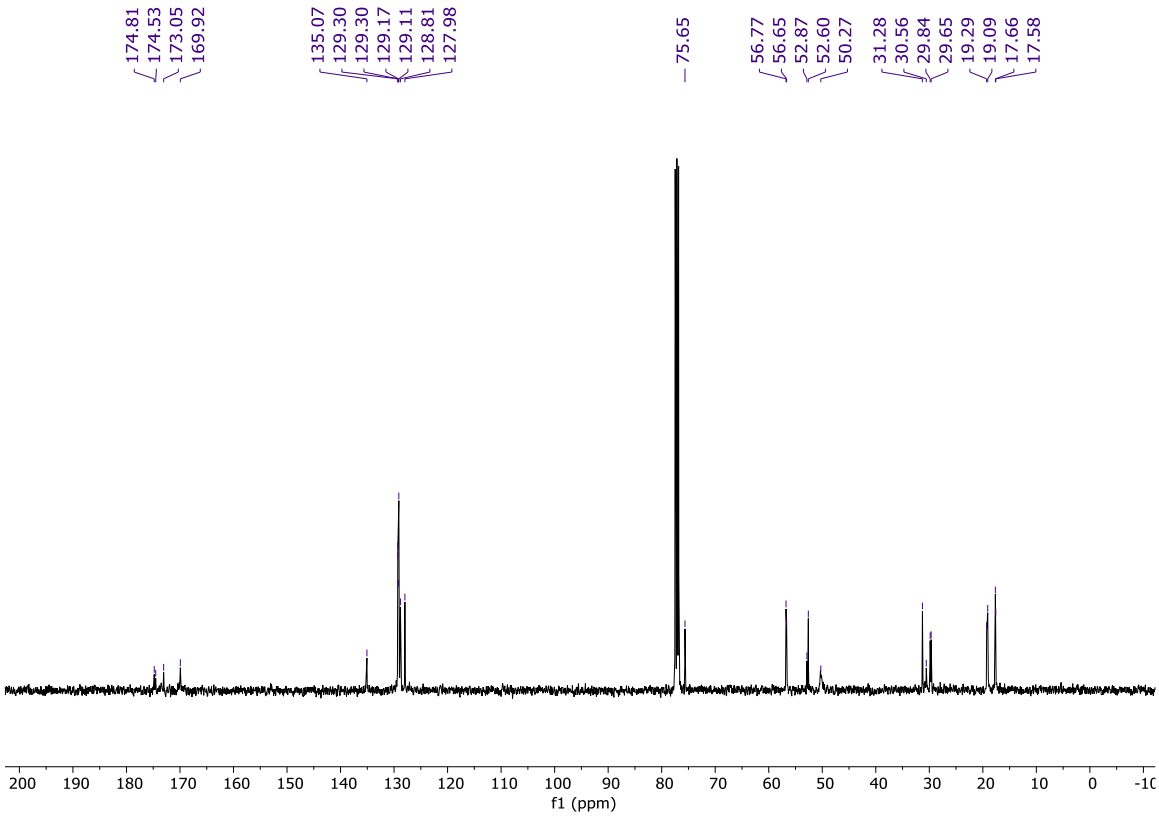
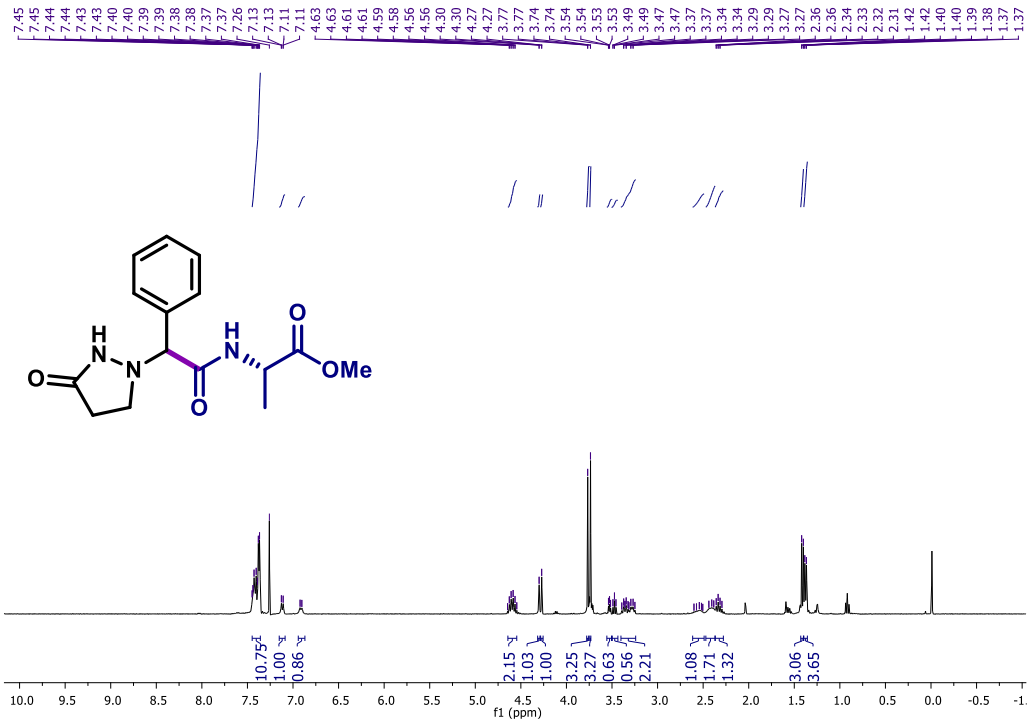
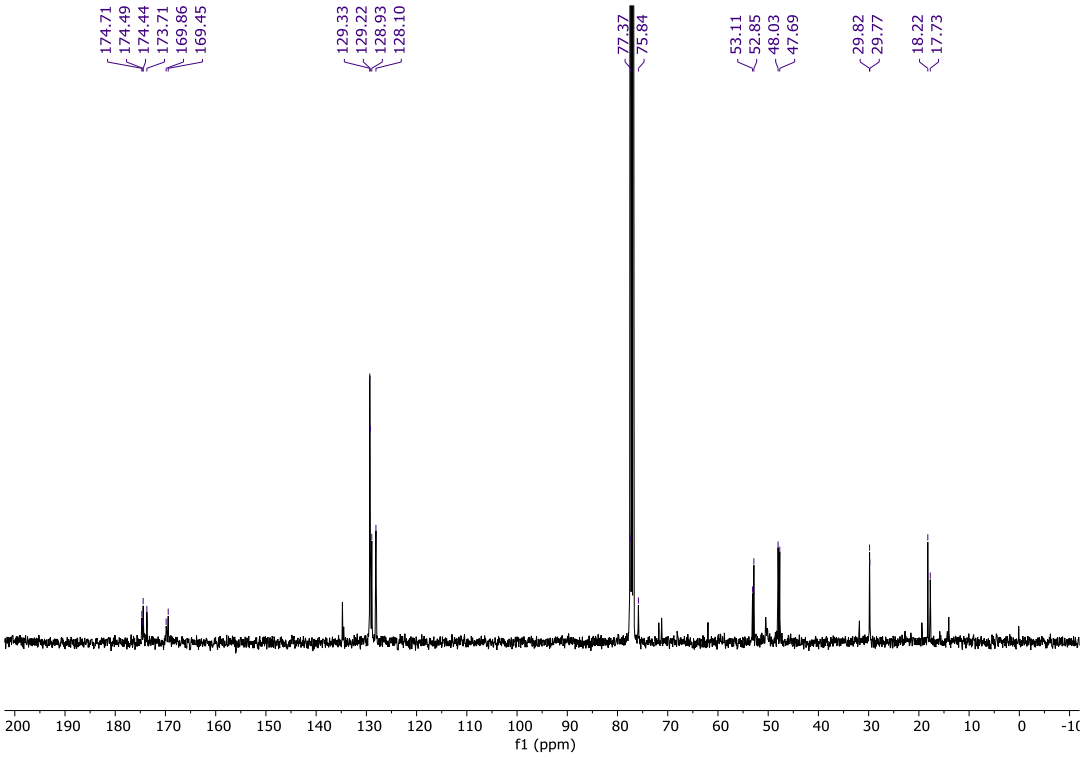


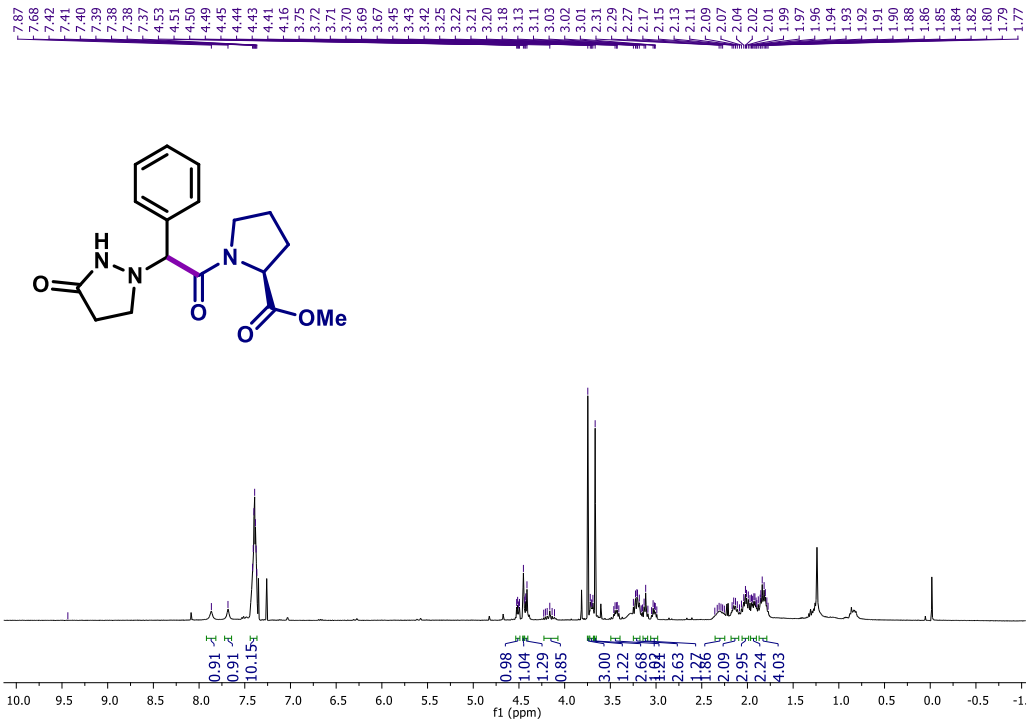
^{13}C NMR ($CDCl_3$, 126 MHz) of 20.



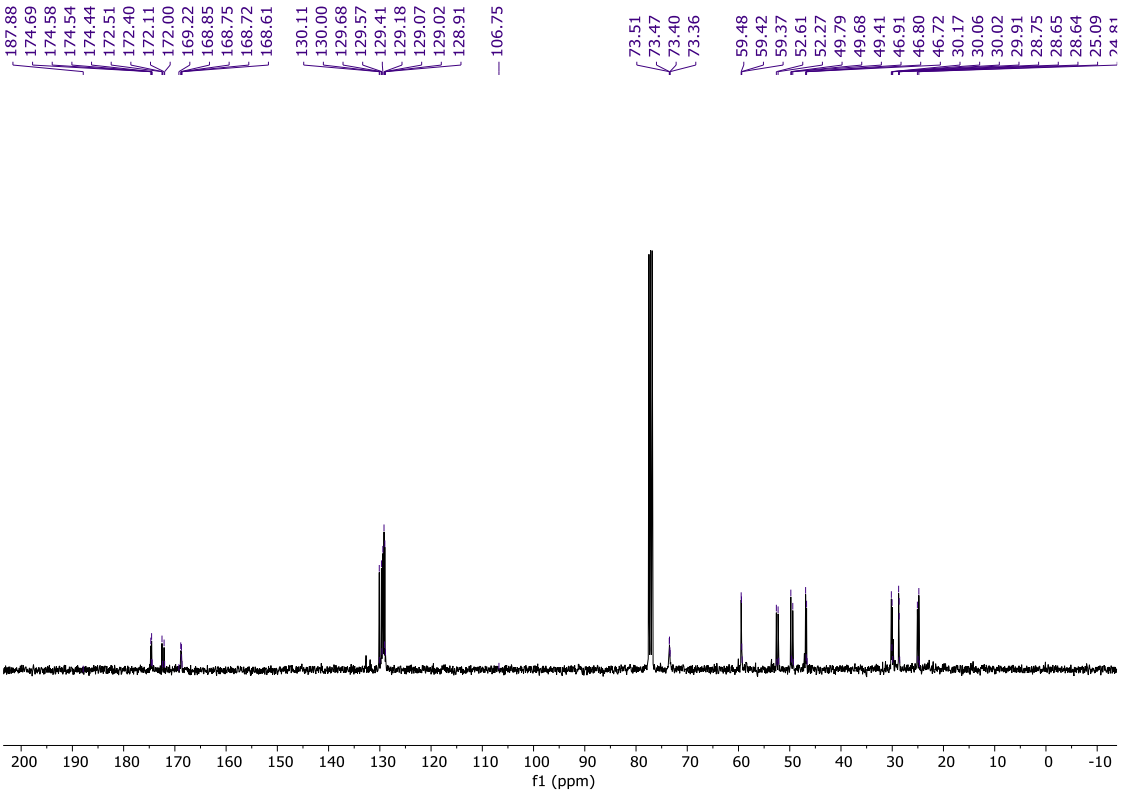
^{1}H NMR ($CDCl_3$, 400 MHz) of 21.



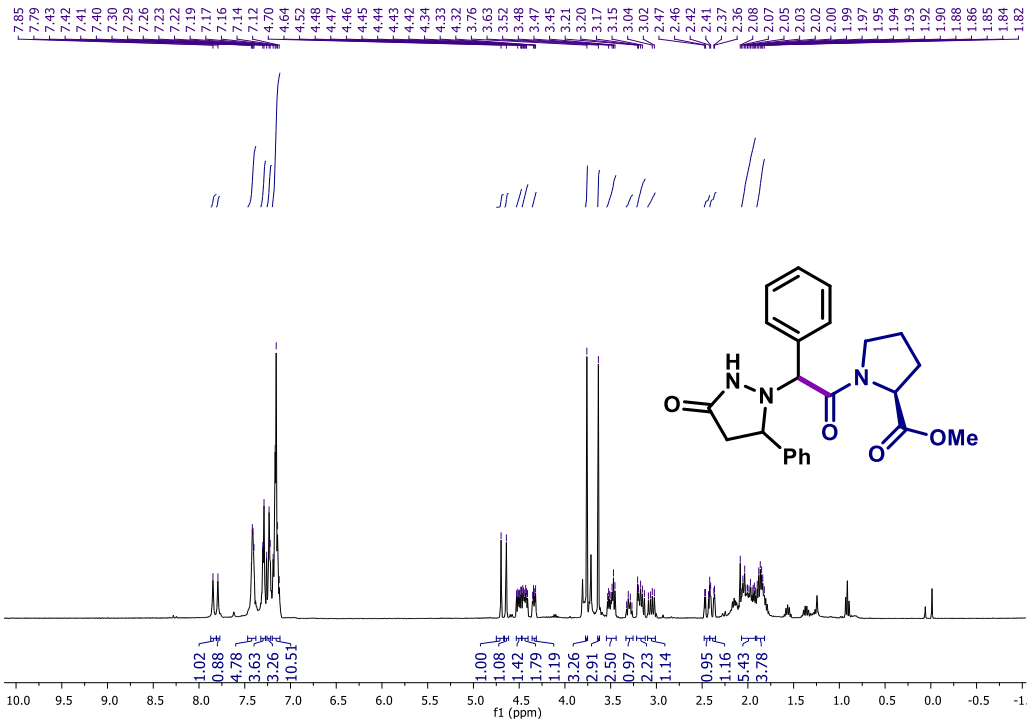
^{13}C NMR ($CDCl_3$, 126 MHz) of 21.



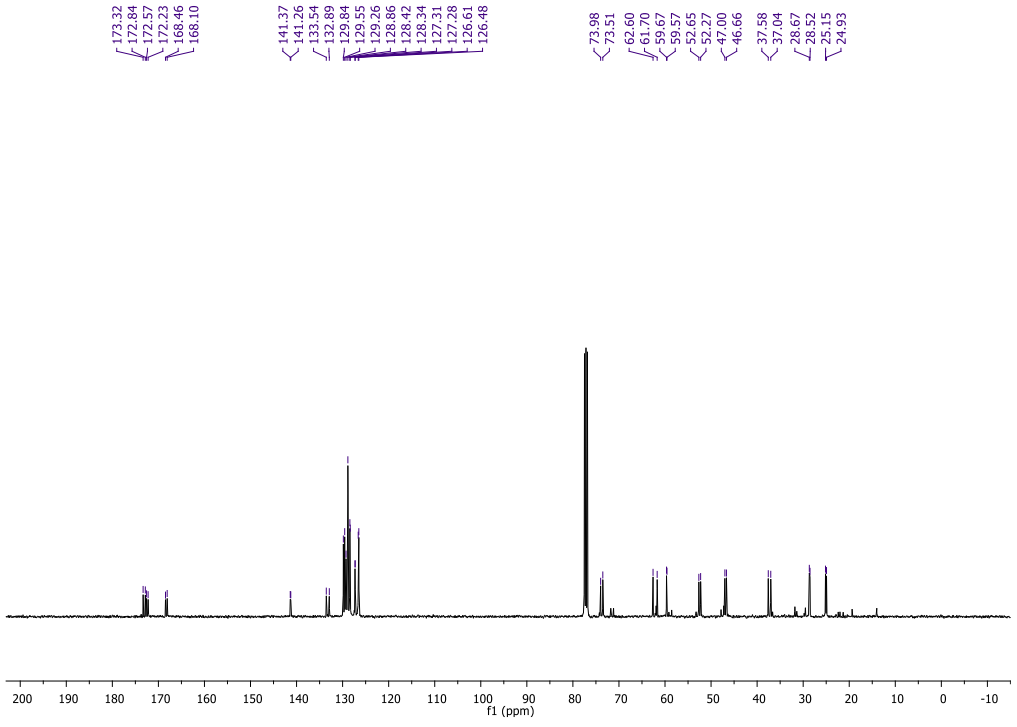
^{1}H NMR ($CDCl_3$, 400 MHz) of 22.



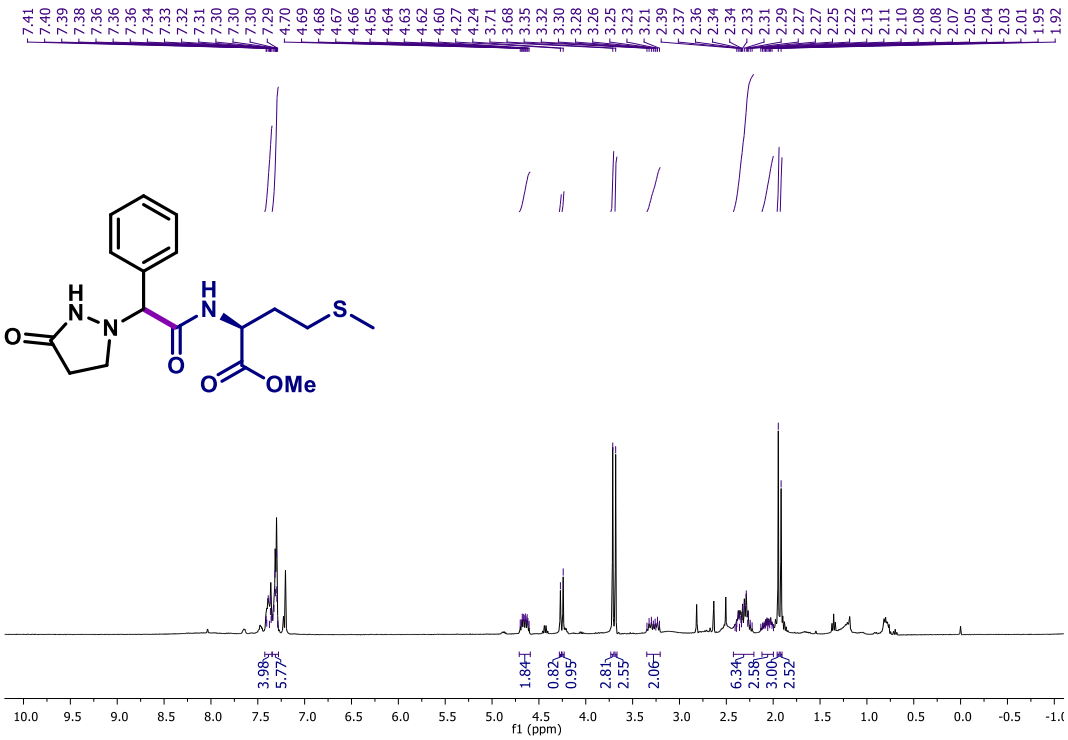
^{13}C NMR ($CDCl_3$, 126 MHz) of 22.



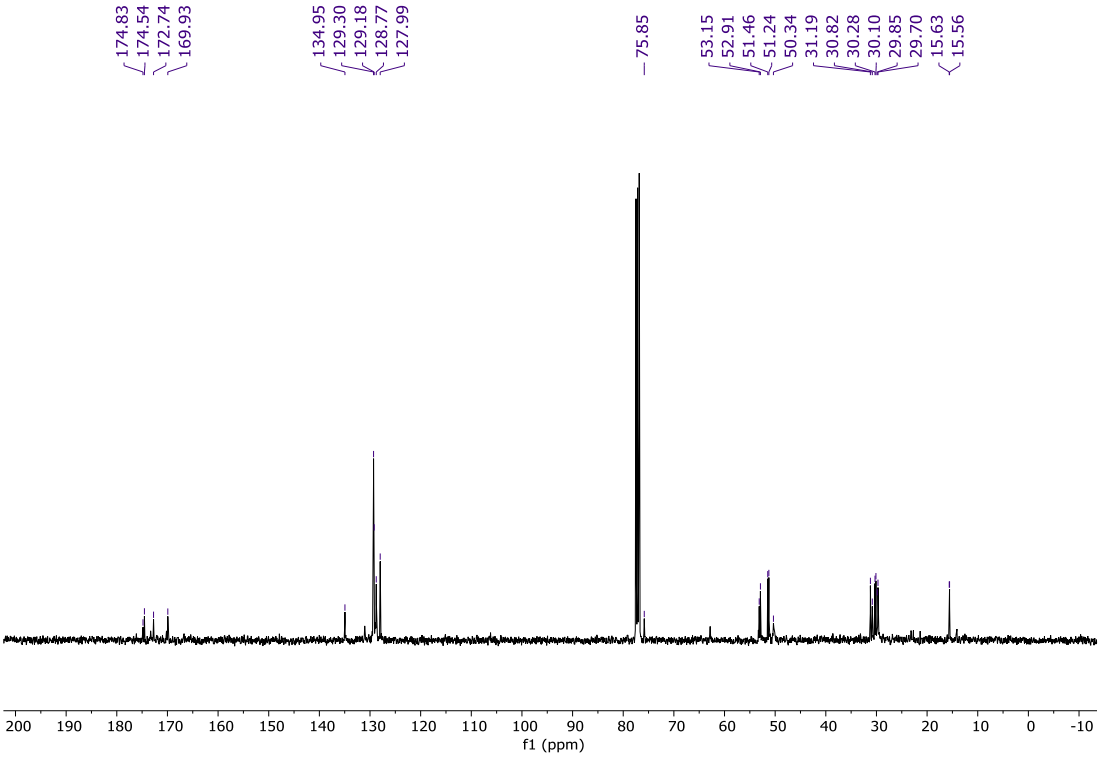
^{1}H NMR ($CDCl_3$, 400 MHz) of 23.



