SUPPORTING INFORMATION

Amberlite IRA900N_3 as a new catalyst for the azidation of α,β-unsaturated ketones under solvent-free conditions

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Experimental Section

All chemicals were purchased and used without any further purification. GC-EIMS analyses were carried out with 70 eV electron energy. All ^{1}H NMR and ^{13}C NMR spectra were recorded at 200 MHz or 400 MHz, and at 50.3 or 100.6 MHz respectively, using a convenient deuterated solvent (reported in the characterization charts) and the residual peak as internal standard, or TMS in the case of $CDCl_3$. IR spectra were recorded with FT-IR instrument, using $CHCl_3$ as solvent. Thin Layer Cromatography analyses were performed on silica gel on aluminum plates and UV and/or $KMnO_4$ were used as revealing systems. Column chromatographies were performed by using silica gel 230-400 mesh and eluting as reported in the following characterization charts. Amberlite IRA900F was purchased from Aldrich as "Fluoride on polymer support". Trimethylsilyl azide was purchased from Acros (97% pure, d: 0.860 Kg/L)

β-azido ketones ***2a***[1], **2c**[2], **2f**[3], **2g**[3], **2i**[4, 5], **2j**[5] and **2k**[5] are known compounds, products **2b, 2d, 2e, 2h,** and **2l** are new compounds.

Characterization data and copies of the ^{1}H and ^{13}C NMR spectra the compounds **2a-l** are reported below.

References

1 Taylor. S. M.; Zalatan, D. N.; Lerchner, A. M.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2005**, *127*, 1313-1317.

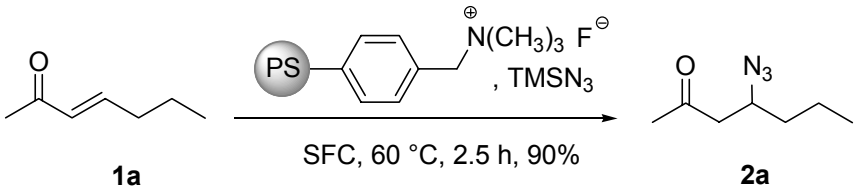
2 Davies, A. J.; Donald, A. S. R.; Marks, R. E. *J. Chem. Soc.* (C) **1967**, *21*, 109-112.

3 Chung, B. Y.; Park, Y. S.; Cho, I. S.; Hyun, B. C. *Bull. Korean Chem. Soc.* **1988**, *9*, 269-70.

4 Xu, L.-W.; Xia, C.-G.; Li, J.-W. Zhou, S.-L. *Tetrahedron Lett.* **2004**, *45*, 1219-1221.

5 Guerin, D. J.; Horstmann, T. E.; Miller, S. J. *Org. Lett.* **1999**, *1*, 1107-1109.

Chem. Name	**4-azidoheptan-2-one (2a)**
Lit. Ref.	*J. Am. Chem. Soc.* **2005**, *127*, 1313-1317



Mol. Wt.: 155

METHOD:
In a screw capped vial equipped with a magnetic stirrer (3*E*)-hept-3-en-2-one (**1a**) (0.116 g, 1.0 mmol), Amberlite IRA900F (0.038 g, 0.10 mmol, 2.6 mmol/g), and azidotrimethylsilane (0.152 mL, 1.1 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 60 °C. After 2.5 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum to give pure 4-azidoheptan-2-one (**2a**) as an oil (90 % yield, 0.140 g).

Mol Formula	$C_7H_{13}N_3O$	**m.p./b.p.**	Oil
Tlc - R_f (eluent)	0.44 (EtOAc/petroleum ether 3/7)		

FT-IR ($CHCl_3$, cm^{-1}): 2122, 1715, 1466, 1404.

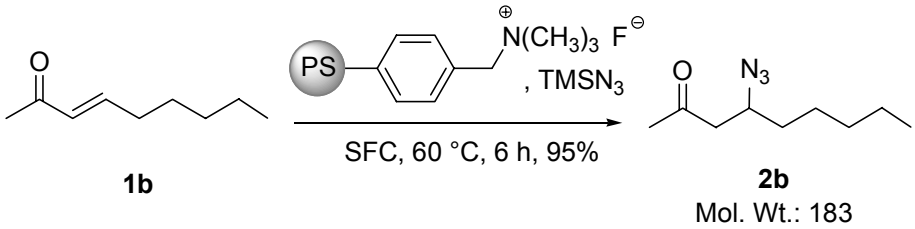
Elemental Analysis: Calcd. C, 54.19; H, 8.39; N, 27.08; found C, 54.39; H, 8.44; N, 27.20.

^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	0.93	3	*t*	6.7
	1.43-1.47	4	*m*	
	2.16	3	*s*	
	2.52	1	*dd*	17.2, 4.6
	2.67	1	*dd*	17.2, 8.4
	3.80-3.85	1	*m*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 13.6, 19.1, 30.5, 36.5, 47.9, 57.8, 205.7.

GC-EIMS (m/z, %): 155 (M^+,< 1), 112 (11), 99 (15), 70 (11), 58 (25), 43 (100).

Chem. Name	**4-azidononan-2-one (2b)**
Lit. Ref.	/



METHOD:
In a screw capped vial equipped with a magnetic stirrer (3*E*)-non-3-en-2-one (**1b**) (0.147 g, 1.0 mmol), Amberlite IRA900F (0.038 g, 0.10 mmol, 2.6 mmol/g), and azidotrimethylsilane (0.152 mL, 1.1 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 60 °C. After 6 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum to give pure 4-azidononan-2-one (**2b**) as an oil (95 % yield, 0.174 g).

Mol Formula	$C_9H_{17}N_3O$	**m.p./b.p.**	Oil
Tlc - R_f (eluent)	0.48 (EtOAc/petroleum ether 3/7)		

FT-IR ($CHCl_3$, cm^{-1}): 2110, 1715, 1468, 1401.

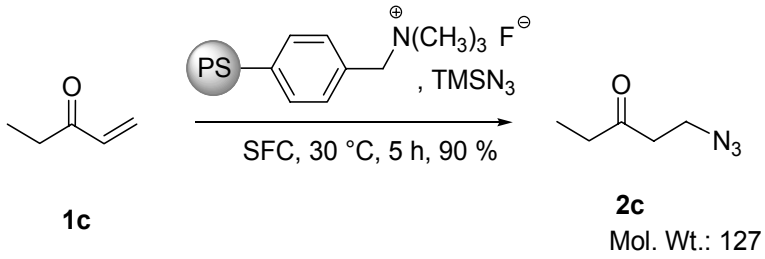
Elemental Analysis: Calcd. C, 58.99; H, 9.35; N, 22.93; found 59.02; H, 9.45; N, 23.01

^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	0.88	3	*t*	6.5
	1.29-1.48	8	*m*	
	2.17	3	*s*	
	2.52	1	*dd*	17.2, 4.9
	2.68	1	*dd*	17.2, 8.1
	3.84	1	*m*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 13.8, 22.3, 25.5, 30.3, 31.3, 34.3, 47.5, 58.0, 205.5.

GC-EIMS (m/z, %): 183 (M^+, nd), 112 (12), 99 (20), 70 (11), 68 (12), , 57 (36), 43 (100).

Chem. Name	**1-azidopentan-3-one (2c)**
Lit. Ref.	*J. Chem. Soc.* (C) **1967**, *21*, 109-112.



METHOD:
In a screw capped vial equipped with a magnetic stirrer pent-1-en-3-one (**1c**) (0.087 g, 1.0 mmol), Amberlite IRA900F (0.038 g, 0.10 mmol, 2.6 mmol/g), and azidotrimethylsilane (0.152 mL, 1.1 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C. After 5 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum to give pure 1-azidopentan-3-one (**2c**) was isolated as an oil (90 % yield, 0.114 g).

Mol Formula	$C_5H_9N_3O$	**m.p./b.p**	Oil
Tlc - R_f (eluent)	0.21 (EtOAc/petroleum ether 1/9)		

FT-IR ($CHCl_3$, cm^{-1}): 2106, 1715, 1603, 1504, 1460, 1411

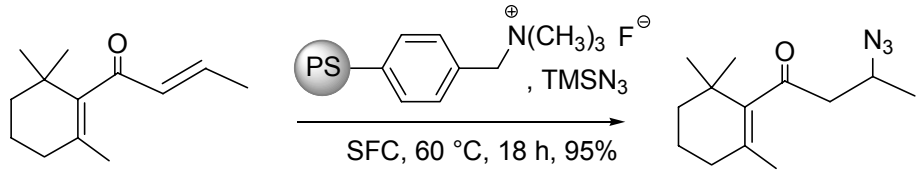
Elemental Analysis: Calcd. C, 47.23; H, 7.13; N, 33.05; found C, 47.15; H, 7.15; N, 33.00.

^{1}H NMR 200 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	1.05	3	*t*	7.3
	2.45	2	*q*	7.3
	2.66	2	*t*	6.3
	3.53	2	*t*	6.3

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 7.5, 36.4, 40.9 45.7, 208.4.

GC-EIMS (m/z, %): 127 (M^+, <1), 99 (6), 72 (45), , 57 (100), 43 (53).

Chem. Name	3-azido-1-(2',6',6'-trimethylcyclohex-1'-en-1'-yl)butan-1-one (2d)
Lit. Ref.	/



1d **2d**
Mol. Wt.: 235

METHOD:
In a screw capped vial equipped with a magnetic stirrer (2*E*)-1-(2',6',6'-trimethylcyclohex-1'-en-1'-yl)butan-1-one **(1g)** (0.214 g, 1.0 mmol), Amberlite IRA900F (0.192 g, 0.50 mmol, 2.6 mmol/g), and azidotrimethylsilane (0.414 mL, 3.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 60 °C. After 18 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum to give pure 3-azido-1-(2,6,6-trimethylcyclohex-1-en-1-yl)butan-1-one **(2d)** was isolated as an oil (95 % yield, 0.223 g).

Mol Formula	$C_{13}H_{21}N_3O$	m.p./b.p.	Oil
Tlc - R_f (eluent)	0.61 (EtOAc/petroleum ether 3/7)		

FT-IR ($CHCl_3$, cm^{-1}): 2119, 1710, 1689, 1458, 1399.

Elemental Analysis: Calcd. C, 66.35; H, 8.99; N, 17.86; found C, 66.23; H, 8.90; N, 17.90.

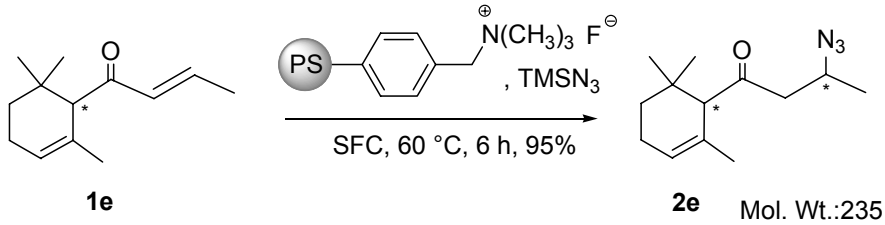
^{1}H NMR 400 MHz $CDCl_3$

δ value	No. H	Mult.	J value/Hz
1.04	3	*s*	
1.07	3	*s*	
1.30	3	*d*	6.6
1.39-1.45	2	*m*	
1.58	3	*s*	
1.58-1.71	2	*m*	
1.95	2	*t*	6.2
2.56	1	*dd*	18.5, 5.4
2.82	1	*dd*	18.5, 7.4
4.10	1	*m*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 18.5, 19.3, 20.3, 28.4, 30.9, 33.0, 38.6, 51.4, 52.7, 129.5, 142.3, 207.4.

GC-EIMS (m/z, %): 235 (M^+, nd), 192 (56), 164 (28), 151 (100), 138 (22), 123 (91), 107 (21), 91 (24), 81 (68), 67 (17), 43 (22).

Chem. Name	3-azido-1-(2’,6’,6’-trimethylcyclohex-2’-en-1’-yl)butan-1-one (2e)
Lit. Ref.	/



METHOD:
In a screw capped vial equipped with a magnetic stirrer (2*E*)-1-(2’,6’,6’-trimethylcyclohex-2’-en-1’-yl)butan-1-one **(1e)** (0.214 g, 1.0 mmol), Amberlite IRA900F (0.096 g, 0.25 mmol, 2.6 mmol/g), and azidotrimethylsilane (0.207 mL, 1.5 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 60 °C. After 6 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum to give a 60/40 mixture of two diastereoisomers of 3-azido-1-(2’,6’,6’-trimethylcyclohex-2’-en-1’-yl)butan-1-one **(2e)** as an oil (95 % yield, 0.223 g).
(2*E*)-1-(2’,6’,6’-trimethylcyclohex-2’-en-1’-yl)butan-1-one (**1e**) is commercially available in a ca. 90/10 mixture with its isomer (**1d**) and therefore the product **2e** has been isolated as inseparable 92/8 mixture with **2d**.

Mol Formula	$C_{13}H_{21}N_3O$	m.p./b.p	Oil
Tlc - R_f (eluent)	0.61 (EtOAc/petroleum ether 3/7)		

FT-IR ($CHCl_3$, cm^{-1}): 2128, 1710, 1450, 1366.

Elemental Analysis: Calcd. C, 65.51; H, 10.15; N, 17.63; found 66.38; H, 9.94; N, 17.87

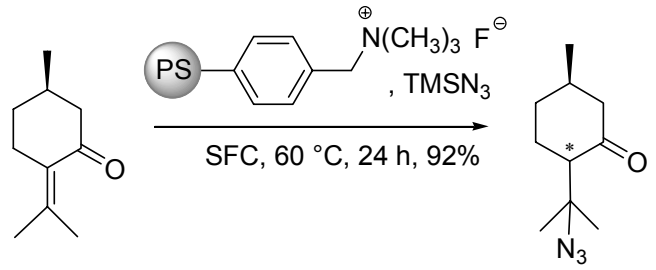
^{1}H NMR 400 MHz $CDCl_3$

δ value	No. H	Mult.	j value/Hz
0.89	3	*s*	
0.90	3	*s*	
0.92	3	*s*	
1.25	3	*d*	2.9
1.27	3	*d*	2.9
1.58	3	*s*	
1.59-1.71	2	*m*	
1.93-2.33	2	*m*	
2.56	1	*dd*	18.2, 5.8
2.69	1	*m*	
2.83	1	*dd*	18.2, 7.4
4.02	1	*m*	
5.60	1	*s*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 19.5, 22.5, 23.3, 27.7, 27.8, 30.6, 30.7, 51.1, 51.2, 52.9, 53.2, 63.6, 63.7, 123.8, 129.6, 210.2, 210.4.

GC-EIMS (m/z, %): 235 (M^+, <1), 192 (11), 124 (13), 123 (100), 122 (13), 108 (18), 107 (24), 95 (14), 93 (10), 91 (15), 84 (16), 81 (50), 79 (11), 69 (11), 67 (10), 43 (12).

Chem. Name	**2-(1'-azido-1'-methylethyl)-5-methylcyclohexan-1-one (2f)**
Lit. Ref.	*Bull. Korean Chem. Soc.* **1988**, *9*, 269-70



1f **2f** Mol. Wt.:195

METHOD:
In a screw capped vial equipped with a magnetic stirrer (5*R*)-5-methyl-2-(1'-methylethylidene)cyclohexan-1-one **(1f)** (0.155 g, 1.0 mmol), Amberlite IRA900F (0.192 g, 0.50 mmol, 2.6 mmol/g), and azidotrimethylsilane (0.207 mL, 1.5 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 60 °C. After 24 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum to give a 60/40 mixture of two diastereoisomers of 2-(1'-azido-1'-methylethyl)-5-methylcyclohexan-1-one (**2f**) as an oil (92 overall % yield, 0.179 g).

Mol Formula	$C_{10}H_{17}N_3O$	**m.p./b.p.**	Oil
Tlc - R_f (eluent)	0.39 (EtOAc/petroleum ether 1/9)		

FT-IR ($CHCl_3$, cm^{-1}): 2115, 1712, 1457, 1388.

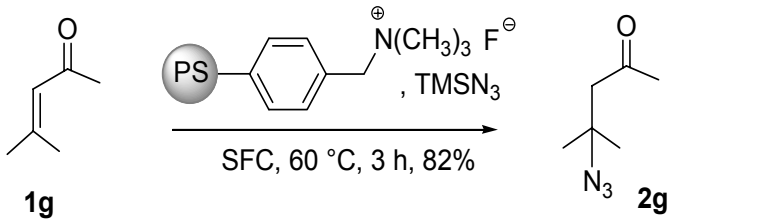
Elemental Analysis: Calcd. C, 61.51; H, 8.78; N, 21.52; found C, 61.48; H, 8.70; N, 21.67.

^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	0.94	3	*d*	6.8
	1.01	3	*d*	6.4
	1.34	6	*s*	
	1.42	6	*s*	
	1.85-2.25	10	*m*	
	2.28-2.47	6	*m*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 18.9, 21.9, 22.0, 22.7, 24.4, 24.7, 24.9, 28.4, 30.6, 32.2, 33.9, 36.0, 49.6, 51.6, 57.8, 57.9, 62.0, 62.1, 209.4, 210.3.

GC-EIMS (m/z, %): 195 (M^+, nd), 153 (11), 109 (20), 69 (31), 56 (100), 43 (4).

Chem. Name	**4-azido-4-methylpentan-2-one (2g)**
Lit. Ref.	*Bull. Korean Chem. Soc.* **1988**, *9*, 269-70



Mol. Wt.: 141

METHOD:
In a screw capped vial equipped with a magnetic stirrer 4-methylpent-3-en-2-one **(1g)** (0.109 g, 1.0 mmol), Amberlite IRA900F (0.096 g, 0.25 mmol, 2.6 mmol/g), and azidotrimethylsilane (0.207 mL, 1.5 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 60 °C. After 3 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum to give pure 4-azido-4-methylpentan-2-one (**2g**) as an oil (82 % yield, 0.116 g).

Mol Formula	$C_6H_{11}N_3O$	**m.p./b.p.**	Oil
Tlc - R_f (eluent)	0.26 (EtOAc/petroleum ether 1/9)		

FT-IR ($CHCl_3$, cm^{-1}): 2104, 1724, 1464, 1368.

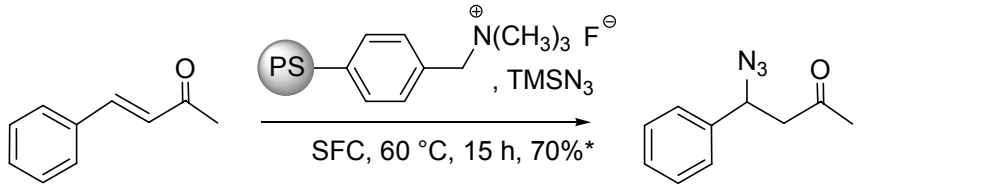
Elemental Analysis: C, 51.05; H, 7.85; N, 29.77; found C, 51.15; H, 7.82; N, 29.62.

^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	1.36	6	*s*	
	2.17	3	*s*	
	2.57	2	*s*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 26.0, 31.7, 53.1, 59.7, 205.8.

GC-EIMS (m/z, %): 141 (M^+, <1), 99 (14), 56 (53), 43 (100).

Chem. Name	4-azido-4-phenylbutan-2-one (2h)
Lit. Ref.	/



1h **2h** Mol. Wt.: 189

METHOD:
In a screw capped vial equipped with a magnetic stirrer (3*E*)-4-phenylbut-3-en-2-one **(1h)** (0.146 g, 1.0 mmol), Amberlite IRA900F (0.192 g, 0.50 mmol, 2.6 mmol/g), and azidotrimethylsilane (0.276 mL, 2.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 60 °C. After 15 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum and the reaction mixture was separated by silica gel column chromatography ($CHCl_3$; silica /sample 15:1) to give pure 4-azido-4-phenylbutan-2-one **(2h)** as an oil (0.085 g, 45% Yield.

*The effective yield calculated considering that 36% of **1h** was recovered after silica gel column chromatgraphy was 70%).

Mol Formula	$C_{10}H_{11}N_3O$	m.p./b.p.	Oil
Tlc - R_f (eluent)	0.51 ($CHCl_3$)		

FT-IR ($CHCl_3$, cm^{-1}): 2111, 1719, 1495, 1455, 1410.

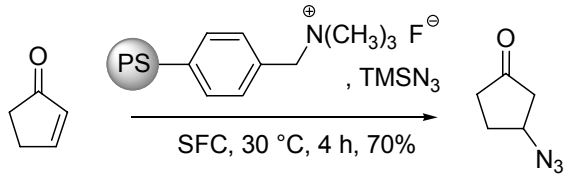
Elemental Analysis: Calcd. C, 63.48; H, 5.86; N, 22.21; found C, 63.40; H, 5.68; N, 22.15.

^{1}H NMR 400 MHz $CDCl_3$	δ value	No. H	Mult.	j value/Hz
	2.16	3	*s*	
	2.75	1	*dd*	17.1, 4.7
	2.98	1	*dd*	17.1, 8.9
	5.03	1	*dd*	8.9, 4.7
	7.31-7.40	5	*m*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 30.5, 49.5, 61.1, 126.7, 128.4, 128.8, 138.8, 204.9.

GC-EIMS (m/z, %): 189 (M^+, nd), 146 (23), 131 (17), 119 (44), 104 (100), 91 (41), 77 (82), 58 (53), 51 (29), 43 (86).

Chem. Name	**3-azido-cyclopentan-1-one (2i)**
Lit. Ref.	*Tetrahedron Lett.* **2004**, *45*, 1219-1221; *Org. Lett.* **1999**, *1*, 1107-1109



1i **2i** Mol. Wt.:125

METHOD:
In a screw capped vial equipped with a magnetic stirrer cyclopent-2-en-1-one (**1i**) (0.084 g, 1.0 mmol), Amberlite IRA900F (0.096 g, 0.25 mmol, 2.6 mmol/g), and azidotrimethylsilane (0.414 mL, 3.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30°C. After 4 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum and the reaction mixture was separated by silica gel column chromatography (8/2 $CHCl_3$/petroleum ether ; silica/sample 30/1) to give pure 3-azido-cyclopentan-1-one (**2i**) as an oil (70 % yield, 0.088 g).

Mol Formula	$C_5H_7N_3O$	**m.p./b.p.**	Oil
Tlc - R_f (eluent)	0.35 ($CHCl_3$/petroleum ether 8/2)		

FT-IR ($CHCl_3$, cm^{-1}): 2111, 1742, 1607, 1452, 1402.

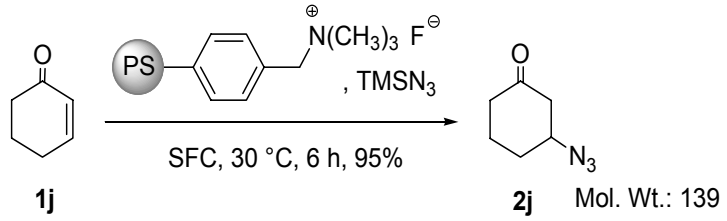
Elemental Analysis: Calcd. C, 47.99; H, 5.64; N, 33.58; found C, 48.30, H, 5.65; N, 33.46.

^{1}H NMR 200 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	2.13-2.32	5	*m*	
	2.44	1	*dd*	18.3, 6.3
	4.29	1	*m*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 28.8, 35.7, 44.0, 58.8, 214.9.

GC-EIMS (m/z, %): 125 (M+, 29), 82 (10), 68 (46), 55 (100), 43 (12).

Chem. Name	**3-azidocyclohexan-1-one (2j)**
Lit. Ref.	*Org. Lett.* **1999**, *1*, 1107-1109



METHOD:
In a screw capped vial equipped with a magnetic stirrer cyclohex-2-enone (**1j**) (0.101 g, 1.0 mmol) (0.101 g, 1.0 mmol), Amberlite IRA900F (0.096 g, 0.25 mmol, 2.6 mmol/g), and azidotrimethylsilane (0.207 mL, 1.5 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C. After 6 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum to give pure 3-azidocyclohexan-1-one (**2j**) as an oil (95 % yield, 0.132 g).

Mol Formula	$C_6H_9N_3O$	**m.p./b.p.**	Oil
Tlc - R_f (eluent)	0.31 (EtOAc/*n*-Hexane 2/8)		

FT-IR ($CHCl_3$, cm^{-1}): 2108, 1720, 1489

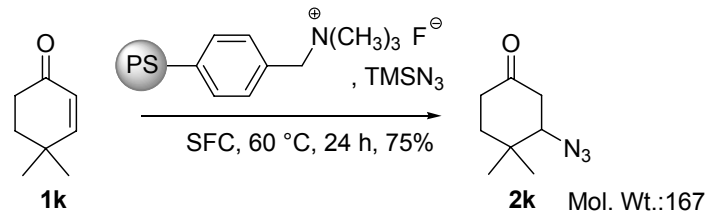
Elemental Analysis: Calcd. C, 51.80; H, 6.47; N, 30.21; found C, 51.63; H, 6.38; N, 30.18.

^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	1.67-1.80	2	*m*	
	1.98-2.10	2	*m*	
	2.33	2	*t*	5.1
	2.37	1	*dd*	14.3, 8.4
	2.64	1	*dd*	14.3, 4.5
	3.87	1	*m*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 21.2, 29.6, 40.5, 46.4, 59.4, 207.4

GC-EIMS (m/z, %): 139 (M^+, 42), 97 (13), 82 (29), 69 (38), 55 (100), 43 (22).

Chem. Name	**3-azido-4,4-dimethylcyclohexan-1-one (2k)**
Lit. Ref.	*Org. Lett*. **1999**, *1*, 1107-1109



METHOD:
In a screw capped vial equipped with a magnetic stirrer 4,4-dimethylcyclohex-2-en-1-one (**1k**) (0.128 g, 1.0 mmol), Amberlite IRA900F (0.096 g, 0.25 mmol, 2.6 mmol/g), and azidotrimethylsilane (0.414 mL, 3.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 60 °C. After 24 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum and the reaction mixture was separated by silica gel column chromatography ($CHCl_3$/petroleum ether 9/1; silica gel/sample 30/1) to give pure 3-azido-4,4-dimethylcyclohexan-1-one (**2k**) as an oil (75 % yield, 0.125 g).

Mol Formula	$C_8H_{13}N_3O$	**m.p./b.p.**	Oil
Tlc - R_f (eluent)	0.42 ($CHCl_3$)		

FT-IR ($CHCl_3$, cm^{-1}): 2100, 1707, 1468, 1390.

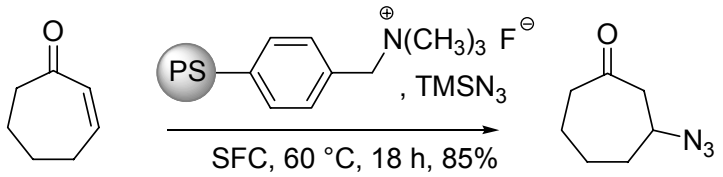
Elemental Analysis: Calcd. C, 57.46; H, 7.84; N, 25.13; found C, 57.59; H, 7.80; N, 25.23.

^{1}H NMR 200 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	1.05	3	*s*	
	1.29	3	*s*	
	1.35-1.57	1	*m*	
	1.72-1.85	1	*m*	
	2.28-2.36	2	*m*	
	2.47	1	*dd*	14.9, 9.2
	2.66	1	*dd*	14.9, 4.6
	3.48	1	*dd*	4.7, 9.2

^{13}C NMR (50.3 MHz, $CDCl_3$) δ : 21.0, 26.8, 34.2, 34.4, 37.2, 42.4, 68.3, 208.0.

GC-EIMS (m/z, %): 167 (M^+, 17), 112 (87), 97 (73), 69 (89), 55 (100), 43 (88).

Chem. Name	3-azidocycloheptan-1-one (2l)
Lit. Ref.	/



1l **2l**

Mol. Wt.: 153

METHOD:
In a screw capped vial equipped with a magnetic stirrer cyclohept-2-en-1-one (**1l**) (0.138 g, 1.0 mmol), Amberlite IRA900F (0.192 g, 0. 50 mmol, 2.6 mmol/g), and azidotrimethylsilane (0.414 mL, 3.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 60 °C. After 18 h, ethyl acetate was added, the catalyst was recovered by filtration and the organic solvent was evaporated under vacuum to give pure 3-azidocycloheptan-1-one (**2l**) was isolated as an oil (85 % yield, 0.130 g).

Mol Formula	$C_7H_{11}N_3O$	m.p./b.p.	Oil
Tlc - R_f (eluent)	0.24 ($CHCl_3$/petroleum ether 9/1)		

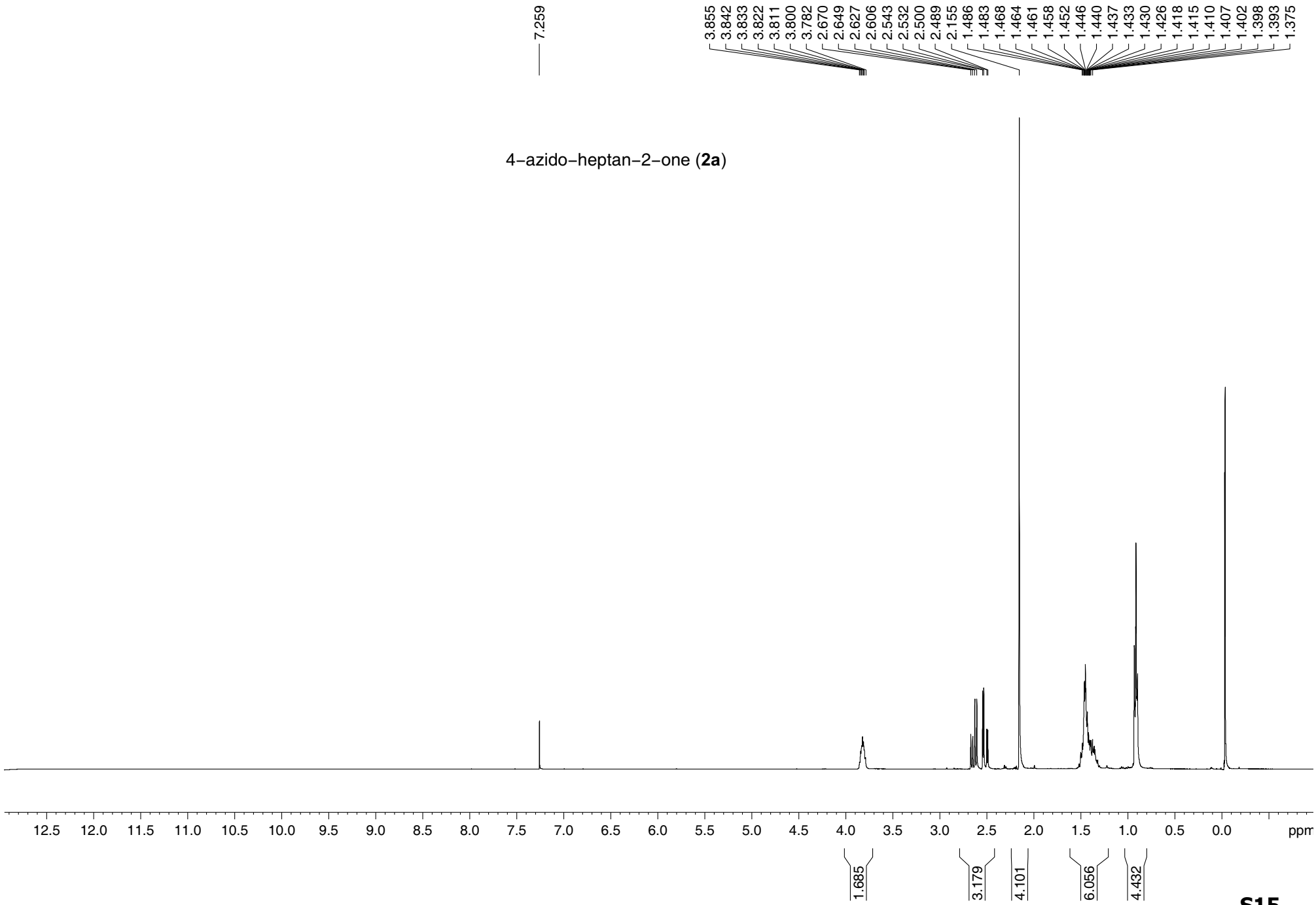
FT-IR ($CHCl_3$, cm^{-1}): 2102, 1700, 1457.

