Supporting Information

Photogenerated donor-donor diazo compounds enable facile access to spirocyclopropanes

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1 General information

All NMR spectra were recorded at room temperature using a Bruker Avance 300 (300 MHz for ^{1}H, 75 MHz for ^{13}C), a Bruker Avance 400 (400 MHz for ^{1}H, 101 MHz for ^{13}C), or a Bruker Avance 600 (600 MHz for ^{1}H, 150 MHz for ^{13}C) NMR spectrometer. All chemical shifts are reported in δ-scale as parts per million [ppm] (multiplicity, coupling constant *J*, number of protons) relative to the solvent residual peaks as the internal standard. Coupling constants *J* are given in Hertz [Hz]. Abbreviations used for signal multiplicity: ^{1}H-NMR: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, and m = multiplet. High resolution mass spectra (HRMS) were obtained from the central analytic mass spectrometry facilities of the Faculty of Chemistry and Pharmacy, Regensburg University, and are reported according to the IUPAC recommendations 2013. All mass spectra were recorded on a Finnigan MAT 95, Thermo Quest Finnigan TSQ 7000, Finnigan MATSSQ 710 A or an Agilent Q-TOF 6540 UHD instrument. GC measurements were performed on a GC 7890 from Agilent Technologies. Data acquisition and evaluation was done with Agilent ChemStation Rev.C.01.04. [35]. Analytical TLC was performed on silica gel coated alumina plates (MN TLC sheets ALUGRAM® Xtra SIL G/UV254). Visualization was done by UV light (254 or 366 nm). If necessary, potassium permanganate was used for chemical staining. Purification by column chromatography was performed with silica gel 60 M (40-63 µm, 230-440 mesh, Merck) on a Biotage® Isolera TM Spektra One device. Photocatalytic reactions were performed with 365 nm LEDs (SSC VIOSYS UV 365nm CUN66A1B (λ = 365 nm (± 15 nm), 3.6 V, 700 mA). The sample was irradiated with a LED through the vial's plane bottom side and cooled from the side using custom-made aluminum cooling blocks connected to a thermostat (Figure S1). Gram-scale reactions were in a classic glass tube photochemical reactor setup irradiated from the outside with 12x 365 nm LEDs (Inolux IN-C68QABTMU2 (λ = 365 nm (± 15 nm), 14 V, 700 mA) (Figure S2). The glass tube with reaction mixture was thermostated at 25 °C, the LED Block cooled by air. UV–Vis and fluorescence measurements were performed with a Varian Cary 100 UV/Vis spectrophotometer and FluoroMax-4 spectrofluorometer, respectively. Commercially available starting materials and solvents were used without further purification.

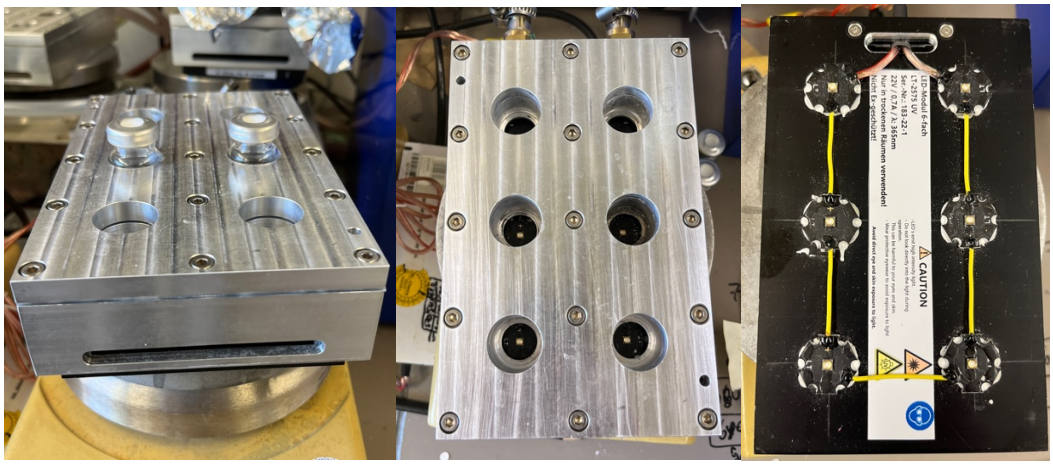


Figure S1. Photochemical set-up for regular-scale reactions.

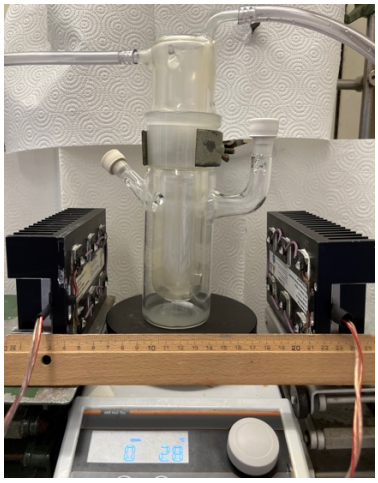
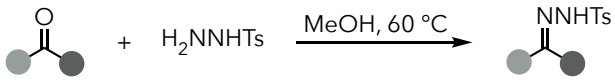


Figure S2. Photochemical set-up for large-scale reactions; ruler added for scale.

2 Synthesis of Starting Materials

2.1 Synthesis of *N*-tosylhydrazones

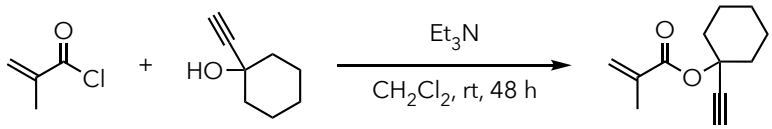


S1 **S2** **1**

N-Tosylhydrazones **1** were prepared according to a reported procedure.[1] To a stirred solution of tosylhydrazide (**S2**, 10 mmol, 1.0 eq.) in MeOH (10 mL) at 60 °C, aldehyde, or ketone (**S1**, 10 mmol, 1.0 eq.) was added dropwise (or portion wise if solid). The reaction progress was monitored by TLC. Then, the mixture was cooled with an ice bath. If the product precipitated when cooled, the solid was filtered of, washed with ice cold MeOH and dried *in vacuo*. If the product did not precipitate, the solvent was removed directly under reduced pressure, and the crude mixture was either directly used or further purified by recrystallization.

2.2 Synthesis of alkenes

1-Ethynylcyclohexyl methacrylate (2h).



S3 **S4** **2h**

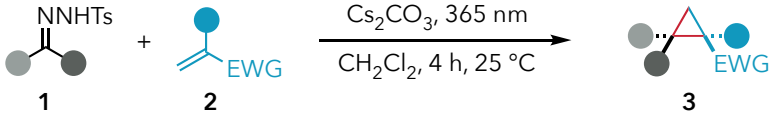
2h was synthesized according to a modified literature procedure.[2]
Methacryloyl chloride (**S3**, 12.0 mmol, 1.2 eq.) was added dropwise to a solution of 1-ethynyl-1-cyclohexanol (**S4**, 10.0 mmol, 1.0 eq.) and triethylamine (13.0 mmol, 1.3 eq.) in dry dichloromethane (50 mL) at 0 °C. The reaction mixture was warmed up to room temperature and stirred for 2 days. Afterwards, the solution was treated with saturated aqueous $NaHCO_3$, washed with water and brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting oil was purified by chromatography (5% EtOAc in PE) yielding titled compound as a colorless oil (408 mg, 2.10 mmol, 21%).

^{1}H NMR (300 MHz, CDCl3) δ = 6.17 – 6.01 (m, 1H), 5.61 – 5.48 (m, 1H), 2.60 (s, 1H), 2.19 – 2.06 (m, 2H), 2.03 – 1.88 (m, 5H), 1.68 – 1.58 (m, 4H), 1.55 – 1.35 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.5, 137.0, 125.3, 83.8, 75.0, 74.1, 36.9, 34.1, 25.1, 22.3, 18.3, 14.0.

The analytical data are consistent with those reported in the literature.[3]

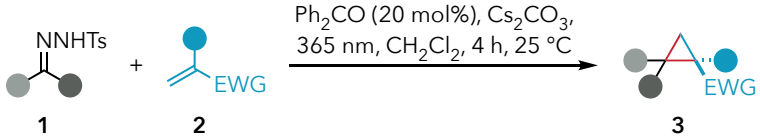
3 Experimental Procedures

3.1 General Procedure A – One-Pot Cyclopropanation



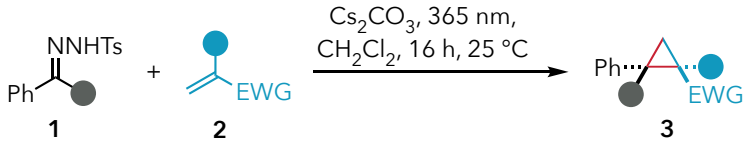
To a 5 mL snap vial with a magnetic stirring bar, tosylhydrazones (**1**, 300 µmol, 1.5 eq.), Cs_2CO_3 (300 µmol, 1.5 eq.) and alkene (**2**, 200 µmol, 1.0 eq., if solid) were added. The vial was evacuated and back filled with N_2 for three times. Then dry CH_2Cl_2 (2 mL) and alkene (**2**, 200 µmol, 1.0 eq., if liquid) was added by syringe, and the mixture was irradiated with a 365 nm LED at 25 °C. After 4 h, the mixture was quenched with water and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was then washed with H_2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum. The residue was purified by silica gel column chromatography to give the desired product.

3.2 General Procedure B – One-Pot Cyclopropanation with Ph_2CO



To a 5 mL snap vial with a magnetic stirring bar, tosylhydrazones (**1**, 300 µmol, 1.5 eq.), Cs_2CO_3 (300 µmol, 1.5 eq.), benzophenone (40 µmol, 20 mol%) and alkene (**2**, 200 µmol, 1.0 eq., if solid) were added. The vial was evacuated and back filled with N_2 for three times. Then dry CH_2Cl_2 (2 mL) and alkene (**2**, 200 µmol, 1.0 eq., if liquid) was added by syringe, and the mixture was irradiated with a 365 nm LED at 25 °C. After 4 h, the mixture was quenched with water and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was then washed with H_2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum. The residue was purified by silica gel column chromatography to give the desired product.

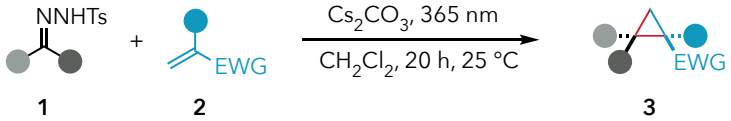
3.3 General Procedure C – One-Pot Cyclopropanation Benzylic NNHTs



1 2 3

To a 5 mL snap vial with a magnetic stirring bar, tosylhydrazones (**1**, 400 µmol, 2.0 eq.), Cs_2CO_3 (300 µmol, 1.5 eq) and alkene (**2**, 200 µmol, 1.0 eq., if solid) were added. The vial was evacuated and back filled with N_2 for three times. Then dry CH_2Cl_2 (2 mL) and alkene (**2**, 200 µmol, 1.0 eq., if liquid) was added by syringe, and the mixture was irradiated with a 365 nm LED at 25 °C. After 16 h, the mixture was quenched with water and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was then washed with H_2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum. The residue was purified by silica gel column chromatography to give the desired product.

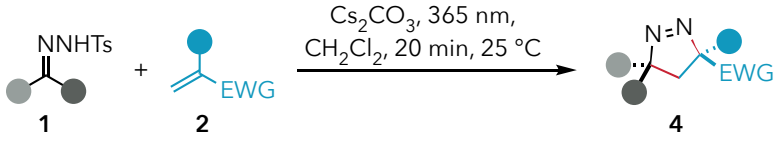
3.4 General Procedure D – Large Scale Cyclopropanation



1 2 3

To a 5 mL snap vial with a magnetic stirring bar, tosylhydrazones (**1**, 10.5 mmol, 1.5 eq.), Cs_2CO_3 (10.5 mmol, 1.5 eq.) and alkene (**2**, 7.00 mmol, 1.0 eq., if solid) were added. The vial was evacuated and back filled with N_2 for three times. Then dry CH_2Cl_2 (70 mL) and alkene (**2**, 7.00 mmol, 1.0 eq., if liquid) was added by syringe, and the mixture was irradiated with a 365 nm LED at 25 °C. After 20 h, the mixture was quenched with water and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was then washed with H_2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum. The residue was purified by silica gel column chromatography to give the desired product.

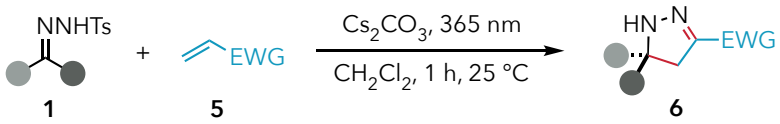
3.5 General Procedure E – Δ^1-pyrazolines



1 2 4

To a 5 mL snap vial with a magnetic stirring bar, tosylhydrazones (**1**, 300 µmol, 1.5 eq.), Cs_2CO_3 (300 µmol, 1.5 eq.) and alkene (**4**, 200 µmol, 1.0 eq., if solid) were added. The vial was evacuated and back filled with N_2 for three times. Then dry CH_2Cl_2 (2 mL) and alkene (**4**, 200 µmol, 1.0 eq., if liquid) was added by syringe, and the mixture was irradiated with a 365 nm LED at 25 °C. After 20 min, the mixture was quenched by addition of water and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was then washed with H_2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum. The residue was purified by silica gel flash chromatography to give the desired product.

3.6 General Procedure F – Δ^2-pyrazolines

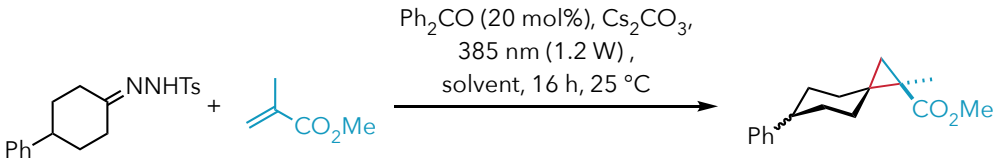


1 **5** **6**

To a 5 mL snap vial with a magnetic stirring bar, tosylhydrazones (**1**, 240 µmol, 1.2 eq.), Cs_2CO_3 (300 µmol, 1.5 eq.) and alkene (**2**, 200 µmol, 1.0 eq., if solid) were added. The vial was evacuated and back filled with N_2 for three times. Then dry CH_2Cl_2 (2 mL) and alkene (**2**, 200 µmol, 1.0 eq., if liquid) was added by syringe, and the mixture was irradiated with a 365 nm LED at 25 °C. After 1 h, the mixture was quenched by addition of water and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was then washed with H_2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum to give the desired product.

4 Optimization details

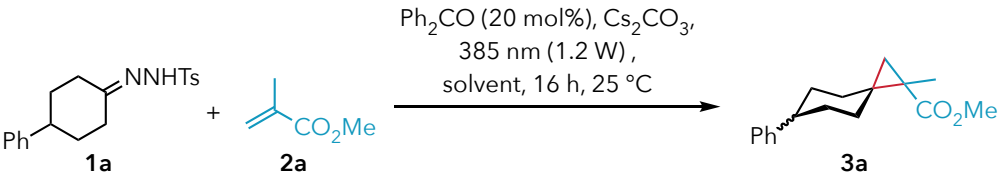
4.1 Optimization of the reaction of tosylhydrazone **1a** with alkene **2a**



1a **2a** **3a**

To a 5 mL snap vial with a magnetic stirring bar, tosylhydrazones (**1**, 240 µmol, 1.2 eq.), Cs_2CO_3 (300 µmol, 1.5 eq.), benzophenone (40.0 µmol, 20 mol%) and alkene (**2**, 200 µmol, 1.0 eq., if solid) were added. The vial was evacuated and back filled with N_2 for three times. Then dry solvent (2 mL) and alkene (**2**, 200 µmol, 1.0 eq., if liquid) was added by syringe, and the mixture was irradiated with a 365 nm LED at 25 °C. After 16 h, *n*-dodecane (20 µL) was added as internal standard and the yield determined by GC-FID.

Table S1. Screening of solvents.

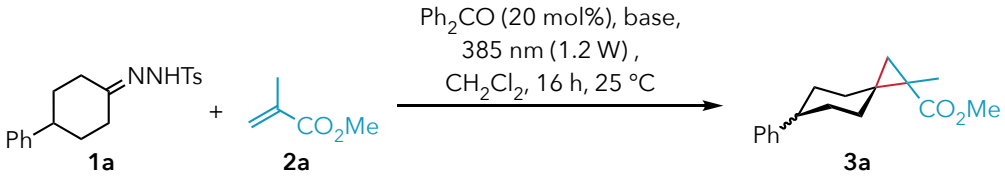


1a **2a** **3a**

#	Solvent	Yield[a]
1	**CH_2Cl_2**	**80%**
2	THF	42%
3	MeCN	63%
4	DMSO	n.d.
5	PhMe	73%
6	MeOH	29%

1a (240 µmol, 1.2 eq.), **2a** (200 µmol, 1.0 eq.), Cs_2CO_3 (300 µmol, 1.5 eq.), Ph_2CO (40 µmol, 20 mol%), dry solvent (2.0 mL), 16 h, 25 °C. a Yield determined by GC-FID with *n*-dodecane as internal std. d.r. = 1:1 unless otherwise stated. n.d. = not detected.

Table S2. Screening of bases.

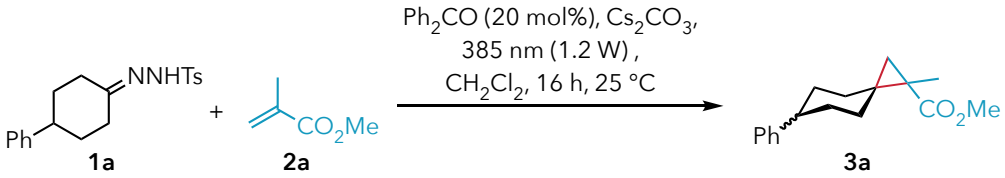


1a **2a** **3a**

#	Base	Yield[a]
1	**Cs_2CO_3**	**80%**
2	DBU	55%
3	TMG	36%

1a (240 µmol, 1.2 eq.), **2a** (200 µmol, 1.0 eq.), base (300 µmol, 1.5 eq.), Ph_2CO (40 µmol, 20 mol%), dry CH_2Cl_2 (2.0 mL), 16 h, 25 °C. [a] Yield determined by GC-FID with *n*-dodecane as internal std. d.r. = 1:1 unless otherwise stated.

Table S3. Screening of ratio of **1a** with **2a** and amount of base.

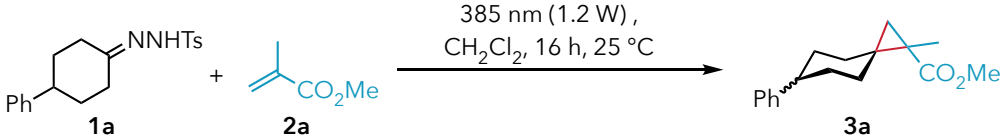


1a **2a** **3a**

#	**1a** : **2a**	Eq. Cs_2CO_3	Yield[a]
1	1.0:1.2	1.5	65%
2	1.0:1.0	1.5	62%
3	1.2:1.0	1.5	80%
4	1.2:1.0	1.2	71%
5	**1.5:1.0**	**1.5**	**88%**
6	1.5:1.0	--	n.d.
7	1.75:1.0	2.0	88%
8	2.0:1.0	2.0	88%

1a (240 µmol, 1.2 eq.), **2a** (200 µmol, 1.0 eq.), Cs_2CO_3 (300 µmol, 1.5 eq.), Ph_2CO (40 µmol, 20 mol%), dry CH_2Cl_2 (2.0 mL), 16 h, 25 °C. [a] Yield determined by GC-FID with *n*-dodecane as internal std. d.r. = 1:1 unless otherwise stated. n.d. = not detected.

Table S4. Screening of Ph_2CO loading.

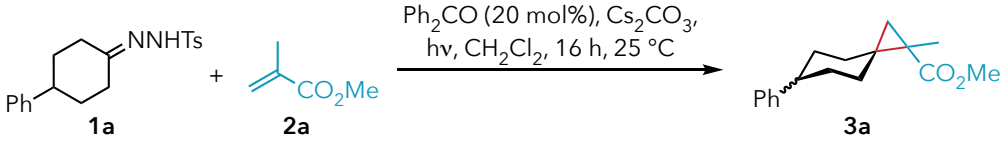


1a **2a** **3a**

#	Ph_2CO	Yield[a]	d.r.
1	20 mol%	88%	1:1
2	10 mol%	89%	1:1
3	5 mol%	92%	1.1:1
4	0 mol%	92%	2.3:1

1a (300 µmol, 1.5 eq.), 2a (200 µmol, 1.0 eq.), Cs_2CO_3 (300 µmol, 1.5 eq.), Ph_2CO, dry CH_2Cl_2 (2.0 mL), 16 h, 25 °C. [a] Yield determined by GC-FID with n-dodecane as internal std. d.r. = 1:1 unless otherwise stated.

Table S5. Screening of light source.



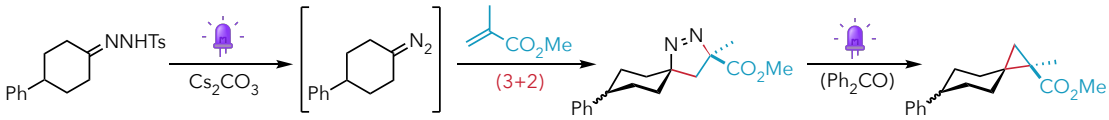
#	hv	Yield[a]
1	385 nm (1.2 W)	88%
2	365 nm (0.6 W)	90%
3	Dark (60 °C)[b]	n.d.
4	Dark (80 °C)[b]	6%
5	Dark (80 °C)[c]	8%
6	Dark (110 °C)[c]	94%

1a (300 µmol, 1.5 eq.), **2a** (200 µmol, 1.0 eq.), Cs_2CO_3 (300 µmol, 1.5 eq.), Ph_2CO (20 mol%), dry CH_2Cl_2 (2.0 mL), 16 h, 25 °C. [a] Yield determined by GC-FID with n-dodecane as internal std. d.r. = 1:1 unless otherwise stated. n.d. = not detected. [b] 1,2-DCE used as solvent. [c] PhMe used as solvent

5 Mechanistic investigations

To have a deeper look into the relationship between catalyst loading, light source and reaction time, kinetic investigations were conducted by *ex-situ* ^{1}H-NMR spectroscopy. After full conversion was observed by ^{1}H-NMR, the yield was determined by GC-FID, giving 90±2% yield for all five shown reaction conditions. The kinetic investigation could not be conducted with GC-FID as Δ^1-pyrazolines (initial cycloaddition product) decompose upon heating forming the desired cyclopropane moiety, falsifying the results.

Proposed reaction pathway:



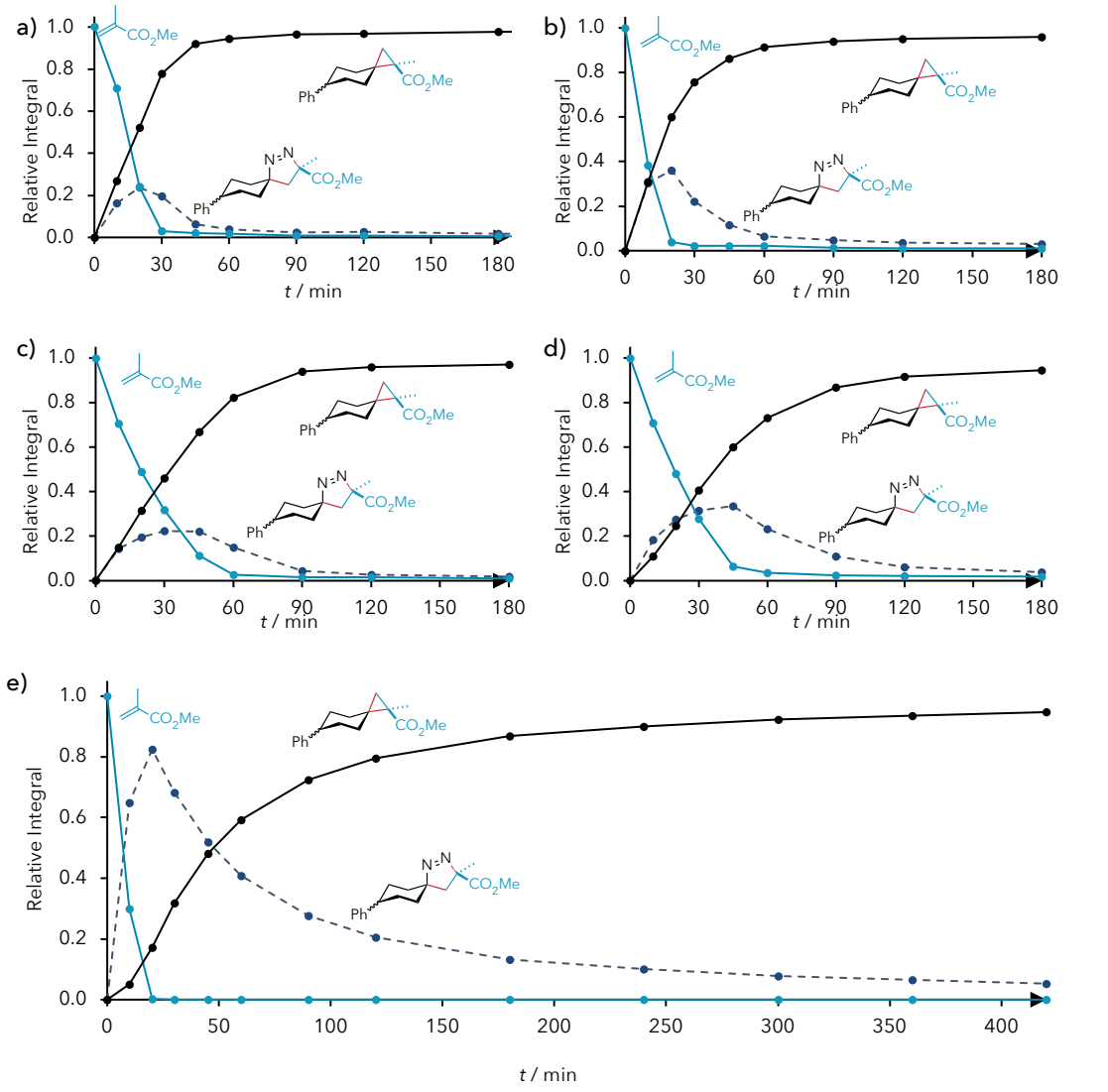


Figure S3. Kinetic profile of the cycloaddition reaction followed by nitrogen extrusion. **a)** Ph_2CO (20 mol%), 365 nm (0.6 W). **b)** Ph_2CO (10 mol%), 365 nm (0.6 W). c) Ph_2CO (20 mol%), 385 nm (1.2 W). **d)** Ph_2CO (10 mol%), 385 nm (1.2 W). **e)** no Ph_2CO, 365 nm (0.6 W).

Even though the reaction also proceeds under irraditaion with a 385 nm LED, kinetic profiles c) and d) show significant slower reaction rates than their 365 nm counterparts even though the optical power is higher (1.2 W vs. 0.6 W). This could indicate the reaction to only proceed with a 385 nm LED due to the deviation of ±15 nm around the emmision maximum. As irradiation with 365 nm did show faster reaction times and better theoretical overlap with the absorption curves of the reactands employed (deprotonated tosylhydrazone[4], benzophenone[5] and *in-situ* formed Δ^1-pyrazoline (Figure S4)), we opted to use the 365 nm LED.

To gain mechanistic insights, the UV-vis spectrum of isolated spiro-pyrazoline **4a** was measured and the cuvette then submitted to irradiation with the standard 365 nm LED used for the reactions (Figure S4). The pyrazoline showed an absorbance maximum of λ_{max} = 334 nm that decreased significantly after irradiation, indicating decomposition of pyrazoline **4a**, presumably towards cyclopropane **3a**.

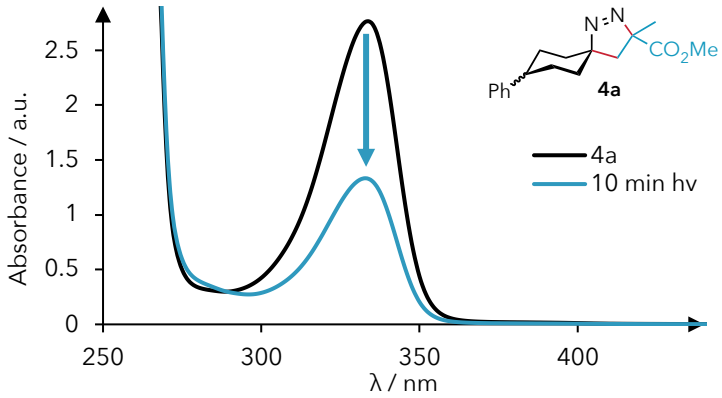


Figure S4. UV-Vis spectrum of spiro-Δ^1-pyrazoline **4a** (black). The mixture was submitted to irradiation with the standard 365 nm LED setup (0.6 W) for 10 min and then measured again (blue).

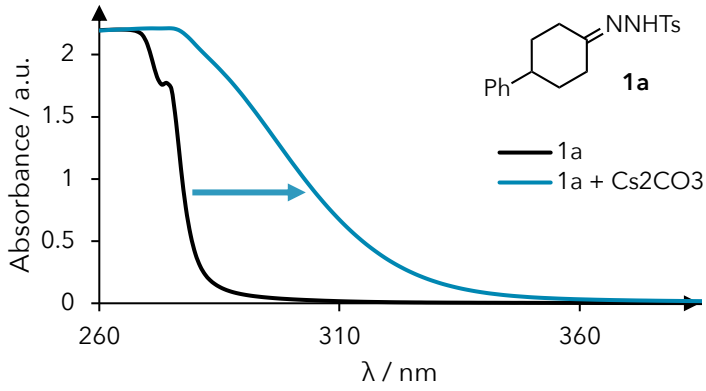


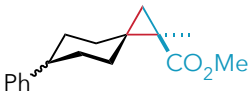
Figure S5. UV-Vis spectrum of tosylhydrazone **1a** (black) and **1a** with Cs_2CO_3 base (blue). Deprotonation of tosylhydrazones causes a significant shift in absorption (indicated by the blue arrow) as was previously reported by our group.[4]

6 Characterization of Products

6.1 Cyclopropanes

Methyl 1-methyl-6-phenylspiro[2.5]octane-1-carboxylate (3a).

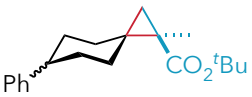
Following general procedure B, the product was obtained as a colorless oil (47.8 mg, 185 µmol, 92%, d.r. = 1:1). Purification was achieved by silica column chromatography (CH_2Cl_2).



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 – 7.26 (m, 2H), 7.23 – 7.14 (m, 3H), 3.68 (s, 1.6H), 3.66 (s, 1.4H), 2.65 – 2.44 (m, 1H), 1.95 – 1.30 (m, 12H), 0.61 – 0.36 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.3, 174.9, 147.2, 147.2, 128.5, 128.4, 126.9, 126.1, 126.1, 51.9, 51.8, 44.3, 44.3, 33.5, 33.3, 33.2, 32.2, 31.7, 31.4, 31.2, 31.0, 30.7, 29.3, 28.8, 25.7, 25.0, 16.6, 16.1.
HRMS (EI): Calcd. for $C_{17}H_{22}O_2$ $[M]^+$: 258.16143, Found: 258.16124.

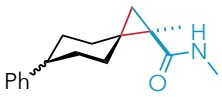
***tert*-Butyl 1-methyl-6-phenylspiro[2.5]octane-1-carboxylate (3b).**

Following general procedure B, the product was obtained as a colorless oil (54.3 mg, 181 µmol, 90%, d.r. = 1:1). Purification was achieved by silica column chromatography (CH_2Cl_2/PE 1:1).



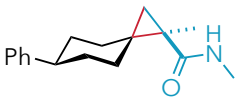
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53 – 7.27 (m, 2H), 7.26 – 7.17 (m, 3H), 2.58 (m, 1H), 2.05 – 1.50 (m, 8H), 1.48 (s, 4.5H), 1.47 (s, 4.5H), 1.40 (s, 1.5H), 1.32 (s, 1.5H), 1.29 (d, *J*=4.6, 0.5H), 1.27 (dd, *J*=4.5, 1.4, 0.5H), 0.43 (d, *J*=4.5, 0.5H), 0.40 (dd, *J*=4.5, 1.1, 0.5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.03, 173.79, 147.50, 147.40, 128.48, 128.45, 126.98, 126.96, 126.06, 80.11, 79.99, 44.47, 44.40, 33.77, 33.50, 33.40, 33.37, 32.29, 31.62, 31.54, 30.63, 30.35, 30.28, 30.17, 29.91, 28.34, 28.28, 24.89, 24.21, 16.93, 16.35.
HRMS (EI): Calcd. for $C_{20}H_{28}O_2$ $[M]^+$: 329.2224, Found: 329.2226.

_N_,1-Dimethyl-6-phenylspiro[2.5]octane-1-carboxamide (3c).



Following general procedure A with 16 h reaction time, the product was obtained as two diasteromers **3c'** and **3c''**. **3c'** was isolated as a white solid (36.4 mg, 141 µmol, 71%). **3c''** was isolated as a 2:1 mixture with **3c'** and a white solid (6.8 mg, 26.4 µmol, 13%). In total, **3c** was isolated as white solids (43.2 mg, 168 µmol, 84%, d.r. = 8.6:1). Purification was achieved by silica column chromatography (EtOAc in PE 40%→60%). Diastereomers were assigned according to analogous literature ^{1}H-NMR spectra.[6]

Diastereomer **3c'**:

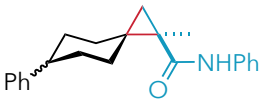


^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 – 7.26 (m, 2H), 7.25 – 7.21 (m, 2H), 7.21 – 7.15 (m, 1H), 5.76 (br, 1H), 2.84 (d, *J*=4.8, 3H), 2.58 (tt, *J*=12.1, 3.5, 1H), 1.99 – 1.89 (m, 1H), 1.85 – 1.67 (m, 3H), 1.63 – 1.47 (m, 4H), 1.42 (s, 3H), 1.24 (d, *J*=4.6, 1H), 0.39 (d, *J*=4.6, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.47, 147.23, 128.39, 126.96, 126.02, 44.13, 33.97, 33.14, 32.05, 31.81, 30.50, 29.09, 26.76, 24.28, 17.75.

HRMS (EI): Calcd. for $C_{17}H_{22}NO$ $[M]^+$: 257.17742, Found: 257.17737.

1-Methyl-_N_,6-diphenylspiro[2.5]octane-1-carboxamide (3d).



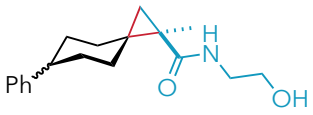
Following general procedure A, the product was obtained as a white solid (64.8 mg, 200 µmol, 100%, d.r. = 5:1). Purification was achieved by silica column chromatography (PE/EtOAc 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (td, *J*=9.0, 1.3, 2H), 7.33 (m, 1H), 7.29 – 7.06 (m, 7H), 7.00 (ddt, *J*=7.2, 6.0, 1.2, 1H), 2.48 (dtt, *J*=31.3, 16.1, 3.7, 1H), 2.01 – 1.09 (m, 12H), 0.55 – 0.28 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 172.0, 147.2, 147.0, 138.2, 138.1, 129.1, 129.0, 128.4, 128.4, 126.9, 126.1, 126.0, 124.3, 124.2, 120.2, 119.9, 44.3, 44.0, 34.1, 33.4, 33.2, 33.0, 32.0, 31.9, 31.9, 31.6, 31.3, 29.9, 29.6, 24.6, 23.8, 17.8, 17.2.