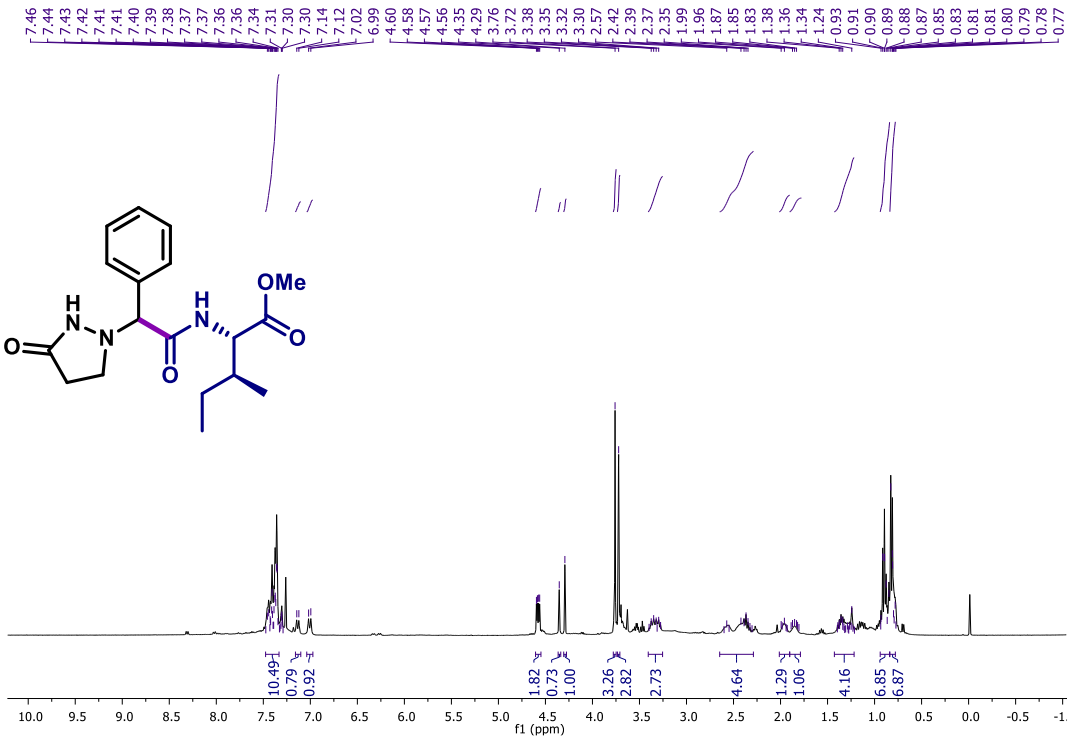
^{13}C NMR ($CDCl_3$, 126 MHz) of 23.



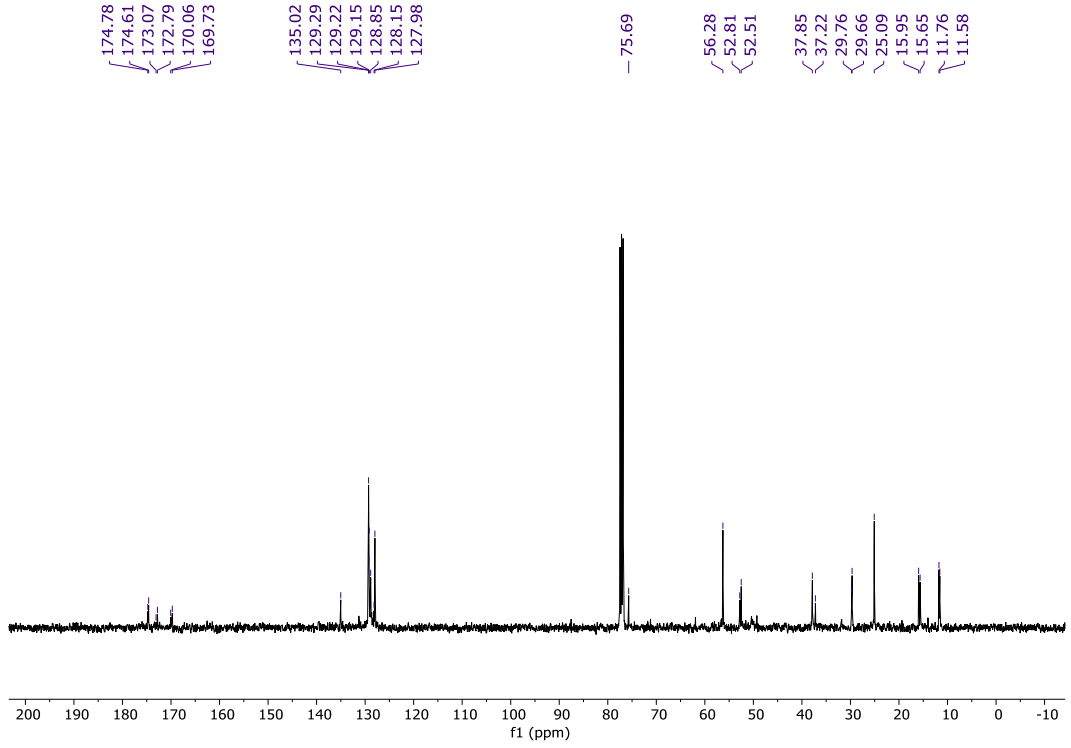
^{1}H NMR ($CDCl_3$, 400 MHz) of 24.



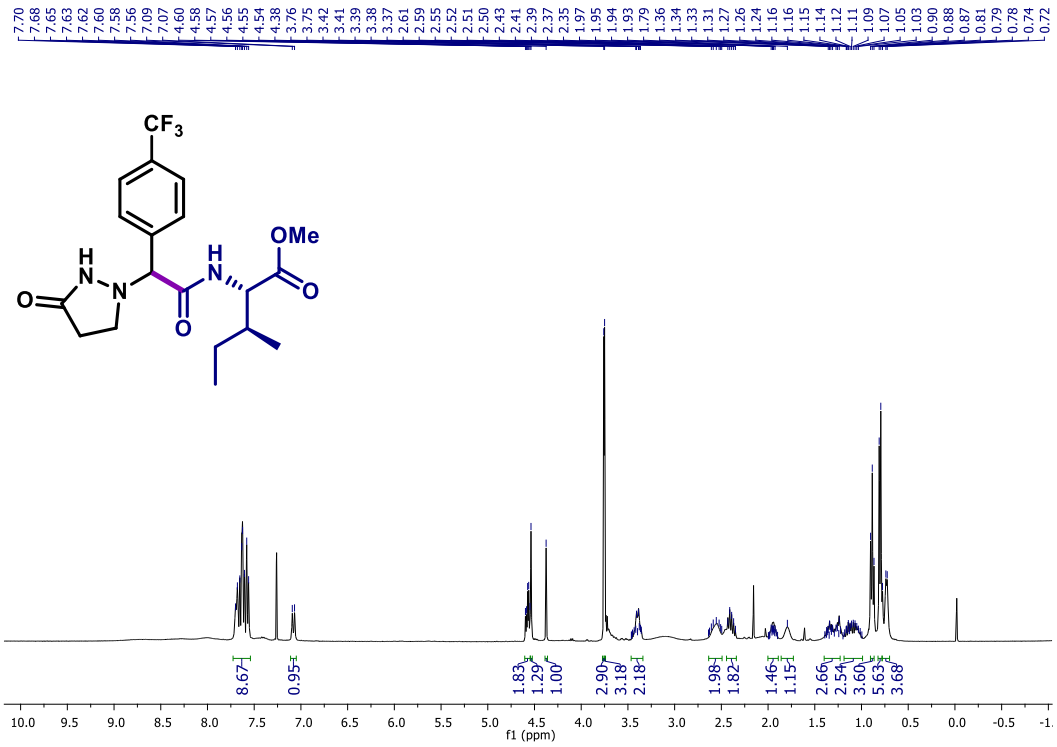
^{13}C NMR ($CDCl_3$, 126 MHz) of 24.



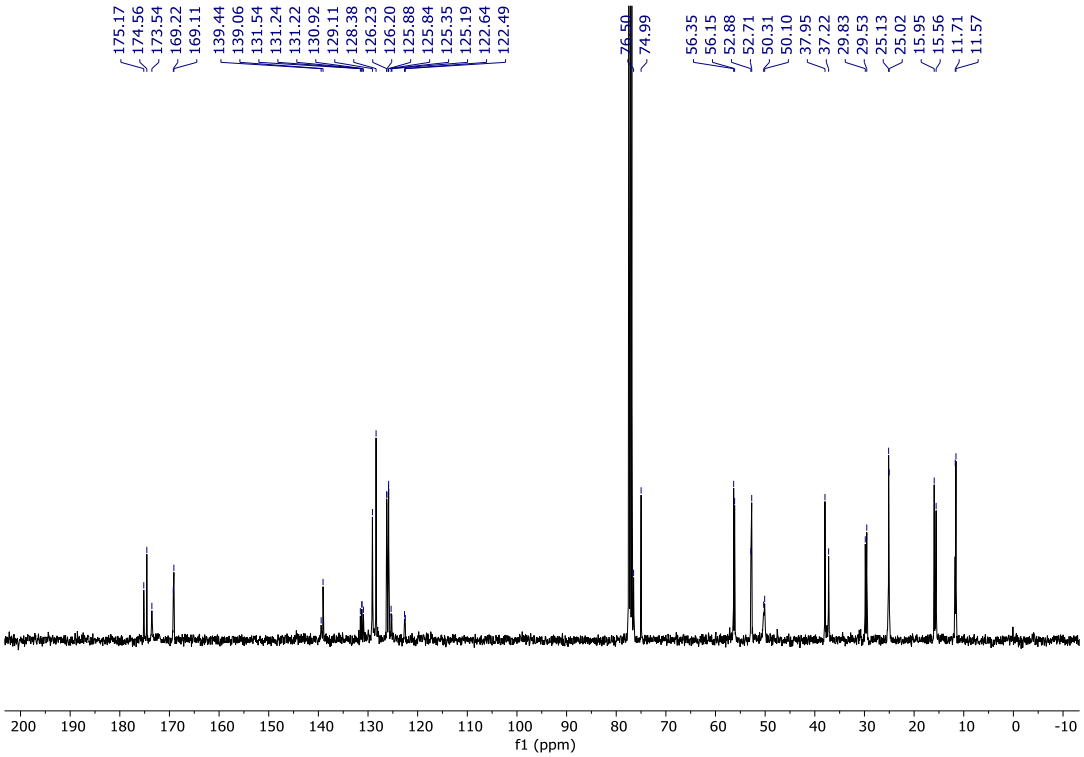
^{1}H NMR ($CDCl_3$, 400 MHz) of 25.



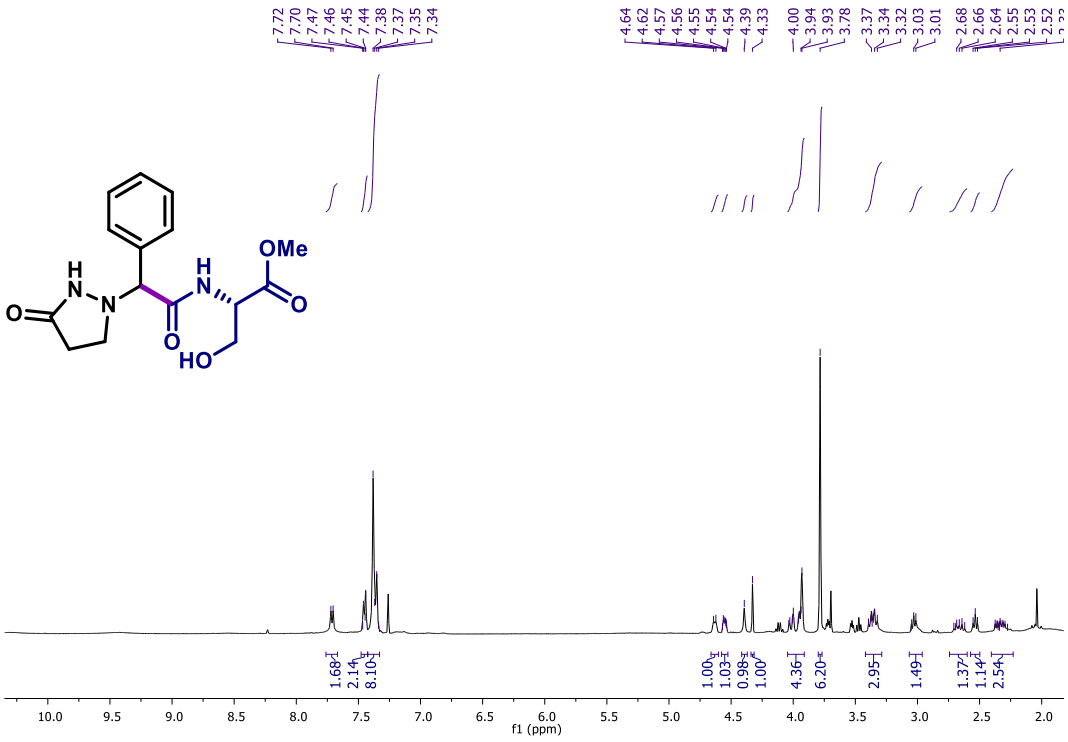
^{13}C NMR ($CDCl_3$, 126 MHz) of 25.



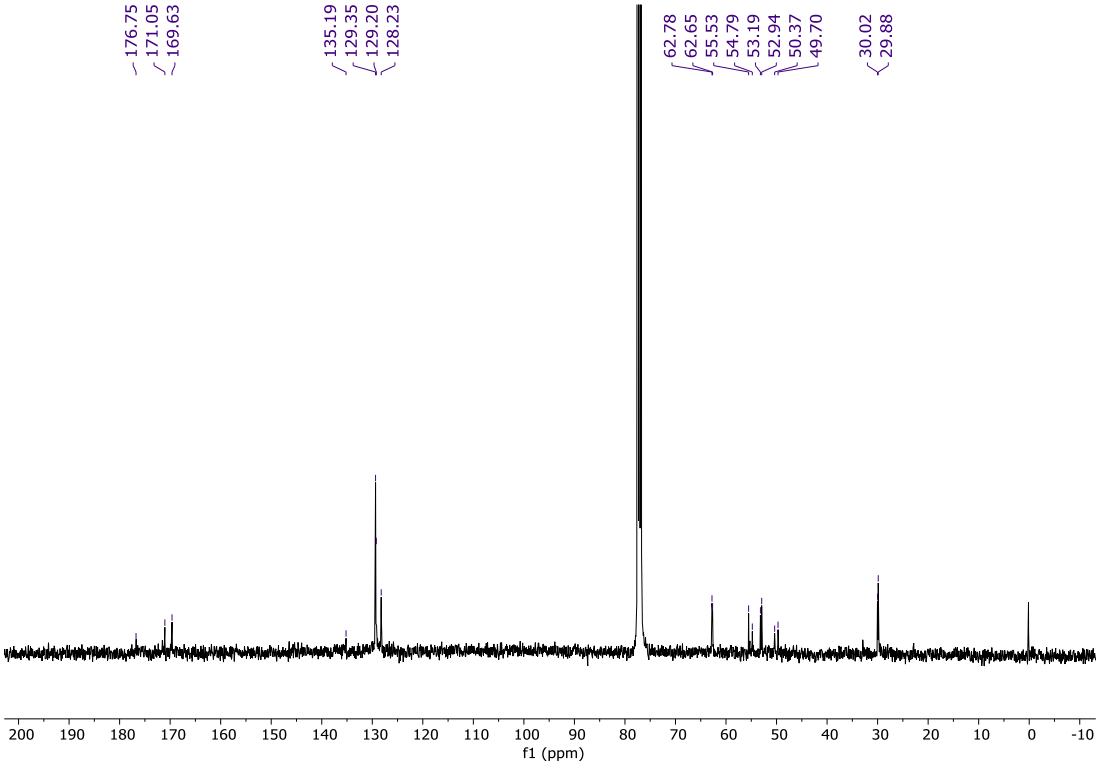
^{1}H NMR ($CDCl_3$, 400 MHz) of 26.



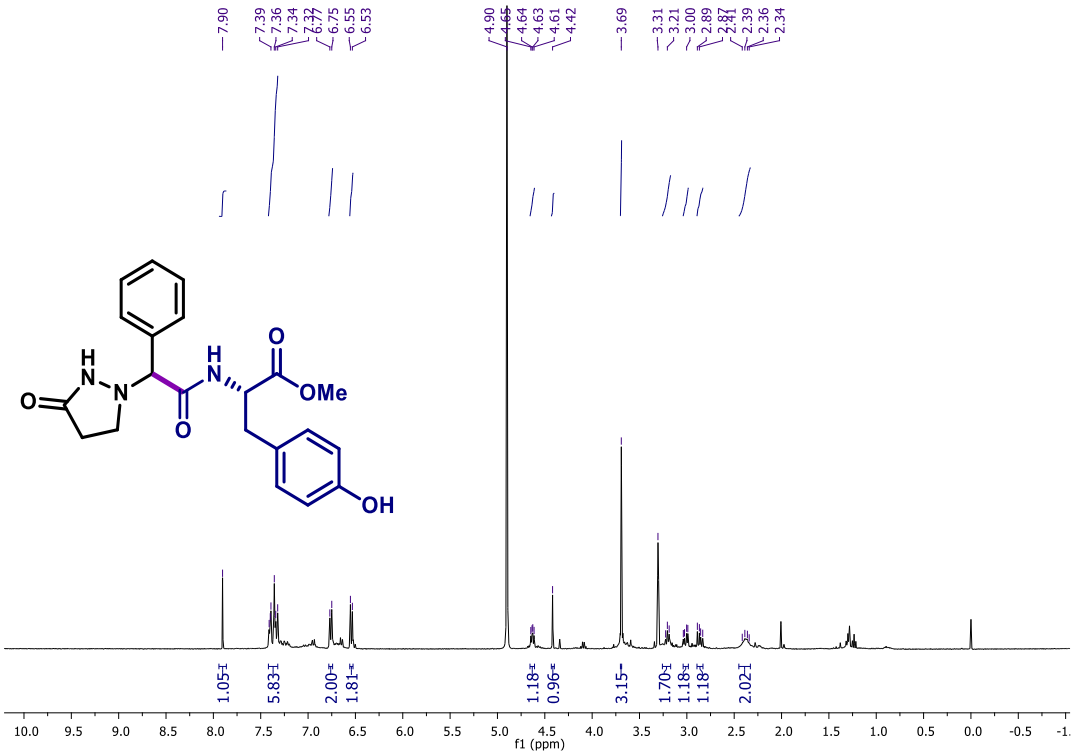
^{13}C NMR ($CDCl_3$, 126 MHz) of 26.



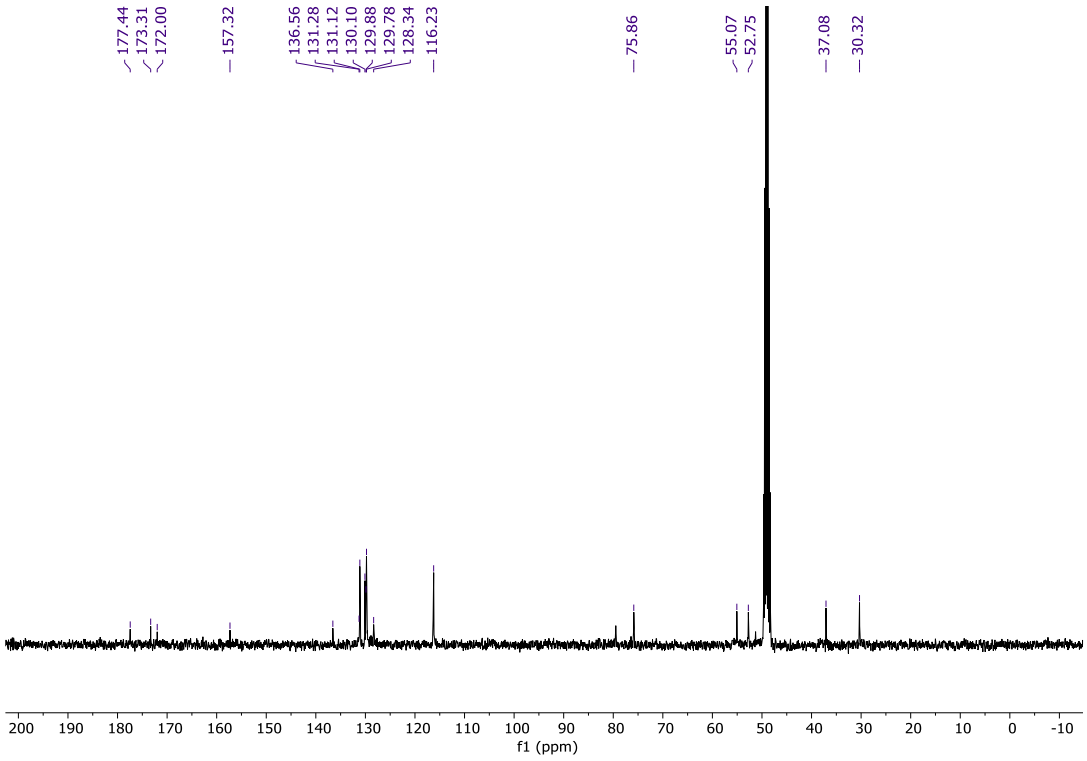
^{1}H NMR ($CDCl_3$, 400 MHz) of 27.



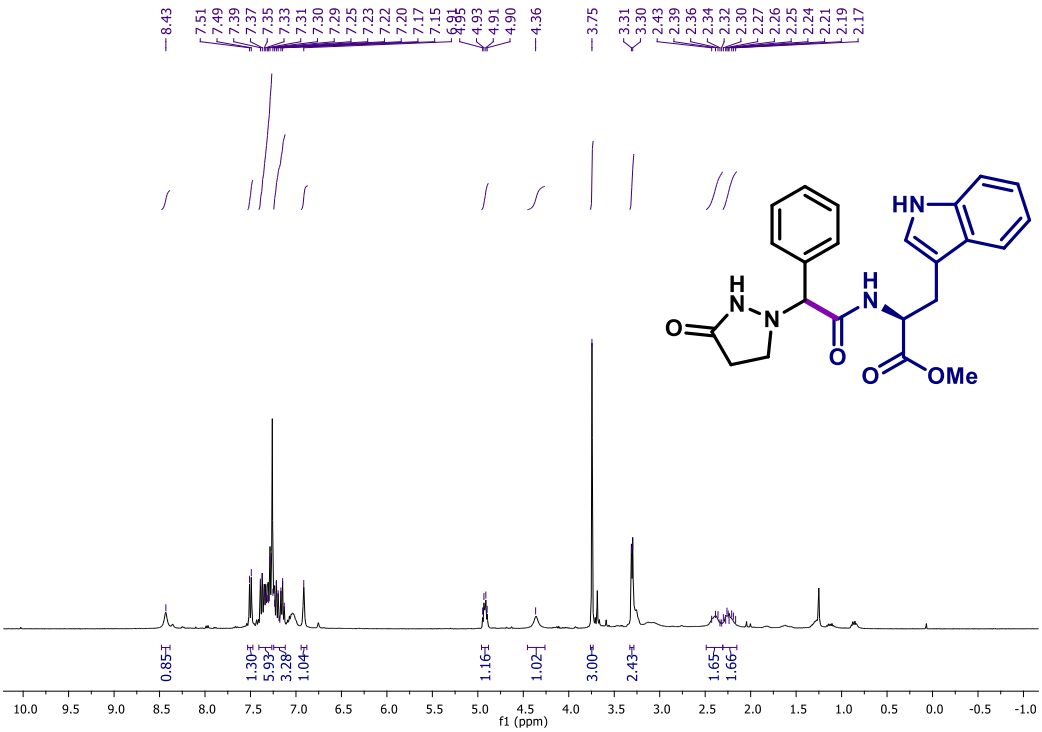
^{13}C NMR ($CDCl_3$, 126 MHz) of 27.



