Supporting Information

ICl-Mediated Functional Group Interconversion from Methyl Homopropargyl Ether to α-Iodo-γ-chloroketone

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1. X-Ray Data and Crystal Structure of **3a** (CCDC 2179135)

Sample preparation: 30 mg of **3a** (light yellow solid) was added to a 10 mL test tube and dissolved in minimal amount of ethyl acetate. Hexane (3 mL) was added to the test tube along the wall. The test tube was loosely capped with a rubber septum and kept at 4 °C. A single crystal was obtained after 5 days.

Cambridge Crystallographic Data Centre deposition number for **3a**: CCDC 2179135. The data can be obtained free from Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

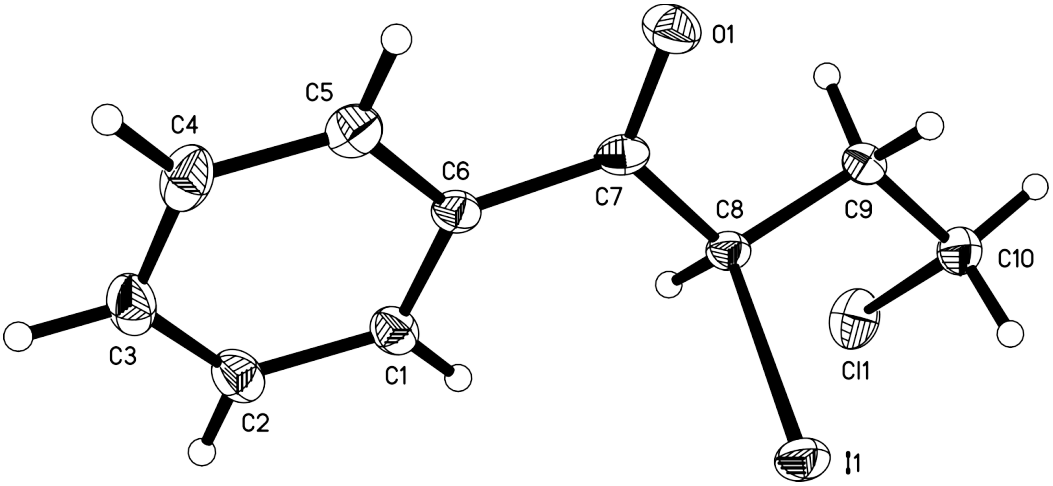

Figure S1. ORTEP drawing of **3a** with complete numbering of atoms, with the ellipsoid contour drawn at the 50% probability level.

Crystal Structure Report for 3a

A colorless block-like specimen of $C_{10}H_{10}ClIO$, approximate dimensions 0.120 mm x 0.200 mm x 0.220 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.
The total exposure time was 0.11 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 13557 reflections to a maximum θ angle of 33.84° (0.64 Å resolution), of which 4312 were independent (average redundancy 3.144, completeness = 99.5%, R_{int} = 4.68%, R_{sig} = 4.51%) and 3455 (80.13%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.1071(7) Å, b = 5.5083(3) Å, c = 17.5919(9) Å, β = 95.7832(18)°, volume = 1070.82(10) $Å^3$, are based upon the refinement of the XYZ-centroids of 5626 reflections above 20 σ(I) with 7.375° < 2θ < 67.65°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.693. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5400 and 0.7000.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/n 1, with Z = 4 for the formula unit, $C_{10}H_{10}ClIO$. The final anisotropic full-

matrix least-squares refinement on F^2 with 118 variables converged at R1 = 3.54%, for the observed data and wR2 = 8.80% for all data. The goodness-of-fit was 1.080. The largest peak in the final difference electron density synthesis was 1.195 $e^-/Å^3$ and the largest hole was -1.790 $e^-/Å^3$ with an RMS deviation of 0.178 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.914 g/cm^3 and F(000), 592 e^-.

Table S1. Sample and crystal data for 3a.

Chemical formula	$C_{10}H_{10}ClIO$	
Formula weight	308.53 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.120 x 0.200 x 0.220 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 11.1071(7) Å	α = 90°
	b = 5.5083(3) Å	β = 95.7832(18)°
	c = 17.5919(9) Å	γ = 90°
Volume	1070.82(10) $Å^3$	
Z	4	
Density (calculated)	1.914 g/cm^3	
Absorption coefficient	3.198 mm^{-1}	
F(000)	592	

Table S2. Data collection and structure refinement for 3a.

Theta range for data collection	2.28 to 33.84°
Index ranges	-16<=h<=17, -8<=k<=7, -27<=l<=27
Reflections collected	13557
Independent reflections	4312 [R(int) = 0.0468]
Coverage of independent reflections	99.5%
Absorption correction	Multi-Scan
Max. and min. transmission	0.7000 and 0.5400
Structure solution technique	direct methods
Structure solution program	XT, VERSION 2014/5
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	4312 / 0 / 118

Goodness-of-fit on F^2	1.080
Δ/σ_{max}	0.002
Final R indices	3455 data; R1 = 0.0354, wR2 = 0.0796 $I>2\sigma(I)$ all data R1 = 0.0501, wR2 = 0.0880
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0356P)^2+0.9631P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	1.195 and -1.790 eÅ^{-3}
R.M.S. deviation from mean	0.178 eÅ^{-3}

2. Computational Methods

DFT electronic structure calculations were performed using the ωB97XD[1] functional coupled with the LANL2DZ basis set (which uses D95V on first row[2] and Los Alamos ECP plus DZ on Na-La and Hf-Bi[3]). Geometries of reactants, transition states (TSs) and products were fully optimized by calculating force constants at every step. TSs were verified as first-order saddle points by frequency calculations, and the transition vector with the imaginary frequency corresponds to the anticipated reaction coordinate. Intrinsic reaction coordinate (IRC) calculations were carried out to further verify that each TS was connected to the correct reactant/product minima. Thermal corrections and enthalpies for reaction structures were calculated using the standard statistical thermodynamical methods using the unscaled ωB97XD vibrational frequencies and the rigid rotor and harmonic oscillator approximations. Reaction enthalpies reported for each pathway include zero-point energies (ZPEs) and thermal corrections to 298 K. Reactions in the diethylether solvent were calculated using the SMD solvation model.[4] For a relaxed 2D-PES scan, all bond lengths and bond angles were fully optimized at each step, except for the two scanning reaction coordinates which were each varied continuously from 4.0 to 1.6 Å, at a step size of 0.1 Å.
DFT calculations were carried out using the Gaussian 16 suite of program.[5] All theoretical jobs were completed at a Linux computational cluster equipped with 20 nodes of dual Intel Xeon 28-core 2.7 GHz processors. Schematic reaction coordinate in Figure 1 was prepared using SigmaPlot v.14. Griding (using Kriging method) and analysis of PES raw data and plotting of contour map and 3D surface in Figure 2 were accomplished using the Surfer software v. 9.

3. Cartesian coordinates and energies of reaction structures in Fig. 1 in the Main Text, which were calculated at the SMD(solvent = diethylether)//ωB97XD/LANL2DZ level of theory

5

C1	0.364094	0.849674	-0.011513
O2	0.720335	2.299772	-0.110287
C3	-0.558660	3.132209	0.009306
C4	-1.681160	2.093634	-0.108388
C5	1.918807	2.829519	0.619192
H6	1.760479	2.690784	1.689678
H7	2.783180	2.277277	0.259904
H8	1.987433	3.879944	0.342394

H9 -0.509574 3.612803 0.986695
H10 -0.510421 3.854987 -0.801409
C11 1.495706 -0.085220 -0.015673
C12 2.412801 -0.078328 -1.086217
C13 1.646154 -1.003290 1.040056
C14 3.477406 -0.986927 -1.094645
H15 2.288349 0.622166 -1.906146
C16 2.709268 -1.916603 1.020386
H17 0.939239 -1.004040 1.862976
C18 3.624819 -1.908110 -0.043596
H19 4.182147 -0.985260 -1.918562
H20 2.822619 -2.629579 1.829185
H21 4.446026 -2.616541 -0.056187
C22 -0.968113 0.759120 -0.015234
H23 -2.416055 2.212142 0.690052
H24 -2.201057 2.169428 -1.065992
I25 -2.037392 -1.030120 -0.054950

Zero-point correction= 0.208651 (Hartree/Particle)
Thermal correction to Energy= 0.220829
Thermal correction to Enthalpy= 0.221773
Thermal correction to Gibbs Free Energy= 0.168265
Sum of electronic and zero-point Energies= -512.330593
Sum of electronic and thermal Energies= -512.318414
Sum of electronic and thermal Enthalpies= -512.317470
Sum of electronic and thermal Free Energies= -512.370978

Cl^-

Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.015023
Sum of electronic and zero-point Energies= -15.095051
Sum of electronic and thermal Energies= -15.093635
Sum of electronic and thermal Enthalpies= -15.092691
Sum of electronic and thermal Free Energies= -15.110074

TS5-6

C1 -0.171577 0.638779 -0.510214
O2 -0.940990 1.702300 -1.024164
C3 -2.884116 0.666288 -1.173821
C4 -2.322561 -0.608079 -0.656042
C5 -0.715781 3.058301 -0.497360
H6 -0.758071 3.053231 0.591752

H7 0.243951 3.426307 -0.868434
H8 -1.533076 3.657810 -0.895343
H9 -3.814542 1.037793 -0.762990
H10 -2.607946 1.001311 -2.166881
C11 1.247837 0.928389 -0.181526
C12 2.136269 1.334938 -1.194514
C13 1.696934 0.830762 1.147143
C14 3.472036 1.621829 -0.881367
H15 1.786122 1.415530 -2.219054
C16 3.033271 1.120410 1.457987
H17 1.004058 0.531266 1.926498
C18 3.922290 1.514340 0.445196
H19 4.157587 1.925693 -1.665226
H20 3.376940 1.042260 2.483832
H21 4.956680 1.736164 0.686319
C22 -0.827036 -0.533661 -0.422445
H23 -2.826382 -0.914458 0.261714
H24 -2.524332 -1.357532 -1.441477
I25 0.128064 -2.348960 0.074164
Cl26 -3.073285 1.816902 1.360805

Zero-point correction= 0.205069 (Hartree/Particle)
Thermal correction to Energy= 0.219350
Thermal correction to Enthalpy= 0.220294
Thermal correction to Gibbs Free Energy= 0.160718
Sum of electronic and zero-point Energies= -527.429293
Sum of electronic and thermal Energies= -527.415012
Sum of electronic and thermal Enthalpies= -527.414068
Sum of electronic and thermal Free Energies= -527.473645

6
C1 0.373512 0.935809 -0.554259
O2 0.307680 2.252570 -1.039843
C3 -2.660376 1.866726 -0.161390
C4 -2.079008 0.829338 -1.118094
C5 0.970210 3.290436 -0.251771
H6 0.580418 3.308963 0.772223
H7 2.053963 3.141153 -0.227948
H8 0.738249 4.229274 -0.755073
H9 -3.584716 2.292693 -0.549055
H10 -1.948074 2.650344 0.085689
C11 1.704855 0.475603 -0.069595
C12 2.810430 0.502418 -0.940756
C13 1.881853 0.065375 1.263775
C14 4.074607 0.099322 -0.487943

H15 2.677044 0.827213 -1.967969
C16 3.147461 -0.334591 1.716798
H17 1.032631 0.056400 1.939848
C18 4.245541 -0.320630 0.841735
H19 4.919703 0.110653 -1.168300
H20 3.275942 -0.652486 2.746105
H21 5.224028 -0.632703 1.192144
C22 -0.769990 0.221930 -0.645435
H23 -2.820442 0.050875 -1.309877
H24 -1.905951 1.353169 -2.067458
I25 -0.785012 -1.870150 -0.249691
Cl26 -3.134892 1.092435 1.488450

Zero-point correction= 0.207664 (Hartree/Particle)
Thermal correction to Energy= 0.222223
Thermal correction to Enthalpy= 0.223167
Thermal correction to Gibbs Free Energy= 0.162319
Sum of electronic and zero-point Energies= -527.503326
Sum of electronic and thermal Energies= -527.488767
Sum of electronic and thermal Enthalpies= -527.487822
Sum of electronic and thermal Free Energies= -527.548670

TS5-7
C1 0.387523 0.370079 -0.613995
O2 1.022617 1.537737 -1.121021
C3 -0.036161 2.556604 -1.407600
C4 -1.355354 1.955380 -0.879819
C5 2.778571 2.182279 -0.016680
H6 3.006907 1.744739 0.946423
H7 3.092281 1.639068 -0.898424
H8 2.732535 3.262834 -0.082786
H9 0.252334 3.465005 -0.882657
H10 -0.029780 2.698650 -2.489279
C11 1.303913 -0.743409 -0.311391
C12 2.250737 -1.155998 -1.269612
C13 1.267403 -1.370399 0.947697
C14 3.138399 -2.199767 -0.977081
H15 2.282437 -0.669529 -2.239489
C16 2.155543 -2.416479 1.236099
H17 0.559514 -1.033579 1.696577
C18 3.090834 -2.833893 0.276101
H19 3.859746 -2.520198 -1.721262
H20 2.123709 -2.896274 2.208422
H21 3.778486 -3.642061 0.502794
C22 -0.939027 0.546730 -0.506532

H23 -1.719371 2.489006 0.002563
H24 -2.135633 1.960674 -1.645551
I25 -2.350941 -0.868522 0.106736
Cl26 0.844793 2.699099 1.708866

Zero-point correction= 0.205460 (Hartree/Particle)
Thermal correction to Energy= 0.219727
Thermal correction to Enthalpy= 0.220672
Thermal correction to Gibbs Free Energy= 0.161507
Sum of electronic and zero-point Energies= -527.422259
Sum of electronic and thermal Energies= -527.407992
Sum of electronic and thermal Enthalpies= -527.407048
Sum of electronic and thermal Free Energies= -527.466212

7
C1 0.402390 1.100530 0.138087
O2 0.641876 2.483029 0.227878
C3 -0.661487 3.185985 0.113575
C4 -1.748918 2.091649 0.226814
H5 -0.698379 3.925600 0.913075
H6 -0.676629 3.686080 -0.857718
C7 1.629734 0.282334 0.088212
C8 2.766643 0.799942 -0.565817
C9 1.705357 -0.984116 0.699742
C10 3.949003 0.051798 -0.629414
H11 2.717550 1.783010 -1.020074
C12 2.890614 -1.730738 0.634602
H13 0.853800 -1.379957 1.241489
C14 4.013996 -1.218391 -0.033011
H15 4.816436 0.458267 -1.138849
H16 2.938558 -2.703880 1.111749
H17 4.930982 -1.796592 -0.081044
C18 -0.919114 0.821349 0.105057
H19 -2.277413 2.124758 1.185496
H20 -2.491447 2.176406 -0.571170
I21 -1.875807 -1.029056 -0.137228

Zero-point correction= 0.167486 (Hartree/Particle)
Thermal correction to Energy= 0.177789
Thermal correction to Enthalpy= 0.178733
Thermal correction to Gibbs Free Energy= 0.128773
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Sum of electronic and thermal Energies= -472.682536
Sum of electronic and thermal Enthalpies= -472.681592
Sum of electronic and thermal Free Energies= -472.731552

CH_3Cl

C1	-1.181774	0.000114	0.000022
H2	-1.506390	1.034187	0.090917
H3	-1.505838	-0.438450	-0.941062
H4	-1.506842	-0.596305	0.849621
Cl5	0.682924	-0.000007	0.000023

Zero-point correction=	0.038460 (Hartree/Particle)
Thermal correction to Energy=	0.041488
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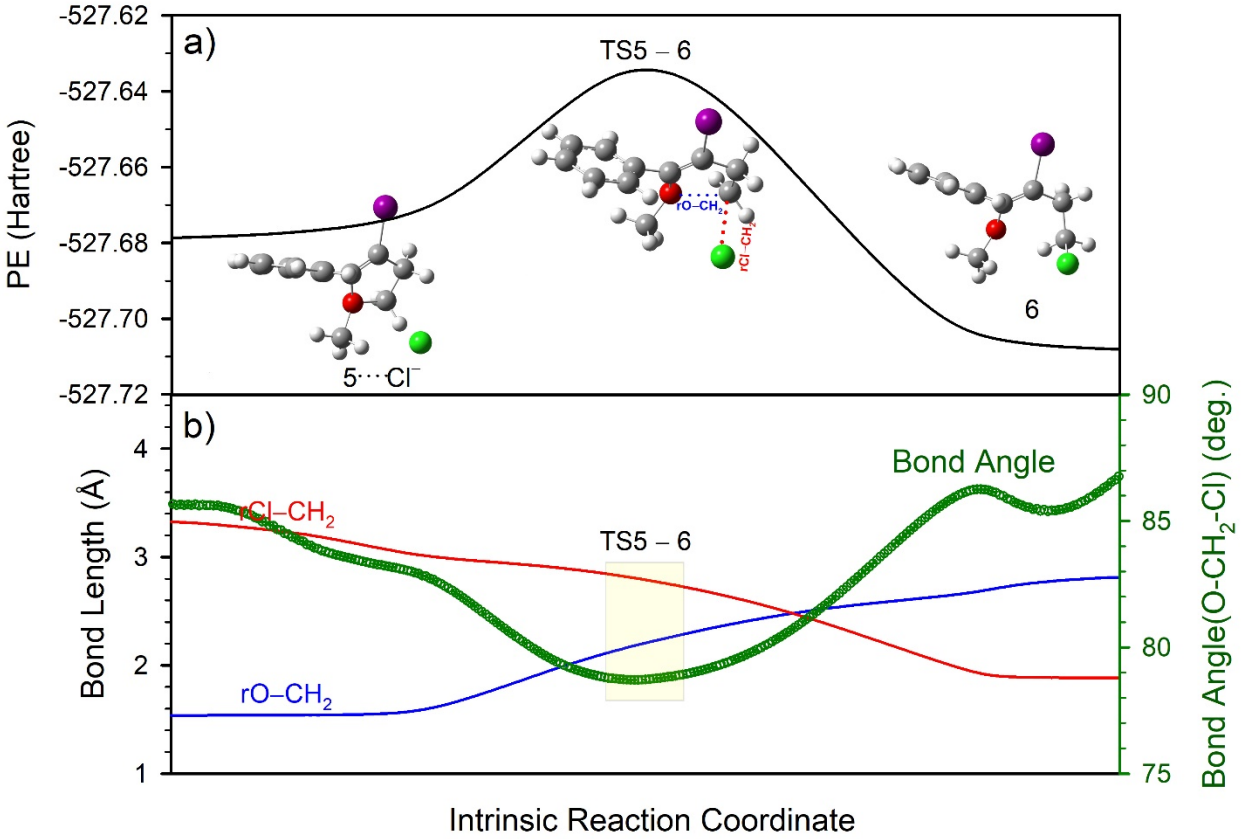

Figure S2. Intrinsic Reaction coordinate and the bond length and bond angle change for the S_Ni reaction path: **5** to **6**.

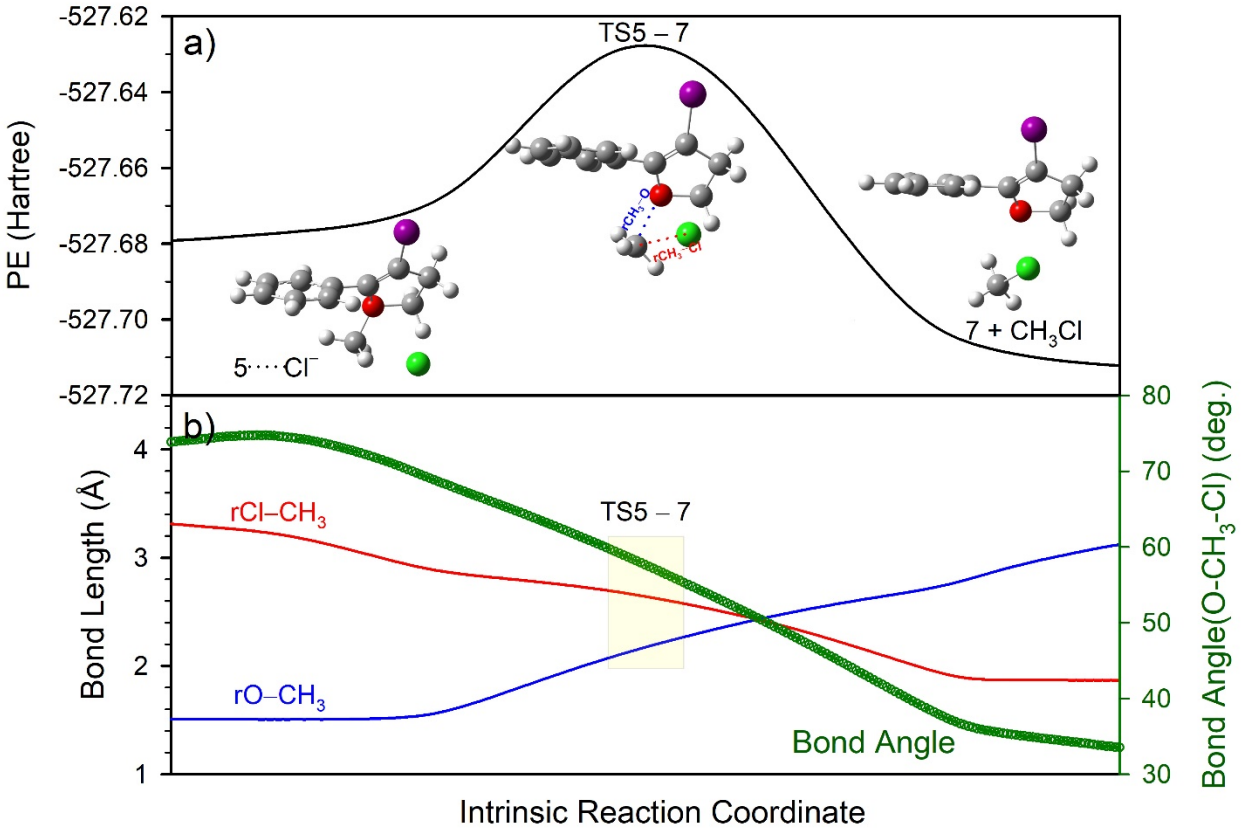

Figure S3. Intrinsic Reaction coordinate and the bond length and bond angle change for the S_Ni reaction path: **5** to **7**.

4. References

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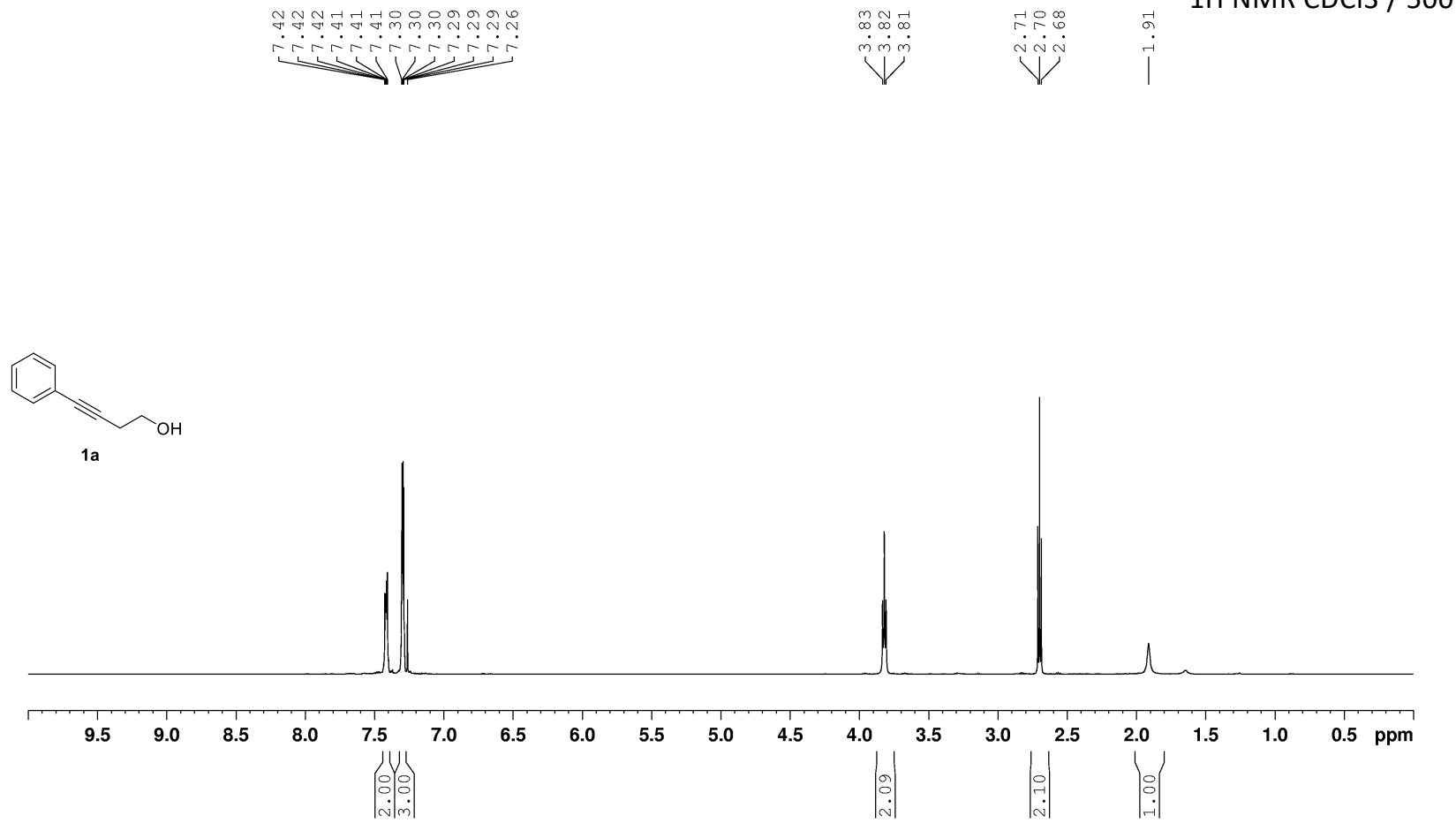
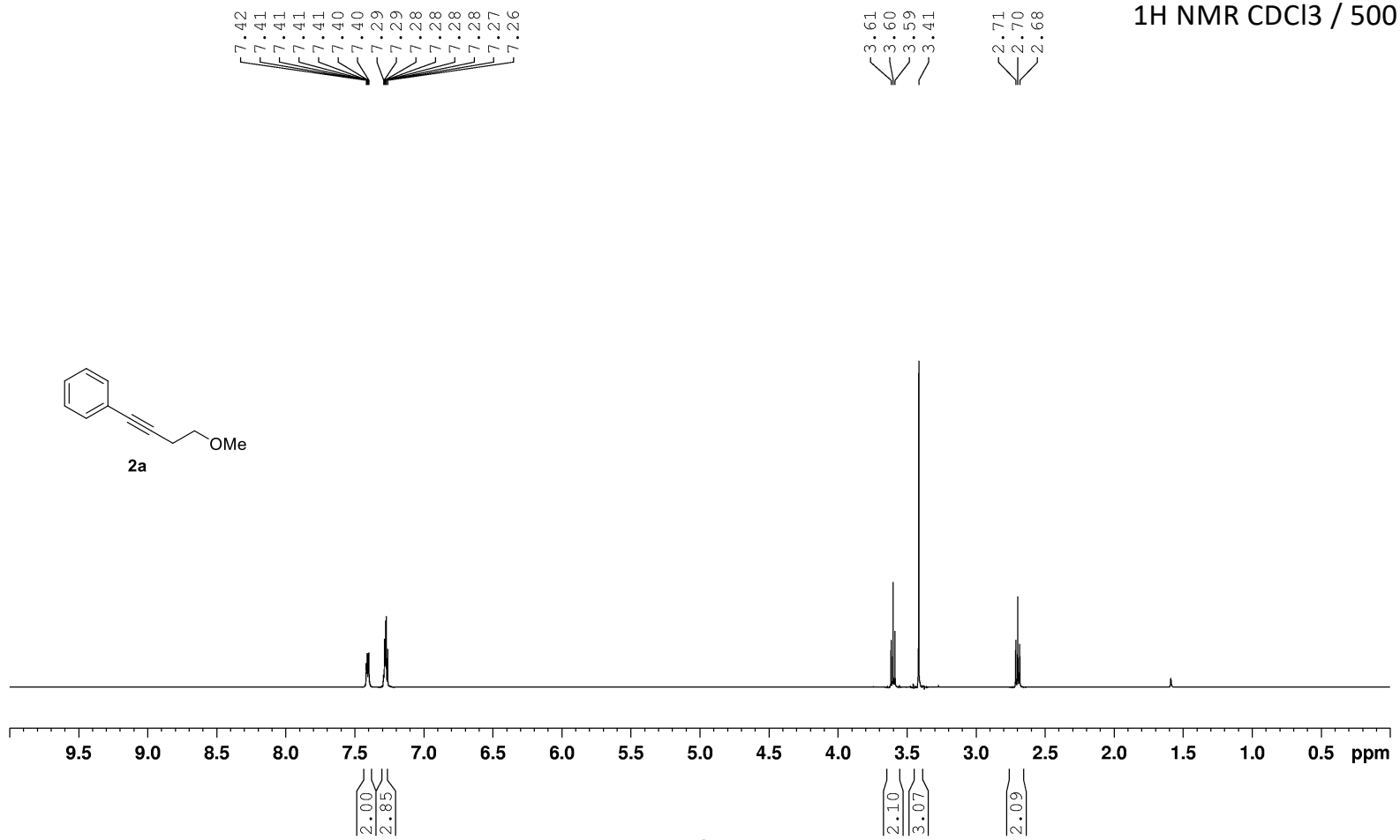
5. Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra for Compounds **1a, 2a–2o, 3a–3o, and 4a**