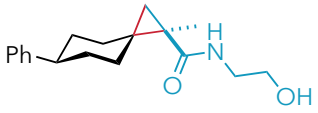
HRMS (ESI): Calcd. for $C_{22}H_{25}NO$ $[M+H]^+$: 320.2009, Found: 320.2008.

***N*-(2-hydroxyethyl)-1-methyl-6-phenylspiro[2.5]octane-1-carboxamide (3e).**



Following general procedure A with 16 h reaction time, the product was obtained as two diasteromers **3e'** and **3e''**. **3e'** was isolated as a white solid (38.2 mg, 133 µmol, 67%). **3e''** was isolated as a 2:1 mixture with **3e'** and a white solid (5.9 mg, 20.5 µmol, 10%). In total. **3e** was isolated as a white solid (44.1 mg, 153 µmol, 77%, d.r. = 10.3:1). Purification was achieved by silica column chromatography (EtOAc in PE 75%→100%). Diastereomers were assigned according to analogous literature ^{1}H-NMR spectra.[6]

Diastereomer **3e'**:

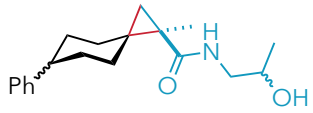


^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 – 7.26 (m, 2H), 7.25 – 7.21 (m, 2H), 7.21 – 7.15 (m, 1H), 5.76 (br, 1H), 2.84 (d, *J*=4.8, 3H), 2.58 (tt, *J*=12.1, 3.5, 1H), 1.99 – 1.89 (m, 1H), 1.85 – 1.67 (m, 3H), 1.63 – 1.47 (m, 4H), 1.42 (s, 3H), 1.24 (d, *J*=4.6, 1H), 0.39 (d, *J*=4.6, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.47, 147.23, 128.39, 126.96, 126.02, 44.13, 33.97, 33.14, 32.05, 31.81, 30.50, 29.09, 26.76, 24.28, 17.75.

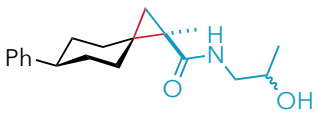
HRMS (ESI): Calcd. for $C_{18}H_{25}NO_2$ $[M+H]^+$: 288.1958, Found: 288.1964.

***N*-(2-hydroxypropyl)-1-methyl-6-phenylspiro[2.5]octane-1-carboxamide (3f).**



Following general procedure A with 16 h reaction time, the major diastereomeric mixture **3f'** of the product was obtained as a white solid (44.7 mg, 148 µmol, 74%, d.r. = 1:1). The minor diastereomeric mixture **3f''** was obtained as a white solid (7.1 mg, 23.6 µmol, 12%, d.r. = 1:1). In total the product was gained as white solids (51.8 mg, 172 µmol, 86%, d.r. = 6.3:1:1). Purification was achieved by silica column chromatography (EtOAc in PE 75%→100%). Diastereomers were assigned according to analogous literature ^{1}H-NMR spectra.[6]

Diastereomeric mixture **3f'**:

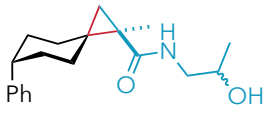


^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 (t, *J*=7.7 Hz, 2H), 7.25 – 7.20 (m, 2H), 7.17 (td, *J*=7.0, 1.6, 1H), 6.46 – 6.01 (m, 1H), 4.02 – 3.75 (m, 1H), 3.47 (dddd, *J*=26.1, 14.0, 6.5, 3.0, 1H), 3.34 – 2.72 (m, 2H), 2.57 (tt, *J*=12.0, 3.5, 1H), 1.98 – 1.88 (m, 1H), 1.88 – 1.68 (m, 3H), 1.63 – 1.47 (m, 4H), 1.46 – 1.37 (m, 3H), 1.25 (dd, *J*=4.6, 3.3, 1H), 1.17 (d, *J*=6.3, 3H), 0.41 (d, *J*=4.6, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.37, 175.14, 147.22, 147.15, 128.42, 128.40, 126.95, 126.03, 67.96, 67.74, 47.59, 47.38, 44.21, 44.14, 34.05, 33.99, 33.09, 33.03, 32.02, 31.75, 30.46, 30.44, 29.38, 29.35, 24.40, 21.19, 21.16, 17.77, 17.73.

HRMS (ESI): Calcd. for $C_{19}H_{27}NO_2$ $[M+H]^+$: 302.2115, Found: 302.2118.

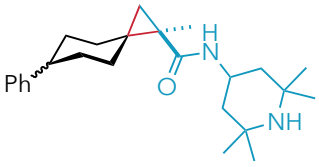
Diastereomeric mixture **3f''**:



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 (dd, *J*=7.9, 6.9, 2H), 7.25 – 7.14 (m, 3H), 6.08 (t, *J*=6.0, 1H), 3.92 (ddd, *J*=7.2, 6.2, 2.9, 1H), 3.45 (dddd, *J*=35.2, 14.1, 6.5, 2.9, 1H), 3.16 (dddd, *J*=33.0, 14.1, 7.4, 5.3, 1H), 2.53 (tt, *J*=11.7, 3.4, 1H), 2.01 – 1.48 (m, 7H), 1.42 – 1.15 (m, 9H), 0.42 (dd, *J*=4.7, 1.4, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.35, 175.28, 147.28, 128.47, 128.44, 126.97, 126.12, 68.10, 67.96, 47.53, 47.48, 44.38, 33.43, 33.41, 33.23, 31.79, 31.76, 31.38, 31.36, 30.85, 30.80, 29.18, 29.12, 23.72, 23.66, 21.16, 21.14, 17.38, 17.33.
HRMS (ESI): Calcd. for $C_{19}H_{27}NO_2$ $[M+H]^+$: 302.2115, Found: 302.2119.

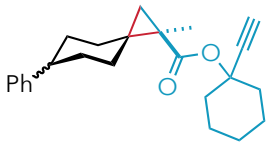
1-Methyl-6-phenyl-*N*-(2,2,6,6-tetramethylpiperidin-4-yl)spiro[2.5]octane-1-carboxamide (3g).



Following general procedure A with 16 h reaction time, the product was obtained as a white solid (45.5 mg, 119 µmol, 60%, d.r. = 5.3:1). Purification was achieved by Biotage® Sfär KP-Amino 11g column chromatography (EtOAc in PE 50%→100%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 (t, *J*=7.5, 2H), 7.24 – 7.13 (m, 3H), 5.46 (d, *J*=8.0, 0.84H), 5.36 (d, *J*=8.0, 0.16H), 4.29 (tdt, *J*=12.1, 7.9, 3.8, 1H), 2.76 – 2.09 (m, 3H), 1.94 – 1.68 (m, 6H), 1.65 – 1.45 (m, 4H), 1.40 (s, 3H), 1.27 (s, 6H), 1.20 (d, *J*=4.6, f1H), 1.15 (d, *J*=6.4, 6H), 1.00 (q, *J*=12.7, 2H), 0.38 (d, *J*=4.7, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.05, 172.92, 147.21, 147.17, 128.33, 126.86, 126.84, 125.98, 125.95, 51.68, 51.64, 45.13, 45.01, 44.30, 44.13, 42.46, 34.55, 34.02, 33.29, 33.08, 31.96, 31.69, 31.59, 31.25, 30.68, 30.42, 29.03, 28.72, 28.23, 28.20, 24.89, 24.16, 17.71, 17.24.
HRMS (ESI): Calcd. for $C_{25}H_{38}N_2O$ $[M+H]^+$: 383.3057, Found: 383.3062.

1-Ethynylcyclohexyl 1-methyl-6-phenylspiro[2.5]octane-1-carboxylate (3h).

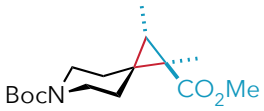


Following general procedure B, the product was obtained as a white solid (54.0 mg, 154 µmol, 77%, d.r. = 1:1). Purification was achieved by silica column chromatography (EtOAc in PE 0%→5%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 (d, *J*=8.1, 2H), 7.23 – 7.15 (m, 3H), 2.74 – 2.39 (m, 2H), 2.18 – 2.01 (m, 2H), 1.99 – 1.27 (m, 20H), 0.45 (d, *J*=4.6, 0.5H), 0.43 (d, *J*=4.5, 0.5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 172.6, 147.5, 147.3, 128.5, 127.0, 127.0, 126.1, 126.0, 84.3, 84.0, 74.9, 74.8, 74.1, 73.9, 44.5, 44.4, 37.6, 37.2, 37.0, 36.8, 33.9, 33.5, 33.4, 32.3, 31.9, 31.8, 31.7, 31.3, 31.2, 31.1, 30.6, 29.8, 29.4, 25.3, 25.3, 24.7, 22.6, 22.5, 22.5, 22.5, 16.7, 16.1.
HRMS (ESI): Calcd. for $C_{24}H_{30}O_2$ $[M+H]^+$: 351.2319, Found: 351.2318.

6-(*tert*-Butyl) 1-methyl 1,2-dimethyl-6-azaspiro[2.5]octane-1,6-dicarboxylate (3i).

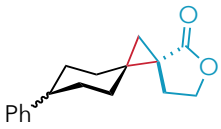
Following general procedure A with 16 h reaction time, the product was obtained as a colorless oil (45.7 mg, 154 µmol, 77%). Purification was achieved by silica column chromatography (PE/EtOAc 5:1). Relative stereo configuration was assigned by NOESY-NMR spectroscopy.



^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.65 (s, 3H), 3.51 – 3.41 (m, 1H), 3.40 – 3.31 (m, 1H), 3.31 – 3.23 (m, 2H), 1.59 (q, *J*=6.6, 1H), 1.44 (s, 13H), 1.19 (s, 3H), 1.00 (d, *J*=6.6, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.0, 155.0, 79.5, 51.9, 43.7, 43.4, 31.7, 31.6, 30.5, 28.6, 26.4, 25.8, 10.3, 8.2.
HRMS (ESI): Calcd. for $C_{16}H_{27}NO_4$ $[M+H]^+$: 298.2013, Found: 298.2008.

9-Phenyl-2-oxadispiro[4.0.5^6.1^5]dodecan-1-one (3j).

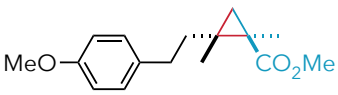
Following general procedure B, the product was obtained as a colorless oil (41.7 mg, 163 µmol, 81%, d.r. = 1:1). Purification was achieved by silica column chromatography (PE/EtOAc 4:1).



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 – 7.16 (m, 5H), 4.64 – 4.24 (m, 2H), 2.79 – 2.57 (m, 1H), 2.47 – 2.20 (m, 3H), 2.13 – 1.88 (m, 3H), 1.88 – 1.61 (m, 2H), 1.51 – 1.20 (m, 3H), 1.01 – 0.85 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 178.4, 178.4, 146.9, 146.7, 128.5, 128.5, 126.9, 126.8, 126.2, 126.2, 65.8, 65.6, 44.2, 43.7, 33.9, 33.8, 33.6, 33.2, 33.2, 33.0, 29.0, 28.7, 28.5, 28.2, 27.3, 27.2, 27.0, 26.5.
HRMS (EI): Calcd. for $C_{17}H_{20}O_2$ $[M]^+$: 256.14578, Found: 256.14597.

Methyl 2-(4-methoxyphenethyl)-1,2-dimethylcyclopropane-1-carboxylate (3k).

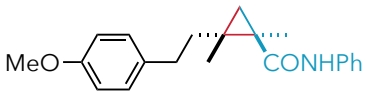
Following general procedure B, the product was obtained as a colorless oil (36.2 mg, 138 µmol, 69%, d.r. = 1:1). Purification was achieved by silica column chromatography (EtOAc in PE 0%→20%).



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.07 (dd, *J*=21.6, 8.6, 2H), 6.82 (dd, *J*=11.1, 8.6, 2H), 3.79 (s, 1.5H), 3.78 (s, 1.5H), 3.69 (s, 1.5H), 3.67 (s, 1.5H), 2.67 (dd, *J*=9.3, 7.6, 1H), 2.64 – 2.54 (m, 0.5H), 2.41 (ddd, *J*=13.6, 9.9, 6.7, 0.5H), 1.79 – 1.57 (m, 2H), 1.39 (d, *J*=4.9, 0.5H), 1.38 (s, 1.5H), 1.35 (s, 1.5H), 1.31 (d, *J*=4.7, 0.5H), 1.24 (s, 1.5H), 1.17 (s, 1.5H), 0.49 – 0.43 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.13, 175.01, 157.79, 157.68, 134.55, 129.17, 129.12, 113.83, 113.74, 55.28, 55.25, 51.77, 51.70, 38.27, 37.47, 32.49, 32.38, 29.40, 28.79, 28.51, 27.87, 27.28, 26.37, 19.23, 18.34, 17.01, 16.63.
HRMS (EI): Calcd. for $C_{16}H_{22}O_3$ $[M]^+$: 262.15635, Found: 262.15627.

2-(4-methoxyphenethyl)-1,2-dimethyl-*N*-phenylcyclopropane-1-carboxamide (3l).

Following general procedure B, the product was obtained as a white solid (58.8 mg, 182 μmol, 91%, d.r. = 1:1). Purification was achieved by silica column chromatography (EtOAc in PE 0%→25%).



^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.52 (ddt, *J*=7.9, 2.2, 1.1, 2H), 7.39 – 7.28 (m, 2H), 7.23 – 6.68 (m, 6H), 3.81 (s, 1.6H), 3.73 (s, 1.4H), 2.73 (t, *J*=8.0, 1H), 2.63 (ddd, *J*=9.1, 6.5, 2.0, 1H), 1.88 – 1.57 (m, 2H), 1.48 (s, 1.3H), 1.35 (d, *J*=4.8, 0.5H), 1.31 (s, 1.5H), 1.28 (s, 1.5H), 1.24 (d, *J*=4.8, 0.5H), 1.21 (s, 1.5H), 0.44 (d, *J*=4.8, 0.4H), 0.40 (d, *J*=4.8, 0.5H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 172.07, 172.04, 157.95, 157.66, 138.25, 134.50, 134.47, 129.54, 129.35, 129.03, 129.01, 124.12, 124.09, 119.87, 119.83, 113.91, 113.74, 55.36, 55.26, 37.97, 37.32, 32.57, 32.39, 32.30, 31.30, 27.43, 26.30, 25.58, 25.00, 19.24, 18.73, 18.25, 18.14.
HRMS (ESI): Calcd. for $C_{21}H_{25}NO_2$ $[M+H]^+$: 324.1958, Found: 324.1962.

1,2,2-Trimethyl-*N*-phenylcyclopropane-1-carboxamide (3m).

Following general procedure B, the product was obtained as a white solid (38.9 mg, 191 μmol, 96%). Purification was achieved by silica column chromatography (EtOAc in PE 0%→20%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 – 7.49 (m, 2H), 7.39 – 7.27 (m, 3H), 7.13 – 7.04 (m, 1H), 1.45 (s, 3H), 1.26 (d, *J*=4.8, 1H), 1.20 (s, 3H), 1.13 (s, 3H), 0.43 (d, *J*=4.7, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.31, 138.29, 129.06, 124.14, 119.89, 31.36, 25.72, 23.10, 22.04, 21.40, 18.04.
HRMS (ESI): Calcd. for $C_{13}H_{17}NO$ $[M+H]^+$: 204.1383, Found: 204.1386.

2,2-Dibenzyl-1-methyl-*N*-phenylcyclopropane-1-carboxamide (3n).

Following general procedure B, the product was obtained as a white solid (70.6 mg, 199 μmol, 99%). Purification was achieved by silica column chromatography (EtOAc in PE 0%→20%).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.61 – 7.50 (m, 2H), 7.49 (br, 1H), 7.42 – 7.z08 (m, 11H), 7.04 (dd, *J*=7.6, 1.8, 2H), 2.99 (d, *J*=14.7, 1H), 2.92 (d, *J*=16.3, 1H), 2.69 (d, *J*=16.2, 1H), 2.54 (d, *J*=14.8, 1H), 1.68 (d, *J*=5.1, 1H), 1.64 (s, 3H), 0.77 (dd, *J*=5.1, 1.0, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.83, 139.72, 139.05, 137.93, 129.49, 129.13, 129.05, 128.57, 128.20, 126.22, 126.17, 124.52, 120.18, 37.60, 36.64, 32.14, 31.69, 24.64, 19.18.
HRMS (ESI): Calcd. for $C_{25}H_{25}NO$ $[M+H]^+$: 356.2009, Found: 356.2014.

1,2-Dimethyl-*N*,2-diphenylcyclopropane-1-carboxamide (3o).

Following general procedure C, the product was obtained as separate diastereomers **3o'** and **3o''**. **3o'** was isolated as a white solid (16.4 mg, 61.8 µmol, 31%), **3o''** was isolated as a white solid (14.9 mg, 56.2 µmol, 28%). In total the product was gained as white solids (31.3 mg, 118 µmol, 59%, d.r. = 1:1). Purification was achieved by silica column chromatography (EtOAc in PE 0% → 25%). Diasteromers were assigned by NOESY-NMR spectroscopy.

Diasteromer **3o'**:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 – 7.50 (m, 2H), 7.40 (br, 1H), 7.35 – 7.16 (m, 7H), 7.13 – 7.04 (m, 1H), 1.55 (d, *J*=5.1, 1H), 1.43 (s, 3H), 1.14 (d, *J*=5.1, 1H), 1.03 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.54, 142.96, 138.16, 129.16, 128.87, 128.58, 126.69, 124.41, 120.03, 33.47, 32.51, 23.78, 23.26, 20.09.

HRMS (ESI): Calcd. for $C_{18}H_{19}NO$ $[M+H]^+$: 266.1539, Found: 266.1543.

Diasteromer **3o''**:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 – 7.08 (m, 7H), 7.06 – 6.92 (m, 3H), 6.85 (s, 1H), 2.06 (d, *J*=5.4, 1H), 1.65 (s, 3H), 1.54 (s, 3H), 0.87 (d, *J*=5.4, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.97, 143.58, 137.70, 128.78, 128.58, 128.37, 126.73, 124.18, 120.52, 33.43, 32.13, 25.01, 23.52, 17.69.

HRMS (ESI): Calcd. for $C_{18}H_{19}NO$ $[M+H]^+$: 266.1539, Found: 266.1538.

2-Isopropyl-1-methyl-N,2-diphenylcyclopropane-1-carboxamide (3p).

Following general procedure C, the product was obtained as separate diastereomers **3p'** and **3p''**. **3p'** was isolated as a white solid (14.2 mg, 48.4 µmol, 24%), **3p''** was isolated as a white solid (13.8 mg, 47.0 µmol, 24%). In total the product was gained as white solids (28.0 mg, 95.4 µmol, 48%, d.r. = 1:1). Purification was achieved by silica column chromatography (EtOAc in PE 0% → 10%). Diasteromers were assigned by NOESY-NMR analysis.

Diasteromer **3p'**:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 – 7.53 (m, 2H), 7.50 (br, 1H), 7.40 – 7.18 (m, 7H), 7.16 – 7.10 (m, 1H), 1.76 (h, *J*=6.8, 1H), 1.60 (d, *J*=4.7, 1H), 1.14 (s, 3H), 1.00 (d, *J*=4.7, 1H), 0.91 (d, *J*=6.8, 3H), 0.80 (d, *J*=6.9, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.40, 137.99, 137.44, 131.76, 129.07, 126.64, 124.30, 120.00, 43.66, 33.00, 32.61, 25.43, 21.25, 20.54, 19.96.

HRMS (ESI): Calcd. for $C_{20}H_{23}NO$ $[M+H]^+$: 294.1852, Found: 294.1857.

Diasteromer **3p''**:

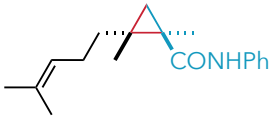
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26 – 7.14 (m, 7H), 7.07 – 6.91 (m, 3H), 6.75 (s, 1H), 1.82 (d, *J*=5.3, 1H), 1.81 – 1.64 (m, 4H), 1.01 (d, *J*=6.8, 3H), 0.90 (d, *J*=5.3, 1H), 0.86 (d, *J*=6.9, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.36, 138.16, 137.66, 131.50, 128.75, 127.72, 126.96, 124.14, 120.51, 43.24, 33.73, 32.86, 26.10, 20.46, 20.34, 16.97.

HRMS (ESI): Calcd. for $C_{20}H_{23}NO$ $[M+H]^+$: 294.1852, Found: 294.1852.

1,2-Dimethyl-2-(4-methylpent-3-en-1-yl)-*N*-phenylcyclopropane-1-carboxamide (3q).

Following general procedure B, the product was obtained as a white solid (42.4 mg, 156 µmol, 78%). Purification was achieved by silica column chromatography (EtOAc in PE 0%→20%).



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 – 7.46 (m, 2H), 7.41 – 7.26 (m, 3H), 7.18 – 7.05 (m, 1H), 5.22 – 5.12 (m, 0.5H), 5.10 – 4.96 (m, 0.5H), 2.18 – 1.97 (m, 2H), 1.77 – 1.40 (m, 11H), 1.32 (d, *J*=4.9, 0.6H), 1.23 – 1.15 (m, 1.9H), 1.11 (s, 1.5H), 0.43 (d, *J*=4.8, 0.5H), 0.41 (d, *J*=4.7, 0.5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.27, 172.19, 138.32, 138.27, 131.82, 131.41, 129.07, 129.03, 124.45, 124.39, 124.16, 124.09, 119.88, 35.55, 35.05, 32.28, 31.41, 27.45, 26.49, 25.90, 25.77, 25.67, 25.43, 25.08, 19.22, 18.49, 18.28, 18.17, 17.79, 17.63.

HRMS (ESI): Calcd. for $C_{18}H_{25}NO$ $[M+H]^+$: 272.2009, Found: 272.2013.

1,2-Dimethyl-*N*-phenyl-[1,1'-bi(cyclopropane)]-2-carboxamide (3r).

Following general procedure B, the product was obtained as separate diastereomers **3r'** and **3r''**. **3r'** was isolated as a white solid (19.7 mg, 85.9 µmol, 43%), **3r''** was isolated as a white solid (18.4 mg, 80.2 µmol, 40%). In total the product was gained as white solids (38.1 mg, 166 µmol, 83%, d.r. = 1:1). Purification was achieved by silica column chromatography (EtOAc in PE 0%→20%). Diasteromers were assigned by NOESY-NMR analysis.

Diasteromer **3r'**:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 – 7.49 (m, 2H), 7.37 – 7.28 (m, 3H), 7.09 (ddt, *J*=7.6, 7.0, 1.2, 1H), 1.52 (s, 3H), 1.14 (s, 3H), 1.06 (d, *J*=5.1, 1H), 0.97 (tt, *J*=8.3, 5.3, 1H), 0.62 – 0.55 (m, 1H), 0.49 (ddt, *J*=9.5, 8.2, 2.2, 1H), 0.39 (d, *J*=5.1, 1H), 0.20 (ddt, *J*=5.4, 3.5, 1.7, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.2, 138.3, 129.1, 124.2, 119.9, 32.3, 28.5, 21.3, 20.1, 17.3, 14.6, 5.5, 3.1.

HRMS (ESI): Calcd. for $C_{15}H_{19}NO$ $[M+H]^+$: 230.1539, Found: 230.1541.

Diasteromer **3r''**:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 – 7.45 (m, 2H), 7.34 – 7.28 (m, 2H), 7.24 (s, 1H), 7.11 – 7.04 (m, 1H), 1.47 (s, 3H), 1.17 (s, 3H), 1.06 (d, *J*=5.2, 1H), 0.90 (tt, *J*=8.3, 5.3, 1H), 0.48 – 0.38 (m, 1H), 0.26 (d, *J*=5.1, 1H), 0.36 – 0.09 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.0, 138.4, 129.1, 124.1, 119.9, 32.6, 26.7, 21.6, 19.0, 18.7, 15.6, 3.7, 2.5.
HRMS (ESI): Calcd. for $C_{15}H_{19}NO$ $[M+H]^+$: 230.1539, Found: 230.1544.

***tert*-butyl 1-methyl-1-(phenylcarbamoyl)-6-azaspiro[2.5]octane-6-carboxylate (3s).**

Following general procedure B, the product was obtained as a white solid (67.9 mg, 197 µmol, 99%). Purification was achieved by silica column chromatography (EtOAc in PE 10%→45%).

Following general procedure D, the product was obtained as a white solid (2.35 g, 6.82 mmol, 98%). Purification was achieved by silica column chromatography (EtOAc in PE 10%→45%).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.53 – 7.44 (m, 2H), 7.37 – 7.27 (m, 3H), 7.10 (ddt, J=7.8, 7.0, 1.2, 1H), 3.88 – 3.56 (m, 2H), 3.16 (dddd, J=19.1, 13.0, 9.5, 3.4, 2H), 1.74 (ddd, J=13.3, 9.5, 4.0, 1H), 1.66 – 1.56 (m, 1H), 1.49 – 1.35 (m, 15H), 0.52 (dd, J=4.9, 1.0, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.40, 154.94, 138.04, 129.04, 124.35, 120.06, 79.55, 31.14, 31.09, 30.94, 28.63, 28.54, 23.33, 17.22.
HRMS (ESI): Calcd. for $C_{20}H_{28}N_2O_3$ $[M+H]^+$: 345.2173, Found: 345.2179.

1-Methyl-*N*-phenylspiro[2.3]hexane-1-carboxamide (3t).

Following general procedure B, the product was obtained as a white solid (32.2 mg, 150 µmol, 75%). Purification was achieved by silica column chromatography (EtOAc in PE 5%→35%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 – 7.46 (m, 2H), 7.34 (s, 1H), 7.30 (t, *J*=8.0, 2H), 7.12 – 7.04 (m, 1H), 2.42 – 2.20 (m, 2H), 2.20 – 2.01 (m, 2H), 1.91 (ddt, *J*=12.5, 8.8, 4.4, 2H), 1.54 (d, *J*=4.6, 1H), 1.32 (s, 3H), 0.67 (d, *J*=4.6, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.5, 138.2, 129.0, 124.1, 120.0, 34.0, 28.3, 27.9, 27.5, 27.1, 16.8, 15.8.
HRMS (ESI): Calcd. for $C_{14}H_{17}NO$ $[M+H]^+$: 216.1383, Found: 216.1382.

1-Methyl-*N*-phenylspiro[2.4]heptane-1-carboxamide (3u).

Following general procedure B, the product was obtained as a white solid (36.5 mg, 159 µmol, 80%). Purification was achieved by silica column chromatography (EtOAc in PE 0%→25%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54 – 7.49 (m, 2H), 7.35 (s, 1H), 7.30 (dd, *J*=8.5, 7.4, 2H), 7.11 – 7.04 (m, 1H), 1.92 – 1.30 (m, 8H), 1.49 (d, *J*=4.4, 1H), 1.44 (s, 3H), 0.57 (d, *J*=4.5, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.2, 138.3, 129.0, 124.1, 119.9, 35.4, 32.7, 32.2, 29.9, 27.3, 26.6, 26.5, 18.6.
HRMS (ESI): Calcd. for $C_{15}H_{19}NO$ $[M+H]^+$: 230.1539, Found: 230.1538.

1-Methyl-*N*-phenylspiro[2.5]octane-1-carboxamide (3v).

Following general procedure B, the product was obtained as a white solid (47.0 mg, 193 µmol, 97%). Purification was achieved by silica column chromatography (EtOAc in PE 0%→15%).

^{1}H NMR (400 MHz, CDCl3) δ = 7.55 – 7.48 (m, 2H), 7.36 (s, 1H), 7.32 – 7.27 (m, 2H), 7.08 (ddt, J=7.6, 7.0, 1.1, 1H), 1.64 – 1.31 (m, 13H), 1.22 (d, J=4.7, 1H), 0.40 (d, J=4.7, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.2, 138.3, 129.0, 124.1, 119.9, 32.0, 31.9, 31.5, 30.3, 26.4, 26.1, 25.7, 24.1, 17.3.
HRMS (ESI): Calcd. for $C_{16}H_{21}NO$ $[M+H]^+$: 244.1696, Found: 244.1696.

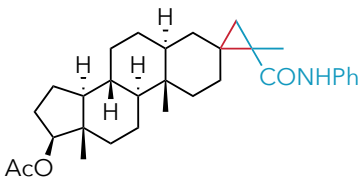
1-Methyl-*N*-phenylspiro[2.6]nonane-1-carboxamide (3w).

Following general procedure B, the product was obtained as a white solid (45.6 mg, 177 µmol, 89%). Purification was achieved by silica column chromatography (EtOAc in PE 0%→15%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 – 7.47 (m, 2H), 7.35 (s, 1H), 7.33 – 7.27 (m, 2H), 7.18 – 6.99 (m, 1H), 1.82 – 1.38 (m, 15H), 1.29 (d, *J*=4.7, 1H), 0.44 (d, *J*=4.7, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.4, 138.3, 129.1, 124.1, 119.9, 34.2, 33.9, 32.7, 31.6, 28.5, 28.4, 26.5, 26.4, 26.3, 18.4.
HRMS (ESI): Calcd. for $C_{17}H_{23}NO$ $[M+H]^+$: 258.1852, Found: 258.1851.

(5*S*,8*R*,9*S*,10*S*,13*S*,14*S*,17*S*)-2',10,13-trimethyl-2'-(phenylcarbamoyl)hexadeca-hydrospiro[cyclopenta[*a*]phenanthrene-3,1'-cyclopropan]-17-yl acetate (3x).

Following general procedure B, the product was obtained as a white solid (95.1 mg, 199 μmol, 99%, d.r. = 1:1). Purification was achieved by silica column chromatography (EtOAc in PE 0%→25%).



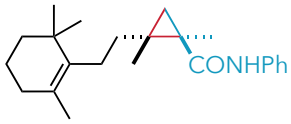
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 – 7.39 (m, 2H), 7.32 (td, *J*=6.8, 4.0, 4H), 7.10 (td, *J*=7.4, 1.1, 1H), 4.57 (ddd, *J*=9.2, 7.8, 4.4, 1H), 2.23 – 2.10 (m, 1H), 2.05 – 1.98 (m, 3H), 1.95 – 0.71 (m, 31H), 0.50 – 0.22 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.1, 172.1, 171.3, 138.1, 138.0, 129.0, 129.0, 124.2, 124.1, 120.3, 119.9, 82.9, 82.9, 54.7, 54.6, 50.8, 46.8, 46.5, 42.6, 42.6, 38.6, 38.0, 37.0, 36.9, 36.0, 36.0, 35.3, 35.3, 33.8, 33.8, 32.0, 31.6, 31.6, 30.6, 30.3, 28.6, 28.4, 27.6, 27.5, 27.4, 27.2, 24.2, 24.1, 23.5, 23.5, 21.2, 20.5, 20.4, 17.8, 17.6, 12.1, 11.8, 11.7.

HRMS (ESI): Calcd. for $C_{31}H_{43}NO_3$ $[M+H]^+$: 478.3316, Found: 478.3323.

1,2-dimethyl-*N*-phenyl-2-(2-(2,6,6-trimethylcyclohex-1-en-1-yl)ethyl)cyclo-propane-1-carboxamide (3y).

Following general procedure B, the product was obtained as a white solid (67.2 mg, 198 μmol, 99%, d.r. = 1:1). Purification was achieved by silica column chromatography (EtOAc in PE 0%→10%).



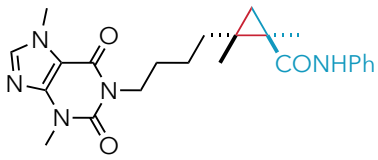
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 – 7.46 (m, 2H), 7.42 – 7.25 (m, 3H), 7.17 – 7.01 (m, 1H), 2.36 – 1.85 (m, 4H), 1.82 (t, *J*=6.4, 1H), 1.60 (s, 3H), 1.50 – 1.38 (m, 6H), 1.40 – 1.27 (m, 2H), 1.30 – 1.12 (m, 4H), 1.07 – 0.93 (m, 4H), 0.91 – 0.89 (m, 2H), 0.46 (d, *J*=4.8, 0.5H), 0.41 (d, *J*=4.7, 0.5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.24, 172.13, 138.43, 138.25, 136.98, 136.70, 129.04, 128.97, 127.23, 127.16, 124.16, 123.96, 119.92, 119.69, 39.94, 39.90, 35.63, 35.38, 35.14, 35.03, 32.90, 32.83, 32.50, 31.70, 28.85, 28.78, 28.68, 28.65, 28.03, 27.22, 25.92, 25.78, 25.14, 24.90, 19.96, 19.80, 19.62, 19.58, 19.06, 18.47, 18.34, 18.28.

HRMS (ESI): Calcd. for $C_{23}H_{33}NO$ $[M+H]^+$: 340.2635, Found: 340.2637.

2-(4-(3,7-Dimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1*H*-purin-1-yl)butyl)-1,2-dimethyl-*N*-phenyl-cyclopropane-1-carboxamide (3z).

Following general procedure B, the product was obtained as a white solid (82.5 mg, 195 µmol, 97%). Purification was achieved by silica column chromatography (MeOH in CH_2Cl_2 5%→15%).



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 – 7.44 (m, 3H), 7.41 (d, *J*=7.7, 1H), 7.32 – 7.20 (m, 2H), 7.11 – 6.98 (m, 1H), 4.05 – 3.85 (m, 5H), 3.55 (s, 1.7H), 3.52 (s, 1.3H), 1.72 – 1.41 (m, 8.5H), 1.30 (d, *J*=4.8, 0.6H), 1.28 – 1.21 (m, 0.5H), 1.18 (d, *J*=4.8, 0.6H), 1.14 (s, 1.3H), 1.06 (s, 1.7H), 0.41 (d, *J*=4.8, 0.5H), 0.37 (d, *J*=4.8, 0.4H).

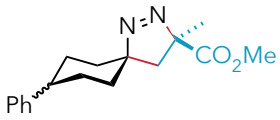
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.21, 155.34, 155.26, 151.55, 151.49, 148.76, 148.63, 141.54, 141.36, 138.30, 138.22, 128.96, 128.91, 124.05, 123.98, 119.97, 119.91, 107.73, 107.69, 41.40, 41.36, 34.77, 34.44, 33.66, 33.64, 32.10, 31.39, 29.80, 29.76, 28.16, 28.14, 27.18, 26.52, 25.08, 24.98, 24.39, 24.35, 19.09, 18.36, 18.23, 17.95.

HRMS (ESI): Calcd. for $C_{23}H_{29}N_5O_3$ $[M+H]^+$: 424.2343, Found: 424.2348.

6.2 Δ^1-Pyrazolines

Methyl 3-methyl-8-phenyl-1,2-diazaspiro[4.5]dec-1-ene-3-carboxylate (4a).

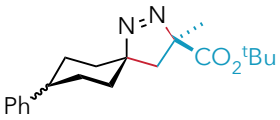
Following general procedure E, the product was obtained as a colorless oil (34.4 mg, 120 µmol, 60%, d.r. = 5.2:1). Purification was achieved by silica column chromatography (EtOAc in PE 0%→15%).