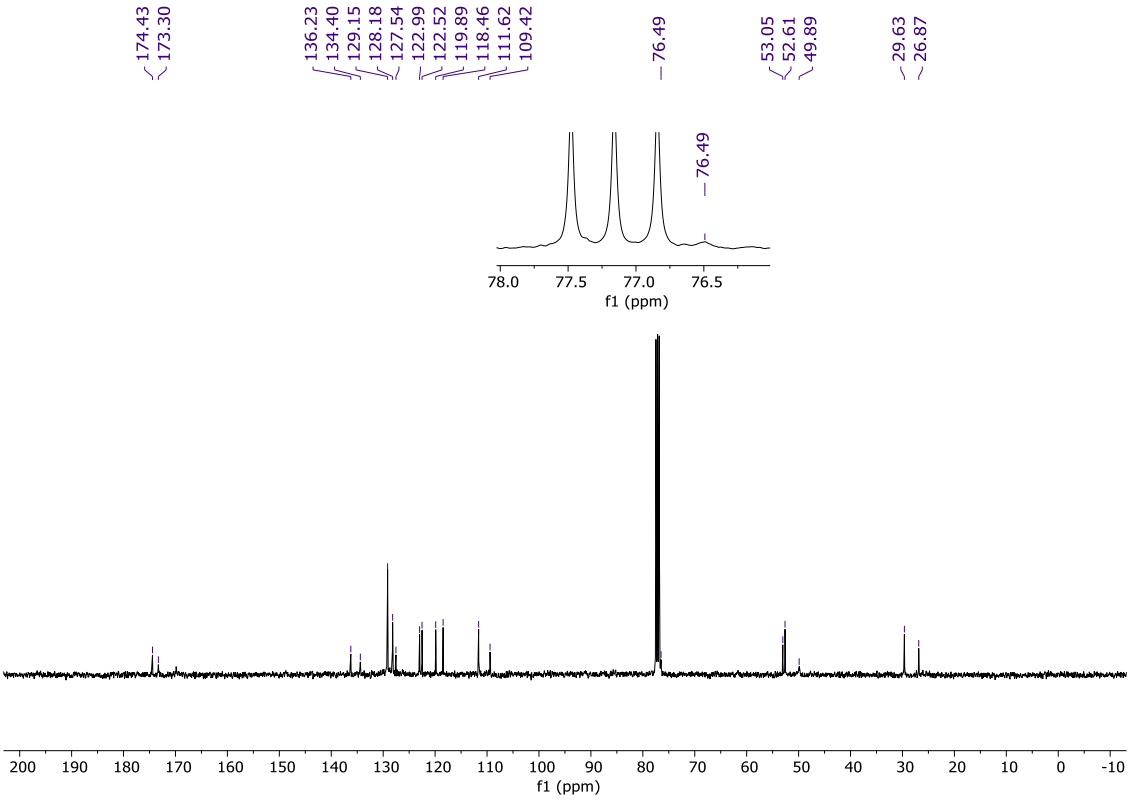
^{1}H NMR (CD_3OD, 400 MHz) of 28.



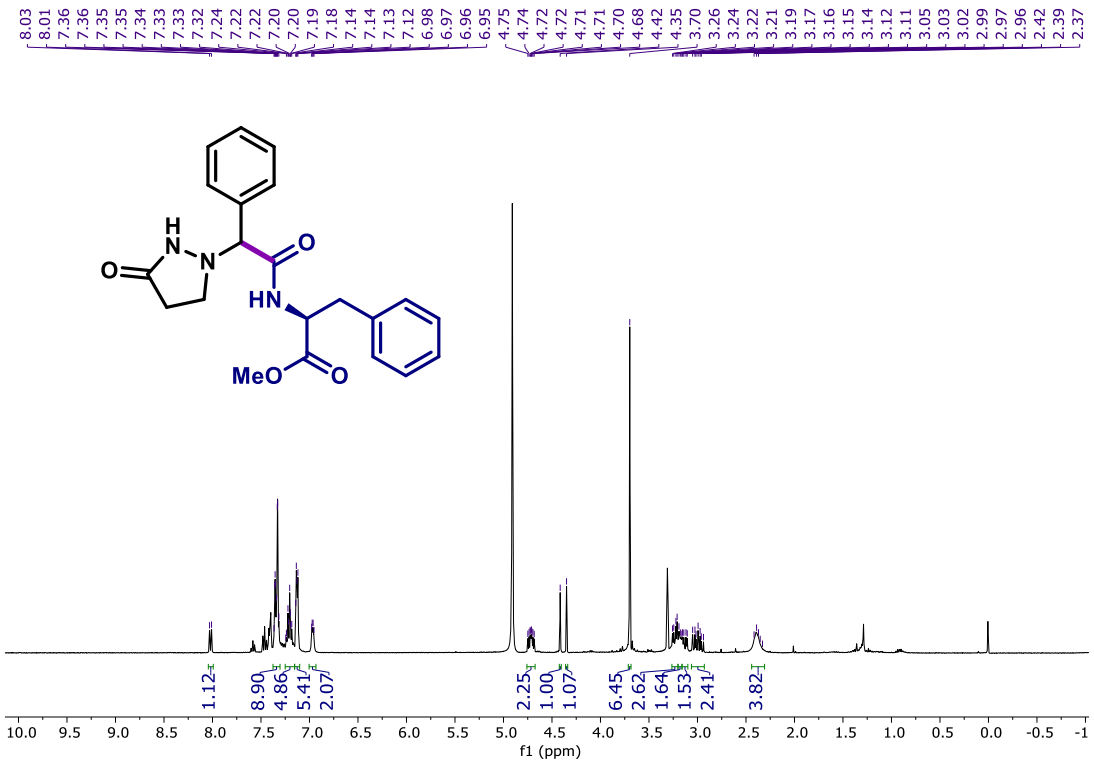
^{13}C NMR (CD_3OD, 126 MHz) of 28.



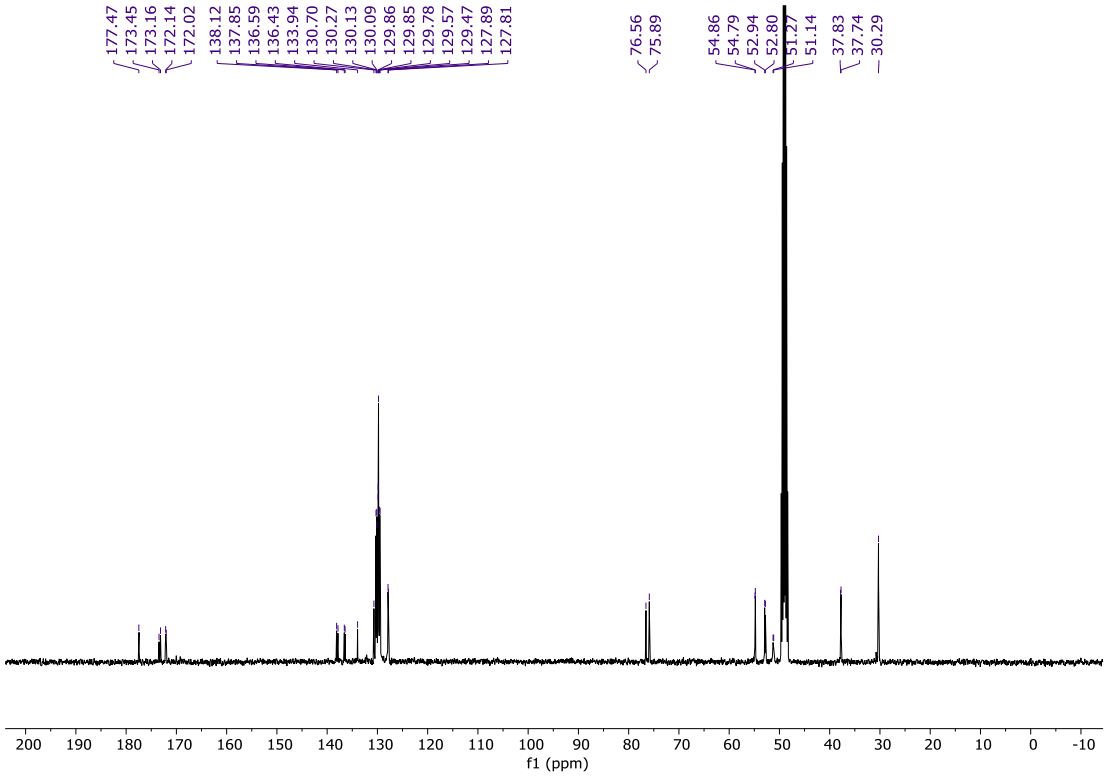
^{1}H NMR ($CDCl_3$, 400 MHz) of 29.



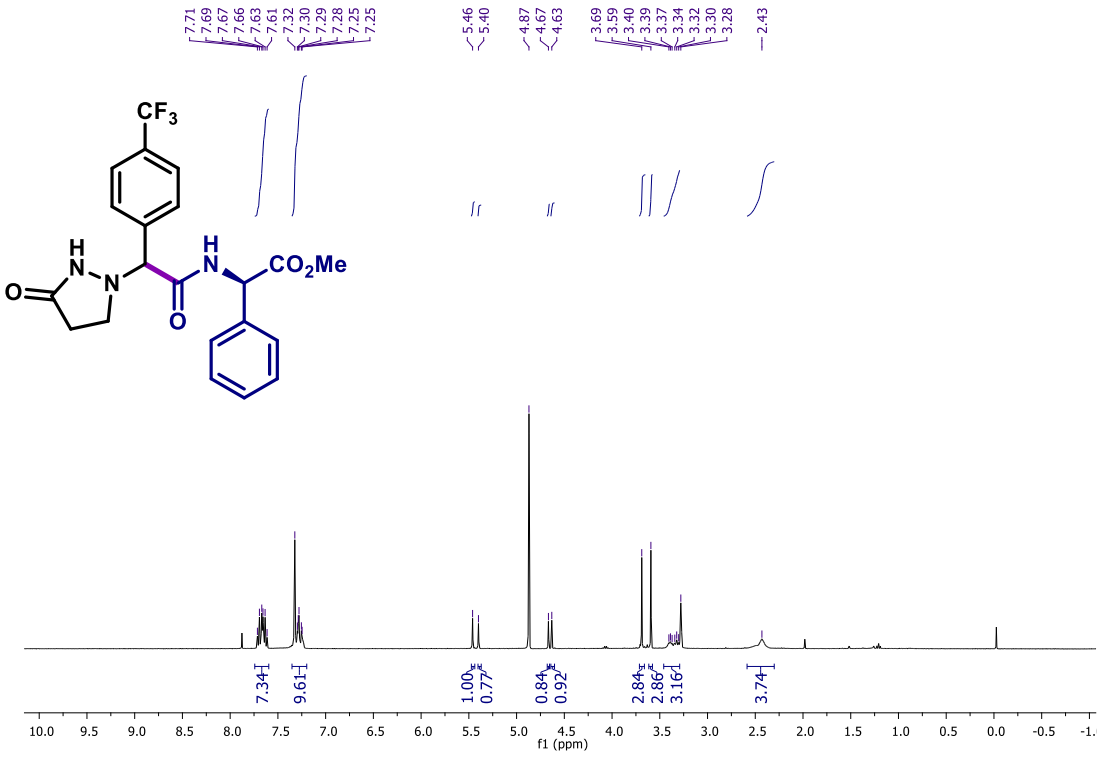
^{13}C NMR ($CDCl_3$, 126 MHz) of 29.



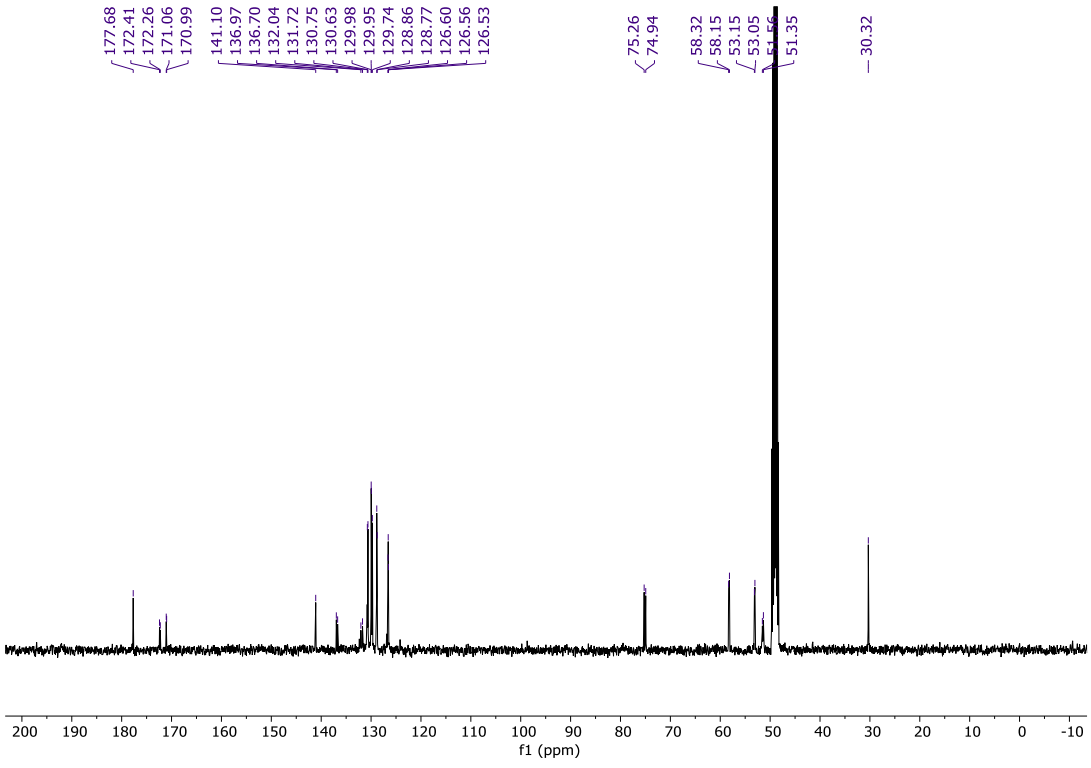
^{1}H NMR (CD_3OD, 400 MHz) of 30.



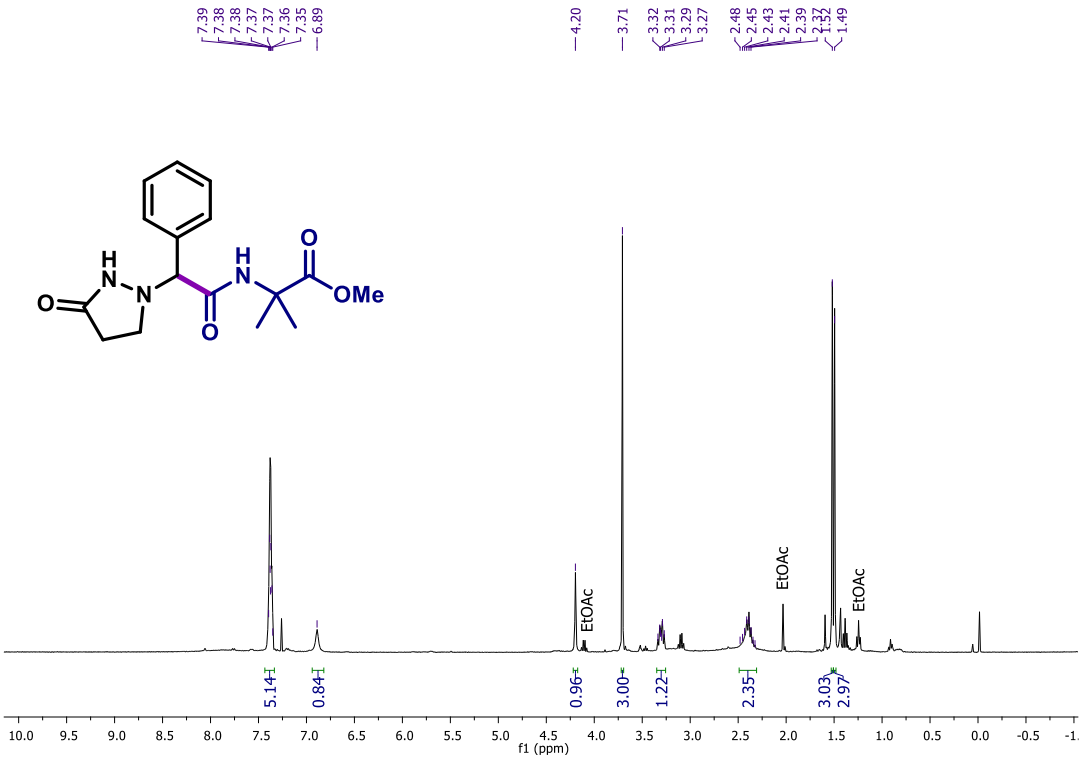
^{13}C NMR (CD_3OD, 126 MHz) of 30.



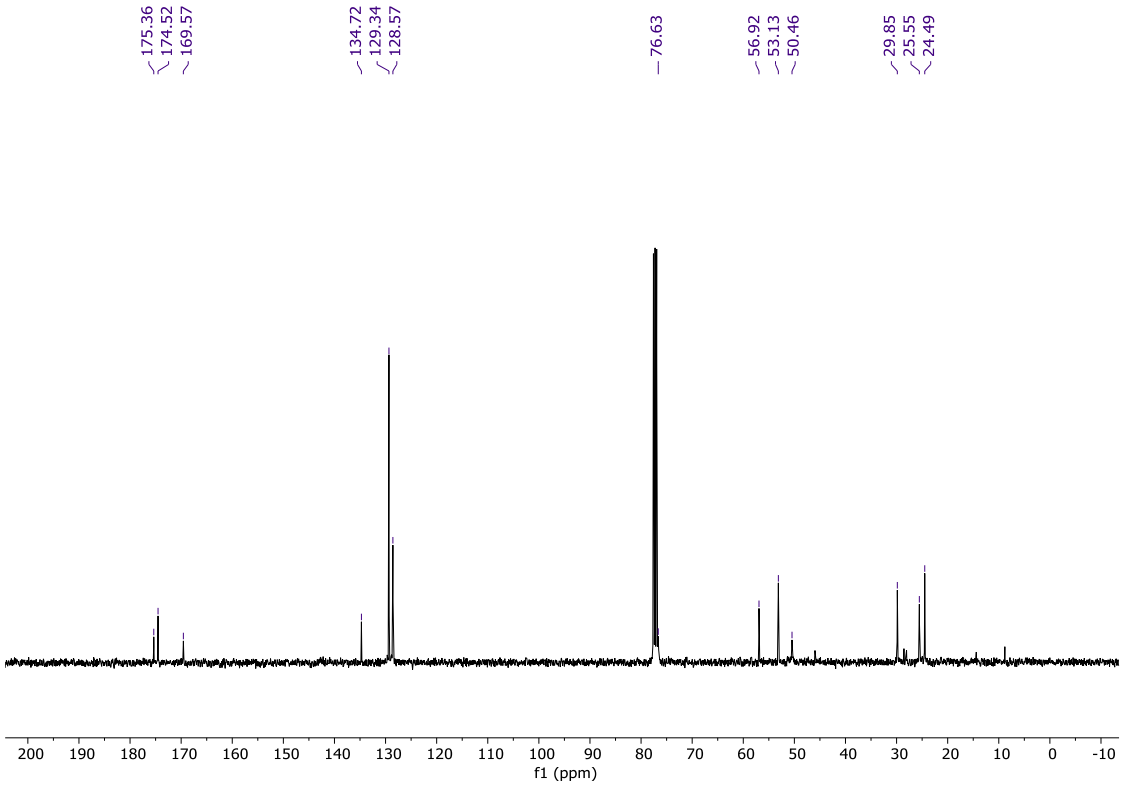
^{1}H NMR (CD_3OD, 400 MHz) of 31.



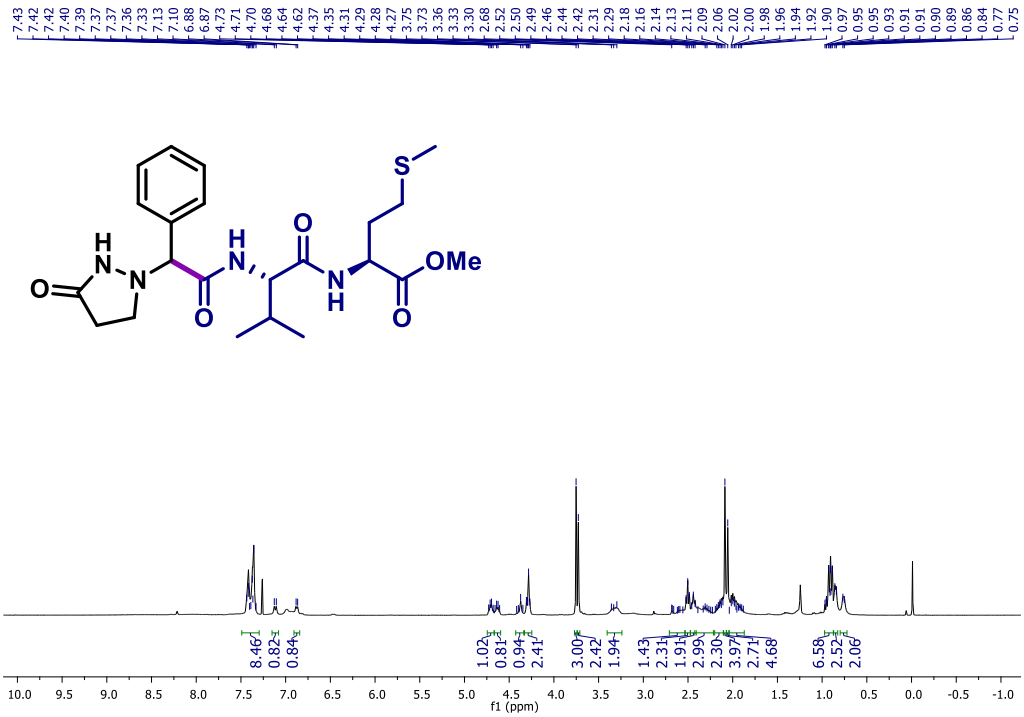
^{13}C NMR (CD_3OD, 126 MHz) of 31.



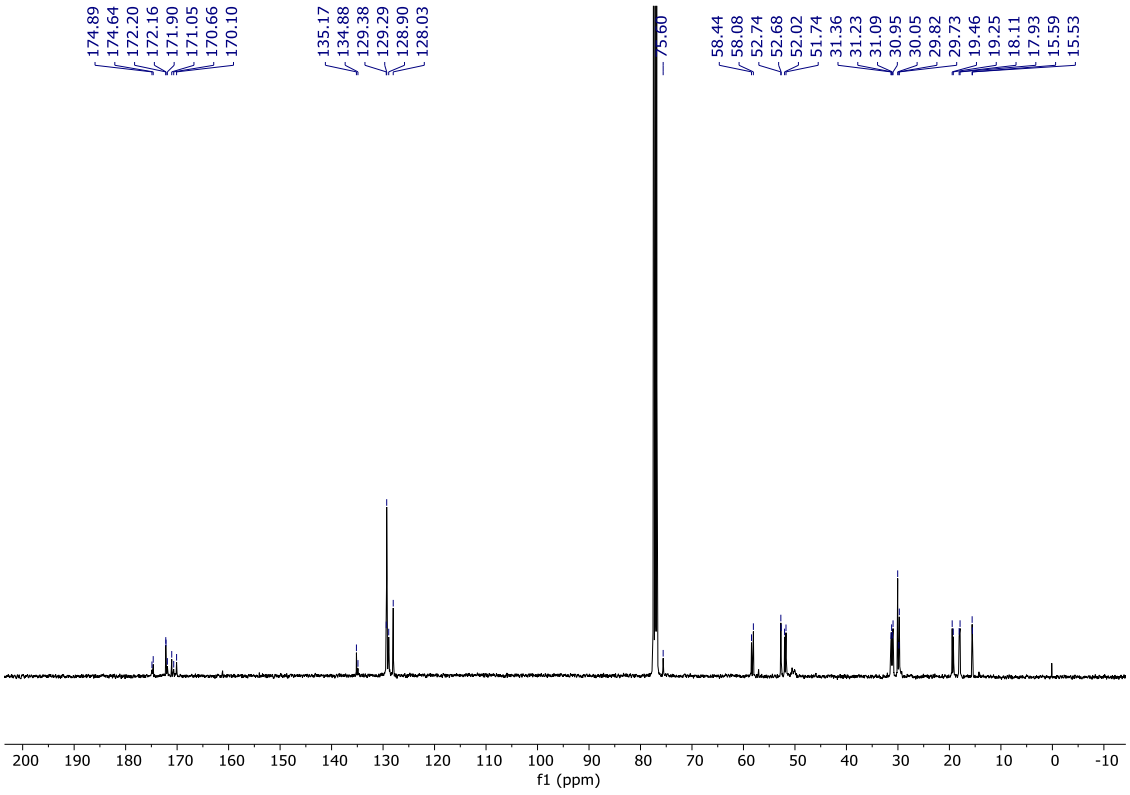
^{1}H NMR ($CDCl_3$, 400 MHz) of 32.