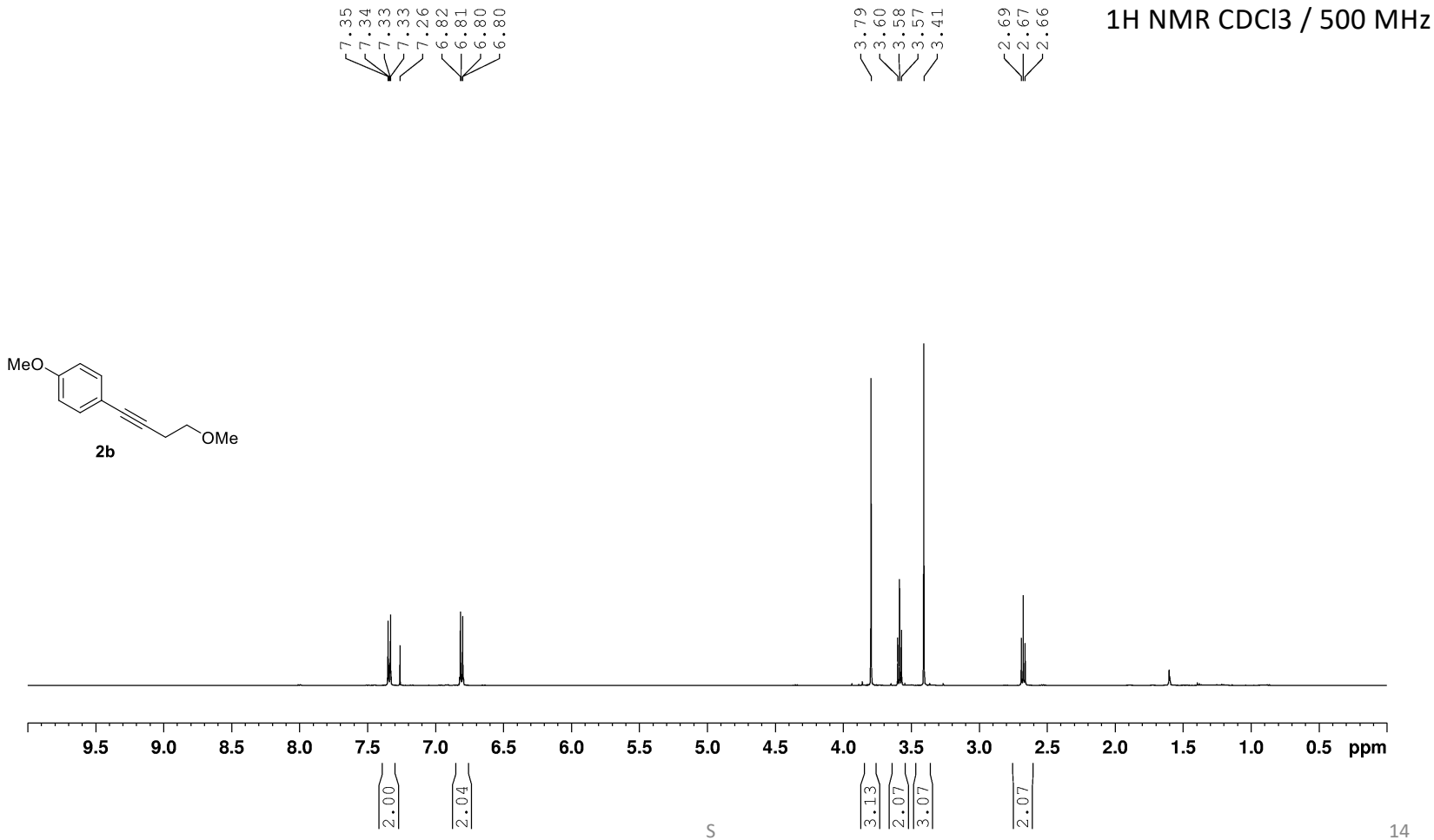
1H NMR CDCl3 / 500 MHz



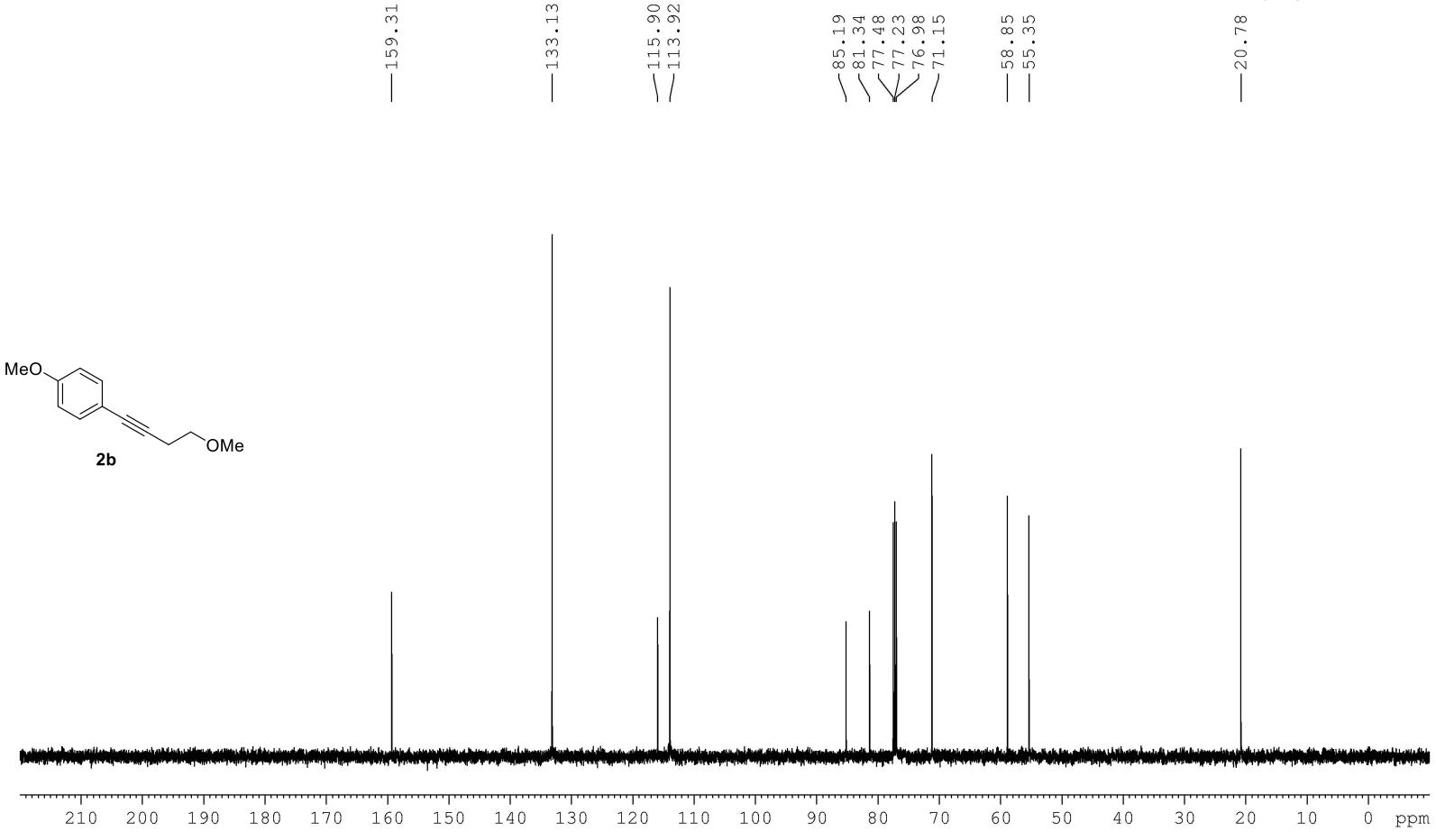
1H NMR CDCl3 / 500 MHz



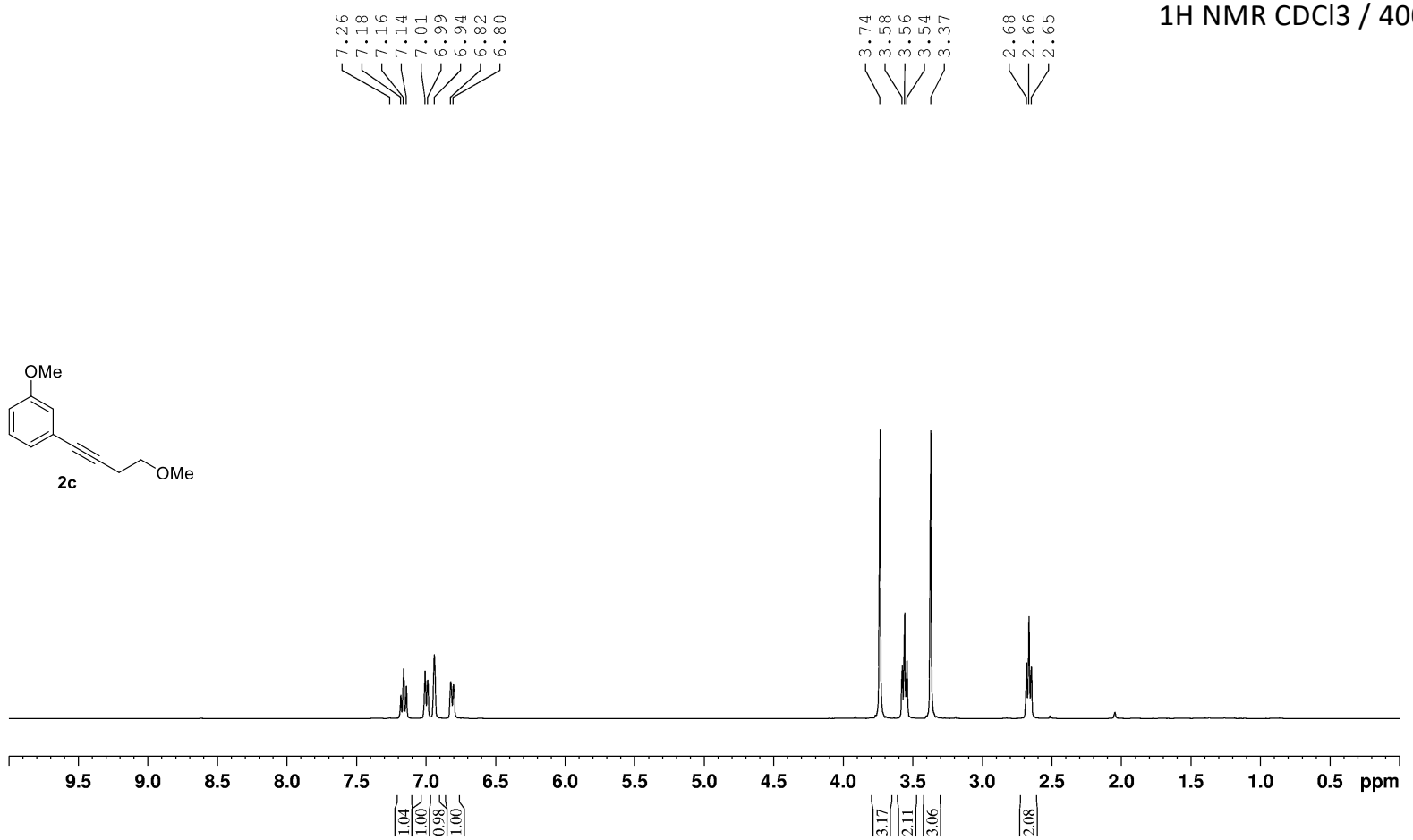
1H NMR CDCl3 / 500 MHz



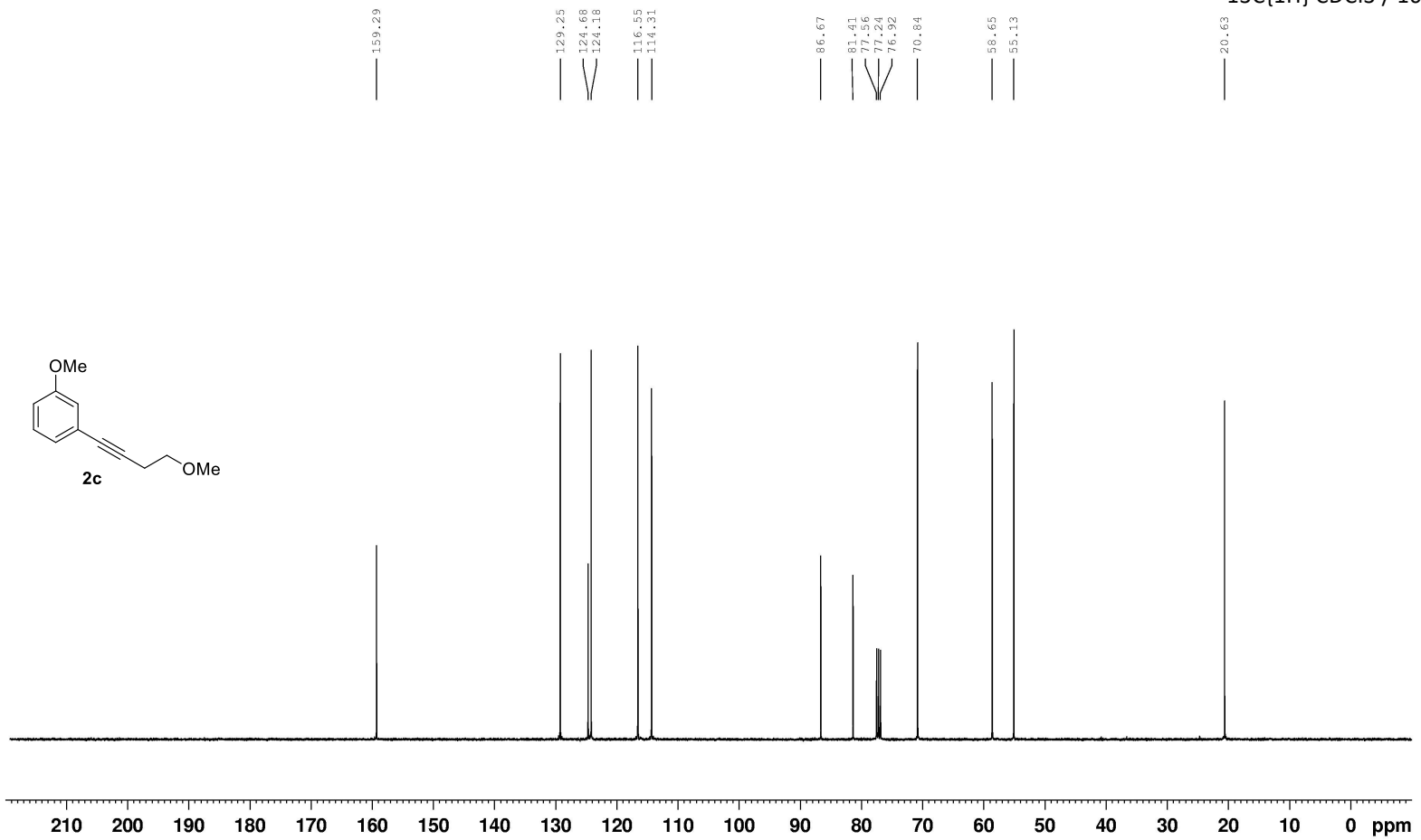
13C{1H} CDCl3 / 125 MHz



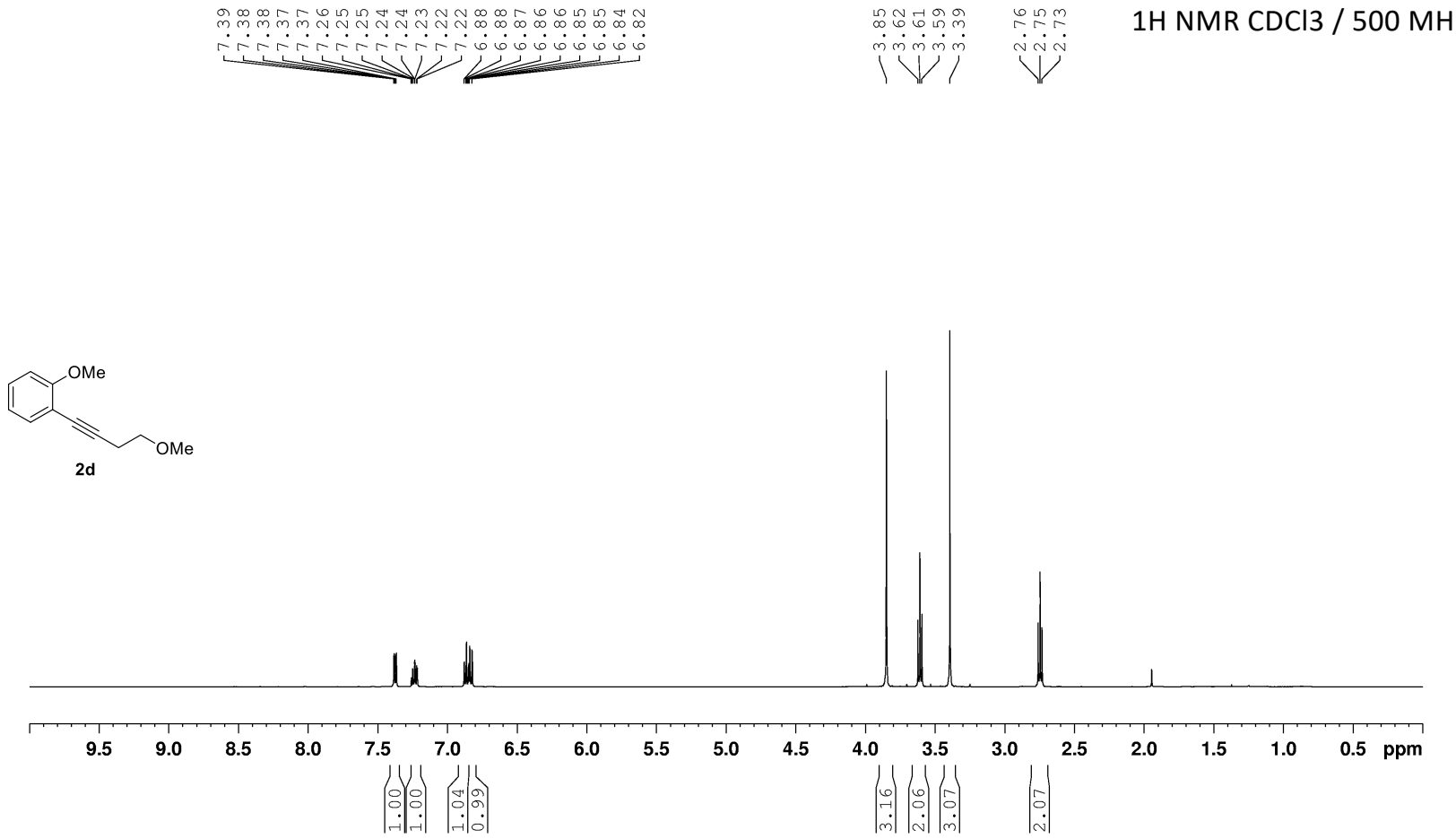
1H NMR CDCl3 / 400 MHz



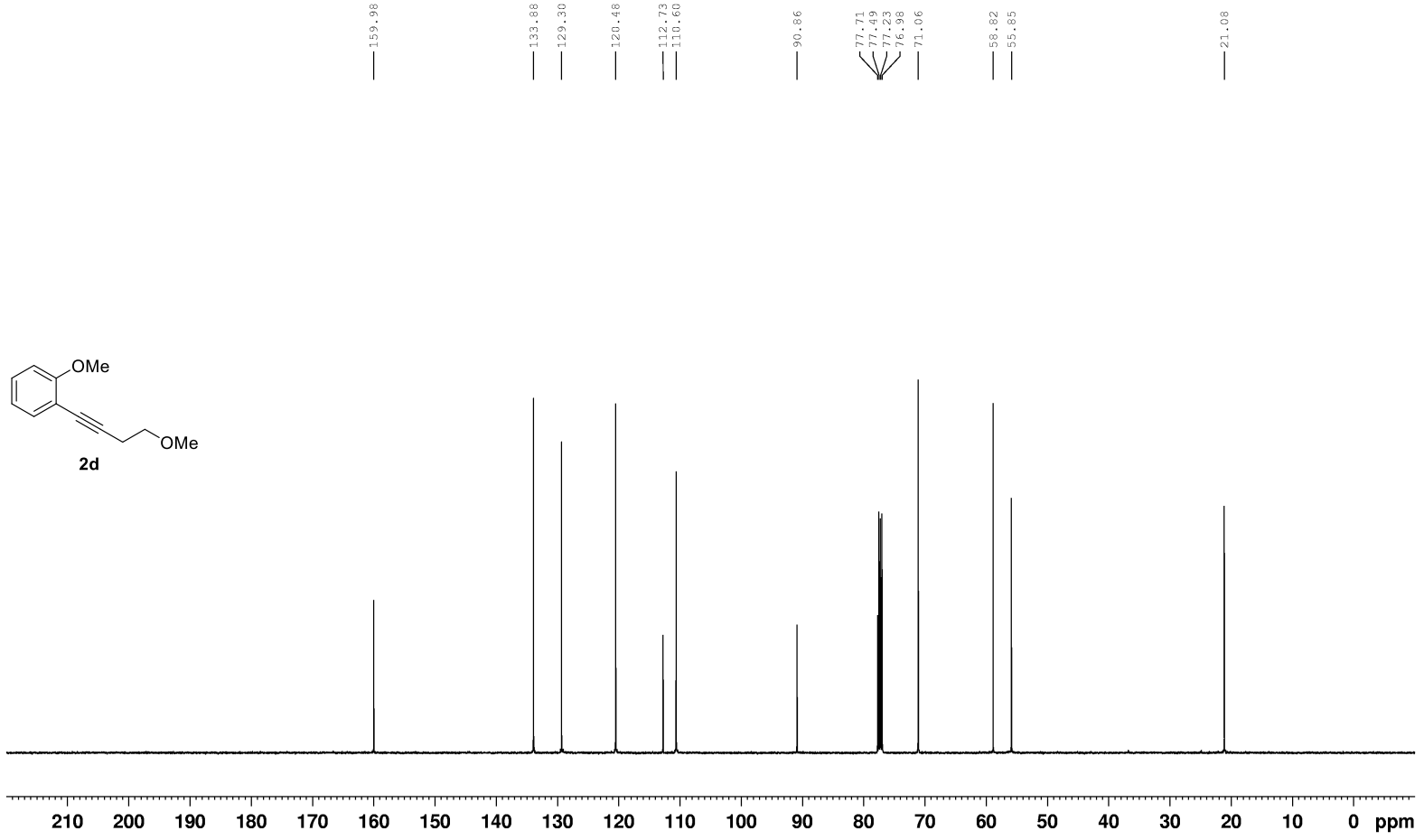
13C{1H} CDCl3 / 100 MHz



1H NMR CDCl3 / 500 MHz



13C{1H} CDCl3 / 125 MHz



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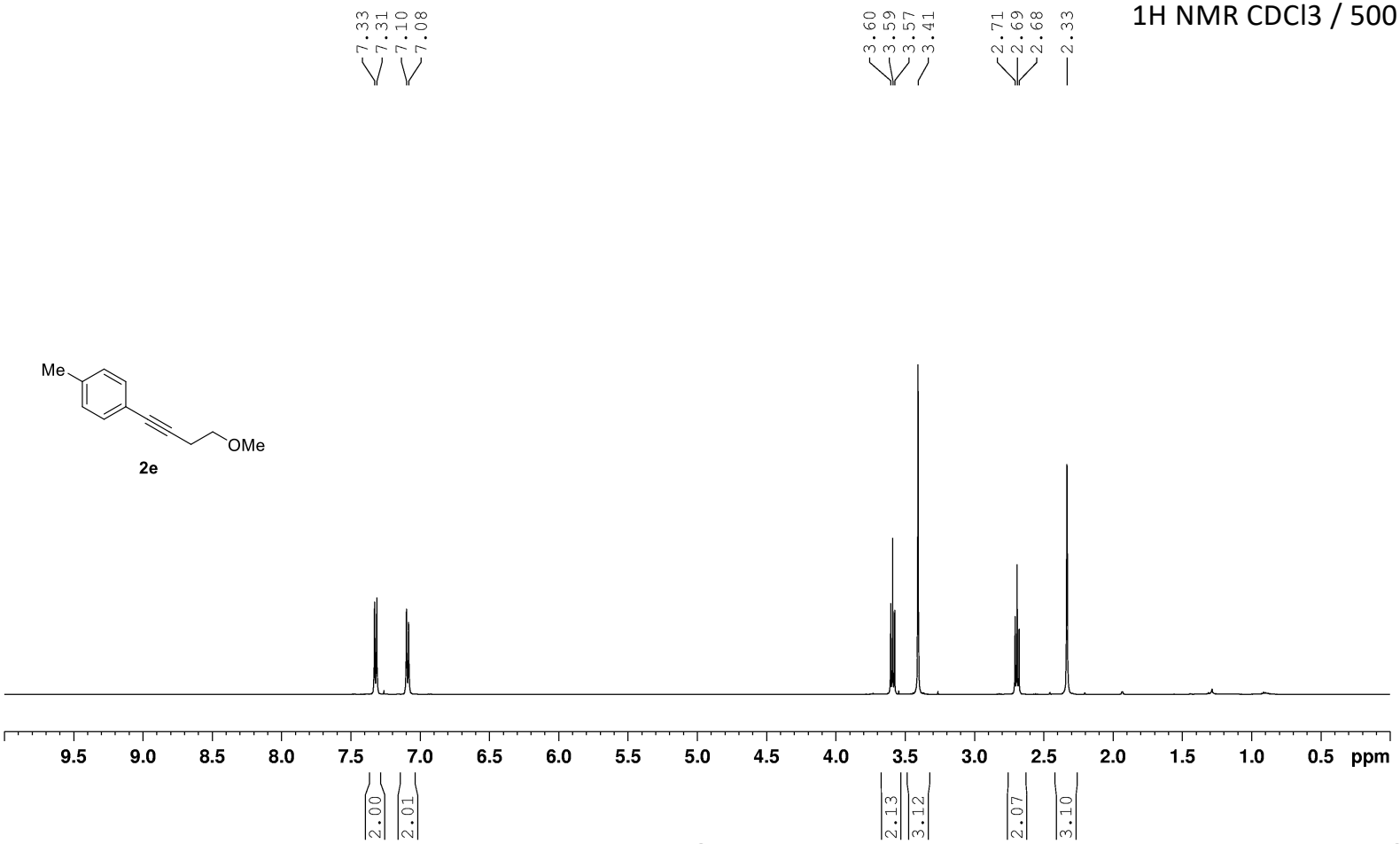

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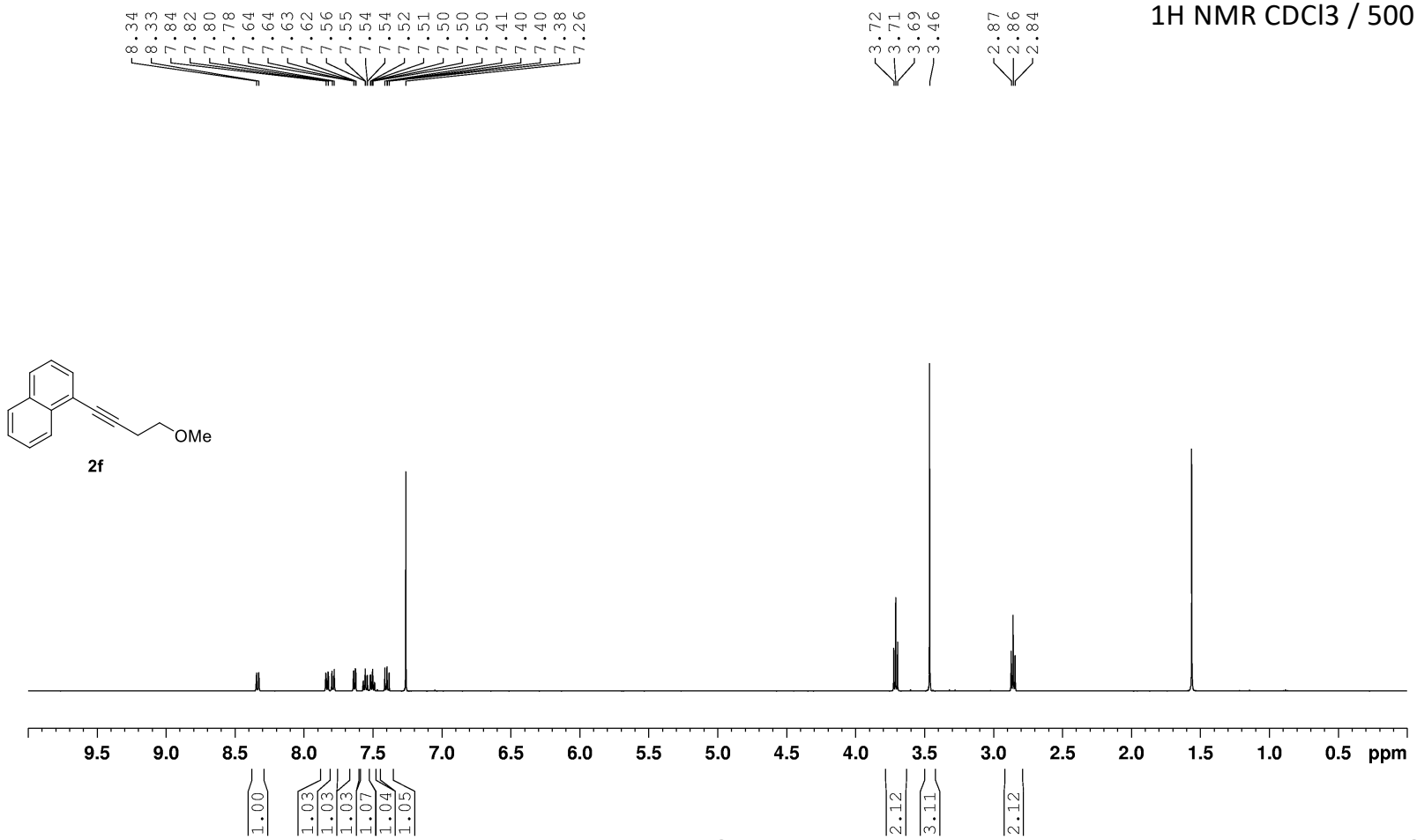
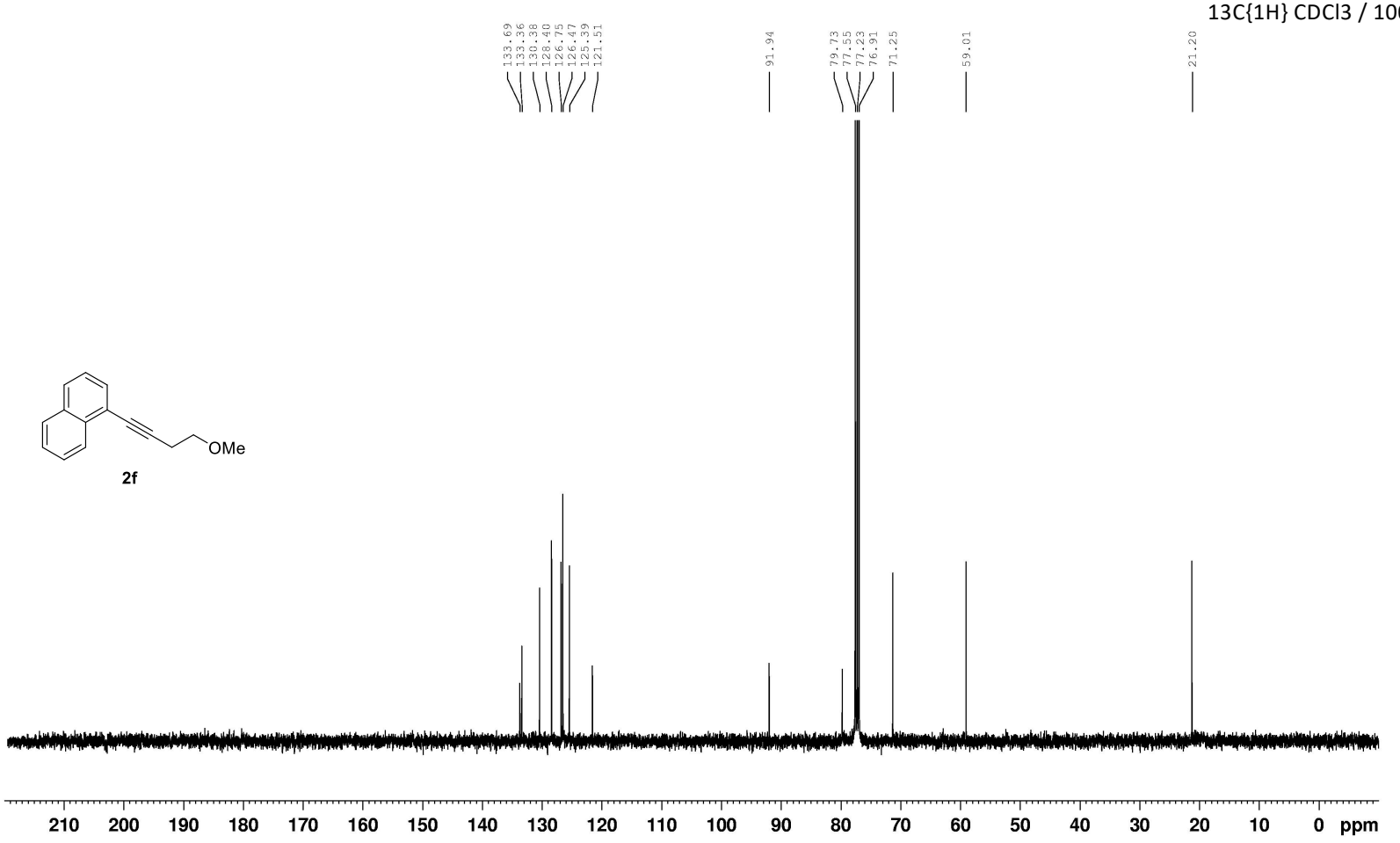
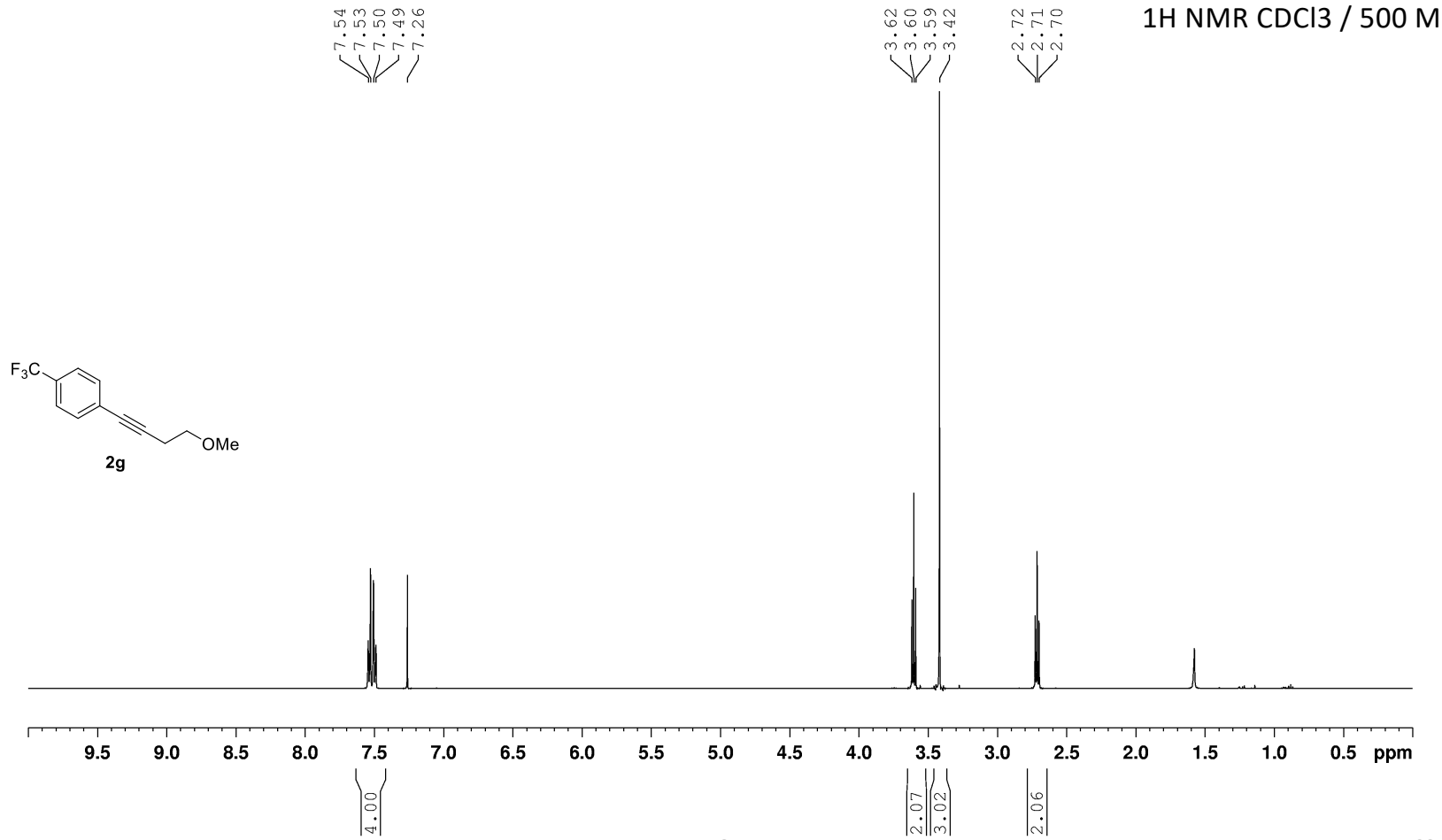