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 – 7.12 (m, 5H), 3.72 (s, 0.5H), 3.71 (s, 2.5H), 2.69 (tt, *J*=12.5, 3.2, 1H), 2.50 – 2.21 (m, 2H), 2.10 (d, *J*=13.0, 0.1H), 1.93 (d, *J*=13.0, 0.9H), 2.05 – 1.39 (m, 5H), 1.61 (s, 0.5H), 1.59 (s, 2.5H), 1.37 (d, *J*=12.9, 0.1H), 1.23 (d, *J*=13.0, 0.9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.95, 146.82, 128.58, 128.51, 127.07, 126.81, 126.41, 126.23, 96.50, 95.70, 94.42, 94.12, 52.99, 52.90, 43.93, 43.03, 42.29, 38.66, 38.43, 37.89, 35.88, 34.71, 31.20, 31.02, 30.86, 30.72, 24.54, 24.11.
HRMS (ESI): Calcd. for $C_{17}H_{22}N_2O_2$ $[M+H]^+$: 287.1754, Found: 287.1756.

***tert*-Butyl 3-methyl-8-phenyl-1,2-diazaspiro[4.5]dec-1-ene-3-carboxylate (4b).**

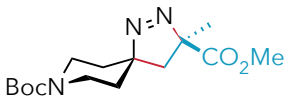
Following general procedure E, the product was obtained as a white solid (38.3 mg, 117 µmol, 58%, d.r. = 5.6:1). Purification was achieved by silica column chromatography (EtOAc in PE 0%→20%).



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 – 7.17 (m, 5H), 2.74 (tt, *J*=12.3, 3.3, 1H), 2.41 (dtd, *J*=26.0, 12.7, 3.4, 1H), 2.11 – 1.30 (m, 6H), 1.62 (s, 0.5H), 1.59 (s, 2.5H), 1.47 (s, 9H), 1.25 (d, *J*=12.9, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.4, 170.3, 146.8, 146.3, 128.5, 128.4, 127.0, 126.7, 126.3, 126.1, 96.2, 96.1, 94.6, 94.0, 82.2, 82.1, 43.9, 43.0, 42.5, 38.7, 38.7, 37.8, 35.9, 34.6, 31.2, 30.9, 30.8, 30.7, 27.9, 24.2, 23.8.
HRMS (ESI): Calcd. for $C_{20}H_{28}N_2O_2$ $[M+H]^+$: 329.2224, Found: 329.2227.

8-(*tert*-Butyl) 3-methyl 3-methyl-1,2,8-triazaspiro[4.5]dec-1-ene-3,8-dicarboxylate (4c).

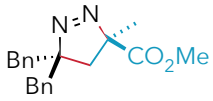
Following general procedure E, the product was obtained as a colorless oil (42.8 mg, 137 µmol, 69%). Purification was achieved by silica column chromatography (EtOAc in PE 20%→35%).



^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.91 (dddd, *J*=16.5, 13.8, 6.9, 4.1, 2H), 3.75 (s, 3H), 3.43 – 3.24 (m, 2H), 2.07 – 1.94 (m, 3H), 1.63 (s, 3H), 1.59 – 1.48 (m, 2H), 1.46 (s, 9H), 1.29 (d, *J*=13.1, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.4, 154.7, 95.4, 94.2, 79.8, 53.0, 39.4, 36.0, 35.0, 28.4, 24.1.
HRMS (ESI): Calcd. for $C_{15}H_{25}N_3O_4$ $[M+H]^+$: 312.1918, Found: 312.1921.

Methyl 5,5-dibenzyl-3-methyl-4,5-dihydro-3*H*-pyrazole-3-carboxylate (4d).

Following general procedure E, the product was obtained as a white solid (53.6 mg, 166 µmol, 83%). Purification was achieved by silica column chromatography (EtOAc in PE 0%→20%).

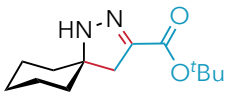


^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 – 7.11 (m, 8H), 7.10 – 7.00 (m, 2H), 3.69 (d, *J*=13.8, 1H), 3.49 (s, 3H), 3.29 (d, *J*=13.6, 1H), 3.09 (d, *J*=13.7, 1H), 2.86 (d, *J*=13.8, 1H), 2.04 (d, *J*=13.4, 1H), 1.22 (d, *J*=13.5, 1H), 0.69 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.9, 136.3, 136.1, 131.1, 131.0, 128.4, 127.1, 126.8, 100.0, 97.0, 52.8, 45.2, 44.2, 33.1, 22.5.
HRMS (ESI): Calcd. for $C_{20}H_{22}N_2O_2$ $[M+H]^+$: 323.1754, Found: 323.1759.

6.3 Δ^2-Pyrazolines

***tert*-Butyl 1,2-diazaspiro[4.5]dec-2-ene-3-carboxylate (6a).**

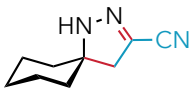
Following general procedure F, the product was obtained as a colorless oil (47.4 mg, 199 µmol, 99%).



^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.94 (s, 1H), 2.67 (s, 2H), 1.78 – 1.11 (m, 19H).
^{13}C NMR (101 MHz, CDCl3) δ 162.63, 143.20, 81.52, 67.74, 36.77, 28.28, 25.29, 23.25.
HRMS (ESI): Calcd. for $C_{13}H_{22}N_2O_2$ [M+H]+: 239.1754, Found: 239.1755.

1,2-Diazaspiro[4.5]dec-2-ene-3-carbonitrile (6b).

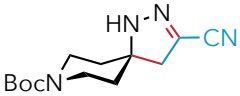
Following general procedure F, the product was obtained as a yellow oil (32.4 mg, 199 µmol, 99%).



^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.23 (s, 1H), 2.68 (s, 2H), 1.67 – 1.52 (m, 6H), 1.51 – 1.35 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 122.20, 115.39, 68.09, 43.94, 36.38, 25.04, 23.11.
HRMS (EI): Calcd. for $C_9H_{13}N_3$ $[M]^+$: 163.11040, Found: 163.11030.

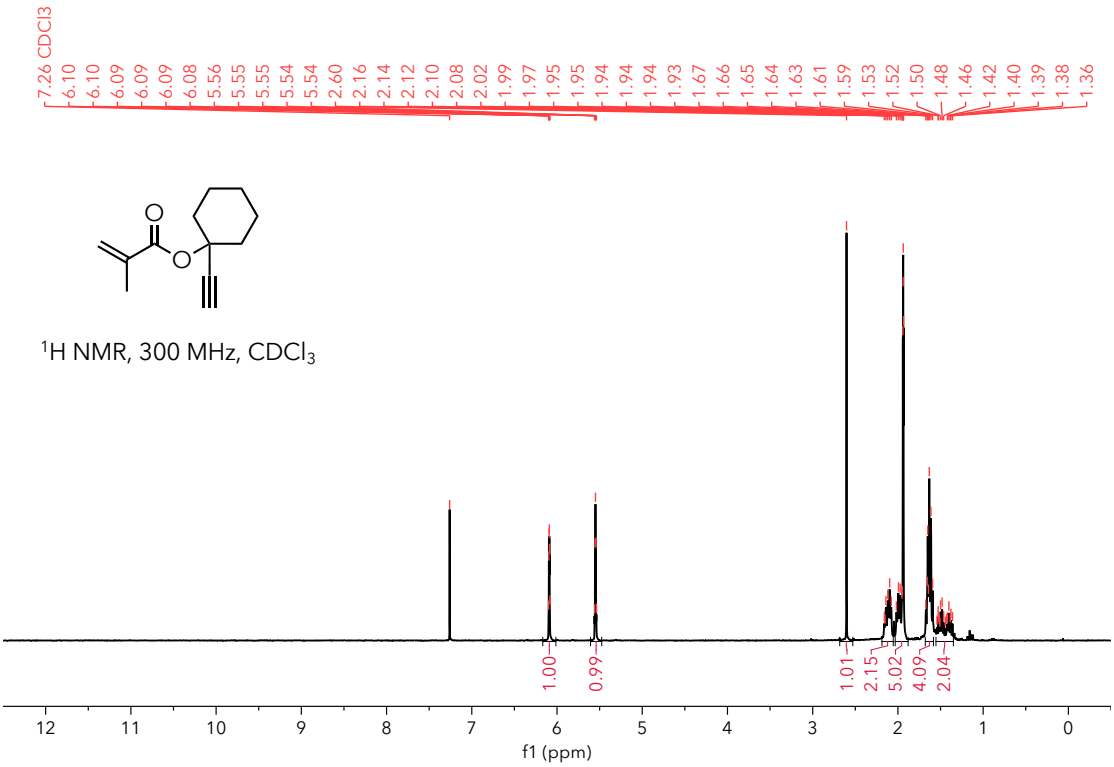
***tert*-Butyl 3-cyano-1,2,8-triazaspiro[4.5]dec-2-ene-8-carboxylate (6c).**

Following general procedure F, the product was obtained as a colorless oil (52.1 mg, 197 µmol, 99%).

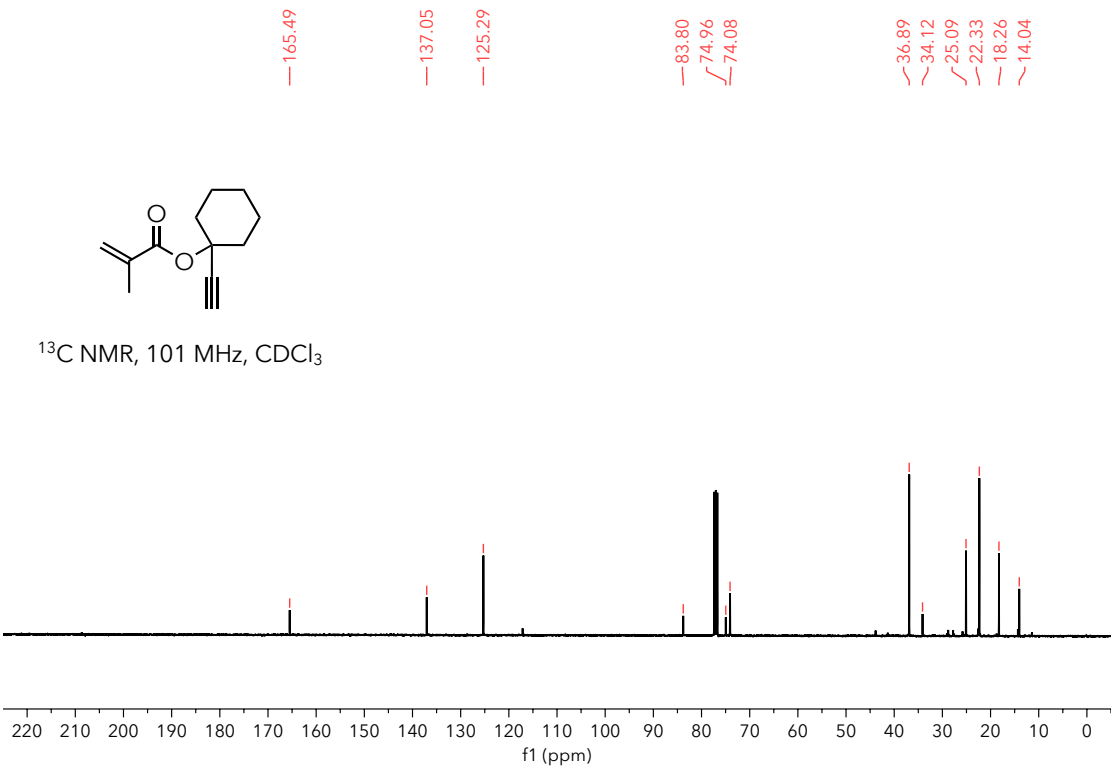


^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.52 (s, 1H), 3.63 (dt, *J*=14.2, 5.0, 2H), 3.22 (ddd, *J*=14.0, 8.0, 4.6, 2H), 2.74 (s, 2H), 1.66 (dt, *J*=10.2, 4.0, 4H), 1.43 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.54, 121.96, 114.98, 80.22, 66.33, 43.08, 35.63, 28.45.
HRMS (ESI): Calcd. for $C_{13}H_{20}N_4O_2$ [M+H]+: 265.1659, Found: 265.1662.

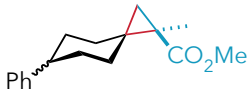
7 NMR Spectra



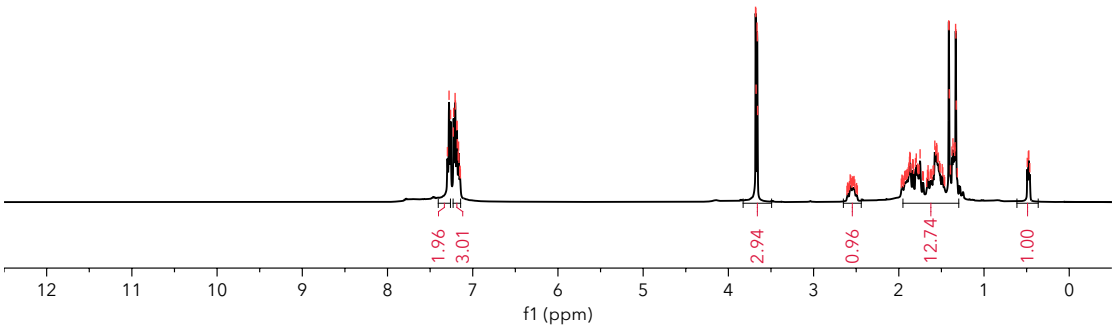
^{1}H NMR, 300 MHz, $CDCl_3$

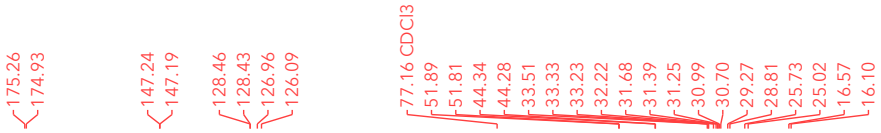


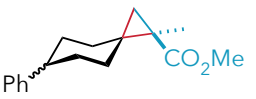
^{13}C NMR, 101 MHz, $CDCl_3$



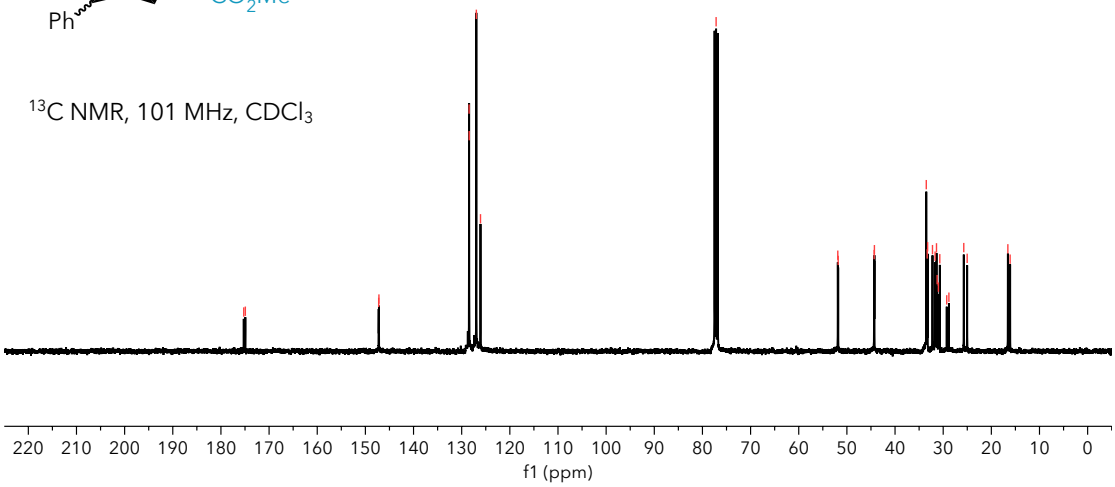
^{1}H NMR, 400 MHz, $CDCl_3$

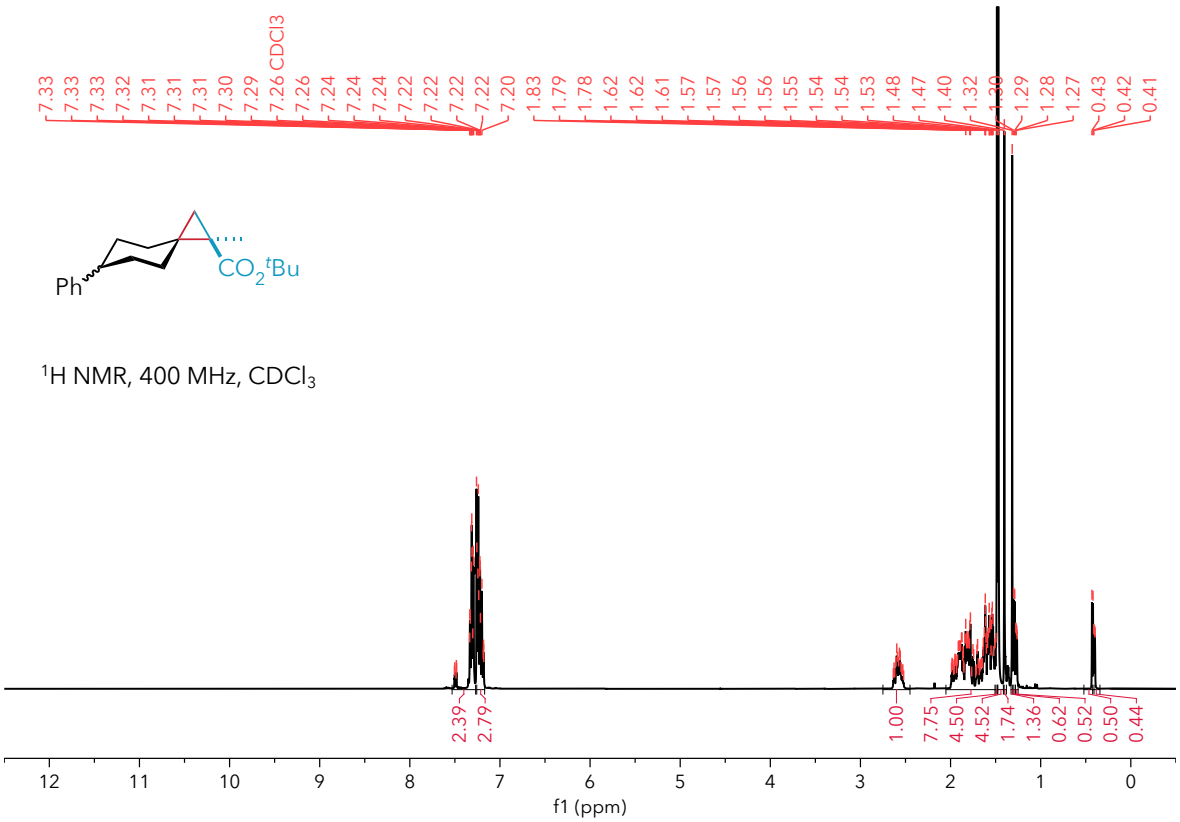


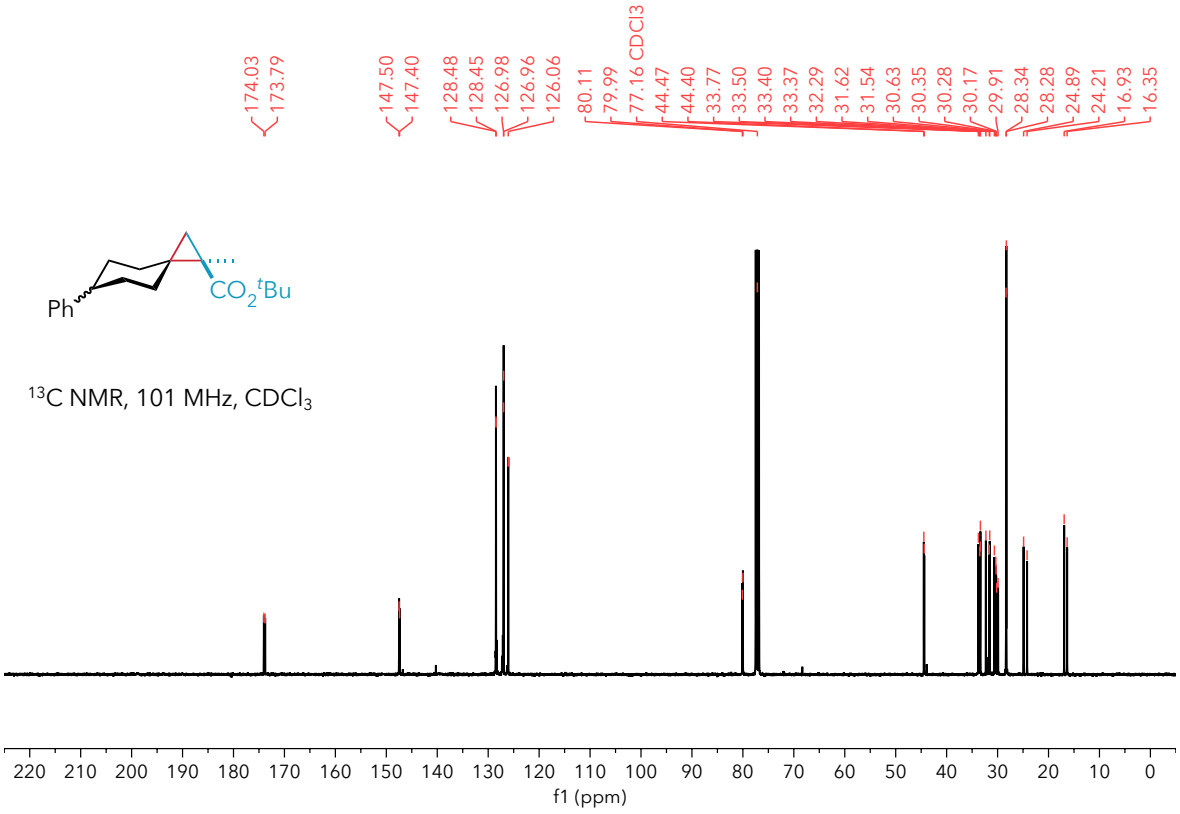


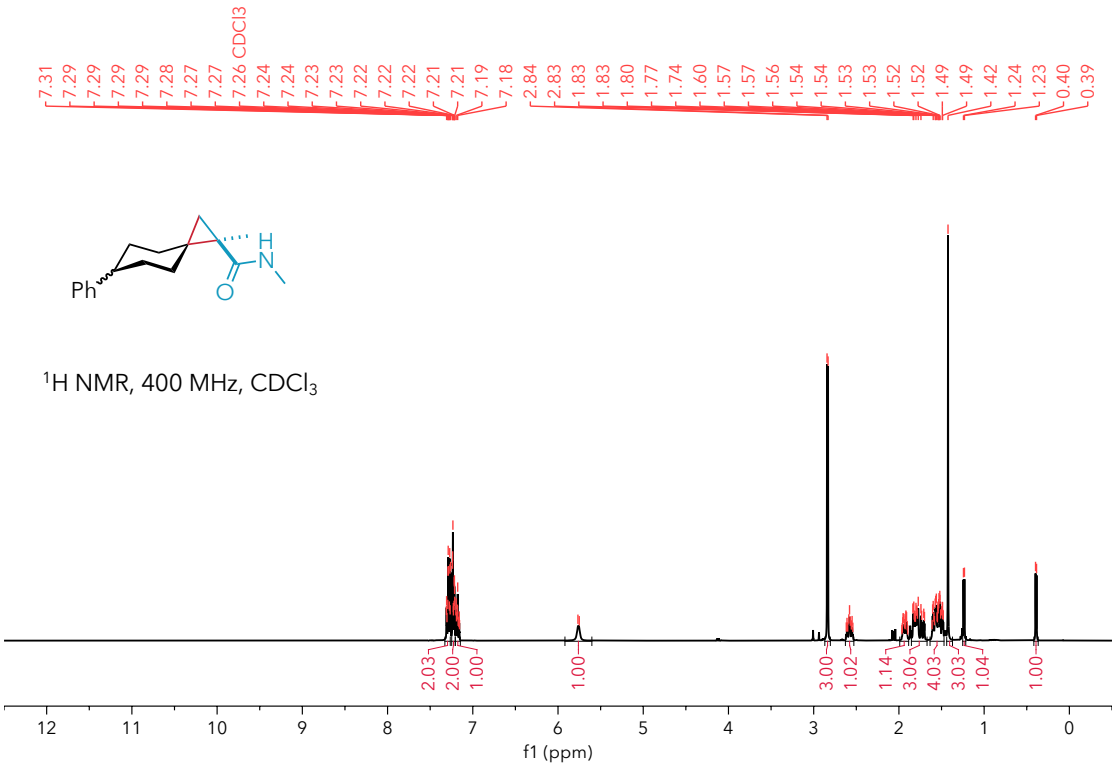


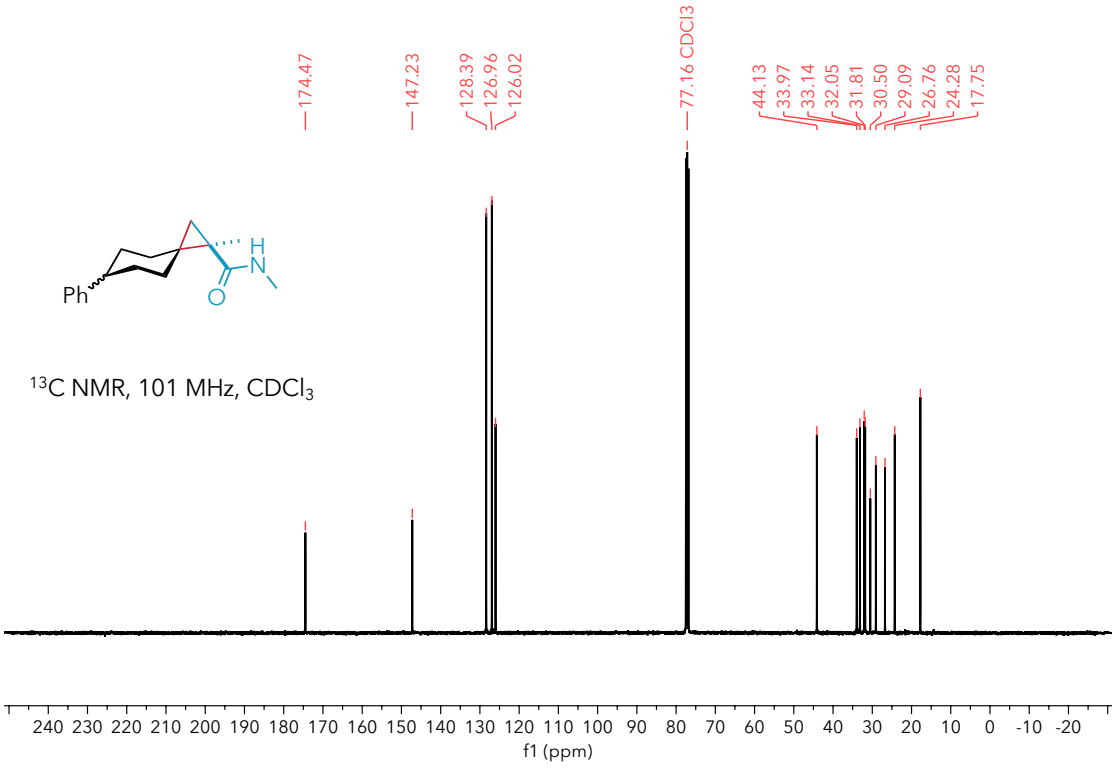
^{13}C NMR, 101 MHz, $CDCl_3$

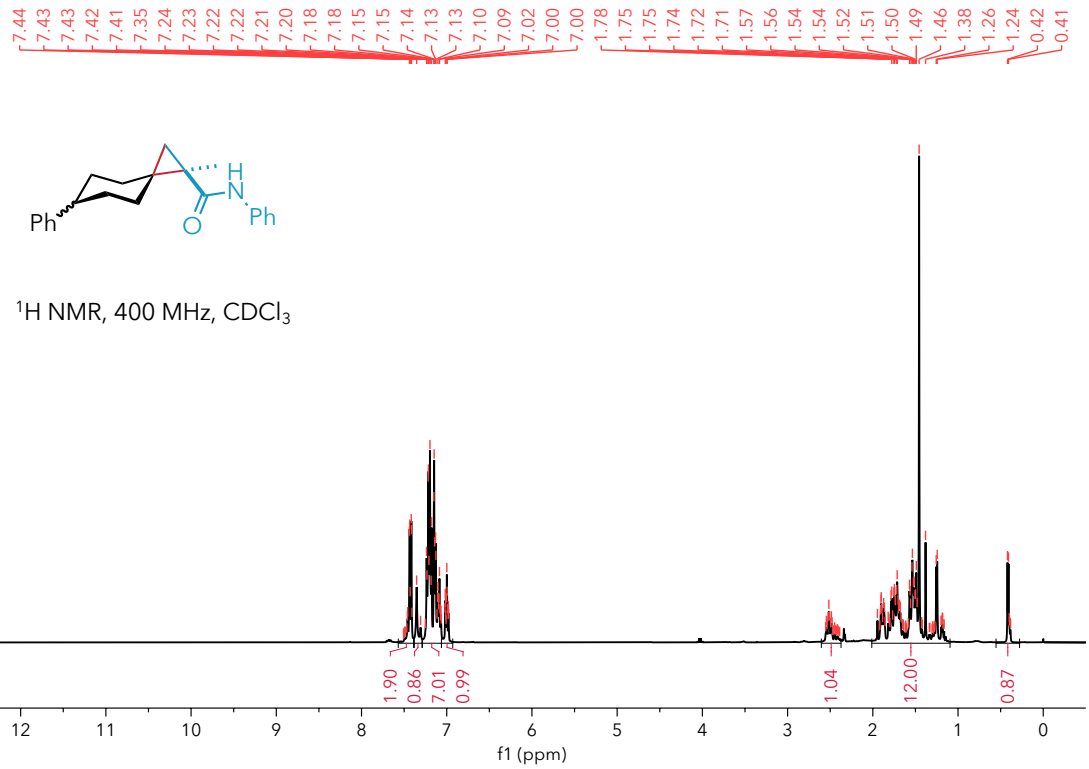



7.33 7.33 7.33 7.32 7.31 7.31 7.31 7.30 7.29 7.26 CDCl3 7.26 7.24 7.24 7.24 7.22 7.22 7.22 7.22 7.20 1.83 1.79 1.78 1.62 1.61 1.57 1.57 1.56 1.56 1.55 1.54 1.54 1.53 1.48 1.47 1.40 1.32 1.30 1.29 1.28 1.27 0.43 0.42 0.41
Ph
CO2tBu
1H NMR, 400 MHz, CDCl3
2.39 2.79 1.00 7.75 4.50 4.52 1.74 1.36 0.62 0.52 0.50 0.44
12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

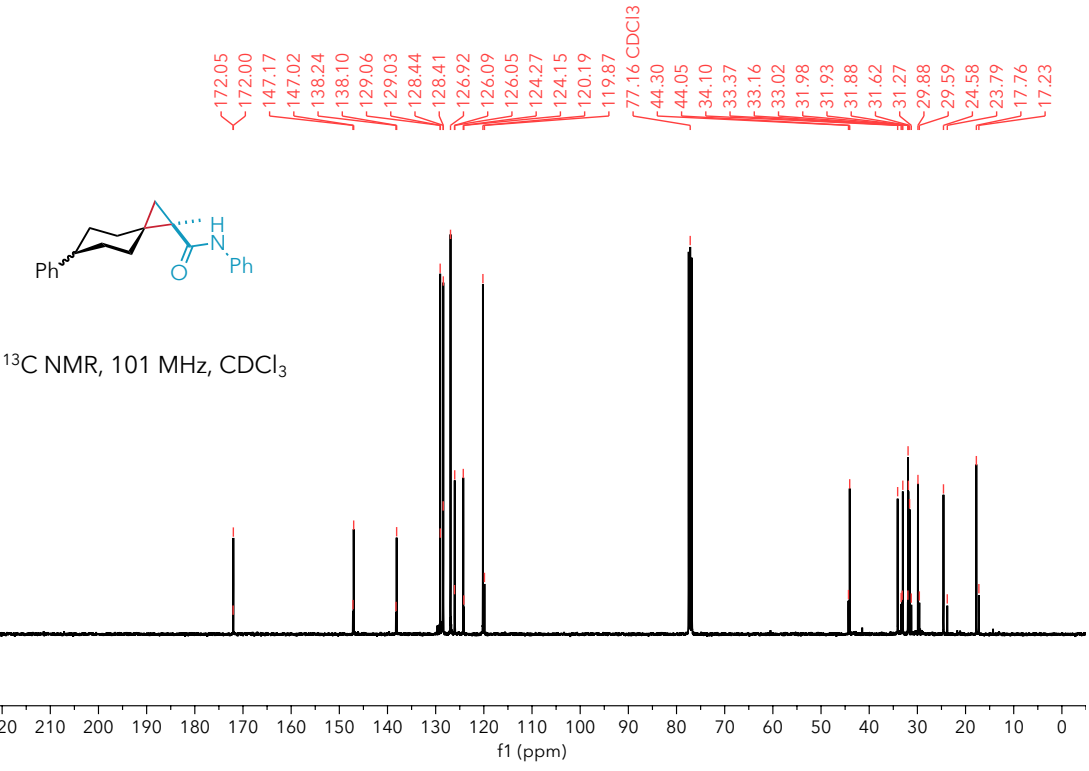

174.03 173.79 147.50 147.40 128.48 128.45 126.98 126.96 126.06 80.11 79.99 77.16 CDCl3 44.47 44.40 33.77 33.50 33.40 33.37 32.29 31.62 31.54 30.63 30.35 30.28 30.17 29.91 28.34 28.28 24.89 24.21 16.93 16.35
Ph
CO2tBu
13C NMR, 101 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.31
7.29
7.29
7.29
7.29
7.28
7.27
7.27
7.26 CDCl3
7.24
7.24
7.23
7.23
7.22
7.22
7.22
7.21
7.21
7.19
7.18
2.84
2.83
1.83
1.83
1.80
1.77
1.74
1.60
1.57
1.57
1.56
1.54
1.54
1.53
1.53
1.52
1.52
1.49
1.49
1.42
1.24
1.23
0.40
0.39
Ph
H
N
O
1H NMR, 400 MHz, CDCl3
2.03
2.00
1.00
1.00
3.00
1.02
1.14
3.06
4.03
3.03
1.04
1.00
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

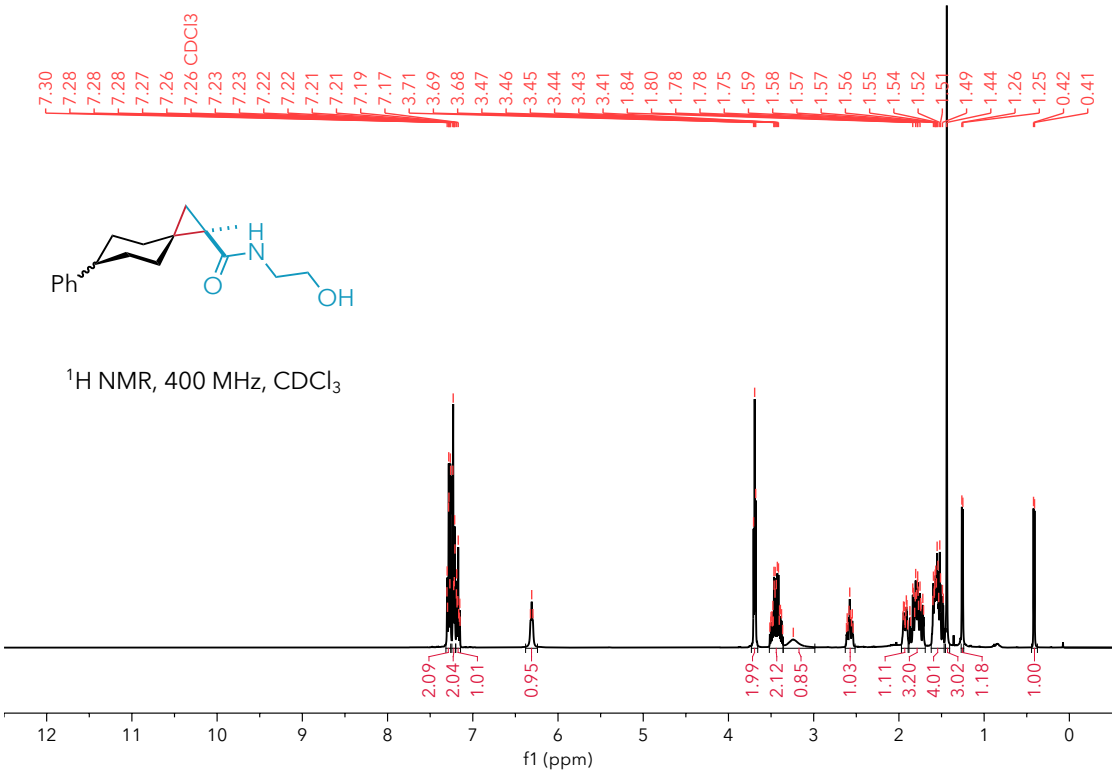

174.47
147.23
128.39
126.96
126.02
77.16 CDCl3
44.13
33.97
33.14
32.05
31.81
30.50
29.09
26.76
24.28
17.75
Ph
H
N
O
13C NMR, 101 MHz, CDCl3
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

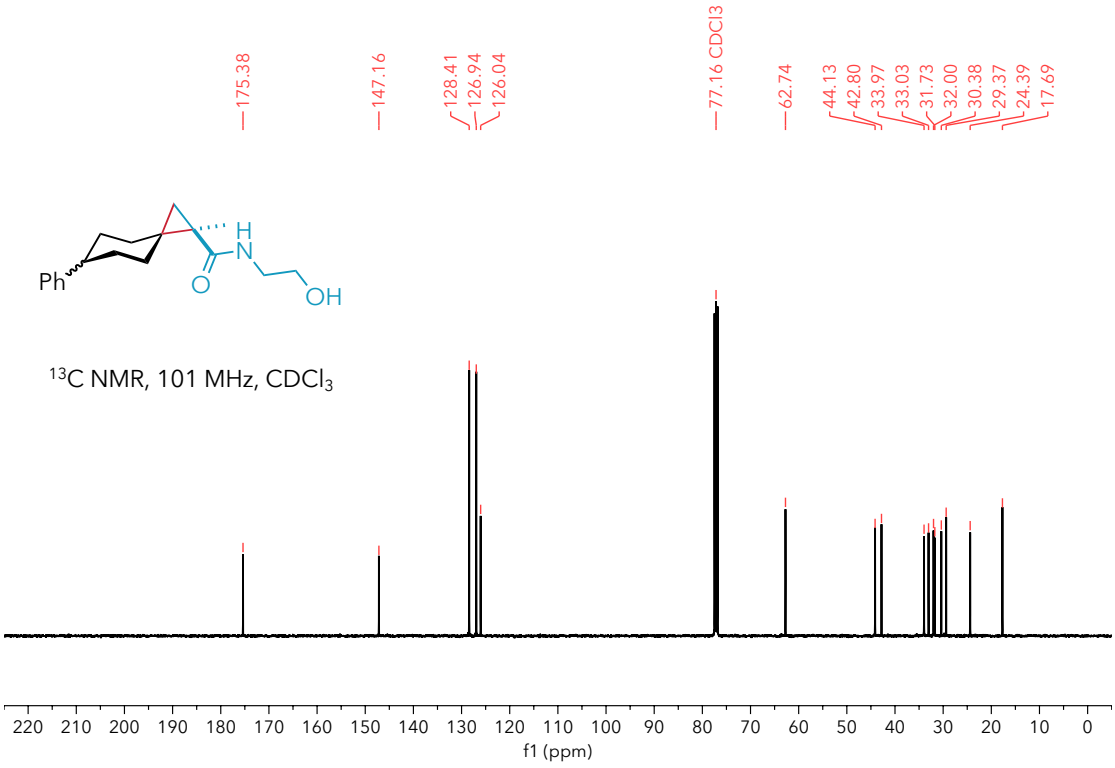


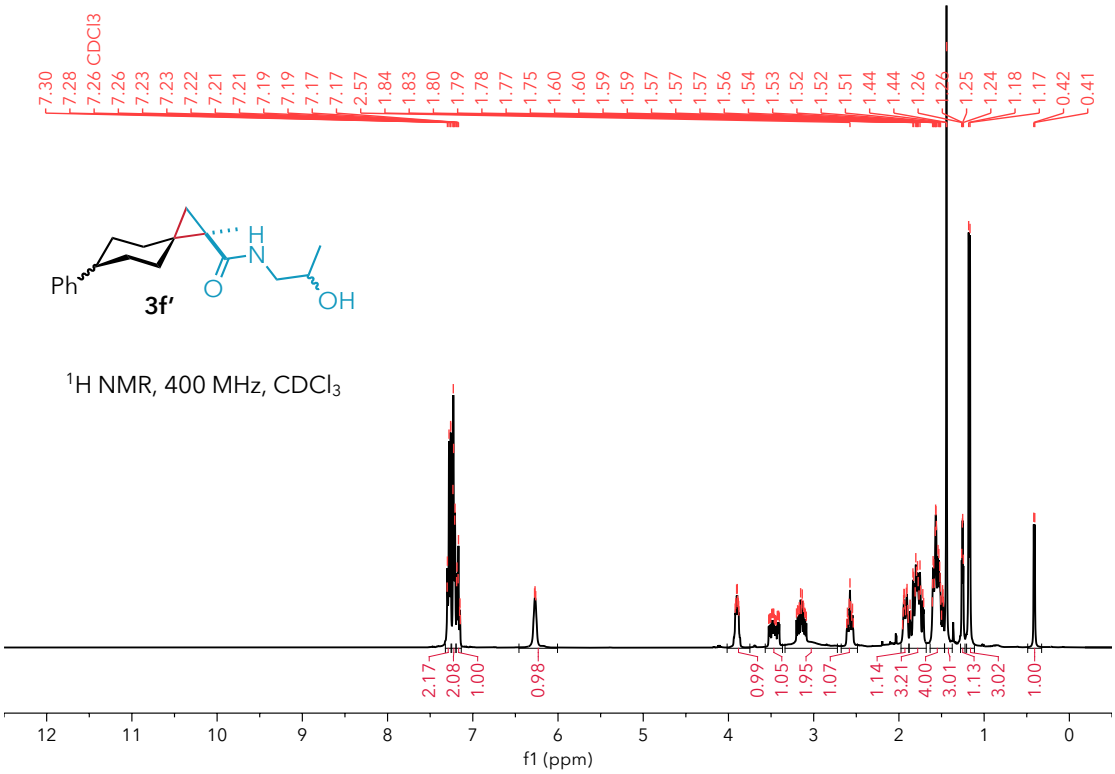
^{1}H NMR, 400 MHz, $CDCl_3$



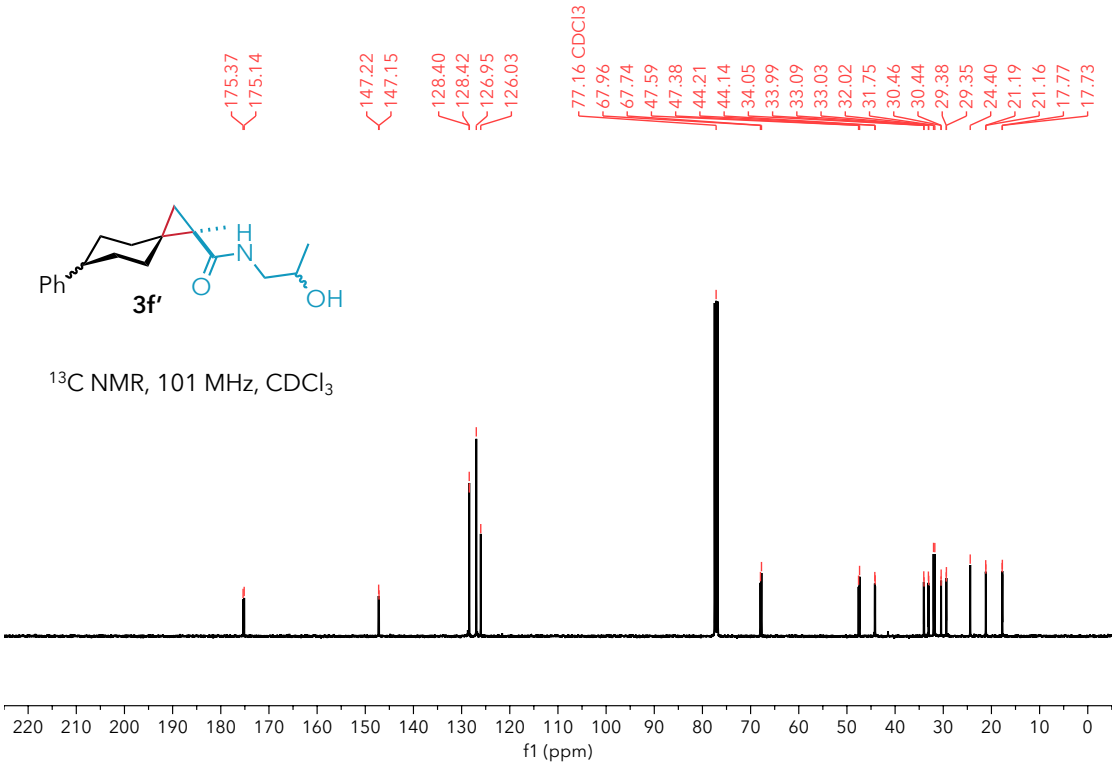
^{13}C NMR, 101 MHz, $CDCl_3$


7.30
7.28
7.28
7.28
7.27
7.26
7.26 CDCl3
7.23
7.23
7.22
7.22
7.21
7.21
7.19
7.17
3.71
3.69
3.68
3.47
3.46
3.45
3.44
3.43
3.41
1.84
1.80
1.78
1.78
1.75
1.59
1.58
1.57
1.57
1.56
1.55
1.54
1.52
1.51
1.49
1.44
1.26
1.25
0.42
0.41
Ph
H
N
O
OH
1H NMR, 400 MHz, CDCl3
2.09
2.04
1.01
0.95
1.99
2.12
0.85
1.03
1.11
3.20
4.01
3.02
1.18
1.00
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

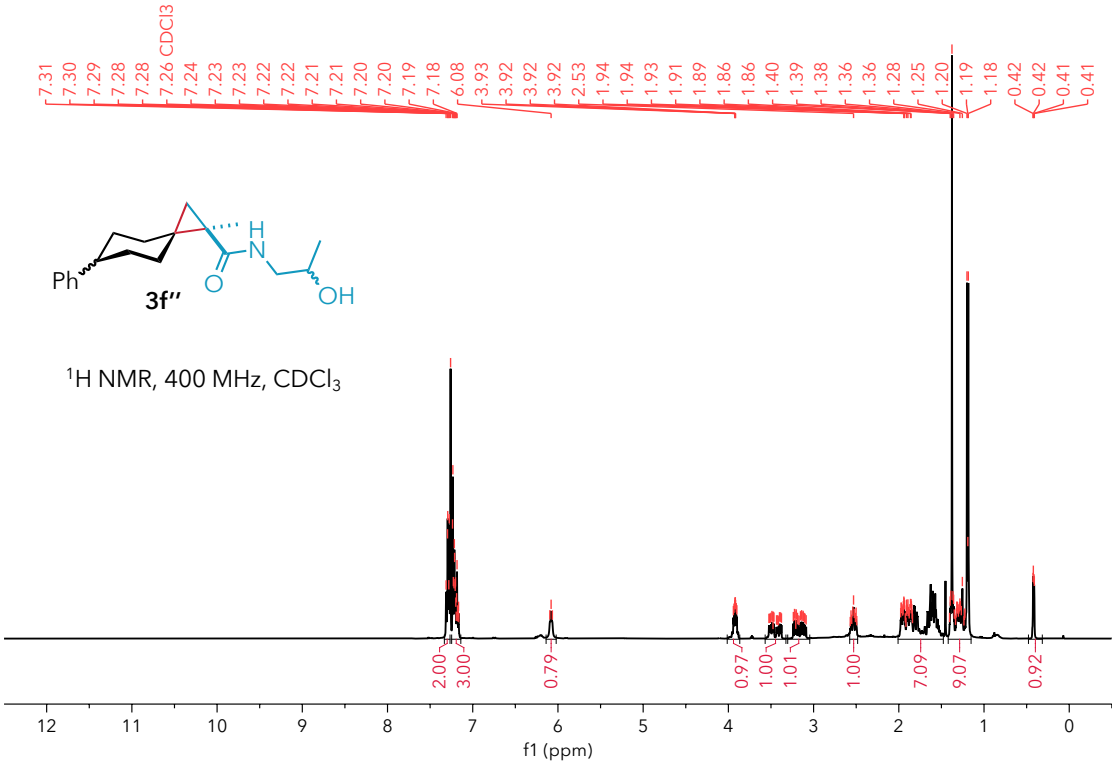

175.38
147.16
128.41
126.94
126.04
77.16 CDCl3
62.74
44.13
42.80
33.97
33.03
31.73
32.00
30.38
29.37
24.39
17.69
Ph
H
N
O
OH
13C NMR, 101 MHz, CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



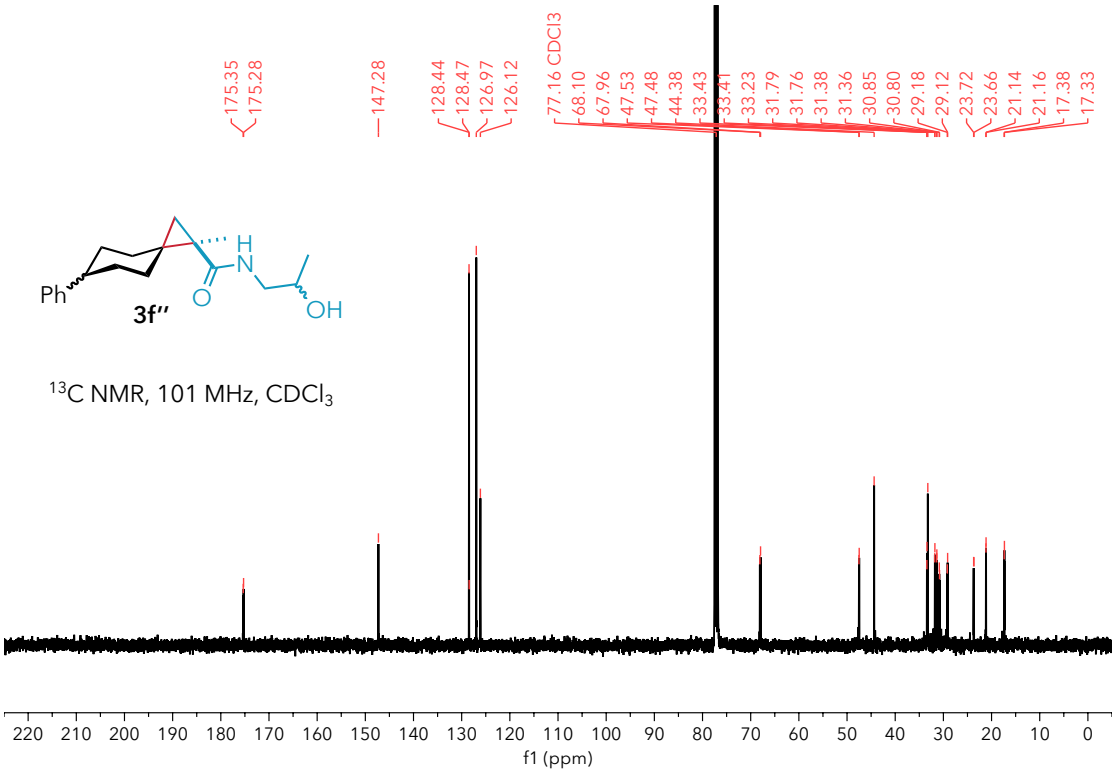
^{1}H NMR, 400 MHz, $CDCl_3$



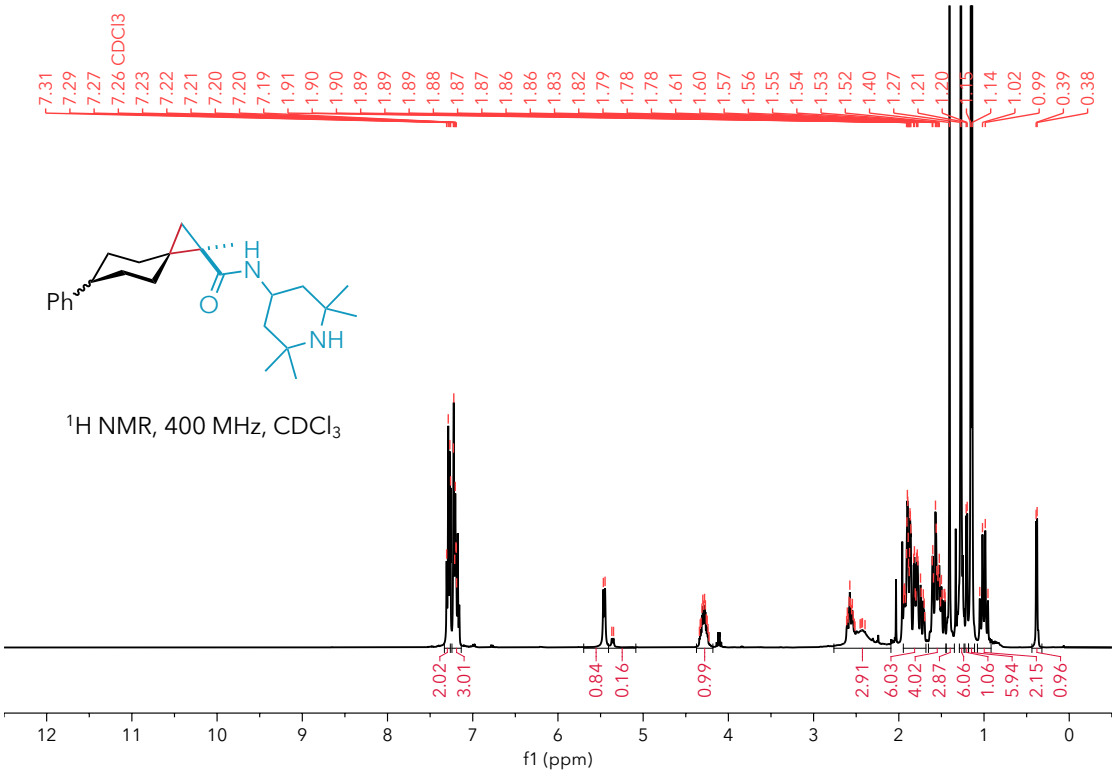
^{13}C NMR, 101 MHz, $CDCl_3$



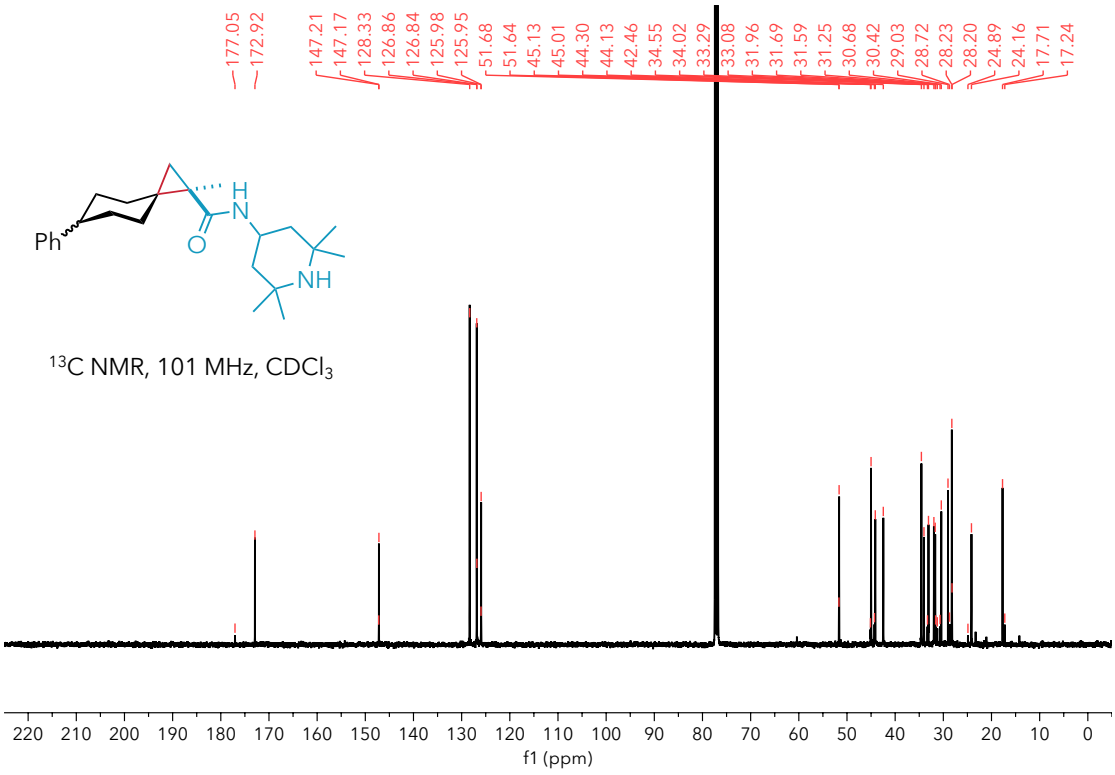
^{1}H NMR, 400 MHz, $CDCl_3$



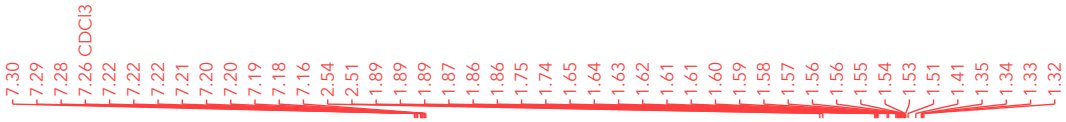
^{13}C NMR, 101 MHz, $CDCl_3$

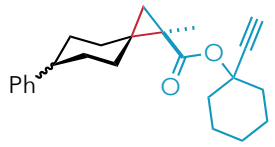


^{1}H NMR, 400 MHz, $CDCl_3$

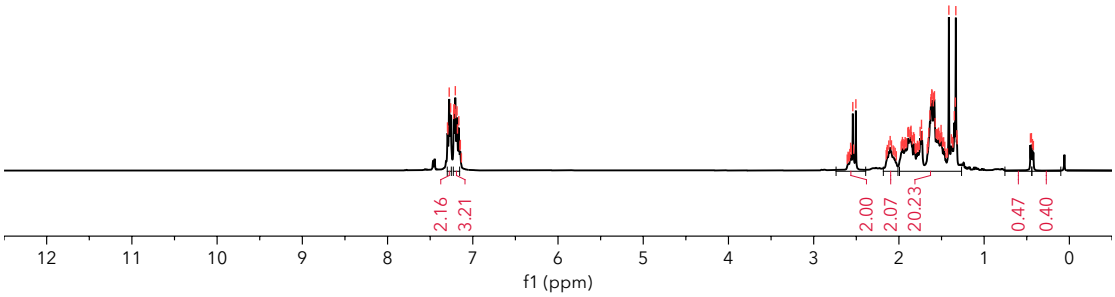


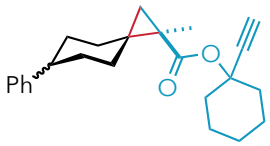
^{13}C NMR, 101 MHz, $CDCl_3$



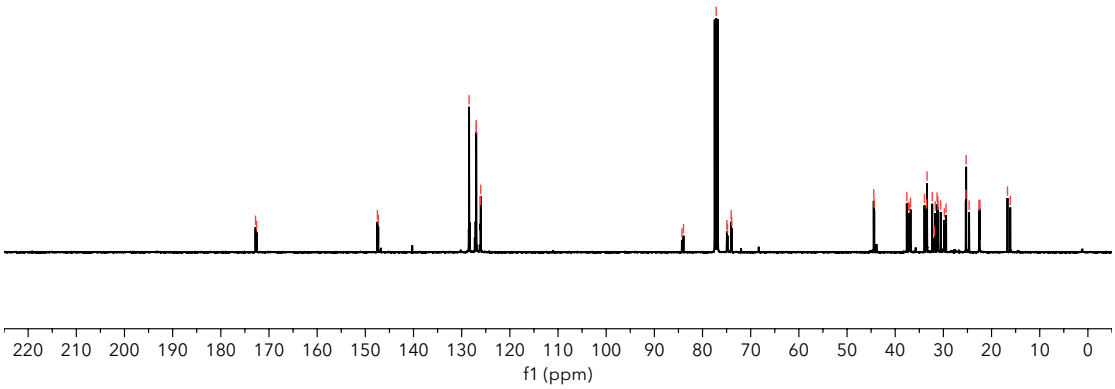


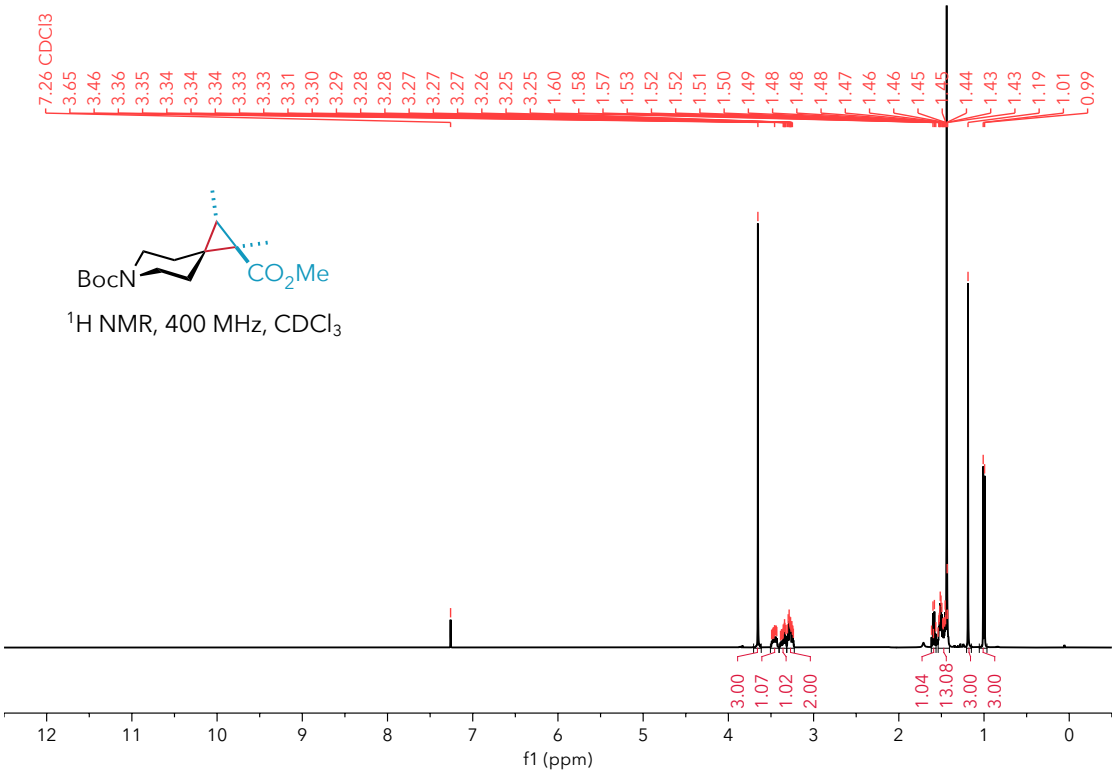
^{1}H NMR, 400 MHz, $CDCl_3$

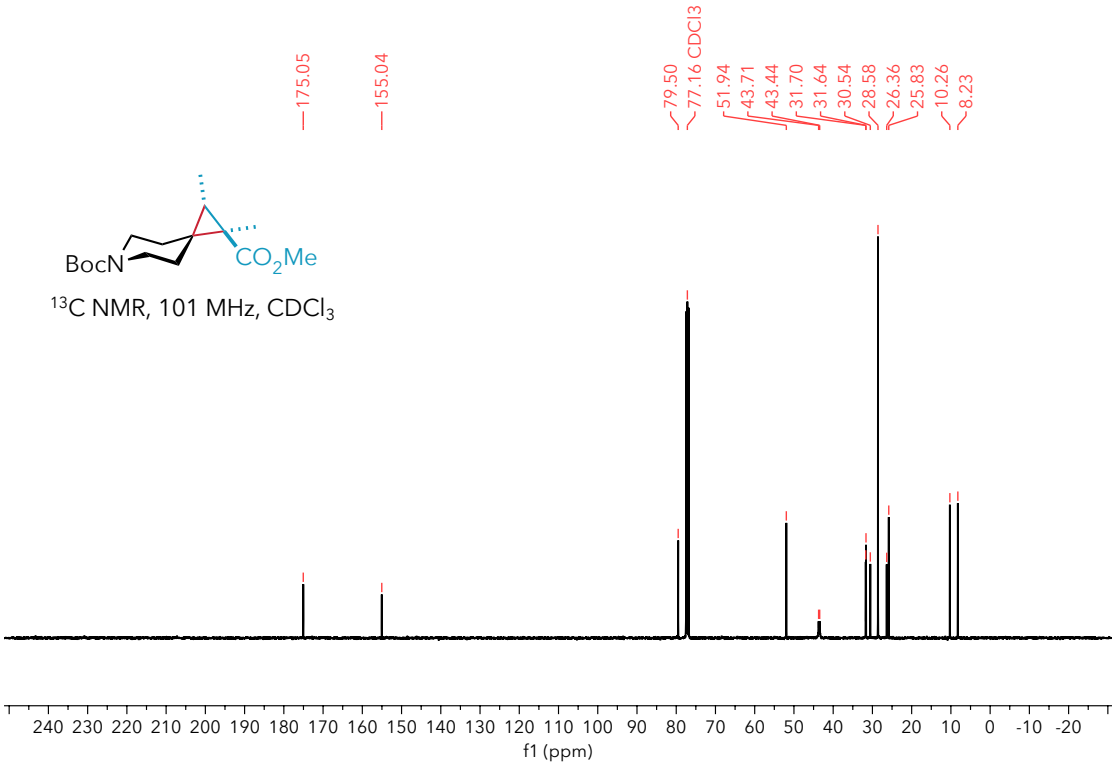


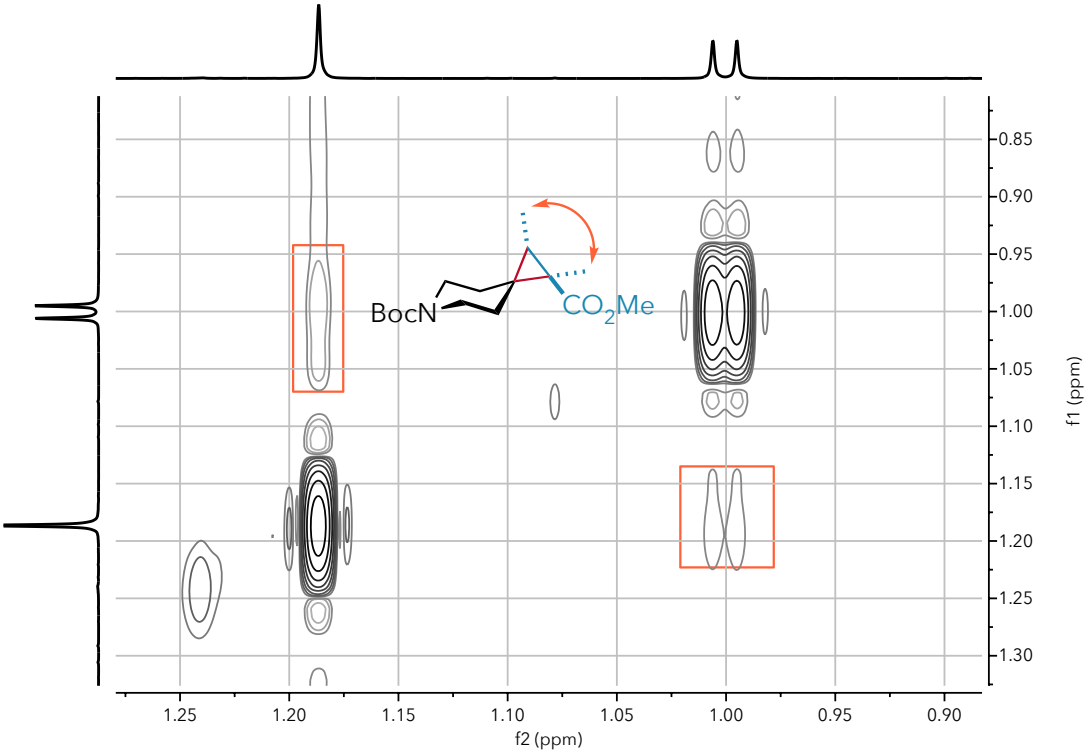


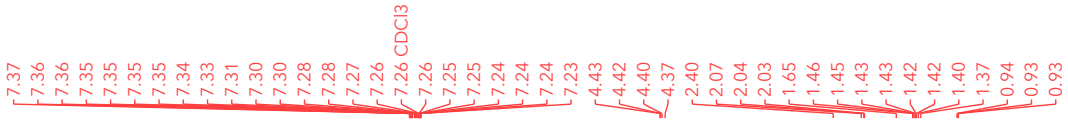
^{13}C NMR, 101 MHz, $CDCl_3$

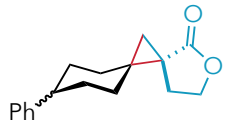



7.26 CDCl3
3.65
3.46
3.36
3.35
3.34
3.34
3.34
3.33
3.33
3.31
3.30
3.29
3.28
3.28
3.27
3.27
3.27
3.26
3.25
3.25
1.60
1.58
1.57
1.53
1.52
1.52
1.51
1.50
1.49
1.48
1.48
1.48
1.47
1.46
1.46
1.45
1.45
1.44
1.43
1.43
1.19
1.01
0.99
BocN
CO2Me
1H NMR, 400 MHz, CDCl3
3.00
1.07
1.02
2.00
1.04
13.08
3.00
3.00
12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

