Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

New Gold-Catalysed Azidation of Allenes

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General experimental details:

All reagents were purchased from commercial sources and used without further purification, unless noted otherwise. Solvents were dried using nitrogen atmosphere and used fresh every day for reaction. Deuterated solvents were acquired from Apollo Scientific Limited and stored over molecular sieves. All the preparative working procedures were carried out under absence of moisture and air under nitrogen atmosphere. Glassware, standard Schlenk tubes, and Schlenk tubes from Carouse 12 Plus Reaction Station from Radleys were flame-dried and flushed with nitrogen. Thin layer chromatography was performed on Aluminium oxide TLC-Cards with Fluorescent indicator 254 nm over aluminium oxide matrix from Sigma-Aldrich, and on Silica TLC-plates (60 F_{254} Merk), and components were visualize by illumination with UV light (λ = 254 nm), or by staining with potassium permanganate solution. Purification of allenes was performed by flash column chromatography using silica gel from Macherey-Nagel GmbH & Co. KG (particle size of 40 to 63 μm) as stationary phase. Purification of products was performed by flash column chromatography using Aluminum Oxide activated, basic, Brockmann I of pore size 58 Å, pH 9.5 ± 0.5 in H_2O. Accurate weights were obtained with a Denver Instrument SI-234. Reactions under microwave irradiation were carried out in a Biotage Initiator$^+$ Microwave system. ^{1}H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ on a Bruker Avance III 500 MHz NMR spectrometer, fitted with a 5mm broadband observed, BBFO^{plus} Z-gradient SmartProbe^{TM} probe or using a Bruker Avance III nanobay 400 MHz NMR spectrometer, fitted with a 5mm broadband observe BBFO^{plus} Z-gradient probe. Calibration was made using the deuterated solvent (δH = 7.26 ppm and δC = 77.36 ppm).[1] Chemical shifts (δ) are given in parts per million (ppm) and coupling constants values (J) are given in Hertz (Hz). Abbreviations for multiplicities are as follows: (s) singlet, (d) doublet, (dd) doublet doublet, (t) triplet, (q) quartet, (m) multiplet. ^{13}C NMR was recorded using broad-band proton decoupling. Low resolution mass spectra were recorded using electrospray (ESI) technique in the positive and negative ion mode with a Shimadzu LCMS spectrometer. Phenomenex pre-column filter (Security Guard, ODS C18, 4 x 3 mm i.d.) was used to prevent rapid deterioration of the pre-column. Elution was carried out using a mobile phase comprising methanol, at a flow rate of 0.2 mL min-1. All solvents were HPLC grade. High resolution mass spectra were obtained

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[1] H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997**,** ***62****,* 7512-7515.

from the EPSRC Mass Spectrometry Service at the University of Swansea by FTMS technique. Melting points were measured with a BÜCHI Melting Point B-545. Infrared spectra were acquired using a Perkin Elmer System 400 FT-IR spectrophotometer. Solid samples were run as thin films of their solution in DCM. Liquid samples were run neat.

Synthesis of starting materials:

Allenes **1a**, **1h**, are commercially available (Sigma-Aldrich) and were used without further purification. Allenes **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, and **1n** were prepared from the corresponding alkynes by Crabbé reaction[2] using the microwave version.[3] Allene **1i** was performed by a modified Crabbé reaction.[4] Allenes **1j**, **1k**, **1l**, and **1m**, were synthesised by a modified Crabbé homologation under microwave conditions.[5] Allenes **1o** and **1p** were synthesised by a modified cadmium iodide allenylation of terminal alkynes with aldehydes.[6]

Crabbé reaction under microwave conditions: propargyl-derivative (1.0 Eq.), HCHO (2.5 Eq.), CuBr (0.3 Eq.), $i\mathrm{Pr_2NH}$ (2 Eq.), in dioxane heated under microwave at 150 ^{o}C for 10 min. Straight purification by column chromatography (silica) gave the corresponding allene derivatives in yields: **(1b)** 49%, (**1c**) 45%, **(1d)** 43%, **(1e)** 53%, **(1f)** 89%, **(1g)** 88%, **(1n)** 35%.

Synthesis of **1i**: 1-Decyne (1.0 Eq.), benzaldehyde (1.8 Eq.), Morpholine (1.4 Eq.), ZnI_2 (0.8 Eq.), in Toluene, reflux at 130ºC during 7.2 h. The solution was filtered through Celite washing with Et_2O and purification by silica column chromatography using hexane as eluent, gave the corresponding allene **1i** in 50% yield.

Crabbé homologation for 1,3-disubstituted allenes under microwave conditions: Microwave vial (2-5 ml), 1-Alkyne (1.0 Eq.), aldehyde (1.5 Eq.), Cy_2NH (1.51 Eq.), CuI (0.1 Eq.) in Toluene at 200ºC, following conversion reaction by TLC. Straight purification by silica column chromatography gave the corresponding 1,3-disubstituted allenes in **(1j)** 28%, **(1k)** 63%, **(1l)** 39%, **(1m)** 77% yield.

Cadmium iodide allenylation of terminal alkynes with aldehydes: CdI_2 (0.8 Eq.) was added in a previously dried-vacuum schlenk flask under inert atmosphere in a globe

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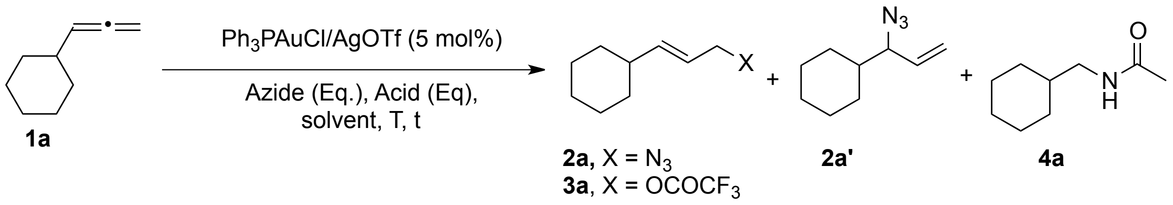
[2] P. Crabbé, B. Nassim and M.-T. Robert-Lopes, *Org. Synth. Coll.*, 1990, **7**, 276; 1985, **63**, 203.
[3] H. Nakamura, T. Sugiishi and Y. Tanaka, *Tetrahedron Lett.*, 2008, **49**, 7230-7233.
[4] J. Kuang and S. Ma, *J. Am. Chem. Soc.* 2010, **132**, 1786-1787.
[5] S. Kitagaki, M. Komizu and C. Mukai, *Synlett* 2011, **8**, 1129-1132.
[6] X. Tang, C. Zhu, T. Cao, J. Kuang, W. Lin, S. Ni, J. Zhang and S. Ma, *Nat. Comm.*, 2013, **4**:2450.

box. Then the corresponding alkyne (1 Eq.), aldehyde (1.8 Eq.), and pyrrolidine (1.4 Eq.) were dissolved in dry Toluene (0.24 M) at 130 ºC during 4 h. Straight purification by silica column chromatography gave the corresponding 1,3-disubstituted allenes in **(1o)** 30%, **(1p)** 29% yield.

All these allenes were prepared according to described procedures and their NMR spectra were fully accordance with the described products.

Table 1S. Optimisation of conditions: different azides, acids and solvents.



Entry	Azide (Eq.)	Acid (Eq.)	Solvent	T (°C)	time (h)	Conversion (%)
1	NaN_3 (1.5)	H_2O (2)	THF	30	20	n.r.
2	NaN_3 (1.5)	HCl (2)	THF	30	21	n.r.
3	NaN_3 (3)	H_2SO_4 (3)	DCM	30	48	11, **2a** 9, **4a**
4	NaN_3 (3)	AcOH (3)	THF	30	48	n.r.
5	NaN_3 (3)	HCl (3)	DCM	30	21	n.r.
6	$TMSN_3$ (1.5)	AcOH (1.5)	DCM	30	19	7, **2a**
7	$TMSN_3$ (3)	H_2O (3)	THF	30	20	n.r.
8	$TMSN_3$ (3)	H_2O (3)	DCM	30	22	20, **2a:2a':3a':4a**, 5.9:1:3:5.3
9	$TMSN_3$ (3)	H_2SO_4 (3)	DCM	30	18	50, **2a** (Decomposition of **1a** and **2a** at 48 h)[a]
10	$TMSN_3$ (3)	H_2SO_4 (3)/H_2O (5)	DCM	30	18	38, **2a:2a':4**, 1.7:1:1.2[b]
11	$TMSN_3$ (3)	CF_3COOH (3)	DCM	30	18	100, **2a:2a':3a:4a**, 5:1:4:4
12	$TMSN_3$ (3)	CF_3SO_3H (3)	DCM	30	18	Decomposition

[a] Similar results were obtained with the phosphite-gold complex. [b] Reaction carried out with $(PhO)_3PAuCl$ as catalysts.

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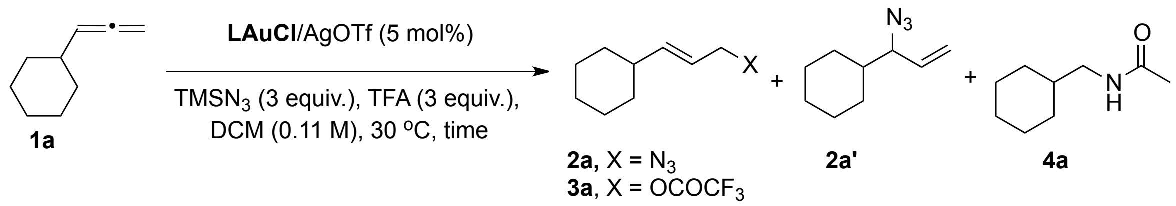
Table 2S. Optimisation of catalyst



Entry	Gold complex[a]	Time (h)	Conversion (%)	Ratio **2a:2a':3a:4a**
1	NHC-1	48	20	1:0:1.3:0
2	NHC-2	48	20	1:0:1.3:0
3	NHC-3	48	10	1:0:0:0
4	Cat-Au SbF_6[b]	48	65	1.3:0:10:1
5	$(PhO)_3PAuCl$	22	100	8.5:1:1:4.5

[a] See Figure 1 for the structure of the gold complexes. [b] Reaction without silver salt added.

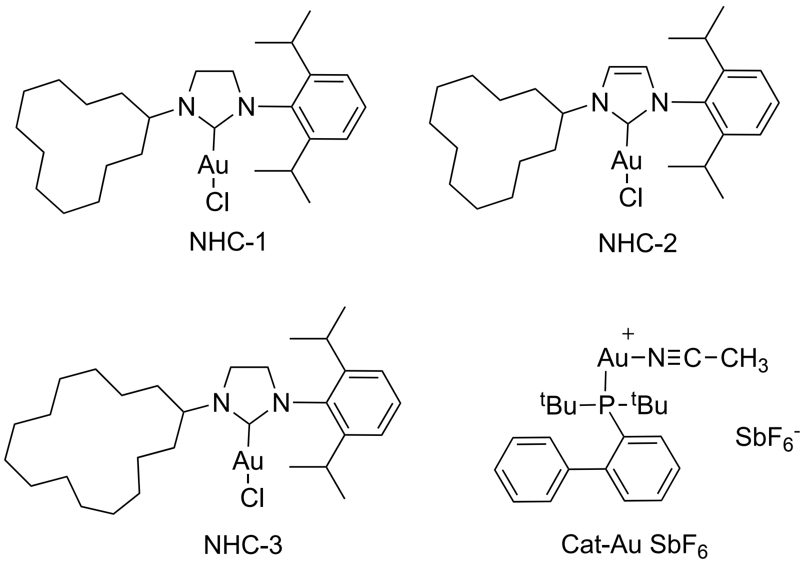


Figure 1. Gold(I) complexes screened in the hydroazidation of allenes.

Gold complexes NHC-1, NHC-2, and NHC-3 were synthesised in Prof. Hashmi's laboratories following their reported procedures.[7]

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[7] (a) A. S. K. Hashmi, T. Hengst, C. Lothschutz and F. Rominger, *Adv. Synth. Catal.* 2010, **352**, 1315-1337; (b) A. S. K. Hashmi, C. Lothschutz, C. Bohling, T. Hengst, C. Hubbert and F. Rominger, *Adv. Synth. Catal.* 2010, **352**, 3001-3012.

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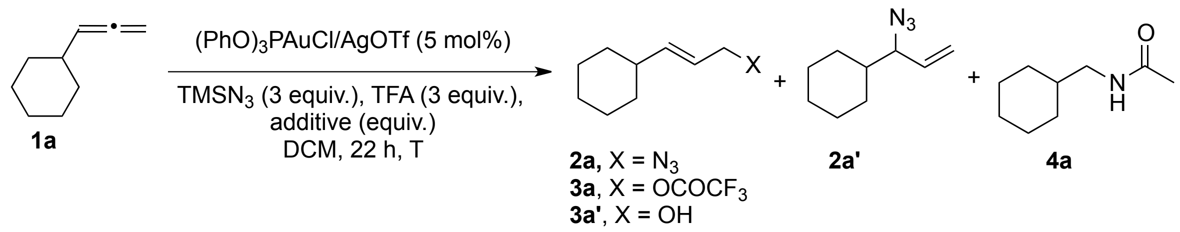
Table 3S. Final optimisation: concentration, temperature, purification.



Entry	Additive (Eq.)	Concentration (M)	T (°C)	Isolated Yield (Ratio 2a:2a')	Isolated Yield (Ratio 4a)	(Ratio 3a)	(Ratio 3a')	Method of Purification
1[a]	¬	0.11	30	(6.6:1)	¬	(0.9)	¬	Silica
2[a]	¬	0.27	30	(2.1:1)	(1.04)	(0.6)	¬	Silica
3	H_2O (3)	0.41	30	37% (3.2:1)	13% (2.1)	(0.25)	(0.09)	Silica
4	H_2O (5)	0.41	30	41% (3.4:1)	15% (2.2)	(0.24)	(0.17)	Silica
5[b]	H_2O (5)	0.41	40	46% (3.7:1)	14% (2.0)	(0.33)	(0.32)	Basic Alumina
6	CH_3COOH (5)	0.41	r.t.	46% (3.8:1)	8% (2.0)	(0.22)	(0.25)	Basic Alumina
7	NH_4OH (5)	0.41	r.t.	40% (4.0:1)	12% (2.4)	(0.38)	(0.22)	Basic Alumina
8	MeOH (5)	0.41	r.t.	43% (4.1:1)	12% (1.44)	(0.25)	(0.15)	Basic Alumina
9	H_2O (5)	0.41	0	61% (0.75:1)	9% (0.38)	(0.05)	(0.01)	Basic Alumina
10	**H_2O (5)**	**0.41**	**r.t.**	**59% (3.7:1)**	**15% (2.1)**	**(0.17)**	**(0.22)**	**Basic Alumina**

[a] After 22h, conversion ≈ 25%. [b] Carried out under microwave heating during 4 hours.

Reaction in the absence of acid, gave low conversion (≈ 30%) to the allyl azides **2a**:**2a'**, as a 7.3:1 mixture. Reaction without the gold complex and/or the silver salt, reaction in the presence of gold complex and TfOH (no silver), and reaction in the absence of gold and silver but in the presence of 5 mol% TfOH gave no conversion.

We have evidence of formation of vinyl triflates and ketones in the reaction of allenes and stoichiometric amounts of TfOH.[8] See for example:

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[8] L. Cooper, M. P. Muñoz, *unpublished results*. For electrophilic addition to allenes, see: W. Smadja, *Chem. Rev.*, 1983, **83**, 263-320.

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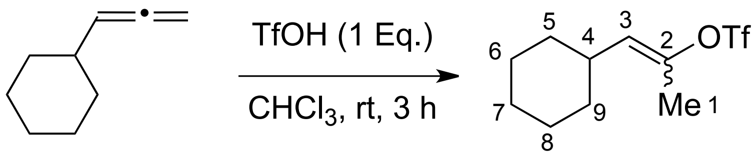

1a **8a**

100 conversion
E/Z, 2:1

Cyclohexylallene (100 mg, 0.818 mmol) was dissolved in dry chloroform (2 mL) and added to a schlenk. TfOH (71 μl, 0.80 mmol) was added slowly. The reaction mixture was stirred for 3 hours at room temperature. Work up with DCM and Water was carried out. A short filtration was carried out with hexane: diethyl ether (20:1). The solvent was evaporated and the mixture was tentatively characterised without further purification by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and 2D NMR experiments HSQC and NOESY. All the attempts to purify the mixture by silica column chromatography gave decomposition so we couldn't obtain a pure sample for HRMS.

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 5.38 (d, J = 9.94 Hz, 1H, H3, major), 5.07 (d, J = 9.94 Hz, 1H, H3, minor), 2.39(m, 1H, minor), 2.07 (m, 1H, major), 2.04 (s, 3H, H1, major), 2.03 (s, 3H, H1, minor), 1.75 - 1.60 (m, 6H), 1.30 - 1.00 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 207 (Cq, C2), 145.53 (CF_3, major), 143.47 (CF_3, minor), 127.59 (CH, C3, major), 127.45 (CH, C3, minor), 36.58 (CH, C4, major), 35.51 (CH, C4, minor), 32.75 (CH_2, x 2, major), 32.54 (CH_2, x 2, minor), 25,91 (CH_2), 25.81 (CH_2 x 2), 25.67 (CH_2 x 2), 25.59 (CH_2), 19.95 (CH_3, C1, minor), 16.33 (CH_3, C1, major). ^{19}F NMR (470 MHz, $CDCl_3$, ppm) δ = -73.91 (OTf, major), - 74.98 (OTf, minor).

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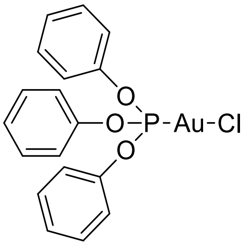
Synthesis of chloro (triphenylphosphite) gold(I): [9,10]

The synthesis was undertaken according to the procedure described by Toste and co-workers. Under nitrogen atmosphere, $AuCl_3$ (125 mg, 0.41 mmol, 1.0 Eq.) was dissolved in 2.5 ml of absolute methanol. The solution was stirred for a few minutes at 0 ºC and under exclusion of light. Me_2S, (76 µl, 1.03 mmol, 2.5 Eq.) was added dropwise. The decolouration of the solution and formation of a white precipitation could be observed immediately. The reaction was stirred for 1 hour and then the stirring was stopped and the solid left to settle. The yellow solution was extracted with a syringe and the solid was washed with MeOH (2.0 ml), Et_2O (2.0 ml), and with petroleum ether (2.0 ml). The solvent was removed by syringe in all cases and after the last washed, the vial was dried by vacuum for a few minutes. Dry chloroform (2.5 ml) was added to the solid and stirred in the dark at 0ºC for a few minutes. Then, a solution of $(PhO)_3P$ (119 µl, 0.45 mmol, 1.1 Eq) in hexane (3.7 ml) was added dropwise whereby the white solid dissolved. The solution was stirred for 1h at room temperature. After complete reaction the solvent was removed in vacuum, triturated with hexane and filtered by vacuum. 154 mg, 0.28 mmol of a beige powder was obtained (69%).

Chloro (triphenylphospite) gold(I)



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.37 – 7.32 (m, 2H; H_{Ar}), 7.25 – 7.20 (m, 1H; H_{Ar}), 7.17 – 7.13 (m, 2H; H_{Ar}). ^{31}P NMR (202 MHz, $CDCl_3$, 25 °C) δ = 109.96.

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[9] P. Mauleon, R. M.Zeldin, A. Z. Gonzalez and F. D. Toste, *J. Am. Chem. Soc.*, 2009, **131**, 6348-6349.
[10] L.-P. Liu, B. Xu, M. S. Mashuta and G. B. Hammond, *J. Am.Chem. Soc.*, 2008, **130**, 17642-17643.

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General procedure for gold-catalysed hydroazidation of allenes under best reaction conditions:

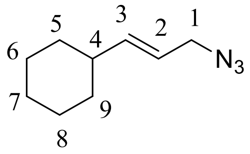
$(PhO)_3PAuCl$, (0.05 Eq.) and silver triflate (0.05 Eq) were added into a previously dried-vacuum schlenk flask under N_2. The solids were dissolved in dry dichloromethane (0.41 M) and stirred for a few minutes at 0 ºC. Then, the corresponding allene (1 Eq.) was added dropwise neat or dissolved in DCM at 0 ºC and under stirring. $TMSN_3$ (3 Eq.), distilled water (5 Eq.), and trifluoroacetic acid (3 Eq.) were then added dropwise at 0 ºC. The mixture was then warmed up and stirred at room temperature until complete conversion, followed by TLC. The crude was filtered through Celite, and washed with dichloromethane. The solvent was removed under vacuum, and the product was purified by column chromatography over basic alumina using Hexane / Et_2O or EtOAc as eluent.
Yields were lowered in some cases due to purification issues.

All the products obtained were air stable and in solution, but we recommend to keep them in the fridge or freezer and in the dark.

Characterisation of products:

Products obtained from the gold-catalysed hydroazidation of different allenes using the procedure described before.

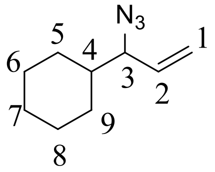
Allyl azide **2a**



From allene **1a** (119 µl, 0.82 mmol), $(PhO)_3PAuCl$ (22 mg, 0.04 mmol), silver triflate (10 mg, 0.04 mmol), $TMSN_3$ (323 µl, 2.45 mmol), distilled water (74 µl, 4.09 mmol), trifluoroacetic acid (196 µl, 2.45 mmol) and 2.0 ml dry DCM. Obtained after column chromatography, Hex/EtOAc, 90:1 then 2:1: **2a:2a'** (3.7:1), 80 mg, 0.48 mmol, 59% (pale yellow oil), and **4a**, 19 mg, 0.12 mmol, 15% (yellow oil).
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 5.73 - 5.68 (m, 1H; H-3), 5.44 (dtd, J = 15.4, 6.7, 1.3 Hz, 1H; H-2), 3.69 (d, J = 6.7 Hz, 2H; H-1), 2.05 - 1.97 (m, 1H; H-4), 1.77 - 1.63 (m, 5H; H-5 to H-9), 1.32 - 0.94 (m, 5H; H-5 to H-9). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)

δ = 143.40 (CH; C-3), 120.45 (CH; C-2), 53.29 (CH$_2$; C-1), 40.79 (CH; C-4), 33.14 (2x CH$_2$; C-5 and C-9), 26.41 (CH$_2$; C-7), 26.25 (CH$_2$; C-6 and C-8).

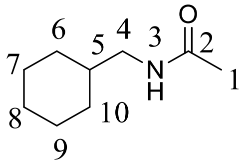
Allyl azide **2a’**



^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS) δ = 5.76 (m, 1H; H-2), 5.31- 5.21 (m, 2H; H-1), 3.60 (t, J = 7.7 Hz, 1H; H-3), 1.69 - 1.78 (m, 5H; H-5 to H-9), 1.38 (m, 1H; H-4), 0.83-1.30 (m, 5H; H-5 to H-9). ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C) δ = 134.80 (CH; C-2), 119.24 (CH$_2$; C-1), 71.34 (CH; C-3), 42.01 (CH; C-4), 29.74 (CH$_2$), 29.61 (CH$_2$), 26.65 (CH$_2$). The other carbon signals of the cyclohexyl ring overlapped with signals from compound **2a**.

2a and **2a’**: IR (Film, cm^{-1}): $\tilde{\nu}$ = 740, 802, 971, 1260, 1450, 1646, 2097, 2853, 2924, 3434. MS (ESI$^+$ in MeOH): m/z (%): 138.0 [M-N$_2$+H]$^+$. HRMS (FTMS + APCI) Calc. for $C_9H_{16}N_3$ [M+H]$^+$: 166.1339. Found: 166.1336. Calc. for $C_9H_{16}N_1$ [M-N$_2$+H]$^+$: 138.1277. Found: 138.1276.

Amide **4a**[11]



^{1}H NMR (500 MHz, CDCl3, 25 °C, TMS) δ = 5.50 (s$_{\text{broad}}$, 1H; NH-3), 3.08 (t, J = 6.4 Hz, 2H; H-4), 1.98 (s, 3H, H-1), 1.78 – 1.62 (m, 5H; H-6 to H-10), 1.50 – 1.38 (m, 1H; H-5), 1.29 – 1.09 (m, 3H; H-5 to H-10), 0.99 – 0.83 (m, 2H; H-5 to H-10). ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C) δ = 170.38 (C$_q$; C-2), 46.21 (CH$_2$; C-4), 38.22 (CH; C-5), 31.16 (CH$_2$; C-6 to C-10), 26.72 (CH$_2$; C-6 to C-10), 26.13(CH$_2$; C-6 to C-10), 23.75 (CH$_3$; C-1). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3592, 3583, 3289, 3090, 2922, 2851, 1653, 1560, 1448, 1301, 991. HRMS

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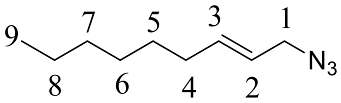
[11] R. Pelagalli, M. Feroci, I. Chiarotto and S. Vecchioa, *Green Chem.*, 2012, **14**, 2251.

(FTMS + APCI in DCM + NH_4OAc) Calc. for $C_9H_{18}O_1N_1$ $[M + H]^+$: 156.1383. Found: 156.1380.

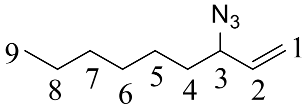
Allyl azide **2b**



From allene **1b** (100 mg, 0.80 mmol), $(PhO)_3PAuCl$ (22 mg, 0.04 mmol), silver triflate (10 mg, 0.04 mmol), $TMSN_3$ (318 µl, 2.42 mmol), distilled water (73 µl, 4.02 mmol), trifluoroacetic acid (193 µl, 2.42 mmol) and 2.0 ml dry DCM. Obtained after column chromatography, Hex/Et_2O, 60:1 then 2:1: **2b:2b'** (1.9:1), 65 mg, 0.38 mmol, 48% (pale yellow oil) and **4b**, 9 mg, 0.06 mmol, 16% (pale yellow liquid).

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ = 5.79 - 5.72 (m, 1H; H-3), 5.51 (dtt, J = 15.0, 6.7, 1.4 Hz, 1H; H-2), 3.70 (d, J = 6.7 Hz, 2H; H-1), 2.12 - 2.05 (m, 2H; H-4), 1.43 - 1.35 (m, 2H; H-5), 1.35 - 1.23 (m, 6H; H-6 to H-8), 0.88 (t, J = 6.6 Hz, 3H; H-9). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 137.65 (CH; C-3), 123.02 (CH; C-2), 53.25 (CH_2; C-1), 32.58 (CH_2; C-4), 32.01 (CH_2; C-5), 29.37 (CH_2), 29.09 (CH_2), 22.93 (CH_2), 14.41 (CH_3; C-9).

Allyl azide **2b'**

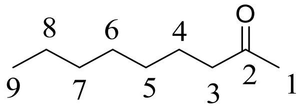


^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ = 5.74 - 5.69 (m, 1H; H-2), 5.28 - 5.24 (m, 2H; H-1), 3.83 - 3.77 (m, 1H; H-3), 1.59 - 1.46 (m, 2H; H-4), 1.44 - 1.38 (m, 2H; H-5), 1.35 - 1.23 (m, 6H; H-6 to H-8), 0.91 - 0.85 (m, 3H; H-9). ^{13}C NMR (126 MHz, $CDCl_{3,}$ 25 ^{o}C) δ = 136.31 (CH; C-2), 118.23 (CH_2; C-1), 65.46 (CH; C-3), 34.61 (CH_2; C-4), 29.27 (CH_2; C-5), 29.17 (CH_2), 26.09 (CH_2), 22.90(CH_2), 14.38 (CH_3; C-9).

2b and **2b'**: IR (Film, cm^{-1}) $\tilde{\nu}$ = 2958, 2929, 2857, 2097, 1643, 1237, 969. HRMS (FTMS + APCI) Calc. for $C_9H_{18}N_1$ $[M\text{-}N_2\text{+}H]^+$: 140.1434. Found: 140.1430.

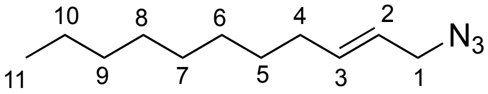
Supporting Information

Ketone **4b**[12,13]



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 2.40 (t, J = 7.5 Hz, 2H; H-3), 2.12 (s, 3H; H-1), 1.52 - 1.58 (m, 2H; H-4), 1.20 - 1.35 (m, 8H; H-5 to H-8), 0.87 (t, J = 7.0 Hz; 3H, H-9). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ = 209.75 (C_q; C-2), 44.18 (CH_2; C-3), 32.02 (CH_2), 30.19 (CH_2), 29.49 (CH_2), 29.41 (CH_2), 24.23 (CH_2), 22.95 (CH_2), 14.41 (CH_3; C-9).

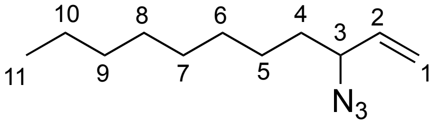
Allyl azide **2c**



From allene **1c** (50 mg, 0.33 mmol), $(PhO)_3PAuCl$ (9 mg, 0.02 mmol), silver triflate (4 mg, 0.02 mmol), $TMSN_3$ (131 µl, 0.98 mmol), trifluoroacetic acid (75 µl, 0.98 mmol) and 4.0 ml dry DCM. Obtained after column chromatography, Hexane then Hex/Et_2O, 5:1: **2c:2c'** (1.8:1), 30 mg, 0.15 mmol, 47% (colourless oil).

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 5.79 - 5.72 (m, 1H; H-3), 5.52 (m, 1H; H-2), 3.69 (d, J = 6.7 Hz, 2H; H-1), 2.08 (m, 2H; H-4), 1.61 - 1.46 (m, 2H; H-5), 1.40 - 1.27 (m, 10H; H-6 to H-8), 0.88 (t, J = 6.8 Hz, 3H; H-9). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ = 137.66 (CH; C-3), 123.00 (CH; C-2), 53.26 (CH_2; C-1), 32.59 (CH_2; C-4), 32.22 (CH_2), 29.77 (CH_2), 29.60 (CH_2), 29.44 (CH_2), 29.41 (CH_2), 23.00 (CH_2), 14.41 (CH_3; C-9).

Allyl azide **2c'**



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 5.74 (m, 1H; H-2), 5.26 (m, 2H; H-1), 3.80 (m, 1H; H-3), 1.59 - 1.23 (m, 12H; H-6 to H-8), 0.88 (t, J = 6.8 Hz, 3H; H-9). Protons on the cyclohexyl ring overlapped with protons of **2c**. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ = 136.30 (CH; C-2), 118.24 (CH_2; C-1), 65.47 (CH; C-3), 34.62 (CH_2), 32.19 (CH_2), 30.06 (CH_2), 29.79 (CH_2), 29.62 (CH_2), 29.56 (CH_2), 26.15 (CH_2), 14.45 (CH_3; C-9).

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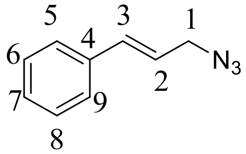
[12] V. V. Negrebetskii, *Russ. J. Gen. Chem.*, 1993, **63**, 1436-1440.

[13] A. Arase, M. Hoshi and Y Masuda, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 209-213.

Supporting Information

2c and **2c'**: IR (Film, cm^{-1}) ṽ = 2957, 2926, 2855, 2098, 1645, 1242, 970. HRMS (FTMS + APCI) Calc. for $C_{11}H_{22}N$ [M-N_2+H]$^+$: 168.1747. Found: 168.1743. Calc. for $C_{11}H_{22}N_3$ [M + H]$^+$: 196.1808. Found: 196.1805.

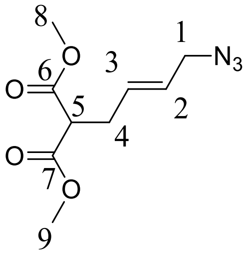
Allyl azide **2d**[14,15,16,17,18]



From allene **1d** (100 mg, 0.86 mmol), $(PhO)_3PAuCl$ (23 mg, 0.04 mmol), silver triflate (11 mg, 0.04 mmol), $TMSN_3$ (340 µl, 2.58 mmol), distilled water (78 µl, 4.30 mmol), trifluoroacetic acid (207 µl, 2.58 mmol) and 2.1 ml dry DCM. Obtained after column chromatography, Hex/Et_2O, 20:1: **2d**, 85 mg, 0.53 mmol, 62% (yellow oil).

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.44 - 7.39 (m, 2H; H-5 and H-9), 7.37 - 7.32 (m, 2H; H-6 and H-8), 7.31 - 7.27 (m, 1H; H-7), 6.66 (d, J = 15.8 Hz, 1H; H-3), 6.25 (dt, J = 15.8, 6.7 Hz, 1H; H-2), 3.95 (dd, J = 6.7, 0.7 Hz, 2H; H-1). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ = 136.34 (C_q; C-4), 134.89 (CH; C-3), 129.00 (CH_{Ar}; C-5 and C-9), 128.52 (CH_{Ar}; C-7), 126.98 (CH_{Ar}; C-6 and C-8), 122.73 (CH; C-2), 53.35 (CH_2; C-1). IR (Film, cm^{-1}) ṽ = 3029, 2927, 2099, 1702, 1654, 1598, 1492, 1235, 967, 747, 693. MS-EI: $C_9H_9N_3$ m/z (%) 159 [M$^+$] (3), 118 (31), 117 (100), 115 (32), 105 (20), 91 (28), 77 (20).

Allyl azide **2e**[19]



From allene **1e** (100 mg, 0.54 mmol), $(PhO)_3PAuCl$ (15 mg, 0.03 mmol), silver triflate (7 mg, 0.03 mmol), $TMSN_3$ (214 µl, 1.63 mmol), distilled water, (49 µl, 2.72 mmol), trifluoroacetic acid (130 µl, 1.63 mmol) and 1.3 ml dry DCM. Obtained after column

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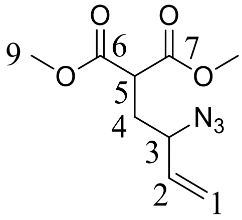
[14] E. Manhart and K. von Werner, *Synthesis,* 1978, 705-706.
[15] A. Jayanthi, V. K. Gumaste and A. R. A. S. Deshmukh, *Synlett,* 2004, 979-982.
[16] S. Murahashi, Y. Taniguchi, Y. Imada and Y. Tanigawa, *J. Org. Chem.,* 1989, **54**, 3292-3303.
[17] M. Rueping, C. Vila and U. Uria, *Org. Lett.,* 2012, **14**, 768-771.
[18] M. R. Maddani, S. K. Moorthy and K. R. Prabhu, *Tetrahedron,* 2010, **66**, 329-333.
[19] S.-I. Murahashi, Y. Taniguchi, Y. Imada and Y. Tanigawa, *J. Org. Chem.,* 1989, **14**, 3301.

chromatography, Hex/EtOAc, 30:1 then 2:1: **2e:2e’** (3.8:1), 53 mg, 0.23 mmol, 43% (yellow oil), and **4e’**, 19 mg, 0.09 mmol, 17% (yellow oil).

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 5.78 - 5.68 (m, 1H; H-3 or H-2), 5.68 - 5.59 (m, 1H; H-3 or H-2), 3.74 (s, 6H; H-8 and H-9), 3.69 (d, J = 6.3 Hz, 2H; H-1), 3.47 (t, J = 7.5 Hz, 1H; H-5), 2.68 (m, 2H; H-4). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ = 169.40 (C_q; C-6 and C-7), 131.80 (CH; C-3), 126.74 (CH; C-2), 52.98 (CH_2; C-1), 52.70 (CH; C-5), 51.74 (CH_2; C-4), 31.75 (CH_3; C-8 or C-9), 30.05 (CH_3; C-8 or C-9).

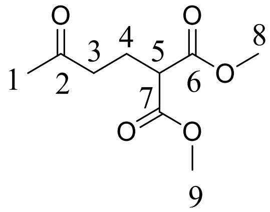
Allyl azide **2e’**



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 5.63 - 5.60 (m, 1H; H-2), 5.35 - 5.31 (m, 2H; H-1), 3.75 (s, 6H; H-8 and H-9), 3.55 (dd, J = 8.2, 6.5 Hz, 1H; H-3), 3.46 - 3.42 (m, 1H; H-5), 2.19 - 2.03 (m, 2H; H-4). ^{13}C NMR signals could not be extracted from the spectra of the mixture **2e+2e’** due to the low concentration of **2e’**.

2e and **2e’**: IR (Film, cm^{-1}) $\tilde{\nu}$ = 2924, 2853, 2099, 1736, 1437, 1260, 973, 801, 749. MS (ESI^+ in MeOH): m/z = 225.05 $C_9H_{15}KO_4$ $[M-N_3+K^++H]^+$. HRMS (FTMS + p NSI) (DCM / MeOH + NH_4OAc): Calc. for $C_9H_{17}N_4O_4$ $[M+NH_4]^+$: 245.1244 Found: 245.1247.

Ketone **4e’**[20]



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 3.73 (s, 6H; H-8 and H-9), 3.43 (t, J = 7.2 Hz, 1H; H-5), 2.53 (t, J = 7.2 Hz, 2H; H-3), 2.16 (m, 2H; H-4), 2.13 (s, 3H; H-1). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ = 207.43 (C_q; C-2), 169.85 (C_q; C-6 and C-7), 52.89 (CH_3; C-8 and C-9), 50.64 (CH; C-5), 40.72 (CH_2; C-3), 30.26 (CH_3; C-1), 22.83 (CH_2; C-

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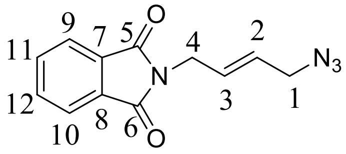
[20] M. R. Saidi, N. Azizib, E. Akbaria, F. Ebrahimia, *J. Mol. Catal.,* 2008, **292**, 44-48.

4). IR (Film, cm^{-1}) ṽ = 2941, 2854, 1732, 1642, 1436, 1275,1156, 750. HRMS (FTMS + p APCI). Calc. for $C_9H_{18}NO_5$ $[M+NH_4]^+$: 220.1179 Found: 220.1176.

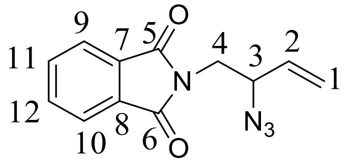
Allyl azide **2f**



From allene **1f** (100 mg, 0.50 mmol), $(PhO)_3PAuCl$ (14 mg, 0.02 mmol), silver triflate (6 mg, 0.02 mmol), $TMSN_3$ (198 µl, 1.51 mmol), distilled water (45 µl, 2.51 mmol), trifluoroacetic acid (172 µl, 1.51 mmol) and 1.2 ml dry DCM. Obtained after column chromatography, Hex/EtOAc, 10:1 then 2:1: **2f**, 55 mg, 0.23 mmol, 48% (yellow oil), **2f'**, 9 mg, 0.04 mmol, 7% (yellow oil) and **4f'**, 35 mg, 0.16 mmol, 32%, (white solid).

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.89 - 7.84 (m, 2H; H_{Ar}), 7.75 - 7.71 (m, 2H; H_{Ar}), 5.88 - 5.81(dtt, J = 15.4, 5.6, 1.1 Hz, 1H; H-3), 5.81 - 5.85 (dtt, J = 15.4, 5.6, 1.1 Hz, 1H; H-2), 4.33 (dd, J = 5.6, 1.1 Hz, 2H; H-4), 3.77 (d, J = 5.6 Hz, 2H; H-1); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ = 168.14 (C_q; C-5 and C-6), 134.42 (CH_{Ar}), 132.41 (C_q; C-7 and C-8), 128.63 (CH; C-3), 127.55 (CH; C-2), 123.74 (CH_{Ar}), 52.27 (CH_2; C-1), 39.10 (CH_2; C-4).

Allyl azide **2f'**

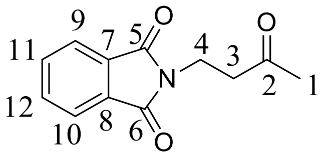


^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.89 – 7.85 (m, 2H; H_{Ar}), 7.77 – 7.69 (m, 2H; H_{Ar}), 5.86 – 5.77 (m, 1H; H-2), 5.42 – 5.38 (m, 1H; H-1), 5.38 – 5.36 (m, 1H; H-1), 4.37 – 4.30 (m, 1H; H-3), 3.83 (dd, J = 13.9, 8.3 Hz, 1H; H-4), 3.72 (dd, J = 13.9, 6.3 Hz, 1H; H-4). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ = 168.36 (C_q; C-5 and C-6), 134.54 (2x CH_{Ar}), 132.90 (CH; C-2) 132.20 (2x C_q, C-7 and C-8), 123.86 (2x CH_{Ar}), 121.41 (CH_2; C-1), 62.73 (CH; C-3), 41.07 (CH_2; C-4). IR (Film, cm^{-1}) ṽ = 2923, 2852, 2098, 1771, 1717, 1614, 1466, 1426, 1391, 717. HRMS (FTMS + p NSI), ((DCM)/MeOH + NH_4OAc): Calc. for $C_{12}H_{14}N_5O_2$ $[M+NH_4]^+$: 260.1142 Found: 260.1143.

Supporting Information

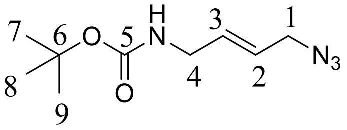
2f and **2f'**: IR (Film, cm^{-1}) $\tilde{\nu}$ = 2922, 2851, 2097, 1771, 1710, 1466, 1426, 1391, 1187, 949, 711. HRMS (FTMS + p NSI) (DCM / MeOH + NH_4OAc): Calc. for $C_{12}H_{14}N_5O_2$ $[M+NH_4]^+$: 260.1142 Found: 260.1145.

Ketone **4f'**[21,22]



^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.85 – 7.81 (m, 2H; H-11 and H-12), 7.73 – 7.69 (m, 2H; H-9 and H-10), 3.98 – 3.93 (m, 2H; H-4), 2.87 (t, J = 7.4 Hz; 1H, H-3), 2.18 (s, 3H; H-1). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ = 206.13 (C_q; C-2), 168.44 (C_q; C-5 and C-6), 134.35 (CH_{Ar}), 132.40 (C_q; C-7 and C-8), 123.63 (CH_{Ar}), 41.95 (CH_2; C-3), 33.32 (CH_2; C-4), 30.27 (CH_3; C-1). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3465, 2957, 2926, 2856, 1709, 1634, 1467, 1435, 1260, 1029, 797, 718. HRMS (FTMS + p APCI), ((DCM)/MeOH + NH_4OAc): Calc. for $C_{12}H_{12}NO_3$ $[M+ H]^+$: 218.0812 Found: 218.0810. M. p.= 111 °C.

Allyl azide **2g**



From allene **1g** (100 mg, 0.39 mmol), $(PhO)_3PAuCl$ (11 mg, 0.02 mmol), silver triflate (5 mg, 0.02 mmol), $TMSN_3$ (154 µl, 1.17 mmol), distilled water (35 µl, 1.96 mmol), trifluoroacetic acid (94 µl, 1.17 mmol) and 957 µl dry DCM. Obtained after column chromatography, Hex/EtOAc, 10:1: **2g**, 32 mg, 0.15 mmol, 38%, (yellow oil).

^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 5.78 (m, 1H; H-3 or H-2), 5.74 (m, 1H; H-3 or H-2), 4.13 (m, 2H; H-4 or H-1), 4.08 (m, 2H; H-4 or H-1), 1.47 (s, 9H; *t*-Bu H-7, H-8 and H-9). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ = 154.66 (C_q; C-5), 126.22 (CH; C-3 or C-2), 126.11 (CH; C-2 or C-3), 79.61 (CH; C-6), 53.44 (CH_2; C-1 or C-4), 53.18 (CH_2; C-1 or C-4), 28.87 (3 x CH_3; C-7, C-8 and C-9). IR (Film, cm^{-1}) $\tilde{\nu}$ = 3332 (broad), 2976, 2925, 2853, 2100, 1706, 1685, 1609, 1410, 1368, 1257, 1170, 1140, 887, 765. HRMS of this compound could not be obtained due to rapid decomposition of this product.