Elemental Analysis: Calcd. C, 54.89; H, 7.24; N, 27.43; found C, 55.00; H, 7.21; N, 27.45.

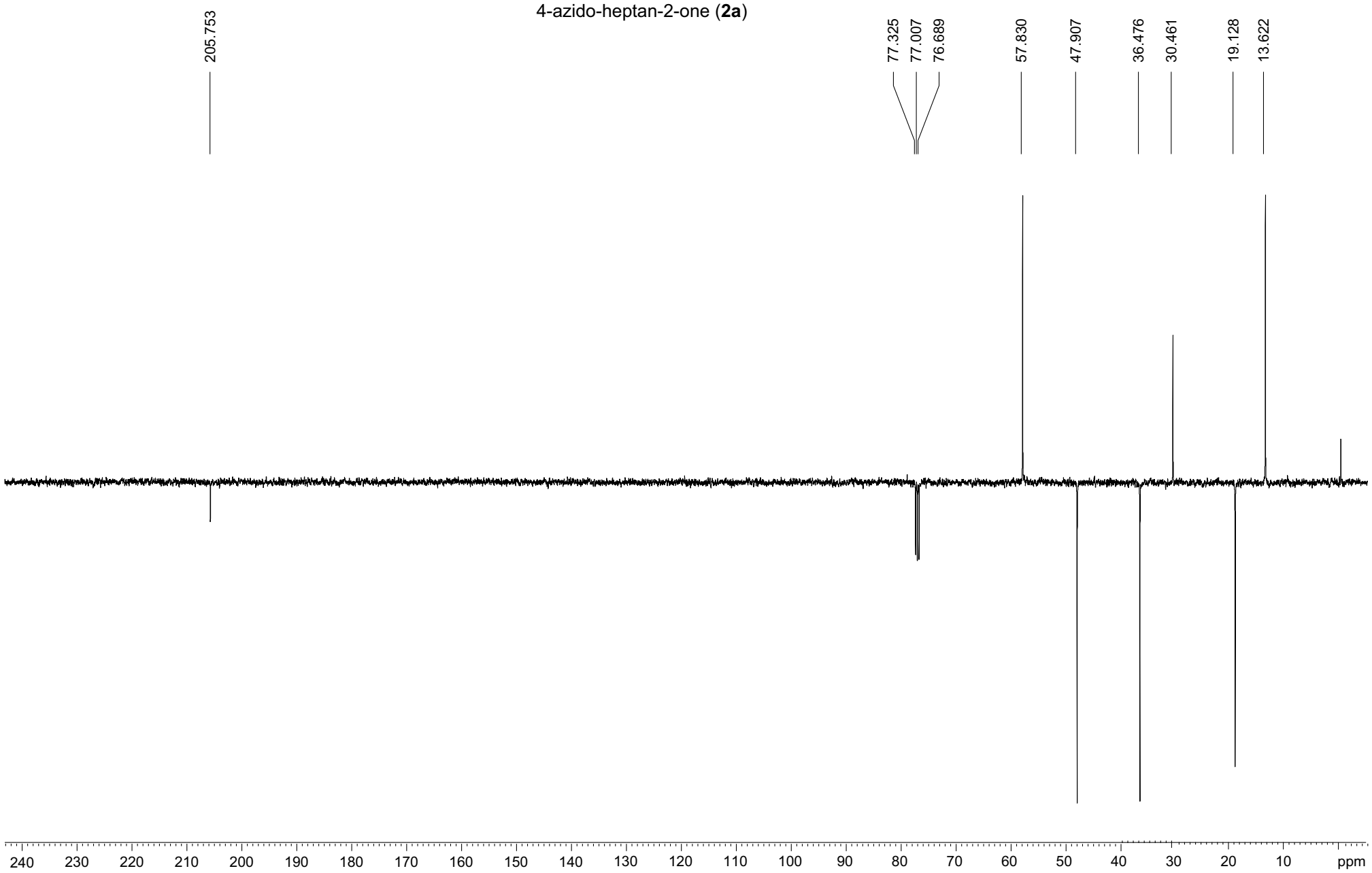
^{1}H NMR 400 MHz $CDCl_3$	δ value	No. H	Mult.	j value/Hz
	1.58-1.60	1	*m*	
	1.71-1.82	2	*m*	
	1.82-1.89	2	*m*	
	1.88-1.96	1	*m*	
	2.38-2.52	2	*m*	
	2.69-2.72	2	*m*	
	3.78	1	*m*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 23.3, 25.2, 35.4, 43.9, 48.2, 57.6, 210.1.

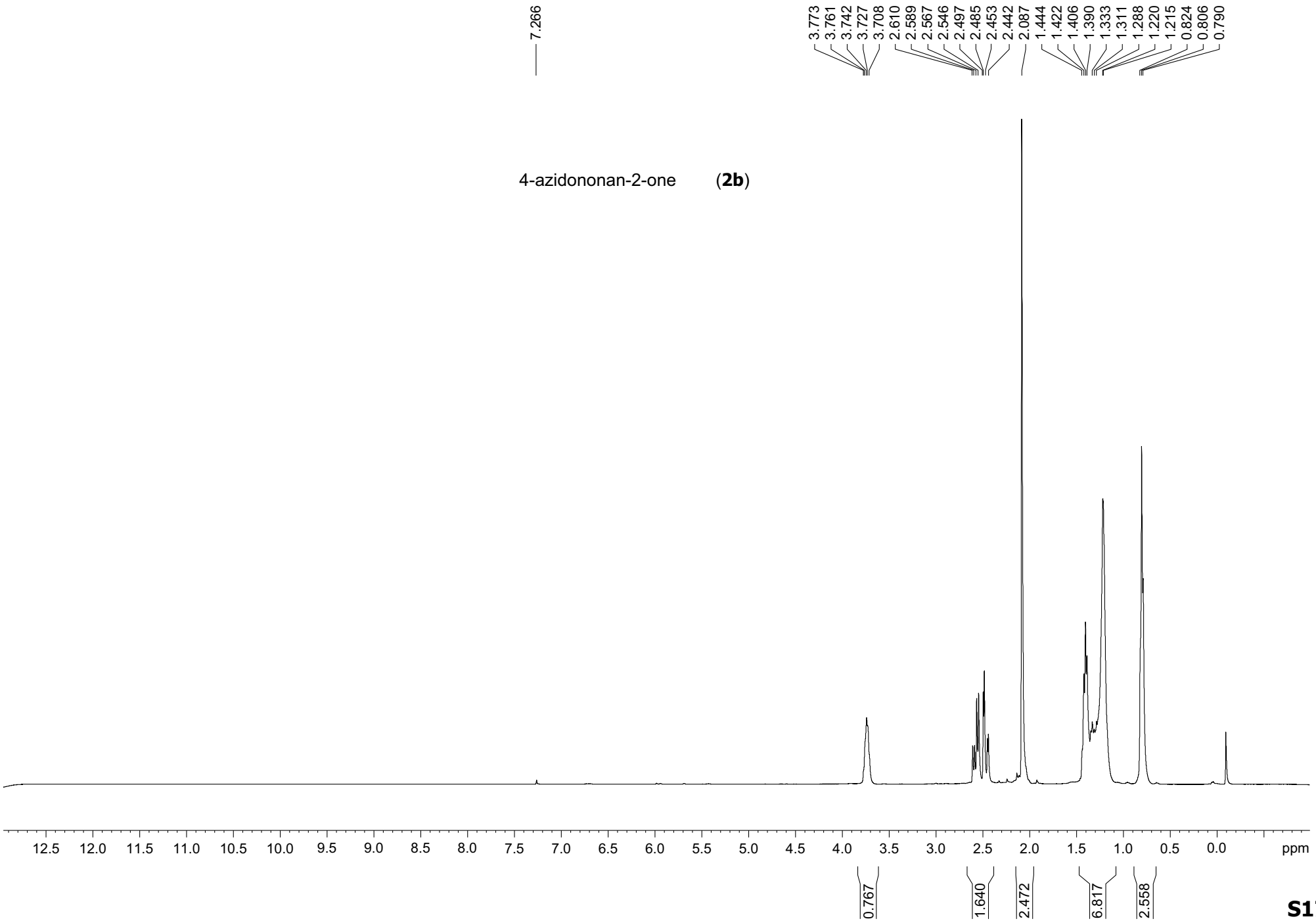
GC-EIMS (m/z, %): 153 (M^+, <1), 96 (28), 82 (28), 69 (36), 55 (100), 54 (42), 43 (28).


7.259
3.855
3.842
3.833
3.822
3.811
3.800
3.782
2.670
2.649
2.627
2.606
2.543
2.532
2.500
2.489
2.155
1.486
1.483
1.468
1.464
1.461
1.458
1.452
1.446
1.440
1.437
1.433
1.430
1.426
1.418
1.415
1.410
1.407
1.402
1.398
1.393
1.375
4−azido−heptan−2−one (2a)
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.685
3.179
4.101
6.056
4.432

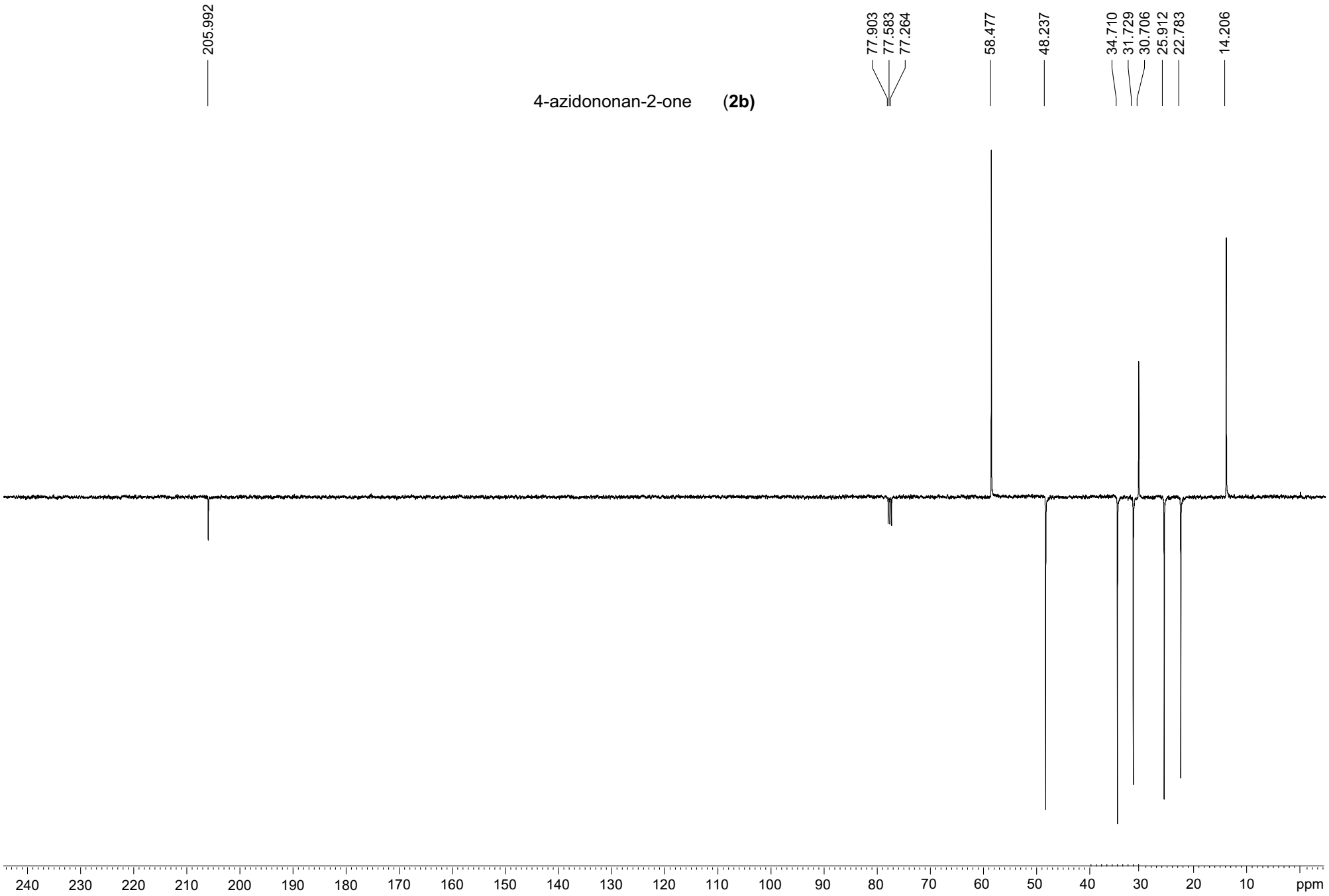
4-azido-heptan-2-one (**2a**)



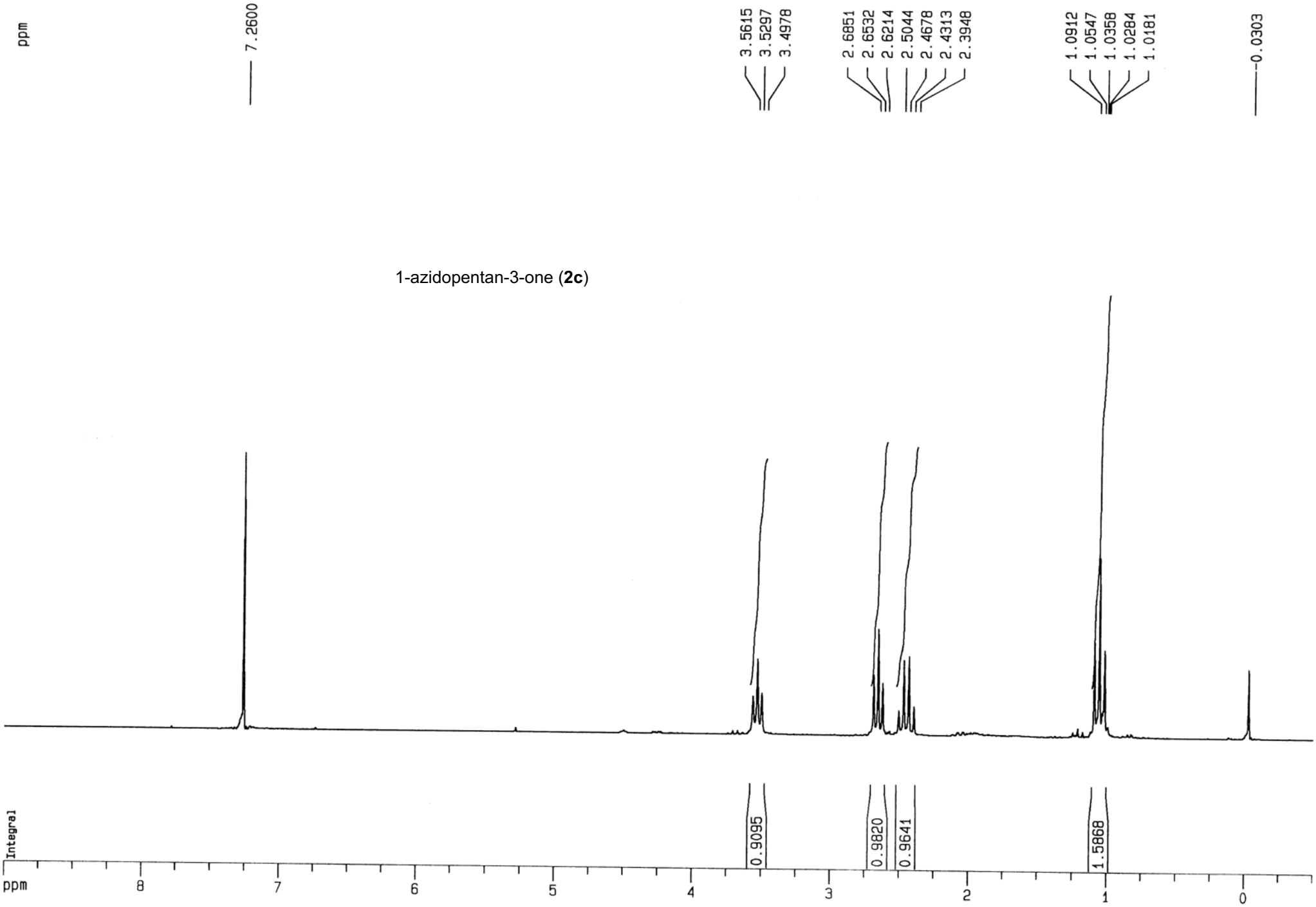
4-azidononan-2-one (**2b**)