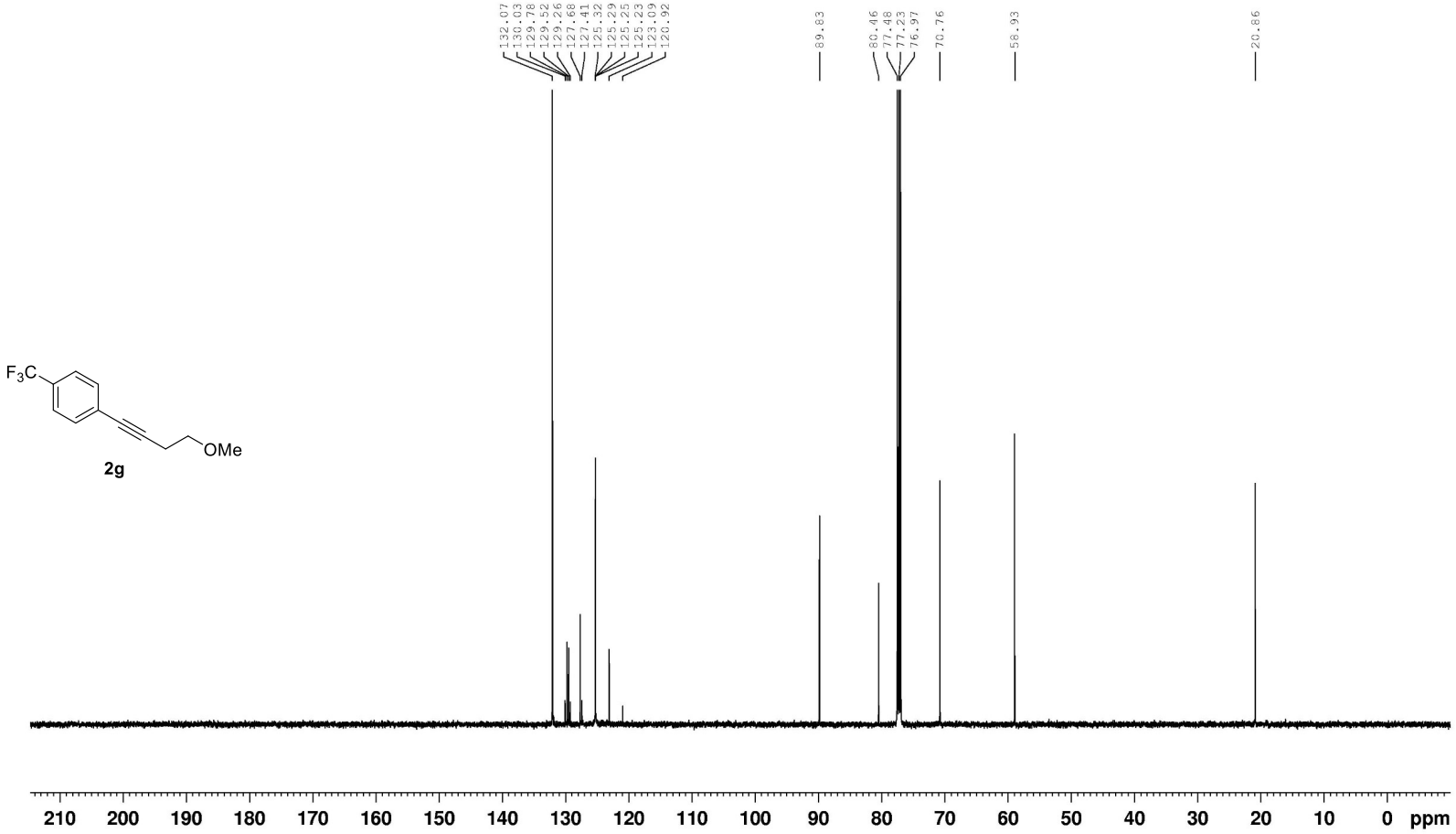
13C{1H} CDCl3 / 100 MHz



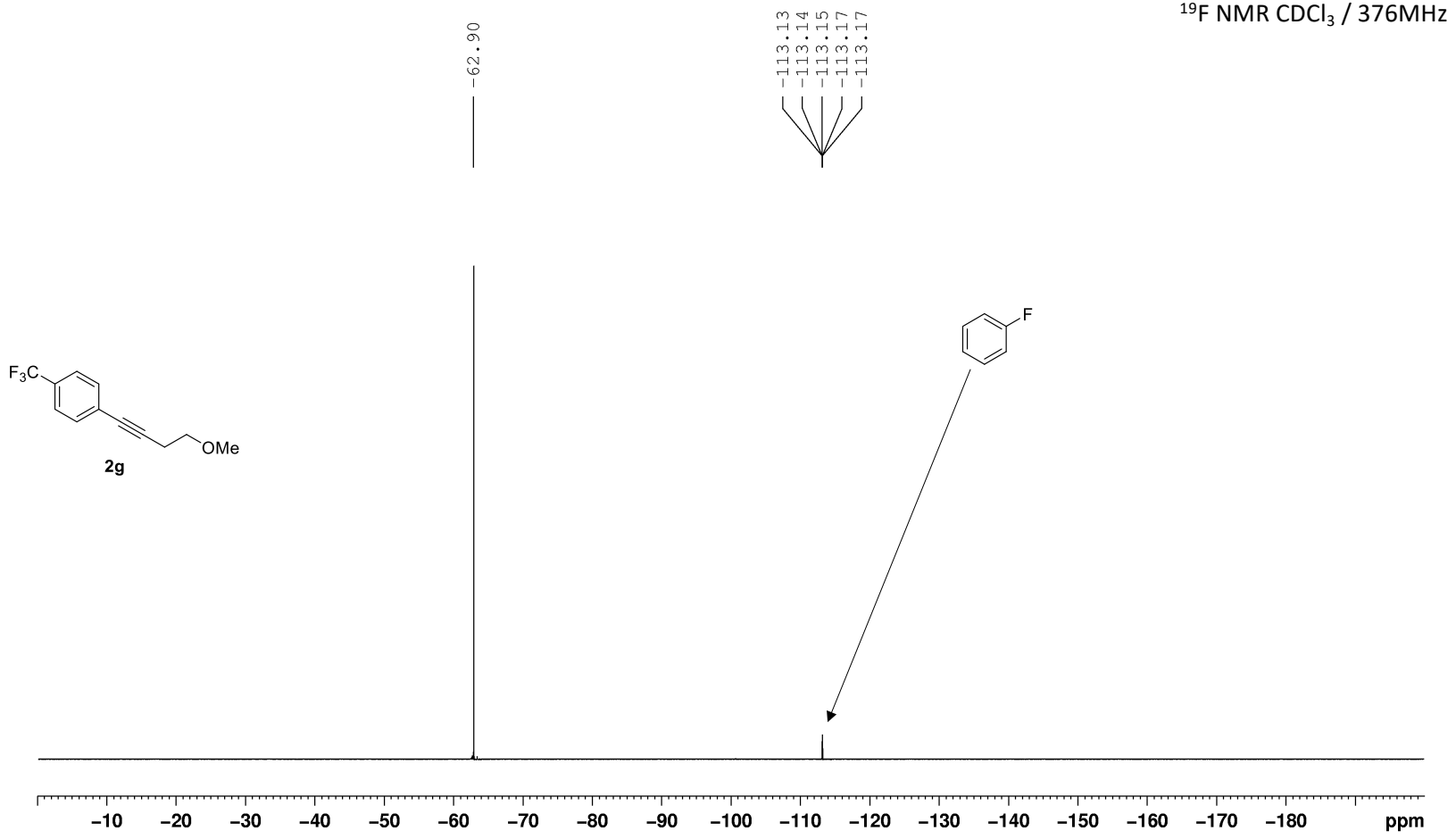
1H NMR CDCl3 / 500 MHz



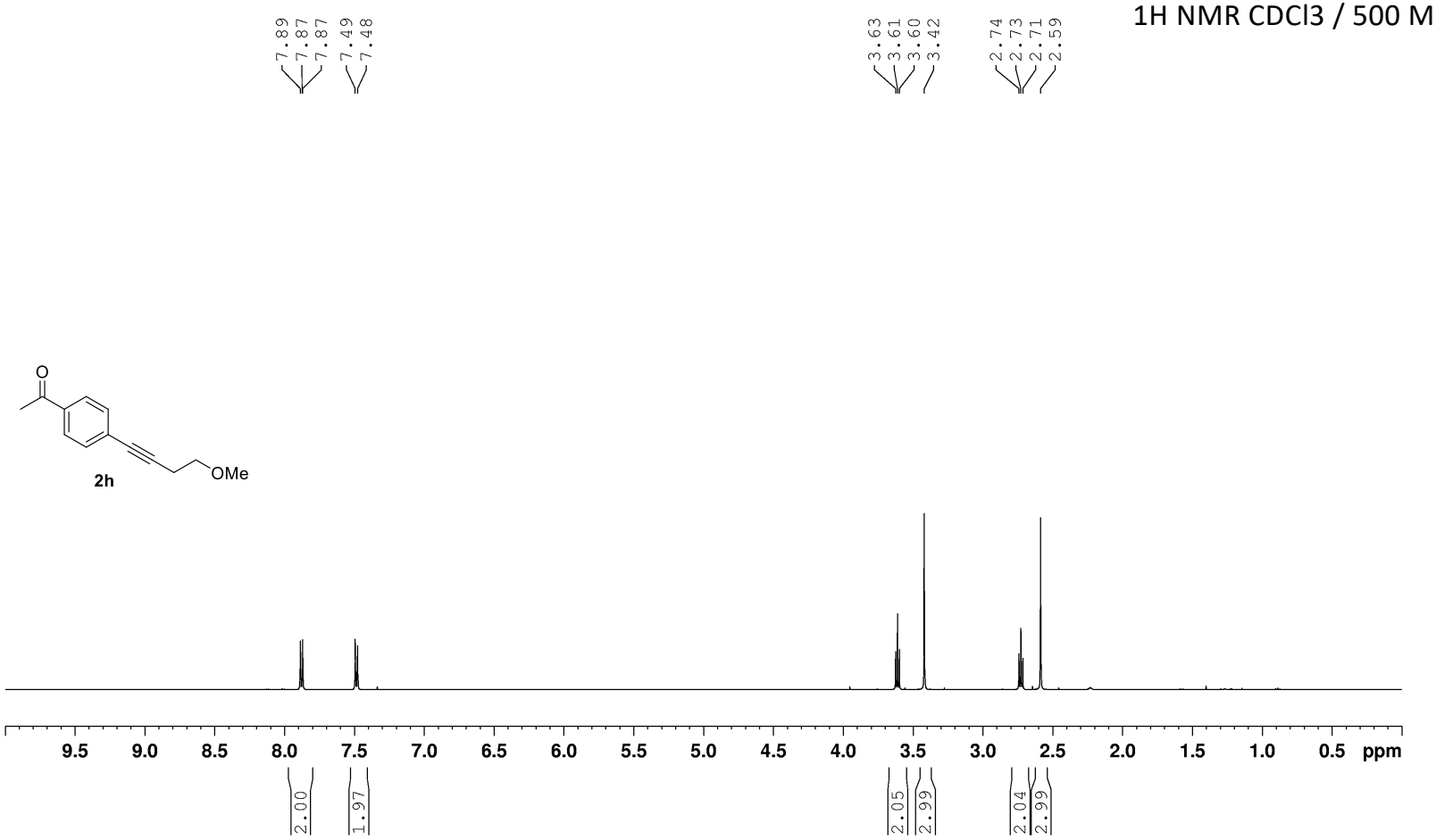
13C{1H} CDCl3 / 125 MHz



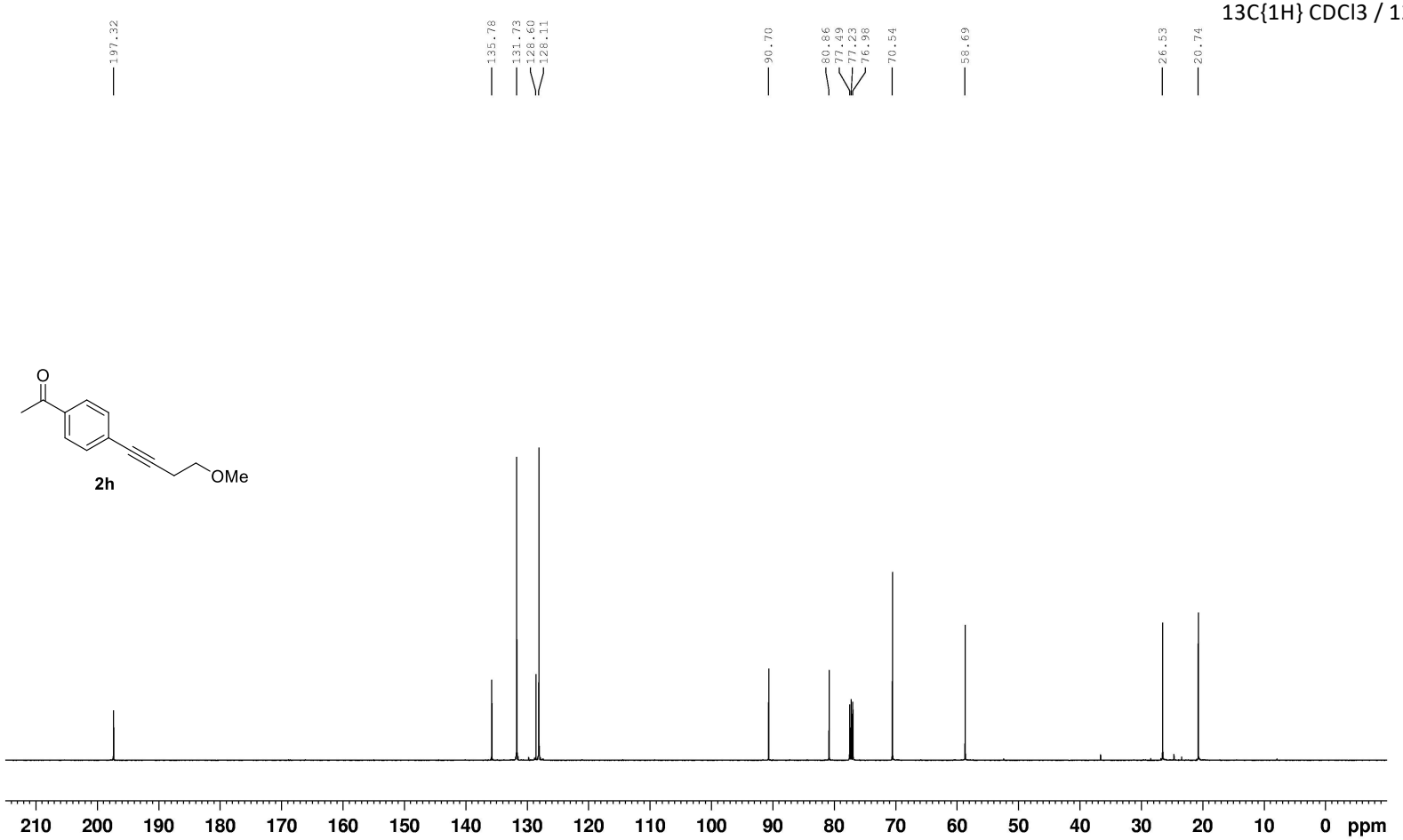
^{19}F NMR $CDCl_3$ / 376MHz



1H NMR CDCl3 / 500 MHz



13C{1H} CDCl3 / 125 MHz



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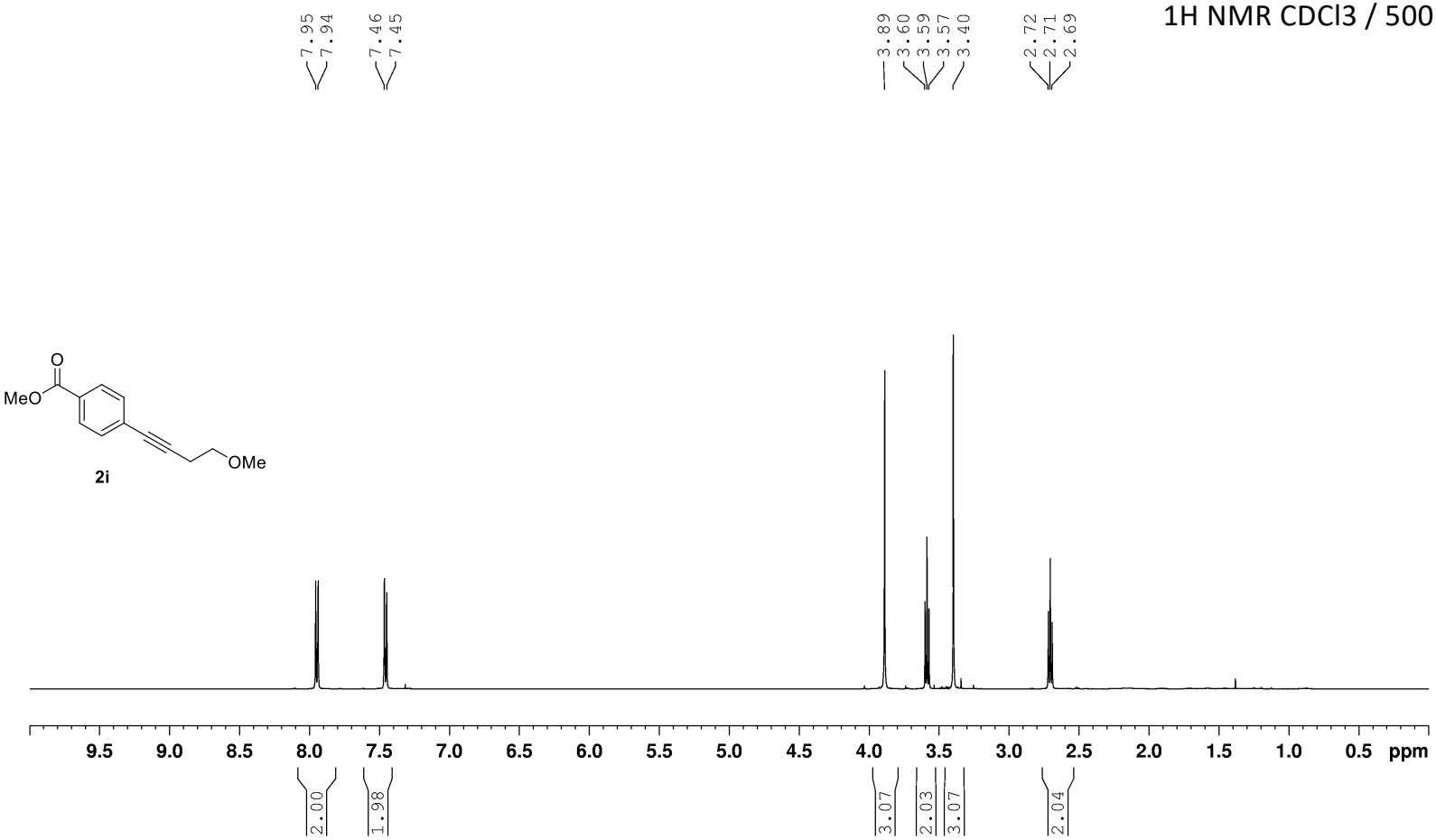
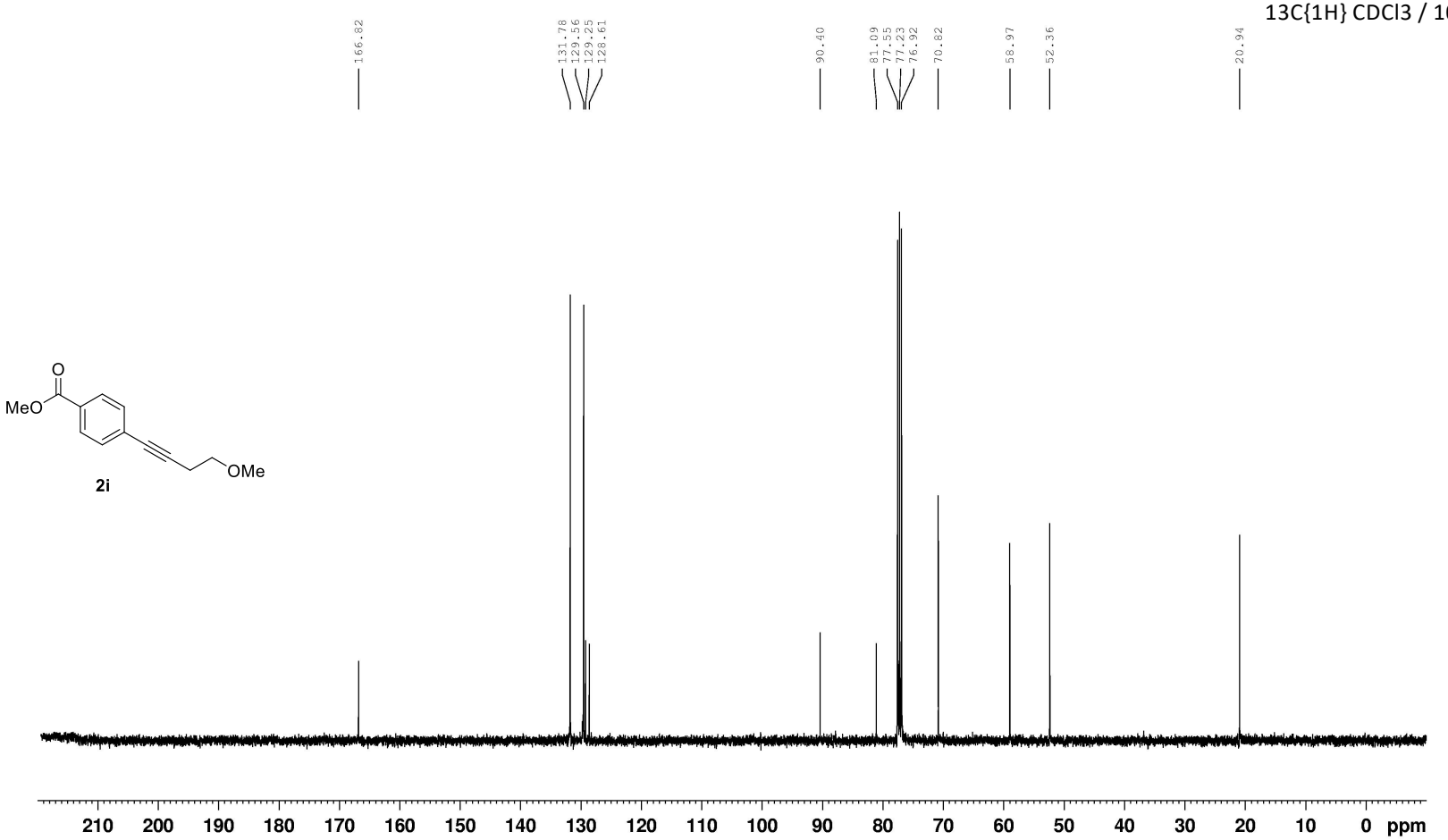
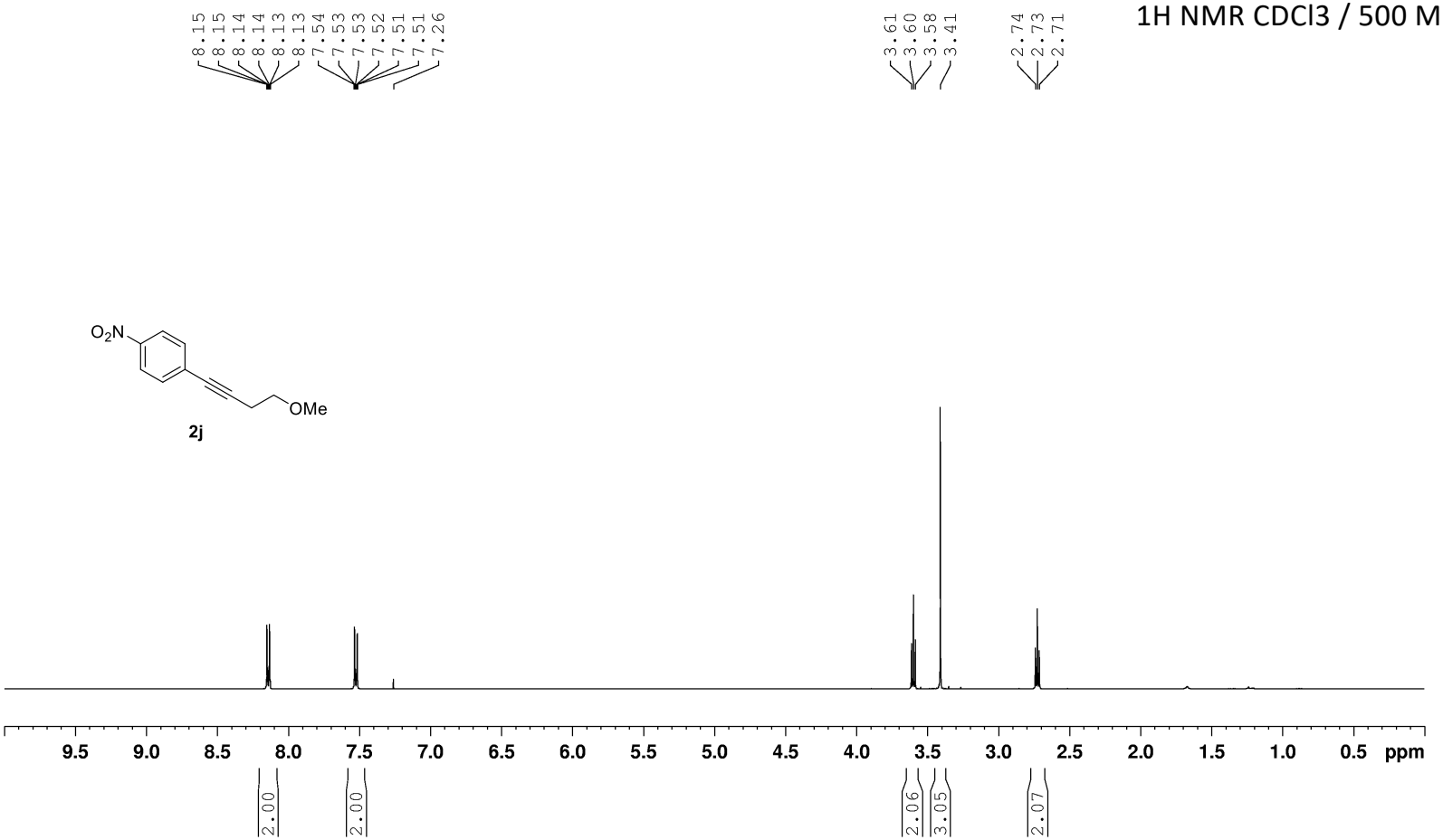