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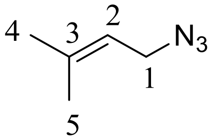
[21] F. Liu,A. Martin-Mingot, M.-P. Jouannetaud, C. Bachmann, G. Frapper, F. Zunino and S. Thibaudeau, *J. Org. Chem*., 2011, **76**, 1460–1463.

[22] M. Viscontini, W. Kaiser and H. A. Leidner, *Helv. Chim. Acta,* 1965, **48***,* 1221-1225.

Supporting Information

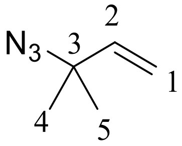
Allyl azide **2h**[23,24]



From allene **1h** (20 mg, 0.29 mmol), $(PhO)_3PAuCl$ (8 mg, 0.01 mmol), silver triflate (4 mg, 0.01 mmol), $TMSN_3$ (116 µl, 0.88 mmol), distilled water (26 µl, 1.47 mmol), trifluoroacetic acid (70 µl, 0.88 mmol) and 718 µl dry DCM. Obtained: 100% conversion **2h:2h'** (3.7:1). This product could not be isolated due to volatility issues.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ = 5.35 - 5.29 (m, 1H; H-2), 3.76 (d, J = 7.5 Hz, 2H; H-1), 1.79 (s, 3H; H-4 or H-5), 1.71 (s, 3H; H-4 or H-5). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ = 130.91(C_q; C-3), 117.42 (CH; C-2), 48.48 (CH_2; C-1), 25.90 (CH_3; C-4 or C-5), 18.25 (CH_3; C-4 or C-5).

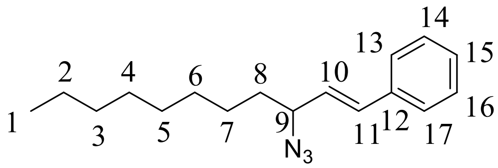
Allyl azide **2h'**



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 5.85 (dd, J = 17.3, 10.6 Hz, 1H; H-2), 5.22 (dd, J = 17.3, 0.5 Hz, 1H; H-1), 5.16 (dd, J = 10.6, 0.5 Hz, 1H; H-1), 1.33 (s, 6H; H-4 and H-5). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ = 141.33 (CH; C-2), 114.26 (CH_2; C-1), 62.57 (C_q; C-3), 26.25 (2x CH_3; C-4 and C-5).

2h and **2h'**: IR (Film, cm^{-1}) $\tilde{\nu}$ = 2962, 2905, 2109, 1679, 1587, 1484, 1261, 1092, 1025, 940, 799, 687.

Allyl azide **2i**



From allene **1i** (100 mg, 0.44 mmol), $(PhO)_3PAuCl$ (12 mg, 0.02 mmol), silver triflate (6 mg, 0.02 mmol), $TMSN_3$ (173 µl, 1.31 mmol), distilled water (39 µl, 2.19 mmol),

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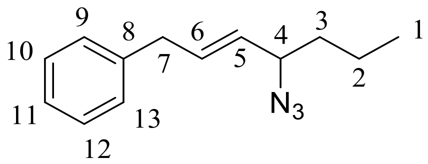
[23] A. V. Malkov, P. Spoor, V. Vinader and P. Kočovsky, *J. Org. Chem.*, 1999, **64**, 5308-5311.
[24] T. Kanai, Y. Kanagawa and Y. Ishii, *J. Org. Chem.*, 1990, **55**, 3274-3277.

trifluoroacetic acid (105 µl, 1.31 mmol) and 1.1 ml dry DCM. Obtained after column chromatography, using as eluent hexane: **2i**, 91 mg, 0.33 mmol, 76%, (yellow oil).

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.43 - 7.40 (m, 2H; H-17 and H-13), 7.37 - 7.32 (m, 2H; H-16 and H-14), 7.30 - 7.26 (m, 1H; H-15), 6.61 (d, J = 15.8 Hz, 1H; H-11), 6.12 (dd, J = 15.8, 8.1 Hz, 1H; H-10), 4.00 (q, J = 7.2 Hz, 1H; H-9), 1.70 - 1.56 (m, 2H; H-8), 1.45 - 1.36 (m, 2H; H-7), 1.36 - 1.23 (m, 10H; H-6, H-5, H-4, H-3 and H-2), 0.91 - 0.87 (m, 3H; H-1). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ = 136.44 (C_q; C-12), 133.44 (CH; C-11), 128.98 (CH_{Ar}; C-14 and C-16), 128.41 (CH_{Ar}; C-15), 127.67 (CH; C-10), 126.98 (CH_{Ar}; C-13 and C-17), 65.27 (CH; C-9), 35.14 (CH_2; C-8), 32.18 (CH_2; C-7), 29.79 (CH_2), 29.64 (CH_2), 29.56 (CH_2), 26.25 (CH_2), 22.99 (CH_2), 14.43 (CH_3; C-1). IR (Film, cm^{-1}) $\tilde{\nu}$ = 3061, 3028, 2957, 2927, 2856, 2097, 1800, 1599, 1494, 1466, 1450, 1260, 1095, 966, 803, 749, 692. HRMS (FTMS + p APCI) (DCM + NH_4OAc): Calc. for $C_{17}H_{26}N_1$ [M–N_2 + H]$^+$: 244.2060 Found: 244.2056, Calc. for $C_{17}H_{25}$ [M–N_3]$^+$: 229.1951 Found: 229.1948

Allyl azide **2j**

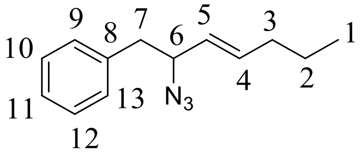


From allene **1j** (100 mg, 0.58 mmol), $(PhO)_3PAuCl$ (16 mg, 0.03 mmol), silver triflate (7 mg, 0.03 mmol), $TMSN_3$ (229 µl, 1.74 mmol), distilled water (52 µl, 2.90 mmol), trifluoroacetic acid (139 µl, 1.74 mmol) and 1.4 ml dry DCM. Obtained after column chromatography, using as eluent hexane: **2j:2j’** (1.3:1), 84 mg, 0.39 mmol, 67%, (yellow oil).

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.35 - 7.25 (m, 2H; H_{Ar}), 7.25 - 7.22 (m, 1H; H_{Ar}), 7.21 - 7.17 (m, 2H; H_{Ar}), 5.90 - 5.84 (m, 1H; H-6), 5.49 - 5.44 (m, 1H; H-5), 3.84 (dd, J = 14.7, 7.3 Hz, 1H; H-4), 3.49 - 3.38 (m, 2H; H-7), 1.59 - 1.44 (m, 2H; H-3), 1.44 - 1.33 (m, 2H; H-2), 0.88 (t, J = 7.3 Hz, 3H; H-1). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ = 139.91 (C_q; C-8), 133.92 (CH; C-6), 129.66 (CH; C-5), 128.91 (2x CH_{Ar}), 128.86 (2x CH_{Ar}), 126.98 (CH_{Ar}; C-11), 64.66 (CH; C-4), 38.93 (CH_2; C-7), 37.05 (CH_2; C-3), 22.58 (CH_2; C-2), 14.07 (CH_3; C-1).

Supporting Information

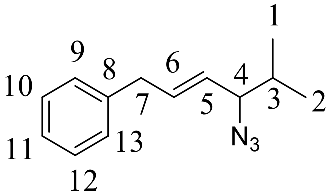
Allyl azide **2j'**



^{1}H NMR (500 MHz, CDCl$_3$, 25 ^{o}C, TMS) δ = 7.35 - 7.28 (m, 2H; H$_{Ar}$), 7.25 - 7.22 (m, 1H; H$_{Ar}$-11), 7.21 - 7.17 (m 2H; H$_{Ar}$), 5.70 - 5.63 (m, 1H; H-4), 5.43 - 5.39 (m, 1H; H-5), 4.05 (dd, J = 14.8, 7.3 Hz, 1H; H-6), 2.80 (d, J = 7.3 Hz, 2H; H-7), 2.08 - 2.00 (m, 2H; H-3), 1.44 - 1.33 (m, 2H; H-2), 0.92 (t, J = 7.3 Hz, 3H; H-1). ^{13}C NMR (126 MHz, CDCl$_3$, 25 ^{o}C) δ = 137.88 (C$_q$; C-8), 136.10 (CH; C-4), 129.80 (2x CH$_{Ar}$), 128.69 (2x CH$_{Ar}$), 127.46 (CH; C-5), 126.60 (CH$_{Ar}$; C-11), 66.12 (CH; C-6), 41.67 (CH$_2$; C-7), 34.55 (CH$_2$; C-3) 19.50 (CH$_2$; C-2), 13.84 (CH$_3$; C-1).

2j and **2j'**: IR (Film, cm^{-1}) ṽ =3029, 2960, 2931, 2873, 2097, 1603, 1454, 1237, 970, 747, 698. HRMS (FTMS + p APCI): Calc. for $C_{13}H_{21}N_4$ $[M+NH_4]^+$: 233.1761 Found: 233.1760.

Allyl azide **2k**

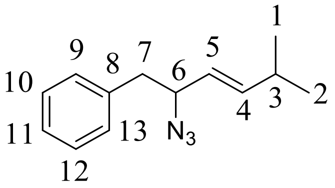


From allene **1k** (86 mg, 0.50 mmol), (PhO)$_3$PAuCl (14 mg, 0.02 mmol), silver triflate (6 mg, 0.02 mmol), TMSN$_3$ (197 µl, 1.50 mmol), distilled water (45 µl, 2.50 mmol), trifluoroacetic acid (120 µl, 1.50 mmol) and 1.2 ml dry DCM. Obtained after column chromatography, using as eluent hexane: **2k:2k'** (1.67:1), 59 mg, 0.27 mmol, 55%, (yellow oil).

^{1}H NMR (500 MHz, CDCl$_3$, 25 ^{o}C, TMS) δ = 7.34 - 7.29 (m, 2H; H$_{Ar}$), 7.25 - 7.17 (m, 3H; H$_{Ar}$), 5.88 (dtd, J = 15.2, 6.9, 0.6 Hz, 1H; H-6), 5.48 (ddt, J = 15.2, 8.5, 1.5 Hz, 1H; H-5), 3.63 (dd, J = 8.5, 6.9 Hz, 1H; H-4), 3.48 - 3.44 (m, 2H; H-7), 1.79 - 1.67 (m, 1H; H-3), 0.95 (d, J = 6.9 Hz, 3H; H-1 or H-2), 0.91 (d, J = 6.9 Hz, 3H; H-1 or H-2). ^{13}C NMR (126 MHz, CDCl$_3$, 25 ^{o}C) δ = 139.95 (C$_q$; C-8), 134.99 (CH; C-6), 128.90 (2x CH$_{Ar}$), 128.85 (2x CH$_{Ar}$), 127.98 (CH; C-5), 126.59 (CH$_{Ar}$; C-11), 71.32 (CH; C-4), 39.03 (CH$_2$; C-7), 32.85 (CH; C-3), 19.23 (CH$_3$; C-1 or C-2), 19.22 (CH$_3$; C-1 or C-2).

Supporting Information

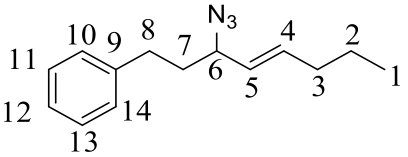
Allyl azide **2k'**



^{1}H NMR (500 MHz, CDCl$_3$, 25 ^{o}C, TMS) δ = 7.36 - 7.28 (m, 2H; H$_{Ar}$), 7.25 - 7.18 (m, 3H; H$_{Ar}$), 5.64 (ddd, J = 15.4, 6.8, 0.6 Hz, 1H; H-4), 5.37 (ddd, J = 15.4, 8.1, 1.3 Hz, 1H; H-5), 4.06 - 4.00 (m, 1H; H-6), 2.83 - 2.79 (m, 2H; H-7), 2.32 (dqd, J = 13.4, 6.8, 1.3 Hz, 1H; H-3), 1.00 (d, J = 6.8 Hz, 3H; H-1 or H-2), 0.99 (d, J = 6.8 Hz, 3H; H-1 or H-2). ^{13}C NMR (126 MHz, CDCl$_3$, 25 ^{o}C) δ = 143.23 (CH; C-4), 137.88 (C$_q$; C-8), 129.83 (2x CH$_{Ar}$), 128.66 (2x CH$_{Ar}$), 126.97 (CH$_{Ar}$; C-11), 124.30 (CH; C-5), 65.99 (CH; C-6), 41.71 (CH$_2$; C-7), 31.22 (CH; C-3), 22.73 (CH$_3$; C-1 or C-2), 22.60 (CH$_3$; C-1 or C-2).

2k and **2k'**: IR (Film, cm^{-1}) $\tilde{\nu}$ = 3064, 3030, 2962, 2929, 2095, 1454, 1260, 1094, 1029, 803, 699, 666. HRMS (FTMS + p APCI): Calc. for $C_{13}H_{21}N_4$ [M+NH$_4$]$^+$: 233.1761 Found: 233.1760.

Allyl azide **2l**

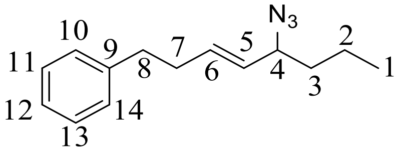


From allene **1l** (100 mg, 0.54 mmol), (PhO)$_3$PAuCl (15 mg, 0.03 mmol), silver triflate (7 mg, 0.03 mmol), TMSN$_3$ (212 µl, 1.61 mmol), distilled water (48 µl, 2.69 mmol), trifluoroacetic acid (129 µl, 1.61 mmol) and 1.3 ml dry DCM. Obtained after column chromatography, using as eluent hexane: **2l:2l'** (1.13:1), 85 mg, 0.37 mmol, 70%, (yellow oil).

^{1}H NMR (500 MHz, CDCl$_3$, 25 ^{o}C, TMS) δ = 7.33 - 7.27 (m, 2H; H$_{Ar}$), 7.23 - 7.16 (m, 3H; H$_{Ar}$), 5.74 - 5.67 (m, 1H; H-4), 5.44 - 5.38 (m, 1H; H-5), 3.82 - 3.78 (m, 1H; H-6), 2.70 - 2.65 (m, 2H; H-8), 2.11 - 2.05 (m, 2H; H-3), 1.91 - 1.75 (m, 2H; H-7), 1.47 - 1.41 (m, 2H; H-2), 0.93 (t, J = 7.4 Hz; 3H, H-1). ^{13}C NMR (126 MHz, CDCl$_3$, 25 ^{o}C) δ = 141.53 (C$_q$; C-9), 136.15 (CH; C-4), 128.80 (4x CH$_{Ar}$), 127.84 (CH; C-5), 126.36 (CH$_{Ar}$; C-12), 64.34 (CH; C-6), 36.61 (CH$_2$; C-7), 34.60 (CH$_2$; C-3), 32.43 (CH$_2$; C-8), 22.65 (CH$_2$; C-2), 13.89 (CH$_3$; C-1).

Supporting Information

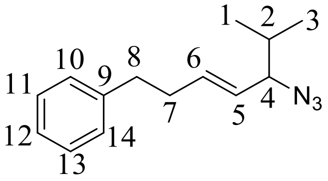
Allyl azide **2l'**



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.33 - 7.27 (m, 2H; H_{Ar}), 7.23 - 7.16 (m, 3H; H_{Ar}), 5.77 - 5.68 (m, 1H; H-6), 5.41 - 5.33 (m, 1H; H-5), 3.78 - 3.74 (m, 1H; H-4), 2.77 - 2.70 (m, 2H; H-8), 2.47 - 2.37 (m, 2H; H-7), 1.55 - 1.47 (m, 2H; H-3), 1.36 - 1.25 (m, 2H; H-2), 0.90 (t, J = 7.4 Hz, 3H; H-1). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ = 141.75 (C_q; C-9), 134.49 (CH; C-6), 128.86 (CH; C-5), 128.80 (2x CH_{Ar}), 128.68 (2x CH_{Ar}), 126.26 (CH_{Ar}; C-12), 64.78 (CH; C-4), 37.02 (CH_2; C-3), 36.05 (CH_2; C-8), 34.29 (CH_2; C-7), 19.41 (CH_2; C-2), 14.05 (CH_3; C-1).

2l and **2l'**: IR (Film, cm^{-1}) $\tilde{\nu}$ = 3064, 3028, 2960, 2932, 2873, 2095, 1666, 1604, 1455, 1238, 1030, 970, 912, 747. HRMS (FTMS+ p APCI) Calc. for $C_{14}H_{23}N_4$ $[M+NH_4]^+$: 247.1917. Found 247.1917, Calc. for $C_{14}H_{20}N_1$ $[M–N_2+H]^+$: 202.1590. Found 202.1591.

Allyl azide **2m**

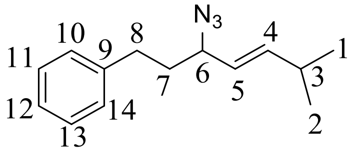


From allene **1m** (100 mg, 0.54 mmol), $(PhO)_3PAuCl$ (15 mg, 0.03 mmol), silver triflate (7 mg, 0.03 mmol), $TMSN_3$ (212 µl, 1.61 mmol), distilled water (48 µl, 2.69 mmol), trifluoroacetic acid (129 µl, 1.61 mmol) and 1.3 ml dry DCM. Obtained after column chromatography, using as eluent hexane: **2m:2m'** (1:1), 98 mg, 0.43 mmol, 80%, (yellow oil).

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.33 - 7.27 (m, 2H; H_{Ar}), 7.23 - 7.16 (m, 3H; H_{Ar}), 5.76 - 5.71 (m, 1H; H-6), 5.43 - 5.37 (m, 1H; H-5), 3.55 (dd, J = 8.5, 6.8 Hz, 1H; H-4), 2.80 - 2.71 (m, 2H; H-8), 2.49 - 2.40 (m, 2H; H-7), 1.67 (dq, J = 13.5, 6.8 Hz, 1H; H-2), 0.90 (d, J = 6.8 Hz, 3H; H-1 or H-3), 0.84 (d, J = 6.8 Hz 3H; H-1 or H-3). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ = 141.53 (C_q; C-9), 135.55 (CH; C-6), 128.80 (2x CH_{Ar}), 128.69 (2x CH_{Ar}), 127.13 (CH; C-5), 126.36 (CH_{Ar}; C-12), 71.48 (CH; C-4), 36.10 (CH_2;

C-8), 34.34 (CH_2; C-7), 32.77 (CH; C-2), 19.18 (CH_3; C-1 or C-3), 19.13 (CH_3; C-1 or C-3).

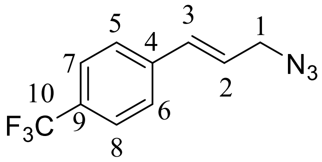
Allyl azide **2m'**



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.33 - 7.27 (m, 2H; H_{Ar}), 7.23 - 7.16 (m, 3H; H_{Ar}), 5.71 - 5.67 (m, 1H; H-4), 5.38 - 5.32 (m, 1H; H-5), 3.80 - 3.73 (m, 1H; H-6), 2.71 - 2.64 (m, 2H; H-8), 2.39 - 2.32 (m, 1H; H-3), 1.91 - 1.75 (m, 2H; H-7), 1.04 (dd, *J* = 6.8, 2.0 Hz, 6H; H-1 and H-2). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ = 143.43 (CH; C-4), 141.73 (C_q; C-9), 128.80 (CH_{Ar}), 126.26 (CH_{Ar}; C-12) 124.61 (CH; C-5), 64.21 (CH; C-6), 36.61 (CH_2; C-7), 32.43 (CH_2; C-8), 31.28 (CH; C-3), 22.83 (CH_3; C-1 or C-2), 22.71 (CH_3; C-1 or C-2).

2m and **2m'**: IR (Film, cm^{-1}) $\tilde{\nu}$ = 3064, 3028, 2961, 2927, 2870, 2095, 1603, 1496, 1454, 1367, 1241, 971, 747, 699. HRMS (FTMS+ p APCI) Calc. for $C_{14}H_{23}N_4$ $[M+NH_4]^+$: 247.1917. Found: 247.1917.

Allyl azide **2n**[25]



From allene **1n** (100 mg, 0.54 mmol), $(PhO)_3PAuCl$ (15 mg, 0.03 mmol), silver triflate (7 mg, 0.03 mmol), $TMSN_3$ (214 µl, 1.63 mmol), distilled water (49 µl, 2.72 mmol), trifluoroacetic acid (186 µl, 1.63 mmol) and 1.3 ml dry DCM. The reaction was then warm up at 30 °C during 60 h. Obtained after column chromatography, Hex/Et_2O, 80:1, 91.1 mg, 0.40 mmol, 74% (pale yellow oil).

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.59 (d, *J* = 8.2 Hz, 2H; H-7 and H-8), 7.50 (d, *J* = 8.2 Hz, 2H; H-5 and H-6), 6.69 (d, *J* = 15.8 Hz, 1H; H-3), 6.33 (dt, *J* = 15.8, 6.4 Hz, 1H; H-2), 3.99 (dd, *J* = 6.4, 0.8 Hz, 2H; H-1). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ =

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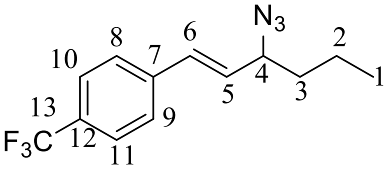
[25] Y. Uozumi, T. Suzuka, R. Kawade, and H. Takenaka, *Synlett*, 2006, **13**, 2109-2113.

139.82 (C_q; C-4), 133.13 (CH; C-3), 130.33 (q, J = 32.4 Hz, C_q; C-9), 127.14 (CH_{Ar}; C-5 and C-6), 126.00 (q, J = 3.8 Hz, CH_{Ar}-7 and CH_{Ar}-8), 125.63 (CH; C-2), 124.42 (q, J = 271.9 Hz, C-F) , 53.07 (CH_2; C-1). ^{19}F NMR (471 MHz, $CDCl_3$) δ = -62.59. IR (Film, cm^{-1}): ṽ = 3042, 2927, 2855, 2644, 2510, 2102, 1616, 1415, 1326, 1124, 1016, 853.

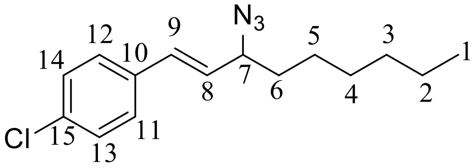
Allyl azide **2o**



From allene **1o** (99.8 mg, 0.44 mmol), $(PhO)_3PAuCl$ (12 mg, 0.02 mmol), silver triflate (6 mg, 0.02 mmol), $TMSN_3$ (174 µl, 1.32 mmol), distilled water (40 µl, 2.21 mmol), trifluoroacetic acid (106 µl, 1.32 mmol) and 1.1 ml dry DCM. The reaction was then warm up at 30 °C during 60 h. Obtained after column chromatography, Pentane/Et_2O, 80:1, 79 mg, 0.30 mmol, 67% (yellow oil).

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.59 (d, J = 8.2 Hz, 2H; H-10 and H-11), 7.50 (d, J = 8.2 Hz, 2H; H-8 and H-9), 6.64 (d, J = 15.8 Hz, 1H; H-6), 6.20 (dd, J = 15.8, 7.8 Hz, 1H; H-5), 4.07 – 4.01 (m, 1H; H-4), 1.71 – 1.55 (m, 2H; H-3), 1.51 – 1.37 (m, 2H; H-2), 0.96 (t, J = 7.3 Hz, 3H; H-1). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ = 139.90 (C_q, C-7), 131.85 (CH; C-6), 130.43 (CH; C-5), 130.24 (q, J = 32.5 Hz; C_q; C-12), 127.14 (CH_{Ar}; C-8 and C-9), 125.97 (q, J = 3.8 Hz; CH_{Ar}; C-11 and C-10), 124.44 (q, J = 271.9 Hz; CF; C-13), 64.61 (CH; C-4), 37.05 (CH_2; C-3), 19.47 (CH_2; C-2), 14.08 (CH_3; C-1). ^{19}F NMR (471 MHz, $CDCl_3$) δ = -62.58. IR (Film, cm^{-1}): ṽ = 2963, 2936, 2876, 2647, 2483, 2327, 2100, 1617, 1325, 1166, 1067, 1030, 967. HRMS (APCI (ASAP)) with added NH_4OAc: Calc. for $C_{13}H_{15}F_3N$ $[M–N_2+H]^+$: 242.1151. Found: 242.1148. Calc. for $C_{13}H_{14}F_3$ $[M–N_3]^+$: 227.1042. Found: 227.1040. Calc. for $C_{13}H_{14}F_3N$ $[M]^+$: 269.1140. Found: 269.1143.

Allyl azide **2p**



Supporting Information

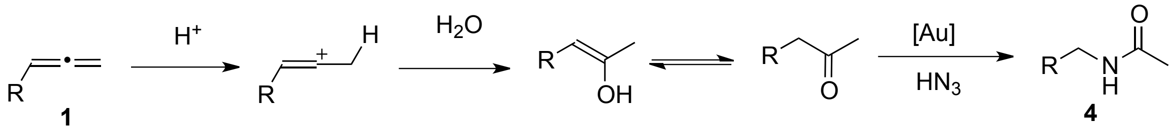
From allene **1p** (106.7 mg, 0.46 mmol), $(PhO)_3PAuCl$ (12 mg, 0.02 mmol), silver triflate (6 mg, 0.02 mmol), $TMSN_3$ (180 µl, 1.37 mmol), distilled water (41 µl, 2.28 mmol), trifluoroacetic acid (109 µl, 1.37 mmol) and 1.1 ml dry DCM. Obtained after column chromatography, Hex/Et_2O, 80:1, 91.1 mg, 0.33 mmol, 72% (yellow oil).

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.34 – 7.32 (m, 2H; H-13 and H-14), 7.31 – 7.29 (m, 2H; H-11 and H-12), 6.55 (d, J = 15.8 Hz, 1H; H-9), 6.08 (dd, J = 15.8, 8.0 Hz, 1H; H-8), 4.01 – 3.95 (m, 1H; H-7), 1.70 – 1.53 (m, 2H; H-6), 1.44 – 1.21 (m, 8H; H-5 to H-2), 0.89 (t, J = 7.0 Hz, 3H; H-1). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ = 134.93 (C_q), 134.10 (C_q), 132.11 (CH; C-9), 129.17 (2x CH_{Ar}), 128.41 (CH; C-8), 128.18 (2x CH_{Ar}), 65.09 (CH; C-7), 35.08 (CH_2; C-6), 32.02 (CH_2; C-5), 29.30 (CH_2; C-4), 26.20 (CH_2; C-3), 22.91 (CH_2; C-2), 14.39 (CH_3; C-1). IR (Film, cm^{-1}): $\tilde{\nu}$ = 2956, 2929, 2857, 2730, 2583, 2470, 2097, 1491, 1238, 1091, 967. HRMS (APCI (ASAP)) with added NH_4OAc: Calc. for $C_{15}H_{21}{}^{35}ClN$ $[M{-}N_2{+}H]^+$: 250.1357. Found: 250.1354. Calc. for $C_{15}H_{21}{}^{37}ClN$ $[M{-}N_2{+}H]^+$: 252.1328. Found: 252.1323. Calc. for $C_{15}H_{20}{}^{35}Cl$ $[M{-}N_3]^+$: 235.1248. Found: 235.1247. Calc. for $C_{15}H_{20}{}^{37}Cl$ $[M{-}N_3]^+$: 237.1219. Found: 237.1215. $C_{15}H_{20}{}^{35}ClN_3$ $[M]^+$: 277.1346 Found: 277.1346.

Supporting Information

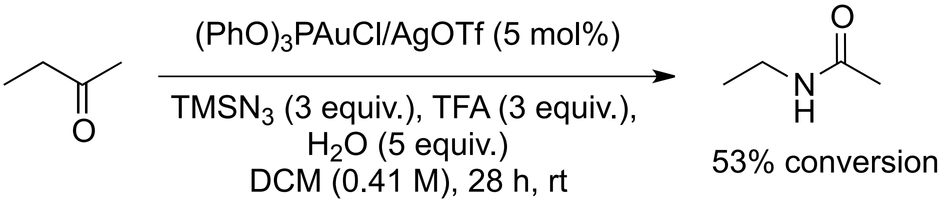
Proposed mechanism for formation of amide 4a

Amide **4a** was obtained as by-product in the reaction with cyclohexylallene **1a**. We propose that this amide comes from a gold-catalysed Schmidt reaction of the corresponding ketone with the *in situ* formed hydrazoic acid.[26] The ketone can be formed by protonation of the allene by the strong acid and attack of water into the central carbon of the allenic system, which is supported by the isolation of methyl ketones **4b'**, **4e'** and **4f'** in the reaction with allenes **1b, 1e** and **1f** (entries 2, 5, and 6, Table 1 in the main manuscript).[8]



Gold-catalysed Schmidt reaction of ethyl methyl ketone.

To further test this hypothesis we carried out the reaction of commercially available ethyl methyl ketone, under our reaction conditions, and we observed 53% conversion to the corresponding amide in 28 h.[27]



$(PhO)_3PAuCl$ (0.05 Eq., 16 mg, 0.03 mmol.) and silver triflate (0.05 Eq., 8 mg, 0,03 mmol) were added into a previously dried-vacuum schlenk flask under N_2. The solids were dissolved in dry dichloromethane (1.4 ml, 0.41 M) and stirred for a few minutes at 0ºC. Then ethyl methyl ketone (1 Eq., 62 µl, 0.58 mmol) was added dropwise at 0ºC and under stirring. $TMSN_3$ (3 Eq., 229 µl, 1.74 mmol), distilled water, (5 Eq., 52 µl, 2.90 mmol), and trifluoroacetic acid, (3 Eq., 139 µl, 1.74 mmol) were added dropwise at 0ºC. The mixture was then warmed up and stirred at room temperature during 28h. The reaction was stopped at 28h with 53% conversion of *N*-ethylacetamide. The crude was filtered through Celite,

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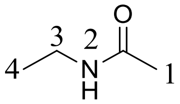
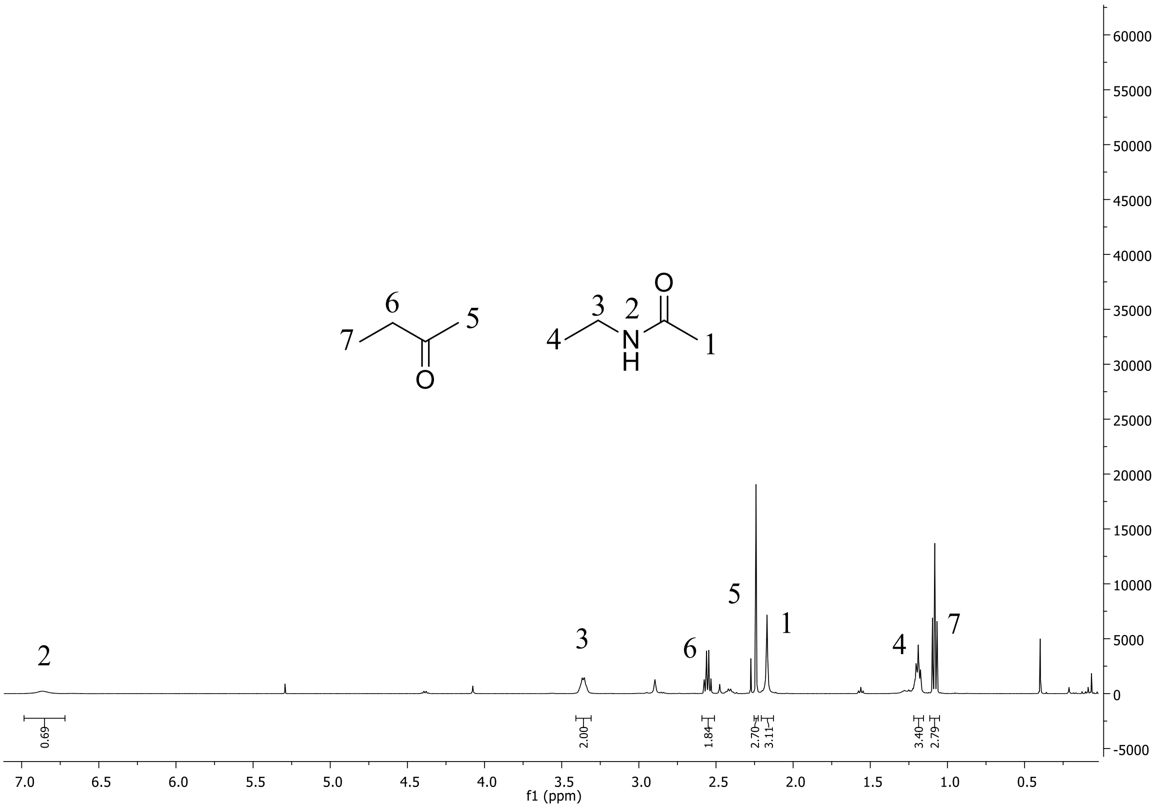
[26] K. F. Z. Schmidt, *Angew. Chem. Int. Ed. Engl.*, 1923, **36**, 511.
[27] C. Qin, P. Feng, Y. Ou, T. Shen, T. Wang and N. Jiao, *Angew. Chem. Int. Ed.*, 2013, **52**, 7850-78-54.

and washed with dichloromethane. The solvent was removed by vacuum, and the crude was analysed without purification by NMR.

N-ethylacetamide.[28,29]



^{1}H NMR (500 MHz, CDCl$_3$, 25 ºC, TMS) δ = 6.87 (broad s, 1H; *N*H-2), 3.41 - 3.32 (m, 2H; H-3), 2.17 (s, 3H; H-1), 1.19 (t, *J* = 7.2 Hz, 3H; H-4).



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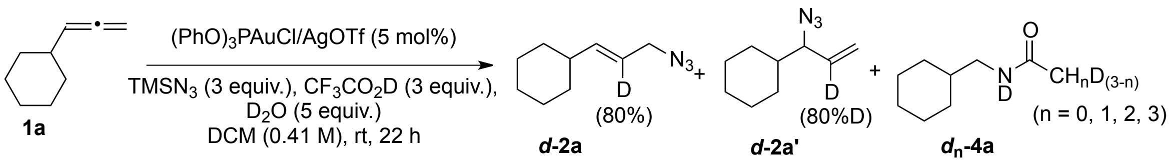
[28] M. Avalos, R.Babiano, J. L. Barneto, J. L. Bravo, P.Cintas, J. L. Jimenez and J. C. Palacios, *J. Org. Chem.,* 2001, **66***,* 7275-7282.

[29] A. R. Katritzky, A. E. Hayden, K. Kirichenko, P. Pelphrey and Y. Ji, *J. Org. Chem*., 2004, **69**, 5108-5111.

Supporting Information

Deuteration experiment:

We also carried out deuterium-labelling experiments to support the protonation of the allene in the terminal position by the acid. Thus, reaction with *d*-TFA and D_2O gave the allyl azides ***d*-2a** and ***d*-2a'** with high deuterium incorporation in the expected positions, also confirming the involvement of vinyl-gold intermediates, and the amide **4a** was obtained as a mixture of compounds with different deuterium incorporation in the methyl group, as well as deuteration in the amidic nitrogen, observed before purification.



Experimental procedure for the deuteration experiment:

$(PhO)_3PAuCl$ (0.05 Eq., 22 mg, 0.04 mmol) and silver triflate (0.05 Eq., 10.5 mg, 0.04 mmol) were added into a previously washed with D_2O and dried-vacuum schlenk flask under N_2. The solids were dissolved in dry dichloromethane (2.0 ml, 0.41 M) and stirred for a few minutes at 0ºC. Then, allene **1a** (1 Eq., 119 µl, 0.82 mmol) was added dropwise to schlenk flask. $TMSN_3$ (3 Eq., 323 µl, 2.45 mmol), D_2O (5 Eq., 74 µl, 4.09 mmol) and *d*-TFA (3 Eq., 189 µl, 2.45 mmol) were added dropwise at 0ºC and under stirring. The mixture was then warmed up and stirred at room temperature during 22h. The crude was filtered through celite and the solvent was removed by vacuum. The mixture was analysed by ^1H and ^2H NMR without purification in $CDCl_3$.

We observed deuterium incorporation in the following positions:

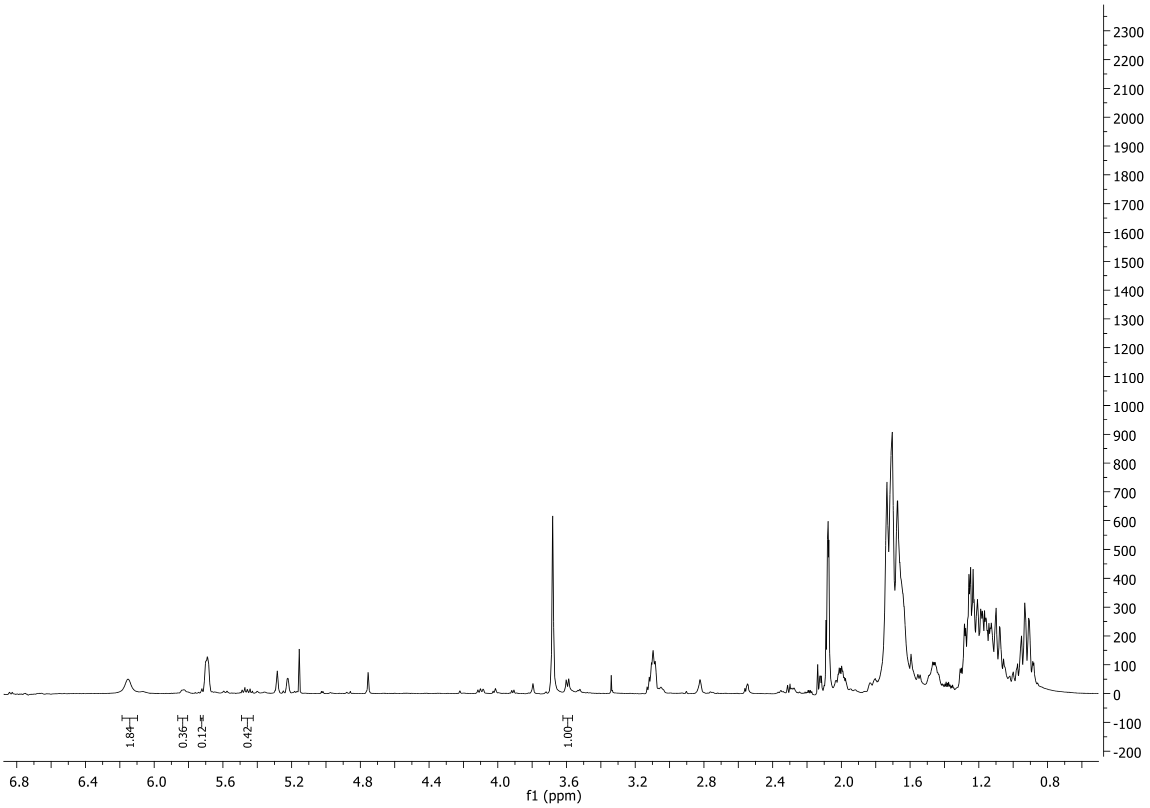
2a: the signal at 5.44 ppm showed 80% of deuterium incorporation.

2a': the signal at 5.76 ppm showed 80% of deuterium incorporation.

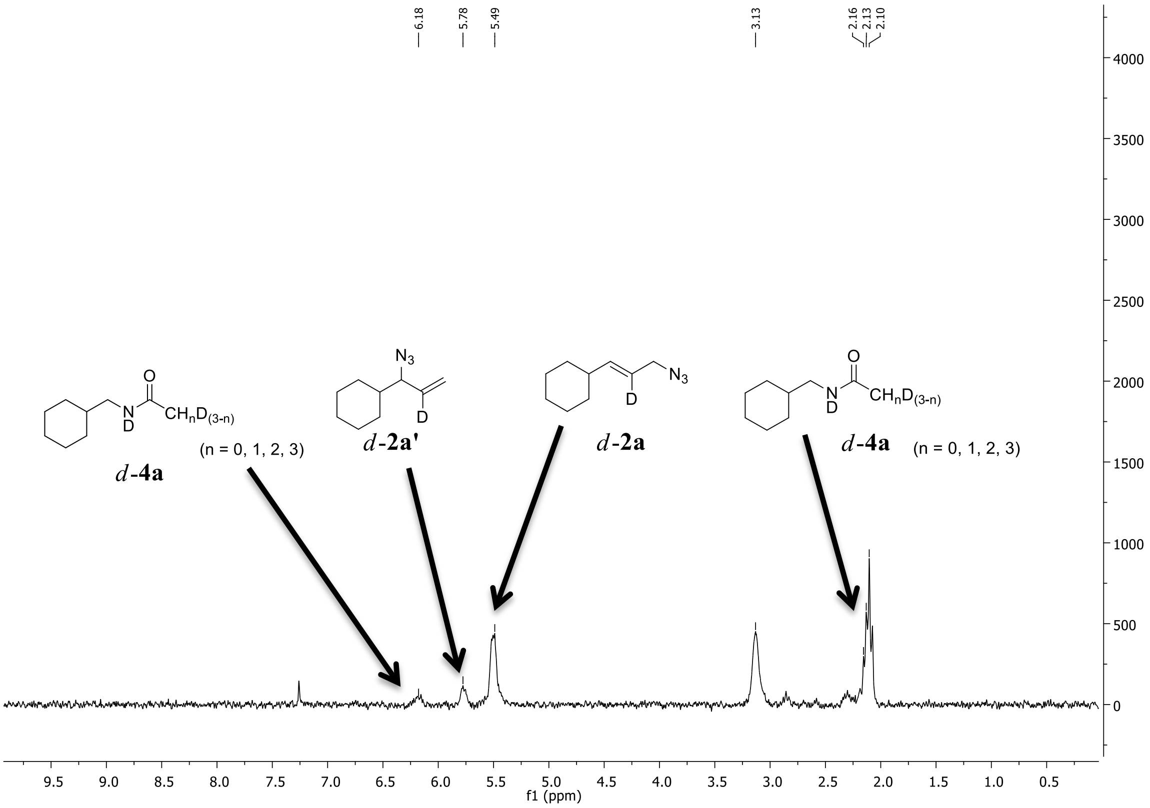
4a: we observed deuterium incorporation at the amidic proton 5.50 ppm, before purification and a mixture of d_0, d_1, d_2, d_3 in the signal at 1.98 ppm (methyl group).

Supporting Information

^{1}H NMR in $CDCl_3$:



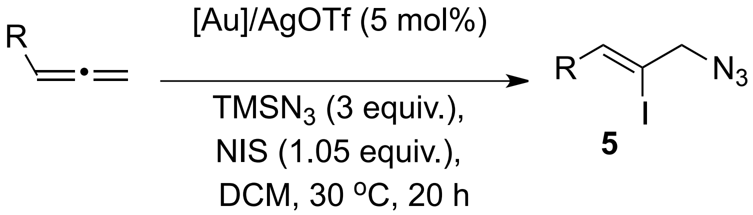
^{2}H NMR in $CHCl_3$:



Supporting Information

General procedure for gold-catalysed iodoazidation of allenes:

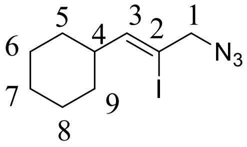
Gold(I)-complex (5 mol%), silver triflate (5 mol%) and NIS (1.05 Eq.) were added into a previously dried-vacuum schlenk flask under N_2. The corresponding allene (1 Eq.) in dry dichloromethane (0.1 M) and $TMSN_3$ (3 Eq.) were added and stirred for a few minutes at 0ºC. The mixture was then warmed up at 30 ºC and stirred at that temperature until complete conversion, followed by TLC. The crude was filtered through Celite, and washed with dichloromethane. The solvent was removed by vacuum, and the product was purified by column chromatography over silica gel using Hexane/Et_2O as eluent.



Entry	Allene	[Au]	Conversion (%)	Isolated yield (%)
1	R = Cy, **1a**	$(PhO)_3PAuCl$	71	--
2	R = Cy, **1a**	NHC-1	84	73, **5a**
3	R = Cy, **1a**	NHC-2	78	--
4	R = Cy, **1a**	NHC-3	83	65, **5a**
5	R = Cy, **1a**	Cat-Au SbF_6	46	--
6	R = Cy, **1a**	Ph_3PAuCl	100 (*E*/*Z* = 1:1)	60, *Z*-**5a**
7	R = *n*-octyl, **1c**	NHC-1	100	40, **5c**

[a] See Figure 1 in SI for structure of gold-complexes.

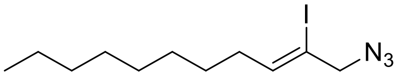
Vinyl-iodide **5a**



R_f in hexane/ethyl acetate (20:1): 0.73. ^{1}H NMR (400 MHz, $CDCl_3$, 25° C, TMS) δ = 5.68 (d, J = 8.6 Hz, 1H; H-3), 4.05 (s, 2H; H-1), 2.22-2.32 (m, 1H; H-4), 1.63-1.77 (m, 5H; H-5 to H-9), 1.11-1.40 (m, 5H; H-5 to H-9). ^{13}C NMR (101 MHz, $CDCl_3$, 25° C) δ = 145.09 (CH; C-3), 96.48 (C_q; C-2), 62.51 (CH_2; C-1), 45.05 (CH; C-4), 31.50 (2x CH_2; C-5 and C-9), 25.78 (CH_2; C-7), 25.46 (2x CH_2; C-6 and C-8). IR (Film, cm^{-1}): ṽ = 2926, 2815, 2096, 1635, 1448, 1318, 1260, 1060, 1029, 893, 838, 802, 689, 559. MS (ESI$^+$ in MeOH): *m/z* (%) = 264.0 $[M-N_2+H]^+$. HRMS (FTMS + APCI) (DCM + NH_4OAc) Calcd. for $C_9H_{18}IN_4$ $[M+NH_4]^+$, 309.0569. Found, 309.0571.

Supporting Information

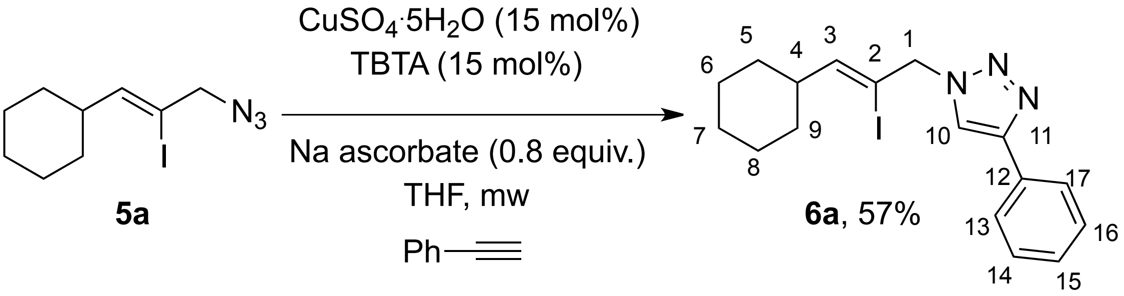
Vinyl-iodide **5c**



R_f in hexane/ethyl acetate (20:1): 0.68. ^{1}H NMR (500 MHz, $CDCl_3$, 25° C, TMS) δ = 5.87 (tt, J = 6.6, 0.9 Hz, 1H), 4.08 (s, 2H), 2.18 (m, 2H), 1.30-1.27 (m, 12H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, 25° C) δ = 139.21 (CH), 98.17 (C_q), 61.54 (CH_2), 34.91 (CH_2), 30.81 (CH_2), 28.35 (CH_2), 28.16 (CH_2), 28.08 (CH_2), 27.00 (CH_2), 21.63 (CH_2), 13.07 (CH_3). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3419, 2955, 2925, 2855, 2099, 1639, 1465, 1269, 1237, 1132, 889, 829, 722. MS (ESI$^+$ in MeOH): *m/z* = 321.0 $[M]^+$, 322.0 $[M+H]^+$. HRMS (FTMS ($DCM+NH_4OAc$)): Calcd. for $C_{11}H_{20}IN_3$ $[M^+]$, 321.0696. Found, 321.0693. Calculated for $C_{11}H_{21}IN$ $[M-N_2+H]^+$, 294.0713. Found, 294.0714.

Orthogonal functionalization of allenes by using the gold-catalysed azidation methodology

Click reaction of vinyl iodide 5a

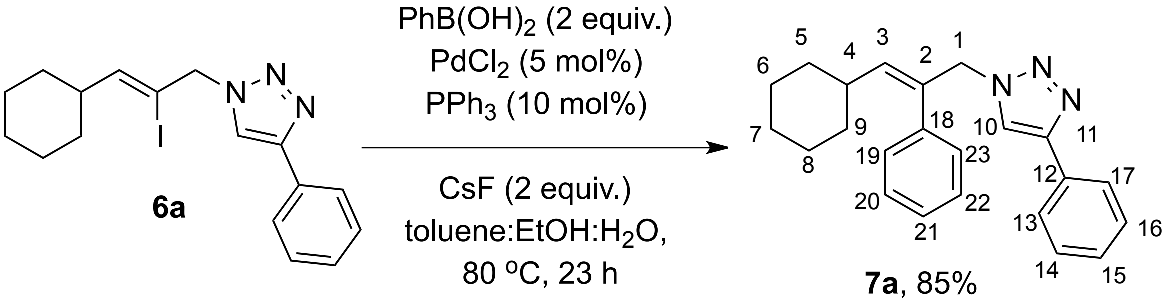


Copper (II) sulfate pentahydrate (15 mol%, 9 mg, 0.04 mmol), sodium ascorbate (0.8 Eq., 38 mg, 0.19 mmol) and tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA) (15 mol%, 19 mg, 0.04 mmol) were added into a (2.0-5.0 ml) microwave vial. To the solids (*Z*)-(3-azido-2-iodoprop-1-en-1-yl)cyclohexane **5a** (1.0 Eq., 70 mg, 0.24 mmol) dissolved in DMF (3 ml) and phenylacetylene (1.0 Eq., 30 µl, 0.24 mmol) were added. The suspension was heated in the microwave at 70 °C for 1h. The reaction mixture was quenched with water and extracted with dichloromethane (x 3). The combined organic phases were dried over anhydrous sodium sulfate and filtrated. After removing the solvent in vacuum the product was separated and purified by column chromatography over silica gel with hexane/ethyl acetate (5:1 then 3:1) as eluent. After evaporating the solvent **6a** was obtained as a pale yellow solid (54 mg, 57 %).

Supporting Information

^{1}H NMR (500 MHz, $CDCl_3$, 25° C, TMS) δ = 7.77 (d, J = 7.5 Hz, 2H; H-13 and H-17), 7.72 (s, 1H; H-10), 7.35 (t, J = 7.5 Hz, 2H; H-14 and H-16), 7.26 (t, J = 7.5 Hz, 1H; H-15), 5.70 (d, J = 8.5 Hz ,1H; H-3,), 5.17 (s, 2H; H-1), 2.20 (m, 1H; H-4), 1.65 (m, 4H; H-5 and H-9), 1.15 (m, 6H; H6, H-7 and H-8). ^{13}C NMR (126 MHz, $CDCl_3$, 25° C) δ = 147.92 (C_q; C-11), 146.46 (CH; C-3), 130.46 (C_q; C-12), 128.77 (2x CH_{Ar}; C-14 and C-16), 128.16 (CH_{Ar}; C-15), 125.73 (2x CH_{Ar}; C-13 and C-17), 119.54 (CH; C-10),95.32 (C_q; C-2), 61.70 (CH_2; C-1), 45.10 (CH; C-4),31.13 (2x CH_2; C-5 and C-9), 25.66 (CH_2; C-7),25.35 (2x CH_2; C-6 and C-8). IR (Film, cm^{-1}): $\tilde{\nu}$ = 509, 694, 762, 973, 1044, 1075, 1225, 1345, 1447, 1638, 2850, 2923, 3423. HRMS (FTMS (DCM / MeOH + NH_4OAc)): Calc. for $C_{17}H_{20}IN_3$ $[M+H]^+$, 394.0775. Found, 394.0775.

Suzuki-Miyaura cross-coupling of vinyl iodide 6a



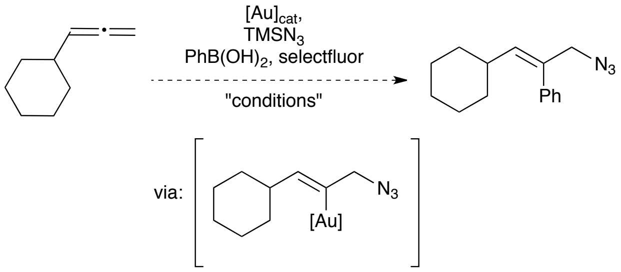
Phenylboronic acid (2.0 Eq., 22 mg, 0.18 mmol), $PdCl_2$ (5 mol%, 0.8 mg, 0.005 mmol), PPh_3 (10 mol%, 2.4 mg, 0.009 mmol) and CsF (2.0 Eq., 27 mg, 0.18 mmol) were added into a flushed schlenk flask under N_2. To the solids (Z)-1-(3-cyclohexyl-2-iodoallyl)-4-phenyl-1H-1,2,3-triazole **6a** (1.0 Eq., 36 mg, 0.09 mmol) dissolved in a mixture of toluene:EtOH:H_2O (1.3 ml : 1.3 ml : 0.4 ml) was added. The mixture was degassed by bubbling N_2 into the solution for 5 min and then stirred at 80 °C for 18h. The reaction mixture was quenched with water and extracted with dichloromethane (x 3). The combined organic phases were dried over anhydrous sodium sulfate and filtrated. After removing the solvent in vacuum the product was separated and purified by column chromatography over silica gel and hexane/ethyl acetate (5:1) as eluent. After evaporating the solvent **7a** was obtained as of a white-yellow solid (26 mg, 85 %).

Rf in hexane/ethyl acetate (3:1): 0.51. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.68 (dd, J = 7.4, 1.2 Hz, 2H; H-13 and H-17), 7.47 (s, 1H; H-10), 7.31(t, J = 7.4 Hz, 2H; H-14 and H-16), 7.27-7.20 (m, 2H; H-20 and H-22), 7.20-7.13 (m, 2H; H-15 and H-21), 7.00 (dd, J = 6.8, 1.5 Hz, 2H; H-19 and H-23), 5.54 (d, J = 10.1 Hz; 1H, H-3), 5.11 (s, 2H; H-1), 2.01 (m, 1H; H-4), 1.58 (m, 5H; H-5 to H-9), 1.06 (m, 5H; H-5 to H-9). ^{13}C NMR (126

MHz, CDCl3, 25 ºC) δ = 147.74 (C_q, C-11), 139.78 (CH; C-3), 137.55(C_q, C-18), 133.16 (C_q, C-2), 130.86 (C_q; C-12), 128.87 (2x CH_{Ar}), 128.67 (2x CH_{Ar}), 128.41 (2x CH_{Ar}), 128.13 (CH_{Ar}; C-15), 127.74 (CH_{Ar}; C-21), 125.80 (2x CH_{Ar}; C-13 and C-17), 119.51 (CH; C-10), 57.89 (CH_2; C-1), 37.68 (CH; C-4), 33.05 (2x CH_2; C-6 and C-8), 25.91 (CH_2; C-7), 25.53 (2x CH_2; C-5 and C-9). IR (Film, cm^{-1}): ṽ = 764, 973, 1646, 1675, 1225, 1338, 1444, 2850, 2924. HRMS (FTMS (DCM / MeOH + NH_4OAc)): Calc. for $C_{23}H_{25}N_3$ $[M+H]^+$, 344.2127. Found, 344.2121. M. p.: 129 ºC.

Attempts to trap the vinyl-gold intermediate via oxidative cross-coupling:

We have unsuccessfully attempted the reaction to engage the vinyl-gold intermediate in a cross-coupling reaction as reported by Zhang *et al.*[30] However, the substrates and reaction conditions reported by Zhang are quite different from our catalytic system and more detailed tuning of the reaction might be needed to get a successful outcome. Further efforts into this and other couplings are being made in our lab, as we believe that this transformation will indeed enhance the synthetic utility of this reaction.



- The oxidative cross-coupling was attempted using **Zhang's conditions**:

Ph_3PAuCl, (0.05 Eq., 10 mg, 0.02 mmol), selectfluor (2 Eq., 290 mg, 0.82 mmol), $PhB(OH)_2$ (4 Eq., 200 mg, 1.64 mmol) were added into a previously dried-vacuum schlenk flask under N_2. The solids were dissolved in dry acetonitrile / H_2O (20:1) (0.05 M) and stirred for a few minutes at 0 ºC. Then, allene **1a** (1 Eq., 60 µl, 0.41 mmol) was added drop wise neat at 0 ºC and under stirring. $TMSN_3$ (3 Eq., 161 µl, 1.23 mmol), was then added drop wise at 0 ºC. The mixture was then warmed up at 80 ºC . The reaction was followed by TLC, and after 6 h the crude was filtered through Celite and a pad $MgSO_4$, and washed with dichloromethane. The solvent was removed under vacuum, and the crude was

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[30] G. Zhang, Y. Peng, L. Cui, and L. Zhang, *Angew. Chem. Int. Ed.*, **2009**, *48*, 3112-3115.

analysed by NMR. No signals corresponding of the expected product were observed. The allene signals disappeared possibly by decomposition at 80 ^{o}C.

- A second experiment was carried out under the conditions of **our azidation reaction**: $(PhO)_3PAuCl$, (0.05 Eq., 11 mg, 0.02 mmol), silver triflate (0.05 Eq., 5 mg, 0.02 mmol), selectfluor (2 Eq., 290 mg, 0.82 mmol), $PhB(OH)_2$ (4 Eq., 200 mg, 1.64 mmol) were added into a previously dried-vacuum schlenk flask under N_2. The solids were dissolved in dry DCM (0.41 M) and stirred for a few minutes at 0 ºC. Then, allene **1a** (1 Eq., 60 µl, 0.41 mmol) was added drop wise neat at 0 ºC and under stirring. $TMSN_3$ (3 Eq., 161 µl, 1.23 mmol), was then added drop wise at 0 ºC. The mixture was then warmed up and stirred at room temperature. The reaction was followed by TLC, and after 6 h the crude was filtered through Celite, and washed with dichloromethane. The solvent was removed under vacuum and the crude was analysed by NMR. Signals of the unreacted allene and phenyl boronic acid were observed.

Supporting Information

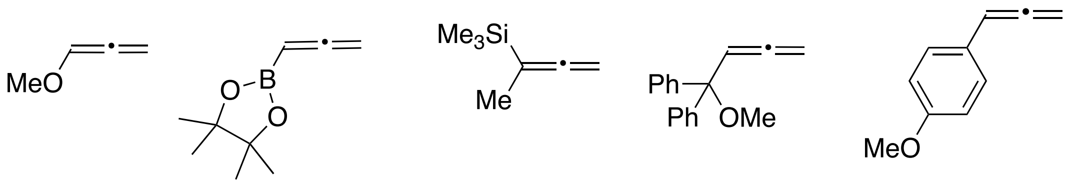
Allenes that did not work in the reaction

Allenes bearing oxygen and groups sensitive to acidic conditions gave decomposition products (equation a).

Interestingly, ethyl 2,3-butanodionate and ethyl 2,3-pentanodionate gave very slow reaction and only traces of the corresponding allyl azides were observed after 5 days of reaction (equation b).

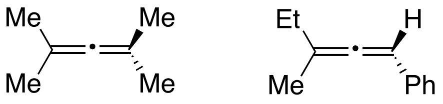
Tri- and tetra-substituted allenes gave traces of the azidation products, but side reactions are observed. More investigations are being carried out in our lab with these allenes (equation c).

a)



b)

c)



Supporting Information

Synthesis of gold-azide complex

$(PhO)_3PAuCl$ (15 mg, 0.027 mmol, 1 Eq.), and AgOTf (7 mg, 0.027 mmol, 1 Eq.) were dissolved in DCM (2 ml) under N_2. An excess of $TMSN_3$ (29 μl, 0.216 mmol, 8 Eq.) was added and the mixture stirred at room temperature for 1h. The mixture was filtered through celite, the solvent was evaporated and the solid washed with hexane to remove excess of azide to give $(PhO)_3PAuN_3$ as a gummy oil. This complex has to be kept in the fridge and in the dark and decomposes very quickly. No HRMS could be obtained due to fast decomposition. All the attempts to crystallise the complex have failed so far.

^1H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS): $\delta = 7.43$ (app t, $J = 7.4$ Hz, 2H), 7.31 (tq, $J = 7.4, 1.2$ Hz, 1H), 7.23 (app dd, $J = 7.4, 1.2$ Hz, 2H). ^{31}P NMR (202 MHz, $CDCl_3$, 25° C): $\delta = 105.80$ ppm. IR (Film, cm^{-1}): $\tilde{\nu} = 2059.66$ (υ_{as} N_3^-).[31]

Stoichiometric NMR Experiments

Three parallel experiments were designed using stoichiometric amounts of all the components and the order of addition of the different components of the reaction were varied as follows:

A) $(PhO)_3PAuCl$ + AgOTf + $TMSN_3$ + Allene **1a** + TFA + H_2O

B) $(PhO)_3PAuCl$ + AgOTf + Allene **1a** + $TMSN_3$ + TFA

C) $(PhO)_3PAuCl$ + AgOTf + TFA + $TMSN_3$ + Allene **1a**

^1H, ^{31}P NMR and ^{19}F NMR spectra were recorded at room temperature after each addition and after several time intervals in between additions.

The following amounts were used in $CDCl_3$ (0.7 ml):

$(PhO)_3PAuCl$ (5 mg, 0.009 mmol)

AgOTf (2 mg, 0.009 mmol)

$TMSN_3$ (1 μl, 0.009 mmol)

Allene **1a** (1 mg, 0.009 mmol)

TFA (1 μl, 0.009 mmol)

H_2O (1 μl, 0.05 mmol, 6 Eq.)

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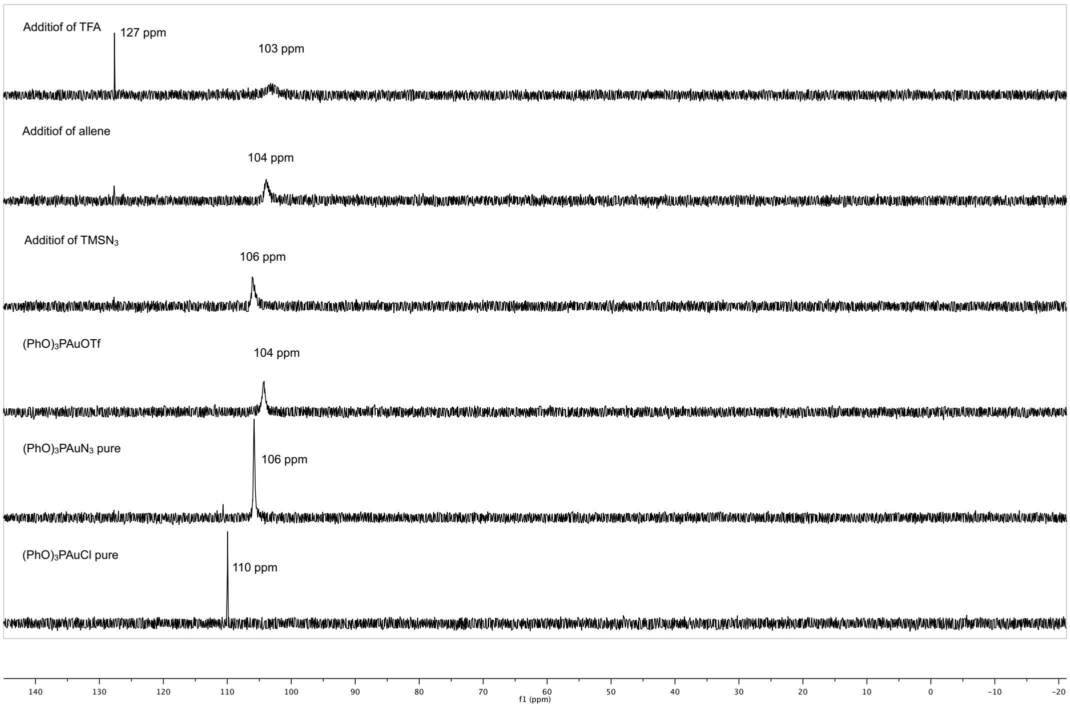
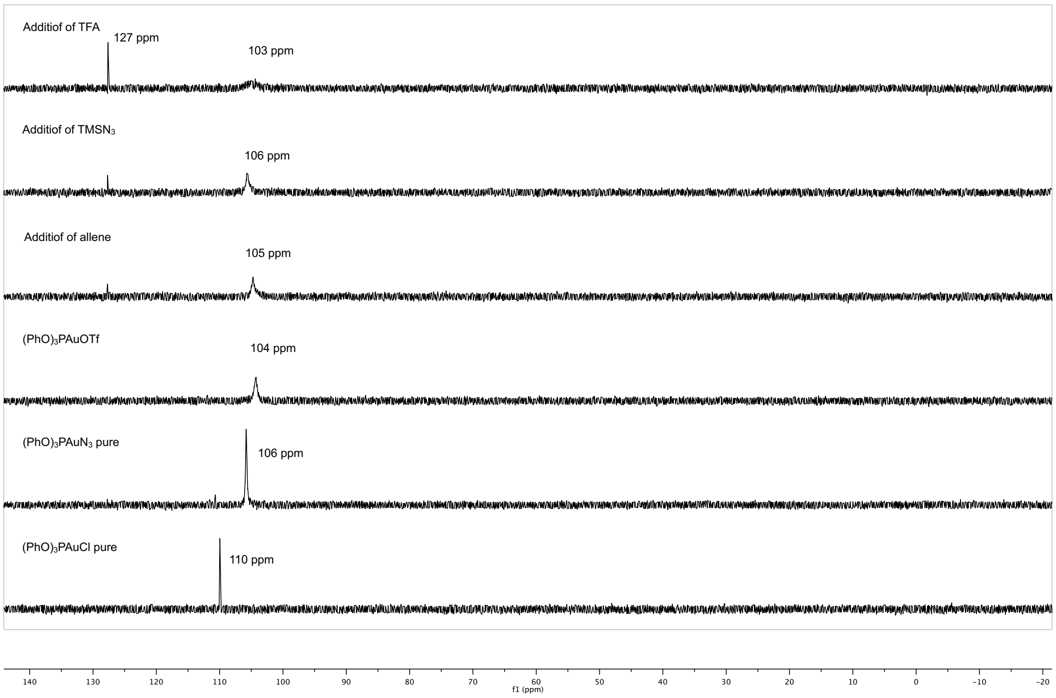
[31] R_3PAuN_3 complexes have been reported with similar IR bands, for Ph_3PAuN_3 (2050 cm^{-1}), see: W. Beck *et al.*, *Z. Anorg. Allg. Chem.*, 2001, **627**, 1669-1674; for Cy_3PAuN_3 (2049 cm^{-1}), see: D. V. Partyka, *PNAS*, 2008, **105**, 14293-14297.

Supporting Information

^{31}P NMR profile of Experiment A:

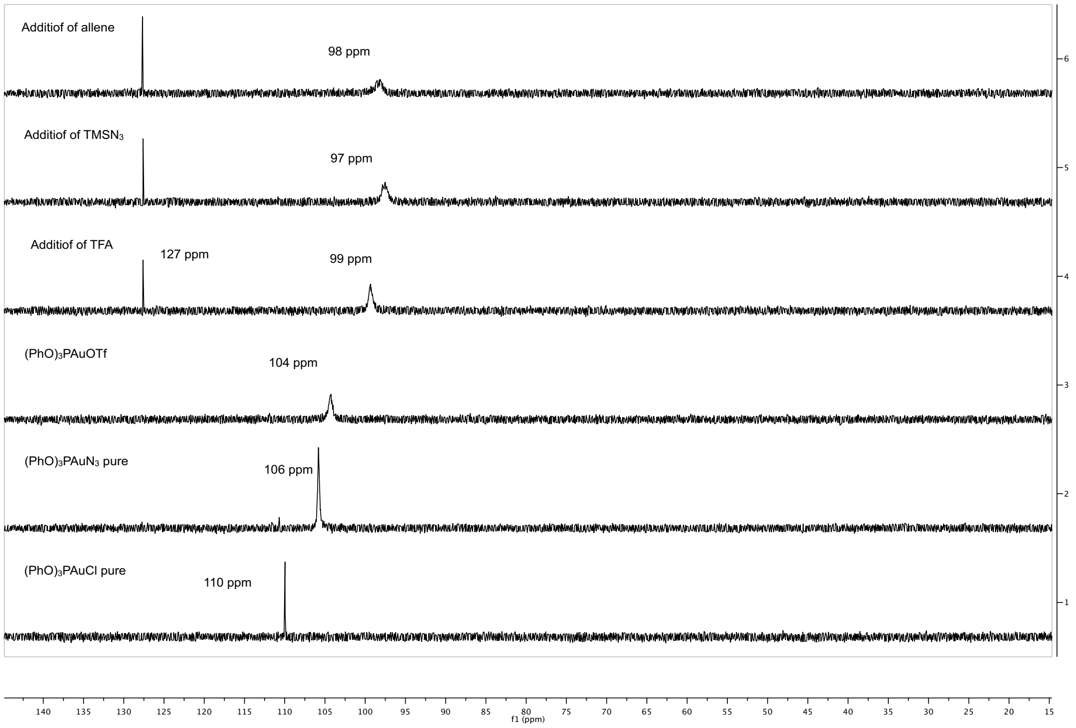


^{31}P NMR profile of Experiment B:



Supporting Information

^{31}P NMR profile of Experiment C:



Supporting Information

^{1}H NMR profile of Experiment A:

The signals used to measure integrals are:

Allene **1a**: 5.07 ppm (q, *J* = 6.5 Hz, 1H)

E-Allyl azide **2a**: 3.69 ppm (d, *J* = 6.70 Hz, 2H)

Allyl azide **2a'**: 3.60 ppm (t, *J* = 7.73 Hz, 1H)

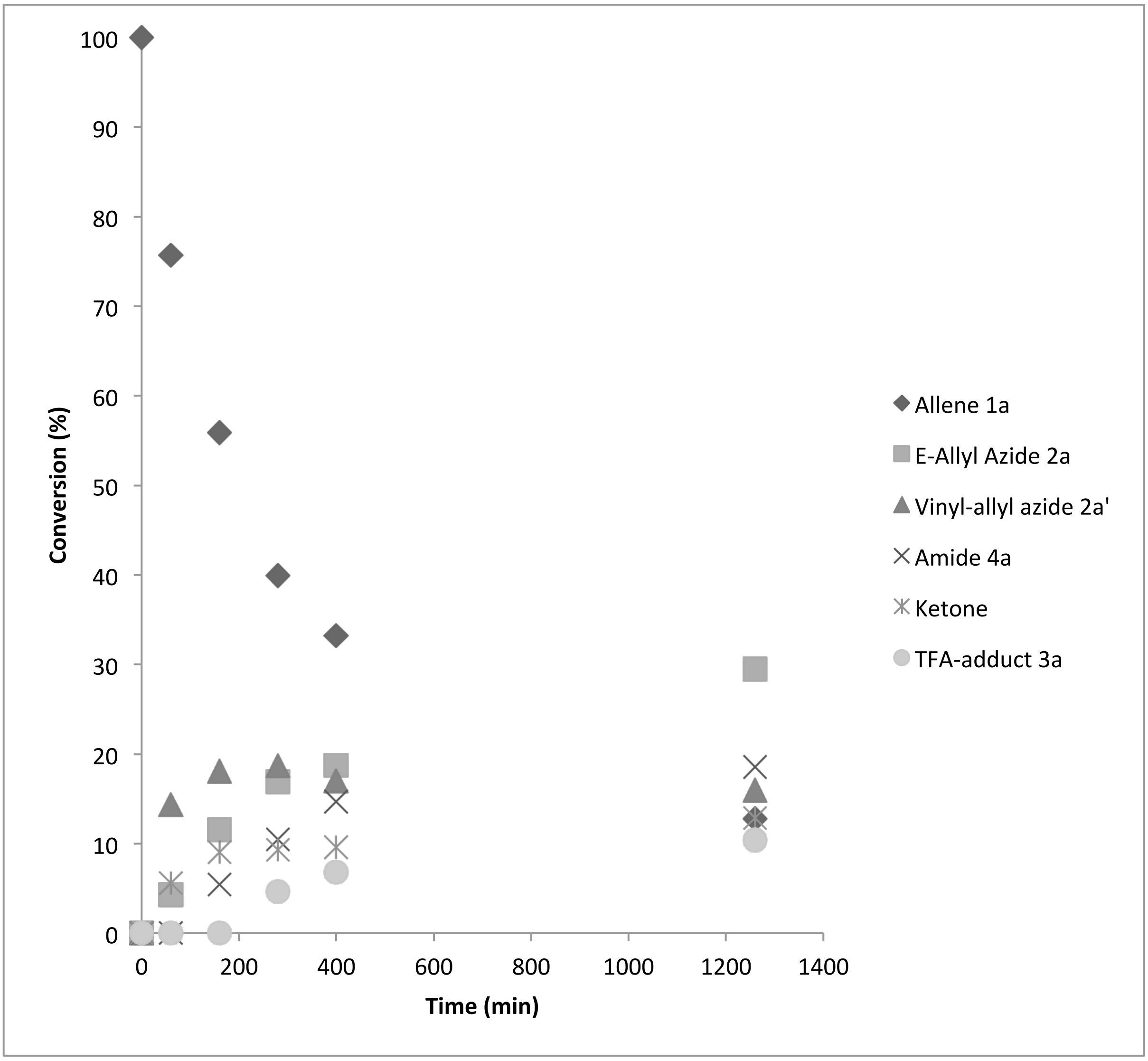
Amide **4a**: 3.10 ppm (t, *J* = 6.44 Hz, 2H)

Ketone: 3.38 ppm (m, 2H)

TFA-adduct **3a**: 4.77 (d, *J* = 6.76 Hz, 2H)

		^{1}H NMR integral (1 H)					
Addition	**time (min)**	**Allene 1a**	**E-Allyl Azide 2a**	**Allyl azide 2a'**	**Amide 4a**	**Ketone**	**TFA-adduct 3a**
AgOTf	0						
	30						
$TMSN_3$	75						
	105						
Allene	145						
	205	5.27	0.3	1	0	0.39	0
TFA	285				0		
	305	3.09	0.64	1	0.3	0.5	0
	425	2.14	0.90	1	0.56	0.5	0.25
H_2O	485						
	545	1.96	1.10	1	0.86	0.56	0.4
	1405	0.8	1.84	1	1.16	0.80	0.65
		Conversion (%)					
Addition	**Time (min)**	**Allene 1a**	**E-Allyl Azide 2a**	**Allyl azide 2a'**	**Amide 4a**	**Ketone**	**TFA-adduct 3a**
AgOTf							
$TMSN_3$							
Allene	0	100	0	0	0	0	0
	60	75.72	4.31	14.37	0.00	5.60	0.00
TFA							
	160	55.88	11.57	18.08	5.42	9.04	0.00
	280	39.96	16.90	18.67	10.46	9.34	4.67
H_2O							
	400	33.25	18.74	16.96	14.67	9.58	6.79
	1260	12.78	29.47	15.97	18.53	12.86	10.38

Supporting Information

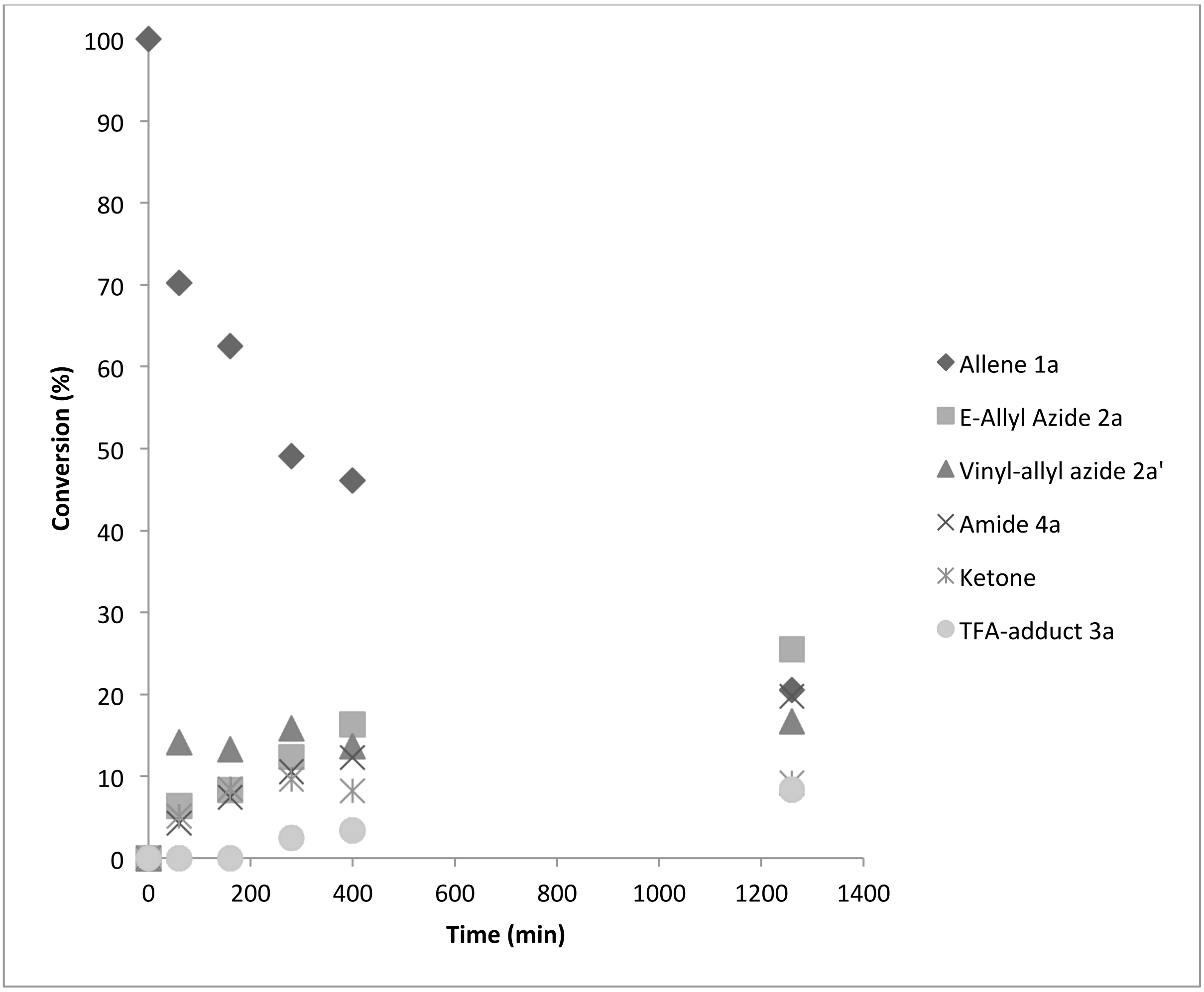


Supporting Information

^{1}H NMR profile of Experiment B:

		^{1}H NMR integral (1 H)					
Addition	**Time (min)**	**Allene 1a**	**E-Allyl Azide 2a**	**Allyl azide 2a'**	**Amide 4a**	**Ketone**	**TFA-adduct 3a**
AgOTf	0						
	30						
Allene	75						
	105						
TMSN$_3$	145						
	205	4.97	0.45	1	0.3	0.36	0
TFA	285						
	305	4.71	0.62	1	0.56	0.63	0
	425	3.09	0.78	1	0.66	0.60	0.15
	545	3.37	1.19	1	0.89	0.6	0.25
	1405	1.23	1.52	1	1.18	0.55	0.5
		Conversion (%)					
Addition	**Time (min)**	**Allene 1a**	**E-Allyl Azide 2a**	**Allyl azide 2a'**	**Amide 4a**	**Ketone**	**TFA-adduct 3a**
AgOTf							
Allene							
TMSN$_3$	0	100	0	0	0	0	0
	60	70.20	6.36	14.12	4.24	5.08	0.00
TFA							
	160	62.55	8.30	13.28	7.44	8.43	0.00
	280	49.09	12.39	15.89	10.56	9.61	2.46
	400	46.10	16.35	13.68	12.24	8.21	3.42
	1260	20.55	25.48	16.71	19.72	9.19	8.35

Supporting Information

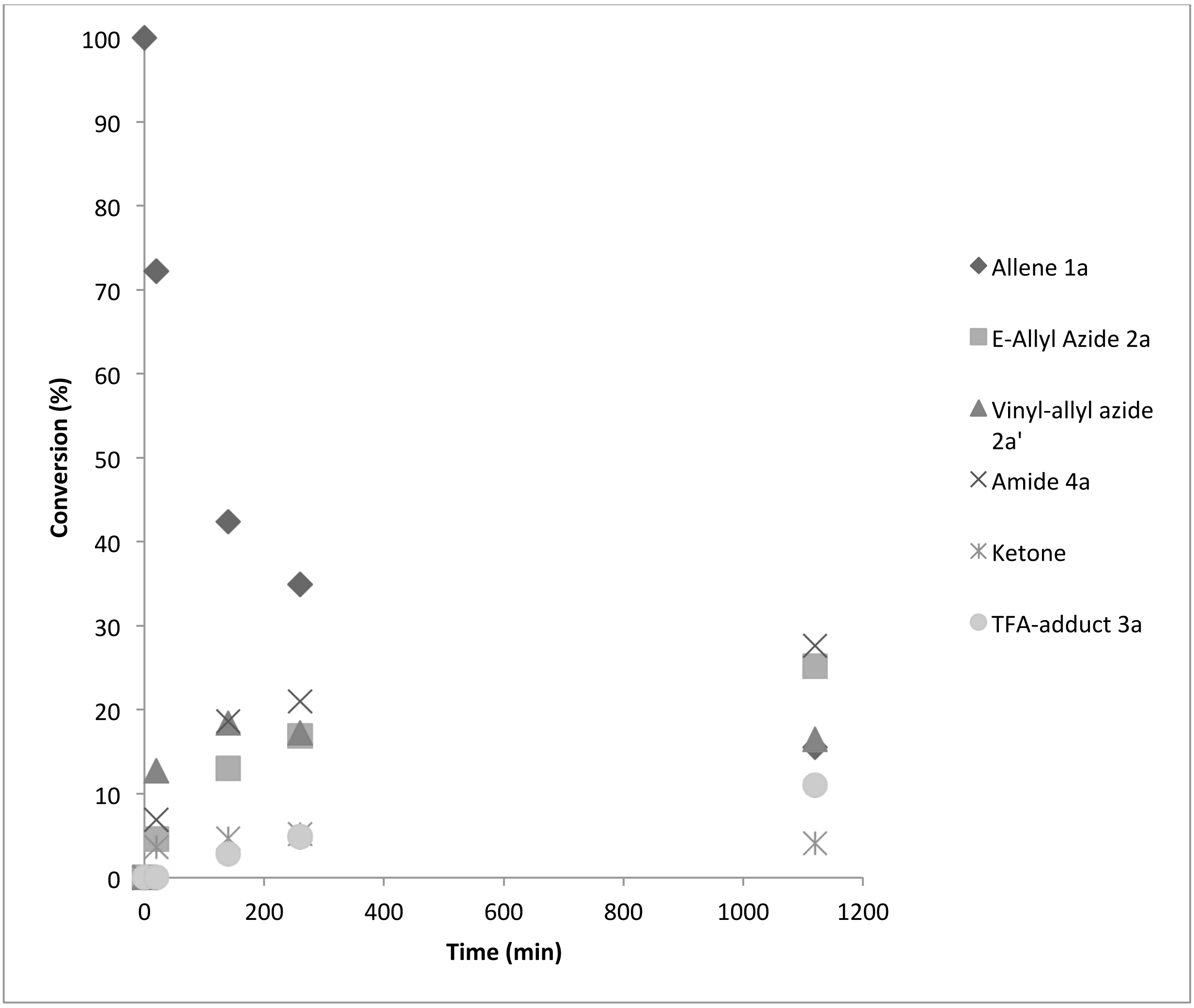


Supporting Information

^{1}H NMR profile of Experiment C:

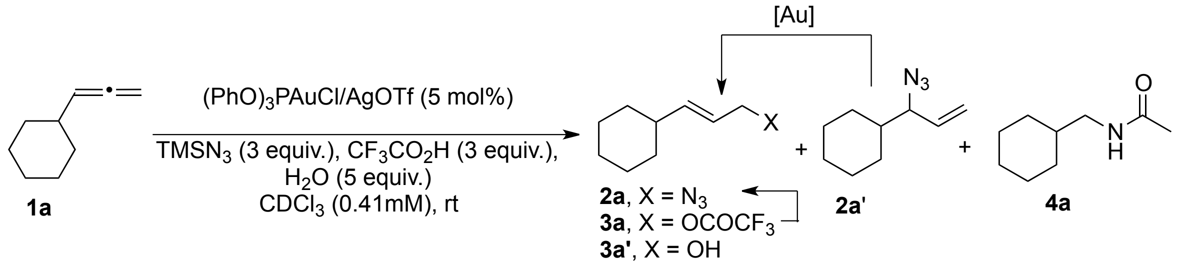
		^{1}H NMR integral					
Addition	**time (min)**	**Allene 1a**	**E-Allyl Azide 2a**	**Allyl azide 2a'**	**Amide 4a**	**Ketone**	**TFA-adduct 3a**
AgOTf	0						
	30						
TFA	75						
	105						
$TMSN_3$	145						
	205						
Allene	285						
	305	5.68	0.36	1	0.54	0.28	0
	425	2.3	0.70	1	1.01	0.25	0.15
	545	2.03	0.98	1	1.22	0.3	0.28
	1405	0.94	1.53	1	1.68	0.25	0.67
		Conversion (%)					
Addition	**Time (min)**	**Allene 1a**	**E-Allyl Azide 2a**	**Allyl azide 2a'**	**Amide 4a**	**Ketone**	**TFA-adduct 3a**
AgOTf							
TFA							
$TMSN_3$							
Allene	0	100	0	0	0	0	0
	20	72.17	4.64	12.71	6.86	3.62	0.00
	140	42.40	13.00	18.43	18.62	4.70	2.86
	260	34.91	16.85	17.20	20.98	5.16	4.90
	1120	15.56	25.19	16.46	27.65	4.12	11.03

Supporting Information



Supporting Information

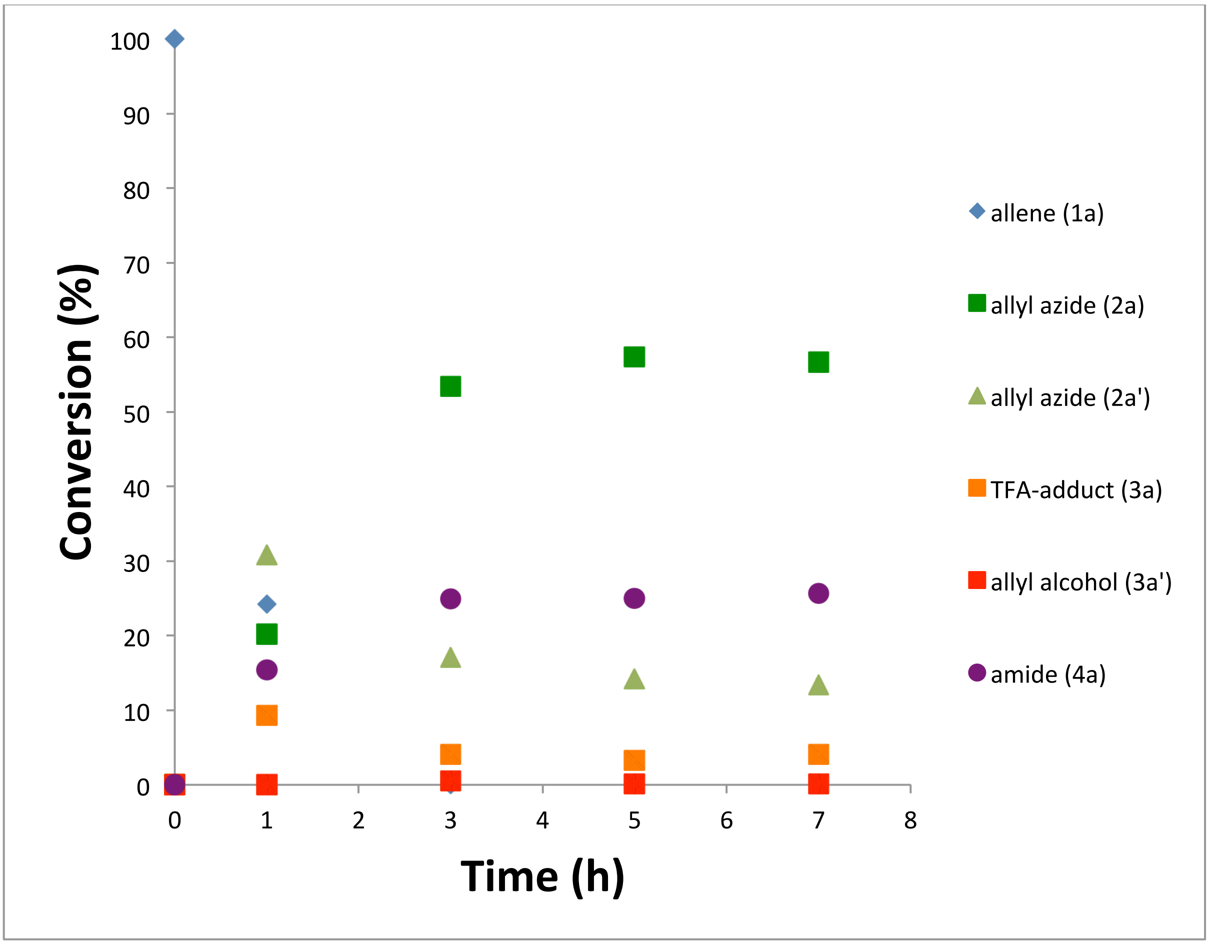
Catalytic NMR experiment:



$(PhO)_3PAuCl$, (0.05 Eq., 22 mg, 0.04 mmol), silver triflate, (0.05 Eq., 10.5 mg, 0.04 mmol) and (1 Eq., 119 µl, 0.82 mmol) of allene **1a** in $CDCl_3$ (2.0 ml, 0.41 mM) were added into a previously dried-vacuum schlenk flask under N_2 and stirred for a few minutes at 0ºC. $TMSN_3$, (3 Eq., 323 µl, 2.45 mmol), distilled water, (5 Eq., 74 µl, 4.09 mmol), and trifluoroacetic acid, (3 Eq., 196 µl, 114.02 mmol) were added drop wise at 0ºC. The mixture was then warmed up and stirred at room temperature during 22h. Samples (0.1 mL) were extracted directly from the schlenk according to the time with a syringe and diluted with $CDCl_3$ for the NMR experiment.

	^{1}H NMR integrals (1H)					
Time (h)	**Allene 1a**	**Allyl Azide 2a**	**Allyl Azide 2a'**	**3a (TFA)**	**3a' (OH)**	**Amide 4a**
0	1	0	0	0	0	0
1	0.785	0.65	1	0.3	0	0.5
3	0	3.12	1	0.24	0.03	1.46
5	0	4.03	1	0.23	0.01	1.75
7	0	4.21	1	0.3	0.01	1.91
9	0	4.38	1	0.33	0.11	2.17
11	0	4.23	1	0.33	0.11	2.12
22	0	4.22	1	0.35	0.12	1.71
	Conversion (%)					
Time (h)	**Allene 1a**	**Allyl Azide 2a**	**Allyl Azide 2a'**	**3a (TFA)**	**3a' (OH)**	**Amide 4a**
0	100	0	0	0	0	0
1	24.23	20.22	30.86	9.26	0.00	15.43
3	0.00	53.37	17.08	4.10	0.51	24.94
5	0.00	57.37	14.23	3.27	0.14	24.98
7	0.00	56.66	13.46	4.04	0.13	25.71
9	0.00	54.85	12.51	4.13	1.38	27.14
11	0.00	54.30	12.84	4.24	1.41	27.21
22	0.00	57.03	13.51	4.73	1.62	23.11

Supporting Information



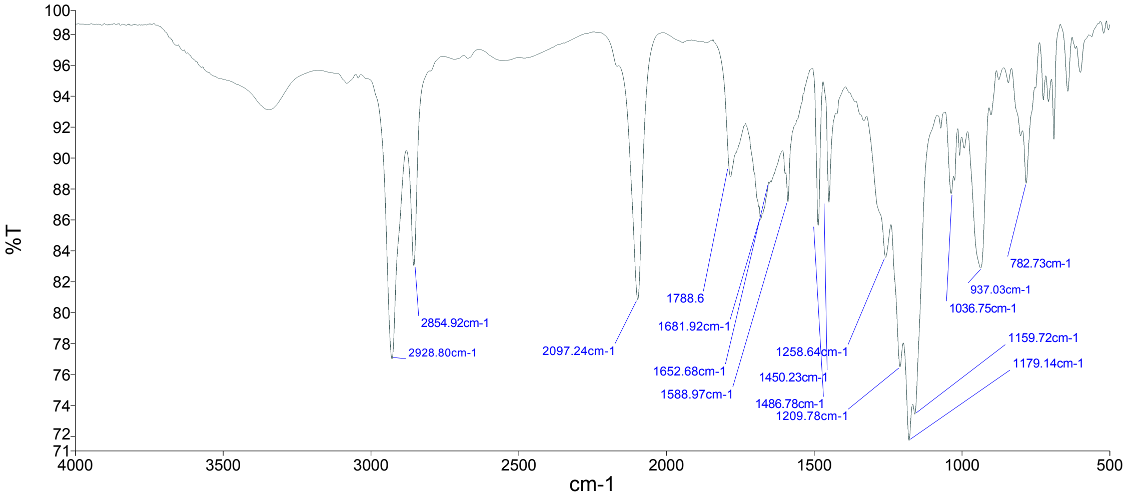
Supporting Information

Catalytic IR experiment:

$(PhO)_3PAuCl$, (0.14 Eq., 31 mg, 0.06 mmol) and silver triflate (0.14 Eq., 15 mg, 0.06 mmol) were added into a previously dried-vacuum schlenk flask under N_2. The solids were dissolved in $CDCl_3$ dry over molecular sieves (3A) (0.41 M) and stirred for a few minutes at 0 ºC. Then, allene **1a** (1 Eq., 60 µl, 0.41 mmol) was added drop wise neat at 0 ºC and under stirring. $TMSN_3$ (3 Eq., 161 µl, 1.23 mmol), distilled water (5 Eq., 37 µl, 2.05 mmol), and trifluoroacetic acid (3 Eq., 98 µl, 1.23 mmol) were then added drop wise at 0 ºC. The mixture was then warmed up and stirred at room temperature. Drops of the reaction mixture were transferred directly form the schlenk to the IR disc according to the time, and the IR experiments were run neat in the following minutes.

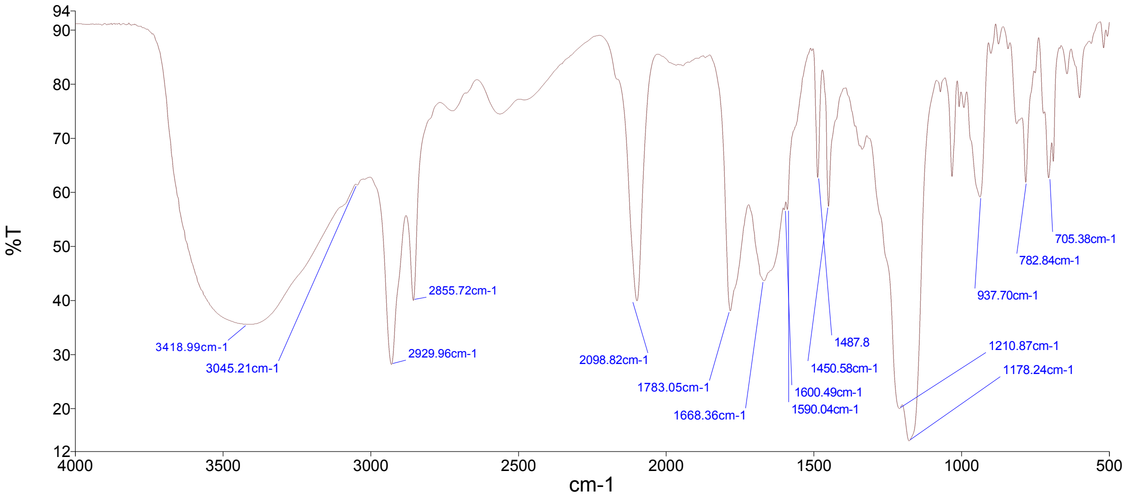
Copies of the IR spectra at some of the times analysed are shown below: The peak of the azide in the final product (2097 cm^{-1}) is observed from the beginning of the reaction, overlapping with the possible peak of the Au-N_3 at 2060 cm^{-1}. No clear conclusion about the formation of Au-N_3 complexes can be extracted from this experiment.

30 min

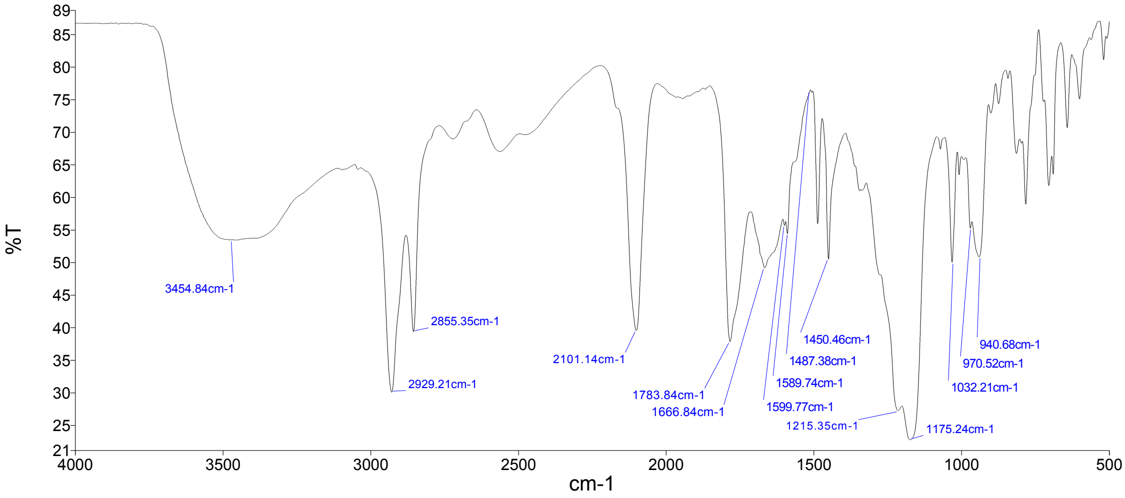


Supporting Information

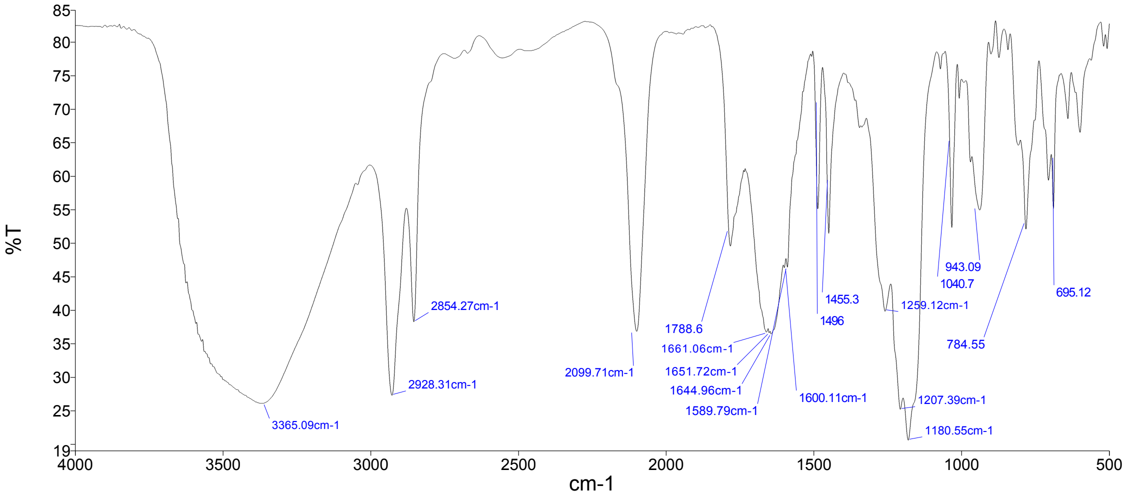
1h 45 min



6 h



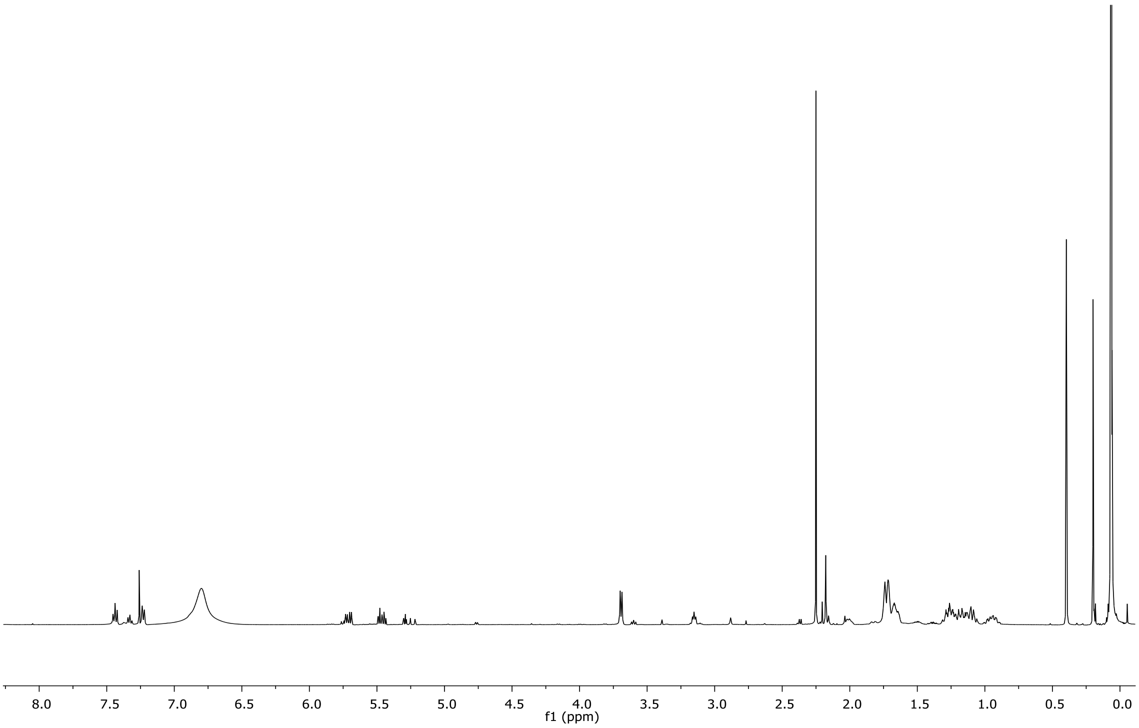
9h 30 min



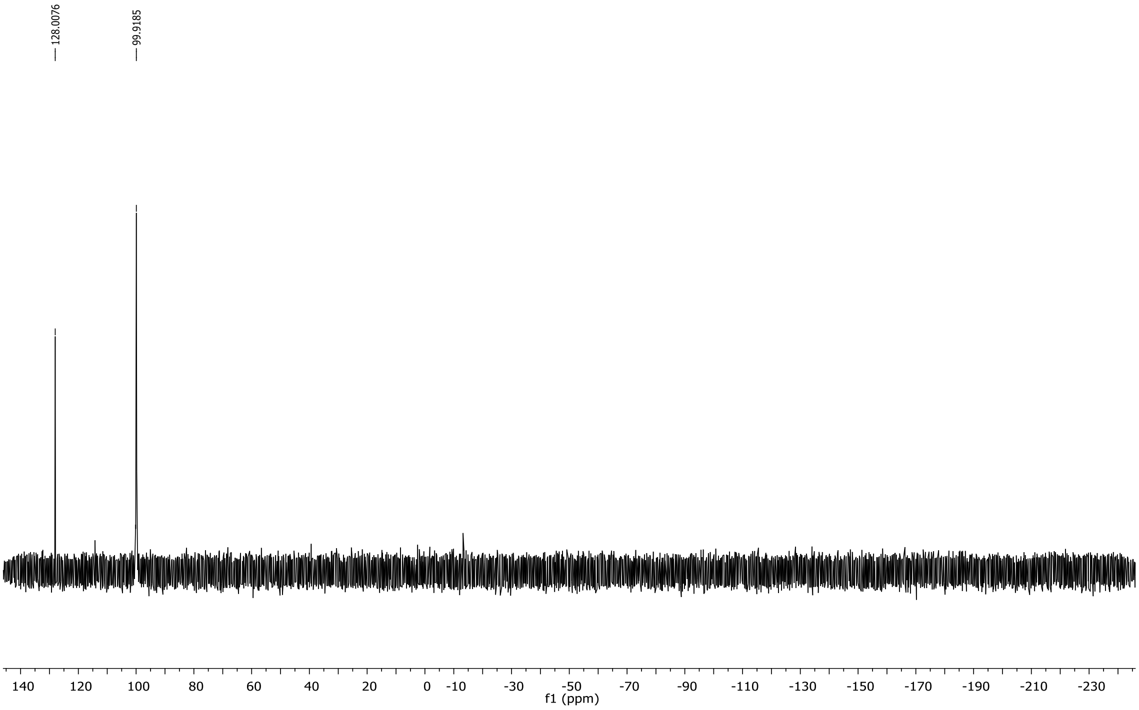
Supporting Information

After 9.5 h, the mixture was filtered through celite, and analysed directly by ^{1}H and ^{31}P NMR. The spectra are shown bellow and are consistent with the previous experiments.

^{1}H NMR (Crude of reaction, 9h 30 min)



^{31}P NMR (Crude of reaction, 9h 30 min)



SI – NMR Spectra

New Gold-Catalysed Azidation of Allenes

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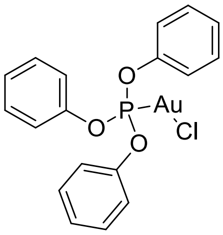
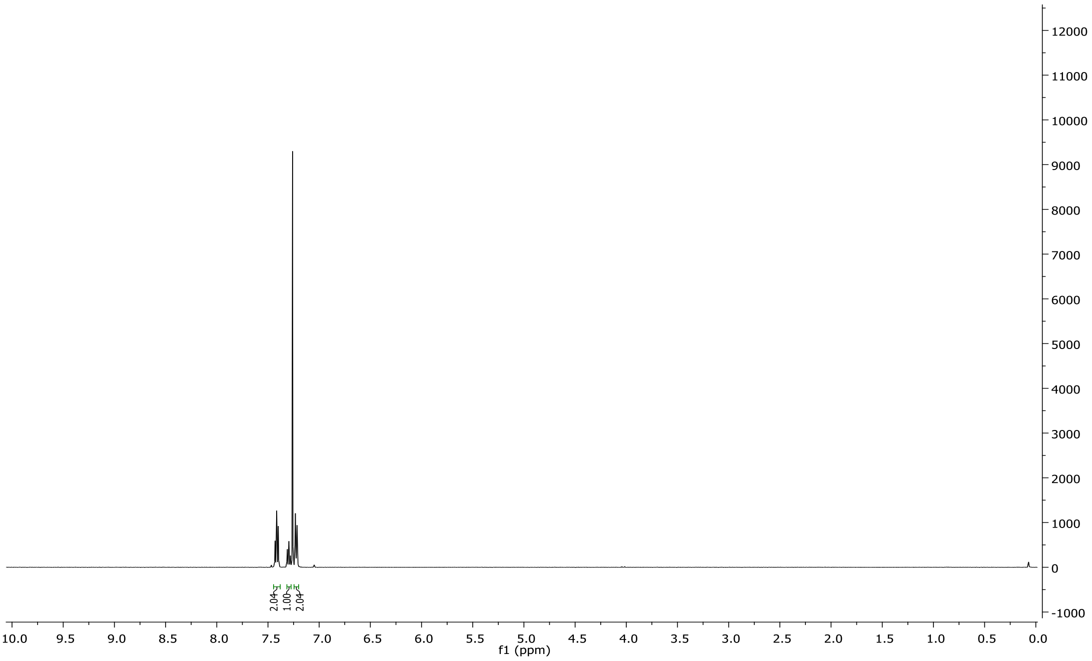
NMR Spectra

SI – NMR Spectra

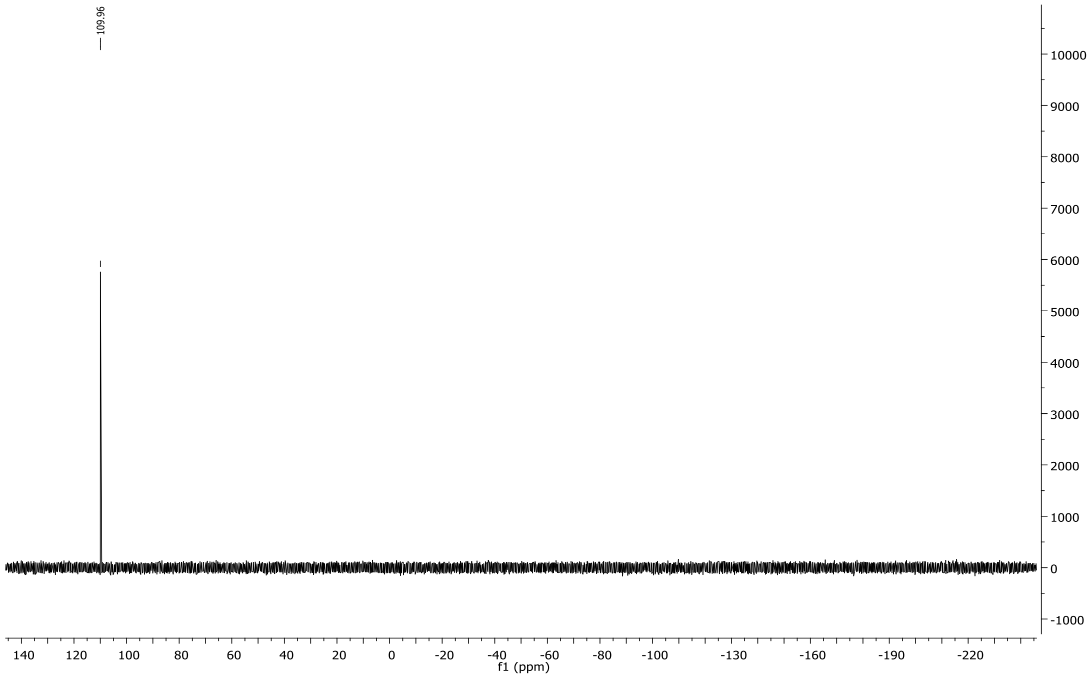
Chloro (triphenylphosphite) gold (I)



^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

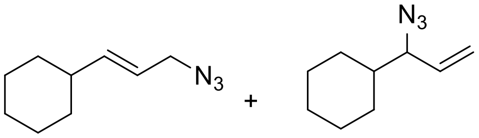


^{31}P NMR (202 MHz, $CDCl_3$, 25 ^{o}C)

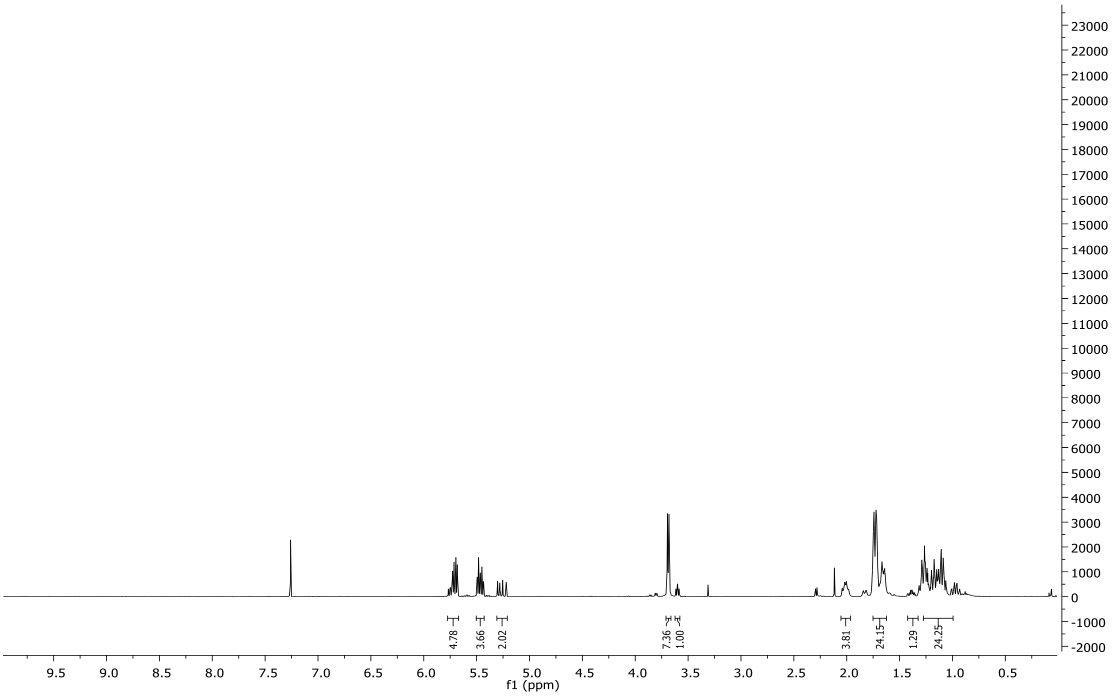


SI – NMR Spectra

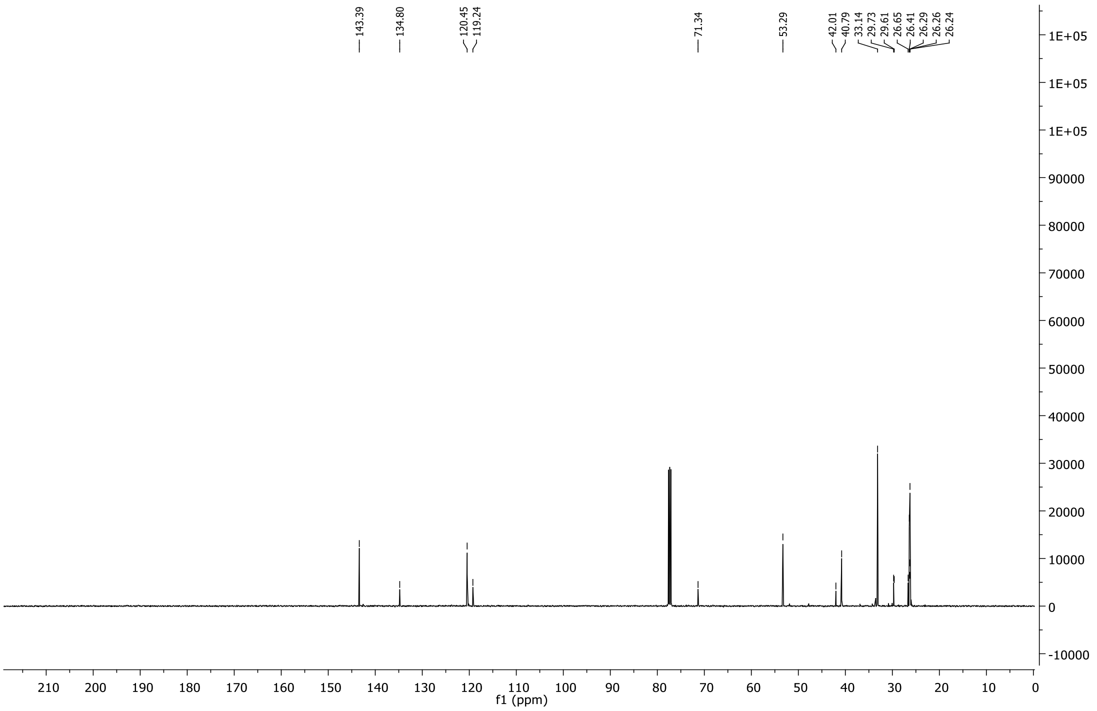
Allyl azides **2a** and **2a'** (3.7:1):



^{1}H NMR (500 MHz, CDCl$_3$, 25 ^{o}C)

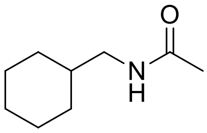


^{13}C NMR (126 MHz, CDCl$_3$, 25 ^{o}C)

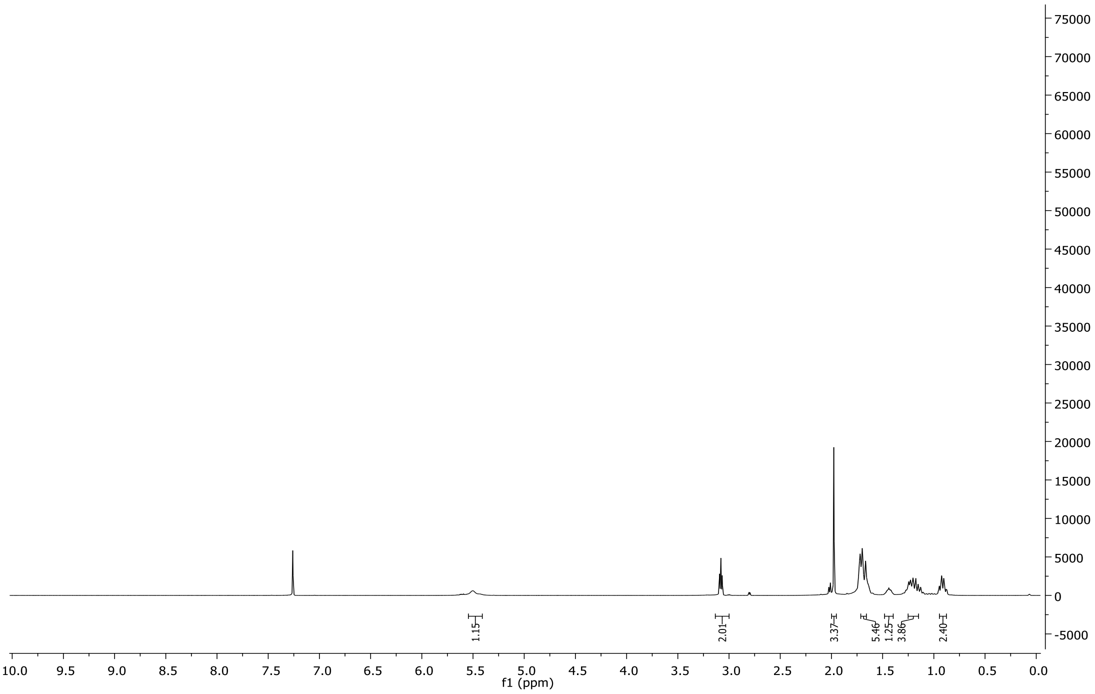


SI – NMR Spectra

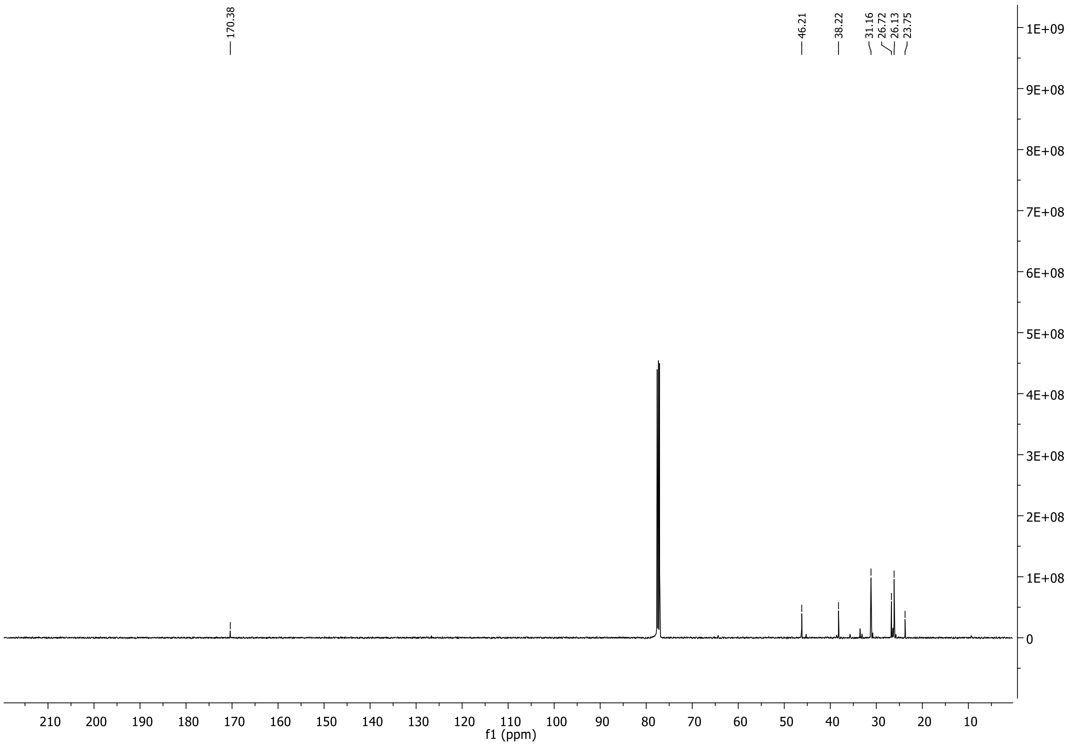
Amide **4a:**



^{1}H NMR (500 MHz, CDCl$_3$, 25 ^{o}C)

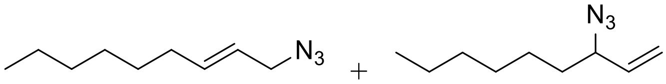


^{13}C NMR (126 MHz, CDCl$_3$, 25 ^{o}C)

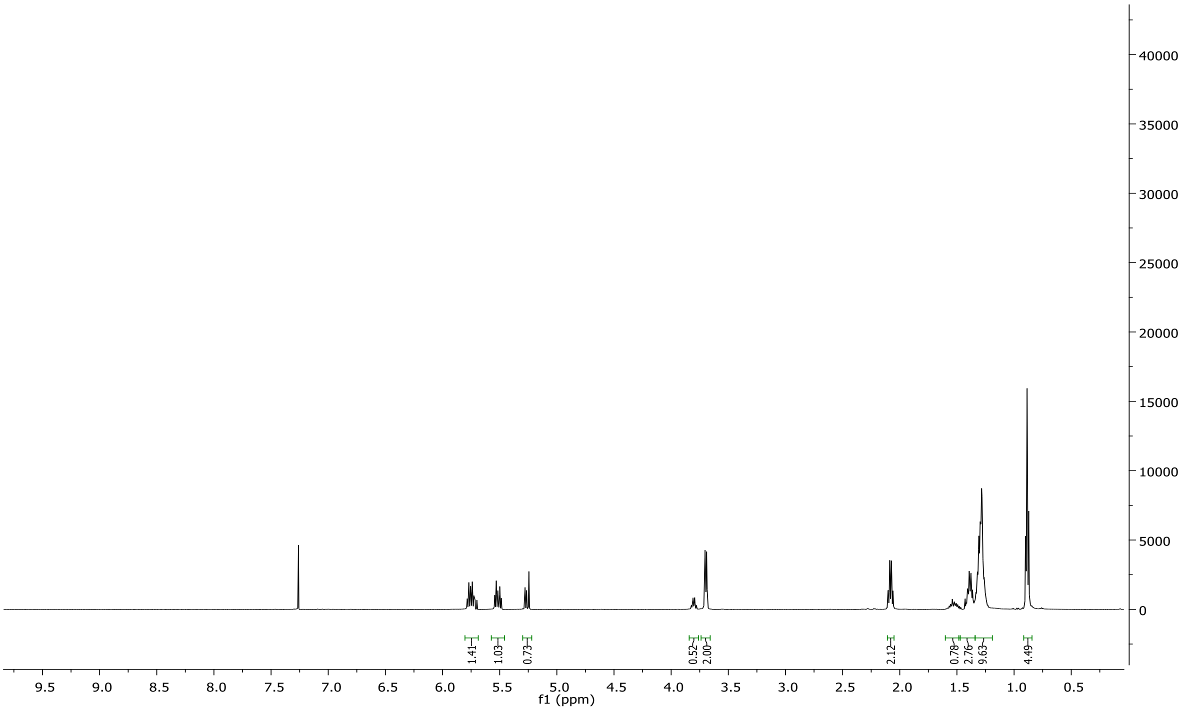


SI – NMR Spectra

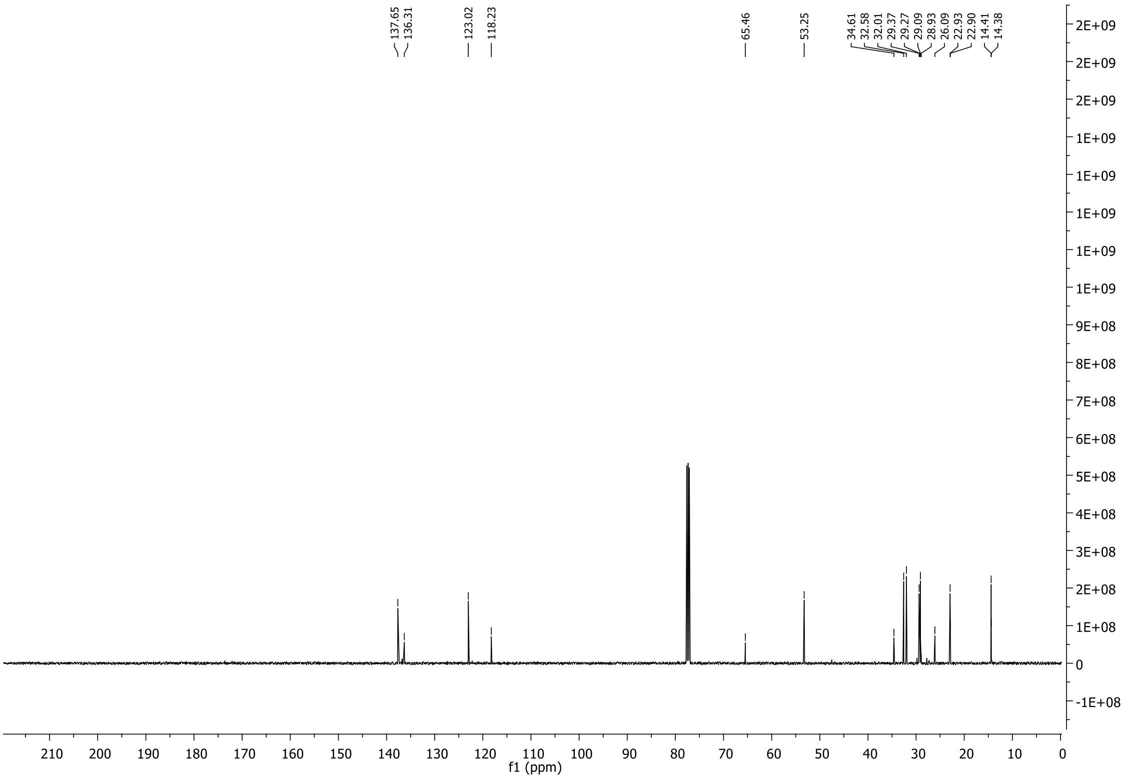
Allyl azides **2b** and **2b'** (1.9:1):



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C)

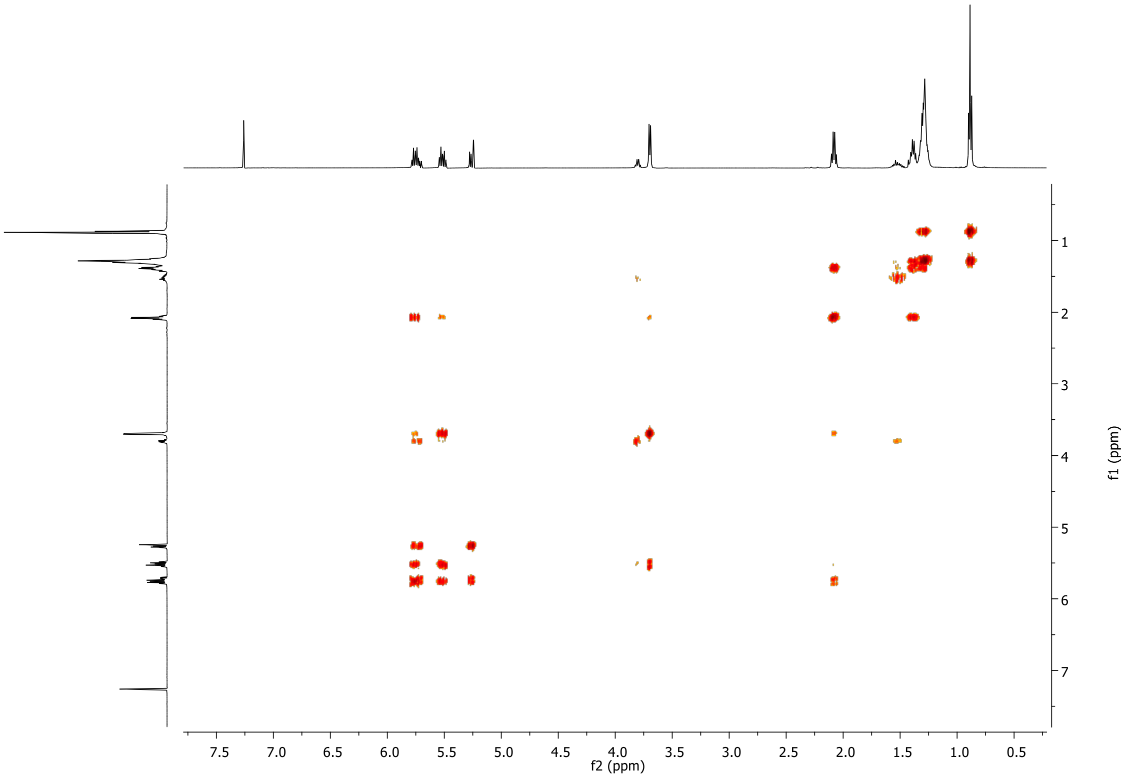


^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)

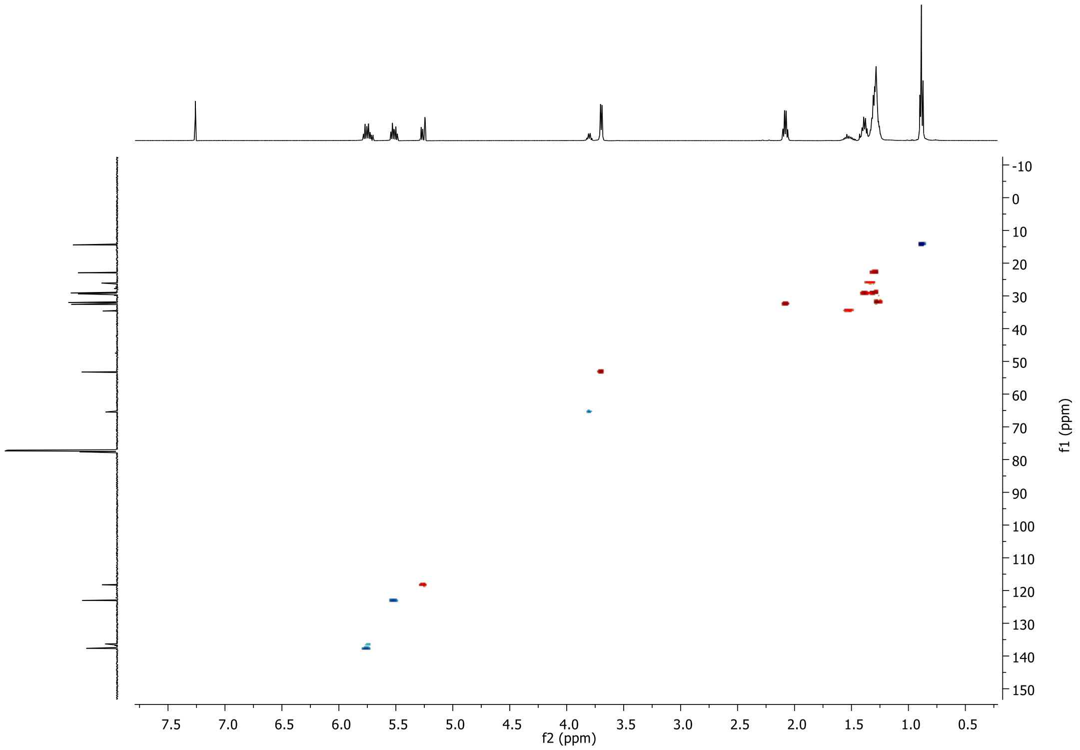


SI – NMR Spectra

2D gCOSY ($CDCl_3$):

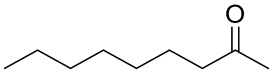


2D HSQC ($CDCl_3$):

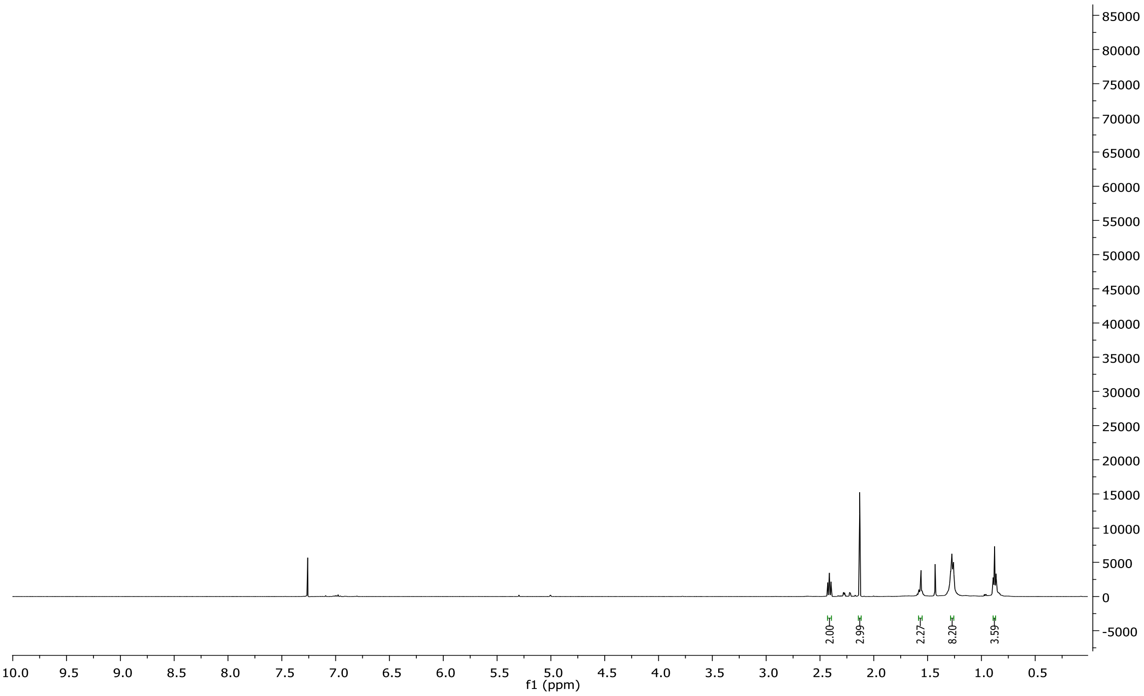


SI – NMR Spectra

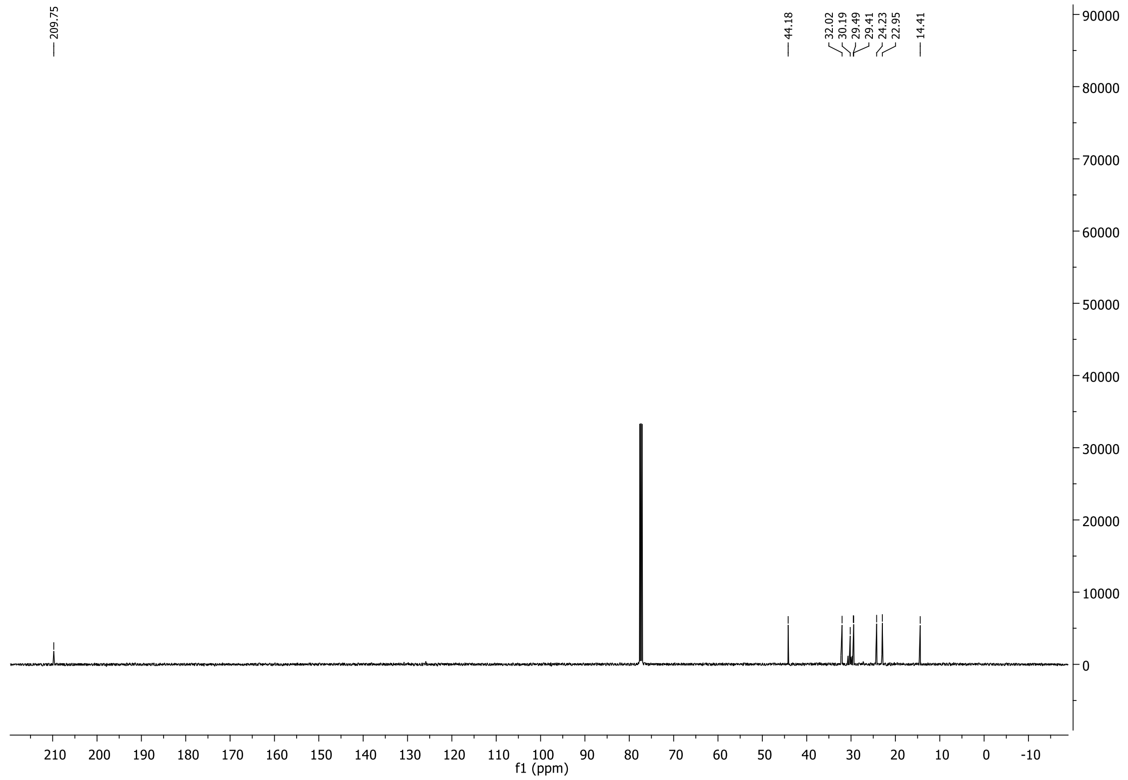
Ketone **4b'**:



^{1}H NMR (500 MHz, CDCl$_3$, 25 ^{o}C)

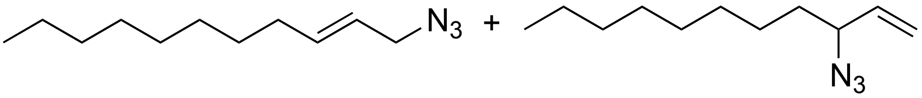


^{13}C NMR (126 MHz, CDCl$_3$, 25 ^{o}C)

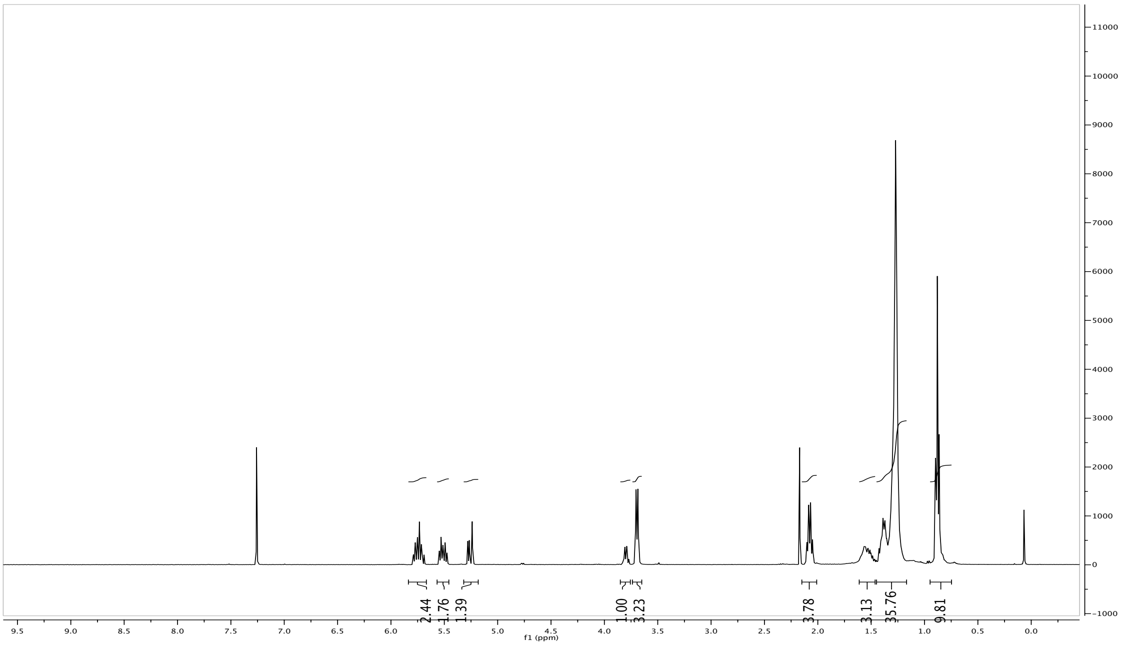


SI – NMR Spectra

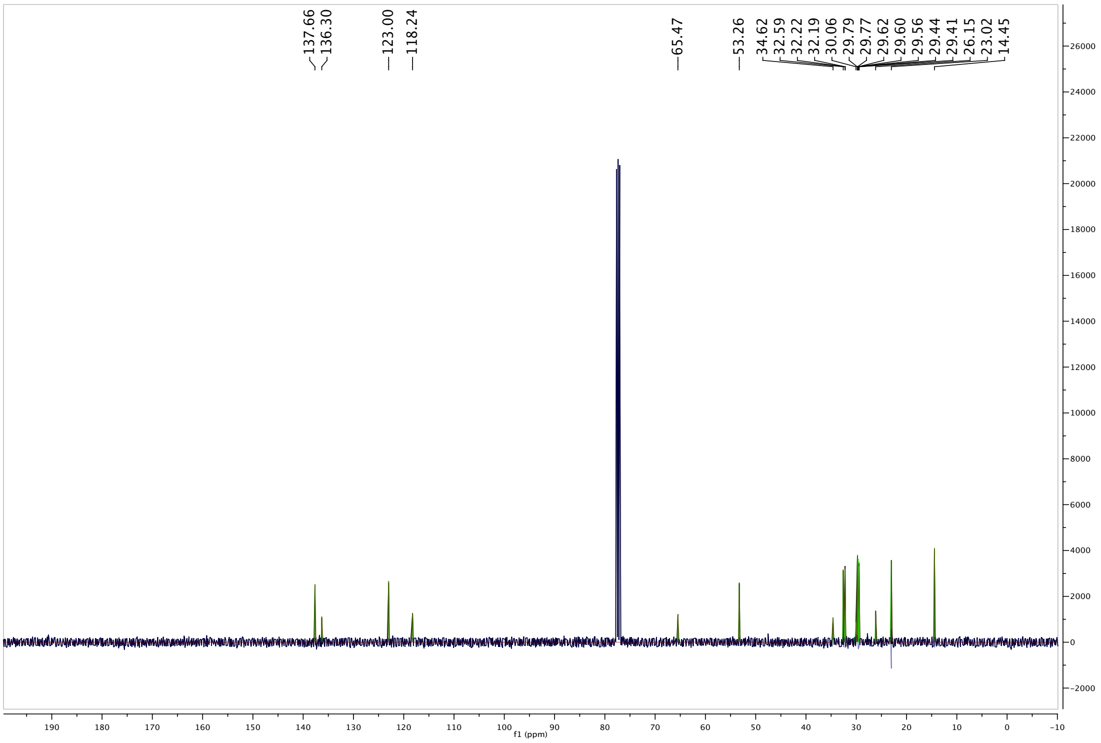
Allyl azides **2c** and **2c'** (1.8:1)



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C)

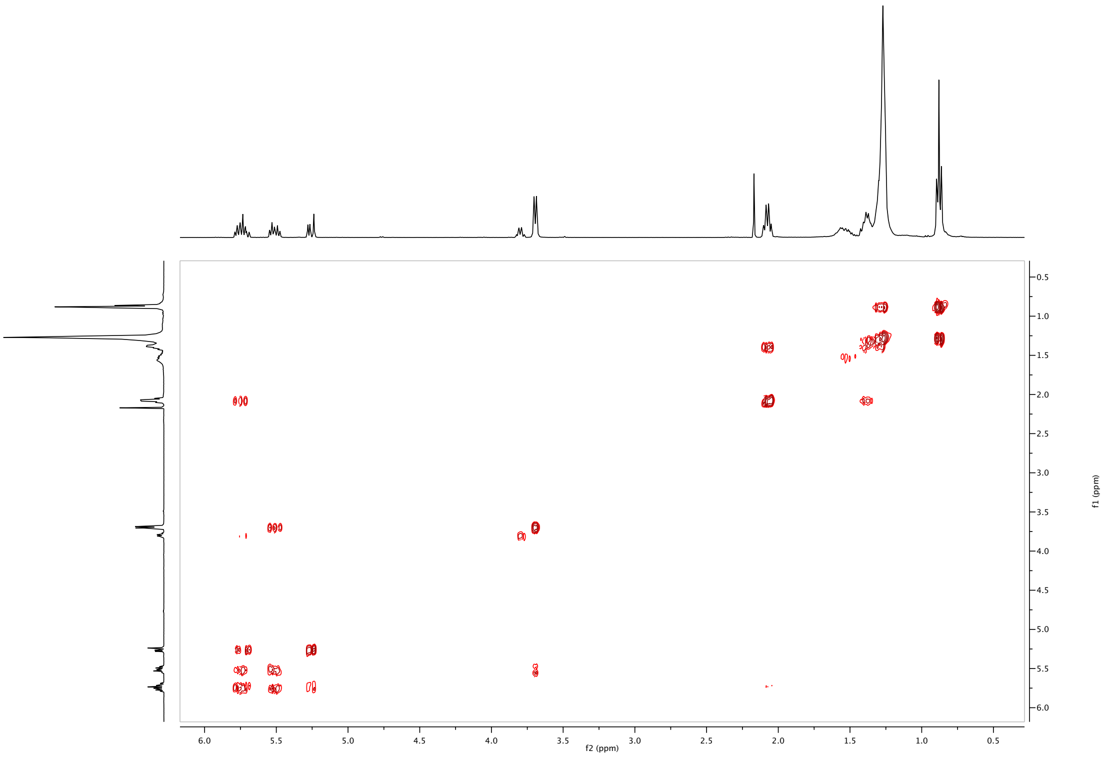


^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)

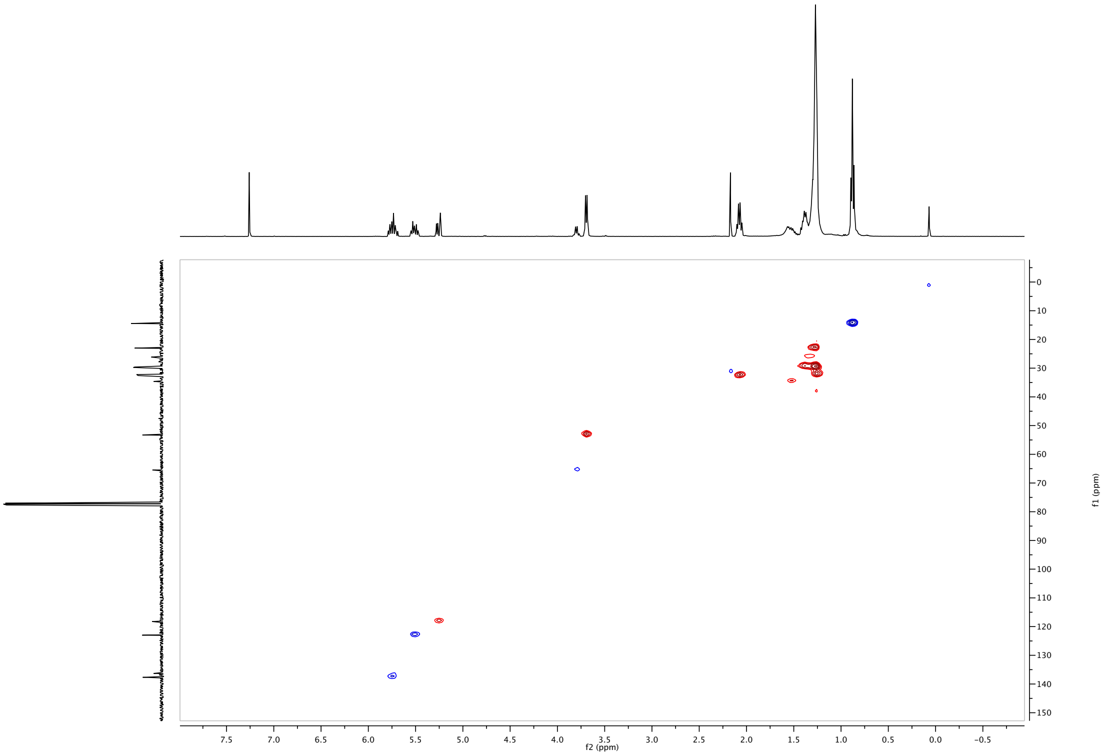


SI – NMR Spectra

2D gCOSY ($CDCl_3$):

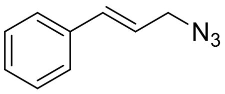


2D HSQC ($CDCl_3$):

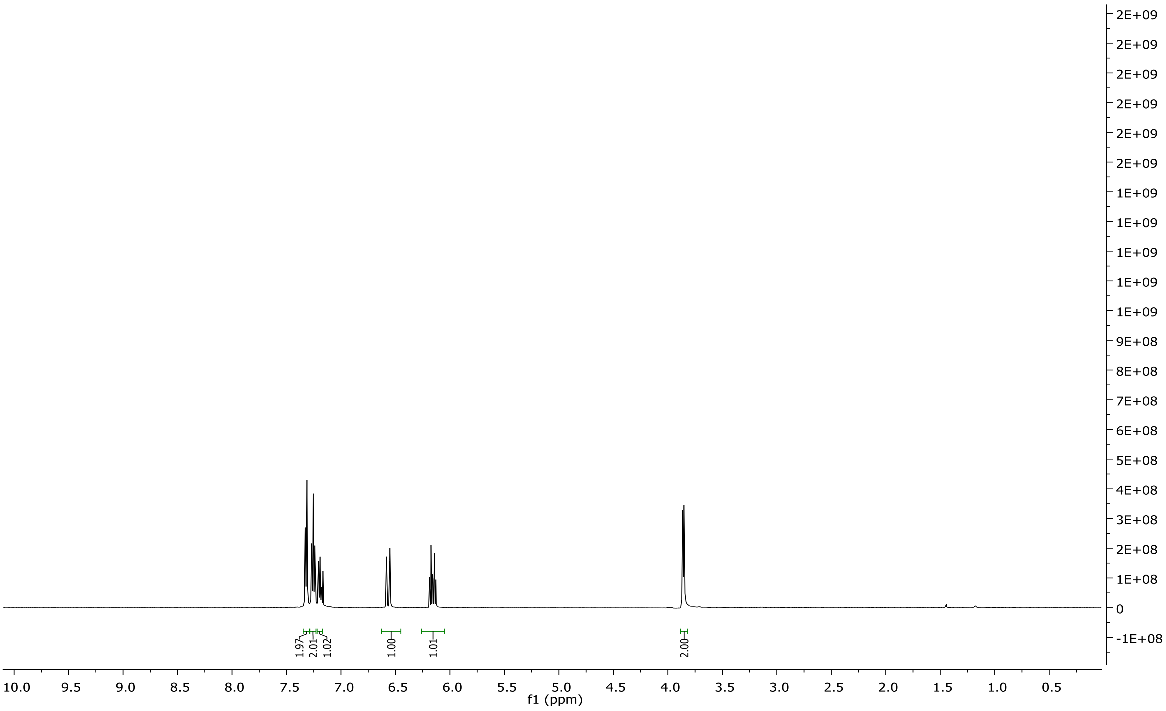


SI – NMR Spectra

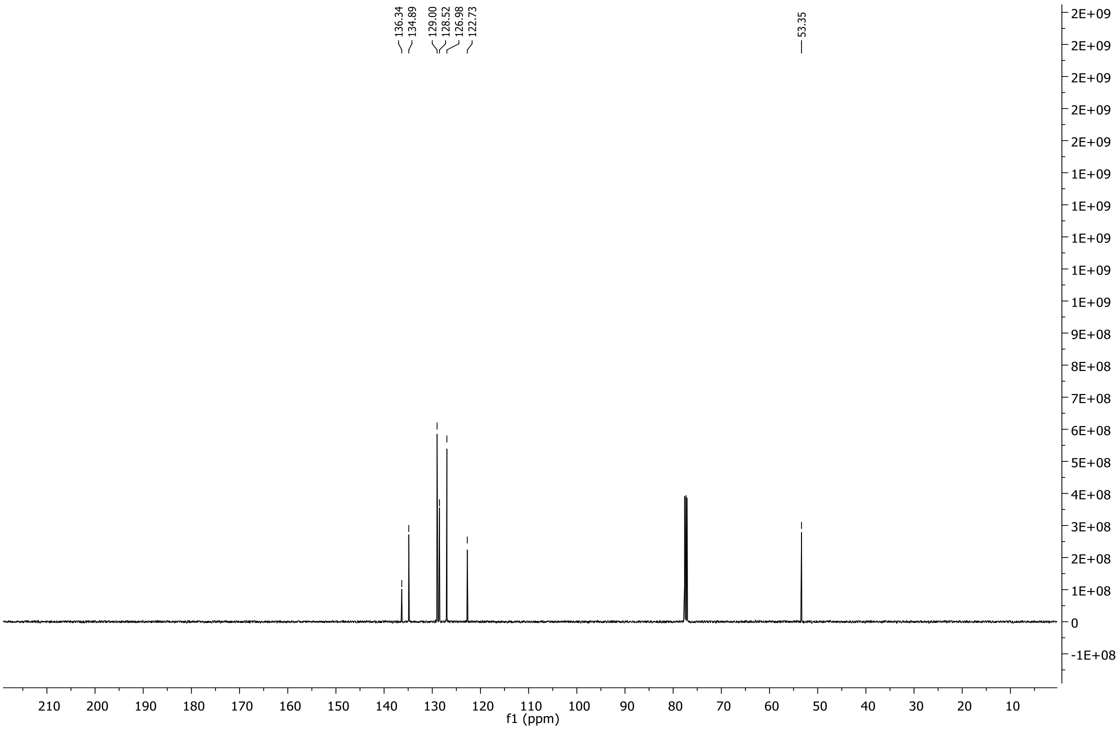
Allyl azide **2d**



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C)

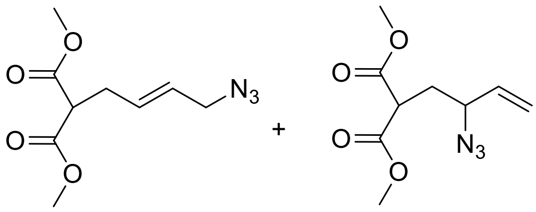


^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)

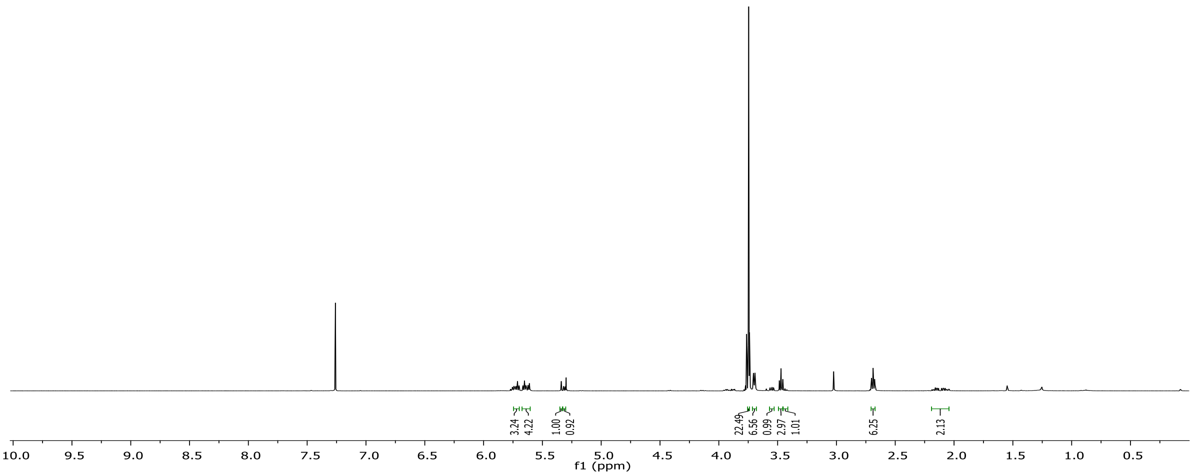


SI – NMR Spectra

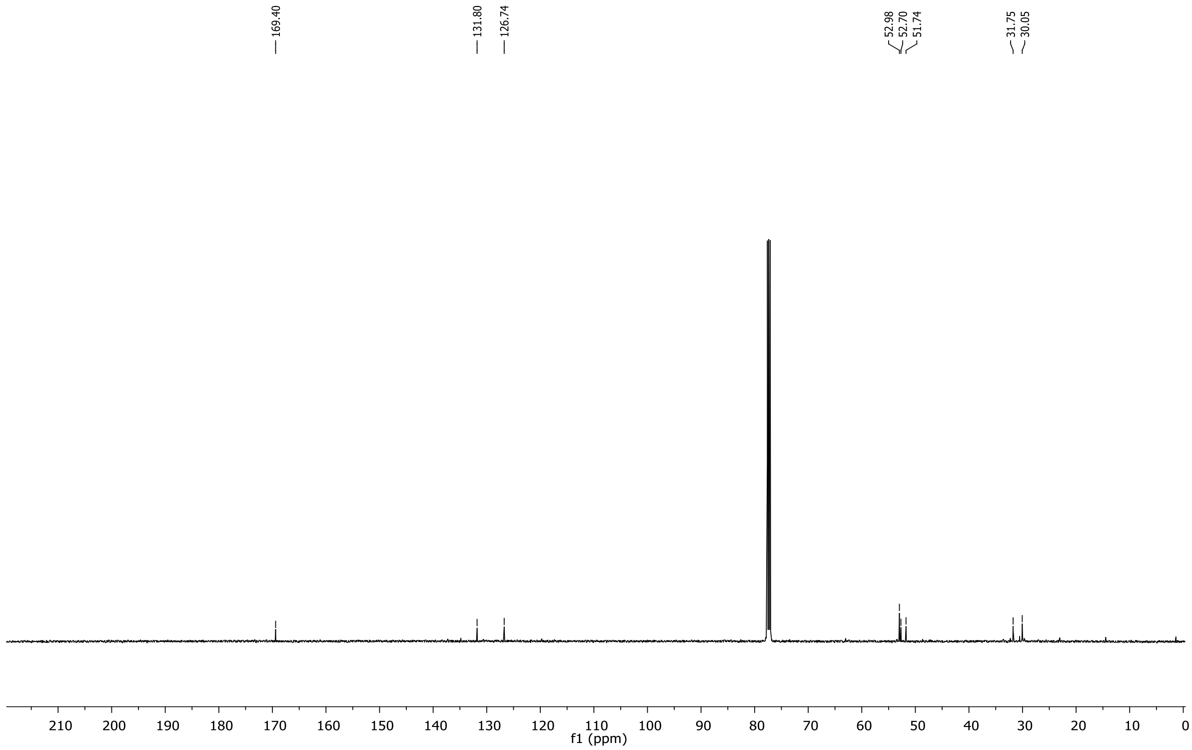
Allyl azides **2e** and **2e'** (3.8:1):



^{1}H NMR (500 MHz, CDCl$_3$, 25 ^{o}C)

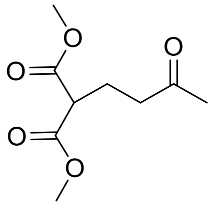


^{13}C NMR (126 MHz, CDCl$_3$, 25 ^{o}C)

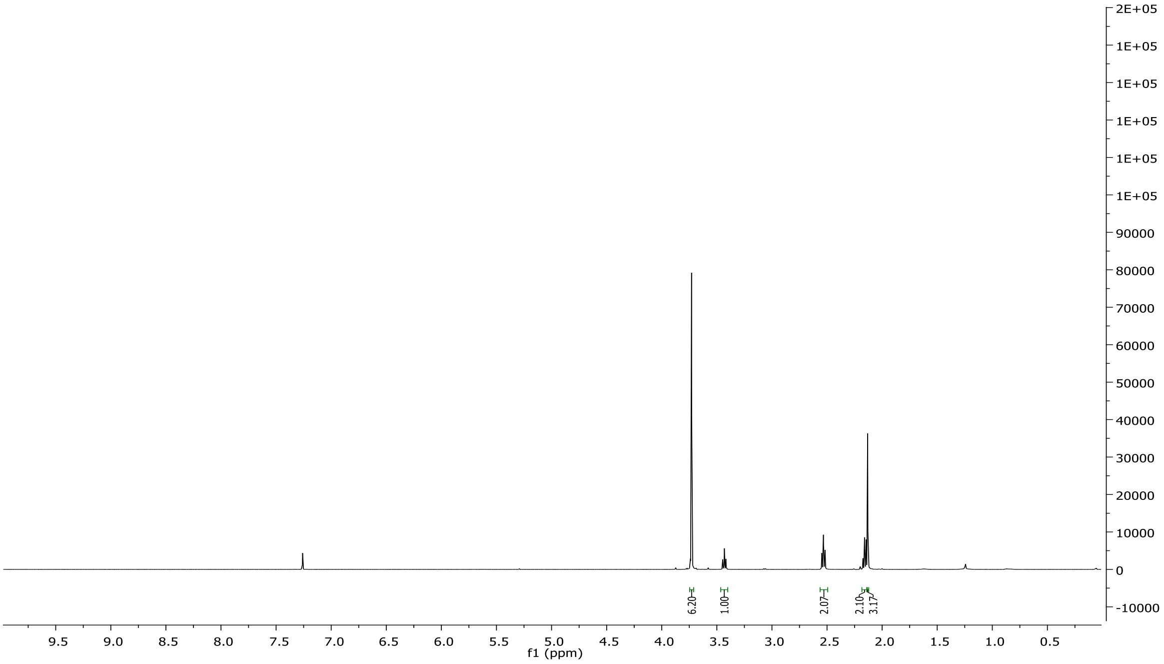


SI – NMR Spectra

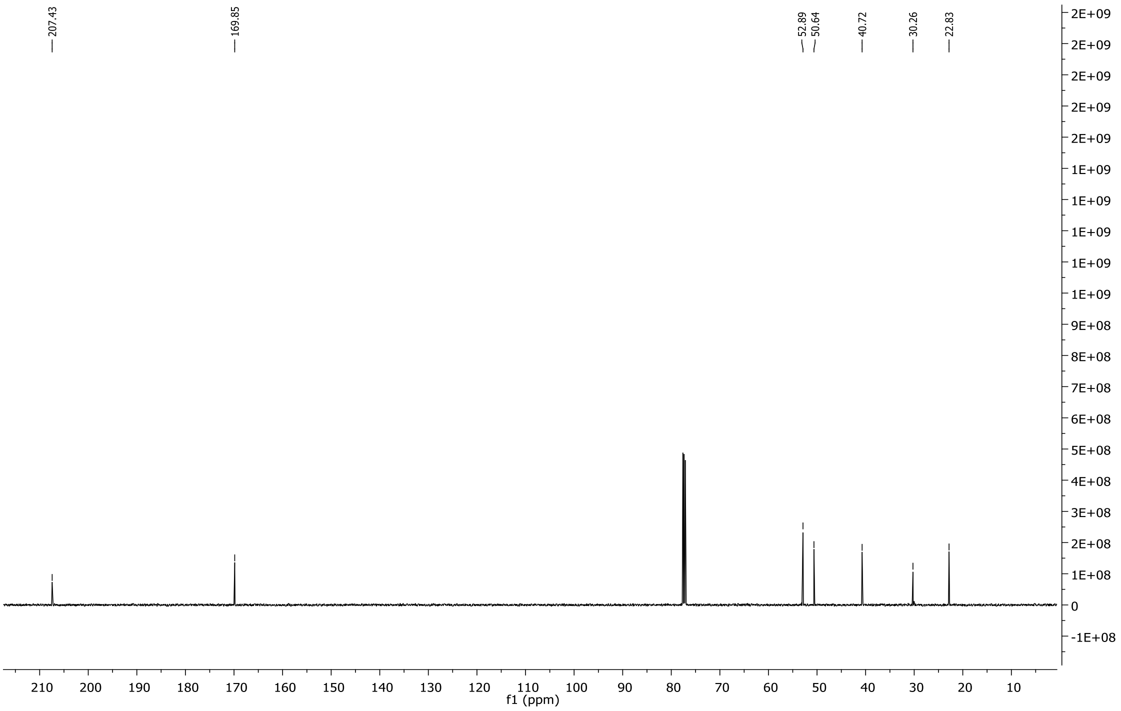
Ketone **4e'**:



^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

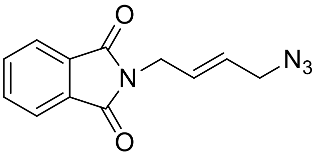


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)

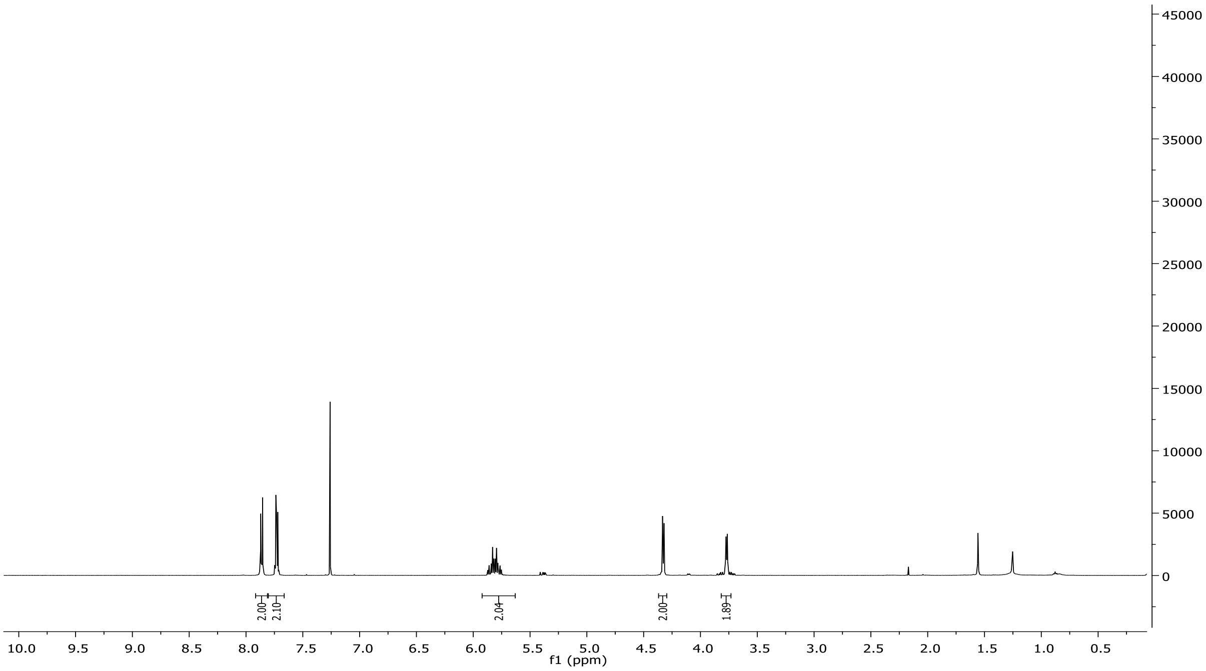


SI – NMR Spectra

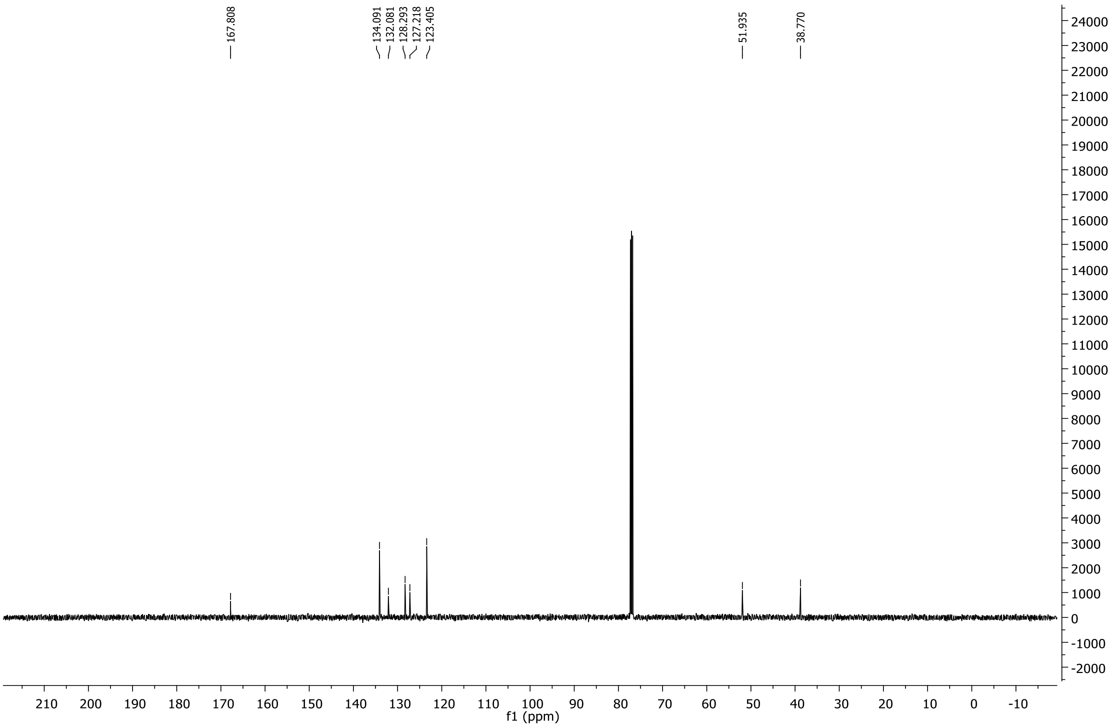
Allyl azide **2f:**



^{1}H NMR (500 MHz, CDCl$_3$, 25 ^{o}C)

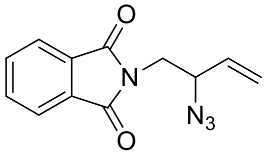


^{13}C NMR (126 MHz, CDCl$_3$, 25 ^{o}C)

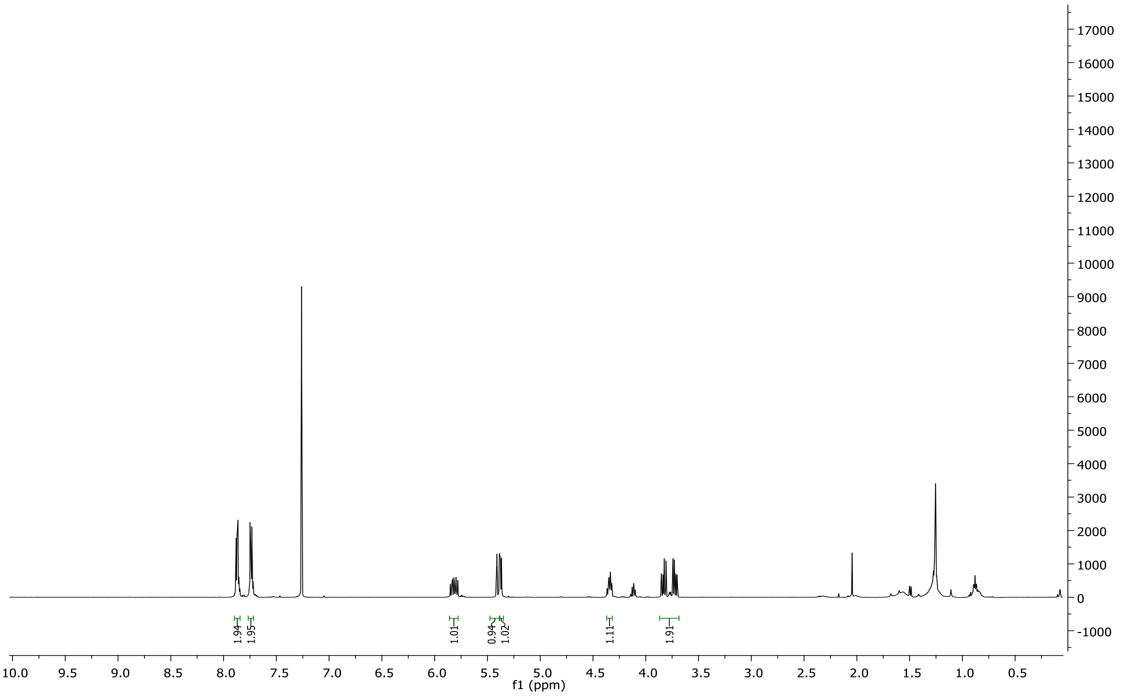


SI – NMR Spectra

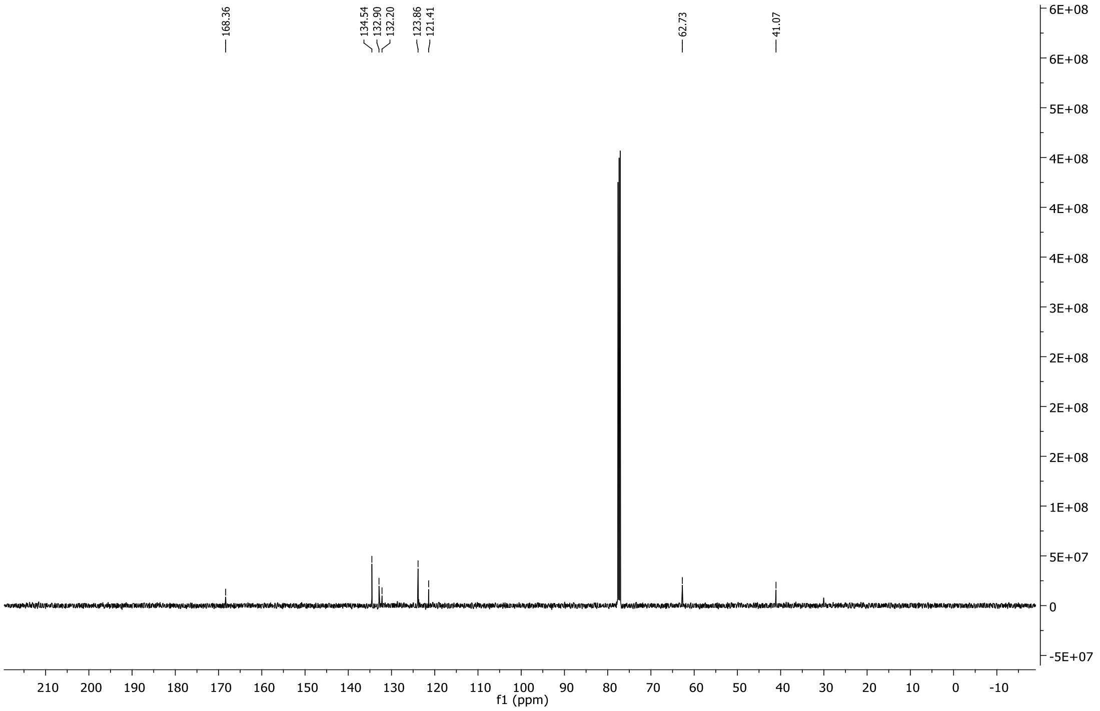
Allyl azide **2f'**:



^{1}H NMR (500 MHz, CDCl$_3$, 25 ^{o}C)

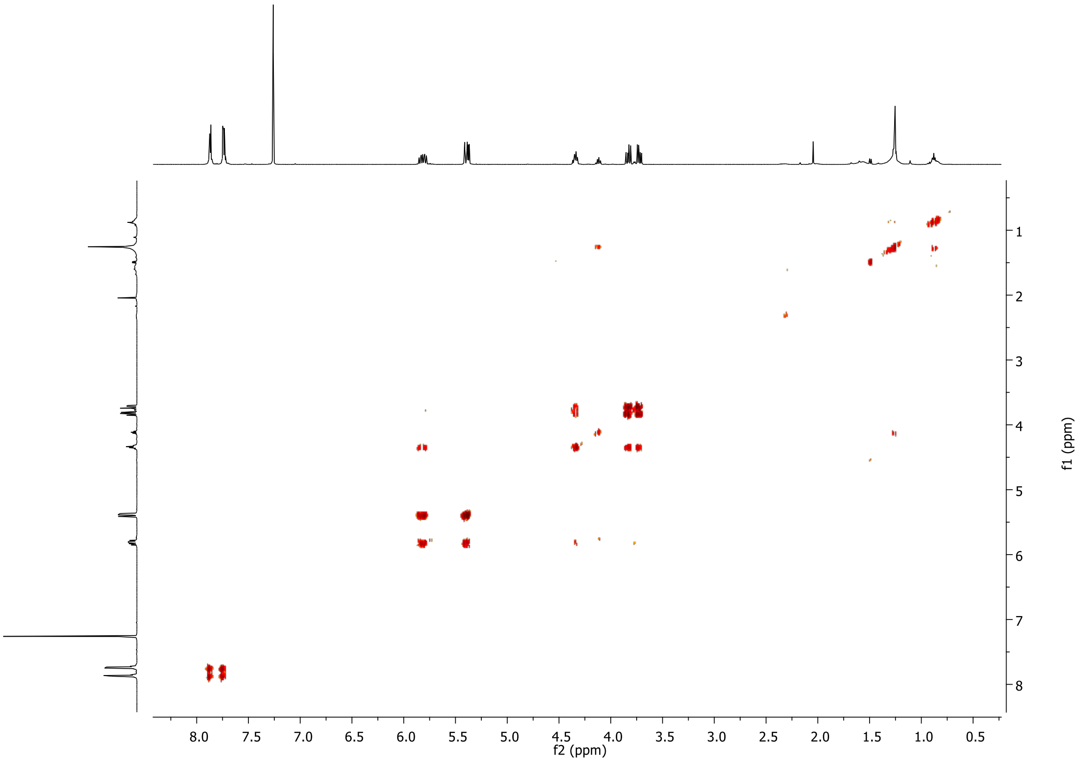


^{13}C NMR (126 MHz, CDCl$_3$, 25 ^{o}C)



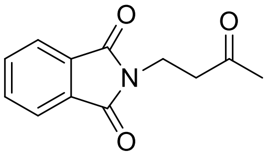
SI – NMR Spectra

2D gCOSY ($CDCl_3$):

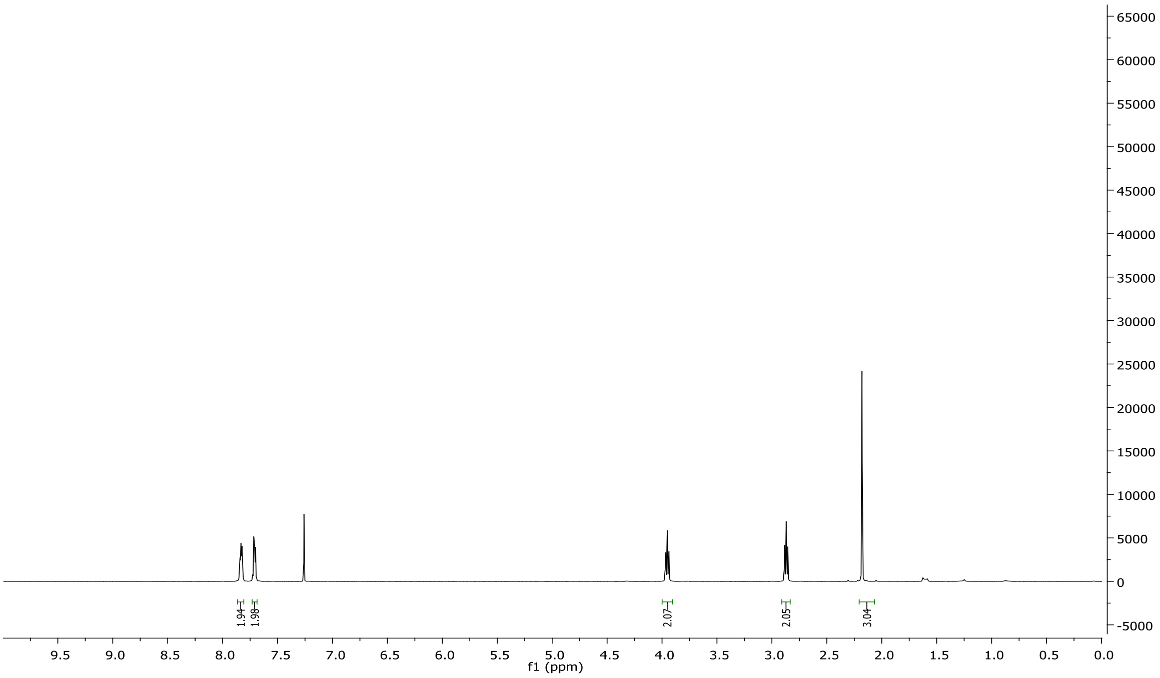


SI – NMR Spectra

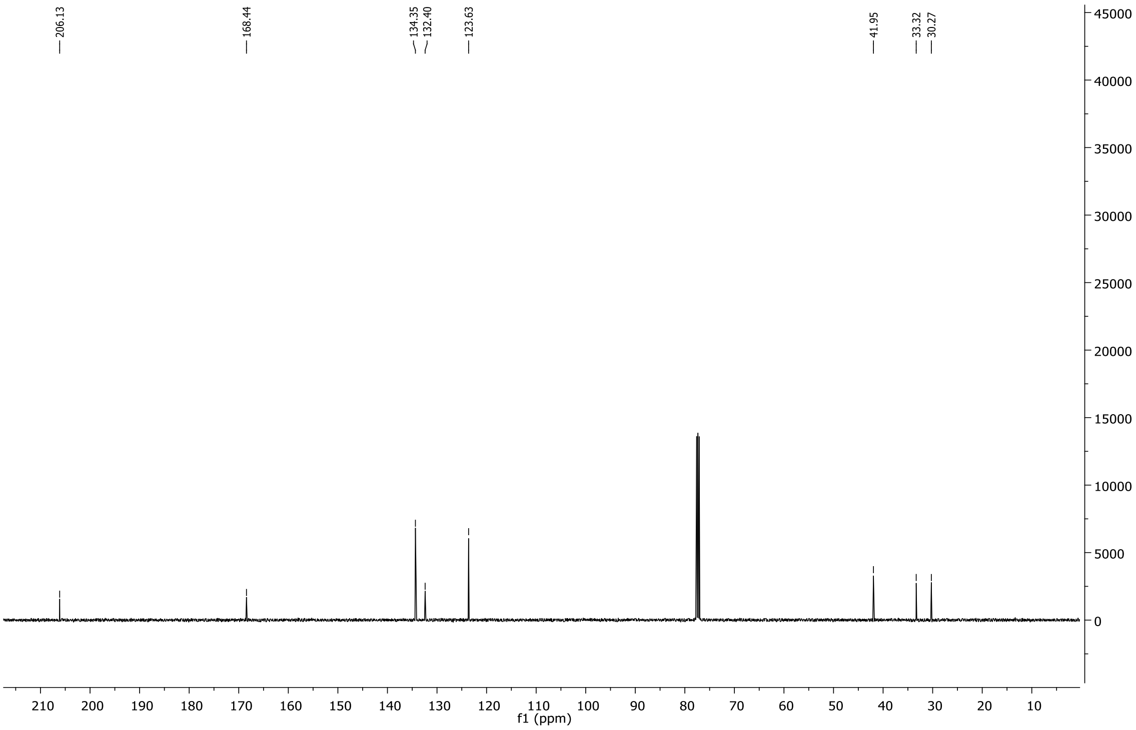
Ketone **4f'**:



^{1}H NMR (500 MHz, CDCl$_3$, 25 ^{o}C)

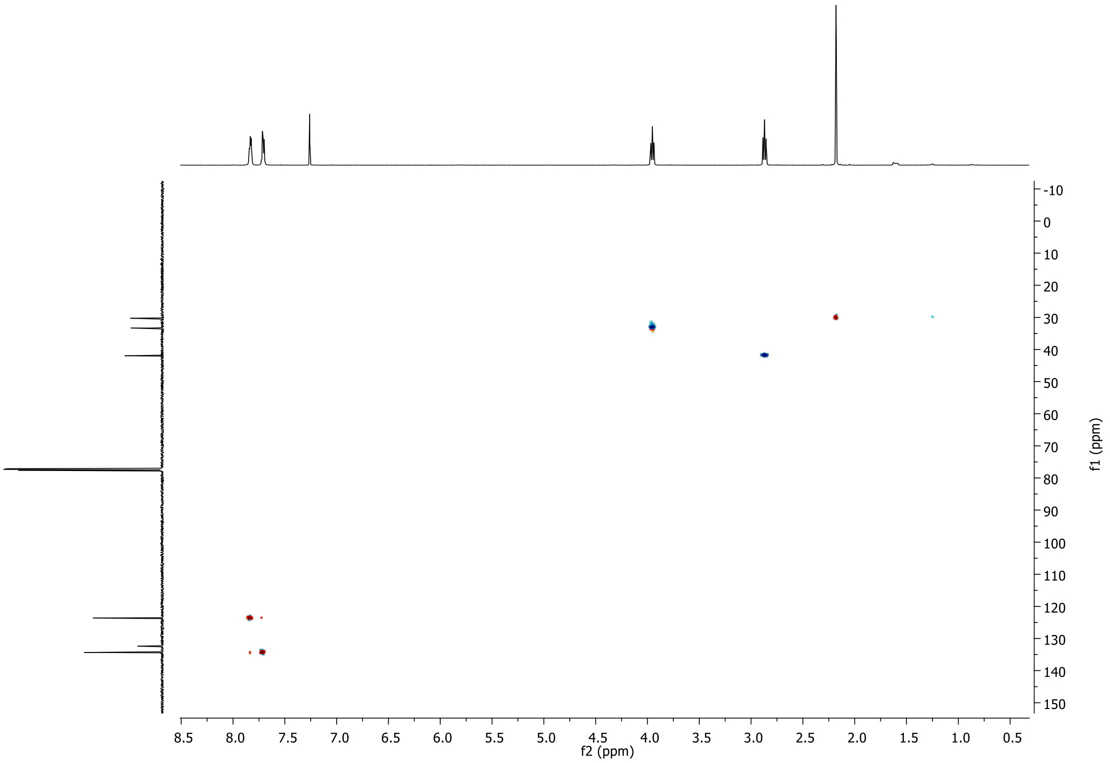


^{13}C NMR (126 MHz, CDCl$_3$, 25 ^{o}C)



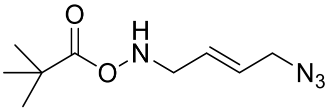
SI – NMR Spectra

2D HSQC ($CDCl_3$):

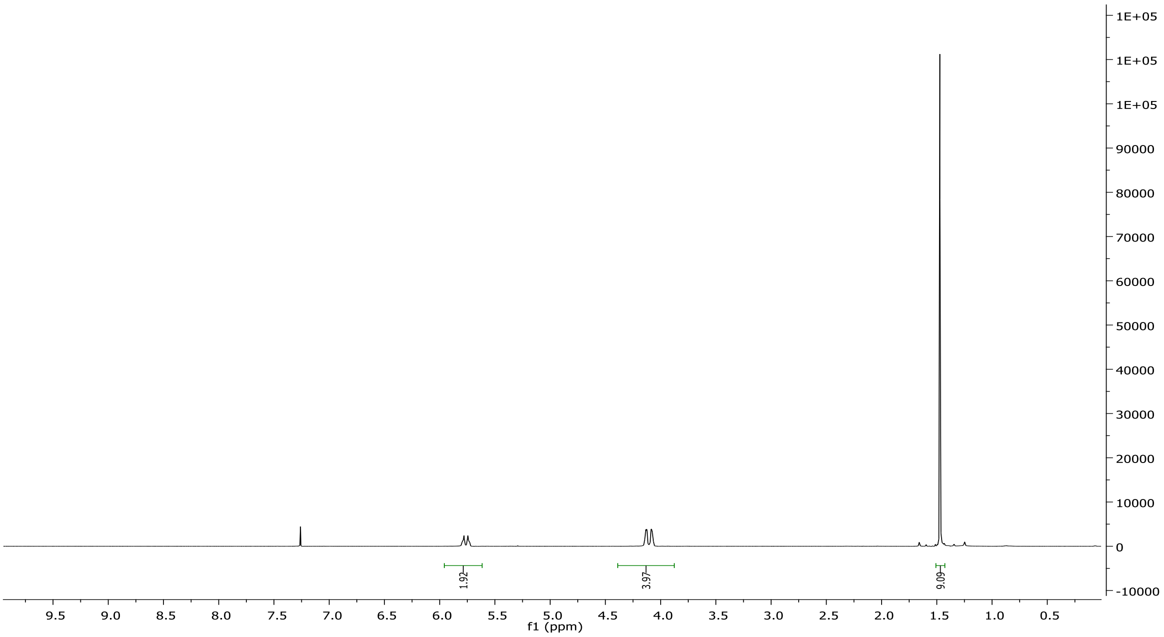


SI – NMR Spectra

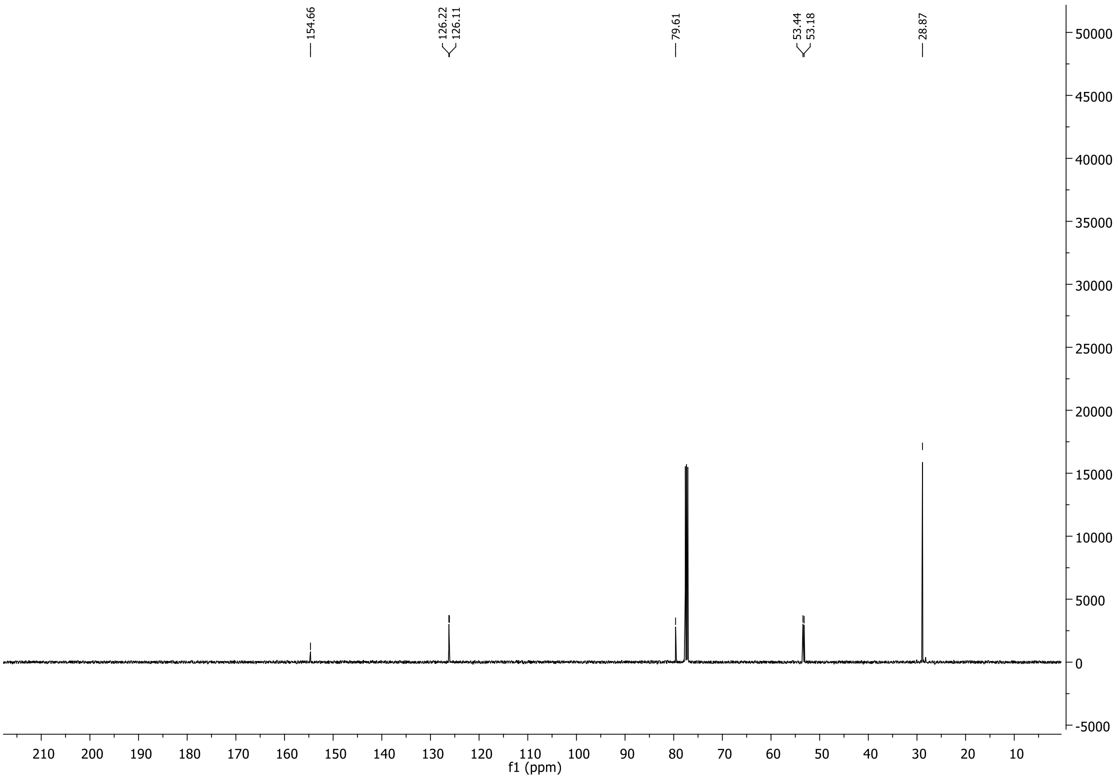
Allyl azide **2g:**



^{1}H NMR (500 MHz, $CDCl_3$, 25 ^oC)

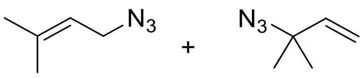


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^oC)

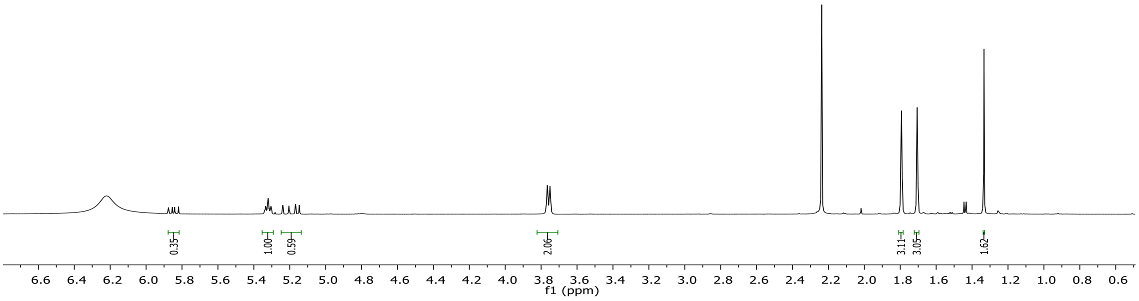


SI – NMR Spectra

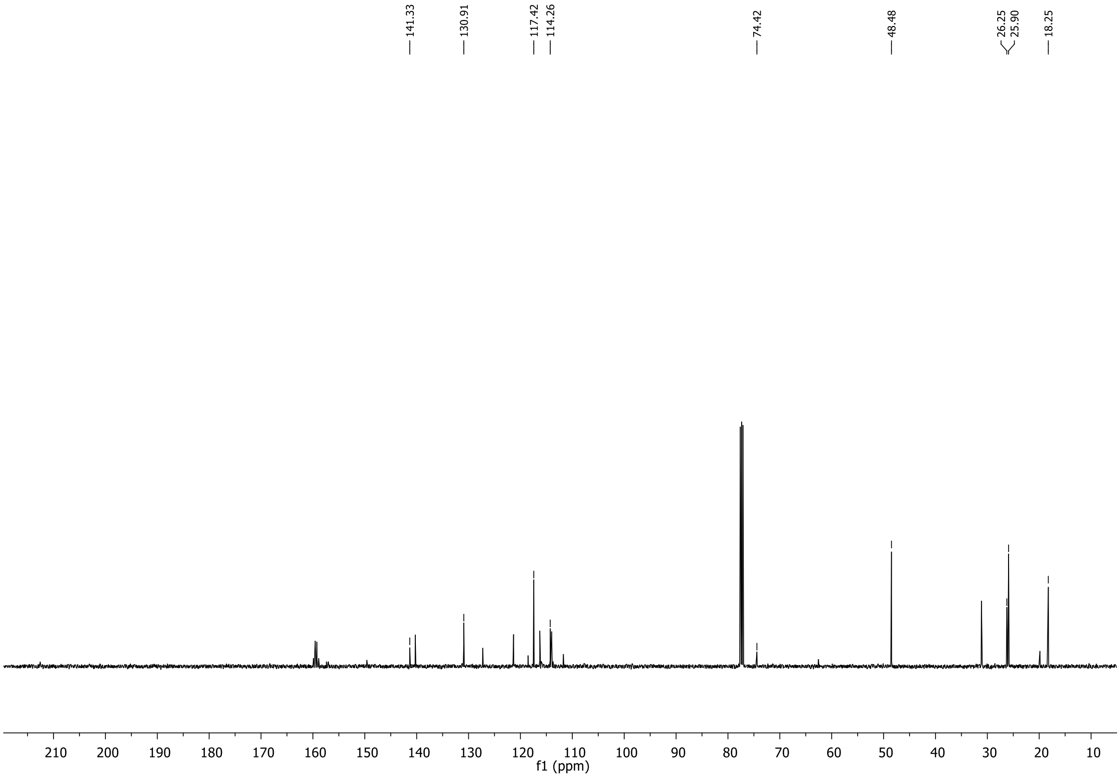
Allyl azides **2h** and **2h'** (3.7:1):



^{1}H NMR (500 MHz, CDCl$_3$, 25 ^{o}C)

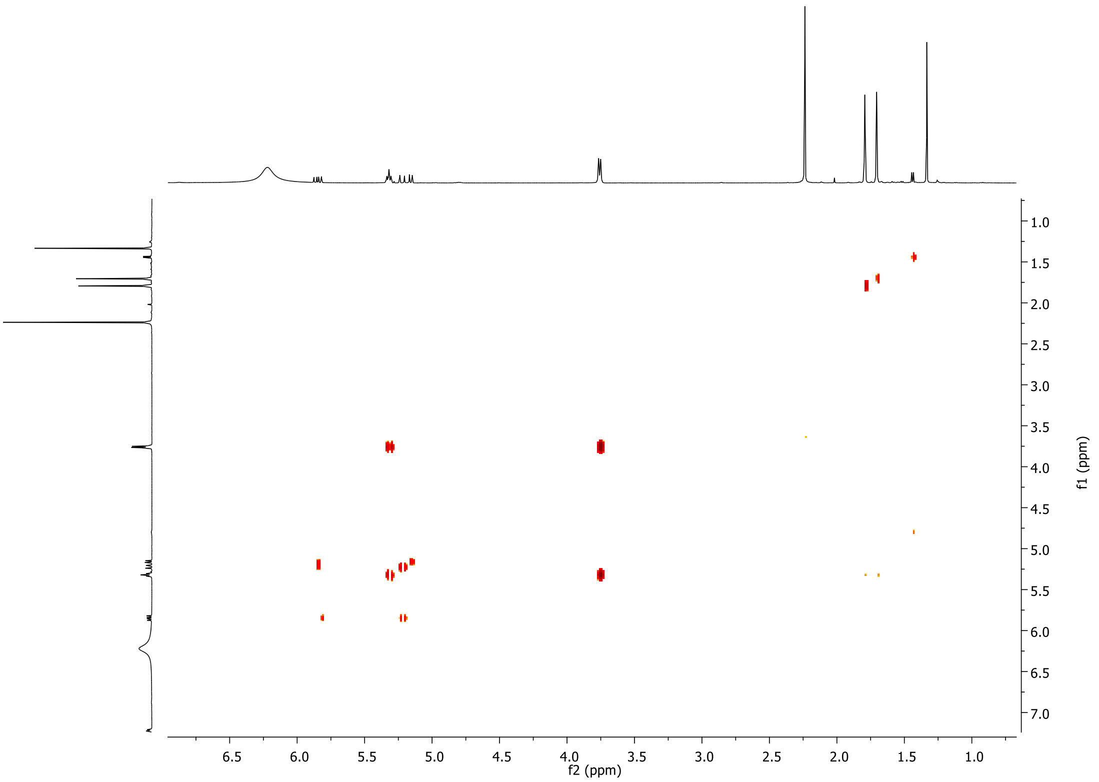


^{13}C NMR (126 MHz, CDCl$_3$, 25 ^{o}C)

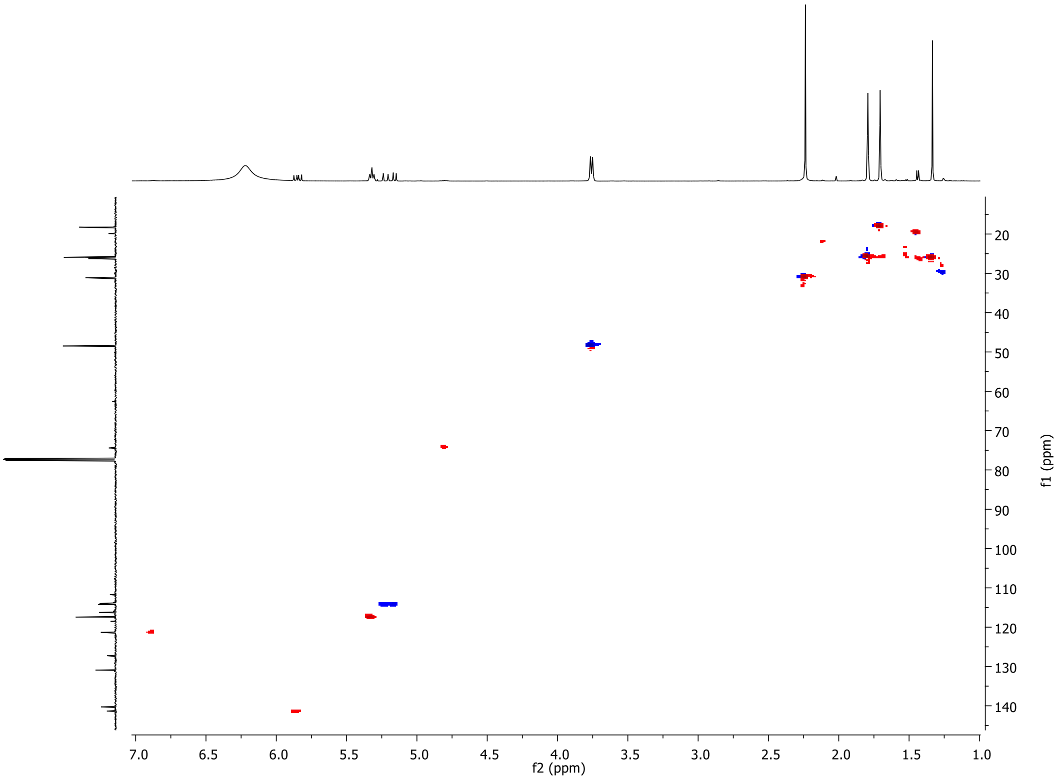


SI – NMR Spectra

2D gCOSY ($CDCl_3$):

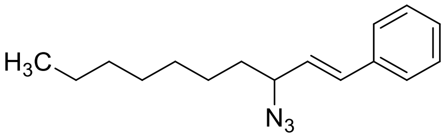


2D HSQC ($CDCl_3$):

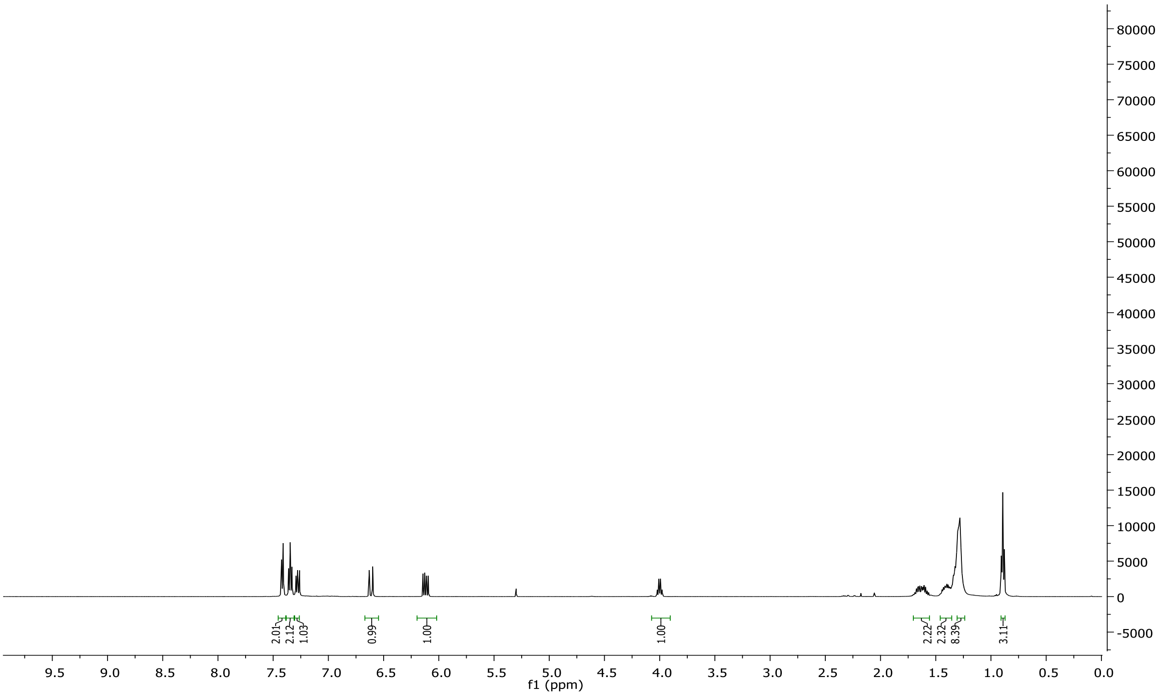


SI – NMR Spectra

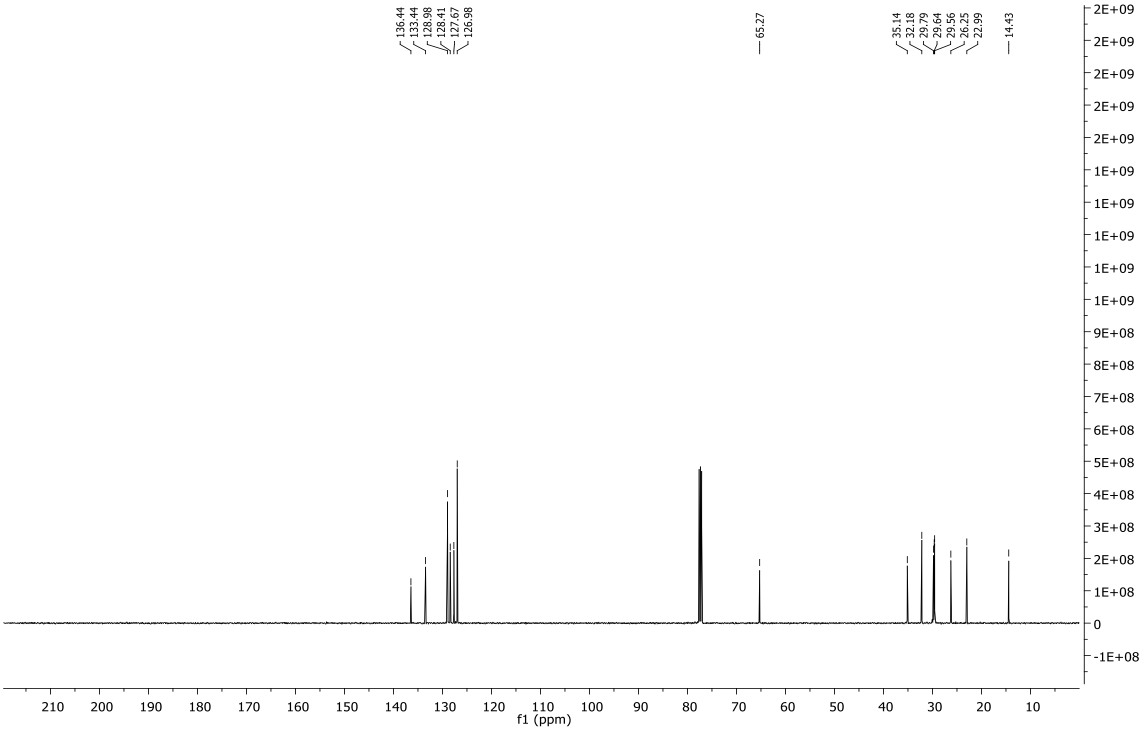
Allyl azide **2i:**



^{1}H NMR (500 MHz, CDCl$_3$, 25 ^{o}C)

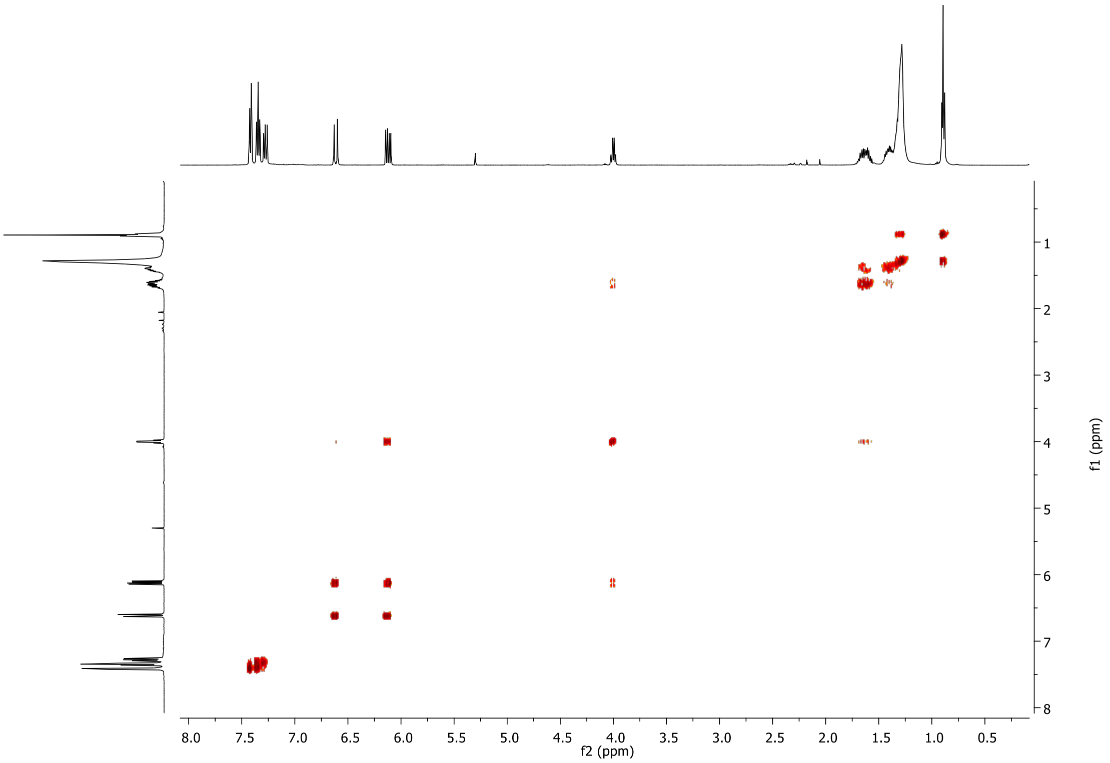


^{13}C NMR (126 MHz, CDCl$_3$, 25 ^{o}C)

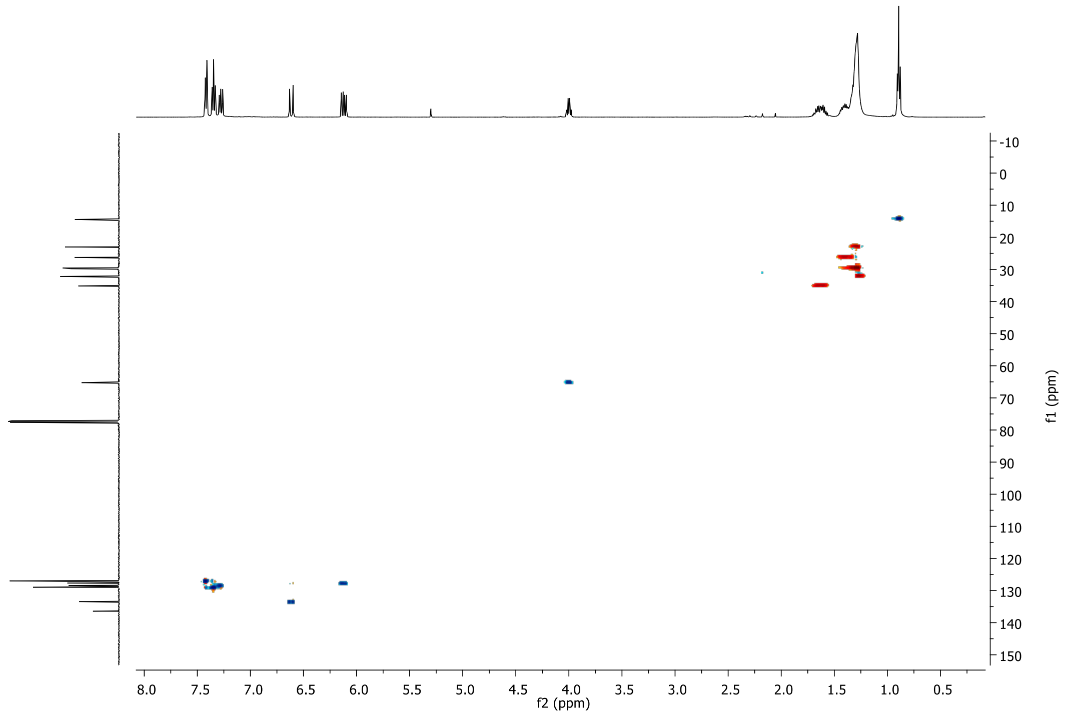


SI – NMR Spectra

2D gCOSY ($CDCl_3$):

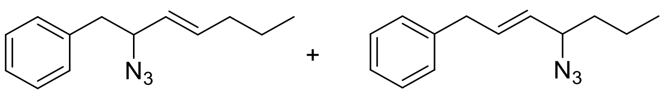


2D HSQC ($CDCl_3$):

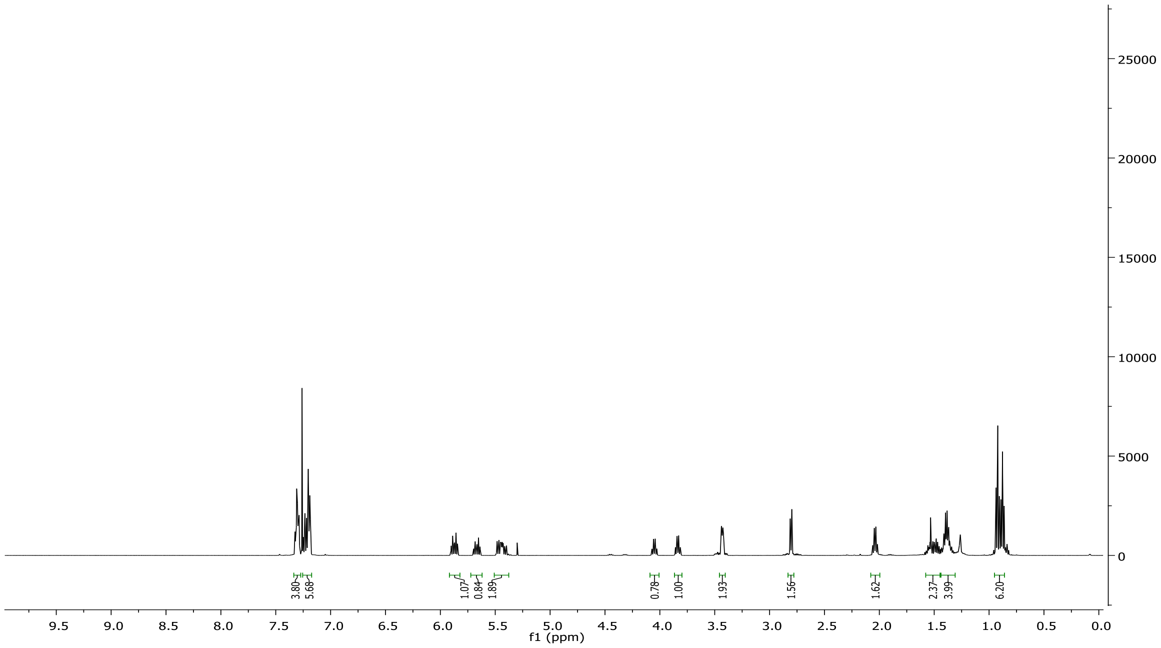


SI – NMR Spectra

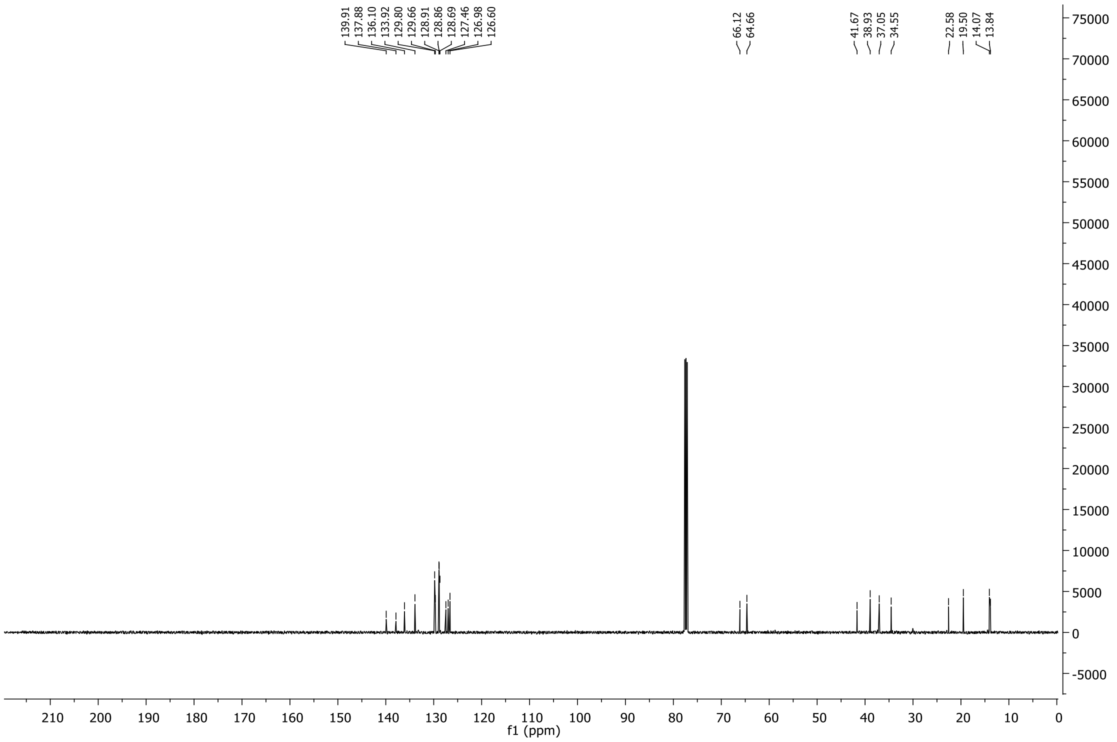
Allyl azide **2j and 2j':**



^{1}H NMR (500 MHz, CDCl$_3$, 25 ^{o}C)

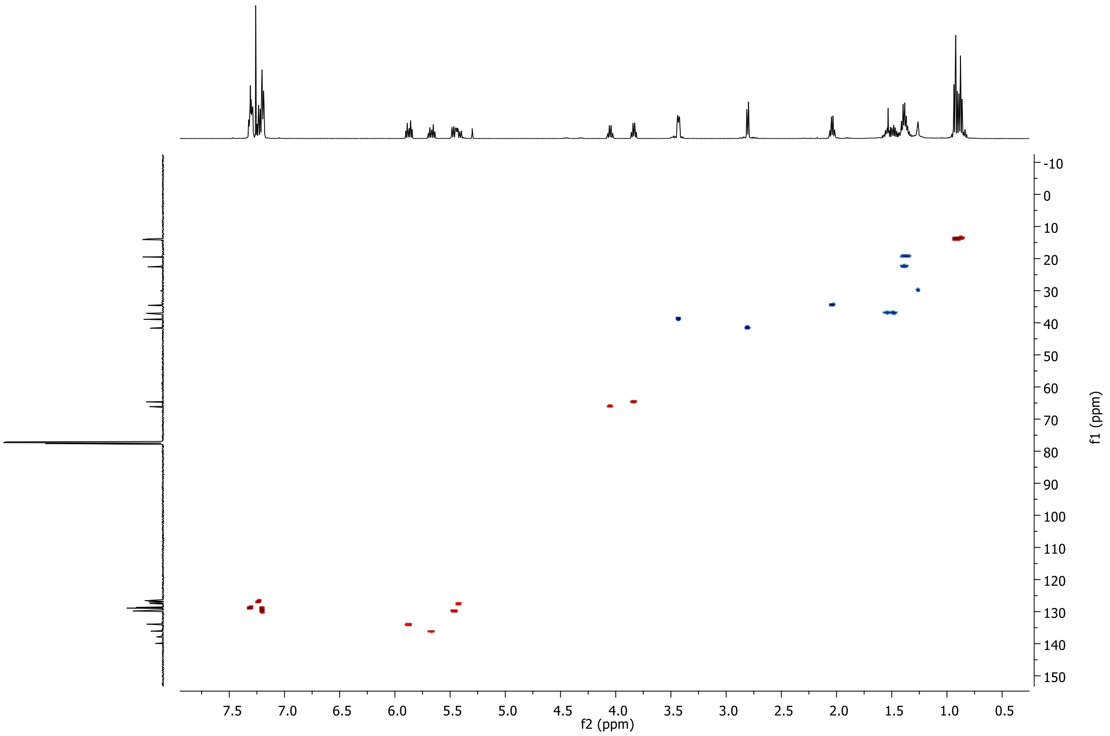


^{13}C NMR (126 MHz, CDCl$_3$, 25 ^{o}C)



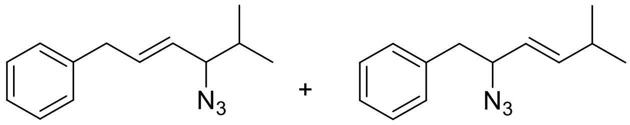
SI – NMR Spectra

2D HSQC ($CDCl_3$):

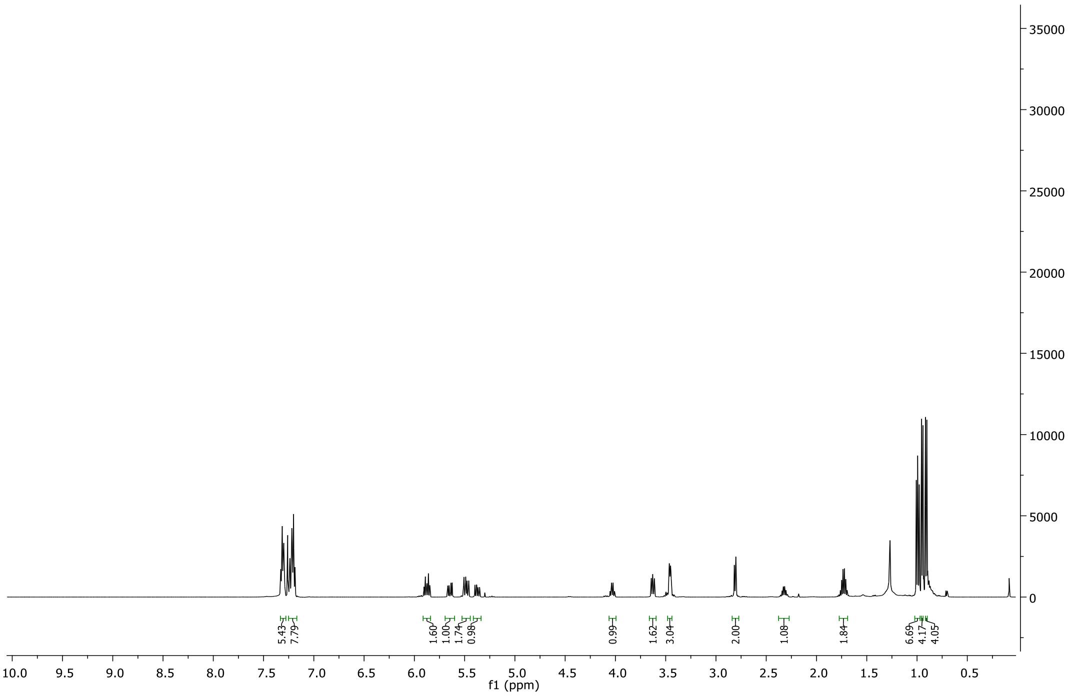


SI – NMR Spectra

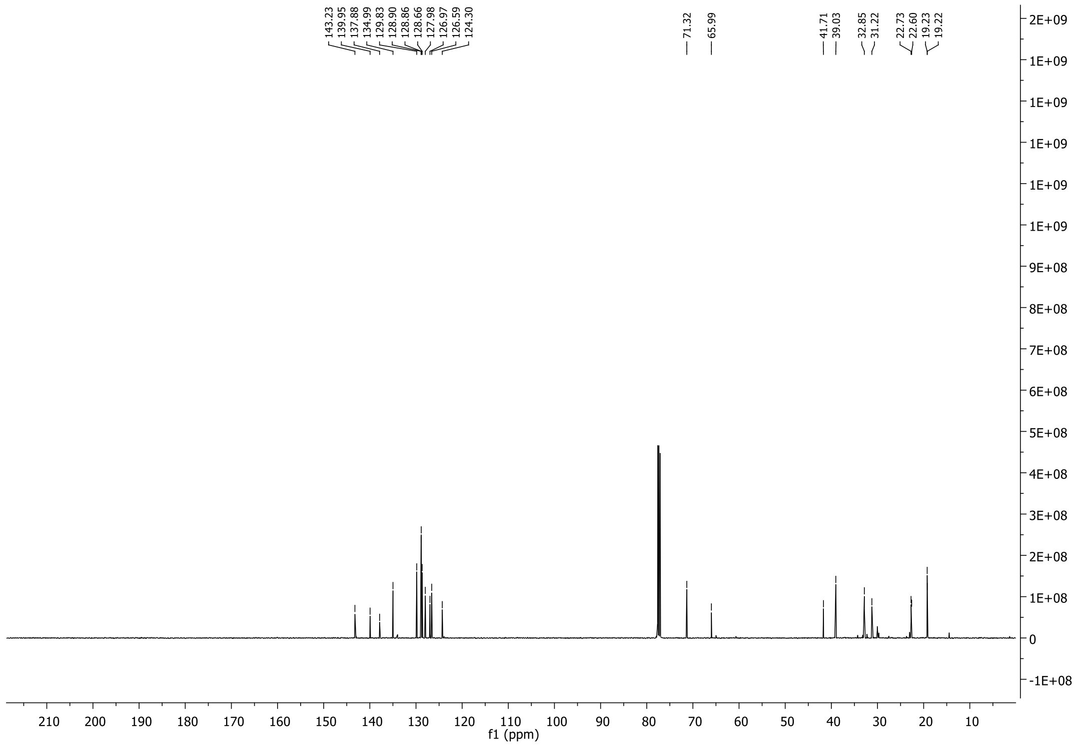
Allyl azides **2k and 2k' (:**



^{1}H NMR (500 MHz, CDCl$_3$, 25 ^{o}C)

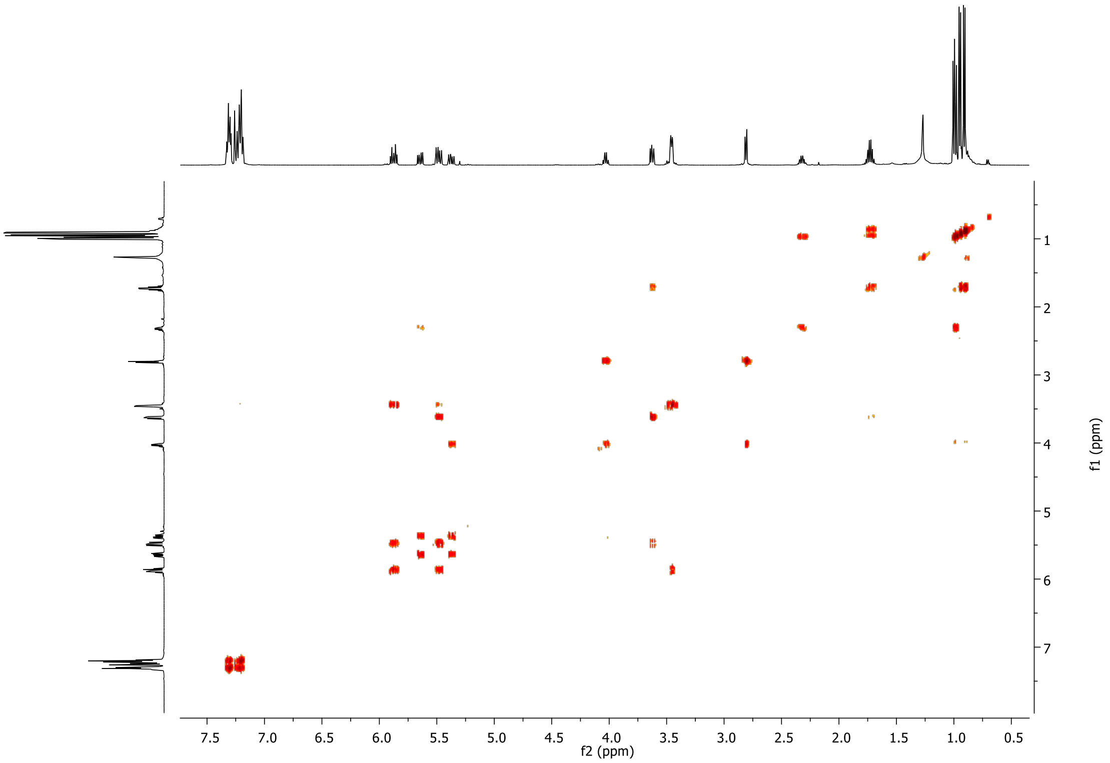


^{13}C NMR (126 MHz, CDCl$_3$, 25 ^{o}C)

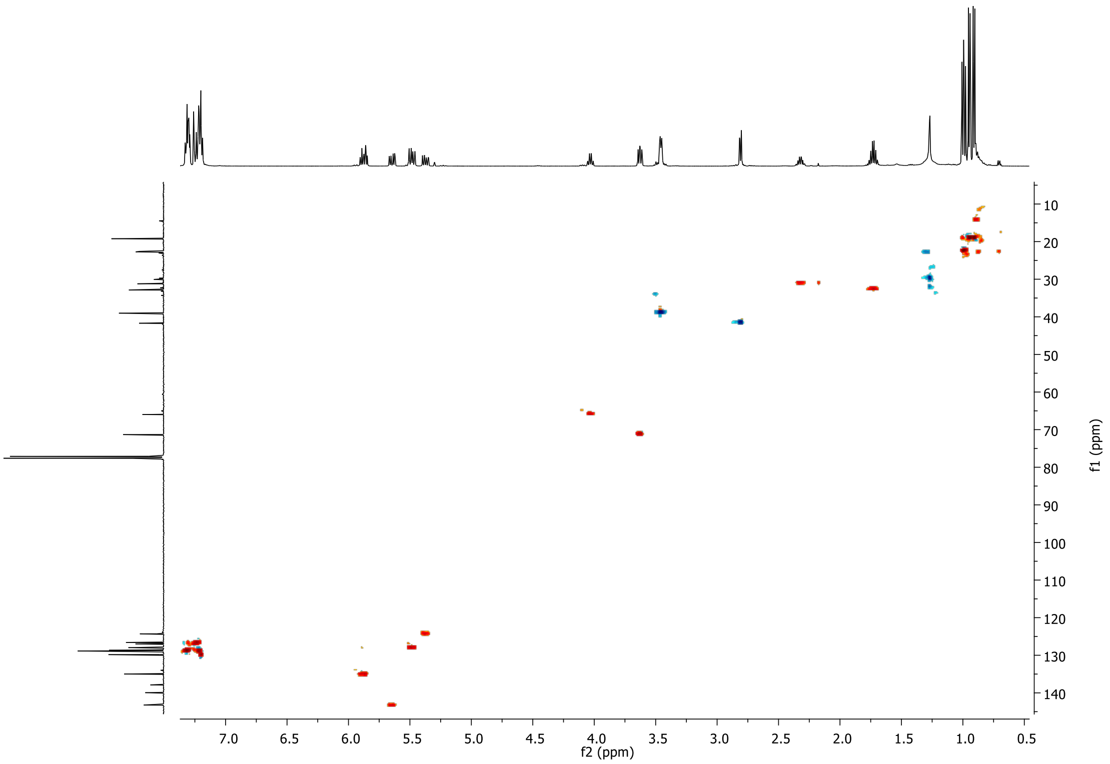


SI – NMR Spectra

2D gCOSY ($CDCl_3$):

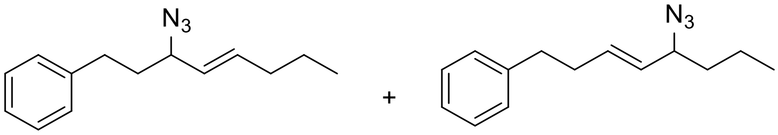


2D HSQC ($CDCl_3$):

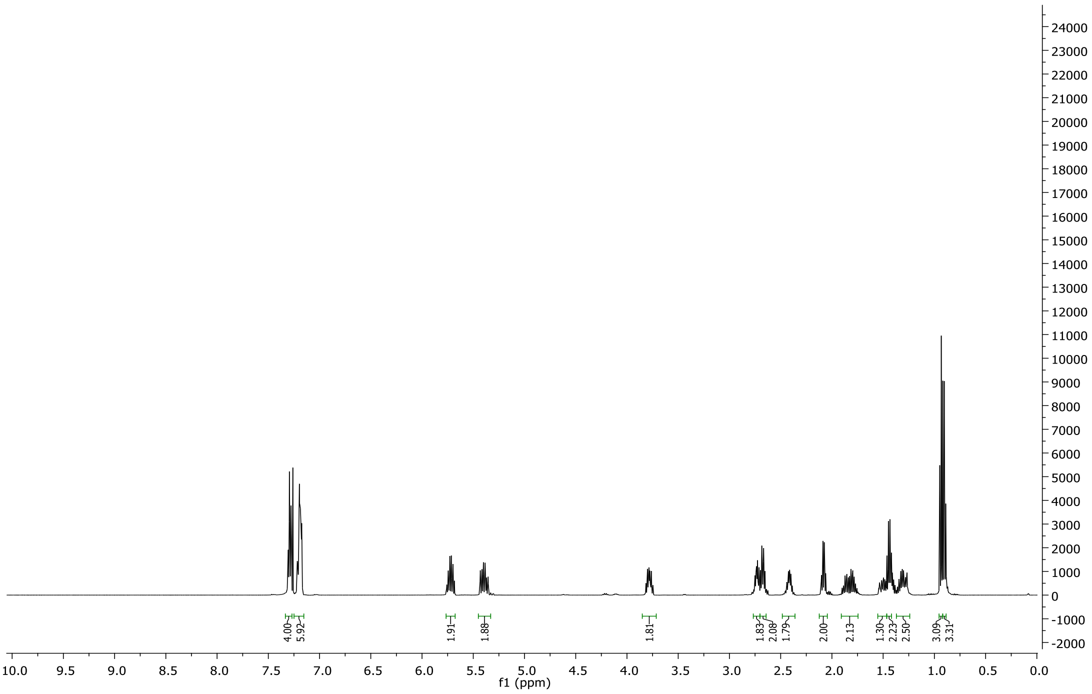


SI – NMR Spectra

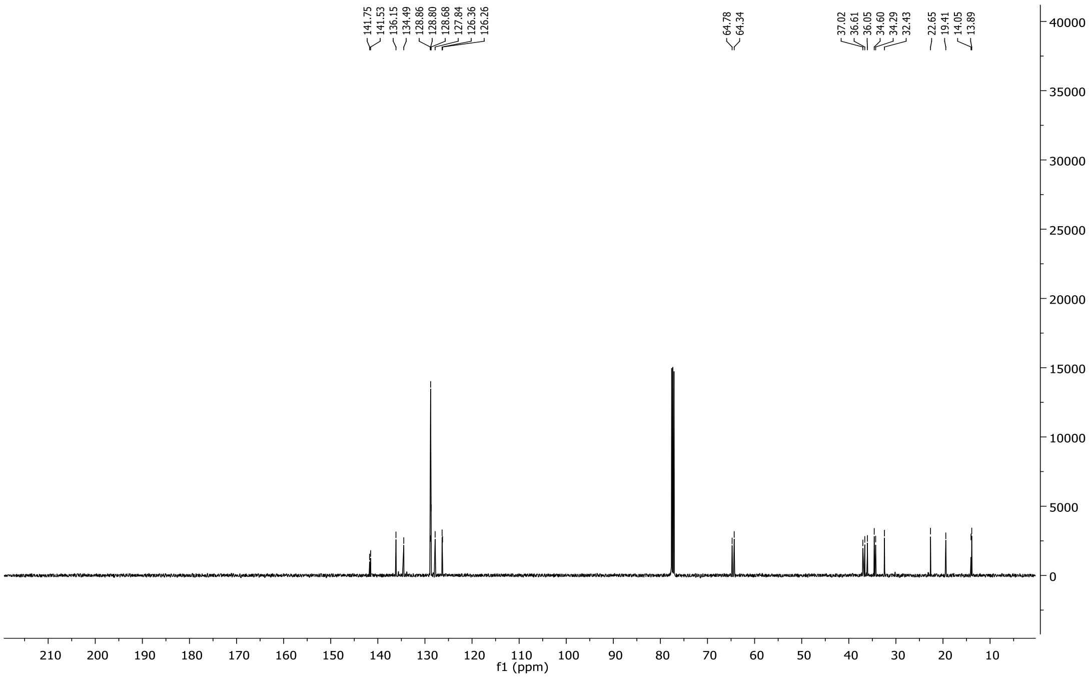
Allyl azides **2l** and **2l'** (1:1.13):



^{1}H NMR (500 MHz, CDCl$_3$, 25 ^{o}C)

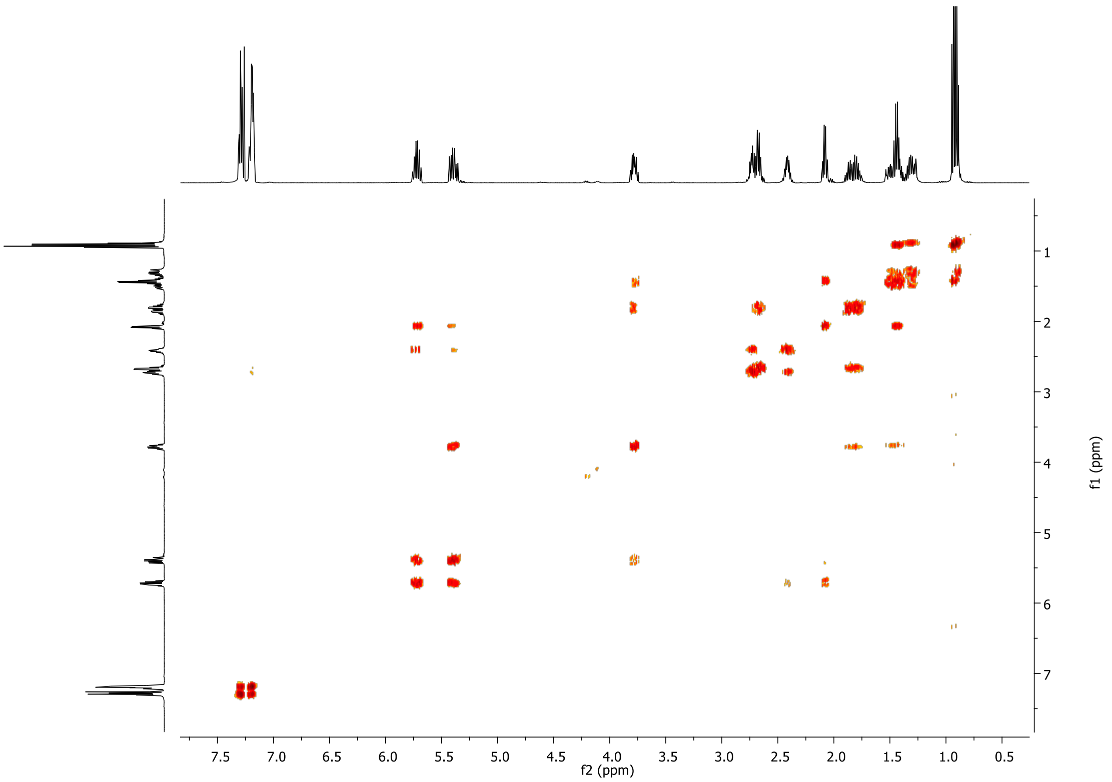


^{13}C NMR (126 MHz, CDCl$_3$, 25 ^{o}C)

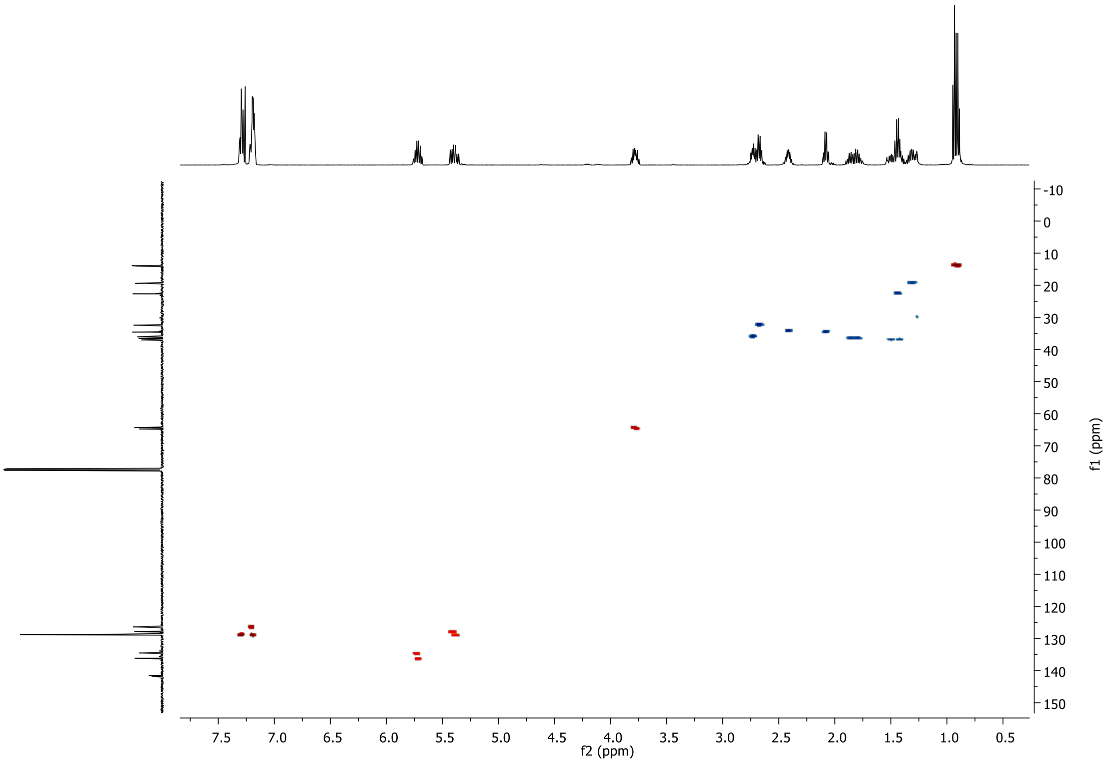


SI – NMR Spectra

2D gCOSY ($CDCl_3$):

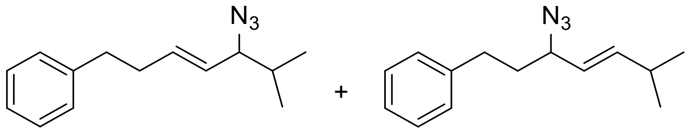


2D HSQC ($CDCl_3$):

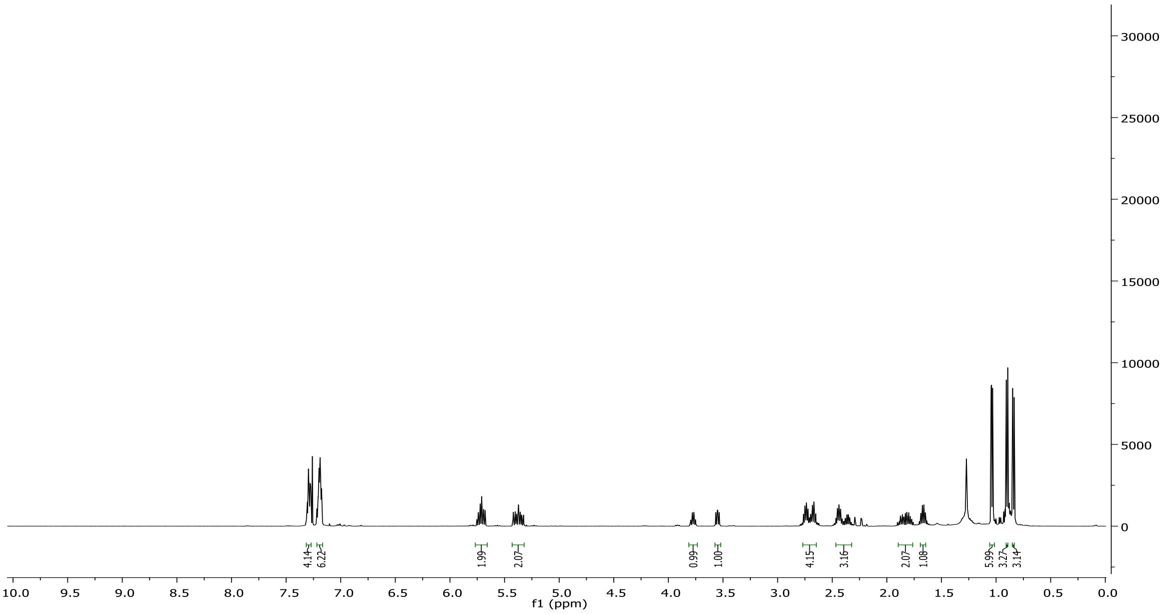


SI – NMR Spectra

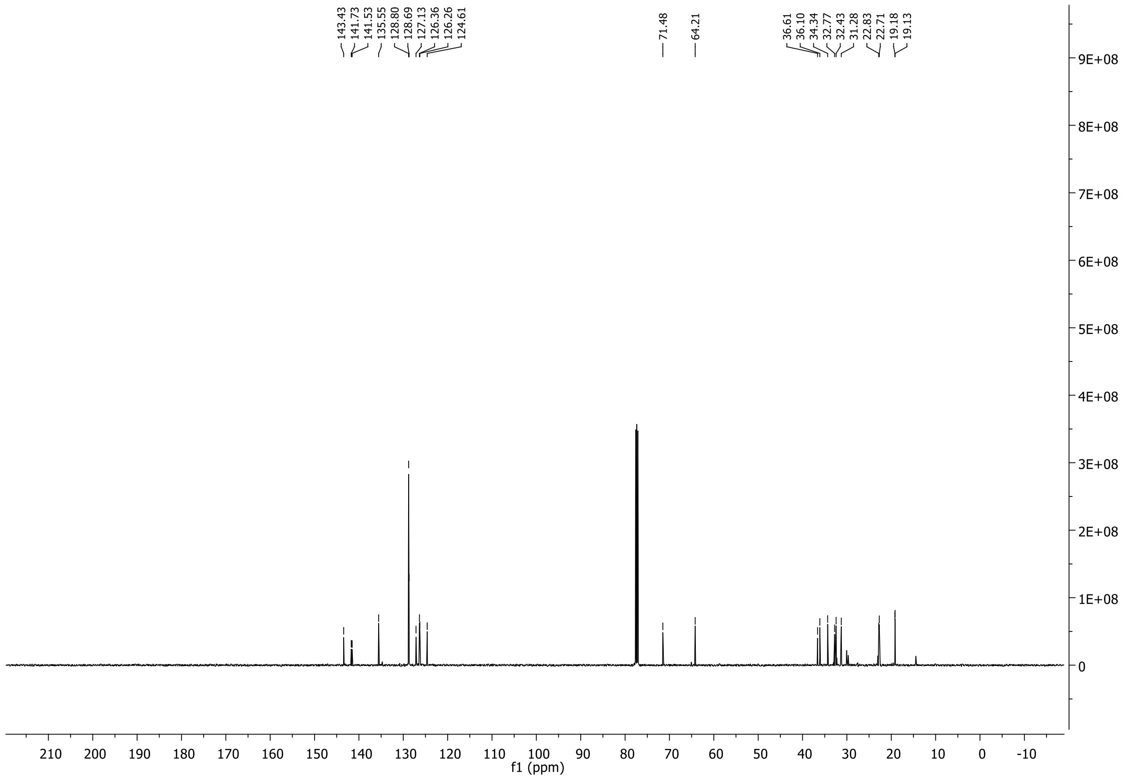
Allyl azide **2m** and **2m'** (1:1):



^{1}H NMR (500 MHz, CDCl$_3$, 25 ^{o}C)

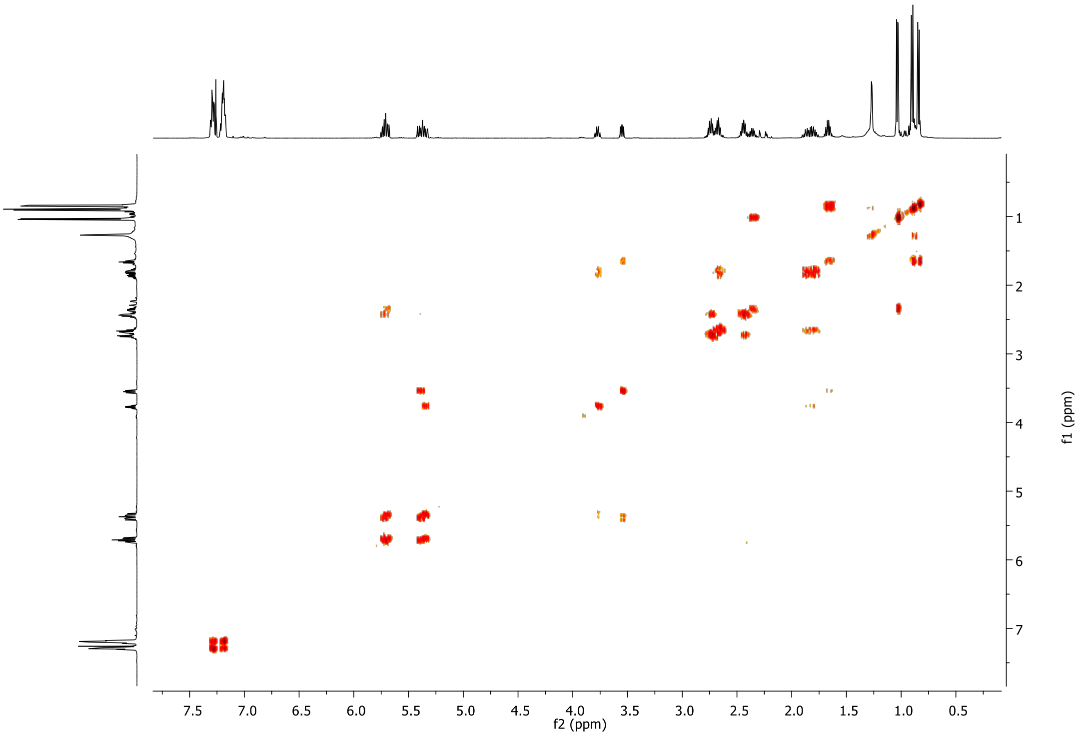


^{13}C NMR (126 MHz, CDCl$_3$, 25 ^{o}C)

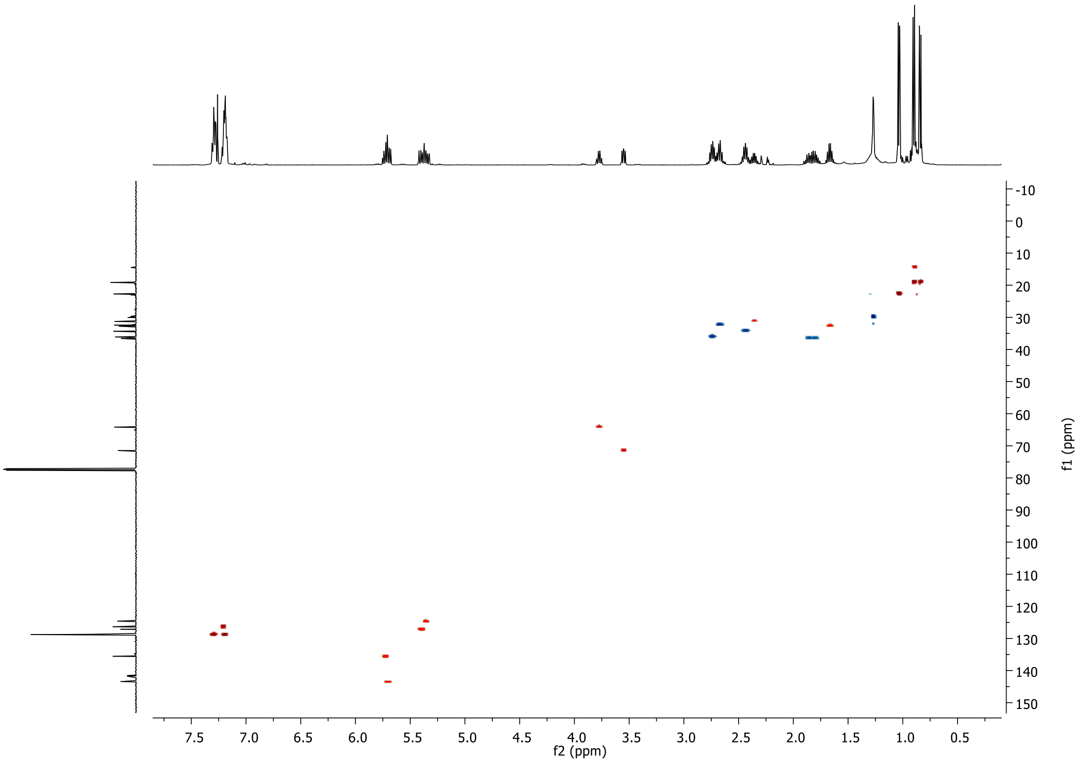


SI – NMR Spectra

2D gCOSY ($CDCl_3$):

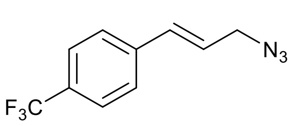


2D HSQC ($CDCl_3$):

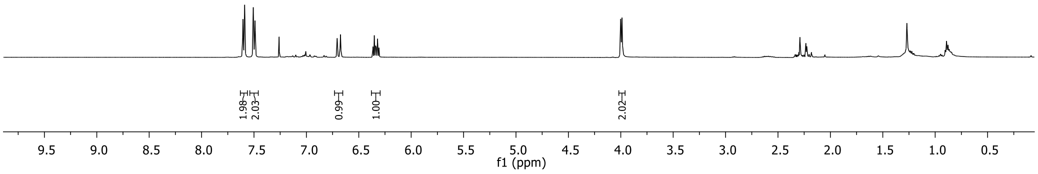


SI – NMR Spectra

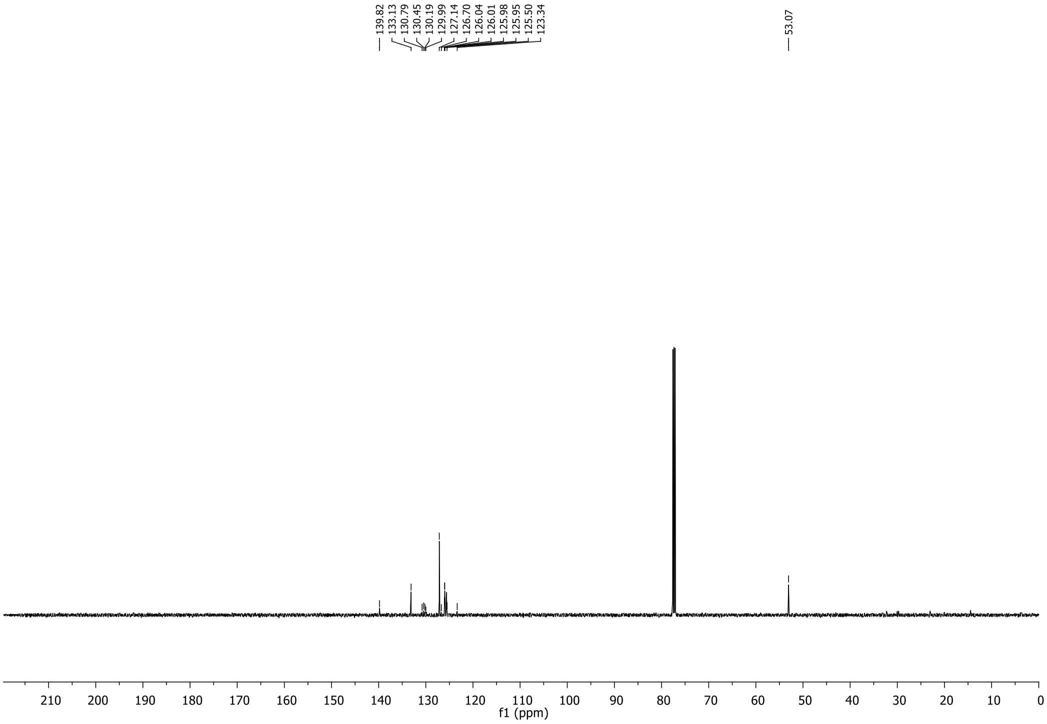
Allyl azide **2n**:



^{1}H NMR (500 MHz, CDCl$_3$, 25 ^{o}C)

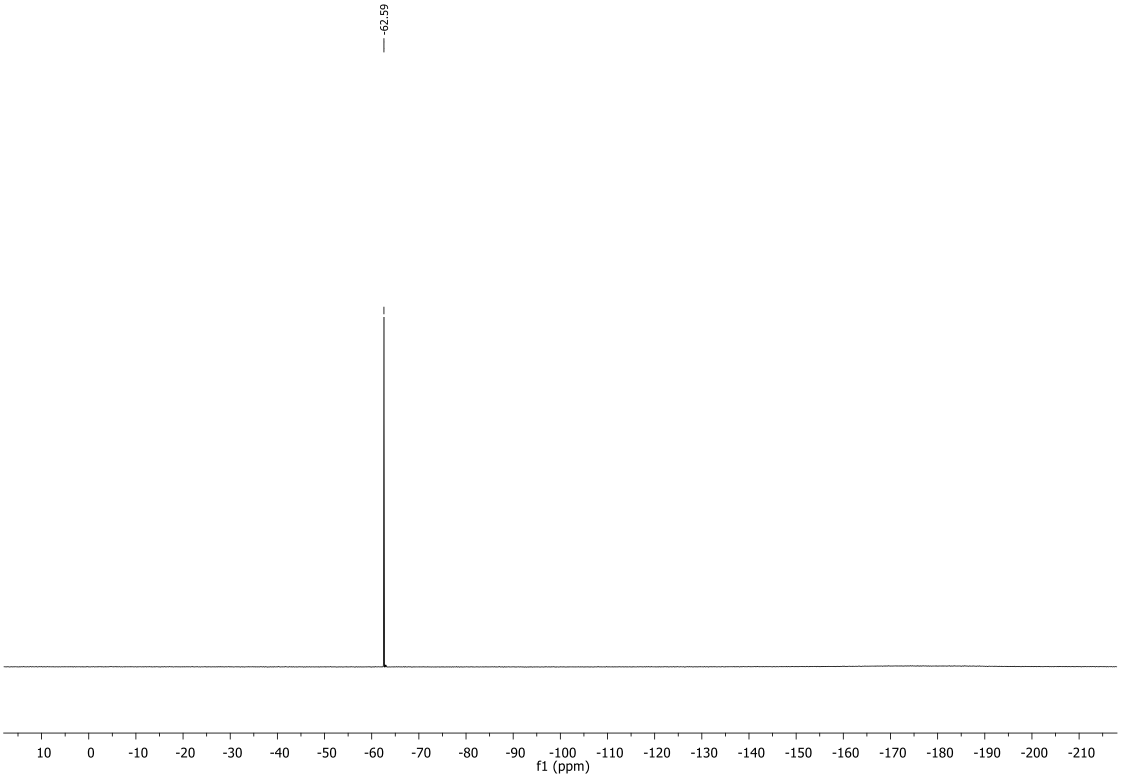


^{13}C NMR (126 MHz, CDCl$_3$, 25 ^{o}C)

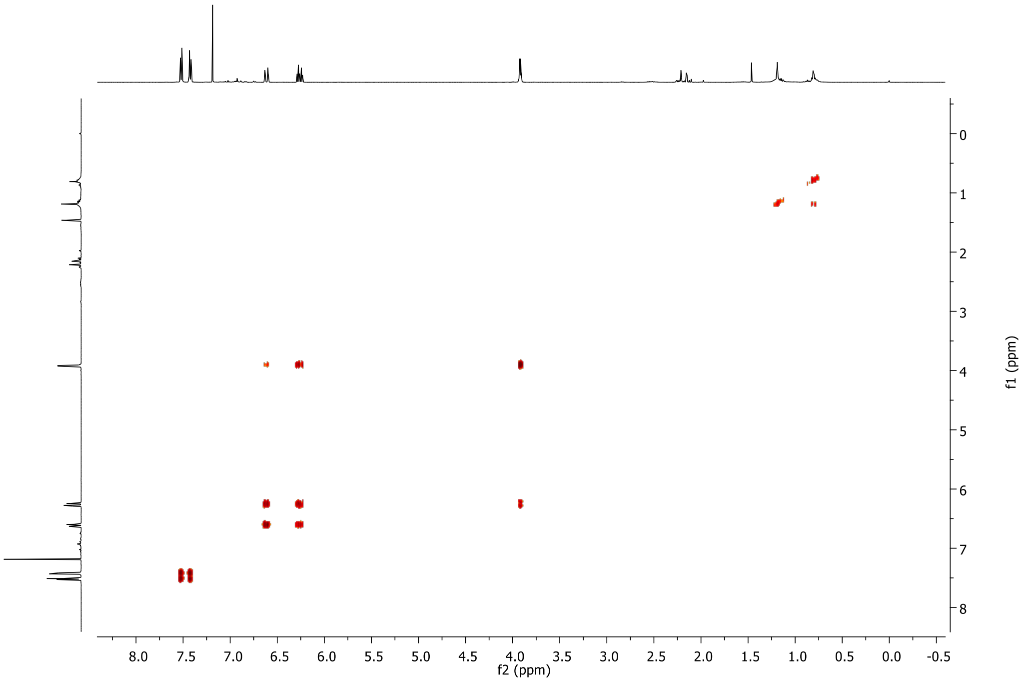


SI – NMR Spectra

^{19}F NMR (471 MHz, $CDCl_3$, 25 °C)

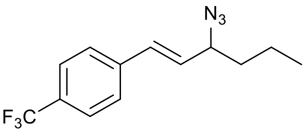


2D gCOSY ($CDCl_3$):

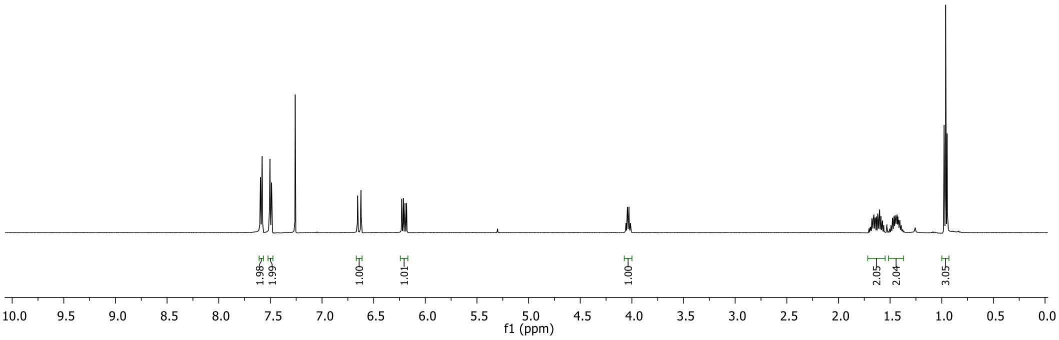


SI – NMR Spectra

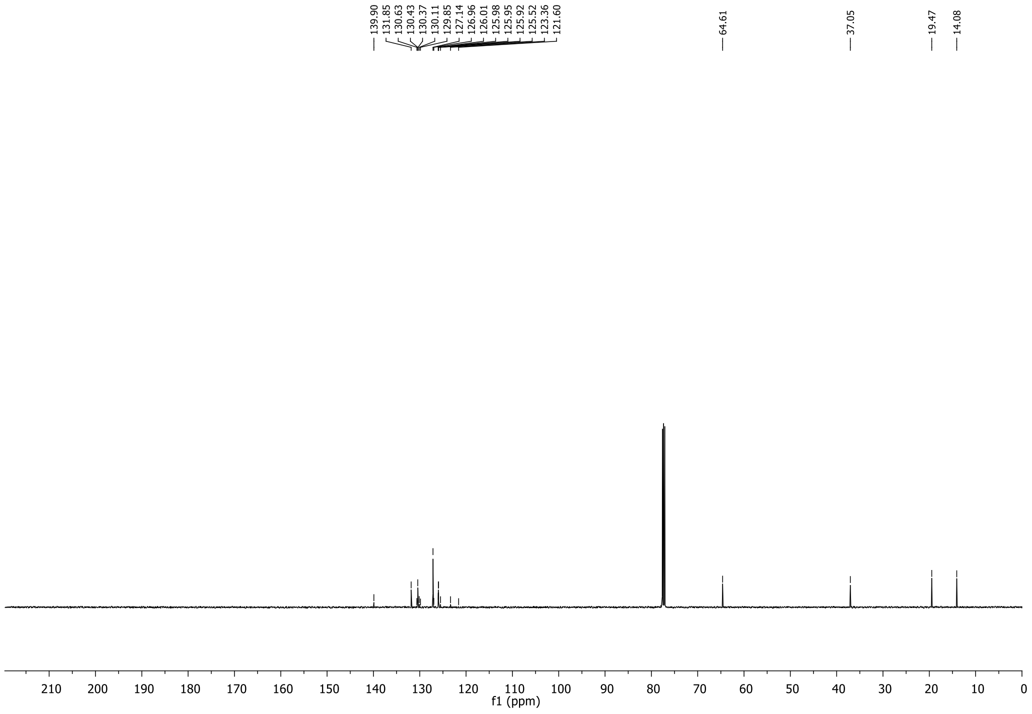
Allyl azide **2O**:



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C)

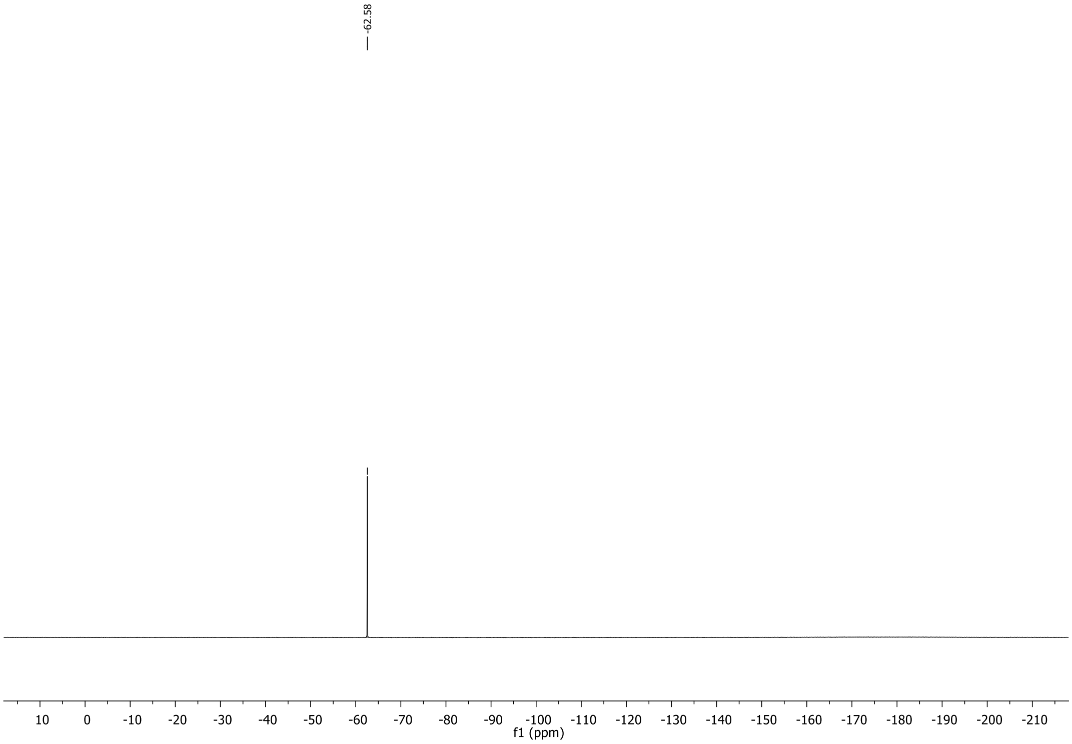


^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)



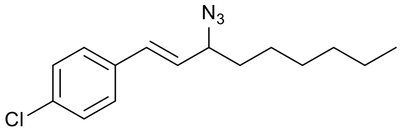
SI – NMR Spectra

^{19}F NMR (471 MHz, $CDCl_3$, 25 °C)

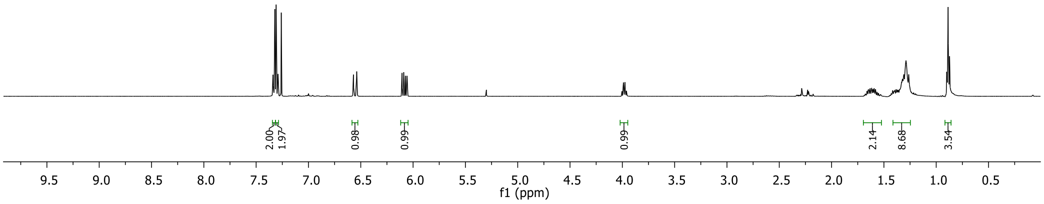


SI – NMR Spectra

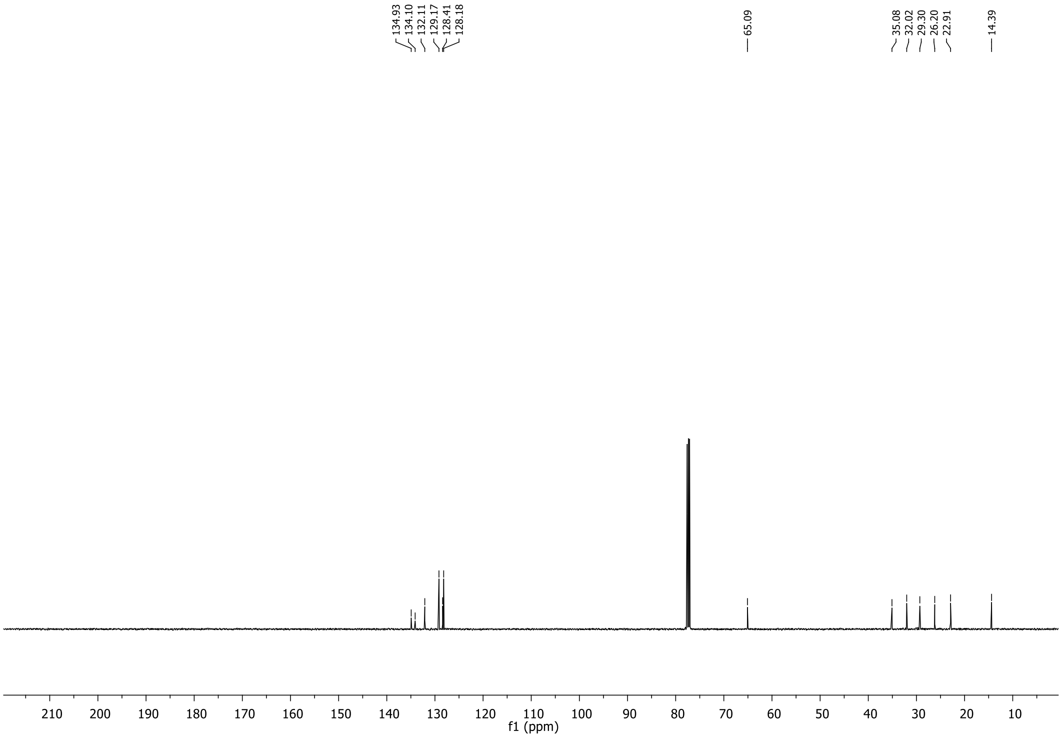
Allyl azide **2P**:



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C)

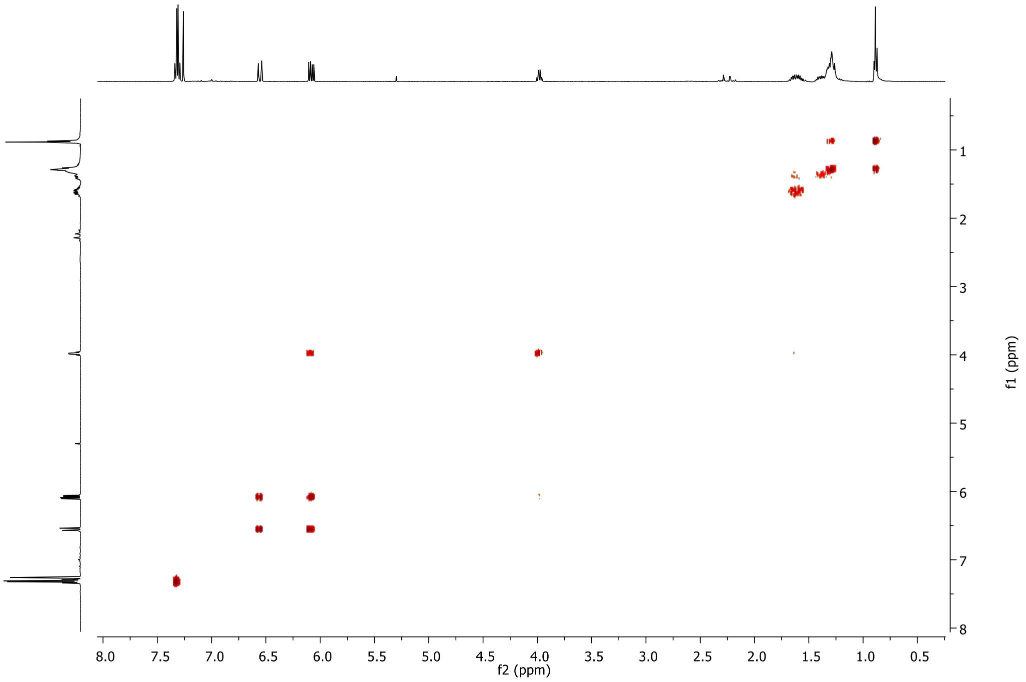


^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)

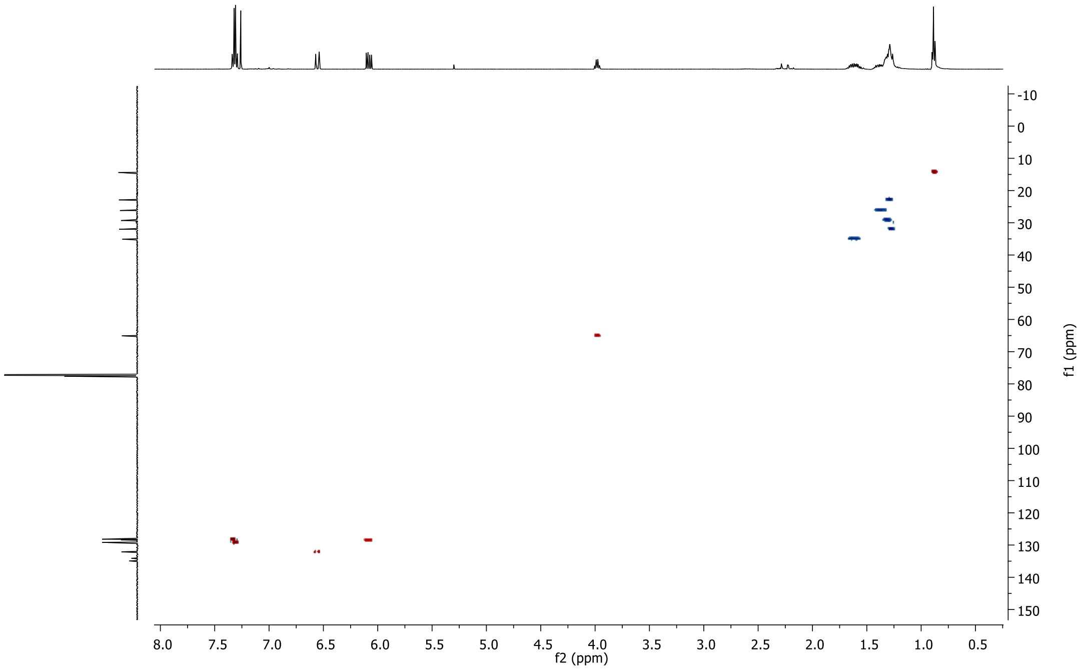


SI – NMR Spectra

2D gCOSY ($CDCl_3$):

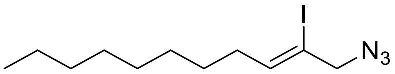


2D HSQC ($CDCl_3$):

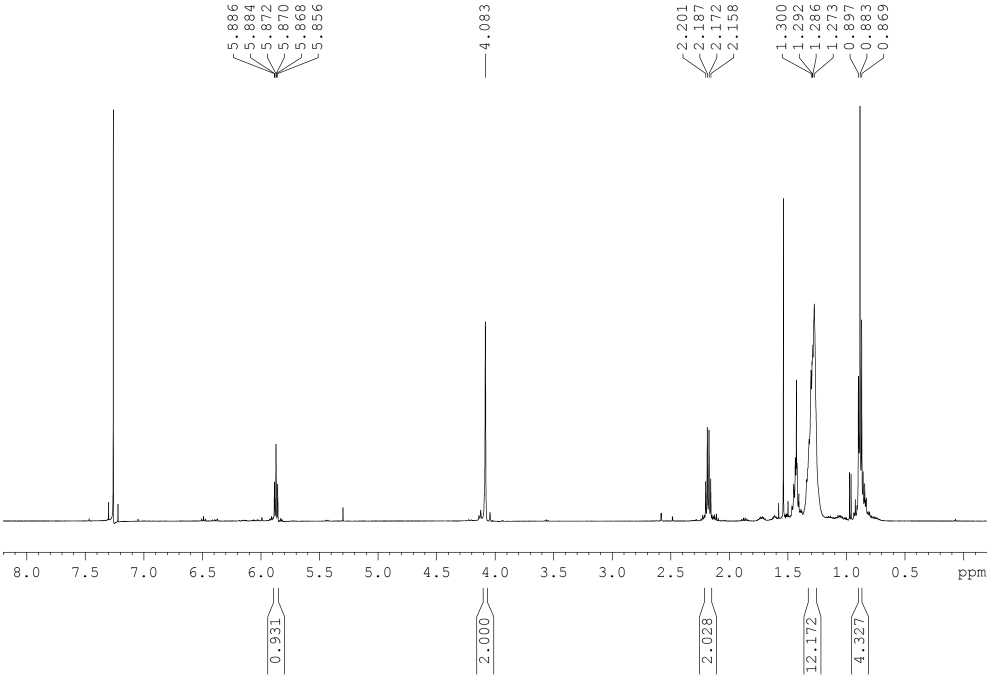


SI – NMR Spectra

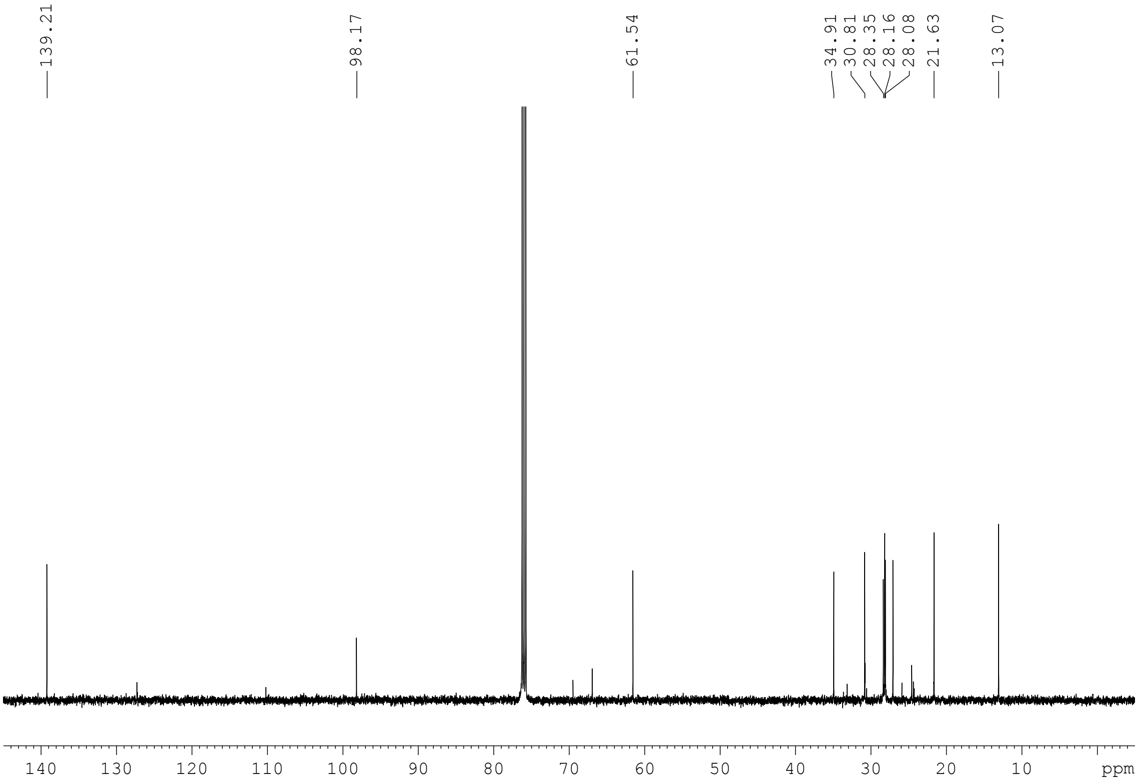
Vinyl-iodide **5c:**



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C)

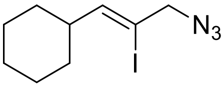


^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)

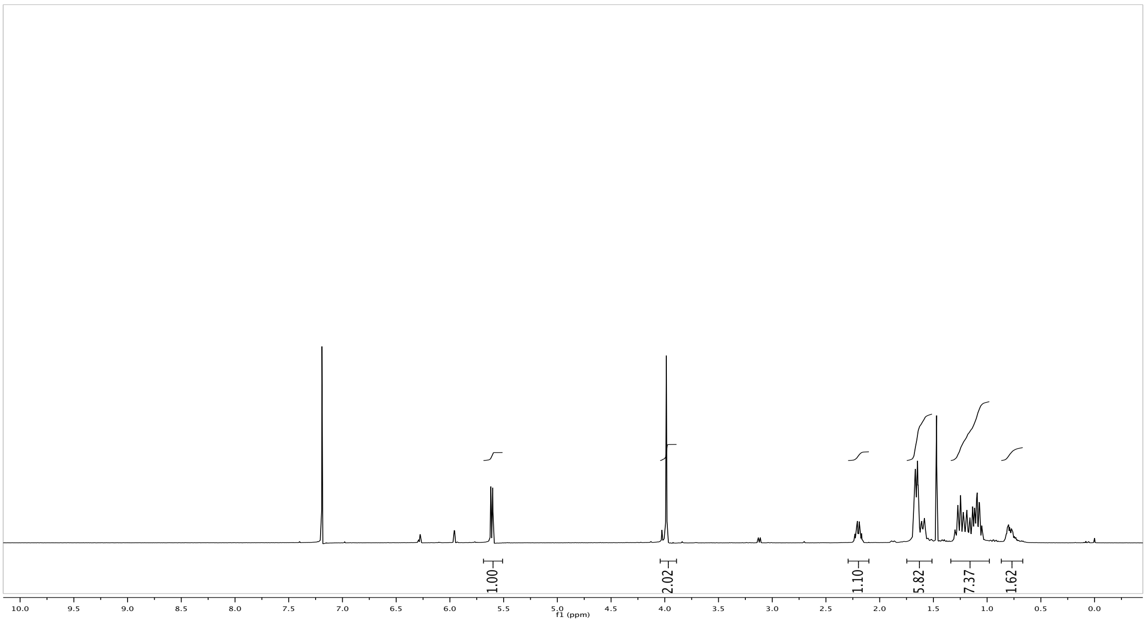


SI – NMR Spectra

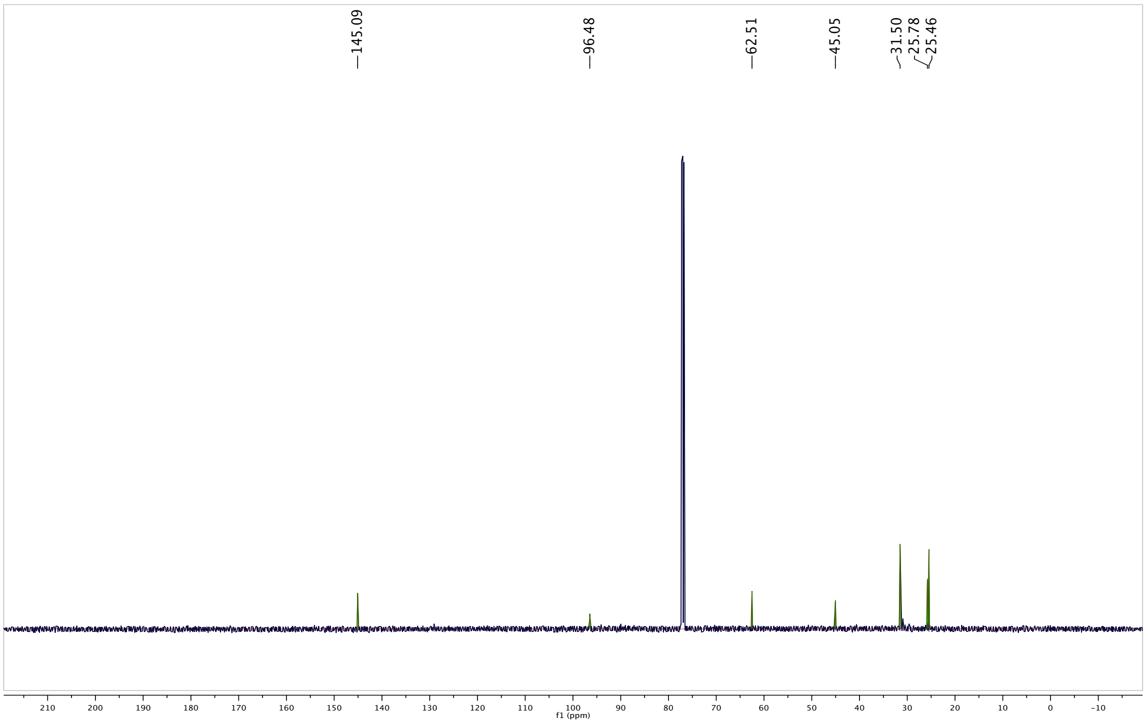
Vinyl-iodide **5a:**



^{1}H NMR (500 MHz, CDCl$_3$, 25 ^{o}C)

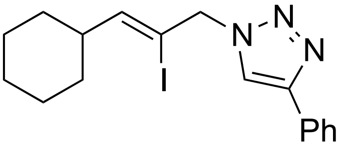


^{13}C NMR (126 MHz, CDCl$_3$, 25 ^{o}C)

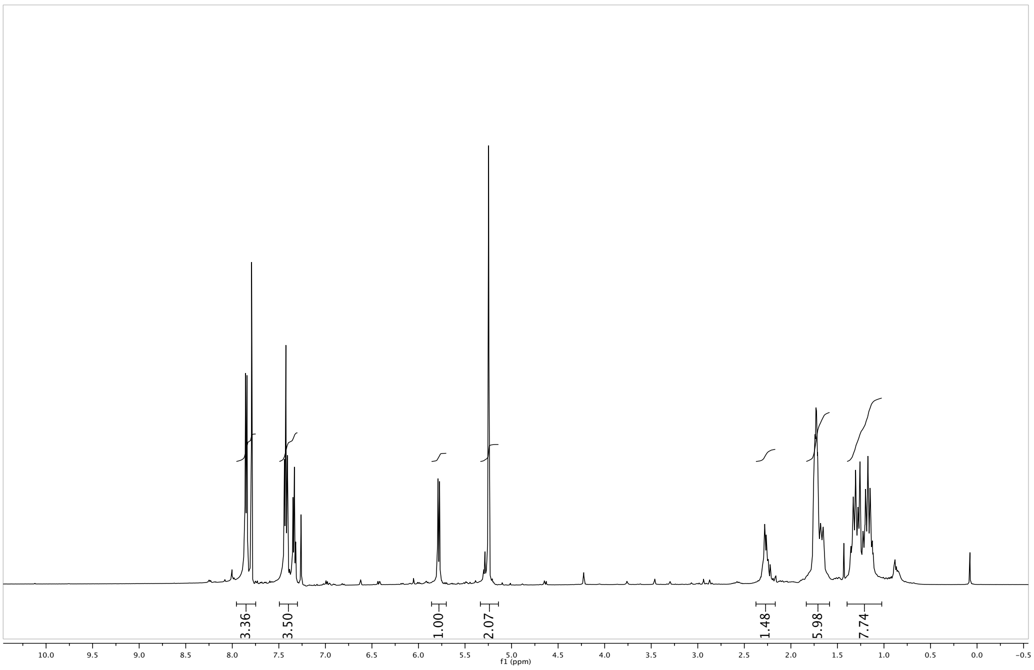


SI – NMR Spectra

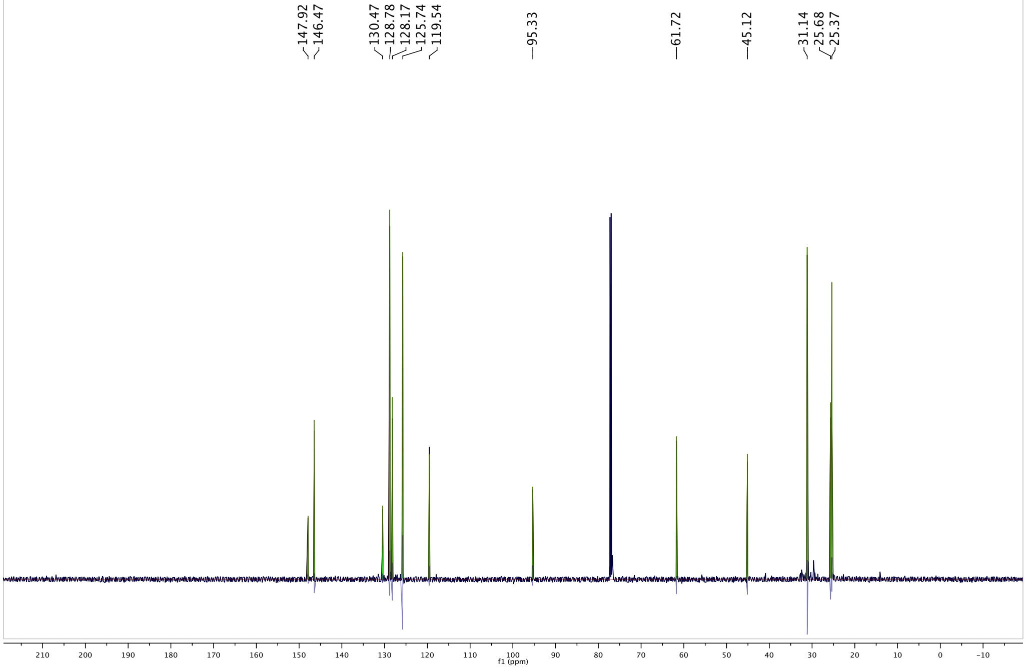
Triazole-vinyl-iodide **6a:**



^{1}H NMR (500 MHz, CDCl$_3$, 25 ^{o}C)

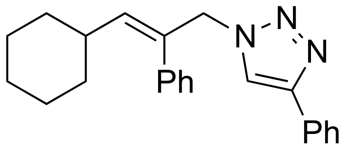


^{13}C NMR (126 MHz, CDCl$_3$, 25 ^{o}C)

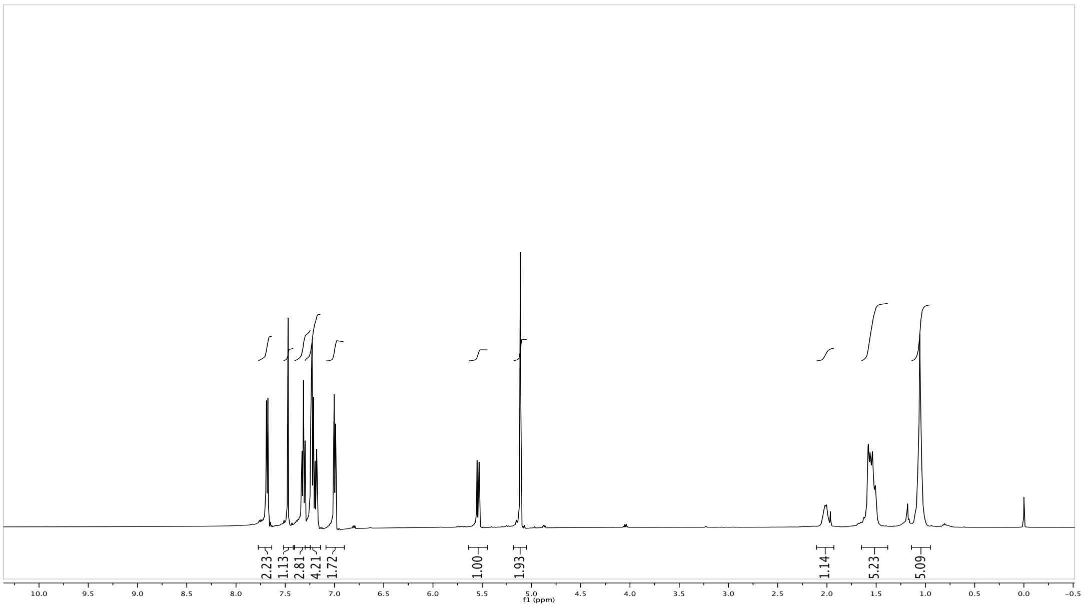


SI – NMR Spectra

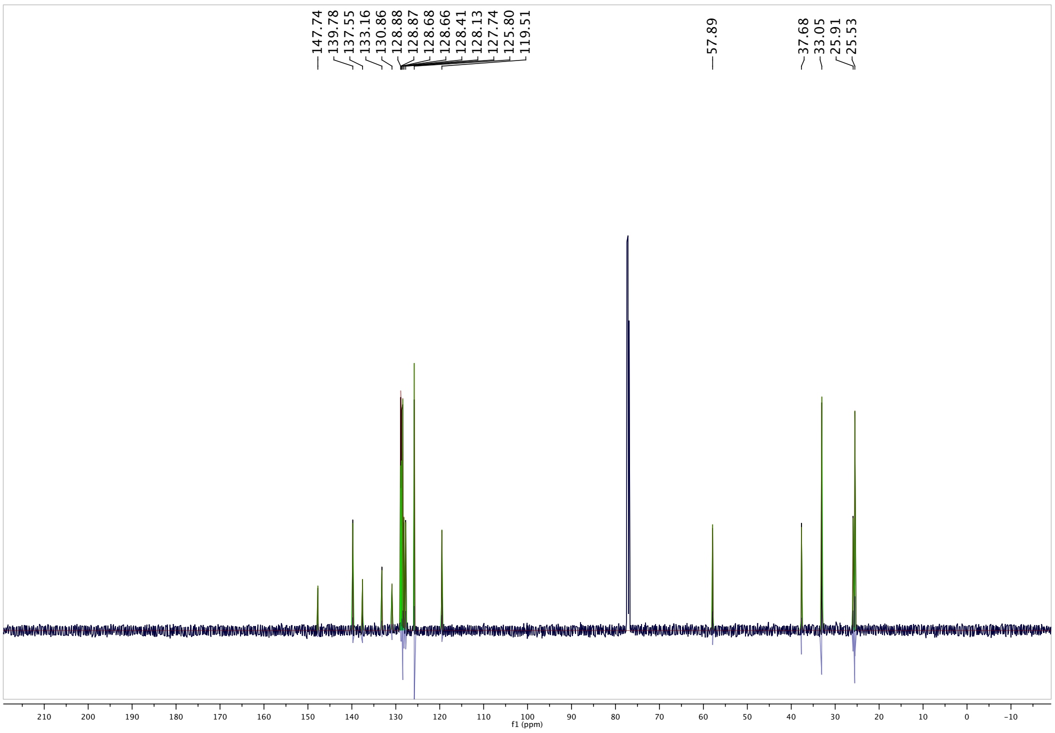
Triazole **7a:**



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C)

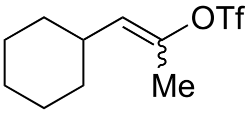


^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)



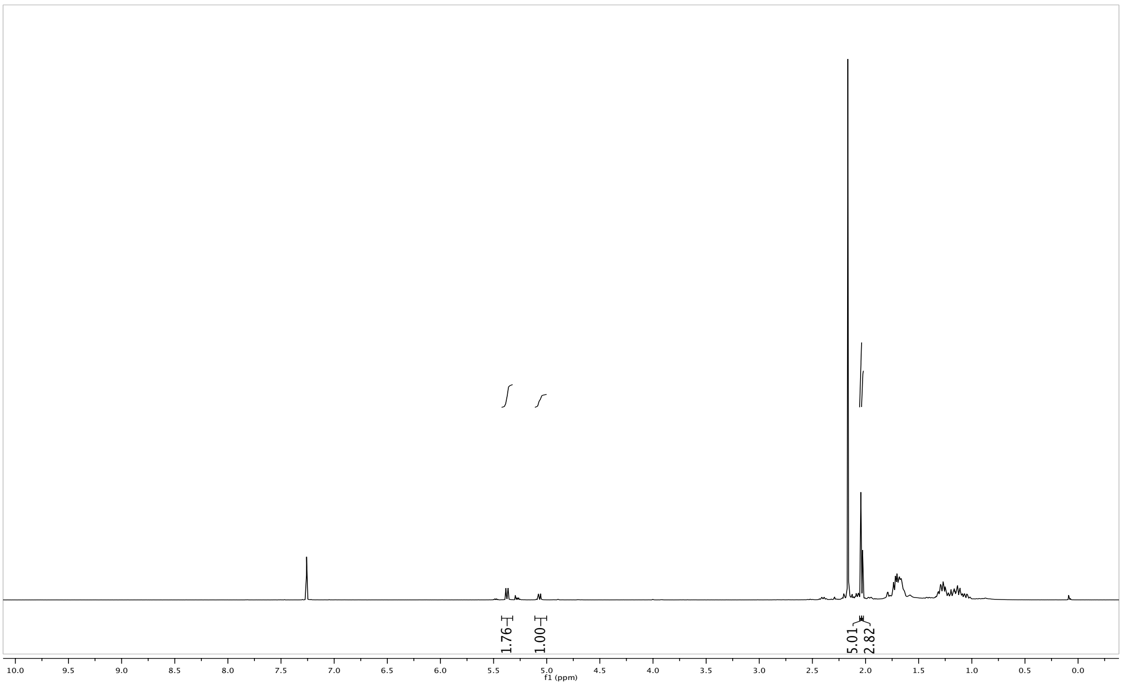
SI – NMR Spectra

Vinyl triflate **8a**:

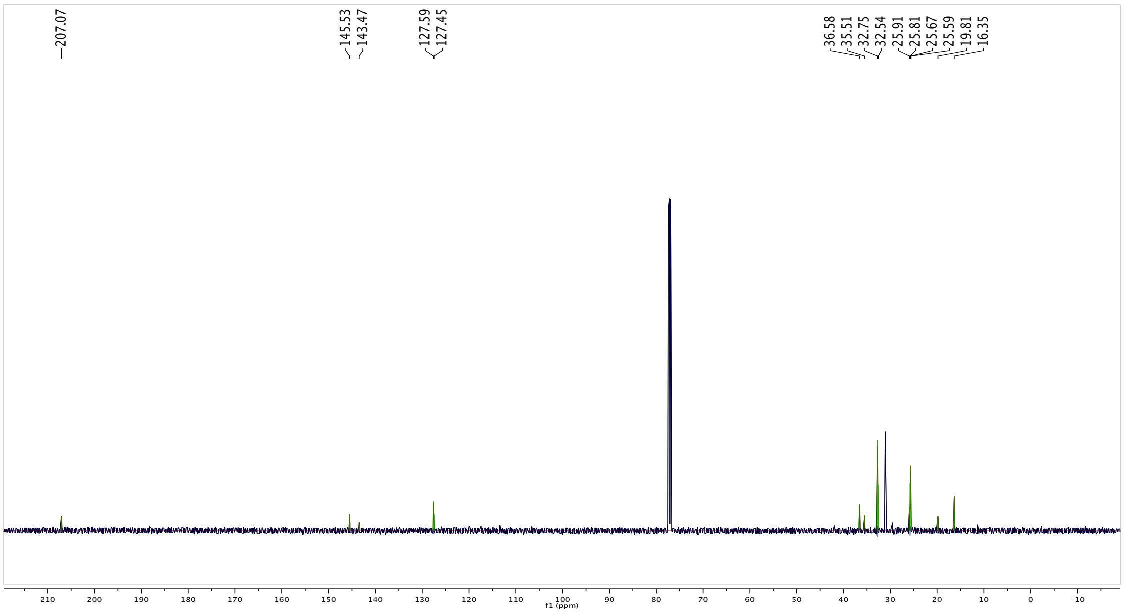


E/*Z*, 2:1

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C)

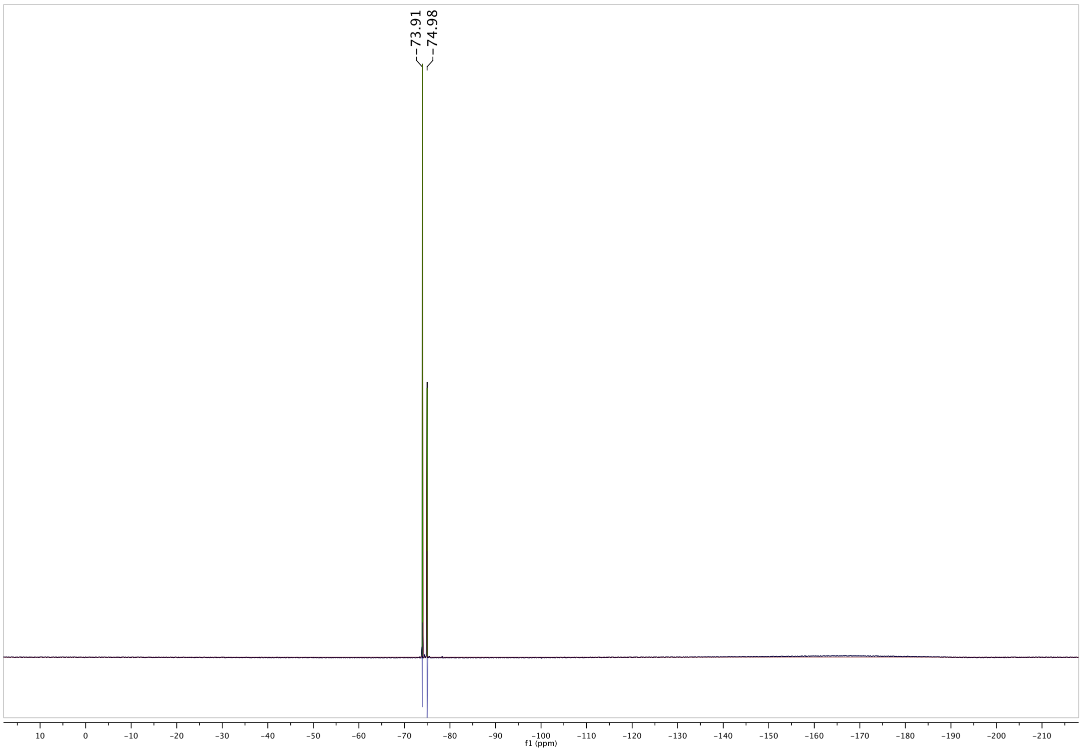


^{13}C NMR (126 MHz, $CDCl_3$, 25 °C)



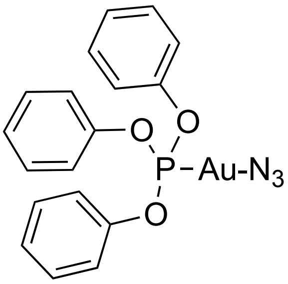
SI – NMR Spectra

^{19}F NMR (470 MHz, CDCl$_3$, 25 ^{o}C)

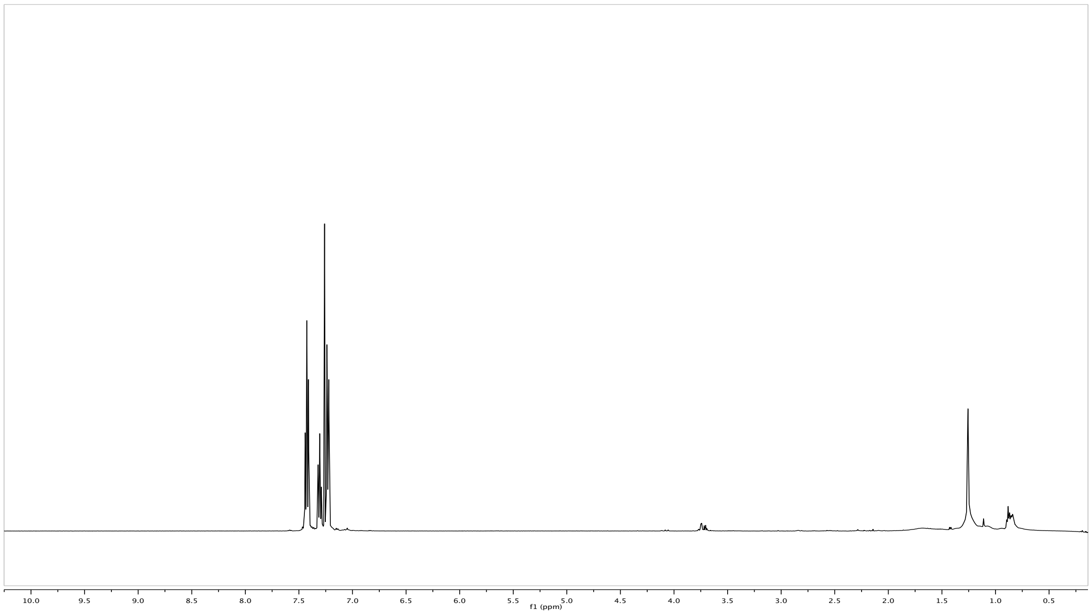


SI – NMR Spectra

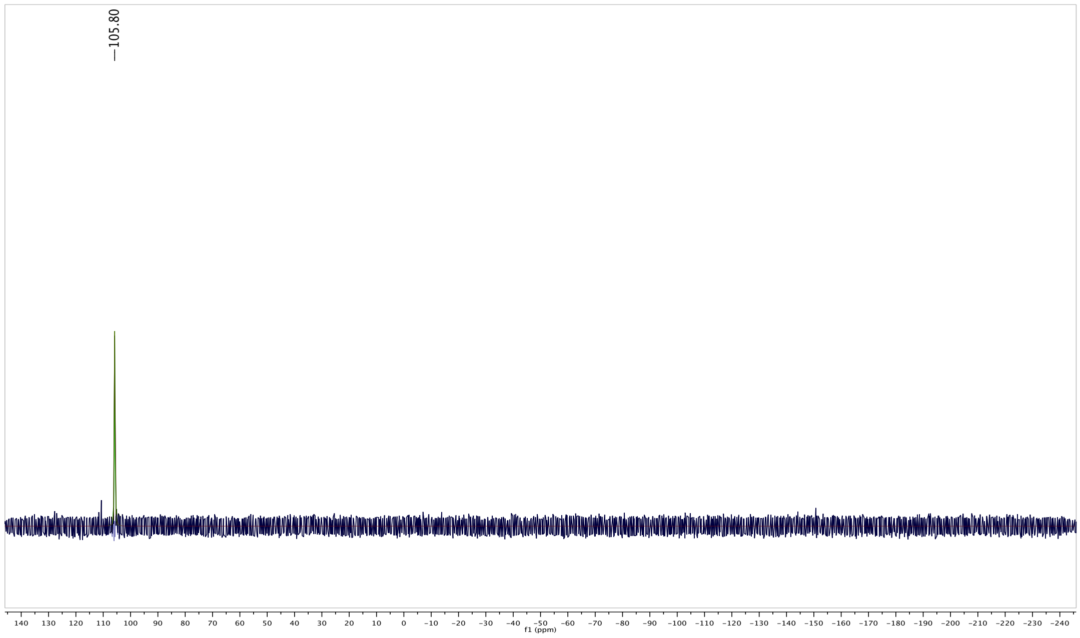
(Triphenylphosphite) gold(I) - azide



^{1}H NMR (500 MHz, CDCl$_3$, 25 ^{o}C)



^{31}P NMR (202 MHz, CDCl$_3$, 25 ^{o}C)



SI – NMR Spectra

IR (Film, cm^{-1})