Direct Synthesis of Butadiynyl-Substituted Pyrroles under Solvent- and Transition Metal-Free Conditions

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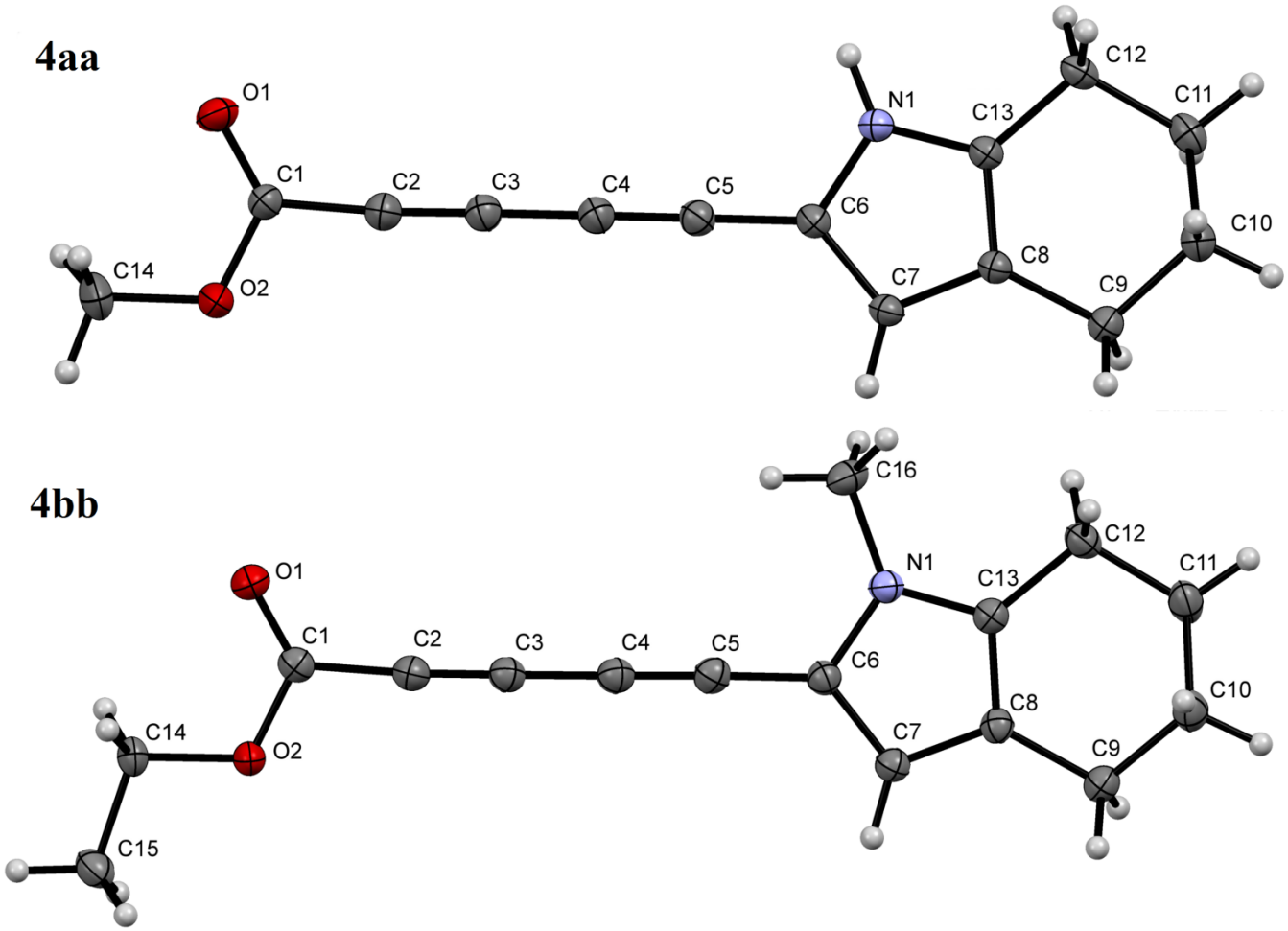
X-ray Crystallography details

Details of X-ray Data Collection and Reduction: X-ray diffraction data were collected using ω scan technique. The space groups were determined from systematic absences and subsequent least-squares refinement. Lorentz and polarization corrections were applied. The structures were solved by direct methods and refined by full-matrix, least-squares on F^2 by use of the SHELXTL Package.[1] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated and added to the structure factor calculations, but were not refined except NH hydrogen atom of **4aa** which position was added from residual electron density peak and refined.

Selected bond lengths for 4aa and 4bb:



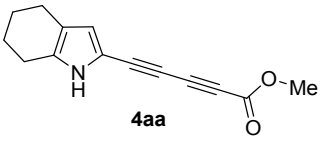
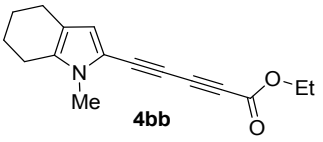
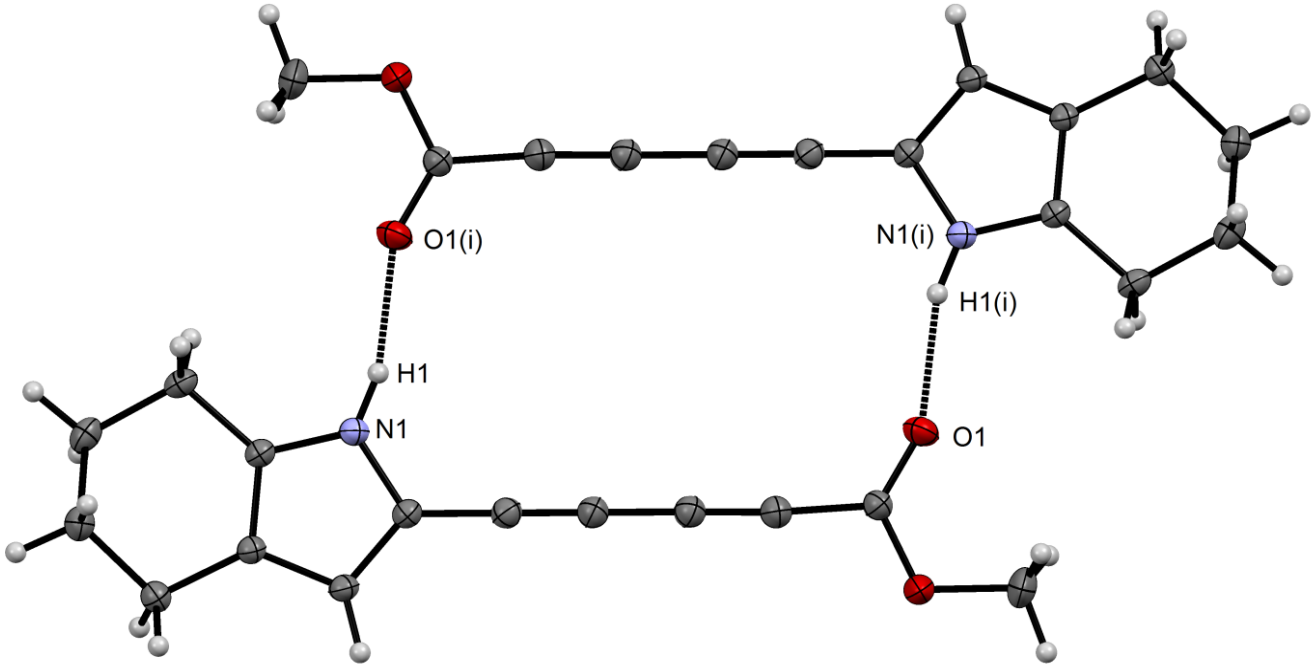
	Bond lengths [Å]	
Bond	 **4aa**	 **4bb**
C1—C2	1.4487 (18)	1.4365 (14)
C2—C3	1.2035 (18)	1.2111 (14)
C3—C4	1.3675 (19)	1.3605 (14)
C4—C5	1.2093 (19)	1.2175 (14)
C5—C6	1.4041 (18)	1.3985 (14)

Table 1. Bond lengths in C1-C6 carbon chain (all lengths in Å).

Packing analysis of 4aa and 4bb: Butadiynes hold a great potential for 1,4-topochemical polymerization[2] and we have here analyzed the packing of the **4aa** and **4bb** compounds. The closest chain-chain separation was analyzed, which is understood as the closest carbon-carbon distance from two neighboring carbon chains. As revealed by thorough analysis the closest distance between two carbon atoms of parallel chains is 5.062 Å for **4aa** and 4.626 Å for **4bb** what strongly exceeds sum of the van der Waals radii. Such huge values exclude the possibility of 1,n-topochemical polymerization. However, during analysis of packing motifs we determined that **4aa** forms dimers in solid state bounded by two hydrogen bonds as presented in the Scheme 1.

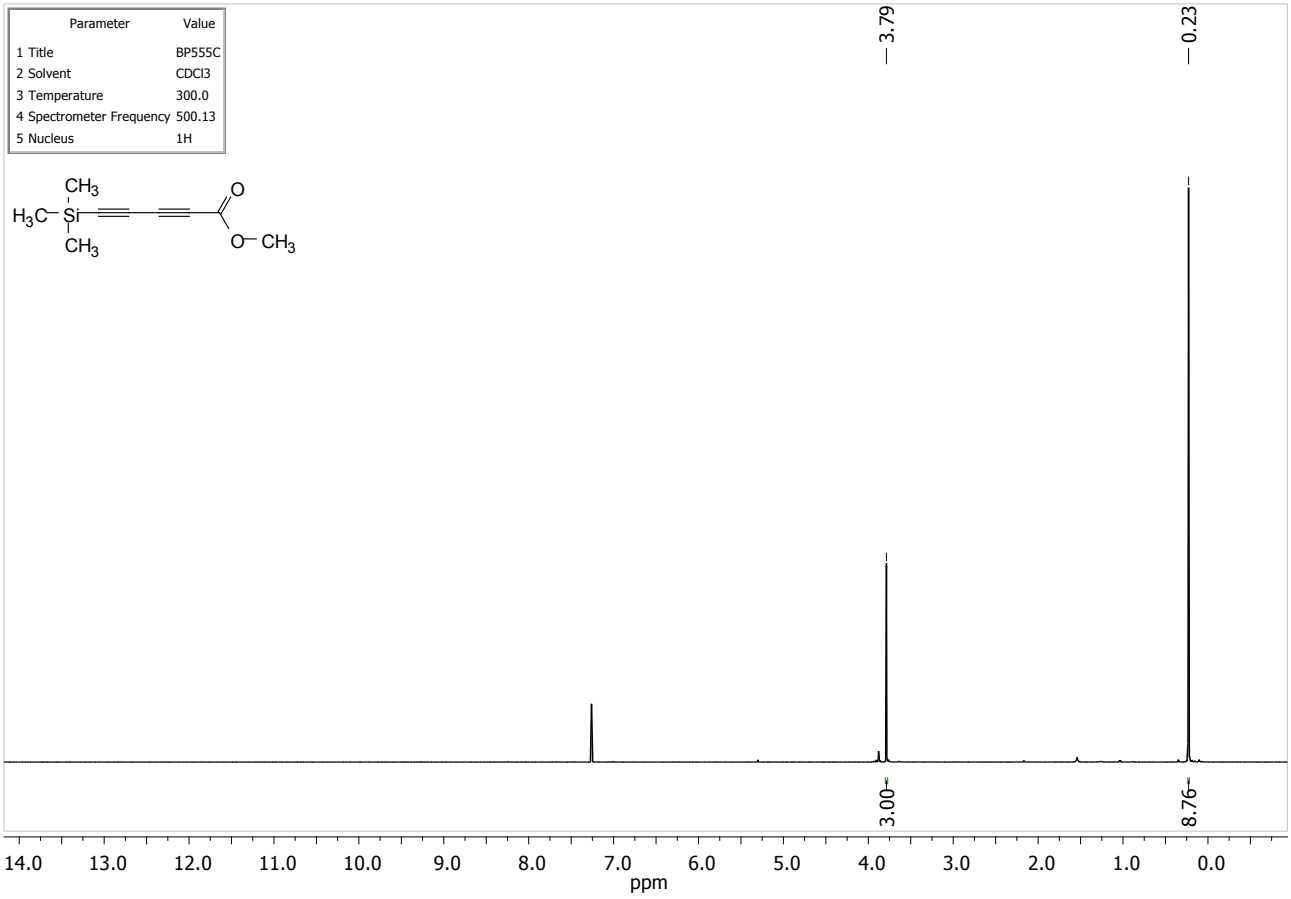


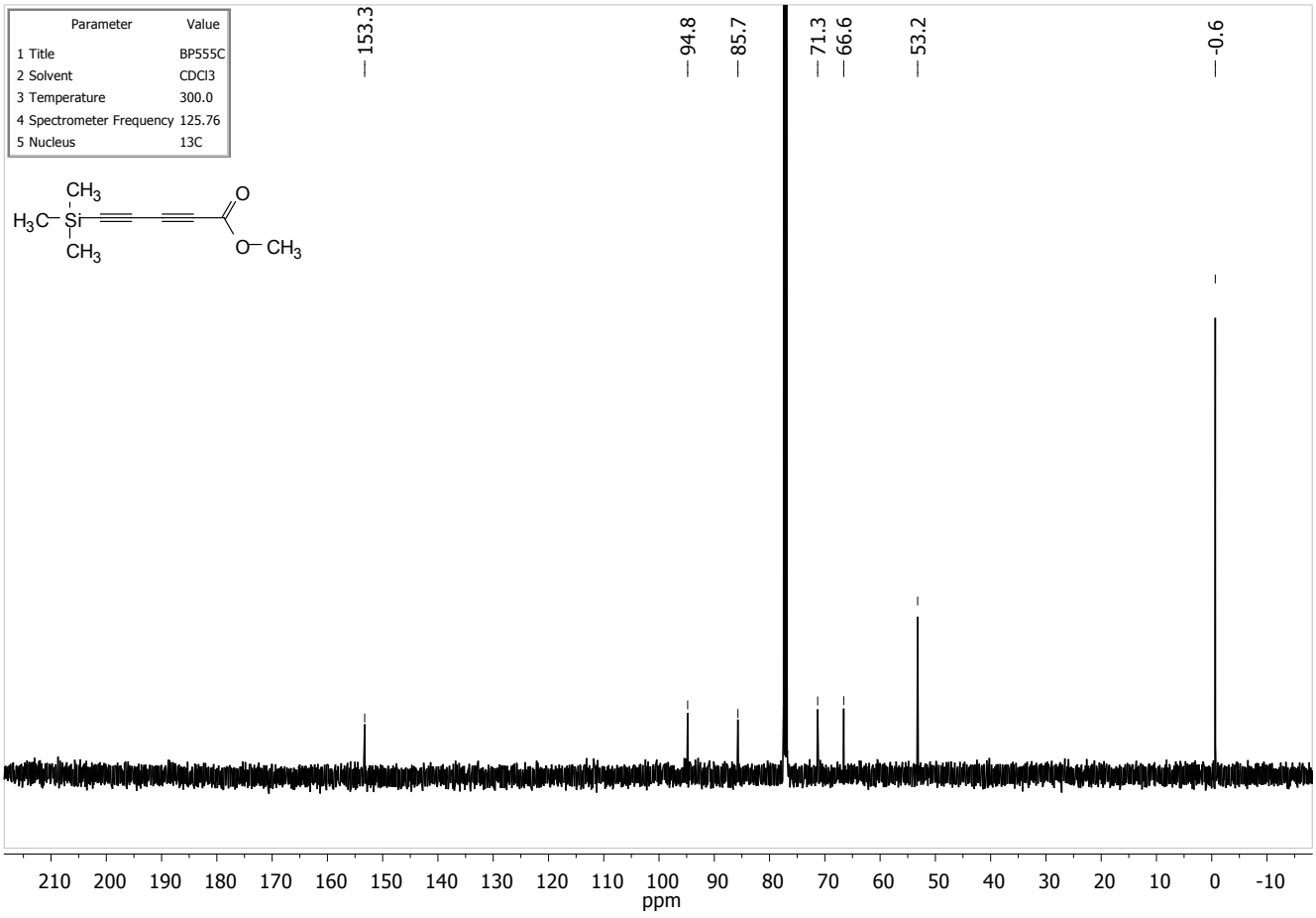
Scheme 1. Packing motif of **4aa**. N-H···O hydrogen bond lengths and angles: N1-H1: 0.904 Å; H1···O1(i): 1.971 Å; N1···O1(i): 2.852 Å; N1—H1···O1(i): 164.5°. Symmetry operations for related atoms are: (i) -x, -y, 2-z. Position of H1 atom was determined from residual electron density map and refined.

	4aa	**4bb**
Empirical formula	$C_{14}H_{13}NO_2$	$C_{16}H_{17}NO_2$
Formula weight	227.25	255.30
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a (Å)	7.887(3)	7.685(2)
b (Å)	8.176(3)	9.000(3)
c (Å)	9.930(3)	11.089(4)
α (°)	77.25(3)	106.45(4)
β (°)	79.07(3)	104.02(3)
γ (°)	77.04(3)	103.26(3)
V (Å^3)	602.0(4)	676.1(4)
Z	2	2
Crystal description	Block, yellow	Plate, purple
Crystal size (mm)	0.60 × 0.31 × 0.08	0.99 × 0.35 × 0.11
d_{calc} (g/cm^3)	1.254	1.254
μ (mm^{-1})	0.08	0.08
F(000)	240	272
Diffractometer	Kuma KM-4	Kuma KM-4
λ (Å)	0.71073	0.71073
T (K)	100	100
Θ min/max (°)	3.0/36.6	2.9/32.6
h, *k*, *l* min/max	-9/13, -13/12, -16/15	-9/9, -12/11, -16/14
Reflections collected	9521	6145
Independent reflections	4548	3201
Reflections with $I>2\sigma(I)$	3499	2525
R (int.)	0.026	0.030
R indices ($F_o^2 > 2\sigma(F_o^2)$)	*R1* = 0.0528	*R1* = 0.0519
	wR2 = 0.1465	*wR2* = 0.01401
R indices (all data)	*R1* = 0.0656	*R1* = 0.0631
	wR2 = 0.1534	*wR2* = 0.1474
GooF	1.07	1.06
$\Delta\rho_{max}/\Delta\rho_{min}$ (e·Å^{-3})	0.45/-0.37	0.30/-0.37

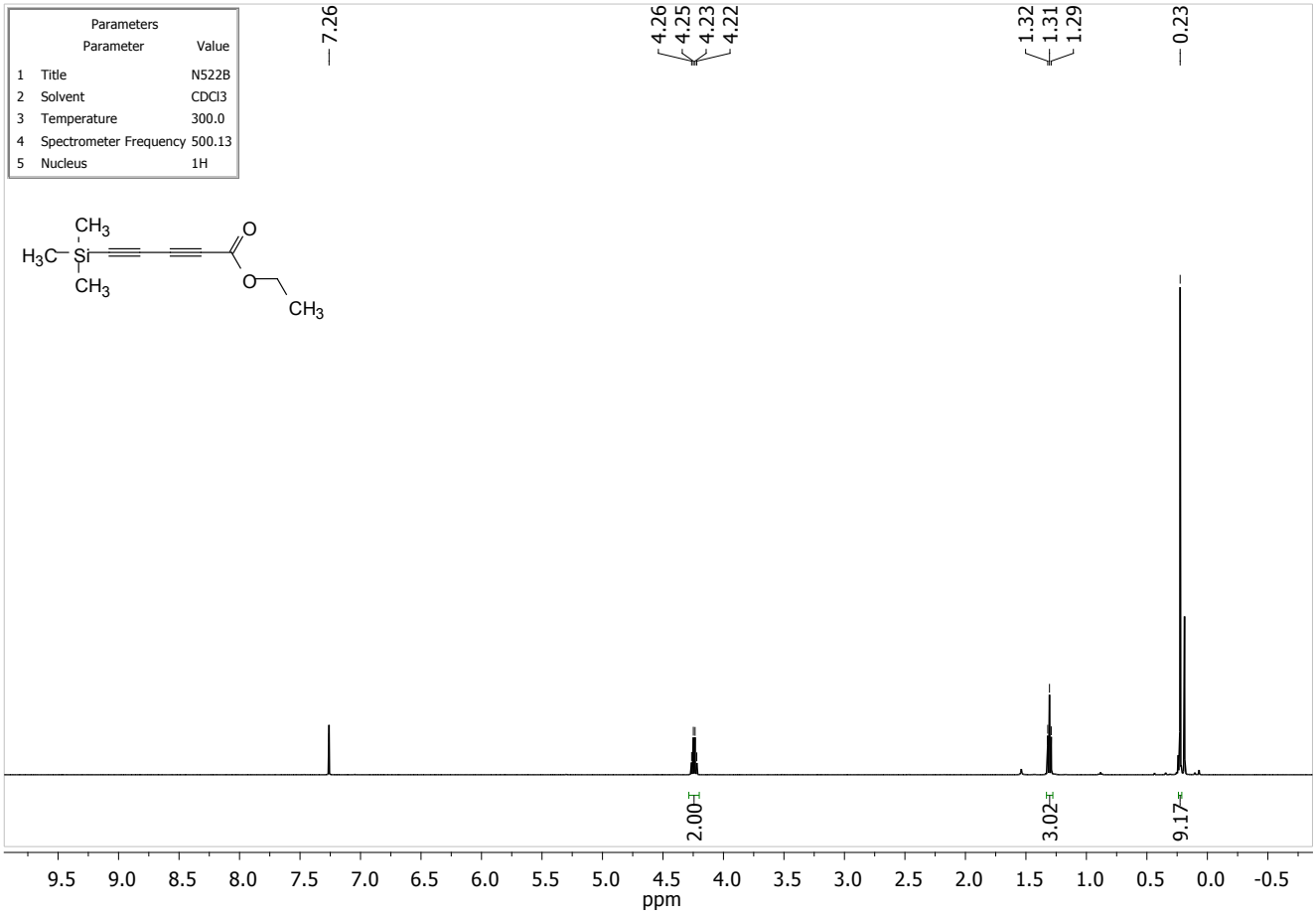
NMR Spectra

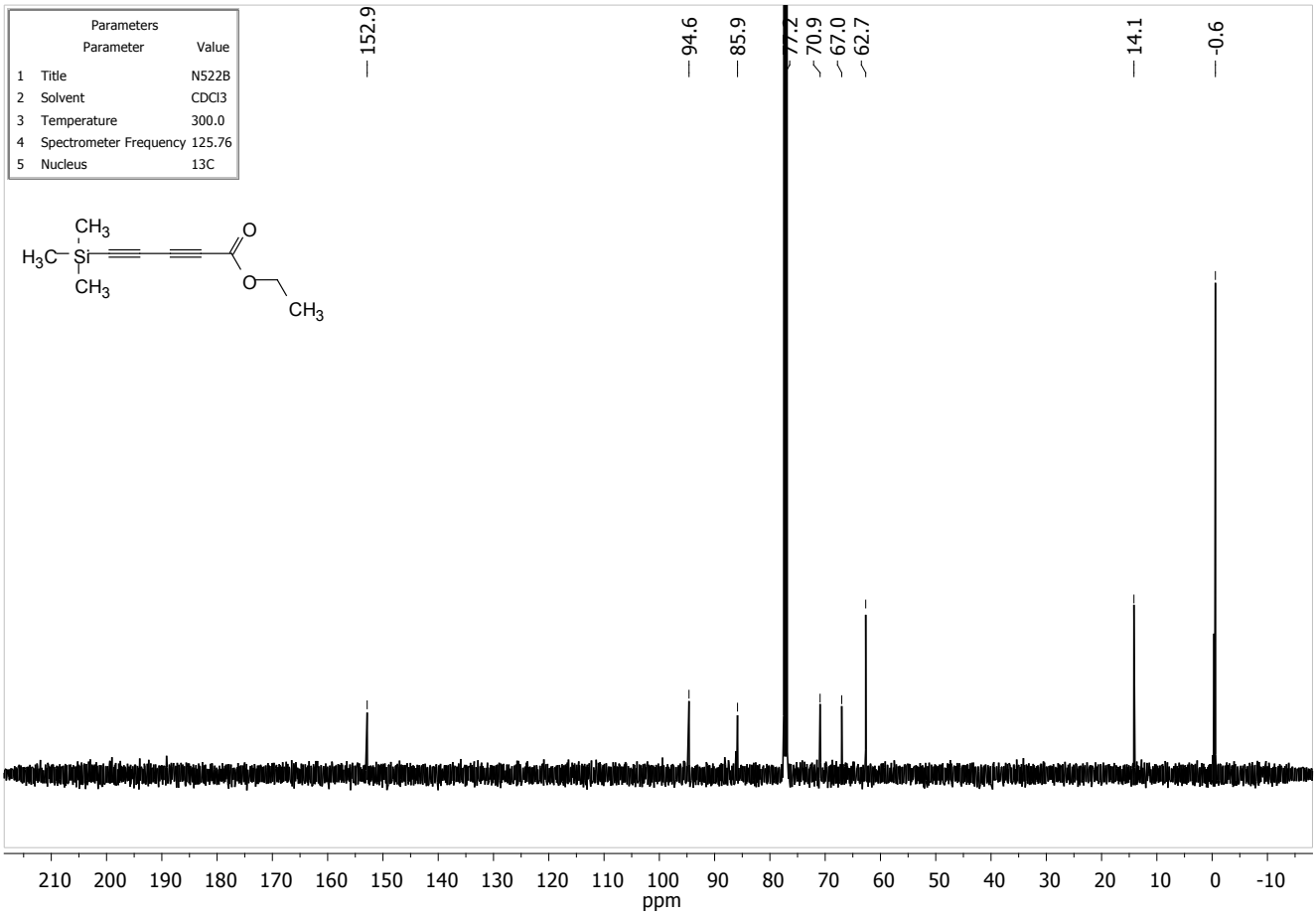
Methyl 5-(trimethylsilyl)penta-2,4-diynoate (3a)



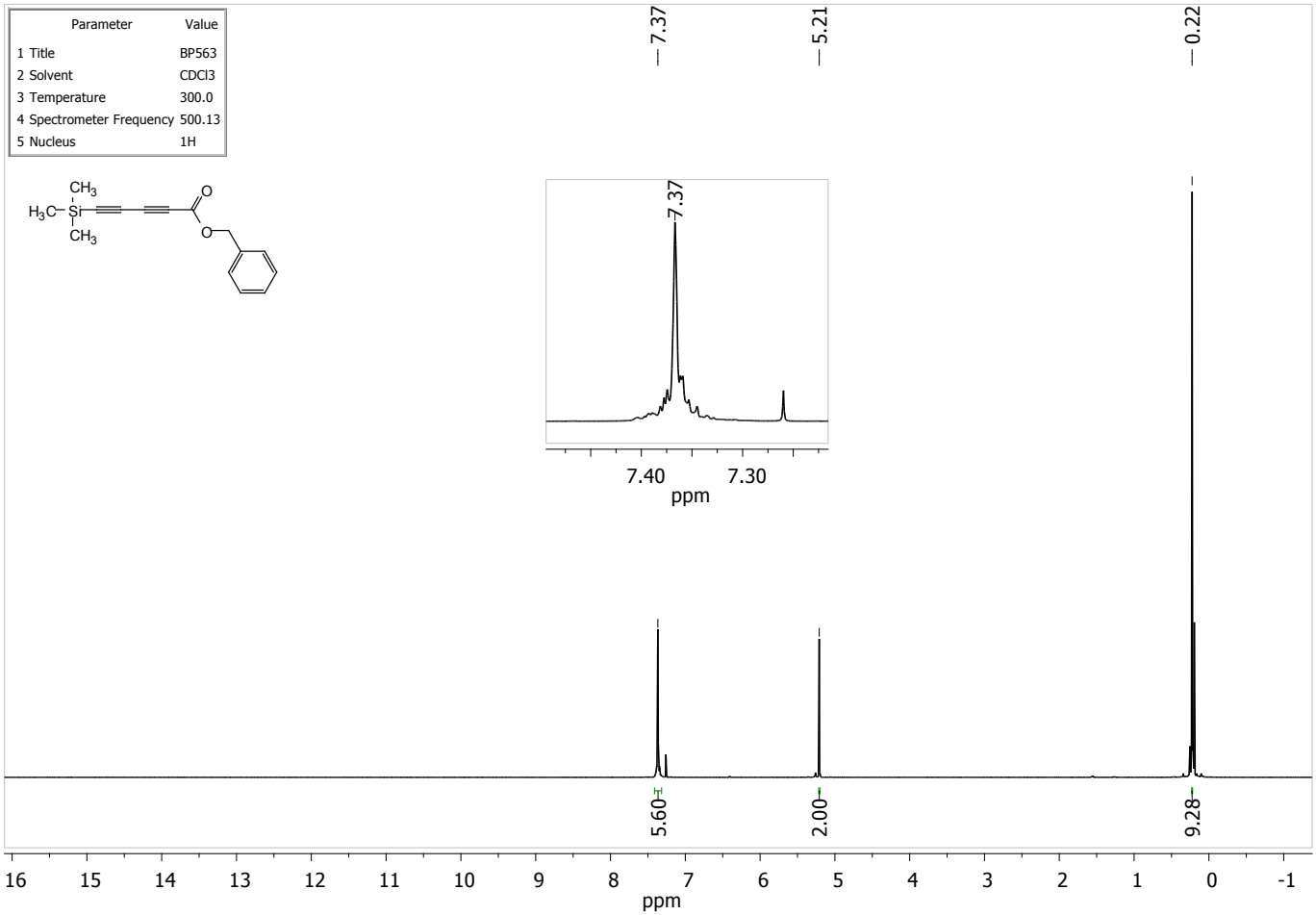


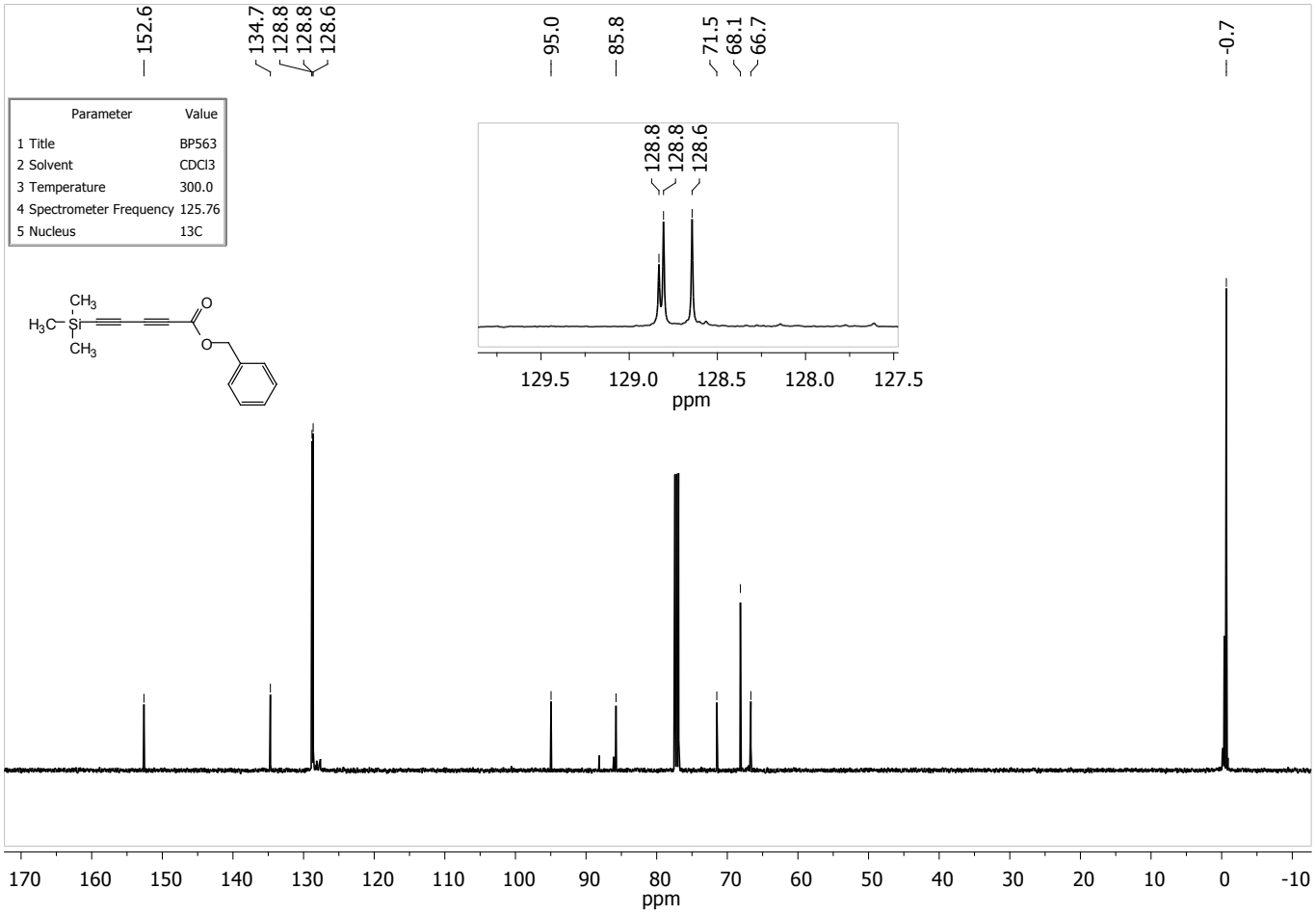
Ethyl 5-(trimethylsilyl)penta-2,4-diynoate (3b)



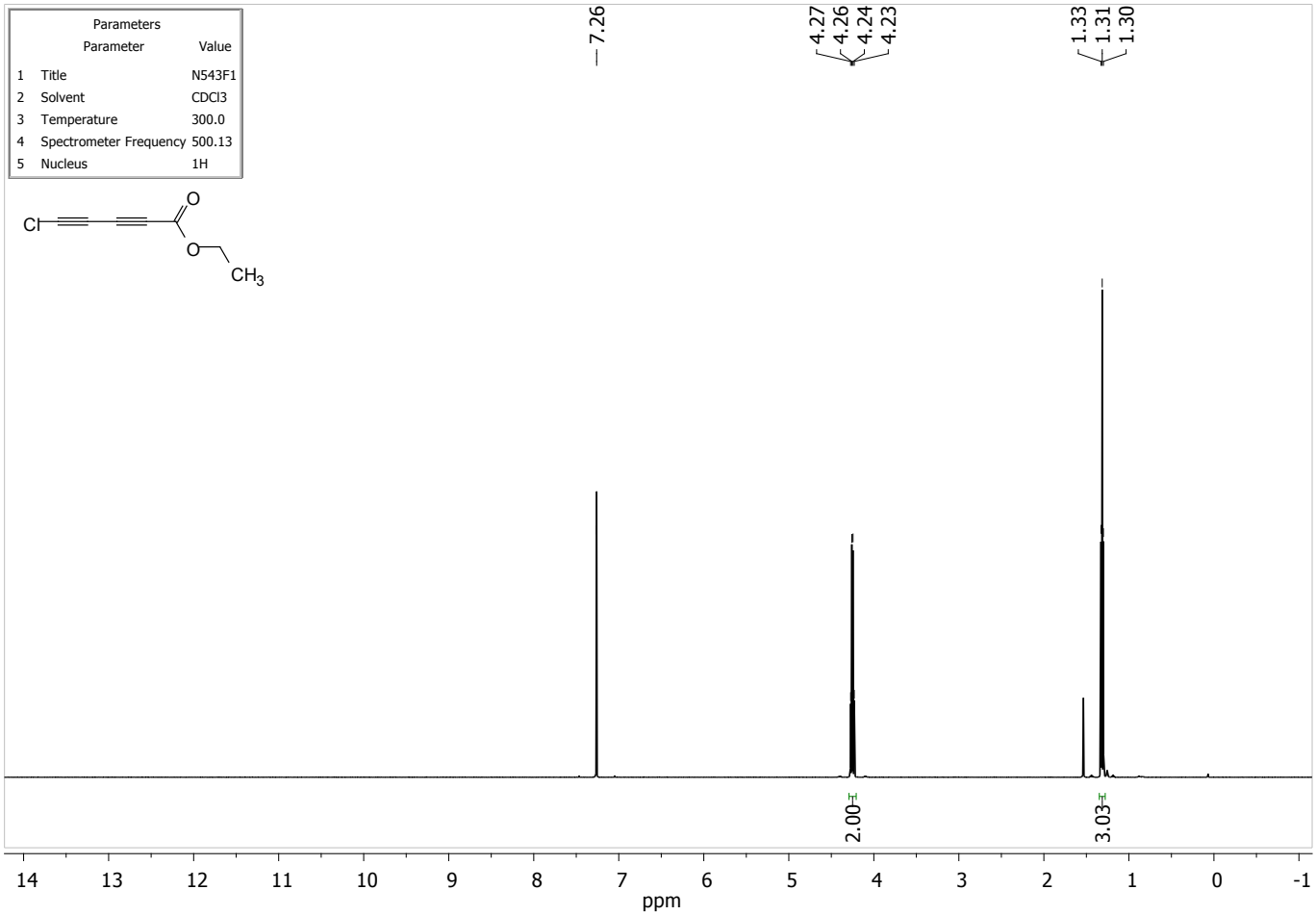


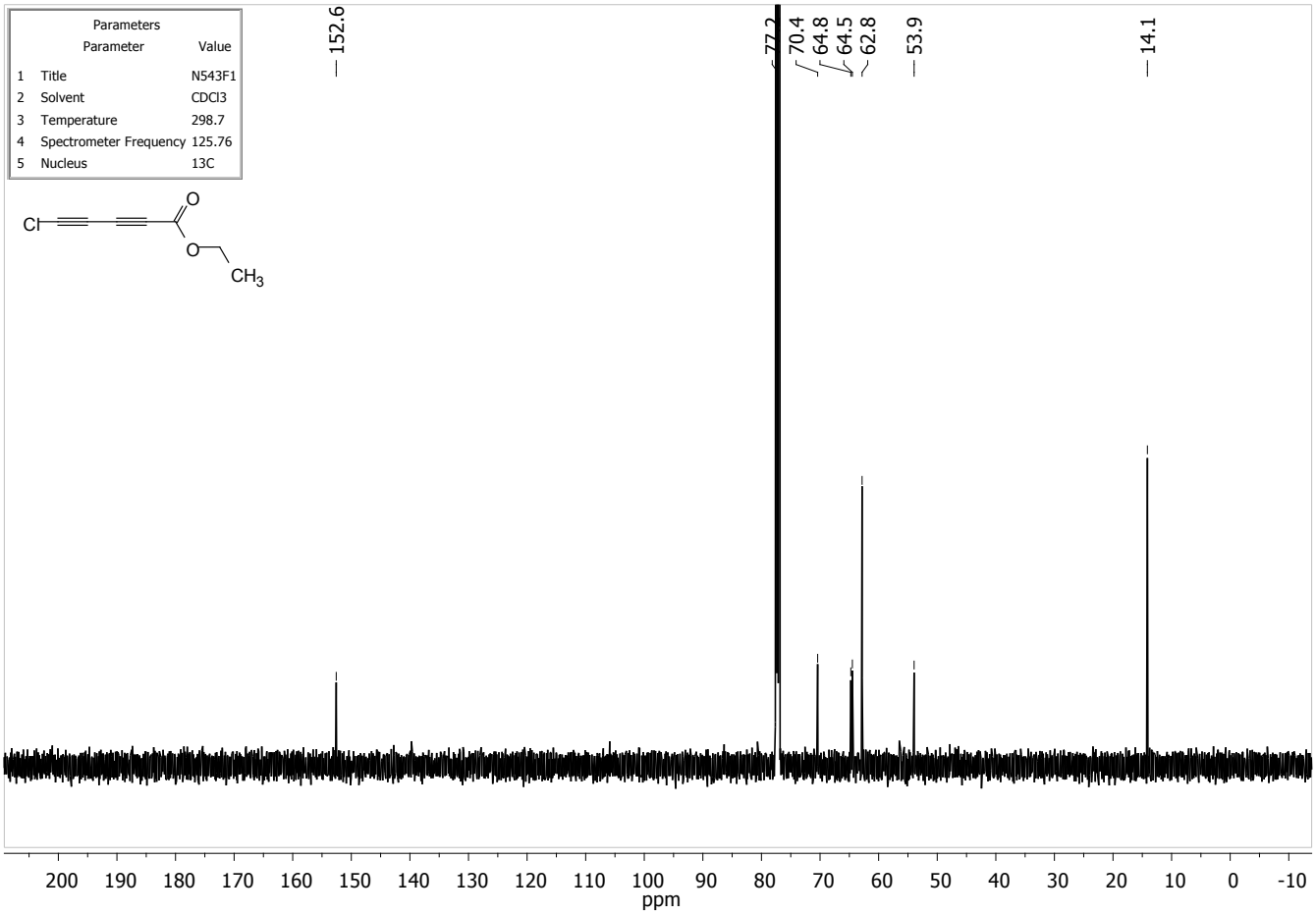
Benzyl 5-(trimethylsilyl)penta-2,4-diynoate (3c)



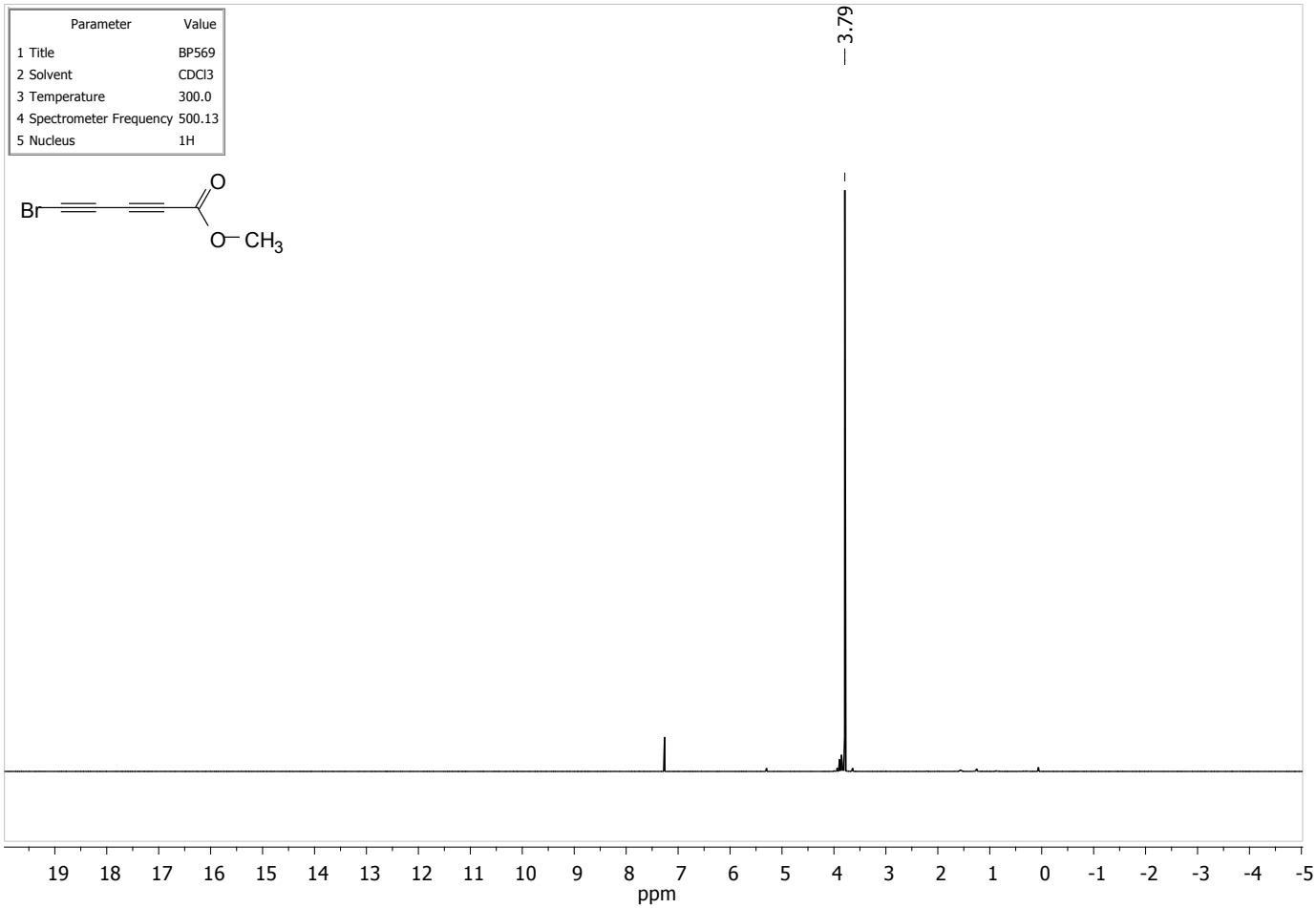


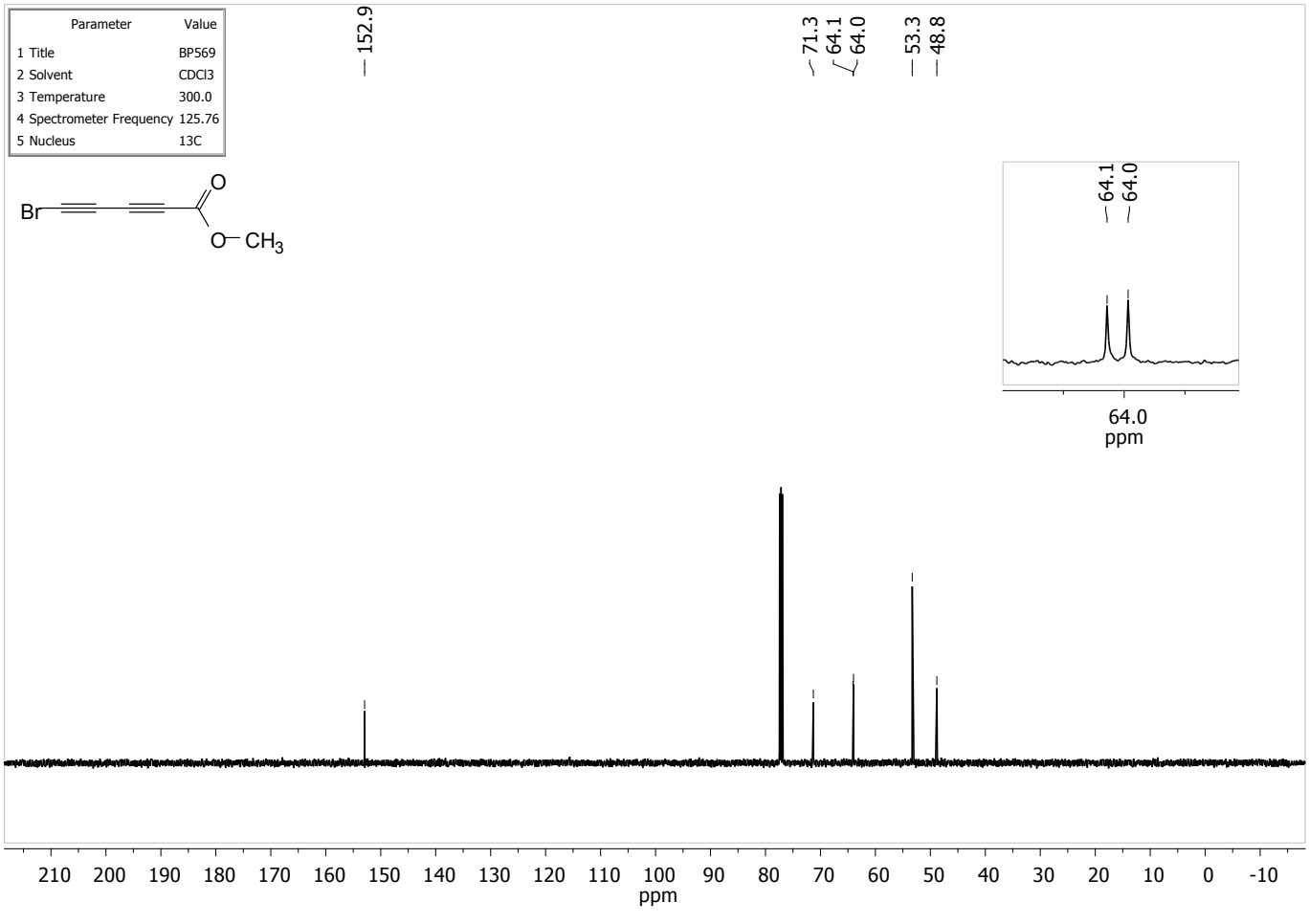
Ethyl 5-chloropenta-2,4-diynoate (2b-Cl)



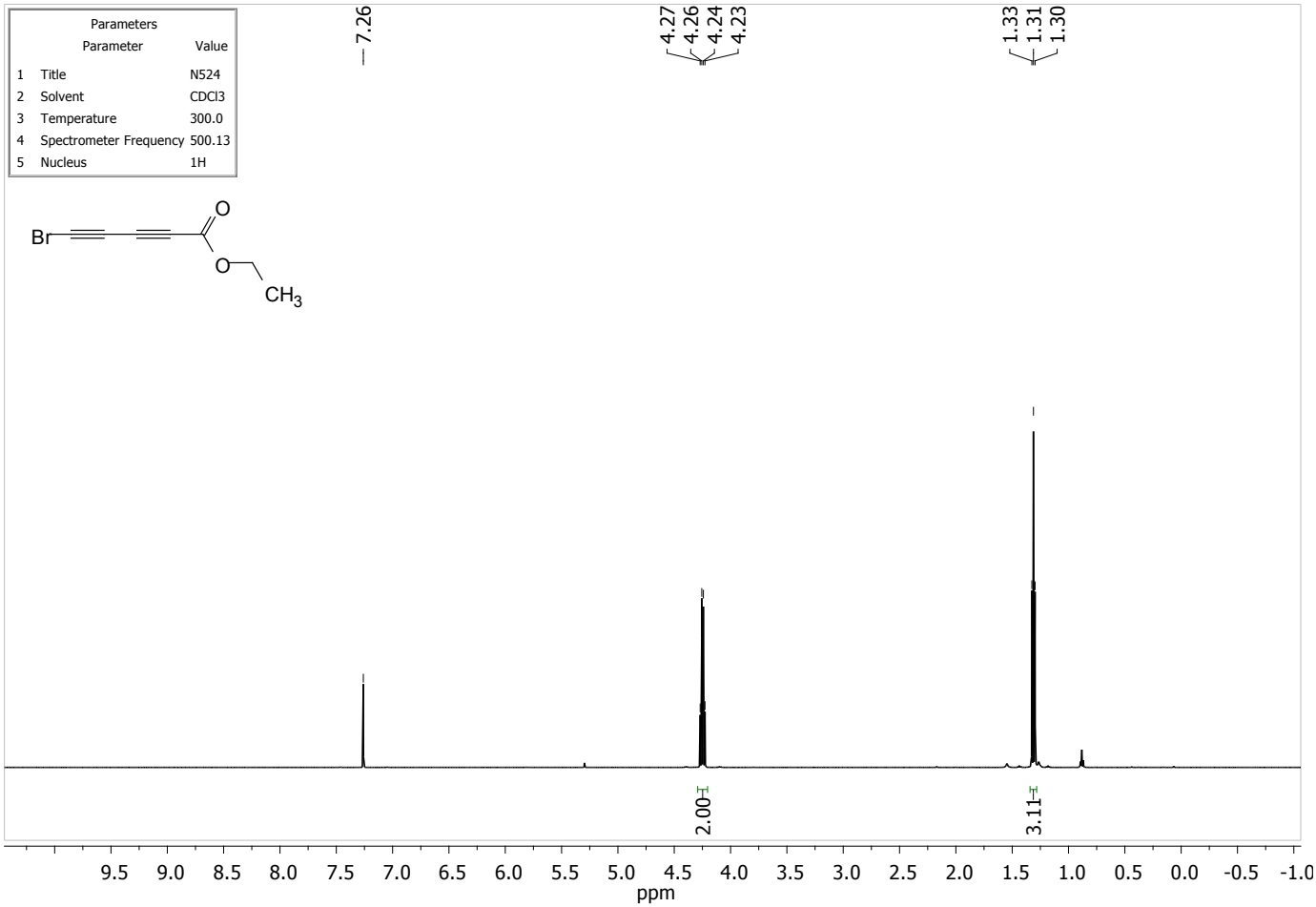


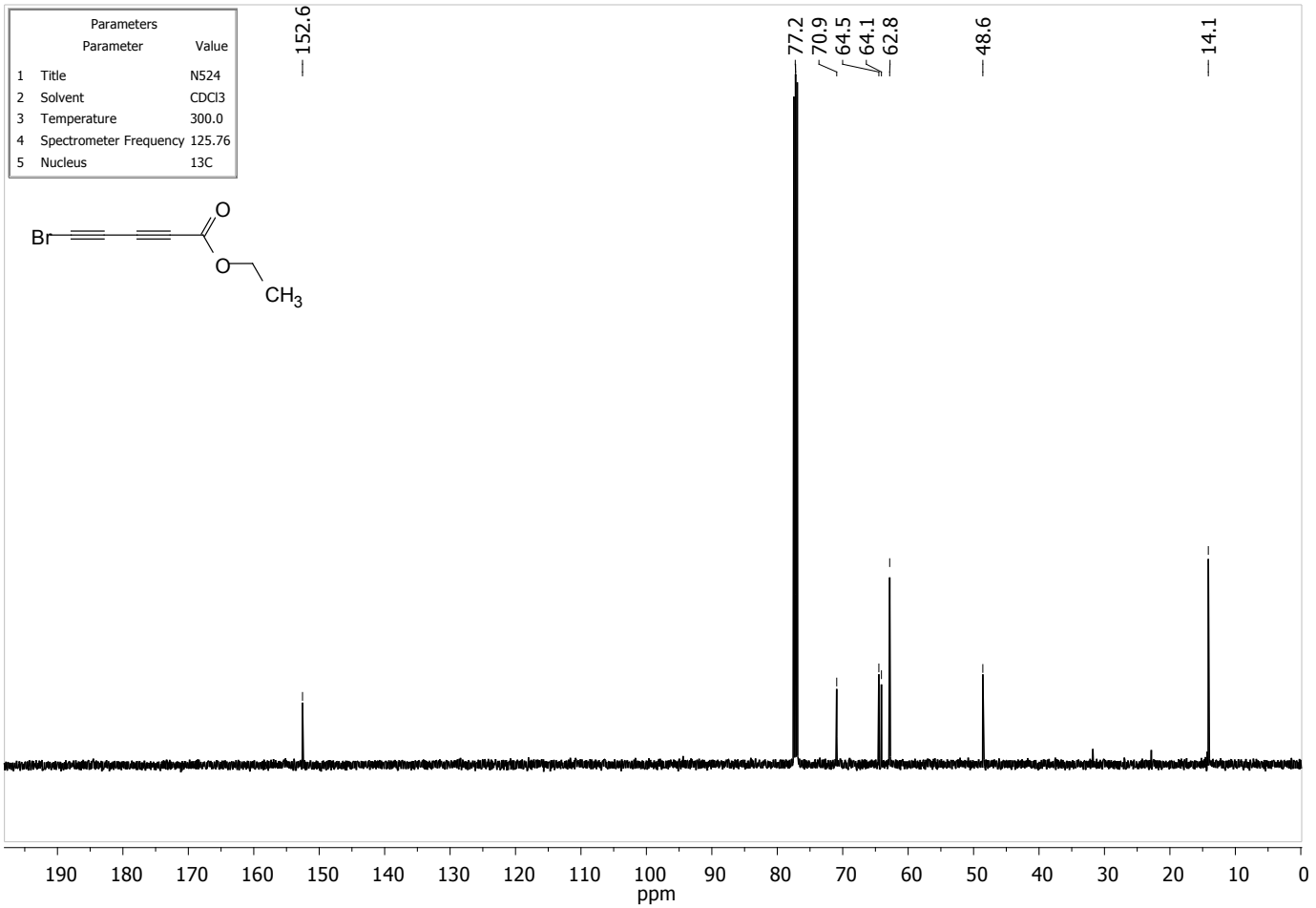
Methyl 5-bromopenta-2,4-diynoate (2a-Br**)**



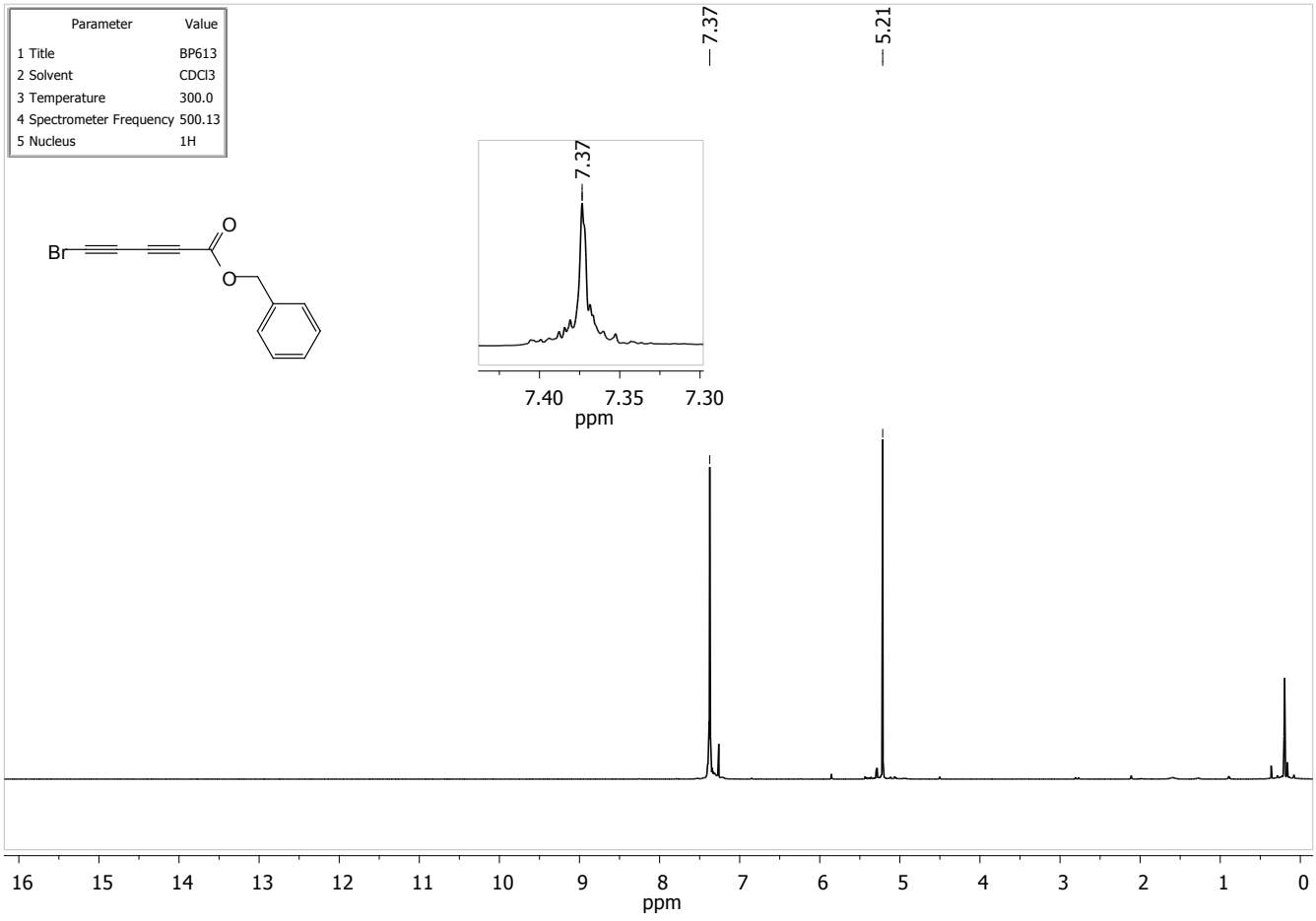


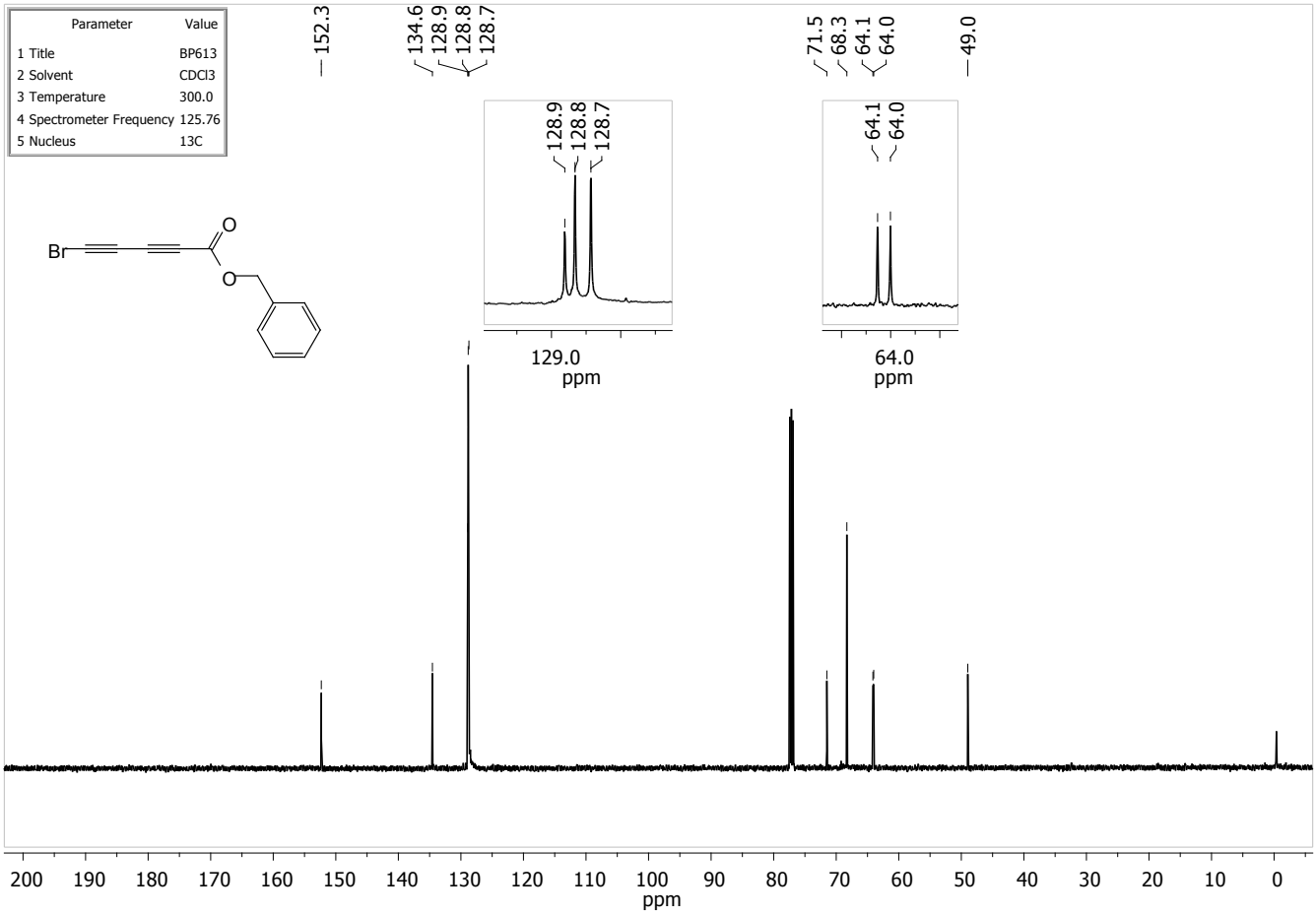
Ethyl 5-bromopenta-2,4-diynoate (2b-Br)





Benzyl 5-bromopenta-2,4-diynoate (2c-Br)





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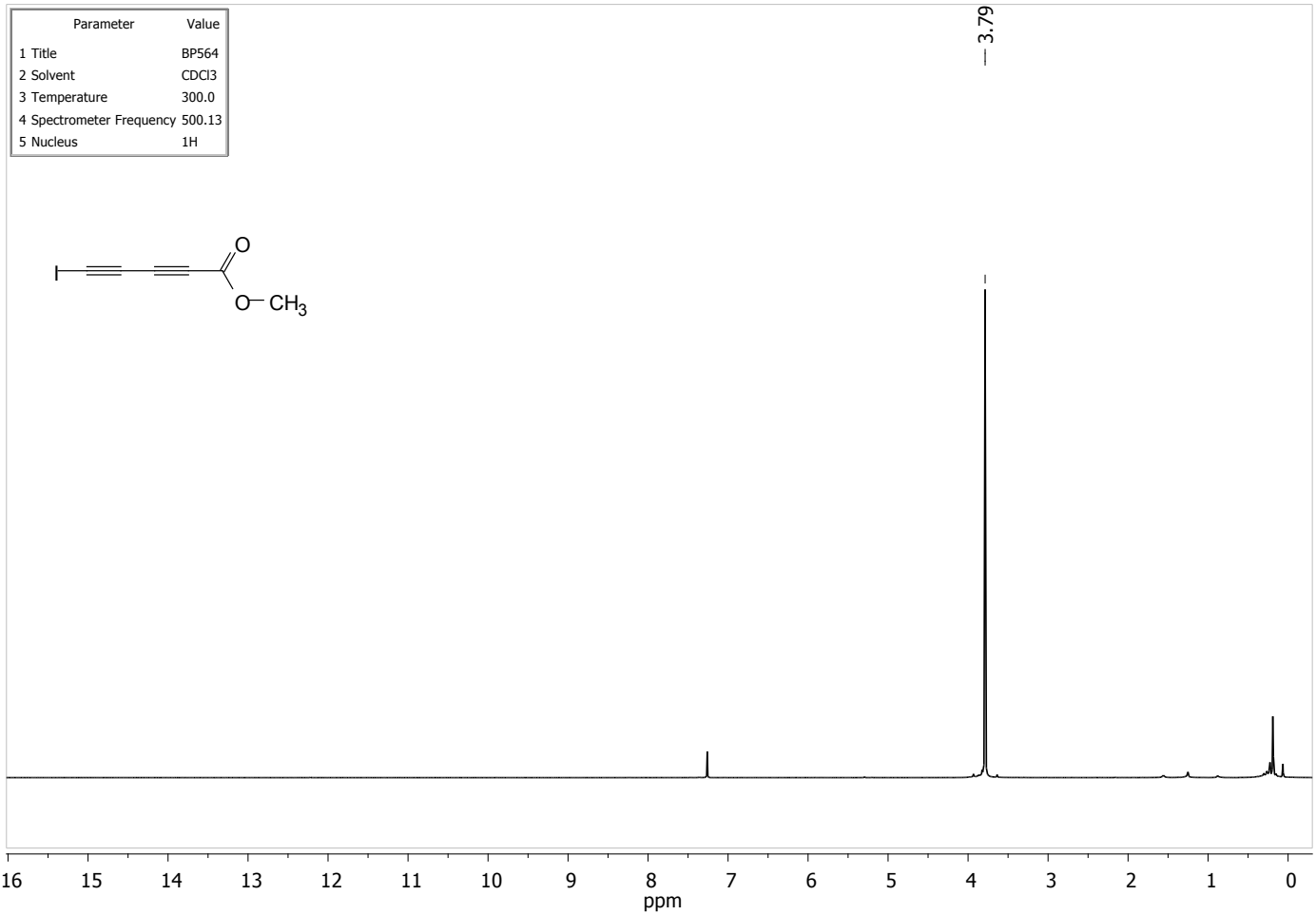
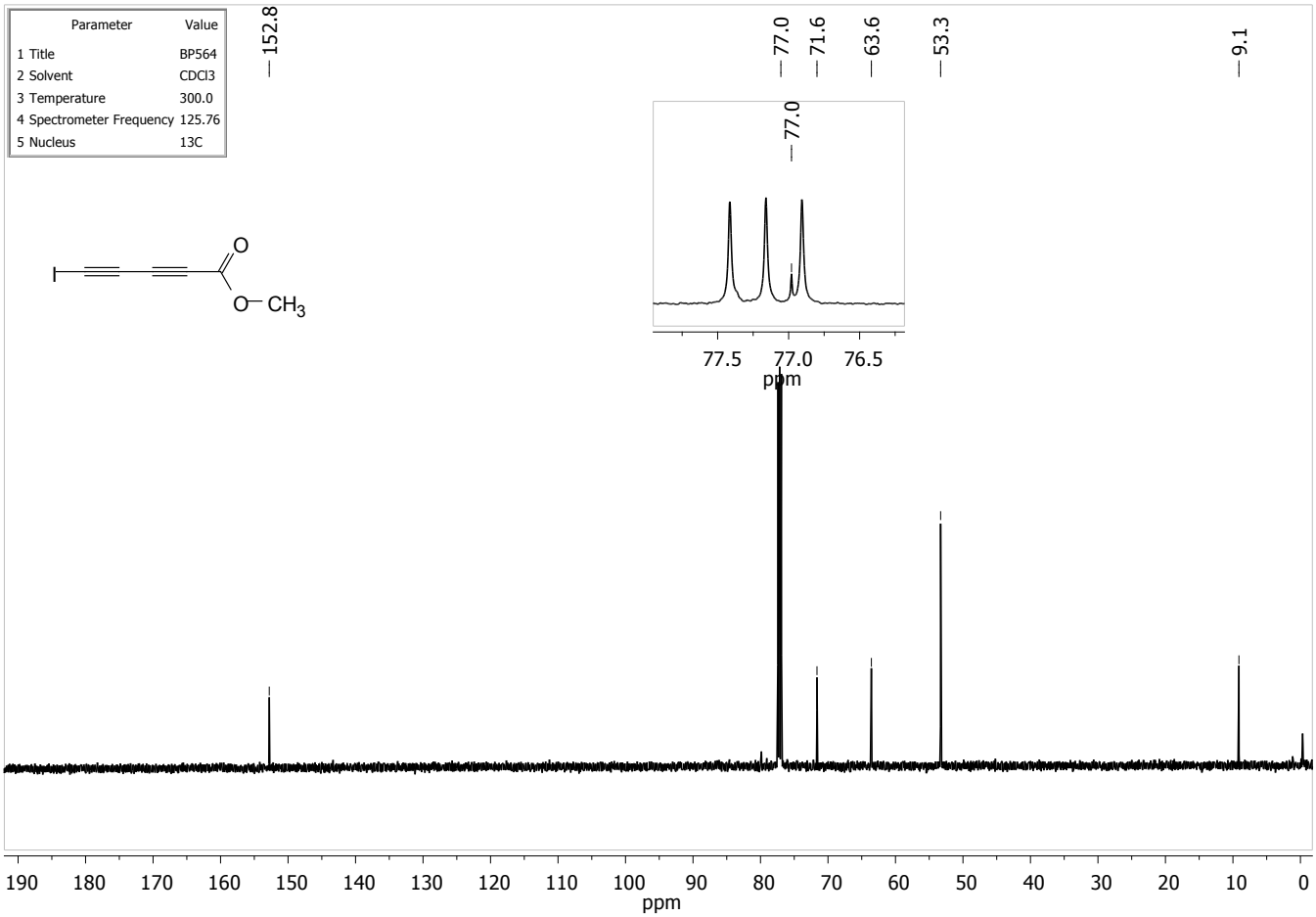
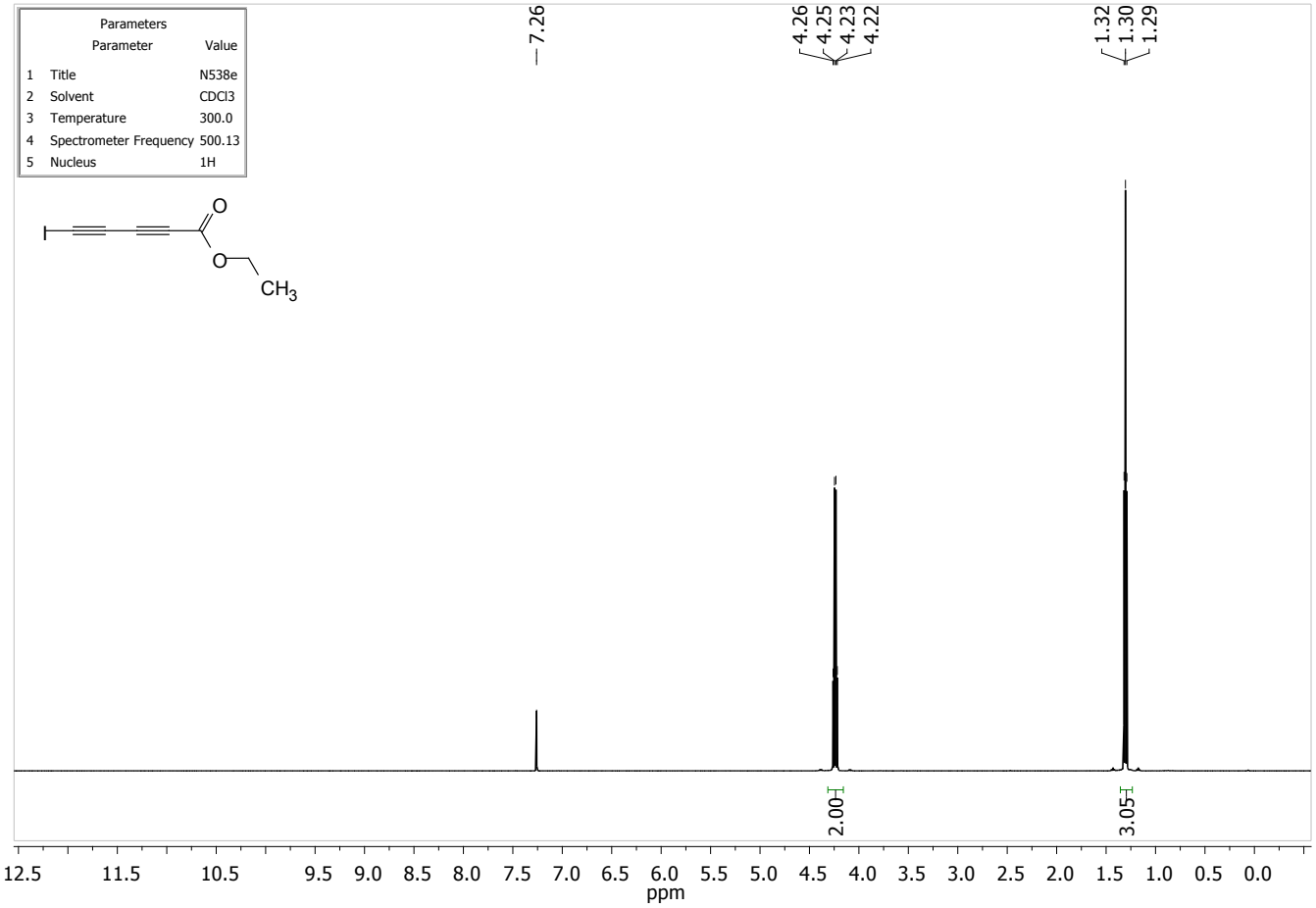
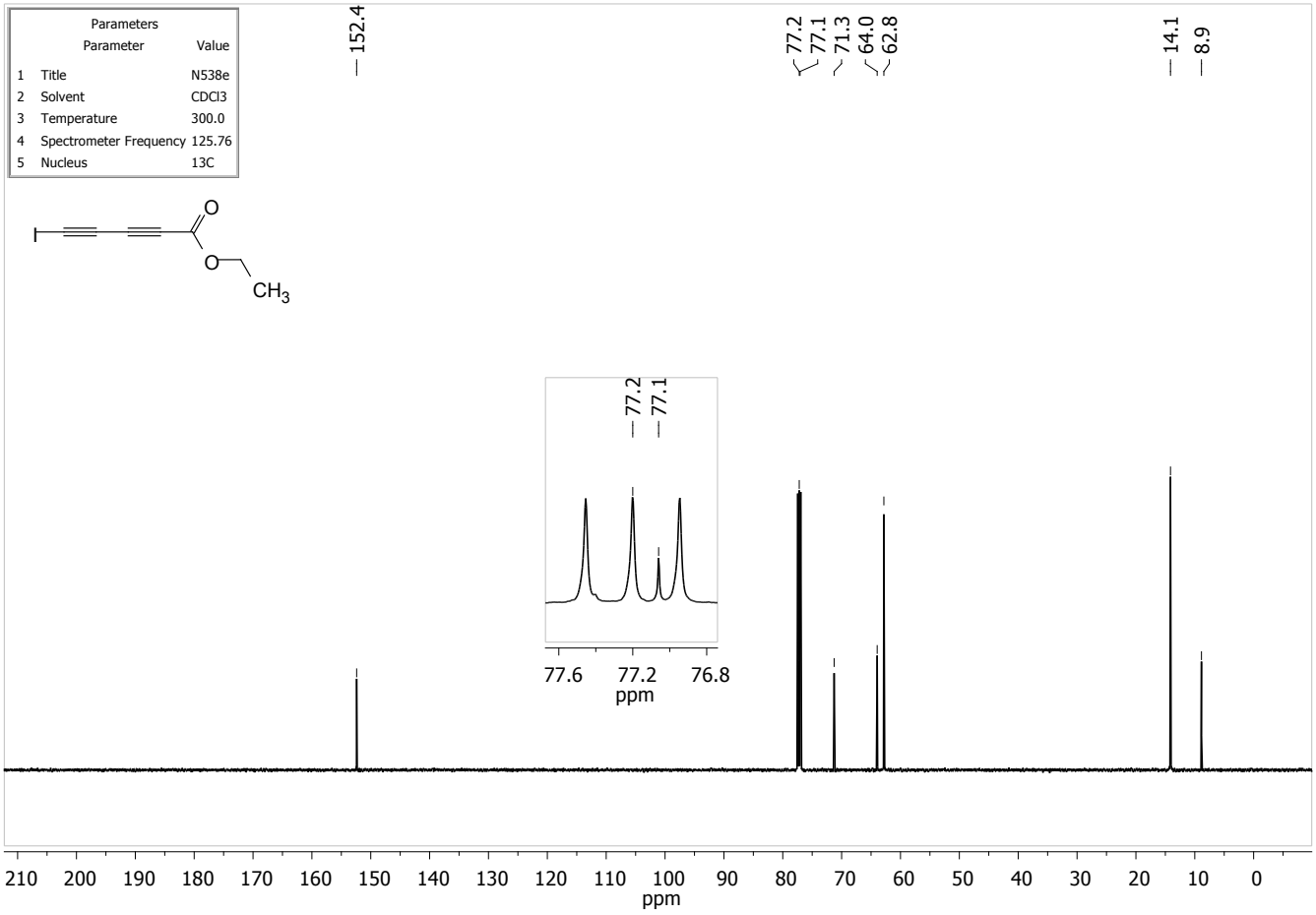


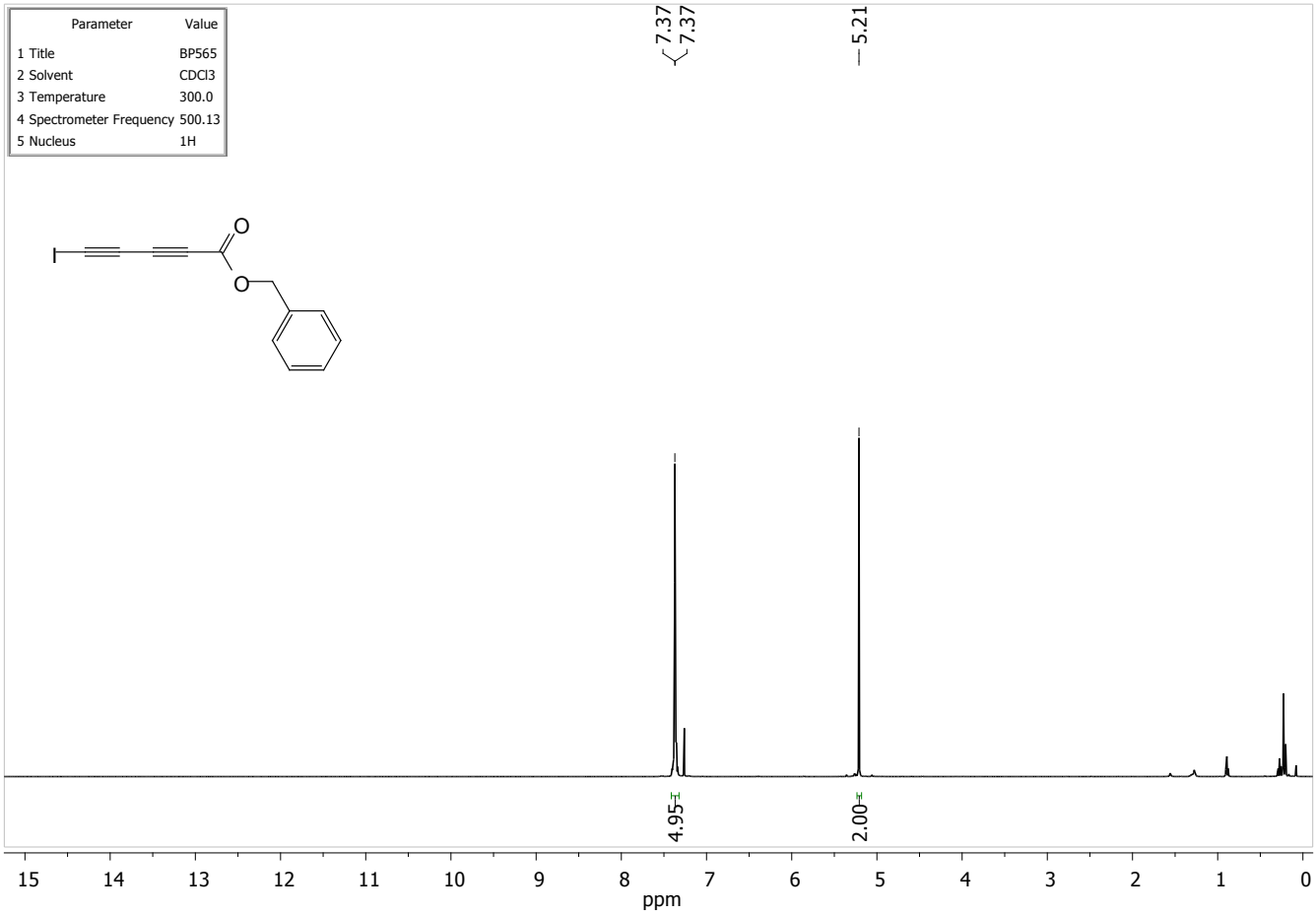


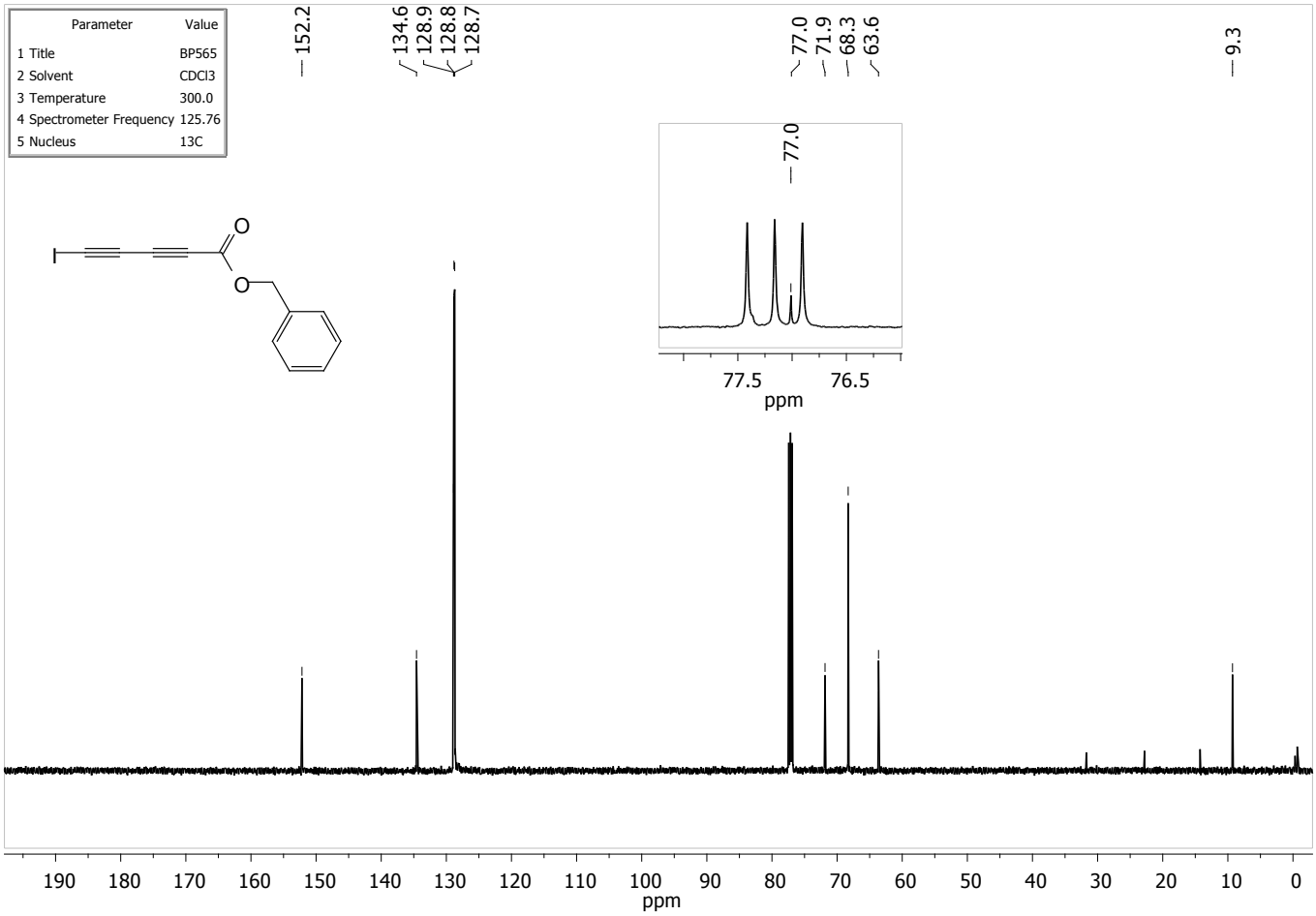
Ethyl 5-iodopenta-2,4-diynoate (2b-I)



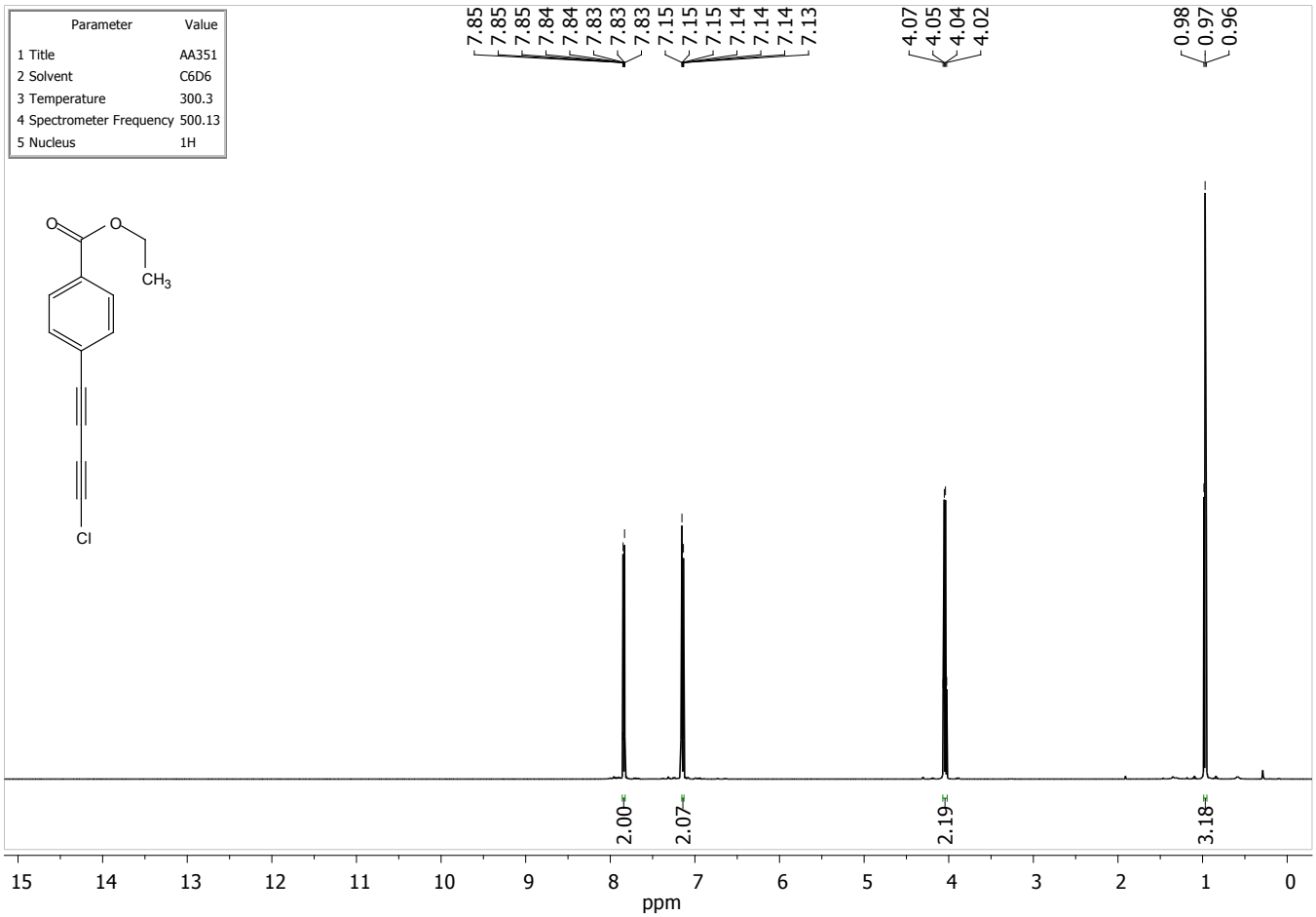


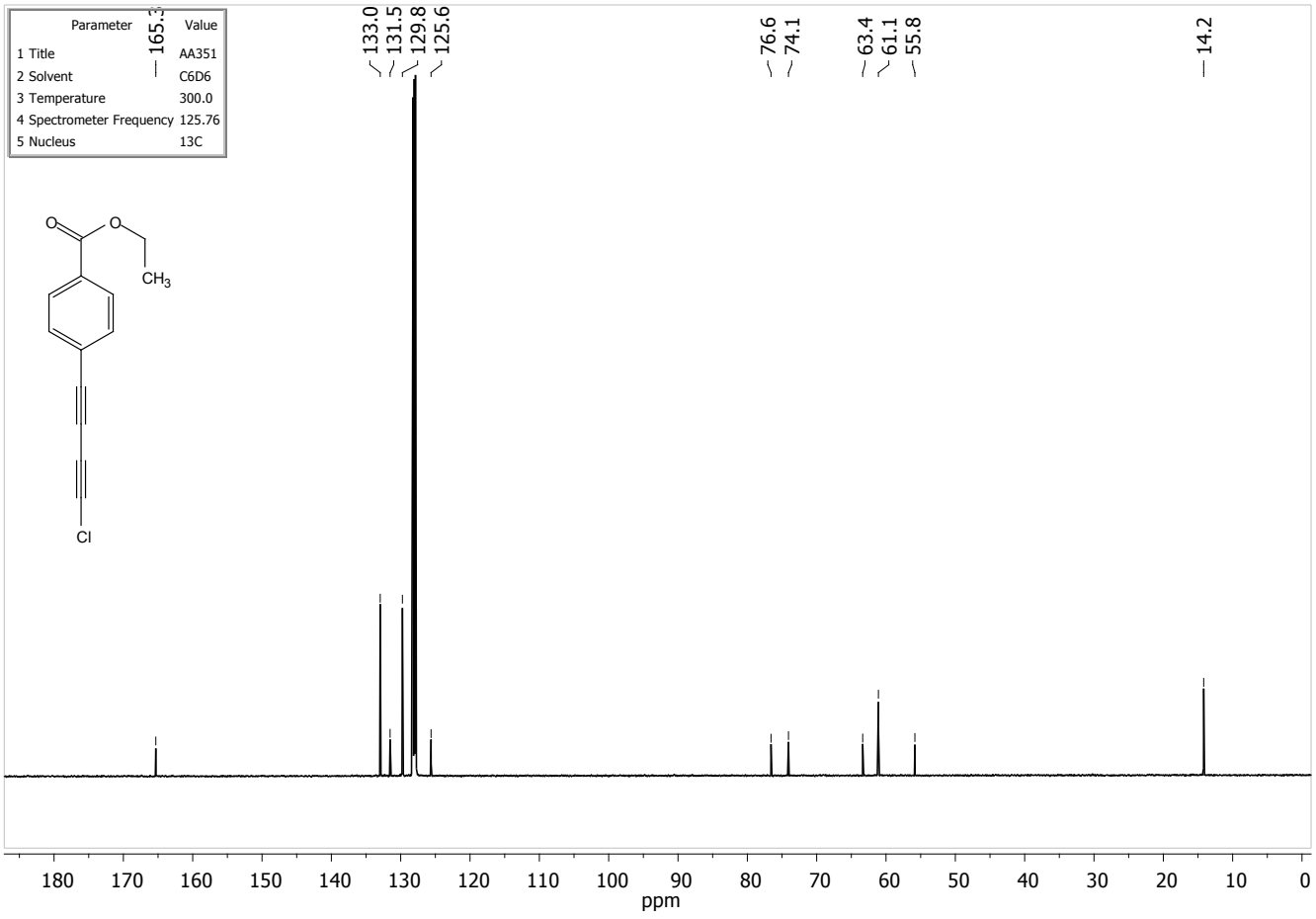
Benzyl 5-iodopenta-2,4-diynoate (2c-I)



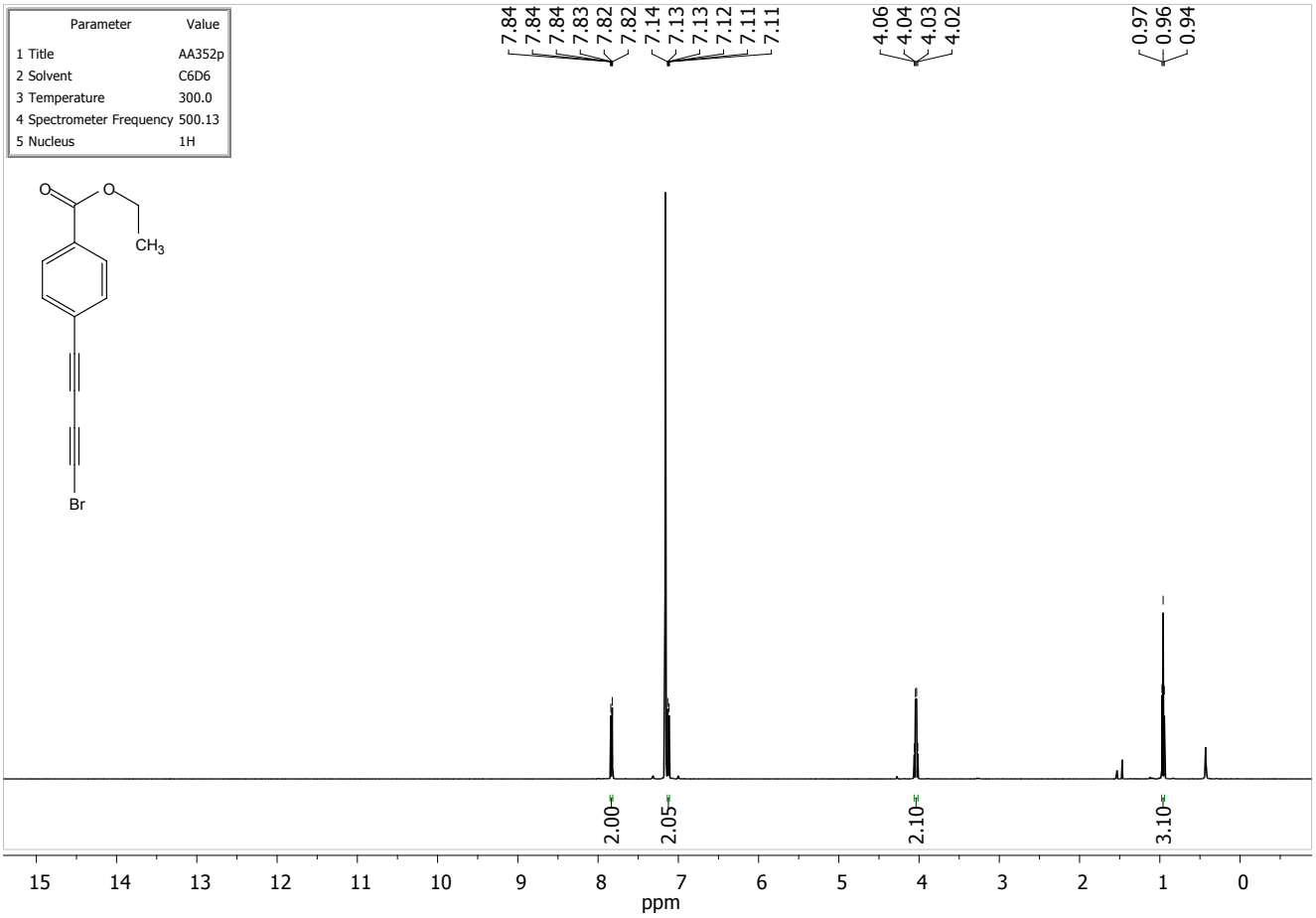


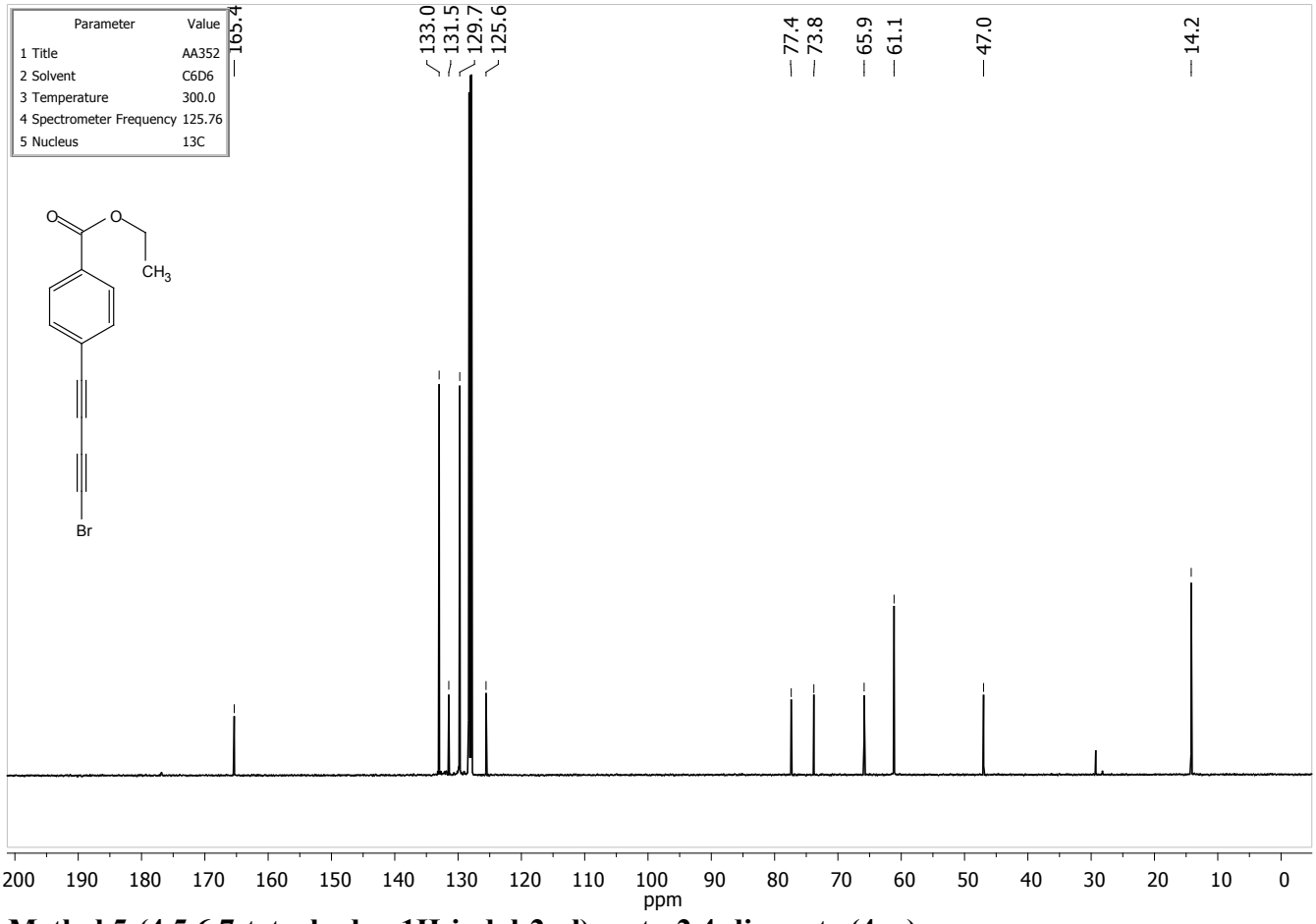
Ethyl 4-(chlorobuta-1,3-diyn-1-yl)benzoate (2d-Cl)



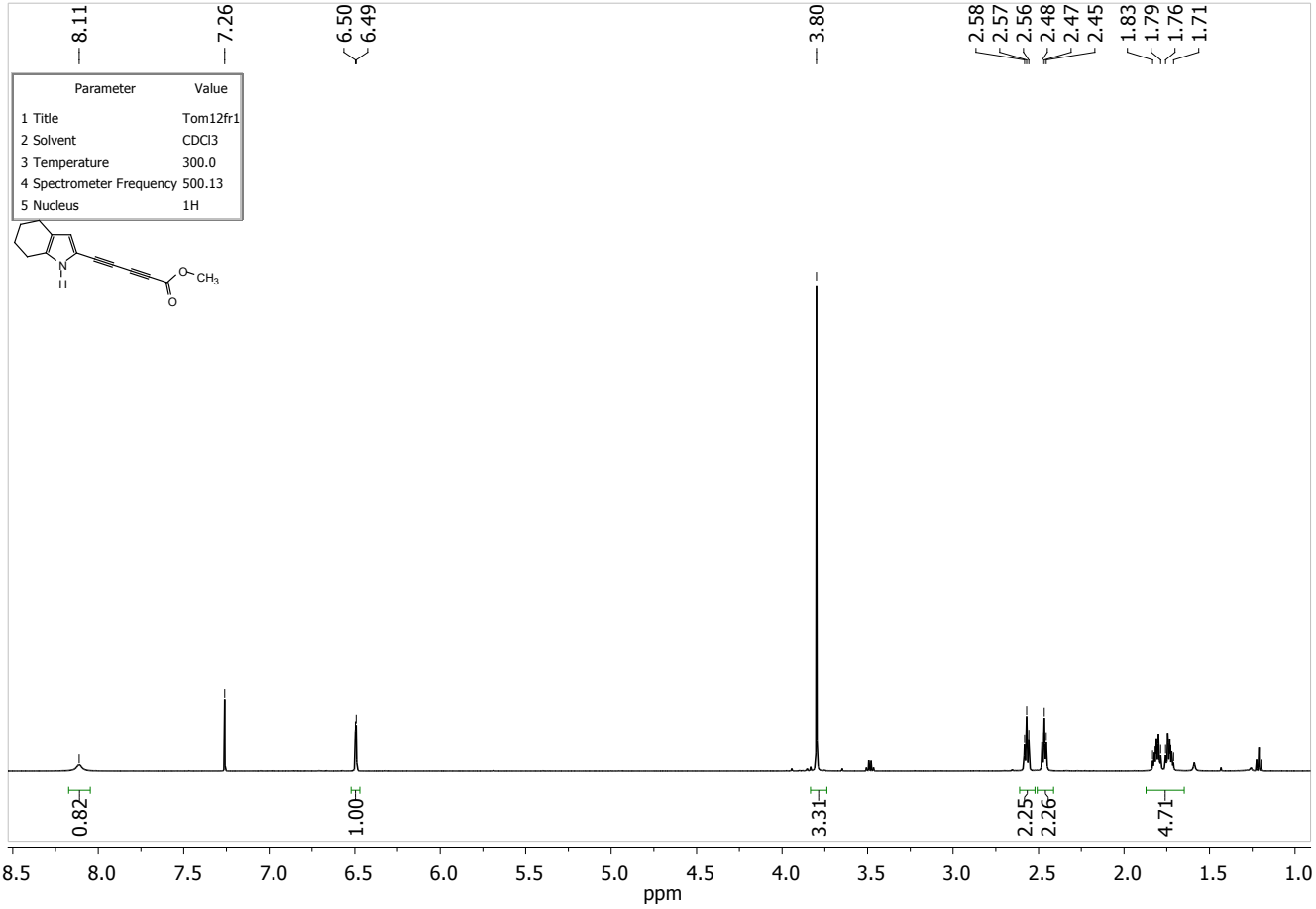


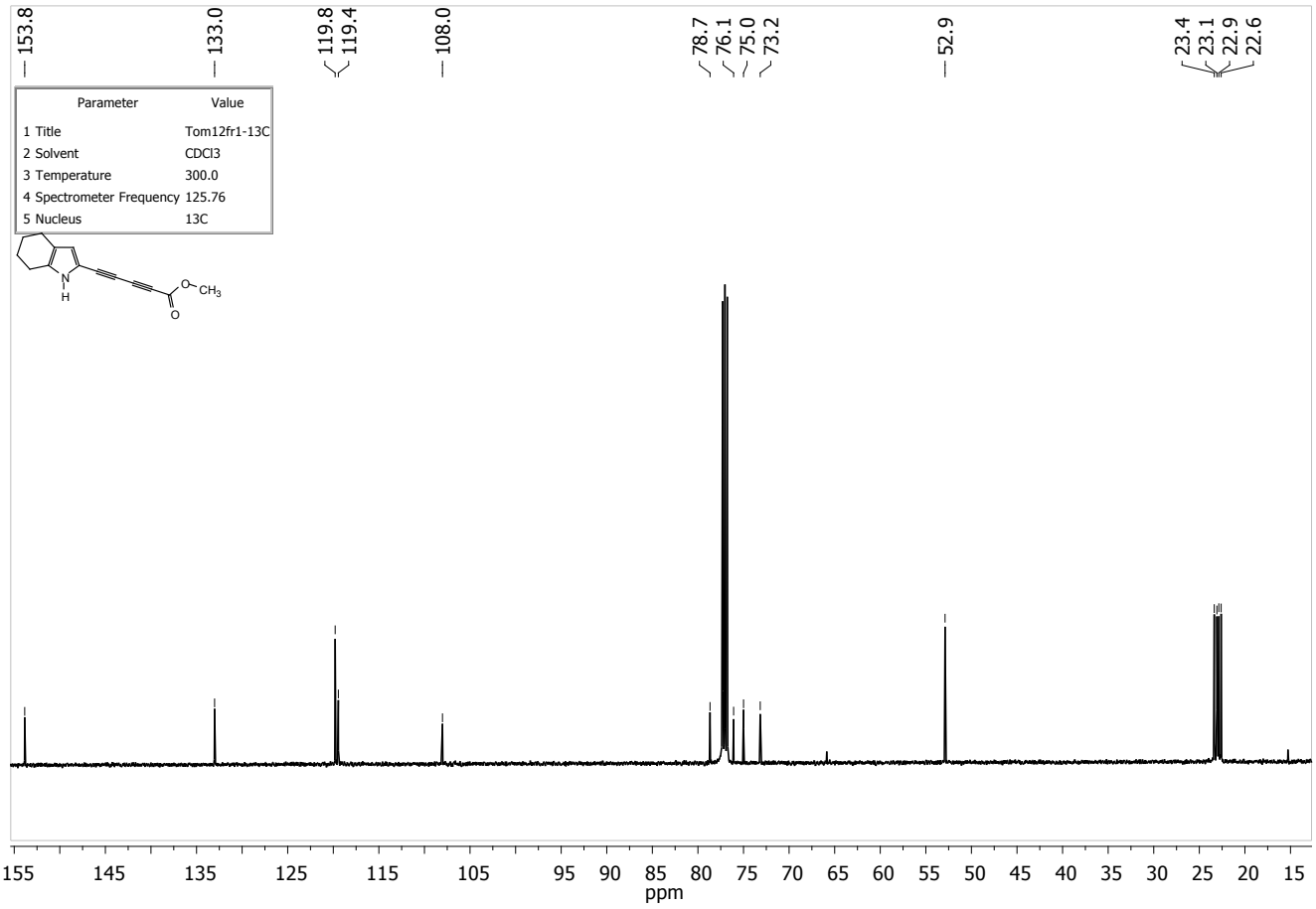
Ethyl 4-(bromobuta-1,3-diyn-1-yl)benzoate (2d-Br)



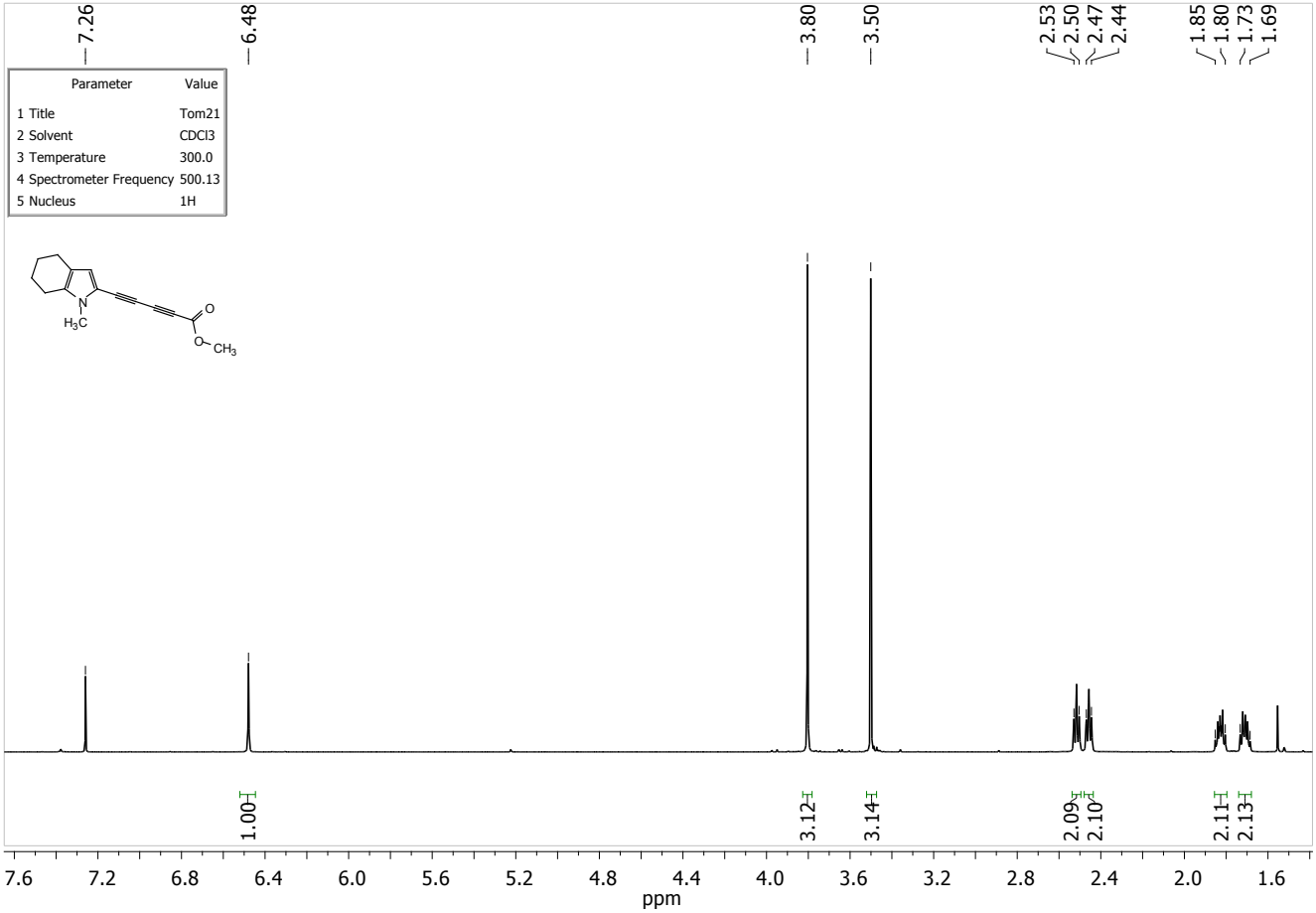


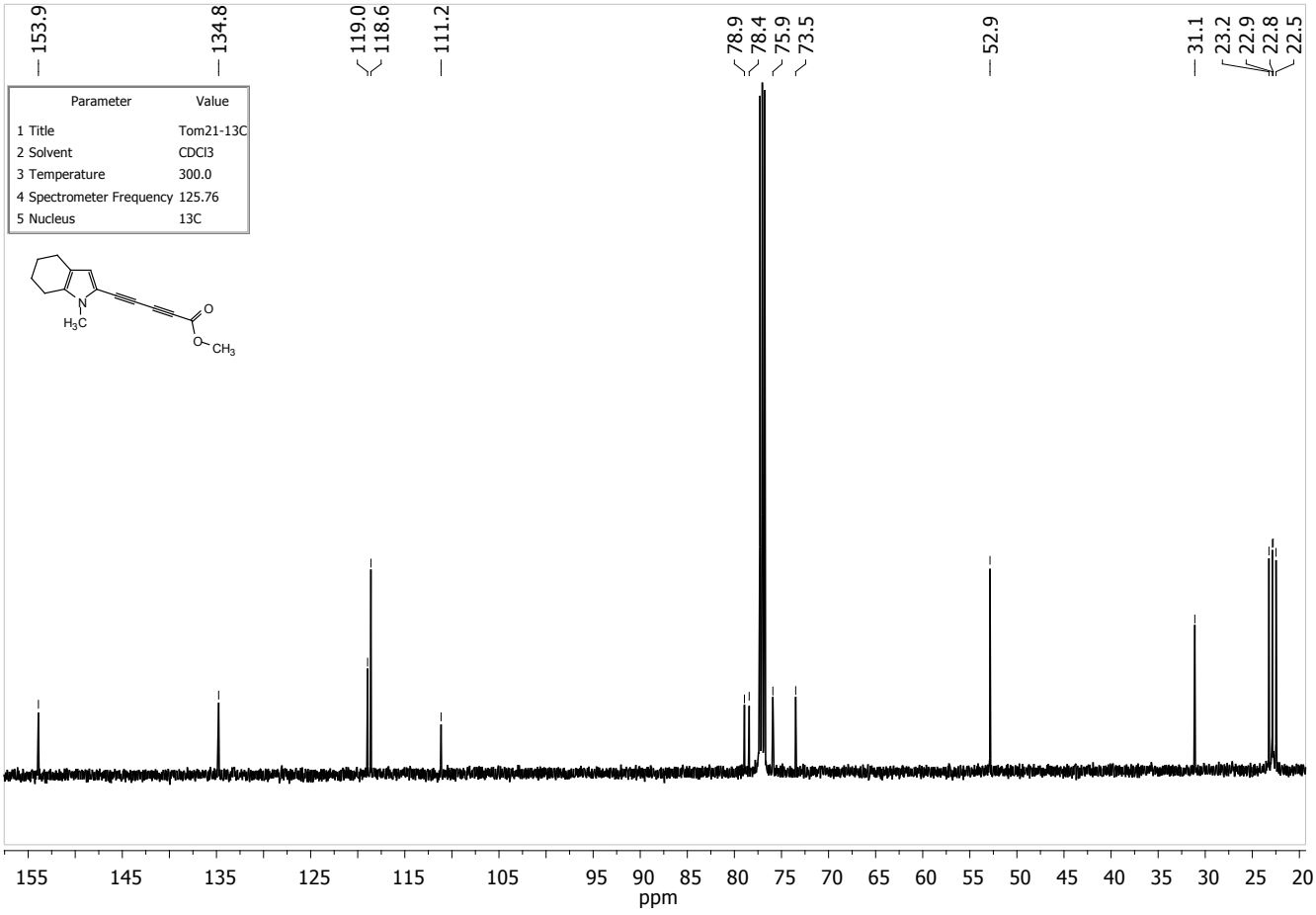
Methyl 5-(4,5,6,7-tetrahydro-1H-indol-2-yl)penta-2,4-diynoate (4aa)



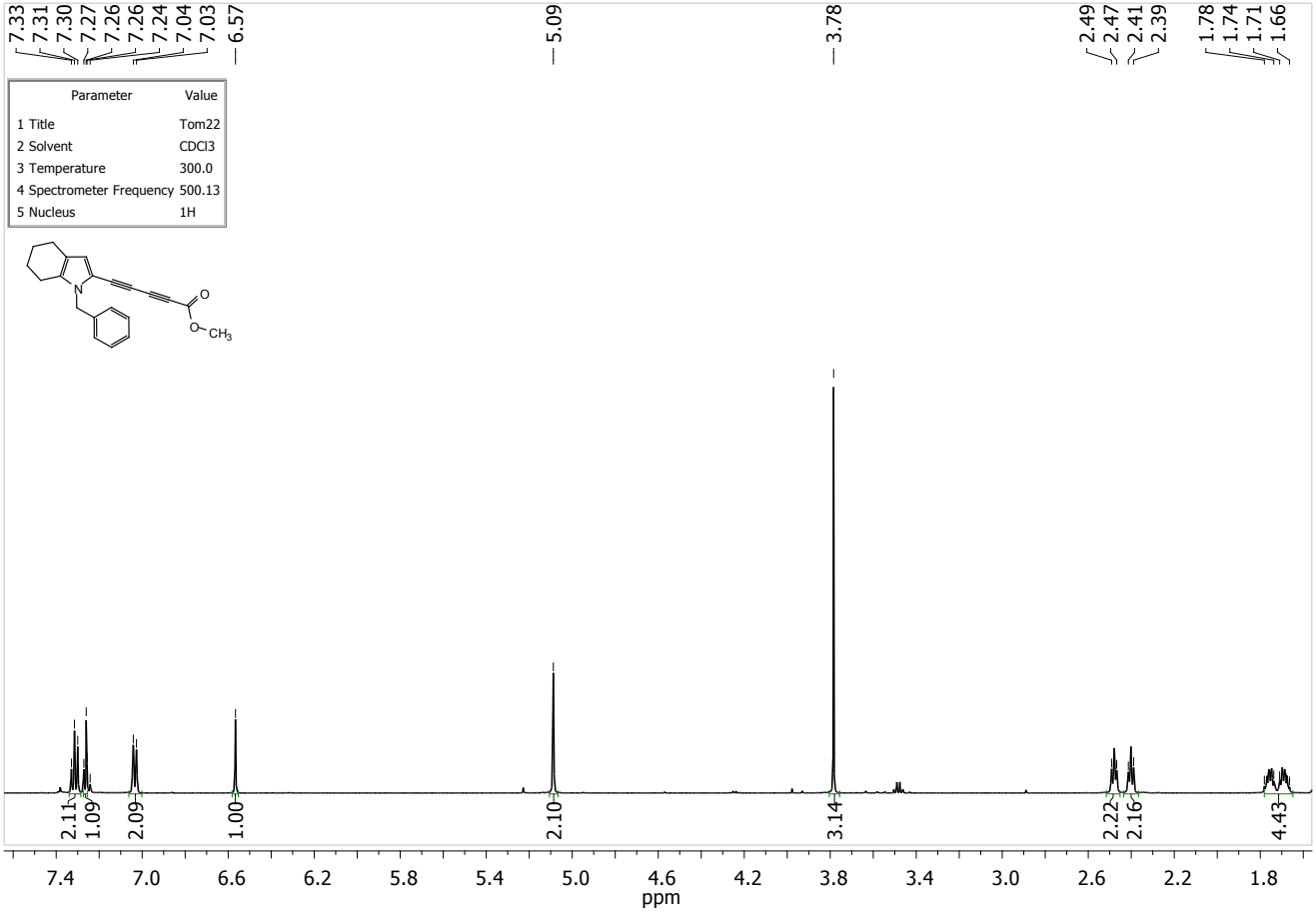


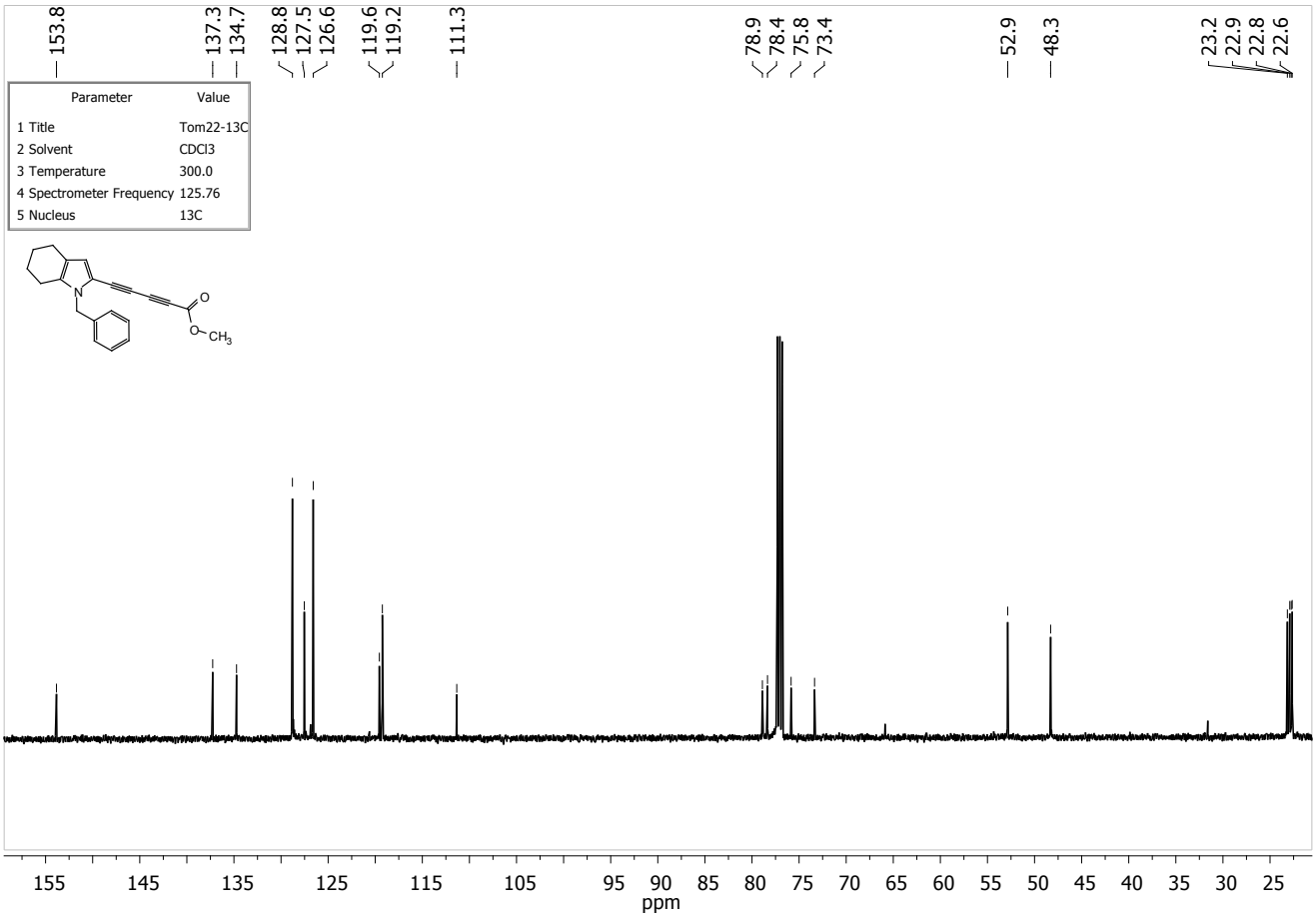
Methyl 5-(1-methyl-4,5,6,7-tetrahydro-1H-indol-2-yl)penta-2,4-diynoate (4ba)



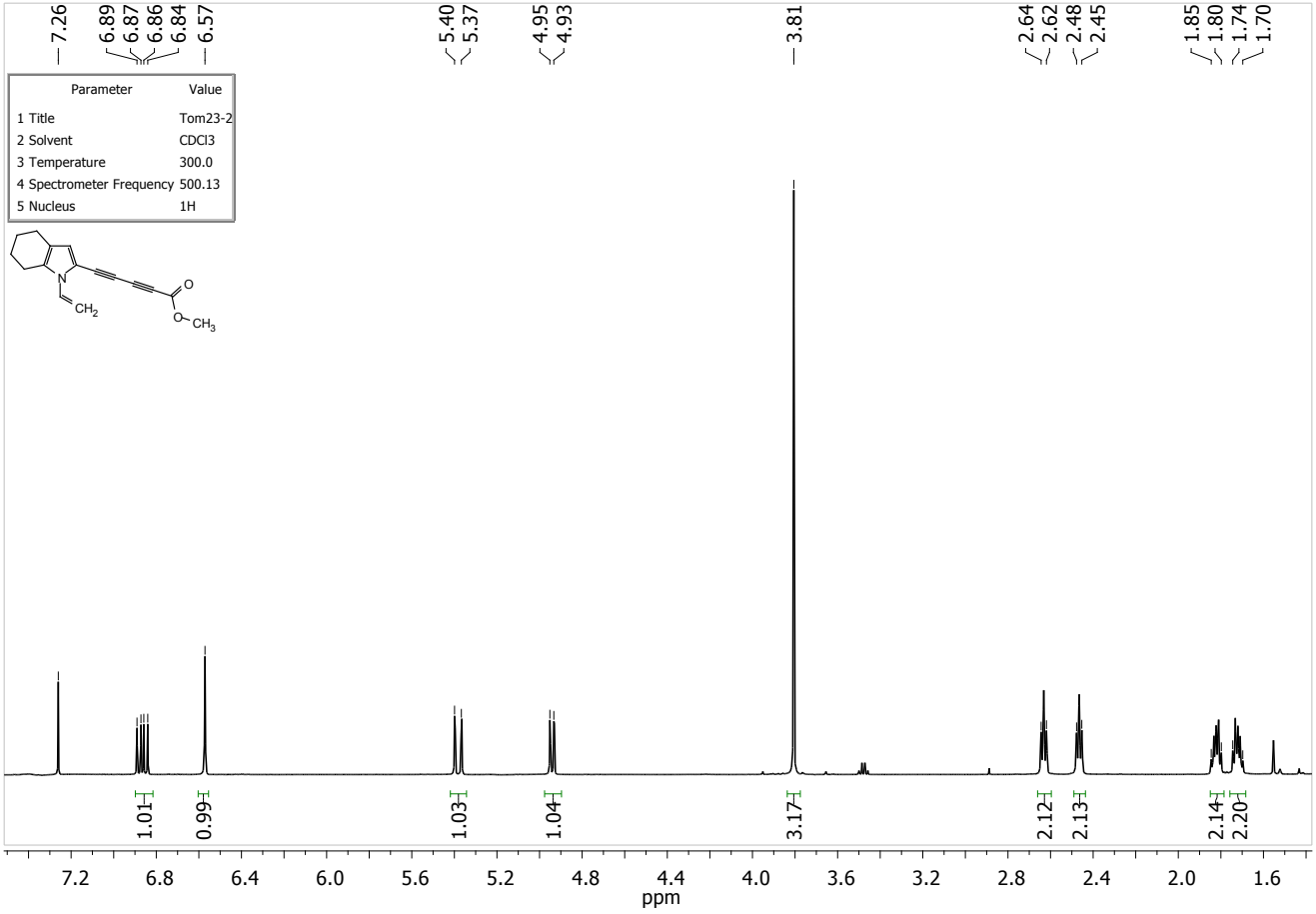


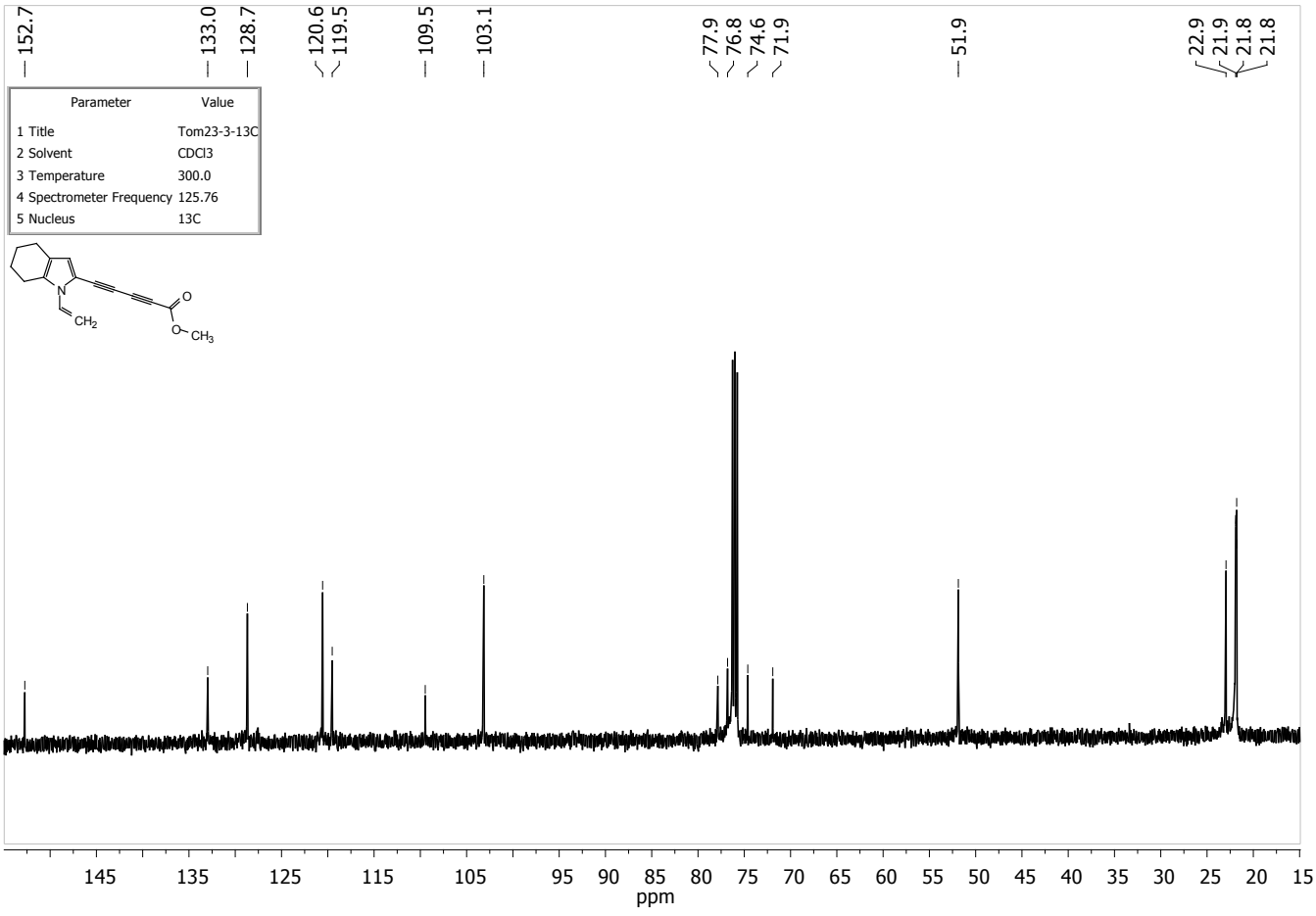
Methyl 5-(1-benzyl-4,5,6,7-tetrahydro-1H-indol-2-yl)penta-2,4-diynoate (4ca)



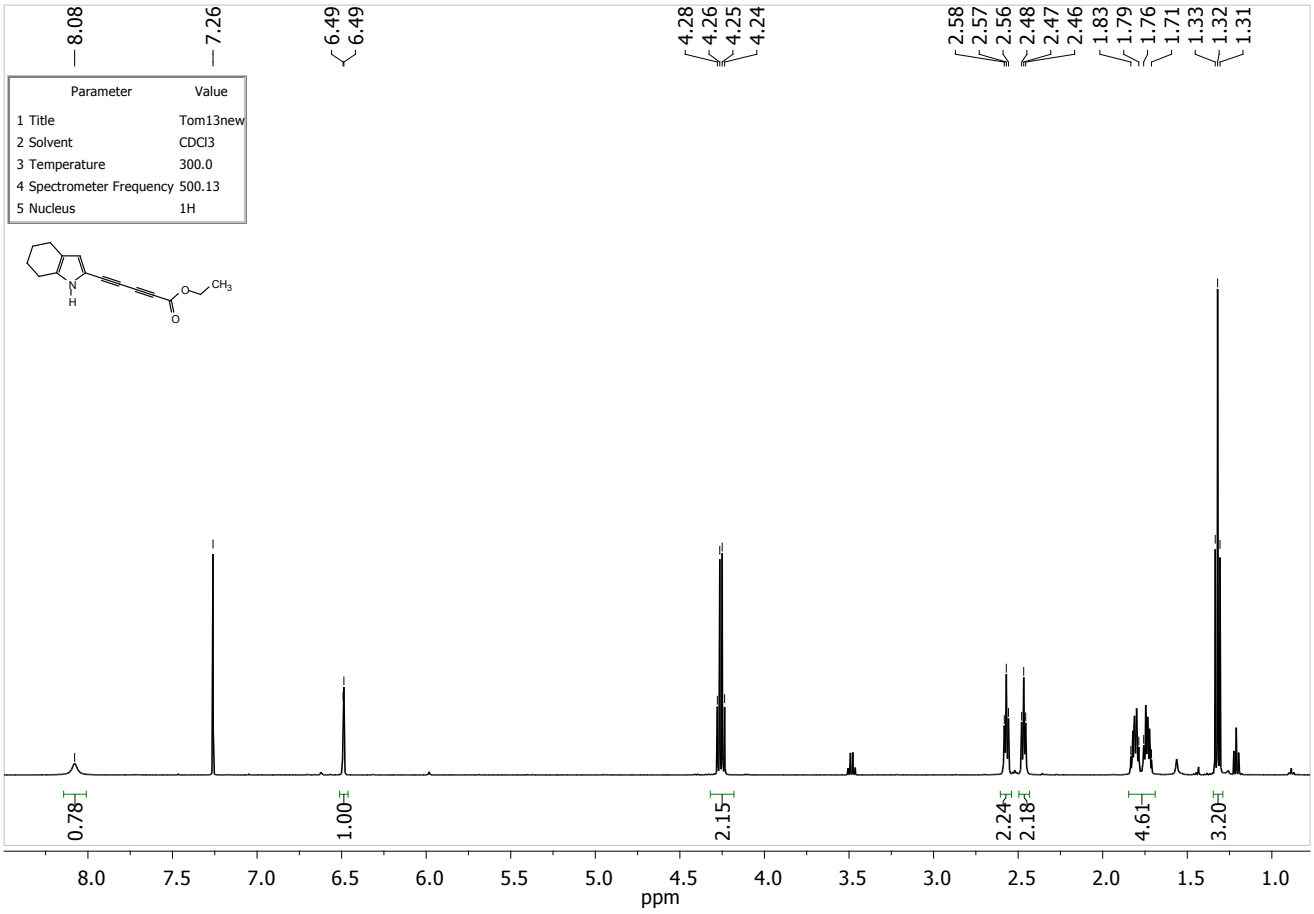


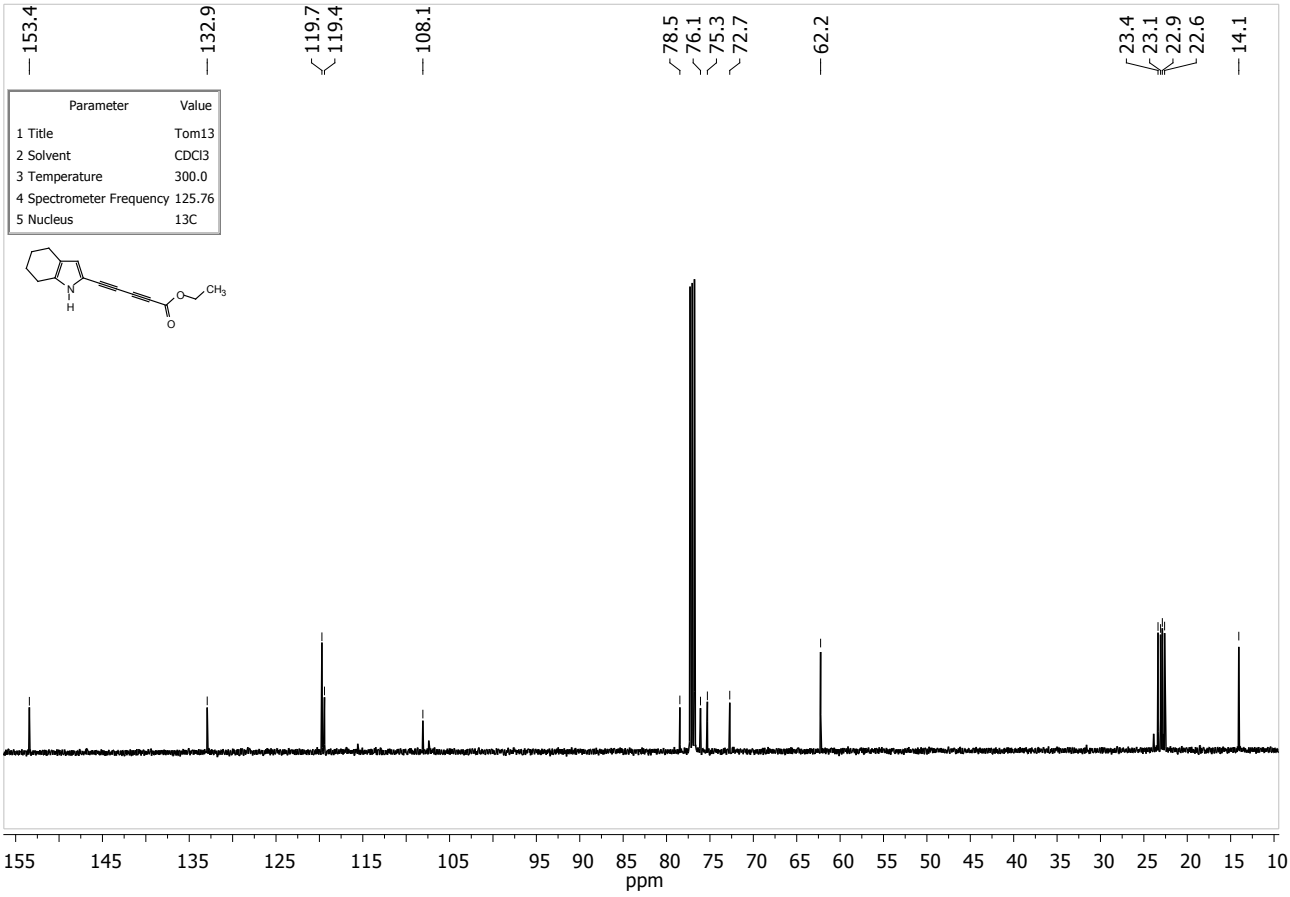
Methyl 5-(1-vinyl-4,5,6,7-tetrahydro-1H-indol-2-yl)penta-2,4-diynoate (4da).



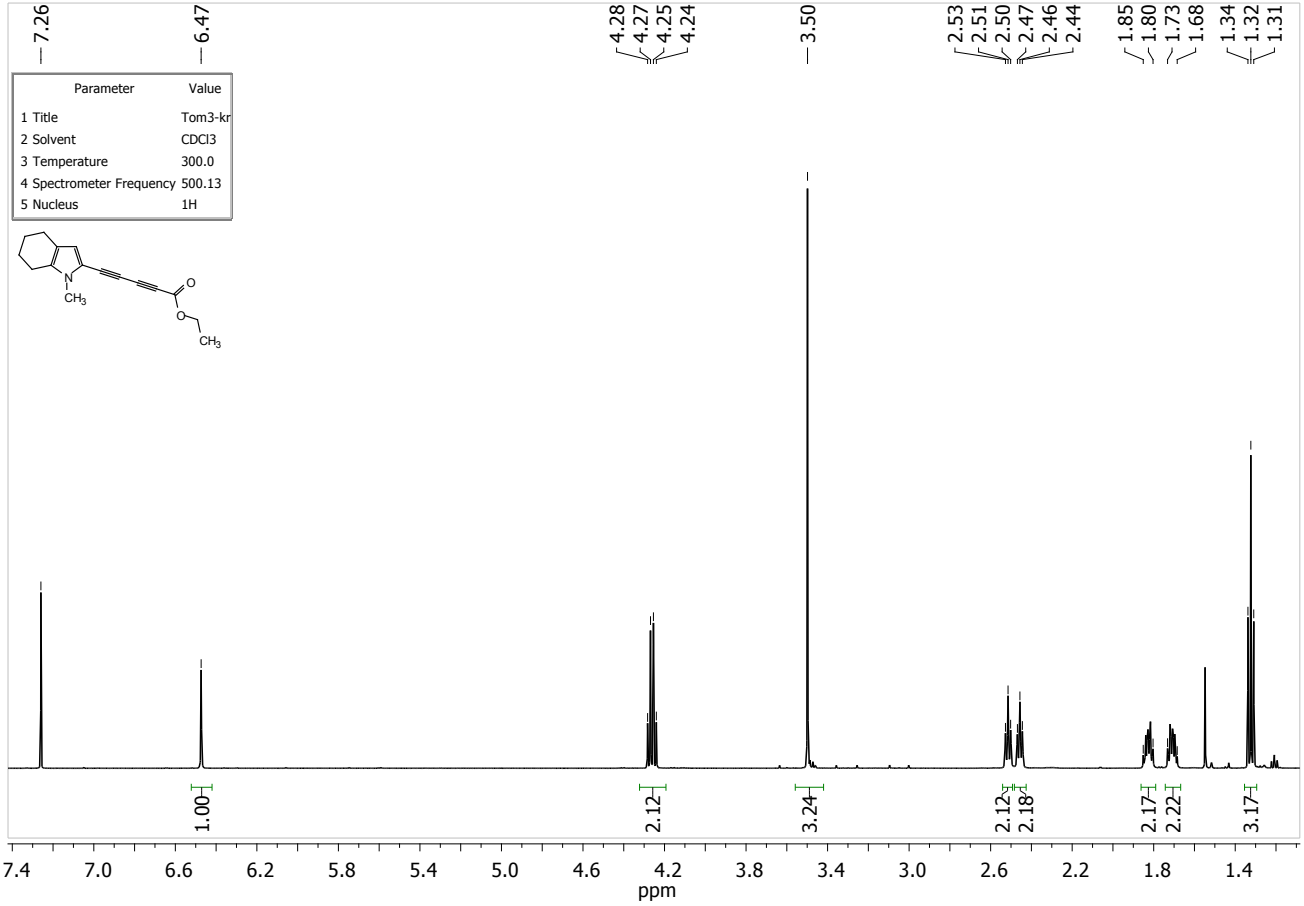


Ethyl 5-(4,5,6,7-tetrahydro-1H-indol-2-yl)penta-2,4-diynoate (4ab).





Ethyl 5-(1-methyl-4,5,6,7-tetrahydro-1H-indol-2-yl)penta-2,4-diynoate (4bb)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1.80
1.73
1.68
1.34
1.32
1.31
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2 Solvent CDCl3
3 Temperature 300.0
4 Spectrometer Frequency 500.13
5 Nucleus 1H
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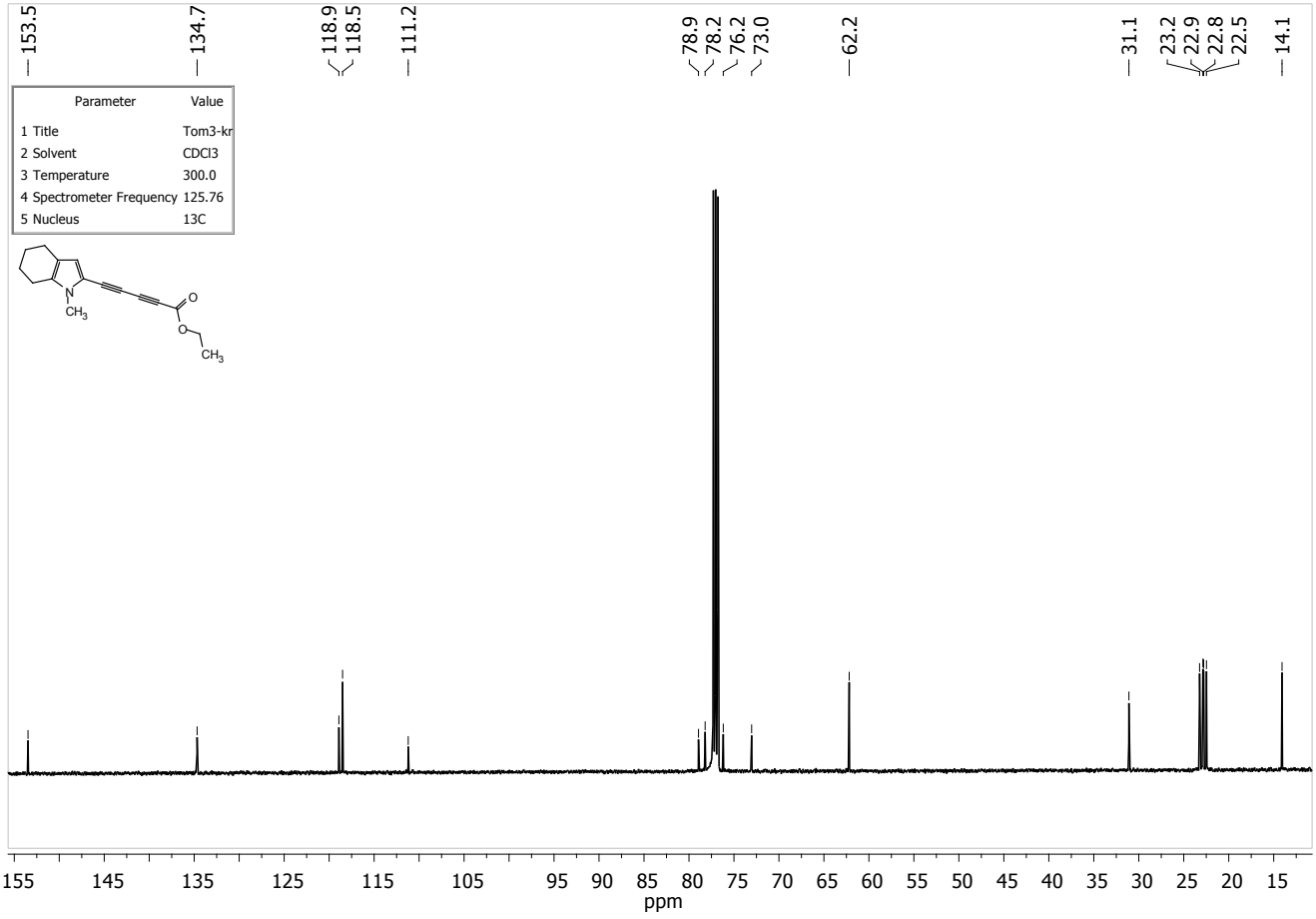
2.12
2.18
2.17
2.22
3.17
ppm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111.2
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73.0
62.2
31.1
23.2
22.9
22.8
22.5
14.1
Parameter Value
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2 Solvent CDCl3
3 Temperature 300.0
4 Spectrometer Frequency 125.76
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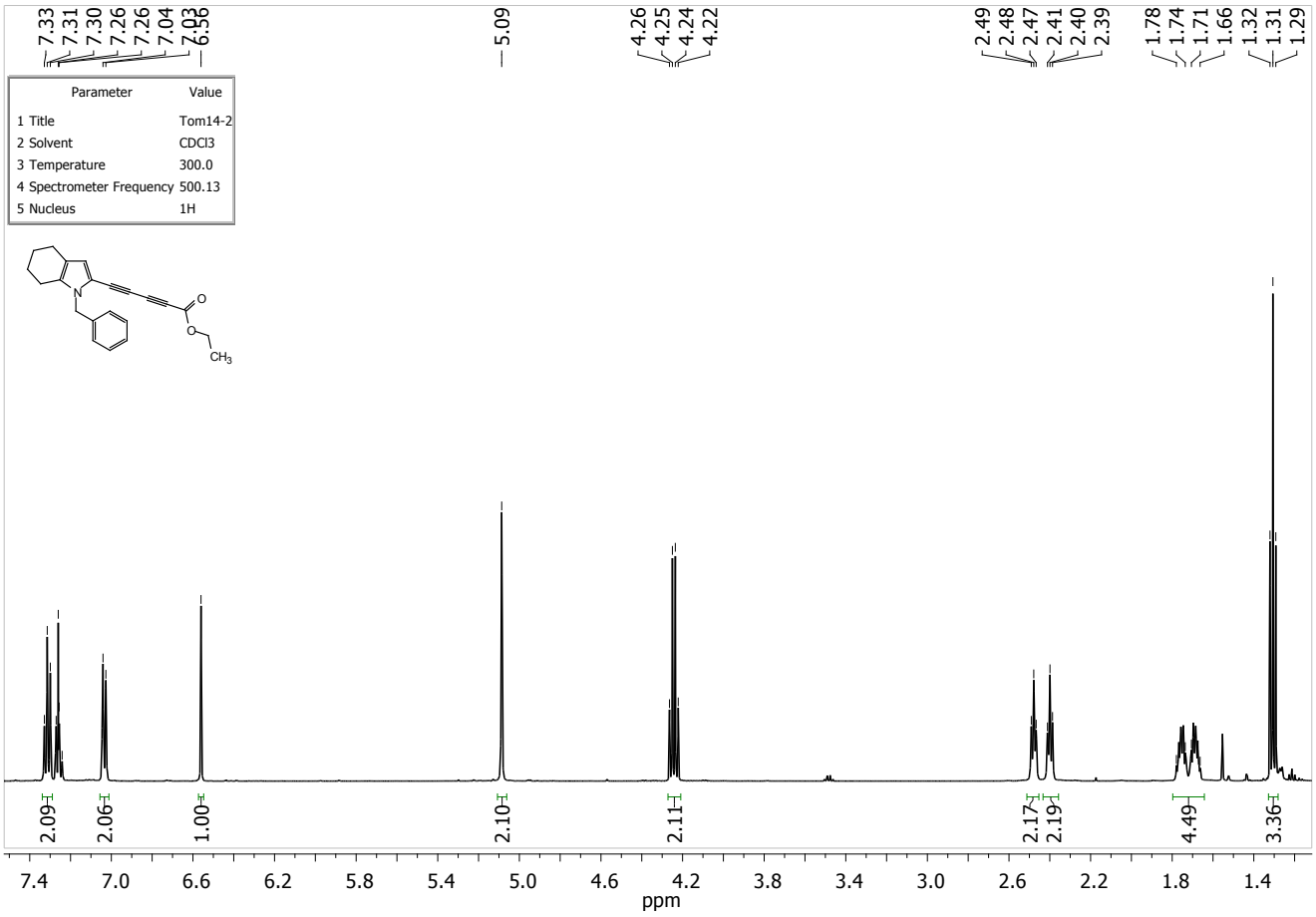
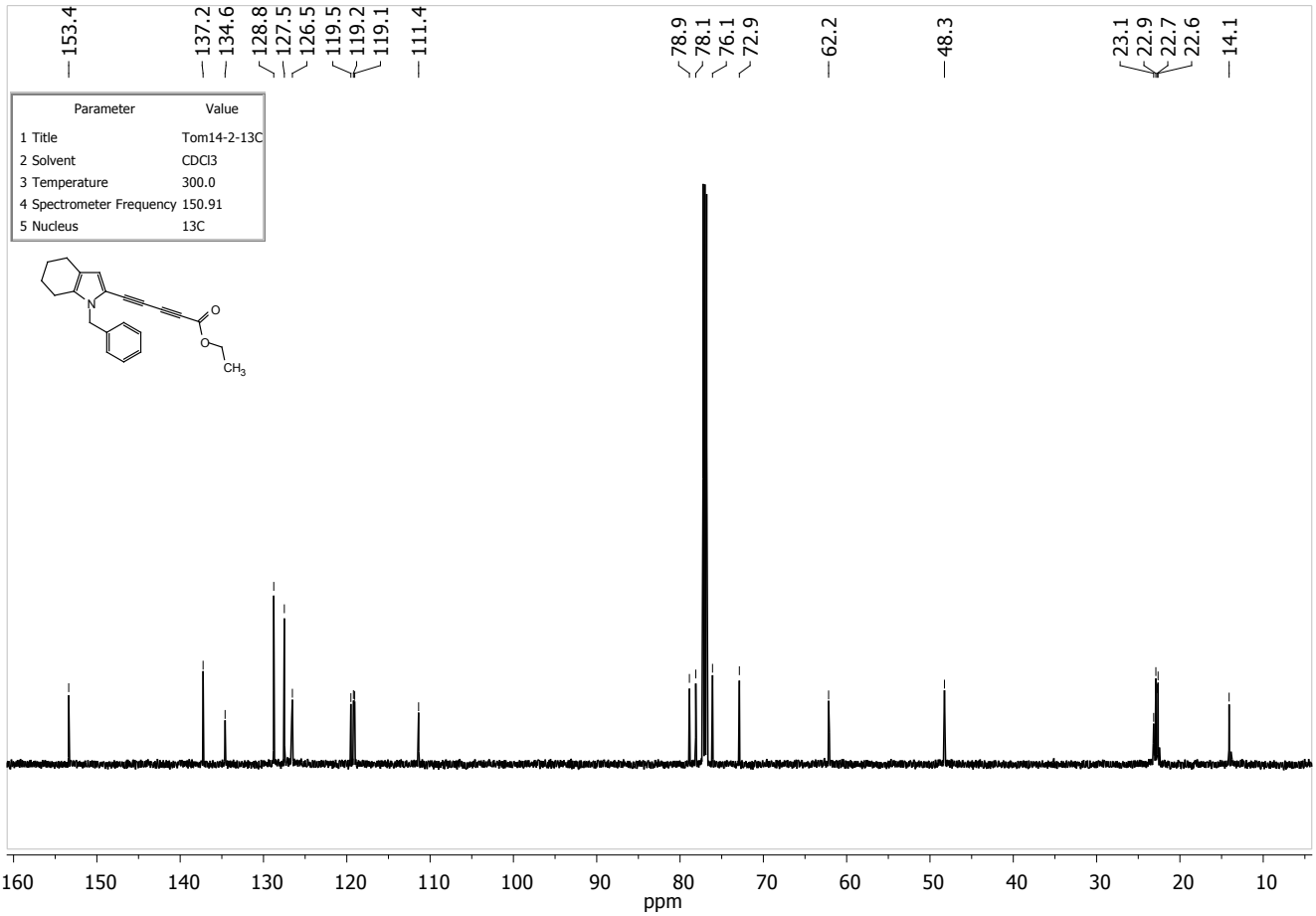
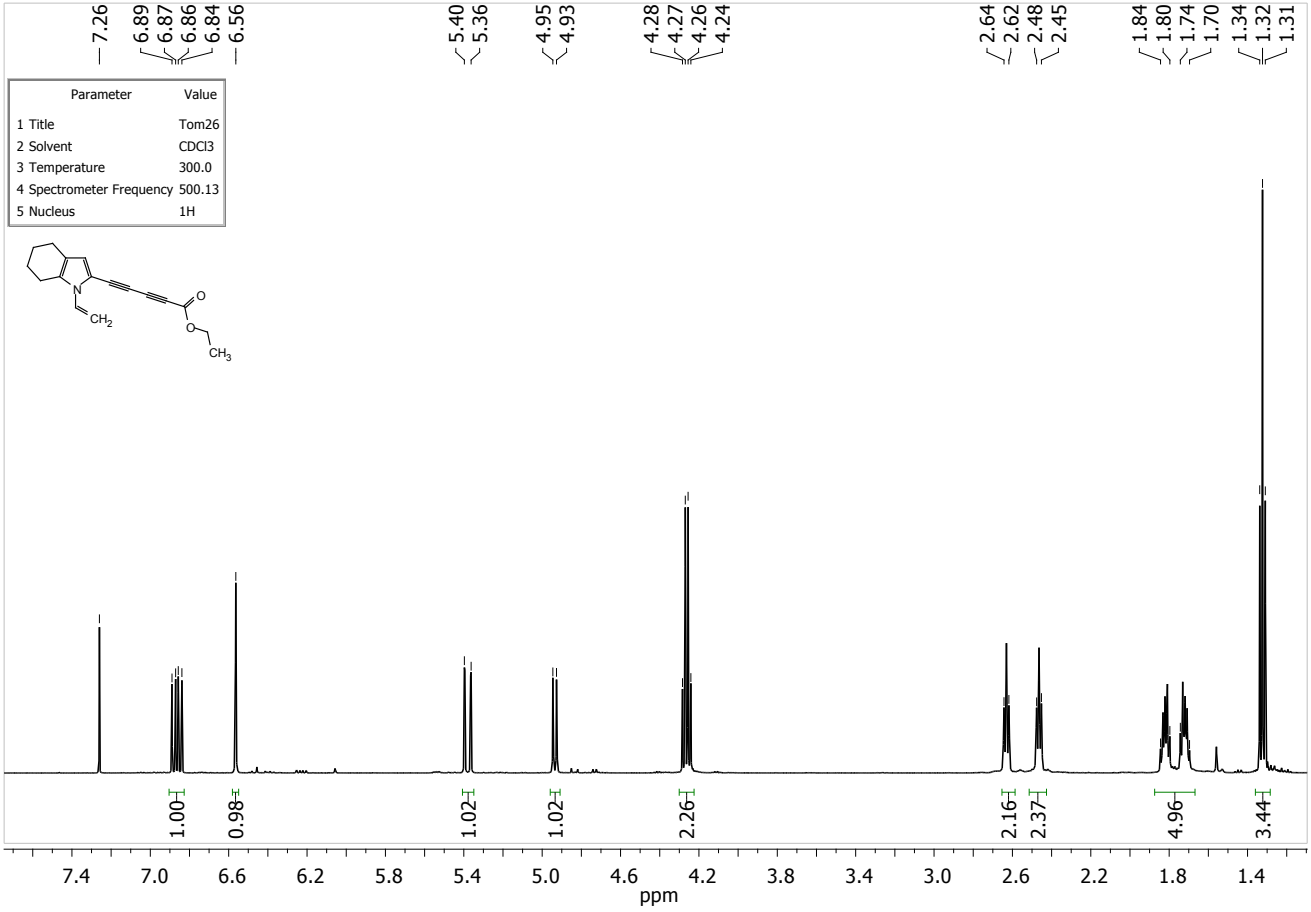
Ethyl 5-(1-benzyl-4,5,6,7-tetrahydro-1H-indol-2-yl)penta-2,4-diynoate (4cb)





Ethyl 5-(1-vinyl-4,5,6,7-tetrahydro-1H-indol-2-yl)penta-2,4-diynoate (4db)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6.56
5.40
5.36
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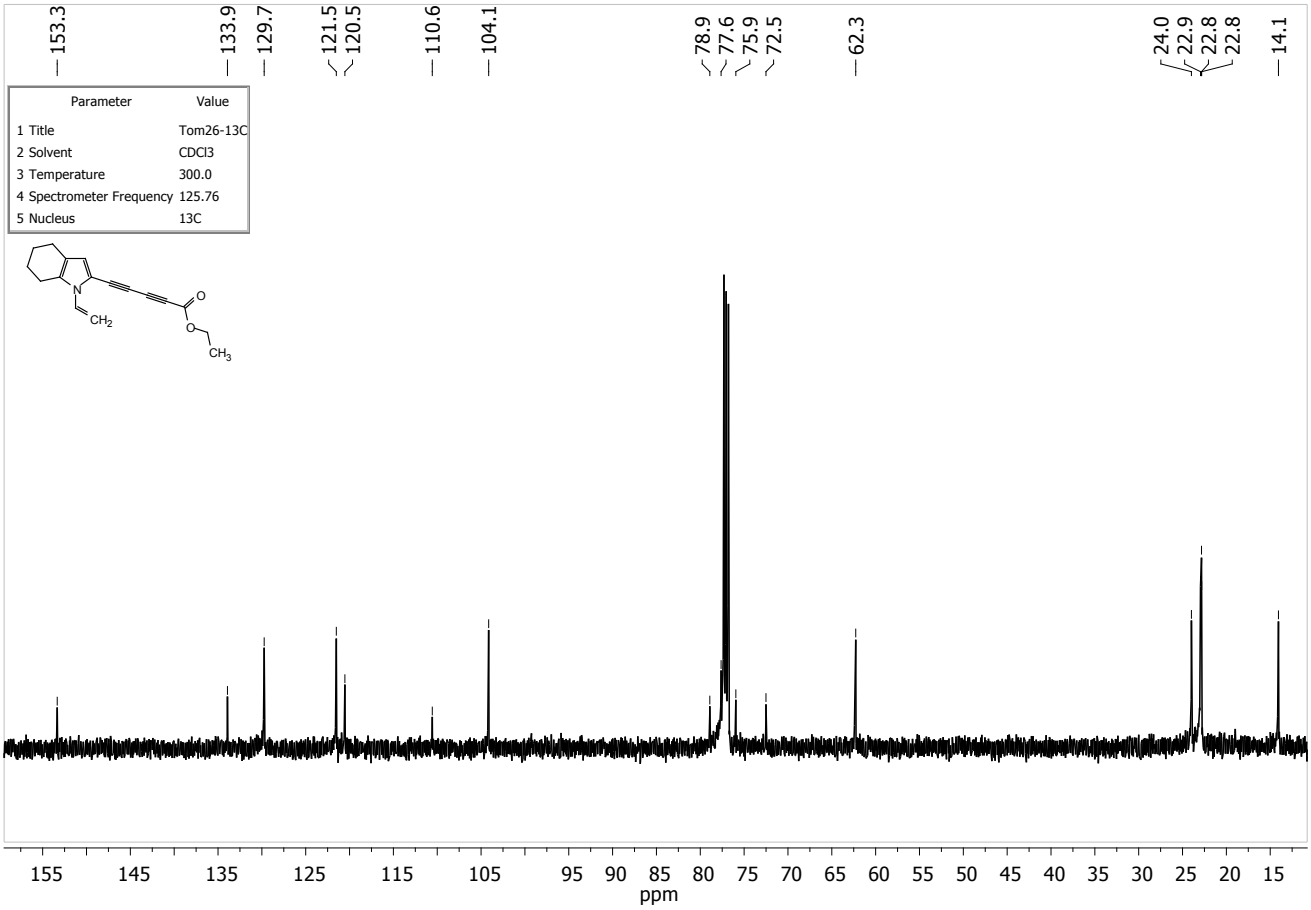
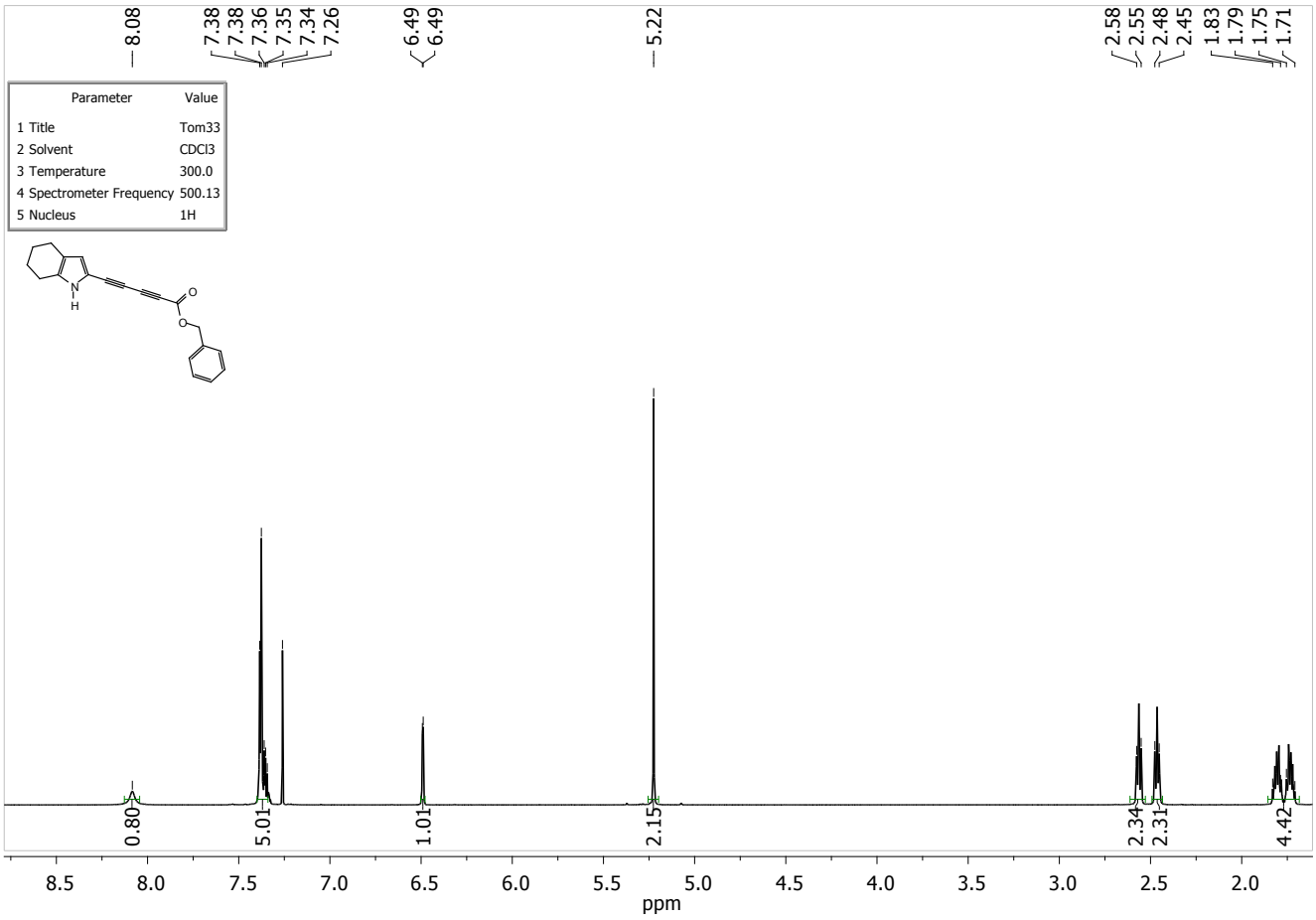
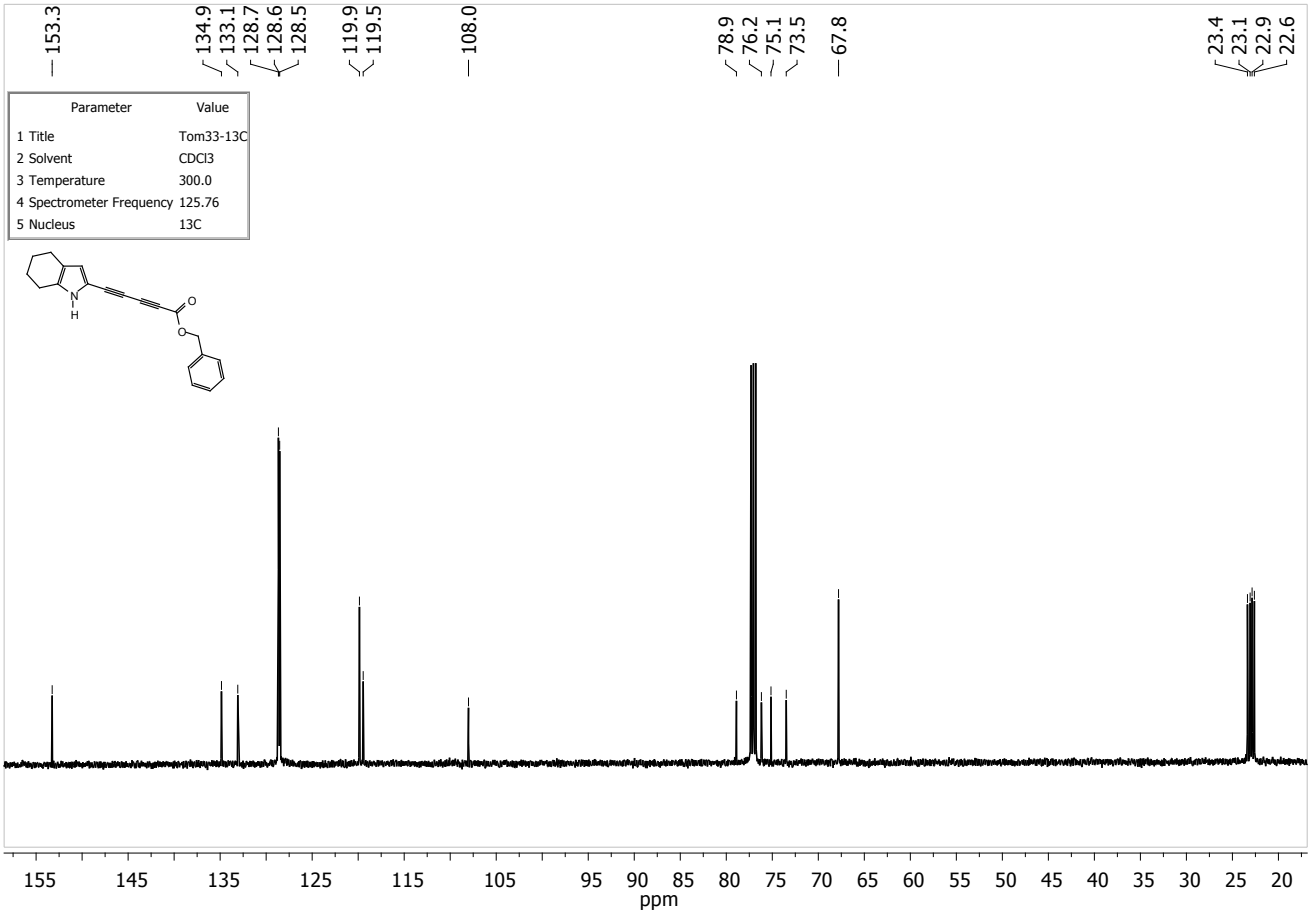
4.93
4.28
4.27
4.26
4.24
2.64
2.62
2.48
2.45
1.84
1.80
1.74
1.70
1.34
1.32
1.31
Parameter Value
1 Title Tom26
2 Solvent CDCl3
3 Temperature 300.0
4 Spectrometer Frequency 500.13
5 Nucleus 1H
1.00
0.98
1.02
1.02
2.26
2.16
2.37
4.96
3.44
7.4 7.0 6.6 6.2 5.8 5.4 5.0 4.6 4.2 3.8 3.4 3.0 2.6 2.2 1.8 1.4
ppm

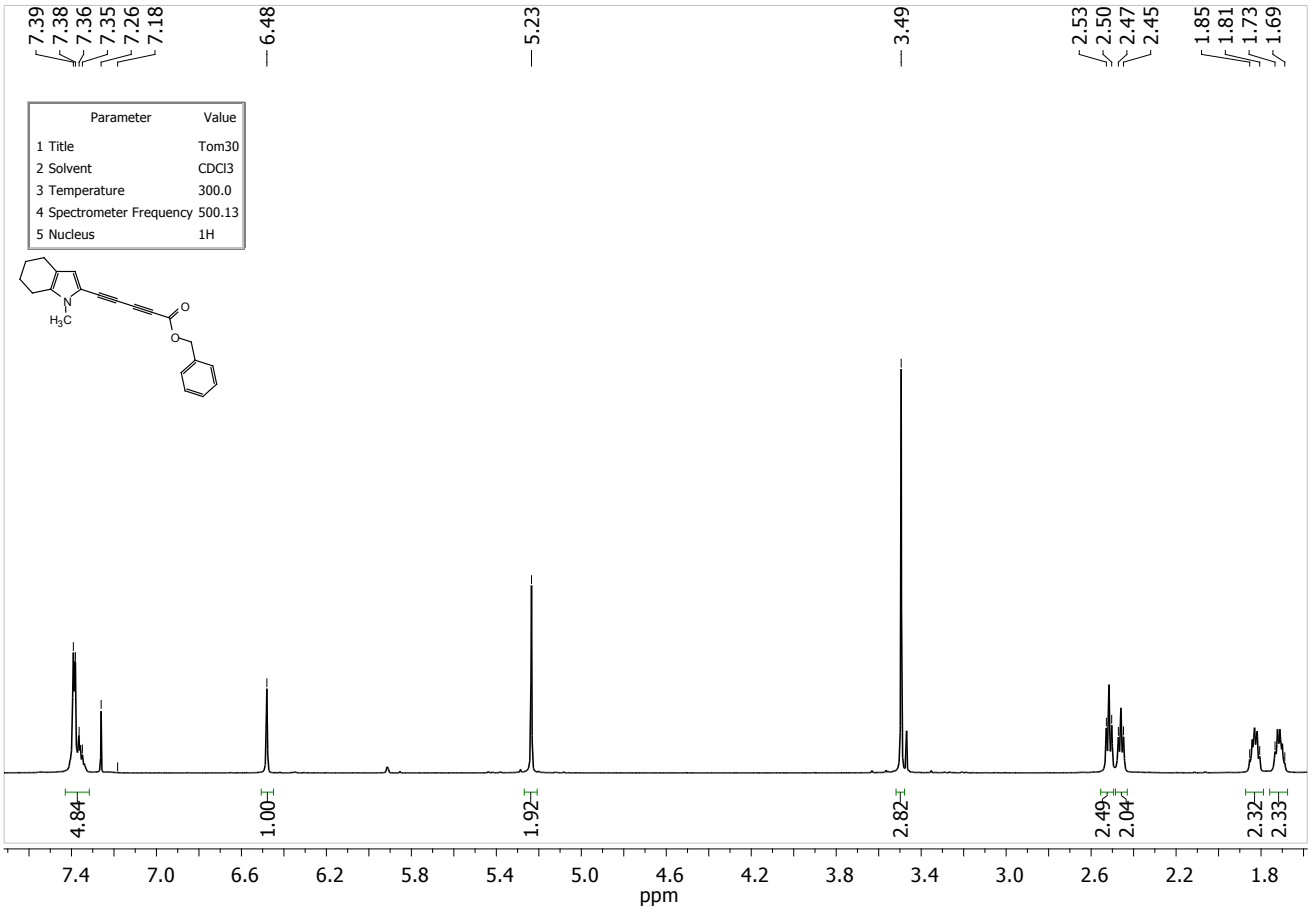

153.3
133.9
129.7
121.5
120.5
110.6
104.1
78.9
77.6
75.9
72.5
62.3
24.0
22.9
22.8
22.8
14.1
Parameter Value
1 Title Tom26-13C
2 Solvent CDCl3
3 Temperature 300.0
4 Spectrometer Frequency 125.76
5 Nucleus 13C
155 145 135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
ppm

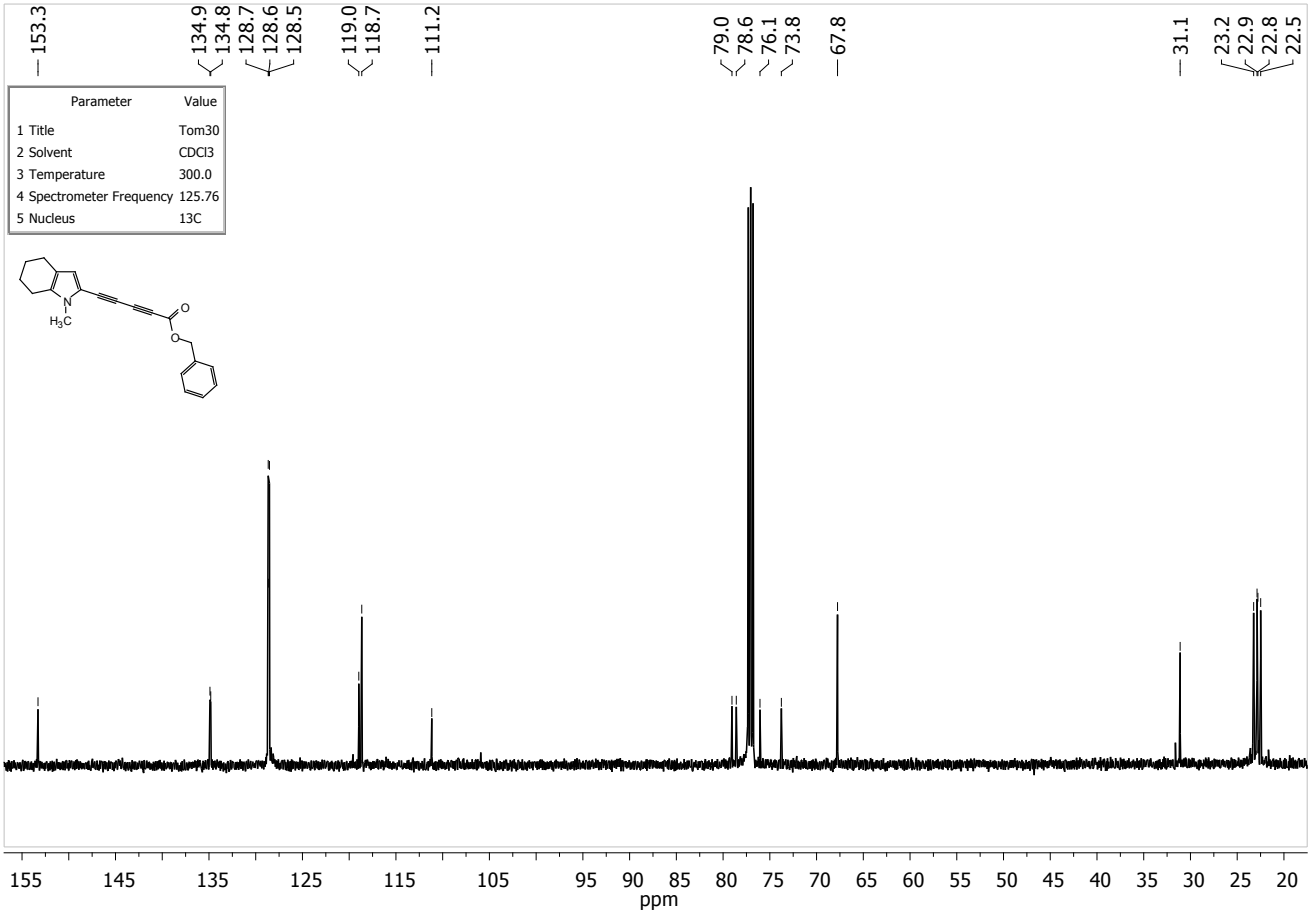
Benzyl 5-(4,5,6,7-tetrahydro-1H-indol-2-yl)penta-2,4-diynoate (4ac)



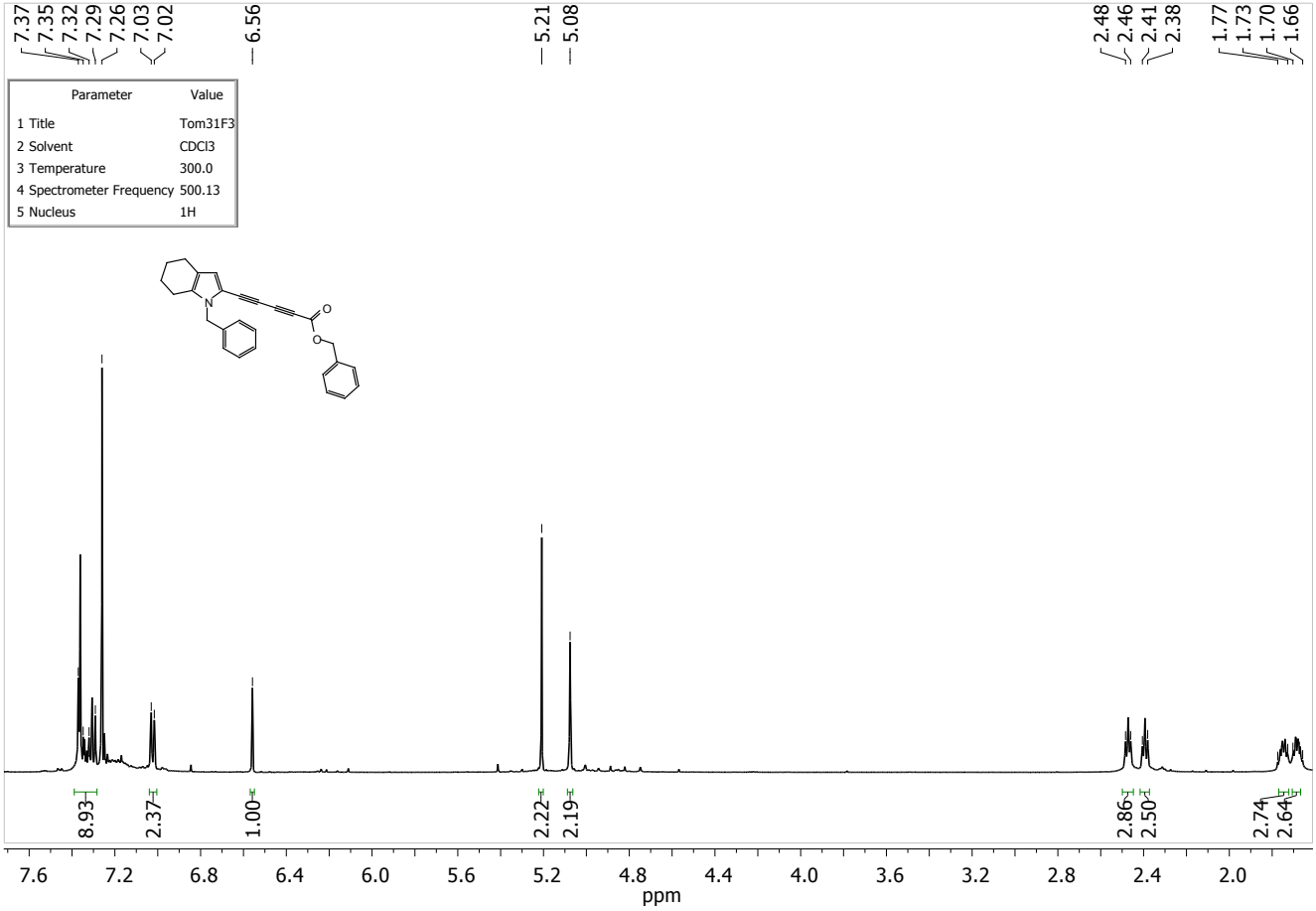


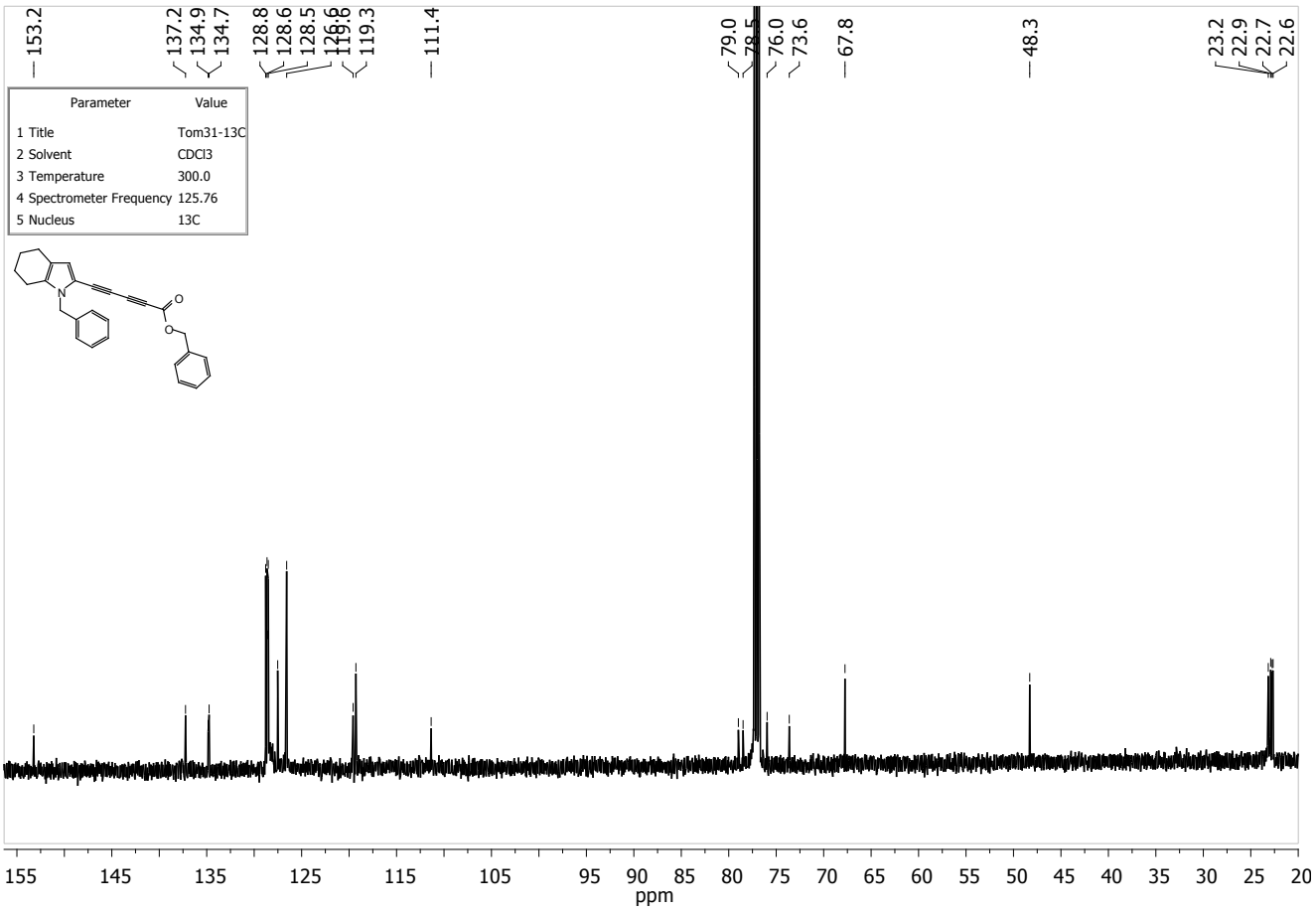
Benzyl 5-(1-methyl-4,5,6,7-tetrahydro-1H-indol-2-yl)penta-2,4-diynoate (4bc)



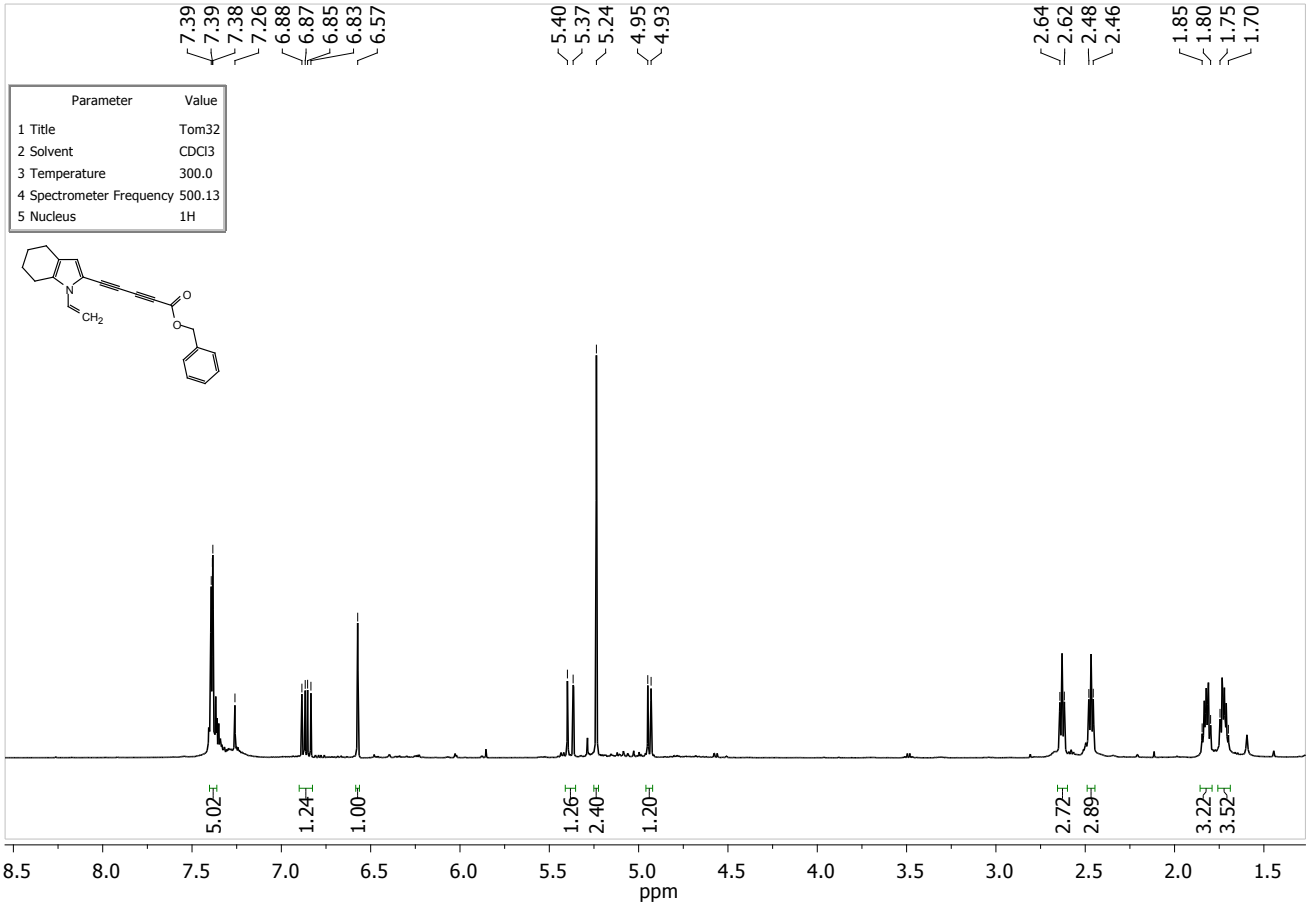


Benzyl 5-(1-benzyl-4,5,6,7-tetrahydro-1H-indol-2-yl)penta-2,4-diynoate (4cc)





Benzyl 5-(1-vinyl-4,5,6,7-tetrahydro-1H-indol-2-yl)penta-2,4-diynoate (4dc)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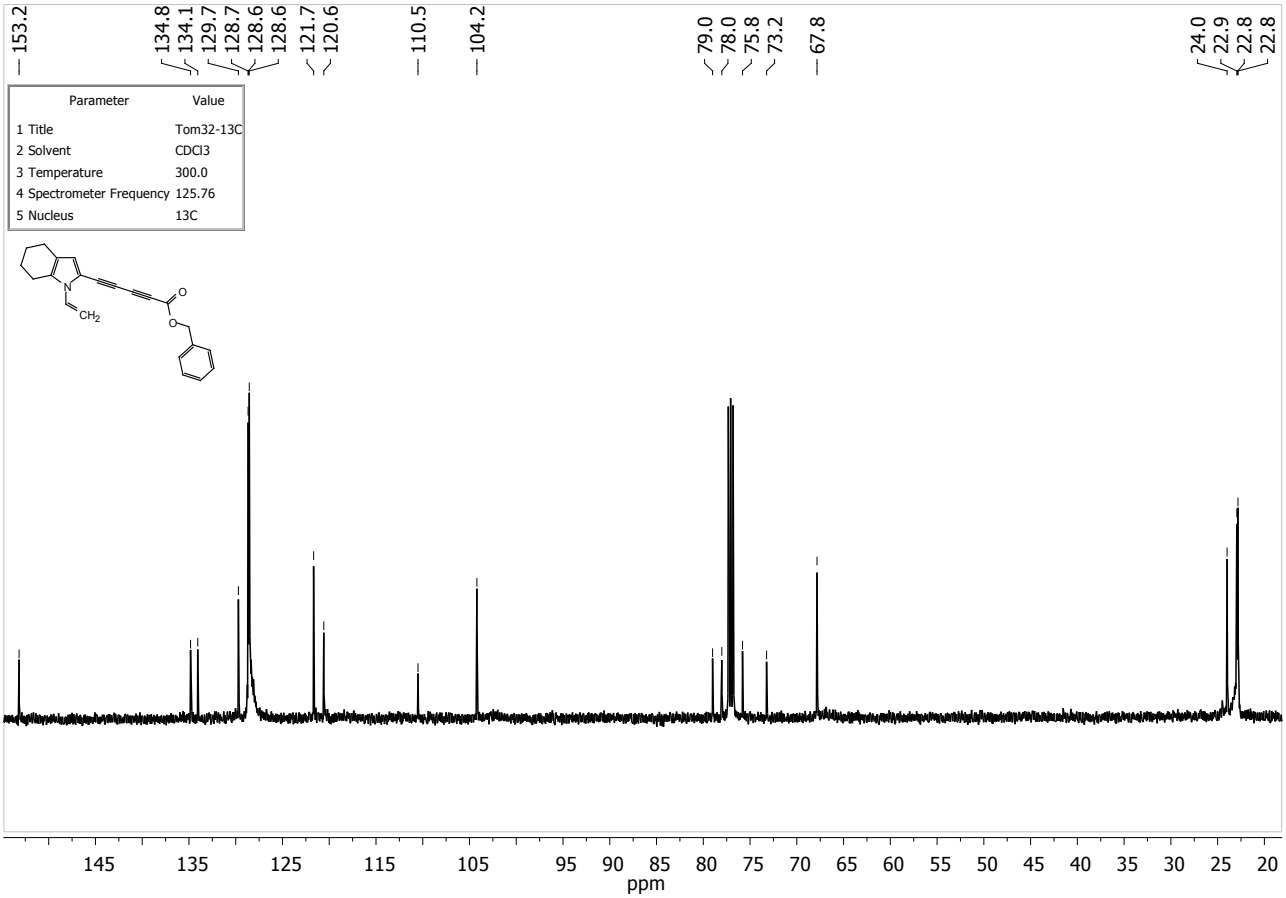
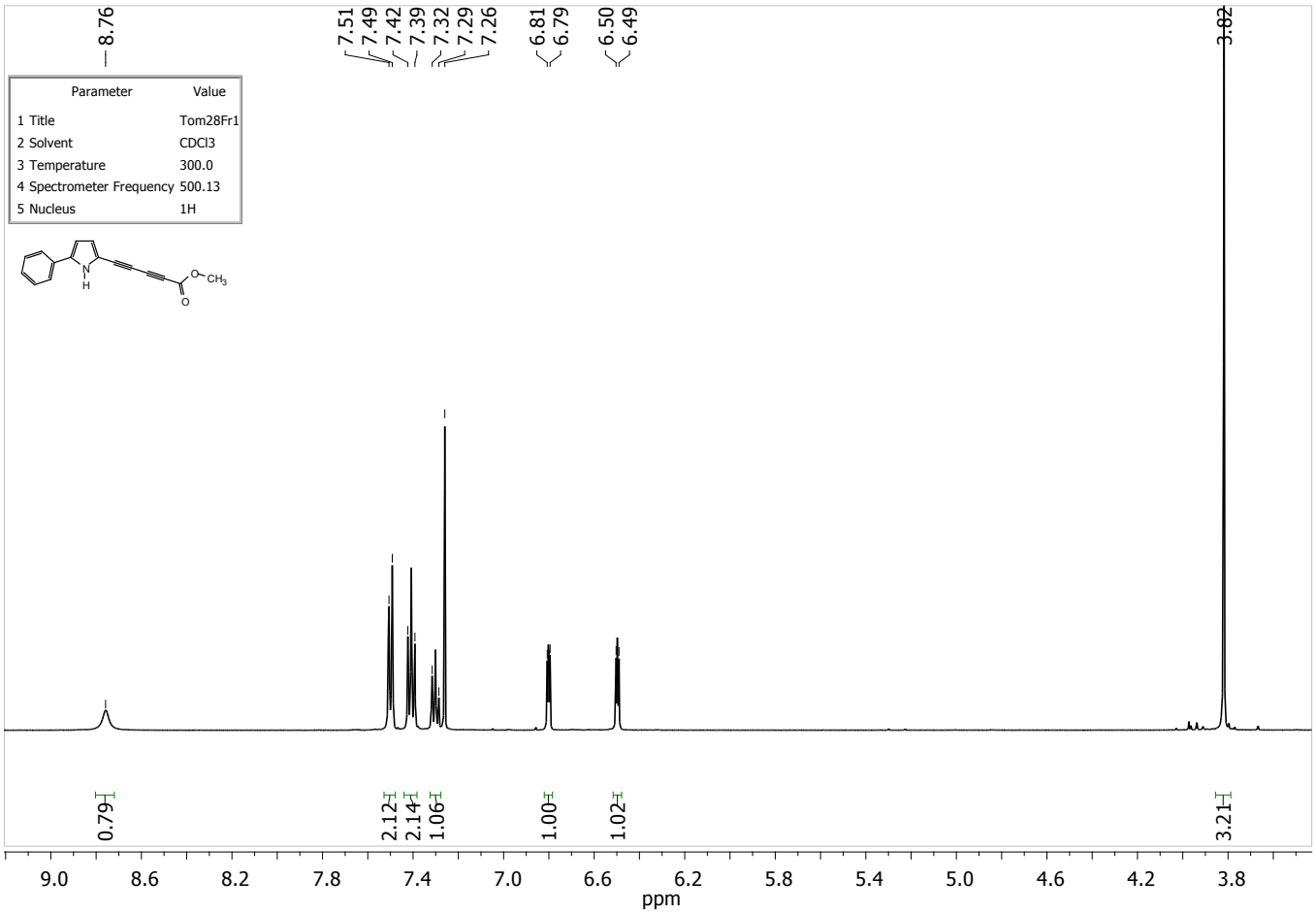
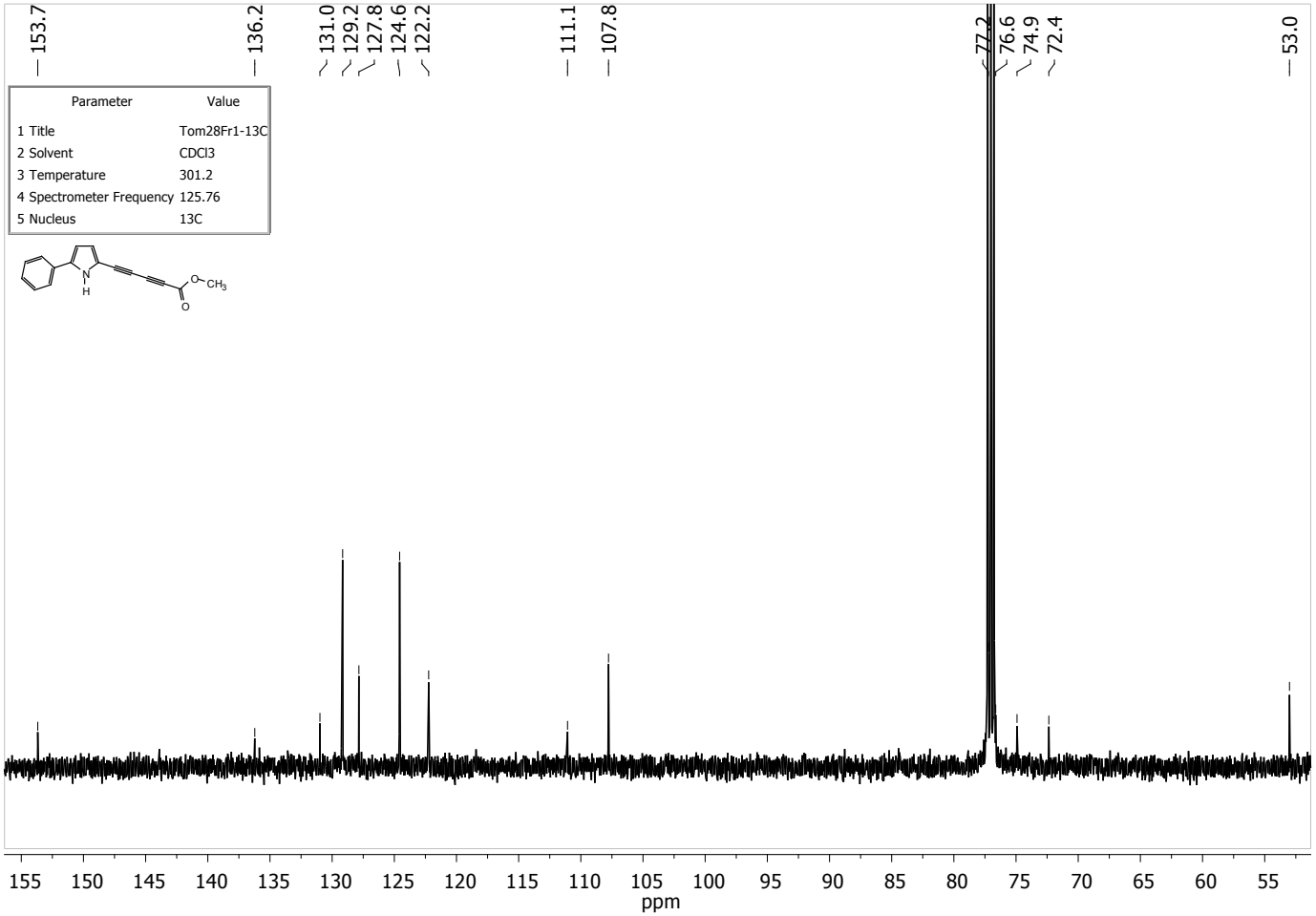
7.38
7.26
6.88
6.87
6.85
6.83
6.57
5.40
5.37
5.24
4.95
4.93
2.64
2.62
2.48
2.46
1.85
1.80
1.75
1.70
Parameter Value
1 Title Tom32
2 Solvent CDCl3
3 Temperature 300.0
4 Spectrometer Frequency 500.13
5 Nucleus 1H
5.02
1.24
1.00
1.26
2.40
1.20
2.72
2.89
3.22
3.52
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
ppm

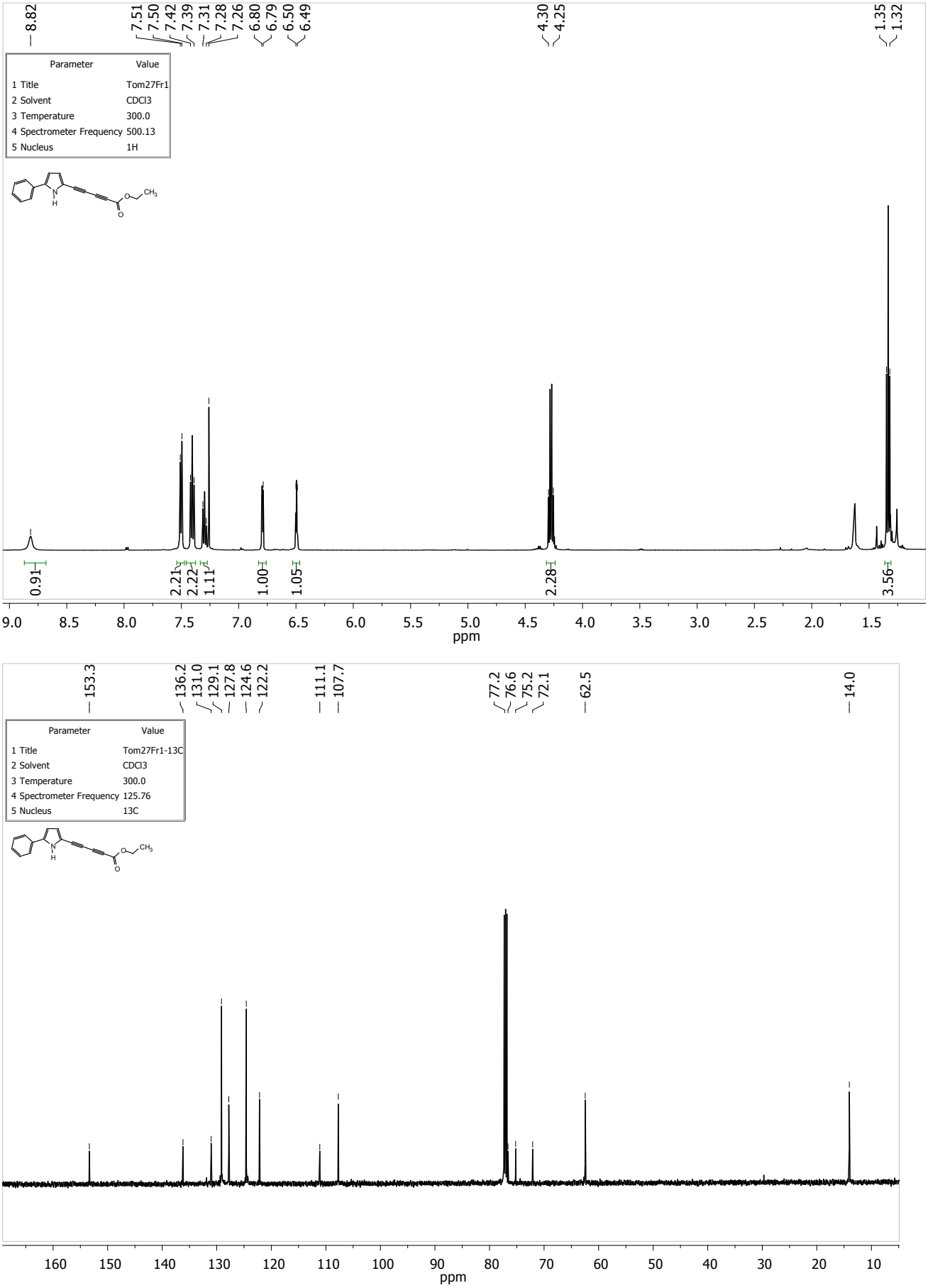

153.2
134.8
134.1
129.7
128.7
128.6
128.6
121.7
120.6
110.5
104.2
79.0
78.0
75.8
73.2
67.8
24.0
22.9
22.8
22.8
Parameter Value
1 Title Tom32-13C
2 Solvent CDCl3
3 Temperature 300.0
4 Spectrometer Frequency 125.76
5 Nucleus 13C
145 135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
ppm

Methyl 5-(5-phenyl-1H-pyrrol-2-yl)penta-2,4-diynoate (4ea)

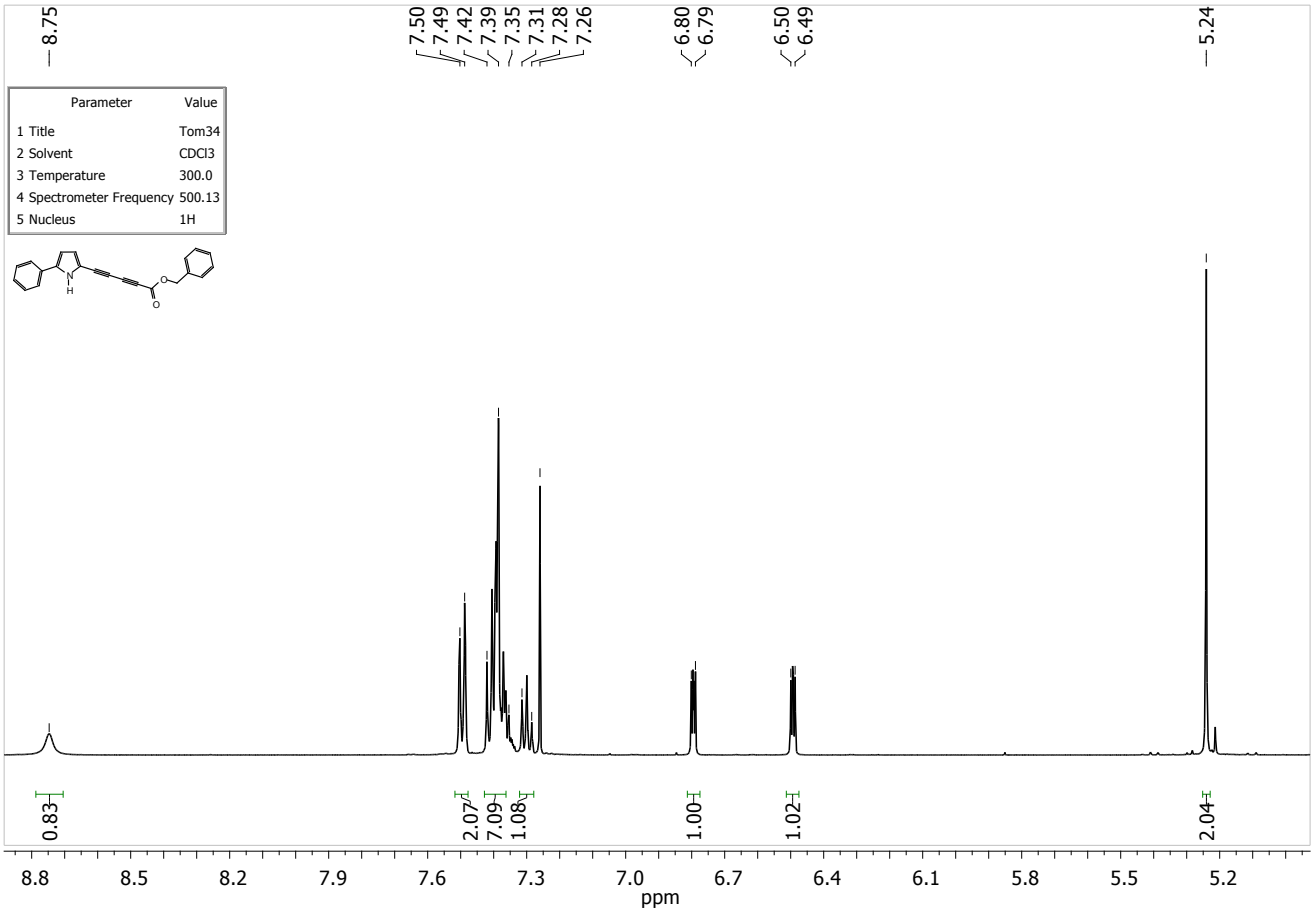


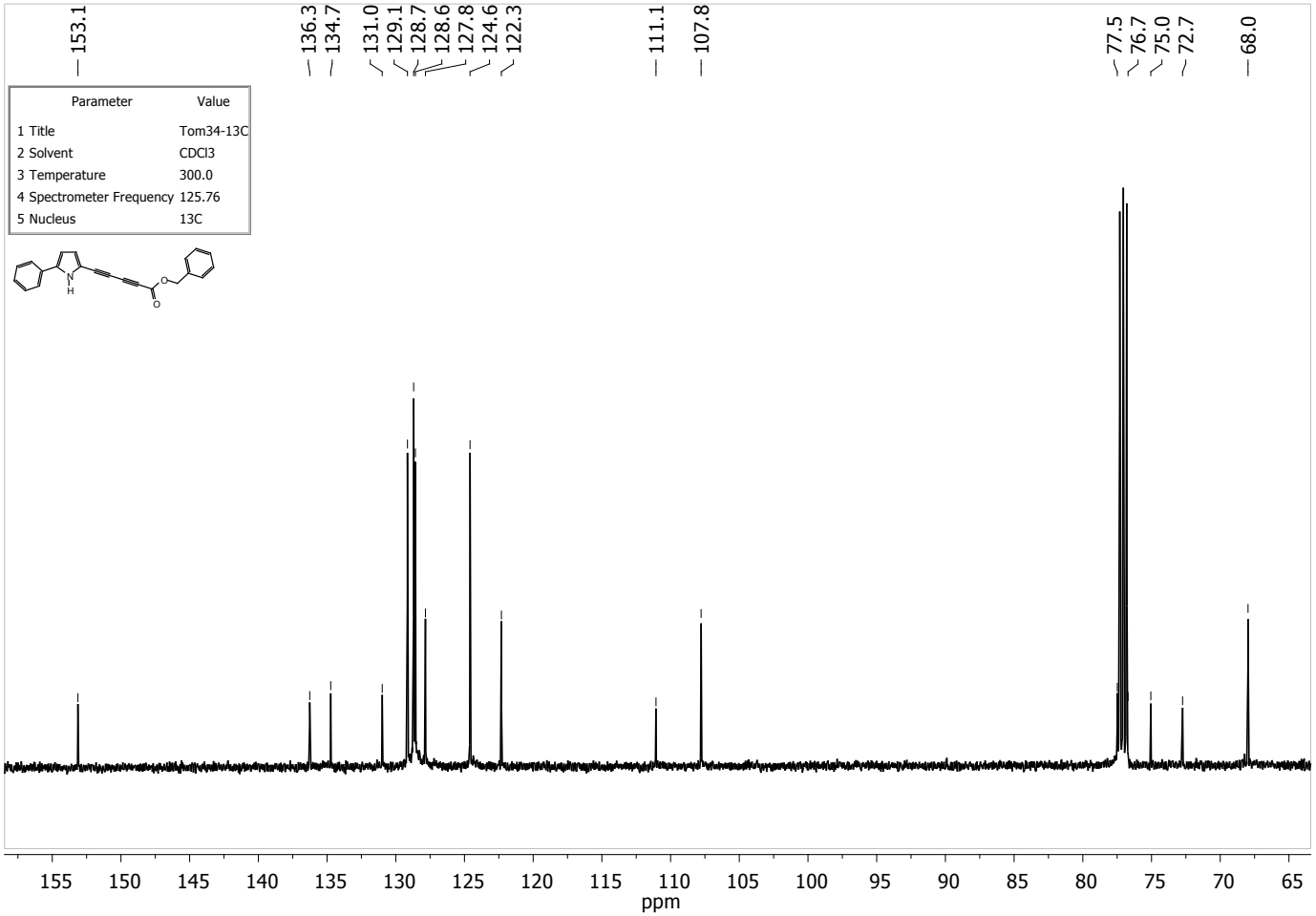


Ethyl 5-(5-phenyl-1H-pyrrol-2-yl)penta-2,4-diynoate (4eb)

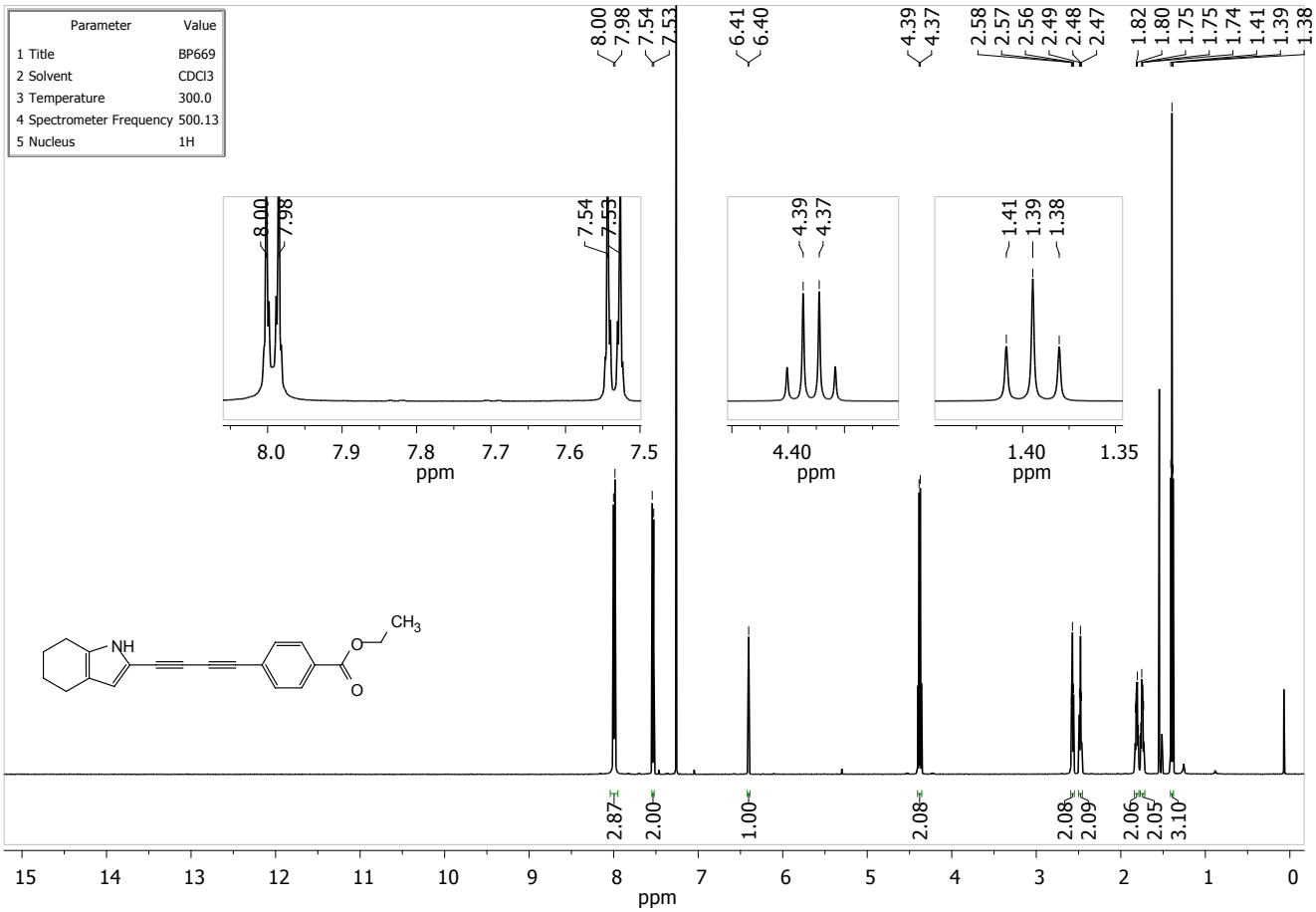


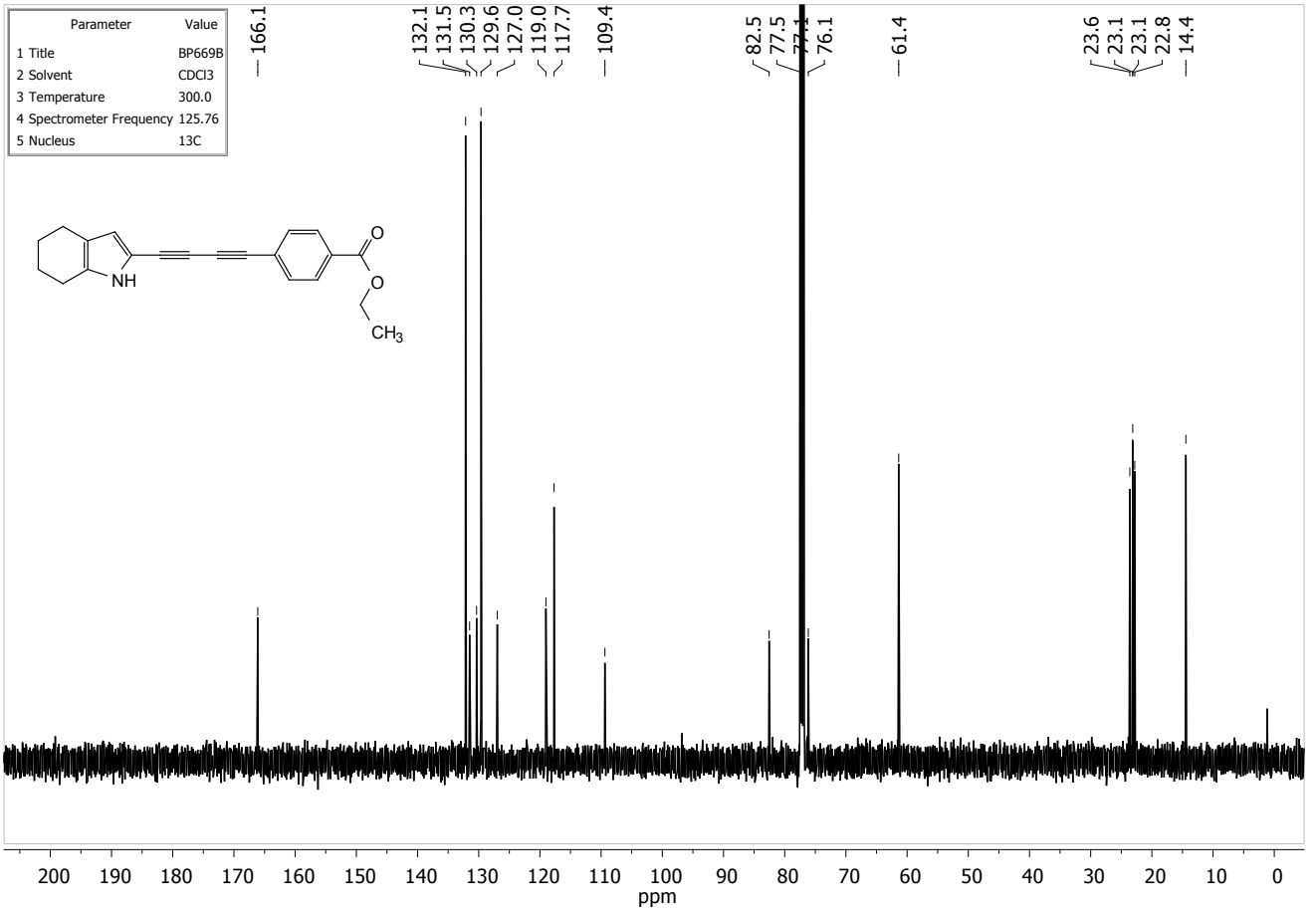
Benzyl 5-(5-phenyl-1H-pyrrol-2-yl)penta-2,4-diynoate (4ec)



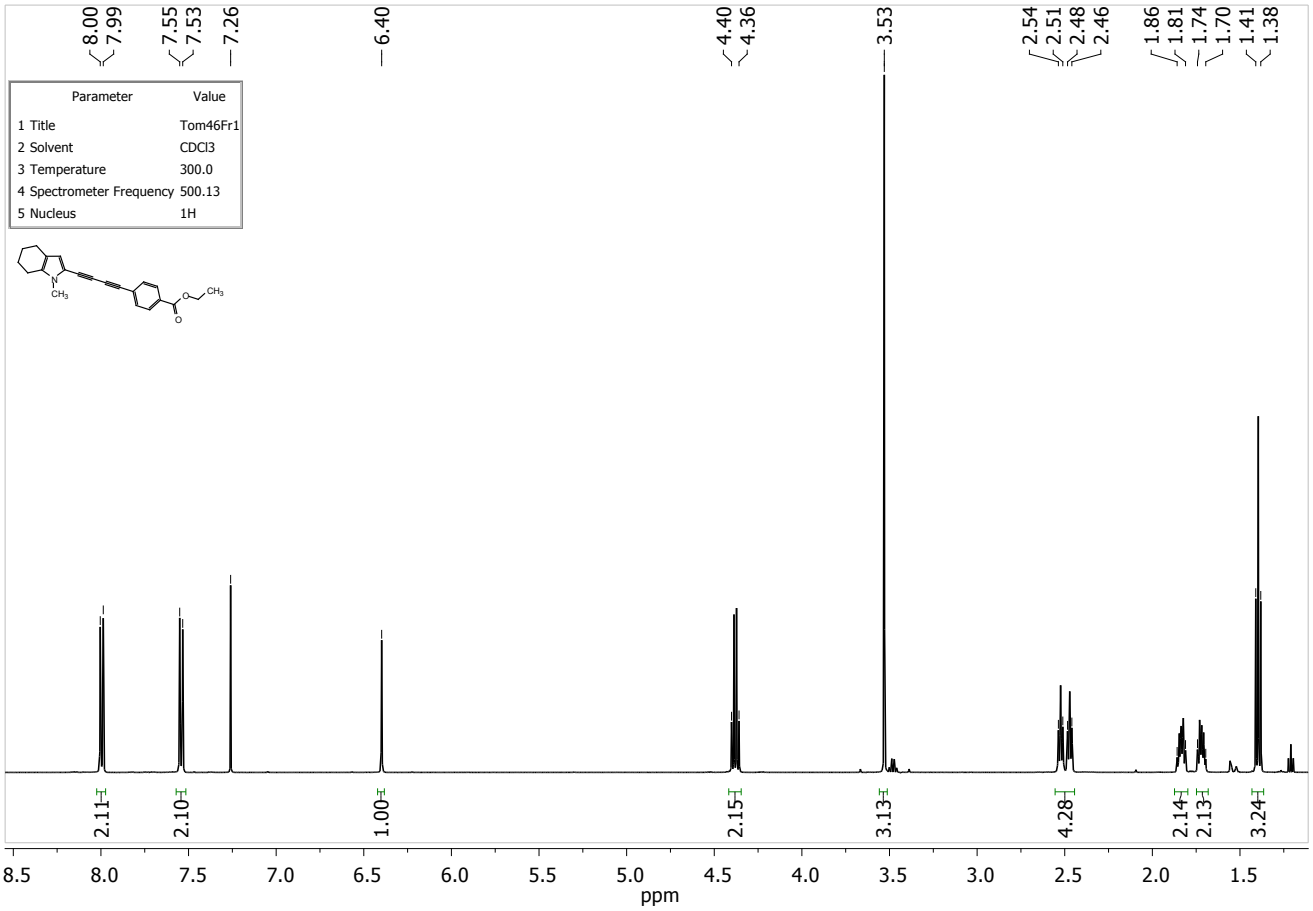


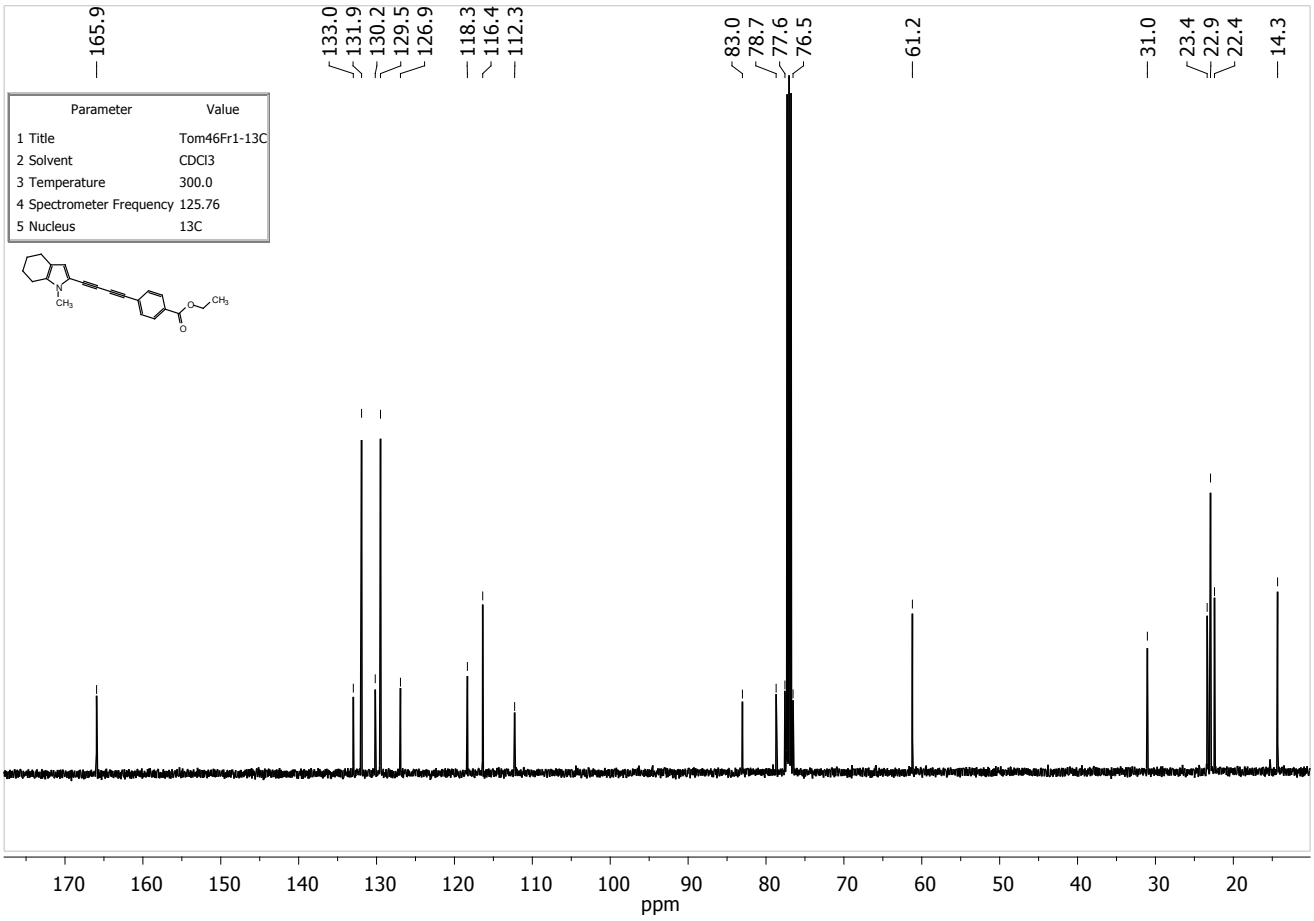
Ethyl 4-((4,5,6,7-tetrahydro-1H-indol-2-yl)buta-1,3-diynyl)benzoate (4ad)



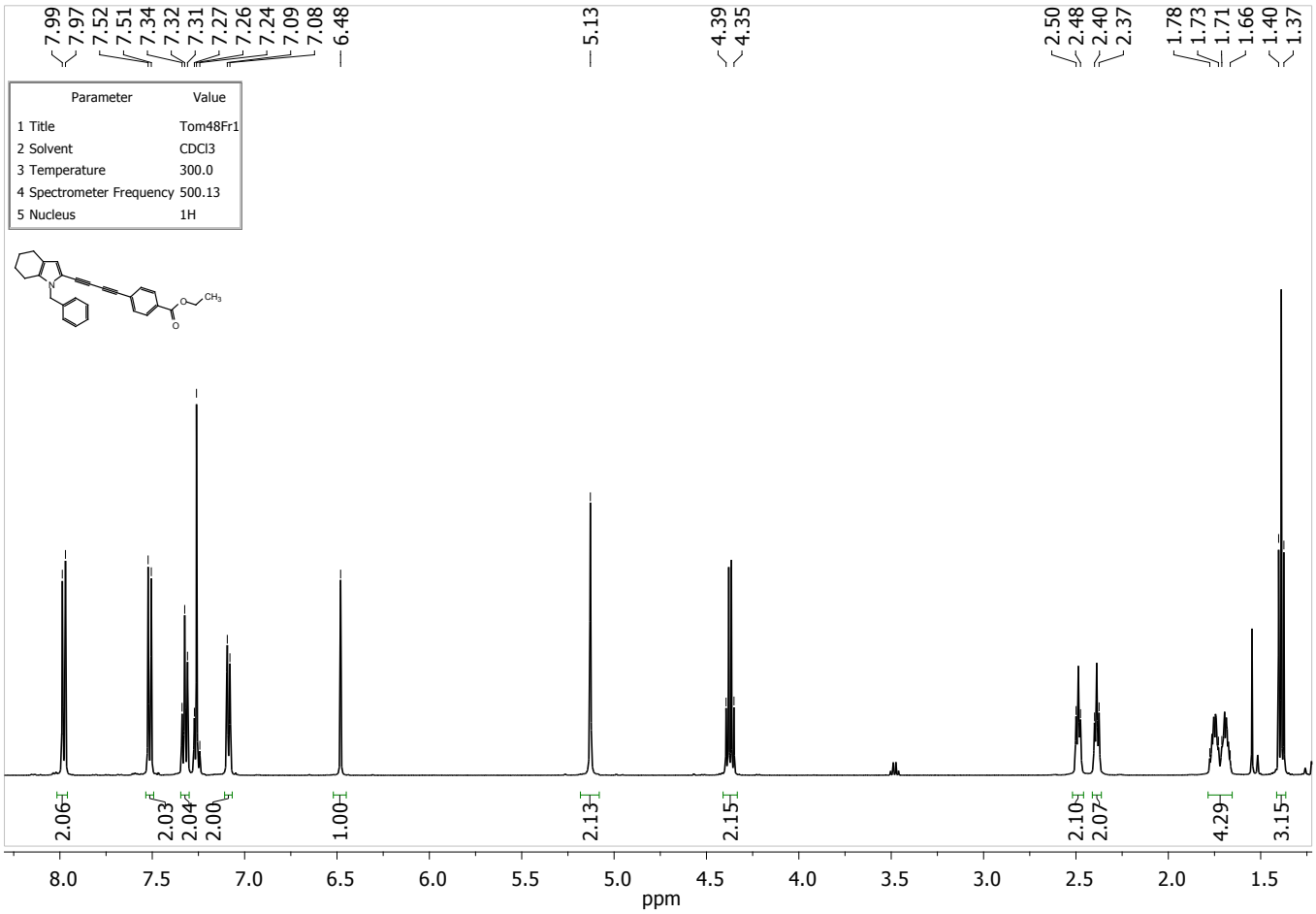


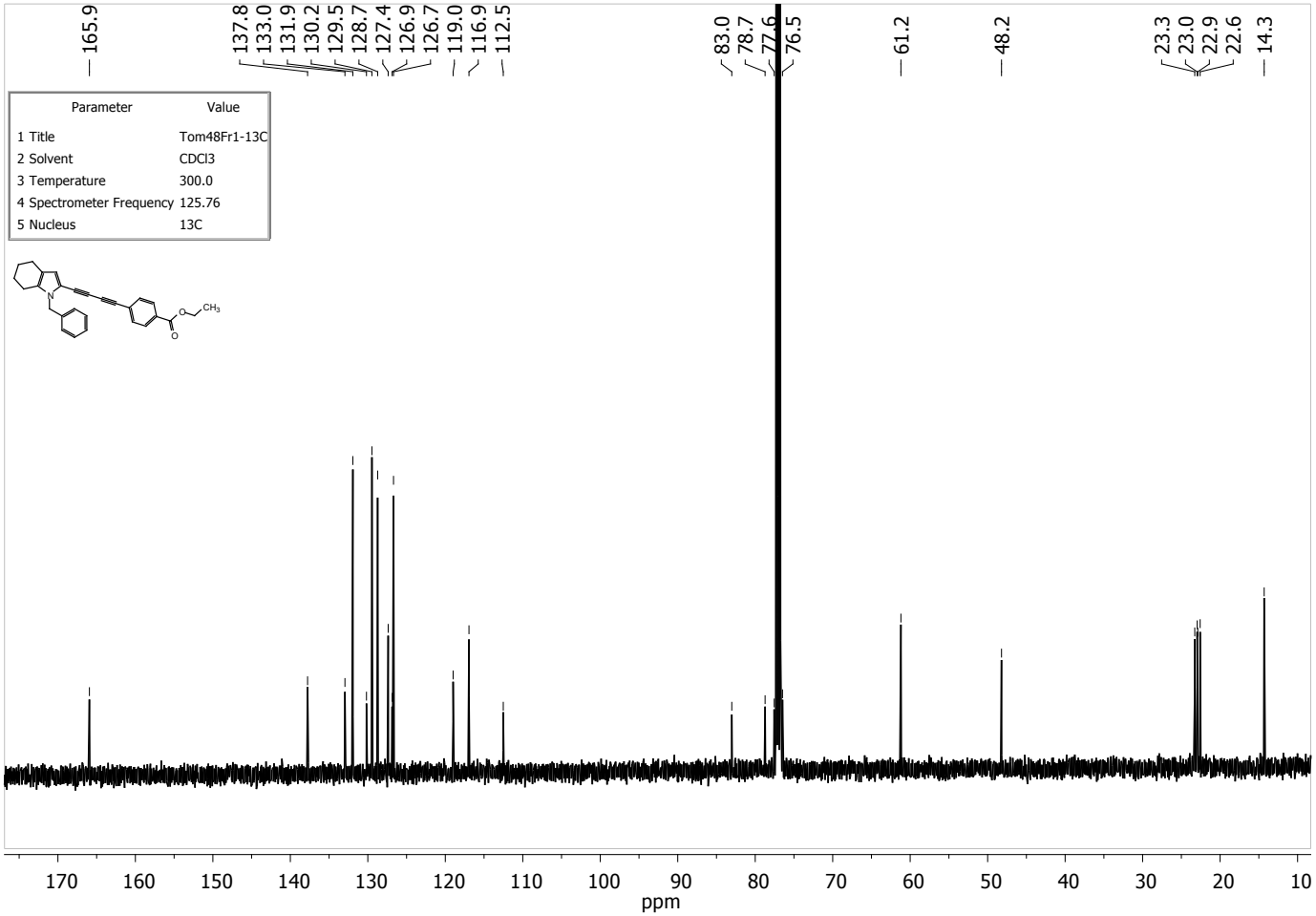
Ethyl 4-((1-methyl-4,5,6,7-tetrahydro-1H-indol-2-yl)buta-1,3-diynyl)benzoate (4bd)



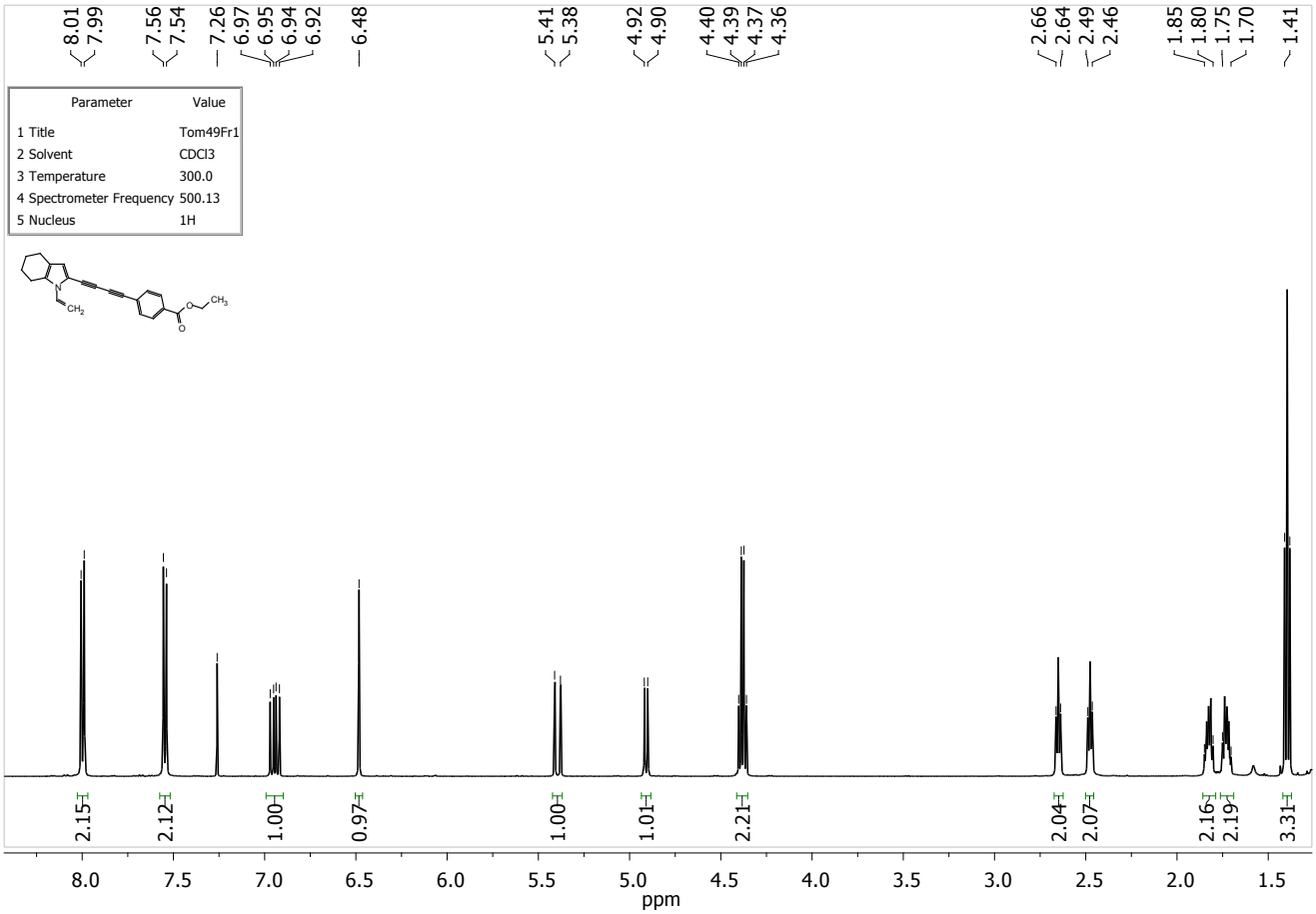


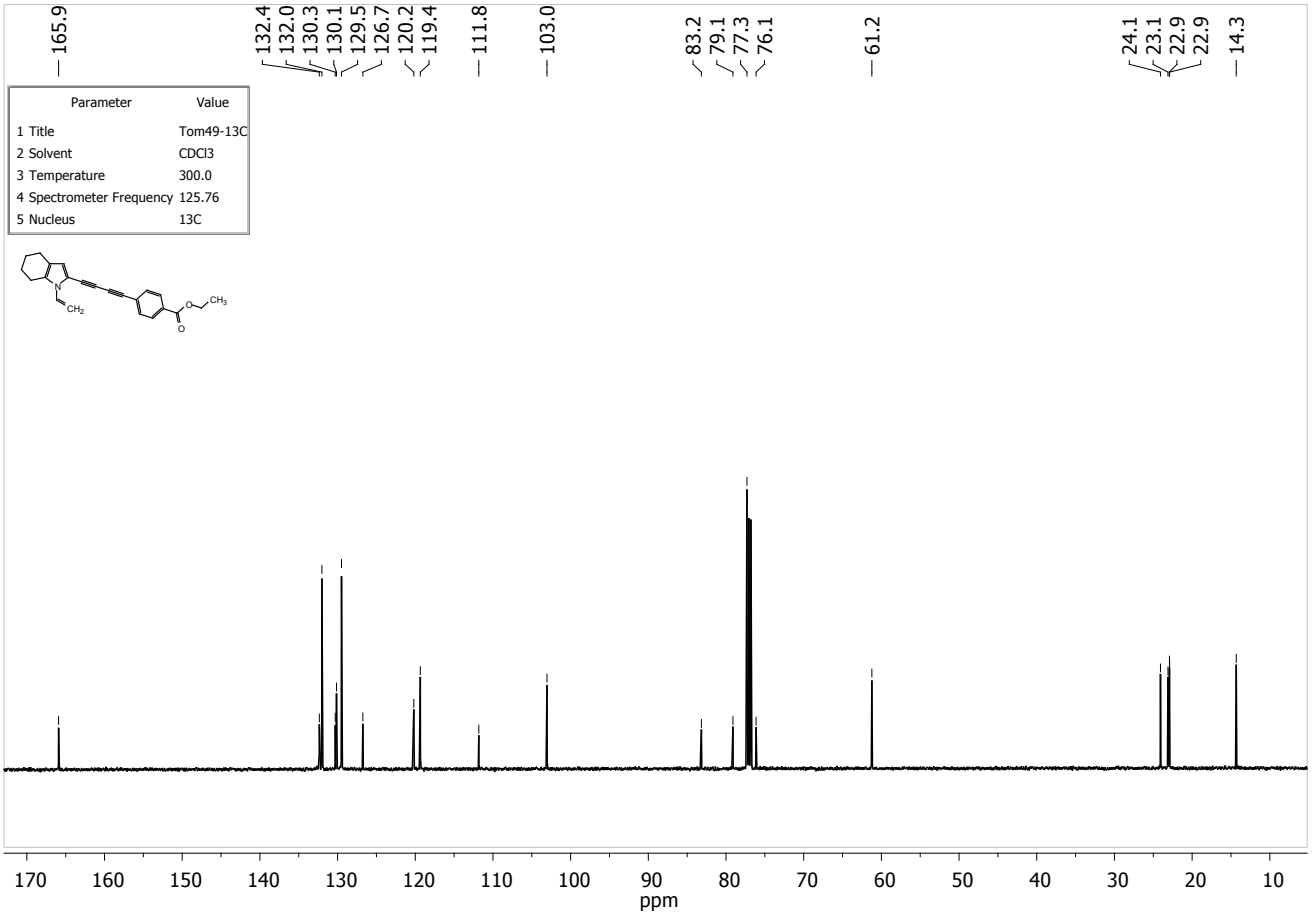
Ethyl 4-((1-benzyl-4,5,6,7-tetrahydro-1H-indol-2-yl)buta-1,3-diynyl)benzoate (4cd)



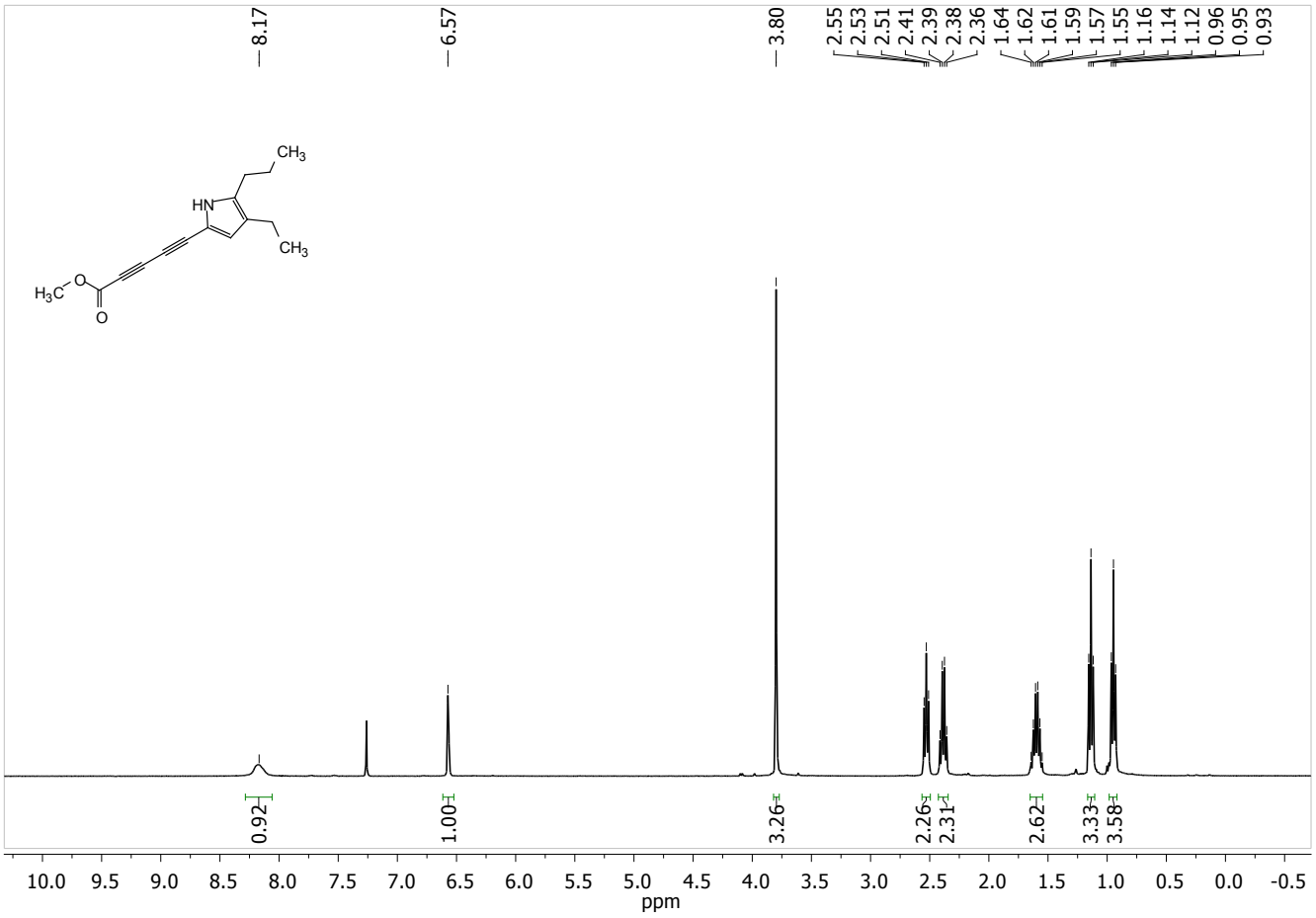


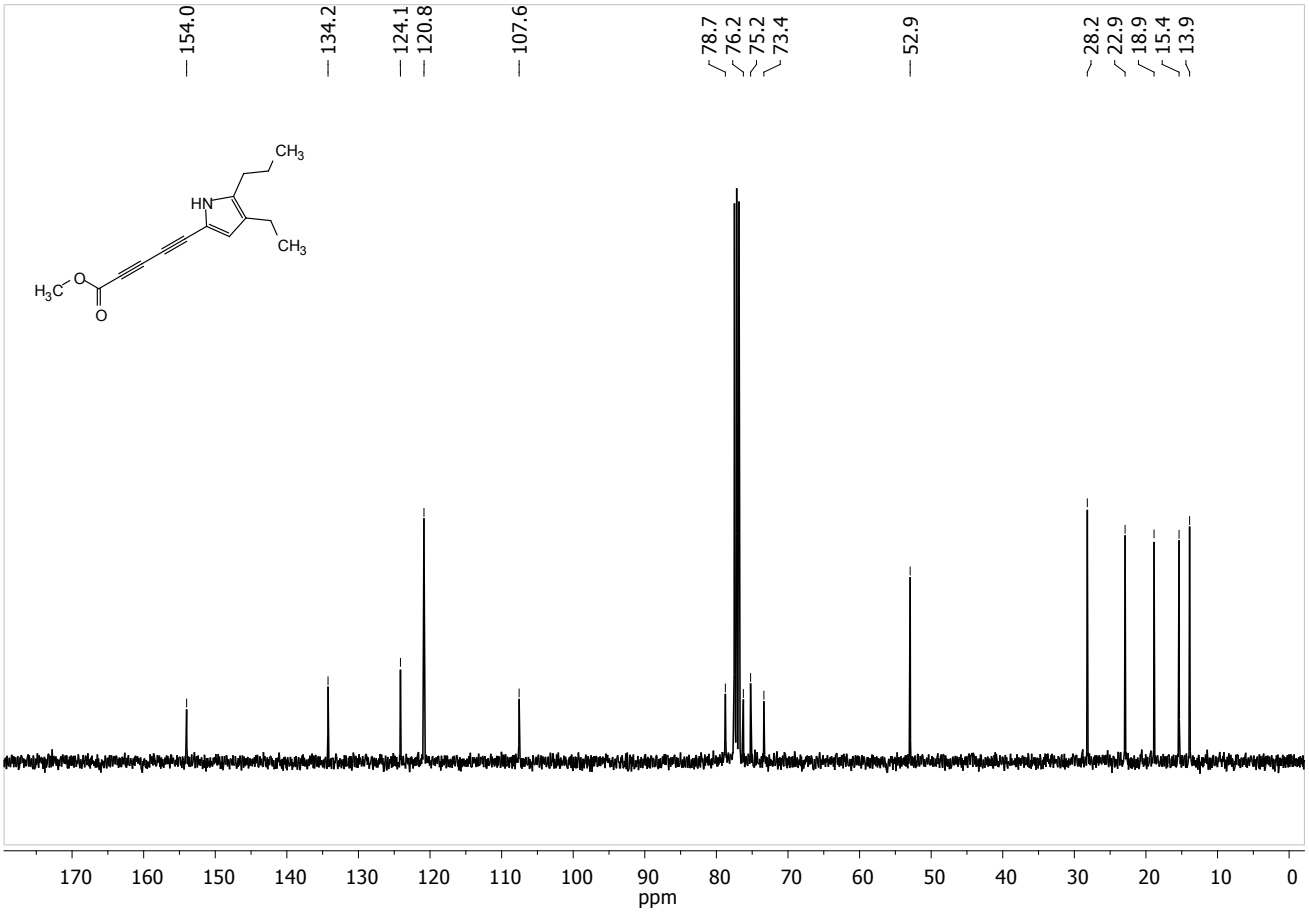
Ethyl 4-((1-vinyl-4,5,6,7-tetrahydro-1H-indol-2-yl)buta-1,3-diynyl)benzoate (4dd)





Methyl 5-(4-ethyl-5-propyl-1H-pyrrol-2-yl)penta-2,4-diynoate (4fa)





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1. Sheldrick, G. M., *Acta Crystallogr. A* **2008,** *64* (Pt 1), 112–122.

2. (a) Sun, A.; Lauher, J. W.; Goroff, N. S., *Science* **2006,** *312*, 1030–1034; (b) Biradha, K.; Santra, R., *Chem. Soc. Rev.* **2013,** *42* (3), 950-967; (c) Deschamps, J.; Balog, M.; Boury, B.; Ben Yahia, M.; Filhol, J. S.; van der Lee, A.; Al Choueiry, A.; Barisien, T.; Legrand, L.; Schott, M.; Dutremez, S. G., *Chem. Mater.* **2010,** *22* (13), 3961-3982.