Electronic Supplementary Material (ESI) for ChemComm.

Iron-catalyzed decarboxylative radical addition to chiral azomethine imines upon visible light

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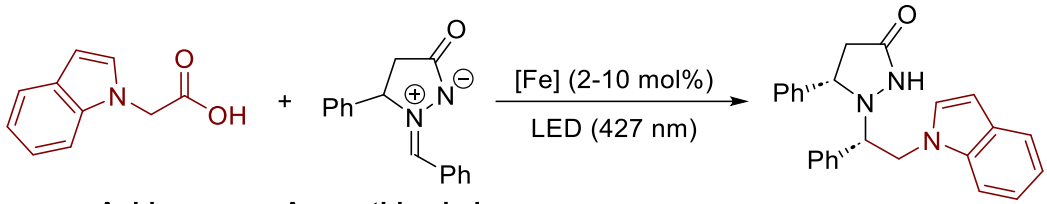
I. General information

Reactions were performed using oven dried glassware under inert atmosphere of nitrogen or argon. Unless otherwise noted, all reagent-grade chemicals and solvents were obtained from commercial suppliers and were used as received. Tetrahydrofuran (THF), toluene, acetonitrile (MeCN) and dichloromethane (CH_2Cl_2) were dried over MBRAUN MB SPS-800 Apparatus. Reactions were monitored by thin-layer chromatography with silica gel 60 F254 pre-coated aluminum plates (0.25 mm). Visualization was performed under UV light, phosphomolybdic acid or $KMnO_4$ oxidation. Chromatographic purification of compounds was achieved with 60 silica gel (40-63 μm). Melting points were measured on a WME Köfler hot-stage (Stuart SMP3) and are uncorrected. Infrared spectra (IR) were recorded on a PerkinElmer Spectrum 100 Series FT-IR spectrometer. Liquids and solids were applied on the Single Reflection Attenuated Total Reflectance (ATR) Accessories. Data are reported in cm^{-1}. ^1H Spectra (300 MHz or 400 MHz) and ^{13}C NMR spectra (75 MHz or 100 MHz) were recorded on a Bruker Avance 300 or NEO400As. Processing and analysis of the spectra were performed with the Topspin 3.6 software from Brucker on a PC workstation. Data appear in the following order: chemical shifts in ppm which were referenced to the internal solvent signal, number of protons, multiplicity (*s*, singlet; *d*, doublet; *t*, triplet; *q*, quadruplet; *dd*, doublet of doublet; *ddd*, doublet of doublet of doublet; *dt*, doublet of triplet; *ddt*, doublet of doublet of triplet; *td*, triplet of doublet; *tdd*, triplet of doublet of doublet; *m*, multiplet; AB_q, AB system) and coupling constant *J* in Hertz. Accurate Mass measurements (HRMS) were performed by the Mass Spectrometry Laboratory of the University of Rouen and were recorded with a Waters LCT 1er XR spectrometer.

II. Investigation of the reaction conditions

1. Optimization at 427 nm

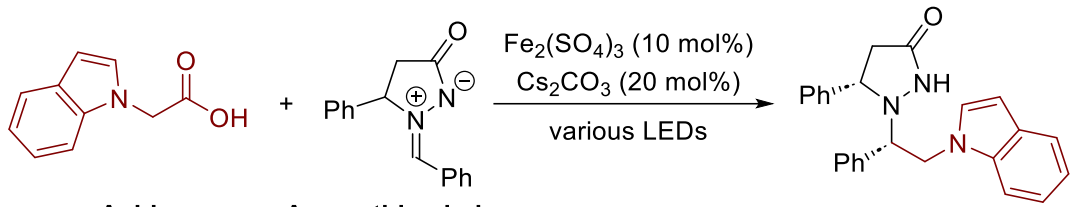


Acid **Azomethine imine**

Entry	[Fe] (mol%)	Acid (equiv)	Base (mol%)	Solvent	Time (h)	Yield[a] (%)	dr[b] (%)
1	$Fe_2(SO_4)_3$ (10)[c]	2	Cs_2CO_3 (20)	DMSO	7	0 (94)[d]	-
2	-	2	Cs_2CO_3 (20)	DMSO	7	5 (65)[d]	-
3	**$Fe_2(SO_4)_3$ (10)**	**2**	**Cs_2CO_3 (20)**	**DMSO**	**7**	**91 (82)[e]**	**86:14**
4	$Fe_2(SO_4)_3$ (10)	2	Cs_2CO_3 (20)	MeCN	7	67 (0)[d]	-
5	-	2	Cs_2CO_3 (20)	MeCN	7	4 (91)[d]	-
6	$Fe_2(SO_4)_3$ (10)	2	Cs_2CO_3 (20)	$(CH_2Cl)_2$	7	26 (57)[d]	-
7	-	2	Cs_2CO_3 (20)	$(CH_2Cl)_2$	7	10 (63)[d]	-
8	$Fe_2(SO_4)_3$ (10)	2	Na_2CO_3 (20)	DMSO	7	84 (0)[d]	-
9	$Fe_2(SO_4)_3$ (10)	2	DBU (20)	DMSO	7	75 (0)[d]	-
10	$Fe_2(SO_4)_3$ (10)	2	-	DMSO	7	84 (75)[e]	87:13
11	**$Fe_2(SO_4)_3$ (10)**	**1.5**	**Cs_2CO_3 (20)**	**DMSO**	**7**	**95 (90)[e]**	**86:14**
12	$Fe_2(SO_4)_3$ (10)	1.0	Cs_2CO_3 (20)	DMSO	7	45 (21)[d]	-
13	$Fe_2(SO_4)_3.H_2O$ (10)	1.5	Cs_2CO_3 (20)	DMSO	7	90 (0)[d]	-
14	$Fe(acac)_3$ (10)	1.5	Cs_2CO_3 (20)	DMSO	7	89 (0)[d]	-
15	$Fe(NO_3)_3.H_2O$ (10)	1.5	Cs_2CO_3 (20)	DMSO	7	81 (0)[d]	-
16	$Fe_2(SO_4)_3$ (5)	1.5	Cs_2CO_3 (20)	DMSO	7	81 (0)[d]	-
17	$Fe_2(SO_4)_3$ (2)	1.5	Cs_2CO_3 (20)	DMSO	7	84 (76)[e]	85:15
18	$Fe_2(SO_4)_3$ (1)	1.5	Cs_2CO_3 (20)	DMSO	7	79 (0)[d]	-
19	$Fe_2(SO_4)_3$ (2)	1.5	Cs_2CO_3 (20)	DMSO	24	90	88:12

Table S1. The reaction was carried out with the azomethine imine (0.2 mmol) in the given solvent (0.1 M versus azomethine imine) at 25-30 °C (temperature regulated using a fan and monitored with a thermometer). EvoluChem 18 W LEDs 427 nm was used at 6 cm from the reaction flask with temperature controlled by a fan (~ 25-30 °C). [a]Yield of both diastereoisomers was determined on the crude mixture by ^{1}H NMR with Bn_2O as an internal standard. [b]Diastereoisomeric ratio (dr) determined by ^{1}H NMR (after purification by column chromatography or by HPLC/MS on the crude). [c]Without LED irradiation. [d]Yield (remaining percentage) of azomethine imine determined on the crude mixture by ^{1}H NMR with Bn_2O as an internal standard. [e]Isolated yield after column chromatography. [f]On 1 mmol scale.

2. *Optimization at various wavelengths*



Acid **Azomethine imine**

Entry	[Fe] (mol%)	Acid (equiv)	LED (nm)	Solvent	Temp, time (°C,h)	Yield[a] (%)	dr[b] (%)
1	-[c]	2	405	DMSO	30, 7	6 (22)[d]	-
2	-	2	405	DMSO	30, 7	52 (0)[d]	-
3	$Fe_2(SO_4)_3$ (10)	2	405	DMSO	30, 7	81 (76)[e]	85:15
4	$Fe_2(SO_4)_3$ (10)[c]	2	405	DMSO	30, 7	66 (17)[d]	-
5	$Fe_2(SO_4)_3$ (10)[f]	2	405	DMSO	30, 7	78 (0)[d]	-
6	-[f]	2	405	DMSO	30, 7	8 (24)[d]	-
7	$Fe_2(SO_4)_3$ (10)	2	405	MeCN	30, 7	69 (0)[d] (66)[e]	86:14
8	-	2	405	MeCN	30, 7	6 (39)[d]	-
9	$Fe_2(SO_4)_3$ (10)[g]	2	405	MeCN	30, 7	1 (58)[d]	-
10	$Fe_2(SO_4)_3$ (10)	2	425	DMSO	30, 7	97 (0)[d]	-
11	$Fe_2(SO_4)_3$ (10)	2	427	DMSO	30, 7	91 (82)[e]	86:14
12	$Fe_2(SO_4)_3$ (10)	2	450-455	DMSO	30, 7	89 (0)[d] (86)[e]	87:13
13	$Fe_2(SO_4)_3$ (10)	2	525-530	DMSO	30, 7	62 (19)[d]	-
14	$Fe_2(SO_4)_3$ (10)	2	427	DMSO	15, 7	87 (80)[e]	88:12
15	$Fe_2(SO_4)_3$ (10)	1.5	427	DMSO	15, 7 (under air)	22 (0)[d]	-

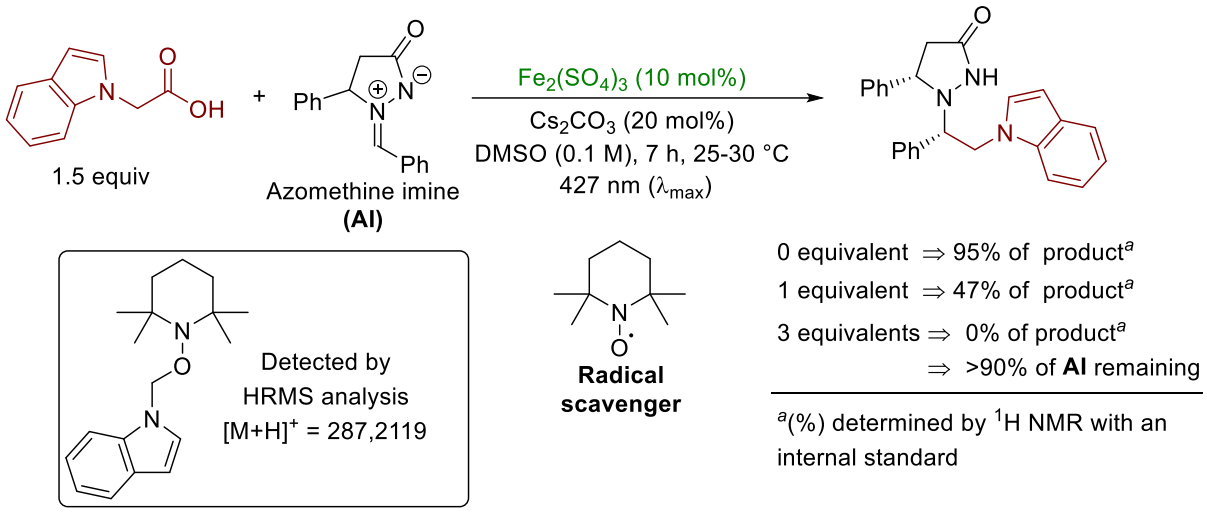
Table S2. The reaction was carried out with the azomethine imine (0.2 mmol) in the given solvent (0.1 M) at 25-30 °C (temperature regulated using a fan and monitored with a thermometer). EvoluChem 18 W LEDs were used at 6 cm from the reaction flask with temperature controlled by a fan (~ 25-30 °C). [a]Yield of both diastereoisomers determined on the crude mixture by ^{1}H NMR with Bn_2O as an internal standard. [b]Diastereoisomeric ratio (dr) determined by ^{1}H NMR (after purification by column chromatography or by HPLC/MS on the crude). [c]Without base. [d]Yield (remaining percentage) of azomethine imine determined on the crude mixture by ^{1}H NMR with Bn_2O as an internal standard. [e]Isolated yield after column chromatography. [f]Use of $CsHCO_3$ (0.2 equiv.) instead of Cs_2CO_3. [g]Use of K_2CO_3 (0.2 equiv.) instead of Cs_2CO_3.

III. Mechanistic investigation

1. Control experiments

a. TEMPO inhibition

TEMPO inhibited the formation of the addition product by likely quenching the radical species originated from the decarboxylative process as testified by HRMS analysis of the crude reaction mixture. The reaction performed under air also led to a decreased yield of 20%.



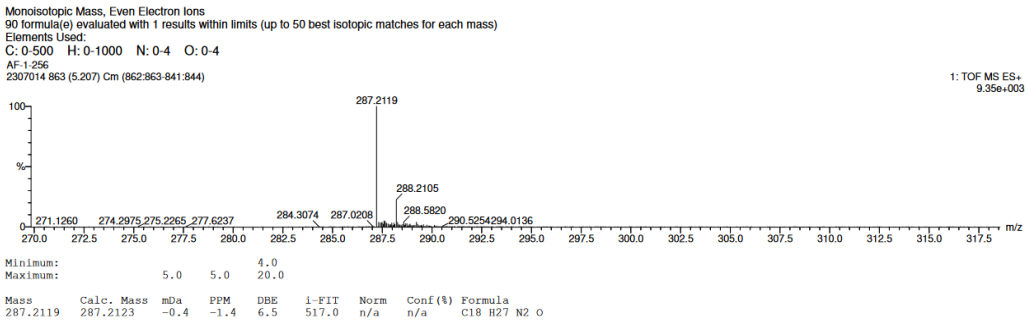


Figure S1. Trapping experiment

b. ON/OFF experiment

Radical addition on azomethine imine was started under the standard conditions. After 30 min, the light irradiation was stopped for 30 min. The process was repeated two more times and the NMR yield of product was measured over time. In the absence of light, no evolution of the formation of the product was observed, suggesting that light is necessary for the reaction to proceed. This also demonstrates that an extensive radical chain mechanism should not be predominant, even though we cannot rule out a very rapid and short chain radical mechanism through a HAT process. Light interruptions were not deleterious as the reaction could start again once the irradiation was restored.

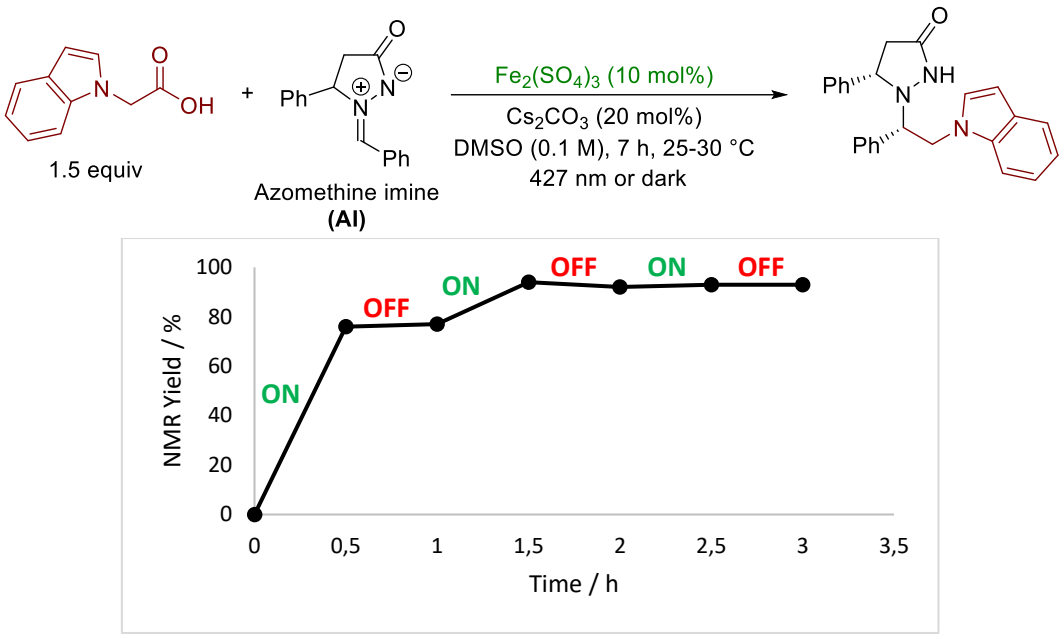
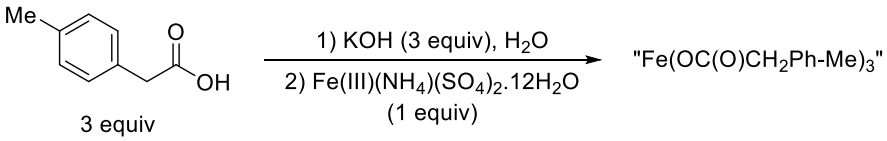


Figure S2. ON/OFF experiments

2. Iron complex synthesis and characterization



Scheme S3. Formation of the iron complex

The iron complex was synthesized following a modified procedure.[1] To a suspension of *p*-Me-benzylcarboxylic acid (3 equiv, 5.17 mmol) in deionized water (5 mL) was added crushed KOH (3 equiv. 5.17mmol) in one portion to achieve a clear solution (heating gently with the heat gun and let stirred for 15 min). A solution of $Fe(NH_4)(SO_4)_2.12H_2O$ (1 equiv., 1.72 mmol) in deionized water (4 mL) was added dropwise to the carboxylate solution under vigorous stirring. The tricarboxylate immediately precipitated as a red sticky solid and then was dissolved in chloroform and the phases separated. The organic phase was dried over $MgSO_4$, concentrated under vacuum and the resulting waxy solid further dried under the pump, with some pentane to remove traces of the solvent to deliver the complex as a red powder in 84% yield (730 mg). HRMS (API^-): calcd for $C_{27}H_{27}O_6{}^{56}Fe$ [$(M+e)^-$]: 503.1157; Found: 503.1159.

[1] Innocent, M.; Lalande, G.; Cam, F.; Aubineau, T.; Guérinot, A. *Eur. J. Org. Chem.* **2023**, e202300892.

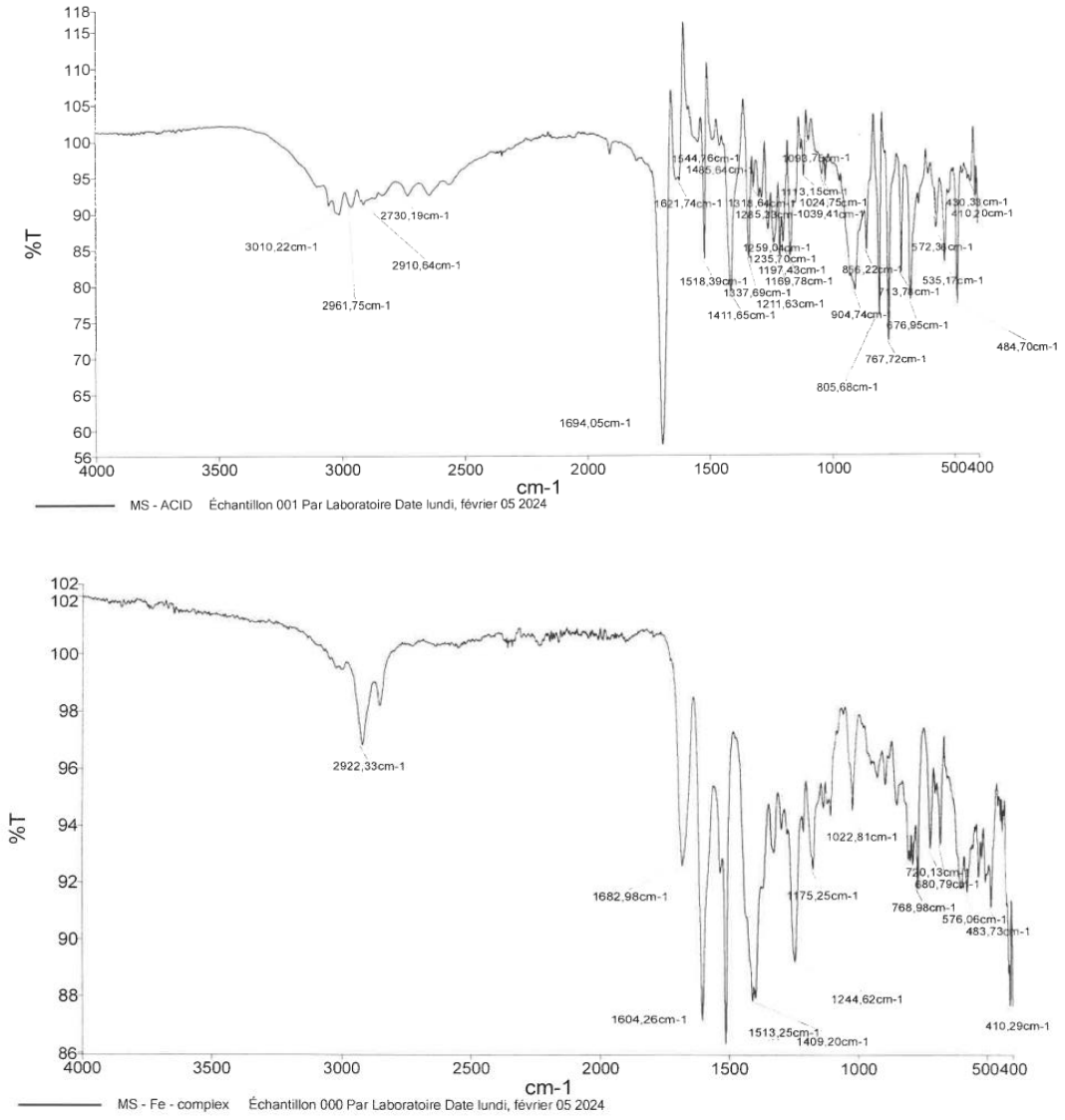
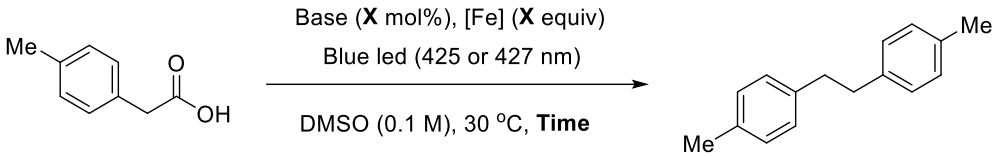


Figure S3. IR spectra of (1) p-Me-benzylcarboxylic acid and (2) iron complex.

The formation of the iron complex was attested by the net decrease of the band at 1694 cm^{-1} ($\nu_{C=O}$ of carboxylic acid) and the concomitant apparition of two bands at 1604 and 1513 cm^{-1}, which are characteristic of metal carboxylates.

c. Dimerization experiments

Dimerization experiments, in order to probe the generation of radical species upon ion-catalyzed decarboxylation reaction conditions, were carried out both with $Fe_2(SO_4)_3$ and $Fe(acac)_3$, the latter afforded a better solubility properties.



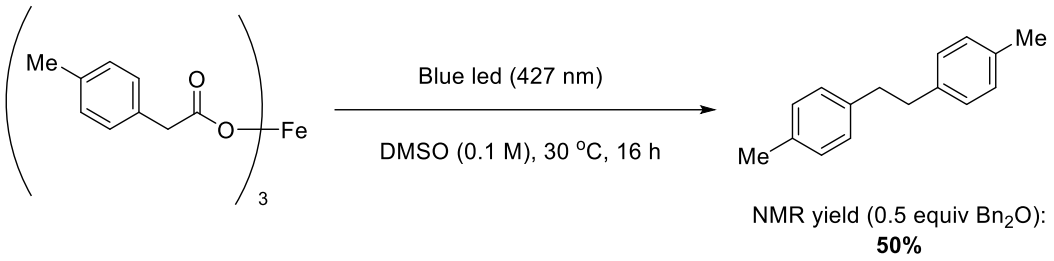
Acid
1.5 equiv

Dimer

Entry	[Fe] (Equiv)	Base, mol%	Time, h	Blue led, nm	Acid,[a] %	Dimer,[a] %
1.	$Fe_2(SO_4)_3$ (0.1 equiv)	20 mol% [b]	7 h	425 nm	91%	<1%
2.	$Fe_2(SO_4)_3$ 1.5 equiv	20 mol% [b]	7 h	427 nm	83%	7%
3.	-	20 mol% [b]	7 h	427 nm	79%	-
4.	$Fe(acac)_3$ [d] 1.5 equiv	20 mol% [b]	7 h	427 nm	79%	10%
5.	$Fe(acac)_3$ [d] 1.5 equiv	1.5 equiv [c]	20 h	427 nm	94%	3%
6.	$Fe(acac)_3$ [d] 1.5 equiv	20 mol% [b]	20 h	380 nm	74%	13%
7.	$Fe(acac)_3$ [d] 1.5 equiv	-	20 h	380 nm	98%	-
8.	$Fe(acac)_3$ [d] 1.5 equiv	1.5 equiv [b]	20 h	427 nm	97%	-

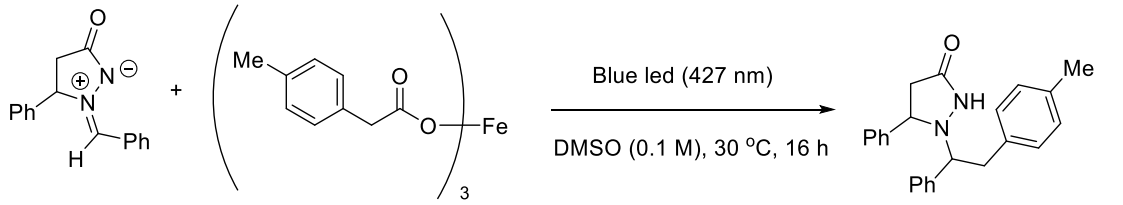
Table S3. The reaction was carried out with the 2-(p-tolyl)acetic acid (0.3 mmol) in DMSO (0.1 M) at 30 °C (temperature regulated using a fan and monitored with a thermometer). EvoluChem 18 W LEDs were used at 6 cm from the reaction flask with temperature controlled by a fan (~ 25-30 °C). [a]Yield of the acid or dimer was determined on the crude mixture by ^1H NMR with Bn_2O as an internal standard. [b]With Cs_2CO_3 as the base. [c]Carboxylate was pre-synthesized with 1.5 equiv of NaH (90%) in THF, then the solvent removed, iron (III) was added, dissolved in DMSO and irradiated overnight. [d]*Work-up*: reaction mixture was put into the solution of citric acid (10%) and extracted 3 times with DCM. The organic layers were dried over $MgSO_4$ and the solvent was removed under the reduced pressure. The NMR Yield was measured with an Bn_2O as an internal standard.

Dimerization experiment was also carried out on the pre-prepared iron complex $Fe(OC(O)CH_2(p\text{-}Me)Ph)_3$ which was engaged into the reaction according to the scheme below. The resulted dimer was obtained with 50% NMR Yield (Bn_2O as an internal standard). The chemical shifts of the ^1H NMR analysis are in a well agreement with the previously reported.[2]



NMR yield (0.5 equiv Bn_2O):
50%

The reaction was also performed in the presence of azomethine imine, allowing the formation the desired product with the 75% NMR yield. Interestingly, no traces of the dimer were observed.



1 equiv 0.5 equiv

NMR Yield (Bn_2O 0.5 equiv):
75% (dr 75:25)

[2] Chen, T.; Yang, L.; Li, L.; Huang, K.W. *Tetrahedron* **2012**, 6152-6157.

3. *UV-vis analyses*

All UV-vis measurements were recorded on an Agilent Technologies Cary 60 scan spectrophotometer using a baseline correction in a rectangular quartz cell (Hellma Analytics, standard cell, stoppered, light path of 10.00 mm, chamber volume of 3.5 mL). All samples were dissolved with a specific concentration of 0.01 M in DMSO and further diluted in the cuvette to obtain a concentration of 0.07, 0.3 or 1 mM. UV-vis spectra of 4-methylbenzylcarboxylic acid (0.07 mM; violet line), azomethine imine (0.07 mM; red line), iron complex (*p*-**$MeC_6H_4CH_2CO_2)_3Fe$** (0.07 mM; dark blue and 1 mM; light blue), iron sulfate (Fe_2SO_4; 0.3 mM; orange line) and a mixture of iron complex and azomethine imine (0.07 mM; green line) were recorded.

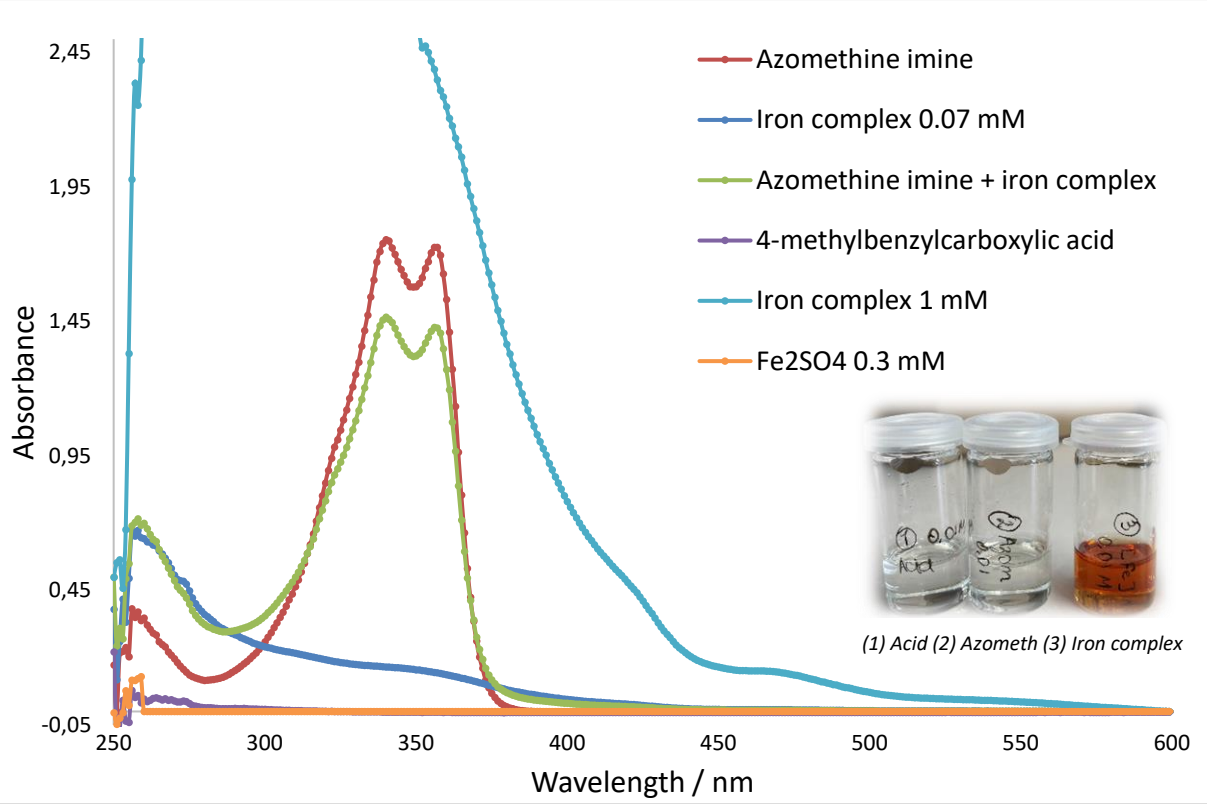


Figure S4. UV-vis spectra

4. *Cyclic voltammetry experiments*

Cyclic voltammetry (CV) measurements were recorded using a standard three-electrode setup in 14.0 mL of either MeCN or DMF with Bu_4NBF_4 (0.1 M) as the supporting electrolyte and substrate (0.01 M) at room temperature. The working electrode was a platinum electrode (200 µm diameter), the counter electrode was a platinum wire, and the reference was a Saturated-Calomel-Electrode (SCE) at a sweep rate of 200 $mV.s^{-1}$.

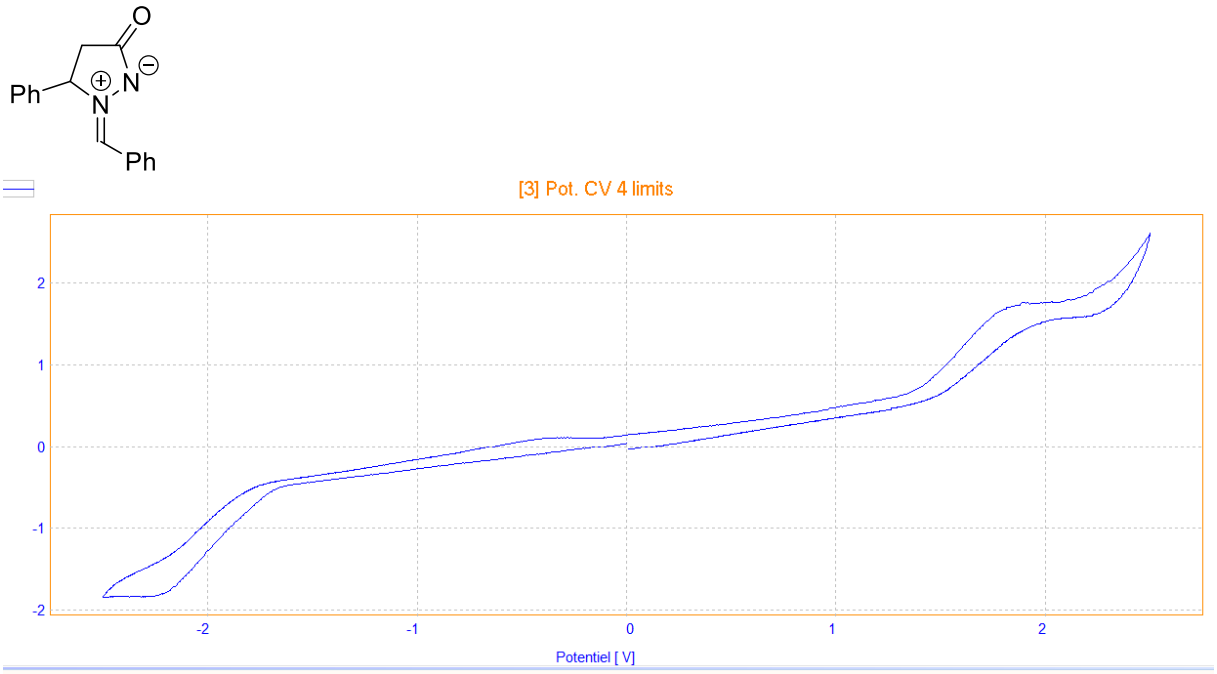


Figure S5. CV spectra of azomethine imine in MeCN.

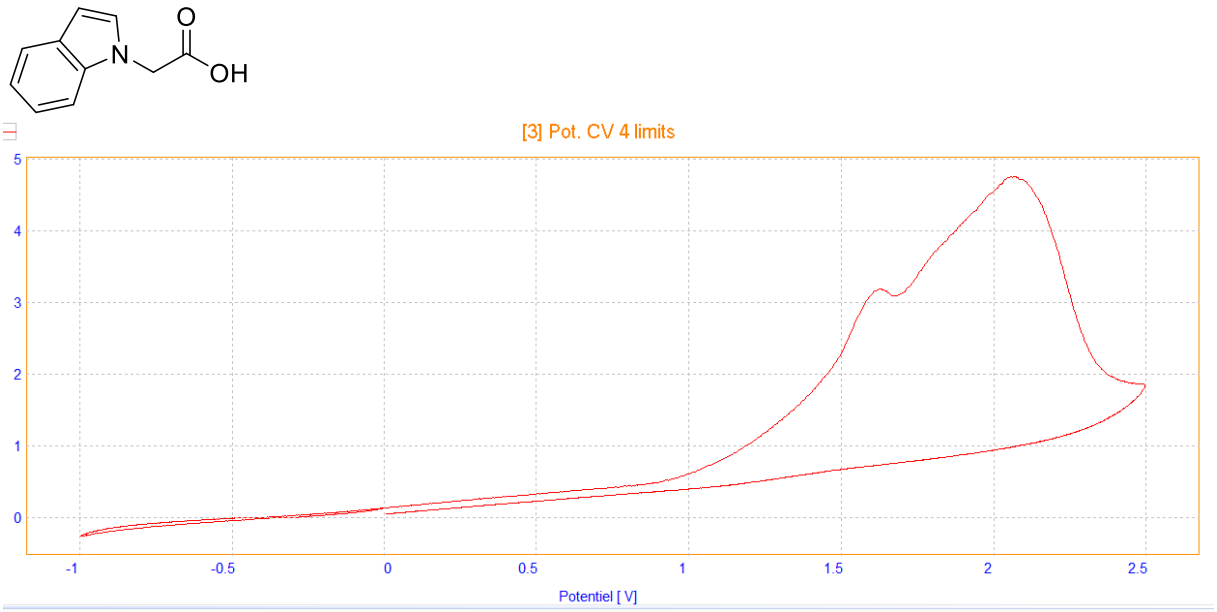
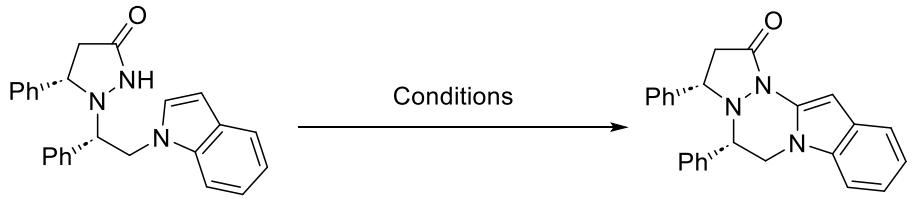
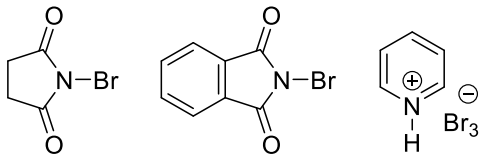


Figure S6. CV spectra of indole acetic acid in MeCN.

IV. Cyclization investigation





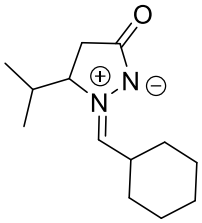
Entry	Reagent (equiv)	Solvent (equiv)	Temp, time (°C, h)	Yield[a] (%)
1	NBS (1)	$(CH_2Cl)_2$	60, 4	33
2	NBS (1)	$(CH_2Cl)_2$	40, 4	0
3	NBS (2)	$(CH_2Cl)_2$	40, 4	23[b]
4	NBS (1)	MeCN	60, 4	59
5	PhtlBr (1)	MeCN	60, 4	51
6	Br_2 (1)	MeCN	60, 4	68
7	Br_2 (1)	MeCN	60, 2	77
8	NBS (1)	MeCN	50, 4	80
9	$PyrBr_3$ (1)	MeCN	60, 4	83 (93)[c]
10	$PyrBr_3$ (1)	MeCN	60, 2	68
11	$PyrBr_3$ (1)	MeCN	50, 4	57

Table S3. The reaction was carried with the hydrazine precursor (0.05 mmol) in the given solvent (0.05 M) under the nitrogen. [a]Yield determined on the crude mixture by ^1H NMR with Bn_2O as an internal standard. [B]Extensive decomposition (many side products) in these conditions. [c]Isolated yield after purification by column chromatography.

V. Experimental procedures

Synthesis of azomethine imines

The starting azomethine imine **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g, 1k** were synthesized following the literature procedure.[3]



(Z)-2-(cyclohexylmethylene)-3-isopropyl-5-oxopyrazolidin-2-ium-1-ide (1k) was synthesized and isolated according to the literature procedure[3] by silica gel column chromatography using CH_2Cl_2:MeOH (96:4) as eluent to give **1k** (0.30 g, 67% yield) as a white solid. mp=156-157°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.34 – 6.28 (m, 1H), 4.38 – 4.30 (m, 1H), 3.26 – 3.12 (m, 1H), 2.75 (dd, *J* = 16.7, 9.6 Hz, 1H), 2.48 (dd, *J* = 16.7, 4.1 Hz, 1H), 2.20 – 2.07 (m, 1H), 2.03 – 1.86 (m, 2H), 1.80 – 1.62 (m, 3H), 1.46 – 1.31 (m, 2H), 1.24 (q, *J* = 12.2 Hz, 3H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 182.8 (C), 142.5 (CH), 73.3 (CH), 37.8 (CH), 32.9 (CH), 31.8 (CH_2), 29.0 (CH_2), 28.6 (CH_2), 25.8 (CH_2), 25.1 (CH_2), 25.0 (CH_2), 18.7 (CH_3), 14.6 (CH_3). HRMS (ESI^+): calcd for $C_{13}H_{23}ON_2$ [$(M+H)^+$]: 223.1805 Found: 223.1806.

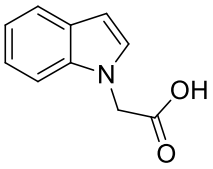
General procedure 1: synthesis of carboxylic acid

Indole acetic acid derivatives were synthesized using a modified procedure.[4,5]

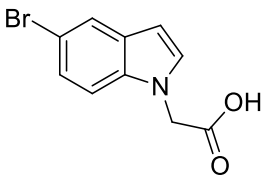
To a solution of 1*H*-indole derivative (1 equiv) in anhydrous THF (40 mL), were added ethyl bromoacetate (1.5 equiv), Cs_2CO_3 (1.5 equiv) and benzyltriethylammonium chloride (10 mol%). The mixture was vigorously stirred at room temperature for 75 hours. The reaction was then filtered and the solvent was removed under reduced pressure to give the corresponding ester which was used in the next step without purification. The crude was dissolved in a mixture of 1,4-dioxane (20 mL)/NaOH (1 M, 20 mL). The mixture was stirred at

[3] Leleu, L.; Martzel, T.; Fall, A.; Sanselme, M.; Levacher, V.; Oudeyer, S.; Brière, J. F. *Chem. Commun*. **2022**, *58*, 6100-6103 and references cited therein.
[4] Brogan, J. T.; Stoops, S. L.; Lindsley, C. W. *ACS Chem. Neurosci.* **2012**, *3*, 658–664.
[5] Wu, L.; Lu, K.; Packiarajan, M.; Jubian, V.; Chandrasena, G.; Wolinksky, T. C.; Walker, M. W. *Bioorg. Med. Chem. Lett*. **2012**, *22*, 2167–2171.

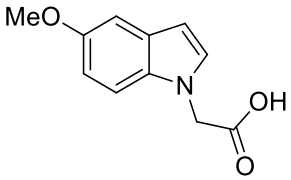
room temperature overnight. Then the reaction was acidified with HCl (2 N, 30 mL) and the organic phase was extracted with ethyl acetate (3 x 40 mL). The organic phase were recombined and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography to give the corresponding carboxylic acid, whose analyses correspond to the one reported in the literature.[3,4]



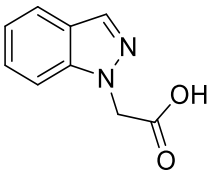
2-(1*H*-indol-1-yl)acetic acid (2a) was synthesized following the general procedure 1 using 1*H*-indole (5.0 g, 42.7 mmol, 1 equiv). The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (from 6/4 to 5/5, R_f = 0.10) as eluent to give **2a** (4.5 g, 60% yield) as a brown solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.94 (s, 1H), 7.37 (dq, *J* = 8.2, 0.9 Hz, 1H), 7.37 (dq, *J* = 8.2, 0.9 Hz, 1H), 7.33 (d, *J* = 3.2 Hz, 1H), 7.11 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.02 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.44 (dd, *J* = 3.2, 0.8 Hz, 1H), 5.01 (s, 2H).



2-(5-bromo-1*H*-indol-1-yl)acetic acid (2b) was synthesized following the general procedure 1 using 5-bromo-1*H*-indole (1.0 g, 5.1 mmol, 1 equiv). The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (from 6/4 to 5/5, R_f = 0.10) as eluent to give **2b** (0.4 g, 31% yield) as a brown solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 13.01 (s, 1H), 7.73 (d, *J* = 2.3 Hz, 1H), 7.38 (dd, *J* = 6.0, 2.8 Hz, 2H), 7.28 – 7.17 (m, 1H), 6.43 (d, *J* = 2.9 Hz, 1H), 5.03 (s, 2H).



2-(5-methoxy-1*H*-indol-1-yl)acetic acid (2c) was synthesized following the general procedure 1 using 5-methoxy-1*H*-indole (1.0 g, 6.8 mmol, 1 equiv). The crude product was purified by silica gel column chromatography using acetic acid/ethyl acetate (1/9, R_f = 0.40) as eluent to give **2c** (0.45 g, 33% yield) as a brown solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.89 (s, 1H), 7.32 – 7.17 (m, 2H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.75 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.34 (dd, *J* = 3.1, 0.8 Hz, 1H), 4.95 (s, 2H), 3.75 (s, 3H)

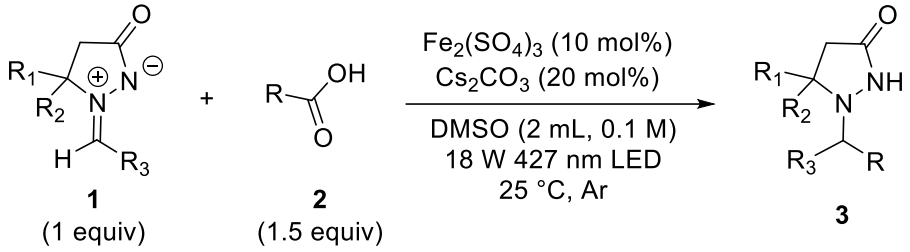


2-(1H-indazol-1-yl)acetic acid (2d) was synthesized following the previously described procedure.[6] *t*-BuOK (368 mg, 3.3 mmol, 1.4 equiv) was added to a solution of indazole (277 mg, 2.3 mmol, 1 equiv) in THF at 0 °C. The reaction mixture was warmed to rt, stirred over 1 h and then recooled to 0 °C. After 15 min, excess of ethyl bromoacetate (470 mg, 312 µL, 1.2 equiv, 2.8 mmol) was added and the reaction mixture was allowed to warm to rt and stirred for 4 h. The solvent was removed under reduced pressure and the residue was redissolved in EtOAc, washed with water and brine and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated in vacuo. The resulting oil was purified by column chromatography (2:3 ether/petroleum ether) to give ethyl 2-(1H-indazol-1-yl)acetate (209 mg, 44% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.06 (s, 1H, H_{Ar}), 7.78 – 7.73 (m, 1H), 7.44 – 7.38 (m, 1H), 7.37 – 7.32 (m, 1H), 7.21 – 7.15 (m, 1H), 5.16 (s, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 4H). Indazole ester (209 mg, 1.02 mmol, 1 equiv) and excess aqueous NaOH solution (10 M, 4 mL) was stirred at reflux for 5 h. After cooling, the mixture was acidified with 10% aqueous HCl solution (to pH=2) and the aqueous layer was extracted with EtOAc. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and the solvent removed in vacuo. Desired product **2d** was obtained as white solid (159 mg, 88%),

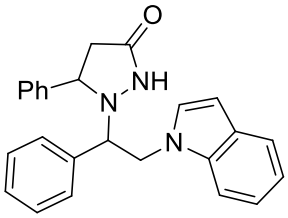
[6] Teixeira, F.C.; Ramos, H.; Antunes, I.F.; Curto, M.J.M.; Duarte, M.T.; Bento, I. *Molecules* **2006**, 11, 867-889.

clean to use without further purification. **^{1}H NMR (400 MHz, DMSO-d_6):** δ 13.01 (br.s, 1H), 8.08 (s, 1H), 7.80 – 7.73 (m, 1H), 7.67 – 7.59 (m, 1H), 7.43 – 7.30 (m, 1H), 7.20 – 7.10 (m, 1H), 5.26 (s, 2H).

General procedure 2: Photochemical reaction

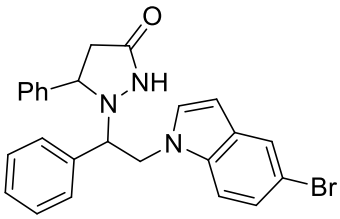


To a sealed tube equipped with a magnetic stir bar were introduced, azomethine imine **1** (0.2 mmol, 1 equiv), carboxylic acid **2** (0.3 mmol, 1.5 equiv), ferric sulfate $Fe_2(SO_4)_3$ (8.0 mg, 0.02 mmol, 10 mol%), cesium carbonate (13.1 mg, 0.04 mmol, 20 mol%) and DMSO (2 mL, 0.1 M). The mixture was degassed by sparging with argon for 10 minutes with an outlet needle and then irradiated using EvoluChem 18 W, 427 nm LEDs (approximately 6 cm away from the light source) and a mini fan at room temperature for 7 or 20 hours depending on the substrate. The reaction mixture was then diluted with water (15 mL) and brine (15 mL). The organic phase was extracted three times with ethyl acetate (3 x 15 mL), dried over Na_2SO_4, concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to give the desired product **3** using indicated solvent system.

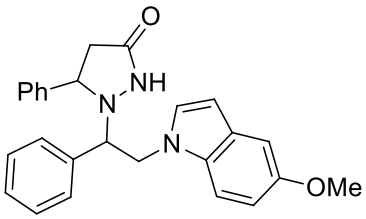


1-(2-(1*H*-indol-1-yl)-1-phenylethyl)-5-phenylpyrazolidin-3-one (3aa) was synthesized following the general procedure 2 using (*Z*)-2-benzylidene-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1a** (50.0 mg, 0.2 mmol, 1 equiv) and 2-(1*H*-indol-1-yl)acetic acid **2a** (52.5 mg, 0.3 mmol, 1.5 equiv) for 7 h. The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl acetate (7/3, R_f = 0.26) as eluent to give **3aa** (68.3 mg, 87:13 dr, 90% yield) as a light-yellow solid. A bigger scale was performed involving azomethine imine **1a** (250.0 mg,

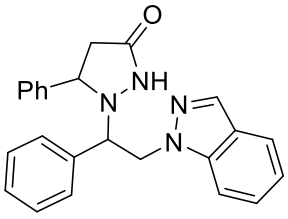
1.0 mmol, 1 equiv), **2a** (262.5 mg, 0.3 mmol, 1.5 equiv), ferric sulfate $Fe_2(SO_4)_3$ (20.0 mg, 0.01 mmol, 5 mol%) and cesium carbonate (65.5 mg, 0.2 mmol, 20 mol%) in DMSO (10 mL, 0.1 M) to afford a light-yellow solid (320.0 mg, 88:12 dr, 84% yield). The main diastereoisomer of **3aa** was isolated by precipitation in *n*-pentane. mp = 167-168°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.65 – 7.48 (m, 1H), 7.36 – 6.95 (m, 13H), 6.50 (d, *J* = 3.2 Hz, 1H), 6.28 (dd, *J* = 3.2, 0.8 Hz, 1H), 4.79 (q, *J* = 8.7 Hz, 1H), 4.46 – 4.14 (m, 3H), 3.17 (dd, *J* = 17.0, 8.7 Hz, 1H), 2.38 (dd, *J* = 17.0, 2.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.4 (C), 141.4 (C), 138.3 (C), 136.0 (C), 128.8 (C), 128.7 (CH), 128.5 (CH), 128.1 (CH), 127.6 (CH), 126.3 (CH), 121.7 (CH), 121.0 (CH), 119.5 (CH), 109.2 (CH), 101.3 (CH), 71.7 (CH), 63.3 (CH), 51.0 (CH_2), 36.3 (CH_2). HRMS (ESI$^+$): calcd for $C_{25}H_{23}N_3O$ [(M+H)$^+$]: 382.1875; Found: 382.1908.



1-(2-(5-bromo-1*H*-indol-1-yl)-1-phenylethyl)-5-phenylpyrazolidin-3-one (3ab) was synthesized following the general procedure 2 using (*Z*)-2-benzylidene-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1a** (50.0 mg, 0.2 mmol, 1 equiv) and 2-(5-bromo-1*H*-indol-1-yl)acetic acid **2b** (76.2 mg, 0.3 mmol, 1.5 equiv) for 7 h. The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl acetate (7/3, R_f = 0.23) as eluent to give **3ab** (77.7 mg, 86:14 dr, 84% yield) as a light-yellow solid. mp = 188-189°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.71 (d, *J* = 1.8 Hz, 0.17H, minor diast), 7.67 (d, *J* = 1.8 Hz, 1H), 7.40 – 7.11 (m, 12H), 7.07 – 7.00 (m, 2H), 6.97 (d, *J* = 8.7 Hz, 1H), 6.89 (m, 0.20H, minor diast), 6.53 (d, *J* = 3.2 Hz, 1H), 6.37 – 6.29 (m, 0.16H, minor diast), 6.24 (dd, *J* = 3.2, 0.8 Hz, 1H), 4.70 (t, *J* = 9.9 Hz, 1H), 4.40 (d, *J* = 8.1 Hz, 1H), 4.35 – 4.20 (m, 2H), 4.13 (d, *J* = 7.3 Hz, 0.19H, minor diast), 3.18 (dd, *J* = 17.0, 8.6 Hz, 1H), 2.57 (dd, *J* = 16.9, 8.9 Hz, 0.17H, minor diast), 2.39 (dd, *J* = 17.0, 2.0 Hz, 1H), 2.34 – 2.27 (m, 0.12H, minor diast). ^{13}C NMR (75 MHz, $CDCl_3$, peaks of minor diast not described) δ 176.5 (C), 141.2 (C), 138.0 (C), 134.7 (C), 130.1 (C), 130.1 (C), 129.6 (CH), 128.9 (3CH), 128.8 (CH), 128.0 (CH), 127.7 (CH), 126.2 (CH), 124.5 (CH), 123.4 (CH), 112.8 (CH), 110.6 (CH), 101.0 (CH), 71.9 (CH), 63.4 (CH), 51.1 (CH_2), 36.3 (CH_2). HRMS (ESI$^+$): calcd for $C_{25}H_{22}BrN_3O$ [(M+H)$^+$]: 460.0980; 462.0959 Found: 460.1034; 462.1023.

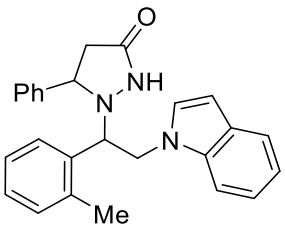


1-(2-(5-methoxy-1*H*-indol-1-yl)-1-phenylethyl)-5-phenylpyrazolidin-3-one (3ac) was synthesized following the general procedure 2 using (*Z*)-2-benzylidene-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1a** (50.0 mg, 0.2 mmol, 1 equiv) and 2-(5-methoxy-1*H*-indol-1-yl)acetic acid **2c** (61.5 mg, 0.3 mmol, 1.5 equiv) for 7 h. The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl acetate (6/4, R_f = 0.23) as eluent to give **3ac** (52.2 mg, 90:10 dr, 63% yield) as a light-yellow solid. The main diastereoisomer of **3ac** was isolated by precipitation in *n*-pentane. mp = 162-163°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.33 – 7.15 (m, 11H), 7.12 – 7.01 (m, 4H), 6.79 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.53 (d, *J* = 3.1 Hz, 1H), 6.24 (d, *J* = 3.1 Hz, 1H), 4.69 (q, *J* = 9.3 Hz, 1H), 4.38 (dd, *J* = 8.6, 2.1 Hz, 1H), 4.27 (d, *J* = 10.7 Hz, 2H), 3.83 (s, 3H), 3.12 (dd, *J* = 17.0, 8.6 Hz, 1H), 2.35 (dd, *J* = 17.0, 2.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2 (C), 154.1 (C), 141.3 (C), 138.3 (C), 131.3 (C), 128.9 (2C), 128.7 (CH), 128.1 (CH), 127.7 (CH), 126.3 (CH), 112.0 (CH), 110. (CH), 102.8 (CH), 101.1 (CH), 71.6 (CH), 63.6 (CH), 55.9 (OCH_3), 51.3 (CH_2), 36.1 (CH_2). HRMS (ESI$^+$): calcd for $C_{26}H_{25}N_3O_2$ [$(M+H)^+$]: 412.1980 Found: 412.2009.

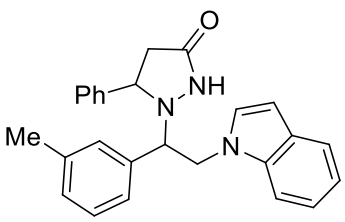


1-(2-(1H-indazol-1-yl)-1-phenylethyl)-5-phenylpyrazolidin-3-one (3ad) was synthesized following the general procedure 2 using (*Z*)-2-benzylidene-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1a** (50.1 mg, 0.2 mmol, 1 equiv) and 2-(1H-indazol-1-yl)acetic acid **2d** (52.9 mg, 0.3 mmol, 1.5 equiv) for 7 h. The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl acetate/MeOH (6/4, then pure EtOAc with 5% MeOH) as eluent to give the mixture of major and minor diastereisomers **3ad** (57.4 mg, dr 87:13, 76%) as a white solid. Remark: It turned out to be difficult to remove traces of solvents even after a prolonged time under vacuum. However, the main diastereomer was obtained by recrystallization from

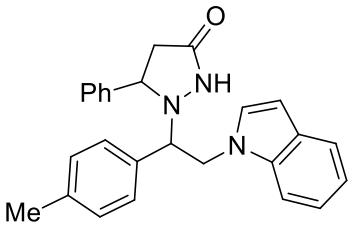
EtOAc/*n*-pentane at -25 °C as a white solid. mp = 89-90°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (brs, 1H), 7.60 – 7.55 (m, 1H), 7.35 – 7.27 (m, 3H), 7.25 – 7.05 (m, 7H), 6.93 – 6.86 (m, 2H), 6.66 – 6.61 (m, 1H), 6.38 – 6.33 (m, 1H), 4.70 (dd, *J* = 14.1, 5.1 Hz, 1H), 4.47 – 4.37 (m, 2H), 4.35 – 4.24 (m, 1H), 3.02 (dd, *J* = 17.0, 8.7 Hz, 1H), 2.36 (dd, *J* = 17.0, 2.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 176.1 (C), 141.3 (C), 138.7 (C), 136.0 (C), 128.8 (CH), 128.7 (C), 128.5 (CH), 127.8 (CH), 127.0 (CH), 126.4 (CH), 124.3 (CH), 121.8 (CH), 121.2 (CH), 119.6 (CH), 109.2 (CH), 101.6 (CH), 66.8 (CH), 63.4 (CH), 50.3 (CH_2), 36.6 (CH_2). HRMS (ESI$^+$): calcd for $C_{24}H_{23}ON_4$ [(M+H)$^+$]: 383.1866 Found: 383.1867.



1-(2-(1H-indol-1-yl)-1-(o-tolyl)ethyl)-5-phenylpyrazolidin-3-one (3ba) was synthesized following the general procedure 2 using (*Z*)-2-(3-methylbenzylidene)-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1b** (52.9 mg, 0.2 mmol, 1 equiv) and 2-(1*H*-indol-1-yl)acetic acid **2a** (52.6 mg, 0.3 mmol, 1.5 equiv) for 7 h. The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl acetate (7/3, R_f = 0.44) as eluent to give the main diastereoisomer of **3ba** (58.8 mg, >96:4 dr, 74% yield) as a light-yellow solid. mp = 182-183°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.50 – 7.42 (m, 1H), 7.33 – 7.27 (m, 2H), 7.25 – 7.04 (m, 8H), 7.01 – 6.93 (m, 1H), 6.44 (d, *J* = 3.1 Hz, 1H), 6.31 (d, *J* = 3.1 Hz, 1H), 4.82 (dd, *J* = 13.9, 4.1 Hz, 1H), 4.60 (dd, *J* = 8.9, 4.1 Hz, 1H), 4.36 – 4.22 (m, 2H), 3.22 (dd, *J* = 17.0, 8.5 Hz, 1H), 2.43 (d, *J* = 17.0 Hz, 1H), 1.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5 (C), 141.2 (C), 137.4 (C), 137.2 (C), 136.2 (C), 130.7 (CH), 128.8 (CH), 128.6 (C), 128.3 (CH), 128.2 (CH), 127.7 (CH), 127.2 (CH), 126.9 (CH), 126.4 (CH), 121.9 (CH), 121.1 (CH), 119.7 (CH), 109.0 (CH), 101.7 (CH), 66.8 (CH), 63.6 (CH), 51.4 (CH_2), 36.0 (CH_2), 19.3 (CH_3). HRMS (ESI$^+$): calcd for $C_{26}H_{25}N_3O$ [(M+H)$^+$]: 396.2062; Found: 396.2076.

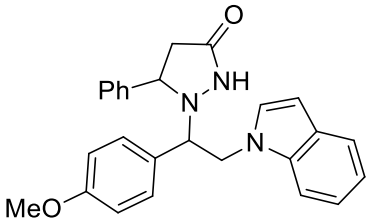


1-(2-(1*H*-indol-1-yl)-1-(m-tolyl)ethyl)-5-phenylpyrazolidin-3-one (3ca) was synthesized following the general procedure 2 using (*Z*)-2-(3-methylbenzylidene)-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1c** (52.9 mg, 0.2 mmol, 1 equiv) and 2-(1*H*-indol-1-yl)acetic acid **2a** (52.6 mg, 0.3 mmol, 1.5 equiv) for 7 h. The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl acetate (7/3, R_f = 0.22) as eluent to give **3ca** (70.7 mg, 84:16 dr, 84% yield) as a light-yellow solid. mp = 211-212°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.68 – 7.52 (m, 1H), 7.36 – 7.00 (m, 9H), 6.94 – 6.86 (m, 2H), 6.84 (s, 1H), 6.54 (d, *J* = 3.2 Hz, 1H), 6.39 (dd, *J* = 3.1, 0.8 Hz, 0.18H, minor diast), 6.32 (dd, *J* = 3.2, 0.8 Hz, 1H), 4.74 (dd, *J* = 12.6, 3.2 Hz, 1H), 4.71 – 4.60 (m, 0.22H), 4.44 – 4.21 (m, 3H), 4.13 (t, *J* = 7.2 Hz, 0.19H), 3.13 (dd, *J* = 17.0, 8.6 Hz, 1H), 2.58 (dd, *J* = 16.7, 8.9 Hz, 0.19H), 2.41 (d, *J* = 2.4 Hz, 1H), 2.35 (d, *J* = 2.3 Hz, 1H), 2.33 (s, 0.64H, minor diast), 2.30 – 2.24 (m, 0.17H, minor diast), 2.17 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, peaks of minor diast not described) δ 176.3 (C), 141.4 (C), 138.5 (C), 138.2 (C), 136.0 (2C), 129.4 (C), 129.0 ($2CH_{Ar}$), 128.8 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 127.6 (CH), 126.5 (CH), 126.3 (CH), 125.1 (CH), 121.7 (CH), 121.0 (CH), 119.5 (CH), 109.2 (CH), 101.3 (CH), 71.7 (CH), 63.4 (CH), 51.0 (CH_2), 36.3 (CH_2), 21.3 (CH_3). HRMS (ESI$^+$): calcd for $C_{26}H_{25}N_3O$ [$(M+H)^+$]: 396.2031; Found: 396.2059.

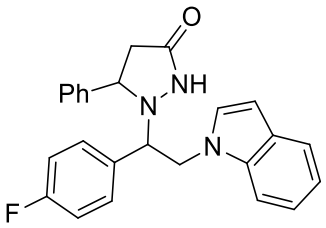


1-(2-(1*H*-indol-1-yl)-1-(*p*-tolyl)ethyl)-5-phenylpyrazolidin-3-one (3da) was synthesized following the general procedure 2 using (*Z*)-2-(4-methylbenzylidene)-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1d** (52.9 mg, 0.2 mmaqol, 1 equiv) and 2-(1*H*-indol-1-yl)acetic acid **2a** (52.6 mg, 0.3 mmol, 1.5 equiv) for 7 h. The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl acetate (7/3, R_f = 0.31) as eluent to give **3da** (66.5 mg, 84:16 dr, 84% yield) as a light-yellow solid. mp = 143-144°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.37 (s, 1H), 7.64 – 7.58 (m, 0.17H, minor diast), 7.58 – 7.53 (m, 1H), 7.32 – 7.13 (m, 8H), 7.07 (tdd, *J* = 8.5, 5.6, 1.5 Hz, 3H), 7.00 – 6.90 (m, 4H), 6.50 (d, *J* = 3.2 Hz, 1H), 6.41 (d, *J* = 3.2 Hz, 0.14H, minor diast), 6.28 (dd, *J* = 3.2, 0.8 Hz, 1H), 4.81 – 4.67 (m, 1H), 4.37 (dd, *J* = 8.6, 2.2 Hz, 1H), 4.32 – 4.19 (m, 2H), 4.11 (dd, *J* = 8.5, 6.2 Hz, 0.16H), 3.12 (dd, *J* = 17.0, 8.6 Hz, 1H),

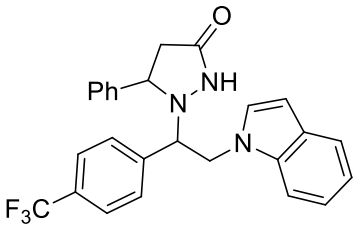
2.51 – 2.40 (m, 0.17H, minor diast), 2.36 (s, 0.44H,CH_3, minor diast), 2.35 (dd, *J* = 17.0, 2.2 Hz, 1H), 2.26 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, peaks of minor diast not described) *δ* 176.38 (C), 141.47 (C), 138.48 (C), 136.04 (C), 135.21 (C), 129.57 (CH), 128.72 (CH), 128.59 (C), 128.02 (CH), 127.59 (CH), 121.67 (CH), 121.00 (CH), 119.47 (CH), 109.31 (CH), 101.27 (CH), 71.38 (CH), 63.07 (CH), 50.94 (CH_2), 36.35 (CH_2), 21.27 (CH_3). HRMS (ESI$^+$): calcd for $C_{26}H_{25}N_3O$ [(M+H)$^+$]: 396.2031; Found: 396.2070.



1-(2-(1*H*-indol-1-yl)-1-(4-methoxyphenyl)ethyl)-5-phenylpyrazolidin-3-one (3ea) was synthesized following the general procedure 2 using (*Z*)-2-(4-methoxybenzylidene)-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1d** (65.1 mg, 0.2 mmol, 1 equiv) and 2-(1*H*-indol-1-yl)acetic acid **2a** (52.5 mg, 0.3 mmol, 1.5 equiv) for 7 h. The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl acetate (7/3, R_f = 0.23) as eluent to give **3ea** (78.3 mg, 88:12 dr, 95% yield) as a light-yellow solid. The main diastereoisomer of **3ea** was isolated by a second silica gel column chromatography using *n*-pentane/ethyl acetate (7/3) as eluent (36.0 mg, 44% yield). mp = 140-141°C . ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.82 (brs, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.35 – 6.97 (m, 12H), 6.74 (d, *J* = 8.4 Hz, 2H), 6.53 (d, *J* = 3.2 Hz, 1H), 6.38 – 6.18 (m, 1H), 4.71 (q, *J* = 8.2 Hz, 1H), 4.41 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.31 – 4.19 (m, 2H), 3.75 (s, 3H), 3.09 (dd, *J* = 17.0, 8.6 Hz, 1H), 2.35 (dd, *J* = 17.0, 2.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 176.3 (C), 159.8 (C), 141.4 (C), 136.0 (C), 130.1 (C), 129.2 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 127.6 (CH), 126.3 (CH), 121.7 (CH), 121.0 (CH), 119.5 (CH), 114.2 (CH), 109.3 (CH), 101.3 (CH), 71.0 (CH), 63.2 (CH), 55.3 (OCH_3), 51.0 (CH_2), 36.2 (CH_2). HRMS (ESI$^+$): calcd for $C_{26}H_{25}N_3O_2$ [(M+H)$^+$]: 412.1980; Found: 412.2028.

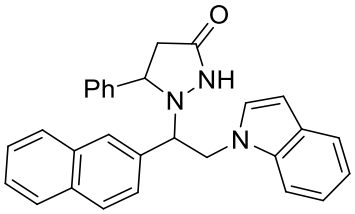


1-(1-(4-fluorophenyl)-2-(1*H*-indol-1-yl)ethyl)-5-phenylpyrazolidin-3-one (3fa) was synthesized following the general procedure 2 using (*Z*)-2-(4-fluorobenzylidene)-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1e** (53.7 mg, 0.2 mmol, 1 equiv) and 2-(1*H*-indol-1-yl)acetic acid **2a** (52.5 mg, 0.3 mmol, 1.5 equiv) for 7 h. The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl acetate (7/3, R_f = 0.25) as eluent to give **3fa** (69.7 mg, 82:18 dr, 87% yield) as a light-yellow solid. The main diastereoisomer of **3fa** was isolated by a second silica gel column chromatography using *n*-pentane/ethyl acetate (7/3) as eluent (21.60 mg, 27% yield, 96:4 dr). mp = 103-104°C . ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.64 – 7.47 (m, 1H), 7.40 – 6.94 (m, 10H), 6.84 (t, *J* = 8.5 Hz, 2H), 6.51 (d, *J* = 3.2 Hz, 1H), 6.31 (d, *J* = 3.1 Hz, 1H), 4.77 (dd, *J* = 12.5, 2.8 Hz, 1H), 4.42 – 4.05 (m, 3H), 3.20 (dd, *J* = 17.0, 8.7 Hz, 1H), 2.40 (dd, *J* = 17.0, 2.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, peaks of minor diast not described) δ 176.3 (C), 162.81 (d, $^1J_{C\text{-}F}$ = 247.7 Hz, C), 141.2 (C), 135.9 (C), 134.0 (d, $^4J_{C\text{-}F}$ = 3.3 Hz, C), 130.9 (d, $^3J_{C\text{-}F}$ = 7.9 Hz, CH), 129.7 (d, $^2J_{C\text{-}F}$ = 8.0 Hz, CH), 128.8 (CH), 128.6 (C), 128.3 (CH), 127.7 (CH), 126.2 (CH), 121.8 (CH), 121.1 (CH), 119.6 (CH), 116.0 (CH), 115.7 (CH), 109.2 (CH), 101.6 (CH), 71.0 (CH), 63.7 (CH), 51.1 (CH_2), 36.5 (CH_2). ^{19}F NMR (282 MHz, $CDCl_3$) δ_F -112.3 (minor diast), -112.8. HRMS (ESI^+): calcd for $C_{25}H_{22}FN_3O$ [$(M+H)^+$]: 400.1780; Found: 400.1827.

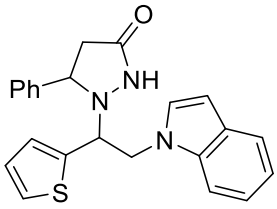


1-(2-(1*H*-indol-1-yl)-1-(4-(trifluoromethyl)phenyl)ethyl)-5-phenylpyrazolidin-3-one (3ga) was synthesized following the general procedure 2 using (*Z*)-5-oxo-3-phenyl-2-(4-(trifluoromethyl)benzylidene)pyrazolidin-2-ium-1-ide **1f** (63.7 mg, 0.2 mmol, 1 equiv) and 2-(1*H*-indol-1-yl)acetic acid **2a** (52.6 mg, 0.3 mmol, 1.5 equiv) for 7 h. The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl acetate (1/1 to 3/7, R_f = 0.35) as eluent and washed with heptane to give **3ga** (62.0 mg, 74:26 dr, 69% yield) as a light-

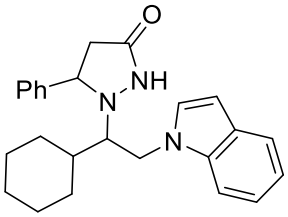
yellow solid. The main diastereoisomer of **3ga** was isolated by a second silica gel column chromatography using *n*-pentane/ethyl acetate (7/3) as eluent (29.9 mg, 30% yield). mp = 104-105°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.63 – 7.52 (m, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.22 (m, 4H), 7.22 – 7.00 (m, 7H), 6.51 (d, *J* = 3.2 Hz, 1H), 6.32 (d, *J* = 3.2 Hz, 1H), 4.81 (dd, *J* = 13.7, 4.0 Hz, 1H), 4.39 (dd, *J* = 8.7, 3.9 Hz, 1H), 4.28 (td, *J* = 8.8, 5.9 Hz, 2H), 3.23 (dd, *J* = 17.0, 8.7 Hz, 1H), 2.42 (dd, *J* = 17.1, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.26 (C), 142.38 (C), 140.99 (C), 135.99 (C), 130.90 (q, $^{2}J_{C\text{-}F}$ = 32.5 Hz, C), 128.89 (CH), 128.62 (CH), 128.42 (CH), 128.26 (CH), 127.86 (CH), 126.24 (CH), 125.70 (q, $^{3}J_{C\text{-}F}$ = 3.5 Hz, CH), 123.90 (q, $^{1}J_{C\text{-}F}$ = 272.3 Hz, C), 121.92 (CH), 121.20 (CH), 119.73 (CH), 109.07 (CH), 101.87 (CH), 71.36 (CH), 64.28 (CH), 50.97 (CH_2), 36.80 (CH_2). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7. HRMS (ESI$^+$): calcd for $C_{26}H_{22}F_3N_3O$ [(M+H)$^+$]: 450.1749; Found: 450.1804.



1-(2-(1*H*-indol-1-yl)-1-(naphthalen-2-yl)ethyl)-5-phenylpyrazolidin-3-one (3ha) was synthesized following the general procedure 2 using (*Z*)-2-(naphthalen-2-ylmethylene)-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1g** (60.0 mg, 0.2 mmol, 1 equiv) and 2-(1*H*-indol-1-yl)acetic acid **2a** (52.6 mg, 0.3 mmol, 1.5 equiv) for 7 h. The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl acetate (6/4, R_f = 0.28) as eluent to give **3ha** (63.2 mg, 83:17 dr, 73% yield) as a light-yellow solid. The main diastereoisomer of **3ha** was isolated by precipitation in *n*-pentane. mp = 204-205°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 19.0, 8.1 Hz, 2H), 7.61 (dd, *J* = 26.4, 7.7 Hz, 2H), 7.53 – 7.42 (m, 4H), 7.36 – 7.21 (m, 10H), 7.19 – 7.13 (m, 3H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.45 (d, *J* = 3.2 Hz, 1H), 6.25 (d, *J* = 3.1 Hz, 1H), 4.83 (dd, *J* = 13.9, 4.6 Hz, 1H), 4.49 (dd, *J* = 8.4, 4.6 Hz, 1H), 4.45 – 4.35 (m, 2H), 3.16 (dd, *J* = 17.0, 8.5 Hz, 1H), 2.37 (dd, *J* = 17.0, 2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4 (C), 141.1 (C), 136.0 (C), 135.8 (C), 133.4 (C), 133.2 (C), 129.0 (C), 128.7 (CH), 128.5 (CH), 128.1 (CH), 128.0 (CH), 127.8 (CH), 127.7 (CH), 126.5 (CH), 126.3 (CH), 124.9 (CH), 121.8 (CH), 121.2 (CH), 119.6 (CH), 109.2 (CH), 101.6 (CH), 71.7 (CH), 63.7 (CH), 51.0 (CH_2), 35.9 (CH_2). HRMS (ESI$^+$): calcd for $C_{29}H_{25}N_3O$ [(M+H)$^+$]: 432.2031; Found: 432.2061.

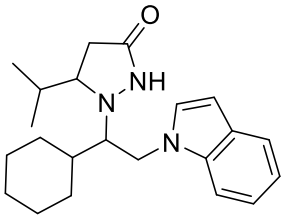


1-(2-(1H-indol-1-yl)-1-(thiophen-2-yl)ethyl)-5-phenylpyrazolidin-3-one (3ia) was synthesized following the general procedure 2 using (Z)-5-oxo-3-phenyl-2-(thiophen-2-ylmethylene)pyrazolidin-2-ium-1-ide **1i** (51.2 mg, 0.2 mmol, 1 equiv) and 2-(1*H*-indol-1-yl)acetic acid **2a** (52.5 mg, 0.3 mmol, 1.5 equiv) for 7 h. The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl acetate (6/4) as eluent to give **3ia** (60.3 mg, 87:13 dr, 78% yield) as a light-yellow solid. Washing with *n*-pentane delivered the desired product **3ia** with a dr of 90:10. mp = 150-151°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (brs, 1H, NH), 8.05 (s, 1H), 7.70 – 7.63 (m, 1H), 7.25 – 6.95 (m, 11 H), 6.46 – 6.28 (m, 1H), 4.96 (dd, *J* = 14.9, 4.6 Hz, 1H), 4.63 (dd, *J* = 14.9, 3.2 Hz, 1H), 4.49 – 4.42 (m, 1H), 4.32 (d, *J* = 7.6 Hz, 1H), 3.34 (dd, *J* = 16.8, 8.7 Hz, 1H), 2.34 (dd, *J* = 16.8, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0 (C), 141.8 (C), 140.5(C), 138.7 (C), 133.6 (CH), 128.9 (CH), 128.6 (CH), 128.5 (CH), 128.0 (CH), 127.3 (CH), 126.3 (CH), 126.2 (CH), 123.5 (C), 121.0 (CH), 120.6 (CH), 108.9 (CH), 70.9 (CH), 63.9 (CH), 53.3 (CH_2), 37.0 (CH_2). HRMS (ESI^+): calcd for $C_{23}H_{22}N_3O^{32}S$ [$(M+H)^+$]: 388.1478; Found: 388.1481.

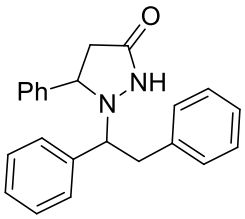


1-(1-cyclohexyl-2-(1H-indol-1-yl)ethyl)-5-phenylpyrazolidin-3-one (3ja) was synthesized following the general procedure 2 using (Z)-2-(cyclohexylmethylene)-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1j** (51.3 mg, 0.2 mmol, 1 equiv) and 2-(1*H*-indol-1-yl)acetic acid **2a** (52.6 mg, 0.3 mmol, 1.5 equiv) for 7 h. The crude product (83:17 dr) was purified by silica gel column chromatography using PE/ethyl acetate (6/4) as eluent to give the major diastereisomer of **3ja** (42.3 mg, 55% yield) as a light-yellow solid. mp = 195-196°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (brs, 1H), 7.71 – 7.66 (m, 1H), 7.33 – 7.28 (m, 1H), 7.25 – 7.22 (m, 1H), 7.22 – 7.12 (m, 5H), 6.87 – 6.79 (m, 2H), 6.60 – 6.54 (m, 1H), 4.63 (dd, *J* = 15.0, 9.1 Hz,

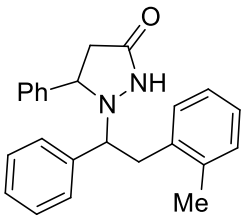
1H), 4.27 (dd, *J* = 15.0, 4.3 Hz, 1H), 3.34 – 3.24 (m, 1H), 3.12 – 3.00 (m, 1H), 2.45 (dd, *J* = 17.0, 8.8 Hz, 1H), 2.32 (dd, *J* = 16.9, 10.9 Hz, 1H), 2.07 – 1.98 (m, 1H), 1.83 – 1.75 (m, 1H), 1.73 – 1.55 (m, 3H), 1.50 – 1.42 (m, 1H), 1.40 – 1.19 (m, 4H), 1.16 – 1.08 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.9 (C), 139.8 (C), 135.8 (C), 129.1 (C), 128.6 (CH), 128.5 (CH), 128.1 (CH), 127.8 (CH), 122.1 (CH), 121.5 (CH), 119.93, 109.9 (CH), 102.1 (CH), 64.8 (CH), 63.6 (CH), 44.1 (CH_2), 41.1 (CH), 40.7 (CH_2), 31.3 (CH_2), 29.7 (CH_2), 26.42 (CH_2), 26.36 (CH_2), 26.32 (CH_2). HRMS (ESI$^+$): calcd for $C_{25}H_{30}N_3O$ [(M+H)$^+$]: 388.2389; Found: 388.2386.



1-(1-cyclohexyl-2-(1H-indol-1-yl)ethyl)-5-isopropylpyrazolidin-3-one (3ka) was synthesized following the general procedure 2 using (Z)-2-(cyclohexylmethylene)-3-isopropyl-5-oxopyrazolidin-2-ium-1-ide **1k** (43.3 mg, 0.2 mmol, 1 equiv) and 2-(1H-indazol-1-yl)acetic acid **2d** (51.2 mg, 0.3 mmol, 1.5 equiv) for 7 h. The crude product (93:7 dr) was purified by silica gel column chromatography using PE/ethyl acetate (6/4) as eluent to give the main diastereomer of **3ka** (43.1 mg, >96:4 dr, 62% yield) as a yellow-brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (brs, 1H), 7.71 – 7.55 (m, 1H), 7.38 – 7.30 (m, 1H), 7.25 – 7.19 (m, 1H), 7.16 – 7.08 (m, 2H), 6.54 – 6.48 (m, 1H), 4.46 (dd, *J* = 14.8, 8.5 Hz, 1H), 4.26 (dd, *J* = 14.9, 4.8 Hz, 1H), 3.23 – 3.12 (m, 1H), 2.65 – 2.56 (m, 1H), 2.14 – 2.04 (m, 2H), 1.93 (dd, *J* = 17.5, 5.6 Hz, 1H), 1.89 – 1.81 (m, 1H), 1.81 – 1.66 (m, 3H), 1.59 – 1.48 (m, 1H), 1.48 – 1.37 (m, 1H), 1.36 – 1.16 (m, 5H), 0.81 (d, *J* = 6.7 Hz, 3H), 0.70 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 175.3 (C), 136.1 (C), 129.0 (C), 128.6 (CH), 121.9 (CH), 121.4 (CH), 119.7 (CH), 109.4 (CH), 102.0 (CH), 68.2 (CH), 67.3 (CH), 44.6 (CH_2), 41.5 (CH), 32.7 (CH_2), 32.5 (CH), 31.4 (CH_2), 30.2 (CH_2), 26.54 (CH_2), 26.48 (CH_2), 26.46 (CH_2), 17.8 (CH_3), 17.1 (CH_3). HRMS (ESI$^+$): calcd for $C_{22}H_{32}N_3O$ [(M+H)$^+$]: 354.2545 Found: 354.2543.

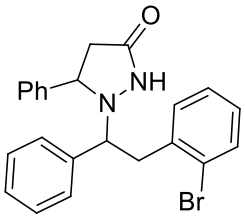


1-(1,2-diphenylethyl)-5-phenylpyrazolidin-3-one (3ae) was synthesized following the general procedure 2 using (*Z*)-2-benzylidene-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1a** (50.0 mg, 0.2 mmol, 1 equiv) and 2-phenylacetic acid **2e** (40.8 mg, 0.3 mmol, 1.5 equiv) for 20 h. The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl acetate (9/1, R_f = 0.22) as eluent to give **3ae** (37.9 mg, 94:6 dr, 58% yield) as a white solid. A second purification using the same conditions allowed to give the main diastereoisomer of **3ae**. mp = 135-136°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.08 (m, 13H), 6.84 (dd, *J* = 6.6, 2.9 Hz, 2H), 4.42 (d, *J* = 7.8 Hz, 1H), 4.06 (dd, *J* = 9.7, 4.6 Hz, 1H), 3.33 (dd, *J* = 12.9, 4.6 Hz, 1H), 3.08 (dd, *J* = 16.9, 8.6 Hz, 1H), 2.93 (dd, *J* = 12.9, 9.7 Hz, 1H), 2.33 (dd, *J* = 16.9, 2.0 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 175.5 (C), 141.7 (C), 139.4 (C), 137.7 (C), 129.6 (CH), 128.6 (CH), 128.5 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 127.5 (CH), 126.4 (CH), 126.3 (CH), 74.1 (CH), 63.0 (CH), 41.2 (CH_2), 36.0 (CH_2). HRMS (ESI$^+$): calcd for $C_{23}H_{22}N_2O$ [(M+H)$^+$]: 343.1766; Found: 343.1819.

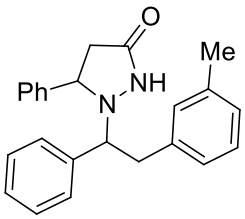


5-phenyl-1-(1-phenyl-2-(*o*-tolyl)ethyl)pyrazolidin-3-one (3af) was synthesized following the general procedure 2 using (*Z*)-2-benzylidene-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1a** (50.0 mg, 0.2 mmol, 1 equiv) and 2-(*o*-tolyl)acetic acid (45.1 mg, 0.3 mmol, 1.5 equiv) for 20 h. The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl acetate (8/2, R_f = 0.20) as eluent to give **3af** (55.0 mg, 94:6 dr, 77% yield) as a white solid. The main diastereoisomer of **3af** was isolated by precipitation in *n*-pentane. mp = 124-125°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.35 – 7.14 (m, 8H) 7.11 – 7.07 (m, 2H), 7.03 (dd, *J* = 4.0, 1.1 Hz, 2H), 6.93 (dt, *J* = 8.7, 4.2 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 4.39 (dd, *J* = 8.6, 2.0 Hz, 1H), 4.03 (dd, *J* = 10.0, 4.1 Hz, 1H), 3.38 (dd, *J* = 13.0, 4.1 Hz, 1H), 3.16 (dd, *J* = 16.9, 8.7 Hz, 1H), 2.92 (dd, *J* = 13.0, 10.0 Hz, 1H), 2.35 (dd, *J* = 16.9, 2.1 Hz, 1H), 2.07 (s, 3H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 175.6 (C), 141.8 (C), 139.7 (C), 136.5 (C), 136.0 (C), 130.6 (CH), 130.2 (CH), 128.6 (CH), 128.4 ($CH_)$, 128.0 (CH), 127.4 (CH), 126.5 (CH), 126.4 (CH), 125.6 (CH), 73.3 (CH_2), 63.2 (CH_2), 38.7 (CH), 36.1 (CH), 19.4 (CH_3). HRMS (ESI^+): calcd for $C_{24}H_{24}N_2O$ [$(M+H)^+$]: 357.1922; Found: 357.1967.

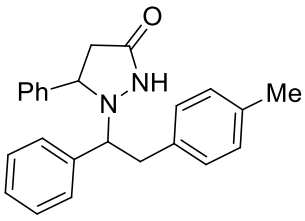


1-(2-(2-bromophenyl)-1-phenylethyl)-5-phenylpyrazolidin-3-one (3ag) was synthesized following the general procedure 2 using (*Z*)-2-benzylidene-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1a** (50.0 mg, 0.2 mmol, 1 equiv) and 2-(2-bromophenyl)acetic acid (51.1 mg, 0.3 mmol, 1.5 equiv) for 20 h. The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl acetate (8/2 to 7/3, R_f = 0.20) as eluent to give **3ag** (49.9 mg, 88:12 dr, 59% yield) as a white solid. mp = 118-119°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.53 – 7.05 (m, 14H), 7.03 – 6.87 (m, 2H), 6.71 (dt, *J* = 7.6, 1.3 Hz, 1H), 4.40 (dd, *J* = 8.7, 2.1 Hz, 1H), 4.01 (dd, *J* = 9.7, 4.7 Hz, 1H), 3.28 (dd, *J* = 12.9, 4.7 Hz, 1H), 3.07 (dd, *J* = 17.0, 8.7 Hz, 1H), 2.88 (dd, *J* = 12.9, 9.7 Hz, 1H), 2.35 (dd, *J* = 17.0, 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9 (C), 141.6 (C), 140.1 (C), 138.6 (CH), 136.6 (CH), 130.4 (CH), 130.1 (CH), 129.6 (CH), 129.4 (CH), 128.6 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 127.5 (CH), 126.3 (CH), 122.1 (CH), 73.9 (CH), 62.6 (CH), 40.8 (CH_2), 36.5 (CH_2). HRMS (ESI^+): calcd for $C_{23}H_{21}BrN_2O$ [$(M+H)^+$]: 421.0871, 423.0850; Found: 421.0927, 423.0911.

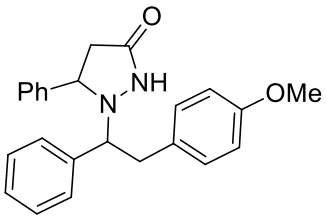


5-phenyl-1-(1-phenyl-2-(*m*-tolyl)ethyl)pyrazolidin-3-one (3ah) was synthesized following the general procedure 2 using (*Z*)-2-benzylidene-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1a** (50.0 mg, 0.2 mmol, 1 equiv) and 2-(*m*-tolyl)acetic acid (45.1 mg, 0.3 mmol, 1.5 equiv) for 20 h. The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl

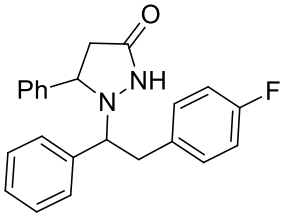
acetate (8/2, R_f = 0.27) as eluent to give **3ah** (45.0 mg, 90:10 dr, 63% yield) as a white solid. The main diastereoisomer of **3ah** was isolated by precipitation in *n*-pentane. mp = 128-129°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.11 (m, 10H) 7.02 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.69 – 6.60 (m, 2H) , 4.42 (dd, *J* = 8.5, 2.1 Hz, 1H), 4.05 (dd, *J* = 9.4, 4.8 Hz, 1H), 3.27 (dd, *J* = 12.9, 4.9 Hz, 1H), 3.04 (dd, *J* = 16.9, 8.6 Hz, 1H), 2.90 (dd, *J* = 12.9, 9.4 Hz, 1H), 2.32 (dd, *J* = 16.9, 2.1 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3 (C), 141.7 (C), 139.5 (C), 137.8 (C), 137.7 (C), 130.5 (CH), 128.6 (CH), 128.5 (CH), 128.5 (CH), 128.1 (CH), 127.5 (CH), 127.1 (CH), 126.6 (CH), 126.4 (CH), 74.0 (CH), 63.0 (CH), 41.1 (CH_2), 36.0 (CH_2), 21.4 (CH_3). HRMS (ESI^+): calcd for $C_{24}H_{24}N_2O$ [$(M+H)^+$]: 357.1922; Found: 357.1967.



5-phenyl-1-(1-phenyl-2-(*p*-tolyl)ethyl)pyrazolidin-3-one (3ai) was synthesized following the general procedure 2 using (*Z*)-2-benzylidene-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1a** (50.0 mg, 0.2 mmol, 1 equiv) and 2-(*p*-tolyl)acetic acid (45.1 mg, 0.3 mmol, 1.5 equiv) for 20 h. The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl acetate (9/1, R_f = 0.19) as eluent to give **3ai** (37.9 mg, 93:7 dr, 84% yield) as a white solid. The main diastereoisomer of **3ai** was isolated by precipitation in *n*-pentane. The corresponding product **3ai** was also obtained from the synthesized complex $Fe(OC(O)CH_2(p\text{-}Me)Ph)_3$ by irradiating with 427 nm visible light in DMSO under the argon for 20 hours. The NMR yield was measured with a Bn_2O (0.5 equiv) as an internal standard, indicating the formation of the desired product with 75% NMR yield (dr 75:25). mp = 129-130°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (brs, 1H), 7.38 – 7.07 (m, 10H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.74 – 6.70 (m, 2H), 4.40 (dd, *J* = 8.7, 2.2 Hz, 1H), 4.02 (dd, *J* = 9.7, 4.6 Hz, 1H), 3.28 (dd, *J* = 13.0, 4.5 Hz, 1H), 3.06 (dd, *J* = 16.9, 8.7 Hz, 1H), 2.90 (dd, *J* = 13.0, 9.7 Hz, 1H), 2.37 – 2.29 (m, 1H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4 (C), 141.7 (C), 139.4 (C), 135.8 (C), 134.6 (C), 129.4 (CH), 129.3 (CH), 129.0 (CH), 128.9 (CH), 128.6 (2CH), 128.5 (CH), 128.1 (CH), 127.5 (CH), 126.6 (CH), 126.4 (CH), 74.1 (CH), 62.9 (CH), 40.7 (CH_2), 36.1 (CH_2), 21.1 (CH_3). HRMS (ESI^+): calcd for $C_{24}H_{24}N_2O$ [$(M+H)^+$]: 357.1922; Found: 357.1971.

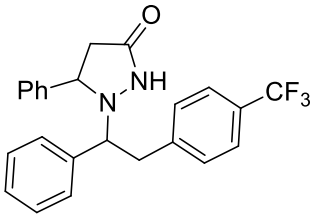


1-(2-(4-methoxyphenyl)-1-phenylethyl)-5-phenylpyrazolidin-3-one (3aj) was synthesized following the general procedure 2 using (*Z*)-2-benzylidene-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1a** (50.0 mg, 0.2 mmol, 1 equiv) and 2-(4-methoxyphenyl)acetic acid (49.8 mg, 0.3 mmol, 1.5 equiv) for 20 h. The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl acetate (8/2 to 7/3, R_f = 0.11) as eluent to give **3aj** (49.5 mg, 96:4 dr, 67% yield) as a white solid. The main diastereoisomer of **3aj** was isolated by precipitation in *n*-pentane. mp = 184-185°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.07 (m, 10H), 6.76 – 6.70 (m, 2H), 6.70 – 6.61 (m, 2H), 4.40 (dd, *J* = 8.6, 2.0 Hz, 1H),4.00 (dd, *J* = 9.7, 4.6 Hz, 1H), 3.73 (s, 3H),3.27 (dd, *J* = 13.0, 4.5 Hz, 1H), 3.08 (dd, *J* = 16.9, 8.7 Hz, 1H), 2.87 (dd, *J* = 13.0, 9.7 Hz, 1H), 2.33 (dd, *J* = 16.9, 2.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4 (C), 158.1 (C), 141.7 (C), 139.5 (C), 130.5 (C), 129.7 (CH), 128.6 (CH), 128.5 (CH), 128.5 (CH), 128.0 (CH), 127.5 (CH), 126.4 (CH), 113.6 (CH), 74.3 (CH), 63.0 (CH), 55.2 (OCH_3), 40.3 (CH_2), 36.0 (CH_2). HRMS (ESI^+): calcd for $C_{24}H_{24}N_2O_2$ [$(M+H)^+$]: 373.1871; Found: 373.1927.

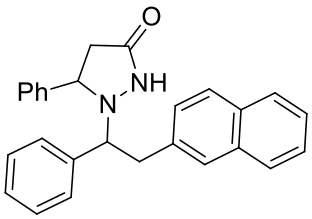


1-(2-(4-fluorophenyl)-1-phenylethyl)-5-phenylpyrazolidin-3-one (3ak) was synthesized following the general procedure 2 using (*Z*)-2-benzylidene-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1a** (50.0 mg, 0.2 mmol, 1 equiv) and 2-(4-fluorophenyl)acetic acid (49.8 mg, 0.3 mmol, 1.5 equiv) for 20 h. The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl acetate (8/2 to 7/3, R_f = 0.18) as eluent to give **3ak** (66.7 mg, 90:10 dr, 90% yield) as a white solid. mp = 134-135°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.01 (m, 11H), 6.83 – 6.73 (m, 4H) 4.39 (dd, *J* = 8.7, 2.1 Hz, 1H), 3.99 (dd, *J* = 9.9, 4.5 Hz, 1H), 3.30 (dd, *J* = 13.0, 4.4 Hz, 1H), 3.11 (dd, *J* = 17.0, 8.7 Hz, 1H), 2.89 (dd, *J* = 13.0, 9.9 Hz, 1H), 2.35 (dd, *J* = 17.0, 2.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.6 (C), 141.86 (C), 135.1 (d, $^1J_{C\text{-}F}$ = 79.3 Hz, C), 129.5 (C),

129.3 (d, $^{3}J_{C\text{-}F}$ = 2.0 Hz, CH), 128.8 (CH), 128.6 (CH), 128.4 (CH), 127.73 (d, $^{2}J_{Cz\text{-}F}$ = 43.1 Hz, CH), 126.7 (CH), 126.41 (CH), 74.1 (CH), 62.7 (CH), 40.6 (CH_2), 36.4 (CH_2). ^{19}F NMR (376 MHz, $CDCl_3$) δ_F -115.6, -116.8. HRMS (ESI$^+$): calcd for $C_{23}H_{21}FN_2O$ [(M+H)$^+$]: 361.1671; Found: 361.1703.

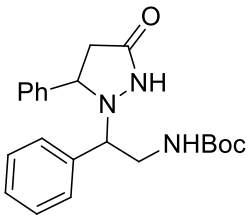


5-phenyl-1-(1-phenyl-2-(4-(trifluoromethyl)phenyl)ethyl)pyrazolidin-3-one (3al) was synthesized following the general procedure 2 using (*Z*)-2-benzylidene-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1a** (50.0 mg, 0.2 mmol, 1 equiv) and 2-(4-(trifluoromethyl)phenyl)acetic acid (61.2 mg, 0.3 mmol, 1.5 equiv). The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl acetate (8/2 to 7/3, R_f = 0.20) as eluent to give **3al** (26.5 mg, 90:10 dr, 32%) yield) as a colorless solid. The main diastereoisomer of **3al** was isolated by precipitation in *n*-pentane. mp = 194-195°C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.43 – 7.15 (m, 10H), 7.10 (dq, *J* = 6.0, 2.6 Hz, 2H), 6.92 (d, *J* = 7.9 Hz, 2H), 4.41 (dd, *J* = 8.6, 2.1 Hz, 1H), 4.04 (dd, *J* = 9.9, 4.5 Hz, 1H), 3.39 (dd, *J* = 12.9, 4.5 Hz, 1H), 3.09 (dd, *J* = 17.0, 8.7 Hz, 1H), 2.99 (dd, *J* = 12.9, 9.8 Hz, 1H), 2.35 (dd, *J* = 17.0, 2.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 175.82 (C), 141.92 (C), 141.62 (C), 138.74 (C), 128.71 (q, $J_{C\text{-}F}$ = 3.0 Hz, CH), 128.4 (C), 128.18 (q, $^{1}J_{C\text{-}F}$= 270.0 Hz, CF_3), 127.6 (CH), 125.69 (CH), 125.09 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz, CH), 122.99 (CH), 73.91 (CH), 62.95 (CH), 41.10 (CH_2), 36.24 (CH_2). ^{19}F NMR (376 MHz, $CDCl_3$) δ_F -62.4. HRMS (ESI$^+$): calcd for $C_{24}H_{21}F_3N_2O$ [(M+H)$^+$]: 411.1640; Found: 411.1699.

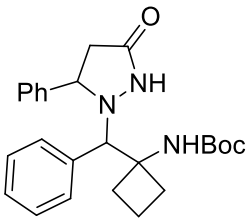


1-(2-(naphthalen-2-yl)-1-phenylethyl)-5-phenylpyrazolidin-3-one (3am) was synthesized following the general procedure 2 using (*Z*)-2-benzylidene-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1a** (50.0 mg, 0.2 mmol, 1 equiv) and 2-(naphthalen-2-yl)acetic acid (55.8 mg, 0.3 mmol, 1.5 equiv) for 20 h. The crude product was purified by silica gel column chromatography using

n-pentane/ethyl acetate (8/2 to 7/3, R_f = 0.33) as eluent to give **3am** (51.8 mg, 92:8 dr, 66% yield) as a white solid. mp = 175-176°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.85 – 7.69 (m, 1H), 7.69 – 7.57 (m, 2H), 7.47 – 7.09 (m, 14H), 6.95 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.45 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.16 (dd, *J* = 9.7, 4.6 Hz, 1H), 3.51 (dd, *J* = 12.9, 4.5 Hz, 1H), 3.15 – 2.98 (m, 2H), 2.35 (dd, *J* = 16.9, 2.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7 (C), 141.9 (C), 139.2 (C), 135.4 (C), 133.4 (C), 132.1 (C), 128.8 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.6 (CH), 127.4 (CH), 126.7 (CH), 126.4 (CH), 125.8 (CH), 125.8 (CH), 125.4 (CH), 74.1 (CH), 62.7 (CH), 41.3 (CH_2), 36.49 (CH_2). HRMS (ESI$^+$): calcd for $C_{27}H_{24}N_2O$ [$(M+H)^+$]: 393.1922; Found: 393.1978.

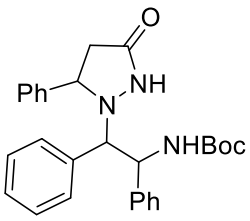


***tert*-butyl (2-(3-oxo-5-phenylpyrazolidin-1-yl)-2-phenylethyl)carbamate (3an)** was synthesized following the general procedure 2 using (*Z*)-2-benzylidene-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1a** (50.0 mg, 0.2 mmol, 1 equiv) and Boc-glycine (52.5 mg, 0.3 mmol, 1.5 equiv) for 20 h. The crude product was purified by two consecutive silica gel column chromatographies using CH_2Cl_2/Et_2O (8/2, R_f = 0.43) and *n*-pentane/ethyl acetate (9/1, R_f = 0.11) as eluent to give **3an** (39.6 mg, >96:4 dr, 52% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.25 (m, 10H), 4.47 (dd, *J* = 9.5, 4.1 Hz, 1H), 4.29 (d, *J* = 8.5 Hz, 1H), 4.14 – 4.06 (m, 1H), 4.02 (q, *J* = 2.7 Hz, 1H), 3.27 (dd, *J* = 16.7, 8.7 Hz, 1H), 2.97 (ddd, *J* = 14.6, 4.3, 2.0 Hz, 1H), 2.40 – 2.12 (m, 1H), 1.50 (s, 9H). ^{1}H NMR was consistent with the literature.[3]

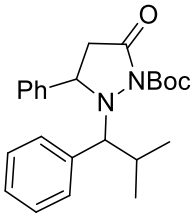


***tert*-butyl (1-((3-oxo-5-phenylpyrazolidin-1-yl)(phenyl)methyl)cyclobutyl)carbamate (3ao)** was synthesized following the general procedure 2 using (*Z*)-2-benzylidene-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1a** (50.0 mg, 0.2 mmol, 1 equiv) and 1-((tert-

butoxycarbonyl)amino)cyclobutanecarboxylic acid (64.5 mg, 0.3 mmol, 1.5 equiv) for 20 h. The crude product was purified by two consecutive silica gel column chromatographies using CH_2Cl_2/Et_2O (8/2, R_f = 0.43) and *n*-pentane/ethyl acetate (6/4, R_f = 0.33) as eluent to give **3ao** (29.0 mg, >96:4 dr, 47% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.14 (s, 1H), 7.30 – 7.11 (m, 10H), 4.42 (s, 1H, NHBoc), 4.16 (dd, *J* = 8.5, 1.4 Hz, 1H), 4.02 (s, 1H), 3.32 (ddd, *J* = 16.6, 8.7, 1.0 Hz, 1H), 3.12 – 2.94 (m, 1H), 2.54 – 2.35 (m, 1H), 2.22 (dt, *J* = 16.6, 1.1 Hz, 1H), 2.18 – 1.97 (m, 2H), 1.91 – 1.73 (m, 1H), 1.54 (s, 9H), 1.13 – 0.98 (m, 1H). ^{1}H NMR was consistent with the literature.[3]



***tert*-butyl (1-(3-oxo-5-phenylpyrazolidin-1-yl)-1,3-diphenylpropan-2-yl)carbamate (3ap)** was synthesized following the general procedure 2 using (*Z*)-2-benzylidene-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1a** (50.0 mg, 0.2 mmol, 1 equiv) and Boc-Phenylalanine (79.5 mg, 0.3 mmol, 1.5 equiv) for 20 h. The crude product was purified by two consecutive silica gel column chromatographies using CH_2Cl_2/Et_2O (8/2, R_f = 0.43) and *n*-pentane/ethyl acetate (9/1, R_f = 0.23) as eluent to give **3ap** (20.2 mg, main diastereoisomer, 21% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.49 – 7.08 (m, 19H), 4.51 – 4.28 (m, 2H), 4.13 (d, *J* = 6.1 Hz, 1H), 3.16 (dd, *J* = 14.3, 4.2 Hz, 1H), 2.48 – 2.20 (m, 1H), 2.20 – 2.00 (m, 1H), 1.32 (s, 9H). ^{1}H NMR was consistent with the literature.[3]

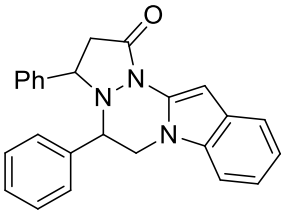


***tert*-butyl 2-(2-methyl-1-phenylpropyl)-5-oxo-3-phenylpyrazolidine-1-carboxylate (4aq)** was synthesized following the general procedure 2 using (*Z*)-2-benzylidene-5-oxo-3-phenylpyrazolidin-2-ium-1-ide **1a** (50.0 mg, 0.2 mmol, 1 equiv) and isobutyric acid (55.8 mg, 0.3 mmol, 1.5 equiv) for 20 h. Then, after removal of solvent under reduced pressure, the

crude reaction was dissolved in CH_2Cl_2 (2 mL). Boc_2O (131.0 mg, 0.6 mmol, 3 equiv) in CH_2Cl_2 (1 mL) was added a dropwise following by DMAP (2.4 mg, 0.02 mmol, 0.1 equiv) and the reaction was stirred at room temperature for 16 hours. The crude product was purified by two consecutive silica gel column chromatographies using CH_2Cl_2/Et_2O (8/2 to 7/3, R_f = 0.53) and *n*-pentane/ethyl acetate (9/1, R_f = 0.15) as eluent to give **4aq** (14.0 mg, >96:4 dr, 30% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.18 (m, 14H), 4.54 (d, *J* = 8.6 Hz, 1H), 3.80 (d, *J* = 10.2 Hz, 1H), 2.31 (dq, *J* = 10.2, 6.5 Hz, 1H), 2.03 (dd, *J* = 17.5, 1.4 Hz, 1H), 1.87 (dd, *J* = 17.5, 8.7 Hz, 1H), 1.65 (s, 9H), 1.21 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 6.5 Hz, 3H). ^{1}H NMR was consistent with the literature.[3]

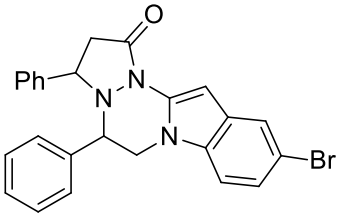
General procedure 3: Cyclization reaction

In a sealed tube, a mixture of **3aa** or **3ab** and pyridinium tribromide (16.8 mg, 0.05 mmol, 1 equiv) in anhydrous acetonitrile (1 mL) under nitrogen was heated at 60 °C for 4 hours. Then, a saturated solution of $Na_2S_2O_3$ (10 mL) was added and the organic phase was extracted with ethyl acetate (2 x 15 mL). After removal of solvent under reduced pressure, the crude was purified by silica gel column chromatography.



3,5-diphenyl-2,3,6,6a-tetrahydroindeno[2,1-c]pyrazolo[1,2-a]pyridazin-1(5H)-one (5aa) was synthesized following the general procedure 3 using **3aa** (+/-, 95:05 dr, 20.0 mg, 0.05 mmol, 1 equiv). The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl acetate (9/1, R_f = 0.45) as eluent to give **5aa** (18.0 mg, >96:4 dr, 93% yield) as a white solid. mp = 267°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 1H), 7.18 – 7.08 (m, 6H), 7.07 – 6.99 (m, 5H), 6.97 (s, 1H), 6.96 – 6.91 (m, 2H), 4.30 – 4.17 (m, 4H), 3.09 (dd, *J* = 17.3, 9.0 Hz, 1H), 2.81 (dd, *J* = 17.3, 10.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4 (C), 140.6 (C), 134.3 (C), 132.4 (C), 130.8 (C), 129.3 (C), 129.2 (CH), 128.4 (CH), 128.2 (CH), 127.9 (CH), 127.4 (CH), 127.2 (CH), 121.0 (CH), 120.7 (CH), 120.5 (CH), 108.4 (CH), 88.16 (CH), 68.3 (CH), 65.7

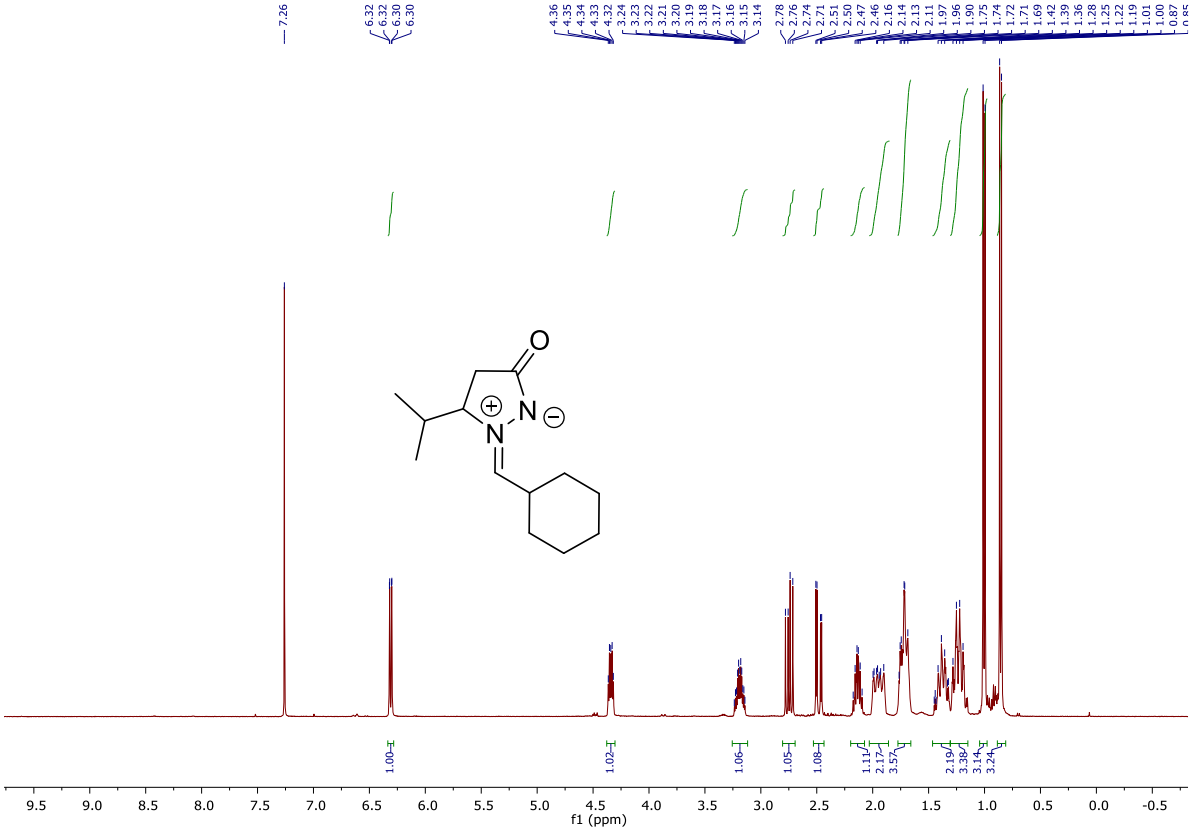
(CH), 48.25 (CH_2), 41.1 (CH_2). HRMS (ESI^+): calcd for $C_{25}H_{21}N_3O$ [$(M+H)^+$]: 380.1718; Found: 380.1765.