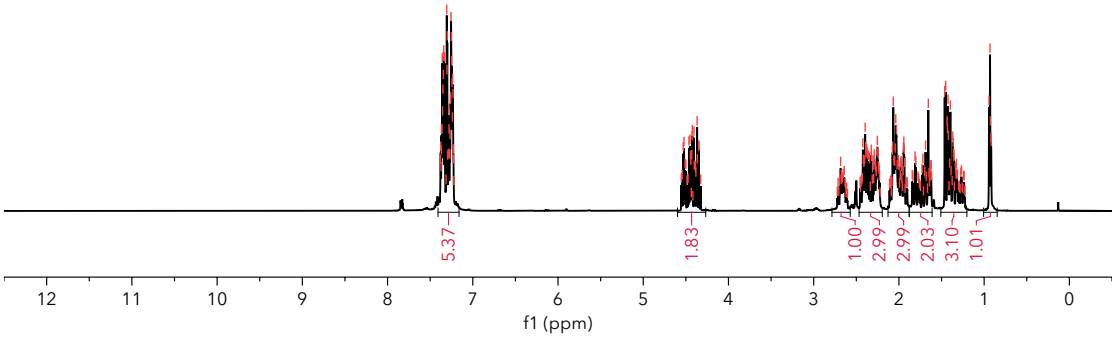

175.05
155.04
79.50
77.16 CDCl3
51.94
43.71
43.44
31.70
31.64
30.54
28.58
26.36
25.83
10.26
8.23
BocN
CO2Me
13C NMR, 101 MHz, CDCl3
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

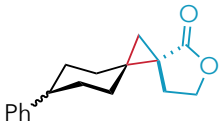

BocN
CO2Me
0.85
0.90
0.95
1.00
1.05
1.10
1.15
1.20
1.25
1.30
f1 (ppm)
1.25
1.20
1.15
1.10
1.05
1.00
0.95
0.90
f2 (ppm)



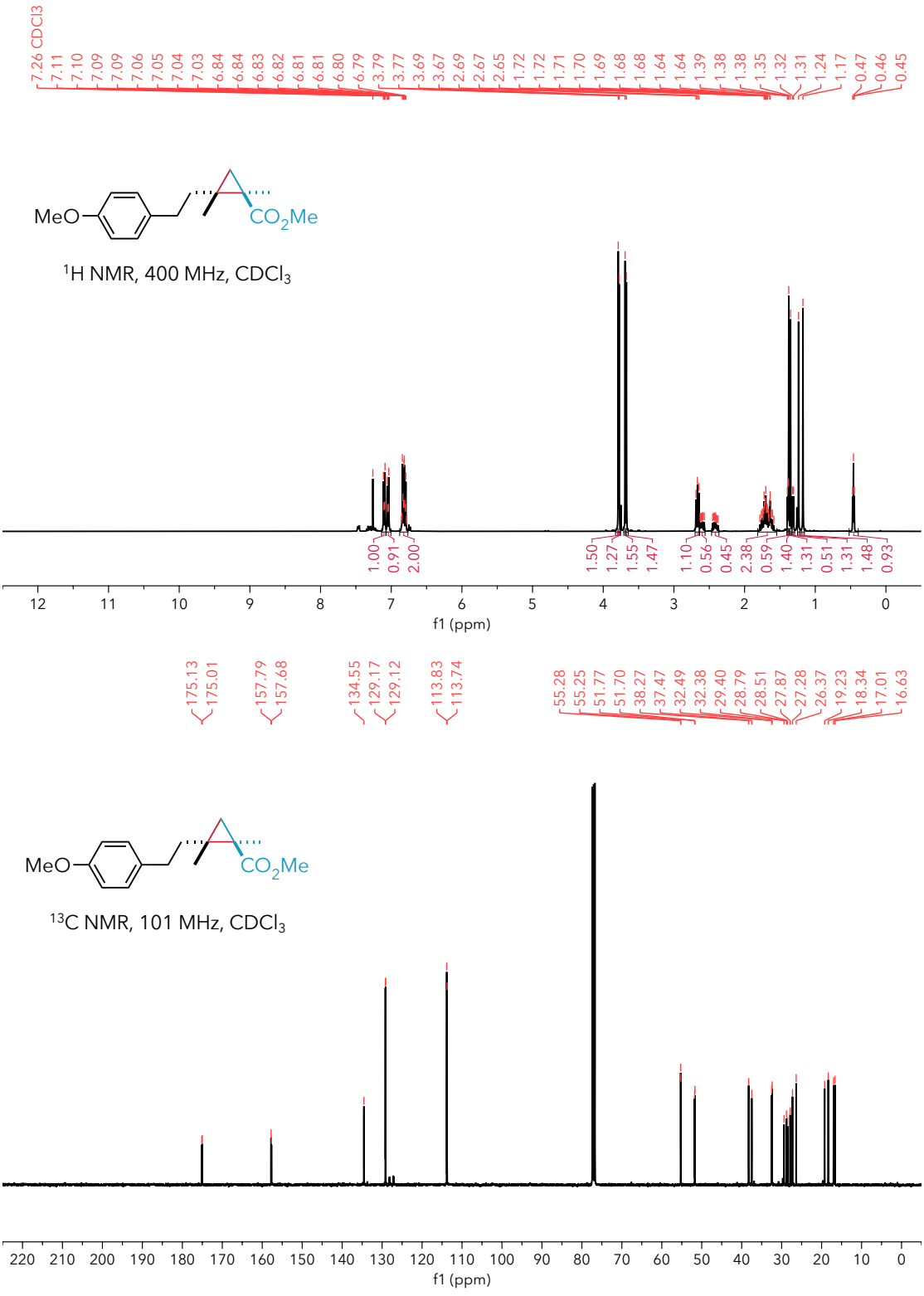


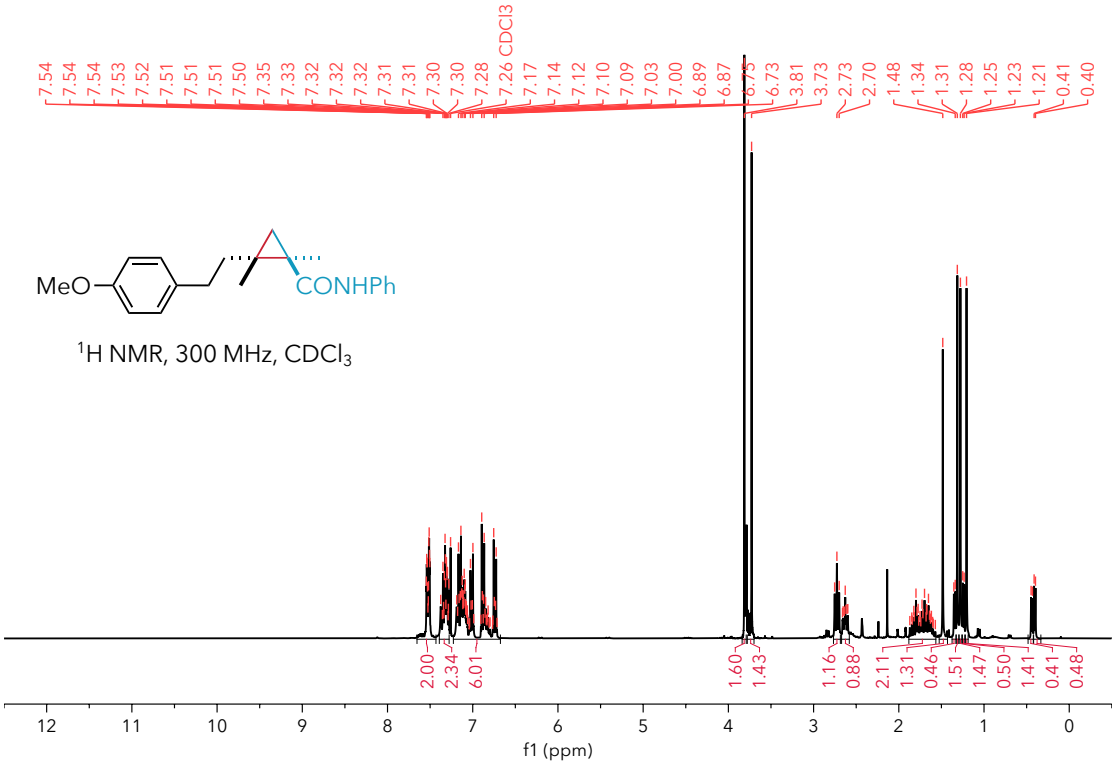
^{1}H NMR, 400 MHz, $CDCl_3$



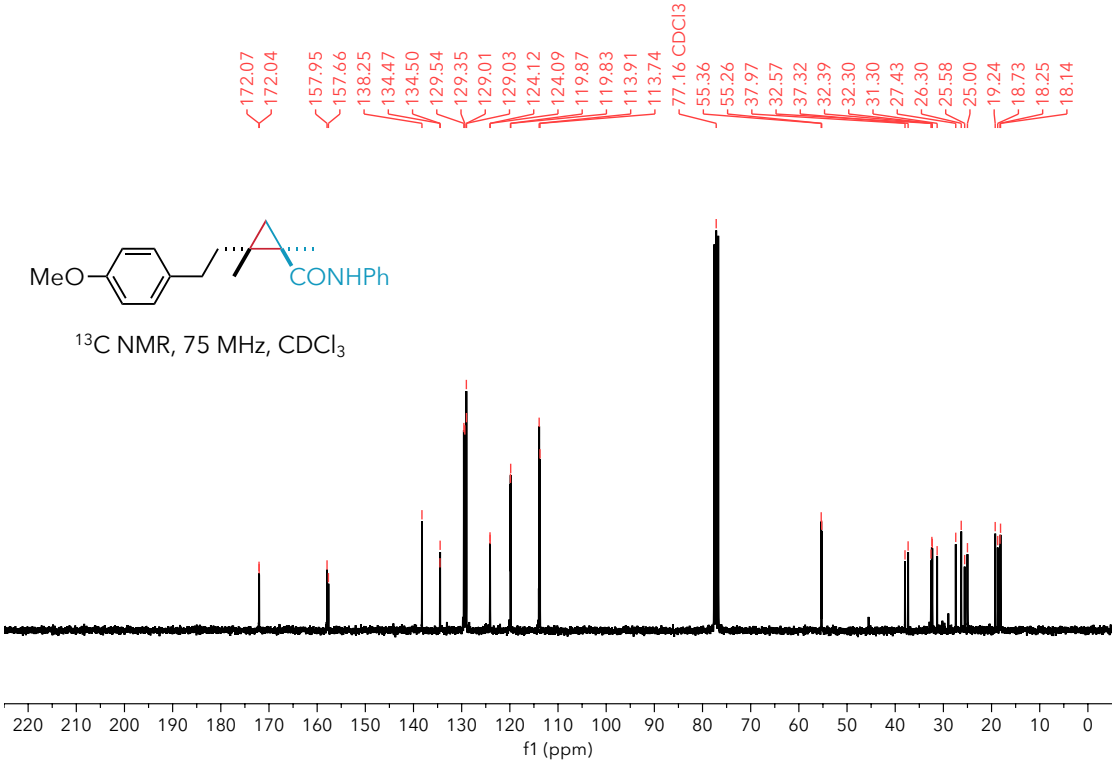


^{13}C NMR, 101 MHz, $CDCl_3$

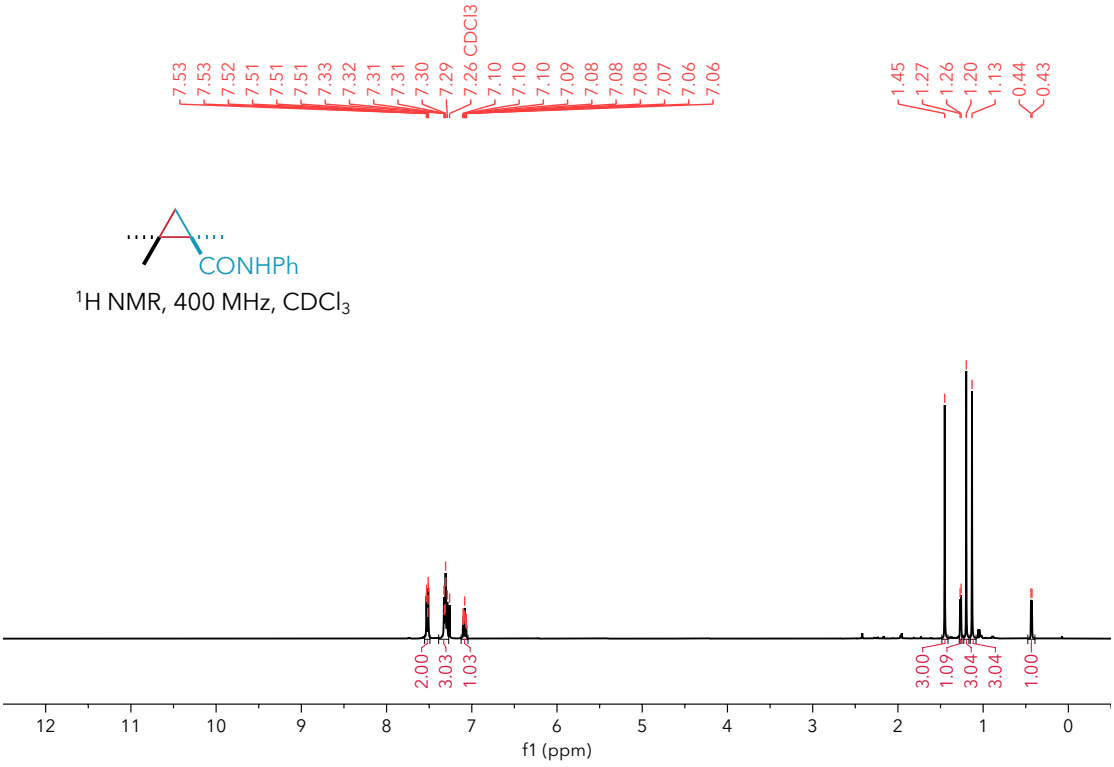

7.26 CDCl3
7.11
7.10
7.09
7.09
7.06
7.05
7.04
7.03
6.84
6.84
6.83
6.82
6.81
6.80
6.79
3.79
3.77
3.69
3.67
2.69
2.67
2.65
1.72
1.72
1.71
1.70
1.69
1.68
1.68
1.64
1.64
1.39
1.38
1.38
1.35
1.32
1.31
1.24
1.17
0.47
0.46
0.45
MeO
CO2Me
1H NMR, 400 MHz, CDCl3
1.00
0.91
2.00
1.50
1.27
1.55
1.47
1.10
0.56
0.45
2.38
0.59
1.40
1.31
0.51
1.31
1.48
0.93
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
175.13
175.01
157.79
157.68
134.55
129.17
129.12
113.83
113.74
55.28
55.25
51.77
51.70
38.27
37.47
32.49
32.38
29.40
28.79
28.51
27.87
27.28
26.37
19.23
18.34
17.01
16.63
MeO
CO2Me
13C NMR, 101 MHz, CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

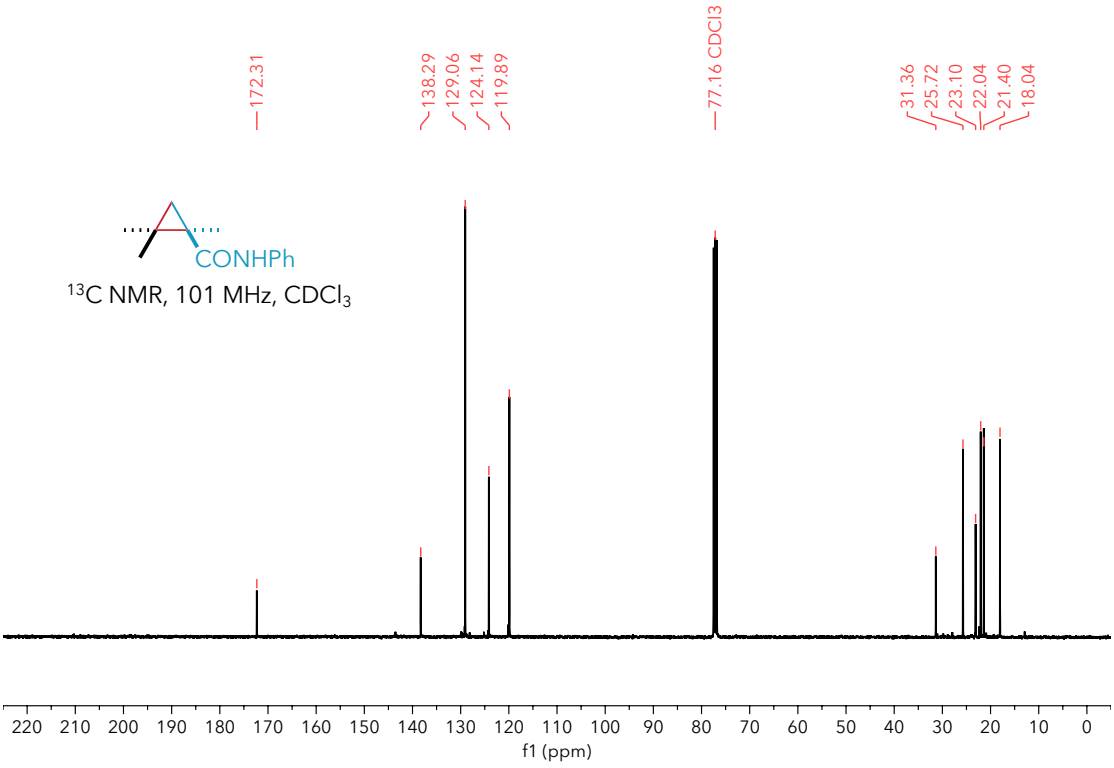


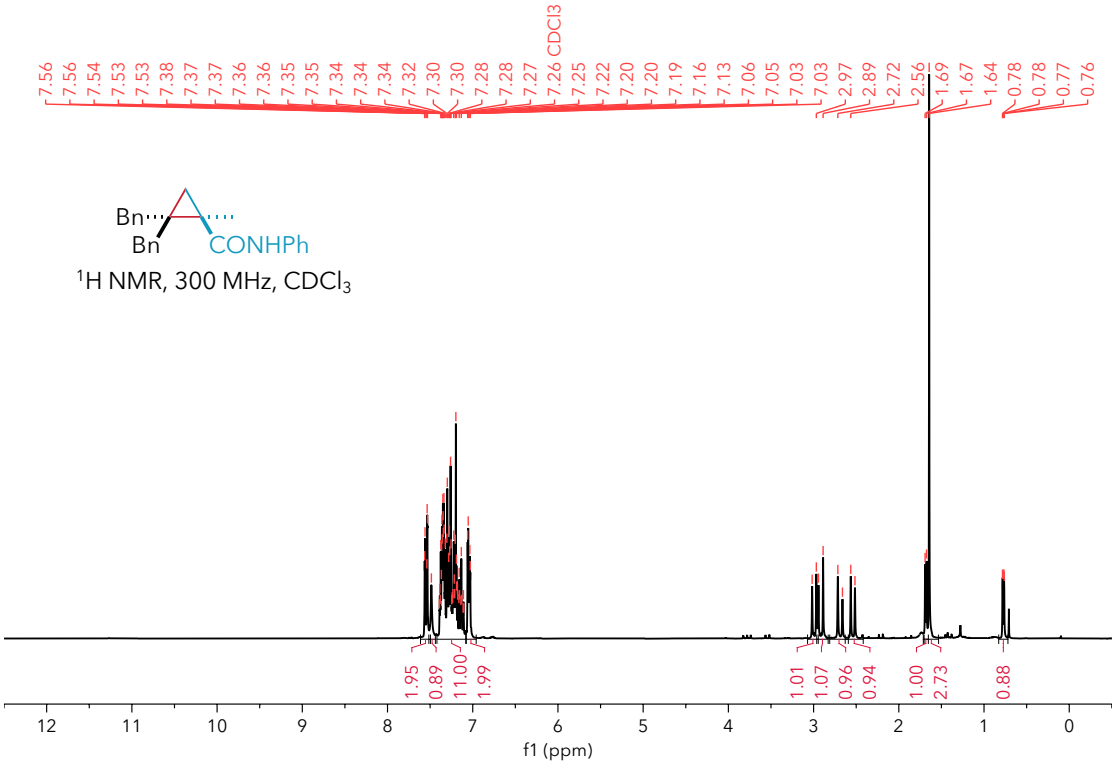
^{1}H NMR, 300 MHz, $CDCl_3$

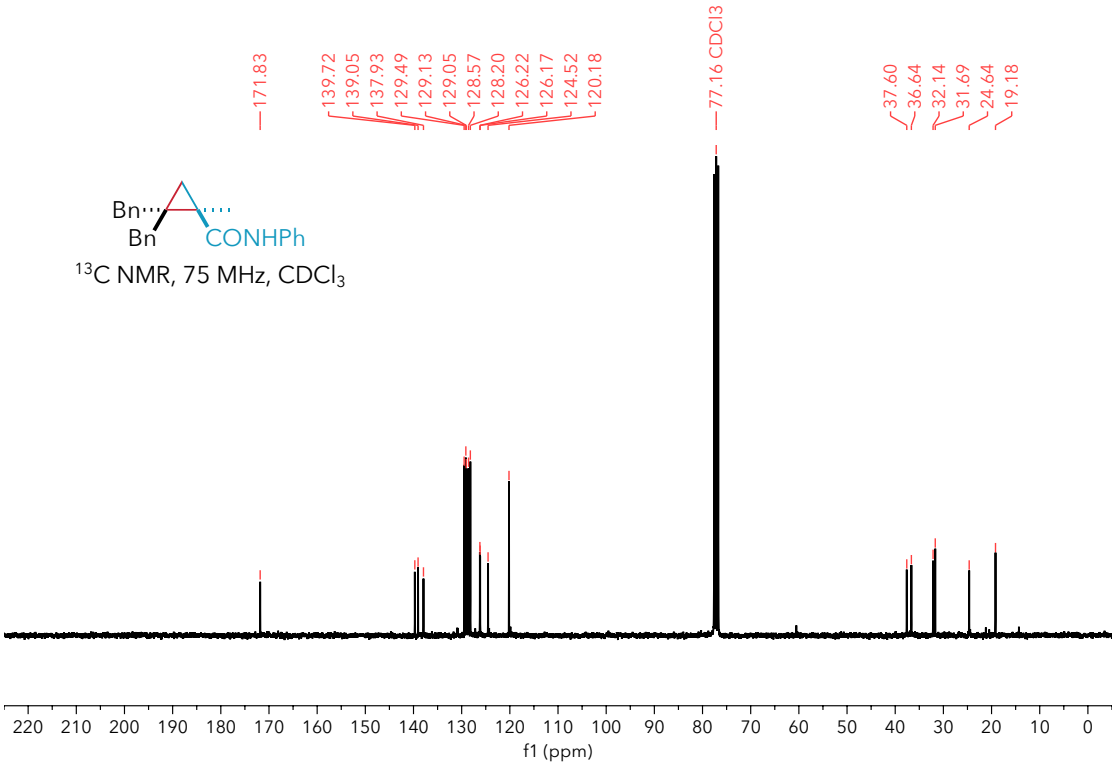


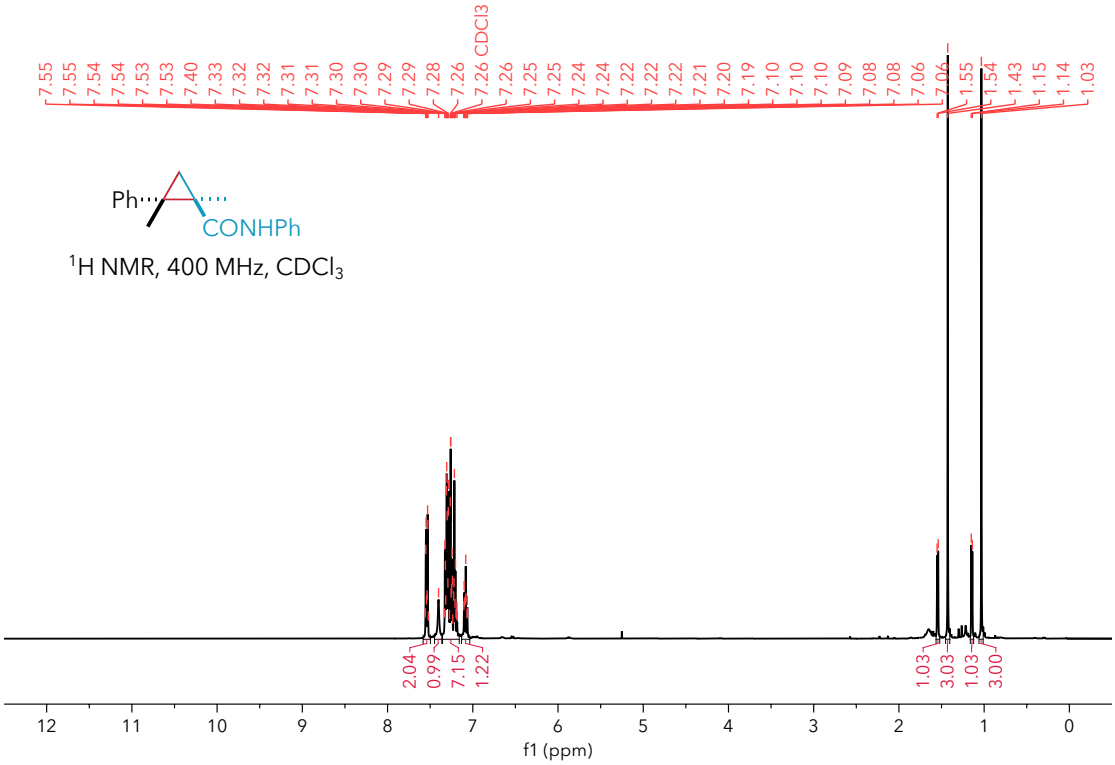
^{13}C NMR, 75 MHz, $CDCl_3$


7.53
7.53
7.52
7.51
7.51
7.51
7.33
7.32
7.31
7.31
7.30
7.29
7.26 CDCl3
7.10
7.10
7.10
7.09
7.08
7.08
7.08
7.07
7.06
7.06
1.45
1.27
1.26
1.20
1.13
0.44
0.43
CONHPh
^{1}H NMR, 400 MHz, $CDCl_3$
2.00
3.03
1.03
3.00
1.09
3.04
3.04
1.00
12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

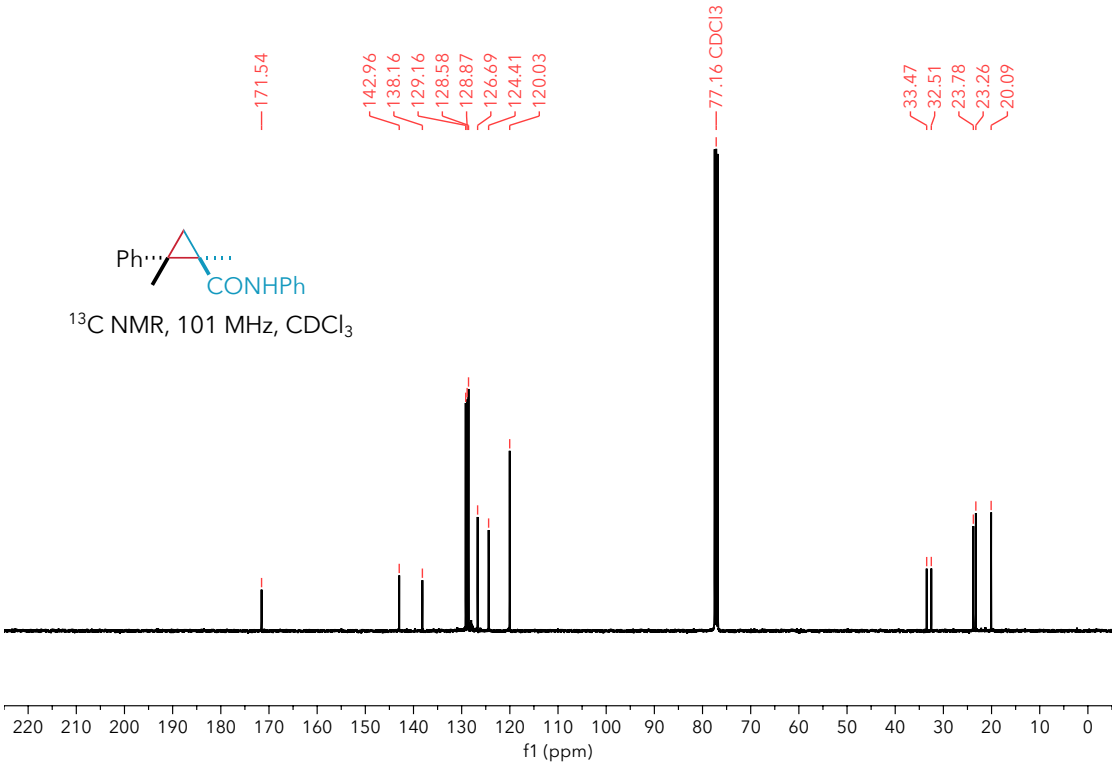

172.31
138.29
129.06
124.14
119.89
77.16 CDCl3
31.36
25.72
23.10
22.04
21.40
18.04
CONHPh
^{13}C NMR, 101 MHz, $CDCl_3$
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.56 7.56 7.54 7.53 7.53 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.34 7.32 7.30 7.30 7.28 7.28 7.27 7.26 CDCl3 7.25 7.22 7.20 7.20 7.19 7.16 7.13 7.06 7.05 7.03 7.03 2.97 2.89 2.72 2.56 1.69 1.67 1.64 0.78 0.78 0.77 0.76
Bn
Bn
CONHPh
1H NMR, 300 MHz, CDCl3
1.95 0.89 11.00 1.99 1.01 1.07 0.96 0.94 1.00 2.73 0.88
12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

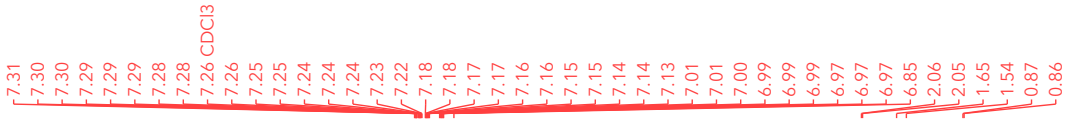

171.83 139.72 139.05 137.93 129.49 129.13 129.05 128.57 128.20 126.22 126.17 124.52 120.18 77.16 CDCl3 37.60 36.64 32.14 31.69 24.64 19.18
Bn
Bn
CONHPh
13C NMR, 75 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



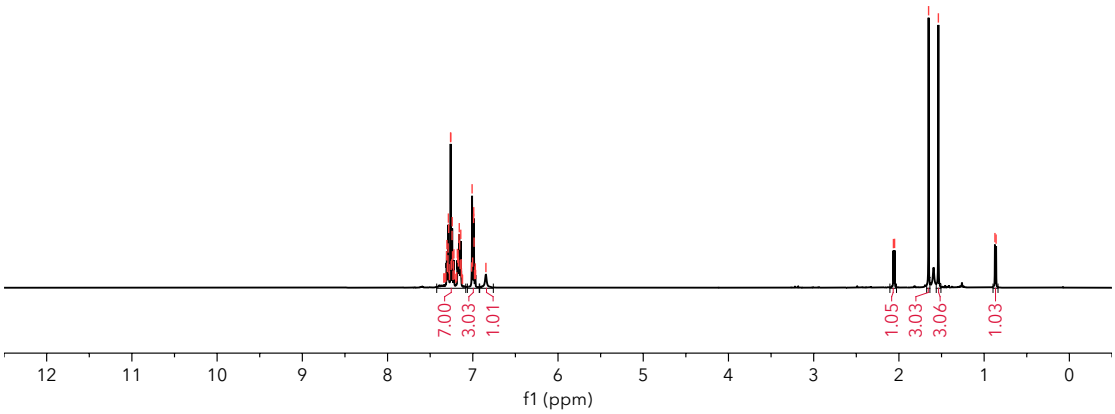
^{1}H NMR, 400 MHz, $CDCl_3$

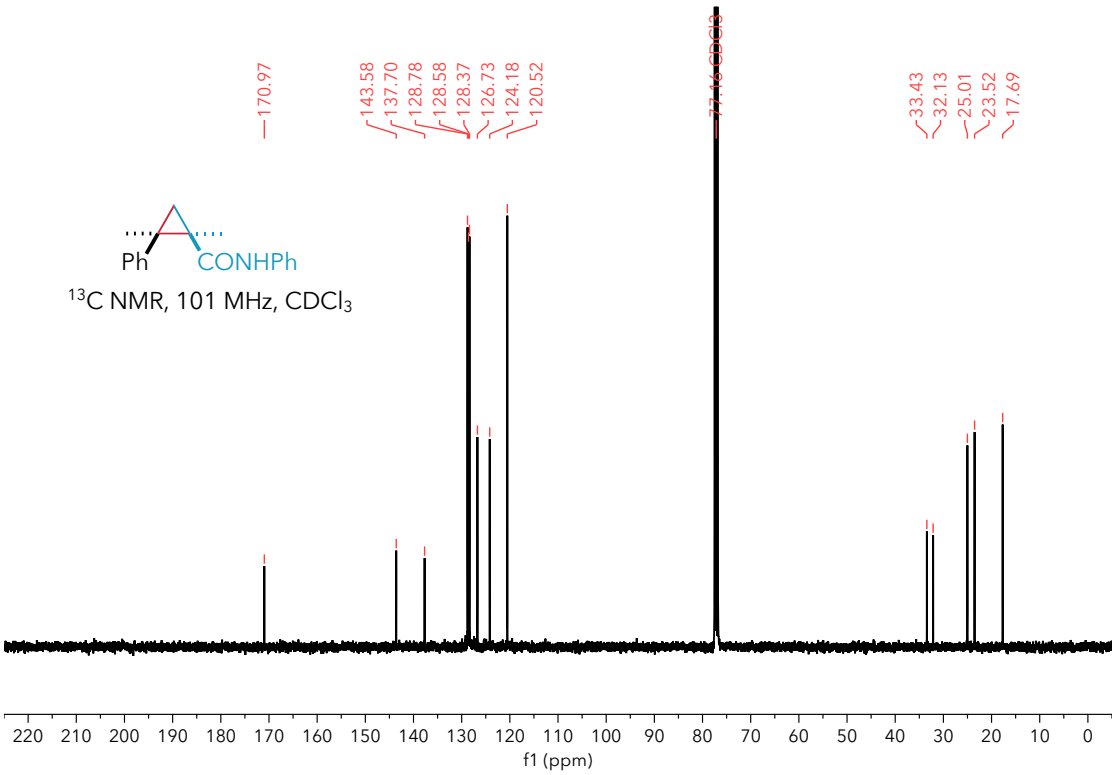


^{13}C NMR, 101 MHz, $CDCl_3$

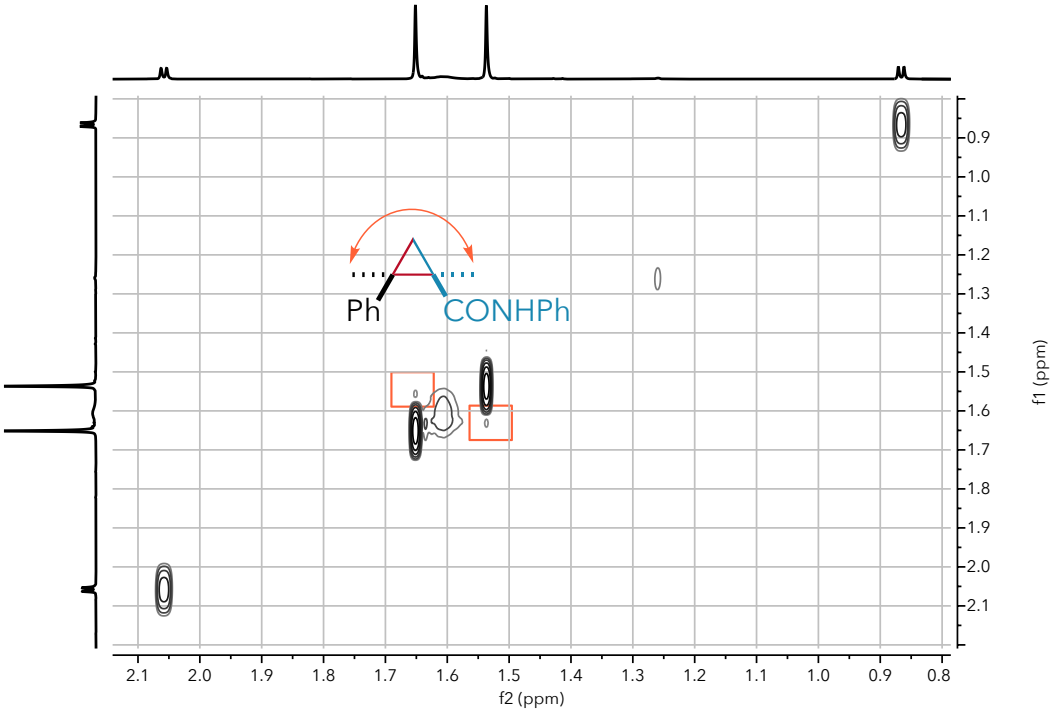


^{1}H NMR, 400 MHz, $CDCl_3$



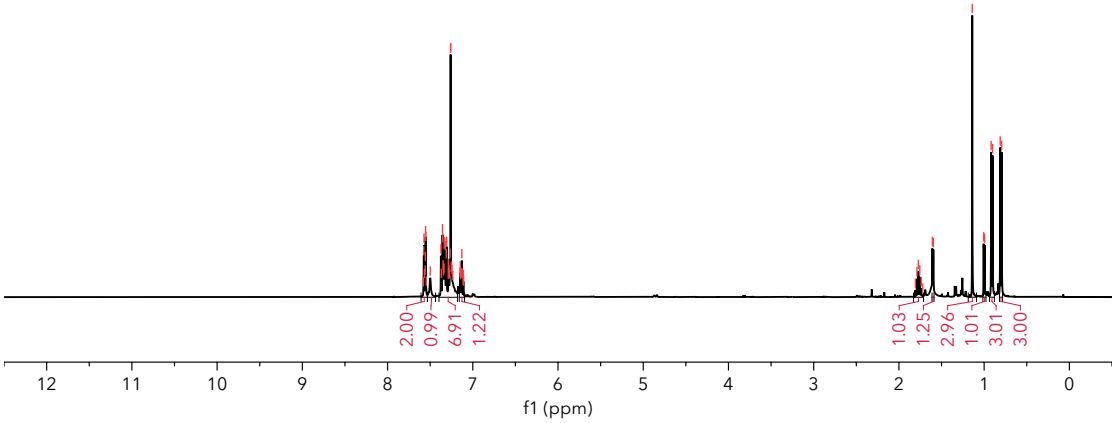


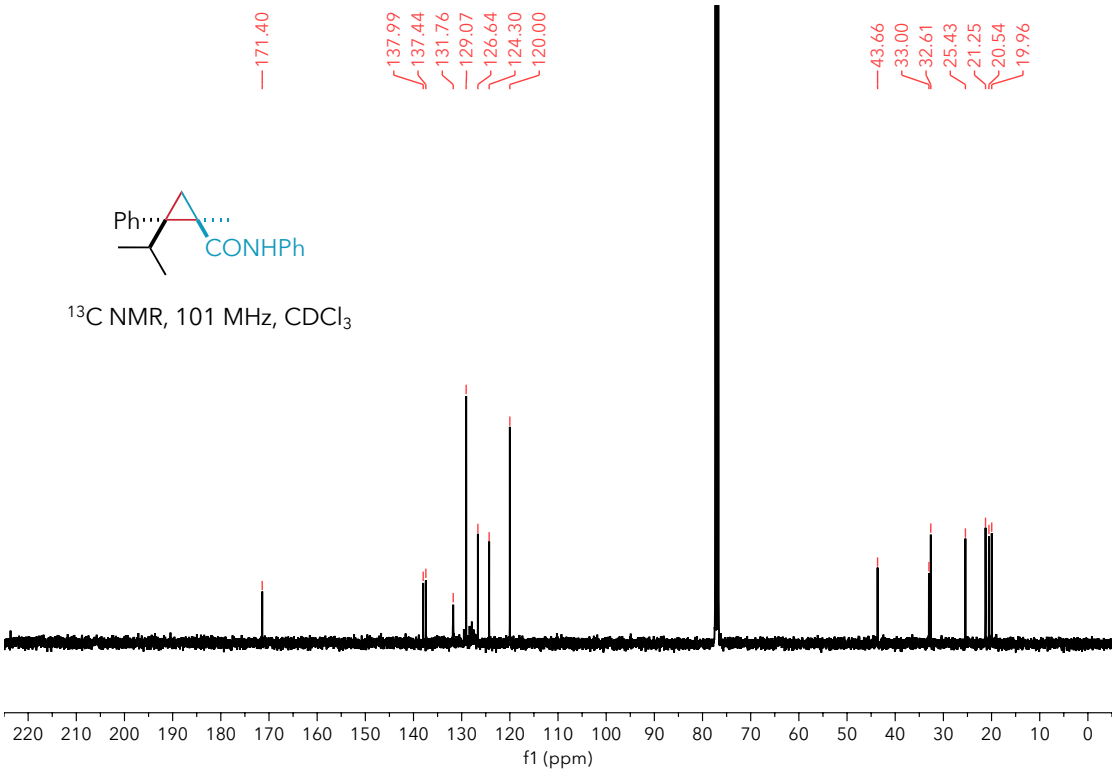
^{13}C NMR, 101 MHz, $CDCl_3$



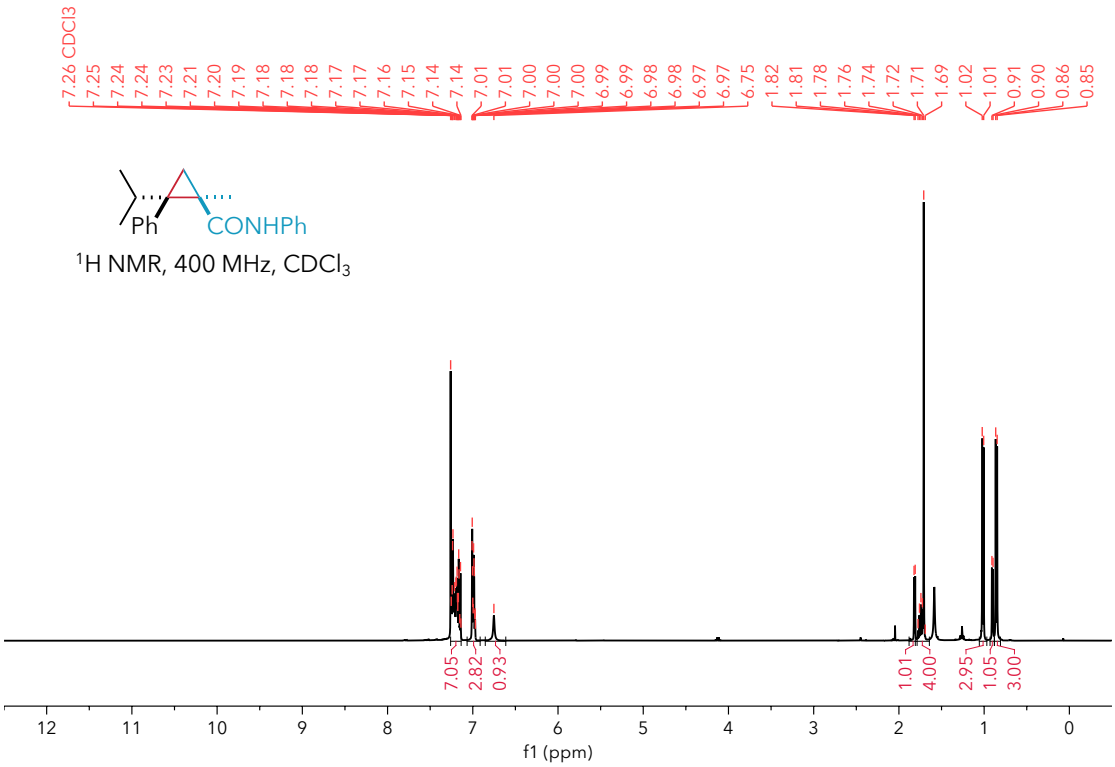
2D-NOESY-NMR spectrum of compound **3o''**. Measured at 600 MHz in $CDCl_3$.

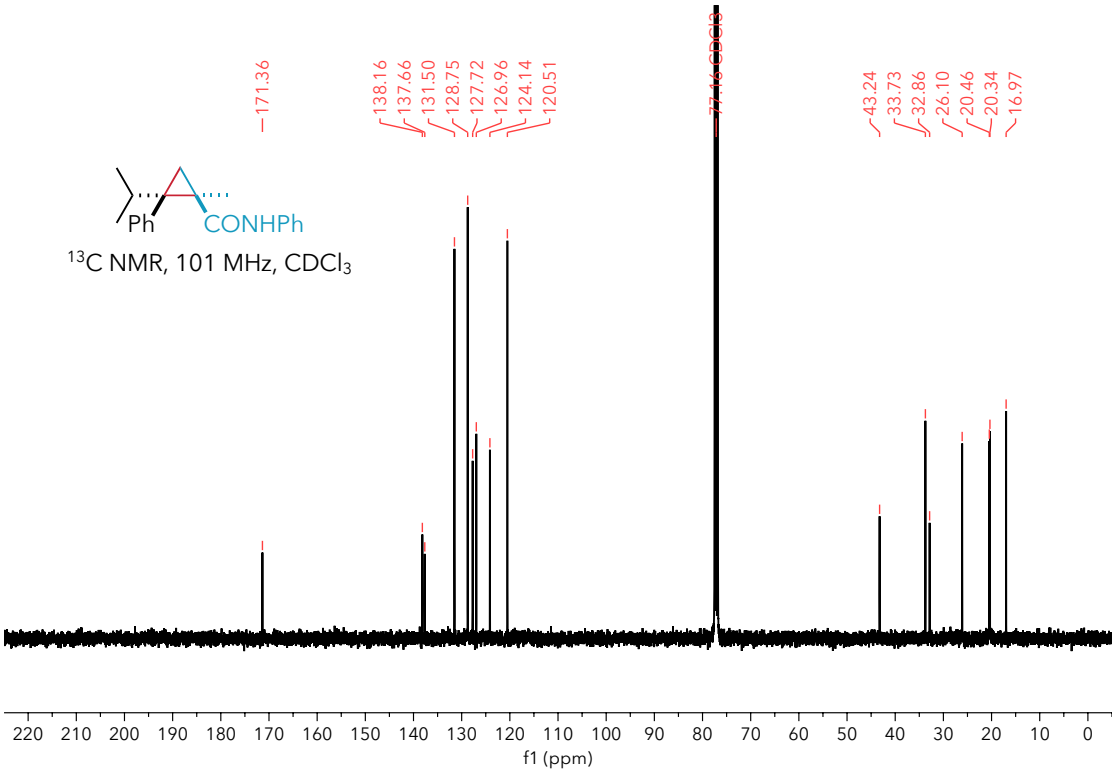
^{1}H NMR, 400 MHz, $CDCl_3$

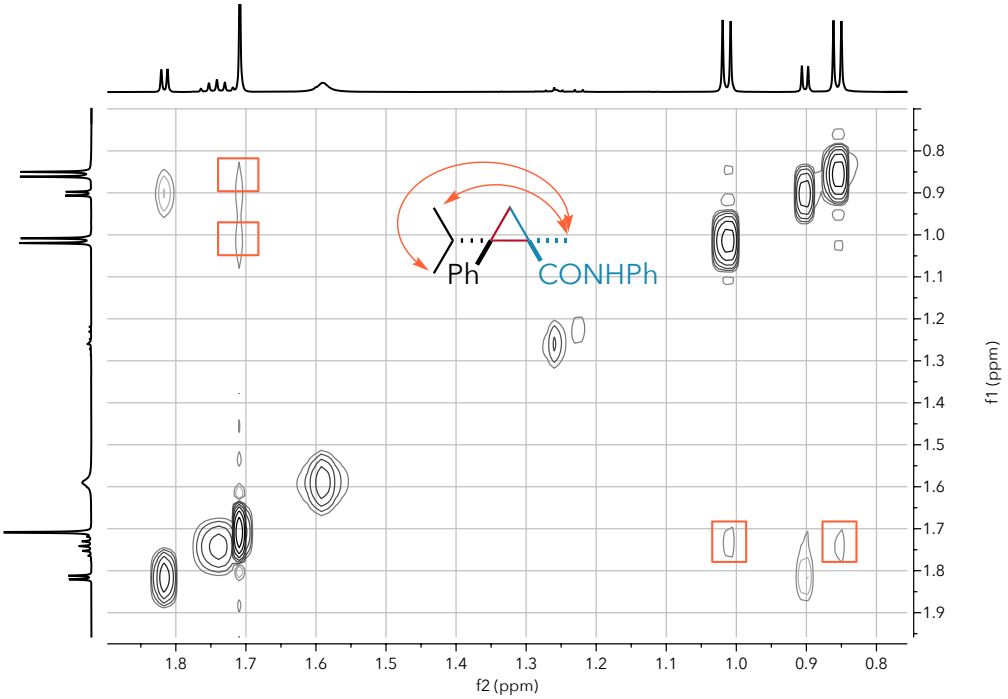




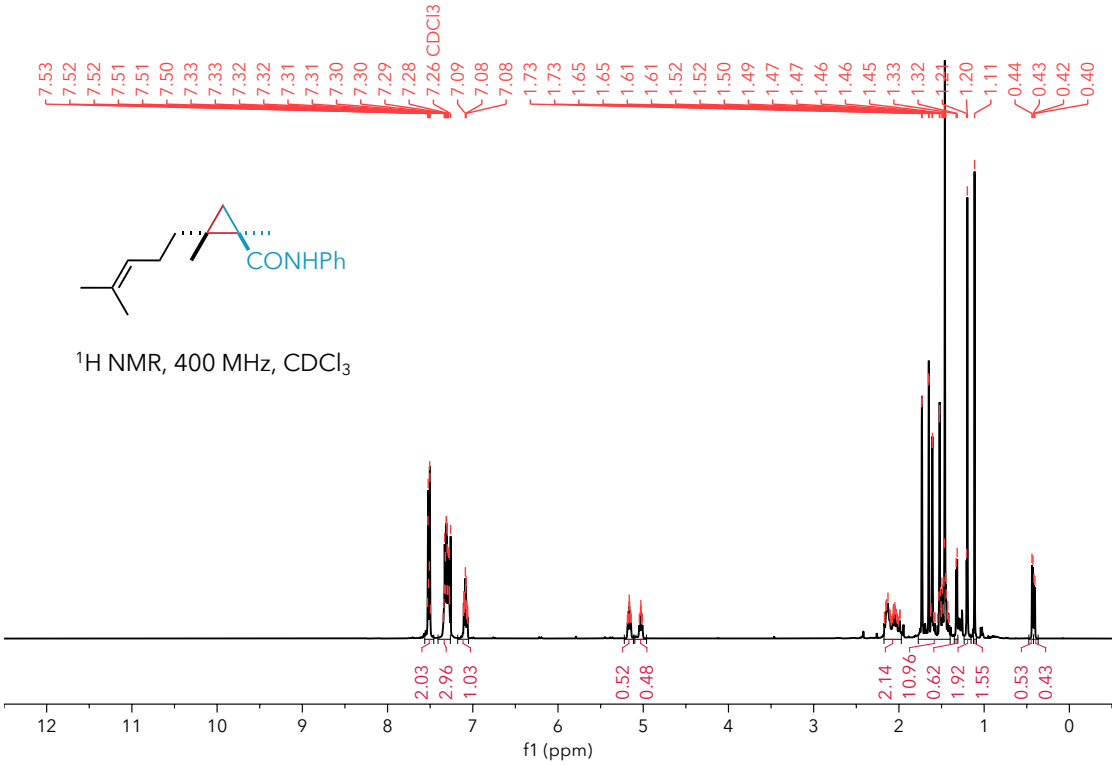
^{13}C NMR, 101 MHz, $CDCl_3$


7.26 CDCl3
7.25
7.24
7.24
7.23
7.21
7.20
7.19
7.18
7.18
7.18
7.17
7.17
7.16
7.15
7.14
7.14
7.01
7.01
7.00
7.00
7.00
6.99
6.99
6.98
6.98
6.97
6.97
6.75
1.82
1.81
1.78
1.76
1.74
1.72
1.71
1.69
1.02
1.01
0.91
0.90
0.86
0.85
Ph
CONHPh
^{1}H NMR, 400 MHz, $CDCl_3$
7.05
2.82
0.93
1.01
4.00
2.95
1.05
3.00
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

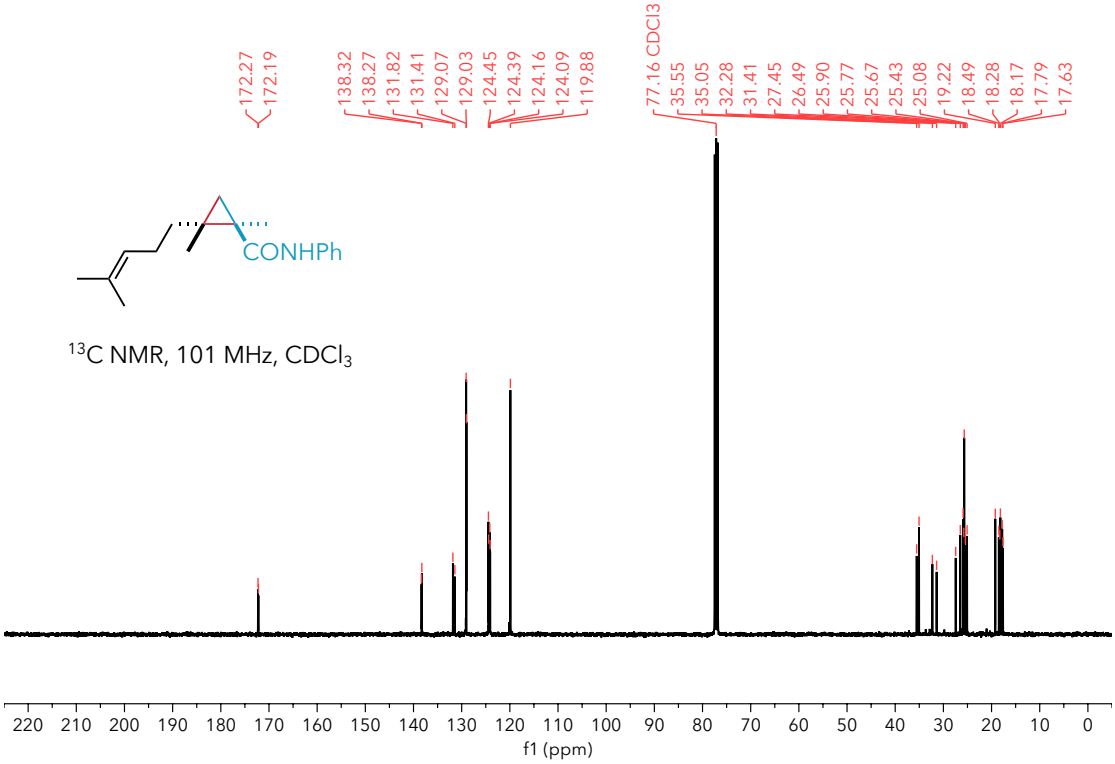

171.36
138.16
137.66
131.50
128.75
127.72
126.96
124.14
120.51
77.16
77.00
76.84
43.24
33.73
32.86
26.10
20.46
20.34
16.97
Ph
CONHPh
^{13}C NMR, 101 MHz, $CDCl_3$
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



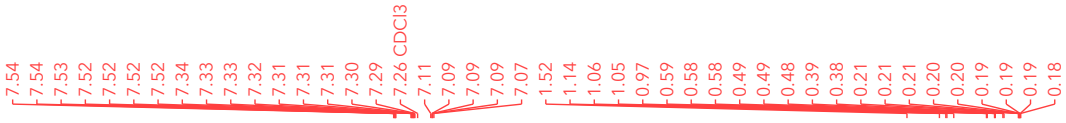
2D-NOESY-NMR spectrum of compound **3p''**. Measured at 600 MHz in $CDCl_3$.



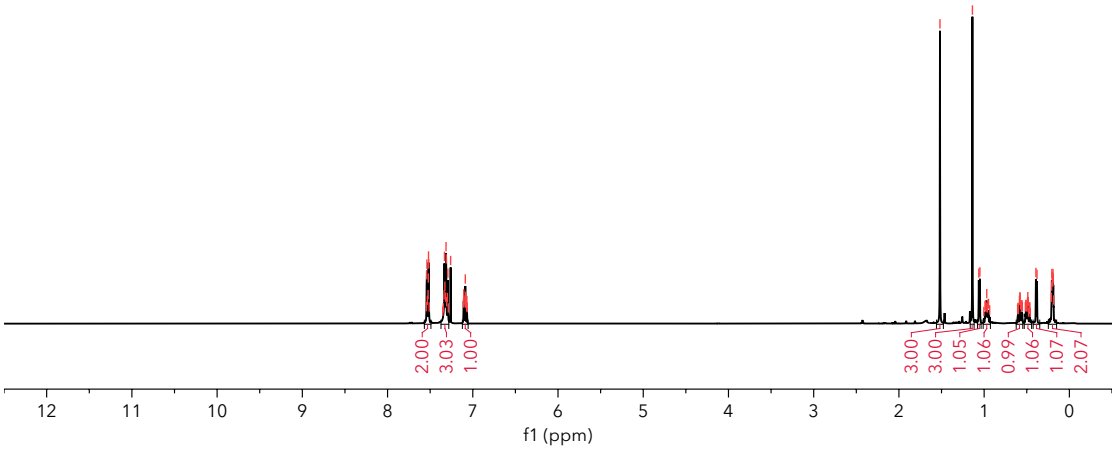
^{1}H NMR, 400 MHz, $CDCl_3$

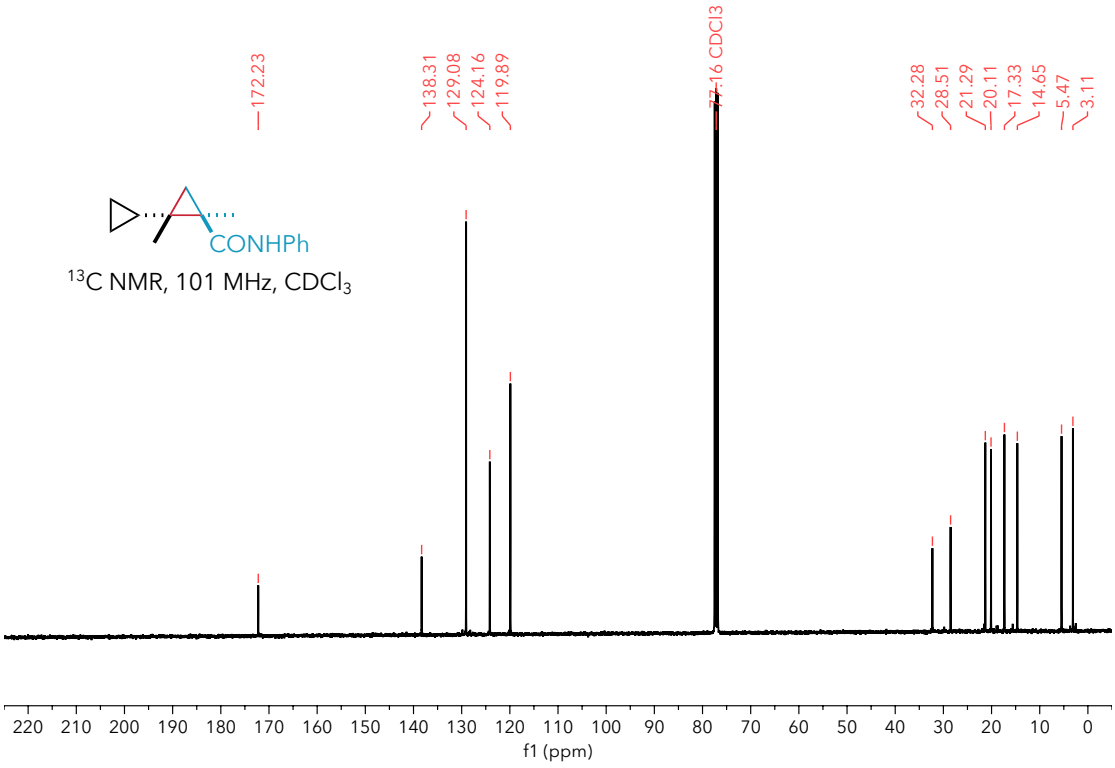


^{13}C NMR, 101 MHz, $CDCl_3$

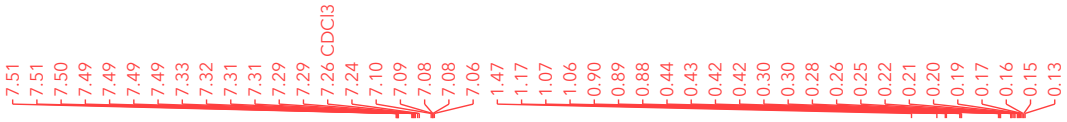


^{1}H NMR, 400 MHz, $CDCl_3$

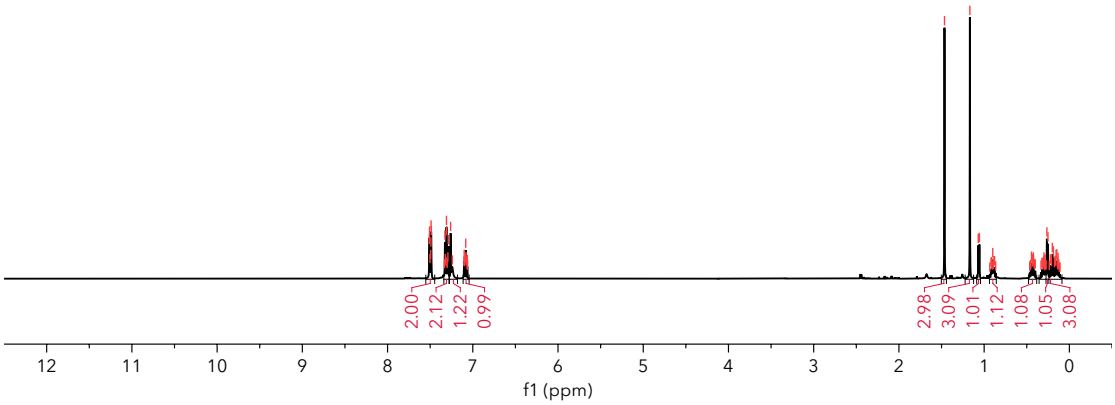


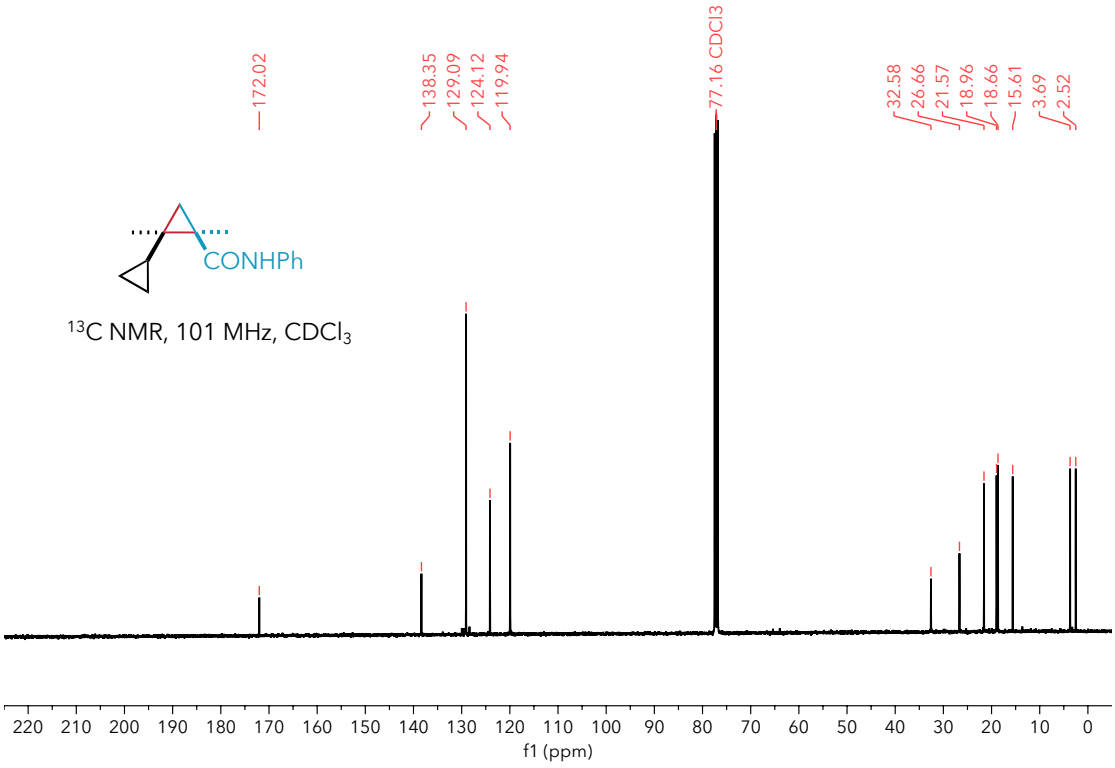


^{13}C NMR, 101 MHz, $CDCl_3$

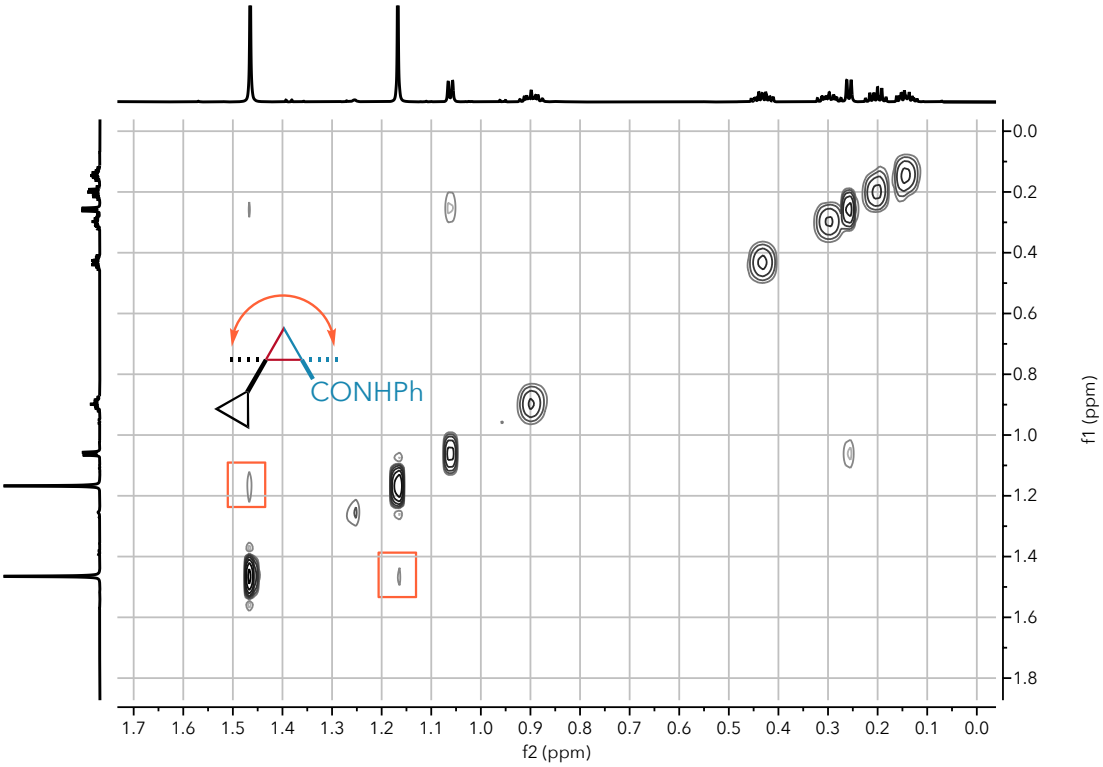


^{1}H NMR, 400 MHz, $CDCl_3$

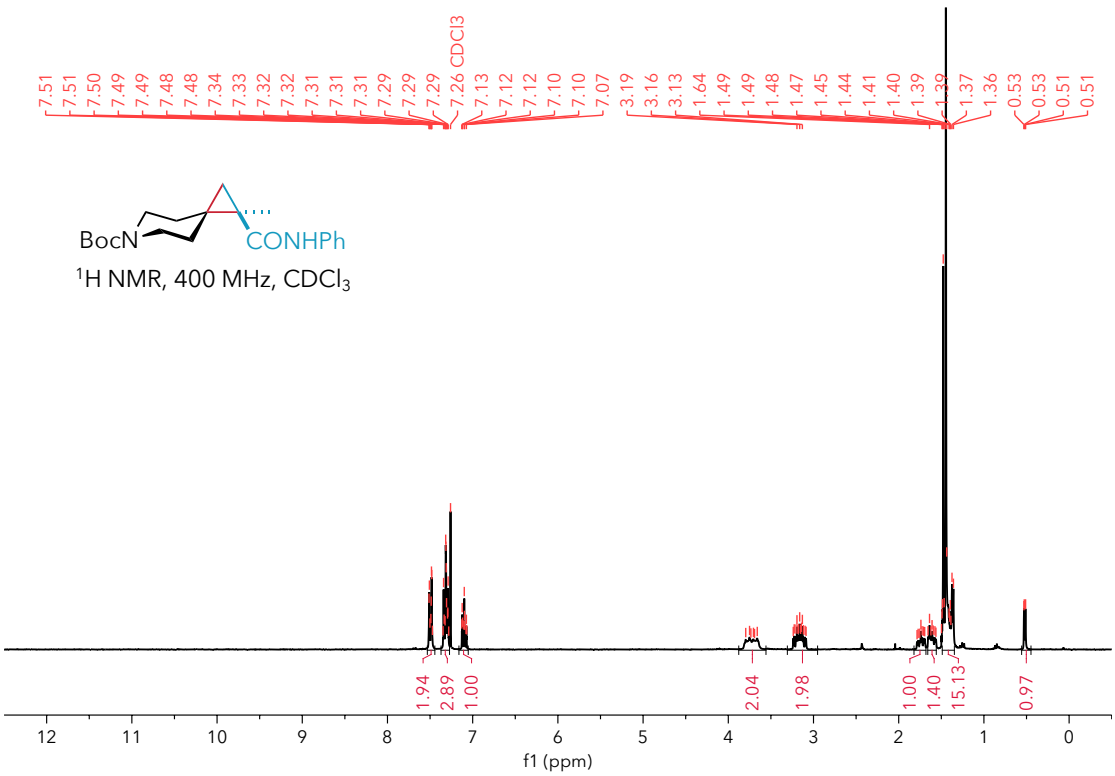


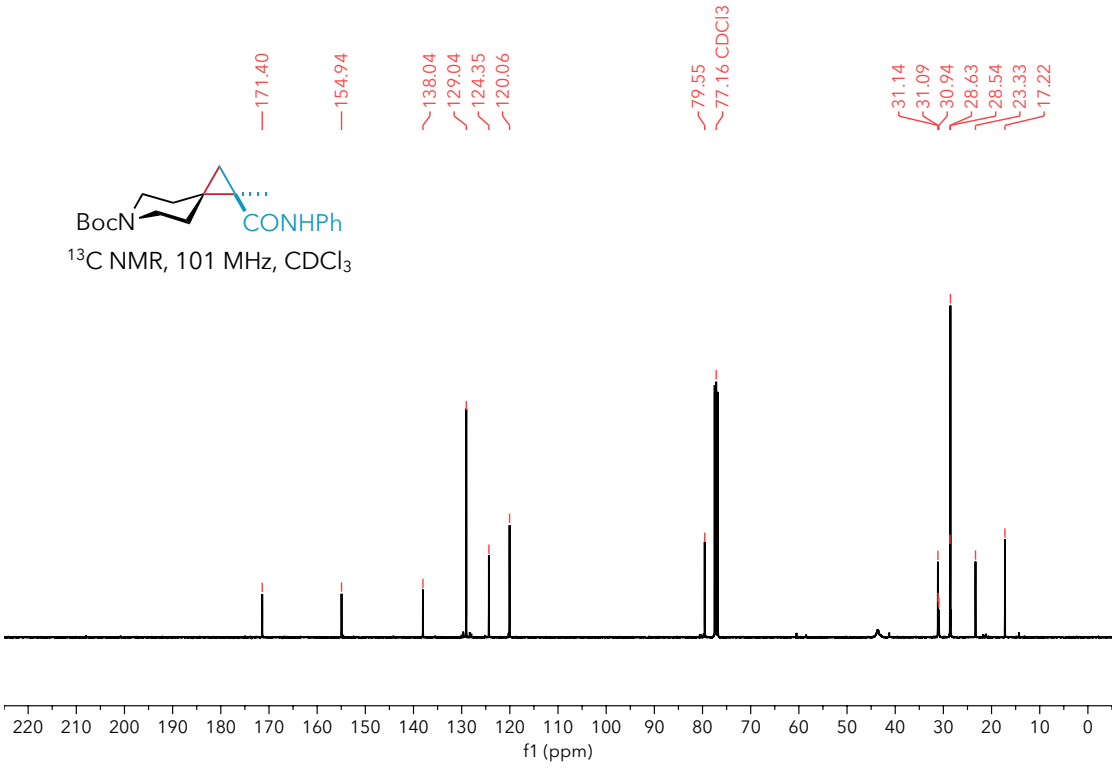


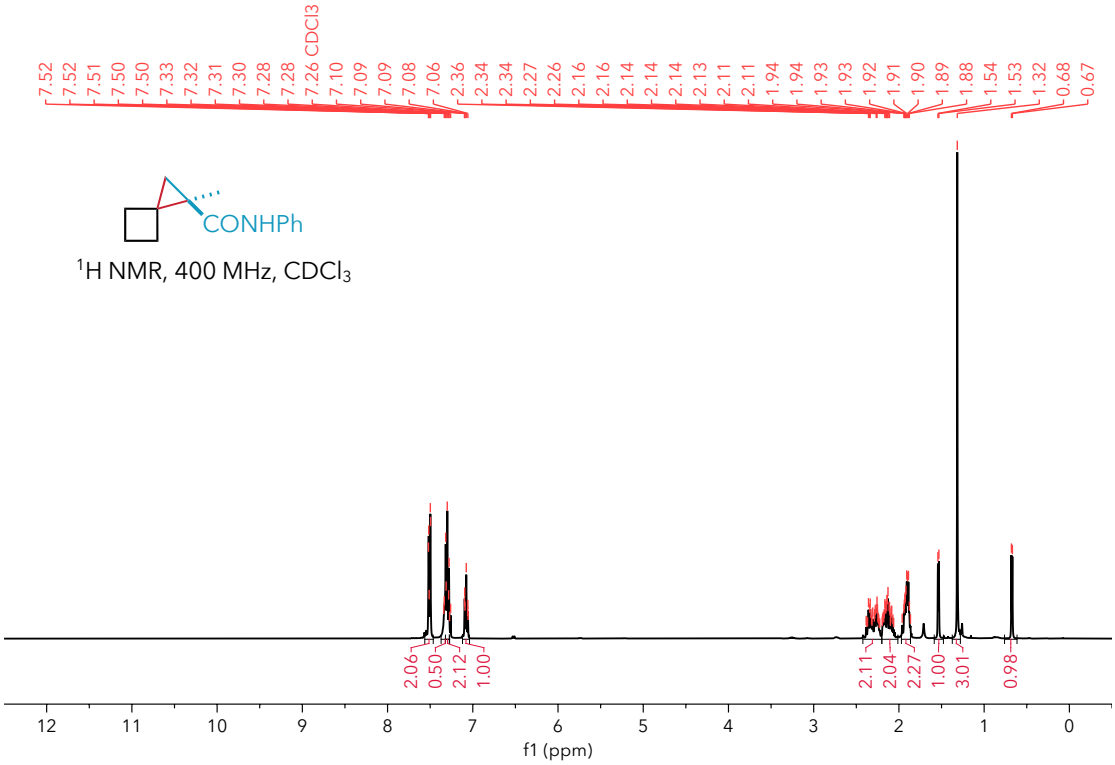
^{13}C NMR, 101 MHz, $CDCl_3$

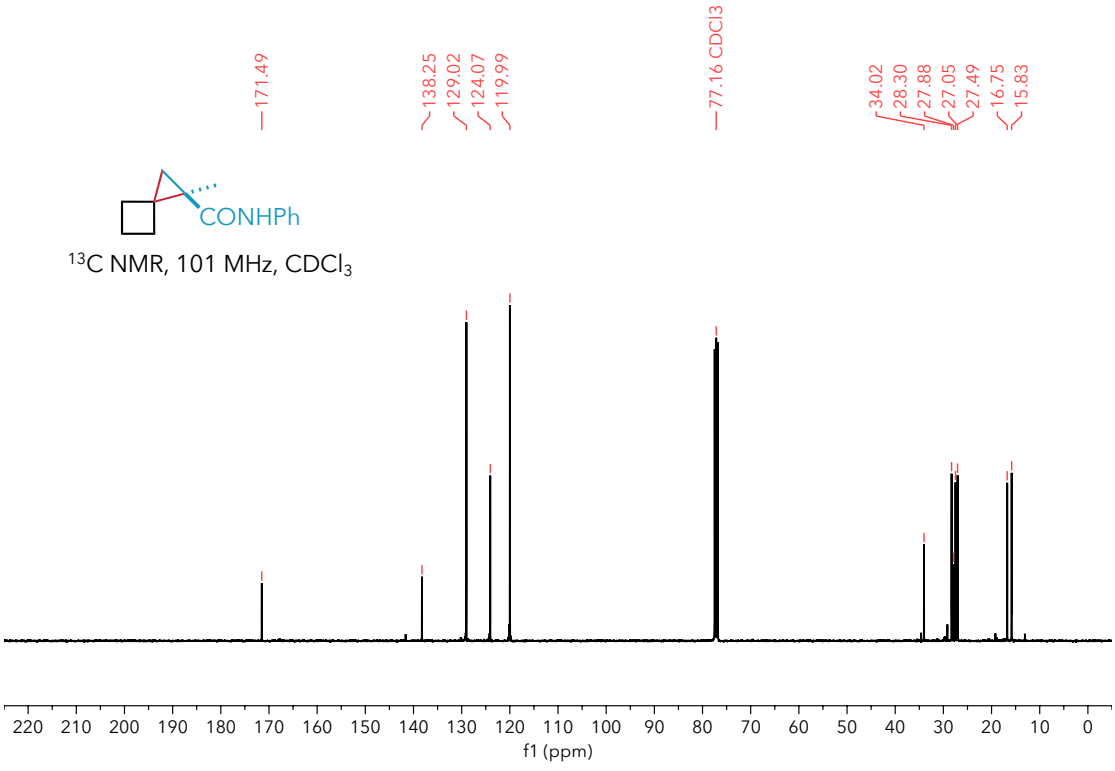


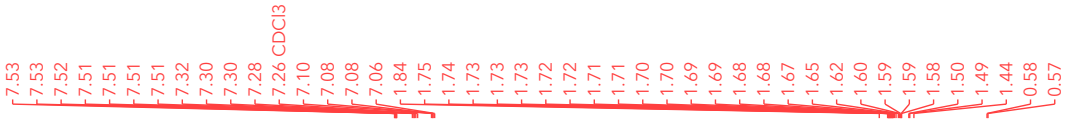
NOESY-NMR spectrum of compound **3r''**. Measured at 600 MHz in $CDCl_3$.


7.51
7.51
7.50
7.49
7.49
7.48
7.48
7.34
7.33
7.32
7.32
7.31
7.31
7.31
7.29
7.29
7.29
7.26 CDCl3
7.13
7.12
7.12
7.10
7.10
7.07
3.19
3.16
3.13
1.64
1.49
1.49
1.48
1.47
1.45
1.44
1.41
1.40
1.39
1.39
1.37
1.36
0.53
0.53
0.51
0.51
BocN
CONHPh
1H NMR, 400 MHz, CDCl3
1.94
2.89
1.00
2.04
1.98
1.00
1.40
15.13
0.97
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

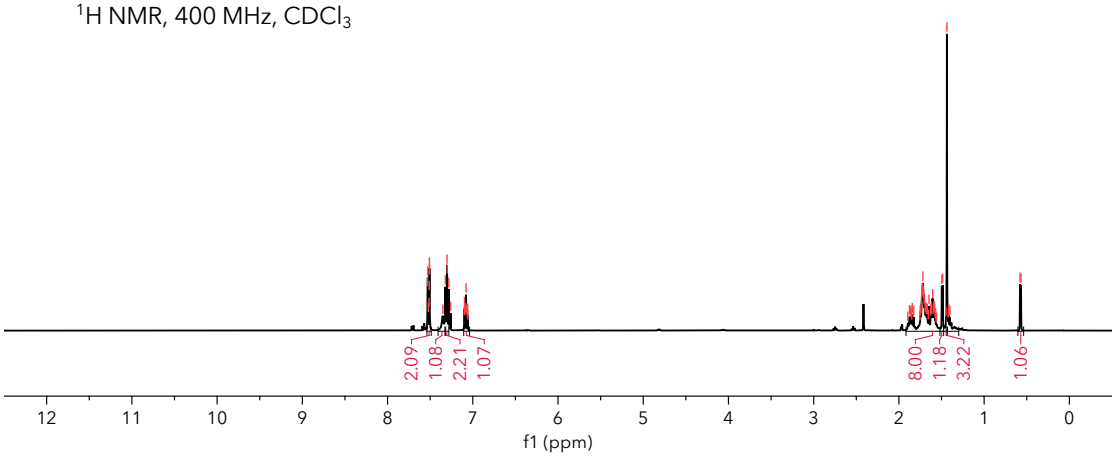

171.40
154.94
138.04
129.04
124.35
120.06
79.55
77.16 CDCl3
31.14
31.09
30.94
28.63
28.54
23.33
17.22
BocN
CONHPh
13C NMR, 101 MHz, CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.52
7.52
7.51
7.50
7.50
7.33
7.32
7.31
7.30
7.28
7.28
7.26 CDCl3
7.10
7.09
7.09
7.08
7.06
2.36
2.34
2.34
2.27
2.26
2.16
2.16
2.14
2.14
2.14
2.13
2.11
2.11
1.94
1.94
1.93
1.93
1.92
1.91
1.90
1.89
1.88
1.54
1.53
1.32
0.68
0.67
CONHPh
1H NMR, 400 MHz, CDCl3
2.06
0.50
2.12
1.00
2.11
2.04
2.27
1.00
3.01
0.98
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

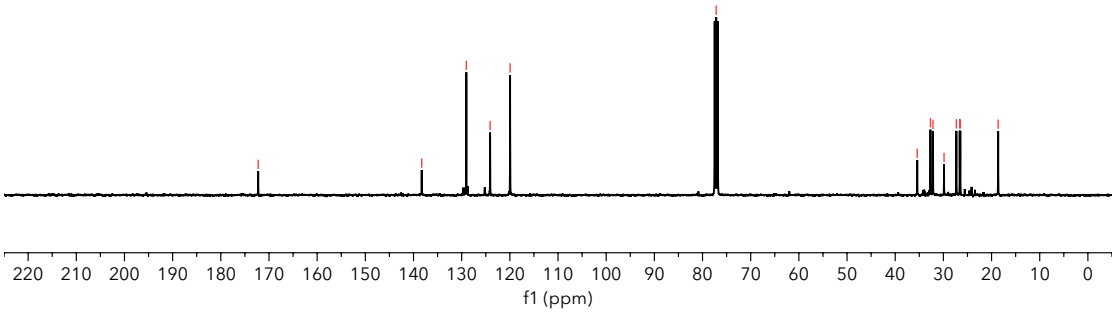

171.49
138.25
129.02
124.07
119.99
77.16 CDCl3
34.02
28.30
27.88
27.05
27.49
16.75
15.83
CONHPh
13C NMR, 101 MHz, CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

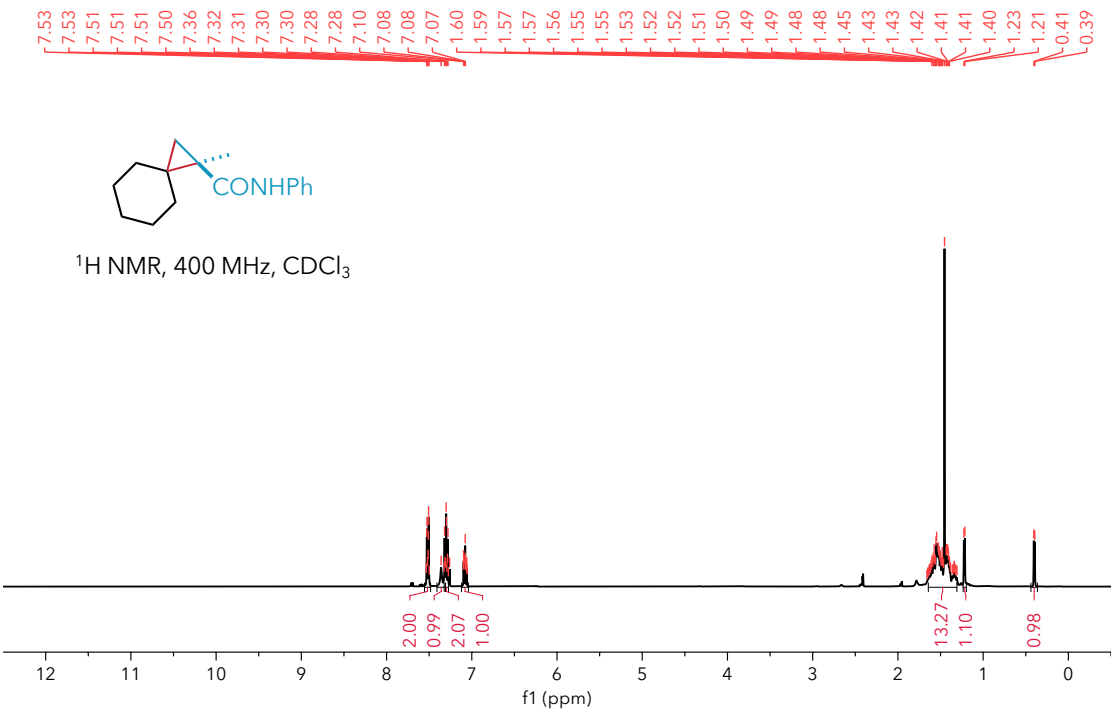


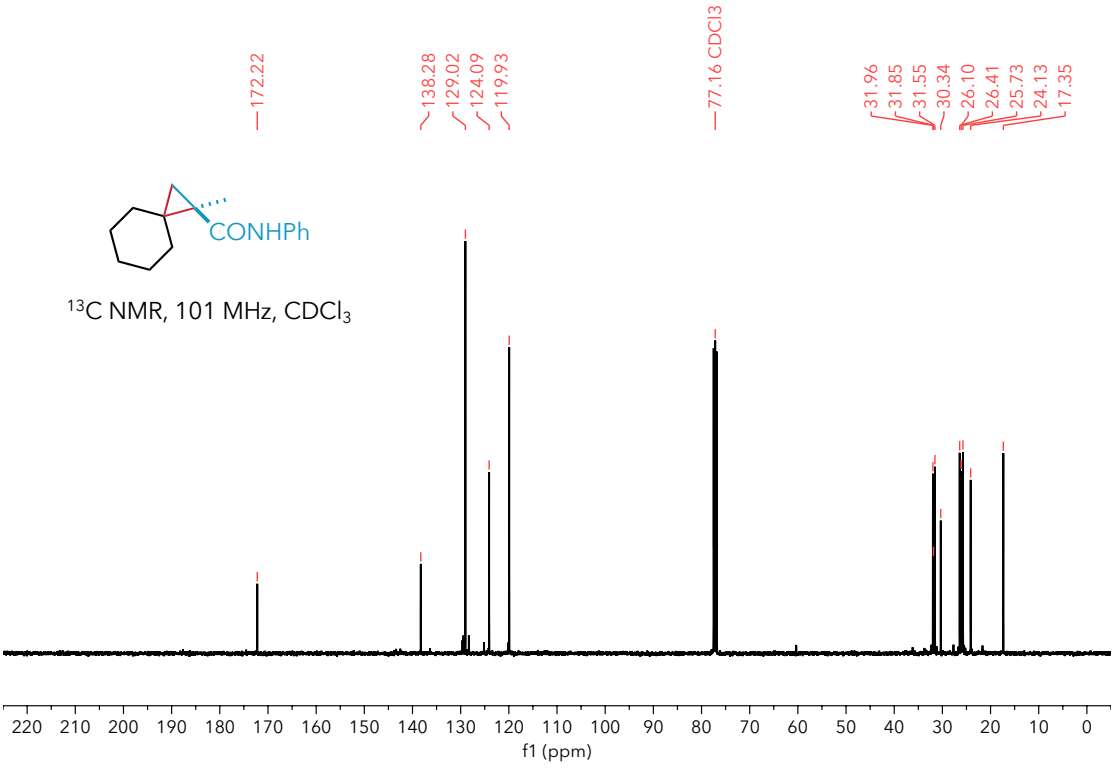
^{1}H NMR, 400 MHz, $CDCl_3$

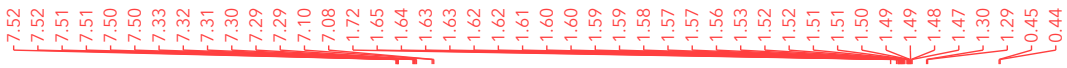


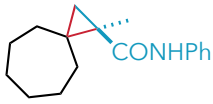
^{13}C NMR, 101 MHz, $CDCl_3$



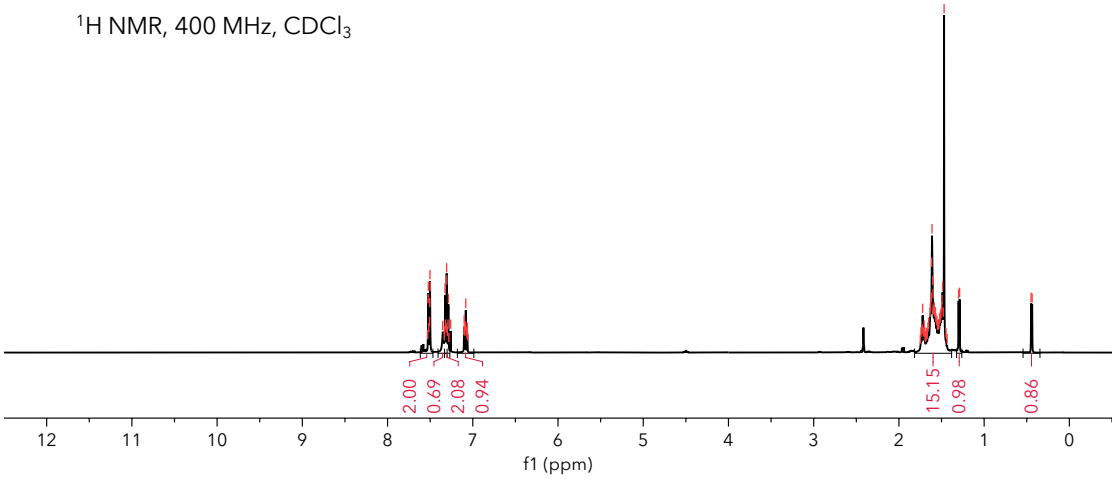

7.53
7.53
7.51
7.51
7.51
7.50
7.36
7.32
7.31
7.30
7.30
7.28
7.28
7.10
7.08
7.08
7.07
1.60
1.59
1.57
1.57
1.56
1.55
1.55
1.53
1.52
1.52
1.51
1.50
1.49
1.49
1.48
1.48
1.45
1.43
1.43
1.42
1.41
1.41
1.40
1.23
1.21
0.41
0.39
CONHPh
^{1}H NMR, 400 MHz, $CDCl_3$
2.00
0.99
2.07
1.00
13.27
1.10
0.98
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


172.22
138.28
129.02
124.09
119.93
77.16 CDCl3
31.96
31.85
31.55
30.34
26.10
26.41
25.73
24.13
17.35
CONHPh
^{13}C NMR, 101 MHz, $CDCl_3$
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

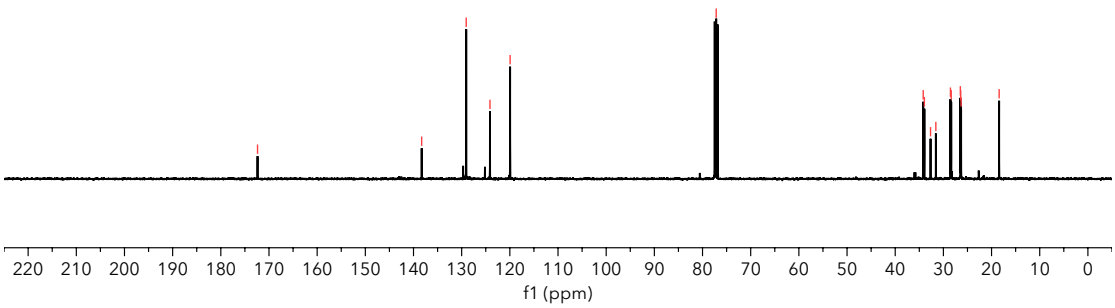


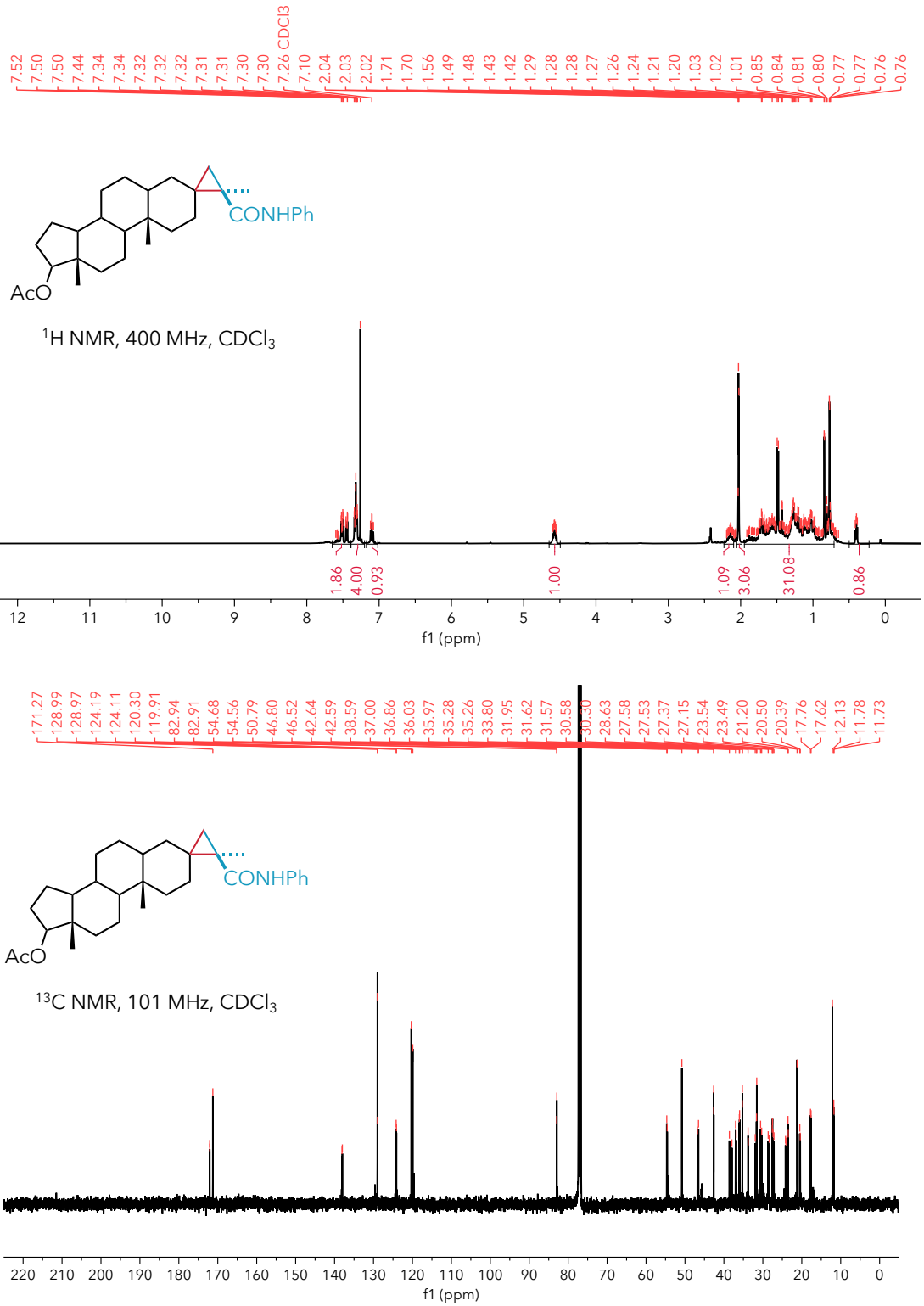


^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 101 MHz, $CDCl_3$

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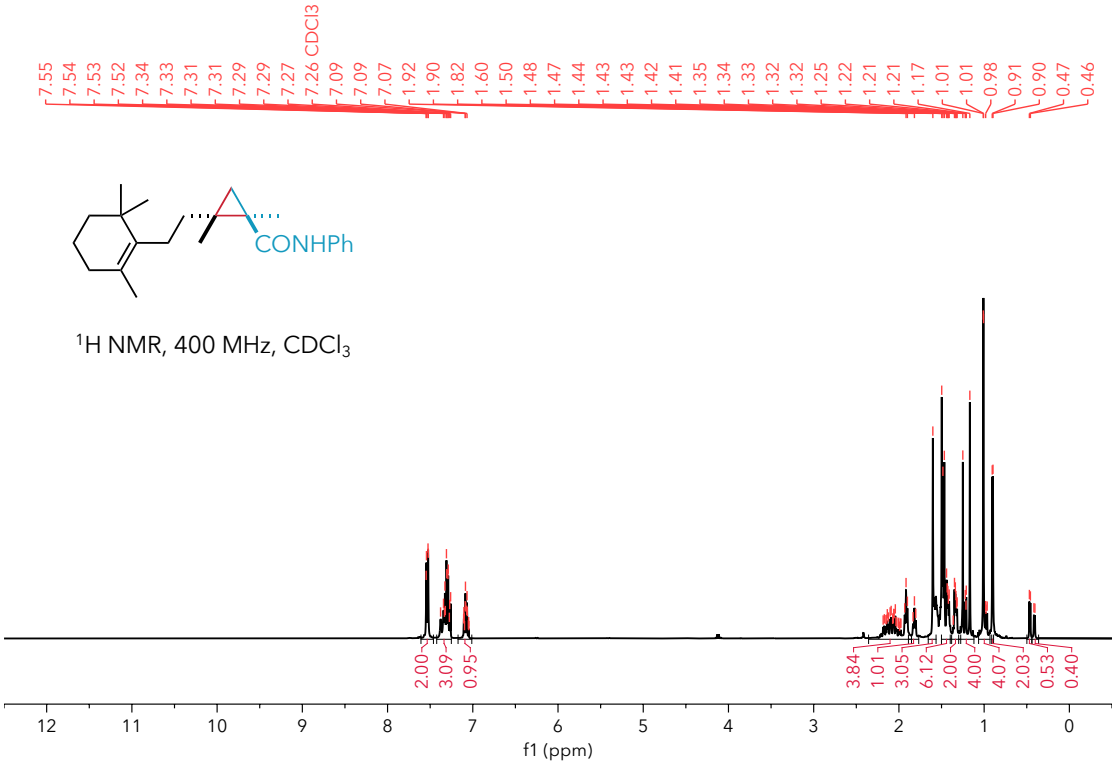
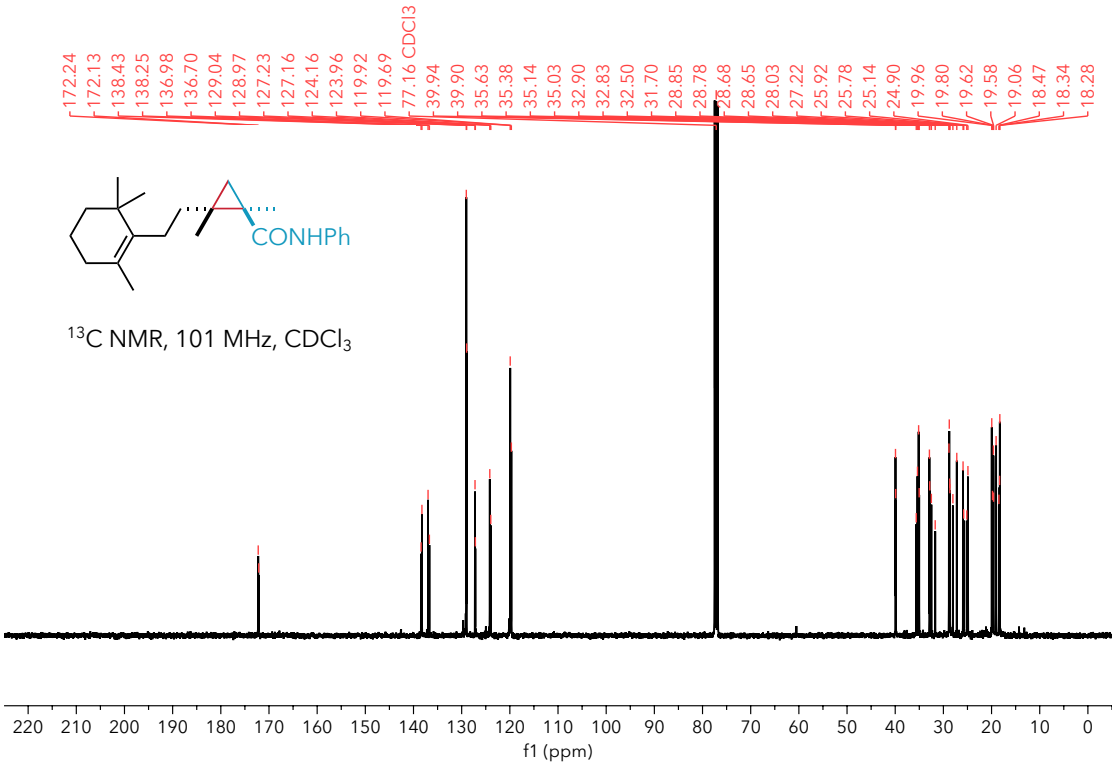
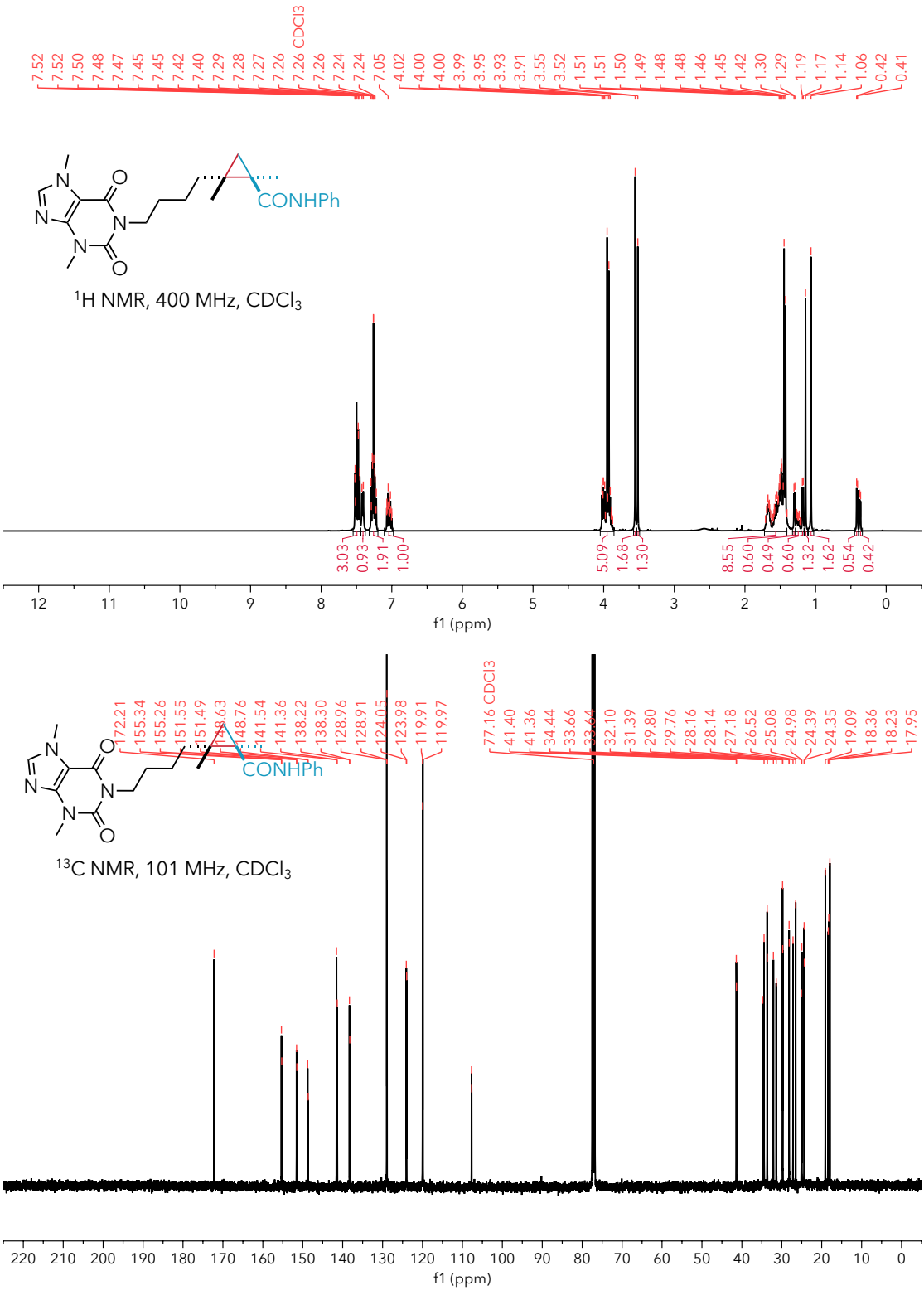
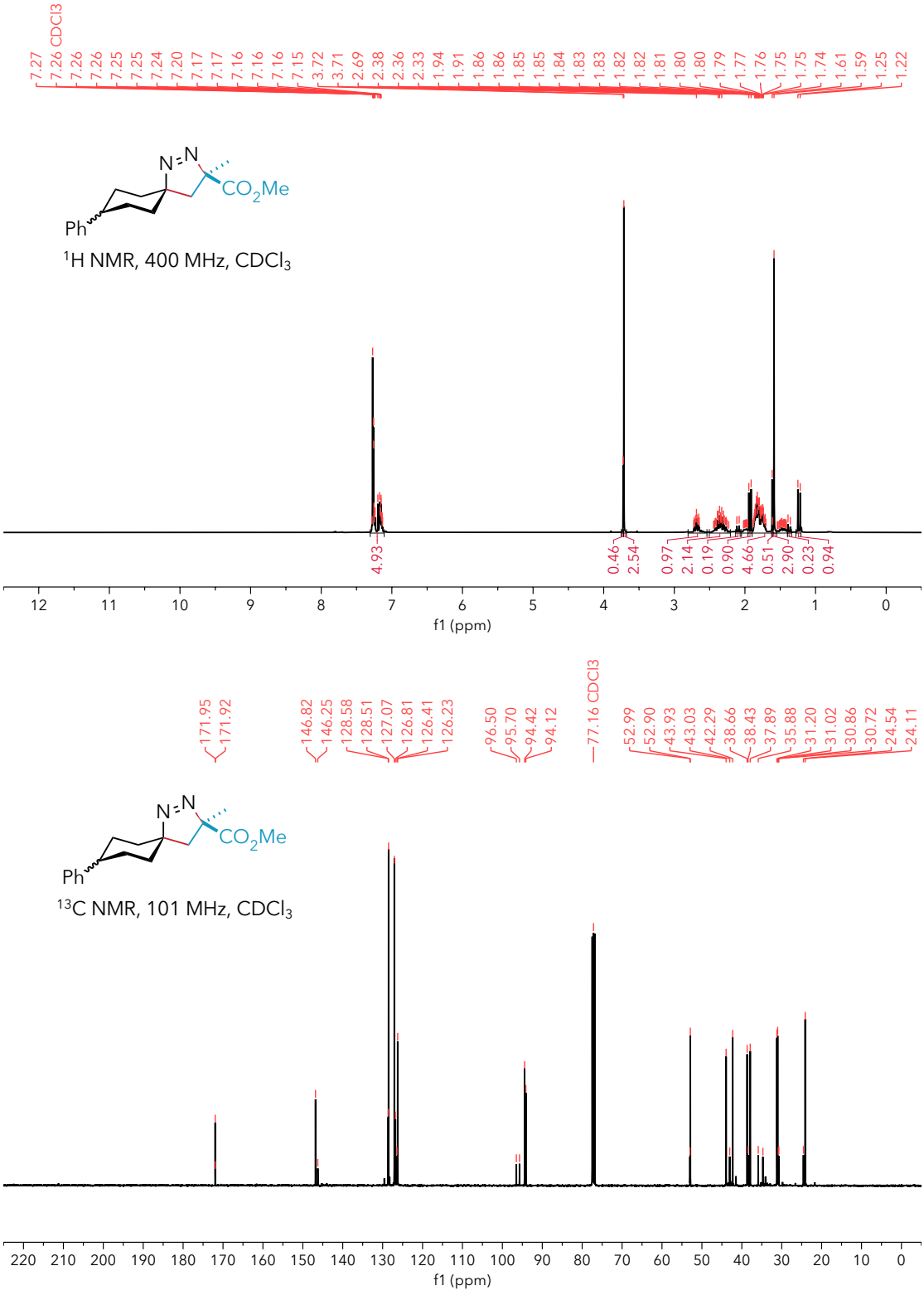
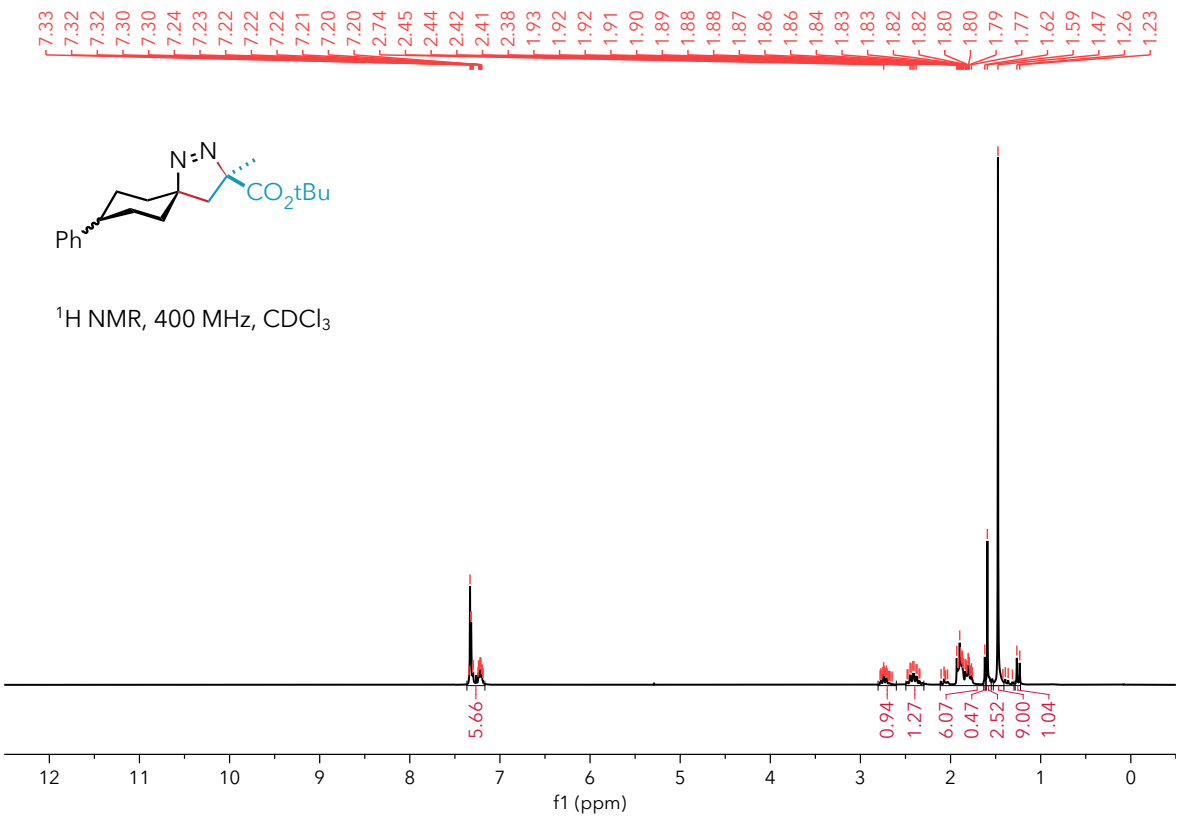
CONHPh
AcO
1H NMR, 400 MHz, CDCl3
1.86 4.00 0.93 1.00 1.09 3.06 31.08 0.86
12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
171.27 128.99 128.97 124.19 124.11 120.30 119.91 82.94 82.91 54.68 54.56 50.79 46.80 46.52 42.64 42.59 38.59 37.00 36.86 36.03 35.97 35.28 35.26 33.80 31.95 31.62 31.57 30.58 30.30 28.63 27.58 27.53 27.37 27.15 23.54 23.49 21.20 20.50 20.39 17.76 17.62 12.13 11.78 11.73
CONHPh
AcO
13C NMR, 101 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

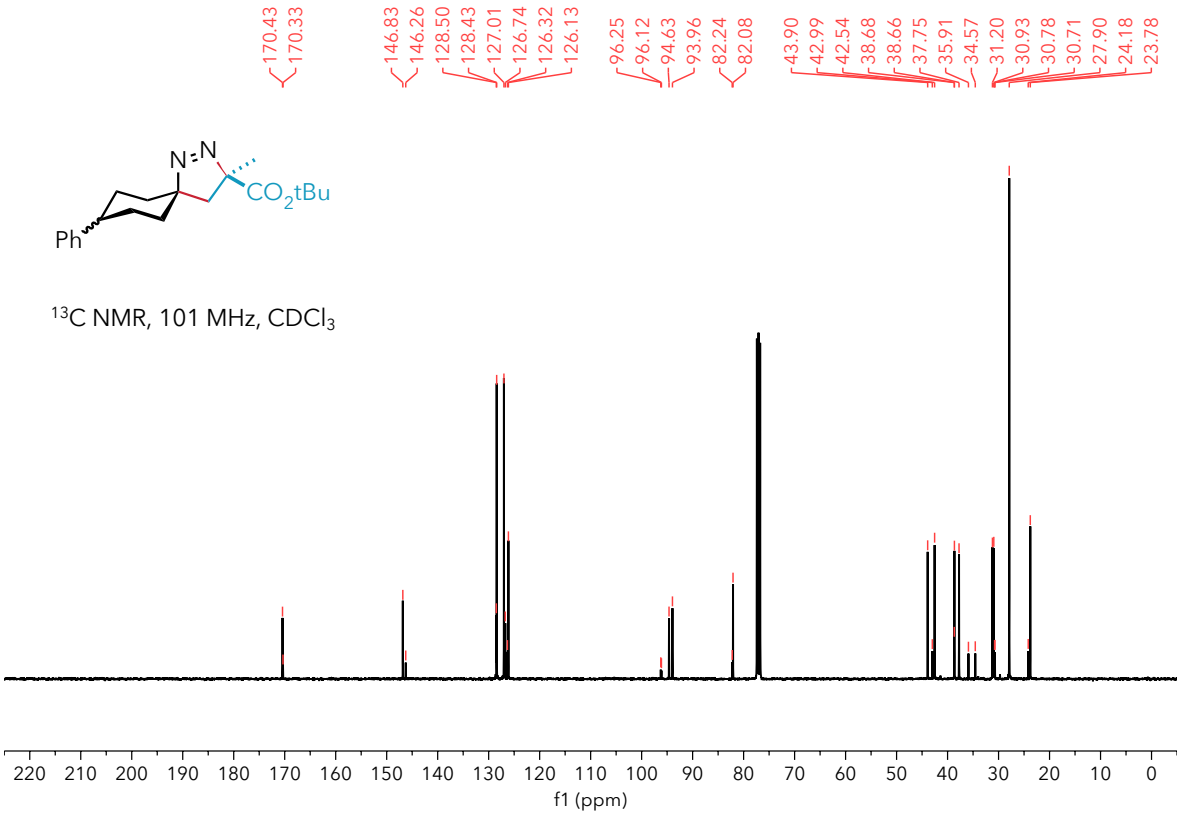

7.55 7.54 7.53 7.52 7.34 7.33 7.31 7.31 7.29 7.29 7.27 7.26 CDCl3 7.09 7.07 1.92 1.90 1.82 1.60 1.50 1.48 1.47 1.44 1.43 1.43 1.42 1.41 1.35 1.34 1.33 1.32 1.32 1.25 1.22 1.21 1.21 1.17 1.01 1.01 0.98 0.91 0.90 0.47 0.46
CONHPh
^{1}H NMR, 400 MHz, $CDCl_3$
2.00 3.09 0.95 3.84 1.01 3.05 6.12 2.00 4.00 4.07 2.03 0.53 0.40
12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

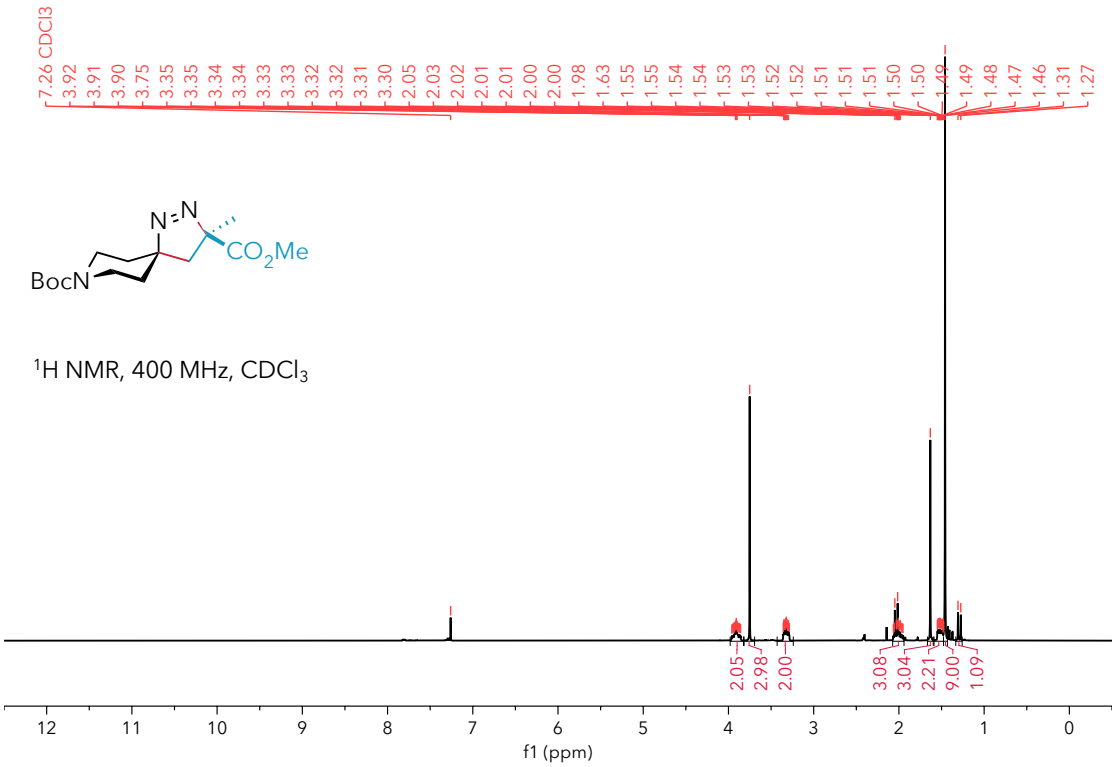

172.24 172.13 138.43 138.25 136.98 136.70 129.04 128.97 127.23 127.16 124.16 123.96 119.92 119.69 77.16 CDCl3 39.94 39.90 35.63 35.38 35.14 35.03 32.90 32.83 32.50 31.70 28.85 28.78 28.68 28.65 28.03 27.22 25.92 25.78 25.14 24.90 19.96 19.80 19.62 19.58 19.06 18.47 18.34 18.28
CONHPh
^{13}C NMR, 101 MHz, $CDCl_3$
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

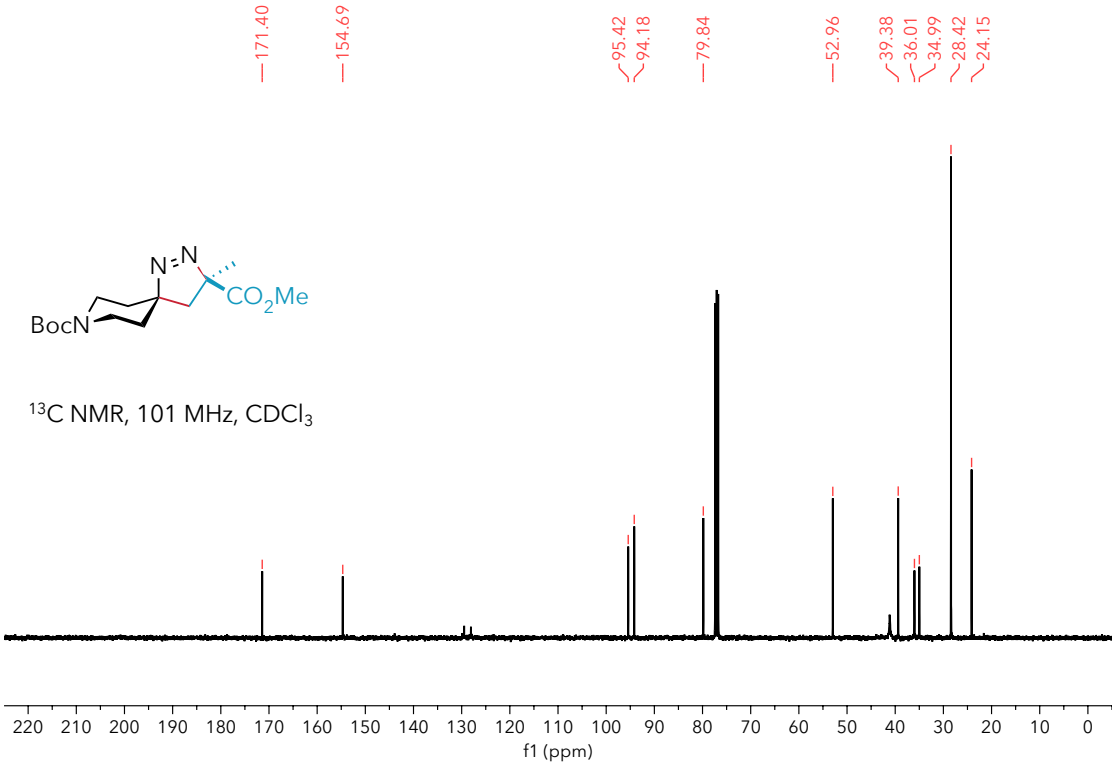

7.52 7.52 7.50 7.48 7.47 7.45 7.45 7.42 7.40 7.29 7.28 7.27 7.26 7.26 CDCl3 7.26 7.24 7.24 7.05 4.02 4.00 4.00 3.99 3.95 3.93 3.91 3.55 3.52 1.51 1.51 1.50 1.49 1.48 1.48 1.46 1.45 1.42 1.30 1.29 1.19 1.17 1.14 1.06 0.42 0.41
CONHPh
1H NMR, 400 MHz, CDCl3
3.03 0.93 1.91 1.00 5.09 1.68 1.30 8.55 0.60 0.49 0.60 1.32 1.62 0.54 0.42
12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
172.21 155.34 155.26 151.55 151.49 148.63 148.76 141.54 141.36 138.22 138.30 128.96 128.91 124.05 123.98 119.91 119.97
77.16 CDCl3 41.40 41.36 34.44 33.66 33.64 32.10 31.39 29.80 29.76 28.16 28.14 27.18 26.52 25.08 24.98 24.39 24.35 19.09 18.36 18.23 17.95
CONHPh
13C NMR, 101 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

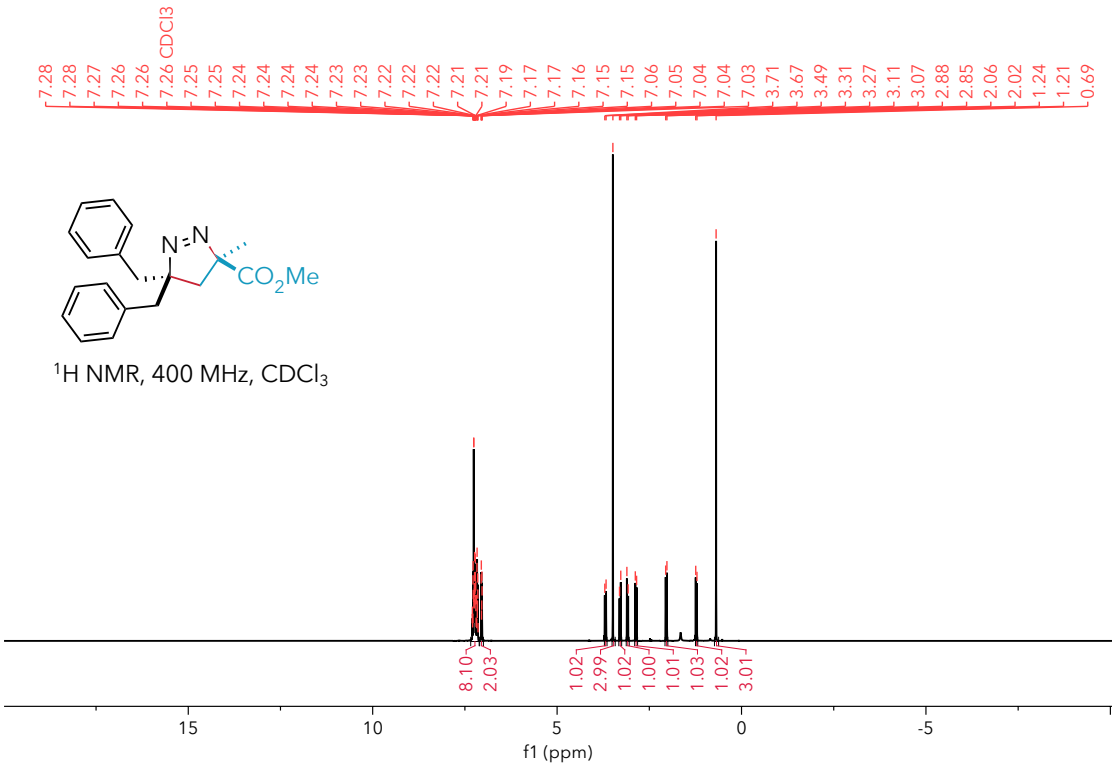

7.27
7.26 CDCl3
7.26
7.26
7.25
7.25
7.24
7.20
7.17
7.17
7.16
7.16
7.16
7.15
3.72
3.71
2.69
2.38
2.36
2.33
1.94
1.91
1.86
1.86
1.85
1.85
1.84
1.83
1.83
1.82
1.82
1.81
1.80
1.80
1.79
1.77
1.76
1.75
1.75
1.74
1.61
1.59
1.25
1.22
N
N
CO2Me
Ph
1H NMR, 400 MHz, CDCl3
4.93
0.46
2.54
0.97
2.14
0.19
0.90
4.66
0.51
2.90
0.23
0.94
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
171.95
171.92
146.82
146.25
128.58
128.51
127.07
126.81
126.41
126.23
96.50
95.70
94.42
94.12
77.16 CDCl3
52.99
52.90
43.93
43.03
42.29
38.66
38.43
37.89
35.88
31.20
31.02
30.86
30.72
24.54
24.11
N
N
CO2Me
Ph
13C NMR, 101 MHz, CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.33
7.32
7.32
7.30
7.30
7.24
7.23
7.22
7.22
7.22
7.21
7.20
7.20
2.74
2.45
2.44
2.42
2.41
2.38
1.93
1.92
1.92
1.91
1.90
1.89
1.88
1.88
1.87
1.86
1.86
1.84
1.83
1.83
1.82
1.82
1.80
1.80
1.79
1.77
1.62
1.59
1.47
1.26
1.23
N
N
CO2tBu
Ph
1H NMR, 400 MHz, CDCl3
5.66
0.94
1.27
6.07
0.47
2.52
9.00
1.04
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

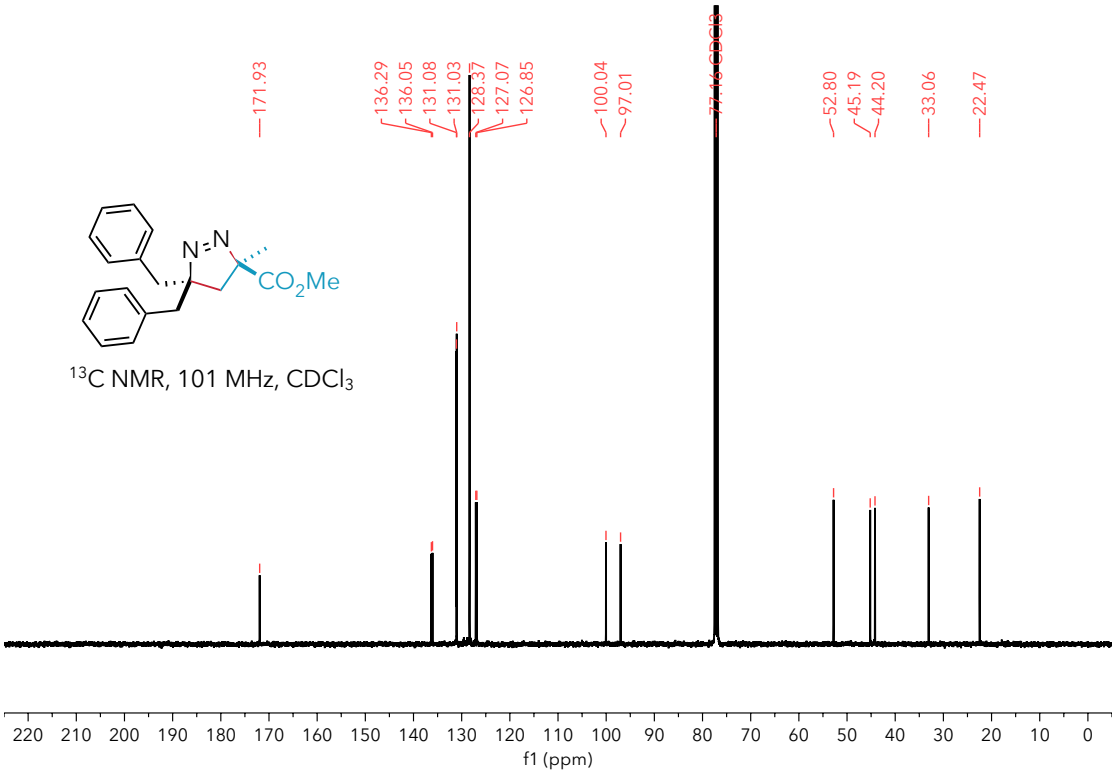

170.43
170.33
146.83
146.26
128.50
128.43
127.01
126.74
126.32
126.13
96.25
96.12
94.63
93.96
82.24
82.08
43.90
42.99
42.54
38.68
38.66
37.75
35.91
34.57
31.20
30.93
30.78
30.71
27.90
24.18
23.78
N
N
CO2tBu
Ph
13C NMR, 101 MHz, CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26 CDCl3
3.92
3.91
3.90
3.75
3.35
3.35
3.34
3.34
3.33
3.33
3.32
3.32
3.31
3.30
2.05
2.03
2.02
2.01
2.01
2.00
2.00
1.98
1.63
1.55
1.55
1.54
1.54
1.53
1.53
1.52
1.52
1.51
1.51
1.51
1.50
1.50
1.49
1.49
1.48
1.47
1.46
1.31
1.27
N
N
CO2Me
BocN
1H NMR, 400 MHz, CDCl3
2.05
2.98
2.00
3.08
3.04
2.21
9.00
1.09
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

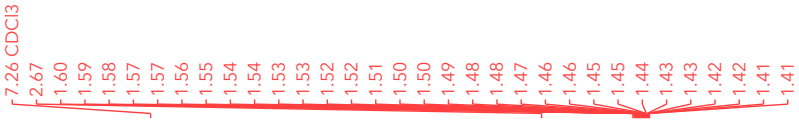

171.40
154.69
95.42
94.18
79.84
52.96
39.38
36.01
34.99
28.42
24.15
N
N
CO2Me
BocN
13C NMR, 101 MHz, CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

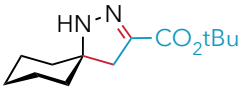


^{1}H NMR, 400 MHz, $CDCl_3$

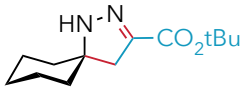


^{13}C NMR, 101 MHz, $CDCl_3$

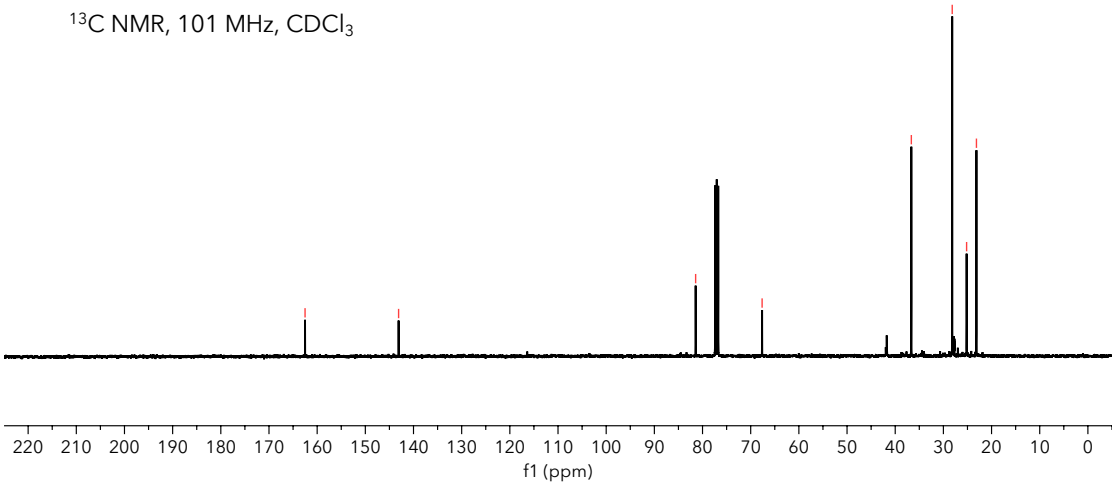


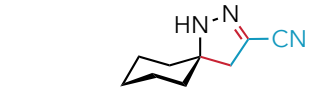


^{1}H NMR, 400 MHz, $CDCl_3$



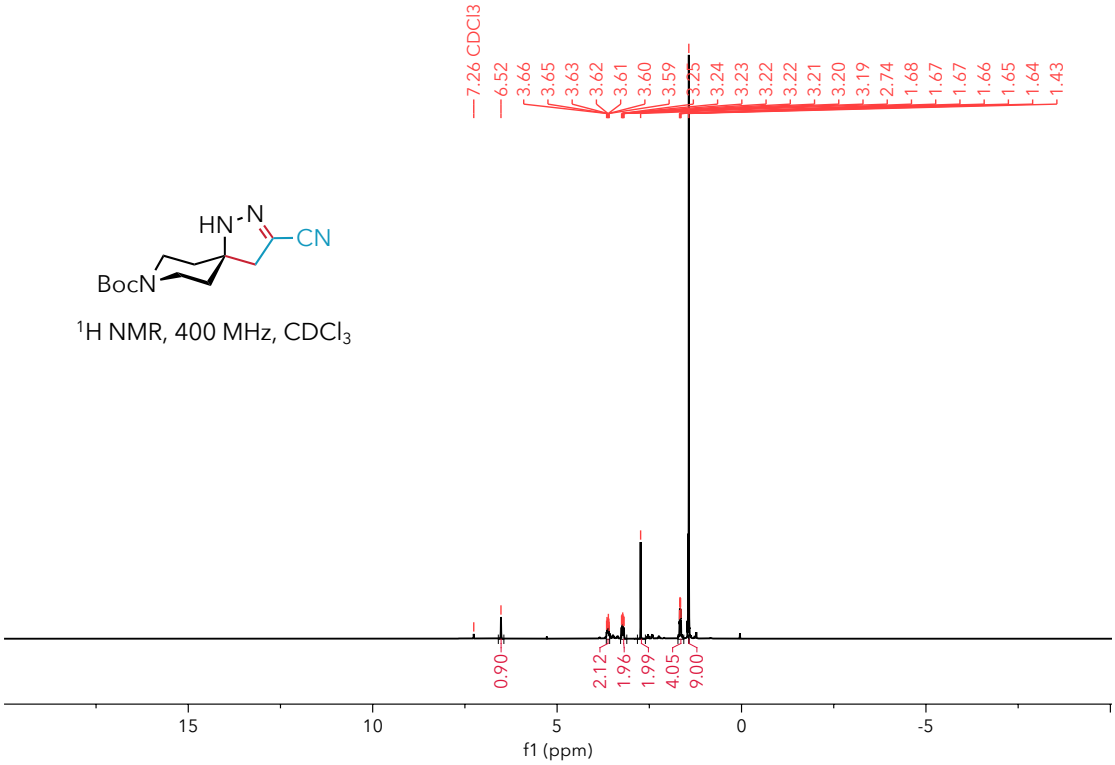
^{13}C NMR, 101 MHz, $CDCl_3$



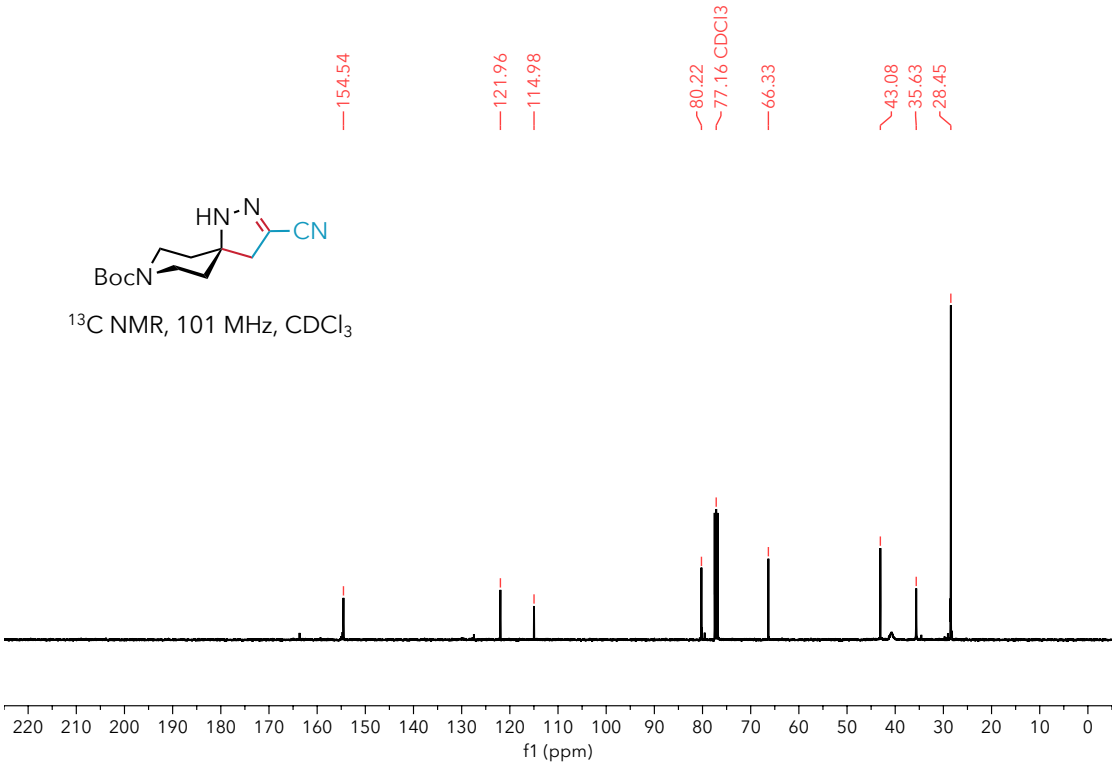


^{1}H NMR, 400 MHz, $CDCl_3$

^{13}C NMR, 101 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 101 MHz, $CDCl_3$

8 References

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5 A. N. Terenin and V. L. Ermolaev, *Dokl. Akad. Nauk SSSR*, 1952, **85**, 547–550.

6 N. D. C. Tappin, W. Michalska, S. Rohrbach and P. Renaud, *Angew Chem Int Ed*, 2019, **58**, 14240–14244.