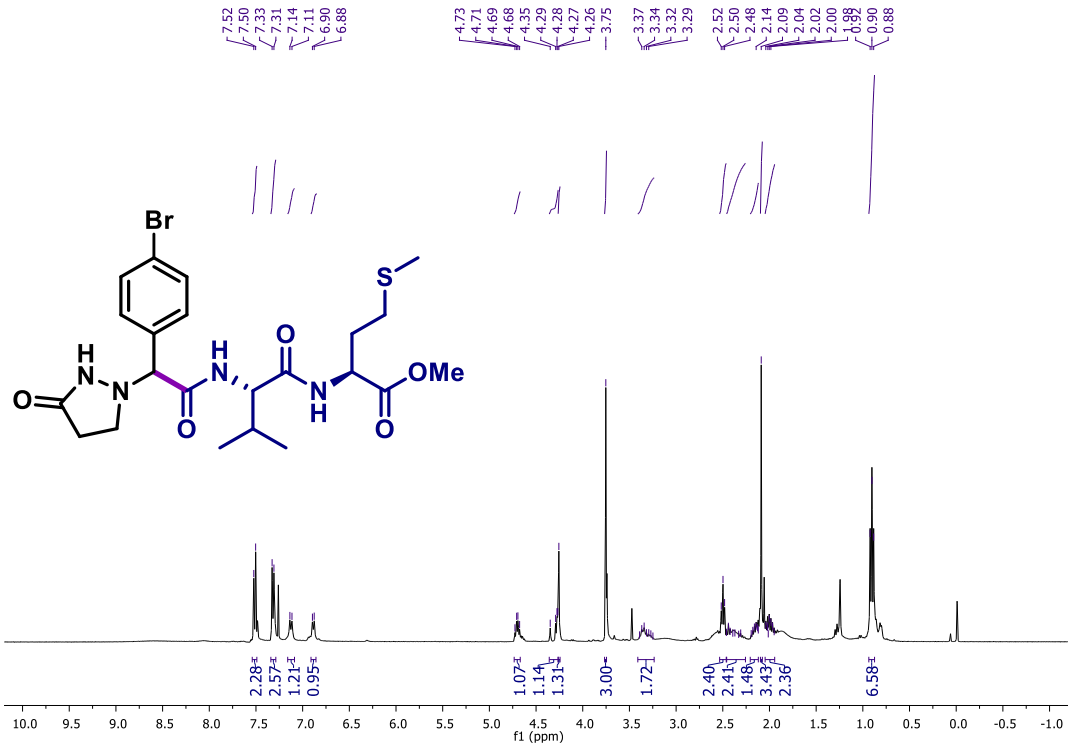
^{13}C NMR ($CDCl_3$, 126 MHz) of 32.



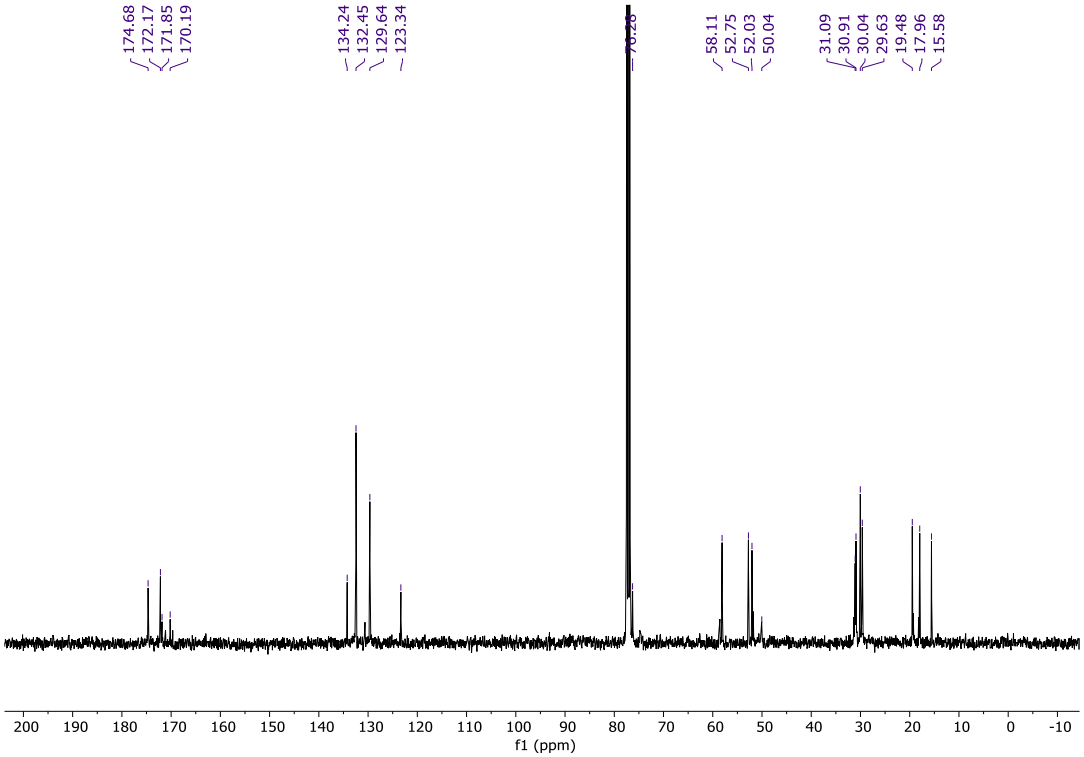
^{1}H NMR ($CDCl_3$, 400 MHz) of 33.



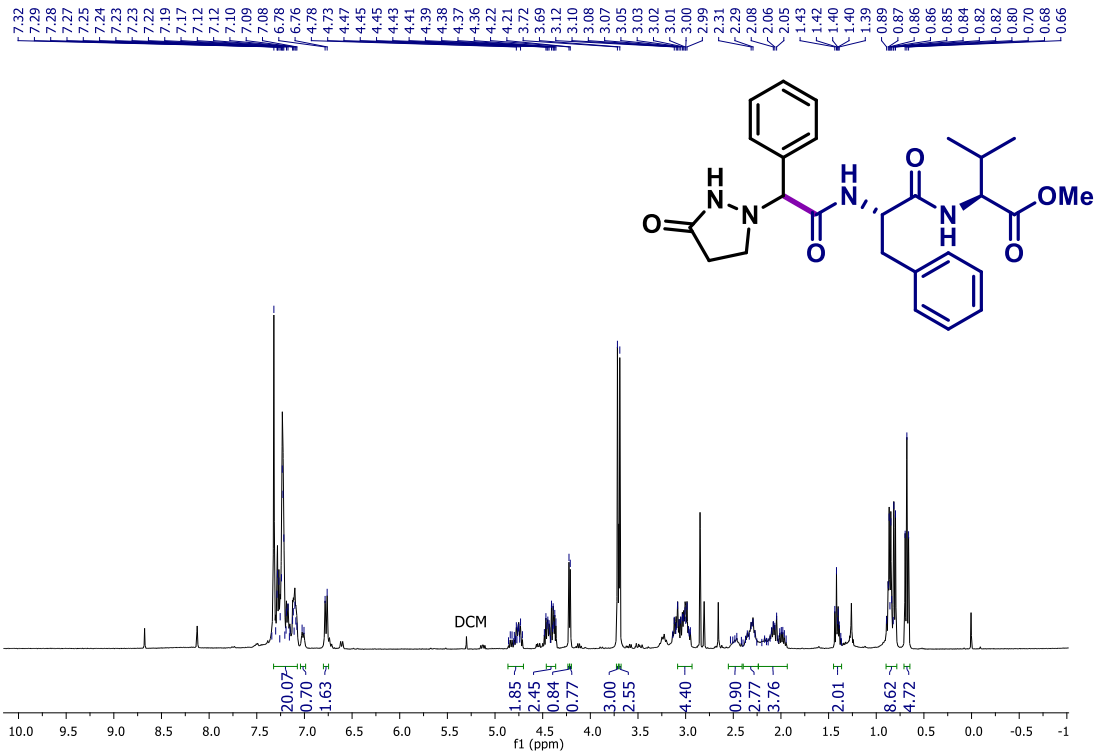
^{13}C NMR ($CDCl_3$, 126 MHz) of 33.



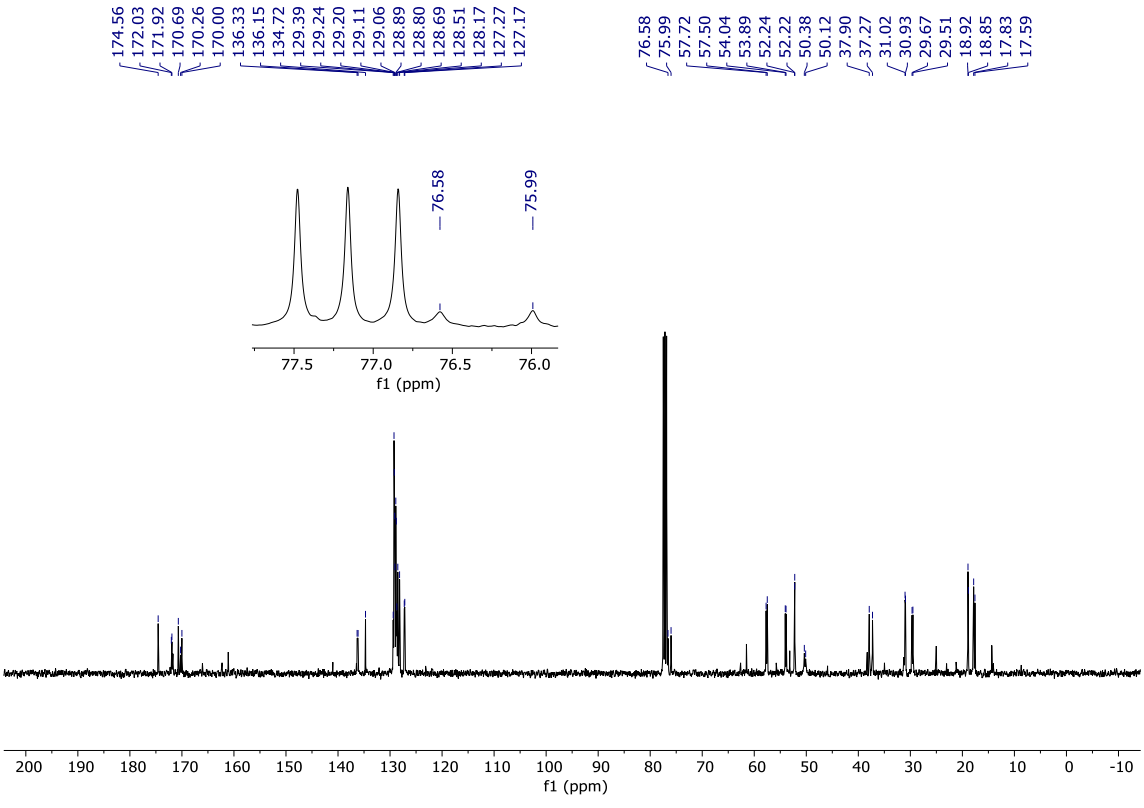
^{1}H NMR ($CDCl_3$, 400 MHz) of 34.



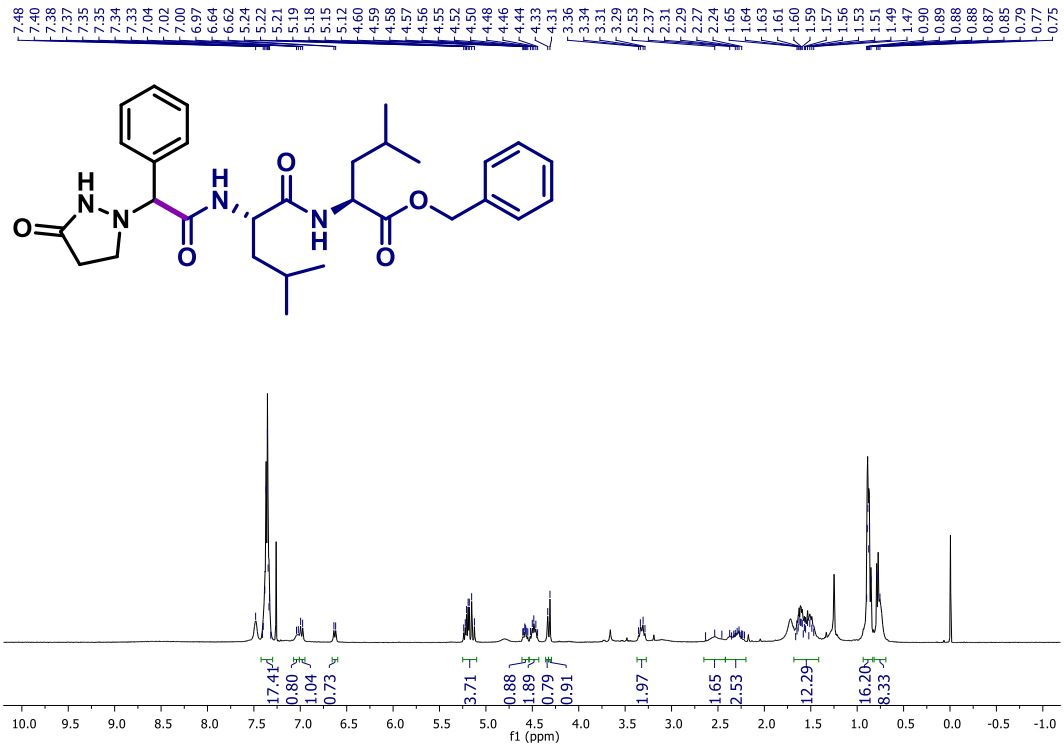
^{13}C NMR ($CDCl_3$, 126 MHz) of 34.



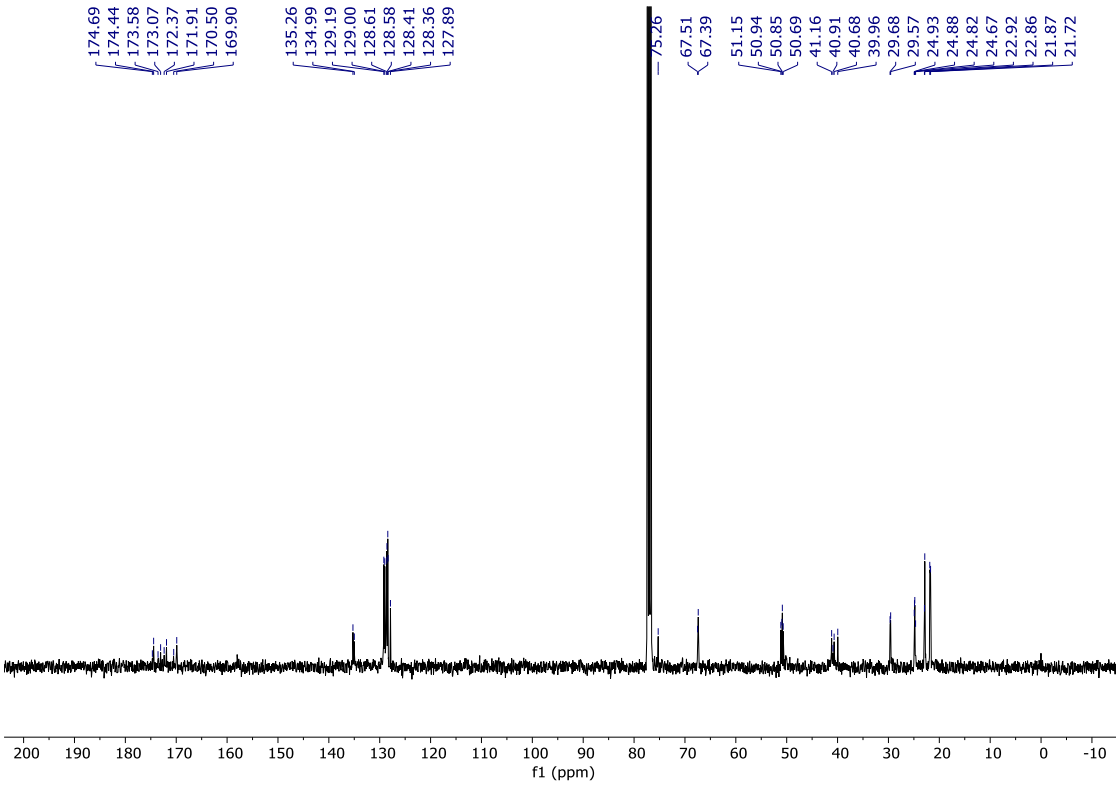
^{1}H NMR ($CDCl_3$, 400 MHz) of 35.



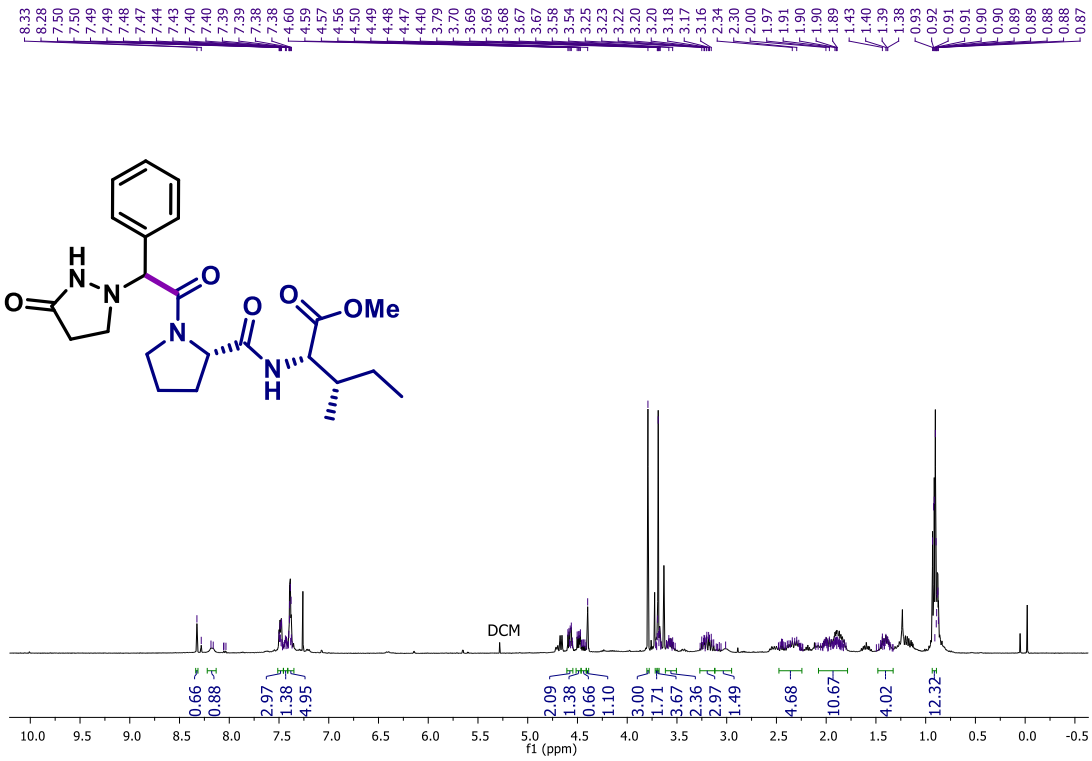
^{13}C NMR ($CDCl_3$, 126 MHz) of 35.



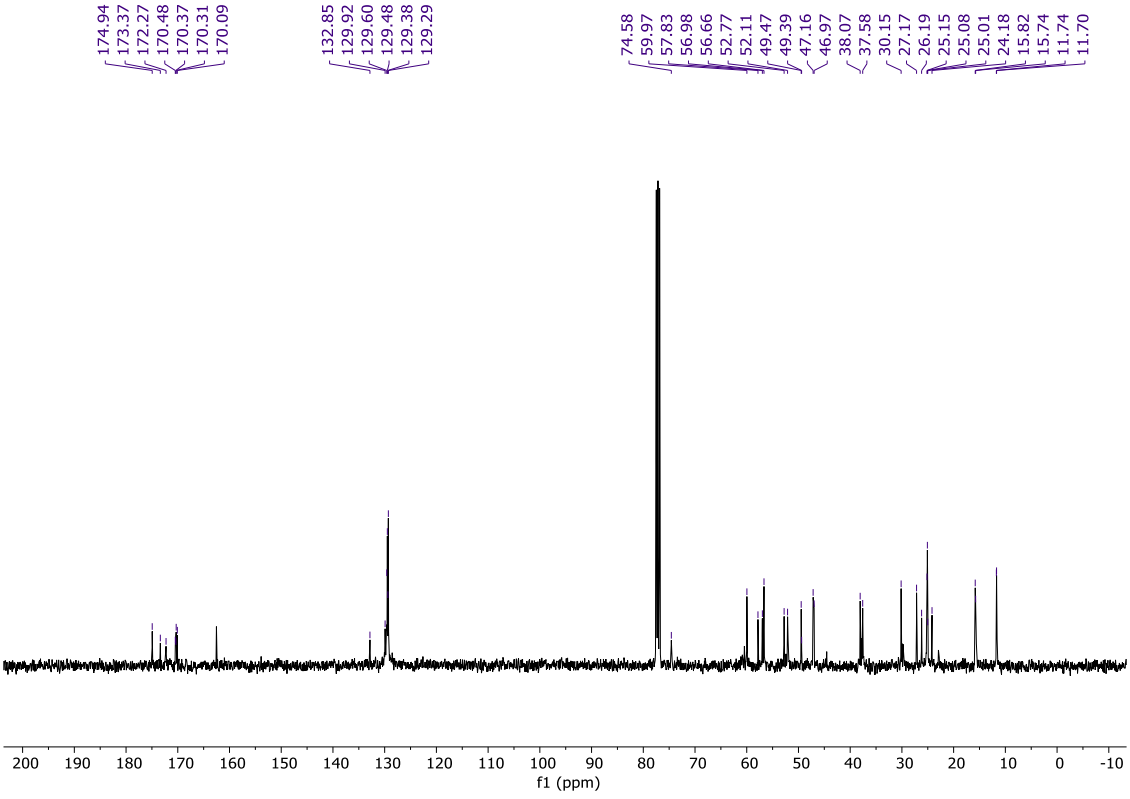
^{1}H NMR ($CDCl_3$, 400 MHz) of 36.



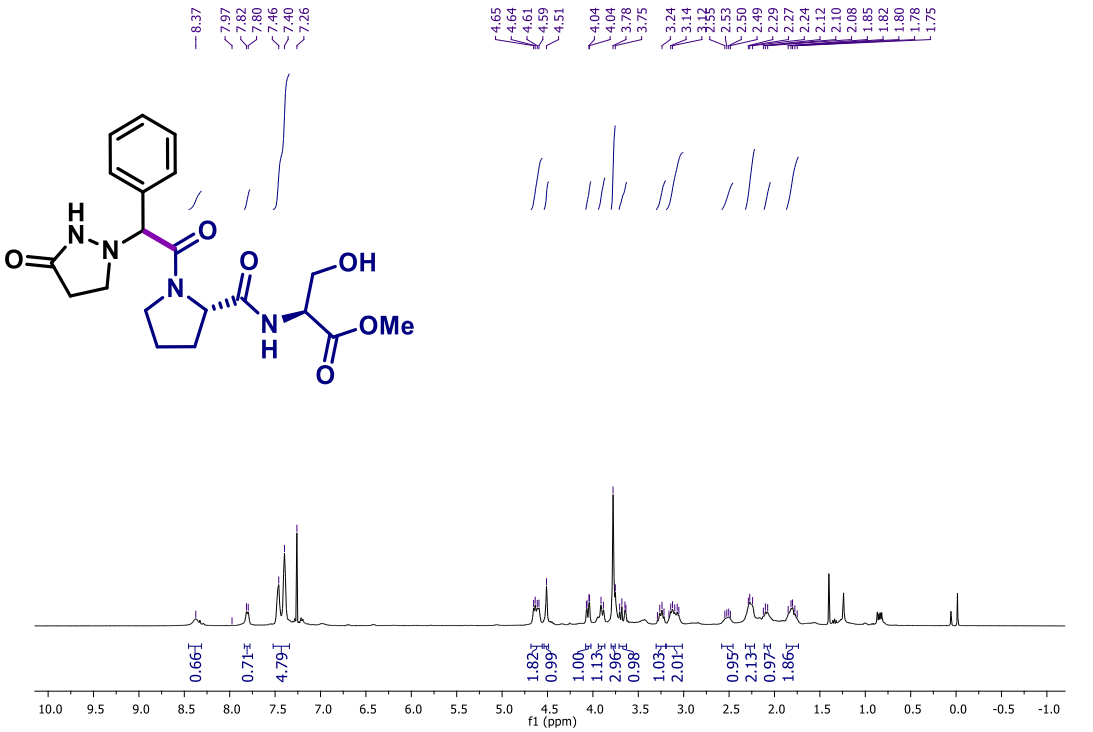
^{13}C NMR ($CDCl_3$, 126 MHz) of 36.



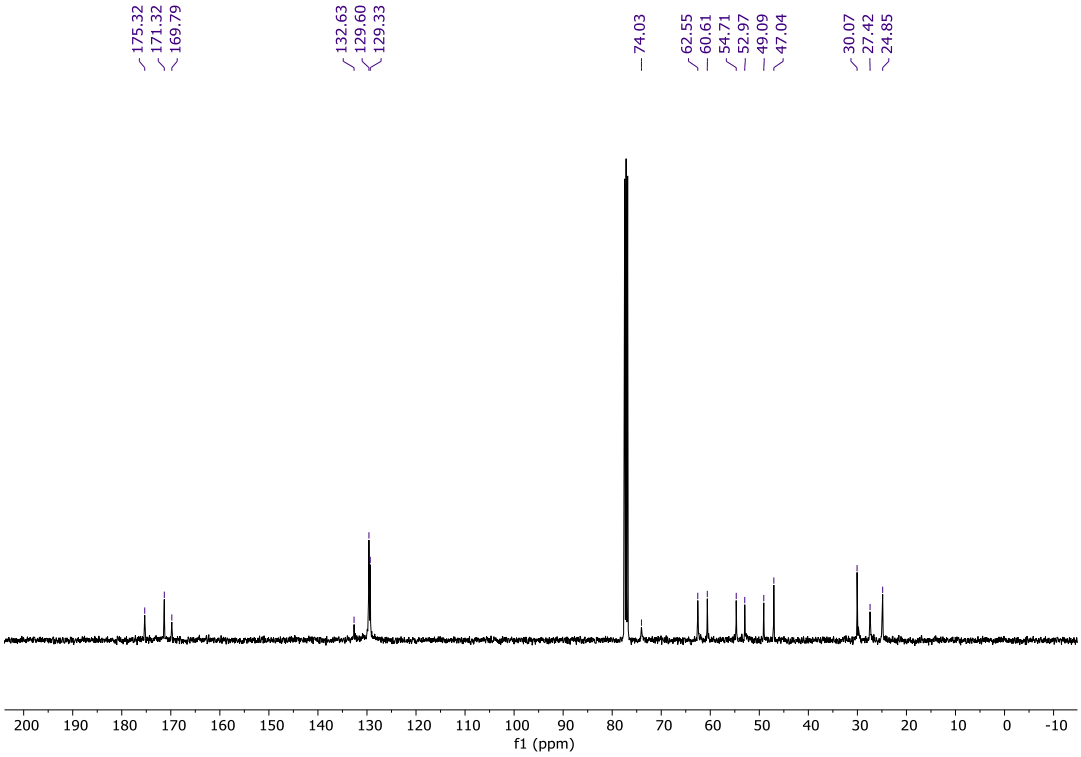
^{1}H NMR ($CDCl_3$, 400 MHz) of 37.



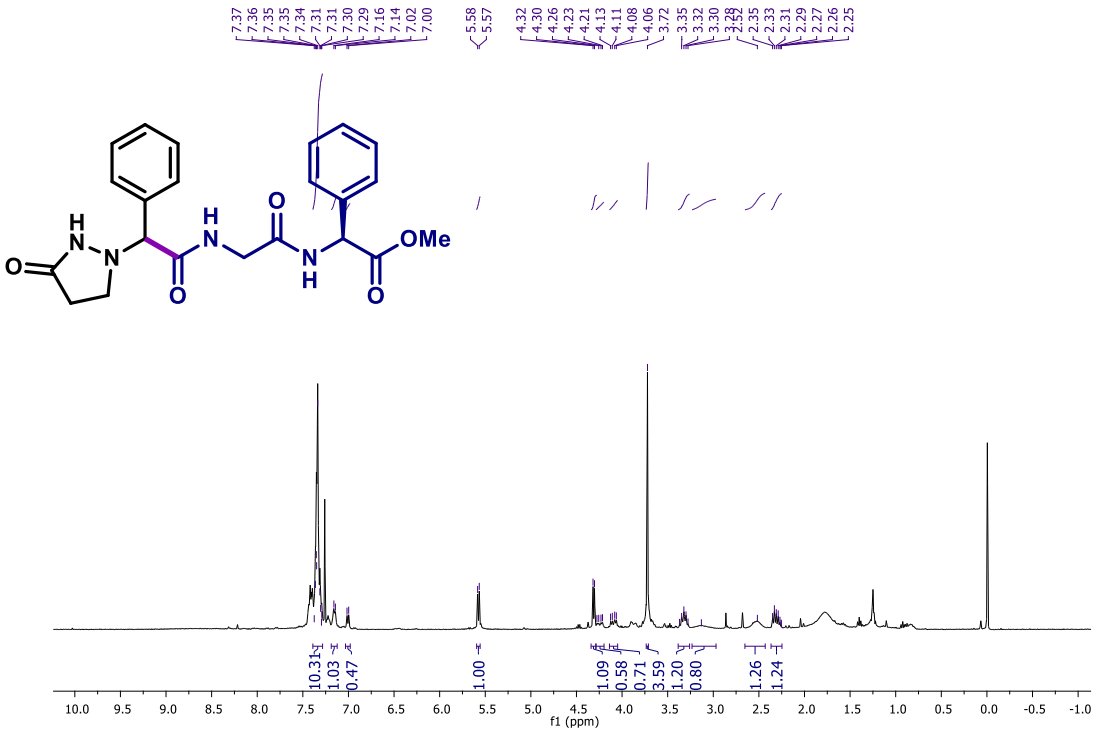
^{13}C NMR ($CDCl_3$, 126 MHz) of 37.



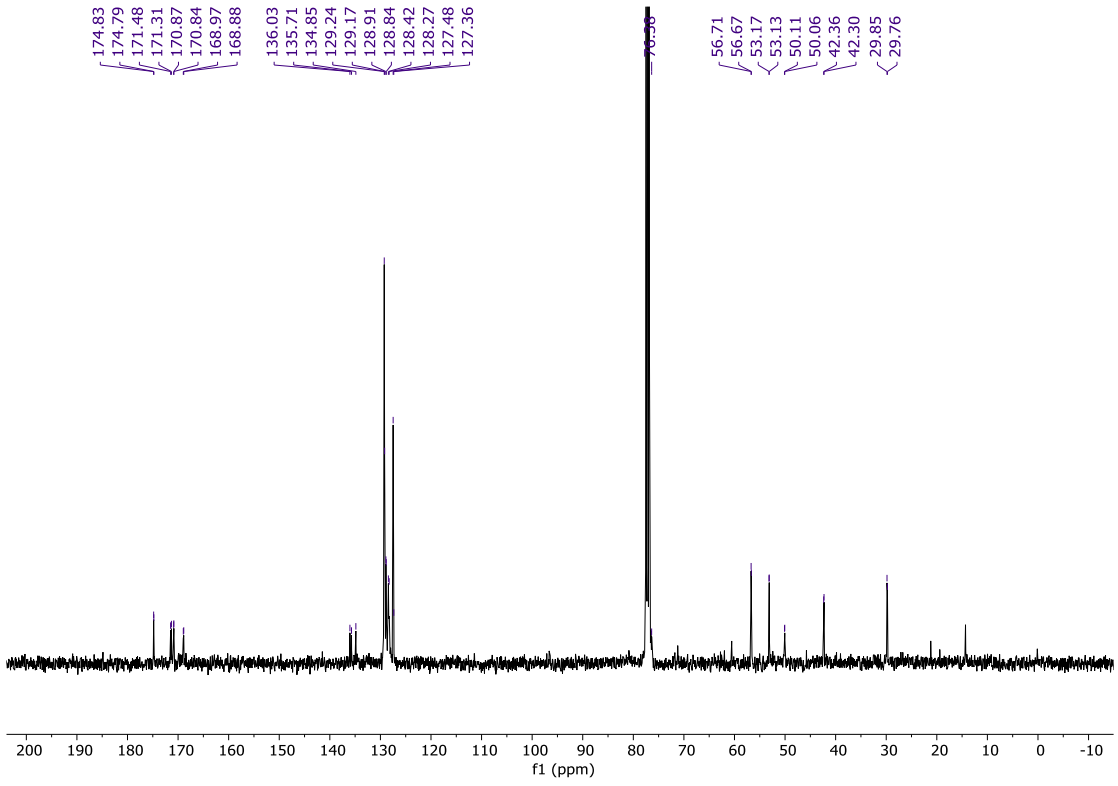
^{1}H NMR ($CDCl_3$, 400 MHz) of 38.



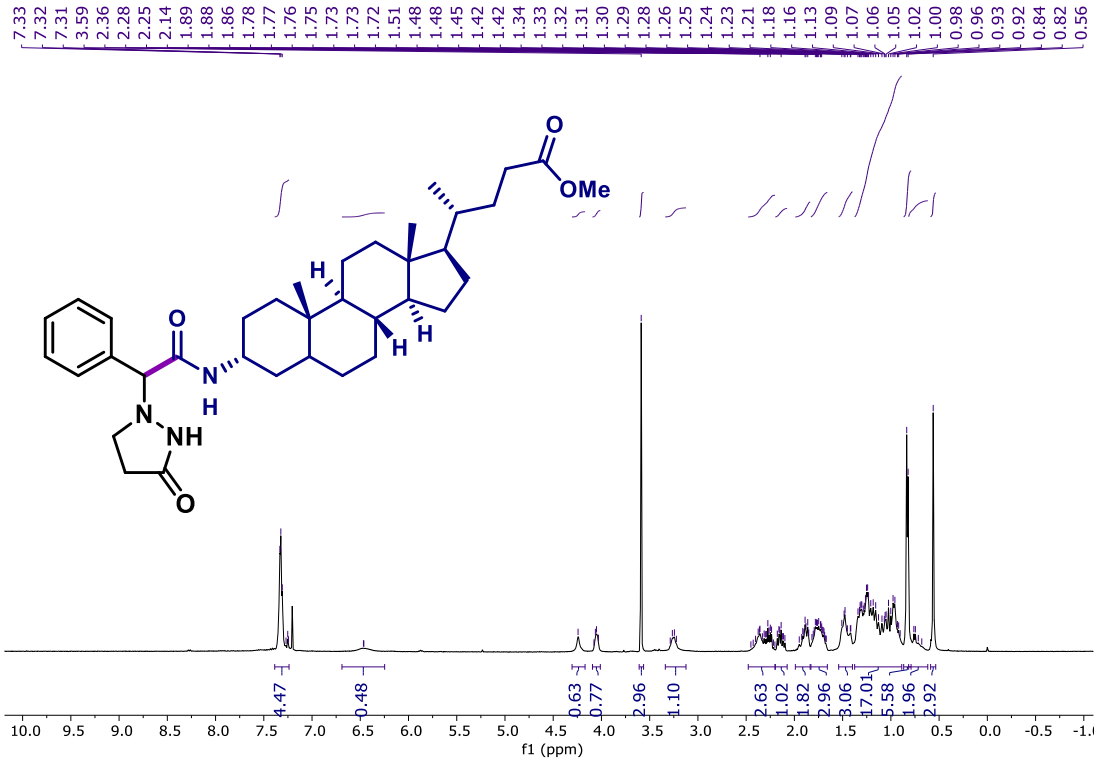
^{3}C NMR ($CDCl_3$, 126 MHz) of 38.



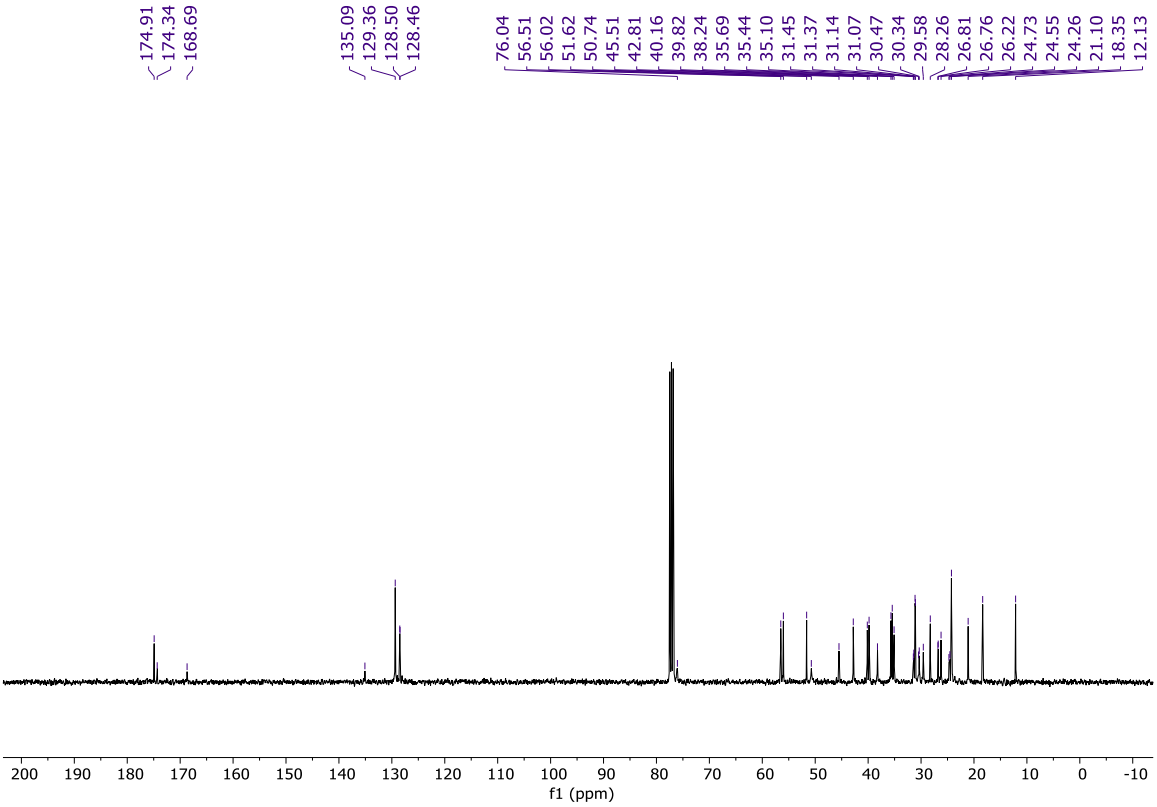
^{1}H NMR ($CDCl_3$, 400 MHz) of 39.



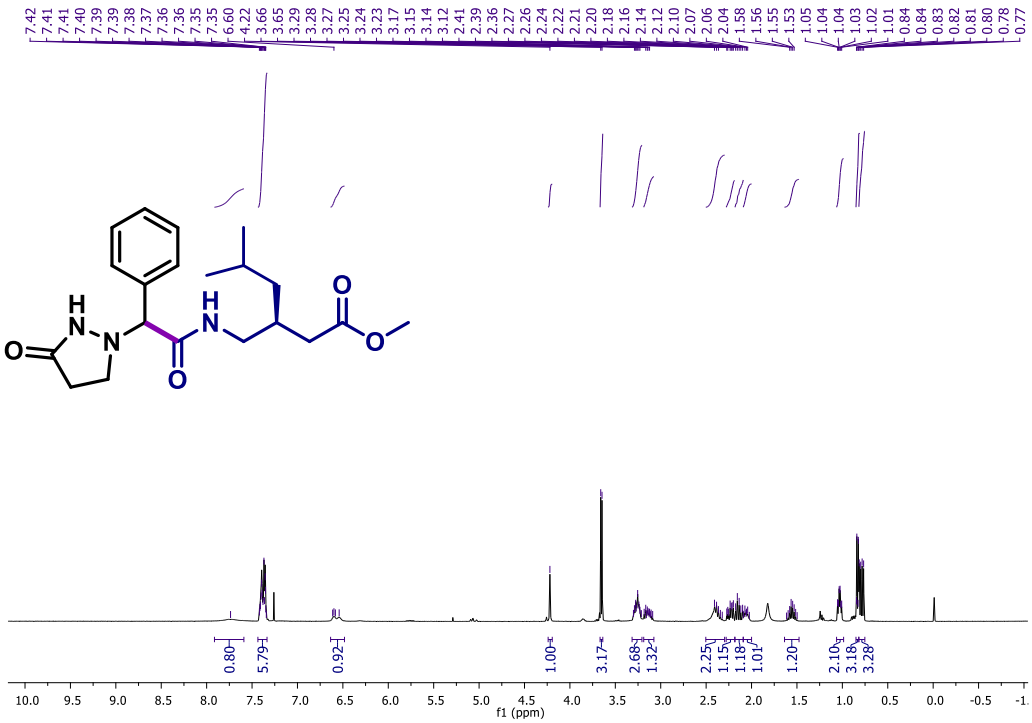
^{13}C NMR ($CDCl_3$, 126 MHz) of 39.



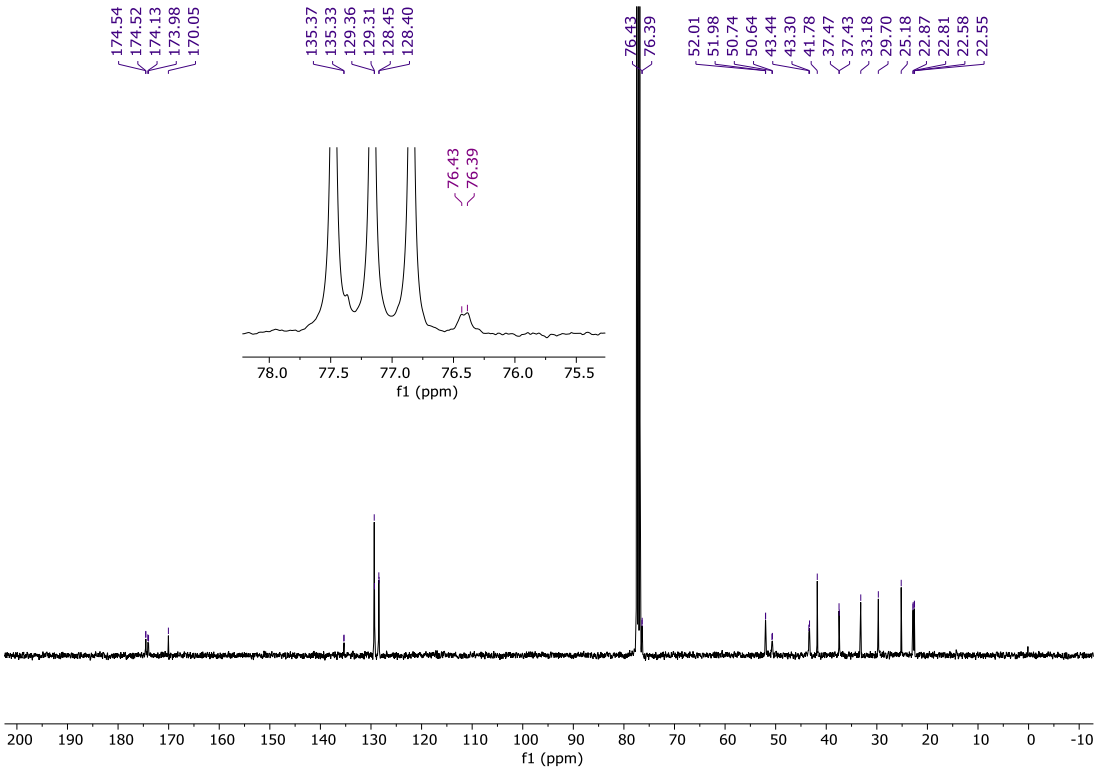
^{1}H NMR ($CDCl_3$, 400 MHz) of 40.



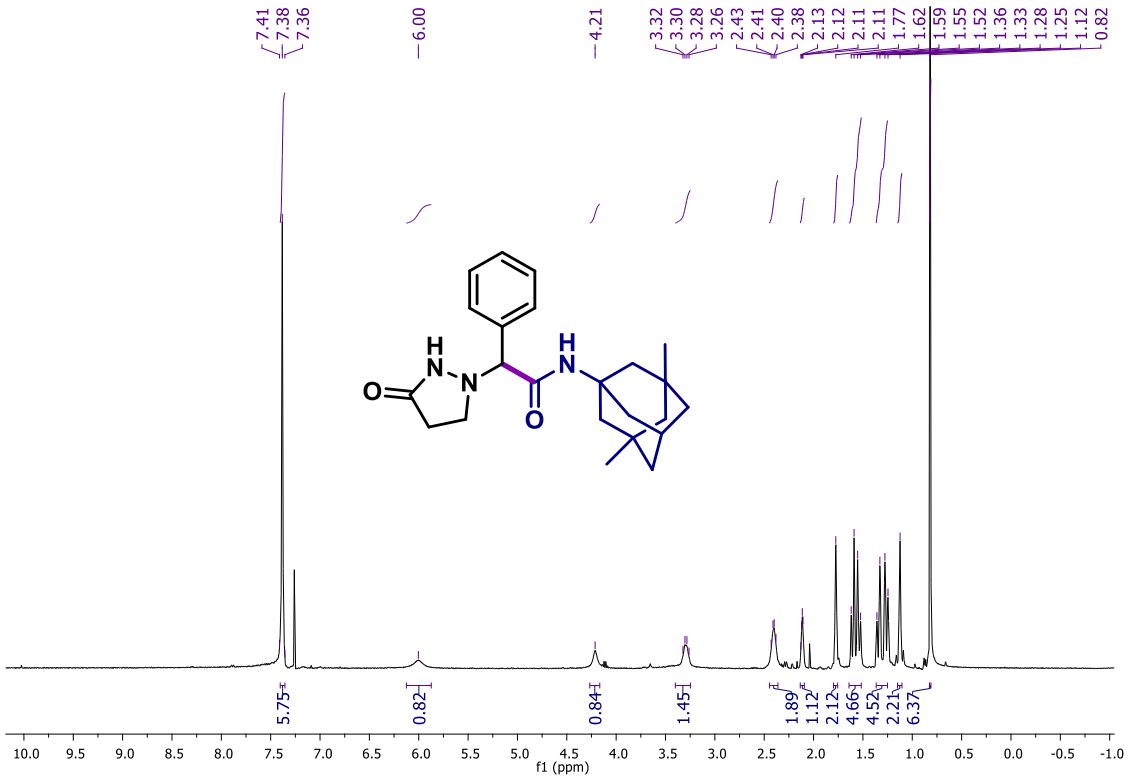
^{13}C NMR ($CDCl_3$, 126 MHz) of 40.



