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Diamine Synthesis via the Nitrogen-Directed Azidation of σ- and π-C-C Bonds

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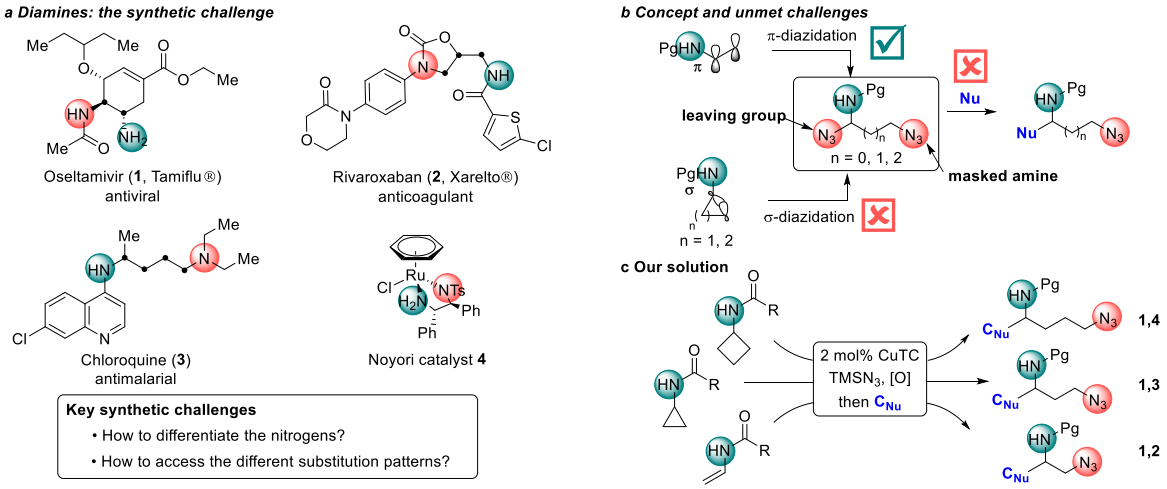
ABSTRACT: Diamines are essential building blocks for the synthesis of agrochemicals, drugs and organic materials, yet their synthesis remains challenging, as both nitrogens need to be differentiated and diverse substitution patterns (1,2-, 1,3 or 1,4) are required. We report herein a new strategy giving access to 1,2-, 1,3- and 1,4- amido azides as orthogonally protected diamines based on the nitrogen-directed diazidation of alkenes, cyclopropanes and cyclobutanes. Commercially available copper thiophene-2-carboxylate (CuTc, 2 mol%) as catalyst promoted the diazidation of both π and σ C-C bonds within 10 minutes in presence of readily available oxidants and trimethylsilyl azide. Selective substitution of the formed α-amino azide by carbon nucleophiles (electron-rich aromatic, malonate, organosilicon, organoboron, organozinc and organomagnesium compounds) was then achieved in a one-pot fashion, leading to the formation of 1,2-, 1,3- and 1,4-diamines with the amino groups protected orthogonally as an amide/carbamate and an azide.

Diamines are an important class of compounds found in pharmaceuticals such as Oseltamivir (**1**), Rivaroxaban (**2**) or Chloroquine (**3**), organocatalysts, chiral ligands, as in Noyori catalyst **4**, and materials (Scheme 1a).[1-4] Two key challenges currently hamper access to these building blocks: 1) A way to differentiate the two nitrogen functionalities and 2) A general access to the different substitution patterns (1,2-, 1,3- or 1,4-), which are currently synthesized using fundamentally different disconnections. To answer these challenges, we considered an approach based on the diazidation of nitrogen-substituted alkenes and strained rings (Scheme 1b). The amine in the starting material would play a key role in this strategy: First, it will act as an activating group to promote the diazidation of an adjacent π or σ C-C bond. Second, it will accelerate the dissociation of the azide at the aminal position for the introduction of nucleophiles. Finally, it will remain in the product as an orthogonally protected amine, whereas the second nitrogen functionality would be in the form of an azide, one of the synthetically most useful functional groups.[5,6]

When considering precedence for our strategy, only the π-diazidation step has been realized so far.[7-17] Diazidation of alkenes is attractive because of a quick access to diamines after reduction, but selective reaction of one of the two azido groups is difficult.[18,19] Introducing simultaneously an azide and another nitrogen functionality on an alkene is promising, but has been realized only in a few reports.[17,20-23]



Scheme 1. (a) Diamines: essential building blocks, but a synthetic challenge. (b) Our concept starting from nitrogen-substituted alkenes and strained rings. (c) Our solution: copper-catalyzed synthesis of 1,2-, 1,3- and 1,4- amido azides.

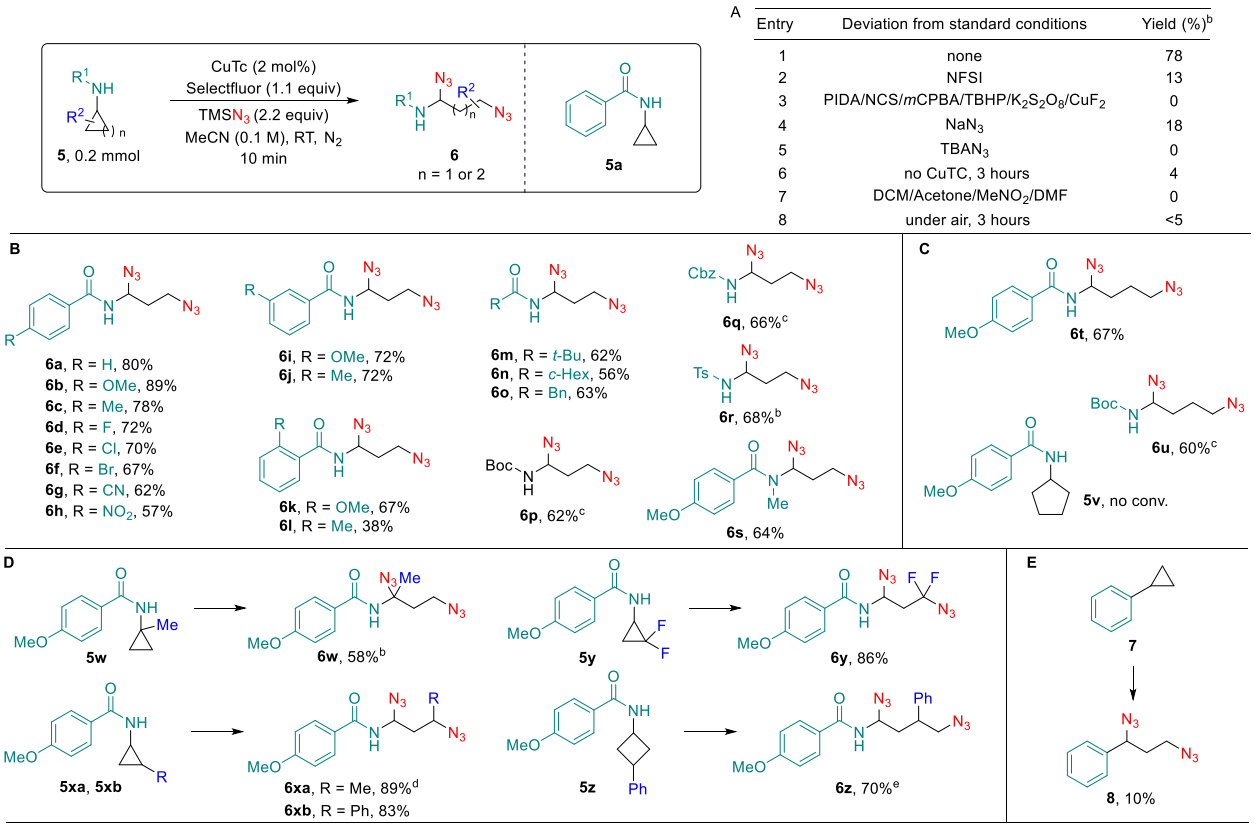
In contrast to the diazidation of π bonds, the envisaged σ bond diazidation of cyclopropanes or cylobutanes to give either 1,3- or 1,4-diazides was unprecedented. Only the diaminations of arylcyclopropanes to form 1,3-ditosylamides or 1,3-azidoimides have been reported.[24,25] This may be due to the lower reactivity of cyclopropane/cyclobutane σ bonds compared to alkene π bonds.[26] Among recent efforts in ring-opening reactions of aminocyclopropanes and aminocyclobutanes,[27,28] our group and others have used oxidative ring-opening to access multi-functionalized building blocks.[29-35] For extending this strategy to the diazidation of aminocyclopropanes, two challenges needed to be considered: 1) the choice of a catalyst to promote both oxidative ring-opening and azide transfer; 2) the functionalization of α-azido amides by carbon nucleophiles, which was unprecedented. Indeed, only three examples using thiophenol,[36] amine[37] and silyl hydride[10] as heteronucleophiles have been reported.

Herein, we show that the C-C diazidation challenge can be solved for both π and σ bonds by the use of a copper catalyst[38-42] (commercially available copper thiophene-2-carboxylate, CuTc, 2 mol%), an oxidant and $TMSN_3$ as azide source (Scheme 1c). We then developed simple conditions for the one-pot addition of a broad range of carbon nucleophiles, resulting in a general access to 1,2-, 1,3- and 1,4- amido azides.

Based on our previous work,[32-34] aminocyclopropane **5a** was selected as the model substrate for the ring-opening azidation reaction with $TMSN_3$ as azide source (Table 1). Photoredox conditions using benzophenone as catalyst and Selectfluor as oxidant[34] afforded a mixture of diazidation product **6a** and a fluorination byproduct (see Scheme S2 in SI). A broad screening of reaction conditions showed that copper salts were uniquely able to suppress fluorination and promote the azidation reaction (see Table S1 in SI). After optimization, **6a** could be obtained in 78% yield in 10 minutes with 2.2 equivalents of $TMSN_3$ when using CuTc as catalyst in acetonitrile (Table 1A, entry 1). The reaction proceeded with low conversion when NFSI was used instead of Selectfluor (Table 1A, entry 2). Other oxidants failed to afford **6a** (Table 1A, entry 3). NaN_3 and $TBAN_3$ were examined, but were less efficient than $TMSN_3$ (Table 1A, entries 4 and 5). Almost no reaction took place in the absence of CuTc (Table 1A, entry 6). The reaction failed in other solvents and it was sensitive to air (Table 1A, entries 7 and 8).

With optimal conditions in hand, we examined the scope of substituents on nitrogen (Table 1B). On benzamides, substituents could be introduced in *para* (**6b-h**), *meta* (**6i-j**) and *ortho* position (**6k-l**). Electron-rich (**6b-c**), electron-poor (**6g-h**) and halogen substituents (**6d-f**) were all well tolerated.

Table 1. Optimization and scope of the diazidation reaction[a]



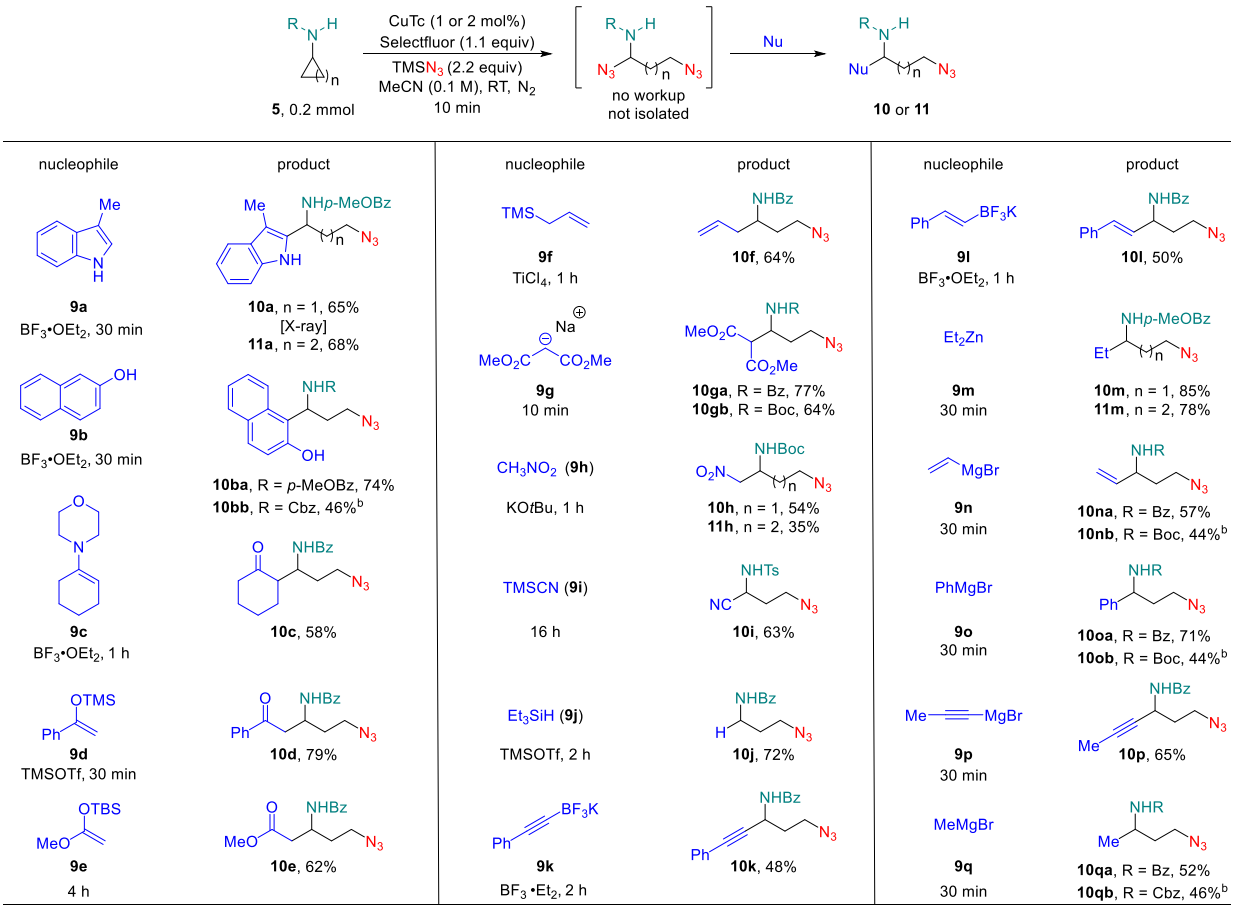
A		
Entry	Deviation from standard conditions	Yield (%)[b]
1	none	78
2	NFSI	13
3	PIDA/NCS/*m*CPBA/TBHP/$K_2S_2O_8$/CuF_2	0
4	NaN_3	18
5	$TBAN_3$	0
6	no CuTC, 3 hours	4
7	DCM/Acetone/$MeNO_2$/DMF	0
8	under air, 3 hours	<5

[a]Isolated yield on a scale of 0.2 mmol. [b]Yield determined by ^1H NMR using CH_2Br_2 as internal standard. [c]1 mol% CuTc was used. [d]6 mol% CuTc was used. [e]0.1 mmol scale.

Substrates bearing alkyl amides underwent diazidation to give **6m-o** in 56-63% yield. Carbamate protected aminocyclopropanes afforded products **6p** and **6q** in 62% and 66% yield respectively. From tosyl protected substrate **5r**, diazidation product **6r** was observed by ^{1}H NMR, but purification by column chromatography led to decomposition. An alkyl-substituted benzamide gave diazide **6s** in 64% yield. The reaction conditions were also successful in the case of aminocyclobutanes, leading to 1,4-diazides **6t** and **6u** in 67% and 60% yield (Table 1C). Ring strain was shown to be an essential driving force, as aminocyclopentane **5v** did not react. Importantly, the transformation was not limited to unsubstituted small rings. 1-Methyl, 2-methyl and 2-phenyl substituted aminocyclopropanes **5w**, **5xa** and **5xb** gave the diazide products **6w**, **6xa** and **6xb** in 58-89% yield (Table 1D). Product **6w** was observed by ^{1}H NMR, but it was not stable enough to be isolated. From *gem*-difluoro aminocyclopropane **5y**, difluoroazide **6y** was obtained in 86% yield. For all substrates, selective cleavage of the more-substituted σ-bond to give the more stable radical was observed. 3-Phenyl substituted aminocyclobutane **5z** yielded only C1-C2 bond cleavage product **6z** in 70% yield. Cyclopropylbenzene **7** gave diazidation product **8** in 10% yield (Table 1E). In contrast, only the aminoazidation product had been observed in Zhang's previous work using NFSI as oxidant.[25]

We then turned towards the one-pot nucleophilic substitution of the α-amino azide. After the diazidation step was complete, carbon nucleophiles[43] were added directly to the reaction mixture (Table 2). To our delight, the α-amino azide was readily replaced by numerous nucleophiles with or without Lewis acid activation. Friedel-Crafts reactions took place in 46-74% yield with 3-methyl indole (**9a**) or 2-naphthol (**9b**) and boron trifluoride etherate as Lewis acid to give diamines **10a** and **10b**. Mannich-type reactions with enamine **9c** or enol ethers **9d** and **9e** gave products **10c-e** in 58-79% yield. Allyltrimethylsilane (**9f**) was also a good nucleophile in presence of titanium tetrachloride. More reactive nucleophiles, such as malonate **9g** and nitronate **9h**, reacted directly with the α-amino azide without the need for Lewis acid activation. Trimethylsilyl cyanide (**9i**) and triethylsilane (**9j**) gave cyano amine **10i** and reduced amine **10j** in 63 and 72% yield respectively. A Petasis-type reaction using tetrafluoroborate salts **9k** and **9l** as nucleophiles led to the formation of propargylic amine **10k** and allylic amine **10l** in 48 and 50% yield in presence of boron trifluoride etherate.

Table 2. One-pot diazidation-nucleophilic substitution for 1,3-and 1,4-diamine synthesis[a]

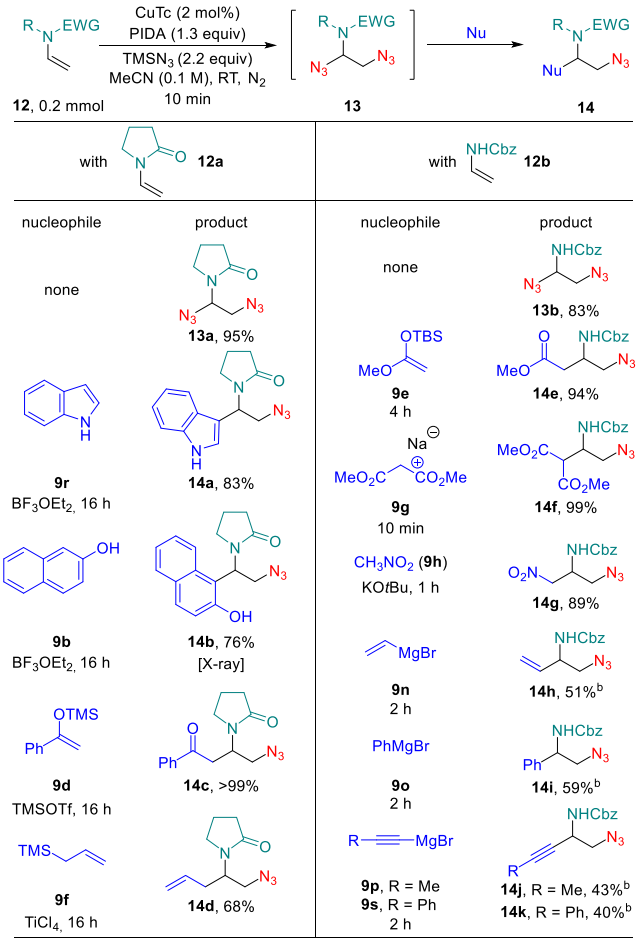


[a]Isolated yield on a scale of 0.2 mmol, nucleophilic substitution at room temperature for the indicated time. [b]Nucleophilic substitution at -20 °C for 2 hours.

Organozinc reagents, such as diethylzinc (**9m**) could be used to introduce an alkyl chain without Lewis acid activation. Commercially available organomagnesium reagents enabled the introduction of vinyl, aryl, alkynyl and alkyl substituents (products **10n-q**). This diazidation-nucleophilic substitution process was successfully extended to aminocyclobutanes to give 1,4-diamines **11a**, **11h** and **11m** in 35-78% yield.

We then applied our nucleophilic substitution protocol with carbon nucleophiles to diazides derived from enamides. Rather than using one of the reported methods to access the diazides,[10,11,15] we wondered if our copper-catalyzed diazidation method could be applied. In fact, the copper-catalyzed diazidation of styrenes has already been reported.[8,9,13,14] Best results were obtained with PIDA as oxidant using CuTc as catalyst, and product **13a** was isolated in 95% yield starting from enamide **12a** (Table 3, see Table S6 in SI for more details). The reaction proceeded even without CuTc, although the isolated yield decreased to 78%. These conditions were also suitable for enecarbamate **12b** and product **13b** was isolated in 83% yield in the presence of CuTc, compared to 67% in its absence.

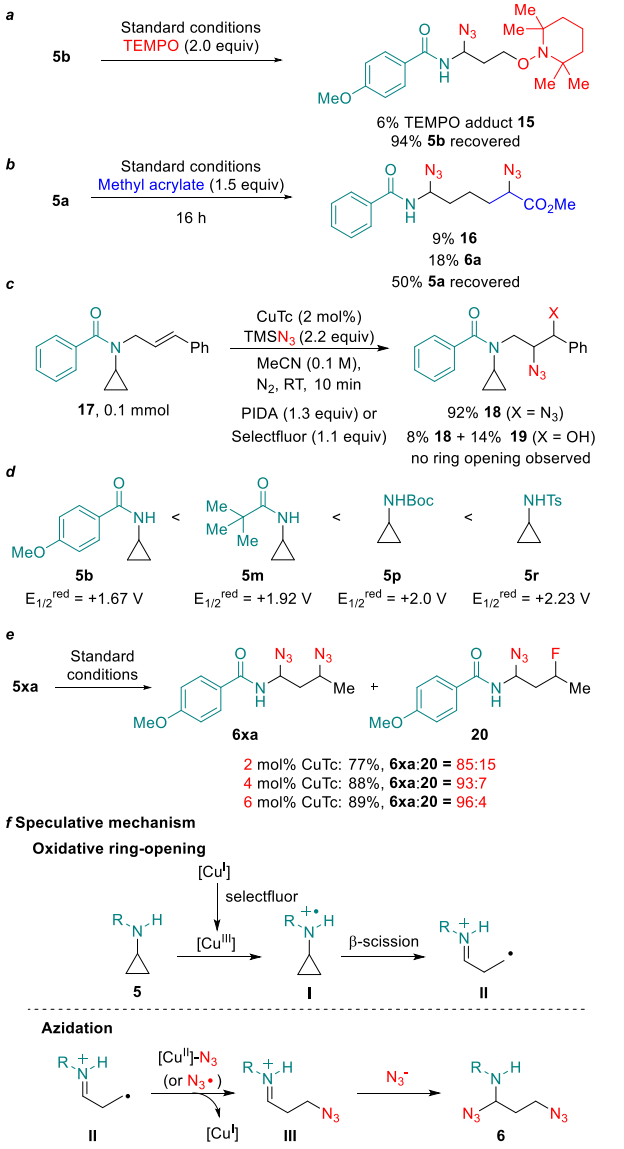
Table 3. Diazidation of enamides and enecarbamates and one-pot addition of nucleophiles[a]



[a]Isolated yield on a scale of 0.2 mmol, nucleophilic substitution at room temperature for the indicated time. [b]Nucleophilic substitution at -20 °C.

Different nucleophiles were then incorporated into the α-amino position. Friedel-Crafts reactions with indole (**9r**) and 2-naphthol (**9b**) gave **14a** and **14b** in 83% and 76% yield respectively. Enol ether (**9d**) and allyltrimethylsilane (**9f**) were also good nucleophiles. For enecarbamate **12b**, β-amino acid derivative **14e** was obtained by using enol ether **9e** as nucleophile. Sodium malonate gave **14f** in 99% yield. When nitromethane was used as nucleophile, 1,2,3-trifunctionalized propane **14g** bearing three nitrogen atoms in different oxidation states was formed. Different organomagnesium reagents were also examined and isolated yields for products **14h-14k** ranged from 40% to 59%.

Preliminary mechanistic experiments were then performed (Scheme 2). In the presence of the radical inhibitor 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), 6% of TEMPO adduct **15** could be isolated, while 94% of **5b** was recovered (Scheme 2a). When methyl acrylate was added, 1,5-diazide product **16** was isolated in 9% yield (Scheme 2b).



Scheme 2. Studies on the catalytic ring-opening azidation and speculative mechanism.

In order to compare the reactivity of the σ and π bonds, we synthesized substrate **17** bearing a cyclopropyl ring and a cinnamyl group on the nitrogen. Using PIDA/$TMSN_3$, 92% of alkene diazidation product **18** was isolated; with Selectfluor/$TMSN_3$, 8% of **18** as well as 14% alkene hydroxyazidation byproduct **19** were isolated (Scheme 2c). In both cases, no ring-opening product was observed. Cyclic voltammetry experiments were then performed to measure the redox potential of substrates **5b**, **5m**, **5p** and **5r** and the values ranged from +1.67 to +2.23 V vs SCE in CH_3CN (Scheme 2d). Therefore, Selectfluor ($E_{1/2}^{Red}$ = +0.33 V and +0.79 V vs SCE in CH_3CN, for two successive SET processes)[34] should not be able to oxidize the aminocyclopropanes directly. When **5xa** was used as substrate, a small amount of fluorination side product **20** was observed in addition to **6xa**. Interestingly, the ratio between **6xa** and **20** was increased by adding more CuTc, indicating that the copper catalyst played a role for azido group transfer (Scheme 2e). Finally, no asymmetric induction was observed in presence of a chiral CN-BOX ligand with 2-phenyl substituted aminocyclopropane **5xb** (See Scheme S8 in SI).[17,42,44]

Based on these results, together with literature precedence on Selectfluor-oxidized Cu(III) species[45-48] and a recent report on copper-catalyzed benzylic C-H azidation,[41] we propose a speculative mechanism in Scheme 2f. The reaction would be initiated by oxidation of CuTc by Selectfluor to form a fleeting Cu(III) species, which then oxidizes aminocyclopropane **5** to give aminium radical **I**. Carbon radical **II** is then formed after β-scission. In a second step, the azide could be transferred from a Cu(II)-N_3 complex to **II**, regenerating a Cu(I) complex. A rebound-type mechanism with a Cu(III)-N_3 complex first oxidizing **5** and then transferring the azide to **II** can be considered, although we have no experimental support for it at this stage. Alternatively, the generation of a free azide radical that recombines with **II** can also be envisaged. In the latter case, the role of copper in the azidation step would be just to increase the concentration of the free azido radical. The azidation of **II** would then lead to iminium **III**, which would be intercepted by an azide nucleophile to deliver diazidation product **6**.

In summary, we have developed a diazidation-nucleophilic substitution sequence for the synthesis of orthogonally protected 1,2-, 1,3-, and 1,4-diamines starting from enamides/enecarbamates, aminocyclopropanes and aminocyclobutanes respectively. The first step was enabled by a copper-catalyzed diazidation proceeding in high yields within 10 minutes at room temperature using commercially available reagents. The obtained α-amino azides functioned then as masked imines for accessing a broad range of protected diamines in the form of an amide/carbamate and an azide by addition of carbon-based nucleophiles. Our new strategy to access diamines further highlights the potential of C-C functionalizations of strained carbocycles for the selective synthesis of multi-functionalized building blocks, as well as shines light on the potential of α-amido azides as masked imines.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge. Crystallographic data for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre, under deposition numbers CCDC 2085561 (**10a**) and 2085562 (**14b**). Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/structures/.

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Notes

The authors declare no competing financial interests.

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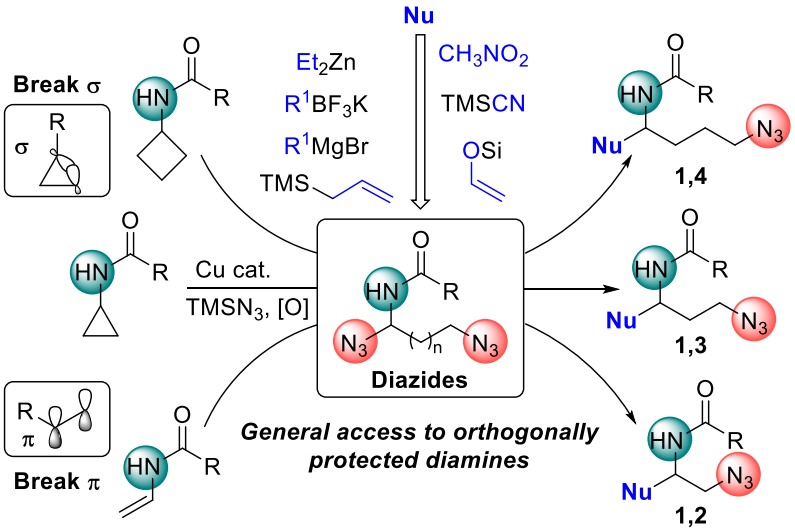
Nu
Et2Zn
R1BF3K
R1MgBr
TMS
CH3NO2
TMSCN
OSi
Break σ
Break π
Cu cat.
TMSN3, [O]
Diazides
General access to orthogonally protected diamines
1,4
1,3
1,2

Supporting Information for

Diamine Synthesis via the Nitrogen-Directed Azidation of σ- and π- C-C Bonds

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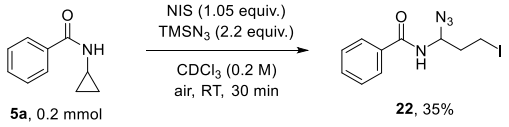
1. General Methods

For quantitative flash chromatography, distilled technical grade solvents were used. THF, Et_2O, toluene, hexane and CH_2Cl_2 were dried by passage over activated alumina under nitrogen atmosphere (H_2O content < 7 ppm, Karl-Fischer titration). All chemicals were purchased and used as received unless stated otherwise. Chromatographic purification was performed as flash chromatography using Macherey-Nagel silica 40-63, 60 Å, using the solvents indicated as eluent with 0.1-0.5 bar pressure. TLC was performed on Merck silica gel 60 F254 TLC plastic or aluminium plates and visualized with UV light, permanganate stain. Melting points were measured on a calibrated Büchi B-540 melting point apparatus using open glass capillaries. ^{1}H-NMR spectra were recorded at room temperature on a Brucker DPX-400 400 MHz spectrometer in $CDCl_3$, Acetone-d_6, CD_3CN or CD_3OD, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm, the internal acetone signal at 2.09 ppm, the internal acetonitrile signal at 1.94 ppm and the internal methanol signal at 3.34 ppm as standard. The data is being reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, p = quintet, m = multiplet or unresolved, br = broad signal, integration, coupling constant(s) in Hz, interpretation). ^{13}C-NMR spectra were recorded with 1H-decoupling on a Brucker DPX-400 101 MHz spectrometer in $CDCl_3$, Acetone-d_6, CD_3CN or CD_3OD, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm, Acetone-d_6 signal at 29.8 ppm, CD_3CN signal at 1.3 ppm or CD_3OD signal at 49.0 ppm as standard. Infrared spectra were recorded on a JASCO FT-IR B4100 or a Bruker Alpha-P spectrophotometer with an ATR device and a ZnSe prism and are reported as cm-1 (w = weak, m = medium, s = strong). High resolution mass spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL on a MICROMASS (ESI) Q-TOF Ultima API. HPLC measurements were done on a Agilent 1260 Infinity autosampler using a CHIRALPAK IA, IB, IC or IF column from DAICEL Chemical. The specific solvents and concentrations (in g/100 mL) are indicated.

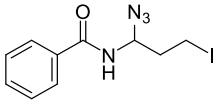
2. Reaction discovery and optimization

2.1 Reaction discovery

Scheme S1 (Azidation attempts with intercepted HLF reaction)



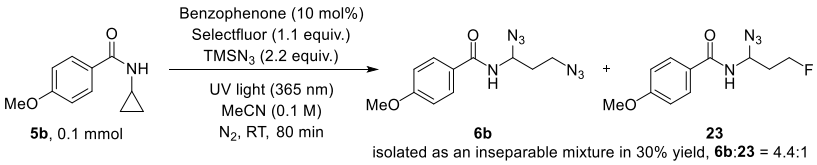
***N*-(1-Azido-3-iodopropyl)benzamide** (**22**).



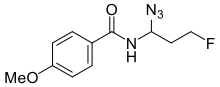
In a 12*75 mm Borosilicate glass tube, *N*-cyclopropylbenzamide **5a** (32.2 mg, 0.200 mmol) and *N*-iodosuccinimide (47.2 mg, 0.210 mmol, 1.05 equiv.) were added. $CDCl_3$ (1.0 mL, 0.2 M) was added, followed by the addition of $TMSN_3$ (94% purity purchased from TCI, 62.0 µL, 0.440 mmol, 2.2 equiv.). The reaction mixture was stirred at room temperature for 30 minutes. *N*-(1-Azido-3-iodopropyl)benzamide **22** (23.0 mg, 70.0 µmol, 35%) was obtained as a yellow solid after purification by column chromatography (SiO_2, pentanes/EtOAc 3:1).

R_f: 0.45 (silica, pentanes:ethyl acetate 3:1);
Mp: 98-99 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 – 7.76 (m, 2H, Ar*H*), 7.58 – 7.52 (m, 1H, Ar*H*), 7.49 – 7.43 (m, 2H, Ar*H*), 6.76 (d, *J* = 9.1 Hz, 1H, N*H*), 5.89 (dt, *J* = 9.0, 6.7 Hz, 1H, C*H*), 3.30 – 3.16 (m, 2H, CH_2I), 2.31 – 2.16 (m, 2H, CH_2CH$_2$I);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.5, 132.8, 132.4, 128.8, 127.2, 67.5, 38.0, -1.8;
IR (film): $\tilde{\nu}$ = 3293 (m), 2109 (s), 1650 (s), 1523 (s), 1241 (s), 701 (m);
HRMS (ESI) calcd. for $C_{10}H_{11}IN_4NaO^+$ $[M+Na]^+$ 352.9870; Found 352.9878.

Scheme S2 (Azidation attempts with benzophenone photocatalyst)



***N*-(1-azido-3-fluoropropyl)-4-methoxybenzamide** (**23**).



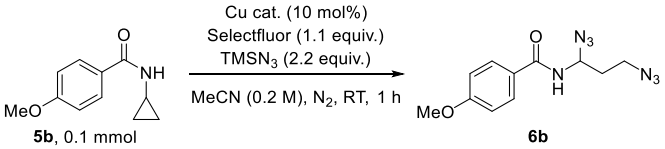
In a 12*75 mm Borosilicate glass tube, *N*-cyclopropyl-4-methoxybenzamide **5b** (19.1 mg, 0.100 mmol), Selectfluor (39.0 mg, 0.110 mmol, 1.1 equiv.) and benzophenone (1.8 mg, 0.010 mmol, 0.10 equiv.) were added. The tube was then closed with a rubber septum and sealed off with parafilm. Evacuate-refill cycle with nitrogen were performed three times to remove O_2 and extra-dry acetonitrile (1.0 mL) was added under nitrogen atmosphere, followed by the addition of $TMSN_3$ (94% purity purchased from

TCI, 31.0 µL, 0.220 mmol, 2.2 equiv.). The mixture was then stirred at room temperature under 365 nm irradiation in Rayonet Reactor for 80 minutes. A mixture of **6b** and **23** was obtained in roughly 30% yield in a ratio of 4.4:1 after purification by column chromatography (SiO_2, pentanes/EtOAc 3:1).

Compound **23** was not obtained in a pure form due to coelution with **6b**, but its existence was confirmed by:
^{19}F NMR (376 MHz, $CDCl_3$): δ = -218.8.

Table S1 (Azidation attempts with Copper catalyst)

Formation of diazidation product **6b** was observed when copper catalysts were used as catalyst, while no fluorination byproduct **23** was observed in these cases.

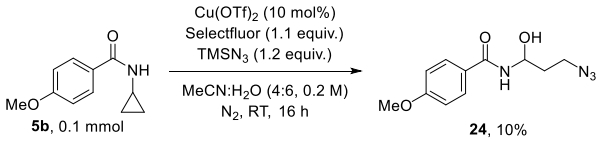


Entry	Catalyst	yield[a]
1	$Cu(OTf)_2$	74%
2	CuOAc	74%
3	$Cu(OTf)_2$ Benzene complex (5 mol%)	32%
4	$Cu(OAc)_2$	87%
5	$Cu(OAc)_2$ (2 mol%)	93%

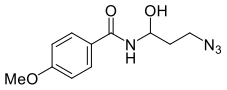
[a] ^{1}H NMR yield using CH_2Br_2 as internal standard.

Scheme S3 (Water as nucleophile)

For substrates **5b**, water was initially used as nucleophile. However, low conversion was observed.



***N*-(3-Azido-1-hydroxypropyl)-4-methoxybenzamide** (**24**).



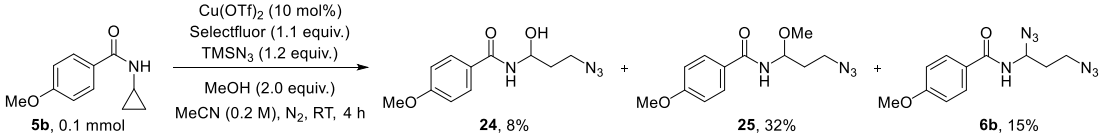
In a 12*75 mm Borosilicate glass tube, *N*-cyclopropyl-4-methoxybenzamide **5b** (38.2 mg, 0.200 mmol), Selectfluor (78.0 mg, 0.220 mmol, 1.1 equiv.) and CuTc (0.8 mg, 0.004 mmol, 0.02 equiv.) were measured on analytical balance. The tube was then closed with a rubber septum and sealed off with parafilm. Acetonitrile-water (v:v=1:1, 1.0 mL, 0.2 M) was added and freeze-pump-nitrogen thaw three times were performed to remove O_2, followed by the addition of $TMSN_3$ (94% purity purchased from TCI, 34.0 µL, 0.240 mmol, 1.2 equiv.). The reaction mixture was stirred at room temperature for 3 hours. Upon completion, the mixture was quenched by the addition of water (10 mL). The aqueous layer was then extracted with dichloromethane (10 mL x 3). The organic extract was dried over Na_2SO_4, filtered and concentrated in vacuo. *N*-(3-Azido-1-hydroxypropyl)-4-methoxybenzamide **24** (4.9 mg, 0.020

mmol, 10%) was obtained as a white solid after purification by column chromatography (SiO_2, pentanes/EtOAc 1:1).

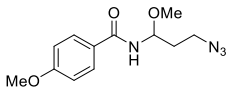
R_f: 0.25 (silica, pentanes:ethyl acetate 1:1);
^{1}H NMR (800 MHz, $CDCl_3$): δ = 7.79 – 7.70 (m, 2H, Ar*H*), 7.07 (d, *J* = 6.6 Hz, 1H, N*H*), 7.00 – 6.90 (m, 2H, Ar*H*), 5.63 (dtd, *J* = 8.7, 5.6, 3.2 Hz, 1H, C*H*), 3.95 (d, *J* = 3.3 Hz, 1H, O*H*), 3.86 (s, 3H, OCH_3), 3.73 (ddd, *J* = 12.4, 7.2, 5.2 Hz, 1H, CH_2N_3), 3.57 (ddd, *J* = 12.4, 7.1, 5.2 Hz, 1H, CH_2N_3), 2.06 – 1.94 (m, 2H, C$H_2CH_2N_3$);
^{13}C NMR (201 MHz, $CDCl_3$): δ = 168.1, 162.7, 128.9, 125.5, 113.9, 73.4, 55.5, 47.2, 33.6;
IR (film): $\tilde{\nu}$ = 3316 (w), 2958 (m), 2105 (m), 1654 (s), 1612 (s), 1257 (s), 1037 (m);
HRMS (ESI) calcd. for $C_{11}H_{14}N_4NaO_3^+$ $[M+Na]^+$ 273.0958; Found 273.0954.

Scheme S4 (Methanol as nucleophile)

Good conversion of **5b** was observed when methanol was used as nucleophile but three different products were isolated by prep TLC. The yield of diazidation product **6b** can be increased by performing the reaction in the absence of MeOH, and with excess of $TMSN_3$.



***N*-(3-Azido-1-methoxypropyl)-4-methoxybenzamide** (**25**).

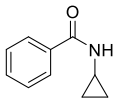


In a 12*75 mm Borosilicate glass tube, *N*-cyclopropyl-4-methoxybenzamide **5b** (38.2 mg, 0.200 mmol), Selectfluor (78.0 mg, 0.220 mmol, 1.1 equiv.) and CuTc (0.8 mg, 0.004 mmol, 0.02 equiv.) were measured on analytical balance. The tube was then closed with a rubber septum and sealed off with parafilm. Evacuate-refill cycle three times with nitrogen were performed to remove O_2 and extra dry acetonitrile (1.0 mL, 0.2 M) was added under nitrogen atmosphere, followed by the addition of MeOH (16.0 µL, 0.240 mmol, 2.0 equiv.) and $TMSN_3$ (94% purity purchased from TCI, 34.0 µL, 0.240 mmol, 1.2 equiv.). The reaction mixture was stirred at room temperature for 4 hours. Upon completion, the mixture was quenched by the addition of water (10 mL). The aqueous layer was then extracted with dichloromethane (10 mL x 3). The organic extract was dried over Na_2SO_4, filtered and concentrated in vacuo. *N*-(3-Azido-1-methoxypropyl)-4-methoxybenzamide **25** (16.8 mg, 64.0 µmol, 32%) was obtained as a white solid after purification by column chromatography (SiO_2, pentanes/EtOAc 2:1).

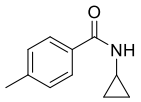
R_f: 0.39 (silica, pentanes:ethyl acetate 2:1);
Mp: 72-75 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 – 7.74 (m, 2H, Ar*H*), 6.97 – 6.91 (m, 2H, Ar*H*), 6.52 (d, *J* = 9.6 Hz, 1H, N*H*), 5.48 (dt, *J* = 9.5, 5.7 Hz, 1H, C*H*), 3.86 (s, 3H, ArOCH_3), 3.61 – 3.43 (m, 2H, CH_2N_3), 3.41 (s, 3H, OCH_3), 2.02 – 1.92 (m, 2H, C$H_2CH_2N_3$);
^{13}C NMR (101 MHz, Acetone-d_6): δ = 167.2, 163.3, 130.1, 127.4, 114.3, 79.8, 55.8, 55.7, 48.5, 35.2;
IR (film): $\tilde{\nu}$ = 3311 (w), 2939 (w), 2098 (s), 1641 (s), 1497 (s), 1257 (s), 1077 (s), 848 (m);
HRMS (ESI) calcd. for $C_{12}H_{16}N_4NaO_3^+$ $[M+Na]^+$ 287.1115; Found 287.1118.

2.2 Optimization

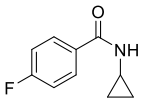
With $Cu(OAc)_2$ as catalyst, other substrates were screened to check whether this reaction is general enough or not. However, poor conversion was encountered for the substrates shown below. Therefore, a second round of optimization was conducted using **5a** as substrate.



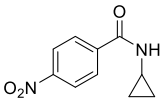
5a, 16% conv.



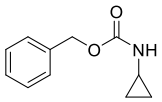
5c, 10% conv.



5d, 10% conv.

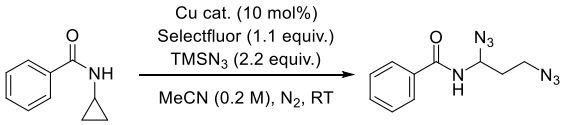


5h, 6% conv.



5q, 32% conv.

Table S2 (Catalyst screening)

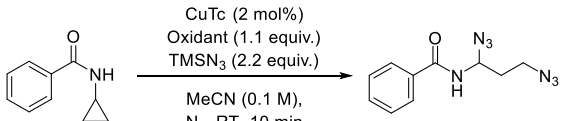


5a, 0.2 mmol — **6a**

Entry	Catalyst	NMR yield[a]
1	CuBr	26%
2	CuCl	16%
3	CuCN	20%
4	$Cu(MeCN)_4BF_4$	24%
5	$Cu(OTf)_2$ Benzene complex	32%
6	CuTc (20 mol%)	48%
7	CuTc (5 mol%)	74%
8	CuTc (2 mol%), MeCN (0.1 M)	78%

[a] ^1H NMR yield using CH_2Br_2 as internal standard.

Table S3 (Oxidant screening)

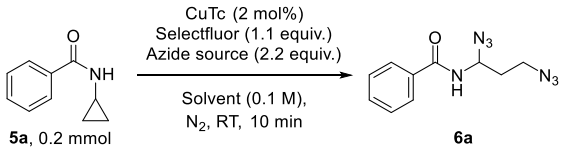


5a, 0.2 mmol — **6a**

Entry	Oxidant	NMR yield[a]
1	Selectfluor	78%
2	NFSI	13%
3	PIDA	0
4	NCS	0
5	*m*CPBA	0
6	$K_2S_2O_8$	0
7	TBHP	0
8	CuF_2	0
9	O_2 from air	<5%

[a] ^1H NMR yield using CH_2Br_2 as internal standard.

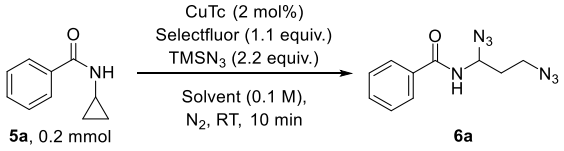
Table S4 (Azide screening)



Entry	Azide source	NMR yield[a]
1	$TMSN_3$	78%
2	NaN_3	18%
3	$TBAN_3$	0

[a] ^1H NMR yield using CH_2Br_2 as internal standard.

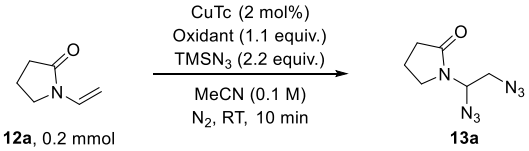
Table S5 (Solvent screening)



Entry	Solvent	NMR yield[a]
1	MeCN	78%
2	DCM	0
3	Acetone	0
4	CH_3NO_2	0
5	DMF	0

[a] ^1H NMR yield using CH_2Br_2 as internal standard.

Table S6 (Optimization for enamide)



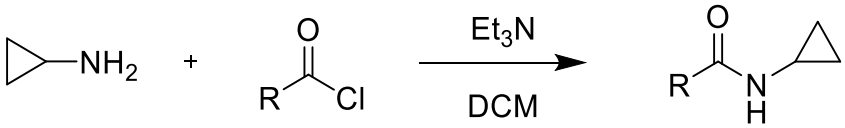
Entry	Oxidant	NMR yield[a]
1	Selectfluor	degradation
2	NFSI	messy
3	TBHP	No reaction
4	$K_2S_2O_8$	No reaction
5	NCS	50%
6	*m*CPBA	30%
7	PIDA	70%
8	PIDA (1.3 equiv.)	88% (95%[b])

[a] ^1H NMR yield using CH_2Br_2 as internal standard. [b] Isolated yield.

3. Preparation of starting materials

3.1 Synthesis of the aminocyclopropanes

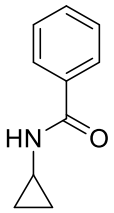
General Procedure A (GP A):



Following a modified version of a reported procedure,[1] to a solution of cyclopropylamine (0.70 mL, 10 mmol, 1.1 equiv.) and triethylamine (1.40 mL, 10.0 mmol, 1.1 equiv.) in dichloromethane (10 mL) was slowly added a solution of acyl chloride (9.09 mmol, 1.0 equiv.) in dichloromethane (10 mL) at 0 °C. The reaction mixture was stirred at room temperature usually for 16 hours. Upon completion, the mixture was quenched by the addition of 1 N HCl (10 mL). The aqueous layer was then extracted with dichloromethane. The organic extract was washed with 1 M NaOH (10 mL) and brine (10 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. In most cases, the crude product was pure enough to be used as such, without further purification.

The synthesis of the substrates (except compound **5f**, **5j**, **5l**, **5n**, **5w** and **5u**) has already been described by our group[2][3][4]. The procedures are taken from our previous publications to facilitate reproduction of the results by having all data in the same file.

***N*-Cyclopropylbenzamide** (**5a**).



Following GP A, using benzoyl chloride (1.28 g, 9.09 mmol), *N*-cyclopropylbenzamide (**5a**) was obtained as a white solid (1.38 g, 8.57 mmol, 94%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 – 7.67 (m, 2H, Ar*H*), 7.49 – 7.43 (m, 1H, Ar*H*), 7.41 – 7.34 (m, 2H, Ar*H*), 6.46 (s, 1H, N*H*), 2.88 (tq, *J* = 7.1, 3.7 Hz, 1H, C*H*), 0.87 – 0.78 (m, 2H, CH_2), 0.66 – 0.50 (m, 2H, CH_2).

^{1}H NMR data correspond to the reported values. [5]

***N*-Cyclopropyl-4-methoxybenzamide** (**5b**)

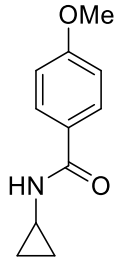
[1] Baburajan, P.; Elango, K. P. *Tetrahedron Lett.* **2014**, *55*, 1006-1010.

[2] Wang, M.-M.; Waser, J. *Angew. Chem. Int. Ed.* **2019**, *58*, 13880-13884.

[3] Wang, M.-M.; Waser, J. *Angew. Chem. Int. Ed.* **2020**, *59*, 16420-16424.

[4] Wang, M.-M.; Jeon, S.; Waser, J. *Org. Lett.* **2020**, *22*, 9123-9127.

[5] Sureshbabu, P.; Sadaf, A.; Chaudhary, P.; Kandasamy, J. *Org. Biomol. Chem.* **2019**, *17*, 845-850.

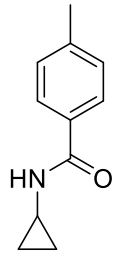


Following GP A, using 4-methoxybenzoyl chloride (1.55 g, 9.09 mmol), *N*-cyclopropyl-4-methoxybenzamide (**5b**) was obtained as a white solid (1.90 g, 8.99 mmol, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.66 (d, *J* = 8.8 Hz, 2H, Ar*H*), 6.94 – 6.85 (d, *J* = 8.8 Hz, 2H, Ar*H*), 6.21 (s, 1H, N*H*), 3.84 (s, 3H, OCH_3), 2.88 (tq, *J* = 7.1, 3.6 Hz, 1H, C*H*), 0.85 (td, *J* = 7.0, 5.3 Hz, 2H, CH_2), 0.65 – 0.55 (m, 2H, CH_2).

^{1}H NMR data correspond to the reported values.[1]

***N*-cyclopropyl-4-methylbenzamide** (**5c**).

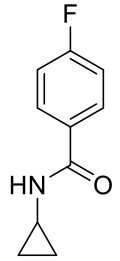


Following GP A, using 4-methylbenzoyl chloride (1.41 g, 9.09 mmol), *N*-cyclopropyl-4-methylbenzamide (**5c**) was obtained as a white solid (1.51 g, 8.62 mmol, 95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 – 7.55 (m, 2H, Ar*H*), 7.23 – 7.11 (m, 2H, Ar*H*), 6.33 (d, *J* = 39.2 Hz, 1H, N*H*), 2.88 (tt, *J* = 7.2, 3.5 Hz, 1H, C*H*), 2.37 (d, *J* = 3.1 Hz, 3H, CH_3), 0.92 – 0.75 (m, 2H, CH_2), 0.68 – 0.54 (m, 2H, CH_2).

^{1}H NMR data correspond to the reported values. [6]

***N*-Cyclopropyl-4-fluorobenzamide** (**5d**).



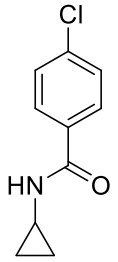
Following GP A, using 4-fluorobenzoyl chloride (1.44 g, 9.09 mmol), *N*-cyclopropyl-4-fluorobenzamide (**5d**) was obtained as a white solid (1.50 g, 8.36 mmol, 92%).

[6] Zhang, Y.; Liu, B.; Gou, Z.; Li, Y.; Zhang, X.; Wang, Y.; Yu, S.; Li, Y.; Sun, D. *Bioorg. Med. Chem. Lett.* **2015**, *25*, 791-794.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 – 7.70 (m, 2H, Ar*H*), 7.12 – 7.01 (m, 2H, Ar*H*), 6.37 (s, 1H, N*H*), 2.87 (tq, *J* = 7.1, 3.6 Hz, 1H, C*H*), 0.84 (td, *J* = 7.0, 5.3 Hz, 2H, CH_2), 0.65 – 0.56 (m, 2H, CH_2).

^{1}H NMR data correspond to the reported values. [7]

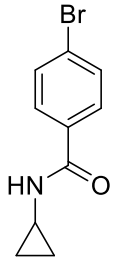
4-Chloro-*N*-cyclopropylbenzamide (**5e**).



Following GP A, using 4-chlorobenzoyl chloride (1.59 g, 9.09 mmol), 4-chloro-*N*-cyclopropylbenzamide (**5e**) was obtained as a white solid (1.65 g, 8.43 mmol, 93%).

R_f: 0.59 (silica, pentanes:ethyl acetate 2:3);
Mp: 133-135 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 – 7.64 (m, 2H, Ar*H*), 7.41 – 7.35 (m, 2H, Ar*H*), 6.27 (s, 1H, N*H*), 2.88 (tt, *J* = 7.1, 3.5 Hz, 1H, C*H*), 0.90 – 0.83 (m, 2H, CH_2), 0.66 – 0.55 (m, 2H, CH_2);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.8, 137.7, 132.7, 128.8, 128.3, 23.2, 6.8;
IR (film): $\tilde{\nu}$ = 3309 (m), 1639 (s), 1528 (m), 1484 (m), 1312 (m), 1093 (m), 847 (m);
HRMS (ESI) calcd. for $C_{10}H_{10}ClNNaO^+$ $[M+Na]^+$ 218.0343; Found 218.0344.

4-Bromo-*N*-cyclopropylbenzamide (**5f**).



Following GP A, using 4-bromobenzoyl chloride (1.59 g, 9.09 mmol), 4-bromo-*N*-cyclopropylbenzamide (**5f**) was obtained as a white solid (2.14 g, 8.92 mmol, 98%).

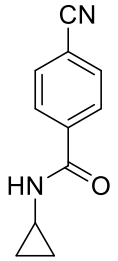
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 – 7.57 (m, 2H, Ar*H*), 7.57 – 7.48 (m, 2H, Ar*H*), 6.34 (s, 1H, N*H*), 2.88 (tq, *J* = 7.1, 3.7 Hz, 1H, C*H*), 0.94 – 0.76 (m, 2H, CH_2), 0.70 – 0.51 (m, 2H, CH_2);

^{1}H NMR data correspond to the reported values. [8]

4-Cyano-*N*-cyclopropylbenzamide (**5g**).

[7] Kondo, H.; Itami, K.; Yamaguchi, J. *Chem. Sci.* **2017**, *8*, 3799-3803.

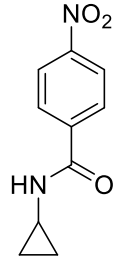
[8] Muth, F.; Gunther, M.; Bauer, S. M.; Doring, E.; Fischer, S.; Maier, J.; Druckes, P.; Koppler, J.; Trappe, J.; Rothbauer, U.; Koch, P.; Laufer, S. A. *J. Med. Chem.* **2015**, *58*, 443-456.



Following GP A, using 4-cyanobenzoyl chloride (1.51 g, 9.09 mmol), 4-cyano-*N*-cyclopropylbenzamide (**5g**) was obtained as a white solid (1.60 g, 8.59 mmol, 95%).

R_f: 0.33 (silica, pentanes:ethyl acetate 1:1);
Mp: 159-161 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.77 – 7.64 (m, 2H, Ar*H*), 6.34 (d, *J* = 38.4 Hz, 1H, N*H*), 2.91 (tq, *J* = 7.0, 3.6 Hz, 1H, C*H*), 1.09 – 0.73 (m, 2H, CH_2), 0.70 – 0.52 (m, 2H, CH_2); **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 167.0, 138.3, 132.4, 127.6, 118.0, 115.1, 23.3, 6.8;
IR (film): $\tilde{\nu}$ = 3275 (m), 3015 (w), 2230 (m), 1632 (s), 1532 (s), 1499 (m), 1313 (m), 1284 (m), 1018 (w), 858 (m);
HRMS (ESI) calcd. for $C_{11}H_{11}N_2O^+$ $[M+H]^+$ 187.0866; Found 187.0862.

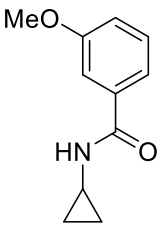
***N*-Cyclopropyl-4-nitrobenzamide** (**5h**).



Following GP A, using 4-nitrobenzoyl chloride (1.69 g, 9.09 mmol), *N*-cyclopropyl-4-nitrobenzamide (**5h**) was obtained as a pale yellow solid (1.71 g, 8.27 mmol, 91%).

R_f: 0.31 (silica, pentanes:ethyl acetate 1:1);
Mp: 176-177 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 – 8.22 (m, 2H, Ar*H*), 7.94 – 7.86 (m, 2H, Ar*H*), 6.41 (s, 1H, N*H*), 2.92 (tq, *J* = 7.2, 3.7 Hz, 1H, C*H*), 0.91 (td, *J* = 7.1, 5.4 Hz, 2H, CH_2), 0.70 – 0.59 (m, 2H, CH_2);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.8, 149.6, 139.9, 128.0, 123.8, 23.4, 6.8;
IR (film, cm^{-1}): $\tilde{\nu}$ = 3280 (m), 1639 (s), 1597 (w), 1533 (m), 1514 (s), 1350 (m), 1308 (m);
HRMS (APCI) m/z: $[M + H]^+$ Calcd for $C_{10}H_{11}N_2O_3^+$ 207.0764; Found 207.0761.

***N*-Cyclopropyl-3-methoxybenzamide** (**5i**).



Following GP A, using 3-methoxybenzoyl chloride (1.55 g, 9.09 mmol), *N*-cyclopropyl-3-methoxybenzamide (**5i**) was obtained as a pale yellow solid (1.88 g, 8.90 mmol, 98%).

R_f: 0.31 (silica, pentanes:ethyl acetate 1:1);

Mp: 74-76 °C;

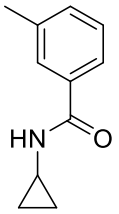
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (s, 1H, Ar*H*), 7.23 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.19 (d, *J* = 7.7 Hz, 1H, Ar*H*), 6.96 (ddd, *J* = 8.0, 2.7, 1.2 Hz, 1H, Ar*H*), 6.39 (s, 1H, N*H*), 3.78 (s, 1H, OCH_3), 2.84 (tt, *J* = 7.2, 3.5 Hz, 1H, C*H*), 0.92 – 0.69 (m, 2H, CH_2), 0.65 – 0.43 (m, 2H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.8, 159.7, 135.8, 129.4, 118.6, 117.6, 112.2, 55.4, 23.1, 6.7;

IR (film): $\tilde{\nu}$ = 3295 (w), 1638 (m), 1582 (m), 1527 (m), 1485 (m), 1286 (m), 1247 (m), 1040 (m), 732 (s);

HRMS (ESI) calcd. for $C_{11}H_{13}NNaO_2^+$ $[M+Na]^+$ 214.0838; Found 214.0842.

***N*-Cyclopropyl-3-methylbenzamide** (**5j**).



Following GP A, using 3-methylbenzoyl chloride (1.41 g, 9.09 mmol), *N*-cyclopropyl-3-methoxybenzamide (**5j**) was obtained as a white solid (1.52 g, 8.69 mmol, 96%).

R_f: 0.35 (silica, pentanes:ethyl acetate 1:1);

Mp: 95-97 °C;

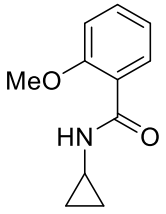
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 – 7.54 (m, 1H, Ar*H*), 7.49 (qd, *J* = 4.6, 3.9, 1.8 Hz, 1H, Ar*H*), 7.30 – 7.25 (m, 2H, Ar*H*), 6.34 (d, *J* = 28.2 Hz, 1H, N*H*), 2.93 – 2.83 (m, 1H, C*H*), 2.45 – 2.27 (m, 3H, CH_3), 0.92 – 0.75 (m, 2H, CH_2), 0.69 – 0.53 (m, 2H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.1, 138.3, 134.4, 132.2, 128.4, 127.6, 123.8, 23.1, 21.3, 6.8;

IR (film): $\tilde{\nu}$ = 3293 (m), 3016 (w), 1635 (s), 1535 (s), 1303 (m), 744 (m);

HRMS (ESI) calcd. for $C_{11}H_{13}NNaO^+$ $[M+Na]^+$ 198.0889; Found 198.0889.

***N*-Cyclopropyl-2-methoxybenzamide** (**5k**).



Following GP A, using 2-methoxybenzoyl chloride (0.853 g, 5.00 mmol), *N*-cyclopropyl-3-methoxybenzamide (**5k**) was obtained as a colorless solid (0.586 g, 3.06 mmol, 61%) after purification by column chromatography on silica using 1:1 pentanes:ethyl acetate as eluent.

R_f: 0.36 (silica, pentanes:ethyl acetate 1:1);

Mp: 56-58 °C;

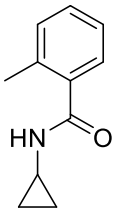
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (dq, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.89 (s, 1H, N*H*), 7.40 (ddq, *J* = 8.7, 7.3, 1.6 Hz, 1H, Ar*H*), 7.04 (ddt, *J* = 8.9, 7.6, 1.5 Hz, 1H, Ar*H*), 6.92 (dq, *J* = 8.3, 1.2 Hz, 1H, Ar*H*), 3.91 (s, 3H, OCH_3), 2.91 (tq, *J* = 7.4, 3.8 Hz, 1H, C*H*), 0.86 – 0.78 (m, 2H, CH_2), 0.61 – 0.52 (m, 2H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.5, 157.3, 132.6, 132.1, 121.3, 121.2, 111.2, 55.8, 22.7, 6.7;

IR (film): $\tilde{\nu}$ = 3393 (w), 3002 (w), 1651 (s), 1600 (m), 1525 (s), 1484 (s), 1295 (m), 1240 (s), 1020 (m), 756 (m);

HRMS (ESI) calcd. for $C_{11}H_{13}NNaO_2^+$ $[M+Na]^+$ 214.0838; Found 214.0843.

***N*-Cyclopropyl-2-methylbenzamide** (**5l**).

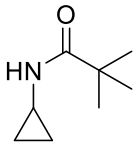


Following GP A, using 2-methylbenzoyl chloride (1.41 g, 9.09 mmol), *N*-cyclopropyl-3-methoxybenzamide (**5l**) was obtained as a white solid (1.56 g, 8.91 mmol, 98%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 – 7.27 (m, 2H, Ar*H*), 7.22 – 7.12 (m, 2H, Ar*H*), 5.90 (s, 1H, N*H*), 2.88 (tq, *J* = 7.2, 3.7 Hz, 1H, C*H*), 2.42 (s, 3H, CH_3), 0.93 – 0.78 (m, 2H, CH_2), 0.65 – 0.47 (m, 2H, CH_2).

^{1}H NMR data correspond to the reported values.[9]

***N*-Cyclopropylpivalamide** (**5m**).

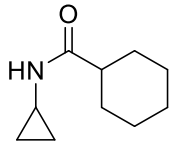


Following GP A, using pivaloyl chloride (1.32 g, 11.0 mmol), *N*-cyclopropylpivalamide (**5m**) was obtained as a white solid (0.90 g, 6.37 mmol, 64%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.71 (s, 1H, N*H*), 2.76 – 2.60 (m, 1H, C*H*), 1.16 (s, 9H, CH_3), 0.86 – 0.71 (m, 2H, CH_2), 0.57 – 0.36 (m, 2H, CH_2).

^{1}H NMR data correspond to the reported values.[10]

***N*-Cyclopropylcyclohexanecarboxamide** (**5n**).



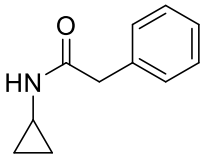
Following GP A, using cyclohexanecarbonyl chloride (1.33 g, 9.09 mmol), *N*-cyclopropylcyclohexanecarboxamide (**5n**) was obtained as a white solid (1.43 g, 8.54 mmol, 94%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.60 (brs, 1H, N*H*), 2.69 (tq, *J* = 7.2, 3.6 Hz, 1H, C*H*), 2.00 (tt, *J* = 11.8, 3.4 Hz, 1H, C*H*), 1.87 – 1.58 (m, 5H, CH_2), 1.40 (qd, *J* = 11.9, 2.8 Hz, 2H, CH_2), 1.30 – 1.11 (m, 3H, CH_2), 0.75 (dd, *J* = 6.8, 1.9 Hz, 2H, CH_2), 0.56 – 0.35 (m, 2H, CH_2).

^{1}H NMR data correspond to the reported values.[10]

***N*-Cyclopropyl-2-phenylacetamide** (**5o**).

[9] Jeffery, J. L.; Bartlett, E. S.; Sarpong, R. *Angew. Chem. Int. Ed.* **2013**, *52*, 2194-2197.
[10] Miyamura, S.; Araki, M.; Suzuki, T.; Yamaguchi, J.; Itami. K. *Angew. Chem. Int. Ed.* **2015**, *54*, 846-851.

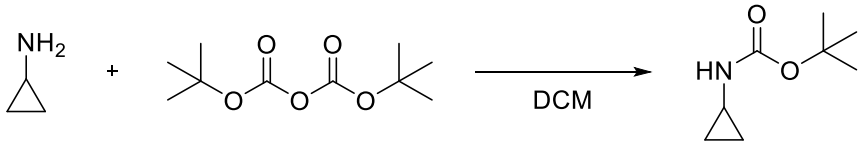


Following GP A, using 2-phenylacetyl chloride (1.41 g, 9.09 mmol), *N*-cyclopropyl-2-phenylacetamide (**5o**) was obtained as a white solid (1.52 g, 8.67mmol, 95%).

R_f: 0.36 (silica, dichloromethane:ethyl acetate 4:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 – 7.27 (m, 3H, Ar*H*), 7.23 (dd, *J* = 6.8, 1.8 Hz, 2H, Ar*H*), 5.44 (s, 1H, N*H*), 3.54 (s, 2H, CH_2), 2.66 (tq, *J* = 7.1, 3.6 Hz, 1H, C*H*), 0.75 – 0.67 (m, 2H, CH_2), 0.44 – 0.33 (m, 2H, CH_2).

^{1}H NMR data correspond to the reported values.[11]

***tert*-Butyl cyclopropylcarbamate** (**5p**).

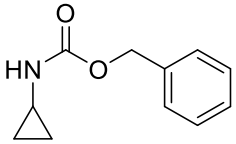


Following a modified version of a reported procedure,[12] to a solution of cyclopropylamine (1.40 mL, 20.0 mmol, 1.0 equiv.) in dichloromethane (20 mL) was slowly added a solution of di-*tert*-butyl dicarbonate (4.85 g, 22.0 mmol, 1.1 equiv.) in dichloromethane (20 mL) at 0 °C. The reaction mixture was stirred at for 16 hours room temperature. Upon completion, the mixture was quenched by addition of 1 N HCl (10 mL). The aqueous layer was then extracted with dichloromethane. The organic layer was washed with 1 M NaOH (10 mL) and brine (10 mL), and dried over Na_2SO_4, filtered and concentrated *in vacuo*. *tert*-Butyl cyclopropylcarbamate **5p** was obtained as a white solid (3.11 g, 19.8 mmol, 99%), which was pure enough to be used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.70 (brs, 1H, N*H*), 2.57 – 2.47 (m, 1H, C*H*), 1.44 (s, 9H, CH_3), 0.72 – 0.63 (m, 2H, CH_2), 0.53 – 0.39 (m, 2H, CH_2).

^{1}H NMR data correspond to the reported values. [12]

Benzyl cyclopropylcarbamate (5q).



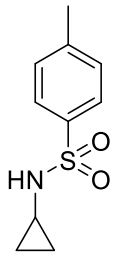
Following GP A, using benzyl chloroformate (1.55 g, 9.09 mmol), benzyl cyclopropylcarbamate (**5q**) was obtained as a colorless solid (1.72 g, 9.00 mmol, 99%).

^{1}H NMR (400 MHz, CDCl3): δ = 7.41 – 7.29 (m, 5H, Ar*H*), 5.10 (s, 2H, CH_2), 5.01 – 4.80 (m, 1H, N*H*), 2.60 (ttd, *J* = 7.0, 3.6, 2.0 Hz, 1H, C*H*), 0.76 – 0.69 (m, 2H, CH_2), 0.55 – 0.49 (m, 2H, CH_2).

[11] Tam, E.; Rita.; Liu, Y.; Chen, A. *Eur. J. Org. Chem.* **2015**, 1100-1107.
[12] Tars, K.; Leitan, J.; Kazaks, A.; Zelencova, D.; Liepinsh, E.; Kuka, J.; Makrecka, M.; Lola, D.; Andrianovs, V.; Gustina, D.; Grinberga, S.; Liepinsh, E.; Kalvinsh, I.; Dambrova, M.; Loza, E.; Pugovics, O. *J. Med. Chem.* **2014**, *57*, 2213-2236.

^{1}H NMR data correspond to the reported values.[13]

***N*-cyclopropyl-4-methylbenzenesulfonamide** (**5r**).



Following GP A, using tosyl chloride (1.73 g, 9.09 mmol), *N*-cyclopropyl-4-methylbenzenesulfonamide (**5r**) was obtained as a colorless solid (1.90 g, 9.00 mmol, 99%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.32 (d, *J* = 8.0 Hz, 2H, Ar*H*), 4.94 (s, 1H, N*H*), 2.43 (s, 3H, CH_3), 2.23 (tt, *J* = 6.6, 3.7 Hz, 1H, C*H*), 0.65 – 0.52 (m, 4H, CH_2).

^{1}H NMR data correspond to the reported values.[14]

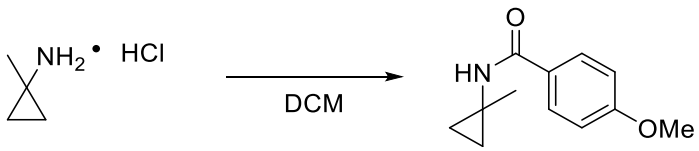
***N*-Cyclopropyl-4-methoxy-*N*-methylbenzamide** (**5s**).

Following a modified version of a reported procedure,[1] to a solution of *N*-cyclopropyl-methylamine hydrochloride (323 mg, 3.00 mmol, 1.1 equiv.) and triethylamine (0.84 mL, 6.0 mmol, 2.1 equiv.) in dichloromethane (10 mL) was slowly added a solution of 4-methoxybenzoyl chloride (478 mg, 2.80 mmol, 1.0 equiv.) in dichloromethane (10 mL) at 0 °C. The reaction mixture was stirred at room temperature for 16 hours. Upon completion, the mixture was quenched by the addition of 1 N HCl (10 mL). The aqueous layer was then extracted with dichloromethane. The organic extract was washed with 1 M NaOH (10 mL) and brine (10 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. *N*-cyclopropyl-4-methoxy-*N*-methylbenzamide (**5s**) was obtained as a yellow oil (560 mg, 2.73 mmol, 97%) which solidified during storage.

R_f: 0.40 (silica, pentanes:ethyl acetate 2:3);
Mp: 59-61 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 – 7.43 (m, 2H, Ar*H*), 6.94 – 6.82 (m, 2H, Ar*H*), 3.83 (s, 3H, OCH_3), 3.07 (s, 3H, NCH_3), 2.82 (tt, *J* = 7.0, 3.9 Hz, 1H, C*H*), 0.63 (d, *J* = 6.7 Hz, 2H, CH_2), 0.47 (p, *J* = 5.8, 5.0 Hz, 2H, CH_2);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.2, 160.6, 129.4, 129.4, 113.1, 55.2, 35.6, 33.1, 9.4;
IR (film): $\tilde{\nu}$ = 3010 (w), 2936(w), 1626 (s), 1607 (s), 1381 (s), 1250 (s), 1172 (m), 1027 (m), 842 (m);
HRMS (ESI) calcd. for $C_{12}H_{15}NNaO_2^+$ $[M + Na]^+$ 228.0995; Found 228.0999.

4-Methoxy-*N*-(1-methylcyclopropyl)benzamide (**5w**)

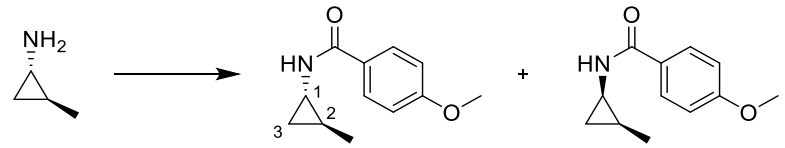
[13] Shaw, M. H.; McCreanor, N. G.; Whittingham, W. G.; Bower, J. F. J. Am. Chem. Soc. 2015, 137, 463-468.
[14] O'Sullivan, S.; Doni, E.; Tuttle, T.; Murphy. J. A. *Angew. Chem. Int. Ed.* **2014**, *53*, 474-478.



Following a modified version of a reported procedure,[1] to a solution of 1-methylcyclopropan-1-amine hydrochloride (396 mg, 3.68 mmol, 1.1 equiv.) and triethylamine (1.0 mL, 7.2 mmol, 2.1 equiv.) in dichloromethane (10 mL) was slowly added a solution of 4-methoxybenzoyl chloride (586 mg, 3.43 mmol, 1.0 equiv.) in dichloromethane (10 mL) at 0 °C. The reaction mixture was stirred at room temperature for 16 hours. Upon completion, the mixture was quenched by the addition of 1 N HCl (10 mL). The aqueous layer was then extracted with dichloromethane. The organic extract was washed with 1 M NaOH (10 mL) and brine (10 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. 4-Methoxy-*N*-(1-methylcyclopropyl)benzamide **5w** (689 mg, 3.36 mmol, 98%) was obtained as a white solid.

R_f: 0.44 (silica, pentanes:ethyl acetate 2:3);
Mp: 130-132 °C;
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 – 7.63 (m, 2H, Ar*H*), 6.92 – 6.85 (m, 2H, Ar*H*), 6.53 – 6.35 (m, 1H, N*H*), 3.83 (d, *J* = 1.5 Hz, 3H, OCH_3, due to rotamers), 1.46 (s, 3H, CH_3), 0.86 – 0.80 (m, 2H, CH_2), 0.74 – 0.68 (m, 2H, CH_2);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.1, 162.0, 128.6, 127.1, 113.6, 55.4, 29.5, 22.9, 14.6;
IR (film): $\tilde{\nu}$ = 3286 (m), 2962 (w), 1634 (s), 1605 (s), 1499 (s), 1252 (s), 1029 (m), 841 (m);
HRMS (ESI) calcd. for $C_{12}H_{15}NNaO_2^+$ $[M+Na]^+$ 228.0995; Found 228.0996.

4-Methoxy-*N*-2-methylcyclopropyl)benzamide (**5xa**).



Following a modified version of a reported procedure,[1] to a solution of 2-methylcyclopropan-1-amine (250 mg, 3.52 mmol, 4:1 d.r., ordered from Fluorochem) and Et_3N (0.54 mL, 3.9 mmol, 1.1 equiv.) in dichloromethane (10 mL) was slowly added a solution of 4-methoxybenzoyl chloride (658 mg, 3.87 mmol, 1.1 equiv.) in dichloromethane (5 mL) at 0 °C. The reaction mixture was stirred at room temperature usually for 16 hours. Upon completion, the mixture was quenched by the addition of 1 N HCl (10 mL). The aqueous layer was then extracted with dichloromethane. The organic extract was washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. 4-Methoxy-*N*-2-methylcyclopropyl)benzamide **5xa** was obtained as a white solid (655 mg, 3.20 mmol, 4:1 d.r., 91%) after first purification by column chromatography on silica using 3:2 pentanes:ethyl acetate as eluent. Second purification was performed by column chromatography on silica using 3:2 pentanes:ethyl acetate as eluent, ***trans*-5xa** (272 mg) and ***cis*-5xa** (79 mg) were obtained separately, together with the rest of product **5xa** recovered as a mixture of diastereomers.

4-Methoxy-*N*-*trans*-2-methylcyclopropyl)benzamide (***trans*-5xa**)
R_f: 0.37 (silica, pentanes:ethyl acetate 1:1);
Mp: 94-96 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 – 7.62 (m, 2H, Ar*H*), 6.94 – 6.83 (m, 2H, Ar*H*), 6.20 (s, 1H, N*H*), 3.83 (s, 3H, OCH_3), 2.56 (dq, *J* = 6.9, 3.4 Hz, 1H, NC*H*), 1.13 (d, *J* = 6.1 Hz, 3H, CH_3), 0.95 (ddt, *J* = 12.2, 6.2, 3.2 Hz, 1H, C*H*CH_3), 0.73 (ddd, *J* = 9.2, 5.4, 3.8 Hz, 1H, CH_2), 0.61 (dt, *J* = 7.2, 5.7 Hz, 1H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.1, 162.1, 128.6, 126.7, 113.6, 55.4, 30.4, 17.2, 14.9 (signals of C2 and C3 are overlapped).
IR (film): $\tilde{\nu}$ = 3274 (m), 3003 (w), 2952 (w), 1624 (s), 1606 (s), 1574 (m), 1541 (s), 1254 (s), 1031 (m), 843 (m);
HRMS (APCI) calcd. for $C_{12}H_{15}NNaO_2^+$ $[M+Na]^+$ 228.0995; Found 228.0993.

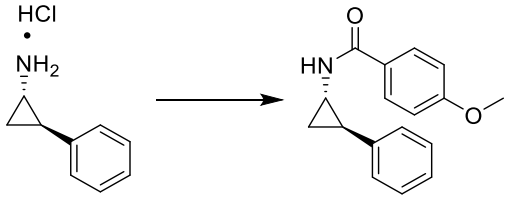
4-Methoxy-*N*-*cis*-2-methylcyclopropyl)benzamide (***cis*-5xa**)

R_f: 0.26 (silica, pentanes:ethyl acetate 1:1);

Mp: 89-91 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 – 7.69 (m, 2H, Ar*H*), 6.92 – 6.87 (m, 2H, Ar*H*), 6.07 (s, 1H, N*H*), 3.84 (s, 3H, OCH_3), 2.90 (dddd, *J* = 9.9, 7.0, 4.0, 3.0 Hz, 1H, NC*H*), 1.15 – 1.07 (m, 4H, CH_3 + CH_2), 1.03 (dddd, *J* = 8.8, 5.4, 3.2, 1.2 Hz, 1H, CH_2), 0.26 – 0.15 (m, 1H, C*H*CH_3).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.7, 162.1, 128.6, 126.9, 113.7, 55.4, 27.5, 13.2, 12.5, 11.7.
IR (film): $\tilde{\nu}$ = 3292 (m), 2958 (w), 1631 (s), 1606 (s), 1499 (s), 1252 (s), 1178 (m), 1028 (m), 844 (m);
HRMS (APCI) calcd. for $C_{12}H_{15}NNaO_2^+$ $[M+Na]^+$ 228.0995; Found 228.0993.

4-Methoxy-*N*-(*trans*-2-phenylcyclopropyl)benzamide (**5xb**).



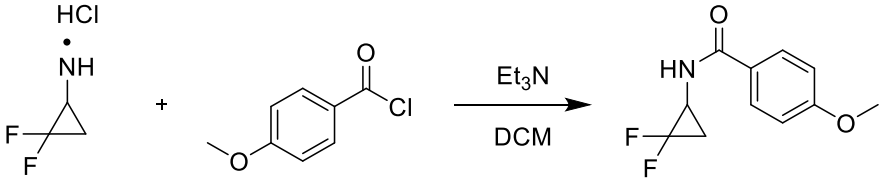
Following a modified version of a reported procedure,[1] to a solution of *trans*-2-phenylcyclopropylamine hydrochloride (635 mg, 3.74 mmol, 1.1 equiv., ordered from Acros) and triethylamine (1.0 mL, 7.2 mmol, 2.0 equiv.) in dichloromethane (10 mL) was slowly added a solution of 4-methoxybenzoyl chloride (607 mg, 3.56 mmol, 1.0 equiv.) in dichloromethane (10 mL) at 0 °C. The reaction mixture was stirred at room temperature for 16 hours. Upon completion, the mixture was quenched by the addition of 1 N HCl (10 mL). The aqueous layer was then extracted with dichloromethane. The organic extract was washed with 1 M NaOH (10 mL) and brine (10 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. 4-Methoxy-*N*-(*trans*-2-phenylcyclopropyl)benzamide (**5xb**) was obtained as a white solid (0.92 g, 3.4 mmol, 97%).

R_f: 0.50 (silica, pentanes:ethyl acetate 1:1);

Mp: 153-155 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 – 7.65 (m, 2H, Ar*H*), 7.31 – 7.26 (m, 2H, Ar*H*), 7.24 – 7.15 (m, 3H, Ar*H*), 6.97 – 6.83 (m, 2H, Ar*H*), 6.39 (s, 1H, N*H*), 3.84 (s, 3H, OCH_3), 3.06 (tt, *J* = 7.4, 3.4 Hz, 1H, NC*H*), 2.16 (ddd, *J* = 9.8, 6.3, 3.4 Hz, 1H, PhC*H*), 1.38 – 1.20 (m, 2H, CH_2);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.1, 162.2, 140.4, 128.7, 128.4, 126.6, 126.5, 126.1, 113.7, 55.4, 32.5, 24.9, 16.3;
IR (film): $\tilde{\nu}$ = 3291 (w), 1632 (s), 1606 (s), 1500 (s), 1255 (s), 1029 (m), 845 (m);
HRMS (ESI) calcd. for $C_{17}H_{17}NNaO_2^+$ $[M+Na]^+$ 290.1151; Found 290.1151.

***N*-(2,2-Difluorocyclopropyl)-4-methoxybenzamide** (**5y**).

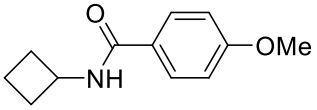


Following a modified version of a reported procedure,[1] to a solution of 2,2-difluorocyclopropylamine hydrochloride (250 mg, 1.93 mmol, 1.0 equiv., ordered from Fluorochem) and triethylamine (0.60 mL, 4.3 mmol, 2.2 equiv.) in dichloromethane (10 mL) was slowly added a solution of 4-methoxybenzoyl chloride (370 mg, 2.17 mmol, 1.1 equiv.) in dichloromethane (5 mL) at 0 °C. The reaction mixture was stirred at room temperature usually for 16 hours. Upon completion, the mixture was quenched by the addition of 1 N HCl (10 mL). The aqueous layer was then extracted with dichloromethane. The organic extract was washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. *N*-(2,2-difluorocyclopropyl)-4-methoxybenzamide (**5y**) was obtained as a white solid (320 mg, 1.41 mmol, 73%) after purification by column chromatography on silica using 2:1 pentanes:ethyl acetate as eluent.

R_f: 0.25 (silica, pentanes:ethyl acetate 2:1);
Mp: 128-129 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.7 Hz, 2H, Ar*H*), 6.91 (d, *J* = 8.7 Hz, 2H, Ar*H*), 6.39 (s, 1H, N*H*), 3.84 (s, 3H, OCH_3), 3.51 (dtq, *J* = 12.1, 5.9, 3.4, 3.0 Hz, 1H, C*H*), 1.87 (dtd, *J* = 13.5, 9.3, 6.4 Hz, 1H, CH_2), 1.50 – 1.35 (m, 1H, CH_2);
^{13}C NMR (101 MHz, $CDCl_3$): δ = ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.8, 162.6, 128.9, 125.5, 113.8, 111.1 (dd, *J* = 291.4, 284.3 Hz), 55.4, 30.8 (dd, *J* = 15.0, 9.4 Hz), 19.3 (t, *J* = 9.9 Hz);
^{19}F NMR (376 MHz, $CDCl_3$): δ = -131.2 (d, *J* = 162.2 Hz, 1F), -143.6 (d, *J* = 162.2 Hz, 1F);
IR (film): $\tilde{\nu}$ = 3307 (m), 1638 (s), 1608 (m), 1500 (s), 1471 (m), 1257 (s), 1222 (s), 1014 (m), 845 (m);
HRMS (ESI) calcd. for $C_{11}H_{12}F_2NO_2^+$ $[M+H]^+$ 228.0831; Found 228.0843.

3.2 Synthesis of the aminocyclobutanes

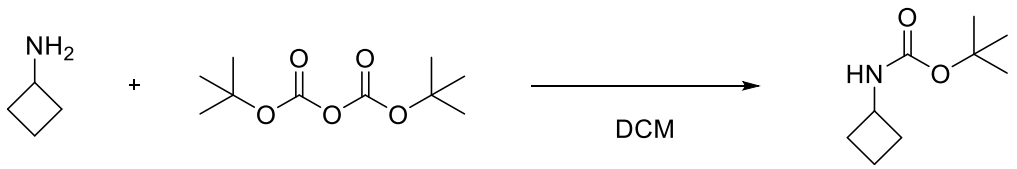
***N*-Cyclobutyl-4-methoxybenzamide** (**5t**)



Following GP A, using cyclobutylamine (523 mg, 7.40 mmol, 1.1 equiv.) and 4-methoxybenzoyl chloride (1.19 g, 7.00 mmol, 1.0 equiv.), *N*-cyclobutyl-4-methoxybenzamide **5t** was obtained as a white solid (1.08 g, 5.27 mmol, 75%).

R_f: 0.44 (silica, pentanes:ethyl acetate 1:1);
Mp: 126-128 °C;
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 – 7.61 (m, 2H, Ar*H*), 7.00 – 6.82 (m, 2H, Ar*H*), 6.16 (s, 1H, N*H*), 4.58 (h, *J* = 8.1 Hz, 1H, C*H*), 3.84 (s, 3H, OCH_3), 2.53 – 2.32 (m, 2H, $CH_2CH_2CH_2$), 2.02 – 1.86 (m, 2H, CH_2), 1.76 (tt, *J* = 11.4, 6.5 Hz, 2H, CH_2);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.0, 162.1, 128.6, 126.8, 113.7, 55.4, 45.1, 31.4, 15.2;
IR (film): $\tilde{\nu}$ = 3305 (w), 2941 (w), 1628 (s), 1607 (s), 1503 (s), 1253 (s), 1030 (m), 844 (m);
HRMS (ESI) calcd. for $C_{12}H_{16}NO_2^+$ $[M+H]^+$ 206.1176; Found 206.1175.

***tert*-Butyl cyclobutylcarbamate** (**5u**).

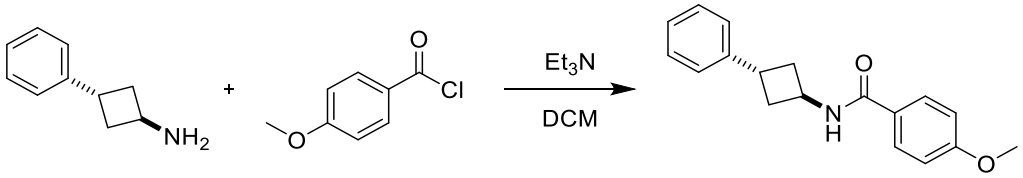


Following a modified version of a reported procedure,[12] to a solution of cyclobutylamine (1.70 mL, 20.0 mmol, 1.0 equiv.) in dichloromethane (20 mL) was slowly added a solution of di-*tert*-butyl dicarbonate (4.85 g, 22.0 mmol, 1.1 equiv.) in dichloromethane (20 mL) at 0 °C. The reaction mixture was stirred at for 16 hours room temperature. Upon completion, the mixture was quenched by addition of 1 N HCl (10 mL). The aqueous layer was then extracted with dichloromethane. The organic layer was washed with 1 M NaOH (10 mL) and brine (10 mL), and dried over Na_2SO_4, filtered and concentrated *in vacuo*. *tert*-Butyl cyclobutylcarbamate **5u** was obtained as a white solid (3.41 g, 19.9 mmol, 99%), which was pure enough to be used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.66 (s, 1H, N*H*), 4.29 – 3.91 (m, 1H, C*H*), 2.30 (q, *J* = 8.8 Hz, 2H, CH_2), 1.88 – 1.72 (m, 2H, CH_2), 1.72 – 1.53 (m, 2H, CH_2), 1.43 (s, 9H, CH_3).

^{1}H NMR data correspond to the reported values.[15]

4-Methoxy-*N*-(*trans*-3-phenylcyclobutyl)benzamide (**5z**).



Following a modified version of a reported procedure,[1] to a solution of trans-3-phenylcyclobutan-1-amine (250 mg, 1.70 mmol, 1.0 equiv., ordered from Fluorochem) and triethylamine (0.27 mL, 1.9 mmol, 1.1 equiv.) in dichloromethane (10 mL) was slowly added a solution of 4-methoxybenzoyl chloride (320 mg, 1.88 mmol, 1.1 equiv.) in dichloromethane (5 mL) at 0 °C. The reaction mixture was stirred at room temperature usually for 16 hours. Upon completion, the mixture was quenched by the addition of 1 N HCl (10 mL). The aqueous layer was then extracted with dichloromethane. The organic extract was washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. 4-Methoxy-*N*-(*trans*-3-phenylcyclobutyl)benzamide **5z** was obtained as a white solid (448 mg, 1.59 mmol, 94%) after purification by column chromatography on silica using 1:1 pentanes:ethyl acetate as eluent.

R_f: 0.50 (silica, pentanes:ethyl acetate 1:1);
Mp: 164-166 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 – 7.71 (m, 2H, Ar*H*), 7.39 – 7.26 (m, 4H, Ar*H*), 7.26 – 7.17 (m, 1H, Ar*H*), 6.98 – 6.87 (m, 2H, Ar*H*), 6.36 (d, *J* = 6.9 Hz, 1H, N*H*), 4.71 (ddtd, *J* = 14.2, 7.9, 6.3, 1.3 Hz, 1H, NC*H*), 3.86 (s, 3H, OCH_3), 3.71 – 3.57 (m, 1H, PhC*H*), 2.74 – 2.61 (m, 2H, CH_2), 2.55 – 2.43 (m, 2H, CH_2);
^{13}C NMR (101 MHz, $CDCl_3$): δ 166.5, 162.1, 144.8, 128.7, 128.5, 126.8, 126.5, 126.0, 113.7, 55.4, 43.7, 36.9, 34.6;
IR (film): $\tilde{\nu}$ = 3338 (m), 2938 (w), 1628 (s), 1605 (m), 1499 (s), 1251 (s), 1031 (m);
HRMS (ESI) calcd. for $C_{18}H_{20}NO_2^+$ $[M+H]^+$ 282.1489; Found 282.1480.

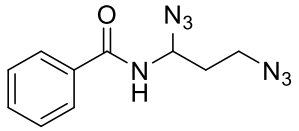
[15] Li, P.; Ma, N.; Wang, Z.; Dai, Q.; Hu, C. *J. Org. Chem.* **2018**, 83, 8233-8240.

4. Scope of the 1,3- and 1,4-difunctionalization reaction

General Procedure B (GP B):

In a 12*75 mm Borosilicate glass tube, the corresponding aminocyclopropane (0.200 mmol, 1.0 equiv.), Selectfluor (78.0 mg, 0.220 mmol, 1.1 equiv.) and CuTc (0.8 mg, 0.004 mmol, 0.02 equiv.) were measured on analytical balance. The tube was then closed with a rubber septum and sealed off with parafilm. Evacuate-refill cycle three times with nitrogen were performed to remove O_2 and extra-dry acetonitrile (2.0 mL, 0.1 M) was added under nitrogen atmosphere, followed by the addition of $TMSN_3$ (94% purity purchased from TCI, 62.0 µL, 0.440 mmol, 2.2 equiv.). The reaction mixture was stirred at room temperature for 10 minutes. Upon completion, the mixture was quenched by the addition of water (10 mL). The aqueous layer was then extracted with dichloromethane (10 mL x 3). The organic extract was dried over Na_2SO_4, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, pentanes/EtOAc).

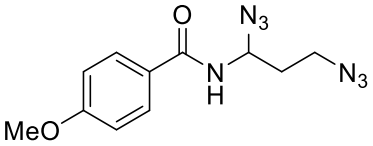
***N*-(1,3-Diazidopropyl)benzamide** (**6a**).



Following GP B, starting from *N*-cyclopropylbenzamide **5a** (32.2 mg, 0.200 mmol), *N*-(1,3-diazidopropyl)benzamide **6a** (39.3 mg, 0.160 mmol, 80%) was obtained as a yellow oil after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.41 (silica, pentanes:ethyl acetate 3:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 – 7.79 (m, 2H, Ar*H*), 7.58 – 7.52 (m, 1H, Ar*H*), 7.49 – 7.43 (m, 2H, Ar*H*), 7.19 (d, *J* = 9.0 Hz, 1H, N*H*), 5.92 (dt, *J* = 8.9, 5.8 Hz, 1H, C*H*), 3.66 (dt, *J* = 12.8, 6.5 Hz, 1H, CH_2N_3), 3.54 (dt, *J* = 12.6, 5.8 Hz, 1H, CH_2N_3), 1.95 (q, *J* = 5.9 Hz, 2H, C$H_2CH_2N_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.4, 132.9, 132.3, 128.8, 127.1, 65.1, 47.3, 33.2;
IR (film): $\tilde{\nu}$ = 3672 (w), 3311 (w), 2975 (m), 2903 (m), 2110 (s), 1653 (m), 1521 (m), 1065 (s);
HRMS (ESI) calcd. for $C_{10}H_{11}N_7NaO^+$ $[M+Na]^+$ 268.0917; Found 268.0920.

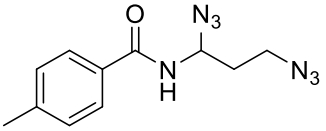
***N*-(1,3-Diazidopropyl)-4-methoxybenzamide** (**6b**).



Following GP B, starting from *N*-cyclopropyl-4-methoxybenzamide **5b** (38.2 mg, 0.200 mmol), *N*-(1,3-diazidopropyl)-4-methoxybenzamide **6b** (49.0 mg, 0.178 mmol, 89%) was obtained as a yellow oil after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.36 (silica, pentanes:ethyl acetate 3:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 – 7.75 (m, 2H, Ar*H*), 7.15 (d, *J* = 8.9 Hz, 1H, N*H*), 6.95 – 6.89 (m, 2H, Ar*H*), 5.89 (dt, *J* = 8.9, 5.9 Hz, 1H, C*H*), 3.85 (s, 3H, OCH_3), 3.64 (dt, *J* = 12.9, 6.4 Hz, 1H, CH_2N_3), 3.52 (dt, *J* = 12.6, 5.9 Hz, 1H, CH_2N_3), 1.94 (q, *J* = 6.1 Hz, 2H, C$H_2CH_2N_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.9, 162.8, 129.1, 125.0, 113.9, 65.1, 55.4, 47.4, 33.2;
IR (film): $\tilde{\nu}$ = 2975 (w), 2903 (w), 2110 (s), 1665 (s), 1497 (s), 1269 (s);
HRMS (ESI) calcd. for $C_{11}H_{13}N_7NaO_2^+$ $[M+Na]^+$ 298.1023; Found 298.1023.

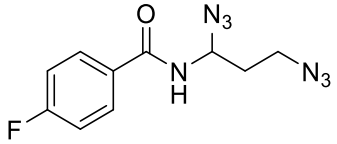
***N*-(1,3-Diazidopropyl)-4-methylbenzamide** (**6c**).



Following GP B, starting from *N*-cyclopropyl-4-methylbenzamide **5c** (35.0 mg, 0.200 mmol), *N*-(1,3-diazidopropyl)-4-methylbenzamide **6c** (40.7 mg, 0.157 mmol, 78%) was obtained as a colorless oil after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.41 (silica, pentanes:ethyl acetate 3:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 – 7.68 (m, 2H, Ar*H*), 7.27 – 7.24 (m, 2H, Ar*H*), 7.14 (d, *J* = 9.0 Hz, 1H, N*H*), 5.91 (dt, *J* = 8.9, 5.9 Hz, 1H, C*H*), 3.65 (dt, *J* = 12.8, 6.5 Hz, 1H, CH_2N$_3$), 3.53 (dt, *J* = 12.5, 5.9 Hz, 1H, CH_2N$_3$), 2.41 (s, 3H, CH_3), 1.95 (q, *J* = 6.1 Hz, 2H, CH_2CH$_2$N$_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.4, 142.9, 130.0, 129.4, 127.2, 65.0, 47.4, 33.2, 21.5;
IR (film): $\tilde{\nu}$ = 3303 (w), 2926 (w), 2092 (s), 1641 (s), 1526 (s), 1498 (m), 1239 (s), 835 (m);
HRMS (APCI) calcd. for $C_{11}H_{13}N_7NaO^+$ $[M+Na]^+$ 282.1074; Found 282.1071.

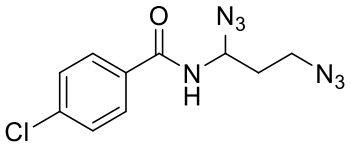
***N*-(1,3-Diazidopropyl)-4-fluorobenzamide** (**6d**).



Following GP B, starting from *N*-cyclopropyl-4-fluorobenzamide **5d** (41.4 mg, 0.200 mmol), *N*-(1,3-diazidopropyl)-4-fluorobenzamide **6d** (37.9 mg, 0.144 mmol, 72%) was obtained as a pale yellow solid after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.45 (silica, pentanes:ethyl acetate 3:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 – 7.77 (m, 2H, Ar*H*), 7.22 (d, *J* = 8.9 Hz, 1H, N*H*), 7.13 (t, *J* = 8.5 Hz, 2H, Ar*H*), 5.89 (dt, *J* = 8.9, 5.8 Hz, 1H, C*H*), 3.67 (dt, *J* = 12.8, 6.4 Hz, 1H, CH_2N$_3$), 3.54 (dt, *J* = 12.2, 5.7 Hz, 1H, CH_2N$_3$), 1.95 (q, *J* = 6.0 Hz, 2H, CH_2CH$_2$N$_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.4, 165.2 (d, *J* = 253.1 Hz), 129.6 (d, *J* = 9.0 Hz), 129.0 (d, *J* = 3.2 Hz), 115.9 (d, *J* = 22.0 Hz), 65.2, 47.3, 33.1;
^{19}F NMR (376 MHz, $CDCl_3$): δ = -106.5;
IR (film): $\tilde{\nu}$ = 3303 (w), 2925 (w), 2095 (s), 1645 (m), 1498 (m), 1234 (s), 882 (m);
HRMS (ESI) calcd. for $C_{10}H_{10}FN_4O^+$ $[M-N_3]^+$ 221.0833; Found 221.0835.

4-Chloro-*N*-(1,3-diazidopropyl)benzamide (**6e**).

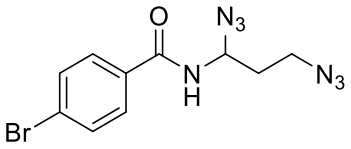


Following GP B, starting from 4-chloro-*N*-cyclopropylbenzamide **5e** (39.0 mg, 0.200 mmol), 4-chloro-*N*-(1,3-diazidopropyl)benzamide **6e** (39.2 mg, 0.141 mmol, 70%) was obtained as a beige solid after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.52 (silica, pentanes:ethyl acetate 3:1);

Mp: 81-83 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 – 7.75 (m, 2H, Ar*H*), 7.49 – 7.45 (m, 2H, Ar*H*), 7.21 (d, *J* = 9.0 Hz, 1H, N*H*), 5.92 (dt, *J* = 8.8, 5.7 Hz, 1H, C*H*), 3.71 (dt, *J* = 12.8, 6.5 Hz, 1H, CH_2N_3), 3.57 (dt, *J* = 12.6, 5.8 Hz, 1H, CH_2N_3), 1.98 (q, *J* = 5.9 Hz, 2H, C$H_2CH_2N_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.4, 138.7, 131.3, 129.1, 128.6, 65.2, 47.3, 33.1;
IR (film): $\tilde{\nu}$ = 3292 (w), 2104 (s), 1648 (m), 1527 (m), 1485 (m), 1244 (m), 1091 (m), 846 (m);
HRMS (ESI) calcd. for $C_{10}H_{10}ClN_7NaO^+$ $[M+Na]^+$ 302.0528; Found 302.0531.

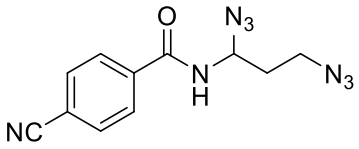
4-Bromo-*N*-(1,3-diazidopropyl)benzamide (**6f**).



Following GP B, starting from 4-bromo-*N*-cyclopropylbenzamide **5f** (47.8 mg, 0.200 mmol), 4-bromo-*N*-(1,3-diazidopropyl)benzamide **6f** (43.5 mg, 0.135 mmol, 67%) was obtained as a beige solid after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.48 (silica, pentanes:ethyl acetate 3:1);
Mp: 88-91 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 – 7.65 (m, 2H, Ar*H*), 7.63 – 7.58 (m, 2H, Ar*H*), 7.18 (d, *J* = 8.8 Hz, 1H, N*H*), 5.89 (dt, *J* = 8.8, 5.7 Hz, 1H, C*H*), 3.68 (dt, *J* = 12.8, 6.4 Hz, 1H, CH_2N_3), 3.55 (dt, *J* = 12.6, 5.7 Hz, 1H, CH_2N_3), 1.95 (q, *J* = 5.9 Hz, 2H, C$H_2CH_2N_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.5, 132.0, 131.7, 128.7, 127.2, 65.2, 47.3, 33.1;
IR (film): $\tilde{\nu}$ = 3293 (w), 2104 (s), 1648 (m), 1527 (m), 1482 (m), 1245 (m), 1070 (w), 844 (w);
HRMS (ESI) calcd. for $C_{10}H_{10}Br^{79}N_4O^+$ $[M-N_3]^+$ 281.0032; Found 281.0039.

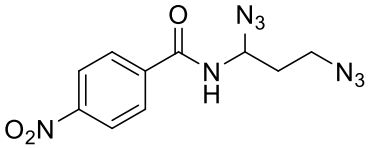
4-Cyano-*N*-(1,3-diazidopropyl)benzamide (**6g**).



Following GP B, starting from 4-cyano-*N*-cyclopropylbenzamide **5g** (37.2 mg, 0.200 mmol), 4-cyano-*N*-(1,3-diazidopropyl)benzamide **6g** (33.5 mg, 0.124 mmol, 62%) was obtained as a pale yellow oil after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.33 (silica, pentanes:ethyl acetate 3:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 – 7.89 (m, 2H, Ar*H*), 7.80 – 7.74 (m, 2H, Ar*H*), 7.34 (d, *J* = 8.7 Hz, 1H, N*H*), 5.90 (dt, *J* = 8.7, 5.6 Hz, 1H, C*H*), 3.76 – 3.64 (m, 1H, CH_2N_3), 3.57 (dt, *J* = 12.7, 5.6 Hz, 1H, CH_2N_3), 1.97 (dt, *J* = 6.3, 5.5 Hz, 2H, C$H_2CH_2N_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.7, 136.8, 132.6, 127.9, 117.8, 115.8, 65.3, 47.2, 32.9;
IR (film): $\tilde{\nu}$ = 3322 (w), 2232 (w), 2104 (s), 1653 (m), 1530 (m), 1496 (m), 1280 (m), 1244 (m), 857 (m);
HRMS (APCI) calcd. for $C_{11}H_{10}N_5O^+$ $[M-N_3]^+$ 228.0880; Found 228.0876.

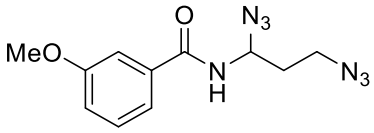
***N*-(1,3-Diazidopropyl)-4-nitrobenzamide** (**6h**).



Following GP B, starting from *N*-cyclopropyl-4-nitrobenzamide **5h** (41.2 mg, 0.200 mmol), *N*-(1,3-diazidopropyl)-4-nitrobenzamide **6h** (33.1 mg, 0.114 mmol, 57%) was obtained as a yellow solid after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.50 (silica, pentanes:ethyl acetate 3:1);
Mp: 88-91 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 – 8.28 (m, 2H, Ar*H*), 8.01 – 7.95 (m, 2H, Ar*H*), 7.38 (d, *J* = 8.7 Hz, 1H, N*H*), 5.92 (dt, *J* = 8.7, 5.6 Hz, 1H, C*H*), 3.73 (dt, *J* = 12.8, 6.2 Hz, 1H, CH_2N_3), 3.58 (dt, *J* = 12.6, 5.5 Hz, 1H, CH_2N_3), 1.98 (dt, *J* = 6.2, 5.4 Hz, 2H, C$H_2CH_2N_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.5, 150.0, 138.4, 128.4, 124.0, 65.4, 47.2, 32.9;
IR (film): $\tilde{\nu}$ = 3294 (w), 2095 (s), 1652 (m), 1522 (s), 1344 (m), 1240 (m), 867 (m);
HRMS (APCI) calcd. for $C_{10}H_{10}N_5O_3^+$ $[M\text{-}N_3]^+$ 248.0778; Found 248.0776.

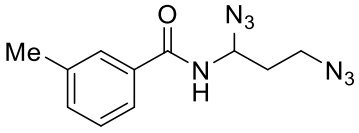
***N*-(1,3-Diazidopropyl)-3-methoxybenzamide** (**6i**).



Following GP B, starting from *N*-cyclopropyl-3-methoxybenzamide **5i** (38.2 mg, 0.200 mmol), *N*-(1,3-diazidopropyl)-3-methoxybenzamide **6i** (39.4 mg, 0.143 mmol, 72%) was obtained as a yellow oil after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.45 (silica, pentanes:ethyl acetate 3:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (dd, *J* = 2.7, 1.5 Hz, 1H, Ar*H*), 7.32 – 7.27 (m, 1H, Ar*H*), 7.26 – 7.23 (m, 1H, Ar*H*), 7.09 (d, *J* = 9.1 Hz, 1H, N*H*), 7.04 – 6.99 (m, 1H, Ar*H*), 5.84 (dt, *J* = 8.9, 5.8 Hz, 1H, C*H*), 3.78 (s, 3H, OCH_3), 3.59 (dt, *J* = 12.8, 6.5 Hz, 1H, CH_2N_3), 3.47 (dt, *J* = 12.7, 5.9 Hz, 1H, CH_2N_3), 1.88 (q, *J* = 6.0 Hz, 2H, C$H_2CH_2N_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.3, 159.9, 134.3, 129.7, 118.8, 118.6, 112.5, 65.1, 55.5, 47.3, 33.2;
IR (film): $\tilde{\nu}$ = 3305 (w), 2940 (w), 2099 (s), 1647 (m), 1583 (m), 1523 (m), 1289 (m), 1246 (m);
HRMS (ESI) calcd. for $C_{11}H_{13}N_7NaO_2^+$ $[M+Na]^+$ 298.1023; Found 298.1029.

***N*-(1,3-Diazidopropyl)-3-methylbenzamide** (**6j**).

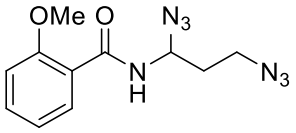


Following GP B, starting from *N*-cyclopropyl-3-methylbenzamide **5j** (35.0 mg, 0.200 mmol), *N*-(1,3-diazidopropyl)-3-methylbenzamide **6j** (37.2 mg, 0.144 mmol, 72%) was obtained as a pale yellow oil after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.48 (silica, pentanes:ethyl acetate 3:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 2.1 Hz, 1H, Ar*H*), 7.58 (dt, *J* = 6.8, 2.2 Hz, 1H, Ar*H*), 7.38 – 7.31 (m, 2H, Ar*H*), 7.18 – 7.04 (s, 1H, N*H*), 5.98 – 5.83 (m, 1H, C*H*), 3.71 – 3.60 (m, 1H, CH_2N_3), 3.60 – 3.48 (m, 1H, CH_2N_3), 2.40 (s, 3H, CH_3), 1.95 (q, *J* = 6.1 Hz, 2H, C$H_2CH_2N_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ 167.6, 138.7, 133.1, 132.9, 128.6, 128.0, 124.0, 65.0, 47.3, 33.2, 21.3;
IR (film): $\tilde{\nu}$ = 3291 (w), 2926 (w), 2094 (s), 1643 (m), 1519 (m), 1242 (m), 1096 (m);
HRMS (ESI) calcd. for $C_{11}H_{13}N_7NaO^+$ $[M+Na]^+$ 282.1074; Found 282.1073.

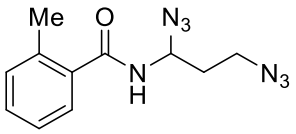
***N*-(1,3-Diazidopropyl)-2-methoxybenzamide** (**6k**).



Following GP B, starting from *N*-cyclopropyl-2-methoxybenzamide **5k** (38.2 mg, 0.200 mmol), *N*-(1,3-diazidopropyl)-2-methoxybenzamide **6k** (37.0 mg, 0.135 mmol, 67%) was obtained as a pale yellow oil after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.32 (silica, pentanes:ethyl acetate 3:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62 (d, *J* = 8.7 Hz, 1H, N*H*), 8.25 – 8.19 (m, 1H, Ar*H*), 7.54 – 7.46 (m, 1H, Ar*H*), 7.10 (ddd, *J* = 8.3, 7.3, 1.0 Hz, 1H, Ar*H*), 7.00 (dd, *J* = 8.4, 1.0 Hz, 1H, Ar*H*), 5.95 (dt, *J* = 8.7, 6.0 Hz, 1H, C*H*), 3.99 (s, 3H, OCH_3), 3.65 – 3.38 (m, 2H, CH_2N_3), 1.95 (q, *J* = 6.3 Hz, 2H, C$H_2CH_2N_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.5, 157.7, 133.7, 132.6, 121.5, 120.1, 111.4, 64.6, 56.0, 47.2, 33.5;
IR (film): $\tilde{\nu}$ = 3362 (w), 2945 (w), 2100 (s), 1658 (m), 1514 (m), 1482 (m), 1240 (m), 1020 (m);
HRMS (ESI) calcd. for $C_{11}H_{13}N_7NaO_2^+$ $[M+Na]^+$ 298.1023; Found 298.1030.

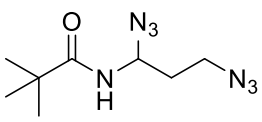
***N*-(1,3-Diazidopropyl)-2-methylbenzamide** (**6l**).



Following GP B, starting from *N*-cyclopropyl-2-methylbenzamide **5l** (35.0 mg, 0.200 mmol), *N*-(1,3-Diazidopropyl)-2-methylbenzamide **6l** (19.5 mg, 0.075 mmol, 38%) was obtained as a colorless oil after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.48 (silica, pentanes:ethyl acetate 3:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 – 7.33 (m, 2H, Ar*H*), 7.27 – 7.21 (m, 2H, Ar*H*), 6.68 (d, *J* = 8.9 Hz, 1H, N*H*), 5.90 (dt, *J* = 9.2, 6.0 Hz, 1H, C*H*), 3.57 (ddt, *J* = 39.3, 12.2, 6.2 Hz, 2H, CH_2N_3), 2.48 (s, 3H, CH_3), 1.91 (q, *J* = 6.2 Hz, 2H, C$H_2CH_2N_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.8, 136.6, 134.7, 131.3, 130.7, 126.7, 125.9, 64.4, 47.3, 33.2, 19.9;
IR (film): $\tilde{\nu}$ = 3268 (w), 2928 (w), 2100 (s), 1649 (m), 1516 (m), 1242 (m), 742 (m);
HRMS (ESI) calcd. for $C_{11}H_{13}N_7NaO^+$ $[M+Na]^+$ 282.1074; Found 282.1081.

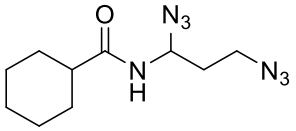
***N*-(1,3-Diazidopropyl)pivalamide** (**6m**).



Following GP B, starting from *N*-cyclopropylpivalamide **5m** (28.2 mg, 0.200 mmol), *N*-(1,3-diazidopropyl)pivalamide **6m** (27.8 mg, 0.124 mmol, 62%) was obtained as a yellow gel after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.33 (silica, pentanes:ethyl acetate 4:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.58 (s, 1H, N*H*), 5.77 – 5.64 (m, 1H, C*H*), 3.60 (dtd, *J* = 12.9, 6.7, 2.4 Hz, 1H, CH_2N_3), 3.47 (dtd, *J* = 13.3, 5.7, 1.5 Hz, 1H, CH_2N_3), 1.84 (q, *J* = 6.0 Hz, 2H, C$H_2CH_2N_3$), 1.24 (s, 9H, C(CH_3)$_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.9, 64.3, 47.3, 39.0, 33.0, 27.5;
IR (film): $\tilde{\nu}$ = 3333 (w), 2969 (w), 2098 (s), 1654 (m), 1513 (m), 1246 (m);
HRMS (ESI) calcd. for $C_8H_{15}N_7NaO^+$ $[M+Na]^+$ 248.1230; Found 248.1230.

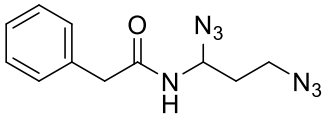
***N*-(1,3-diazidopropyl)cyclohexanecarboxamide** (**6n**).



Following GP B, starting from *N*-cyclopropylcyclohexanecarboxamide **5n** (33.4 mg, 0.200 mmol), *N*-(1,3-diazidopropyl)cyclohexanecarboxamide **6n** (28.3 mg, 0.124 mmol, 62%) was obtained as a beige solid after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.52 (silica, pentanes:ethyl acetate 3:1);
Mp: 43-45 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.35 (d, *J* = 9.1 Hz, 1H, N*H*), 5.71 (dt, *J* = 9.1, 6.0 Hz, 1H, NC*H*), 3.55 (dt, *J* = 12.9, 6.5 Hz, 1H, CH_2N_3), 3.45 (dt, *J* = 12.5, 6.1 Hz, 1H, CH_2N_3), 2.16 (tt, *J* = 11.7, 3.5 Hz, 1H, C(O)C*H*), 1.95 – 1.78 (m, 6H, CH_2), 1.53 – 1.41 (m, 2H, CH_2), 1.36 – 1.17 (m, 4H, CH_2);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.4, 64.0, 47.3, 45.3, 33.2, 29.9, 29.4, 25.6, 25.5 (one less carbon peak due to overlapping);
IR (film): $\tilde{\nu}$ = 3279 (w), 2931 (m), 2099 (s), 1655 (m), 1526 (m), 1255 (m);
HRMS (ESI) calcd. for $C_{10}H_{17}N_7NaO^+$ $[M+Na]^+$ 274.1387; Found 274.1377.

***N*-(1,3-Diazidopropyl)-2-phenylacetamide** (**6o**).

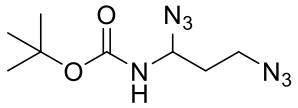


Following GP B, starting from *N*-cyclopropyl-2-phenylacetamide **5o** (35.0 mg, 0.200 mmol), *N*-(1,3-Diazidopropyl)-2-phenylacetamide **6o** (32.5 mg, 0.125 mmol, 63%) was obtained as a yellow solid after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.30 (silica, pentanes:ethyl acetate 3:1);
Mp: 54-56 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 – 7.37 (m, 2H, Ar*H*), 7.36 – 7.31 (m, 1H, Ar*H*), 7.30 – 7.26 (m, 2H, Ar*H*), 6.36 (d, *J* = 8.7 Hz, 1H, N*H*), 5.67 (dt, *J* = 9.0, 5.6 Hz, 1H, C*H*), 3.71 – 3.61 (m, 2H, PhCH_2), 3.45 (ddd, *J* = 13.0, 7.2, 5.9 Hz, 1H, CH_2N_3), 3.36 (dt, *J* = 12.6, 5.7 Hz, 1H, CH_2N_3), 1.69 (dd, *J* = 6.6, 4.9 Hz, 2H, C$H_2CH_2N_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.5, 133.8, 129.5, 129.2, 127.7, 64.4, 46.9, 43.5, 32.7;
IR (film): $\tilde{\nu}$ = 3277 (w), 2097 (s), 1656 (m), 1532 (m), 1242 (m), 696 (m);

HRMS (ESI) calcd. for $C_{11}H_{13}N_7NaO^+$ $[M+Na]^+$ 282.1074; Found 282.1073.

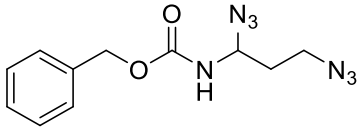
***tert*-Butyl (1,3-diazidopropyl)carbamate** (**6p**).



Following GP B, starting from *tert*-butyl cyclopropylcarbamate **5p** (31.4 mg, 0.200 mmol) with CuTc (0.4 mg, 0.002 mmol, 0.01 equiv.), *tert*-Butyl (1,3-diazidopropyl)carbamate **6p** (29.7 mg, 0.123 mmol, 62%) was obtained as a colorless oil after purification by column chromatography on silica using 10:1 pentanes:ethyl acetate as eluent.

R_f: 0.38 (silica, pentanes:ethyl acetate 10:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.54 – 5.12 (m, 2H, N*H* + C*H*), 3.46 (qt, *J* = 12.7, 6.4 Hz, 2H, CH_2N$_3$), 1.80 (q, *J* = 6.4 Hz, 2H, CH_2CH$_2$N$_3$), 1.47 (s, 9H, C(CH$_3$)$_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.8, 81.0, 66.5, 47.3, 33.6, 28.1;
IR (film): $\tilde{\nu}$ = 3323 (w), 2987 (m), 2098 (s), 1701 (s), 1509 (m), 1257 (s), 1161 (s);
HRMS (ESI) calcd. for $C_8H_{15}N_7NaO_2^+$ $[M+Na]^+$ 264.1179; Found 264.1180.

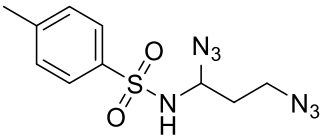
Benzyl (1,3-diazidopropyl)carbamate (**6q**).



Following GP B, starting from benzyl cyclopropylcarbamate **5q** (38.2 mg, 0.200 mmol) with CuTc (0.4 mg, 0.002 mmol, 0.01 equiv.), benzyl (1,3-diazidopropyl)carbamate **6q** (36.2 mg, 0.132 mmol, 66%) was obtained as a colorless oil after purification by column chromatography on silica using 5:1 pentanes:ethyl acetate as eluent.

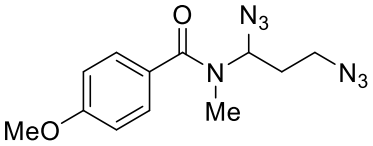
R_f: 0.53 (silica, pentanes:ethyl acetate 5:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 – 7.34 (m, 5H, Ar*H*), 5.63 (d, *J* = 9.7 Hz, 1H, N*H*), 5.48 (p, *J* = 6.7 Hz, 1H, C*H*), 5.16 (s, 2H, OCH_2), 3.54 – 3.40 (m, 2H, CH_2N$_3$), 1.82 (q, *J* = 6.4 Hz, 2H, CH_2CH$_2$N$_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.6, 135.6, 128.6, 128.4, 128.3, 67.5, 66.9, 47.1, 33.4;
IR (film): $\tilde{\nu}$ = 3672 (w), 3323 (w), 2975 (s), 2098 (s), 1713 (s), 1245 (s), 1065 (s);
HRMS (ESI) calcd. for $C_{11}H_{13}N_7NaO_2^+$ $[M+Na]^+$ 298.1023; Found 298.1028.

***N*-(1,3-diazidopropyl)-4-methylbenzenesulfonamide** (**6r**).



Following GP B, starting from *N*-cyclopropyl-4-methylbenzenesulfonamide **5r** (42.2 mg, 0.200 mmol), N-(1,3-diazidopropyl)-4-methylbenzenesulfonamide **6r** was formed in 68% yield based on crude ^{1}H NMR after workup, but purification by column chromatography on silica led to decomposition. Please refer to compound **10i** for one-pot nucleophilic substitution via **6r**.

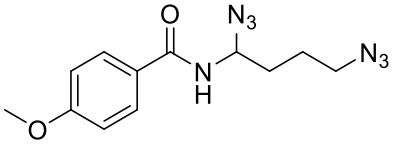
***N*-(1,3-Diazidopropyl)-4-methoxy-N-methylbenzamide** (**6s**).



Following GP B, starting from *N*-cyclopropyl-4-methoxy-*N*-methylbenzamide **5s** (41.0 mg, 0.200 mmol), *N*-(1,3-diazidopropyl)-4-methoxy-N-methylbenzamide **6s** (37.1 mg, 0.128 mmol, 64%) was obtained as a pale yellow oil after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.26 (silica, pentanes:ethyl acetate 3:1);
^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ = 7.52 – 7.34 (m, 2H, Ar*H*), 6.99 – 6.90 (m, 2H, Ar*H*), 6.36 – 5.51 (br, 1H, C*H*), 3.85 (s, 3H, OCH_3), 3.38 (dd, *J* = 12.4, 5.9 Hz, 2H, CH_2N$_3$), 2.99 (s, 3H, NCH_3), 2.02 – 1.79 (m, 2H, CH_2CH$_2$N$_3$);
^{13}C NMR (101 MHz, $CDCl_3$, 298K): δ = 172.5, 161.3, 129.4, 126.9, 113.9, 55.4, 47.4, 31.7 (two carbon signals are not resolved due to rotamers, which can be observed by measuring NMR experiment in Acetone-d_6 at 261.7 K);
IR (film): $\tilde{\nu}$ = 2963 (w), 2097 (s), 1641 (m), 1607 (m), 1251 (s), 1064 (m), 1028 (m), 842 (m);
HRMS (ESI) calcd. for $C_{12}H_{15}N_7NaO_2^+$ [M+Na]$^+$ 312.1179; Found 312.1187.

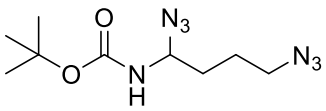
***N*-(1,4-Diazidobutyl)-4-methoxybenzamide** (**6t**).



Following GP B, starting from *N*-cyclobutyl-4-methoxybenzamide **5t** (41.0 mg, 0.200 mmol), *N*-(1,4-diazidobutyl)-4-methoxybenzamide **6t** (39.0 mg, 0.135 mmol, 67%) was obtained as a white solid after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.30 (silica, pentanes:ethyl acetate 3:1);
Mp: 58-61 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 – 7.69 (m, 2H, Ar*H*), 6.89 – 6.85 (m, 2H, Ar*H*), 6.52 (d, *J* = 9.1 Hz, 1H, N*H*), 5.68 (dt, *J* = 8.9, 6.5 Hz, 1H, C*H*), 3.79 (s, 3H, OCH_3), 3.33 – 3.28 (m, 2H, CH_2N$_3$), 1.76 – 1.63 (m, 4H, CH_2CH_2);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.9, 162.8, 129.1, 125.1, 113.9, 66.6, 55.5, 50.7, 32.0, 24.7;
IR (film): $\tilde{\nu}$ = 3296(w), 2933 (w), 2097 (s), 1638 (m), 1605 (s), 1500 (s), 1254 (s), 1177 (m), 1029 (m), 845 (m);
HRMS (APCI) calcd. for $C_{12}H_{15}N_7NaO_2^+$ [M+Na]$^+$ 312.1179; Found 312.1174.

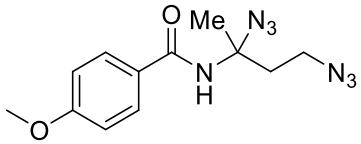
***tert*-Butyl (1,4-diazidobutyl)carbamate** (**6u**).



Following GP B, starting from *tert*-butyl cyclobutylcarbamate **5u** (34.2 mg, 0.200 mmol) with CuTc (0.4 mg, 0.002 mmol, 0.01 equiv.), *tert*-Butyl (1,4-diazidopropyl)carbamate **6u** (30.5 mg, 0.120 mmol, 60%) was obtained as a colorless oil after purification by column chromatography on silica using 8:1 pentanes:ethyl acetate as eluent.

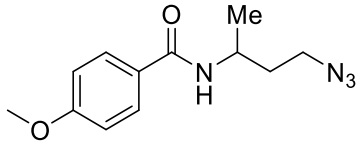
R_f: 0.31 (silica, pentanes:ethyl acetate 8:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.34 – 4.97 (m, 2H, N*H* + C*H*), 3.32 (t, *J* = 6.1 Hz, 2H, CH_2N_3), 1.67 (tdd, *J* = 13.4, 10.2, 6.2 Hz, 4H, CH_2), 1.46 (s, 9H, C$(CH_3)_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.8, 80.8, 68.2, 50.7, 31.9, 28.1, 24.6;
IR (film): $\tilde{\nu}$ = 3667 (w), 3340 (w), 2973 (s), 2102 (s), 1704 (s), 1508 (m), 1253 (s), 1060 (s);
HRMS (ESI) calcd. for $C_9H_{17}N_7NaO_2^+$ $[M+Na]^+$ 278.1336; Found 278.1338.

***N*-(2,4-Diazidobutan-2-yl)-4-methoxybenzamide** (**6w**).



Following GP B, starting from 4-methoxy-*N*-(1-methylcyclopropyl)benzamide **5w** (41.0 mg, 0.200 mmol), *N*-(2,4-diazidobutan-2-yl)-4-methoxybenzamide **6w** was formed in 58% yield based on crude ^{1}H NMR after workup, but purification by column chromatography on silica led to decomposition. Therefore, one-pot reduction by trimethylsilane was performed as shown below to form **26**.

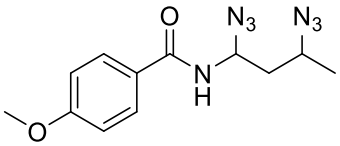
***N*-(4-azidobutan-2-yl)-4-methoxybenzamide** (**26**).



Following GP C, starting from 4-methoxy-*N*-(1-methylcyclopropyl)benzamide **5w** (41.0 mg, 0.200 mmol), after diazidation step is finished, triethylsilane (32.0 µL, 0.200 mmol, 1.0 equiv.) and TMSOTf (36.0 µL, 0.200 mmol, 1.0 equiv.) were added to the crude. The reaction mixture was stirred at room temperature for 2 hours. *N*-(4-azidobutan-2-yl)-4-methoxybenzamide **26** (22.4 mg, 90.3 µmol, 45%) was obtained as a white solid after purification by column chromatography on silica using 1:1 pentanes:ethyl acetate as eluent.

R_f: 0.37 (silica, pentanes:ethyl acetate 1:1);
Mp: 61-63 °C;
^{1}H NMR (800 MHz, $CDCl_3$): δ = 7.77 – 7.66 (m, 2H, Ar*H*), 6.96 – 6.86 (m, 2H, Ar*H*), 6.07 (d, *J* = 8.4 Hz, 1H, N*H*), 4.30 (tdd, *J* = 8.2, 6.6, 5.0 Hz, 1H, C*H*), 3.84 (s, 3H, OCH_3), 3.49 – 3.36 (m, 2H, N_3CH_2), 1.90 – 1.75 (m, 2H, $N_3CH_2CH_2$), 1.28 (d, *J* = 6.7 Hz, 3H, CH_3);
^{13}C NMR (201 MHz, $CDCl_3$): δ = 166.4, 162.1, 128.6, 126.8, 113.7, 55.4, 48.7, 43.8, 35.8, 20.9;
IR (film): $\tilde{\nu}$ = 3313(w), 2977 (s), 2098 (s), 1631 (s), 1500 (s), 1257 (s), 1045 (s), 852 (m);
HRMS (ESI) calcd. for $C_{12}H_{16}N_4NaO_2^+$ $[M+Na]^+$ 271.1165; Found 271.1169.

***N*-(1,3-Diazidobutyl)-4-methoxybenzamide** (**6xa**).

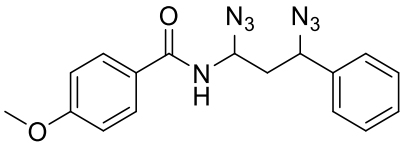


Following GP B, starting from 4-methoxy-*N*-(trans-2-methylcyclopropyl)benzamide **5xa** (41.0 mg, 0.200 mmol) with CuTc (2.4 mg, 0.012 mmol, 0.06 equiv.), *N*-(1,3-diazidobutyl)-4-methoxybenzamide **6xa**

(51.6 mg, 0.179 mmol, 89%) was obtained as a yellow gel after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.23 (silica, pentanes:ethyl acetate 3:1);
^{1}H NMR (400 MHz, $CDCl_3$; mixture of diastereoisomers in a ratio of 1.1:1, signals corresponding to the two regioisomers are partially resolved): δ = 7.78 (ddd, *J* = 10.1, 4.9, 2.7 Hz, 4H, Ar*H*, major + minor), 7.62 – 7.35 (m, 1H, N*H*, minor), 7.00 – 6.89 (m, 4H, Ar*H*, major + minor), 6.59 (t, *J* = 18.1 Hz, 1H, N*H*, major), 5.96 – 5.81 (m, 2H, NC*H*, major + minor), 3.99 (dd, *J* = 6.5, 3.5 Hz, 1H, MeC*H*, minor), 3.86 (s, 6H, OCH_3, major +minor), 3.75 – 3.66 (m, 1H, MeC*H*, major), 1.96 – 1.71 (m, 4H, CH_2, major +minor), 1.37 (dd, *J* = 8.2, 6.5 Hz, 6H, CH_3, major +minor);
^{13}C NMR (101 MHz, $CDCl_3$; mixture of diastereoisomers in a ratio of 1.1:1, signals corresponding to the two regioisomers are partially resolved): δ = 166.8, 166.7, 162.8, 162.8, 129.1, 125.2, 114.0, 65.2, 64.7, 55.5, 54.3, 53.7, 41.0, 39.7, 19.6, 19.3;
IR (film): $\tilde{\nu}$ = 3307(w), 2971 (w), 2098 (s), 1640 (m), 1605 (m), 1500 (s), 1252 (s), 1029 (m);
HRMS (ESI) calcd. for $C_{12}H_{15}N_7NaO_2^+$ $[M+Na]^+$ 312.1179; Found 312.1180.

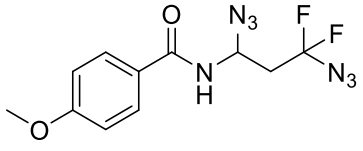
***N*-(1,3-Diazido-3-phenylpropyl)-4-methoxybenzamide** (**6xb**).



Following GP B, starting from 4-methoxy-*N*-(trans-2-phenylcyclopropyl)benzamide **5xb** (53.4 mg, 0.200 mmol), *N*-(1,3-diazido-3-phenylpropyl)-4-methoxybenzamide **6xb** (58.0 mg, 0.165 mmol, 83%) was obtained as a yellow solid after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.43 (silica, pentanes:ethyl acetate 3:1);
Mp: 81-84 °C;
^{1}H NMR (400 MHz, $CDCl_3$; mixture of diastereoisomers in a ratio of 1.2:1, signals corresponding to the two regioisomers are partially resolved): δ = 7.81 – 7.75 (m, 2H, Ar*H*, major), 7.70 – 7.62 (m, 2H, Ar*H*, minor), 7.59 – 7.53 (m, 1H, N*H*, major), 7.46 – 7.30 (m, 10H, Ar*H*, major + minor), 6.97 – 6.92 (m, 2H, Ar*H*, major), 6.92 – 6.87 (m, 2H, Ar*H*, minor), 6.66 (d, *J* = 8.9 Hz, 1H, N*H*, minor), 5.91 (ddd, *J* = 8.9, 7.6, 5.6 Hz, 1H, NC*H*, minor), 5.85 (ddd, *J* = 8.9, 5.8, 4.5 Hz, 1H, NC*H*, major), 4.88 (dd, *J* = 9.2, 5.0 Hz, 1H, PhC*H*, major), 4.71 (dd, *J* = 9.1, 5.2 Hz, 1H, PhC*H*, minor), 3.86 (s, 3H, OCH_3, major), 3.84 (s, 3H, OCH_3, minor), 2.22 – 1.95 (m, 4H, CH_2, major + minor);
^{13}C NMR (101 MHz, $CDCl_3$; mixture of diastereoisomers in a ratio of 1.2:1, signals corresponding to the two regioisomers are partially resolved): δ = 166.8, 166.8, 162.8, 162.8, 138.5, 137.9, 129.3, 129.2, 129.1, 129.1, 129.0, 128.9, 126.9, 125.1, 125.0, 113.9, 113.8, 65.0, 64.8, 62.3, 62.2, 55.4, 55.4, 40.9, 39.9;
IR (film): $\tilde{\nu}$ = 3307(w), 2100 (s), 1643 (m), 1605 (m), 1502 (s), 1255 (s), 1177 (m), 1029 (m);
HRMS (ESI) calcd. for $C_{17}H_{17}N_7NaO_2^+$ $[M+Na]^+$ 374.1336; Found 374.1345.

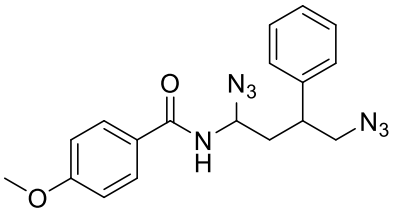
***N*-(1,3-Diazido-3,3-difluoropropyl)-4-methoxybenzamide** (**6y**).



Following GP B, starting from *N*-(2,2-difluorocyclopropyl)-4-methoxybenzamide **5y** (45.4 mg, 0.200 mmol), *N*-(1,3-diazido-3,3-difluoropropyl)-4-methoxybenzamide **6y** (53.8 mg, 0.173 mmol, 86%) was obtained as a beige solid after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.43 (silica, pentanes:ethyl acetate 3:1);
Mp: 58-61 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 – 7.75 (m, 2H, Ar*H*), 6.97 – 6.93 (m, 2H, Ar*H*), 6.77 (d, *J* = 9.1 Hz, 1H, N*H*), 6.00 (ddd, *J* = 8.8, 7.1, 5.7 Hz, 1H, C*H*), 3.86 (s, 3H, CH_3), 2.43 (tdd, *J* = 11.1, 6.4, 2.9 Hz, 2H, CH_2);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.8, 163.0, 129.1, 124.8, 121.9 (t, *J* = 266.9 Hz), 114.0, 62.2 (t, *J* = 4.1 Hz), 55.5, 40.1 (t, *J* = 26.7 Hz);
^{19}F NMR (377 MHz, $CDCl_3$): δ = -69.1;
IR (film): $\tilde{\nu}$ = 3312(w), 2936 (w), 2142 (s), 1652 (m), 1601 (s), 1502 (m), 1250 (s), 1171 (s);
HRMS (ESI) calcd. for $C_{11}H_{11}F_2N_7NaO_2^+$ $[M+Na]^+$ 334.0834; Found 334.0838.

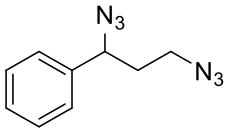
***N*-(1,4-Diazido-3-phenylbutyl)-4-methoxybenzamide** (**6z**).



Following GP B, starting from 4-methoxy-*N*-(*trans*-3-phenylcyclobutyl)benzamide **5z** (28.1 mg, 0.100 mmol), *N*-(1,4-diazido-3-phenylbutyl)-4-methoxybenzamide **6z** (25.7 mg, 0.070 mmol, 70%) was obtained as a colorless oil after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.43 (silica, pentanes:ethyl acetate 3:1);
^{1}H NMR (400 MHz, $CDCl_3$; mixture of diastereoisomers in a ratio of 1:1, signals corresponding to the two regioisomers are partially resolved): δ = 7.59 – 7.54 (m, 2H, Ar*H*), 7.43 – 7.37 (m, 4H, Ar*H*), 7.36 – 7.32 (m, 3H, Ar*H*), 7.31 – 7.26 (m, 3H, Ar*H*), 7.25 – 7.22 (m, 2H, Ar*H*), 6.89 – 6.80 (m, 4H, Ar*H*), 6.49 (d, *J* = 8.7 Hz, 1H, N*H*), 6.40 (d, *J* = 9.1 Hz, 1H, N*H*), 5.75 (ddd, *J* = 9.2, 7.1, 4.1 Hz, 1H, C*H*), 5.49 (td, *J* = 8.7, 5.8 Hz, 1H, C*H*), 3.84 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 3.55 (dt, *J* = 12.1, 7.0 Hz, 2H, N_3CH_2), 3.45 (ddd, *J* = 15.1, 12.1, 7.4 Hz, 2H, N_3CH_2), 3.14 (ddt, *J* = 10.5, 7.2, 3.7 Hz, 1H, PhC*H*), 3.07 (ddt, *J* = 10.9, 7.0, 3.7 Hz, 1H, PhC*H*), 2.26 – 2.12 (m, 2H, CH_2), 2.06 (tdd, *J* = 13.8, 10.3, 5.0 Hz, 2H, CH_2);
^{13}C NMR (101 MHz, $CDCl_3$; mixture of diastereoisomers in a ratio of 1:1, signals corresponding to the two regioisomers are partially resolved): δ = 166.7, 166.5, 162.7, 140.7, 140.0, 129.5, 129.2, 129.0, 128.9, 128.8, 127.9, 127.8, 127.7, 127.6, 125.0, 124.9, 113.7, 113.7, 66.0, 65.4, 56.8, 56.6, 55.4, 55.3, 42.4, 41.3, 37.8, 37.5;
IR (film): $\tilde{\nu}$ = 3303(w), 2934 (w), 2097 (s), 1641 (m), 1605 (m), 1499 (m), 1254 (s), 1176 (m), 1028 (m);
HRMS (ESI) calcd. for $C_{18}H_{19}N_7NaO_2^+$ $[M+Na]^+$ 388.1492; Found 388.1496.

(1,3-Diazidopropyl)benzene (**8**).

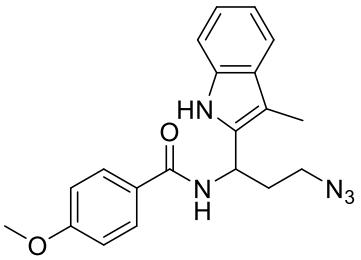


Following GP B, starting from cyclopropylbenzene **7** (25.1 µL, 0.200 mmol), (1,3-diazidopropyl)benzene **8** (4.0 mg, 0.020 mmol, 10%) was obtained as a colorless oil after purification by column chromatography on silica using pentanes as eluent.

R_f: 0.32 (silica, pentanes);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (ddt, *J* = 8.0, 6.5, 1.3 Hz, 2H, Ar*H*), 7.38 – 7.35 (m, 1H, Ar*H*), 7.32 (tt, *J* = 5.6, 1.4 Hz, 2H, Ar*H*), 4.61 (dd, *J* = 8.6, 5.9 Hz, 1H, C*H*), 3.48 – 3.29 (m, 2H, CH_2N_3), 2.10 – 1.88 (m, 2H, C$H_2CH_2N_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.6, 129.0, 128.6, 126.9, 63.2, 48.1, 35.5;
IR (film): $\tilde{\nu}$ = 2963 (m), 2098 (s), 1245 (m), 1053 (m), 908 (m);
HRMS (ESI) calcd. for $C_9H_{11}N_4^+$ $[M+H-N_2]^+$ 175.0978; Found 175.0965.

General Procedure C (GP C):
In a 12*75 mm Borosilicate glass tube, the corresponding aminocyclopropane (0.200 mmol, 1.0 equiv.), Selectfluor (78.0 mg, 0.220 mmol, 1.1 equiv.) and CuTc (0.8 mg, 0.004 mmol, 0.02 equiv.) were measured on analytical balance. The tube was then closed with a rubber septum and sealed off with parafilm. Evacuate-refill cycle with nitrogen were performed three times to remove O_2 and extra-dry acetonitrile (2.0 mL, 0.1 M) was added under nitrogen atmosphere, followed by the addition of $TMSN_3$ (94% purity purchased from TCI, 62.0 µL, 0.440 mmol, 2.2 equiv.). The reaction mixture was stirred at room temperature for 10 minutes before nucleophile (and if needed the Lewis acid/base) was added. The nucleophilc substitution step was not sensitive to air and nucleophile can be added directly by injection if it is in liquid state or by removing the cap and adding from the top if it is in solid state. The progress of the reaction was monitored by TLC. Upon completion, the mixture was quenched by the addition of water (10 mL). The aqueous layer was then extracted with dichloromethane (10 mL x 3). The organic extract was dried over Na_2SO_4, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, pentanes/EtOAc).

***N*-(3-Azido-1-(3-methyl-1H-indol-2-yl)propyl)-4-methoxybenzamide** (**10a**).

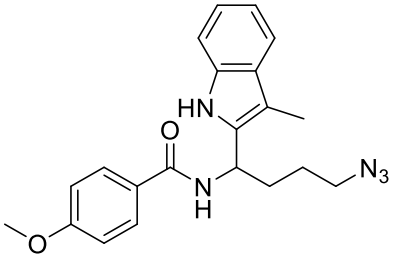


Following GP C, starting from *N*-cyclopropyl-4-methoxybenzamide **5b** (38.2 mg, 0.200 mmol), after diazidation step is finished, 3-methylindole (39.4 mg, 0.300 mmol, 1.5 equiv.) and boron trifluoride etherate (25.0 µL, 0.200 mmol, 1.0 equiv.) were added to the crude. The reaction mixture was stirred at room temperature for 30 minutes. *N*-(3-Azido-1-(3-methyl-1H-indol-2-yl)propyl)-4-methoxybenzamide **10a** (47.3 mg, 0.130 mmol, 65%) was obtained as a yellow solid after purification by column chromatography on silica using 3:2 pentanes:ethyl acetate as eluent.

R_f: 0.45 (silica, pentanes:ethyl acetate 3:2);
Mp: 152-155 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.13 (s, 1H, indole N*H*), 7.75 – 7.70 (m, 2H, Ar*H*), 7.54 – 7.50 (m, 1H, Ar*H*), 7.32 (dt, *J* = 8.1, 1.0 Hz, 1H, Ar*H*), 7.17 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H, Ar*H*), 7.10 (ddd, *J* = 8.0, 7.0,

1.1 Hz, 1H, Ar*H*), 6.93 – 6.89 (m, 2H, Ar*H*), 6.75 (d, *J* = 7.1 Hz, 1H, N*H*), 5.16 (q, *J* = 7.4 Hz, 1H, C*H*), 3.84 (s, 3H, OCH_3), 3.44 (ddd, *J* = 12.5, 7.0, 5.6 Hz, 1H, CH_2N_3), 3.31 (ddd, *J* = 12.6, 7.2, 5.6 Hz, 1H, CH_2N_3), 2.56 – 2.40 (m, 2H, C$H_2CH_2N_3$), 2.34 (s, 3H, CH_3);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.9, 162.5, 135.4, 133.1, 128.8, 128.5, 126.1, 122.2, 119.2, 118.7, 113.9, 111.0, 108.3, 55.4, 48.8, 46.2, 32.8, 8.7;
IR (film): $\tilde{\nu}$ = 3672 (w), 3323 (m), 2975 (s), 2098 (s), 1617 (s), 1497 (m), 1257 (s), 1065 (s);
HRMS (ESI) calcd. for $C_{20}H_{21}N_5NaO_2^+$ $[M+Na]^+$ 386.1587; Found 386.1588.

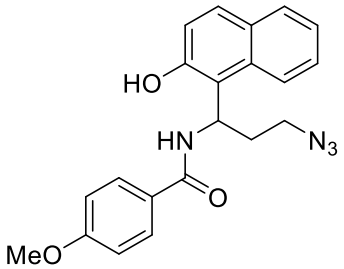
***N*-(4-Azido-1-(3-methyl-1H-indol-2-yl)butyl)-4-methoxybenzamide** (**11a**).



Following GP C, starting from *N*-cyclobutyl-4-methoxybenzamide **5t** (41.0 mg, 0.200 mmol), after diazidation step is finished, 3-methylindole (39.4 mg, 0.300 mmol, 1.5 equiv.) and boron trifluoride etherate (25.0 µL, 0.200 mmol, 1.0 equiv.) were added to the crude. The reaction mixture was stirred at room temperature for 30 minutes. *N*-(4-Azido-1-(3-methyl-1H-indol-2-yl)butyl)-4-methoxybenzamide **11a** (51.4 mg, 0.136 mmol, 68%) was obtained as a beige solid after purification by column chromatography on silica using 3:2 pentanes:ethyl acetate as eluent.

R_f: 0.37 (silica, pentanes:ethyl acetate 3:2);
Mp: 160-164 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.93 (s, 1H, indole N*H*), 7.72 – 7.67 (m, 2H, Ar*H*), 7.52 (dd, *J* = 7.8, 1.2 Hz, 1H, Ar*H*), 7.27 – 7.24 (m, 1H, Ar*H*), 7.15 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 1H, Ar*H*), 7.09 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H, Ar*H*), 6.87 – 6.81 (m, 2H, Ar*H*), 6.79 (d, *J* = 7.5 Hz, 1H, N*H*), 5.22 (q, *J* = 7.8 Hz, 1H, C*H*), 3.80 (s, 3H, OCH_3), 3.29 (t, *J* = 6.6 Hz, 2H, CH_2N_3), 2.33 (s, 3H, CH_3), 2.29 – 2.13 (m, 2H, CH_2), 1.71 – 1.55 (m, 2H, CH_2);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.3, 162.4, 135.4, 133.6, 128.8, 128.7, 126.3, 122.1, 119.2, 118.7, 113.8, 110.9, 108.2, 55.4, 51.1, 47.6, 31.6, 26.0, 8.8;
IR (film): $\tilde{\nu}$ = 3316 (m), 2938 (w), 2102 (s), 1616 (s), 1500 (s), 1261 (s), 1029 (w);
HRMS (ESI) calcd. for $C_{21}H_{23}N_5NaO_2^+$ $[M+Na]^+$ 400.1744; Found 400.1745.

***N*-(3-Azido-1-(2-hydroxynaphthalen-1-yl)propyl)-4-methoxybenzamide** (**10ba**).

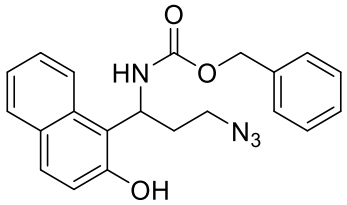


Following GP C, starting from *N*-cyclopropyl-4-methoxybenzamide **5b** (38.2 mg, 0.200 mmol), after diazidation step is finished, 2-naphthol (43.2 mg, 0.300 mmol, 1.5 equiv.) and boron trifluoride etherate (25.0 µL, 0.200 mmol, 1.0 equiv.) were added to the crude. The reaction mixture was stirred at room temperature for 30 minutes. *N*-(3-Azido-1-(2-hydroxynaphthalen-1-yl)propyl)-4-

methoxybenzamide **10ba** (56.0 mg, 0.149 mmol, 74%) was obtained as a white solid after purification by column chromatography on silica using 1:1 pentanes:ethyl acetate as eluent.

R_f: 0.27 (silica, pentanes:ethyl acetate 1:1);
Mp: 187-190 °C;
^{1}H NMR (400 MHz, Acetone-d_6): δ = 9.55 (s, 1H, naphthol O*H*), 8.39 (d, *J* = 8.8 Hz, 1H, N*H*), 8.31 (d, *J* = 8.7 Hz, 1H, Ar*H*), 7.88 – 7.78 (m, 3H, Ar*H*), 7.75 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.54 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H, Ar*H*), 7.33 (ddd, *J* = 8.0, 6.8, 1.0 Hz, 1H, Ar*H*), 7.26 (d, *J* = 8.9 Hz, 1H, Ar*H*), 7.01 – 6.90 (m, 2H, Ar*H*), 6.34 (q, *J* = 8.1 Hz, 1H, NC*H*), 3.82 (s, 3H, OCH_3), 3.52 (dt, *J* = 12.3, 7.0 Hz, 1H, CH_2N$_3$), 3.42 (dt, *J* = 12.6, 6.6 Hz, 1H, CH_2N$_3$), 2.63 – 2.44 (m, 1H, CH_2CH$_2$N$_3$), 2.28 (dq, *J* = 13.6, 6.8 Hz, 1H, CH_2CH$_2$N$_3$);
^{13}C NMR (101 MHz, Acetone-d_6): δ = 166.5, 163.1, 154.0, 133.4, 130.1, 130.0, 129.6, 129.5, 128.0, 127.6, 123.9, 123.3, 120.2, 119.5, 114.4, 55.8, 49.8, 45.7, 34.4;
IR (film): $\tilde{\nu}$ = 3137 (m), 2932 (w), 2097 (s), 1627 (s), 1606 (s), 1501 (s), 1259 (s), 1029 (m);
HRMS (ESI) calcd. for $C_{21}H_{20}N_4NaO_3^+$ [M+Na]$^+$ 399.1428; Found 399.1426.

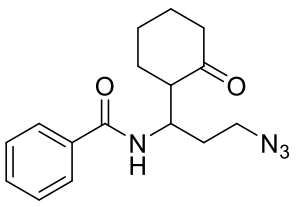
Benzyl (3-azido-1-(2-hydroxynaphthalen-1-yl)propyl)carbamate (**10bb**).



Following GP C, starting from benzyl cyclopropylcarbamate **5q** (38.2 mg, 0.200 mmol), after diazidation step is finished, the crude was cooled down to -20 °C before 2-naphthol (43.2 mg, 0.300 mmol, 1.5 equiv.) and boron trifluoride etherate (25.0 µL, 0.200 mmol, 1.0 equiv.) were added to the crude. The reaction mixture was stirred at -20 °C for 2 hours. Benzyl (3-azido-1-(2-hydroxynaphthalen-1-yl)propyl)carbamate **10bb** (35.0 mg, 0.093 mmol, 46%) was obtained as a white solid after purification by column chromatography on silica using 4:1 pentanes:ethyl acetate as eluent.

R_f: 0.30 (silica, pentanes:ethyl acetate 4:1);
MP: 149-150 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (s, 1H, Ar*H*), 7.76 (dd, *J* = 8.1, 1.3 Hz, 1H, Ar*H*), 7.65 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.49 (ddd, *J* = 8.5, 6.7, 1.4 Hz, 1H, Ar*H*), 7.39 – 7.31 (m, 6H, Ar*H*), 7.04 (d, *J* = 8.8 Hz, 1H, Ar*H*), 5.85 (dt, *J* = 9.4, 7.2 Hz, 1H, NC*H*), 5.20 (d, *J* = 9.6 Hz, 2H, PhCH_2), 3.32 (ddt, *J* = 47.1, 12.5, 6.6 Hz, 2H, CH_2N$_3$), 2.42 – 2.13 (m, 2H, CH_2CH$_2$N$_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.0, 136.0, 131.9, 129.6, 129.0, 128.7, 128.5, 128.3, 128.2, 128.1, 128.0, 127.2, 123.3, 121.9, 118.2, 67.5, 48.8, 47.0, 33.9;
IR (film): $\tilde{\nu}$ = 3277 (m), 2097 (s), 1687 (s), 1516 (s), 1329 (m), 1271 (m);
HRMS (ESI) calcd. for $C_{21}H_{20}N_4NaO_3^+$ [M+Na]$^+$ 399.1428; Found 399.1435.

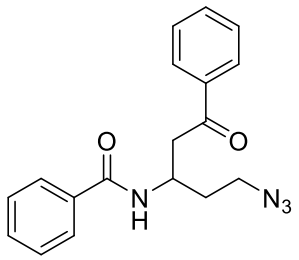
***N*-(3-Azido-1-(2-oxocyclohexyl)propyl)benzamide** (**10c**).



Following GP C, starting from *N*-cyclopropylbenzamide **5a** (32.2 mg, 0.200 mmol), after diazidation step is finished, 1-morpholinocyclohexane (100 µL, 0.600 mmol, 3.0 equiv.) and boron trifluoride etherate (75.0 µL, 0.600 mmol, 3.0 equiv.) were added to the crude. The reaction mixture was stirred at room temperature for 1 hour. *N*-(3-Azido-1-(2-oxocyclohexyl)propyl)benzamide **10c** (35.1 mg, 0.117 mmol, 58%) was obtained as a beige solid after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.30 (silica, pentanes:ethyl acetate 3:1);
Mp: 93-96 °C;
^{1}H NMR (400 MHz, CDCl3; mixture of two diastereoisomers in a 1.7:1 ratio: the signals corresponding to the two diastereoisomers are partially resolved): δ = 7.77 (ddd, *J* = 7.6, 6.0, 1.4 Hz, 2H, Ar*H*), 7.54 – 7.47 (m, 1H, Ar*H*), 7.44 (dtd, *J* = 8.7, 4.3, 2.3 Hz, 2H, Ar*H*), 7.09 (d, *J* = 9.8 Hz, 1H, N*H*, major:minor = 1.7:1), 4.31 (qdd, *J* = 11.0, 4.5, 2.6 Hz, 1H, NC*H*), 3.50 – 3.28 (m, 2H, CH_2N_3), 2.72 (dddd, *J* = 17.5, 12.3, 5.4, 1.8 Hz, 1H, C(O)C*H*), 2.48 – 2.01 (m, 5H, CH_2), 2.00 – 1.62 (m, 5H, CH_2);
^{13}C NMR (101 MHz, $CDCl_3$; mixture of two diastereoisomers in a 1.7:1 ratio: the signals corresponding to the two diastereoisomers are partially resolved): δ = 214.4, 213.2, 167.1, 166.7, 134.1, 134.1, 131.6, 128.6, 126.9, 54.5, 54.0, 49.0, 48.9, 48.7, 48.2, 43.3, 42.5, 33.7, 33.1, 30.9, 29.5, 28.4, 27.0, 25.1, 24.8;
IR (film): $\tilde{\nu}$ = 3315 (w), 2936 (m), 2093 (s), 1703 (s), 1636 (s), 1527 (s), 1308 (m), 1258 (m);
HRMS (ESI) calcd. for $C_{16}H_{20}N_4NaO_2^+$ $[M+Na]^+$ 323.1478; Found 323.1477.

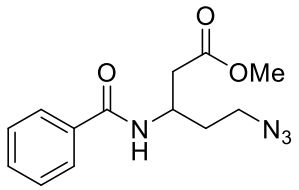
***N*-(5-Azido-1-oxo-1-phenylpentan-3-yl)benzamide** (**10d**).



Following GP C, starting from *N*-cyclopropylbenzamide **5a** (32.2 mg, 0.200 mmol), after diazidation step is finished, trimethyl((1-phenylvinyl)oxy)silane (82.0 µL, 0.400 mmol, 2.0 equiv.) and TMSOTf (72.0 µL, 0.400 mmol, 2.0 equiv.) were added to the crude. The reaction mixture was stirred at room temperature for 30 minutes. *N*-(5-Azido-1-oxo-1-phenylpentan-3-yl)benzamide **10d** (51.1 mg, 0.159 mmol, 79%) was obtained as a yellow solid after purification by column chromatography on silica using 2:1 pentanes:ethyl acetate as eluent.

R_f: 0.32 (silica, pentanes:ethyl acetate 2:1);
Mp: 81-84 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 – 7.94 (m, 2H, Ar*H*), 7.82 – 7.75 (m, 2H, Ar*H*), 7.62 – 7.57 (m, 1H, Ar*H*), 7.46 (ddd, *J* = 19.5, 8.1, 6.5 Hz, 5H, Ar*H*), 7.26 – 7.22 (m, 1H, N*H*), 4.68 (tq, *J* = 9.4, 4.8 Hz, 1H, NC*H*), 3.56 (dd, *J* = 17.6, 4.2 Hz, 1H, C(O)CH_2), 3.47 (dd, *J* = 7.4, 6.0 Hz, 2H, CH_2N_3), 3.29 (dd, *J* = 17.6, 5.5 Hz, 1H, C(O)CH_2), 2.20 (ddt, *J* = 14.2, 9.4, 6.0 Hz, 1H, C$H_2CH_2N_3$), 1.95 (dtd, *J* = 14.4, 7.4, 4.7 Hz, 1H, C$H_2CH_2N_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.5, 167.0, 136.6, 134.2, 133.7, 131.6, 128.8, 128.6, 128.1, 126.9, 48.9, 45.0, 41.5, 33.0;
IR (film): $\tilde{\nu}$ = 3310 (w), 3061 (w), 2095 (s), 1682 (s), 1636 (s), 1534 (s), 1306 (m), 690 (s);
HRMS (ESI) calcd. for $C_{18}H_{19}N_4O_2^+$ $[M+H]^+$ 323.1503; Found 323.1498.

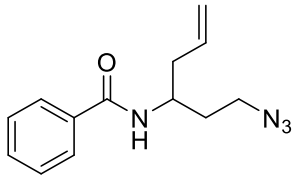
Methyl 5-azido-3-benzamidopentanoate (**10e**).



Following GP C, starting from *N*-cyclopropylbenzamide **5a** (32.2 mg, 0.200 mmol), after diazidation step is finished, *tert*-butyl[(1-methoxyvinyl)oxy]dimethylsilane (132 µL, 0.600 mmol, 3.0 equiv.) was added to the crude. The reaction mixture was stirred at room temperature for 4 hours. Methyl 5-azido-3-benzamidopentanoate **10e** (34.0 mg, 0.123 mmol, 62%) was obtained as a colorless oil after purification by column chromatography on silica using 1:1 pentanes:ethyl acetate as eluent.

R_f: 0.47 (silica, pentanes:ethyl acetate 1:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (dq, *J* = 8.1, 1.7, 1.2 Hz, 2H, Ar*H*), 7.54 – 7.48 (m, 1H, Ar*H*), 7.44 (ddd, *J* = 8.1, 6.2, 1.3 Hz, 2H, Ar*H*), 7.08 (d, *J* = 9.0 Hz, 1H, N*H*), 4.65 – 4.47 (m, 1H, NC*H*), 3.72 (s, 3H, OCH_3), 3.50 – 3.39 (m, 2H, CH_2N_3), 2.79 – 2.65 (m, 2H, C$H_2CO_2CH_3$), 2.07 – 1.96 (m, 1H, C$H_2CH_2N_3$), 1.94 – 1.82 (m, 1H, C$H_2CH_2N_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.4, 166.8, 134.1, 131.7, 128.6, 126.9, 51.9, 48.7, 44.3, 37.9, 33.3;
IR (film): $\tilde{\nu}$ = 3309 (w), 2951 (m), 2098 (s), 1736 (s), 1638 (s), 1534 (s), 1307 (m), 1263 (m);
HRMS (ESI) calcd. for $C_{13}H_{16}N_4NaO_3^+$ $[M+Na]^+$ 299.1115; Found 299.1114.

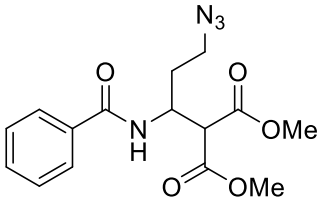
***N*-(1-Azidohex-5-en-3-yl)benzamide** (**10f**).



Following GP C, starting from *N*-cyclopropylbenzamide **5a** (32.2 mg, 0.200 mmol), after diazidation step is finished, allyltrimethylsilane (64.0 µL, 0.400 mmol, 2.0 equiv.) and $TiCl_4$ (55.0 µL, 0.500 mmol, 2.5 equiv.) were added to the crude. The reaction mixture was stirred at room temperature for 1 hour. *N*-(1-Azidohex-5-en-3-yl)benzamide **10f** (31.2 mg, 0. 128 mmol, 64%) was obtained as a grey solid after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.39 (silica, pentanes:ethyl acetate 3:1);
Mp: 54-57 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 – 7.69 (m, 2H, Ar*H*), 7.53 – 7.47 (m, 1H, Ar*H*), 7.46 – 7.38 (m, 2H, Ar*H*), 6.15 (d, *J* = 8.7 Hz, 1H, N*H*), 5.82 (ddt, *J* = 16.5, 10.8, 7.1 Hz, 1H, vinylC*H*), 5.21 – 5.09 (m, 2H, vinylCH_2), 4.31 (ttd, *J* = 8.8, 6.4, 4.5 Hz, 1H, NC*H*), 3.51 – 3.35 (m, 2H, CH_2N_3), 2.47 – 2.30 (m, 2H, allylic CH_2), 1.93 (dtd, *J* = 14.2, 7.5, 4.5 Hz, 1H, C$H_2CH_2N_3$), 1.79 (dddd, *J* = 14.4, 8.9, 7.1, 6.0 Hz, 1H, C$H_2CH_2N_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.1, 134.5, 133.7, 131.5, 128.6, 126.8, 118.6, 48.7, 47.1, 39.1, 33.6;
IR (film): $\tilde{\nu}$ = 3293 (w), 2930 (w), 2094 (s), 1633 (s), 1536 (s), 1305 (m), 917 (w);
HRMS (ESI) calcd. for $C_{13}H_{17}N_4O^+$ $[M+H]^+$ 245.1397 Found 245.1394.

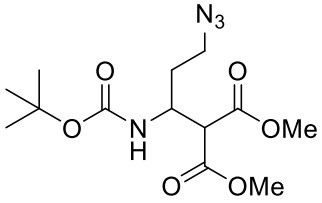
Dimethyl 2-(3-azido-1-benzamidopropyl)malonate (**10ga**).



Following GP C, starting from *N*-cyclopropylbenzamide **5a** (32.2 mg, 0.200 mmol), after diazidation step is finished, a solution of dimethyl malonate (46.0 µL, 0.400 mmol, 2.0 equiv.) and sodium hydride 60% dispersion mineral oil (16.0 mg, 0.400 mmol, 2.0 equiv.) in THF (0.5 mL) was added dropwise to the crude. The reaction mixture was stirred at room temperature for 10 minutes. Dimethyl 2-(3-azido-1-benzamidopropyl)malonate **10ga** (51.2 mg, 0.153 mmol, 77%) was obtained as a grey solid after purification by column chromatography on silica using 1:1 pentanes:ethyl acetate as eluent.

R_f: 0.45 (silica, pentanes:ethyl acetate 1:1);
Mp: 57-59 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 – 7.73 (m, 2H, Ar*H*), 7.54 – 7.48 (m, 1H, Ar*H*), 7.46 – 7.41 (m, 2H, Ar*H*), 7.33 (d, *J* = 9.5 Hz, 1H, N*H*), 4.90 (tdd, *J* = 9.6, 4.7, 3.8 Hz, 1H, NC*H*), 3.82 (s, 3H, OCH_3), 3.79 (d, *J* = 3.8 Hz, 1H, C*H*), 3.71 (s, 3H, OCH_3), 3.44 (dd, *J* = 7.5, 6.2 Hz, 2H, CH_2N_3), 2.06 – 1.82 (m, 2H, C$H_2CH_3N_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.1, 167.8, 167.0, 133.9, 131.7, 128.6, 127.0, 54.3, 53.0, 52.8, 48.5, 47.0, 32.8;
IR (film): $\tilde{\nu}$ = 3306 (m), 2954 (m), 2096 (s), 1732 (s), 1642 (s), 1523 (s), 1257 (s), 1158 (s), 712 (m);
HRMS (ESI) calcd. for $C_{15}H_{18}N_4NaO_5^+$ $[M+Na]^+$ 357.1169; Found 357.1179.

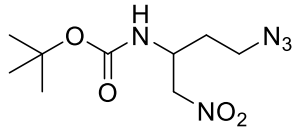
Dimethyl 2-(3-azido-1-((*tert*-butoxycarbonyl)amino)propyl)malonate (**10gb**).



Following GP C, starting from *tert*-butyl cyclopropylcarbamate **5p** (31.4 mg, 0.200 mmol), after diazidation step is finished, a solution of dimethyl malonate (46.0 µL, 0.400 mmol, 2.0 equiv.) and sodium hydride 60% dispersion mineral oil (16.0 mg, 0.400 mmol, 2.0 equiv.) in THF (0.5 mL) was added dropwise to the crude. The reaction mixture was stirred at room temperature for 10 minutes. Dimethyl 2-(3-azido-1-((*tert*-butoxycarbonyl)amino)propyl)malonate **10gb** (42.5 mg, 0.129 mmol, 64%) was obtained as a white solid after purification by column chromatography on silica using 5:1 pentanes:ethyl acetate as eluent.

R_f: 0.30 (silica, pentanes:ethyl acetate 5:1);
Mp: 78-81 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.37 (d, *J* = 10.0 Hz, 1H, N*H*), 4.34 (td, *J* = 9.8, 4.8 Hz, 1H, NC*H*), 3.77 (d, *J* = 1.4 Hz, 3H, OCH_3), 3.73 (d, *J* = 1.5 Hz, 3H, OCH_3), 3.66 (d, *J* = 4.2 Hz, 1H, C*H*), 3.48 – 3.30 (m, 2H, CH_2N_3), 1.82 (dtd, *J* = 19.4, 7.3, 3.5 Hz, 2H, C$H_2CH_3N_3$), 1.42 (s, 9H, C(CH_3)$_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.5, 167.9, 155.3, 79.8, 54.8, 52.8, 52.6, 48.5, 47.9, 32.6, 28.2;
IR (film): $\tilde{\nu}$ = 3376 (w), 2955 (m), 2097 (s), 1734 (s), 1713 (s), 1500 (m), 1242 (s), 1161 (s);
HRMS (ESI) calcd. for $C_{13}H_{22}N_4NaO_6^+$ $[M+Na]^+$ 353.1432; Found 353.1432.

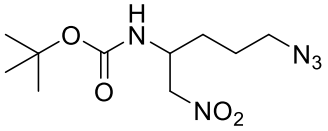
***tert*-Butyl (4-azido-1-nitrobutan-2-yl)carbamate** (**10h**).



Following GP C, starting from *tert*-butyl cyclopropylcarbamate **5p** (31.4 mg, 0.200 mmol), after diazidation step is finished, CH_3NO_2 (22.0 µL, 0.400 mmol, 2.0 equiv.) was added to the crude followed by the addition of KO*t*Bu 1.0M in *t*BuOH (0.40 mL, 0.40 mmol, 2.0 equiv.). The reaction mixture was stirred at room temperature for 1 hour. *tert*-Butyl (4-azido-1-nitrobutan-2-yl)carbamate **10h** (28.0 mg, 0.108 mmol, 54%) was obtained as a white solid after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.45 (silica, pentanes:ethyl acetate 3:1);
Mp: 49-53 °C;
^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.97 (d, *J* = 8.7 Hz, 1H, N*H*), 4.63 (dd, *J* = 13.0, 5.7 Hz, 1H, NO_2CH_2), 4.56 (dd, *J* = 13.1, 4.4 Hz, 1H, NO_2CH_2), 4.24 (tt, *J* = 9.5, 4.7 Hz, 1H, NC*H*), 3.47 (dtt, *J* = 17.9, 12.9, 6.9 Hz, 2H, CH_2N_3), 1.97 – 1.78 (m, 2H, $CH_2CH_3N_3$), 1.44 (s, 9H, $C(CH_3)_3$);
^{13}C NMR (151 MHz, $CDCl_3$): δ = 154.9, 80.6, 77.9, 48.0, 47.0, 30.8, 28.2;
IR (film): $\tilde{\nu}$ = 3339 (w), 2979 (w), 2100 (s), 1692 (s), 1554 (s), 1367 (s), 1165 (s), 1062 (w);
HRMS (ESI) calcd. for $C_9H_{17}N_5NaO_4^+$ $[M+Na]^+$ 282.1173; Found 282.1176.

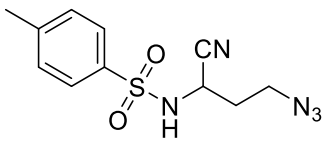
***tert*-Butyl (5-azido-1-nitropentan-2-yl)carbamate** (**11h**).



Following GP C, starting from *tert*-butyl cyclobutylcarbamate **5u** (34.2 mg, 0.200 mmol), after diazidation step is finished, CH_3NO_2 (22.0 µL, 0.400 mmol, 2.0 equiv.) was added to the crude followed by the addition of KO*t*Bu 1.0 M in *t*BuOH (0.40 mL, 0.40 mmol, 2.0 equiv.). The reaction mixture was stirred at room temperature for 1 hour. *tert*-Butyl (5-azido-1-nitropentan-2-yl)carbamate **11h** (19.0 mg, 0.070 mmol, 35%) was obtained as a colorless oil after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.33 (silica, pentanes:ethyl acetate 6:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.88 (d, *J* = 8.9 Hz, 1H, N*H*), 4.61 – 4.38 (m, 2H, NO_2CH_2), 4.13 (td, *J* = 8.3, 4.0 Hz, 1H, NC*H*), 3.45 – 3.19 (m, 2H, CH_2N_3), 1.67 (ddt, *J* = 9.3, 7.2, 3.5 Hz, 4H, CH_2), 1.44 (s, 9H, $C(CH_3)_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.0, 80.4, 78.3, 50.7, 48.7, 29.0, 28.2, 25.4;
IR (film): $\tilde{\nu}$ = 3667 (w), 3340 (m), 2973 (s), 2098 (s), 1697 (s), 1550 (s), 1373 (s), 1253 (s), 1064 (s);
HRMS (ESI) calcd. for $C_{10}H_{19}N_5NaO_4^+$ $[M+Na]^+$ 296.1329; Found 296.1332.

***N*-(3-Azido-1-cyanopropyl)-4-methylbenzenesulfonamide** (**10i**).

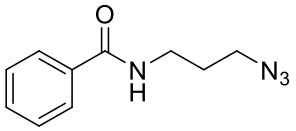


Following GP C, starting from *N*-cyclopropyl-4-methylbenzenesulfonamide **5r** (42.2 mg, 0.200 mmol), after diazidation step is finished, TMSCN (38.0 µL, 0.300 mmol, 1.5 equiv.) was added to the crude. The reaction mixture was stirred at room temperature for 30 minutes. *N*-(3-Azido-1-cyanopropyl)-4-

methylbenzenesulfonamide **10i** (35.1 mg, 0.126 mmol, 63%) was obtained as a beige solid after purification by column chromatography on silica using 1:1 pentanes:ethyl acetate as eluent.

R_f: 0.50 (silica, pentanes:ethyl acetate 1:1);
Mp: 113-116 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 – 7.73 (m, 2H, Ar*H*), 7.37 (d, *J* = 8.1 Hz, 2H, Ar*H*), 5.39 (d, *J* = 9.8 Hz, 1H, N*H*), 4.42 (ddd, *J* = 9.8, 7.2, 6.2 Hz, 1H, NC*H*), 3.64 – 3.49 (m, 2H, CH_2N$_3$), 2.45 (s, 3H, CH_3), 2.02 (dtd, *J* = 7.6, 5.8, 2.4 Hz, 2H, CH_2CH$_2$N$_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.9, 135.7, 130.2, 127.3, 116.7, 46.9, 42.3, 33.0, 21.7;
IR (film): $\tilde{\nu}$ = 3275 (m), 2929 (w), 2105 (s), 1336 (s), 1161 (s), 1090 (s), 815 (m);
HRMS (ESI) calcd. for $C_{11}H_{13}N_5NaO_2S^+$ $[M+Na]^+$ 302.0682; Found 302.0684.

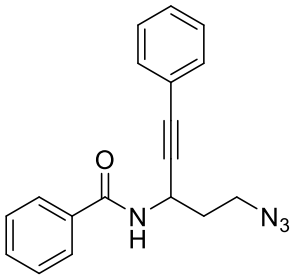
***N*-(3-Azidopropyl)benzamide** (**10j**).



Following GP C, starting from *N*-cyclopropylbenzamide **5a** (32.2 mg, 0.200 mmol), after diazidation step is finished, triethylsilane (32.0 µL, 0.200 mmol, 1.0 equiv.) and TMSOTf (36.0 µL, 0.200 mmol, 1.0 equiv.) were added to the crude. The reaction mixture was stirred at room temperature for 2 hours. *N*-(3-Azidopropyl)benzamide **10j** (29.2 mg, 0.143 mmol, 72%) was obtained as a colorless oil after purification by column chromatography on silica using 2:1 pentanes:ethyl acetate as eluent.

R_f: 0.26 (silica, pentanes:ethyl acetate 2:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 – 7.72 (m, 2H, Ar*H*), 7.52 – 7.45 (m, 1H, Ar*H*), 7.44 – 7.37 (m, 2H, Ar*H*), 6.79 – 6.47 (m, 1H, N*H*), 3.53 (qd, *J* = 6.7, 3.2 Hz, 2H, NCH_2), 3.42 (qd, *J* = 6.2, 5.4, 2.5 Hz, 2H, CH_2N$_3$), 1.90 (dddd, *J* = 8.2, 6.6, 4.2, 2.0 Hz, 2H, CH_2CH$_2$N$_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.7, 134.3, 131.5, 128.5, 126.8, 49.5, 37.7, 28.7;
IR (film): $\tilde{\nu}$ = 3310 (m), 2932 (w), 2092 (s), 1636 (s), 1537 (s), 1291 (m), 669 (m);
HRMS (ESI) calcd. for $C_{10}H_{12}N_4NaO^+$ $[M+Na]^+$ 227.0903; Found 227.0908.

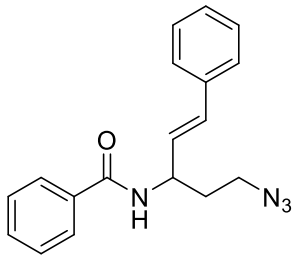
***N*-(5-Azido-1-phenylpent-1-yn-3-yl)benzamide** (**10k**).



Following GP C, starting from *N*-cyclopropylbenzamide **5a** (32.2 mg, 0.200 mmol), after diazidation step is finished, potassium phenylethynyltrifluoroborate (83.2 mg, 0.400 mmol, 2.0 equiv.) and boron trifluoride etherate (100 µL, 0.800 mmol, 4.0 equiv.) were added to the crude. The reaction mixture was stirred at room temperature for 2 hours. *N*-(5-Azido-1-phenylpent-1-yn-3-yl)benzamide **10k** (28.8 mg, 0. 095 mmol, 48%) was obtained as a yellow oil after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.43 (silica, pentanes:ethyl acetate 3:1);
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.84 – 7.79 (m, 2H, Ar*H*), 7.55 – 7.51 (m, 1H, Ar*H*), 7.48 – 7.42 (m, 4H, Ar*H*), 7.35 – 7.29 (m, 3H, Ar*H*), 6.60 (d, *J* = 8.2 Hz, 1H, N*H*), 5.37 (dt, *J* = 8.2, 6.3 Hz, 1H, NC*H*), 3.72 – 3.66 (m, 1H, CH_2N$_3$), 3.60 (dt, *J* = 12.6, 6.4 Hz, 1H, CH_2N$_3$), 2.23 – 2.07 (m, 2H, CH_2CH$_2$N$_3$);
^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.3, 133.7, 131.9, 131.8, 128.7, 128.7, 128.3, 127.0, 122.1, 86.6, 84.5, 48.4, 40.7, 34.7;
IR (film): $\tilde{\nu}$ = 3293 (m), 3060 (w), 2927 (w), 2096 (s), 1637 (s), 1527 (s), 1443 (m), 1279 (m);
HRMS (ESI) calcd. for $C_{18}H_{16}N_4NaO^+$ [M+Na]$^+$ 327.1216; Found 327.1222.

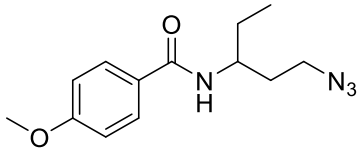
(*E*)-*N*-(5-Azido-1-phenylpent-1-en-3-yl)benzamide (**10l**).



Following GP C, starting from *N*-cyclopropylbenzamide **5a** (32.2 mg, 0.200 mmol), after diazidation step is finished, potassium trans-styryltrifluoroborate (73.6 mg, 0.400 mmol, 2.0 equiv.) and boron trifluoride etherate (100 µL, 0.800 mmol, 4.0 equiv.) were added to the crude. The reaction mixture was stirred at room temperature for 1 hour. (E)-*N*-(5-Azido-1-phenylpent-1-en-3-yl)benzamide **10l** (30.8 mg, 0.100 mmol, 50%) was obtained as a yellow gel after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.37 (silica, pentanes:ethyl acetate 3:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 – 7.77 (m, 2H, Ar*H*), 7.55 – 7.49 (m, 1H, Ar*H*), 7.48 – 7.41 (m, 2H, Ar*H*), 7.39 – 7.34 (m, 2H, Ar*H*), 7.34 – 7.28 (m, 2H, Ar*H*), 7.27 – 7.24 (m, 1H, Ar*H*), 6.62 (dd, *J* = 15.9, 1.3 Hz, 1H, vinylC*H*), 6.47 (d, *J* = 8.3 Hz, 1H, N*H*), 6.20 (dd, *J* = 15.9, 6.5 Hz, 1H, vinylC*H*), 4.97 (dqd, *J* = 8.0, 6.5, 1.4 Hz, 1H, NLC*H*), 3.59 – 3.41 (m, 2H, CH_2N$_3$), 2.04 (qd, *J* = 6.8, 3.0 Hz, 2H, CH_2CH$_2$N$_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.7, 136.2, 134.3, 131.7, 131.6, 128.6, 128.6, 128.1, 127.9, 126.9, 126.5, 49.7, 48.5, 34.1;
IR (film): $\tilde{\nu}$ = 3301 (w), 3027 (w), 2929 (w), 2096 (s), 1634 (s), 1532 (s), 1304 (m), 966 (m);
HRMS (ESI) calcd. for $C_{18}H_{18}N_4NaO^+$ [M+Na]$^+$ 329.1373; Found 329.1372.

***N*-(1-Azidopentan-3-yl)-4-methoxybenzamide** (**10m**).

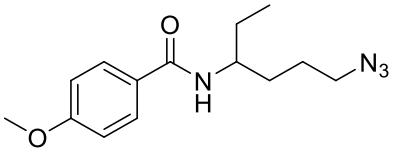


Following GP C, starting from *N*-cyclopropyl-4-methoxybenzamide **5b** (38.2 mg, 0.200 mmol), after diazidation step is finished, diethylzinc solution 1.0M in hexanes (0.30 mL, 0.30 mmol, 1.5 equiv.) was added to the crude. The reaction mixture was stirred at room temperature for 30 minutes. *N*-(1-Azidopentan-3-yl)-4-methoxybenzamide **10m** (44.6 mg, 0.170 mmol, 85%) was obtained as a beige solid after purification by column chromatography on silica using 2:1 pentanes:ethyl acetate as eluent.

R_f: 0.33 (silica, pentanes:ethyl acetate 2:1);
Mp: 73-76 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 – 7.68 (m, 2H, Ar*H*), 6.96 – 6.86 (m, 2H, Ar*H*), 6.03 (d, *J* = 9.0 Hz, 1H, N*H*), 4.17 – 4.09 (m, 1H, C*H*), 3.84 (s, 3H, OCH_3), 3.41 (tt, *J* = 12.3, 7.0 Hz, 2H, CH_2N$_3$), 1.90 (dtd, *J* = 14.1, 7.6, 4.2 Hz, 1H, CH_2CH$_2$N$_3$), 1.73 (dddd, *J* = 14.3, 8.9, 7.2, 5.8 Hz, 1H, CH_2CH$_2$N$_3$), 1.59 (ddt, *J* = 28.8, 13.8, 7.5 Hz, 2H, CH_2CH$_3$), 0.96 (t, *J* = 7.4 Hz, 3H, CH_3);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.8, 162.1, 128.6, 126.8, 113.7, 55.4, 49.1, 48.7, 33.9, 28.0, 10.4;
IR (film): $\tilde{\nu}$ = 3305 (m), 2964 (m), 2933 (m), 2096 (s), 1629 (s), 1506 (s), 1255 (s), 1029 (m), 841 (m);
HRMS (ESI) calcd. for $C_{13}H_{18}N_4NaO_2^+$ [M+Na]$^+$ 285.1322; Found 285.1317.

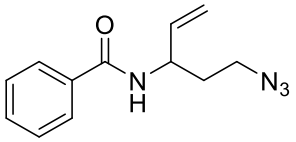
***N*-(6-Azidohexan-3-yl)-4-methoxybenzamide** (**11m**).



Following GP C, starting from *N*-cyclobutyl-4-methoxybenzamide **5t** (41.0 mg, 0.200 mmol), after diazidation step is finished, diethylzinc solution 1.0M in hexanes (0.30 mL, 0.30 mmol, 1.5 equiv.) was added to the crude. The reaction mixture was stirred at room temperature for 30 minutes. *N*-(6-Azidohexan-3-yl)-4-methoxybenzamide **11m** (43.3 mg, 0.157 mmol, 78%) was obtained as a white solid after purification by column chromatography on silica using 2:1 pentanes:ethyl acetate as eluent.

R_f: 0.28 (silica, pentanes:ethyl acetate 2:1);
Mp: 55-58 °C;
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.75 – 7.69 (m, 2H, Ar*H*), 6.94 – 6.91 (m, 2H, Ar*H*), 5.88 – 5.65 (m, 1H, N*H*), 4.08 (qd, *J* = 9.0, 4.5 Hz, 1H, C*H*), 3.85 (s, 3H, OCH_3), 3.33 (td, *J* = 6.3, 3.8 Hz, 2H, CH_2N$_3$), 1.68 (qtd, *J* = 15.2, 7.6, 3.3 Hz, 4H, CH_2), 1.55 – 1.46 (m, 2H, CH_2), 0.97 (t, *J* = 7.4 Hz, 3H, CH_3);
^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.8, 162.1, 128.5, 126.9, 113.7, 55.4, 51.3, 50.4, 32.2, 28.4, 25.5, 10.4;
IR (film): $\tilde{\nu}$ = 3307 (w), 2961 (w), 2933 (w), 2093 (s), 1627 (s), 1505 (s), 1250 (s), 1030 (m), 844 (m);
HRMS (ESI) calcd. for $C_{14}H_{20}N_4NaO_2^+$ [M+Na]$^+$ 299.1478; Found 299.1480.

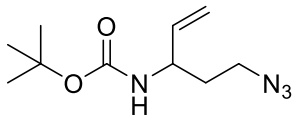
***N*-(5-Azidopent-1-en-3-yl)benzamide** (**10na**).



Following GP C, starting from *N*-cyclopropylbenzamide **5a** (32.2 mg, 0.200 mmol), after diazidation step is finished, vinylmagnesium bromide solution 1.0 M in THF (0.30 mL, 0.30 mmol, 1.5 equiv.) was added to the crude. The reaction mixture was stirred at room temperature for 30 minutes. *N*-(5-Azidopent-1-en-3-yl)benzamide **10na** (26.3 mg, 0.130 mmol, 57%) was obtained as a yellow oil after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.32 (silica, pentanes:ethyl acetate 3:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 – 7.76 (m, 2H, Ar*H*), 7.52 – 7.47 (m, 1H, Ar*H*), 7.44 – 7.39 (m, 2H, Ar*H*), 6.53 (d, *J* = 8.4 Hz, 1H, N*H*), 5.85 (ddd, *J* = 17.2, 10.4, 5.7 Hz, 1H, vinylC*H*), 5.32 – 5.15 (m, 2H, vinylCH_2), 4.79 (dddt, *J* = 14.6, 7.2, 5.6, 1.6 Hz, 1H, NC*H*), 3.44 (h, *J* = 5.7 Hz, 2H, CH_2N$_3$), 2.01 – 1.82 (m, 2H, CH_2CH$_2$N$_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.8, 136.9, 134.2, 131.5, 128.5, 126.9, 116.0, 49.9, 48.4, 33.5;
IR (film): $\tilde{\nu}$ = 3293 (w), 2929 (w), 2094 (s), 1632 (s), 1528 (s), 1290 (s), 921 (m);
HRMS (ESI) calcd. for $C_{12}H_{15}N_2O^+$ [M+H]$^+$ 203.1179; Found 203.1192.

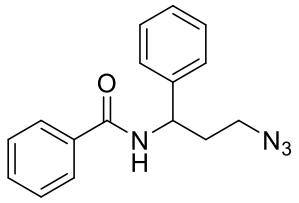
***tert*-Butyl (5-azidopent-1-en-3-yl)carbamate** (**10nb**).



Following GP C, starting from *tert*-butyl cyclopropylcarbamate **5p** (31.4 mg, 0.200 mmol), after diazidation step is finished, the crude was cooled down to -20 °C before vinylmagnesium bromide solution 1.0M in THF (0.30 mL, 0.30 mmol, 1.5 equiv.) was added dropwise. The reaction mixture was stirred at -20 °C for 2 hours. *tert*-Butyl (5-azidopent-1-en-3-yl)carbamate **10nb** (20.0 mg, 0.088 mmol, 44%) was obtained as a colorless oil after purification by column chromatography on silica using 10:1 pentanes:ethyl acetate as eluent.

R_f: 0.33 (silica, pentanes:ethyl acetate 10:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.76 (ddd, *J* = 16.6, 10.4, 5.7 Hz, 1H, vinylC*H*), 5.26 – 5.09 (m, 2H, vinylCH_2), 4.55 (s, 1H, N*H*), 4.26 – 4.15 (m, 1H, NC*H*), 3.41 – 3.32 (m, 2H, CH_2N_3), 1.79 (dh, *J* = 28.8, 6.9 Hz, 2H, C$H_2CH_2N_3$), 1.45 (s, 9H, C(CH_3)$_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.2, 137.7, 115.4, 79.7, 50.7, 48.3, 34.1, 28.4;
IR (film): $\tilde{\nu}$ = 3337 (w), 2978 (w), 2097 (s), 1690 (s), 1516 (s), 1366 (s), 1248 (s), 1168 (s);
HRMS (ESI) calcd. for $C_{10}H_{18}N_4NaO_2^+$ $[M+Na]^+$ 249.1322; Found 249.1325.

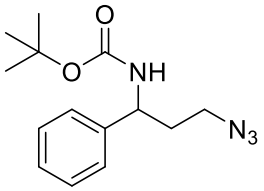
***N*-(3-Azido-1-phenylpropyl)benzamide** (**10oa**).



Following GP C, starting from *N*-cyclopropylbenzamide **5a** (32.2 mg, 0.200 mmol), after diazidation step is finished, phenylmagnesium bromide solution 3.0 M in diethyl ether (0.10 mL, 0.30 mmol, 1.5 equiv.) was added to the crude. The reaction mixture was stirred at room temperature for 30 minutes. *N*-(3-Azido-1-phenylpropyl)benzamide **10oa** (39.5 mg, 0.141 mmol, 71%) was obtained as a beige solid after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.45 (silica, pentanes:ethyl acetate 3:1);
Mp: 84-86 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 – 7.75 (m, 2H, Ar*H*), 7.53 – 7.48 (m, 1H, Ar*H*), 7.46 – 7.40 (m, 2H, Ar*H*), 7.37 (dtd, *J* = 7.5, 6.5, 1.6 Hz, 4H, Ar*H*), 7.33 – 7.27 (m, 1H, Ar*H*), 6.69 (d, *J* = 7.9 Hz, 1H, N*H*), 5.33 (td, *J* = 7.6, 6.2 Hz, 1H, NC*H*), 3.38 (t, *J* = 6.8 Hz, 2H, CH_2N_3), 2.29 – 2.09 (m, 2H, C$H_2CH_2N_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.7, 140.7, 134.2, 131.6, 129.0, 128.6, 127.8, 126.9, 126.5, 52.0, 48.6, 35.0;
IR (film): $\tilde{\nu}$ = 3291 (w), 3061 (w), 2093 (s), 1633 (s), 1529 (s), 1292 (s), 696 (s);
HRMS (ESI) calcd. for $C_{16}H_{16}N_4NaO^+$ $[M+Na]^+$ 303.1216; Found 303.1216.

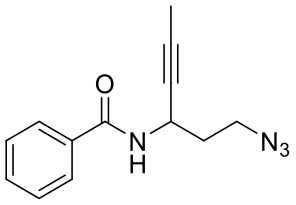
***tert*-Butyl (3-azido-1-phenylpropyl)carbamate** (**10ob**).



Following GP C, starting from *tert*-butyl cyclopropylcarbamate **5p** (31.4 mg, 0.200 mmol), after diazidation step is finished, the crude was cooled down to -20 °C before phenylmagnesium bromide solution 3.0M in diethyl ether (0.10 mL, 0.30 mmol, 1.5 equiv.) was added dropwise. The reaction mixture was stirred at -20 °C for 2 hours. *tert*-Butyl (3-azido-1-phenylpropyl)carbamate **10ob** (24.5 mg, 89.0 µmol, 44%) was obtained as a white solid after purification by column chromatography on silica using 10:1 pentanes:ethyl acetate as eluent.

R_f: 0.36 (silica, pentanes:ethyl acetate 10:1);
MP: 84-84.5 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 – 7.25 (m, 5H, Ar*H*), 5.01 – 4.83 (m, 1H, N*H*), 4.83 – 4.65 (m, 1H, NC*H*), 3.29 (tt, *J* = 9.8, 5.0 Hz, 2H, CH_2N_3), 2.13 – 1.88 (m, 2H, $CH_2CH_2N_3$), 1.42 (s, 9H, $C(CH_3)_3$);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.1, 141.5, 128.8, 127.6, 126.3, 79.7, 52.7, 48.5, 35.8, 28.3;
IR (film): $\tilde{\nu}$ = 3343 (w), 2977 (m), 2096 (s), 1696 (s), 1512 (m), 1167 (s), 700 (m);
HRMS (ESI) calcd. for $C_{14}H_{20}N_4NaO_2^+$ $[M+Na]^+$ 299.1478; Found 299.1486.

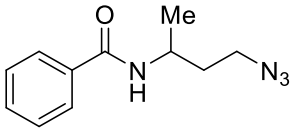
***N*-(1-Azidohex-4-yn-3-yl)benzamide** (**10p**).



Following GP C, starting from *N*-cyclopropylbenzamide **5a** (32.2 mg, 0.200 mmol), after diazidation step is finished, 1-propynylmagnesium bromide solution 0.5M in THF (0.60 mL, 0.30 mmol, 1.5 equiv.) was added to the crude. The reaction mixture was stirred at room temperature for 30 minutes. *N*-(1-Azidohex-4-yn-3-yl)benzamide **10p** (31.5 mg, 0.130 mmol, 65%) was obtained as a colorless oil after purification by column chromatography on silica using 4:1 pentanes:ethyl acetate as eluent.

R_f: 0.26 (silica, pentanes:ethyl acetate 4:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 – 7.74 (m, 2H, Ar*H*), 7.52 – 7.47 (m, 1H, Ar*H*), 7.45 – 7.39 (m, 2H, Ar*H*), 6.57 (d, *J* = 8.0 Hz, 1H, N*H*), 5.04 (dddd, *J* = 10.3, 8.1, 5.9, 2.4 Hz, 1H, NC*H*), 3.63 – 3.43 (m, 2H, CH_2N_3), 2.09 – 1.93 (m, 2H, $CH_2CH_2N_3$), 1.83 (d, *J* = 2.3 Hz, 3H, CH_3);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.3, 133.8, 131.7, 128.5, 127.0, 80.5, 76.8, 48.3, 40.3, 34.7, 3.5;
IR (film): $\tilde{\nu}$ = 3292 (w), 2920 (w), 2092 (s), 1634 (s), 1523 (s), 1263 (s), 1155 (m);
HRMS (ESI) calcd. for $C_{13}H_{14}N_4NaO^+$ $[M+Na]^+$ 265.1060; Found 265.1059.

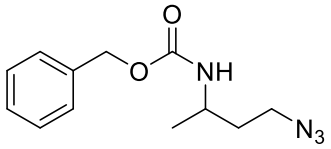
***N*-(4-Azidobutan-2-yl)benzamide** (**10qa**).



Following GP C, starting from *N*-cyclopropylbenzamide **5a** (32.2 mg, 0.200 mmol), after diazidation step is finished, methylmagnesium bromide solution 3.0 M in THF (0.10 mL, 0.30 mmol, 1.5 equiv.) was added to the crude. The reaction mixture was stirred at room temperature for 30 minutes. *N*-(4-Azidobutan-2-yl)benzamide **10qa** (22.6 mg, 0.104 mmol, 52%) was obtained as a pale yellow oil after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.29 (silica, pentanes:ethyl acetate 3:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 – 7.72 (m, 2H, Ar*H*), 7.51 – 7.46 (m, 1H, Ar*H*), 7.43 – 7.38 (m, 2H, Ar*H*), 6.27 (d, *J* = 8.4 Hz, 1H, N*H*), 4.31 (tdd, *J* = 8.1, 6.7, 5.4 Hz, 1H, NC*H*), 3.49 – 3.36 (m, 2H, CH_2N$_3$), 1.89 – 1.77 (m, 2H, CH_2CH$_2$N$_3$), 1.28 (d, *J* = 6.7 Hz, 3H, CH_3);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.9, 134.5, 131.4, 128.5, 126.8, 48.6, 43.9, 35.7, 20.8;
IR (film): $\tilde{\nu}$ = 3303 (w), 2971 (w), 2093 (s), 1633 (s), 1535 (s), 1289 (m), 694 (m);
HRMS (ESI) calcd. for $C_{11}H_{14}N_4NaO^+$ $[M+Na]^+$ 241.1060; Found 241.1062.

Benzyl (4-azidobutan-2-yl)carbamate (**10qb**).



Following GP C, starting from benzyl cyclopropylcarbamate **5q** (38.2 mg, 0.200 mmol), after diazidation step is finished, the crude was cooled down to -20 °C before methylmagnesium bromide solution 3.0 M in THF (0.10 mL, 0.30 mmol, 1.5 equiv.) was added drpwise. The reaction mixture was stirred at -20 °C for 2 hours. Benzyl (4-azidobutan-2-yl)carbamate **10qb** (23.0 mg, 93.0 µmol, 46%) was obtained as a colorless oil after purification by column chromatography on silica using 4:1 pentanes:ethyl acetate as eluent.

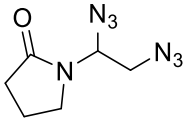
R_f: 0.45 (silica, pentanes:ethyl acetate 4:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 – 7.28 (m, 5H, Ar*H*), 5.09 (s, 2H, PhCH_2), 4.78 – 4.43 (m, 1H, N*H*), 3.85 (p, *J* = 7.1 Hz, 1H, NC*H*), 3.36 (t, *J* = 7.0 Hz, 2H, CH_2N$_3$), 1.71 (dq, *J* = 14.7, 7.0 Hz, 2H, CH_2CH$_2$N$_3$), 1.19 (d, *J* = 6.7 Hz, 3H, CH_3);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.7, 136.4, 128.5, 128.1, 128.1, 66.7, 48.4, 45.1, 36.0, 21.1;
IR (film): $\tilde{\nu}$ = 3326 (w), 2969 (m), 2096 (s), 1695 (s), 1529 (m), 1245 (s), 1072 (m);
HRMS (ESI) calcd. for $C_{12}H_{16}N_4NaO_2^+$ $[M+Na]^+$ 271.1165; Found 271.1167.

5. Scope of the 1,2-difunctionalization reaction

General Procedure D (GP D):
In a 12*75 mm Borosilicate glass tube, the corresponding enamide **12a** or enecarbamate **12b** (0.200 mmol, 1.0 equiv.), (Diacetoxyiodo)benzene (83.7 mg, 0.260 mmol, 1.3 equiv.) and CuTc (0.8 mg, 0.004 mmol, 0.02 equiv.) were measured on analytical balance. The tube was then closed with a rubber septum and sealed off with parafilm. Evacuate-refill cycle three times with nitrogen were performed to remove O_2 and extra-dry acetonitrile (2.0 mL, 0.1 M) was added under nitrogen atmosphere, followed by the addition of $TMSN_3$ (94% purity purchased from TCI, 62.0 µL, 0.440 mmol, 2.2 equiv.). The reaction mixture was stirred at room temperature for 10 minutes. Upon completion, the mixture was quenched by the addition of water (10 mL). The aqueous layer was then extracted with

dichloromethane (10 mL x 3). The organic extract was dried over Na_2SO_4, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, pentanes/EtOAc).

1-(1,2-Diazidoethyl)pyrrolidin-2-one (**13a**).

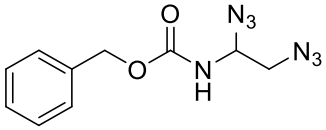


Following GP D, starting from 1-vinylpyrrolidin-2-one **12a** (22.2 mg, 0.200 mmol), 1-(1,2-diazidoethyl)pyrrolidin-2-one **13a** (36.9 mg, 0.189 mmol, 95%) was obtained as a colorless oil after purification by column chromatography on silica using 1:1 pentanes:ethyl acetate as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.80 (t, *J* = 6.6 Hz, 1H, NC*H*), 3.55 – 3.46 (m, 1H, NCH_2), 3.46 – 3.29 (m, 3H, NCH_2 + N_3CH_2), 2.69 – 2.34 (m, 2H, C(O)CH_2), 2.34 – 1.89 (m, 2H, CH_2).

^{1}H NMR data correspond to the reported values.[16]

Benzyl (1,2-diazidoethyl)carbamate (**13b**).



Following GP D, starting from benzyl vinylcarbamate **12b** (35.4 mg, 0.200 mmol), benzyl (1,2-diazidoethyl)carbamate **13b** (43.5 mg, 0.167 mmol, 83%) was obtained as a colorless oil after purification by column chromatography on silica using 6:1 pentanes:ethyl acetate as eluent.

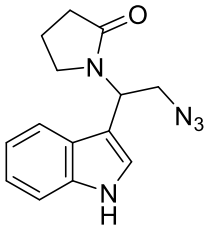
R_f: 0.42 (silica, pentanes:ethyl acetate 6:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 – 7.29 (m, 5H, Ar*H*), 5.74 (d, *J* = 9.7 Hz, 1H, N*H*), 5.47 (dt, *J* = 9.7, 4.2 Hz, 1H, NC*H*), 5.17 (s, 2H, benzylic CH_2), 3.47 (dd, *J* = 12.7, 4.0 Hz, 1H, CH_2N_3), 3.33 (dd, *J* = 12.7, 4.5 Hz, 1H, CH_2N_3);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.4, 135.4, 128.6, 128.5, 128.2, 67.7, 67.2, 53.6;
IR (film): $\tilde{\nu}$ = 3310 (w), 2097 (s), 1698 (s), 1508 (m), 1213 (s), 1045 (m);
HRMS (ESI) calcd. for $C_{10}H_{11}N_7NaO_2^+$ $[M+Na]^+$ 284.0866; Found 284.0867.

General Procedure E (GP E):
In a 12*75 mm Borosilicate glass tube, the corresponding enamide **12a** or enecarbamate **12b** (0.200 mmol, 1.0 equiv.), (Diacetoxyiodo)benzene (83.7 mg, 0.260 mmol, 1.3 equiv.) and CuTc (0.8 mg, 0.004 mmol, 0.02 equiv.) were measured on analytical balance. The tube was then closed with a rubber septum and sealed off with parafilm. Evacuate-refill cycle three times with nitrogen were performed to remove O_2 and extra-dry acetonitrile (2.0 mL, 0.1 M) was added under nitrogen atmosphere, followed by the addition of $TMSN_3$ (94% purity purchased from TCI, 62.0 µL, 0.440 mmol, 2.2 equiv.). The reaction mixture was stirred at room temperature for 10 minutes before nucleophile (and if needed the Lewis acid/base) was added. The nucleophilc substitution step was not sensitive to air and nucleophile can be added directly by injection if it is in liquid state or by removing the cap and adding from the top if it is in solid state. The progress of the reaction was monitored by TLC. Upon completion, the mixture was quenched by the addition of water (10 mL). The aqueous layer was then extracted

[16] Yuan, Y.-A.; Lu, D.-F.; Chen, Y.-R.; Xu, H. *Angew. Chem. Int. Ed.* **2016**, *55*, 534-538.

with dichloromethane (10 mL x 3). The organic extract was dried over Na_2SO_4, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, pentanes/EtOAc).

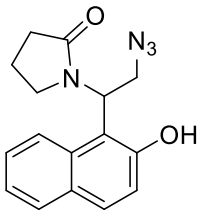
1-(2-Azido-1-(1*H*-indol-3-yl)ethyl)pyrrolidin-2-one (**14a**).



Following GP E, starting from 1-vinyl-2-pyrrolidinone **12a** (22.2 mg, 0.200 mmol), after diazidation step is finished, indole (35.1 mg, 0.300 mmol, 1.5 equiv.) and boron trifluoride etherate (50.0 µL, 0.400 mmol, 2.0 equiv.) were added to the crude. The reaction mixture was stirred at room temperature for 16 hours. 1-(2-Azido-1-(1*H*-indol-3-yl)ethyl)pyrrolidin-2-one **14a** (44.9 mg, 0.167 mmol, 83%) was obtained as a dark red solid after purification by column chromatography on silica using ethyl acetate as eluent.

R_f: 0.44 (silica, ethyl acetate);
Mp: 113-117 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.84 (s, 1H, indole N*H*), 7.60 (d, *J* = 7.9 Hz, 1H, Ar*H*), 7.40 (dt, *J* = 8.2, 0.9 Hz, 1H, Ar*H*), 7.22 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H, Ar*H*), 7.16 (dd, *J* = 2.6, 0.9 Hz, 1H, Ar*H*), 7.11 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H, Ar*H*), 5.81 (ddd, *J* = 8.9, 5.2, 0.9 Hz, 1H, NC*H*), 3.89 (dd, *J* = 12.5, 8.9 Hz, 1H, NCH_2), 3.79 (dd, *J* = 12.5, 5.3 Hz, 1H, NCH_2), 3.32 (ddd, *J* = 9.6, 8.4, 5.4 Hz, 1H, N_3CH_2), 2.98 (ddd, *J* = 9.6, 8.5, 5.9 Hz, 1H, N_3CH_2), 2.56 – 2.36 (m, 2H, C(O)CH_2), 2.04 – 1.90 (m, 1H, CH_2), 1.84 (dddd, *J* = 16.0, 9.5, 4.9, 3.3 Hz, 1H, CH_2);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.5, 136.1, 126.2, 122.7, 122.3, 120.1, 119.0, 111.4, 111.2, 51.1, 47.2, 43.4, 31.4, 17.8;
IR (film): $\tilde{\nu}$ = 3254 (w), 2095 (s), 1658 (s), 1421 (m), 1285 (m), 743 (m);
HRMS (ESI) calcd. for $C_{14}H_{16}N_5O^+$ $[M+H]^+$ 270.1349; Found 270.1358.

1-(2-Azido-1-(2-hydroxynaphthalen-1-yl)ethyl)pyrrolidin-2-one (**14b**).

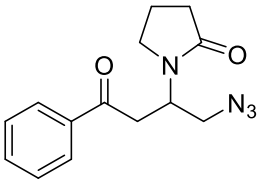


Following GP E, starting from 1-vinyl-2-pyrrolidinone **12a** (22.2 mg, 0.200 mmol), after diazidation step is finished, 2-naphthol (57.6 mg, 0.400 mmol, 2.0 equiv.) and boron trifluoride etherate (50.0 µL, 0.400 mmol, 2.0 equiv.) were added to the crude. The reaction mixture was stirred at room temperature for 16 hours. 1-(2-Azido-1-(2-hydroxynaphthalen-1-yl)ethyl)pyrrolidin-2-one **14b** (44.8 mg, 0.151 mmol, 76%) was obtained as a white solid after purification by recrystallization in dichloromethane and pentanes.

R_f: 0.23 (silica, pentanes:ethyl acetate 1:1);
Mp: 210-212 °C;

^{1}H NMR (500 MHz, Methanol-d_4): δ = 8.13 (d, *J* = 8.7 Hz, 1H, Ar*H*), 7.74 (t, *J* = 7.9 Hz, 2H, Ar*H*), 7.44 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H, Ar*H*), 7.29 (ddd, *J* = 7.9, 6.7, 1.0 Hz, 1H, Ar*H*), 7.10 (d, *J* = 8.9 Hz, 1H, Ar*H*), 6.13 (dd, *J* = 9.1, 5.4 Hz, 1H, NC*H*), 4.41 (dd, *J* = 12.7, 9.2 Hz, 1H, N_3CH_2), 3.97 (dd, *J* = 12.7, 5.3 Hz, 1H, N_3CH_2), 3.75 (ddd, *J* = 10.3, 8.5, 5.4 Hz, 1H, NCH_2), 3.16 (ddd, *J* = 10.3, 8.5, 6.0 Hz, 1H, NCH_2), 2.42 (ddd, *J* = 17.1, 9.6, 6.3 Hz, 1H, CH_2), 2.35 – 2.27 (m, 1H, CH_2), 2.00 (dddd, *J* = 15.4, 12.7, 5.9, 4.3 Hz, 1H, C(O)CH_2), 1.90 – 1.82 (m, 1H, C(O)CH_2);
^{13}C NMR (126 MHz, Methanol-d_4): δ = 177.6, 156.2, 135.2, 131.9, 130.5, 129.7, 128.2, 124.1, 123.5, 119.3, 113.5, 52.8, 51.7, 45.4, 32.0, 18.9;
IR (film): $\tilde{\nu}$ = 3064 (w), 2098 (s), 1646 (s), 1435 (m), 1243 (m), 818 (m);
HRMS (ESI) calcd. for $C_{16}H_{16}N_4NaO_2^+$ $[M+Na]^+$ 319.1165; Found 319.1166.

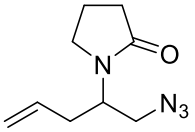
1-(1-Azido-4-oxo-4-phenylbutan-2-yl)pyrrolidin-2-one (**14c**).



Following GP E, starting from 1-vinyl-2-pyrrolidinone **12a** (22.2 mg, 0.200 mmol), after diazidation step is finished, trimethyl((1-phenylvinyl)oxy)silane (82.0 µL, 0.400 mmol, 2.0 equiv.) and TMSOTf (72.0 µL, 0.400 mmol, 2.0 equiv.) were added to the crude. The reaction mixture was stirred at room temperature for 16 hours. 1-(1-Azido-4-oxo-4-phenylbutan-2-yl)pyrrolidin-2-one **14c** (54.4 mg, 0.200 mmol, >99%) was obtained as a yellow solid after purification by column chromatography on silica using ethyl acetate as eluent.

R_f: 0.41 (silica, ethyl acetate);
Mp: 40-42 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 – 7.84 (m, 2H, Ar*H*), 7.59 – 7.50 (m, 1H, Ar*H*), 7.44 (dd, *J* = 8.4, 7.0 Hz, 2H, Ar*H*), 4.38 (tt, *J* = 8.0, 5.4 Hz, 1H, NC*H*), 3.83 (dd, *J* = 12.4, 8.4 Hz, 1H, N_3CH_2), 3.62 (dd, *J* = 17.1, 7.7 Hz, 1H, PhC(O)CH_2), 3.58 – 3.52 (m, 1H, NCH_2), 3.52 – 3.41 (m, 2H, N_3CH_2 + NCH_2), 3.20 (dd, *J* = 17.2, 5.8 Hz, 1H, PhC(O)CH_2), 2.39 – 2.26 (m, 2H, C(O)CH_2), 2.03 – 1.95 (m, 2H, CH_2);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.0, 175.6, 136.3, 133.5, 128.7, 128.0, 51.9, 50.1, 47.5, 38.1, 31.5, 18.6;
IR (film): $\tilde{\nu}$ = 2921 (w), 2099 (s), 1684 (s), 1285 (m), 757 (w);
HRMS (ESI) calcd. for $C_{14}H_{17}N_4O_2^+$ $[M+H]^+$ 273.1346; Found 273.1348.

1-(1-Azidopent-4-en-2-yl)pyrrolidin-2-one (**14d**).

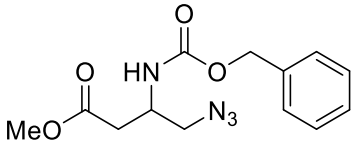


Following GP E, starting from 1-vinyl-2-pyrrolidinone **12a** (22.2 mg, 0.200 mmol), after diazidation step is finished, allyltrimethylsilane (63.0 µL, 0.400 mmol, 2.0 equiv.) and $TiCl_4$ (55.0 µL, 0.500 mmol, 2.5 equiv.) were added to the crude. The reaction mixture was stirred at room temperature for 16 hours. 1-(1-Azidopent-4-en-2-yl)pyrrolidin-2-one **14d** (26.4 mg, 0.136 mmol, 68%) was obtained as a yellow oil after purification by column chromatography on silica using pentanes:ethyl acetate 2:3 as eluent.

R_f: 0.25 (silica, pentanes:ethyl acetate 2:3);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.70 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H, vinyl C*H*), 5.17 – 5.01 (m, 2H, vinyl CH_2), 4.28 (qd, *J* = 7.7, 4.6 Hz, 1H, NC*H*), 3.45 (dd, *J* = 12.7, 7.9 Hz, 1H, N_3CH_2), 3.41 – 3.29 (m, 3H, N_3CH_2 + NCH_2), 2.39 (ddd, *J* = 8.4, 7.0, 2.6 Hz, 2H, C(O)CH_2), 2.32 (ddt, *J* = 8.0, 6.9, 1.4 Hz, 2H, allyl CH_2), 2.07 – 1.92 (m, 2H, CH_2);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.5, 133.6, 118.0, 52.2, 50.6, 43.6, 34.0, 31.2, 18.4;
IR (film): $\tilde{\nu}$ = 2976 (w), 2098 (s), 1681 (s), 1421 (m), 1284 (m), 920 (w);
HRMS (ESI) calcd. for $C_9H_{14}N_4NaO^+$ $[M+Na]^+$ 217.1060; Found 217.1065.

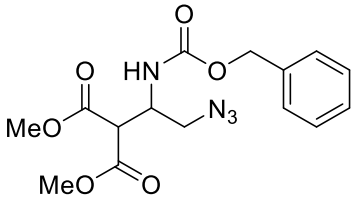
Methyl 4-azido-3-(((benzyloxy)carbonyl)amino)butanoate (**14e**).



Following GP E, starting from benzyl vinylcarbamate **12b** (35.4 mg, 0.200 mmol), after diazidation step is finished, *tert*-butyl[(1-methoxyvinyl)oxy]dimethylsilane (132 µL, 0.600 mmol, 3.0 equiv.) was added to the crude. The reaction mixture was stirred at room temperature for 4 hours. Methyl 4-azido-3-(((benzyloxy)carbonyl)amino)butanoate **14e** (54.7 mg, 0.187 mmol, 94%) was obtained as a colorless oil after purification by column chromatography on silica using pentanes:ethyl acetate 3:1 as eluent.

R_f: 0.35 (silica, pentanes:ethyl acetate 3:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 – 7.29 (m, 5H, Ar*H*), 5.42 (s, 1H, N*H*), 5.10 (s, 2H, benzylic CH_2), 4.17 (dt, *J* = 8.7, 5.5 Hz, 1H, NC*H*), 3.68 (s, 3H, OCH_3), 3.60 – 3.43 (m, 2H, N_3CH_2), 2.62 (dd, *J* = 6.0, 2.9 Hz, 2H, C(O)CH_2);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.2, 155.5, 136.1, 128.5, 128.2, 128.1, 66.9, 53.4, 51.9, 47.5, 35.8;
IR (film): $\tilde{\nu}$ = 3329 (w), 2953 (w), 2098 (s), 1697 (s), 1522 (s), 1214 (s), 1050 (s), 737 (m);
HRMS (ESI) calcd. for $C_{13}H_{16}N_4NaO_4^+$ $[M+Na]^+$ 315.1064; Found 315.1066.

Dimethyl 2-(2-azido-1-(((benzyloxy)carbonyl)amino)ethyl)malonate (**14f**).

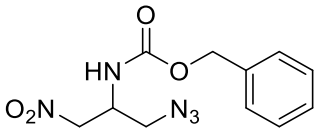


Following GP E, starting from benzyl vinylcarbamate **12b** (35.4 mg, 0.200 mmol), after diazidation step is finished, a solution of dimethyl malonate (46.0 µL, 0.400 mmol, 2.0 equiv.) and sodium hydride 60% dispersion mineral oil (16.0 mg, 0.400 mmol, 2.0 equiv.) in THF (0.5 mL) was added dropwise to the crude. The reaction mixture was stirred at room temperature for 10 minutes. Dimethyl 2-(2-azido-1-(((benzyloxy)carbonyl)amino)ethyl)malonate **14f** (69.4 mg, 0.198 mmol, 99%) was obtained as a colorless oil after purification by column chromatography on silica using pentanes:ethyl acetate 3:1 as eluent.

R_f: 0.30 (silica, pentanes:ethyl acetate 3:1);
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41 – 7.28 (m, 5H, Ar*H*), 5.77 (d, *J* = 9.6 Hz, 1H, N*H*), 5.10 (s, 2H, benzylic CH_2), 4.52 – 4.42 (m, 1H, NC*H*), 3.77 (d, *J* = 4.9 Hz, 1H, C*H*), 3.76 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 3.63 (dd, *J* = 12.3, 5.9 Hz, 1H, N_3CH_2), 3.45 (dd, *J* = 12.4, 6.8 Hz, 1H, N_3CH_2);
^{13}C NMR (151 MHz, $CDCl_3$): δ = 168.1, 167.4, 155.6, 136.1, 128.5, 128.2, 128.0, 67.0, 53.0, 52.9, 52.5, 51.9, 50.1;

IR (film): $\tilde{\nu}$ = 3361 (w), 2954 (w), 2101 (s), 1722 (s), 1506 (m), 1218 (s), 1059 (m);
HRMS (ESI) calcd. for $C_{15}H_{18}N_4NaO_6^+$ [M+Na]$^+$ 373.1119; Found 373.1115.

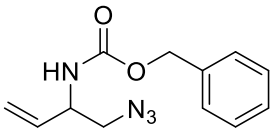
Benzyl (1-azido-3-nitropropan-2-yl)carbamate (**14g**).



Following GP E, starting from benzyl vinylcarbamate **12b** (35.4 mg, 0.200 mmol), after diazidation step is finished, CH_3NO_2 (22.0 µL, 0.400 mmol, 2.0 equiv.) was added to the crude followed by the addition of KO*t*Bu 1.0M in *t*BuOH (0.40 mL, 0.40 mmol, 2.0 equiv.). The reaction mixture was stirred at room temperature for 1 hour. Benzyl (1-azido-3-nitropropan-2-yl)carbamate **14g** (49.7 mg, 0.178 mmol, 89%) was obtained as a colorless oil after purification by column chromatography on silica using pentanes:ethyl acetate 3:1 as eluent.

R_f: 0.39 (silica, pentanes:ethyl acetate 3:1);
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.40 – 7.30 (m, 5H, Ar*H*), 5.36 (d, *J* = 8.5 Hz, 1H, N*H*), 5.12 (s, 2H, benzylic CH_2), 4.63 (dd, *J* = 13.3, 6.2 Hz, 1H, NO_2CH_2), 4.53 (dd, *J* = 13.3, 5.3 Hz, 1H, NO_2CH_2), 4.41 (dt, *J* = 8.8, 5.6 Hz, 1H, NC*H*), 3.67 (dd, *J* = 12.6, 5.0 Hz, 1H, N_3CH_2), 3.59 (dd, *J* = 12.6, 6.2 Hz, 1H, N_3CH_2);
^{13}C NMR (151 MHz, $CDCl_3$): δ = 155.3, 135.6, 128.6, 128.4, 128.2, 75.0, 67.5, 51.3, 48.7;
IR (film): $\tilde{\nu}$ = 3310 (w), 2106 (s), 1698 (s), 1554 (s), 1259 (m), 1063 (w);
HRMS (ESI) calcd. for $C_{11}H_{13}N_5NaO_4^+$ [M+Na]$^+$ 302.0860; Found 302.0865.

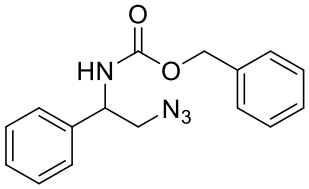
Benzyl (1-azidobut-3-en-2-yl)carbamate (**14h**).



Following GP E, starting from benzyl vinylcarbamate **12b** (35.4 mg, 0.200 mmol), after diazidation step is finished, the crude was cooled down to -20 °C before vinylmagnesium bromide solution 1.0 M in THF (0.30 mL, 0.30 mmol, 1.5 equiv.) was added dropwise. The reaction mixture was stirred at -20 °C for 2 hours. Benzyl (1-azidobut-3-en-2-yl)carbamate **14h** (25.2 mg, 0.102 mmol, 51%) was obtained as a colorless oil after purification by column chromatography on silica using pentanes:ethyl acetate 7:1 as eluent.

R_f: 0.33 (silica, pentanes:ethyl acetate 7:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 – 7.33 (m, 5H, Ar*H*), 5.82 (ddd, *J* = 17.3, 10.5, 5.5 Hz, 1H, vinyl C*H*), 5.34 – 5.20 (m, 2H, vinyl CH_2), 5.13 (s, 2H, PhCH_2), 5.08 – 4.79 (m, 1H, N*H*), 4.48 – 4.36 (m, 1H, NC*H*), 3.48 (qd, *J* = 12.5, 4.7 Hz, 2H, CH_2N_3);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.6, 136.1, 134.9, 128.5, 128.2, 128.1, 117.3, 67.0, 54.6, 52.7;
IR (film): $\tilde{\nu}$ = 3328 (w), 2099 (s), 1699 (s), 1522 (m), 1241 (m);
HRMS (ESI) calcd. for $C_{12}H_{14}N_4NaO_2^+$ [M+Na]$^+$ 269.1009; Found 269.1017.

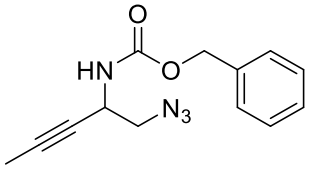
Benzyl (2-azido-1-phenylethyl)carbamate (**14i**).



Following GP E, starting from benzyl vinylcarbamate **12b** (35.4 mg, 0.200 mmol), after diazidation step is finished, the crude was cooled down to -20 °C before phenylmagnesium bromide solution 3.0 M in diethyl ether (0.10 mL, 0.30 mmol, 1.5 equiv.) was added dropwise. The reaction mixture was stirred at -20 °C for 2 hours. Benzyl (2-azido-1-phenylethyl)carbamate **14i** (35.2 mg, 0.119 mmol, 59%) was obtained as a colorless oil after purification by column chromatography on silica using pentanes:ethyl acetate 7:1 as eluent.

R_f: 0.34 (silica, pentanes:ethyl acetate 7:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 – 7.30 (m, 10H, Ar*H*), 5.41 (d, *J* = 8.0 Hz, 1H, N*H*), 5.12 (d, *J* = 5.4 Hz, 2H, PhCH_2), 5.02 – 4.83 (m, 1H, NC*H*), 3.65 (t, *J* = 5.8 Hz, 2H, CH_2N_3);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.6, 138.8, 136.1, 128.9, 128.5, 128.5, 128.2, 128.2, 126.5, 67.1, 55.5, 54.5;
IR (film): $\tilde{\nu}$ = 3319 (w), 2097 (s), 1693 (s), 1523 (m), 1241 (s), 1043 (m);
HRMS (ESI) calcd. for $C_{16}H_{16}N_4NaO_2^+$ $[M+Na]^+$ 319.1165; Found 319.1170.

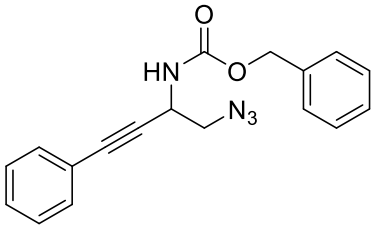
Benzyl (1-azidopent-3-yn-2-yl)carbamate (**14j**).



Following GP E, starting from benzyl vinylcarbamate **12b** (35.4 mg, 0.200 mmol), after diazidation step is finished, the crude was cooled down to -20 °C before 1-propynylmagnesium bromide solution 0.5 M in THF (0.60 mL, 0.30 mmol, 1.5 equiv.) was added dropwise. The reaction mixture was stirred at -20 °C for 2 hours. Benzyl (1-azidopent-3-yn-2-yl)carbamate **14j** (22.0 mg, 85.0 µmol, 43%) was obtained as a colorless oil after purification by column chromatography on silica using pentanes:ethyl acetate 7:1 as eluent.

R_f: 0.38 (silica, pentanes:ethyl acetate 7:1);
^{1}H NMR (400 MHz, $CDCl_3$; a mixture of rotamers in a ratio of 1:1 was observed, which was partly resolved): δ = 7.40 – 7.30 (m, 5H, Ar*H*), 5.13 (t, *J* = 5.9 Hz, 3H, PhCH_2 + N*H*), 4.63 (s, 1H, NC*H*), 3.43 (t, *J* = 5.2 Hz, 2H, CH_2N_3), 1.83 (d, *J* = 2.3 Hz, 3H, CH_3);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.2, 136.0, 128.5, 128.2, 128.1, 81.6, 75.3, 67.1, 55.1, 43.8, 3.5;
IR (film): $\tilde{\nu}$ = 3327 (w), 2969 (m), 2099 (s), 1700 (s), 1508 (s), 1237 (s), 1051 (m);
HRMS (ESI) calcd. for $C_{13}H_{14}N_4NaO_2^+$ $[M+Na]^+$ 281.1009; Found 281.1014.

Benzyl (1-azido-4-phenylbut-3-yn-2-yl)carbamate (**14k**).

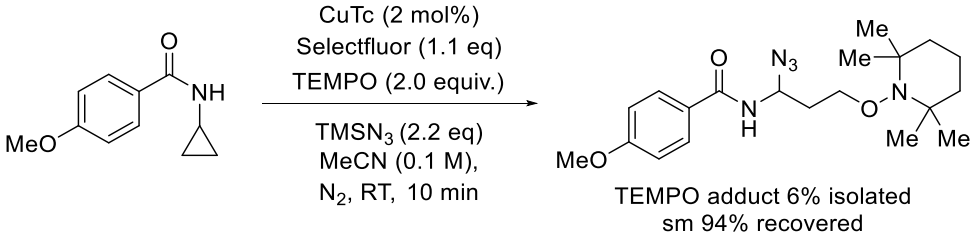


Following GP E, starting from benzyl vinylcarbamate **12b** (35.4 mg, 0.200 mmol), after diazidation step is finished, the crude was cooled down to -20 °C before 1-propynylmagnesium bromide solution 1.0 M in THF (0.30 mL, 0.30 mmol, 1.5 equiv.) was added dropwise. The reaction mixture was stirred at -20 °C for 2 hours. Benzyl (1-azido-4-phenylbut-3-yn-2-yl)carbamate **14k** (25.7 mg, 80.0 µmol, 40%) was obtained as a colorless oil after purification by column chromatography on silica using pentanes:ethyl acetate 7:1 as eluent.

R_f: 0.38 (silica, pentanes:ethyl acetate 7:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 – 7.29 (m, 10H, Ar*H*), 5.29 (d, *J* = 8.6 Hz, 1H, N*H*), 5.22 – 5.12 (m, 2H, PhCH_2), 4.94 (dd, *J* = 8.6, 4.6 Hz, 1H, NC*H*), 3.56 (qd, *J* = 12.2, 4.9 Hz, 2H, CH_2N_3);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.2, 135.9, 131.8, 128.8, 128.6, 128.3, 128.3, 128.2, 121.8, 85.0, 84.9, 67.3, 55.0, 44.4;
IR (film): $\tilde{\nu}$ = 3321 (w), 2101 (s), 1702 (s), 1518 (m), 1239 (s), 1046 (m);
HRMS (ESI) calcd. for $C_{18}H_{16}N_4NaO_2^+$ $[M+Na]^+$ 343.1165; Found 343.1165.

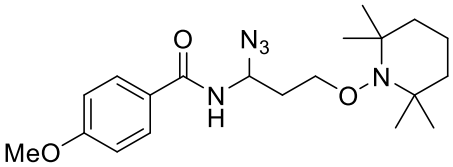
6. Mechanistic studies

6.1 Scheme S5 (TEMPO experiment)



Following GP B, starting from *N*-cyclopropyl-4-methoxybenzamide **5b** (38.2 mg, 0.200 mmol), TEMPO (62.4 mg, 0.400 mmol, 2.0 equiv.) was added since the beginning. After stirring for 10 minutes, *N*-(1-azido-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propyl)-4-methoxybenzamide **15** (5.0 mg, 0.012 mmol, 6%) was obtained as a white solid after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

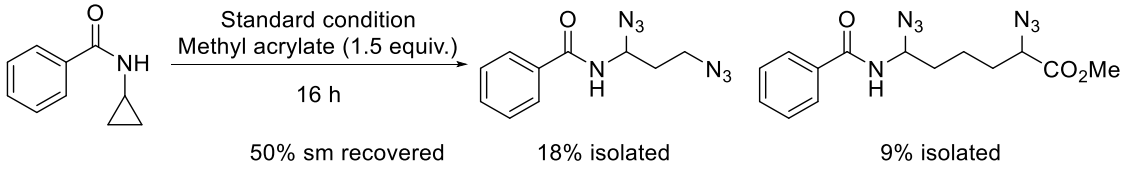
***N*-(1-Azido-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propyl)-4-methoxybenzamide** (**15**).



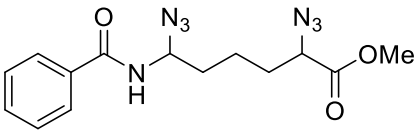
R_f: 0.44 (silica, pentanes:ethyl acetate 3:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 – 7.74 (m, 2H, Ar*H*), 7.51 (d, *J* = 8.5 Hz, 1H, N*H*), 6.98 – 6.88 (m, 2H, Ar*H*), 5.93 (ddd, *J* = 8.9, 5.6, 3.8 Hz, 1H, NC*H*), 4.21 (td, *J* = 9.9, 2.8 Hz, 1H, OCH_2), 3.91 – 3.87 (m, 1H, OCH_2), 3.86 (s, 3H, OCH_3), 2.04 (ddt, *J* = 14.1, 10.1, 3.9 Hz, 1H, CH_2CH$_2$O), 1.89 (dtd, *J* = 14.4, 5.2, 2.9 Hz, 1H, CH_2CH$_2$O), 1.57 – 1.45 (m, 6H, CH_2CH_2CH_2), 1.27 – 1.07 (m, 12H, 4 x CH_3);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.0, 162.6, 129.1, 125.6, 113.7, 72.7, 65.6, 59.9, 59.8, 55.4, 39.8, 39.6, 33.0, 33.0, 32.7, 20.8, 20.3, 17.0;
IR (film): $\tilde{\nu}$ = 3308 (w), 2931 (m), 2105 (s), 1644 (m), 1606 (m), 1502 (s), 1256 (s), 1030 (m);
HRMS (ESI) calcd. for $C_{20}H_{32}N_5O_3^+$ $[M+H]^+$ 390.2500; Found 390.2506.

6.2 Scheme S6 (Using Methyl acrylate as radical trapping reagent)



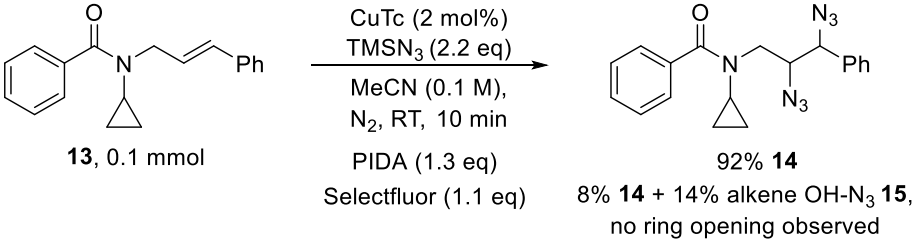
Methyl 2,6-diazido-6-benzamidohexanoate (**16**).



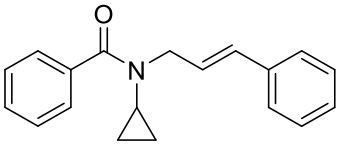
Following GP B, starting from *N*-cyclopropyl-benzamide **5a** (32.2 mg, 0.200 mmol), methyl acrylate (27.0 µL, 0.300 mmol, 1.5 equiv.) was added since the beginning. After stirring for 10 minutes, Methyl 2,6-diazido-6-benzamidohexanoate **16** (6.0 mg, 0.018 mmol, 9%) was obtained as a colorless oil after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.27 (silica, pentanes:ethyl acetate 3:1);
^{1}H NMR (400 MHz, $CDCl_3$; mixture of two diastereoisomers in a 1:1 ratio: the signals corresponding to the two diastereoisomers are not resolved): δ = 7.81 (dt, *J* = 8.4, 1.3 Hz, 2H, Ar*H*), 7.60 – 7.53 (m, 1H, Ar*H*), 7.50 – 7.44 (m, 2H, Ar*H*), 6.59 – 6.40 (m, 1H, N*H*), 5.75 (dt, *J* = 9.1, 6.7 Hz, 1H, NC*H*), 3.90 (dd, *J* = 8.2, 5.2 Hz, 1H, N_3C*H*), 3.80 (d, *J* = 3.5 Hz, 3H, OCH_3), 1.95 – 1.71 (m, 4H, CH_2), 1.62 – 1.55 (m, 2H, CH_2);
^{13}C NMR (101 MHz, $CDCl_3$; mixture of two diastereoisomers in a 1:1 ratio: the signals corresponding to the two diastereoisomers are partially resolved): δ = 170.7, 167.4, 133.0, 132.3, 128.8, 127.1, 66.7, 66.7, 61.7, 52.7, 34.1, 30.6, 21.4;
IR (film): $\tilde{\nu}$ = 3312 (w), 2954 (w), 2102 (s), 1741 (m), 1647 (m), 1523 (s), 1242 (m), 715 (m);
HRMS (ESI) calcd. for $C_{14}H_{17}N_7NaO_3^+$ $[M+Na]^+$ 354.1285; Found 354.1282.

6.3 Scheme S7 (Comparing reactivity of cyclopropyl ring with C=C bond)



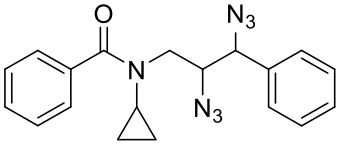
***N*-Cinnamyl-*N*-cyclopropylbenzamide** (**17**).



Following a modified version of a reported procedure,[17] to a solution of Cinnamyl bromide (709 mg, 3.60 mmol, 1.2 equiv.) and NaH (60% dispersion in mineral oil, 156 mg, 3.90 mmol, 1.3 equiv.) in THF (10 mL) was slowly added a solution of *N*-cyclopropyl-benzamide **5a** (483 mg, 3.00 mmol) in THF (5 mL) at 0 °C. The reaction mixture was stirred at room temperature for 16 hours. Upon completion, the mixture was quenched by addition of 1 N HCl (10 mL). The aqueous layer was then extracted with dichloromethane. The organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. *N*-Cinnamyl-*N*-cyclopropylbenzamide **17** was obtained as a yellow oil (773 mg, 2.79 mmol, 93%) after purification by column chromatography on silica using 3:1 pentanes:ethyl acetate as eluent.

R_f: 0.30 (silica, pentanes:ethyl acetate 3:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 – 7.46 (m, 2H, Ar*H*), 7.44 – 7.36 (m, 5H, Ar*H*), 7.36 – 7.30 (m, 2H, Ar*H*), 7.28 – 7.25 (m, 1H, Ar*H*), 6.59 (d, *J* = 15.9 Hz, 1H, vinyl C*H*), 6.34 (s, 1H, vinyl C*H*), 4.30 (s, 2H, NCH_2), 2.80 (tt, *J* = 6.9, 4.0 Hz, 1H, C*H*), 0.57 (d, *J* = 34.6 Hz, 4H, CH_2);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.4, 137.3, 136.7, 132.6, 129.5, 128.6, 128.0, 127.7, 127.2, 126.4, 125.2, 49.8, 31.6, 9.7;
IR (film): $\tilde{\nu}$ = 3025 (w), 1631 (s), 1402 (s), 1289 (m), 965 (m), 697 (s);
HRMS (ESI) calcd. for $C_{19}H_{19}NNaO^+$ $[M+Na]^+$ 300.1359; Found 300.1372.

***N*-Cyclopropyl-*N*-(2,3-diazido-3-phenylpropyl)benzamide** (**18**).

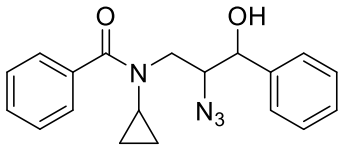


Following GP D, starting from *N*-Cinnamyl-*N*-cyclopropylbenzamide **17** (27.7 mg, 0.100 mmol), *N*-cyclopropyl-*N*-(2,3-diazido-3-phenylpropyl)benzamide **18** (39.2 mg, 0.092 mmol, 92%) was obtained as a colorless oil after purification by column chromatography on silica using 2:1 pentanes:ethyl acetate as eluent.

R_f: 0.59 (silica, pentanes:ethyl acetate 2:1);
^{1}H NMR (400 MHz, $CDCl_3$; mixture of two diastereoisomers in a 1.2:1 ratio: the signals corresponding to the two diastereoisomers are partially resolved): δ = 7.57 – 7.30 (m, 10H, Ar*H*), 4.66 (d, *J* = 6.4 Hz, 1H, benzylic C*H* minor), 4.55 (d, *J* = 6.9 Hz, 1H, benzylic C*H* major), 4.25 (q, *J* = 8.9 Hz, 1H, N_3C*H*), 3.94 (d, *J* = 13.9 Hz, 1H, NCH_2 minor), 3.64 (d, *J* = 13.3 Hz, 1H, NCH_2 major), 3.39 (d, *J* = 9.9 Hz, 1H, NCH_2 major), 3.35 (d, *J* = 9.9 Hz, 1H, NCH_2 minor), 2.95 – 2.78 (m, 1H, C*H*), 0.74 – 0.49 (m, 2H, CH_2), 0.49 – 0.32 (m, 2H, CH_2);
^{13}C NMR (101 MHz, $CDCl_3$; mixture of two diastereoisomers in a 1.2:1 ratio: the signals corresponding to the two diastereoisomers are partially resolved): δ = 172.8, 136.8, 136.7, 135.6, 135.3, 129.8, 129.8, 129.2, 129.1, 129.1, 129.0, 128.0, 128.0, 127.6, 127.4, 127.2, 127.1, 68.0, 67.3, 64.2, 63.8, 50.5, 49.5, 33.5, 11.1, 10.3;
IR (film): $\tilde{\nu}$ = 3062 (w), 2095 (s), 1631 (s), 1401 (m), 1248 (m), 699 (s);
HRMS (ESI) calcd. for $C_{19}H_{20}N_7O^+$ $[M+H]^+$ 362.1724; Found 362.1722.

[17] Park, Y.; Beak, P. *Tetrahedron* **1996**, *52*, 12333-12350.

***N*-(2-azido-3-hydroxy-3-phenylpropyl)-*N*-cyclopropylbenzamide (19).**

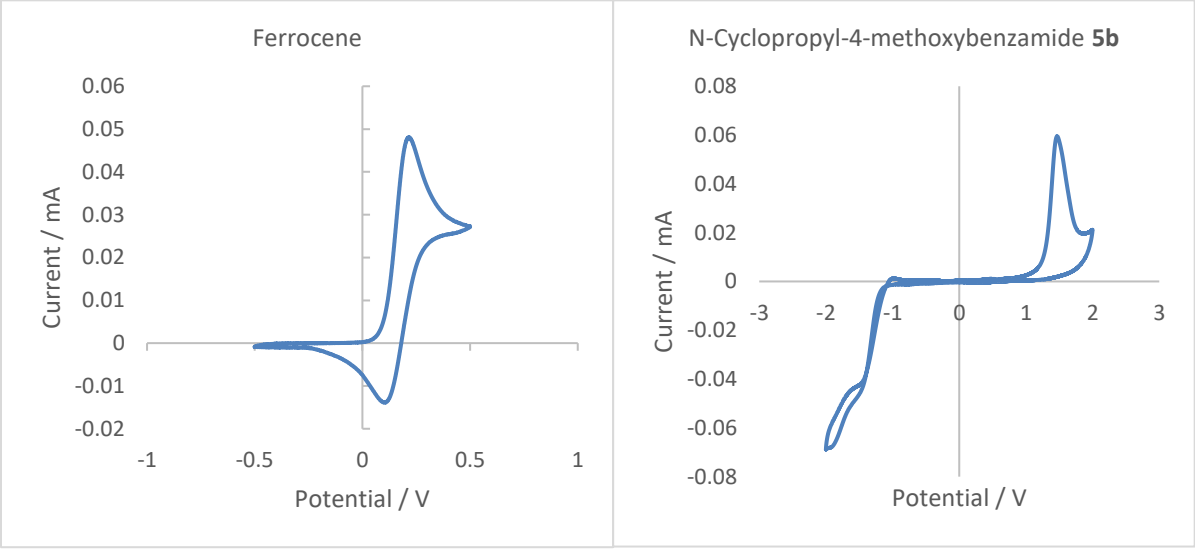


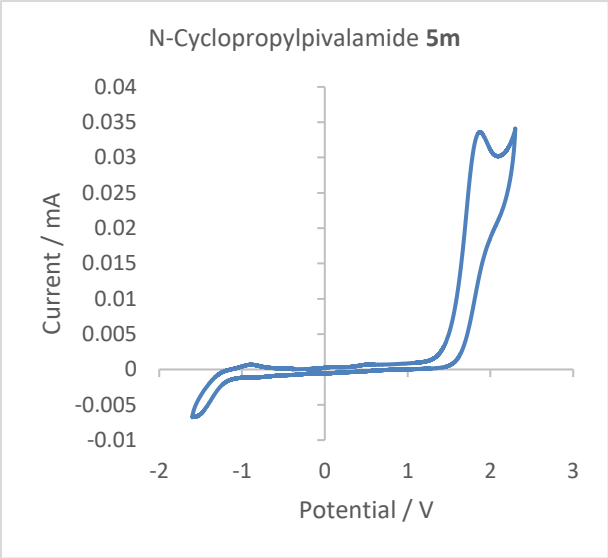
Following GP B, starting from *N*-Cinnamyl-*N*-cyclopropylbenzamide **17** (27.7 mg, 0.100 mmol), N-cyclopropyl-N-(2,3-diazido-3-phenylpropyl)benzamide **18** (3.0 mg, 0.008 mmol, 8%) and *N*-(2-azido-3-hydroxy-3-phenylpropyl)-*N*-cyclopropylbenzamide **19** (5.0 mg, 0.014 mmol, 14%, d.r. 4:1, only the major diastereoisomer was fully characterized) was obtained as a white solid after purification by preparative TLC on silica using 2:1 pentanes:ethyl acetate as eluent.

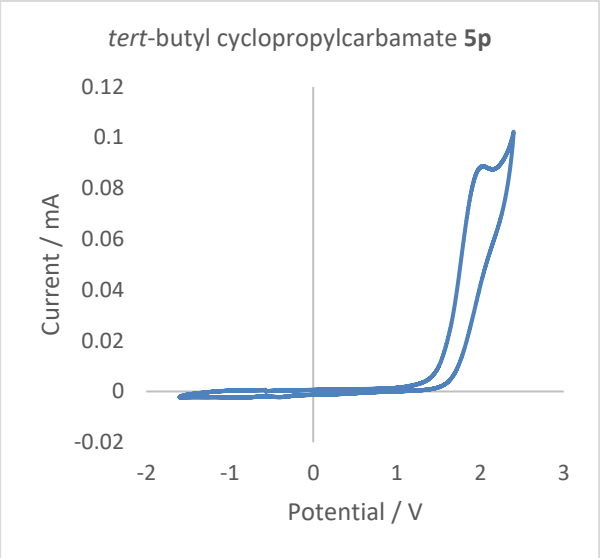
R_f: 0.27 (silica, pentanes:ethyl acetate 2:1);
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.54 – 7.31 (m, 10H, Ar*H*), 4.68 (d, *J* = 5.9 Hz, 1H, OC*H*), 4.08 (ddd, *J* = 8.2, 5.9, 1.9 Hz, 1H, N_3CH), 4.04 – 3.84 (m, 1H, NCH_2), 3.55 (dd, *J* = 14.3, 1.9 Hz, 1H, NCH_2), 2.78 (tt, *J* = 7.1, 4.0 Hz, 1H, NC*H*), 0.60 – 0.11 (m, 4H, CH_2);
^{13}C NMR (151 MHz, $CDCl_3$): δ = 175.1, 136.3, 136.3, 130.0, 128.8, 128.5, 128.0, 127.4, 127.4, 75.7, 68.7, 52.5, 34.1, 10.4, 8.7;
IR (film): $\tilde{\nu}$ = 3343 (w), 2924 (w), 2101 (s), 1614 (m), 1414 (m), 1287 (w), 700 (m);
HRMS (ESI) calcd. for $C_{19}H_{21}N_4O_2^+$ $[M+H]^+$ 337.1659; Found 337.1668.

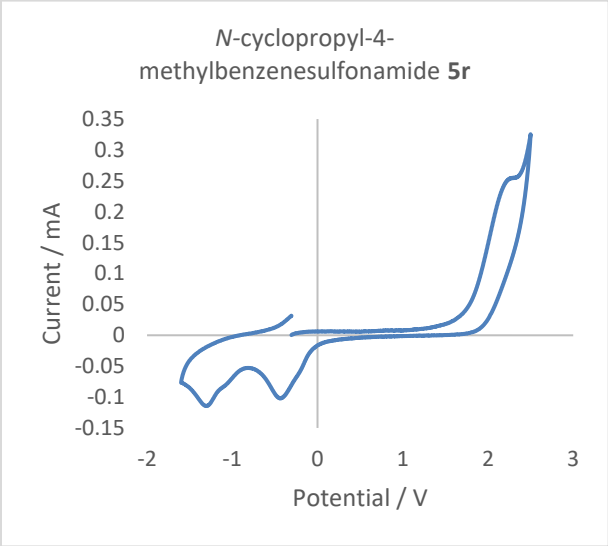
6.4 Cyclic voltammetry experiments

Procedure: Cyclic voltammetry was performed with a Biologic SP-150 Potentiostat, with a three-electrode cell configuration: a glassy carbon electrode as the working electrode, Pt wire as the counter electrode and a Ag/Ag^+ quasi-reference electrode with 0.01 M $AgBF_4$ in acetonitrile. Bu_4NPF_6 was employed as the electrolyte and acetonitrile was used as solvent.
Ferrocene was used to calibrate the potential of Ag/Ag^+ quasi-reference electrode.





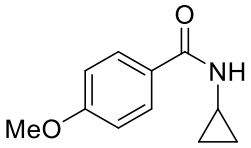




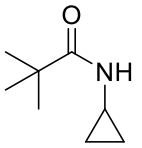
Result:

$E_{1/2}^{red}$(**5b**)= +1.67 V vs SCE in MeCN; $E_{1/2}^{red}$(**5m**)= +1.92 V vs SCE in MeCN;

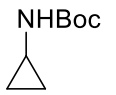
$E_{1/2}^{red}$(**5p**)= +2.0 V vs SCE in MeCN; $E_{1/2}^{red}$(**5r**)= +2.23 V vs SCE in MeCN.



$E_{1/2}^{red}$ = +1.67 V



$E_{1/2}^{red}$ = +1.92 V

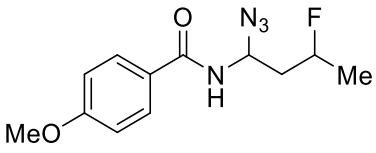


$E_{1/2}^{red}$ = +2.0 V

$E_{1/2}^{red}$ = +2.23 V

6.5 Fluorination byproduct

***N*-(1-Azido-3-fluorobutyl)-4-methoxybenzamide (20)**

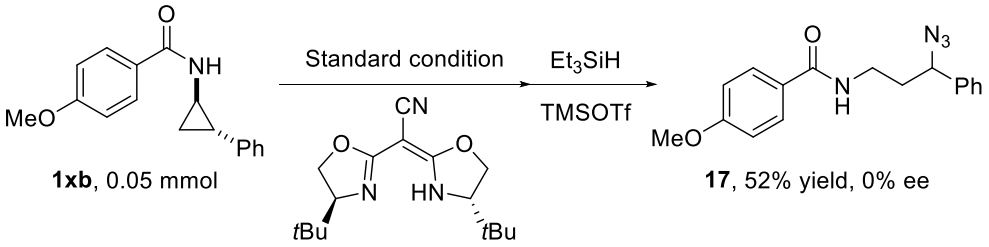


Following modified GP B, starting from 4-methoxy-*N*-(trans-2-methylcyclopropyl)benzamide **5xa** (41.0 mg, 0.200 mmol) with insufficient amount of CuTc catalyst, *N*-(1-Azido-3-fluorobutyl)-4-methoxybenzamide **20** can be observed, which co-eluted with diazidation product **6xa** during purification by column chromatography. Therefore, no pure **20** was obtained, but its existence was confirmed by:

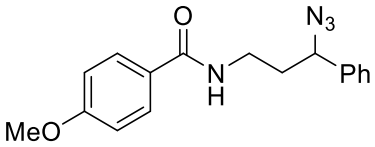
^{19}F NMR (376 MHz, $CDCl_3$): δ = -171.6, -174.0;

HRMS: (ESI) calcd. for $C_{12}H_{15}FN_4NaO_2^+$ $[M+Na]^+$ 289.1071; Found 289.1072.

6.6 Scheme S8 (Asymmetric azidation attempts)



***N*-(3-azido-3-phenylpropyl)-4-methoxybenzamide** (**21**).



Following modified GP C, CuTc (0.40 mg, 2.0 µmol, 0.04 equiv.), 4-methoxy-*N*-(trans-2-phenylcyclopropyl)benzamide **5xb** (13.4 mg, 50.0 µmol) and (*E*)-2-((*S*)-4-(*tert*-butyl)-4,5-dihydrooxazol-2-yl)-2-((*S*)-4-(tert-butyl)oxazolidin-2-ylidene)acetonitrile (0.73 mg, 2.5 µmol, 0.05 equiv.) were measured on analytical balance. The tube was then closed with a rubber septum and sealed off with parafilm. Evacuate-refill cycle three times with nitrogen were performed to remove O_2 and extra-dry acetonitrile (0.5 mL) was added under nitrogen atmosphere, followed by the addition of $TMSN_3$ (94% purity purchased from TCI, 16.0 µL, 0.110 mmol, 2.2 equiv.). The mixture was stirred at room temperature for 20 minutes before a solution of Selectfluor (19.5 mg, 55.0 µmol, 1.1 equiv.) in acetonitrile (0.5 mL) was added by syringe. The reaction mixture was stirred at room temperature for 10 minutes. After the diazidation step is finished, triethylsilane (8.0 µL, 0.050 mmol, 1.0 equiv.) and TMSOTf (9.0 µL, 0.050 mmol, 1.0 equiv.) were added to the crude. The reaction mixture was stirred at room temperature for 2 hours. *N*-(3-azido-3-phenylpropyl)-4-methoxybenzamide **21** was obtained as a white solid (8.0 mg, 0.026 mmol, 52%) after purification by preparative TLC on silica using 1:1 pentanes:ethyl acetate as eluent. Chiral HPLC conditions: er = 49.8:50.2; Chiralpak IB 80:20 Hexane/ iPrOH, 1.0 mL/min, 31 min. tr (minor) = 20.6 min. and tr (major) = 24.9 min. λ = 260 cm^{-1}.

R_f: 0.28 (silica, pentanes:ethyl acetate 1:1);

Mp: 81-82 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 – 7.61 (m, 2H, Ar*H*), 7.46 – 7.37 (m, 2H, Ar*H*), 7.37 – 7.30 (m, 3H, Ar*H*), 6.97 – 6.83 (m, 2H, Ar*H*), 6.32 – 6.18 (m, 1H, N*H*), 4.60 (t, *J* = 7.1 Hz, 1H, N_3CH), 3.85 (s, 3H, OCH_3), 3.59 – 3.45 (m, 2H, NCH_2), 2.16 – 2.02 (m, 2H, CH_2);

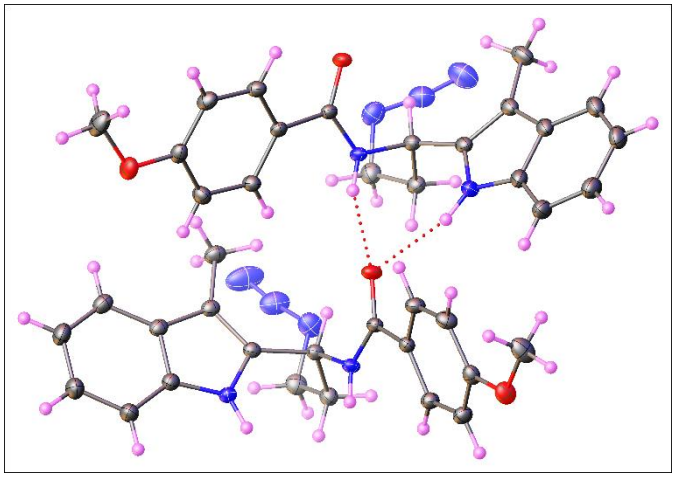
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.9, 162.2, 139.0, 129.0, 128.6, 128.6, 126.8, 126.6, 113.7, 64.8, 55.4, 37.4, 35.9;

IR (film): $\tilde{\nu}$ = 3312 (w), 2932 (w), 2095 (s), 1630 (m), 1503 (s), 1254 (s), 1030 (m);

HRMS (ESI) calcd. for $C_{17}H_{18}N_4NaO_2^+$ $[M+Na]^+$ 333.1322; Found 333.1328.

7. X-ray structure of xx

Crystal Data and Experimental (**10a**, Thermal ellipsoids are shown at the 50% level)

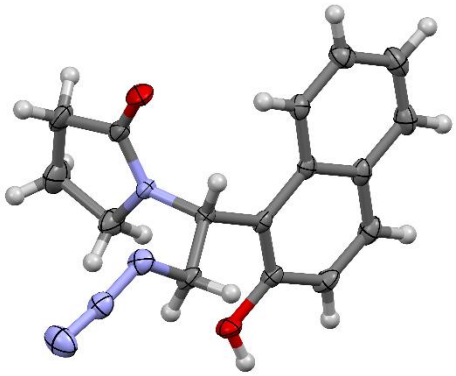


A single crystals was grown by slow diffusion of the solvent of **10a** in $CDCl_3$. Supplementary crystallographic data for this compound have been deposited at Cambridge Crystallographic Data Centre (2085561) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Experimental. Single colourless prism crystals of **10a** (**mw-4-16-4**) were used as supplied. A suitable crystal with dimensions 0.34 × 0.09 × 0.07 mm^3 was selected and mounted on a SuperNova, Dual, Cu at home/near, Atlas diffractometer. The crystal was kept at a steady T = 140.01(10) K during data collection. The structure was solved with the ShelXT 2018/2 (Sheldrick, 2015) solution program using dual methods and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F^2.

Crystal Data. $C_{20}H_{21}N_5O_2$, M_r = 363.42, monoclinic, $P2_1/c$ (No. 14), a = 9.77714(16) Å, b = 28.6855(5) Å, c = 13.2347(2) Å, β = 91.2051(16)°, α = γ = 90°, V = 3711.00(11) $Å^3$, T = 140.01(10) K, Z = 8, Z' = 2, μ(Cu K_α) = 0.708, 31976 reflections measured, 7180 unique (R_{int} = 0.0364) which were used in all calculations. The final wR_2 was 0.1198 (all data) and R_1 was 0.0427 (I≥2 σ(I)).

Crystal Data and Experimental (**14b**, Thermal ellipsoids are shown at the 50% level)



After purification of xx by recrystallization in dichloromethane and pentanes, single crystals were obtained and measured directly. Supplementary crystallographic data for this compound have been deposited at Cambridge Crystallographic Data Centre (2085562) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Experimental. Single clear pale colourless prism crystals of **14b** (**mw-4-143-1**) were used as supplied. A suitable crystal with dimensions 0.19 × 0.14 × 0.08 mm^3 was selected and mounted on a SuperNova, Dual, Cu at home/near, Atlas diffractometer. The crystal was kept at a steady T = 140.00(10) K during data collection. The structure was solved with the ShelXT (Sheldrick, 2015) solution program using dual methods and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F^2.

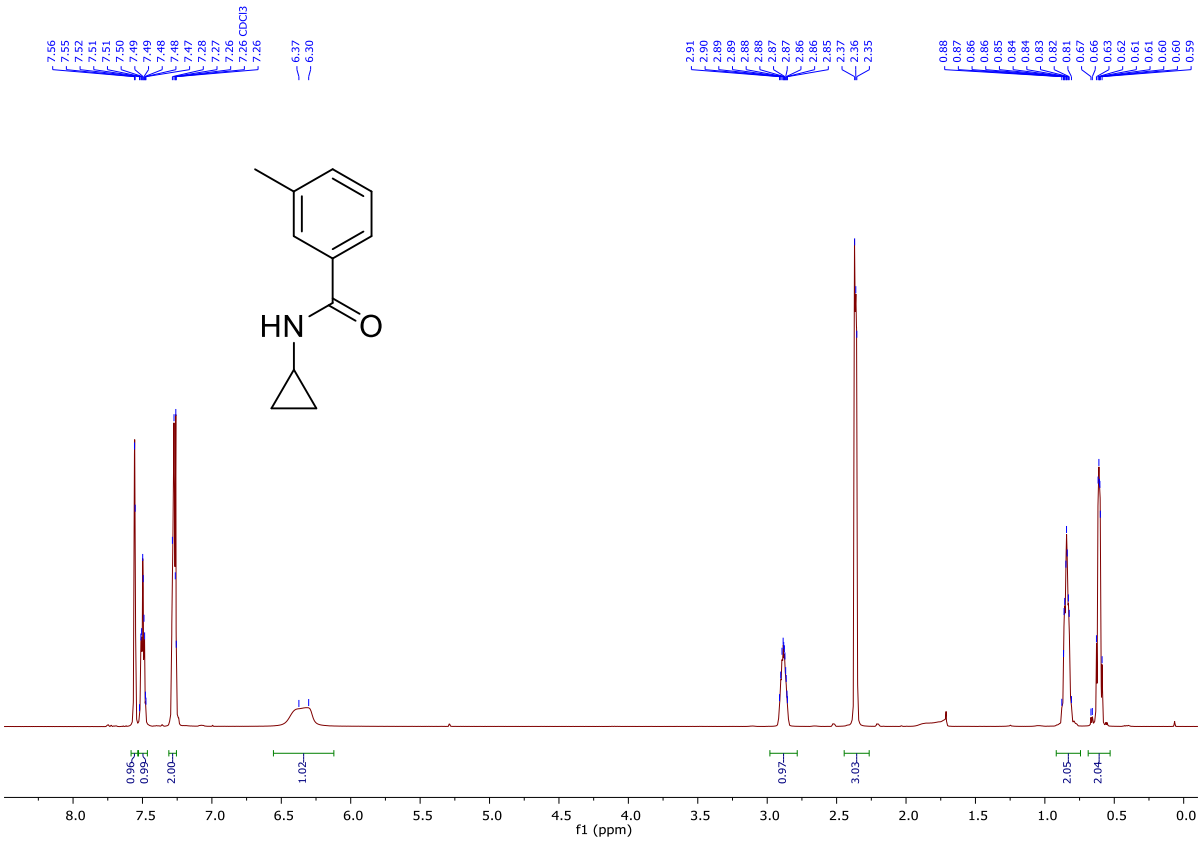
Crystal Data. $C_{16}H_{16}N_4O_2$, M_r = 296.33, monoclinic, $P2_1/c$ (No. 14), a = 8.19152(19) Å, b = 21.2742(5) Å, c = 8.40359(19) Å, β = 97.861(2)°, $\alpha = \gamma$ = 90°, V = 1450.71(6) Å^3, T = 140.00(10) K, Z = 4, Z' = 1, μ(Cu K$_\alpha$) = 0.758, 8484 reflections measured, 3016 unique (R_{int} = 0.0166) which were used in all calculations. The final wR_2 was 0.1009 (all data) and R_1 was 0.0363 (I≥2 σ(I)).

Compound	**10a** (**MW-4-16-4**)	**Compound**	**14b** (**mw-4-143-1**)
Formula	$C_{20}H_{21}N_5O_2$	Formula	$C_{16}H_{16}N_4O_2$
$D_{calc.}$/ g cm^{-3}	1.301	$D_{calc.}$/ g cm^{-3}	1.357
μ/mm^{-1}	0.708	μ/mm^{-1}	0.758
Formula Weight	363.42	Formula Weight	296.33
Colour	colourless	Colour	clear pale colourless
Shape	prism	Shape	prism
Size/mm^3	0.34×0.09×0.07	Size/mm^3	0.19×0.14×0.08
T/K	140.01(10)	T/K	140.00(10)
Crystal System	monoclinic	Crystal System	monoclinic
Space Group	$P2_1/c$	Space Group	$P2_1/c$
a/Å	9.77714(16)	a/Å	8.19152(19)
b/Å	28.6855(5)	b/Å	21.2742(5)
c/Å	13.2347(2)	c/Å	8.40359(19)
α/°	90	α/°	90
β/°	91.2051(16)	β/°	97.861(2)
γ/°	90	γ/°	90
V/Å^3	3711.00(11)	V/Å^3	1450.71(6)
Z	8	Z	4
Z'	2	Z'	1
Wavelength/Å	1.54184	Wavelength/Å	1.54184
Radiation type	Cu$K\alpha$	Radiation type	Cu K$_\alpha$
Θ_{min}/°	3.081	Θ_{min}/°	4.156
Θ_{max}/°	71.750	Θ_{max}/°	76.485
Measured Refl's.	31976	Measured Refl's.	8484
Indep't Refl's	7180	Indep't Refl's	3016
Refl's I≥2σ(I)	5795	Refl's I≥2 σ(I)	2720
R_{int}	0.0364	R_{int}	0.0166
Parameters	507	Parameters	264
Restraints	0	Restraints	0
Largest Peak/e Å^{-3}	0.196	Largest Peak	0.279
Deepest Hole/e Å^{-3}	-0.262	Deepest Hole	-0.177
GooF	1.030	GooF	1.024
wR_2 (all data)	0.1198	wR_2 (all data)	0.1009
wR_2	0.1110	wR_2	0.0975
R_1 (all data)	0.0541	R_1 (all data)	0.0403
R_1	0.0427	R_1	0.0363

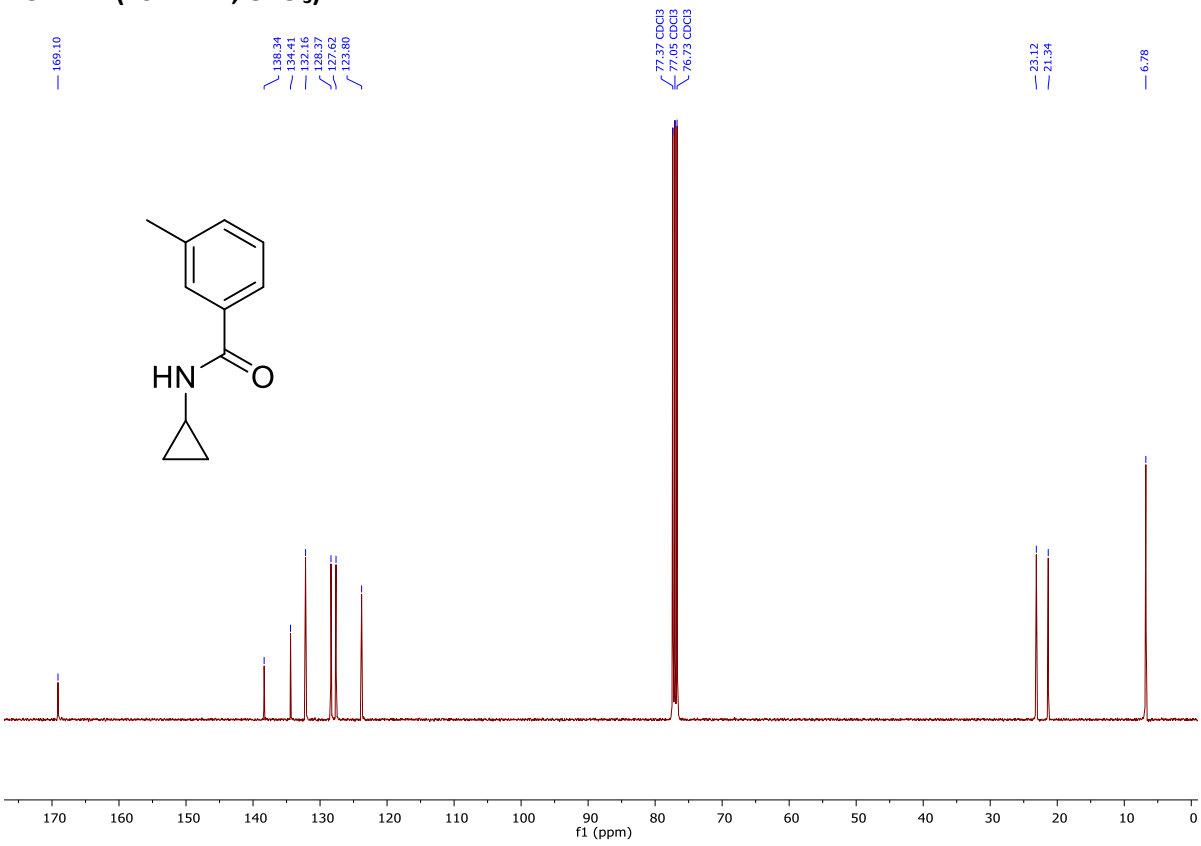
8. NMR spectra of new compounds

_N_-Cyclopropyl-3-methylbenzamide (5j)

^{1}H-NMR (400 MHz, $CDCl_3$)

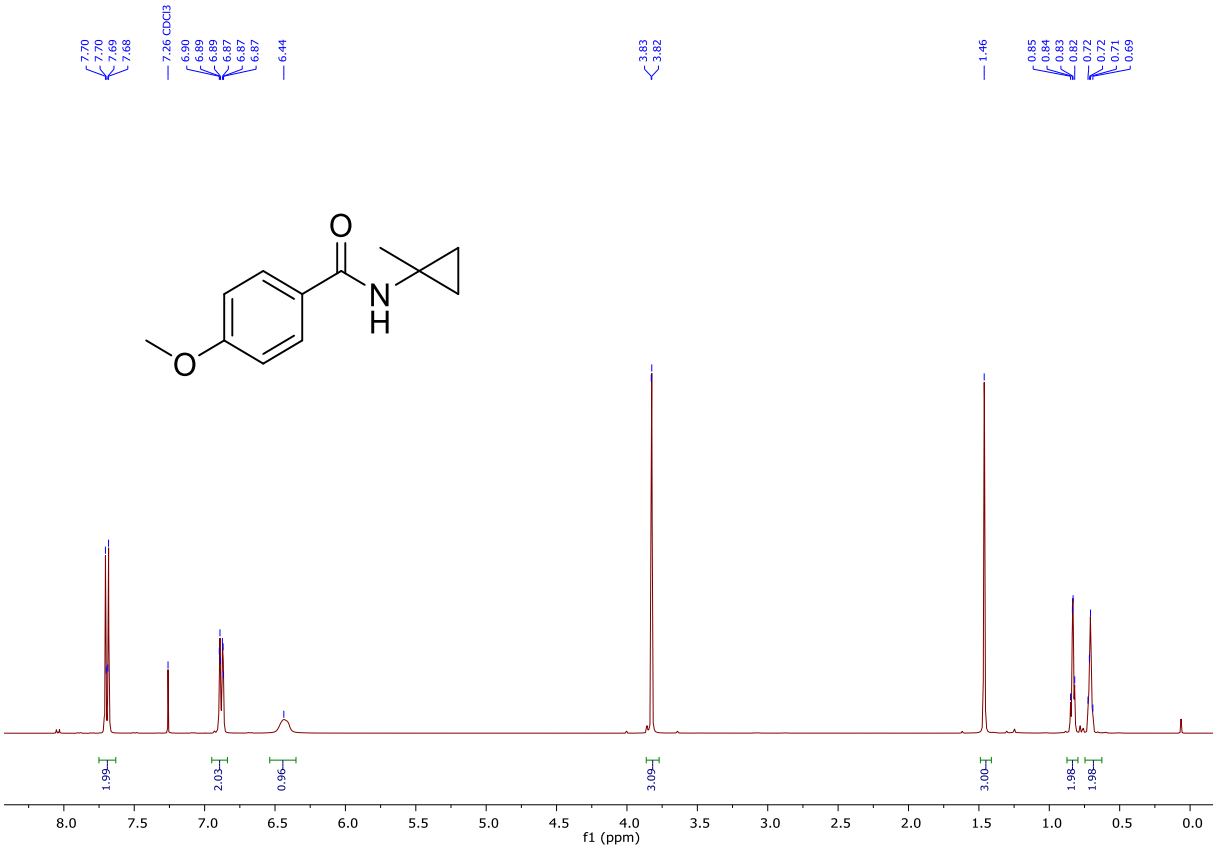


^{13}C-NMR (101 MHz, $CDCl_3$)

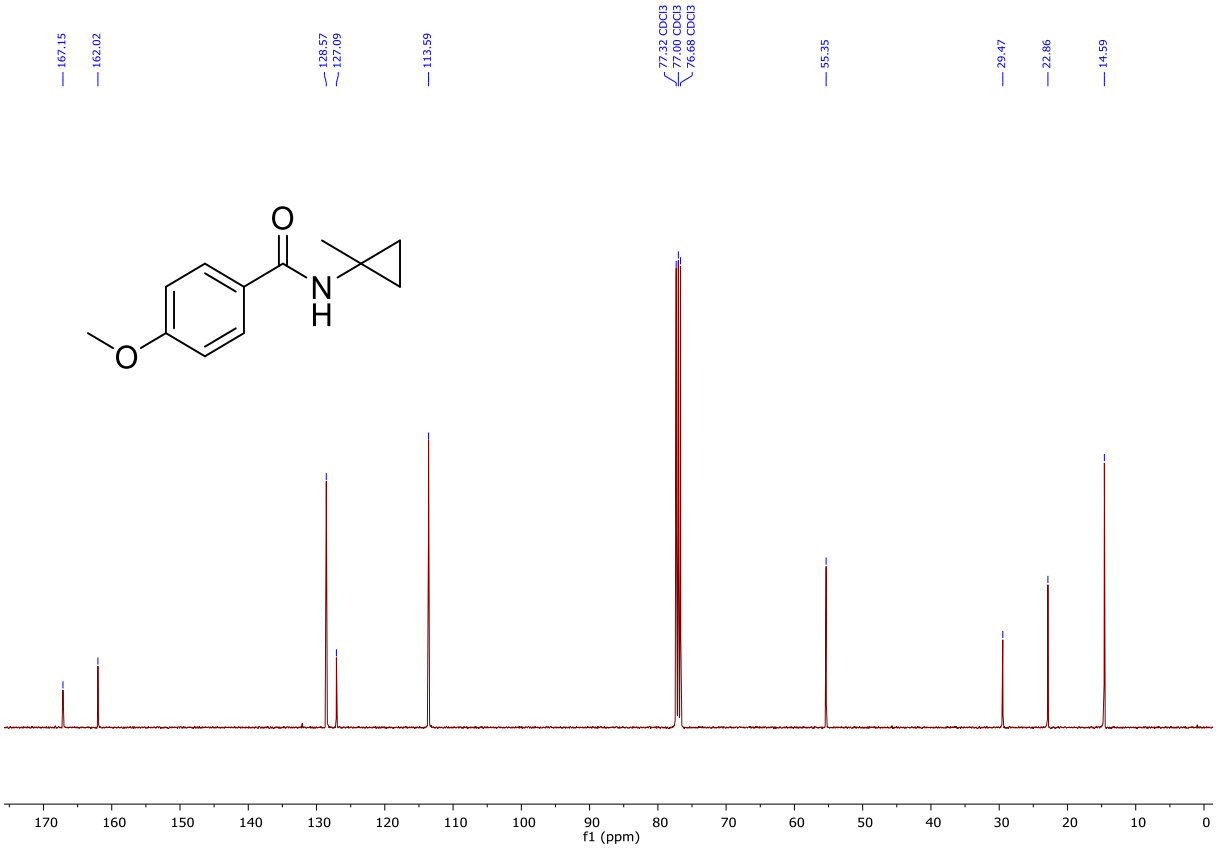


4-Methoxy-*N*-(1-methylcyclopropyl)benzamide (5w)

^{1}H-NMR (400 MHz, $CDCl_3$)

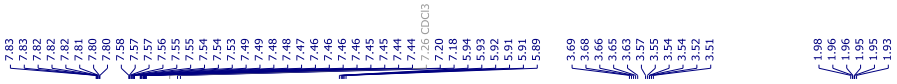


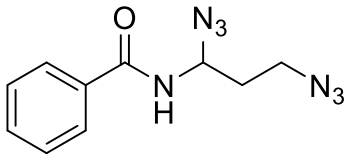
^{13}C-NMR (101 MHz, $CDCl_3$)

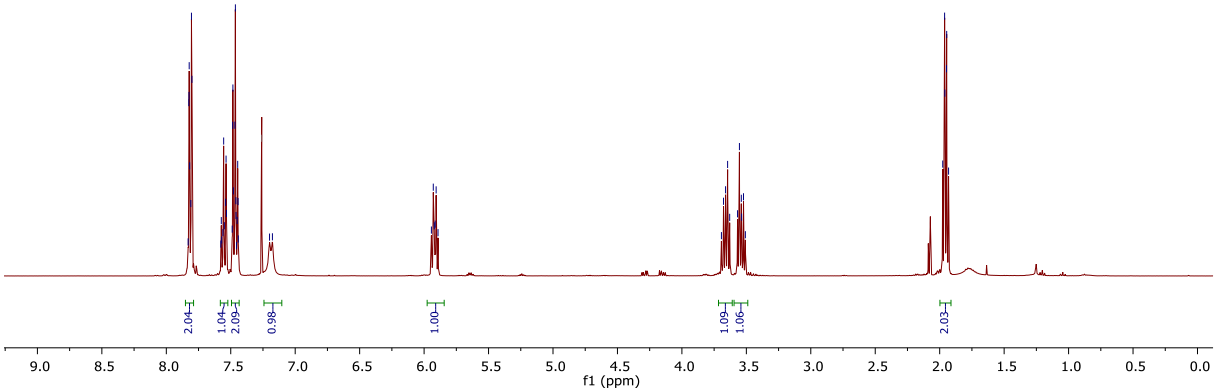


***N*-(1,3-Diazidopropyl)benzamide (6a)**

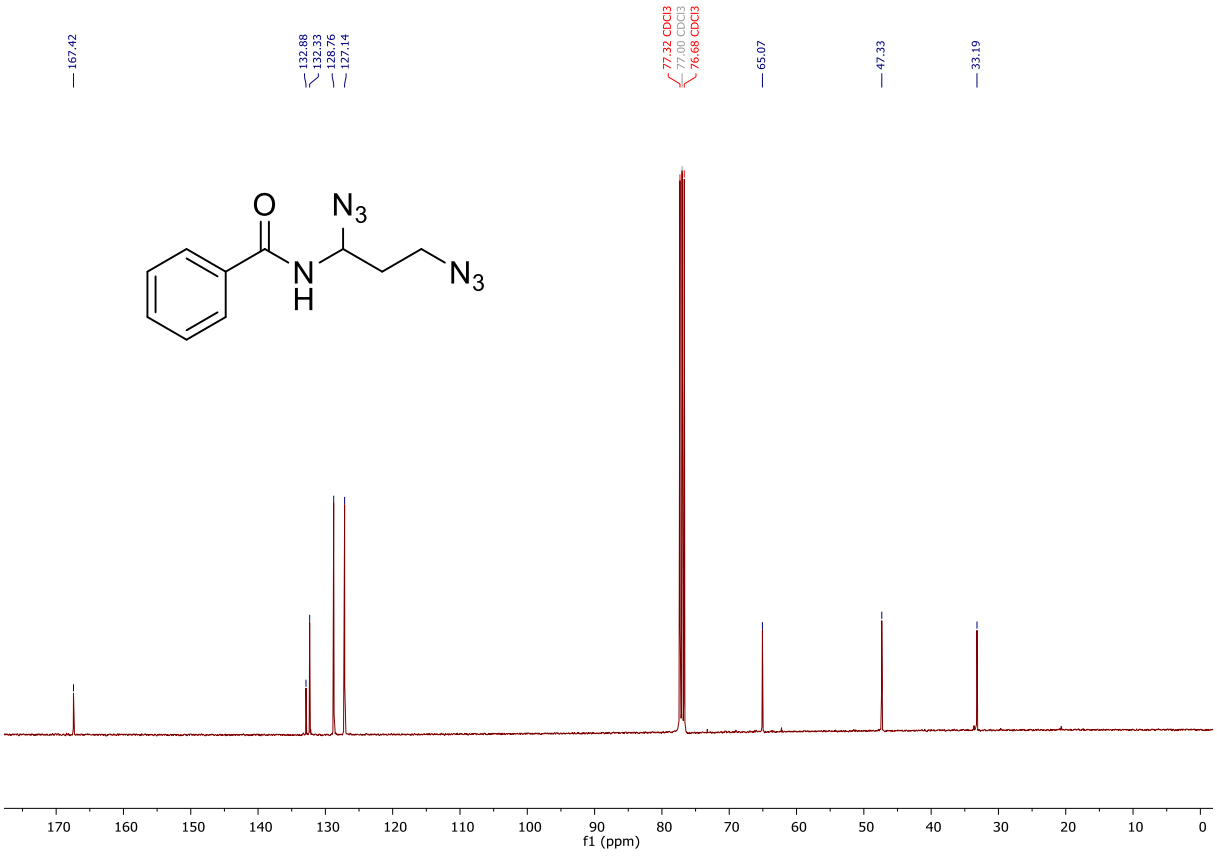
^{1}H-NMR (400 MHz, $CDCl_3$)





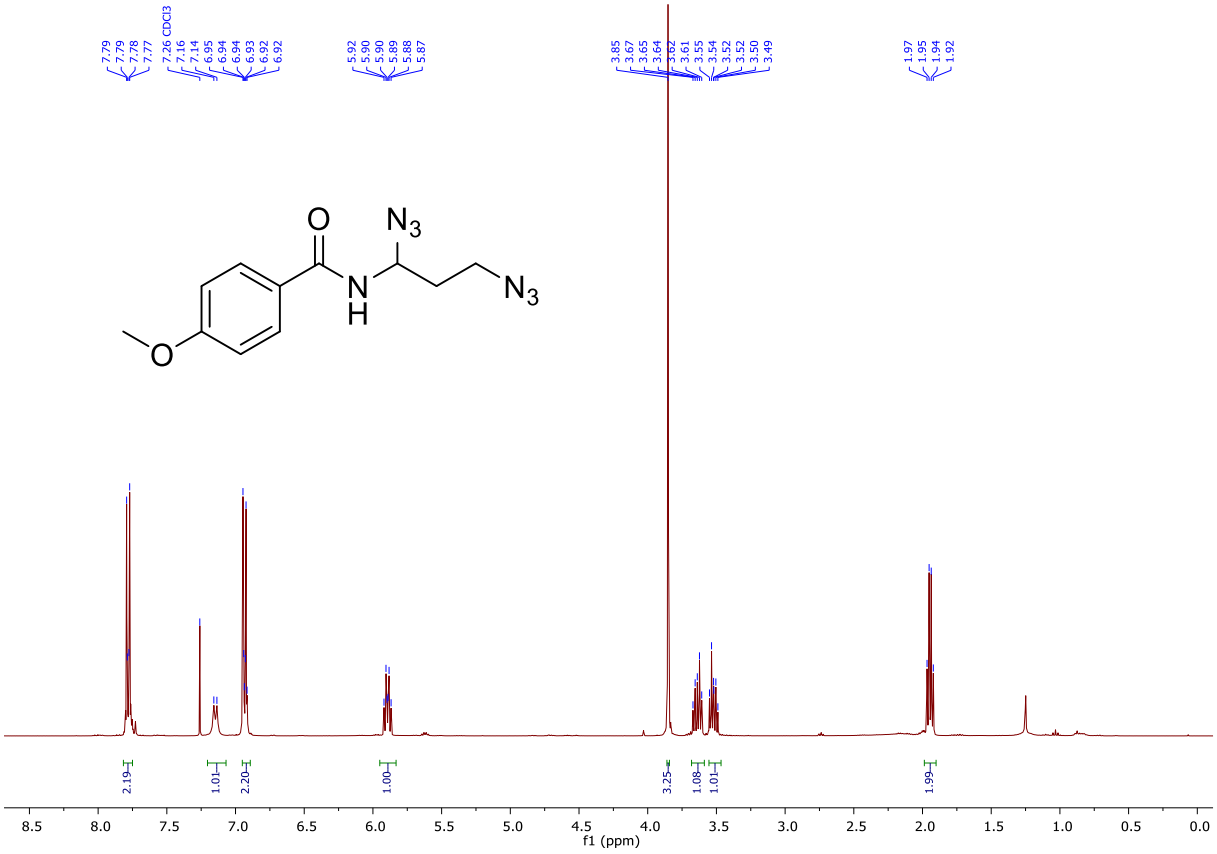


^{13}C-NMR (101 MHz, $CDCl_3$)

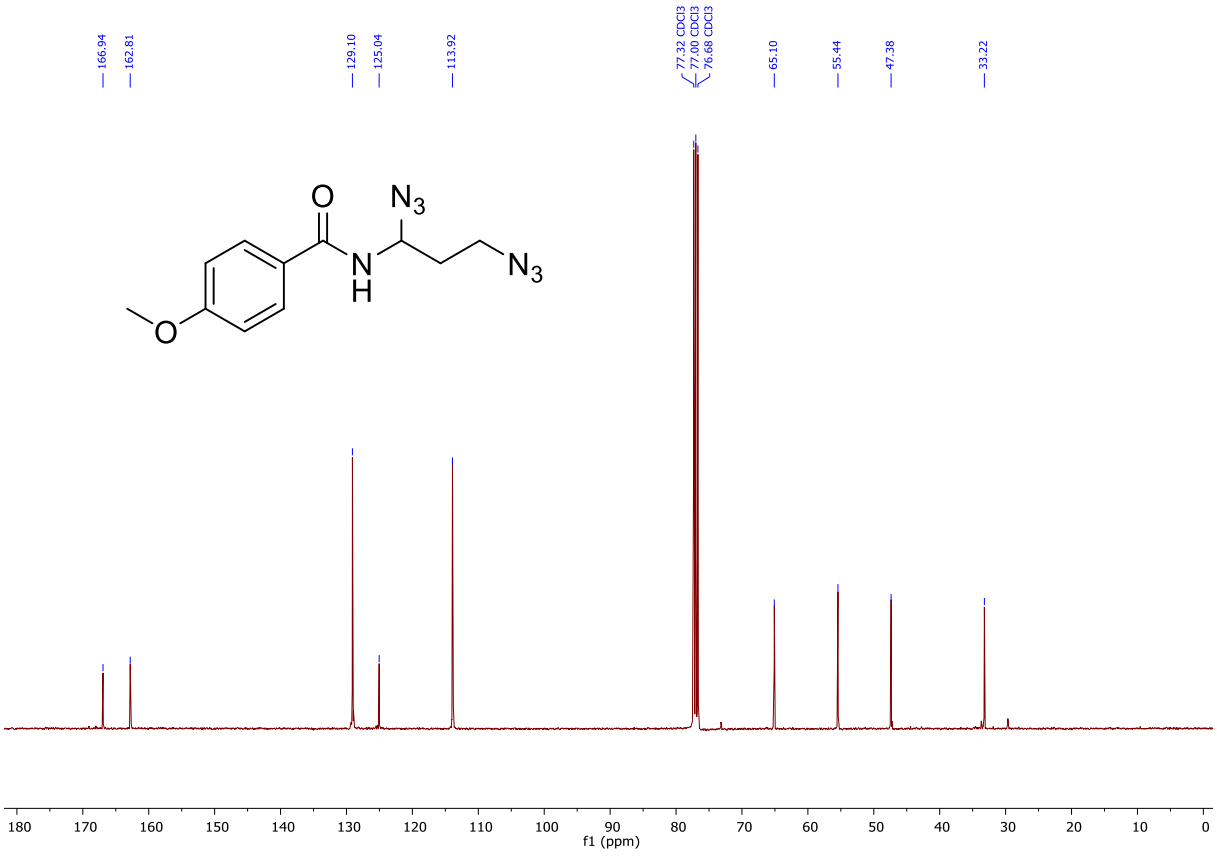


***N*-(1,3-Diazidopropyl)-4-methoxybenzamide (6b)**

^{1}H-NMR (400 MHz, $CDCl_3$)

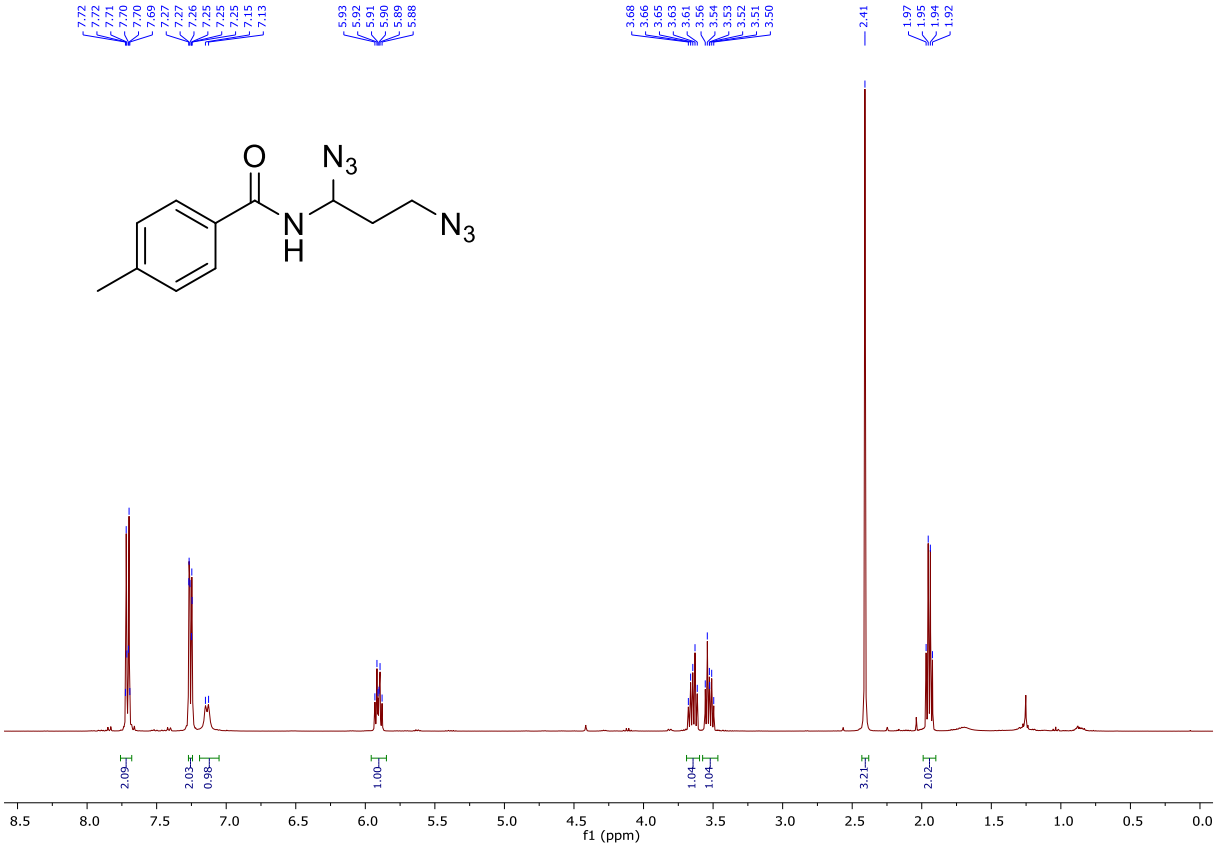


^{13}C-NMR (101 MHz, $CDCl_3$)

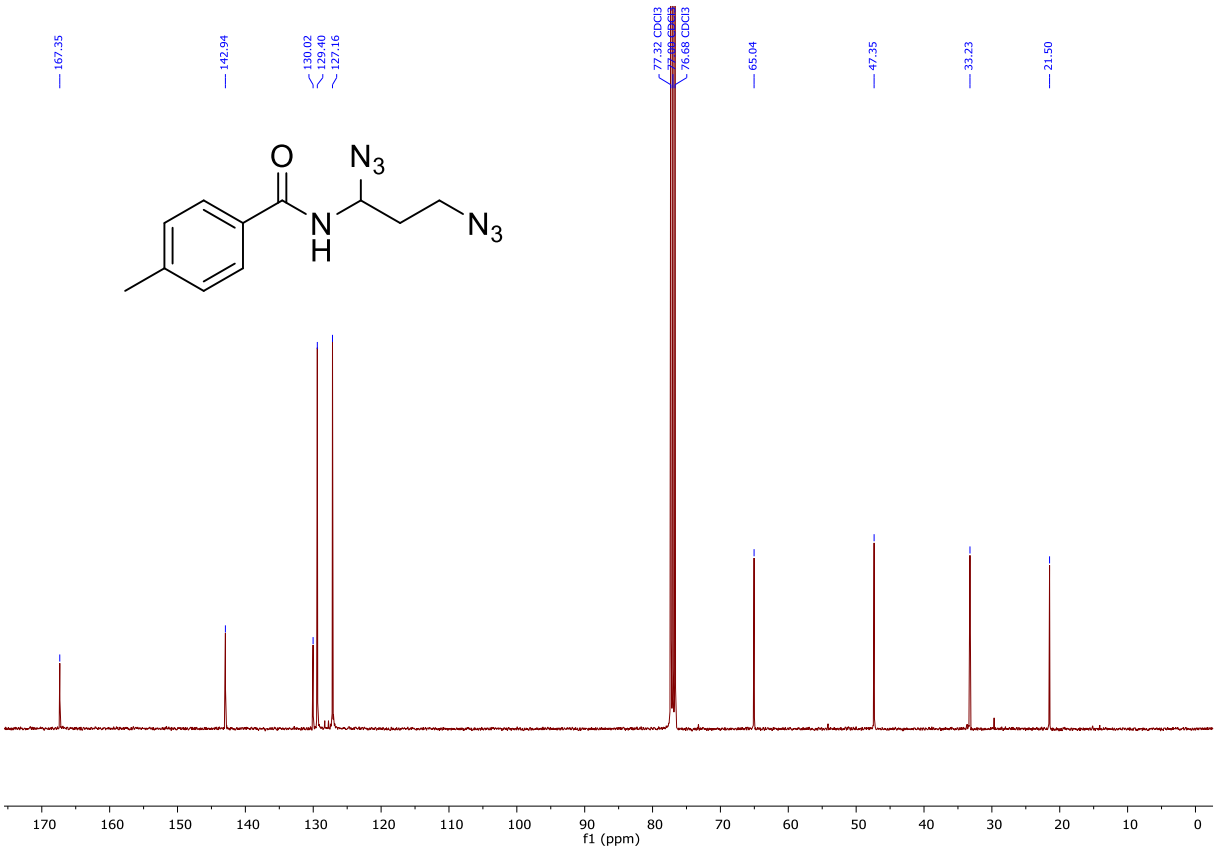


***N*-(1,3-Diazidopropyl)-4-methylbenzamide (6c)**

^{1}H-NMR (400 MHz, $CDCl_3$)