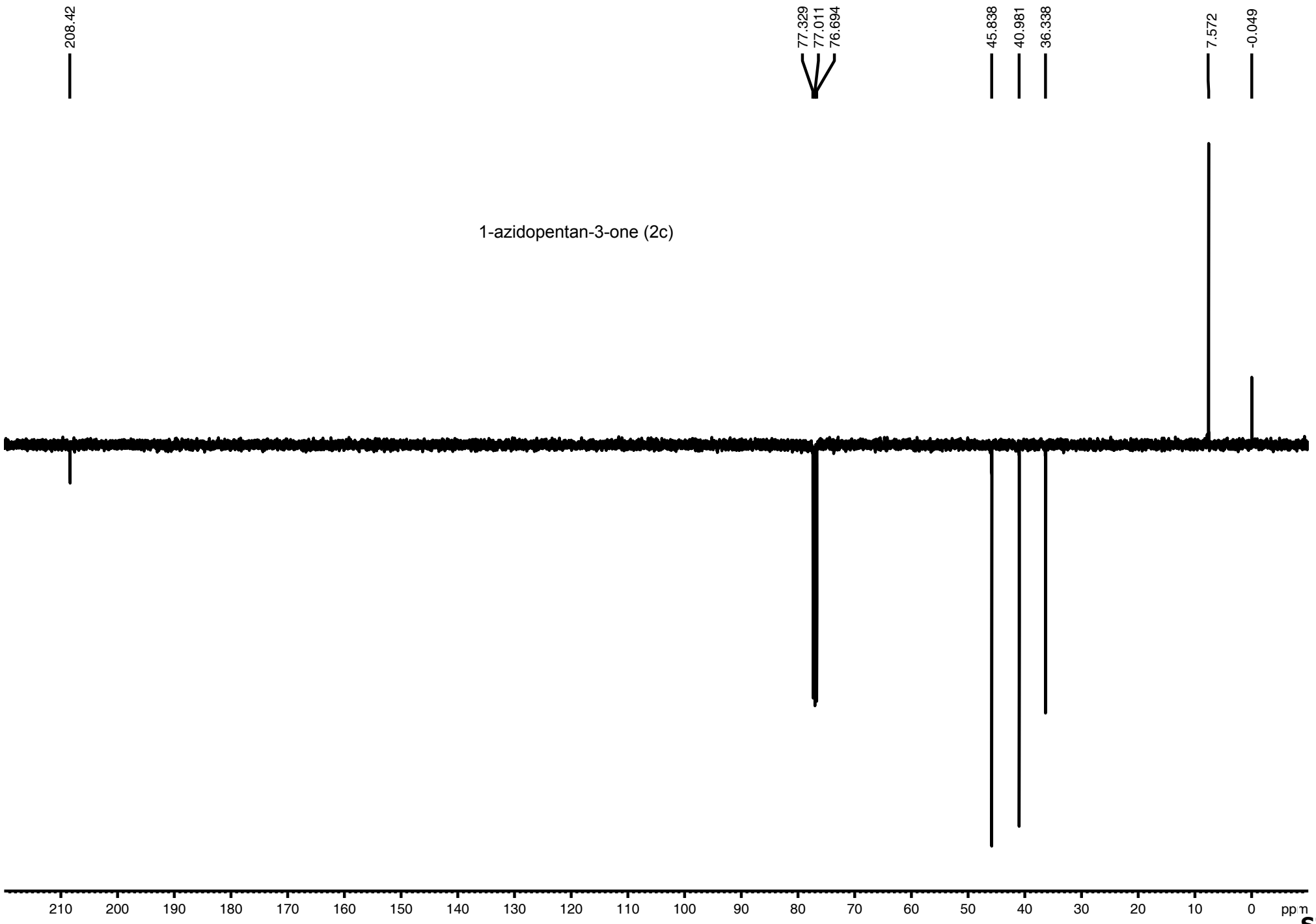


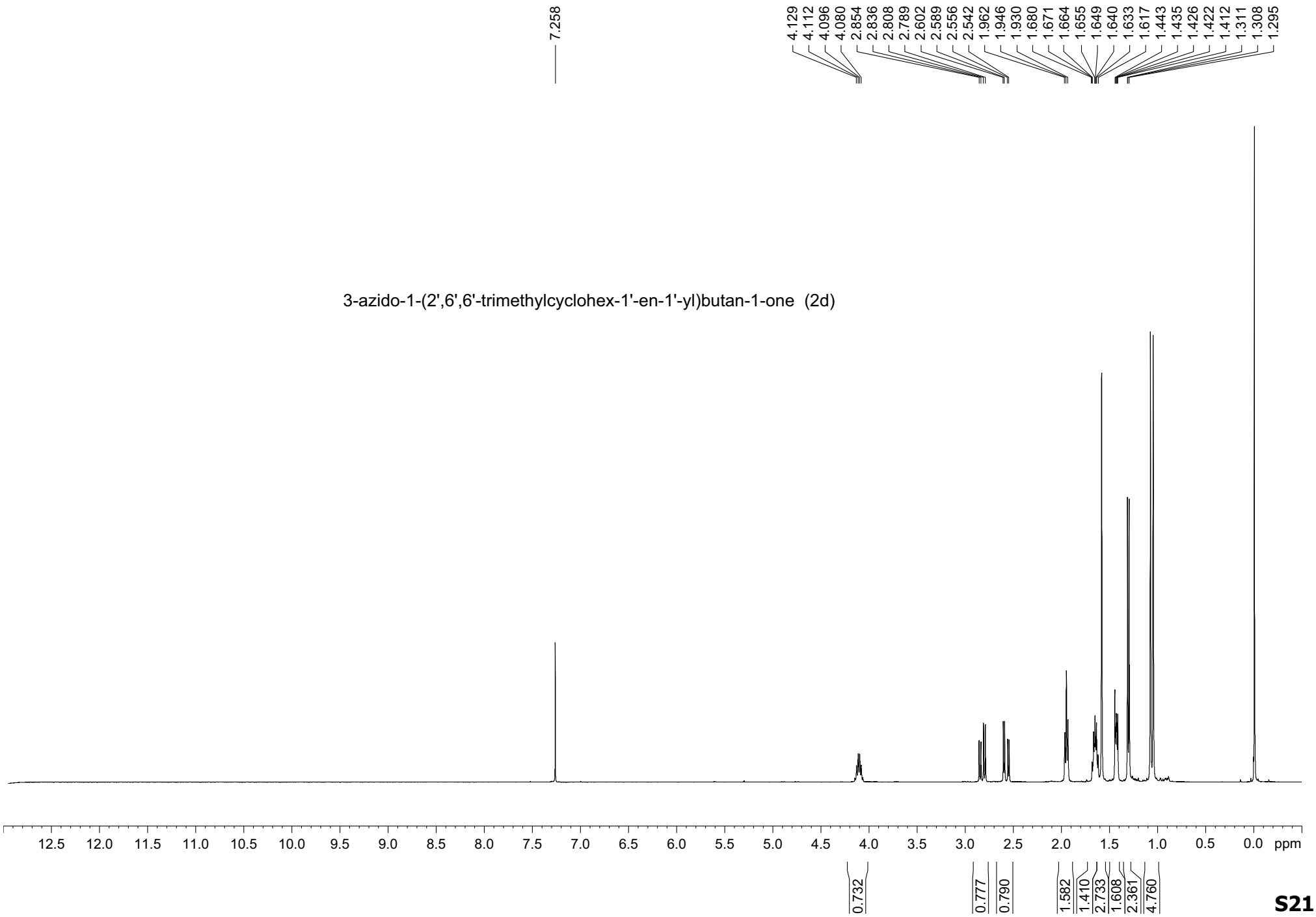
4-azidononan-2-one (**2b**)

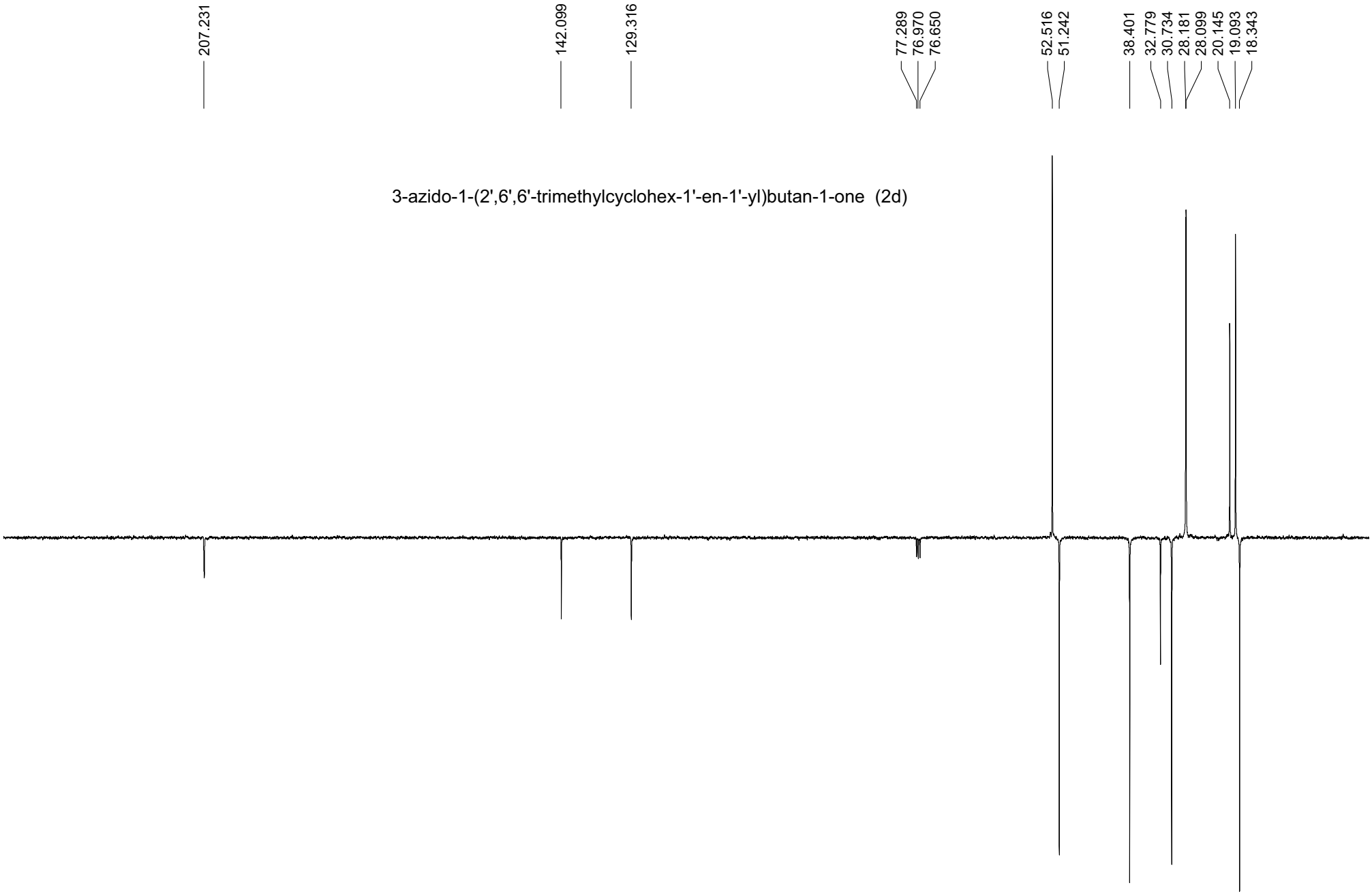


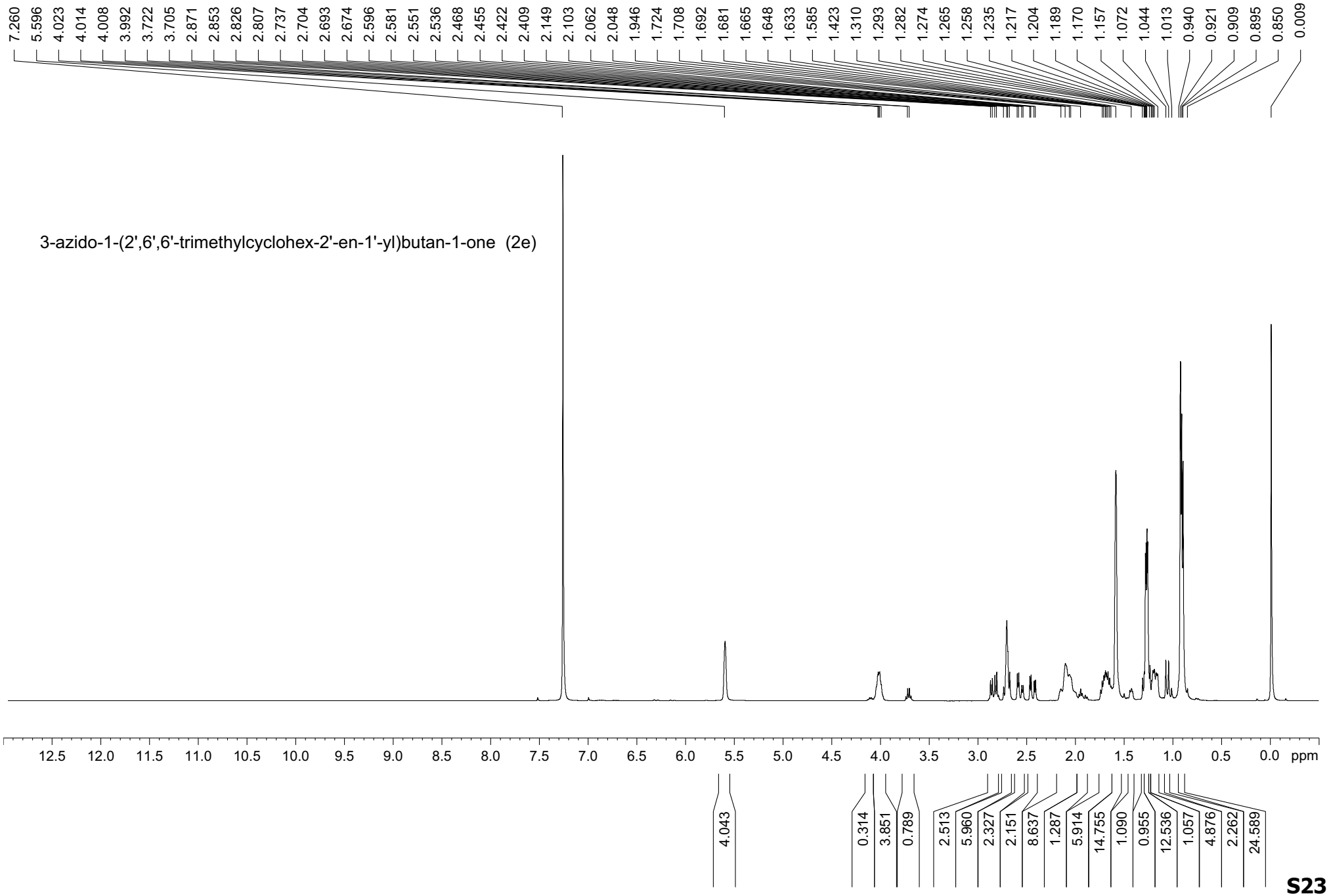
1-azidopentan-3-one (**2c**)



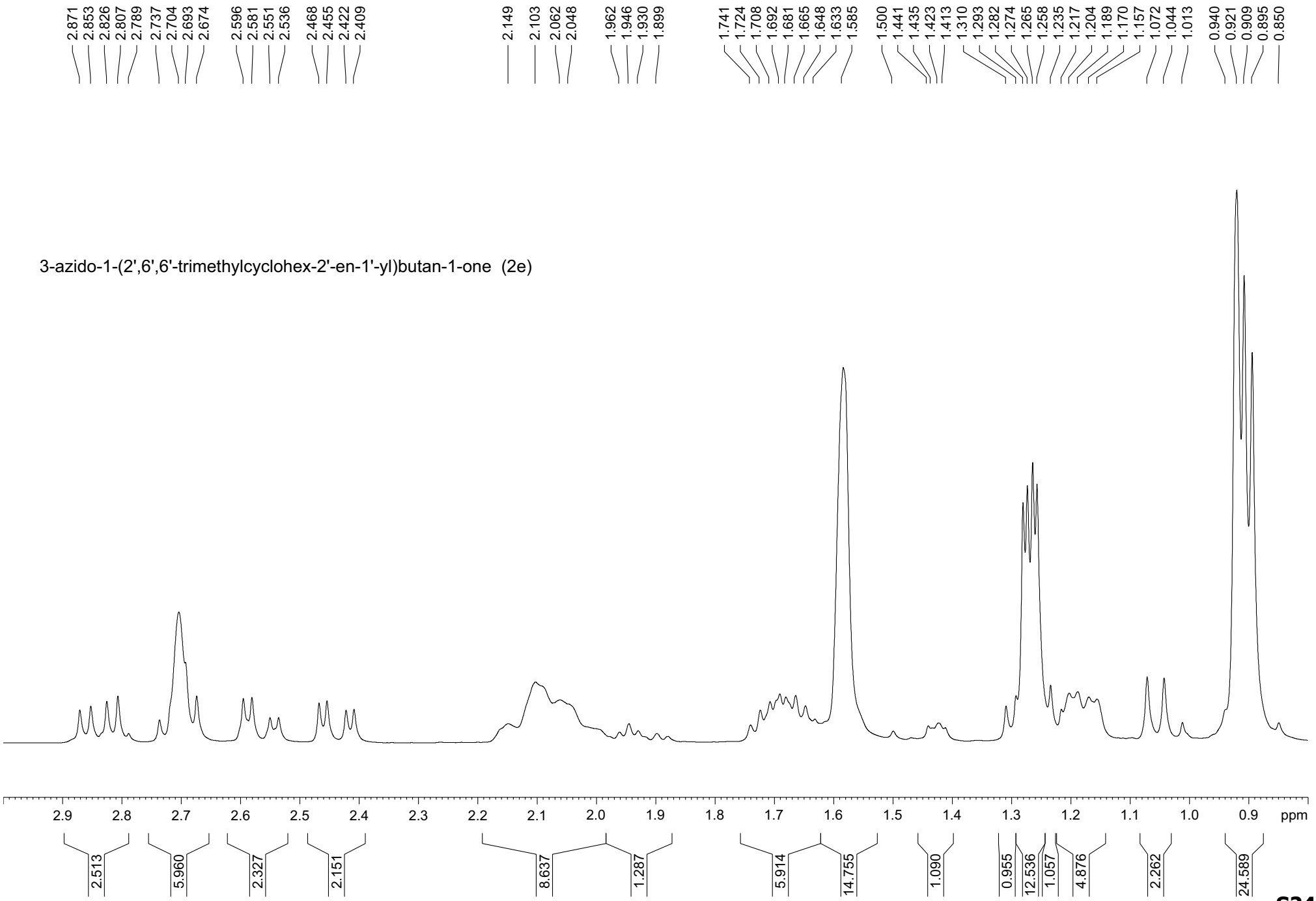

208.42
77.329
77.011
76.694
45.838
40.981
36.338
7.572
-0.049
1-azidopentan-3-one (2c)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

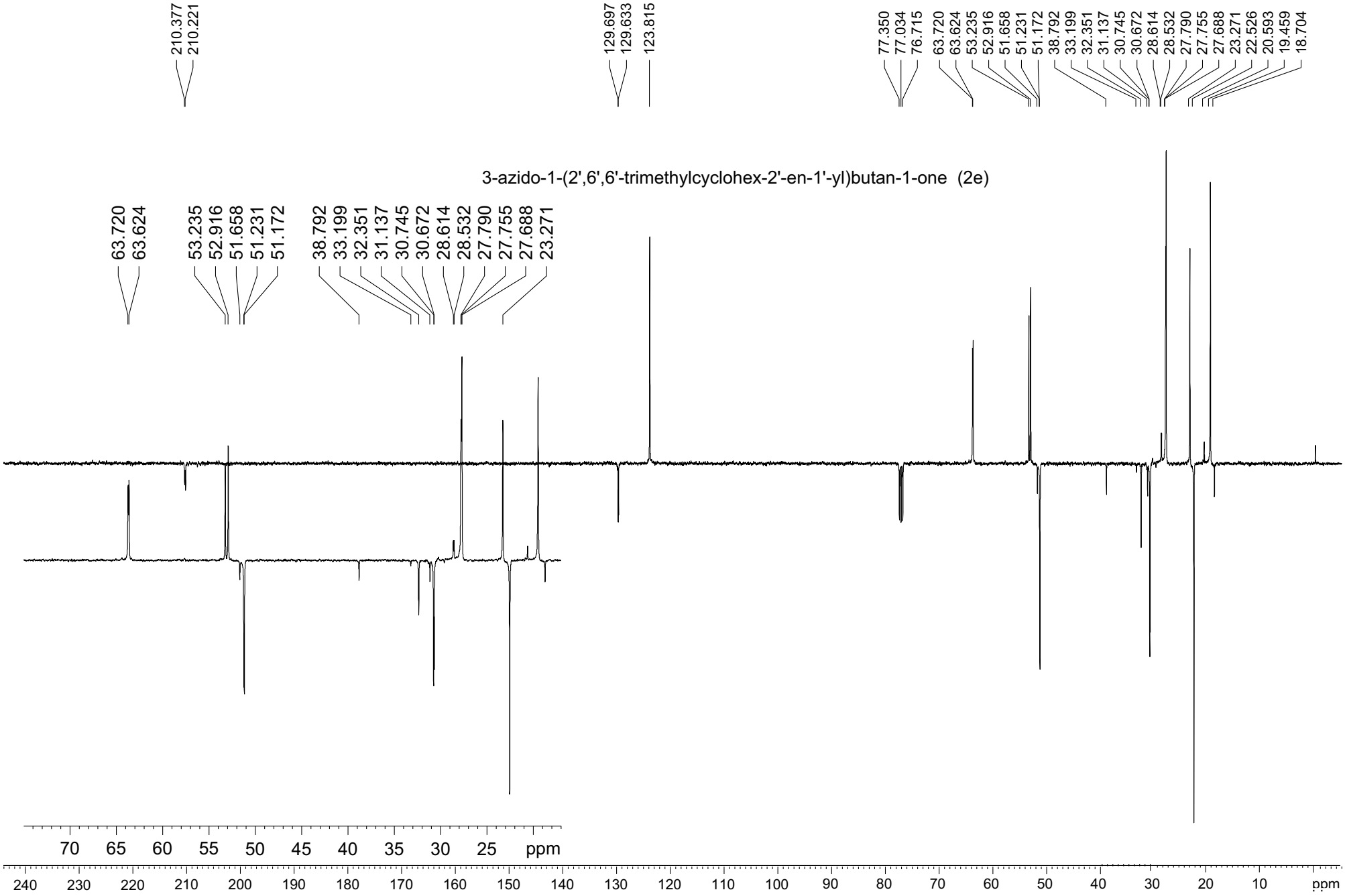

7.258
4.129
4.112
4.096
4.080
2.854
2.836
2.808
2.789
2.602
2.589
2.556
2.542
1.962
1.946
1.930
1.680
1.671
1.664
1.655
1.649
1.640
1.633
1.617
1.443
1.435
1.426
1.422
1.412
1.311
1.308
1.295
3-azido-1-(2',6',6'-trimethylcyclohex-1'-en-1'-yl)butan-1-one (2d)
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.732
0.777
0.790
1.582
1.410
2.733
1.608
2.361
4.760

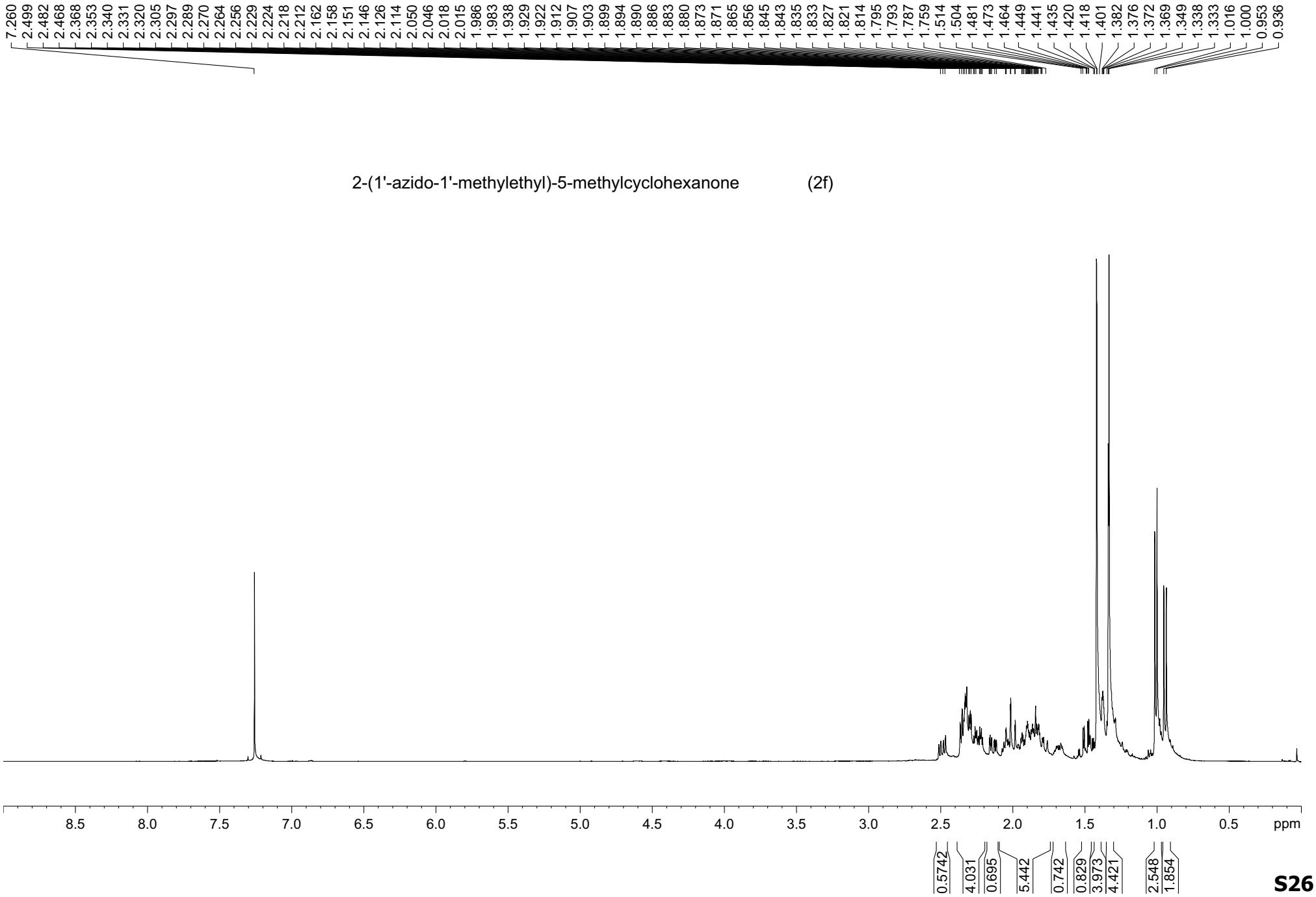

207.231
142.099
129.316
77.289
76.970
76.650
52.516
51.242
38.401
32.779
30.734
28.181
28.099
20.145
19.093
18.343
3-azido-1-(2',6',6'-trimethylcyclohex-1'-en-1'-yl)butan-1-one (2d)


7.260
5.596
4.023
4.014
4.008
3.992
3.722
3.705
2.871
2.853
2.826
2.807
2.737
2.704
2.693
2.674
2.596
2.581
2.551
2.536
2.468
2.455
2.422
2.409
2.149
2.103
2.062
2.048
1.946
1.724
1.708
1.692
1.681
1.665
1.648
1.633
1.585
1.423
1.310
1.293
1.282
1.274
1.265
1.258
1.235
1.217
1.204
1.189
1.170
1.157
1.072
1.044
1.013
0.940
0.921
0.909
0.895
0.850
0.009
3-azido-1-(2',6',6'-trimethylcyclohex-2'-en-1'-yl)butan-1-one (2e)
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.043
0.314
3.851
0.789
2.513
5.960
2.327
2.151
8.637
1.287
5.914
14.755
1.090
0.955
12.536
1.057
4.876
2.262
24.589

3-azido-1-(2',6',6'-trimethylcyclohex-2'-en-1'-yl)butan-1-one (2e)

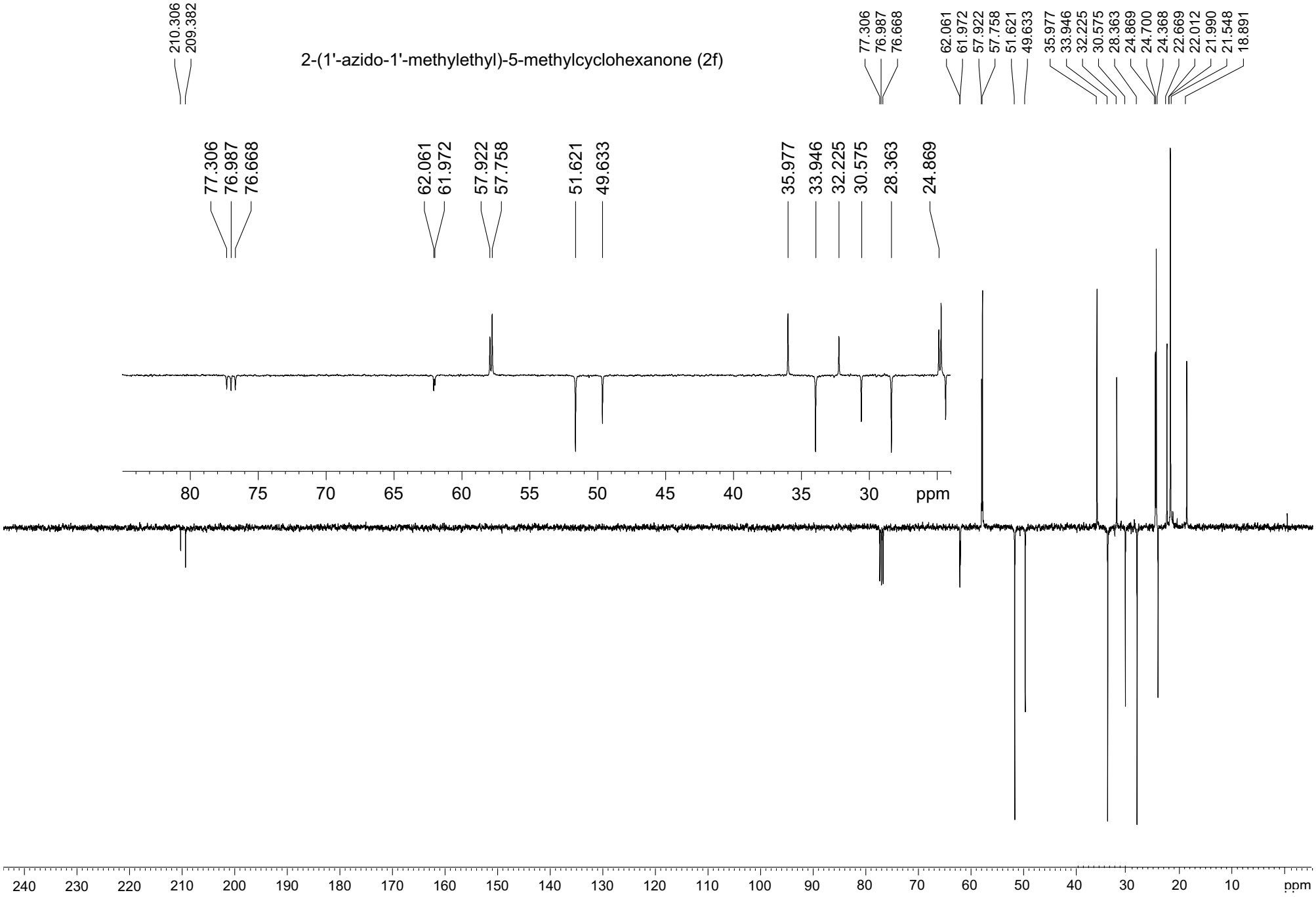



3-azido-1-(2',6',6'-trimethylcyclohex-2'-en-1'-yl)butan-1-one (2e)
210.377
210.221
129.697
129.633
123.815
77.350
77.034
76.715
63.720
63.624
53.235
52.916
51.658
51.231
51.172
38.792
33.199
32.351
31.137
30.745
30.672
28.614
28.532
27.790
27.755
27.688
23.271
22.526
20.593
19.459
18.704
70 65 60 55 50 45 40 35 30 25 ppm
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

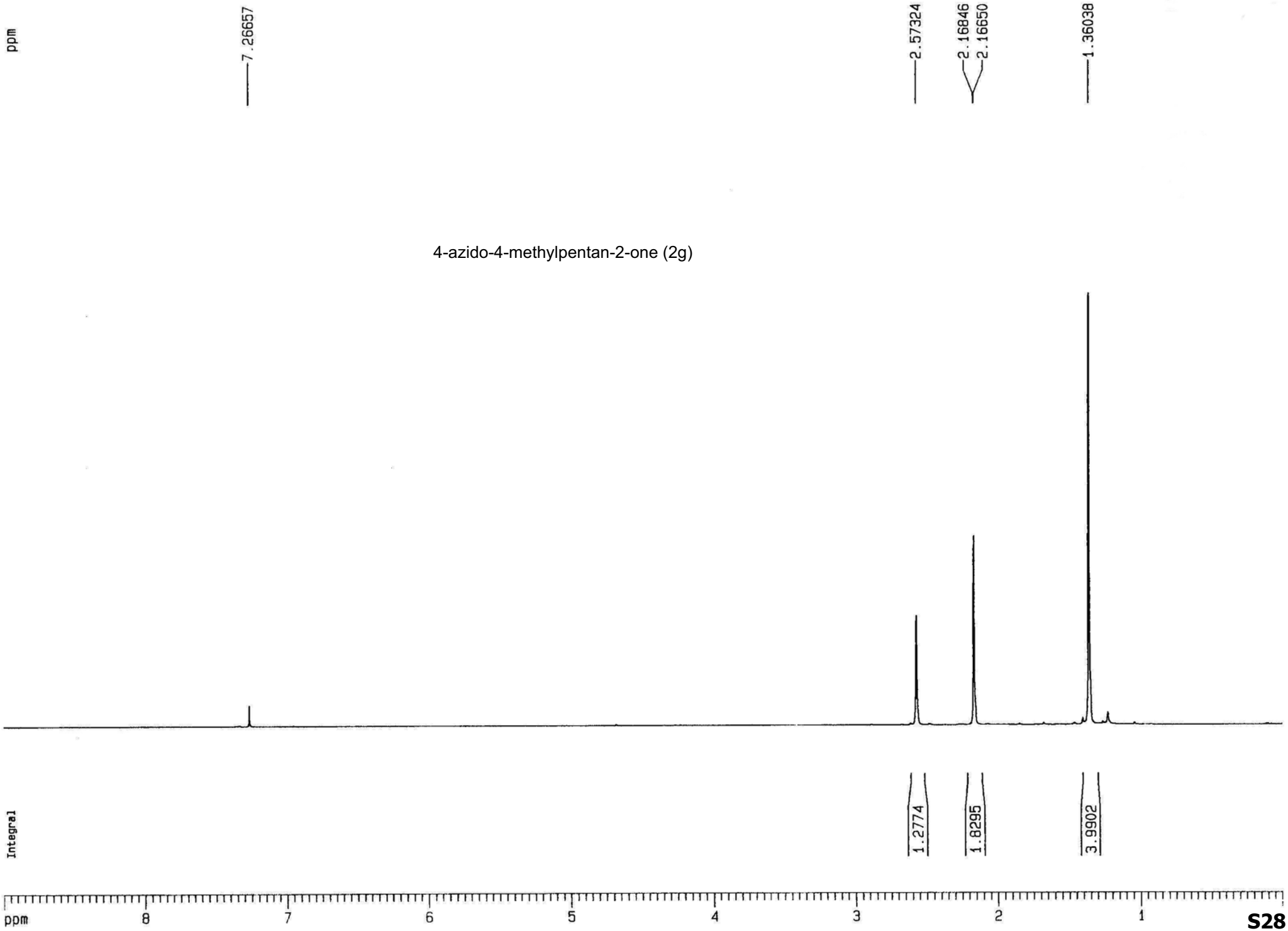


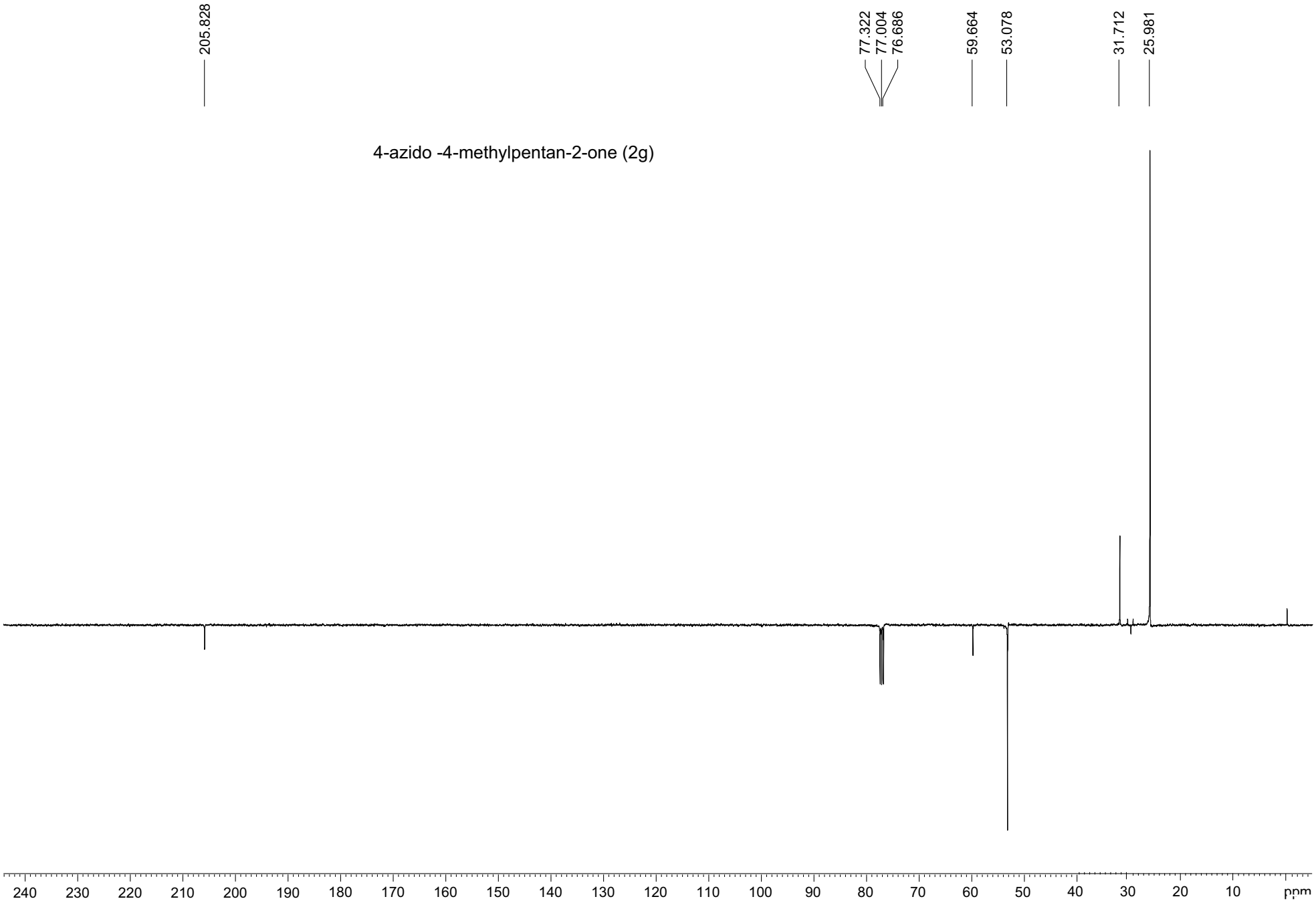
2-(1'-azido-1'-methylethyl)-5-methylcyclohexanone (2f)

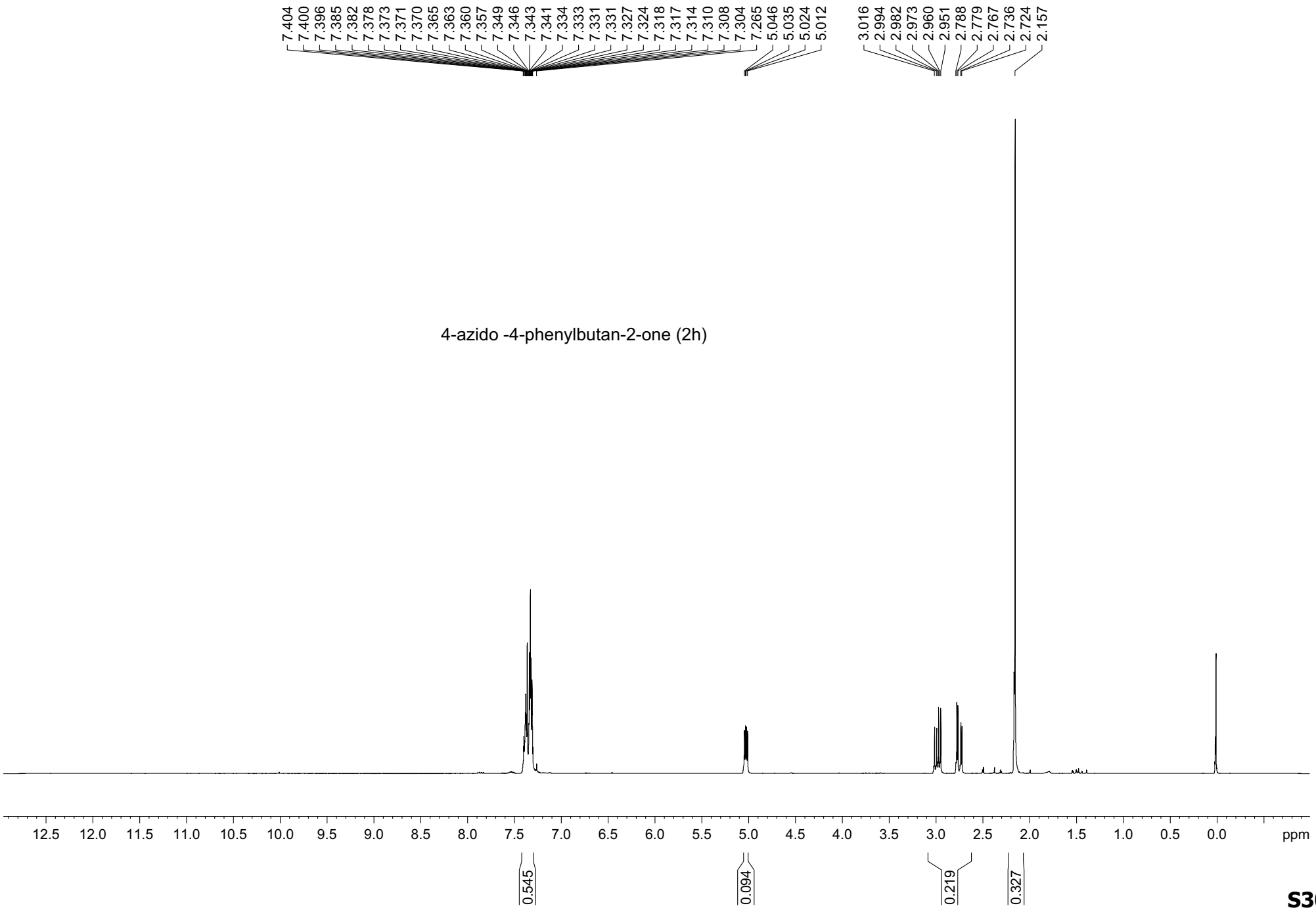
2-(1'-azido-1'-methylethyl)-5-methylcyclohexanone (2f)

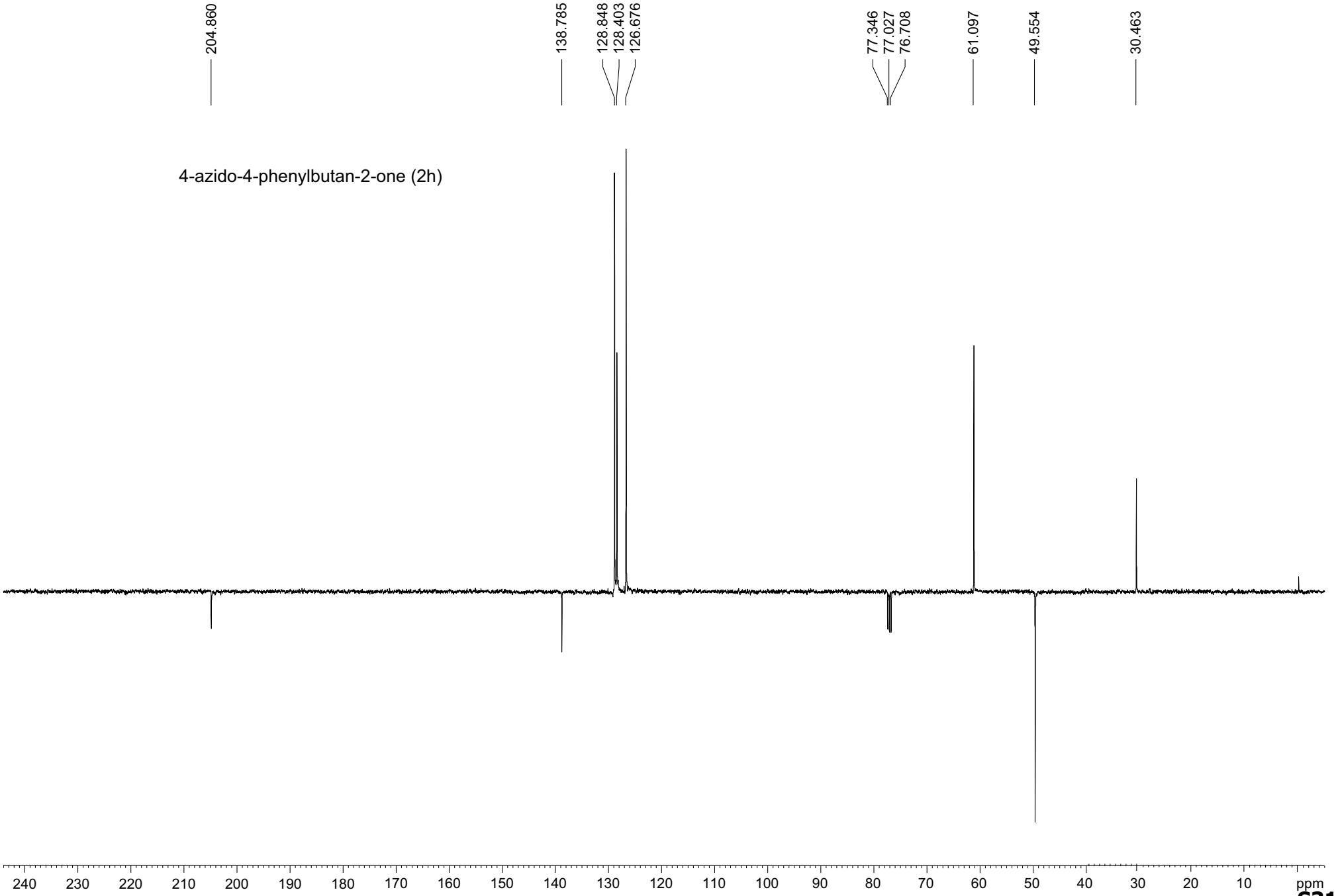


4-azido-4-methylpentan-2-one (2g)

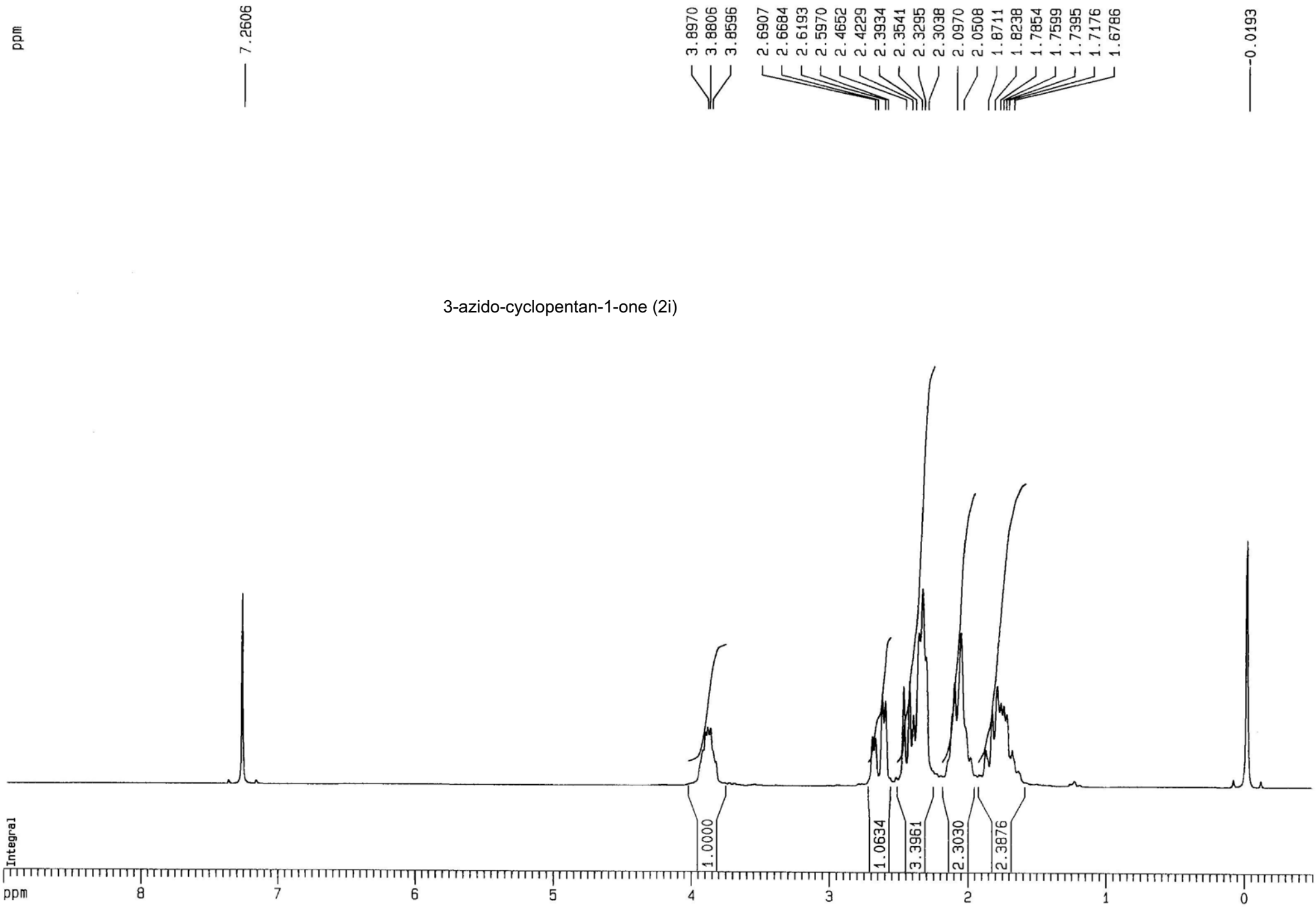



205.828
77.322
77.004
76.686
59.664
53.078
31.712
25.981
4-azido -4-methylpentan-2-one (2g)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

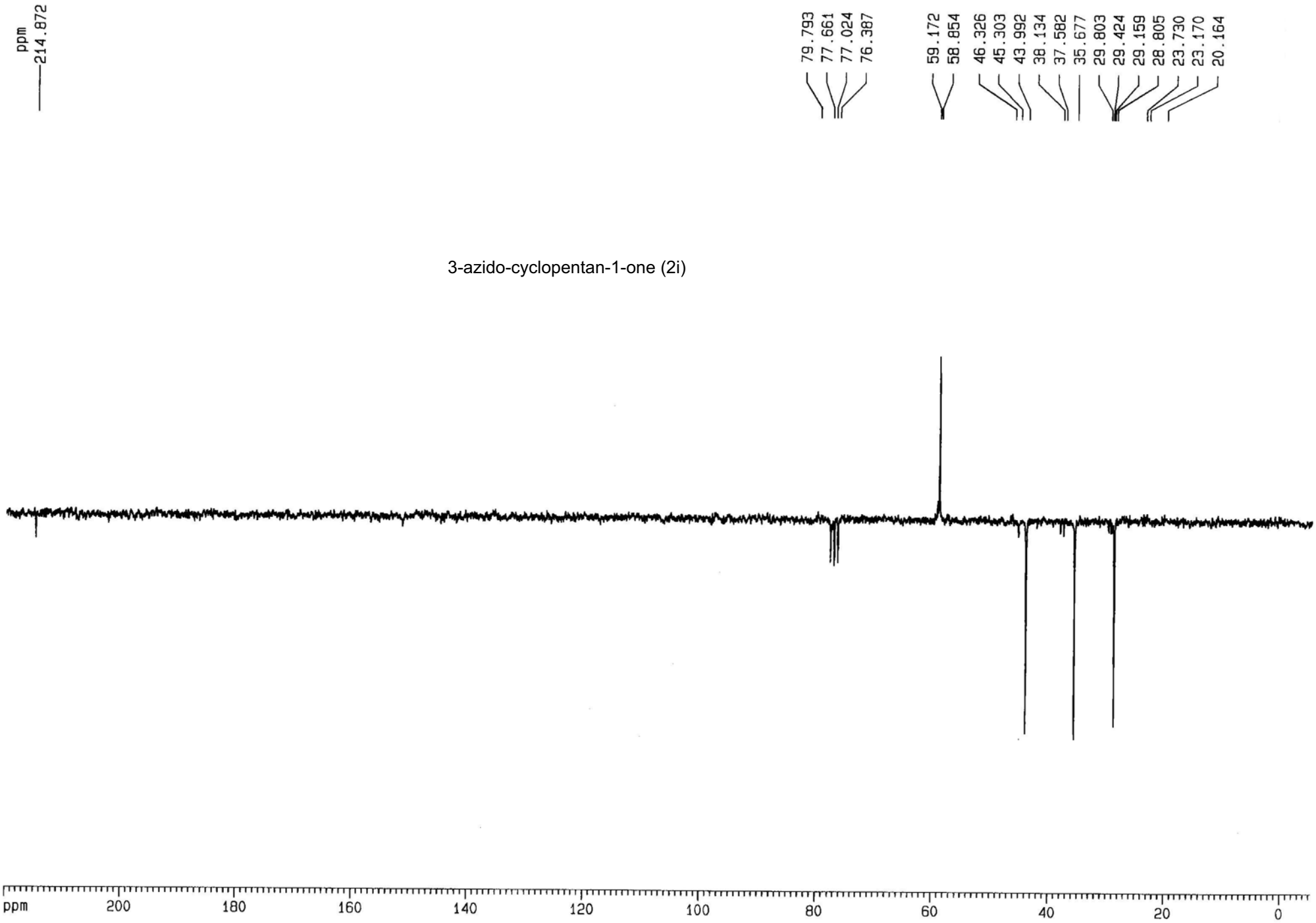

7.404
7.400
7.396
7.385
7.382
7.378
7.373
7.371
7.370
7.365
7.363
7.360
7.357
7.349
7.346
7.343
7.341
7.334
7.333
7.331
7.331
7.327
7.324
7.318
7.317
7.314
7.310
7.308
7.304
7.265
5.046
5.035
5.024
5.012
3.016
2.994
2.982
2.973
2.960
2.951
2.788
2.779
2.767
2.736
2.724
2.157
4-azido -4-phenylbutan-2-one (2h)
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.545
0.094
0.219
0.327


204.860
138.785
128.848
128.403
126.676
77.346
77.027
76.708
61.097
49.554
30.463
4-azido-4-phenylbutan-2-one (2h)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

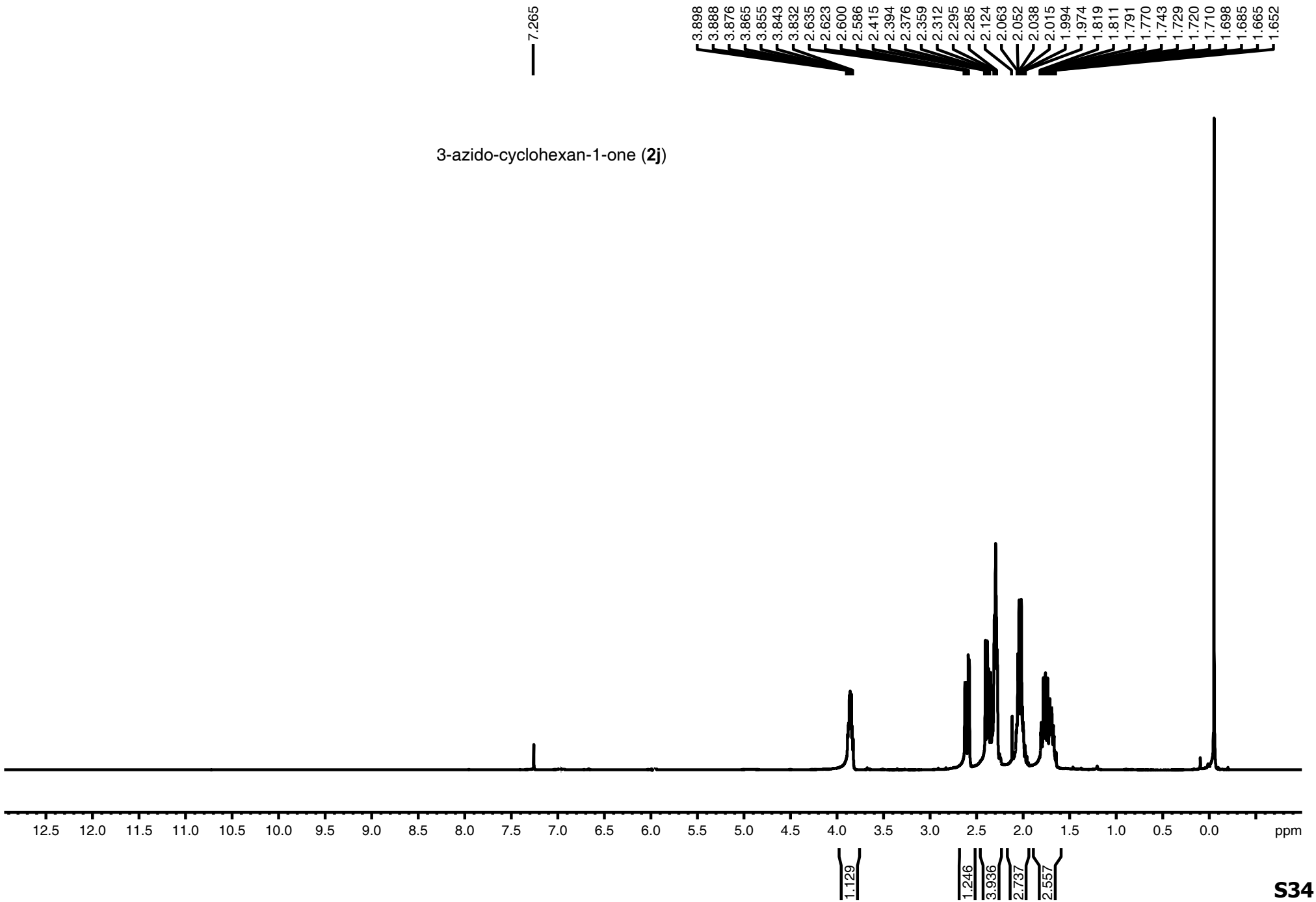
3-azido-cyclopentan-1-one (2i)



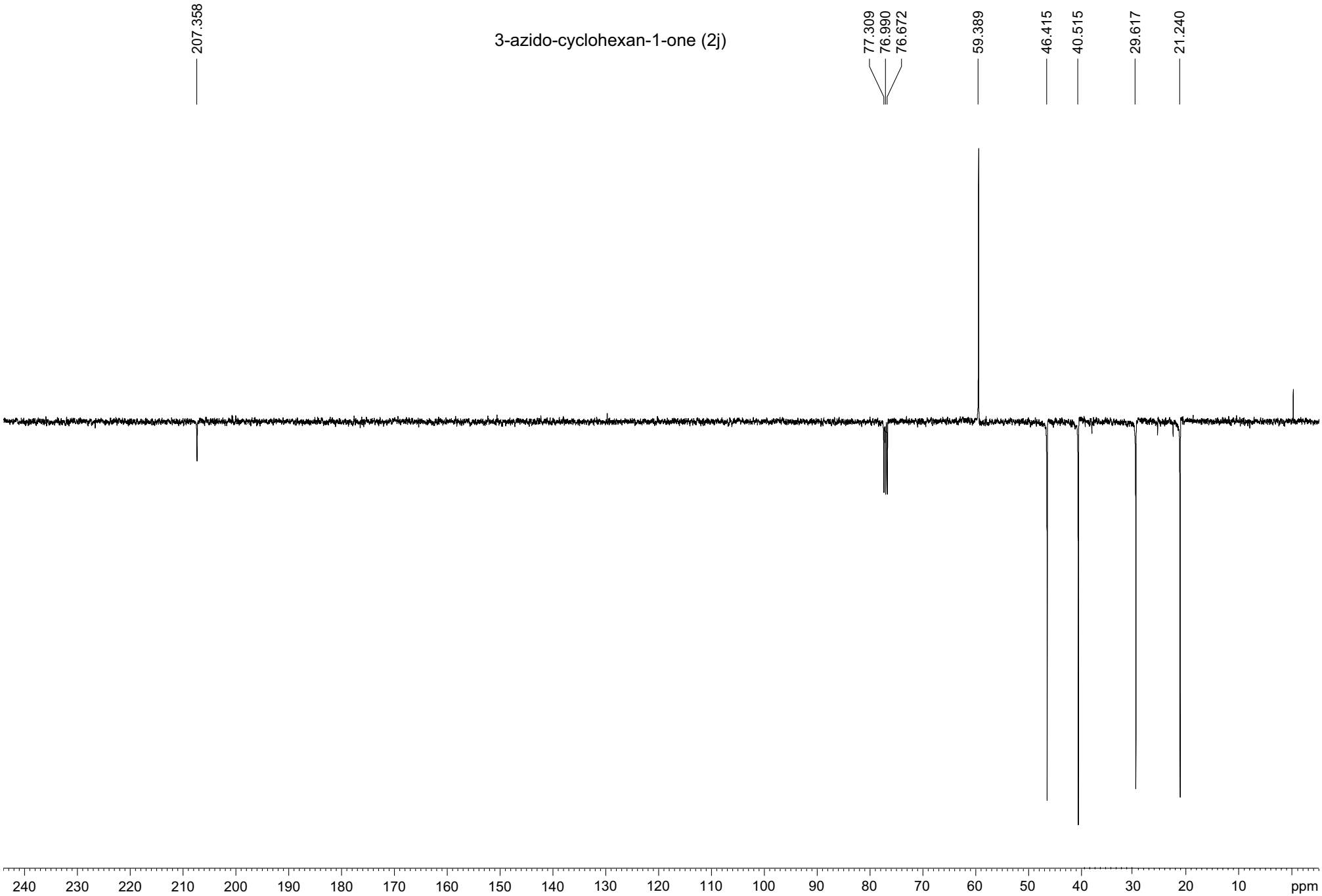
3-azido-cyclopentan-1-one (2i)



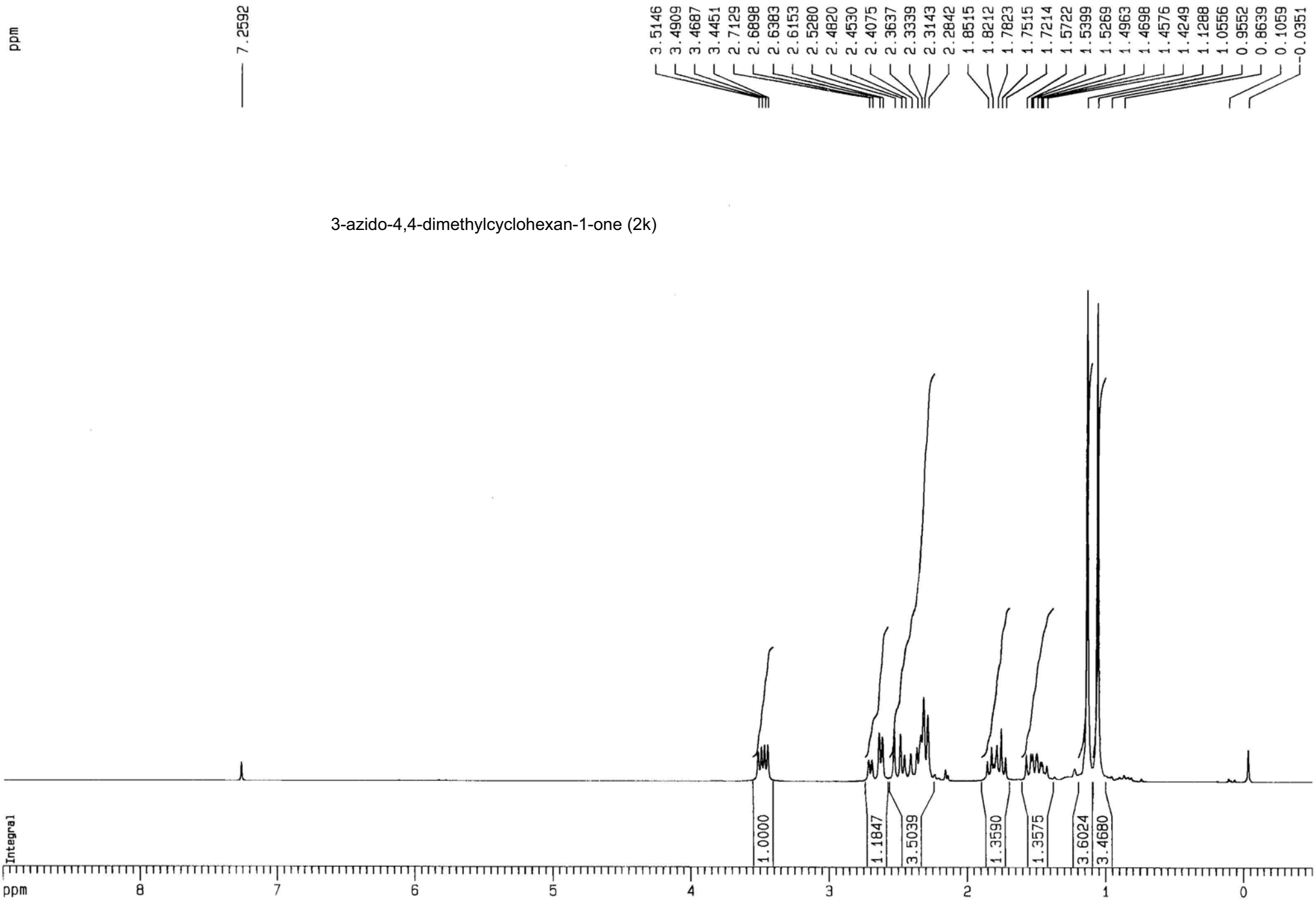
3-azido-cyclohexan-1-one (**2j**)



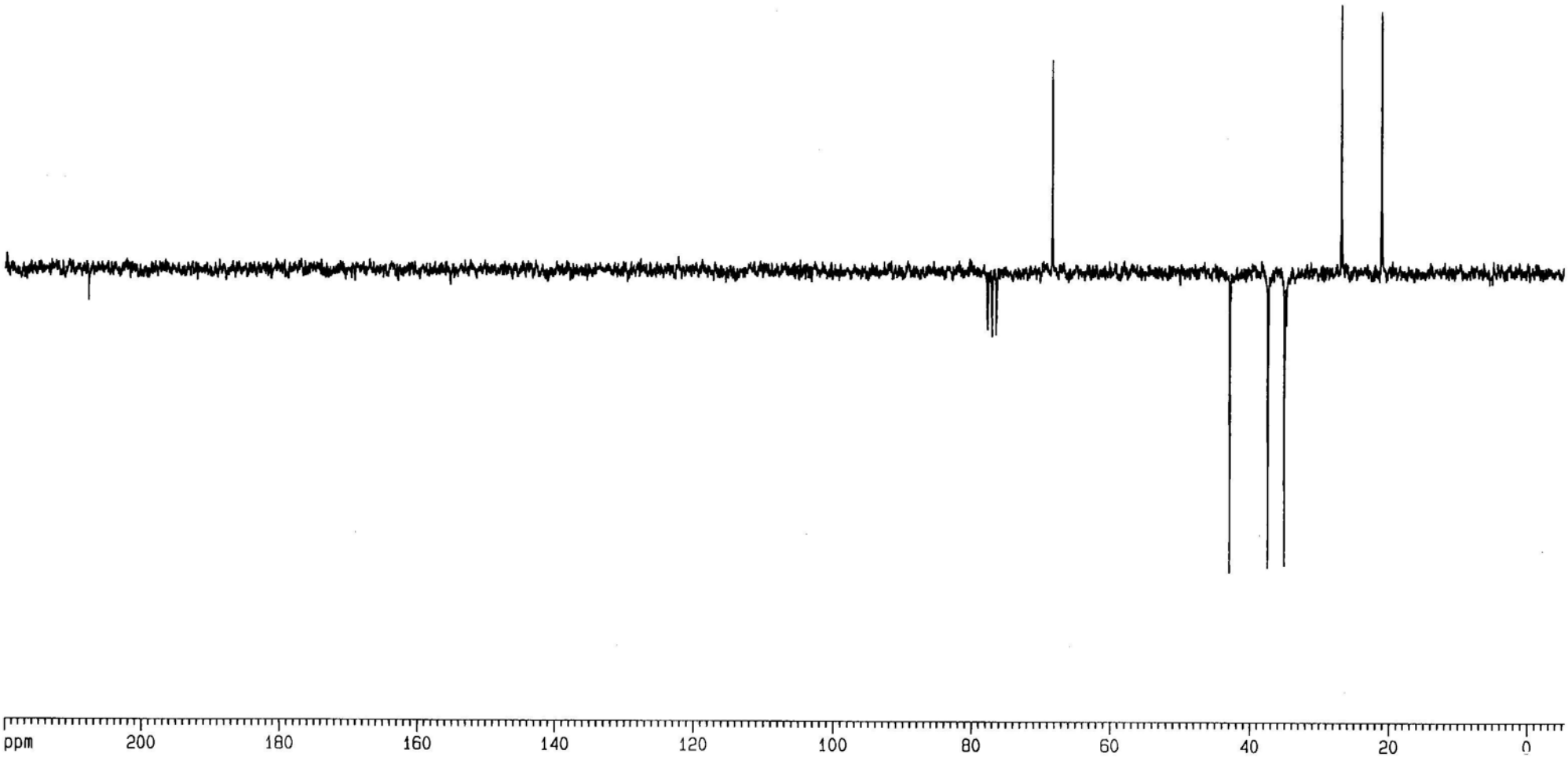
3-azido-cyclohexan-1-one (2j)

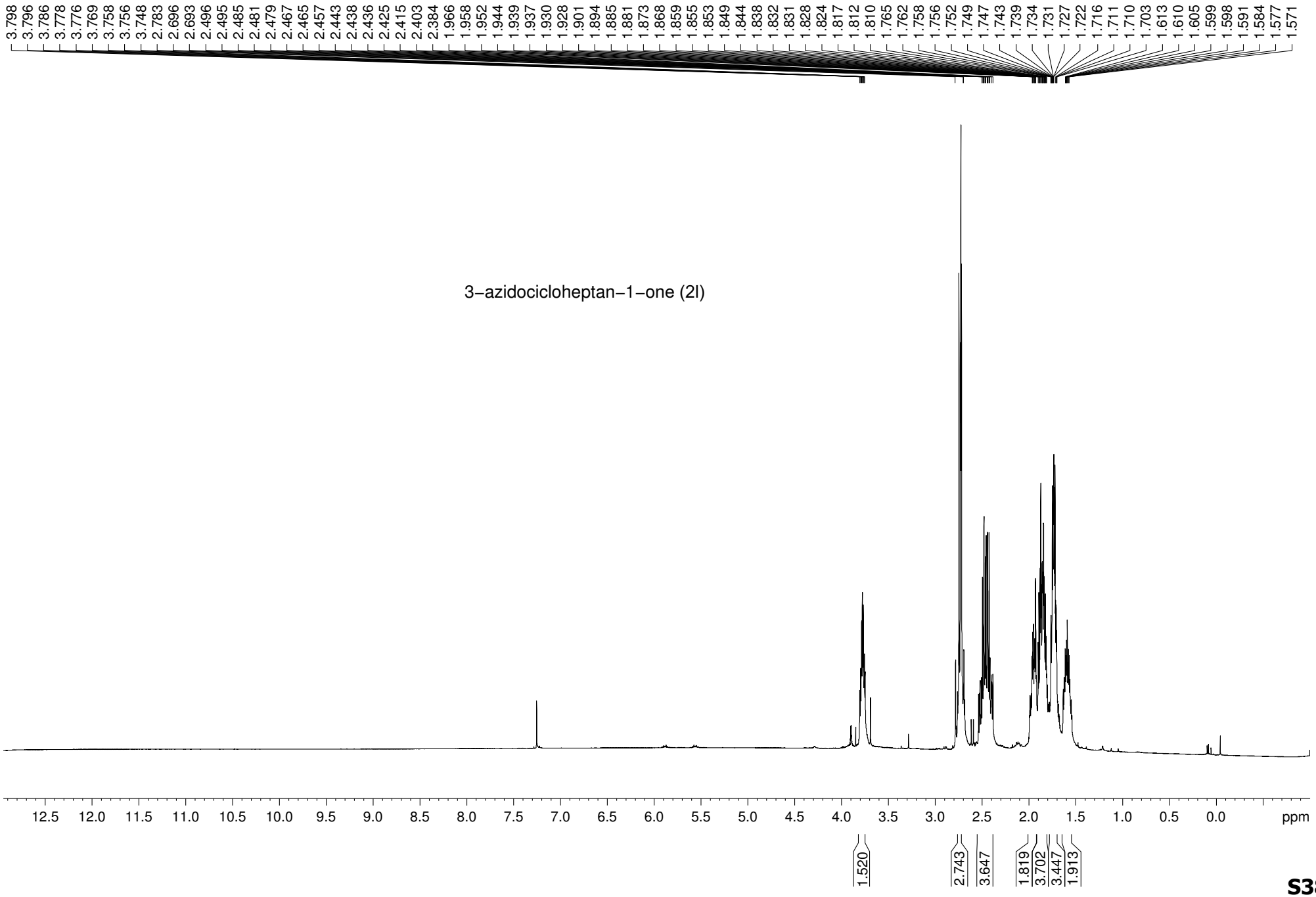


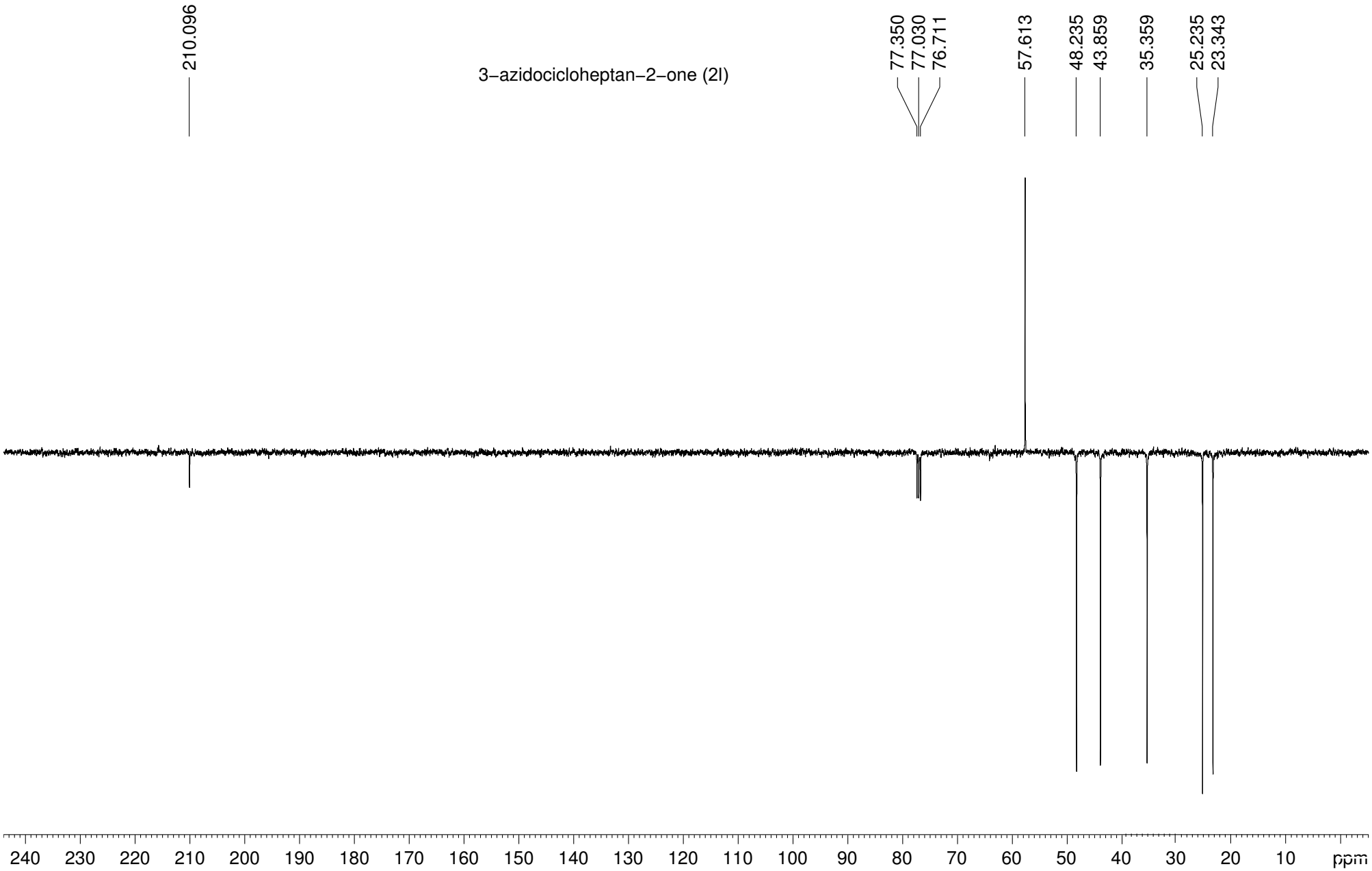
3-azido-4,4-dimethylcyclohexan-1-one (2k)



3-azido-4,4-dimethylcyclohexan-1-one (2k)




3.798
3.796
3.786
3.778
3.776
3.769
3.758
3.756
3.748
2.783
2.696
2.693
2.496
2.495
2.485
2.481
2.479
2.467
2.465
2.457
2.443
2.438
2.436
2.425
2.415
2.403
2.384
1.966
1.958
1.952
1.944
1.939
1.937
1.930
1.928
1.901
1.894
1.885
1.881
1.873
1.868
1.859
1.855
1.853
1.849
1.844
1.838
1.832
1.831
1.828
1.824
1.817
1.812
1.810
1.765
1.762
1.758
1.756
1.752
1.749
1.747
1.743
1.739
1.734
1.731
1.727
1.722
1.716
1.711
1.710
1.703
1.613
1.610
1.605
1.599
1.598
1.591
1.584
1.577
1.571
3−azidocicloheptan−1−one (2l)
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.520
2.743
3.647
1.819
3.702
3.447
1.913


3−azidocicloheptan−2−one (2l)
210.096
77.350
77.030
76.711
57.613
48.235
43.859
35.359
25.235
23.343
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm