

Electronic Supplementary Information

for

Organocatalytic Alkylation and

Photoorganocatalyst-Free Acylation of

Azomethine Imines by Hantzsch Esters

under Blue LED Light

Jiacheng Li,^b Jongkonporn Phetcharawetch,^{b,c} Minghao Qi,^{b,d} Sara Helen Kyne,^e Chutima

Kuhakarn,^c Bingwei Zhong,^{a*} and Philip Wai Hong Chan^{a,b*}

^a Department of Biological Environment, Jiyang College of Zhejiang A&F University,
Zhuji 311800, China

^b School of Chemistry, Monash University, Clayton, Victoria 3800, Australia

^c Department of Chemistry and Center of Excellence for Innovation in Chemistry
(PERCH-CIC), Faculty of Science, Mahidol University, Bangkok 10400, Thailand

^d School of Science, Monash University Malaysia, Bandar Sunway, Subang Jaya,
Selangor, Malaysia

^e School of Chemistry, University of New South Wales, Sydney, New South Wales
2052, Australia

Email: phil.chan@monash.edu

Table of Contents

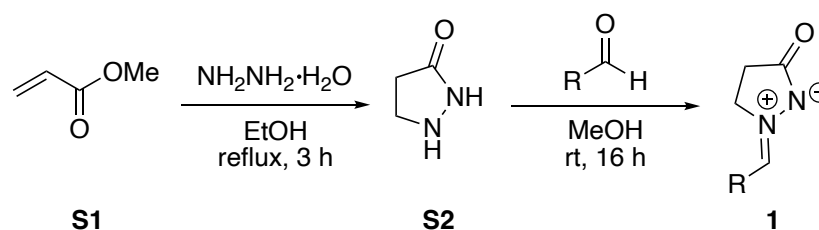
1. General Information	S1
2. Experimental Procedures.....	S2
2.1 General procedure for the synthesis of azomethine imines (1a–q).....	S2
2.2 General procedure for the synthesis of 4-alkyl-substituted DHPs (2a–o).....	S2
2.3 General procedure for the synthesis of 2i	S4
2.4 General procedure for the synthesis of 4-acyl-substituted DHPs (4a–o)	S5
2.5 Procedure for the synthesis of 4CzPN.....	S6
2.6 Procedure for the synthesis of DPZ.....	S7
2.7 General procedure for the 4-CzPN-catalysed photoredox reaction of 1 and 2	S8
2.8 General procedure for the photoredox reaction of 1a and 4	S8
2.9 Procedure for the gramme-scale reaction of 1a and 2a	S9
2.10 Procedures for the selective transformations of 3aa and 5aa	S9
3. Control Experiments.....	S12
3.1 Control reactions with 1a and 2a	S12
3.2 Deuterium labelling experiments	S13
3.3 UV-vis spectroscopic measurements.....	S15
4. Compound Analytical Data	S16
5. ¹ H, ¹³ C and ¹⁹ F NMR Spectra.....	S65
6. References	S174

1. General Information

All reactions were performed in oven-dried glassware under a nitrogen atmosphere. All photoreactions were performed using a blue LED light source (456 nm, 50 W). Photoreactions were prepared in a nitrogen-filled glovebox and set up with three lamps (10 cm distance from the reaction flask) and the temperature maintained by fan cooling. Unless specified, all reagents and starting materials were purchased from commercial companies and used as received. Anhydrous solvents were freshly degassed following standard procedures using three freeze-pump-thaw cycles. Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel plates. Visualisation was achieved by UV light (254 nm). Flash chromatography was performed using silica gel and gradient solvent system (eluent: 40-60 °C fraction of petroleum benzine:EtOAc). ^1H , ^{13}C and ^{19}F NMR spectra were recorded on 400 and 600 MHz spectrometers. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: s (singlet), br s (broad singlet), d (doublet), t (triplet), dd (doublet of doublets), dt (doublet of triplets), ddd (doublet of doublet of doublets), ddt (doublet of doublet of triplets), dtt (doublet of triplet of triplets), ddq (doublet of doublet of quintets), dddd (doublet of doublet of doublet of doublets), dtd (doublet of triplet of doublets), dt (doublet of triplets), dp (doublet of pentents), dq (doublet of quintets), td (triplet of doublets), tdd (triplet of doublet of doublets), tt (triplet of triplets), qd (quintet of doublets), qt (quintet of triplets) or m (multiplet). The number of protons (n) for a given resonance is indicated by $n\text{H}$ and coupling constants are reported as a J value in Hz. Infrared spectra were recorded on an FTIR spectrometer (thin film). High resolution mass spectra (HRMS) were obtained on a LC/HRMS TOF spectrometer using simultaneous electrospray (ESI).

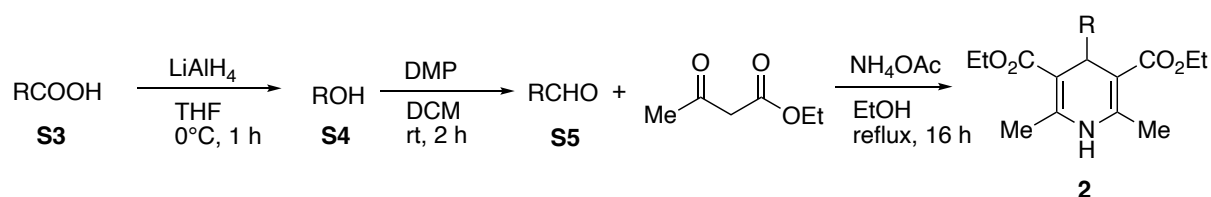
2. Experimental Procedures

2.1 General procedure for the synthesis of azomethine imines (1a–q)^{S1}



To a round bottom flask containing a magnetic stirring bar was added hydrazine hydrate (1.0 mL, 20 mmol, 1.0 equiv.) in EtOH (20 mL). Methyl acrylate (2.0 mL, 22.5 mmol, 1.1 equiv.) was added at 0 °C and the resulting reaction mixture was stirred for 30 min before heating at reflux for 3 h. On completion, the solvent was removed under reduced pressure and the resulting residue (**S2**) was used in the next step without further purification. The residue (**S2**) was dissolved in MeOH (5 mL) and the appropriate aldehyde (30 mmol, 1.5 equiv.) was added. The reaction was stirred at room temperature for 14 h. Upon completion, the solvent was removed under reduced pressure and the ensuing residue was recrystallised from hot EtOH (Et₂O was added to aid crystallisation if required). The crystals were filtered and dried under vacuum to afford the title compound.

2.2 General procedure for the synthesis of 4-alkyl-substituted DHPs (2a–o)^{S2-S4}



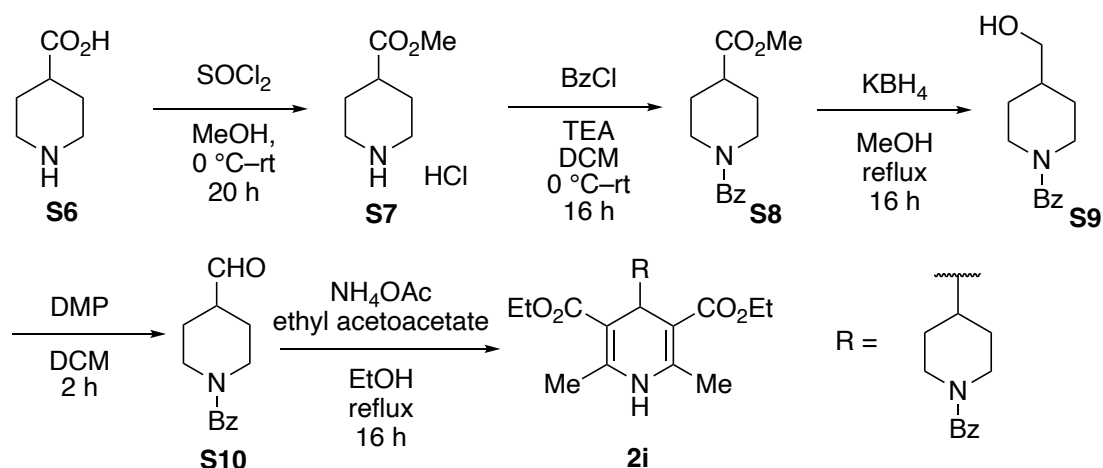
To a round bottom flask containing a magnetic stirring bar and the appropriate carboxylic acid (**S3**, 10 mmol, 1.0 equiv.) in freshly distilled THF (20 mL) was added LiAlH_4 solution (2.0 M in THF, 6.0 mL, 12 mmol, 1.2 equiv.) slowly at 0 °C. The reaction mixture was stirred at 0 °C for a further 1 h. Upon completion, the reaction mixture was quenched by addition of cold water until no more hydrogen gas formed. The reaction mixture was extracted with EtOAc (3

× 20 mL). The combined organic phase was washed with brine (20 mL), dried over anhydrous Na₂SO₄ and concentrated *in vacuo* to give the corresponding **S4**, which was used in the next step without further purification.

To **S4** (10 mmol, 1.0 equiv.) in DCM (50 mL) was added DMP (6.4 g, 15 mmol, 1.2 equiv.). The reaction mixture was stirred at room temperature for 2 h. Upon completion, the reaction mixture was quenched by addition of saturated sodium thiosulfate (50 mL) and stirred until the organic phase become clear (approximately 30 min). Then, the organic phase was washed with brine (20 mL), dried over anhydrous Na₂SO₄ and concentrated *in vacuo* to give a residue that was purified by flash column chromatography on silica gel (eluent: petroleum benzine:EtOAc = 10:1) to provide **S5**.

To a round bottom flask containing a magnetic stirring bar and the appropriate aldehyde **S5** (5.0 mmol, 1.0 equiv.) in EtOH (10 mL) was added ethyl acetoacetate (1.27 mL, 10 mmol, 2.0 equiv.) and ammonium acetate (385 mg, 5 mmol, 1.0 equiv.). The reaction mixture was heated to reflux and stirred at this temperature for 16 h. Upon completion, the reaction mixture was concentrated *in vacuo*. The crude residue was dissolved in EtOAc (20 mL) and washed with brine (20 mL). The aqueous phase was extracted with EtOAc (2 × 50 mL). The combined organic phase was washed with brine (20 mL), dried over anhydrous Na₂SO₄ and concentrated *in vacuo* to give a residue that was purified by flash column chromatography on silica gel (eluent: petroleum benzine:EtOAc = 4:1) to provide the title compound.

2.3 General procedure for the synthesis of 2i^{S3-S7}



To a round bottom flask containing a magnetic stirring bar and **S6** (1.9 g, 15 mmol, 1.0 equiv.) in MeOH (20 mL) was added SOCl_2 (2.0 mL, 27 mmol, 1.8 equiv.) dropwise at 0 °C and the reaction mixture was stirred at room temperature for 20 h. Upon completion, the reaction mixture was concentrated *in vacuo* to afford **S7** in quantitative yield, which was used in the next step without further purification.

To **S7** (6.0 g, 15 mmol, 1.0 equiv.) in DCM (50 mL) was added TEA (6.5 mL, 45 mmol, 3.0 equiv.), followed by BzCl (1.9 mL, 16.5 mmol, 1.1 equiv.). The reaction mixture was stirred at room temperature for 16 h. Upon completion, the reaction was quenched by addition of water (50 mL) and extracted with EtOAc (3 × 20 mL). The combined organic phase was washed with brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to give a residue that was purified by flash column chromatography on silica gel (eluent: petroleum benzine:EtOAc = 4:1) to provide **S8** in 97% yield (3.6 g) as a white solid.

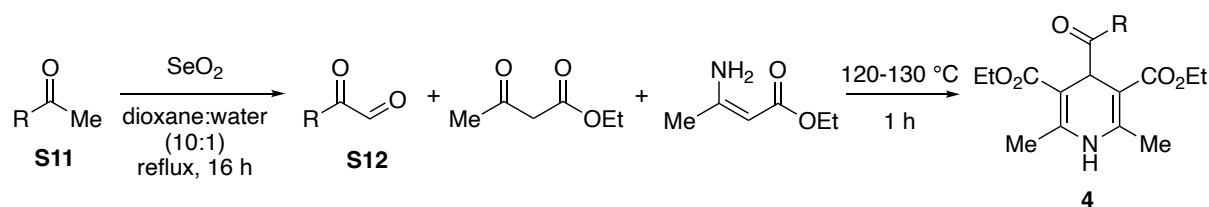
To **S8** (3.6 g, 14.6 mmol, 1.0 equiv.) in MeOH was added KBH_4 (1.2 g, 22.2 mmol, 1.5 equiv.) portion-wise and the reaction mixture refluxed for 16 h. Upon completion, the reaction mixture was quenched by addition water (20 mL) and the excess methanol removed *in vacuo*. The aqueous phase was extracted with EtOAc (3 × 50 mL). The combined organic phase was

washed with brine (20 mL), dried over anhydrous Na₂SO₄ and concentrated *in vacuo* to afford **S9** in 90% yield, which was used in the next step without further purification.

To **S9** (2.9 g, 13.2 mmol, 1.0 equiv.) in DCM (50 mL) was added DMP (8.3 g, 19.8 mmol, 1.2 equiv.). The reaction mixture was stirred at room temperature for 2 h. Upon completion, the reaction mixture was quenched by addition of saturated sodium thiosulfate (50 mL) and stirred until the organic phase become clear (approximately 30 min). Then, the organic phase was washed with brine (20 mL), dried over anhydrous Na₂SO₄ and concentrated *in vacuo* to give a residue that was purified by flash column chromatography on silica gel (eluent: petroleum benzene:EtOAc = 4:1) to provide **S10** in 83% yield (2.4 g) as a yellow solid.

To a round bottom flask containing a magnetic stirring bar and **S10** (2.4 g, 11 mmol, 1.0 equiv.) in EtOH (20 mL) was added ethyl acetoacetate (2.86 mL, 22 mmol, 2.0 equiv.) and ammonium acetate (852 mg, 11 mmol, 1.0 equiv.). The reaction mixture was heated to reflux and stirred at this temperature for 16 h. Upon completion, the reaction mixture was concentrated *in vacuo*. The crude residue was dissolved in EtOAc (20 mL) and washed with brine (20 mL). The aqueous phase was extracted with EtOAc (2 × 50 mL). The combined organic phase was washed with brine (20 mL), dried over anhydrous Na₂SO₄ and concentrated *in vacuo* to give a residue that was purified by flash column chromatography on silica gel (eluent: petroleum benzene:EtOAc = 2:1) to provide the title compound **2i** (2.0 g, 42% yield) as yellow solid.

2.4 General procedure for the synthesis of 4-acyl-substituted DHPs (**4a–o**)^{S8}

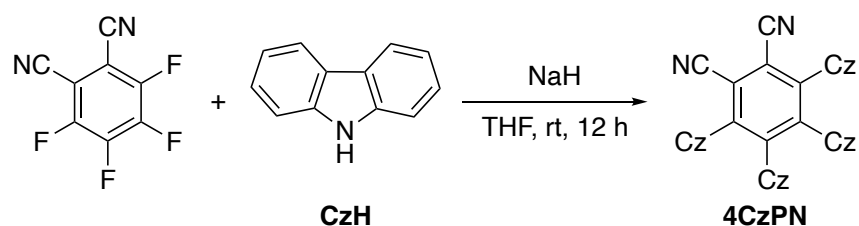


To a round bottom flask containing a magnetic stirring bar and the appropriate ketone **S11** (10 mmol, 1.0 equiv.) in dioxane (20 mL) and water (2 mL) was added SeO₂ (1.3 g, 12 mmol, 1.2 equiv.) and the reaction mixture was heated to reflux for 24 h. Upon completion, the reaction

mixture was filtered through a thin pad of celite to remove the dark insoluble impurities. The filtrate was concentrated *in vacuo* and the residue was used in the next step without further purification.

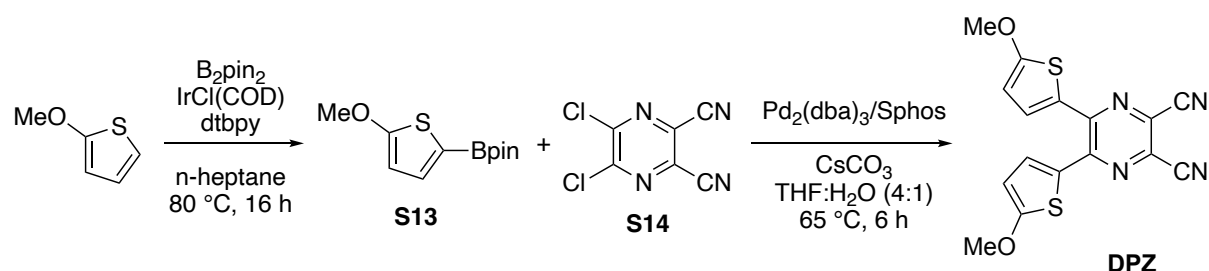
A solution of α -keto aldehyde **S12** (5.0 mmol, 1.0 equiv.) in ethyl acetoacetate (0.65 mL, 5.0 mmol, 1.0 equiv.) was stirred at 130 °C for 5–15 min. The reaction mixture was cooled to 80 °C, ethyl 3-aminocrotonate (0.65 g, 5.0 mmol, 1.0 equiv.) was added portion-wise (exothermic reaction), and then the reaction mixture was heated to 120 °C for another 5–15 min and monitored by TLC. The residue was cooled to ambient temperature and the corresponding **4** was purified by flash column chromatography on silica gel (eluent: petroleum benzine:EtOAc = 4:1) to provide the title compound.

2.5 Procedure for the synthesis of **4CzPN**^{S9}



To a round bottom flask containing a magnetic stirring bar and carbazole (0.84 g, 5.0 mmol, 5.0 equiv.) in THF (20 mL), was slowly added NaH (60% in oil, 0.60 g, 15.0 mmol, 15 equiv.). The reaction mixture was stirred at room temperature for 30 min, then tetrafluorophthalonitrile (0.20 g, 1.00 mmol, 1.0 equiv.) was added and the resulting reaction mixture stirred at room temperature for 12 h. Upon completion, the reaction mixture was quenched with water (2 mL) and concentrated *in vacuo*. The residue was washed with water (20 mL) and EtOH (20 mL), then recrystallised from petroleum benzine/dichloromethane. The crystals were filtered and dried under vacuum to provide the title compound **4CzPN** (0.71 g, 90% yield) as yellow solid.

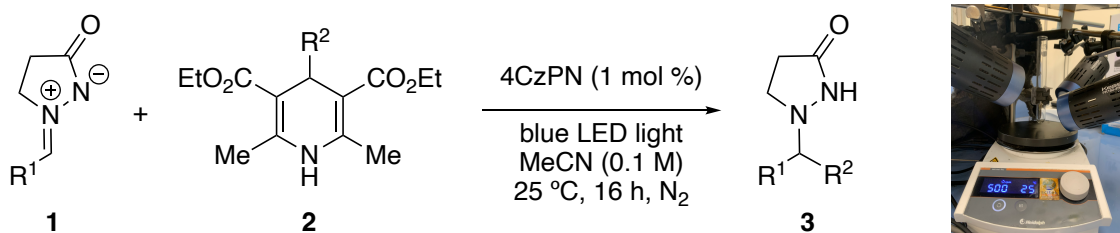
S2.6 Procedure for the synthesis of DPZ^{S10}



To a round bottom flask containing a magnetic stirring bar and bis(pinacolate)diboron (508 mg, 2.0 mmol, 1 equiv.) in *n*-heptane (6 mL) were added 2-methoxythiophene (2.3 g, 20.0 mmol), $\text{IrCl}(\text{COD})$ (12 mg, 0.03 mmol, 0.015 equiv.) and dtbpy (8 mg, 0.03 mmol, 0.015 equiv.) and the reaction mixture stirred at 80 °C for 16 h. Upon completion, the reaction mixture was diluted with toluene (20 mL) and washed with brine (20 mL). The organic phase was concentrated *in vacuo* to give a residue that was purified by flash column chromatography on silica gel (eluent: petroleum benzine:EtOAc = 10:1) to provide (5-methoxythiophen-2-yl)boronic acid pinacol ester **S13** in 75% yield (170 mg) as a yellow solid.

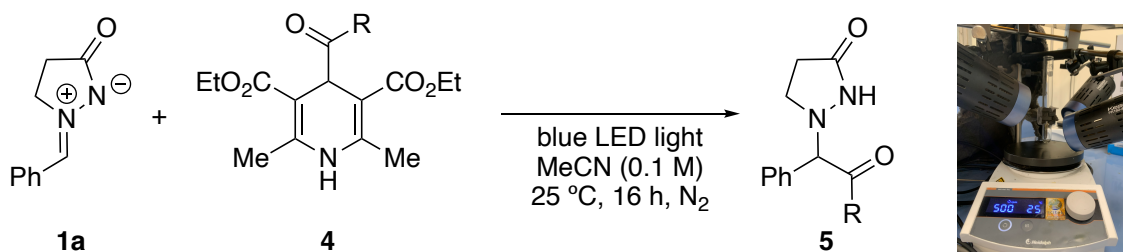
To a round bottom flask containing a magnetic stirring bar, 5,6-dichloropyrazine-2,3-dicarbonitrile (147 mg, 0.74 mmol, 1 equiv.) and (5-methoxythiophen-2-yl)boronic acid pinacol ester (360 mg, 1.5 mmol, 2 equiv.) were dissolved in a THF/water mixture (4:1; 20 mL). Nitrogen was bubbled through the reaction mixture for 15 min whereupon $\text{Pd}_2(\text{dba})_3$ (34 mg, 0.037 mmol, 0.05 equiv.), SPhos (16 mg, 0.037 mmol, 0.05 equiv.) and Cs_2CO_3 (506 mg, 1.5 mmol, 2 equiv.) were added and the reaction mixture stirred at 65 °C for 6 h. Upon completion, the reaction mixture was diluted with water (20 mL) and extracted with dichloromethane (3×20 mL). The combined organic phase was washed with brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to give a residue that was purified by filtration through a short plug of silica gel (eluent: dichloromethane:*n*-hexane = gradient 1:2 to 2:1) and subsequent recrystallisation from dichloromethane/*n*-hexane to provide the title compound **DPZ** (184 mg, 70% yield) as orange solid.

2.7 General procedure for the 4-CzPN-catalysed photoredox reaction of 1 and 2



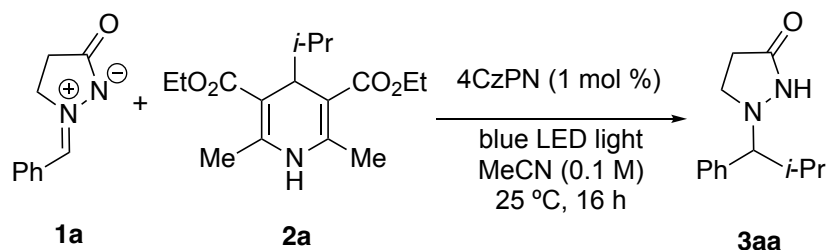
To a 10 mL glass screw cap reaction tube equipped with a magnetic stirring bar, was added azomethine imine **1** (0.3 mmol, 1.0 equiv.), DHP **2** (0.6 mmol, 2.0 equiv.) and 4CzPN (0.003 mmol, 1 mol %). The reaction tube was transferred to an inert atmosphere glovebox and anhydrous degassed MeCN (3.0 mL, 0.1 M) were added *via* a gastight syringe. The reaction tube was sealed, and the reaction mixture stirred under blue LED light irradiation (456 nm, 10 cm distance from the lamp) at 25 °C (maintained by fan cooling) for 16 h. Upon completion, the reaction mixture was concentrated *in vacuo*. The crude residue was purified by flash column chromatography on silica gel (eluent: EtOAc) to provide the title compound.

2.8 General procedure for the photoredox reaction of 1a and 4



To a 10 mL glass screw cap reaction tube equipped with a magnetic stirring bar, was added the azomethine imine **1** (0.3 mmol, 1.0 equiv.) and DHP **4** (0.6 mmol, 2.0 equiv.). The reaction tube was transferred to an inert atmosphere glovebox and anhydrous degassed MeCN (0.1 M, 3.0 mL) were added *via* a gastight syringe. The reaction tube was sealed, and the reaction mixture stirred under blue LED light irradiation (456 nm, 10 cm distance from the lamp) at 25 °C (maintained by fan cooling) for 16 h. Upon completion, the reaction mixture was concentrated *in vacuo*. The crude residue was purified by flash column chromatography on silica gel (eluent: EtOAc) to provide the title compound.

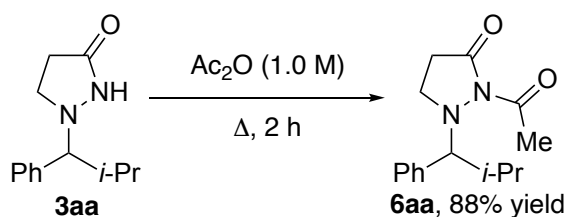
2.9 Procedure for the gramme-scale reaction of **1a** and **2a**



To a 100 mL round bottle flask equipped with a magnetic stirring bar, was added azomethine imine **1a** (0.88 g, 5 mmol, 1.0 equiv.), DHP **2a** (1.9 g, 6.5 mmol, 1.5 equiv.) and 4CzPN (40 mg, 0.05 mmol, 1 mol %). The round bottle flask was transferred to an inert atmosphere glovebox and anhydrous degassed MeCN (50 mL, 0.1 M) were added *via* a syringe. The round bottle flask was sealed, and the reaction mixture stirred under blue LED light irradiation (456 nm, 10 cm distance from the lamp) at 25 °C (maintained by fan cooling) for 16 h. Upon completion, the reaction mixture was concentrated *in vacuo*. The crude residue was purified by flash column chromatography on silica gel (eluent: EtOAc) to provide the **3aa** (1.9 g, 99% yield).

2.10 Procedures for the selective transformations of **3aa** and **5aa**

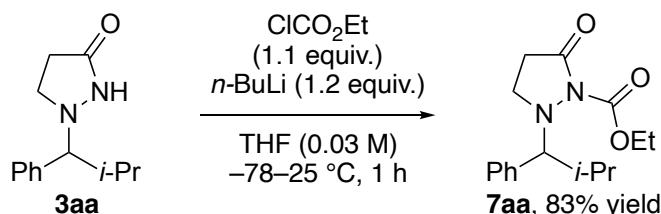
2.10.1 Procedure for the *N*-amidation of **3aa**^{S11-14}



To a round bottom flask containing a magnetic stirring bar, was added **3aa** (65.4 mg, 0.3 mmol, 1.0 equiv.) in acetic anhydride (0.3 mL, 3.0 mmol, 10.0 equiv.). The reaction mixture was stirred under reflux for 2 h. Upon completion, the reaction mixture was quenched by the addition of saturated NaHCO₃ (20 mL). The aqueous phase was extracted with EtOAc (3 × 20 mL). The combined organic phase was washed with brine (20 mL), dried over anhydrous Na₂SO₄ and concentrated *in vacuo* to give a residue that was purified by flash column

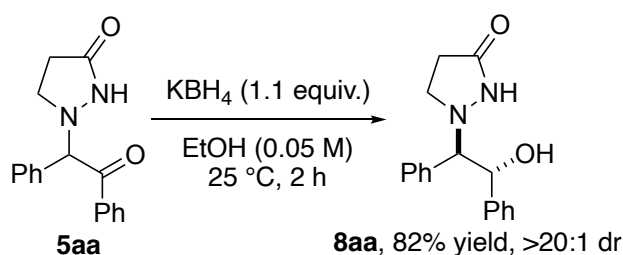
chromatography on silica gel (eluent: EtOAc) to provide **6aa** (68.7 mg, 88% yield) as white solid.

2.10.2 Procedure for the *N*-carbamation of **3aa**^{S11-14}



To a round bottom flask containing a magnetic stirring bar, was added **3aa** (65.4 mg, 0.3 mmol, 1.0 equiv.) in THF (10 mL). *n*BuLi (2.0 M in 0.18 mL, 0.36 mmol, 1.2 equiv.) was added dropwise at $-78\text{ }^\circ\text{C}$. The reaction mixture was stirred at this temperature for 1 h before adding ClCO_2Et (0.036 mL, 0.33 mmol, 1.1 equiv.) and the reaction mixture was stirred at room temperature for a further 1 h. Upon completion, the reaction mixture was quenched by the addition of water (10 mL). The aqueous phase was extracted with EtOAc ($3 \times 20\text{ mL}$). The combined organic phase was washed with brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to give a residue that was purified by flash column chromatography on silica gel (eluent: EtOAc) to provide **7aa** (72.3 mg, 83% yield) as yellow wax.

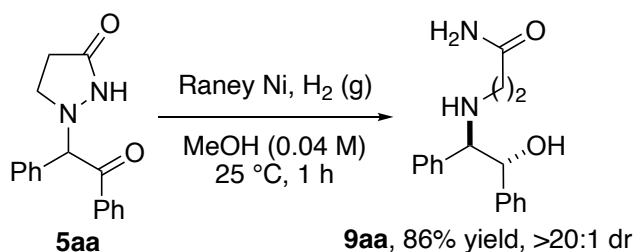
2.10.3 Procedure for the reduction of **5aa**^{S11-14}



To a round bottom flask containing a magnetic stirring bar, was added KBH_4 (18 mg, 1.1 equiv.), pyrazolidin-3-one **1a** (84 mg, 0.3 mmol) in EtOH (0.5 M, 6 mL), and the resulting reaction mixture was stirred at room temperature for 2 h. Upon completion, the reaction mixture was quenched by the addition of water (10 mL). The aqueous phase was extracted with EtOAc ($3 \times 10\text{ mL}$). The combined organic phase was washed with water (10 mL), brine (20

mL), dried over anhydrous Na₂SO₄ and concentrated *in vacuo* to give a residue that was purified by flash column chromatography on silica gel (eluent: dichloromethane:methanol = 9:1) to provide **8aa** (70 mg, 82% yield) as white solid.

2.10.4 Procedure for the reductive ring-opening of **5aa**^{S11-14}

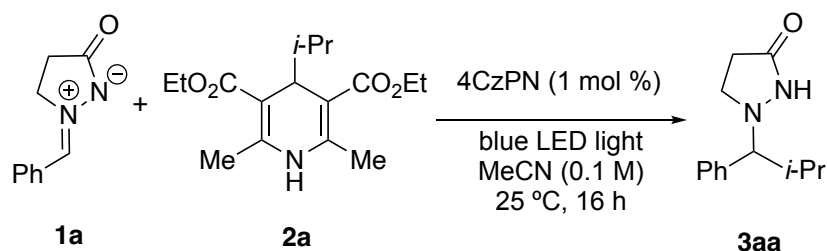


To a round bottom flask containing a magnetic stirring bar, was added Raney nickel (400 mg in 2 mL MeOH) and **5aa** (84 mg, 0.3 mmol, 1 equiv.) in MeOH (7 mL). The reaction mixture was stirred at room temperature for 1 h under a hydrogen atmosphere. Upon completion, the reaction mixture was filtered through Celite, and washed with MeOH (20 mL) to remove the Raney-nickel. The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel (eluent: dichloromethane:methanol = 9:1) to provide **9aa** (73 mg, 86% yield) as white solid.

3. Control Experiments

3.1 Control reactions with 1a and 2a

Table S1. Reactions of 1a and 2a deviated from the optimised 4CzPN-catalysed conditions^a

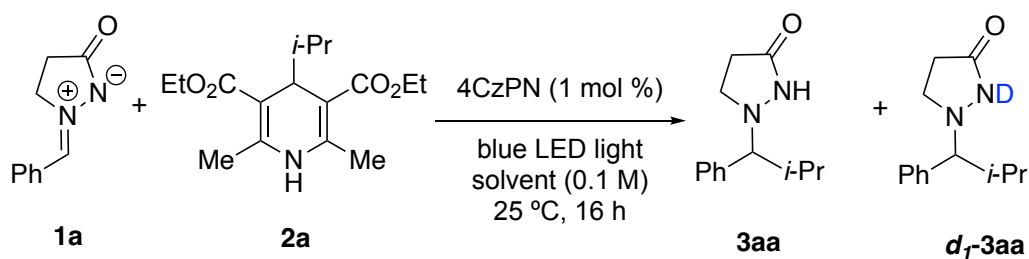


entry	deviation from the standard reaction conditions	yield (%)
1	no light	— ^b
2	no 4CzPN	— ^b
3	BHT (3.0 equiv.)	99%
4	TEMPO (3.0 equiv.)	— ^b

^a Unless stated otherwise, all reactions were performed with **1a** (0.3 mmol), **2a** (0.6 mmol, 2.0 equiv.), 4CzPN (1 mol %) in MeCN (0.1 M, 3 mL) under blue LED light ($\lambda_{\text{max}} = 456 \text{ nm}$) and nitrogen atmosphere at 25 °C for 16 h. ^b No reaction detected by TLC analysis and ¹H NMR measurements.

3.2 Deuterium labelling experiments

Table S2. Control experiments with **1a** and **2a**^a



entry	solvent	3aa : d₁-3aa ^b
1	MeCN	100:0
2	<i>d</i> ₃ -MeCN	100:0
3	MeCN:D ₂ O (9:1 v/v)	64:36

^a Unless stated otherwise, all reactions were performed with **1a** (0.3 mmol), **2a** (0.6 mmol, 2.0 equiv.), 4CzPN (1 mol %) in solvent (0.1 M, 3 mL) under blue LED light ($\lambda_{\text{max}} = 456 \text{ nm}$) and nitrogen atmosphere at 25 °C for 16 h. ^b Product ratio of **3aa**:**d₁-3aa** was determined by ¹H NMR measurements.

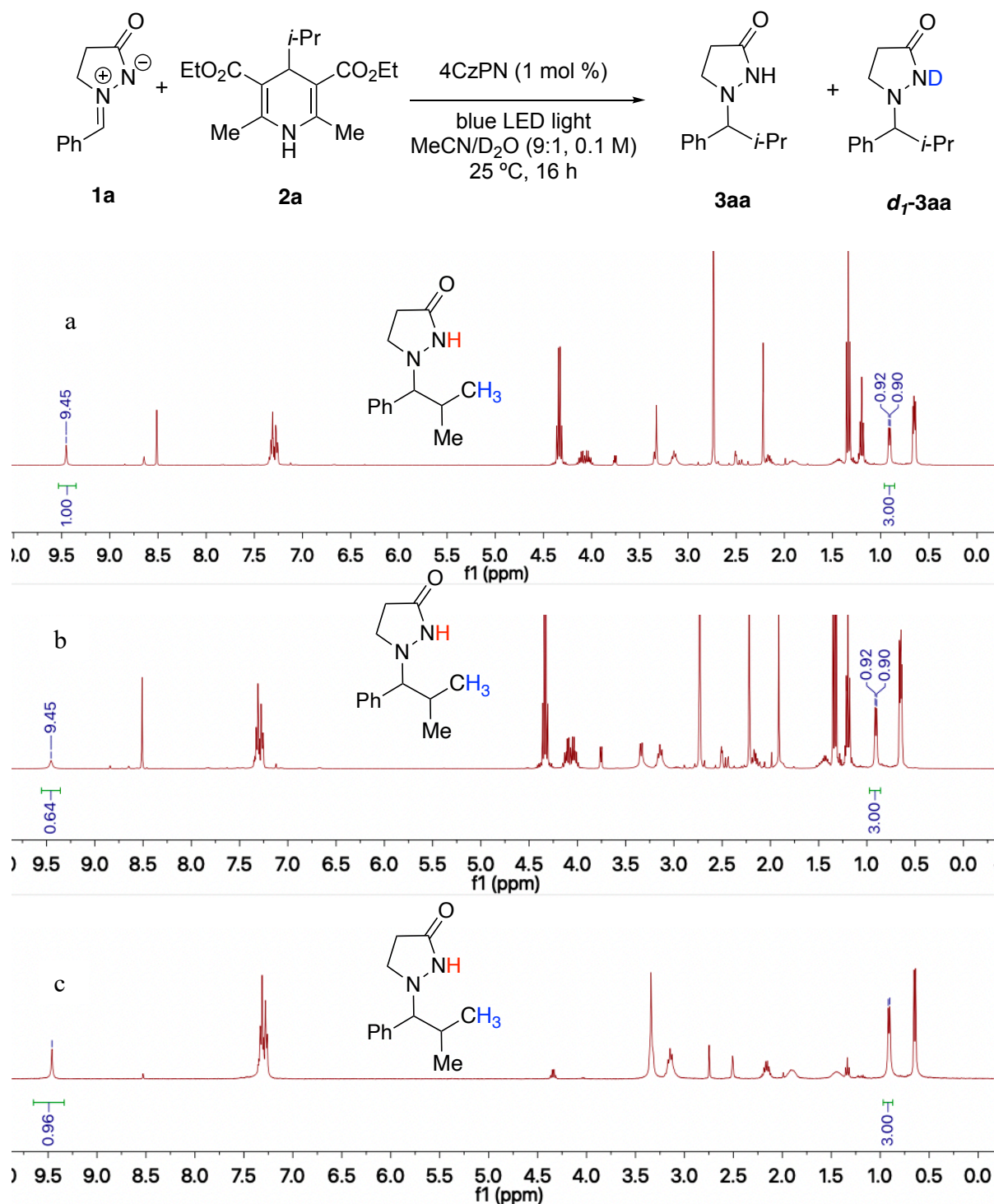
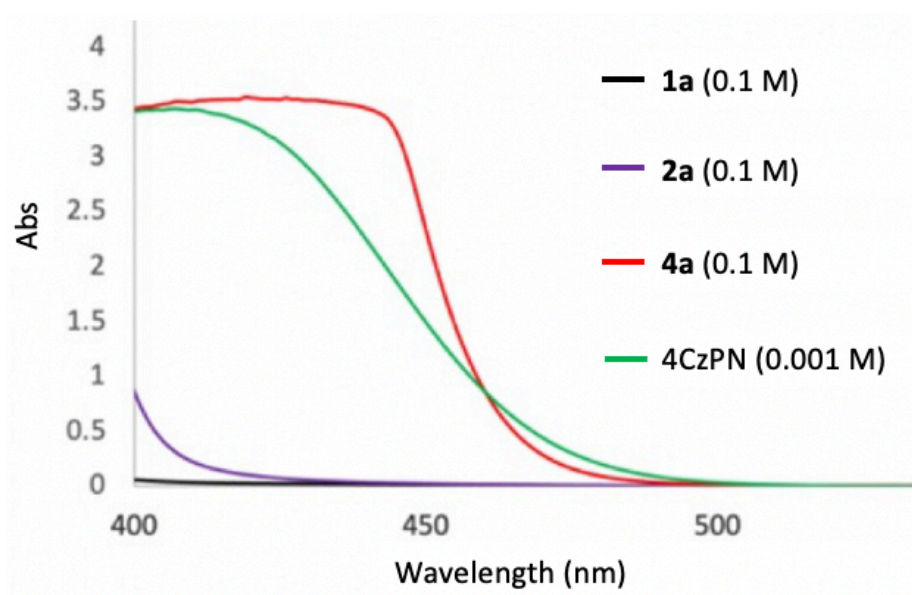


Figure S1. ¹H NMR analysis of deuterium control experiments: (a) reaction performed with **1a** and **2a** in *d*₃-MeCN, ¹H NMR in *d*₃-MeCN; (b) reaction performed with **1a** and **2a** in MeCN:D₂O (9:1), ¹H NMR in CDCl₃; (c) reaction performed with **3aa** in MeCN:D₂O (9:1), ¹H NMR in CDCl₃.

3.3 UV-vis spectroscopic measurements

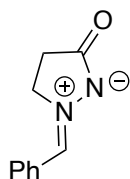
The solution of azomethine imine (**1a**) was prepared by adding **1a** (53.1 mg, 0.3 mmol) in MeCN (3 mL). The solution of DHP-*i*Pr (**2a**) was prepared by adding **2a** (88.6 mg, 0.3 mmol) in MeCN (3 mL). The solution of DHP-COPh (**4a**) was prepared by adding **4a** (107.2 mg, 0.3 mmol) in MeCN (3 mL). The solution of 4CzPN was prepared by adding 4CzPN (2.4 mg, 0.003 mmol) in MeCN (3 mL). The fresh standard solutions were transferred to four separate 4 mL glass cuvettes and scanned from the 300–700 nm region in a UV-vis spectrometer.



Scheme 1. UV-vis spectroscopic measurements of azomethine imine **1a** (0.1 M), DHP **2a** (0.1 M), DHP **4a** (0.1 M) and 4CzPN (0.001 M) in MeCN.

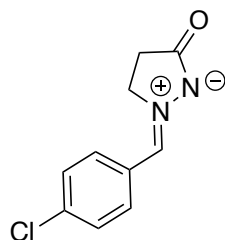
4. Compound Analytical Data

2-Benzylidene-5-oxopyrazolidin-2-ium-1-ide (1a)^{S1}



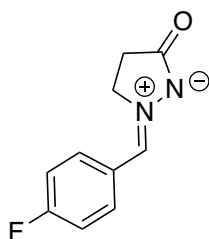
White solid (1.9 g, 55% yield); ¹H NMR (600 MHz, CDCl₃) δ 8.26 (dd, *J* = 7.8, 2.1 Hz, 2H), 7.48 – 7.37 (m, 3H), 7.14 (s, 1H), 4.55 – 4.41 (m, 2H), 2.80 – 2.67 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 184.9 (C=O), 132.7 (C=N), 131.8 (Ar), 131.6 (Ar), 129.2 (Ar), 128.8 (Ar), 57.9 (CH₂), 29.4 (CH₂).

2-(4-Chlorobenzylidene)-5-oxopyrazolidin-2-ium-1-ide (1b)^{S15}



White solid (1.6 g, 40% yield); ¹H NMR (600 MHz, CDCl₃) δ 8.22 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.09 (s, 1H), 4.55 – 4.48 (m, 2H), 2.82 – 2.73 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 184.9 (C=O), 137.8 (C=N), 132.6 (Ar), 131.0 (Ar), 129.2 (Ar), 127.7 (Ar), 58.1 (CH₂), 29.3 (CH₂).

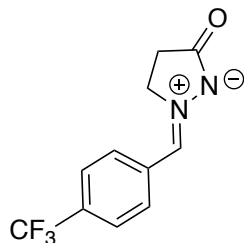
2-(4-Fluorobenzylidene)-5-oxopyrazolidin-2-ium-1-ide (1c)^{S16}



White solid (1.8 g, 47% yield); ¹H NMR (600 MHz, CDCl₃) δ 8.32 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.17 – 7.06 (m, 3H), 4.51 (t, *J* = 8.4 Hz, 2H), 2.84 – 2.73 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 184.9 (C=O), 164.3 (d, *J*_{C-F} = 255.2 Hz, C=N), 134.0 (d, *J*_{C-F} = 9.1 Hz, Ar), 131.34 (Ar),

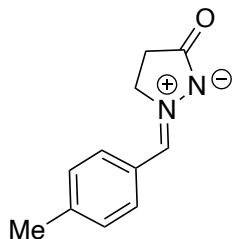
125.6 (d, J_{C-F} = 3.0 Hz, Ar), 116.2 (d, J_{C-F} = 21.1 Hz, Ar), 57.86 (CH₂), 29.36 (CH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ -104.9.

2-(4-(Trifluoromethyl)benzylidene)pyrazolidin-2-ium-1-ide (1d)^{S15}



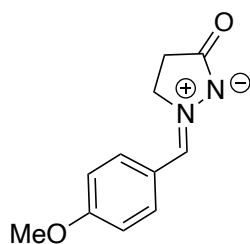
White solid (1.45 g, 30% yield); ¹H NMR (600 MHz, CDCl₃) δ 8.39 (d, J = 8.3 Hz, 2H), 7.67 (d, J = 8.3 Hz, 2H), 7.15 (s, 1H), 4.58 (t, J = 8.1 Hz, 2H), 2.97 – 2.72 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 185.2 (C=O), 132.5 (d, J_{C-F} = 33.2 Hz, Ar), 132.2 (Ar), 131.4 (Ar), 129.9 (Ar), 125.7 (q, J_{C-F} = 3.0 Hz, CF₃), 58.5 (CH₂), 29.1 (CH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ -63.1.

2-(4-Methylbenzylidene)-5-oxopyrazolidin-2-ium-1-ide (1e)^{S17}



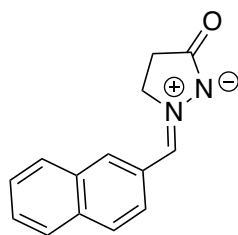
White solid (1.2 g, 32% yield); ¹H NMR (600 MHz, CDCl₃) δ 8.16 (dd, J = 6.1, 2.6 Hz, 2H), 7.23 (dd, J = 5.6, 2.8 Hz, 2H), 7.09 (s, 1H), 4.47 (t, J = 8.3 Hz, 2H), 2.79 – 2.70 (m, 2H), 2.38 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 184.8 (C=O), 142.9 (C=N), 133.0 (Ar), 131.7 (Ar), 129.6 (Ar), 126.6 (Ar), 57.7 (CH₂), 29.5 (CH₂), 21.8 (CH₃).

2-(4-Methoxybenzylidene)-5-oxopyrazolidin-2-ium-1-ide (1f)^{S16}



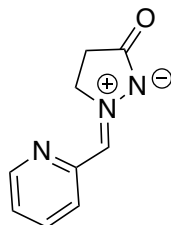
White solid (1.0 g, 25% yield); ¹H NMR (600 MHz, CDCl₃) δ 8.27 – 8.19 (m, 2H), 7.09 (s, 1H), 6.94 – 6.86 (m, 2H), 4.44 (dt, *J* = 7.5, 3.3 Hz, 2H), 3.82 (s, 3H), 2.77 – 2.66 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 184.6 (C=O), 162.4 (C=N), 133.8 (Ar), 133.0 (Ar), 122.1 (Ar), 114.3 (Ar), 57.3 (CH₂), 55.5 (CH₃), 29.6 (CH₂).

2-(Naphthalen-2-ylmethylene)-5-oxopyrazolidin-2-ium-1-ide (1g)^{S17}



White solid (1.8 g, 40% yield); ¹H NMR (600 MHz, CDCl₃) δ 9.06 (s, 1H), 8.08 – 8.00 (m, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.82 (dd, *J* = 14.7, 8.3 Hz, 2H), 7.54 (dd, *J* = 19.2, 7.6 Hz, 2H), 7.20 (s, 1H), 4.53 (t, *J* = 8.1 Hz, 2H), 2.82 (t, *J* = 8.1 Hz, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 185.1 (C=O), 162.3 (C=N), 134.5 (Ar), 133.0 (Ar), 133.0 (Ar), 132.5 (Ar), 129.7 (Ar), 128.5 (Ar), 128.4 (Ar), 127.6 (Ar), 127.1 (Ar), 127.0 (Ar), 126.4 (Ar), 58.0 (CH₂), 29.4 (CH₂).

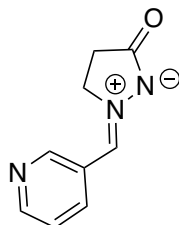
5-Oxo-2-(pyridin-2-ylmethylene)pyrazolidin-2-ium-1-ide (1h)^{S16}



Yellow solid (1.2 g, 33% yield); ¹H NMR (600 MHz, CDCl₃) δ 9.20 (d, *J* = 8.1 Hz, 1H), 8.68 (d, *J* = 4.7 Hz, 1H), 7.83 (td, *J* = 7.9, 1.8 Hz, 1H), 7.37 (s, 1H), 7.33 (ddd, *J* = 7.7, 4.7, 1.2 Hz,

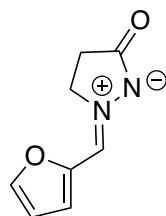
1H), 4.67 – 4.52 (m, 2H), 2.94 – 2.78 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 185.2 (Ar), 150.0 (C=N), 148.1 (Ar), 137.0 (Ar), 132.4 (Ar), 127.7 (Ar), 125.0 (Ar), 58.4 (CH₂), 29.1 (CH₂).

5-Oxo-2-(pyridin-3-ylmethylene)pyrazolidin-2-ium-1-ide (1i)^{S18}



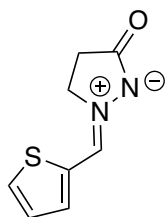
White solid (1.0 g, 29% yield); ¹H NMR (400 MHz, CDCl₃) δ 9.16 (dt, *J* = 8.2, 2.0 Hz, 1H), 8.92 (d, *J* = 2.3 Hz, 1H), 8.62 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.41 (dd, *J* = 8.2, 4.8 Hz, 1H), 7.17 (d, *J* = 1.6 Hz, 1H), 4.66 – 4.51 (m, 2H), 2.90 – 2.77 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 185.1 (C=O), 151.6 (C=N), 151.5 (Ar), 138.1 (Ar), 128.6 (Ar), 125.9 (Ar), 123.9 (Ar), 58.3 (CH₂), 29.3 (CH₂).

2-(Furan-2-ylmethylene)-5-oxopyrazolidin-2-ium-1-ide (1j)^{S19}



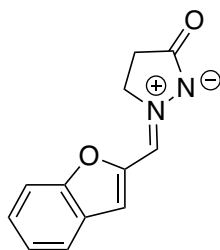
White solid (1.3 g, 40% yield); ¹H NMR (600 MHz, CDCl₃) δ 7.91 (d, *J* = 3.7 Hz, 1H), 7.58 (d, *J* = 1.7 Hz, 1H), 7.21 (d, *J* = 0.8 Hz, 1H), 6.66 – 6.60 (m, 1H), 4.46 (t, *J* = 8.1 Hz, 2H), 2.88 – 2.80 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 184.4 (C=O), 146.2 (C=N), 145.8 (Ar), 121.4 (Ar), 121.1 (Ar), 113.7 (Ar), 56.3 (CH₂), 30.1 (CH₂).

5-Oxo-2-(thiophen-2-ylmethylene)pyrazolidin-2-ium-1-ide (1k)^{S17}



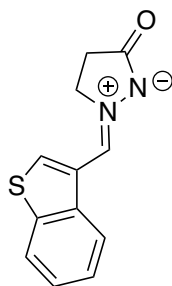
White solid (0.76 g, 21% yield); ¹H NMR (600 MHz, CDCl₃) δ 7.76 (d, *J* = 5.0 Hz, 1H), 7.55 (d, *J* = 3.3 Hz, 1H), 7.49 (s, 1H), 7.17 (dd, *J* = 5.1, 3.9 Hz, 1H), 4.52 – 4.42 (m, 2H), 2.91 – 2.82 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 183.2 (C=O), 135.5 (C=N), 133.2 (Ar), 132.3 (Ar), 127.6 (Ar), 126.6 (Ar), 55.5 (CH₂), 30.5 (CH₂).

2-(Benzofuran-2-ylmethylene)-5-oxopyrazolidin-2-ium-1-ide (1l)



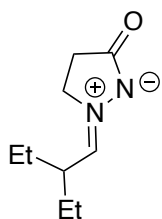
White solid (2.0 g, 48% yield); m.p. 255–256 °C ¹H NMR (600 MHz, CDCl₃) δ 8.34 (s, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.42 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1H), 7.32 – 7.28 (m, 2H), 4.55 (t, *J* = 7.5 Hz, 2H), 2.95 – 2.86 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 184.8 (C=O), 155.5 (C=N), 146.4 (Ar), 128.5 (Ar), 127.6 (Ar), 123.9 (Ar), 123.1 (Ar), 117.3 (Ar), 111.4 (Ar), 57.0 (CH₂), 29.9 (CH₂); HRMS (ESI) calcd. for C₁₂H₁₁N₂O₂ (M⁺ + H): 215.0821, found 251.0818; IR (neat cm⁻¹): 3052, 1672, 1654, 1495, 1274, 1105, 964, 769, 756.

2-(Benzo[*b*]thiophen-3-ylmethylene)-5-oxopyrazolidin-2-ium-1-ide (1m)



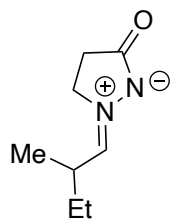
White solid (2.0 g, 44% yield); m.p. 249–250 °C ^1H NMR (600 MHz, CDCl_3) δ 9.55 (s, 1H), 7.86 (dd, $J = 29.6, 8.0$ Hz, 2H), 7.54 – 7.39 (m, 3H), 4.58 (t, $J = 8.1$ Hz, 2H), 2.88 (t, $J = 8.1$ Hz, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 185.0 (C=O), 139.4 (C=N), 137.7 (Ar), 136.8 (Ar), 125.4 (Ar), 125.3 (Ar), 124.1 (Ar), 123.5 (Ar), 123.2 (Ar), 119.9 (Ar), 57.1 (CH_2), 29.9 (CH_2); HRMS (ESI) calcd. for $\text{C}_{12}\text{H}_{11}\text{N}_2\text{OS}$ ($\text{M}^+ + \text{H}$): 231.0592, found 231.0589; IR (neat cm^{-1}): 3157, 3065, 1674, 1601, 1552, 1280, 1106, 953, 741.

2-(2-Ethylbutylidene)-5-oxopyrazolidin-2-ium-1-ide (1n)



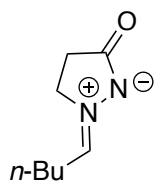
White solid (1.0 g, 30% yield); m.p. 56–57 °C; ^1H NMR (600 MHz, CDCl_3) δ 6.41 (s, 1H), 4.33 (t, $J = 8.2$ Hz, 2H), 3.14 (s, 1H), 2.81 – 2.70 (m, 2H), 1.65 – 1.56 (m, 2H), 1.53 – 1.47 (m, 2H), 0.90 (m, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 183.6 (C=O), 56.3 (CH_2), 42.1 (CH), 30.2 (CH_2), 24.3 (CH_2), 11.6 (CH_3); HRMS (ESI) calcd. for $\text{C}_9\text{H}_{17}\text{N}_2\text{O}$ ($\text{M}^+ + \text{H}$): 169.1341, found 169.1338; IR (neat cm^{-1}): 2961, 2930, 1675, 1601, 1459, 1295, 1080, 951, 790.

2-(2-Methylbutylidene)-5-oxopyrazolidin-2-ium-1-ide (1o)



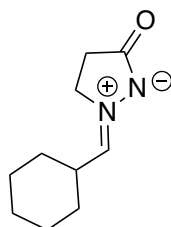
White wax (1.0 g, 30% yield); ^1H NMR (400 MHz, CDCl_3) δ 6.69 (d, $J = 7.9$ Hz, 1H), 4.40 (d, $J = 8.7$ Hz, 2H), 3.08 (p, $J = 7.1$ Hz, 1H), 2.72 – 2.57 (m, 2H), 1.49 (ddq, $J = 35.5, 13.9, 7.2$ Hz, 2H), 1.07 (d, $J = 6.8$ Hz, 3H), 0.86 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 183.5 (C=O), 145.6 (C=N), 55.9 (CH_2), 35.2 (CH_2), 30.1 (CH), 26.4 (CH_2), 15.6 (CH_3), 11.3 (CH_3); HRMS (ESI) calcd. for $\text{C}_8\text{H}_{15}\text{N}_2\text{O}$ ($\text{M}^+ + \text{H}$): 155.1184, found 155.1181; IR (neat cm^{-1}): 3380, 2967, 1675, 1601, 1440, 1221, 1087, 956, 790.

5-Oxo-2-pentylidenepyrazolidin-2-ium-1-ide (1p)^{S20}



White wax (0.34 g, 11% yield); ^1H NMR (400 MHz, CDCl_3) δ 6.55 (t, $J = 6.2$ Hz, 1H), 4.31 (t, $J = 8.4$ Hz, 2H), 2.82 – 2.64 (m, 4H), 1.62 – 1.52 (m, 2H), 1.39 (q, $J = 7.5$ Hz, 2H), 0.92 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 183.5 (C=O), 140.3 (C=N), 56.0 (CH_2), 30.3 (CH_2), 29.2 (CH_2), 27.5 (CH_2), 22.5 (CH_2), 13.6 (CH_3).

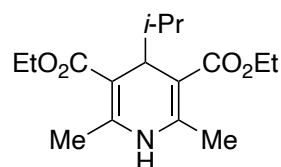
2-(Cyclohexylmethylene)-5-oxopyrazolidin-2-ium-1-ide (1q)^{S17}



White solid (0.72 g, 20% yield); ^1H NMR (600 MHz, CDCl_3) δ 6.39 (d, $J = 5.9$ Hz, 1H), 4.29 (t, $J = 8.3$ Hz, 2H), 3.12 (dtq, $J = 12.0, 8.3, 3.7$ Hz, 1H), 2.73 (ddt, $J = 10.7, 5.9, 2.8$ Hz, 2H),

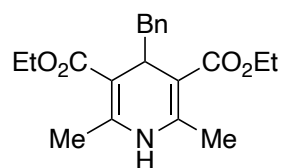
1.91 (d, $J = 12.0$ Hz, 2H), 1.73 – 1.62 (m, 3H), 1.39 – 1.28 (m, 2H), 1.20 (q, $J = 12.8$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 183.5 (C=O), 143.5 (C=N), 56.2 (CH_2), 37.8 (CH_2), 30.1 (CH), 28.6 (CH_2), 25.6 (CH_2), 24.9 (CH_2).

Diethyl 4-isopropyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2a)^{S21}



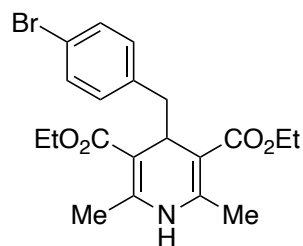
Yellow solid (0.66 g, 45% yield); ^1H NMR (600 MHz, CDCl_3) δ 4.26 – 4.08 (m, 4H), 3.90 (d, $J = 5.4$ Hz, 1H), 2.28 (s, 6H), 1.28 (t, $J = 7.1$ Hz, 6H), 0.73 (d, $J = 6.9$ Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 168.7 (C=O), 144.6 (C=C), 101.8 (C=C), 59.5 (CH), 38.8 (CH_2), 35.5 (CH_2), 19.3 (CH_3), 18.5 (CH_3), 14.4 (CH_3).

Diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2b)^{S21}



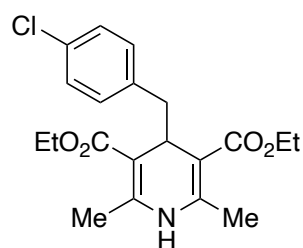
Yellow solid (0.57 g, 33% yield); ^1H NMR (600 MHz, CDCl_3) δ 7.13 (dd, $J = 17.9, 7.3$ Hz, 3H), 7.07 – 6.92 (m, 2H), 5.87 (s, 1H), 4.18 (t, $J = 5.6$ Hz, 1H), 4.11 – 3.93 (m, 4H), 2.56 (d, $J = 5.7$ Hz, 2H), 2.16 (s, 6H), 1.21 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 167.9 (C=O), 145.7 (C=C), 139.3 (Ar), 130.1 (Ar), 127.3 (Ar), 125.6 (Ar), 101.7 (C=C), 59.6 (CH), 42.4 (CH_2), 35.5 (CH_2), 19.1 (CH_3), 14.3 (CH_3).

Diethyl 4-(4-bromobenzyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2c)^{S21}



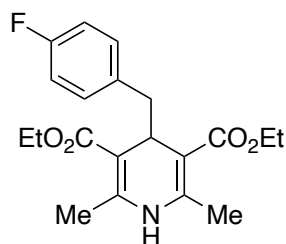
Yellow solid (0.21 g, 10% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 8.3 Hz, 2H), 5.22 (s, 1H), 4.18 (t, *J* = 5.4 Hz, 1H), 4.15 – 4.03 (m, 4H), 2.54 (d, *J* = 5.4 Hz, 2H), 2.17 (s, 6H), 1.25 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 167.7 (C=O), 145.4 (C=C), 138.3 (Ar), 131.8 (Ar), 130.3 (Ar), 119.7 (Ar), 101.6 (C=C), 59.7 (CH), 41.6 (CH₂), 35.4 (CH₂), 19.3 (CH₃), 14.4 (CH₃).

Diethyl 4-(4-chlorobenzyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2d)^{S22}



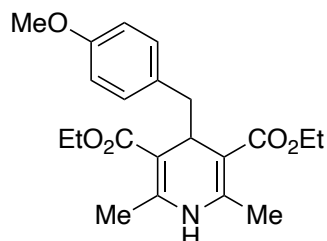
Yellow solid (0.57 g, 30% yield); ¹H NMR (600 MHz, CDCl₃) δ 7.13 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 5.29 (s, 1H), 4.17 (t, *J* = 5.4 Hz, 1H), 4.08 (dddd, *J* = 17.9, 10.8, 7.1, 3.7 Hz, 4H), 2.55 (d, *J* = 5.4 Hz, 2H), 2.17 (s, 6H), 1.24 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 167.7 (C=O), 145.5 (C=C), 137.8 (Ar), 131.6 (Ar), 131.4 (Ar), 127.3 (Ar), 101.6 (C=C), 59.7 (CH), 41.5 (CH₂), 35.4 (d, *J* = 6.5 Hz, CH₂), 19.3 (d, *J* = 2.2 Hz, CH₃), 14.4 (CH₃).

Diethyl 4-(4-fluorobenzyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2e)^{S21}



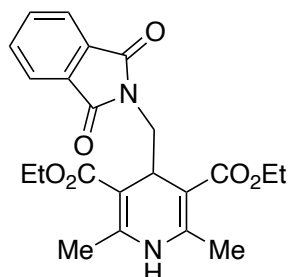
Yellow solid (0.63 g, 35% yield); ¹H NMR (600 MHz, CDCl₃) δ 7.00 – 6.78 (m, 4H), 5.47 (d, *J* = 6.2 Hz, 1H), 4.16 (d, *J* = 1.4 Hz, 1H), 4.07 (ddd, *J* = 9.3, 7.1, 2.3 Hz, 4H), 2.58 – 2.48 (m, 2H), 2.15 (s, 6H), 1.24 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 167.8 (C=O), 161.5 (d, *J*_{C-F} = 242.9 Hz, C=O), 145.6 (C=C), 134.9 (d, *J*_{C-F} = 3.2 Hz, Ar), 131.4 (d, *J*_{C-F} = 7.7 Hz, Ar), 113.9 (d, *J*_{C-F} = 21.0 Hz, Ar), 101.5 (C=C), 59.6 (h, *J*_{C-F} = 5.0 Hz, CH), 41.3 (t, *J*_{C-F} = 4.5 Hz, CH₂), 35.4 (d, *J*_{C-F} = 6.0 Hz, CH₂), 19.2 (CH₃), 14.3 (CH₃). ¹⁹F NMR (376 MHz, CDCl₃) δ –118.2.

Diethyl 4-(4-methoxybenzyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2f)^{S21}



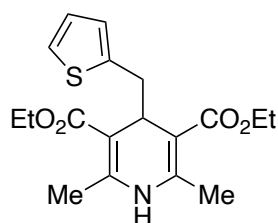
Yellow solid (0.47 g, 25% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.19 (d, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 5.52 (s, 1H), 4.93 (s, 1H), 4.09 (qd, *J* = 7.1, 5.3 Hz, 4H), 3.75 (s, 3H), 2.33 (s, 6H), 1.22 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 167.9 (C=O), 157.9 (Ar), 145.3 (C=C), 131.4 (Ar), 131.0 (Ar), 112.7 (Ar), 101.9 (C=C), 59.6 (CH), 55.24 (d, *J* = 6.0 Hz, CH₃), 41.2 (CH₂), 35.5 (d, *J* = 7.4 Hz, CH₂), 19.2 (CH₃), 14.4 (CH₃).

Diethyl 4-((1,3-dioxoisindolin-2-yl)methyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2g)^{S23}



Yellow solid (1.0 g, 50% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.80 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.67 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.11 (s, 1H), 4.37 (t, *J* = 6.6 Hz, 1H), 4.08 – 3.90 (m, 4H), 3.60 (d, *J* = 6.5 Hz, 2H), 2.28 (s, 6H), 1.19 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 168.5 (C=O), 167.3 (C=O), 146.9 (C=C), 133.7 (Ar), 132.2 (Ar), 122.9 (Ar), 100.2 (C=C), 59.8 (CH), 41.0 (CH₂), 33.1 (CH₂), 19.3 (CH₃), 14.2 (CH₃).

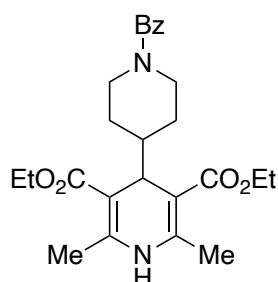
Diethyl 2,6-dimethyl-4-(thiophen-2-ylmethyl)-1,4-dihydropyridine-3,5-dicarboxylate (2h)^{S22}



Yellow solid (0.52 g, 30% yield); ¹H NMR (600 MHz, CDCl₃) δ 7.08 (d, *J* = 5.1 Hz, 1H), 6.86 – 6.82 (m, 1H), 6.61 (d, *J* = 2.9 Hz, 1H), 5.40 (s, 1H), 4.19 (t, *J* = 5.2 Hz, 1H), 4.11 (qdd, *J* = 7.1, 2.3, 0.9 Hz, 4H), 2.82 (d, *J* = 5.2 Hz, 2H), 2.20 (s, 6H), 1.26 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 167.7 (C=O), 145.7 (C=C), 141.4 (Ar), 126.2 (Ar), 126.2 (Ar), 123.8 (Ar), 101.5 (C=C), 59.7 (CH), 36.1 (CH₂), 35.7 (CH₂), 19.4 (CH₃), 14.4 (CH₃).

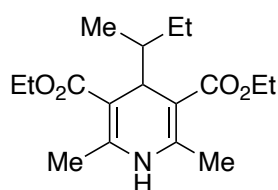
Diethyl 4-(1-benzoylpiperidin-4-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate

(2i)



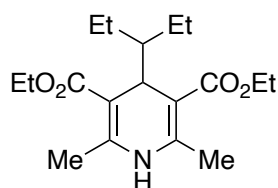
Yellow solid (2.0 g, 42% yield); m.p. 96–97 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.35 (dddd, J = 12.5, 7.0, 2.7, 1.8 Hz, 5H), 6.19 (d, J = 75.6 Hz, 1H), 4.67 (s, 1H), 4.26 – 4.11 (m, 4H), 4.01 (dd, J = 5.6, 2.4 Hz, 1H), 3.68 (s, 1H), 2.81 (d, J = 13.3 Hz, 1H), 2.67 – 2.55 (m, 1H), 2.28 (d, J = 5.0 Hz, 6H), 1.61 (d, J = 13.2 Hz, 1H), 1.47 (dq, J = 9.2, 2.9 Hz, 2H), 1.31 – 1.26 (m, 6H), 1.18 – 1.07 (m, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 170.2 (C=O), 168.2 (C=O), 145.5 (C=C), 136.4 (Ar), 129.4 (Ar), 128.4 (Ar), 126.8 (Ar), 59.8 (CH), 48.4 (CH_2), 43.9 (CH_2), 42.7 (CH_2), 37.4 (CH_2), 37.4 (CH_2), 37.3 (CH_2), 19.4 (CH_3), 14.4 (CH_3), 14.4 (CH); HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{33}\text{N}_2\text{O}_5$ ($\text{M}^+ + \text{H}$): 441.2389, found 441.2398; IR (neat cm^{-1}): 3289, 2936, 1687, 1601, 1443, 1297, 1207, 1084, 1016, 952, 777, 709.

Diethyl 4-(*sec*-butyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2j)^{S24}



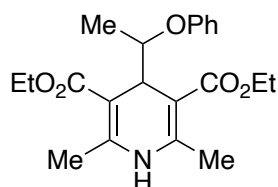
Yellow solid (0.62 g, 40% yield); ^1H NMR (600 MHz, CDCl_3) δ 5.68 (s, 1H), 4.21 – 3.99 (m, 4H), 3.95 (s, 1H), 2.22 (s, 6H), 1.22 (tt, J = 7.1, 1.9 Hz, 7H), 0.93 – 0.85 (m, 1H), 0.77 (ddt, J = 7.5, 4.0, 2.4 Hz, 3H), 0.65 (dt, J = 6.8, 2.0 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.0 (C=O), 168.6 (C=O), 144.7 (C=C), 144.5 (C=C), 102.3 (C=C), 101.3 (C=C), 59.6 (CH), 43.1 (CH_2), 37.5 (CH_2), 25.2 (CH_2), 19.4 (CH_2), 19.3 (CH_2), 14.7 (CH_3), 14.3 (CH_3), 14.3 (CH_3), 12.2 (CH_3).

Diethyl 2,6-dimethyl-4-(pentan-3-yl)-1,4-dihydropyridine-3,5-dicarboxylate (2k)^{S24}



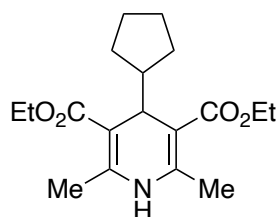
Yellow solid (0.76 g, 47% yield); ¹H NMR (600 MHz, CDCl₃) δ 5.89 (s, 1H), 4.20 – 4.07 (m, 5H), 2.82 (s, 1H), 2.25 (s, 6H), 1.40 – 1.36 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 6H), 1.13 (ddq, *J* = 27.9, 13.9, 7.2 Hz, 4H), 1.01 (tt, *J* = 6.6, 3.3 Hz, 1H), 0.83 (t, *J* = 7.4 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 168.9 (C=O), 144.8 (C=C), 102.0 (C=C), 59.6 (CH), 49.8 (CH₂), 34.5 (CH₂), 21.1 (CH), 19.2 (CH₂), 14.3 (CH₃), 11.7 (CH₃).

Diethyl 2,6-dimethyl-4-(1-phenoxyethyl)-1,4-dihydropyridine-3,5-dicarboxylate (2l)



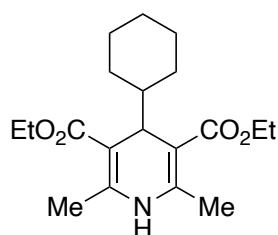
Yellow wax (0.28 g, 15% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.22 (t, *J* = 8.0 Hz, 2H), 6.97 – 6.91 (m, 2H), 6.89 – 6.84 (m, 1H), 5.57 (s, 1H), 4.55 (d, *J* = 4.4 Hz, 1H), 4.38 (dd, *J* = 6.6, 4.6 Hz, 1H), 4.33 – 4.19 (m, 2H), 4.02 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.75 (dq, *J* = 10.7, 7.1 Hz, 1H), 2.29 (d, *J* = 21.2 Hz, 6H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.17 (d, *J* = 6.3 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.8 (C=O), 166.3 (C=O), 156.8 (Ar), 145.3 (C=C), 142.9 (C=C), 127.4 (Ar), 118.1 (Ar), 113.2 (Ar), 97.9 (C=C), 97.1 (C=C), 59.7 (CH), 58.1 (CH), 58.0 (CH), 35.6 (CH₂), 23.0 (CH₂), 17.8 (CH₃), 16.8 (CH₃), 13.5 (CH₃), 12.7 (CH₃), 12.4 (CH₃), 11.8 (CH₃); HRMS (ESI) calcd. for C₂₁H₂₈NO₅ (M⁺ + H): 374.1967, found 374.1966; IR (neat cm⁻¹): 3300, 2956, 1687, 1597, 1440, 1297, 1189, 1083, 997, 952, 771, 710.

Diethyl 4-cyclopentyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2m)^{S25}



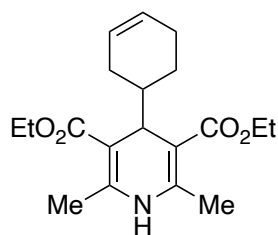
White solid (0.61 g, 38% yield); ¹H NMR (600 MHz, CDCl₃) δ 5.72 (s, 1H), 4.24 – 4.10 (m, 4H), 3.99 (d, *J* = 7.2 Hz, 1H), 2.29 (s, 6H), 1.76 – 1.69 (m, 1H), 1.54 (dtd, *J* = 6.6, 3.8, 2.1 Hz, 2H), 1.50 – 1.43 (m, 2H), 1.42 – 1.36 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 6H), 1.19 – 1.11 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 168.6 (C=O), 144.5 (C=C), 102.8 (C=C), 59.6 (CH), 48.2 (CH₂), 35.8 (CH₂), 28.4 (CH₂), 24.0 (CH), 19.4 (CH₃), 14.4 (CH₃).

Diethyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2n)^{S21}



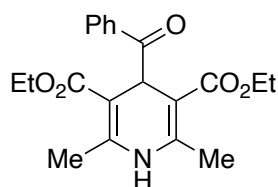
White solid (0.67 g, 40% yield); ¹H NMR (600 MHz, CDCl₃) δ 5.87 (s, 1H), 4.15 (ddq, *J* = 43.8, 10.8, 7.1 Hz, 4H), 3.90 (d, *J* = 5.7 Hz, 1H), 2.28 (s, 6H), 1.63 (d, *J* = 8.1 Hz, 2H), 1.57 – 1.47 (m, 3H), 1.27 (t, *J* = 7.2 Hz, 6H), 1.16 – 1.21 (m, 1H), 1.08 – 1.00 (m, 3H), 0.89 (qd, *J* = 12.6, 12.0, 4.8 Hz, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 168.8 (C=O), 144.6 (C=C), 101.8 (C=C), 59.5 (CH), 45.8 (CH₂), 38.4 (CH₂), 28.8 (CH), 26.7 (CH₂), 26.6 (CH₂), 19.3 (CH₃), 14.4 (CH₃).

Diethyl 4-(cyclohex-3-en-1-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2o)^{S24}



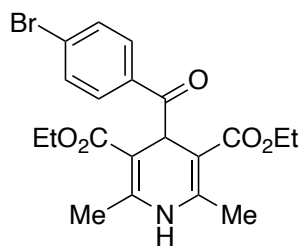
Yellow solid (0.88 g, 53% yield); ¹H NMR (600 MHz, CDCl₃) δ 5.68 (s, 1H), 5.58 (d, *J* = 11.3 Hz, 2H), 4.28 – 4.09 (m, 4H), 4.02 (d, *J* = 5.8 Hz, 1H), 2.30 (d, *J* = 2.6 Hz, 6H), 2.05 – 1.97 (m, 1H), 1.96 – 1.91 (m, 1H), 1.90 – 1.83 (m, 1H), 1.81 – 1.72 (m, 1H), 1.67 – 1.60 (m, 1H), 1.58 – 1.49 (m, 1H), 1.32 – 1.24 (m, 6H), 1.23 – 1.14 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 168.6 (C=O), 168.5 (C=O), 144.8 (C=C), 144.7 (C=C), 127.1 (C=C), 126.7 (C=C), 101.7 (C=C), 59.6 (CH), 41.5 (CH₂), 37.8 (CH₃), 27.5 (CH₂), 26.0 (CH₂), 25.0 (CH), 19.5 (CH₂), 19.4 (CH₃), 14.4 (CH₃).

Diethyl 4-benzoyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4a)^{S8}



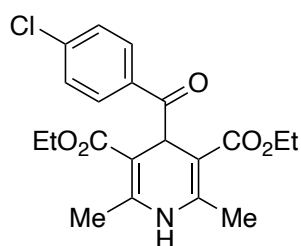
Yellow solid (0.71 g, 40% yield); ¹H NMR (600 MHz, CDCl₃) δ 8.19 – 8.11 (m, 2H), 7.57 – 7.50 (m, 1H), 7.44 (dd, *J* = 8.3, 7.2 Hz, 2H), 7.04 (s, 1H), 5.73 (s, 1H), 3.97 (ddq, *J* = 40.8, 10.9, 7.1 Hz, 4H), 2.28 (s, 6H), 1.03 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 204.4 (C=O), 167.0 (C=O), 147.1 (C=C), 137.0 (Ar), 132.8 (Ar), 129.7 (Ar), 128.0 (Ar), 99.6 (C=C), 59.9 (CH), 41.8 (CH₂), 19.2 (CH₃), 14.1 (CH₃).

Diethyl 4-(4-bromobenzoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4b)^{S26}



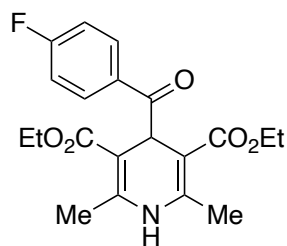
Yellow solid (1.18 g, 54% yield); ¹H NMR (600 MHz, CDCl₃) δ 8.03 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 6.53 (s, 1H), 5.64 (s, 1H), 4.05 – 3.93 (m, 4H), 2.29 (s, 6H), 1.06 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 203.2 (C=O), 166.9 (C=O), 146.9 (C=C), 135.8 (Ar), 131.3 (Ar), 131.2 (Ar), 128.0 (Ar), 99.8 (C=C), 60.0 (CH), 41.7 (CH₂), 19.5 (CH₃), 14.2 (CH₃).

Diethyl 4-(4-chlorobenzoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4c)^{S26}



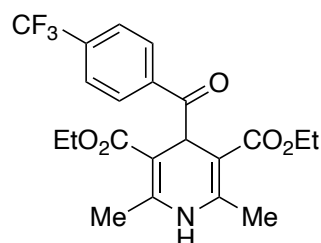
Yellow solid (0.96 g, 49% yield); ¹H NMR (600 MHz, CDCl₃) δ 8.10 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 6.09 (s, 1H), 5.64 (s, 1H), 4.06 – 3.94 (m, 4H), 2.32 (s, 6H), 1.06 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 202.5 (C=O), 166.8 (C=O), 146.6 (C=C), 139.1 (Ar), 135.3 (Ar), 131.1 (Ar), 128.3 (Ar), 100.0 (C=C), 60.0 (CH), 41.6 (CH₂), 19.7 (CH₃), 14.2 (CH₃).

Diethyl 4-(4-fluorobenzoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4d)^{S26}



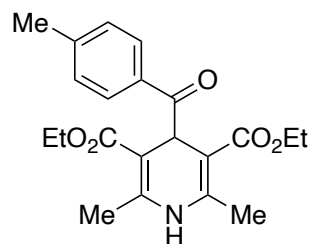
Yellow solid (0.82 g, 47%); ¹H NMR (400 MHz, CDCl₃) δ 8.21 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.11 (t, *J* = 8.7 Hz, 2H), 6.88 (s, 1H), 5.68 (s, 1H), 3.99 (dddd, *J* = 14.9, 9.2, 7.2, 3.8 Hz, 4H), 2.28 (s, 6H), 1.05 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 202.9 (C=O), 166.0 (d, *J*_{C-F} = 252.5 Hz, C=O), 147.0 (C=C), 133.3 (d, *J*_{C-F} = 10.1 Hz, Ar), 132.4 (d, *J*_{C-F} = 10.1 Hz, Ar), 115.2 (Ar), 114.9 (Ar), 99.7 (C=C), 59.9 (CH), 41.7 (CH₂), 19.4 (CH₃), 14.2 (CH₃); ¹⁹F NMR (376 MHz, CDCl₃) δ -105.9.

Diethyl 2,6-dimethyl-4-(4-(trifluoromethyl)benzoyl)-1,4-dihydropyridine-3,5-dicarboxylate (4e)^{S8}



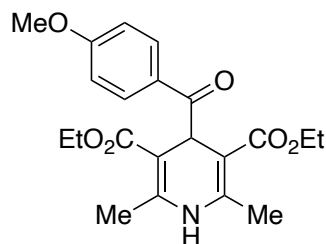
Yellow solid (0.57 g, 27% yield); ¹H NMR (600 MHz, CDCl₃) δ 8.25 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 7.9 Hz, 2H), 6.35 (s, 1H), 5.68 (s, 1H), 4.06 – 3.88 (m, 4H), 2.31 (s, 6H), 1.03 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 203.3 (C=O), 166.8 (C=O), 146.8 (C=C), 140.1 (Ar), 134.0 (q, *J*_{C-F} = 30.2 Hz, Ar), 129.8 (Ar), 125.3 (q, *J*_{C-F} = 15.1 Hz, Ar), 121.1 (q, *J*_{C-F} = 271.8 Hz, CF₃), 99.8 (C=C), 60.1 (CH), 42.2 (CH₂), 19.6 (CH₃); ¹⁹F NMR (376 MHz, CDCl₃) δ -63.1.

Diethyl 2,6-dimethyl-4-(4-methylbenzoyl)-1,4-dihydropyridine-3,5-dicarboxylate (4f)^{S26}



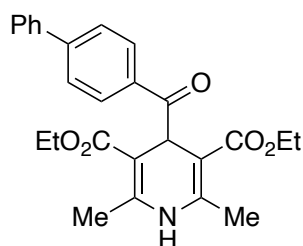
Yellow solid (1.30 g, 70% yield); ¹H NMR (600 MHz, CDCl₃) δ 8.06 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.10 (s, 1H), 5.71 (s, 1H), 3.98 (ddq, *J* = 38.9, 10.9, 7.1 Hz, 4H), 2.40 (s, 3H), 2.27 (s, 6H), 1.05 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 203.8 (C=O), 167.1 (C=O), 147.1 (C=C), 143.6 (Ar), 134.3 (Ar), 129.9 (Ar), 128.7, 99.6 (Ar), 59.8 (CH), 41.5 (CH₂), 21.7 (CH₃), 19.2 (CH₃), 14.1 (CH₃).

Diethyl 4-(4-methoxybenzoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4g)^{S26}



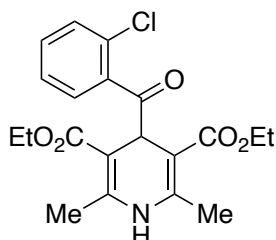
Yellow solid (1.26 g, 65% yield); ¹H NMR (600 MHz, CDCl₃) δ 8.17 (d, *J* = 8.9 Hz, 2H), 7.48 (s, 1H), 6.92 (d, *J* = 8.9 Hz, 2H), 5.70 (s, 1H), 4.06 – 3.91 (m, 4H), 3.85 (s, 3H), 2.25 (s, 6H), 1.06 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 202.9 (C=O), 167.1 (C=O), 163.6 (Ar), 147.2 (C=C), 132.2 (Ar), 129.6 (Ar), 113.2 (Ar), 99.6 (C=C), 59.8 (CH), 55.4 (CH₃), 41.2 (CH₂), 19.1 (CH₃), 14.2 (CH₃).

Diethyl 4-([1,1'-biphenyl]-4-carbonyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4h)^{S26}



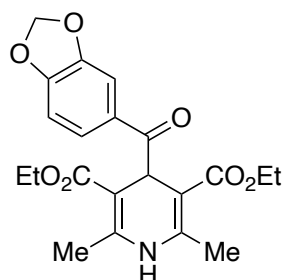
Yellow solid; (0.85 g, 39% yield); ¹H NMR (600 MHz, CDCl₃) δ 8.23 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 7.0 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 6.70 (s, 1H), 5.75 (s, 1H), 4.08 – 3.93 (m, 4H), 2.32 (s, 6H), 1.07 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 203.7 (C=O), 167.0 (C=O), 146.9 (Ar), 145.4 (C=C), 140.2 (Ar), 135.7 (Ar), 130.3 (Ar), 128.9 (Ar), 128.1 (Ar), 127.3 (Ar), 126.6 (Ar), 99.9 (C=C), 60.0 (CH), 41.7 (CH₂), 19.4 (CH₃), 14.2 (CH₃).

Diethyl 4-(2-chlorobenzoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4i)^{S27}



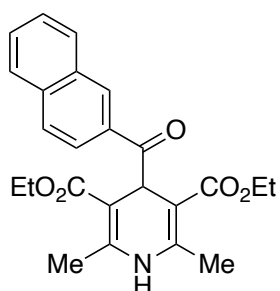
Yellow solid (0.88 g, 45% yield); ¹H NMR (600 MHz, CDCl₃) δ 7.53 (d, *J* = 8.9 Hz, 1H), 7.36 – 7.27 (m, 3H), 6.44 (s, 1H), 5.46 (s, 1H), 4.11 – 3.85 (m, 4H), 2.34 (d, *J* = 2.0 Hz, 6H), 1.12 (td, *J* = 7.1, 1.3 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 200.8 (C=O), 166.8 (C=O), 147.2 (C=C), 139.8 (Ar), 130.9 (Ar), 130.6 (Ar), 129.7 (Ar), 128.7 (Ar), 126.1 (Ar), 97.3 (C=C), 60.0 (CH), 46.6 (CH₂), 19.4 (CH₃), 14.1 (CH₃).

Diethyl 4-(benzo[d][1,3]dioxole-5-carbonyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4j)^{S8}



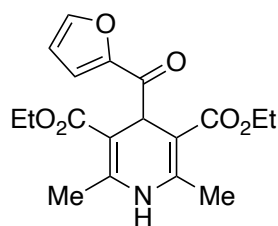
Yellow solid (1.2 g, 60% yield); ¹H NMR (600 MHz, CDCl₃) δ 7.86 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.60 (d, *J* = 1.7 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.02 (s, 2H), 5.63 (s, 1H), 4.10 – 3.96 (m, 4H), 2.28 (s, 6H), 1.11 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 202.0 (C=O), 167.0 (C=O), 151.7 (Ar), 147.7 (C=C), 146.9 (Ar), 131.3 (Ar), 126.4 (Ar), 109.5 (Ar), 107.5 (Ar), 101.7 (C=C), 99.7 (CH₂), 59.9 (CH), 41.4 (CH₂), 19.4 (CH₃), 14.2 (CH₃).

Diethyl 4-(2-naphthoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4k)^{S8}



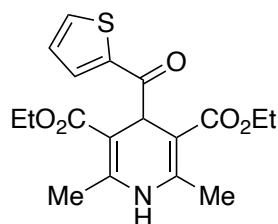
Yellow solid (0.88 g, 43% yield); ¹H NMR (600 MHz, CDCl₃) δ 8.77 (s, 1H), 8.15 (dd, *J* = 8.6, 1.8 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.90 – 7.85 (m, 2H), 7.56 (dddd, *J* = 27.2, 8.1, 6.9, 1.3 Hz, 2H), 6.87 (s, 1H), 5.90 (s, 1H), 3.95 (ddq, *J* = 62.3, 10.9, 7.1 Hz, 4H), 2.33 (s, 6H), 0.98 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 203.9 (C=O), 167.0 (C=O), 147.1 (C=C), 135.6 (Ar), 134.1 (Ar), 132.5 (Ar), 131.7 (Ar), 129.7 (Ar), 128.2 (Ar), 127.7 (Ar), 126.5 (Ar), 125.3 (Ar), 99.8 (C=C), 59.9 (CH), 41.7 (CH₂), 19.4 (CH₃), 14.1 (CH₃).

Diethyl 4-(furan-2-carbonyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4l)^{S28}



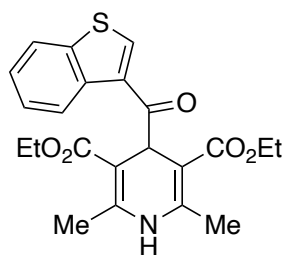
Brown solid (0.42 g, 24% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.64 (s, 1H), 7.50 (d, *J* = 3.6 Hz, 1H), 6.71 (s, 1H), 6.55 (dd, *J* = 3.6, 1.6 Hz, 1H), 5.44 (s, 1H), 4.05 (qd, *J* = 7.2, 2.4 Hz, 4H), 2.29 (s, 6H), 1.11 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 192.3 (C=O), 167.0 (C=O), 152.0 (Ar), 147.3 (Ar), 147.2 (C=C), 120.8 (Ar), 112.2 (Ar), 99.1 (C=C), 59.9 (CH), 42.7 (CH₂), 19.3 (CH₃), 14.2 (CH₃).

Diethyl 2,6-dimethyl-4-(thiophene-2-carbonyl)-1,4-dihydropyridine-3,5-dicarboxylate (4m)^{S26}



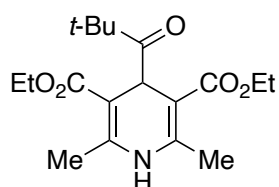
Brown solid (0.63 g, 35% yield); ¹H NMR (600 MHz, CDCl₃) δ 8.12 (d, *J* = 4.0 Hz, 1H), 7.65 (dt, *J* = 4.6, 1.5 Hz, 1H), 7.54 (s, 1H), 7.13 (q, *J* = 4.3 Hz, 1H), 5.56 (s, 1H), 4.03 (ddq, *J* = 10.3, 7.0, 3.6 Hz, 4H), 2.31 – 2.12 (m, 6H), 1.13 – 0.98 (m, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 196.8 (C=O), 167.0 (C=O), 147.5 (Ar), 143.5 (C=C), 135.2 (Ar), 134.7 (Ar), 128.0 (Ar), 99.0 (C=C), 59.9 (CH), 43.4 (CH₂), 19.1 (CH₃), 14.2 (CH₃).

Diethyl 4-(benzo[*b*]thiophene-3-carbonyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4n)



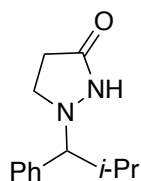
Yellow solid (0.91 g, 44% yield); m.p. 125–126 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.96 (s, 1H), 8.69 (d, $J = 7.2$ Hz, 1H), 7.86 (d, $J = 7.9$ Hz, 1H), 7.49 – 7.36 (m, 2H), 7.29 (d, $J = 4.2$ Hz, 1H), 5.70 (s, 1H), 4.04 (qd, $J = 7.1, 5.1$ Hz, 4H), 2.34 (s, 6H), 1.10 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 198.5 (C=O), 167.1 (C=O), 147.2 (Ar), 140.9 (C=C), 139.5 (Ar), 137.3 (Ar), 133.7 (Ar), 125.7 (Ar), 125.4 (Ar), 125.2 (Ar), 122.3 (Ar), 99.4 (C=C), 60.0 (CH), 44.0 (CH_2), 19.5 (CH_3), 14.3 (CH_3); HRMS (ESI): calcd. for $\text{C}_{22}\text{H}_{24}\text{NO}_5\text{S}$ ($\text{M} + \text{H}$) $^+$ 414.1375, found 414.1407; IR (neat cm^{-1}): 3313, 3223, 3125, 2978, 2924, 1686, 1639, 1491, 1366, 1266, 1188, 1088, 1046, 1019 884, 839, 754.

Diethyl 2,6-dimethyl-4-pivaloyl-1,4-dihydropyridine-3,5-dicarboxylate (4o)^{S27}



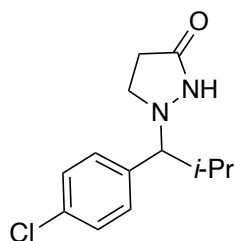
Yellow solid (0.24 g, 14% yield); ^1H NMR (400 MHz, CDCl_3) δ 6.04 (s, 1H), 5.26 (s, 1H), 4.19 (q, $J = 7.1$ Hz, 4H), 2.29 (s, 6H), 1.31 (d, $J = 7.1$ Hz, 6H), 1.20 (s, 9H); ^{13}C NMR (151 MHz, CDCl_3) δ 217.1 (C=O), 167.1 (C=O), 146.4 (C=C), 99.3 (C=C), 60.1 (CH), 43.7 (CH_2), 41.2 (C), 27.1 (CH_3), 19.6 (CH_3), 14.4 (CH_3).

1-(2-Methyl-1-phenylpropyl)pyrazolidin-3-one (3aa)



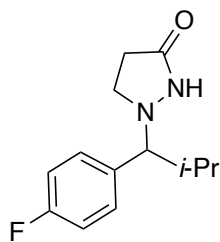
Light yellow solid (65.5 mg, 99% yield); m.p. 112.2–113.2 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.07 (s, 1H), 7.36 – 7.14 (m, 5H), 3.29 (d, J = 6.6 Hz, 2H), 3.12 (dt, J = 11.1, 8.4 Hz, 1H), 2.21 (dt, J = 16.8, 8.4 Hz, 1H), 2.10 (h, J = 6.7 Hz, 1H), 1.98 – 1.85 (m, 1H), 0.84 (d, J = 6.7 Hz, 3H), 0.73 (d, J = 6.7 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 175.5 (C=O), 137.1 (Ar), 129.3 (Ar), 128.2 (Ar), 127.8 (Ar), 77.6 (CH_2), 50.6 (CH), 30.3 (CH_2), 29.4 (CH), 20.5 (CH_3), 17.3 (CH_3); HRMS (ESI) calcd. for $\text{C}_{13}\text{H}_{19}\text{N}_2\text{O}$ ($\text{M}^+ + \text{H}$): 219.1497, found 219.1475; IR (neat cm^{-1}): 3149, 2872, 1716, 1682, 1458, 1366, 1292, 1080, 1015, 761, 711.

1-(1-(4-Chlorophenyl)-2-methylpropyl)pyrazolidin-3-one (3ba)



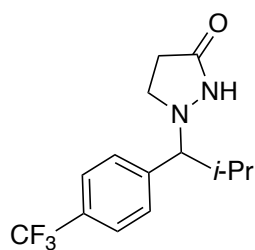
White solid (72.0 mg, 95% yield); m.p. 115.5–116.5 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.72 (s, 1H), 7.30 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 3.34 (d, J = 6.6 Hz, 1H), 3.30 – 3.13 (m, 2H), 2.30 (dt, J = 16.7, 8.3 Hz, 1H), 2.15 (h, J = 6.7 Hz, 1H), 2.00 (dt, J = 16.3, 7.9 Hz, 1H), 0.89 (d, J = 6.8 Hz, 3H), 0.76 (d, J = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 175.7 (C=O), 135.7 (Ar), 133.6 (Ar), 130.6 (Ar), 128.3 (Ar), 76.8 (CH_2), 50.4 (CH), 30.2 (CH_2), 29.4 (CH), 20.4 (CH_3), 17.2 (CH_3); HRMS (ESI) calcd. for $\text{C}_{13}\text{H}_{18}\text{ClN}_2\text{O}$ ($\text{M}^+ + \text{H}$): 253.1108, found 253.1109; IR (neat cm^{-1}): 3161, 3066, 2963, 1681, 1491, 1363, 1298, 1087, 1014, 824, 799, 738.

1-(1-(4-Fluorophenyl)-2-methylpropyl)pyrazolidin-3-one (3ca)



White solid (70.0 mg, 98% yield); m.p. 118–119 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.73 (s, 1H), 7.23 (dd, $J = 8.5, 5.6$ Hz, 2H), 7.01 (t, $J = 8.7$ Hz, 2H), 3.34 (d, $J = 6.7$ Hz, 1H), 3.26 (s, 1H), 3.17 (q, $J = 10.8, 9.6$ Hz, 1H), 2.28 (dt, $J = 16.6, 8.4$ Hz, 1H), 2.15 (h, $J = 6.7$ Hz, 1H), 1.97 (dt, $J = 16.5, 8.0$ Hz, 1H), 0.89 (d, $J = 6.7$ Hz, 3H), 0.76 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 175.7 (C=O), 162.4 (d, $J_{\text{C-F}} = -241.6$ Hz, Ar), 132.9 (d, $J_{\text{C-F}} = 3.2$ Hz, Ar), 130.8 (d, $J_{\text{C-F}} = 7.7$ Hz, Ar), 115.1 (d, $J_{\text{C-F}} = 21.1$ Hz, Ar), 76.7 (CH_2), 50.4 (CH), 30.3 (CH_2), 29.5 (CH), 20.4 (CH_3), 17.3 (CH_3); ^{19}F NMR (376 MHz, CDCl_3) δ -114.5; HRMS (ESI) calcd. for $\text{C}_{13}\text{H}_{18}\text{FN}_2\text{O}$ ($\text{M}^+ + \text{H}$): 237.1403, found 237.1403; IR (neat cm^{-1}): 3145, 3057, 2963, 1694, 1507, 1364, 1220, 1158, 1088, 842, 722.

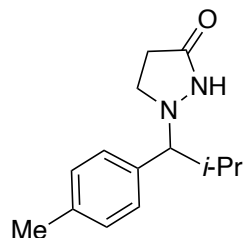
1-(2-Methyl-1-(4-(trifluoromethyl)phenyl)propyl)pyrazolidin-3-one (3da)



White solid (77 mg, 89% yield); m.p. 135.5–136.5 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.58 (s, 1H), 7.74 (d, $J = 7.9$ Hz, 2H), 7.54 (d, $J = 7.9$ Hz, 2H), 3.56 (d, $J = 7.5$ Hz, 1H), 3.29 – 3.03 (m, 2H), 2.24 (h, $J = 6.8$ Hz, 1H), 2.16 – 1.99 (m, 1H), 1.70 – 1.49 (m, 1H), 0.93 (d, $J = 6.6$ Hz, 3H), 0.68 (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$) δ 175.1 (C=O), 143.0 (Ar), 130.6 (Ar), 128.4 (q, $J_{\text{C-F}} = 31.6$ Hz, Ar), 125.7 (Ar), 125.0 (q, $J_{\text{C-F}} = 3.8$ Hz, CF_3), 123.9 (Ar), 75.8 (CH_2), 50.2 (CH), 29.8 (CH_2), 29.1 (CH), 20.8 (CH_3), 18.4 (CH_3); ^{19}F NMR (376 MHz,

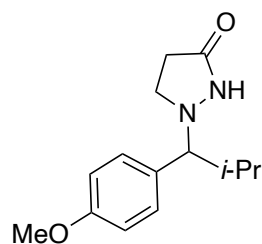
DMSO) δ -60.9; HRMS (ESI) calcd. for $C_{14}H_{18}F_3N_2O$ ($M^+ + H$): 287.1371, found 287.1377; IR (neat cm^{-1}): 3164, 2962, 1679, 1320, 1167, 1115, 1066, 1023, 762, 707.

1-(2-Methyl-1-(*p*-tolyl)pyrazolidin-3-one (3ea)



White solid (70 mg, 99% yield); m.p. 132.4–133.4 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.13 (s, 4H), 3.30 (d, J = 6.9 Hz, 2H), 3.18 (dt, J = 11.1, 8.3 Hz, 1H), 2.33 (s, 3H), 2.29 – 2.08 (m, 2H), 1.94 (dt, J = 16.4, 8.0 Hz, 1H), 0.91 (d, J = 6.7 Hz, 3H), 0.78 (d, J = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.9 (C=O), 152.1 (Ar), 133.4 (Ar), 130.9 (Ar), 129.2 (Ar), 127.7 (Ar), 113.4 (Ar), 84.1 (CH_2), 82.1 (CH), 65.9 (CH_2), 55.5 (CH_3), 28.2 (CH_3), 27.6 (CH_3); HRMS (ESI) calcd. for $C_{14}H_{21}N_2O$ ($M^+ + H$): 233.1654, found 233.1656; IR (neat cm^{-1}): 3145, 2867, 1677, 1427, 1365, 1312, 1185, 1026, 795, 724.

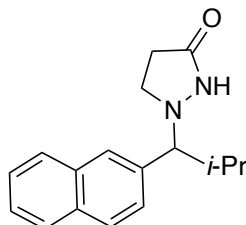
1-(1-(4-Methoxyphenyl)-2-methylpropyl)pyrazolidin-3-one (3fa)



White solid (62.0 mg, 83% yield); m.p. 114.6–115.6 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.17 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 3.79 (s, 3H), 3.30 (t, J = 10.5 Hz, 2H), 3.16 (dt, J = 11.2, 8.3 Hz, 1H), 2.23 (dt, J = 16.6, 8.5 Hz, 1H), 2.12 (dt, J = 13.4, 6.7 Hz, 1H), 1.94 (dt, J = 16.4, 8.1 Hz, 1H), 0.90 (d, J = 6.8 Hz, 3H), 0.77 (d, J = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.6 (C=O), 159.2 (Ar), 130.3 (Ar), 129.1 (Ar), 113.6 (Ar), 77.0 (CH_2), 55.2 (CH_3), 50.4 (CH), 30.4 (CH_2), 29.5 (CH), 20.5 (CH_3), 17.6 (CH_3); HRMS (ESI)

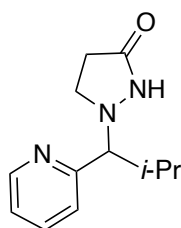
calcd. for $C_{14}H_{21}N_2O$ ($M^+ + H$): 249.1603, found 249.1599; IR (neat cm^{-1}): 2956, 1695, 1655, 1582, 1509, 1248, 1181, 1034, 826, 800.

1-(2-Methyl-1-(naphthalen-2-yl)propyl)pyrazolidin-3-one (3ga)



White solid (77.0 mg, 96% yield); m.p. 146–147 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.90 – 7.77 (m, 3H), 7.73 (s, 1H), 7.54 – 7.41 (m, 3H), 3.55 (d, $J = 6.4$ Hz, 1H), 3.44 – 3.19 (m, 2H), 2.42 – 2.22 (m, 2H), 2.11 – 1.94 (m, 1H), 0.95 (d, $J = 6.7$ Hz, 3H), 0.86 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.5 (C=O), 134.9 (Ar), 133.1 (Ar), 133.0 (Ar), 128.6 (Ar), 127.9 (Ar), 127.7 (Ar), 127.7 (Ar), 127.1 (Ar), 126.2 (Ar), 126.0 (Ar), 77.7 (CH_2), 50.7 (CH), 30.4 (CH_2), 29.7 (CH), 20.6 (CH_3), 17.4 (CH_3); HRMS (ESI) calcd. for $C_{17}H_{21}N_2O$ ($M^+ + H$): 269.1654, found 269.1662; IR (neat cm^{-1}): 3150, 2964, 1681, 1654, 1368, 1068, 790, 743.

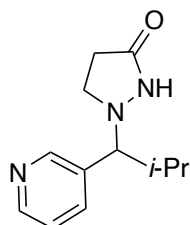
1-(2-Methyl-1-(pyridin-2-yl)propyl)pyrazolidin-3-one (3ha)



White solid (64.4 mg, 98% yield); m.p. 109–110 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.59 – 8.48 (m, 1H), 7.60 (td, $J = 7.7, 1.8$ Hz, 1H), 7.23 (d, $J = 7.8$ Hz, 1H), 7.20 – 7.12 (m, 1H), 3.51 (d, $J = 8.1$ Hz, 1H), 3.40 (ddd, $J = 11.3, 9.1, 7.3$ Hz, 1H), 3.30 (ddd, $J = 11.3, 9.0, 7.5$ Hz, 1H), 2.32 – 2.16 (m, 1H), 2.02 (dq, $J = 17.7, 9.5, 8.8$ Hz, 1H), 1.73 (dt, $J = 16.5, 8.3$ Hz, 1H), 0.96 (d, $J = 6.7$ Hz, 3H), 0.71 (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.0 (C=O), 157.7 (Ar), 149.2 (Ar), 136.0 (Ar), 124.2 (Ar), 122.7 (Ar), 78.1 (CH_2), 49.4 (CH),

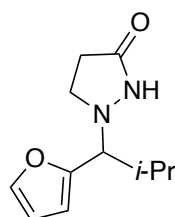
30.2 (CH₂), 29.2 (CH), 20.3 (CH₃), 18.4 (CH₃); HRMS (ESI) calcd. for C₁₂H₁₈N₃O (M⁺ + H): 220.1450, found 220.1450; IR (neat cm⁻¹): 3145, 2953, 1682, 1581, 1482, 1298, 1019, 994, 774, 751.

1-(2-Methyl-1-(pyridin-3-yl)propyl)pyrazolidin-3-one (3ia)



White solid (65.7 mg, 99% yield); m.p. 128.4–129.4 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.11 (s, 1H), 8.50 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.44 (d, *J* = 2.2 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.23 (dd, *J* = 8.0, 4.7 Hz, 1H), 3.36 (d, *J* = 6.7 Hz, 1H), 3.28 – 3.03 (m, 2H), 2.28 (dt, *J* = 16.8, 8.4 Hz, 1H), 2.16 (h, *J* = 6.7 Hz, 1H), 1.94 (dt, *J* = 16.3, 8.1 Hz, 1H), 0.86 (d, *J* = 6.7 Hz, 3H), 0.72 (d, *J* = 6.7 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 175.8 (C=O), 150.5 (Ar), 149.2 (Ar), 136.5 (Ar), 132.7 (Ar), 123.2 (Ar), 74.9 (CH₂), 50.5 (CH), 30.2 (CH₂), 29.4 (CH), 20.3 (CH₃), 17.2 (CH₃); HRMS (ESI) calcd. for C₁₂H₁₈N₃O (M⁺ + H): 220.1450, found 220.1472; IR (neat cm⁻¹): 3149, 2872, 1682, 1458, 1366, 1257, 1080, 1015, 819, 761, 711.

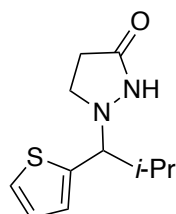
1-(1-(Furan-2-yl)-2-methylpropyl)pyrazolidin-3-one (3ja)



White solid (62.4 mg, 99% yield); m.p. 103.4–104.4 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.84 (s, 1H), 7.41 (dd, *J* = 1.9, 0.8 Hz, 1H), 6.36 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.23 (dd, *J* = 3.2, 0.8 Hz, 1H), 3.51 – 3.42 (m, 1H), 3.36 (d, *J* = 9.7 Hz, 1H), 3.26 (ddd, *J* = 11.7, 9.0, 6.7 Hz, 1H), 2.10 (dp, *J* = 9.6, 6.6 Hz, 1H), 1.92 (ddd, *J* = 16.0, 9.1, 6.6 Hz, 1H), 1.78 (dd, *J* = 16.7, 9.0 Hz, 1H), 1.06 (d, *J* = 6.6 Hz, 3H), 0.81 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 176.4 (C=O),

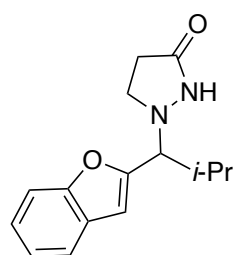
151.8 (Ar), 142.2 (Ar), 110.8 (Ar), 109.9 (Ar), 70.7 (CH₂), 49.5 (CH), 29.8 (CH₂), 29.4 (CH), 20.3 (CH₃), 19.6 (CH₃); HRMS (ESI) calcd. for C₁₁H₁₇N₂O₂ (M⁺ + H): 209.1290, found 209.1282; IR (neat cm⁻¹): 3141, 2962, 1677, 1423, 1371, 1159, 1016, 916, 805, 766.

1-(2-Methyl-1-(thiophen-2-yl)propyl)pyrazolidin-3-one (3ka)



White solid (64.0 mg, 95% yield); m.p. 93.6–94.6 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.75 (s, 1H), 7.29 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.00 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.95 (dd, *J* = 3.4, 1.2 Hz, 1H), 3.60 (d, *J* = 8.3 Hz, 1H), 3.52 – 3.35 (m, 1H), 3.24 (ddd, *J* = 11.4, 9.1, 6.6 Hz, 1H), 2.10 (dddd, *J* = 23.9, 13.4, 8.8, 6.8 Hz, 2H), 1.88 (dt, *J* = 16.9, 8.6 Hz, 1H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.84 (d, *J* = 6.7 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 176.3 (C=O), 139.4 (Ar), 127.3 (Ar), 126.5 (Ar), 125.7 (Ar), 73.1 (CH₂), 50.2 (CH), 31.2 (CH₂), 30.3 (CH), 20.5 (CH₃), 18.9 (CH₃); HRMS (ESI) calcd. for C₁₁H₁₇N₂OS (M⁺ + H): 225.1062, found 225.1057; IR (neat cm⁻¹): 3069, 2962, 1687, 1650, 1459, 1365, 1278, 1231, 1098, 1012, 800, 709.

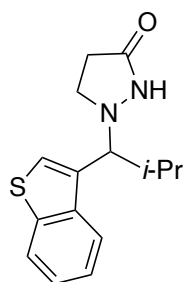
1-(1-(Benzofuran-2-yl)-2-methylpropyl)pyrazolidin-3-one (3la)



White wax (72.0 mg, 93% yield); m.p. 106.1–107.1 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.82 (s, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.21 – 7.17 (m, 1H), 7.15 (td, *J* = 7.4, 1.1 Hz, 1H), 6.60 (s, 1H), 3.47 (d, *J* = 9.1 Hz, 2H), 3.31 (ddd, *J* = 11.5, 9.1, 7.1 Hz, 1H), 2.17 (dp, *J* = 9.0, 6.6 Hz, 1H), 2.00 (ddd, *J* = 16.4, 9.1, 7.1 Hz, 1H), 1.93 – 1.84 (m, 1H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.83 (d, *J* = 6.7 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 176.0 (C=O), 154.8 (Ar),

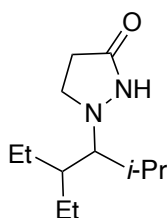
128.1 (Ar), 124.2 (Ar), 122.9 (Ar), 121.0 (Ar), 111.3 (Ar), 106.8 (Ar), 71.2 (CH₂), 49.7 (CH), 30.0 (CH₂), 29.5 (CH), 20.3 (CH₃), 19.3 (CH₃); HRMS (ESI) calcd. for C₁₅H₁₉N₂O₂ (M⁺ + H): 259.1447, found 259.1444; IR (neat cm⁻¹): 3148, 3052, 2957, 1682, 1452, 1365, 1247, 1171, 1008, 937, 744, 675.

1-(1-(Benzo[*b*]thiophen-3-yl)-2-methylpropyl)pyrazolidin-3-one (3ma)



White solid (67.0 mg, 82% yield); m.p. 182.5–183.5 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.58 (s, 1H), 7.95 – 7.84 (m, 2H), 7.38 (dtd, *J* = 15.0, 7.1, 5.9 Hz, 3H), 3.98 (d, *J* = 7.0 Hz, 1H), 3.35 (s, 1H), 3.27 – 3.09 (m, 1H), 2.27 (dt, *J* = 13.3, 6.8 Hz, 2H), 1.95 (s, 1H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.88 (d, *J* = 6.7 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 175.8 (C=O), 140.2 (Ar), 139.6 (Ar), 132.6 (Ar), 124.9 (Ar), 124.5 (Ar), 124.2 (Ar), 122.9 (Ar), 122.1 (Ar), 51.0 (CH), 31.0 (CH₂), 30.3 (CH), 20.7 (CH₃), 18.0 (CH₃); HRMS (ESI) calcd. for C₁₅H₁₉N₂OS (M⁺ + H): 275.1218, found 275.1218; IR (neat cm⁻¹): 3160, 2962, 1709, 1668, 1460, 1424, 1364, 1295, 1243, 1079, 1015, 795, 761, 736.

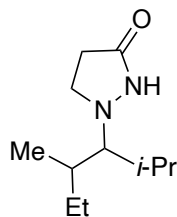
1-(4-Ethyl-2-methylhexan-3-yl)pyrazolidin-3-one (3na)



Colourless wax (16 mg, 25% yield); ¹H NMR (600 MHz, CDCl₃) δ 6.96 (s, 1H), 3.39 – 3.22 (m, 2H), 2.51 (t, *J* = 8.3 Hz, 2H), 2.41 (s, 1H), 2.00 (pd, *J* = 6.9, 4.2 Hz, 1H), 1.56 – 1.49 (m, 1H), 1.48 – 1.42 (m, 1H), 1.41 – 1.36 (m, 1H), 1.34 (dq, *J* = 9.0, 2.5, 2.1 Hz, 1H), 1.30 – 1.19

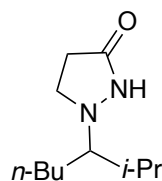
(m, 2H), 1.02 – 0.87 (m, 11H); ^{13}C NMR (151 MHz, CDCl_3) δ 174.4 (C=O), 51.2 (CH_2), 41.8 (CH), 30.4 (CH_2), 27.8 (CH), 24.8 (CH_2), 24.0 (CH_2), 20.8 (CH_3), 20.1 (CH_3), 12.8 (CH_3), 12.7 (CH_3); HRMS (ESI) calcd. for $\text{C}_{12}\text{H}_{25}\text{N}_2\text{O}$ ($\text{M}^+ + \text{H}$): 213.1967, found 213.1959; IR (neat cm^{-1}): 2960, 1740, 1699, 1456, 1369, 1268, 1231, 1043, 833, 757, 749.

1-(2,4-Dimethylhexan-3-yl)pyrazolidin-3-one (3oa)



Colourless wax (30 mg, 50% yield, 1:1 dr); ^1H NMR (400 MHz, CDCl_3) δ 7.56 (s, 1H), 3.38 – 3.24 (m, 2H), 2.58 – 2.45 (m, 2H), 2.30 (ddd, $J = 7.8, 5.4, 3.4$ Hz, 1H), 2.09 – 1.90 (m, 1H), 1.77 – 1.63 (m, 1H), 1.53 – 1.43 (m, 1H), 1.28 – 1.13 (m, 1H), 1.02 – 0.81 (m, 12H); ^{13}C NMR (151 MHz, CDCl_3) δ 174.4 (C=O), 74.4 (CH_2), 51.3 (CH), 50.6 (CH_2), 34.7 (CH_2), 34.4 (CH_2), 30.7 (CH), 30.5 (CH), 28.4 (CH), 27.9 (CH), 27.5 (CH_2), 27.4 (CH_2), 21.5 (CH_2), 20.9 (CH_2), 20.6 (CH_2), 19.9 (CH_3), 16.8 (CH_3), 16.6 (CH_3), 12.3 (CH_3); HRMS (ESI) calcd. for $\text{C}_{11}\text{H}_{23}\text{N}_2\text{O}$ ($\text{M}^+ + \text{H}$): 199.1810, found 199.1808; IR (neat cm^{-1}): 3148, 2959, 1678, 1459, 1369, 1303, 1072, 744, 701.

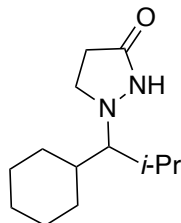
1-(2-Methylheptan-3-yl)pyrazolidin-3-one (3pa)



Colourless wax (50 mg, 84% yield); ^1H NMR (400 MHz, CDCl_3) δ 8.49 (s, 1H), 3.26 (t, $J = 8.4$ Hz, 2H), 2.48 (td, $J = 8.3, 4.9$ Hz, 2H), 2.29 (d, $J = 4.6$ Hz, 1H), 1.90 – 1.77 (m, 1H), 1.45 – 1.25 (m, 6H), 0.89 (m, 9H); ^{13}C NMR (151 MHz, CDCl_3) δ 174.6 (C=O), 71.4 (CH_2), 49.5 (CH), 31.5 (CH_2), 30.9 (CH_2), 29.8 (CH_2), 26.8 (CH_2), 23.1 (CH), 19.8 (CH_3), 17.8 (CH_3), 14.0

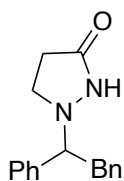
(CH₃); HRMS (ESI) calcd. for C₁₁H₂₃N₂O (M⁺ + H): 199.1810, found 199.1809; IR (neat cm⁻¹): 3162, 2956, 1682, 1504, 1365, 1255, 1039, 735.

1-(1-Cyclohexyl-2-methylpropyl)pyrazolidin-3-one (3qa)



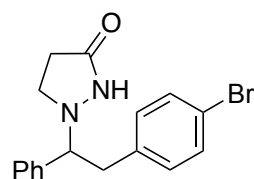
White wax (58 mg, 86% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.73 (s, 1H), 3.31 (t, *J* = 8.5 Hz, 2H), 2.58 – 2.45 (m, 2H), 2.17 (t, *J* = 3.9 Hz, 1H), 1.99 (ddd, *J* = 9.7, 7.0, 3.5 Hz, 1H), 1.78 – 1.56 (m, 6H), 1.31 – 1.06 (m, 5H), 0.96 (dd, *J* = 7.0, 2.5 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 174.2 (C=O), 75.1 (CH₂), 50.8 (CH), 38.3 (CH₂), 31.4 (CH₂), 31.2 (CH), 30.8 (CH), 27.6 (CH₂), 26.8 (CH₂), 26.8 (CH₂), 26.5 (CH₂), 20.8 (CH₃), 20.7 (CH₃); HRMS (ESI) calcd. for C₁₃H₂₅N₂O (M⁺ + H): 225.1961, found 225.1940; IR (neat cm⁻¹): 2924, 1774, 1678, 1439, 1369, 963, 723, 702.

1-(1,2-Diphenylethyl)pyrazolidin-3-one (3ab)



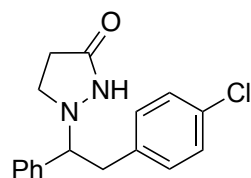
White solid (56.7 mg, 71% yield); m.p. 134.3–135.3 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.70 (s, 1H), 7.18 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.12 – 7.00 (m, 5H), 6.83 (dd, *J* = 7.4, 2.0 Hz, 2H), 3.69 (dd, *J* = 9.5, 4.9 Hz, 1H), 3.33 (s, 1H), 3.22 – 3.10 (m, 2H), 2.86 (dd, *J* = 13.2, 9.5 Hz, 1H), 2.35 (dt, *J* = 17.1, 8.6 Hz, 1H), 2.15 (ddd, *J* = 16.7, 8.7, 6.3 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 175.1 (C=O), 139.0 (Ar), 137.6 (Ar), 129.4 (Ar), 128.6 (Ar), 128.4 (Ar), 128.2 (Ar), 128.1 (Ar), 126.3 (Ar), 74.6 (CH₂), 50.9 (CH), 40.9 (CH₂), 30.2 (CH₂); HRMS (ESI) calcd. for C₁₇H₁₉N₂O (M⁺ + H): 267.1476, found 267.1497; IR (neat cm⁻¹): 3080, 1691, 1450, 1240, 1120, 1089, 954, 803, 715.

1-(2-(4-Bromophenyl)-1-phenylethyl)pyrazolidin-3-one (3ac)



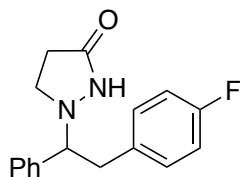
White solid (45 mg, 43% yield); m.p. 194.7–195.7 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.25 – 7.15 (m, 5H), 7.09 (t, J = 3.6 Hz, 2H), 6.69 (d, J = 8.1 Hz, 2H), 3.70 (dd, J = 9.9, 4.8 Hz, 1H), 3.33 (s, 1H), 3.25 – 3.14 (m, 2H), 2.85 (dt, J = 21.2, 9.7 Hz, 1H), 2.35 (dt, J = 16.9, 8.5 Hz, 1H), 2.13 (dt, J = 16.3, 7.8 Hz, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 175.2 (C=O), 136.4 (Ar), 131.2 (Ar), 131.2 (Ar), 128.7 (Ar), 128.5 (Ar), 128.4 (Ar), 120.3 (Ar), 74.3 (CH_2), 50.8 (CH), 40.1 (CH_2), 30.1 (CH_2); HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{18}\text{BrN}_2\text{O}$ ($\text{M}^+ + \text{H}$): 345.0603 and 347.0582, found 345.0612 and 347.0593; IR (neat cm^{-1}): 3151, 3052, 2925, 1671, 1486, 1070, 1012, 808, 753, 700.

1-(2-(4-Chlorophenyl)-1-phenylethyl)pyrazolidin-3-one (3ad)



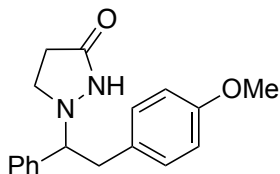
White solid (57 mg, 63% yield); m.p. 177.8–178.8 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.15 (m, 3H), 7.14 – 7.06 (m, 2H), 7.06 – 6.99 (m, 2H), 6.75 (d, J = 8.4 Hz, 2H), 3.71 (dd, J = 9.9, 4.7 Hz, 1H), 3.35 (s, 1H), 3.20 (td, J = 11.4, 8.6 Hz, 2H), 2.87 (dd, J = 13.3, 9.7 Hz, 1H), 2.37 (dt, J = 17.0, 8.6 Hz, 1H), 2.23 – 2.08 (m, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 175.0 (C=O), 135.8 (Ar), 132.2 (Ar), 130.8 (Ar), 128.7 (Ar), 128.6 (Ar), 128.5 (Ar), 128.3 (Ar), 74.4 (CH_2), 50.8 (CH), 39.9 (CH_2), 30.0 (CH_2); HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{18}\text{ClN}_2\text{O}$ ($\text{M}^+ + \text{H}$): 301.1108, found 301.1103; IR (neat cm^{-1}): 3179, 1691, 1489, 1452, 1183, 1092, 1015, 816, 702.

1-(2-(4-Fluorophenyl)-1-phenylethyl)pyrazolidin-3-one (3ae)



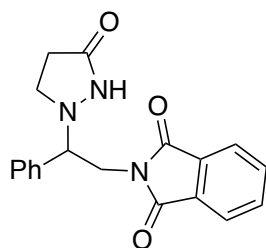
White solid (48 mg, 56% yield); m.p. 150.8–151.8 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.19 (q, $J = 3.0$ Hz, 3H), 7.13 – 7.05 (m, 2H), 6.75 (dt, $J = 8.2, 2.8$ Hz, 4H), 3.70 (dd, $J = 9.8, 4.7$ Hz, 1H), 3.34 (s, 1H), 3.27 – 3.12 (m, 2H), 2.87 (dd, $J = 13.2, 9.8$ Hz, 1H), 2.37 (dt, $J = 16.9, 8.5$ Hz, 1H), 2.15 (dt, $J = 16.1, 7.9$ Hz, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 175.1 (C=O), 161.5 (d, $J_{\text{C-F}} = 241.6$ Hz, Ar), 133.1 (Ar), 130.8 (d, $J_{\text{C-F}} = 7.8$ Hz, Ar), 128.6 (d, $J_{\text{C-F}} = 16.5$ Hz, Ar), 128.4 (Ar), 114.9 (d, $J_{\text{C-F}} = 21.1$ Hz, Ar), 74.6 (CH_2), 50.8 (CH), 39.8 (CH_2), 30.1 (CH_2); ^{19}F NMR (376 MHz, CDCl_3) δ –116.7; HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{18}\text{FN}_2\text{O}$ ($\text{M}^+ + \text{H}$): 285.1403, found 285.1453; IR (neat cm^{-1}): 2935, 1691, 1676, 1508, 1208, 1158, 840, 825, 701.

1-(2-(4-Methoxyphenyl)-1-phenylethyl)pyrazolidin-3-one (3af)



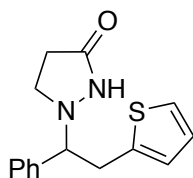
White solid (37.3 mg, 42% yield); m.p. 149.6–150.6 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.00 (s, 1H), 7.18 (dd, $J = 5.1, 1.6$ Hz, 3H), 7.15 – 7.05 (m, 2H), 6.73 (d, $J = 8.6$ Hz, 2H), 6.60 (d, $J = 8.6$ Hz, 2H), 3.65 (s, 4H), 3.29 (s, 1H), 3.21 – 3.07 (m, 2H), 2.80 (dd, $J = 13.4, 9.4$ Hz, 1H), 2.33 (dt, $J = 17.0, 8.6$ Hz, 1H), 2.18 – 2.06 (m, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 175.2 (C=O), 158.0 (Ar), 139.1 (Ar), 130.4 (Ar), 129.7 (Ar), 128.5 (Ar), 128.0 (Ar), 113.5 (Ar), 74.7 (CH_2), 55.1 (CH_3), 50.9 (CH), 40.0 (CH_2), 30.3 (CH_2); HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_2$ ($\text{M}^+ + \text{H}$): 297.1597, found 297.1574; IR (neat cm^{-1}): 3211, 2910, 1692, 1511, 1453, 1244, 1179, 1033, 832, 813, 712, 688.

2-(2-(3-Oxopyrazolidin-1-yl)-2-phenylethyl)isoindoline-1,3-dione (3ag)



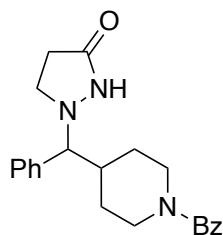
White solid (61 mg, 61% yield); m.p. 245.2–246.2 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.51 (s, 1H), 7.79 (s, 4H), 7.33 (dd, $J = 6.7, 3.0$ Hz, 2H), 7.29 – 7.23 (m, 3H), 4.17 (dd, $J = 8.6, 6.8$ Hz, 1H), 3.99 (qd, $J = 13.8, 7.7$ Hz, 2H), 3.21 (td, $J = 11.1, 10.6, 5.9$ Hz, 2H), 1.94 (dt, $J = 16.4, 8.1$ Hz, 1H), 1.64 (s, 1H); ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$) δ 175.2 (C=O), 167.9 (C=O), 135.0 (Ar), 131.7 (Ar), 129.4 (Ar), 128.7 (Ar), 128.6 (Ar), 123.5 (Ar), 68.0 (CH_2), 49.7 (CH), 40.7 (CH_2), 29.7 (CH_2); HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{18}\text{N}_3\text{O}_3$ ($\text{M}^+ + \text{H}$): 336.1348, found 336.1357; IR (neat cm^{-1}): 3120, 2830, 1773, 1703, 1397, 963, 722, 702.

1-(1-Phenyl-2-(thiophen-2-yl)ethyl)pyrazolidin-3-one (3ah)



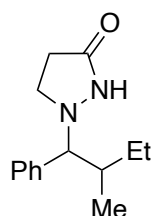
White solid (22 mg, 27% yield); m.p. 111.8–112.8 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.85 (s, 1H), 7.33 – 7.27 (m, 3H), 7.24 (dd, $J = 7.3, 2.3$ Hz, 2H), 7.05 (dd, $J = 5.2, 1.2$ Hz, 1H), 6.79 (dd, $J = 5.1, 3.4$ Hz, 1H), 6.55 (d, $J = 2.3$ Hz, 1H), 3.82 (dd, $J = 9.1, 5.1$ Hz, 1H), 3.45 (dd, $J = 14.6, 5.1$ Hz, 2H), 3.31 – 3.17 (m, 2H), 2.45 – 2.32 (m, 1H), 2.18 (ddd, $J = 16.7, 8.7, 6.4$ Hz, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 175.3 (C=O), 139.6 (Ar), 138.7 (Ar), 128.7 (Ar), 128.5 (Ar), 128.3 (Ar), 126.6 (Ar), 126.2 (Ar), 124.1 (Ar), 73.9 (CH_2), 50.8 (CH), 34.9 (CH_2), 30.1 (CH_2); HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{17}\text{N}_2\text{OS}$ ($\text{M}^+ + \text{H}$): 273.1062, found 273.1066; IR (neat cm^{-1}): 3147, 2931, 1672, 1453, 1356, 1246, 1179, 1031, 831, 751, 699.

1-((1-Benzoylpiperidin-4-yl)(phenyl)methyl)pyrazolidin-3-one (3ai)



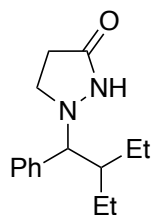
White solid (83.0 mg, 76% yield); m.p. 107.8–108.8 °C; 146–147 °C ^1H NMR (400 MHz, CDCl_3) δ 9.08 (s, 1H), 7.50 – 7.20 (m, 10H), 4.69 (d, J = 29.8 Hz, 1H), 3.71 (d, J = 33.5 Hz, 1H), 3.61 – 3.17 (m, 3H), 3.14 – 2.62 (m, 2H), 2.21 (s, 2H), 2.06 – 1.50 (m, 3H), 1.06 (m, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 175.9 (C=O), 170.2 (C=O), 136.2 (Ar), 129.5 (Ar), 129.3 (Ar), 128.7 (Ar), 128.5 (Ar), 128.4 (Ar), 126.9 (Ar), 126.8 (Ar), 77.3 (CH_2), 77.1 (CH_2), 76.8 (CH_2), 76.2 (CH_2), 50.5 (CH), 47.7 (CH_2), 42.1 (CH_2), 38.0 (CH), 30.9 (CH_2), 30.0 (CH_2); HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{26}\text{N}_3\text{O}_2$ ($\text{M}^+ + \text{H}$): 364.2025, found 364.2038; IR (neat cm^{-1}): 3168, 2933, 1682, 1601, 1438, 1279, 911, 727, 725.

1-(2-Methyl-1-phenylbutyl)pyrazolidin-3-one (3aj)



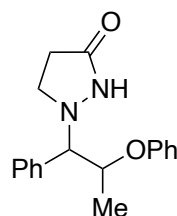
Light yellow wax (69.7 mg, 99% yield, 1:1 dr); ^1H NMR (400 MHz, CDCl_3) δ 7.30 (ddd, J = 14.8, 10.4, 6.7 Hz, 5H), 3.61 – 3.33 (m, 2H), 3.23 (d, J = 9.9 Hz, 1H), 2.33 (ddt, J = 50.8, 16.7, 8.6 Hz, 1H), 2.23 – 1.89 (m, 2H), 1.70 – 1.38 (m, 1H), 0.94 (dd, J = 6.0, 3.9 Hz, 3H), 0.87 – 0.79 (m, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 175.5 (C=O), 175.2 (C=O), 136.9 (Ar), 129.4 (Ar), 129.3 (Ar), 128.3 (Ar), 128.2 (Ar), 127.9 (Ar), 127.9 (Ar), 76.2 (CH_2), 50.6 (CH), 50.5 (CH_2), 36.0 (CH_2), 36.0 (CH_2), 30.2 (CH), 26.9 (CH_2), 24.1 (CH_2), 16.7 (CH_3), 14.1 (CH_3), 11.5 (CH_3), 11.1 (CH_3); HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{21}\text{N}_2\text{O}$ ($\text{M}^+ + \text{H}$): 233.1654, found 233.1665; IR (neat cm^{-1}): 3165, 2962, 1682, 1453, 1370, 1302, 1077, 704.

1-(2-Ethyl-1-phenylbutyl)pyrazolidin-3-one (3ak)



White solid (73.2 mg, 99% yield); m.p. 84.4–85.4 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.87 (s, 1H), 7.22 (t, $J = 7.2$ Hz, 5H), 3.48 (d, $J = 7.3$ Hz, 1H), 3.32 (s, 1H), 3.21 – 3.02 (m, 1H), 2.10 (dt, $J = 16.5, 8.3$ Hz, 1H), 1.80 (dt, $J = 16.4, 8.1$ Hz, 1H), 1.67 (ddd, $J = 9.7, 5.9, 2.6$ Hz, 1H), 1.48 (ddd, $J = 13.5, 7.3, 3.2$ Hz, 1H), 1.43 – 1.34 (m, 1H), 1.27 (dt, $J = 14.1, 7.1$ Hz, 1H), 0.89 (t, $J = 7.4$ Hz, 3H), 0.86 – 0.78 (m, 1H), 0.74 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 175.4 (C=O), 137.4 (Ar), 129.3 (Ar), 128.3 (Ar), 127.8 (Ar), 73.8 (CH_2), 50.5 (CH), 42.2 (CH_2), 30.4 (CH), 22.1 (CH_2), 21.2 (CH_2), 11.2 (CH_3), 11.2 (CH_3); HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{23}\text{N}_2\text{O}$ ($\text{M}^+ + \text{H}$): 247.1810, found 247.1820; IR (neat cm^{-1}): 3167, 2962, 1679, 1454, 1365, 1304, 1077, 914, 733, 704.

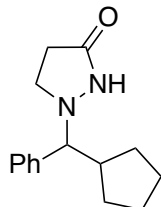
1-(2-Phenoxy-1-phenylpropyl)pyrazolidin-3-one (3al)



White wax (69 mg, 77% yield, 1:1 dr); ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, $J = 123.1$ Hz, 1H), 7.43 – 7.15 (m, 7H), 7.02 – 6.79 (m, 3H), 4.68 (ddt, $J = 27.2, 9.4, 6.2$ Hz, 1H), 3.83 – 3.62 (m, 1H), 3.39 – 2.81 (m, 2H), 2.31 – 2.04 (m, 2H), 1.08 (dd, $J = 116.2, 6.3$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 174.0 (C=O), 173.6 (C=O), 157.0 (Ar), 156.6 (Ar), 136.6 (Ar), 136.2 (Ar), 129.8 (Ar), 129.7 (Ar), 129.4 (Ar), 129.1 (Ar), 128.9 (Ar), 128.7 (Ar), 128.7 (Ar), 128.4 (Ar), 122.0 (Ar), 121.6 (Ar), 116.8 (Ar), 116.3 (Ar), 78.0 (CH_2), 76.4 (CH_2), 76.4 (CH), 74.6 (CH), 52.1 (CH), 51.6 (CH), 30.3 (CH_2), 30.1 (CH_2), 16.9 (CH_3), 15.2 (CH_3); HRMS (ESI)

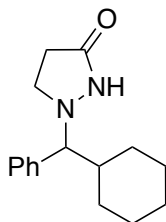
calcd. for $C_{18}H_{21}N_2O_2$ ($M^+ + H$): 297.1603, found 297.1608; IR (neat cm^{-1}): 3170, 2953, 1686, 1598, 1492, 1369, 1229, 1071, 754, 705.

1-(Cyclopentyl(phenyl)methyl)pyrazolidin-3-one (3am)



White solid (73.2 mg, 99% yield); m.p. 126.4–127.4 °C; 1H NMR (600 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.36 – 7.27 (m, 5H), 3.42 (dd, $J = 26.4, 9.9$ Hz, 2H), 3.21 (ddd, $J = 11.5, 9.1, 6.3$ Hz, 1H), 2.39 (dtd, $J = 16.2, 9.0, 7.2$ Hz, 1H), 2.00 – 1.90 (m, 2H), 1.68 (dt, $J = 16.6, 8.4$ Hz, 1H), 1.55 (ddd, $J = 8.8, 6.8, 4.7$ Hz, 2H), 1.51 – 1.39 (m, 4H), 1.00 (ddd, $J = 10.9, 8.9, 5.8$ Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1 (C=O), 138.0 (Ar), 129.3 (Ar), 128.3 (Ar), 127.9 (Ar), 76.1 (CH_2), 49.9 (CH), 41.8 (CH_2), 30.9 (CH), 30.3 (CH_2), 29.9 (CH_2), 25.3 (CH_2), 25.0 (CH_2); HRMS (ESI) calcd. for $C_{15}H_{21}N_2O$ ($M^+ + H$): 245.1654, found 245.1646; IR (neat cm^{-1}): 3160, 2923, 2854, 1674, 1451, 1347, 1295, 1017, 766, 700.

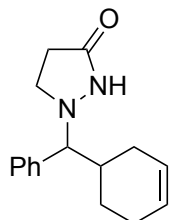
1-(Cyclohexyl(phenyl)methyl)pyrazolidin-3-one (3an)



White solid (51.2 mg, 66% yield); m.p. 162.5–163.5 °C 1H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.28 – 7.03 (m, 5H), 3.37 – 3.20 (m, 2H), 3.12 (q, $J = 9.2$ Hz, 1H), 2.20 (dt, $J = 16.9, 8.5$ Hz, 1H), 1.92 (td, $J = 16.4, 8.2$ Hz, 1H), 1.81 – 1.69 (m, 2H), 1.68 – 1.47 (m, 4H), 1.25 – 1.06 (m, 2H), 1.01 – 0.85 (m, 1H), 0.73 (qd, $J = 13.7, 12.7, 3.6$ Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.4 (C=O), 137.6 (Ar), 129.3 (Ar), 128.2 (Ar), 127.7 (Ar), 50.5 (CH_2), 39.5 (CH), 31.0 (CH_2), 30.3 (CH), 27.9 (CH_2), 26.5 (CH_2), 26.3 (CH_2), 26.0 (CH_2). HRMS (ESI) calcd. for

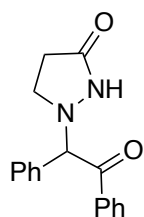
C₁₆H₂₃N₂O (M⁺ + H): 259.1789, found 259.1810; IR (neat cm⁻¹): 3187, 2920, 1675, 1438, 1328, 1295, 1016, 751, 701.

1-(Cyclohex-3-en-1-yl(phenyl)methyl)pyrazolidin-3-one (3ao)



White solid (74 mg, 96% yield, 1:1 dr); m.p. 153–154 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.51 (s, 1H), 7.39 – 7.24 (m, 5H), 5.69 – 5.50 (m, 2H), 3.57 – 3.30 (m, 2H), 3.29 – 3.17 (m, 1H), 2.21 – 1.55 (m, 8H), 1.25 – 1.00 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 175.9 (C=O), 137.1 (Ar), 136.8 (Ar), 129.4 (Ar), 129.4 (Ar), 128.4 (Ar), 128.0 (Ar), 127.0 (Ar), 127.0 (Ar), 126.1 (C=C), 125.9 (C=C), 75.9 (CH₂), 75.8 (CH₂), 35.2 (CH), 35.1 (CH), 30.2 (CH₂), 30.2 (CH₂), 29.4 (CH), 27.5 (CH₂), 26.5 (CH₂), 25.0 (CH₂), 24.8 (CH₂), 24.2 (CH₂); HRMS (ESI) calcd. for C₁₆H₂₁N₂O (M⁺ + H): 257.1648, found 257.1663; IR (neat cm⁻¹): 3144, 3024, 2904, 1681, 1492, 1368, 1075, 1007, 745, 704.

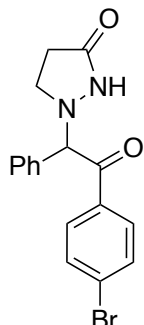
1-(2-Oxo-1,2-diphenylethyl)pyrazolidin-3-one (5aa)



White solid (51.3 mg, 61% yield); m.p. 148–149 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.83 (m, 2H), 7.56 (s, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.42 (dd, *J* = 7.8, 1.9 Hz, 2H), 7.38 – 7.31 (m, 5H), 5.33 (s, 1H), 3.38 (s, 1H), 3.29 (ddd, *J* = 11.3, 8.9, 6.7 Hz, 1H), 2.45 – 2.32 (m, 1H), 2.15 (dd, *J* = 15.6, 7.9 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 196.0 (C=O), 174.9 (C=O), 135.1 (Ar), 133.6 (Ar), 133.1 (Ar), 129.6 (Ar), 129.4 (Ar), 129.3 (Ar), 128.8 (Ar), 128.6 (Ar), 50.0

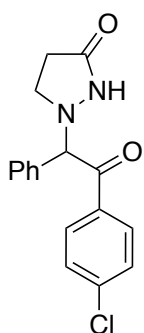
(CH₂), 29.8 (CH₂); HRMS (ESI) calcd. for C₁₇H₁₇N₂O₂ (M⁺ + H): 281.1284, found 281.1268; IR (neat cm⁻¹): 3186, 2937, 1673, 1449, 1352, 1213, 1171, 979, 694.

1-(2-(4-Bromophenyl)-2-oxo-1-phenylethyl)pyrazolidin-3-one (5ab)



White solid (54 mg, 50% yield); m.p. 150 – 151 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.37 (ddd, *J* = 7.9, 4.7, 2.1 Hz, 5H), 5.32 (s, 1H), 3.41 (s, 1H), 3.32 (ddd, *J* = 11.4, 8.9, 6.7 Hz, 1H), 2.39 (s, 1H), 2.17 (s, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 194.9 (C=O), 174.8 (C=O), 133.6 (Ar), 132.0 (Ar), 130.3 (Ar), 129.6 (Ar), 129.6 (Ar), 129.6 (Ar), 129.0 (Ar), 50.0 (CH₂), 29.7 (CH₂); HRMS (ESI): calcd. for C₁₇H₁₆BrN₂O₂ (M⁺ + H) 359.0395 and 361.0375, found 359.0401 and 361.0381; IR (neat cm⁻¹): 3149, 3051, 1686, 1583, 1400, 1355, 1219, 1071, 976, 832, 730, 700.

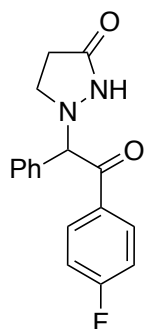
1-(2-(4-Chlorophenyl)-2-oxo-1-phenylethyl)pyrazolidin-3-one (5ac)



White solid (59 mg, 62% yield); m.p. 179 – 180 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.6 Hz, 2H), 7.43 – 7.30 (m, 7H), 5.34 (s, 1H), 3.42 (s, 1H), 3.33 (ddd, *J* = 11.2, 8.8, 6.6 Hz, 1H), 2.49 – 2.32 (m, 1H), 2.25 – 2.06 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 194.7 (C=O), 174.8 (C=O), 140.2 (Ar), 133.2 (Ar), 130.2 (Ar), 129.6 (Ar), 129.6 (Ar), 129.6 (Ar), 129.0 (Ar),

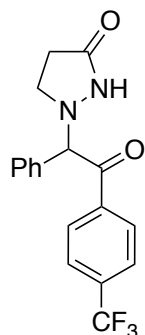
50.0 (CH₂), 29.7 (CH₂); HRMS (ESI): calcd. for C₁₇H₁₆ClN₂O₂ (M⁺ + H) 315.0900, found 315.0900; IR (neat cm⁻¹): 3143, 3050, 2945, 1684, 1585, 1454, 1401, 1355, 1219, 1092, 976, 833, 732, 700.

1-(2-(4-Fluorophenyl)-2-oxo-1-phenylethyl)pyrazolidin-3-one (5ad)



White solid (68 mg, 76% yield); m.p. 131–132 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.99 – 7.86 (m, 2H), 7.68 (s, 1H), 7.44 – 7.30 (m, 5H), 7.02 (t, *J* = 8.6 Hz, 2H), 5.29 (s, 1H), 3.37 (s, 1H), 3.29 (ddd, *J* = 11.3, 9.0, 6.8 Hz, 1H), 2.37 (dd, *J* = 16.6, 8.4 Hz, 1H), 2.14 (dd, *J* = 16.6, 8.4 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 194.4 (C=O), 175.0 (C=O), 165.8 (d, *J*_{C-F} = 256.5 Hz, Ar), 132.9 (Ar), 131.6 (d, *J*_{C-F} = 15.1 Hz, Ar), 131.4 (d, *J*_{C-F} = 15.1 Hz, Ar), 129.6 (Ar), 129.5 (d, *J*_{C-F} = 15.1 Hz, Ar), 115.9 (d, *J*_{C-F} = 15.1 Hz, Ar), 76.7 (CH), 50.0 (CH₂), 29.8 (CH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ –103.6; HRMS (ESI) calcd. for C₁₇H₁₆FN₂O₂ (M⁺ + H): 299.1196, found 299.1203; IR (neat cm⁻¹): 3181, 3049, 1679, 1597, 1509, 1221, 1158, 997, 839, 737, 701.

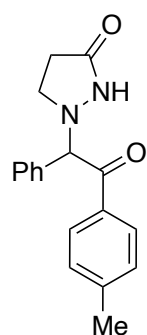
1-(2-Oxo-1-phenyl-2-(4-(trifluoromethyl)phenyl)ethyl)pyrazolidin-3-one (5ae)



White solid (30.3 mg, 29% yield); m.p. 93–94 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.44 – 7.34 (m, 5H), 5.33 (s, 1H), 3.44 (s, 1H), 3.32

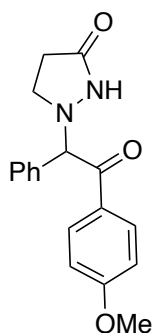
(ddd, $J = 11.3, 9.0, 6.6$ Hz, 1H), 2.42 (s, 1H), 2.16 (s, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 195.1 (C=O), 175.0 (C=O), 137.7 (Ar), 134.7 (q, $J = 30.2$ Hz, Ar), 132.3 (Ar), 129.7 (Ar), 129.6 (Ar), 129.1 (Ar), 125.7 (q, $J_{\text{C-F}} = 15.1$ Hz, Ar), 123.2 (q, $J_{\text{C-F}} = 271.8$ Hz, CF_3), 50.1 (CH_2), 29.7 (CH_2). ^{19}F NMR (376 MHz, CDCl_3) δ -63.3; HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{16}\text{F}_3\text{N}_2\text{O}_2$ ($\text{M}^+ + \text{H}$): 349.1158, found 349.1142; IR (neat cm^{-1}): 3185, 3055, 1687, 1410, 1323, 1161, 1130, 1111, 1066, 982, 840, 699.

1-(2-Oxo-1-phenyl-2-(*p*-tolyl)ethyl)pyrazolidin-3-one (5af)



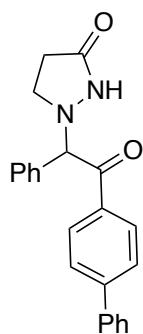
White solid (51 mg, 58% yield); m.p. 174 – 175 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 8.3$ Hz, 2H), 7.46 – 7.41 (m, 2H), 7.36 (ddd, $J = 6.1, 2.6, 1.4$ Hz, 3H), 7.16 (d, $J = 8.3$ Hz, 2H), 5.46 (s, 1H), 3.55 – 3.30 (m, 2H), 2.38 (s, 1H), 2.33 (s, 3H), 2.17 (s, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 195.1 (C=O), 174.4 (C=O), 144.8 (Ar), 132.2 (Ar), 129.8 (Ar), 129.6 (Ar), 129.5 (Ar), 129.4 (Ar), 129.1 (Ar), 49.9 (CH_2), 29.5 (CH_3), 21.7 (CH_2); HRMS (ESI): calcd. for $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_2$ ($\text{M} + \text{H}$) $^+$ 295.1447, found 295.1453; IR (neat cm^{-1}): 3176, 3052, 2882, 2903, 1678, 1604, 1409, 1247, 1227, 1184, 968, 731, 701.

1-(2-(4-Methoxyphenyl)-2-oxo-1-phenylethyl)pyrazolidin-3-one (5ag)



White solid (66 mg, 71% yield); m.p. 159–160 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, J = 8.9 Hz, 2H), 7.53 (s, 1H), 7.41 (dd, J = 7.9, 1.8 Hz, 2H), 7.37 – 7.28 (m, 3H), 6.81 (d, J = 9.0 Hz, 2H), 5.26 (s, 1H), 3.78 (s, 3H), 3.37 (s, 1H), 3.26 (ddd, J = 11.3, 8.9, 6.7 Hz, 1H), 2.37 (s, 1H), 2.14 (s, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 194.4 (C=O), 174.8 (C=O), 163.8 (Ar), 133.5 (Ar), 131.2 (Ar), 129.5 (Ar), 129.3 (Ar), 129.2 (Ar), 127.9 (Ar), 113.9 (Ar), 55.5 (CH_3), 50.0 (CH_2), 29.8 (CH_2); HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_3$ ($\text{M}^+ + \text{H}$): 311.1389, found 311.1373; IR (neat cm^{-1}): 3134, 2963, 1678, 1598, 1574, 1421, 1220, 1176, 1026, 983, 839, 816, 699.

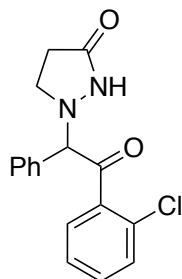
1-(2-([1,1'-Biphenyl]-4-yl)-2-oxo-1-phenylethyl)pyrazolidin-3-one (5ah)



White solid (42.7 mg, 40% yield); m.p. 152–153 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, J = 8.4 Hz, 2H), 7.62 – 7.51 (m, 4H), 7.49 – 7.33 (m, 8H), 5.37 (s, 1H), 3.43 (s, 1H), 3.32 (ddd, J = 11.3, 8.9, 6.6 Hz, 1H), 2.51 – 2.33 (m, 1H), 2.27 – 2.08 (m, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 195.5 (C=O), 174.9 (C=O), 146.3 (Ar), 139.5 (Ar), 133.6 (Ar), 133.1 (Ar), 129.7 (Ar), 129.5 (Ar), 129.4 (Ar), 129.0 (Ar), 128.4 (Ar), 127.3 (Ar), 127.2 (Ar), 50.1 (CH_2), 29.8

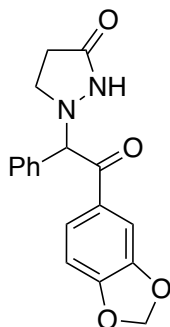
(CH₂); HRMS (ESI) calcd. for C₂₃H₂₁N₂O₂ (M⁺ + H): 357.1603, found 357.1617; IR (neat cm⁻¹): 3051, 1678, 1602, 1408, 1248, 1224, 1180, 984, 759, 690.

1-(2-(2-Chlorophenyl)-2-oxo-1-phenylethyl)pyrazolidin-3-one (5ai)



White solid (53 mg, 56% yield); m.p. 99.5–100.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.41 (s, 1H), 7.29 – 7.17 (m, 7H), 7.06 (td, *J* = 7.4, 1.5 Hz, 1H), 6.90 (dd, *J* = 7.7, 1.6 Hz, 1H), 5.16 (s, 1H), 3.29 (ddd, *J* = 11.2, 8.8, 7.0 Hz, 2H), 2.53 – 2.37 (m, 1H), 2.22 (dt, *J* = 16.7, 8.3 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 199.3 (C=O), 174.9 (C=O), 137.5 (Ar), 132.1 (Ar), 131.7 (Ar), 130.5 (Ar), 130.3 (Ar), 129.6 (Ar), 129.5 (Ar), 129.2 (Ar), 129.1 (Ar), 126.6 (Ar), 80.0 (CH), 50.2 (CH₂), 29.7 (CH₂); HRMS (ESI) calcd. for C₁₇H₁₆ClN₂O (M⁺ + H): 315.0900, found 315.0918; IR (neat cm⁻¹): 3196, 1682, 1590, 1432, 1221, 1185, 1067, 972, 845, 740, 703.

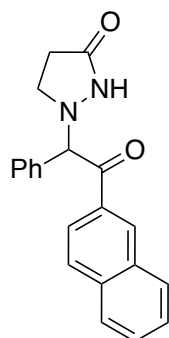
1-(2-(Benzo[d][1,3]dioxol-5-yl)-2-oxo-1-phenylethyl)pyrazolidin-3-one (5aj)



White solid (64 mg, 66% yield); m.p. 164–165 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.56 (s, 1H), 7.50 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.38 – 7.30 (m, 4H), 6.73 (d, *J* = 8.3 Hz, 1H), 5.98 (d, *J* = 1.4 Hz, 2H), 5.25 (s, 1H), 3.38 (s, 1H), 3.27 (ddd, *J* = 11.3, 9.0, 6.7 Hz, 1H), 2.38 (s, 1H), 2.14 (s, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 194.0 (C=O), 174.8 (C=O), 152.2 (Ar), 148.2 (Ar), 133.3 (Ar), 129.6 (Ar), 129.5 (Ar), 129.4 (Ar), 129.3 (Ar), 125.4 (Ar), 108.6

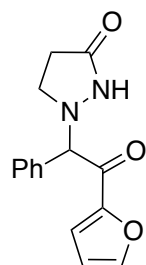
(Ar), 108.0 (Ar), 102.0 (CH₂), 76.5 (CH), 50.0 (CH₂), 29.8 (CH₂); HRMS (ESI) calcd. for C₁₈H₁₇N₂O₄ (M⁺ + H): 325.1188, found 325.1202; IR (neat cm⁻¹): 3046, 2890, 1683, 1485, 1434, 1348, 1254, 1098, 1038, 940, 888, 735, 698.

1-(2-(Naphthalen-2-yl)-2-oxo-1-phenylethyl)pyrazolidin-3-one (5ak)



White solid (71 mg, 72% yield); m.p. 174 – 175 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.43 (s, 1H), 7.94 – 7.85 (m, 2H), 7.78 (dd, *J* = 8.4, 4.0 Hz, 2H), 7.59 – 7.47 (m, 4H), 7.39 – 7.30 (m, 3H), 5.61 (s, 1H), 3.50 (s, 1H), 3.40 (ddd, *J* = 11.1, 8.9, 6.6 Hz, 1H), 2.55 – 2.36 (m, 1H), 2.30 – 2.15 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 195.8 (C=O), 174.7 (C=O), 135.6 (Ar), 132.2 (Ar), 131.0 (Ar), 129.7 (Ar), 129.7 (Ar), 129.5 (Ar), 129.5 (Ar), 129.0 (Ar), 128.6 (Ar), 127.7 (Ar), 127.0 (Ar), 124.1 (Ar), 50.0 (CH₂), 29.7 (CH₂); HRMS (ESI): calcd. for C₂₁H₁₉N₂O₂ (M⁺ + H) 331.1447, found 331.1447; IR (neat cm⁻¹): 3149, 3047, 2923, 1691, 1677, 1467, 1342, 1261, 1216, 1124, 984, 826, 799, 751, 722, 699.

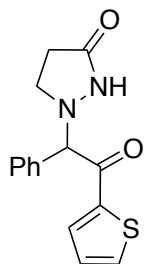
1-(2-(Furan-2-yl)-2-oxo-1-phenylethyl)pyrazolidin-3-one (5al)



White solid (23 mg, 28% yield); m.p. 173 – 174 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.52 (d, *J* = 1.6 Hz, 1H), 7.47 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.39 – 7.31 (m, 3H), 7.21 (d, *J* = 3.7 Hz, 1H), 6.47 (dd, *J* = 3.6, 1.7 Hz, 1H), 5.17 (s, 1H), 3.41 – 3.23 (m, 2H), 2.48 (s, 1H), 2.29 – 2.17 (m,

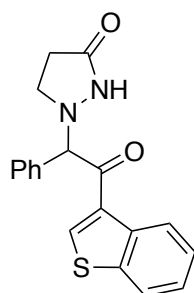
1H); ¹³C NMR (151 MHz, CDCl₃) δ 184.7 (C=O), 174.9 (C=O), 151.1 (Ar), 147.0 (Ar), 133.2 (Ar), 129.5 (Ar), 129.3 (Ar), 129.2 (Ar), 119.2 (Ar), 112.6 (Ar), 50.0 (CH₂), 29.6 (CH₂); HRMS (ESI): calcd. for C₁₅H₁₅N₂O₃ (M⁺ + H) 271.1083, found 271.1085; IR (neat cm⁻¹): 3028, 3118, 3099, 1694, 1660, 1462, 1397, 1274, 1167, 1031, 990, 793, 699.

1-(2-Oxo-1-phenyl-2-(thiophen-2-yl)ethyl)pyrazolidin-3-one (5am)



White solid (40 mg, 47% yield); m.p. 128 – 129 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.71 – 7.67 (m, 1H), 7.60 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.47 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.40 – 7.34 (m, 3H), 7.04 (dd, *J* = 4.9, 3.9 Hz, 1H), 5.13 (s, 1H), 3.36 (s, 1H), 3.29 (ddd, *J* = 11.4, 8.9, 7.0 Hz, 1H), 2.44 (s, 1H), 2.21 (s, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 188.7 (C=O), 174.9 (C=O), 141.5 (Ar), 134.7 (Ar), 133.4 (Ar), 129.5 (Ar), 129.5 (Ar), 129.4 (Ar), 128.3 (Ar), 50.1 (CH₂), 29.7 (CH₂); HRMS (ESI) calcd. for C₁₅H₁₅N₂O₂S (M⁺ + H): 287.0848, found 287.0832; IR (neat cm⁻¹): 3148, 1690, 1663, 1410, 1353, 1222, 1066, 947, 752, 718.

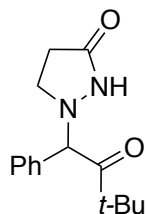
1-(2-(Benzo[*b*]thiophen-3-yl)-2-oxo-1-phenylethyl)pyrazolidin-3-one (5an)



White solid (69 mg, 68% yield); m.p. 181 – 182 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.72 (d, *J* = 8.2 Hz, 1H), 8.29 (s, 1H), 7.82 – 7.74 (m, 1H), 7.56 – 7.46 (m, 3H), 7.42 – 7.33 (m, 4H), 5.46 (s, 1H), 3.43 (dd, *J* = 20.2, 11.8 Hz, 2H), 2.51 – 2.33 (m, 1H), 2.32 – 2.11 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 190.7 (C=O), 174.8 (C=O), 139.3 (Ar), 138.2 (Ar), 136.8 (Ar),

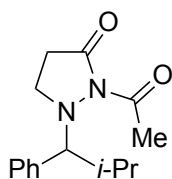
133.6 (Ar), 132.7 (Ar), 129.5 (Ar), 129.5 (Ar), 129.4 (Ar), 126.2 (Ar), 125.8 (Ar), 125.6 (Ar), 122.2 (Ar), 78.0 (CH), 50.1 (CH₂), 29.7 (CH₂); HRMS (ESI): calcd. for C₁₉H₁₇N₂O₂S (M⁺ + H) 337.1011, found 337.1010; IR (neat cm⁻¹): 3177, 3068, 2992, 2891, 1688, 1674, 1490, 1454, 1421, 1145, 1059, 860, 742, 710, 695.

1-(3,3-Dimethyl-2-oxo-1-phenylbutyl)pyrazolidin-3-one (5ao)



White solid (15.6 mg, 20% yield); m.p. 121–122 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.31 (m, 5H), 3.48 (dt, *J* = 11.0, 8.2 Hz, 1H), 3.36 (s, 1H), 3.18 (ddd, *J* = 11.1, 8.8, 7.2 Hz, 1H), 2.13 (ddd, *J* = 16.3, 8.8, 7.2 Hz, 1H), 1.93 (ddd, *J* = 16.5, 8.8, 7.6 Hz, 1H), 1.00 (s, 9H); ¹³C NMR (151 MHz, CDCl₃) δ 175.5 (C=O), 138.4 (Ar), 129.9 (Ar), 128.2 (Ar), 127.7 (Ar), 81.6 (CH), 53.4 (CH₂), 35.5 (CH), 30.4 (CH₂), 29.0 (CH₃); HRMS (ESI) calcd. for C₁₅H₂₁N₂O₂ (M⁺ + H): 261.1597, found 261.1583; IR (neat cm⁻¹): 3176, 2955, 2887, 1703, 1655, 1451, 1369, 1180, 1071, 754, 711.

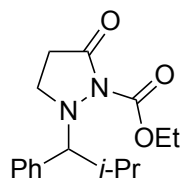
2-Acetyl-1-(2-methyl-1-phenylpropyl)pyrazolidin-3-one (6aa)



White solid (68.7 mg, 88%); m.p. 66 – 67°C; ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.30 (m, 3H), 7.17 (dd, *J* = 6.4, 3.0 Hz, 2H), 3.78 (d, *J* = 10.8 Hz, 1H), 3.43 – 3.31 (m, 2H), 2.49 (s, 3H), 2.35 – 2.24 (m, 1H), 1.93 (ddd, *J* = 17.7, 7.7, 2.6 Hz, 1H), 1.51 – 1.38 (m, 1H), 1.30 (d, *J* = 6.5 Hz, 3H), 0.81 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 175.0 (C=O), 166.9 (C=O), 136.8 (Ar), 129.1 (Ar), 128.8 (Ar), 128.4 (Ar), 72.8 (CH₂), 42.5 (CH₃), 32.1 (CH), 28.5 (CH), 24.9 (CH₂), 20.8 (CH₃), 20.3 (CH₃); HRMS (ESI) calcd. for C₁₅H₂₁N₂O₂ (M⁺ + H):

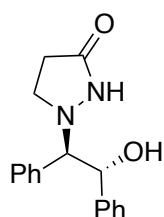
261.1597, found 261.1570; IR (neat cm^{-1}): 2954, 1739, 1701, 1368, 1267, 1232, 1070, 833, 757, 710.

Ethyl 2-(2-methyl-1-phenylpropyl)-5-oxopyrazolidine-1-carboxylate (7aa)



Yellow wax (72.3 mg, 83%); ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.28 (m, 3H), 7.20 (dt, J = 6.8, 2.2 Hz, 2H), 4.47 – 4.28 (m, 2H), 3.61 (dd, J = 10.4, 2.2 Hz, 1H), 3.34 (ddd, J = 11.3, 7.2, 2.3 Hz, 2H), 2.23 (ddt, J = 12.9, 10.4, 4.4 Hz, 1H), 1.84 (ddd, J = 17.6, 7.0, 3.4 Hz, 1H), 1.38 (t, J = 7.1 Hz, 3H), 1.22 (dd, J = 6.5, 2.2 Hz, 3H), 0.80 (dd, J = 6.5, 2.1 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 173.6 (C=O), 150.3 (C=O), 136.3 (Ar), 129.3 (Ar), 128.8 (Ar), 128.8 (Ar), 128.4 (Ar), 128.3 (Ar), 74.6 (CH_2), 63.1 (CH_2), 43.7 (CH), 31.7 (CH_2), 28.5 (CH_2), 20.6 (CH_2), 20.6 (CH_3), 14.4 (CH_3), 14.3 (CH_3); HRMS (ESI) calcd. for $\text{C}_{16}\text{H}_{23}\text{N}_2\text{O}_3$ ($\text{M}^+ + \text{H}$): 291.1702, found 291.1696; IR (neat cm^{-1}): 2960, 1783, 1731, 1274, 1235, 1045, 912, 837, 734, 705.

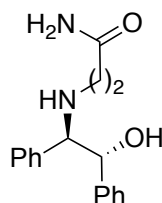
1-(2-Hydroxy-1,2-diphenylethyl)pyrazolidin-3-one (8aa)



White solid (70 mg, 82% yield, > 20:1 dr); m.p. 183 – 184 $^{\circ}\text{C}$; ^1H NMR (600 MHz, CDCl_3) δ 7.25 – 7.21 (m, 1H), 7.21 – 7.14 (m, 5H), 7.05 (d, J = 7.1 Hz, 2H), 7.01 – 6.97 (m, 2H), 5.23 (d, J = 3.6 Hz, 1H), 3.78 (d, J = 3.6 Hz, 1H), 3.30 (dt, J = 11.2, 8.5 Hz, 1H), 3.16 (s, 1H), 2.49 (dt, J = 16.9, 8.5 Hz, 1H), 2.23 (ddd, J = 16.7, 8.7, 6.5 Hz, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 175.3 (C=O), 140.4 (Ar), 134.8 (Ar), 129.7 (Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 127.5 (Ar), 126.6 (Ar), 77.6 (CH_2), 74.3 (CH), 51.4 (CH), 29.9 (CH_2); HRMS (ESI): calcd. for

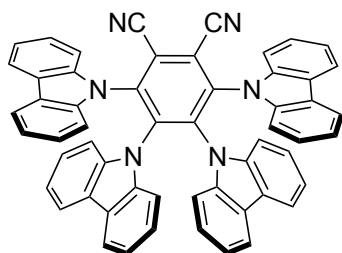
C₁₇H₁₉N₂O₂ (M⁺ + H) 283.1447, found 283.1433; IR (neat cm⁻¹): 3539, 3030, 2797, 1687, 1650, 1453, 1365, 1299, 1193, 1056, 782.

3-((2-Hydroxy-1,2-diphenylethyl)amino)propenamide (9aa)



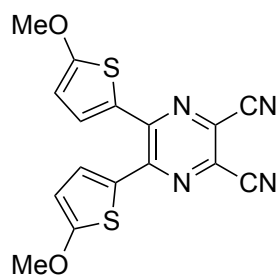
White solid (73 mg, 86% yield, > 20:1 dr); m.p. 249 – 250 °C; ¹H NMR (400 MHz, MeOD–d₄) δ 7.21 – 7.11 (m, 5H), 7.08 (dd, *J* = 5.1, 1.9 Hz, 3H), 6.99 (dd, *J* = 7.0, 2.8 Hz, 2H), 5.15 (d, *J* = 4.2 Hz, 1H), 4.24 (d, *J* = 4.2 Hz, 1H), 3.06 – 2.96 (m, 1H), 2.91 (dt, *J* = 12.8, 6.7 Hz, 1H), 2.55 – 2.46 (m, 2H). ¹³C NMR (151 MHz, MeOD–d₄) δ 176.2 (C=O), 141.9 (Ar), 139.1 (Ar), 128.5 (Ar), 127.6 (Ar), 127.5 (Ar), 127.1 (Ar), 127.0 (Ar), 126.7 (Ar), 76.5 (CH₂), 68.4 (CH), 42.8 (CH), 34.3 (CH₂); HRMS (ESI): calcd. for C₁₇H₂₁N₂O₂ (M⁺ + H) 285.1603, found 285.1595; IR (neat cm⁻¹): 3624, 3564, 3523, 3495, 3421, 3353, 1661, 1548, 1454, 1422, 1387, 1224, 1062, 980.

4CzPN^{S9}



Yellow solid (0.71 g, 90% yield); ¹H NMR (600 MHz, CD₂Cl₂) δ 7.80 (d, *J* = 7.0 Hz, 4H), 7.34 (d, *J* = 7.6 Hz, 4H), 7.26 (d, *J* = 8.0 Hz, 4H), 7.17 – 7.09 (m, 8H), 6.94 (d, *J* = 8.2 Hz, 4H), 6.80 (t, *J* = 7.5 Hz, 4H), 6.63 – 6.59 (m, 4H); ¹³C NMR (151 MHz, (CD₃)₂SO) δ 142.1 (Ar), 141.6 (Ar), 139.2 (Ar), 138.0 (Ar), 125.6 (Ar), 124.5 (Ar), 123.5 (Ar), 123.3 (Ar), 121.6 (Ar), 121.0 (Ar), 120.6 (Ar), 119.8 (Ar), 119.5 (Ar), 113.9 (Ar), 111.7 (CN), 111.6 (CN).

DPZ^{S10}



Orange solid (184 mg, 70% yield); ^1H NMR (600 MHz, CDCl_3) δ 7.68 (d, $J = 4.4$ Hz, 2H), 6.19 (d, $J = 4.4$ Hz, 2H), 4.00 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 173.7 (Ar), 146.6 (Ar), 131.1 (Ar), 126.1 (Ar), 124.5 (Ar), 113.5 (Ar), 106.1 (CN), 60.6 (CH_3).

5. ^1H , ^{13}C and ^{19}F NMR Spectra

Figure S1. ^1H and ^{13}C NMR spectra of 2-benzylidene-5-oxopyrazolidin-2-ium-1-ide (**1a**)

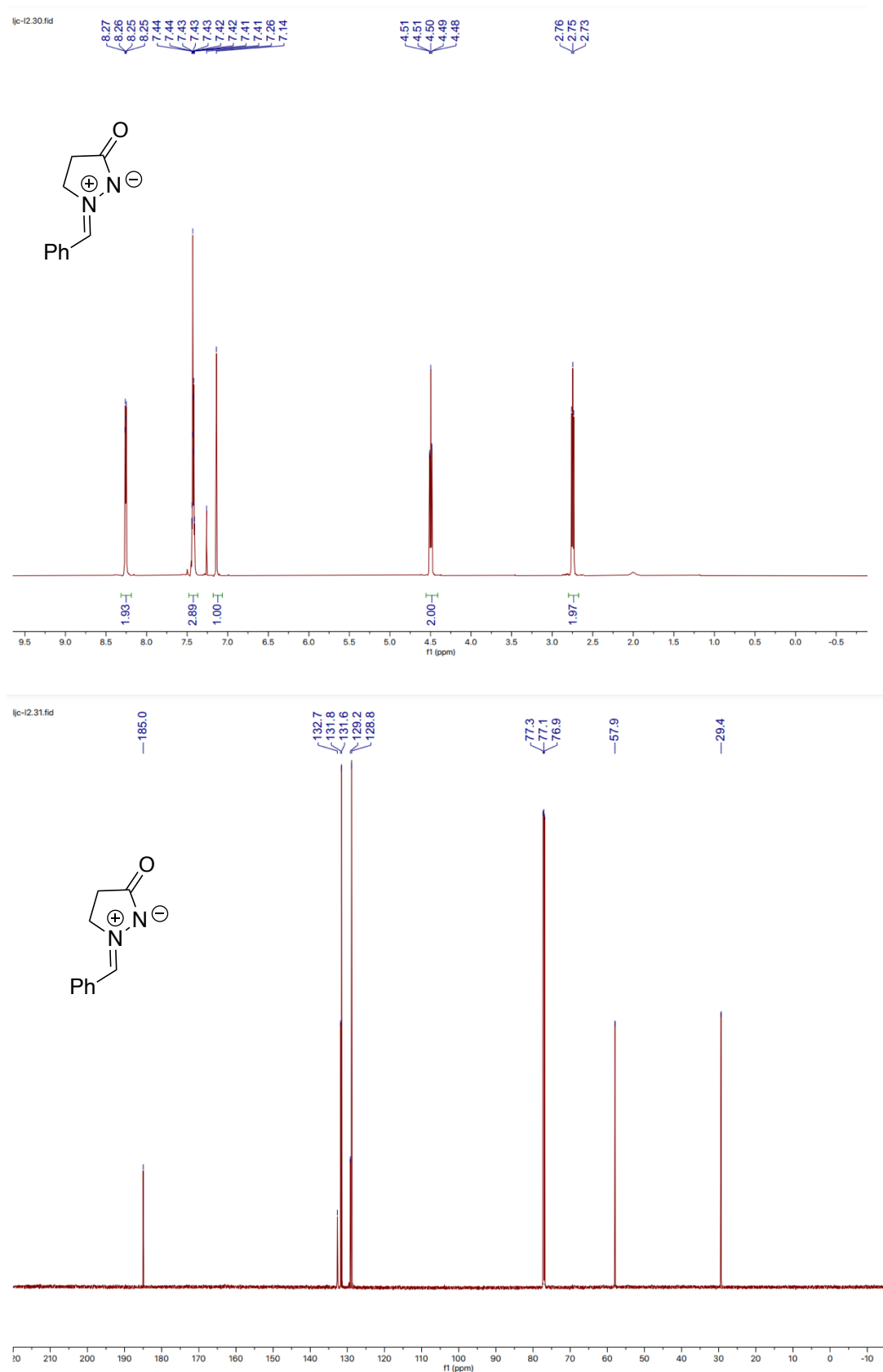


Figure S2. ^1H and ^{13}C NMR spectra of 2-(4-chlorobenzylidene)-5-oxopyrazolidin-2-ium-1-ide
(1b)

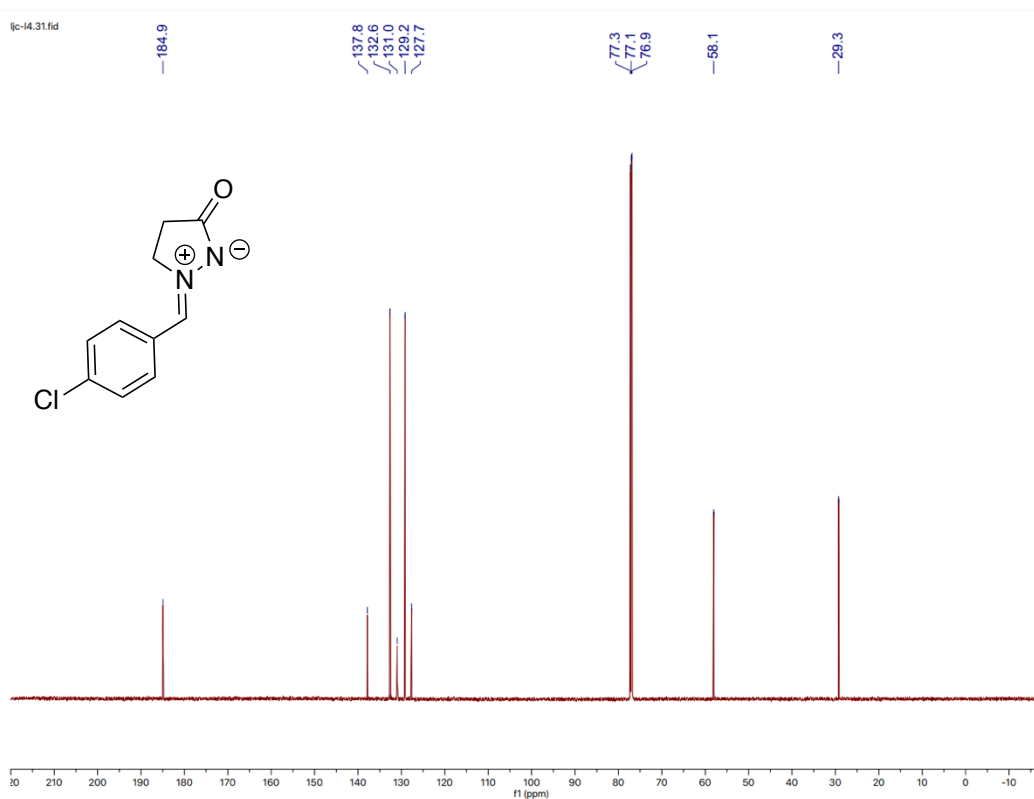
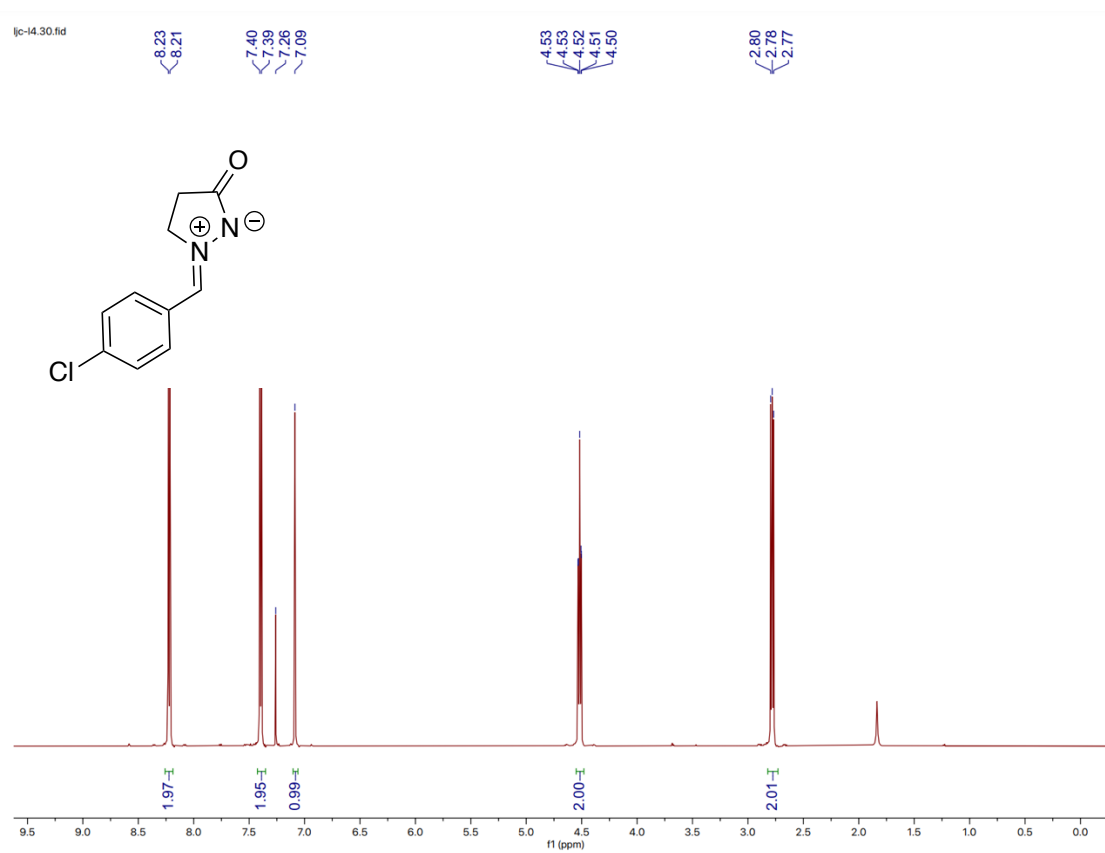
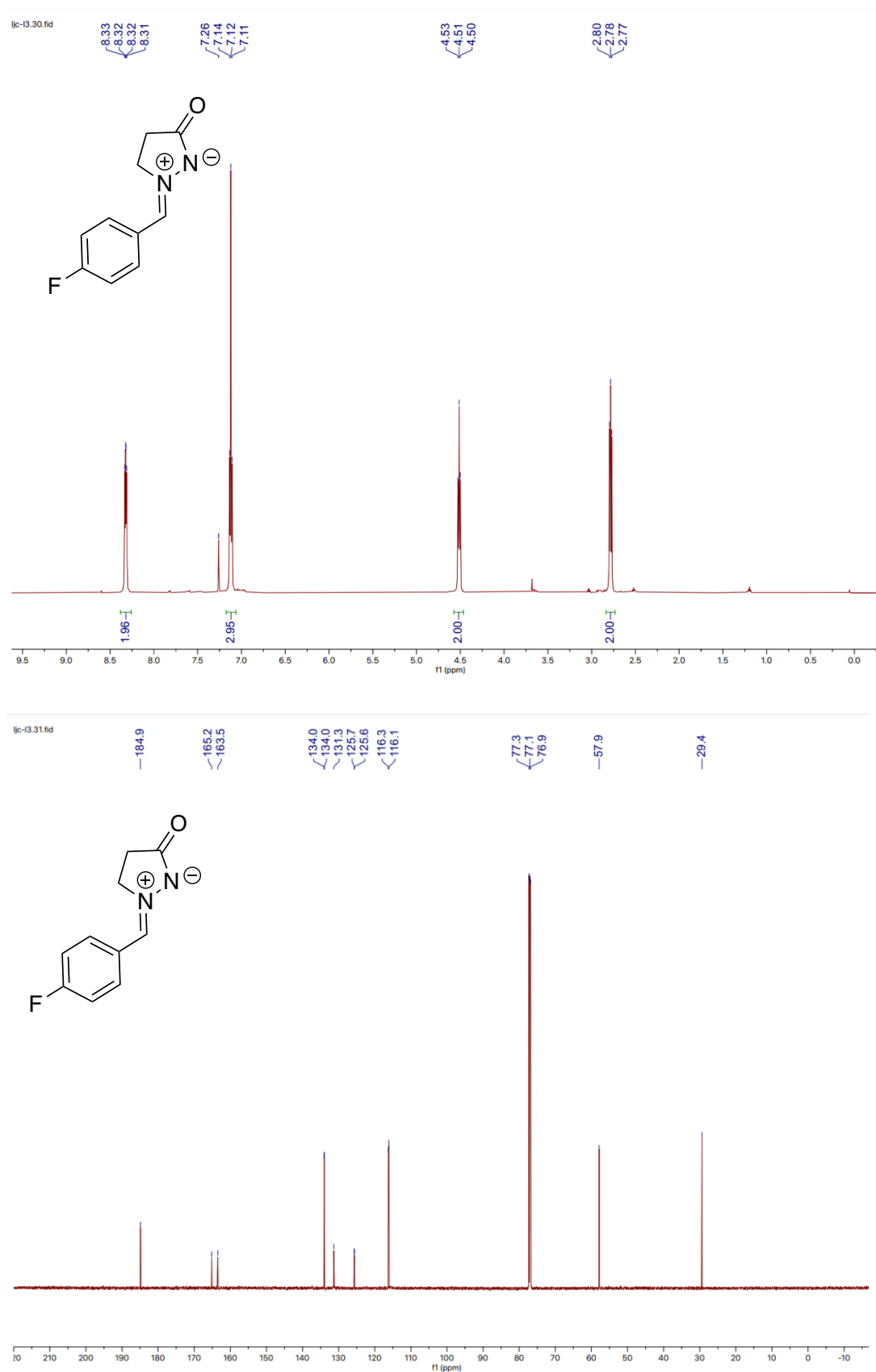


Figure S3. ^1H , ^{13}C and ^{19}F NMR spectra of 2-(4-fluorobenzylidene)-5-oxopyrazolidin-2-ium-1-ide (**1c**)



ljc-13.20.fid

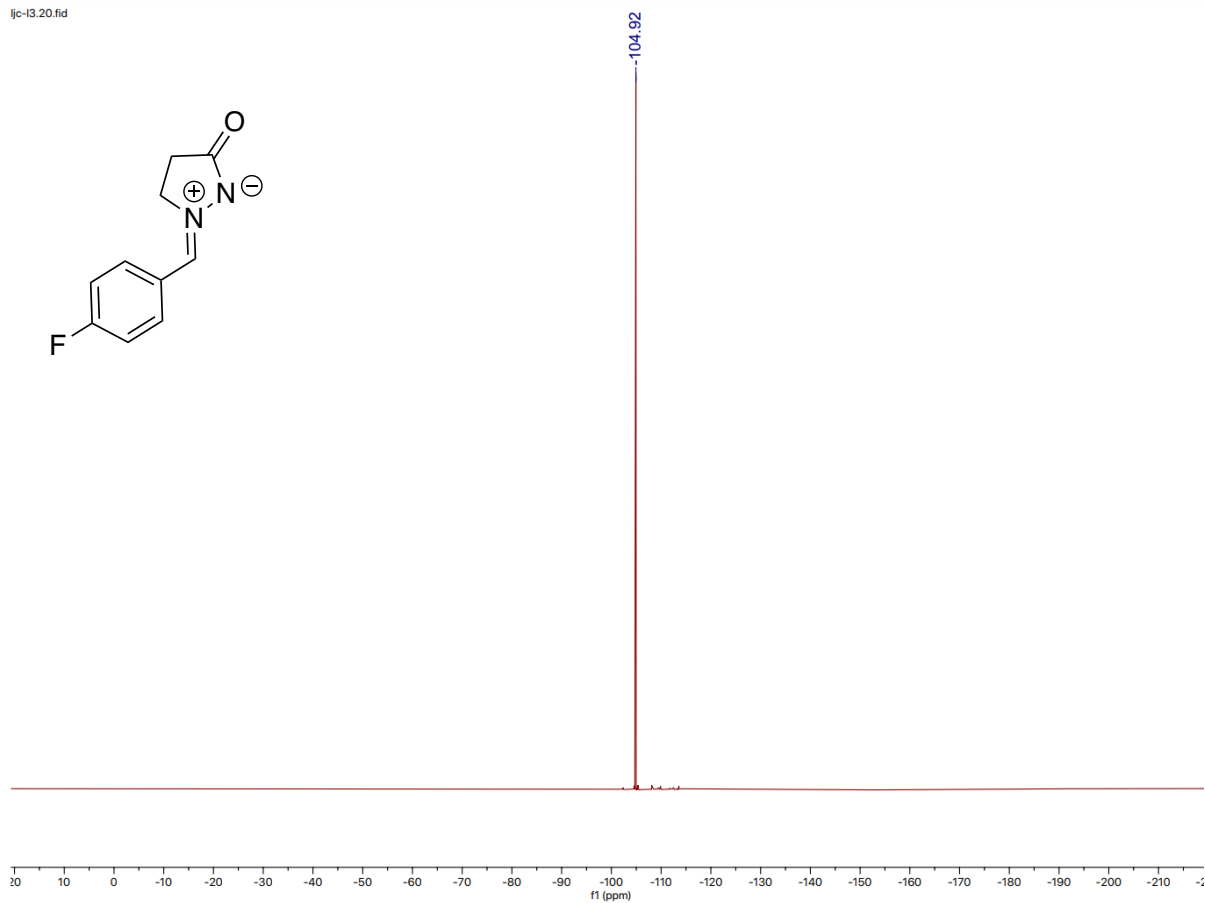
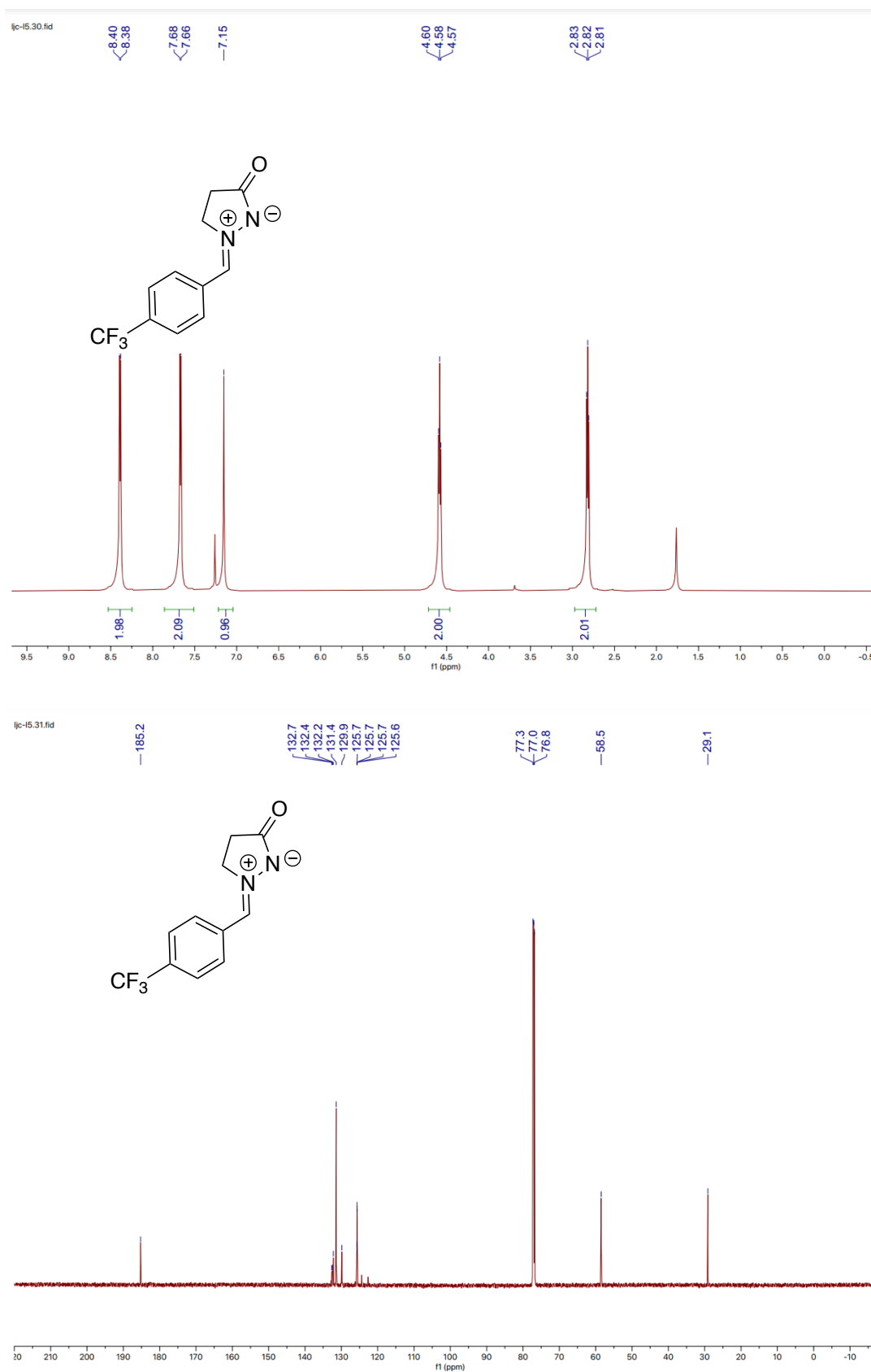


Figure S4. ^1H , ^{13}C and ^{19}F NMR spectra of 2-(4-(trifluoromethyl)benzylidene)pyrazolidin-2-ium-1-ide (**1d**)



ljc-15.20.fid

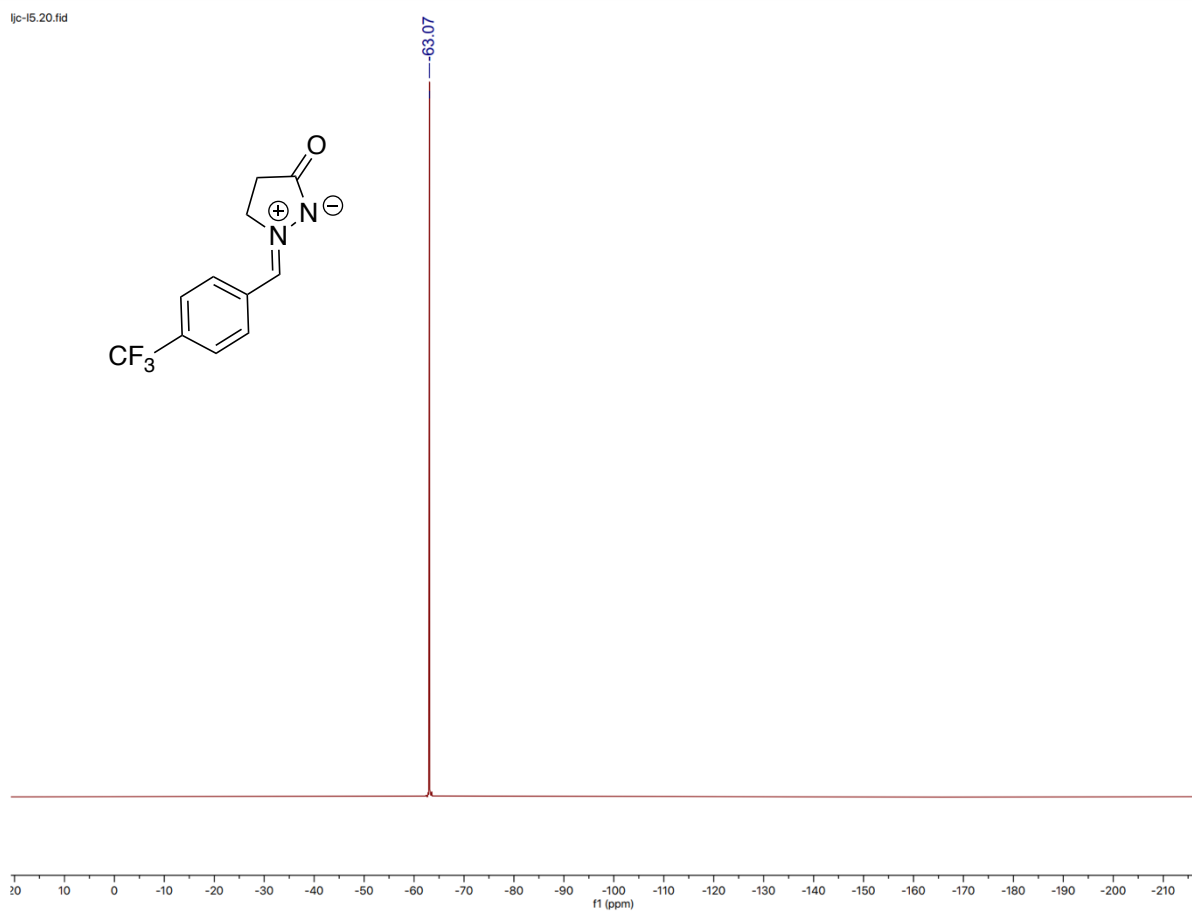


Figure S5. ^1H and ^{13}C NMR spectra of 2-(4-methylbenzylidene)-5-oxopyrazolidin-2-ium-1-ide (**1e**)

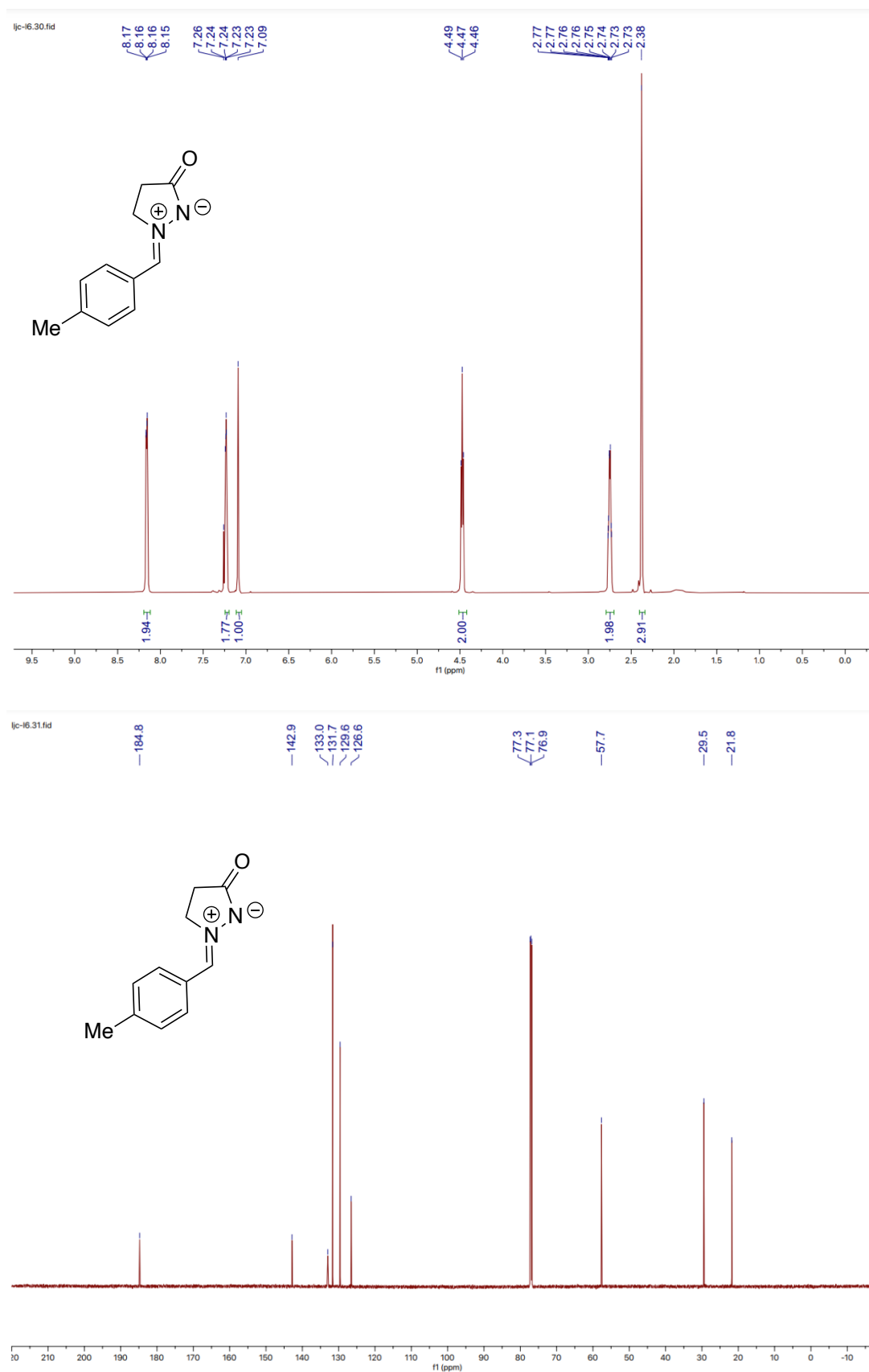


Figure S6. ^1H and ^{13}C NMR spectra of 2-(4-methoxybenzylidene)-5-oxopyrazolidin-2-ium-1-ide (**1f**)

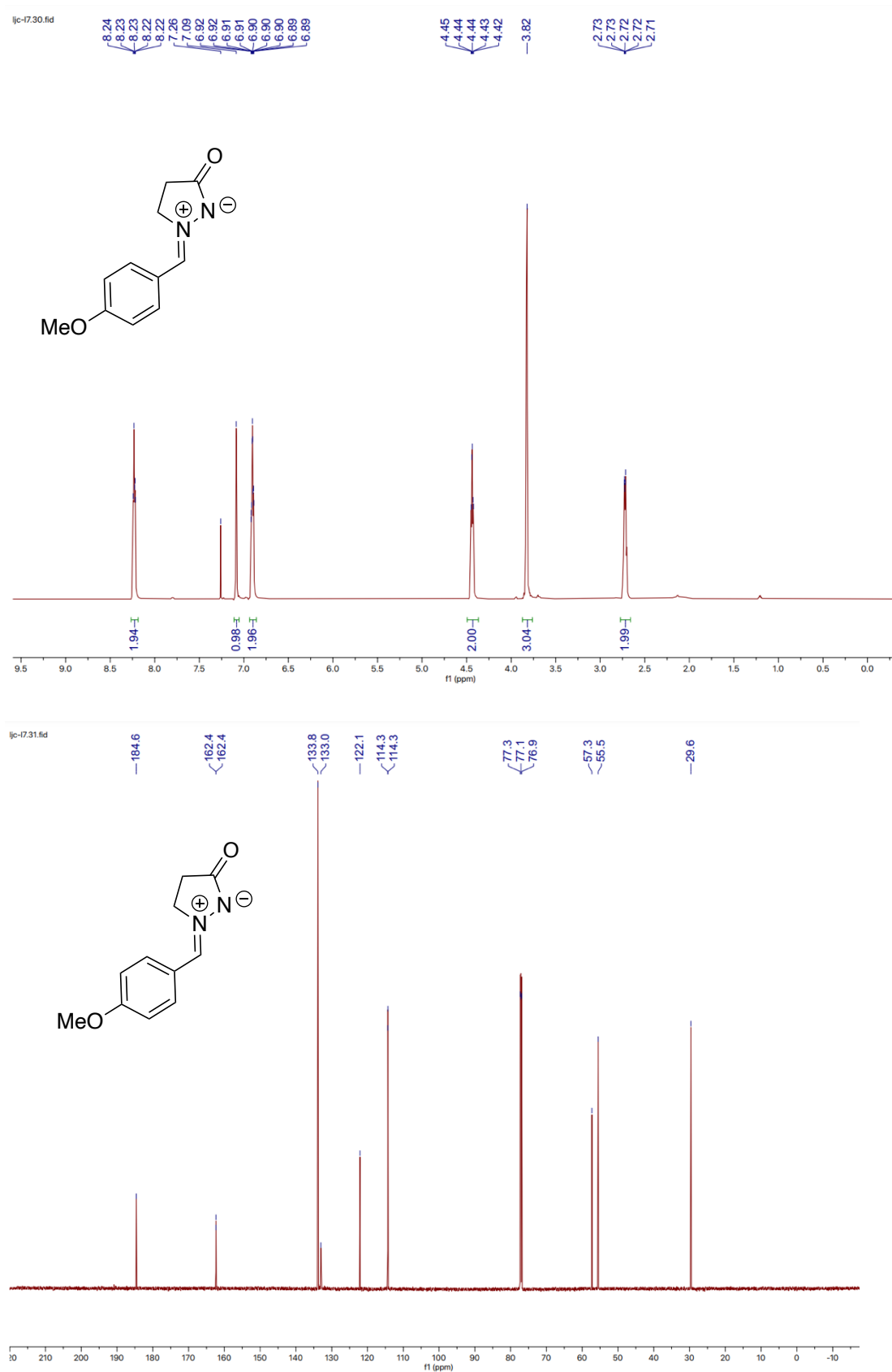


Figure S7. ^1H and ^{13}C NMR spectra of 2-(naphthalen-2-ylmethylene)-5-oxopyrazolidin-2-ium-1-ide (**1g**)

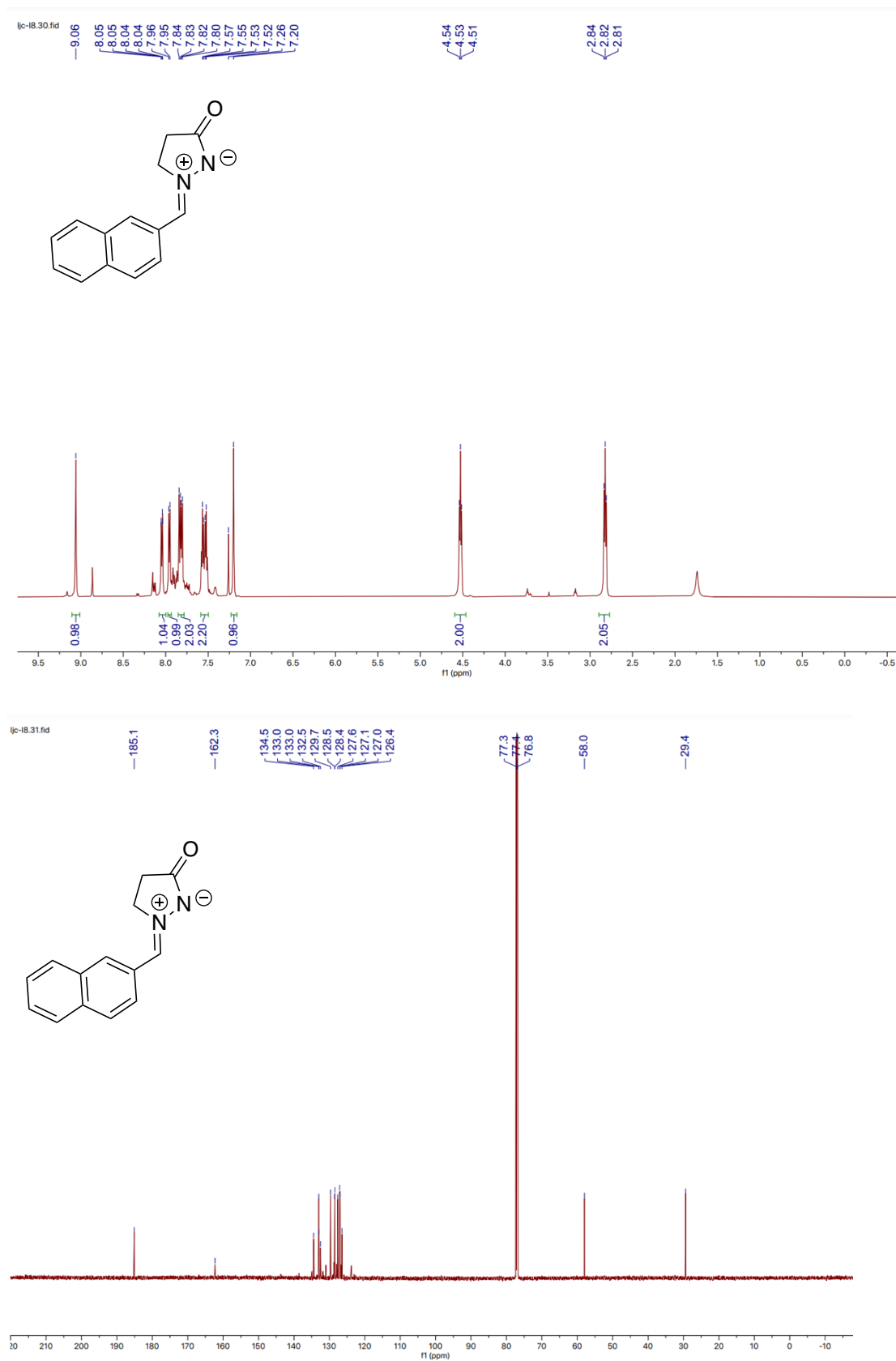


Figure S8. ^1H and ^{13}C NMR spectra of 5-oxo-2-(pyridin-2-ylmethylene)pyrazolidin-2-ium-1-ide (**1h**)

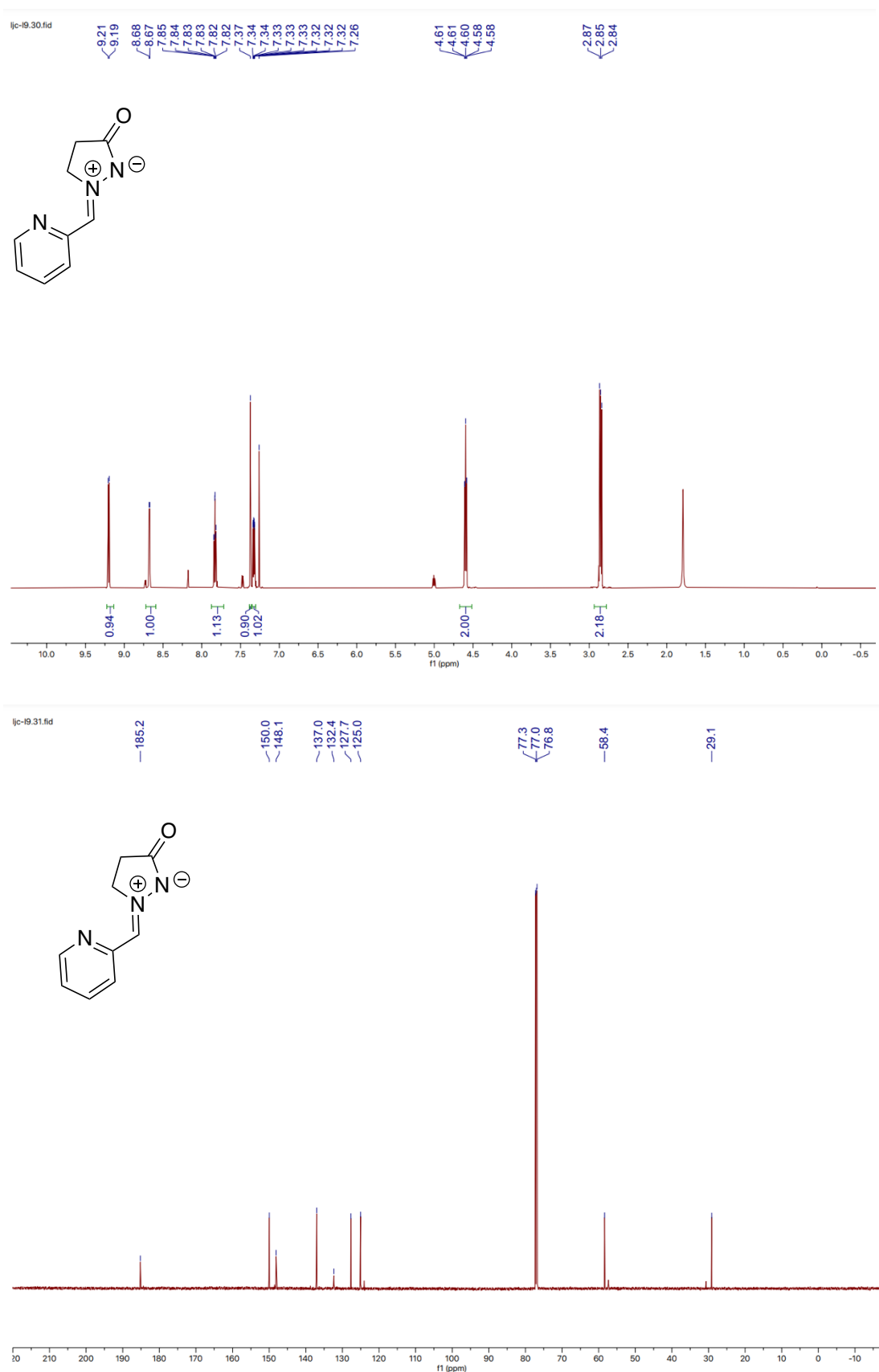


Figure S9. ^1H and ^{13}C NMR spectra of 5-oxo-2-(pyridin-3-ylmethylene)pyrazolidin-2-ium-1-ide (**1i**)

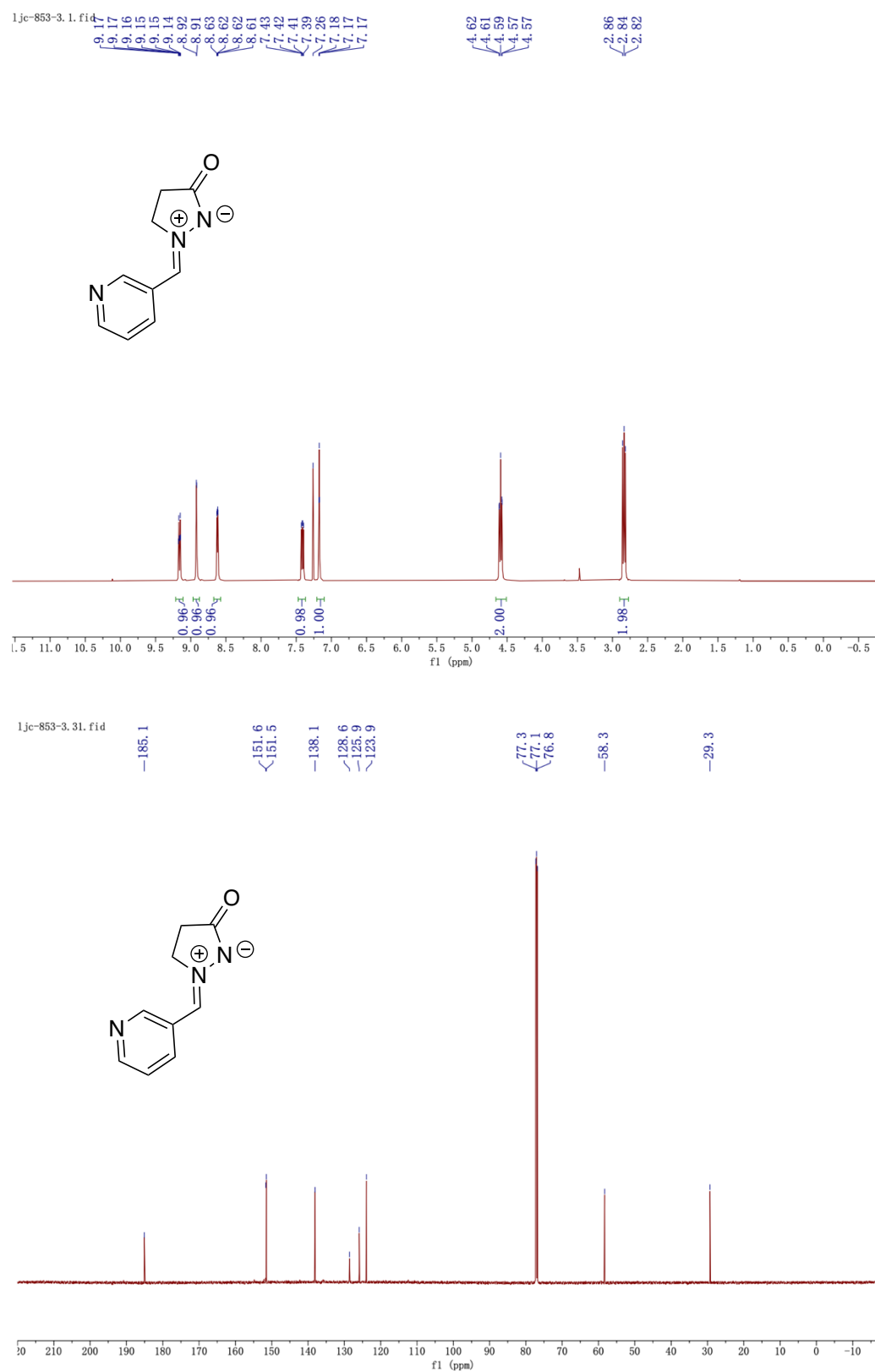


Figure S10. ^1H and ^{13}C NMR spectra of 2-(furan-2-ylmethylene)-5-oxopyrazolidin-2-ium-1-ide (**1j**)

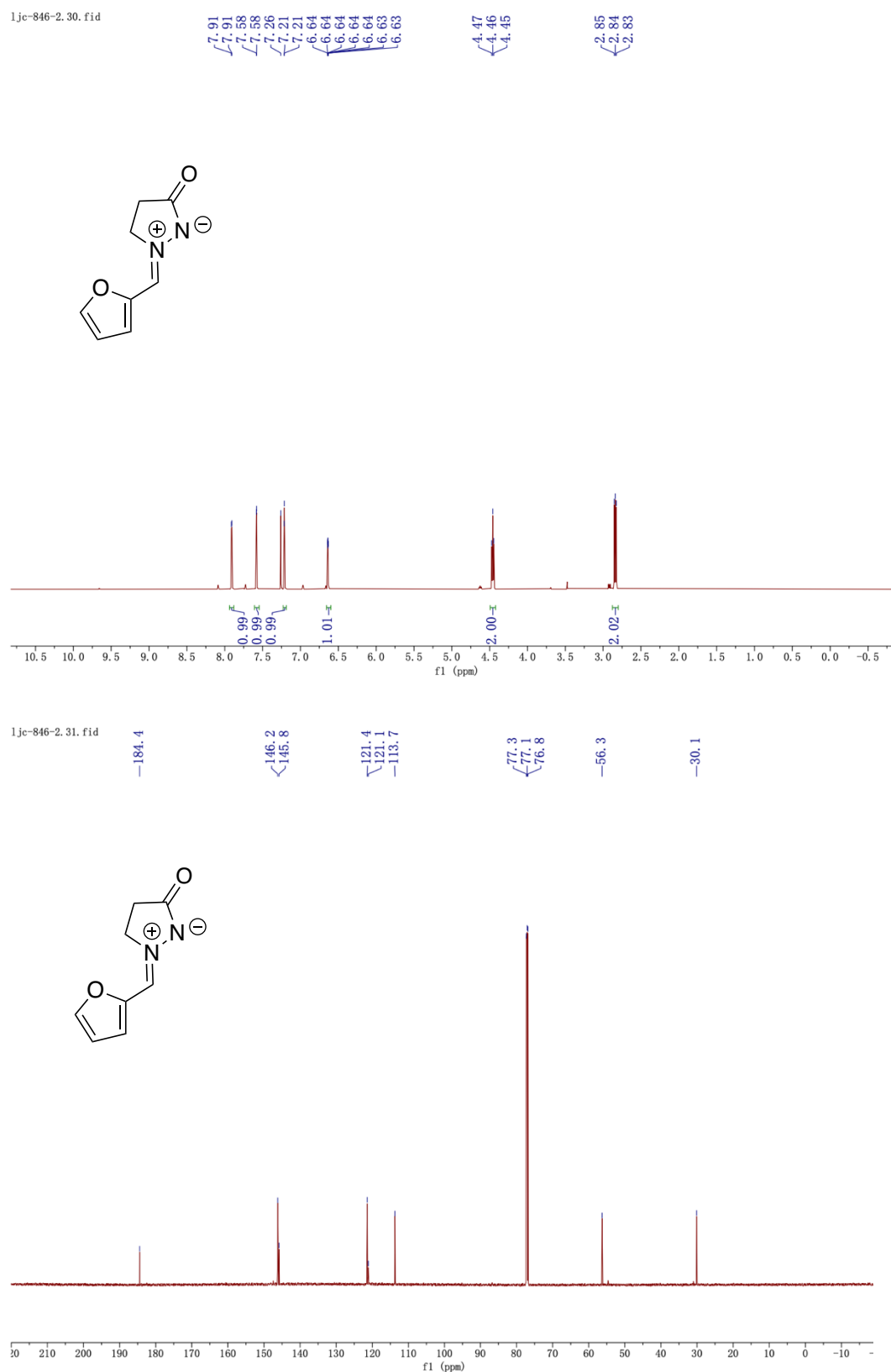


Figure S11. ^1H and ^{13}C NMR spectra of 5-oxo-2-(thiophen-2-ylmethylene)pyrazolidin-2-ium-1-ide (**1k**)

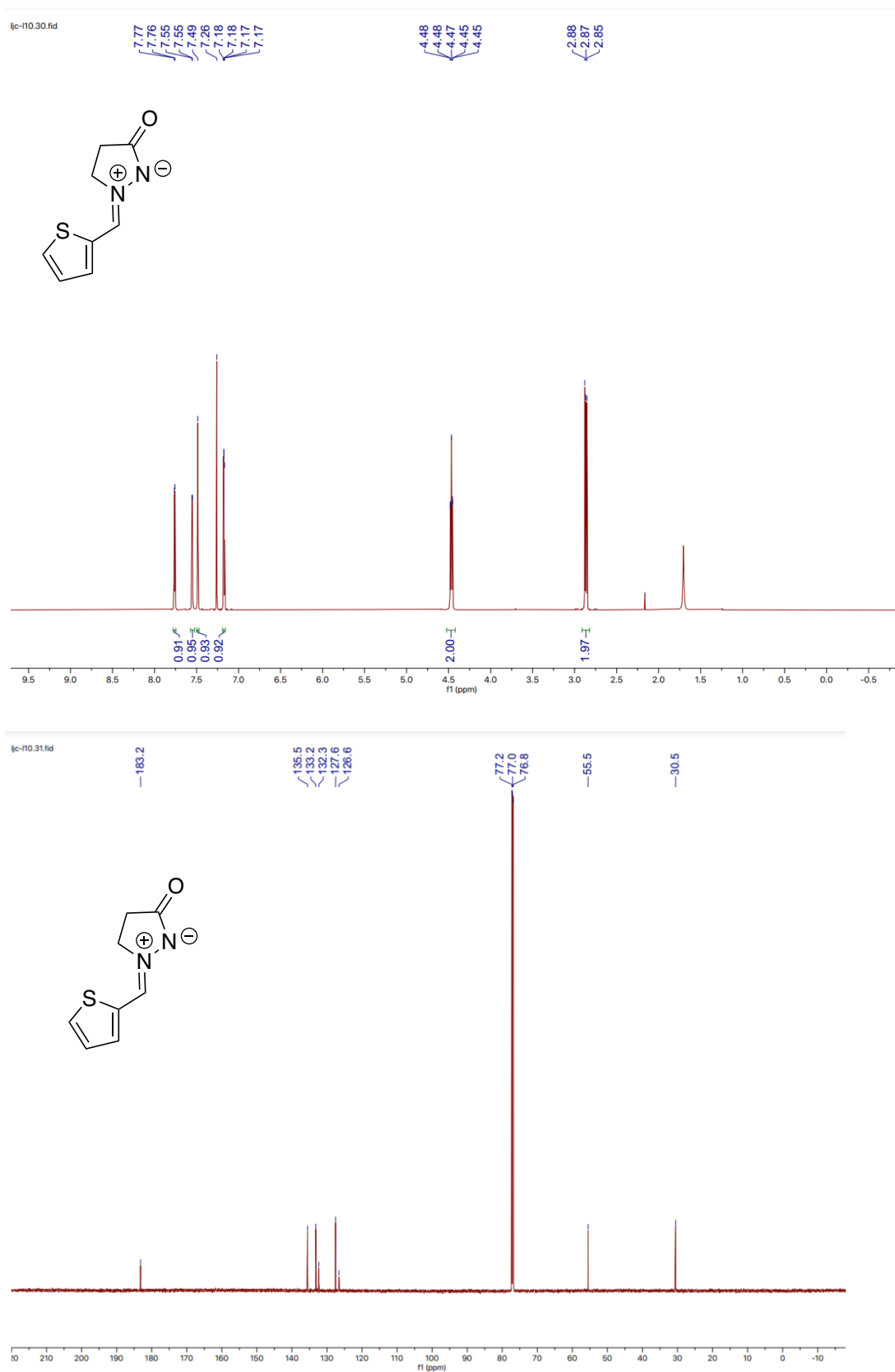


Figure S12. ^1H and ^{13}C NMR spectra of 2-(benzofuran-2-ylmethylene)-5-oxopyrazolidin-2-ium-1-ide (**11**)

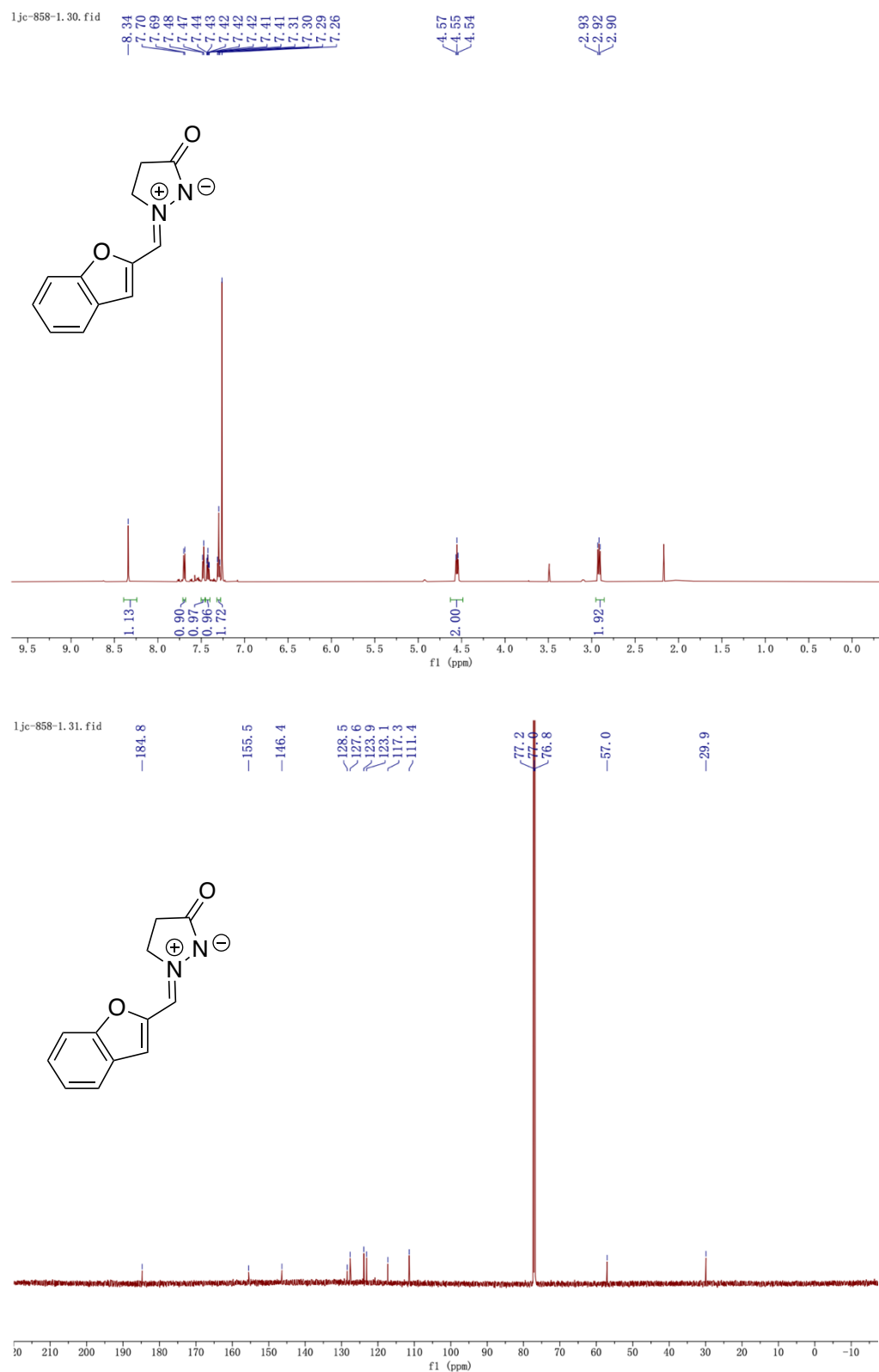


Figure S13. ^1H and ^{13}C NMR spectra of 2-(benzo[*b*]thiophen-3-ylmethylene)-5-oxopyrazolidin-2-ium-1-ide (**1m**)

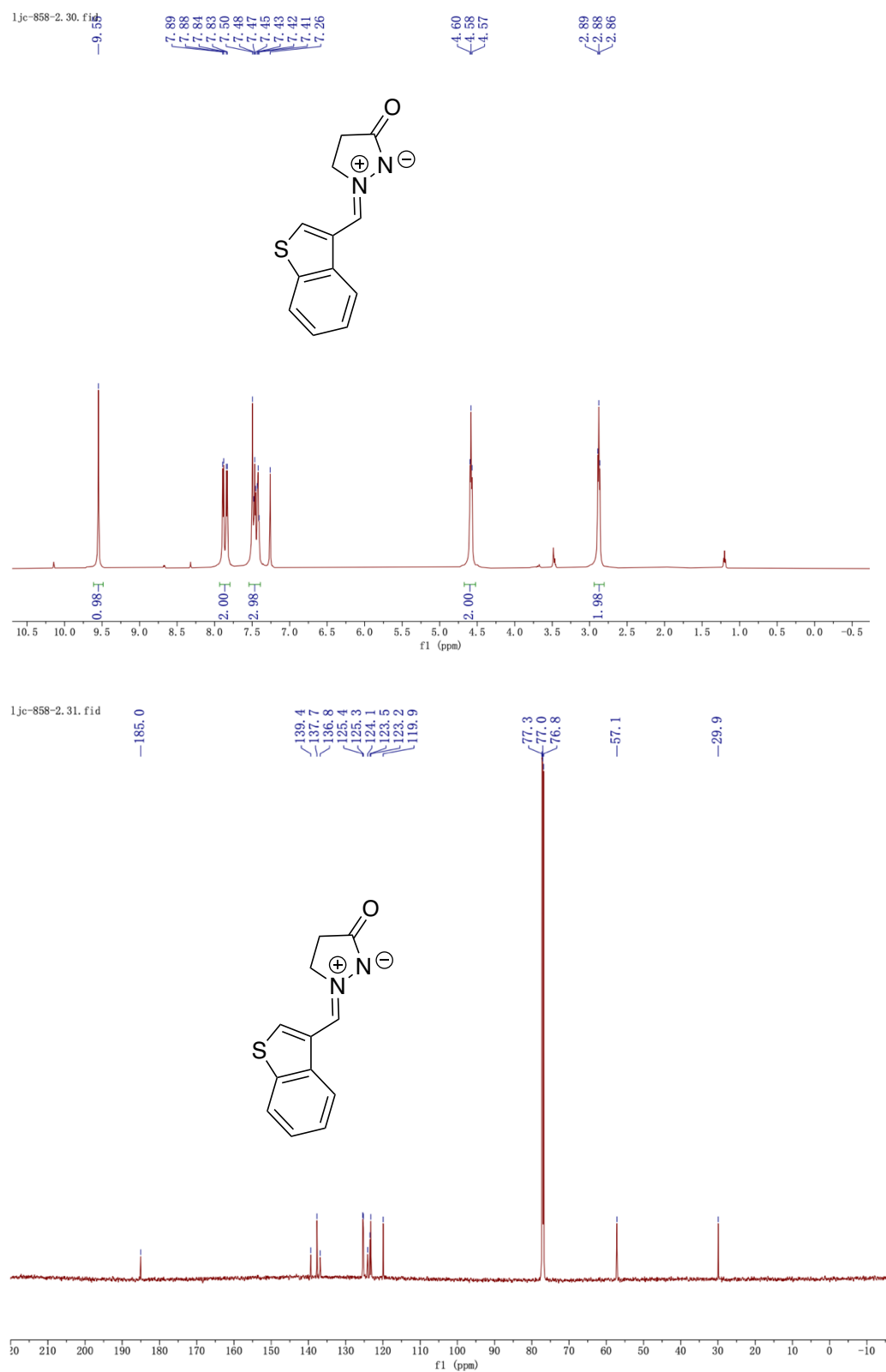


Figure S14. ^1H and ^{13}C NMR spectra of 2-(2-ethylbutylidene)-5-oxopyrazolidin-2-ium-1-ide

(1n)

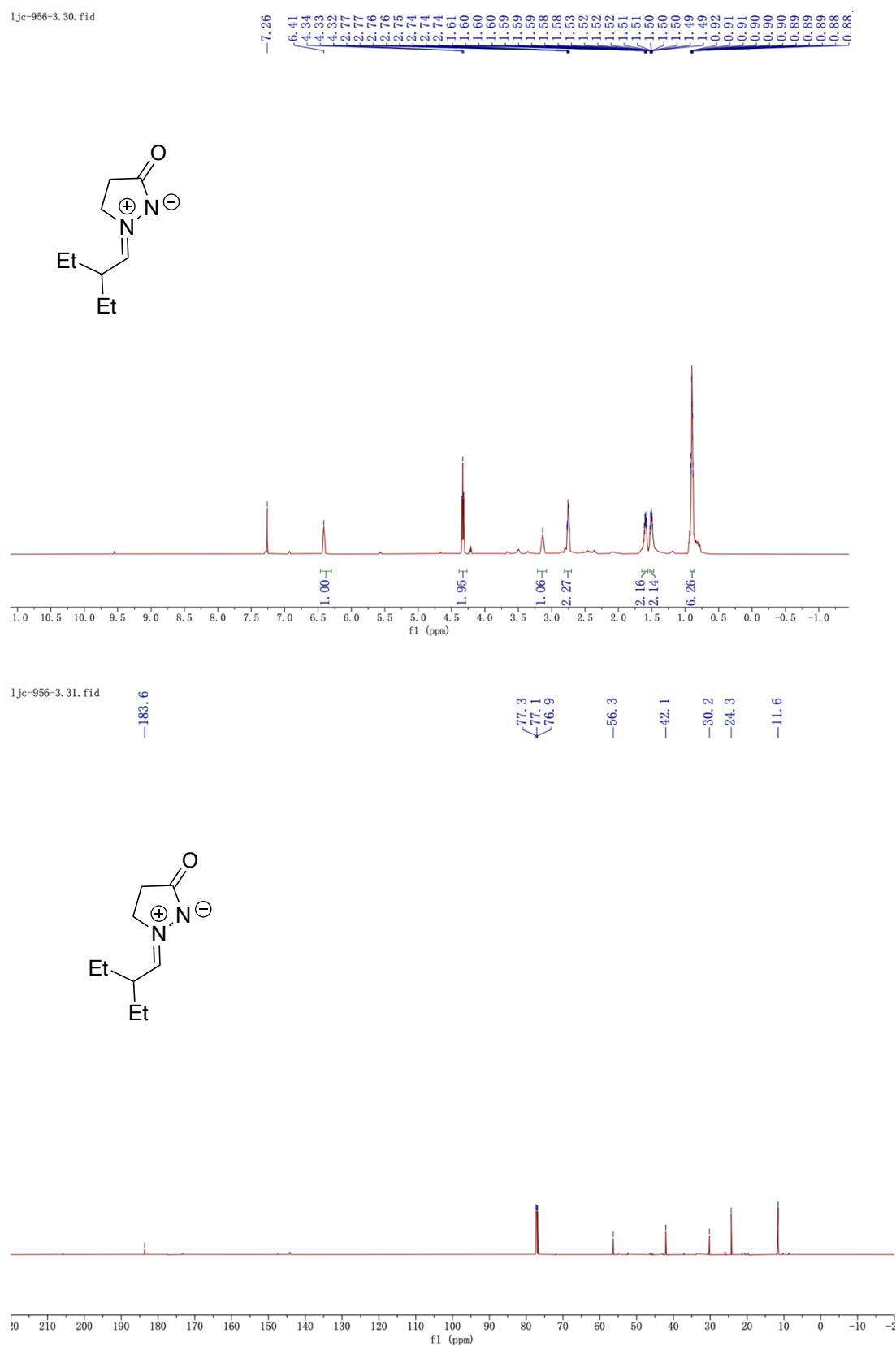


Figure S15. ^1H and ^{13}C NMR spectra of 2-(2-methylbutylidene)-5-oxopyrazolidin-2-ium-1-ide (**1o**)

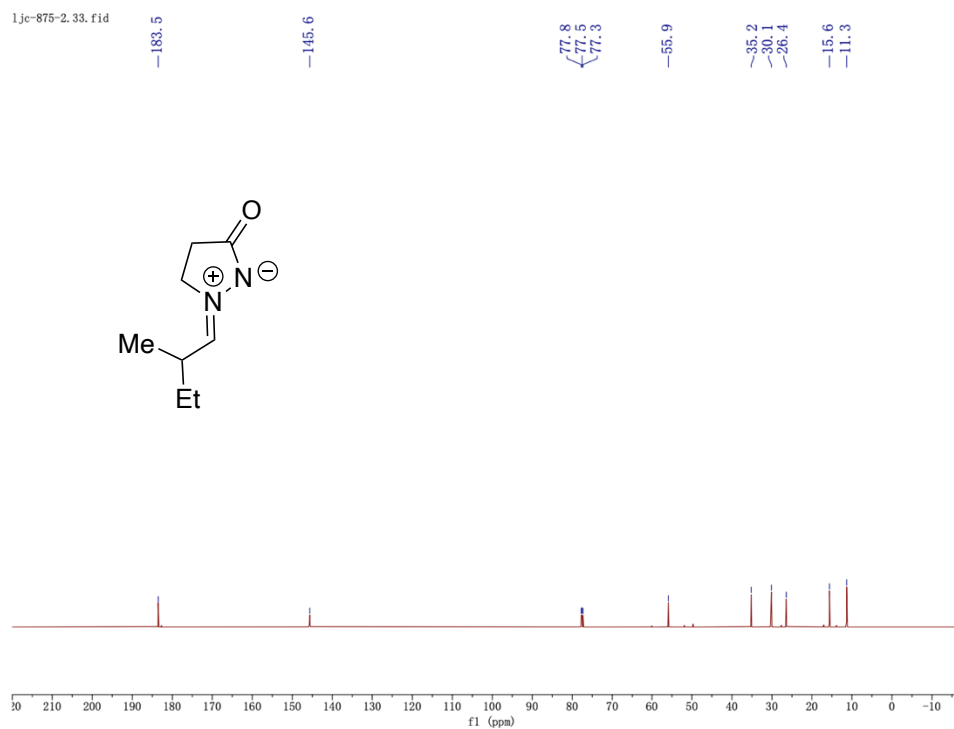
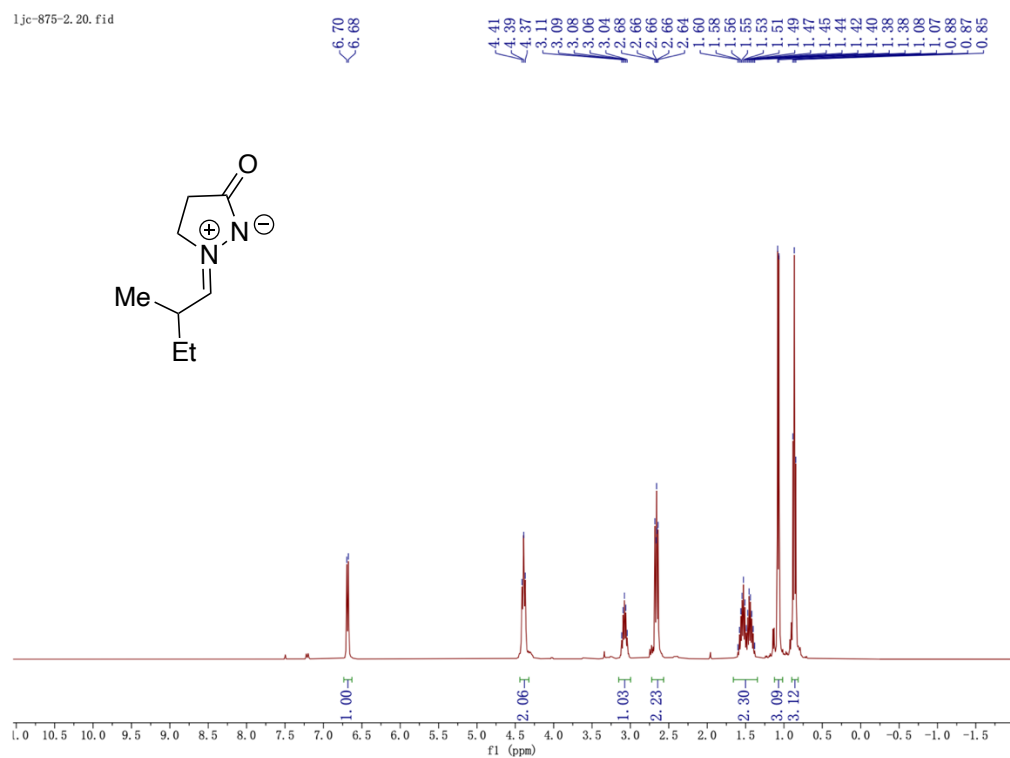


Figure S16. ^1H and ^{13}C NMR spectra of 5-oxo-2-pentylidenepyrazolidin-2-ium-1-ide (**1p**)

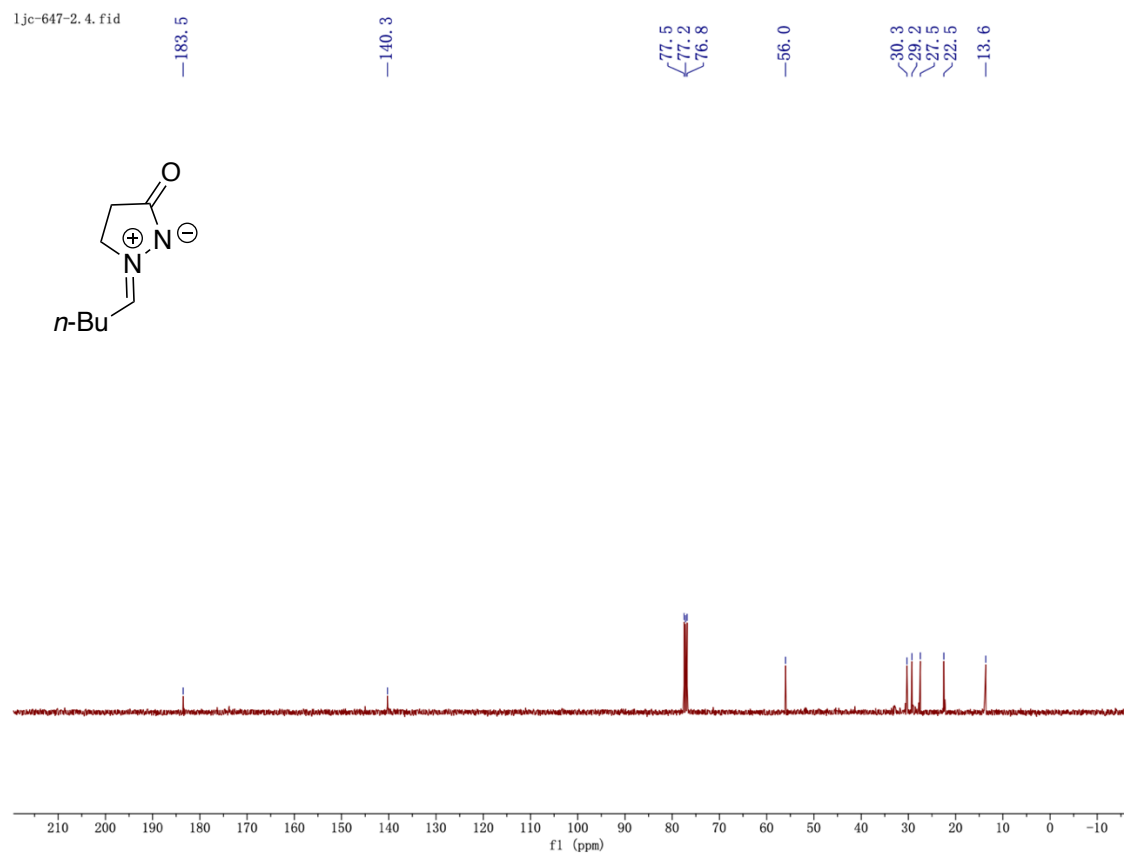
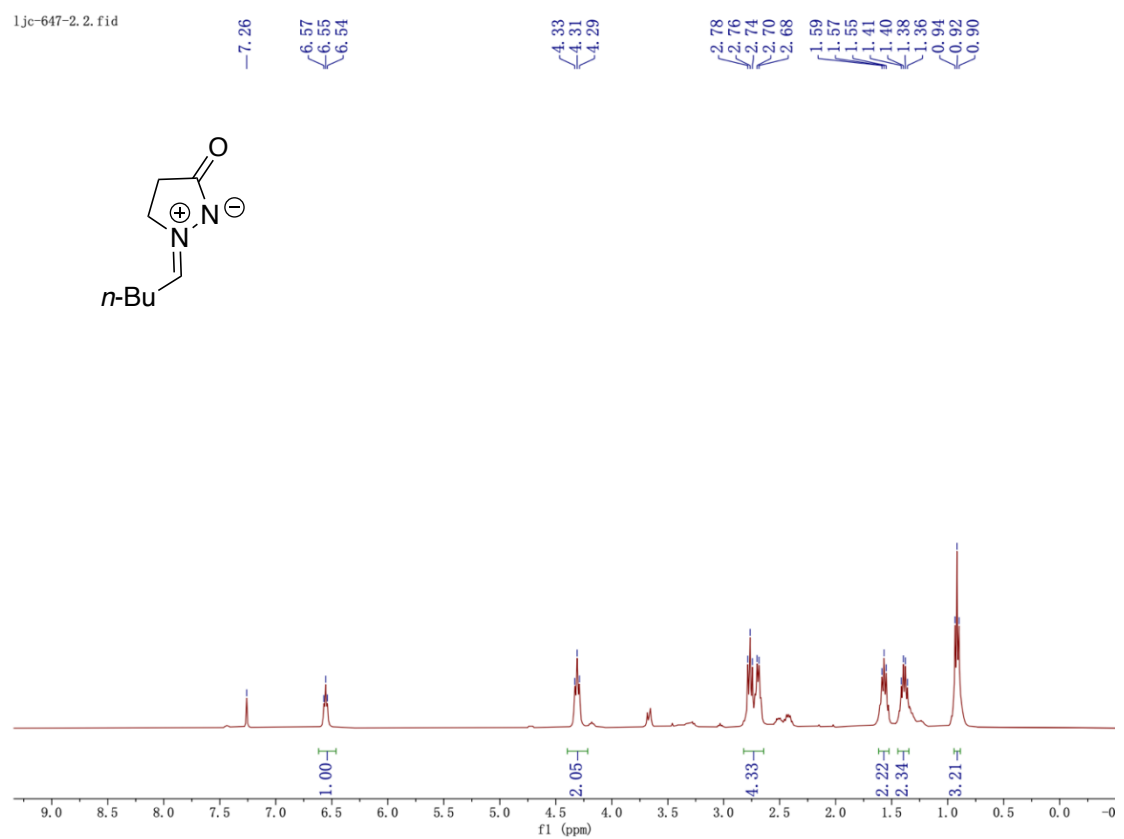


Figure S17. ^1H and ^{13}C NMR spectra of 2-(cyclohexylmethylene)-5-oxopyrazolidin-2-ium-1-ide (**1q**)

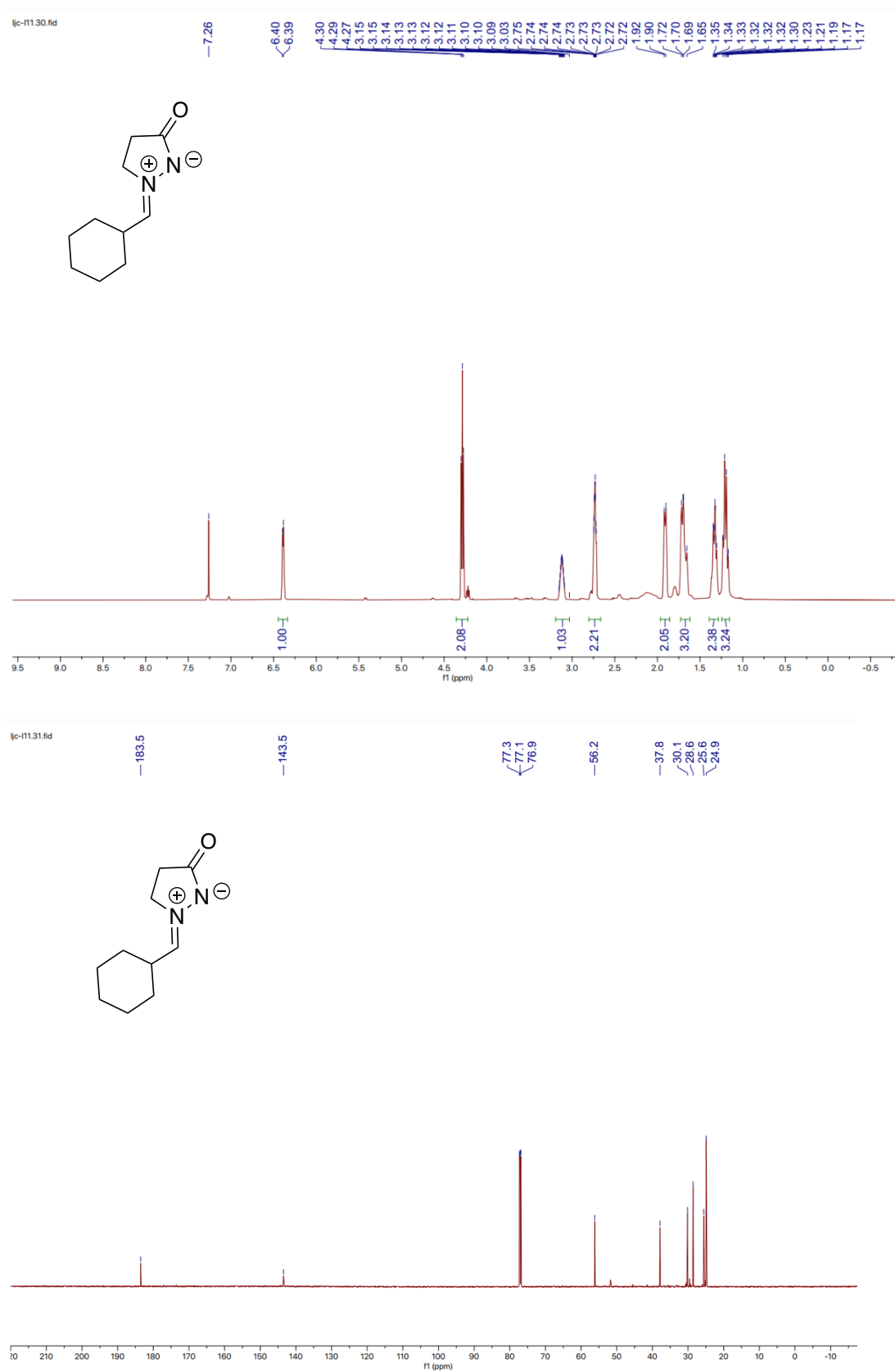


Figure S18. ^1H and ^{13}C NMR spectra of diethyl 4-isopropyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**2a**)

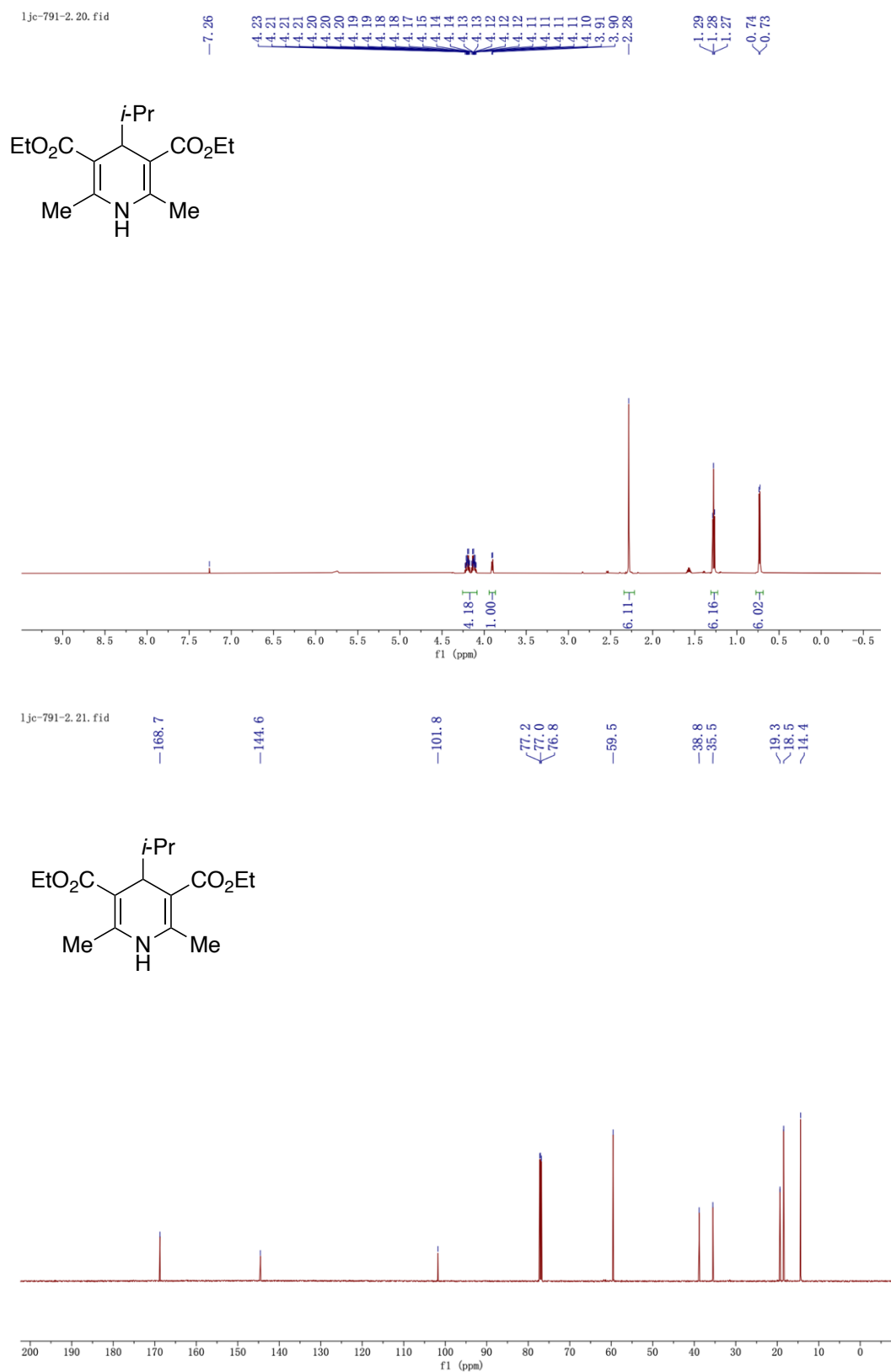


Figure S19. ^1H and ^{13}C NMR spectra of diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**2b**)

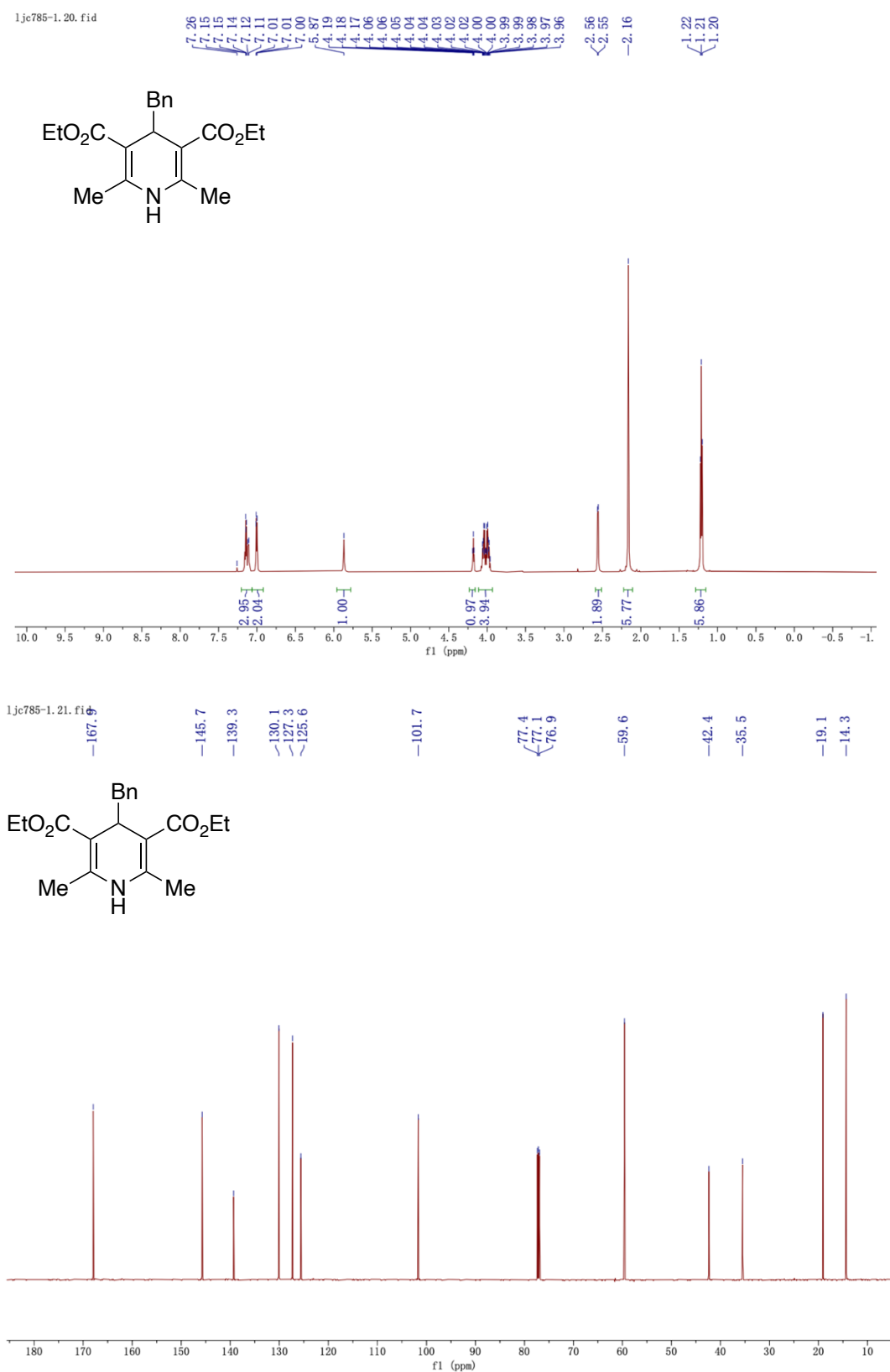


Figure S20. ^1H and ^{13}C NMR spectra of diethyl 4-(4-bromobenzyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**2c**)

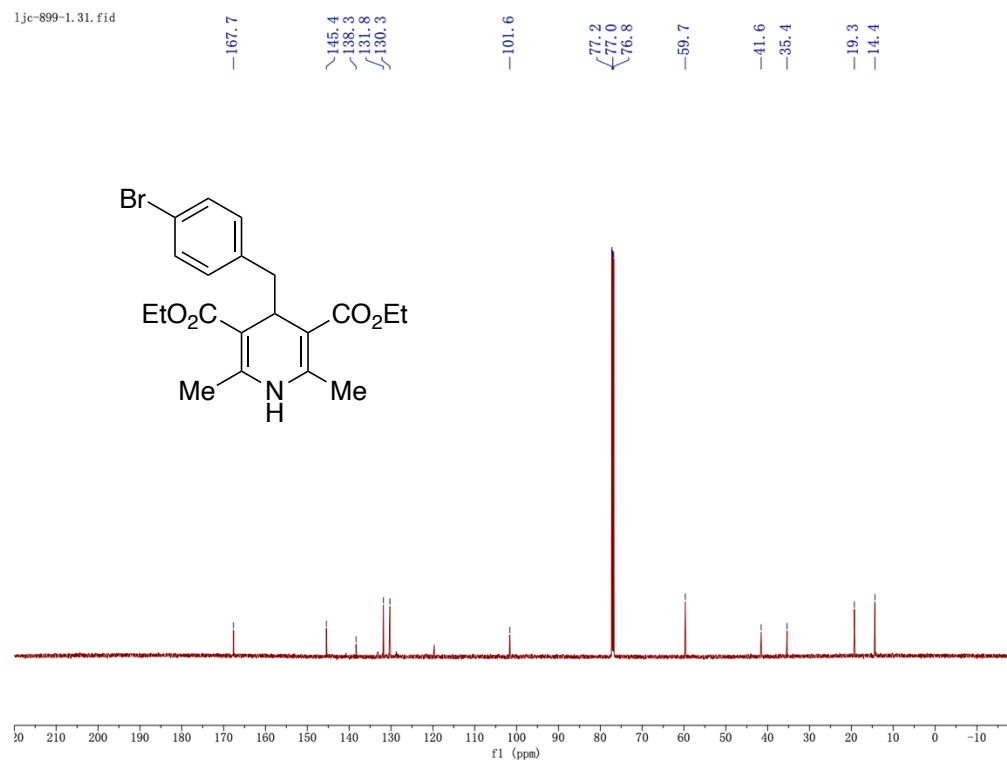
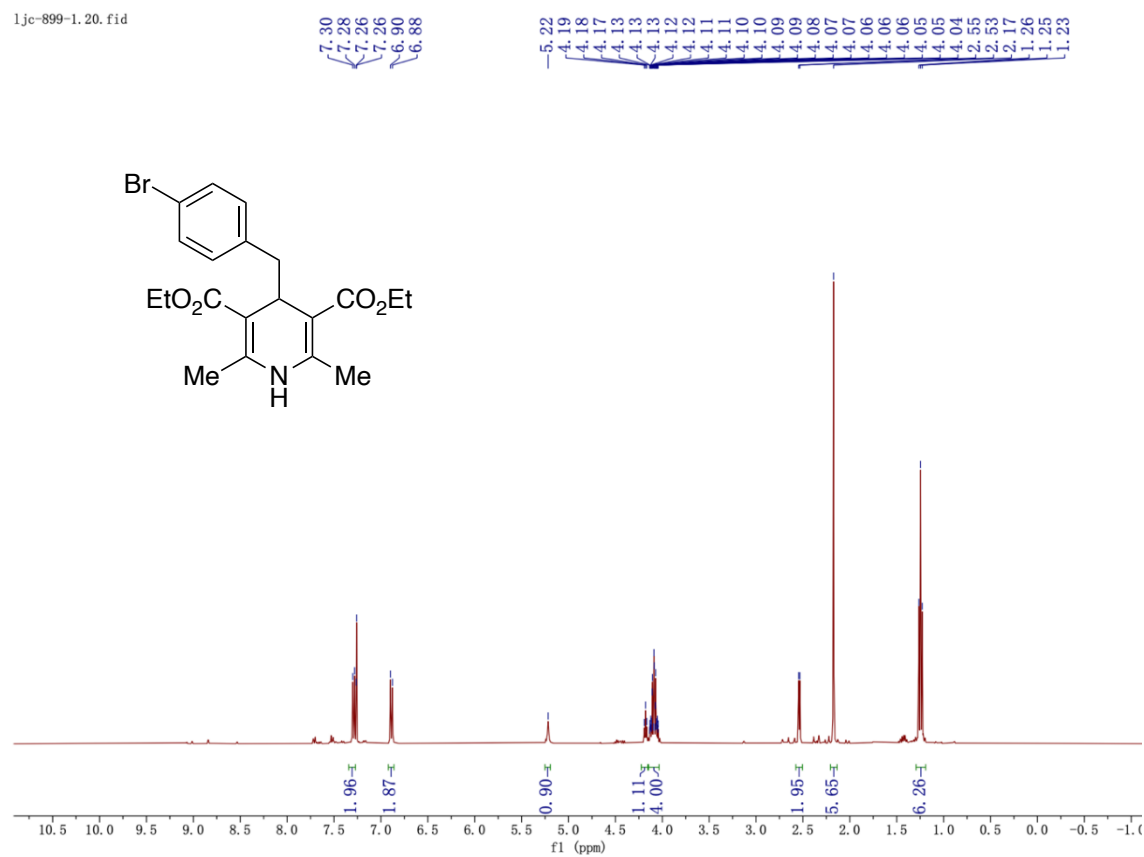


Figure S21. ^1H and ^{13}C NMR spectra of diethyl 4-(4-chlorobenzyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**2d**)

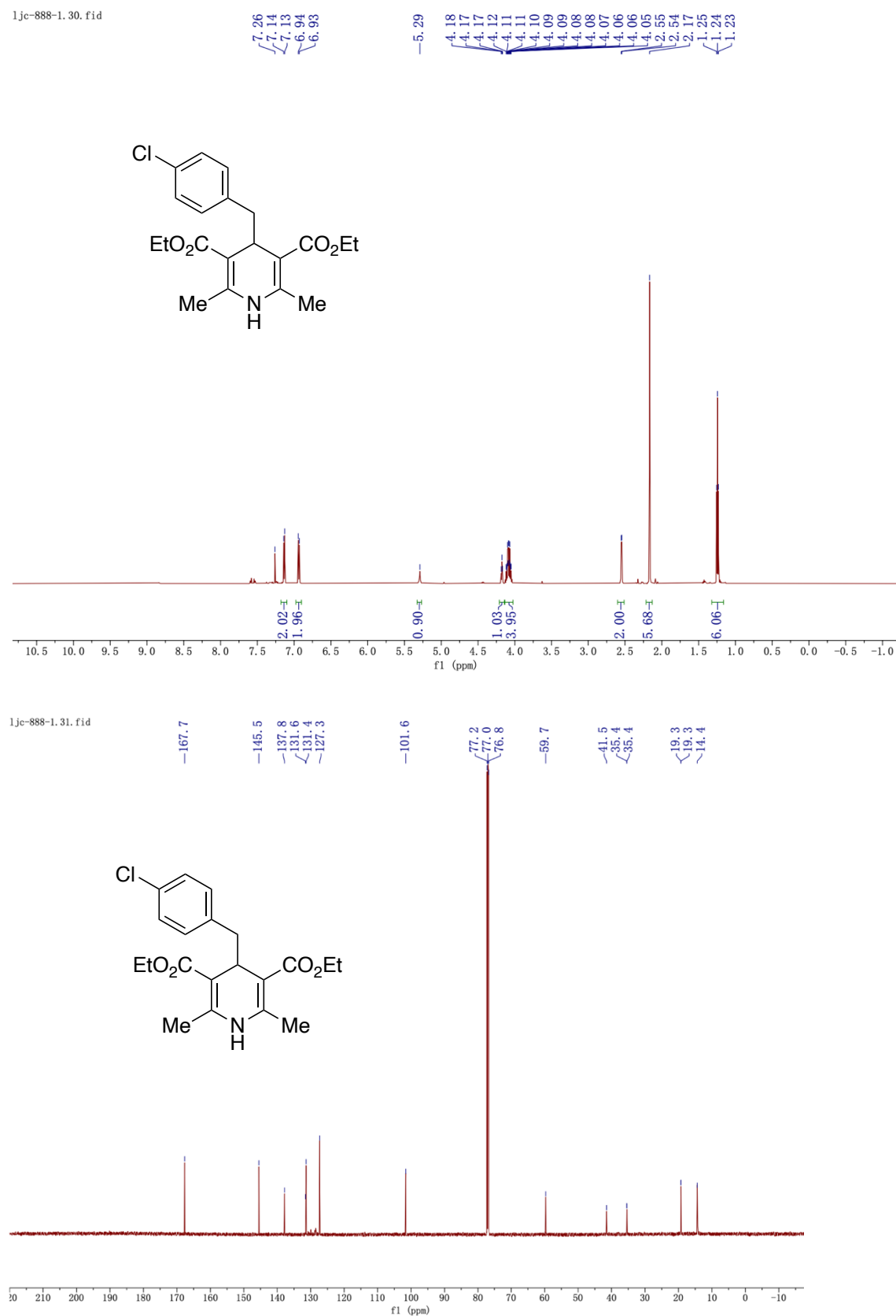
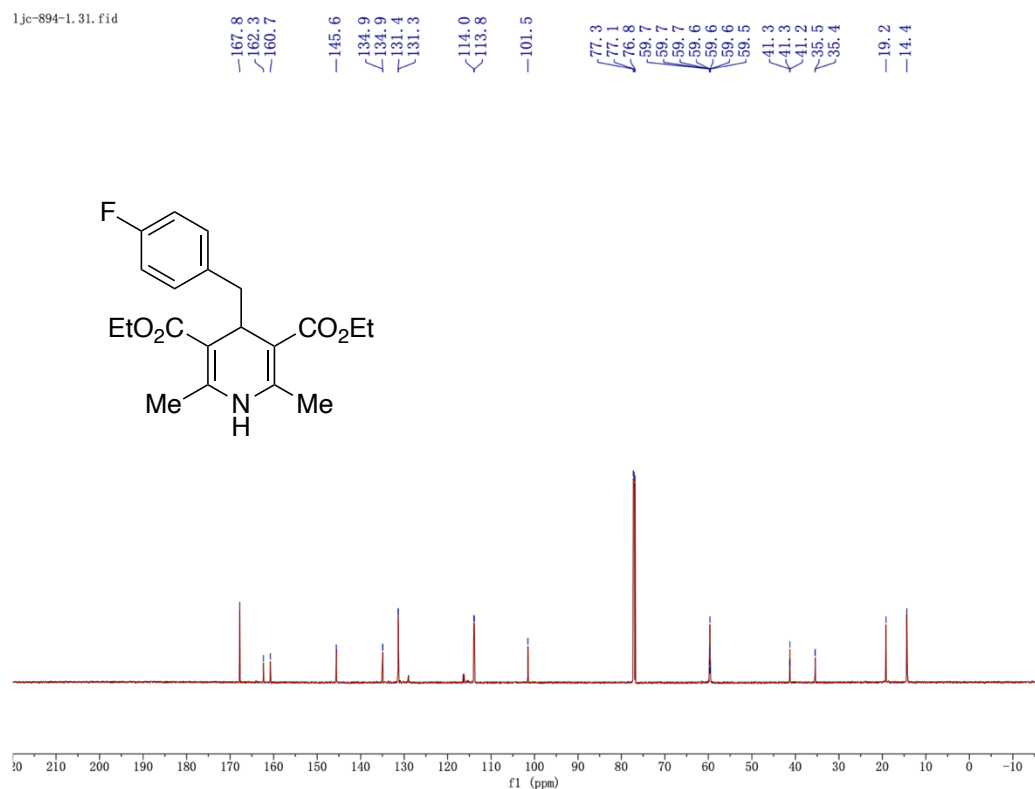
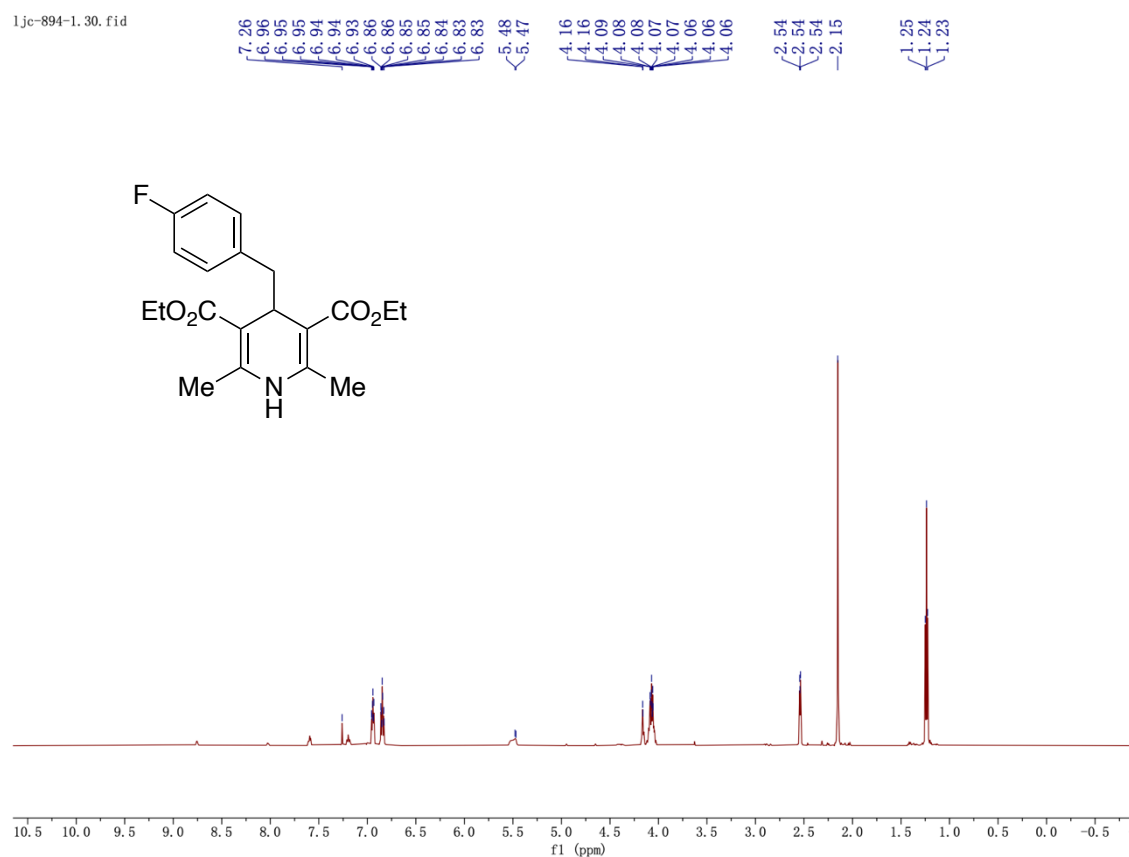


Figure S22. ^1H , ^{13}C and ^{19}F NMR spectra of diethyl 4-(4-fluorobenzyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**2e**)



ljc-894-1.20.fid

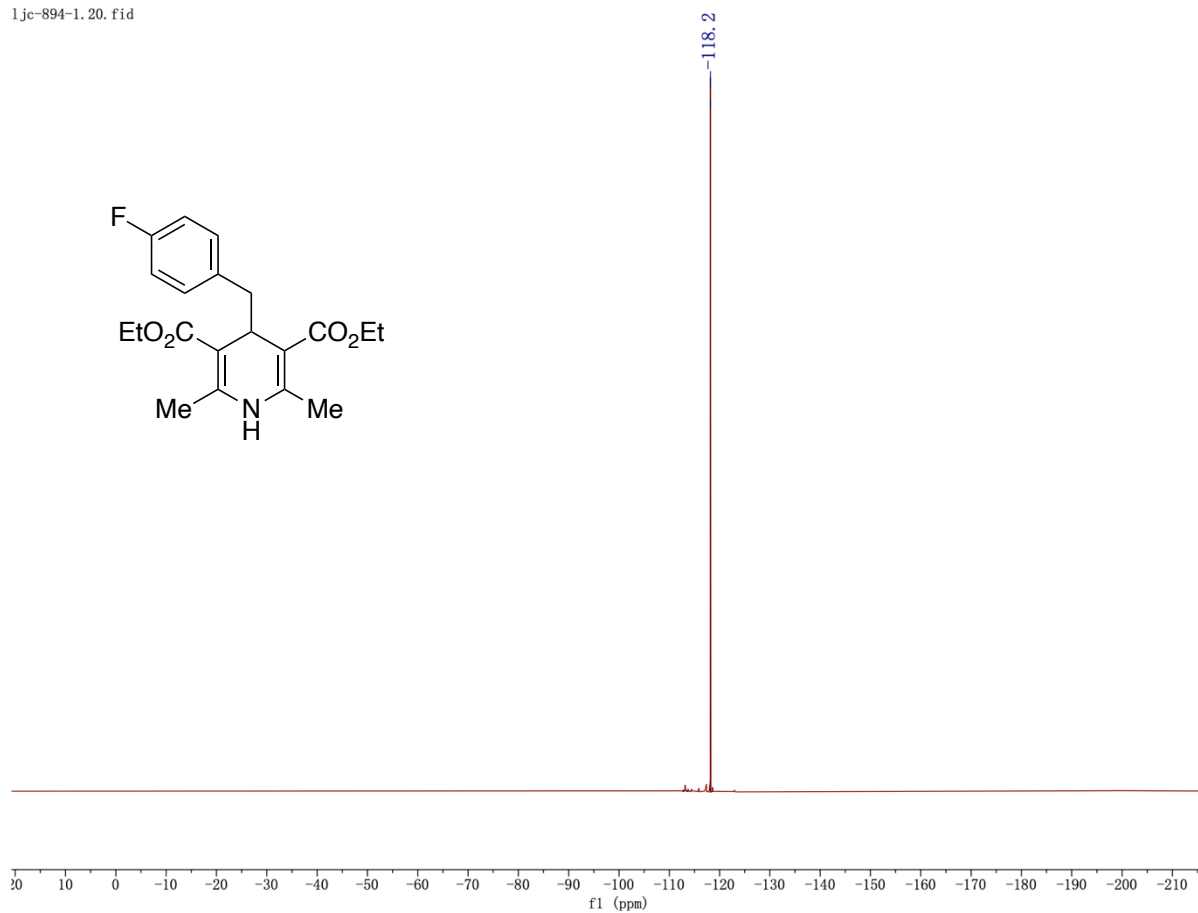


Figure S23. ^1H and ^{13}C NMR spectra of diethyl 4-(4-methoxybenzyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**2f**)

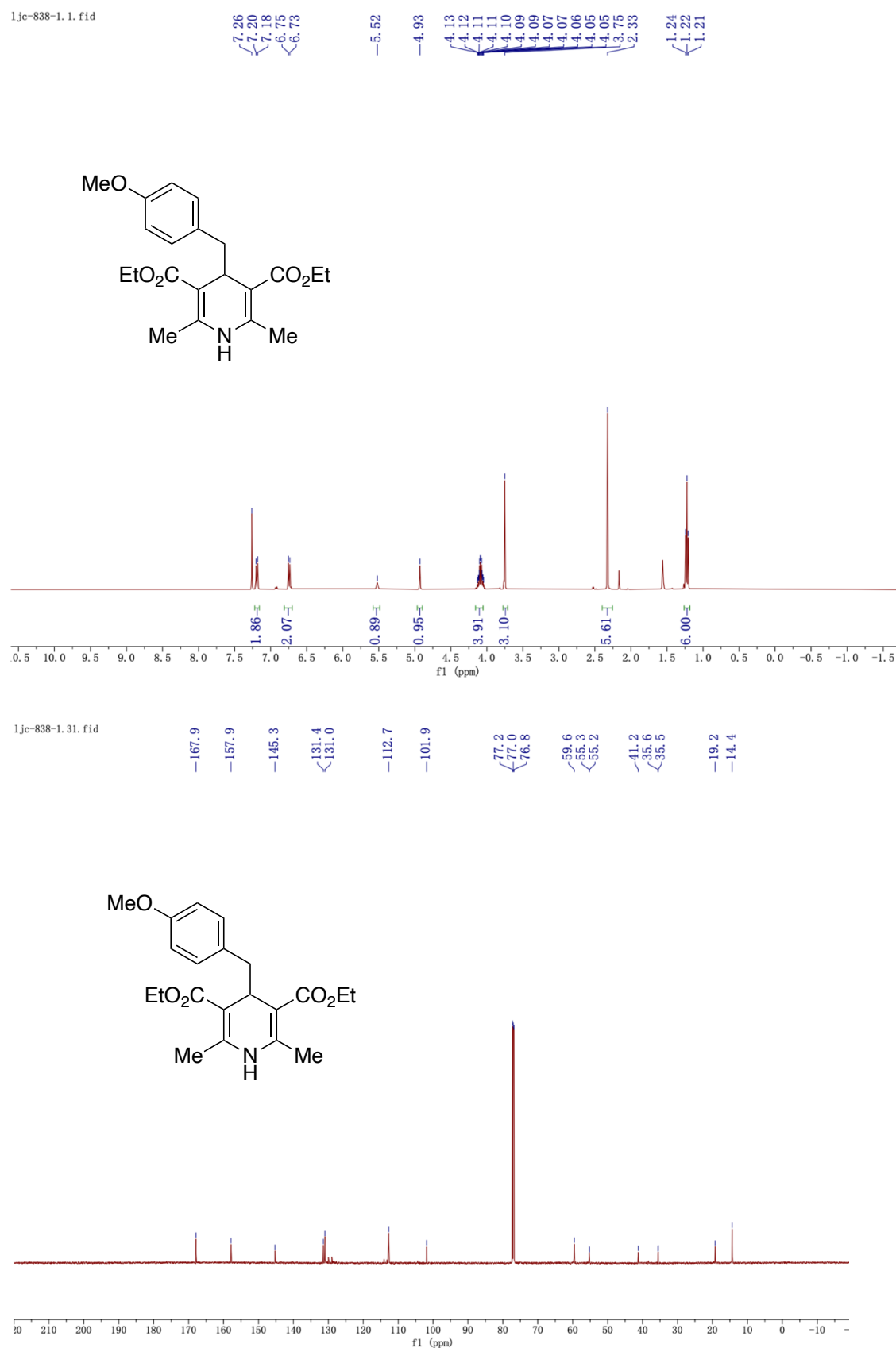


Figure S24. ^1H and ^{13}C NMR spectra of diethyl 4-((1,3-dioxoisindolin-2-yl)methyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**2g**)

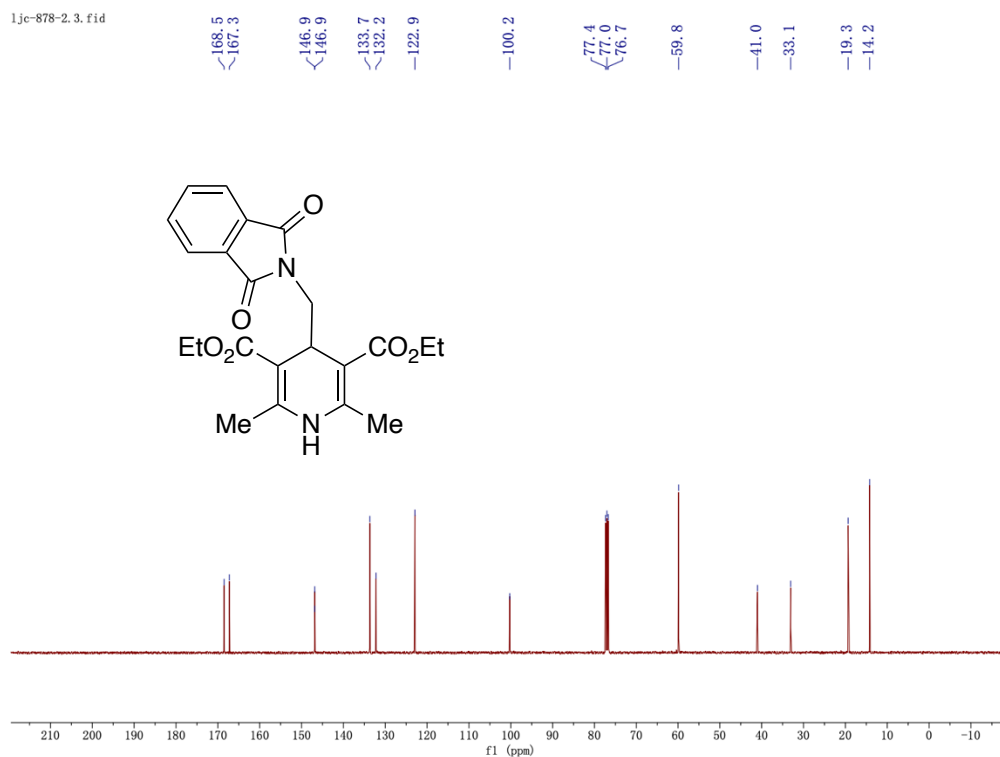
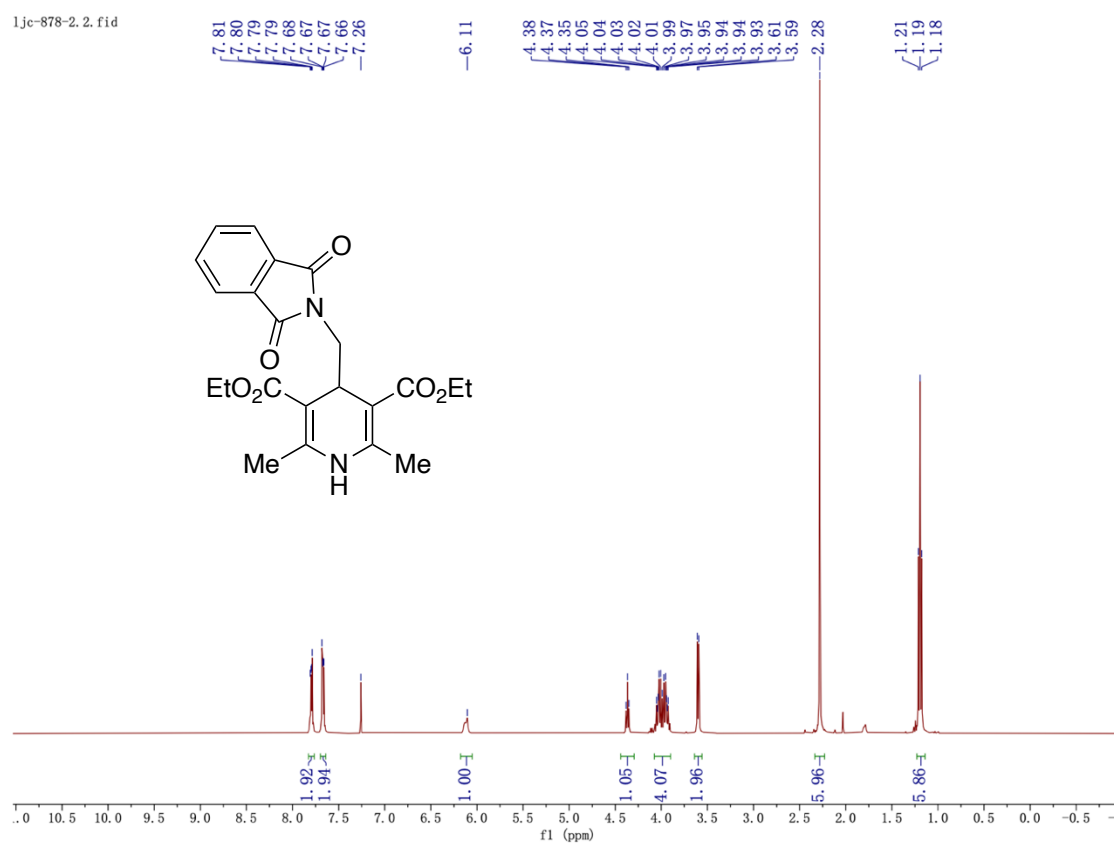
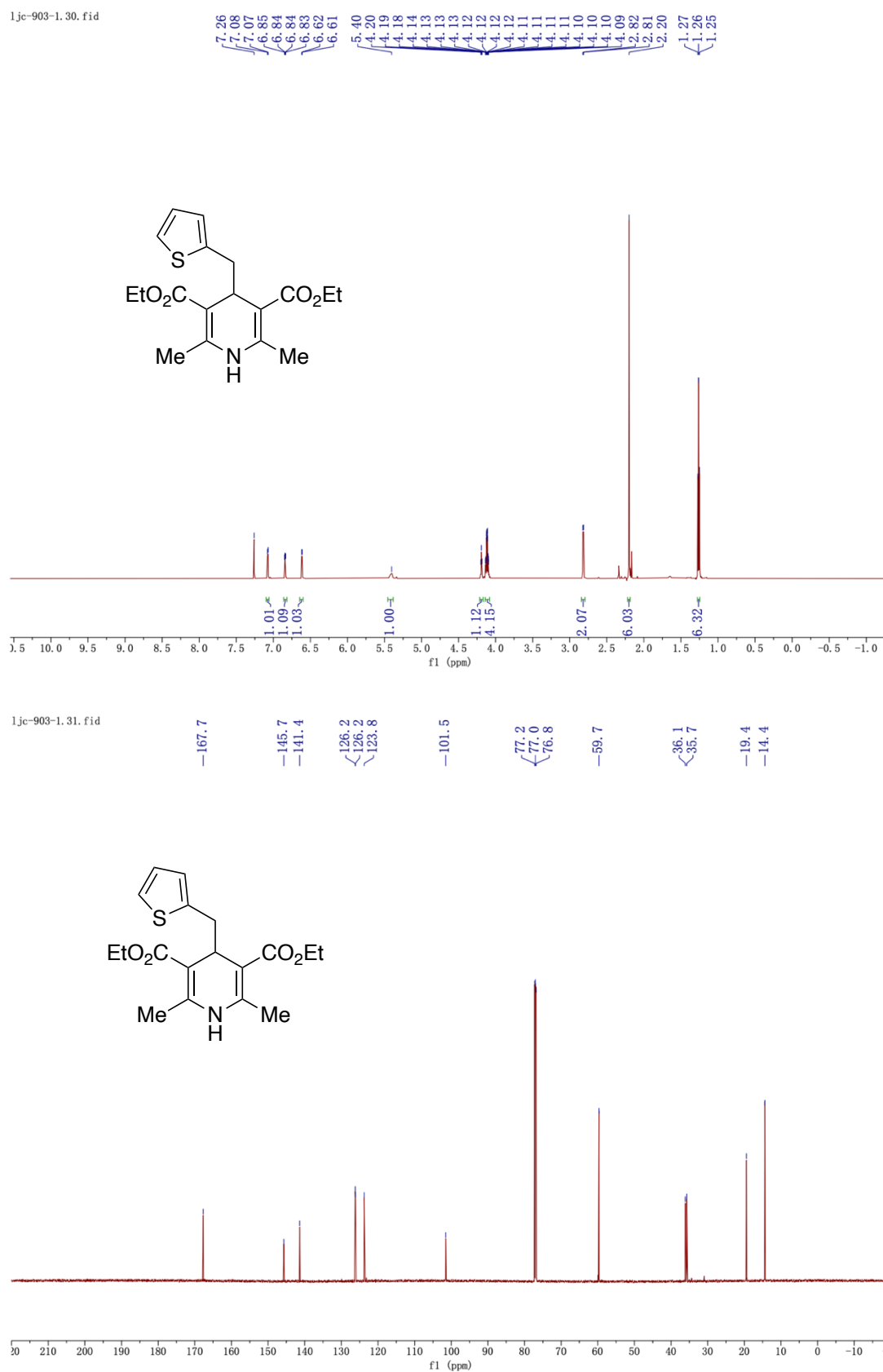


Figure S25. ^1H and ^{13}C NMR spectra of diethyl 2,6-dimethyl-4-(thiophen-2-ylmethyl)-1,4-dihydropyridine-3,5-dicarboxylate (**2h**)



¹H NMR spectrum (400 MHz, CDCl₃) of the compound. The chemical structure is shown above the spectrum. The spectrum displays peaks corresponding to the protons in the molecule, with integration values provided below the baseline.

Chemical structure: CC1=C(C(=O)OCC)C(C(=O)OCC)=C(C1)C2CCN(CC2)C3=CC=CC=C3

¹H NMR peaks (ppm): 7.46, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 4.67, 4.19, 4.18, 4.17, 4.16, 4.15, 4.14, 4.02, 4.01, 4.00, 3.68, 2.82, 2.59, 2.58, 2.29, 2.28, 1.62, 1.60, 1.49, 1.48, 1.48, 1.47, 1.46, 1.29, 1.28, 1.27, 1.14, 1.14, 1.13, 1.13, 1.12, 1.12.

Integration values: 5.38, 1.10, 0.96, 4.05, 1.00, 0.97, 1.04, 5.73, 0.99, 1.98, 6.05, 1.06.



Figure S27. ^1H and ^{13}C NMR spectra of diethyl 4-(*sec*-butyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**2j**)

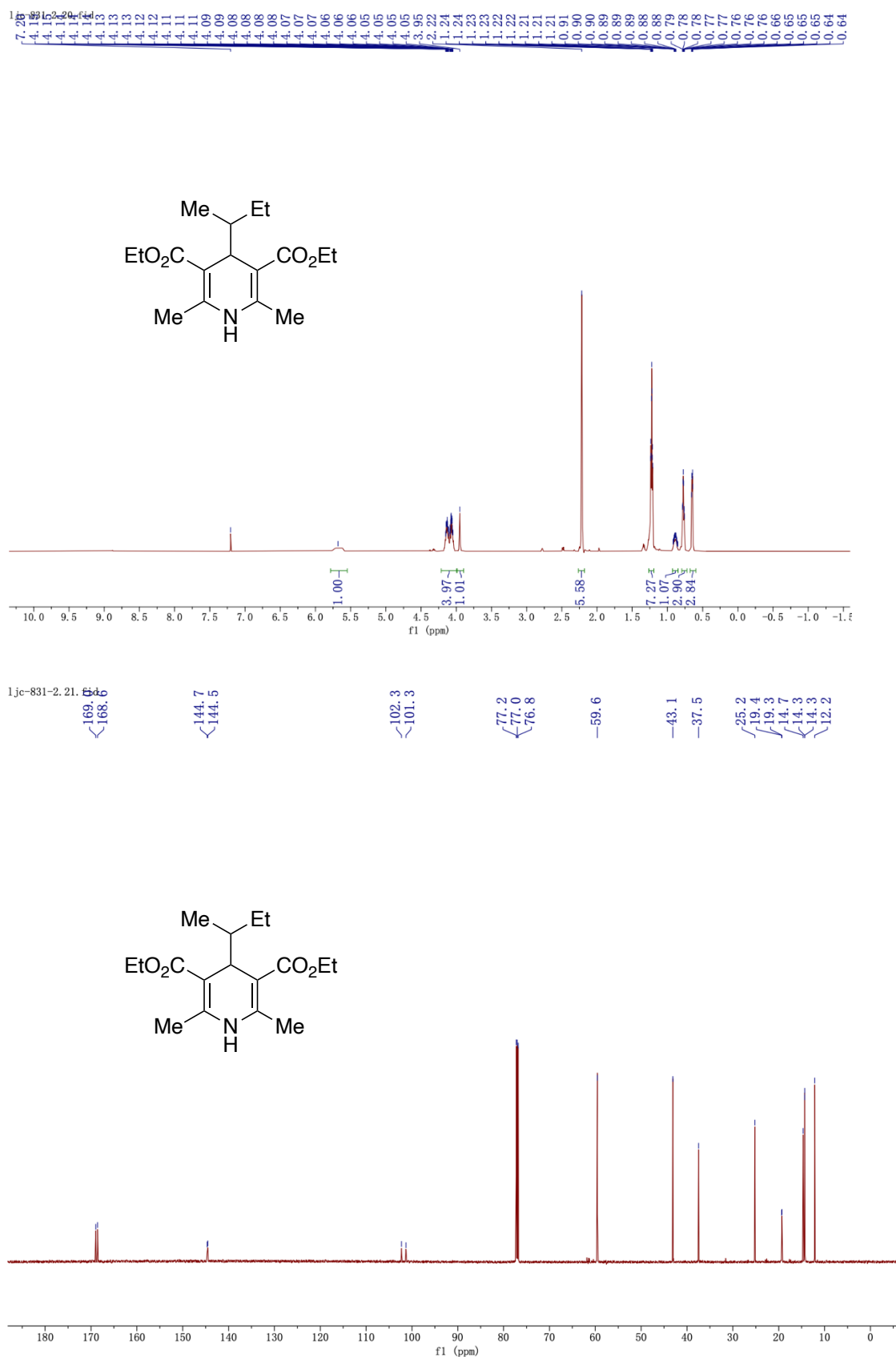


Figure S28. ^1H and ^{13}C NMR spectra of diethyl 2,6-dimethyl-4-(pentan-3-yl)-1,4-dihydropyridine-3,5-dicarboxylate (**2k**)

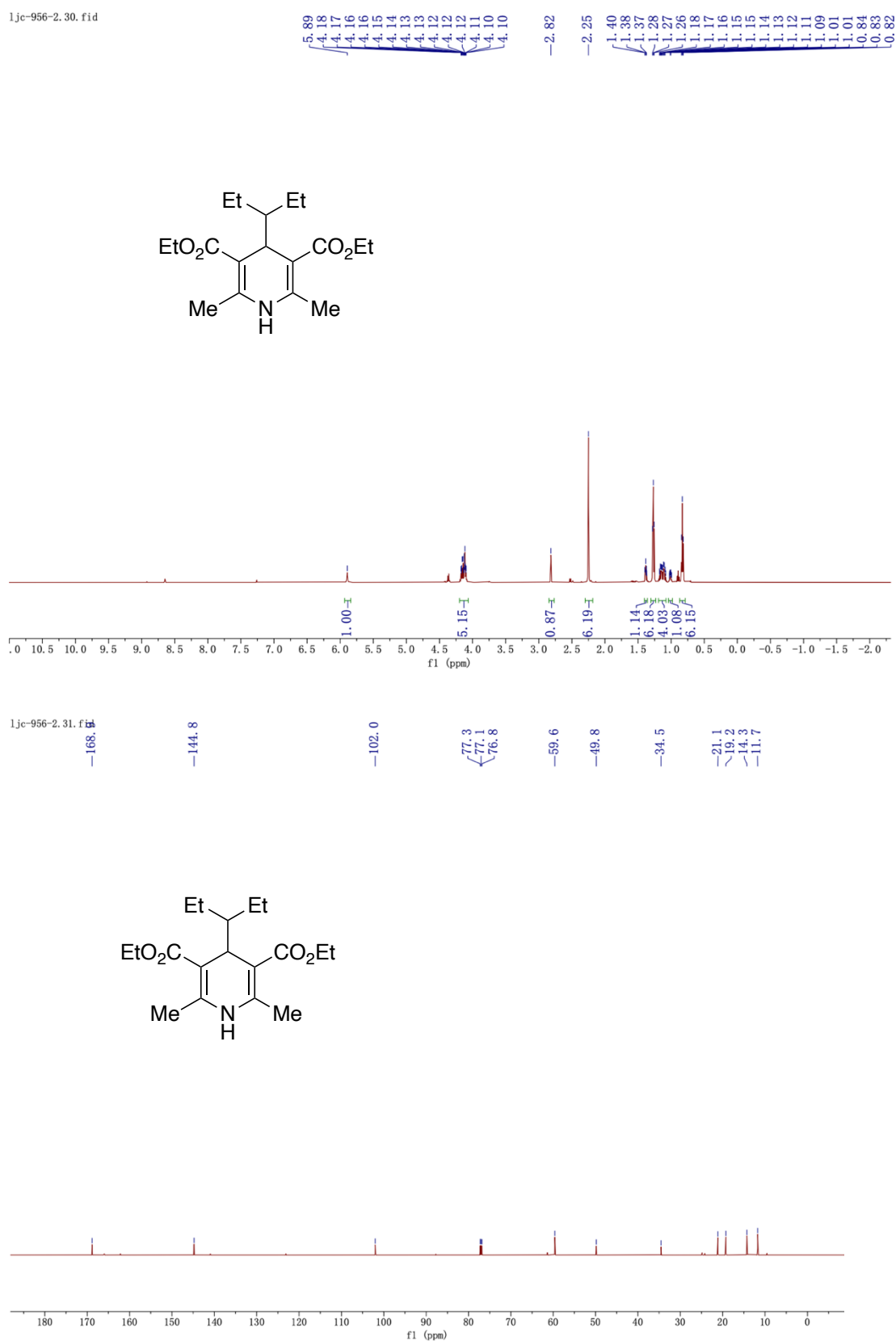


Figure S29. ^1H and ^{13}C NMR spectra of diethyl 2,6-dimethyl-4-(1-phenoxyethyl)-1,4-dihydropyridine-3,5-dicarboxylate (**2I**)

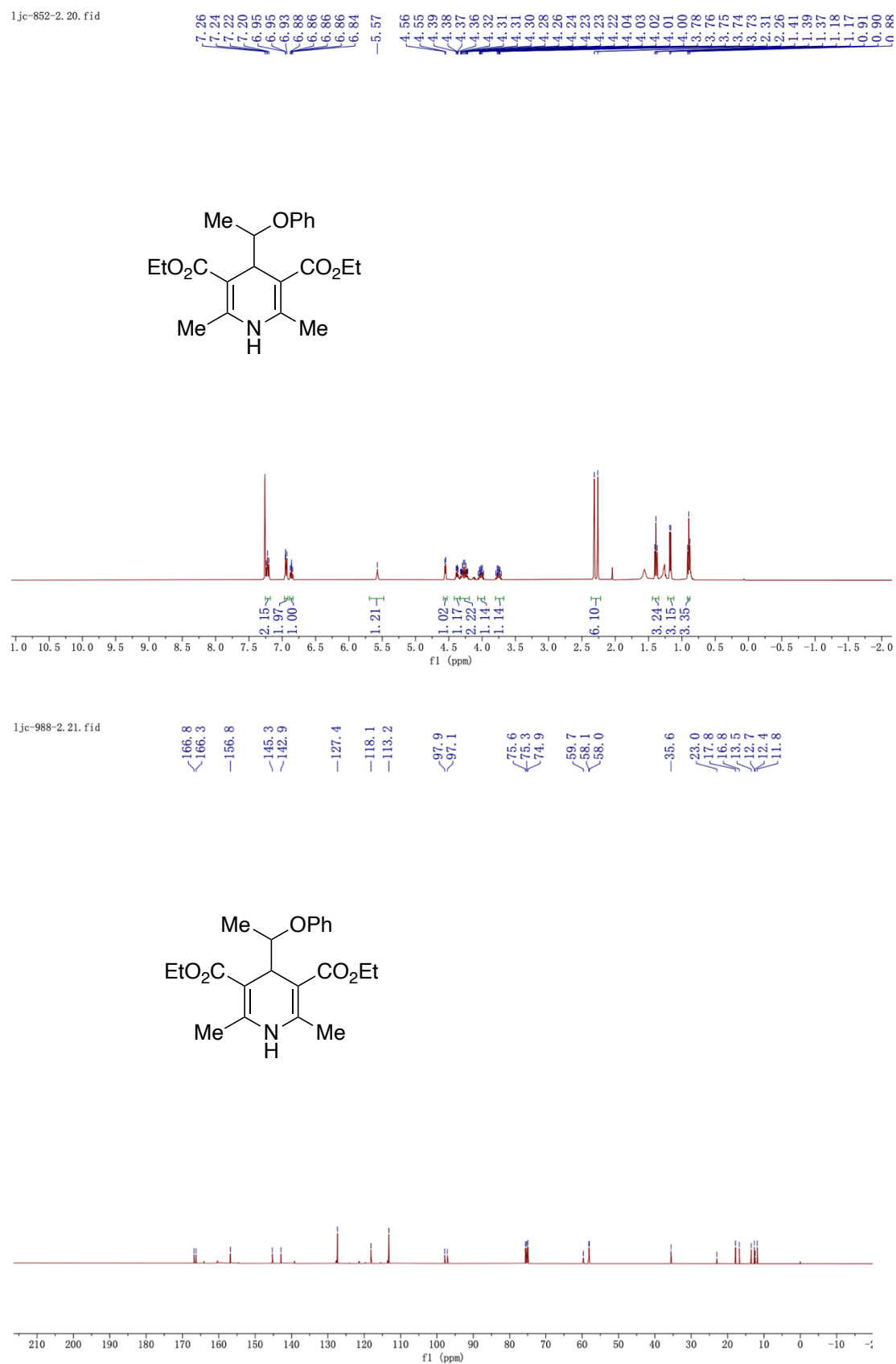


Figure S30. ^1H and ^{13}C NMR spectra of diethyl 4-cyclopentyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**2m**)

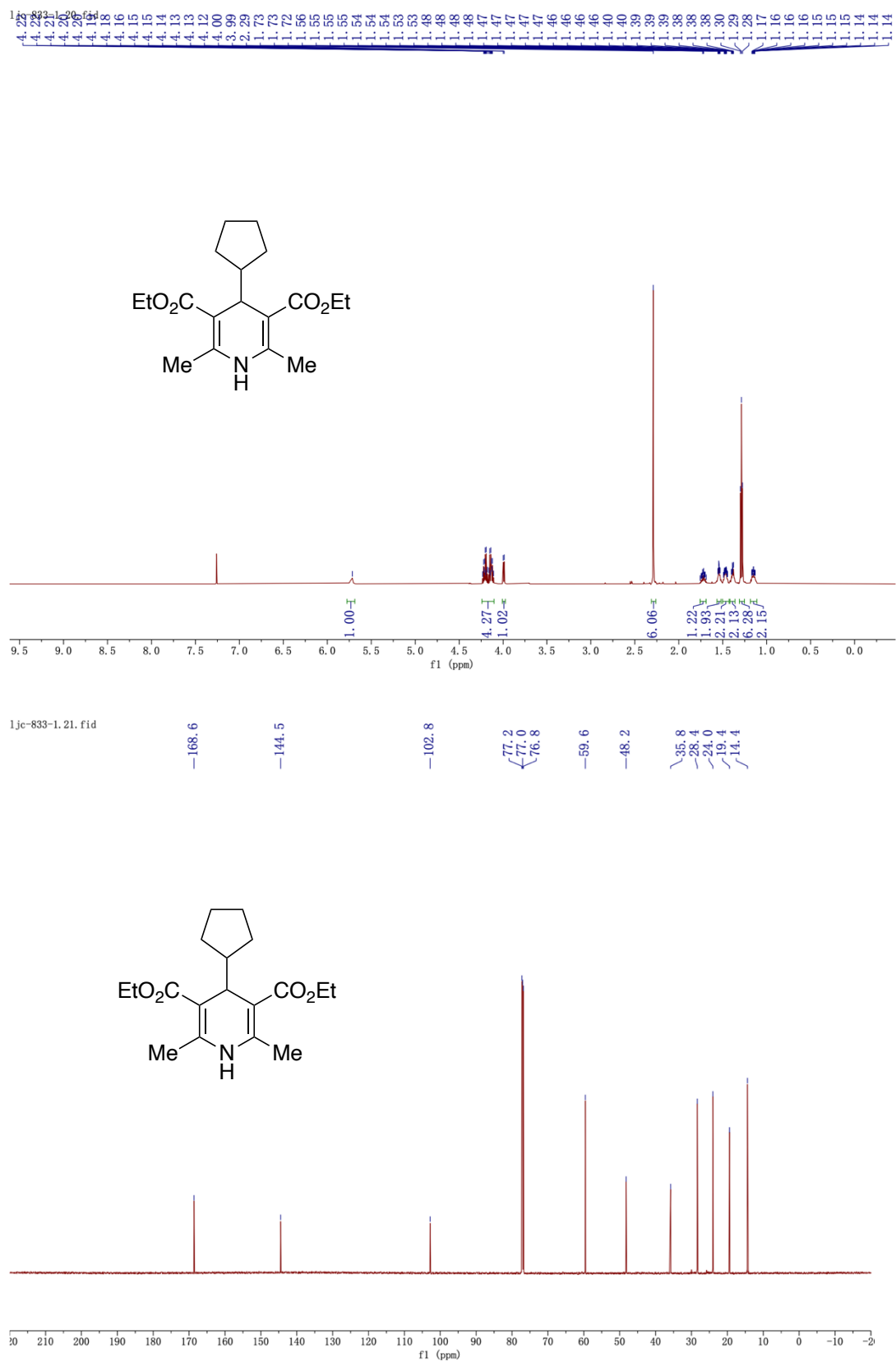


Figure S31. ^1H and ^{13}C NMR spectra of diethyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**2n**)

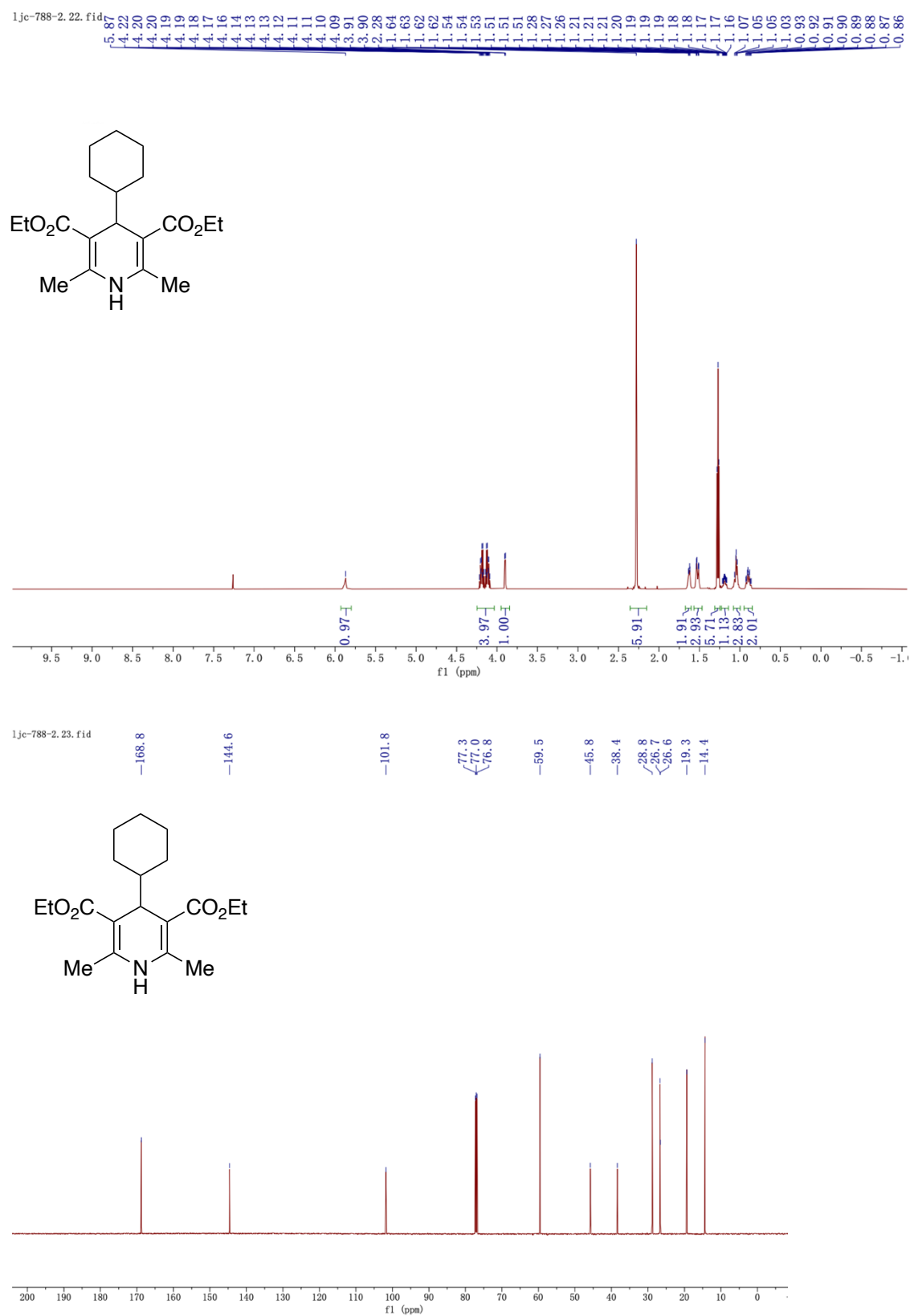


Figure S32. ^1H and ^{13}C NMR spectra of diethyl 4-(cyclohex-3-en-1-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**2o**)

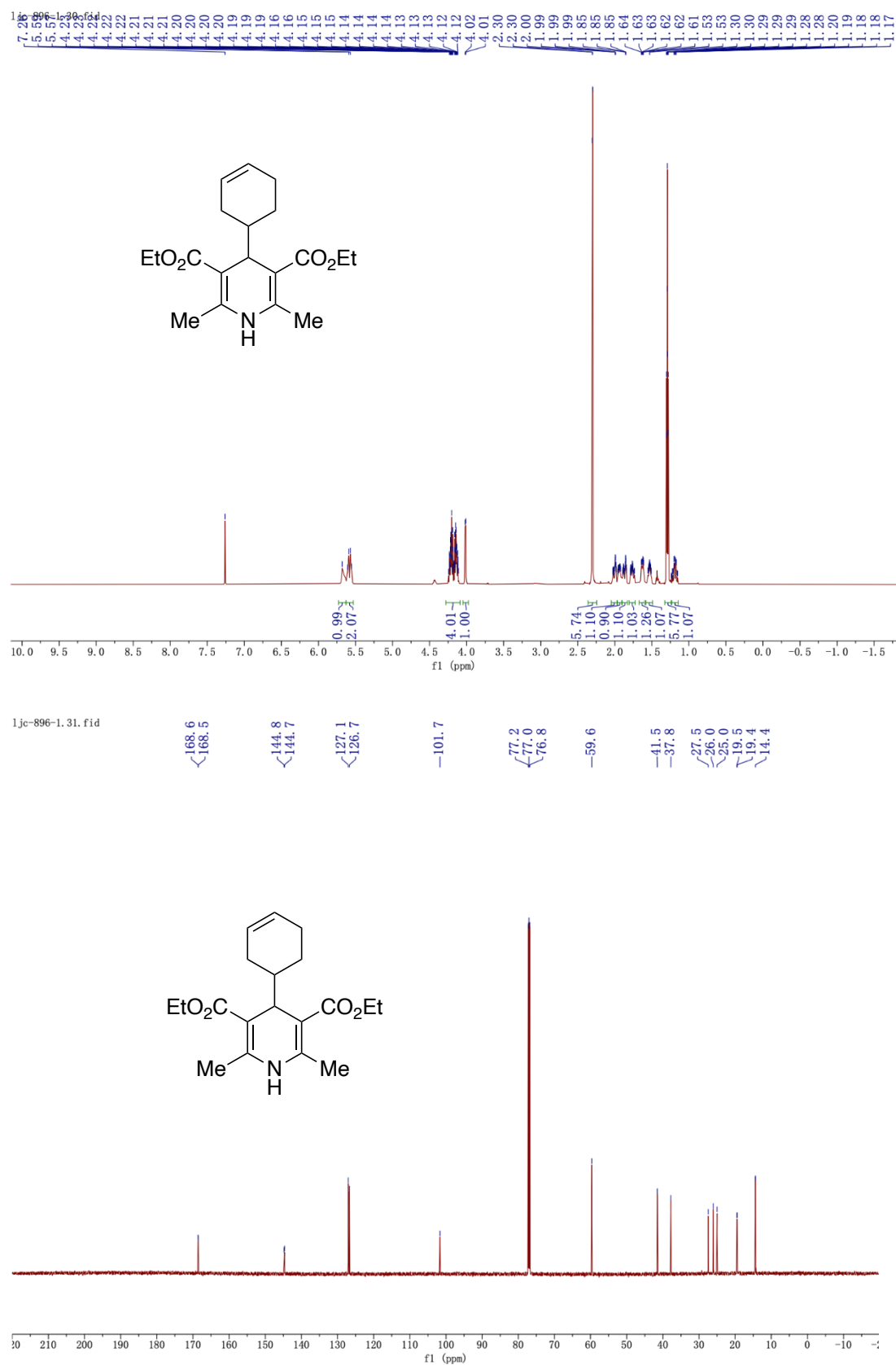


Figure S33. ^1H and ^{13}C NMR spectra of diethyl 4-benzoyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4a**)

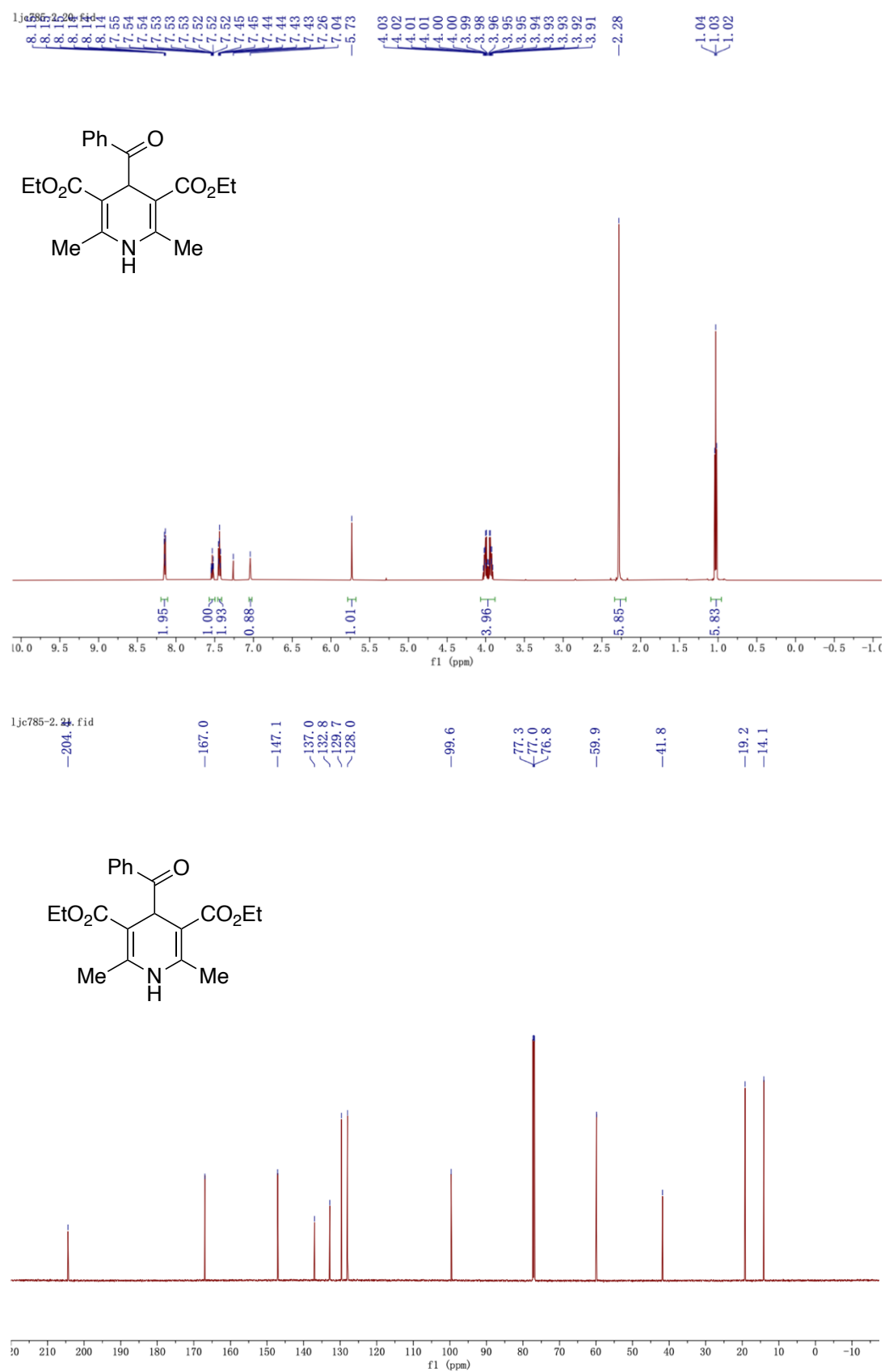


Figure S34. ^1H and ^{13}C NMR spectra of diethyl 4-(4-bromobenzoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4b**)

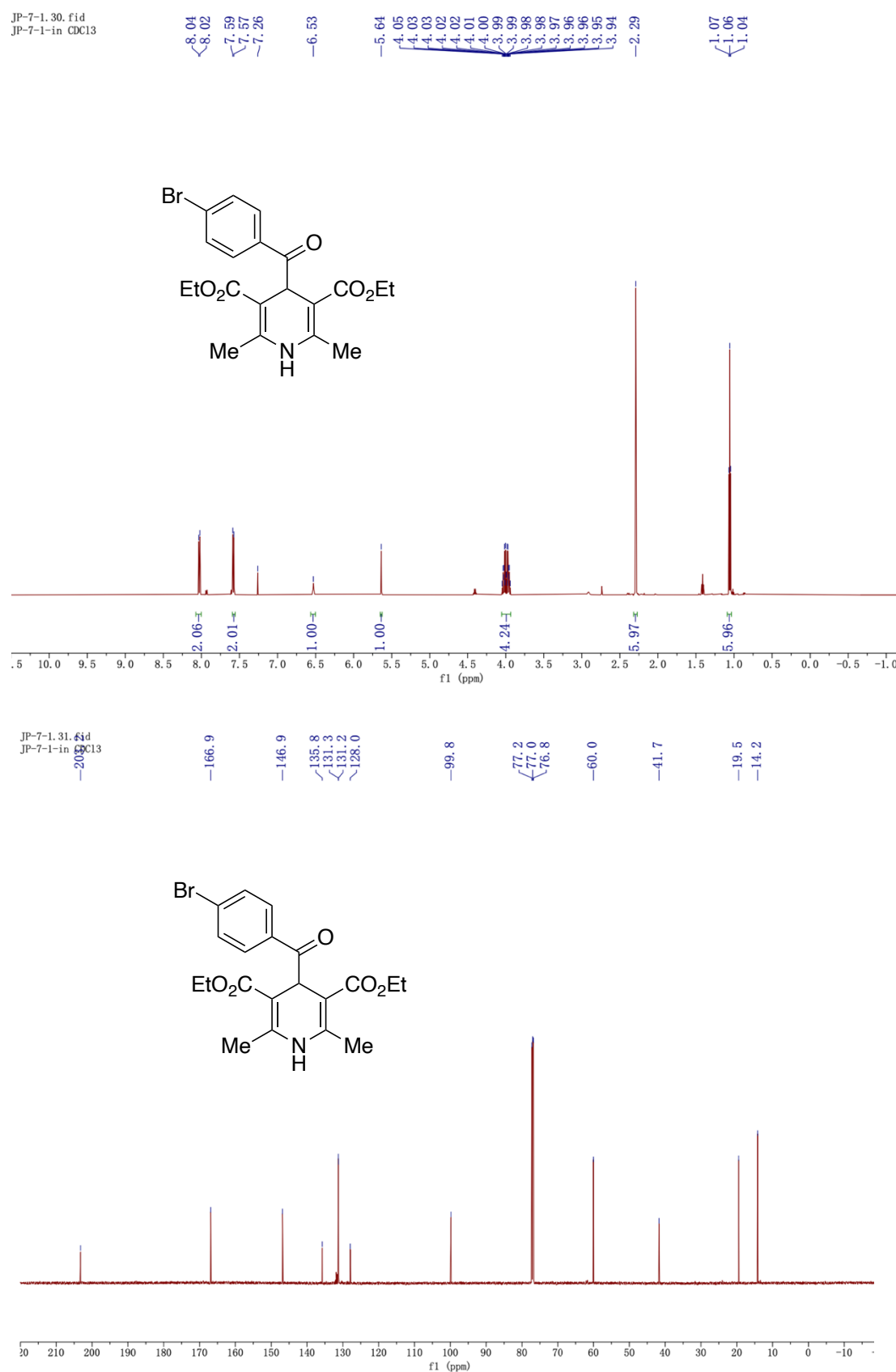


Figure S35. ^1H and ^{13}C NMR spectra of diethyl 4-(4-chlorobenzoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4c**)

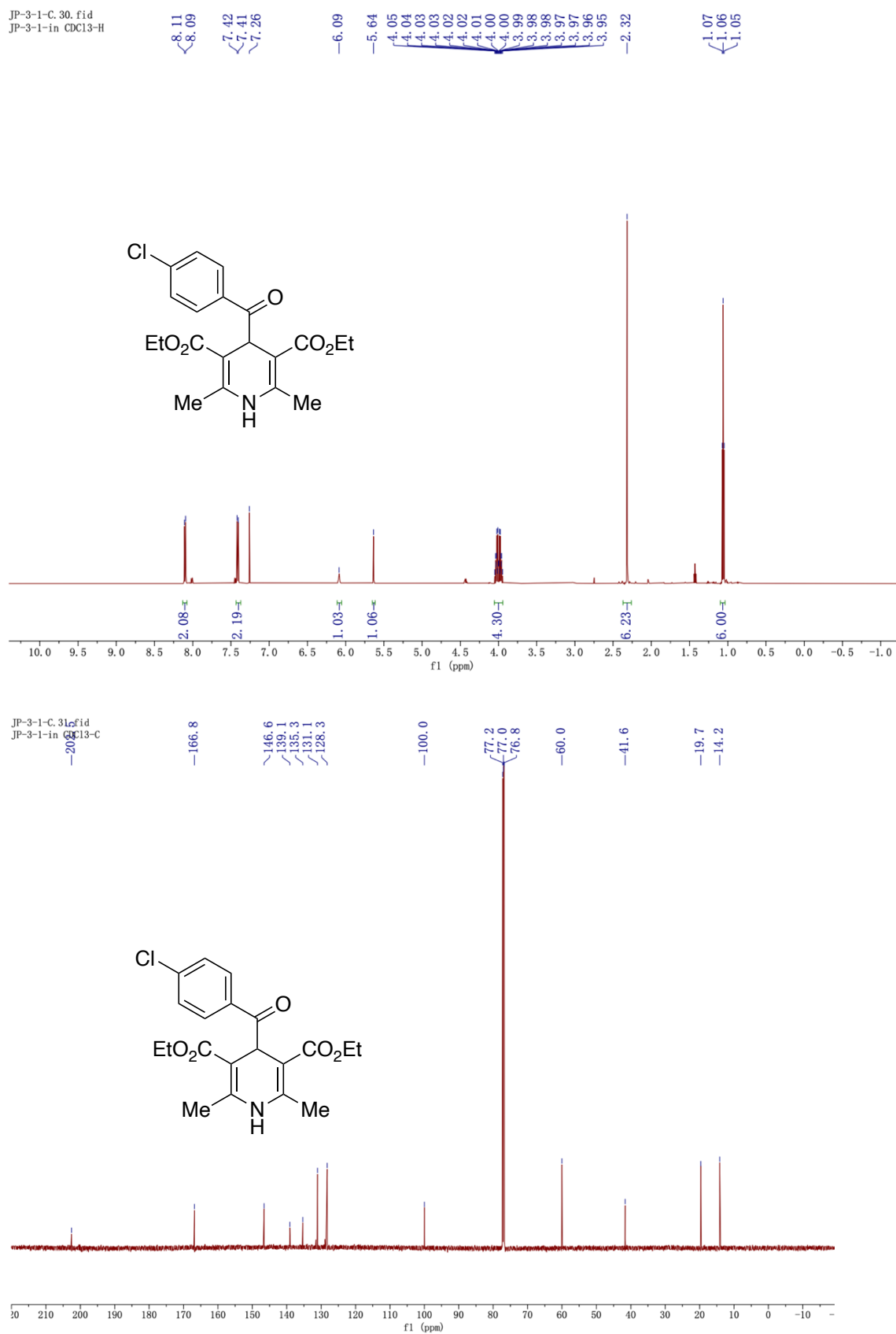
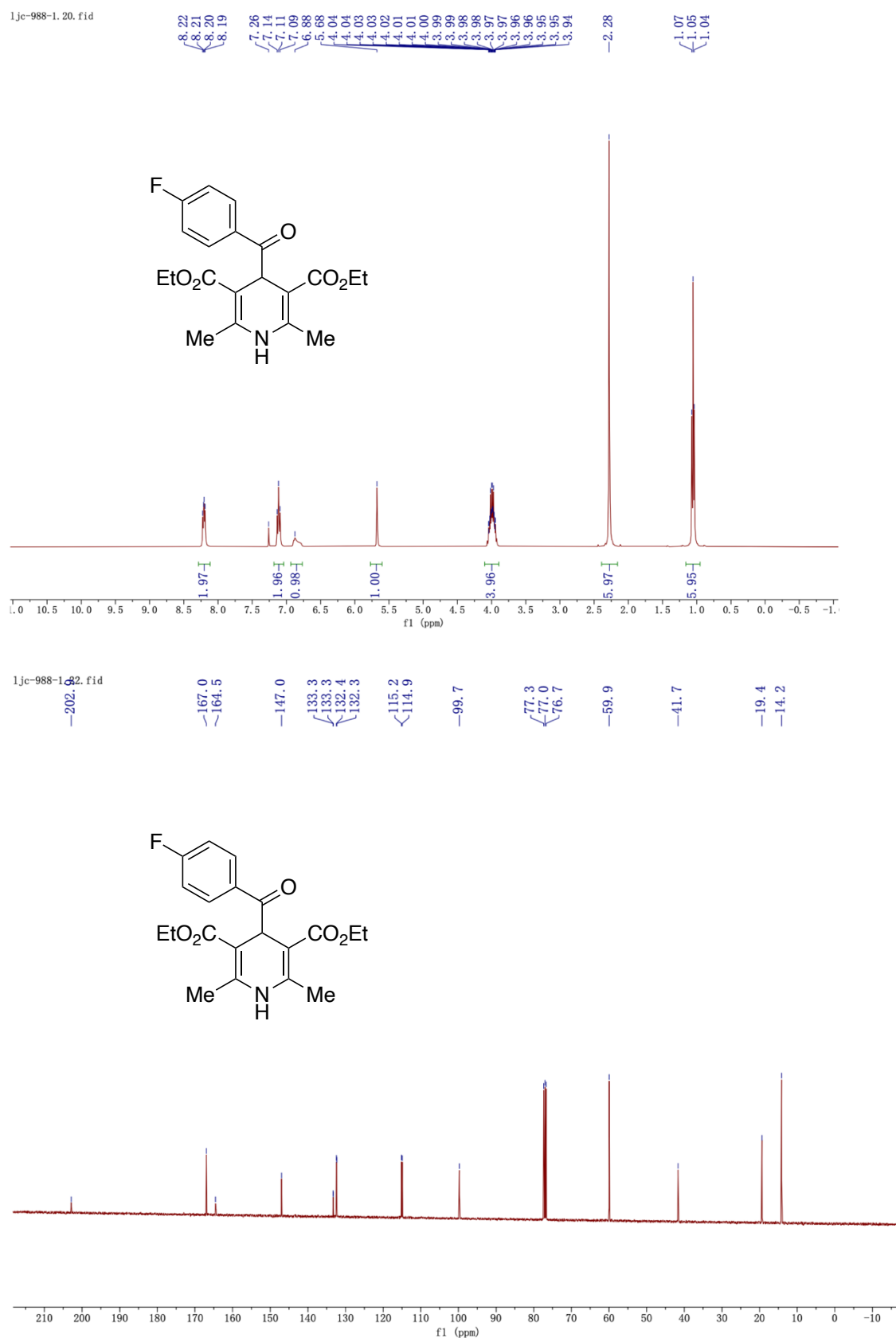


Figure S36. ^1H , ^{13}C and ^{19}F NMR spectra of diethyl 4-(4-fluorobenzoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4d**)



ljc-988-1.21.fid

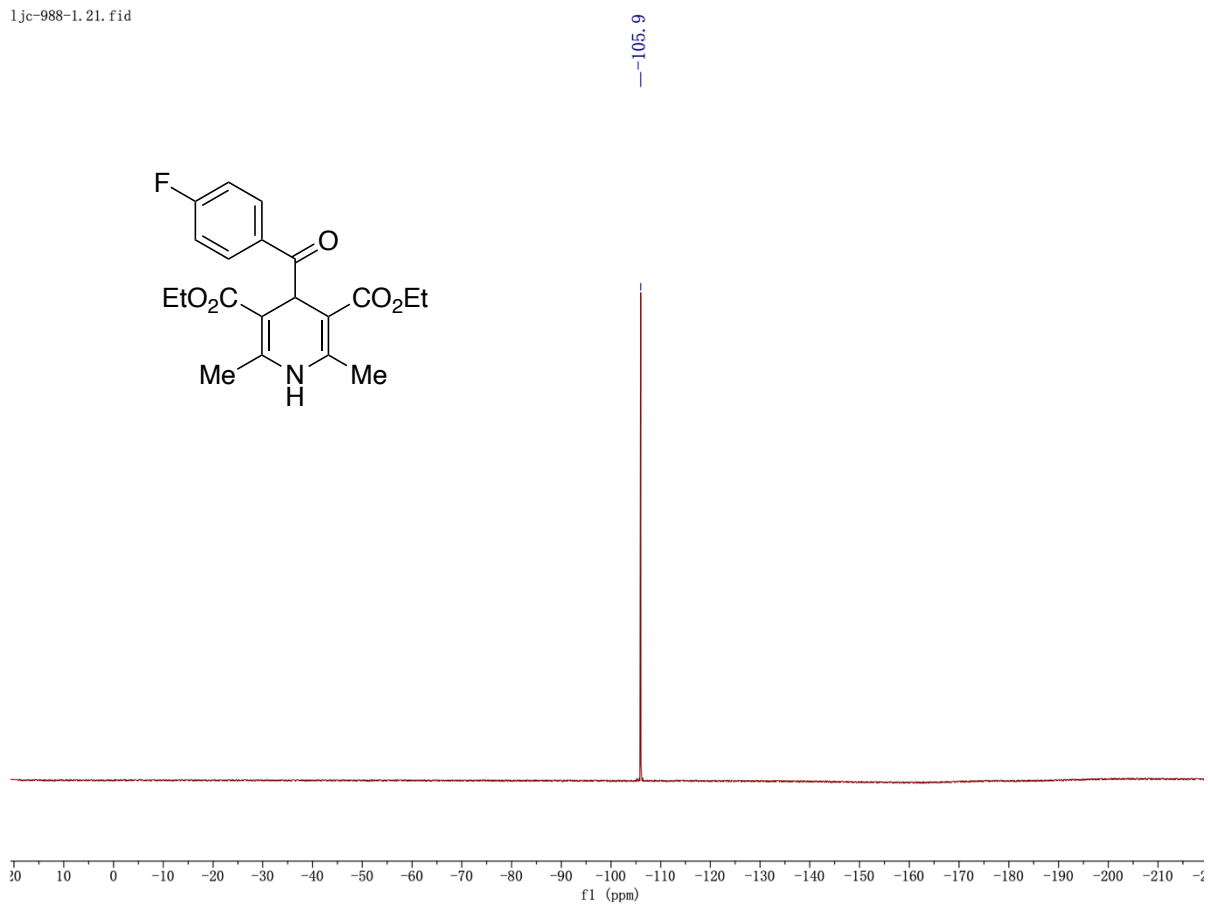
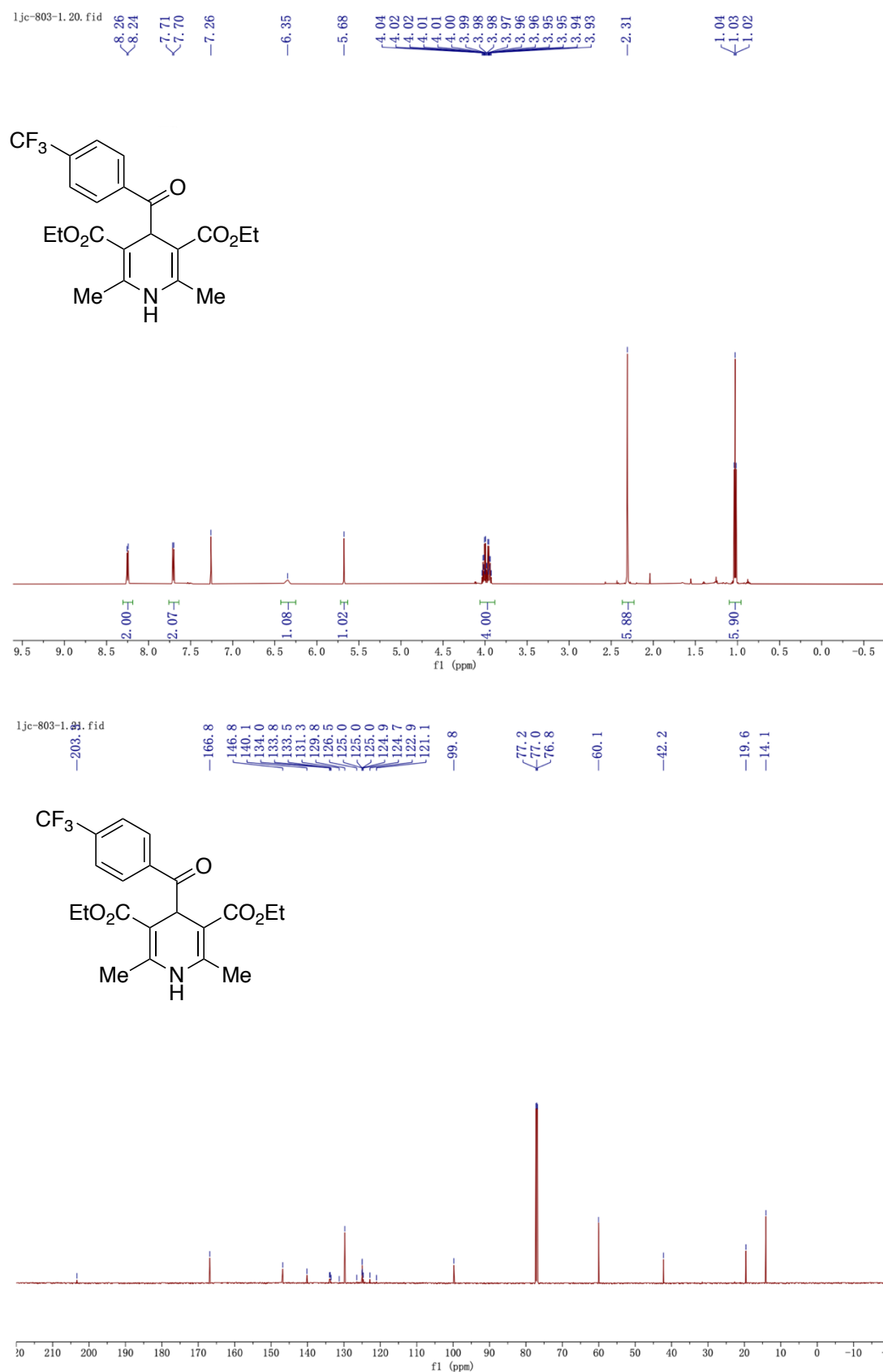


Figure S37. ^1H , ^{13}C and ^{19}F NMR spectra of diethyl 2,6-dimethyl-4-(4-(trifluoromethyl)benzoyl)-1,4-dihydropyridine-3,5-dicarboxylate (**4e**)



1jc-803-1.2.fid

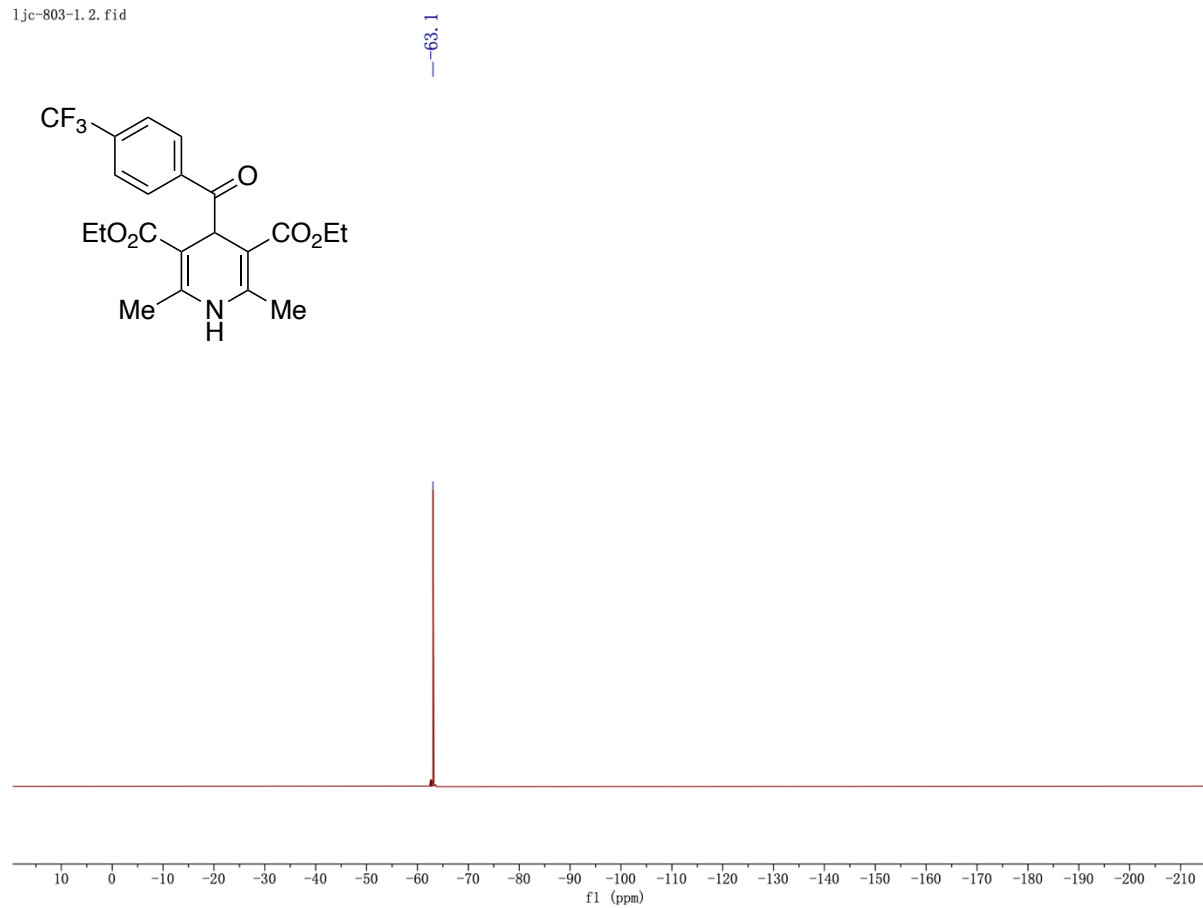


Figure S38. ^1H and ^{13}C NMR spectra of diethyl 2,6-dimethyl-4-(4-methylbenzoyl)-1,4-dihydropyridine-3,5-dicarboxylate (**4f**)

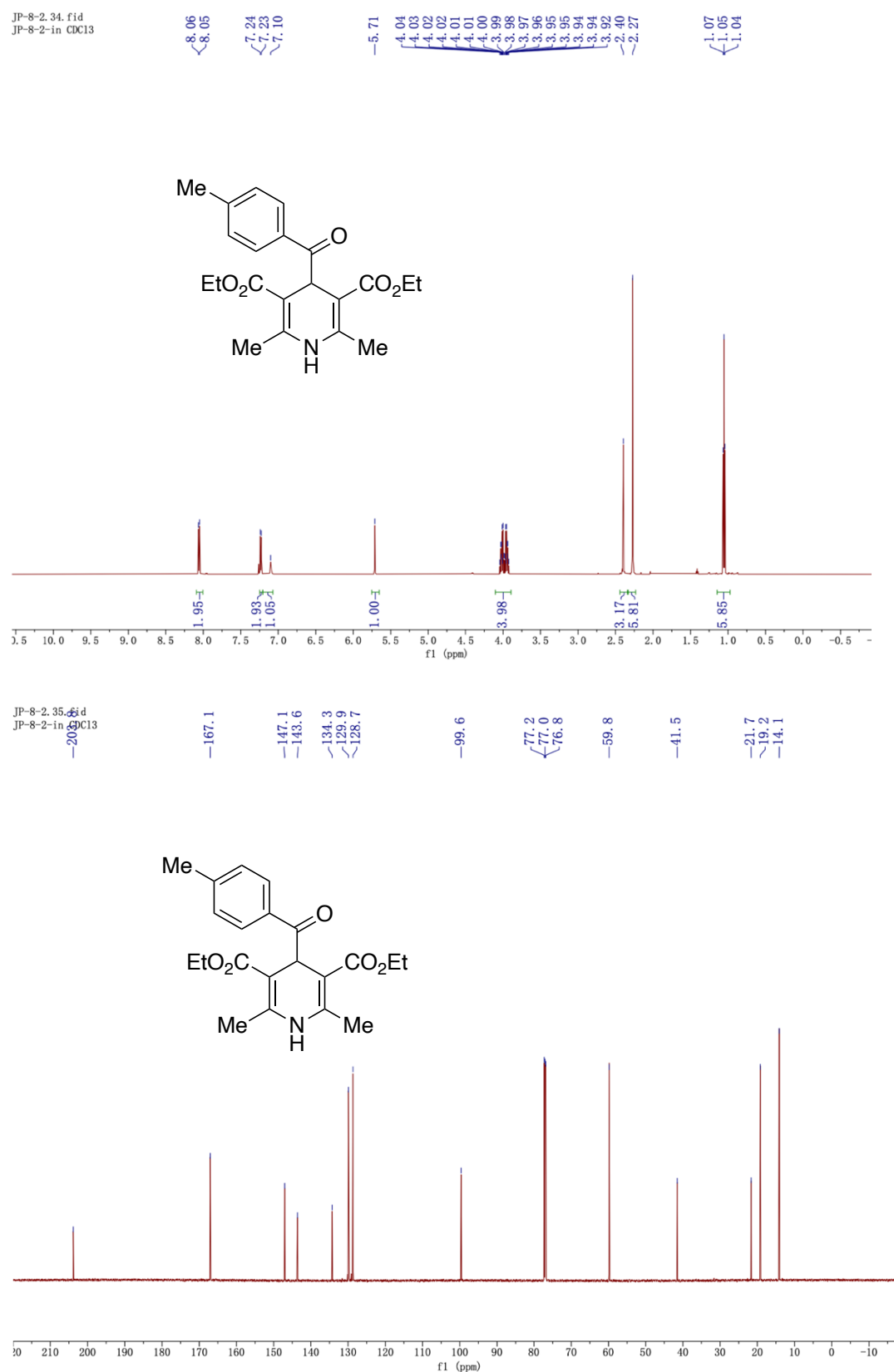


Figure S39. ^1H and ^{13}C NMR spectra of diethyl 4-(4-methoxybenzoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4g**)

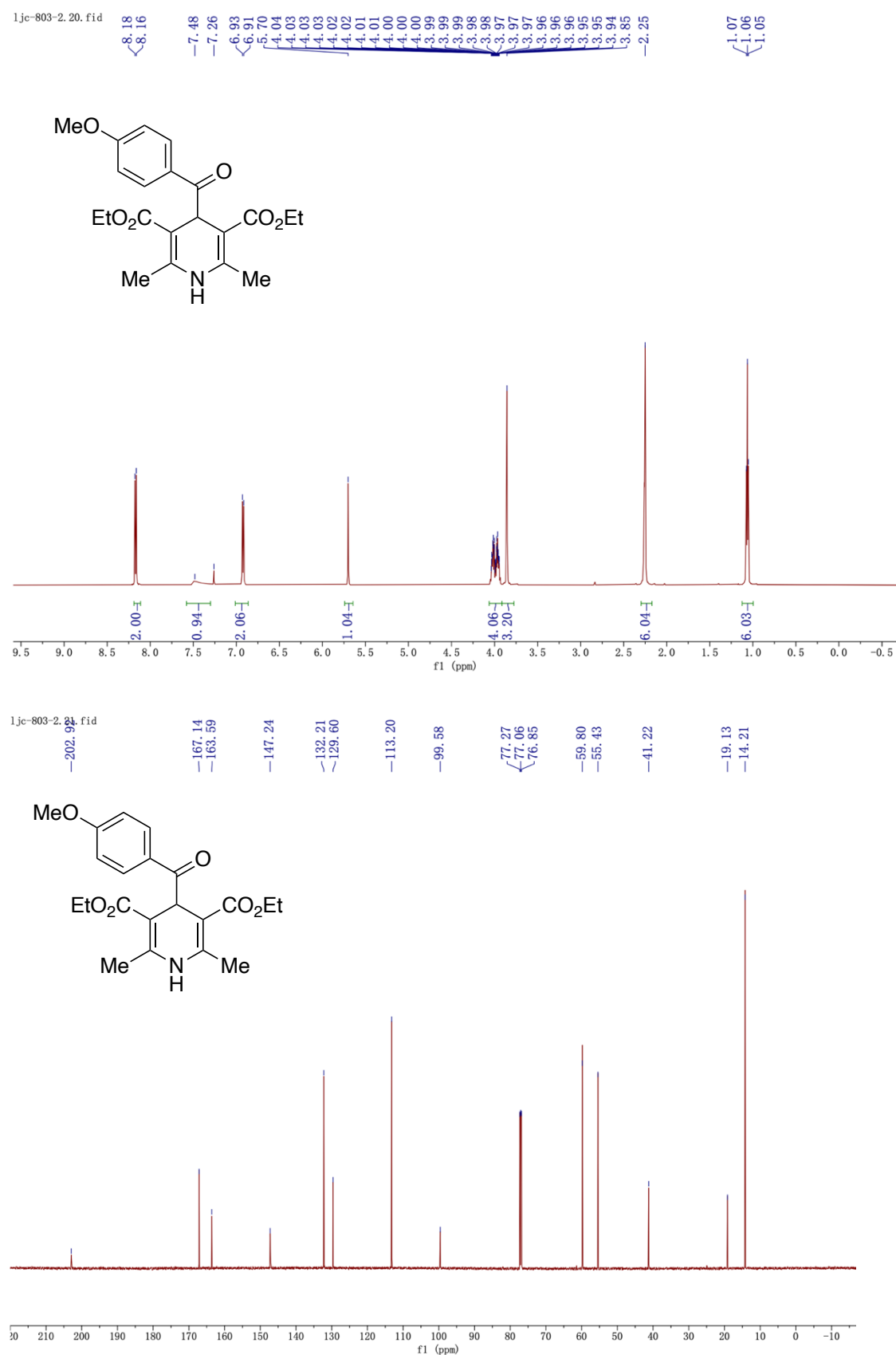


Figure S40. ^1H and ^{13}C NMR spectra of diethyl 4-([1,1'-biphenyl]-4-carbonyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4h**)

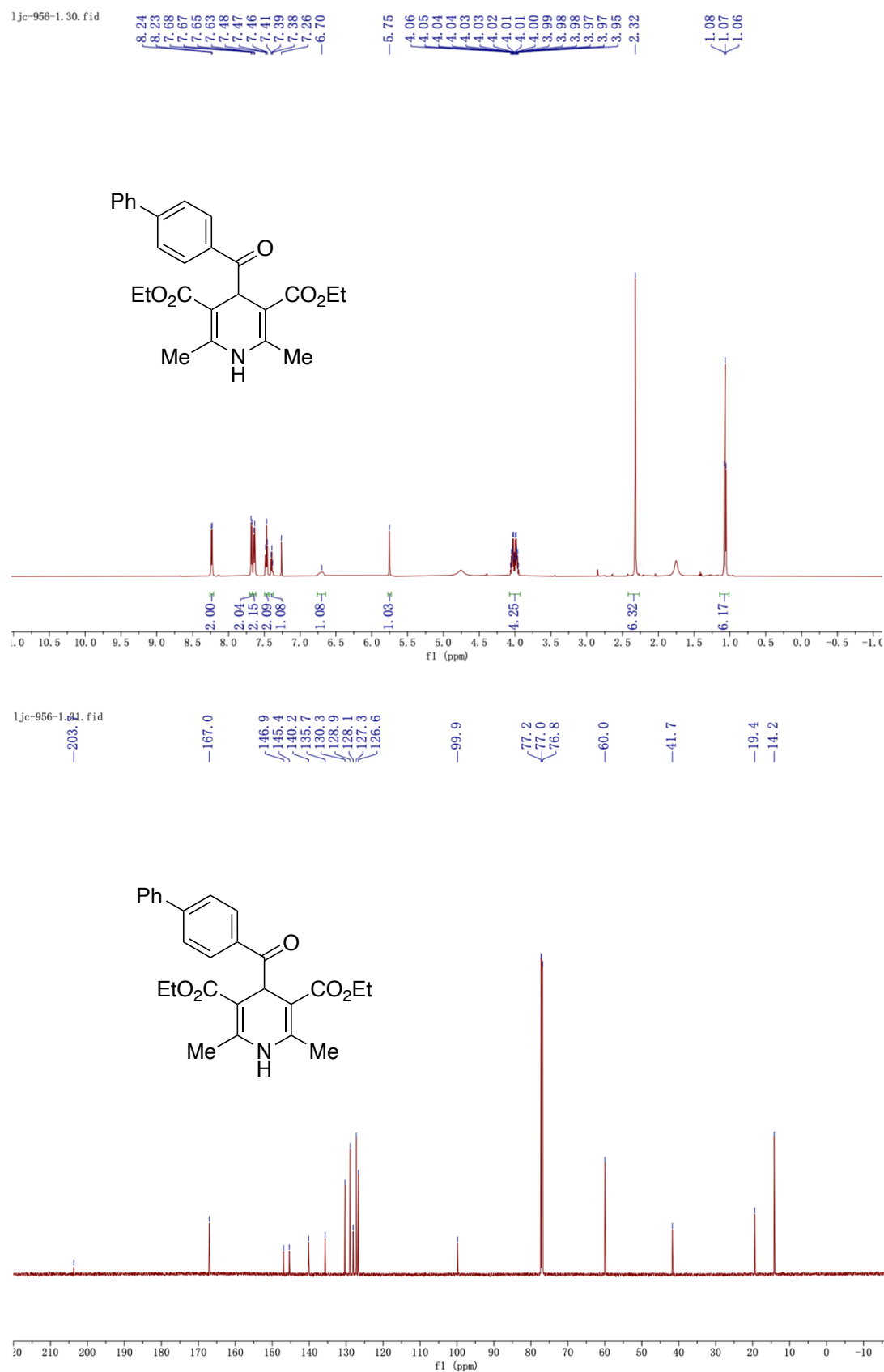


Figure S41. ^1H and ^{13}C NMR spectra of diethyl 4-(2-chlorobenzoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4i**)

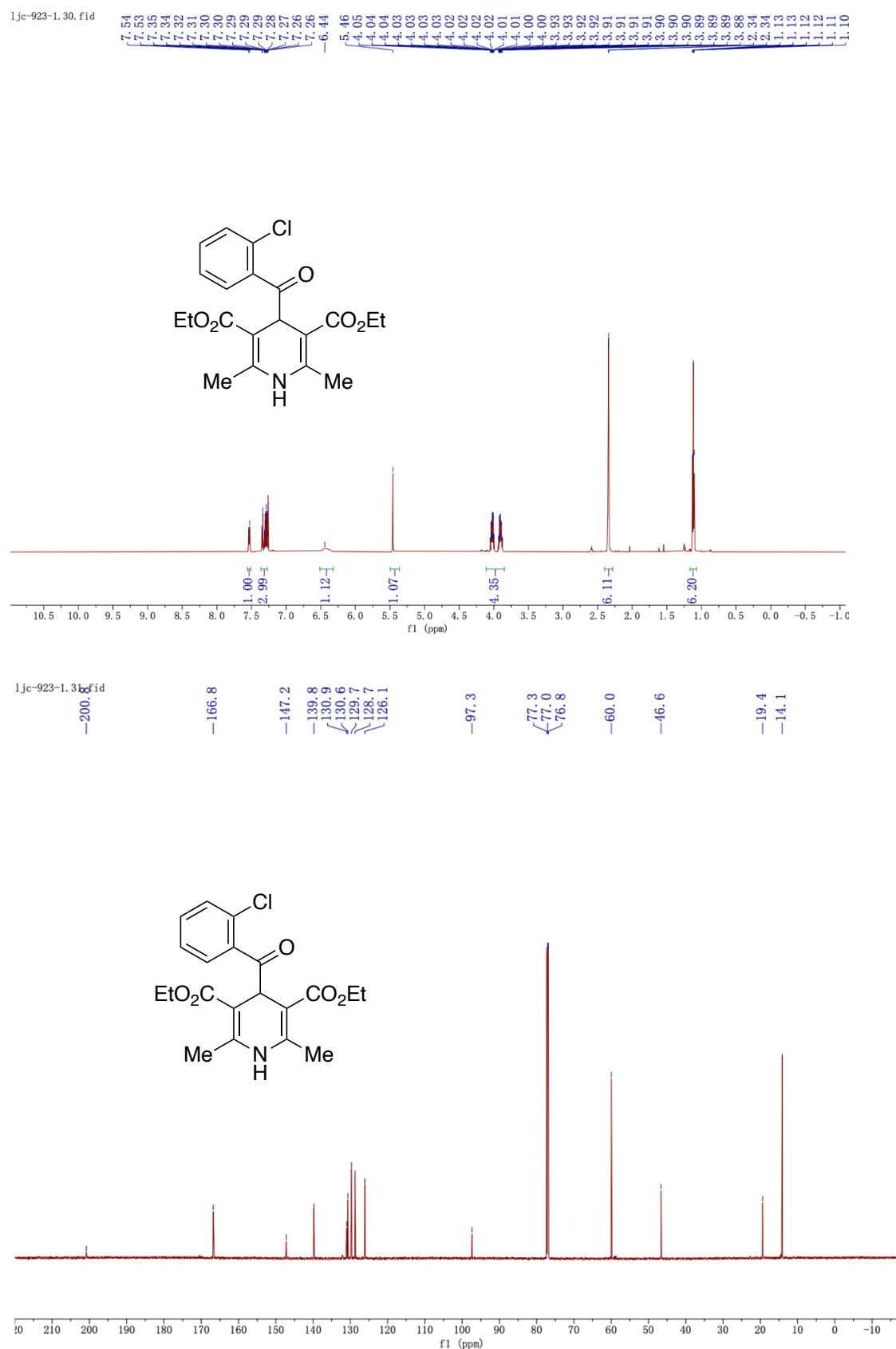


Figure S42. ^1H and ^{13}C NMR spectra of diethyl 4-(benzo[d][1,3]dioxole-5-carbonyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4j**)

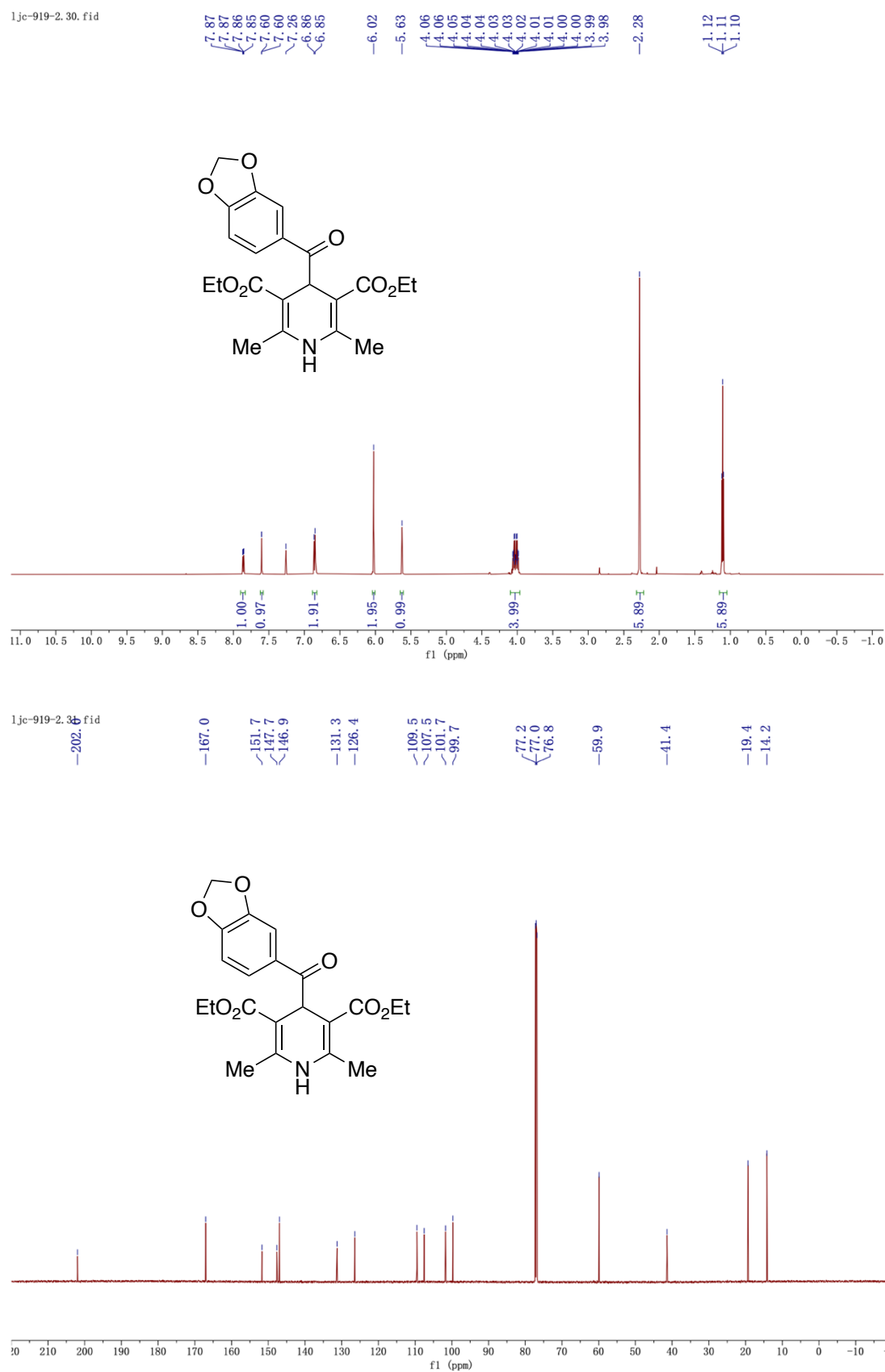


Figure S43. ^1H and ^{13}C NMR spectra of diethyl 4-(2-naphthoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4k**)

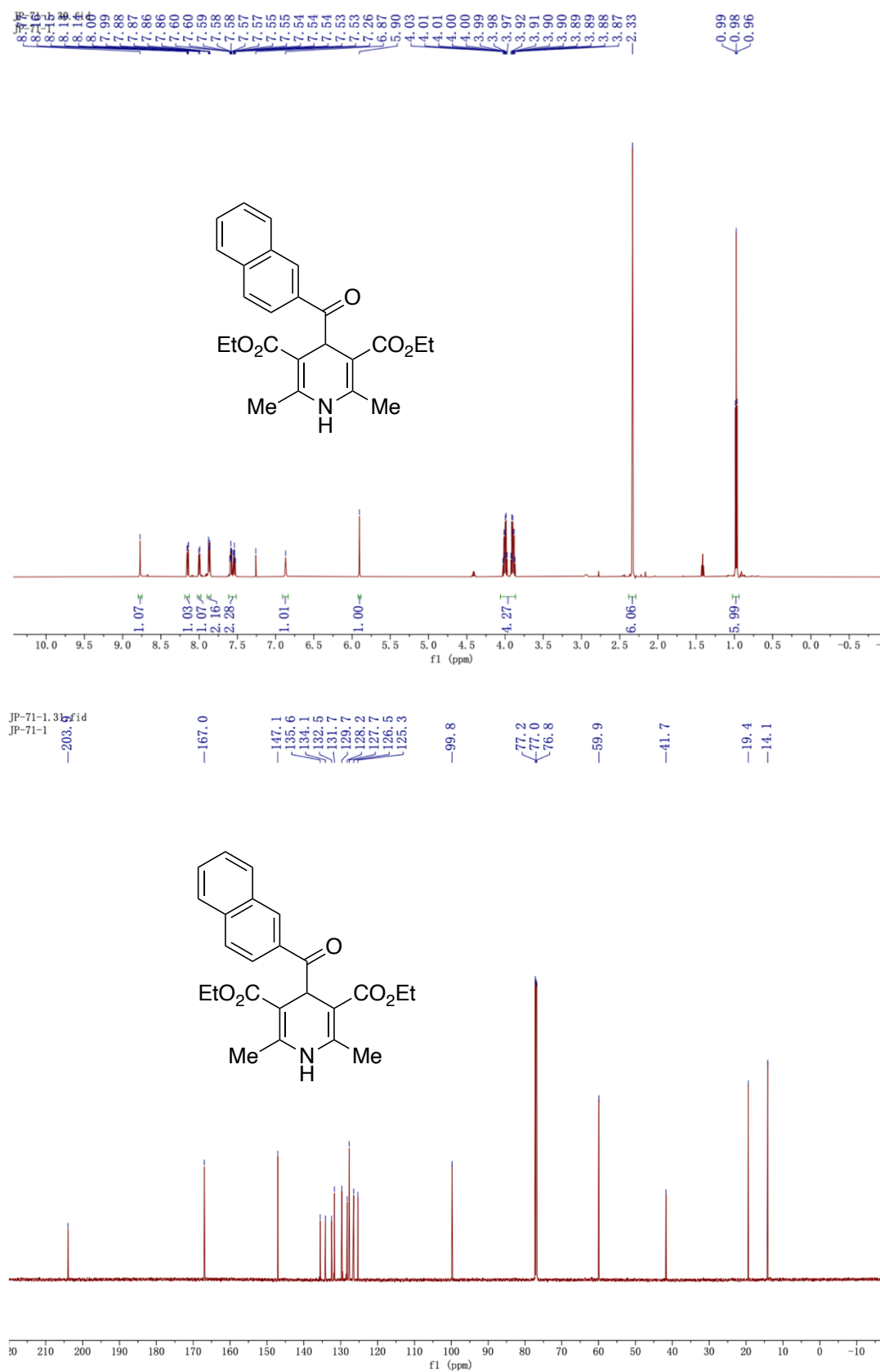


Figure S44. ^1H and ^{13}C NMR spectra of diethyl 4-(furan-2-carbonyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4I**)

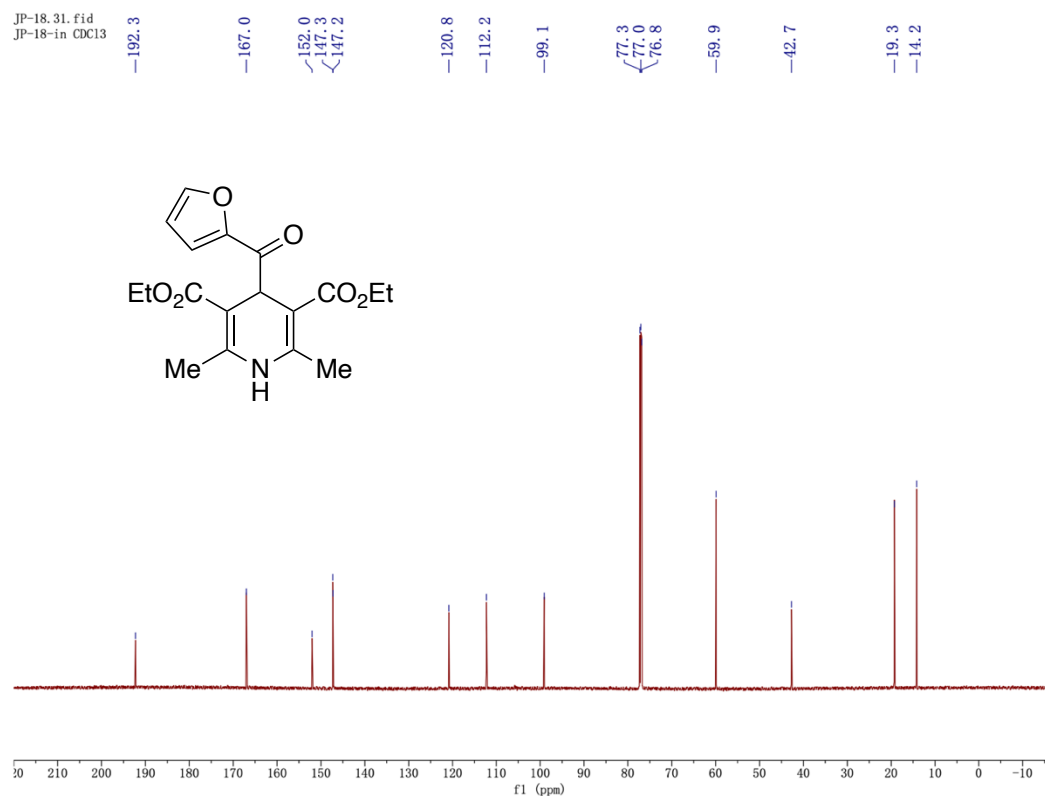
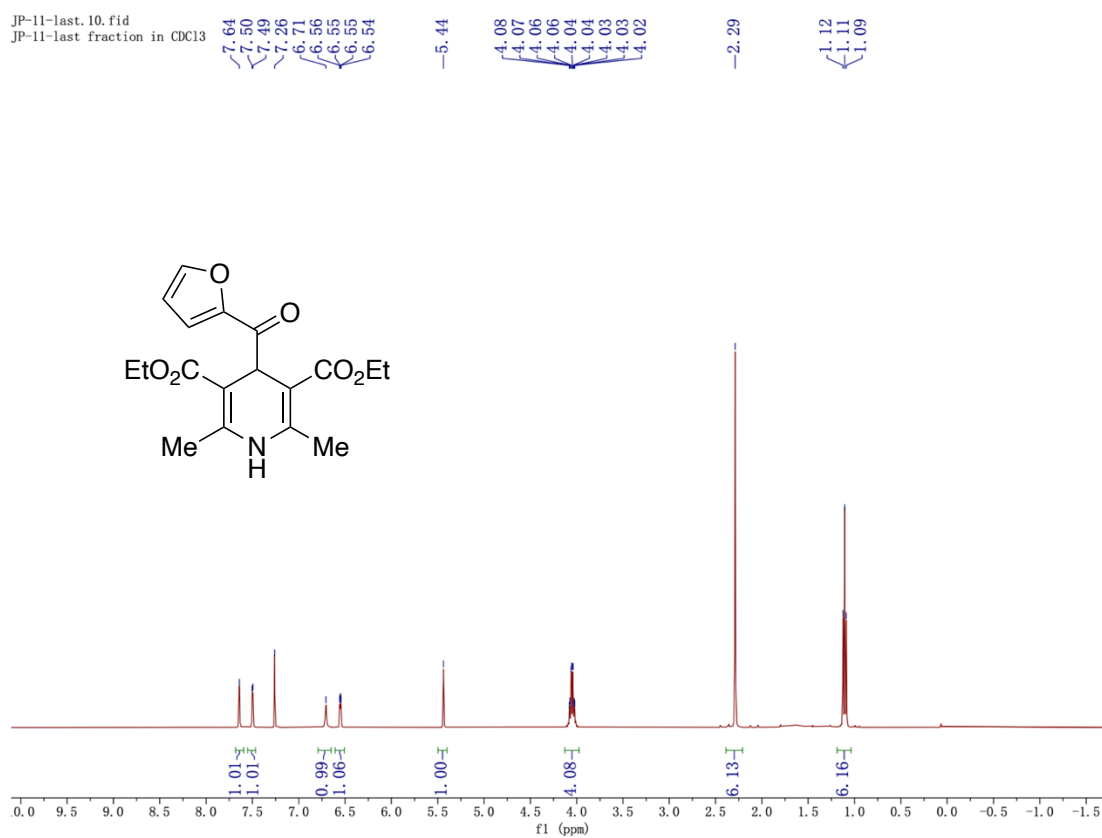


Figure S45. ^1H and ^{13}C NMR spectra of diethyl 2,6-dimethyl-4-(thiophene-2-carbonyl)-1,4-dihydropyridine-3,5-dicarboxylate (**4m**)

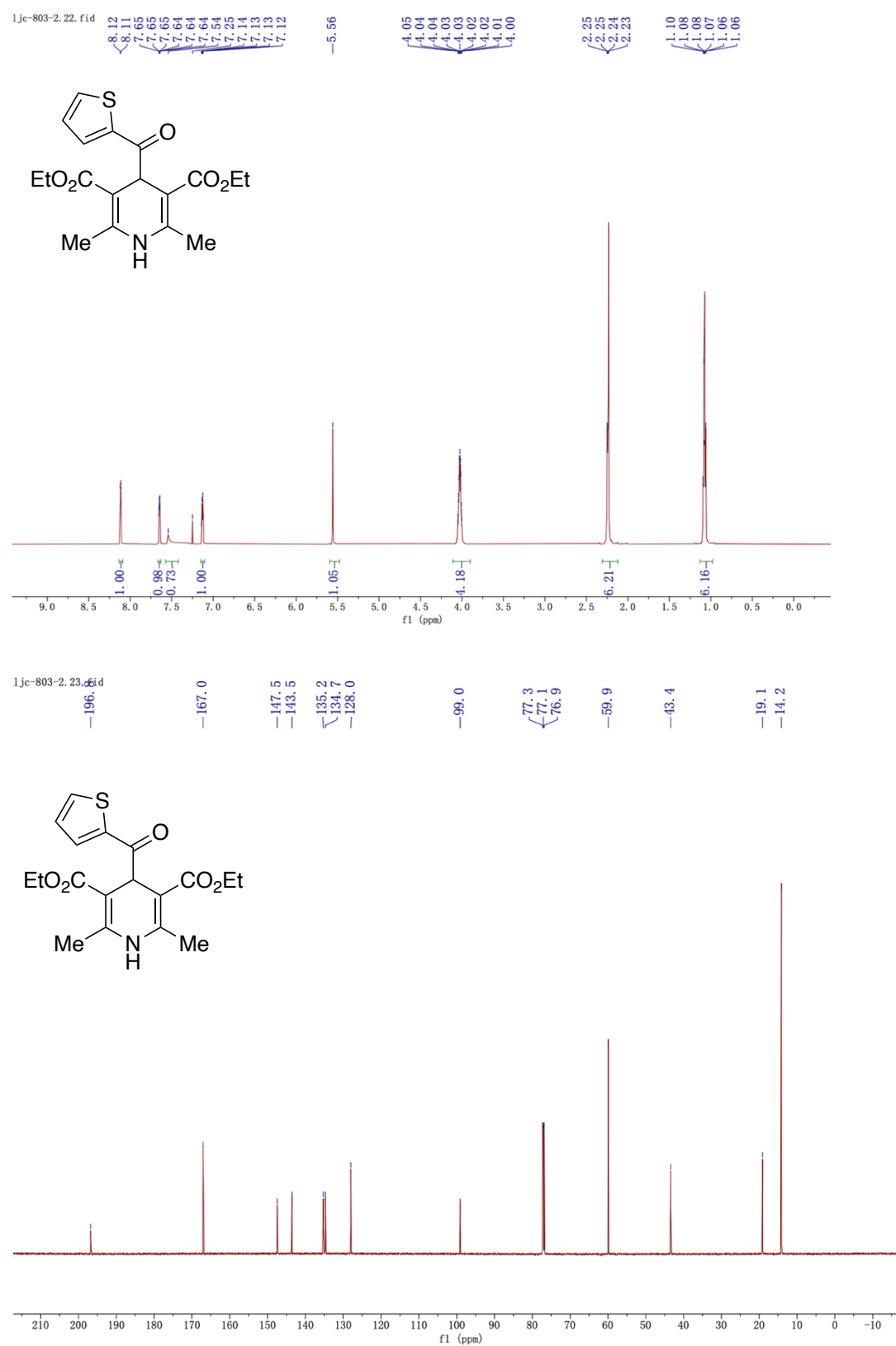


Figure S46. ^1H and ^{13}C NMR spectra of diethyl 4-(benzo[*b*]thiophene-3-carbonyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4n**)

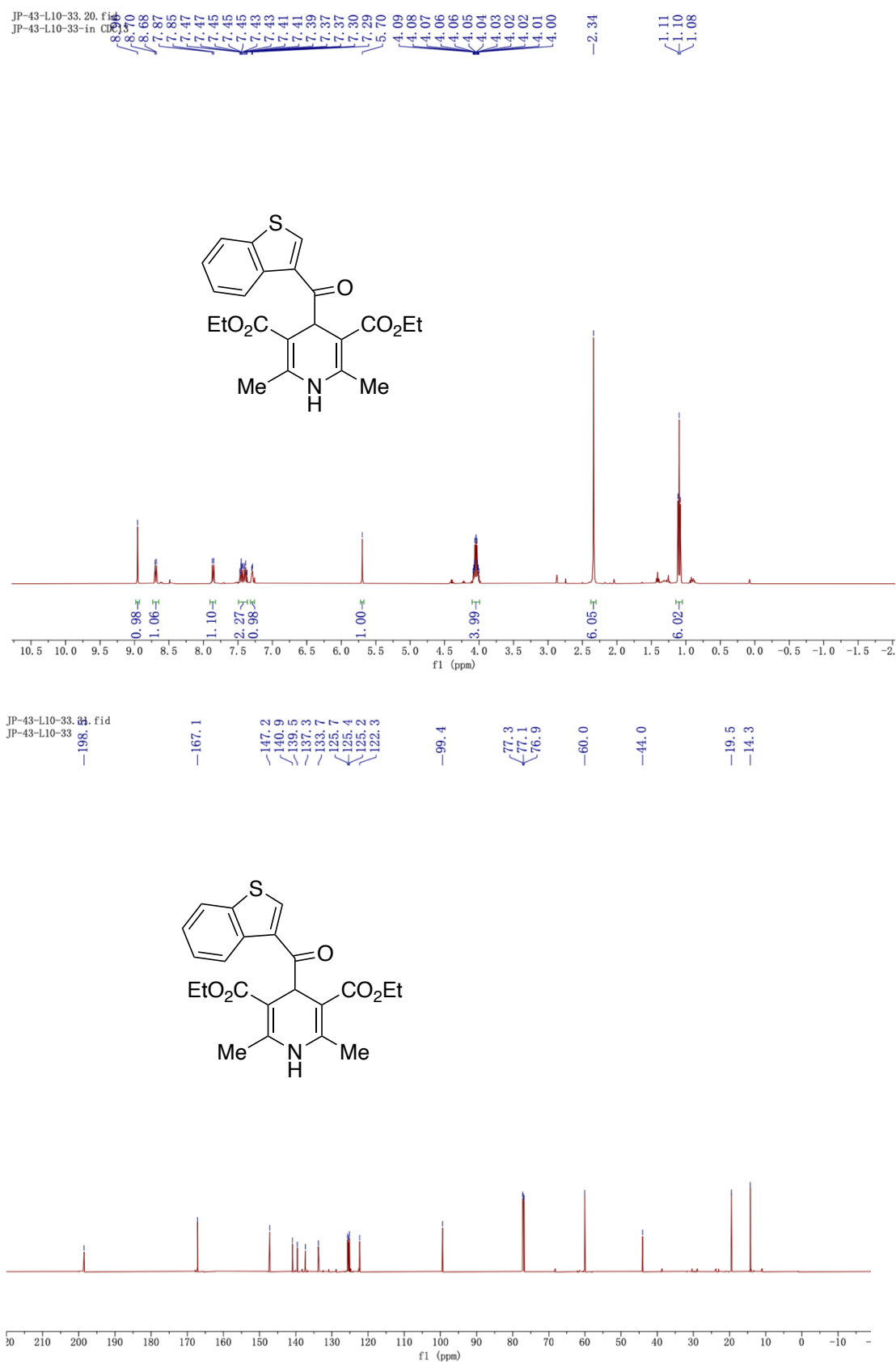


Figure S47. ^1H and ^{13}C NMR spectra of diethyl 2,6-dimethyl-4-pivaloyl-1,4-dihydropyridine-3,5-dicarboxylate (**4o**)

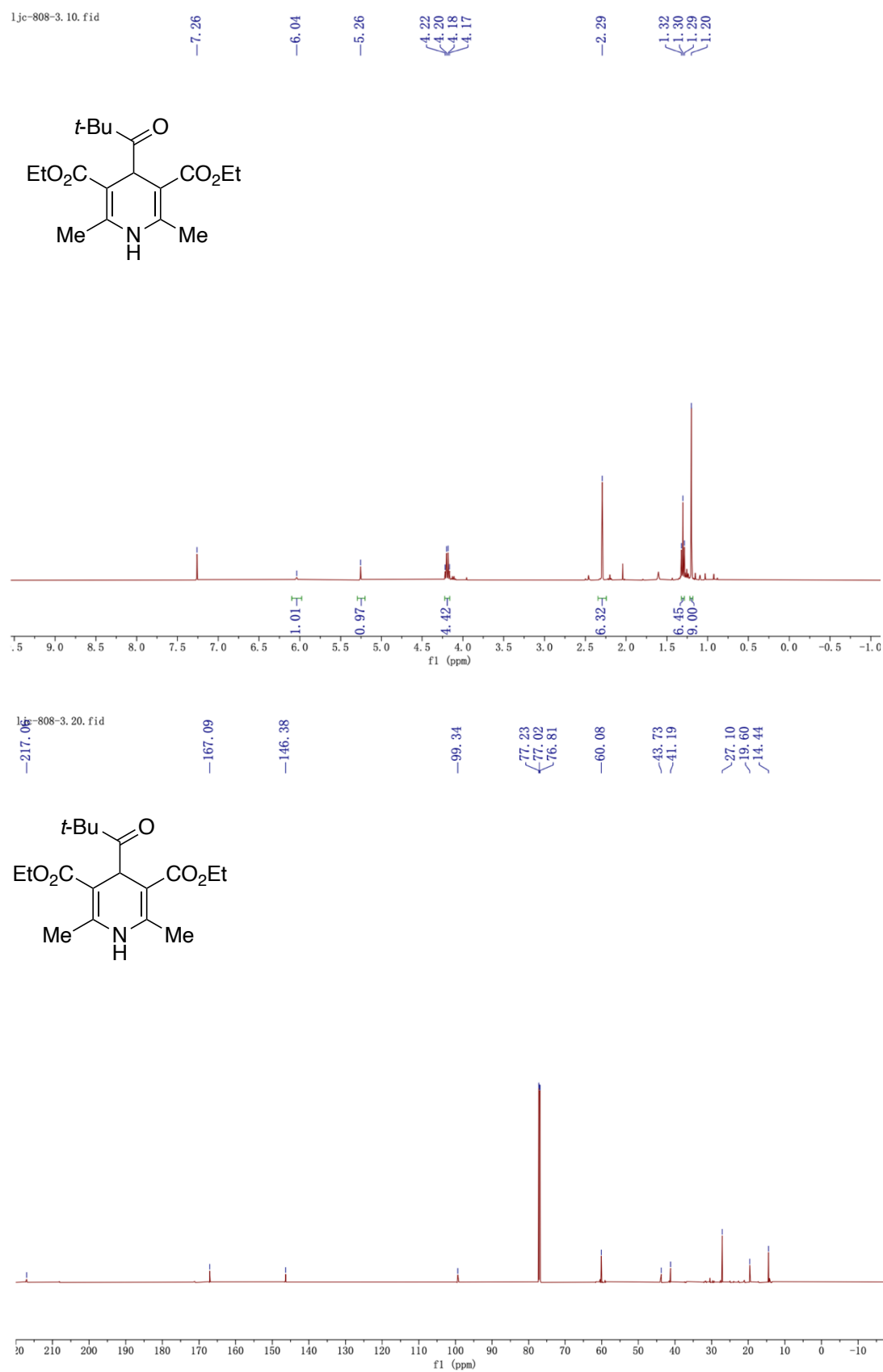


Figure S48. ^1H and ^{13}C NMR spectra of 1-(2-methyl-1-phenylpropyl)pyrazolidin-3-one (**3aa**)

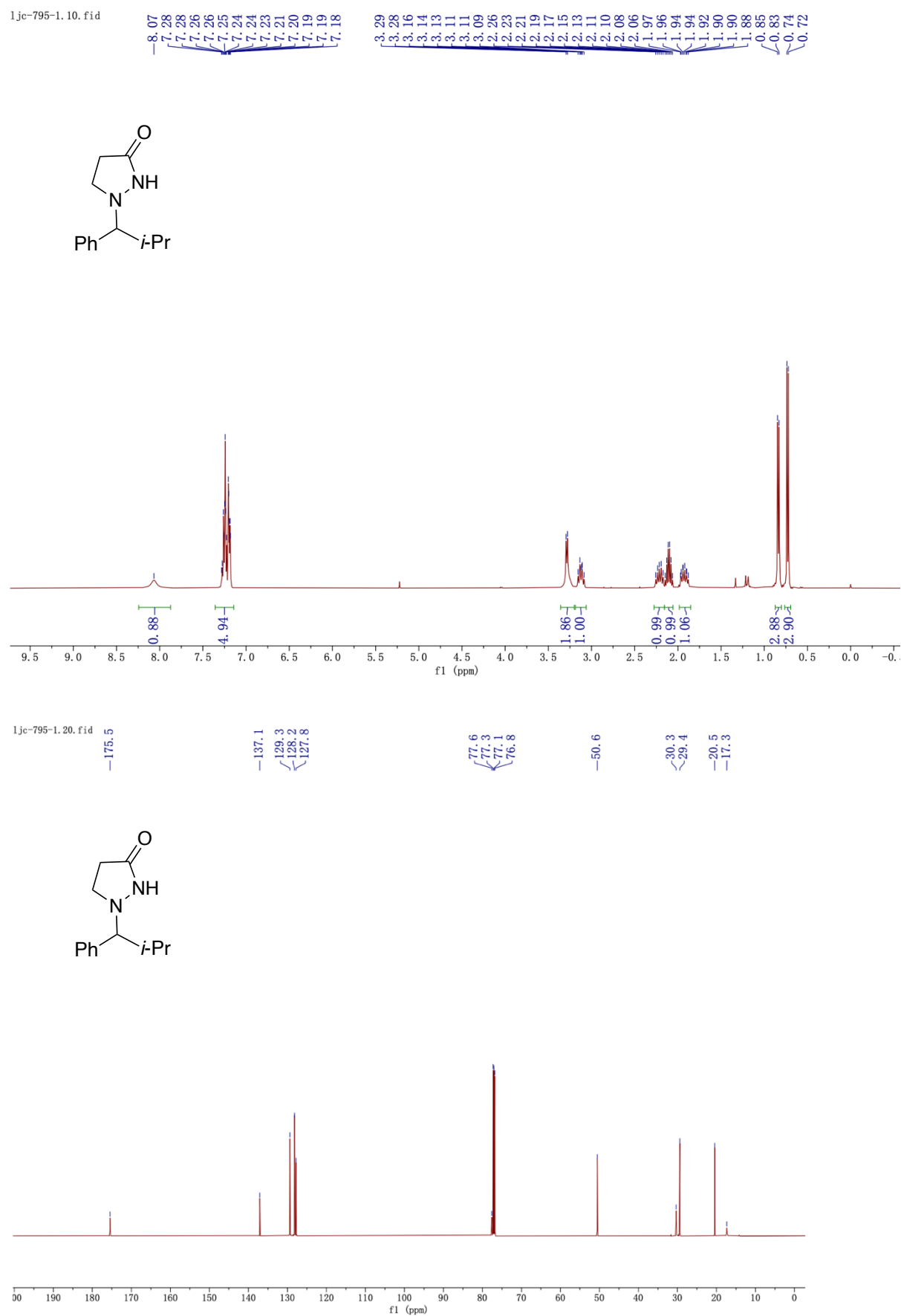


Figure S49. ^1H and ^{13}C NMR spectra of 1-(1-(4-chlorophenyl)-2-methylpropyl)pyrazolidin-3-one (**4ba**)

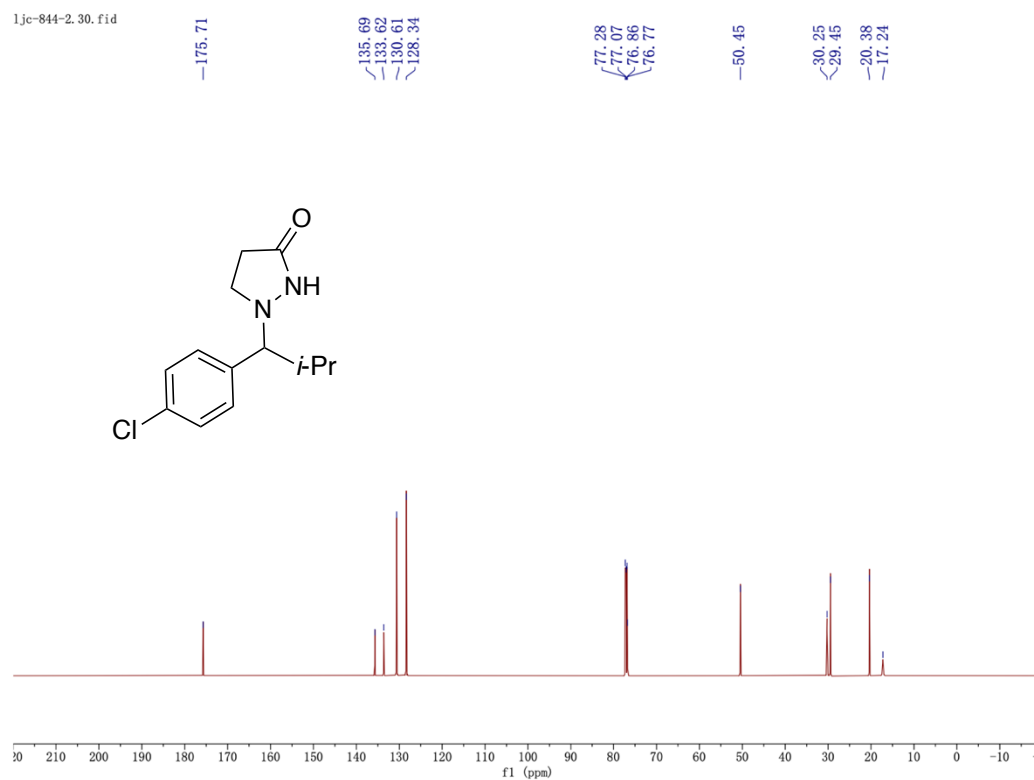
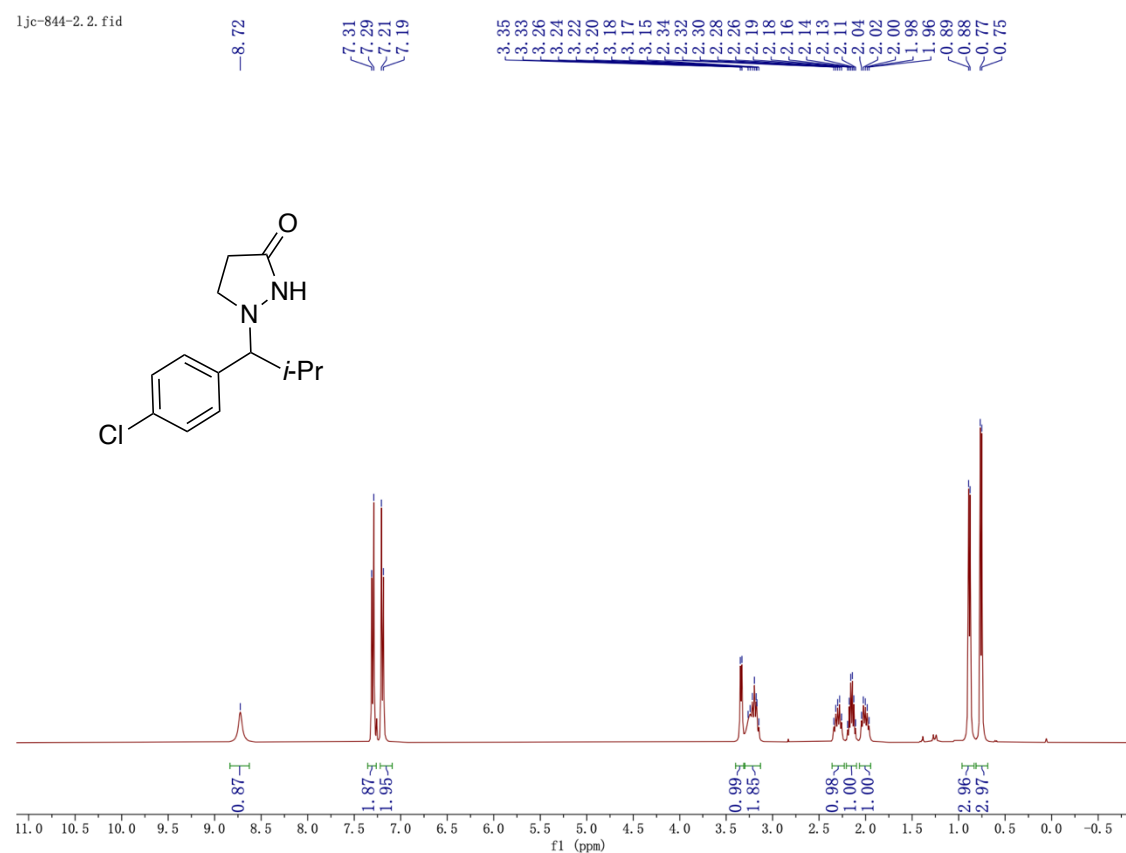
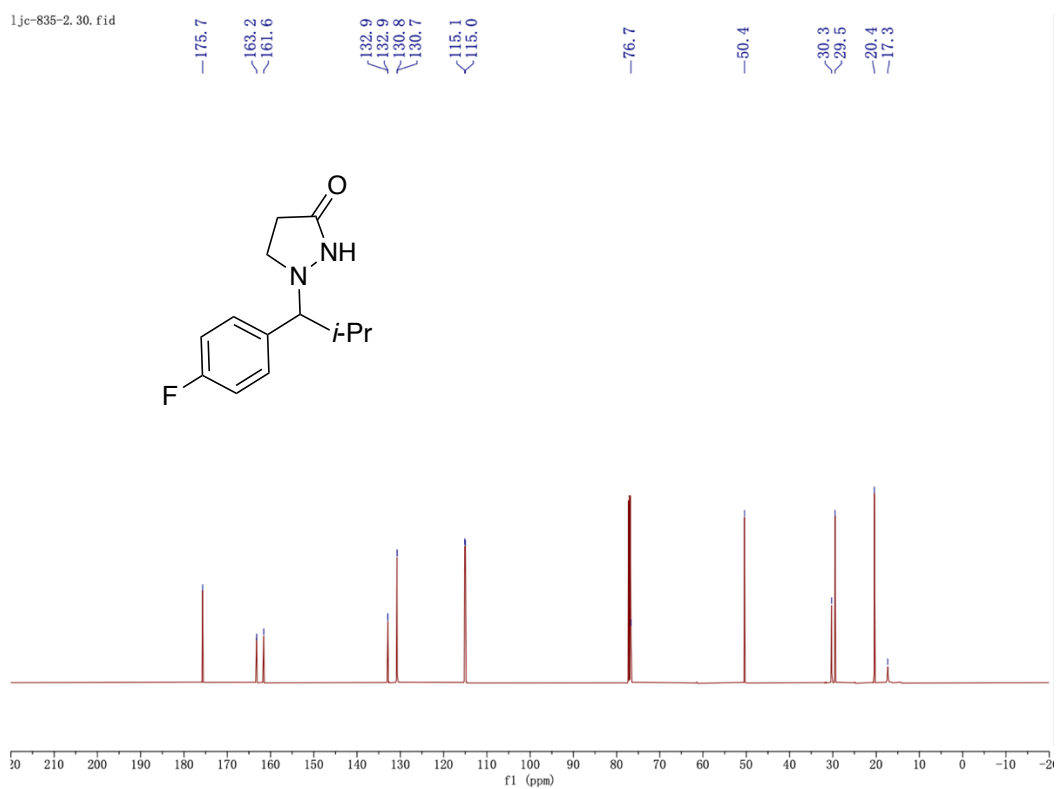
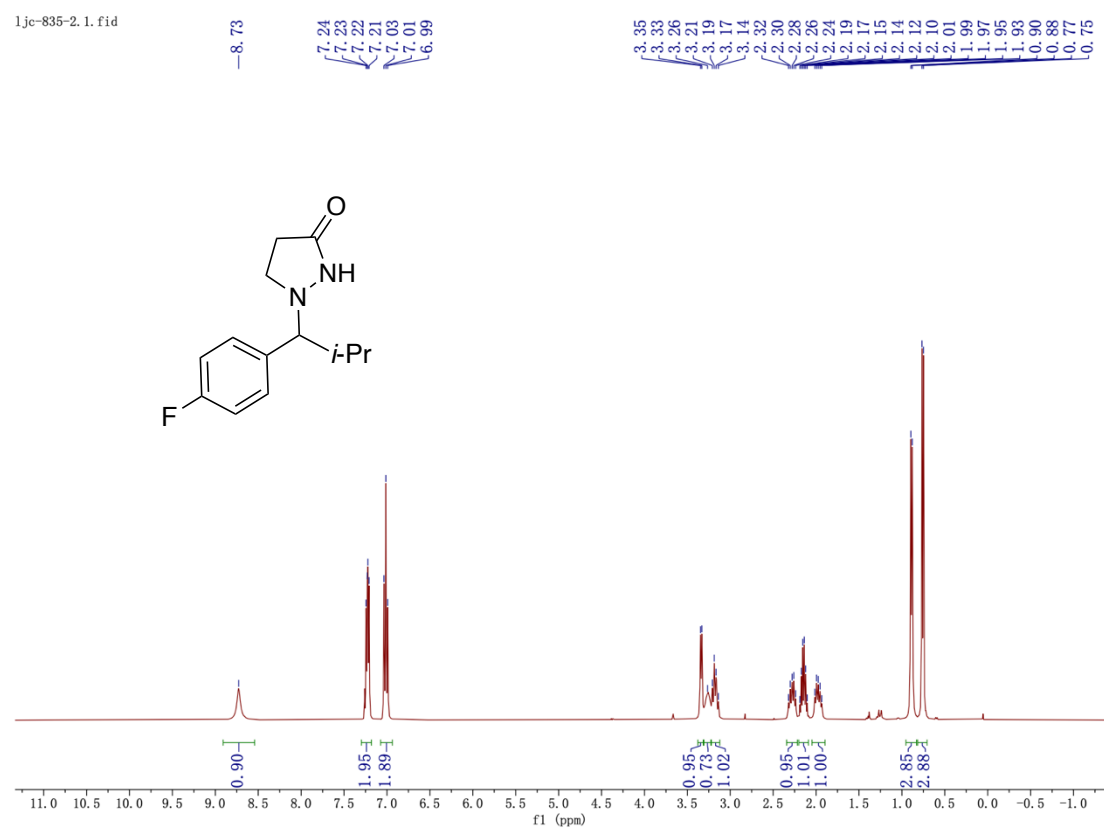


Figure S50. ^1H , ^{13}C and ^{19}F NMR spectra of 1-(1-(4-fluorophenyl)-2-methylpropyl)pyrazolidin-3-one (**4ca**)



ljc-835-2.20.fid
¹⁹F NMR (376 MHz, CDCl₃) δ -114.5.

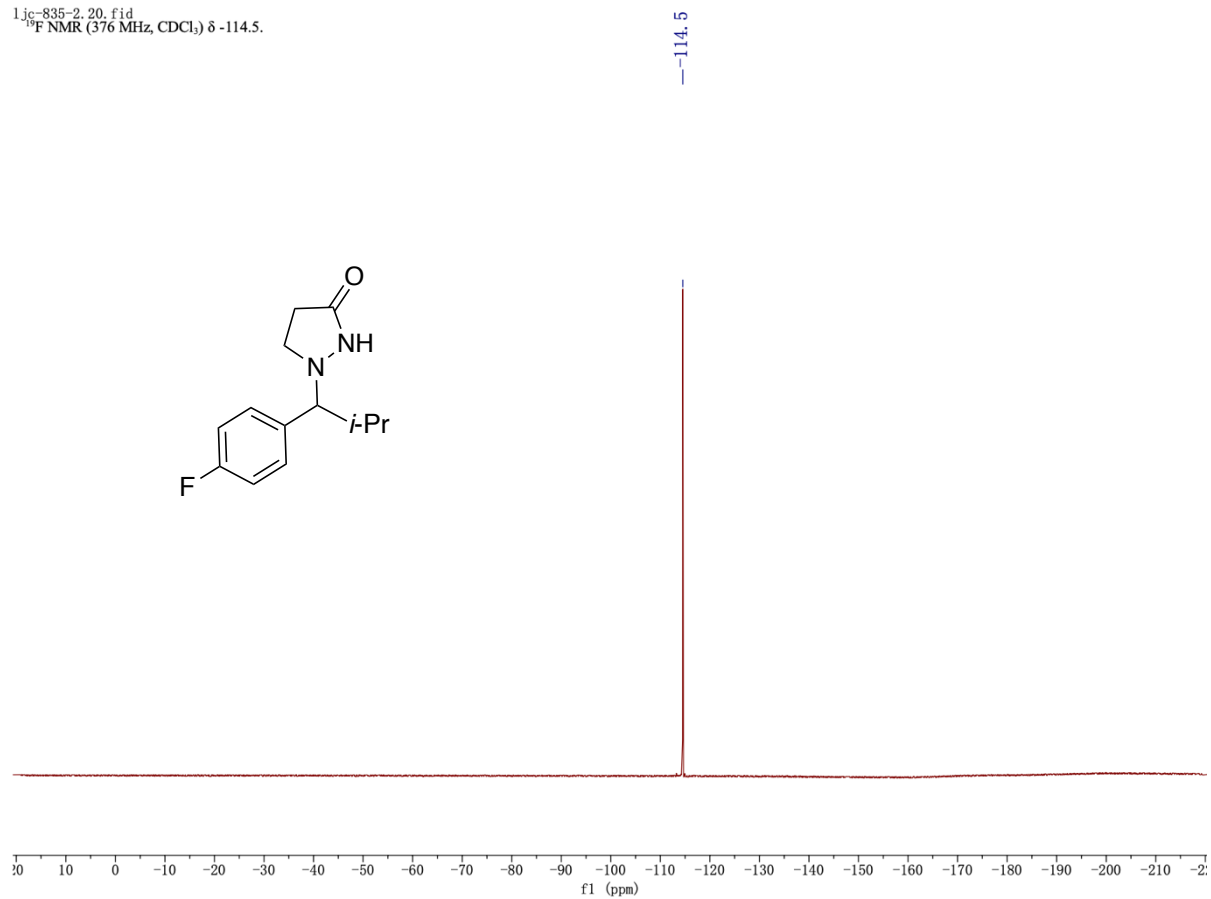
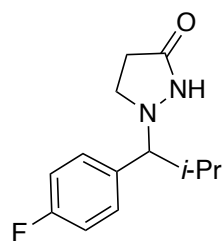
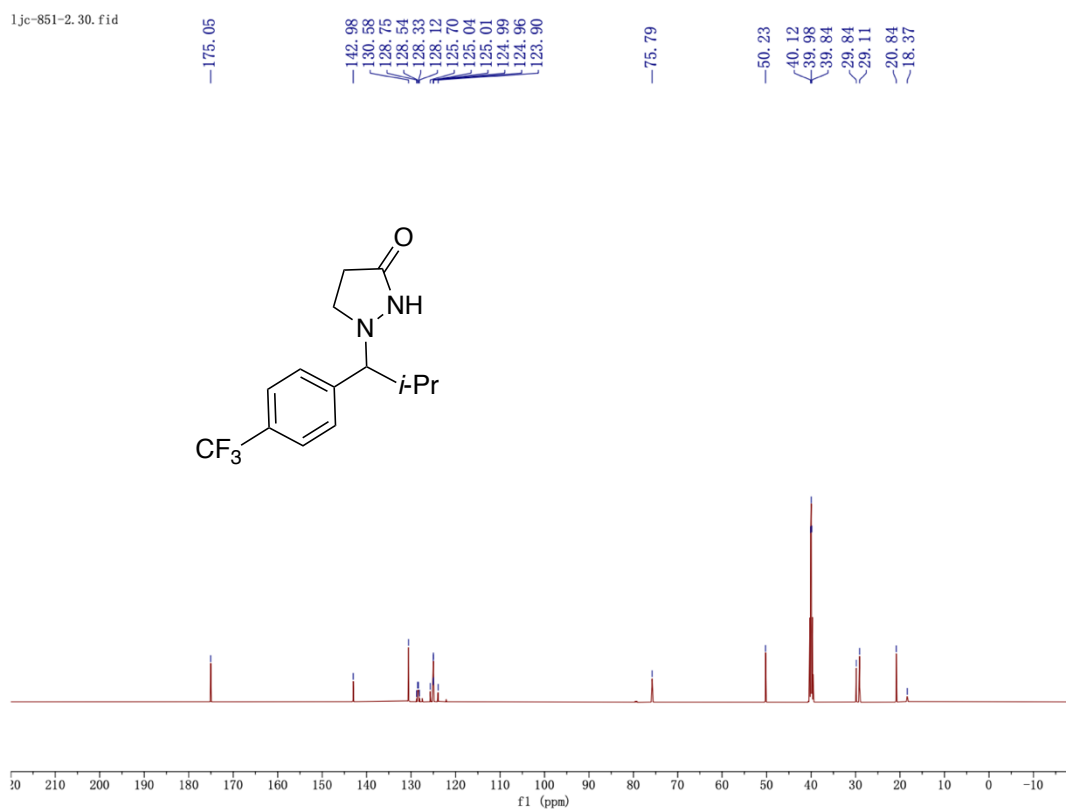
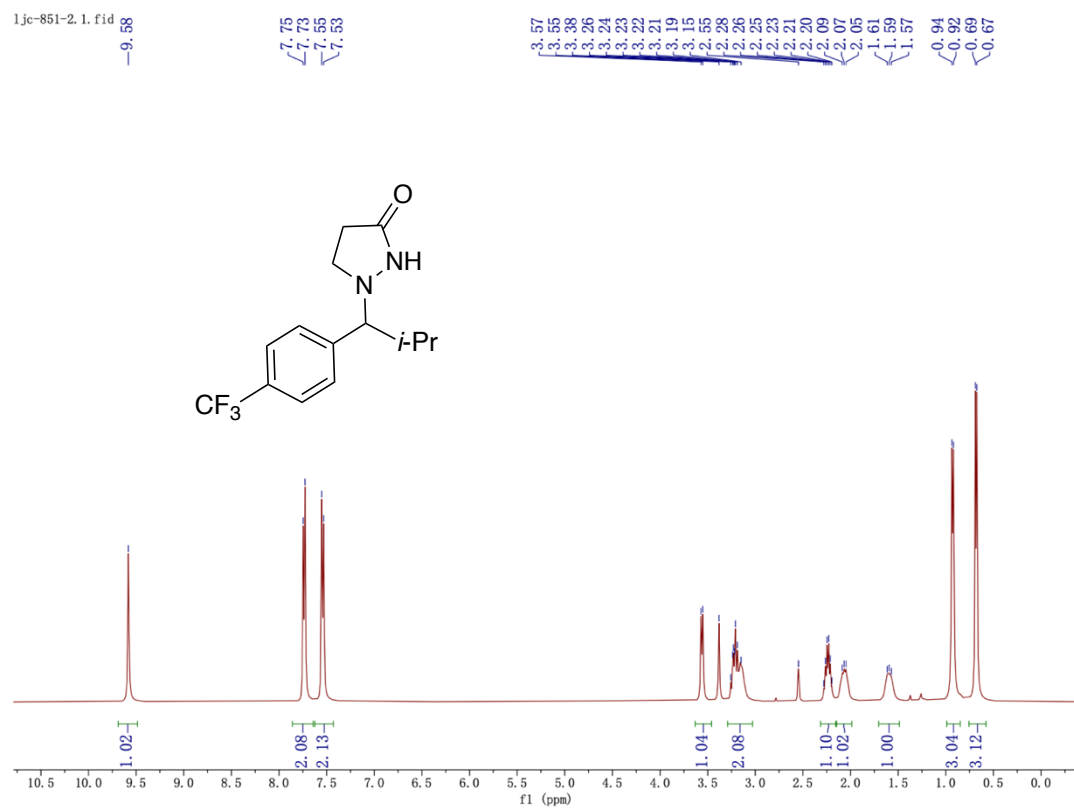


Figure S51. ^1H , ^{13}C and ^{19}F NMR spectra of 1-(2-methyl-1-(4-(trifluoromethyl)phenyl)propyl)pyrazolidin-3-one (**3da**)



ljc-851-2.20.fid

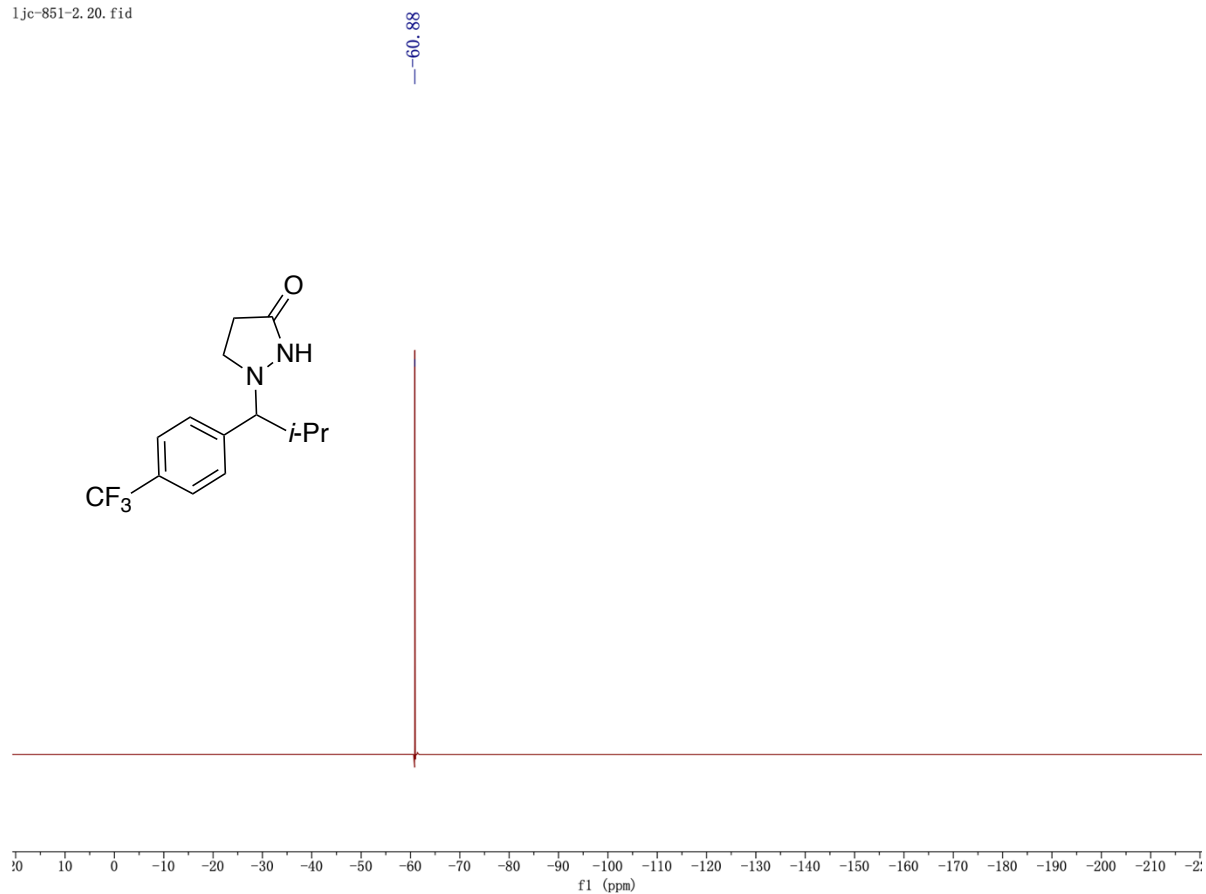


Figure S52. ^1H and ^{13}C NMR spectra of 1-(2-methyl-1-(*p*-tolyl)propyl)pyrazolidin-3-one (**3ea**)

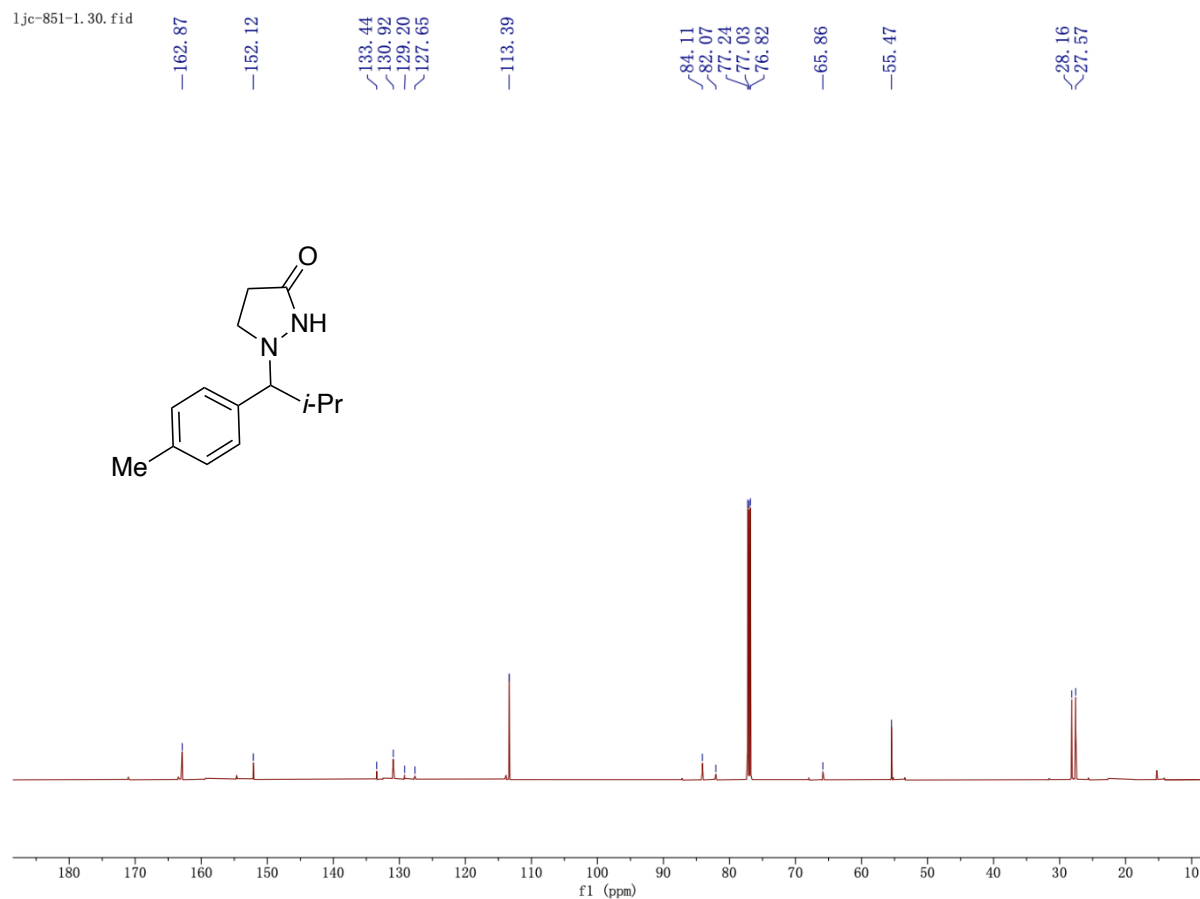
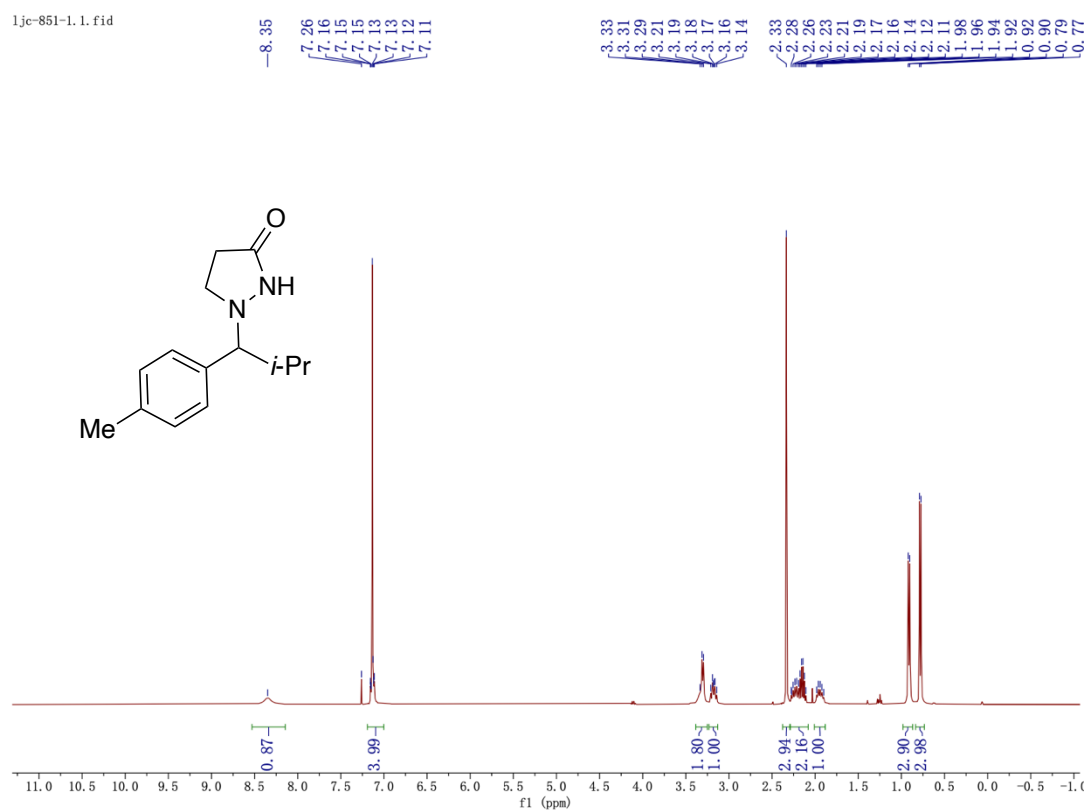


Figure S53. ^1H and ^{13}C NMR spectra of 1-(1-(4-methoxyphenyl)-2-methylpropyl)pyrazolidin-3-one (**3fa**)

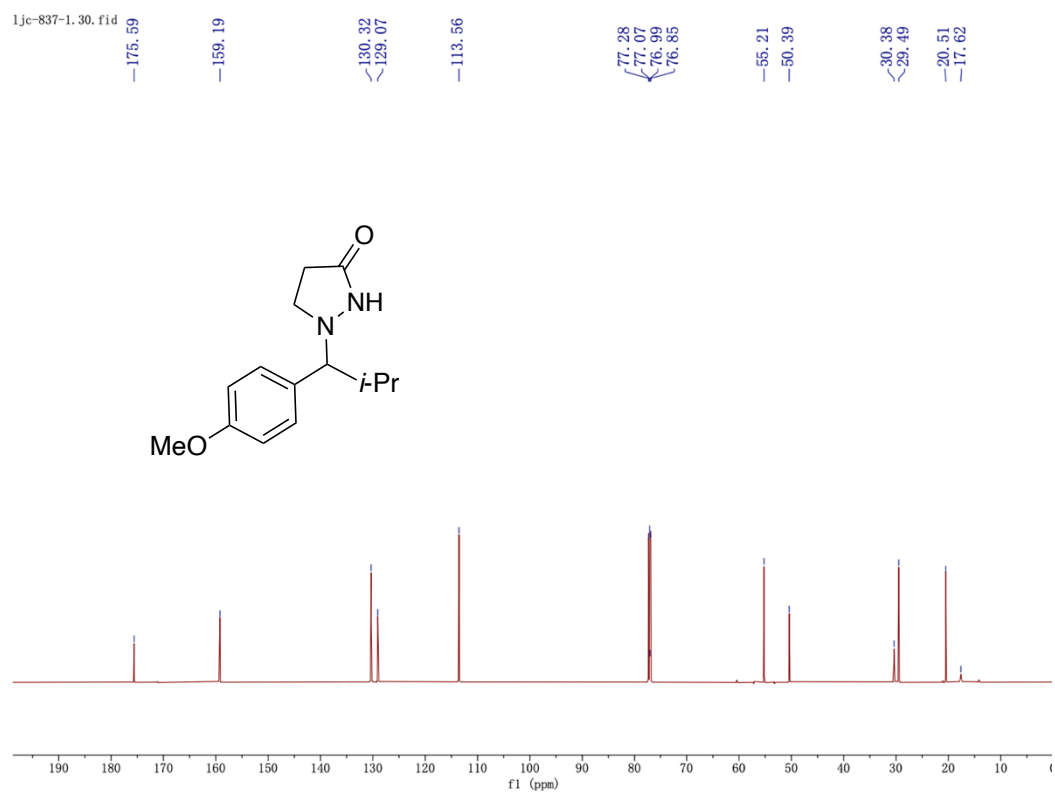
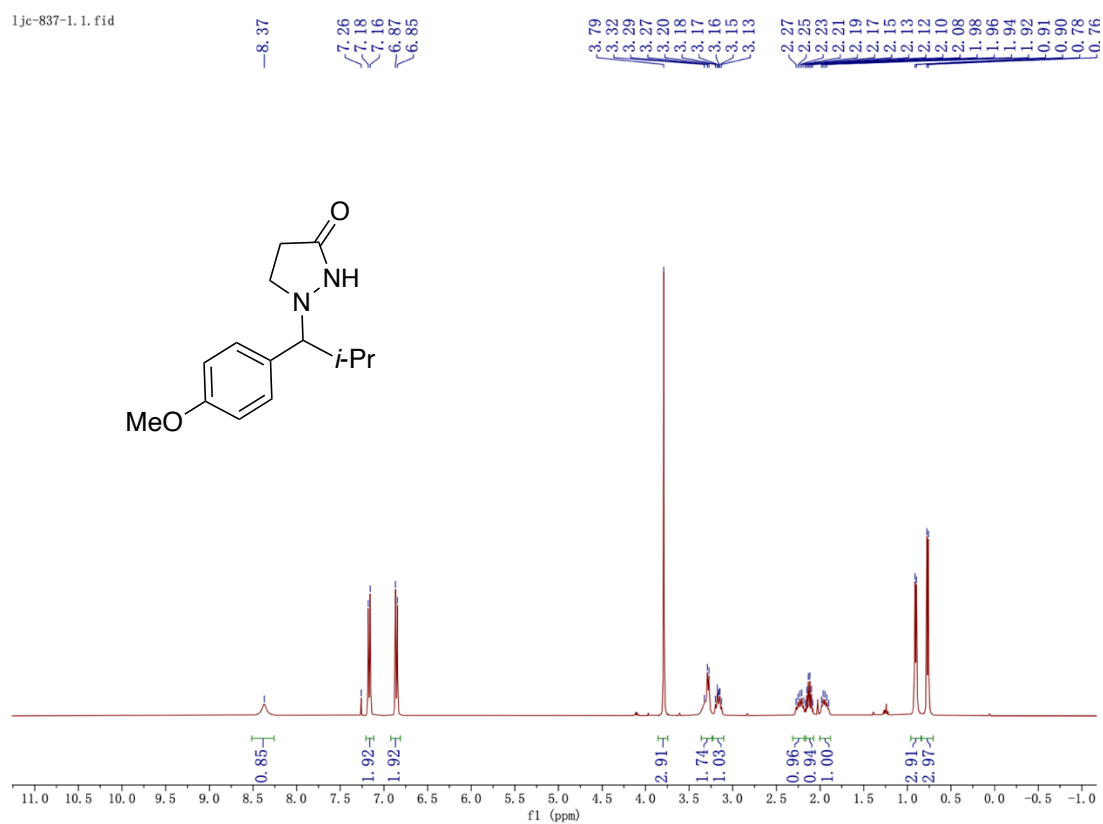


Figure S54. ^1H and ^{13}C NMR spectra of 1-(2-methyl-1-(naphthalen-2-yl)propyl)pyrazolidin-3-one (**3ga**)

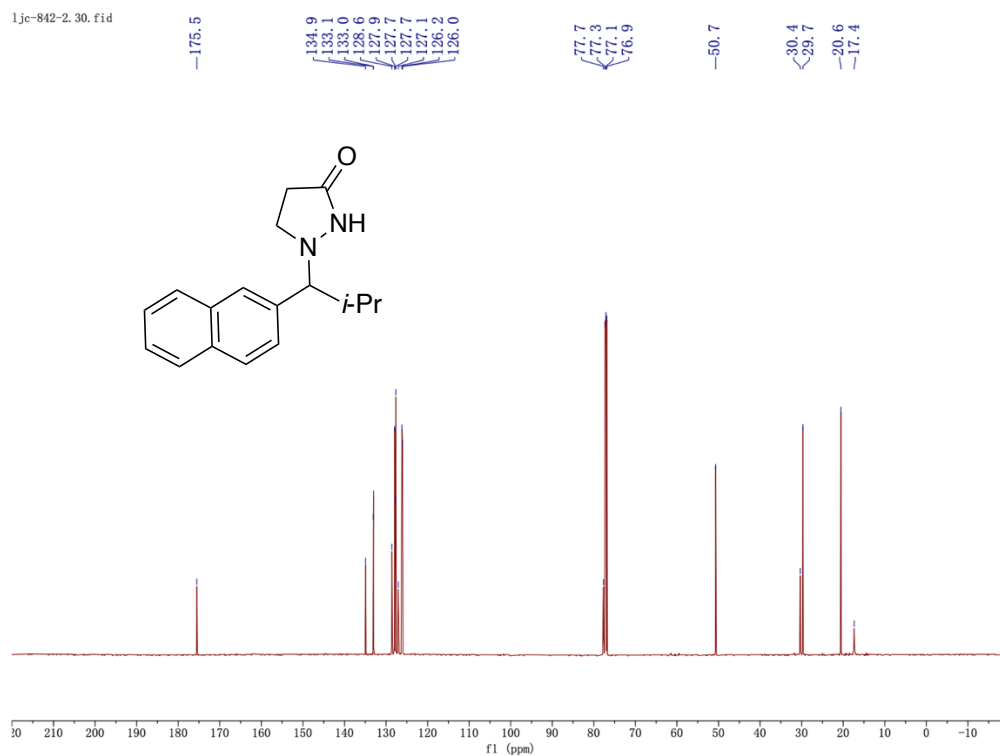
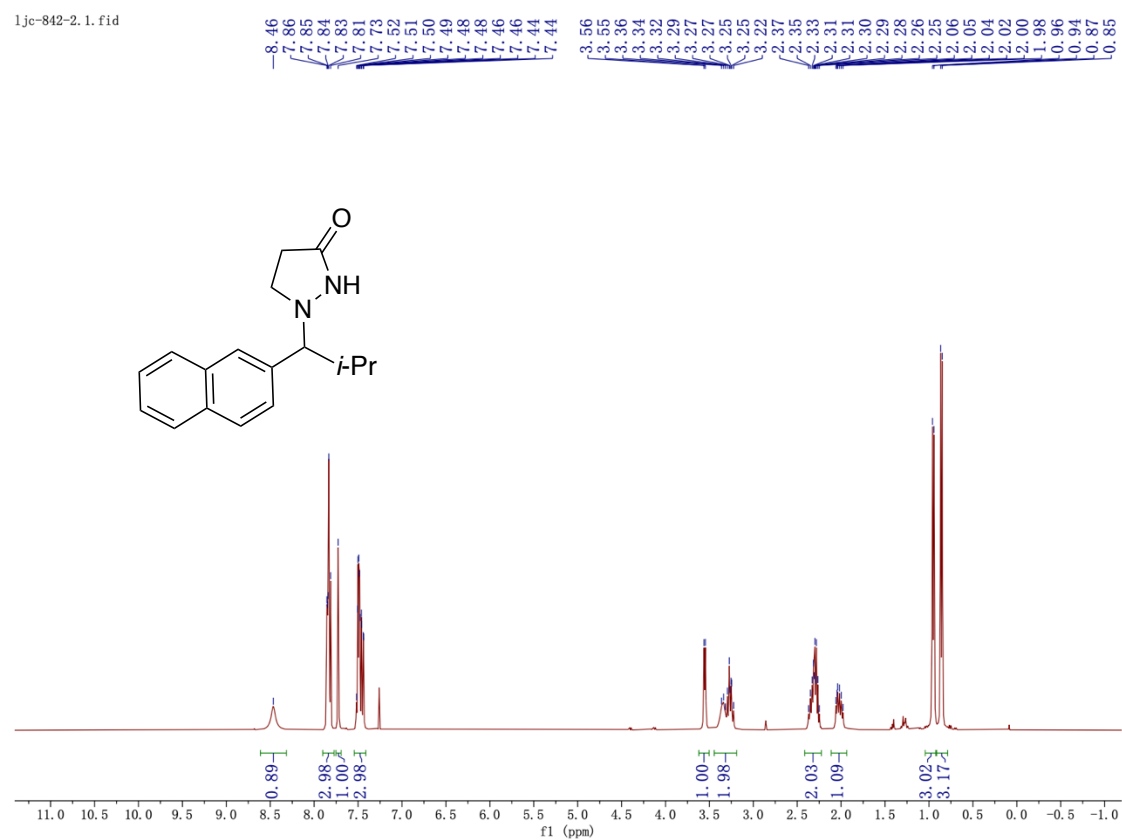


Figure S55. ^1H and ^{13}C NMR spectra of 1-(2-methyl-1-(pyridin-2-yl)propyl)pyrazolidin-3-one
(3ha)

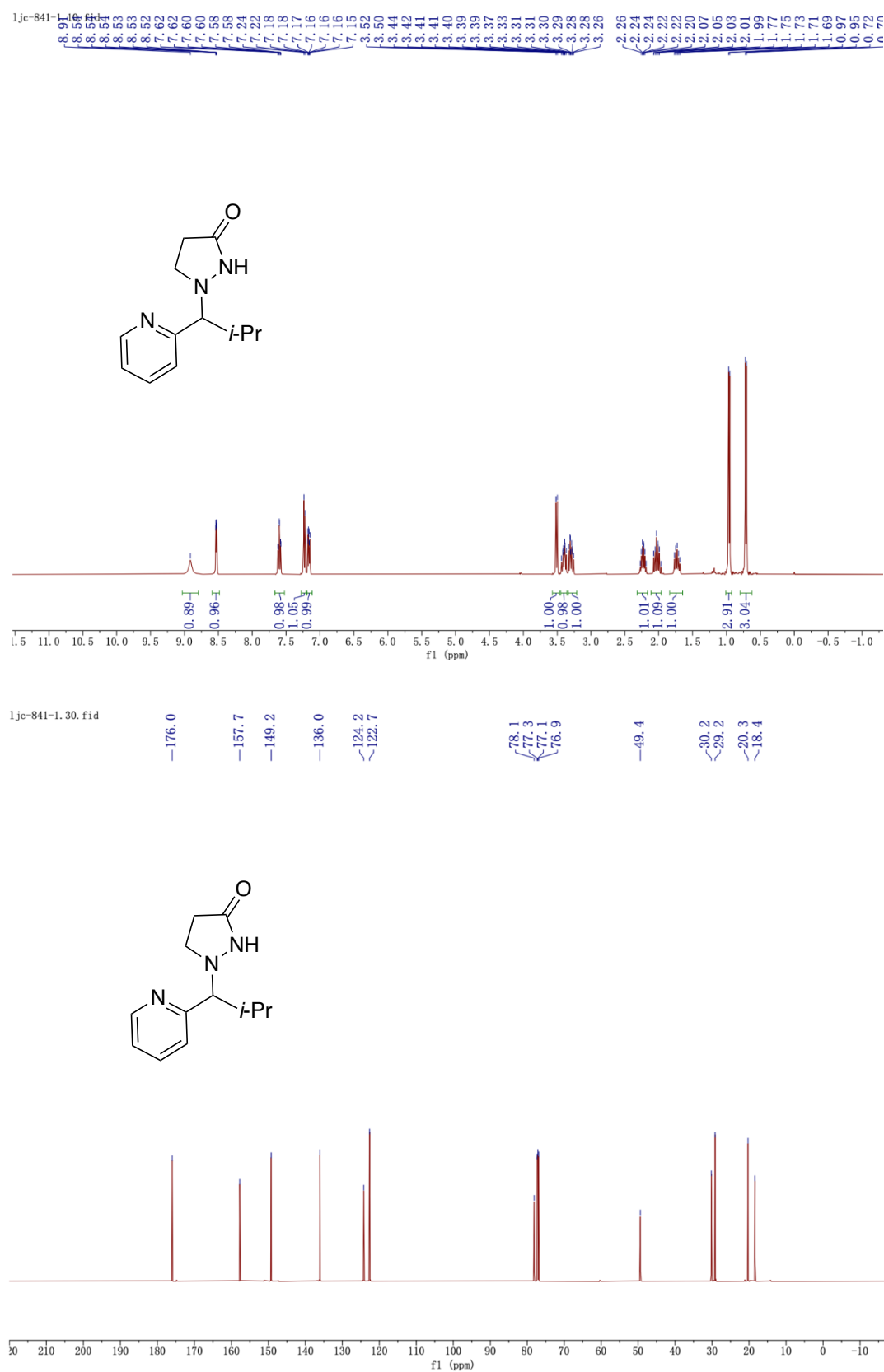


Figure S56. ^1H and ^{13}C NMR spectra of 1-(2-methyl-1-(pyridin-3-yl)propyl)pyrazolidin-3-one
(3ia)

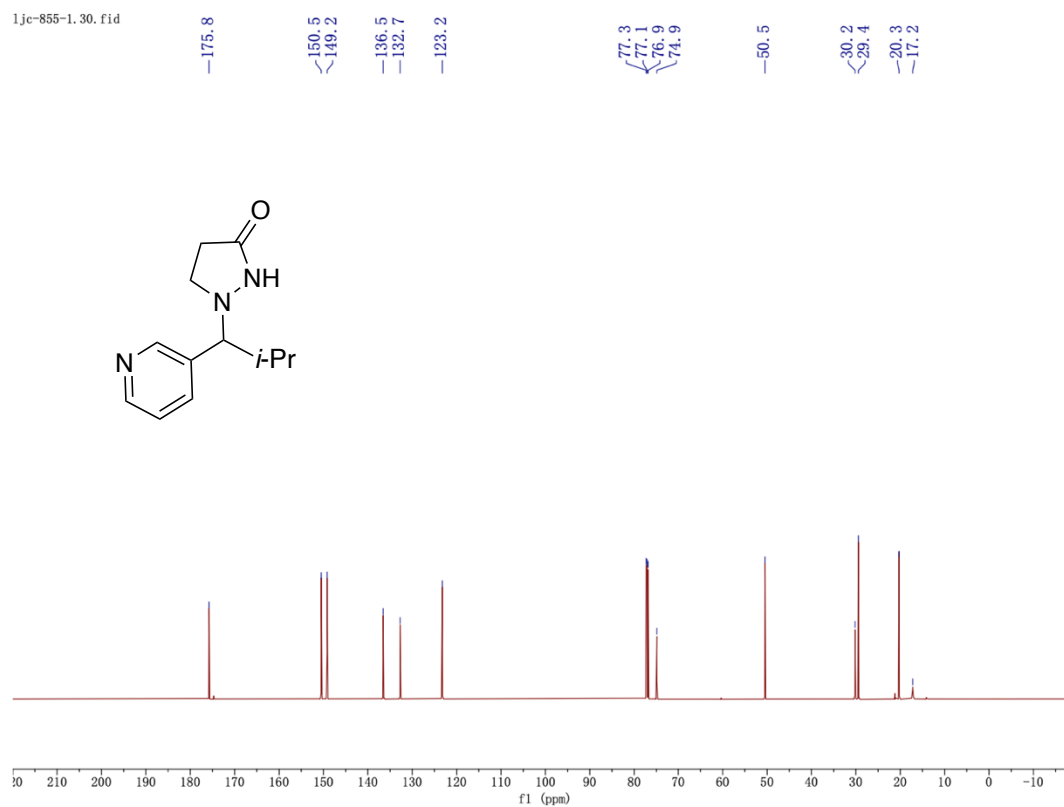
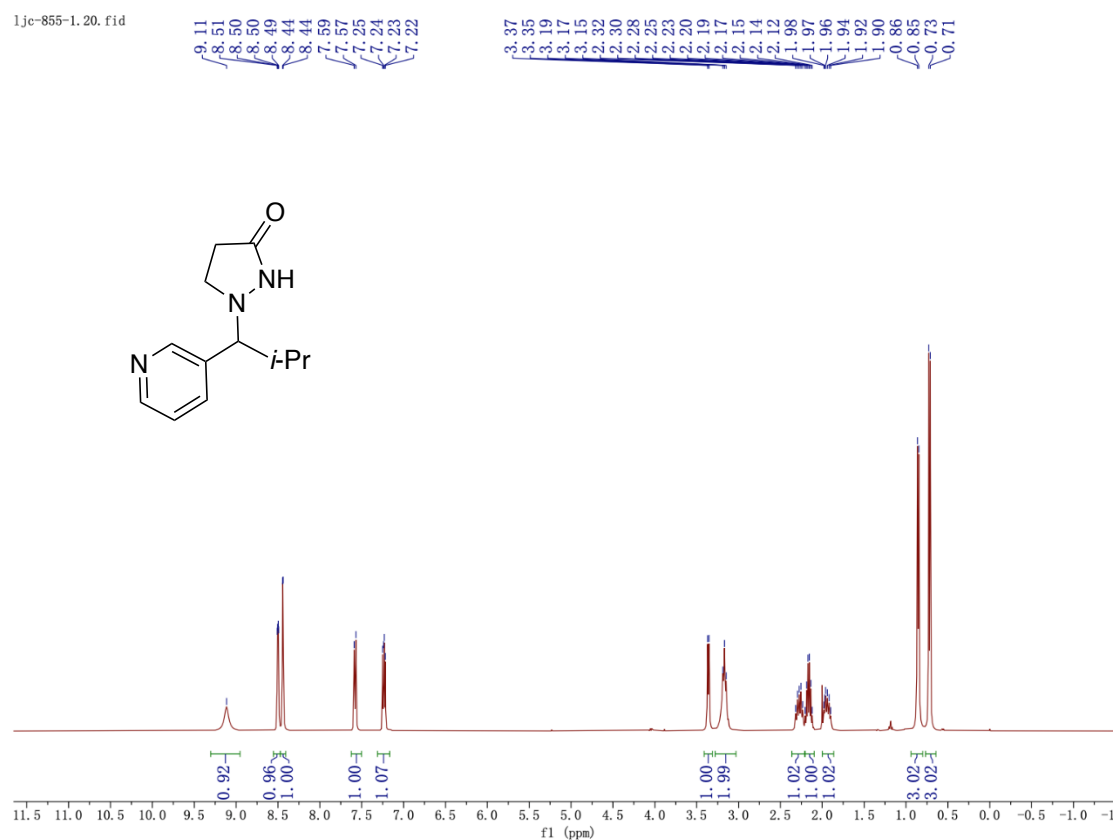


Figure S57. ^1H and ^{13}C NMR spectra of 1-(1-(furan-2-yl)-2-methylpropyl)pyrazolidin-3-one
(3ja)

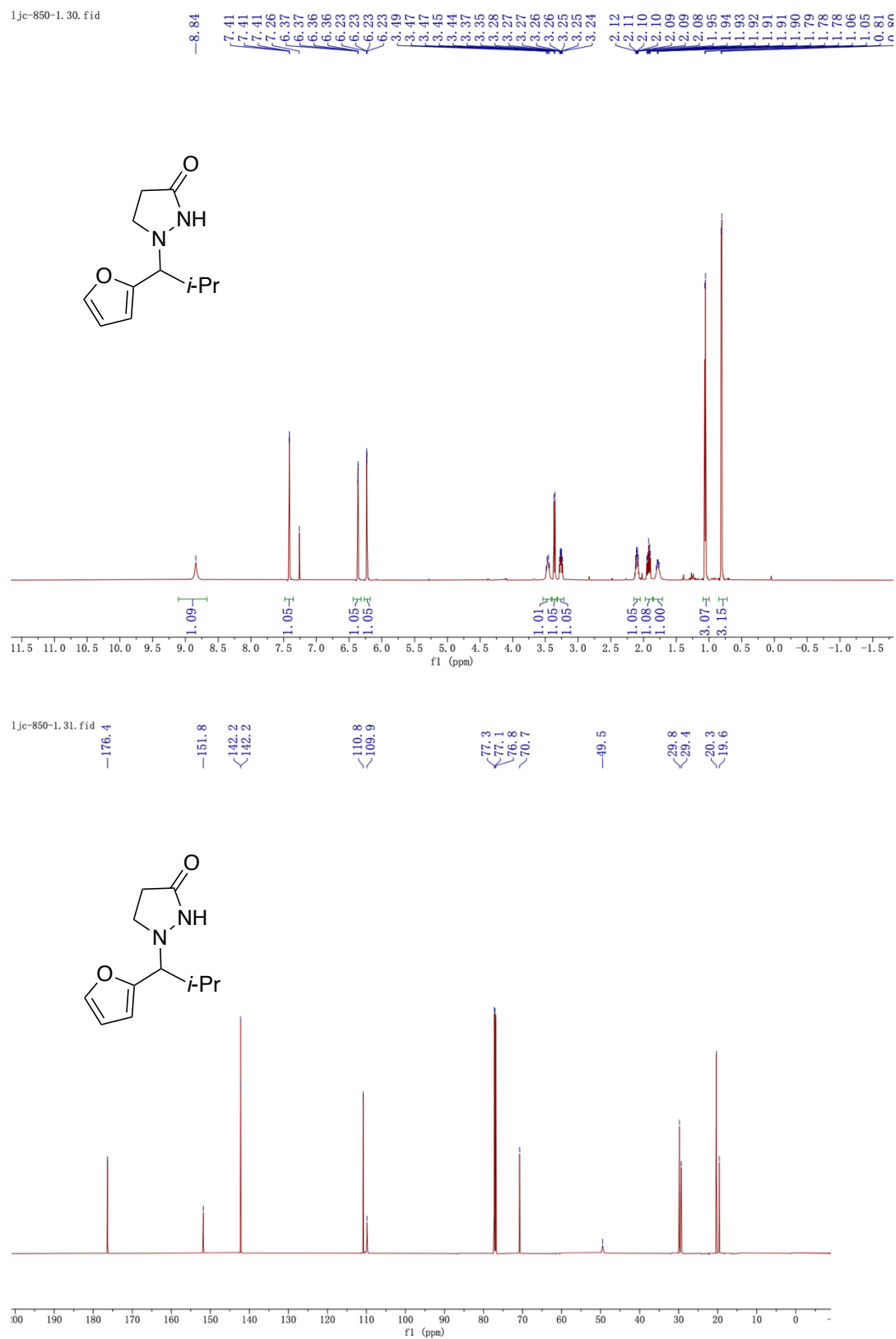


Figure S58. ^1H and ^{13}C NMR spectra of 1-(2-methyl-1-(thiophen-2-yl)propyl)pyrazolidin-3-one (**3ka**)

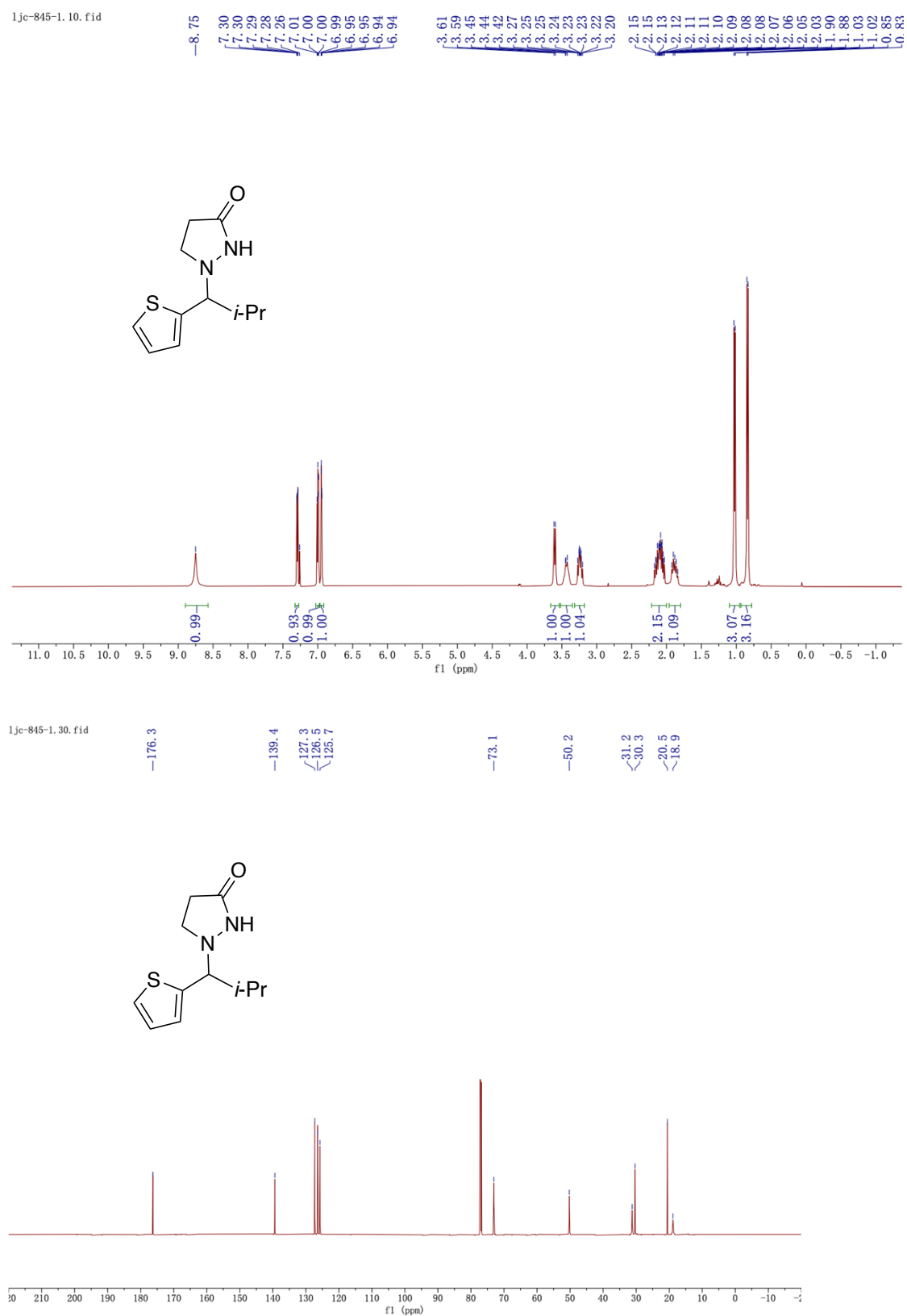


Figure S59. ^1H and ^{13}C NMR spectra of 1-(1-(benzofuran-2-yl)-2-methylpropyl)pyrazolidin-3-one (**3la**)

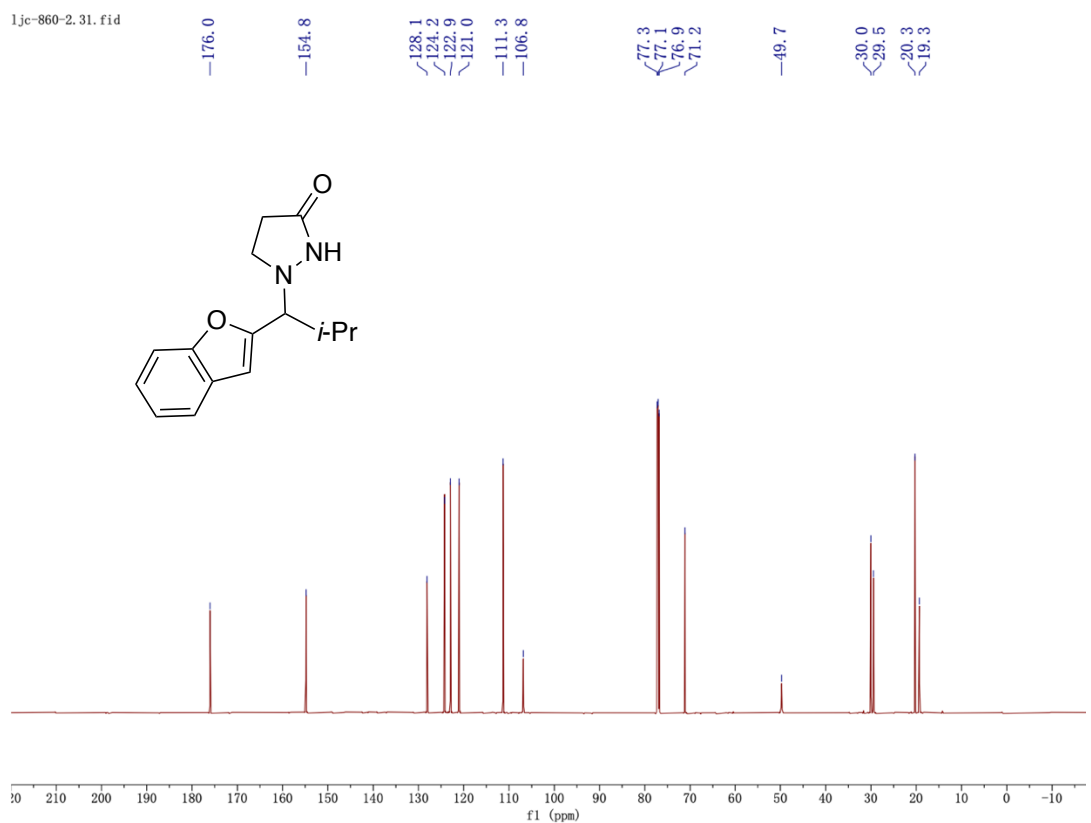
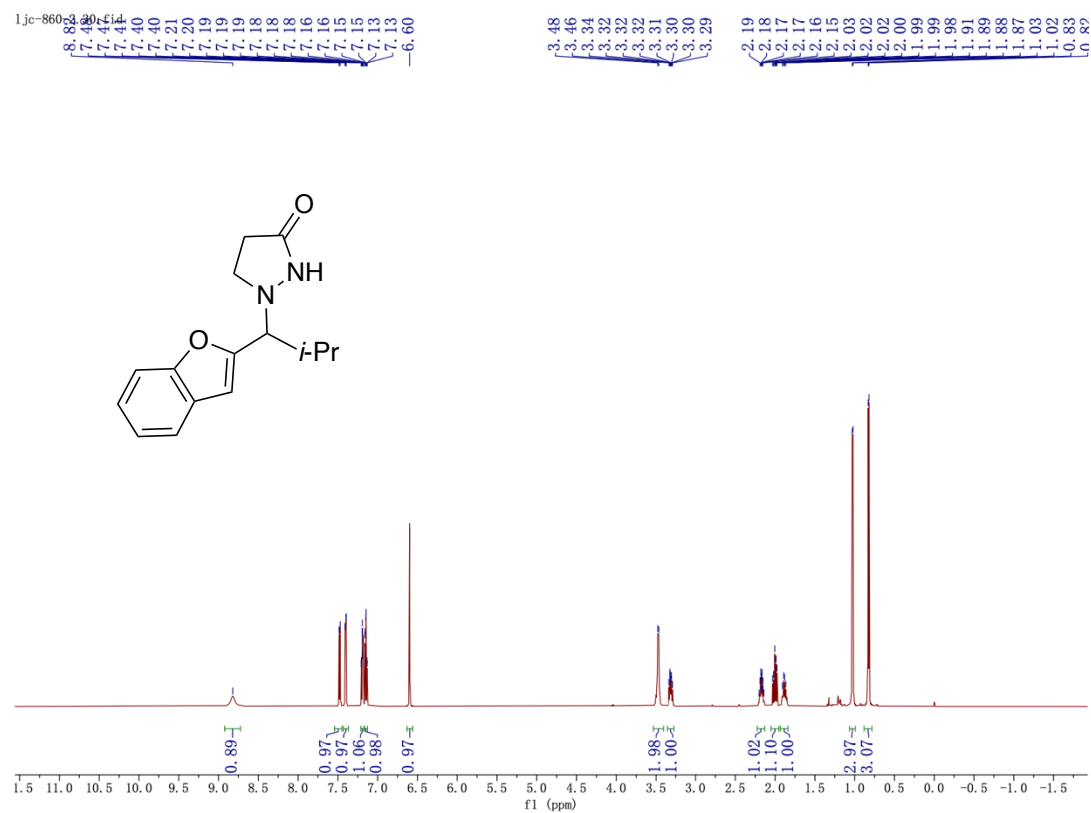
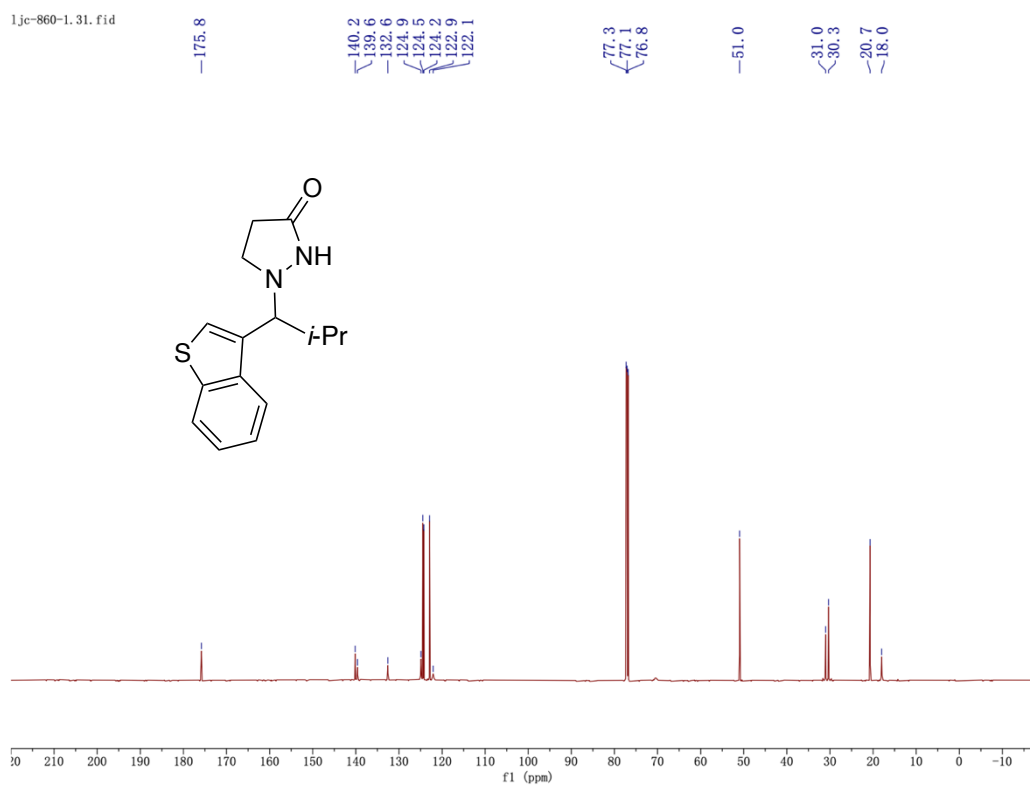
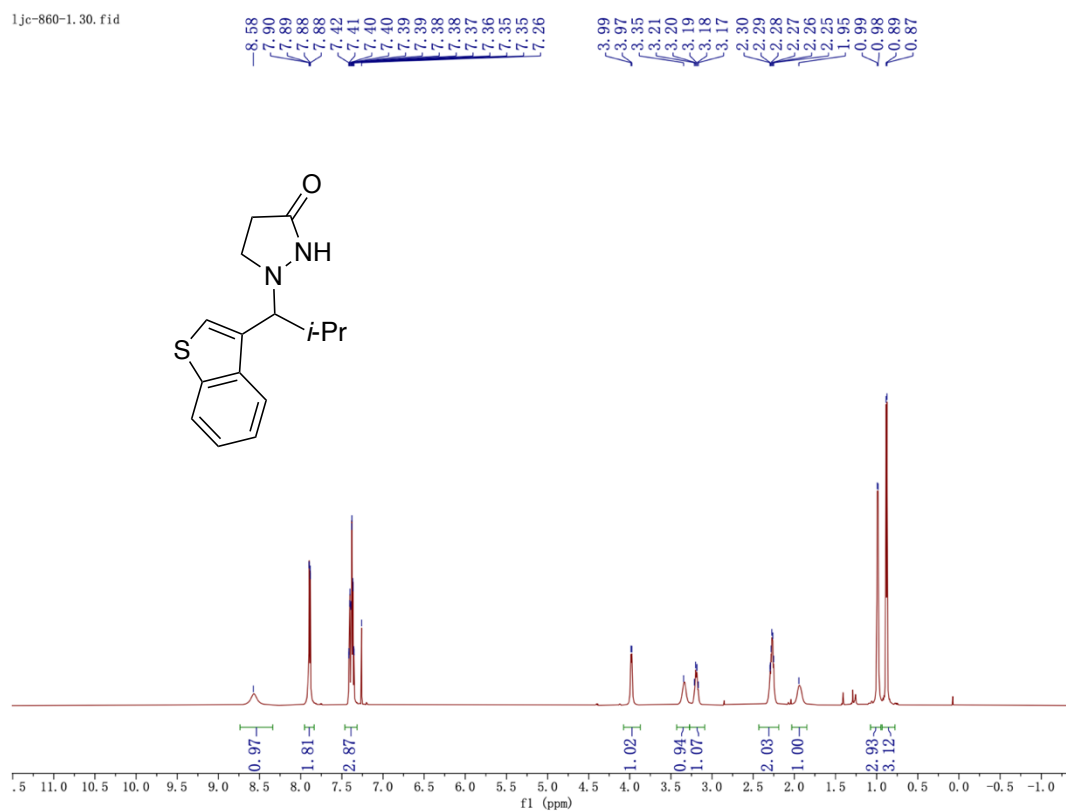


Figure S60. ^1H and ^{13}C NMR spectra of 1-(1-(benzo[*b*]thiophen-3-yl)-2-methylpropyl)pyrazolidin-3-one (**3ma**)



(3na)

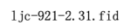


Figure S62. ^1H and ^{13}C NMR spectra of 1-(2,4-dimethylhexan-3-yl)pyrazolidin-3-one (**30a**)

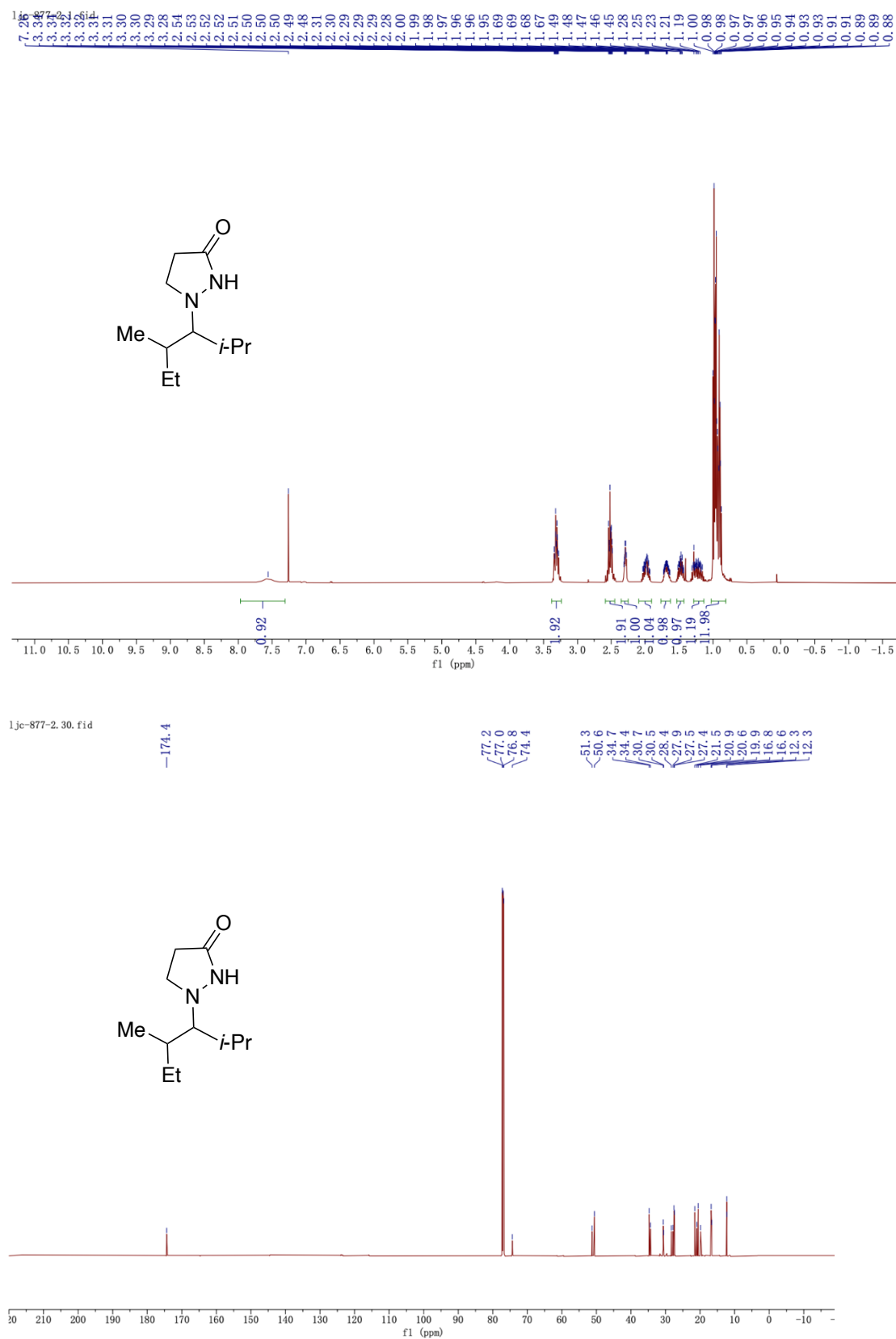


Figure S63. ^1H and ^{13}C NMR spectra of 1-(2-methylheptan-3-yl)pyrazolidin-3-one (**3pa**)

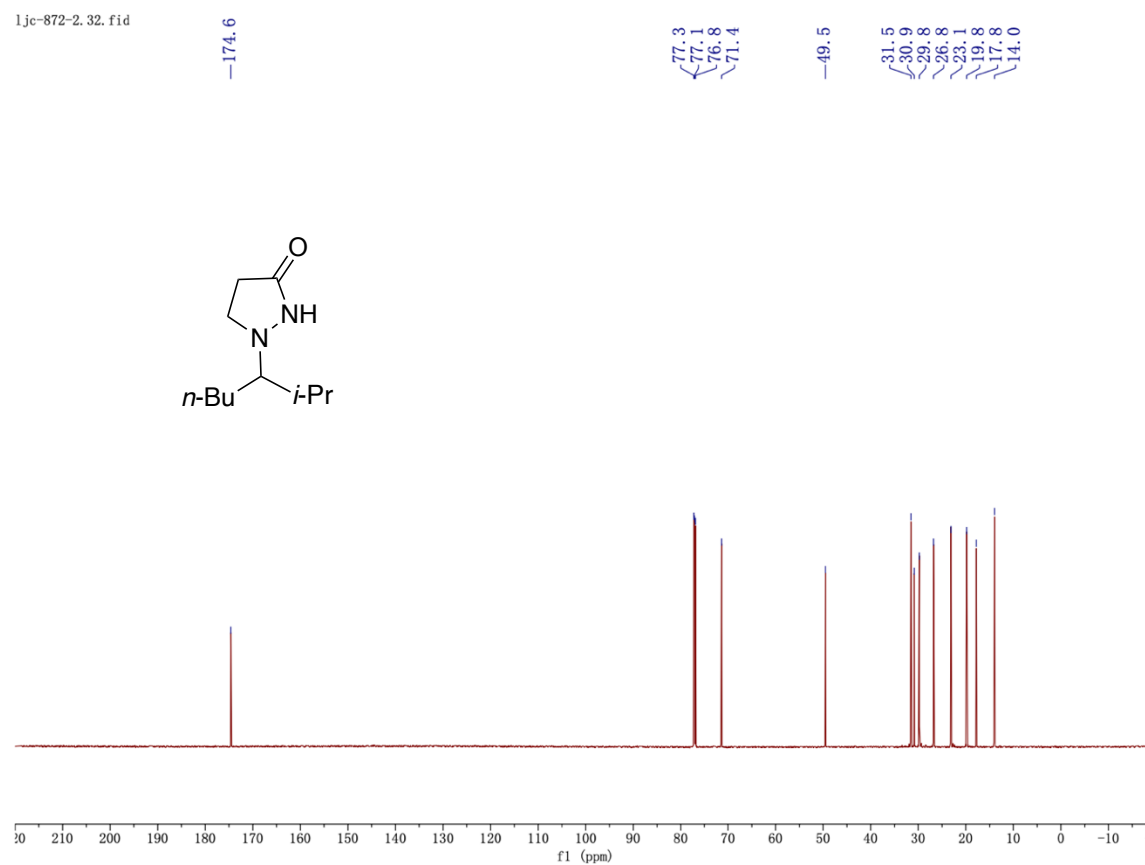
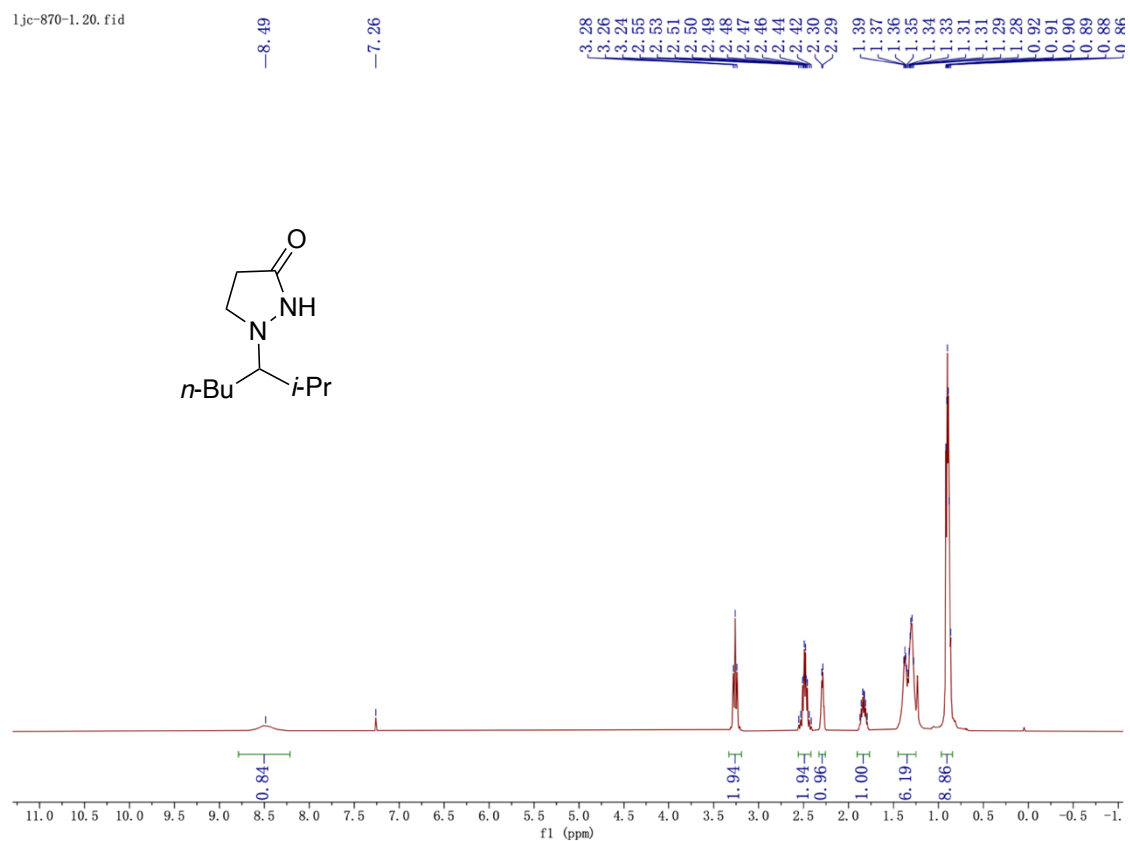


Figure S64. ^1H and ^{13}C NMR spectra of 1-(1-cyclohexyl-2-methylpropyl)pyrazolidin-3-one
(3qa)

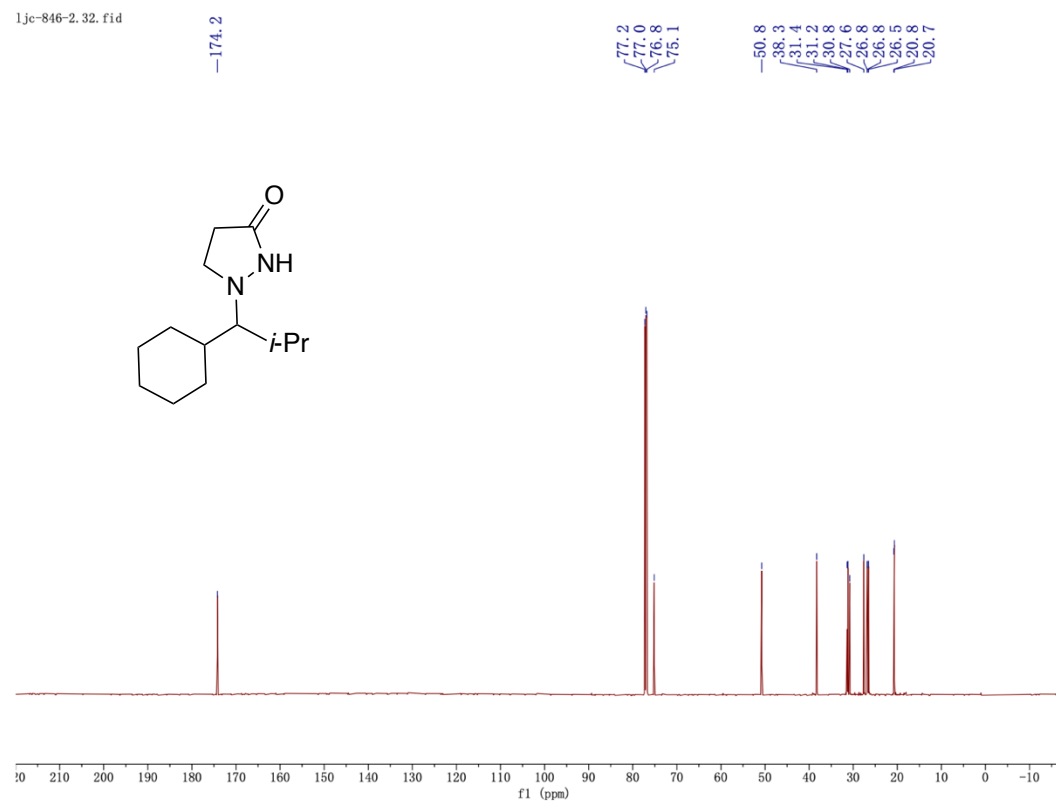
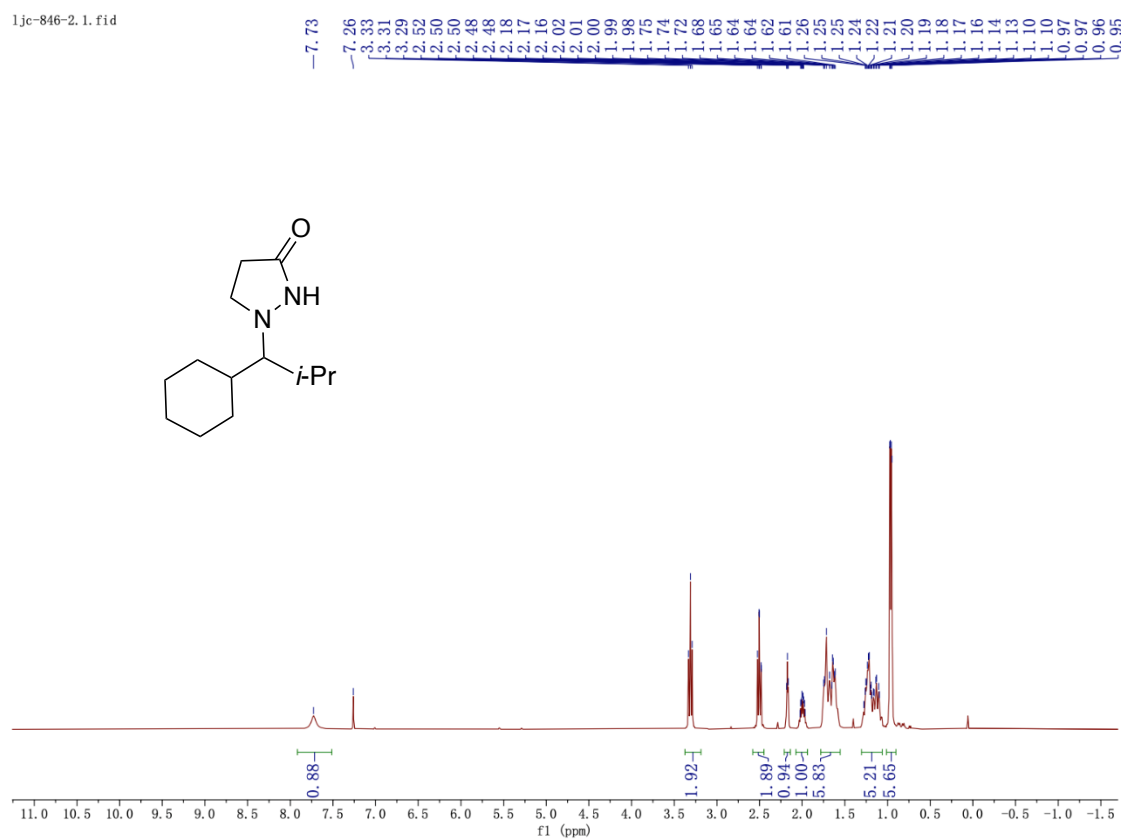


Figure S65. ^1H and ^{13}C NMR spectra of 1-(1,2-diphenylethyl)pyrazolidin-3-one (**3ab**)

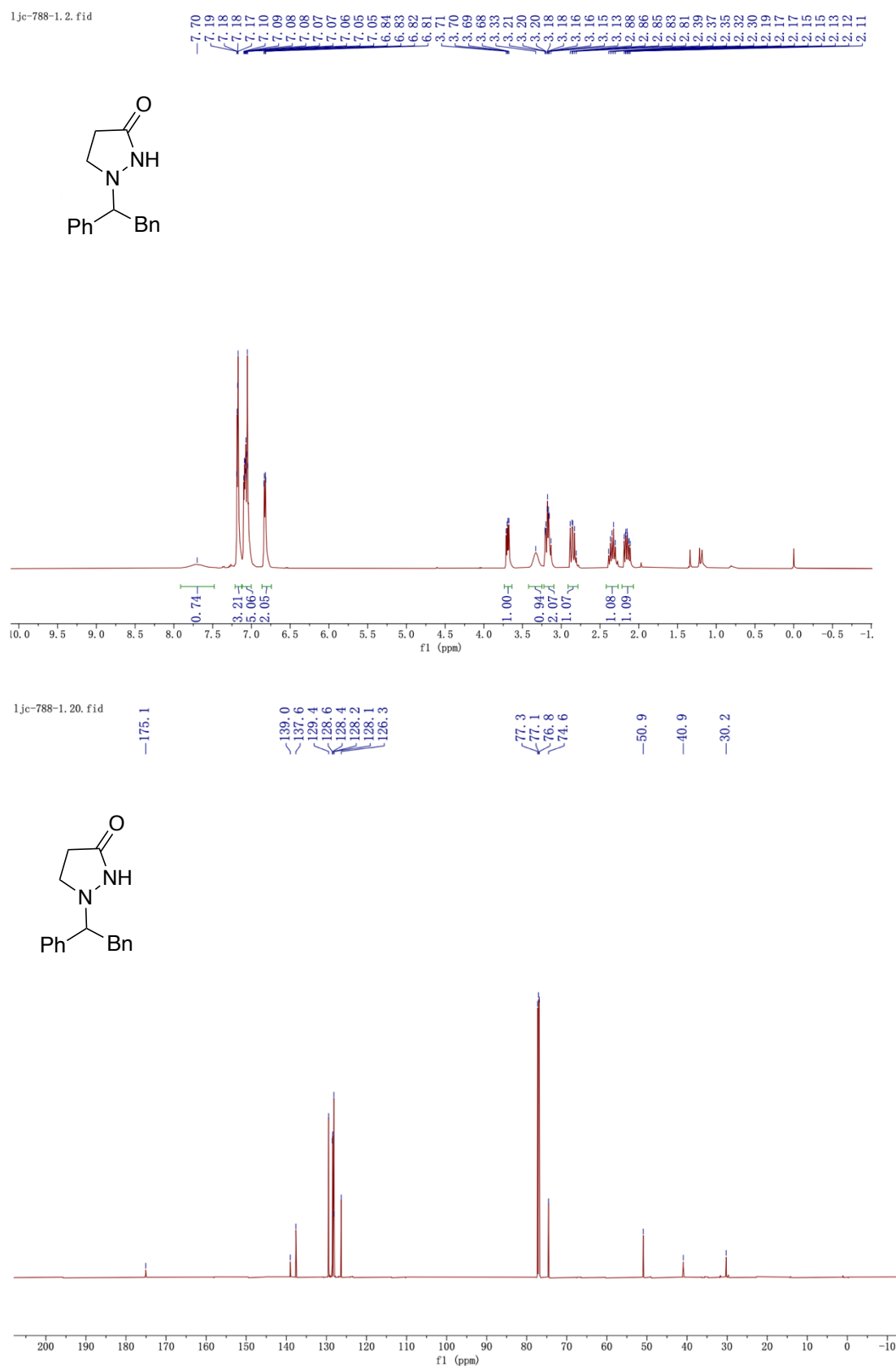


Figure S66. ^1H and ^{13}C NMR spectra of 1-(2-(4-bromophenyl)-1-phenylethyl)pyrazolidin-3-one (**3ac**)

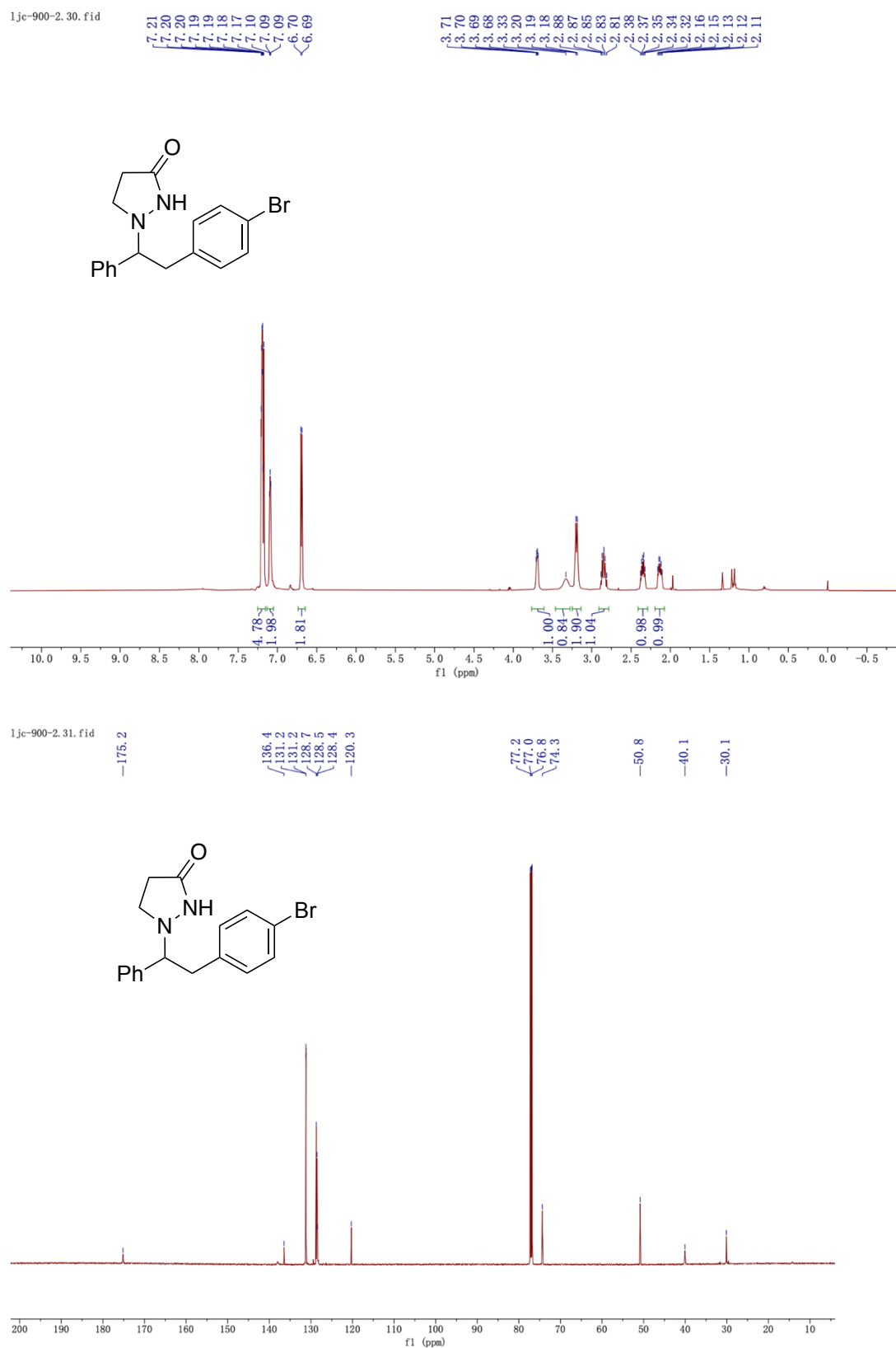


Figure S67. ^1H and ^{13}C NMR spectra of 1-(2-(4-chlorophenyl)-1-phenylethyl)pyrazolidin-3-one (**3ad**)

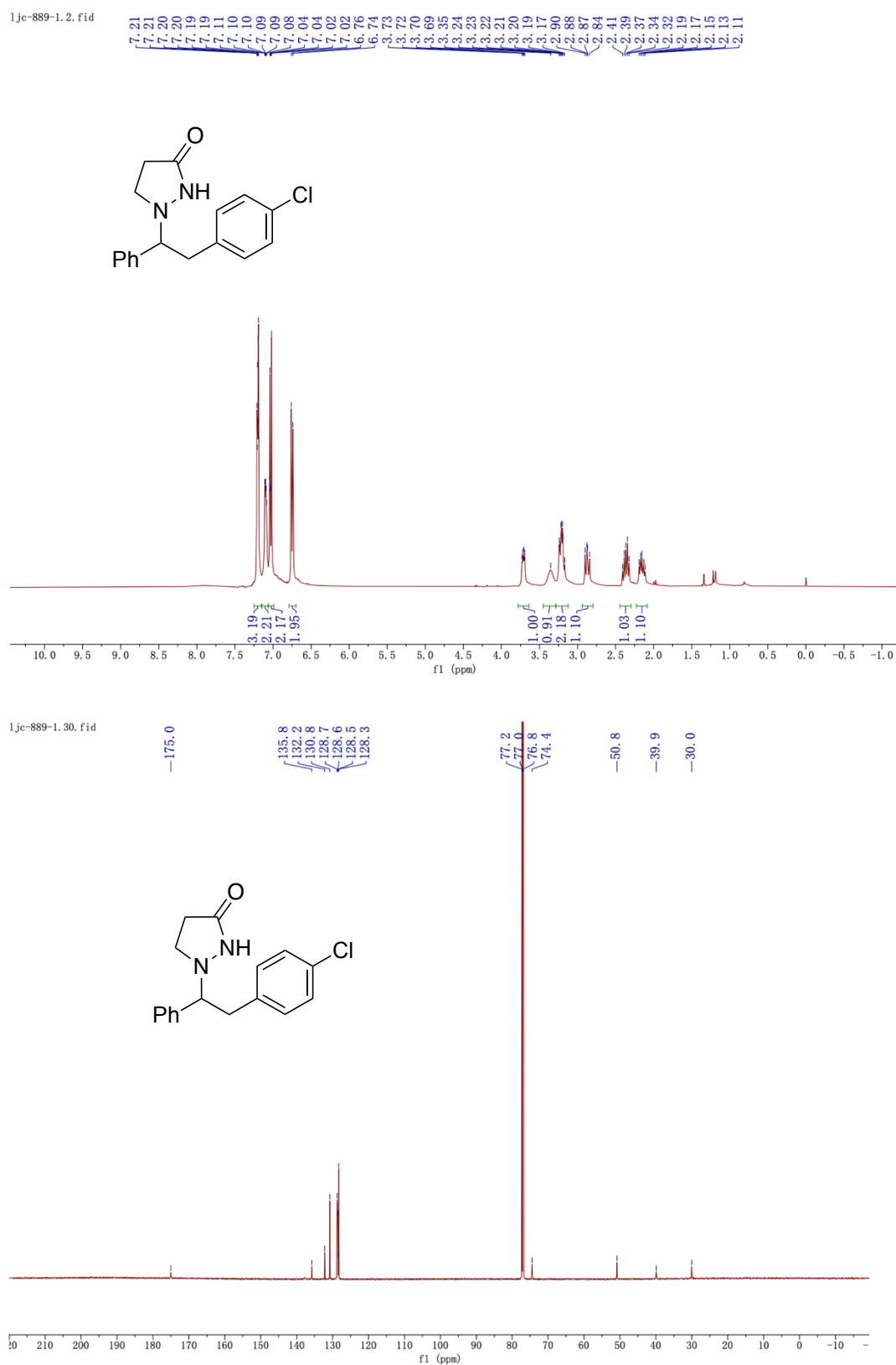
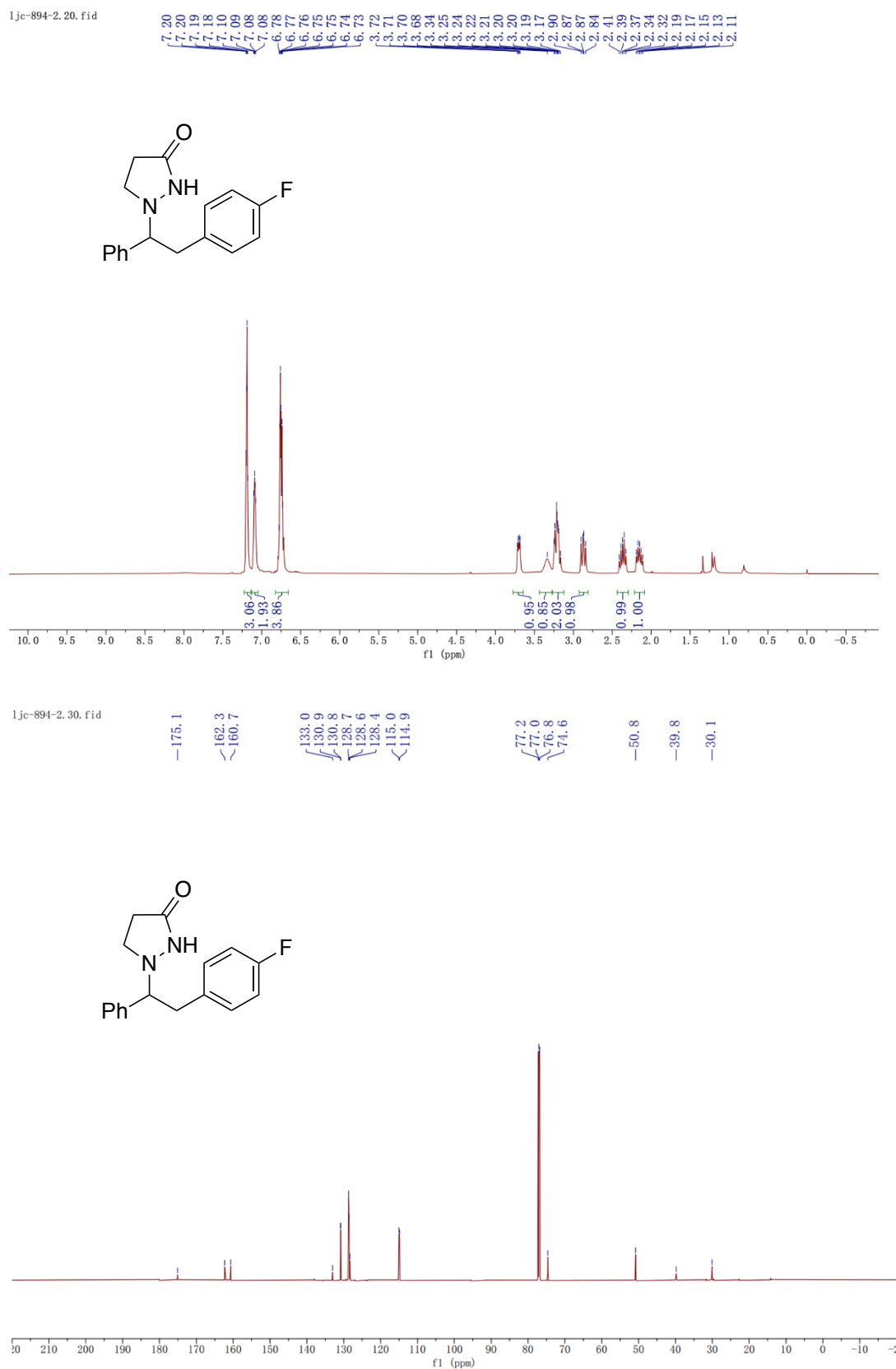


Figure S68. ^1H , ^{13}C and ^{19}F NMR spectra of 1-(2-(4-fluorophenyl)-1-phenylethyl)pyrazolidin-3-one (**3ae**)



ljc-894-2.21.fid

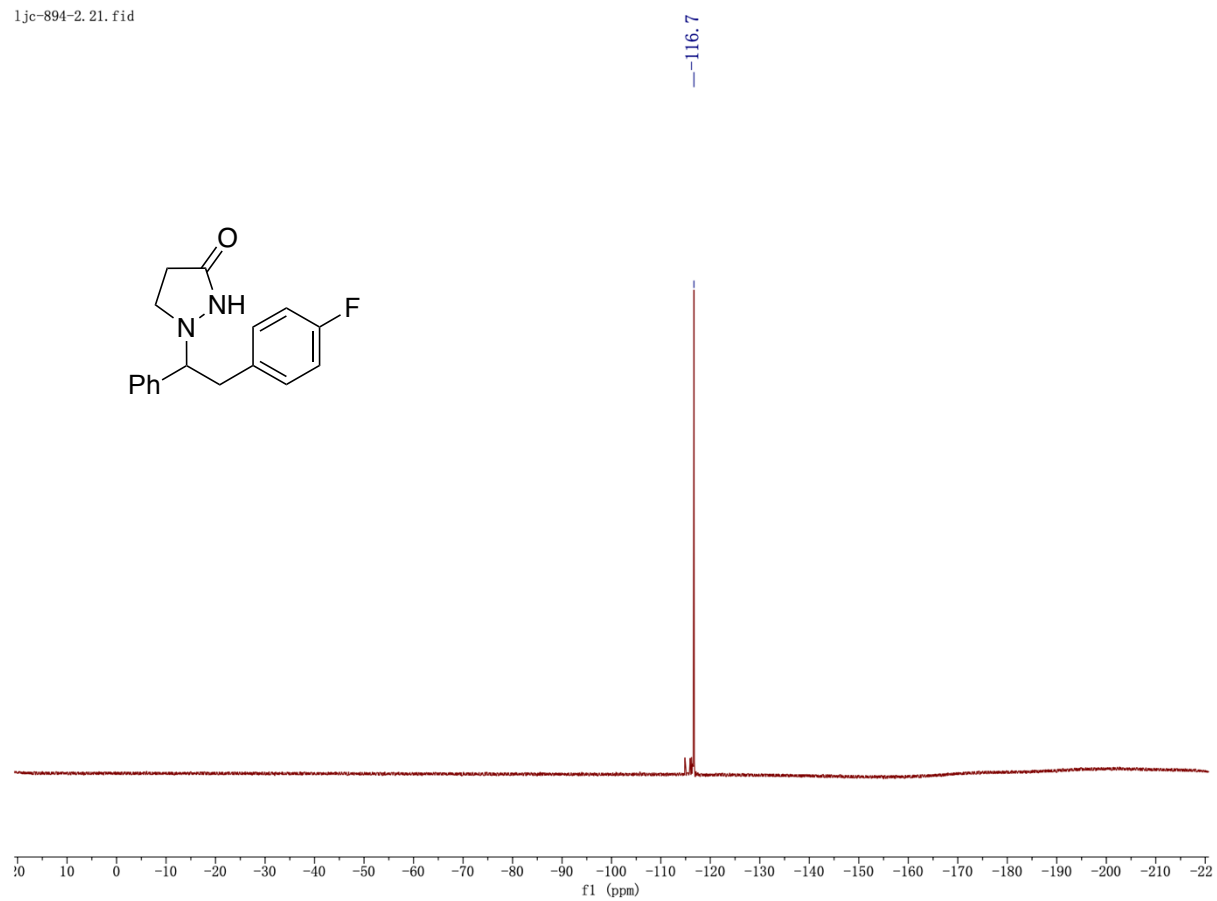


Figure S69. ^1H and ^{13}C NMR spectra of 1-(2-(4-methoxyphenyl)-1-phenylethyl)pyrazolidin-3-one (**3af**)

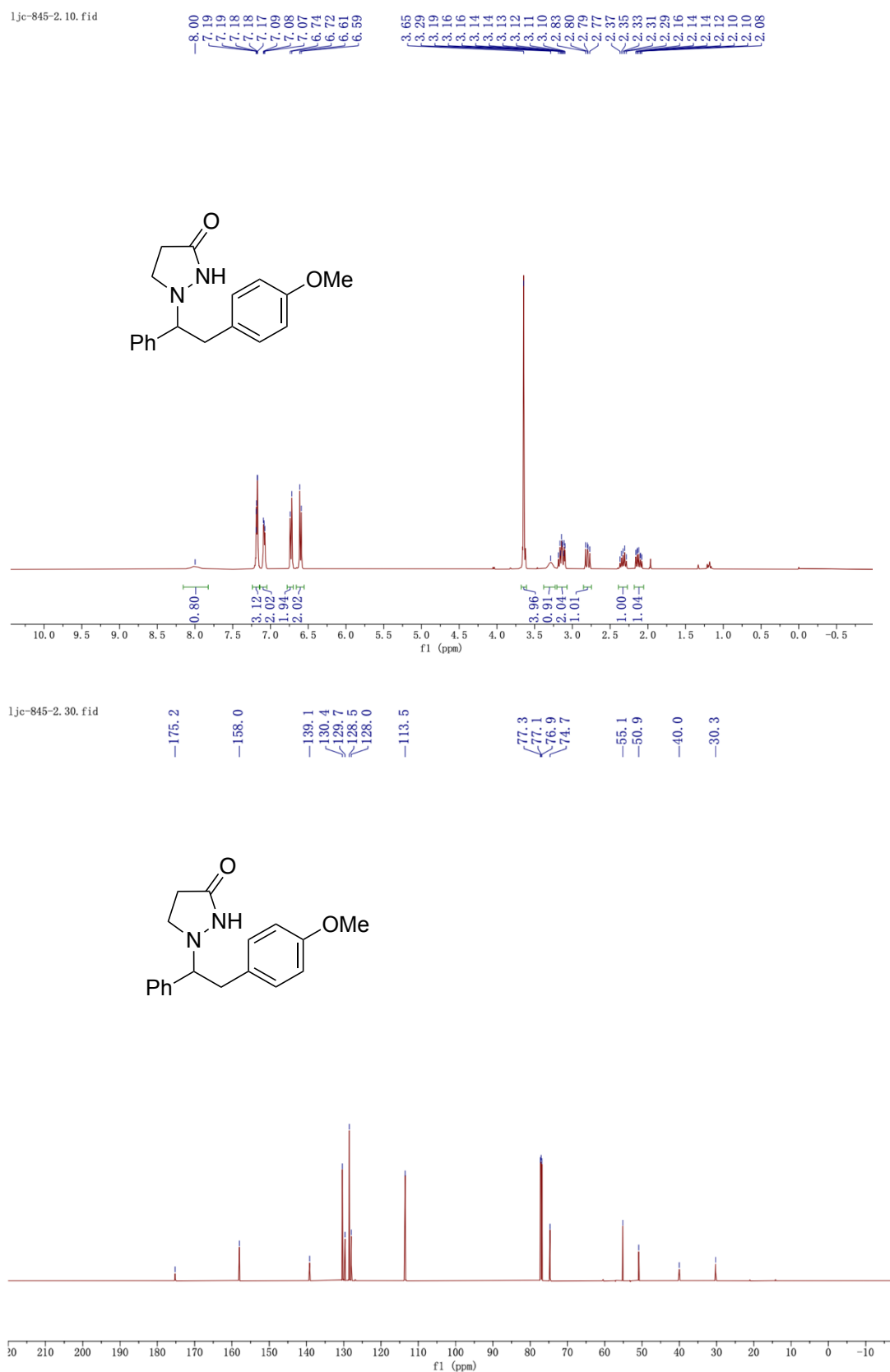


Figure S70. ^1H and ^{13}C NMR spectra of 2-(2-(3-oxopyrazolidin-1-yl)-2-phenylethyl)isoindoline-1,3-dione (**3ag**)

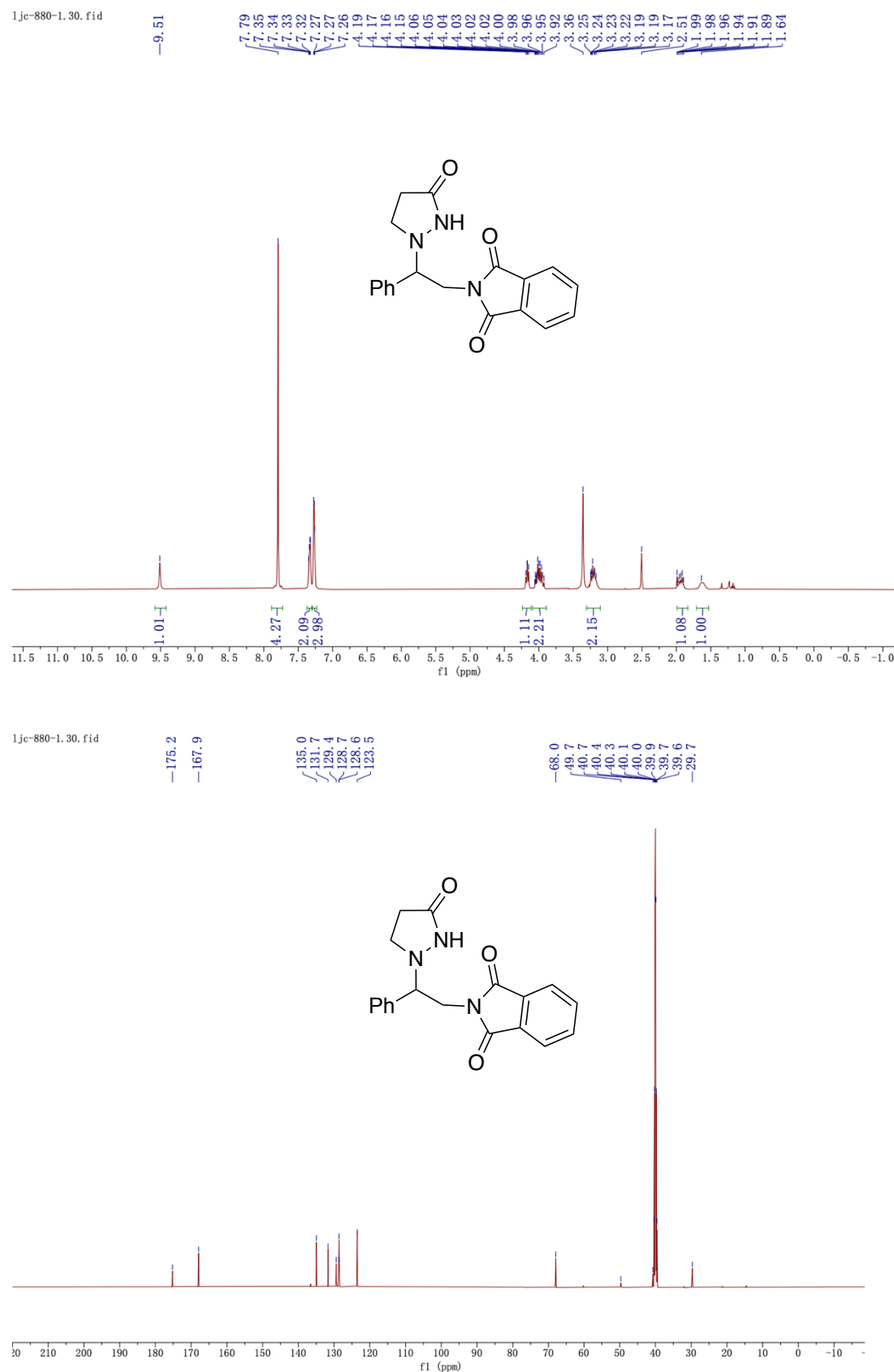


Figure S71. ^1H and ^{13}C NMR spectra of 1-(1-phenyl-2-(thiophen-2-yl)ethyl)pyrazolidin-3-one
(3ah)

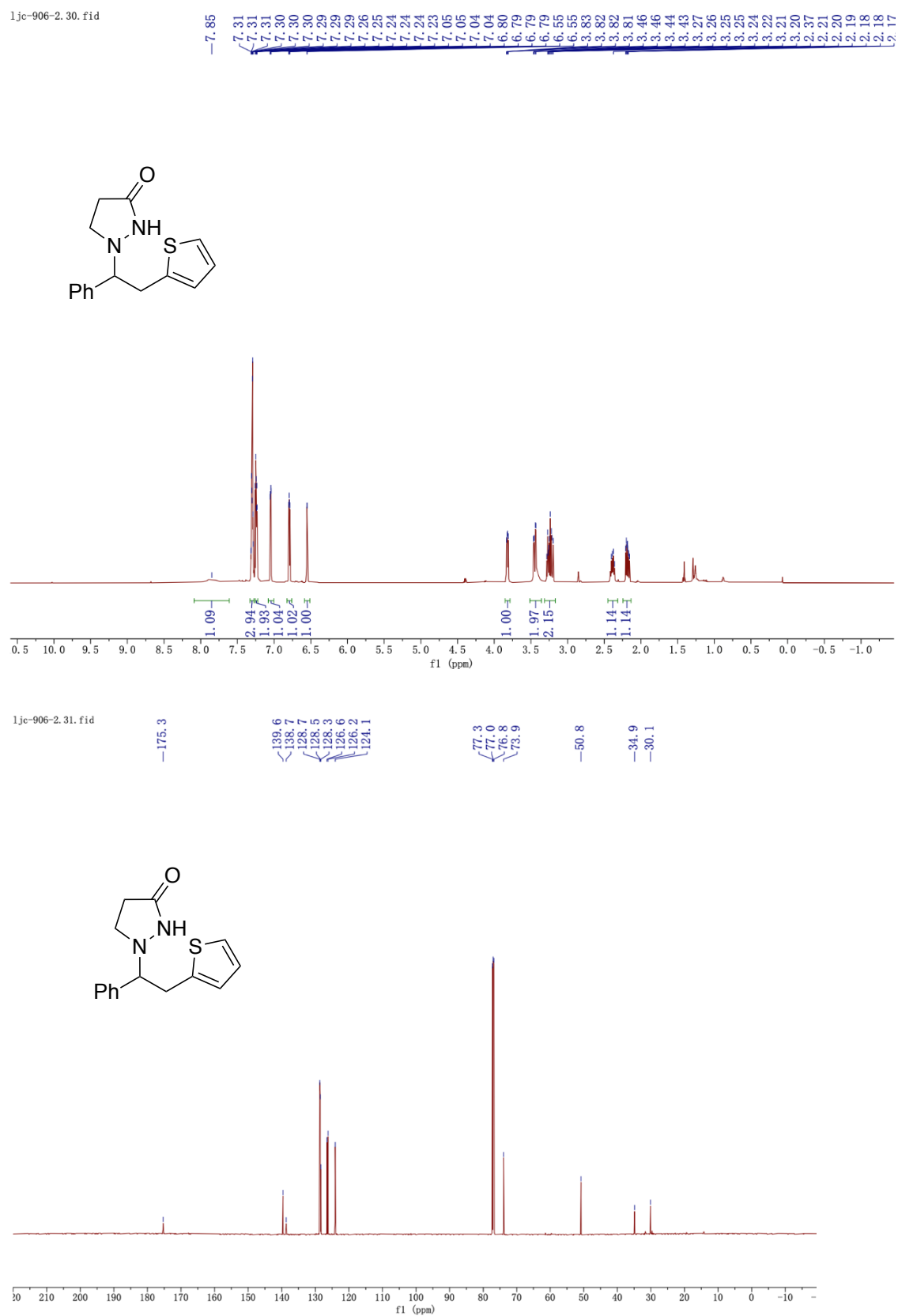


Figure S72. ^1H and ^{13}C NMR spectra of 1-((1-benzoylpiperidin-4-yl)(phenyl)methyl)pyrazolidin-3-one (**3ai**)

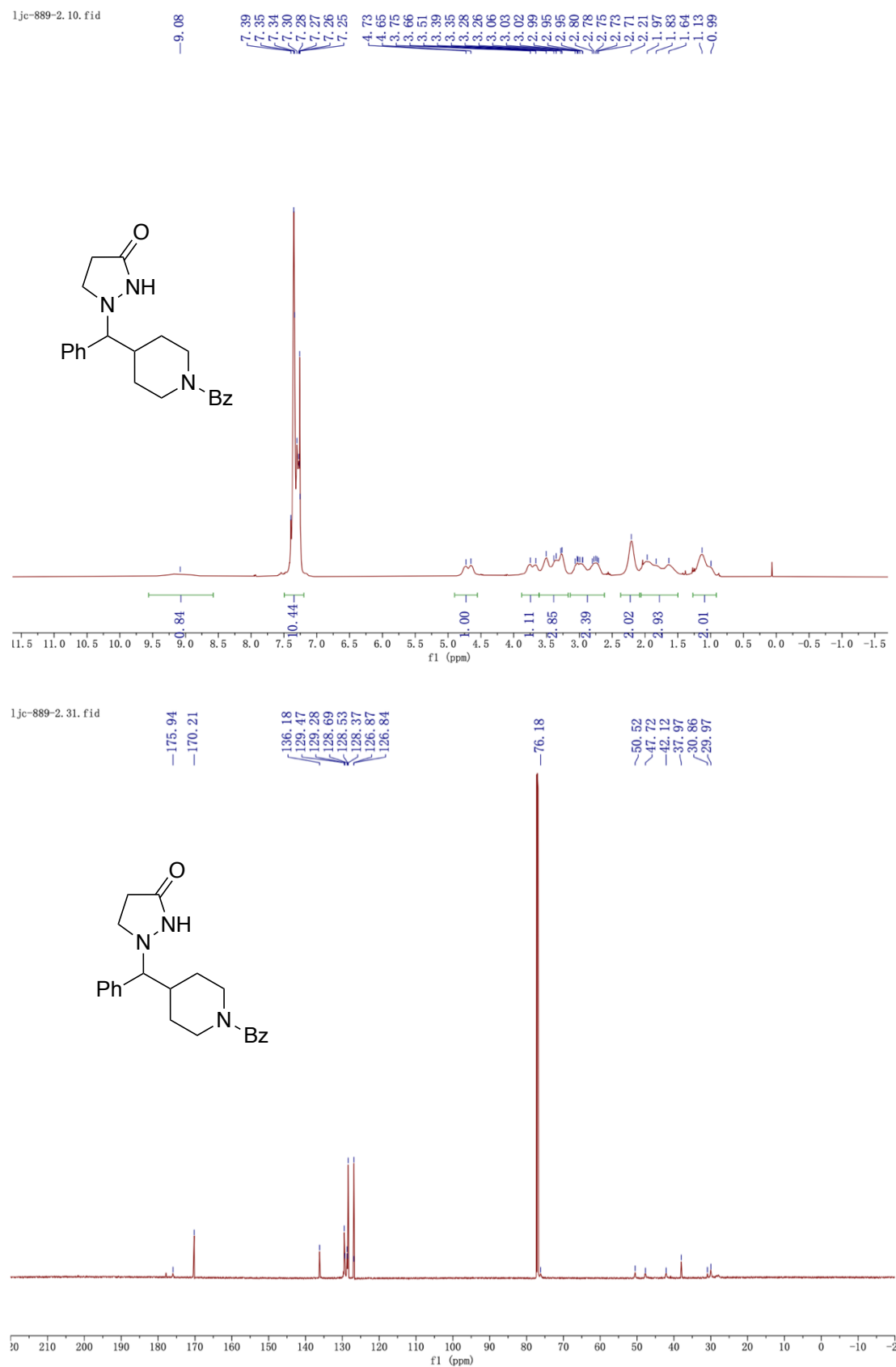


Figure S73. ^1H and ^{13}C NMR spectra of 1-(2-methyl-1-phenylbutyl)pyrazolidin-3-one (**3aj**)

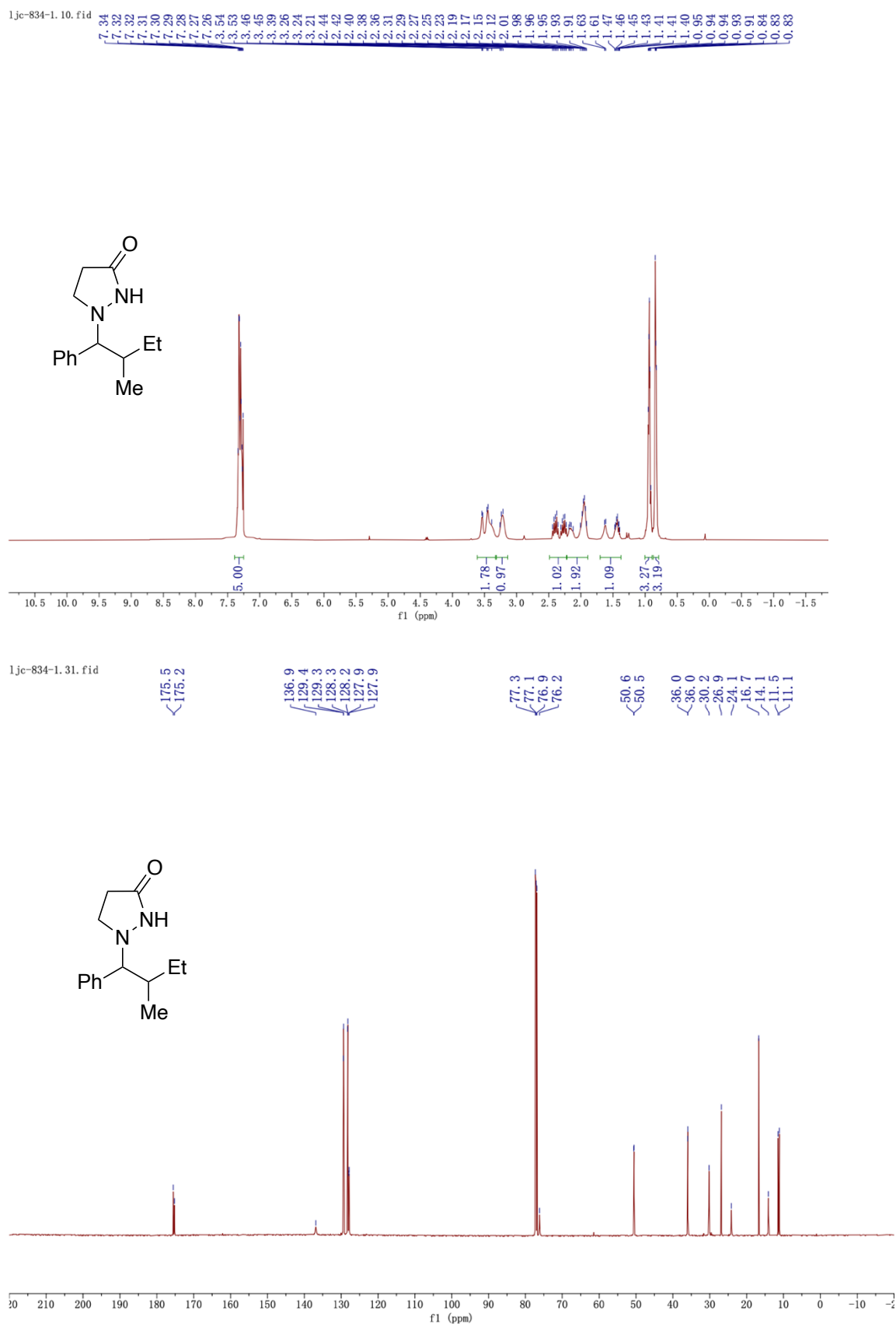


Figure S74. ^1H and ^{13}C NMR spectra of 1-(2-ethyl-1-phenylbutyl)pyrazolidin-3-one (**3ak**)

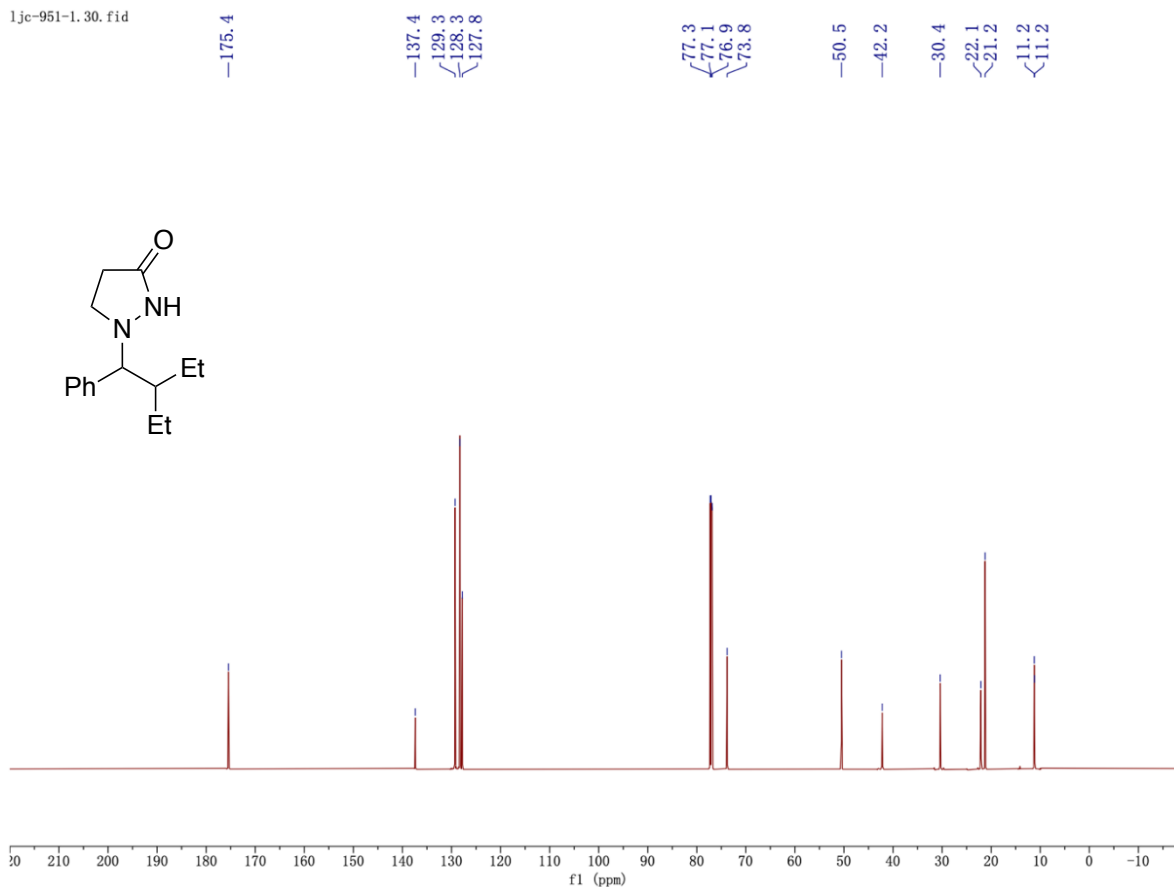
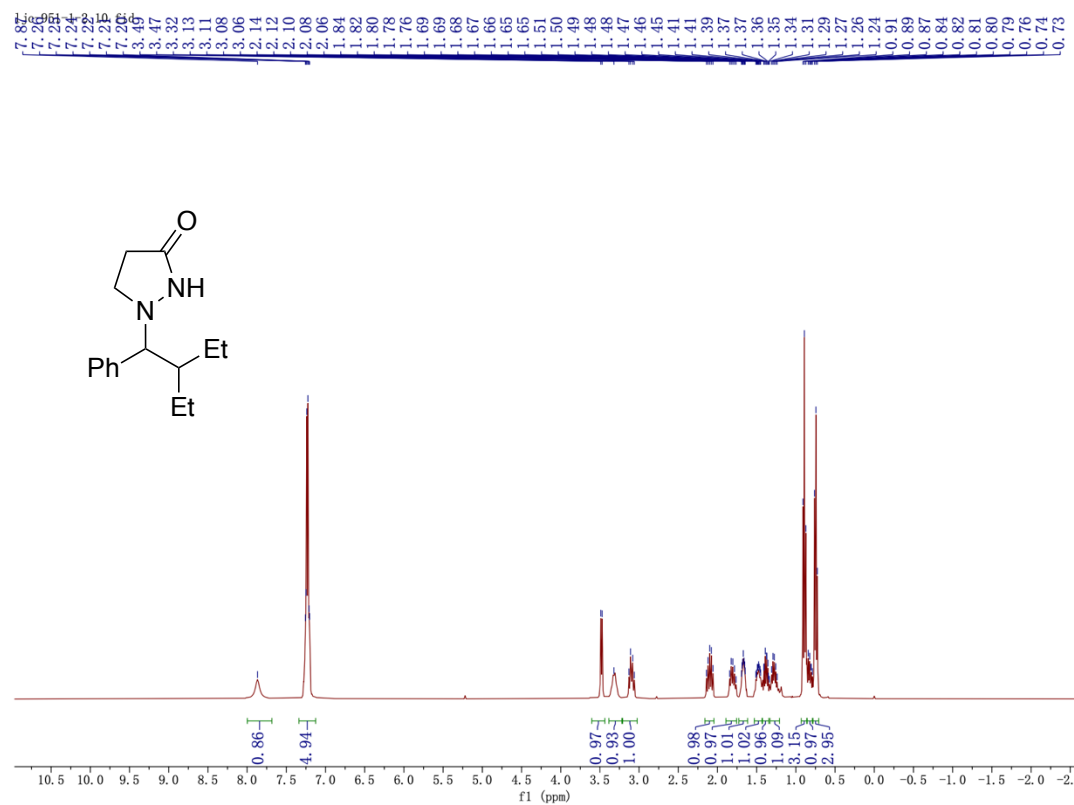


Figure S75. ^1H and ^{13}C NMR spectra of 1-(2-phenoxy-1-phenylpropyl)pyrazolidin-3-one (**3al**)

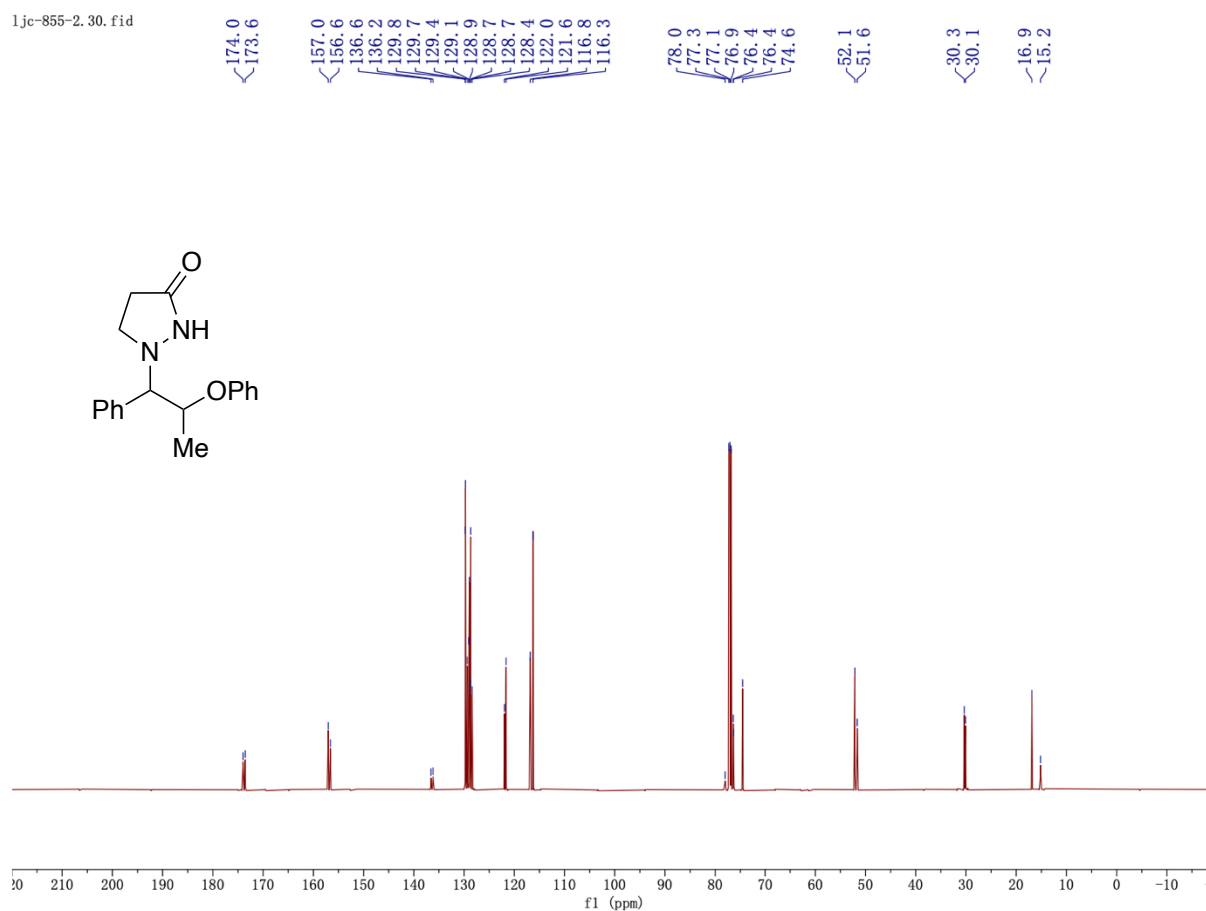
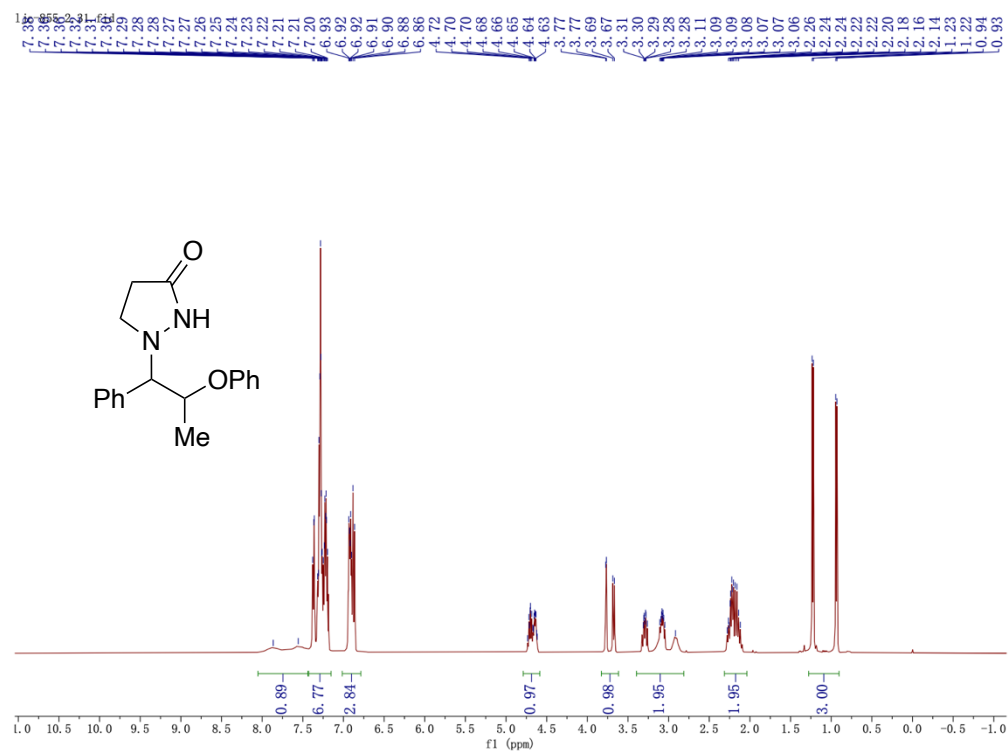


Figure S76. ^1H and ^{13}C NMR spectra of 1-(cyclopentyl(phenyl)methyl)pyrazolidin-3-one
(**3am**)

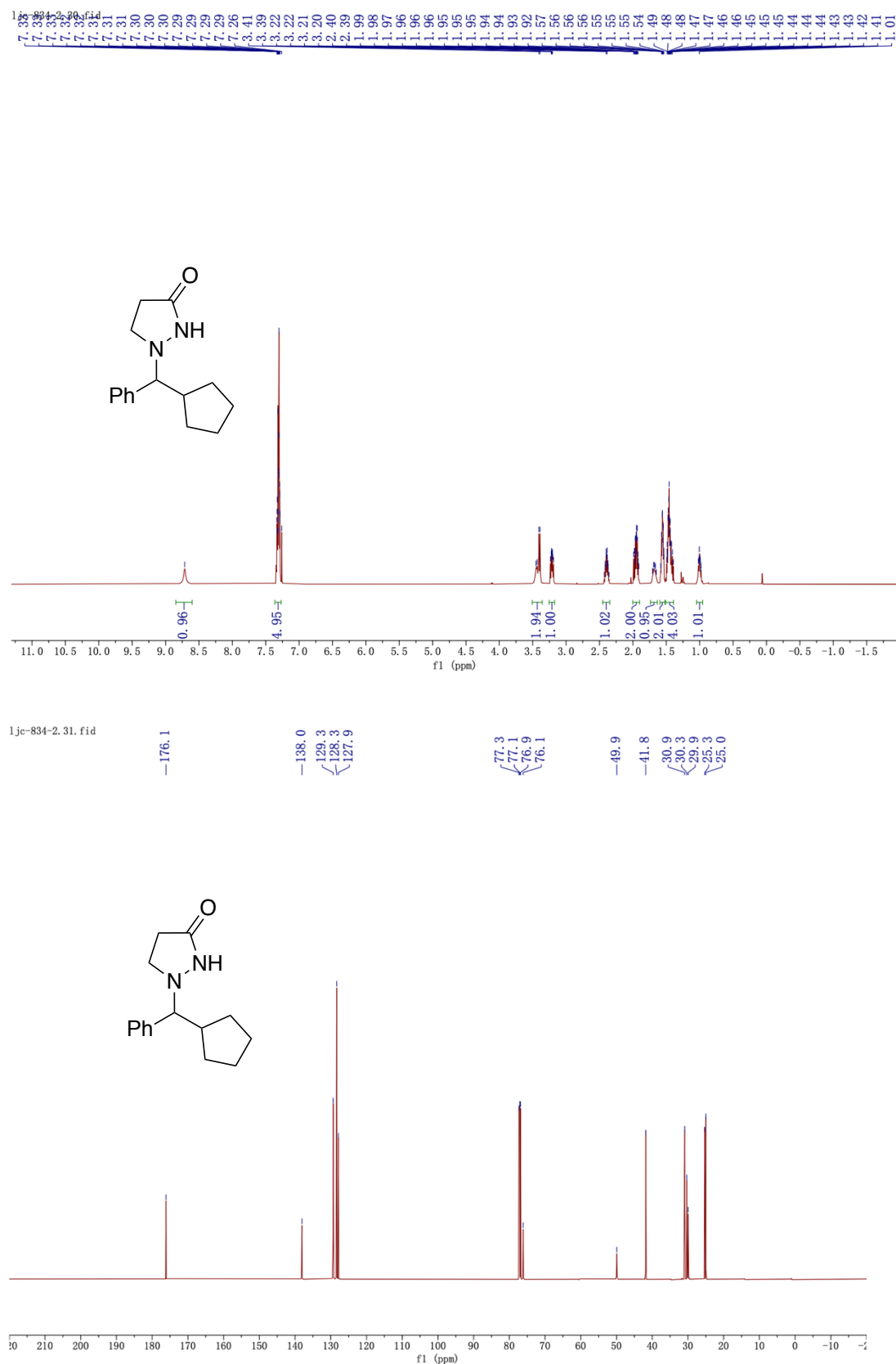
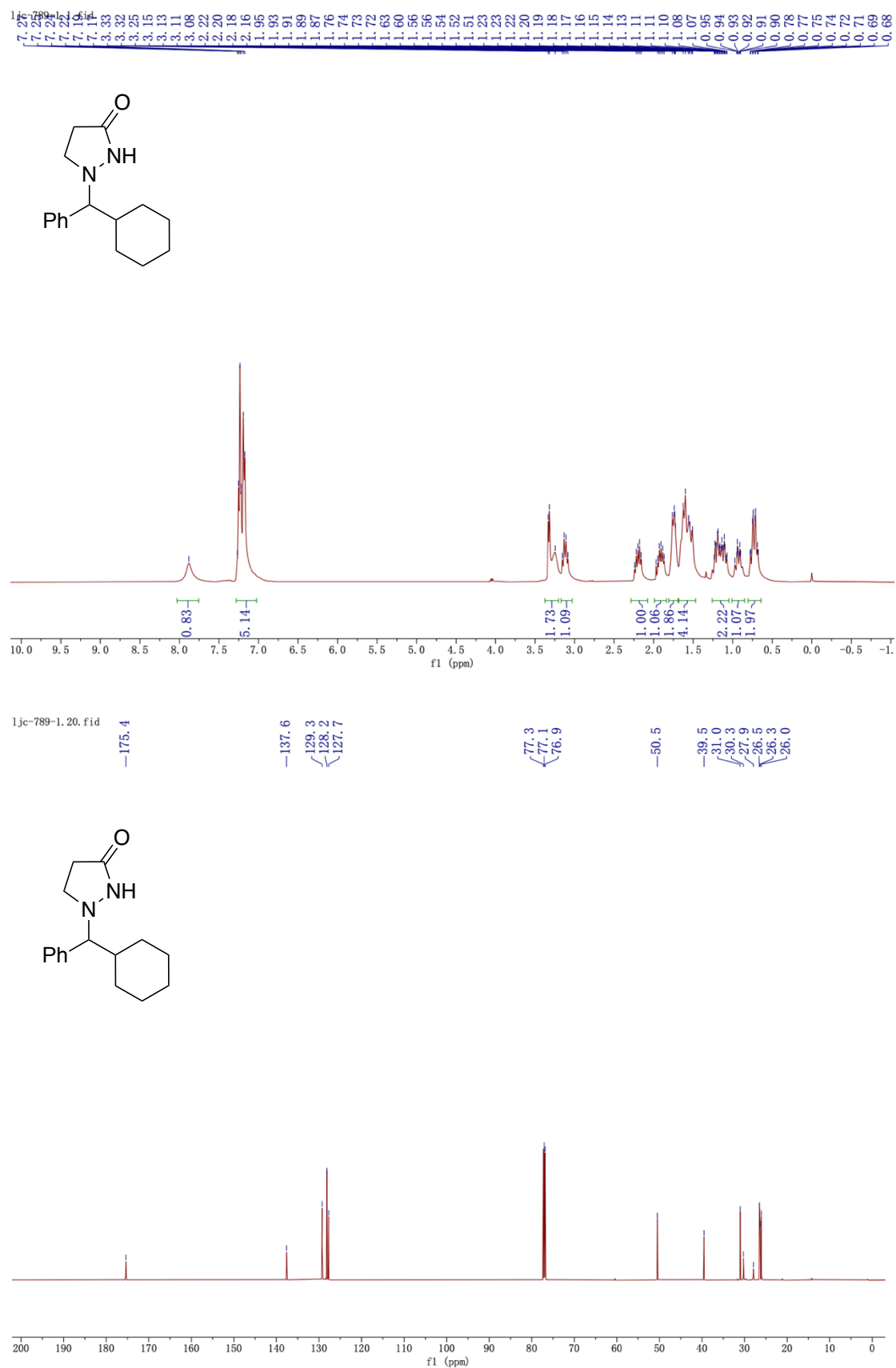


Figure S77. ^1H and ^{13}C NMR spectra of 1-(cyclohexyl(phenyl)methyl)pyrazolidin-3-one (**3an**)



¹H NMR Spectrum (400 MHz, CDCl₃)

Chemical structure: c1ccccc1C2C(=O)NCC2C3=CC=CC=C3

Peak list (ppm): 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 5.64, 5.63, 5.62, 5.61, 5.60, 5.55, 5.55, 5.55, 5.54, 5.53, 5.53, 3.52, 3.50, 3.49, 3.24, 3.24, 3.23, 3.22, 3.21, 2.18, 2.17, 2.15, 2.14, 2.14, 2.13, 2.11, 2.10, 2.09, 2.08, 2.05, 2.04, 2.02, 1.99, 1.98, 1.96, 1.95, 1.92, 1.89, 1.86, 1.85, 1.84, 1.83, 1.81, 1.06, 1.05.

Integration values: 0.90, 5.00, 2.02, 1.94, 0.99, 7.98, 1.09.

¹³C NMR Spectrum (100 MHz, CDCl₃)

Chemical structure: c1ccccc1C2C(=O)NCC2C3=CC=CC=C3

Peak list (ppm): 175.9, 137.1, 136.8, 129.4, 129.4, 128.4, 128.0, 127.0, 126.1, 125.9, 77.3, 77.1, 76.9, 75.9, 75.8, 35.2, 35.1, 30.2, 30.2, 29.4, 27.5, 26.5, 25.0, 24.8, 24.2.

Figure S79. ^1H and ^{13}C NMR spectra of 1-(2-oxo-1,2-diphenylethyl)pyrazolidin-3-one (**5aa**)

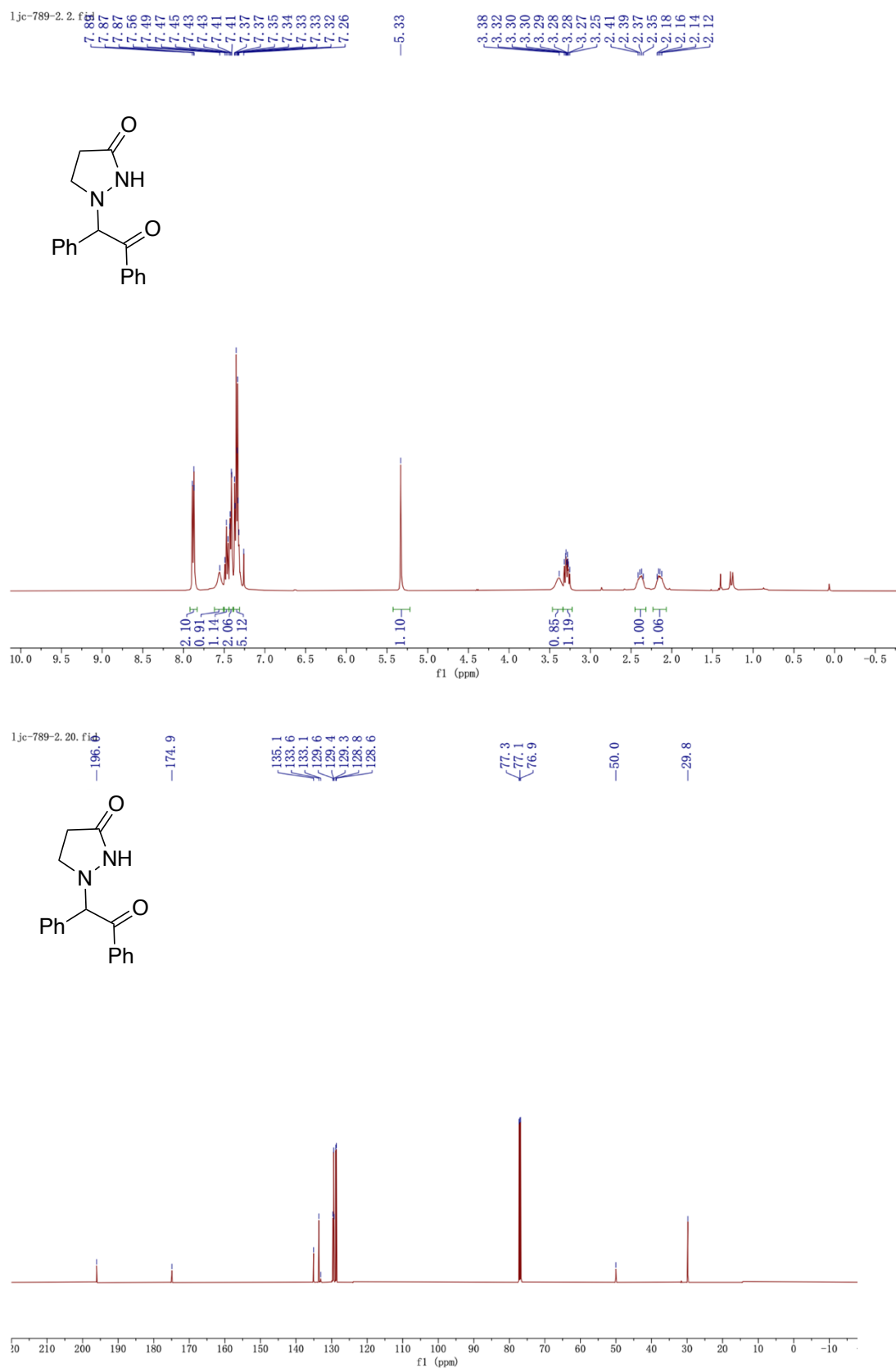


Figure S80. ^1H and ^{13}C NMR spectra of 1-(2-(4-bromophenyl)-2-oxo-1-phenylethyl)pyrazolidin-3-one (**5ab**)

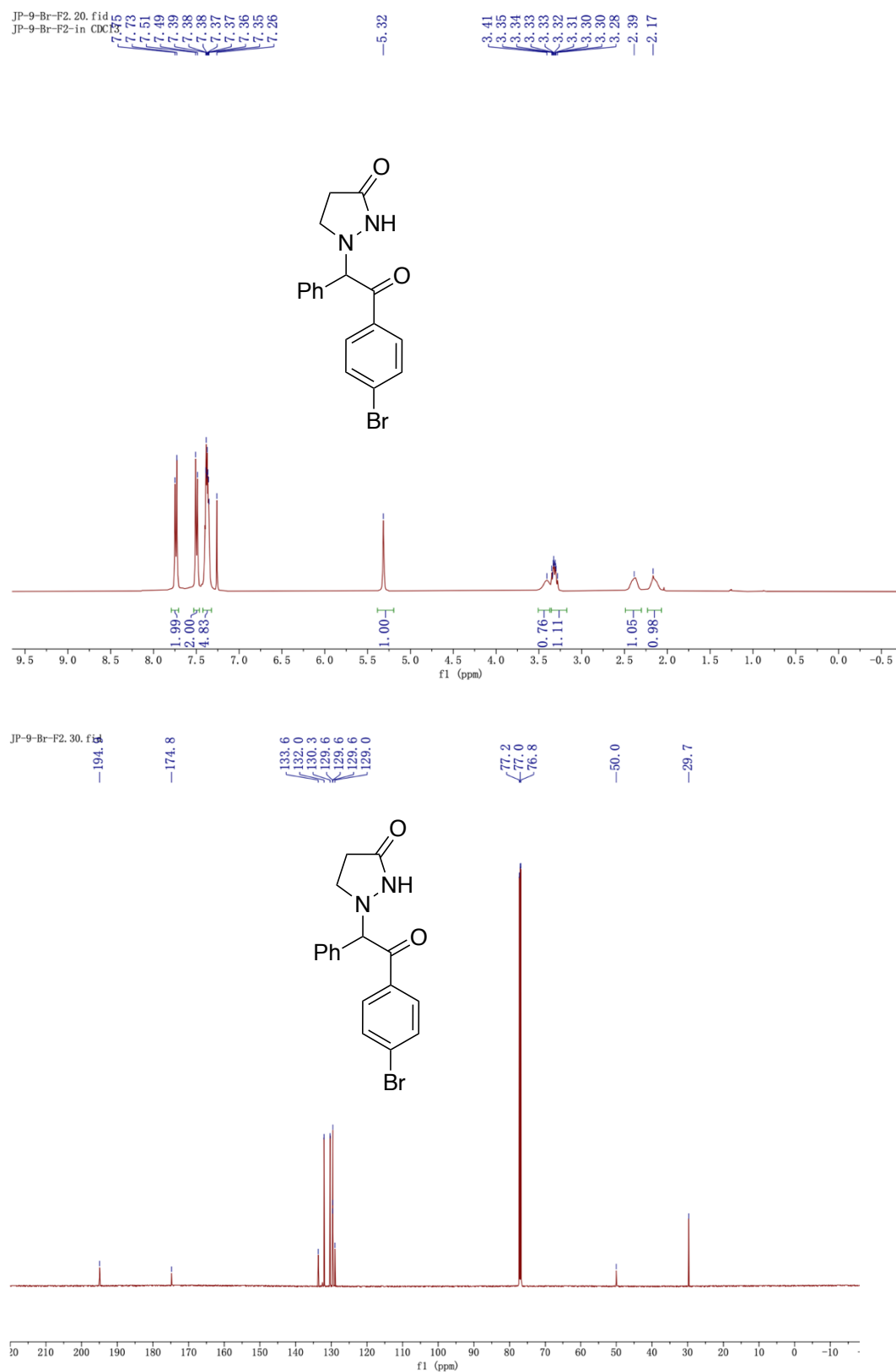


Figure S81. ^1H and ^{13}C NMR spectra of 1-(2-(4-chlorophenyl)-2-oxo-1-phenylethyl)pyrazolidin-3-one (**5ac**)

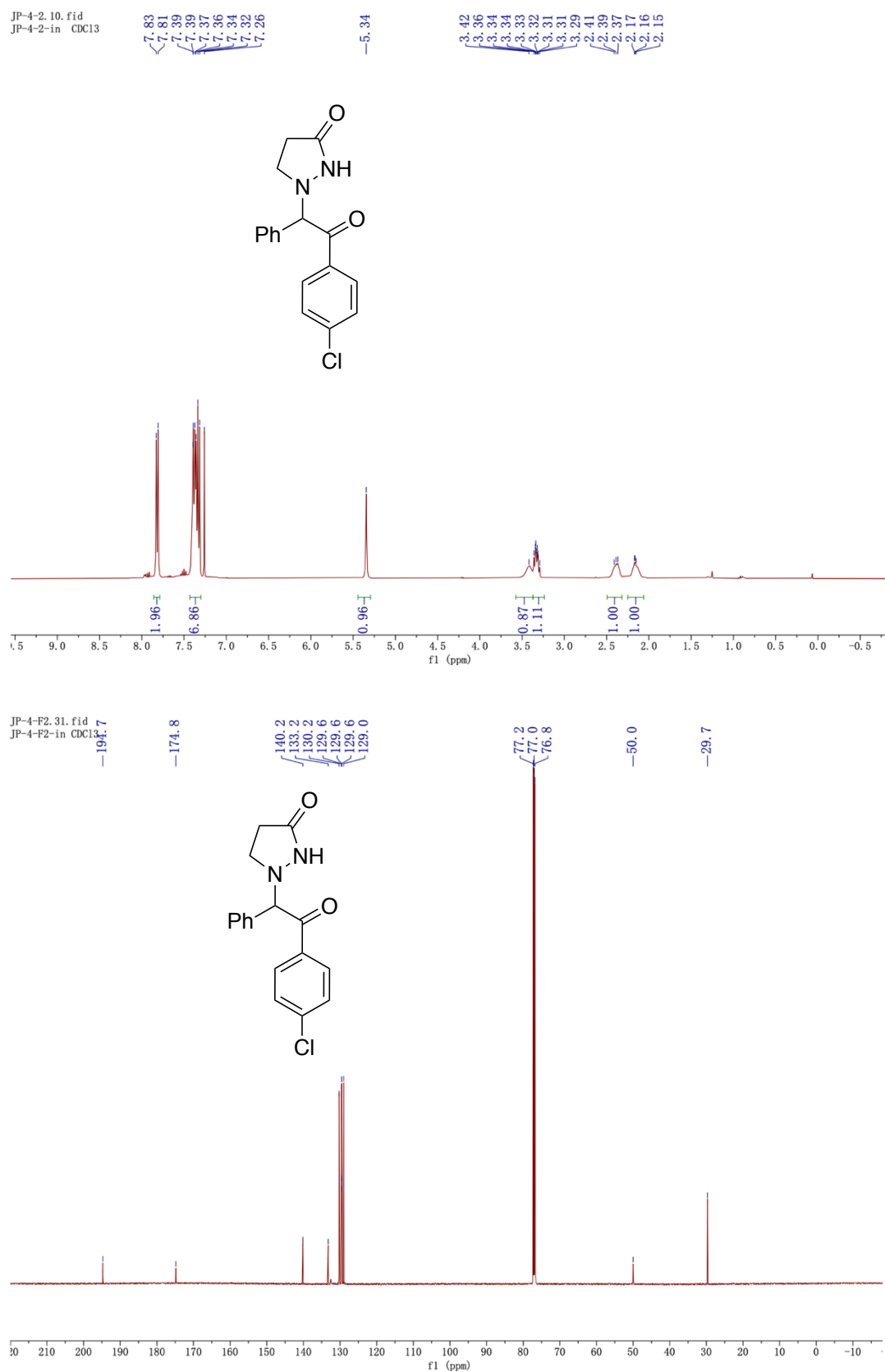
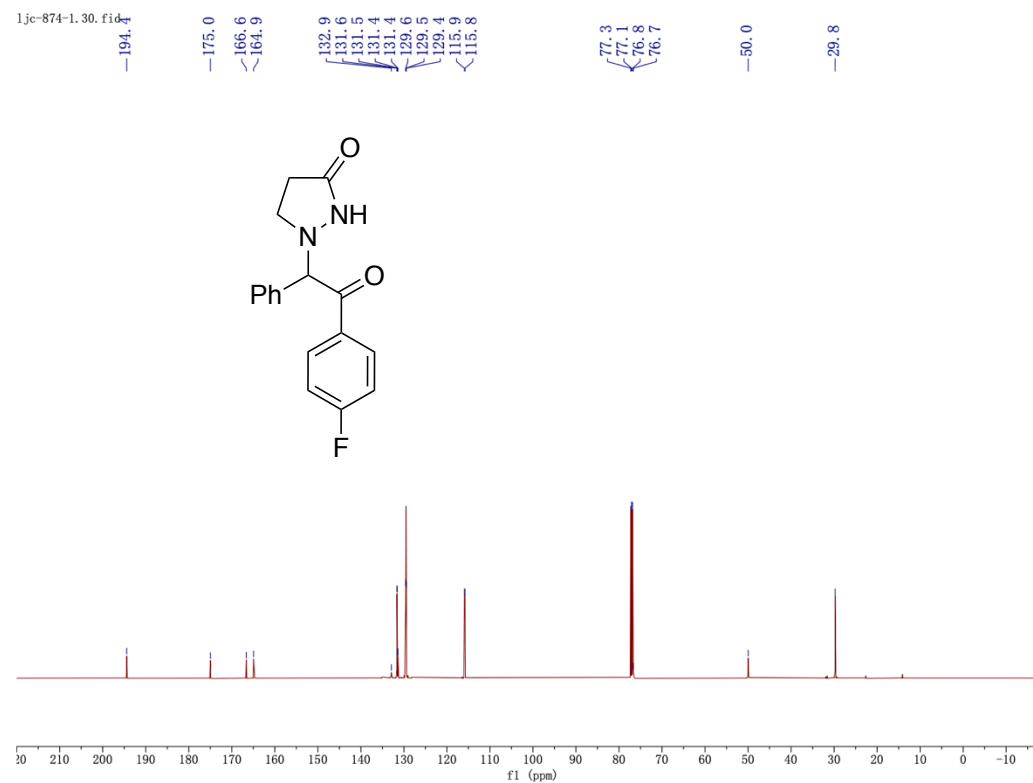
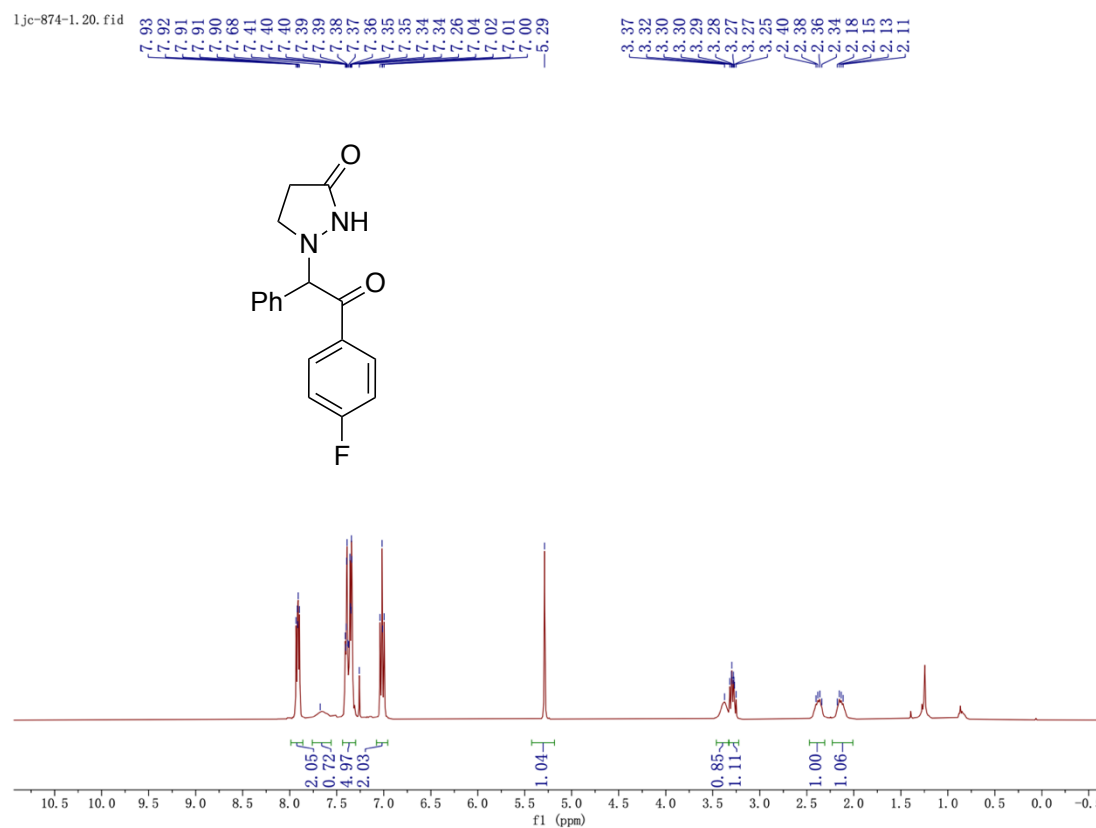
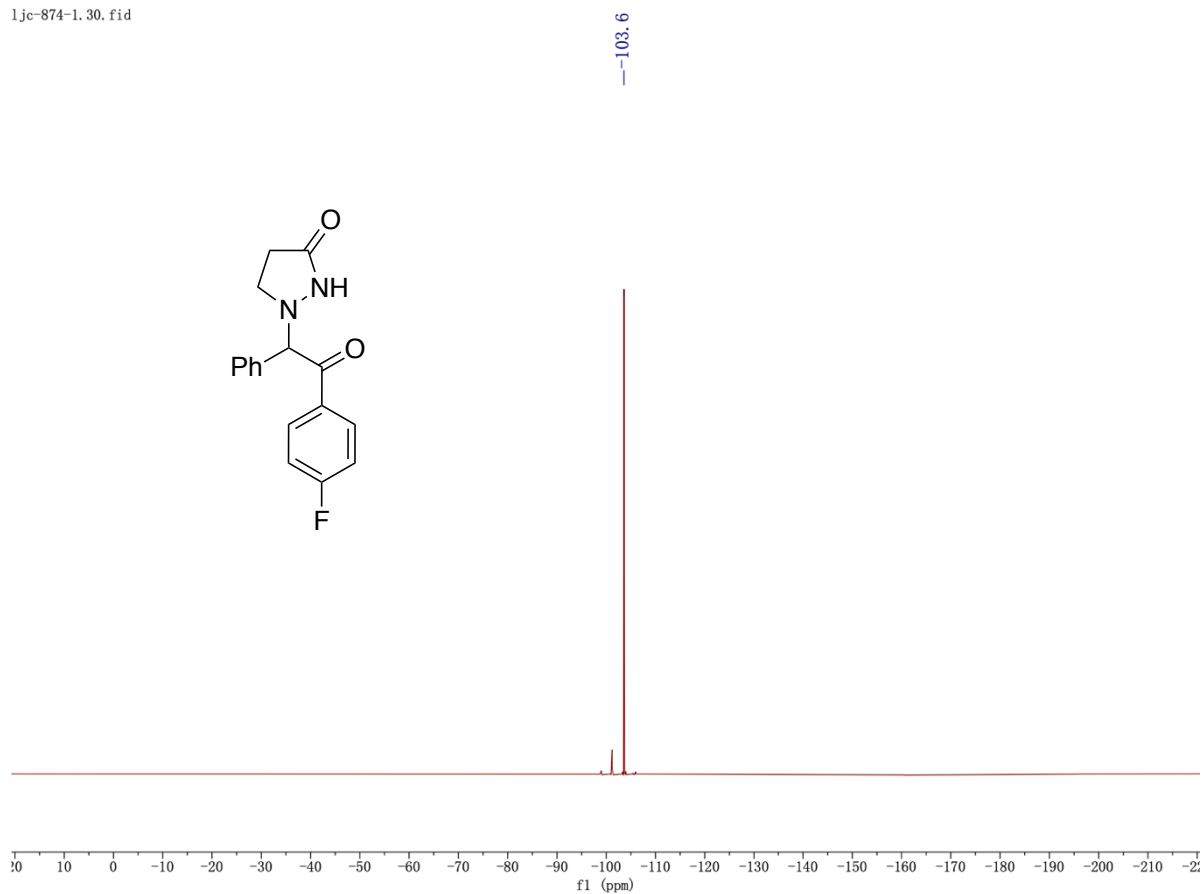


Figure S82. ^1H , ^{13}C and ^{19}F NMR spectra of 1-(2-(4-fluorophenyl)-2-oxo-1-phenylethyl)pyrazolidin-3-one (**5ad**)



1jc-874-1.30.fid



1je-805-1.20. fid

Chemical structure: O=C1CCNC(=O)C1C(=O)c2ccc(C(F)(F)F)cc2C3=CC=CC=C3

¹H NMR spectrum (ppm):

- 7.98, 7.97, 7.63, 7.62, 7.41, 7.41, 7.40, 7.40, 7.40, 7.39, 7.39, 7.38, 7.38, 7.37, 7.37, 7.36, 7.36, 7.26, 5.33 (Aromatic protons)
- 3.44, 3.34, 3.33, 3.33, 3.32, 3.32, 3.31, 3.30 (NH and CH protons)
- 2.42, 2.16 (CF₃ protons)

Integration values (from left to right): 2.00, 2.13, 4.82, 1.04, 0.71, 1.09, 0.92, 0.97.



ljc-805-1.3.fid

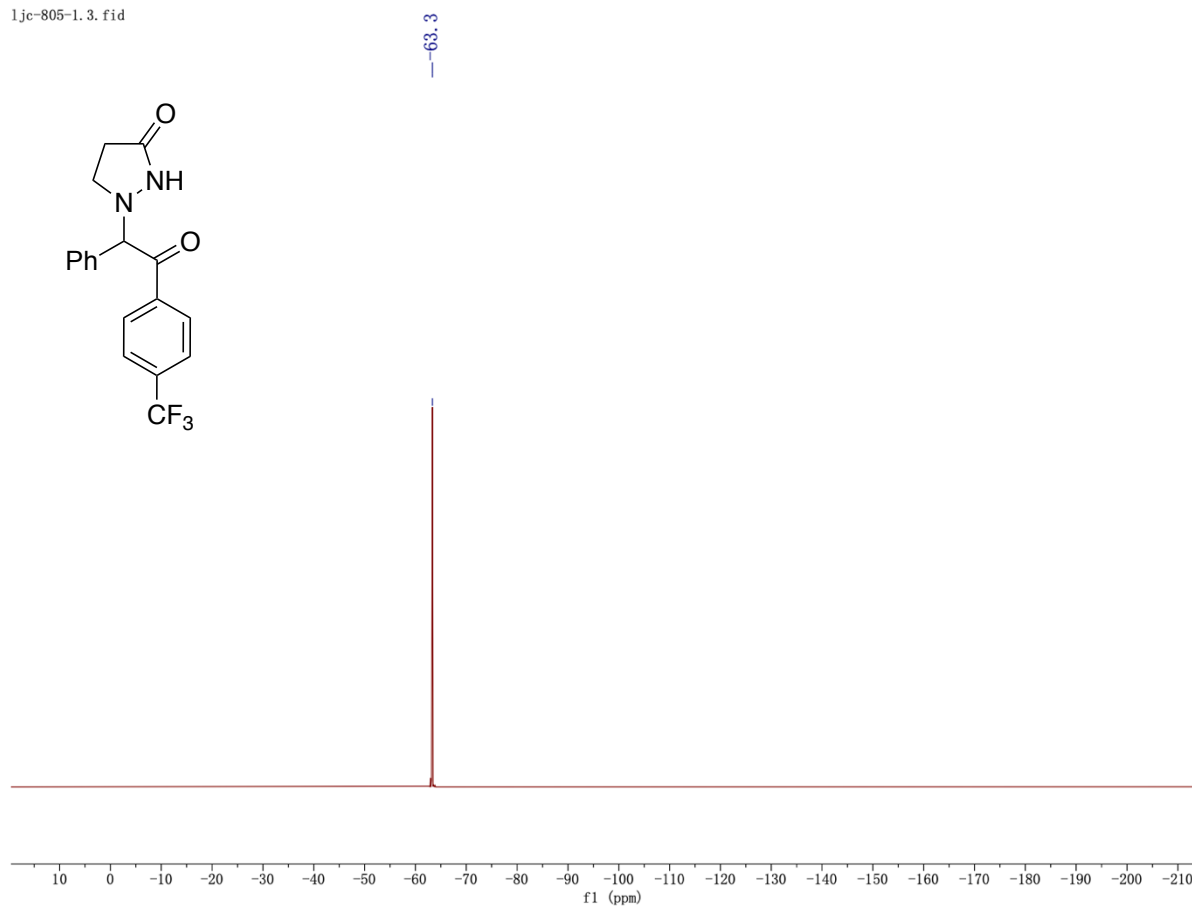


Figure S84. ^1H and ^{13}C NMR spectra of 1-(2-oxo-1-phenyl-2-(*p*-tolyl)ethyl)pyrazolidin-3-one

(5af)

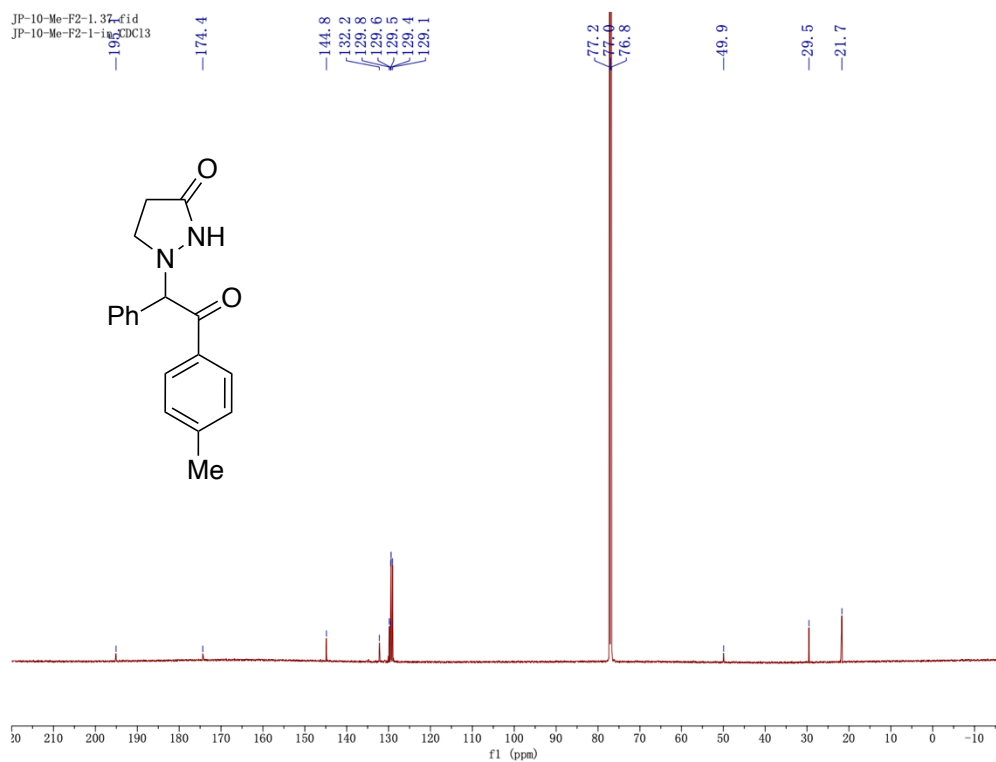
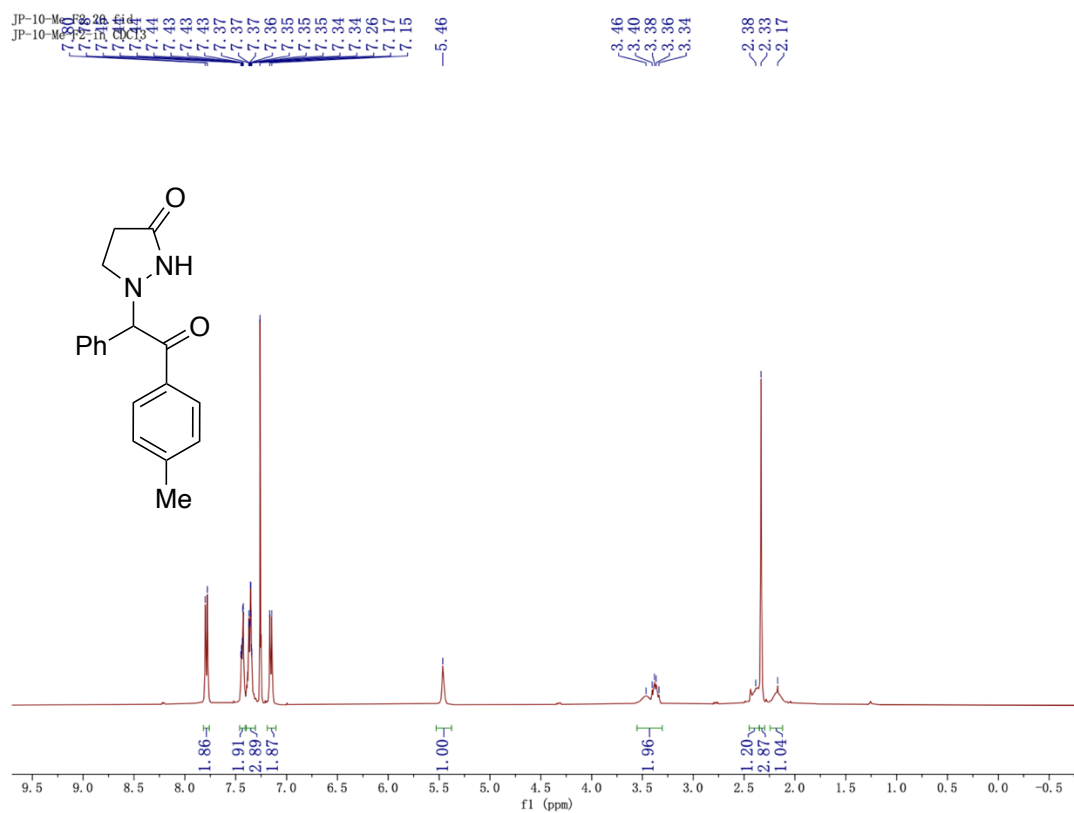
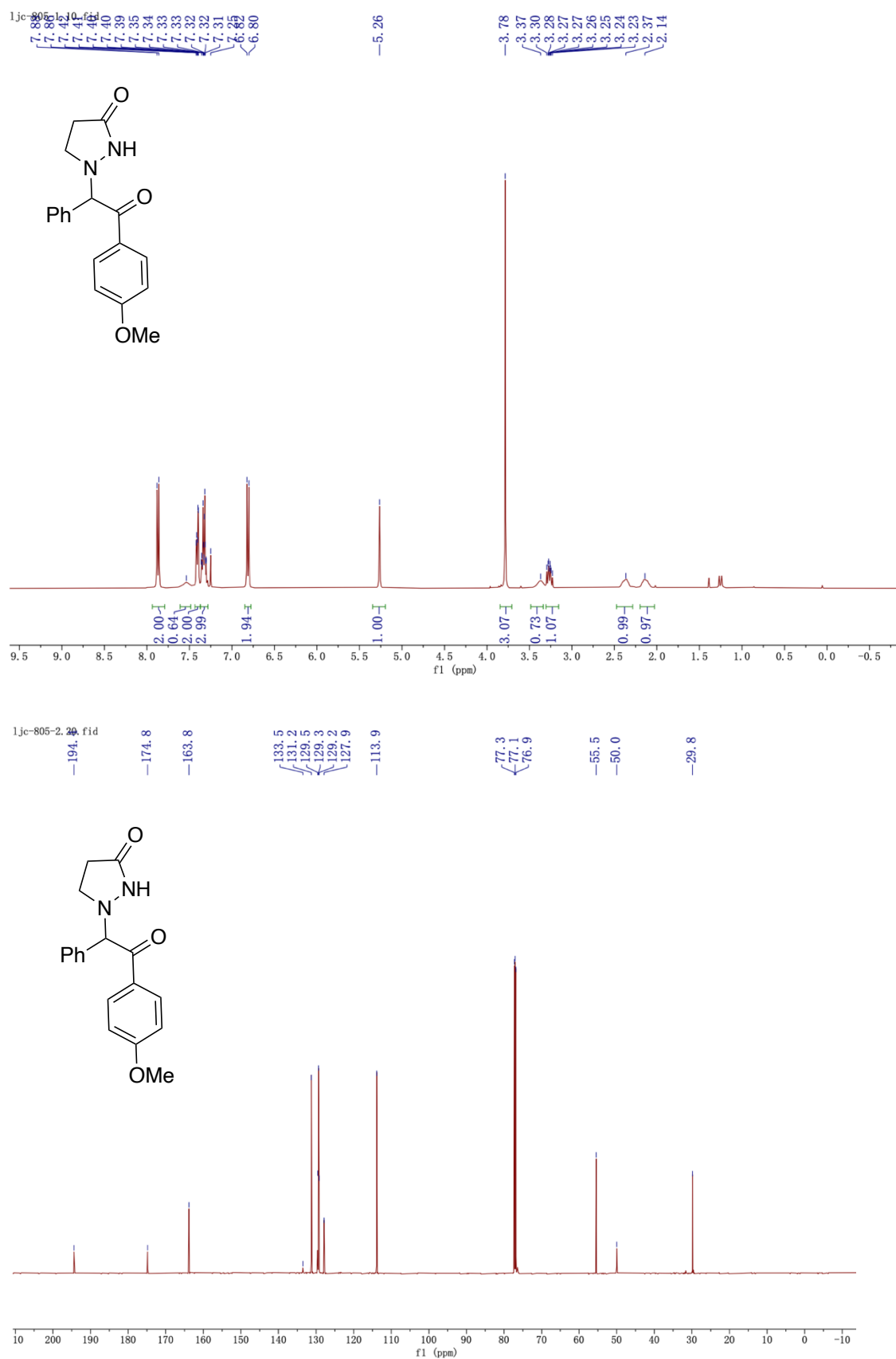


Figure S85. ^1H and ^{13}C NMR spectra of 1-(2-(4-methoxyphenyl)-2-oxo-1-phenylethyl)pyrazolidin-3-one (**5ag**)



1jc-951-1-2.20. f1d

Chemical structure: O=C1CCN(C1C(=O)c2ccc(cc2)c3ccccc3)C4=CC=CC=C4

¹H NMR spectrum (400 MHz, CDCl₃) showing peaks in the aromatic region (7.1-7.8 ppm) and aliphatic region (2.1-3.4 ppm). Integration values are provided below the peaks.

Peak list (ppm): 7.98, 7.96, 7.59, 7.58, 7.57, 7.56, 7.55, 7.54, 7.53, 7.47, 7.46, 7.45, 7.43, 7.43, 7.42, 7.41, 7.40, 7.40, 7.39, 7.38, 7.38, 7.37, 7.37, 7.36, 7.36, 7.35, 7.35, 5.37, 3.43, 3.35, 3.33, 3.33, 3.32, 3.31, 3.30, 3.30, 3.28, 2.44, 2.42, 2.39, 2.19, 2.17, 2.15, 2.15.

Integration values: 1.93, 4.32, 8.02, 1.00, 0.90, 1.14, 1.00, 1.03.



Figure S87. ^1H and ^{13}C NMR spectra of 1-(2-(2-chlorophenyl)-2-oxo-1-phenylethyl)pyrazolidin-3-one (**5ai**)

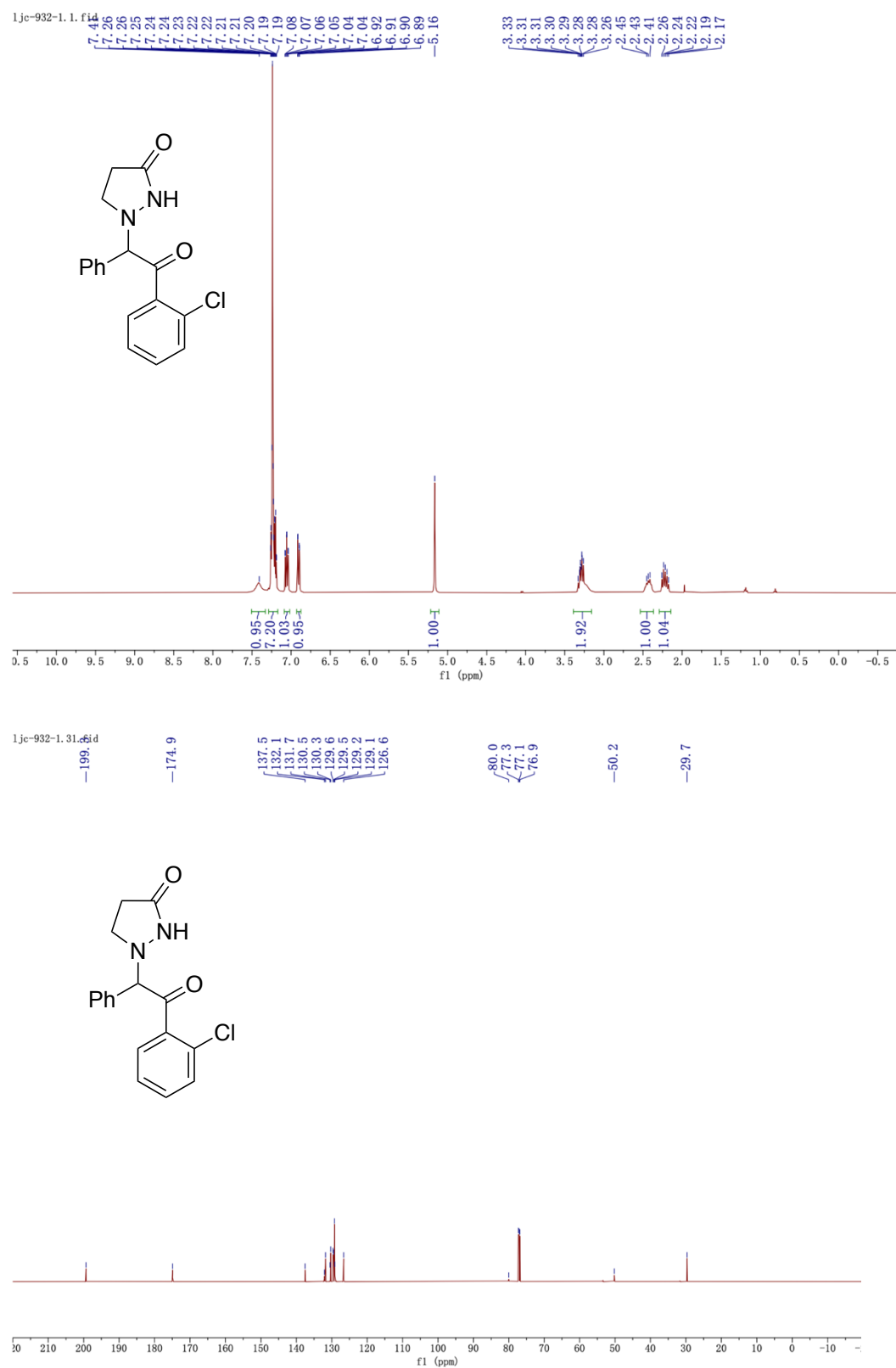


Figure S88. ^1H and ^{13}C NMR spectra of 1-(2-(benzo[*d*][1,3]dioxol-5-yl)-2-oxo-1-phenylethyl)pyrazolidin-3-one (**5aj**)

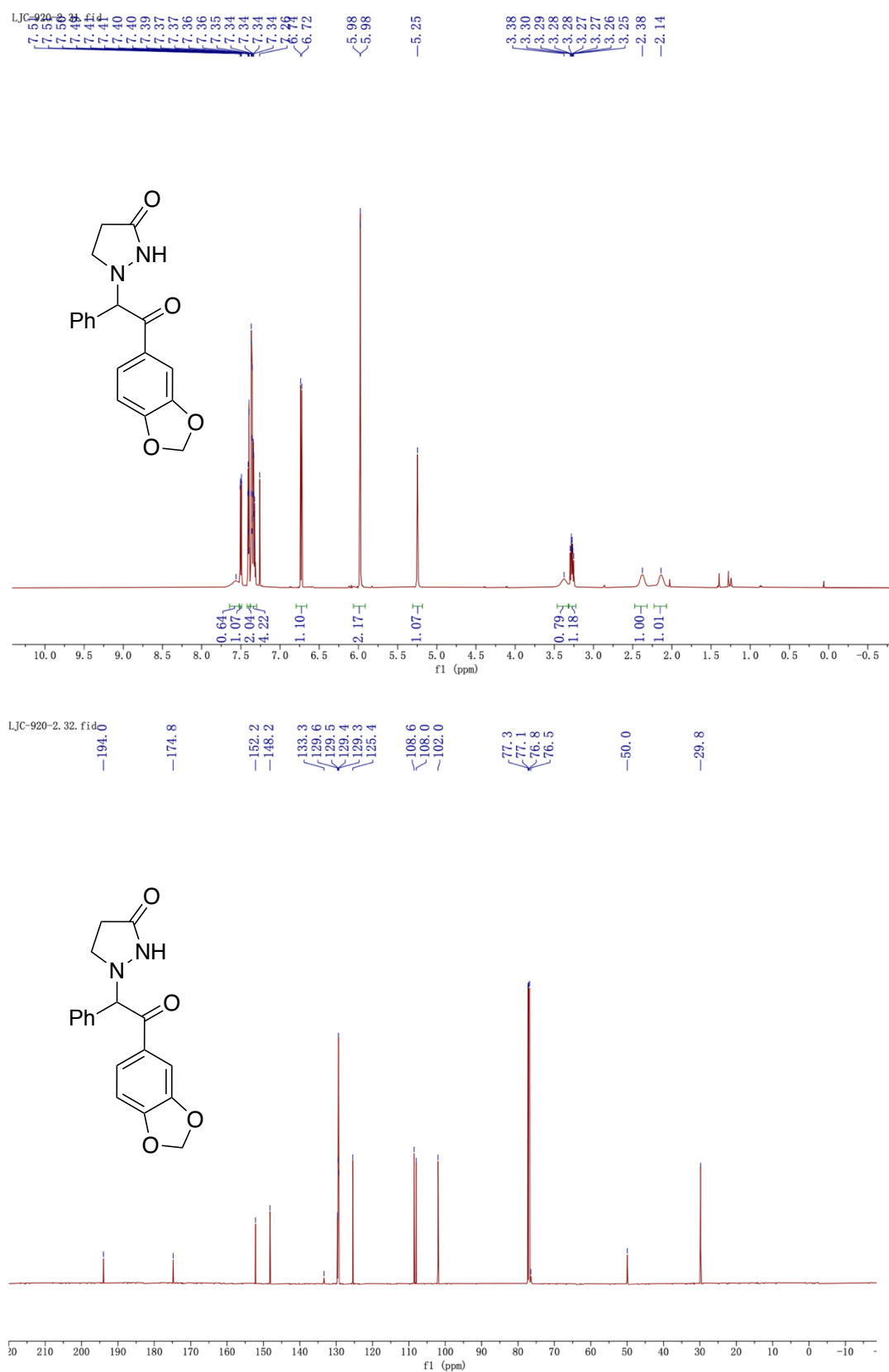
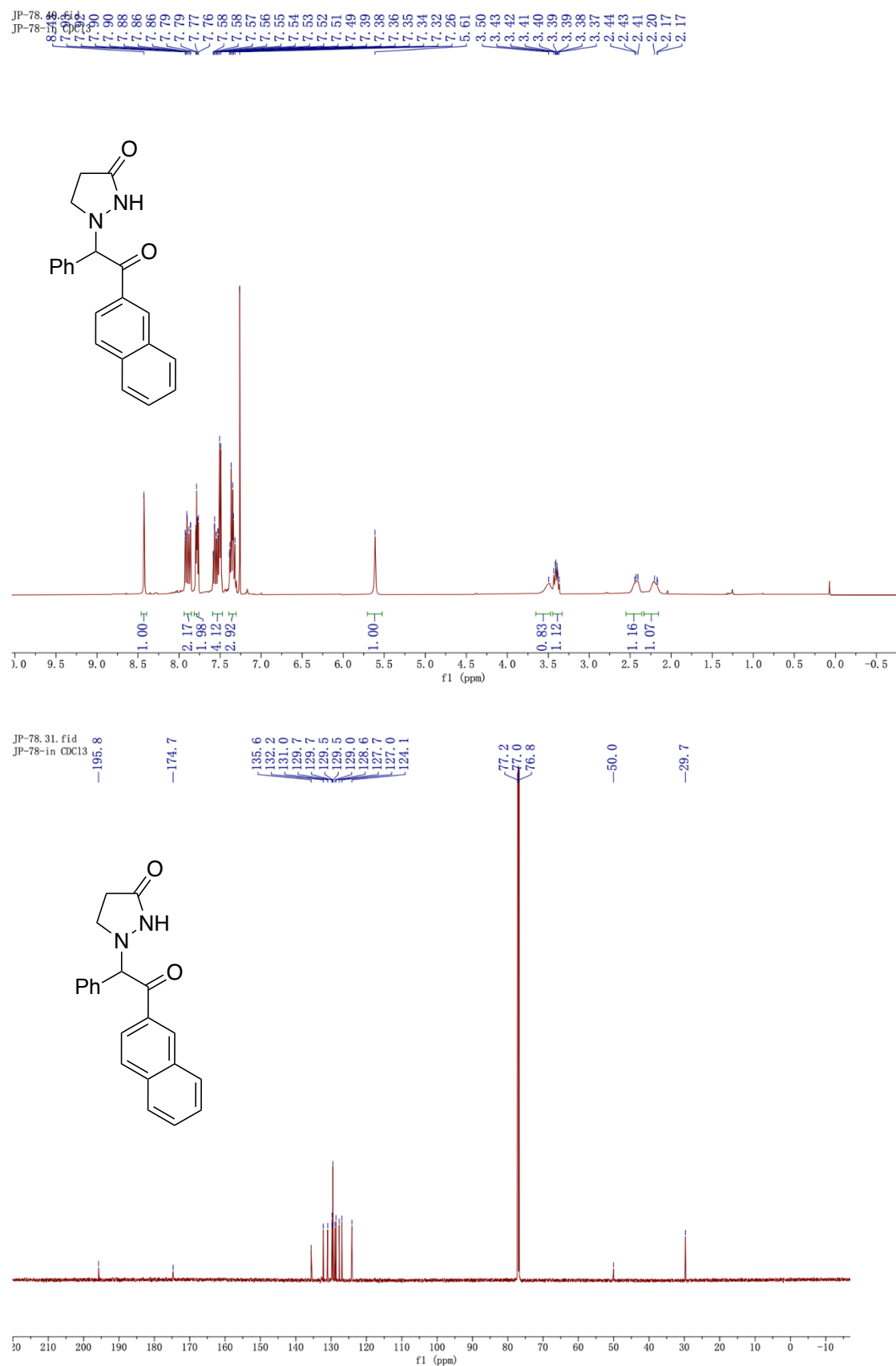
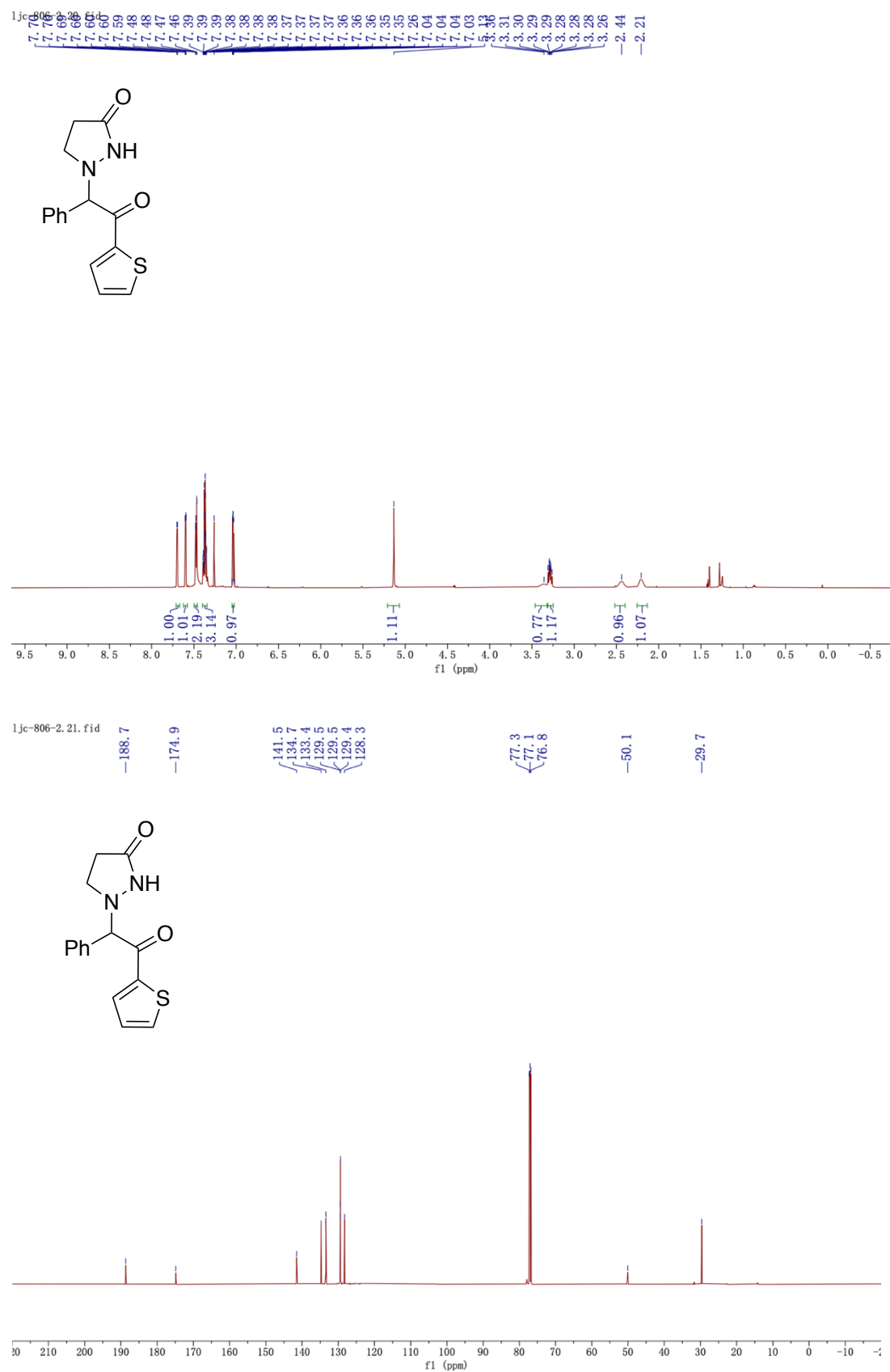


Figure S89. ^1H and ^{13}C NMR spectra of 1-(2-(naphthalen-2-yl)-2-oxo-1-phenylethyl)pyrazolidin-3-one (**5ak**)



[illegible]

Figure S91. ^1H and ^{13}C NMR spectra of 1-(2-oxo-1-phenyl-2-(thiophen-2-yl)ethyl)pyrazolidin-3-one (**5am**)



JP-45-2-10-854
JP-45-2-in

Chemical structure: O=C1CN(C(=O)c2cc3ccccc3s2)CC1c4ccccc4

¹H NMR spectrum (ppm):

- 8.78, 8.76, 8.39, 7.79, 7.77, 7.77, 7.52, 7.51, 7.50, 7.50, 7.49, 7.49, 7.48, 7.48, 7.47, 7.46, 7.41, 7.41, 7.40, 7.40, 7.39, 7.39, 7.38, 7.38, 7.37, 7.36, 7.35, 7.26, 5.46, 3.48, 3.44, 3.42, 3.40, 2.45, 2.43, 2.41, 2.41, 2.22, 2.20, 2.17

Integration values:

- 1.01, 1.00, 1.07, 3.24, 4.07, 1.00, 2.06, 1.05, 1.06



Figure S93. ^1H and ^{13}C NMR spectra of 1-(3,3-dimethyl-2-oxo-1-phenylbutyl)pyrazolidin-3-one (**5ao**)

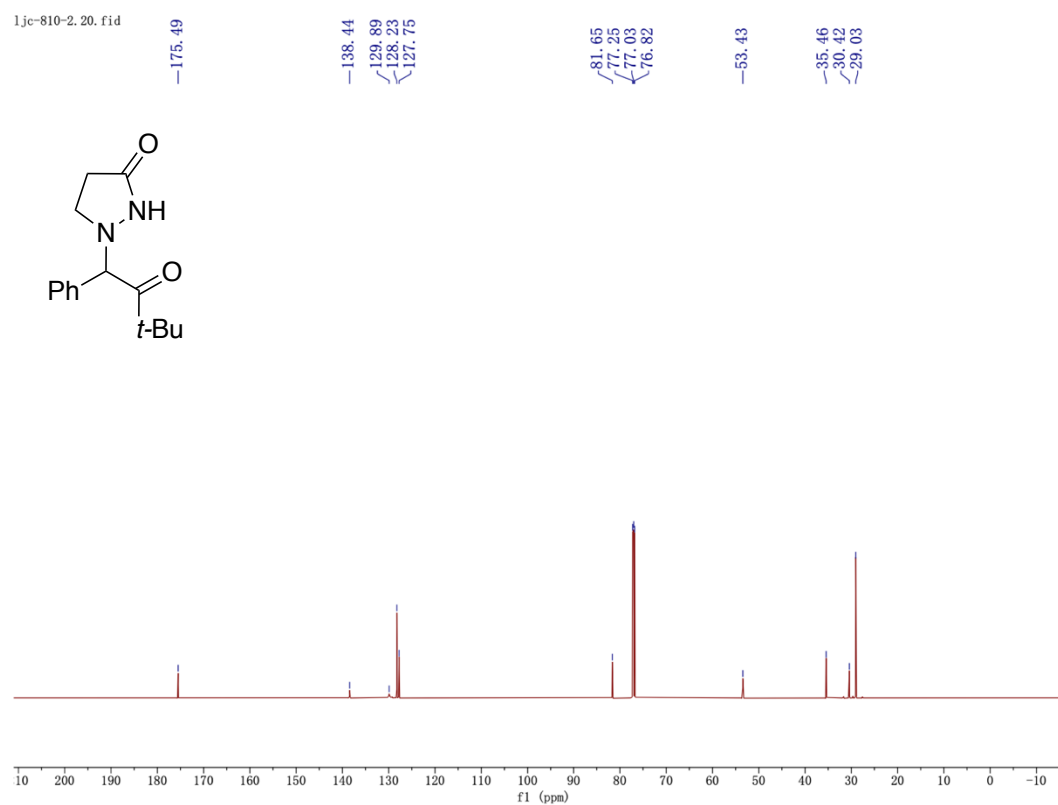
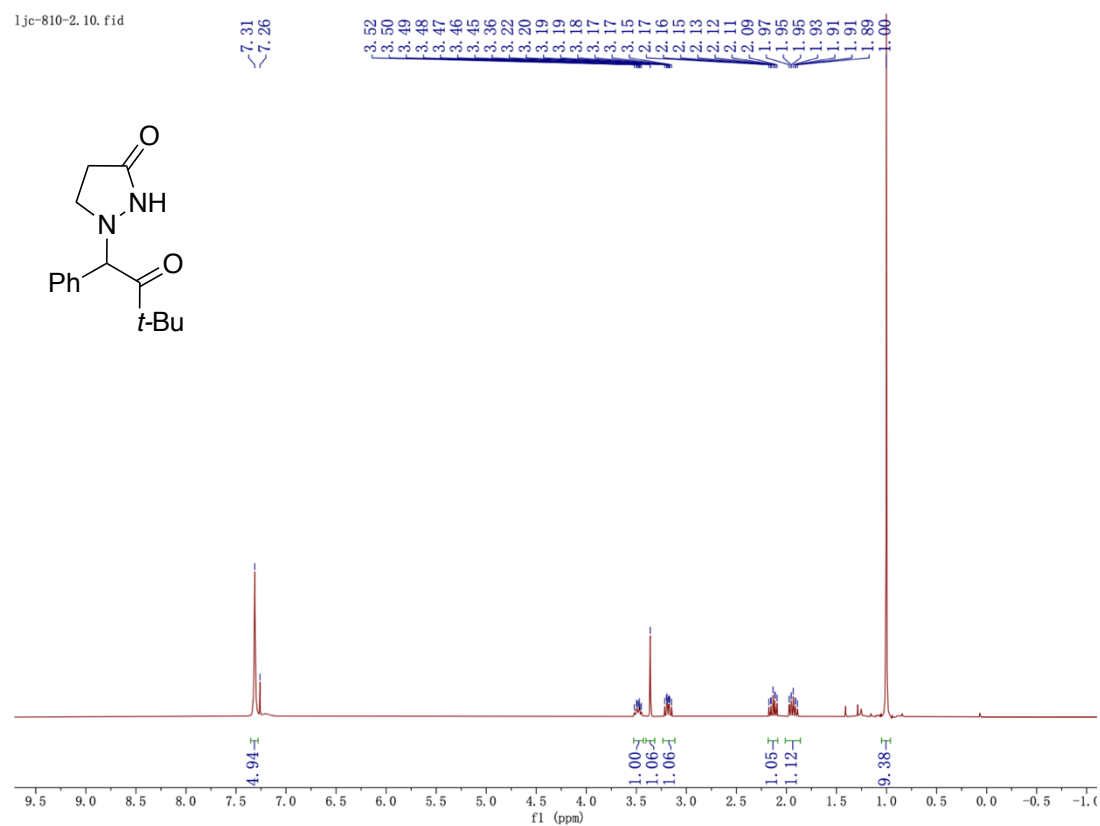
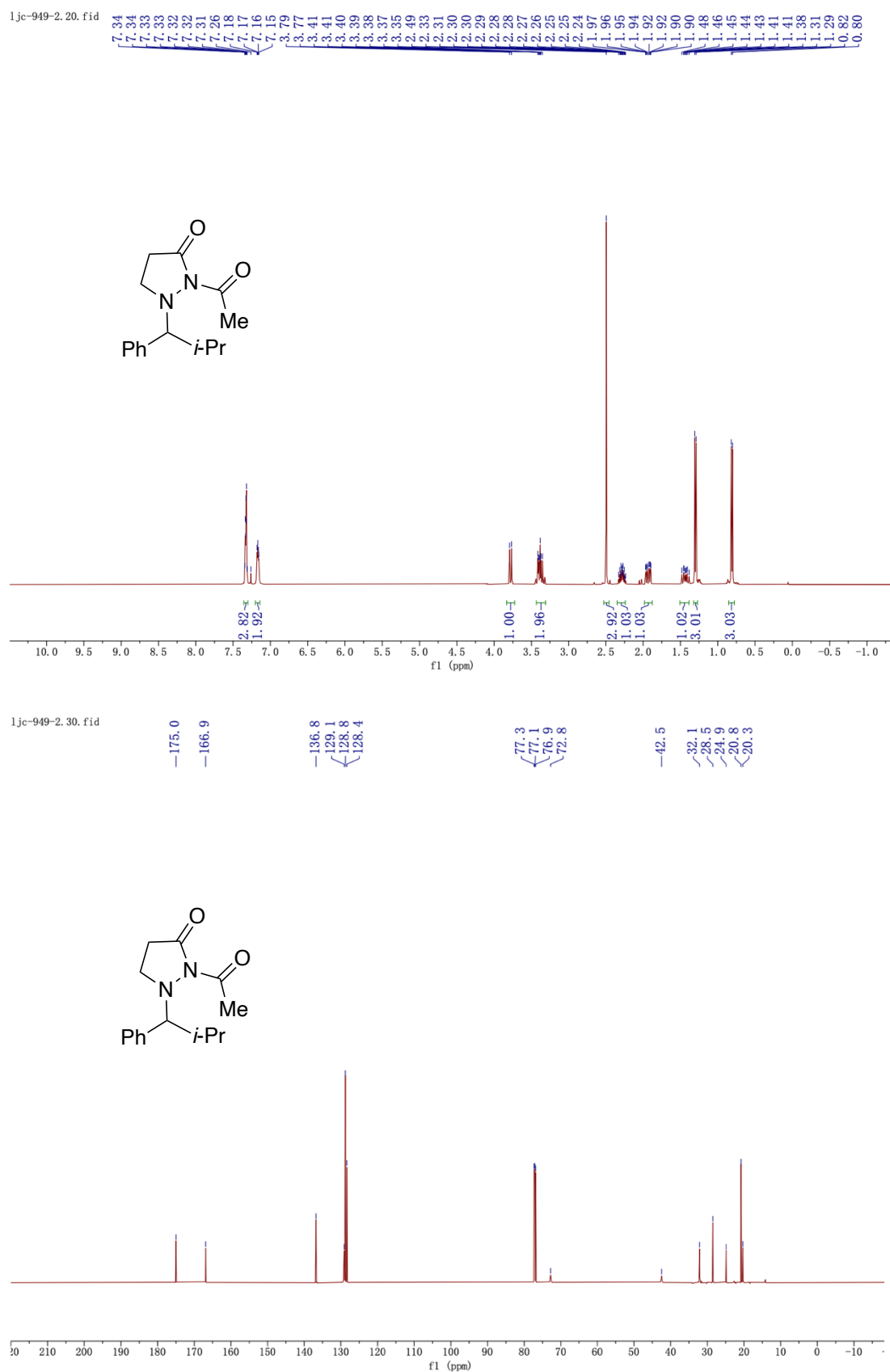


Figure S94. ^1H and ^{13}C NMR spectra of 2-acetyl-1-(2-methyl-1-phenylpropyl)pyrazolidin-3-one (**6aa**)



CCOC(=O)N1CCN(C1Cc2ccccc2)C(C)C

7.32, 7.30, 7.28, 7.26, 7.24, 7.22, 7.20, 7.18, 7.16, 7.14, 7.12, 7.10, 7.08, 7.06, 7.04, 7.02, 7.00, 6.98, 6.96, 6.94, 6.92, 6.90, 6.88, 6.86, 6.84, 6.82, 6.80, 6.78, 6.76, 6.74, 6.72, 6.70, 6.68, 6.66, 6.64, 6.62, 6.60, 6.58, 6.56, 6.54, 6.52, 6.50, 6.48, 6.46, 6.44, 6.42, 6.40, 6.38, 6.36, 6.34, 6.32, 6.30, 6.28, 6.26, 6.24, 6.22, 6.20, 6.18, 6.16, 6.14, 6.12, 6.10, 6.08, 6.06, 6.04, 6.02, 6.00, 5.98, 5.96, 5.94, 5.92, 5.90, 5.88, 5.86, 5.84, 5.82, 5.80, 5.78, 5.76, 5.74, 5.72, 5.70, 5.68, 5.66, 5.64, 5.62, 5.60, 5.58, 5.56, 5.54, 5.52, 5.50, 5.48, 5.46, 5.44, 5.42, 5.40, 5.38, 5.36, 5.34, 5.32, 5.30, 5.28, 5.26, 5.24, 5.22, 5.20, 5.18, 5.16, 5.14, 5.12, 5.10, 5.08, 5.06, 5.04, 5.02, 5.00, 4.98, 4.96, 4.94, 4.92, 4.90, 4.88, 4.86, 4.84, 4.82, 4.80, 4.78, 4.76, 4.74, 4.72, 4.70, 4.68, 4.66, 4.64, 4.62, 4.60, 4.58, 4.56, 4.54, 4.52, 4.50, 4.48, 4.46, 4.44, 4.42, 4.40, 4.38, 4.36, 4.34, 4.32, 4.30, 4.28, 4.26, 4.24, 4.22, 4.20, 4.18, 4.16, 4.14, 4.12, 4.10, 4.08, 4.06, 4.04, 4.02, 4.00, 3.98, 3.96, 3.94, 3.92, 3.90, 3.88, 3.86, 3.84, 3.82, 3.80, 3.78, 3.76, 3.74, 3.72, 3.70, 3.68, 3.66, 3.64, 3.62, 3.60, 3.58, 3.56, 3.54, 3.52, 3.50, 3.48, 3.46, 3.44, 3.42, 3.40, 3.38, 3.36, 3.34, 3.32, 3.30, 3.28, 3.26, 3.24, 3.22, 3.20, 3.18, 3.16, 3.14, 3.12, 3.10, 3.08, 3.06, 3.04, 3.02, 3.00, 2.98, 2.96, 2.94, 2.92, 2.90, 2.88, 2.86, 2.84, 2.82, 2.80, 2.78, 2.76, 2.74, 2.72, 2.70, 2.68, 2.66, 2.64, 2.62, 2.60, 2.58, 2.56, 2.54, 2.52, 2.50, 2.48, 2.46, 2.44, 2.42, 2.40, 2.38, 2.36, 2.34, 2.32, 2.30, 2.28, 2.26, 2.24, 2.22, 2.20, 2.18, 2.16, 2.14, 2.12, 2.10, 2.08, 2.06, 2.04, 2.02, 2.00, 1.98, 1.96, 1.94, 1.92, 1.90, 1.88, 1.86, 1.84, 1.82, 1.80, 1.78, 1.76, 1.74, 1.72, 1.70, 1.68, 1.66, 1.64, 1.62, 1.60, 1.58, 1.56, 1.54, 1.52, 1.50, 1.48, 1.46, 1.44, 1.42, 1.40, 1.38, 1.36, 1.34, 1.32, 1.30, 1.28, 1.26, 1.24, 1.22, 1.20, 1.18, 1.16, 1.14, 1.12, 1.10, 1.08, 1.06, 1.04, 1.02, 1.00, 0.98, 0.96, 0.94, 0.92, 0.90, 0.88, 0.86, 0.84, 0.82, 0.80, 0.78, 0.76, 0.74, 0.72, 0.70, 0.68, 0.66, 0.64, 0.62, 0.60, 0.58, 0.56, 0.54, 0.52, 0.50, 0.48, 0.46, 0.44, 0.42, 0.40, 0.38, 0.36, 0.34, 0.32, 0.30, 0.28, 0.26, 0.24, 0.22, 0.20, 0.18, 0.16, 0.14, 0.12, 0.10, 0.08, 0.06, 0.04, 0.02, 0.00, -0.02, -0.04, -0.06, -0.08, -0.10, -0.12, -0.14, -0.16, -0.18, -0.20, -0.22, -0.24, -0.26, -0.28, -0.30, -0.32, -0.34, -0.36, -0.38, -0.40, -0.42, -0.44, -0.46, -0.48, -0.50, -0.52, -0.54, -0.56, -0.58, -0.60, -0.62, -0.64, -0.66, -0.68, -0.70, -0.72, -0.74, -0.76, -0.78, -0.80, -0.82, -0.84, -0.86, -0.88, -0.90, -0.92, -0.94, -0.96, -0.98, -1.00, -1.02, -1.04, -1.06, -1.08, -1.10, -1.12, -1.14, -1.16, -1.18, -1.20, -1.22, -1.24, -1.26, -1.28, -1.30, -1.32, -1.34, -1.36, -1.38, -1.40, -1.42, -1.44, -1.46, -1.48, -1.50, -1.52, -1.54, -1.56, -1.58, -1.60, -1.62, -1.64, -1.66, -1.68, -1.70, -1.72, -1.74, -1.76, -1.78, -1.80, -1.82, -1.84, -1.86, -1.88, -1.90, -1.92, -1.94, -1.96, -1.98, -2.00, -2.02, -2.04, -2.06, -2.08, -2.10, -2.12, -2.14, -2.16, -2.18, -2.20, -2.22, -2.24, -2.26, -2.28, -2.30, -2.32, -2.34, -2.36, -2.38, -2.40, -2.42, -2.44, -2.46, -2.48, -2.50, -2.52, -2.54, -2.56, -2.58, -2.60, -2.62, -2.64, -2.66, -2.68, -2.70, -2.72, -2.74, -2.76, -2.78, -2.80, -2.82, -2.84, -2.86, -2.88, -2.90, -2.92, -2.94, -2.96, -2.98, -3.00, -3.02, -3.04, -3.06, -3.08, -3.10, -3.12, -3.14, -3.16, -3.18, -3.20, -3.22, -3.24, -3.26, -3.28, -3.30, -3.32, -3.34, -3.36, -3.38, -3.40, -3.42, -3.44, -3.46, -3.48, -3.50, -3.52, -3.54, -3.56, -3.58, -3.60, -3.62, -3.64, -3.66, -3.68, -3.70, -3.72, -3.74, -3.76, -3.78, -3.80, -3.82, -3.84, -3.86, -3.88, -3.90, -3.92, -3.94, -3.96, -3.98, -4.00, -4.02, -4.04, -4.06, -4.08, -4.10, -4.12, -4.14, -4.16, -4.18, -4.20, -4.22, -4.24, -4.26, -4.28, -4.30, -4.32, -4.34, -4.36, -4.38, -4.40, -4.42, -4.44, -4.46, -4.48, -4.50, -4.52, -4.54, -4.56, -4.58, -4.60, -4.62, -4.64, -4.66, -4.68, -4.70, -4.72, -4.74, -4.76, -4.78, -4.80, -4.82, -4.84, -4.86, -4.88, -4.90, -4.92, -4.94, -4.96, -4.98, -5.00, -5.02, -5.04, -5.06, -5.08, -5.10, -5.12, -5.14, -5.16, -5.18, -5.20, -5.22, -5.24, -5.26, -5.28, -5.30, -5.32, -5.34, -5.36, -5.38, -5.40, -5.42, -5.44, -5.46, -5.48, -5.50, -5.52, -5.54, -5.56, -5.58, -5.60, -5.62, -5.64, -5.66, -5.68,



Figure S96. ^1H and ^{13}C NMR spectra of 1-(2-hydroxy-1,2-diphenylethyl)pyrazolidin-3-one
(**8aa**)

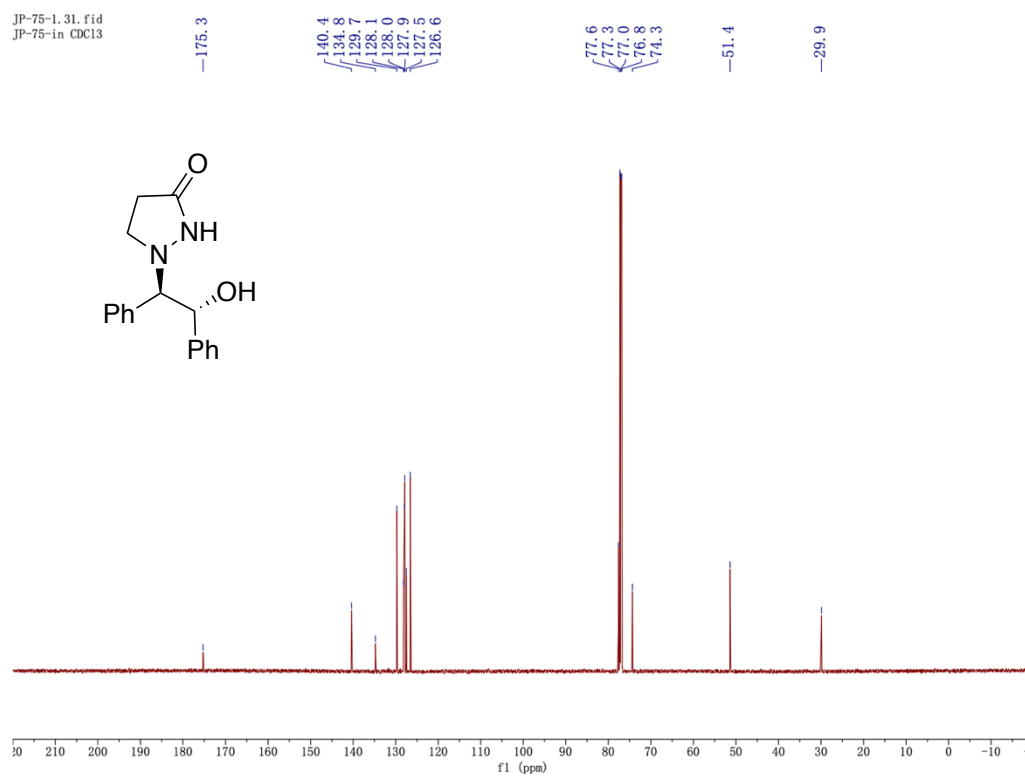
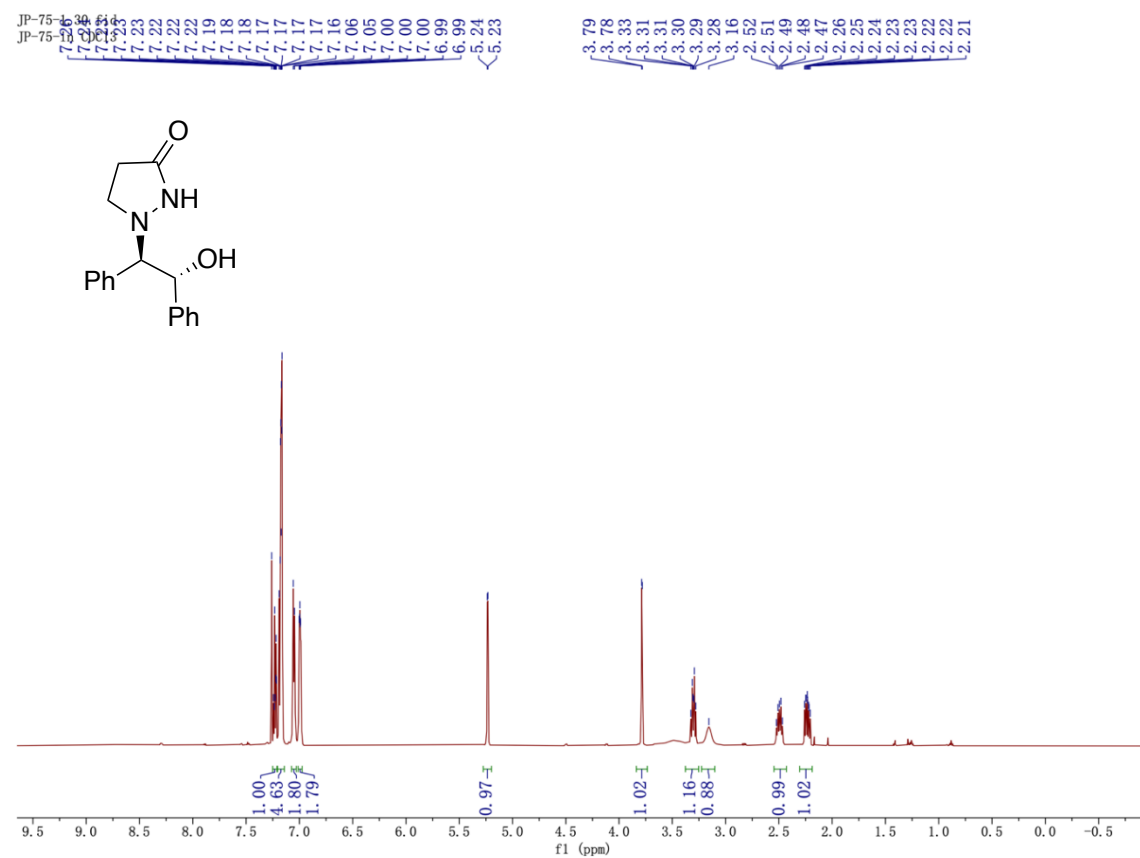


Figure S97. ^1H and ^{13}C NMR spectra of 3-((2-hydroxy-1,2-diphenylethyl)amino)propenamide

(9aa)

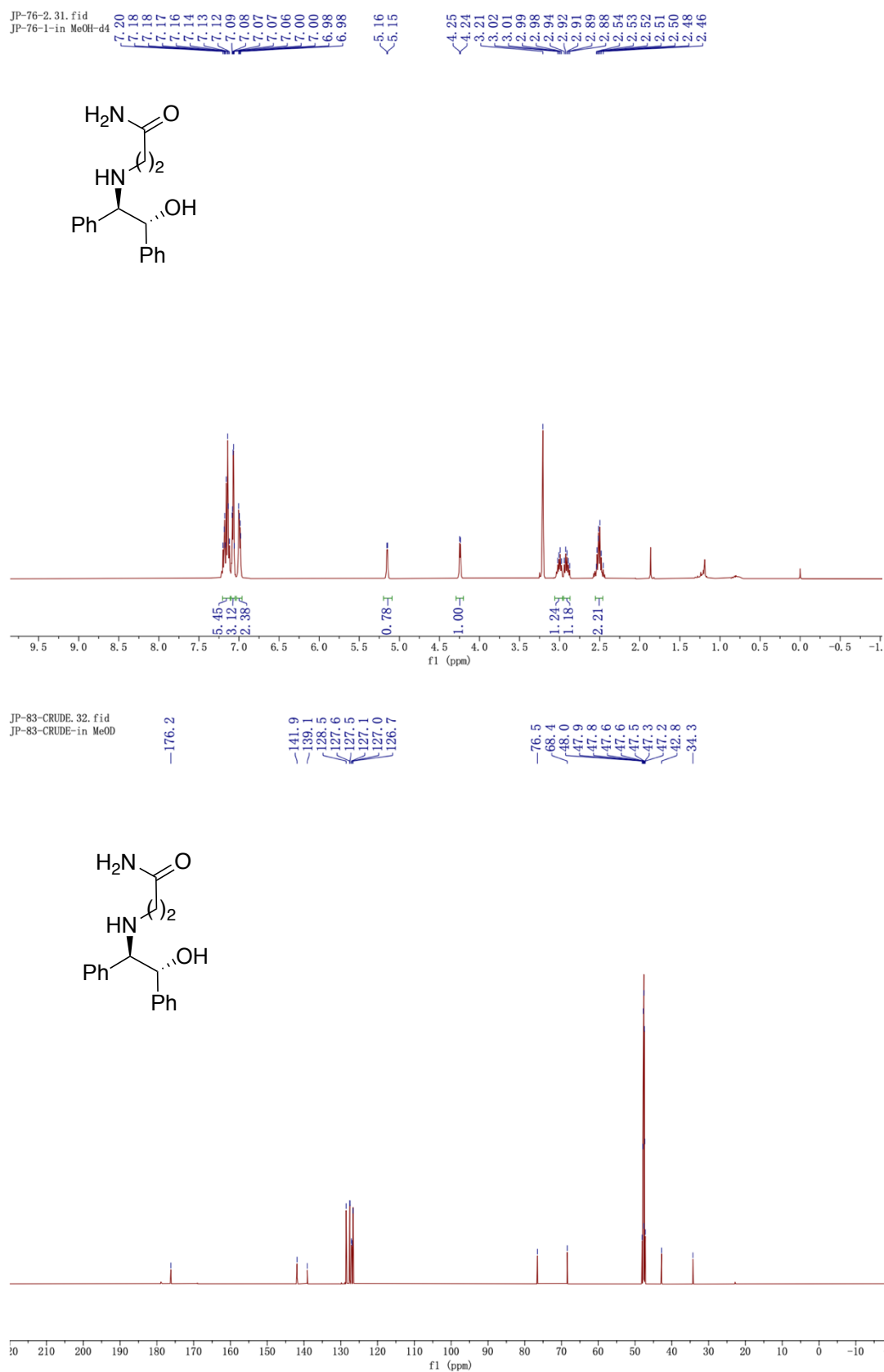


Figure S98. ^1H and ^{13}C NMR spectra of 4CzPN

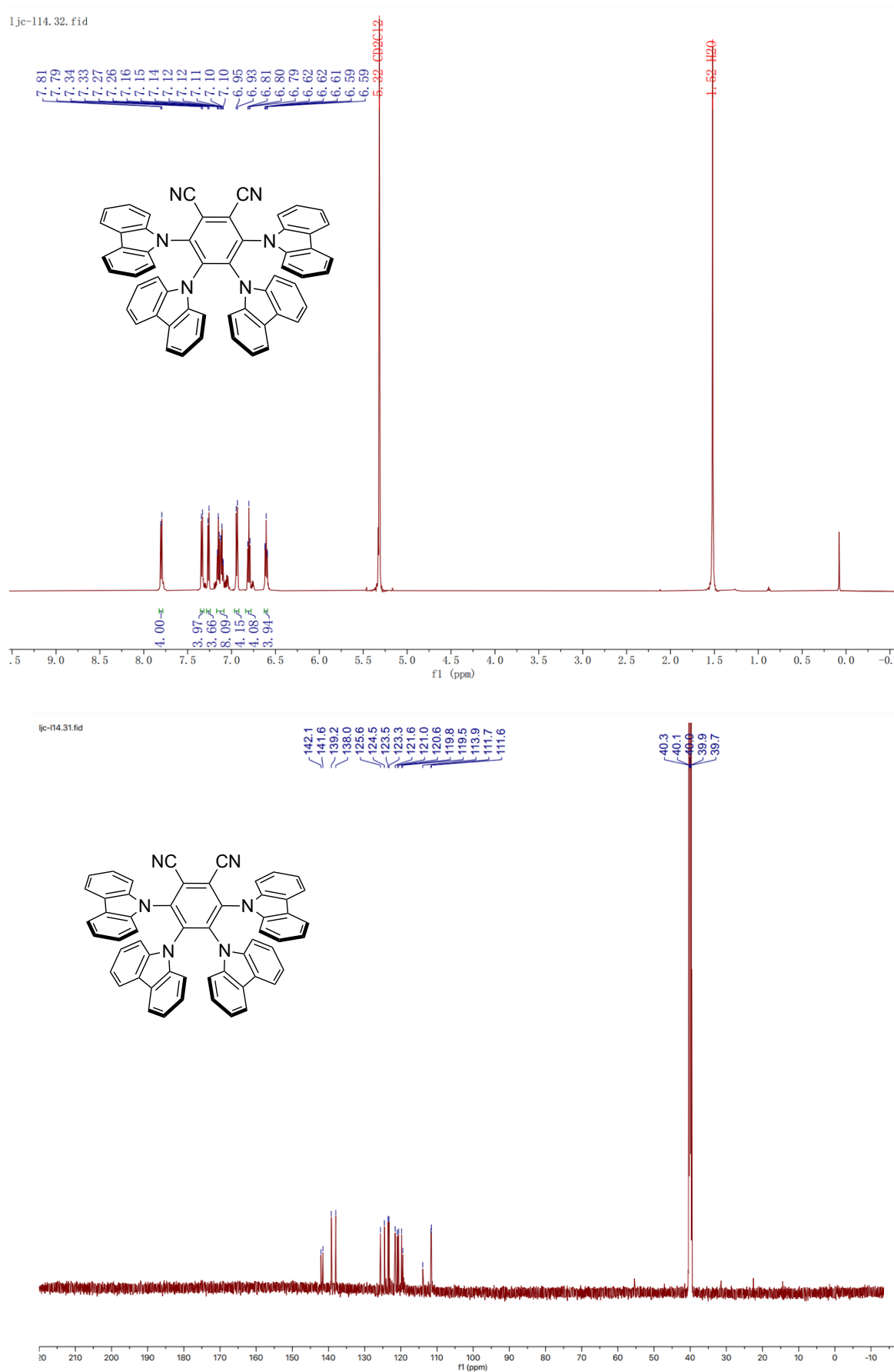
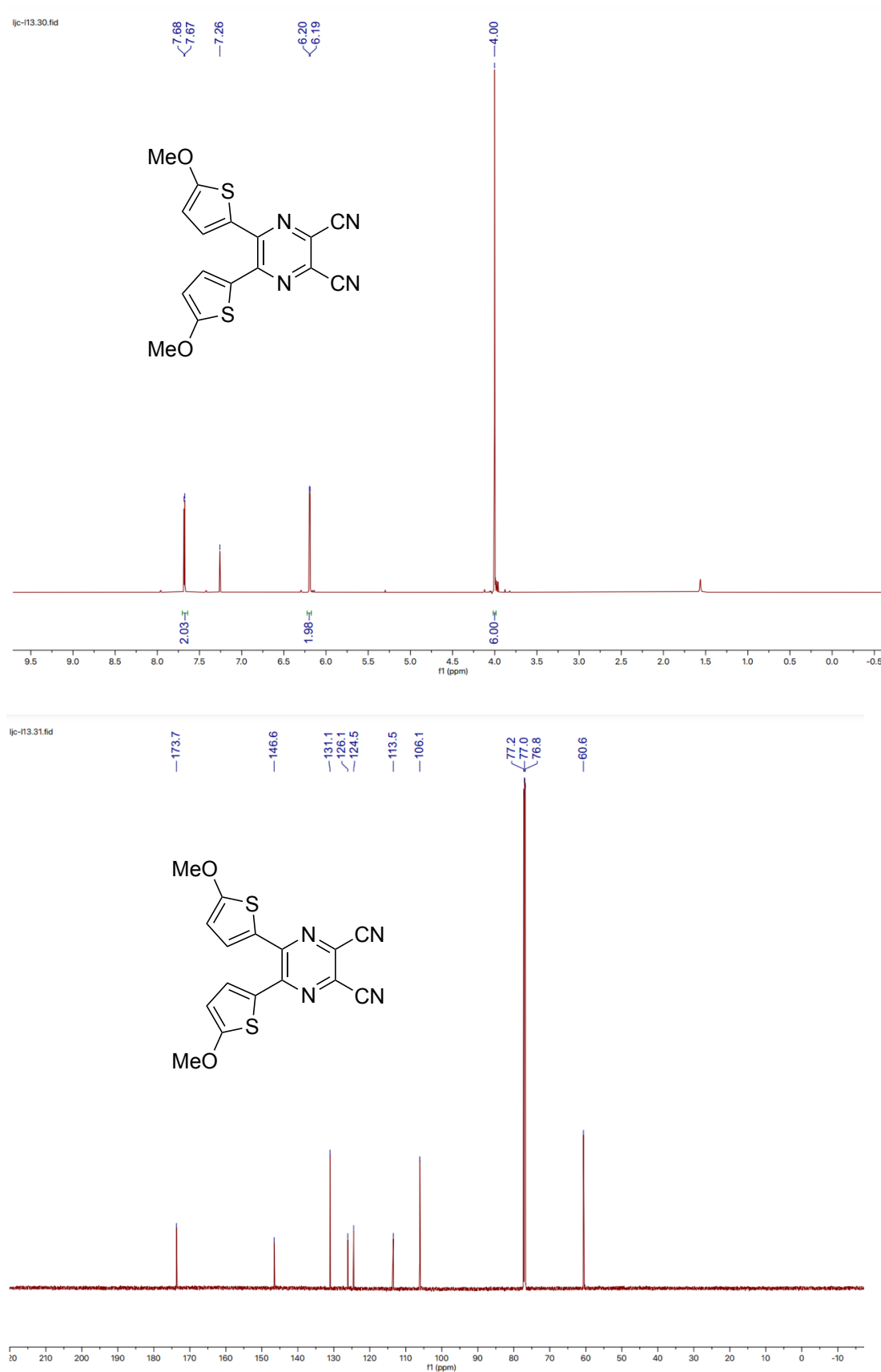


Figure S99. ^1H and ^{13}C NMR spectra of DPZ



6. References

- S1. M. Keller, A. S. S. Sido, P. Pale and J. Sommer, Copper(I) Zeolites as Heterogeneous and Ligand-Free Catalysts: [3 + 2] Cycloaddition of Azomethine Imines, *Chem. Eur. J.*, 2009, **15**, 2810–2817.
- S2. K. J. Jiao, D. Liu, H. X. Ma, H. Qiu, P. Fang, and T. S. Mei, Nickel-Catalyzed Electrochemical Reductive Relay Cross-Coupling of Alkyl Halides to Aryl Halides, *Angew. Chem. Int. Ed.*, 2020, **59**, 6520–6524.
- S3. P. Fristrup, M. Kreis, A. Palmelund, P. O. Norrby and R. Madsen, The Mechanism for the Rhodium-Catalyzed Decarbonylation of Aldehydes: A Combined Experimental and Theoretical Study, *J. Am. Chem. Soc.*, 2008, **130**, 5206–215.
- S4. T. Rossolini, J. A. Leitch, R. Grainger and D. J. Dixon, Photocatalytic Three-Component Umpolung Synthesis of 1,3-Diamines, *Org. Lett.*, 2018, **20**, 6794–6798.
- S5. A. Beuchel, D. Robaa, D. A. Negatu, A. Madani, N. Alvarez, M. D. Zimmerman, A. Richter, L. Mann, S. Hoenke, R. Csuk, T. Dick and P. Imming, Structure–Activity Relationship of Anti-Mykobacterium abscessus Piperidine-4-carboxamides, a New Class of NBTI DNA Gyrase Inhibitors, *ACS Med. Chem. Lett.*, 2022, **13**, 417–427.
- S6. P. Trillo, T. Slagbrand and H. Adolfsson, Straightforward α -Amino Nitrile Synthesis Through Mo(CO)₆-Catalyzed Reductive Functionalization of Carboxamides, *Angew. Chem. Int. Ed.*, 2018, **57**, 12347–12351.
- S7. G. Barbe and A. B. Charette, Highly Chemoselective Metal-Free Reduction of Tertiary Amides, *J. Am. Chem. Soc.*, 2008, **130**, 18–19.
- S8. B. Bieszczad, L. A. Perego and P. Melchiorre, Photochemical C–H Hydroxyalkylation of Quinolines and Isoquinolines, *Angew. Chem. Int. Ed.*, 2019, **58**, 16878–16883.

- S9. J. Li, X. C. Lu, Y. Xu, J. X. Wen, G. Q. Hou and L. Liu, Photoredox Catalysis Enables Decarboxylative Cyclization with Hypervalent Iodine(III) Reagents: Access to 2,5-Disubstituted 1,3,4-Oxadiazoles, *Org. Lett.*, 2020, **22**, 9621–9626.
- S10. Y. Zhao, C. Zhang, K. F. Chin, O. Pytela, G. Wei, H. Liu, F. Bureš and Z. Jiang, Dicyanopyrazine-derived Push–pull Chromophores for Highly Efficient Photoredox Catalysis, *RSC Adv.*, 2014, **4**, 30062–30067.
- S11. J. M. John and S. H. A. Bergens, Highly Active Catalyst for the Hydrogenation of Amides to Alcohols and Amines, *Angew. Chem. Int. Ed.*, 2011, **50**, 10377–10380.
- S12. A. Piperno, C. Carnovale, S. V. Giofrè and D. Iannazzo, Hydrozirconation of Four-, Five-, Six- and Seven-Membered *N*-Alkoxy carbonyl Lactams to Lactamols, *Tetrahedron Lett.*, 2011, **52**, 6880–6882.
- S13. N. Utsumi, N. Arai, K. Kawaguchi, T. Katayama, T. Yasuda, K. Murata and T. Ohkuma, Asymmetric Hydrogenation of Polysubstituted Aromatic Ketones Catalyzed by the DIPSkewphos/PICA Derivative–Ruthenium(II) Complexes, *ChemCatChem.*, 2018, **10**, 3955–3959.
- S14. A. Chan and K. A. Scheidt, Direct Amination of Homoenolates Catalyzed by *N* Heterocyclic Carbenes, *J. Am. Chem. Soc.*, 2008, **130**, 2740–2741.
- S15. S. E. Winterton and J. M. Ready, [3 + 2]-Cycloadditions of Azomethine Imines and Ynolates, *Org. Lett.*, 2016, **18**, 2608–2611.
- S16. W. Zhou, X. X. Li, G. H. Li, Y. Wu and Z. Chen, Gold Catalyzed [3 + 2] Cycloaddition of *N*-Allenyl Amides with Azomethine Imines, *Chem. Commun.*, 2013, **49**, 3552–3554.
- S17. C. Li, C. S. Wang, T. Z. Li, G. J. Mei and F. Shi, Brønsted Acid-Catalyzed (4 + 3) Cyclization of *N,N'*-Cyclic Azomethine Imines with Isatoic Anhydrides, *Org. Lett.*, 2019, **21**, 598–602.

- S18. R. Shintani and T. Hayashi, Palladium-Catalyzed [3 + 3] Cycloaddition of Trimethylenemethane with Azomethine Imines, *J. Am. Chem. Soc.*, 2006, **128**, 6330–6331.
- S19. Q. Du, J. M. Neudörfl and H. G. Schmalz, Chiral Phosphine–Phosphite Ligands in Asymmetric Gold Catalysis: Highly Enantioselective Synthesis of Furo[3,4-d]-Tetrahydropyridazine Derivatives through [3+3]-Cycloaddition, *Chem. Eur. J.*, 2018, **24**, 2379–2383.
- S20. Q. Y. Fang, H. S. Jin, R. B. Wang and L. M. Zhao, DABCO-mediated [3+3] Cycloaddition of Azomethine Imines with In Situ Generated Nitrile Oxides from Hydroximoyl Chlorides, *Chem. Commun.*, 2019, **55**, 10587–10590.
- S21. Z. Bai, H. Zhang, H. Wang, H. Yu, G. Chen and G. He, Enantioselective Alkylamination of Unactivated Alkenes under Copper Catalysis, *J. Am. Chem. Soc.*, 2021, **143**, 1195–1202.
- S22. Q. Y. Wu, Q. Q. Min, G. Z. Ao and F. Liu, Radical alkylation of para-quinone methides with 4-substituted Hantzsch esters/nitriles via organic photoredox catalysis, *Org. Biomol. Chem.*, 2018, **16**, 6391–6394.
- S23. T. van Leeuwen, L. Buzzetti, L. A. Perego and P. Melchiorre, A Redox-Active Nickel Complex that Acts as an Electron Mediator in Photochemical Giese Reactions, *Angew. Chem. Int. Ed.*, 2019, **58**, 4953–4957.
- S24. Á. Gutiérrez-Bonet, C. Remeur, J. K. Matsui and G. A. Molander, Late-Stage C–H Alkylation of Heterocycles and 1,4-Quinones via Oxidative Homolysis of 1,4-Dihydropyridines, *J. Am. Chem. Soc.*, 2017, **139**, 12251–12258.
- S25. X. G. Liu, C. S. Dong, F. Li and B. Zhang, Manganese-Mediated Direct Functionalization of Hantzsch Esters with Alkyl Iodides via an Aromatization–Dearomatization Strategy, *Org. Lett.*, 2021, **23**, 4002–4007.
- S26. X. Luo and P. Wang, Ynonylation of Acyl Radicals by Electroinduced Homolysis of 4-Acyl-1,4-dihydropyridines, *Org. Lett.*, 2021, **23**, 4960–4965.

- S27. L. Liu, Z. Deng, K. Xu, P. Jiang, H. Du and J. Tan, Access to Deuterated Unnatural α -Amino Acids and Peptides by Photochemical Acyl Radical Addition, *Org. Lett.*, 2021, **23**, 5299–5304.
- S28. G. Goti, B. Bieszczad, A. Vega-Peñaloza and P. Melchiorre, Stereocontrolled Synthesis of 1,4-Dicarbonyl Compounds by Photochemical Organocatalytic Acyl Radical Addition to Enals, *Angew. Chem. Int. Ed.*, 2019, **58**, 1213–1217.