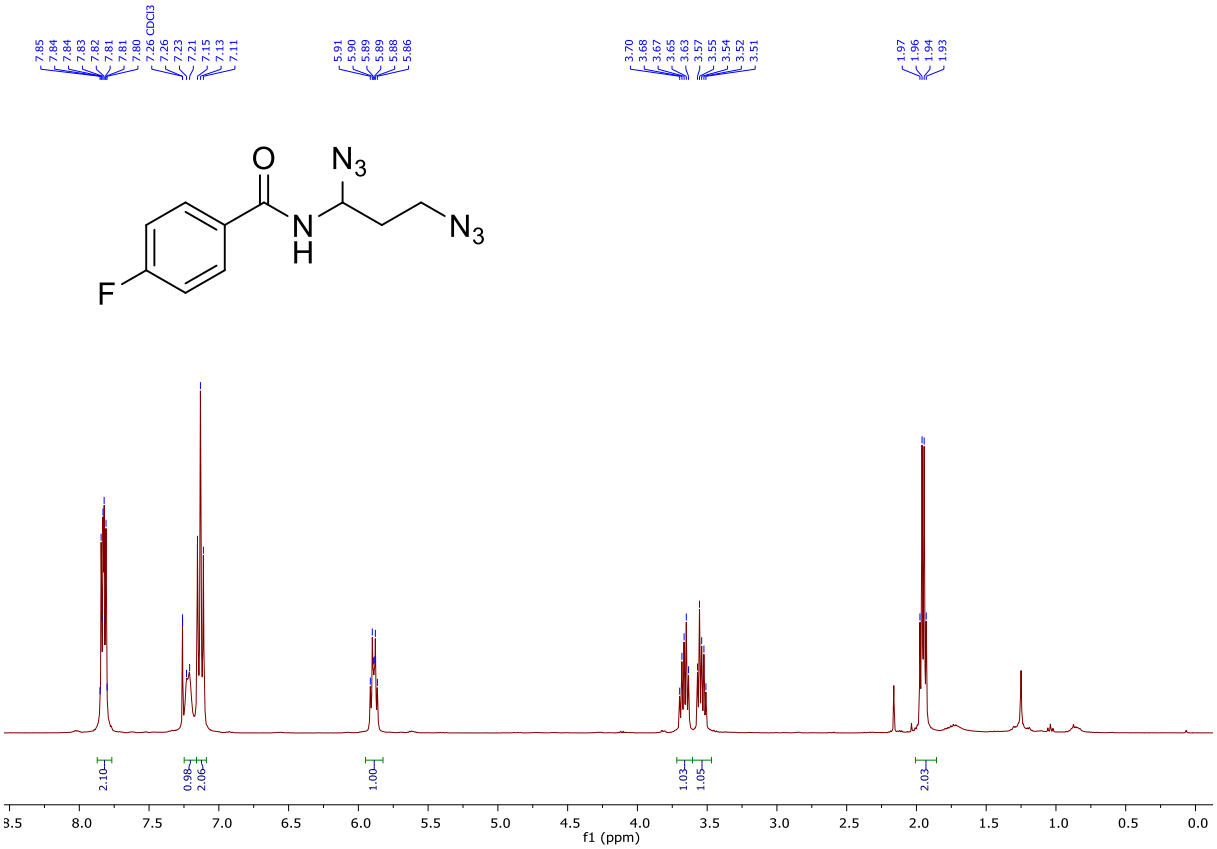


^{13}C-NMR (101 MHz, $CDCl_3$)

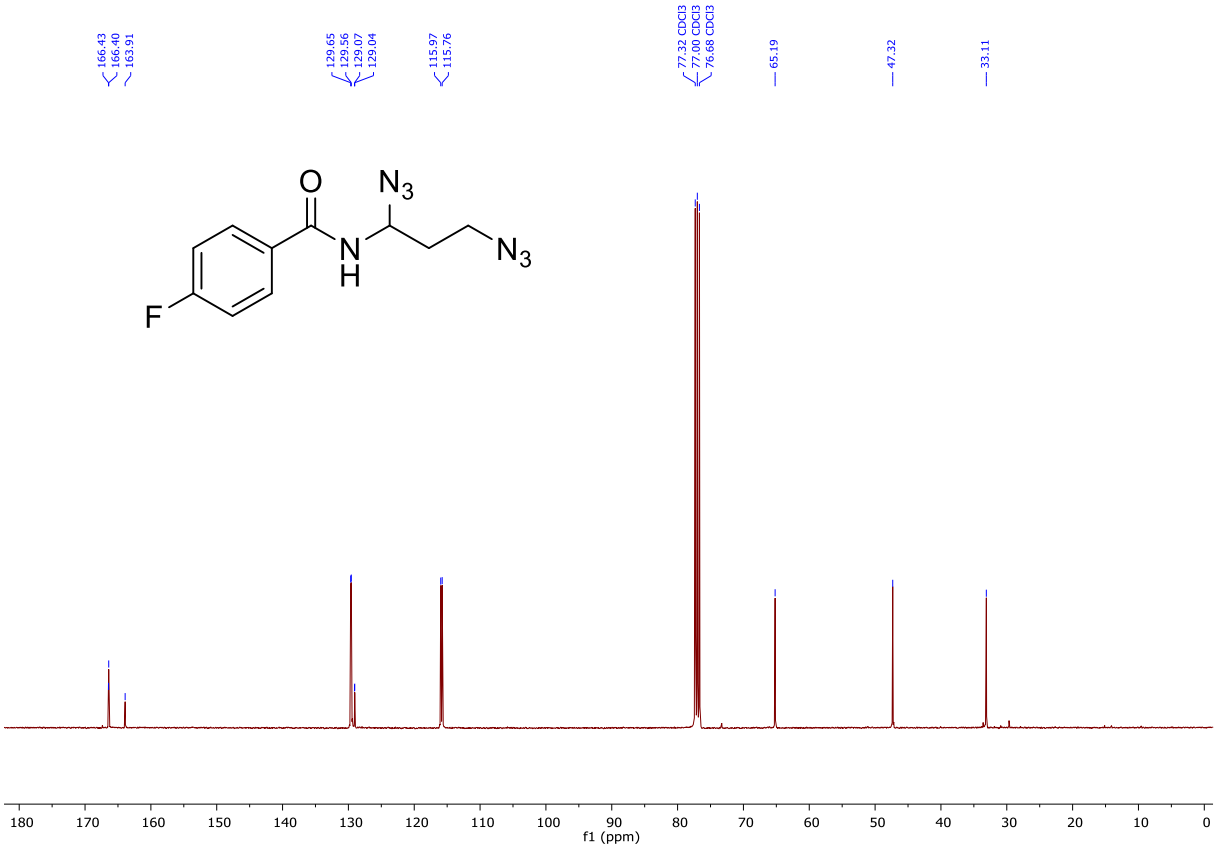


***N*-(1,3-Diazidopropyl)-4-fluorobenzamide (6d)**

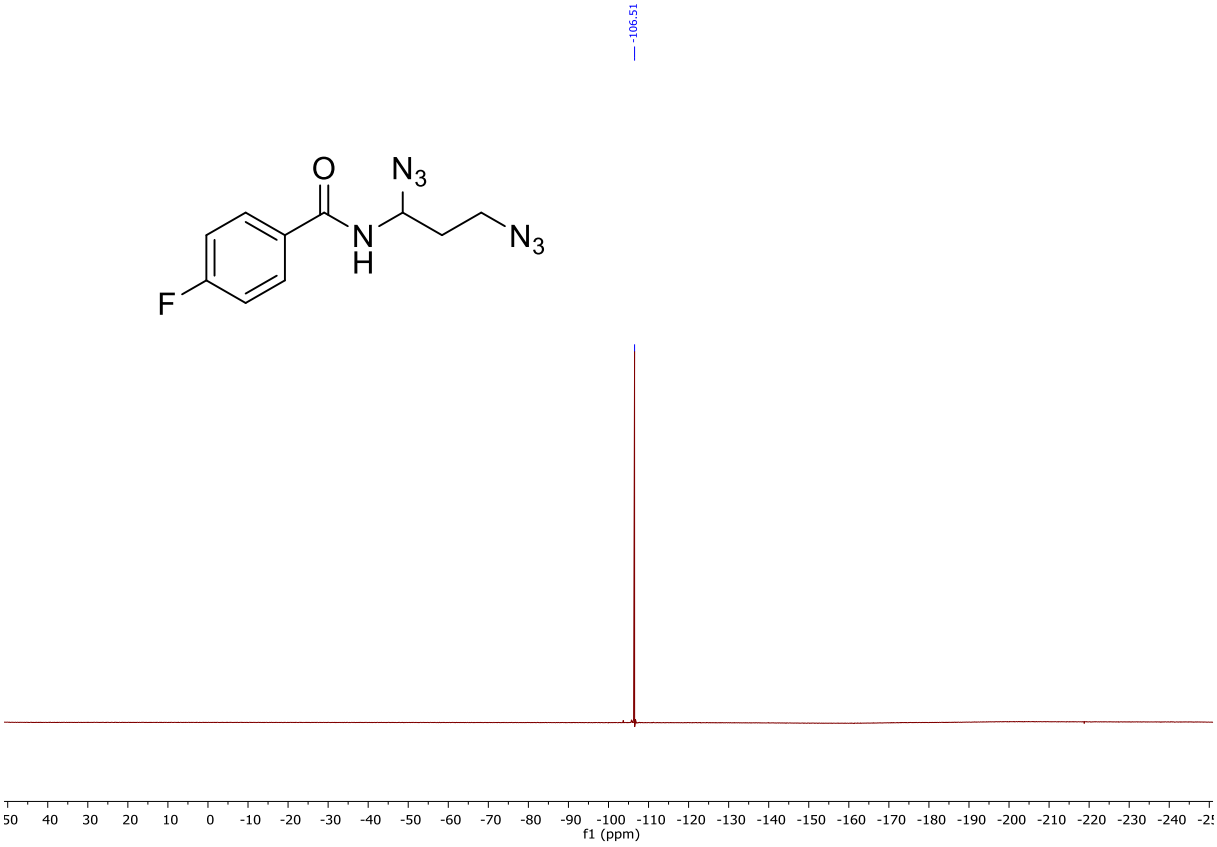
^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (101 MHz, $CDCl_3$)

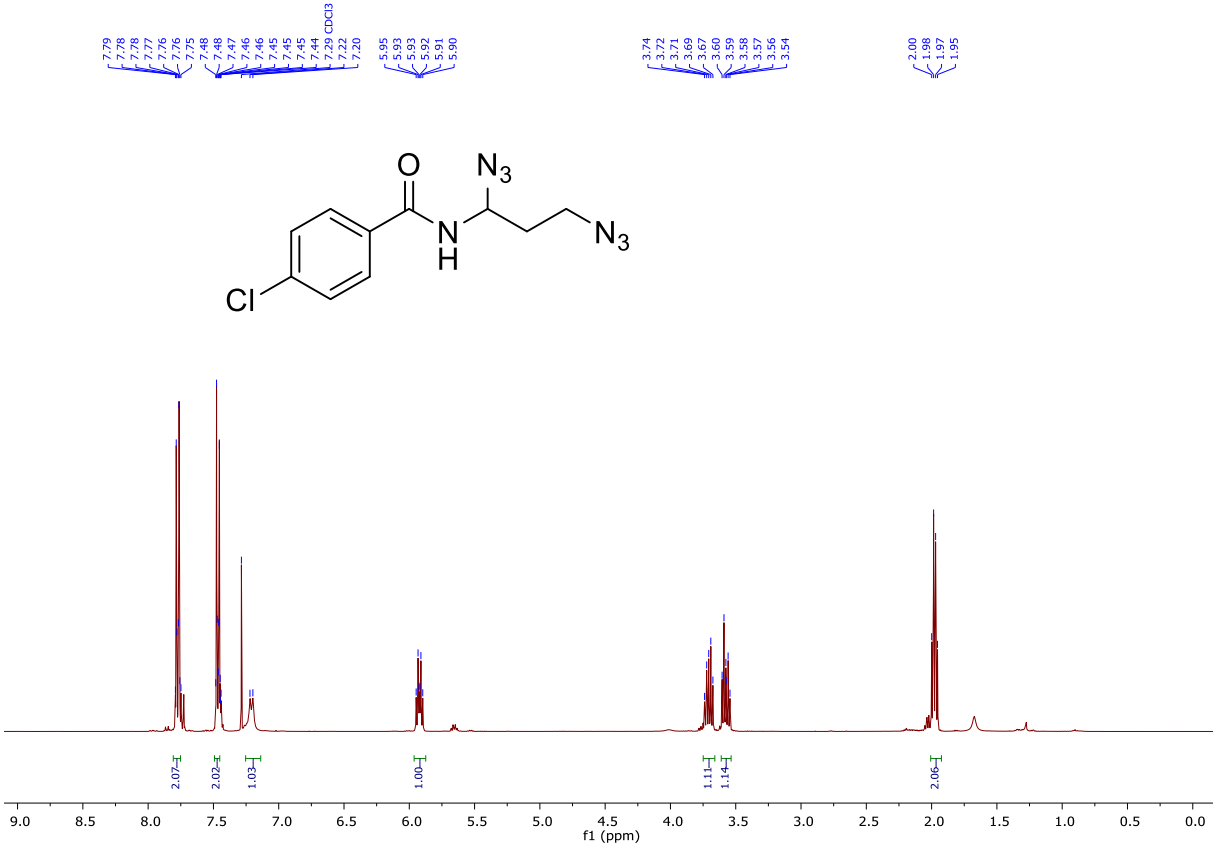


^{19}F-NMR (376 MHz, $CDCl_3$)

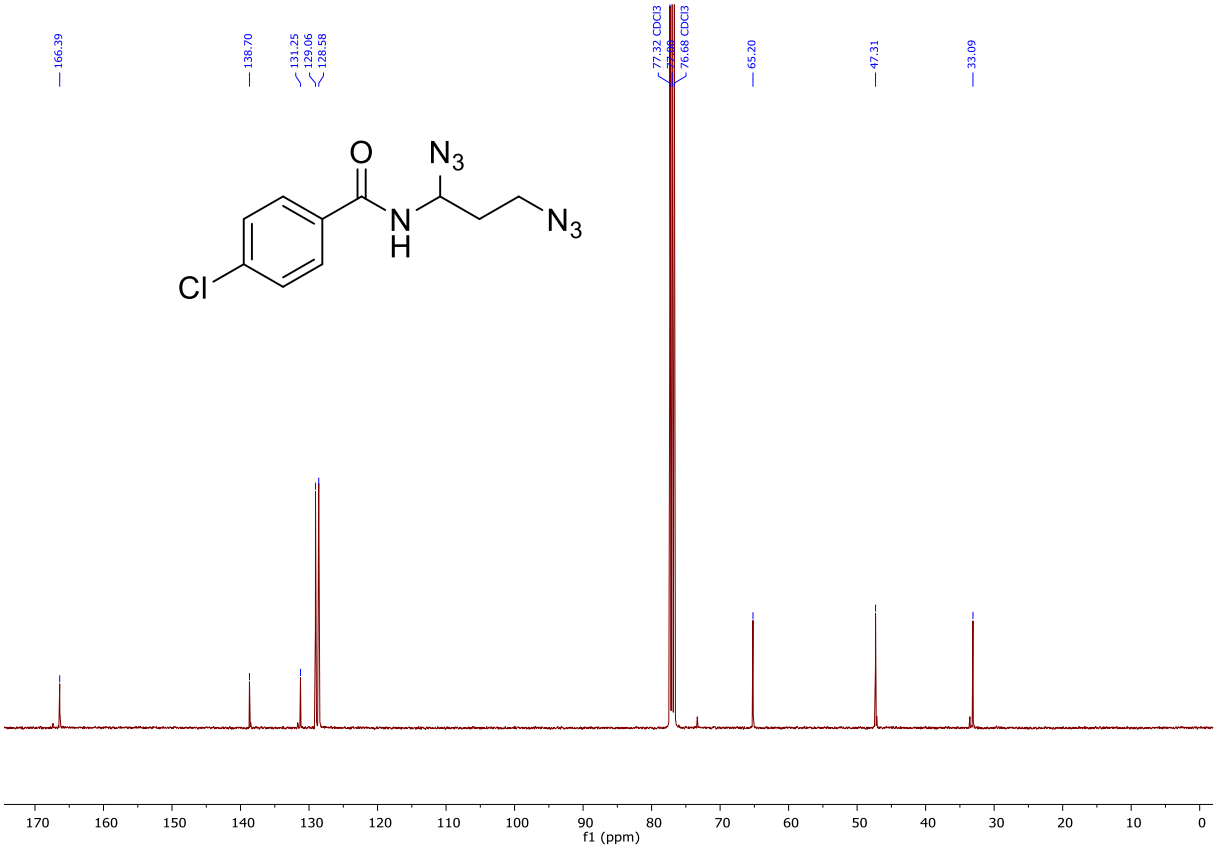


4-Chloro-*N*-(1,3-diazidopropyl)benzamide (6e)

^{1}H-NMR (400 MHz, $CDCl_3$)

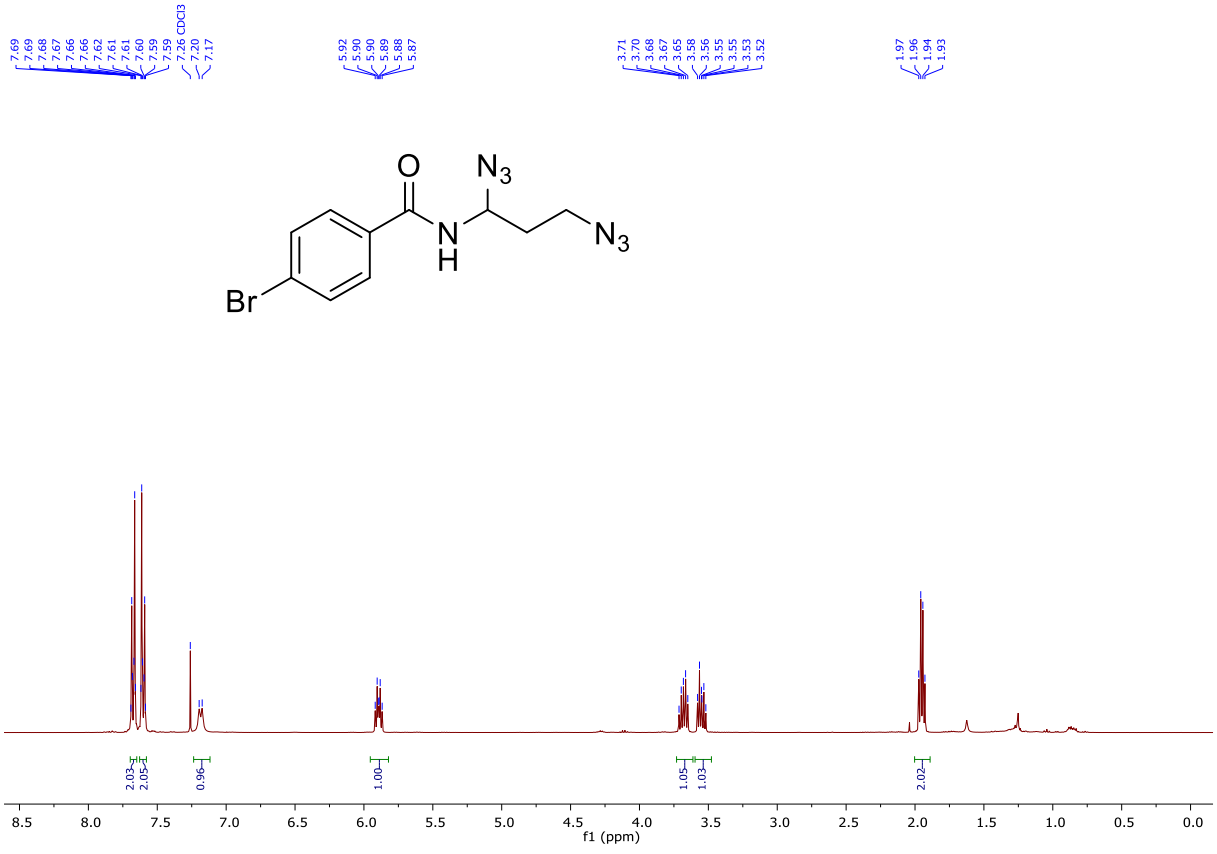


^{13}C-NMR (101 MHz, $CDCl_3$)

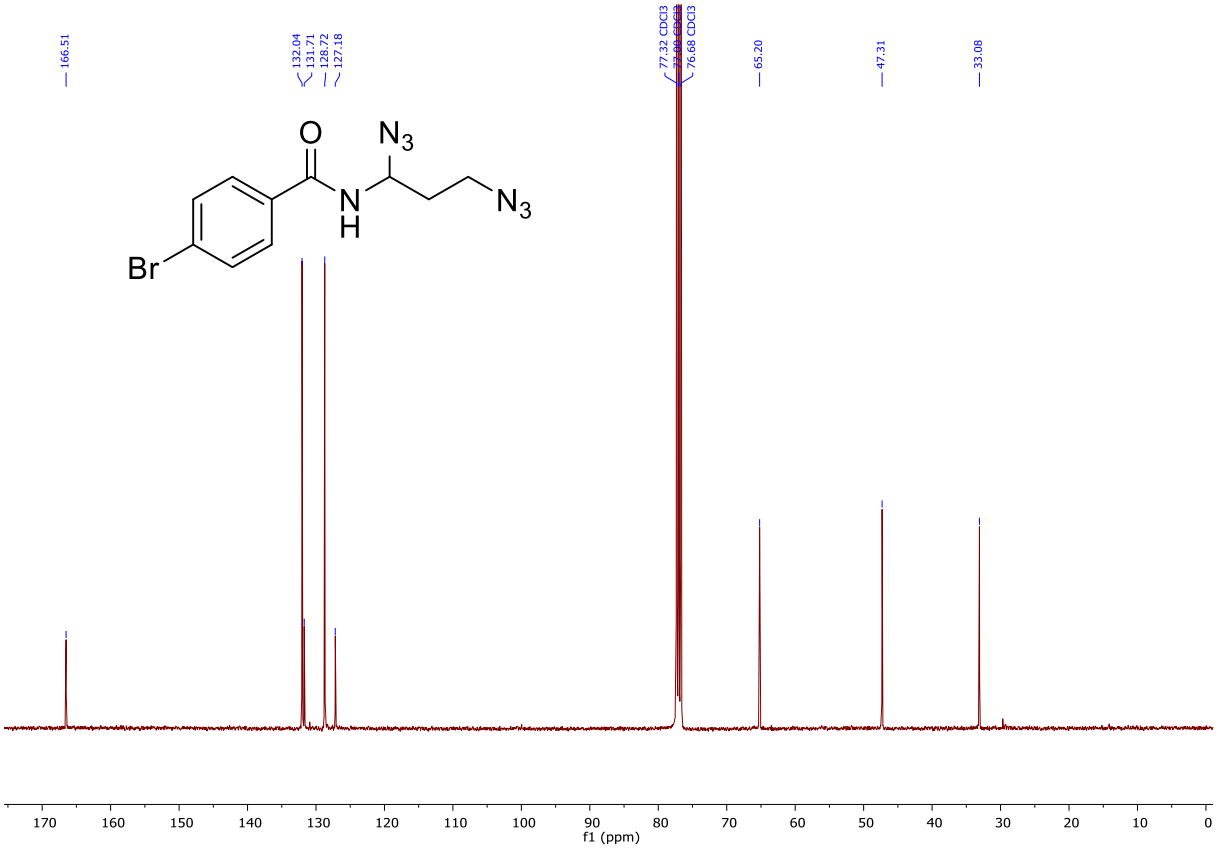


4-Bromo-*N*-(1,3-diazidopropyl)benzamide (6f)

^{1}H-NMR (400 MHz, $CDCl_3$)

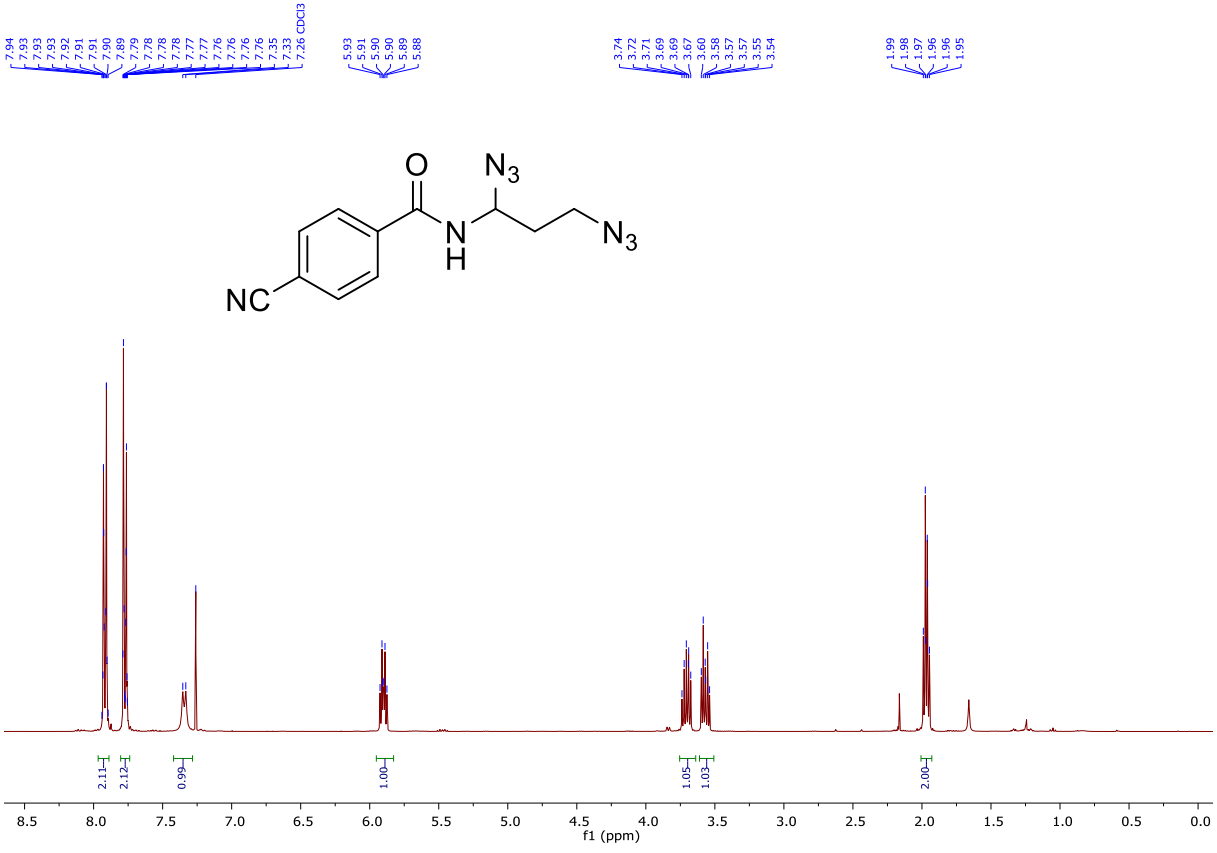


^{13}C-NMR (101 MHz, $CDCl_3$)

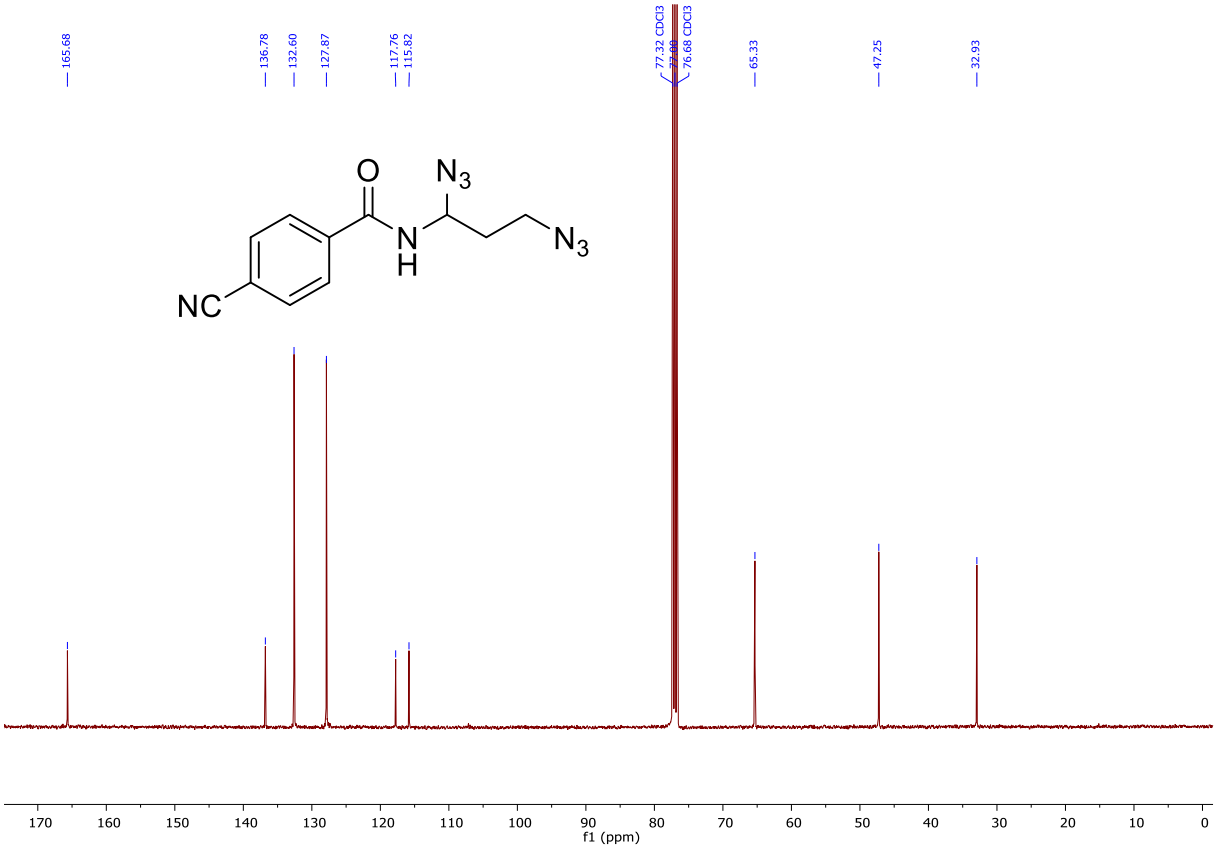


4-Cyano-*N*-(1,3-diazidopropyl)benzamide (6g)

^{1}H-NMR (400 MHz, $CDCl_3$)

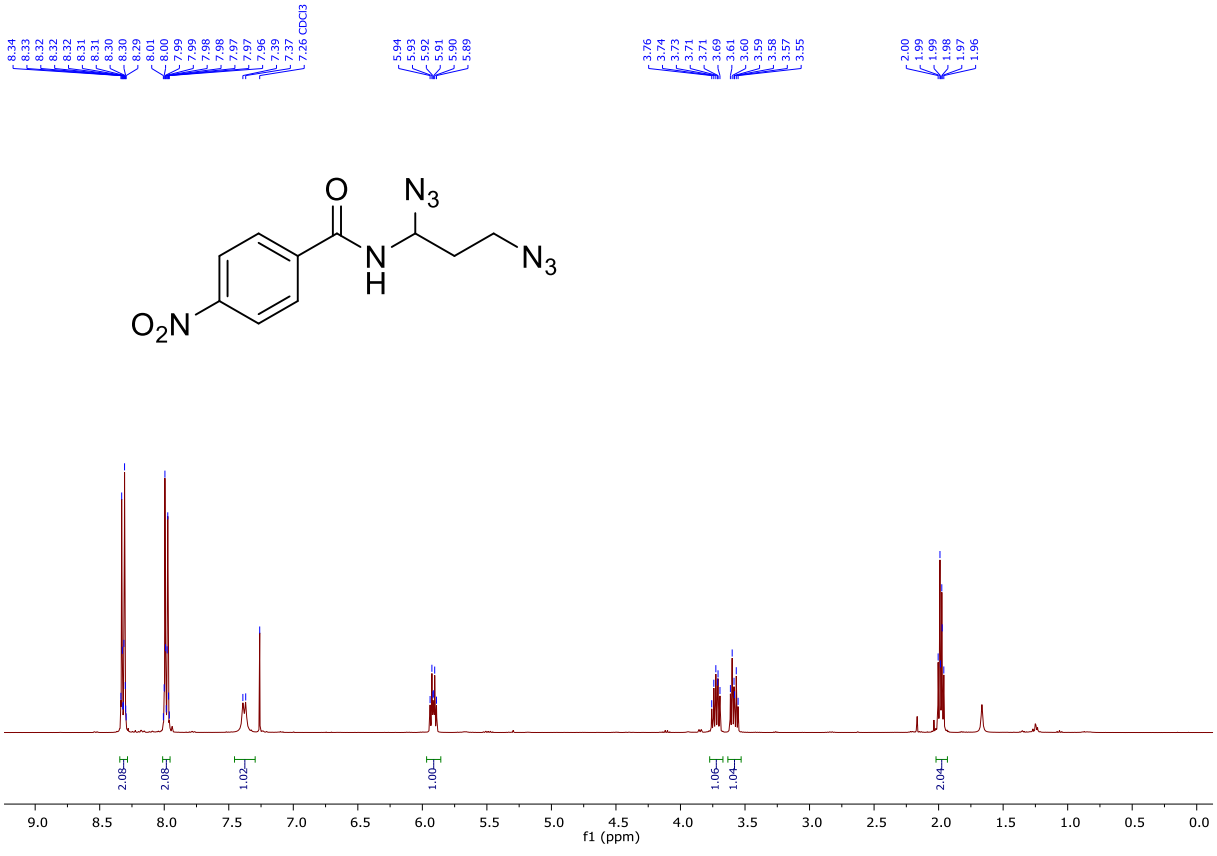


^{13}C-NMR (101 MHz, $CDCl_3$)

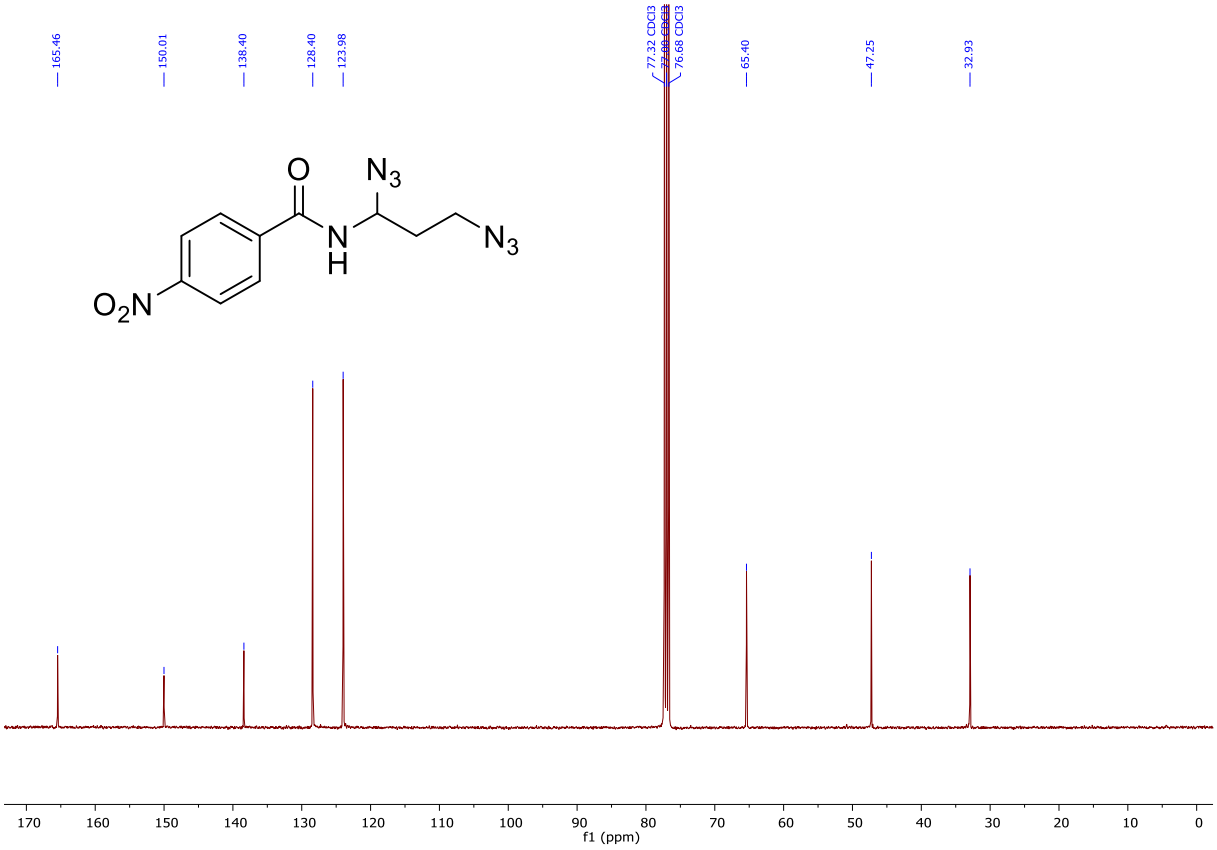


***N*-(1,3-Diazidopropyl)-4-nitrobenzamide (6h)**

^{1}H-NMR (400 MHz, $CDCl_3$)

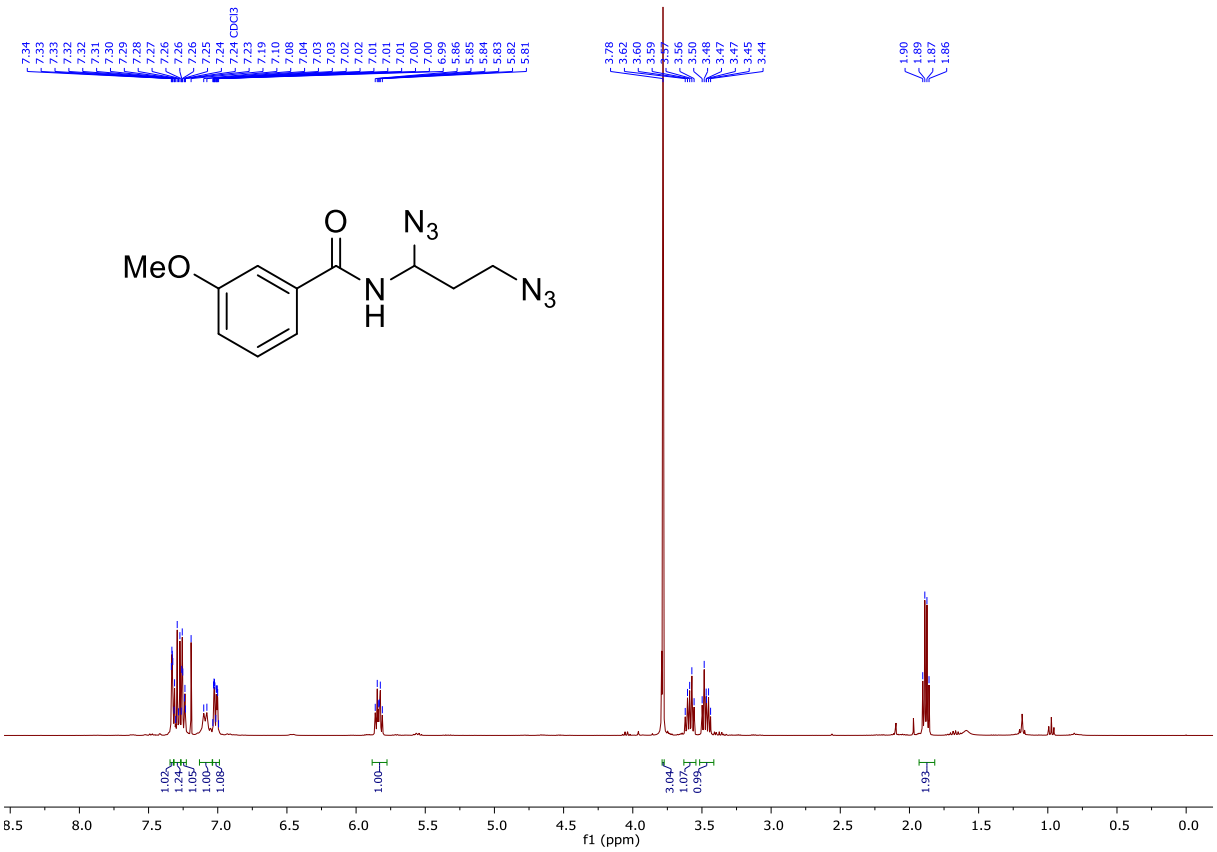


^{13}C-NMR (101 MHz, $CDCl_3$)

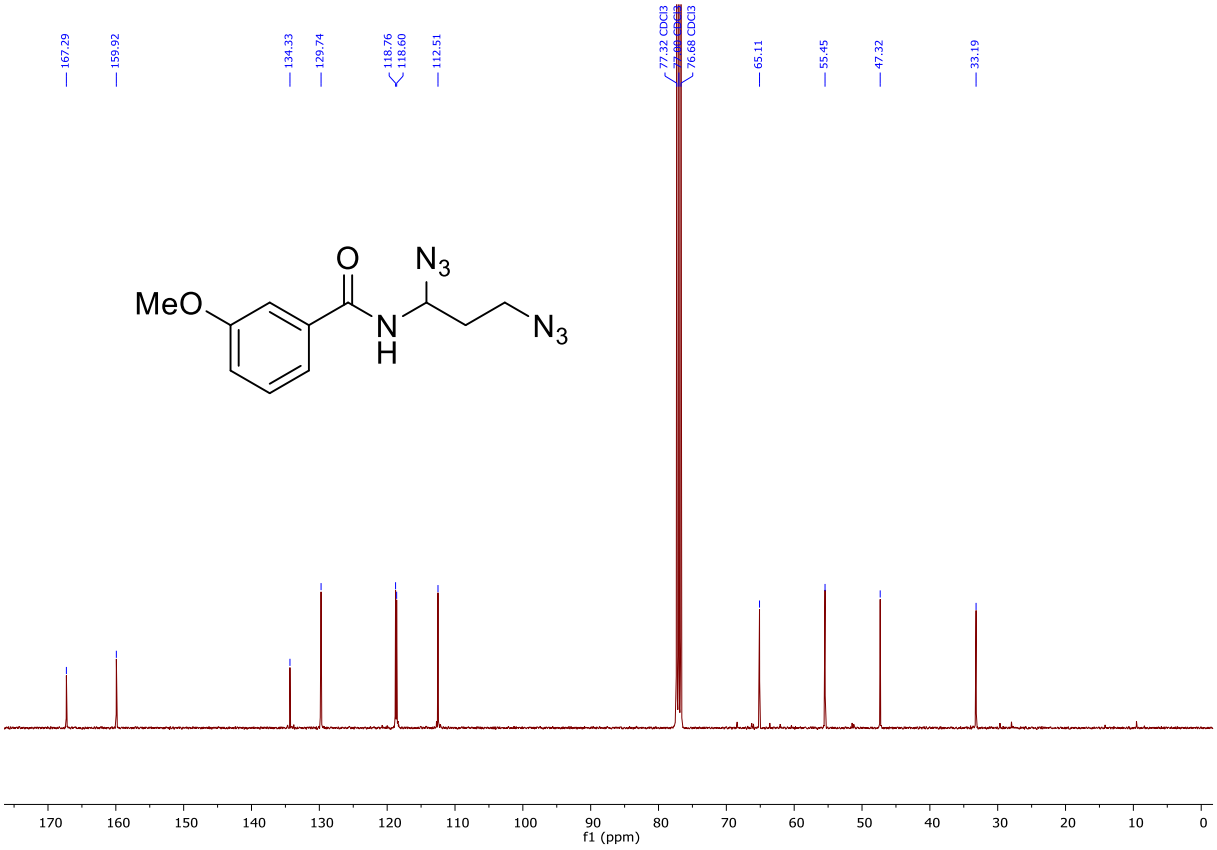


***N*-(1,3-Diazidopropyl)-3-methoxybenzamide (6i)**

^{1}H-NMR (400 MHz, $CDCl_3$)

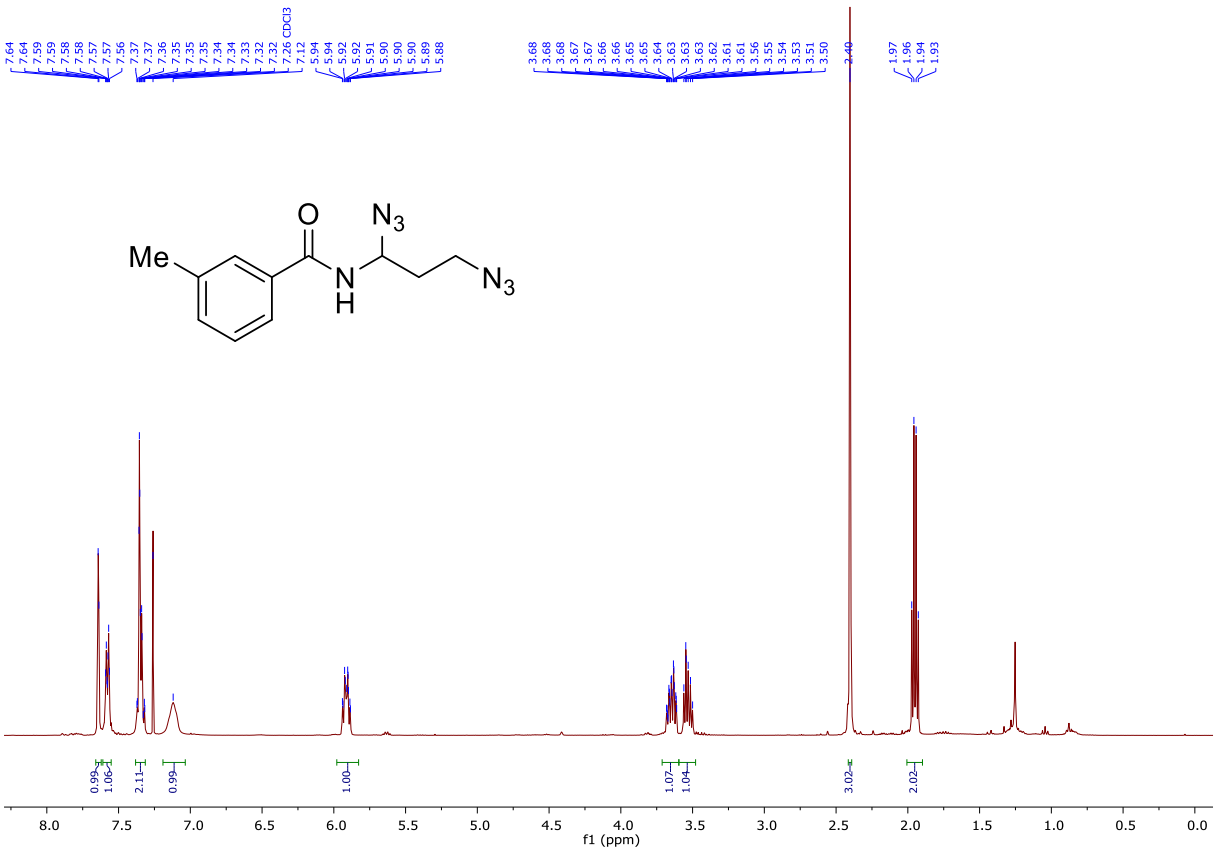


^{13}C-NMR (101 MHz, $CDCl_3$)

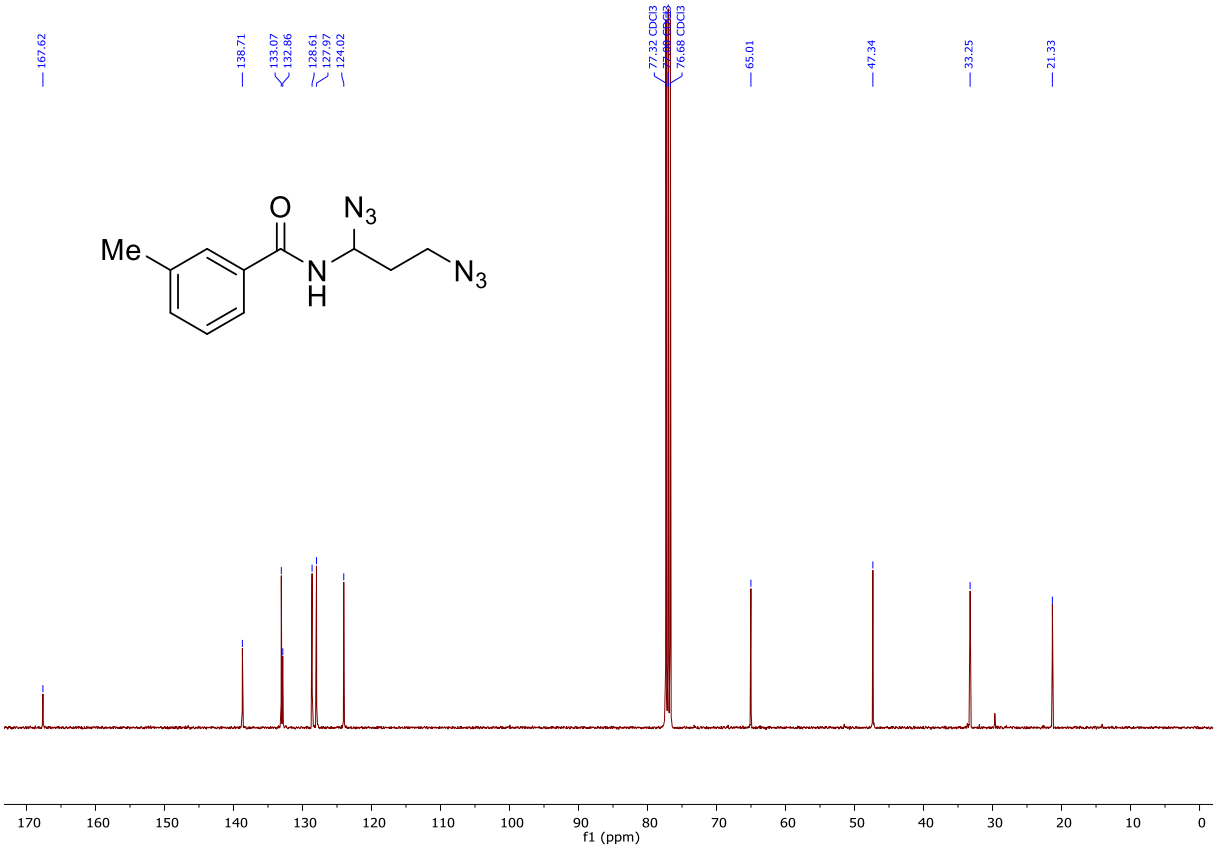


***N*-(1,3-Diazidopropyl)-3-methylbenzamide (6j)**

^{1}H-NMR (400 MHz, $CDCl_3$)

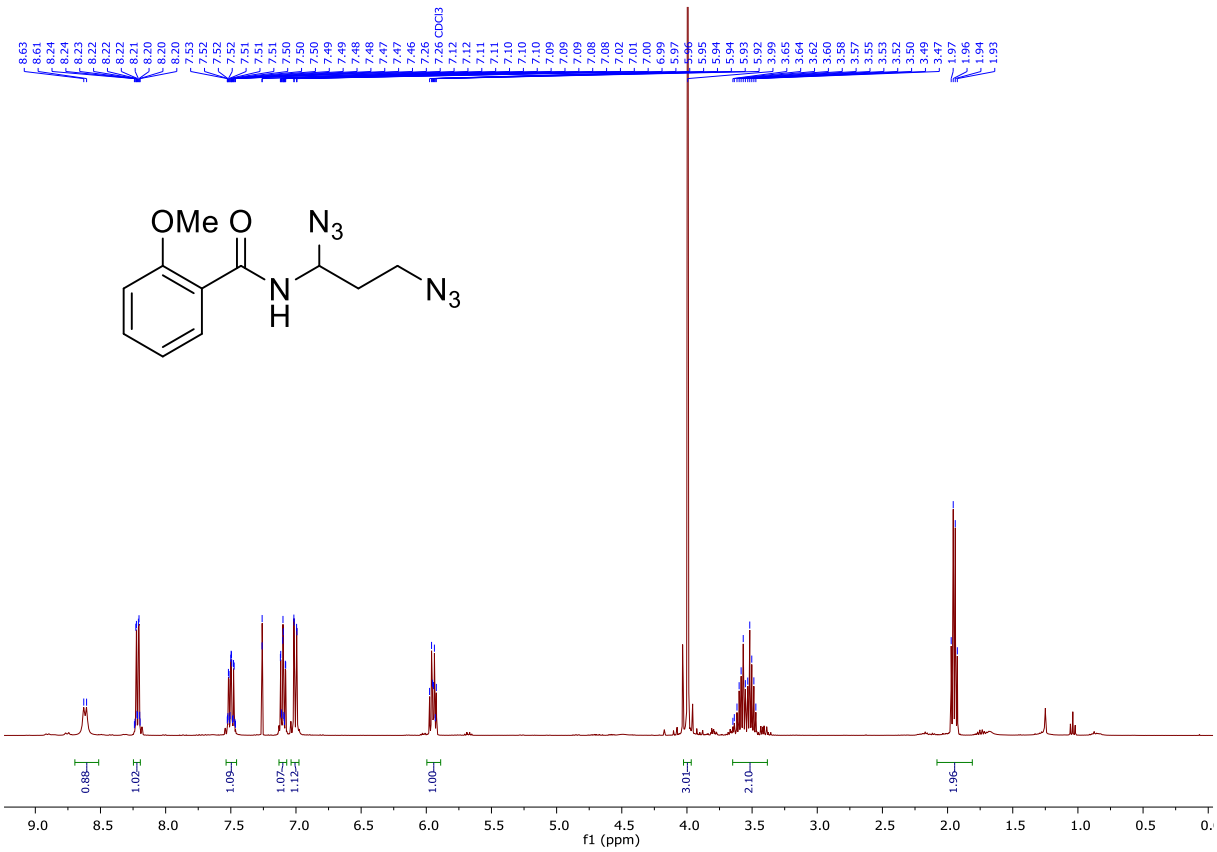


^{13}C-NMR (101 MHz, $CDCl_3$)

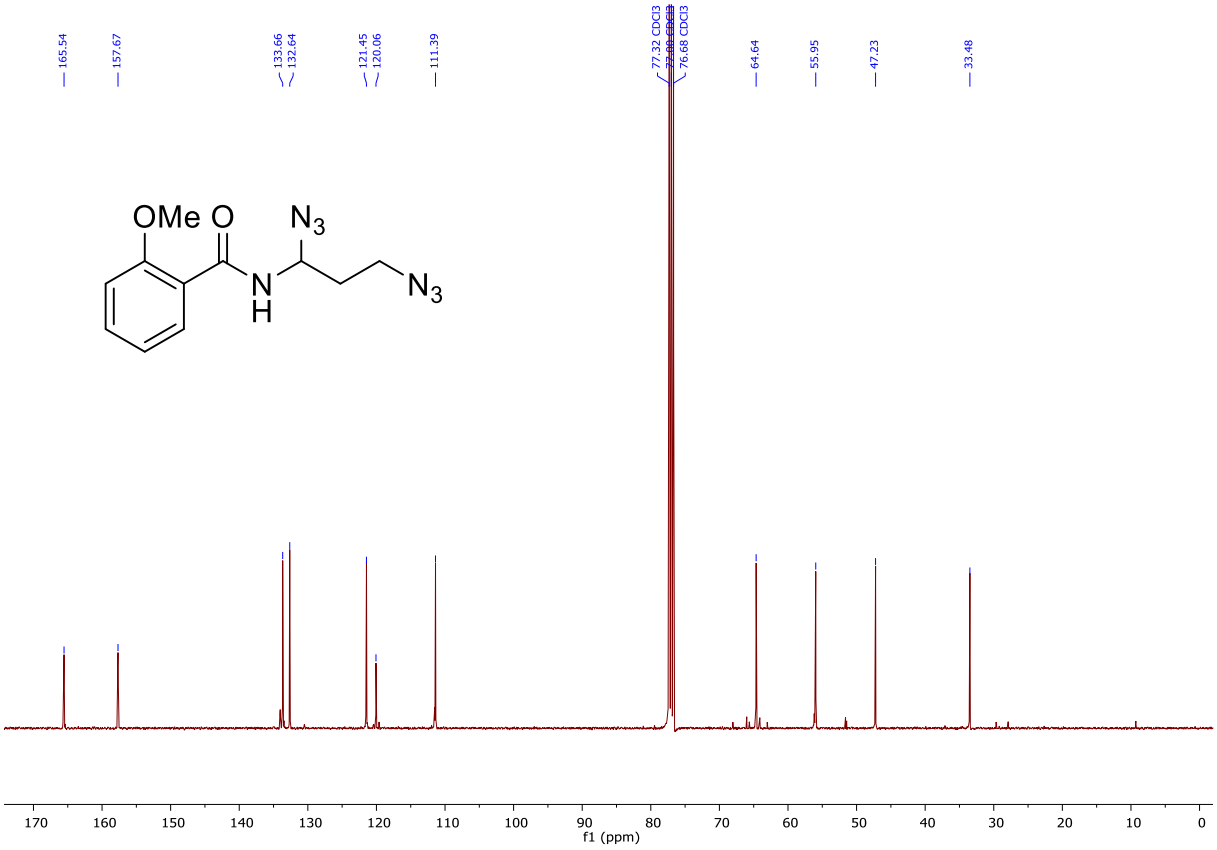


***N*-(1,3-Diazidopropyl)-2-methoxybenzamide (6k)**

^{1}H-NMR (400 MHz, $CDCl_3$)

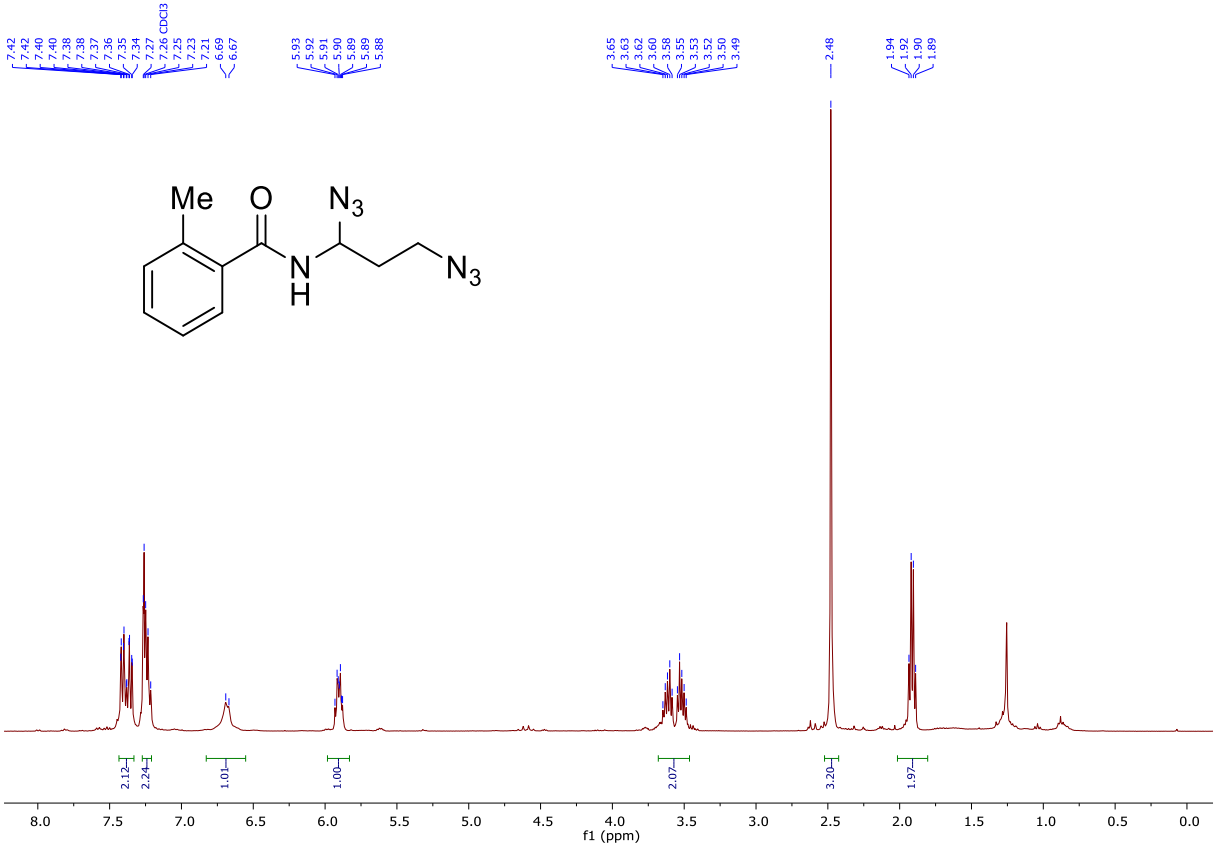


^{13}C-NMR (101 MHz, $CDCl_3$)

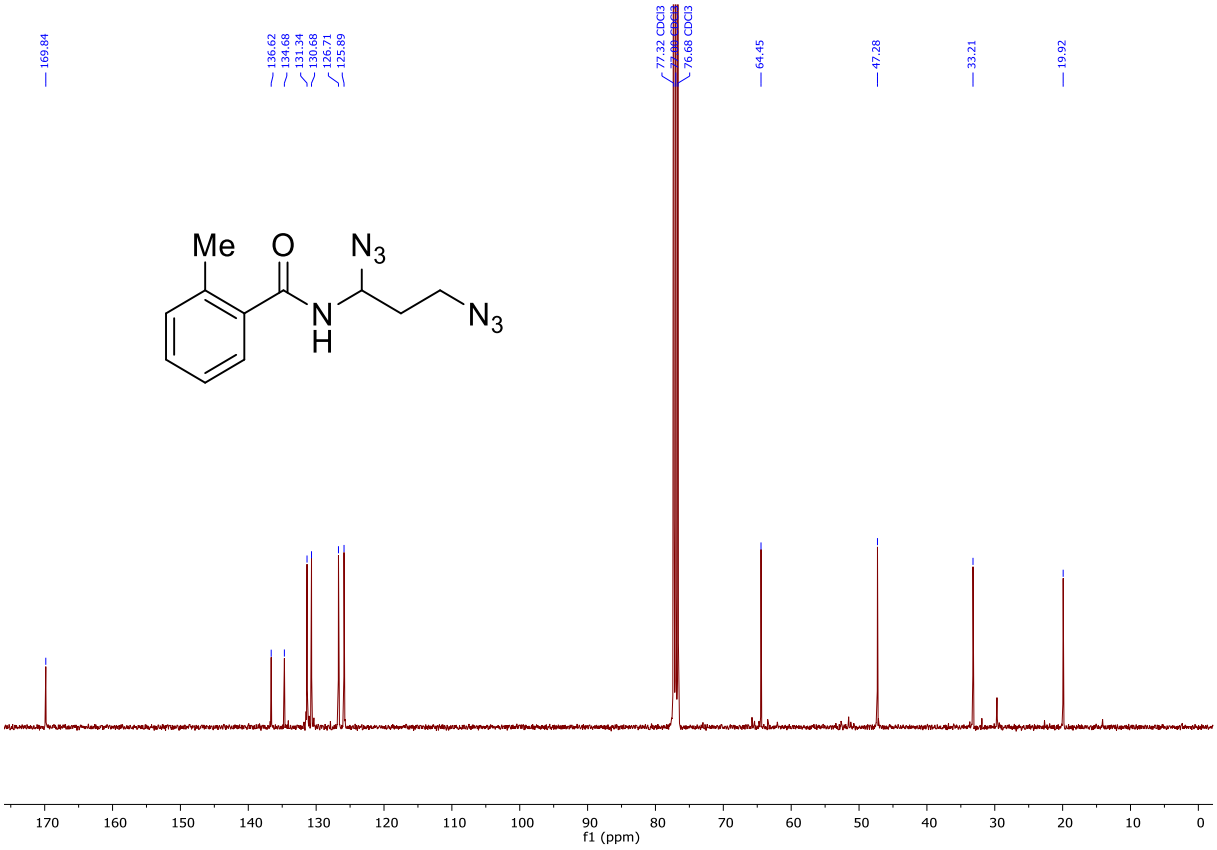


***N*-(1,3-Diazidopropyl)-2-methylbenzamide (6l)**

^{1}H-NMR (400 MHz, $CDCl_3$)

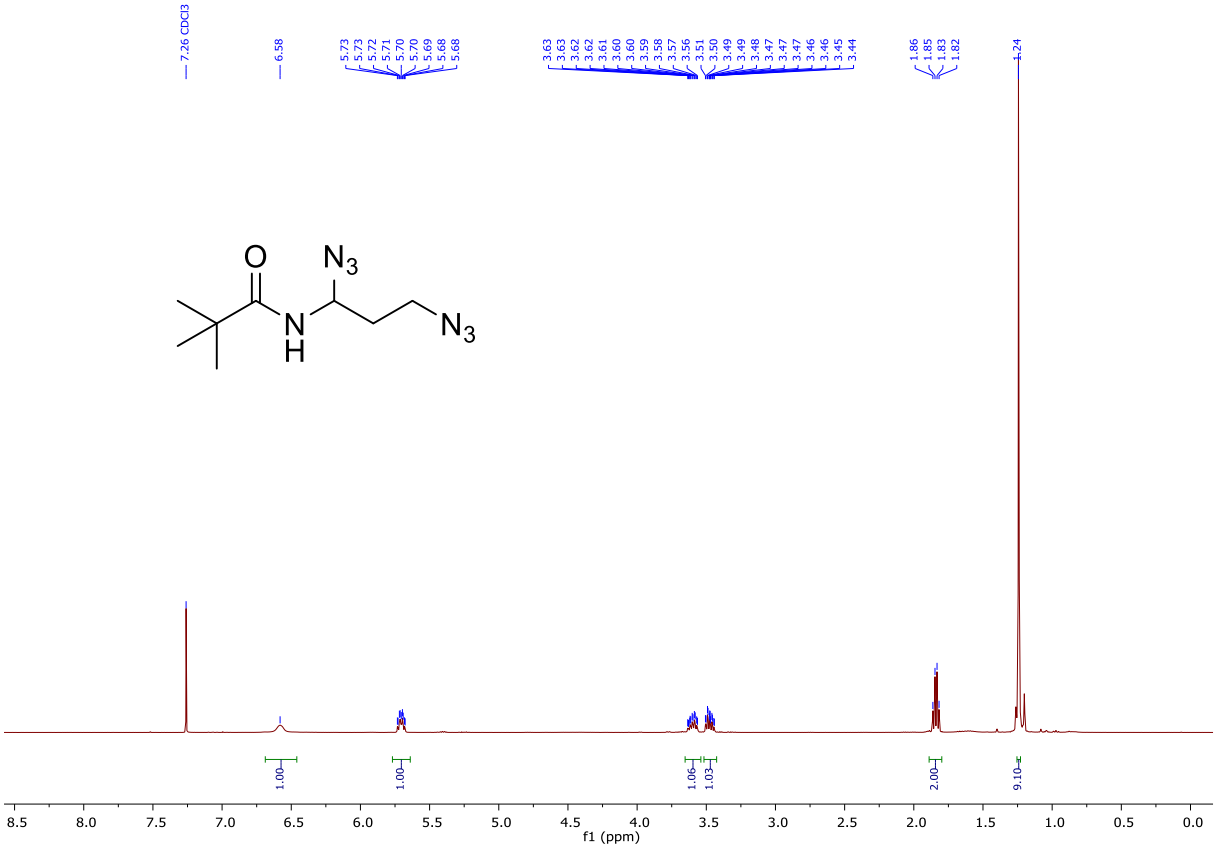


^{13}C-NMR (101 MHz, $CDCl_3$)

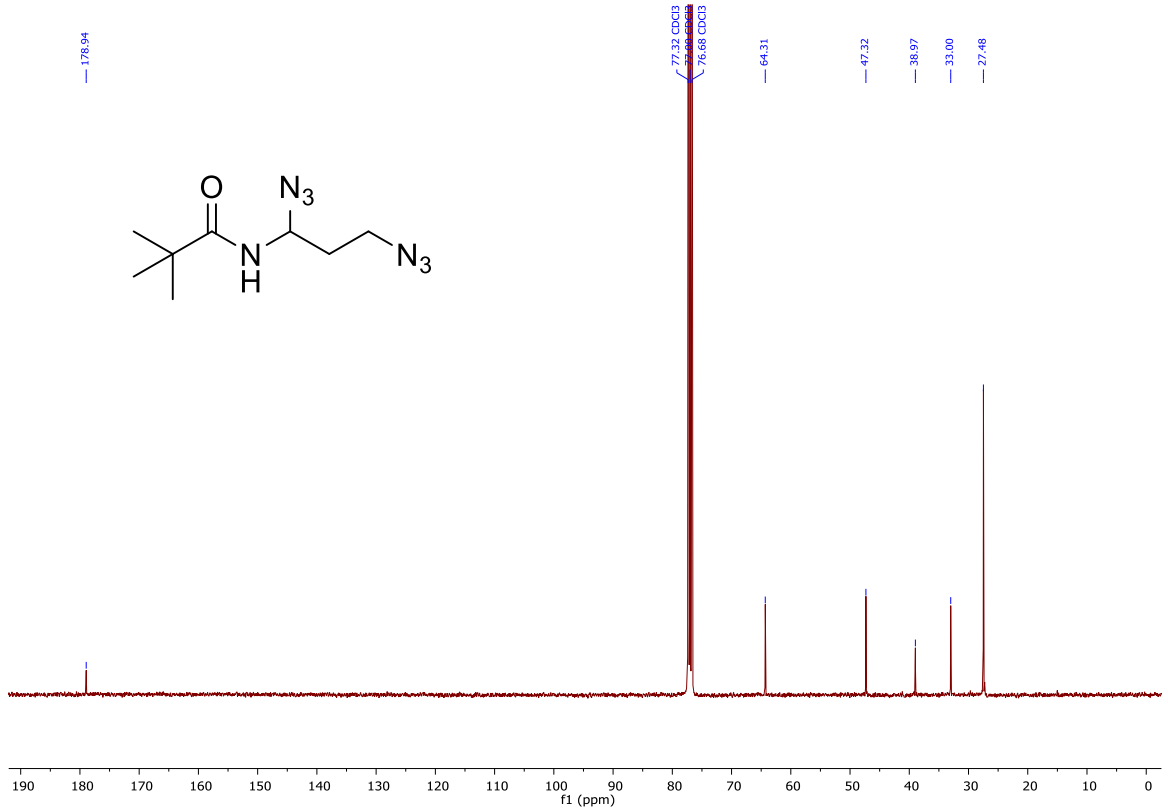


***N*-(1,3-Diazidopropyl)pivalamide (6m)**

^{1}H-NMR (400 MHz, $CDCl_3$)

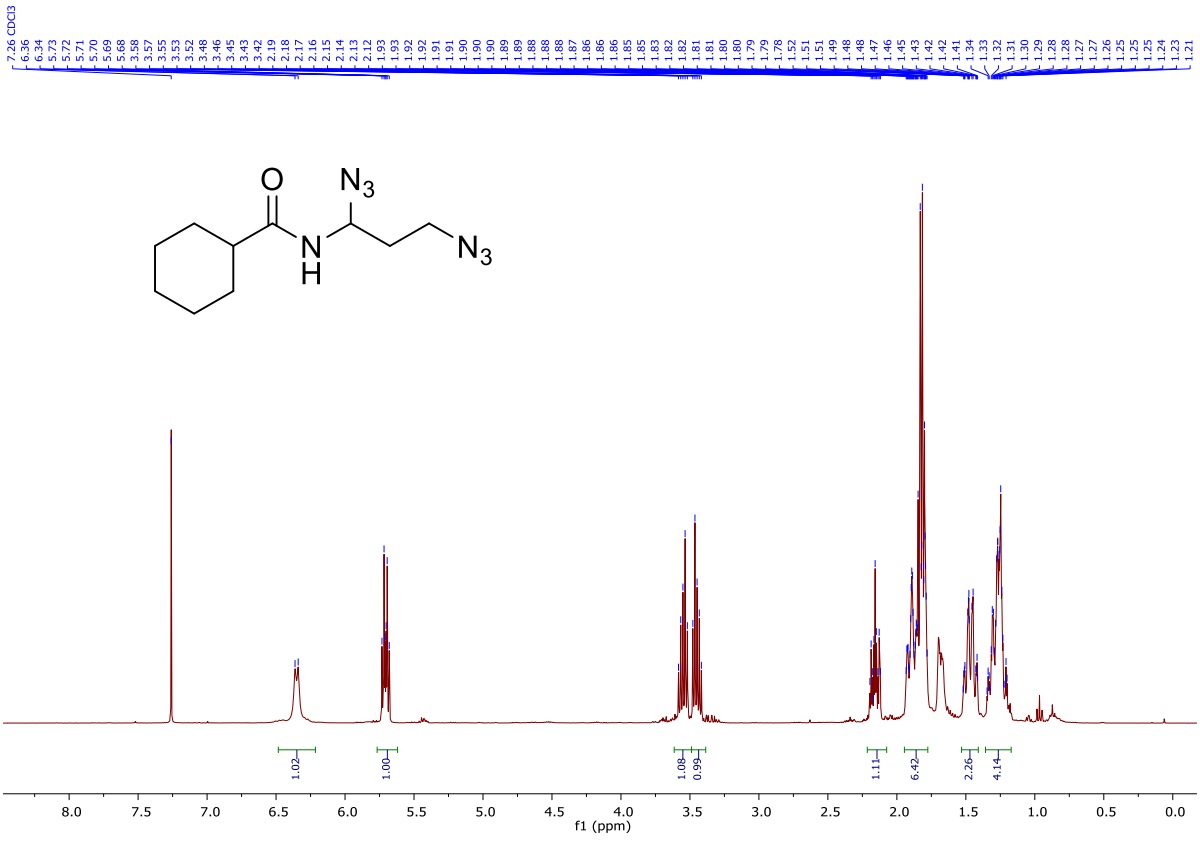


^{13}C-NMR (101 MHz, $CDCl_3$)

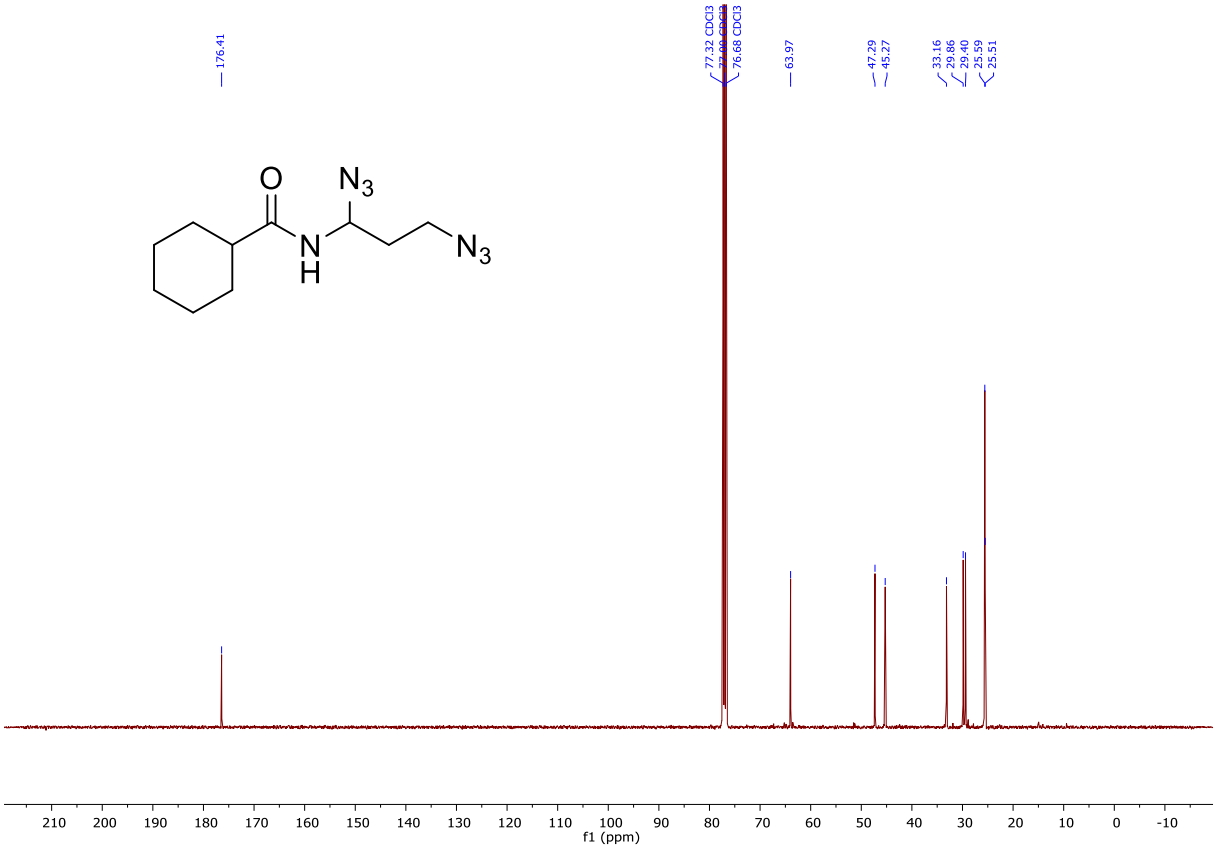


***N*-(1,3-diazidopropyl)cyclohexanecarboxamide (6n)**

^{1}H-NMR (400 MHz, $CDCl_3$)

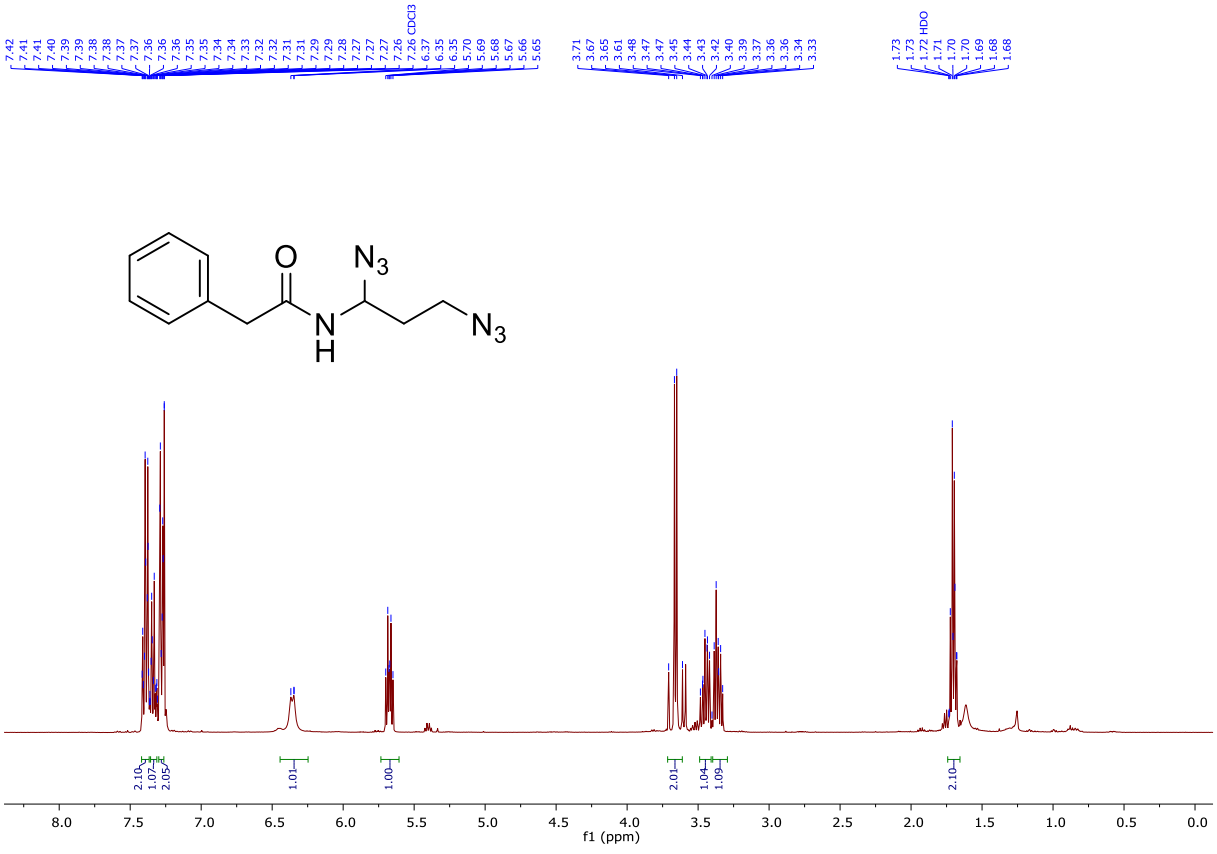


^{13}C-NMR (101 MHz, $CDCl_3$)

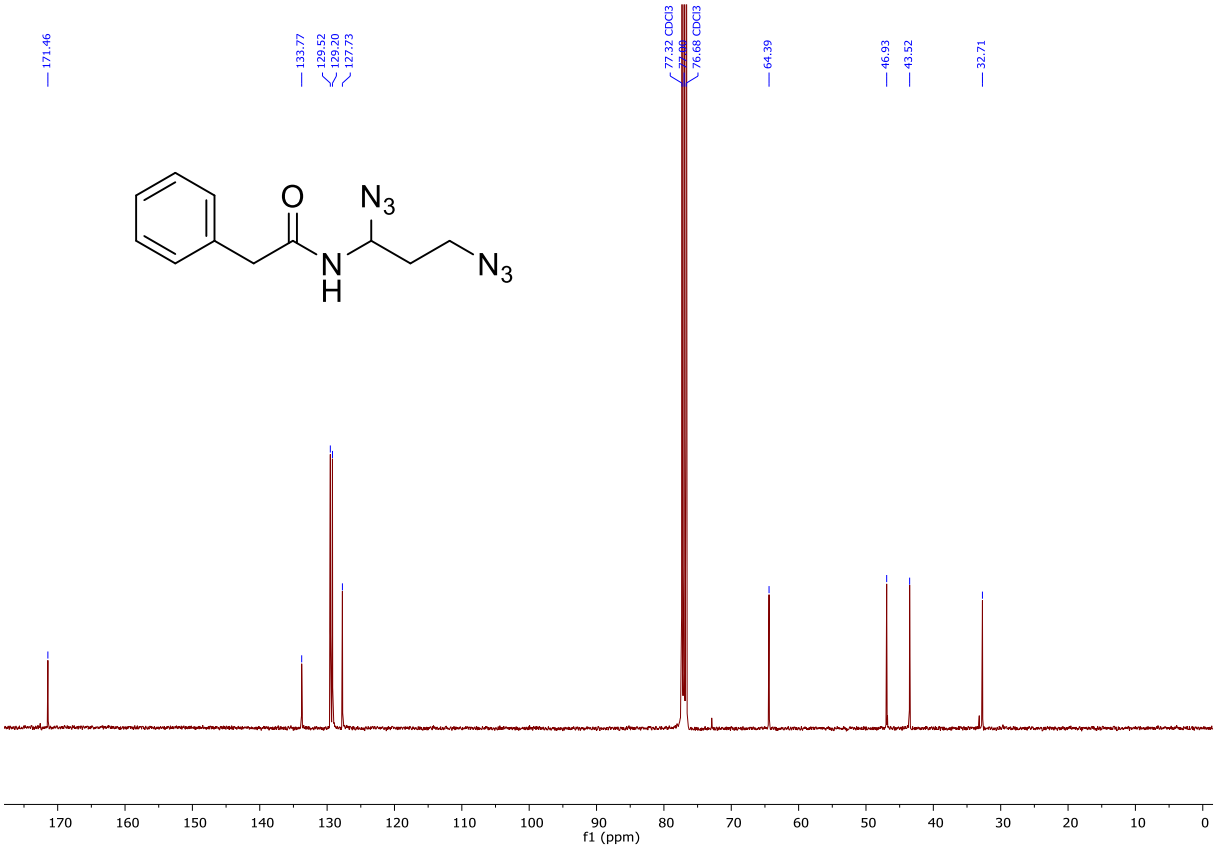


***N*-(1,3-Diazidopropyl)-2-phenylacetamide (6o)**

^{1}H-NMR (400 MHz, $CDCl_3$)

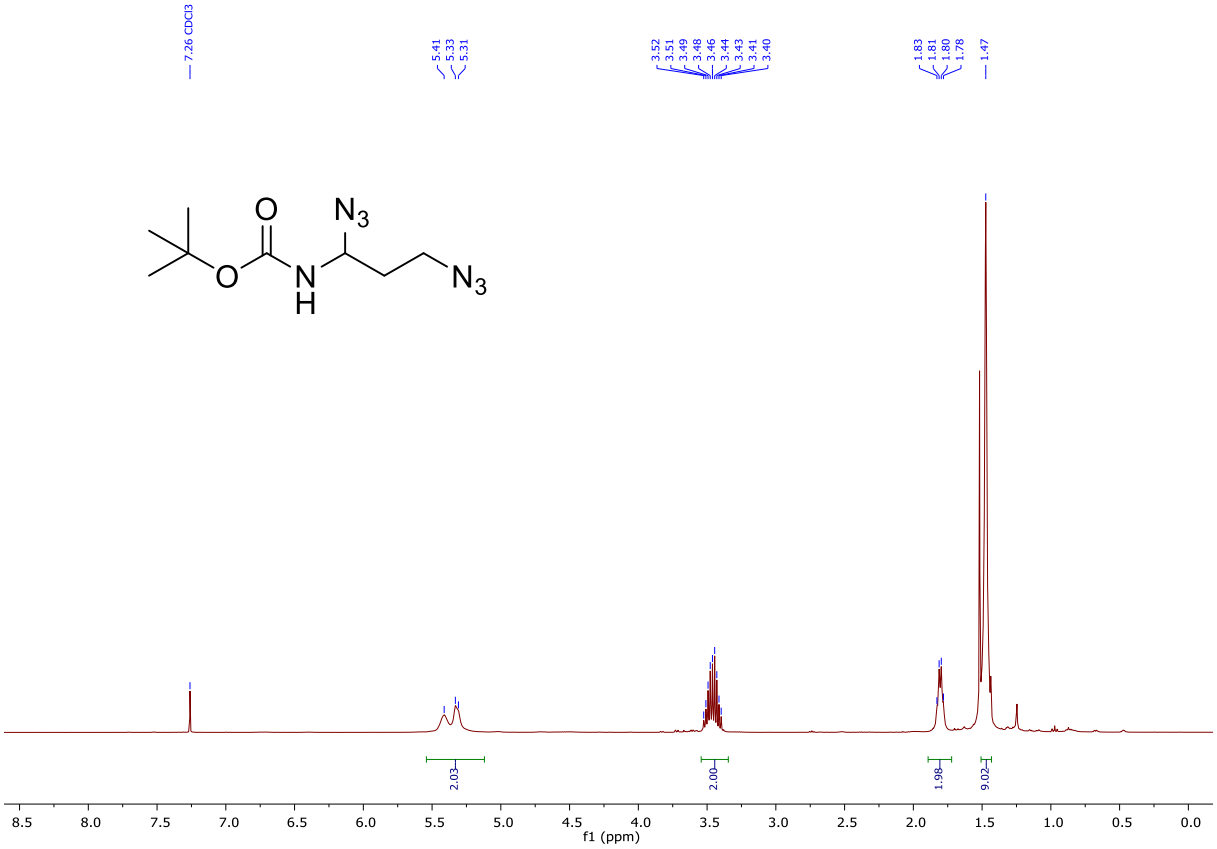


^{13}C-NMR (101 MHz, $CDCl_3$)

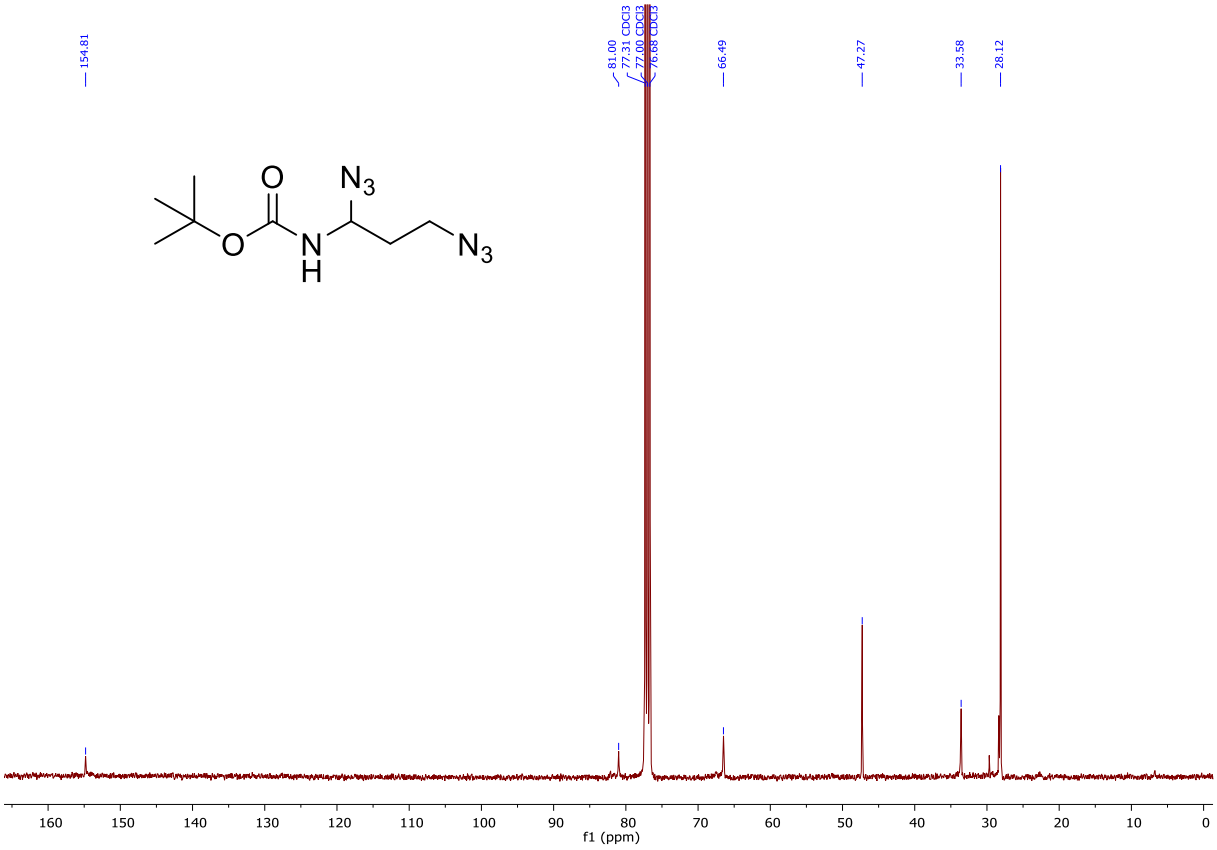


***tert*-Butyl (1,3-diazidopropyl)carbamate (6p)**

^{1}H-NMR (400 MHz, $CDCl_3$)

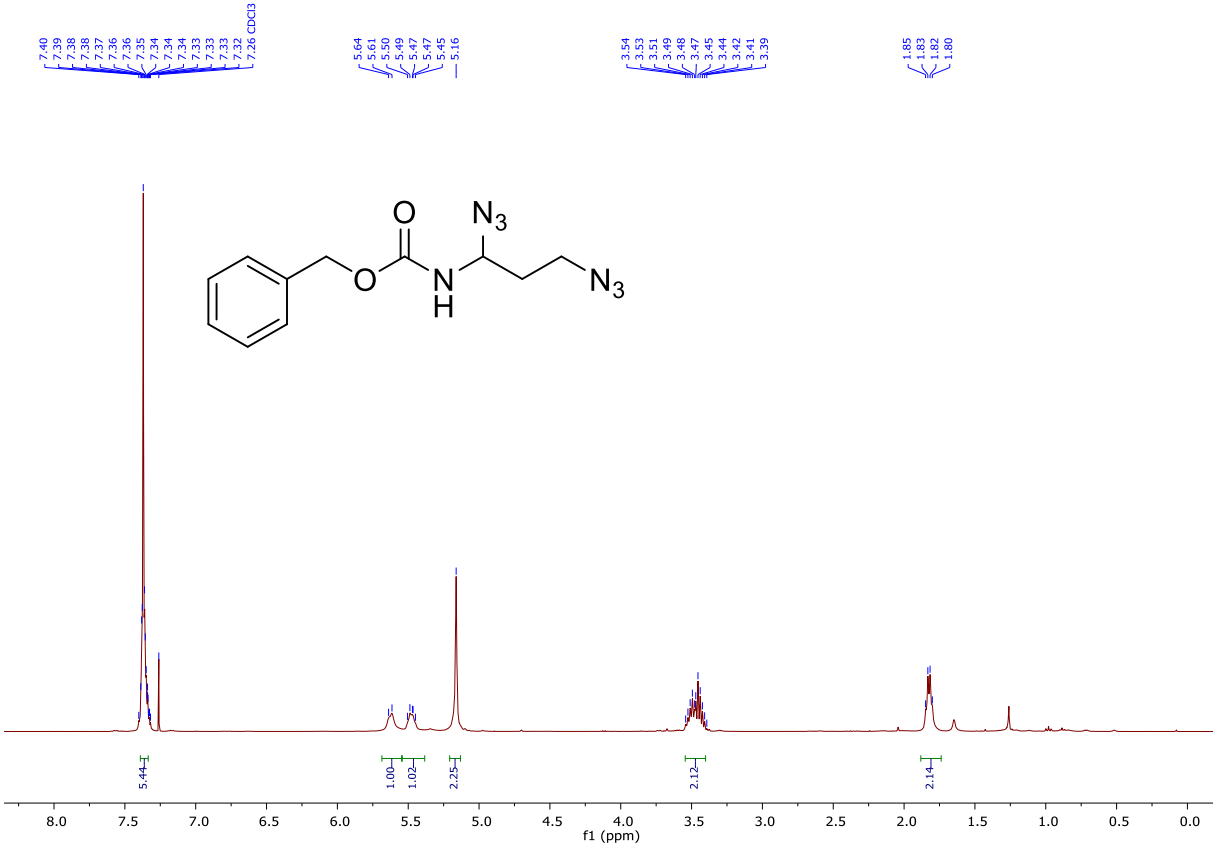


^{13}C-NMR (101 MHz, $CDCl_3$)