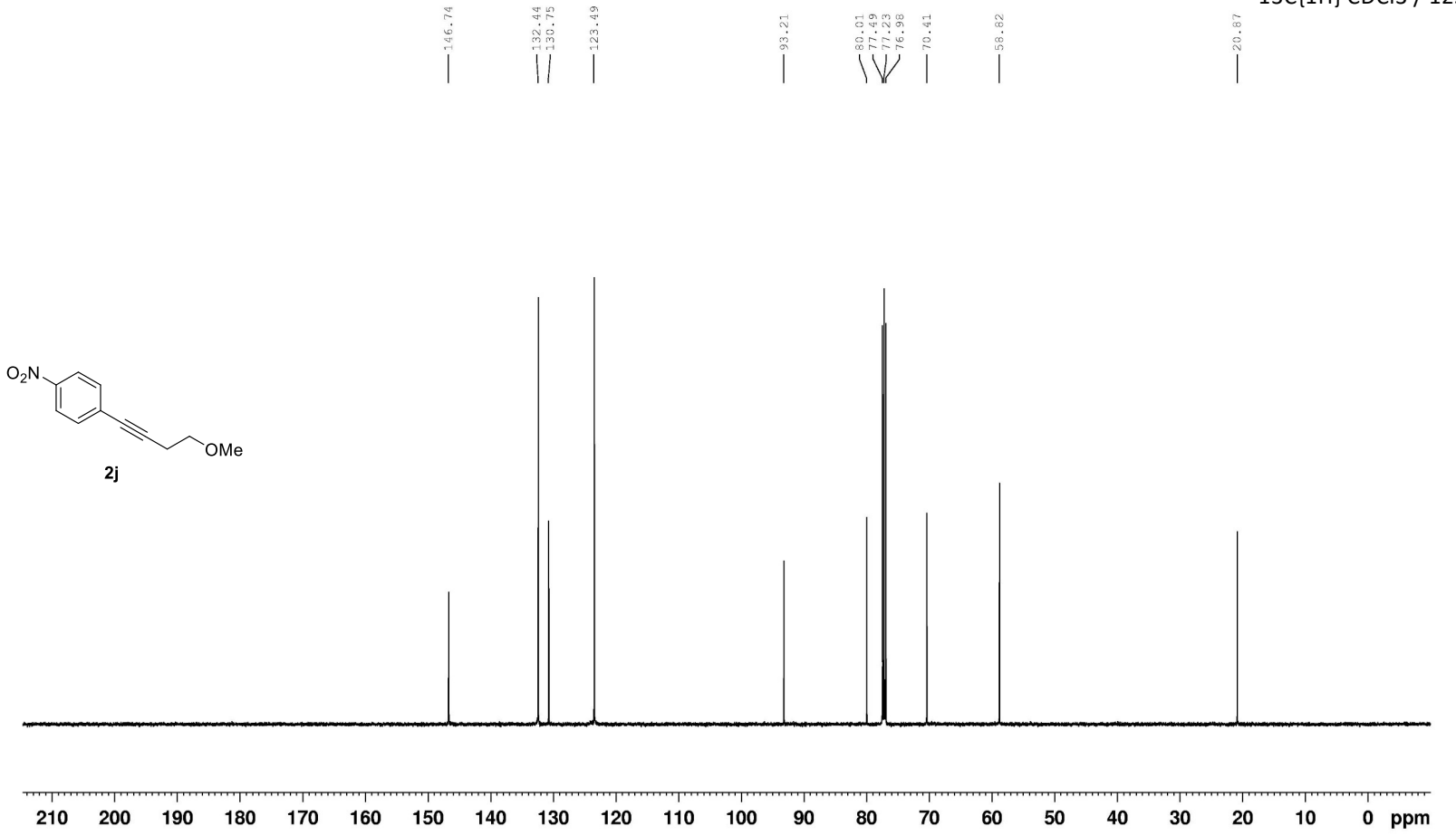
13C{1H} CDCl3 / 100 MHz



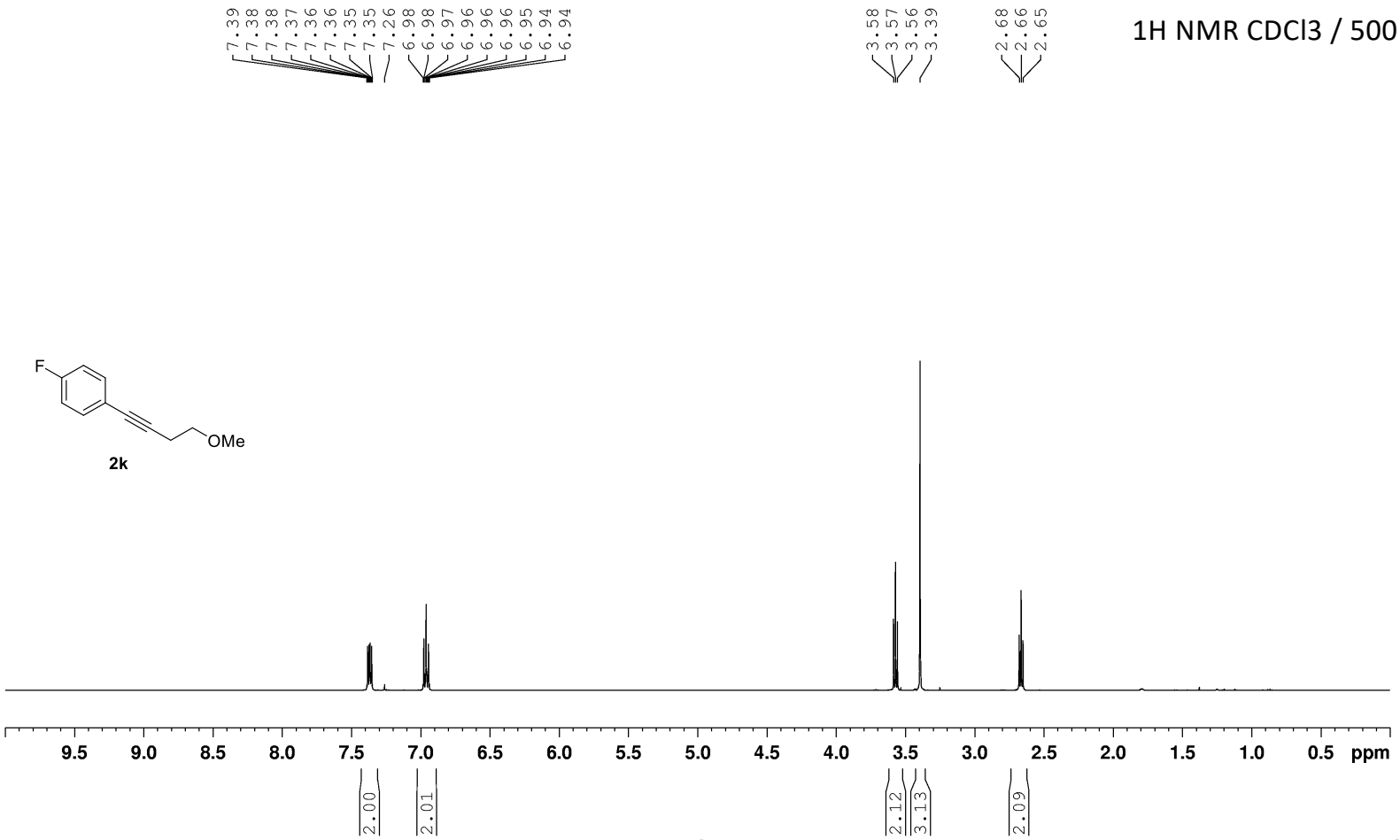
1H NMR CDCl3 / 500 MHz



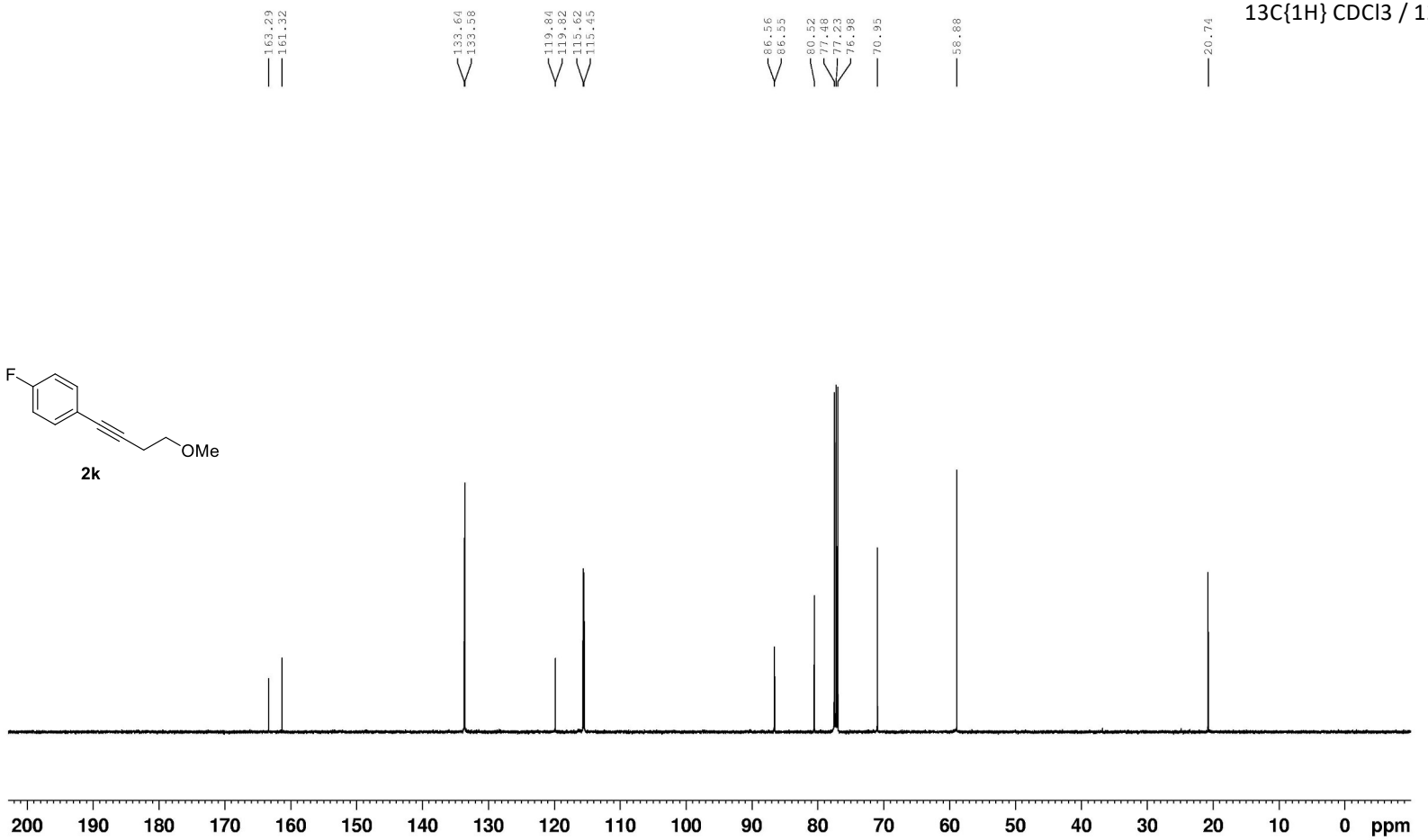
13C{1H} CDCl3 / 125 MHz



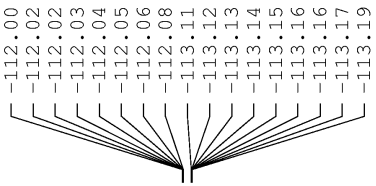
1H NMR CDCl3 / 500 MHz

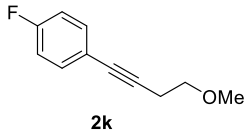


13C{1H} CDCl3 / 125 MHz

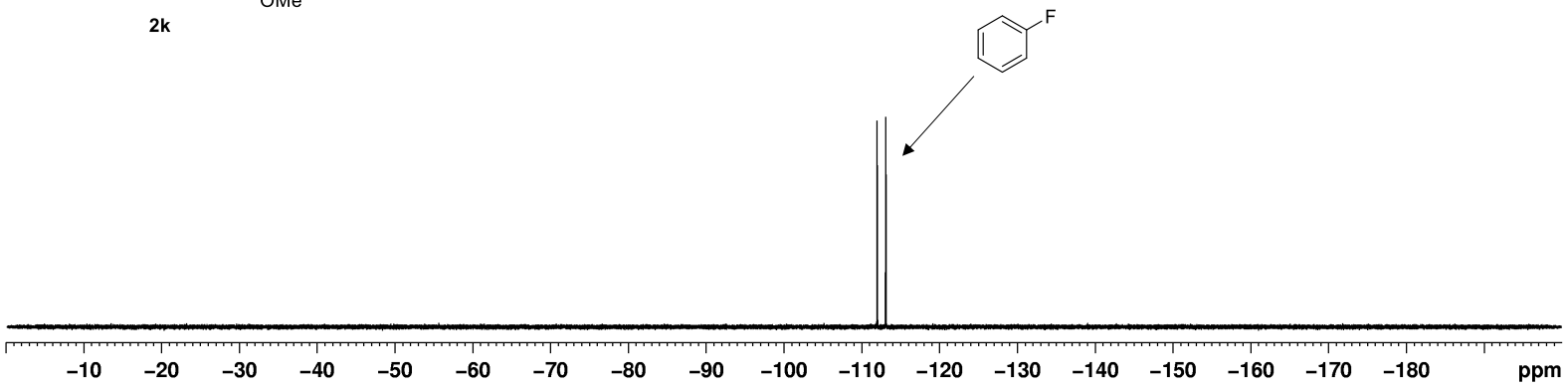


^{19}F NMR $CDCl_3$ / 376MHz

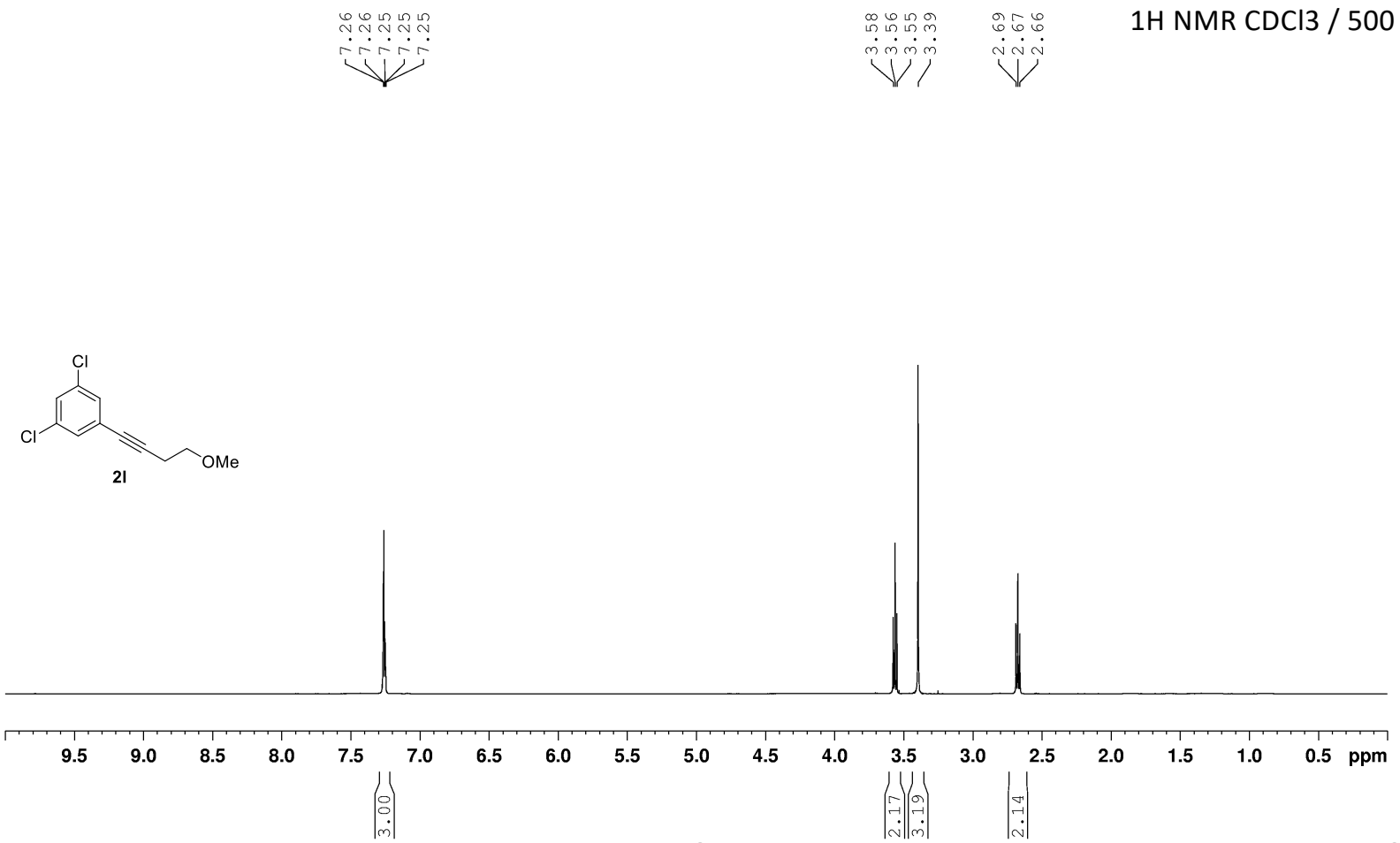




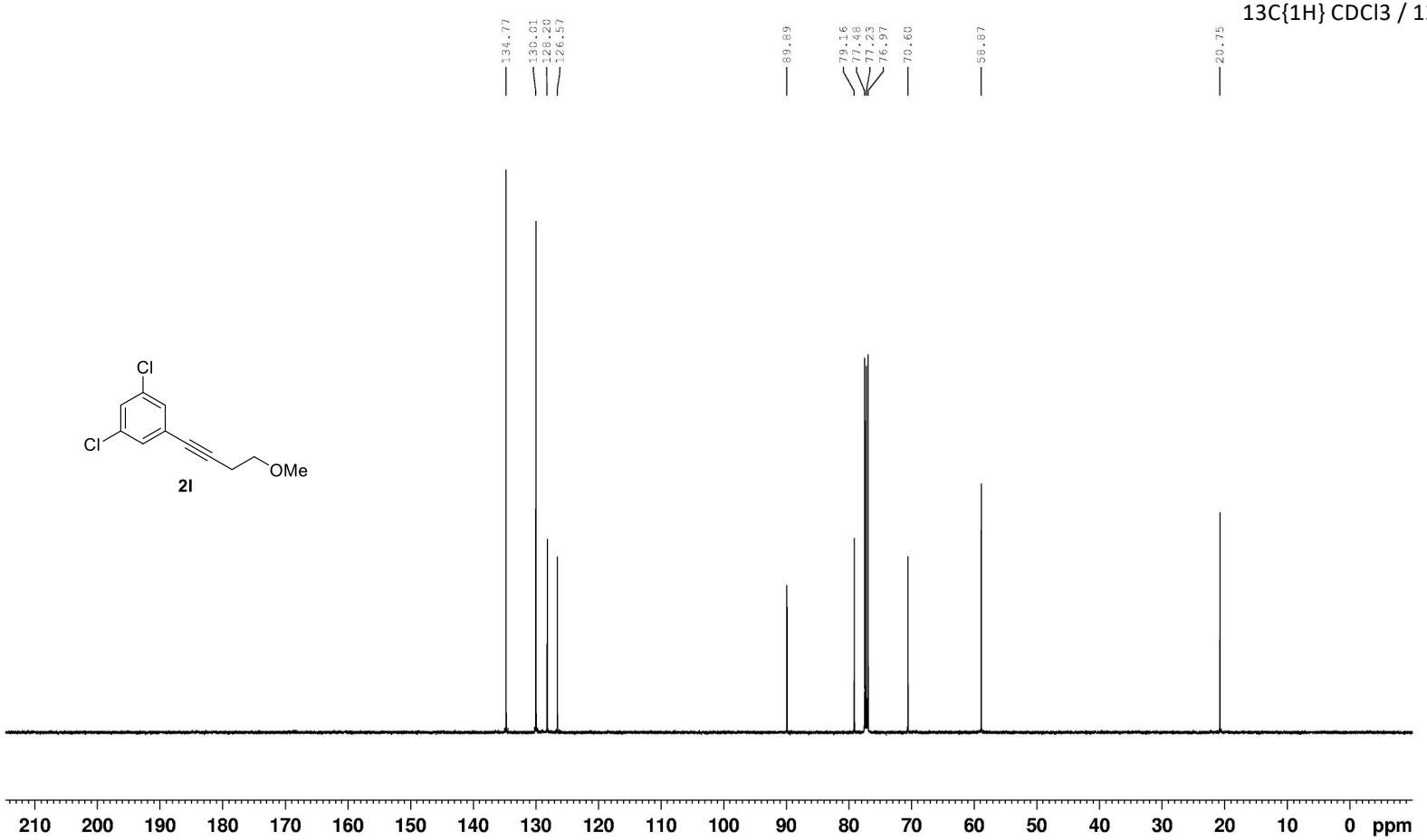
2k



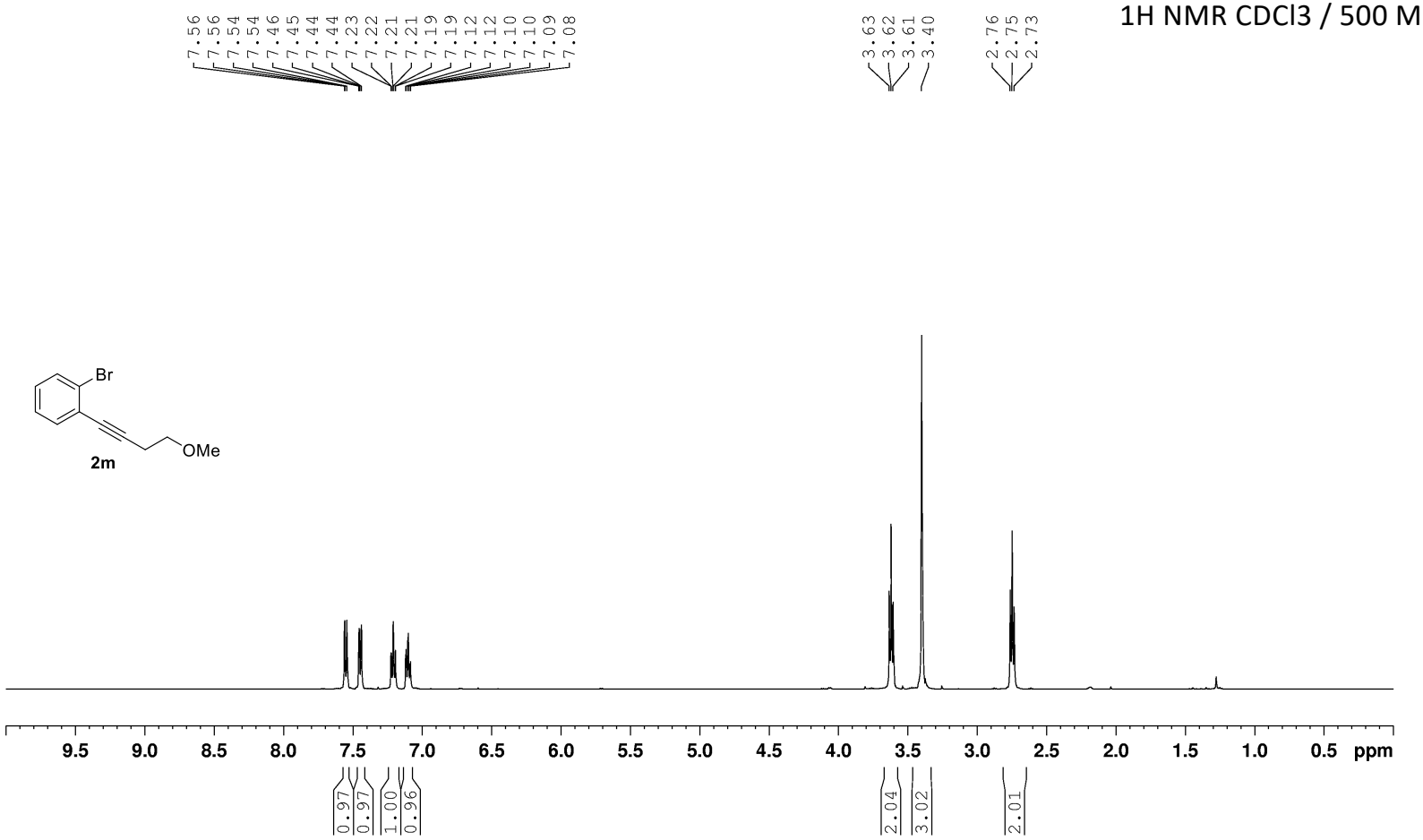
1H NMR CDCl3 / 500 MHz



13C{1H} CDCl3 / 125 MHz



1H NMR CDCl3 / 500 MHz



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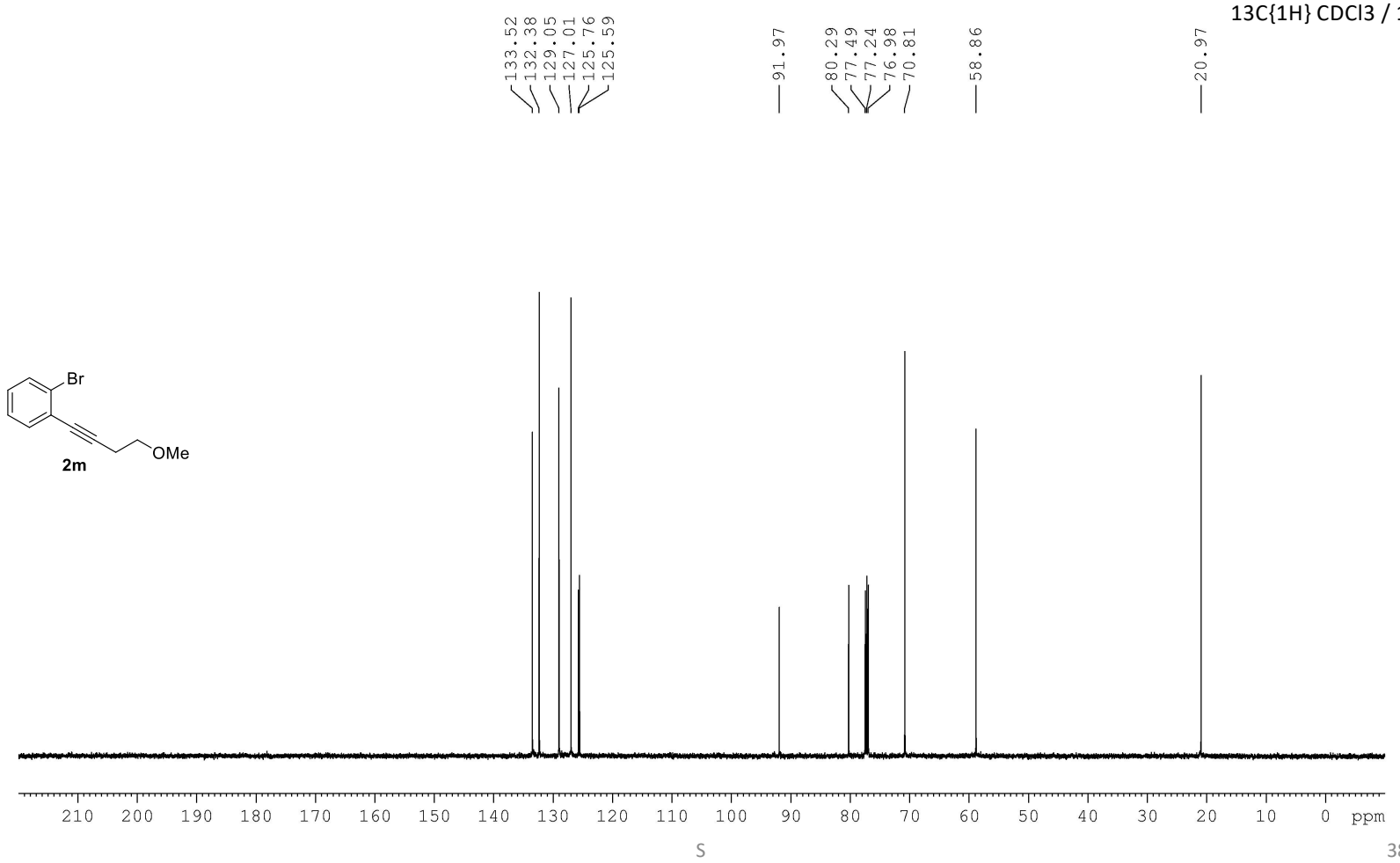
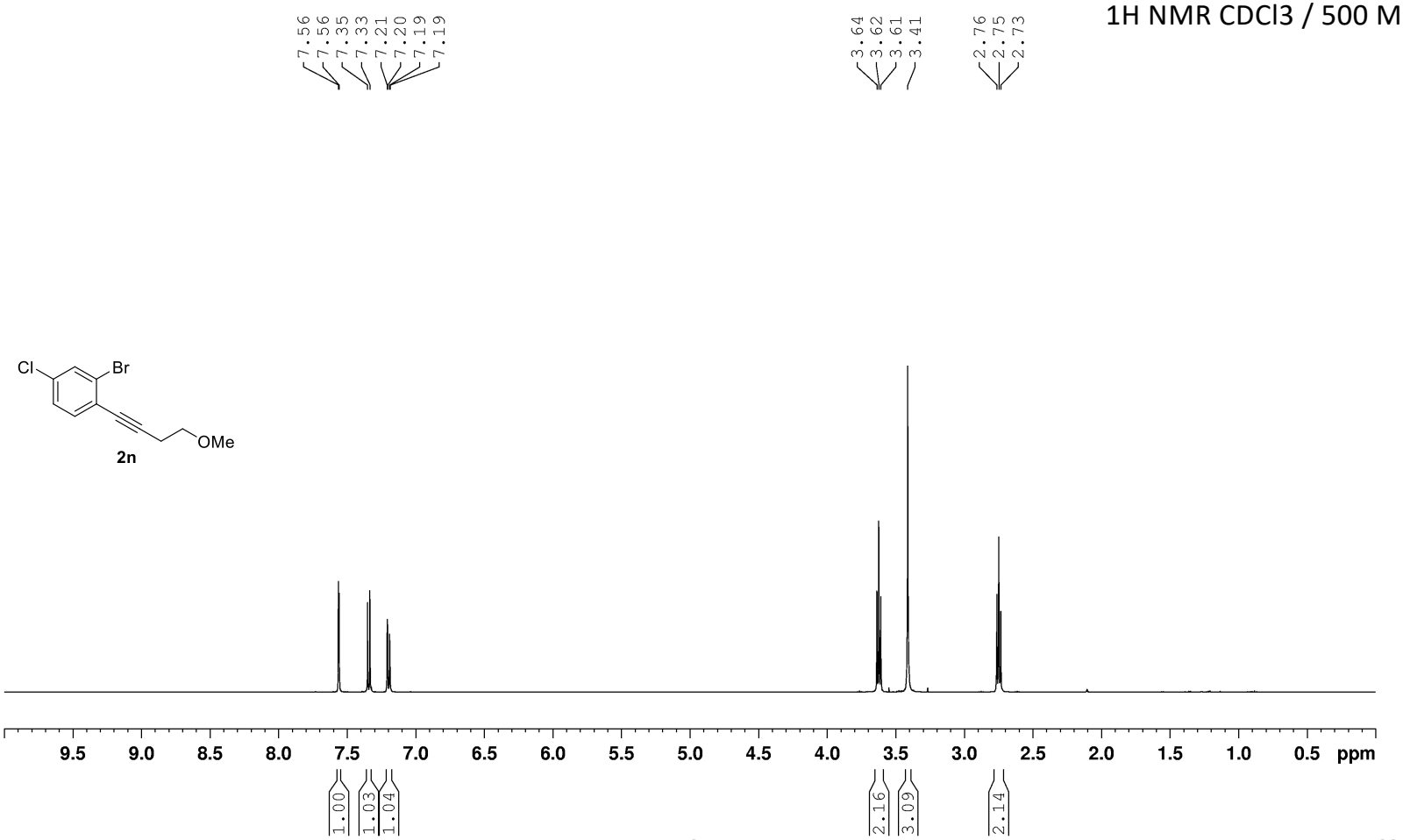
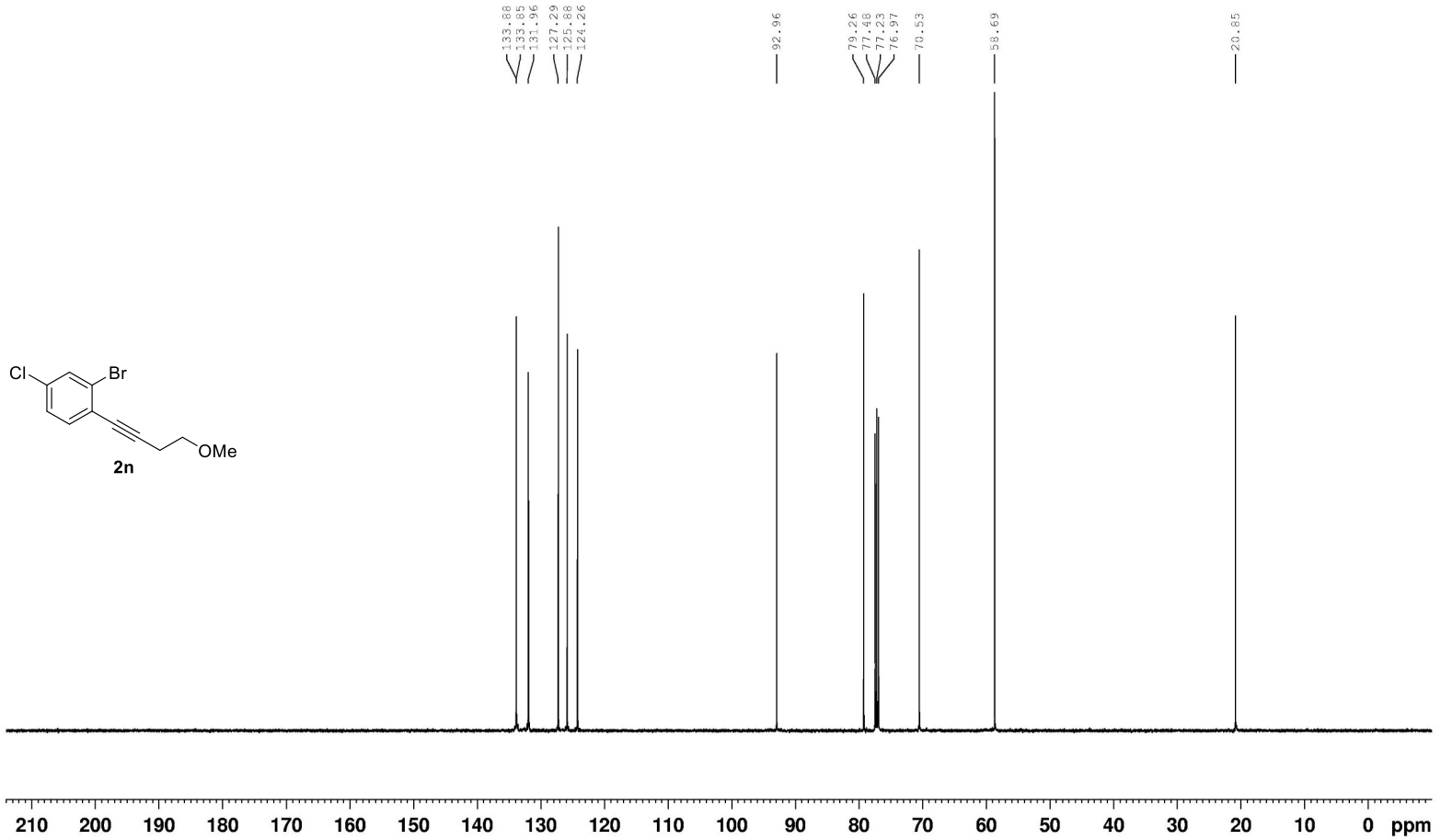


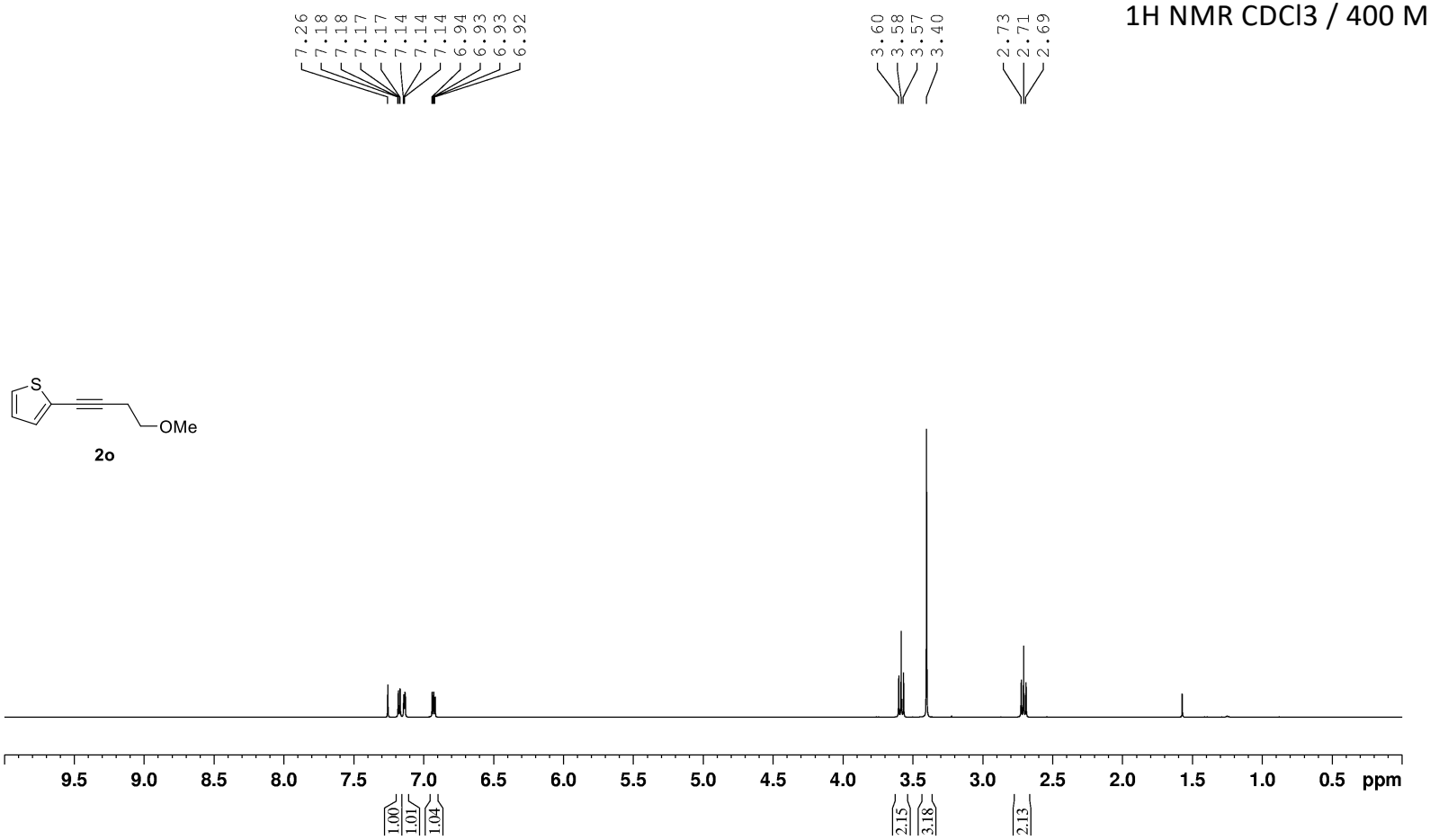
1H NMR CDCl3 / 500 MHz



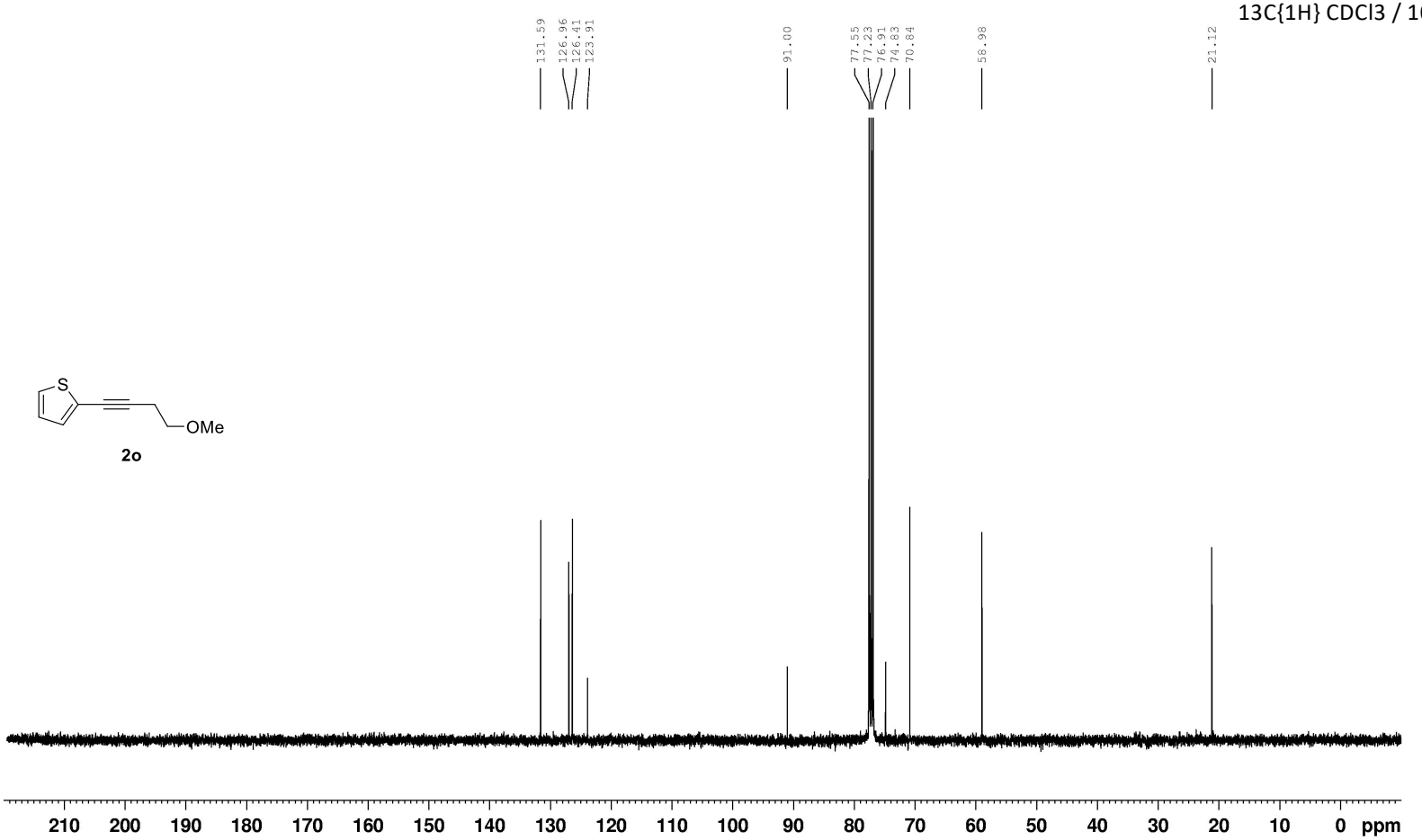
13C{1H} CDCl3 / 125 MHz



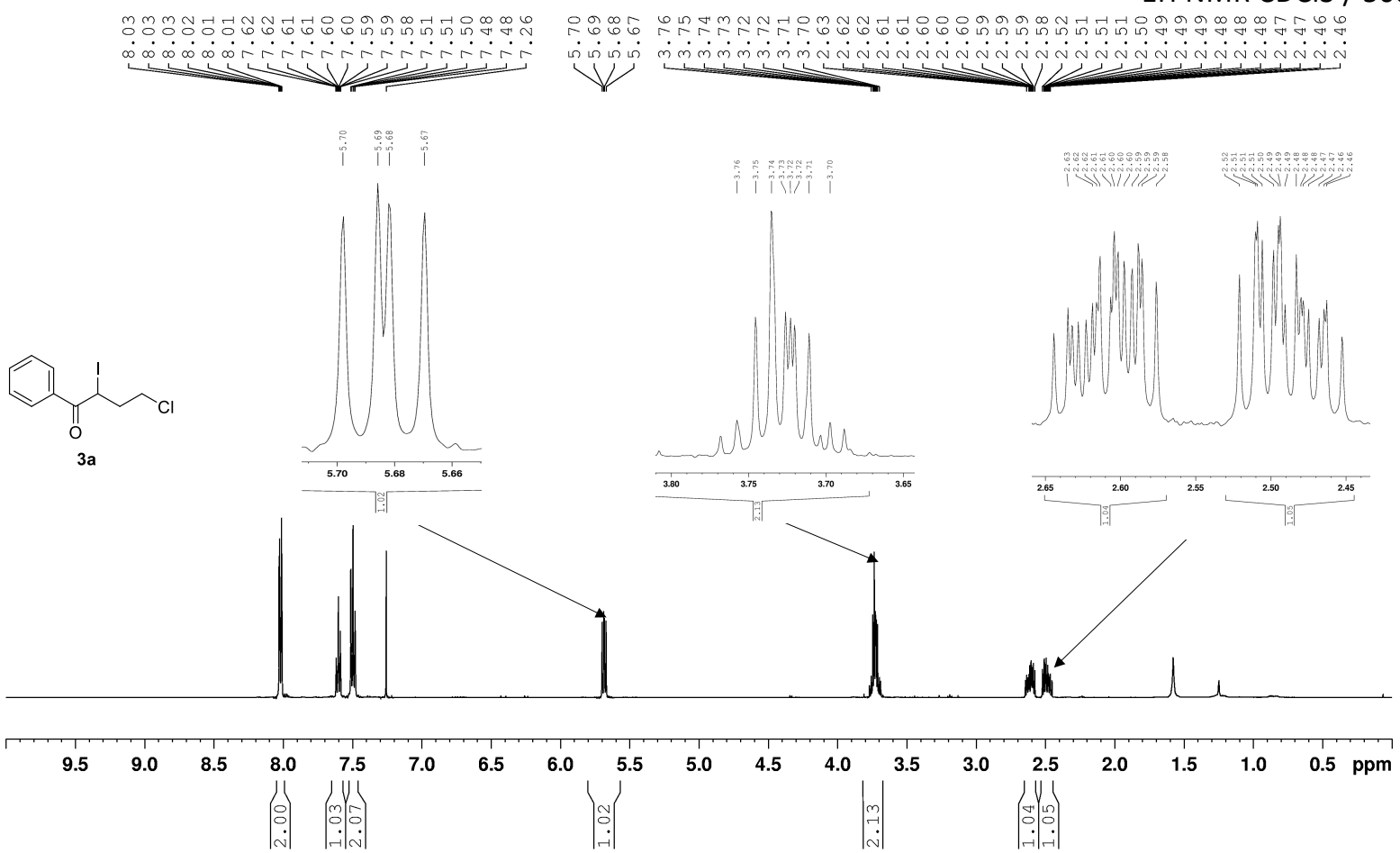
1H NMR CDCl3 / 400 MHz



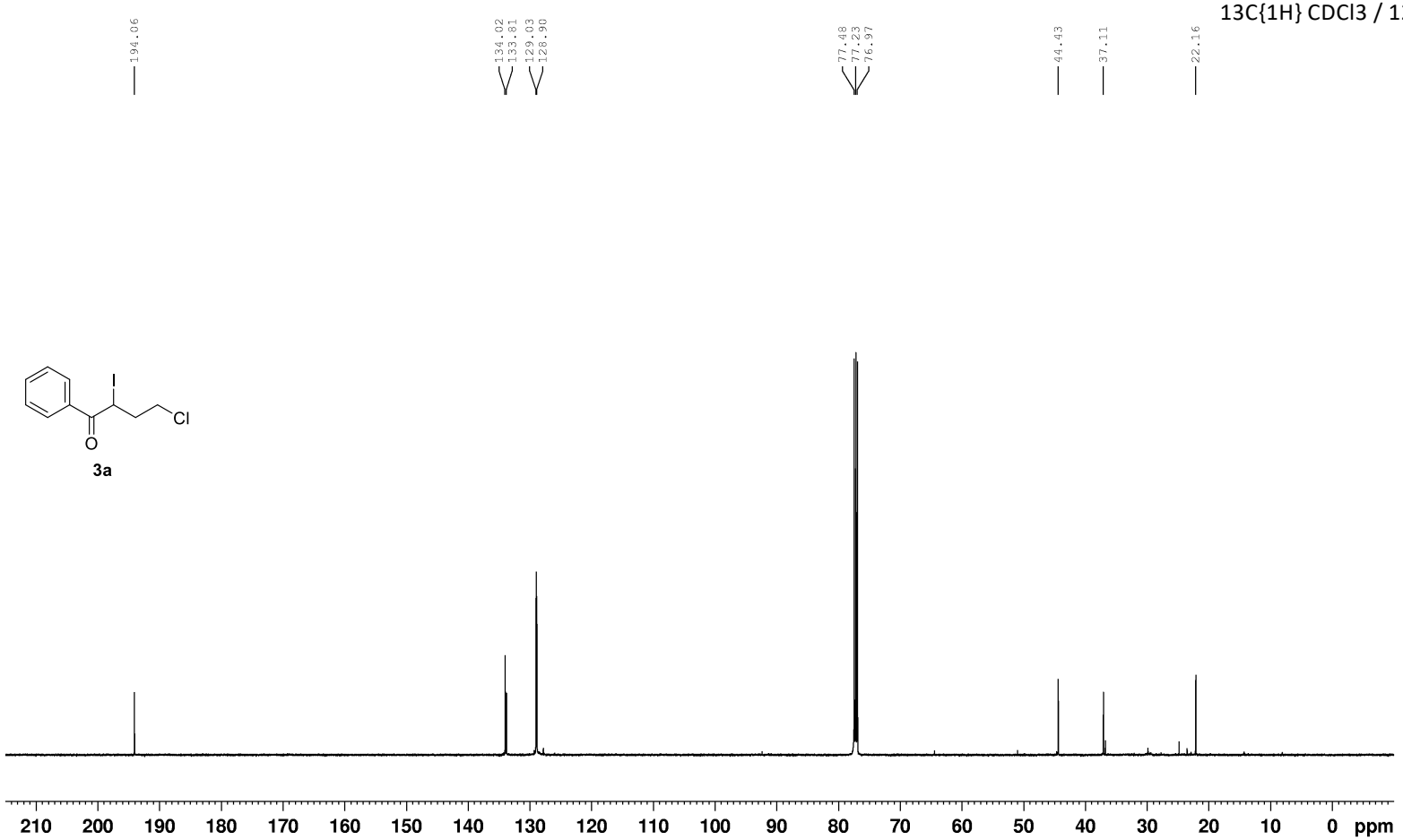
13C{1H} CDCl3 / 100 MHz



1H NMR CDCl3 / 500 MHz



13C{1H} CDCl3 / 125 MHz



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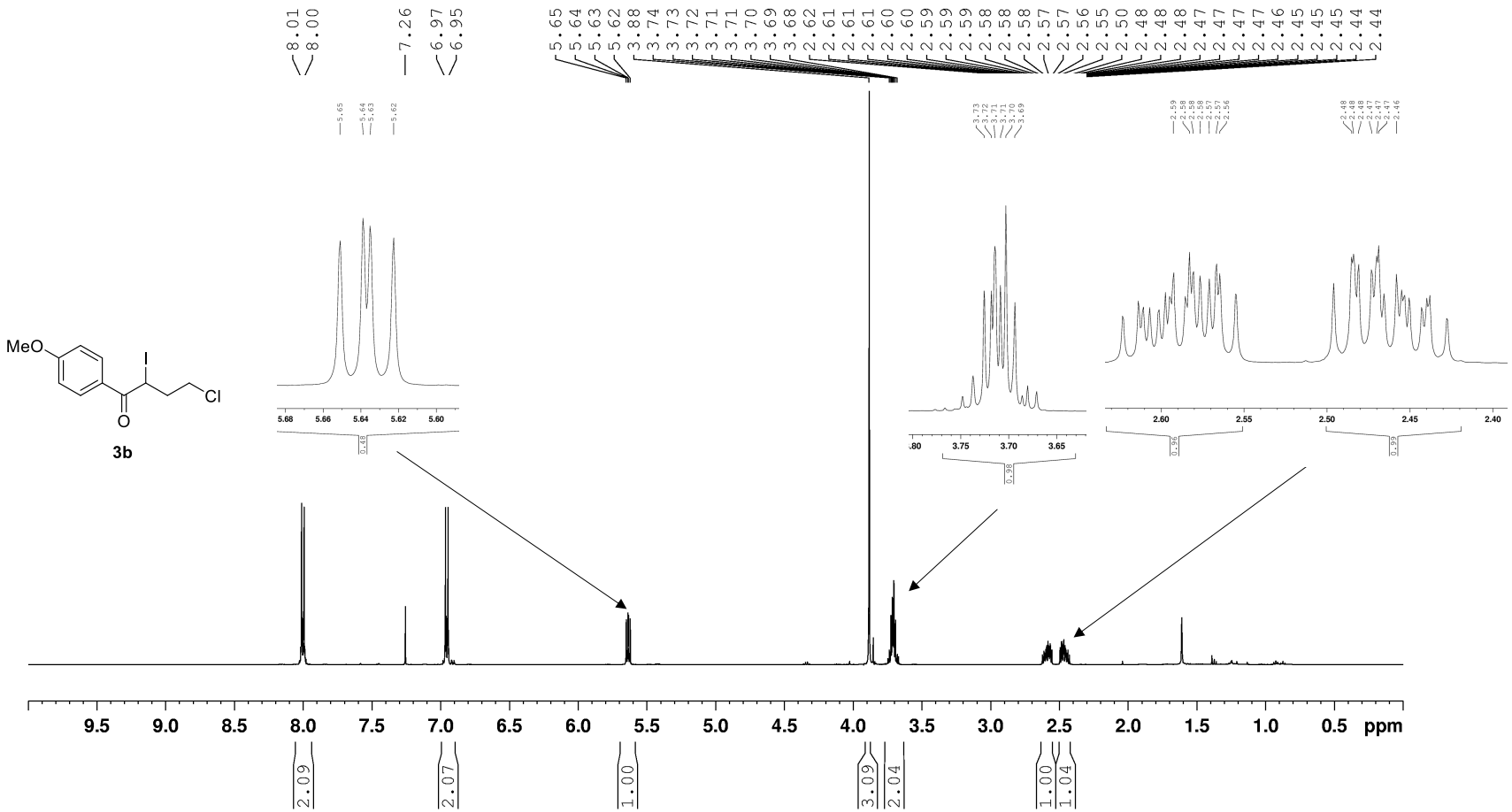
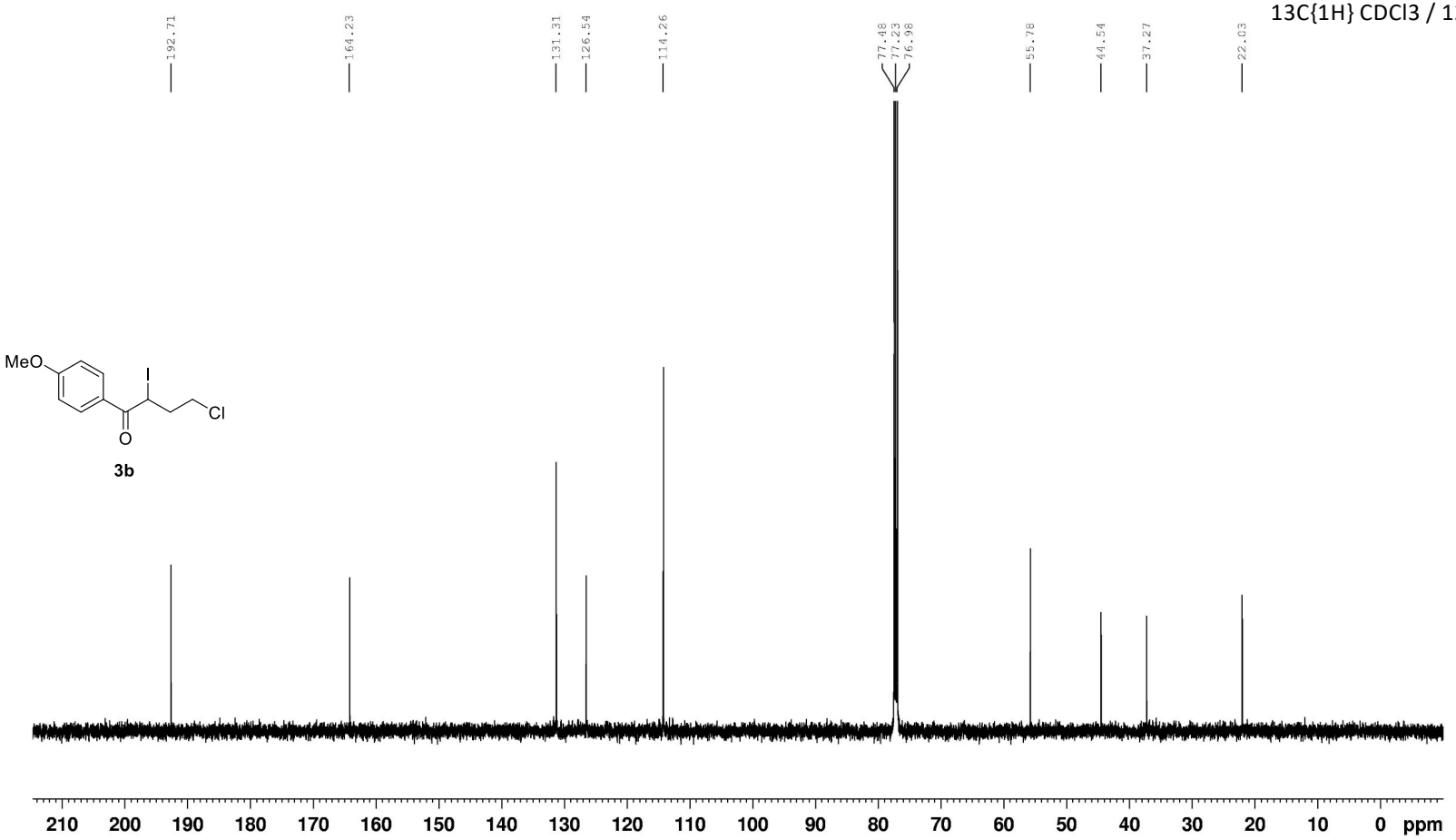


13C{1H} CDCl3 / 125 MHz



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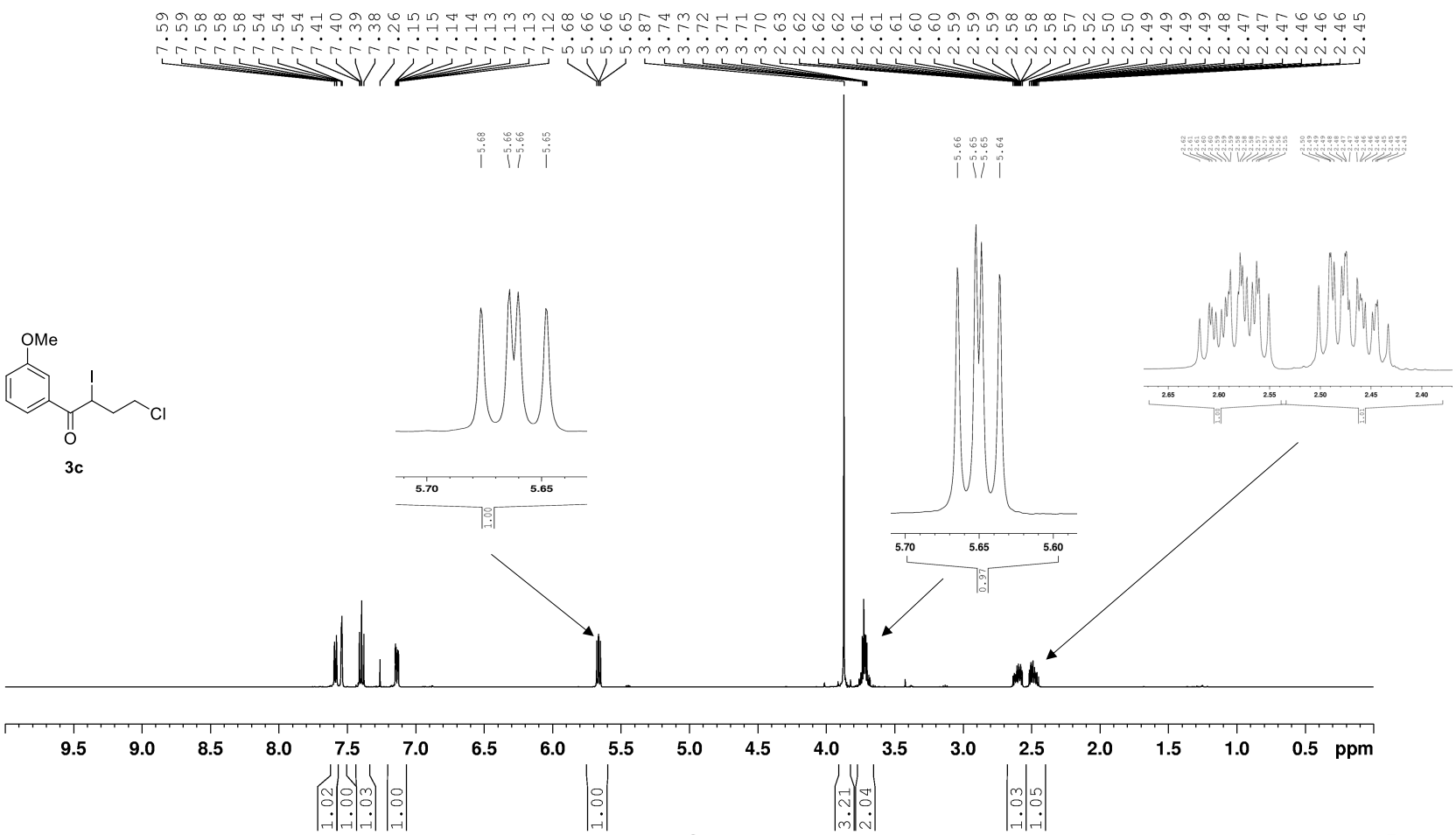

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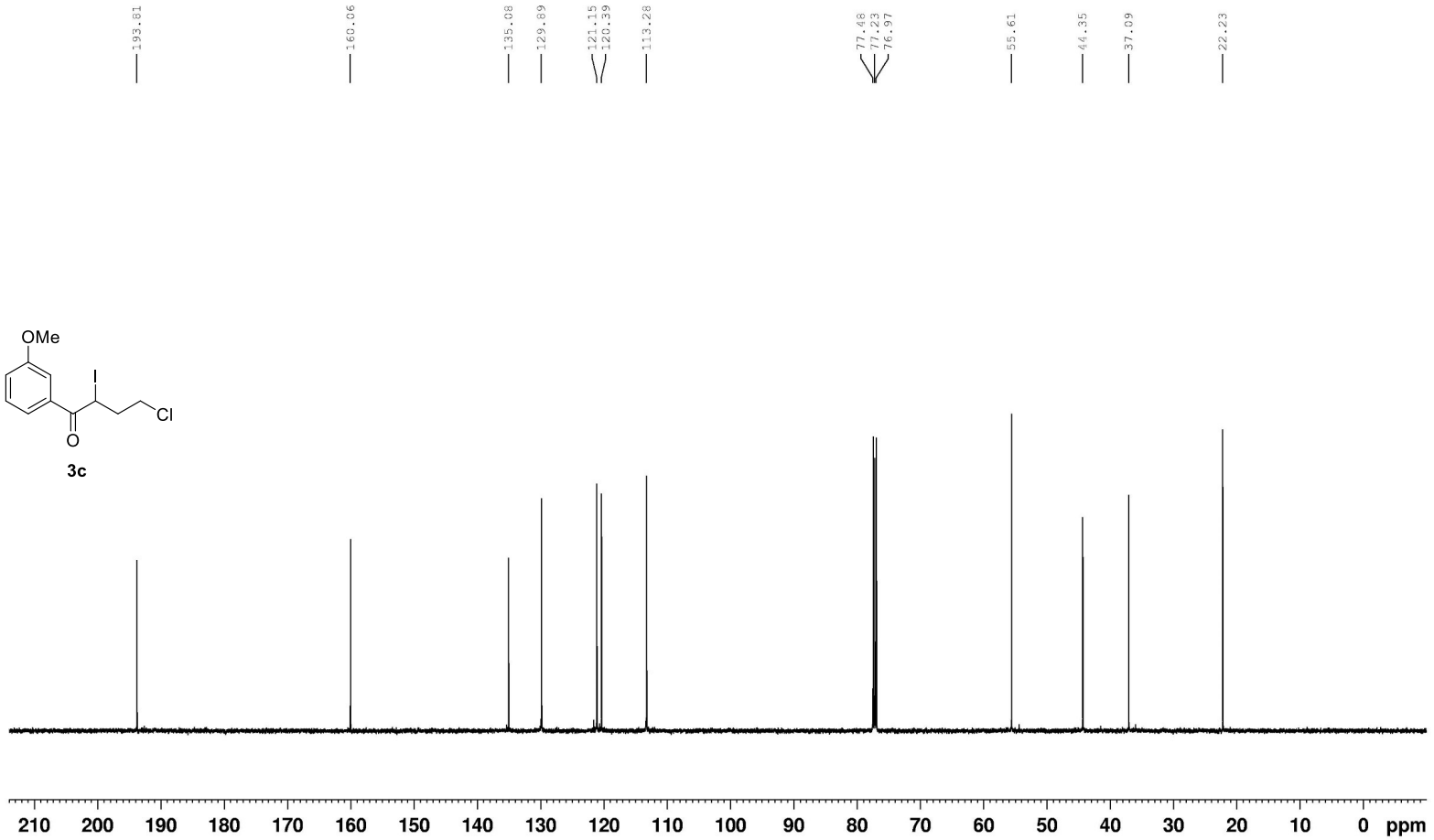

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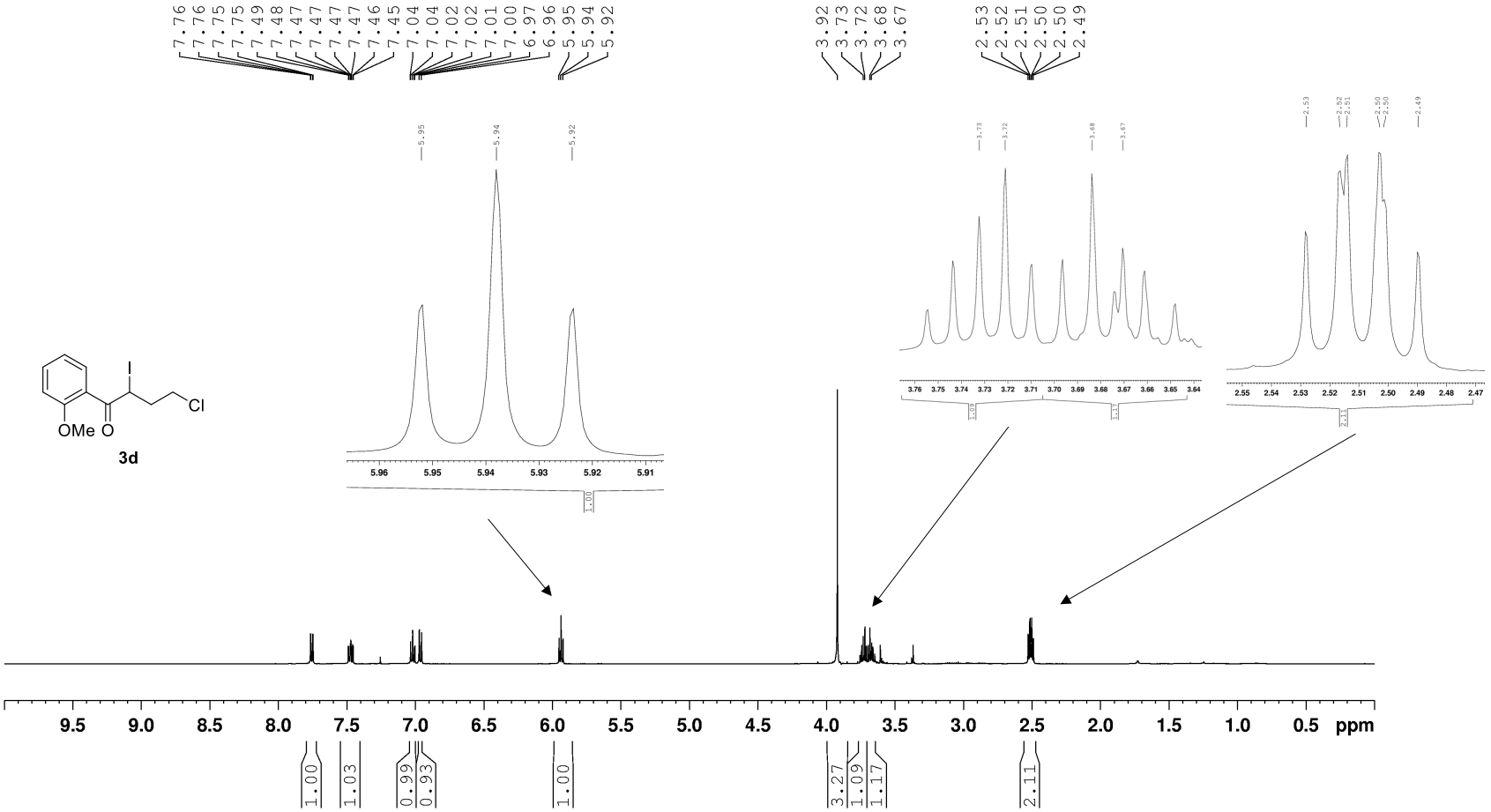

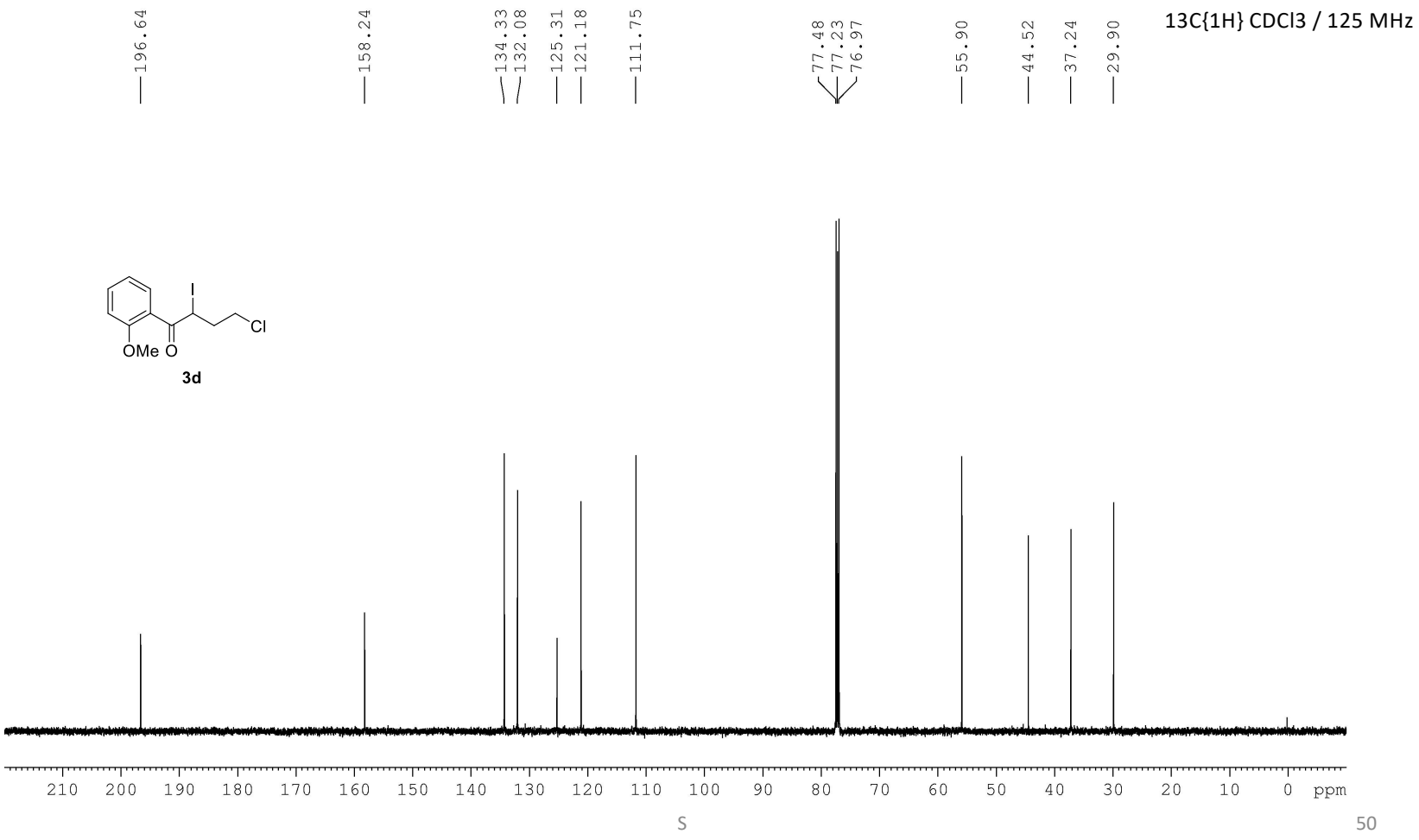
196.64
158.24
134.33
132.08
125.31
121.18
111.75
77.48
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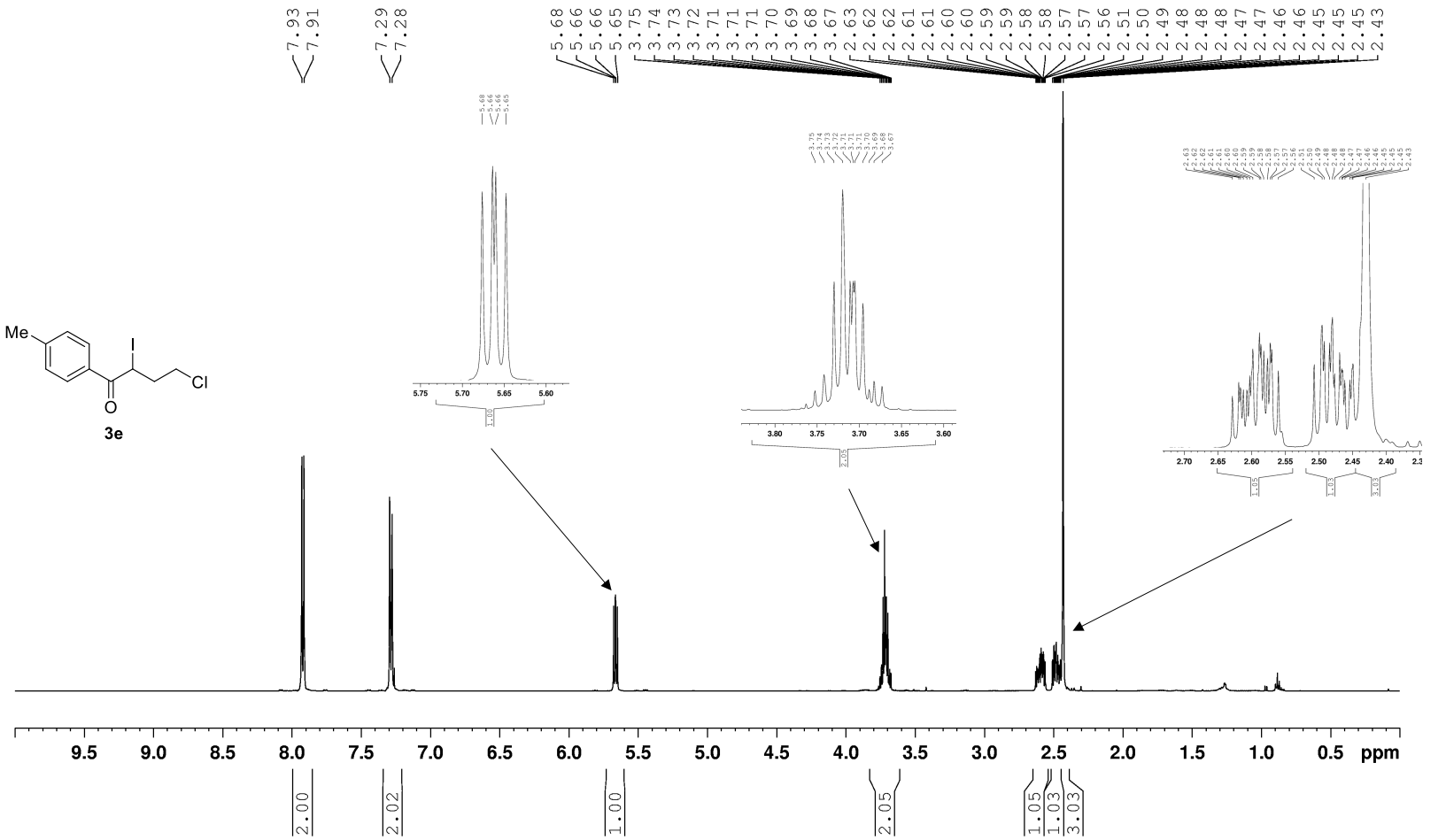
76.97
55.90
44.52
37.24
29.90
13C{1H} CDCl3 / 125 MHz
I
Cl
OMe O
3d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

1H NMR CDCl3 / 500 MHz



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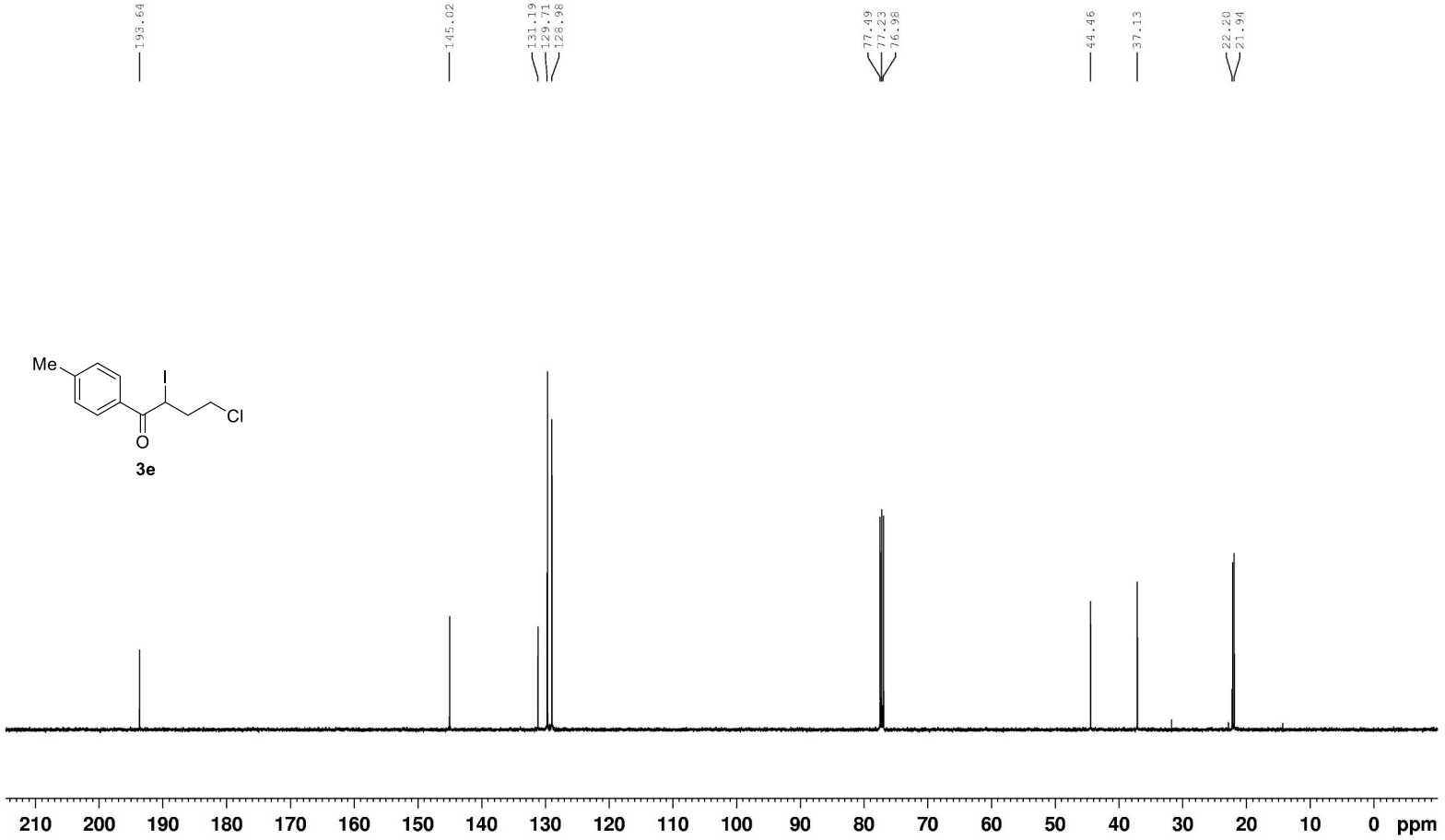

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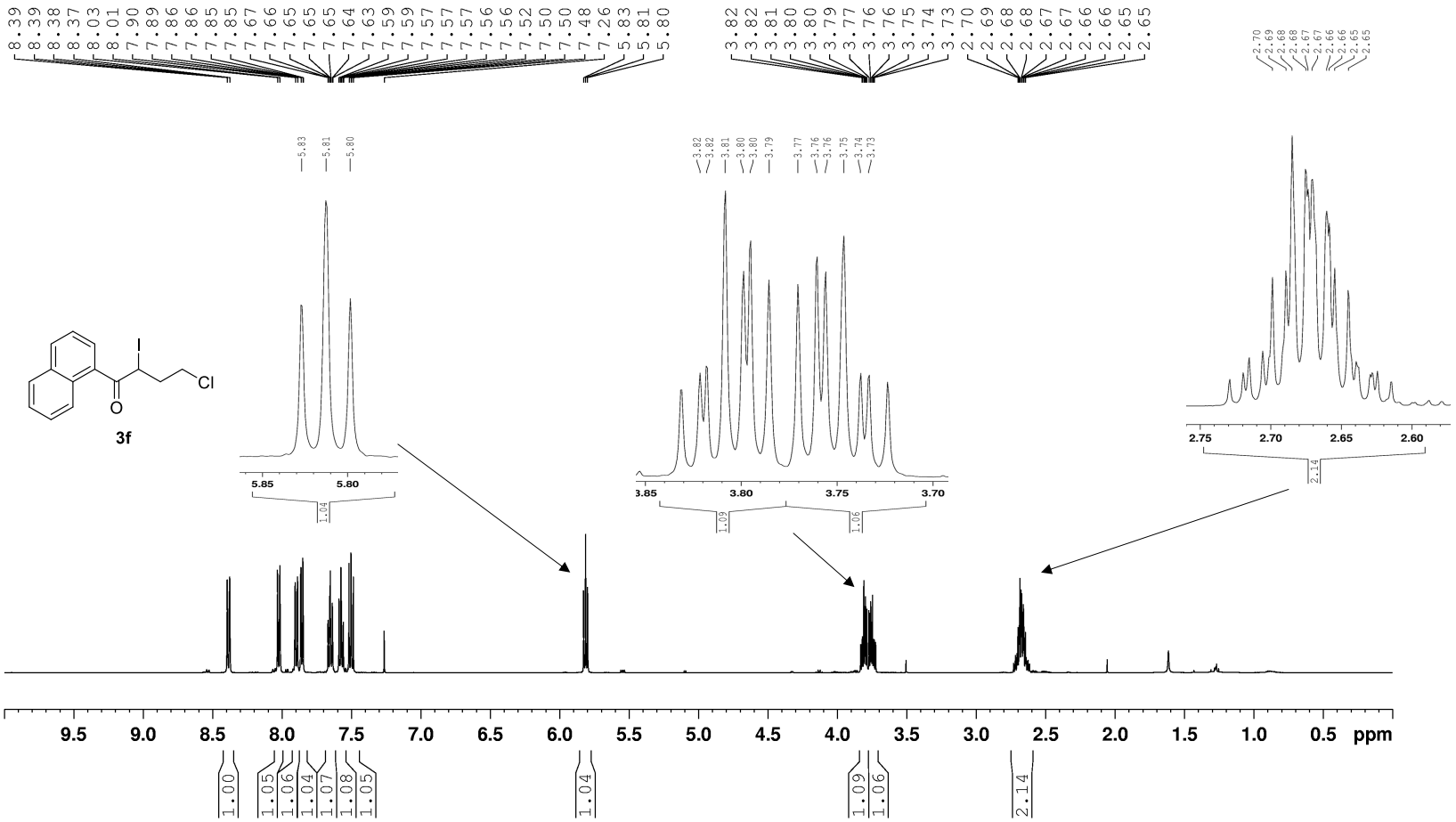

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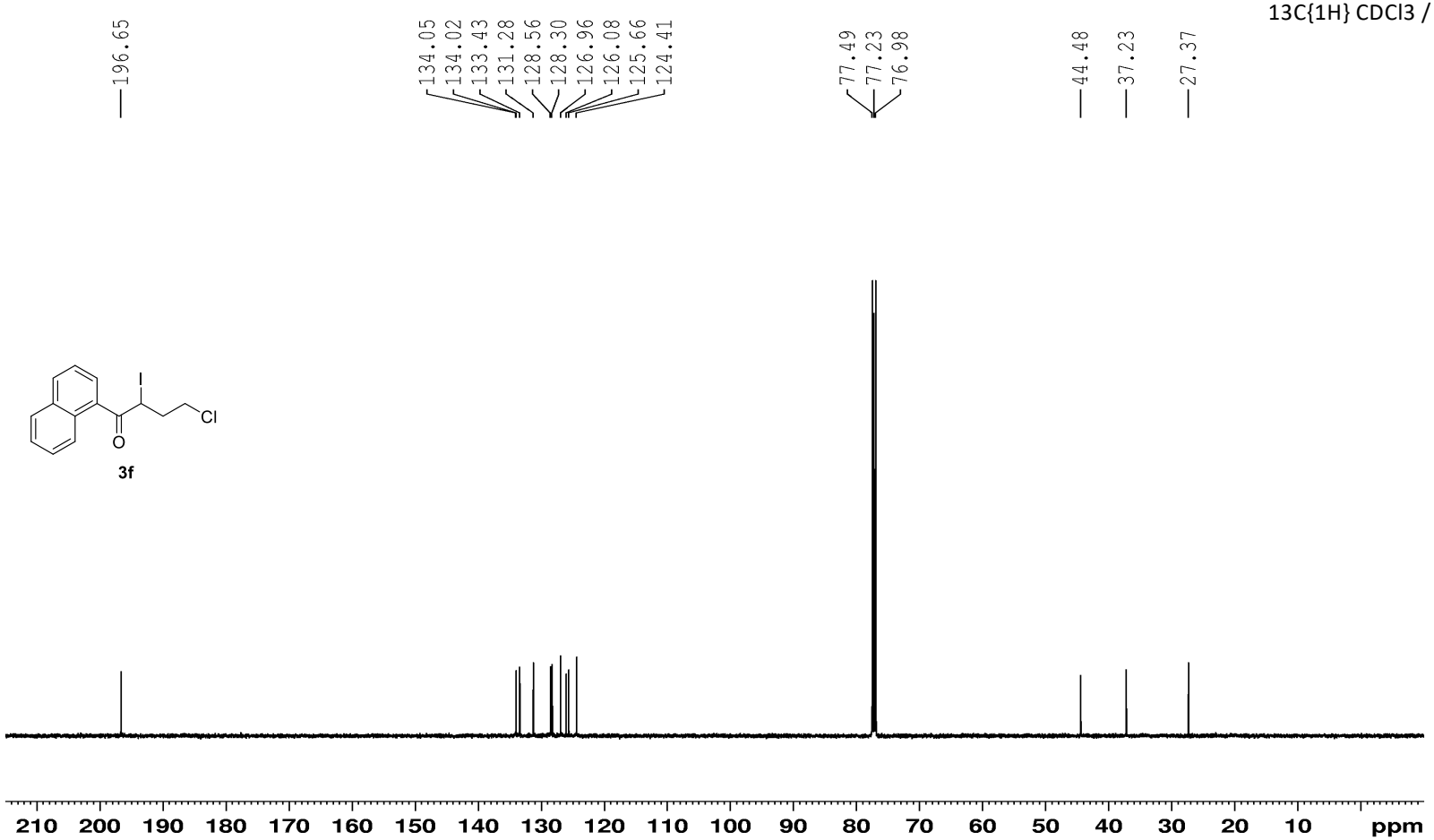

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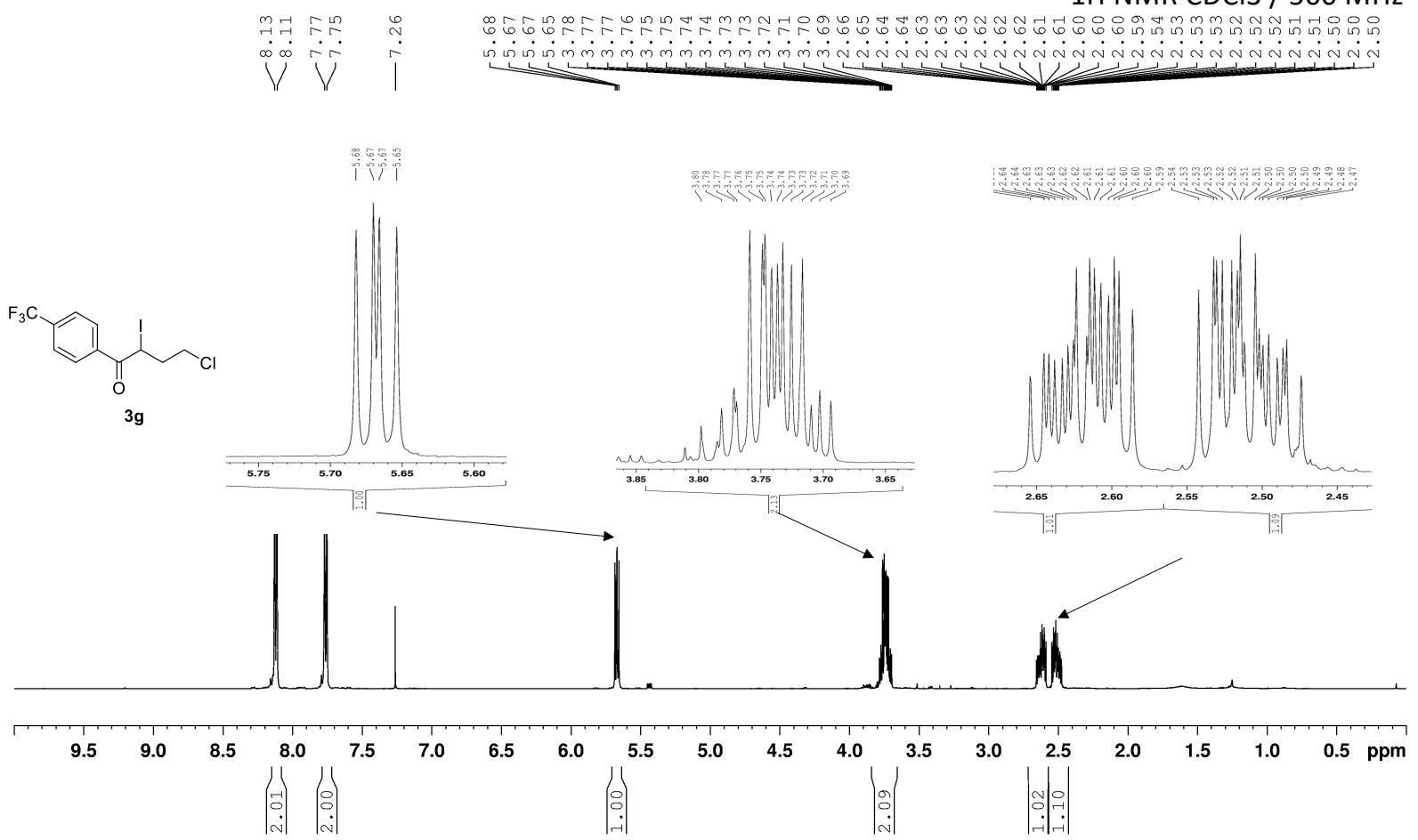
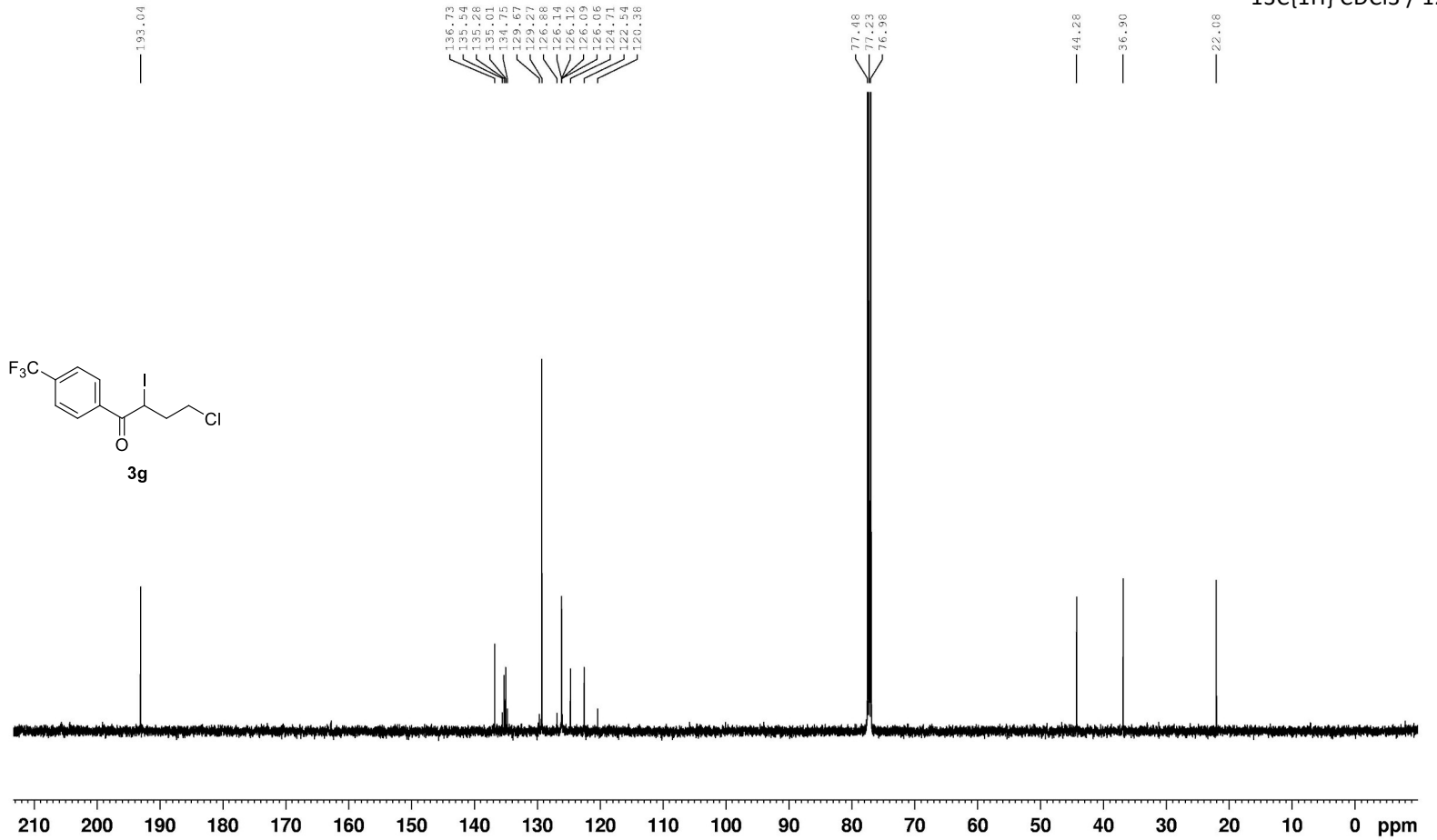
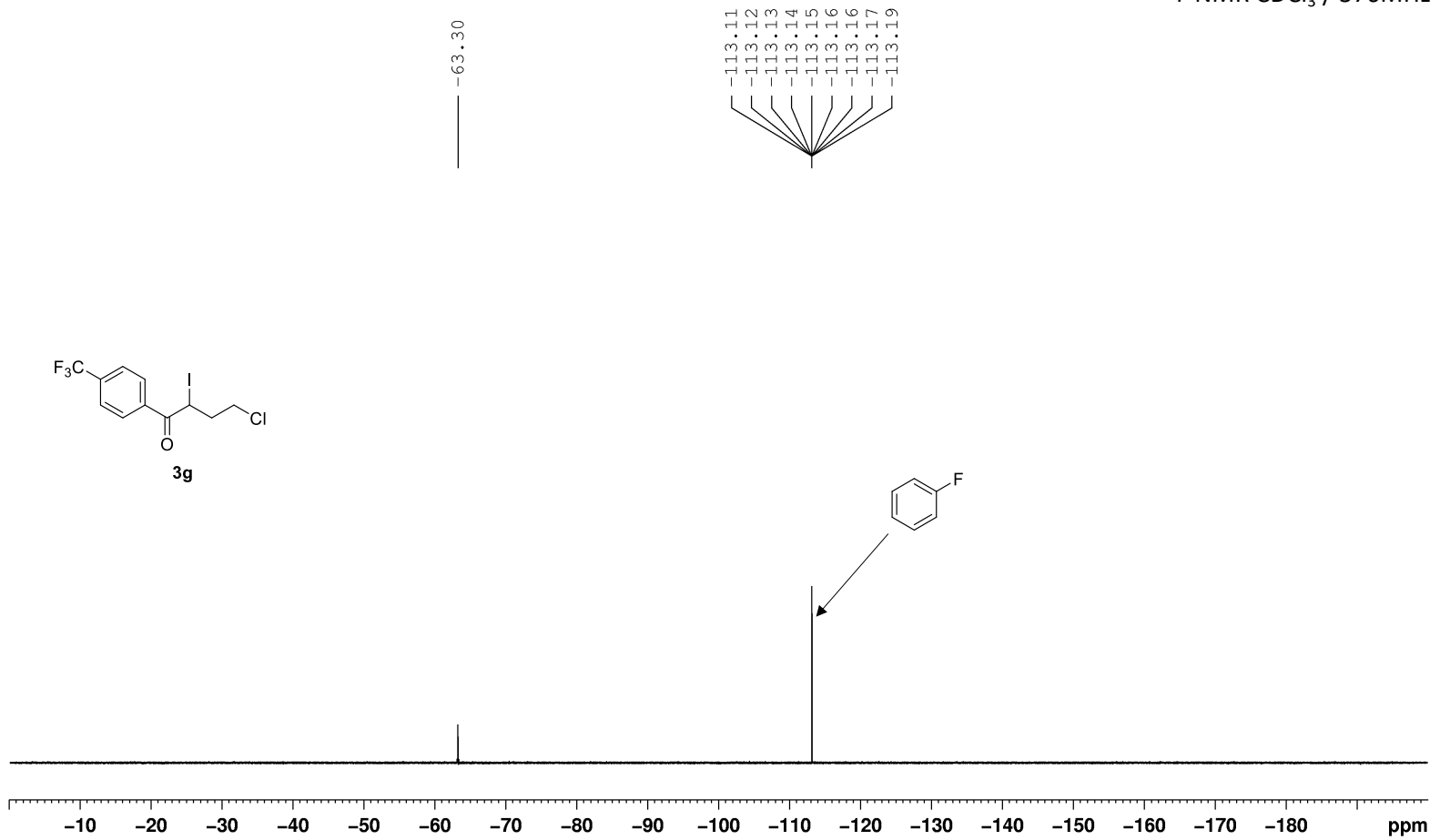


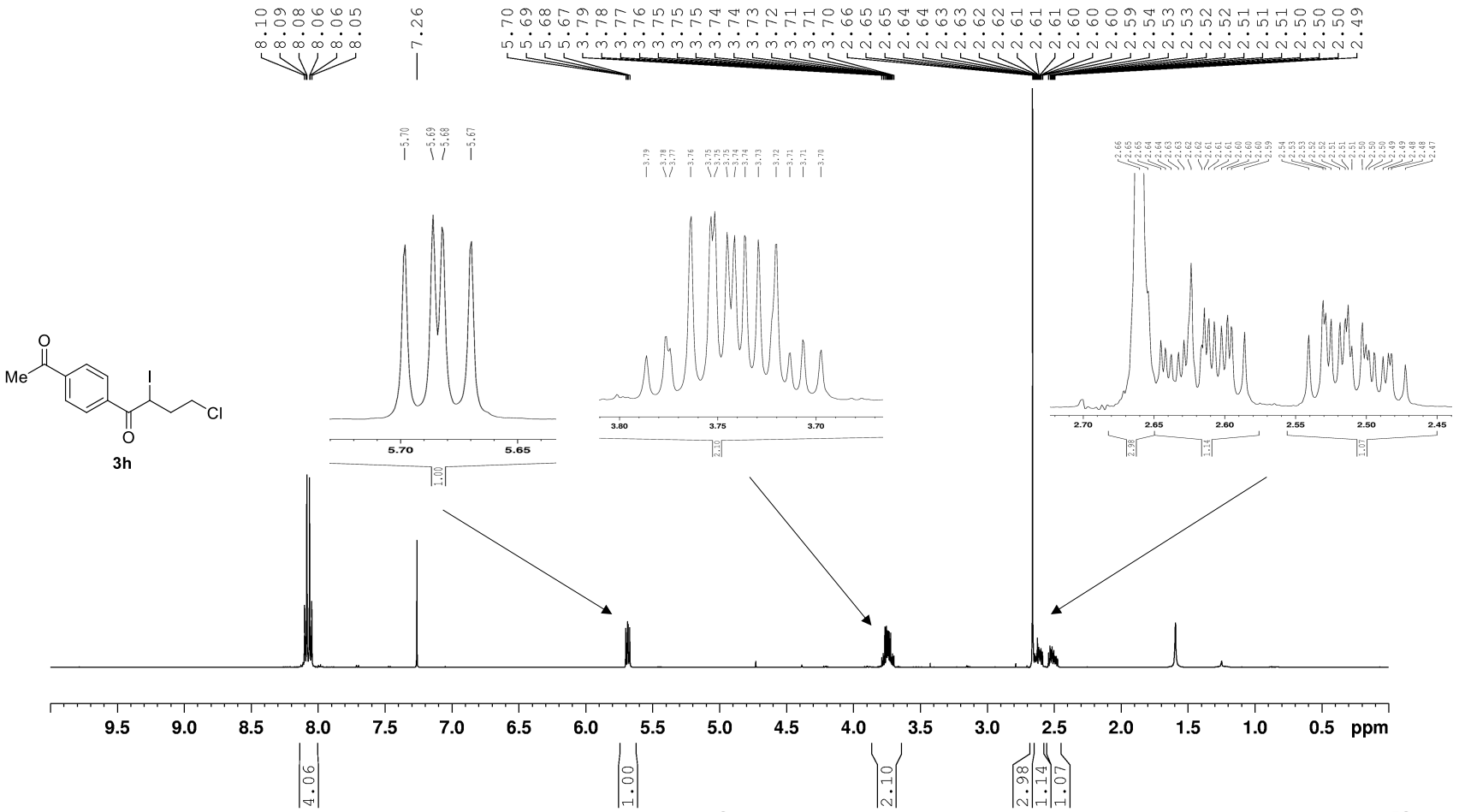
13C{1H} CDCl3 / 125 MHz



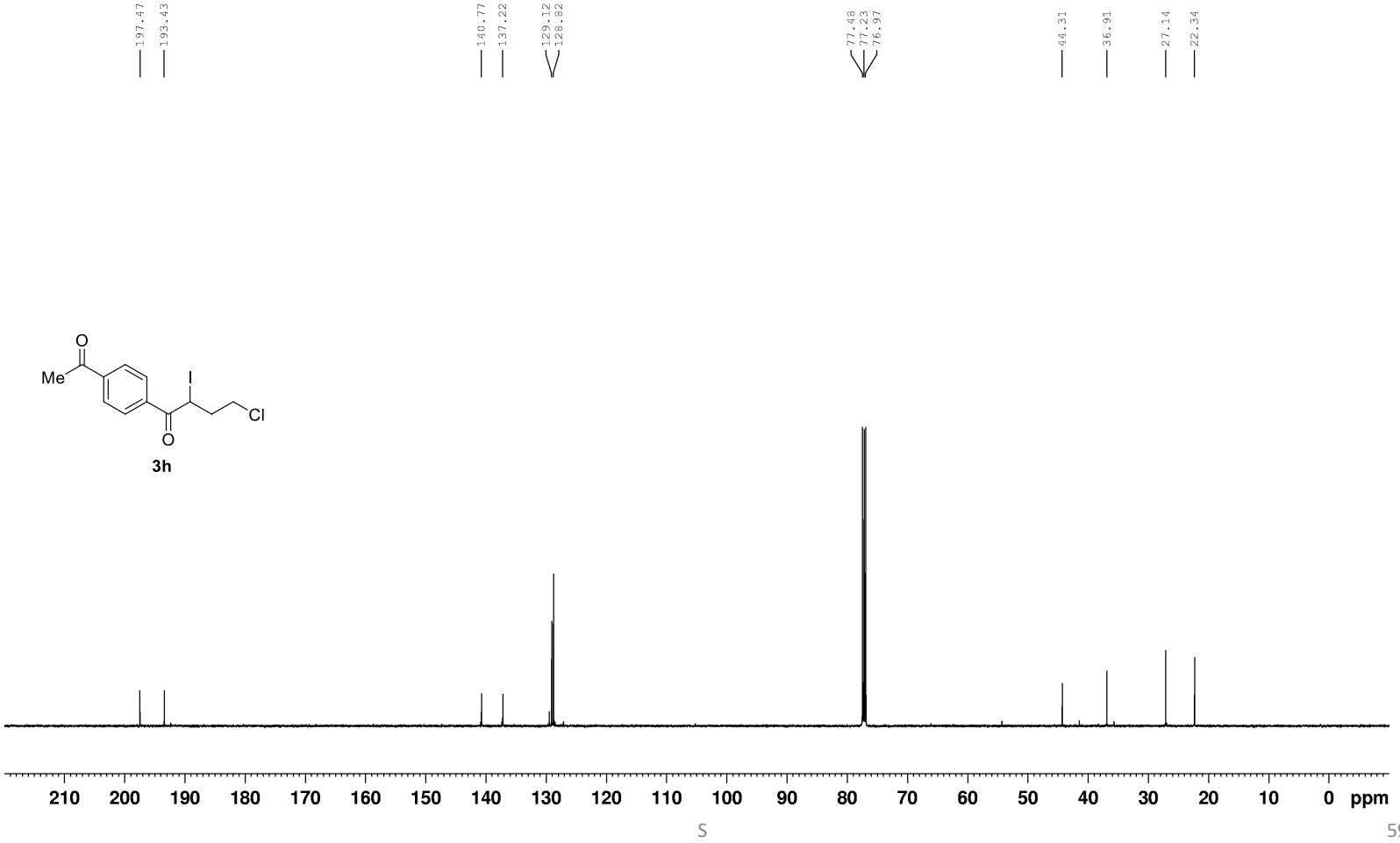
^{19}F NMR $CDCl_3$ / 376MHz



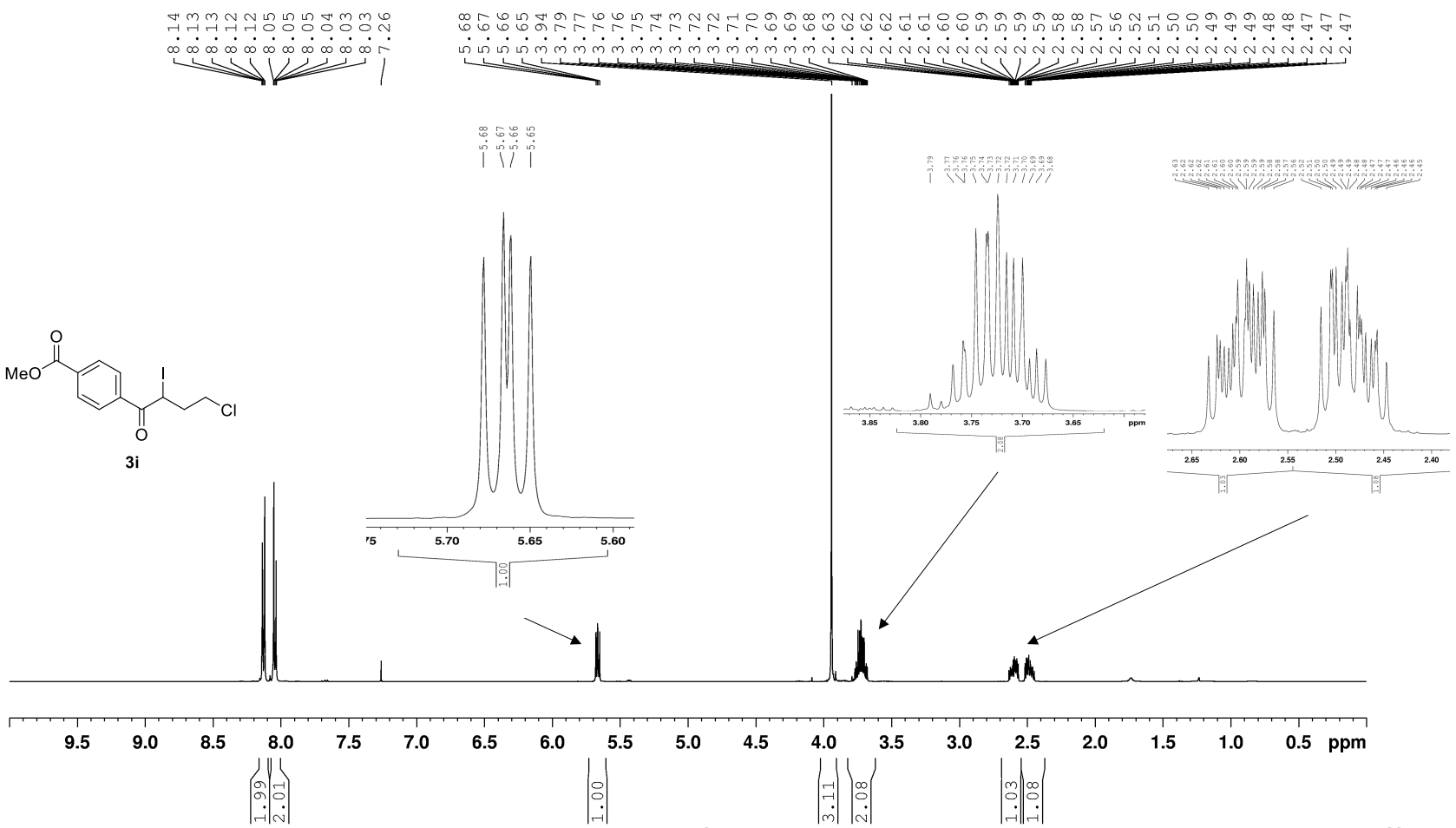
1H NMR CDCl3 / 500 MHz



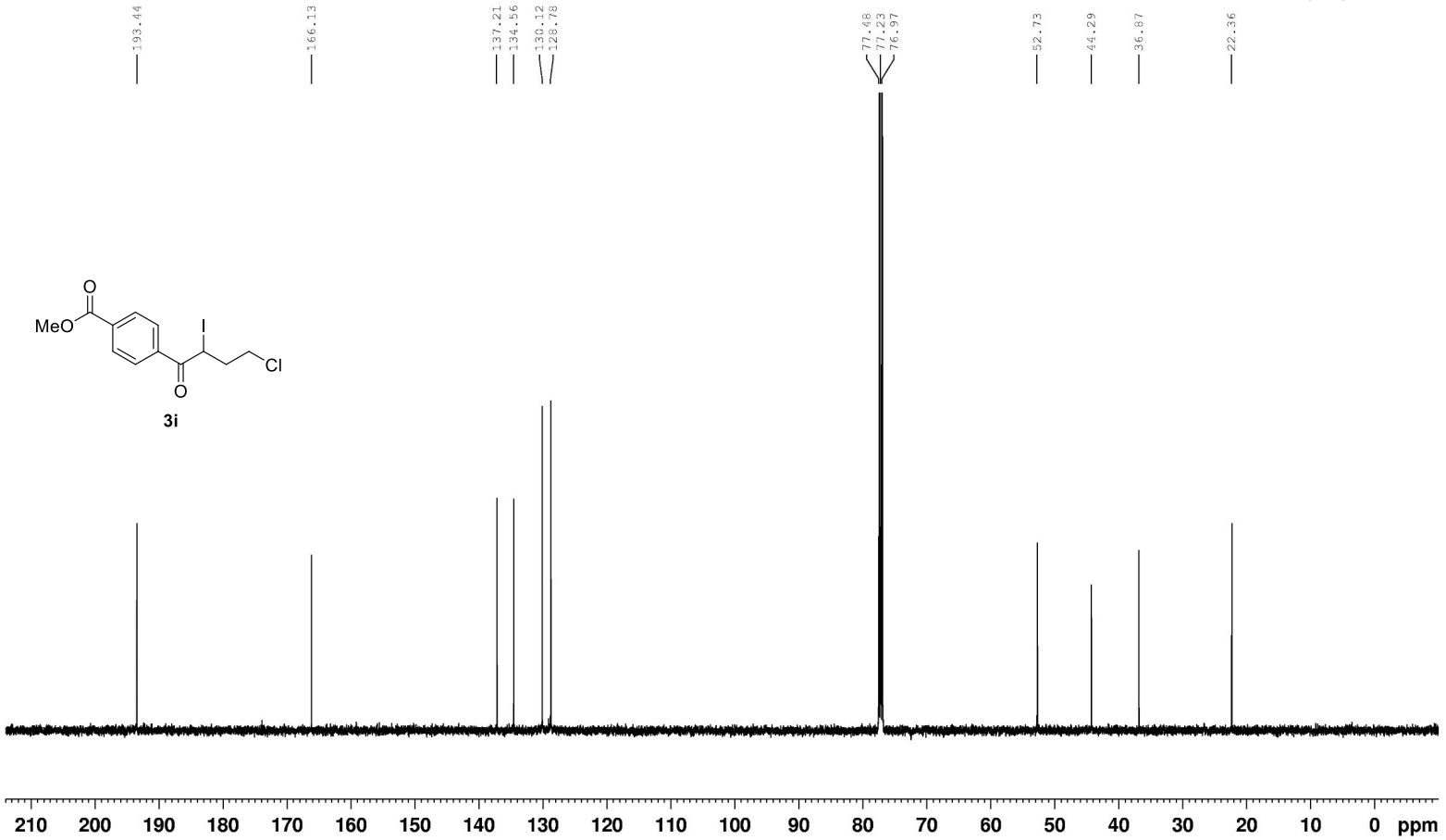
13C{1H} CDCl3 / 125 MHz



1H NMR CDCl3 / 500 MHz



13C{1H} CDCl3 / 125 MHz



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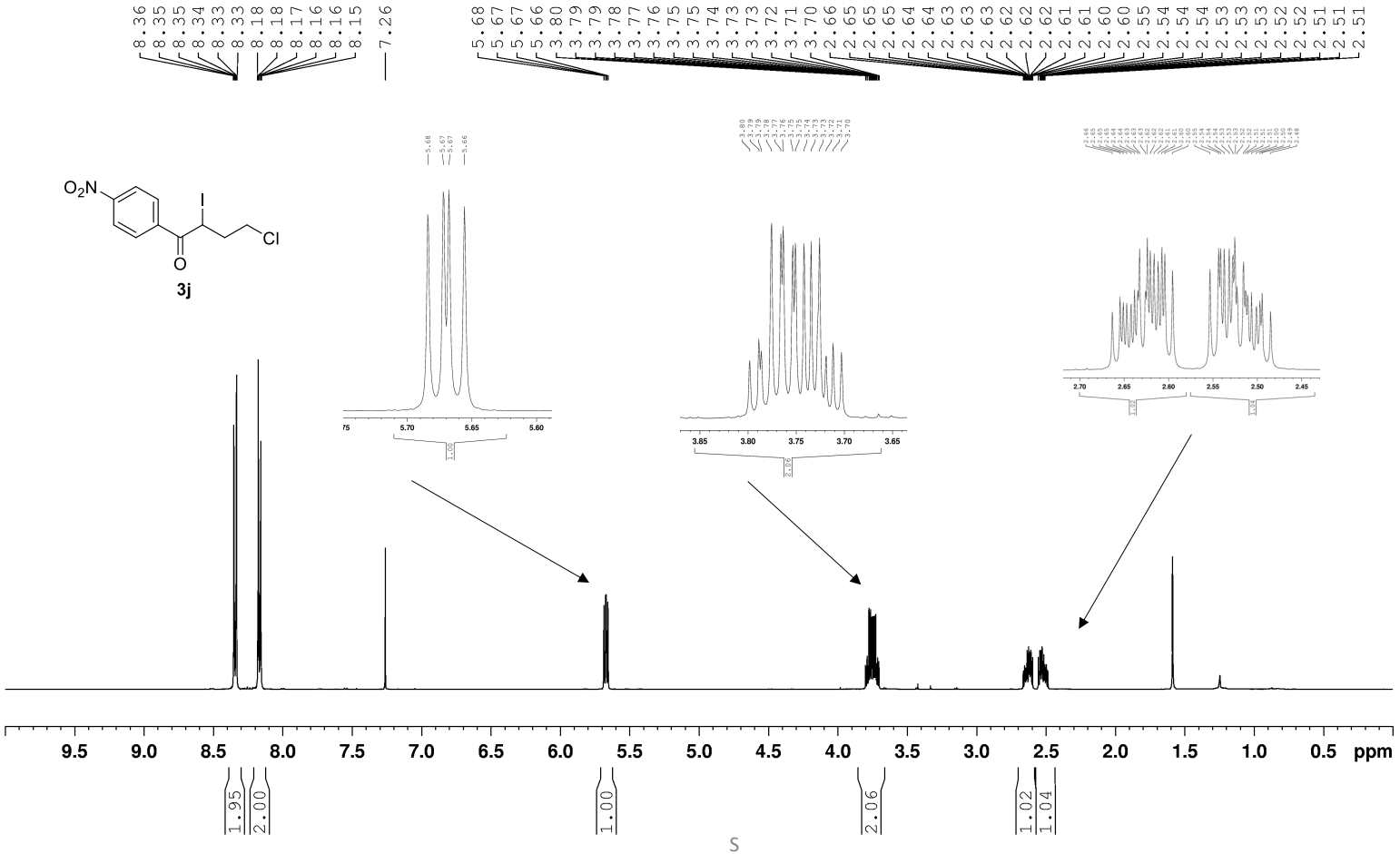
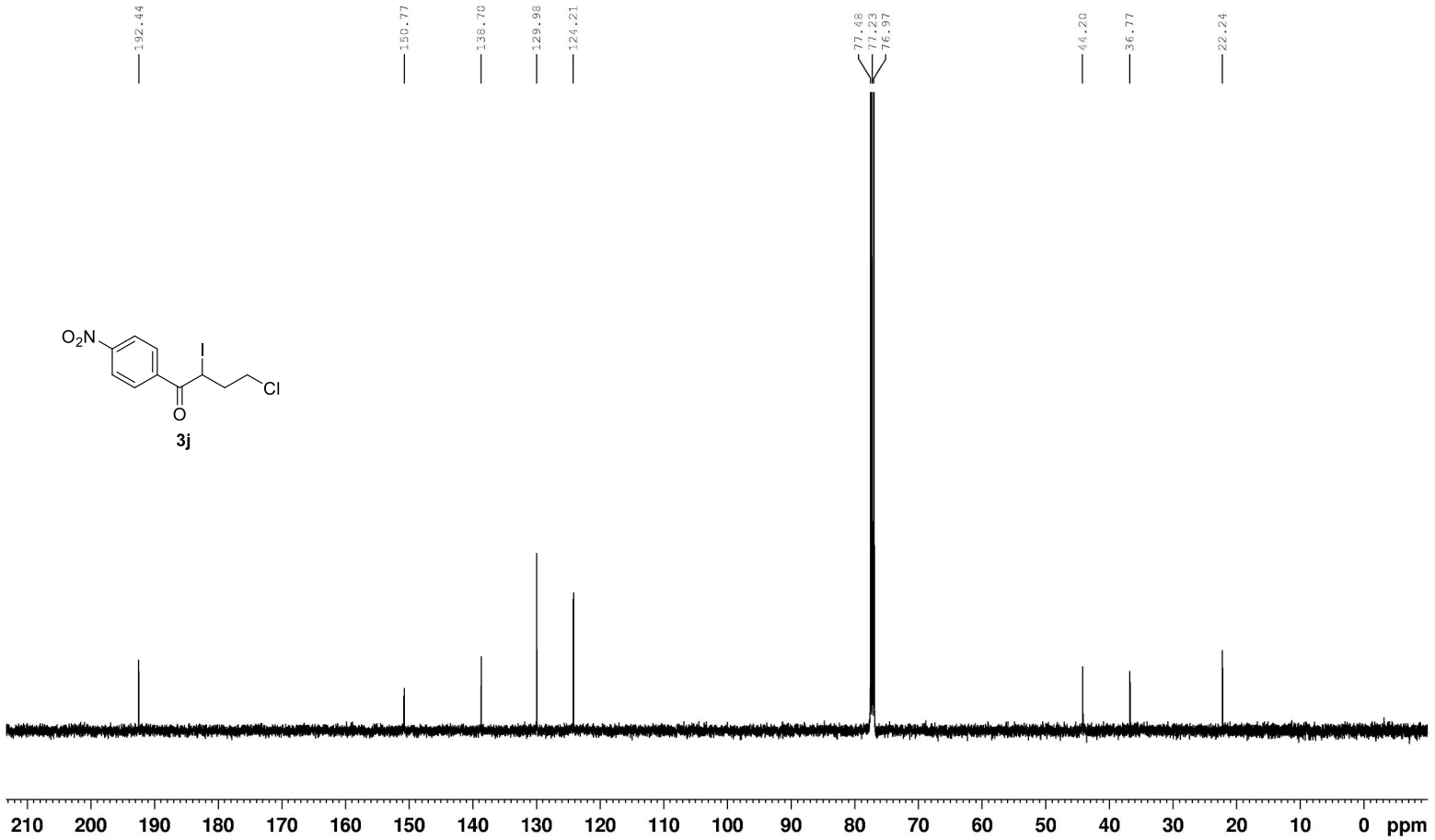


13C{1H} CDCl3 / 125 MHz



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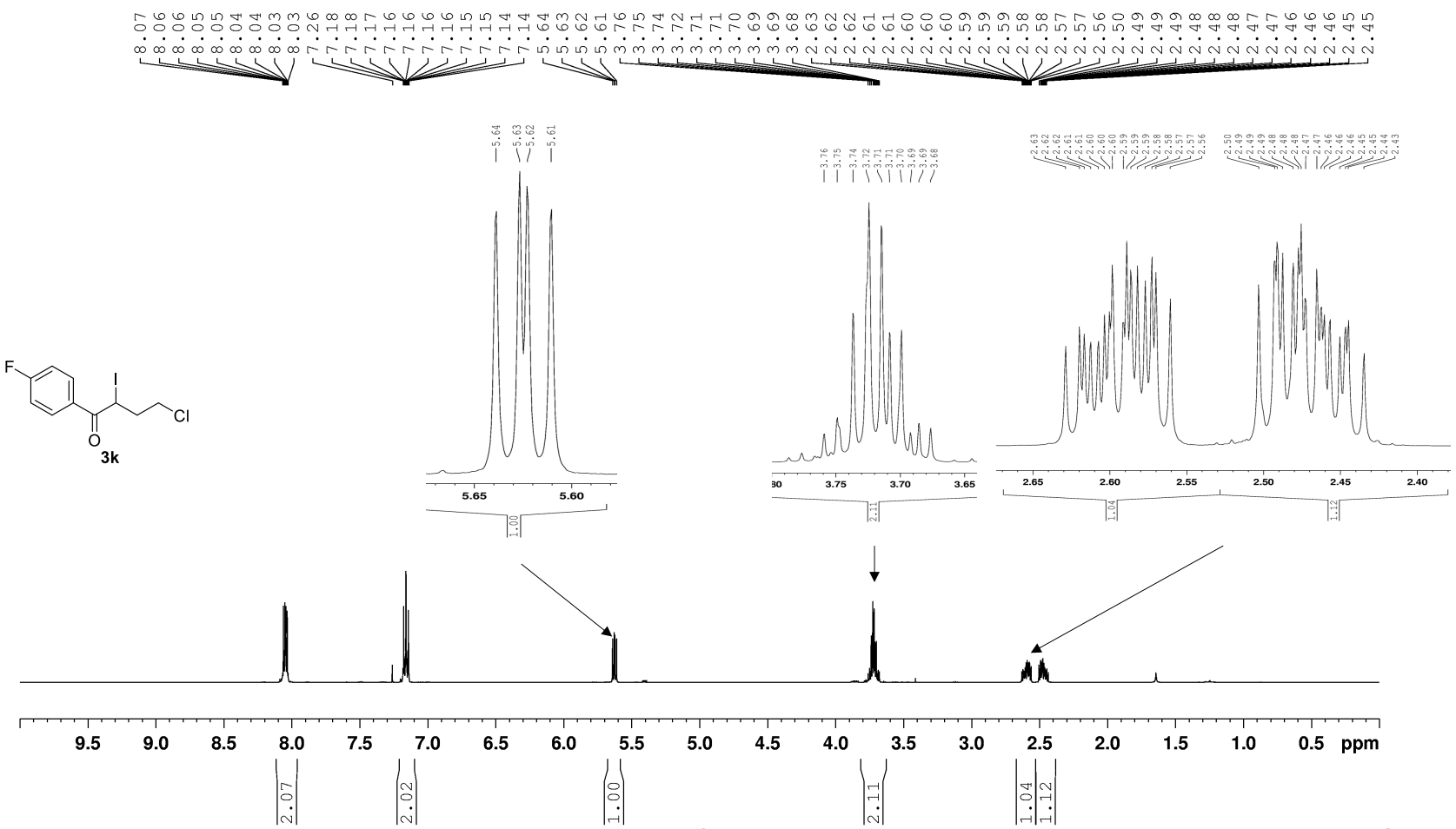
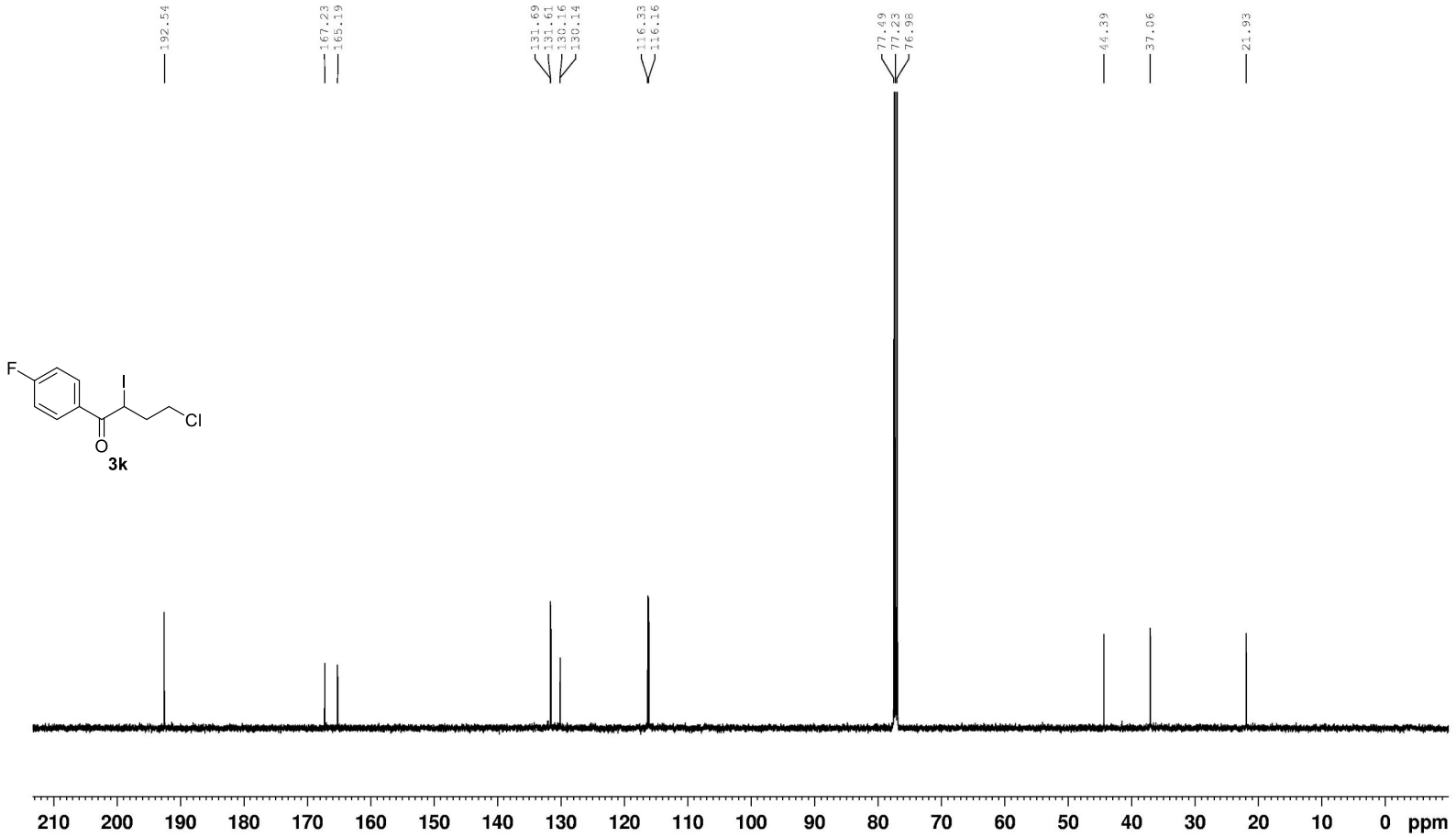
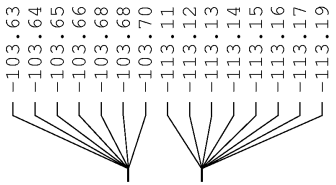
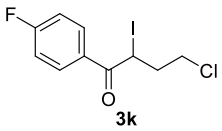