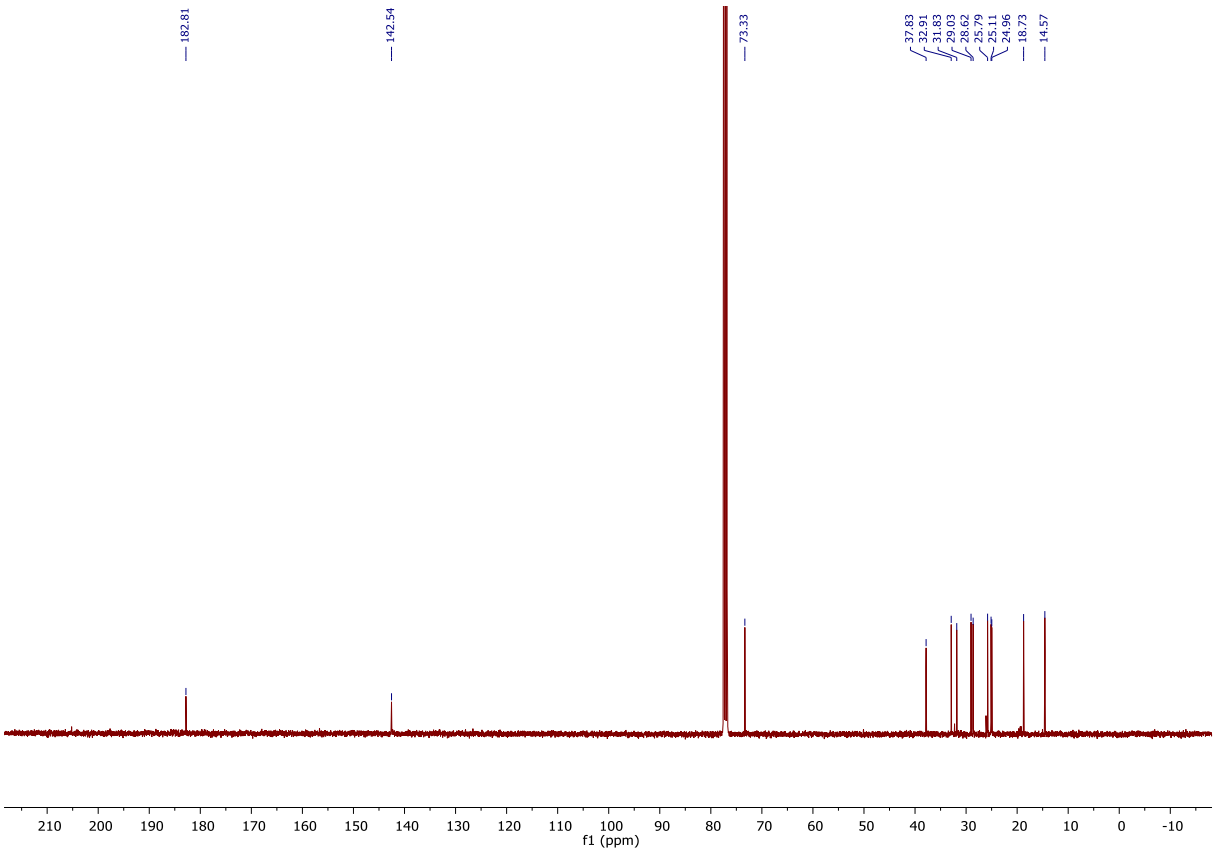


10-bromo-3,5-diphenyl-2,3,5,6-tetrahydro-1H-pyrazolo[1',2':1,2][1,2,4]triazino[4,3-a]indol-1-one (5ab) was synthesized following the general procedure 3 using **3ab** (+/-, 86:14 dr, 22.9 mg, 0.05 mmol, 1 equiv). The crude product was purified by silica gel column chromatography using *n*-pentane/ethyl acetate (8/2, R_f = 0.68) as eluent to give **5ab** (20.0 mg, >96:4 dr, 87% yield) as a white solid. mp = 275°C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 1.8 Hz, 1H), 7.22 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.14 – 6.98 (m, 9H), 6.96 – 6.87 (m, 3H), 4.30 – 4.16 (m, 4H, 3.11 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.82 (dd, *J* = 17.5, 11.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5 (C), 140.4 (C), 133.9 (C), 131.8 (C), 131.1 (C), 129.68 (C), 129.3 (CH), 128.4 (CH), 128.3 (CH), 127.4 (CH), 127.3 (CH), 123.7 (CH), 122.9 (CH), 114.0 (CH), 109.7 (C), 87.54 (CH), 68.2 (CH), 65.9 (CH), 48.2 (CH_2), 41.1 (CH_2). HRMS (ESI^+): calcd for $C_{25}H_{20}BrN_3O$ [$(M+H)^+$]: 458.0823, 460.0803; Found: 458.0856, 460.0804.

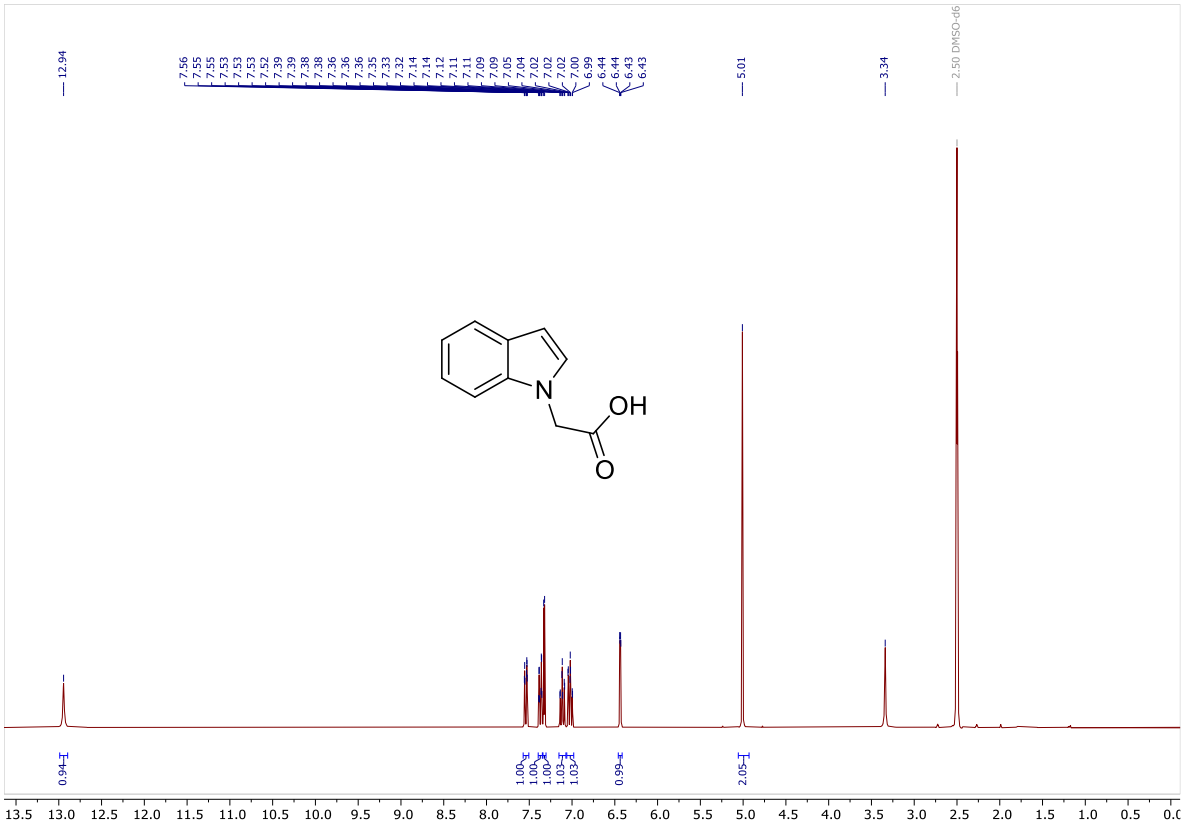
VI. NMR spectra

(*Z*)-2-(cyclohexylmethylene)-3-isopropyl-5-oxopyrazolidin-2-ium-1-ide (1k)

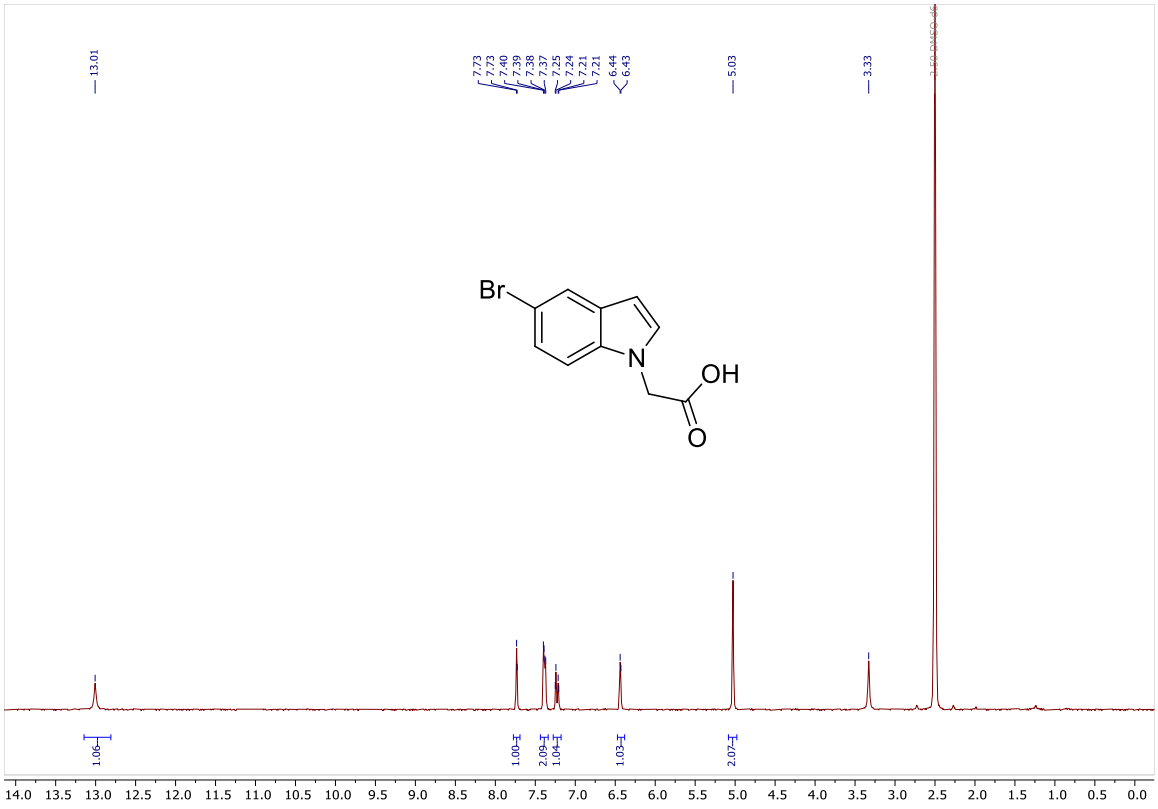




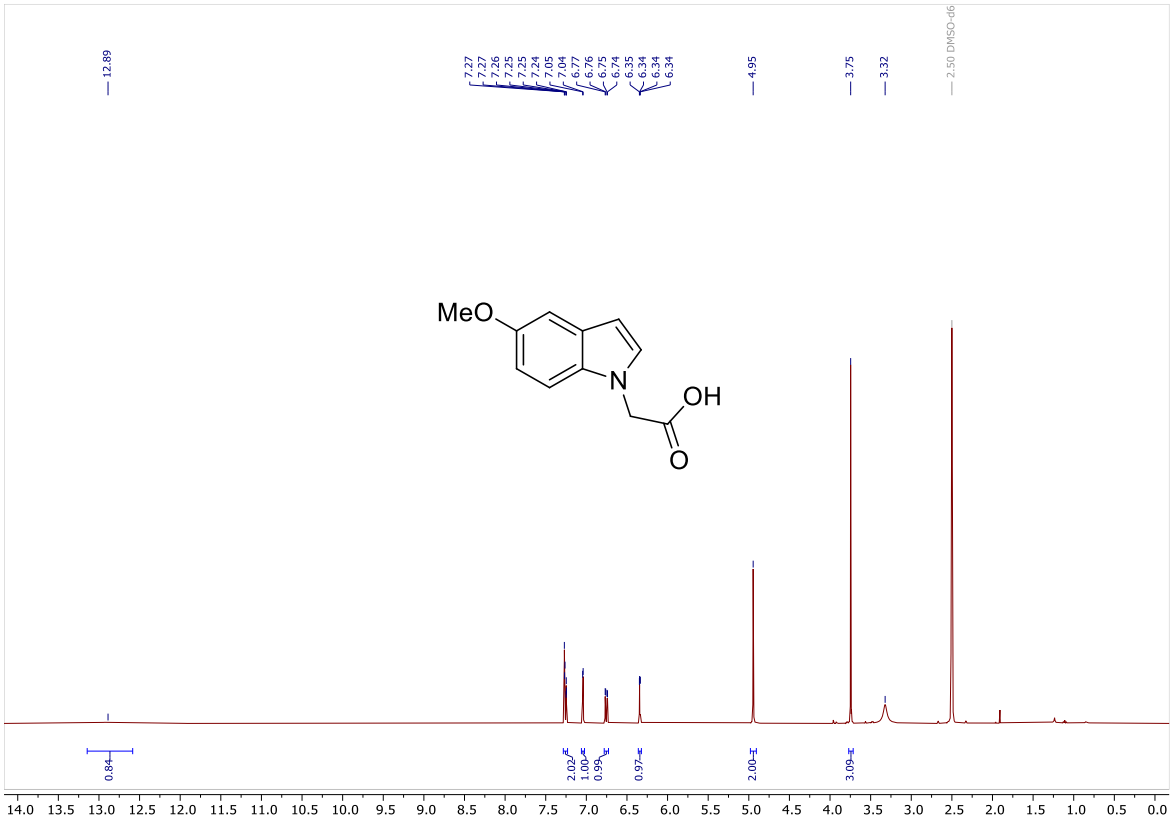
2-(1*H*-indol-1-yl)acetic acid (2a)



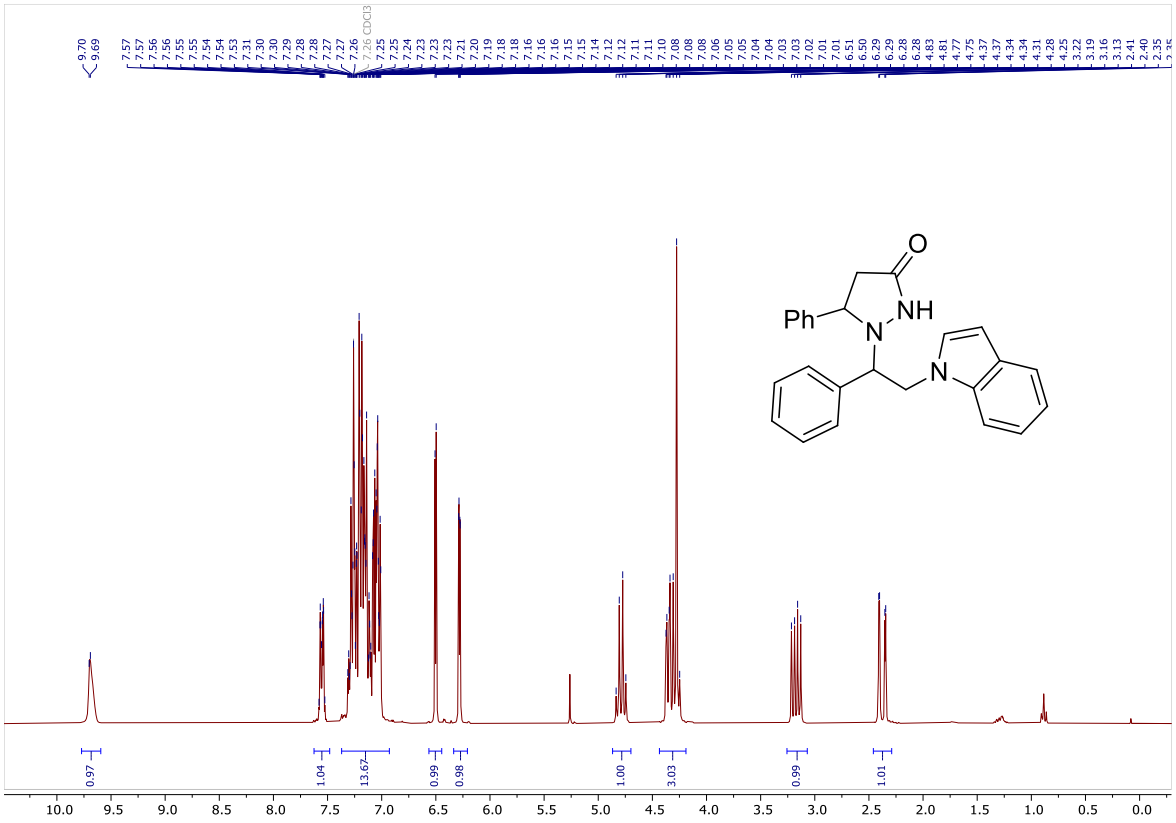
2-(5-bromo-1*H*-indol-1-yl)acetic acid (2b)



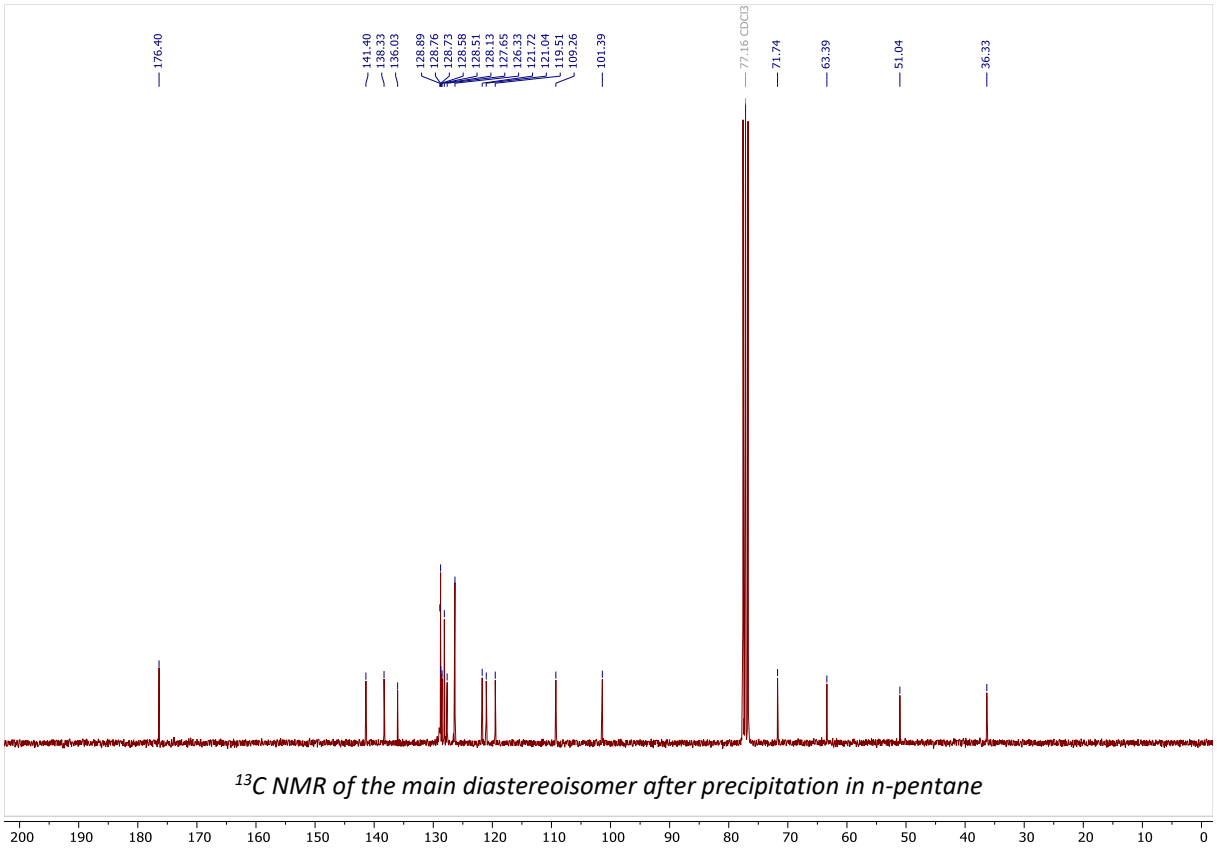
2-(5-methoxy-1*H*-indol-1-yl)acetic acid (2c)



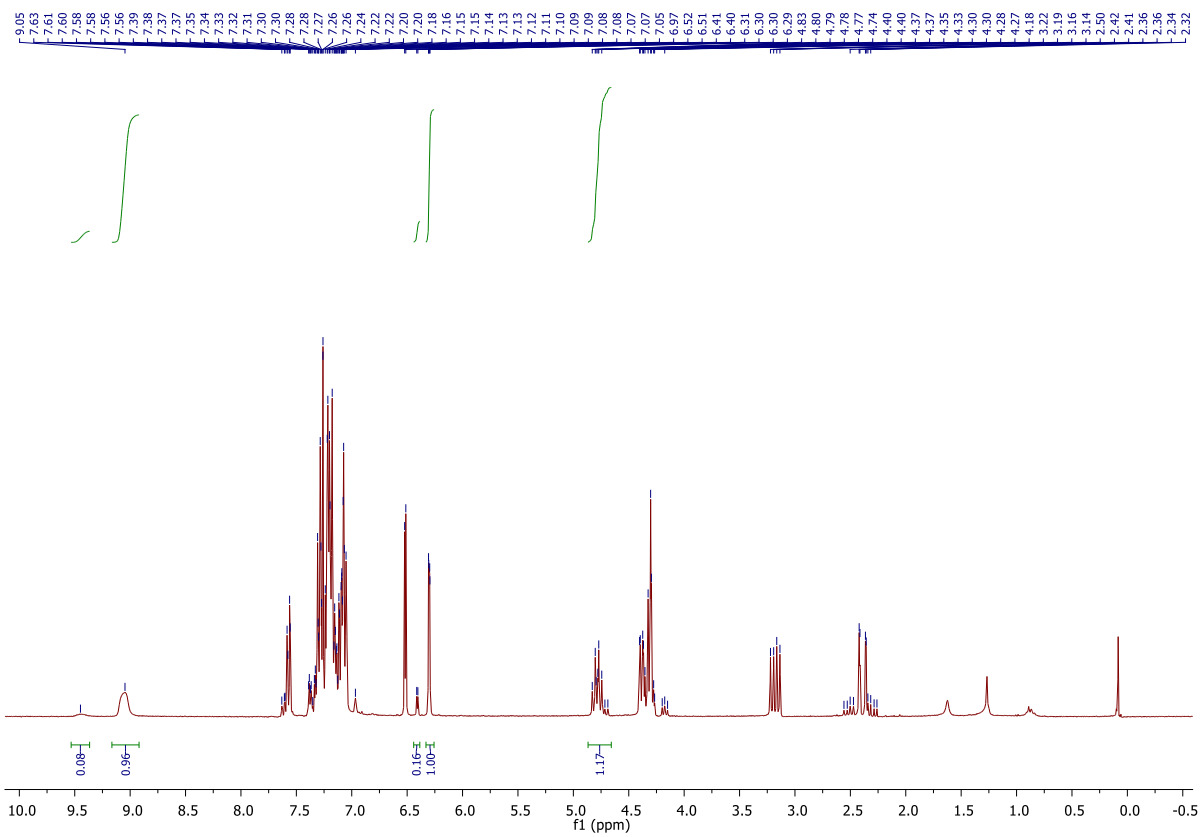
1-(2-(1*H*-indol-1-yl)-1-phenylethyl)-5-phenylpyrazolidin-3-one (3aa)



^{1}H NMR of the main diastereoisomer after precipitation in n-pentane

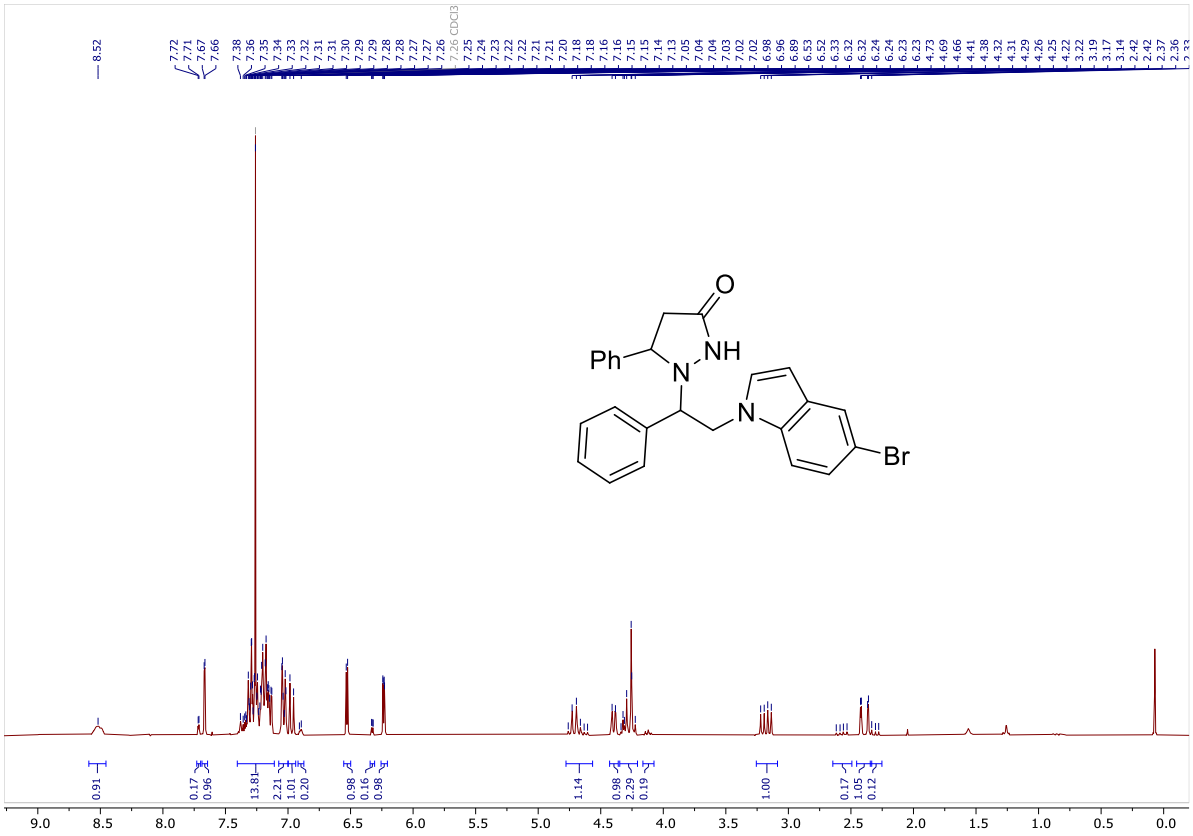


^{13}C NMR of the main diastereoisomer after precipitation in n-pentane

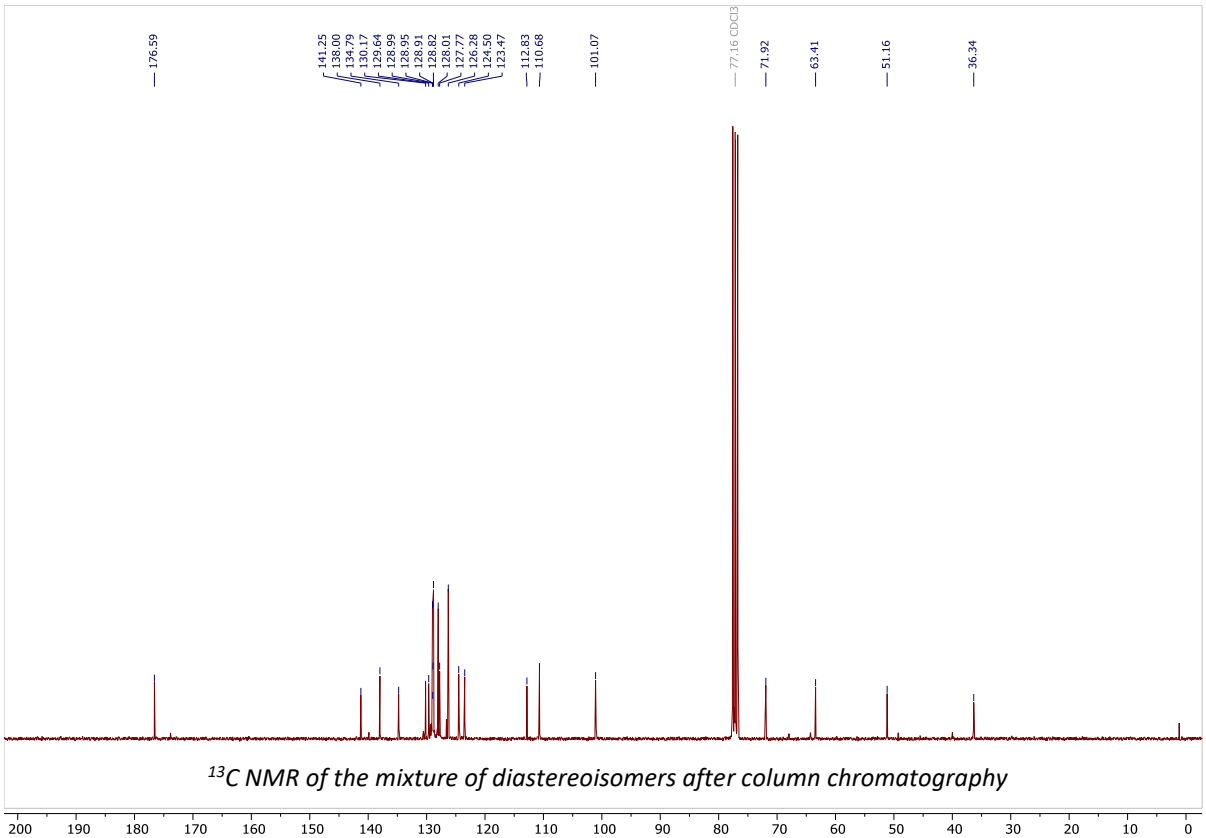


^{1}H NMR of the mixture of diastereoisomers after column chromatography

1-(2-(5-bromo-1*H*-indol-1-yl)-1-phenylethyl)-5-phenylpyrazolidin-3-one (3ab)

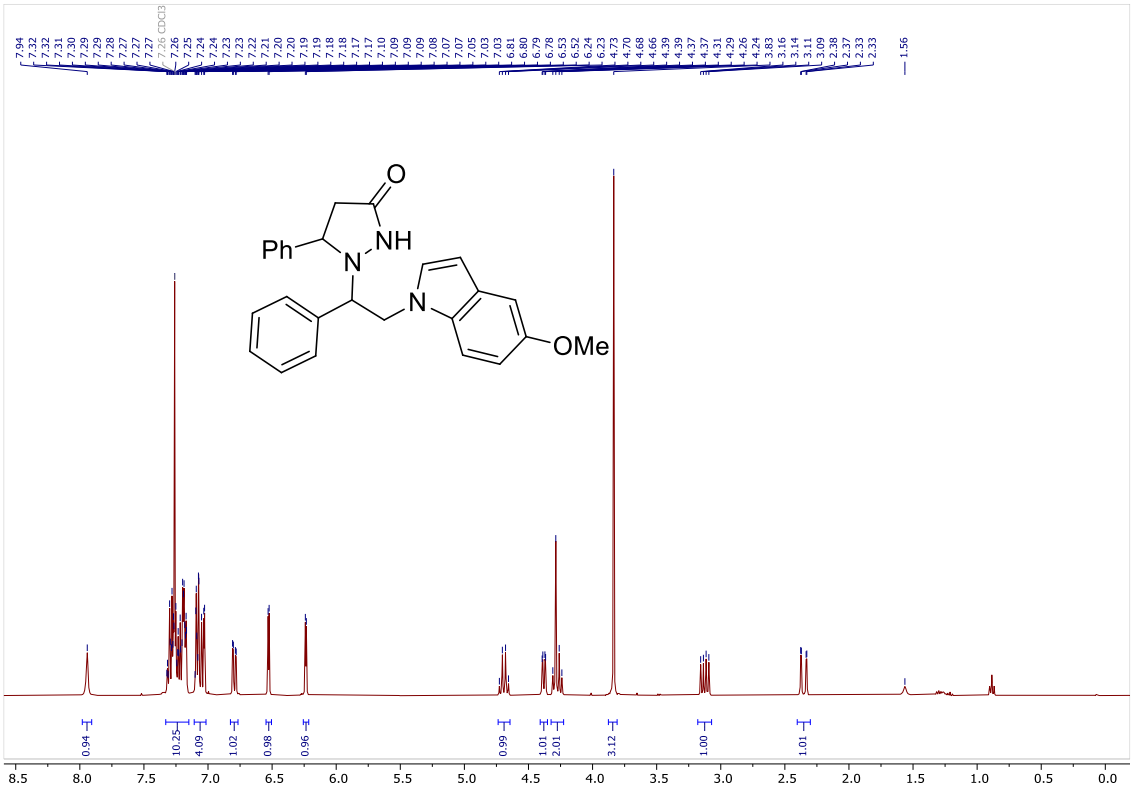


^{1}H NMR of the mixture of diastereoisomers after column chromatography

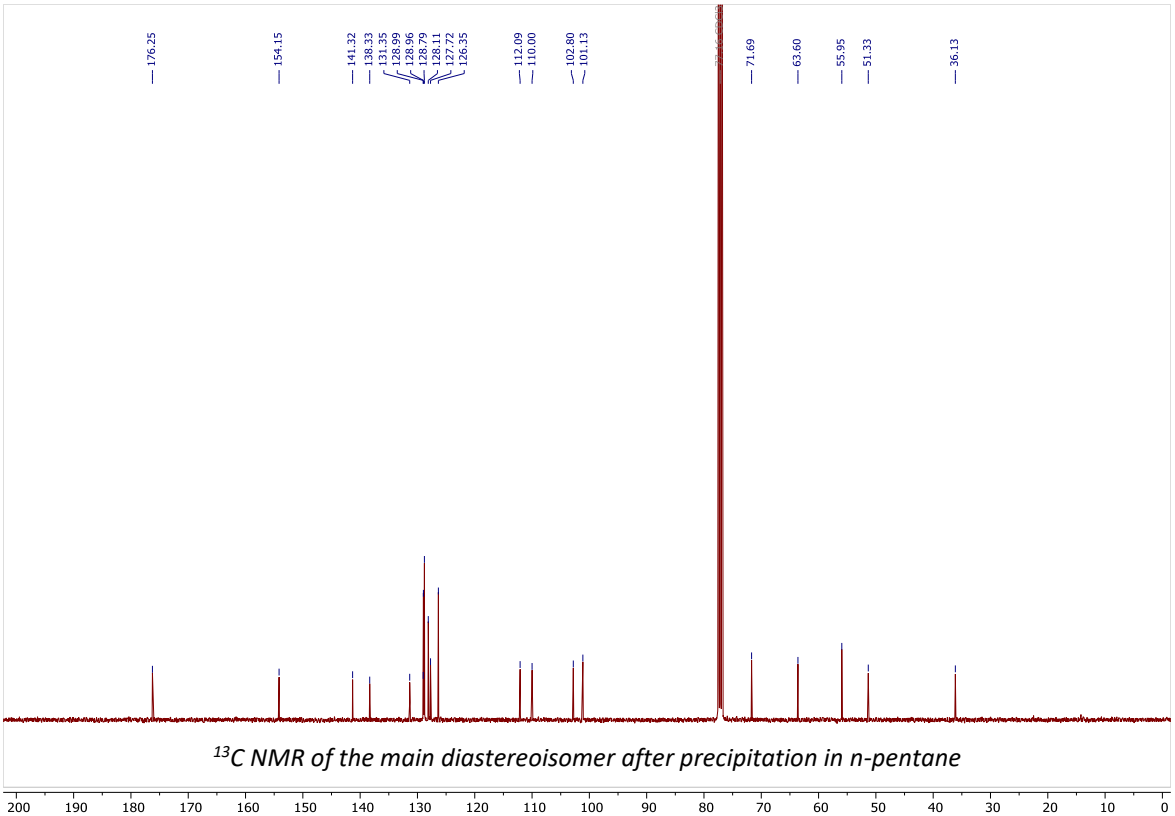


^{13}C NMR of the mixture of diastereoisomers after column chromatography

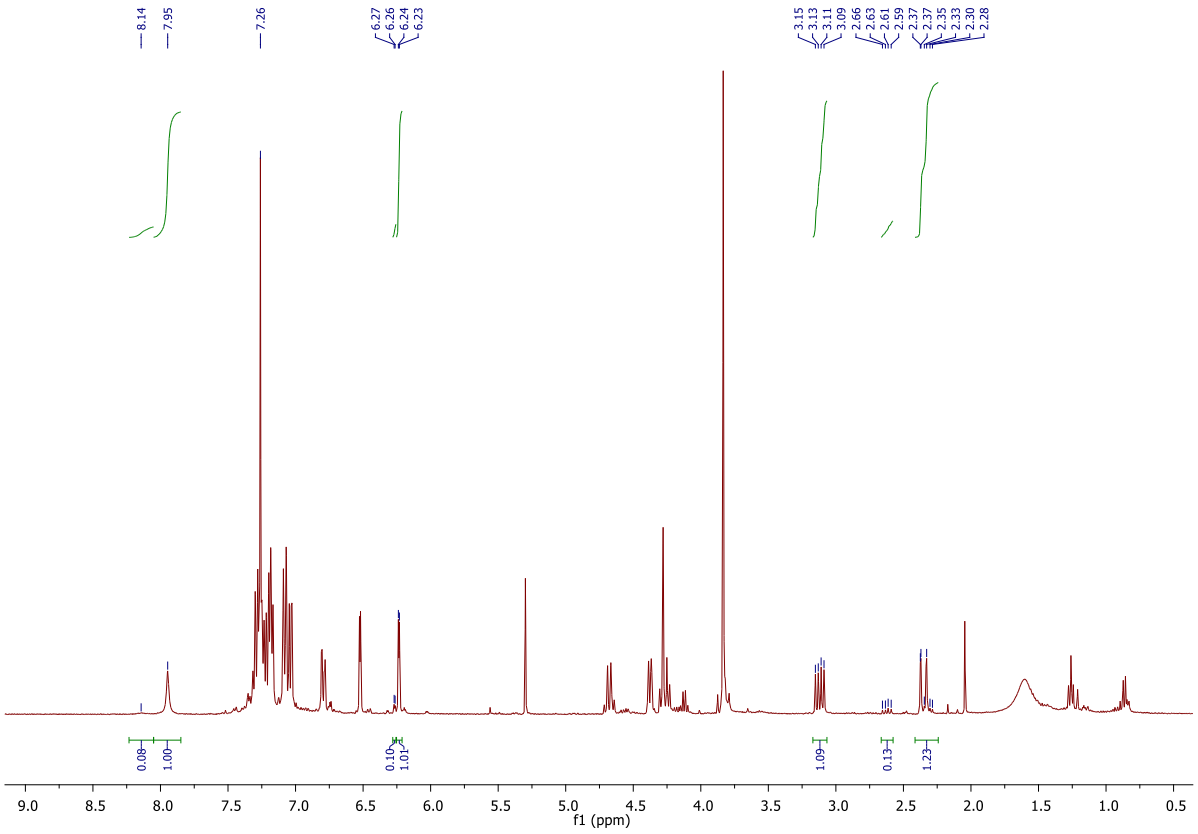
1-(2-(5-methoxy-1*H*-indol-1-yl)-1-phenylethyl)-5-phenylpyrazolidin-3-one (3ac)



^{1}H NMR of the main diastereoisomer after precipitation in n-pentane

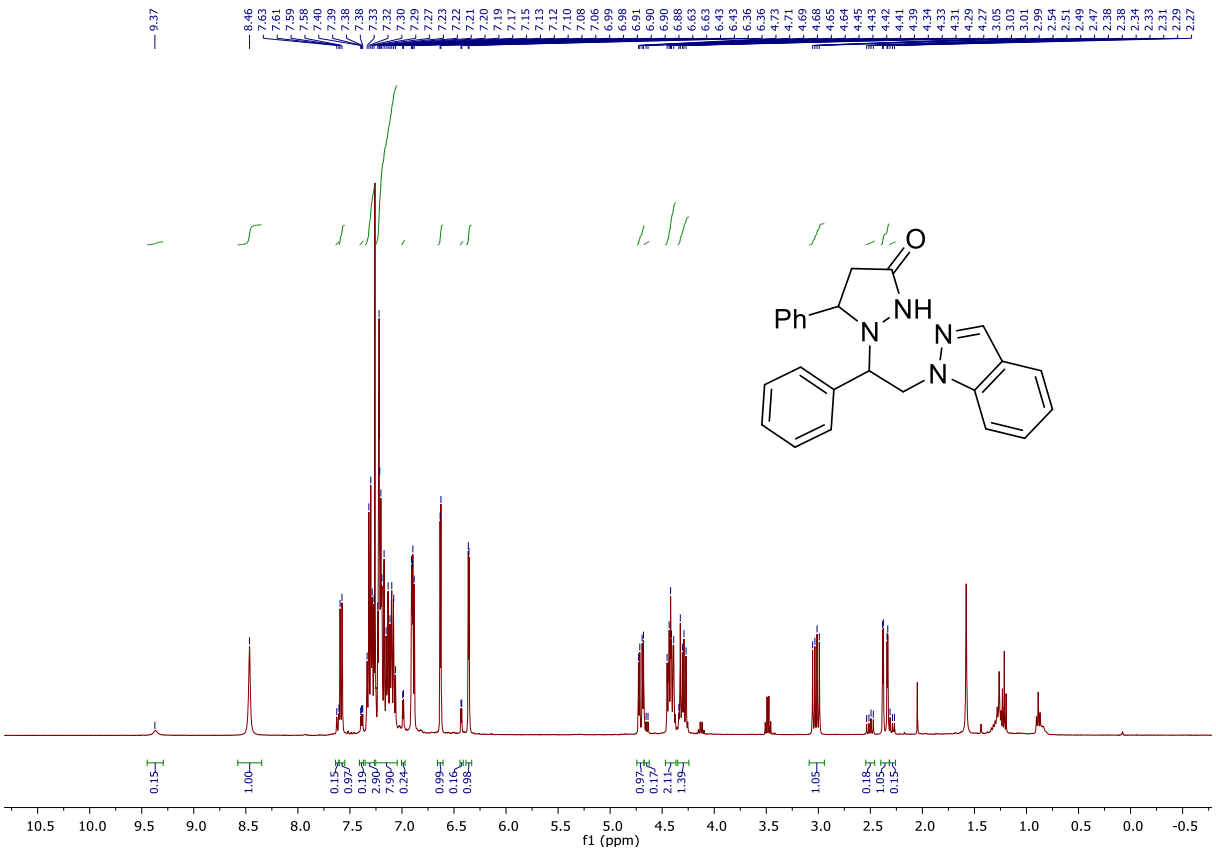


^{13}C NMR of the main diastereoisomer after precipitation in n-pentane

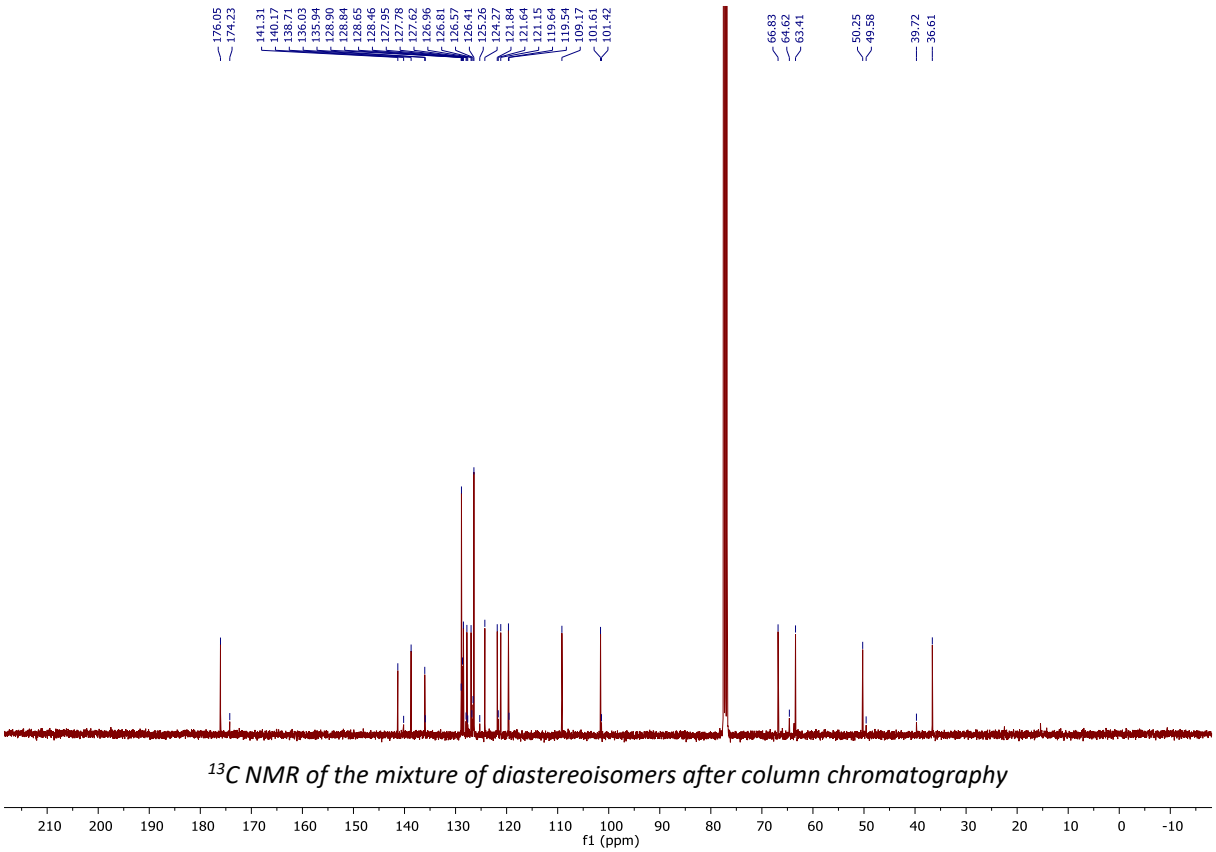


^{1}H NMR of the mixture of diastereoisomers after column chromatography

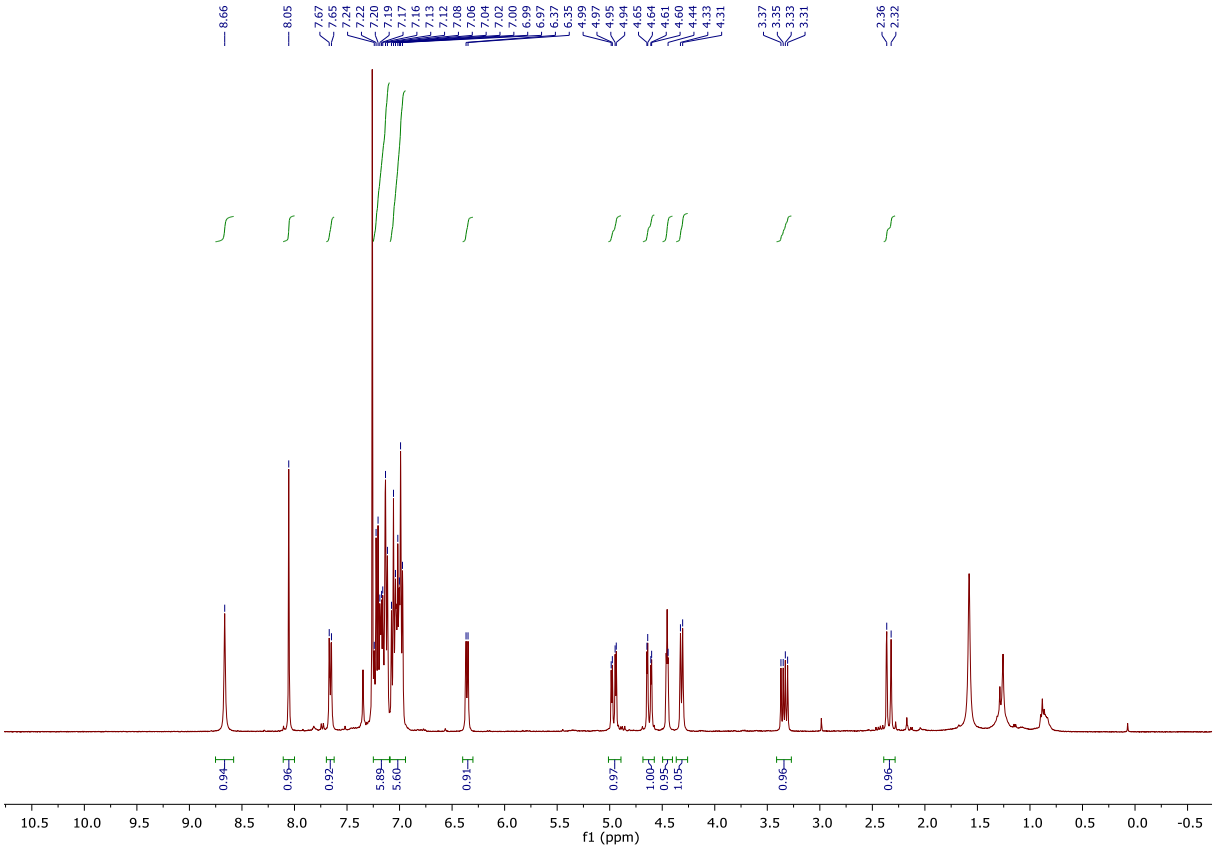
1-(2-(1H-indazol-1-yl)-1-phenylethyl)-5-phenylpyrazolidin-3-one (3ad)



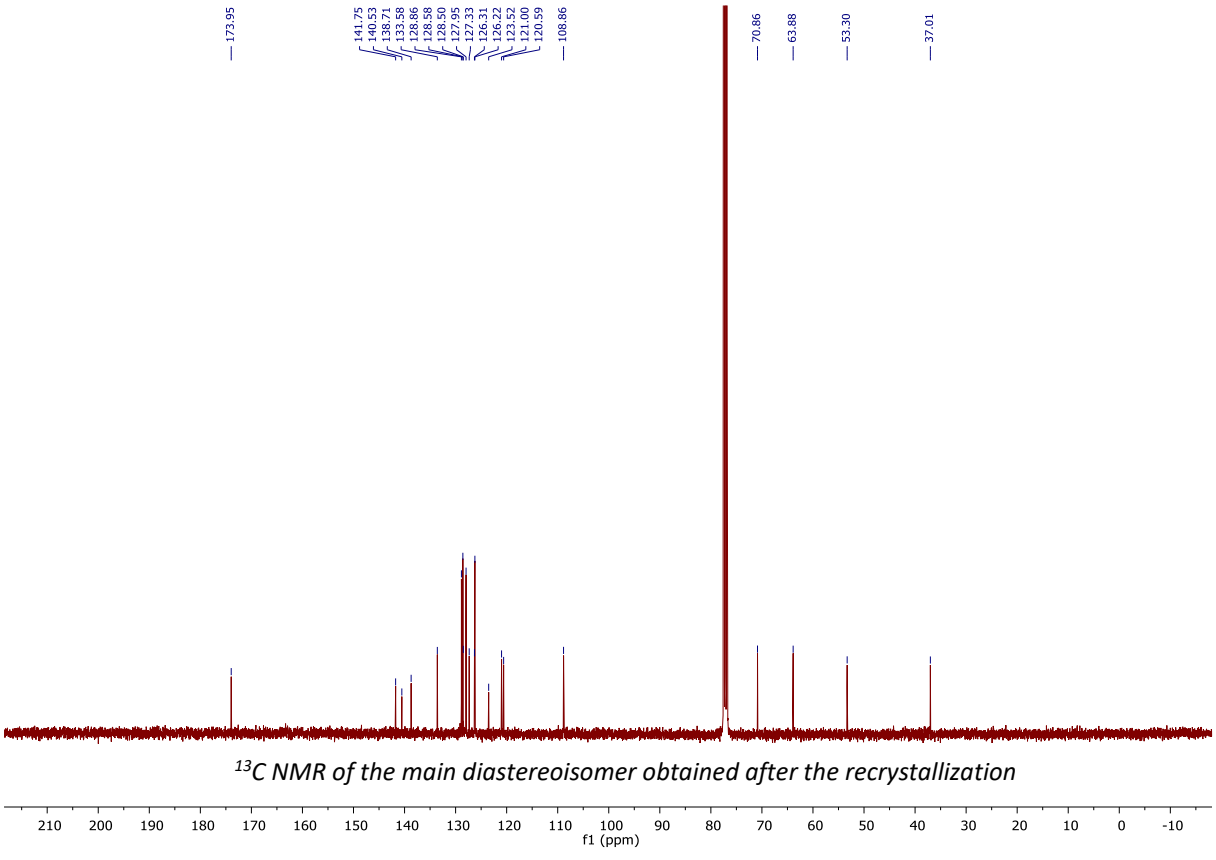
^{1}H NMR of the mixture of diastereoisomers after column chromatography



^{13}C NMR of the mixture of diastereoisomers after column chromatography

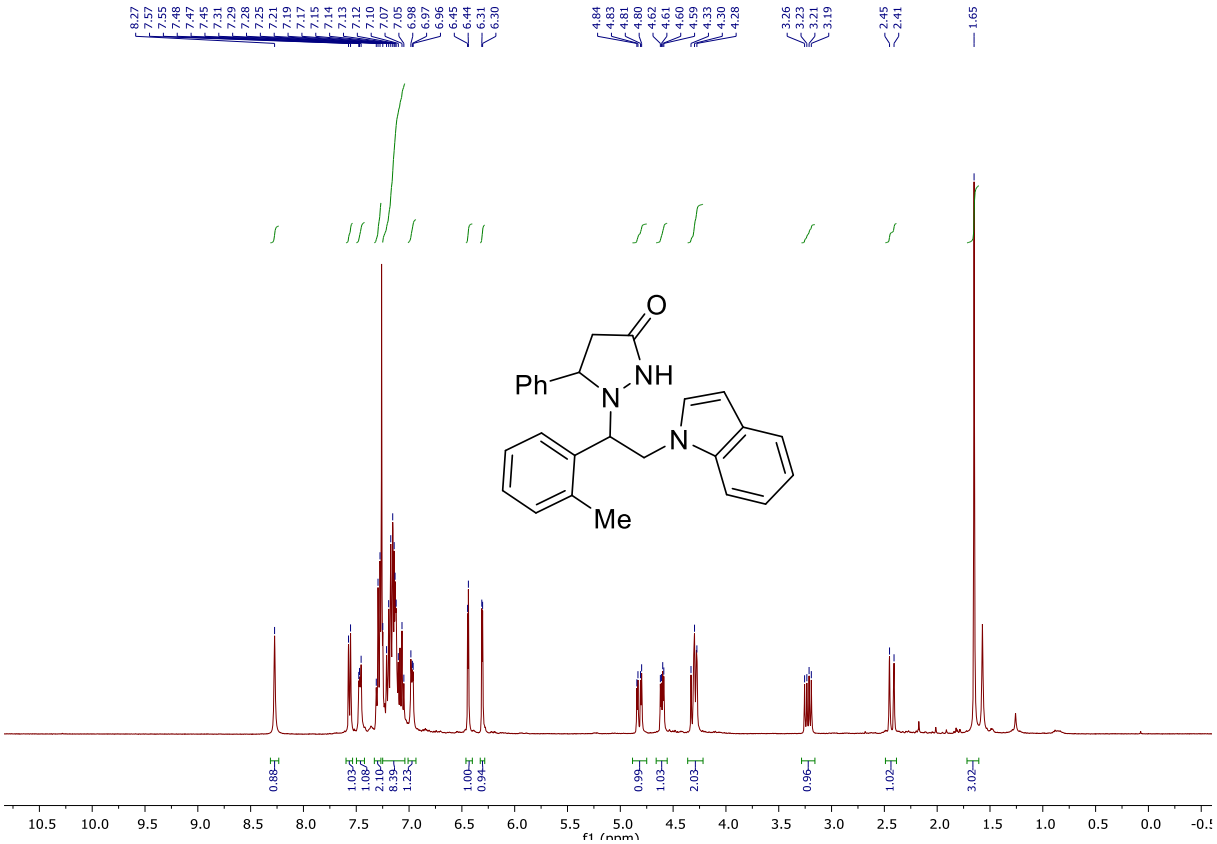


^{1}H NMR of the main diastereoisomer obtained after the recrystallization

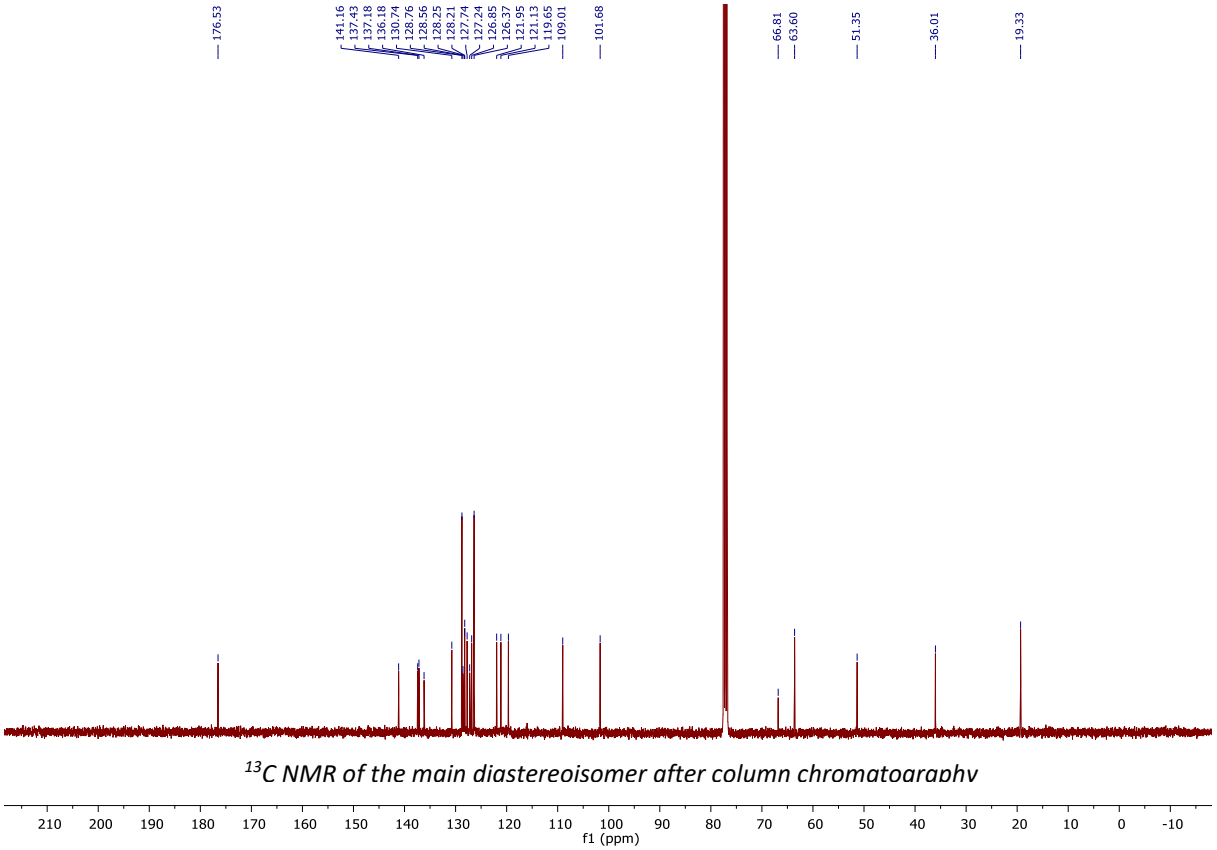


^{13}C NMR of the main diastereoisomer obtained after the recrystallization

1-(2-(1*H*-indol-1-yl)-1-(o-tolyl)ethyl)-5-phenylpyrazolidin-3-one (3ba)

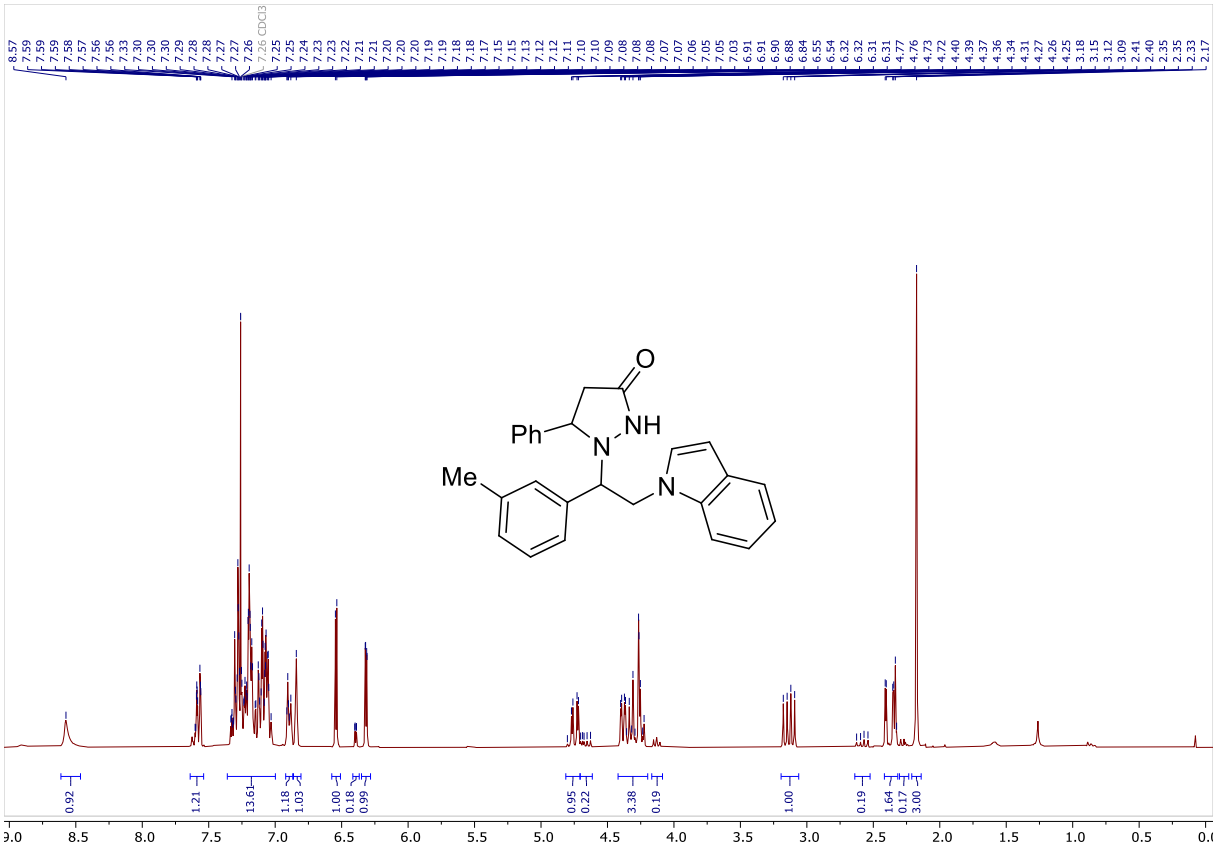


^{1}H NMR of the main diastereoisomer after column chromatography

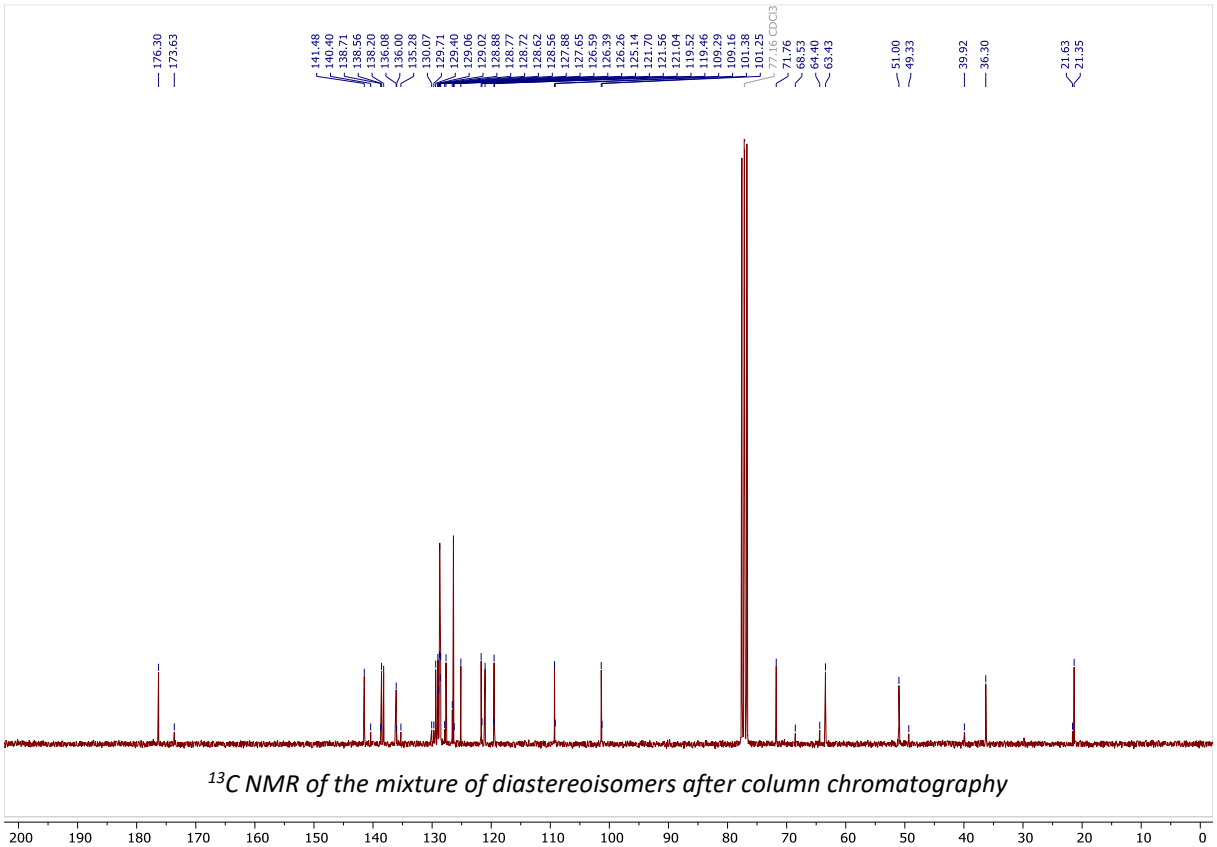


^{13}C NMR of the main diastereoisomer after column chromatography

1-(2-(1*H*-indol-1-yl)-1-(m-tolyl)ethyl)-5-phenylpyrazolidin-3-one (3ca)

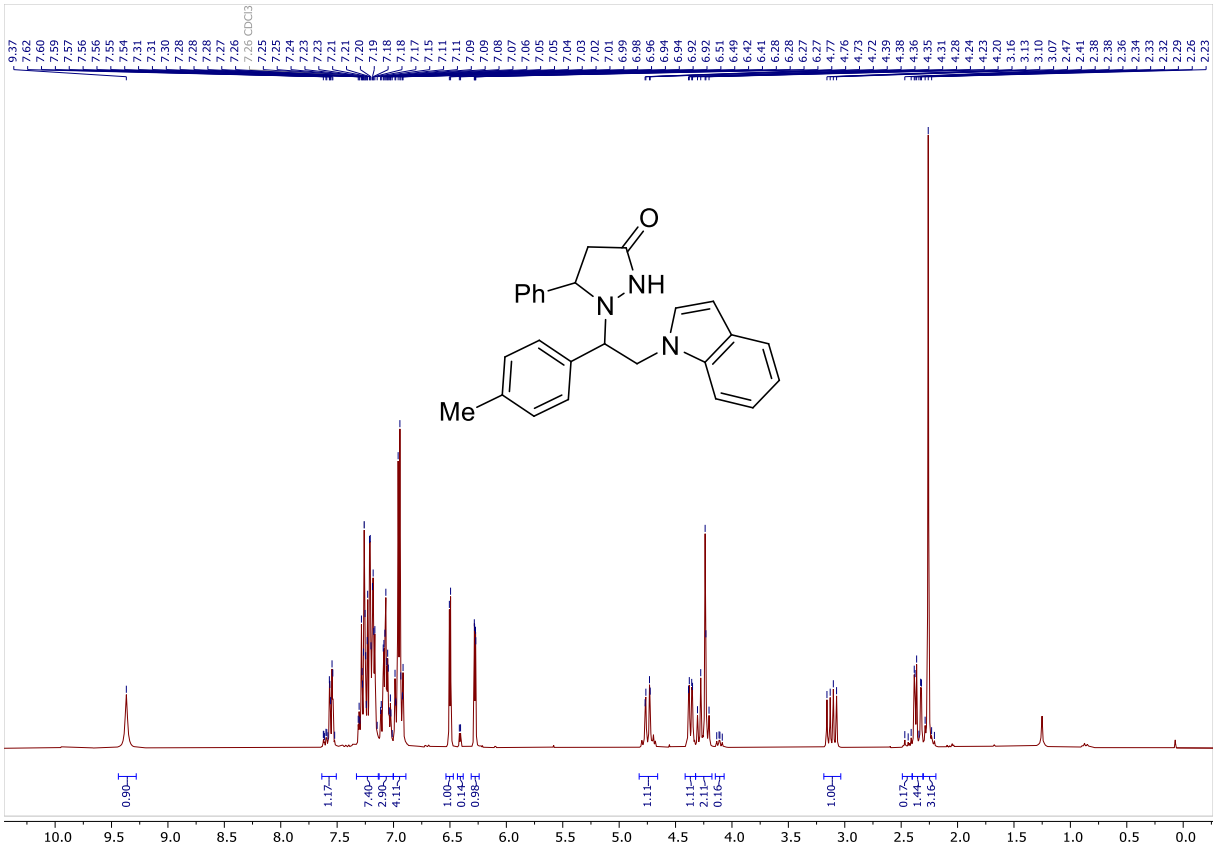


^{1}H NMR of the mixture of diastereoisomers after column chromatography

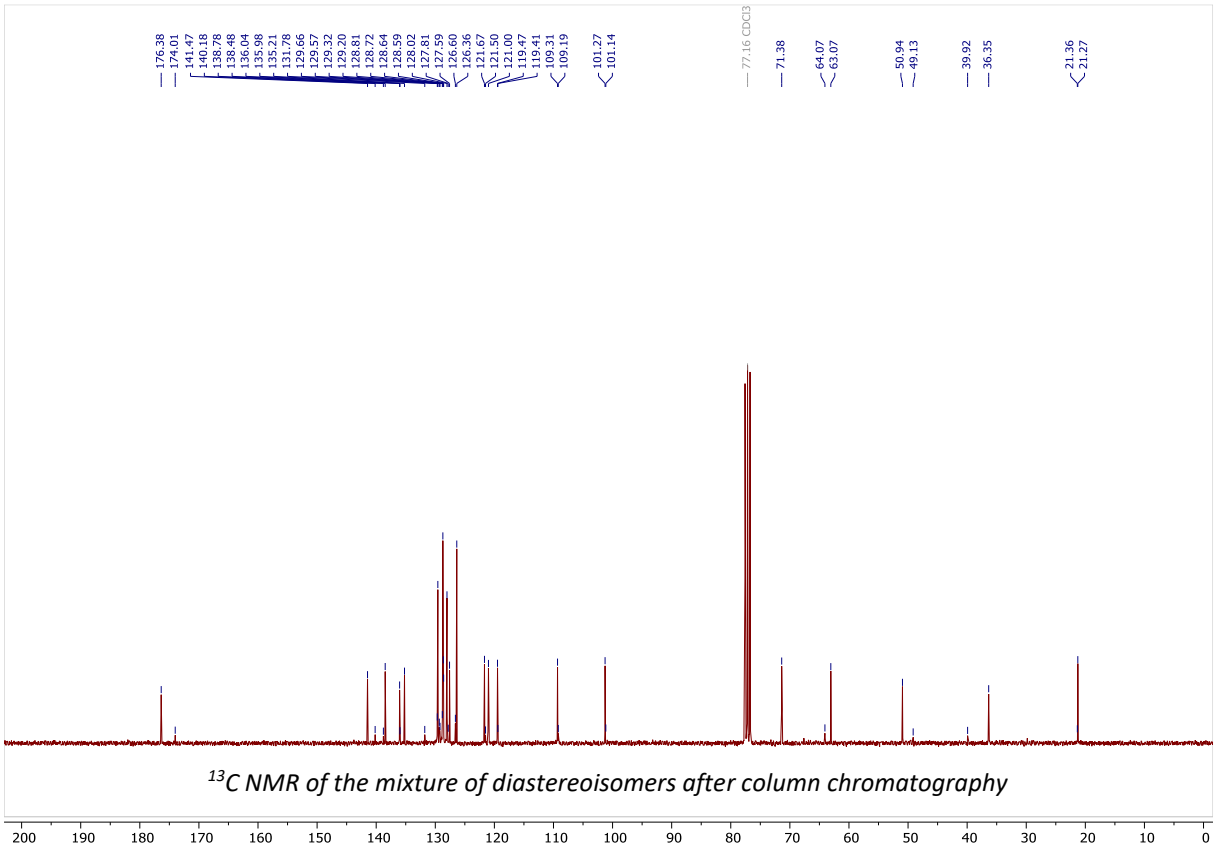


^{13}C NMR of the mixture of diastereoisomers after column chromatography

1-(2-(1*H*-indol-1-yl)-1-(*p*-tolyl)ethyl)-5-phenylpyrazolidin-3-one (3da)

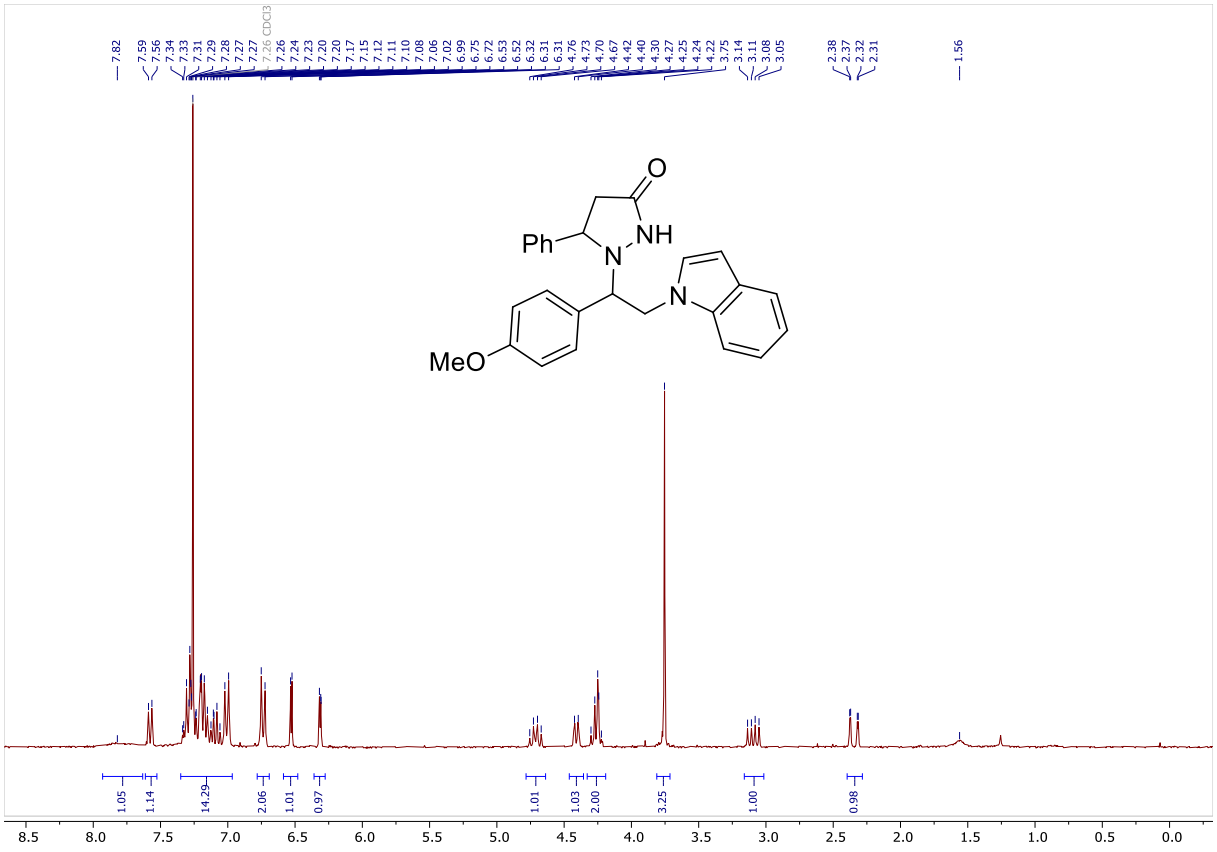


^{1}H NMR of the mixture of diastereoisomers after column chromatography

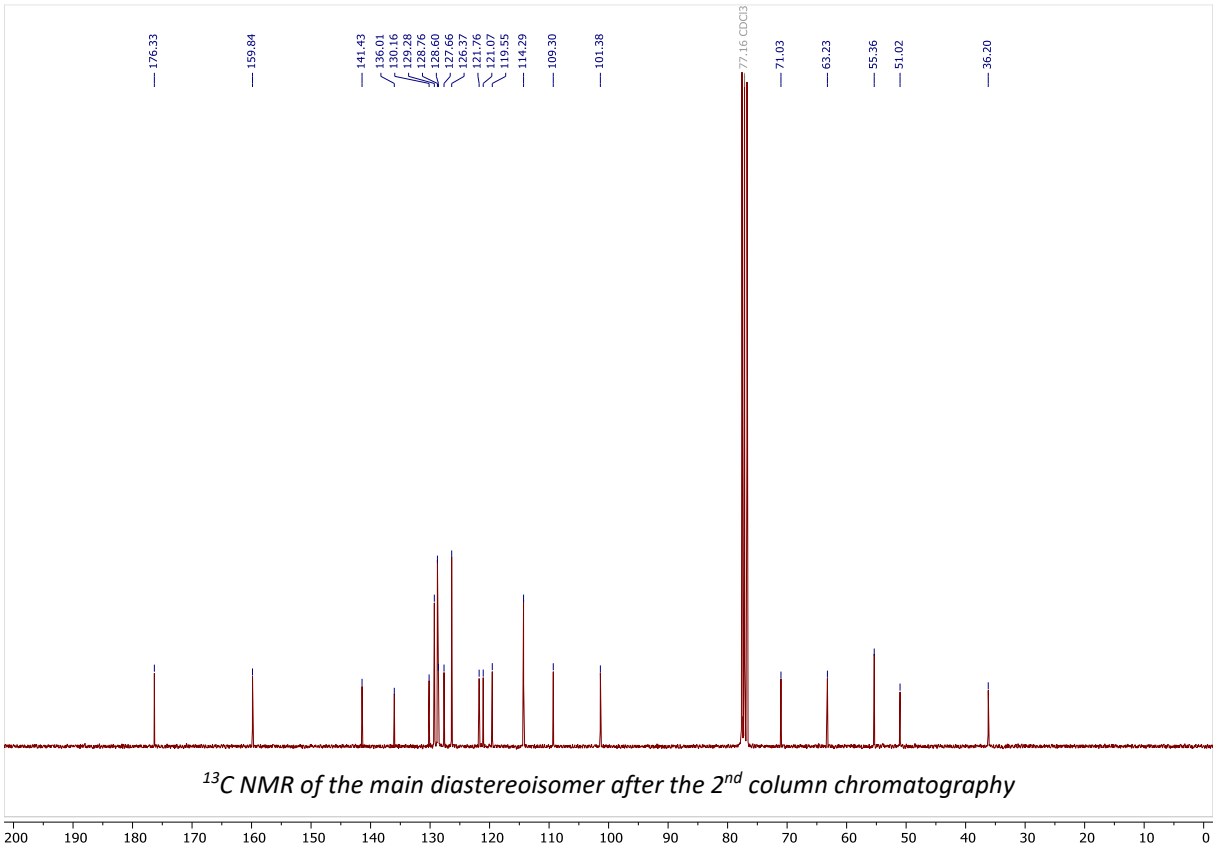


^{13}C NMR of the mixture of diastereoisomers after column chromatography

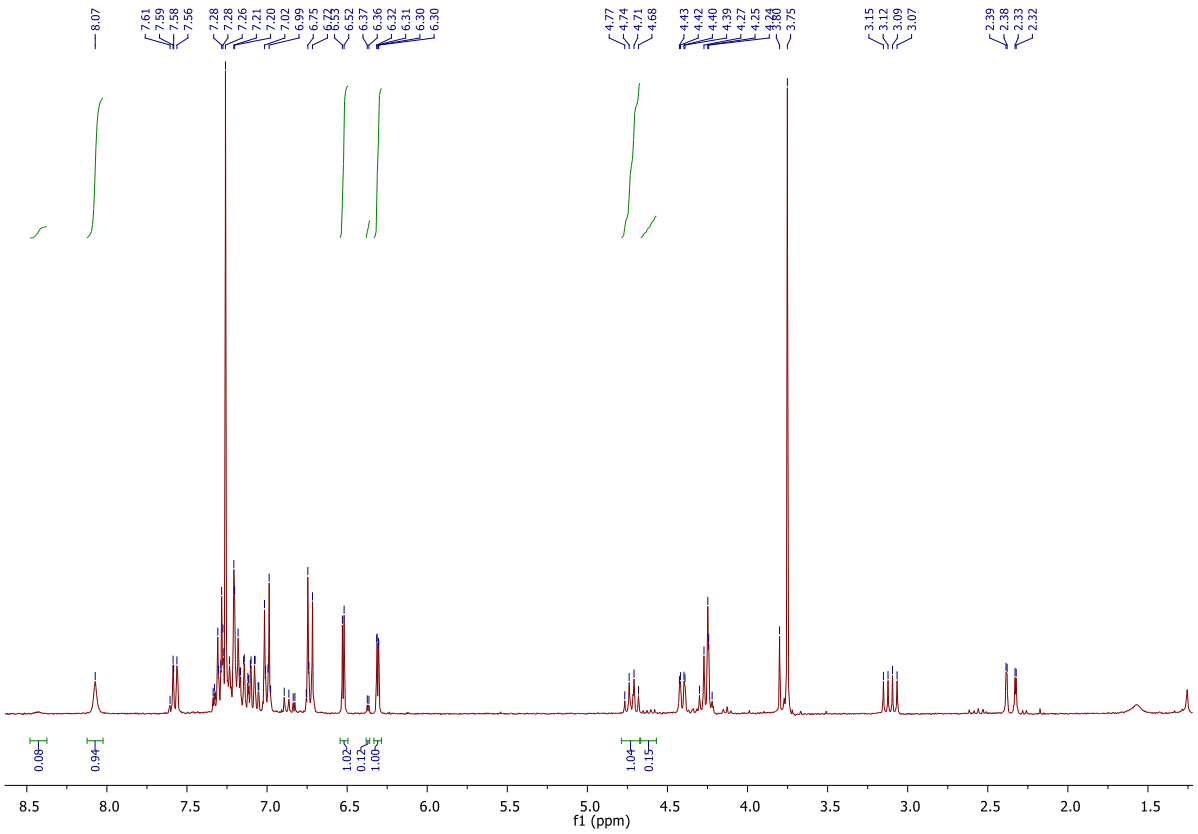
1-(2-(1*H*-indol-1-yl)-1-(4-methoxyphenyl)ethyl)-5-phenylpyrazolidin-3-one (3ea)



^{1}H NMR of the main diastereoisomer after the 2nd column chromatography

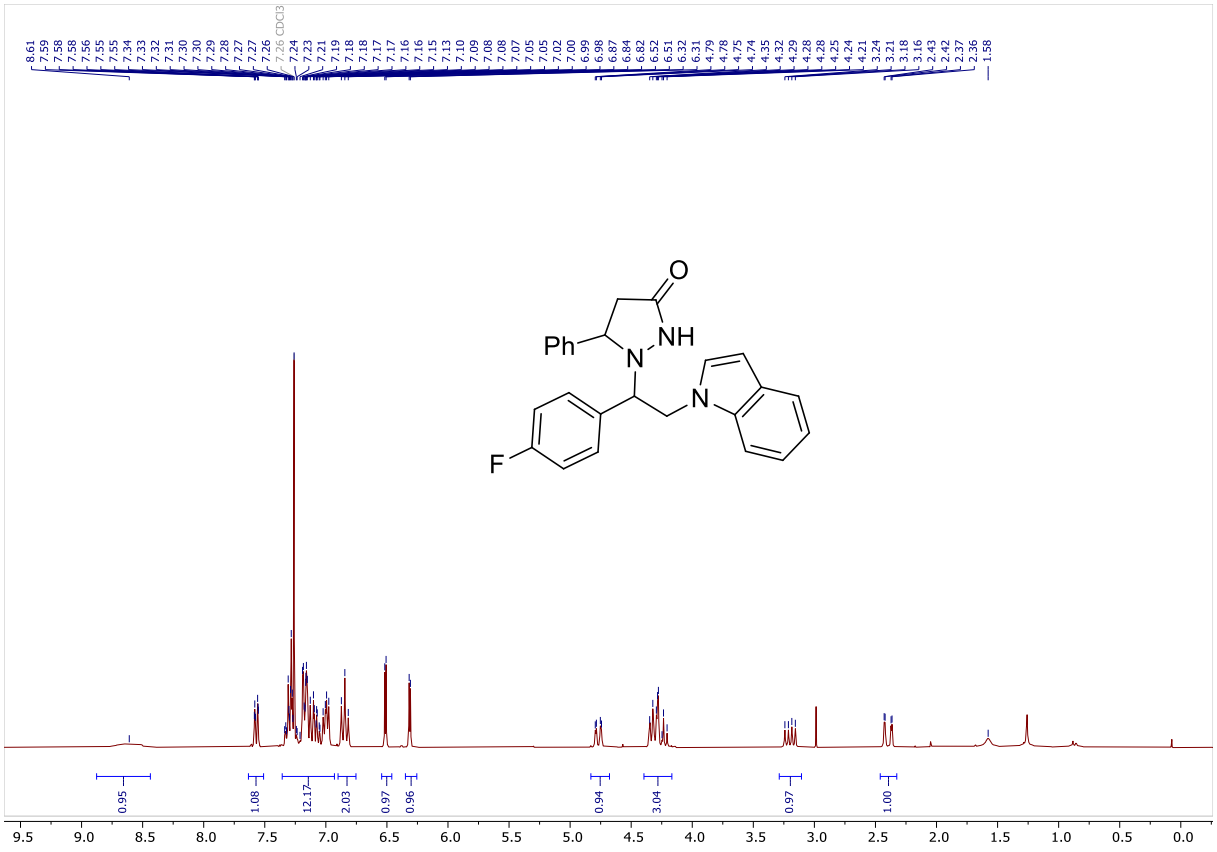


^{13}C NMR of the main diastereoisomer after the 2nd column chromatography

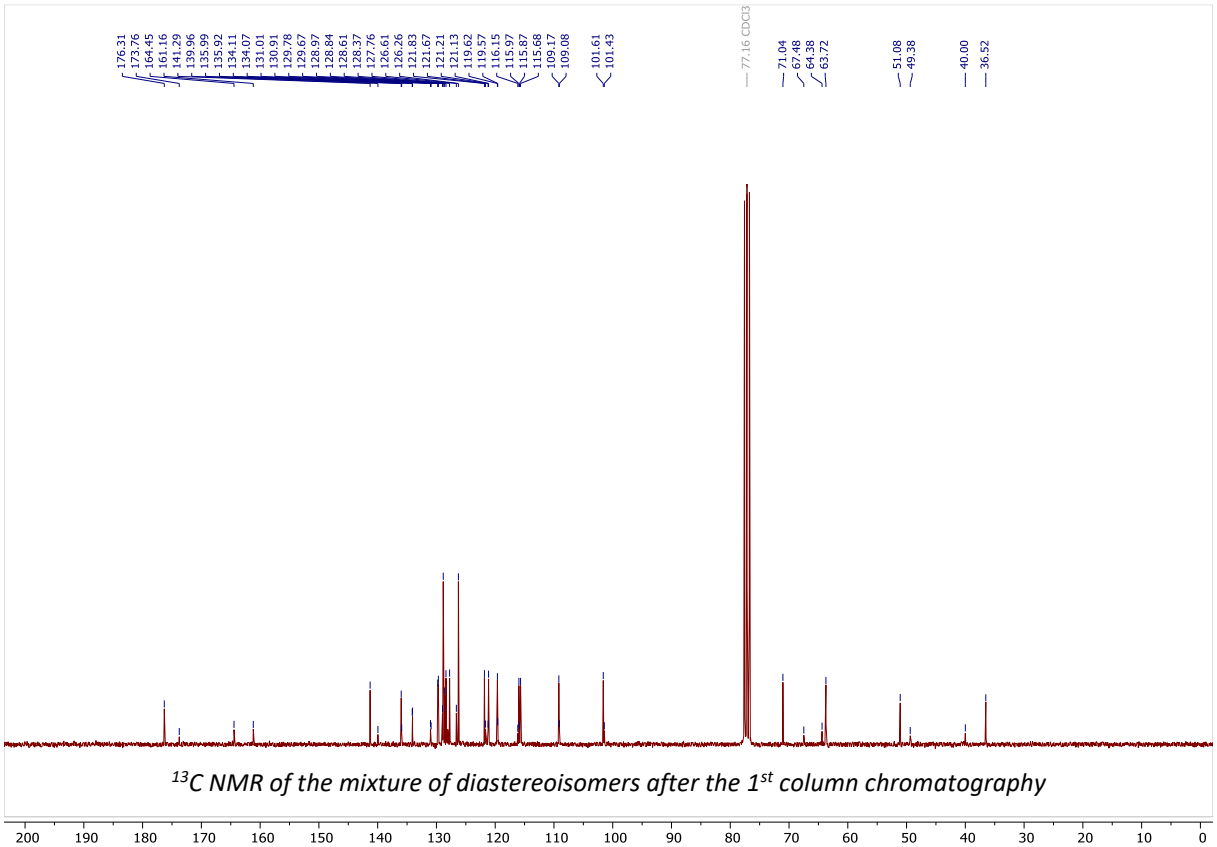


^{1}H NMR of the mixture of diastereoisomers after the 1st column chromatography

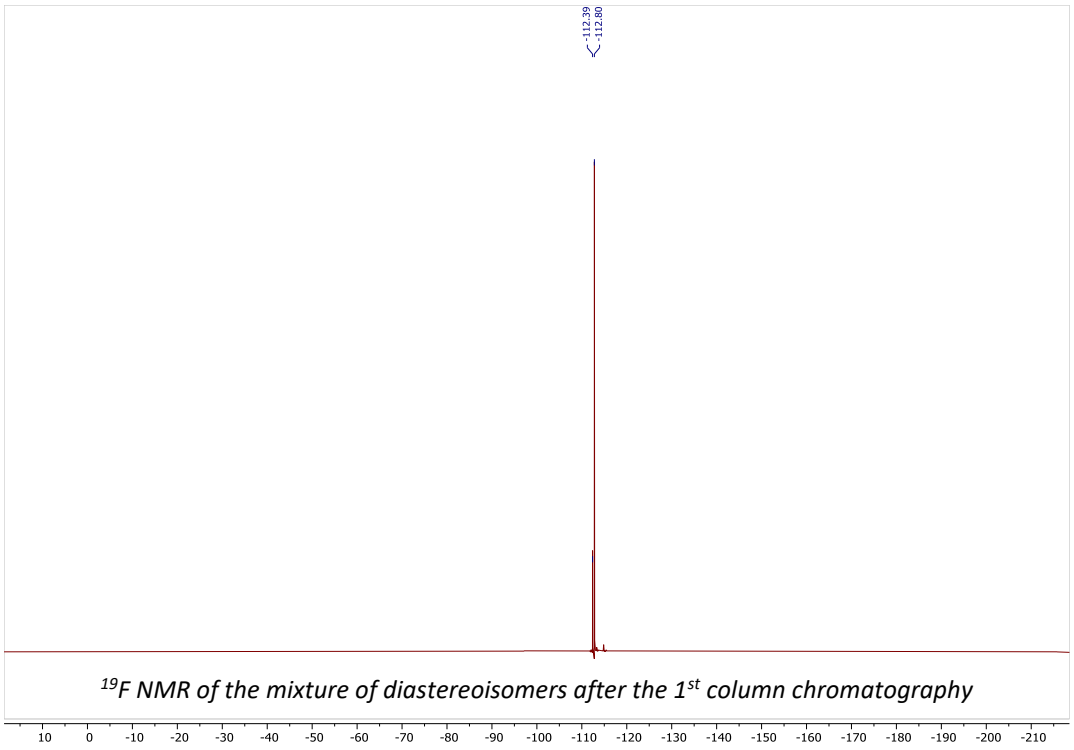
1-(1-(4-fluorophenyl)-2-(1*H*-indol-1-yl)ethyl)-5-phenylpyrazolidin-3-one (3fa)



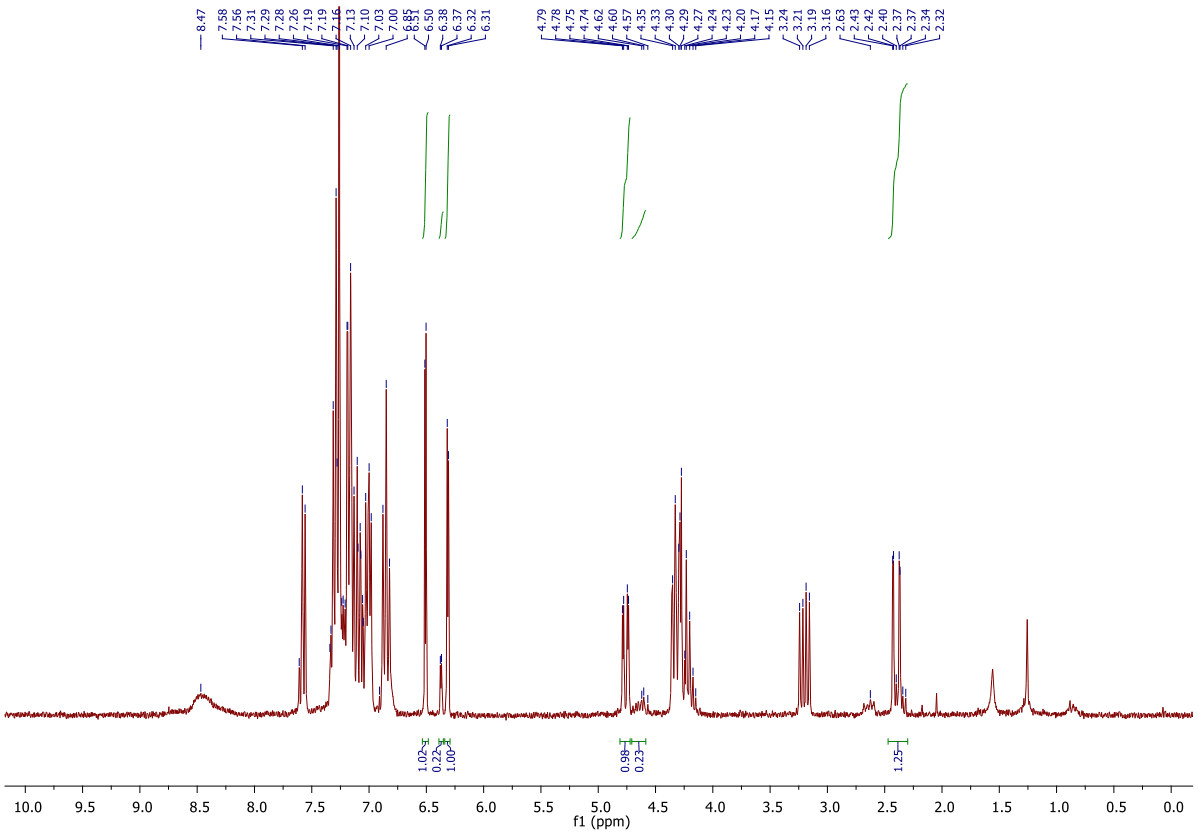
^{1}H NMR of the main diastereoisomer after the 2nd column chromatography



^{13}C NMR of the mixture of diastereoisomers after the 1st column chromatography

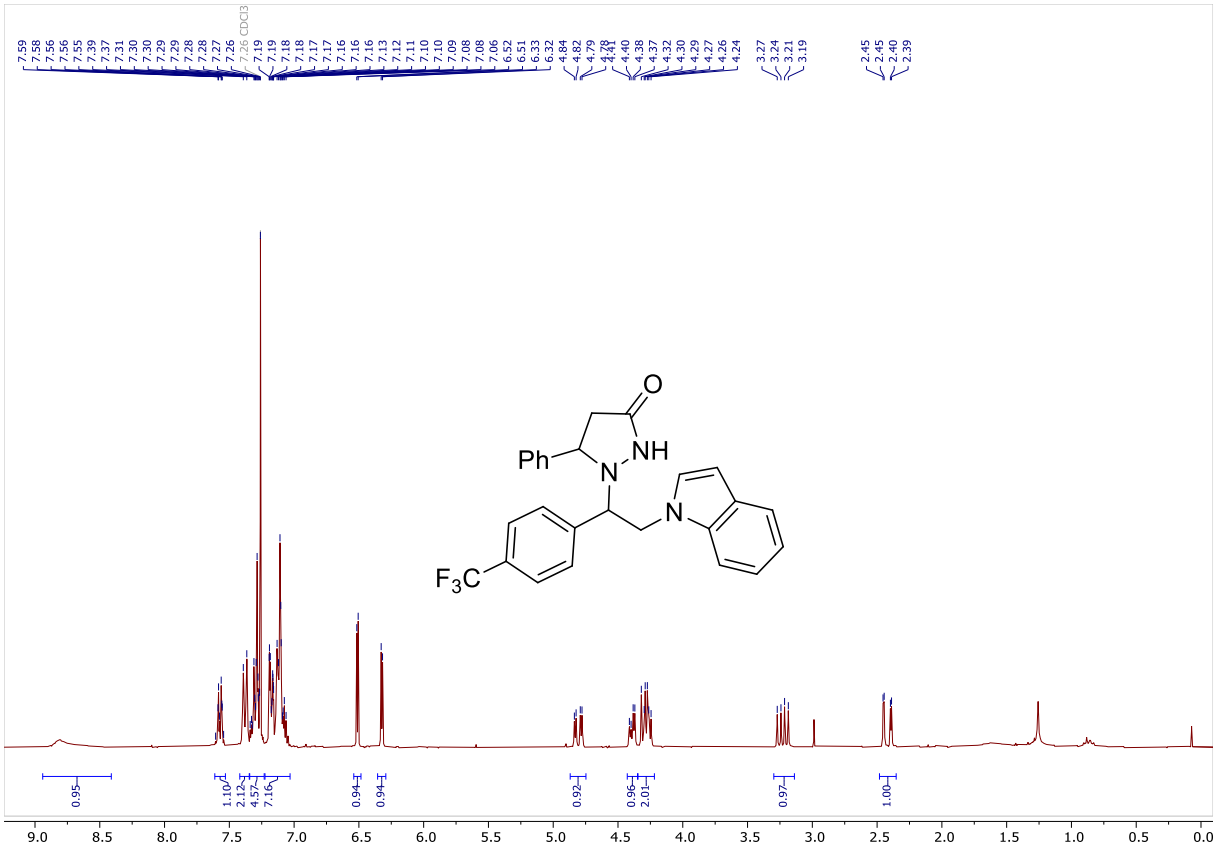


^{19}F NMR of the mixture of diastereoisomers after the 1st column chromatography

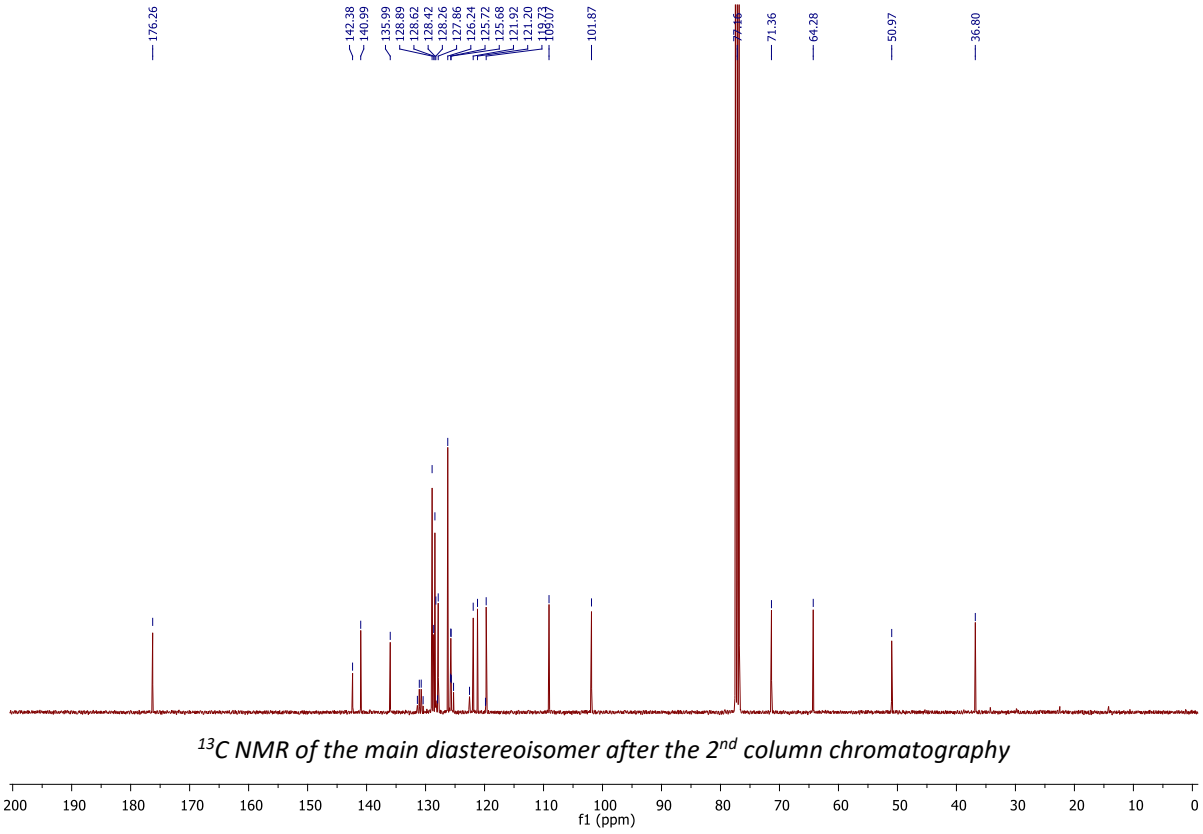


^{1}H NMR of the mixture of diastereoisomers after the 1st column chromatography

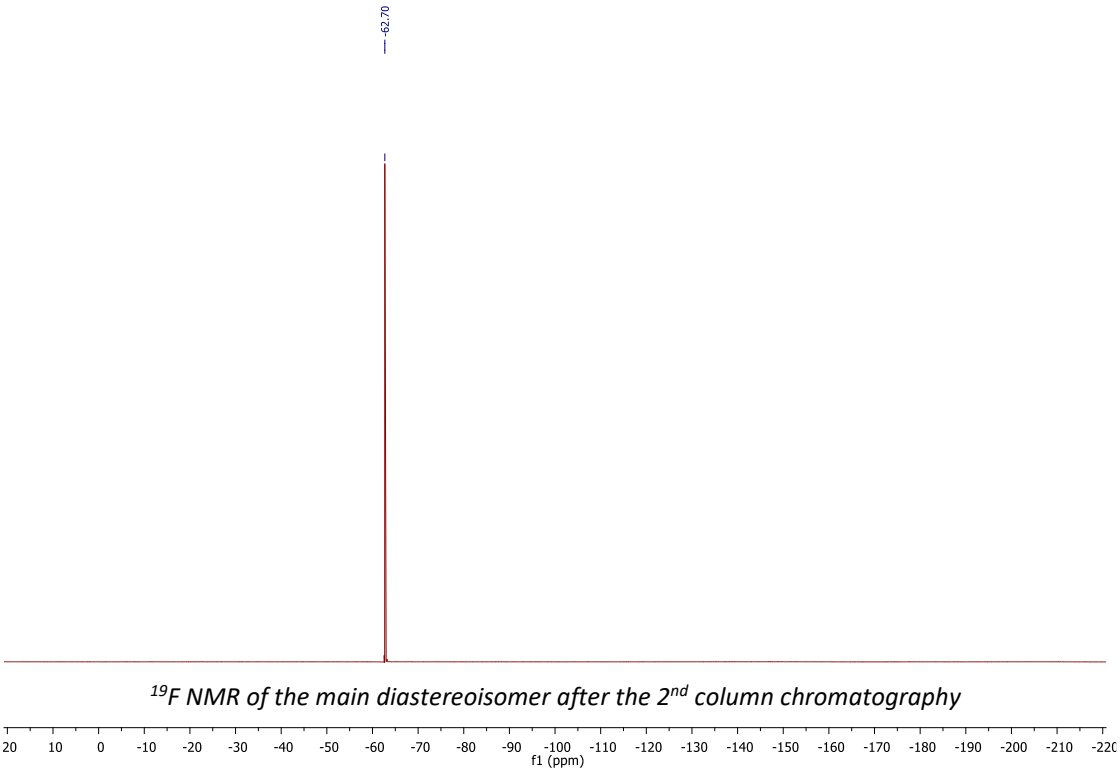
1-(2-(1*H*-indol-1-yl)-1-(4-(trifluoromethyl)phenyl)ethyl)-5-phenylpyrazolidin-3-one (3ga)



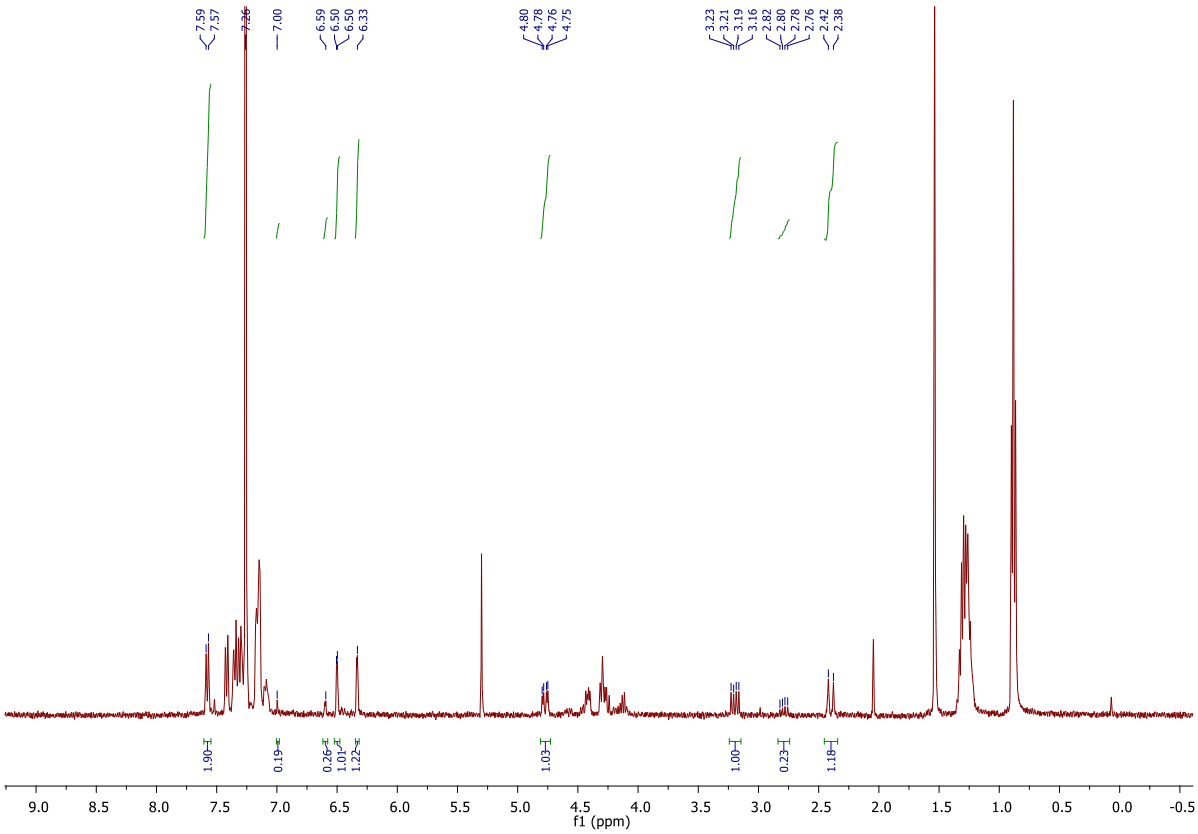
^{1}H NMR of the main diastereoisomer after the 2nd column chromatography



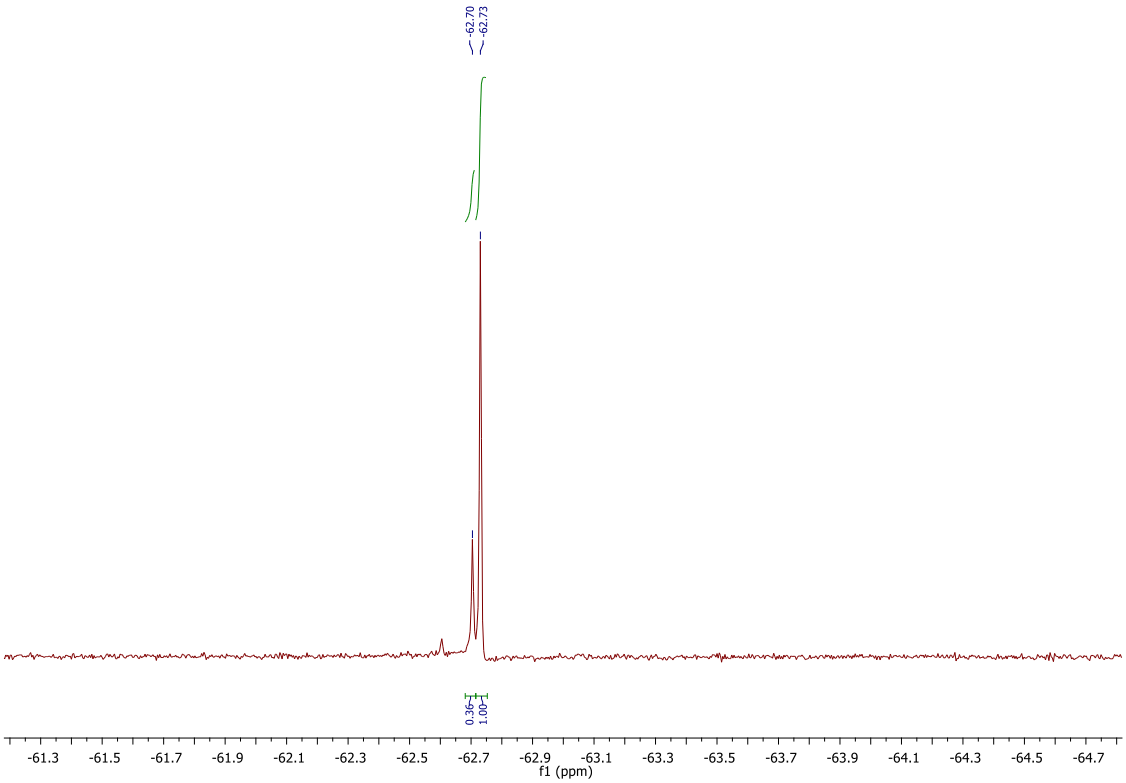
^{13}C NMR of the main diastereoisomer after the 2nd column chromatography



^{19}F NMR of the main diastereoisomer after the 2nd column chromatography

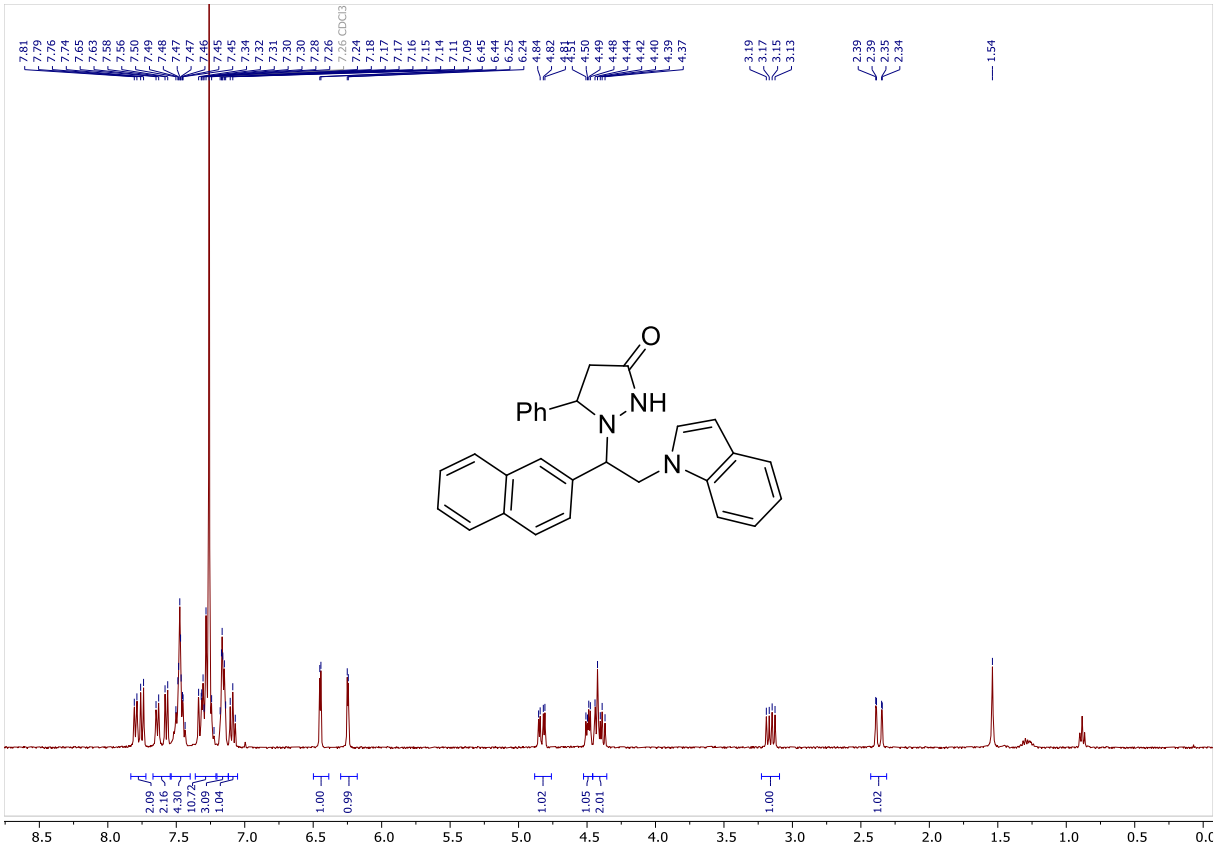


^{1}H NMR of the mixture of diastereoisomers after the 1st column chromatography

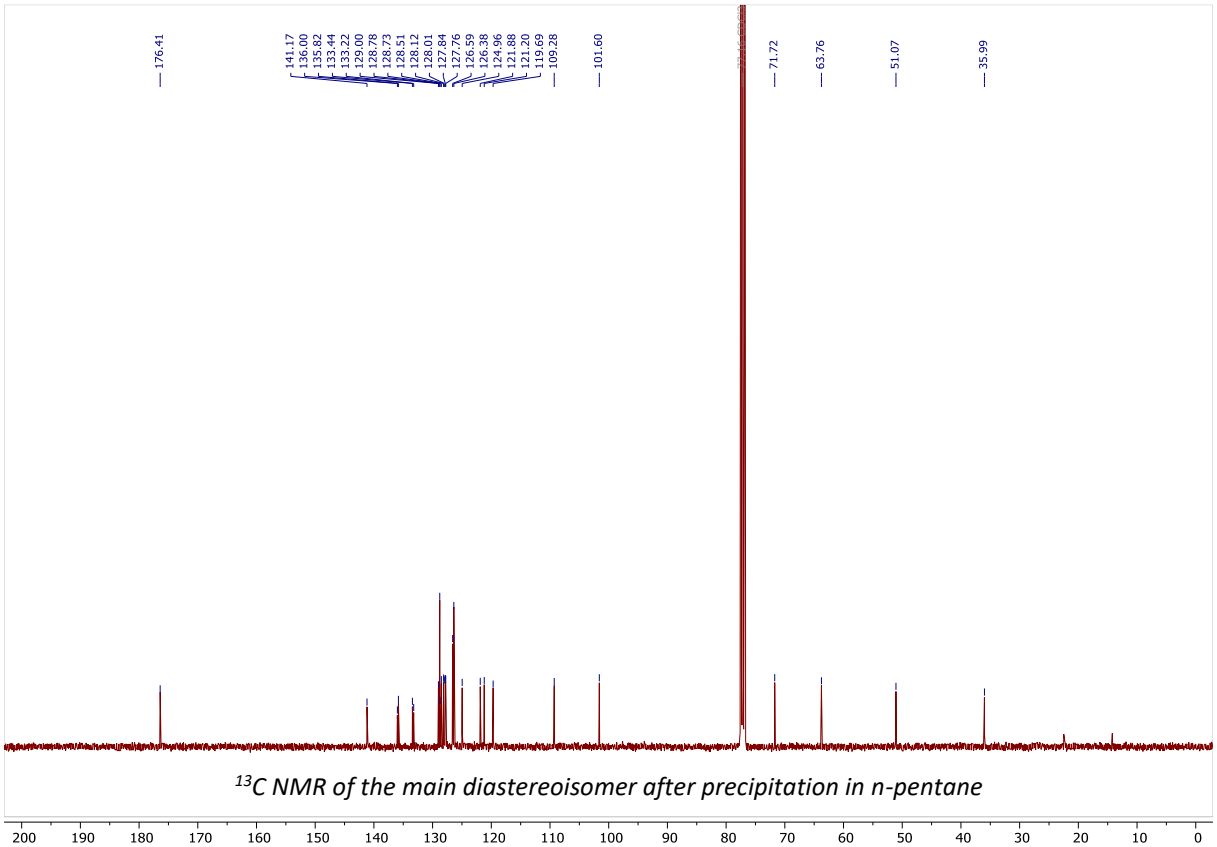


^{19}F NMR of the mixture of diastereoisomers after the 1st column chromatography

1-(2-(1*H*-indol-1-yl)-1-(naphthalen-2-yl)ethyl)-5-phenylpyrazolidin-3-one (3ha)

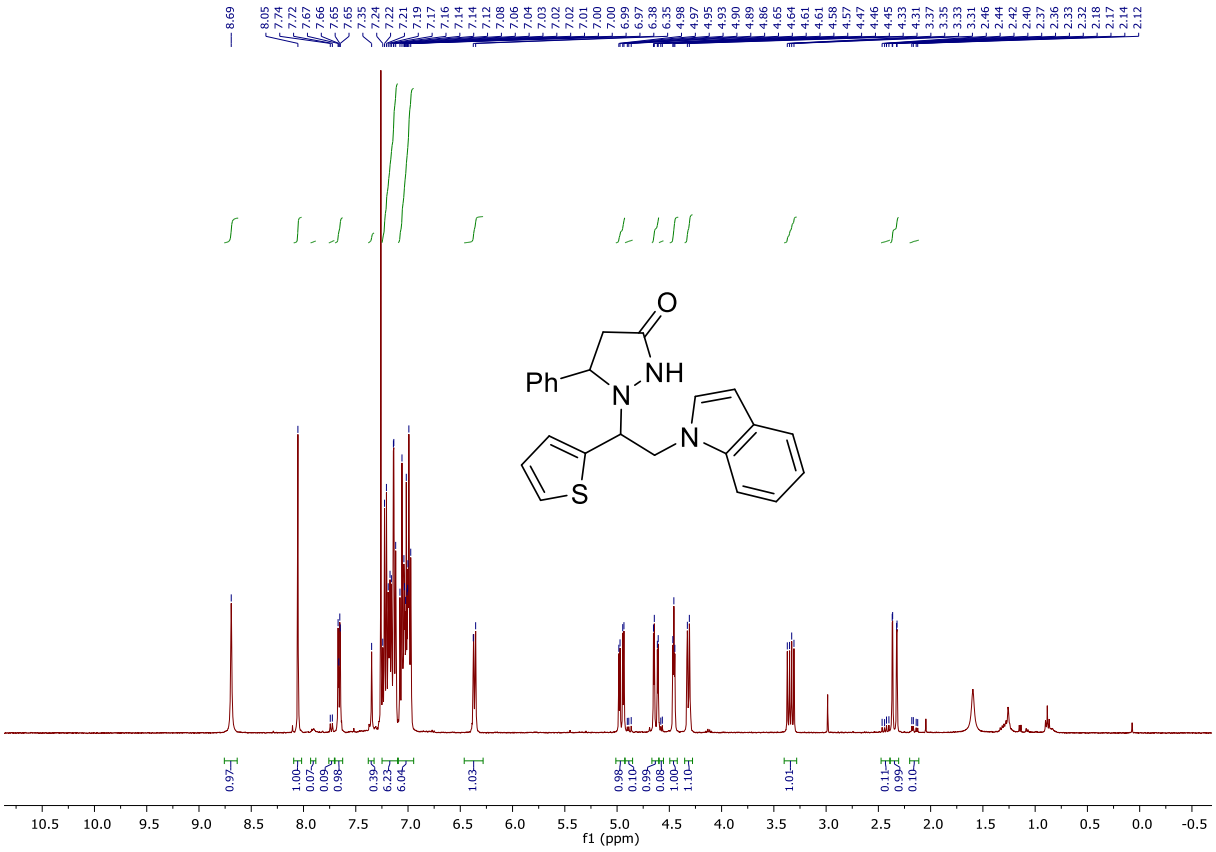


^{1}H NMR of the main diastereoisomer after precipitation in n-pentane

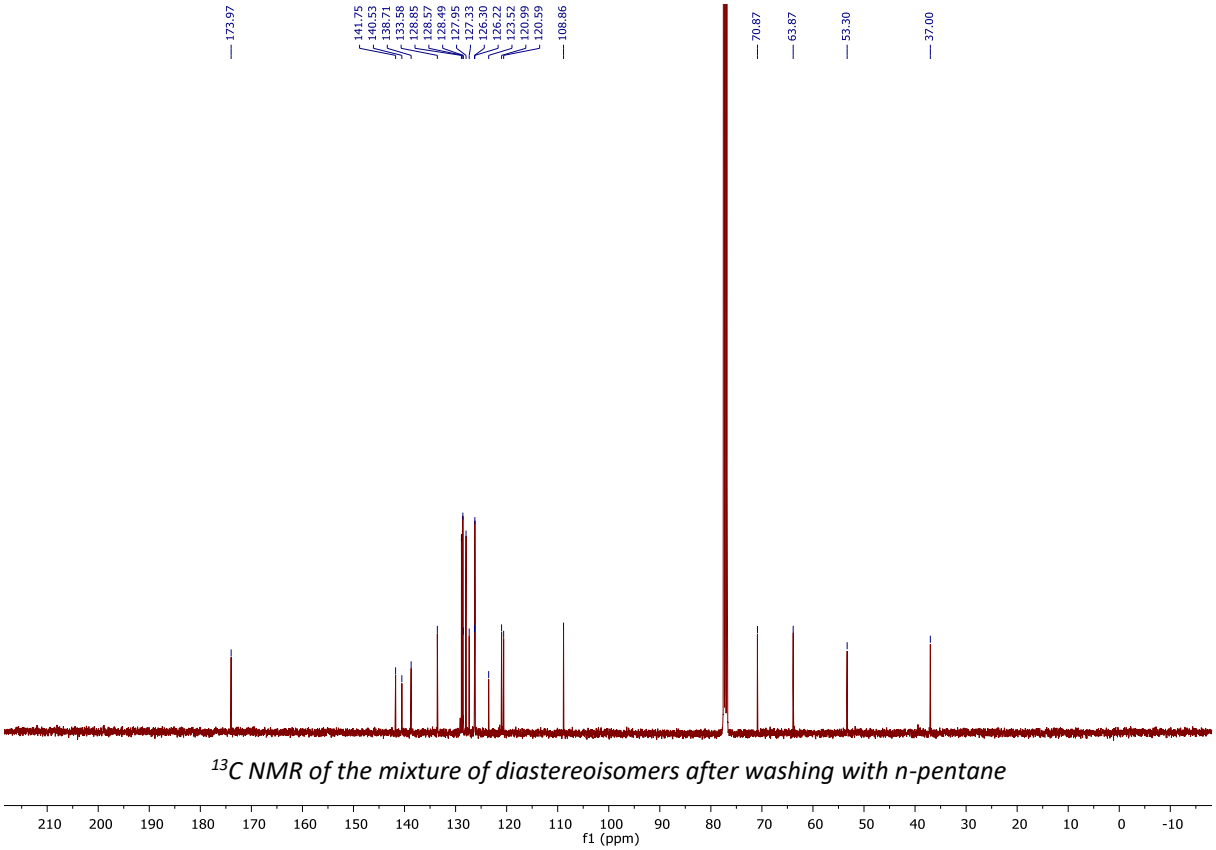


^{13}C NMR of the main diastereoisomer after precipitation in n-pentane

1-(2-(1H-indol-1-yl)-1-(thiophen-2-yl)ethyl)-5-phenylpyrazolidin-3-one (3ia)

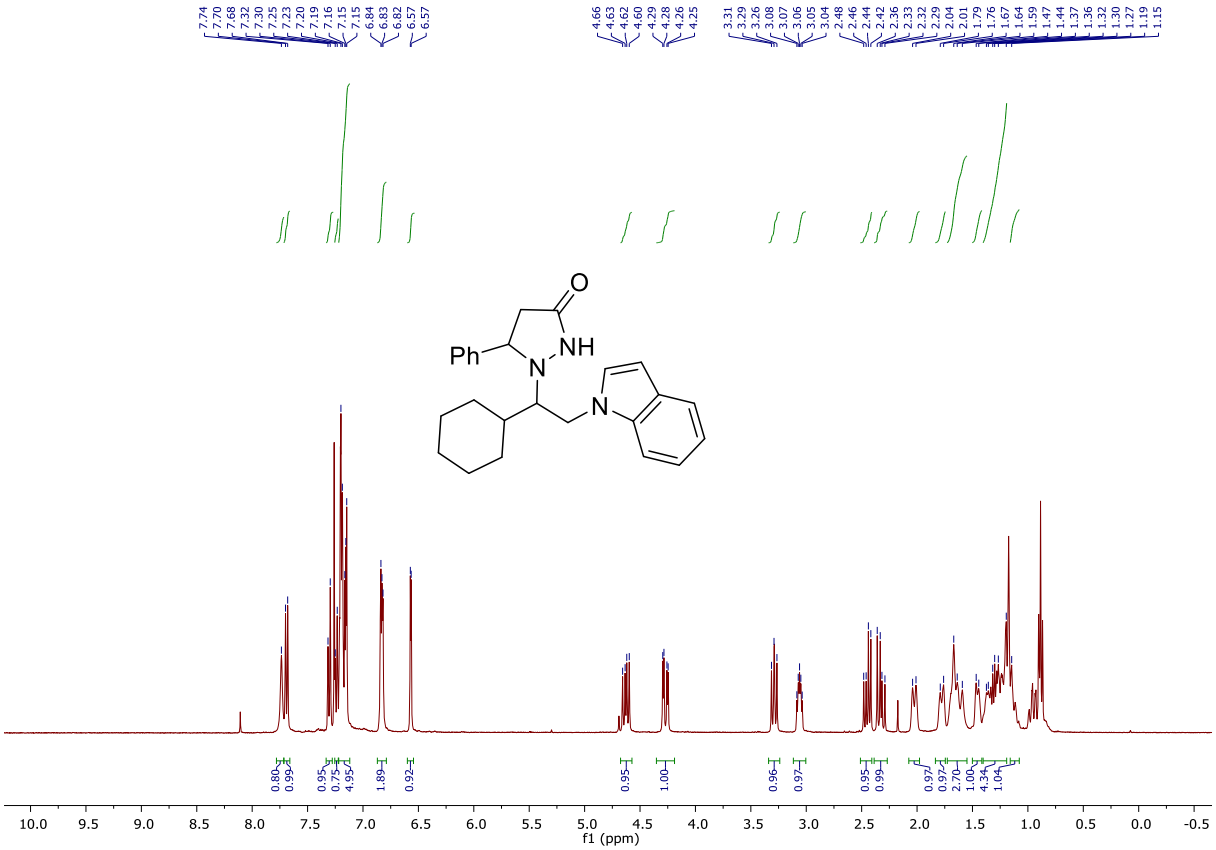


^{1}H NMR of the mixture of diastereoisomers after washing with n-pentane

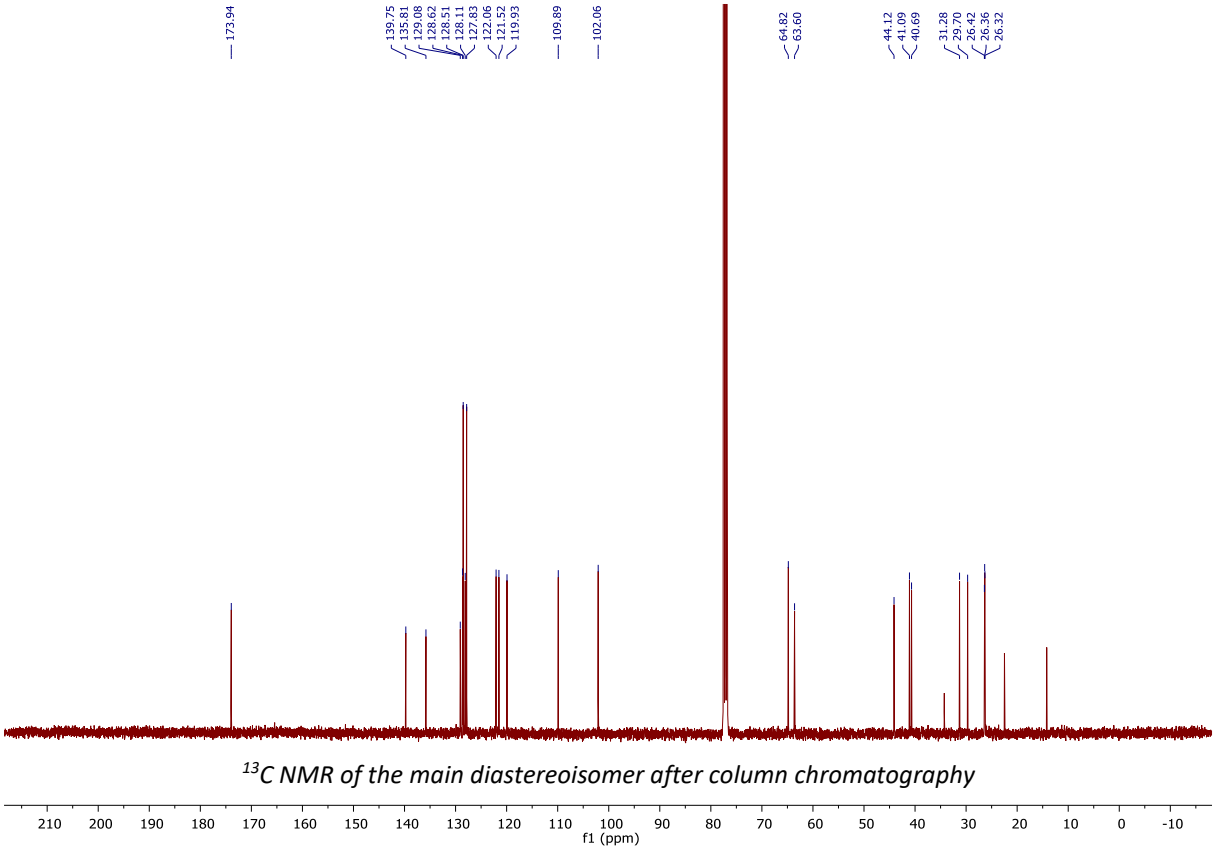


^{13}C NMR of the mixture of diastereoisomers after washing with n-pentane

1-(1-cyclohexyl-2-(1H-indol-1-yl)ethyl)-5-phenylpyrazolidin-3-one (3ja)

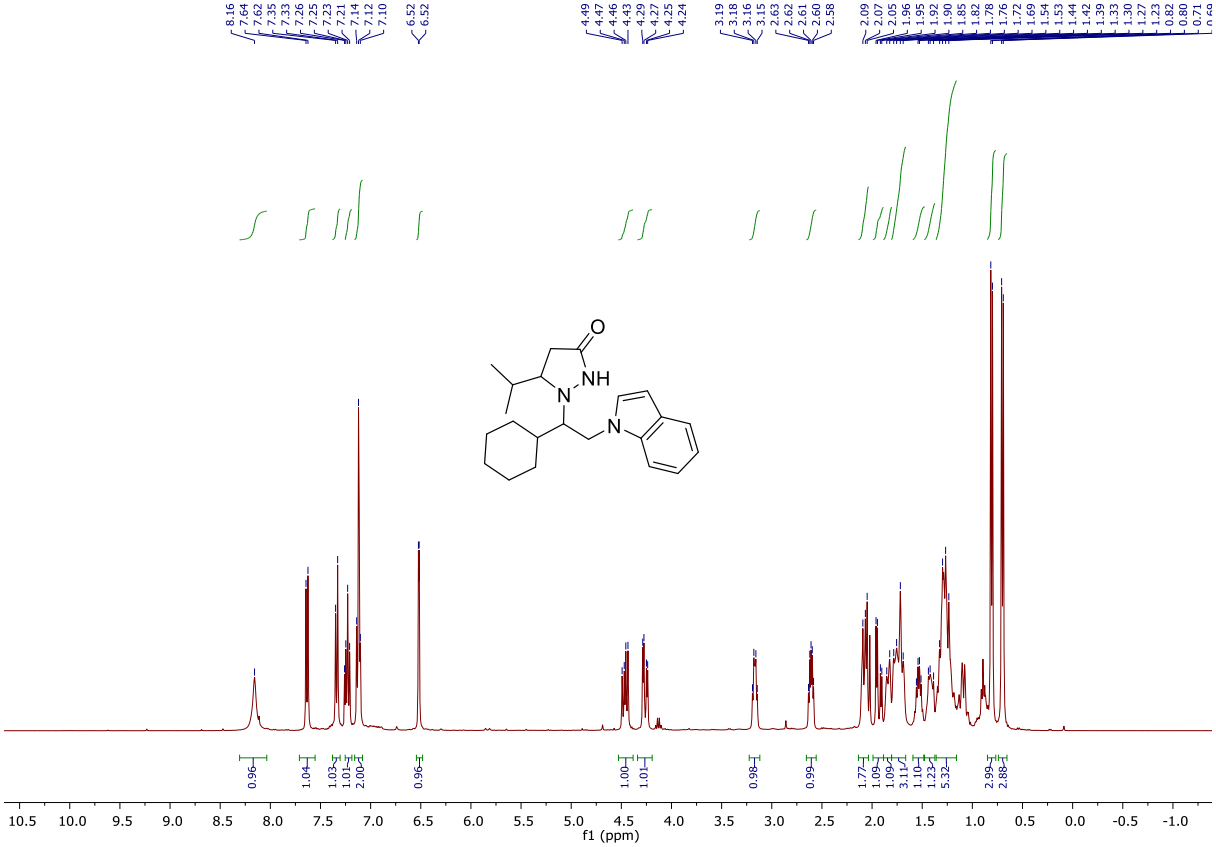


^{1}H NMR of the main diastereoisomer after column chromatography

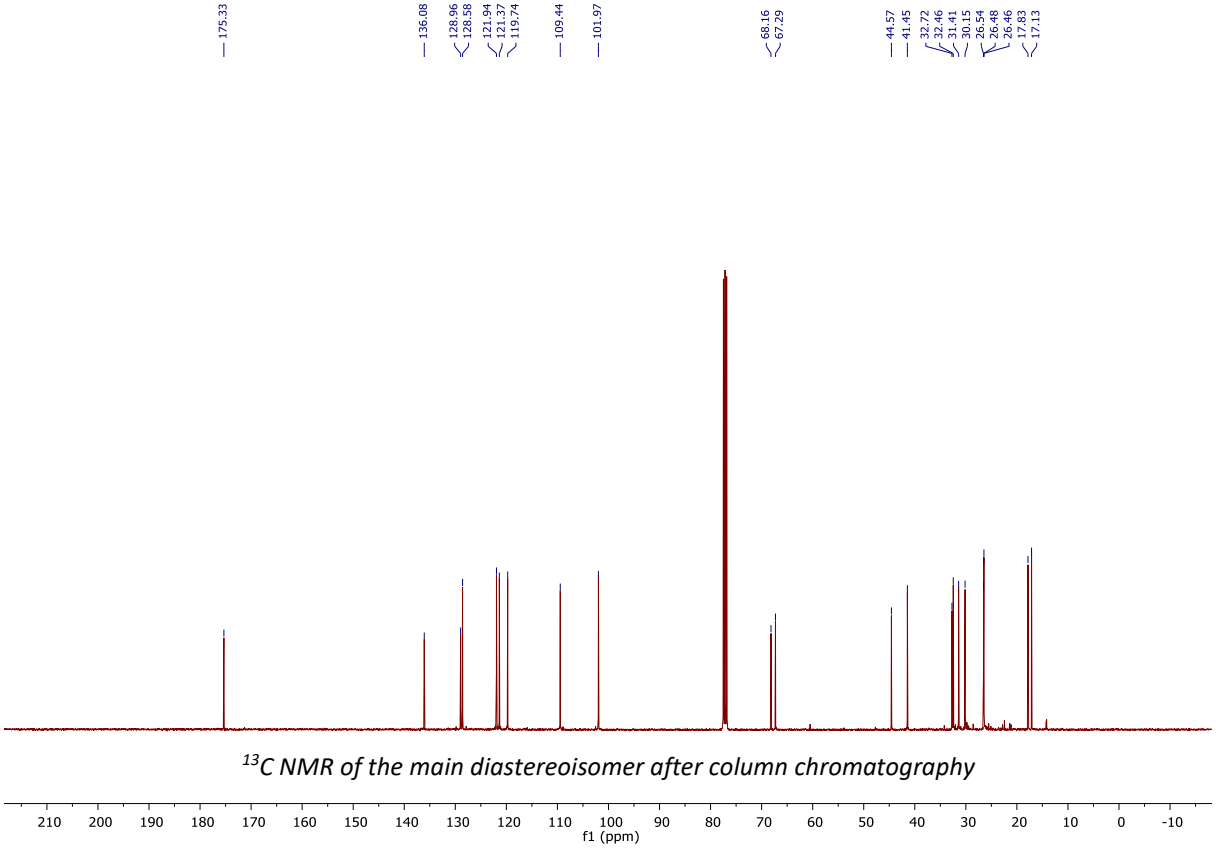


^{13}C NMR of the main diastereoisomer after column chromatography

1-(1-cyclohexyl-2-(1H-indol-1-yl)ethyl)-5-isopropylpyrazolidin-3-one (3ka):

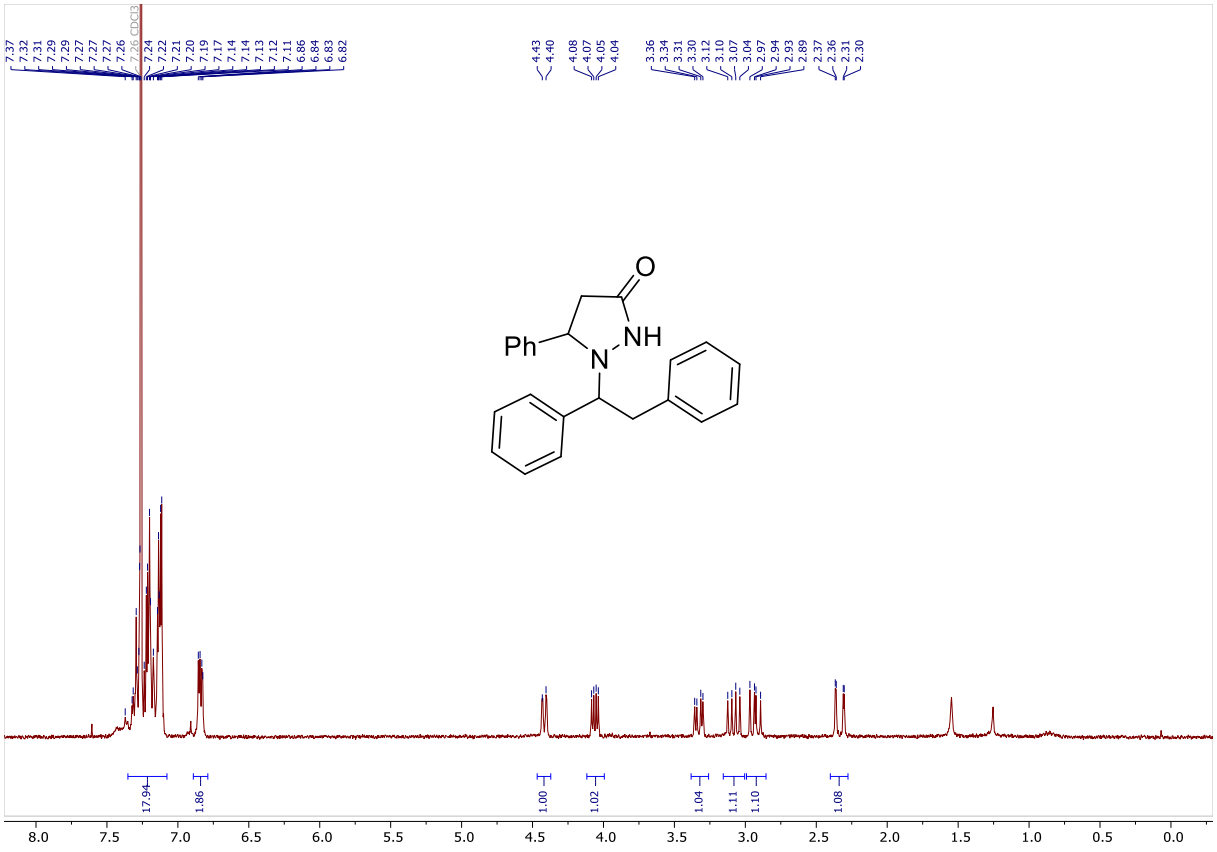


^{1}H NMR of the main diastereoisomer after column chromatography

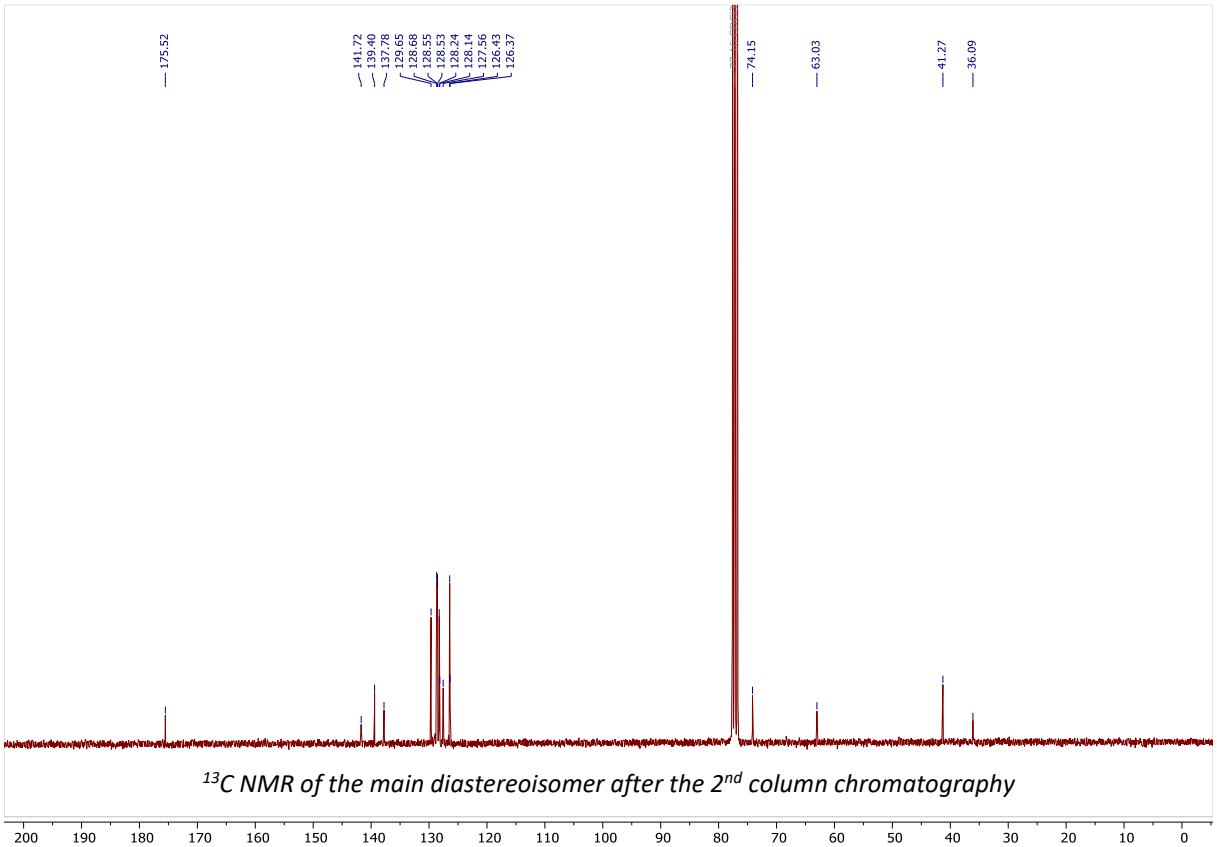


^{13}C NMR of the main diastereoisomer after column chromatography

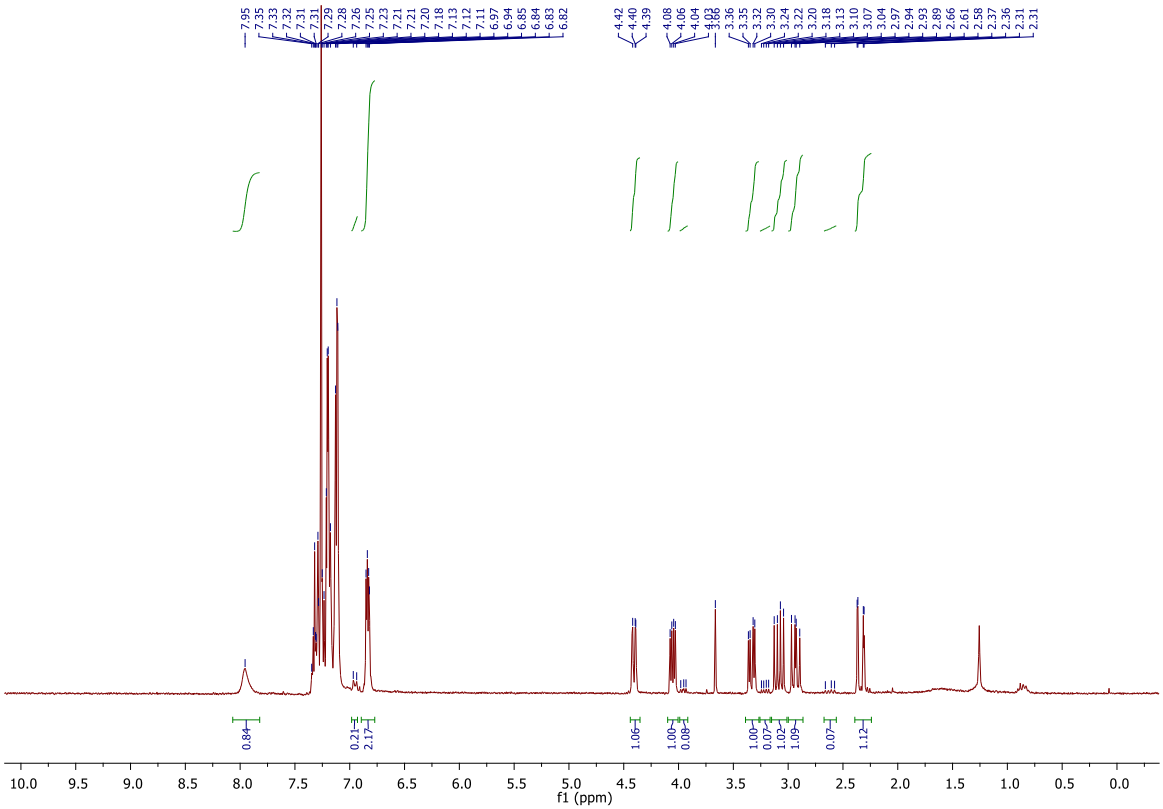
1-(1,2-diphenylethyl)-5-phenylpyrazolidin-3-one (3ae)



^{1}H NMR of the main diastereoisomer after the 2nd column chromatography

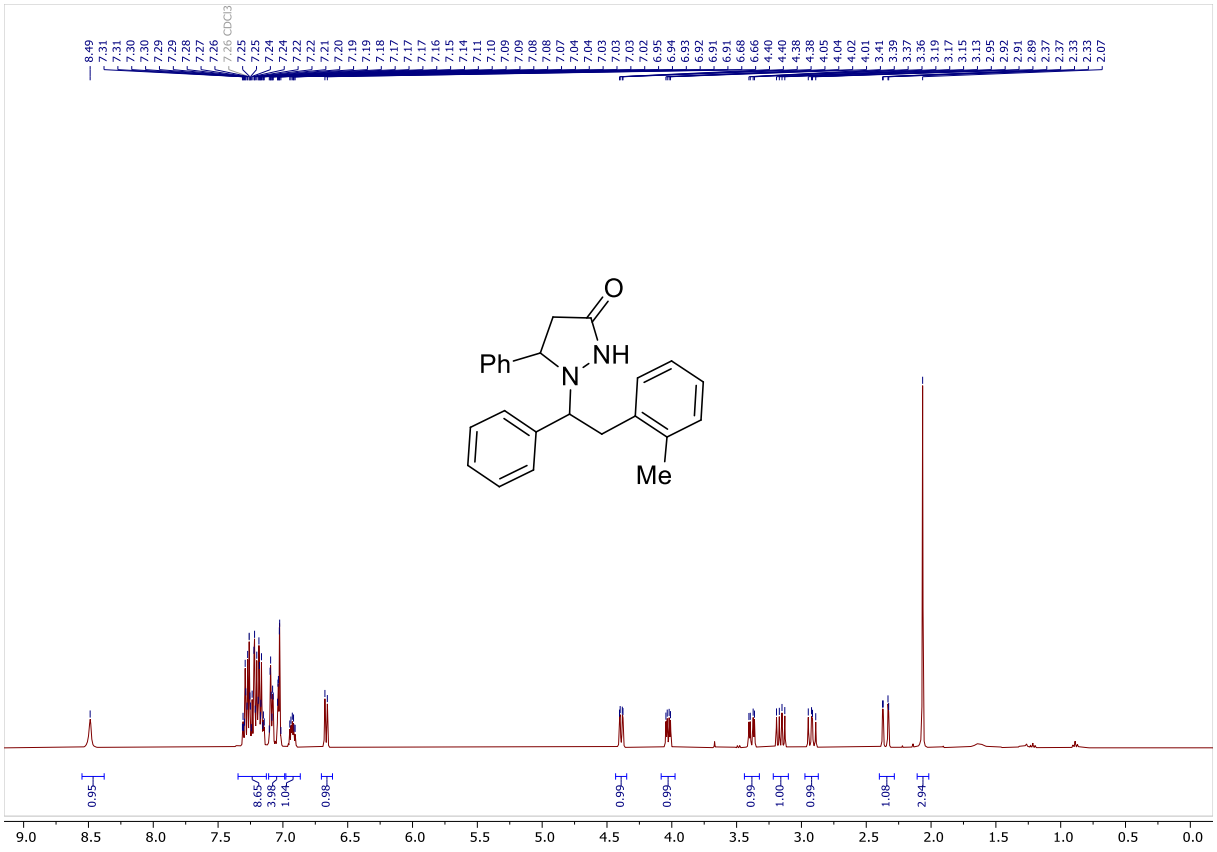


^{13}C NMR of the main diastereoisomer after the 2nd column chromatography

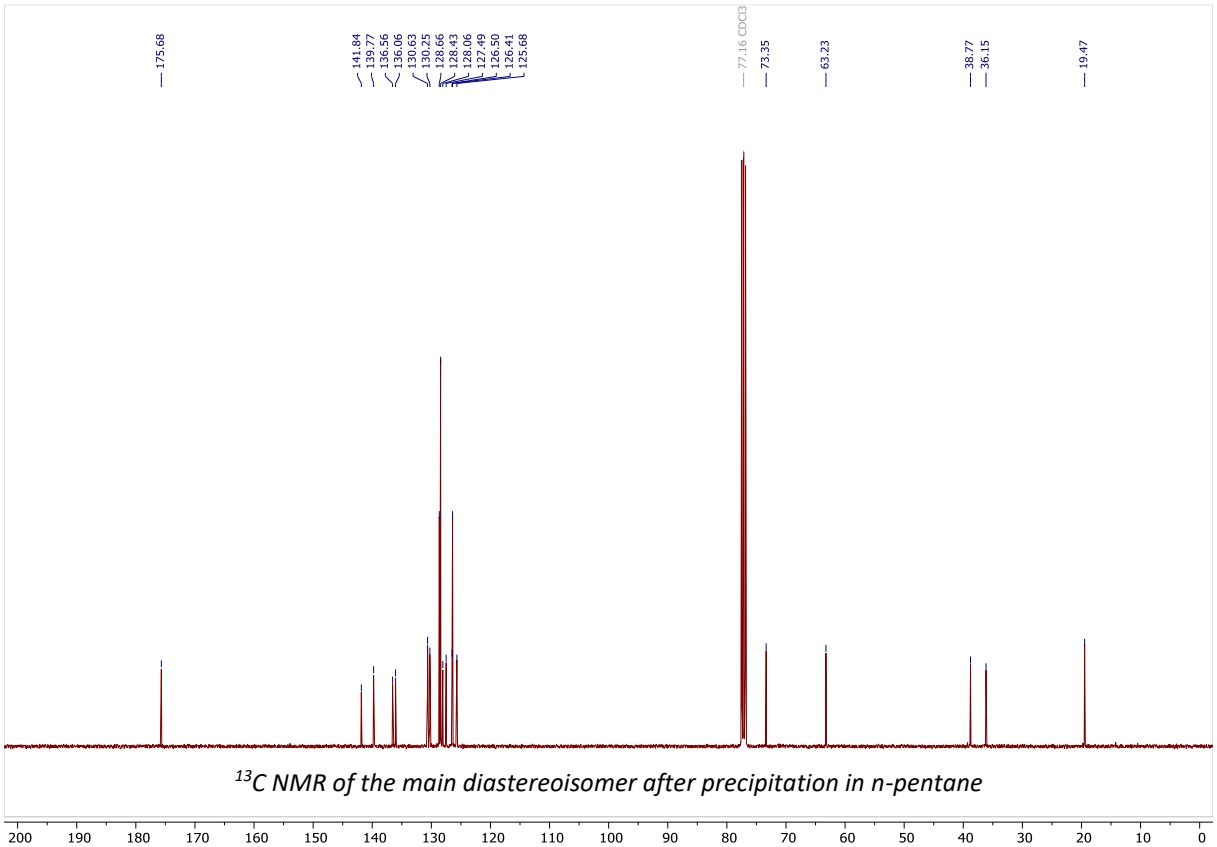


^{1}H NMR of the mixture of diastereoisomers after the 1st column chromatography

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

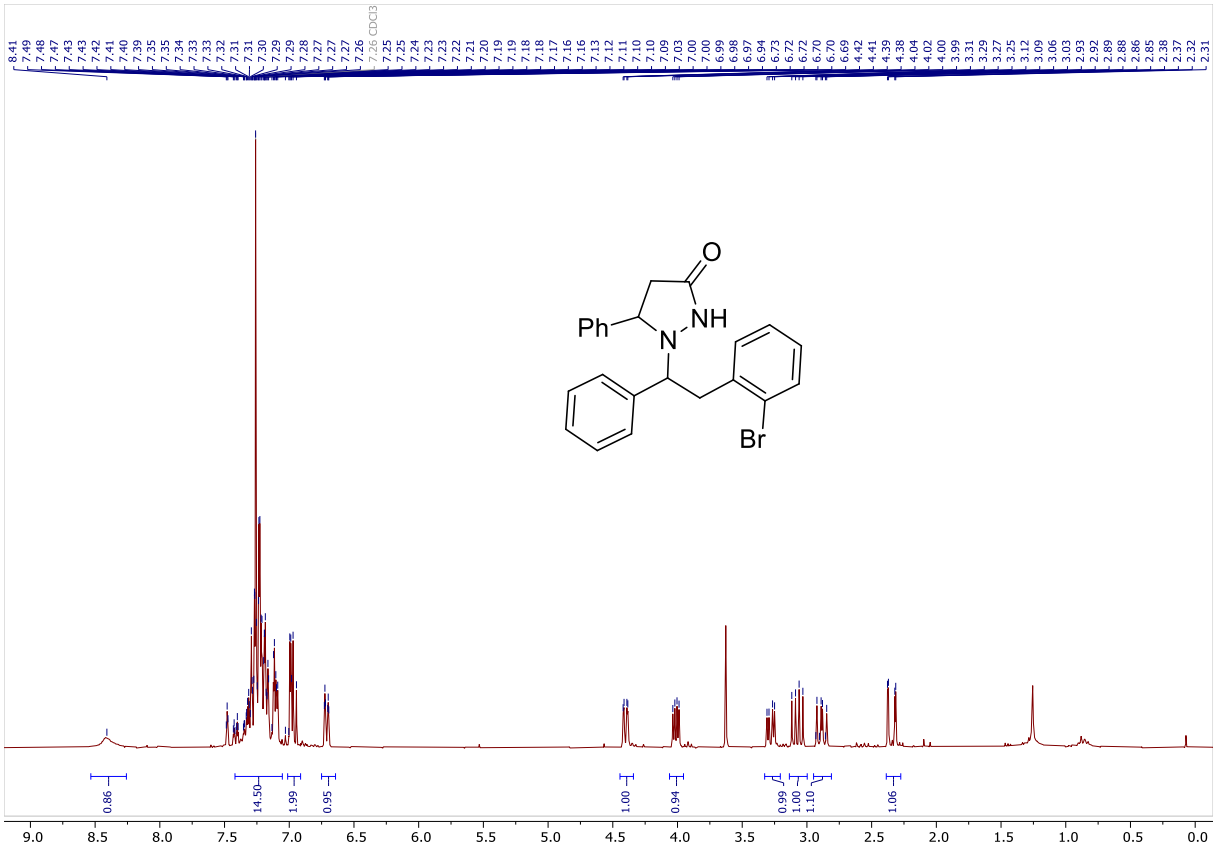


^{1}H NMR of the main diastereoisomer after precipitation in n-pentane

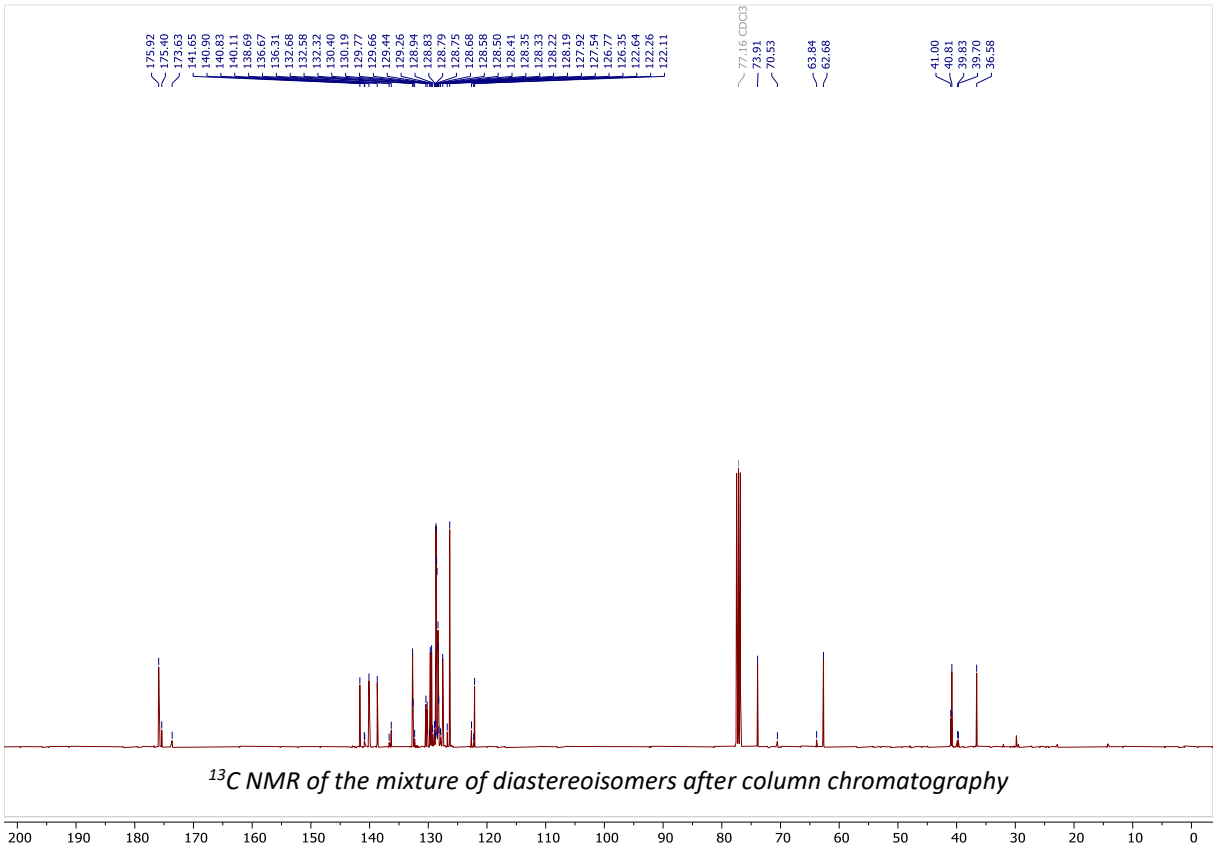


^{13}C NMR of the main diastereoisomer after precipitation in n-pentane

1-(2-(2-bromophenyl)-1-phenylethyl)-5-phenylpyrazolidin-3-one (3ag)

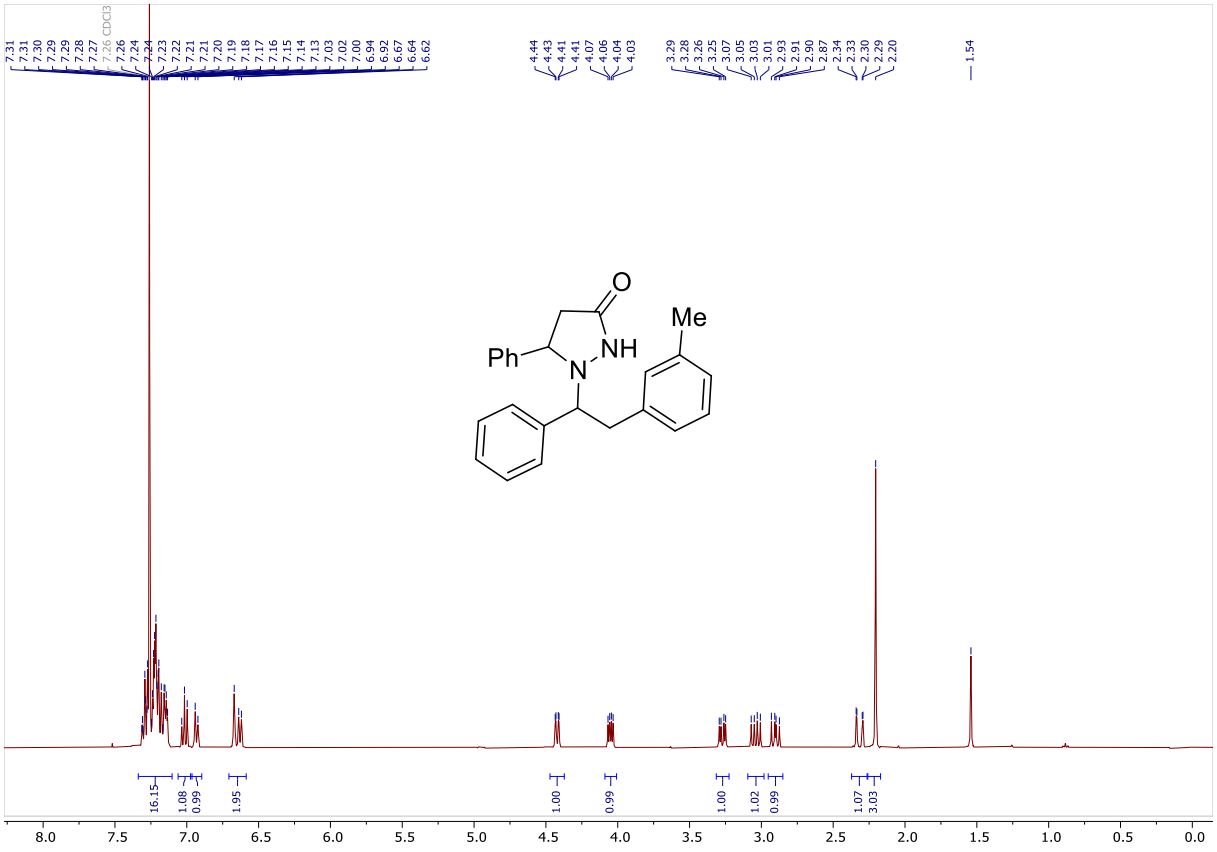


^{1}H NMR of the mixture of diastereoisomers after column chromatography

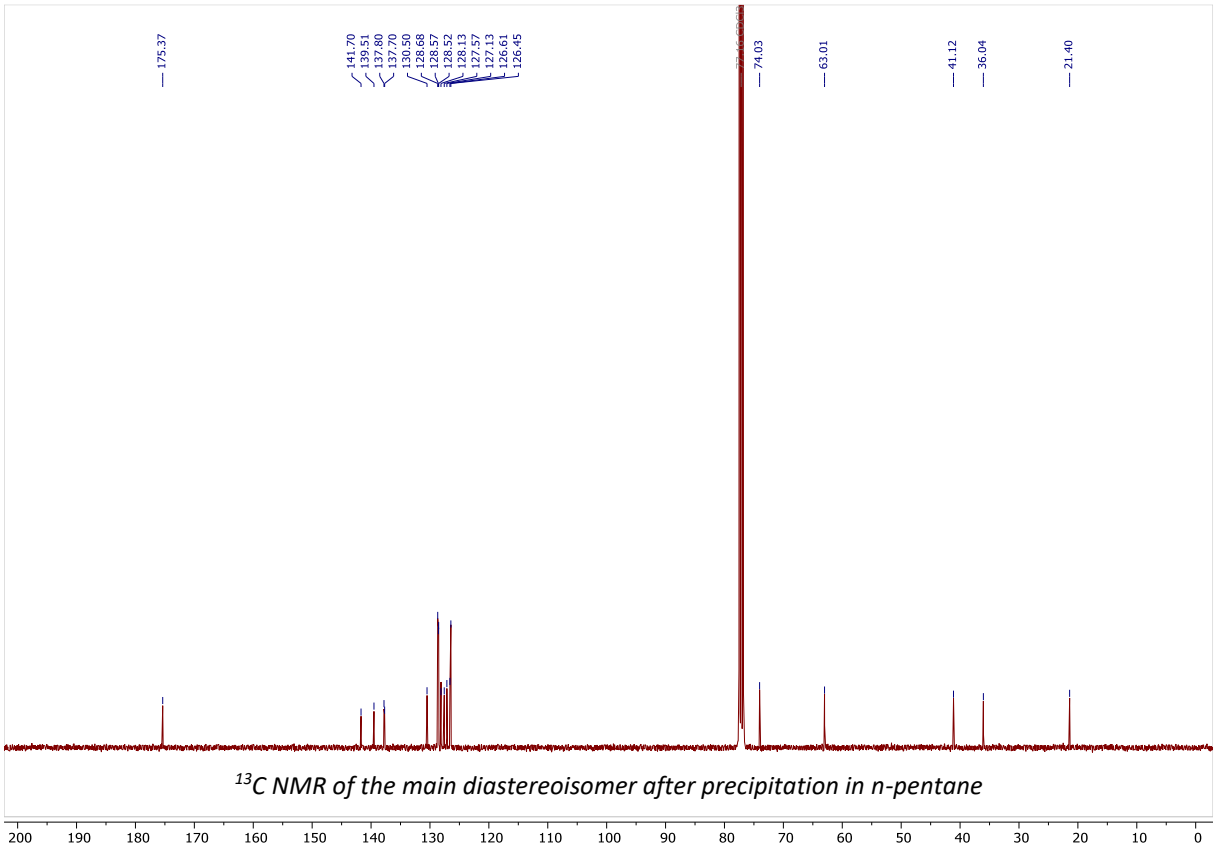


^{13}C NMR of the mixture of diastereoisomers after column chromatography

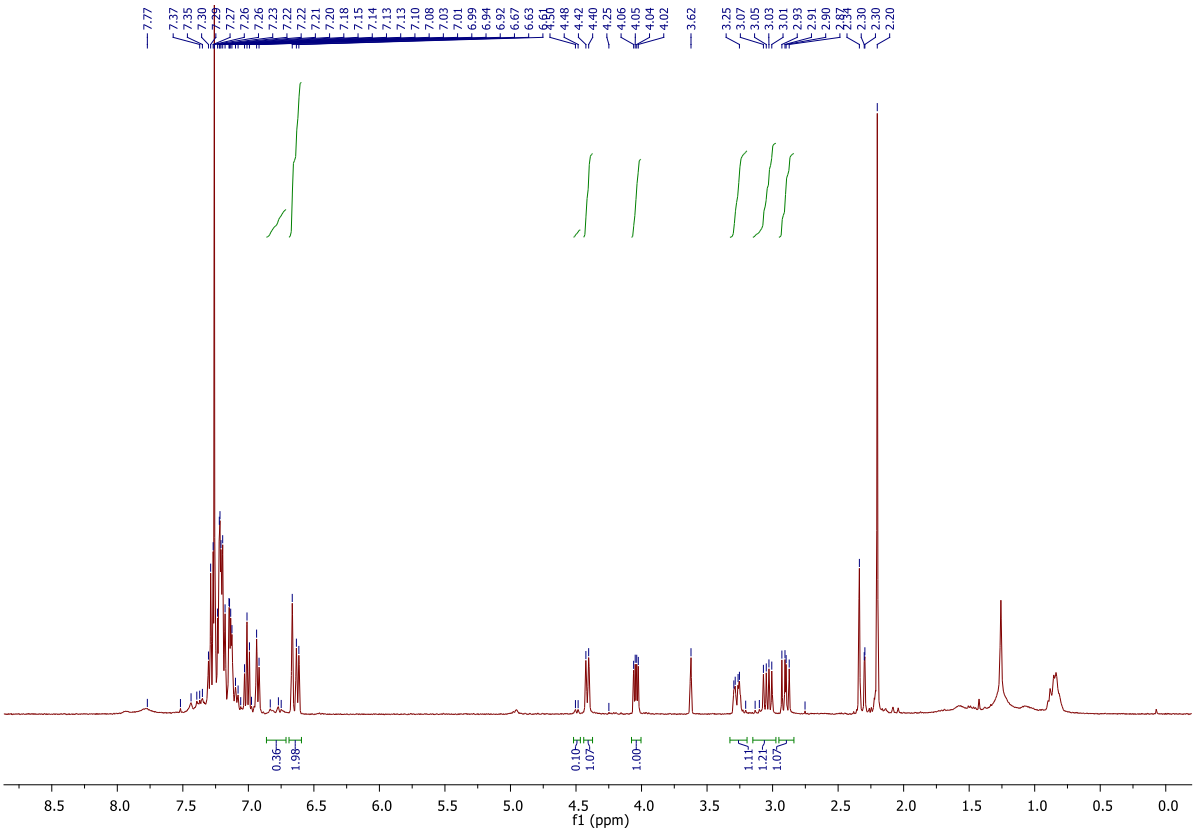
5-phenyl-1-(1-phenyl-2-(*m*-tolyl)ethyl)pyrazolidin-3-one (3ah)



^{1}H NMR of the main diastereoisomer after precipitation in n-pentane

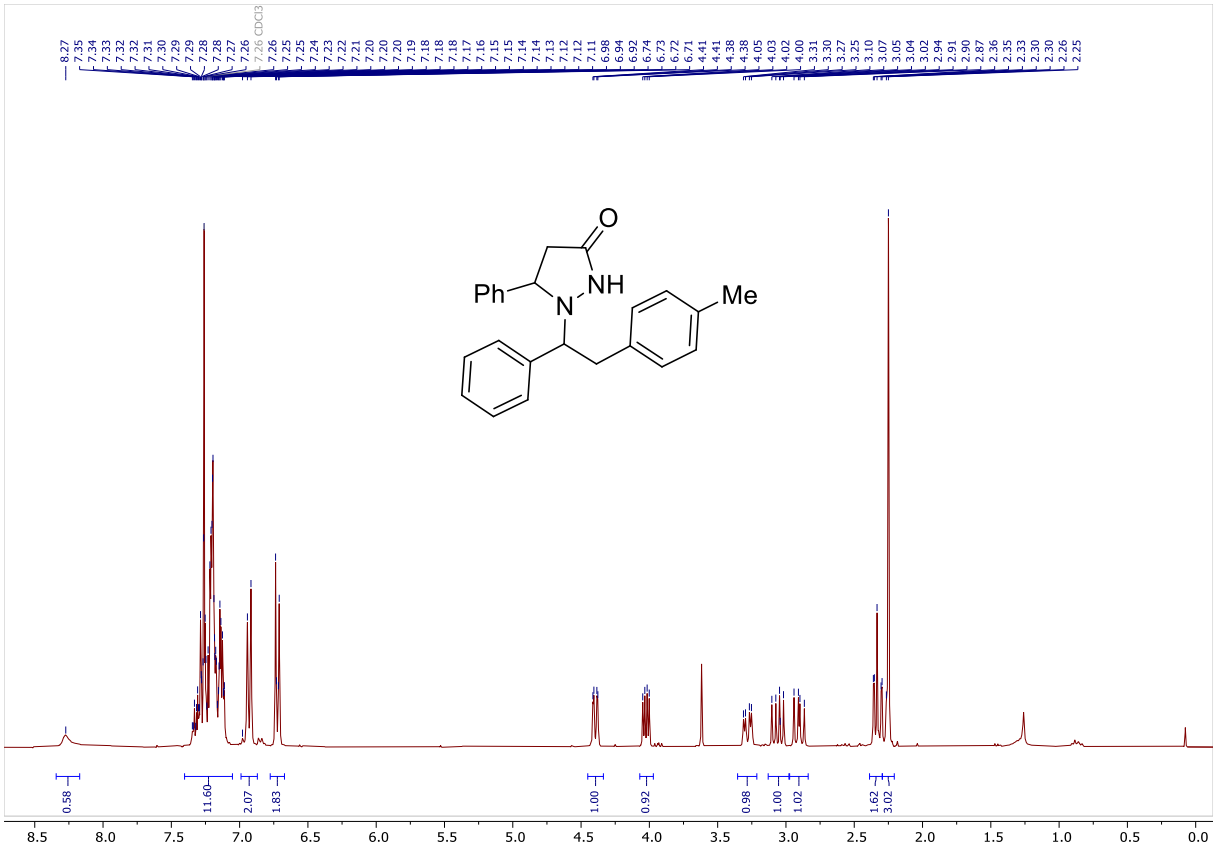


^{13}C NMR of the main diastereoisomer after precipitation in n-pentane

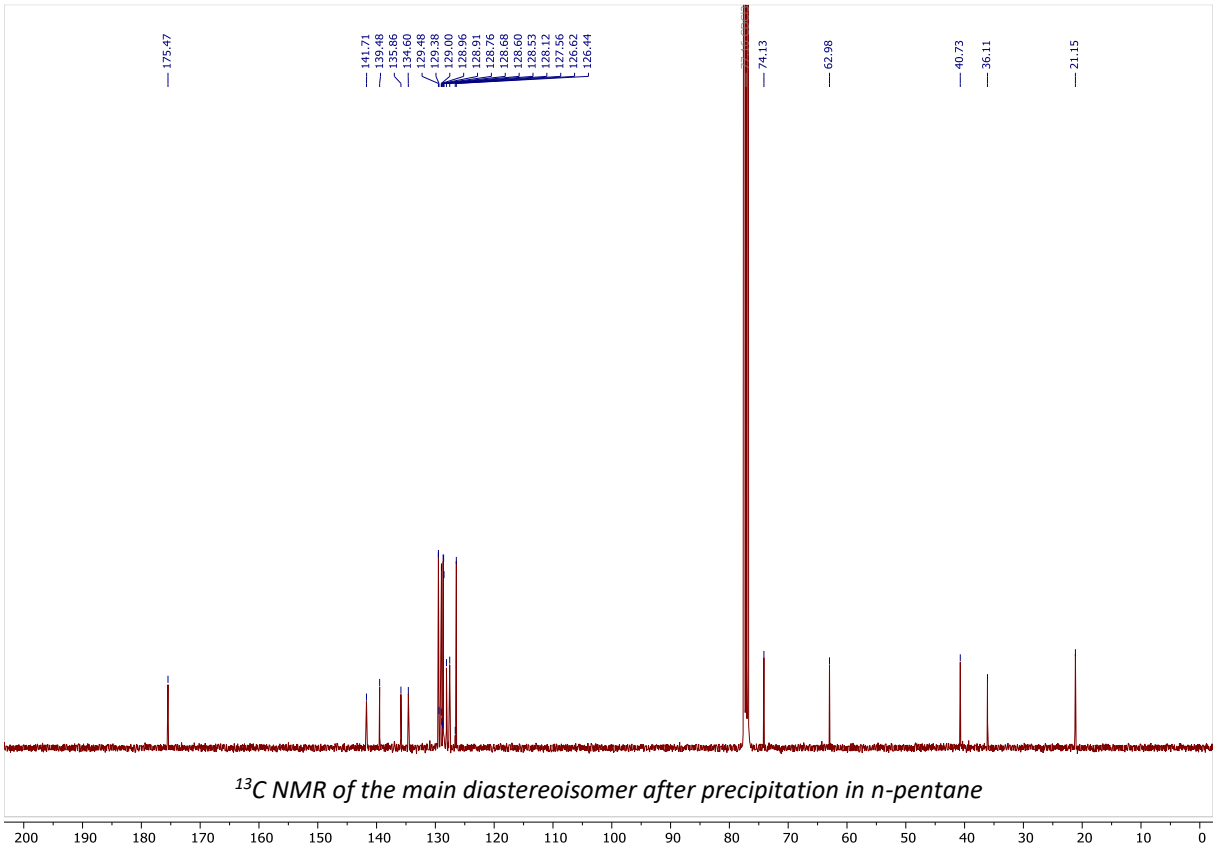


^{1}H NMR of the mixture of diastereoisomers after column chromatography

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

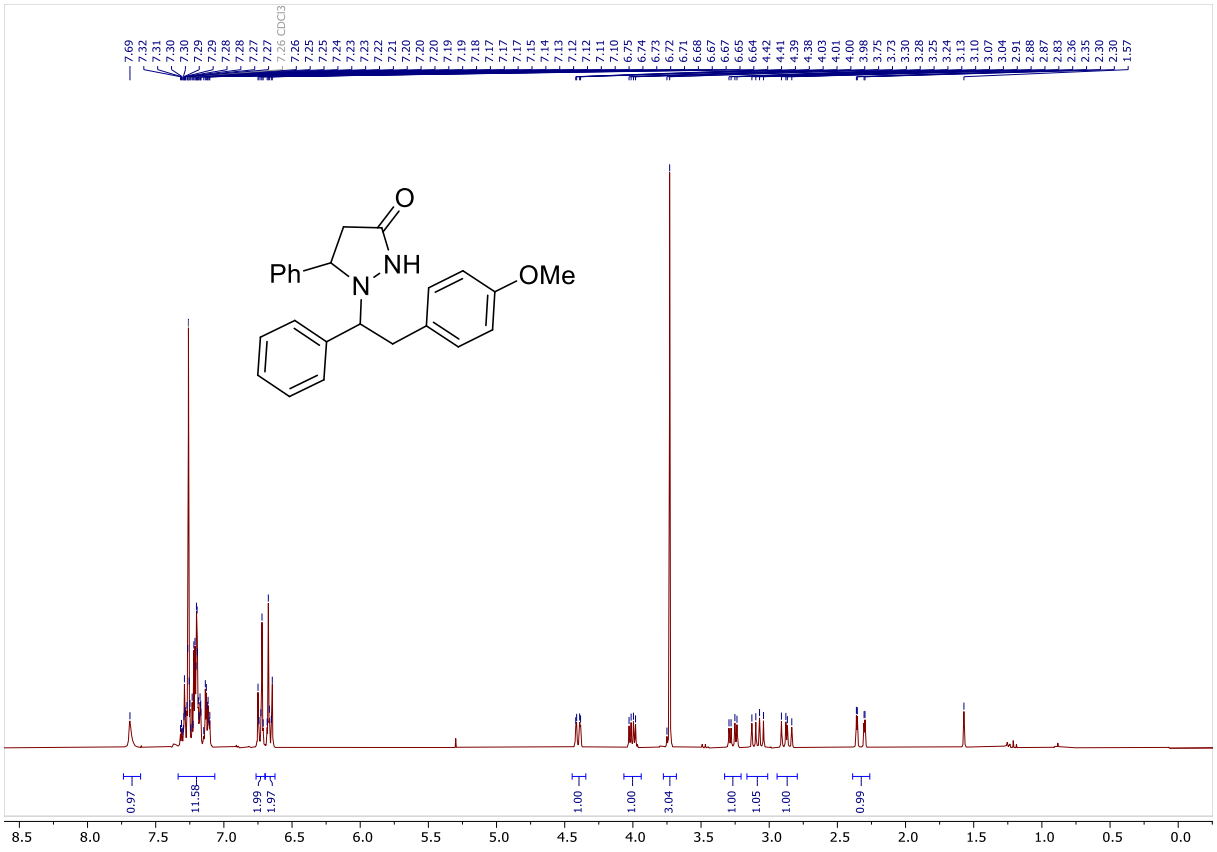


^{1}H NMR of the main diastereoisomer after precipitation in n-pentane

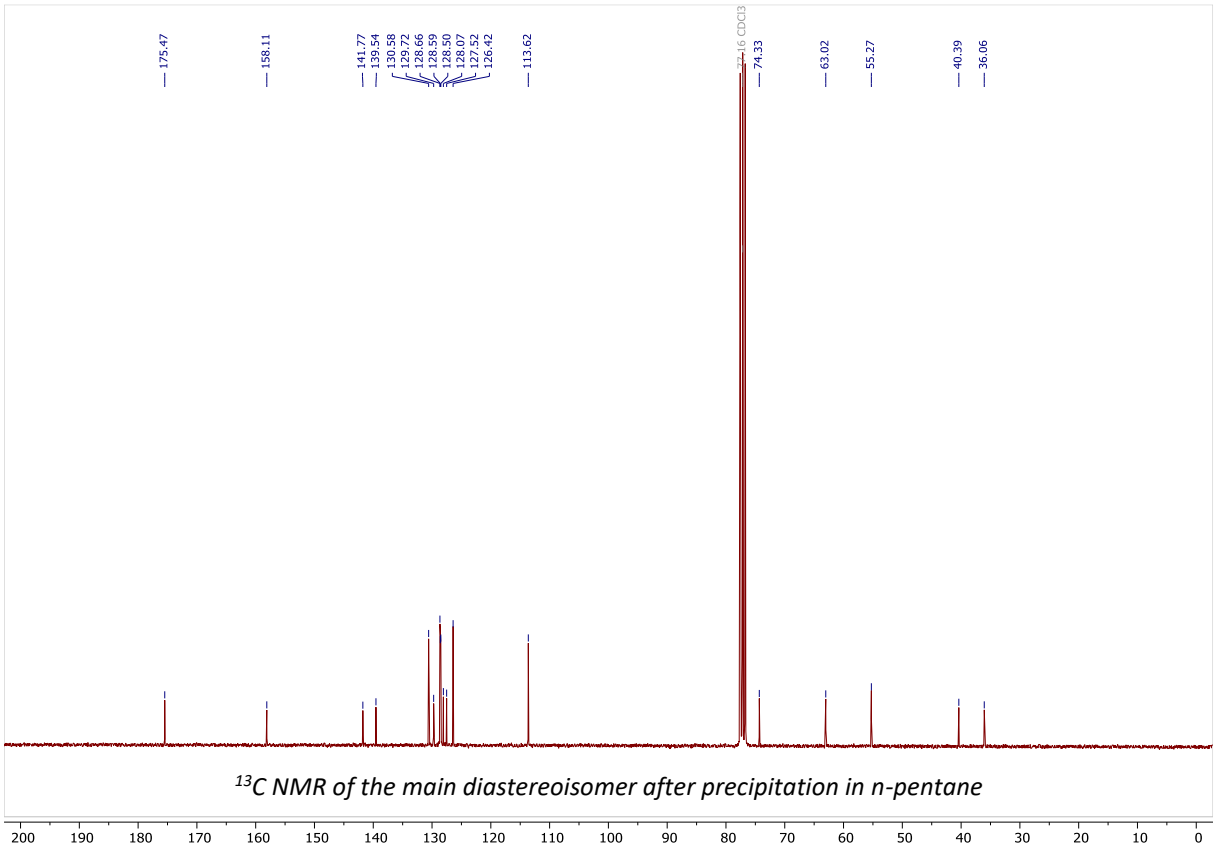


^{13}C NMR of the main diastereoisomer after precipitation in n-pentane

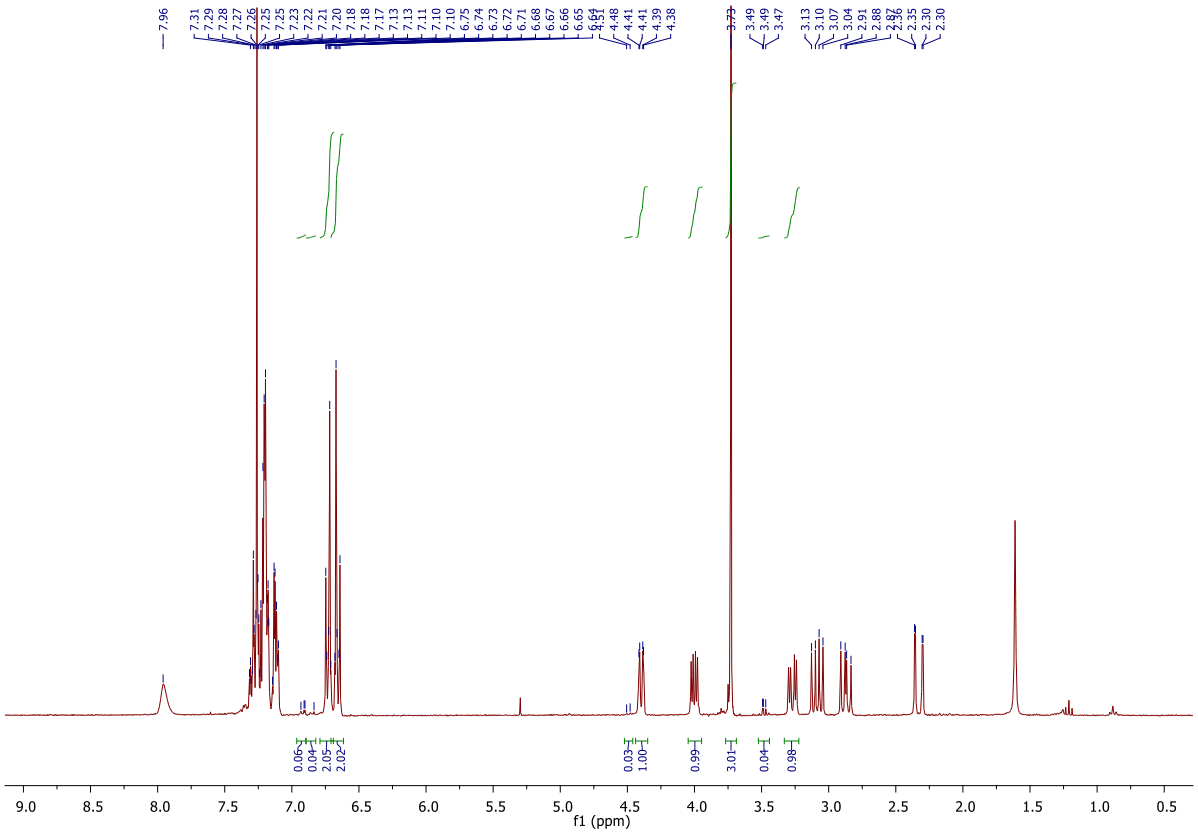
1-(2-(4-methoxyphenyl)-1-phenylethyl)-5-phenylpyrazolidin-3-one (3aj)



^{1}H NMR of the main diastereoisomer after precipitation in n-pentane

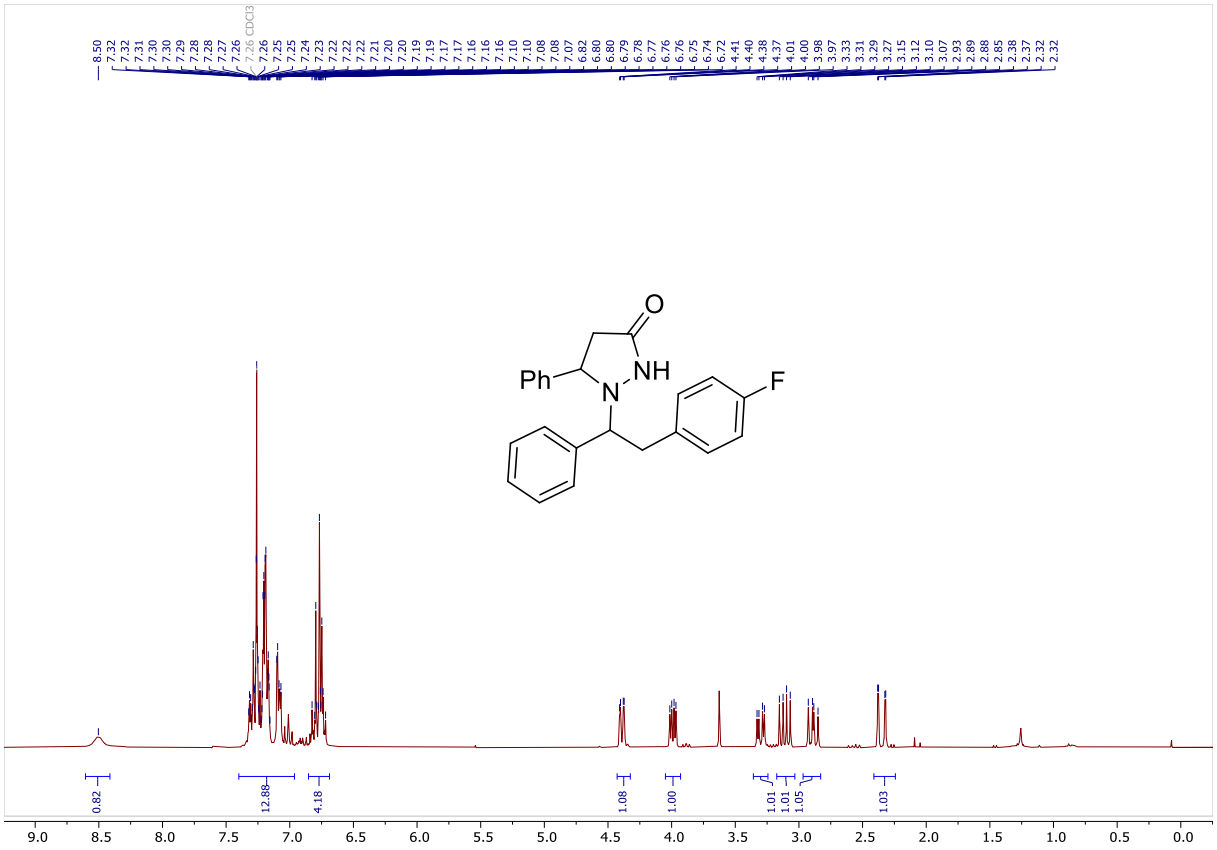


^{13}C NMR of the main diastereoisomer after precipitation in n-pentane

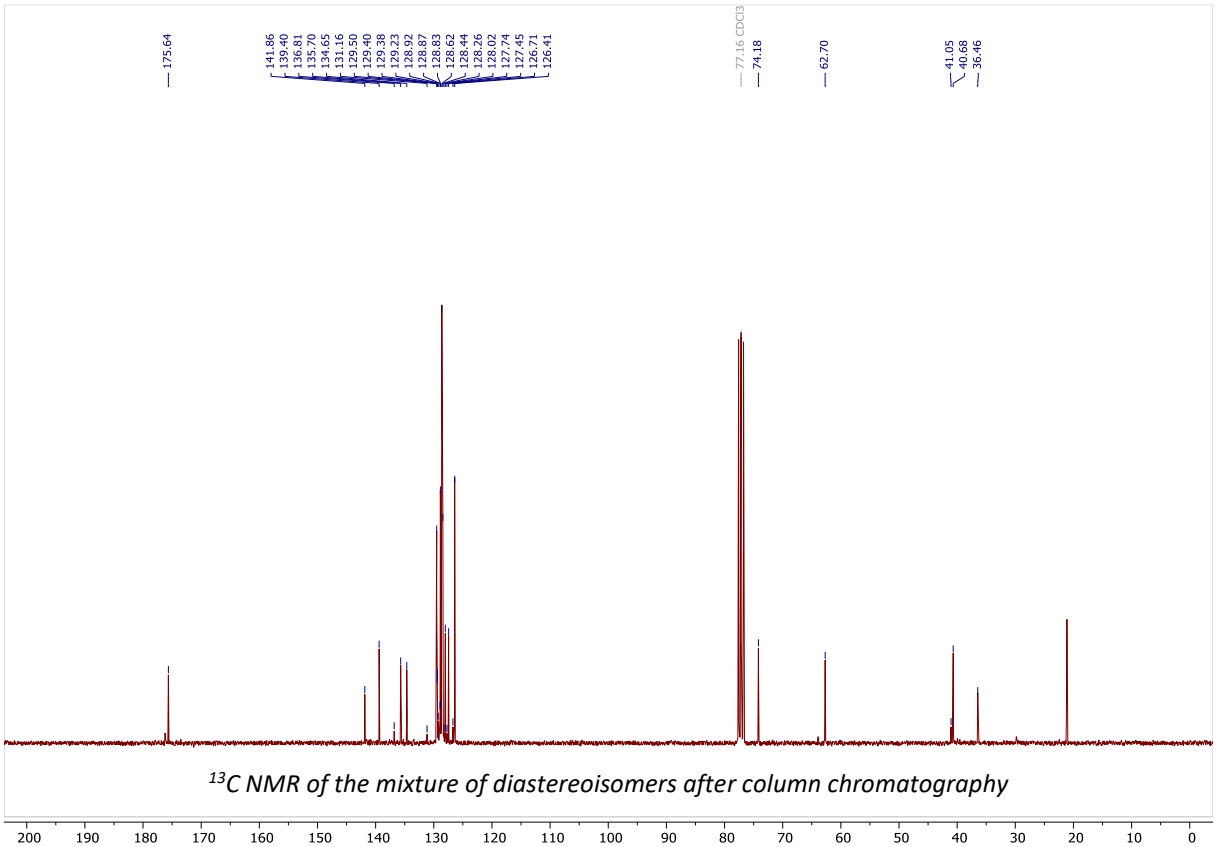


^{1}H NMR of the mixture of diastereoisomers after column chromatography

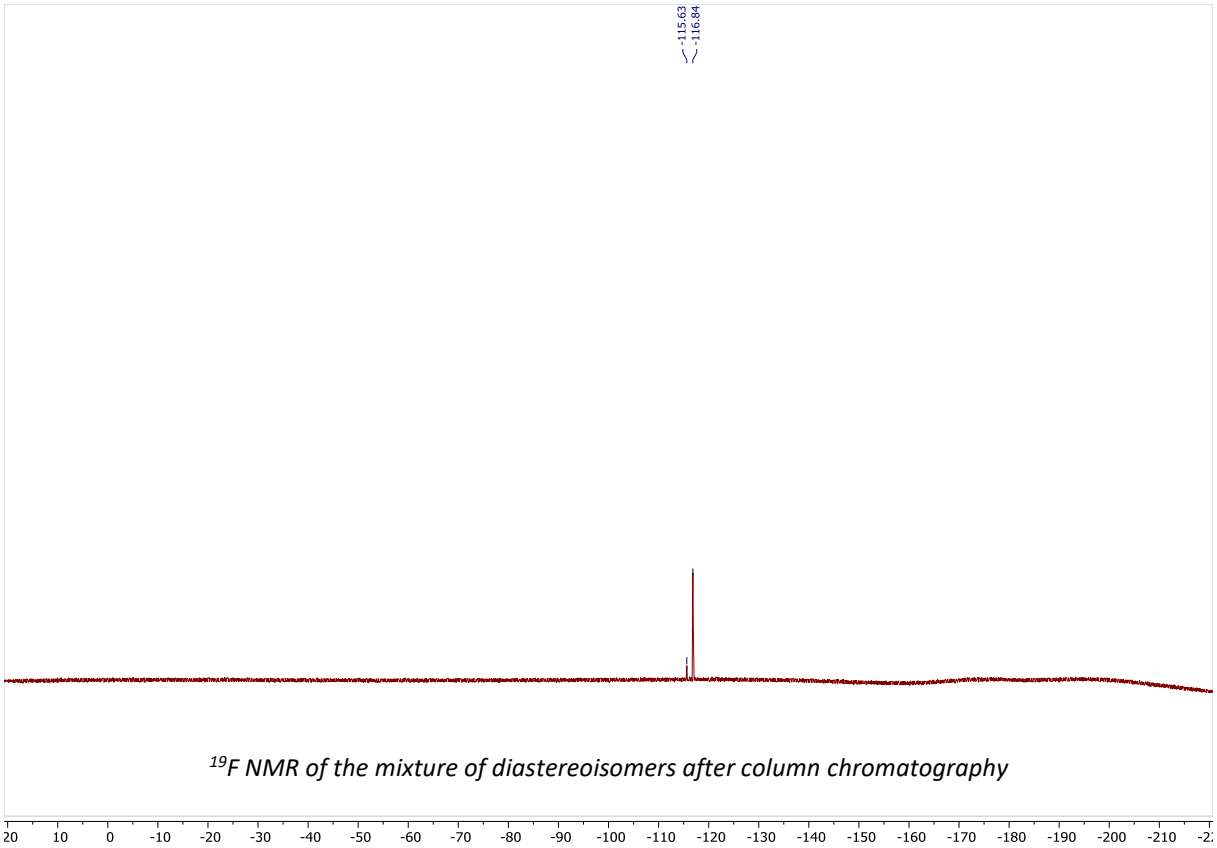
1-(2-(4-fluorophenyl)-1-phenylethyl)-5-phenylpyrazolidin-3-one (3ak)



^{1}H NMR of the mixture of diastereoisomers after column chromatography

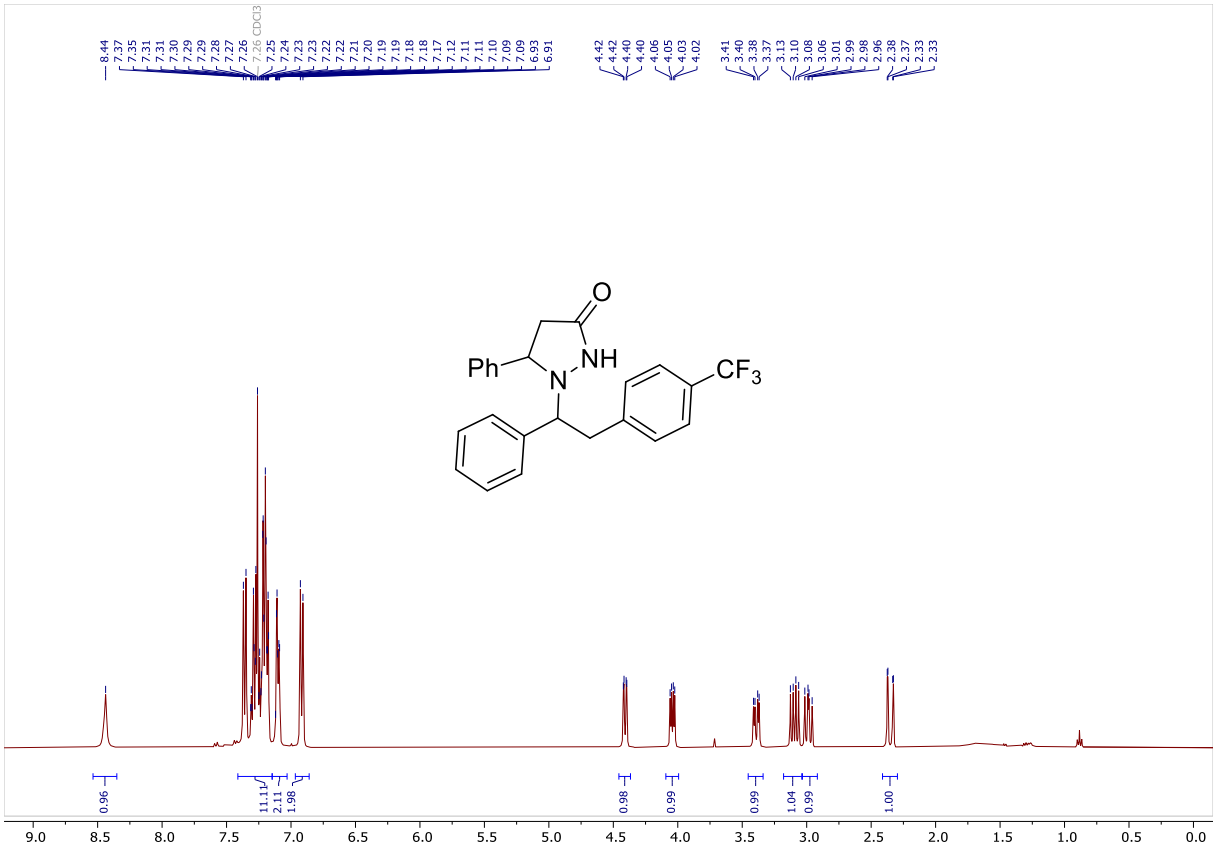


^{13}C NMR of the mixture of diastereoisomers after column chromatography

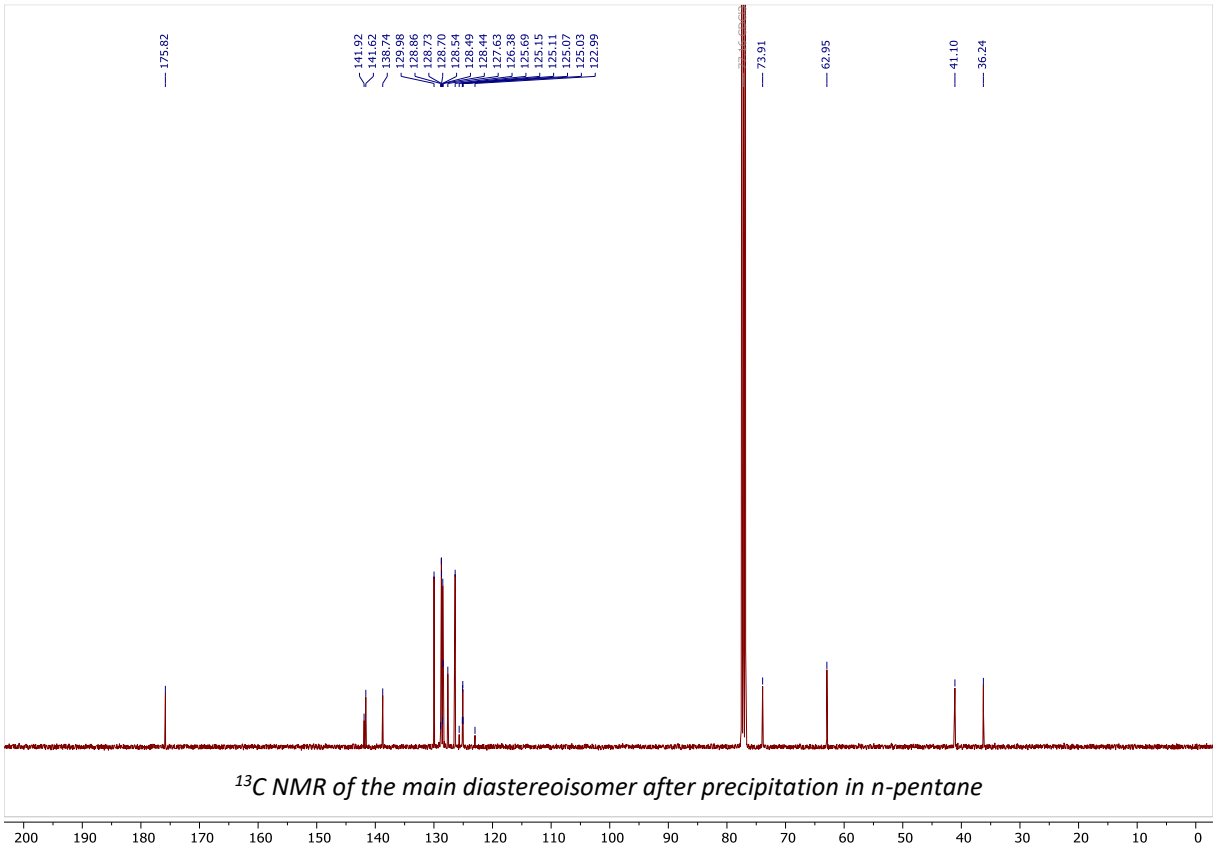


^{19}F NMR of the mixture of diastereoisomers after column chromatography

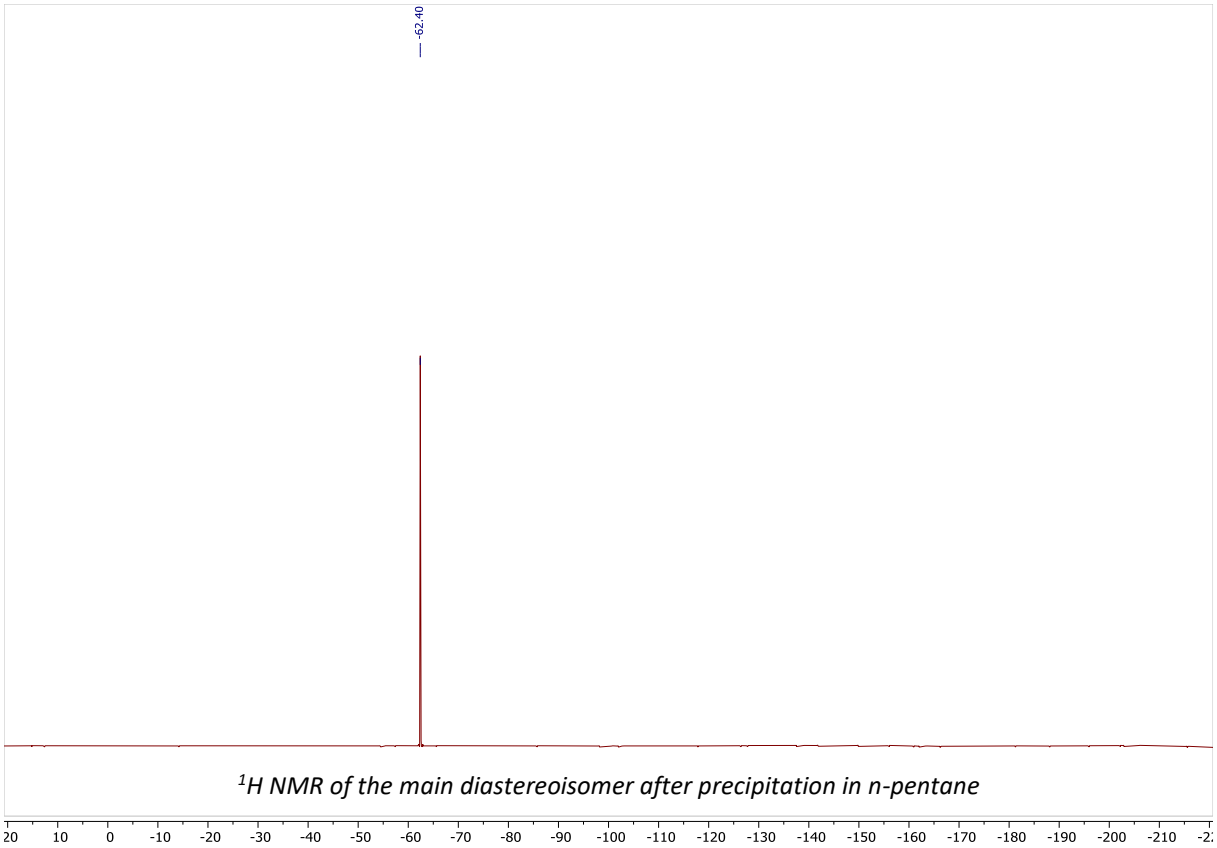
5-phenyl-1-(1-phenyl-2-(4-(trifluoromethyl)phenyl)ethyl)pyrazolidin-3-one (3al)



^{1}H NMR of the main diastereoisomer after precipitation in n-pentane

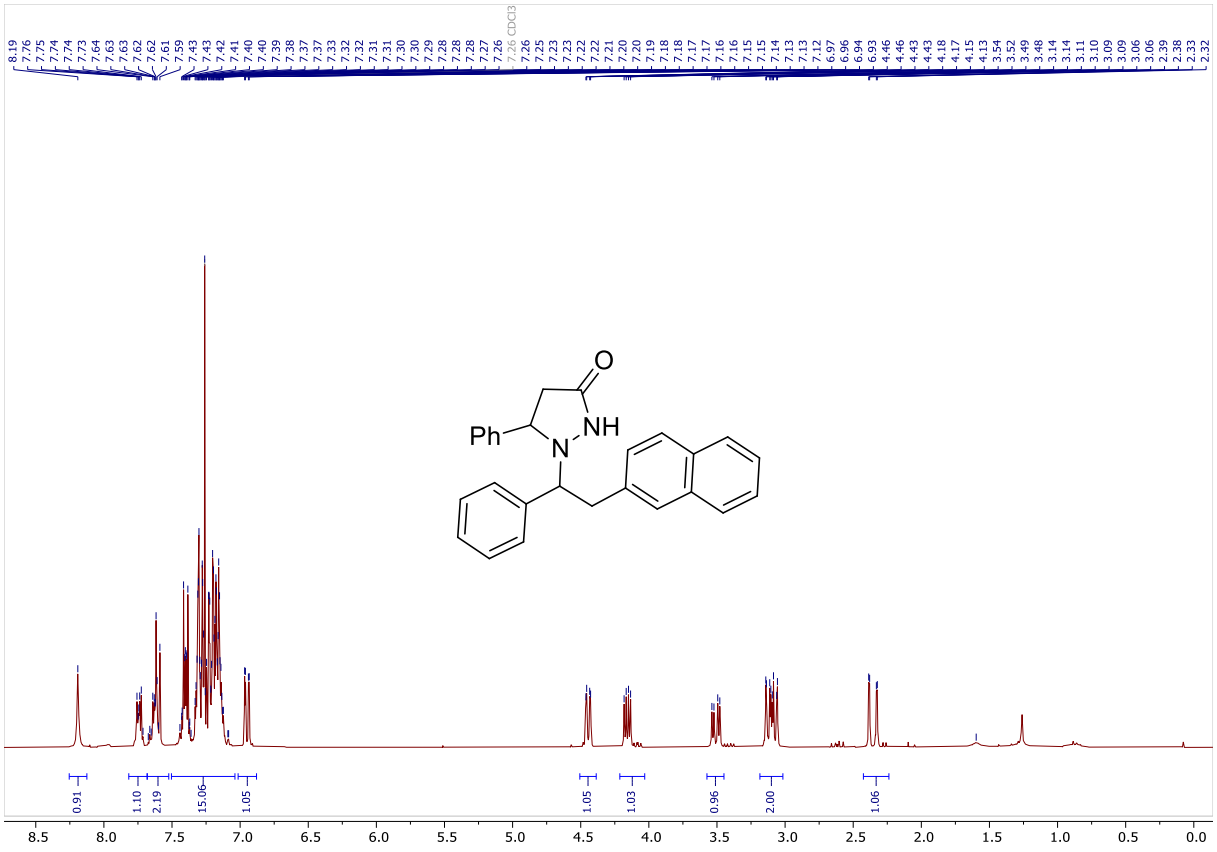


^{13}C NMR of the main diastereoisomer after precipitation in n-pentane

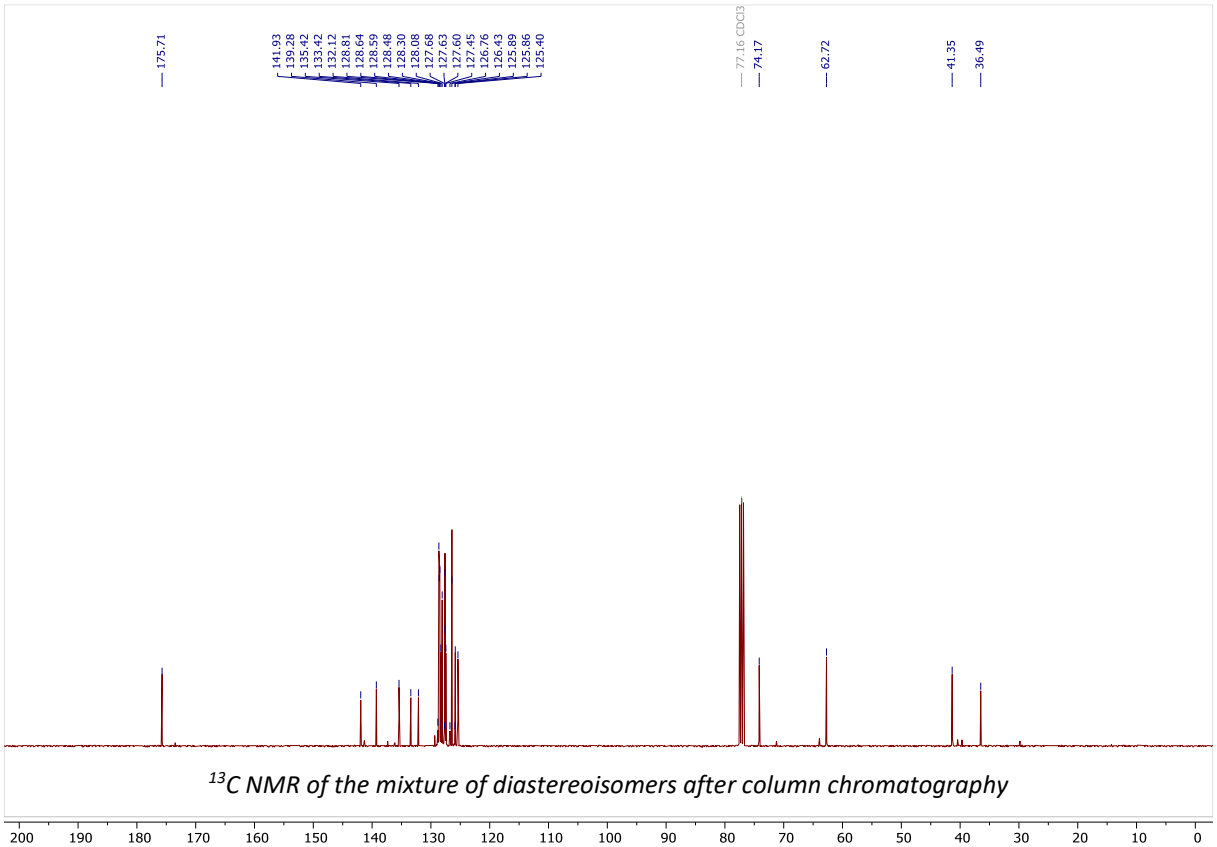


^{1}H NMR of the main diastereoisomer after precipitation in n-pentane

1-(2-(naphthalen-2-yl)-1-phenylethyl)-5-phenylpyrazolidin-3-one (3am)

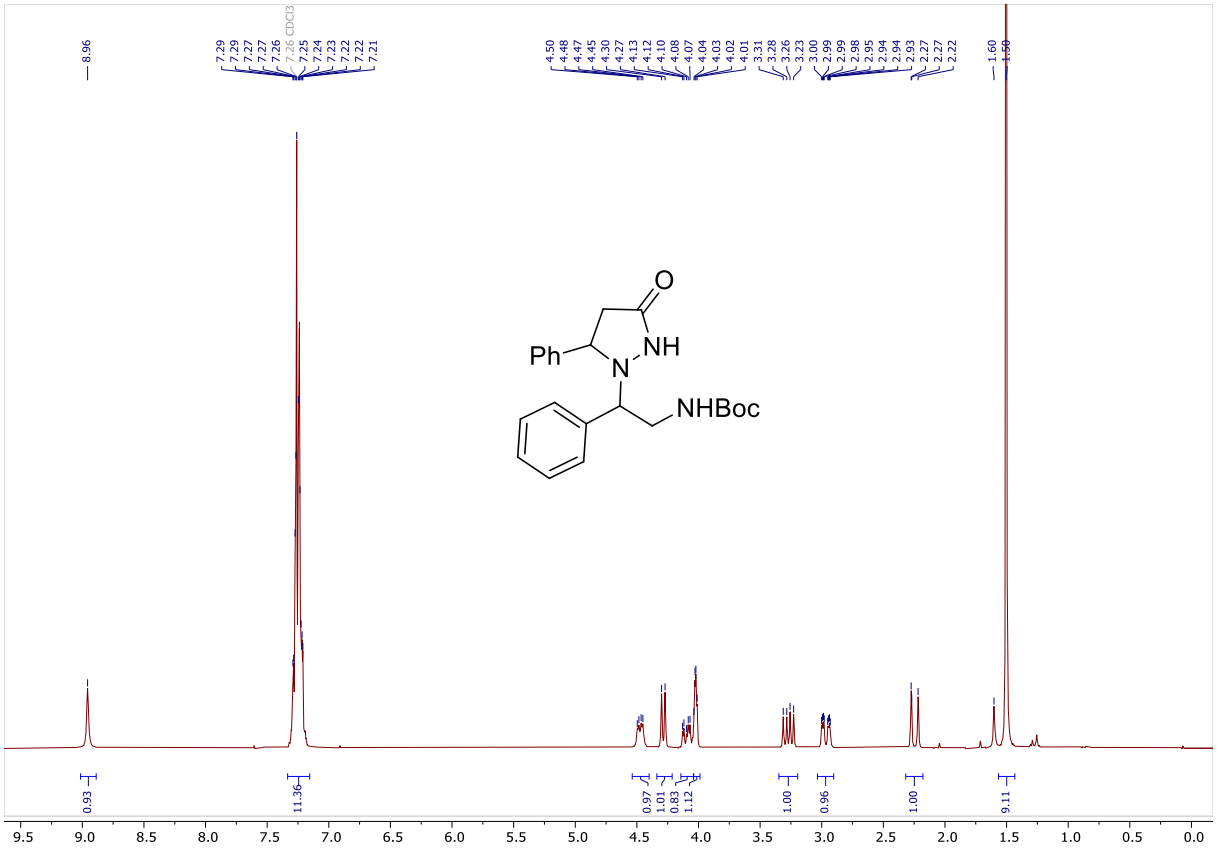


^{1}H NMR of the mixture of diastereoisomers after column chromatography



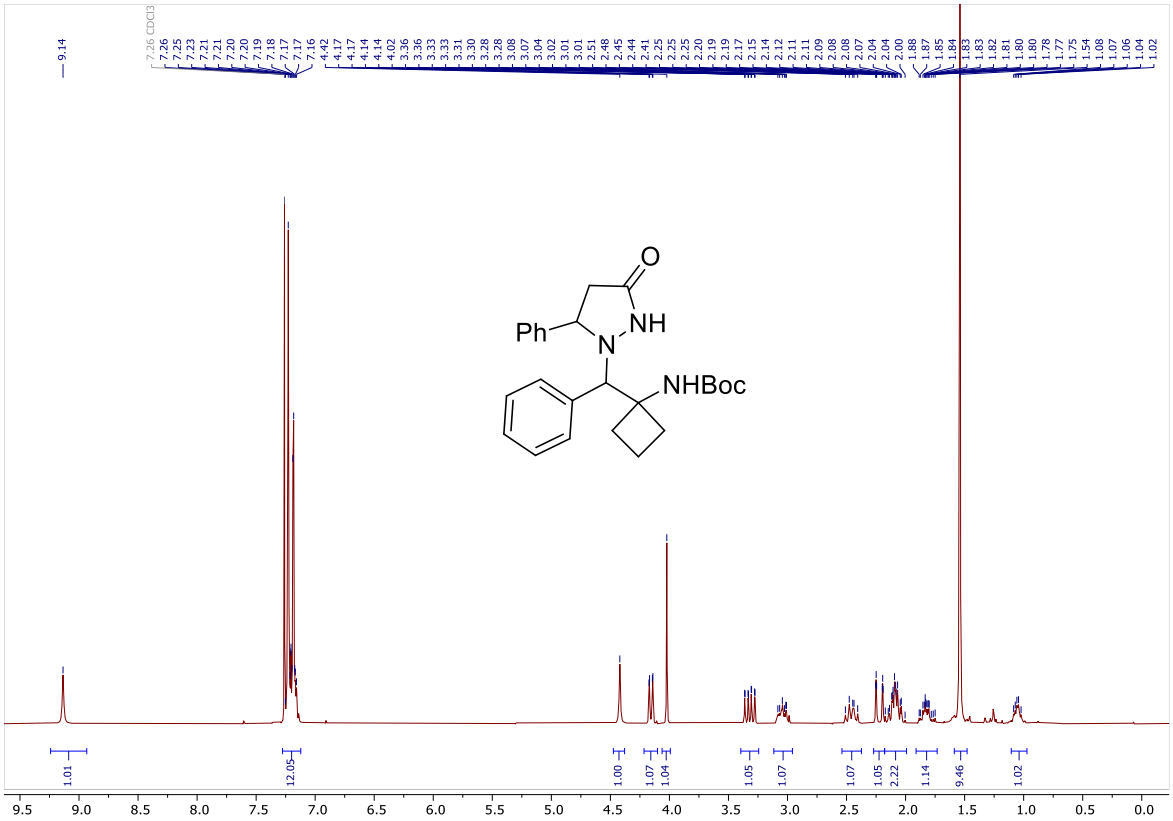
^{13}C NMR of the mixture of diastereoisomers after column chromatography

tert-butyl (2-(3-oxo-5-phenylpyrazolidin-1-yl)-2-phenylethyl)carbamate (3an)



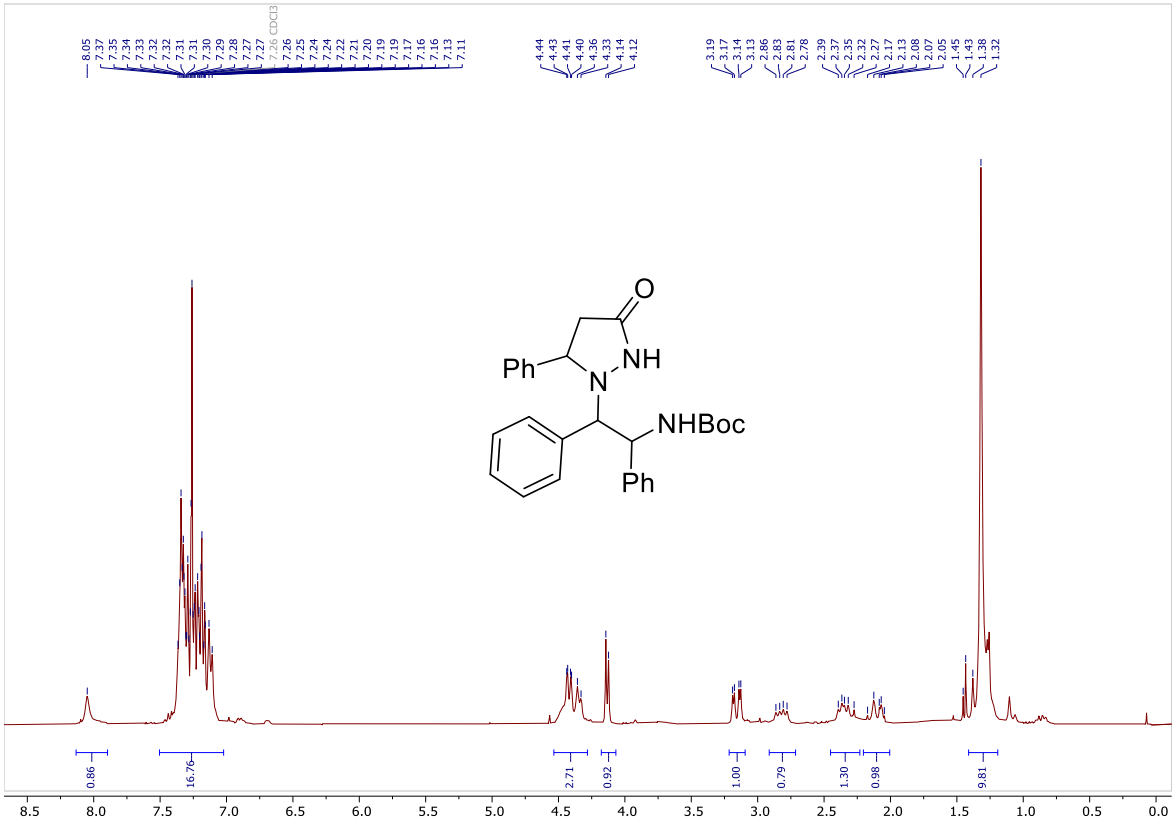
^{1}H NMR of the main diastereoisomer after the 2nd column chromatography

tert-butyl (1-((3-oxo-5-phenylpyrazolidin-1-yl)(phenyl)methyl)cyclobutyl)carbamate (3ao)



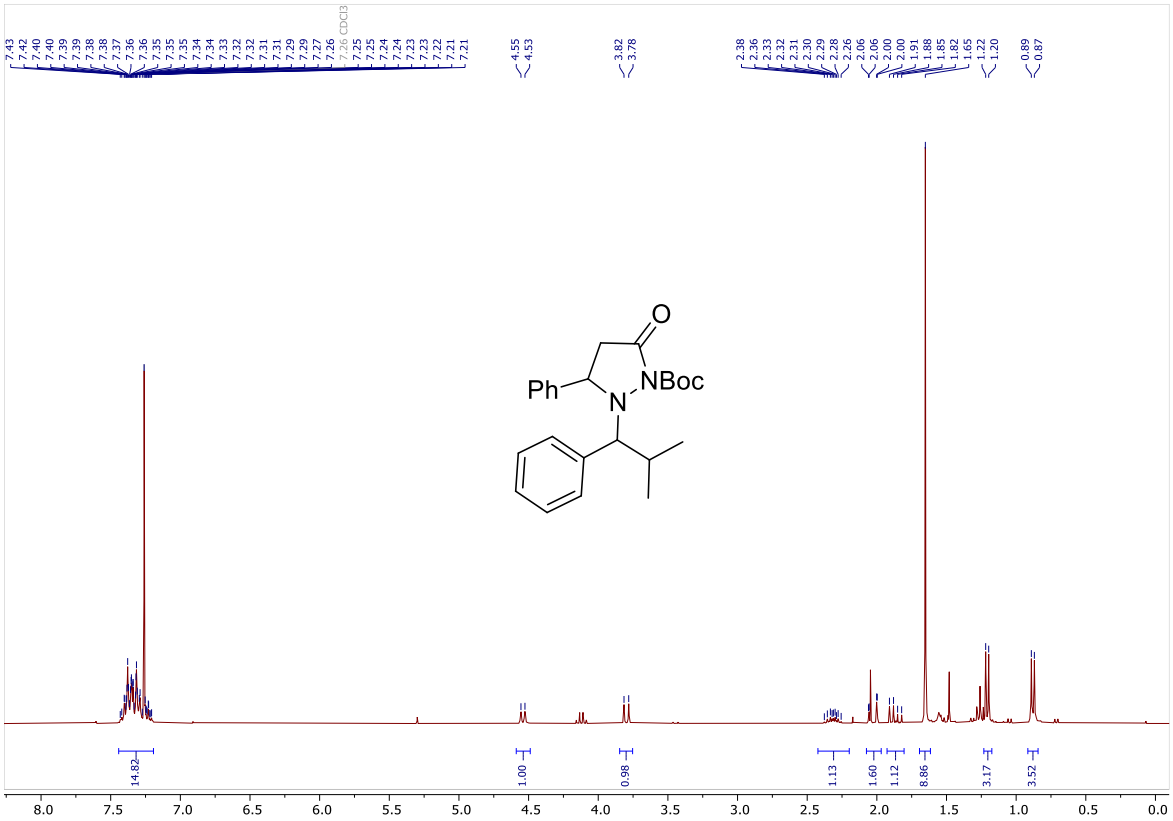
^{1}H NMR of the main diastereoisomer after the 2nd column chromatography

tert-butyl (1-(3-oxo-5-phenylpyrazolidin-1-yl)-1,3-diphenylpropan-2-yl)carbamate (3ap)



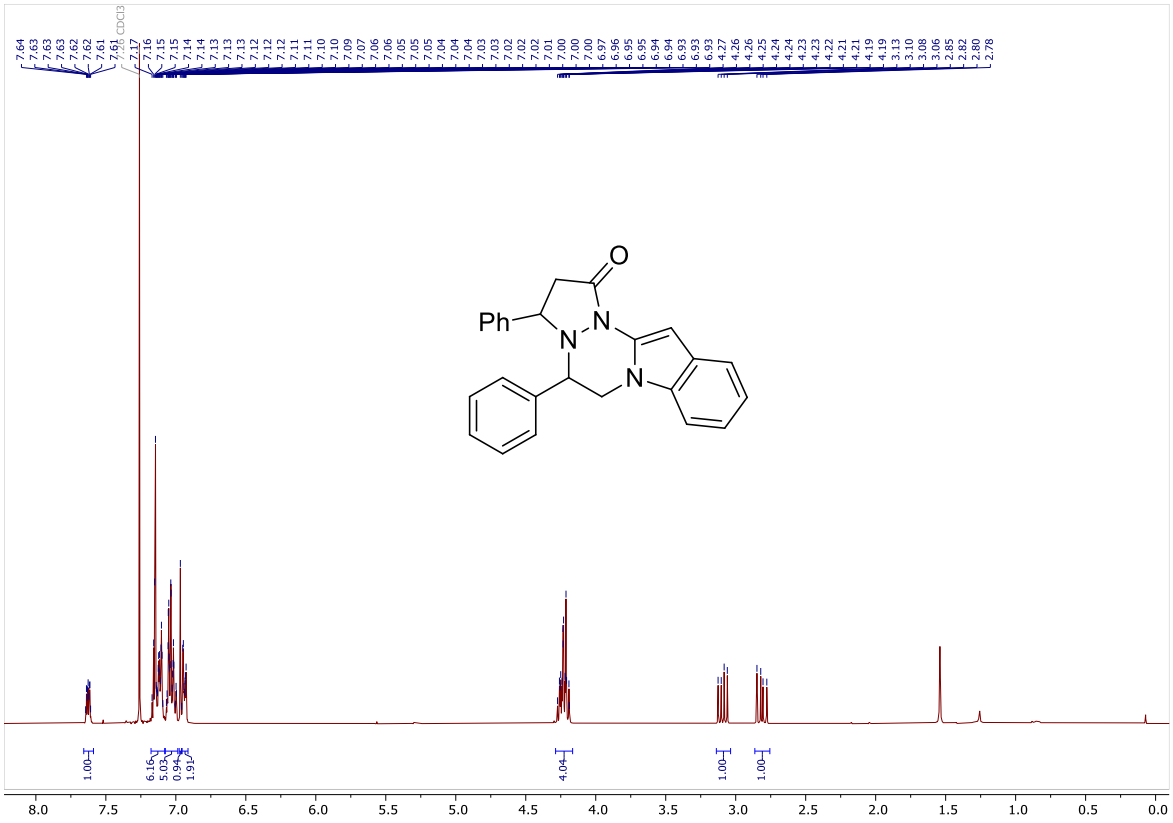
^{1}H NMR of the main diastereoisomer after the 2nd column chromatography

tert-butyl 2-(2-methyl-1-phenylpropyl)-5-oxo-3-phenylpyrazolidine-1-carboxylate (4aq)

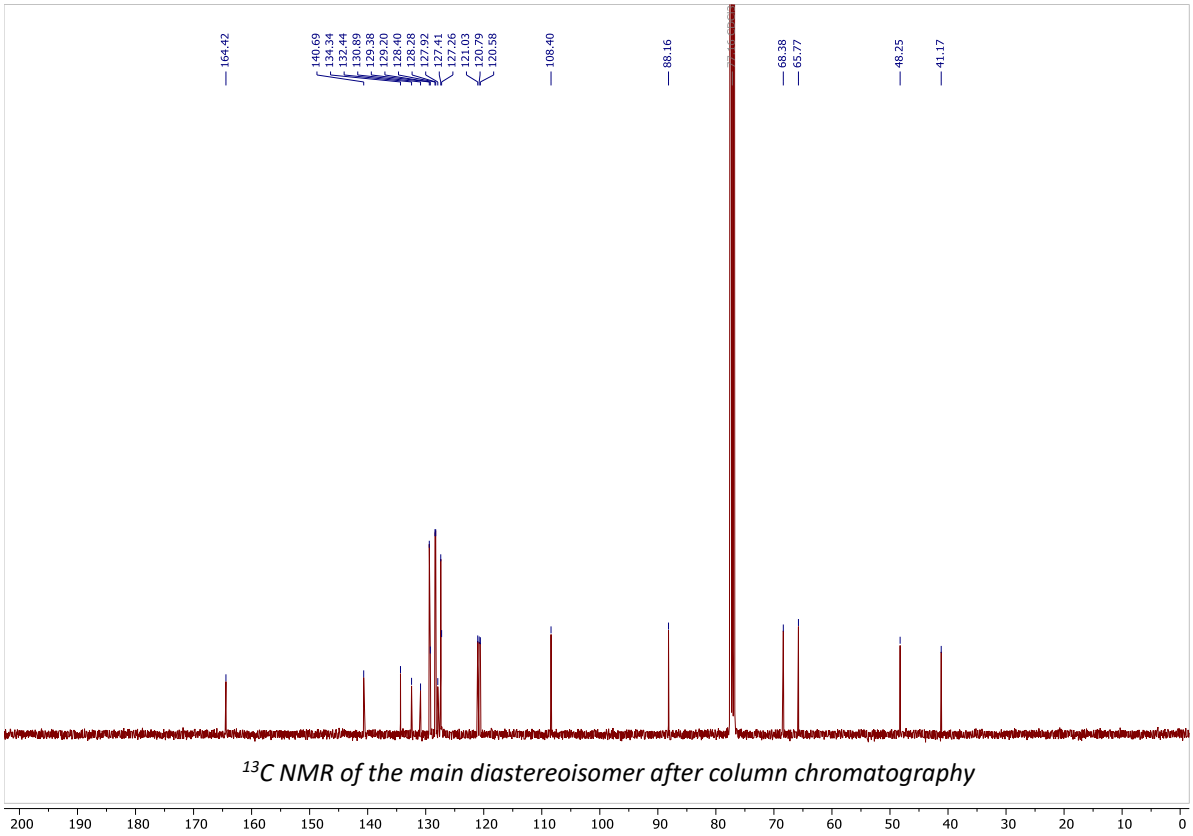


^{1}H NMR of the main diastereoisomer after the 2nd column chromatography

3,5-diphenyl-2,3,6,6a-tetrahydroindeno[2,1-c]pyrazolo[1,2-a]pyridazin-1(5H)-one (5aa)

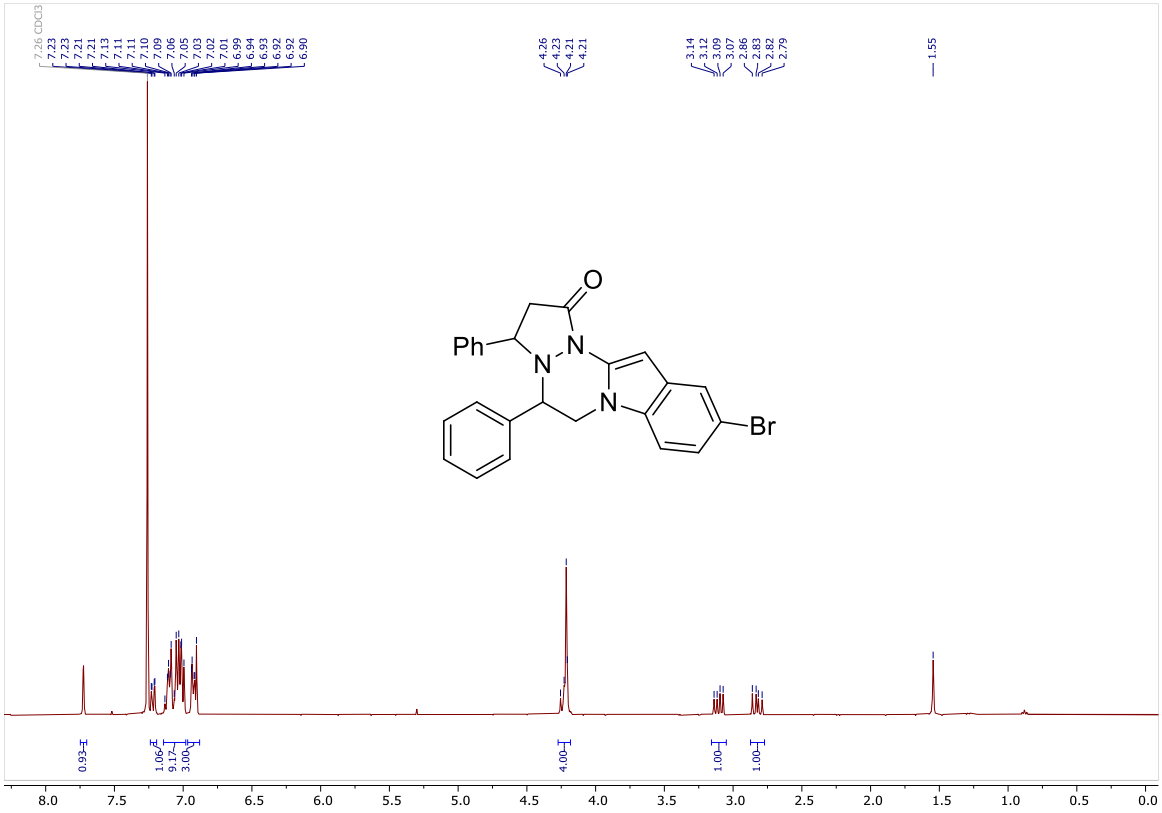


^{1}H NMR of the main diastereoisomer after column chromatography

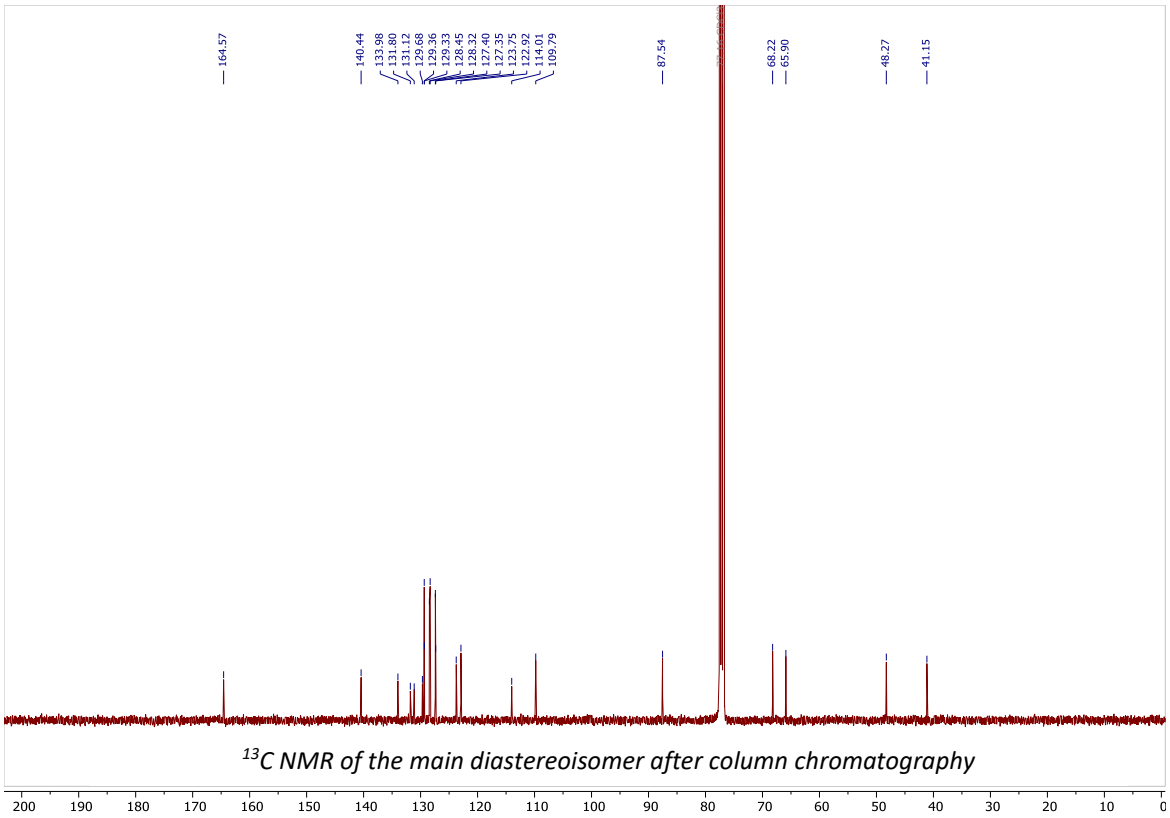


^{13}C NMR of the main diastereoisomer after column chromatography

10-bromo-3,5-diphenyl-2,3,5,6-tetrahydro-1H-pyrazolo[1',2':1,2][1,2,4]triazino[4,3-a]indol-1-one (5ab)



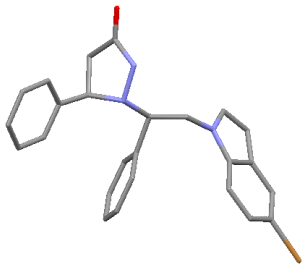
^{1}H NMR of the main diastereoisomer after column chromatography



^{13}C NMR of the main diastereoisomer after column chromatography

VII. X-ray analyses

1-(2-(5-bromo-1*H*-indol-1-yl)-1-phenylethyl)-5-phenylpyrazolidin-3-one (3ab)



Data collection

The crystal structure of **3ab** [$C_{25}H_{22}BrN_3O$] has been determined from single crystal X-Ray diffraction. The chosen crystal was stuck on a glass fibre and mounted on a kappa goniometer of a Bruker D8-VENTURE diffractometer equipped with a PHOTON area detector. A series of exposures were recorded, see Table S5-6. The cell parameters and the orientation matrix of the crystal were preliminary determined by using APEX Software[1]. Data integration and global cell refinement were performed with SAINT Software[2]. Intensities were corrected for Lorentz, polarisation, decay and absorption effects (SADABS Software[2]) and reduced to F_O^2. The program package WinGX[3] was used for space group determination, structure solution and refinement.

Data refinement

The standard space group $P2_1/c$ (n°14) was determined from systematic extinctions and relative F_O^2 of equivalent reflections. The structure was solved by direct methods[4]. Anisotropic displacement parameters were refined for all non-hydrogen atoms. Every Hydrogen atoms were located from subsequent difference Fourier syntheses and placed with geometrical constraints (SHELXL[4]). The final cycle of full-matrix least-square refinement on F^2 was based on 4737 observed reflections and 271 variable parameters and converged with unweighted and weighted agreement factors of: R1 = 0.0668, wR2 = 0.2173 for 4228 reflections with $I>2\sigma I$ and R1 = 0.0712, wR2 = 0.2220 for all data.

Crystallographic data

The crystal data are collected in Table S4. The full crystallographic parameters (atomic coordinates, bond length, angles and anisotropic displacements) are reported in Table S7-13.

Chemical Formula	$C_{25}H_{22}BrN_3O$
Molecular Weight / *g.mol*$^{-1}$	460.36
Crystal System	Monoclinic
Space Group	$P2_1/c$
Z , Z' (asymmetric units per unit cell)	4,1
a / *Å*	5.9460(2)
b / *Å*	22.9810(6)
c / *Å*	16.1913(4)
α / °	90
β / °	96.653(1)
γ / °	90
V / *Å*^{3}	2197.56(11)
d_{calc} / *g.cm*$^{-3}$	1.391
F(000) / *e*$^-$	944
Absorption coefficient μ (Mo$K\alpha_1$) / *mm*$^{-1}$	2.709

Table S4. Crystal data

Structural description

The asymmetric unit is composed of one molecule (figures S3 and S4). The stereogenic centers C10 and C19 are RR (on the figure). The compound crystallizes in a centrosymmetric space group so both enantiomers are present in the solid.

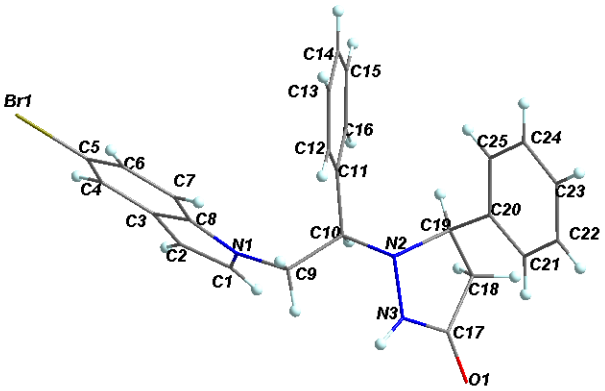


Figure S7. asymmetric unit with atoms labels

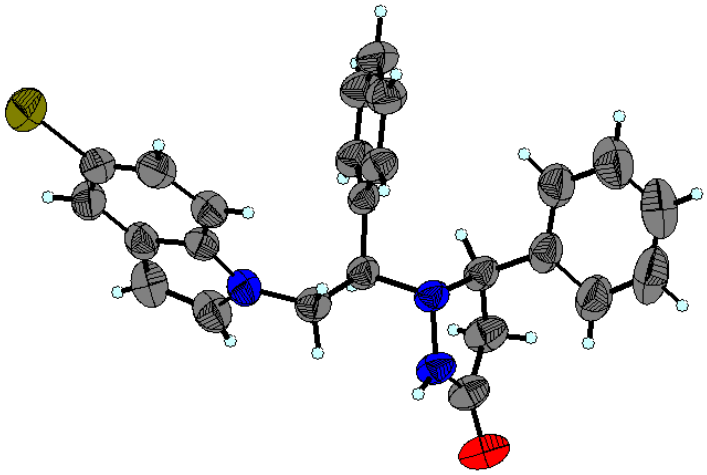


Figure S8. Asymmetric unit in thermal allipsoidal representation (50% of probability)

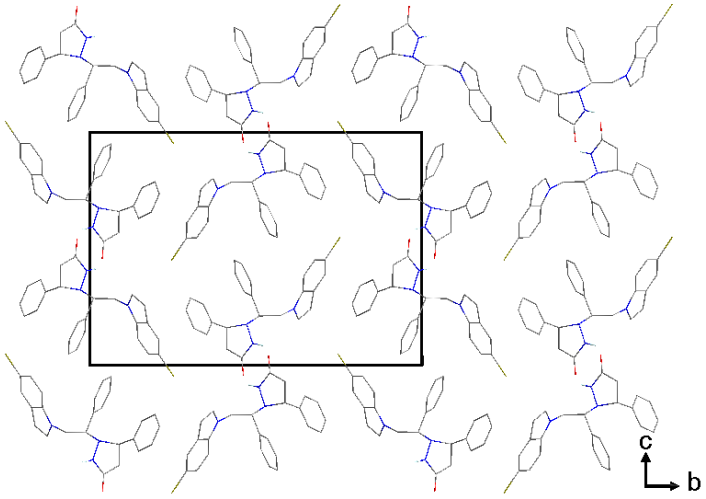


Figure S9. Projection along a axis

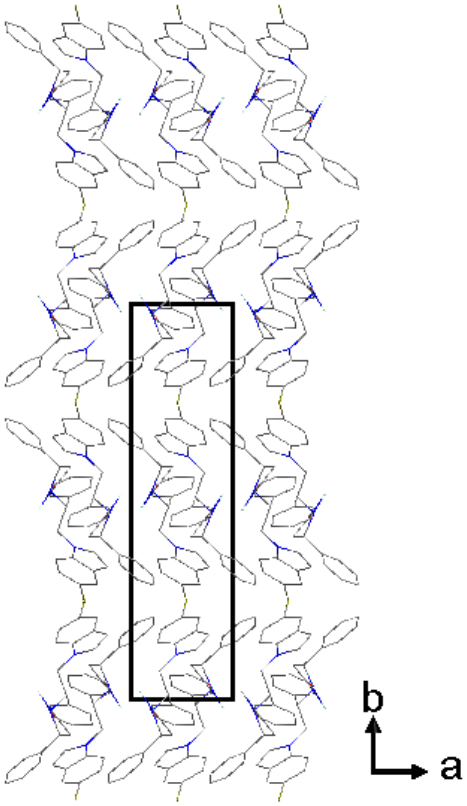


Figure S10. Projection along c axis

Sofwares :

(1)- APEX. V2022.10-1

(2)- SAINT V8.40B Bruker AXS LLC.219

- SADABS – 2016/2 – Bruker AXS area detector scaling and absorption correction

(3)- WinGX: Version 2023.1: An integrated system of Windows Programs for the solution, refinement and analysis of Single Crystal X-Ray Diffraction Data, By LouisJ. Farrugia, Dept. of chemistry, University of Glasgow. L. J. Farrugia (2012) J. Appl. Cryst. 45, 849-854.

(4)-include in WinGX suite :

- SIR 92: A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, J. Appl. Crystallogr., 1994, 27, 435.;

- SHELX & SHELXTL program: G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112-122..

(6)-PowderCell for Windows (version 2.4) by Kraus W. & Nolze G., Federal institute for materials Research and testing, Rudower Chausse 5, 12489 Berlin Germany.

Scan parameters : D=40.000 mm λ = 1.54184Å

Axis	**2θ/°**	**ω/°**	**φ/°**	**χ/°**	**Width/°**	**Frames**
Omega	109.52	-5.2	80	65.5	0.5	245
Omega	109.52	79.76	252	68.5	0.5	162
Omega	109.52	-5.2	160	65.5	0.5	245
Omega	109.52	107.37	160	-44.5	0.5	216
Omega	109.52	-5.2	0	65.5	0.5	245
Omega	109.52	-144.63	-120	-44.5	0.5	216
Omega	-48.14	-153.55	-54	44.5	0.5	216
Omega	109.52	117.31	40	65.5	0.5	245
Omega	109.52	-5.2	-160	65.5	0.5	245
Omega	109.52	-5.2	120	65.5	0.5	245
Phi	109.52	13.46	35.6	24	0.5	367
Omega	94.52	92.37	270	-44.5	0.5	216
Omega	109.52	-5.2	-80	65.5	0.5	245
Omega	109.52	-5.2	-40	65.5	0.5	245
Phi	109.52	102.34	-130.34	-24	0.5	666
Omega	-48.14	-45.55	153	44.5	0.5	216
Omega	-48.14	-55.86	0	-65.5	0.5	192
Omega	79.52	-174.63	0	-44.5	0.5	216
Omega	79.52	-174.63	90	-44.5	0.5	216
Omega	-48.14	-45.55	51	44.5	0.5	216
Omega	-64.52	-169.93	270	44.5	0.5	216
Omega	94.52	-159.63	0	-44.5	0.5	216
Omega	94.52	-159.63	90	-44.5	0.5	216
Phi	-48.14	-45.55	163.6	44.5	0.5	367
Phi	94.52	92.12	360	-44.5	0.5	720
Omega	-48.14	-153.55	0	44.5	0.5	216
Omega	-64.52	-61.93	180	44.5	0.5	216
Phi	79.52	77.12	0	-44.5	0.5	720
Phi	-48.14	-40.95	-20	24	0.5	367
Phi	109.52	107.12	-122.34	-44.5	0.5	666
Phi	-64.52	41.33	360	-44.5	0.5	720
Phi	-49.52	56.33	360	-44.5	0.5	720

Unique reflections [$F_o > 4.0\ \sigma(F_o)$]	4737 (4228)
θ range / °	3.354 to 80.55
hkl range	-7≤h≤6, -29≤k≤29, -20≤l≤20
$R_{int} = \Sigma[\lvert F_O^2 - F_O^2(mean)\rvert] / \Sigma[F_O^2]$	0.05
Completeness to θ = 26.40 / %	99.9

Table S5. Data collection

$R_1 = \Sigma (| |F_O| - |F_C| |) / \Sigma |F_O|$

$wR_2 = [\Sigma [w (F_O^2 - F_C^2)^2] / \Sigma [w (F_O^2)^2]]^{1/2}$

$GooF = [\Sigma [w (F_O^2 - F_C^2)^2] / (n - p)]^{1/2}$

Number of reflections (n) (with $F_O > 4.0\ \sigma(F_O)$)	4228
Number of refined parameters (p) / restraints	271
Final R indices [I>2sigma(I)]	R1 = 0.0668, wR2 = 0.2173
R indices (all data)	R1 = 0.0712, wR2 = 0.2220
Goodness of Fit indicator (Restrained GooF)	1.083
Maximum peak in Final Difference Map / $e^-Å^{-3}$	1.282
Maximum hole in Final Difference Map / $e^-Å^{-3}$	-0.921

Table S6. Refinement data

	x	y	z	U(eq)
C(1)	6462(6)	3717(1)	8032(2)	70(1)
C(2)	7680(6)	3352(2)	7589(2)	72(1)
C(3)	6360(5)	3258(1)	6817(2)	60(1)
C(4)	6711(6)	2924(1)	6117(2)	67(1)
C(5)	5010(7)	2918(1)	5471(2)	70(1)
C(6)	2982(7)	3221(2)	5477(2)	71(1)
C(7)	2616(5)	3558(1)	6160(2)	62(1)
C(8)	4333(5)	3578(1)	6821(2)	54(1)
C(9)	2805(5)	4259(1)	7863(2)	58(1)
C(10)	3690(4)	4887(1)	7880(2)	48(1)
C(11)	3957(4)	5118(1)	7021(2)	47(1)
C(12)	2116(5)	5149(1)	6416(2)	56(1)
C(13)	2302(6)	5411(2)	5652(2)	66(1)
C(14)	4326(6)	5640(2)	5490(2)	72(1)
C(15)	6173(6)	5614(2)	6083(2)	72(1)
C(16)	6000(5)	5350(1)	6844(2)	59(1)
C(17)	2674(5)	5425(1)	9678(2)	58(1)
C(18)	4072(5)	5877(2)	9297(2)	62(1)
C(19)	3045(4)	5883(1)	8385(2)	51(1)
C(20)	1213(5)	6323(1)	8157(2)	57(1)
C(21)	-374(6)	6474(2)	8685(3)	78(1)
C(22)	-2138(7)	6860(2)	8411(4)	96(2)
C(23)	-2254(8)	7099(2)	7632(4)	98(2)
C(24)	-673(8)	6967(2)	7111(3)	92(1)
C(25)	1053(7)	6579(2)	7375(2)	72(1)
Br(1)	5471(1)	2468(1)	4514(1)	107(1)
N(1)	4443(4)	3855(1)	7578(2)	58(1)
N(2)	2050(3)	5277(1)	8239(1)	47(1)
N(3)	1694(4)	5091(1)	9063(1)	54(1)
O(1)	2386(4)	5379(1)	10415(1)	72(1)

Table S7. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2$ x 10^3). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
H(1)	6934	3852	8565	83
H(2)	9099	3195	7761	86
H(4)	8042	2715	6094	80
H(6)	1872	3197	5024	85
H(7)	1274	3764	6176	74
H(9A)	2494	4149	8416	70
H(9B)	1398	4236	7496	70
H(10)	5154	4904	8226	57
H(12)	734	4993	6521	67
H(13)	1050	5430	5252	79
H(14)	4454	5813	4978	87
H(15)	7545	5773	5974	86
H(16)	7265	5329	7239	71
H(18A)	5657	5767	9349	75
H(18B)	3930	6254	9554	75
H(19)	4255	5939	8031	61
H(21)	-270	6320	9219	94
H(22)	-3226	6953	8758	115
H(23)	-3425	7354	7455	118
H(24)	-752	7136	6586	111
H(25)	2124	6488	7020	87
H(3)	909	4788	9153	65

Table S8. Hydrogen coordinates (x10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

C(1)-C(2)	1.365(5)	C(13)-H(13)	0.93
C(1)-N(1)	1.371(4)	C(14)-C(15)	1.374(5)
C(1)-H(1)	0.93	C(14)-H(14)	0.93
C(2)-C(3)	1.413(5)	C(15)-C(16)	1.387(5)
C(2)-H(2)	0.93	C(15)-H(15)	0.93
C(3)-C(4)	1.405(5)	C(16)-H(16)	0.93
C(3)-C(8)	1.412(4)	C(17)-O(1)	1.228(3)
C(4)-C(5)	1.369(5)	C(17)-N(3)	1.336(4)
C(4)-H(4)	0.93	C(17)-C(18)	1.507(4)
C(5)-C(6)	1.393(5)	C(18)-C(19)	1.531(4)
C(5)-Br(1)	1.909(3)	C(18)-H(18A)	0.97
C(6)-C(7)	1.389(5)	C(18)-H(18B)	0.97
C(6)-H(6)	0.93	C(19)-C(20)	1.502(4)
C(7)-C(8)	1.391(5)	C(19)-N(2)	1.520(3)
C(7)-H(7)	0.93	C(19)-H(19)	0.98
C(8)-N(1)	1.375(4)	C(20)-C(21)	1.388(4)
C(9)-N(1)	1.459(4)	C(20)-C(25)	1.390(5)
C(9)-C(10)	1.534(4)	C(21)-C(22)	1.405(6)
C(9)-H(9A)	0.97	C(21)-H(21)	0.93
C(9)-H(9B)	0.97	C(22)-C(23)	1.369(8)
C(10)-N(2)	1.491(3)	C(22)-H(22)	0.93
C(10)-C(11)	1.514(3)	C(23)-C(24)	1.368(8)
C(10)-H(10)	0.98	C(23)-H(23)	0.93
C(11)-C(12)	1.385(4)	C(24)-C(25)	1.389(6)
C(11)-C(16)	1.387(4)	C(24)-H(24)	0.93
C(12)-C(13)	1.390(4)	C(25)-H(25)	0.93
C(12)-H(12)	0.93	N(2)-N(3)	1.440(3)
C(13)-C(14)	1.366(5)	N(3)-H(3)	0.86

Table S9. Bond lengths (Å)

C(2)-C(1)-N(1)	110.2(3)	C(11)-C(10)-C(9)	112.7(2)	C(20)-C(19)-C(18)	116.1(2)
C(2)-C(1)-H(1)	124.9	N(2)-C(10)-H(10)	109.2	N(2)-C(19)-C(18)	104.3(2)
N(1)-C(1)-H(1)	124.9	C(11)-C(10)-H(10)	109.2	C(20)-C(19)-H(19)	109.2
C(1)-C(2)-C(3)	106.5(3)	C(9)-C(10)-H(10)	109.2	N(2)-C(19)-H(19)	109.2
C(1)-C(2)-H(2)	126.7	C(12)-C(11)-C(16)	118.2(3)	C(18)-C(19)-H(19)	109.2
C(3)-C(2)-H(2)	126.7	C(12)-C(11)-C(10)	120.7(2)	C(21)-C(20)-C(25)	118.4(3)
C(4)-C(3)-C(8)	119.7(3)	C(16)-C(11)-C(10)	120.9(2)	C(21)-C(20)-C(19)	122.9(3)
C(4)-C(3)-C(2)	132.6(3)	C(11)-C(12)-C(13)	121.0(3)	C(25)-C(20)-C(19)	118.7(3)
C(8)-C(3)-C(2)	107.7(3)	C(11)-C(12)-H(12)	119.5	C(20)-C(21)-C(22)	119.9(4)
C(5)-C(4)-C(3)	117.2(3)	C(13)-C(12)-H(12)	119.5	C(20)-C(21)-H(21)	120.1
C(5)-C(4)-H(4)	121.4	C(14)-C(13)-C(12)	120.0(3)	C(22)-C(21)-H(21)	120.1
C(3)-C(4)-H(4)	121.4	C(14)-C(13)-H(13)	120	C(23)-C(22)-C(21)	120.0(4)
C(4)-C(5)-C(6)	123.6(3)	C(12)-C(13)-H(13)	120	C(23)-C(22)-H(22)	120
C(4)-C(5)-Br(1)	117.6(3)	C(13)-C(14)-C(15)	119.9(3)	C(21)-C(22)-H(22)	120
C(6)-C(5)-Br(1)	118.8(3)	C(13)-C(14)-H(14)	120	C(24)-C(23)-C(22)	121.0(4)
C(7)-C(6)-C(5)	120.0(3)	C(15)-C(14)-H(14)	120	C(24)-C(23)-H(23)	119.5
C(7)-C(6)-H(6)	120	C(14)-C(15)-C(16)	120.3(3)	C(22)-C(23)-H(23)	119.5
C(5)-C(6)-H(6)	120	C(14)-C(15)-H(15)	119.8	C(23)-C(24)-C(25)	119.2(5)
C(6)-C(7)-C(8)	117.5(3)	C(16)-C(15)-H(15)	119.8	C(23)-C(24)-H(24)	120.4
C(6)-C(7)-H(7)	121.2	C(15)-C(16)-C(11)	120.6(3)	C(25)-C(24)-H(24)	120.4
C(8)-C(7)-H(7)	121.2	C(15)-C(16)-H(16)	119.7	C(24)-C(25)-C(20)	121.5(4)
N(1)-C(8)-C(7)	130.9(3)	C(11)-C(16)-H(16)	119.7	C(24)-C(25)-H(25)	119.3
N(1)-C(8)-C(3)	107.0(3)	O(1)-C(17)-N(3)	125.2(3)	C(20)-C(25)-H(25)	119.3
C(7)-C(8)-C(3)	122.0(3)	O(1)-C(17)-C(18)	127.0(3)	C(1)-N(1)-C(8)	108.6(3)
N(1)-C(9)-C(10)	111.4(2)	N(3)-C(17)-C(18)	107.7(2)	C(1)-N(1)-C(9)	123.5(3)
N(1)-C(9)-H(9A)	109.4	C(17)-C(18)-C(19)	102.9(2)	C(8)-N(1)-C(9)	127.8(3)
C(10)-C(9)-H(9A)	109.4	C(17)-C(18)-H(18A)	111.2	N(3)-N(2)-C(10)	110.8(2)
N(1)-C(9)-H(9B)	109.4	C(19)-C(18)-H(18A)	111.2	N(3)-N(2)-C(19)	102.93(19)
C(10)-C(9)-H(9B)	109.4	C(17)-C(18)-H(18B)	111.2	C(10)-N(2)-C(19)	110.57(18)
H(9A)-C(9)-H(9B)	108	C(19)-C(18)-H(18B)	111.2	C(17)-N(3)-N(2)	115.0(2)
N(2)-C(10)-C(11)	106.9(2)	H(18A)-C(18)-H(18B)	109.1	C(17)-N(3)-H(3)	122.5
N(2)-C(10)-C(9)	109.5(2)	C(20)-C(19)-N(2)	108.7(2)	N(2)-N(3)-H(3)	122.5

Table S10. Angles (°)

	U11	U22	U33	U23	U13	U12
C(1)	77(2)	55(2)	75(2)	2(1)	2(2)	1(1)
C(2)	67(2)	57(2)	90(2)	-1(2)	3(2)	6(1)
C(3)	63(2)	42(1)	77(2)	6(1)	20(1)	-1(1)
C(4)	75(2)	50(2)	79(2)	4(1)	30(2)	6(1)
C(5)	104(2)	49(2)	62(2)	3(1)	28(2)	7(2)
C(6)	92(2)	60(2)	59(2)	5(1)	10(2)	1(2)
C(7)	67(2)	53(2)	66(2)	7(1)	14(1)	3(1)
C(8)	63(2)	41(1)	62(2)	7(1)	20(1)	-5(1)
C(9)	67(2)	50(1)	62(2)	1(1)	26(1)	-4(1)
C(10)	47(1)	49(1)	50(1)	0(1)	13(1)	-2(1)
C(11)	47(1)	46(1)	51(1)	-3(1)	17(1)	-2(1)
C(12)	51(1)	62(2)	56(2)	-1(1)	13(1)	-7(1)
C(13)	75(2)	71(2)	53(2)	1(1)	7(1)	-1(2)
C(14)	89(2)	73(2)	60(2)	8(1)	29(2)	-5(2)
C(15)	63(2)	80(2)	77(2)	6(2)	33(2)	-12(2)
C(16)	48(1)	67(2)	65(2)	0(1)	19(1)	-4(1)
C(17)	50(1)	73(2)	51(1)	-4(1)	13(1)	-9(1)
C(18)	59(2)	73(2)	57(2)	-6(1)	13(1)	-18(1)
C(19)	51(1)	51(1)	53(1)	-6(1)	18(1)	-9(1)
C(20)	57(1)	46(1)	71(2)	-14(1)	19(1)	-7(1)
C(21)	77(2)	61(2)	104(3)	-9(2)	43(2)	-2(2)
C(22)	74(2)	68(2)	154(5)	-30(3)	48(3)	-2(2)
C(23)	81(2)	63(2)	147(5)	-23(3)	-1(3)	11(2)
C(24)	108(3)	68(2)	96(3)	-11(2)	-10(2)	13(2)
C(25)	85(2)	61(2)	71(2)	-10(2)	7(2)	9(2)
Br(1)	165(1)	91(1)	70(1)	-6(1)	27(1)	37(1)
N(1)	67(1)	45(1)	64(1)	2(1)	15(1)	1(1)
N(2)	50(1)	48(1)	47(1)	-1(1)	17(1)	-7(1)
N(3)	55(1)	61(1)	49(1)	0(1)	18(1)	-12(1)
O(1)	68(1)	103(2)	47(1)	-3(1)	12(1)	-21(1)

*Table S11. Anisotropic displacement parameters (Å² x 10^3) The anisotropic displacement factor exponent takes the form: -2 π^2 [h² a*² U11 + ... + 2 h k a* b* U12]*

N(1)-C(1)-C(2)-C(3)	0.2(4)	C(17)-C(18)-C(19)-N(2)	-26.4(3)
C(1)-C(2)-C(3)-C(4)	-179.4(3)	N(2)-C(19)-C(20)-C(21)	80.6(3)
C(1)-C(2)-C(3)-C(8)	-0.1(4)	C(18)-C(19)-C(20)-C(21)	-36.5(4)
C(8)-C(3)-C(4)-C(5)	-1.2(4)	N(2)-C(19)-C(20)-C(25)	-97.3(3)
C(2)-C(3)-C(4)-C(5)	178.0(3)	C(18)-C(19)-C(20)-C(25)	145.5(3)
C(3)-C(4)-C(5)-C(6)	-0.4(5)	C(25)-C(20)-C(21)-C(22)	2.4(5)
C(3)-C(4)-C(5)-Br(1)	179.7(2)	C(19)-C(20)-C(21)-C(22)	-175.6(3)
C(4)-C(5)-C(6)-C(7)	1.1(5)	C(20)-C(21)-C(22)-C(23)	-1.8(6)
Br(1)-C(5)-C(6)-C(7)	-179.0(2)	C(21)-C(22)-C(23)-C(24)	0.1(7)
C(5)-C(6)-C(7)-C(8)	-0.1(5)	C(22)-C(23)-C(24)-C(25)	0.9(7)
C(6)-C(7)-C(8)-N(1)	-177.9(3)	C(23)-C(24)-C(25)-C(20)	-0.3(6)
C(6)-C(7)-C(8)-C(3)	-1.5(4)	C(21)-C(20)-C(25)-C(24)	-1.4(5)
C(4)-C(3)-C(8)-N(1)	179.3(3)	C(19)-C(20)-C(25)-C(24)	176.7(3)
C(2)-C(3)-C(8)-N(1)	0.0(3)	C(2)-C(1)-N(1)-C(8)	-0.2(4)
C(4)-C(3)-C(8)-C(7)	2.2(4)	C(2)-C(1)-N(1)-C(9)	-177.0(3)
C(2)-C(3)-C(8)-C(7)	-177.2(3)	C(7)-C(8)-N(1)-C(1)	177.0(3)
N(1)-C(9)-C(10)-N(2)	-175.5(2)	C(3)-C(8)-N(1)-C(1)	0.1(3)
N(1)-C(9)-C(10)-C(11)	65.8(3)	C(7)-C(8)-N(1)-C(9)	-6.5(5)
N(2)-C(10)-C(11)-C(12)	-60.7(3)	C(3)-C(8)-N(1)-C(9)	176.7(3)
C(9)-C(10)-C(11)-C(12)	59.6(3)	C(10)-C(9)-N(1)-C(1)	69.6(4)
N(2)-C(10)-C(11)-C(16)	113.5(3)	C(10)-C(9)-N(1)-C(8)	-106.5(3)
C(9)-C(10)-C(11)-C(16)	-126.1(3)	C(11)-C(10)-N(2)-N(3)	-179.77(19)
C(16)-C(11)-C(12)-C(13)	-0.5(4)	C(9)-C(10)-N(2)-N(3)	57.9(3)
C(10)-C(11)-C(12)-C(13)	173.9(3)	C(11)-C(10)-N(2)-C(19)	-66.3(3)
C(11)-C(12)-C(13)-C(14)	0.2(5)	C(9)-C(10)-N(2)-C(19)	171.4(2)
C(12)-C(13)-C(14)-C(15)	-0.3(5)	C(20)-C(19)-N(2)-N(3)	-101.0(2)
C(13)-C(14)-C(15)-C(16)	0.7(6)	C(18)-C(19)-N(2)-N(3)	23.5(2)
C(14)-C(15)-C(16)-C(11)	-1.0(5)	C(20)-C(19)-N(2)-C(10)	140.6(2)
C(12)-C(11)-C(16)-C(15)	0.9(4)	C(18)-C(19)-N(2)-C(10)	-94.9(2)
C(10)-C(11)-C(16)-C(15)	-173.5(3)	O(1)-C(17)-N(3)-N(2)	171.9(3)
O(1)-C(17)-C(18)-C(19)	-157.1(3)	C(18)-C(17)-N(3)-N(2)	-5.2(3)
N(3)-C(17)-C(18)-C(19)	20.0(3)	C(10)-N(2)-N(3)-C(17)	106.3(3)
C(17)-C(18)-C(19)-C(20)	93.2(3)	C(19)-N(2)-N(3)-C(17)	-12.0(3)

Table S12. Torsion angles (°)

h	k	l	2θ/°	d/Å	I/rel.	|F(hkl)|
0	1	1	6.70	13.18	11.54	23.84
0	0	2	10.99	8.04	3.83	31.98
0	1	2	11.65	7.59	8.35	35.38
0	3	1	12.79	6.92	14.84	51.86
0	2	2	13.43	6.59	20.97	64.77
1	0	0	14.99	5.91	100.00	223.69
0	4	0	15.41	5.75	27.31	120.25
1	1	0	15.48	5.72	7.55	44.91
-1	1	1	15.84	5.59	8.75	49.49
0	3	2	15.97	5.55	3.86	33.16
0	4	1	16.37	5.41	8.29	49.84
1	2	0	16.87	5.25	12.37	62.76
1	1	1	17.01	5.21	51.48	129.16
-1	2	1	17.20	5.15	69.18	151.41
-1	0	2	17.56	5.05	13.61	97.02
-1	1	2	17.98	4.93	15.81	75.76
0	2	3	18.25	4.86	6.92	50.88
1	2	1	18.29	4.85	3.35	35.46
1	3	0	18.96	4.68	3.95	39.98
0	4	2	18.97	4.67	58.87	154.49
-1	2	2	19.19	4.62	21.55	94.60
-1	3	1	19.26	4.61	29.68	111.39
1	0	2	19.64	4.52	10.62	96.16
0	5	1	20.08	4.42	3.41	39.43
0	3	3	20.20	4.39	3.64	41.00
1	3	1	20.24	4.38	15.33	84.28
1	2	2	21.12	4.20	76.53	196.80
-1	1	3	21.39	4.15	4.81	50.02
1	4	0	21.56	4.12	17.71	96.75
-1	4	1	21.82	4.07	4.71	50.51
0	0	4	22.09	4.02	2.51	52.81
0	5	2	22.26	3.99	51.13	169.94
-1	2	3	22.43	3.96	6.46	60.86
0	1	4	22.43	3.96	11.65	81.77
0	4	3	22.67	3.92	30.32	133.36
1	4	1	22.70	3.91	25.89	123.40
0	2	4	23.42	3.79	4.58	53.63
-1	4	2	23.44	3.79	12.38	88.25
0	6	1	23.86	3.73	12.86	91.66
1	5	0	24.52	3.63	9.31	80.24
-1	5	1	24.76	3.59	7.04	70.49
1	2	3	24.91	3.57	2.91	45.60
0	3	4	24.99	3.56	7.36	72.78

1	4	2	25.06	3.55	5.80	64.78
0	5	3	25.51	3.49	3.41	50.63
-1	1	4	25.59	3.48	11.94	95.04
0	6	2	25.74	3.46	30.26	152.24
-1	4	3	26.18	3.40	7.90	79.18
-1	5	2	26.20	3.40	50.34	200.06
1	5	2	27.67	3.22	4.16	60.92
1	6	0	27.74	3.21	23.77	146.03
-1	3	4	27.88	3.20	8.67	88.69
1	0	4	28.24	3.16	9.29	131.60
1	1	4	28.51	3.13	4.32	64.10
0	6	3	28.62	3.12	2.22	46.12
-1	6	2	29.25	3.05	14.93	122.44
0	5	4	29.49	3.03	8.12	91.10

*Table S13. Calculated reflections from PowderCell**

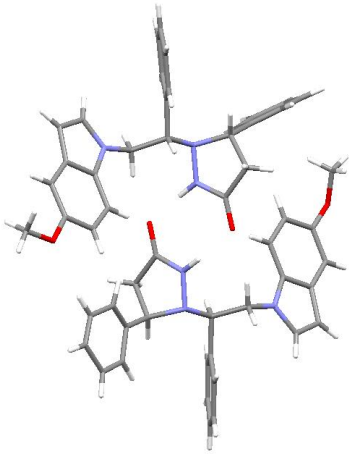
Source: Cu-$K_{\alpha 1}$ (λ = 1.540598 Å)

Condition on reflections: I ≥ 2

Range (2θ): From 3° to 30°

*PowderCell for Windows (version 2.4) by Kraus W. & Nolze G., Federal institute for materials Research and testing, Rudower Chausse 5, 12489 Berlin Germany.

1-(2-(5-bromo-1*H*-indol-1-yl)-1-phenylethyl)-5-phenylpyrazolidin-3-one (3ab)



Data collection

The crystal structure of **3ac** [$C_{26}H_{25}N_3O_2$] has been determined from single crystal X-Ray diffraction. The chosen crystal was stuck on a glass fibre and mounted on a kappa goniometer of a Bruker D8-VENTURE diffractometer equipped with a PHOTON area detector. A series of exposures were recorded, see Table S15-16. The cell parameters and the orientation matrix of the crystal were preliminary determined by using APEX Software[1]. Data integration and global cell refinement were performed with SAINT Software[2]. Intensities were corrected for Lorentz, polarisation, decay and absorption effects (SADABS Software[2]) and reduced to F_O^2. The program package WinGX[3] was used for space group determination, structure solution and refinement.

Data refinement

The standard space group $P2_1/c$ (n°14) was determined from systematic extinctions and relative F_O^2 of equivalent reflections. The structure was solved by direct methods[4]. Anisotropic displacement parameters were refined for all non-hydrogen atoms. Every Hydrogen atoms were located from subsequent difference Fourier syntheses and placed with geometrical constraints (SHELXL[4]). The final cycle of full-matrix least-square refinement on F^2 was based on 4737 observed reflections and 271 variable parameters and converged with unweighted and weighted agreement factors of: R1 = 0.0668, wR2 = 0.2173 for 4228 reflections with $I>2\sigma I$ and R1 = 0.0712, wR2 = 0.2220 for all data.

Crystallographic data

The crystal data are collected in Table S14. The full crystallographic parameters (atomic coordinates, bond length, angles and anisotropic displacements) are reported in Table S17-23.

Chemical Formula	$C_{26}H_{25}N_3O_2$
Molecular Weight / $g.mol^{-1}$	411.49
Crystal System	Monoclinic
Space Group	P21/c
Z , Z' (asymmetric units per unit cell)	4,1
a / *Å*	16.9362(3)
b / *Å*	10.0156(2)
c / *Å*	27.6433(5)
α / °	90
β / °	106.283(1)
γ / °	90
V / $Å^3$	4500.9(2)
d_{calc} / $g.cm^{-3}$	1.214
F(000) / e^-	1744
Absorption coefficient μ (MoKα_1) / mm^{-1}	0.619

Table S14. Crystal data

Structural description

The asymmetric unit is composed of one molecule (figures S7 and S8). The stereogenic centers C10 and C19 are RR (on the figure). The compound crystallizes in a centrosymmetric space group so both enantiomers are present in the solid.

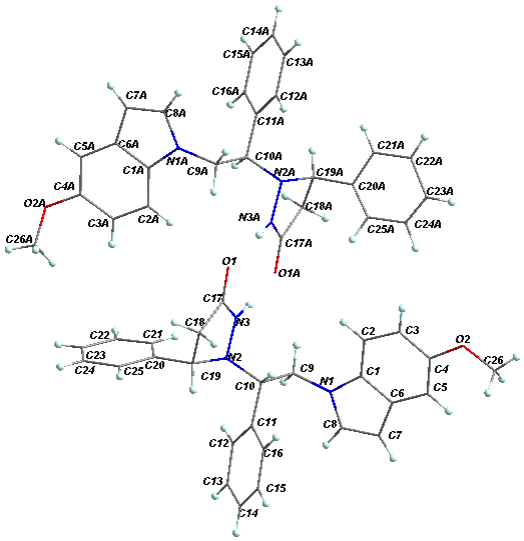


Figure S11. Asymmetric unit with atoms labels

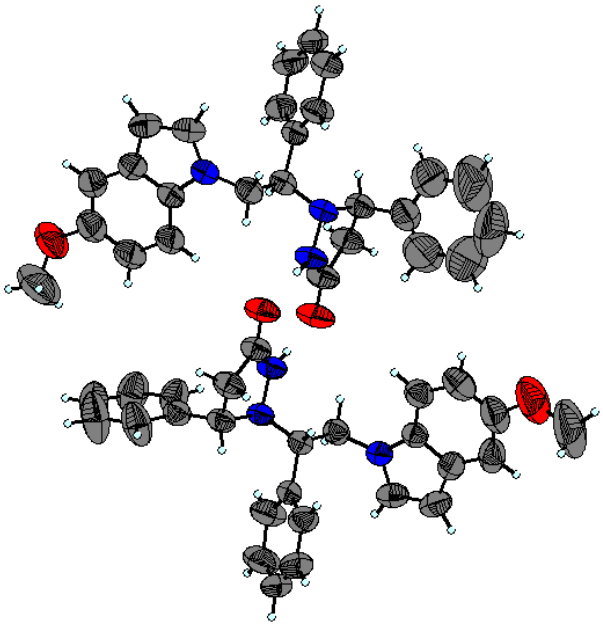


Figure S12. Asymmetric unit in thermal allipsoidal representation (50% of probability)

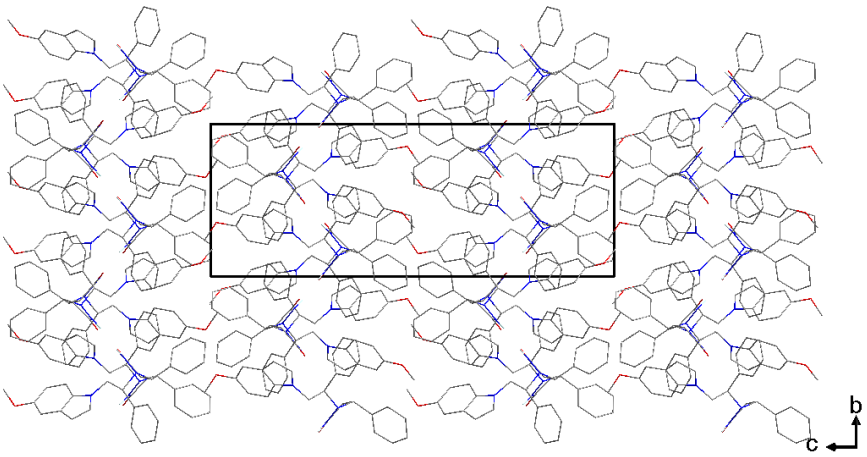


Figure S13. Projection along a axis

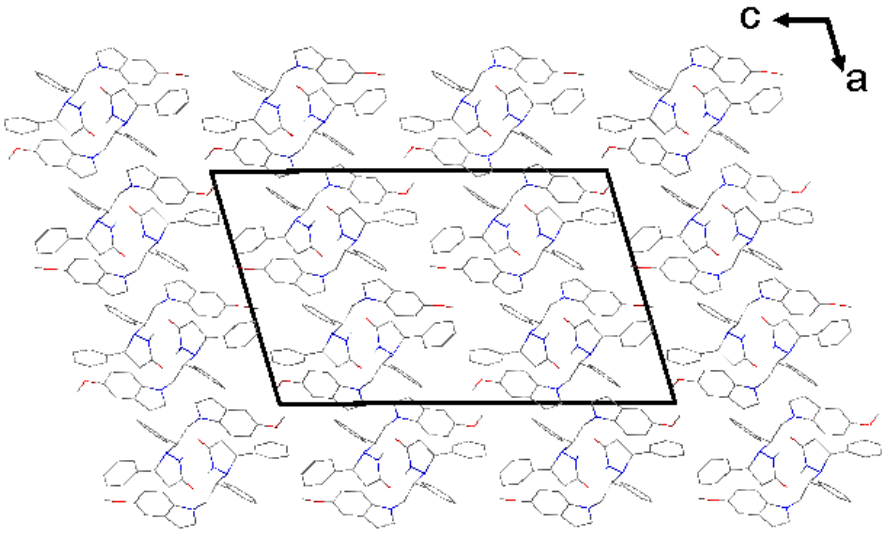


Figure S14. Projection along b axis

Sofwares :

(1)- APEX. V2022.10-1

(2)- SAINT V8.40B Bruker AXS LLC.219

- SADABS – 2016/2 – Bruker AXS area detector scaling and absorption correction

(3)- WinGX: Version 2023.1: An integrated system of Windows Programs for the solution, refinement and analysis of Single Crystal X-Ray Diffraction Data, By LouisJ. Farrugia, Dept. of chemistry, University of Glasgow. L. J. Farrugia (2012) J. Appl. Cryst. 45, 849-854.

(4)-include in WinGX suite :

- SIR 92: A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, J. Appl. Crystallogr., 1994, 27, 435.;

- SHELX & SHELXTL program: G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112-122..

(6)-PowderCell for Windows (version 2.4) by Kraus W. & Nolze G., Federal institute for materials Research and testing, Rudower Chausse 5, 12489 Berlin Germany.

Axis	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames
Phi	55	0	0	54.74	1	180
Phi	55	0	180	54.74	1	180
Omega	-48.14	-45.55	102	44.5	0.5	216
Omega	109.52	-5.2	120	65.5	0.5	245
Phi	109.52	14.28	-194.34	22	0.5	361
Omega	-48.14	-153.55	0	44.5	0.5	216
Omega	109.52	-1.24	252	68.5	0.5	162
Omega	109.52	-1.24	180	68.5	0.5	162
Omega	-48.14	-55.86	0	-65.5	0.5	192
Omega	109.52	215.37	40	-44.5	0.5	216
Omega	109.52	-5.2	160	65.5	0.5	245
Omega	109.52	107.37	80	-44.5	0.5	216
Omega	109.52	-5.2	40	65.5	0.5	245
Omega	109.52	215.37	160	-44.5	0.5	216
Omega	109.52	-5.2	80	65.5	0.5	245
Omega	109.52	107.37	-120	-44.5	0.5	216
Omega	109.52	107.37	-40	-44.5	0.5	216
Omega	-48.14	-153.55	51	44.5	0.5	216
Omega	109.52	-5.2	-160	65.5	0.5	245
Omega	109.52	-5.2	-120	65.5	0.5	245
Omega	109.52	107.37	-80	-44.5	0.5	216
Omega	109.52	215.37	0	-44.5	0.5	216
Omega	109.52	79.76	108	68.5	0.5	162
Omega	109.52	-1.24	324	68.5	0.5	162
Omega	109.52	117.3	-80	65.5	0.5	245
Omega	109.52	-5.2	-40	65.5	0.5	245
Phi	-48.14	-39.51	0	22	0.5	720
Omega	109.52	107.37	120	-44.5	0.5	216
Phi	-48.14	-45.55	0	44.5	0.5	720
Omega	109.52	107.37	-160	-44.5	0.5	216
Omega	109.52	-5.2	0	65.5	0.5	245
Phi	-48.14	-39.51	0	22	0.5	720
Phi	109.52	100.89	0	-22	0.5	720

Unique reflections [$F_o > 4.0\ \sigma(F_o)$]	9831 / 6271
θ range / °	2.718 to 810112
hkl range	-21≤ h≤ 21; -12≤ k≤ 10; -35 ≤ l ≤35
$R_{int} = \Sigma[\lvert F_O^2 - F_O^2(mean)\rvert] / \Sigma[F_O^2]$	0.074
Completeness to θ = 26.40 / %	100.0

Table S15. Data collection. Scan parameters : D=40;045 mm, λ = 1.54184Å

$R_1 = \Sigma (| |F_O| - |F_C| |) / \Sigma |F_O|$

$wR_2 = [\Sigma [w (F_O^2 - F_C^2)^2] / \Sigma [w (F_O^2)^2]]^{1/2}$

$GooF = [\Sigma [w (F_O^2 - F_C^2)^2] / (n - p)]^{1/2}$

Number of reflections (n) (with $F_O > 4.0\ \sigma(F_O)$)	6271
Number of refined parameters (p) / restraints	562
Final R indices [I>2sigma(I)]	R1 = 0.0714, wR2 = 0.2213
R indices (all data)	R1 = 0.1017, wR2 = 0.2454
Goodness of Fit indicator (Restrained GooF)	1.040
Maximum peak in Final Difference Map / $e^-Å^{-3}$	0.498
Maximum hole in Final Difference Map / $e^-Å^{-3}$	-0.286

Table S16. Refinement data

	x	y	z	U(eq)
C(1)	9225(1)	210(2)	8348(1)	59(1)
C(2)	8642(2)	812(3)	8542(1)	77(1)
C(3)	8600(2)	415(4)	9010(1)	101(1)
C(4)	9116(3)	-557(4)	9281(1)	104(1)
C(5)	9711(2)	-1150(3)	9100(1)	94(1)
C(6)	9764(2)	-765(2)	8624(1)	68(1)
C(7)	10269(2)	-1159(2)	8317(1)	81(1)
C(8)	10036(1)	-446(2)	7887(1)	73(1)
C(9)	9026(2)	1355(2)	7512(1)	63(1)
C(10)	8280(1)	789(2)	7109(1)	58(1)
C(11)	8544(1)	-332(2)	6820(1)	59(1)
C(12)	9026(2)	-88(3)	6505(1)	94(1)
C(13)	9312(3)	-1161(4)	6275(1)	111(1)
C(14)	9095(2)	-2454(3)	6362(1)	99(1)
C(15)	8615(2)	-2673(3)	6664(1)	100(1)
C(16)	8343(2)	-1631(2)	6893(1)	79(1)
C(17)	6748(1)	2783(2)	6970(1)	66(1)
C(18)	6432(2)	1723(3)	6577(1)	73(1)
C(19)	7160(1)	1534(2)	6354(1)	63(1)
C(20)	7095(1)	2414(2)	5899(1)	69(1)
C(21)	7588(2)	3512(3)	5902(1)	94(1)
C(22)	7533(2)	4270(4)	5471(1)	113(1)
C(23)	6966(3)	3960(4)	5035(1)	117(1)
C(24)	6465(3)	2889(5)	5021(1)	147(2)
C(25)	6539(3)	2105(4)	5449(1)	119(1)
C(26)	9470(5)	-1823(7)	10036(2)	233(4)
N(1)	9405(1)	396(2)	7898(1)	60(1)
N(2)	7900(1)	1906(2)	6772(1)	57(1)
N(3)	7561(1)	2843(2)	7053(1)	65(1)
O(1)	6349(1)	3488(2)	7180(1)	82(1)
O(2)	8997(3)	-841(4)	9745(1)	170(2)

Table S17-1. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1A)	5661(1)	7867(2)	6574(1)	62(1)
C(2A)	6208(2)	7084(3)	6406(1)	84(1)
C(3A)	6256(2)	7316(4)	5924(1)	99(1)
C(4A)	5770(2)	8290(3)	5615(1)	90(1)
C(5A)	5232(2)	9057(3)	5782(1)	78(1)
C(6A)	5165(1)	8847(2)	6269(1)	66(1)
C(7A)	4664(2)	9391(2)	6552(1)	76(1)
C(8A)	4859(2)	8754(2)	7002(1)	73(1)
C(9A)	5796(2)	6901(2)	7431(1)	65(1)
C(10A)	6578(1)	7456(2)	7805(1)	59(1)
C(11A)	6364(1)	8606(2)	8098(1)	62(1)
C(12A)	5901(2)	8430(3)	8430(1)	86(1)
C(13A)	5708(2)	9517(3)	8688(1)	99(1)
C(14A)	5974(2)	10773(3)	8604(1)	94(1)
C(15A)	6405(2)	10957(3)	8272(1)	95(1)
C(16A)	6599(2)	9888(2)	8020(1)	78(1)
C(17A)	8096(1)	5504(2)	7893(1)	70(1)
C(18A)	8432(2)	6614(3)	8259(1)	76(1)
C(19A)	7764(1)	6774(2)	8530(1)	68(1)
C(20A)	7896(2)	5920(3)	8991(1)	91(1)
C(21A)	7648(4)	6419(6)	9381(2)	168(2)
C(22A)	7751(6)	5649(10)	9823(2)	234(4)
C(23A)	8184(6)	4392(9)	9861(3)	211(4)
C(24A)	8369(9)	4052(8)	9499(3)	332(8)
C(25A)	8181(8)	4746(6)	9053(2)	295(6)
C(26A)	5900(5)	7425(7)	4853(2)	211(3)
N(1A)	5461(1)	7826(2)	7022(1)	64(1)
N(2A)	6983(1)	6352(2)	8144(1)	61(1)
N(3A)	7293(1)	5402(2)	7853(1)	68(1)
O(1A)	8480(1)	4787(2)	7677(1)	88(1)
O(2A)	5812(2)	8526(3)	5133(1)	130(1)

Table S17-2. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
H(2)	8290	1464	8361	92
H(3)	8214	810	9147	121
H(5)	10066	-1786	9289	113
H(7)	10685	-1795	8399	97
H(8)	10271	-516	7621	88
H(9A)	9432	1659	7350	76
H(9B)	8851	2122	7670	76
H(10)	7881	441	7274	69
H(12)	9163	783	6445	112
H(13)	9647	-1005	6066	133
H(14)	9283	-3169	6210	119
H(15)	8465	-3541	6718	119
H(16)	8014	-1805	7104	95
H(18A)	5945	2023	6322	88
H(18B)	6307	903	6727	88
H(19)	7198	595	6262	76
H(21)	7970	3756	6202	113
H(22)	7886	4988	5483	135
H(23)	6918	4472	4748	141
H(24)	6069	2678	4723	177
H(25)	6204	1359	5428	143
H(26A)	9332	-2672	9874	349
H(26B)	9367	-1843	10361	349
H(26C)	10042	-1637	10078	349
H(3B)	7863	3402	7261	78

Table S18-1. Hydrogen coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
H(2A)	6527	6433	6610	101
H(3A)	6619	6815	5801	119
H(5A)	4916	9707	5575	94
H(7A)	4273	10062	6448	91
H(8A)	4618	8922	7259	88
H(9A1)	5925	6064	7293	78
H(9A2)	5386	6722	7607	78
H(10A)	6952	7775	7617	71
H(12A)	5717	7582	8481	103
H(13A)	5400	9397	8915	119
H(14A)	5854	11499	8781	112
H(15A)	6573	11810	8212	114
H(16A)	6898	10030	7789	93
H(18C)	8501	7428	8085	91
H(18D)	8955	6368	8493	91
H(19A)	7724	7714	8619	81
H(21A)	7412	7263	9358	201
H(22A)	7545	5943	10082	281
H(23A)	8310	3882	10154	253
H(24A)	8662	3260	9517	398
H(25A)	8270	4318	8775	355
H(26D)	6435	7040	4993	316
H(26E)	5842	7691	4511	316
H(26F)	5485	6778	4860	316
H(3A1)	6985	4811	7666	81

Table S18-2. Hydrogen coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

C(1)-N(1)	1.374(3)	C(14)-H(14)	0.93
C(1)-C(2)	1.387(3)	C(15)-C(16)	1.367(4)
C(1)-C(6)	1.407(3)	C(15)-H(15)	0.93
C(2)-C(3)	1.375(4)	C(16)-H(16)	0.93
C(2)-H(2)	0.93	C(17)-O(1)	1.229(3)
C(3)-C(4)	1.381(5)	C(17)-N(3)	1.333(3)
C(3)-H(3)	0.93	C(17)-C(18)	1.507(3)
C(4)-C(5)	1.378(5)	C(18)-C(19)	1.537(3)
C(4)-O(2)	1.382(4)	C(18)-H(18A)	0.97
C(5)-C(6)	1.399(4)	C(18)-H(18B)	0.97
C(5)-H(5)	0.93	C(19)-N(2)	1.493(3)
C(6)-C(7)	1.417(4)	C(19)-C(20)	1.515(3)
C(7)-C(8)	1.348(4)	C(19)-H(19)	0.98
C(7)-H(7)	0.93	C(20)-C(25)	1.368(4)
C(8)-N(1)	1.368(3)	C(20)-C(21)	1.379(4)
C(8)-H(8)	0.93	C(21)-C(22)	1.394(4)
C(9)-N(1)	1.445(3)	C(21)-H(21)	0.93
C(9)-C(10)	1.540(3)	C(22)-C(23)	1.348(5)
C(9)-H(9A)	0.97	C(22)-H(22)	0.93
C(9)-H(9B)	0.97	C(23)-C(24)	1.361(6)
C(10)-N(2)	1.483(3)	C(23)-H(23)	0.93
C(10)-C(11)	1.516(3)	C(24)-C(25)	1.396(5)
C(10)-H(10)	0.98	C(24)-H(24)	0.93
C(11)-C(12)	1.373(3)	C(25)-H(25)	0.93
C(11)-C(16)	1.374(3)	C(26)-O(2)	1.378(8)
C(12)-C(13)	1.402(4)	C(26)-H(26A)	0.96
C(12)-H(12)	0.93	C(26)-H(26B)	0.96
C(13)-C(14)	1.385(5)	C(26)-H(26C)	0.96
C(13)-H(13)	0.93	N(2)-N(3)	1.437(2)
C(14)-C(15)	1.336(5)	N(3)-H(3B)	0.86

Table S19-1. Bond lengths (Å)

C(1A)-N(1A)	1.374(3)	C(14A)-H(14A)	0.93
C(1A)-C(2A)	1.389(3)	C(15A)-C(16A)	1.366(4)
C(1A)-C(6A)	1.409(3)	C(15A)-H(15A)	0.93
C(2A)-C(3A)	1.377(4)	C(16A)-H(16A)	0.93
C(2A)-H(2A)	0.93	C(17A)-O(1A)	1.231(3)
C(3A)-C(4A)	1.401(5)	C(17A)-N(3A)	1.336(3)
C(3A)-H(3A)	0.93	C(17A)-C(18A)	1.505(3)
C(4A)-C(5A)	1.366(4)	C(18A)-C(19A)	1.529(3)
C(4A)-O(2A)	1.376(4)	C(18A)-H(18C)	0.97
C(5A)-C(6A)	1.397(3)	C(18A)-H(18D)	0.97
C(5A)-H(5A)	0.93	C(19A)-C(20A)	1.500(4)
C(6A)-C(7A)	1.416(3)	C(19A)-N(2A)	1.508(3)
C(7A)-C(8A)	1.353(4)	C(19A)-H(19A)	0.98
C(7A)-H(7A)	0.93	C(20A)-C(25A)	1.264(6)
C(8A)-N(1A)	1.369(3)	C(20A)-C(21A)	1.358(5)
C(8A)-H(8A)	0.93	C(21A)-C(22A)	1.412(8)
C(9A)-N(1A)	1.447(3)	C(21A)-H(21A)	0.93
C(9A)-C(10A)	1.538(3)	C(22A)-C(23A)	1.446(11)
C(9A)-H(9A1)	0.97	C(22A)-H(22A)	0.93
C(9A)-H(9A2)	0.97	C(23A)-C(24A)	1.178(11)
C(10A)-N(2A)	1.487(3)	C(23A)-H(23A)	0.93
C(10A)-C(11A)	1.509(3)	C(24A)-C(25A)	1.373(8)
C(10A)-H(10A)	0.98	C(24A)-H(24A)	0.93
C(11A)-C(12A)	1.375(3)	C(25A)-H(25A)	0.93
C(11A)-C(16A)	1.380(3)	C(26A)-O(2A)	1.378(6)
C(12A)-C(13A)	1.390(4)	C(26A)-H(26D)	0.96
C(12A)-H(12A)	0.93	C(26A)-H(26E)	0.96
C(13A)-C(14A)	1.378(5)	C(26A)-H(26F)	0.96
C(13A)-H(13A)	0.93	N(2A)-N(3A)	1.437(2)
C(14A)-C(15A)	1.337(5)	N(3A)-H(3A1)	0.86

Table S19-2. Bond lengths (Å)

N(1)-C(1)-C(2)	130.9(2)	C(9)-C(10)-H(10)	109.1	C(25)-C(20)-C(21)	116.6(3)
N(1)-C(1)-C(6)	108.01(19)	C(12)-C(11)-C(16)	118.5(2)	C(25)-C(20)-C(19)	119.6(2)
C(2)-C(1)-C(6)	121.1(2)	C(12)-C(11)-C(10)	121.2(2)	C(21)-C(20)-C(19)	123.8(2)
C(3)-C(2)-C(1)	117.9(3)	C(16)-C(11)-C(10)	120.1(2)	C(20)-C(21)-C(22)	122.2(3)
C(3)-C(2)-H(2)	121	C(11)-C(12)-C(13)	119.6(3)	C(20)-C(21)-H(21)	118.9
C(1)-C(2)-H(2)	121	C(11)-C(12)-H(12)	120.2	C(22)-C(21)-H(21)	118.9
C(2)-C(3)-C(4)	121.5(3)	C(13)-C(12)-H(12)	120.2	C(23)-C(22)-C(21)	119.9(3)
C(2)-C(3)-H(3)	119.3	C(14)-C(13)-C(12)	119.7(3)	C(23)-C(22)-H(22)	120.1
C(4)-C(3)-H(3)	119.3	C(14)-C(13)-H(13)	120.1	C(21)-C(22)-H(22)	120.1
C(5)-C(4)-C(3)	121.6(3)	C(12)-C(13)-H(13)	120.1	C(22)-C(23)-C(24)	119.3(3)
C(5)-C(4)-O(2)	124.0(4)	C(15)-C(14)-C(13)	119.9(3)	C(22)-C(23)-H(23)	120.4
C(3)-C(4)-O(2)	114.4(4)	C(15)-C(14)-H(14)	120	C(24)-C(23)-H(23)	120.4
C(4)-C(5)-C(6)	118.0(3)	C(13)-C(14)-H(14)	120	C(23)-C(24)-C(25)	120.8(3)
C(4)-C(5)-H(5)	121	C(14)-C(15)-C(16)	120.5(3)	C(23)-C(24)-H(24)	119.6
C(6)-C(5)-H(5)	121	C(14)-C(15)-H(15)	119.7	C(25)-C(24)-H(24)	119.6
C(5)-C(6)-C(1)	119.9(3)	C(16)-C(15)-H(15)	119.7	C(20)-C(25)-C(24)	121.2(3)
C(5)-C(6)-C(7)	134.0(3)	C(15)-C(16)-C(11)	121.7(3)	C(20)-C(25)-H(25)	119.4
C(1)-C(6)-C(7)	106.1(2)	C(15)-C(16)-H(16)	119.2	C(24)-C(25)-H(25)	119.4
C(8)-C(7)-C(6)	107.8(2)	C(11)-C(16)-H(16)	119.2	O(2)-C(26)-H(26A)	109.5
C(8)-C(7)-H(7)	126.1	O(1)-C(17)-N(3)	124.87(19)	O(2)-C(26)-H(26B)	109.5
C(6)-C(7)-H(7)	126.1	O(1)-C(17)-C(18)	127.9(2)	H(26A)-C(26)-H(26B)	109.5
C(7)-C(8)-N(1)	110.0(2)	N(3)-C(17)-C(18)	107.24(18)	O(2)-C(26)-H(26C)	109.5
C(7)-C(8)-H(8)	125	C(17)-C(18)-C(19)	102.33(17)	H(26A)-C(26)-H(26C)	109.5
N(1)-C(8)-H(8)	125	C(17)-C(18)-H(18A)	111.3	H(26B)-C(26)-H(26C)	109.5
N(1)-C(9)-C(10)	113.20(16)	C(19)-C(18)-H(18A)	111.3	C(8)-N(1)-C(1)	108.08(19)
N(1)-C(9)-H(9A)	108.9	C(17)-C(18)-H(18B)	111.3	C(8)-N(1)-C(9)	125.6(2)
C(10)-C(9)-H(9A)	108.9	C(19)-C(18)-H(18B)	111.3	C(1)-N(1)-C(9)	126.28(17)
N(1)-C(9)-H(9B)	108.9	H(18A)-C(18)-H(18B)	109.2	N(3)-N(2)-C(10)	108.71(16)
C(10)-C(9)-H(9B)	108.9	N(2)-C(19)-C(20)	110.32(17)	N(3)-N(2)-C(19)	101.95(15)
H(9A)-C(9)-H(9B)	107.8	N(2)-C(19)-C(18)	104.62(17)	C(10)-N(2)-C(19)	114.85(16)
N(2)-C(10)-C(11)	111.54(16)	C(20)-C(19)-C(18)	112.4(2)	C(17)-N(3)-N(2)	115.30(16)
N(2)-C(10)-C(9)	107.52(15)	N(2)-C(19)-H(19)	109.8	C(17)-N(3)-H(3B)	122.3
C(11)-C(10)-C(9)	110.55(18)	C(20)-C(19)-H(19)	109.8	N(2)-N(3)-H(3B)	122.3
N(2)-C(10)-H(10)	109.1	C(18)-C(19)-H(19)	109.8	C(26)-O(2)-C(4)	118.5(5)
C(11)-C(10)-H(10)	109.1				

Table S20-1. Angles (°)

N(1A)-C(1A)-C(2A)	129.9(2)	C(11A)-C(10A)-H(10A)	108.9	C(9A)-C(10A)-H(10A)	108.9
N(1A)-C(1A)-C(6A)	107.81(19)	C(12A)-C(11A)-C(10A)	121.8(2)	C(25A)-C(20A)-C(19A)	127.3(4)
C(2A)-C(1A)-C(6A)	122.2(2)	C(16A)-C(11A)-C(10A)	120.2(2)	C(21A)-C(20A)-C(19A)	117.4(3)
C(3A)-C(2A)-C(1A)	117.1(3)	C(11A)-C(12A)-C(13A)	120.2(3)	C(20A)-C(21A)-C(22A)	119.6(6)
C(3A)-C(2A)-H(2A)	121.5	C(11A)-C(12A)-H(12A)	119.9	C(20A)-C(21A)-H(21A)	120.2
C(1A)-C(2A)-H(2A)	121.5	C(13A)-C(12A)-H(12A)	119.9	C(22A)-C(21A)-H(21A)	120.2
C(2A)-C(3A)-C(4A)	121.5(3)	C(14A)-C(13A)-C(12A)	119.6(3)	C(21A)-C(22A)-C(23A)	118.5(6)
C(2A)-C(3A)-H(3A)	119.3	C(14A)-C(13A)-H(13A)	120.2	C(21A)-C(22A)-H(22A)	120.8
C(4A)-C(3A)-H(3A)	119.3	C(12A)-C(13A)-H(13A)	120.2	C(23A)-C(22A)-H(22A)	120.8
C(5A)-C(4A)-O(2A)	116.8(3)	C(15A)-C(14A)-C(13A)	120.6(2)	C(24A)-C(23A)-C(22A)	116.1(7)
C(5A)-C(4A)-C(3A)	121.3(3)	C(15A)-C(14A)-H(14A)	119.7	C(24A)-C(23A)-H(23A)	122
O(2A)-C(4A)-C(3A)	121.9(3)	C(13A)-C(14A)-H(14A)	119.7	C(22A)-C(23A)-H(23A)	122
C(4A)-C(5A)-C(6A)	118.8(3)	C(14A)-C(15A)-C(16A)	119.9(3)	C(23A)-C(24A)-C(25A)	124.5(9)
C(4A)-C(5A)-H(5A)	120.6	C(14A)-C(15A)-H(15A)	120	C(23A)-C(24A)-H(24A)	117.8
C(6A)-C(5A)-H(5A)	120.6	C(16A)-C(15A)-H(15A)	120	C(25A)-C(24A)-H(24A)	117.8
C(5A)-C(6A)-C(1A)	119.1(2)	C(15A)-C(16A)-C(11A)	121.8(3)	C(20A)-C(25A)-C(24A)	125.2(6)
C(5A)-C(6A)-C(7A)	134.3(2)	C(15A)-C(16A)-H(16A)	119.1	C(20A)-C(25A)-H(25A)	117.4
C(1A)-C(6A)-C(7A)	106.6(2)	C(11A)-C(16A)-H(16A)	119.1	C(24A)-C(25A)-H(25A)	117.4
C(8A)-C(7A)-C(6A)	107.3(2)	O(1A)-C(17A)-N(3A)	125.43(19)	O(2A)-C(26A)-H(26D)	109.5
C(8A)-C(7A)-H(7A)	126.4	O(1A)-C(17A)-C(18A)	127.3(2)	O(2A)-C(26A)-H(26E)	109.5
C(6A)-C(7A)-H(7A)	126.4	N(3A)-C(17A)-C(18A)	107.26(18)	H(26D)-C(26A)-H(26E)	109.5
C(7A)-C(8A)-N(1A)	110.2(2)	C(17A)-C(18A)-C(19A)	102.36(18)	O(2A)-C(26A)-H(26F)	109.5
C(7A)-C(8A)-H(8A)	124.9	C(17A)-C(18A)-H(18C)	111.3	H(26D)-C(26A)-H(26F)	109.5
N(1A)-C(8A)-H(8A)	124.9	C(19A)-C(18A)-H(18C)	111.3	H(26E)-C(26A)-H(26F)	109.5
N(1A)-C(9A)-C(10A)	111.69(17)	C(17A)-C(18A)-H(18D)	111.3	C(8A)-N(1A)-C(1A)	108.1(2)
N(1A)-C(9A)-H(9A1)	109.3	C(19A)-C(18A)-H(18D)	111.3	C(8A)-N(1A)-C(9A)	126.3(2)
C(10A)-C(9A)-H(9A1)	109.3	H(18C)-C(18A)-H(18D)	109.2	C(1A)-N(1A)-C(9A)	125.47(18)
N(1A)-C(9A)-H(9A2)	109.3	C(20A)-C(19A)-N(2A)	109.4(2)	N(3A)-N(2A)-C(10A)	108.42(16)
C(10A)-C(9A)-H(9A2)	109.3	C(20A)-C(19A)-C(18A)	113.7(2)	N(3A)-N(2A)-C(19A)	101.26(16)
H(9A1)-C(9A)-H(9A2)	107.9	N(2A)-C(19A)-C(18A)	104.34(17)	C(10A)-N(2A)-C(19A)	113.29(16)
N(2A)-C(10A)-C(11A)	111.58(17)	C(20A)-C(19A)-H(19A)	109.7	C(17A)-N(3A)-N(2A)	115.22(16)
N(2A)-C(10A)-C(9A)	108.31(16)	N(2A)-C(19A)-H(19A)	109.7	C(17A)-N(3A)-H(3A1)	122.4
C(11A)-C(10A)-C(9A)	110.25(18)	C(18A)-C(19A)-H(19A)	109.7	N(2A)-N(3A)-H(3A1)	122.4
N(2A)-C(10A)-H(10A)	108.9	C(25A)-C(20A)-C(21A)	115.2(5)	C(4A)-O(2A)-C(26A)	116.7(3)
C(12A)-C(11A)-C(16A)	117.9(2)				

Table S20-2. Angles (°)

	U11	U22	U33	U23	U13	U12
C(1)	58(1)	57(1)	59(1)	-7(1)	14(1)	-5(1)
C(2)	74(2)	90(2)	70(1)	-6(1)	25(1)	3(1)
C(3)	114(2)	118(2)	82(2)	-15(2)	47(2)	-8(2)
C(4)	153(3)	95(2)	65(2)	0(2)	30(2)	-25(2)
C(5)	123(2)	69(1)	71(2)	3(1)	-4(2)	-16(2)
C(6)	70(1)	53(1)	72(1)	-3(1)	3(1)	-9(1)
C(7)	66(1)	60(1)	105(2)	-11(1)	7(1)	7(1)
C(8)	61(1)	67(1)	95(2)	-13(1)	28(1)	2(1)
C(9)	75(1)	56(1)	59(1)	-5(1)	18(1)	-5(1)
C(10)	65(1)	53(1)	60(1)	-5(1)	25(1)	-4(1)
C(11)	65(1)	56(1)	56(1)	-6(1)	18(1)	1(1)
C(12)	128(2)	73(1)	101(2)	-11(1)	67(2)	2(2)
C(13)	132(3)	116(3)	103(2)	-25(2)	63(2)	17(2)
C(14)	116(2)	80(2)	91(2)	-18(1)	15(2)	40(2)
C(15)	124(3)	58(1)	112(2)	-11(1)	27(2)	14(1)
C(16)	94(2)	56(1)	90(2)	-4(1)	28(1)	1(1)
C(17)	60(1)	65(1)	76(1)	-19(1)	23(1)	-7(1)
C(18)	65(1)	76(1)	81(2)	-26(1)	23(1)	-17(1)
C(19)	63(1)	57(1)	67(1)	-18(1)	17(1)	-4(1)
C(20)	66(1)	68(1)	68(1)	-12(1)	13(1)	2(1)
C(21)	92(2)	81(2)	90(2)	13(1)	-7(2)	-13(1)
C(22)	115(3)	98(2)	110(2)	26(2)	7(2)	-18(2)
C(23)	131(3)	121(3)	84(2)	22(2)	5(2)	-13(2)
C(24)	162(4)	178(4)	74(2)	13(2)	-12(2)	-72(3)
C(25)	137(3)	133(3)	75(2)	-11(2)	8(2)	-61(2)
C(26)	393(12)	200(6)	86(3)	40(3)	35(5)	-60(7)
N(1)	61(1)	59(1)	63(1)	-5(1)	21(1)	2(1)
N(2)	60(1)	52(1)	60(1)	-14(1)	19(1)	0(1)
N(3)	56(1)	62(1)	76(1)	-25(1)	19(1)	-2(1)
O(1)	64(1)	89(1)	101(1)	-37(1)	34(1)	-7(1)
O(2)	276(5)	159(3)	82(2)	15(2)	63(2)	-34(3)

Table S21-1. Anisotropic displacement parameters ($Å^2$ x 10^3) The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
C(1A)	61(1)	64(1)	62(1)	-12(1)	20(1)	-7(1)
C(2A)	80(2)	105(2)	71(2)	-4(1)	28(1)	18(1)
C(3A)	104(2)	123(2)	82(2)	-8(2)	47(2)	25(2)
C(4A)	109(2)	98(2)	71(2)	-3(1)	35(2)	-6(2)
C(5A)	91(2)	67(1)	75(2)	-1(1)	21(1)	-11(1)
C(6A)	70(1)	54(1)	73(1)	-8(1)	19(1)	-13(1)
C(7A)	82(2)	54(1)	97(2)	-6(1)	34(1)	2(1)
C(8A)	74(1)	61(1)	95(2)	-14(1)	41(1)	-3(1)
C(9A)	70(1)	62(1)	65(1)	-11(1)	23(1)	-11(1)
C(10A)	65(1)	57(1)	63(1)	-11(1)	28(1)	-10(1)
C(11A)	63(1)	59(1)	63(1)	-10(1)	19(1)	-1(1)
C(12A)	113(2)	76(1)	85(2)	-7(1)	54(2)	6(1)
C(13A)	118(2)	109(2)	81(2)	-6(2)	45(2)	32(2)
C(14A)	92(2)	83(2)	87(2)	-28(1)	-6(2)	34(2)
C(15A)	86(2)	64(1)	128(3)	-19(2)	20(2)	10(1)
C(16A)	75(2)	62(1)	96(2)	-8(1)	24(1)	-4(1)
C(17A)	61(1)	68(1)	87(2)	-27(1)	31(1)	-13(1)
C(18A)	64(1)	75(1)	91(2)	-30(1)	26(1)	-15(1)
C(19A)	71(1)	64(1)	68(1)	-19(1)	19(1)	-5(1)
C(20A)	100(2)	95(2)	75(2)	-6(1)	20(2)	-7(2)
C(21A)	211(6)	194(5)	119(3)	39(3)	81(4)	68(4)
C(22A)	278(9)	318(11)	133(5)	77(6)	102(6)	39(9)
C(23A)	263(9)	209(8)	142(5)	87(6)	25(6)	6(6)
C(24A)	660(20)	178(7)	165(6)	90(6)	131(11)	175(11)
C(25A)	640(20)	115(4)	124(4)	25(3)	100(7)	125(7)
C(26A)	360(10)	195(6)	115(3)	-14(4)	127(5)	36(6)
N(1A)	67(1)	64(1)	65(1)	-10(1)	26(1)	-5(1)
N(2A)	64(1)	57(1)	66(1)	-17(1)	28(1)	-5(1)
N(3A)	61(1)	62(1)	85(1)	-30(1)	29(1)	-11(1)
O(1A)	66(1)	92(1)	117(1)	-50(1)	42(1)	-15(1)
O(2A)	186(3)	142(2)	77(1)	-1(1)	61(2)	6(2)

Table S21-2. Anisotropic displacement parameters ($Å^2 \times 10^3$) The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

N(1)-C(1)-C(2)-C(3)	179.8(2)	N(2)-C(19)-C(20)-C(25)	169.7(3)
C(6)-C(1)-C(2)-C(3)	-0.8(4)	C(18)-C(19)-C(20)-C(25)	-74.0(3)
C(1)-C(2)-C(3)-C(4)	-0.3(5)	N(2)-C(19)-C(20)-C(21)	-8.2(3)
C(2)-C(3)-C(4)-C(5)	1.6(5)	C(18)-C(19)-C(20)-C(21)	108.1(3)
C(2)-C(3)-C(4)-O(2)	179.9(3)	C(25)-C(20)-C(21)-C(22)	-0.6(5)
C(3)-C(4)-C(5)-C(6)	-1.7(5)	C(19)-C(20)-C(21)-C(22)	177.4(3)
O(2)-C(4)-C(5)-C(6)	-179.9(3)	C(20)-C(21)-C(22)-C(23)	2.1(6)
C(4)-C(5)-C(6)-C(1)	0.6(4)	C(21)-C(22)-C(23)-C(24)	-1.3(7)
C(4)-C(5)-C(6)-C(7)	-178.5(3)	C(22)-C(23)-C(24)-C(25)	-0.8(8)
N(1)-C(1)-C(6)-C(5)	-179.8(2)	C(21)-C(20)-C(25)-C(24)	-1.6(6)
C(2)-C(1)-C(6)-C(5)	0.6(3)	C(19)-C(20)-C(25)-C(24)	-179.6(4)
N(1)-C(1)-C(6)-C(7)	-0.4(2)	C(23)-C(24)-C(25)-C(20)	2.3(8)
C(2)-C(1)-C(6)-C(7)	-180.0(2)	C(7)-C(8)-N(1)-C(1)	-0.4(3)
C(5)-C(6)-C(7)-C(8)	179.5(3)	C(7)-C(8)-N(1)-C(9)	176.88(19)
C(1)-C(6)-C(7)-C(8)	0.2(3)	C(2)-C(1)-N(1)-C(8)	180.0(2)
C(6)-C(7)-C(8)-N(1)	0.1(3)	C(6)-C(1)-N(1)-C(8)	0.5(2)
N(1)-C(9)-C(10)-N(2)	174.05(16)	C(2)-C(1)-N(1)-C(9)	2.8(4)
N(1)-C(9)-C(10)-C(11)	-64.0(2)	C(6)-C(1)-N(1)-C(9)	-176.72(18)
N(2)-C(10)-C(11)-C(12)	51.8(3)	C(10)-C(9)-N(1)-C(8)	91.2(3)
C(9)-C(10)-C(11)-C(12)	-67.8(3)	C(10)-C(9)-N(1)-C(1)	-92.1(2)
N(2)-C(10)-C(11)-C(16)	-132.2(2)	C(11)-C(10)-N(2)-N(3)	172.03(16)
C(9)-C(10)-C(11)-C(16)	108.2(2)	C(9)-C(10)-N(2)-N(3)	-66.6(2)
C(16)-C(11)-C(12)-C(13)	-1.1(5)	C(11)-C(10)-N(2)-C(19)	58.6(2)
C(10)-C(11)-C(12)-C(13)	174.9(3)	C(9)-C(10)-N(2)-C(19)	179.95(16)
C(11)-C(12)-C(13)-C(14)	1.0(6)	C(20)-C(19)-N(2)-N(3)	93.16(19)
C(12)-C(13)-C(14)-C(15)	-0.1(6)	C(18)-C(19)-N(2)-N(3)	-27.9(2)
C(13)-C(14)-C(15)-C(16)	-0.7(5)	C(20)-C(19)-N(2)-C(10)	-149.49(17)
C(14)-C(15)-C(16)-C(11)	0.6(5)	C(18)-C(19)-N(2)-C(10)	89.4(2)
C(12)-C(11)-C(16)-C(15)	0.4(4)	O(1)-C(17)-N(3)-N(2)	179.0(2)
C(10)-C(11)-C(16)-C(15)	-175.7(3)	C(18)-C(17)-N(3)-N(2)	-1.7(3)
O(1)-C(17)-C(18)-C(19)	163.1(3)	C(10)-N(2)-N(3)-C(17)	-102.4(2)
N(3)-C(17)-C(18)-C(19)	-16.3(3)	C(19)-N(2)-N(3)-C(17)	19.3(2)
C(17)-C(18)-C(19)-N(2)	27.4(2)	C(5)-C(4)-O(2)-C(26)	-3.4(6)
C(17)-C(18)-C(19)-C(20)	-92.3(2)	C(3)-C(4)-O(2)-C(26)	178.4(5)

Table S22-1. Torsion angles (°)

N(1A)-C(1A)-C(2A)-C(3A)	177.1(3)	N(2A)-C(19A)-C(20A)-C(25A)	79.1(8)
C(6A)-C(1A)-C(2A)-C(3A)	0.8(4)	C(18A)-C(19A)-C(20A)-C(25A)	-37.1(8)
C(1A)-C(2A)-C(3A)-C(4A)	-0.5(5)	N(2A)-C(19A)-C(20A)-C(21A)	-97.3(4)
C(2A)-C(3A)-C(4A)-C(5A)	0.5(5)	C(18A)-C(19A)-C(20A)-C(21A)	146.5(4)
C(2A)-C(3A)-C(4A)-O(2A)	-179.7(3)	C(25A)-C(20A)-C(21A)-C(22A)	2.5(10)
O(2A)-C(4A)-C(5A)-C(6A)	179.6(3)	C(19A)-C(20A)-C(21A)-C(22A)	179.4(6)
C(3A)-C(4A)-C(5A)-C(6A)	-0.6(4)	C(20A)-C(21A)-C(22A)-C(23A)	5.2(12)
C(4A)-C(5A)-C(6A)-C(1A)	0.8(3)	C(21A)-C(22A)-C(23A)-C(24A)	-5.5(16)
C(4A)-C(5A)-C(6A)-C(7A)	-176.7(3)	C(22A)-C(23A)-C(24A)-C(25A)	-2(2)
N(1A)-C(1A)-C(6A)-C(5A)	-178.0(2)	C(21A)-C(20A)-C(25A)-C(24A)	-10.6(16)
C(2A)-C(1A)-C(6A)-C(5A)	-0.9(3)	C(19A)-C(20A)-C(25A)-C(24A)	173.0(11)
N(1A)-C(1A)-C(6A)-C(7A)	0.1(2)	C(23A)-C(24A)-C(25A)-C(20A)	11(2)
C(2A)-C(1A)-C(6A)-C(7A)	177.2(2)	C(7A)-C(8A)-N(1A)-C(1A)	0.1(3)
C(5A)-C(6A)-C(7A)-C(8A)	177.7(2)	C(7A)-C(8A)-N(1A)-C(9A)	-176.4(2)
C(1A)-C(6A)-C(7A)-C(8A)	-0.1(3)	C(2A)-C(1A)-N(1A)-C(8A)	-176.9(3)
C(6A)-C(7A)-C(8A)-N(1A)	0.0(3)	C(6A)-C(1A)-N(1A)-C(8A)	-0.1(2)
N(1A)-C(9A)-C(10A)-N(2A)	-167.74(16)	C(2A)-C(1A)-N(1A)-C(9A)	-0.4(4)
N(1A)-C(9A)-C(10A)-C(11A)	69.9(2)	C(6A)-C(1A)-N(1A)-C(9A)	176.40(19)
N(2A)-C(10A)-C(11A)-C(12A)	-54.4(3)	C(10A)-C(9A)-N(1A)-C(8A)	-94.2(3)
C(9A)-C(10A)-C(11A)-C(12A)	66.0(3)	C(10A)-C(9A)-N(1A)-C(1A)	89.9(2)
N(2A)-C(10A)-C(11A)-C(16A)	128.8(2)	C(11A)-C(10A)-N(2A)-N(3A)	-170.27(16)
C(9A)-C(10A)-C(11A)-C(16A)	-110.8(2)	C(9A)-C(10A)-N(2A)-N(3A)	68.2(2)
C(16A)-C(11A)-C(12A)-C(13A)	-2.3(4)	C(11A)-C(10A)-N(2A)-C(19A)	-58.7(2)
C(10A)-C(11A)-C(12A)-C(13A)	-179.2(3)	C(9A)-C(10A)-N(2A)-C(19A)	179.76(17)
C(11A)-C(12A)-C(13A)-C(14A)	0.8(5)	C(20A)-C(19A)-N(2A)-N(3A)	-92.7(2)
C(12A)-C(13A)-C(14A)-C(15A)	1.1(5)	C(18A)-C(19A)-N(2A)-N(3A)	29.3(2)
C(13A)-C(14A)-C(15A)-C(16A)	-1.4(5)	C(20A)-C(19A)-N(2A)-C(10A)	151.4(2)
C(14A)-C(15A)-C(16A)-C(11A)	-0.1(5)	C(18A)-C(19A)-N(2A)-C(10A)	-86.5(2)
C(12A)-C(11A)-C(16A)-C(15A)	2.0(4)	O(1A)-C(17A)-N(3A)-N(2A)	179.8(3)
C(10A)-C(11A)-C(16A)-C(15A)	178.9(3)	C(18A)-C(17A)-N(3A)-N(2A)	1.5(3)
O(1A)-C(17A)-C(18A)-C(19A)	-160.8(3)	C(10A)-N(2A)-N(3A)-C(17A)	99.4(2)
N(3A)-C(17A)-C(18A)-C(19A)	17.5(3)	C(19A)-N(2A)-N(3A)-C(17A)	-20.0(3)
C(17A)-C(18A)-C(19A)-C(20A)	90.2(3)	C(5A)-C(4A)-O(2A)-C(26A)	-141.4(5)
C(17A)-C(18A)-C(19A)-N(2A)	-29.0(3)	C(3A)-C(4A)-O(2A)-C(26A)	38.8(6)

Table S22-2. Torsion angles (°)

h	k	l	2θ/°	d/Å	I/rel.	|F(hkl)|	h	k	l	2θ/°	d/Å	I/rel.	|F(hkl)|
0	0	2	6.66	13.27	100.00	191.97	-2	2	2	20.91	4.25	3.70	83.41
-1	1	1	10.41	8.49	22.93	101.95	1	1	5	20.96	4.23	6.97	114.82
2	0	0	10.88	8.13	3.27	56.89	3	1	2	21.29	4.17	13.93	164.91
-2	0	2	11.05	8.00	4.48	67.65	2	2	1	21.57	4.12	17.97	189.89
0	1	2	11.06	7.99	9.67	70.36	-3	1	5	21.76	4.08	11.39	152.57
1	1	1	11.35	7.79	4.22	47.70	1	2	3	21.82	4.07	3.70	87.15
-1	1	2	11.47	7.71	6.27	58.79	4	0	0	21.85	4.06	4.15	130.85
-2	1	1	13.69	6.47	12.52	99.38	-2	1	6	21.87	4.06	9.90	142.95
-2	1	2	14.16	6.25	64.93	234.18	0	1	6	21.95	4.05	5.96	111.40
2	0	2	14.27	6.20	2.91	70.66	-4	0	4	22.20	4.00	2.81	109.46
-2	0	4	14.67	6.03	9.49	131.25	-4	1	2	22.79	3.90	4.00	94.81
-2	1	3	15.36	5.77	13.82	117.38	-4	1	3	23.12	3.84	2.11	69.98
-1	1	4	15.66	5.65	3.35	58.94	3	1	3	23.26	3.82	20.08	217.18
2	1	2	16.81	5.27	16.53	140.80	4	1	0	23.61	3.77	6.08	121.36
-2	1	4	17.14	5.17	10.09	112.25	1	2	4	23.79	3.74	3.82	96.93
-3	1	1	18.07	4.91	84.94	343.71	3	2	0	24.18	3.68	5.67	120.19
-3	1	2	18.15	4.89	3.69	71.99	-3	2	3	24.36	3.65	2.12	74.08
-1	1	5	18.33	4.84	14.63	144.83	2	2	3	24.45	3.64	17.08	211.03
1	2	0	18.52	4.79	32.37	217.71	4	1	1	24.71	3.60	5.10	116.58
3	1	0	18.60	4.77	29.84	209.94	-2	2	5	24.77	3.59	8.42	150.21
1	2	1	19.10	4.64	9.49	121.65	3	1	4	25.54	3.48	2.98	92.30
-1	2	2	19.17	4.63	13.81	147.35	4	1	2	26.20	3.40	4.34	114.35
-2	1	5	19.35	4.58	2.71	65.88	3	2	2	26.33	3.38	6.62	141.98
2	0	4	19.49	4.55	20.08	255.50	2	2	4	26.44	3.37	4.34	115.56
0	0	6	20.06	4.42	13.25	213.92	-5	1	3	27.89	3.20	3.24	105.61
1	2	2	20.22	4.39	25.73	212.51	3	1	5	28.06	3.18	4.90	130.67
0	2	3	20.36	4.36	3.37	77.47	-5	1	4	28.38	3.14	2.09	86.43
-2	2	1	20.59	4.31	9.13	128.96	4	2	1	29.19	3.06	3.45	114.36

*Table S23. Calculated reflections from PowderCell**

Source: Cu-$K_{\alpha 1}$ (λ = 1.540598 Å)

Condition on reflections: I ≥ 2

Range (2θ): From 3° to 30°

*PowderCell for Windows (version 2.4) by Kraus W. & Nolze G., Federal institute for materials Research and testing, Rudower Chausse 5, 12489 Berlin Germany.