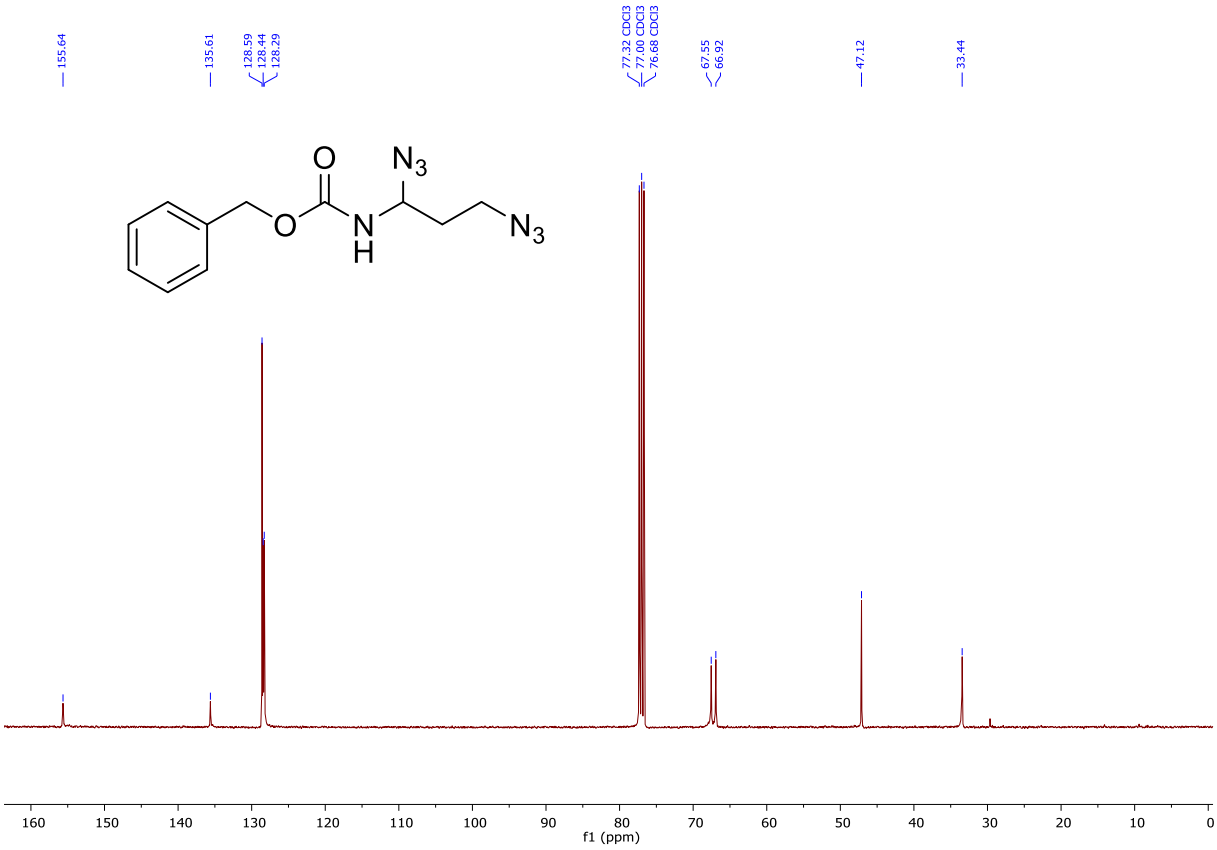


Benzyl (1,3-diazidopropyl)carbamate (6q)

^{1}H-NMR (400 MHz, $CDCl_3$)

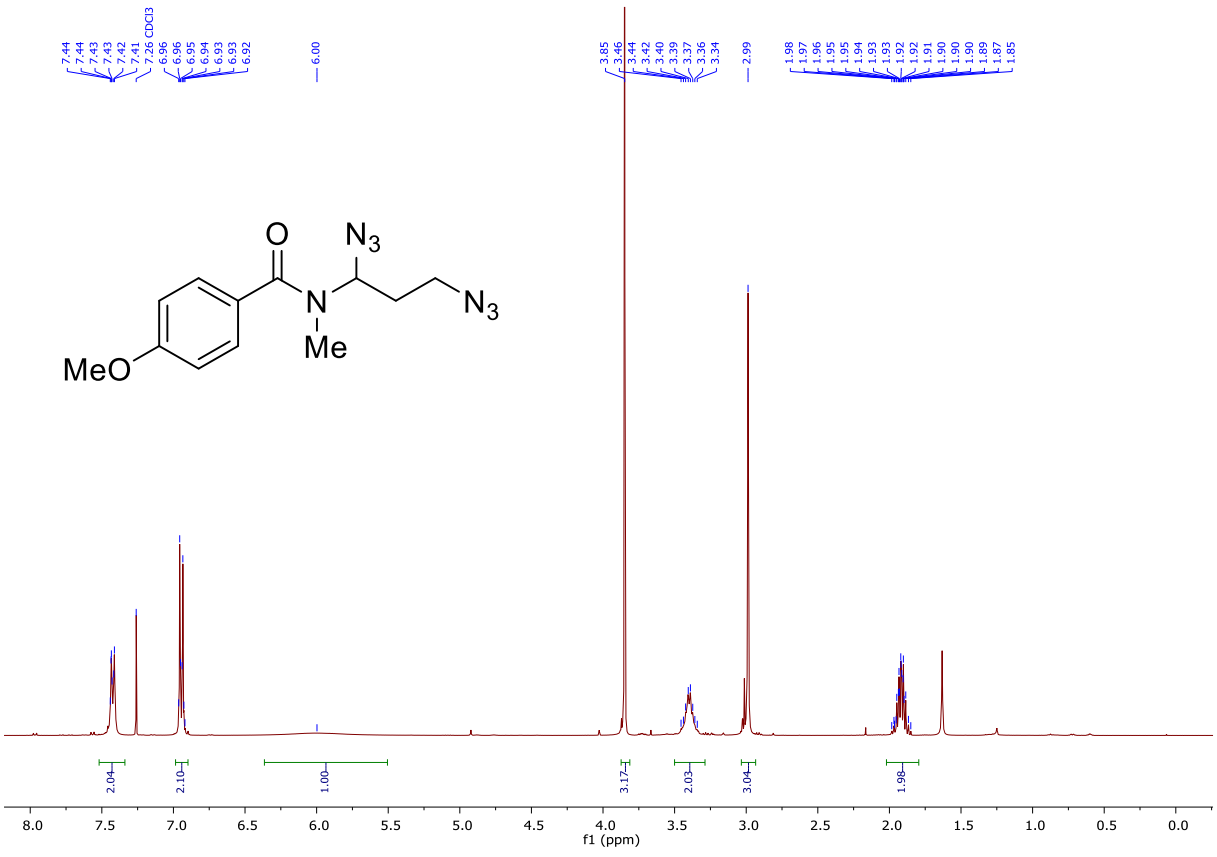


^{13}C-NMR (101 MHz, $CDCl_3$)

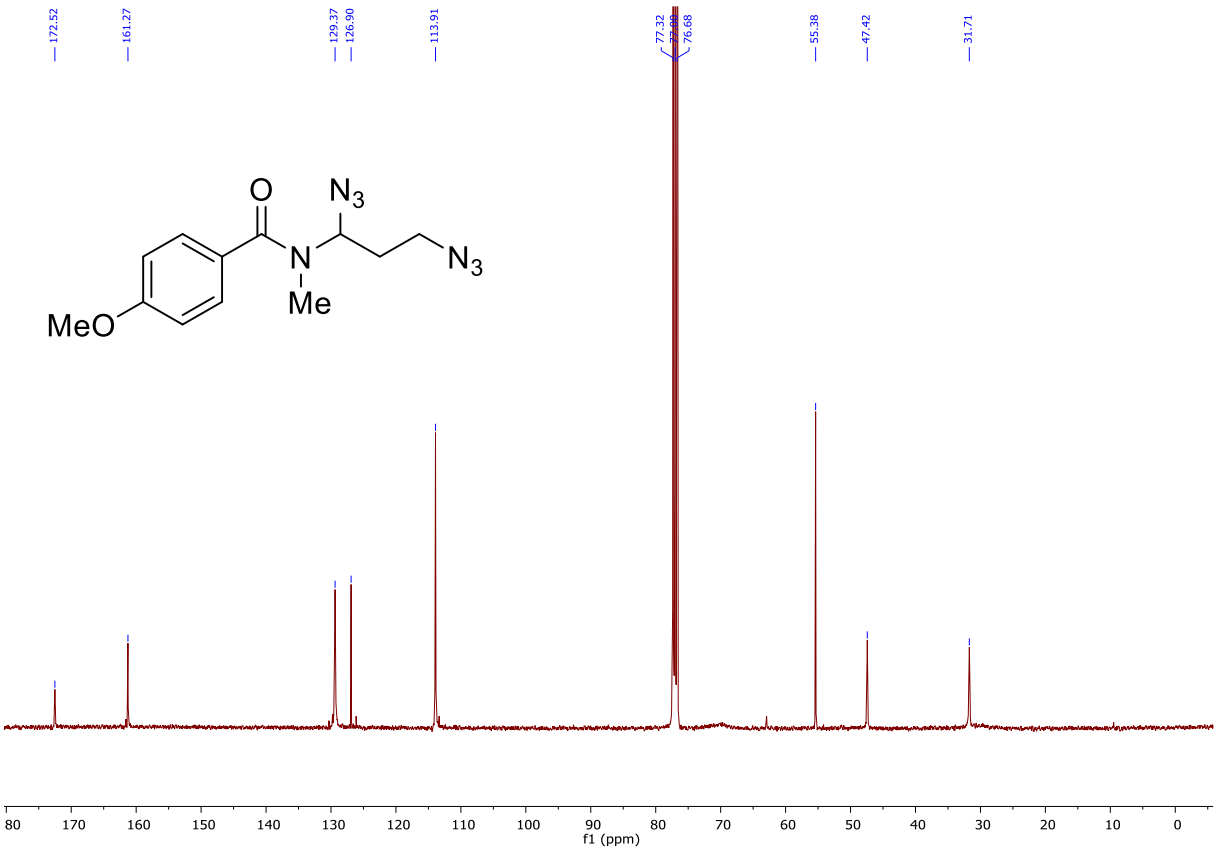


***N*-(1,3-Diazidopropyl)-4-methoxy-N-methylbenzamide (6s)**

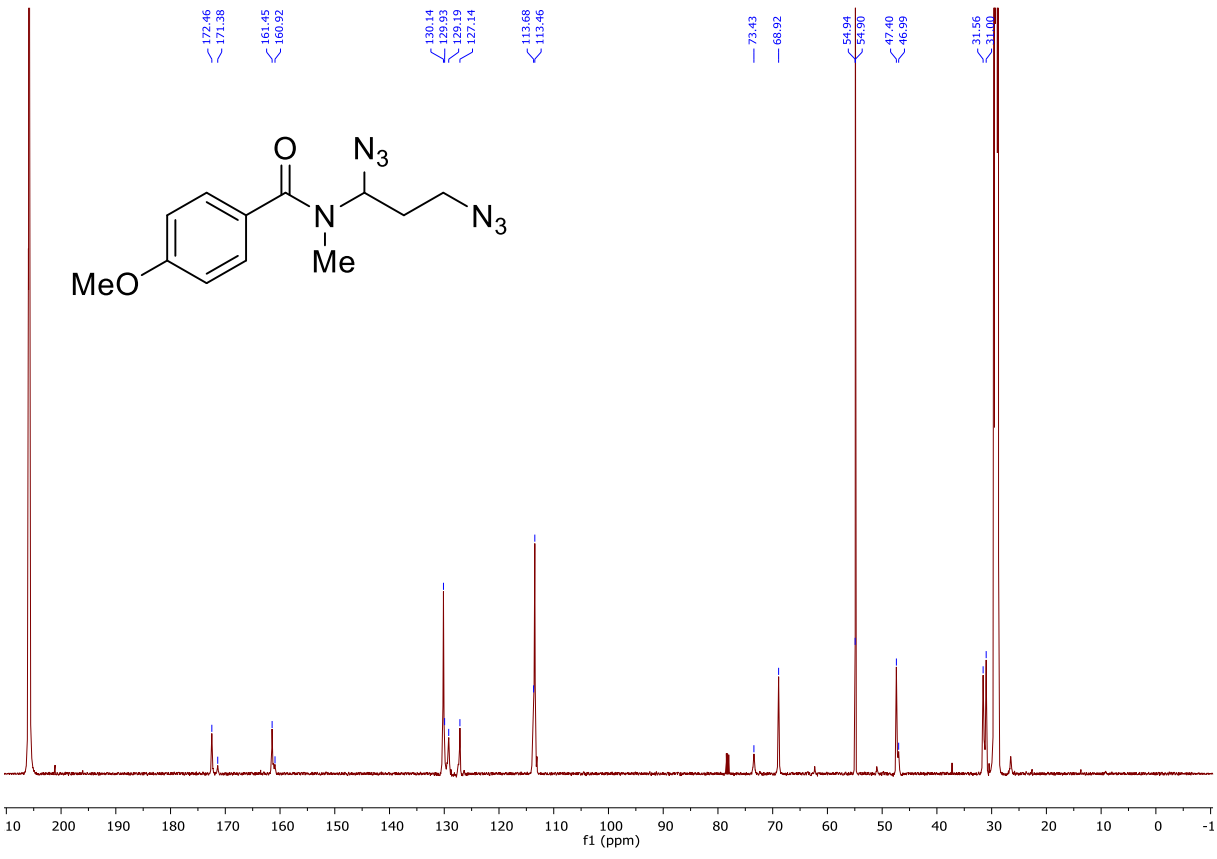
^{1}H-NMR (400 MHz, $CDCl_3$, 298K)



^{13}C-NMR (101 MHz, $CDCl_3$, 298K)

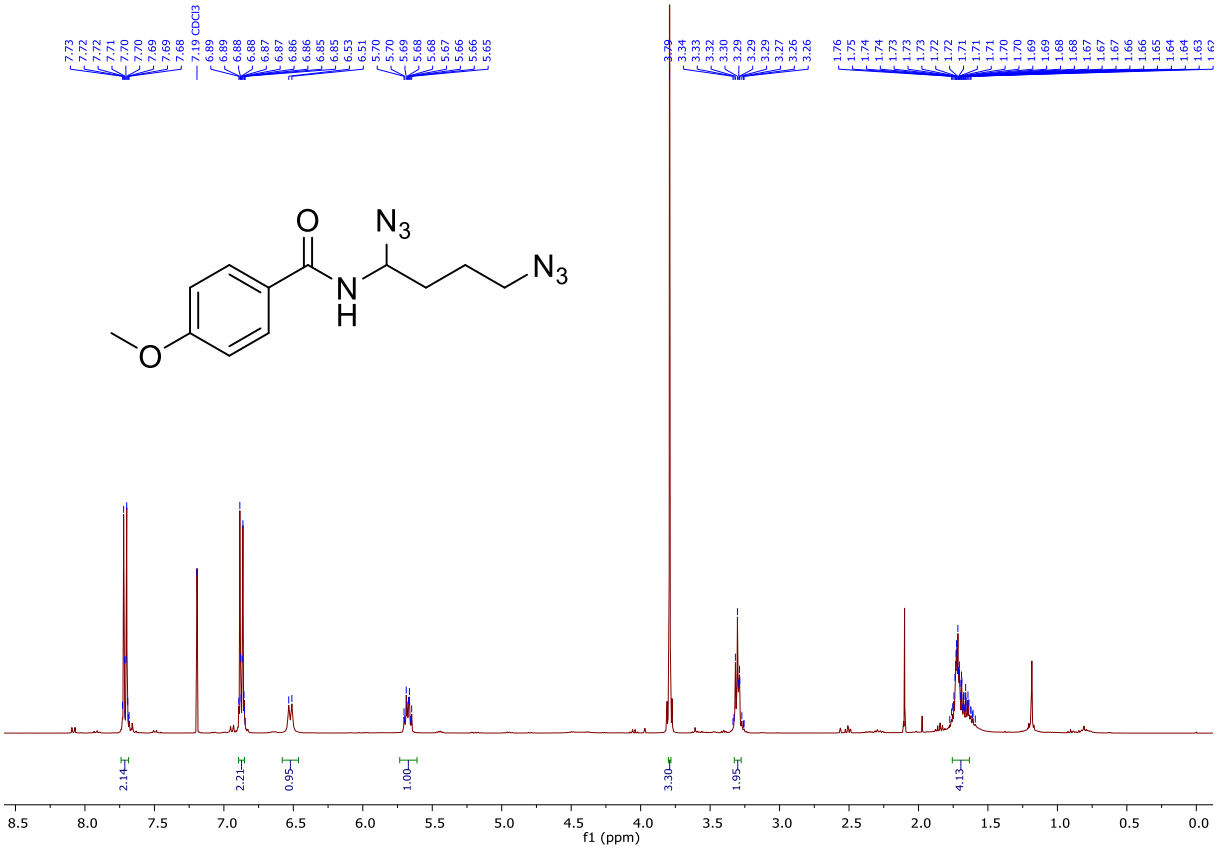


^{13}C-NMR (101 MHz, Acetone-d_6, 261.7 K)

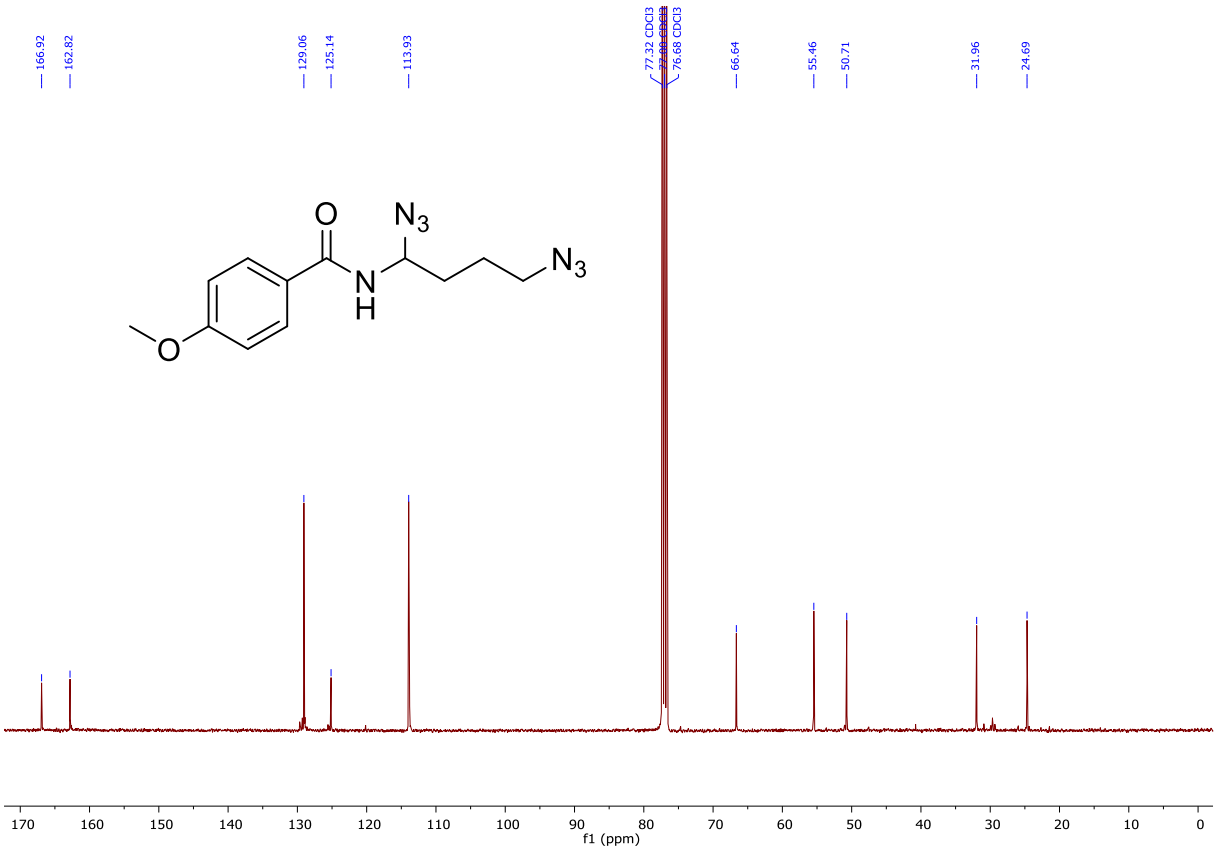


***N*-(1,4-Diazidobutyl)-4-methoxybenzamide (6t)**

^{1}H-NMR (400 MHz, $CDCl_3$)

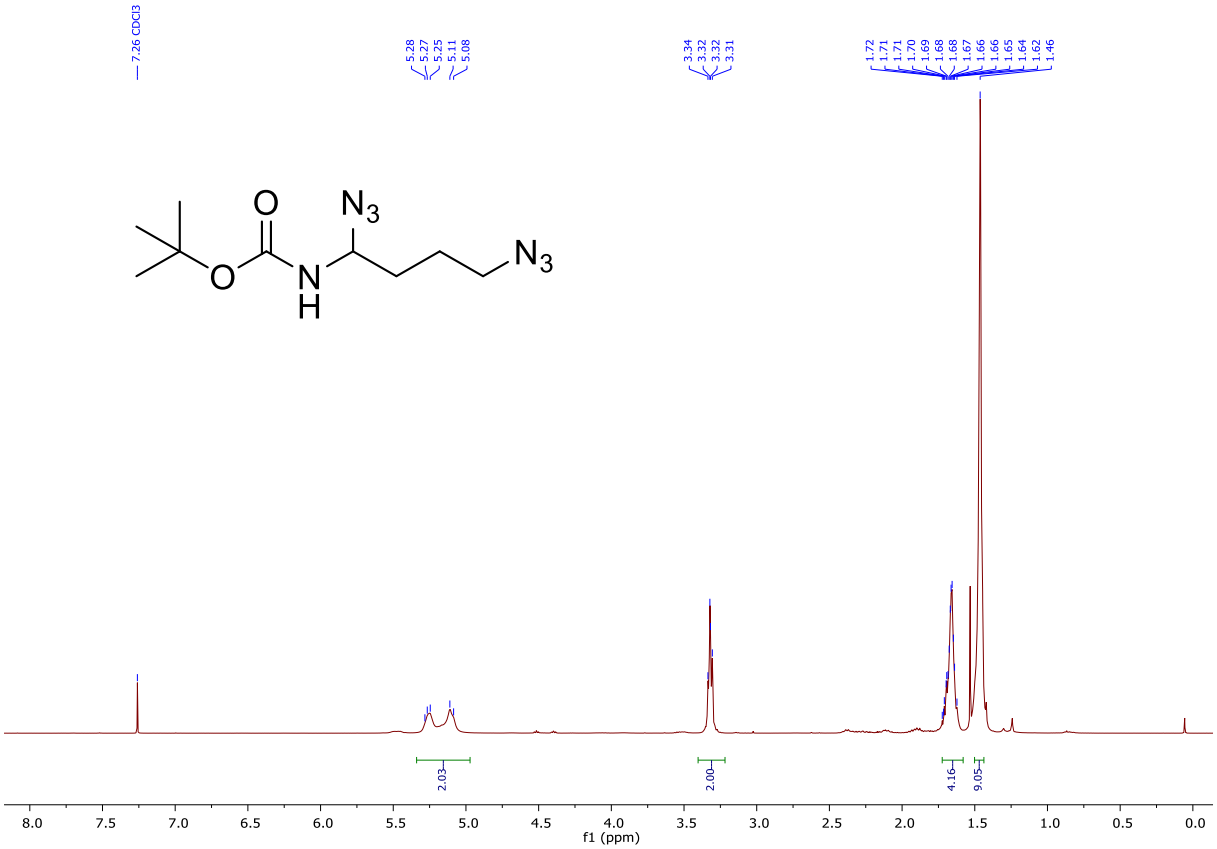


^{13}C-NMR (101 MHz, $CDCl_3$)

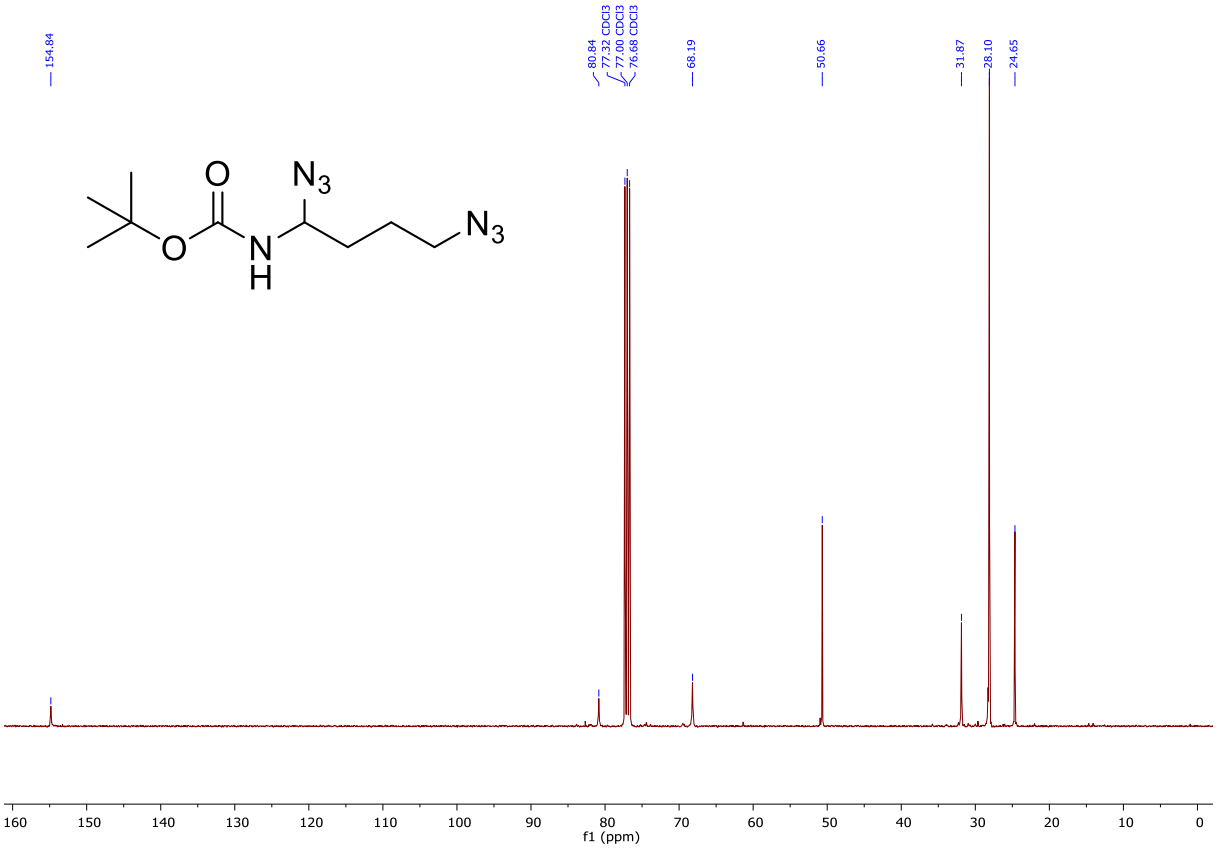


***tert*-Butyl (1,4-diazidobutyl)carbamate (6u)**

^{1}H-NMR (400 MHz, $CDCl_3$)

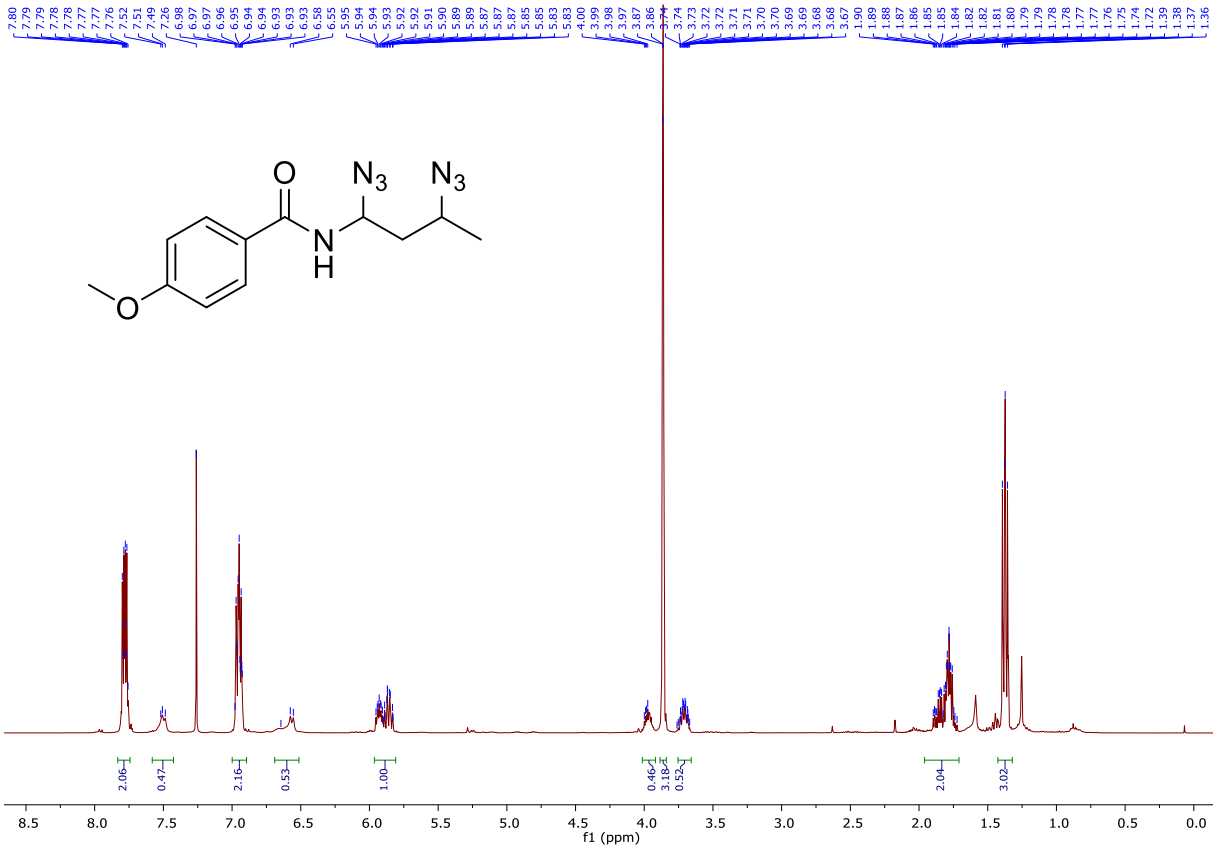


^{13}C-NMR (101 MHz, $CDCl_3$)

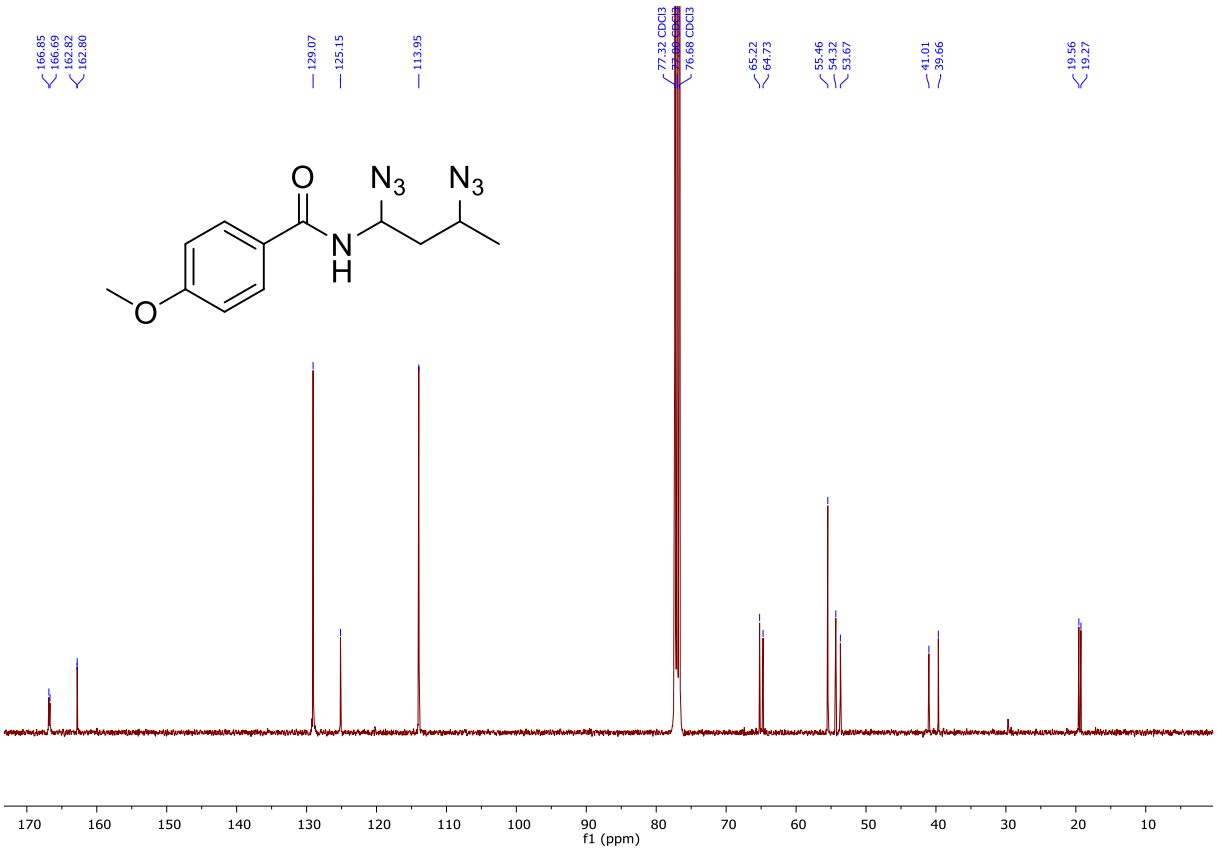


***N*-(1,3-Diazidobutyl)-4-methoxybenzamide (6xa)**

^{1}H-NMR (400 MHz, $CDCl_3$)

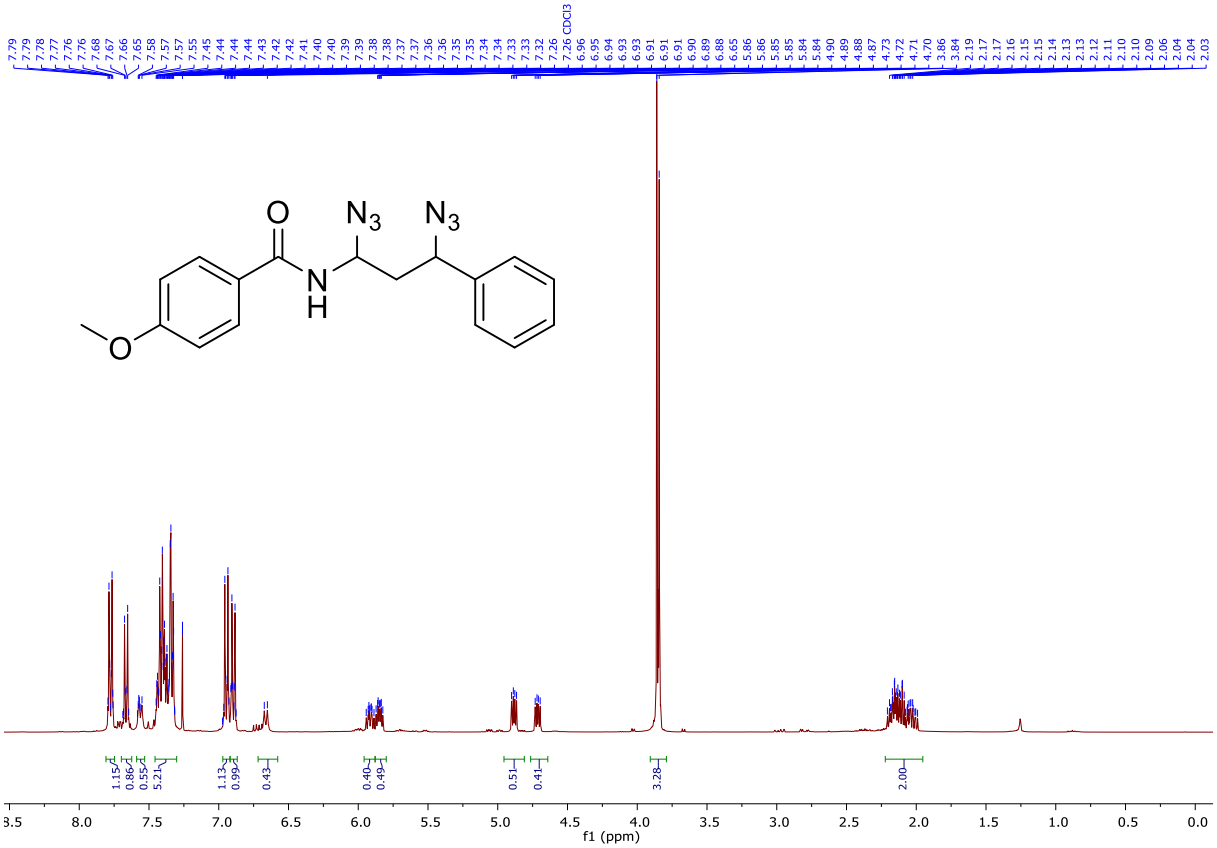


^{13}C-NMR (101 MHz, $CDCl_3$)

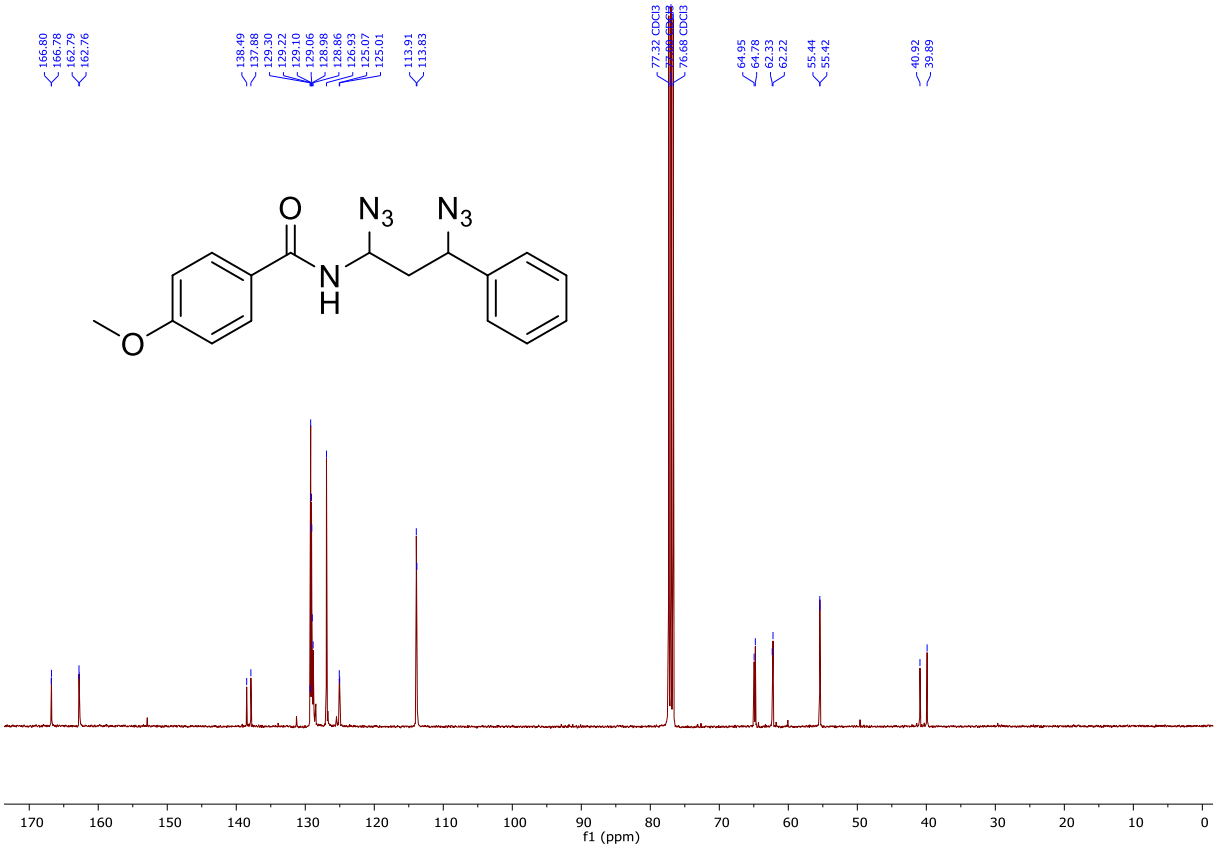


***N*-(1,3-Diazido-3-phenylpropyl)-4-methoxybenzamide (6xb)**

^{1}H-NMR (400 MHz, $CDCl_3$)

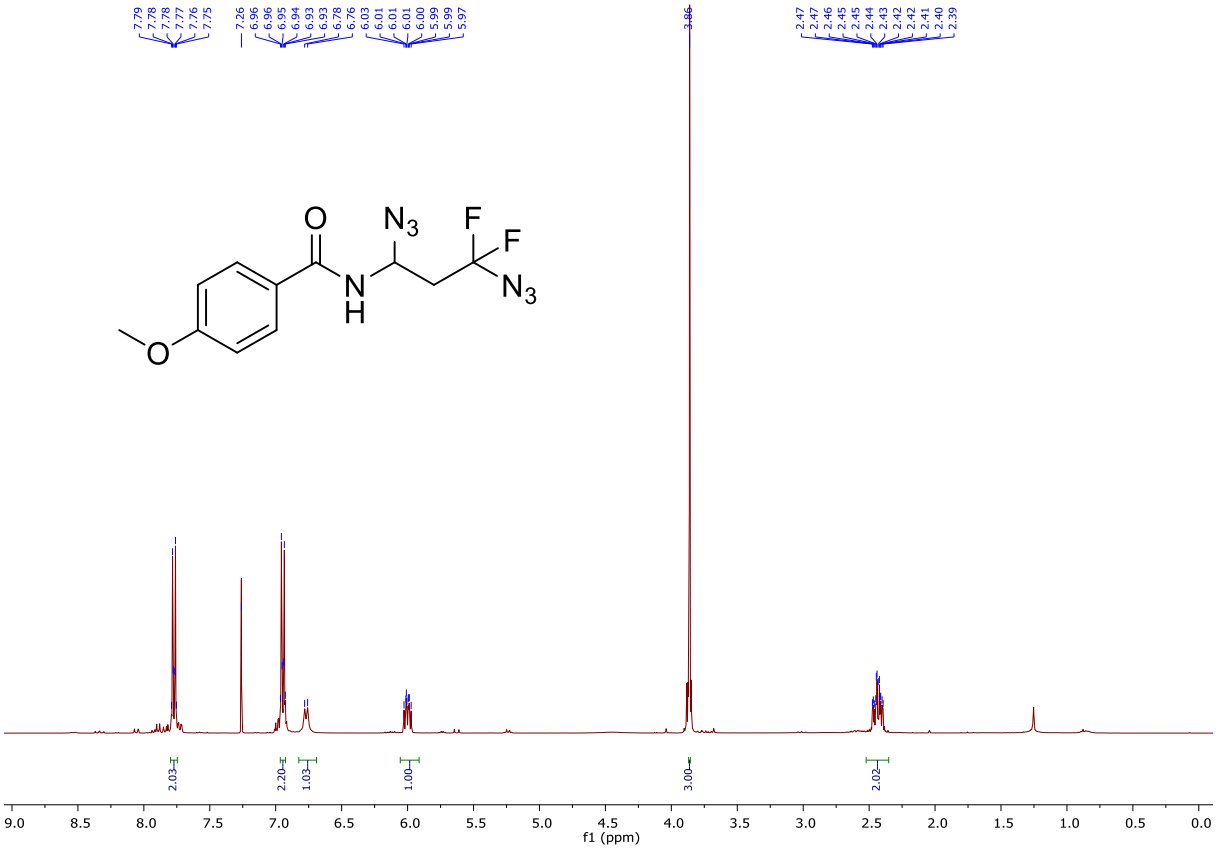


^{13}C-NMR (101 MHz, $CDCl_3$)

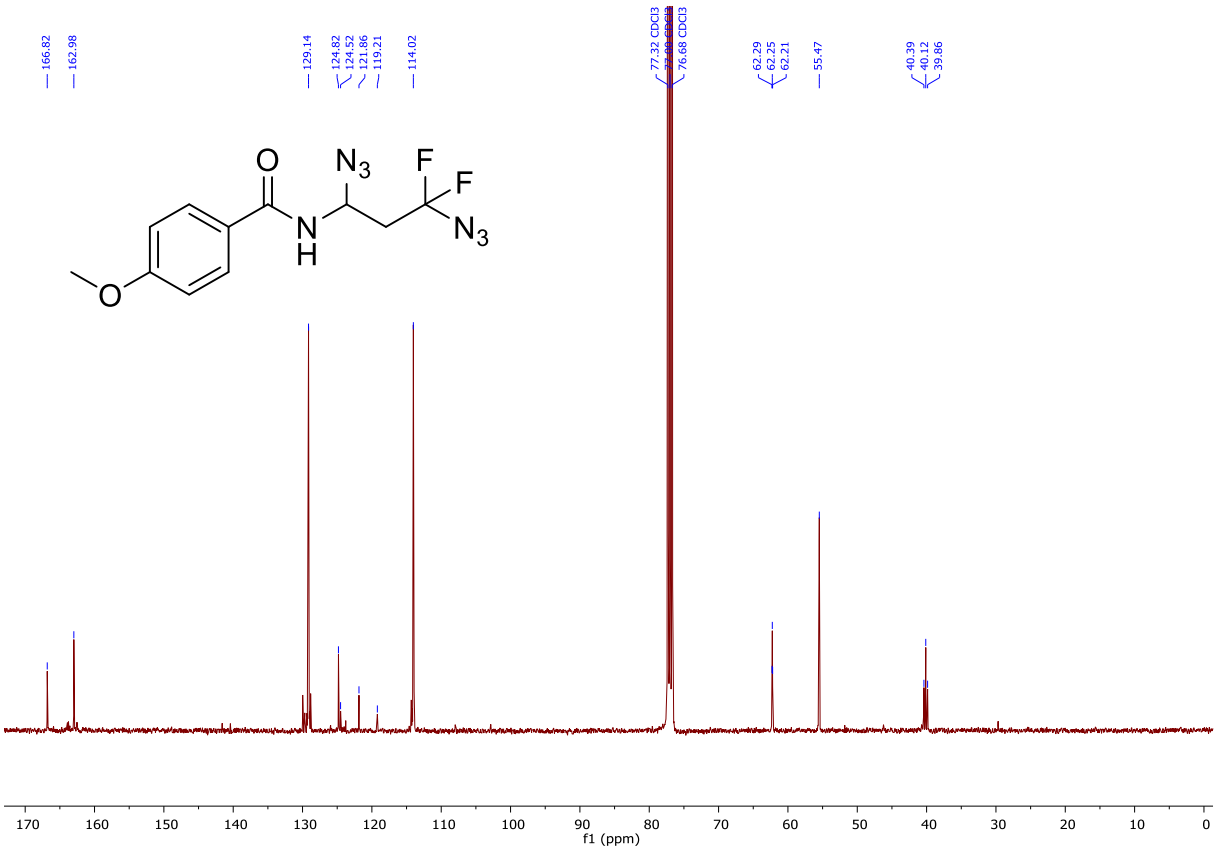


***N*-(1,3-Diazido-3,3-difluoropropyl)-4-methoxybenzamide (6y)**

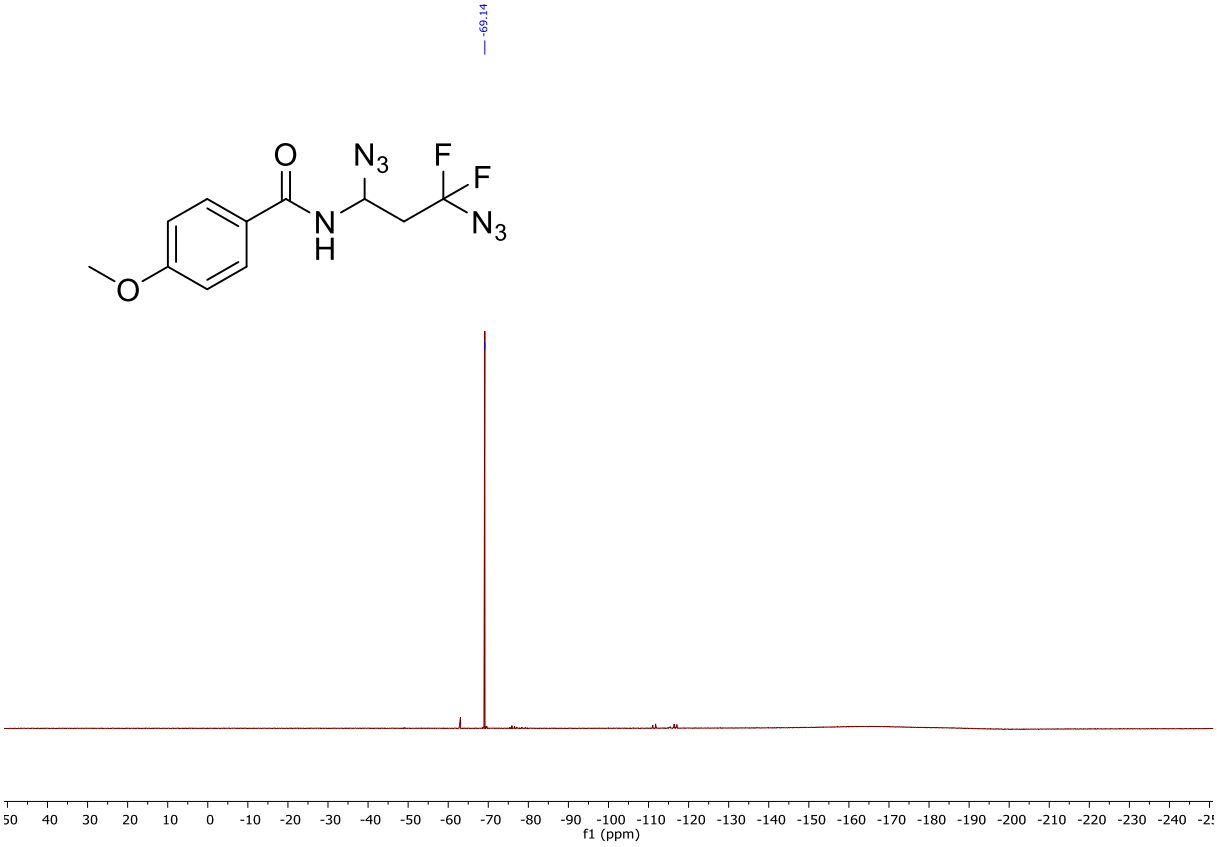
^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (101 MHz, $CDCl_3$)

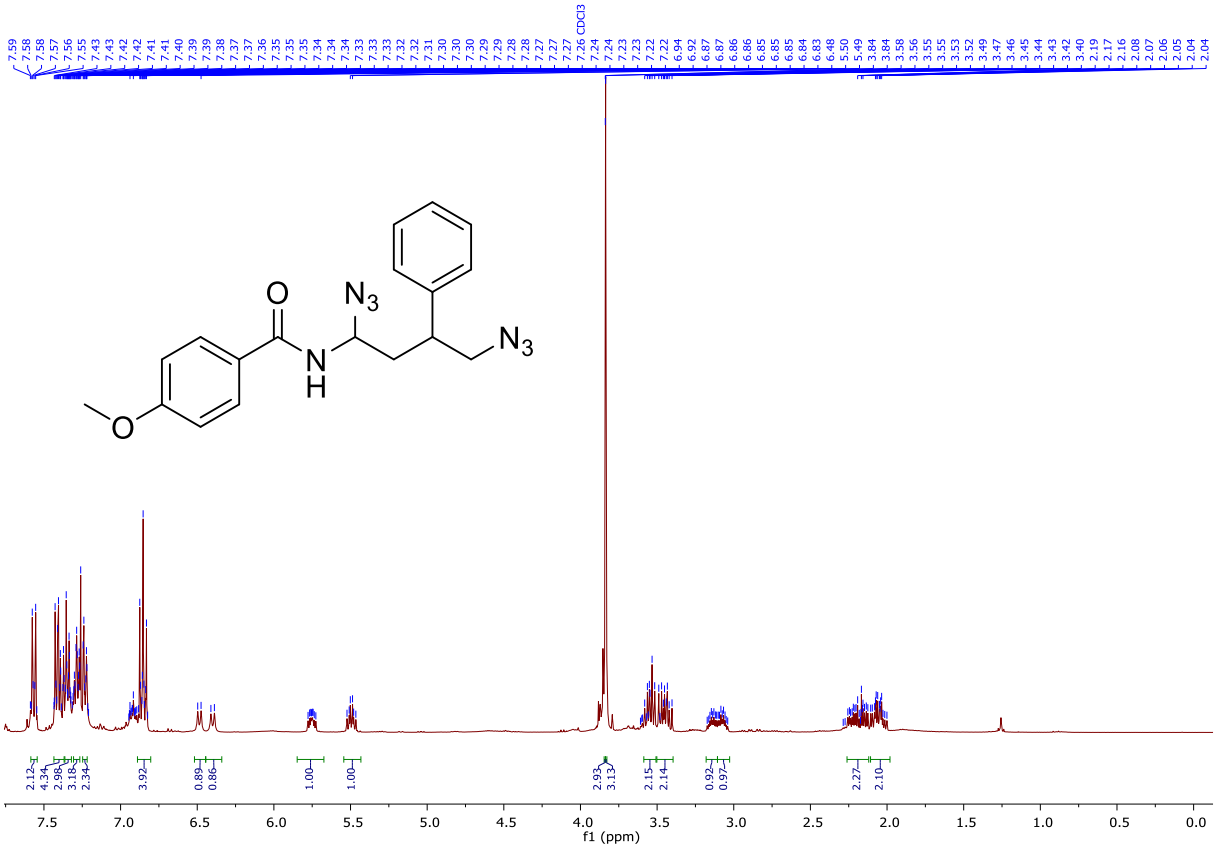


^{19}F-NMR (377 MHz, $CDCl_3$)

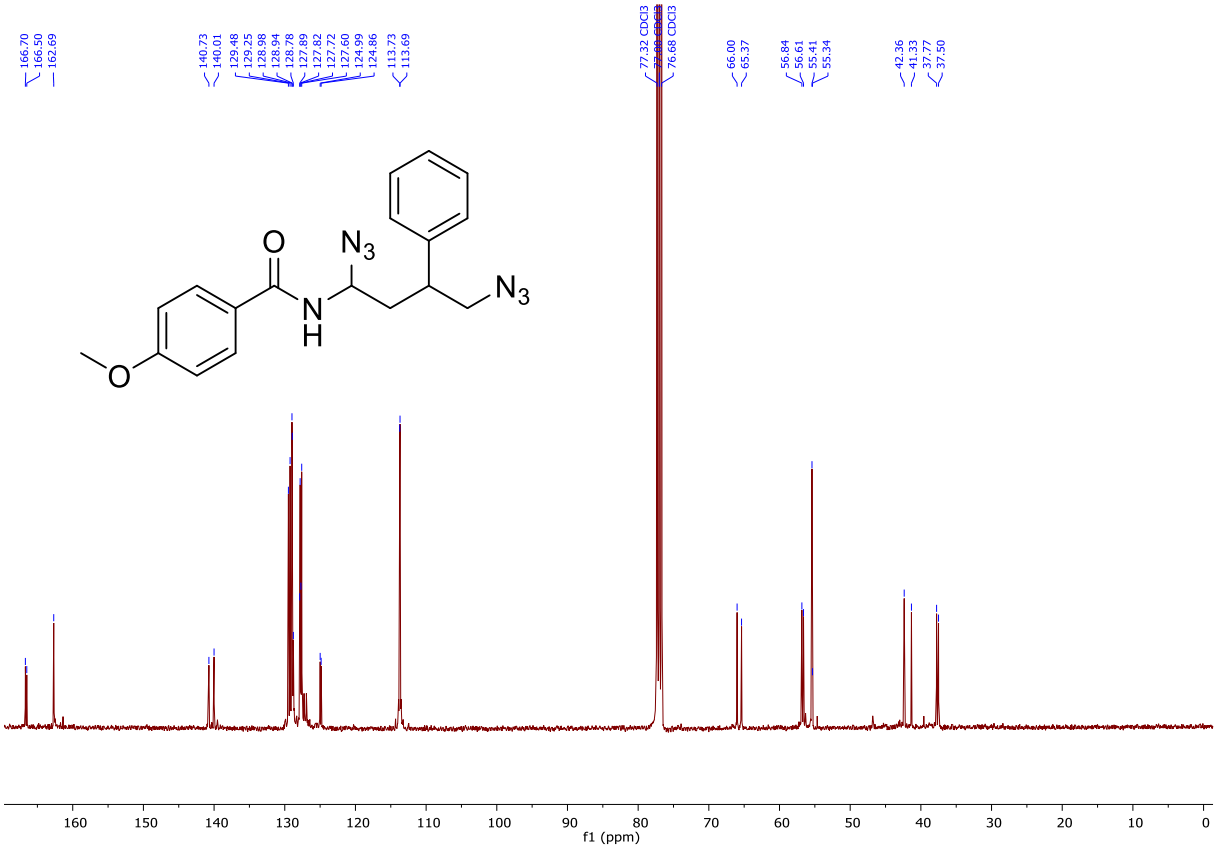


***N*-(1,4-Diazido-3-phenylbutyl)-4-methoxybenzamide (6z)**

^{1}H-NMR (400 MHz, $CDCl_3$)

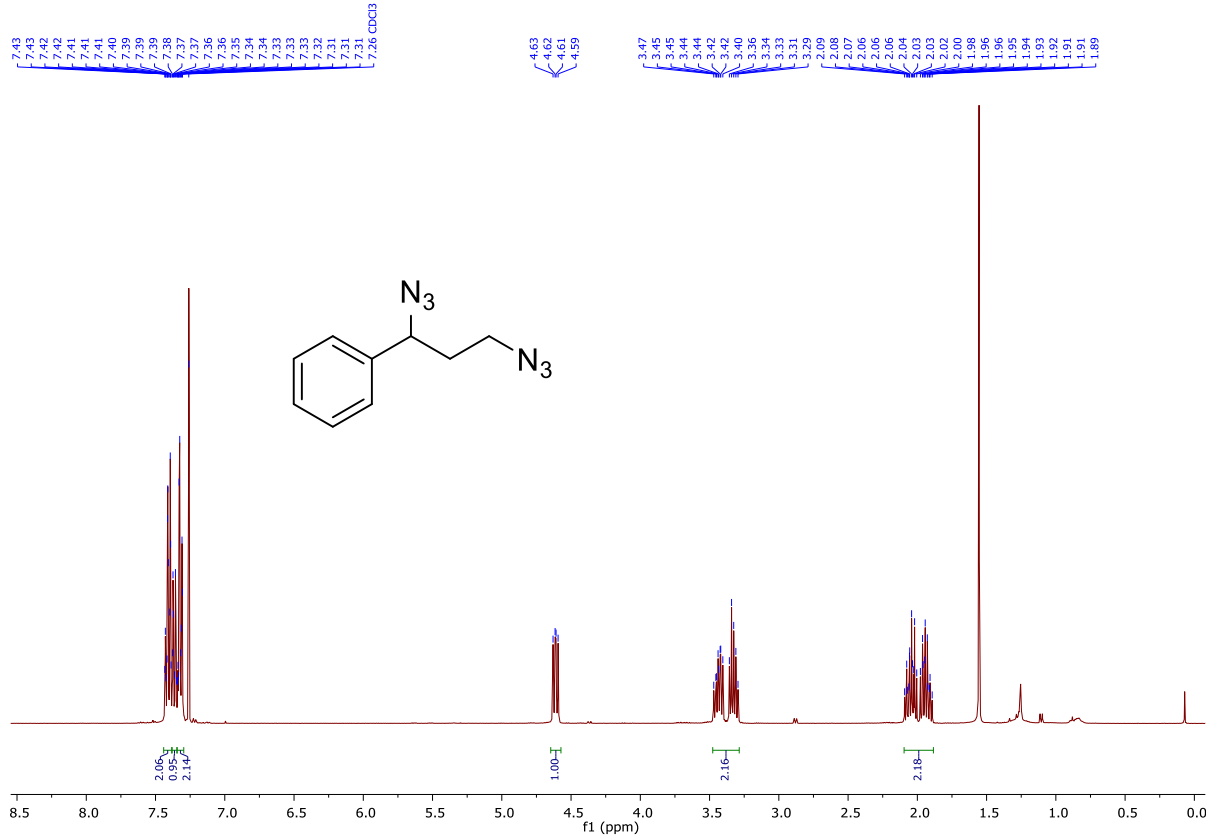


^{13}C-NMR (101 MHz, $CDCl_3$)

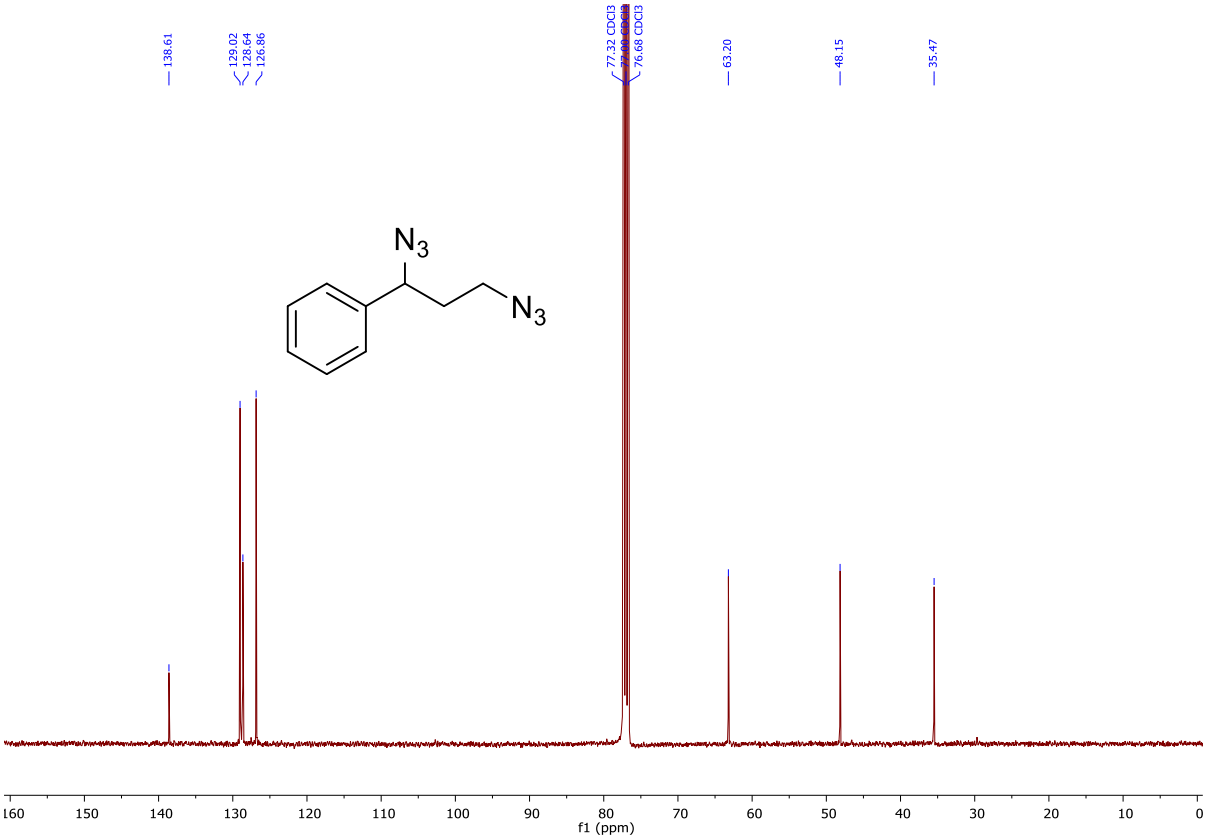


(1,3-Diazidopropyl)benzene (8)

^{1}H-NMR (400 MHz, $CDCl_3$)

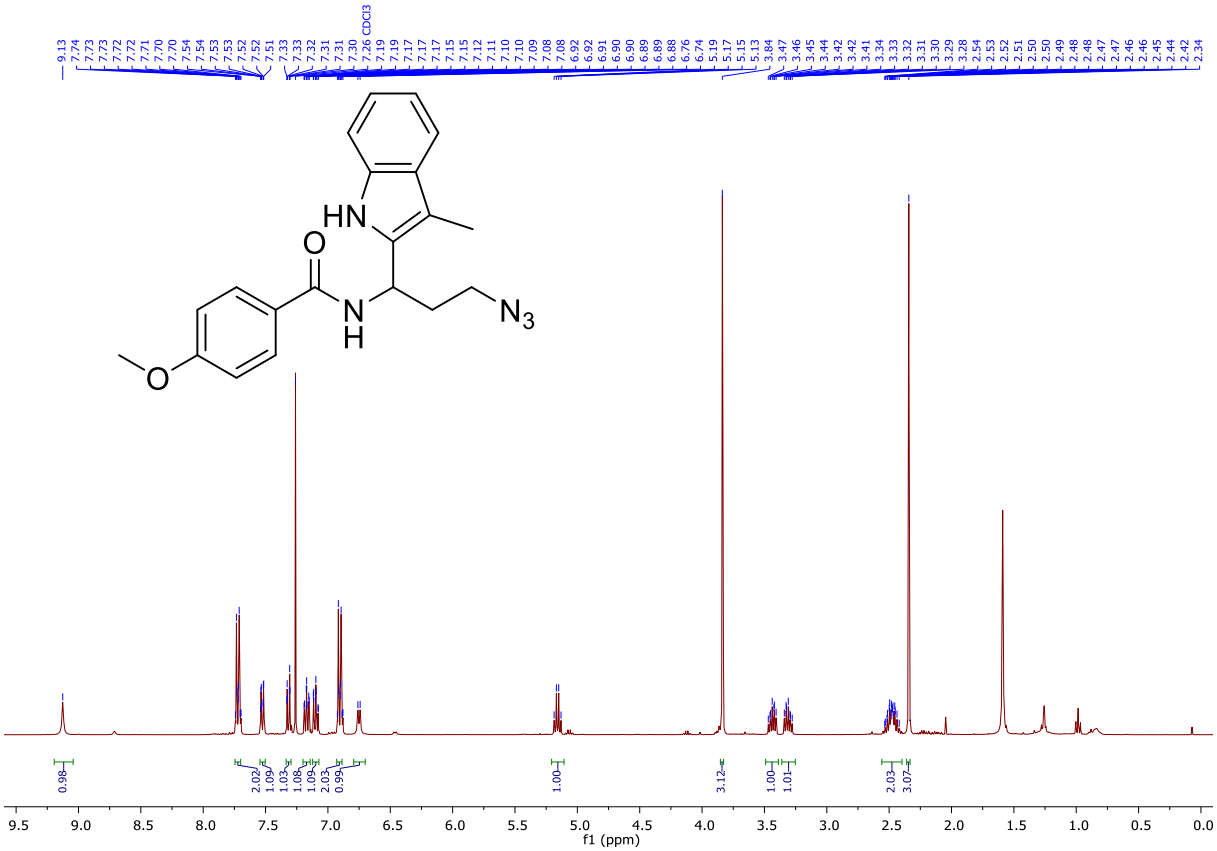


^{13}C-NMR (101 MHz, $CDCl_3$)

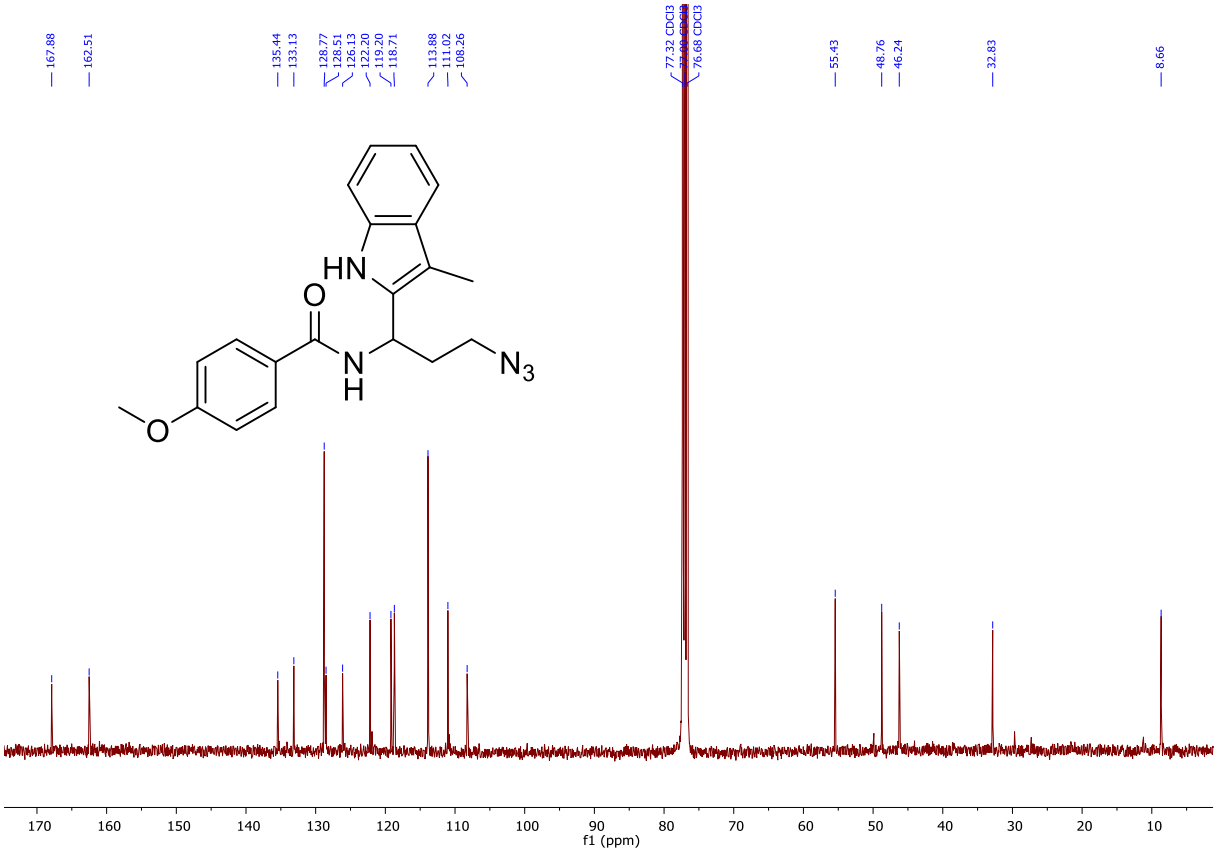


***N*-(3-Azido-1-(3-methyl-1H-indol-2-yl)propyl)-4-methoxybenzamide (10a)**

^{1}H-NMR (400 MHz, $CDCl_3$)

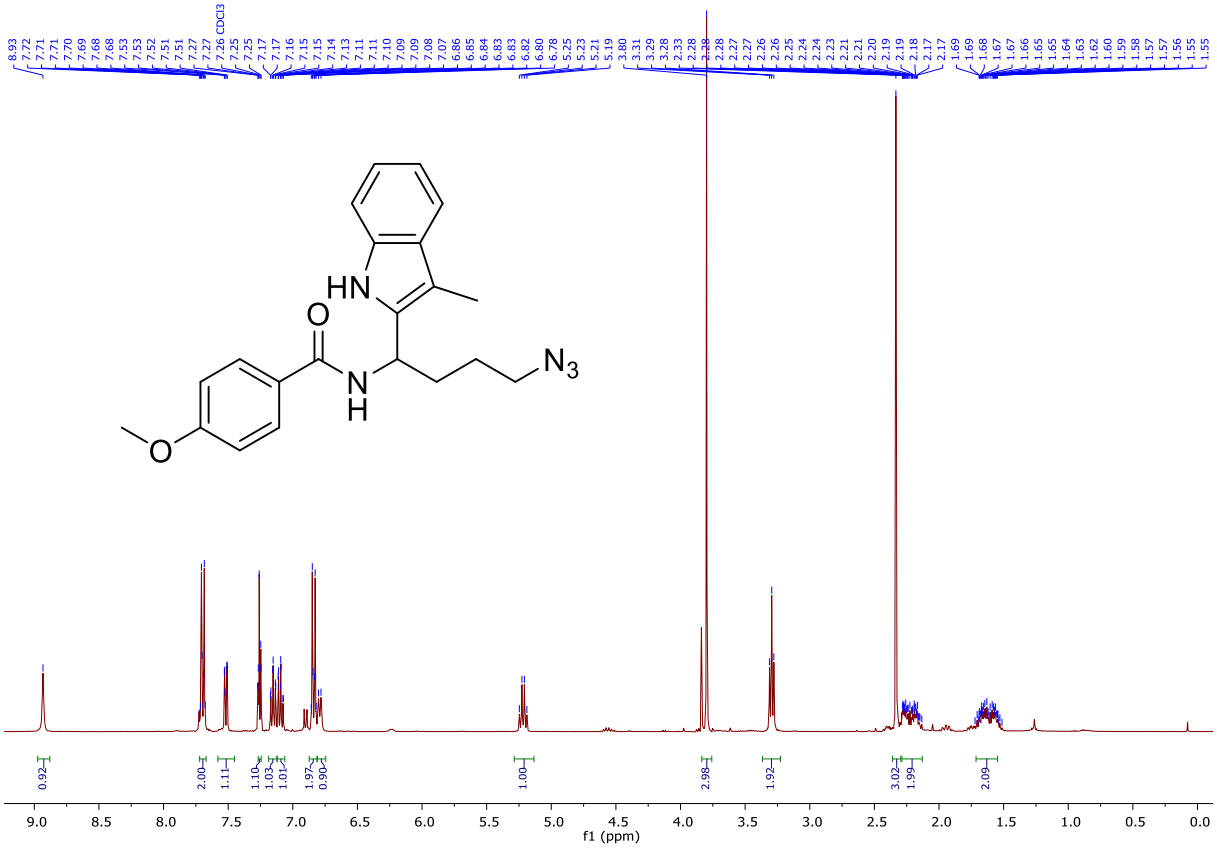


^{13}C-NMR (101 MHz, $CDCl_3$)

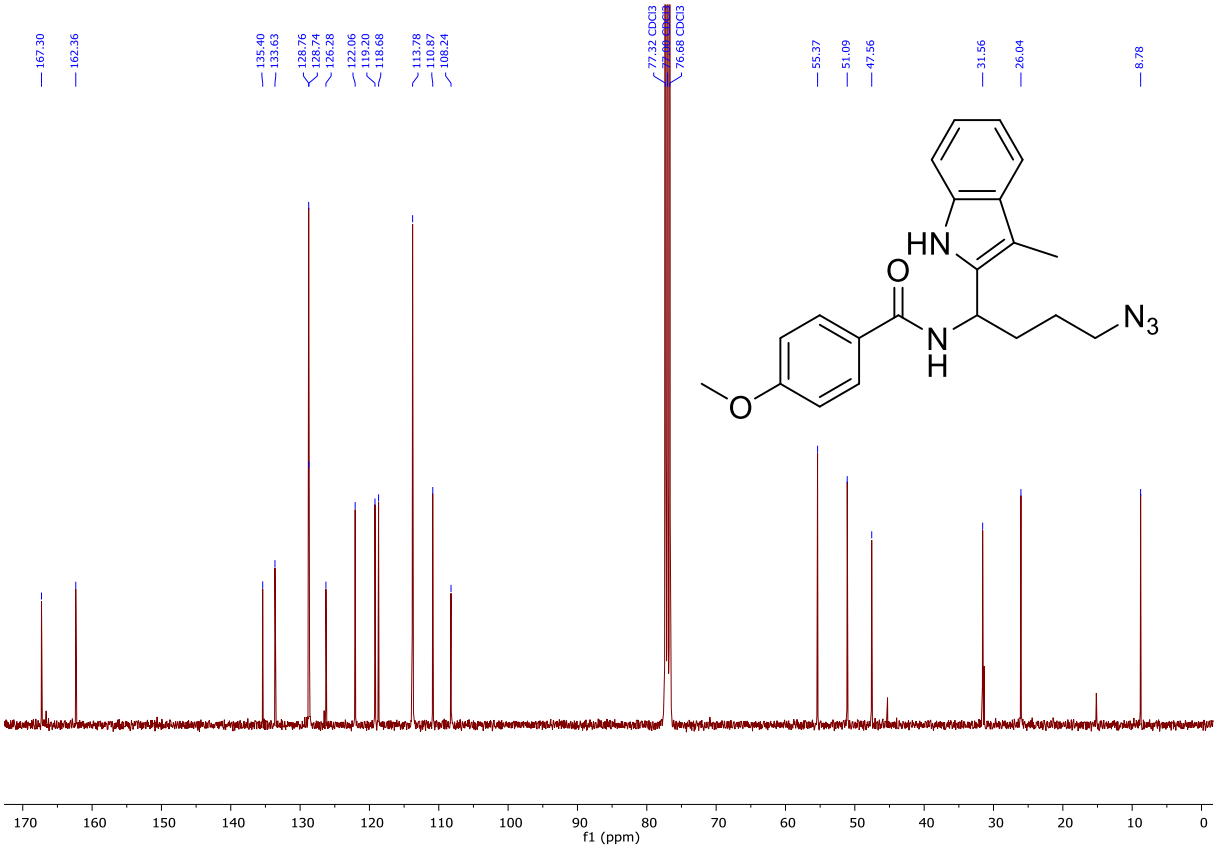


***N*-(4-Azido-1-(3-methyl-1H-indol-2-yl)butyl)-4-methoxybenzamide (11a)**

^{1}H-NMR (400 MHz, $CDCl_3$)

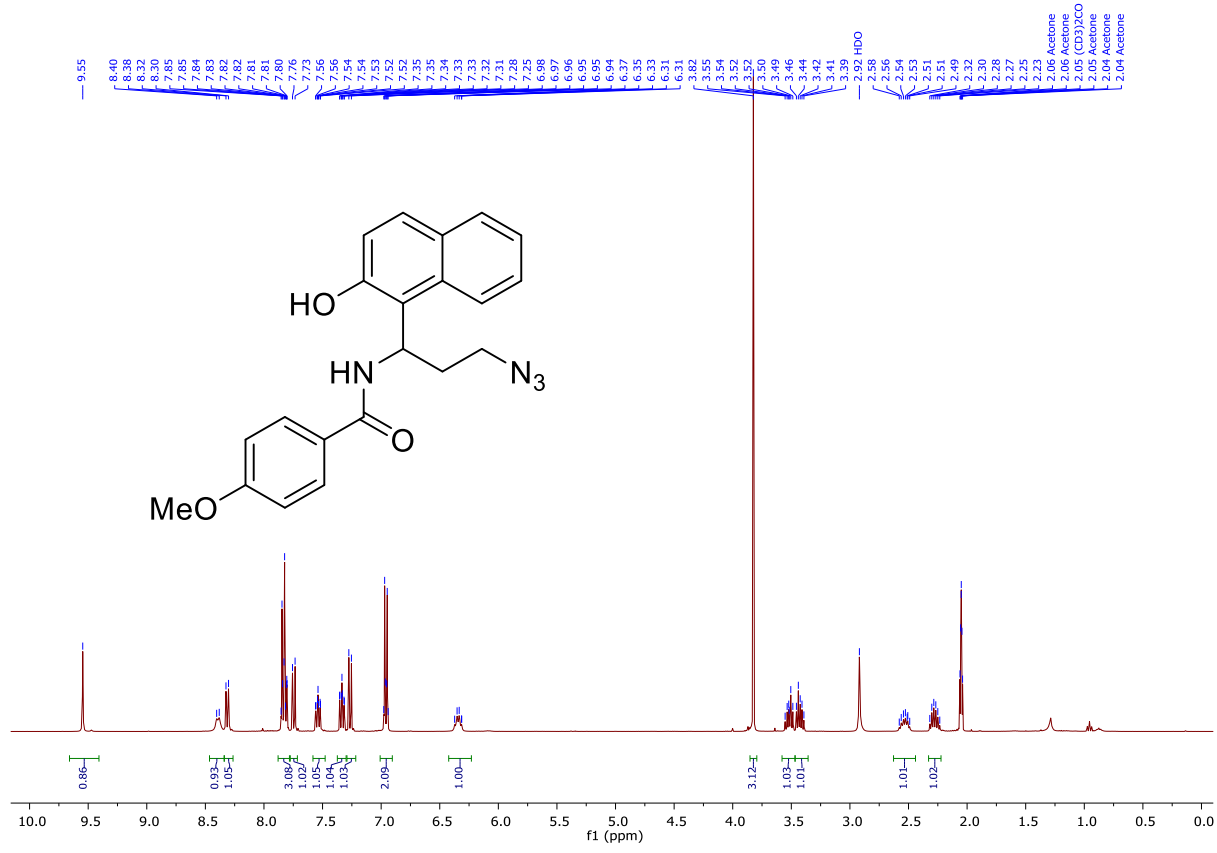


^{13}C-NMR (101 MHz, $CDCl_3$)

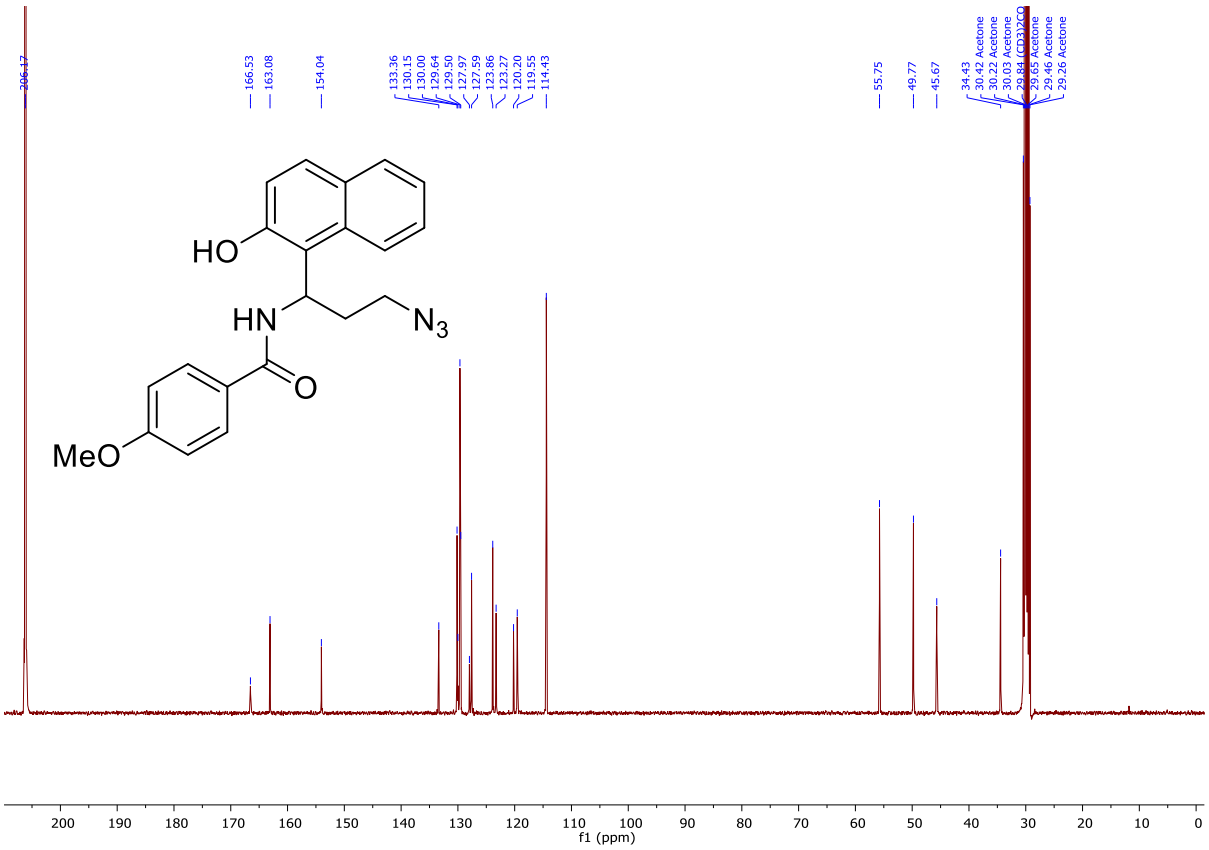


***N*-(3-Azido-1-(2-hydroxynaphthalen-1-yl)propyl)-4-methoxybenzamide (10ba)**

^{1}H-NMR (400 MHz, Acetone-d_6)

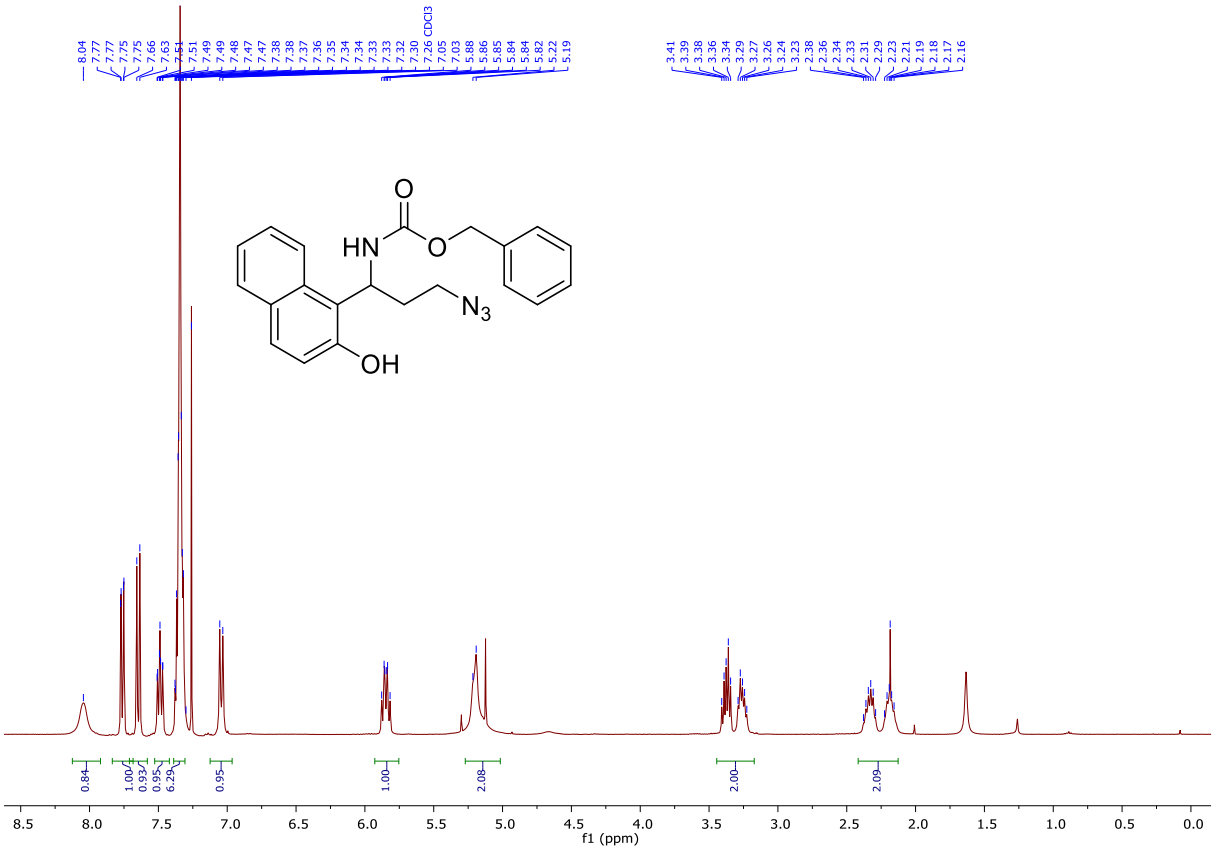


^{13}C-NMR (101 MHz, Acetone-d_6)

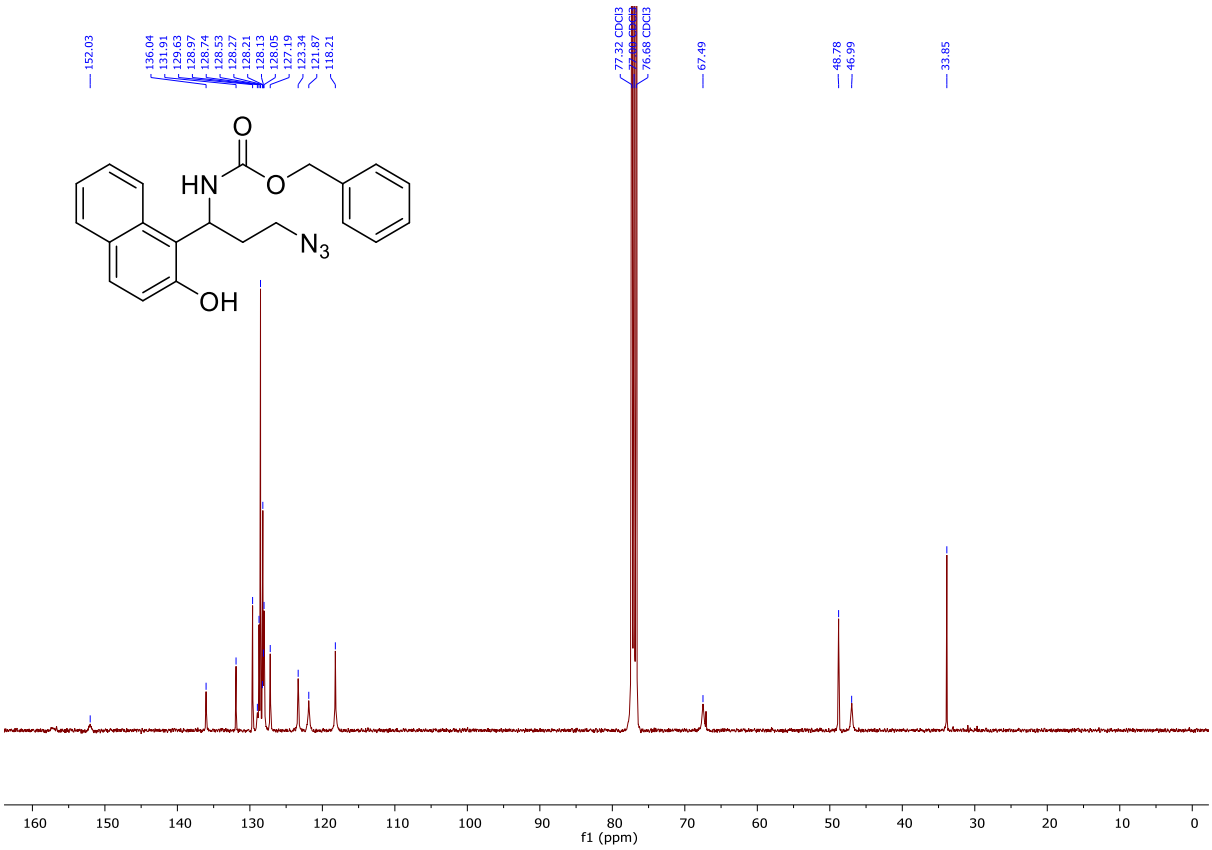


Benzyl (3-azido-1-(2-hydroxynaphthalen-1-yl)propyl)carbamate (10bb)

^{1}H-NMR (400 MHz, $CDCl_3$)

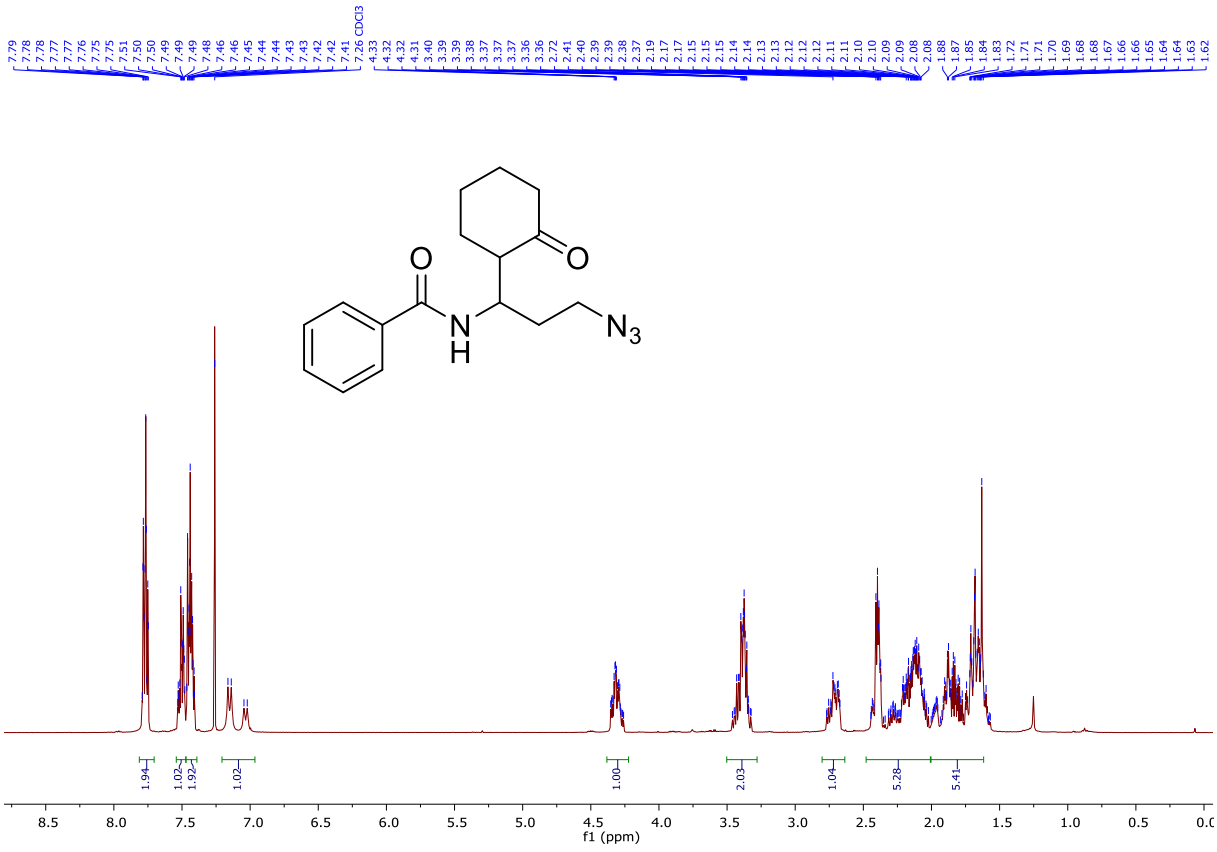


^{13}C-NMR (101 MHz, $CDCl_3$)

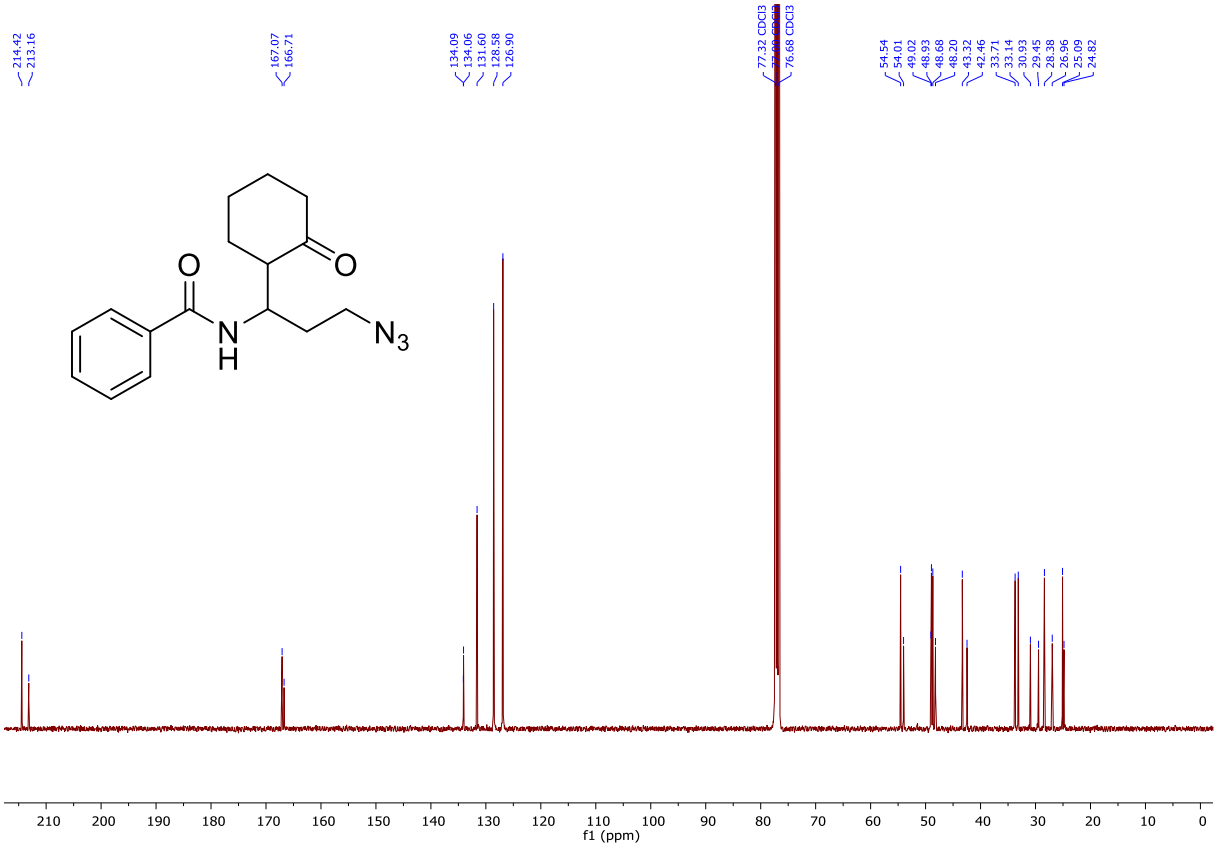


***N*-(3-Azido-1-(2-oxocyclohexyl)propyl)benzamide (10c)**

^{1}H-NMR (400 MHz, $CDCl_3$)

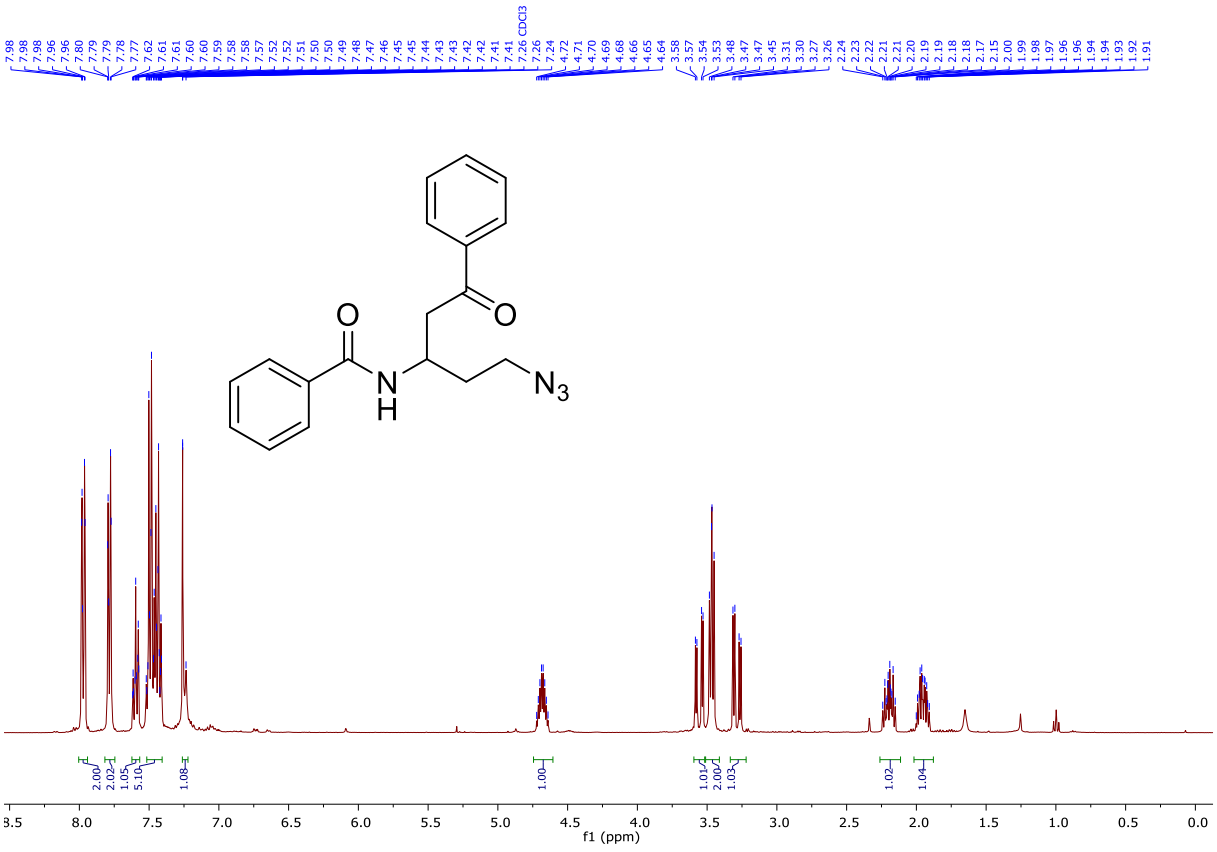


^{13}C-NMR (101 MHz, $CDCl_3$)

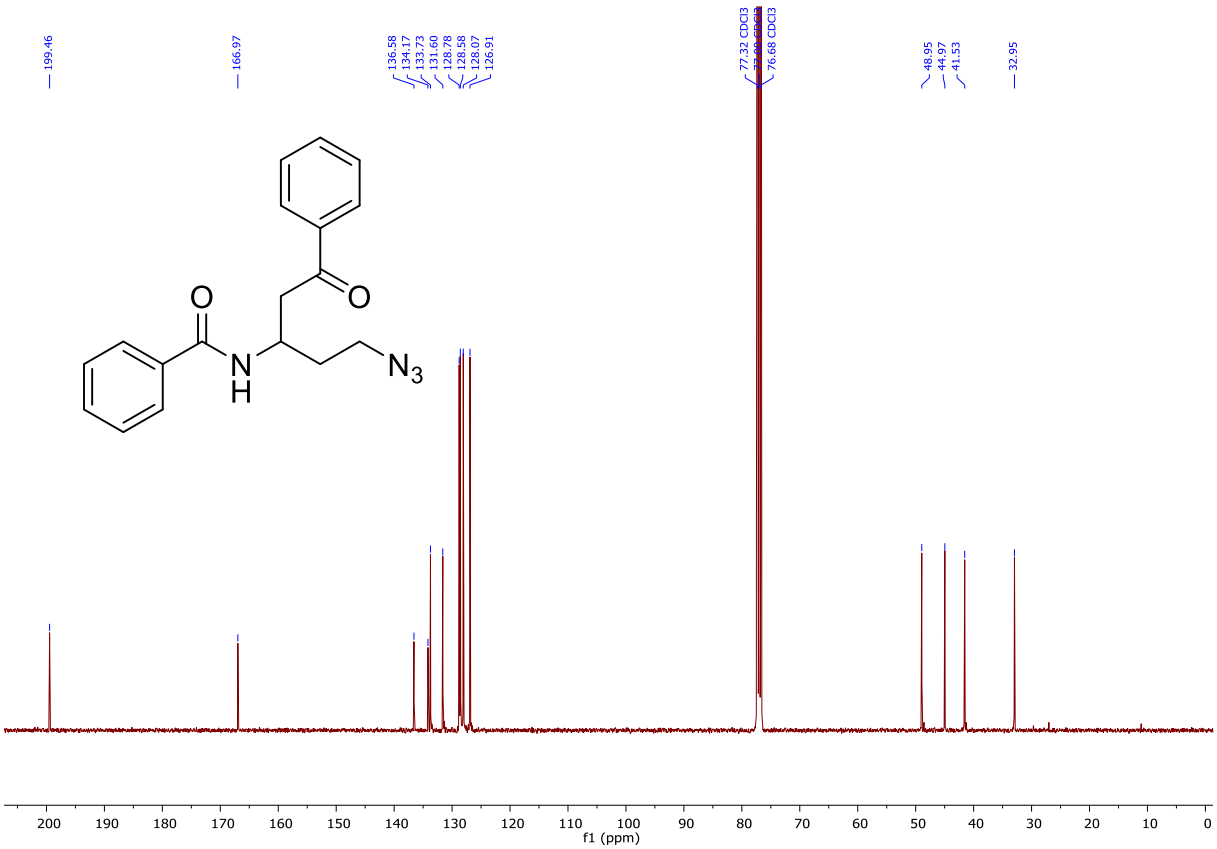


***N*-(5-Azido-1-oxo-1-phenylpentan-3-yl)benzamide (10d)**

^{1}H-NMR (400 MHz, $CDCl_3$)

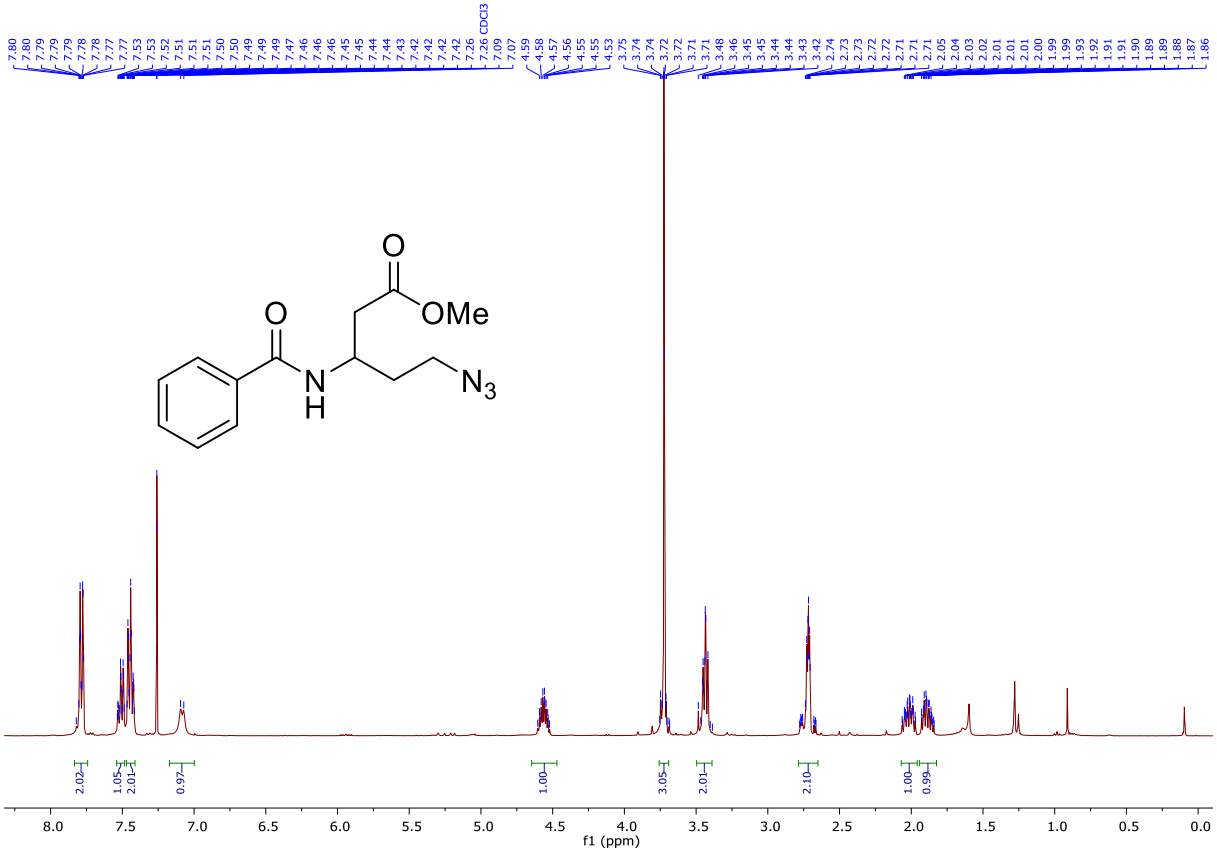


^{13}C-NMR (101 MHz, $CDCl_3$)

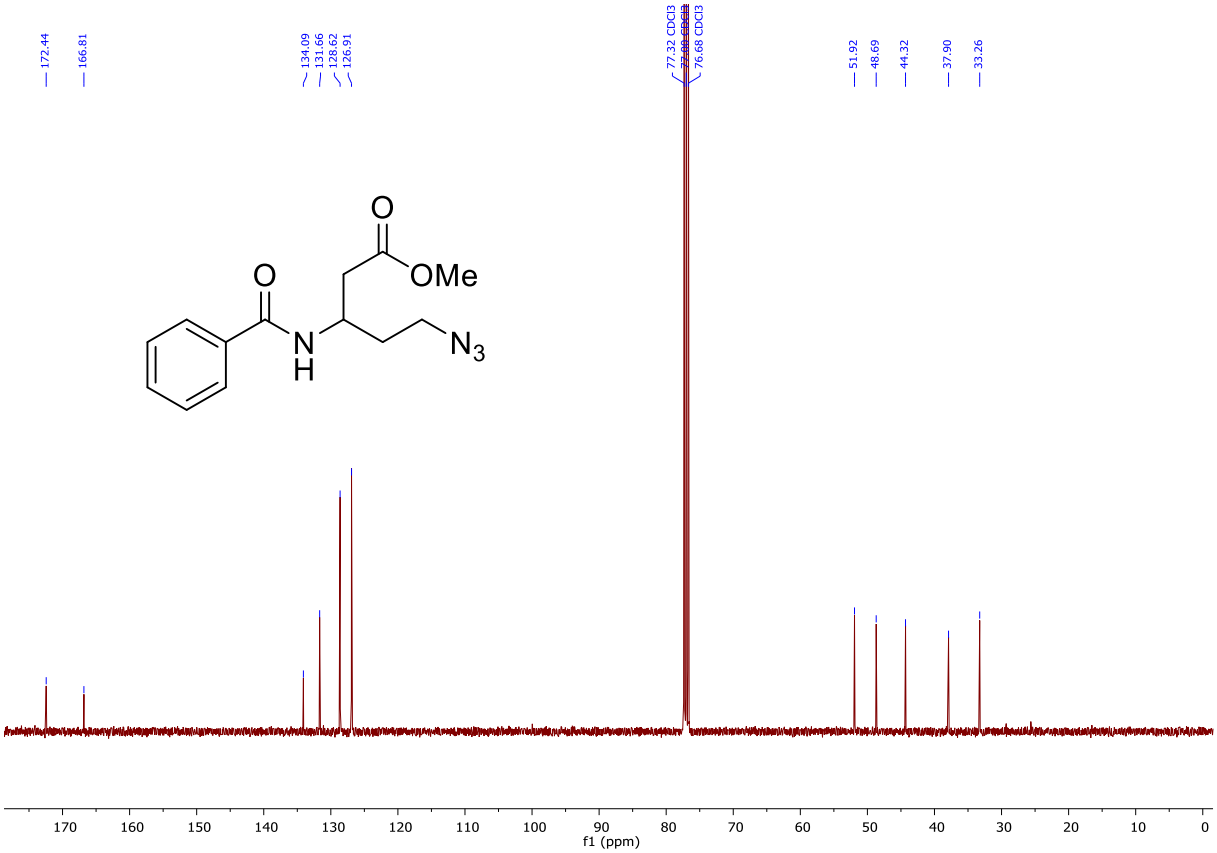


Methyl 5-azido-3-benzamidopentanoate (10e)

^{1}H-NMR (400 MHz, $CDCl_3$)

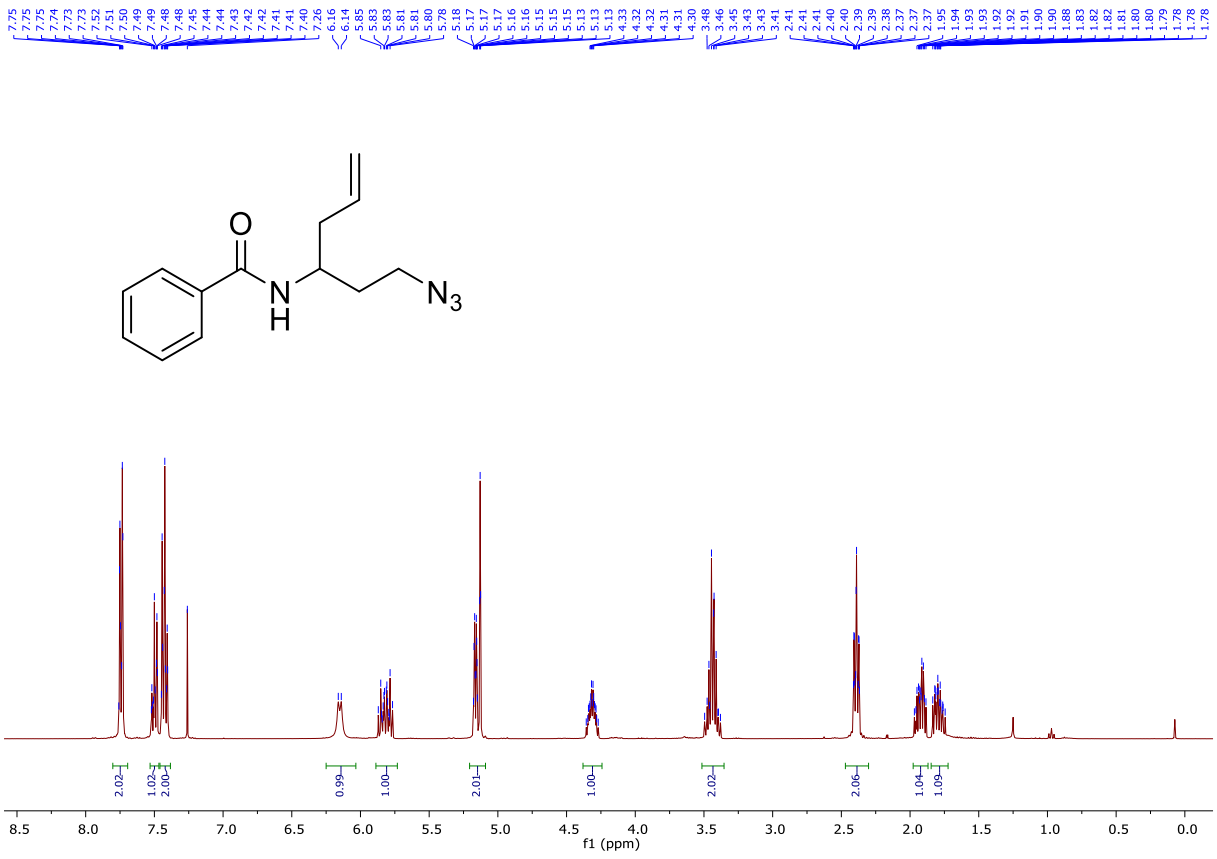


^{13}C-NMR (101 MHz, $CDCl_3$)

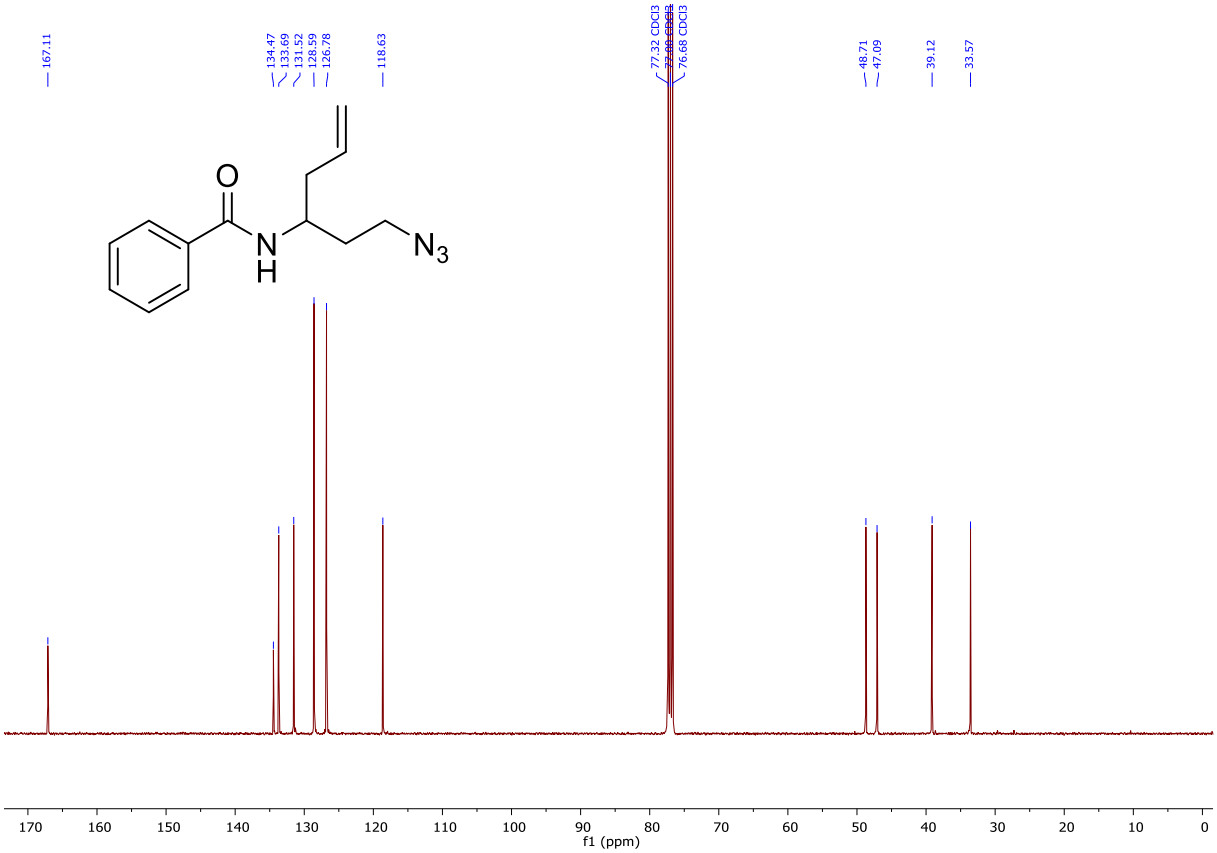


***N*-(1-Azidohex-5-en-3-yl)benzamide (10f)**

^{1}H-NMR (400 MHz, $CDCl_3$)

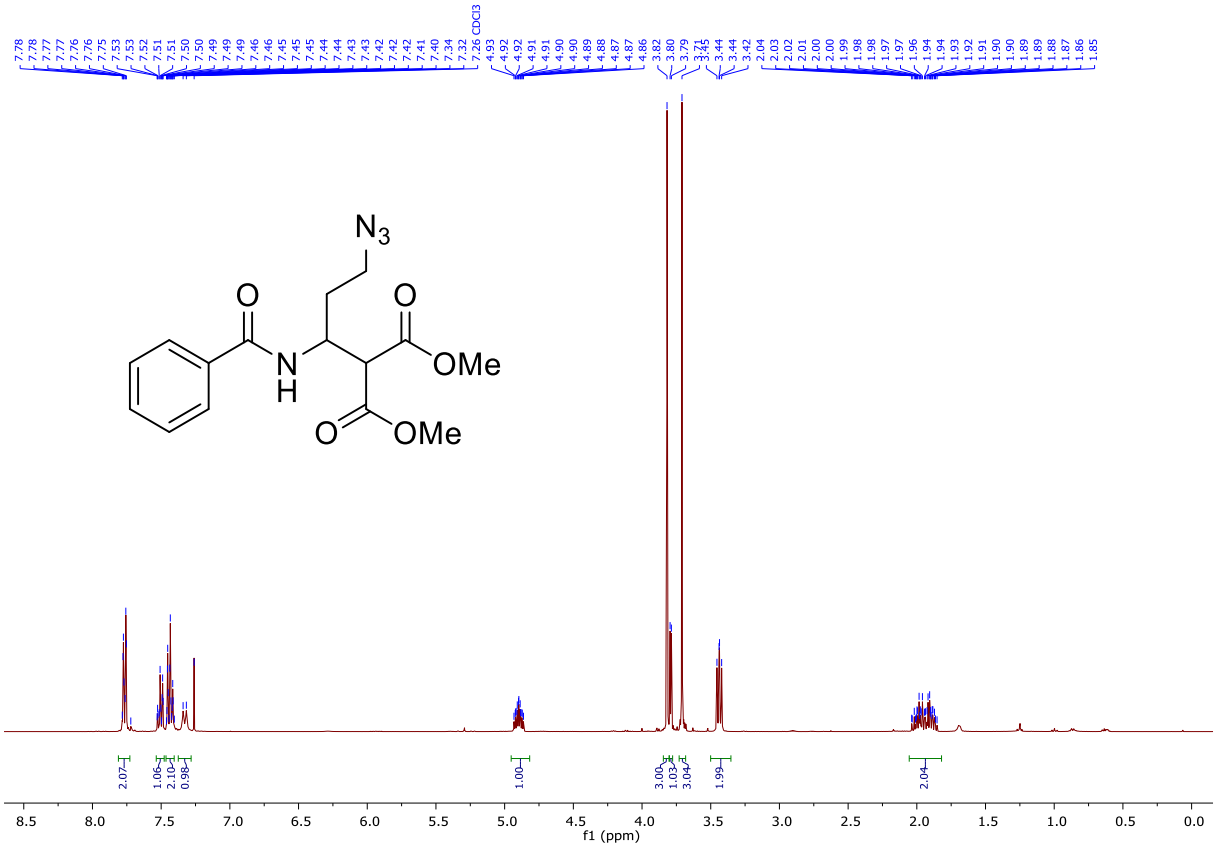


^{13}C-NMR (101 MHz, $CDCl_3$)

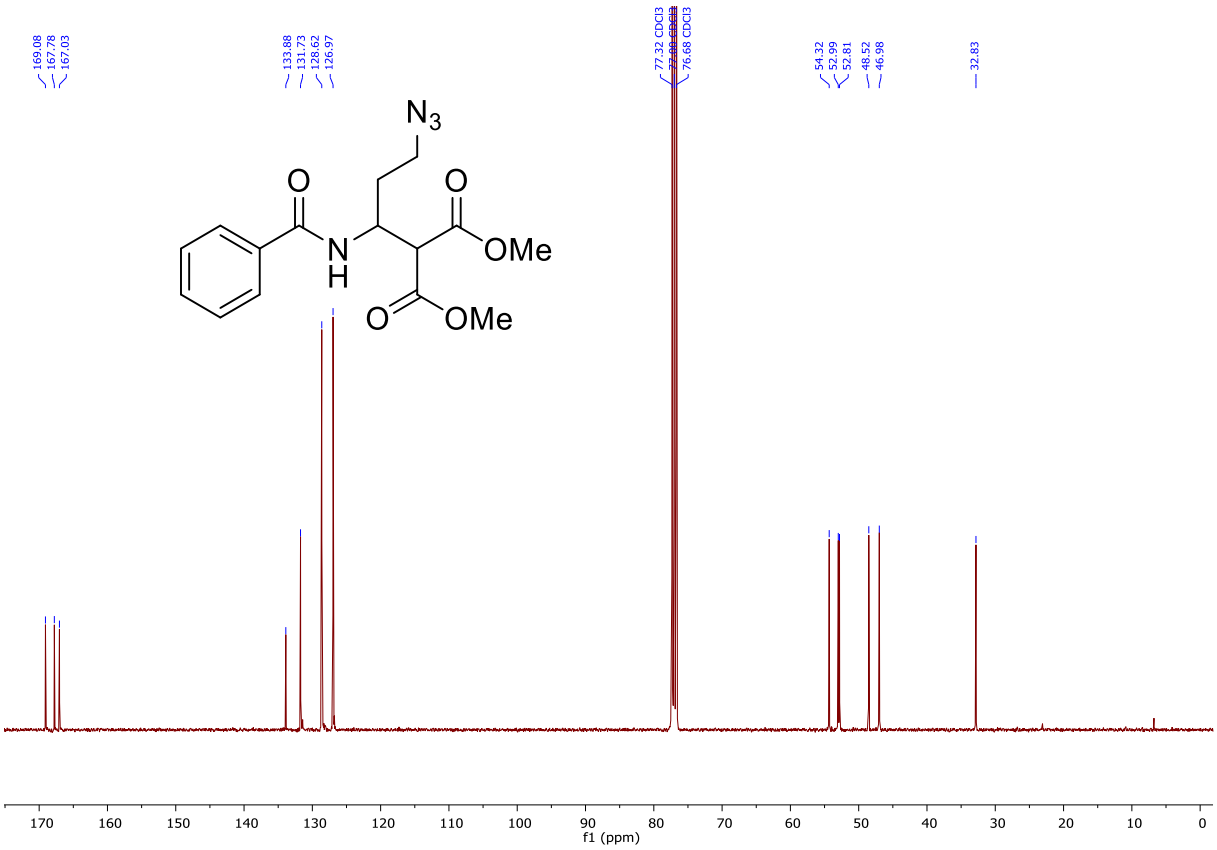


Dimethyl 2-(3-azido-1-benzamidopropyl)malonate (10ga)

^{1}H-NMR (400 MHz, $CDCl_3$)

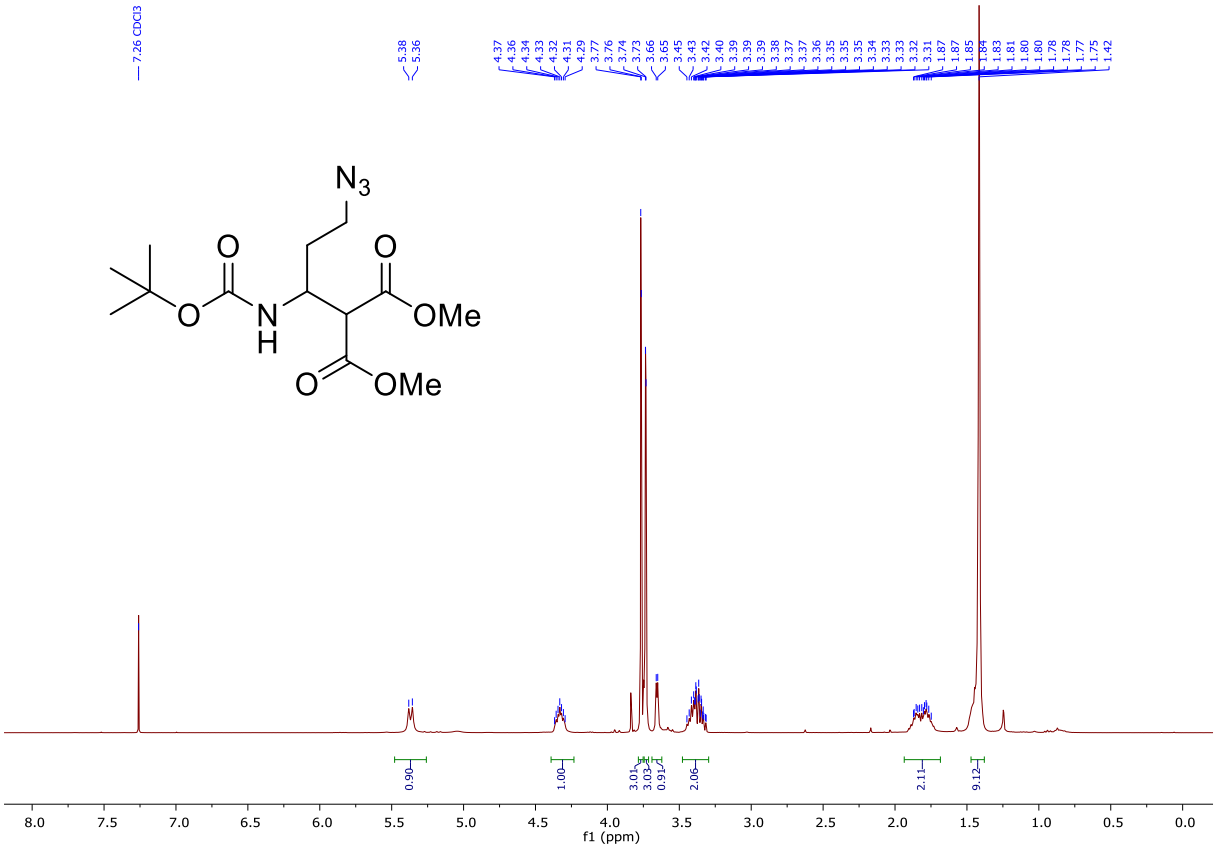


^{13}C-NMR (101 MHz, $CDCl_3$)

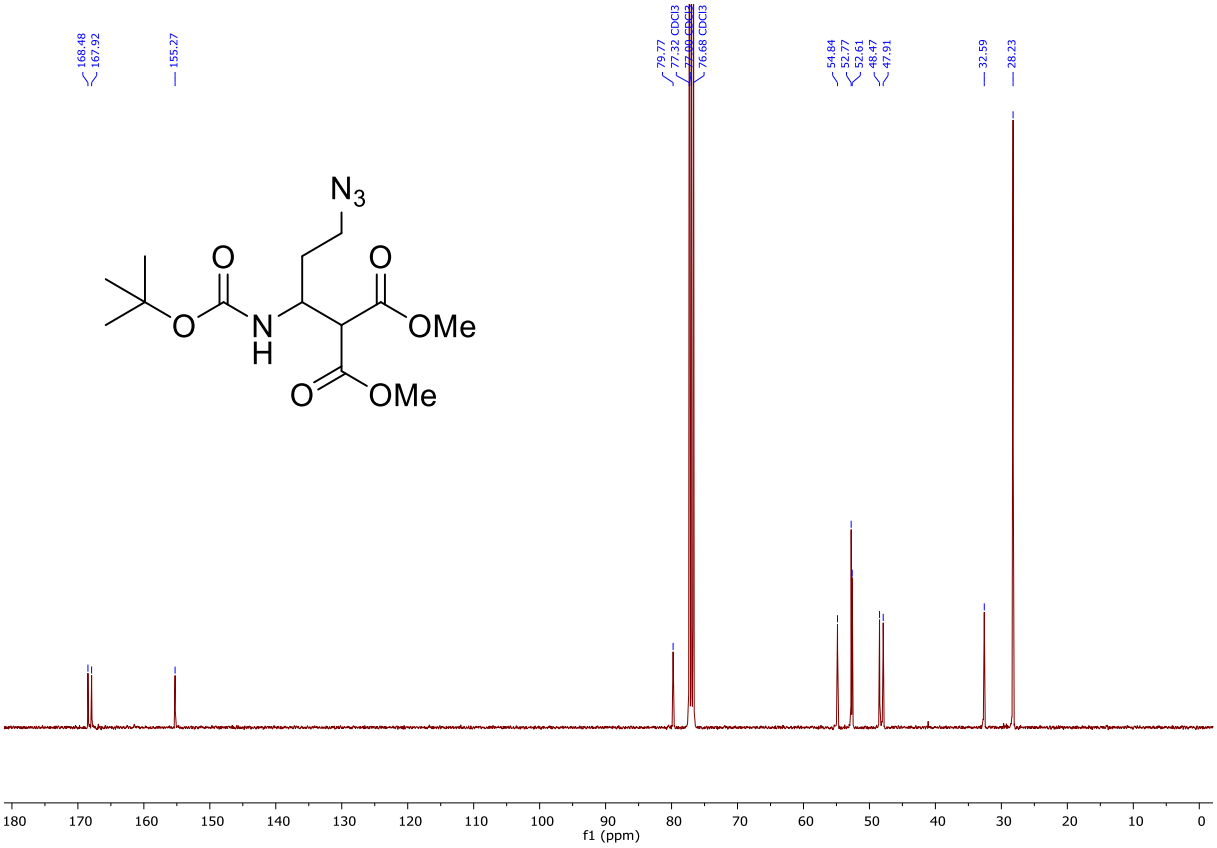


Dimethyl 2-(3-azido-1-((*tert*-butoxycarbonyl)amino)propyl)malonate (10gb)

^{1}H-NMR (400 MHz, $CDCl_3$)

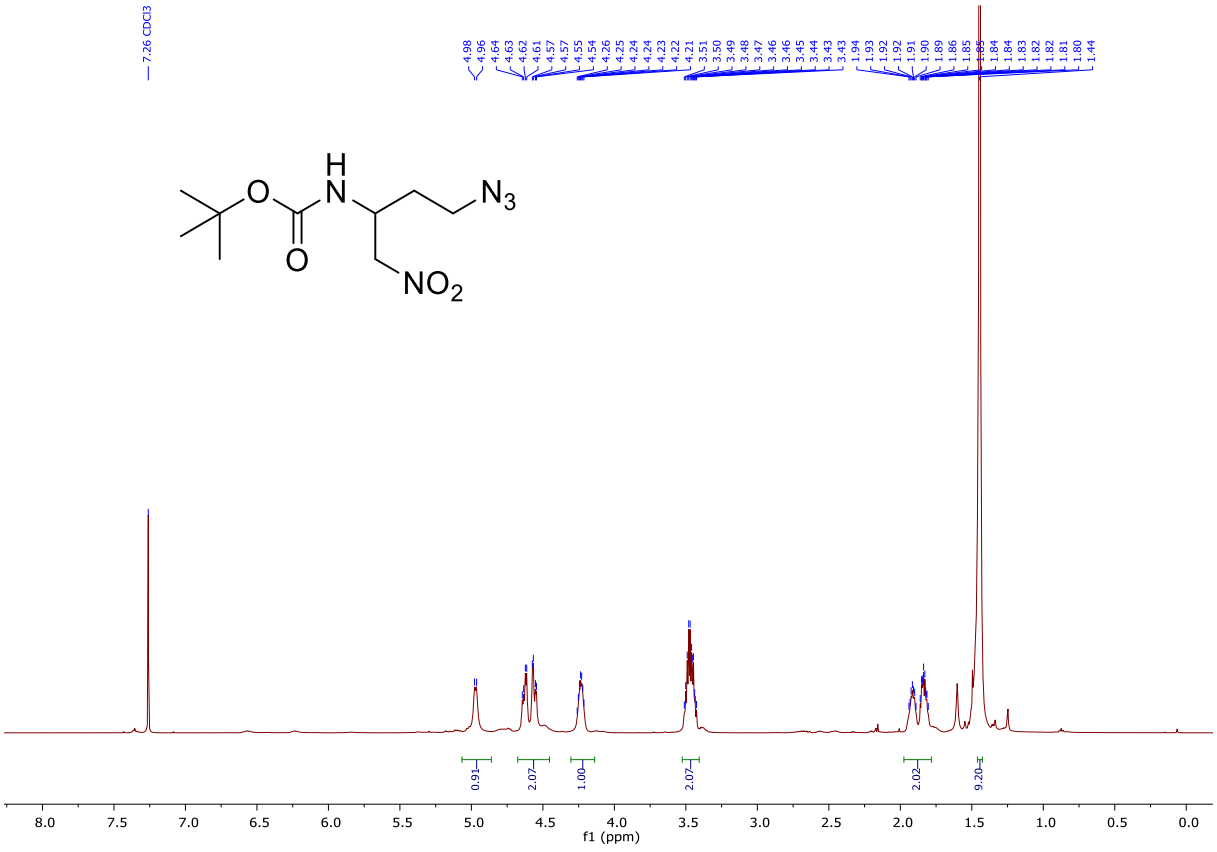


^{13}C-NMR (101 MHz, $CDCl_3$)

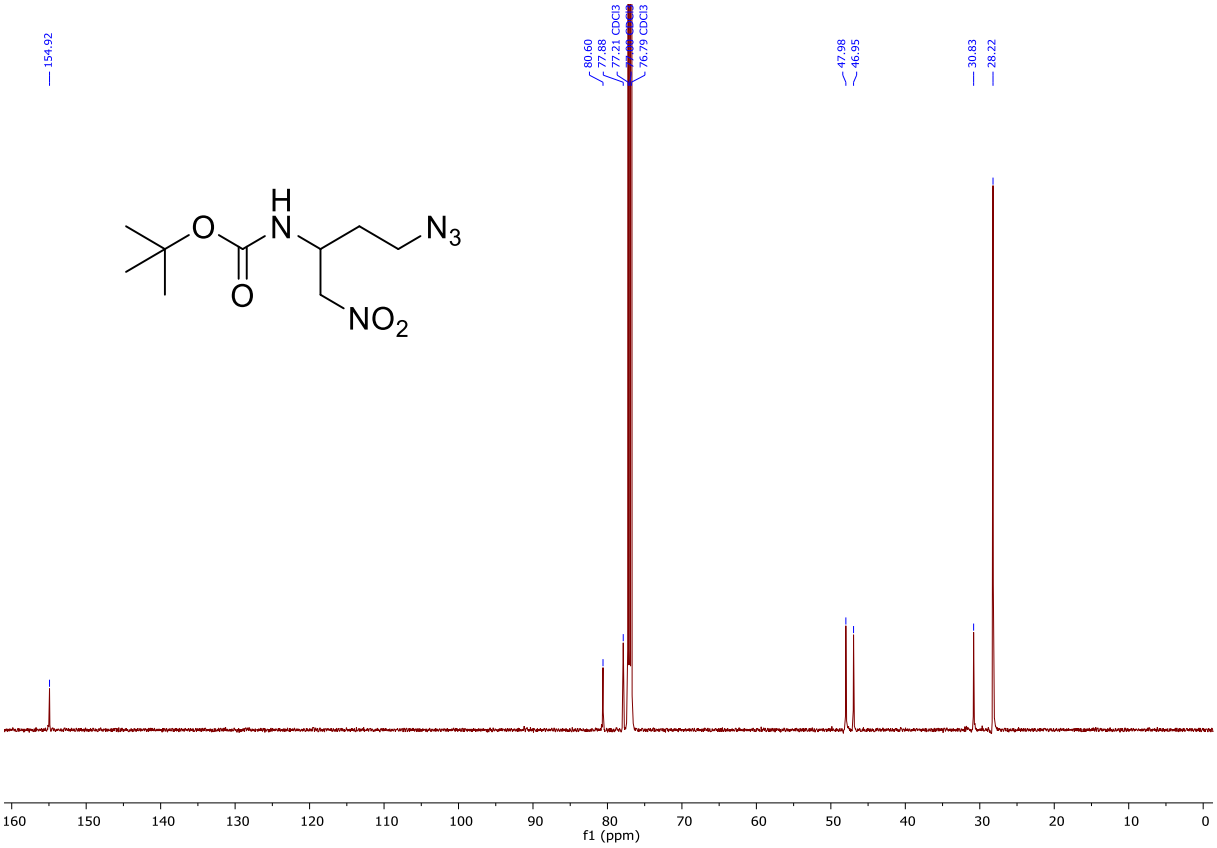


***tert*-Butyl (4-azido-1-nitrobutan-2-yl)carbamate (10h)**

^{1}H-NMR (600 MHz, $CDCl_3$)

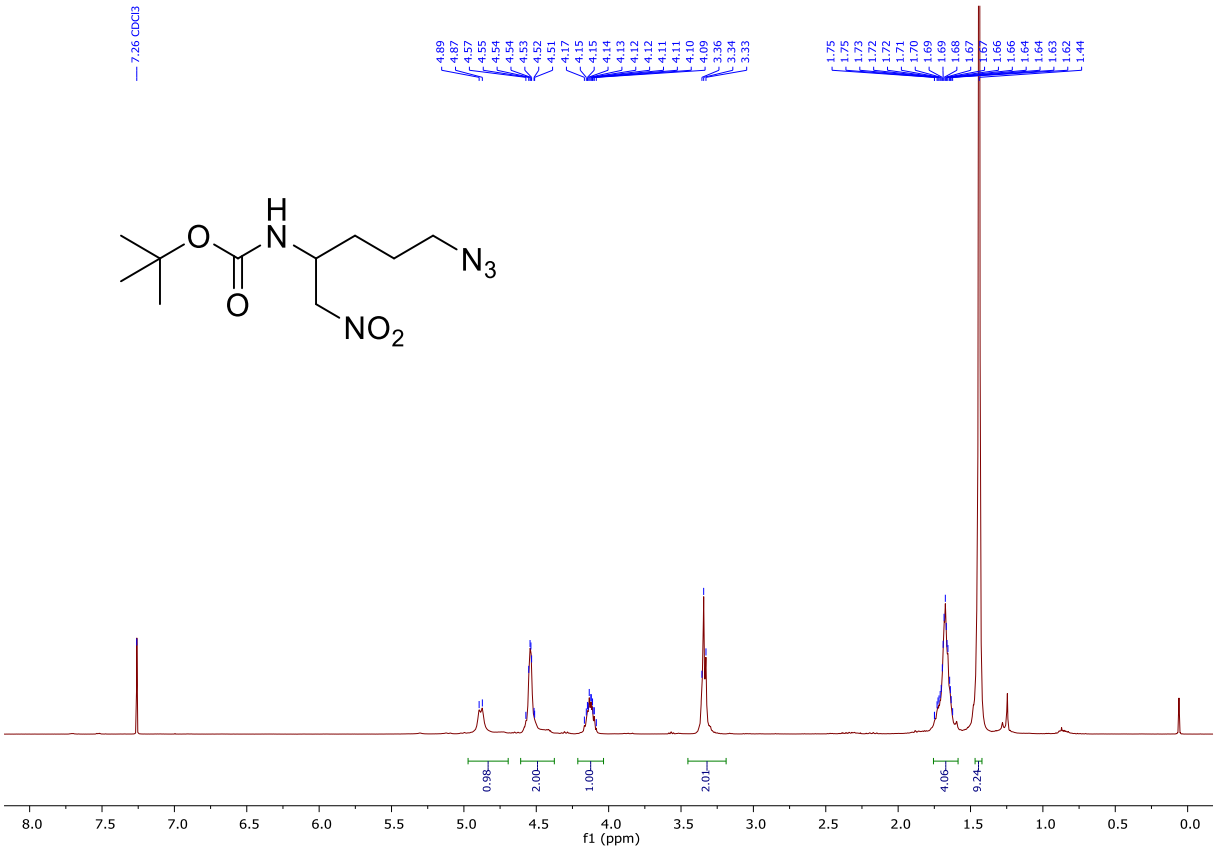


^{13}C-NMR (151 MHz, $CDCl_3$)

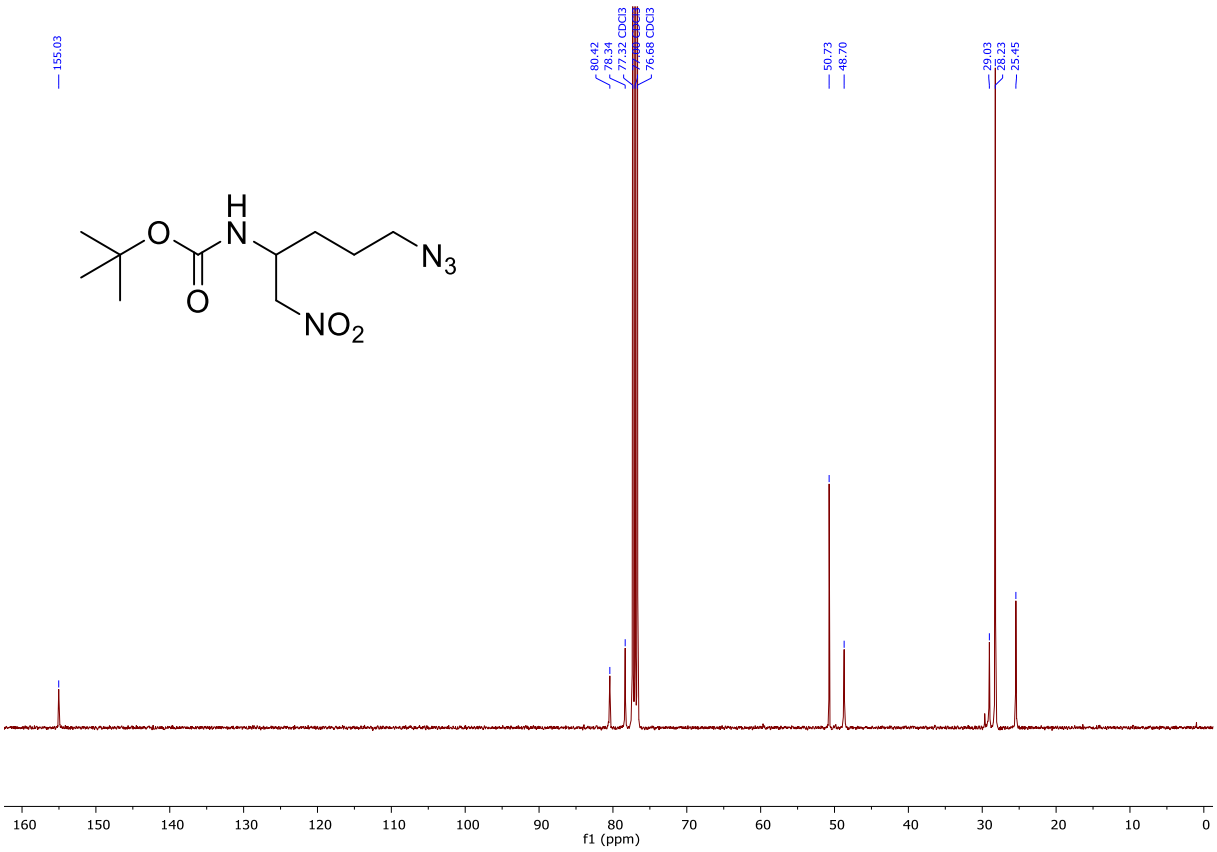


***tert*-Butyl (5-azido-1-nitropentan-2-yl)carbamate (11h)**

^{1}H-NMR (400 MHz, $CDCl_3$)

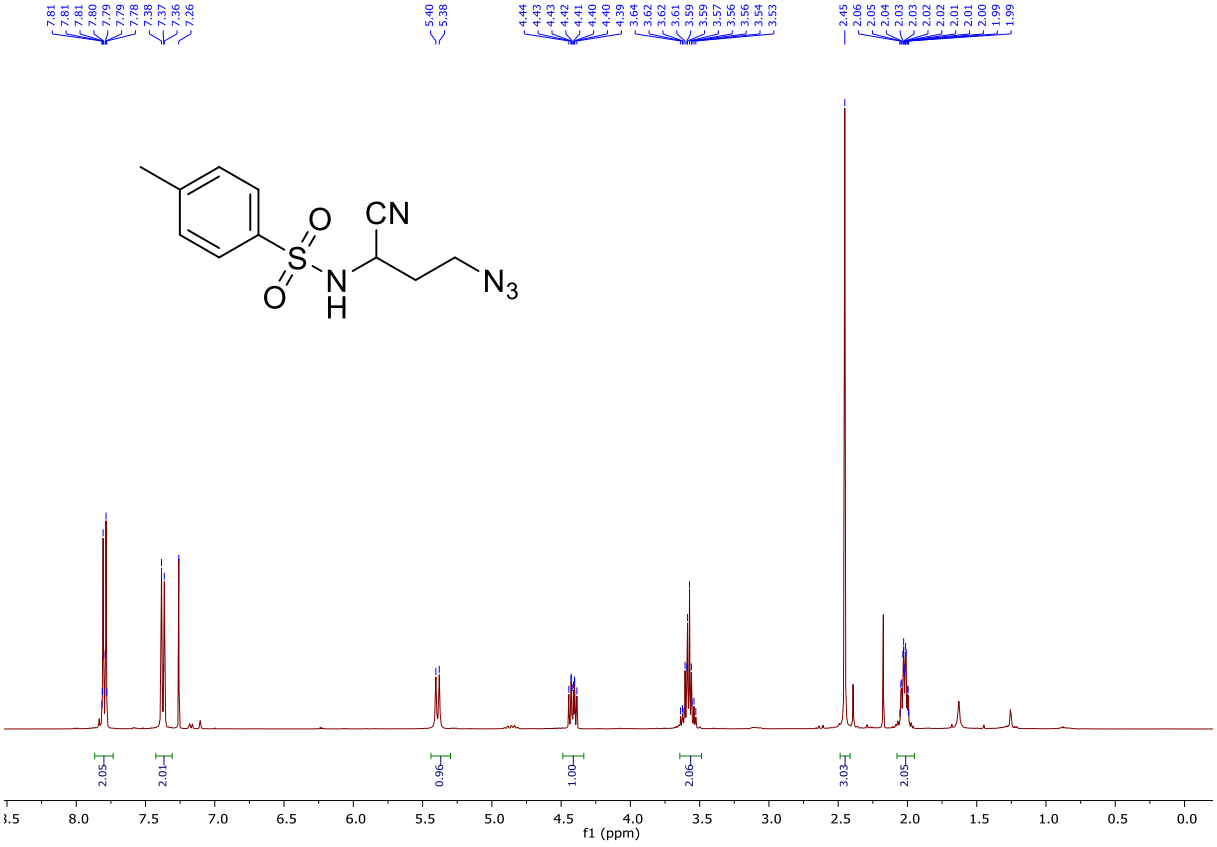


^{13}C-NMR (101 MHz, $CDCl_3$)

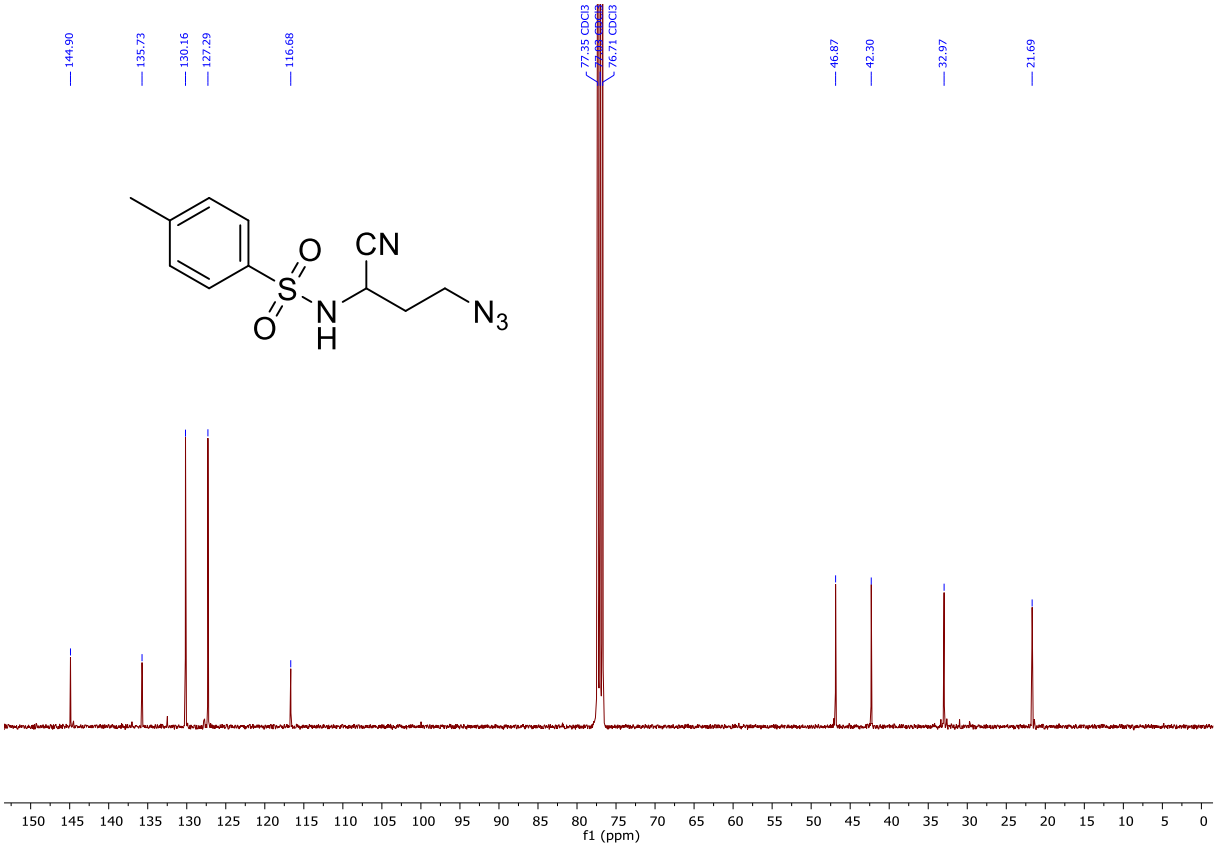


***N*-(3-Azido-1-cyanopropyl)-4-methylbenzenesulfonamide (10i)**

^{1}H-NMR (400 MHz, $CDCl_3$)

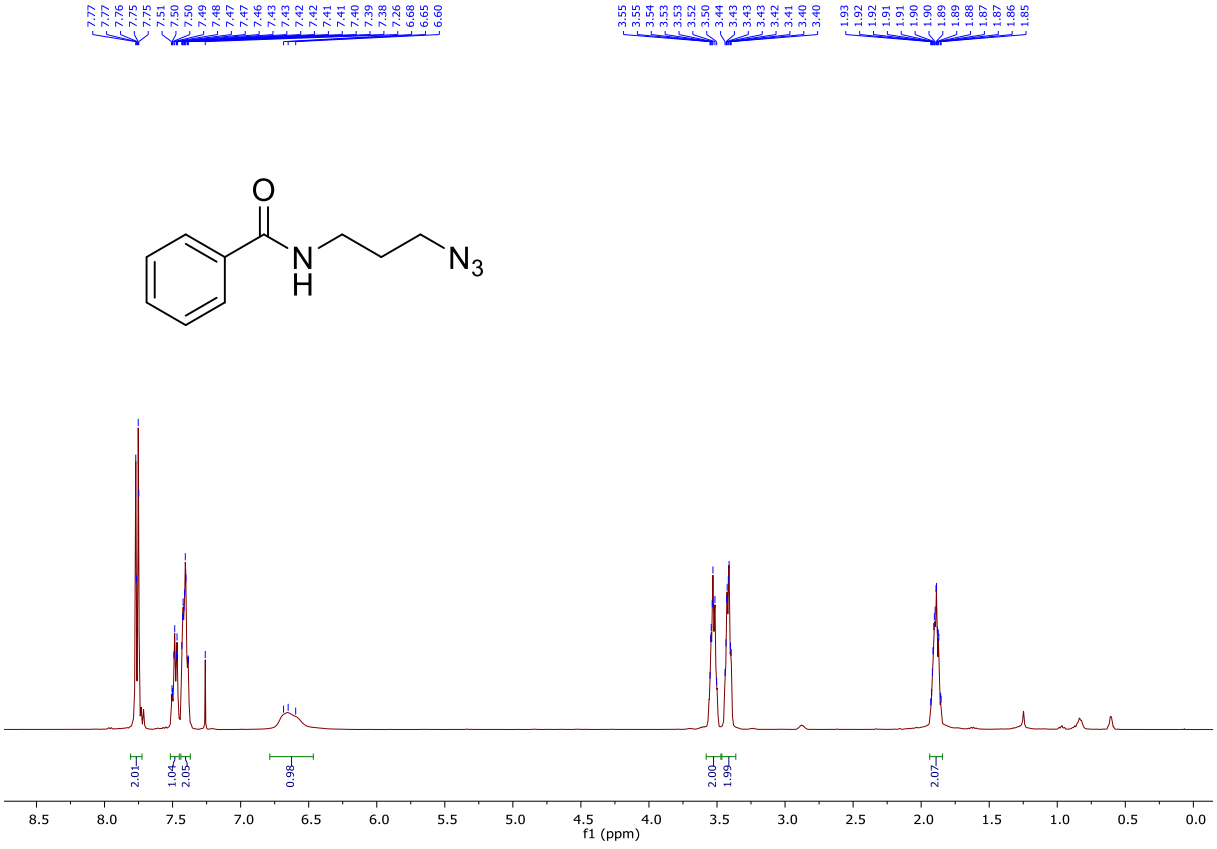


^{13}C-NMR (101 MHz, $CDCl_3$)

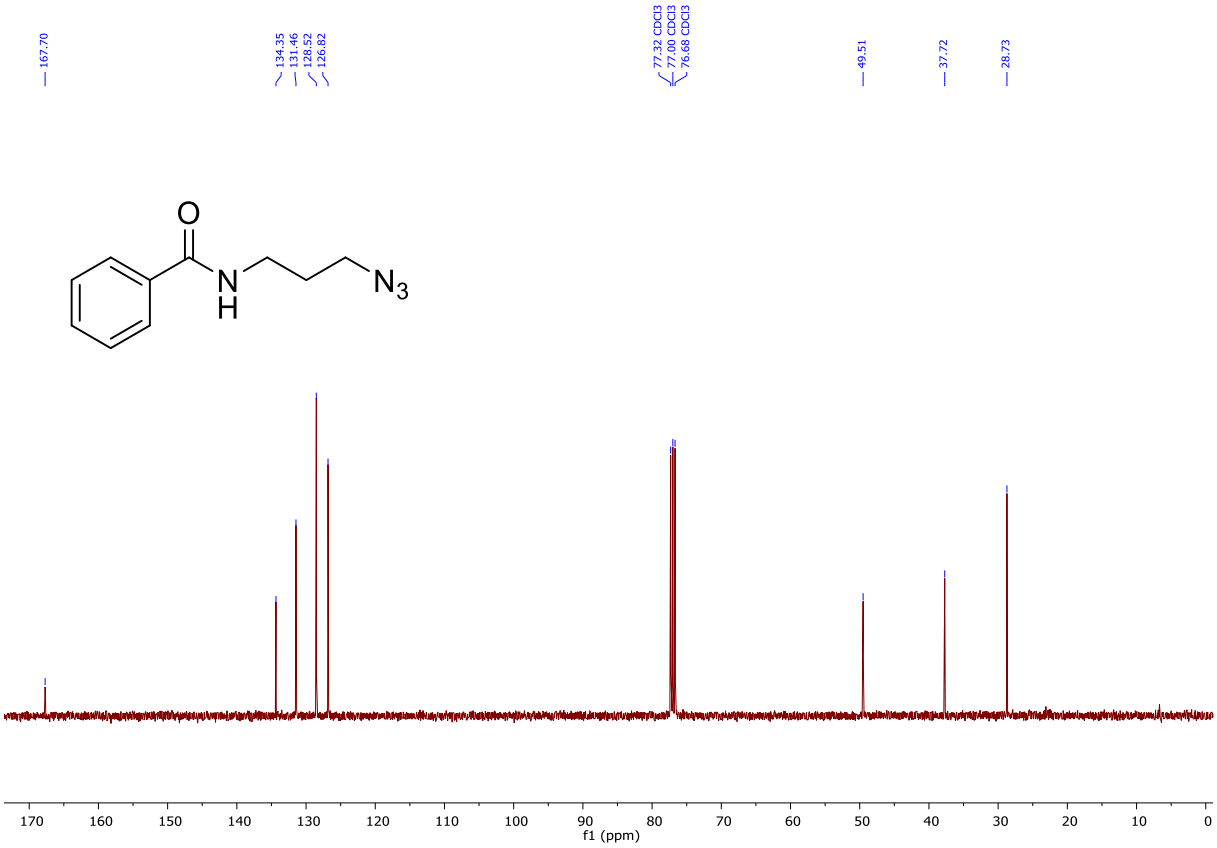


***N*-(3-Azidopropyl)-4-methoxybenzamide (10j)**

^{1}H-NMR (400 MHz, $CDCl_3$)

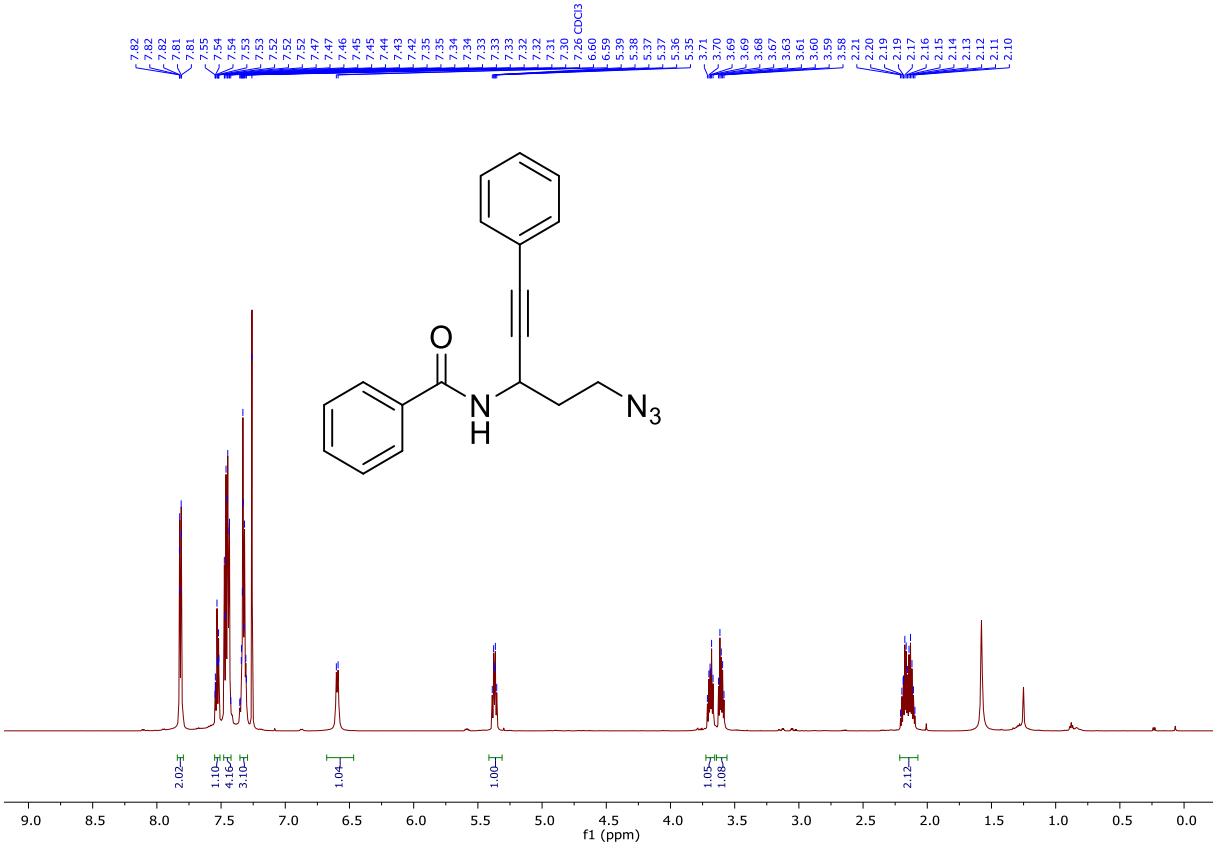


^{13}C-NMR (101 MHz, $CDCl_3$)

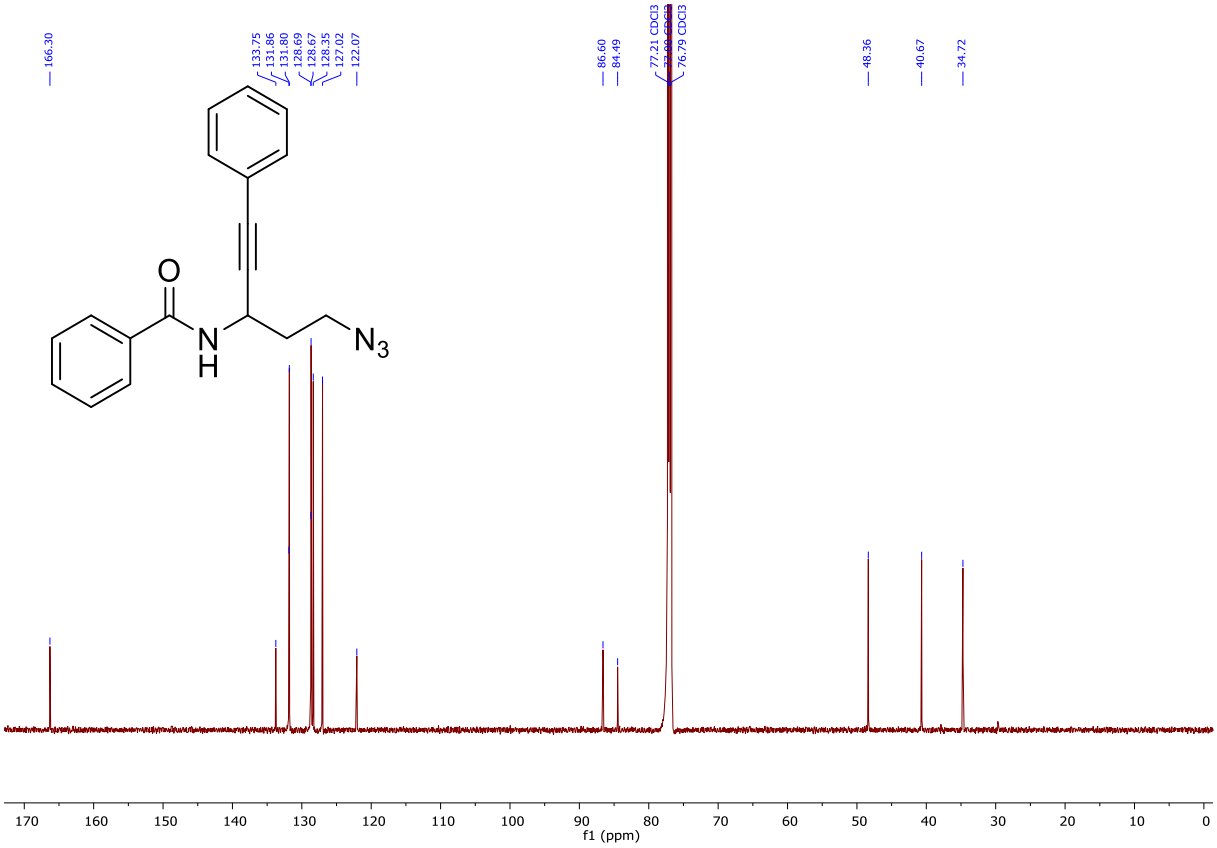


***N*-(5-Azido-1-phenylpent-1-yn-3-yl)benzamide (10k)**

^{1}H-NMR (600 MHz, $CDCl_3$)

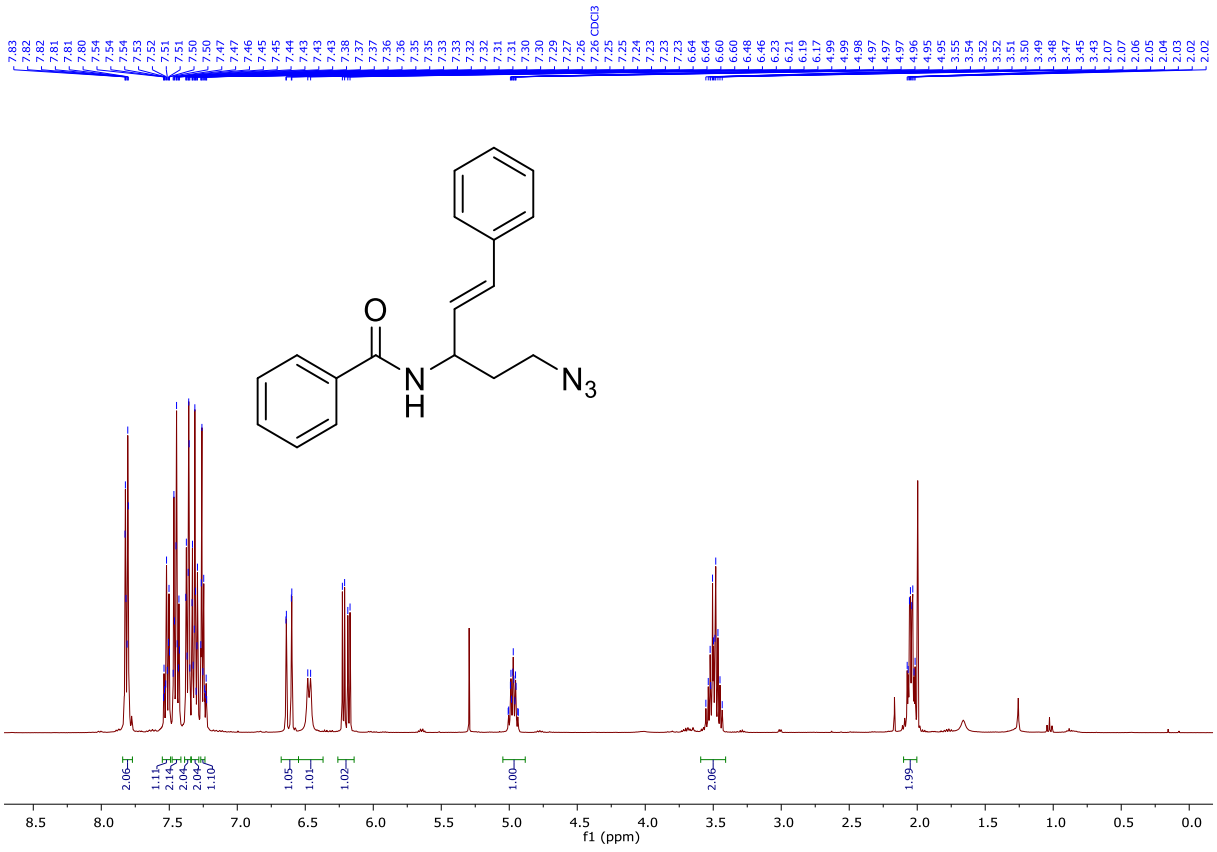


^{13}C-NMR (151 MHz, $CDCl_3$)

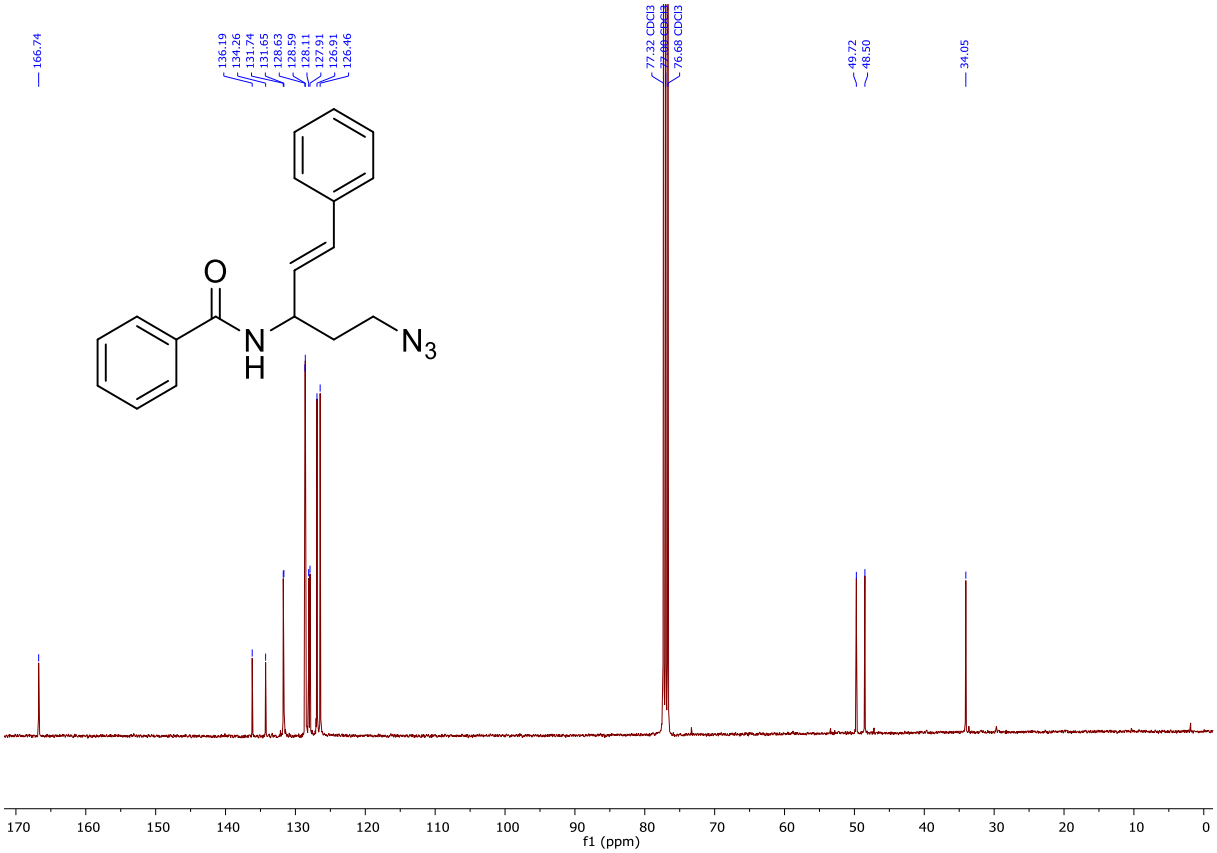


(*E*)-*N*-(5-Azido-1-phenylpent-1-en-3-yl)benzamide (10l)

^{1}H-NMR (400 MHz, $CDCl_3$)

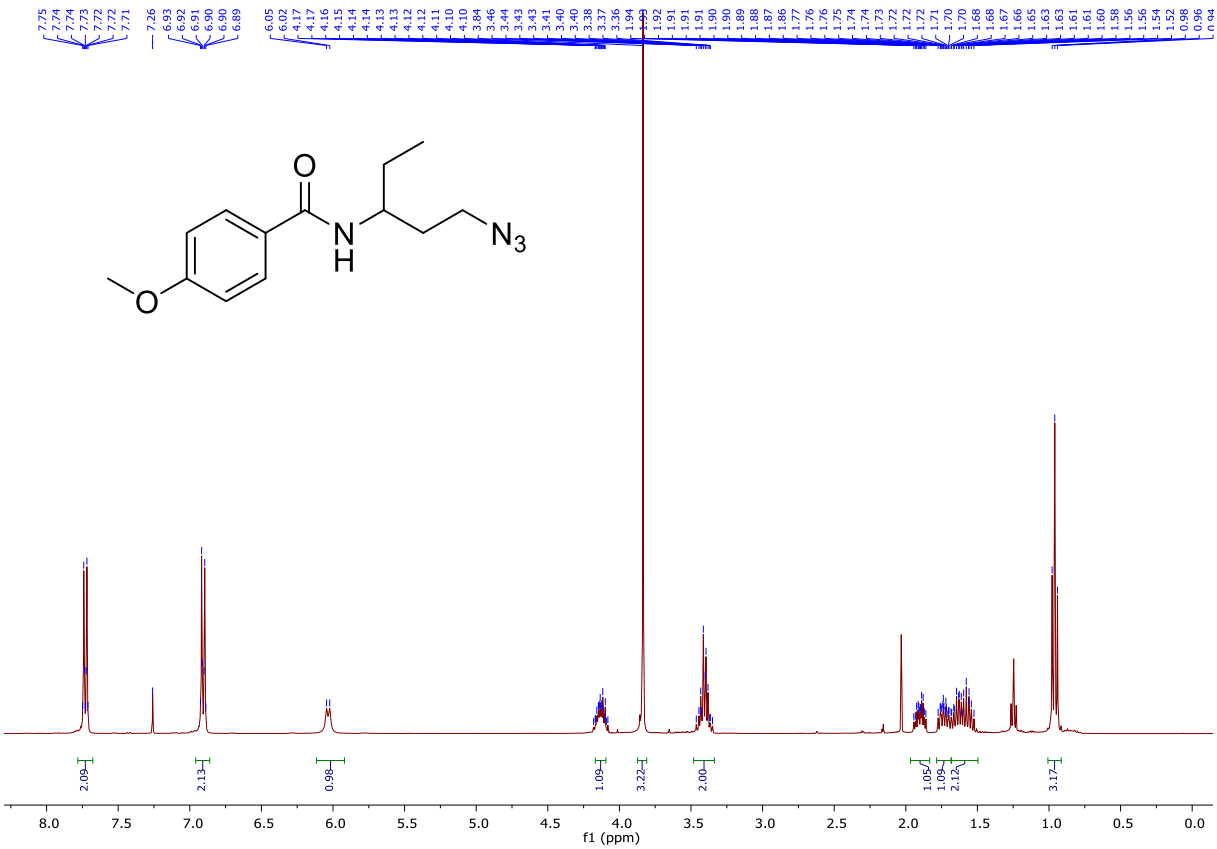


^{13}C-NMR (101 MHz, $CDCl_3$)

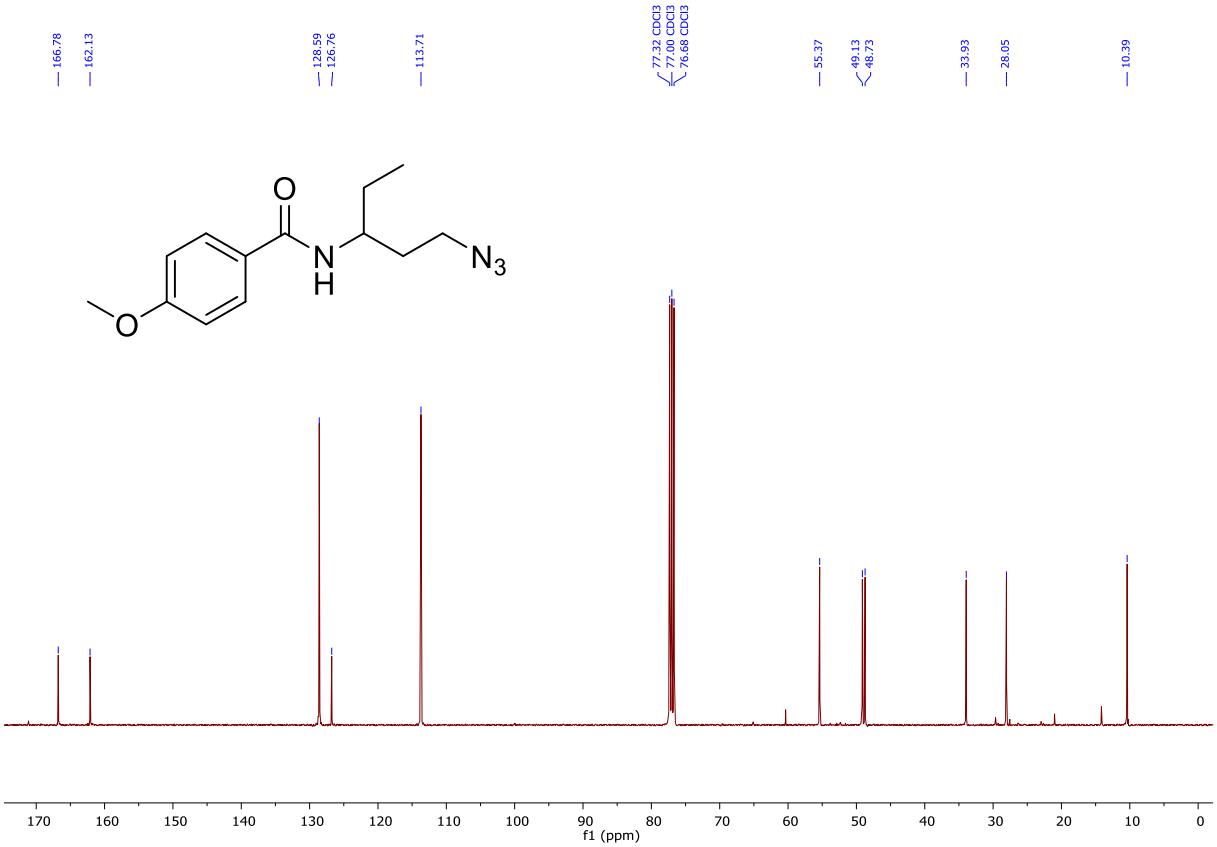


***N*-(1-Azidopentan-3-yl)-4-methoxybenzamide (10m)**

^{1}H-NMR (400 MHz, $CDCl_3$)

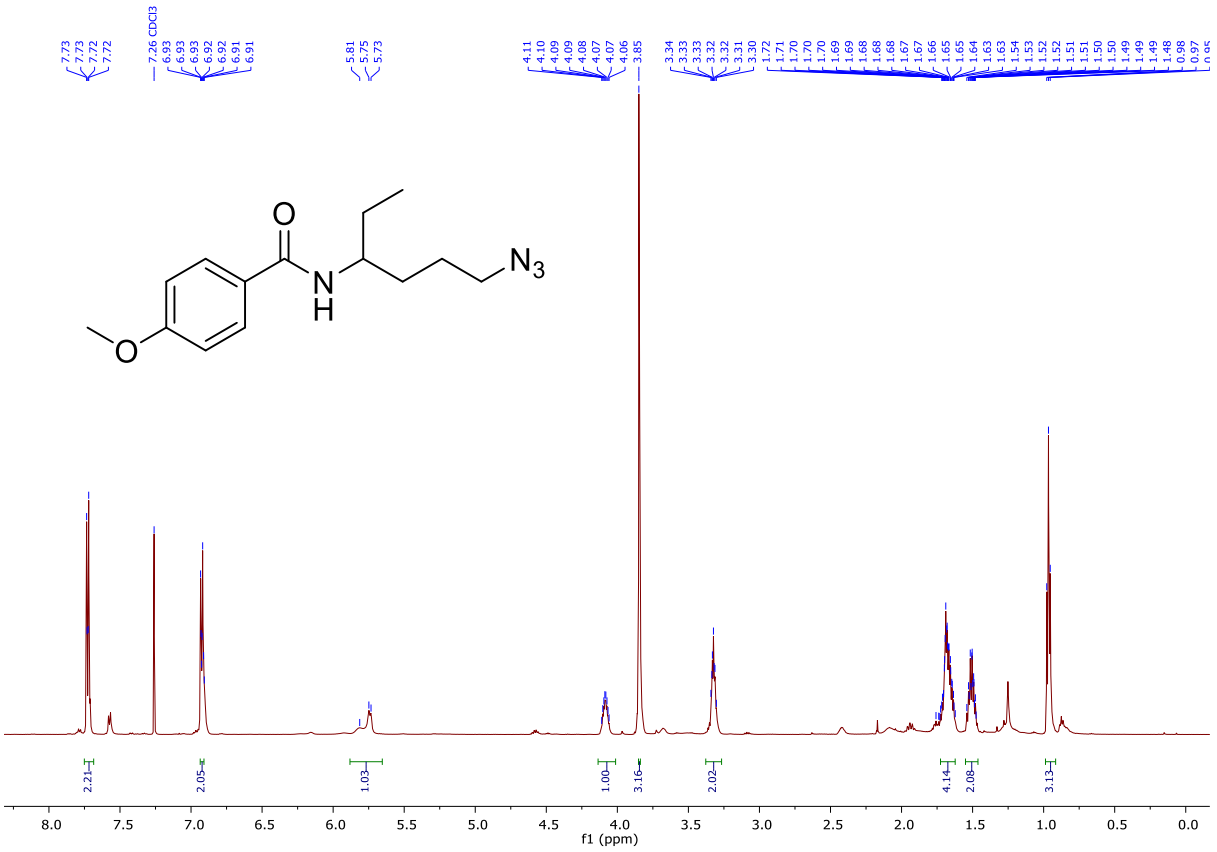


^{13}C-NMR (101 MHz, $CDCl_3$)

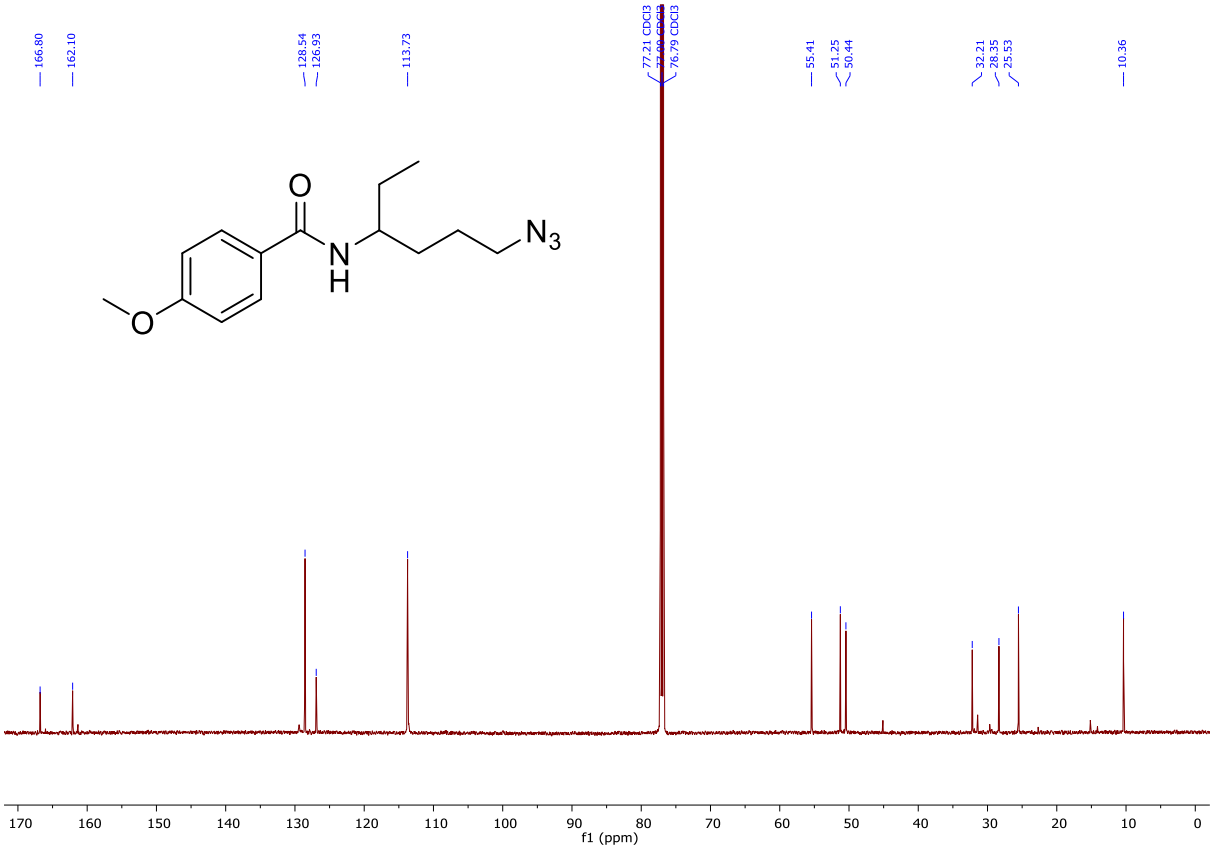


***N*-(6-Azidohexan-3-yl)-4-methoxybenzamide (11m)**

^{1}H-NMR (600 MHz, $CDCl_3$)

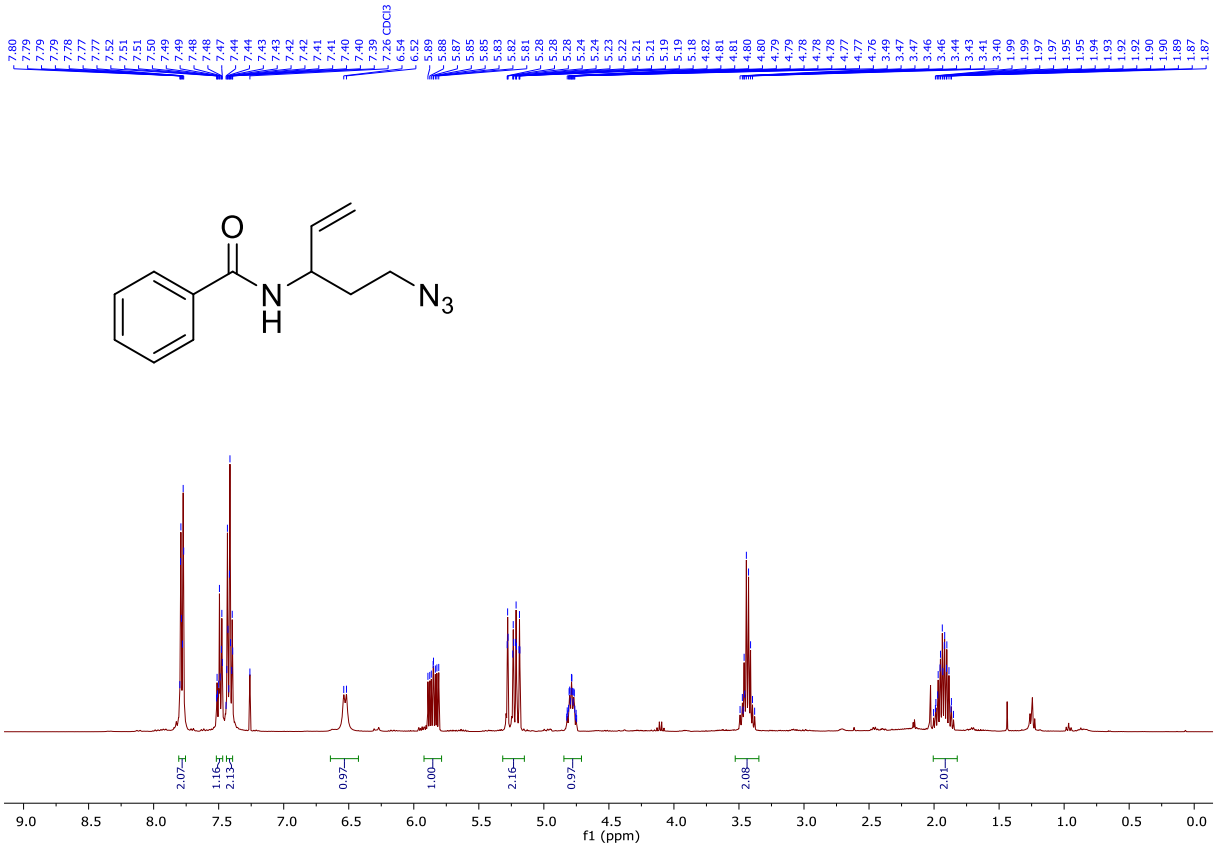


^{13}C-NMR (151 MHz, $CDCl_3$)

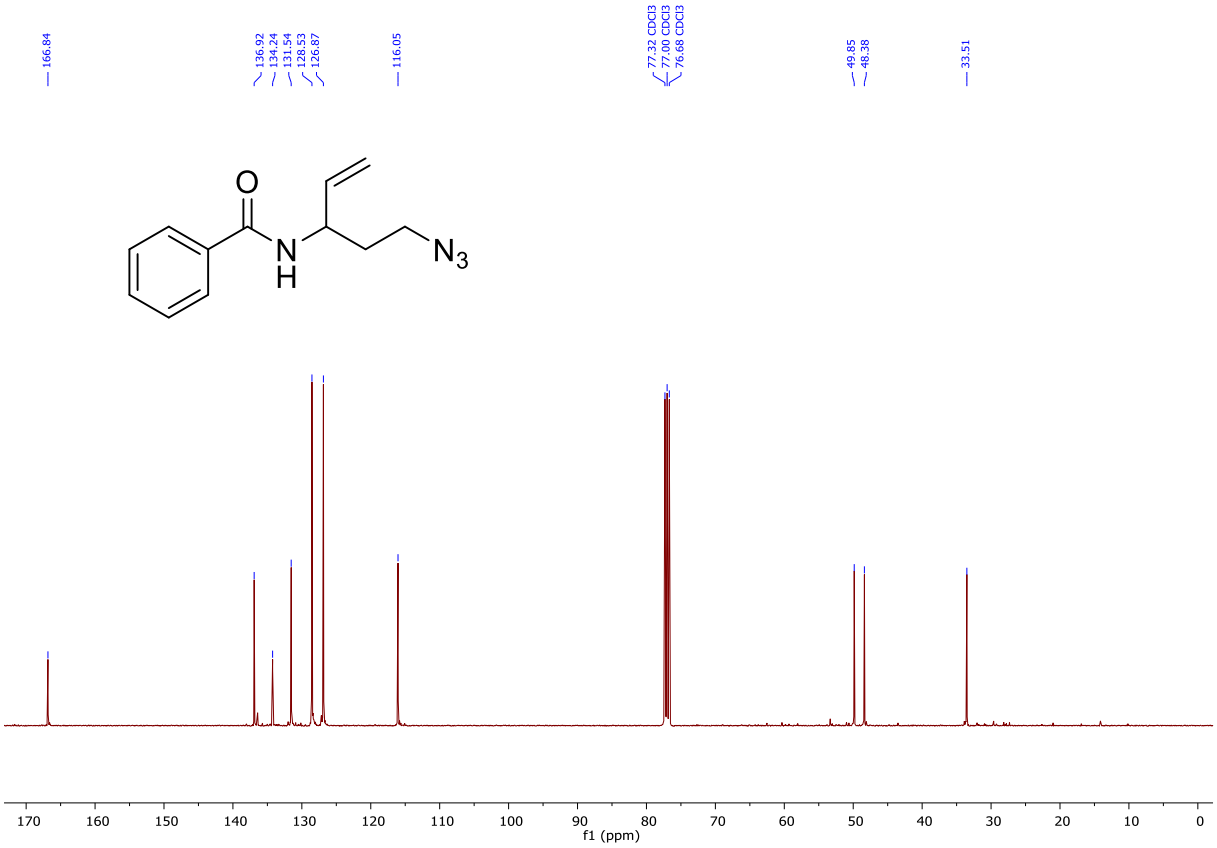


N-(5-Azidopent-1-en-3-yl)benzamide (10na)

^{1}H-NMR (400 MHz, $CDCl_3$)

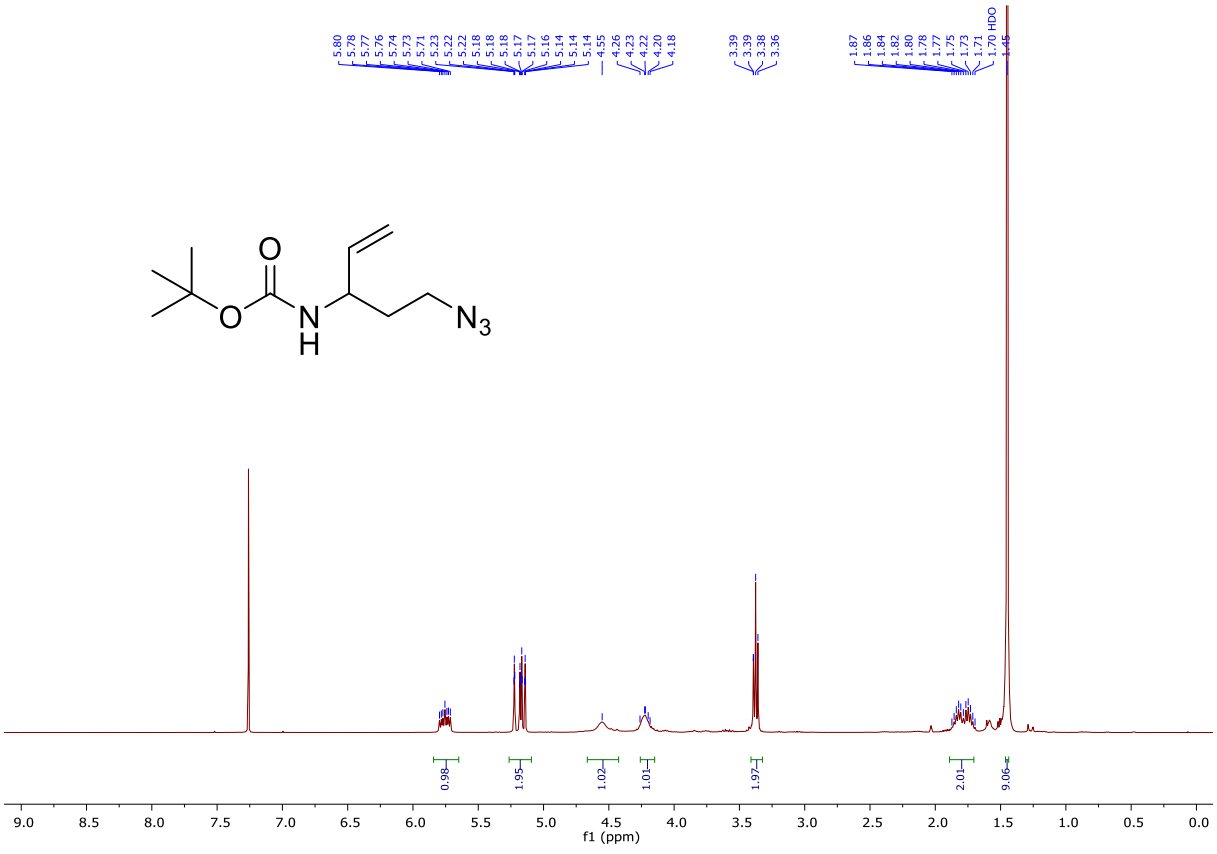


^{13}C-NMR (101 MHz, $CDCl_3$)

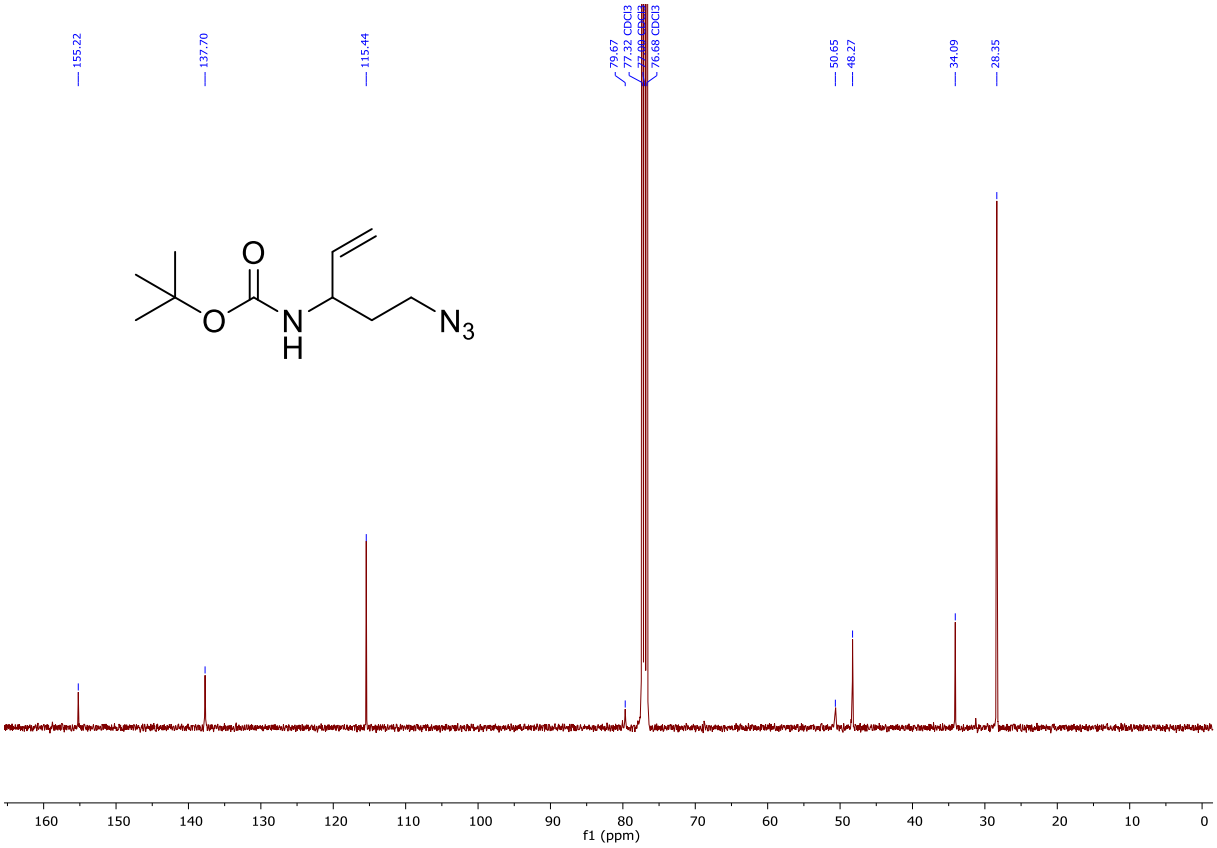


***tert*-Butyl (5-azidopent-1-en-3-yl)carbamate (10nb)**

^{1}H-NMR (400 MHz, $CDCl_3$)

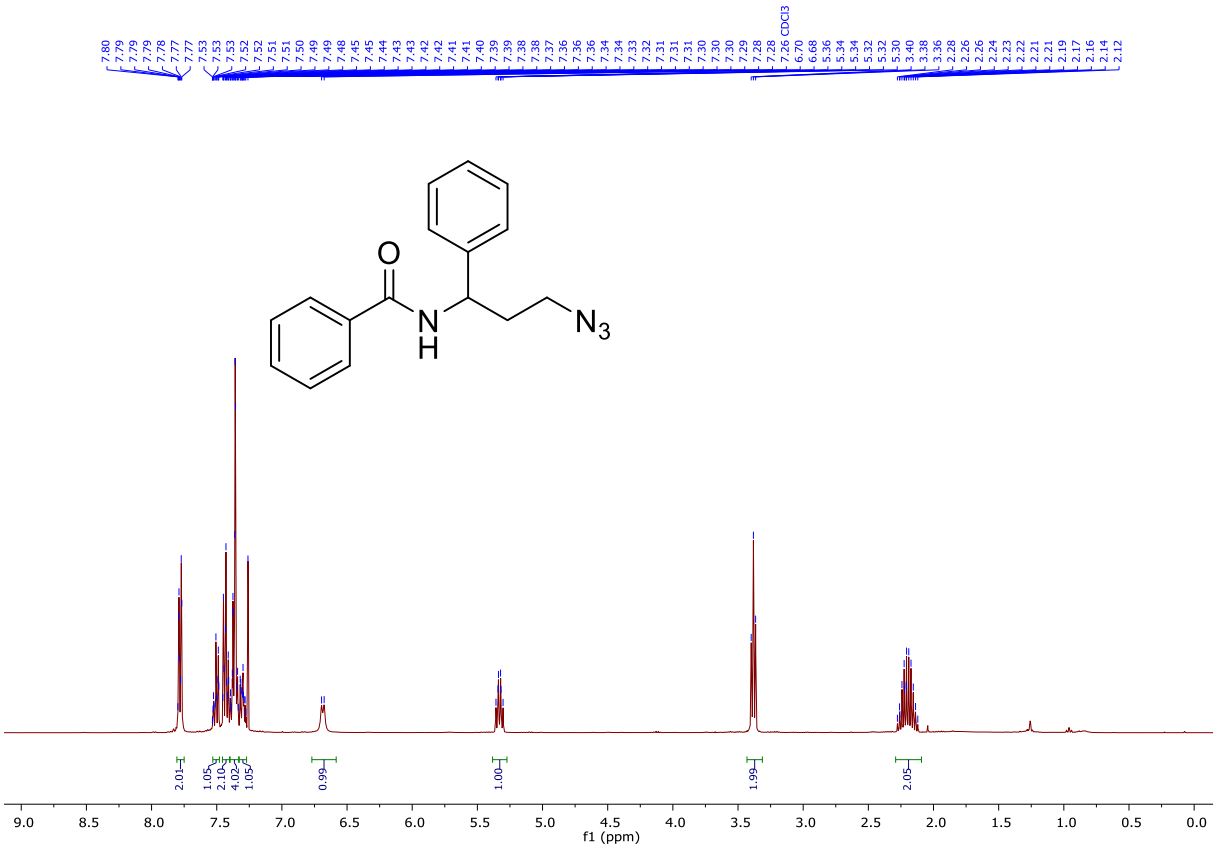


^{13}C-NMR (101 MHz, $CDCl_3$)

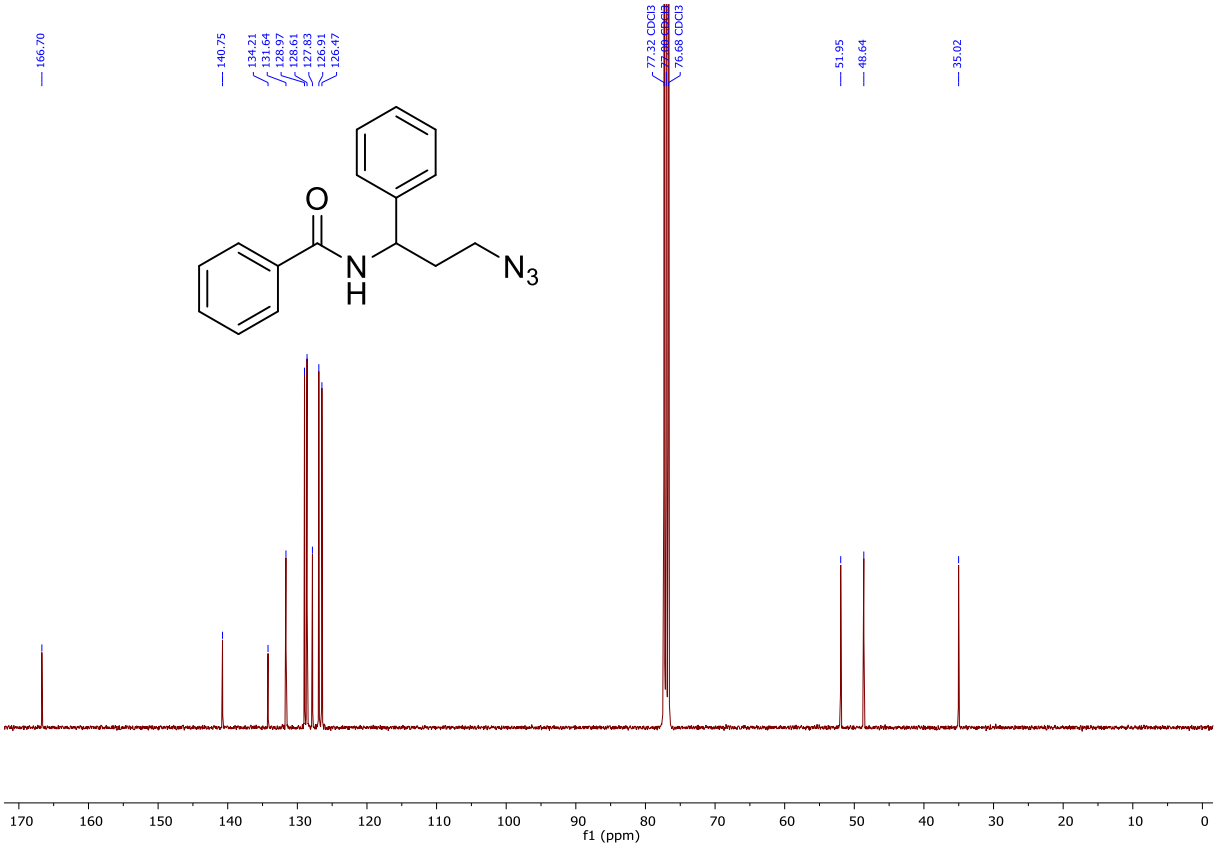


***N*-(3-Azido-1-phenylpropyl)benzamide (10oa)**

^{1}H-NMR (400 MHz, $CDCl_3$)

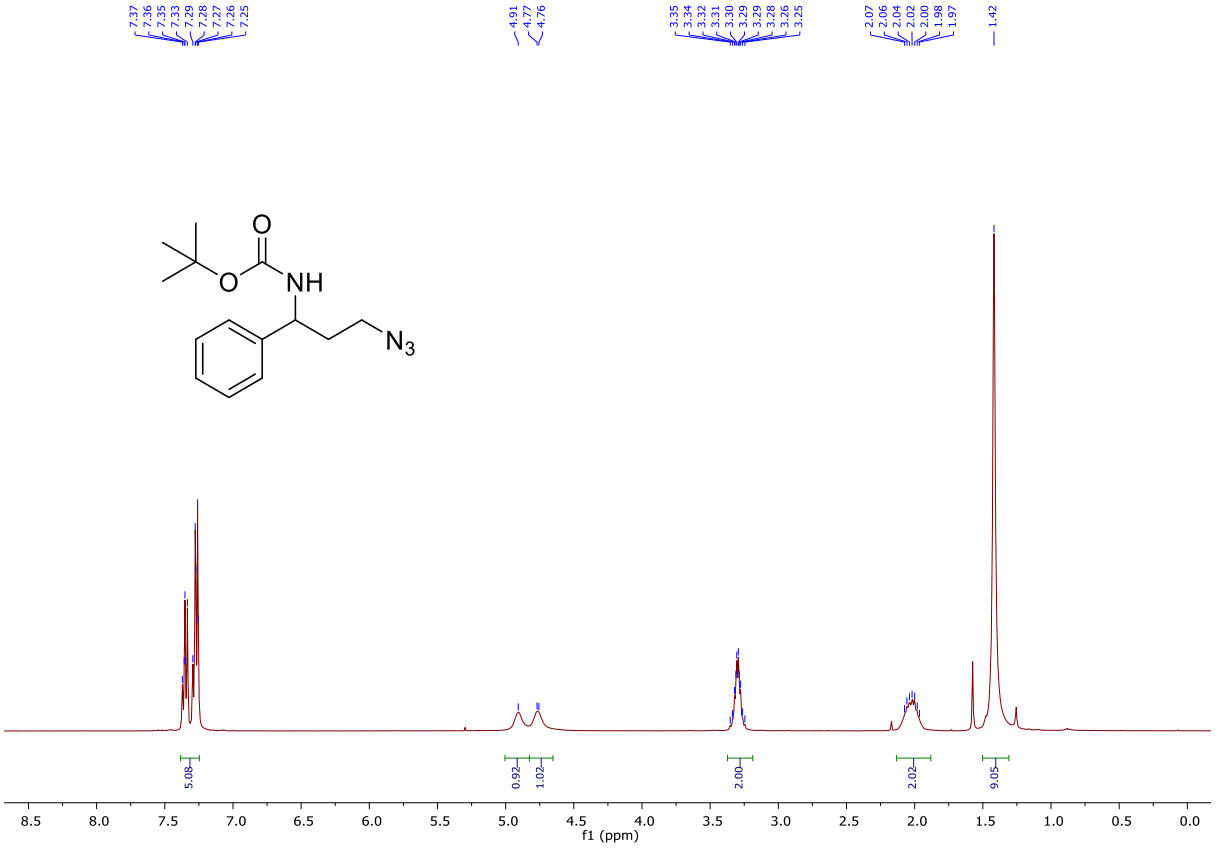


^{13}C-NMR (101 MHz, $CDCl_3$)

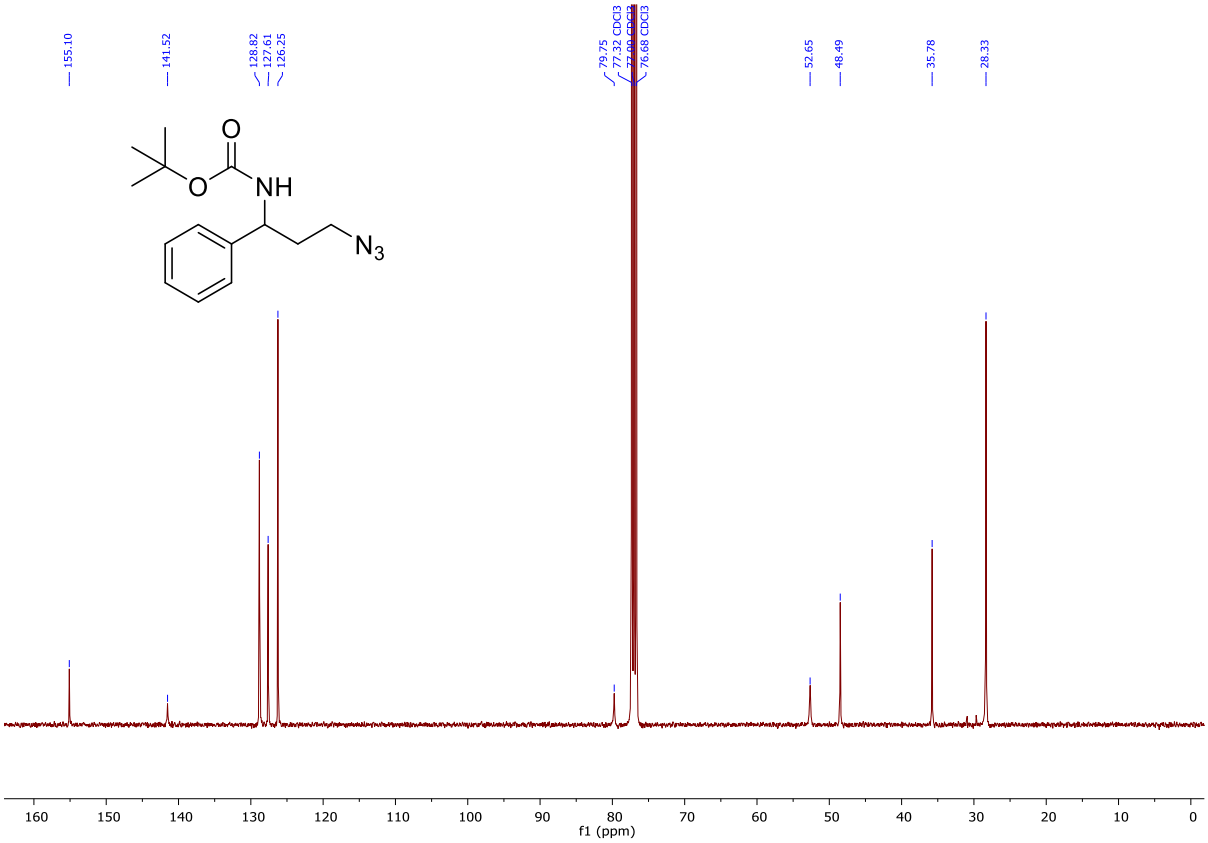


***tert*-Butyl (3-azido-1-phenylpropyl)carbamate (10ob)**

^{1}H-NMR (400 MHz, $CDCl_3$)

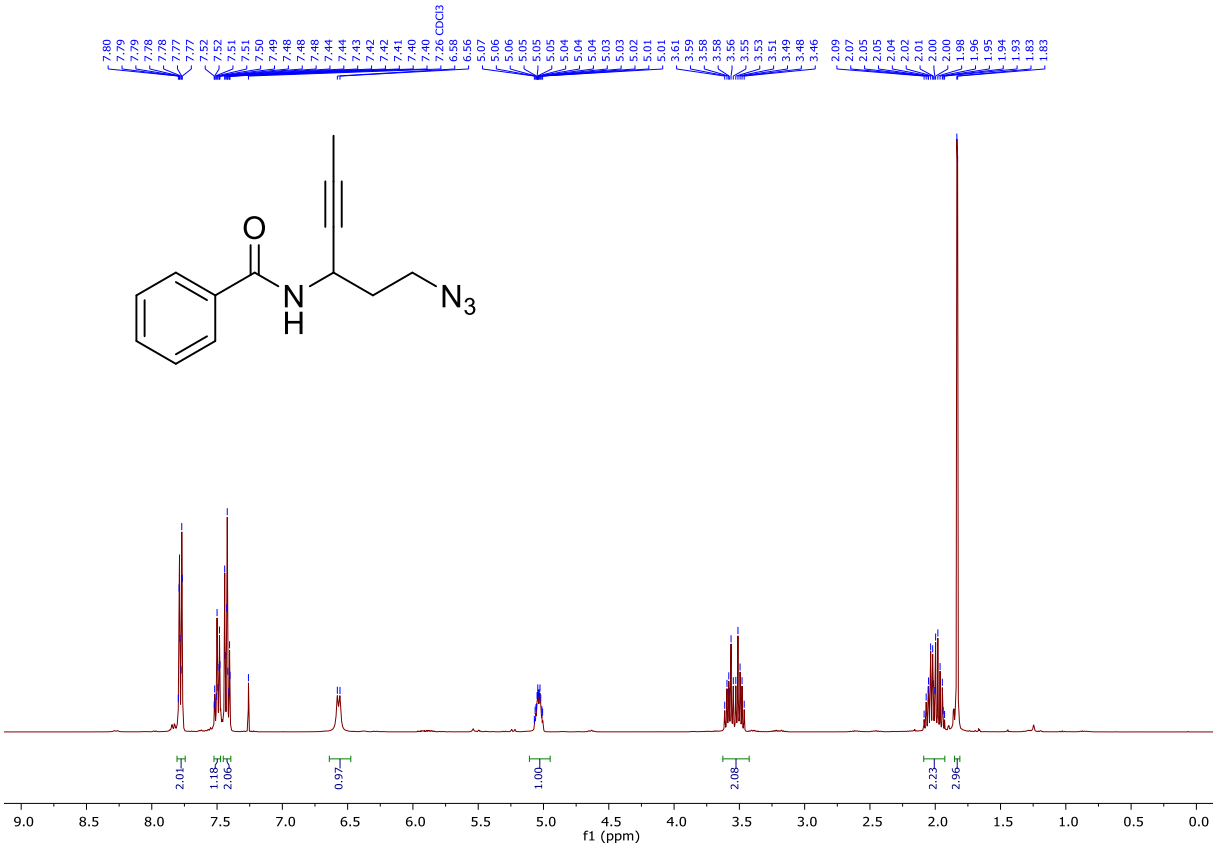


^{13}C-NMR (101 MHz, $CDCl_3$)

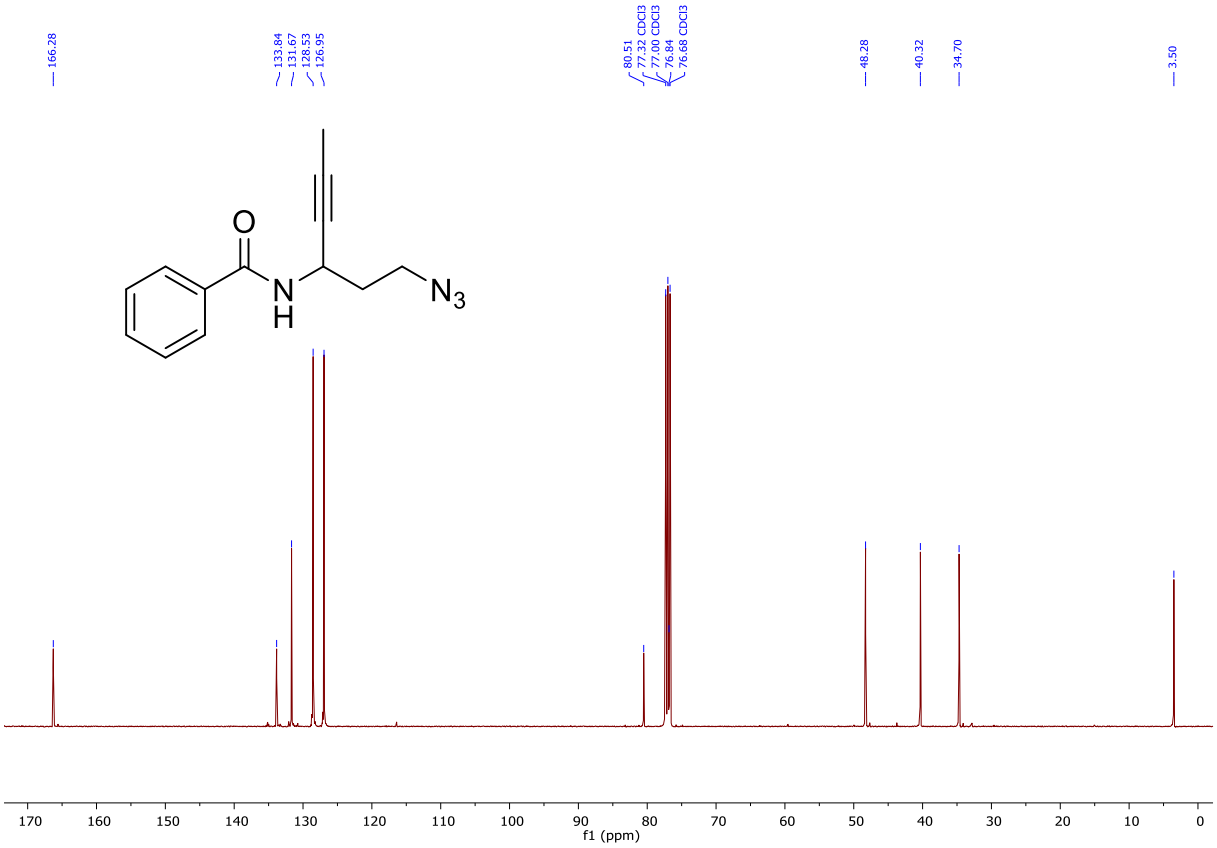


***N*-(1-Azidohex-4-yn-3-yl)benzamide (10p)**

^{1}H-NMR (400 MHz, $CDCl_3$)

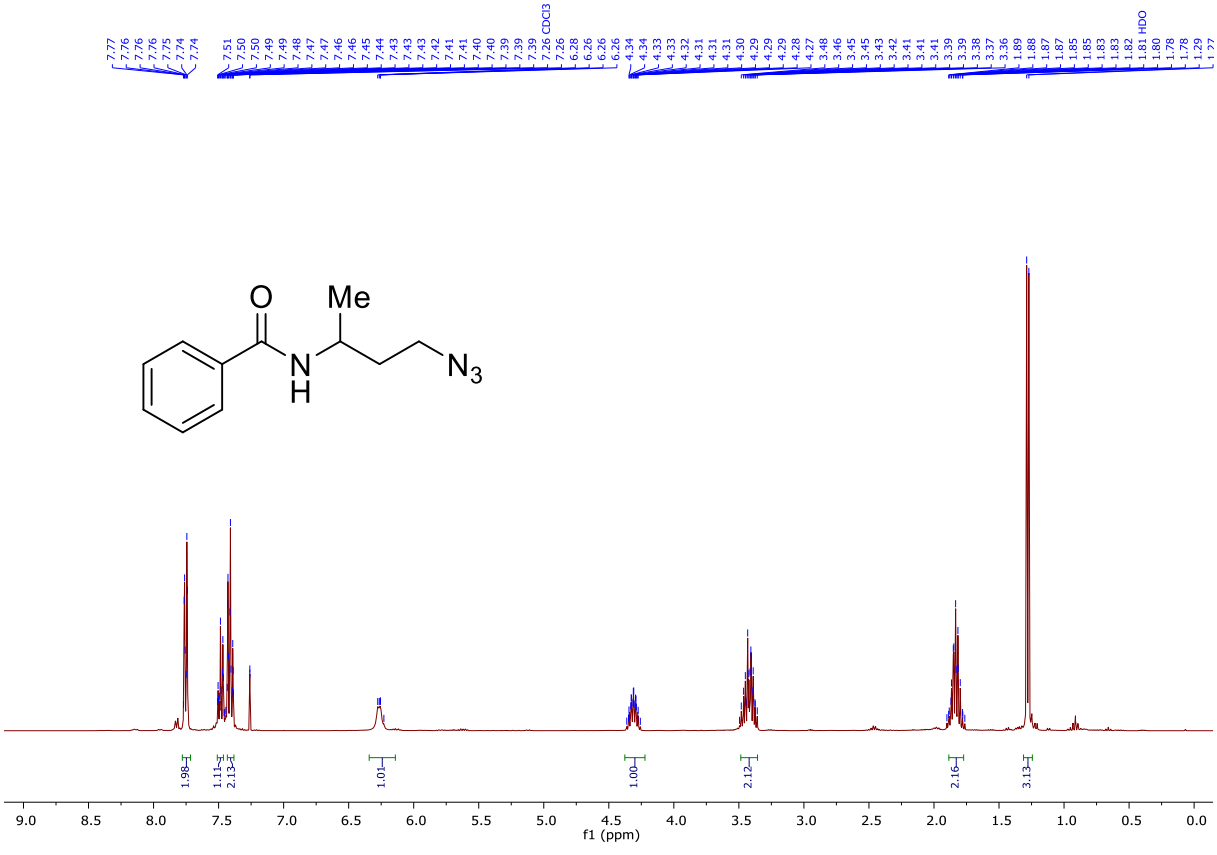


^{13}C-NMR (101 MHz, $CDCl_3$)

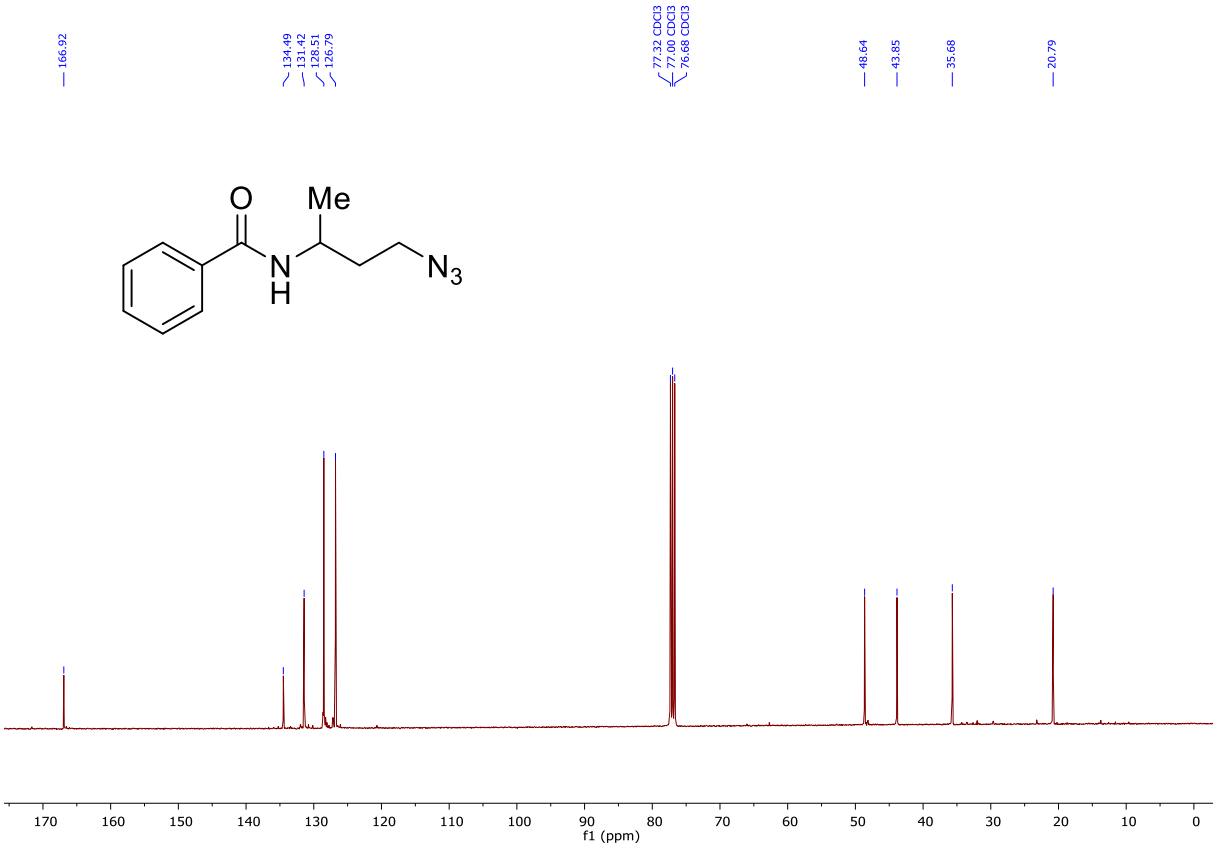


***N*-(4-Azidobutan-2-yl)benzamide (10qa)**

^{1}H-NMR (400 MHz, $CDCl_3$)

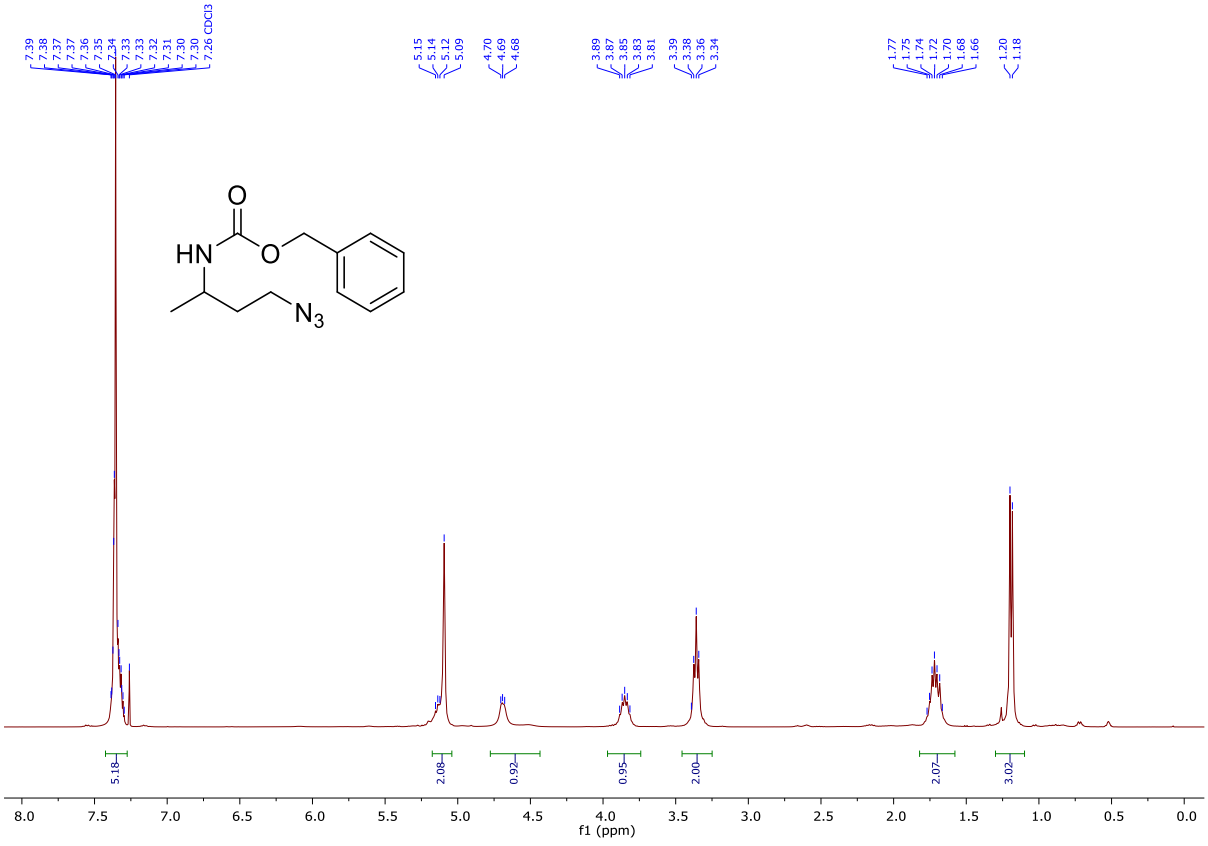


^{13}C-NMR (101 MHz, $CDCl_3$)

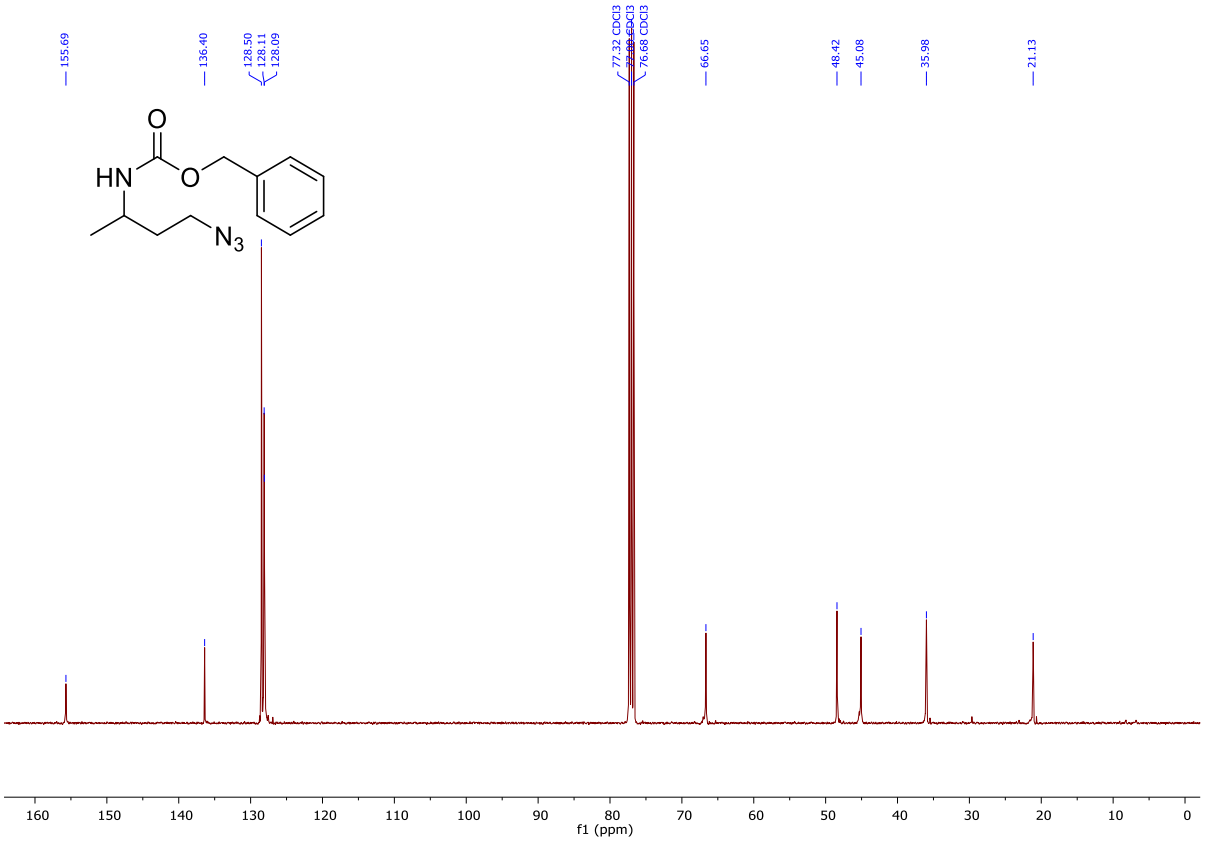


Benzyl (4-azidobutan-2-yl)carbamate (10qb)

^{1}H-NMR (400 MHz, $CDCl_3$)

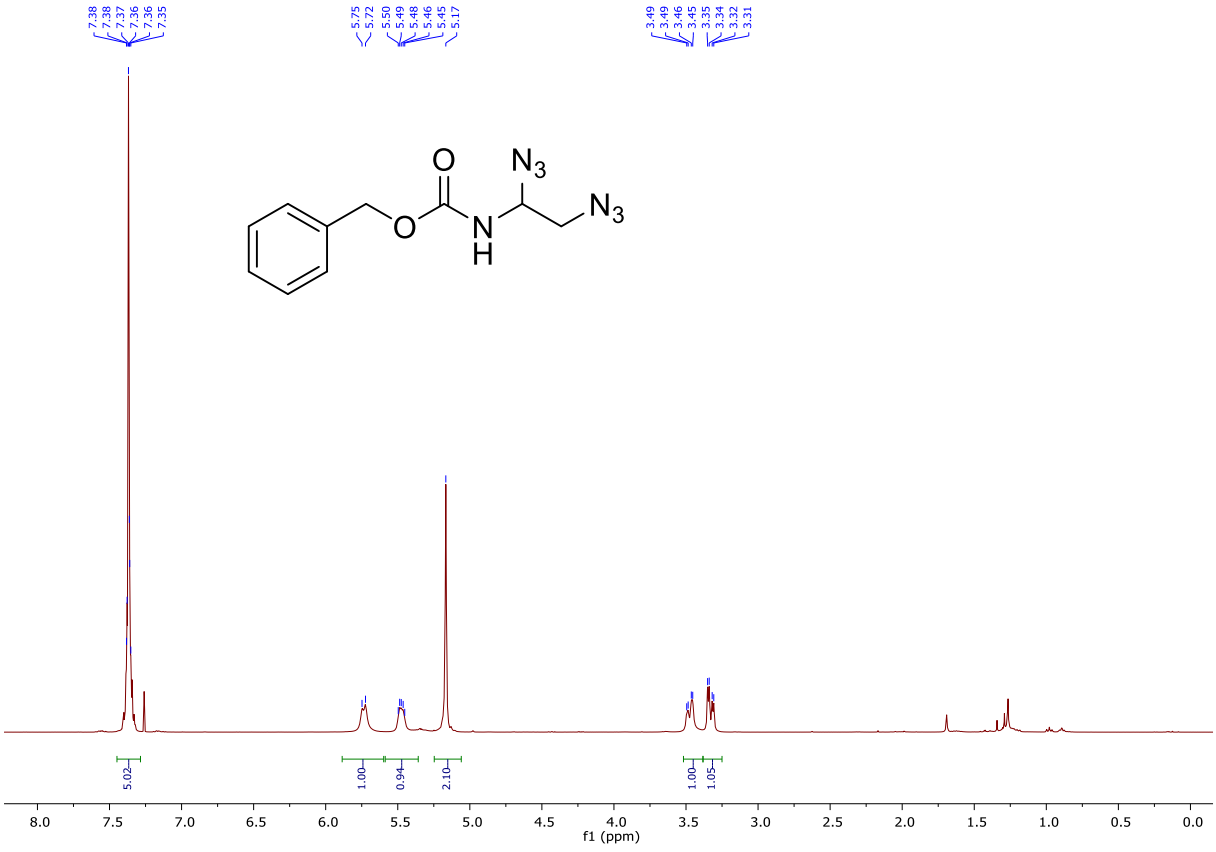


^{13}C-NMR (101 MHz, $CDCl_3$)

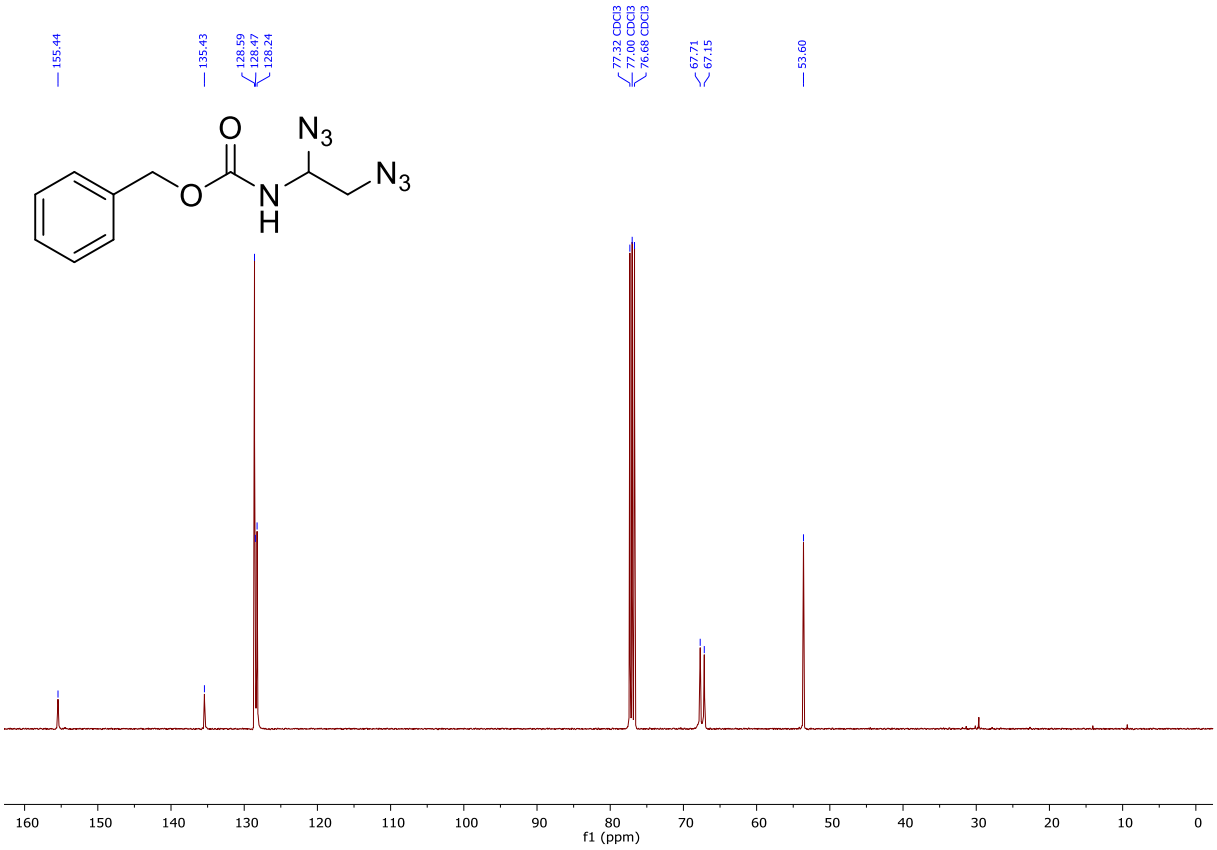


Benzyl (1,2-diazidoethyl)carbamate (13b)

^{1}H-NMR (400 MHz, $CDCl_3$)

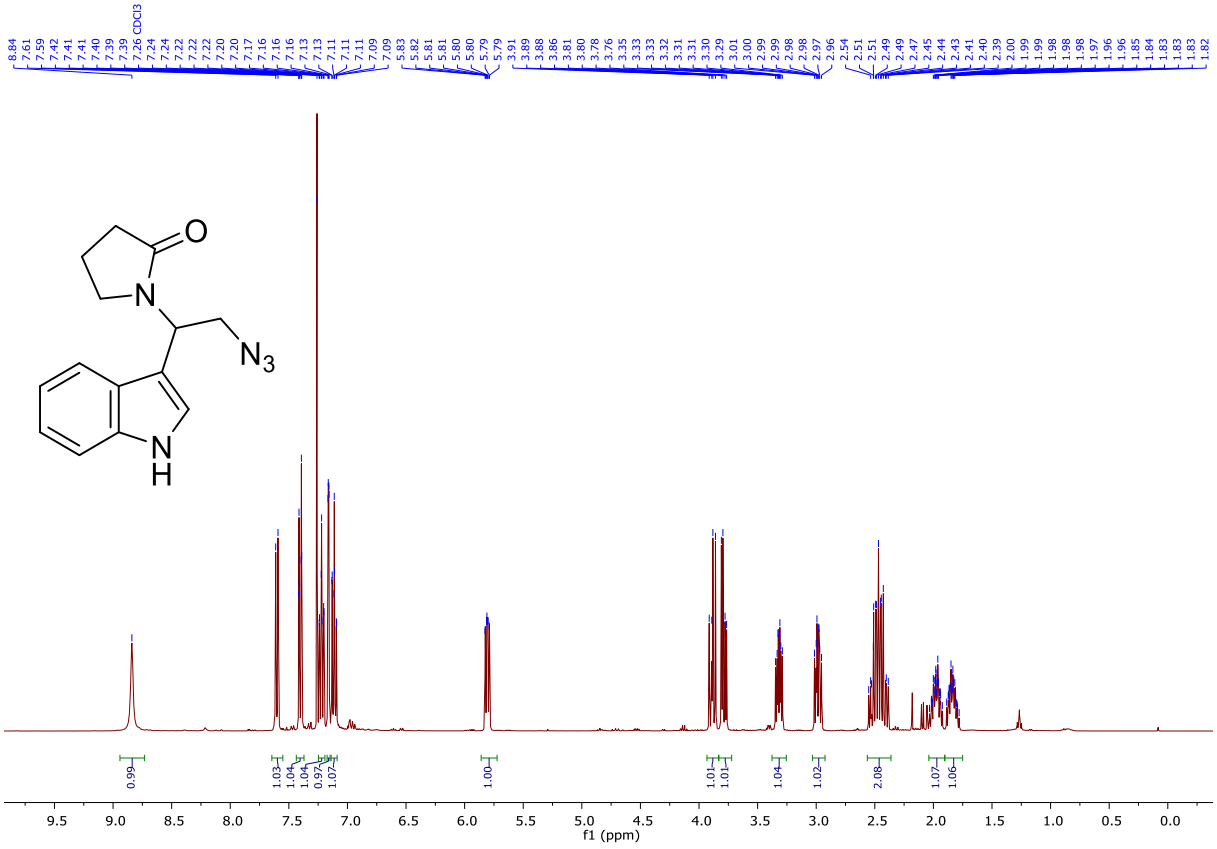


^{13}C-NMR (101 MHz, $CDCl_3$)

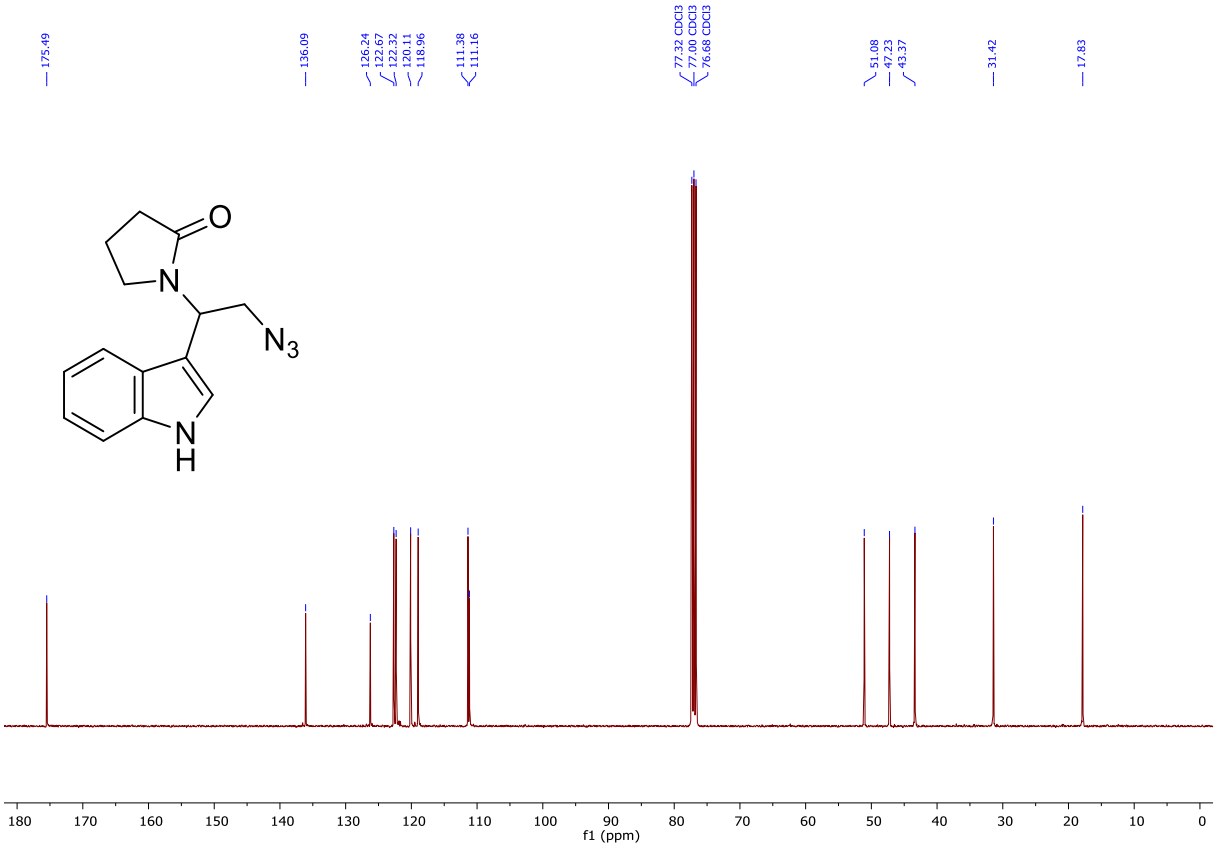


1-(2-Azido-1-(1*H*-indol-3-yl)ethyl)pyrrolidin-2-one (14a)

^{1}H-NMR (400 MHz, $CDCl_3$)

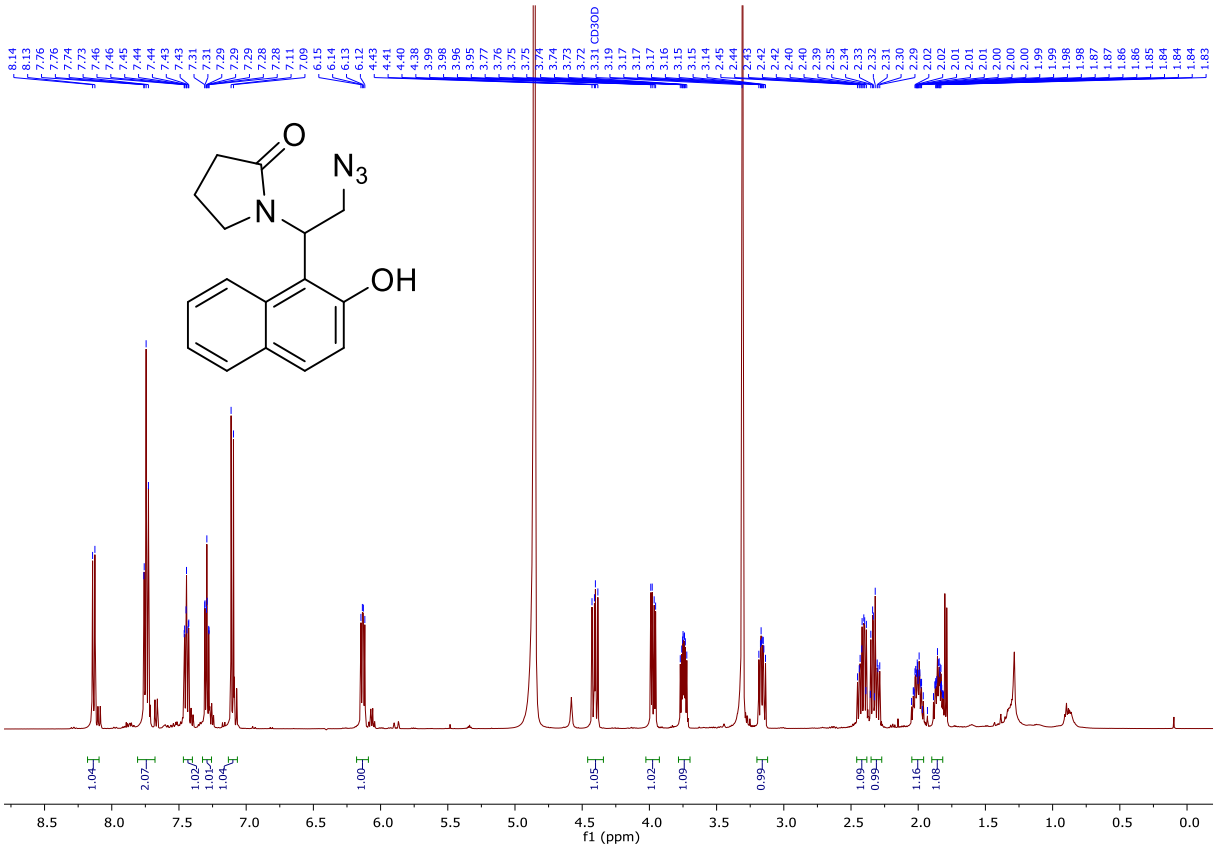


^{13}C-NMR (101 MHz, $CDCl_3$)

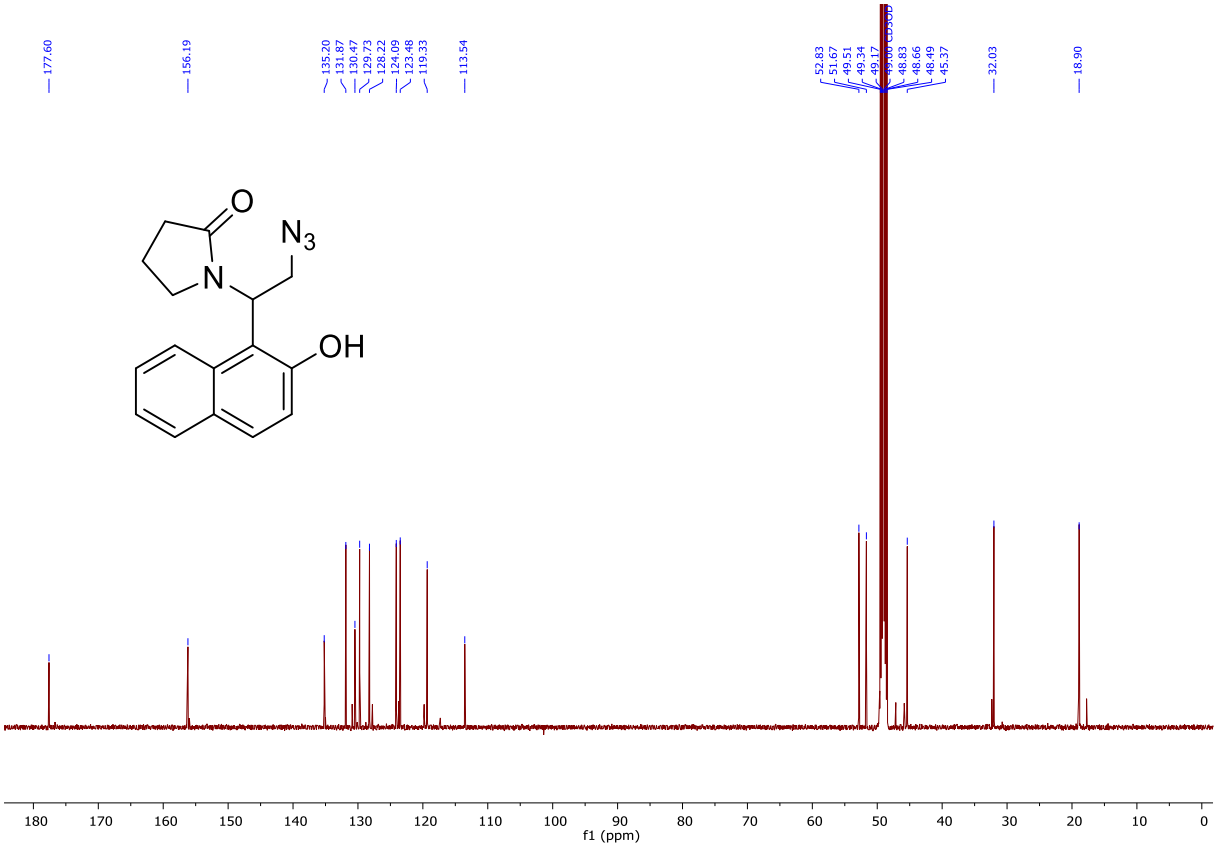


1-(2-Azido-1-(2-hydroxynaphthalen-1-yl)ethyl)pyrrolidin-2-one (14b)

^{1}H-NMR (500 MHz, Methanol-d_4)

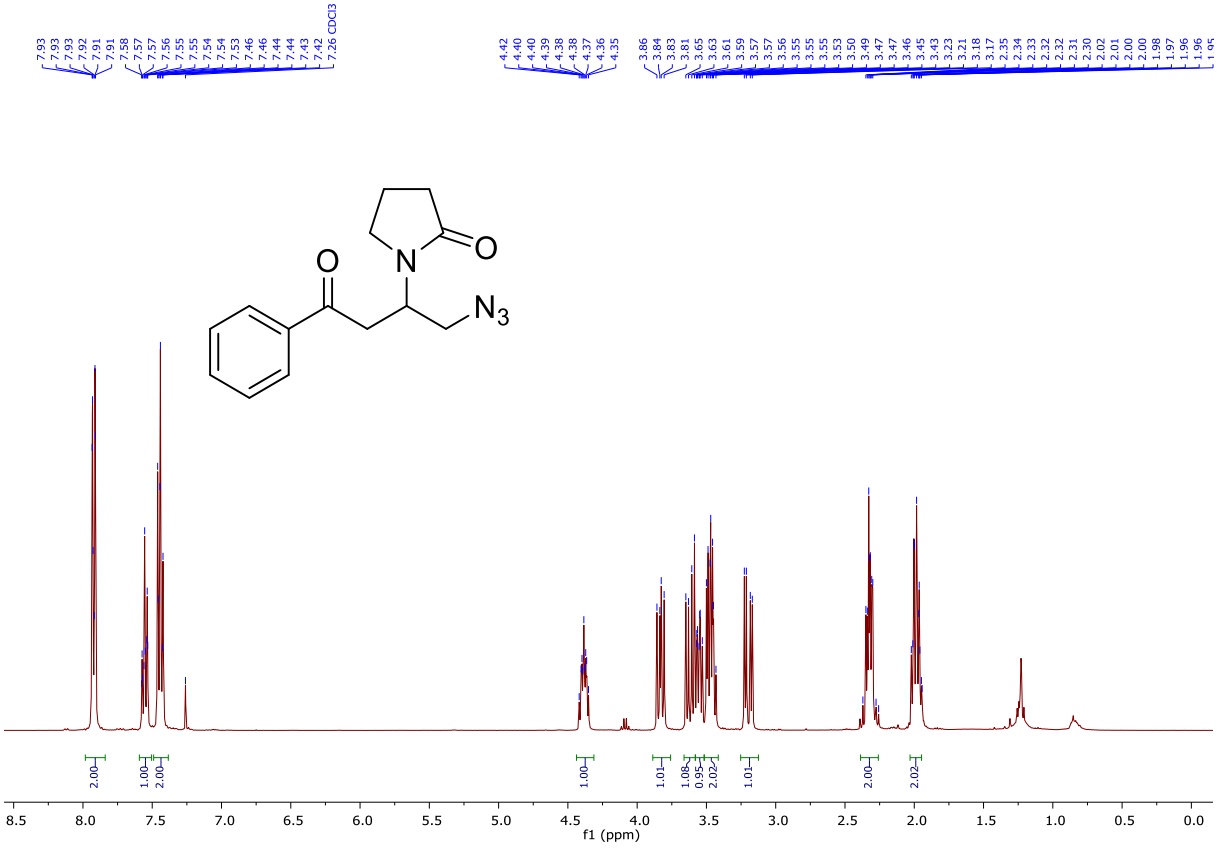


^{13}C-NMR (126 MHz, Methanol-d_4)

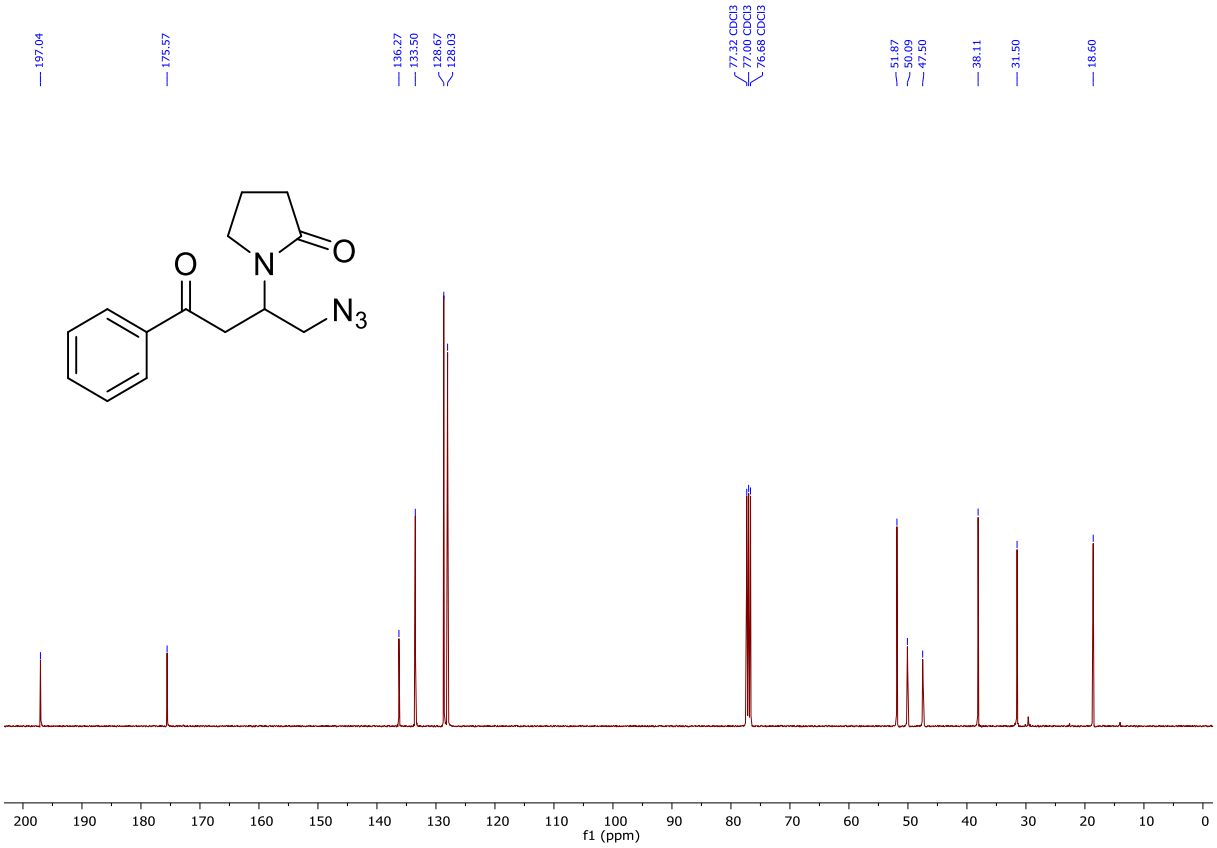


1-(1-Azido-4-oxo-4-phenylbutan-2-yl)pyrrolidin-2-one (14c)

^{1}H-NMR (400 MHz, $CDCl_3$)

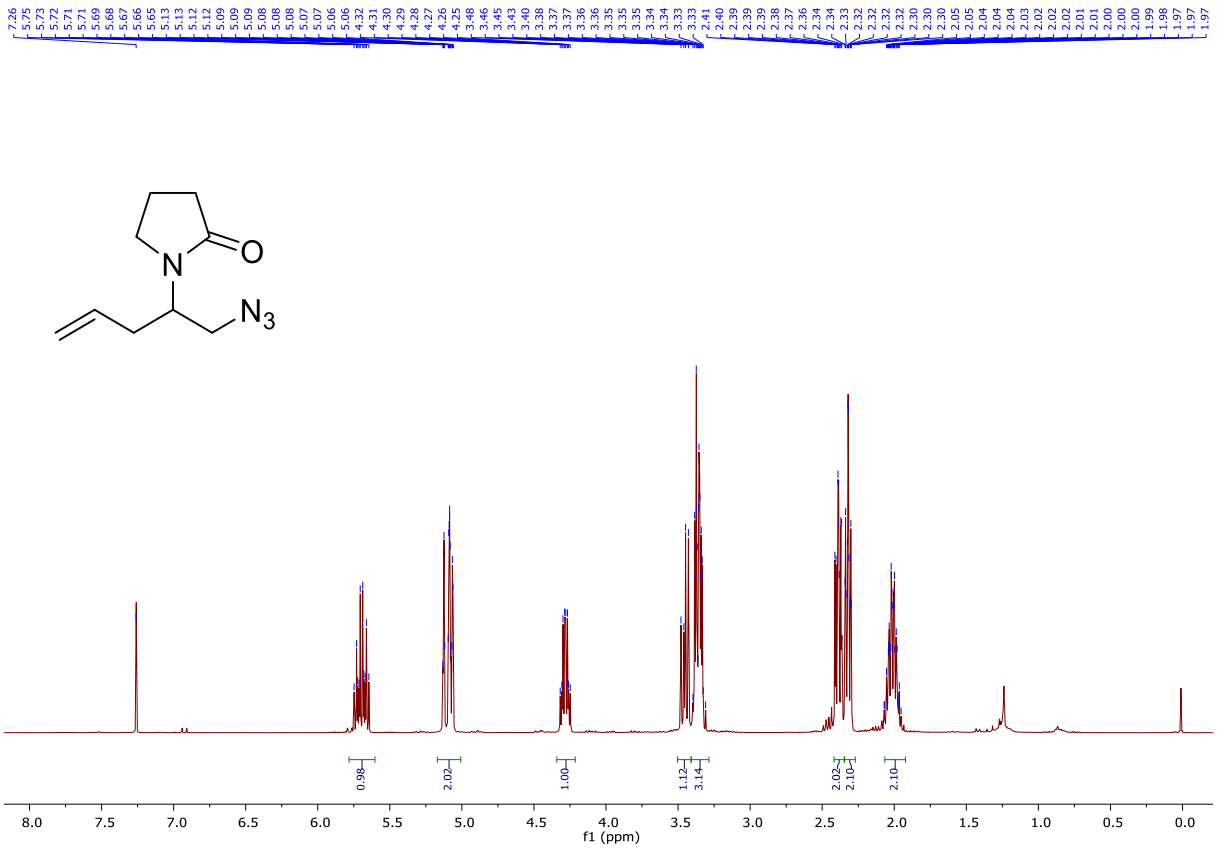


^{13}C-NMR (101 MHz, $CDCl_3$)

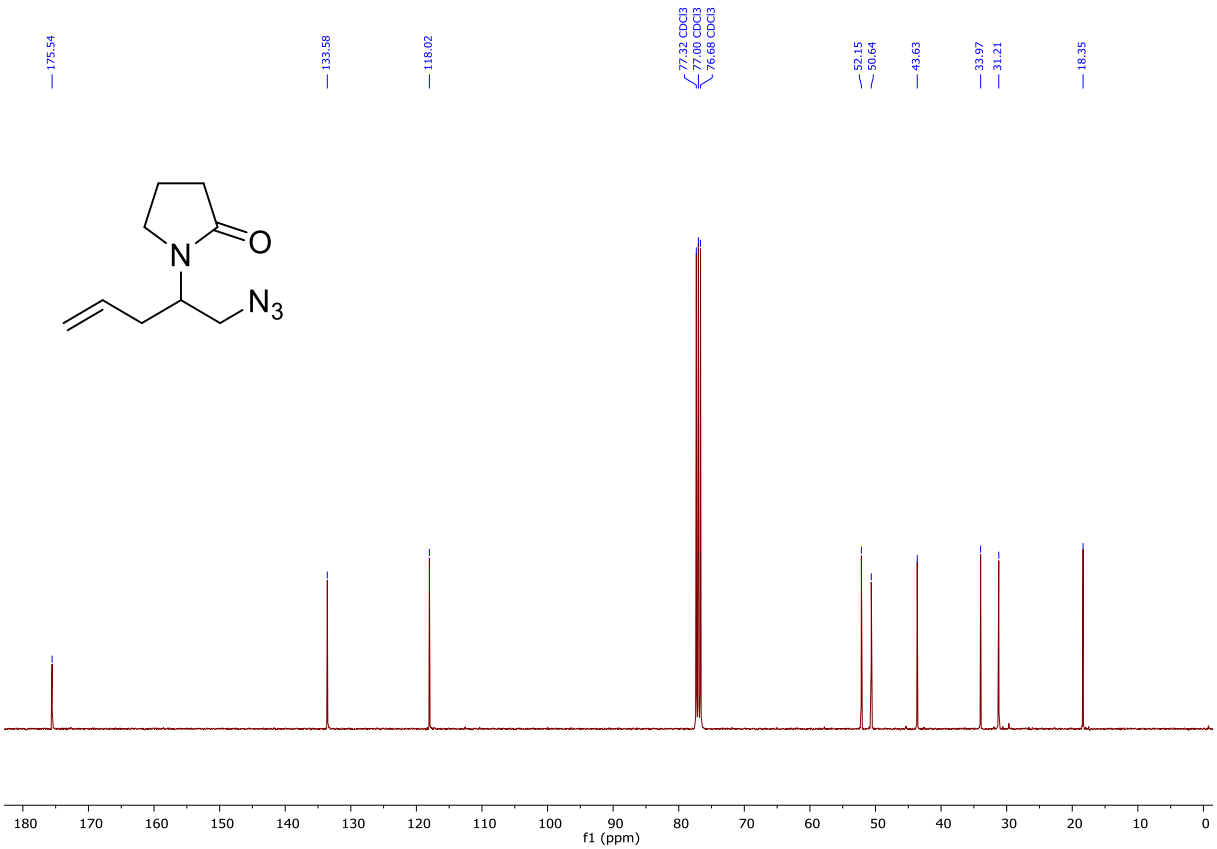


1-(1-Azidopent-4-en-2-yl)pyrrolidin-2-one (14d)

^{1}H-NMR (400 MHz, $CDCl_3$)

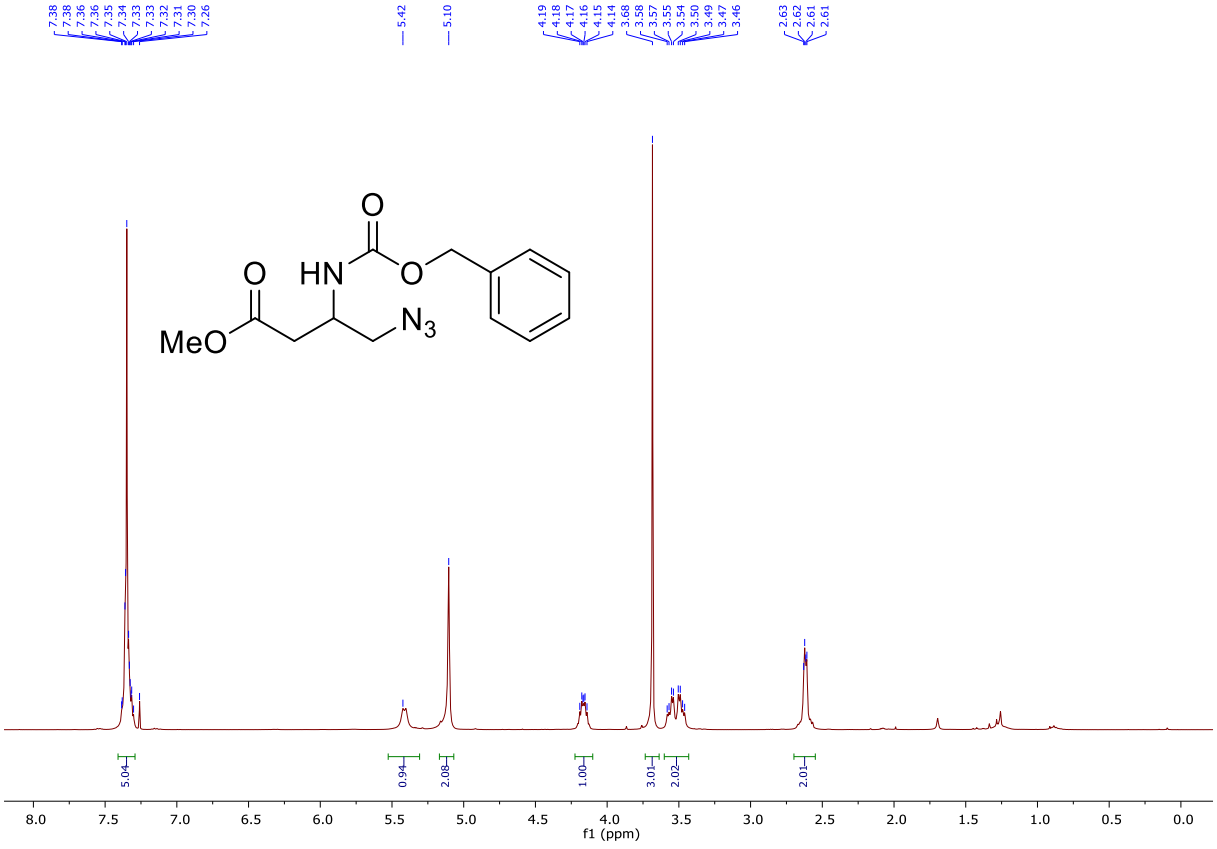


^{13}C-NMR (101 MHz, $CDCl_3$)

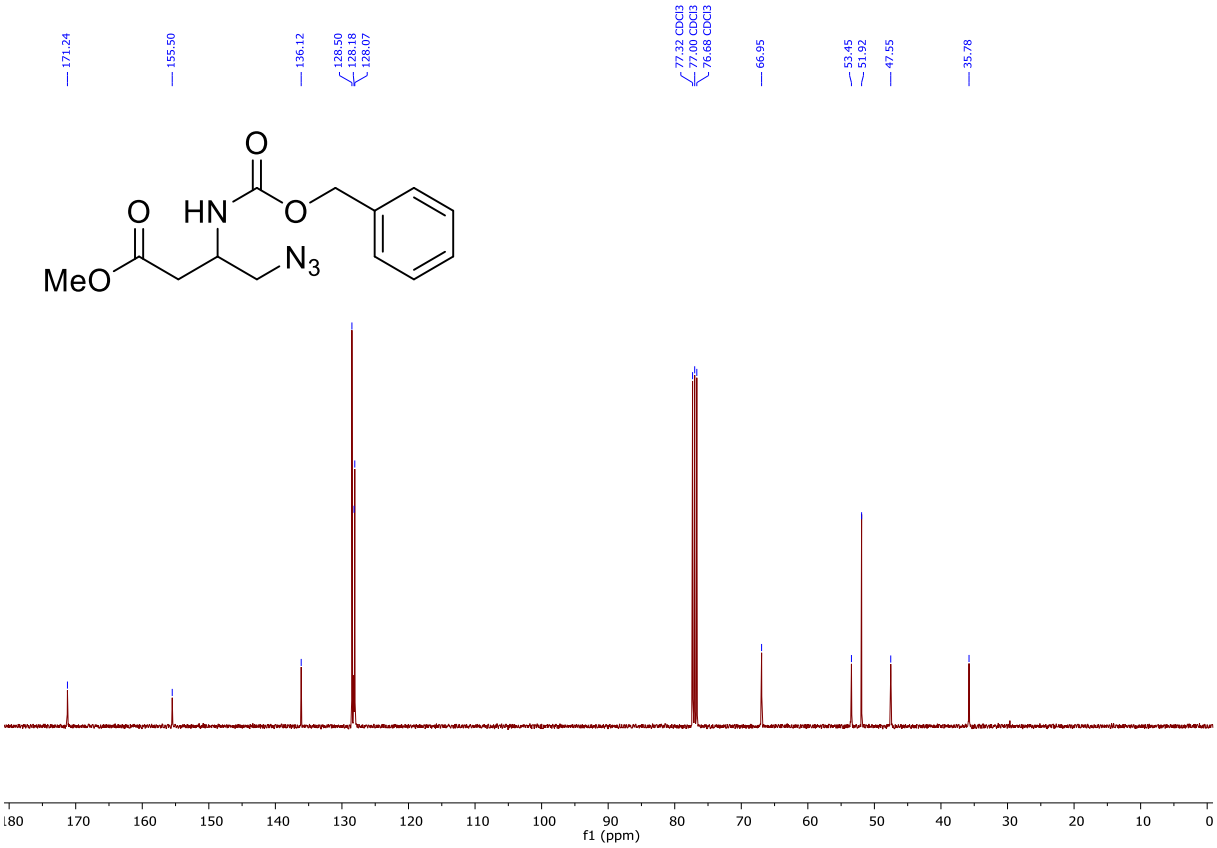


Methyl 4-azido-3-(((benzyloxy)carbonyl)amino)butanoate (14e)

^{1}H-NMR (400 MHz, $CDCl_3$)

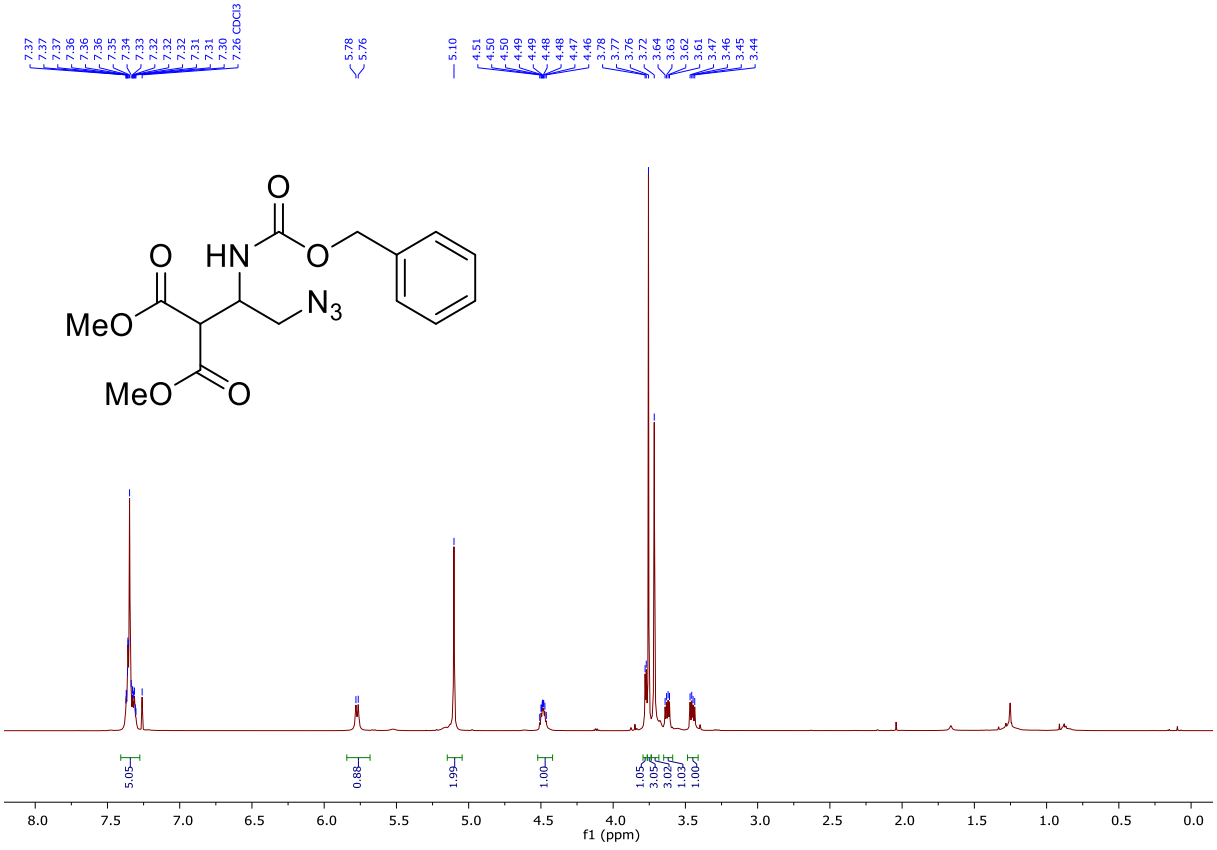


^{13}C-NMR (101 MHz, $CDCl_3$)

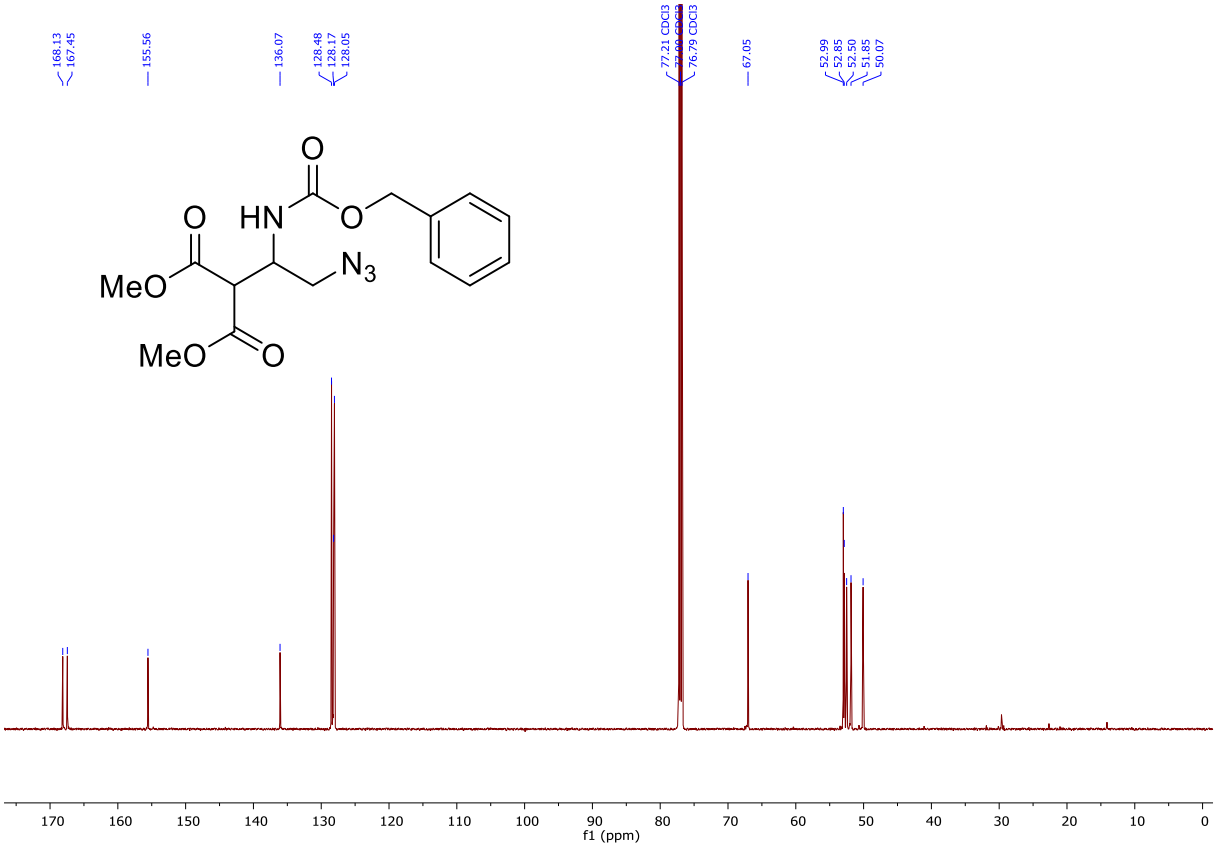


Dimethyl 2-(2-azido-1-(((benzyloxy)carbonyl)amino)ethyl)malonate (14f)

^{1}H-NMR (600 MHz, $CDCl_3$)

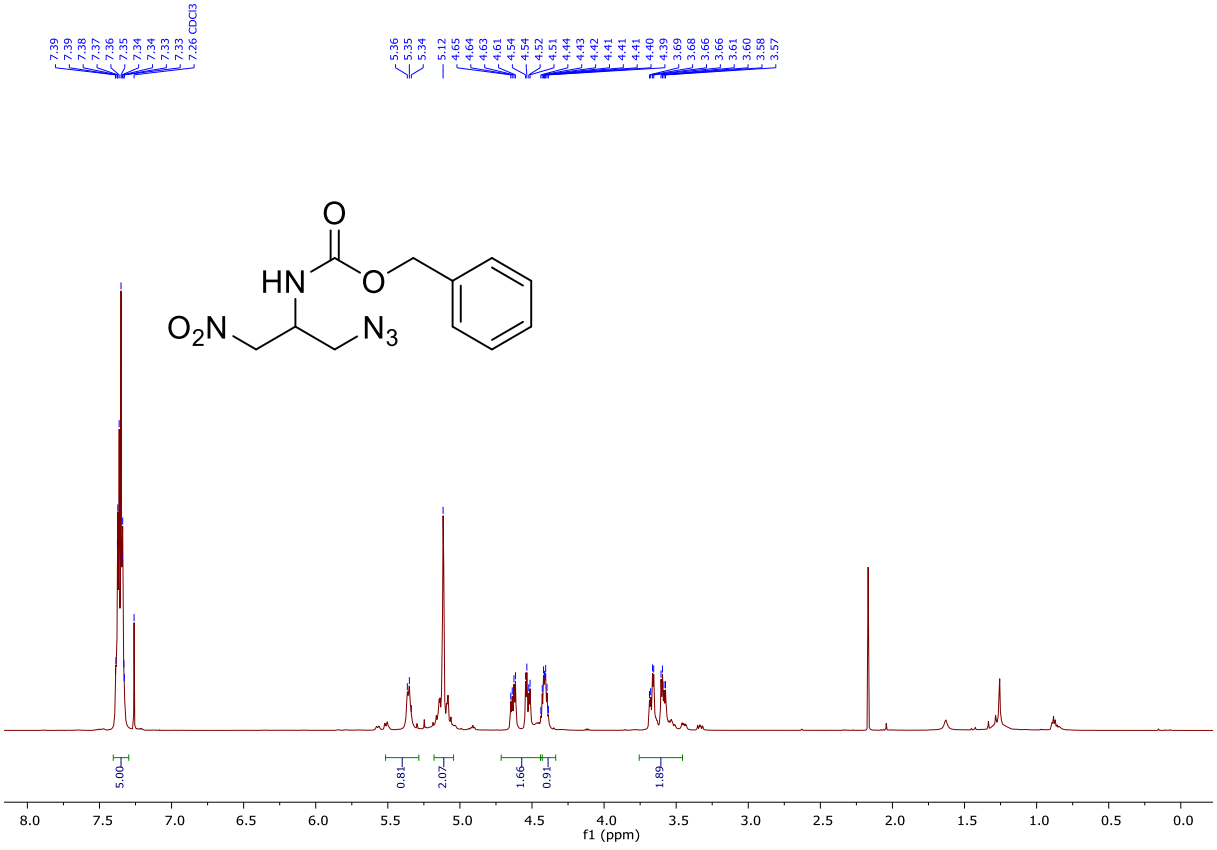


^{13}C-NMR (151 MHz, $CDCl_3$)

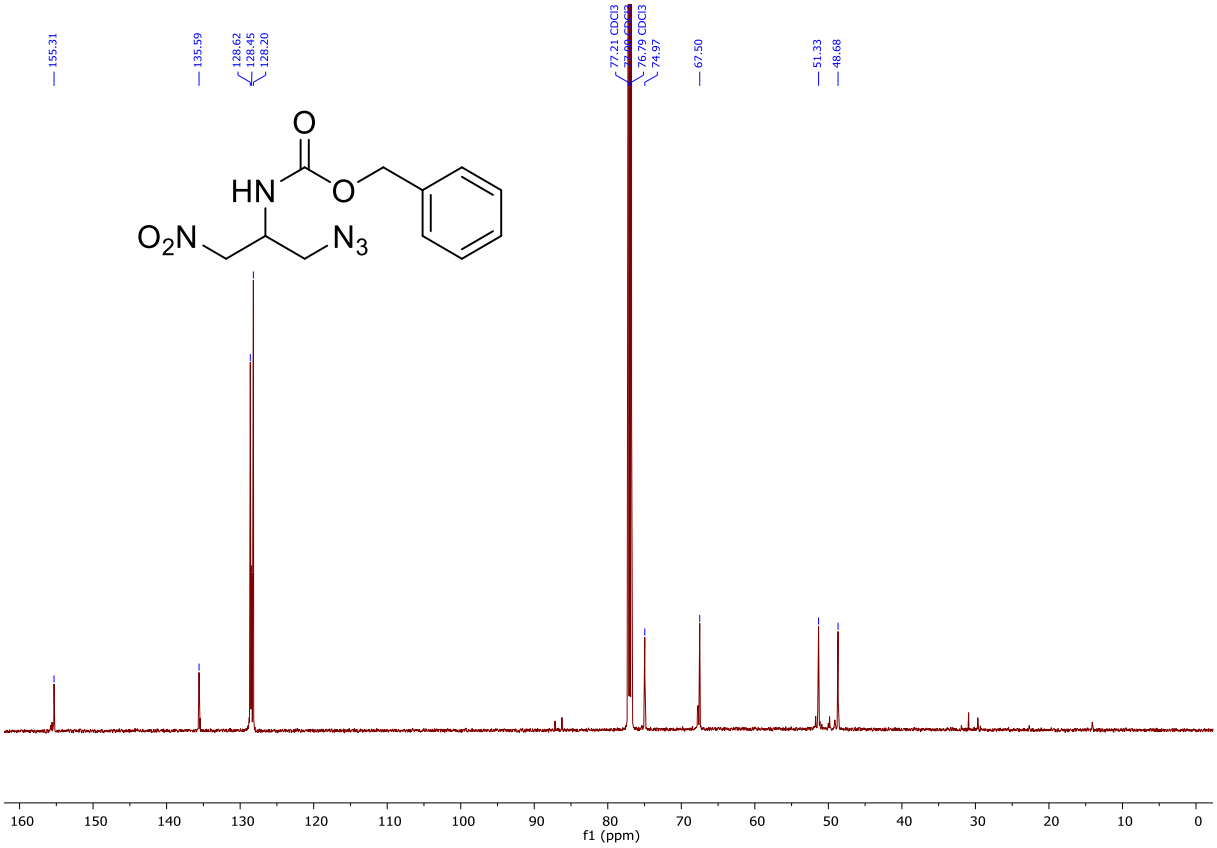


Benzyl (1-azido-3-nitropropan-2-yl)carbamate (14g)

^{1}H-NMR (600 MHz, $CDCl_3$)

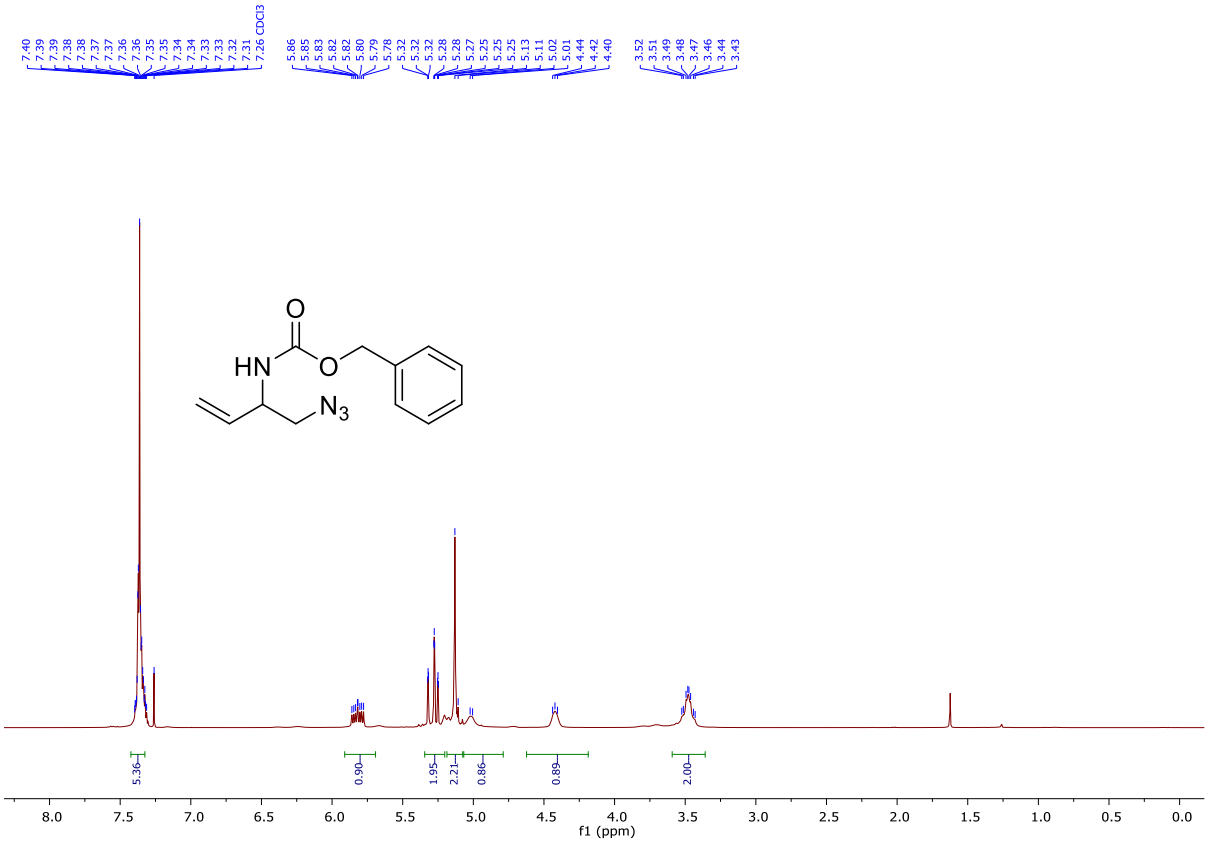


^{13}C-NMR (151 MHz, $CDCl_3$)

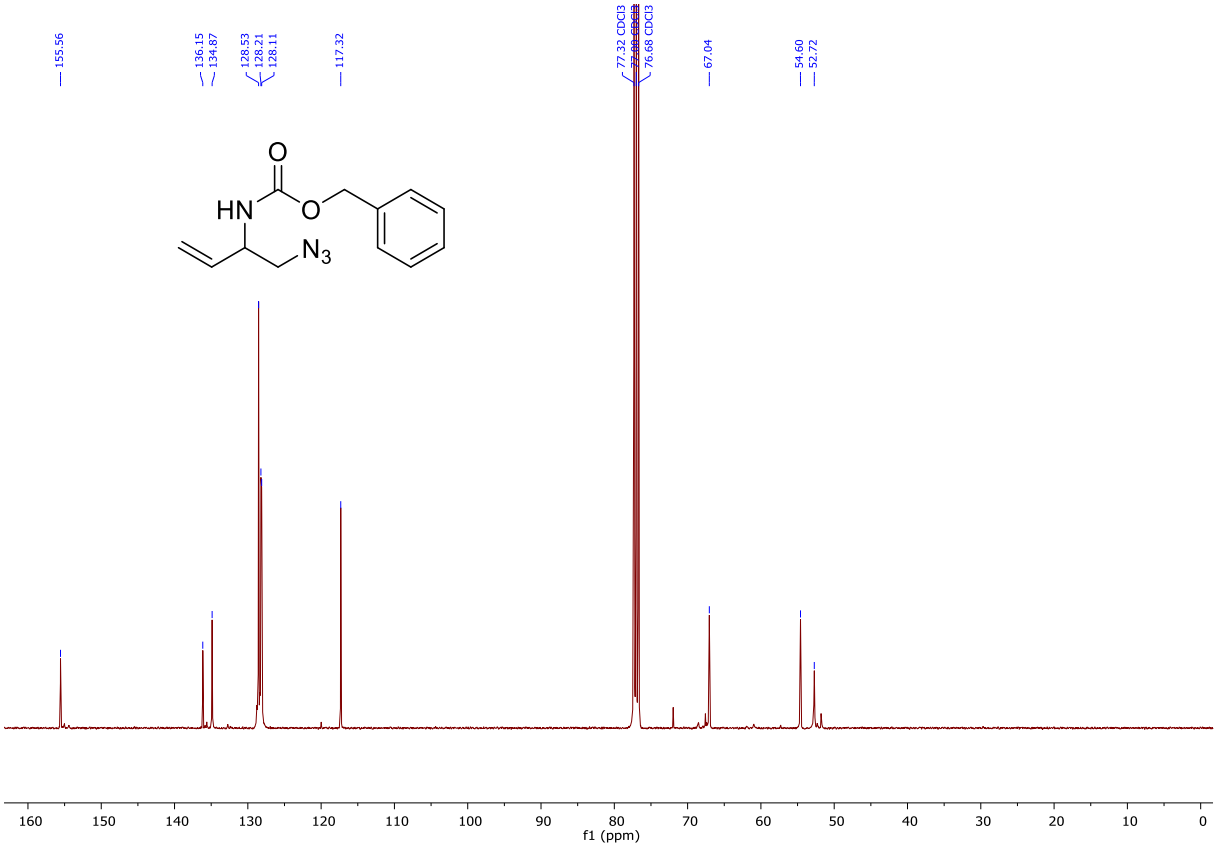


Benzyl (1-azidobut-3-en-2-yl)carbamate (14h)

^{1}H-NMR (400 MHz, $CDCl_3$)

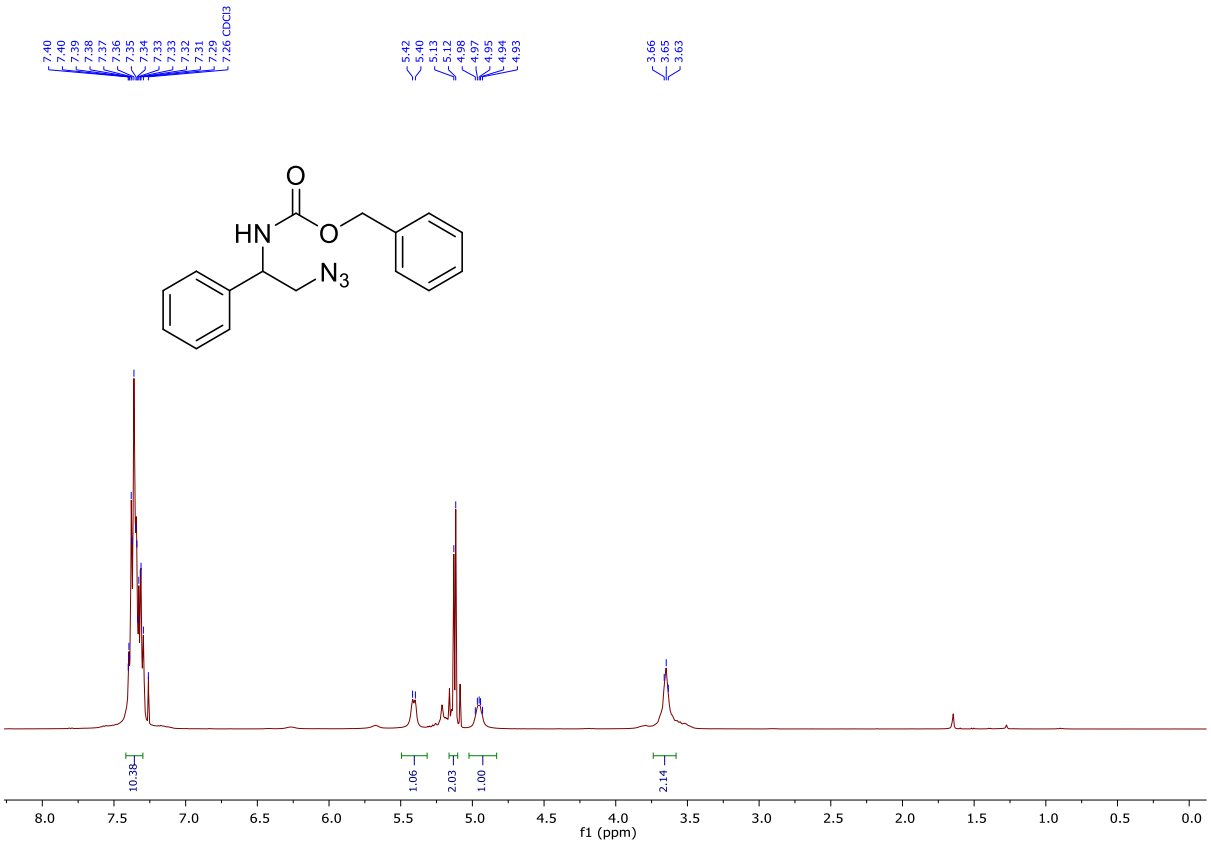


^{13}C-NMR (101 MHz, $CDCl_3$)

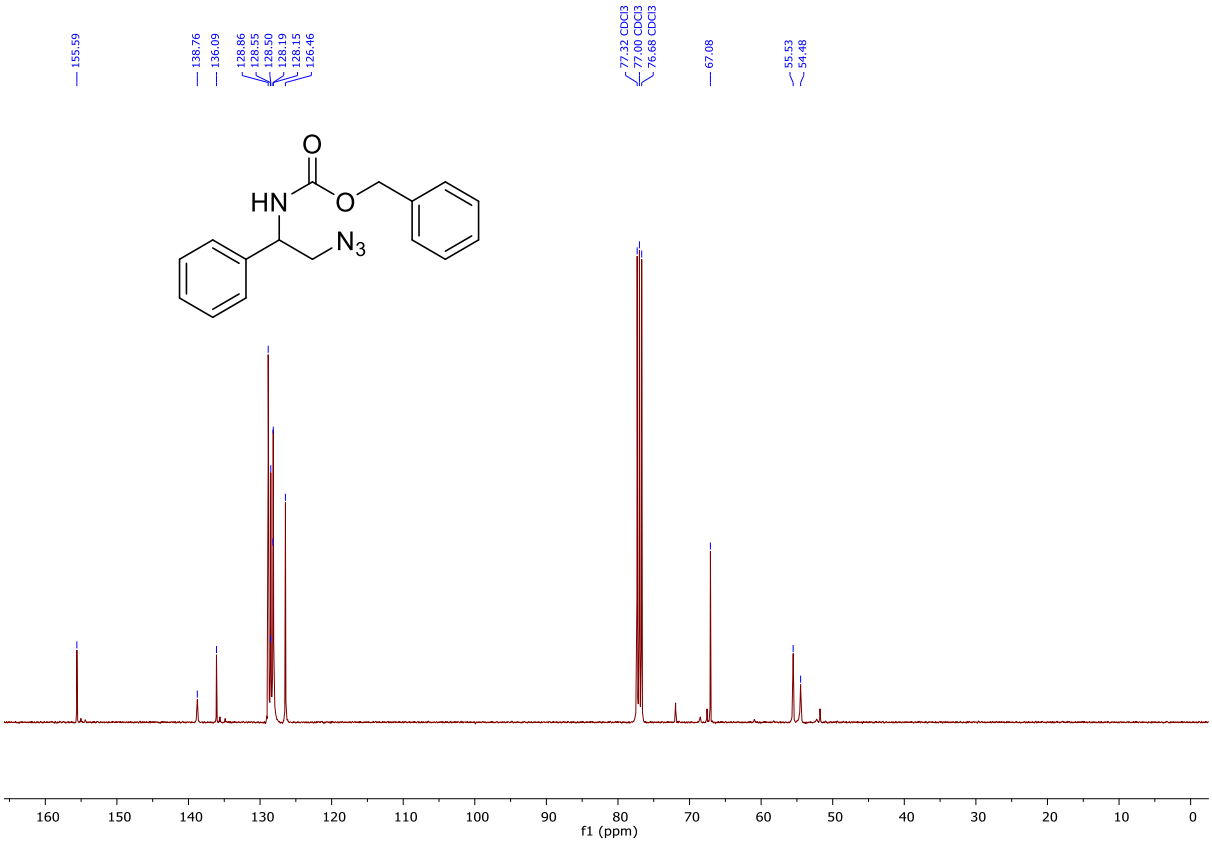


Benzyl (2-azido-1-phenylethyl)carbamate (14i)

^{1}H-NMR (400 MHz, $CDCl_3$)

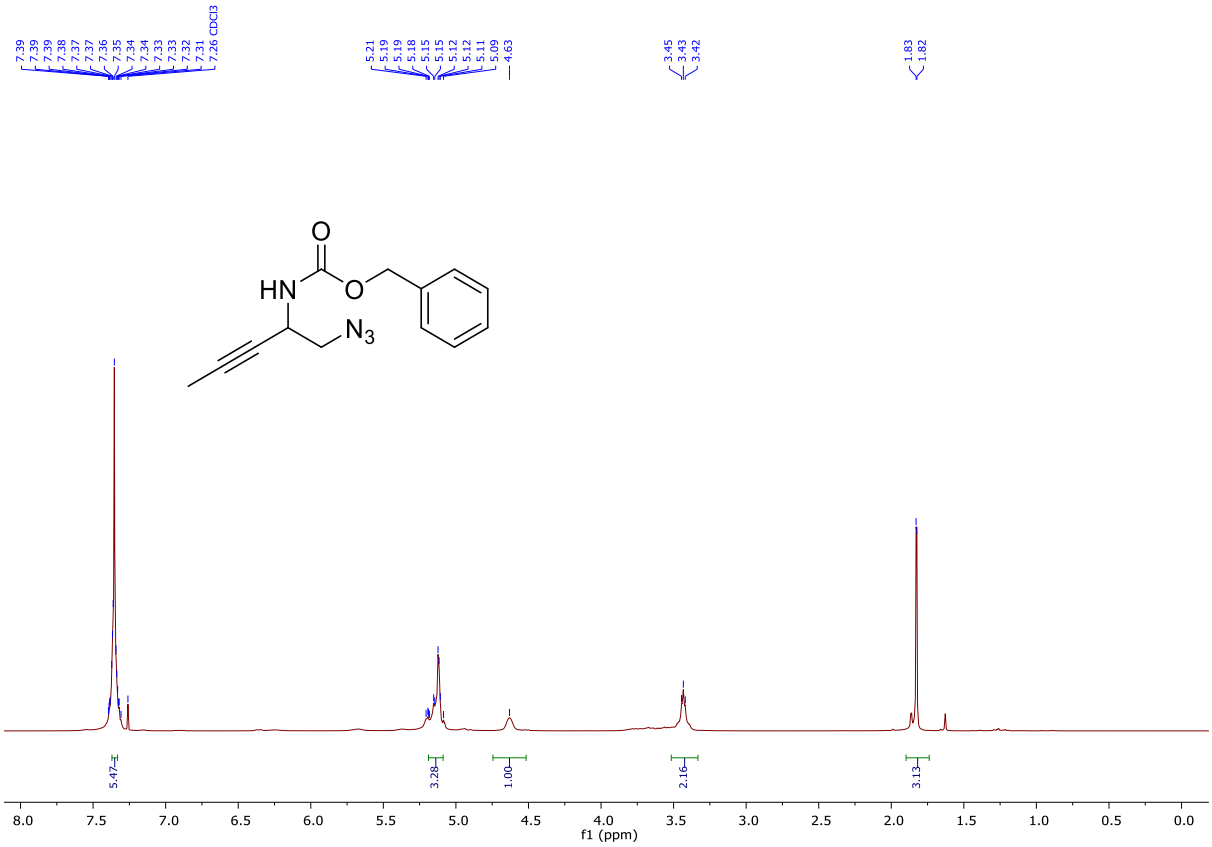


^{13}C-NMR (101 MHz, $CDCl_3$)

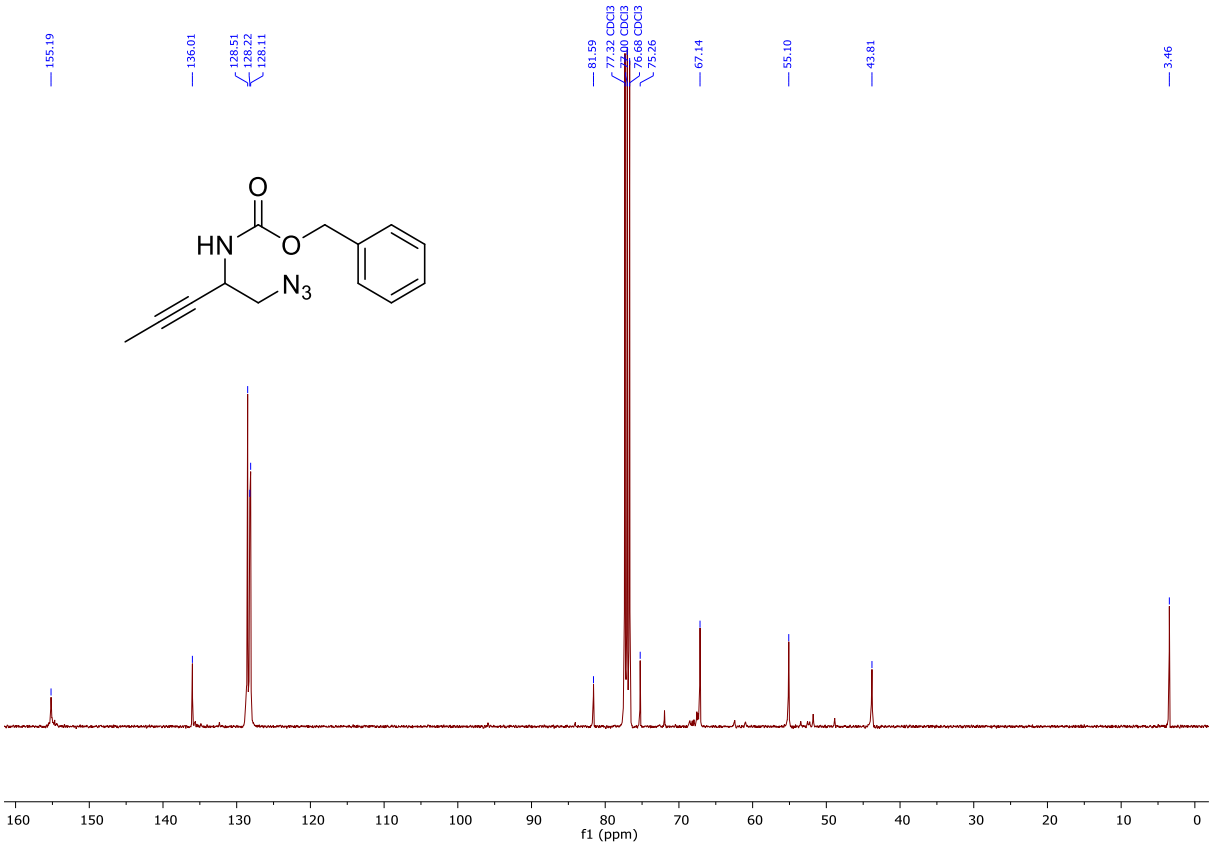


Benzyl (1-azidopent-3-yn-2-yl)carbamate (14j)

^{1}H-NMR (400 MHz, $CDCl_3$)

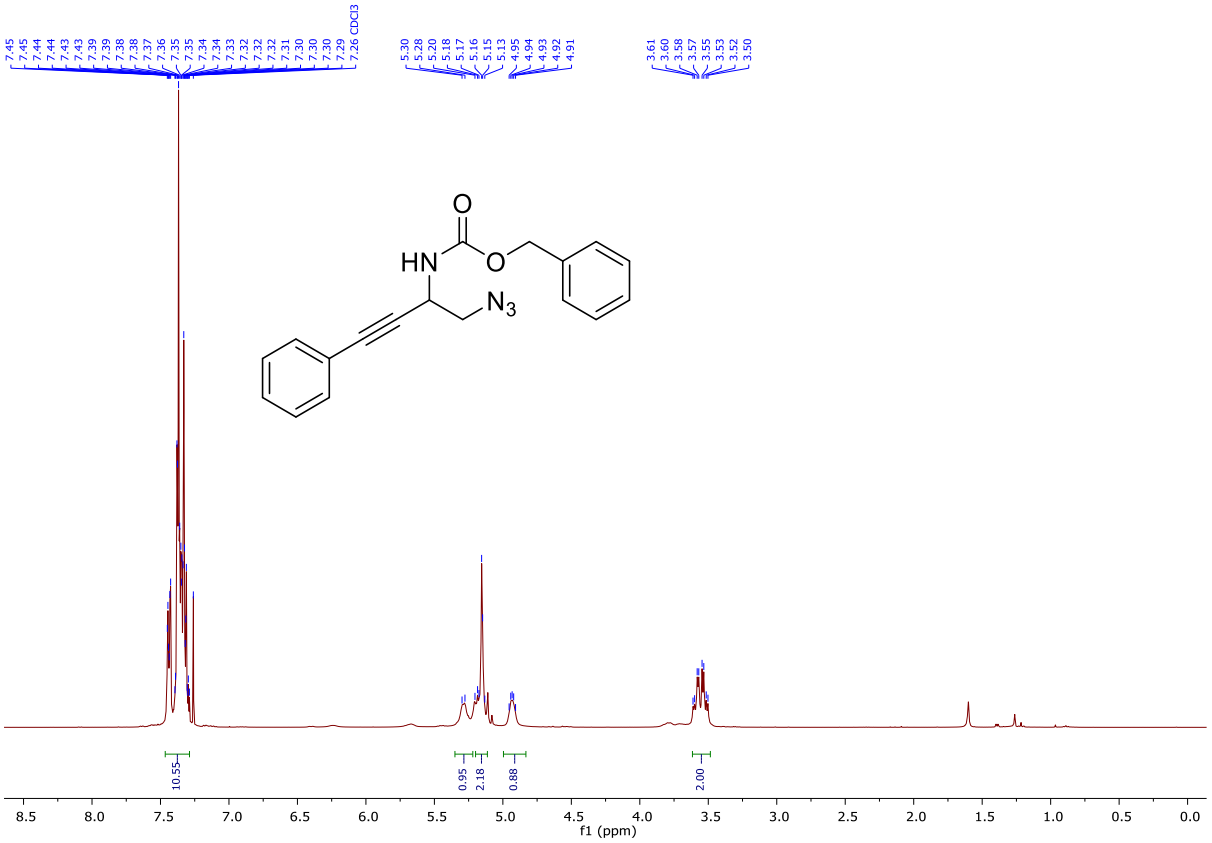


^{13}C-NMR (101 MHz, $CDCl_3$)

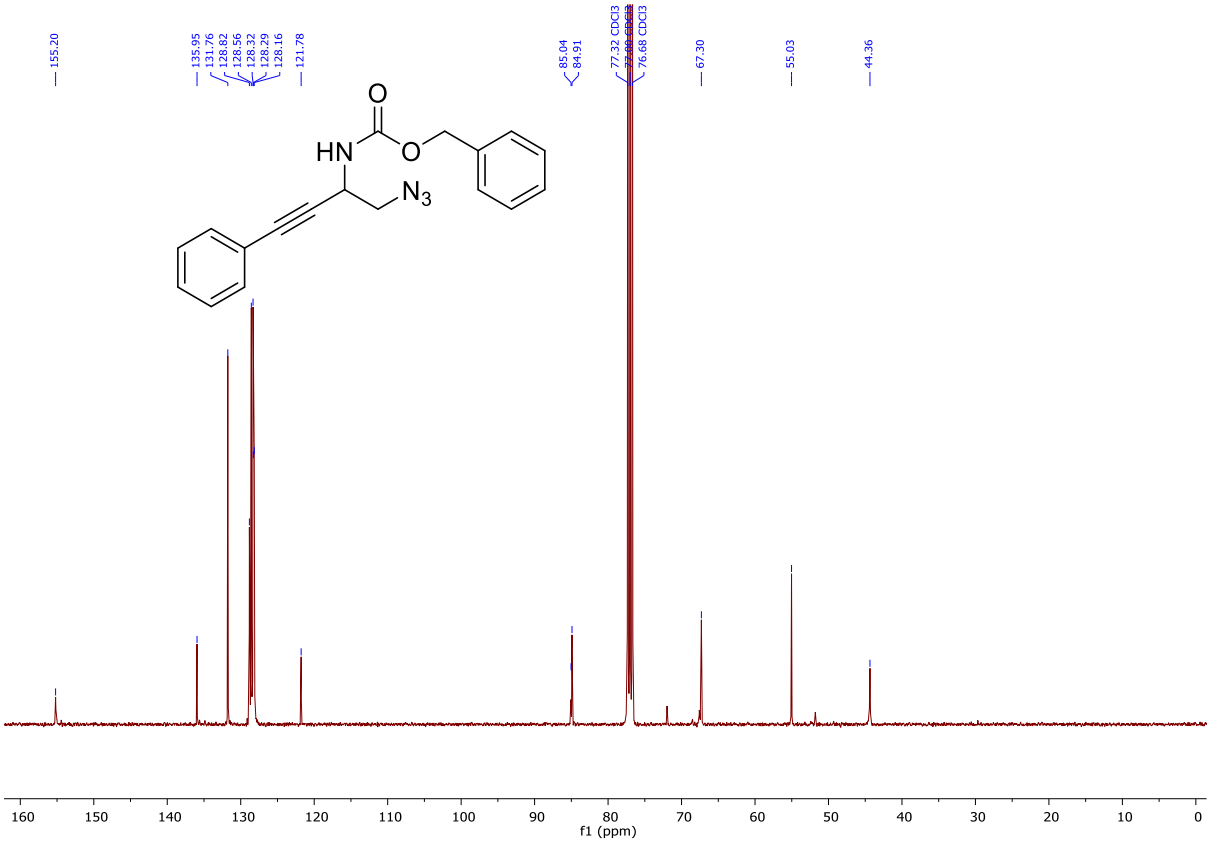


Benzyl (1-azido-4-phenylbut-3-yn-2-yl)carbamate (14k)

^{1}H-NMR (400 MHz, $CDCl_3$)

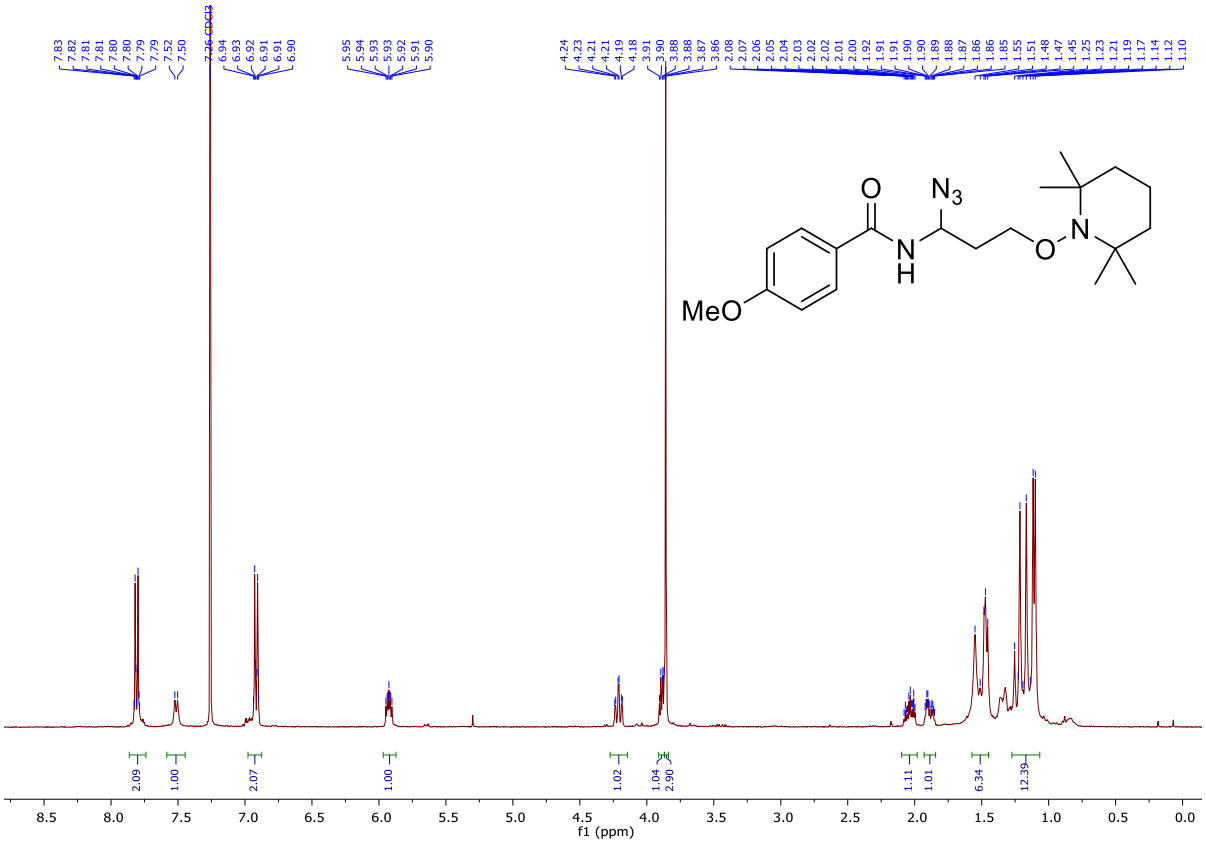


^{13}C-NMR (101 MHz, $CDCl_3$)

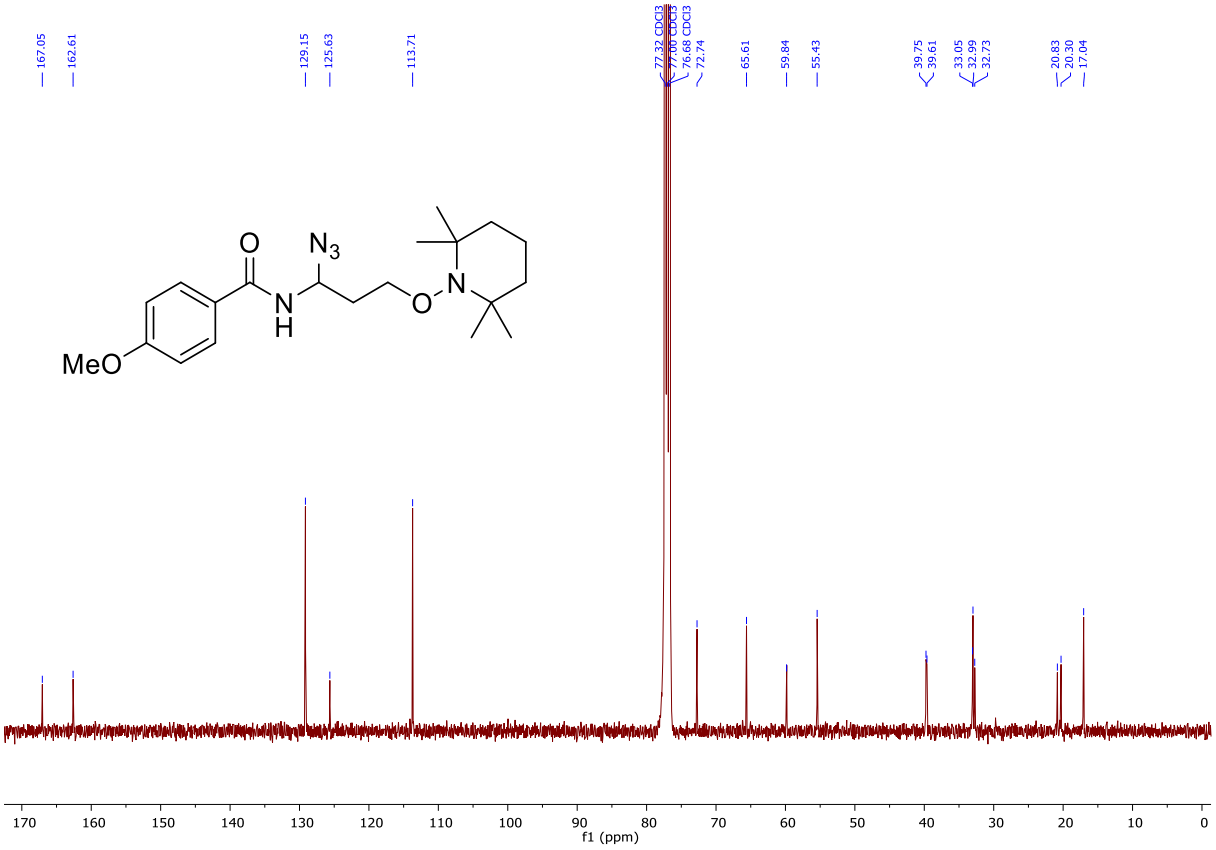


***N*-(1-Azido-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propyl)-4-methoxybenzamide (15)**

^{1}H-NMR (400 MHz, $CDCl_3$)

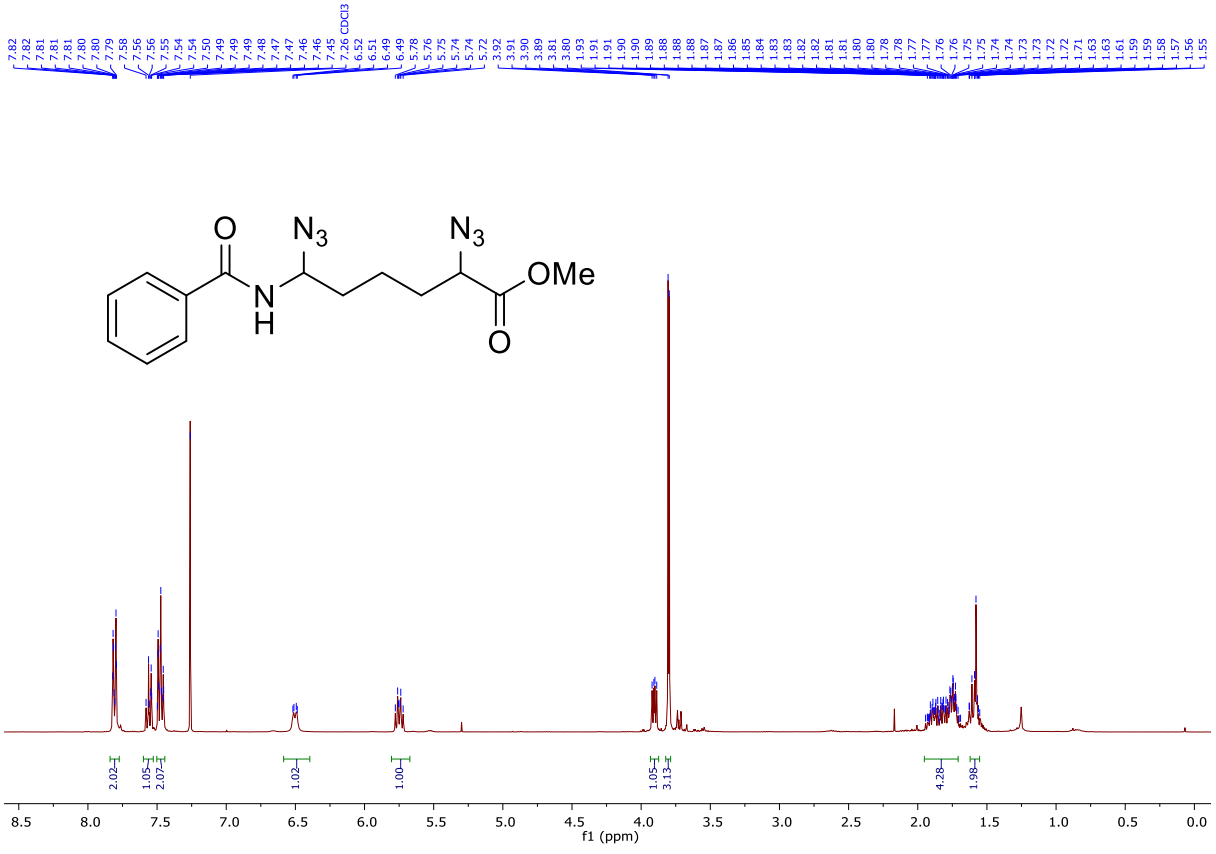


^{13}C-NMR (101 MHz, $CDCl_3$)

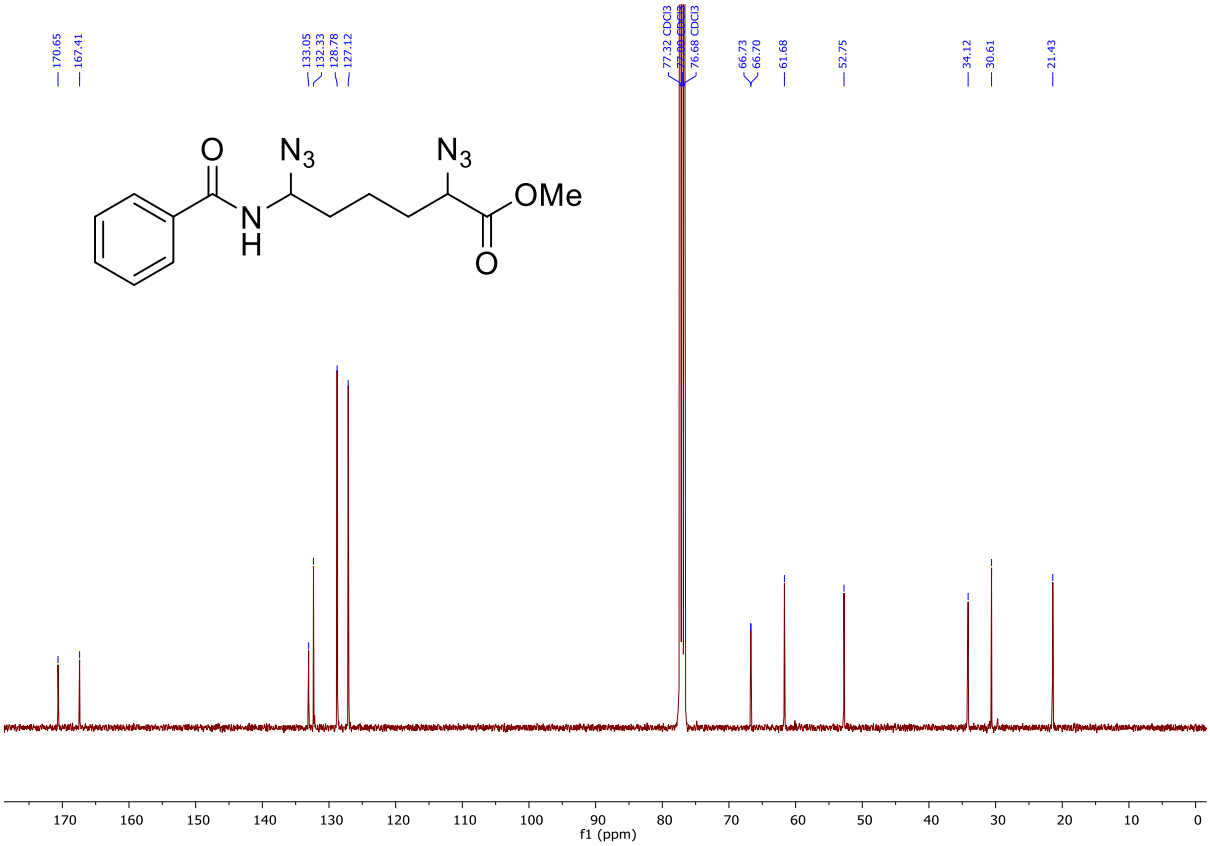


Methyl 2,6-diazido-6-benzamidohexanoate (16)

^{1}H-NMR (400 MHz, $CDCl_3$)

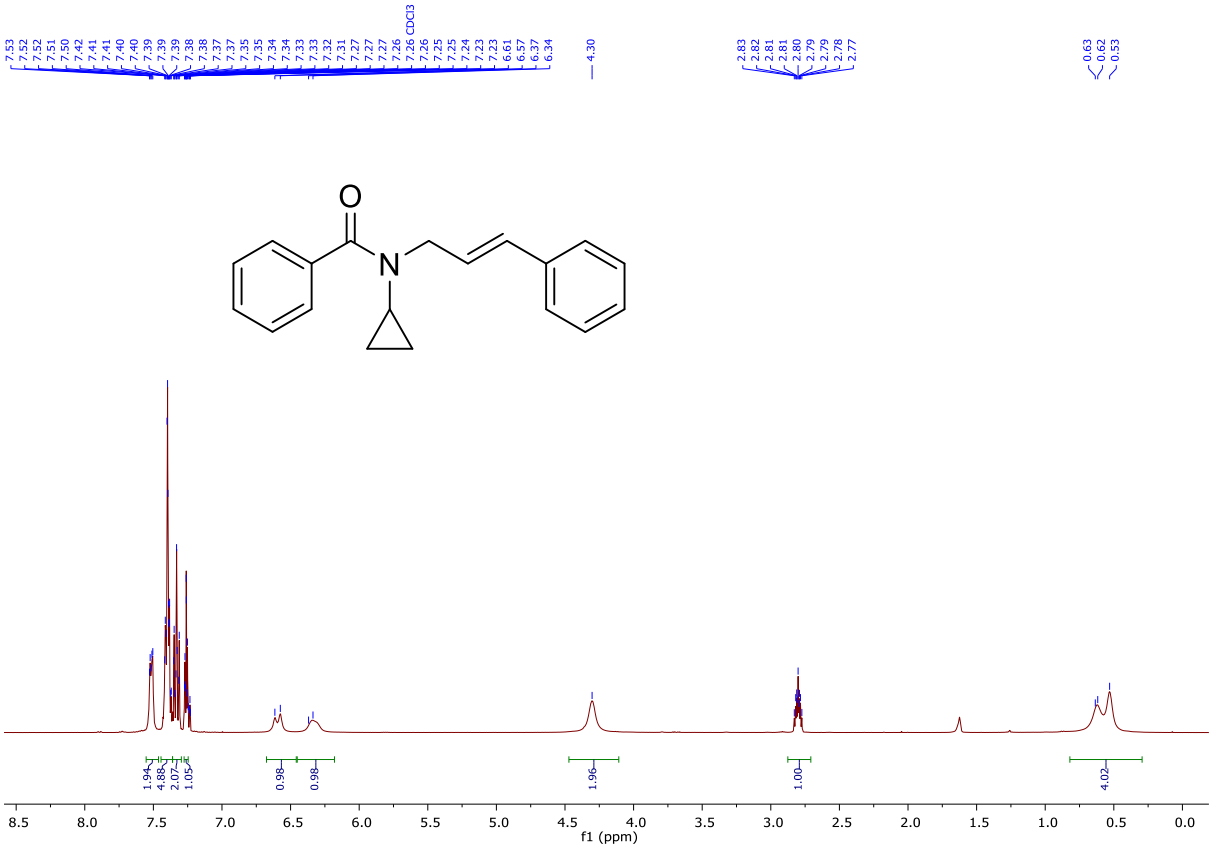


^{13}C-NMR (101 MHz, $CDCl_3$)

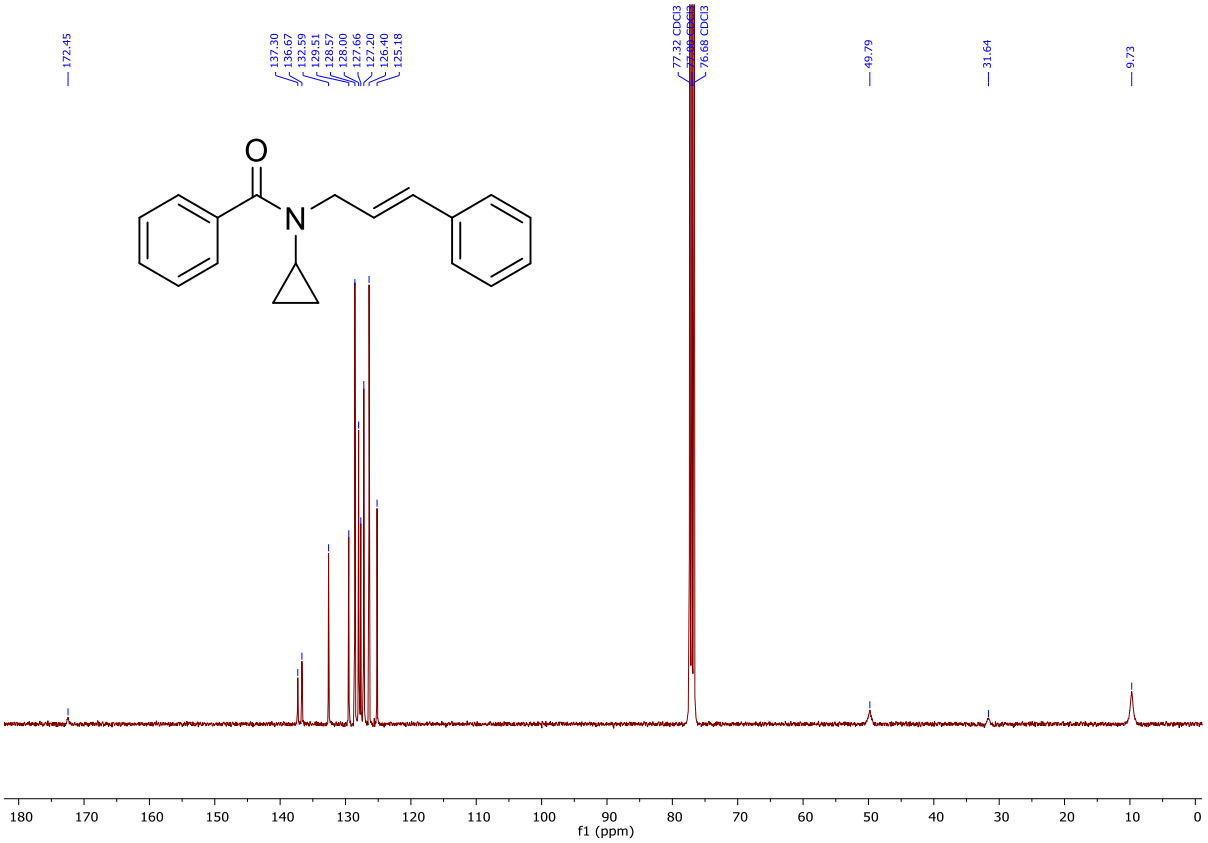


***N*-Cinnamyl-*N*-cyclopropylbenzamide (17)**

^{1}H-NMR (400 MHz, $CDCl_3$)

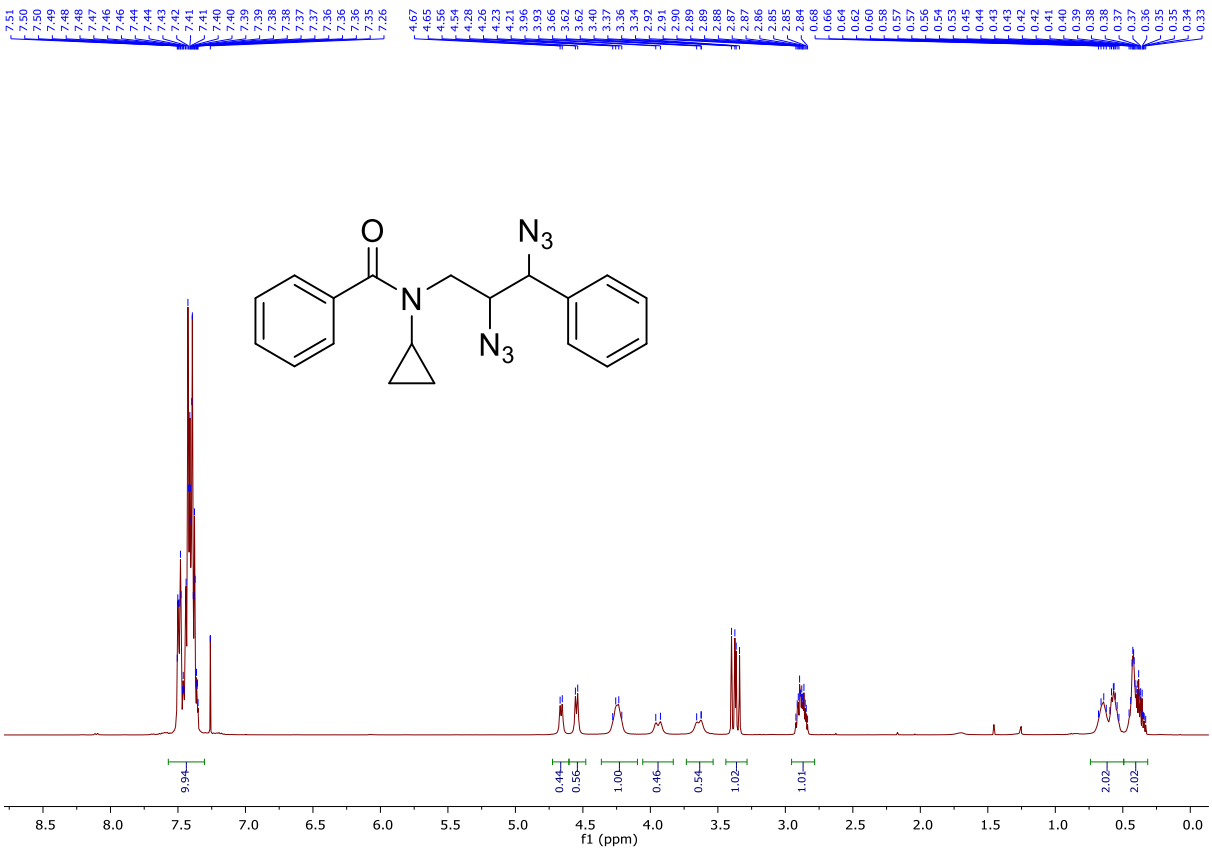


^{13}C-NMR (101 MHz, $CDCl_3$)

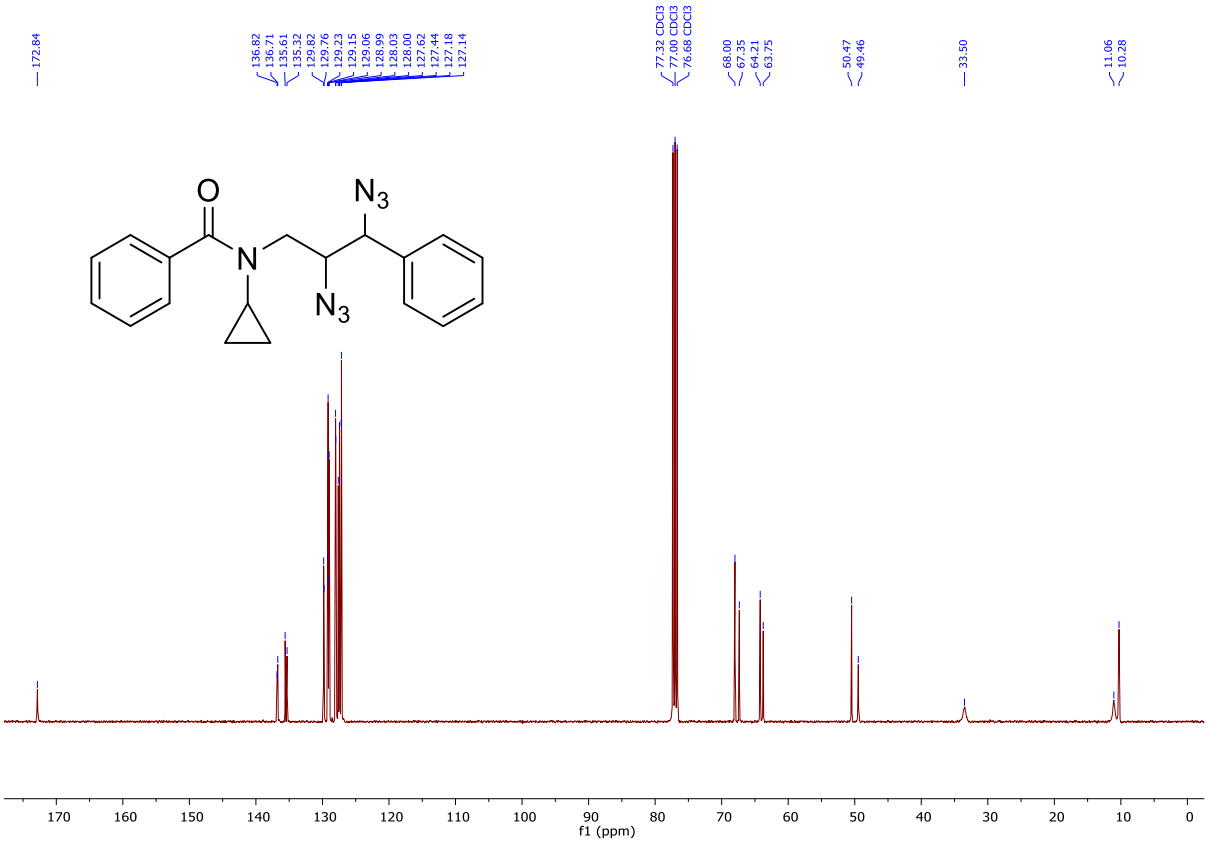


N-Cyclopropyl-N-(2,3-diazido-3-phenylpropyl)benzamide (18)

^{1}H-NMR (400 MHz, $CDCl_3$)

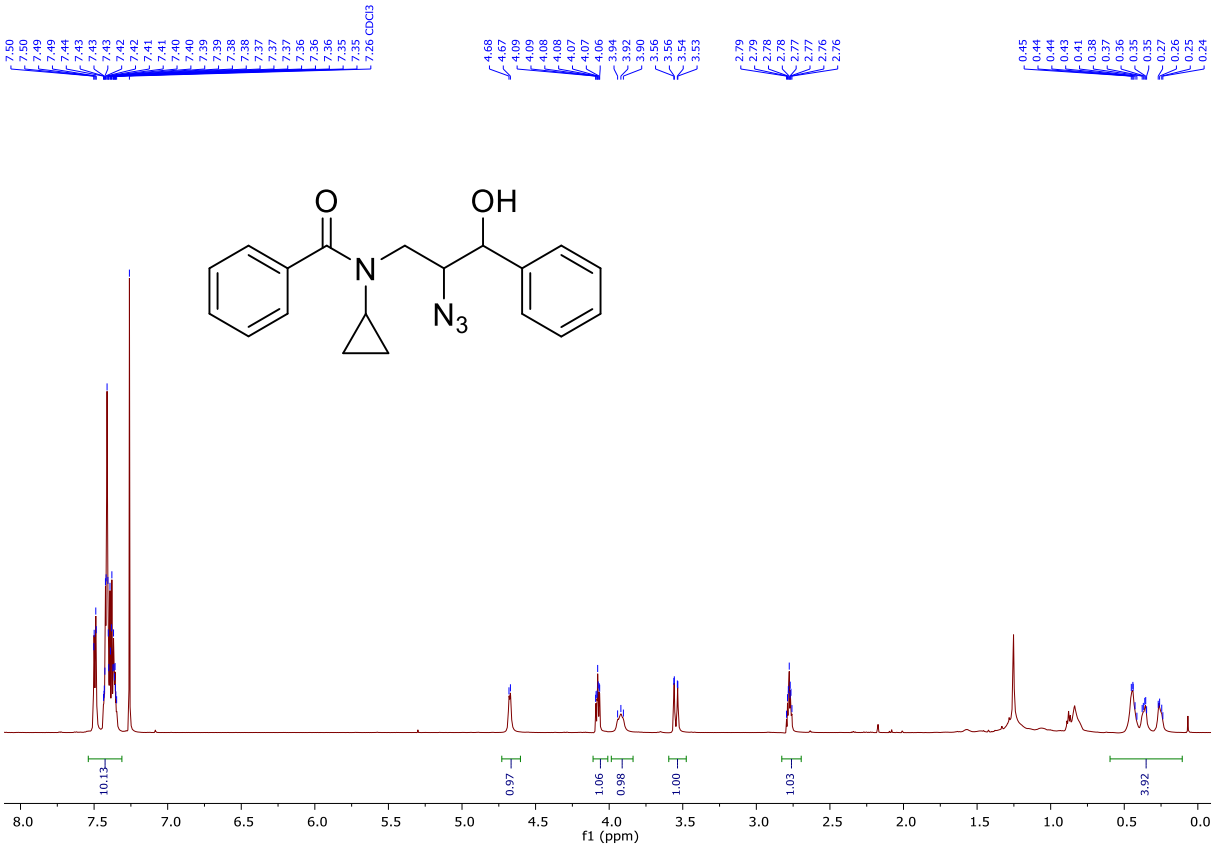


^{13}C-NMR (101 MHz, $CDCl_3$)

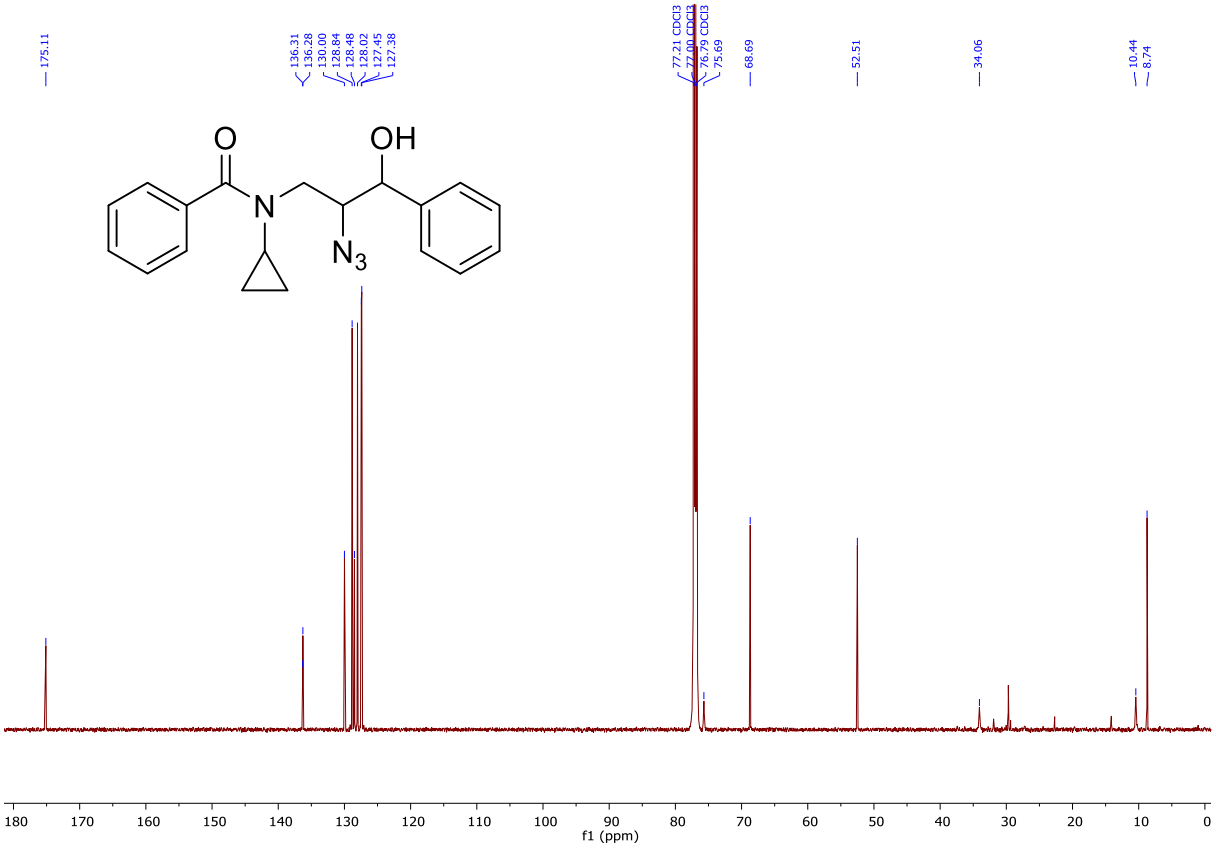


***N*-(2-azido-3-hydroxy-3-phenylpropyl)-*N*-cyclopropylbenzamide (19)**

^{1}H-NMR (600 MHz, $CDCl_3$)

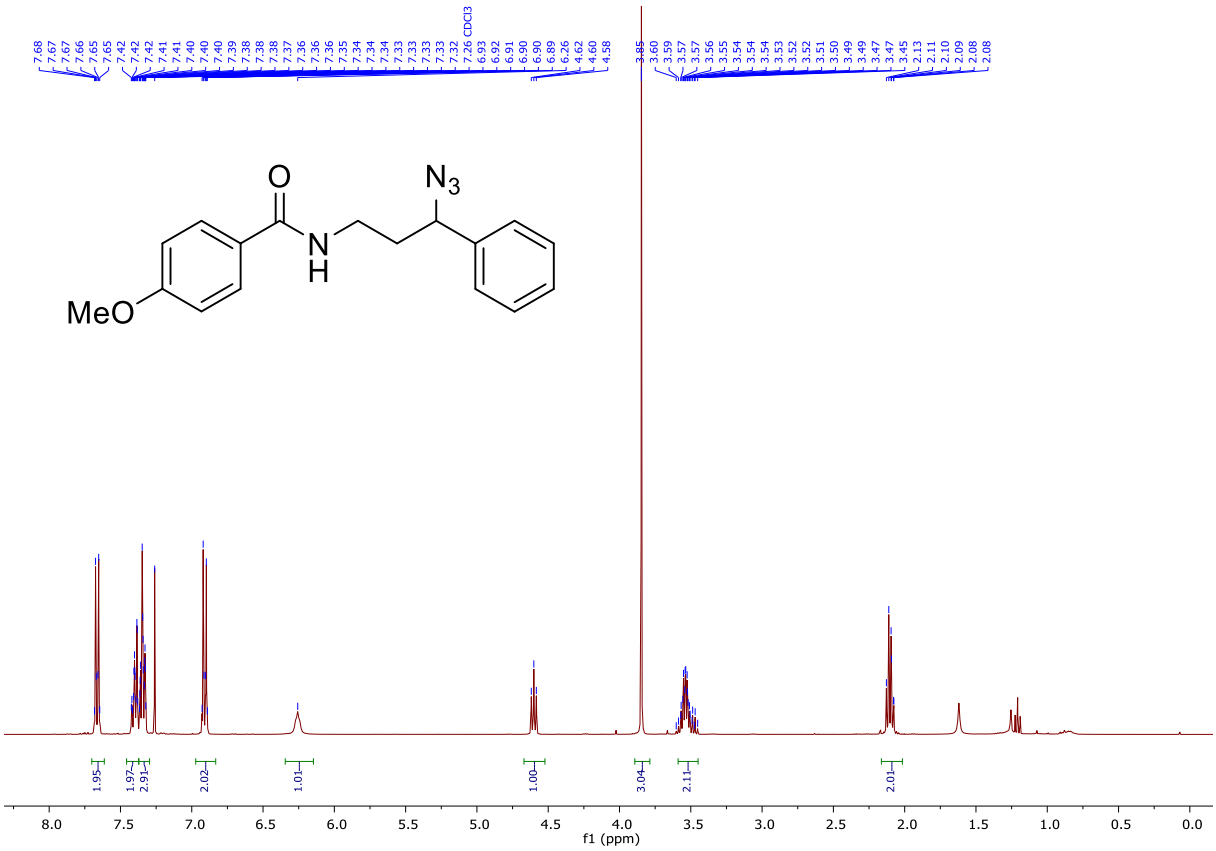


^{13}C-NMR (151 MHz, $CDCl_3$)

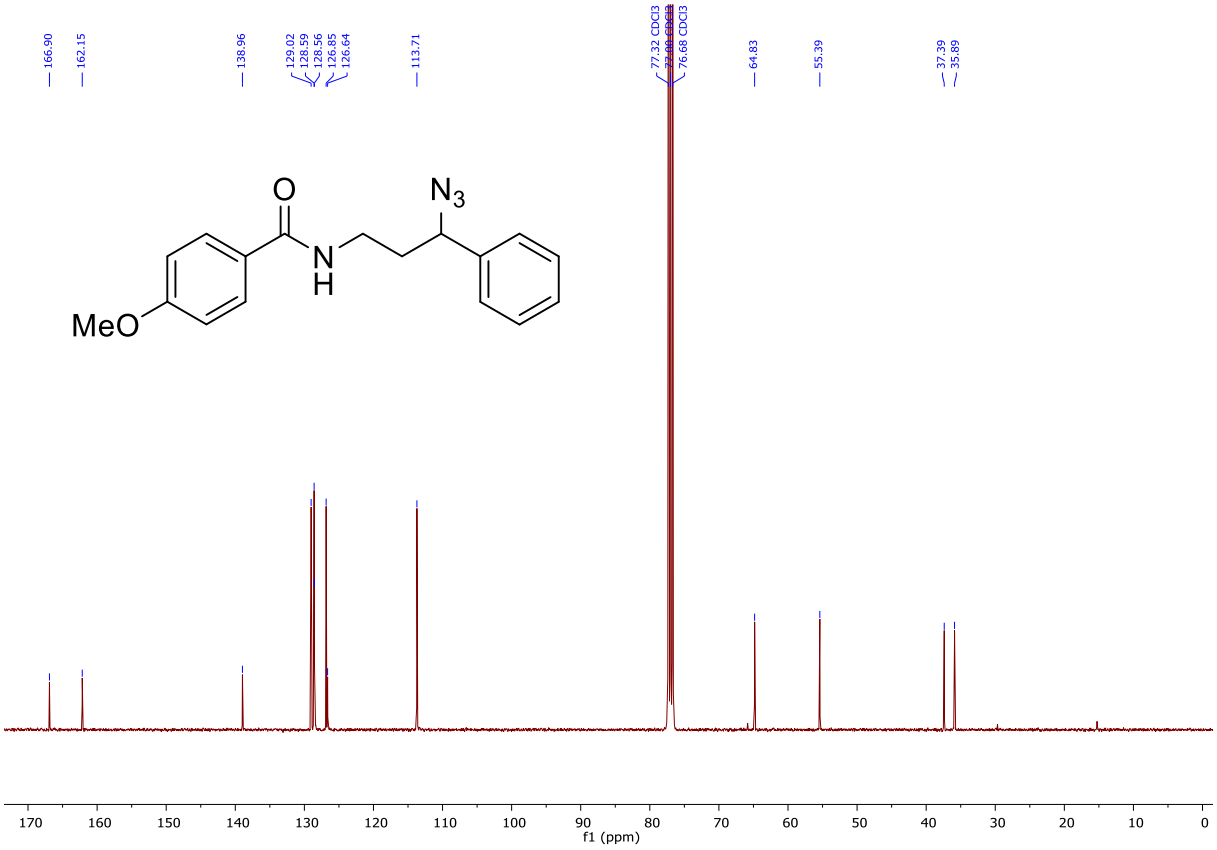


***N*-(3-azido-3-phenylpropyl)-4-methoxybenzamide (21)**

^{1}H-NMR (600 MHz, $CDCl_3$)

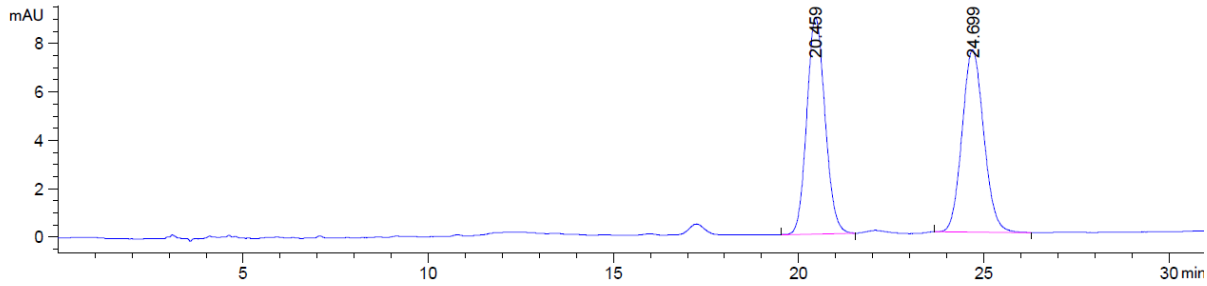


^{13}C-NMR (151 MHz, $CDCl_3$)



HPLC

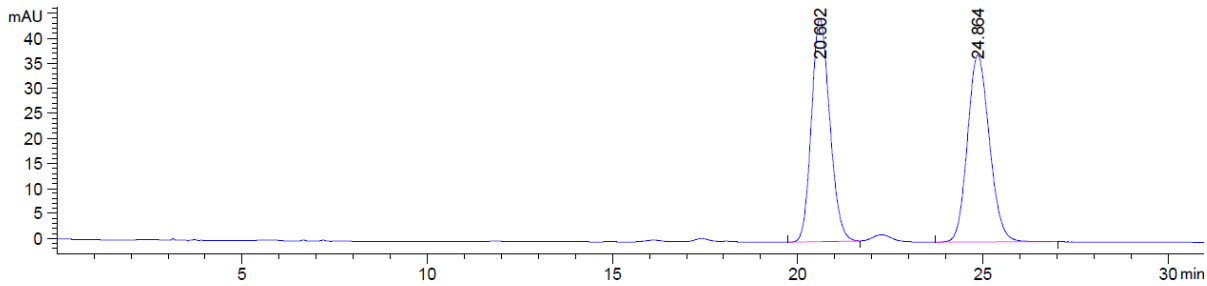
Racemic



Signal 5: DAD1 E, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.459	BB	0.5313	306.83521	8.96500	49.9731
2	24.699	BB	0.6316	307.16583	7.53440	50.0269

With CN-BOX

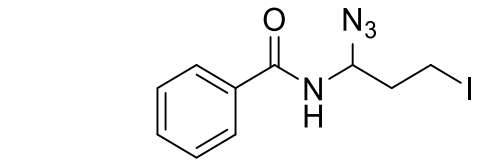


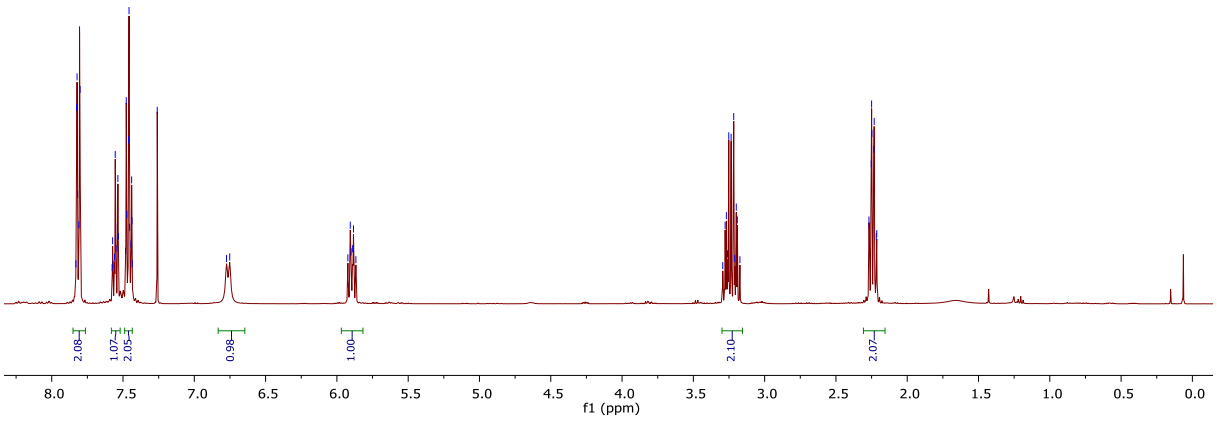
Signal 5: DAD1 E, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.602	BB	0.5300	1527.54224	44.55735	49.8299
2	24.864	BB	0.6410	1537.97205	37.30072	50.1701

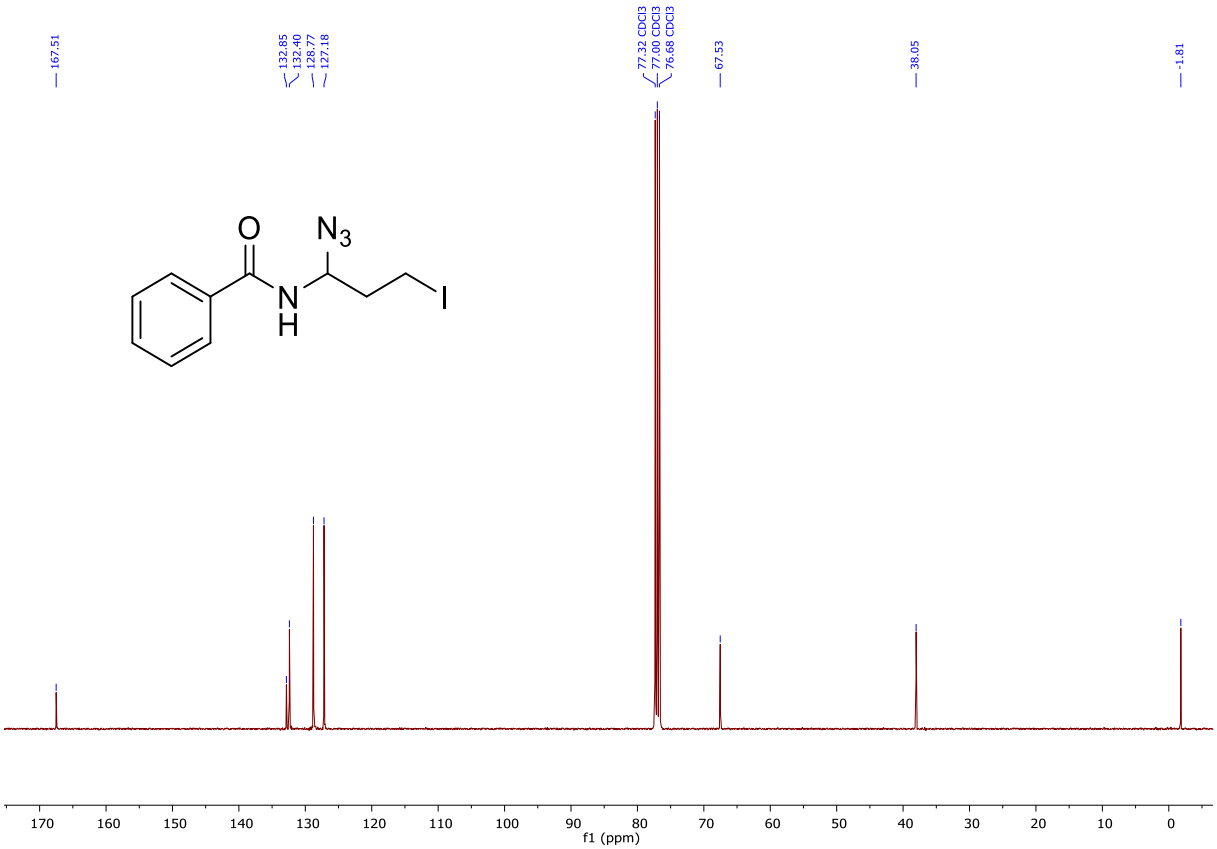
_N_-(1-Azido-3-iodopropyl)benzamide (22)

^{1}H-NMR (400 MHz, $CDCl_3$)



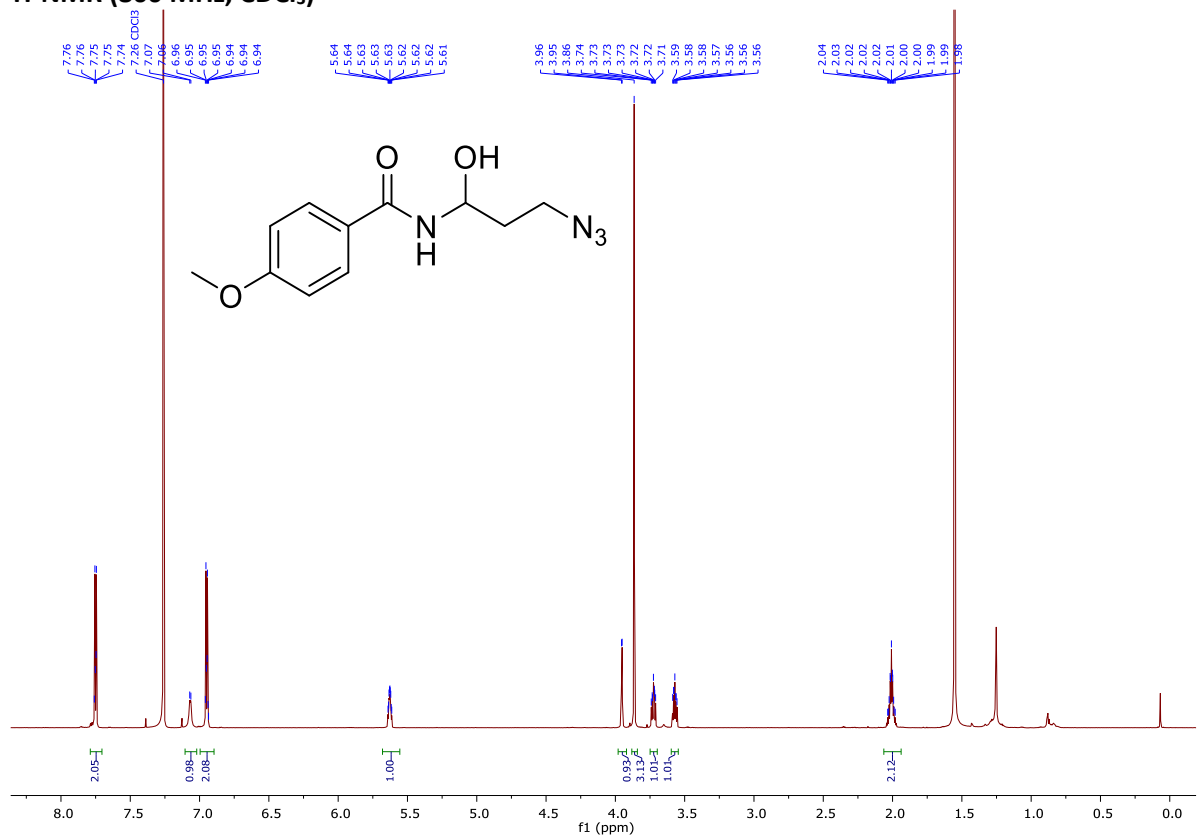


^{13}C-NMR (101 MHz, $CDCl_3$)

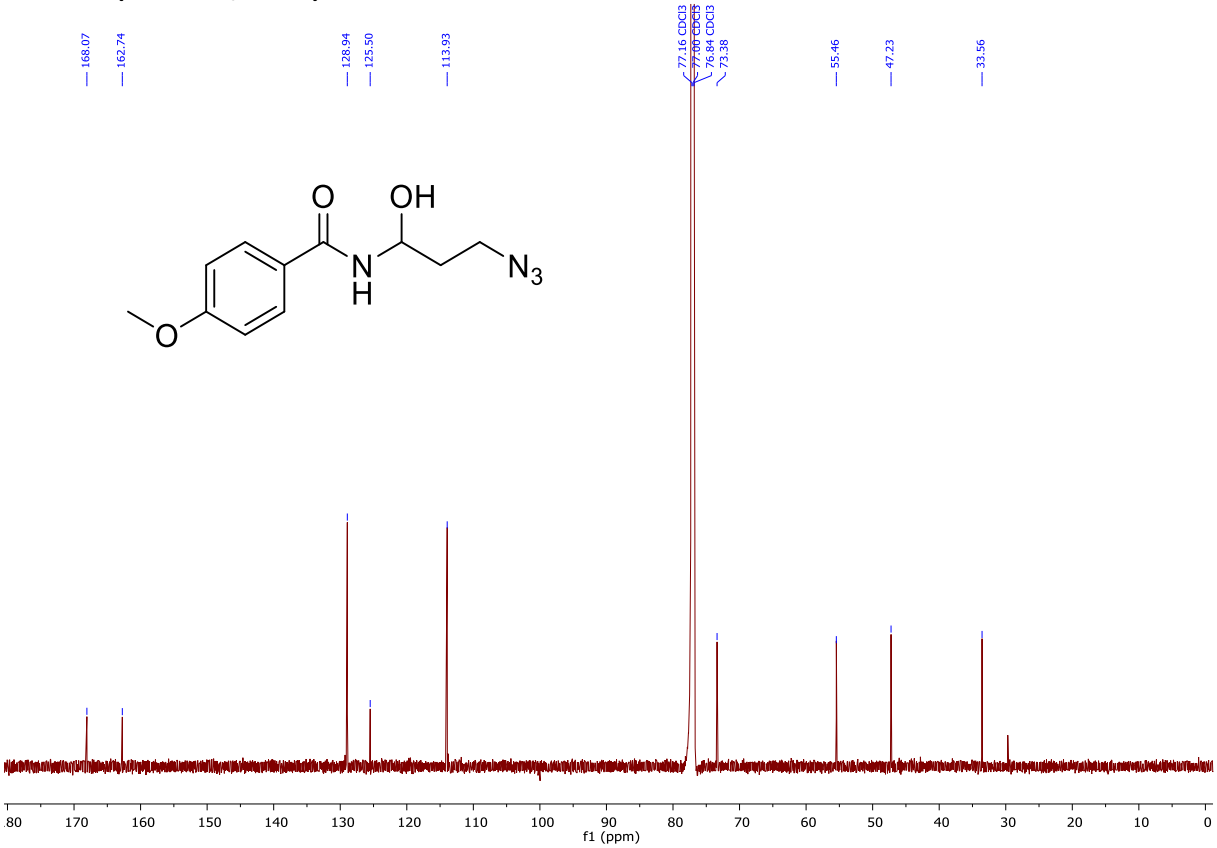


***N*-(3-Azido-1-hydroxypropyl)-4-methoxybenzamide (24)**

^{1}H-NMR (800 MHz, $CDCl_3$)

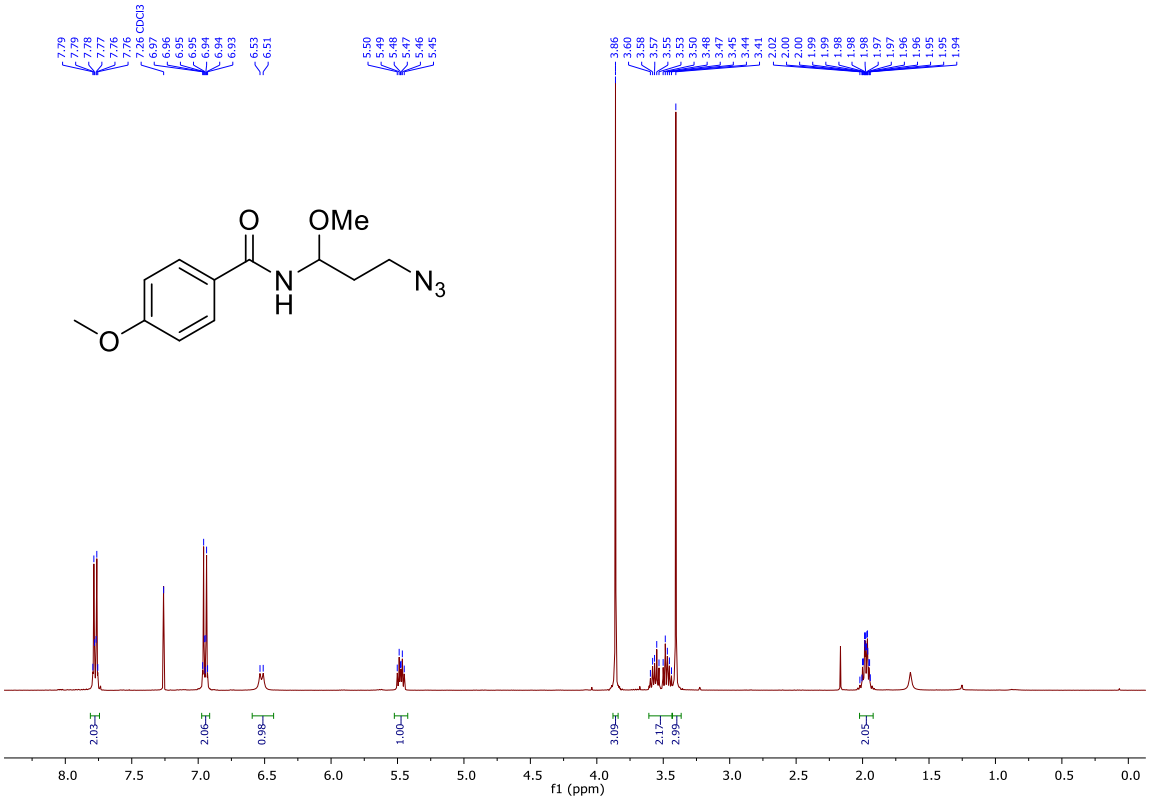


^{13}C-NMR (201 MHz, $CDCl_3$)

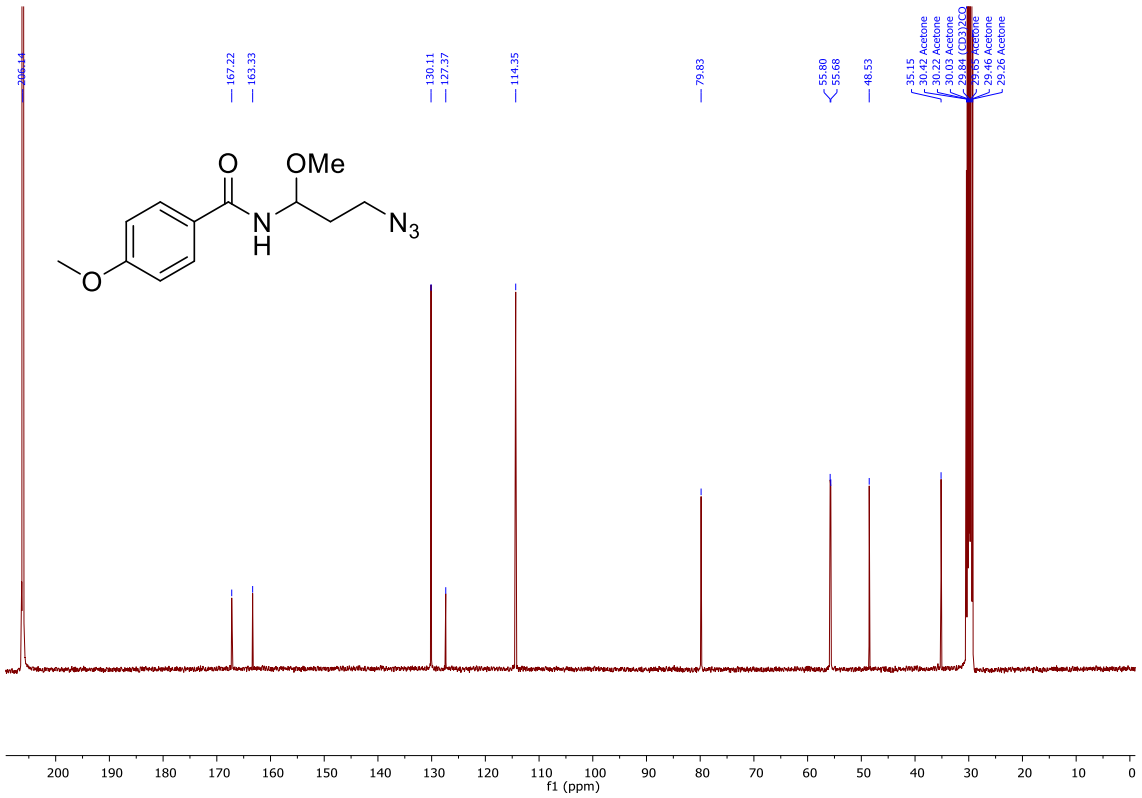


***N*-(3-Azido-1-methoxypropyl)-4-methoxybenzamide (25)**

^{1}H-NMR (400 MHz, $CDCl_3$)

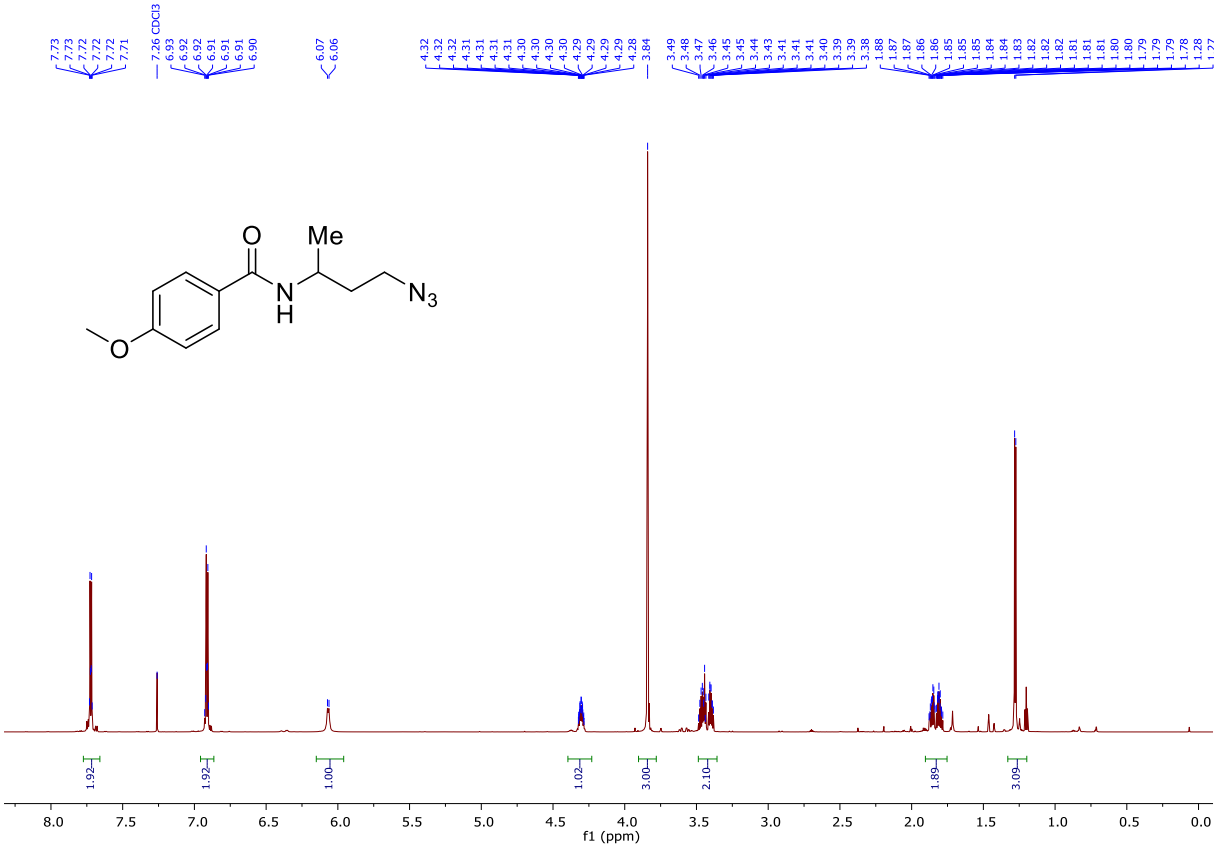


^{13}C-NMR (101 MHz, Acetone-d_6)



***N*-(4-azidobutan-2-yl)-4-methoxybenzamide (26)**

^{1}H-NMR (800 MHz, $CDCl_3$)



^{13}C-NMR (201 MHz, $CDCl_3$)