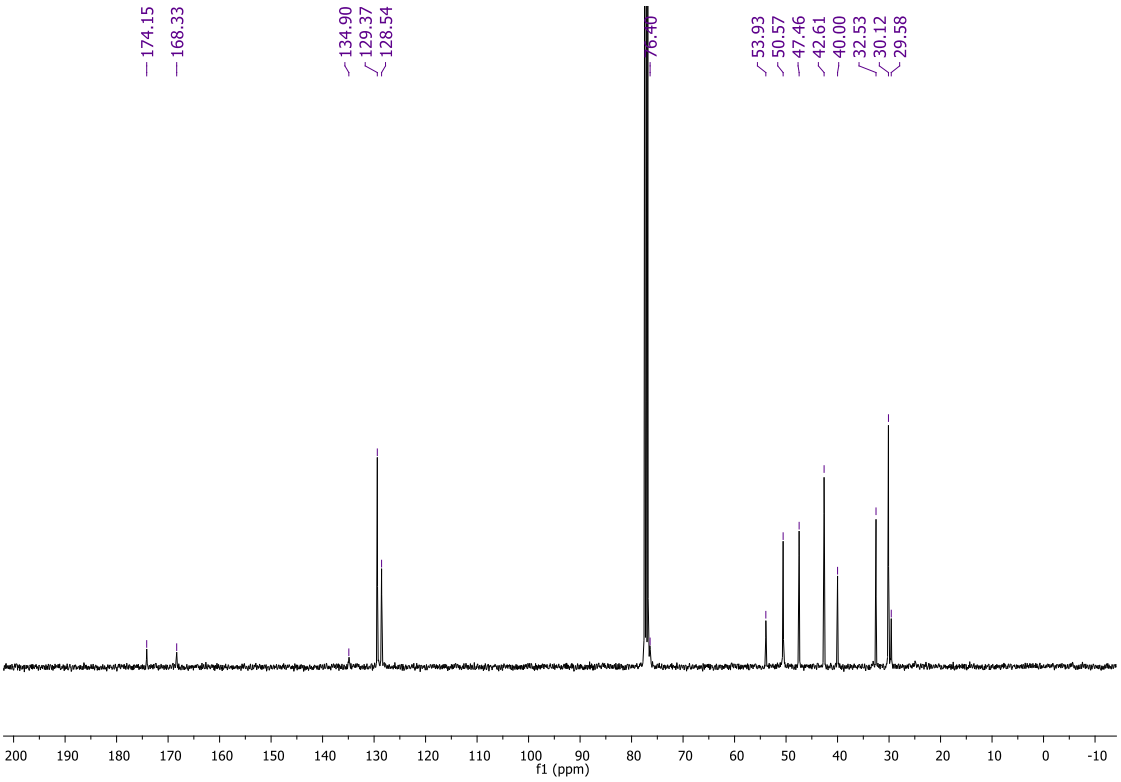
^{1}H NMR (CDCl$_3$, 400 MHz) of 41.



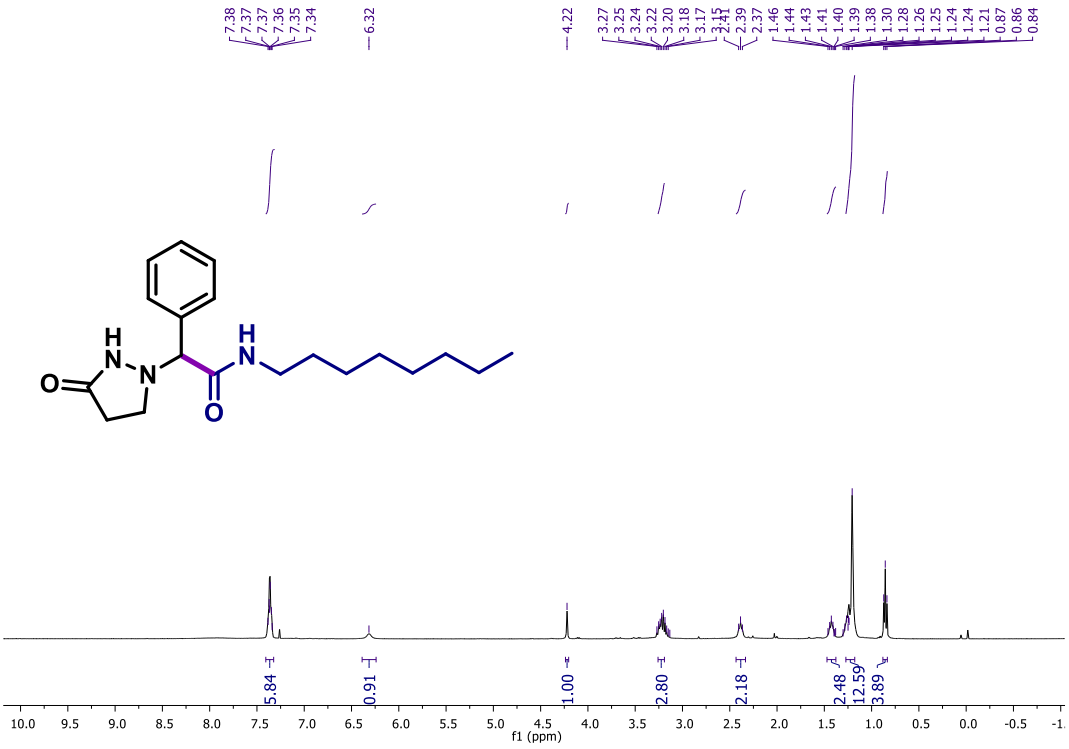
^{13}C NMR (CDCl3, 126 MHz) of 41.



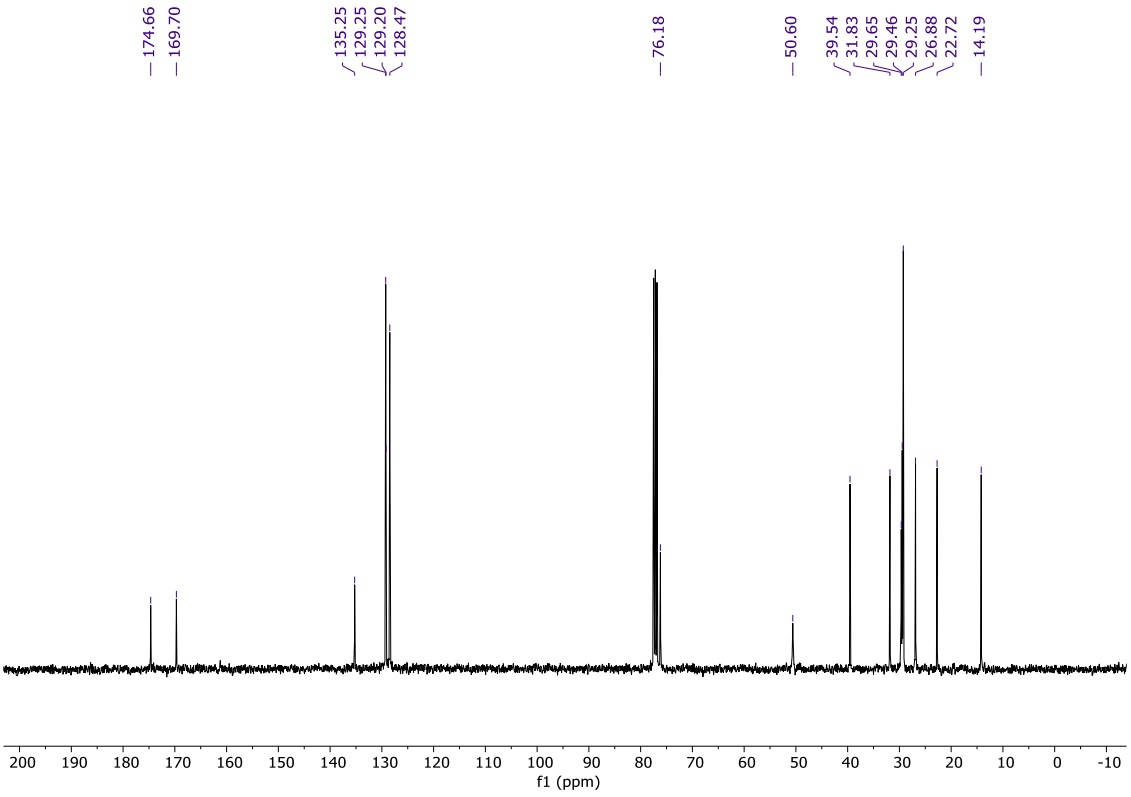
^{1}H NMR ($CDCl_3$, 400 MHz) of 42.



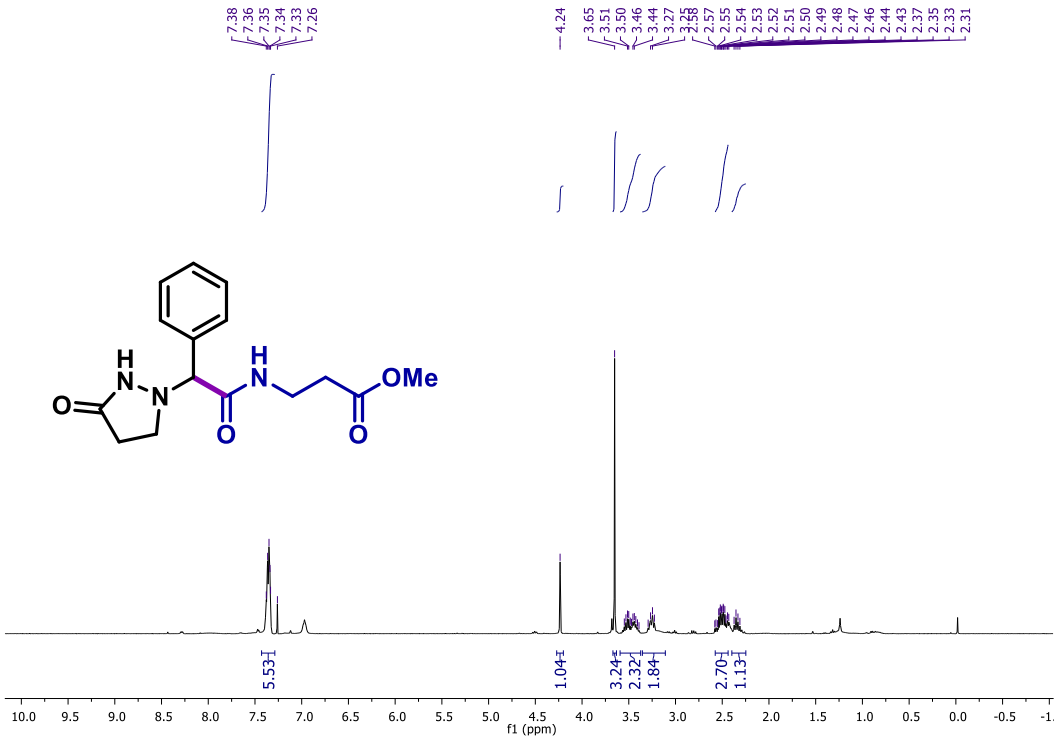
^{13}C NMR (CDCl3, 126 MHz) of 42.



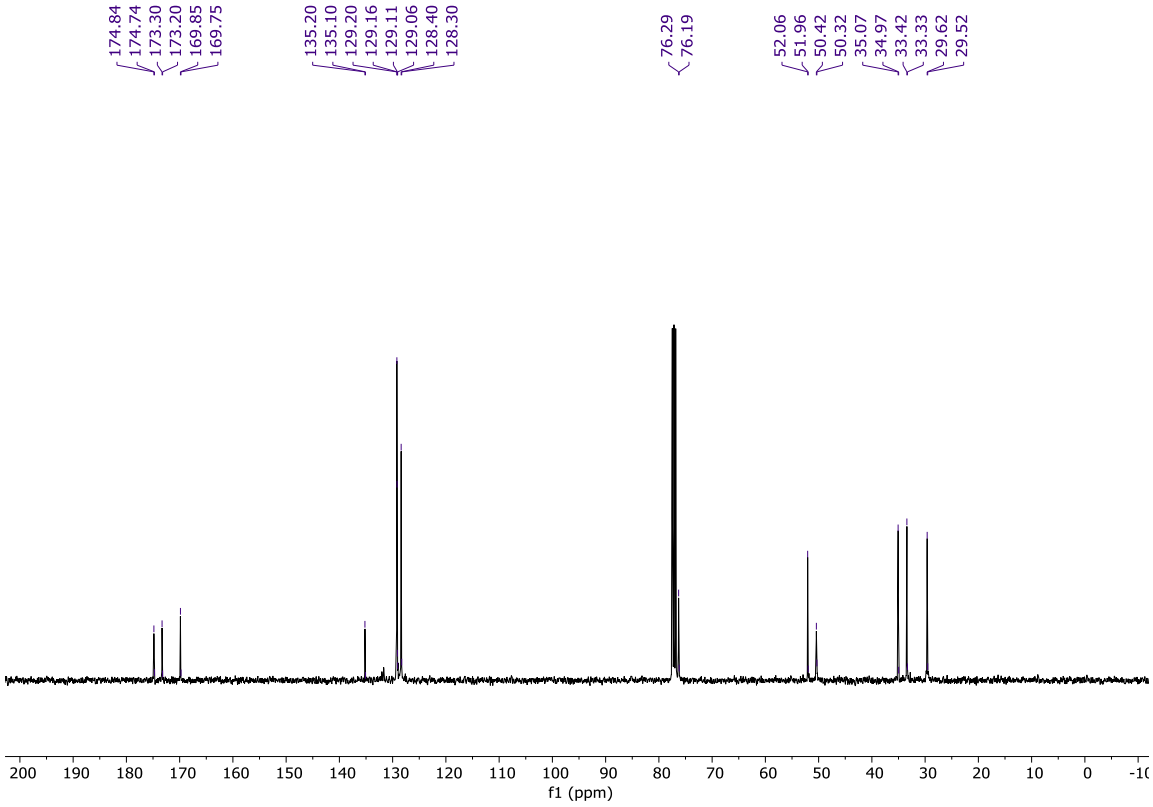
^{1}H NMR ($CDCl_3$, 400 MHz) of 43.



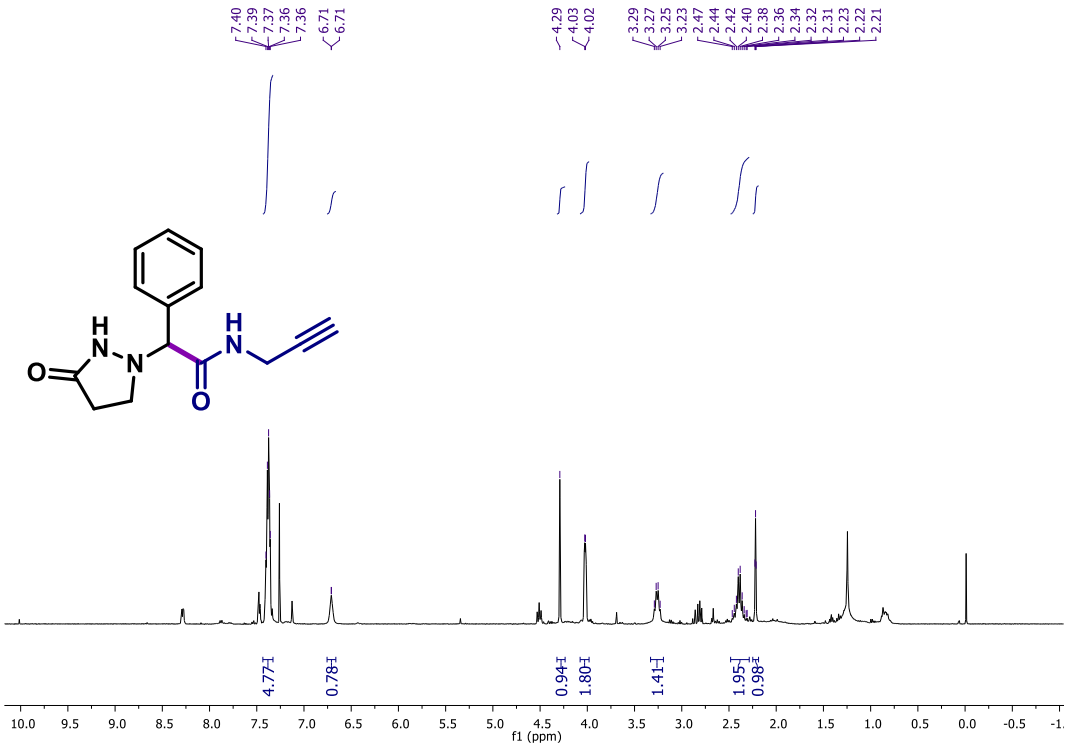
^{1}H NMR ($CDCl_3$, 400 MHz) of 43.



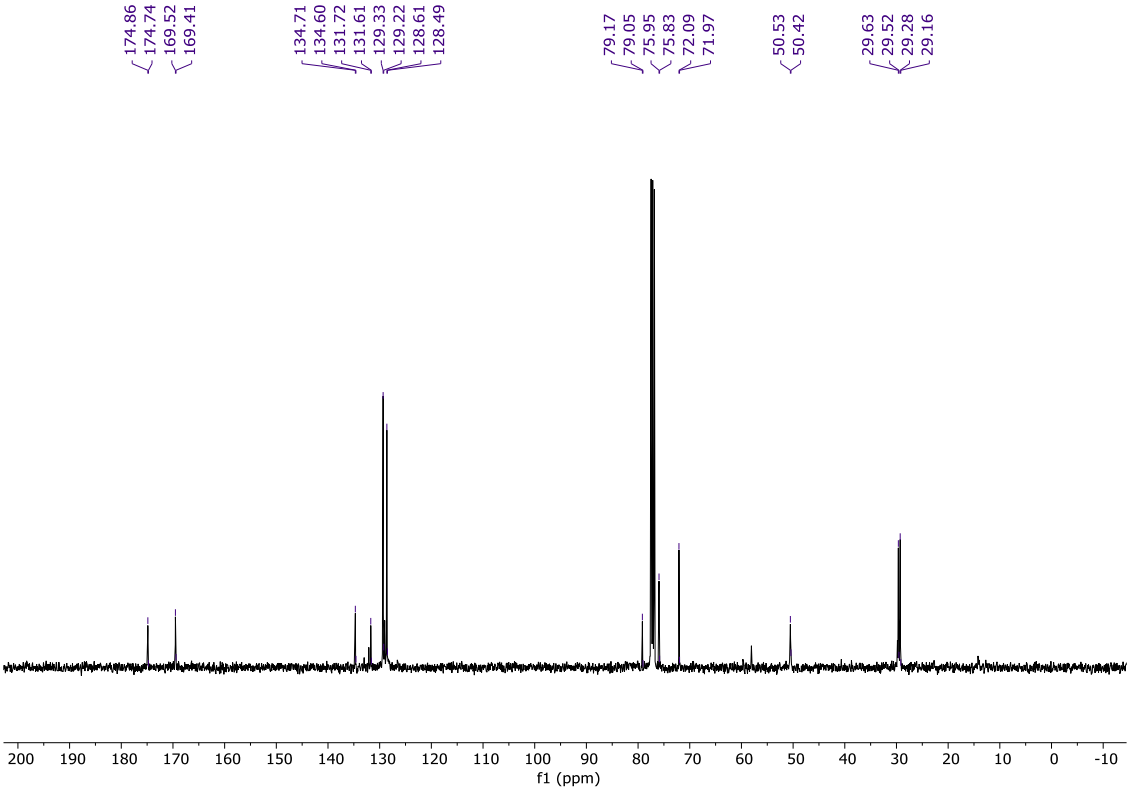
^{1}H NMR ($CDCl_3$, 400 MHz) of 44.



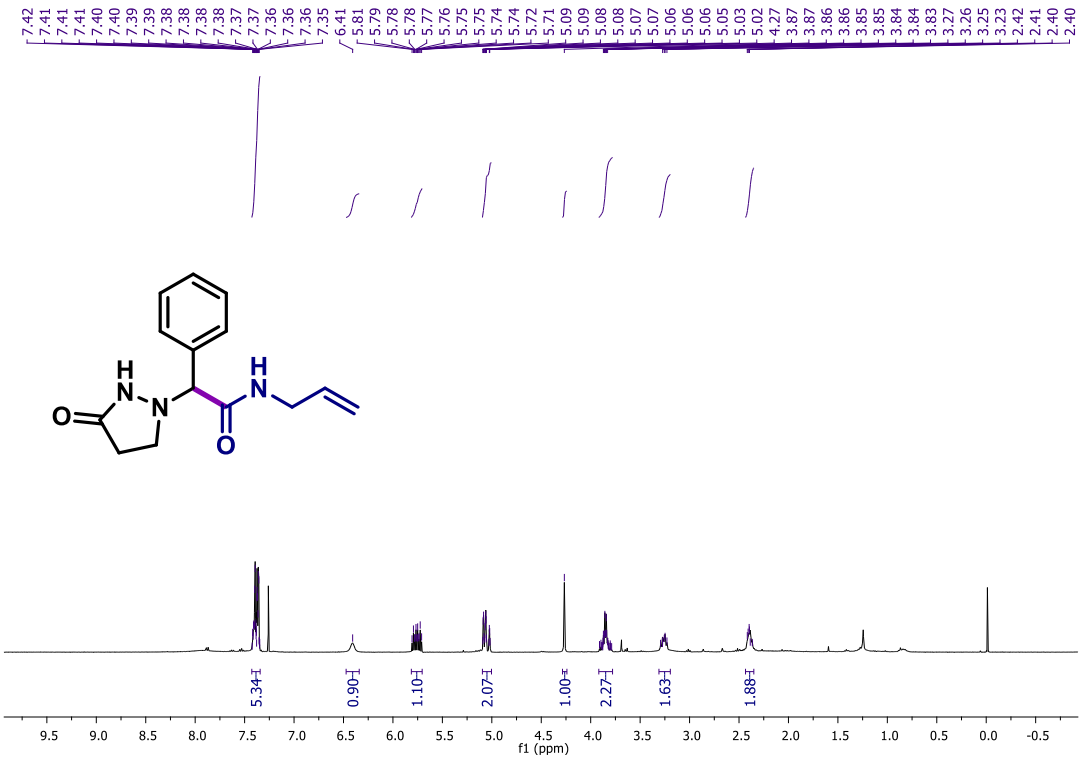
^{13}C NMR ($CDCl_3$, 126 MHz) of 44.



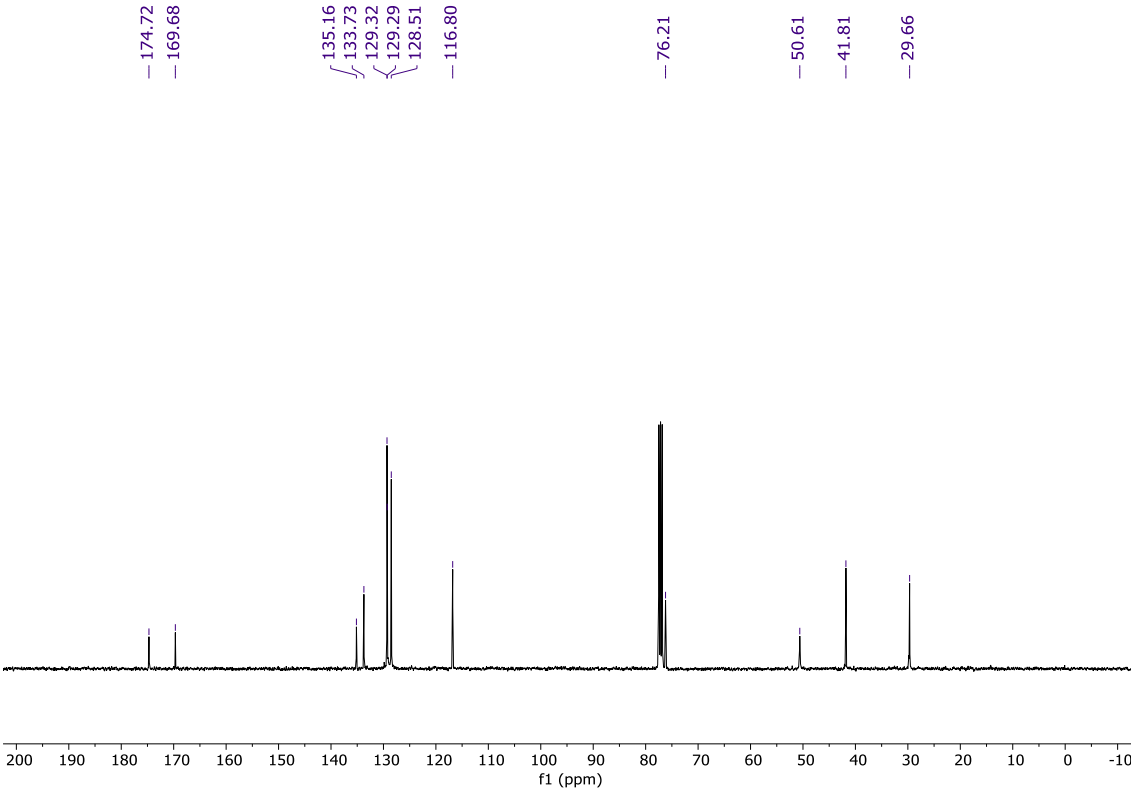
^{1}H NMR ($CDCl_3$, 400 MHz) of 45.



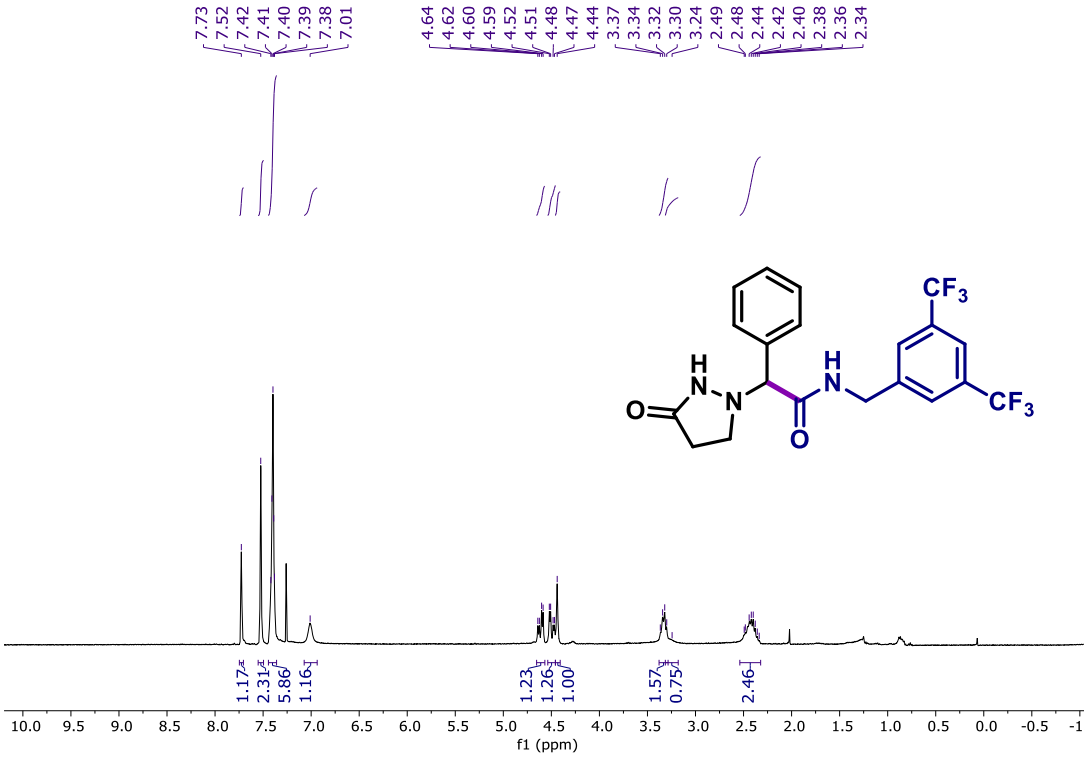
^{13}C NMR ($CDCl_3$, 126 MHz) of 45.



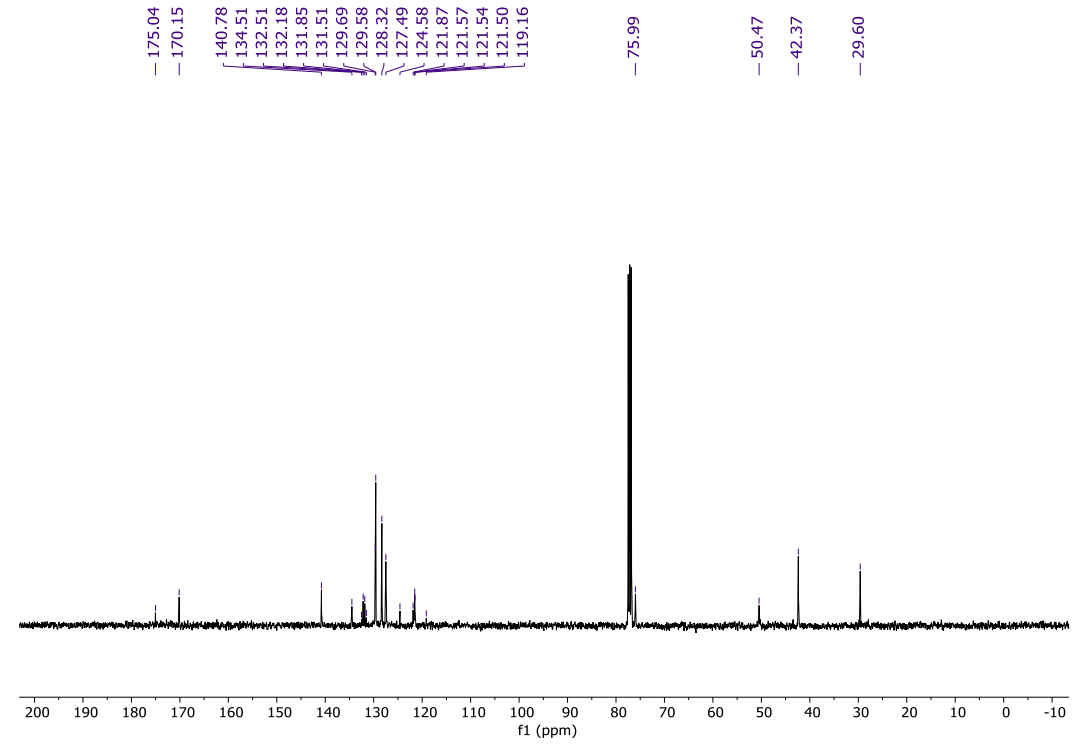
^{1}H NMR ($CDCl_3$, 400 MHz) of 46.



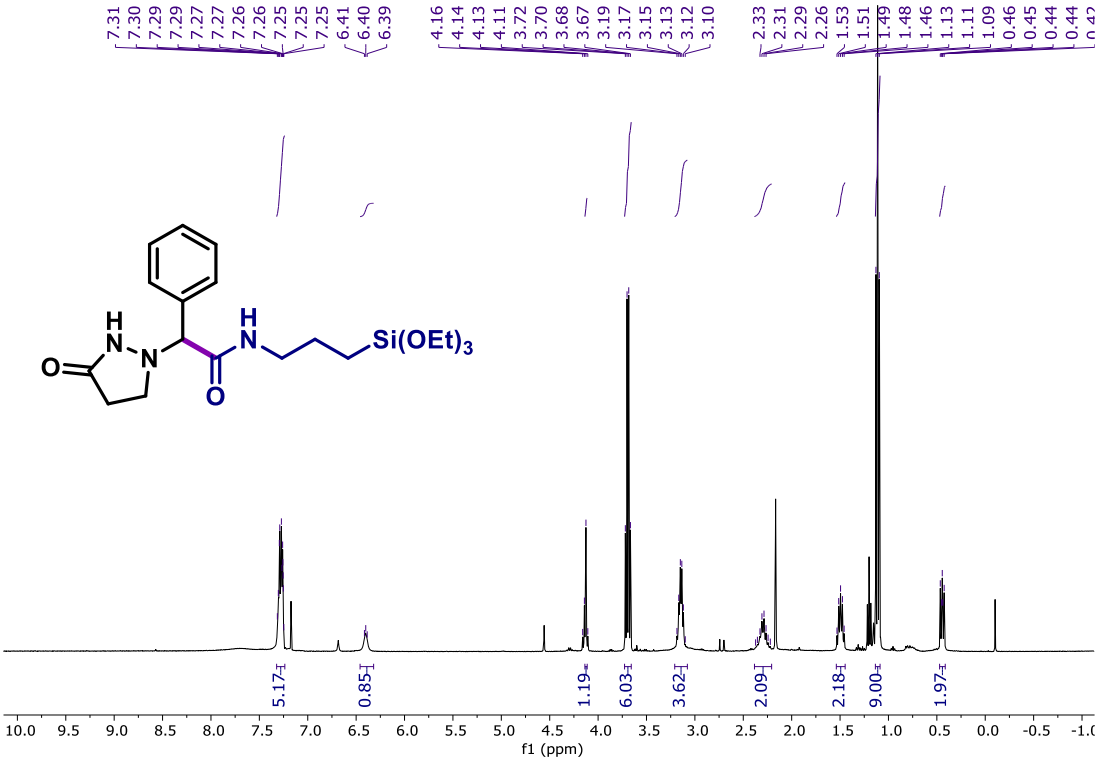
^{13}C NMR ($CDCl_3$, 126 MHz) of 46.



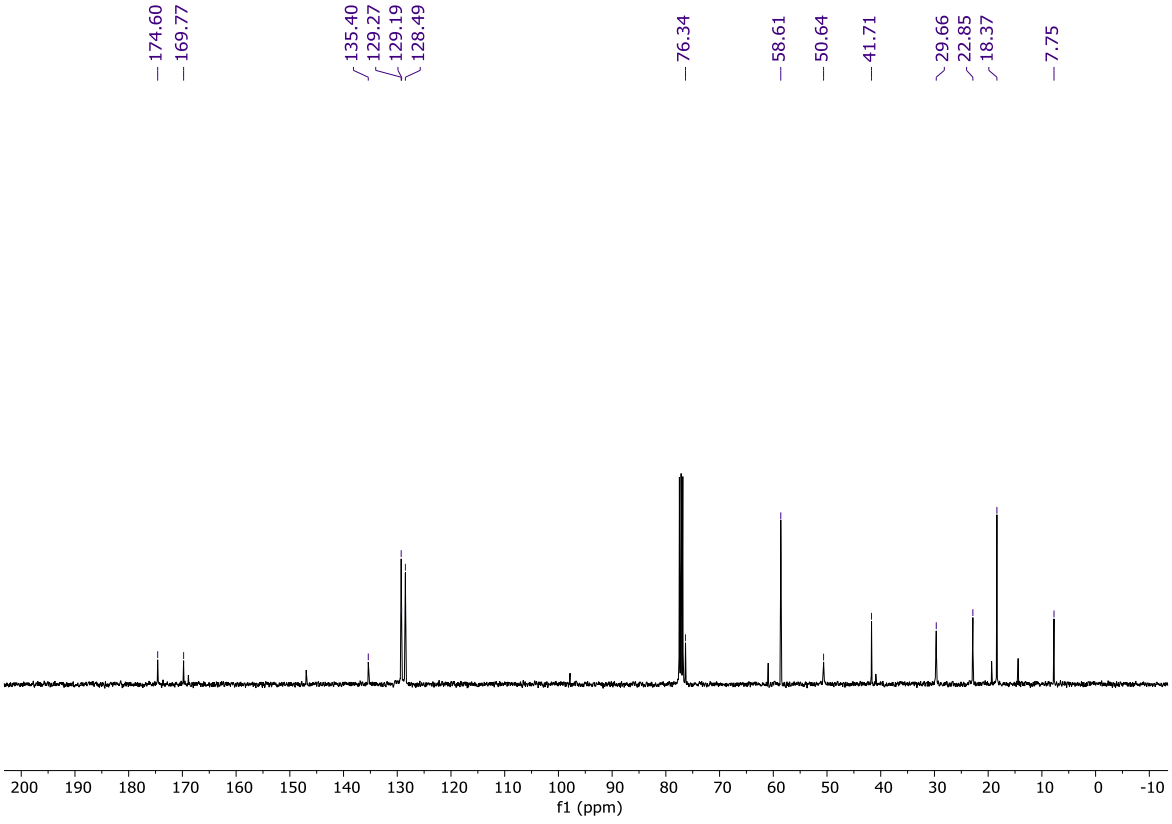
^{1}H NMR ($CDCl_3$, 400 MHz) of 47.



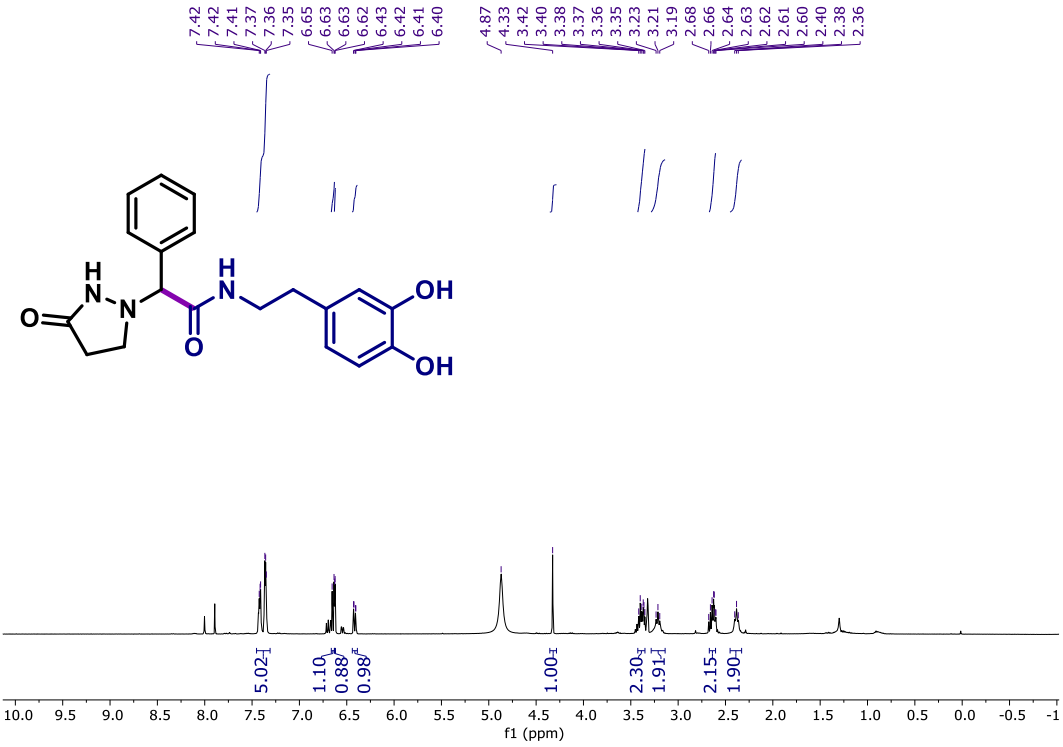
^{13}C NMR ($CDCl_3$, 126 MHz) of 47.



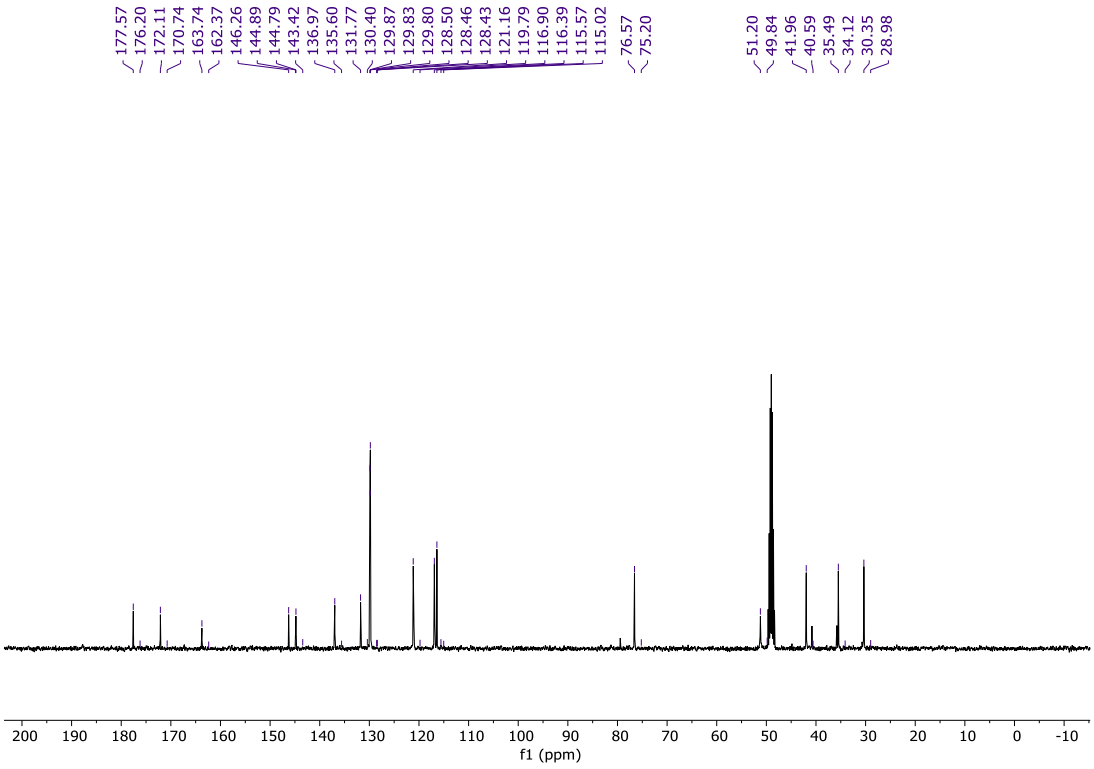
^{1}H NMR ($CDCl_3$, 400 MHz) of 48.



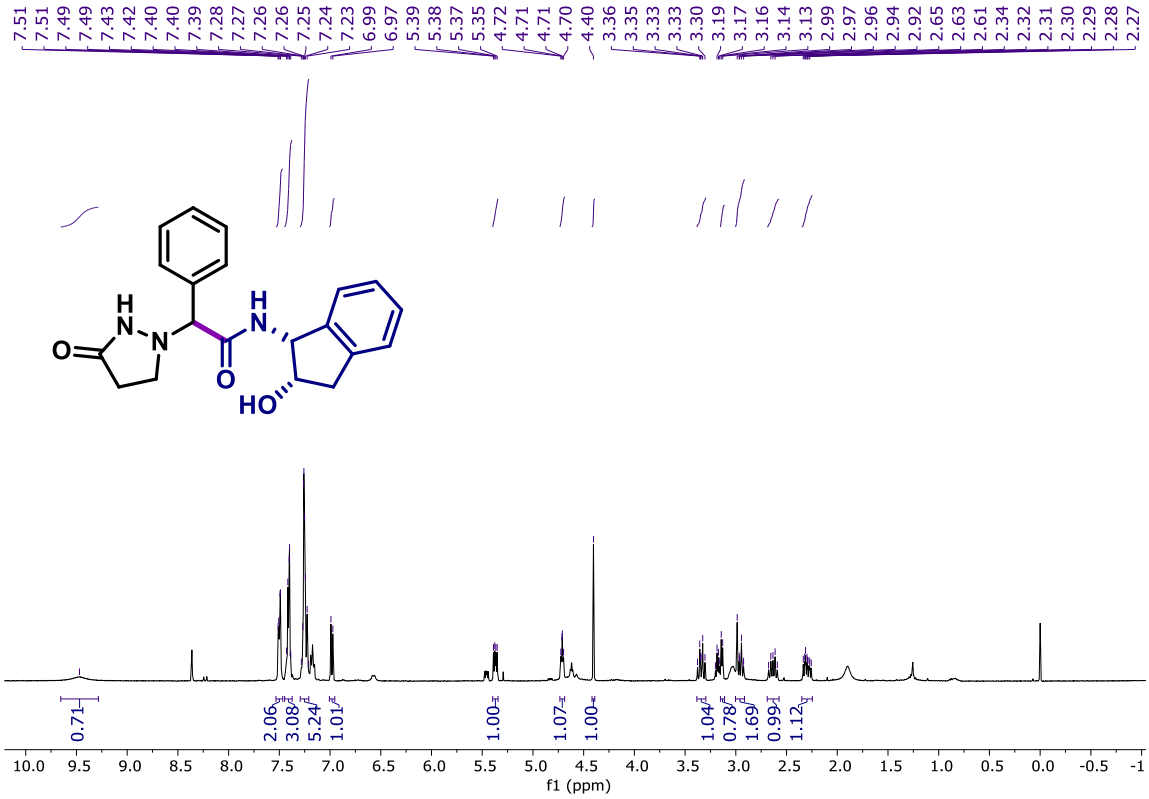
^{13}C NMR ($CDCl_3$, 126 MHz) of 48.



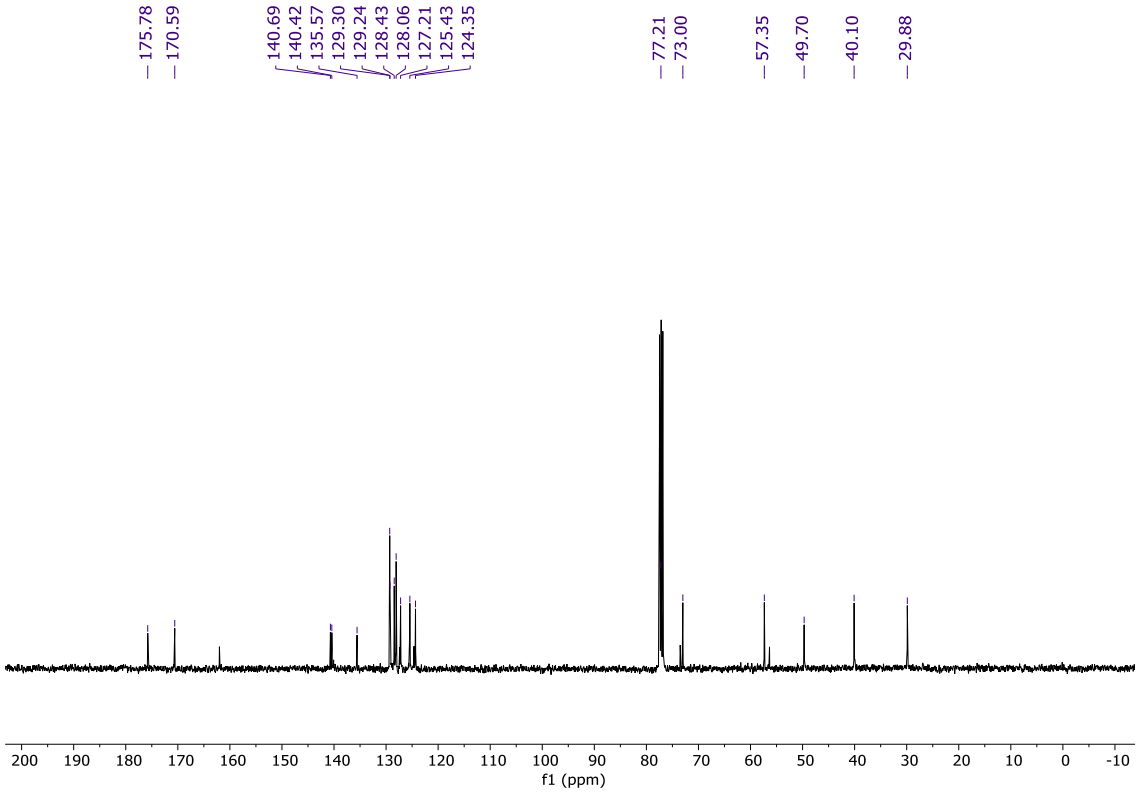
^{1}H NMR (CD_3OD, 400 MHz) of 49.



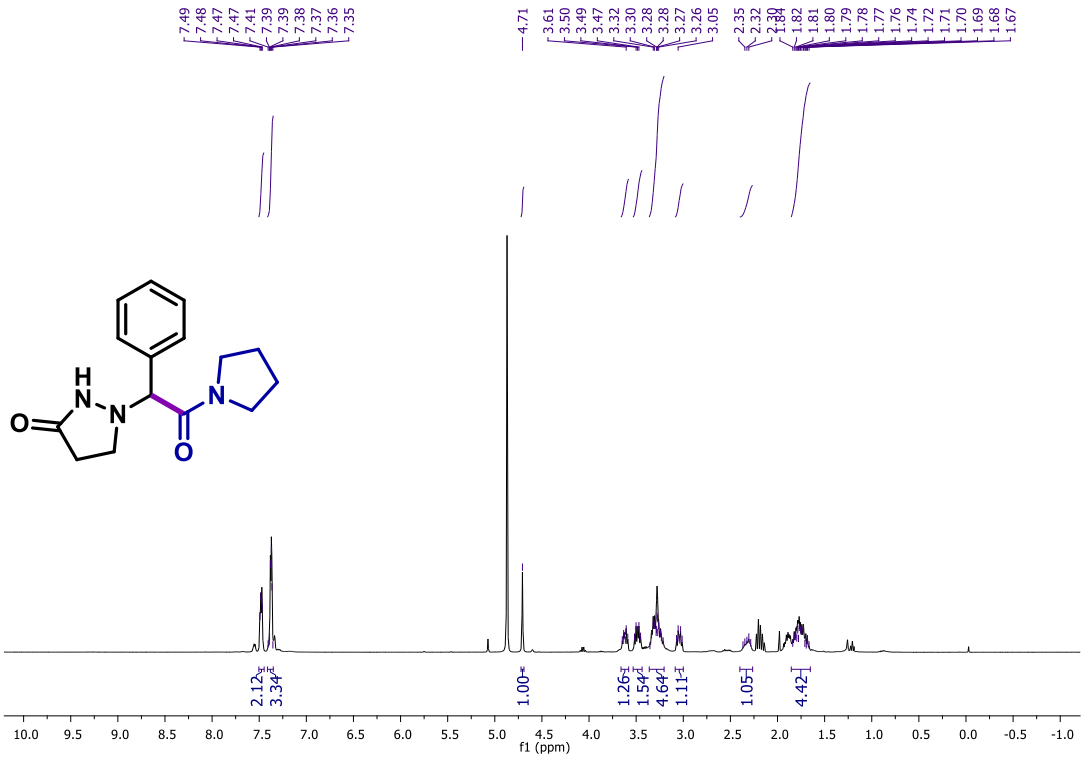
^{13}C NMR (CD_3OD, 126 MHz) of 49.



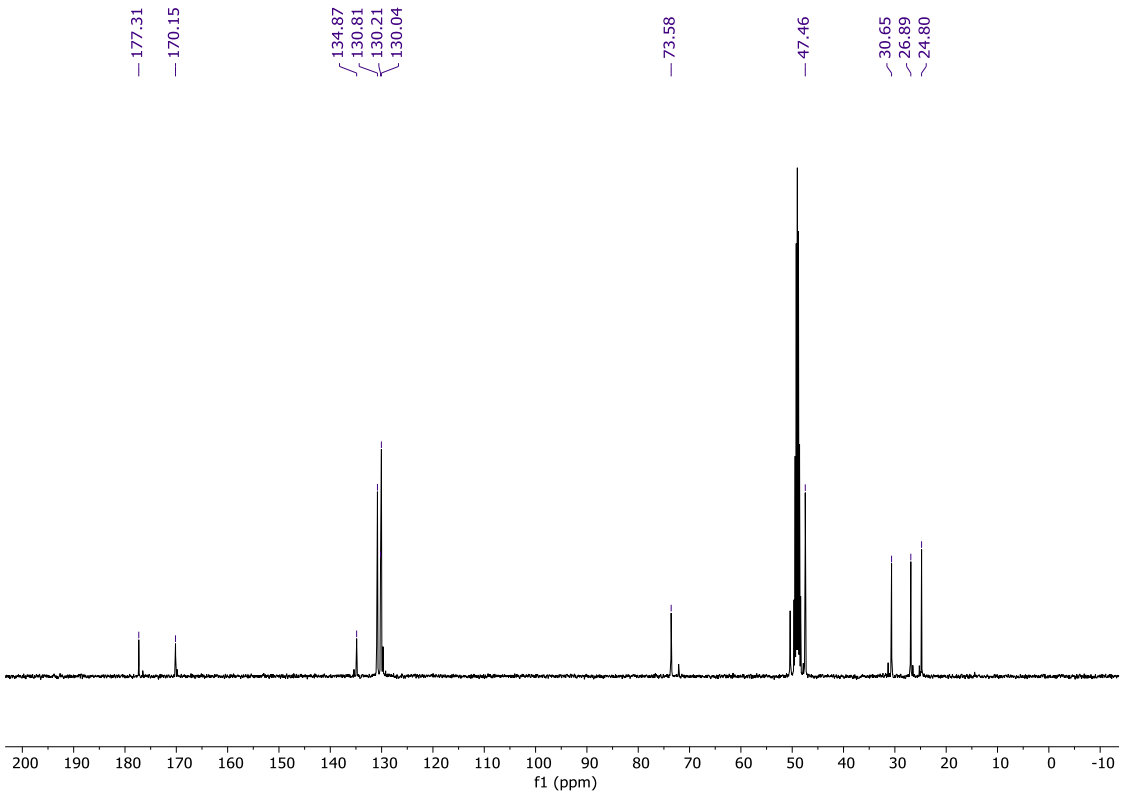
^{1}H NMR ($CDCl_3$, 400 MHz) of 50.



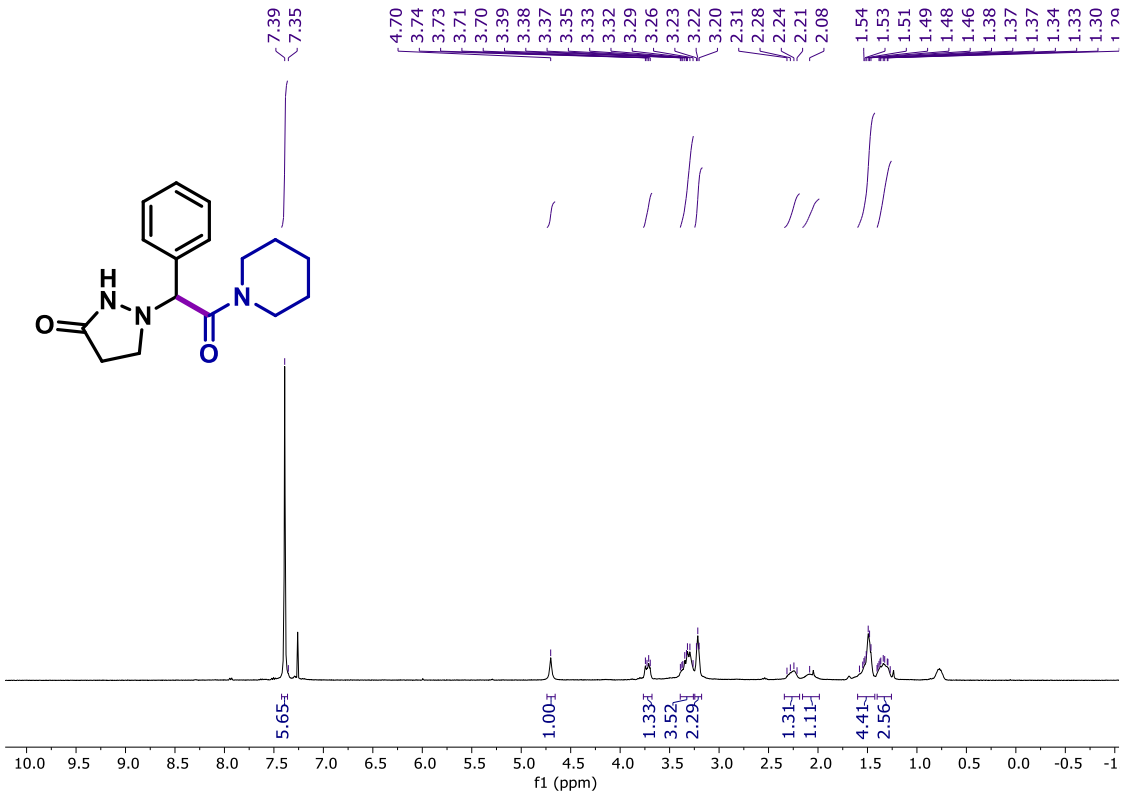
^{13}C NMR ($CDCl_3$, 126 MHz) of 50.



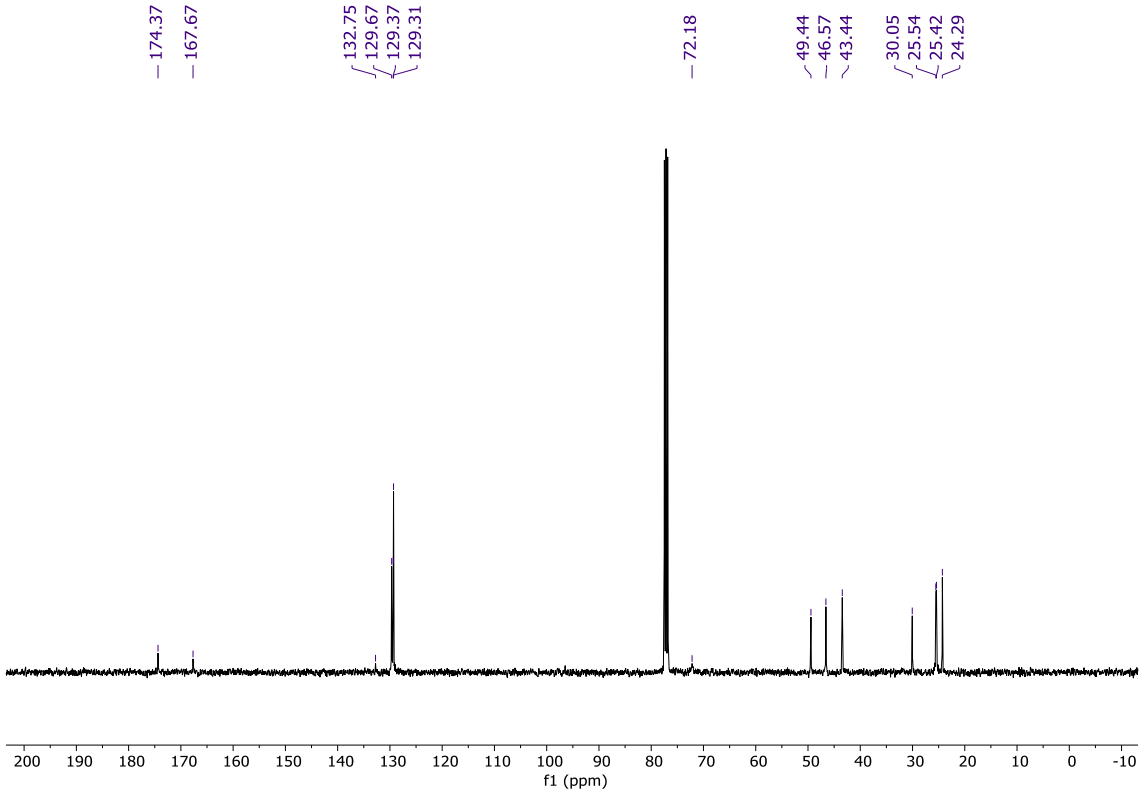
^{1}H NMR ($CDCl_3$, 400 MHz) of 51.



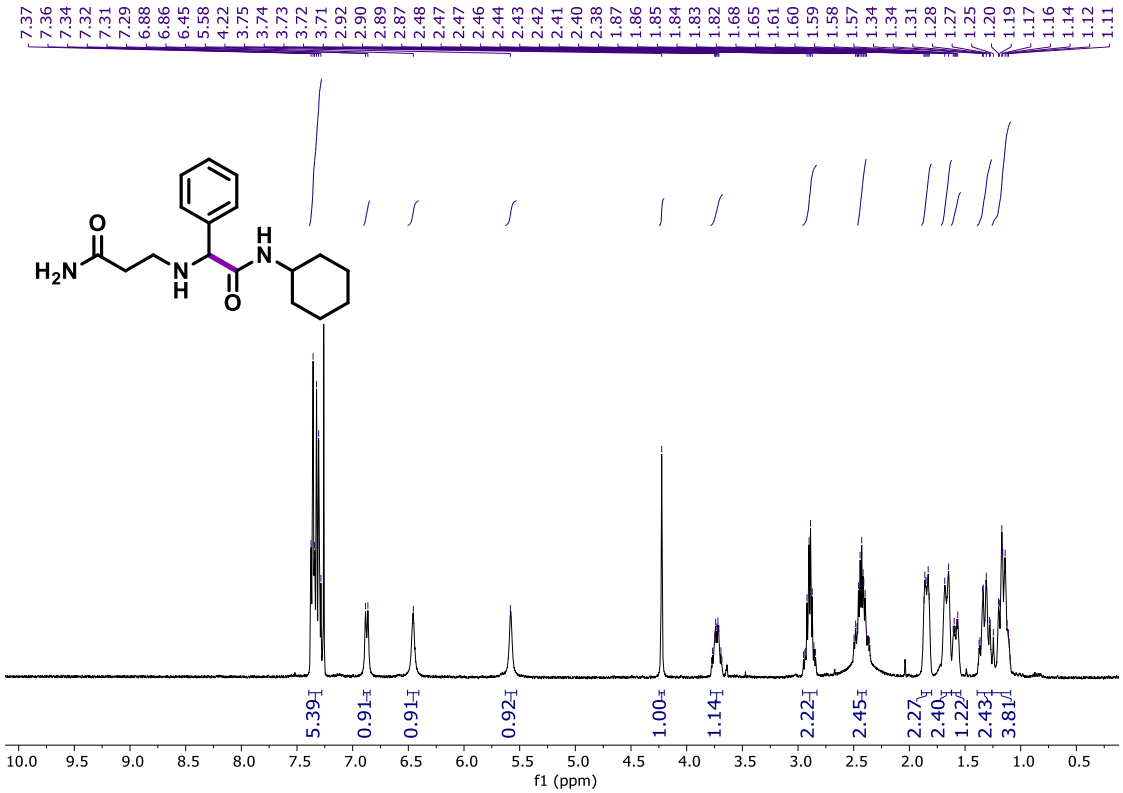
^{13}C NMR ($CDCl_3$, 126 MHz) of 51.



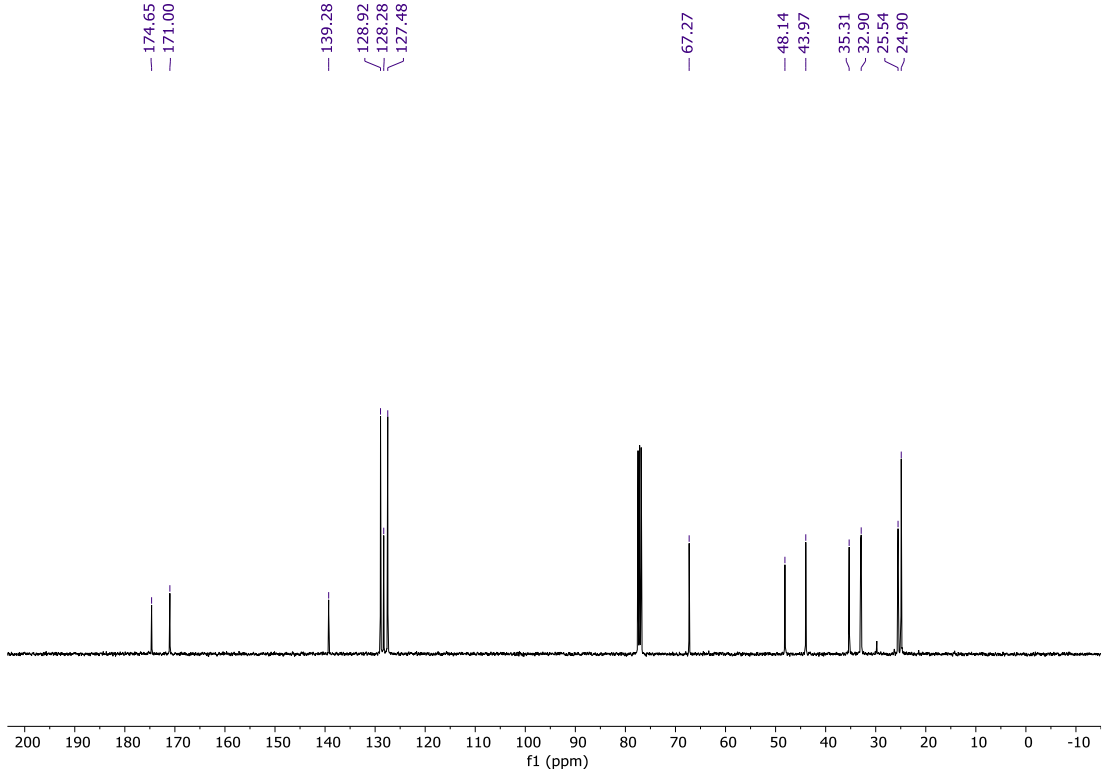
^{1}H NMR ($CDCl_3$, 400 MHz) of 52.



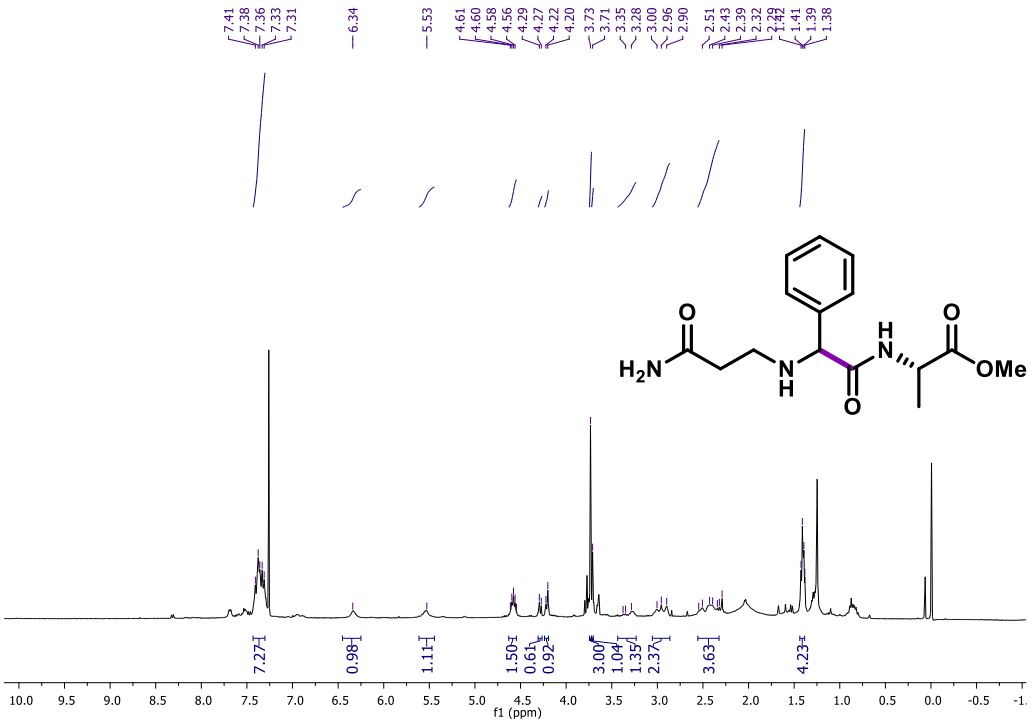
^{13}C NMR ($CDCl_3$, 126 MHz) of 52.



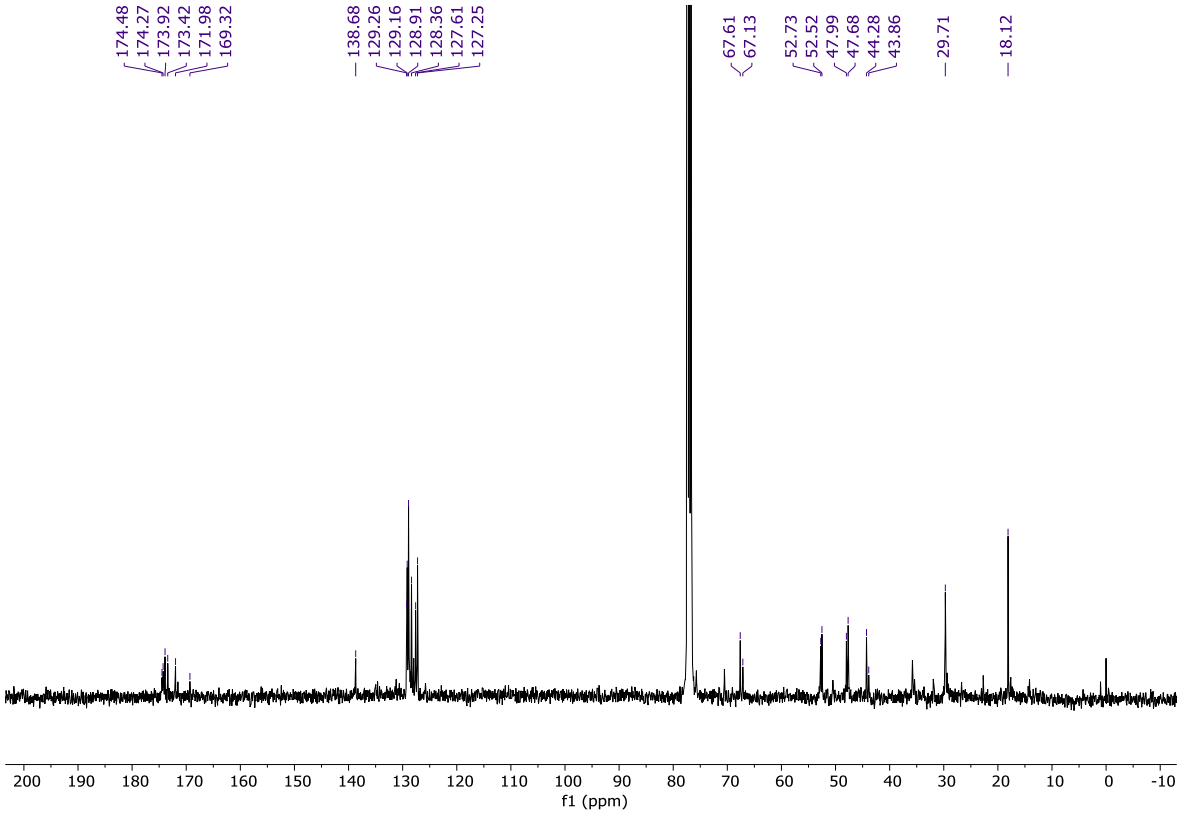
^{1}H NMR ($CDCl_3$, 400 MHz) of 53.



^{13}C NMR ($CDCl_3$, 126 MHz) of 53.



^{1}H NMR ($CDCl_3$, 400 MHz) of 54.



^{13}C NMR ($CDCl_3$, 126 MHz) of 54.