13C{1H} CDCl3 / 125 MHz

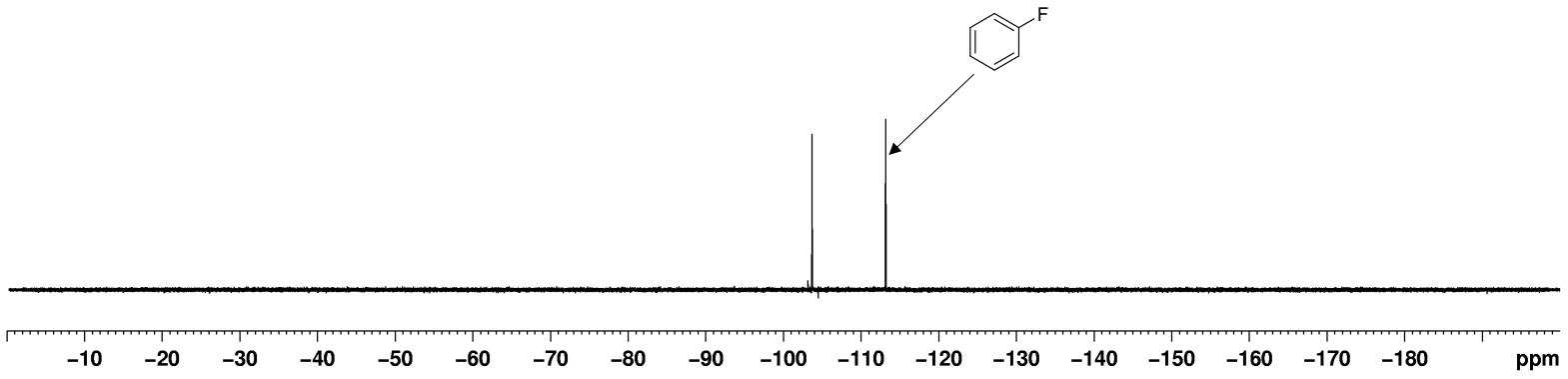


^{19}F NMR $CDCl_3$ / 376MHz

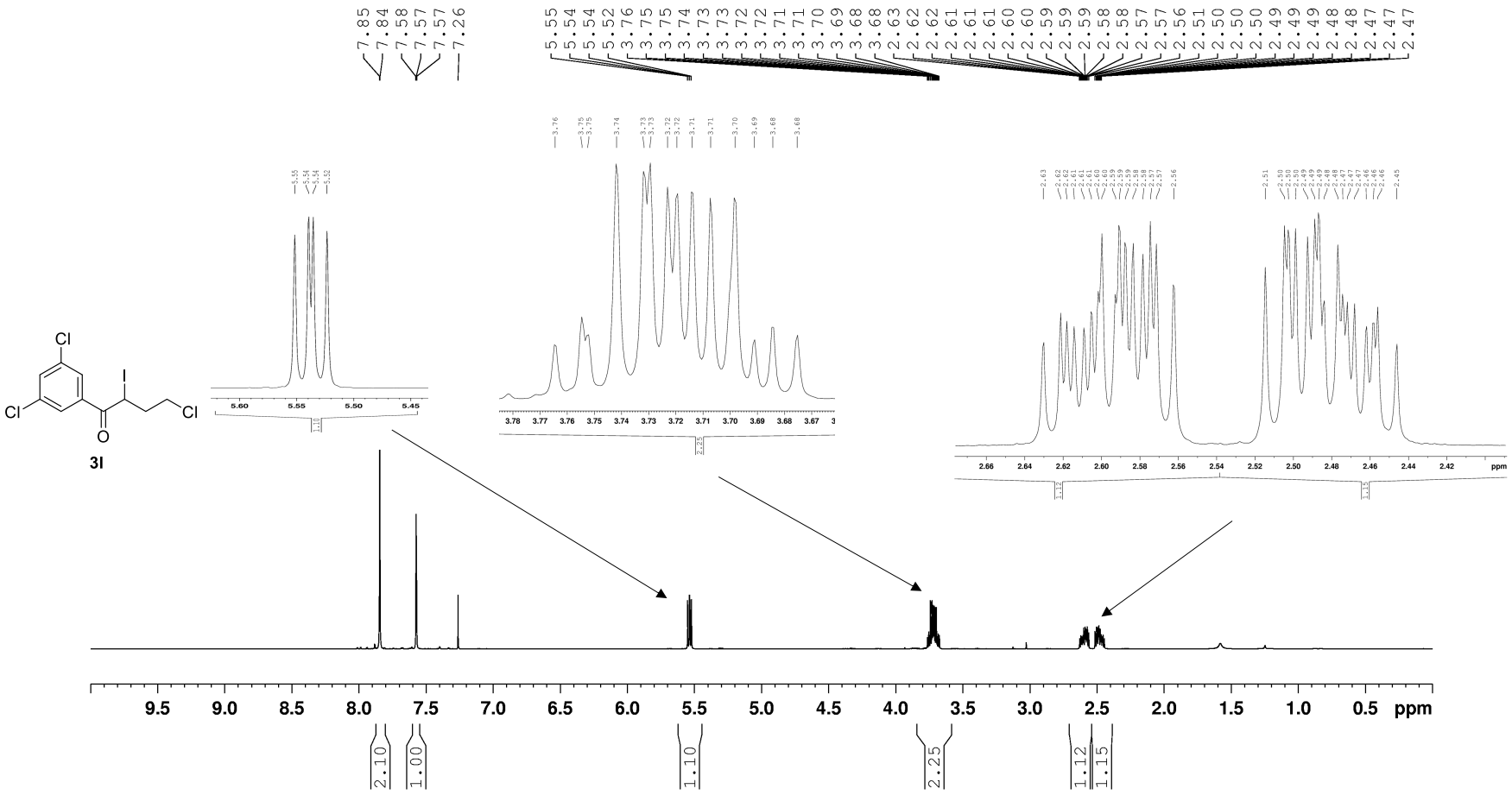




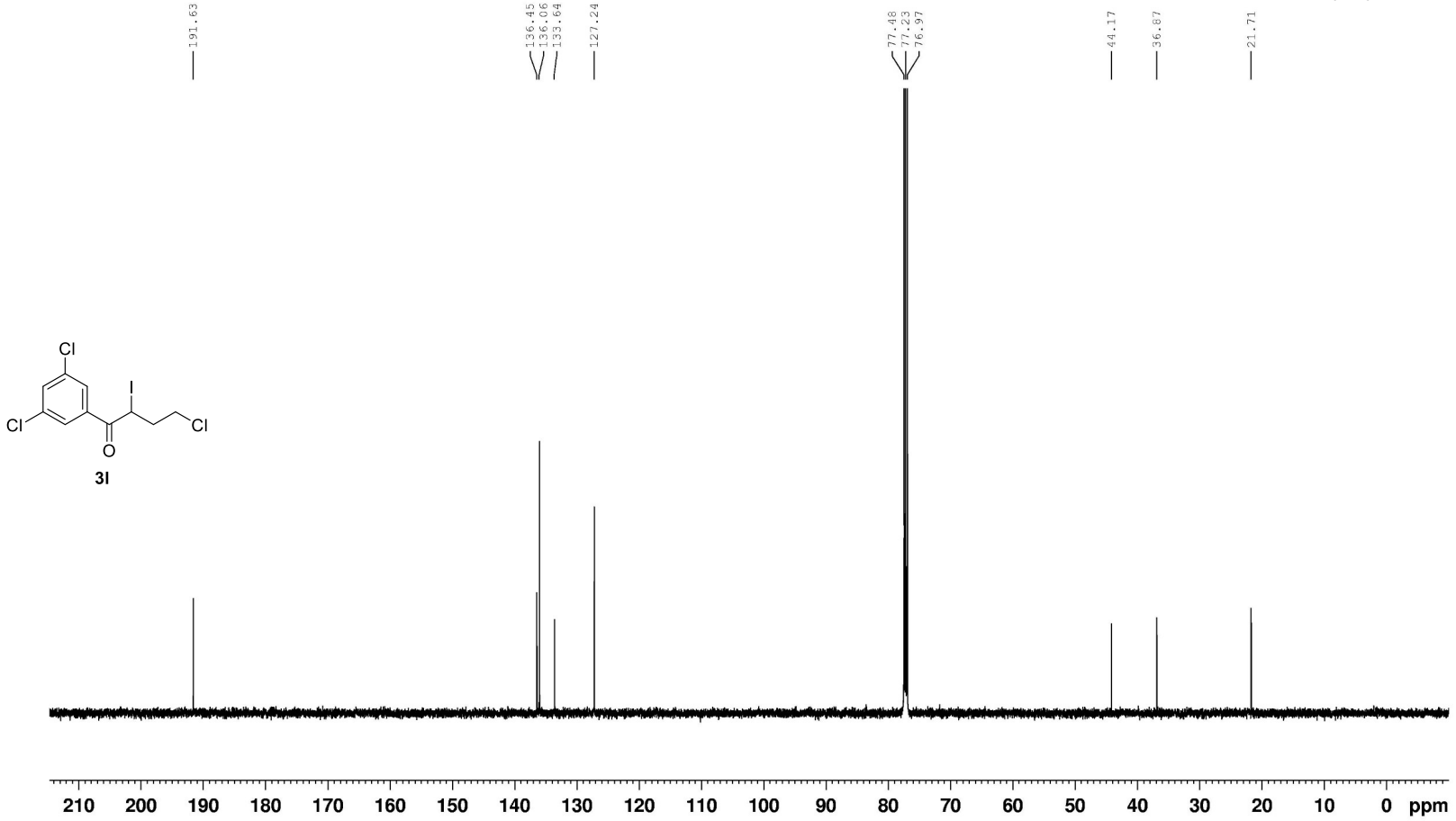
3k



1H NMR CDCl3 / 500 MHz



13C{1H} CDCl3 / 125 MHz



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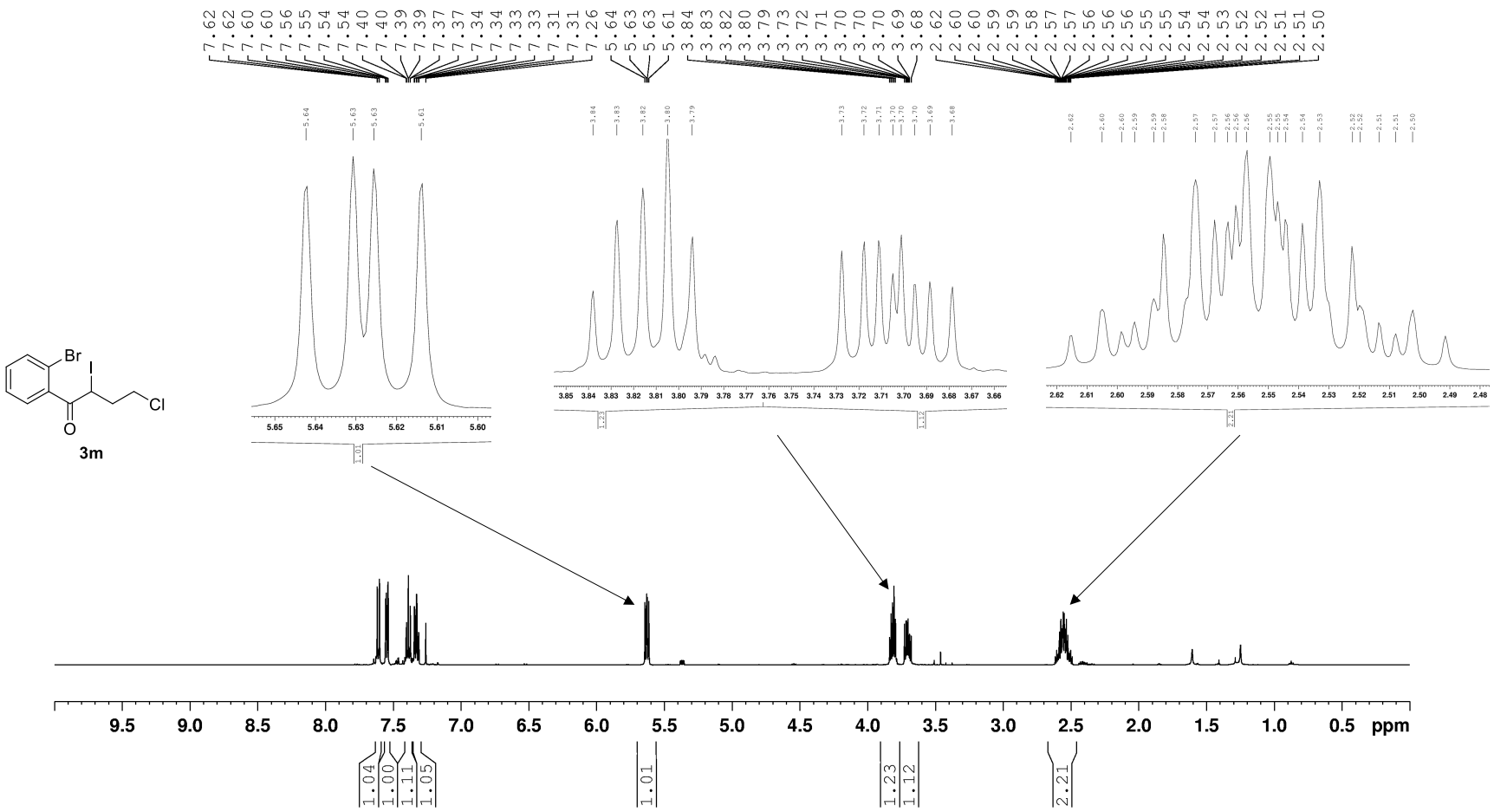
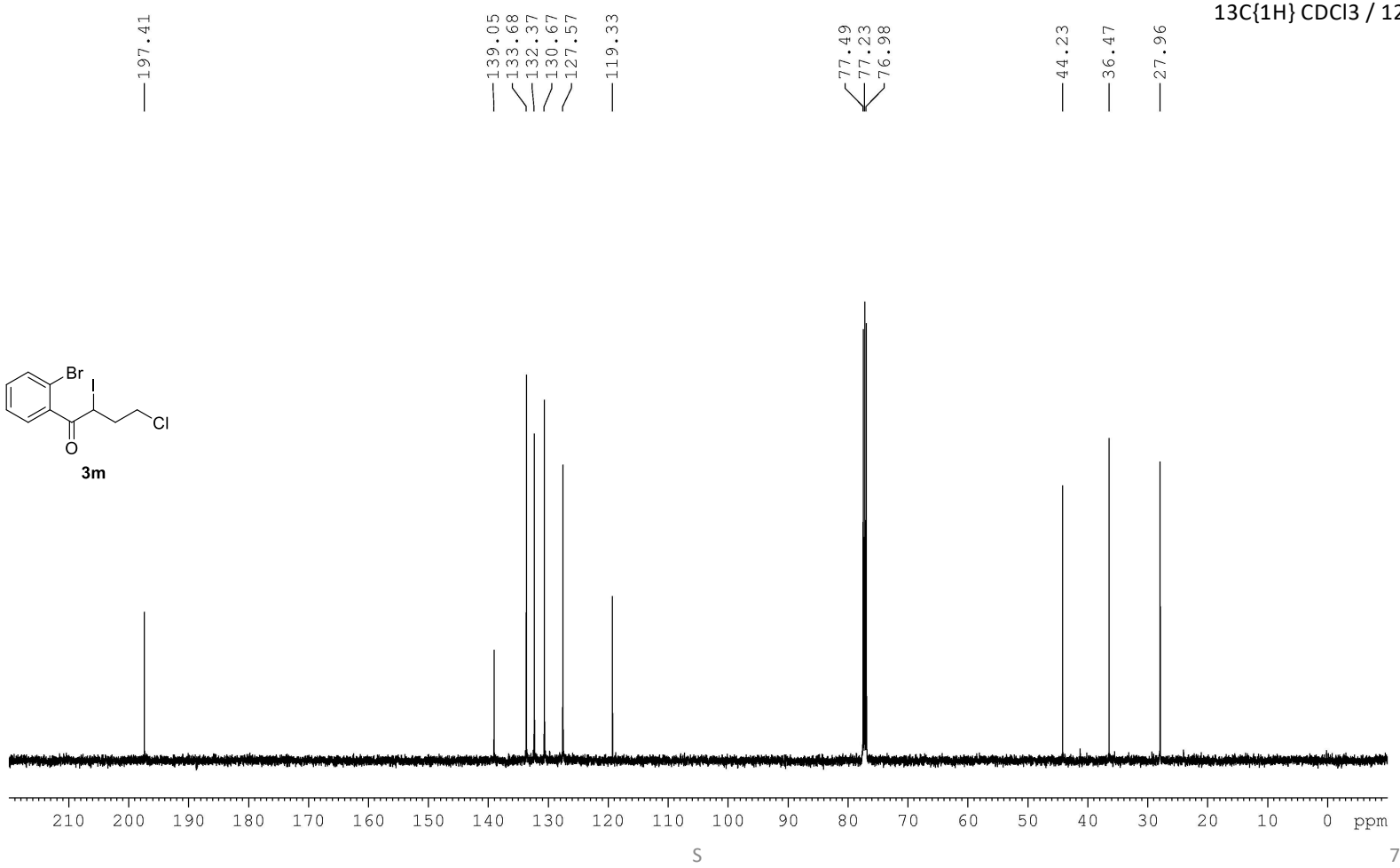
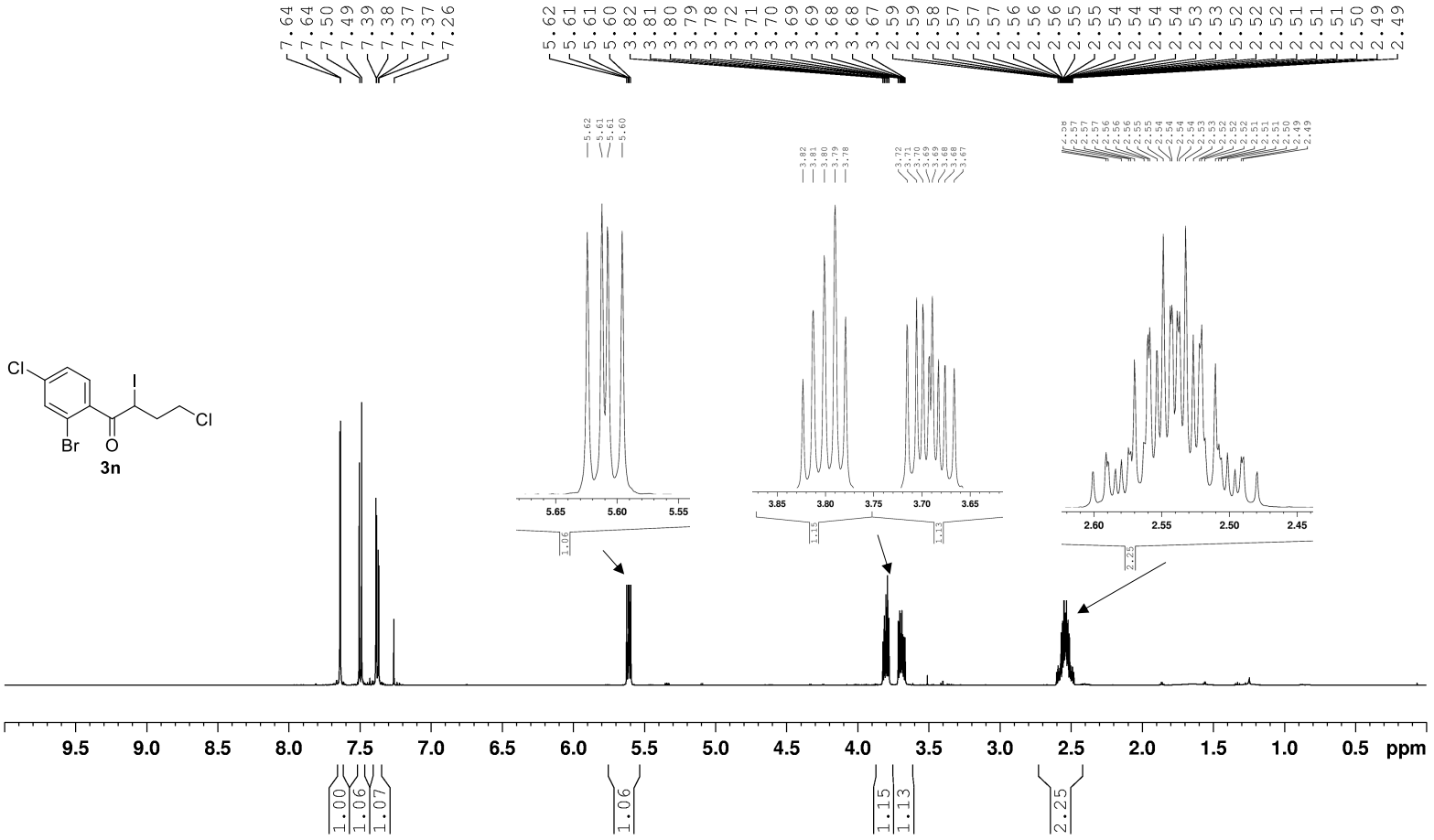


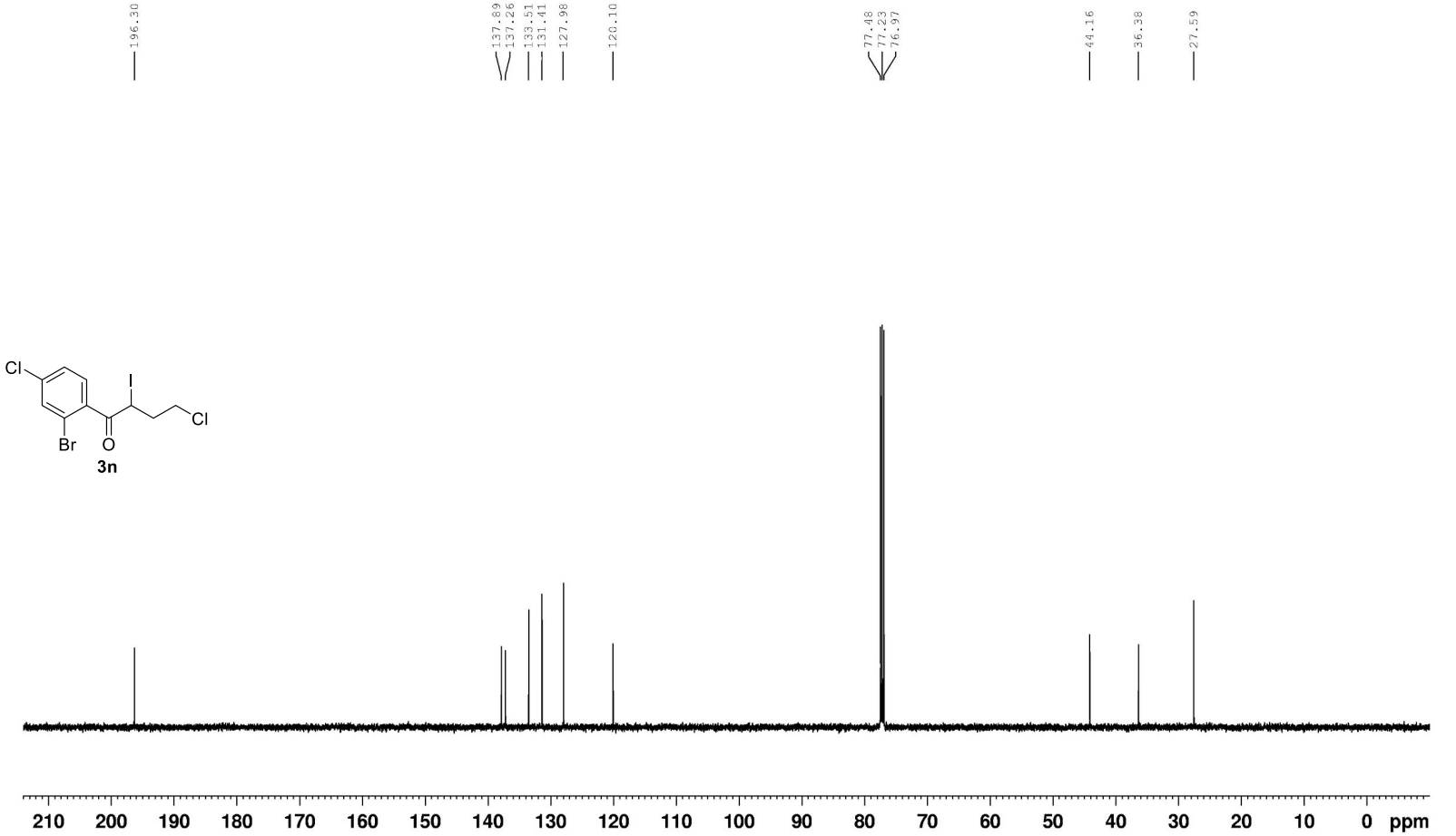
13C{1H} CDCl3 / 125 MHz



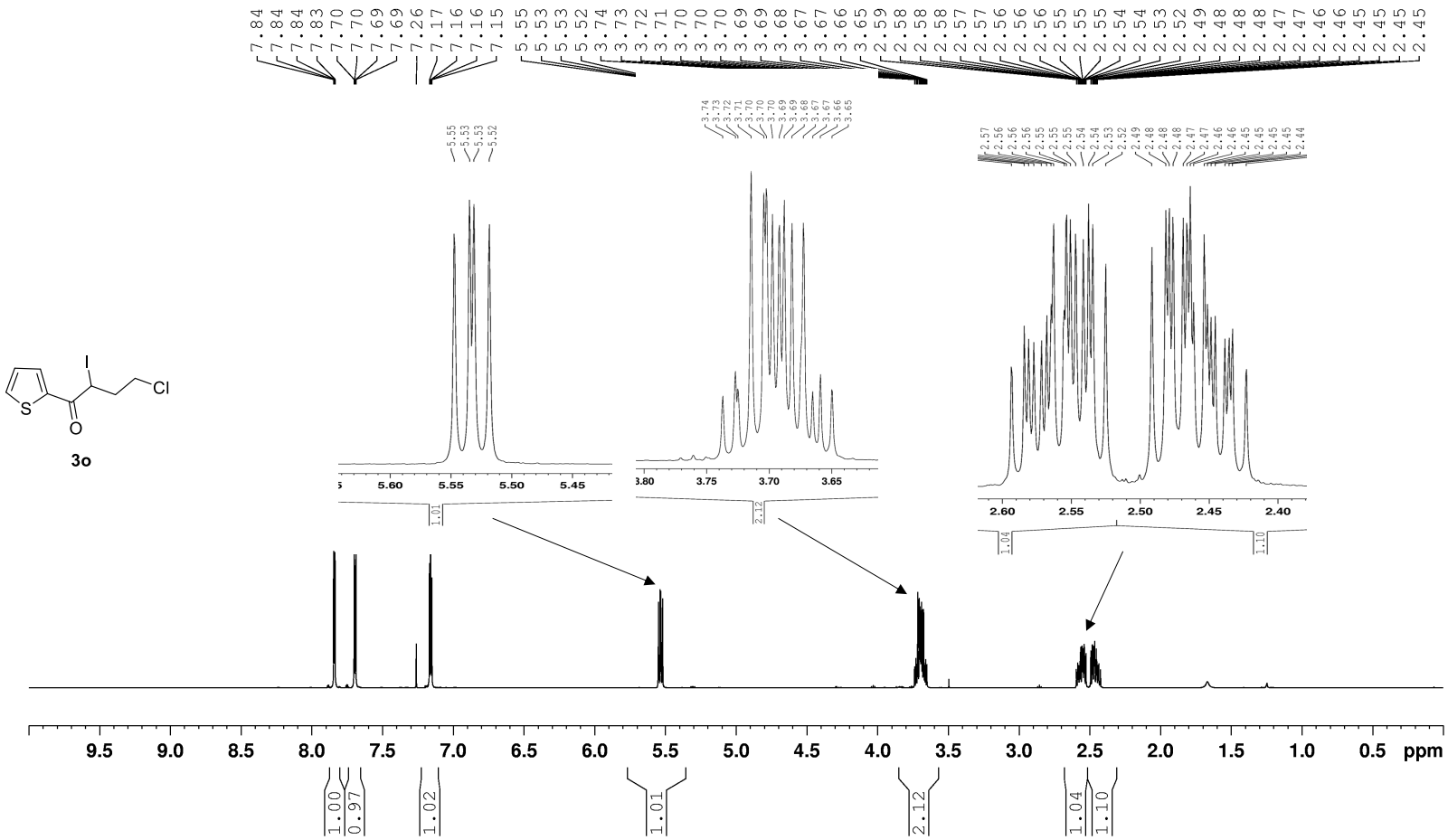
1H NMR CDCl3 / 500 MHz



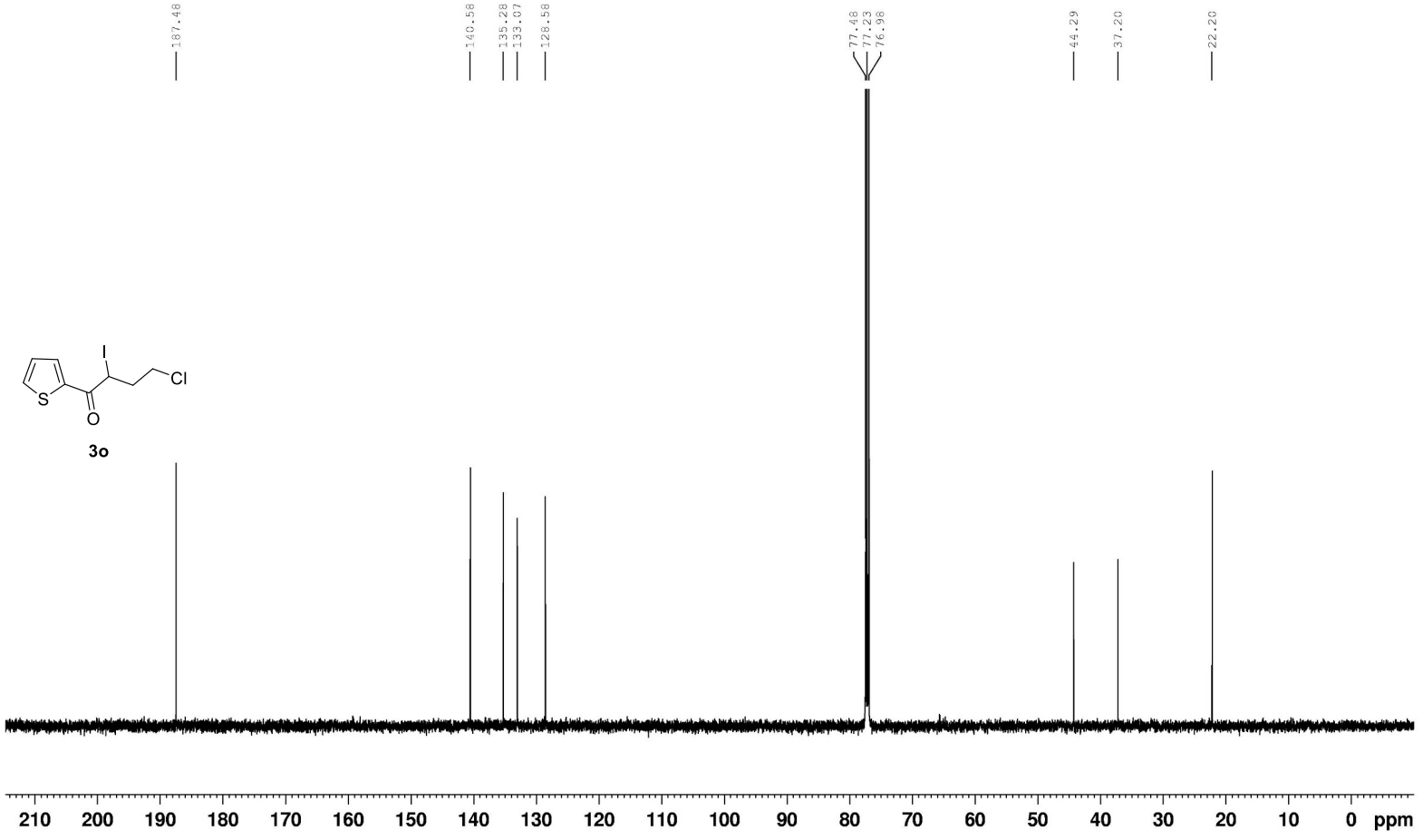
13C{1H} CDCl3 / 125 MHz



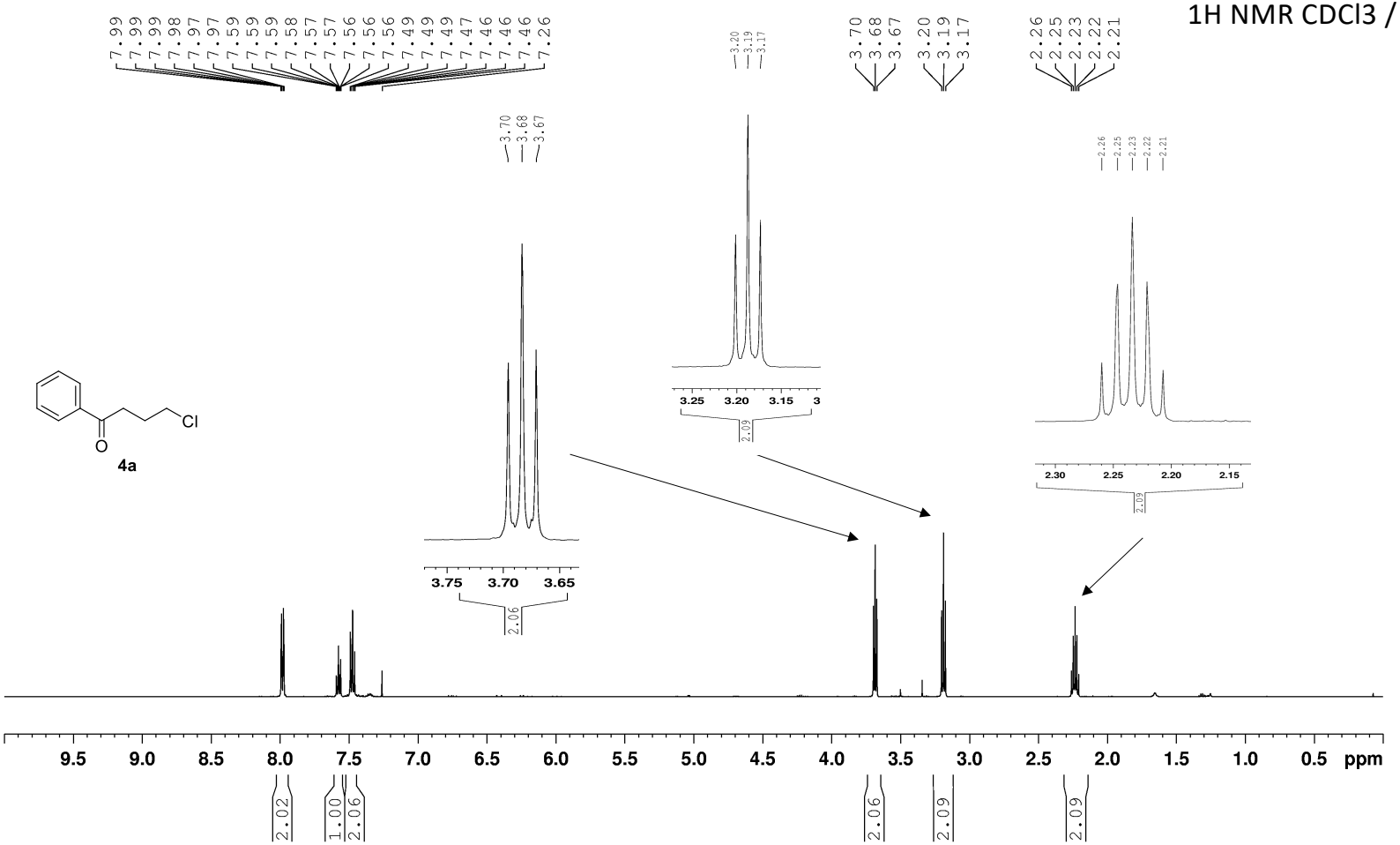
1H NMR CDCl3 / 500 MHz

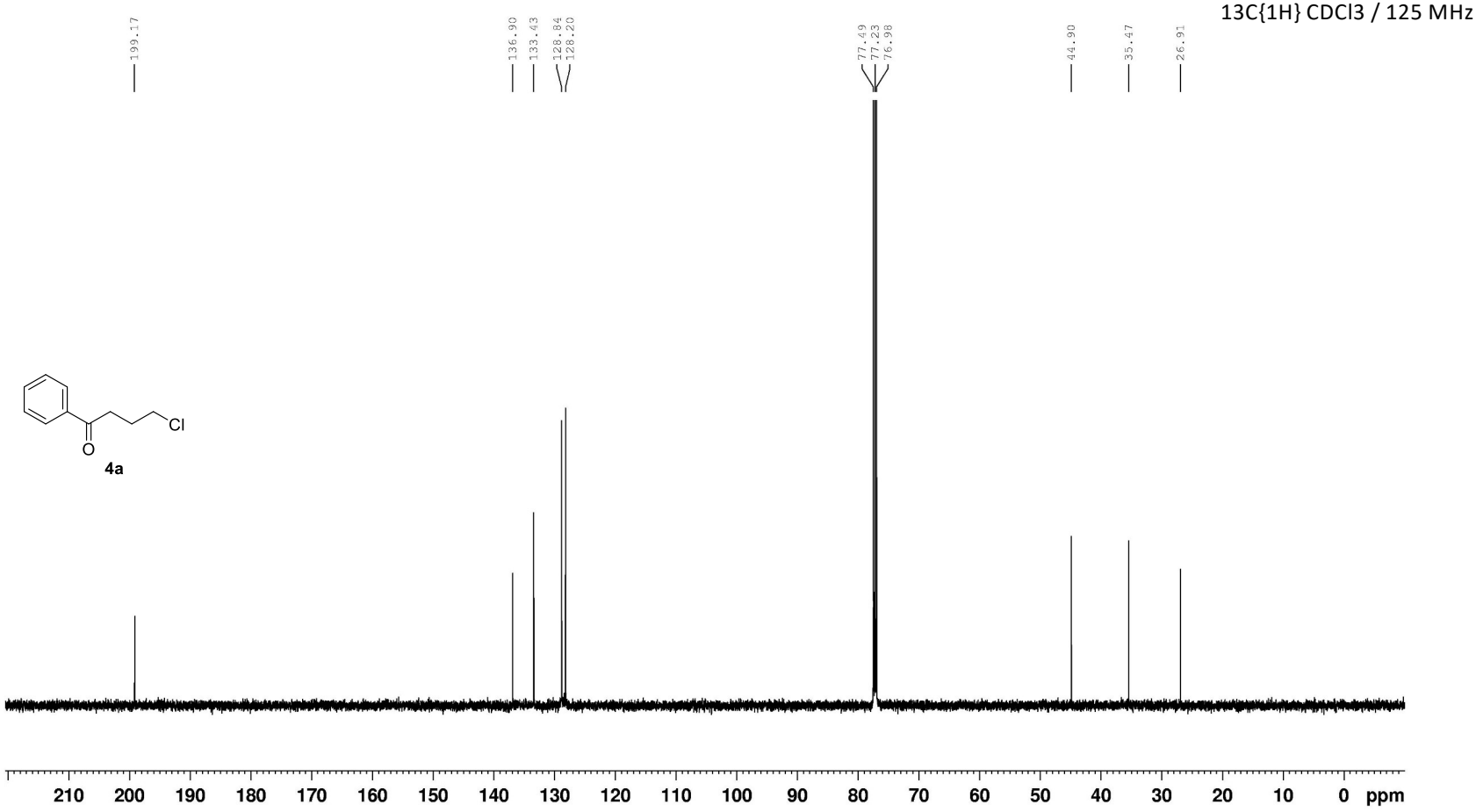


13C{1H} CDCl3 / 125 MHz



1H NMR CDCl3 / 500 MHz




13C{1H} CDCl3 / 125 MHz
199.17
136.90
133.43
128.84
128.20
77.49
77.23
76.98
44.90
35.47
26.91
Cl
O
4a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm