

Supporting Information

Decatungstate as Direct Hydrogen Atom Transfer Photocatalyst for SOMOphilic Alkynylation

Luca Capaldo^{a,b,*} and Davide Ravelli^b

^a Flow Chemistry Group, Van't Hoff Institute for Molecular Sciences (HIMS), University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands

^b PhotoGreen Lab, Department of Chemistry, University of Pavia, Viale Taramelli 12, 27100 Pavia, Italy

Tel: +31 20 525 7143; E-mail: l.capaldo@uva.nl

CONTENT (121 pages)

1. Data cited in the text	3
1.1 Starting materials chart	3
1.2 Screening of reaction conditions.....	4
1.3 Kinetic analysis of the reaction.....	5
1.4 Quantum yield measurement	6
1.5 Deuterium labeling experiments	8
1.6 Proposed mechanism for the formation of 14'	14
1.7 ¹ H-NMR analysis of the reaction crude between 1a and 2l	15
1.8 Computational Analysis.....	16
2. Experimental section.....	17
2.1 General Information.....	17
2.2 Synthesis and characterization of alkynylation reagents	19

2.3 General procedures for the SOMOphilic Alkynylation	29
2.4 Characterization of products 3-31	32
Scope of the H-Donors (1a-q)	32
Scope of the methanesulfonyl alkynes (2a-l).....	37
3. Computational Methods.....	41
General	41
Computational Analysis (see Table S2).....	41
DFT optimized geometries in the gas phase	42
4. References.....	48
5. ^1H -, ^{13}C - and ^{19}F -NMR of compounds I-2	52
6. ^1H -, ^{13}C - and ^{19}F -NMR of compounds 2	68
7. ^1H -, ^{13}C - and ^{19}F -NMR of compounds 3-31	84

1. Data cited in the text

1.1 Starting materials chart

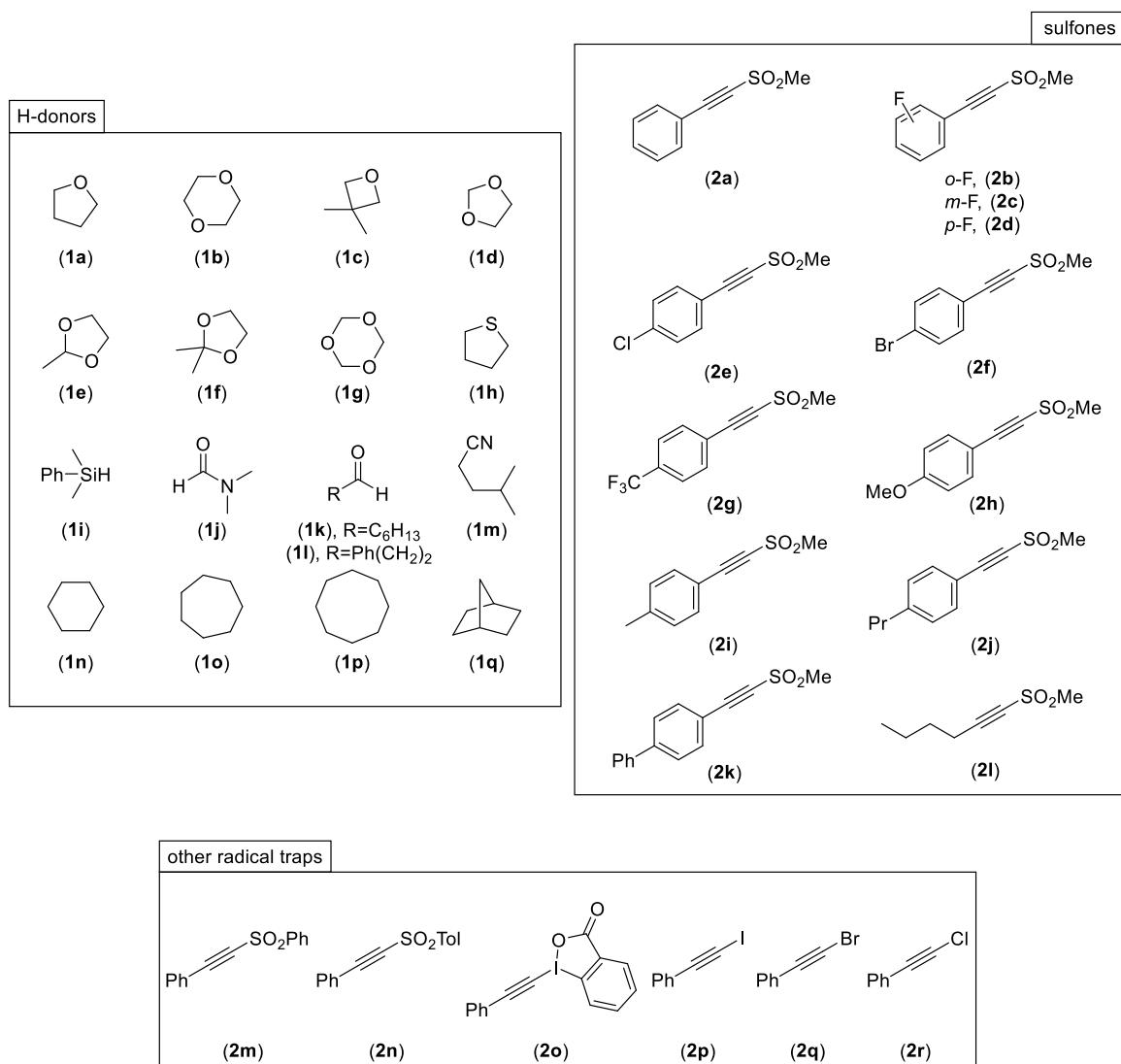
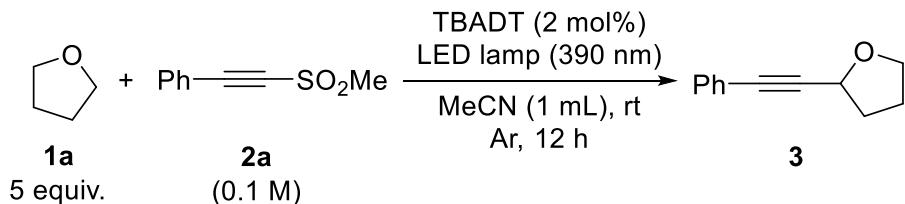


Chart S1. Substrates used in this work.

1.2 Screening of reaction conditions

Table S1. Screening of reaction conditions in terms of photocatalyst loading, solvent and light source.

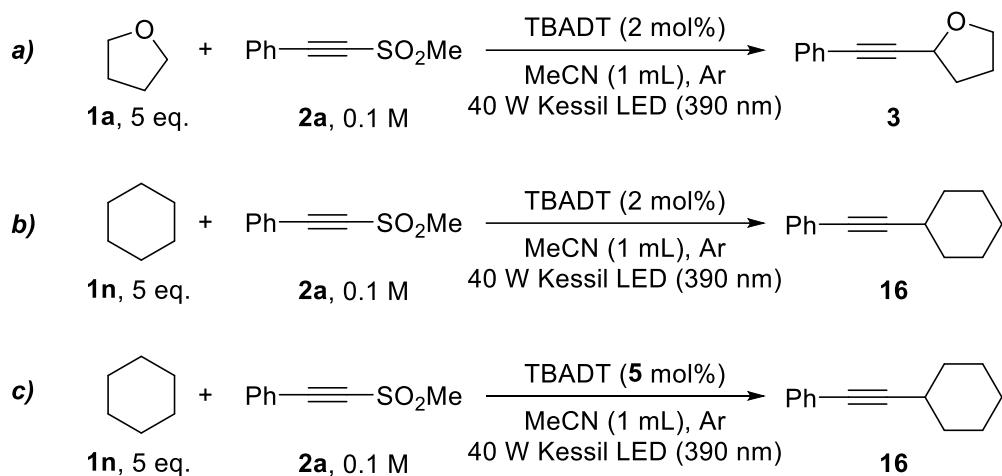


Entry	Variation from conditions	Consumption of 2a	3 , GC Yield
1	none	100%	74%
2	TBADT (1.0 mol%), 24 h	100%	66%
3	TBADT (0.5 mol%), 24 h	100%	65%
4	TBADT (0.1 mol%), 24 h	70%	40%
5	Solvent: MeCN/H ₂ O 9:1	100%	69%
6	Solvent: Me ₂ CO	100%	68%
7	$\lambda = 405$ nm	100%	62%
8	no light	0%	0%
9	no TBADT	0%	traces

Reaction conditions: **2a** (0.1 M), **1a** (5 equiv., 0.5 M), tetrabutylammonium decatungstate (Bu_4N)₄[W₁₀O₃₂] (2 mol%) in 1 mL of the chosen solvent under inert atmosphere (Ar-sparged solution). After irradiation, dodecane (1 $\mu\text{l}/\text{mL}$) was added as external standard and the mixture was filtered through a short SiO_2 plug to remove the catalyst. The resulting solution was then analyzed via GC-FID analysis and yields were calculated by means of calibration curves with authentic samples.

1.3 Kinetic analysis of the reaction

Figure S1 shows the typical kinetic profile of the reaction between tetrahydrofuran (**1a**) and **2a** and between cyclohexane (**1n**) and **2a** (see **Scheme S1a-c**). The reactions were monitored over a period of 24 hours. Small aliquots were subtracted from the reaction mixture at 1, 2, 5, 6, 7, 12 and 24 hours, analysed via GC-FID and consumptions/yields were calculated by means of calibration curves with authentic samples (external standard: dodecane).



Scheme S1. Reactions studied for the kinetic analysis.

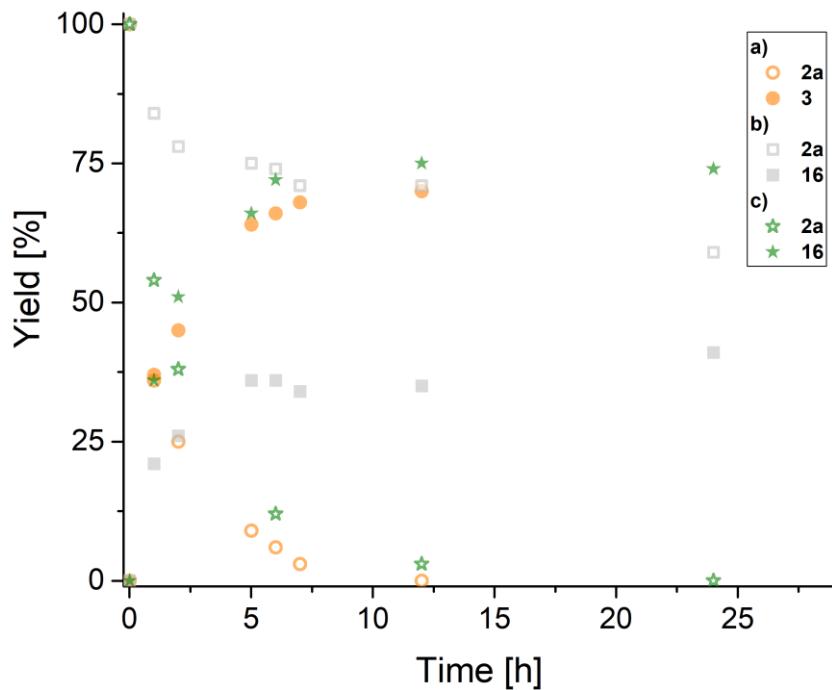


Figure S1. Kinetic profile of reaction **a**) (orange circles), reaction **b**) (grey squares) and reaction **c**) (green stars). SM: Starting Material.

1.4 Quantum yield measurement

Quantum yield (QY) was determined via ferrioxalate actinometry according to a procedure reported in the literature.^{S1,2} Potassium ferrioxalate was prepared according to a procedure reported in the literature.^{S3} In particular, 3.2 g of FeCl_3 were dissolved in 8 mL of distilled H_2O and were added to a hot solution of 12 g of $\text{K}_2\text{C}_2\text{O}_4$ in 20 mL of distilled H_2O . After a couple of minutes at 100°C, the mixture was let cooling down at room temperature and crystallization was triggered with a glass stick. After crystallization was complete, the mother liquor was removed via a Pasteur pipette and the green crystals ($\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$) were dissolved again in 20 mL of distilled H_2O . Potassium ferrioxalate was recrystallized two more times. Light green crystals (4 g, 41%) were obtained, washed with MeOH and dried at 45°C for 1 hour.

As for the actinometry, two solutions were prepared (NB: the following steps were carried out in the dark, with a deep red lamp):

- Ferrioxalate solution: 59 mg in 10 mL of distilled H_2O (0.012 M). For this concentration, the fraction of absorbed photons is >99% and decomposition QY was reported to be ~ 1.2.^{S2}
- o*-phenanthroline solution: 10 mg of *o*-phenanthroline (0.0055 M), 22.5 g of sodium acetate trihydrate in 10 mL (0.016 M) of distilled water.

At this point, 1 mL of solution a) was transferred into a vial. This operation was repeated three times to get 3 identical solutions: one of them was kept in the dark (in a drawer), while the other two were irradiated with the same setup adopted for explorative experiments (see below) for 60 seconds.

After irradiation, 20 μL of each of the three solutions were withdrawn and diluted with 2 mL of solution b) each (*first dilution*). The diluted solutions were then left equilibrating for 1 hour. Afterwards, they were diluted further (1:5) with distilled H_2O (*second dilution*). Then, a dual-beam spectrophotometer was used to read the difference of absorbance (ΔA) between the irradiated solutions and the blank.

Entry	ΔA_1	ΔA_2
1	1.2141	0.2506
2	1.2025	0.2498

ΔA_1 is the difference in absorbance after the first dilution; ΔA_2 is the difference in absorbance after the second dilution.

Then the following formula was used for the calculation of the moles of photons per second ($\text{E} \cdot \text{s}^{-1}$):

$$E \cdot s^{-1} = \frac{\frac{mol_{Fe^{2+} \text{ after irradiation}}}{[Fe^{2+} \text{ in irradiated solutions}}}}{\frac{[Fe^{2+} \text{ after 1st dilution}}{[Fe^{2+} \text{ after 2nd dilution}}}} \times \frac{\frac{\Delta A}{\varepsilon \times l}}{\frac{2.5 \times 10^{-3}L}{0.5 \times 10^{-3}L} \times \frac{2.2 \times 10^{-3}L}{0.02 \times 10^{-3}L} \times 10^{-3}L}{\Phi \times t_{irr}}}$$

Results are reported in the following table. We calculated the quantum yield after of 1 hour, when 3.70×10^{-5} moles of product **3** were formed (**Figure S1**). QY was calculated from the ratio between the moles of product produced after 1 hour and the moles of photon reaching the reaction vial in 1 hour.

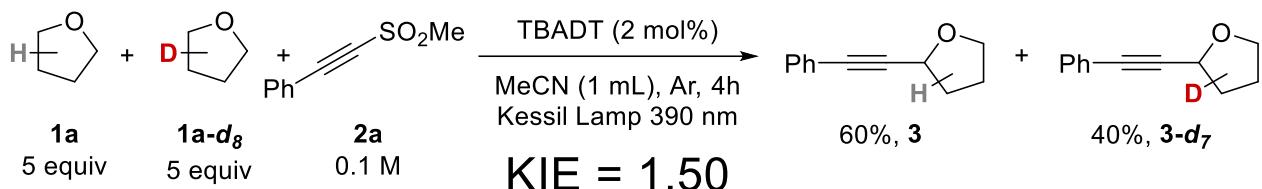
Entry	ΔA_{dil}	$E \text{ s}^{-1}$	$E \text{ h}^{-1}$	mol_{prod}	Φ
1	0.2506	1.53×10^{-7}	5.51×10^{-4}	3.70×10^{-5}	0.07
2	0.2498	1.52×10^{-7}	5.49×10^{-4}	3.70×10^{-5}	0.07

QY was determined to be 0.07, indicating that the process is not a radical-chain reaction.

1.5 Deuterium labeling experiments

Kinetic Isotope Effect for the model reaction

An experiment under the optimized conditions was carried out in the presence of a mixture of protiated **1a** (5.0 equiv) and deuterated THF **1a-d₈** (5.0 equiv, see **Scheme S2** and **Figure S2**). After irradiation, the reaction mixture was filtered through a short silica plug in a pasteur pipette, diluted with dichloromethane and finally analyzed via GC/MS (see Experimental Section below).



Scheme S2. Kinetic Isotope Effect for the model reaction between **1a** and **2a**.

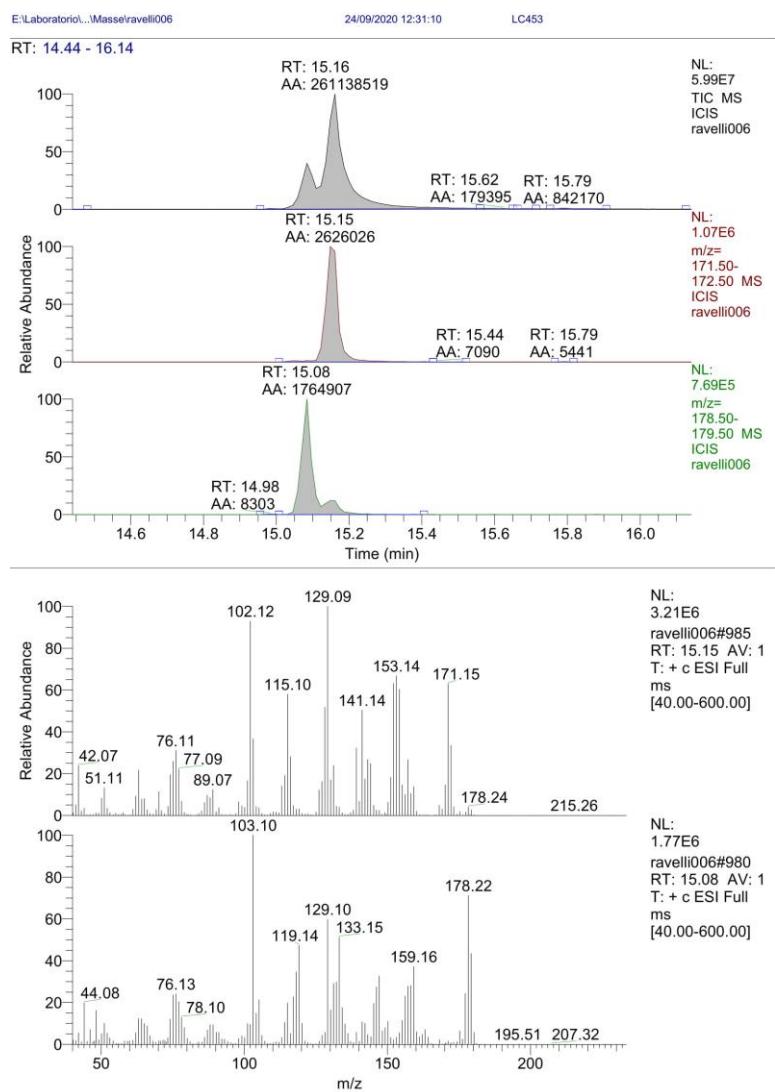
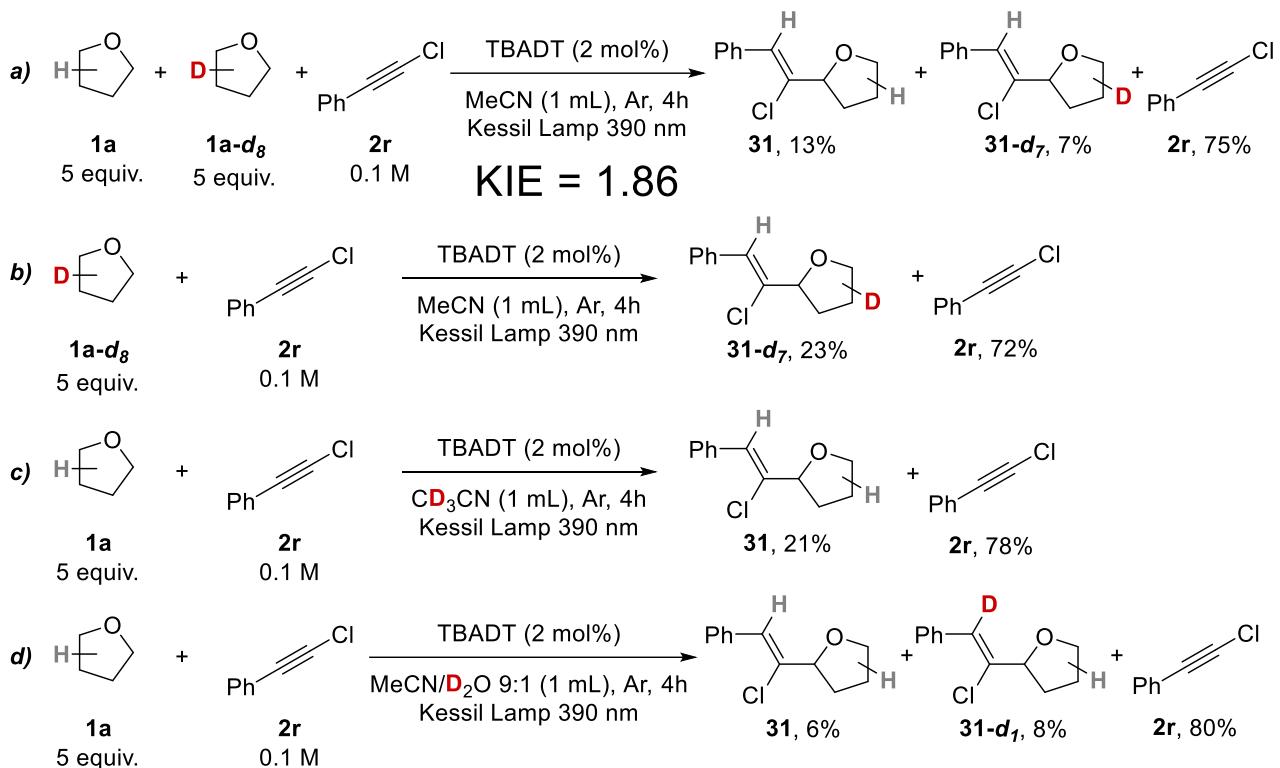


Figure S2. GC/MS analysis results for the reaction reported in **Scheme S2**: chromatogram (TIC), chromatogram (mass range: 171.50 – 172.50 m/z), chromatogram (mass range: 177.50 – 178.50 m/z), mass spectrum for peak at 15.15 min (**3**), mass spectrum for peak at 15.08 (**3-d₇**).

Deuterium labeling

In order to understand the mechanism operating when using chloroalkyne **2r** in the role of radical trap, we performed the experiments listed in **Scheme S3**. All the experiments were interrupted at low conversion of the starting chloroalkyne (< 30%). In particular, we performed:

- experiment **a**) to evaluate the Kinetic Isotope Effect;
- experiment **b**) to assess the origin of the H-atom in the formation of **31**;
- experiment **c**) to exclude that acetonitrile acts as the quencher of the vinyl radical adduct.
- experiment **d**) to actually prove either that a proton scrambling equilibrium at the level of the reduced form of the photocatalyst is operating or an ET/PT sequence is responsible for the closure of the photocatalytic cycle.



Scheme S3. Deuterium labeling experiments in the reaction between **1a** and **2r**.

RT: 16.17 - 17.42

NL:
5.48E7
TIC MS
ravelli002

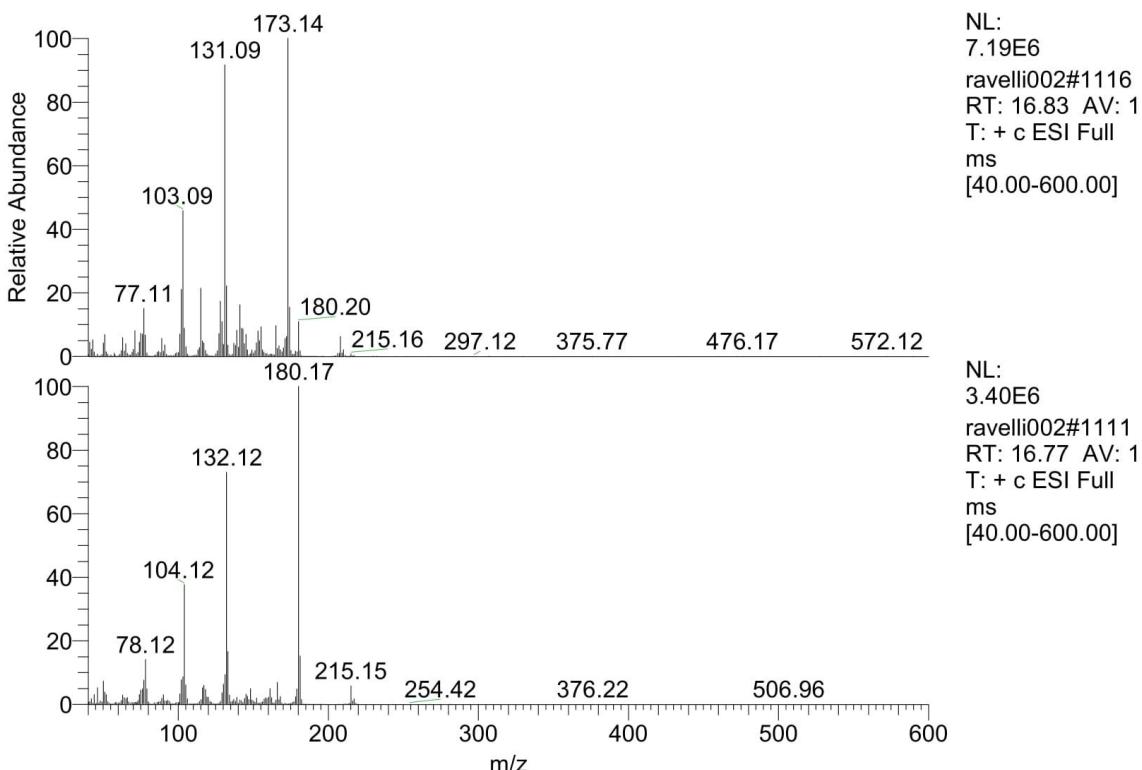
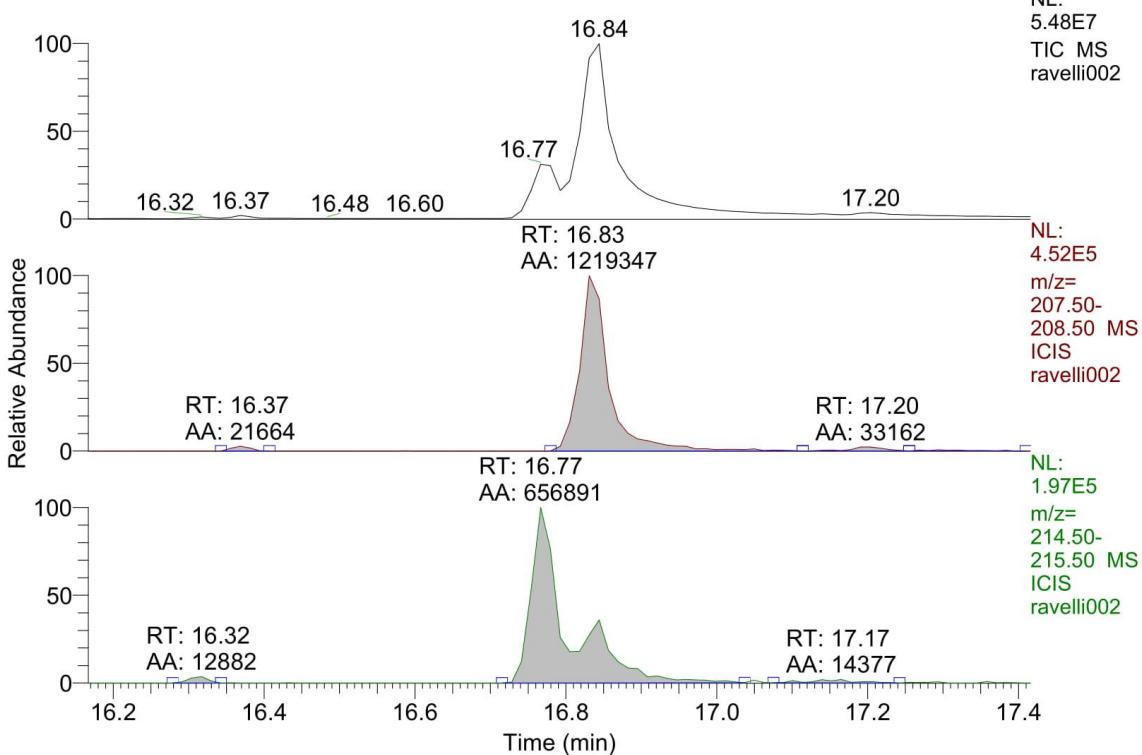


Figure S3. GC/MS analysis results for the reaction reported in **Scheme S3**: chromatogram (TIC), chromatogram (mass range: 207.50 – 208.50 m/z, **31**), chromatogram (mass range: 214.50 – 215.50 m/z, **31-d₇**), mass spectrum for peak at 16.83 min (**31**), mass spectrum for peak at 16.77 (**31-d₇**).

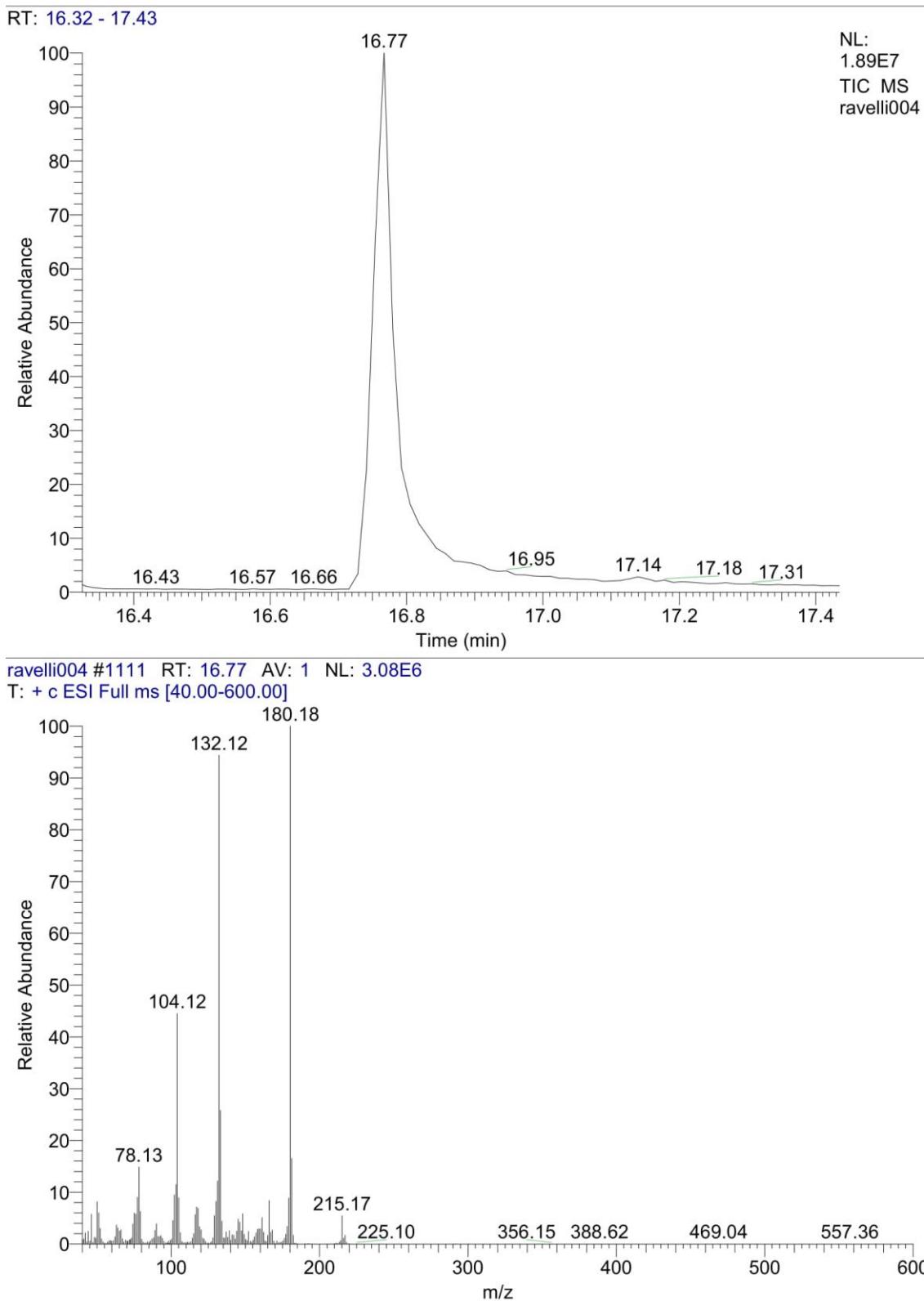
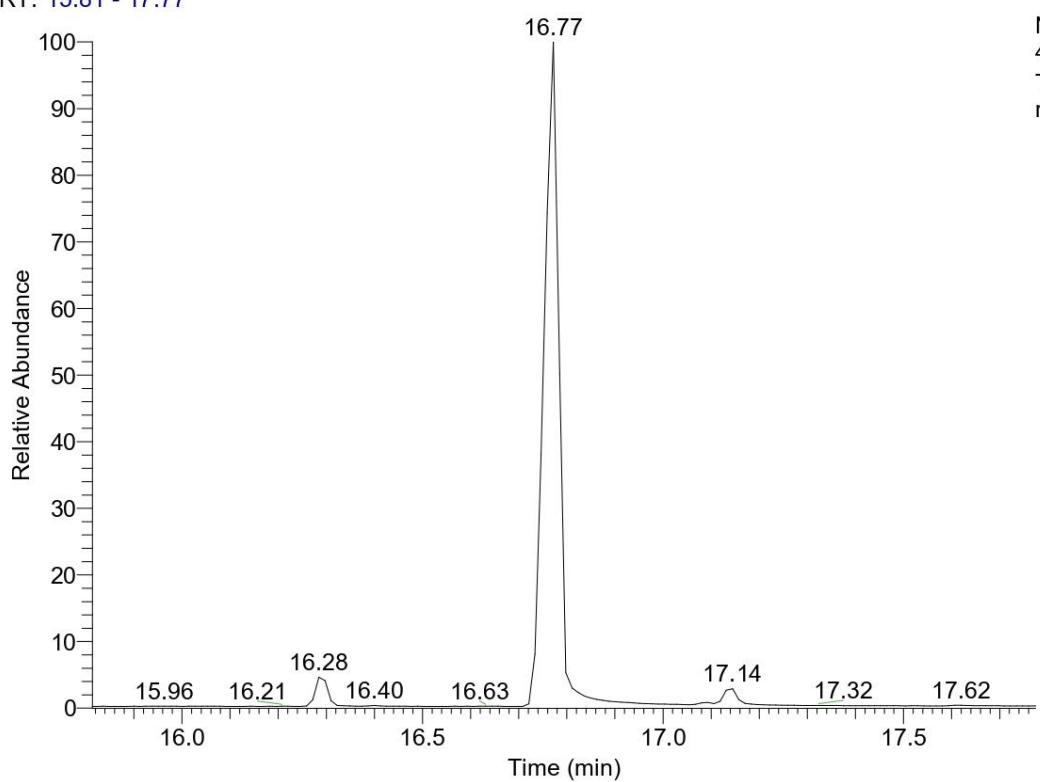


Figure S4. GC/MS analysis results for experiment *b*) in **Scheme S3**: chromatogram (TIC), mass spectrum for peak at 16.77 min (**31-d₇**).

RT: 15.81 - 17.77



NL:
4.90E8
TIC MS
ravelli008

ravelli008 #1113 RT: 16.77 AV: 1 NL: 1.58E8

T: + c ESI Full ms [40.00-600.00]

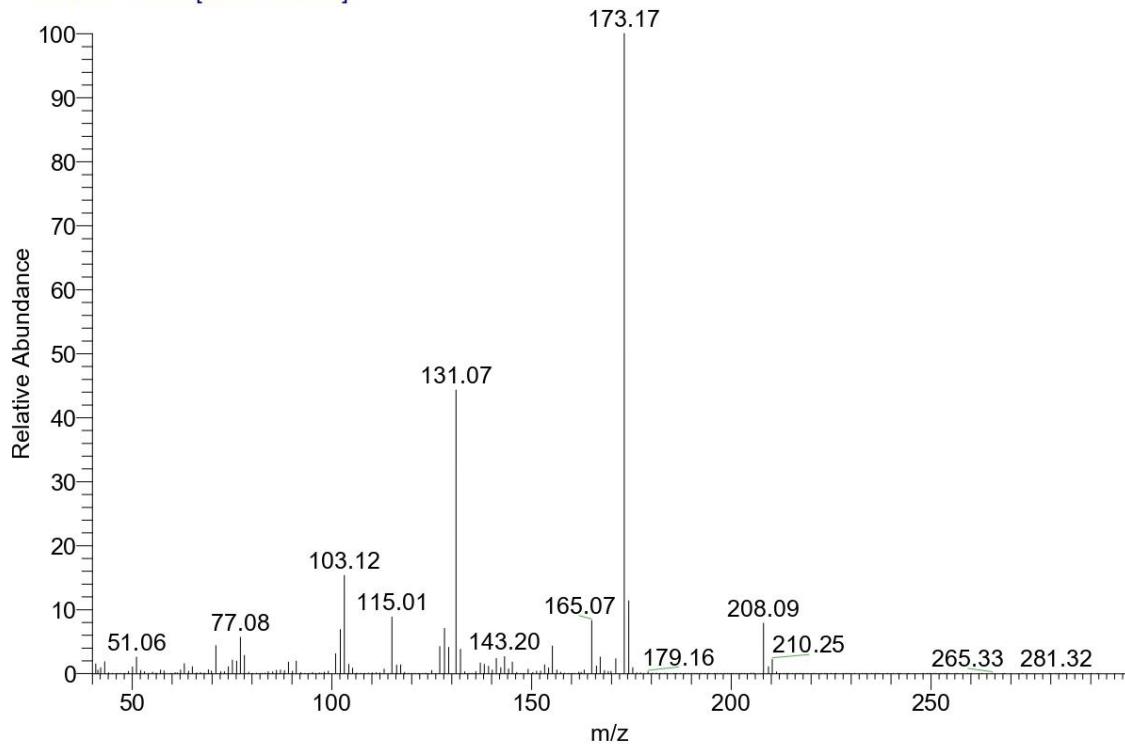
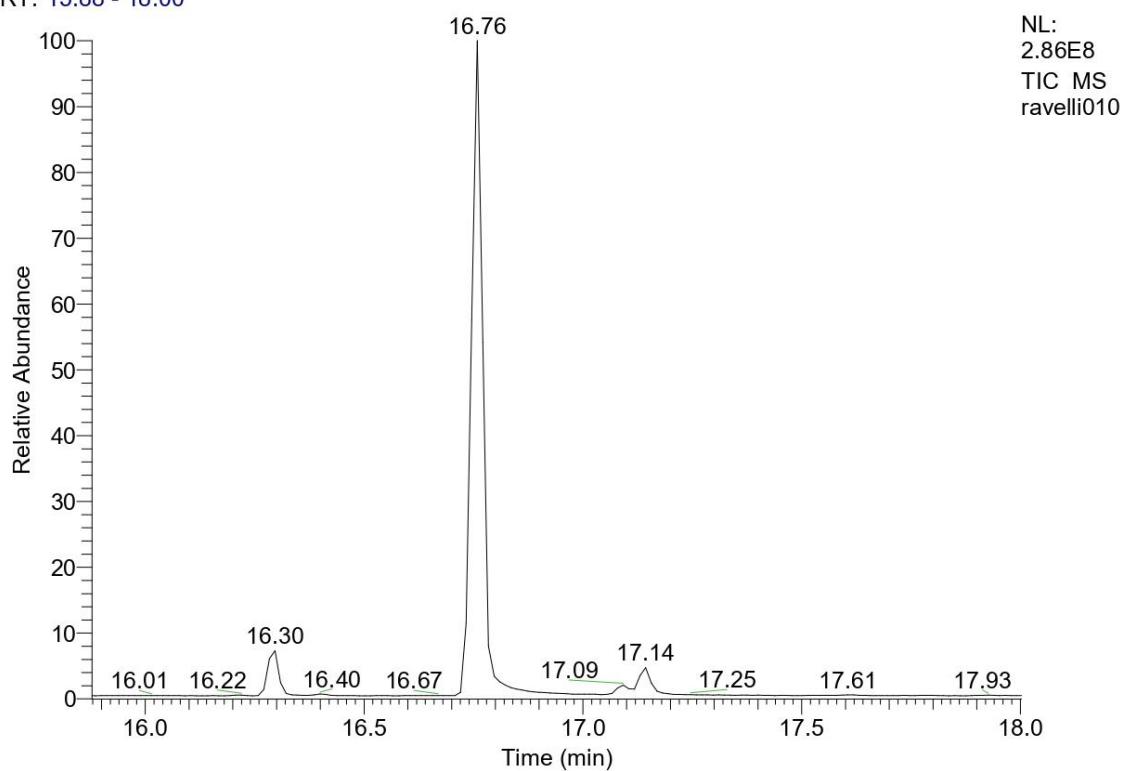


Figure S5. GC/MS analysis results for experiment *c*) in **Scheme S3**: chromatogram (TIC), mass spectrum for peak at 16.77 min (**31**).

RT: 15.88 - 18.00



ravelli010 #1112 RT: 16.76 AV: 1 NL: 6.67E7
 T: + c ESI Full ms [40.00-600.00]

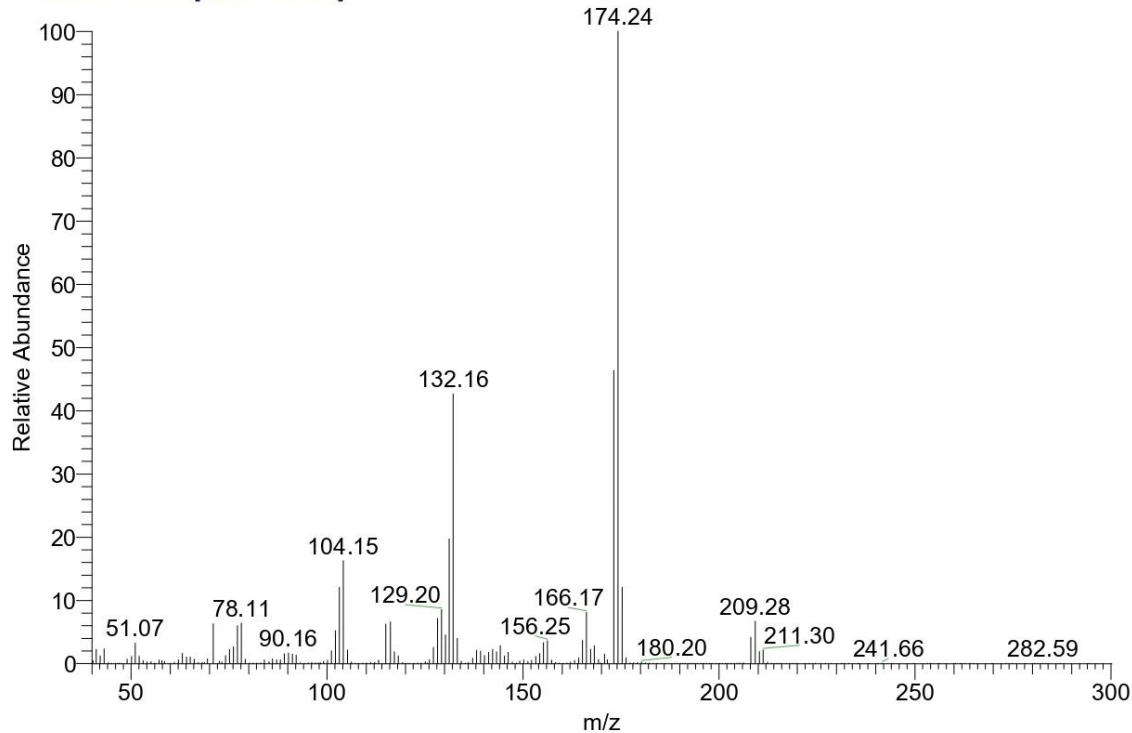
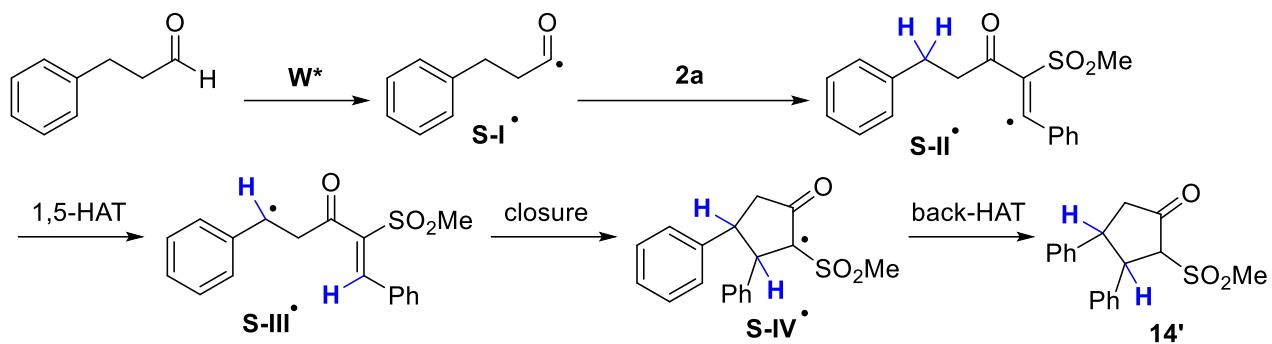


Figure S6. GC/MS analysis results for experiment d) in **Scheme S3**: chromatogram (TIC), mass spectrum for peak at 16.76 min (**31-d1**).

1.6 Proposed mechanism for the formation of **14'**



Scheme S4. Mechanism for the formation of product **14'** when **1l** is used in the role of H-Donor.

In **Scheme S4** an overview of the mechanism leading to the formation of product **14'** is offered. In detail, the first HAT step occurs at the formyl site of 3-phenylpropanal (**1l**) to afford the corresponding acyl radical **S-I[•]**. This intermediate adds onto sulfone **2a** through an ipso attack at the same carbon that bears the sulfonyl group. Thus, the highly reactive C(sp²)-centered radical **S-II[•]** is generated and abstracts intramolecularly a H atom from the benzyl site of the aldehyde to get **S-III[•]** via 1,5-HAT. Finally, ring closure via intramolecular radical addition to form **S-IV[•]** followed by back HAT afford product **14'**.

1.7 ^1H -NMR analysis of the reaction crude between 1a and 2l

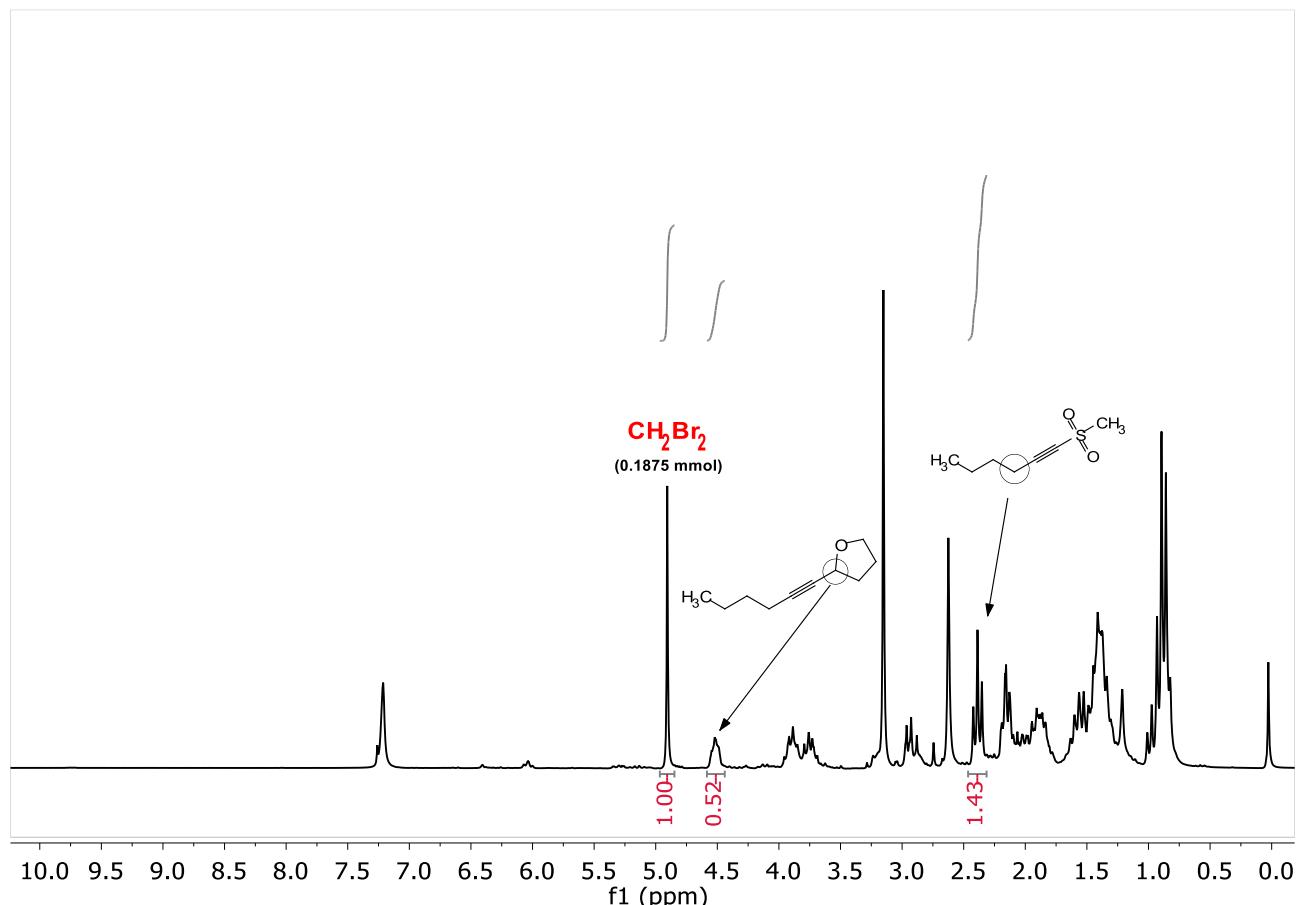


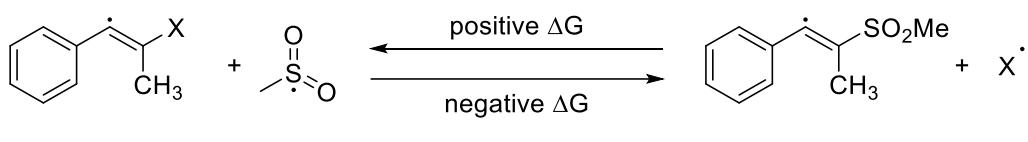
Figure S7. The experiment was run by adopting the explorative setup (vide infra). After 36 h, the reaction was interrupted, the solvent removed and replaced with CDCl_3 . Dibromomethane (CH_2Br_2 : 0.1875 mmol, 32.5 mg, $\rho = 2.5 \text{ g/mL}$) was used as the external standard.

1.8 Computational Analysis

The aptitude of different moieties (X) to act as radicofugal groups (X^\bullet) in the studied process has been evaluated computationally by means of the equation reported in **Table S2**. The methyl-substituted vinyl radicals indicated in the equation formally arise from the addition of a methyl radical onto the considered alkynylating agent. Methyl radical has been chosen as a simplified model of the photogenerated radical intermediates studied in this work and its use has allowed to speed up calculations and to limit the need to perform tedious conformational searches. The validity of such assumption, however, has been fully justified by considering the actual substitution with the 2-tetrahydrofuranyl group (see Computational Methods below).

Thus, by taking the case of the methanesulfonyl group as a reference, the reported equation gives a quantitative measure of the tendency of a given group to stabilize the vinyl radical adduct with respect to its intrinsic stability as a free radical. Specifically, a positive value indicates a weaker radicofugal group aptitude with respect to the methanesulfonyl radical and viceversa. The full set of data is gathered in **Table S2**.

Table S2. Relative stabilization of radicofugal groups.



X^\bullet	ΔG , kcal mol ⁻¹
Cl^\bullet	+20.8
PhSO_2^\bullet	+0.7
MeSO_2^\bullet	0
tolSO_2^\bullet	-0.1

2. Experimental section

2.1 General Information

H-donors **1** were commercially available and used as received, except for oxygenated H-donors **1a-g** and aldehydes **1k,l**, which were distilled prior to use. Acetonitrile (HPLC grade) employed for the photochemical reactions was used as received. TBADT was synthesized as indicated elsewhere.^{S4}

NMR spectra were recorded on a 376 (for ¹⁹F), 300 (for ¹H) or 75 (for ¹³C) MHz spectrometer; the attributions were made based on ¹H and ¹³C NMR. Data for ¹H and ¹⁹F NMR are reported as follows: chemical shift referred to TMS (δ ppm), multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quadruplet, quint = quintuplet, sext = sextuplet, sept = septuplet, m = multiplet), coupling constant (Hz) and integration. Data for ¹³C NMR are reported in terms of chemical shift.

Thin-layer chromatography (TLC) was performed on silica gel 60 F-254 plates. Visualization of the developed plates was performed by fluorescence quenching, 2,4-dinitrophenylhydrazine or KMnO₄ staining.

GC/MS analyses were carried out on a Thermo Scientific DSQII single quadrupole GC/MS system. The injection in the GC/MS system was performed at 250 °C split mode. The initial oven temperature of 80 °C was maintained for 5 min, increased by 10 °C/min to 250 °C and held for 10 min. A Restek Rx-5ms 30 m × 0.25 mm × 0.25 μ m film thickness capillary column was used with helium as the carrier gas at a constant flow rate of 1.0 mL/min. The transfer line temperature was 270 °C and the ion source temperature was 250 °C. Electron ionization mode was used with 70 eV and the ions were registered in full scan mode in a mass range of m/z 40-600 amu. The chromatogram acquisition, detection of mass spectral peaks and their waveform processing were performed using Xcalibur MS Software Version 2.1 (Thermo Scientific Inc.). Assignment of chemical structures to chromatographic peaks was based on the comparison with the databases for GC-MS NIST Mass Spectral Library (NIST 08) and Wiley Registry of Mass Spectral Data (8th Edition). The percentage content of each component was directly computed from the peak areas in the GC/MS chromatogram.

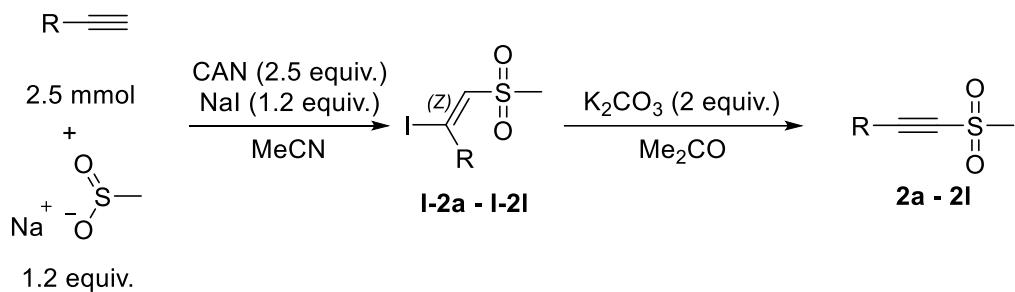
GC-FID analyses were performed on an Agilent 7820A. The injection was performed at 250 °C in split mode. The initial oven temperature of 80 °C was maintained for 2 min, increased by 10 °C/min to 250 °C and held for 5 min. An Agilent HP5 30 m × 0.32 mm × 0.25 µm film thickness capillary column was used with nitrogen as the carrier gas at a constant flow rate of 6.0 mL/min.

The light source for photochemical experiments was a 40 W Kessil LED (centered at 390 nm) at full power (technical specifications at <https://www.kessil.com/science/PR160L>). See section 2.3 for further information.

2.2 Synthesis and characterization of alkynylation reagents

General procedure for the synthesis of methylsulfones (2a-2l)

Sulfones (**2a-2l**) were synthesized according to a procedure adapted from the literature via the 2-step procedure reported below.⁵⁵

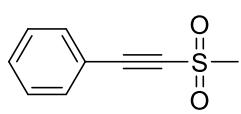


Step 1: An oven-dried 3-necks 100 mL round-bottom flask was charged with sodium methanesulfinate (354 mg, 3.0 mmol, 1.2 equiv.) and NaI (449 mg, 3.0 mmol, 1.2 equiv.) under inert atmosphere (Argon). Dry MeCN (15 mL) was added and the suspension was bubbled with Argon for 10 minutes. While keeping a vigorous stirring, the alkyne was added via syringe (2.5 mmol, 1.0 equiv.), then CAN (3.4 g, 6.25 mmol, 2.5 equiv.) in dry MeCN (25 mL) was added dropwise by means of a pressure-equalizing dropping funnel. The suspension turned to dark red and, after 4 hours, to bright yellow: typically, aromatic alkynes substituted with electron-withdrawing groups reacted faster than the corresponding electron-donating substituted derivatives. The reaction was checked via TLC, GC-FID or NMR (CDCl_3) and, upon completion, quenched with brine (50 mL). Then, the crude mixture was extracted with dichloromethane. The organic phase was washed again with brine (3×30 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure to get iodosulfones **I-2**. These products were typically obtained as a fluffy solid and purified via column chromatography (silica gel, cyclohexane/ethyl acetate mixtures as the eluant).

Step 2: Afterwards, iodosulfones **I-2** were dissolved in Me_2CO (25 mL) and refluxed with K_2CO_3 (2 equiv.) to completion. Reaction was conveniently monitored via GC-FID and, once completed, carbonate was filtered away, acetone was removed via rotary evaporation and the crude was purified via column chromatography (silica gel, cyclohexane/ethyl acetate mixtures as the eluant).

*N.B. 1: The conversion of **I-2** to **2** was also conveniently monitored via NMR (CDCl_3), since the signals for the methyl groups of iodosulfones typically fall below 3 ppm, while those of the final sulfones are more deshielded (> 3 ppm).*

N.B. 2: this synthesis is very sensitive to the purity grade of sodium methanesulfinate, which should be used in >98% grade. Sulfinate should be always stored under inert atmosphere.



((methylsulfonyl)ethynyl)benzene (2a) From 1-ethynylbenzene (274 μ L, 2.5 mmol, 1.0 equiv., ρ = 0.93 g/mL) to get iodosulfone **I-2a** (616 mg, 80%; mp: 99–100 $^{\circ}$ C, lit.^{S6} 99–101 $^{\circ}$ C) as a white solid. **I-2a** was then treated with potassium carbonate (553 mg, 4 mmol, 2.0 equiv.) in refluxing Me₂CO (25 mL) overnight to get **2a** as a yellowish solid (328 mg, 91%; mp: 64–66 $^{\circ}$ C, lit.^{S7} 65–66 $^{\circ}$ C) after column chromatography (silica gel, cyclohexane/ethyl acetate 9:1 as the eluant).

Spectroscopic data for **I-2a** are in accordance with the literature:^{S6}

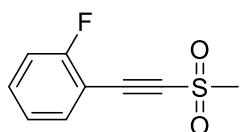
¹H NMR (300 MHz, CDCl₃) δ 7.47 – 7.43 (m, 2H), 7.41 – 7.35 (m, 3H), 7.31 (s, 1H), 2.68 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 140.2, 139.4, 130.3, 128.2, 127.7, 114.8, 43.0.

Spectroscopic data for **2a** are in accordance with the literature:^{S8}

¹H NMR (300 MHz, CDCl₃) δ 7.65 – 7.55 (d, J = 8 Hz, 2H), 7.54 – 7.47 (m, 1H), 7.41 (t, J = 8 Hz, 2H), 3.31 (s, 3 H).

¹³C NMR (75 MHz, CDCl₃) δ 132.6, 131.8, 129.0, 117.2, 91.4, 84.6, 46.5.



1-fluoro-2-((methylsulfonyl)ethynyl)benzene (2b) From 1-ethynyl-2-fluorobenzene (286 μ L, 2.5 mmol, 1.0 equiv., ρ : 1.06 g/mL) to get iodosulfone **I-2b** (303 mg, 37%; mp: 97–99 $^{\circ}$ C, lit.^{S6} 97–99 $^{\circ}$ C) as a yellowish solid. **I-2b** was then treated with potassium carbonate (257 mg, 1.9 mmol, 2.0 equiv.) in refluxing Me₂CO (20 mL) overnight to get **2b** as a yellowish oil that solidified upon standing at -4 $^{\circ}$ C for 20 minutes to give an off-white solid (182 mg, 93%; mp: 63–66 $^{\circ}$ C) after column chromatography (silica gel, cyclohexane/ethyl acetate 8:2 \rightarrow 7:3 as the eluant).

Spectroscopic data for **I-2b** are in accordance with the literature:^{S6}

¹H NMR (300 MHz, CDCl₃) δ 7.41 – 7.29 (m, 2H), 7.38 (s, 1H), 7.22 – 7.15 (m, 1H), 7.12 – 7.02 (m, 1H), 2.84 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 157.1 (d, J = 249 Hz), 141.6, 132.1 (d, J = 8 Hz), 129.7 (d, J = 2 Hz), 127.6 (d, J = 15 Hz), 124.3 (d, J = 4 Hz), 116.0 (d, J = 21 Hz), 106.9, 42.9.

¹⁹F NMR (376 MHz, CDCl₃) δ –112.46 (ddd, J_1 = 10 Hz, J_2 = 7 Hz, J_3 = 5 Hz).

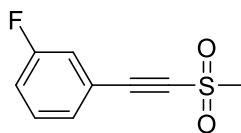
Spectroscopic data for **2b**:

¹H NMR (300 MHz, CDCl₃) δ 7.70 – 7.41 (m, 2H), 7.31 – 7.03 (m, 2H), 3.31 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 157.1 (d, J = 249 Hz), 141.6, 132.1 (d, J = 8 Hz), 129.7 (d, J = 2 Hz), 127.58 (d, J = 15 Hz), 124.3 (d, J = 4 Hz), 116.0 (d, J = 21 Hz), 106.9, 42.9 (d, J = 2 Hz).

¹⁹F NMR (376 MHz, CDCl₃) δ –106.74 (dtd, J_1 = 10 Hz, J_2 = 5 Hz, J_3 = 3 Hz).

Anal. Calcd for C₉H₇FO₂S: C, 54.54; H, 3.56; Found: C, 54.4; H, 3.6.



1-fluoro-3-((methylsulfonyl)ethynyl)benzene (2c) From 1-ethynyl-3-fluorobenzene (286 μ L, 2.5 mmol, 1.0 equiv., ρ : 1.05 g/mL) to get iodosulfone **I-2c** (682 mg, 42%; mp: 104–106 $^{\circ}$ C, lit.^{S6} 103–105 $^{\circ}$ C) as a yellowish solid. **I-2c** was then treated with potassium carbonate (289 mg, 2.1 mmol, 2.0 equiv.)

in refluxing Me₂CO (30 mL) overnight to get **2c** as a yellow oil after column chromatography (silica gel, cyclohexane/ethyl acetate 8:2 as the eluant).

Spectroscopic data for **I-2c** are in accordance with the literature:^{S6}

¹H NMR (300 MHz, CDCl₃) δ 7.37 (td, *J*₁ = 8 Hz, *J*₂ = 6 Hz, 1H), 7.31 (s, 1H), 7.23 (ddd, *J*₁ = 8 Hz, *J*₂ = 2 Hz, *J*₃ = 1 Hz, 1H), 7.14 (dt, *J*₁ = 9 Hz, *J*₂ = 2 Hz, 1H), 7.08 (tdd *J*₁ = 8 Hz, *J*₂ = 3 Hz, *J*₃ = 1 Hz, 1H), 2.75 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 162.0 (d, *J* = 249 Hz), 141.4 (d, *J* = 8 Hz), 140.8, 130.2 (d, *J* = 8 Hz), 123.7 (d, *J* = 3 Hz), 117.5 (d, *J* = 21 Hz), 115.2 (d, *J* = 23 Hz), 112.8 (d, *J* = 2 Hz), 43.4.

¹⁹F NMR (376 MHz, CDCl₃) δ -111.54 -- -111.95 (m).

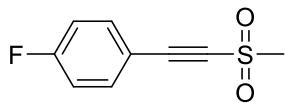
Spectroscopic data for **2c**:

¹H NMR (300 MHz, CDCl₃) δ 7.41 – 7.34 (m, 2H), 7.30 – 7.17 (m, 2H), 3.30 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 162.2 (d, *J* = 249 Hz), 130.8 (d, *J* = 8 Hz), 129.0 (d, *J* = 3 Hz), 119.6 (d, *J* = 24 Hz), 119.4 (d, *J* = 21 Hz), 89.6 (d, *J* = 3 Hz), 85.05.

¹⁹F NMR (376 MHz, CDCl₃) δ -111.11 -- -111.39 (m).

Anal. Calcd. for C₉H₇FO₂S: C, 54.54; H, 3.56; Found: C, 54.5; H, 3.6.



1-fluoro-4-((methylsulfonyl)ethynyl)benzene (2d). From 1-ethynyl-4-fluorobenzene (286 μL, 2.5 mmol, 1.0 equiv., ρ = 1.048 g/mL) to get iodosulfone **I-2d** (420 mg, 52%; mp: 102–104 °C, lit.^{S6} 112–114 °C) as a white fluffy solid. **I-2d** was then treated with potassium carbonate (356 mg, 2.6 mmol, 2.0 equiv.) in refluxing Me₂CO (25 mL) overnight to get **2d** as a yellowish solid (241 mg, 93%; mp: 74–76 °C) after column chromatography (silica gel, cyclohexane/ethyl acetate 8:2 as the eluant).

Spectroscopic data for **I-2d** are in accordance with the literature:^{S6}

¹H NMR (300 MHz, CDCl₃) δ 7.53 – 7.43 (m, 2H), 7.30 (s, 1H), 7.13 – 7.03 (m, 2H), 2.73 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 163.6 (d, *J* = 252 Hz), 140.4, 135.5, 130.4 (d, *J* = 9 Hz), 115.7 (d, *J* = 22 Hz), 113.8, 43.3.

¹⁹F NMR (376 MHz, CDCl₃) δ -109.18 (tt, *J*₁ = 8 Hz, *J*₂ = 5 Hz).

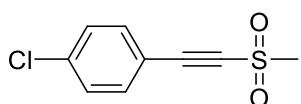
Spectroscopic data for **2d**:

¹H NMR (300 MHz, CDCl₃) δ 7.52 – 7.43 (m, 2H), 7.14 – 7.00 (m, 2H), 2.73 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 164.6 (d, *J* = 256 Hz), 135.4 (d, *J* = 9 Hz), 116.6 (d, *J* = 22 Hz), 113.8 (d, *J* = 4 Hz), 90.6, 84.5 (d, *J* = 2 Hz), 46.9.

¹⁹F NMR (376 MHz, CDCl₃) δ -104.5 (ttd, *J*₁ = 8 Hz, *J*₂ = 5 Hz, *J*₃ = 1 Hz).

Anal. Calcd for C₉H₇FO₂S: C, 54.54; H, 3.56; Found: C, 54.4; H, 3.6.



1-chloro-4-((methylsulfonyl)ethynyl)benzene (2e). From 1-ethynyl-4-chlorobenzene (341 mg, 2.5 mmol, 1.0 equiv.) to get iodosulfone **I-2e** (500 mg, 58%; mp: 132–134 °C; lit.^{S6} 116–117 °C) as a pale yellow solid.

I-2e was then treated with potassium carbonate (403 mg, 2.9 mmol, 2.0 equiv.) in refluxing Me₂CO (25 mL) overnight to get **2e** as a yellowish solid (110 mg, 45%; mp: 101–103 °C) after column chromatography (silica gel, cyclohexane/ethyl acetate 8:2 as the eluant).

Spectroscopic data for **I-2e** are in accordance with those reported in the literature:^{S6}

¹H NMR (300 MHz, CDCl₃) δ 7.38 – 7.29 (m, 5H), 2.70 (s, 3H).

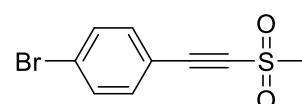
¹³C NMR (75 MHz, CDCl₃) δ 140.5, 137.9, 136.6, 129.4, 128.7, 113.5, 43.3.

Spectroscopic data for **2e**:

¹H NMR (300 MHz, CDCl₃) δ 7.53 (d, *J* = 9 Hz, 2H), 7.41 (d, *J* = 9 Hz, 2H), 3.30 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 138.6, 134.2, 129.5, 116.2, 90.3, 85.5, 46.9.

Anal. Calcd. for C₉H₇ClO₂S: C, 50.36; H, 3.29; Found: C, 50.4; H, 3.3.

**1-bromo-4-((methylsulfonyl)ethynyl)benzene (2f).** From 1-ethynyl-4-bromobenzene (452 mg, 2.5 mmol, 1.0 equiv.) to get iodosulfone **I-2f** (682 mg, 70%) as a beige crystalline solid (mp: 128–130 °C). **I-2f** was then treated with potassium carbonate (483 mg, 3.5 mmol, 2.0 equiv.) in refluxing Me₂CO (30 mL) overnight to get **2f** as a white solid (252 mg, 56%; mp: 116–118 °C) after column chromatography (silica gel, cyclohexane/ethyl acetate 8:2 as the eluant).

Spectroscopic data for **I-2f**:^{S9}

¹H NMR (300 MHz, CDCl₃) δ 7.53 (d, *J* = 9 Hz, 2H), 7.33 (d, *J* = 9 Hz, 2H), 7.31 (s, 1H), 2.75 (s, 3H).

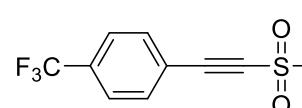
¹³C NMR (75 MHz, CDCl₃) δ 140.9, 138.8, 132.1, 130.0, 125.4, 114.0, 43.8.

Spectroscopic data for **2f**:

¹H NMR (300 MHz, CDCl₃) δ 7.57 (d, *J* = 9 Hz, 2H), 7.45 (d, *J* = 9 Hz, 2H), 3.30 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 134.2, 132.4, 127.0, 116.6, 90.3, 85.5, 46.9.

Anal. Calcd. for C₉H₇BrO₂S: C, 41.72; H, 2.72; Found: C, 41.7; H, 2.7.

**1-((methylsulfonyl)ethynyl)-4-(trifluoromethyl)benzene (2g).** From 1-ethynyl-4-(trifluoromethyl)benzene (408 μL, 2.5 mmol, 1.0 equiv., ρ = 1.043 g/mL) to get iodosulfone **I-2g** (400 mg, 42%; mp: 113–115 °C, lit.^{S6} 113–114 °C) as a mixture of inseparable *Z/E*-isomers as yellowish crystalline solid. **I-2g** (without any further purification, purity 85% by GC) was then treated with potassium carbonate (483 mg, 3.5 mmol, 2.0 equiv.) in refluxing Me₂CO (30 mL) overnight to get **2g** as a white solid (165 mg, 63%; mp: 91–93 °C) after column chromatography (silica gel, cyclohexane/ethyl acetate 7:3 as the eluant).

Spectroscopic data for **I-2g**:^{S6}

Major isomer: ¹H NMR (300 MHz, CDCl₃) δ 7.65 (d, *J* = 8 Hz, 2H), 7.53 (d, *J* = 8 Hz, 2H), 7.36 (s, 1H), 2.78 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 143.0, 140.8, 132.1 (q, *J* = 33 Hz), 128.2, 125.4 (q, *J* = 4 Hz), 123.6 (q, *J* = 274 Hz), 112.7, 43.4.

¹⁹F NMR (376 MHz, CDCl₃) δ –63.38 (m).

Minor isomer: ¹H NMR (300 MHz, CDCl₃) δ 7.65 (d, *J* = 8 Hz, 2H), 7.53 (d, *J* = 8 Hz, 2H), 7.21 (s, 1H), 3.18 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 144.8, 139.1, 132.5 (q, *J* = 20 Hz), 129.0, 125.9 (q, *J* = 4 Hz), 114.9, 42.0. NB: the CF₃ group for the minor isomer could not be detected.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.37 (m).

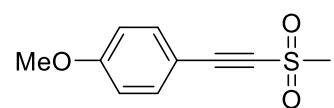
Spectroscopic data for **2g**:

¹H NMR (300 MHz, CDCl₃) δ 7.75 – 7.67 (m, 4H), 7.26 (s, 1H), 3.32 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 133.5 (q, *J* = 32 Hz), 133.3, 126.0 (q, *J* = 4 Hz), 123.44 (q, *J* = 274 Hz), 121.5 (q, *J* = 1 Hz), 89.2, 86.3, 46.9.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.76.

Anal. Calcd. for C₁₀H₇F₃O₂S: C, 48.39; H, 2.84; Found: C, 48.3; H, 2.9.

 **1-methoxy-4-((methylsulfonyl)ethynyl)benzene (2h).** From 1-ethynyl-4-methoxybenzene (324 μL, 2.5 mmol, 1.0 equiv., ρ = 1.019 g/mL) to get iodosulfone **I-2h** (582 mg, 69%) as a yellow oil. **I-2h** was then treated with potassium carbonate (475 mg, 3.4 mmol, 2.0 equiv.) in refluxing Me₂CO (50 mL) overnight to get **2h** as a yellow oil after column chromatography (silica gel, cyclohexane/ethyl acetate 8:2 as the eluant).

Spectroscopic data for **I-2h**:

¹H NMR (300 MHz, CDCl₃) δ 7.47 (d, *J* = 9 Hz, 2H), 7.24 (s, 1H), 6.89 (d, *J* = 9 Hz, 2H), 3.83 (s, 3H), 2.67 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 161.3, 139.5, 131.6, 130.3, 115.6, 113.8, 55.5, 43.0.

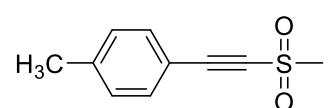
Anal. Calcd. for C₁₀H₁₁IO₃S: C, 35.52; H, 3.28; Found: C, 35.5; H, 3.3.

Spectroscopic data for **2h**:

¹H NMR (300 MHz, CDCl₃) δ 7.53 (d, *J* = 9 Hz, 2H), 6.91 (d, *J* = 9 Hz, 2H), 3.85 (s, 3H), 3.28 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 162.5, 135.0, 114.7, 109.3, 92.9, 83.9, 55.6, 47.0.

Anal. Calcd. for C₁₀H₁₀O₃S: C, 57.13; H, 4.79; Found: C, 57.1; H, 4.8.

 **1-methyl-4-((methylsulfonyl)ethynyl)benzene (2i).** From 1-ethynyl-4-methylbenzene (581 mg, 2.5 mmol, 1.0 equiv.) to get iodosulfone **I-2i** (522 mg, 65%; mp: 129–131 °C, lit.^{S10} 129–130 °C) as a yellowish crystalline solid. **I-2i** was then treated with potassium carbonate (449 mg, 3.2 mmol, 2.0 equiv.) in refluxing Me₂CO (30 mL) overnight to get **2i** as a yellowish solid (175 mg, 56%; mp: 65–67 °C) after column chromatography (silica gel, cyclohexane/ethyl acetate 9:1 as the eluant).

Spectroscopic data for **I-2i** are in accordance with the literature:^{S6}

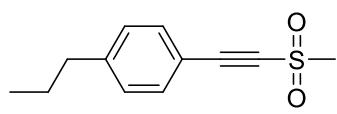
¹H NMR (300 MHz, CDCl₃) δ 7.37 (d, *J* = 8 Hz, 2H), 7.27 (s, 1H), 7.19 (d, *J* = 8 Hz, 2H), 2.66 (s, 3H), 2.37 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 141.1, 140.0, 136.7, 129.2, 128.1, 115.6, 43.1, 21.6.

Spectroscopic data for **2i**:

¹H NMR (300 MHz, CDCl₃) δ 7.47 (d, *J* = 8 Hz, 2H), 7.21 (d, *J* = 8 Hz, 2H), 3.29 (s, 3H), 2.39 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 142.8, 132.9, 129.7, 114.4, 92.3, 84.2, 47.0, 21.9.



1-((methylsulfonyl)ethynyl)-4-propylbenzene (2j). From 1-ethynyl-4-propylbenzene (360 mg, 2.5 mmol, 1.0 equiv.) to get iodosulfone **I-2j** (422 mg, 59%) as an off-white solid (mp: 109–111 °C; lit.^{S6} 123–124 °C). **I-2j** was then treated with potassium carbonate (333 mg, 2.4 mmol, 2.0 equiv.) in refluxing Me₂CO (30 mL) for 36 hours to get **2j** as a yellowish liquid (215 mg, 81%) after column chromatography (silica gel, cyclohexane/ethyl acetate 8:2 as the eluant).

Spectroscopic data for **I-2j** are in accordance with the literature:^{S6}

¹H NMR (300 MHz, CDCl₃) δ 7.39 (d, *J* = 8 Hz, 2H), 7.27 (s, 1H), 7.19 (d, *J* = 8 Hz, 2H), 2.63 (s, 3H), 2.63 – 2.55 (t, *J* = 8 Hz, 2H), 1.64 (h, *J* = 7 Hz, 2H), 0.94 (t, *J* = 7 Hz, 3H).

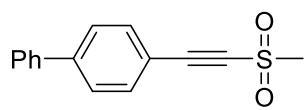
¹³C NMR (75 MHz, CDCl₃) δ 145.8, 140.1, 136.8, 128.5, 128.2, 115.6, 43.0, 38.0, 24.2, 13.9.

Spectroscopic data for **2j**:

¹H NMR (300 MHz, CDCl₃) δ 7.50 (d, *J* = 8 Hz, 2H), 7.22 (d, *J* = 8 Hz, 2H), 3.29 (s, 3H), 2.62 (t, *J* = 8 Hz, 2H), 1.64 (h, *J* = 7 Hz, 2H), 0.93 (t, *J* = 7 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 147.4, 133.0, 129.1, 114.7, 92.4, 84.2, 47.0, 38.2, 24.2, 13.8.

Anal. Calcd. for C₁₂H₁₄O₂S: C, 64.84; H, 6.35; Found: C, 64.9; H, 6.4.



4-((methylsulfonyl)ethynyl)-1,1'-biphenyl (2k). From 4-ethynylbiphenyl (446 mg, 2.5 mmol, 1.0 equiv.) to get iodosulfone **I-2k** (574 mg, 60%; mp: 140–142 °C) as a pale yellow powder. **I-2k** was then treated with potassium carbonate (415 mg, 3.0 mmol, 2.0 equiv.) in refluxing Me₂CO (25 mL) overnight to get **2k** as a beige powder (365 mg, 95%; mp: 143–145 °C) after column chromatography (silica gel, cyclohexane/ethyl acetate 8:2 as the eluant).

Spectroscopic data for **I-2k**:

¹H NMR (300 MHz, CDCl₃) δ 7.71 – 7.52 (m, 6H), 7.51 – 7.38 (m, 3H), 7.33 (s, 1H), 2.73 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 143.4, 140.3, 139.8, 138.3, 129.1, 128.8, 128.2, 127.3, 127.0, 115.0, 43.2.

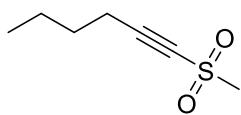
Anal. Calcd. for C₁₅H₁₃IO₂S: C, 46.89; H, 3.41; Found: C, 46.9; H, 3.4.

Spectroscopic data for **2k**:

¹H NMR (300 MHz, CDCl₃) δ 7.70 – 7.56 (m, 6H), 7.52 – 7.37 (m, 3H), 3.32 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 144.7, 139.6, 133.5, 129.2, 128.6, 127.6, 127.3, 116.2, 91.8, 85.1, 47.0.

Anal. Calcd. for C₁₅H₁₂O₂S: C, 70.29; H, 4.72; Found: C, 70.3; H, 4.8.



1-(methylsulfonyl)hex-1-yne (2l). From 1-hexyne (1.14 mL, 10 mmol, 1.0 equiv., $\rho = 0.715$ g/mL) to get iodosulfone **I-2l** (313 mg, 11%) as a colorless oil. **I-2l** was then treated with potassium carbonate (30 mg, 0.4 mmol, 2.0 equiv.) in refluxing Me_2CO (25 mL) overnight to get **2l** as a colorless liquid (108 mg, 61%) after column chromatography (silica gel, cyclohexane/ethyl acetate 9:1 as the eluant).

Spectroscopic data for **I-2l** are in accordance with the literature:^{S6}

^1H NMR (300 MHz, CDCl_3) δ 7.00 (s, 1H), 3.30 – 3.22 (m, 2H), 3.20 (s, 3H), 1.92 – 1.78 (m, 2H), 1.72 – 1.55 (m, 2H), 1.19 (t, $J = 7$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 137.7, 127.5, 43.8, 39.9, 32.2, 21.7, 13.9.

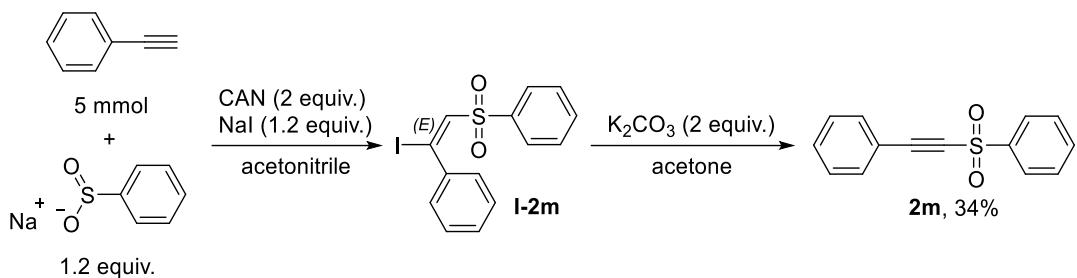
Spectroscopic data for **2l**:

^1H NMR (300 MHz, CDCl_3) δ 3.18 (s, 3H), 2.41 (t, $J = 7$ Hz, 2H), 1.67 – 1.53 (m, 2H), 1.53 – 1.32 (m, 2H), 0.93 (t, $J = 7$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 95.8, 77.4, 46.8, 29.1, 22.1, 18.6, 13.5.

Anal. Calcd. for $\text{C}_7\text{H}_{12}\text{O}_2\text{S}$: C, 52.47; H, 7.55; Found: C, 52.5; H, 7.6.

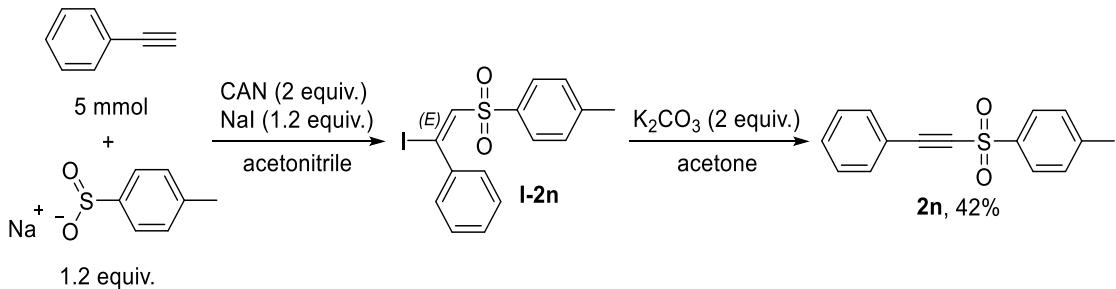
Synthesis of ((phenylethynyl)sulfonyl)benzene (2m)



((Phenylethynyl)sulfonyl)benzene was synthesized as described above for methylsulfones. In particular, sodium benzenesulfinic acid salt (984 mg, 6 mmol, 1.2 equiv.) was used in place of sodium methanesulfinate. **2m** was purified via column chromatography (silica gel, cyclohexane/ethyl acetate 9:1 as the eluant) to get a pale yellow solid (419 mg, 34% yield over two steps; mp: 65-66 °C, lit.^{S8} 66-68 °C). Spectroscopic and characterization data of **2m** are in accordance with the literature.^{S8}

¹H NMR (300 MHz, CDCl_3) δ 8.13 – 8.06 (m, 2H), 7.73 – 7.65 (m, 1H), 7.65 – 7.57 (m, 2H), 7.56 – 7.44 (m, 3H), 7.43 – 7.33 (m, 2H).

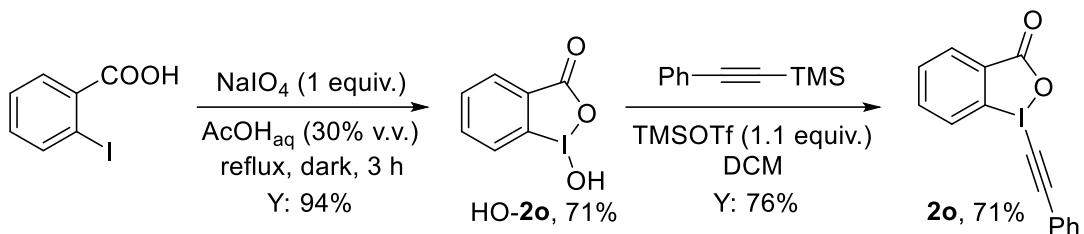
Synthesis of 1-methyl-4-((phenylethynyl)sulfonyl)benzene (2n)



1-methyl-4-((phenylethynyl)sulfonyl)benzene (**2n**) was synthesized as described above for methylsulfones. In particular, sodium *p*-toluenesulfinic acid salt (1.07 g, 6 mmol, 1.2 equiv.) was used in place of sodium methanesulfinate. Iodosulfone **I-2n** was obtained as a red wax and was purified via column chromatography (silica gel, cyclohexane/ethyl acetate 9:1 as the eluant). However, we found that crude **I-2n** could be directly subjected to the second step of the reaction without penalizing the yield. In particular, the red wax was dissolved in Me_2CO (25 mL) and refluxed with K_2CO_3 (1.38 g, 10 mmol, 2 equiv.) for at least 24 hours. Reaction was conveniently monitored via GC-FID and, once completed, carbonate was removed by filtration and acetone via rotary evaporation. The crude was recrystallized from hot cyclohexane to get **2n** as a white solid (537 mg, 42% yield over two steps; mp: 76-78 °C, lit.^{S8} 76-77 °C). Alternatively, **2n** could be purified via column chromatography (silica gel, cyclohexane/ethyl acetate 9:1 as the eluant). Spectroscopic and characterization data of **2n** are in accordance with the literature.^{S8}

¹H NMR (300 MHz, CDCl_3) δ 7.96 (d, $J = 8$ Hz, 2H), 7.55 – 7.43 (m, 3H), 7.43 – 7.32 (m, 4H), 2.47 (s, 3H).

Synthesis of 1-(phenylethynyl)-1,2-benziodoxol-3(1H)-one (2o)



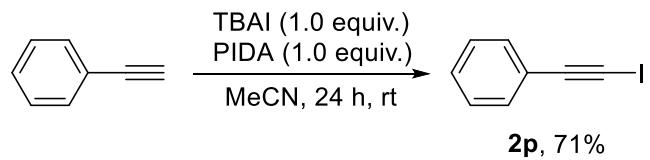
Following a literature procedure,^{S11} NaIO₄ (2.1 g, 10.0 mmol, 1.0 equiv.) and 2-iodobenzoic acid (2.4 g, 10.0 mmol, 1.0 equiv.) were suspended in 30% (v:v) aqueous AcOH (15 mL). The reaction mixture was vigorously stirred and refluxed for 3 h in the dark. Ice-cold water was added and allowed to cool to room temperature. The resulting white solid was filtered, washed with cold water and acetone; after 2 hours of air-drying, HO-**2o** was obtained as a white solid (2.49 g, 94%).

The white solid was then suspended in DCM (100 mL) and TMSOTf (2.6 mL, 14.1 mmol, 1.5 equiv., $\rho = 1.225 \text{ g/mL}$) was added dropwise: the white suspension turned into a yellow solution after 30 seconds. After 1 h of stirring, trimethylsilyl alkyne (2.0 mL, 10.3 mmol, 1.1 equiv., $\rho = 0.886 \text{ g/mL}$) was added dropwise and the solution turned gradually to brown.

After 2 days, the mixture was quenched with water and washed with sat'd NaHCO₃ and dried over MgSO₄. After solvent removal, an orange solid was obtained and recrystallized from MeCN to afford an off-white solid (7.1 g, 76%; mp: 149 °C with decomp., lit.^{S12} 150 °C with decomp.). Spectroscopic data of **2o** are in accordance with the literature.^{S11}

¹H NMR (300 MHz, CDCl₃) δ 8.44 – 8.38 (m, 1H), 8.28 – 8.22 (m, 1H), 7.83 – 7.71 (m, 2H), 7.65 – 7.55 (m, 2H), 7.54 – 7.36 (m, 3H).

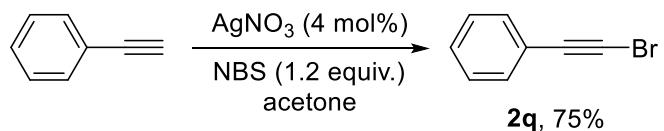
Synthesis of (iodoethynyl)benzene (2p)



Following a literature procedure,^{S13} tetrabutylammonium iodide (TBAI; 400 mg, 1 mmol, 1 equiv.) was suspended in MeCN (10 mL) and ethynylbenzene (110 μ L, 1.0 mmol, 1.0 equiv., $\rho = 0.93 \text{ g/mL}$) was added dropwise. Phenyliodine(III) diacetate (PIDA; 300 mg, 0.9 mmol, 0.9 equiv.) was then added in portions: the mixture was stirred for 24 h at room temperature and then extracted with ethyl acetate and sat'd Na₂S₂O₃. Iodoalkyne **2p** was obtained after column chromatography (pure cyclohexane as the eluant) as a yellowish liquid (160 mg, 71%) to be stored in the dark and at –21 °C. Spectroscopic data of **2p** are in accordance with the literature.^{S13}

¹H NMR (300 MHz, CDCl₃) δ 7.47 – 7.41 (m, 2H), 7.36 – 7.28 (m, 3H).

Synthesis of (bromoethynyl)benzene (2q)

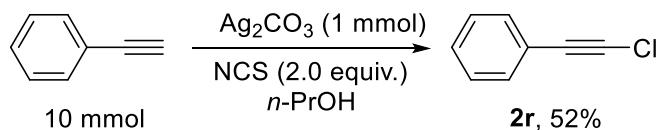


(Bromoethynyl)benzene (**2q**) was synthesized according to a previously reported procedure.^{S14} In particular, phenylacetylene (439 μ L; 4 mmol; 1.0 equiv., $\rho = 0.93$ g/mL) was dissolved in acetone (10 mL) in a 100 mL round-bottom flask. Then, AgNO_3 (34 mg; 0.2 mmol; 0.05 equiv.) was added to get a fine suspension (sonication may be used, if necessary). Finally, *N*-bromosuccinimide (NBS) (854 mg; 4.8 mmol; 1.2 equiv.) was added and the suspension was stirred by means of a magnetic stirrer. After 3 hours, the suspension turned grey and finally yellow, which usually indicated reaction completion. The reaction was constantly monitored via TLC (eluant: pure cyclohexane). Once the reaction was complete, the solvent was removed and the crude product purified via column chromatography (eluant: pure cyclohexane) to yield **2q** as a colorless oil (543 mg, 75% yield; storage at -21 °C is required). Spectroscopic data of **2q** are in accordance with the literature.^{S14}

¹H NMR (300 MHz, CDCl_3) δ 7.51 – 7.42 (m, 2H), 7.37 – 7.28 (m, 3H).

N.B.: NBS was recrystallized from water (24 g in 250 mL) prior to use.

Synthesis of (chloroethynyl)benzene (2r)



(Chloroethynyl)benzene (**2r**) was synthesized by modifying a previously reported procedure.^{S15} In particular, an oven-dried (T: 130 °C, overnight) 100 mL Schlenk flask equipped with a magnetic stirrer was charged with *N*-chlorosuccinimide (NCS) (2.67g, 20.0 mmol, 2.0 equiv.), K_2CO_3 (690 mg, 5.0 mmol, 0.5 equiv.) and Ag_2CO_3 supported on Celite (50% wt; 550 mg, 1.0 mmol, 0.1 equiv.) under inert atmosphere (Argon). Finally, propanol (15 mL) was added. Then, phenylacetylene (1.1 mL, 10.0 mmol, 1.0 equiv., $\rho = 0.93$ g/mL) was added via syringe and the mixture was refluxed for 4 hours. Reaction was monitored via GC-FID and ultimately quenched with brine at 0 °C. The crude was extracted with ethyl acetate (3×50 mL), the organic phases were combined, washed with water, dried over Na_2SO_4 and then the solvent was removed under reduced pressure. Product (720 mg; 53% yield) was obtained as a colorless liquid after column chromatography (eluant: petroleum ether). Spectroscopic data of **2r** are in accordance with the literature.^{S15}

¹H NMR (300 MHz, CDCl_3) δ 7.48 – 7.40 (m, 2H), 7.38 – 7.28 (m, 3H).

2.3 General procedures for the SOMOphilic Alkynylation of Aliphatic Hydrogen Donors via Decatungstate-Photocatalyzed Hydrogen Atom Transfer

To evaluate the broadness of the title reaction, explorative experiments were carried out (**Figure S8**, left). For the isolation of the products, preparative experiments were performed (**Figure S8**, right).



Figure S8. Reaction vessels for explorative (left) and preparative experiments (right).

Explorative runs: In a typical experiment, a MeCN solution (1 mL) of **2a** (0.1 M), **1a** (5.0 equiv, 0.5 M) and tetrabutylammonium decatungstate (TBADT, 2 mol%) was prepared in a borosilicate glass vial (see **Figure S8**, left). The solution was bubbled with inert gas (Argon) for 1 minute prior to irradiation. The vial was put in an Evoluchem apparatus (see **Figure S9**) equipped with a 8-spots holder and irradiated with a 40 W Kessil LED (390 nm) at full power up to reaction completion (reaction was monitored via GC-FID analysis to check the consumption of starting materials and product formation).



Figure S9. Equipment used for explorative experiments.

Preparative runs: In a typical experiment, a MeCN solution (5 mL) of **2a** (0.1 M), **1a** (5.0 equiv, 0.5 M) and tetrabutylammonium decatungstate (TBADT, 2 mol%) was prepared in a Pyrex reaction vessel (see **Figure S8**, right). Solution was bubbled with inert gas (Argon) for 5 minutes prior to irradiation. While maintaining the solution under continuous stirring, a 40 W Kessil LED (390 nm) was positioned 5 cm away from the reaction vessel (see **Figure S10**) and used at full power up to reaction completion (reaction was monitored via GC-FID analysis to check for the consumption of the starting material). After irradiation, the crude mixture was poured into a round-bottom flask and the solvent was removed via rotary evaporation. Afterwards, the crude was adsorbed on SiO_2 and purified via column chromatography.

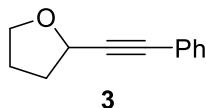


Figure S10. Equipment used for preparative experiments.

2.4 Characterization of products 3-31

*N.B.: NMR spectroscopy was performed in acetone-*d*₆ or CDCl₃, however partial decomposition of the analyzed compounds (in particular, propargylic ethers) was observed in the latter solvent within 24 hours.*

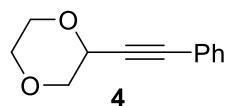
Scope of the H-Donors (1a-q)



2-(phenylethynyl)tetrahydrofuran (3). From freshly distilled tetrahydrofuran **1a** (2.5 mmol, 0.5 M, 5.0 equiv., 200 μ L, ρ = 0.889 g/mL) and **2a** (0.5 mmol, 0.1 M, 1.0 equiv., 90 mg). The crude mixture was purified through column chromatography (SiO₂: cyclohexane/ethyl acetate 9:1) to afford **3** as a colorless oil (61 mg, 71% yield). Spectroscopic data of **3** are in accordance with the literature (CDCl₃ used as the solvent).^{S16}

¹H NMR (300 MHz, acetone-*d*₆) δ 7.58 – 7.14 (m, 5H), 4.76 (dd, J_1 = 7 Hz, J_2 = 5 Hz, 1H), 3.94 – 3.71 (m, 2H), 2.29 – 2.15 (m, 1H), 2.02 – 1.85 (m, 3H).

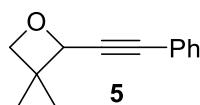
¹³C NMR (75 MHz, acetone-*d*₆) δ 132.4, 129.3, 129.3, 123.9, 90.7, 84.6, 69.0, 68.2, 34.2, 26.1.



2-(phenylethynyl)-1,4-dioxane (4). From freshly distilled 1,4-dioxane **1b** (2.5 mmol, 0.5 M, 5.0 equiv., 214 μ L, ρ = 1.03 g/mL) and **2a** (0.5 mmol, 0.1 M, 1.0 equiv., 90 mg). The crude mixture was purified through column chromatography (SiO₂: cyclohexane/ethyl acetate 95:5) to afford **4** as a colorless oil (57 mg, 61% yield) and 36 mg of starting sulfone (39% yield). Spectroscopic data of **4** are in accordance with the literature (CDCl₃ used as the solvent).^{S17}

¹H NMR (300 MHz, acetone-*d*₆) δ 7.46 – 7.15 (m, 5H), 4.43 (dd, J_1 = 7 Hz, J_2 = 3 Hz, 1H), 3.76 (tt, J_1 = 10 Hz, J_2 = 3 Hz, 2H), 3.64 – 3.28 (m, 4H).

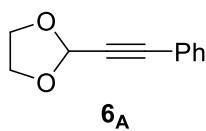
¹³C NMR (75 MHz, acetone-*d*₆) δ 132.5, 129.7, 129.5, 123.3, 86.4, 86.3, 71.0, 67.1, 66.9, 66.0.



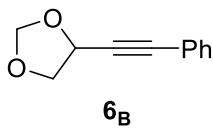
3,3-dimethyl-2-(phenylethynyl)oxetane (5). From freshly distilled 3,3-dimethyloxetane **1c** (2.5 mmol, 0.5 M, 5.0 equiv., 258 μ L, ρ = 0.83 g/mL) and **2a** (0.5 mmol, 0.1 M, 1.0 equiv., 90 mg). TBADT 5 mol% was used. The crude mixture was purified through column chromatography (SiO₂: cyclohexane/ethyl acetate 8:2) to afford **5** as a colorless liquid (33 mg, 35% yield). Spectroscopic data of **5** are in accordance with the literature (CDCl₃ used as the solvent).^{S18}

¹H NMR (300 MHz, acetone-*d*₆) δ 7.54 – 7.46 (m, 2H), 7.40 (q, J = 4 Hz, 3H), 5.16 (s, 1H), 4.30 (d, J = 5 Hz, 1H), 4.18 (d, J = 5 Hz, 1H), 1.39 (s, 3H), 1.32 (s, 3H).

¹³C NMR (75 MHz, acetone-*d*₆) δ 132.5, 129.7, 129.5, 123.6, 90.9, 87.45, 81.9, 80.5, 40.9, 26.1, 23.7.



2-(phenylethynyl)-1,3-dioxolane (6A) and 4-(phenylethynyl)-1,3-dioxolane (6B). From freshly distilled 1,3-dioxolane **1d** (2.5 mmol, 0.5 M, 5.0 equiv., 175 μ L, ρ = 1.06 g/mL) and **2a** (0.5 mmol, 0.1 M, 1.0 equiv., 90 mg). The crude mixture was purified through column chromatography (SiO₂: petroleum ether/methyl *tert*-butyl ether 9:1) to afford a mixture of **6A** and **6B** as a colorless oil (57 mg, ratio 1:1, 67% overall yield). Further



purification afforded pure fractions of each compound. Spectroscopic data of **6A** and **6B** are in accordance with the literature (CDCl₃ used as the solvent).^{S19}

Isomer 6A:

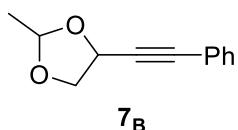
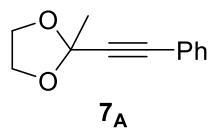
¹H NMR (300 MHz, acetone-d₆) δ 7.56 – 7.45 (m, 2H), 7.44 – 7.37 (m, 3H), 5.86 (s, 1H), 4.11 – 4.01 (m, 2H), 4.01 – 3.90 (m, 2H).

¹³C NMR (75 MHz, acetone-d₆) δ 132.9, 130.3, 129.8, 123.0, 94.3, 86.5, 85.4, 65.4.

Isomer 6B:

¹H NMR (300 MHz, acetone-d₆) δ 7.51 – 7.43 (m, 2H), 7.43 – 7.34 (m, 3H), 5.02 – 4.91 (m, 3H), 4.18 (dd, *J*₁ = 8 Hz, *J*₂ = 6 Hz, 1H), 3.86 (dd, *J*₁ = 8 Hz, *J*₂ = 6 Hz, 1H).

¹³C NMR (75 MHz, acetone-d₆) δ 132.6, 129.8, 129.6, 123.3, 95.7, 87.6, 86.2, 71.4, 66.4.



2-methyl-2-(phenylethynyl)-1,3-dioxolane (7A) and 2-methyl-4-(phenylethynyl)-1,3-dioxolane (7B). From freshly distilled 2-methyl-1,3-dioxolane **1e** (2.5 mmol, 0.5 M, 5.0 equiv., 224 μL, ρ = 0.98 g/mL) and **2a** (0.5 mmol, 0.1 M, 1.0 equiv., 90 mg). The reaction was performed in the presence of NaHCO₃ (42 mg, 0.5 mmol, 0.1 M, 1.0 equiv.) to prevent the hydrolysis of compound **7A**. The crude mixture was purified through column chromatography (SiO₂: petroleum ether/methyl tert-butyl ether 9:1) to afford a mixture of **7A** and **7B** as a colorless oil (71 mg, ratio 3.3:1, 75% overall yield). Further purification afforded pure fractions of each compound: **7A** as a colorless solid (mp: 42–44 °C) and **7B** as a colorless oil. Spectroscopic data of **7A** are in accordance with the literature (CDCl₃ used as the solvent).^{S20}

Isomer 7A:

¹H NMR (300 MHz, acetone-d₆) δ 7.50 – 7.43 (m, 2H), 7.42 – 7.36 (m, 3H), 4.13 – 4.06 (m, 2H), 4.06 – 3.99 (m, 2H), 1.70 (s, 3H).

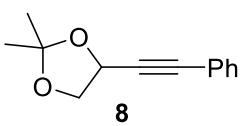
¹³C NMR (75 MHz, acetone-d₆) δ 132.5, 129.6, 129.4, 123.0, 103.2, 88.7, 82.9, 65.3, 26.8.

Isomer 7B:

¹H NMR (300 MHz, acetone-d₆) δ 7.51 – 7.44 (m, 2H), 7.44 – 7.36 (m, 3H), 5.19 (q, *J* = 5 Hz, 1H), 5.01 (dd, *J* = 7 Hz, *J* = 6 Hz, 1H), 4.33 (dd, *J* = 8 Hz, *J* = 7 Hz, 1H), 3.84 (dd, *J* = 8 Hz, *J* = 6 Hz, 1H), 1.34 (d, *J* = 5 Hz, 3H).

¹³C NMR (75 MHz, acetone-d₆) δ 132.8, 130.0, 129.8, 123.6, 102.4, 88.4, 86.6, 72.2, 66.9, 20.0.

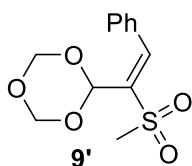
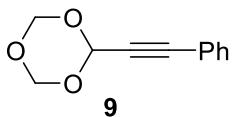
Anal. Calcd. for C₁₂H₁₂O₂: C, 76.57; H, 6.43; Found: C, 76.6; H, 6.5.



2,2-dimethyl-4-(phenylethynyl)-1,3-dioxolane (8). From 2,2-dimethyl-1,3-dioxolane **1f** (2.5 mmol, 0.5 M, 5.0 equiv., 276 μL, ρ = 0.93 g/mL) and **2a** (0.5 mmol, 0.1 M, 1.0 equiv., 90 mg). The crude mixture was purified through column chromatography (SiO₂: petroleum ether/ethyl acetate 95:5) to afford **8** as a colorless oil (69 mg, 68% yield). Spectroscopic data of **8** are in accordance with the literature (CDCl₃ used as the solvent).^{S21}

¹H NMR (300 MHz, acetone-d₆) δ 7.50 – 7.42 (m, 2H), 7.42 – 7.31 (m, 3H), 4.98 (t, *J* = 6.1 Hz, 1H), 4.24 (dd, *J*₁ = 8 Hz, *J*₂ = 6 Hz, 1H), 3.96 (dd, *J*₁ = 8 Hz, *J*₂ = 6 Hz, 1H), 1.46 (s, 3H), 1.34 (s, 3H).

¹³C NMR (75 MHz, acetone-*d*₆) δ 132.4, 129.6, 129.5, 123.4, 110.8, 88.3, 85.7, 70.8, 66.7, 26.7, 26.2.



2-(phenylethynyl)-1,3,5-trioxane (9) and (E)-2-(1-(methylsulfonyl)-2-phenylvinyl)-1,3,5-trioxane (9'). From 1,3,5-trioxane **1g** (2.5 mmol, 0.5 M, 5.0 equiv., 225 mg) and **2a** (0.5 mmol, 0.1 M, 1.0 equiv., 90 mg). The crude mixture was purified through column chromatography (SiO₂: cyclohexane/ethyl acetate 8:2) and products **9** and **9'** were isolated as two colorless oils (**9**: 43 mg, 45% yield; **9'**: 35 mg, 26% yield).

Data for **9**:

¹H NMR (300 MHz, acetone-*d*₆) δ 7.56 – 7.50 (m, 2H), 7.46 – 7.39 (m, 3H), 6.00 (s, 1H), 5.36 (d, *J* = 6 Hz, 2H), 5.20 (d, *J* = 6 Hz, 2H).

¹³C NMR (75 MHz, acetone-*d*₆) δ 132.7, 130.4, 129.6, 122.1, 92.5, 91.4, 87.1, 83.8.

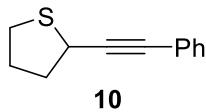
Anal. Calcd. for C₁₁H₁₀O₃: C, 69.46; H, 5.30; Found: C, 69.4; H, 5.4.

Data for **9B**:

¹H NMR (300 MHz, CDCl₃) δ 7.77 (s, 1H), 7.64 – 7.52 (m, 2H), 7.43 – 7.38 (m, 3H), 5.97 (s, 1H), 5.33 (dd, *J*₁ = 15 Hz, *J*₂ = 6 Hz, 4H), 2.90 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 143.2, 136.8, 132.5, 130.0, 129.8, 128.5, 97.5, 93.9, 44.4.

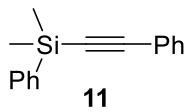
Anal. Calcd. for C₁₂H₁₄O₅S: C, 53.32; H, 5.22; Found: C, 53.3; H, 5.2.



2-(phenylethynyl)tetrahydrothiophene (10). From tetrahydrothiophene **1h** (2.5 mmol, 0.5 M, 5 equiv., 220 μ L, ρ = 1.00 g/mL) and **2a** (0.5 mmol, 0.1 M, 1.0 equiv., 90 mg). The crude mixture was purified through column chromatography (SiO₂: cyclohexane/ethyl acetate 98:2 → 80:20) to afford **10** as a yellowish oil (68 mg, 72% yield). Spectroscopic data of **10** are in accordance with the literature (CDCl₃ used as the solvent).^{S22}

¹H NMR (300 MHz, acetone-*d*₆) δ 7.66 – 6.98 (m, 5H), 4.31 (dd, *J* = 6.4 Hz, 5.5 Hz, 1H), 3.14 – 3.01 (m, 1H), 2.99 – 2.87 (m, 1H), 2.33 – 2.17 (m, 2H), 2.18 – 1.99 (m, 2H).

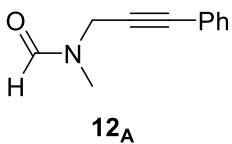
¹³C NMR (75 MHz, acetone-*d*₆) δ 132.3, 129.4, 129.1, 124.4, 91.9, 83.3, 39.8, 37.4, 33.2, 31.2.



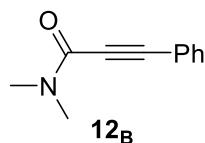
dimethyl(phenyl)(phenylethynyl)silane (11). From dimethylphenylsilane **1i** (1.0 mmol, 0.2 M, 2 equiv., 155 μ L, ρ = 0.89 g/mL) and **2a** (0.5 mmol, 0.1 M, 1.0 equiv., 90 mg). The crude mixture was purified through column chromatography (SiO₂: cyclohexane/ethyl acetate 95:5) to afford **11** as a colorless oil (73 mg, 62% yield). Spectroscopic data of **11** are in accordance with the literature (CDCl₃ used as the solvent).^{S23}

¹H NMR (300 MHz, acetone-*d*₆) δ 7.76 – 7.69 (m, 2H), 7.55 – 7.49 (m, 2H), 7.44 – 7.35 (m, 6H), 0.48 (s, 6H).

¹³C NMR (75 MHz, acetone-*d*₆) δ 137.8, 134.7, 132.9, 130.6, 130.0, 129.6, 129.0, 123.9, 107.8, 92.7, -0.5.



N-methyl-N-(3-phenylprop-2-yn-1-yl)formamide (12A) and N,N-dimethyl-3-phenylpropiolamide (12B). From *N,N*-dimethylformamide **1j** (2.0 mmol, 0.4 M, 4 equiv., 155 μ L, ρ = 0.94 g/mL) and **2a** (0.5 mmol, 0.1 M, 1.0 equiv., 90 mg). The crude mixture was purified through column chromatography (SiO₂: petroleum ether/ethyl acetate 7:3) to isolate **12A** (35 mg, 40% yield) and **12B** (2 mg, 3% yield). Spectroscopic data of **12A**



and **12B** are in accordance with the literature (CDCl₃ used as the solvent).

Data for 12A (mixture of rotamers):^{S24}

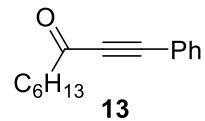
¹H NMR (300 MHz, acetone-d₆) δ 8.19 (s, 1H), 8.07 (s, 1H), 7.58 – 7.41 (m, 4H), 7.42 – 7.31 (m, 6H), 4.41 (s, 2H), 4.39 (s, 2H), 3.11 (s, 3H), 2.94 (s, 3H).

¹³C NMR (75 MHz, acetone-d₆) δ 162.7, 162.6, 132.4, 129.5, 129.4, 129.4, 123.6, 123.3, 85.0, 84.8, 84.8, 83.9, 39.7, 33.7, 33.7, 29.1.

Data for 12B:^{S25}

¹H NMR (300 MHz, acetone-d₆) δ 7.65 – 7.55 (m, 2H), 7.53 – 7.44 (m, 3H), 3.29 (s, 3H), 2.95 (s, 3H).

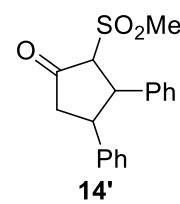
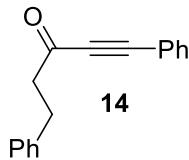
¹³C NMR (75 MHz, acetone-d₆) δ 154.8, 133.4, 131.3, 130.0, 121.9, 89.8, 83.1, 38.6, 34.2.



1-phenylnon-1-yn-3-one (13). From heptaldehyde **1k** (0.5 mmol, 0.1 M, 1 equiv., 71 μL, ρ = 0.81 g/mL) and **2a** (0.5 mmol, 0.1 M, 1.0 equiv., 90 mg). The crude mixture was purified through column chromatography (SiO₂: cyclohexane/ethyl acetate 9:1) to afford **13** as a colorless oil (72 mg, 67% yield). Spectroscopic data of **13** are in accordance with the literature (CDCl₃ used as the solvent).^{S26}

¹H NMR (300 MHz, acetone-d₆) δ 7.65 – 7.60 (m, 2H), 7.58 – 7.43 (m, 3H), 2.67 (t, *J* = 7.3 Hz, 2H), 1.80 – 1.62 (m, 2H), 1.45 – 1.21 (m, 6H), 0.93 – 0.83 (m, 3H).

¹³C NMR (75 MHz, acetone-d₆) δ 187.9, 133.9, 131.9, 130.0, 121.1, 90.2, 88.6, 46.2, 32.5, 29.5, 24.9, 23.3, 14.5.



1,5-diphenylpent-1-yn-3-one (14) and 2-(methylsulfonyl)-3,4-diphenylcyclopentan-1-one (14'). From 3-phenylpropanal **1l** (0.5 mmol, 0.1 M, 1 equiv., 66 μL, ρ = 1.02 g/mL) and **2a** (0.5 mmol, 0.1 M, 1.0 equiv., 90 mg). The crude mixture was purified through column chromatography (SiO₂: cyclohexane/ethyl acetate 9:1) to isolate **14** (51 mg, 44%) and **14'** (51 mg, 32%), both as colorless oils. Spectroscopic data of **14** are in accordance with the literature (CDCl₃ used as the solvent).^{S27}

Data for 14:

¹H NMR (300 MHz, acetone-d₆) δ 7.69 – 7.61 (m, 2H), 7.60 – 7.44 (m, 3H), 7.33 – 7.16 (m, 5H), 3.05 (s, 4H).

¹³C NMR (75 MHz, acetone-d₆) δ 186.9, 141.7, 133.9, 131.9, 129.9, 129.4, 129.4, 127.1, 120.9, 90.8, 88.5, 47.7, 30.7.

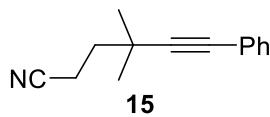
Data for 14' (single stereoisomer):

¹H NMR (300 MHz, CDCl₃) δ 7.16 – 7.06 (m, 6H), 6.75 – 6.69 (m, 4H), 4.50 (dd, *J*₁ = 7 Hz, *J*₂ = 6 Hz, 1H), 4.18 – 4.12 (m, 1H), 4.11 (d, *J* = 6 Hz, 1H), 3.13 (s, 3H), 2.97 (d, *J* = 8 Hz, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 208.2, 138.2, 137.8, 128.5, 128.3, 128.0, 127.9, 127.5, 127.2, 73.0, 47.6, 45.8, 43.5, 41.2.

Anal. Calcd. for C₁₈H₁₈O₃S: C, 68.77; H, 5.77; Found: C, 68.8; H, 5.8.

HSQC and COSY are reported at the end of this document.



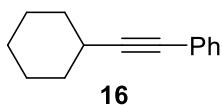
4,4-dimethyl-6-phenylhex-5-ynenitrile (15). From isocaprononitrile **1m** (5.0 mmol, 1.0 M, 10 equiv., 605 μL, ρ = 0.80 g/mL) and **2a** (0.5 mmol, 0.1 M, 1.0 equiv., 90 mg). The crude mixture was purified through column chromatography (SiO₂: cyclohexane/ethyl acetate 90:10) to afford **15** as a colorless oil (59 mg, 60% yield).

¹H NMR (300 MHz, acetone-d₆) δ 7.46 – 7.39 (m, 2H), 7.37 – 7.30 (m,

3H), 2.72 – 2.64 (m, 2H), 1.94 – 1.78 (m, 2H), 1.34 (s, 6H).

¹³C NMR (75 MHz, acetone-*d*₆) δ 132.4, 129.2, 128.8, 124.4, 120.9, 95.4, 82.6, 39.3, 32.3, 29.0, 13.9.

Anal. Calcd. for C₁₄H₁₅N: C, 85.24; H, 7.66; Found: C, 85.2; H, 7.8.

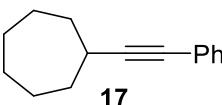


16

(cyclohexylethynyl)benzene (16). From cyclohexane **1n** (2.5 mmol, 0.5 M, 5 equiv., 270 μL, ρ = 0.77 g/mL) and **2a** (0.5 mmol, 0.1 M, 1.0 equiv., 90 mg). TBADT was used 5 mol%. The crude mixture was purified through column chromatography (SiO₂: petroleum ether) to afford **16** as a volatile colorless liquid (69 mg, 75% yield). Spectroscopic data of **16** are in accordance with the literature (in CDCl₃).^{S28}

¹H NMR (300 MHz, acetone-*d*₆) δ 7.39 – 7.33 (m, 2H), 7.33 – 7.25 (m, 3H), 2.58 (td, *J*₁ = 9 Hz, *J*₂ = 5 Hz, 1H), 1.93 – 1.78 (m, 2H), 1.79 – 1.66 (m, 2H), 1.58 – 1.43 (m, 3H), 1.43 – 1.25 (m, 3H).

¹³C NMR (75 MHz, acetone-*d*₆) δ 132.6, 129.57, 128.8, 125.4, 95.2, 81.7, 33.8, 30.6, 26.9, 25.8.

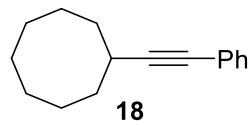


17

(phenylethynyl)cycloheptane (17). From cycloheptane **1o** (2.5 mmol, 0.5 M, 5 equiv., 303 μL, ρ = 0.81 g/mL) and **2a** (0.5 mmol, 0.1 M, 1.0 equiv., 90 mg). TBADT was used 5 mol%. The crude mixture was purified through column chromatography (SiO₂: petroleum ether) to afford **17** as a colorless oil (**17**: 61 mg, 61% yield). Spectroscopic data of **17** are in accordance with the literature.^{S17}

¹H NMR (300 MHz, CDCl₃) δ 7.47 – 7.36 (m, 2H), 7.36 – 7.24 (m, 3H), 2.84 (tt, *J*₁ = 8 Hz, *J*₂ = 4 Hz, 1H), 2.07 – 1.87 (m, 2H), 1.86 – 1.73 (m, 5H), 1.67 – 1.50 (m, 7H).

¹³C NMR (75 MHz, CDCl₃) δ 131.6, 128.3, 127.5, 124.4, 95.3, 80.9, 34.8, 31.8, 28.1, 25.8.

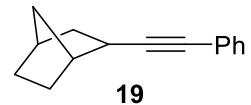


18

(phenylethynyl)cyclooctane (18). From cyclooctane **1p** (2.5 mmol, 0.5 M, 5 equiv., 334 μL, ρ = 0.84 g/mL) and **2a** (0.5 mmol, 0.1 M, 1.0 equiv., 90 mg). TBADT was used 5 mol%. The crude mixture was purified through column chromatography (SiO₂: petroleum ether) to afford **18** as a colorless oil (**18**: 83 mg, 78% yield). Spectroscopic data of **18** are in accordance with the literature.^{S29}

¹H NMR (300 MHz, CDCl₃) δ 7.47 – 7.37 (m, 2H), 7.36 – 7.25 (m, 3H), 2.83 (tt, *J*₁ = 8 Hz, *J*₂ = 4 Hz, 1H), 2.05 – 1.91 (m, 2H), 1.89 – 1.74 (m, 4H), 1.71 – 1.46 (m, 8H).

¹³C NMR (75 MHz, CDCl₃) δ 177.1, 173.7, 173.6, 172.8, 169.8, 140.9, 126.0, 77.2, 76.3, 72.9, 71.0, 70.1.



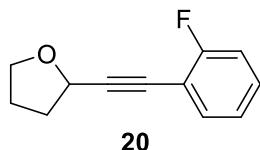
19

2-(phenylethynyl)bicyclo[2.2.1]heptane (19). From norbornane **1q** (2.5 mmol, 0.5 M, 5 equiv., 240 mg) and **2a** (0.5 mmol, 0.1 M, 1.0 equiv., 90 mg). TBADT was used 5 mol%. The crude mixture was purified through column chromatography (SiO₂: petroleum ether) to afford **19** as a colorless oil (**19**: 45 mg, 46% yield). Spectroscopic data of **19** are in accordance with the literature (CDCl₃ used as the solvent).^{S30}

¹H NMR (300 MHz, Acetone-*d*₆) δ 7.38 – 7.34 (m, 2H), 7.34 – 7.28 (m, 3H), 2.48 (ddd, *J*₁ = 9 Hz, *J*₂ = 5 Hz, *J*₃ = 1 Hz, 1H), 2.40 – 2.34 (m, 1H), 2.33 – 2.26 (m, 1H), 1.81 – 1.57 (m, 3H), 1.56 – 1.46 (m, 2H), 1.31 – 1.10 (m, 3H).

¹³C NMR (176 MHz, Acetone-*d*₆) δ 132.1, 129.2, 128.3, 125.1, 96.1, 81.0, 44.5, 40.0, 37.2, 37.0, 34.1, 29.3, 29.2.

Scope of the methanesulfonyl alkynes (2a-l)

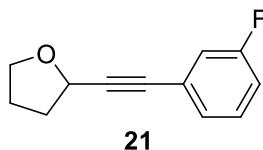


2-((2-fluorophenyl)ethynyl)tetrahydrofuran (20). From tetrahydrofuran **1a** (2.5 mmol, 0.5 M, 5 equiv., 202 μ L, ρ = 0.89 g/mL) and **2b** (0.5 mmol, 0.1 M, 1.0 equiv., 99 mg). The crude mixture was purified through column chromatography (SiO₂: cyclohexane/ethyl acetate 90:10) to afford **20** as a colorless liquid (70 mg, 74% yield). Spectroscopic data of **20** are in accordance with the literature (CDCl₃ used as the solvent).^{S19}

¹H NMR (300 MHz, acetone-*d*₆) δ 7.53 – 7.30 (m, 2H), 7.21 – 7.13 (m, 2H), 4.79 (dd, *J*₁ = 7 Hz, *J*₂ = 5 Hz, 1H), 3.96 – 3.85 (m, 1H), 3.83 – 3.72 (m, 1H), 2.29 – 2.15 (m, 1H), 2.01 – 1.86 (m, 3H).

¹³C NMR (75 MHz, acetone-*d*₆) δ 163.55 (d, *J* = 250 Hz), 134.5 (d, *J* = 1 Hz), 131.4 (d, *J* = 8 Hz), 125.3 (d, *J* = 4 Hz), 116.4 (d, *J* = 21 Hz), 112.2 (d, *J* = 16 Hz), 96.1 (d, *J* = 3 Hz), 78.0, 69.1, 68.3, 34.2, 26.1.

¹⁹F NMR (376 MHz, acetone-*d*₆) δ –112.31 (ddd, *J*₁ = 10 Hz, *J*₂ = 7 Hz, *J*₃ = 5 Hz).

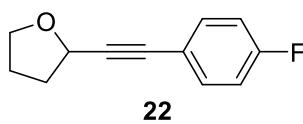


2-((3-fluorophenyl)ethynyl)tetrahydrofuran (21). From tetrahydrofuran **1a** (2.5 mmol, 0.5 M, 5 equiv., 202 μ L, ρ = 0.89 g/mL) and **2c** (0.5 mmol, 0.1 M, 1.0 equiv., 99 mg). The crude mixture was purified through column chromatography (SiO₂: cyclohexane/ethyl acetate 90:10) to afford **21** as a colorless liquid (59 mg, 62% yield). Spectroscopic data of **21** are in accordance with the literature (CDCl₃ used as the solvent).^{S19}

¹H NMR (300 MHz, acetone-*d*₆) δ 7.43 – 7.33 (m, 1H), 7.22 (dt, *J*₁ = 8 Hz, *J*₂ = 1 Hz, 1H), 7.18 – 7.07 (m, 2H), 4.74 (dd, *J*₁ = 7 Hz, *J*₂ = 5 Hz, 1H), 3.91 – 3.81 (m, 1H), 3.79 – 3.69 (m, 1H), 2.28 – 2.12 (m, 1H), 1.95 – 1.83 (m, 3H).

¹³C NMR (75 MHz, acetone-*d*₆) δ 163.6 (d, *J* = 245 Hz), 131.7 (d, *J* = 9 Hz), 128.9 (d, *J* = 3 Hz), 126.2 (d, *J* = 9 Hz), 119.2 (d, *J* = 23 Hz), 116.8 (d, *J* = 21 Hz), 92.1, 93.6 (d, *J* = 3 Hz), 69.2, 68.6, 34.4, 26.4.

¹⁹F NMR (376 MHz, acetone-*d*₆) δ –114.67 – –114.81 (m).

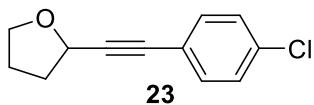


2-((4-fluorophenyl)ethynyl)tetrahydrofuran (22). From tetrahydrofuran **1a** (2.5 mmol, 0.5 M, 5 equiv., 202 μ L, ρ = 0.89 g/mL) and **2d** (0.5 mmol, 0.1 M, 1.0 equiv., 99 mg). The crude mixture was purified through column chromatography (SiO₂: cyclohexane/ethyl acetate 98:2 → 80:20) to afford **22** as a colorless oil (75 mg, 79% yield). Spectroscopic data of **22** are in accordance with the literature (CDCl₃ used as the solvent).^{S19}

¹H NMR (300 MHz, acetone-*d*₆) δ 7.47 (ddt, *J*₁ = 8 Hz, *J*₂ = 5 Hz, *J*₃ = 3 Hz, 2H), 7.32 – 6.97 (m, 2H), 4.75 (dd, *J*₁ = 7 Hz, *J*₂ = 5 Hz, 1H), 3.96 – 3.67 (m, 2H), 2.28 – 2.13 (m, 1H), 2.13 – 1.77 (m, 3H).

¹³C NMR (75 MHz, acetone-*d*₆) δ 163.3 (d, *J* = 248 Hz), 134.5 (d, *J* = 8 Hz), 120.2 (d, *J* = 3 Hz), 116.4 (d, *J* = 22 Hz), 90.4 (d, *J* = 2 Hz), 83.4, 68.9, 68.1, 34.1, 26.0.

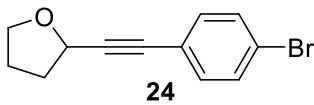
¹⁹F NMR (376 MHz, acetone-*d*₆) δ –113.15 (tt, *J*₁ = 9 Hz, *J*₂ = 5 Hz).



2-((4-chlorophenyl)ethynyl)tetrahydrofuran (23). From tetrahydrofuran **1a** (2.5 mmol, 0.5 M, 5 equiv., 202 μ L, ρ = 0.89 g/mL) and **2e** (0.5 mmol, 0.1 M, 1.0 equiv., 107 mg). The crude mixture was purified through column chromatography (SiO₂: cyclohexane/ethyl acetate 90:10 \rightarrow 80:20) to afford **23** as a colorless liquid (67 mg, 65% yield). Spectroscopic data of **23** are in accordance with the literature (CDCl₃ used as the solvent).^{S19}

¹H NMR (300 MHz, acetone-*d*₆) δ 7.39 (d, *J* = 8 Hz, 2H), 7.35 (d, *J* = 8 Hz, 2H), 4.75 – 4.64 (m, 1H), 3.89 – 3.80 (m, 1H), 3.78 – 3.68 (m, 1H), 2.23 – 2.11 (m, 1H), 2.05 – 1.82 (m, 3H).

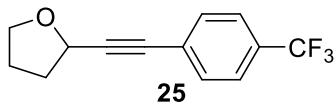
¹³C NMR (75 MHz, acetone-*d*₆) δ 134.7, 133.9, 129.6, 122.6, 91.8, 83.4, 68.9, 68.2, 34.1, 26.0.



2-((4-bromophenyl)ethynyl)tetrahydrofuran (24). From tetrahydrofuran **1a** (2.5 mmol, 0.5 M, 5 equiv., 202 μ L, ρ = 0.89 g/mL) and **2f** (0.5 mmol, 0.1 M, 1.0 equiv., 130 mg). The crude mixture was purified through column chromatography (SiO₂: cyclohexane/ethyl acetate 90:10) to afford **24** as a colorless liquid (78 mg, 62% yield). Spectroscopic data of **24** are in accordance with the literature (CDCl₃ used as the solvent).^{S19}

¹H NMR (300 MHz, acetone-*d*₆) δ 7.57 (d, *J* = 8 Hz, 2H), 7.38 (d, *J* = 8 Hz, 2H), 4.77 (dd, *J*₁ = 7 Hz, *J*₂ = 5 Hz, 1H), 3.97 – 3.85 (m, 1H), 3.85 – 3.71 (m, 1H), 2.31 – 2.17 (m, 1H), 2.11 – 1.84 (m, 3H).

¹³C NMR (75 MHz, acetone-*d*₆) δ 134.3, 132.7, 123.2, 123.0, 92.1, 83.6, 69.1, 68.3, 34.2, 26.2.

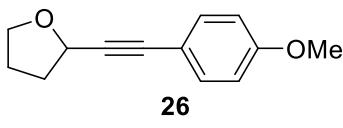


2-((4-(trifluoromethyl)phenyl)ethynyl)tetrahydrofuran (25). From tetrahydrofuran **1a** (2.5 mmol, 0.5 M, 5 equiv., 202 μ L, ρ = 0.89 g/mL) and **2g** (0.5 mmol, 0.1 M, 1.0 equiv., 124 mg). The crude mixture was purified through column chromatography (SiO₂: cyclohexane/ethyl acetate 90:10) to afford **25** as a colorless liquid (53 mg, 46% yield) and **2g** (17 mg, 14% yield). Spectroscopic data of **25** are in accordance with the literature (CDCl₃ used as the solvent).^{S19}

¹H NMR (300 MHz, acetone-*d*₆) δ 7.72 (d, *J* = 8 Hz, 2H), 7.65 (d, *J* = 8 Hz, 2H), 4.81 (dd, *J*₁ = 7 Hz, *J*₂ = 5 Hz, 1H), 3.97 – 3.87 (m, 1H), 3.80 (td, *J*₁ = 8 Hz, *J*₂ = 5 Hz, 1H), 2.33 – 2.18 (m, 1H), 2.13 – 1.88 (m, 3H).

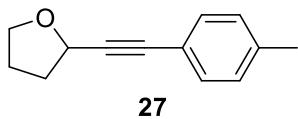
¹³C NMR (75 MHz, acetone-*d*₆) δ 133.1, 130.5 (q, *J* = 32 Hz), 128.1 (q, *J* = 1 Hz), 126.4 (q, *J* = 4 Hz), 125.2 (q, *J* = 269 Hz), 93.6, 83.3, 69.0, 68.4, 34.2, 26.2.

¹⁹F NMR (376 MHz, acetone-*d*₆) δ –63.80.



2-((4-methoxyphenyl)ethynyl)tetrahydrofuran (26). From tetrahydrofuran **1a** (2.5 mmol, 0.5 M, 5 equiv., 202 μ L, ρ = 0.89 g/mL) and **2h** (0.5 mmol, 0.1 M, 1.0 equiv., 105 mg). The crude mixture was purified through column chromatography (SiO₂: cyclohexane/ethyl acetate 80:20) to afford **26** as a colorless liquid (55 mg, 55% yield) and **2h** (13 mg, 12%). Spectroscopic data of **26** are in accordance with the literature (CDCl₃ used as the solvent).^{S19}

¹H NMR (300 MHz, acetone-*d*₆) δ 7.35 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.73 (dd, *J*₁ = 7.1, *J*₂ = 5.0 Hz, 1H), 3.93 – 3.85 (m, 1H), 3.80 (s, 3H), 3.80 – 3.70 (m, 1H), 2.28 – 2.12 (m, 1H), 2.08 – 1.83 (m, 3H).

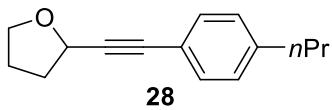


¹³C NMR (75 MHz, acetone-*d*₆) δ 160.8, 133.8, 115.9, 114.9, 89.0, 84.6, 69.1, 68.1, 55.7, 34.2, 26.1.

2-(p-tolylethynyl)tetrahydrofuran (27). From tetrahydrofuran **1a** (2.5 mmol, 0.5 M, 5 equiv., 202 μL, ρ = 0.89 g/mL) and **2i** (0.5 mmol, 0.1 M, 1.0 equiv., 97 mg). The crude mixture was purified through column chromatography (SiO₂: cyclohexane/ethyl acetate 90:10) to afford **27** as a colorless liquid (63 mg, 68% yield). Spectroscopic data of **27** are in accordance with the literature (CDCl₃ used as the solvent).^{S19}

¹H NMR (300 MHz, acetone-*d*₆) δ 7.31 (d, *J* = 8 Hz, 2H), 7.17 (d, *J* = 8 Hz, 2H), 4.75 (dd, *J*₁ = 7 Hz, *J*₂ = 5 Hz, 1H), 3.96 – 3.85 (m, 1H), 3.83 – 3.71 (m, 1H), 2.33 (s, 3H), 2.28 – 2.14 (m, 1H), 2.13 – 1.86 (m, 3H).

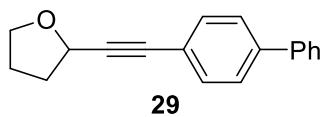
¹³C NMR (75 MHz, acetone-*d*₆) δ 139.2, 132.2, 130.0, 120.8, 89.9, 84.7, 69.0, 68.0, 34.2, 26.0, 21.4.



2-((4-propylphenyl)ethynyl)tetrahydrofuran (28). From tetrahydrofuran **1a** (2.5 mmol, 0.5 M, 5 equiv., 202 μL, ρ = 0.89 g/mL) and **2j** (0.5 mmol, 0.1 M, 1.0 equiv., 111 mg). The crude mixture was purified through column chromatography (SiO₂: cyclohexane/ethyl acetate 95:5) to afford **28** as a colorless liquid (65 mg, 61% yield). Spectroscopic data of **28** are in accordance with the literature (CDCl₃ used as the solvent).^{S19}

¹H NMR (300 MHz, CDCl₃) δ 7.34 (d, *J* = 8 Hz, 2H), 7.20 – 6.94 (m, 2H), 4.80 (dd, *J*₁ = 7 Hz, *J*₂ = 5 Hz, 1H), 4.13 – 3.94 (m, 1H), 3.94 – 3.73 (m, 1H), 2.56 (dd, *J*₁ = 9 Hz, *J*₂ = 7 Hz, 2H), 2.28 – 2.15 (m, 1H), 2.14 – 2.01 (m, 2H), 2.00 – 1.86 (m, 1H), 1.78 – 1.48 (m, 2H), 0.92 (t, *J* = 7 Hz, 3H).

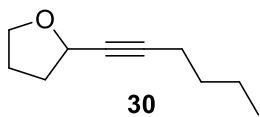
¹³C NMR (75 MHz, CDCl₃) δ 143.2, 131.7, 128.5, 120.1, 88.5, 84.7, 68.8, 68.0, 38.0, 33.6, 25.6, 24.4, 13.8.



2-([1,1'-biphenyl]-4-ylethynyl)tetrahydrofuran (29). From tetrahydrofuran **1a** (2.5 mmol, 0.5 M, 5 equiv., 202 μL, ρ = 0.89 g/mL) and **2k** (0.5 mmol, 0.1 M, 1.0 equiv., 128 mg). The crude mixture was purified through column chromatography (SiO₂: cyclohexane/ethyl acetate 90:10) to afford **29** as a yellowish wax (52 mg, 42% yield). Spectroscopic data of **29** are in accordance with the literature (CDCl₃ used as the solvent).^{S31}

¹H NMR (300 MHz, acetone-*d*₆) δ 7.75 – 7.59 (m, 4H), 7.59 – 7.42 (m, 4H), 7.42 – 7.32 (m, 1H), 4.78 (dd, *J*₁ = 7 Hz, *J*₂ = 5 Hz, 1H), 3.98 – 3.83 (m, 1H), 3.84 – 3.70 (m, 1H), 2.31 – 2.17 (m, 1H), 2.12 – 1.85 (m, 3H).

¹³C NMR (75 MHz, acetone-*d*₆) δ 141.7, 140.9, 132.9, 129.8, 128.6, 127.8, 127.7, 122.8, 91.3, 84.4, 69.0, 68.1, 34.2, 26.0.

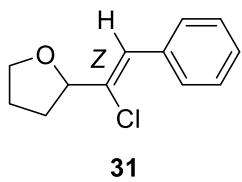


2-(hex-1-yn-1-yl)tetrahydrofuran (30). From tetrahydrofuran **1a** (0.5 mmol, 0.5 M, 5 equiv., 40 μL, ρ = 0.89 g/mL) and **2k** (0.1 mmol, 0.1 M, 1.0 equiv., 16 mg) in MeCN (1 mL). Reaction run under explorative conditions (see **Figure S7**), product not isolated.

NMR yield of **30**: 39%.

Remaining starting material: 53%.

Yield based on remaining starting material (brsm): 83%.



(Z)-2-(1-chloro-2-phenylvinyl)tetrahydrofuran (31). From tetrahydrofuran **1a** (2.5 mmol, 0.5 M, 5 equiv., 202 μ L, $\rho = 0.89$ g/mL) and **2r** (0.5 mmol, 0.1 M, 1.0 equiv., 68 mg). The crude mixture was purified through column chromatography (SiO₂: cyclohexane/ethyl acetate 90:10) to afford **31** as a colorless oil (43 mg, 41% yield) and **2r** (11 mg, 16%). Spectroscopic data of **31** are in accordance with the literature (CDCl₃ used as the solvent).^{S32}
¹H NMR (300 MHz, CDCl₃) δ 7.76 – 7.58 (m, 2H), 7.41 – 7.35 (m, 2H), 7.35 – 7.24 (m, 1H), 6.90 (s, 1H), 4.65 – 4.54 (m, 1H), 4.05 – 3.93 (m, 1H), 3.91 – 3.78 (m, 1H), 2.29 – 2.11 (m, 1H), 2.09 – 1.86 (m, 3H).
¹³C NMR (75 MHz, CDCl₃) δ 135.8, 135.6, 130.1, 129.2, 128.8, 124.5, 82.9, 69.9, 32.0, 26.4.
NOESY is reported at the end of this document.

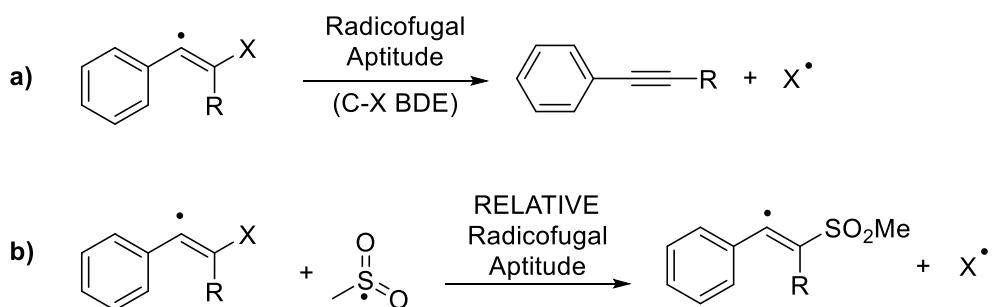
3. Computational Methods

General

All the calculations were carried out using the Gaussian16 (Rev. C.01) program package^{S33} at the CINECA Supercomputer center (Italy). In our investigation, all the structures have been optimized in the gas phase by having recourse to density functional theory (DFT), *viz.* adopting the ω B97XD functional with an unrestricted (U) formalism in the case of open-shell species, along with the def2tzvp basis set. To confirm the nature of the optimized structures, vibrational frequencies have been calculated at the same level of theory as geometry optimizations, and it was verified that they had only real frequencies. For each of the reported structures, a systematic investigation of all of the possible conformations has been carried out. However, only the most stable conformation has been reported and considered for further work.

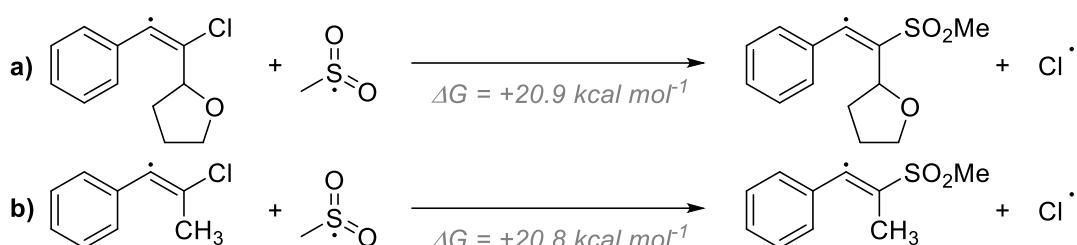
Computational Analysis (see Table S2)

A rigorous determination of the radicofugal aptitude of the considered X groups would have required the calculation of Bond Dissociation Energy (BDE) values for the relevant C–X bonds (X = SO₂R, benziodoxolonyl or halogen; **Scheme S5a**). However, this task calls for the use of high-level calculations with huge computational cost,^{S34} which is well beyond the aim of this work. As a matter of fact, Density Functional Theory methods with unrestricted formalism may suffer from spin contamination, with the immediate consequence that the wavefunction is no longer an eigenfunction of the total spin. Accordingly, DFT approaches are unsuitable to address named objective, since some error may be introduced into the calculation. A good trade-off consists in having recourse to relative models (**Scheme S5b**).^{S35} In doing so, the spin contamination is normalized and the introduced errors cancel out, thus enabling for the evaluation of the relative radicofugal aptitude of X groups with DFT methods.



Scheme S5. Computational models for the evaluation of the absolute radicofugal aptitude via determination of the C–X BDE value (a) and the relative radicofugal aptitude via a relative model with the methanesulfonyl group as the reference (b).

According to the mechanism reported in **Scheme 5** in the main text, the elimination step required to afford product **3** depends on the tendency of the X group to act as a radicofugal group at the level of adduct **I[•]**. Thus, we compared the methanesulfonyl group and the chlorine atom in the role of radicofugal groups (**Scheme S6a**), from which it can be concluded that the former has a stronger radicofugal aptitude compared to the latter. We then extended this calculation to traps **2m-2o** and, in doing so, we replaced the tetrahydrofuran ring with the simpler methyl group to skip the need to perform an extensive conformational search due to the different possible arrangements of the heterocyclic ring. Of course, we checked the implications of this approximation on the energy value (**Scheme S6b**) and, gratifyingly, found that the result was not significantly affected.



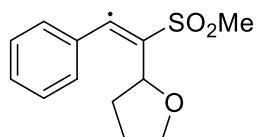
Scheme S6. Comparison of the radicofugal aptitude of methanesulfonyl group and chlorine atom at the level of radical adduct **I[•]** (a) and evaluation of the effect of the replacement of the tetrahydrofuran ring with a less computationally demanding methyl group.

DFT optimized geometries in the gas phase

In all cases, the structures reported below have been optimized at the (U)ωB97XD/def2tzvp level of theory in the gas phase and it was verified that these had no imaginary frequencies.

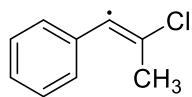
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C	-1.18424000	1.00016300	-0.00004100
C	1.41419500	0.48635100	0.00003500
C	2.10732600	0.26694600	-1.21760100
C	2.10737300	0.26701400	1.21763800
C	3.41668600	-0.15865900	-1.20495200
H	1.59038700	0.43776700	-2.15288700
C	3.41673800	-0.15859300	1.20493900
H	1.59048700	0.43786700	2.15294500
C	4.08109900	-0.37460100	-0.00001200
H	3.93200200	-0.32566100	-2.14228100
H	3.93210000	-0.32554800	2.14225100

H	5.11052300	-0.70764700	-0.00001400
S	-2.18418700	-0.50467200	0.00007800
O	-2.90711300	-0.54124500	1.23985800
O	-2.90789700	-0.54085400	-1.23926400
C	-1.01634000	-1.83653700	-0.00048500
H	-0.40619100	-1.79142500	-0.89916100
H	-0.40540000	-1.79151600	0.89765700
H	-1.62690800	-2.73865100	-0.00024500
C	-2.03164600	2.24382500	-0.00013200
H	-2.67183100	2.26011300	0.88306000
H	-1.39620800	3.12663200	-0.00038300
H	-2.67212100	2.25978900	-0.88311300

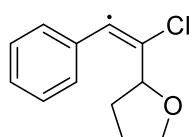


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O	-1.39318500	-1.98998600	1.00063000
C	1.87448100	-0.28848200	0.05916000
C	2.46149300	-0.61240900	-1.19212300
C	2.72712000	-0.13547100	1.18356900
C	3.82503300	-0.76481000	-1.30004200
H	1.82049800	-0.73317000	-2.05545700
C	4.08766200	-0.29297400	1.04916800
H	2.28911700	0.09888600	2.14481100
C	4.64816400	-0.60708500	-0.18710200
H	4.25926100	-1.00935300	-2.26115500
H	4.72596700	-0.17360000	1.91544200
H	5.71889100	-0.73000300	-0.28210500
C	-2.85595400	-0.95433500	-0.56088400
H	-2.35942800	-0.74638000	-1.50933300
H	-3.72881800	-0.30807200	-0.49598600
C	-3.17218600	-2.44256800	-0.43531300
H	-3.46696300	-2.89388300	-1.38194900
H	-3.96724300	-2.61295500	0.29286400
C	-1.85439800	-2.98052900	0.09549700
H	-1.12974600	-3.11973100	-0.71725100
H	-1.94463200	-3.91666000	0.64590200
C	-1.88353000	-0.72235000	0.61241200
H	-2.40329800	-0.27969200	1.46637100
S	-1.22265400	1.89876700	-0.08386900
O	-1.62746800	1.98619500	-1.45845100

O	-2.14546400	2.28696500	0.94621900
C	0.26440200	2.84130200	0.11203200
H	0.63015500	2.73379700	1.13013400
H	1.00435200	2.51417700	-0.61421400
H	-0.02980300	3.87205500	-0.08245900

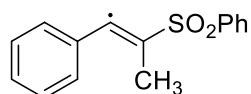


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Cl	-2.63051500	-0.00491100	1.23807700
C	0.69890900	0.00126300	-0.28236200
C	1.41394500	1.21566000	-0.15509800
C	1.41347400	-1.21410600	-0.16449300
C	2.77016900	1.20412600	0.08682100
H	0.87683700	2.15055600	-0.24525100
C	2.76990200	-1.20497200	0.07746100
H	0.87616200	-2.14818600	-0.26173400
C	3.45683800	-0.00109600	0.20372000
H	3.30334900	2.14089700	0.18799100
H	3.30251600	-2.14283000	0.17123700
H	4.52235900	-0.00185100	0.39302200
C	-2.98676500	0.00588200	-1.48168200
H	-3.62299200	-0.87635800	-1.39286600
H	-3.62259200	0.88771900	-1.38656900
H	-2.51546700	0.00924600	-2.46343200



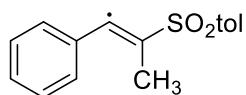
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O	1.71386600	-1.16171800	-1.16394800
C	-1.60696900	0.16474800	-0.01873800
C	-2.13363200	-0.39754400	1.17189400
C	-2.48350700	0.35030300	-1.11769800
C	-3.46251200	-0.74890100	1.24825700
H	-1.47438700	-0.54176700	2.01778200
C	-3.80894700	-0.00827500	-1.01893700
H	-2.09115600	0.77505000	-2.03190600
C	-4.30904800	-0.55871300	0.15874800
H	-3.85062000	-1.17530500	2.16465200
H	-4.46638500	0.13967400	-1.86630300

H	-5.35231800	-0.83780100	0.22710100
C	3.10931100	-0.25102400	0.53422900
H	2.67952900	0.06837000	1.48378500
H	4.06317600	0.25863500	0.41660000
C	3.23654200	-1.77615600	0.47519300
H	3.36313800	-2.22690400	1.45893000
H	4.08039300	-2.07160100	-0.14989000
C	1.93351700	-2.17462900	-0.19851000
H	1.10568800	-2.20368800	0.52231000
H	1.97381400	-3.12852100	-0.72258100
C	2.13748000	0.07172900	-0.62875700
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Cl	1.40831700	2.54083300	0.31079900

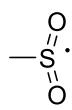


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C	-1.54767800	1.49496700	-0.26708800
C	1.09193700	1.41036000	-0.20060700
C	1.82382200	0.91045100	-1.30375500
C	1.78341400	1.65725200	1.01025200
C	3.17131300	0.65215200	-1.18391000
H	1.30490200	0.71844300	-2.23332700
C	3.13152900	1.39529700	1.10705800
H	1.23280200	2.04326800	1.85802500
C	3.83453900	0.88986300	0.01650100
H	3.71604800	0.25791100	-2.03238600
H	3.64593200	1.58252100	2.04112400
H	4.89381100	0.68546100	0.10104300
S	-2.22922200	-0.11603800	0.20243800
O	-2.68190300	-0.01620500	1.56084500
O	-3.14907400	-0.49901700	-0.83162500
C	-2.61880000	2.51047500	-0.55691100
H	-3.26958900	2.62827300	0.31140400
H	-2.16506100	3.47035300	-0.79422600
H	-3.23315200	2.18120300	-1.39544800
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C	-0.51732200	-1.83173400	-1.04849700
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C	0.61422500	-2.62736100	-1.11031200
H	-1.15847100	-1.69941000	-1.90976200
C	1.41852800	-2.77848500	0.01022800

H	1.71495500	-2.27405300	2.07450000
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H	2.30758700	-3.39375400	-0.04440300

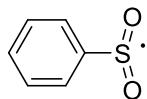


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C	-0.45993300	-1.76817400	-0.22457300
C	-1.30603800	-1.43096300	-1.30671200
C	-1.05448600	-2.21046700	0.98159100
C	-2.67476400	-1.50593300	-1.16913200
H	-0.86223400	-1.09343500	-2.23360200
C	-2.42462100	-2.28149700	1.09721500
H	-0.41535100	-2.47560200	1.81350700
C	-3.24442600	-1.92704900	0.02881100
H	-3.30980200	-1.23136500	-2.00207300
H	-2.86521000	-2.61319100	2.02888300
H	-4.32056800	-1.98544900	0.12765900
S	2.33982900	0.55782800	0.21195300
O	2.81054600	0.54668600	1.56805200
O	3.12157900	1.19391700	-0.81110400
C	3.41094300	-1.85197000	-0.61458800
H	4.07530100	-1.81236300	0.25054500
H	3.22959500	-2.89222700	-0.87651600
H	3.90926600	-1.34940100	-1.44412100
C	0.70553100	1.22196500	0.17594100
C	-0.09945000	1.12107500	1.29939500
C	0.21529800	1.75556500	-1.00513900
C	-1.41848000	1.52763800	1.22307100
H	0.30678400	0.71369900	2.21554600
C	-1.10463700	2.16550500	-1.06329100
H	0.86558400	1.84208500	-1.86553900
C	-1.94444600	2.03834800	0.03959200
H	-2.05545700	1.43558500	2.09448400
H	-1.49325800	2.58126300	-1.98526400
C	-3.39700800	2.40482400	-0.05203100
H	-3.75965300	2.83189000	0.88330800
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H	-3.99309100	1.51207100	-0.25963200

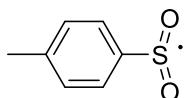


S	0.00000000	0.00000000	0.00000000
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C	0.00000000	0.00000000	1.80488544
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H	-0.50574487	0.90120800	2.14111840
H	-0.50574487	-0.90120800	2.14111840
O	0.56671586	1.26122900	-0.42507543
O	0.56671586	-1.26122900	-0.42507543



S	1.69087900	-0.00018400	-0.24202000
O	2.19003700	1.26419300	0.25284800
O	2.18964600	-1.26404400	0.25463300
C	-0.09040700	0.00023500	-0.08036400
C	-0.76123900	1.21322000	-0.05148300
C	-0.76136700	-1.21318500	-0.05221600
C	-2.14418500	1.20446800	0.03150800
H	-0.20620200	2.14103900	-0.07450600
C	-2.14387700	-1.20459800	0.03064500
H	-0.20577400	-2.14068000	-0.07559400
C	-2.83195800	0.00010700	0.07089000
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H	-3.91254000	-0.00027300	0.13484800



S	2.14509900	-0.00001700	0.22636700
O	2.63851000	-1.26403300	-0.27622900
O	2.63853600	1.26403900	-0.27610900
C	0.36702900	0.00001100	0.09302500
C	-0.31103200	1.20926400	0.07810800
C	-0.31104500	-1.20925800	0.07816100
C	-1.69307900	1.19778800	0.01977900
H	0.23934200	2.14020900	0.09472200
C	-1.69307700	-1.19777000	0.01983100
H	0.23932600	-2.14020200	0.09481400
C	-2.40345500	0.00001700	-0.01123600
H	-2.23053900	2.13819300	-0.00259900
H	-2.23056000	-2.13816400	-0.00250700
C	-3.90201900	-0.00000800	-0.10576800
H	-4.32957000	-0.88390800	0.36742200
H	-4.32951900	0.88469400	0.36596200
H	-4.21637000	-0.00087300	-1.15238900

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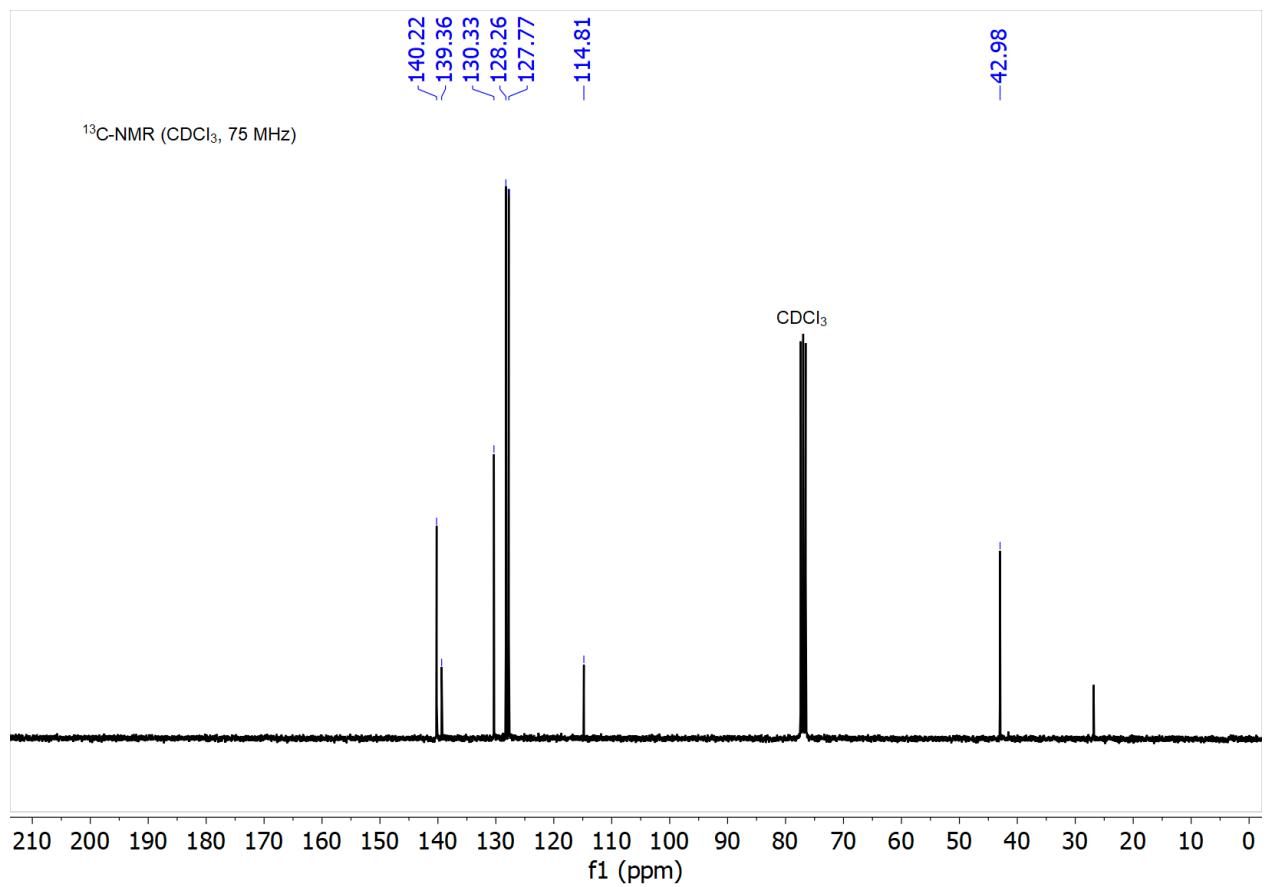
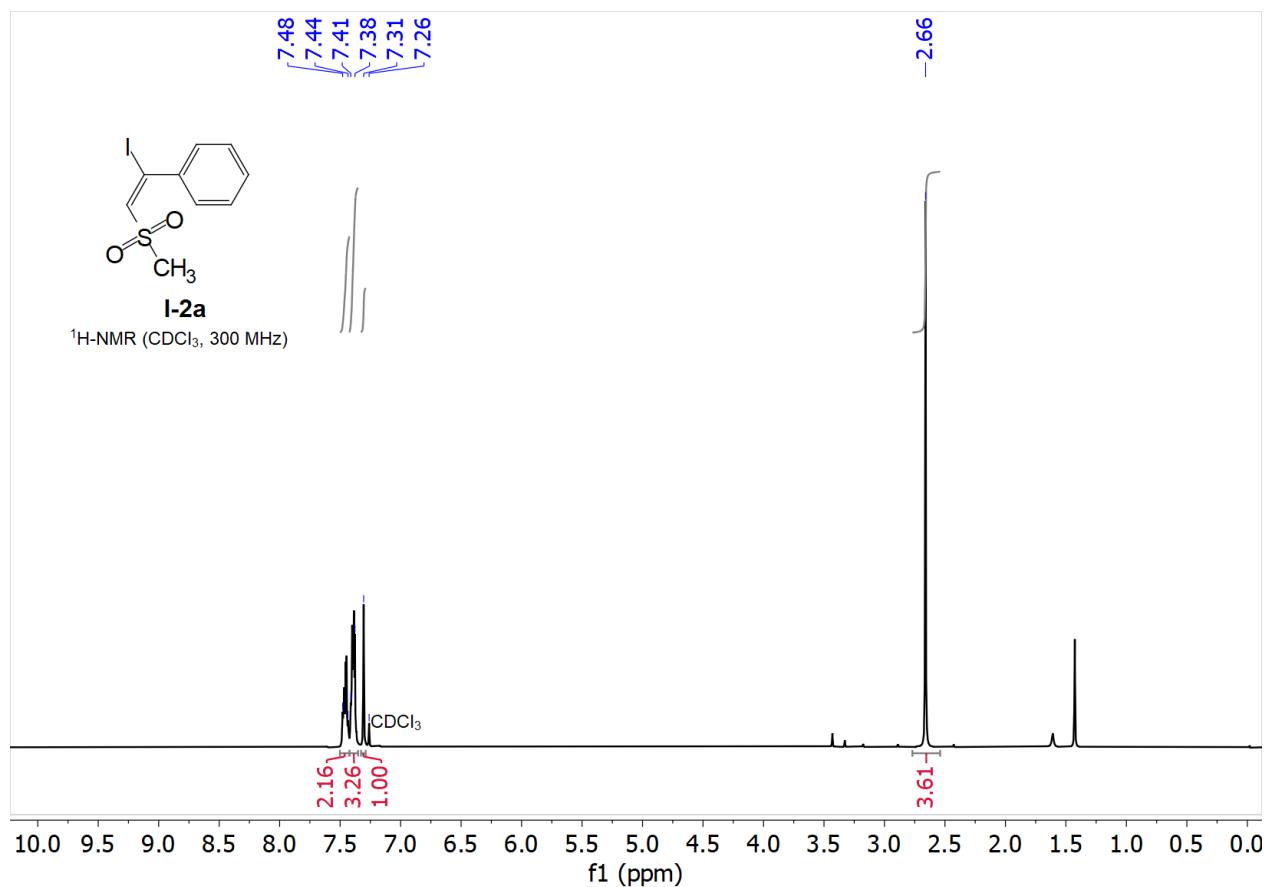
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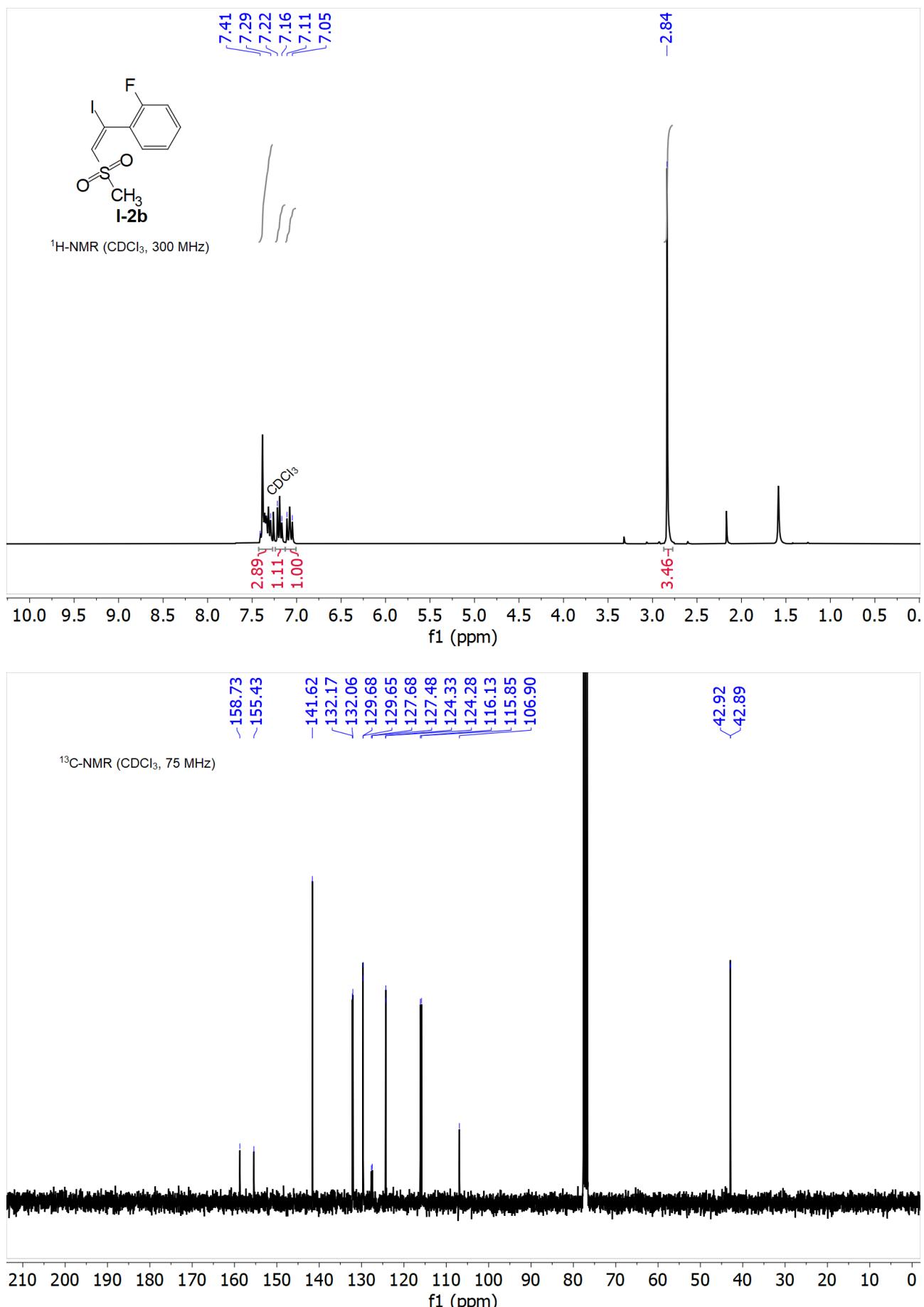
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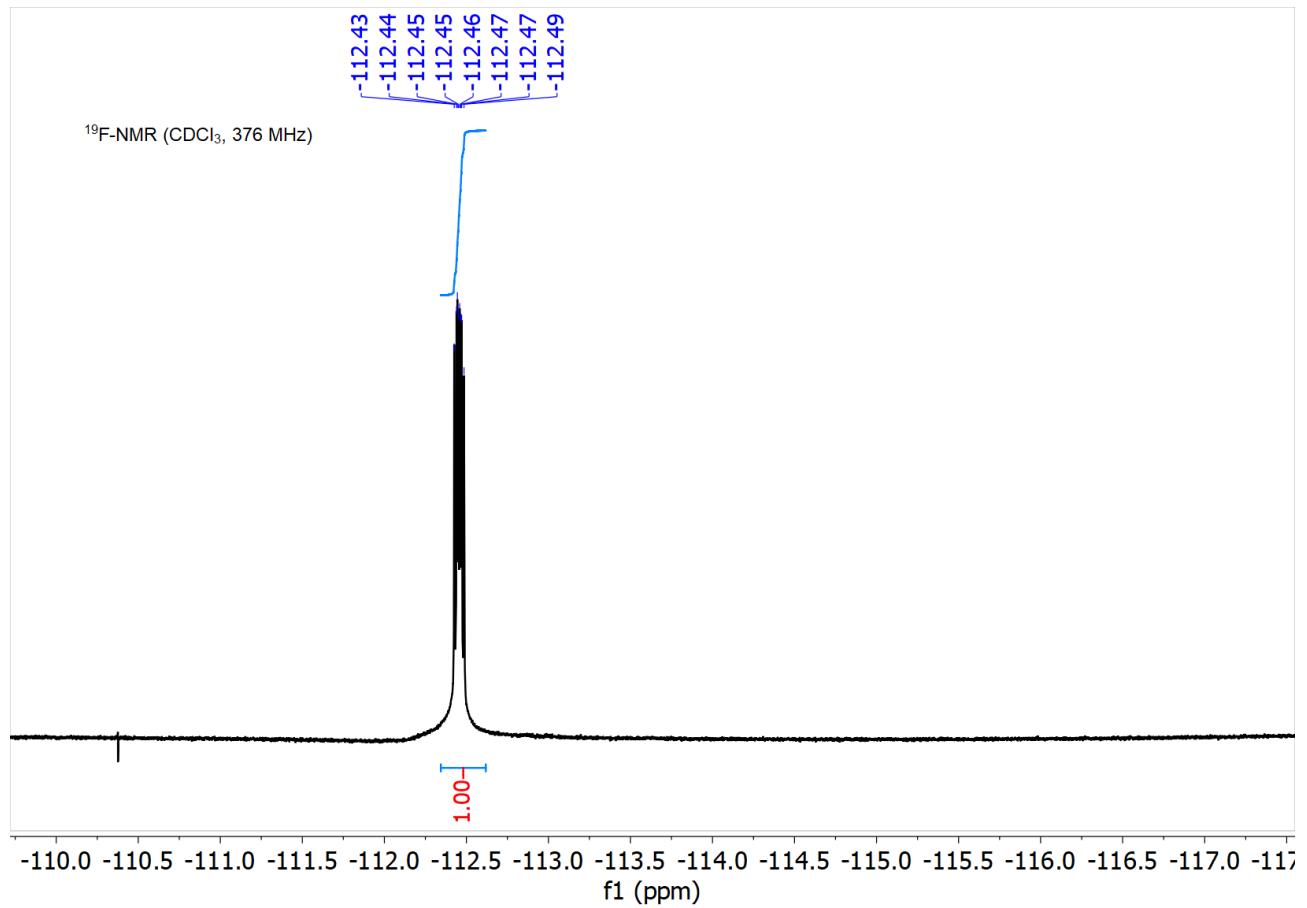
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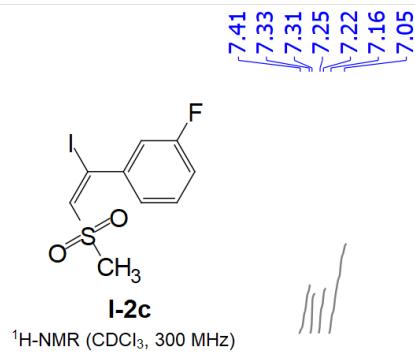
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5. ^1H -, ^{13}C and ^{19}F -NMR of compounds I-2

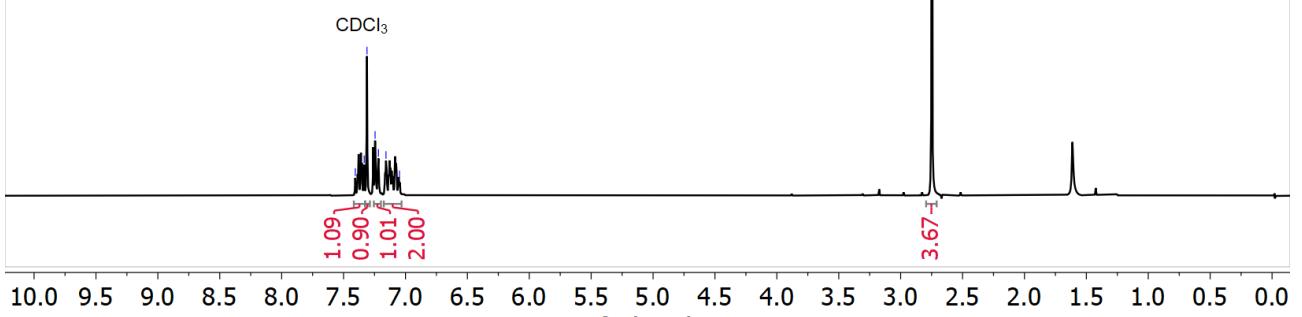




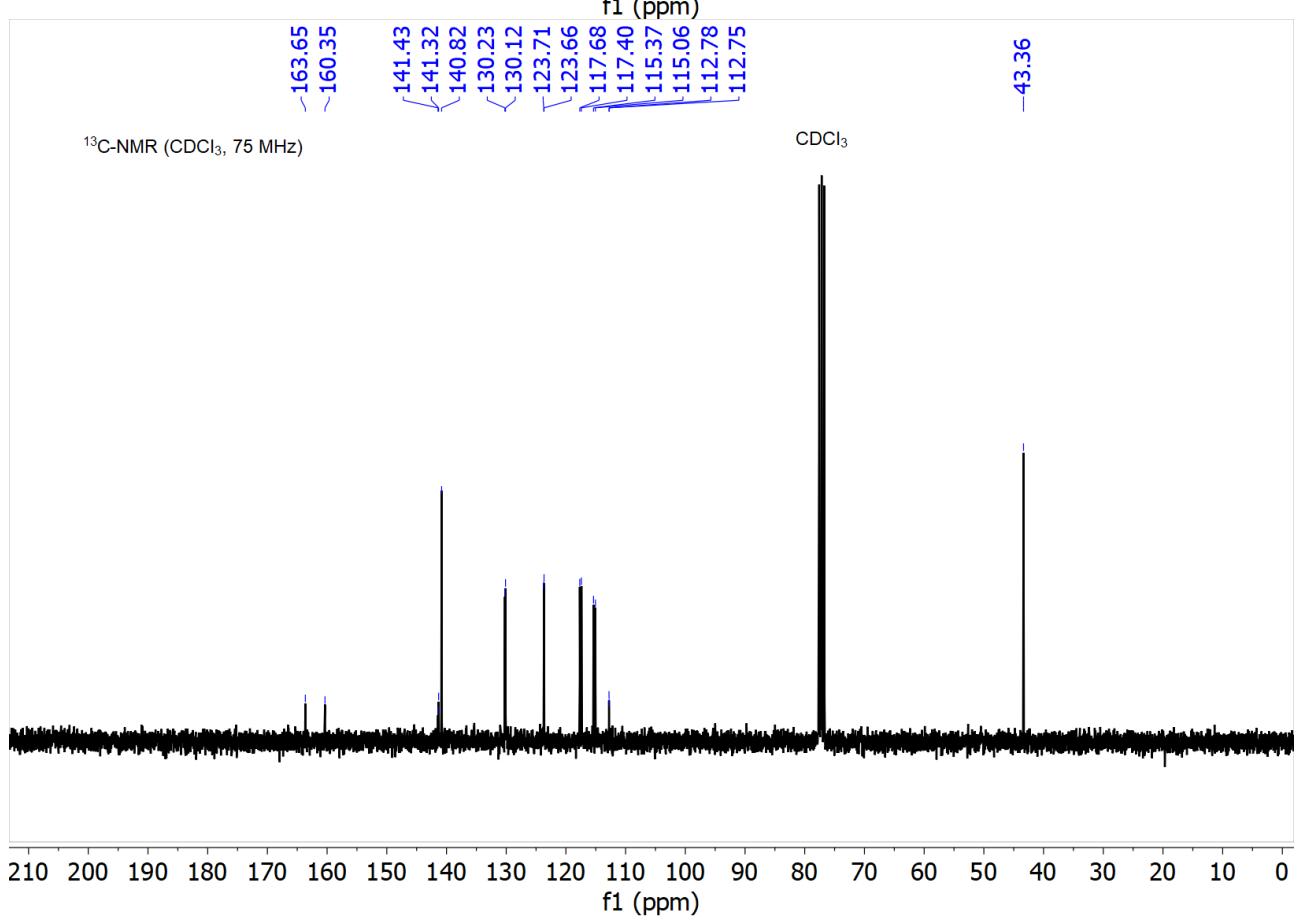


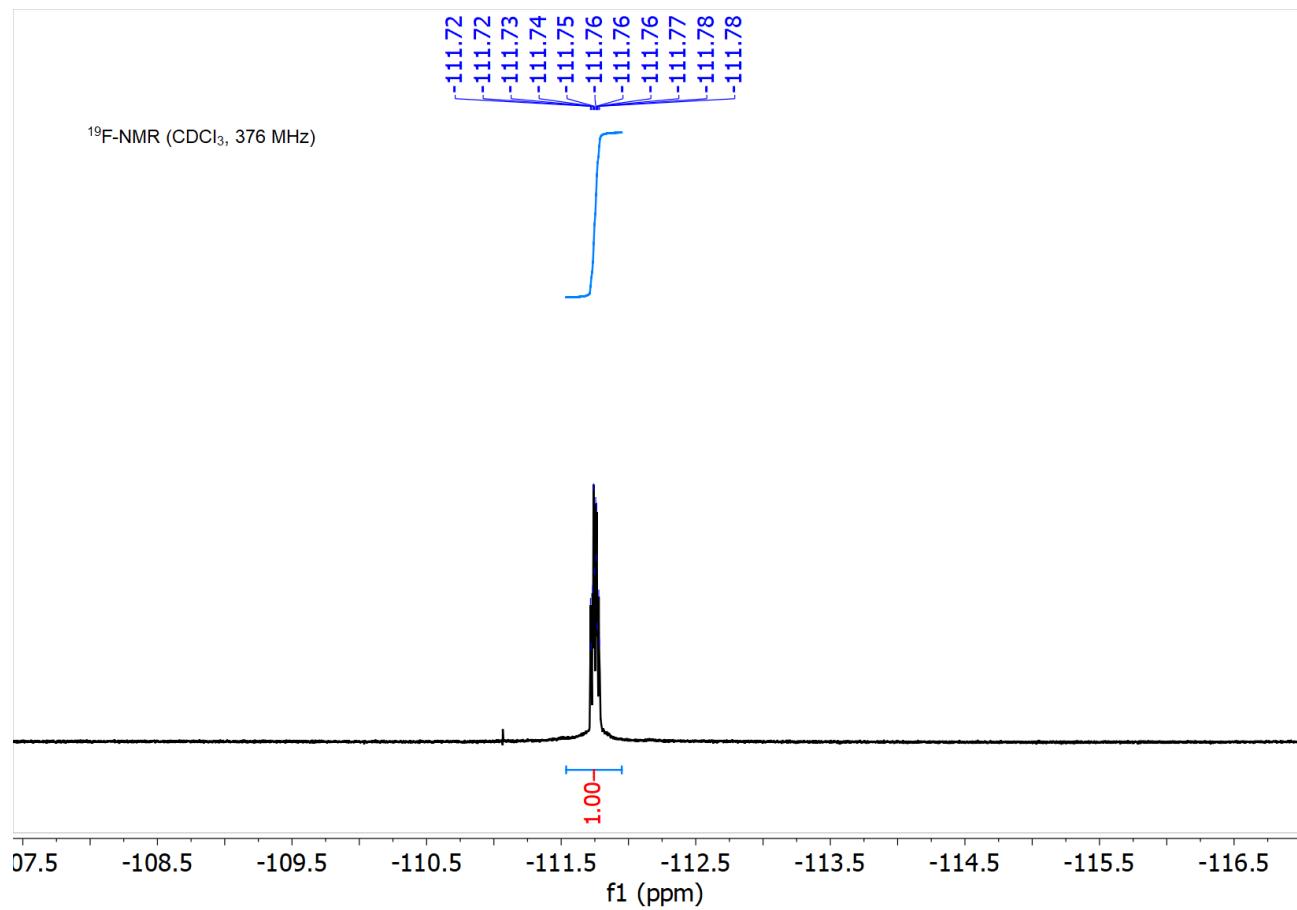


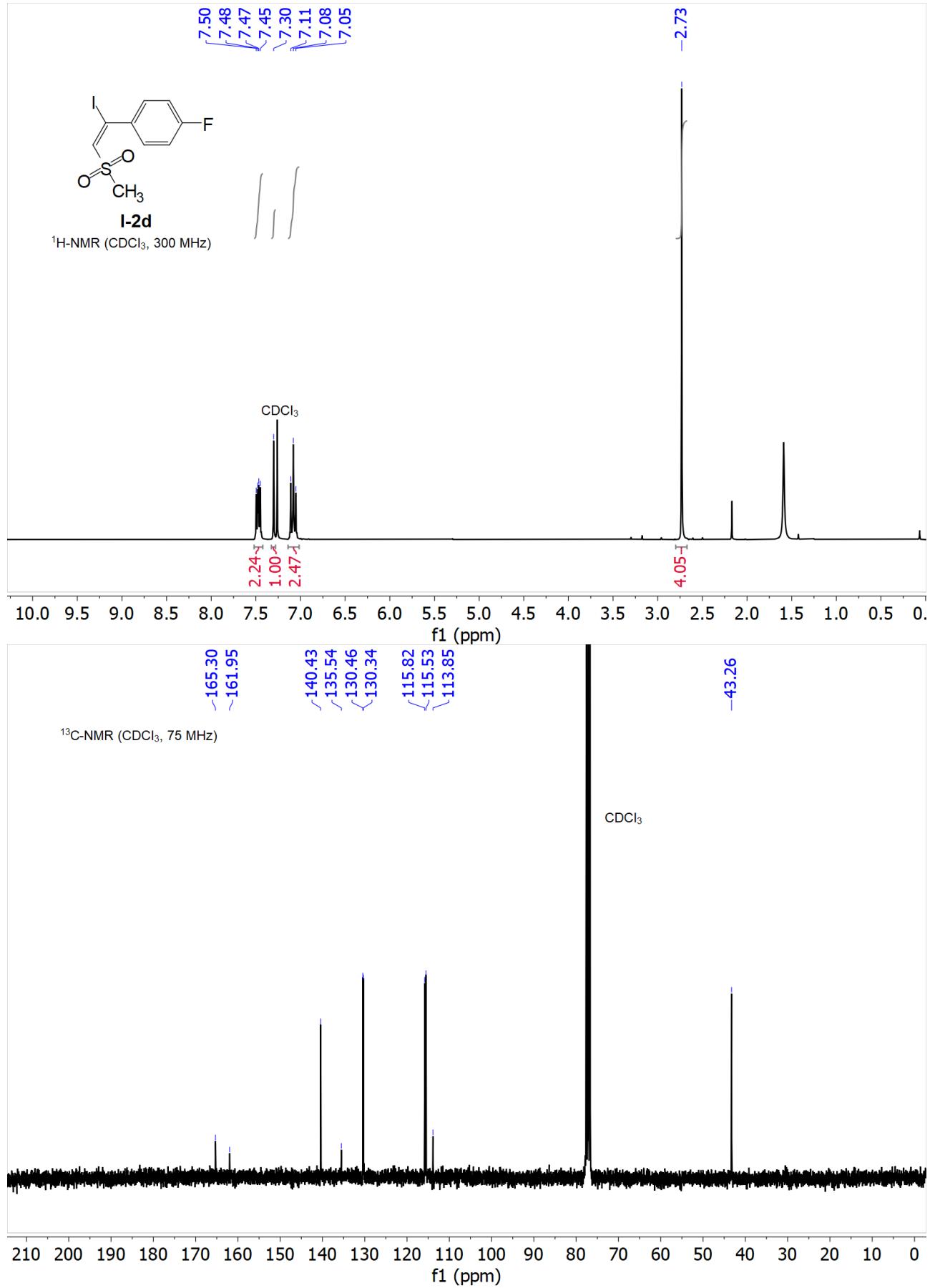
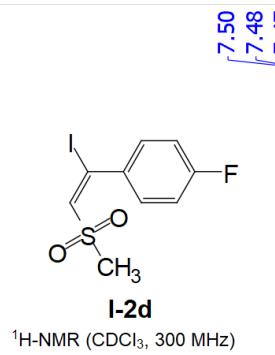
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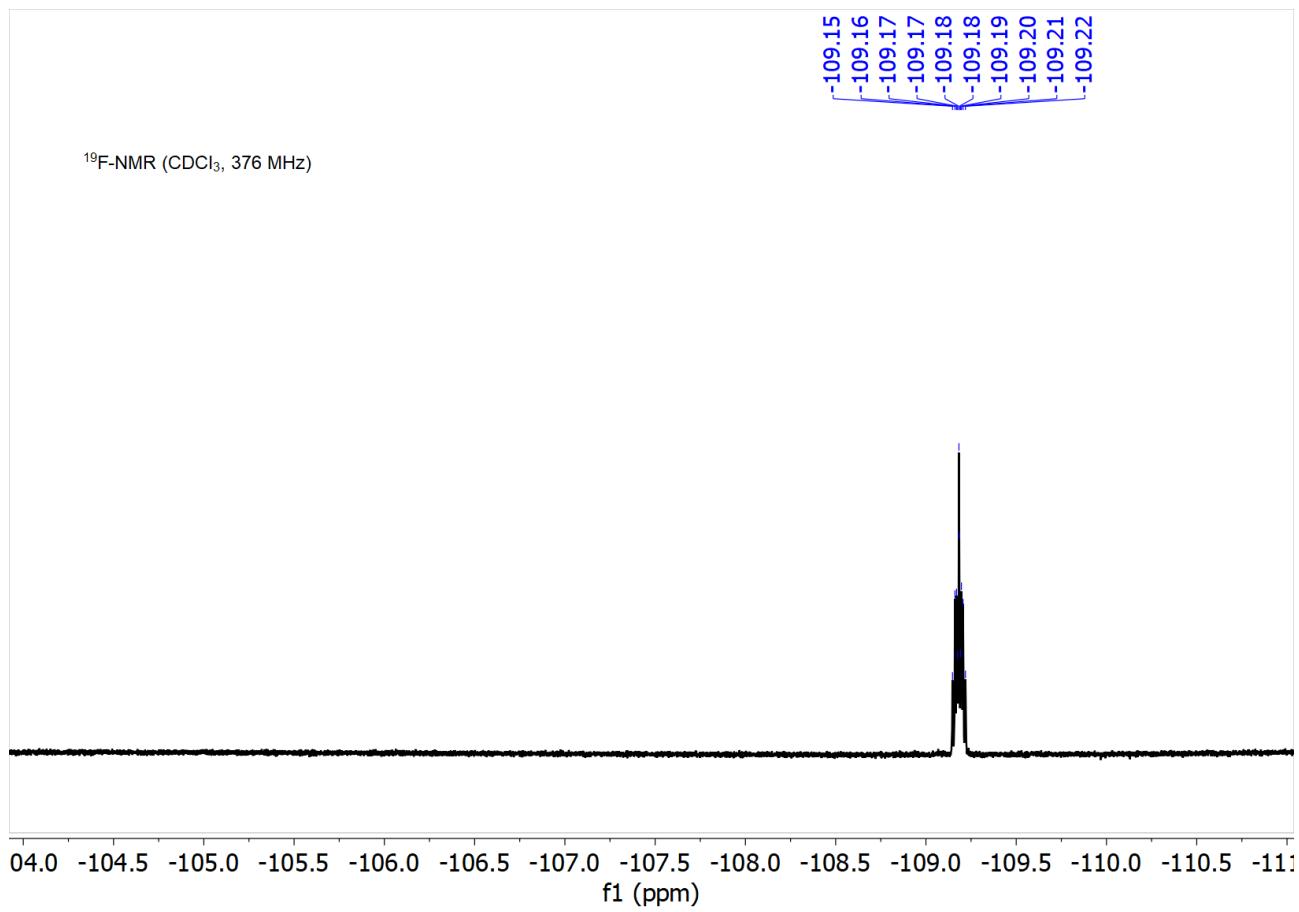


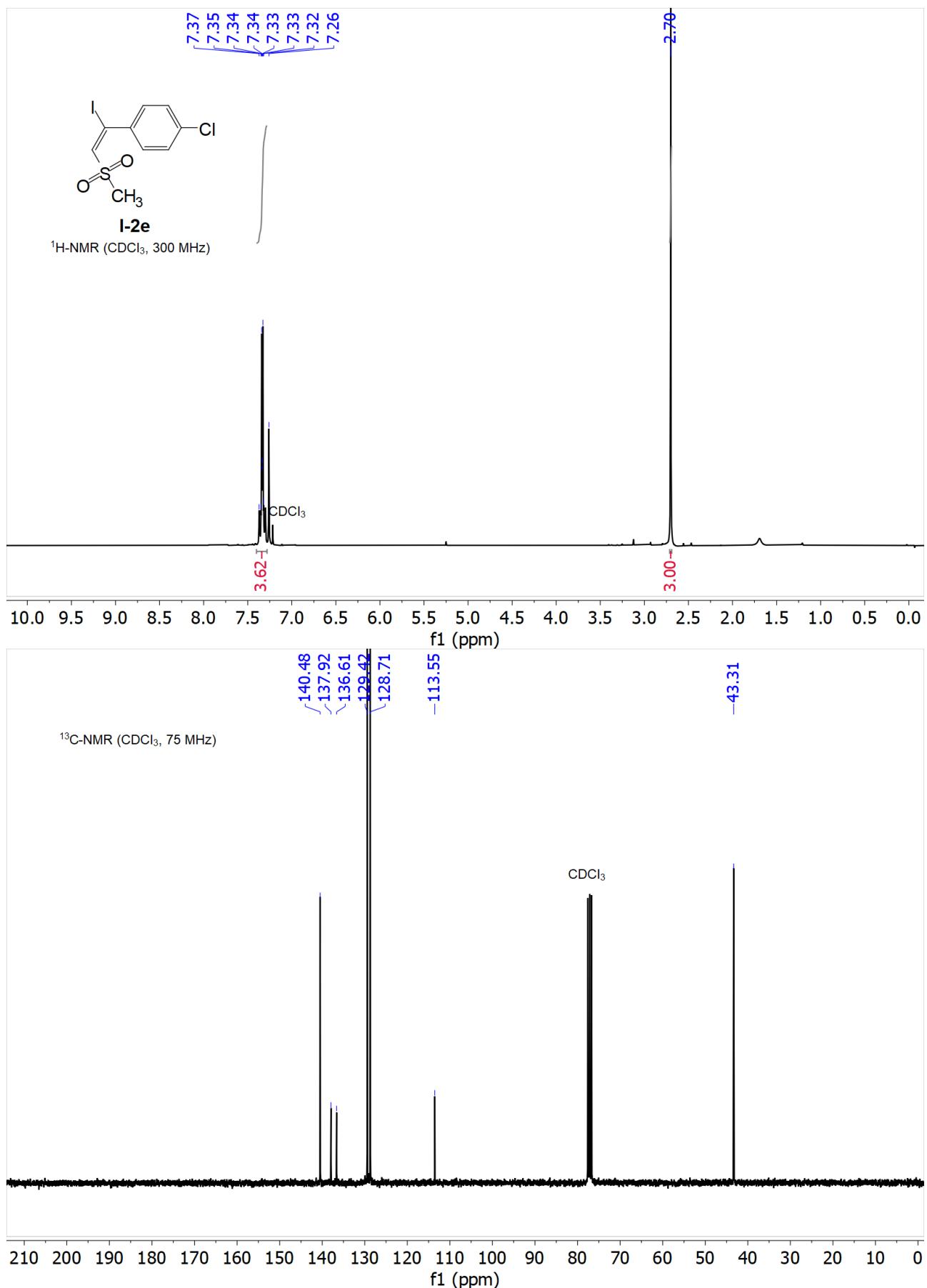
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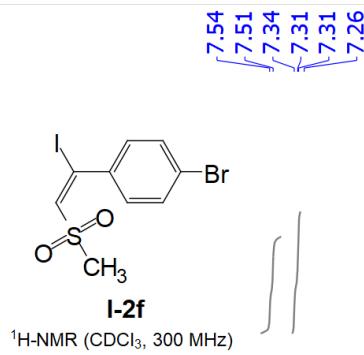




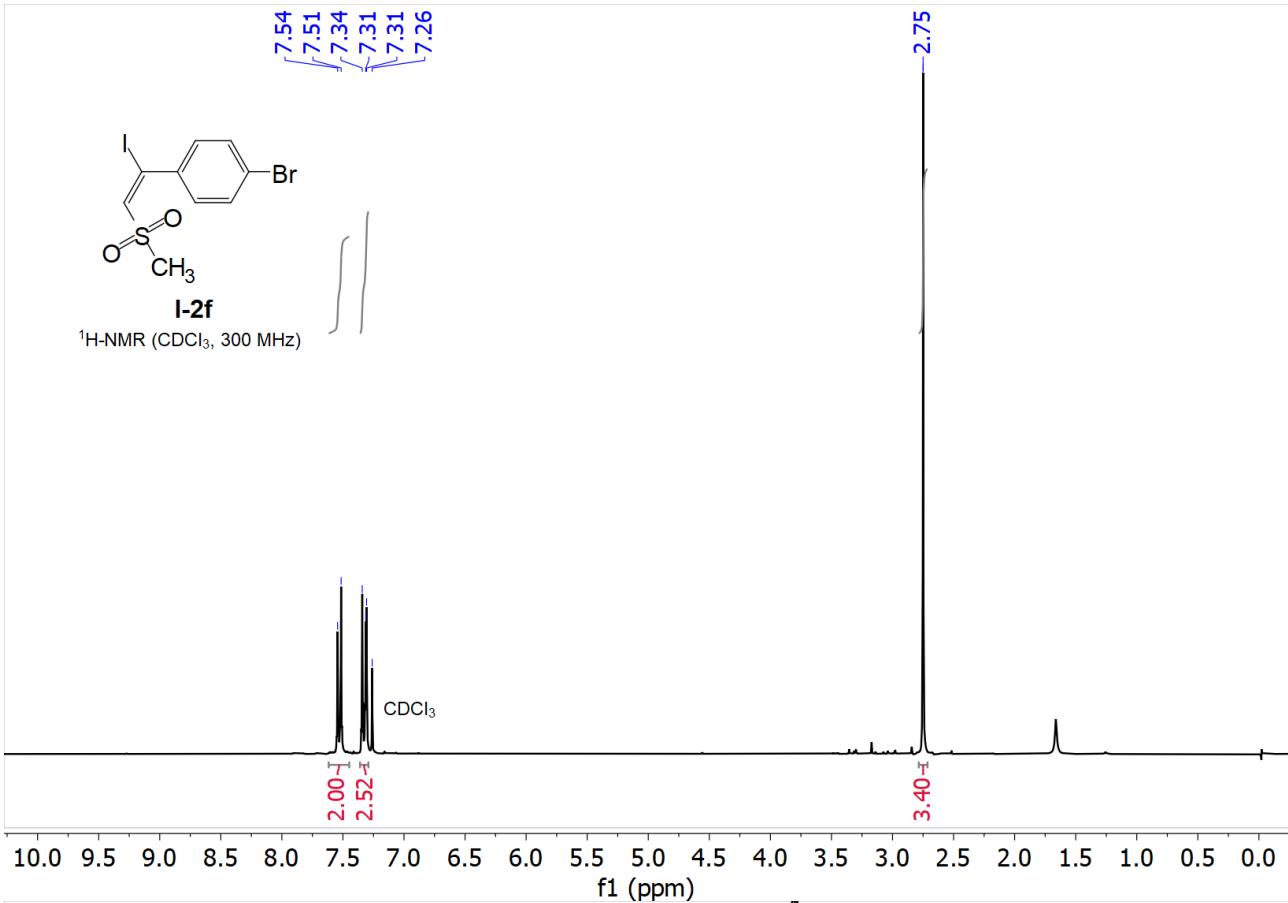




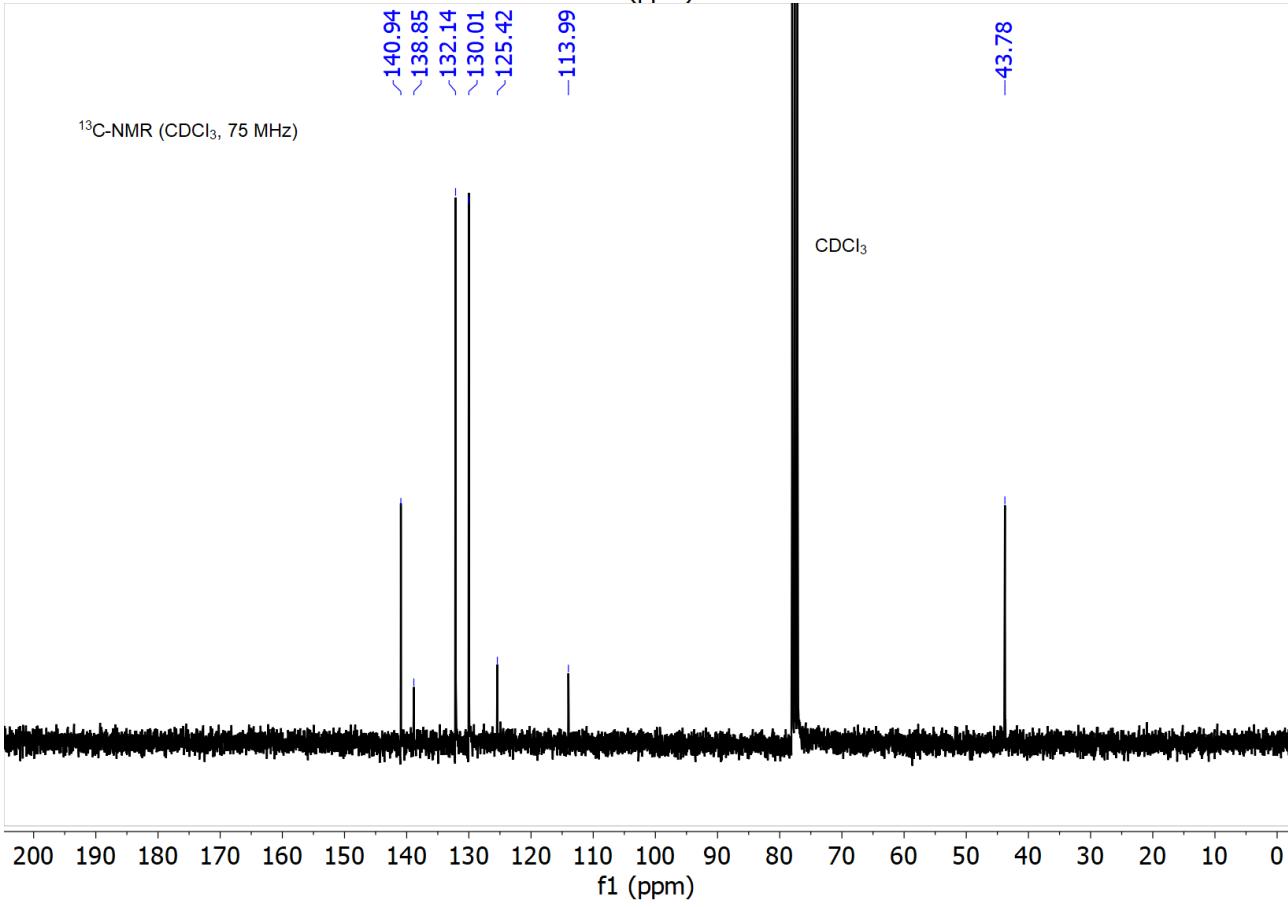


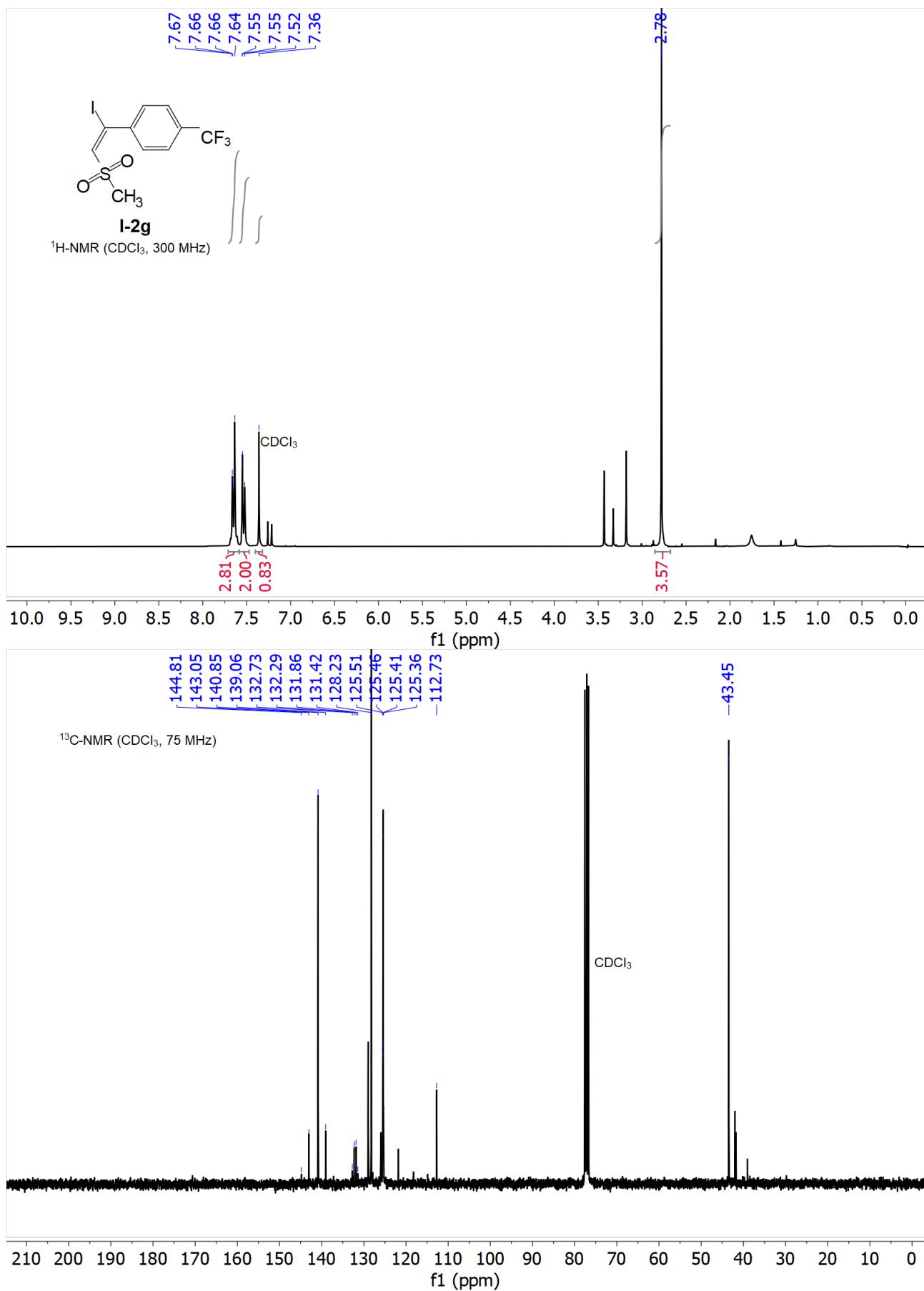


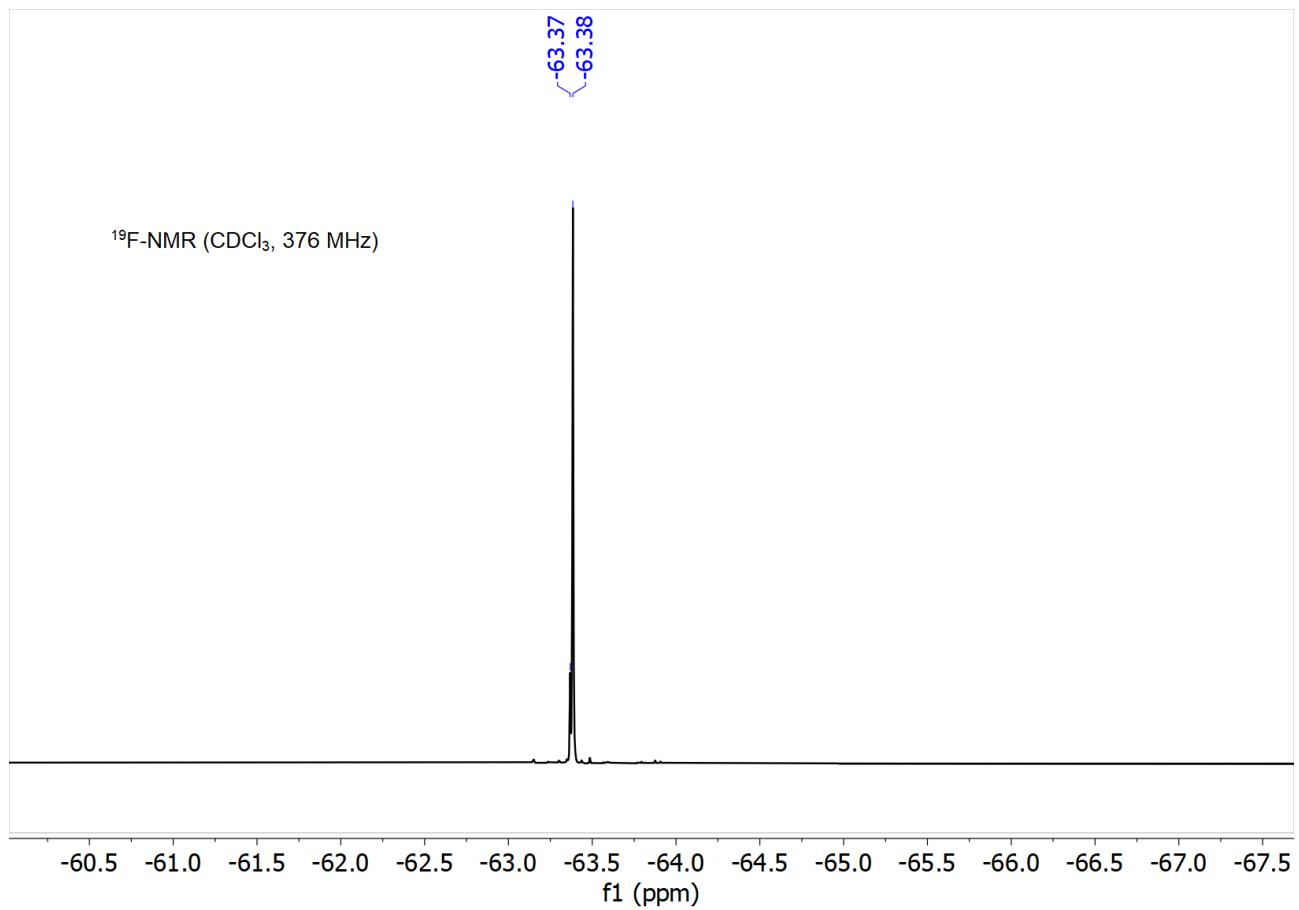
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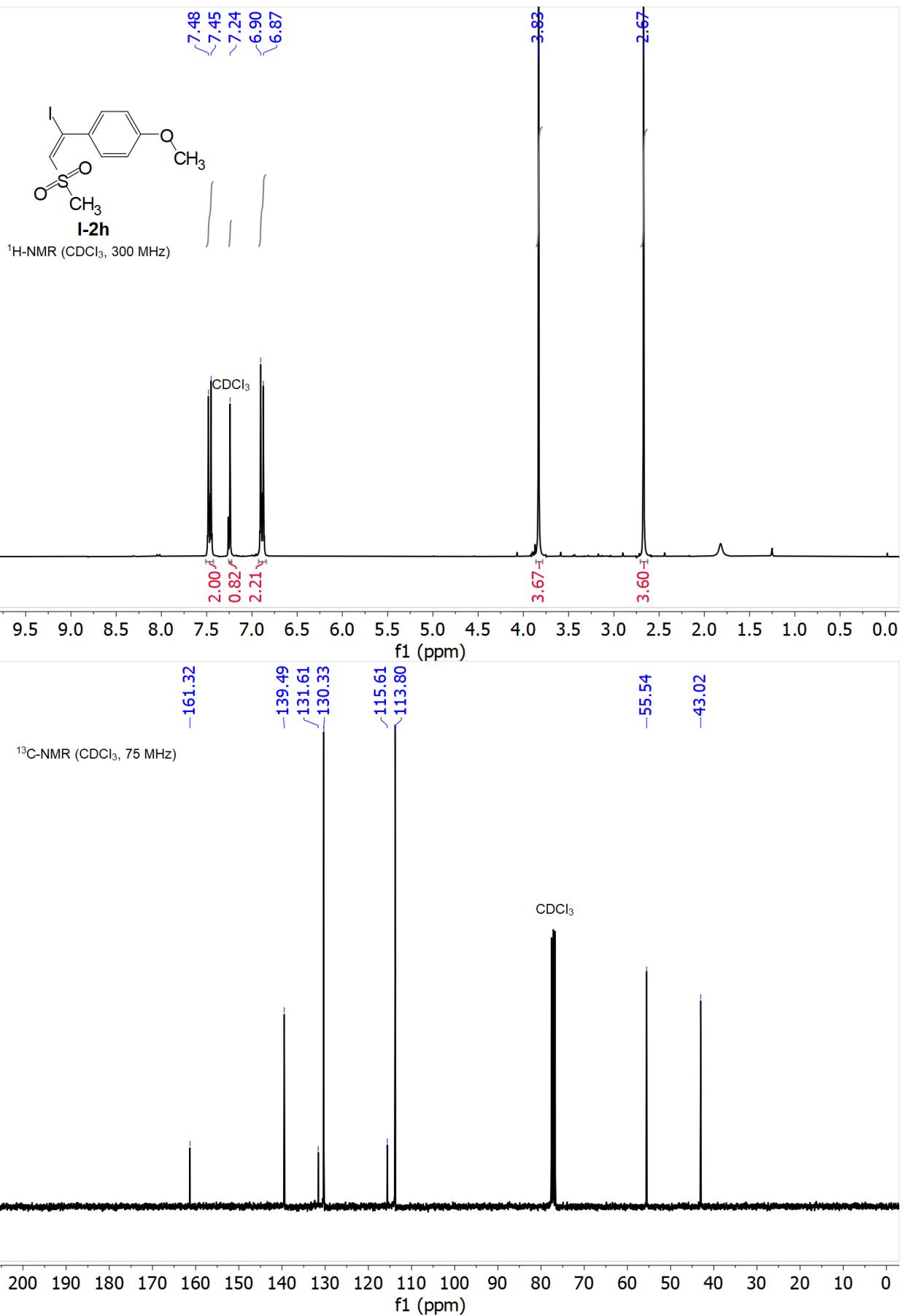


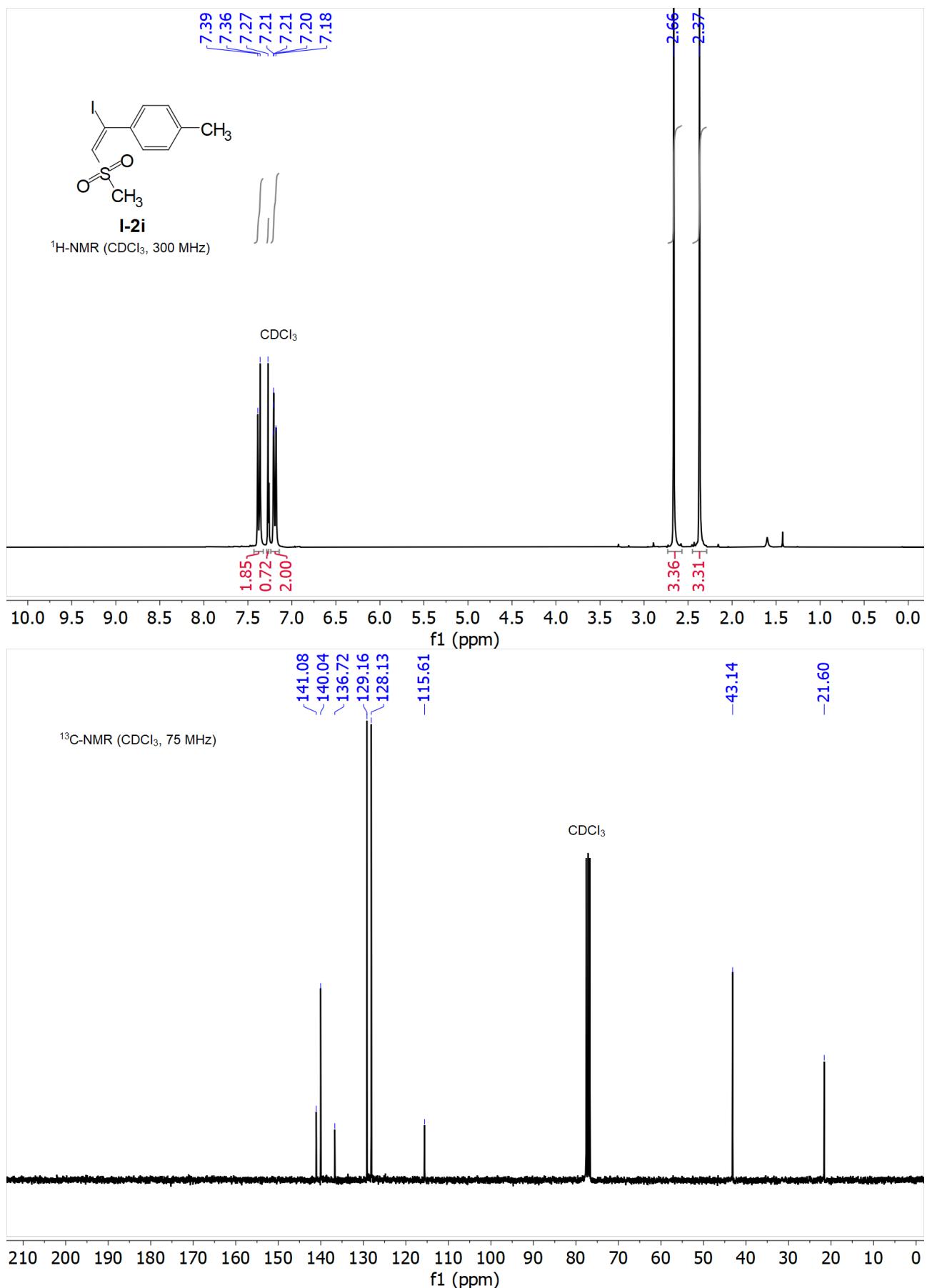
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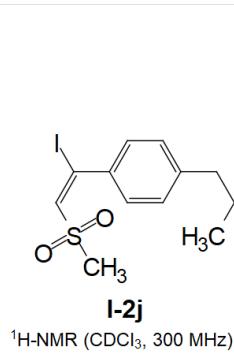




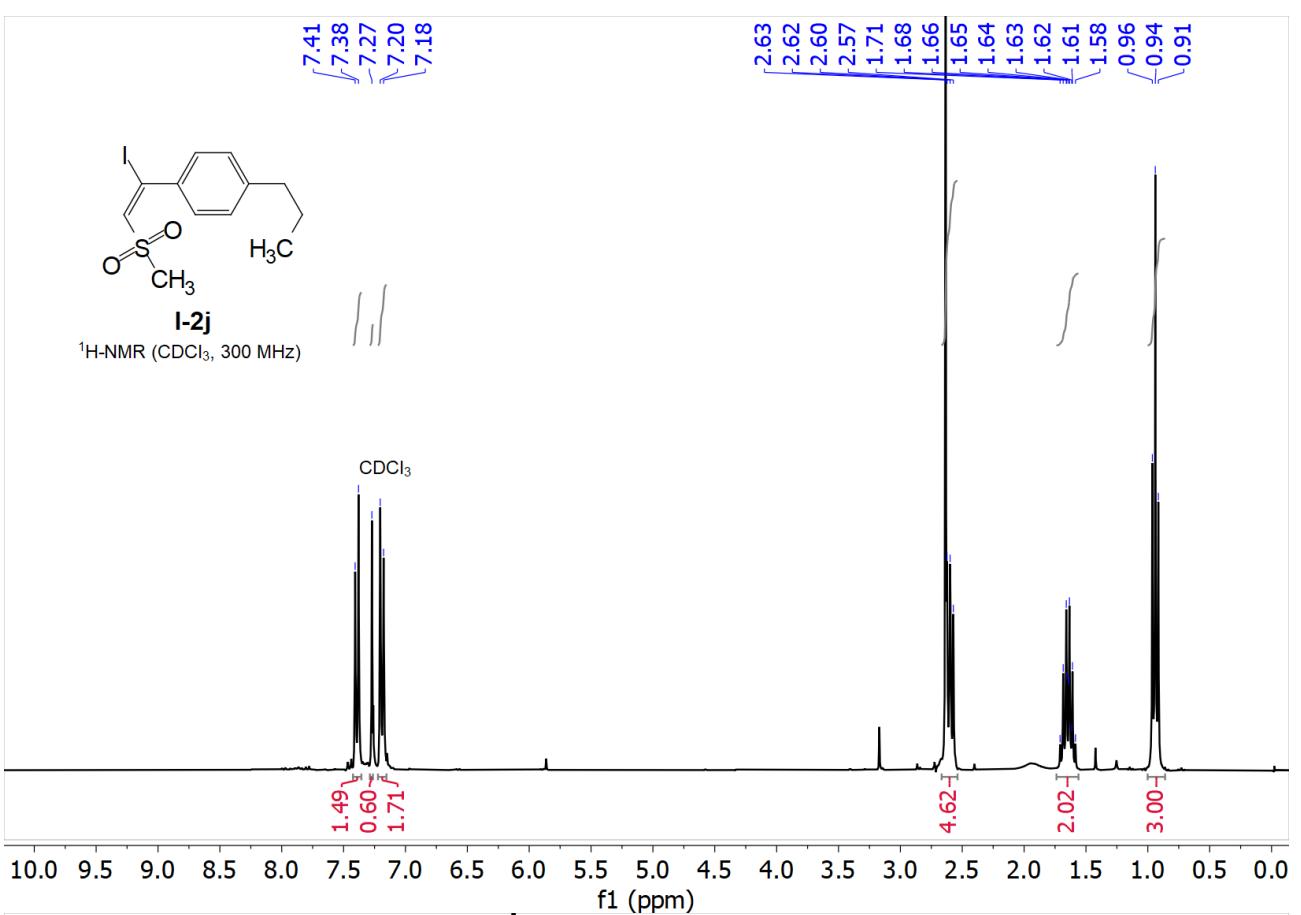




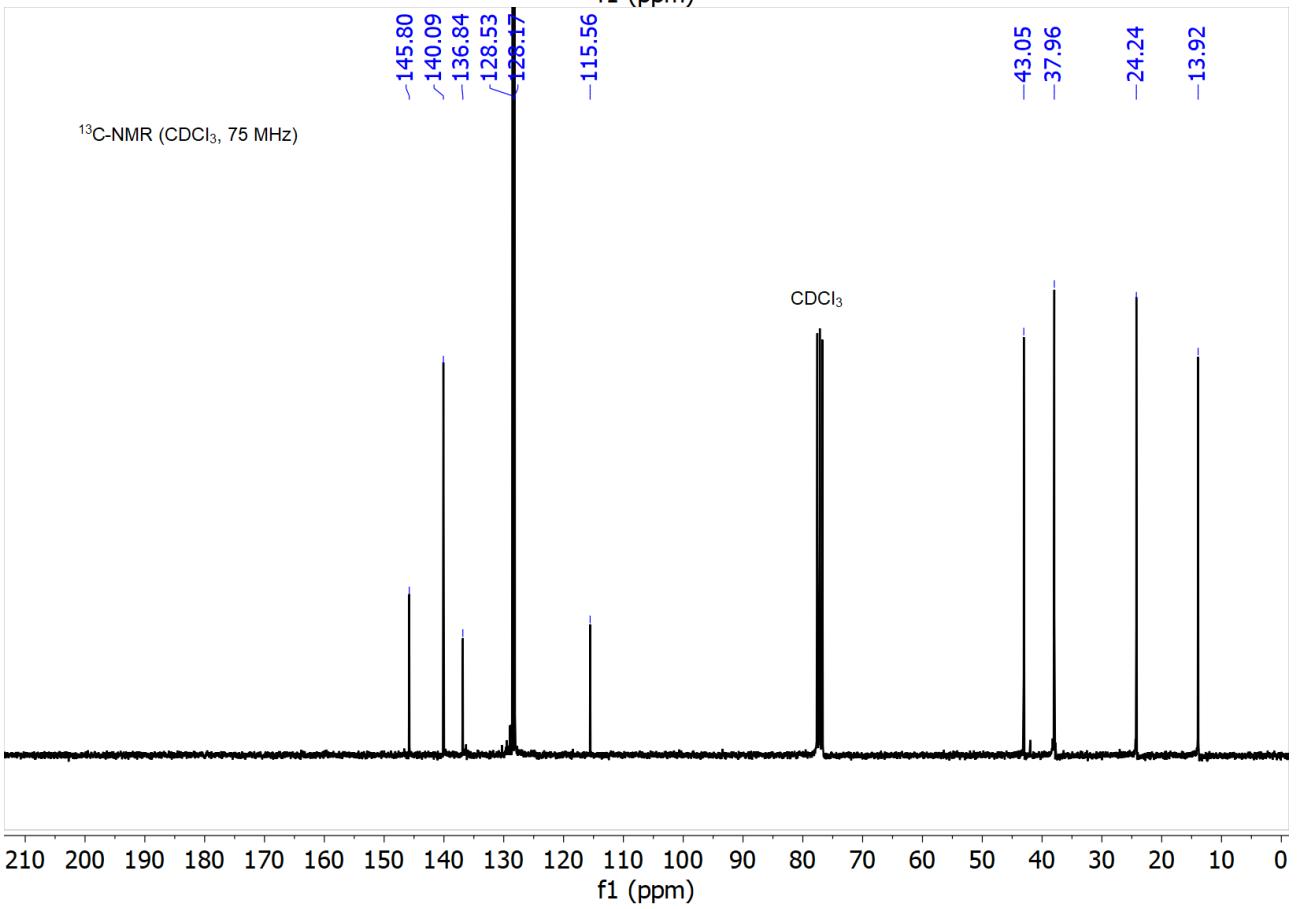


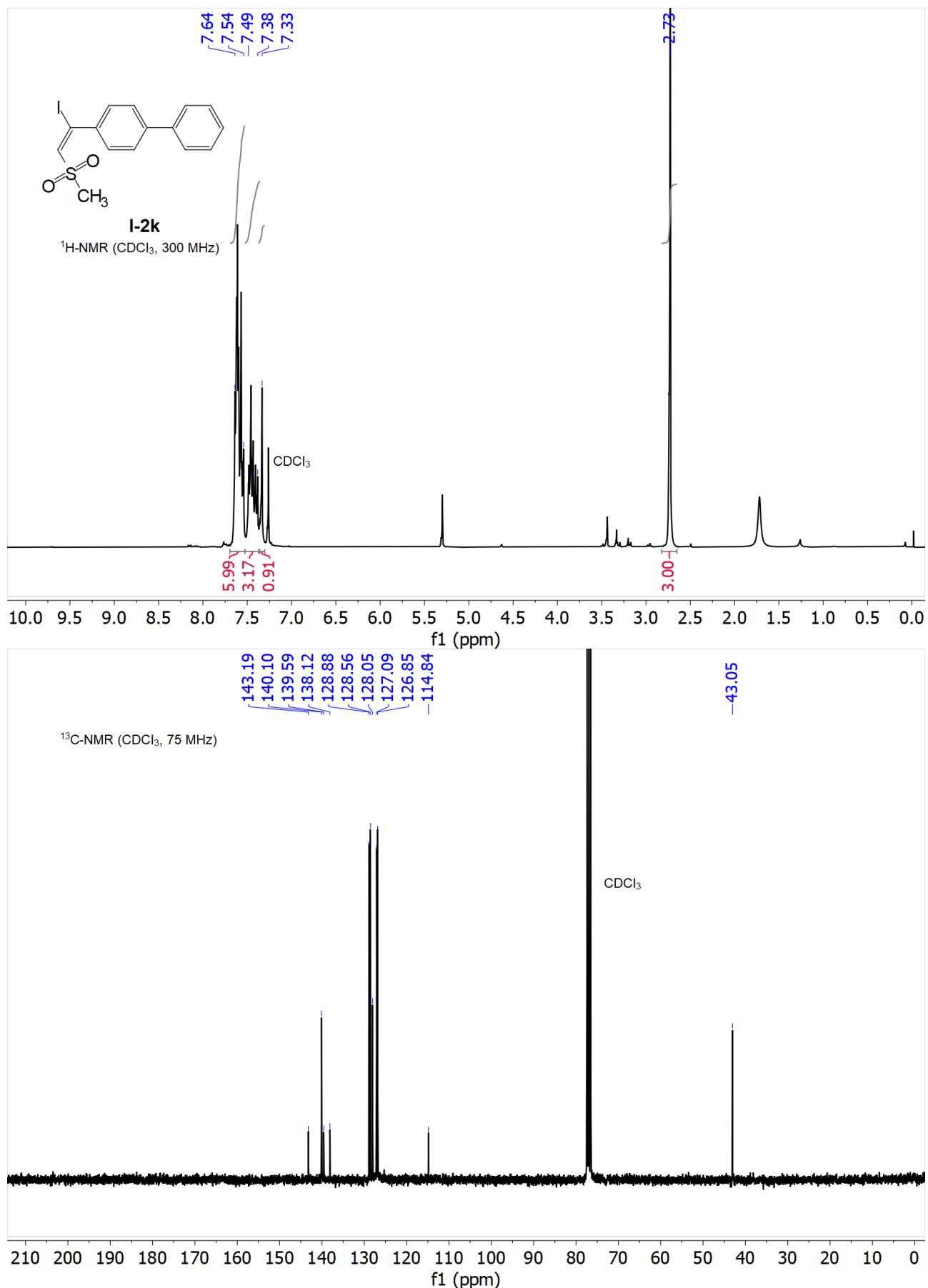


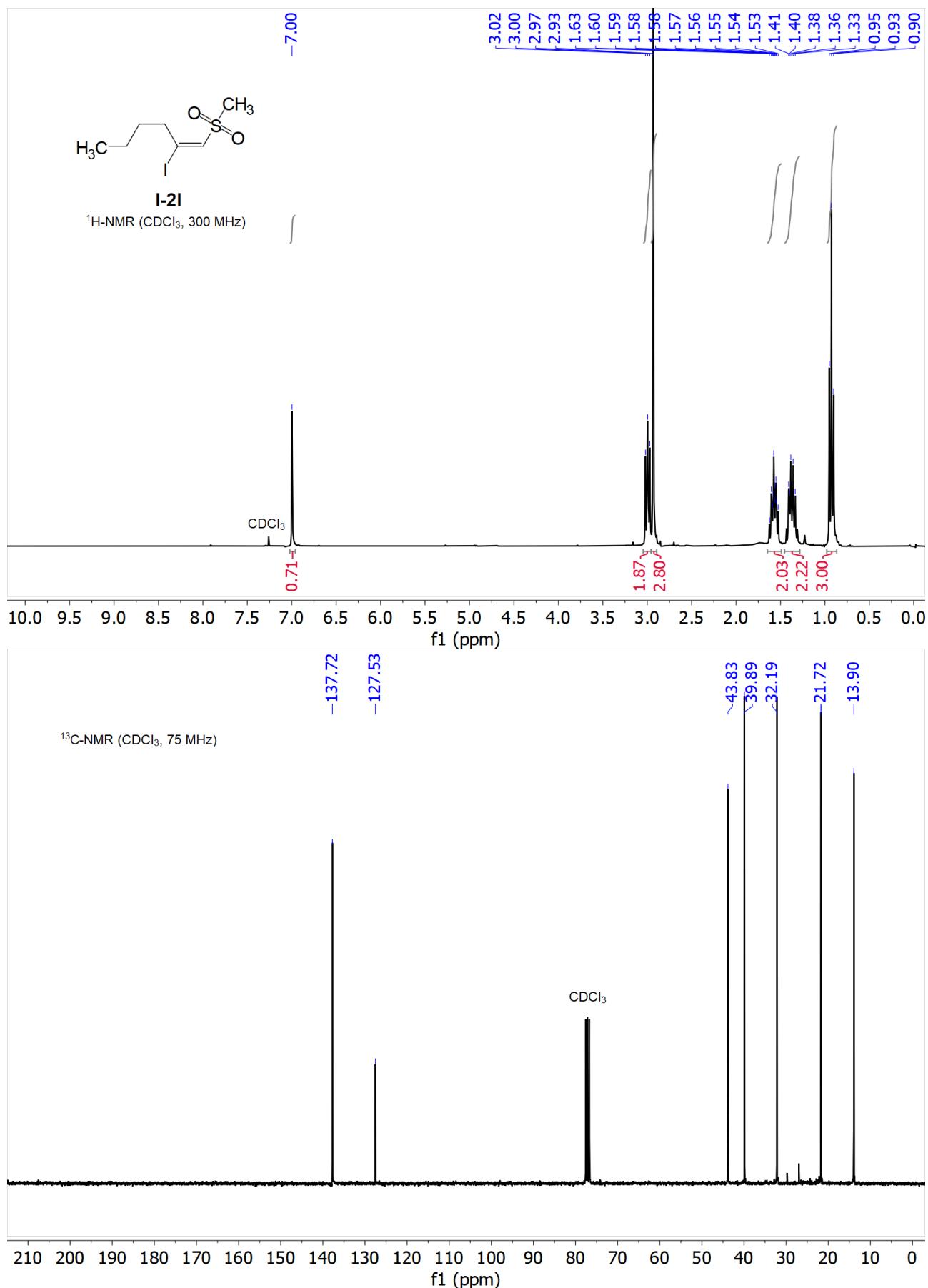
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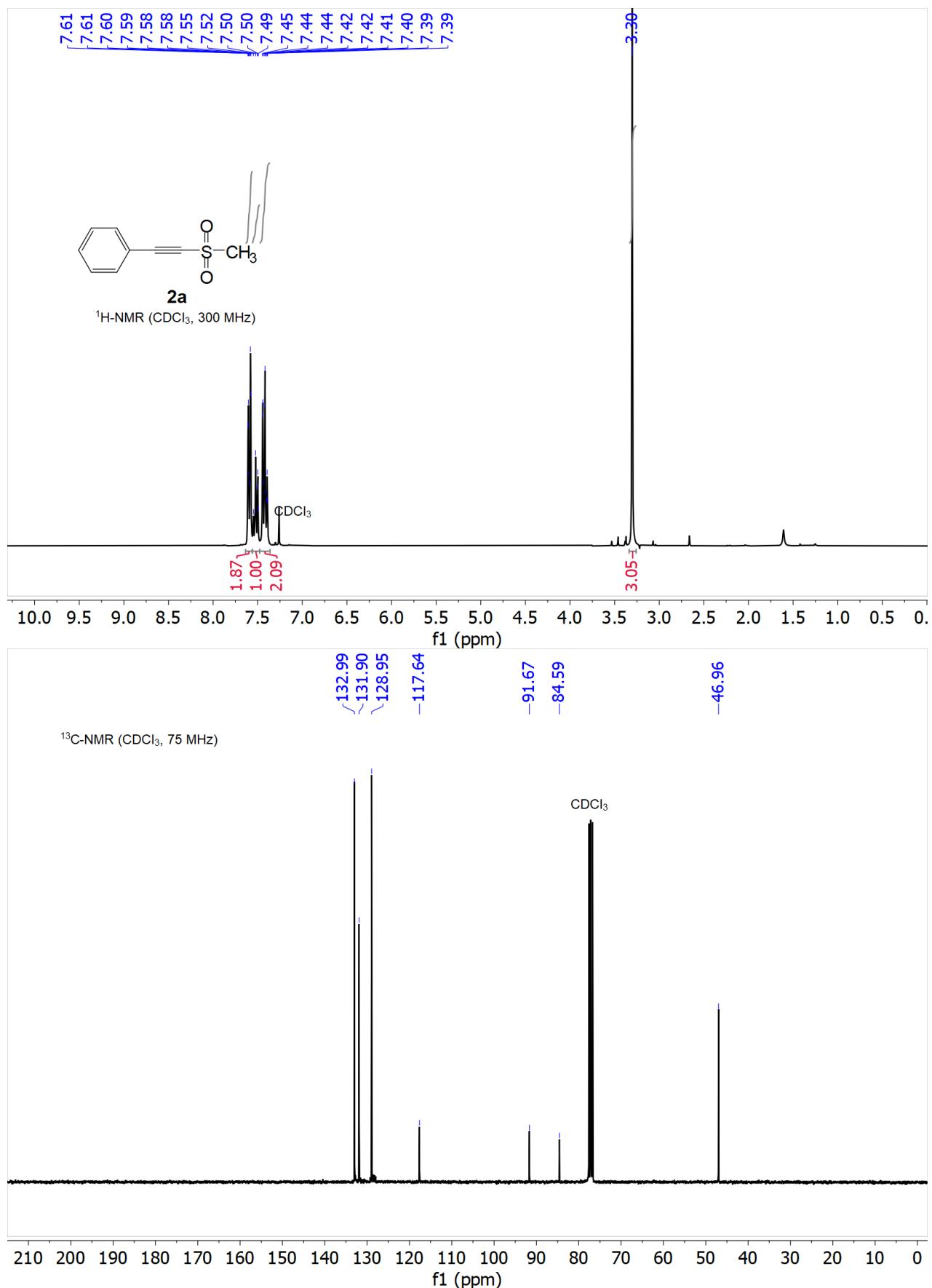
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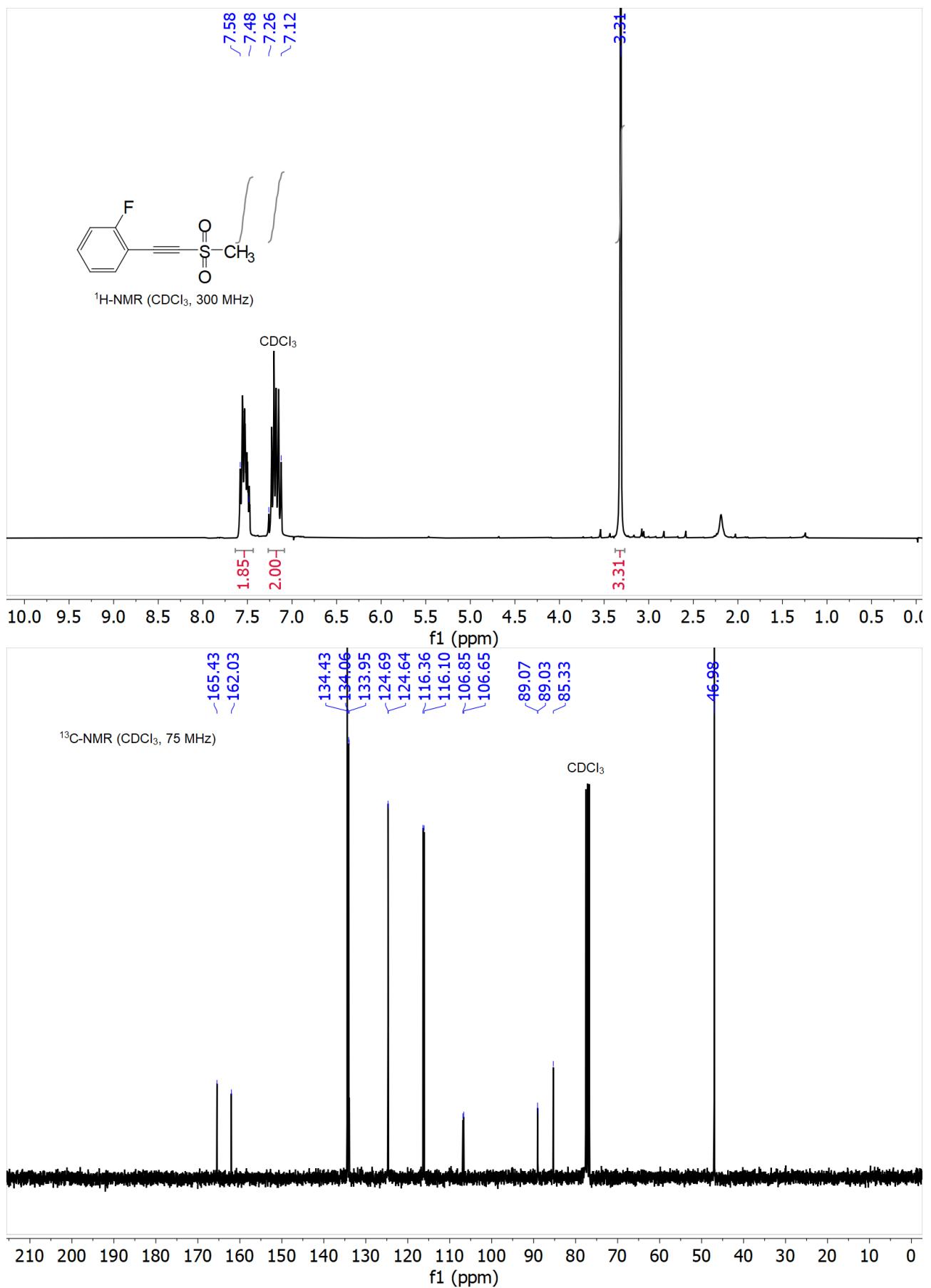


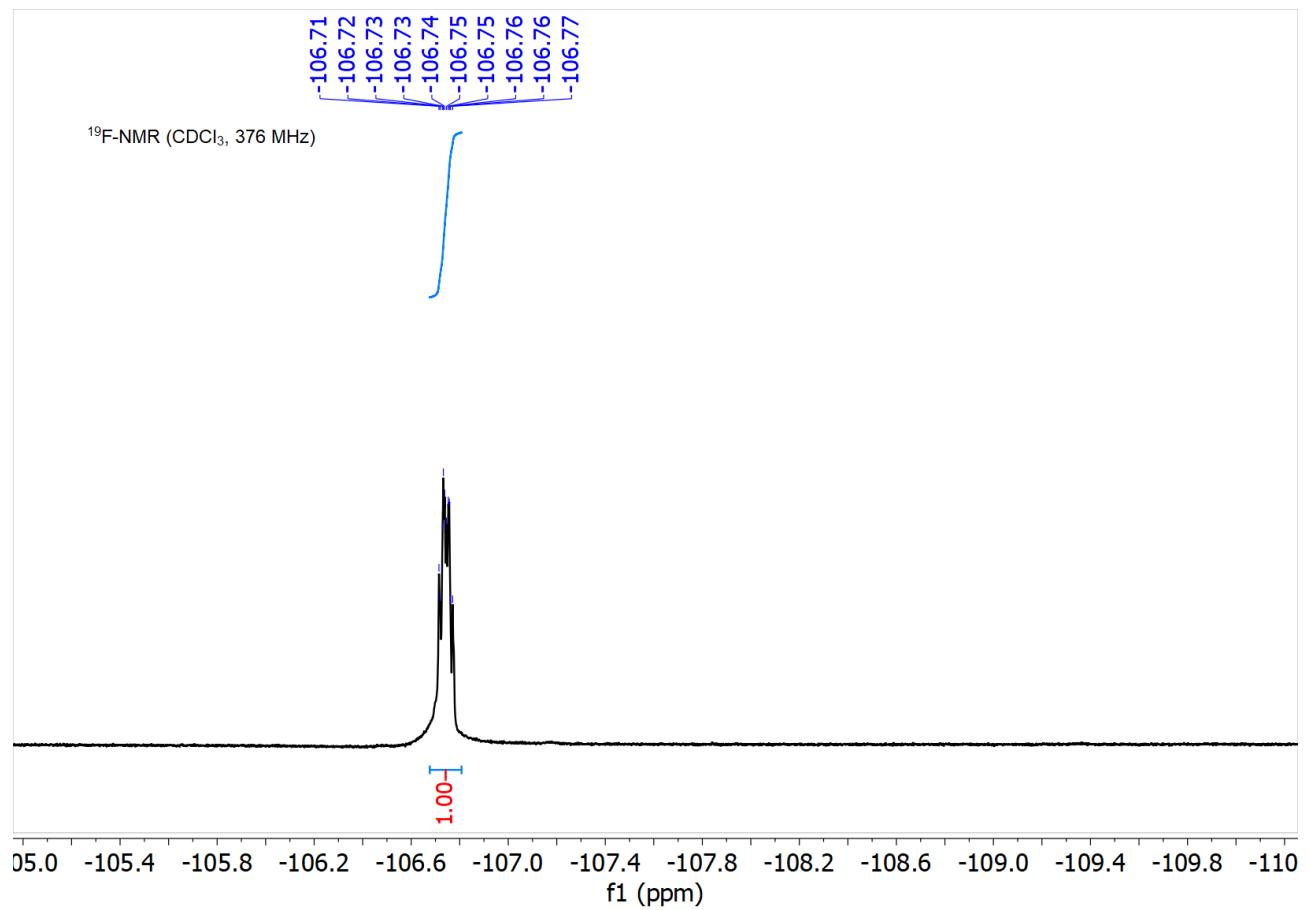


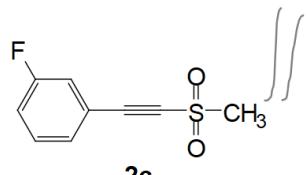


6. ^1H -, ^{13}C and ^{19}F -NMR of compounds 2

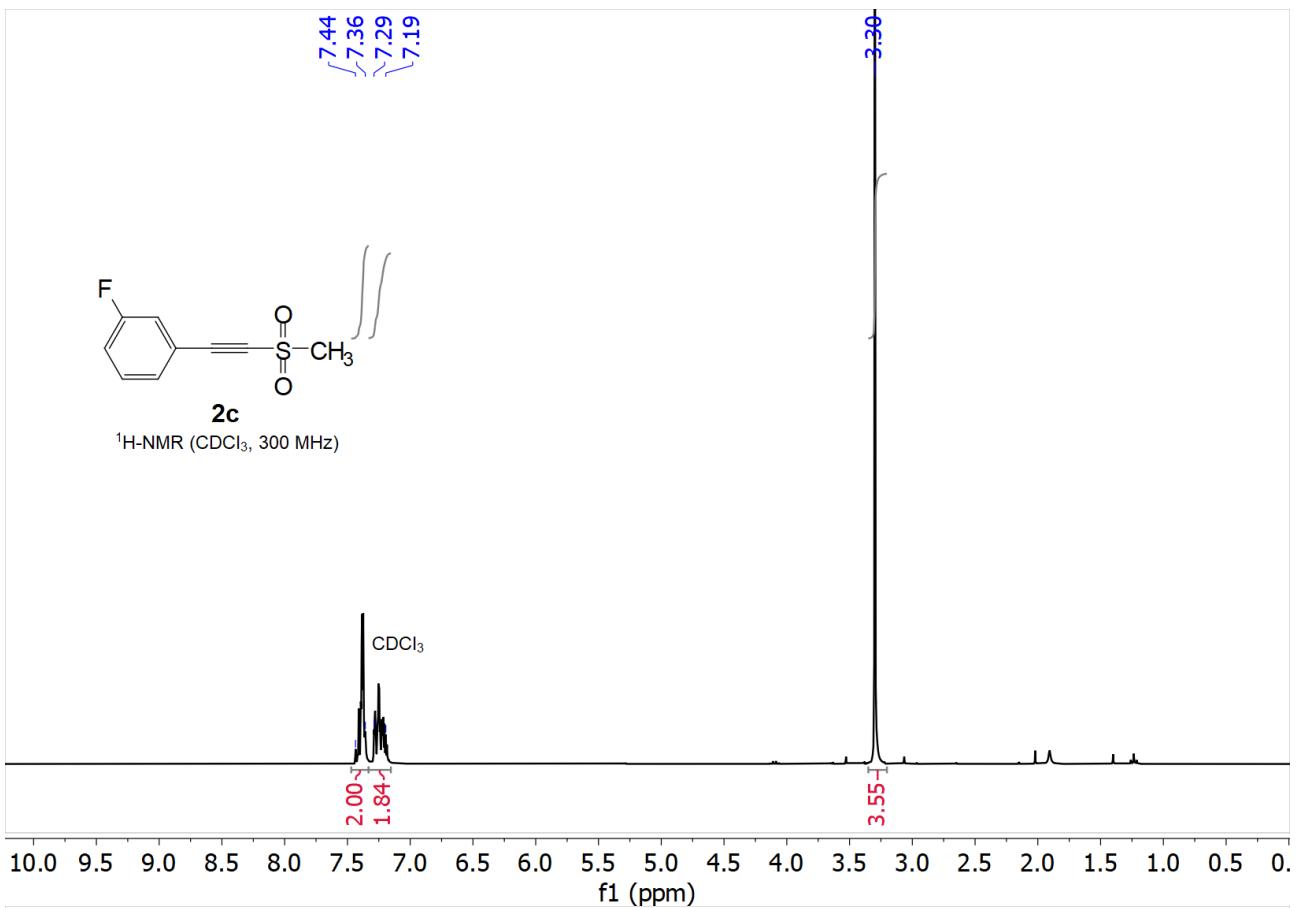




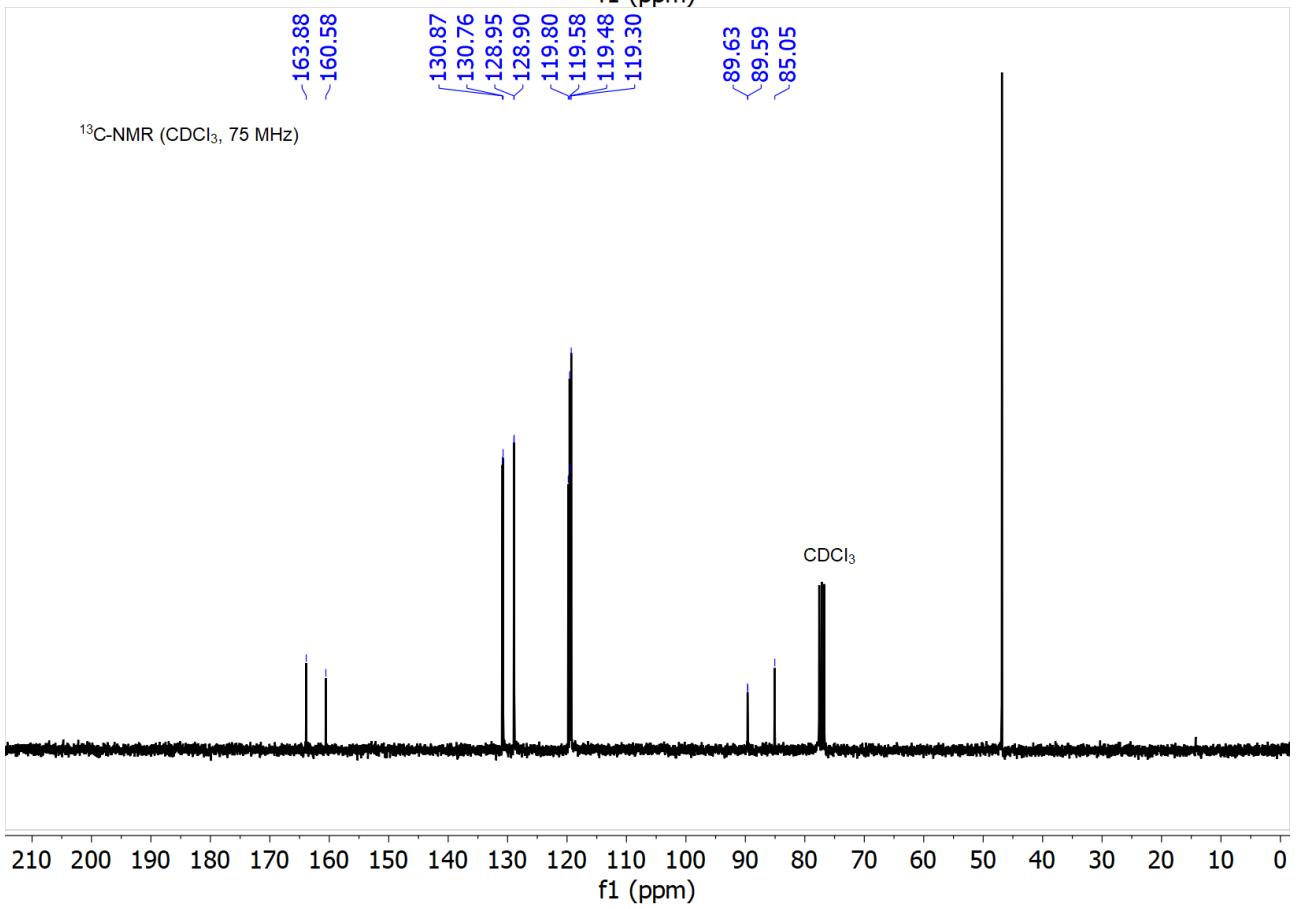


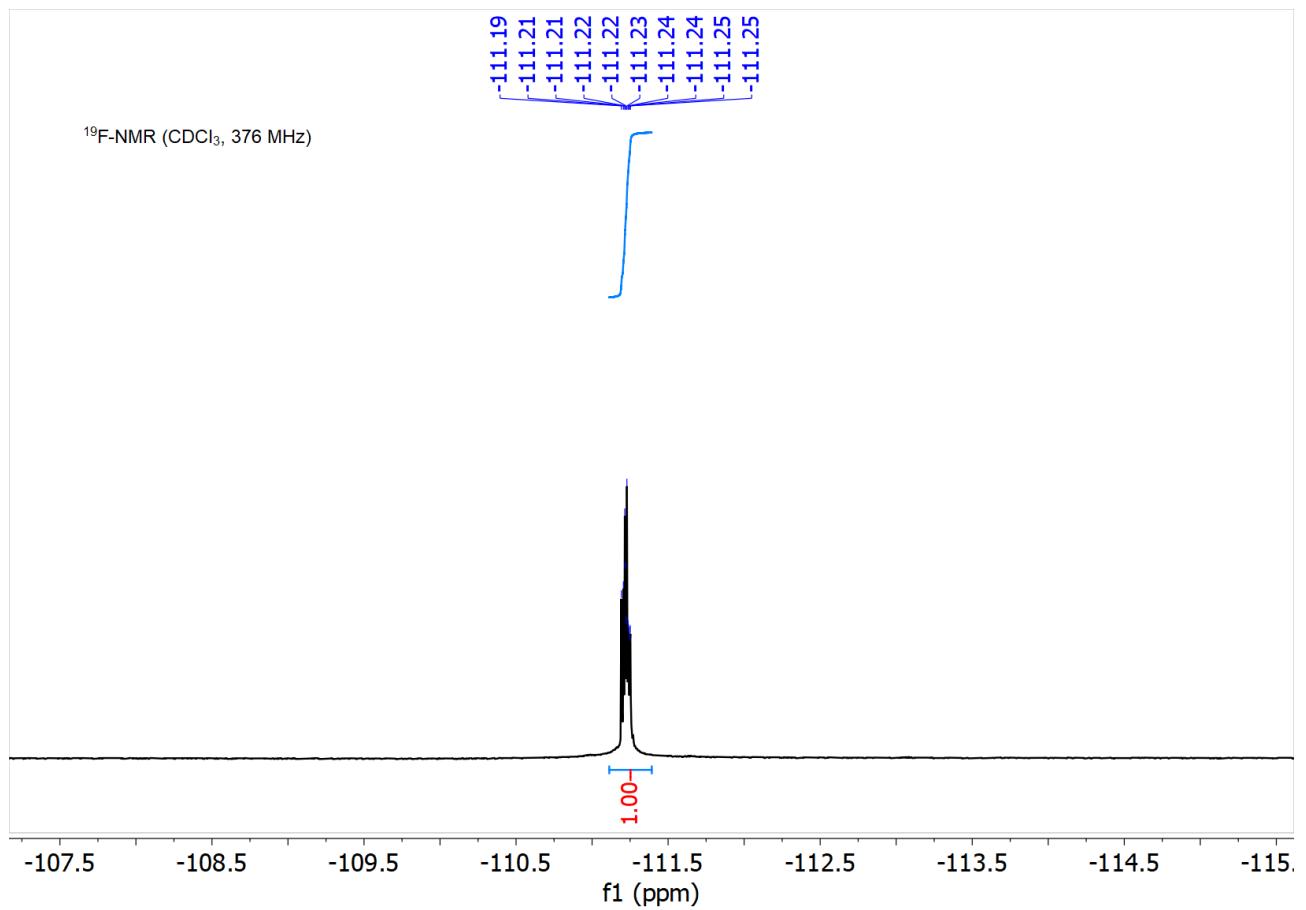


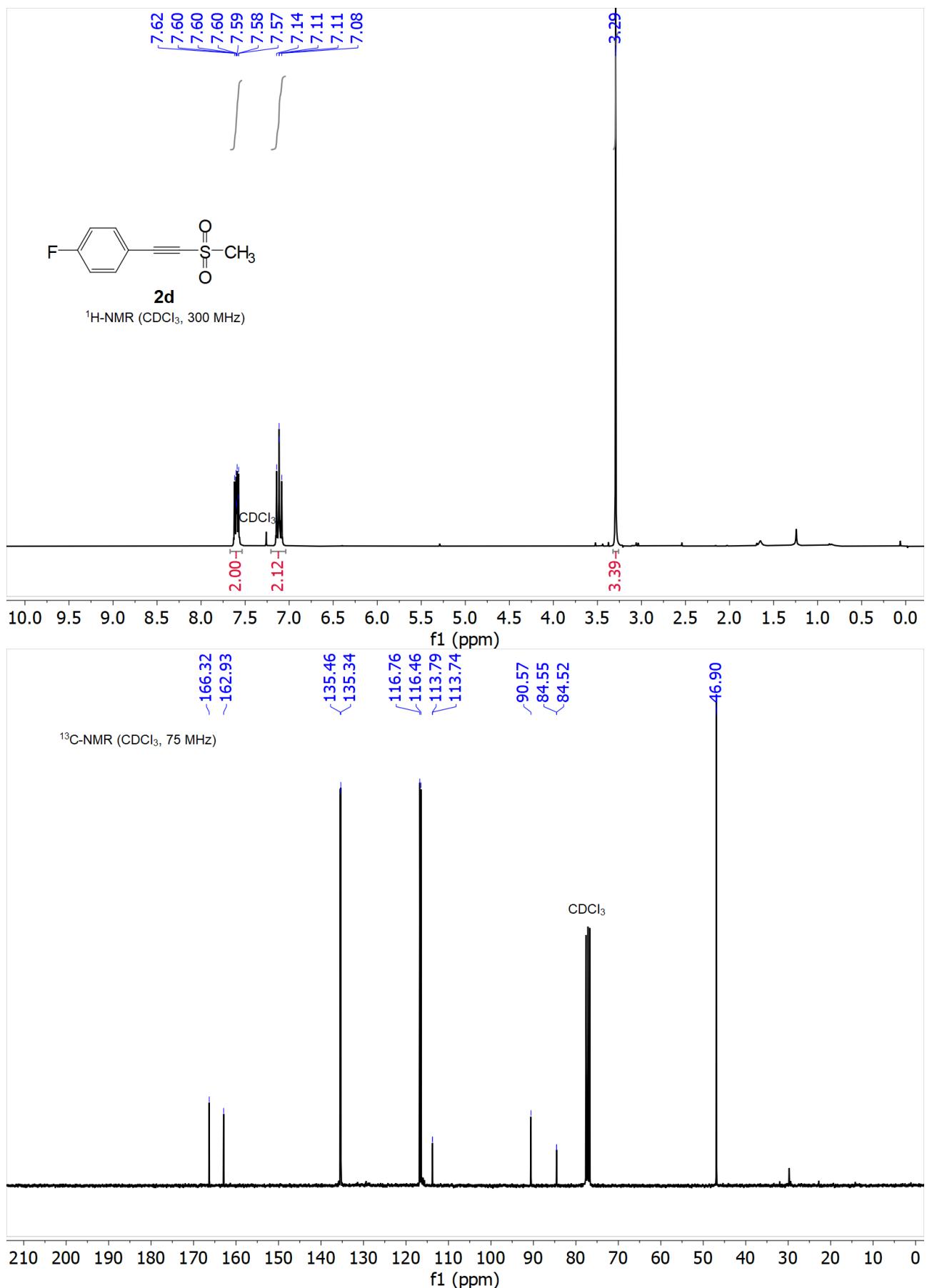
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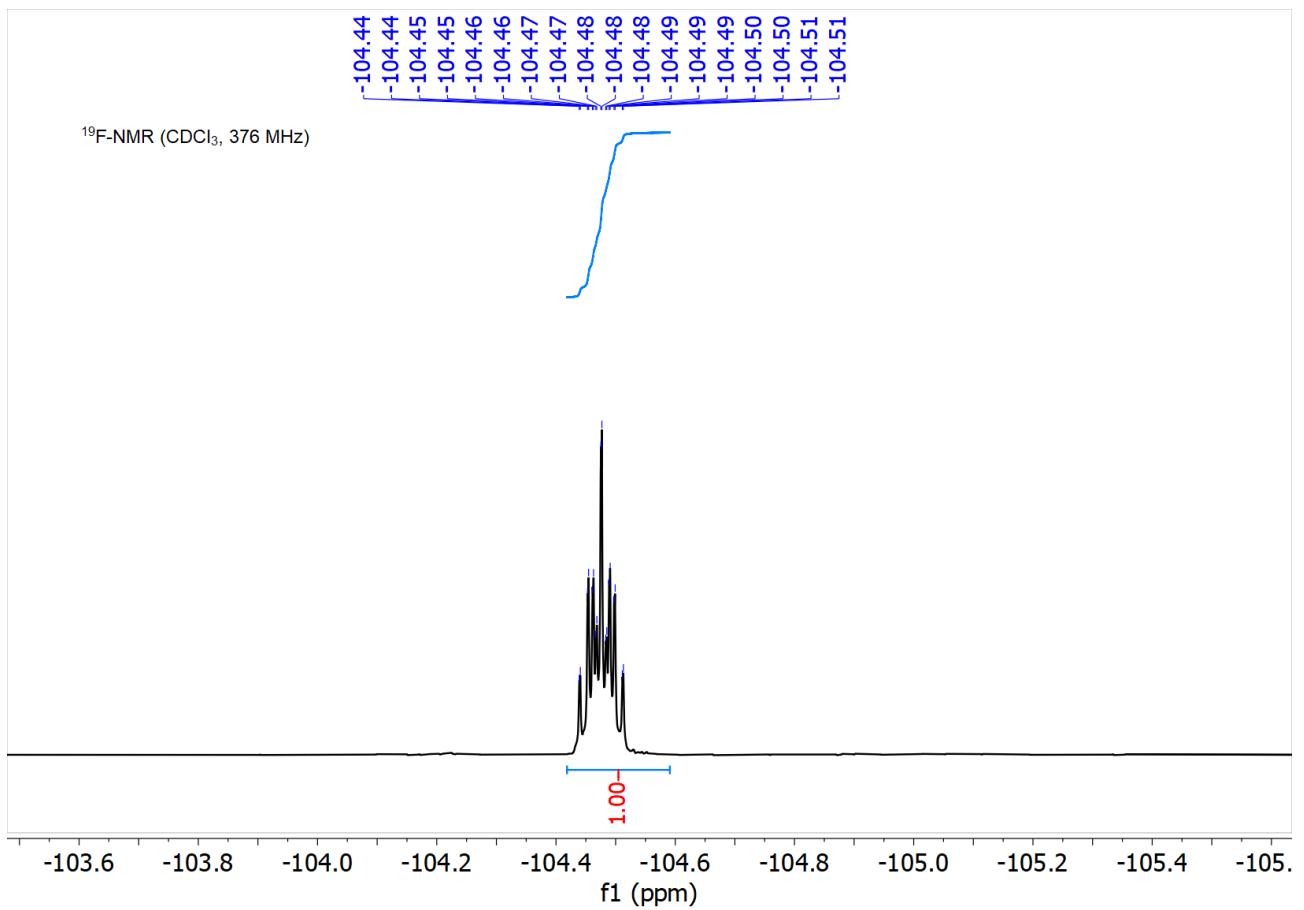


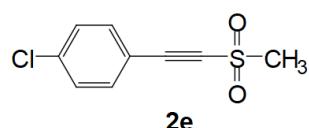
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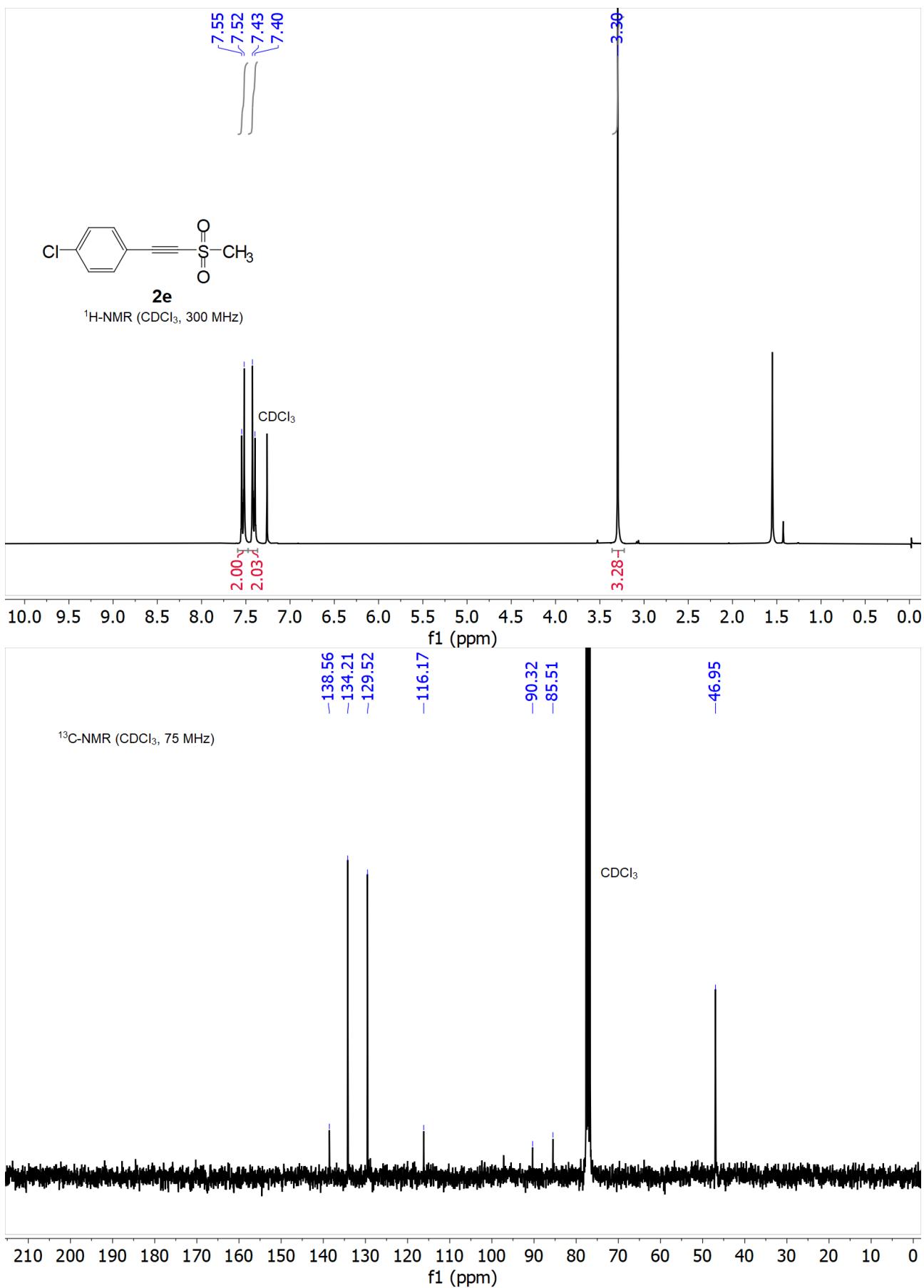


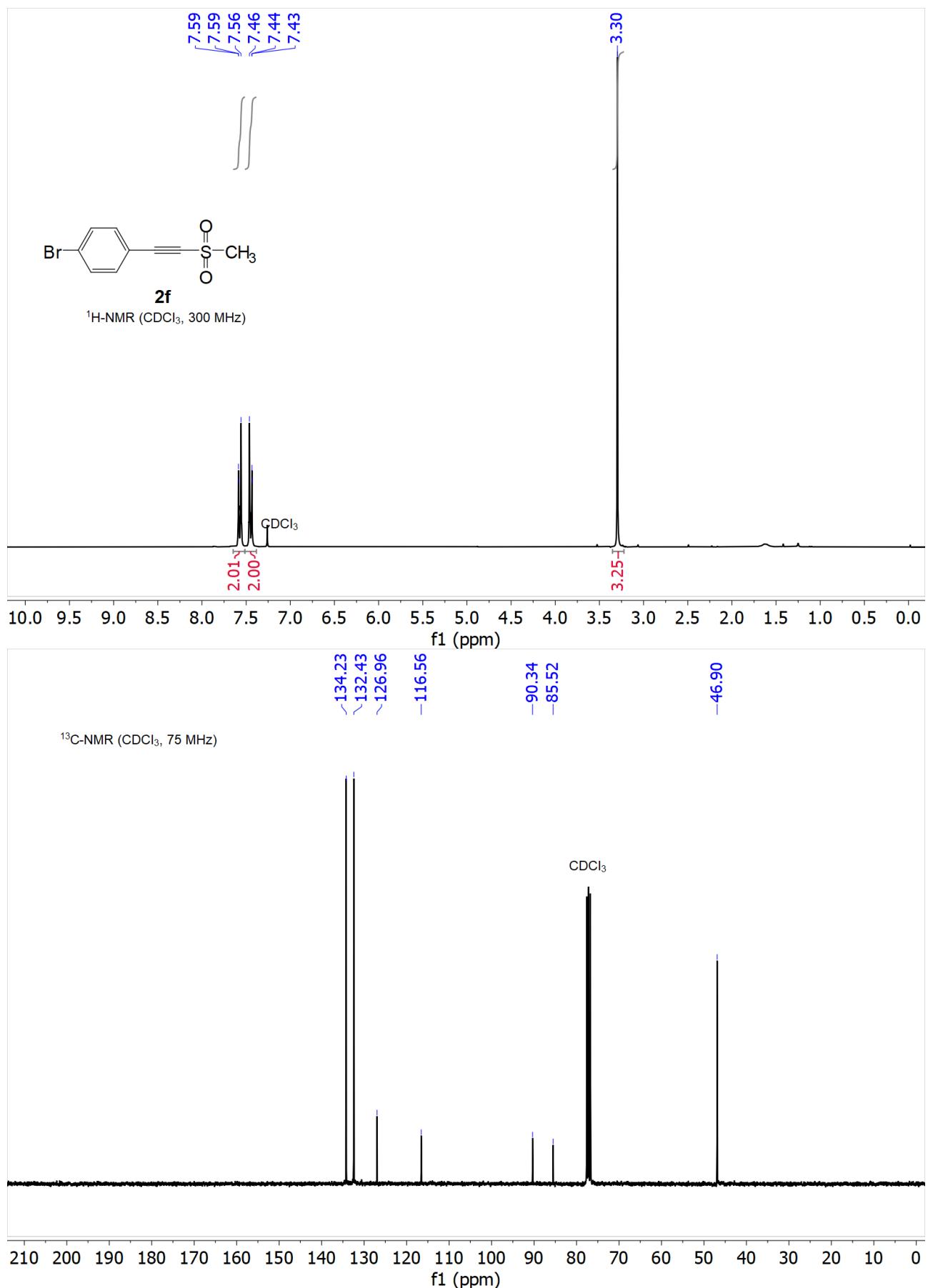


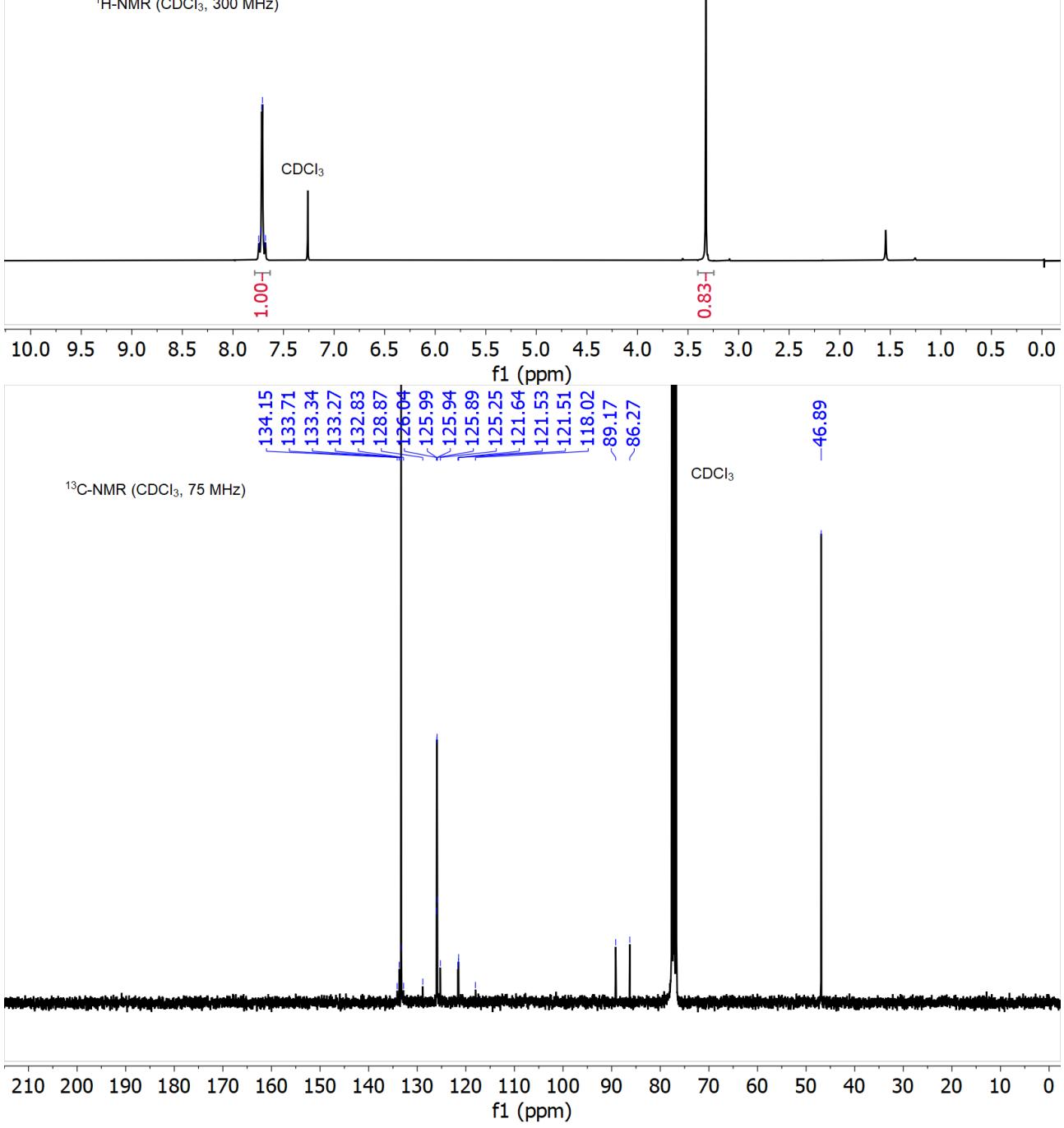
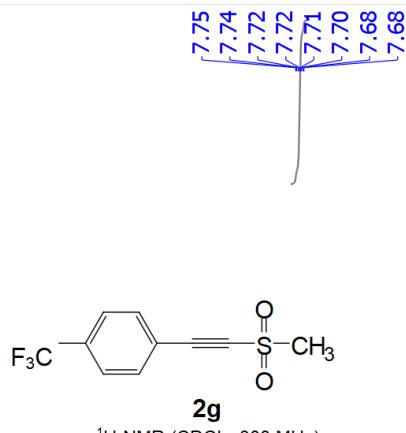




¹H-NMR (CDCl₃, 300 MHz)





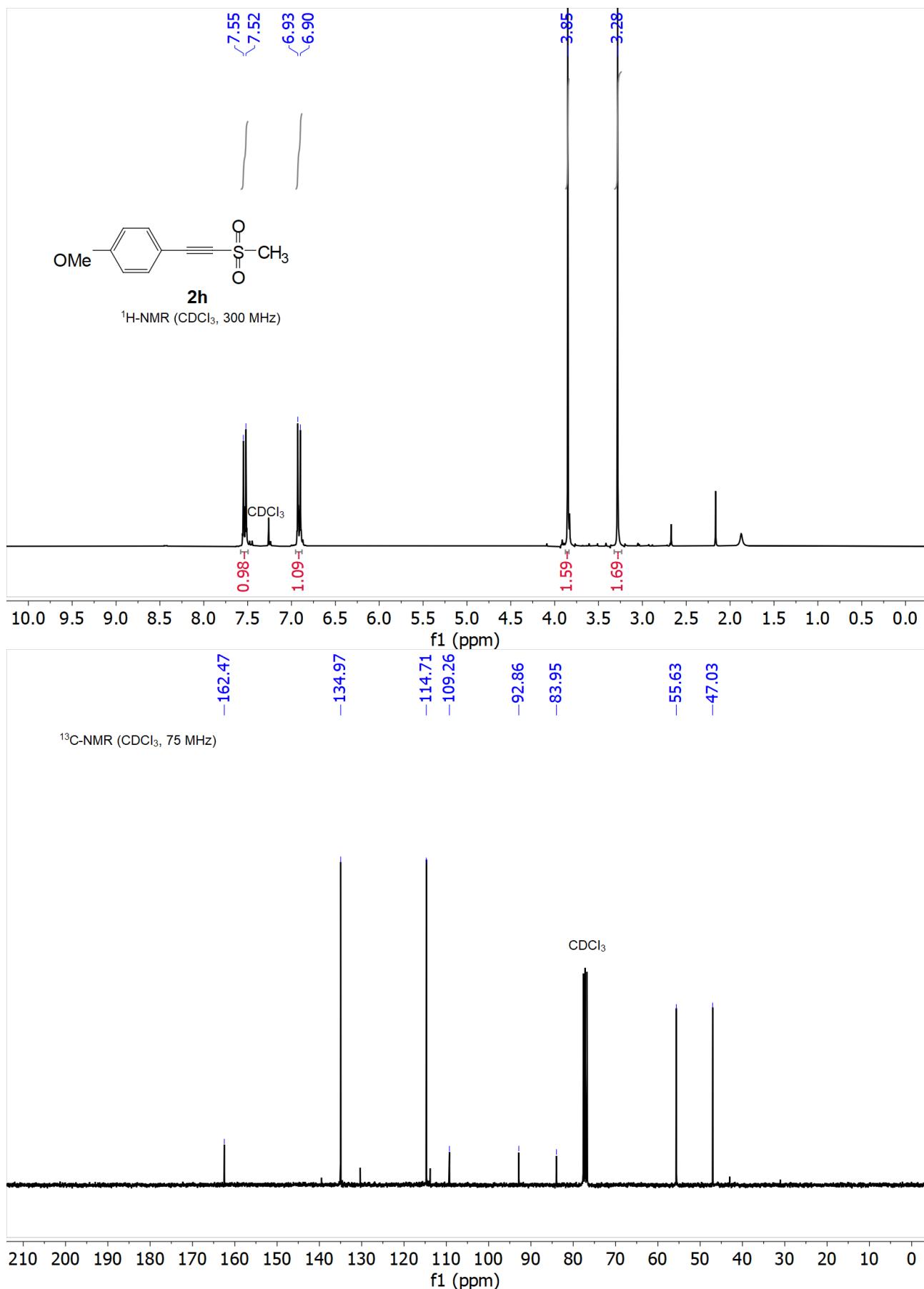


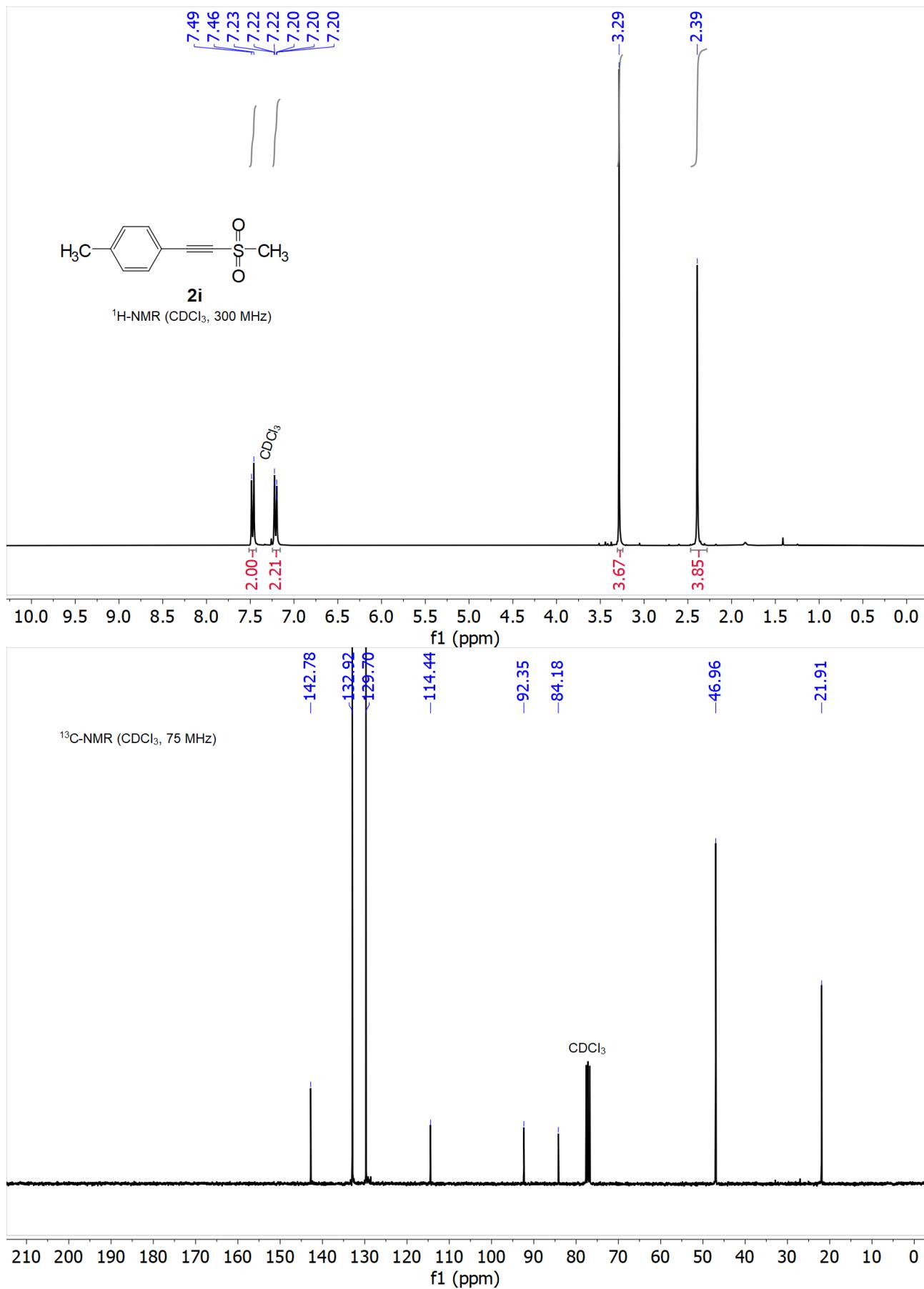
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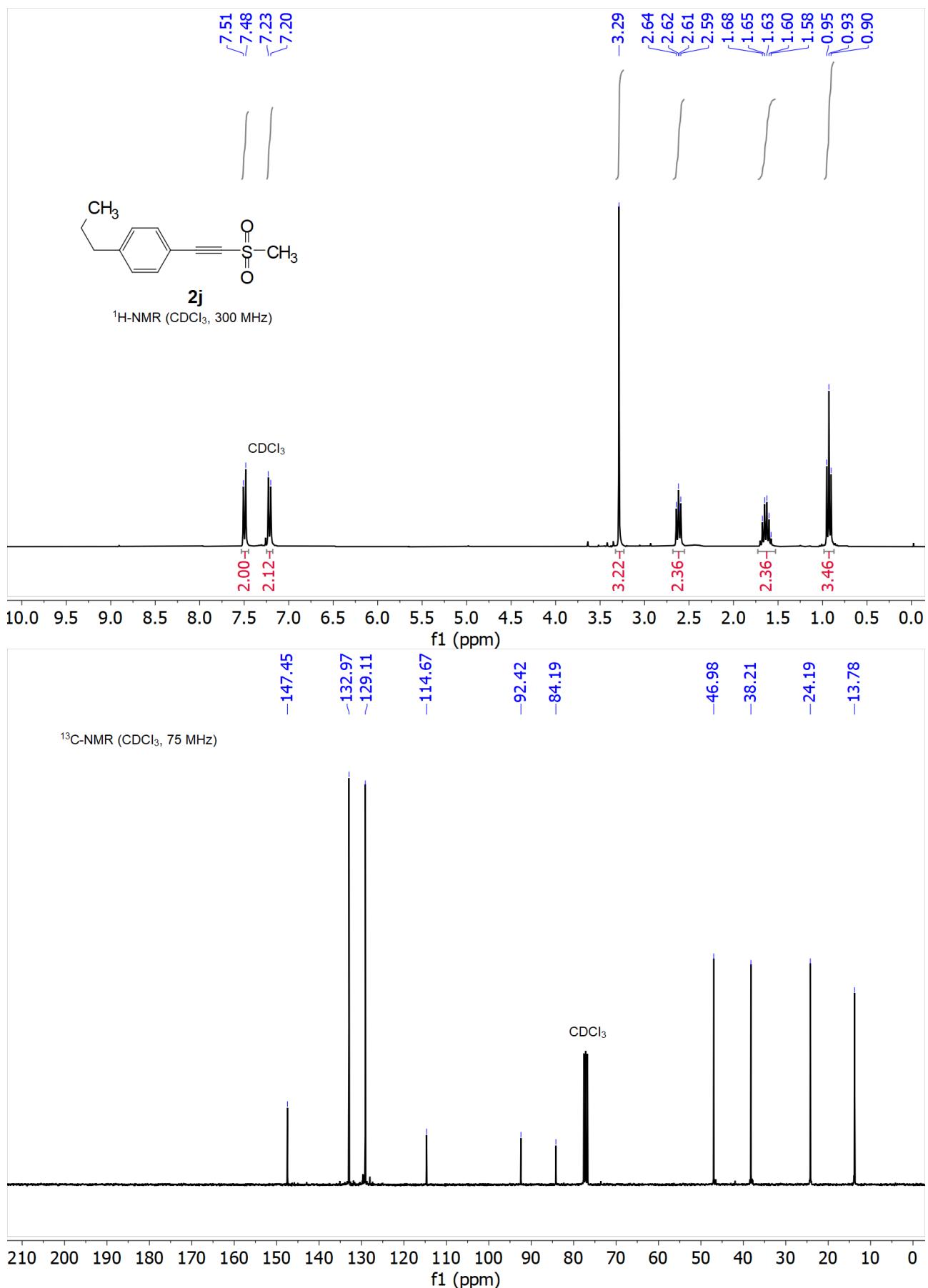
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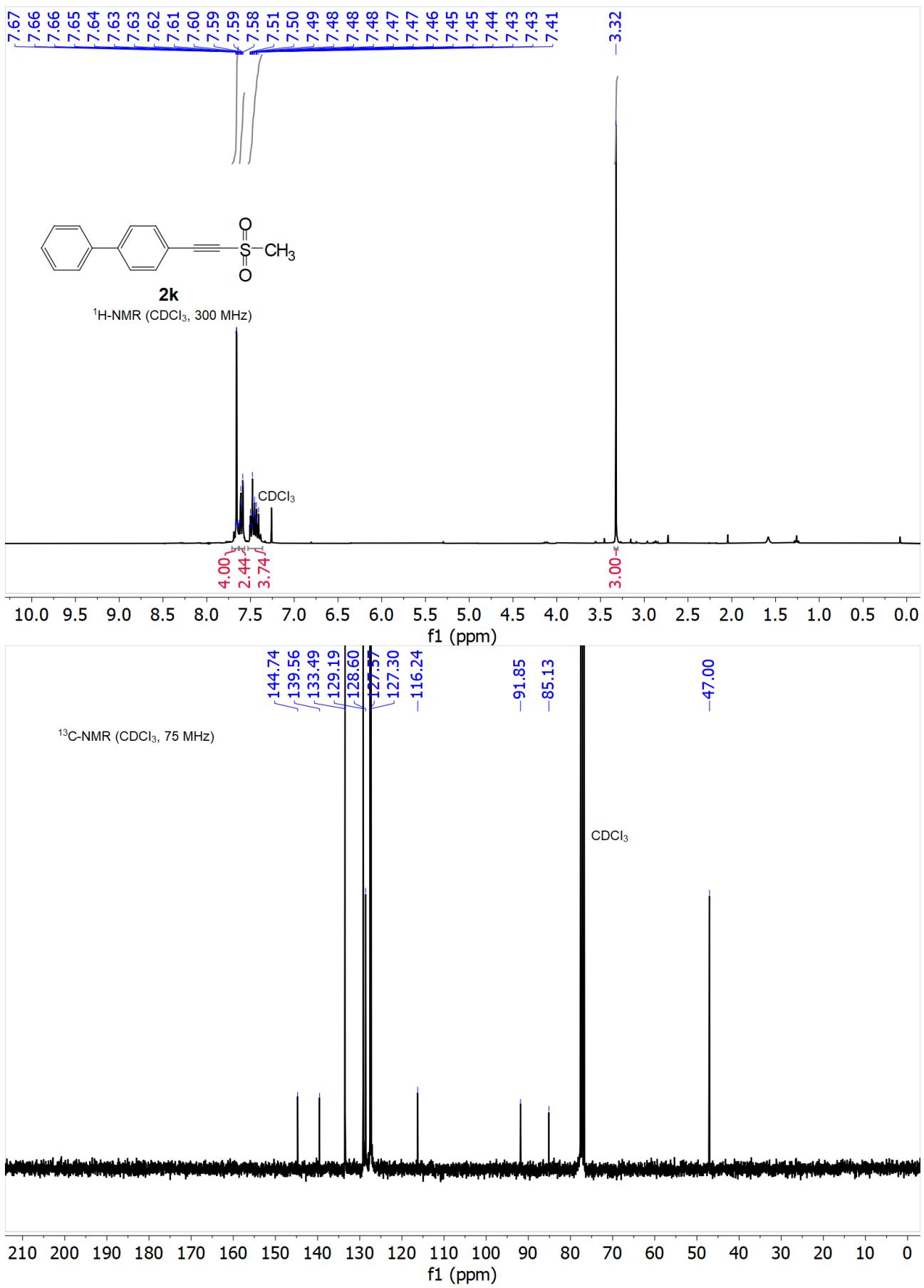
-60.5 -61.0 -61.5 -62.0 -62.5 -63.0 -63.5 -64.0 -64.5 -65.0 -65.5 -66.0 -66.5 -67.0 -67.5

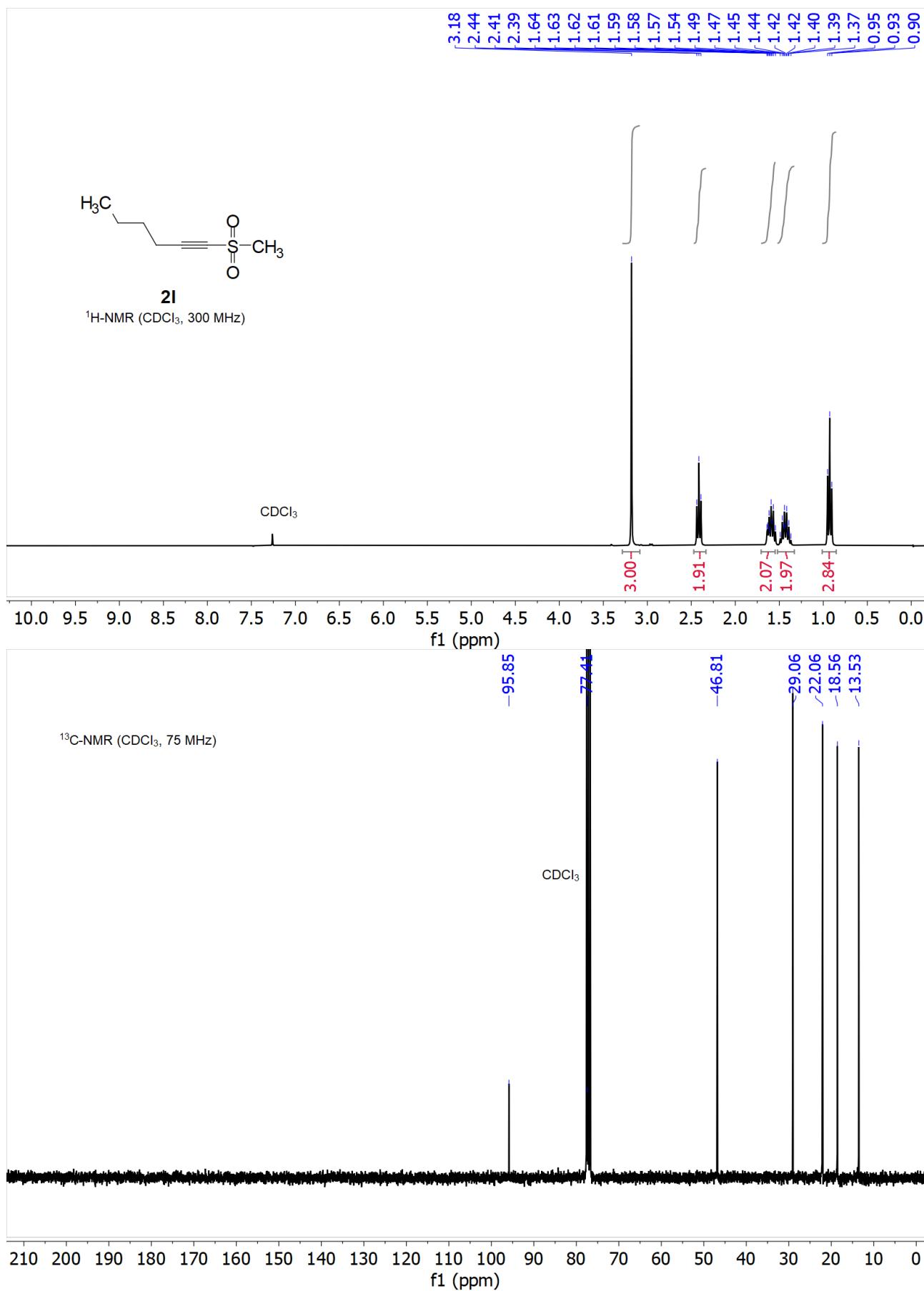
f1 (ppm)



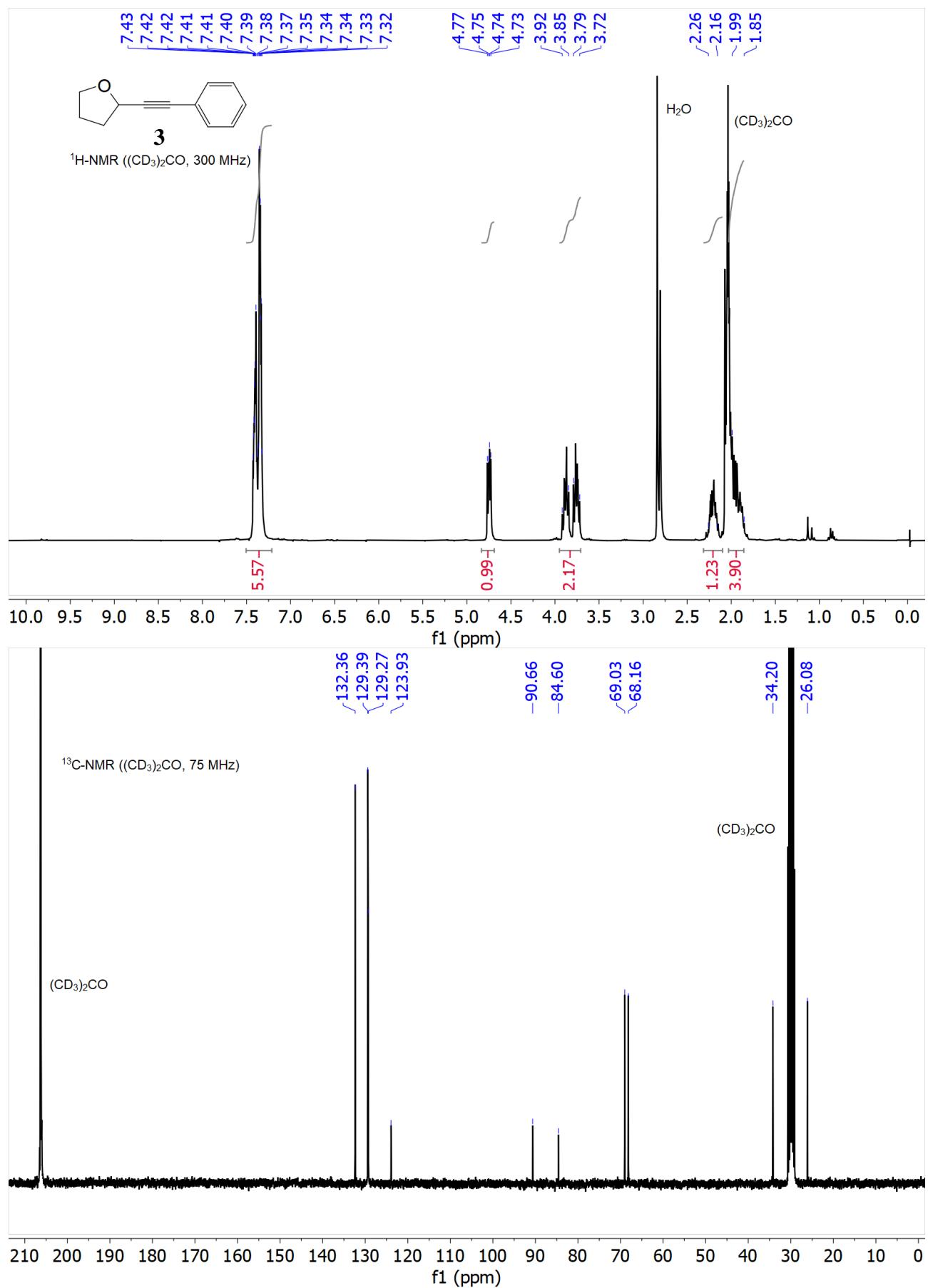


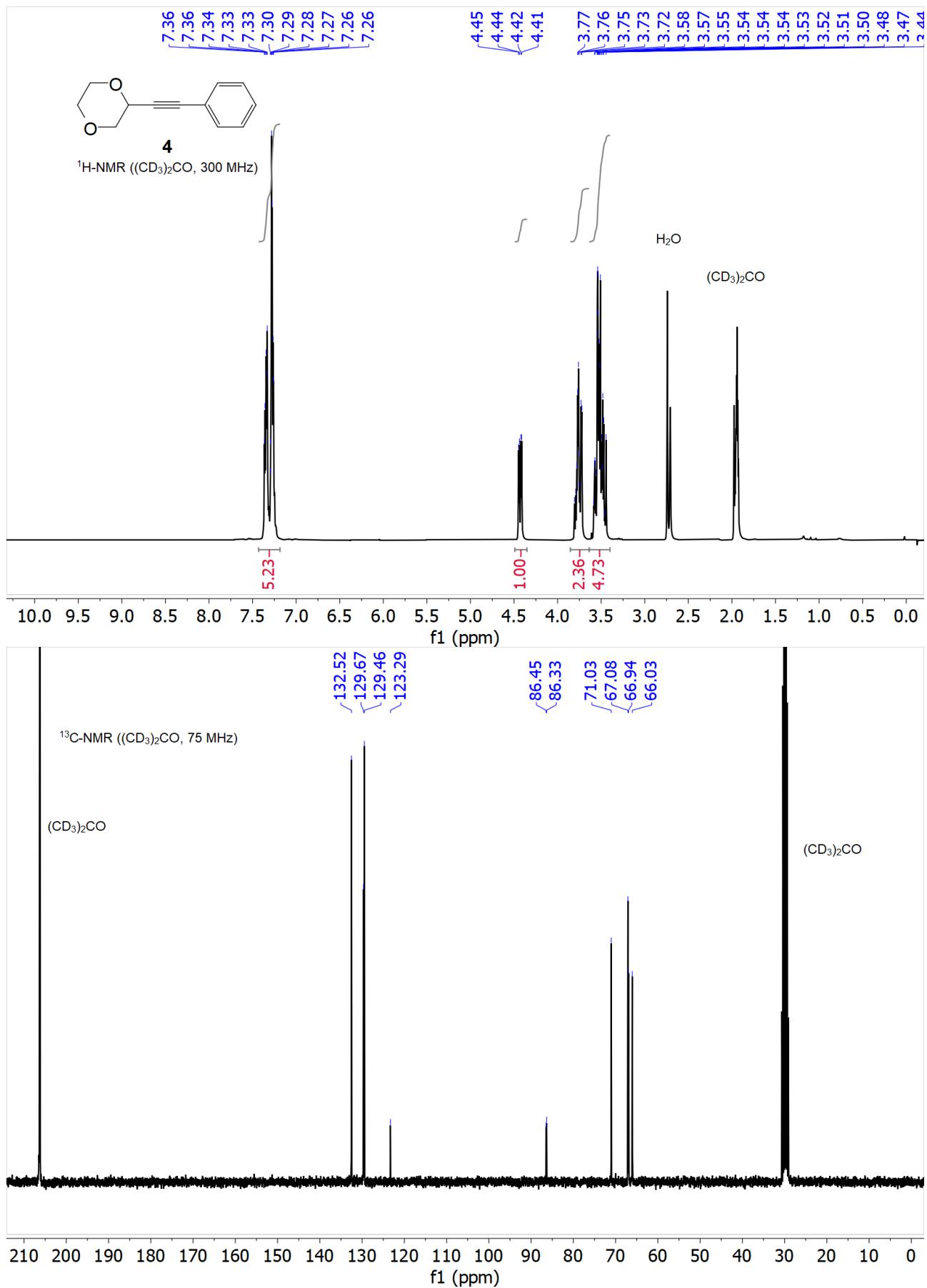


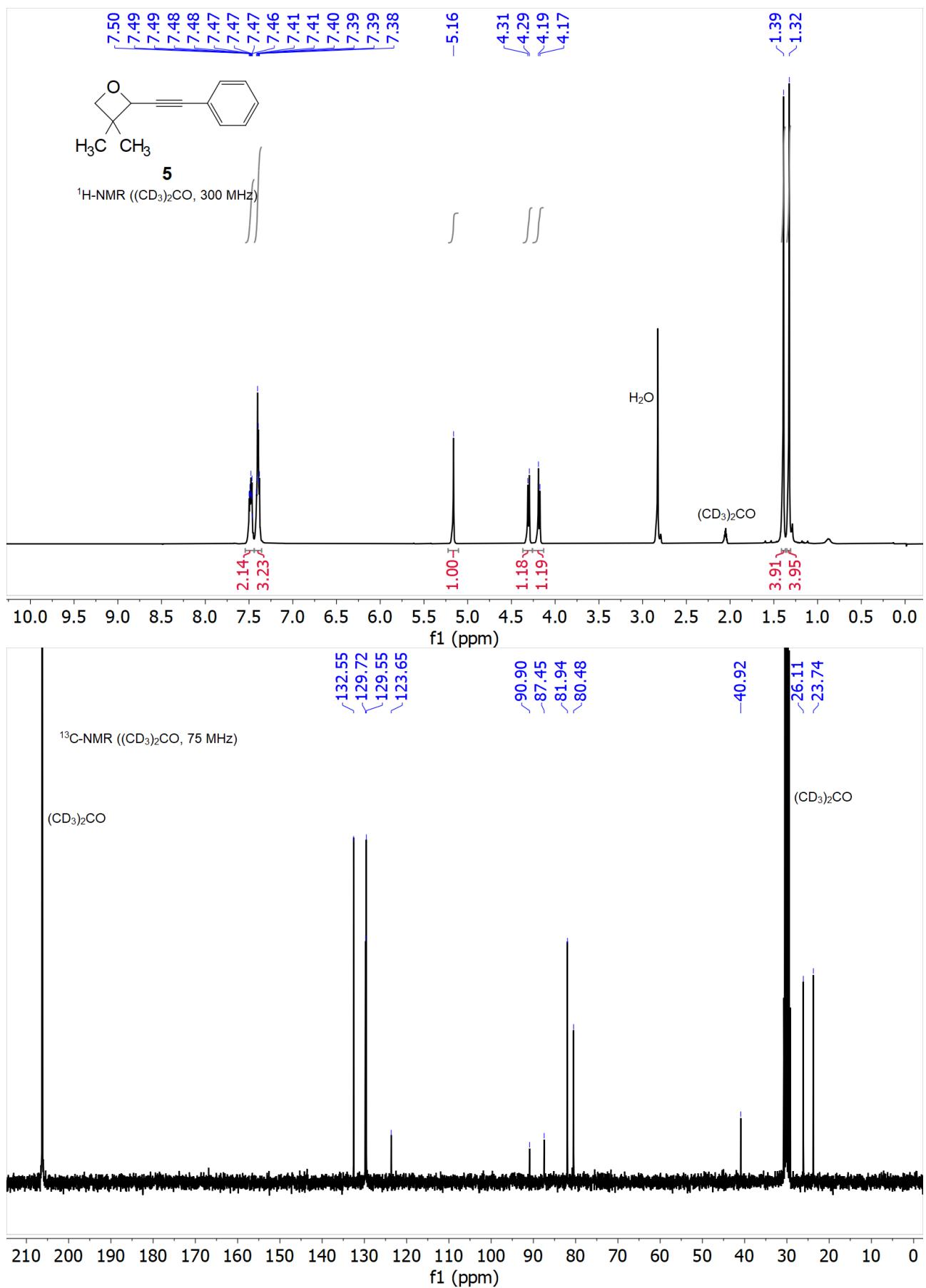


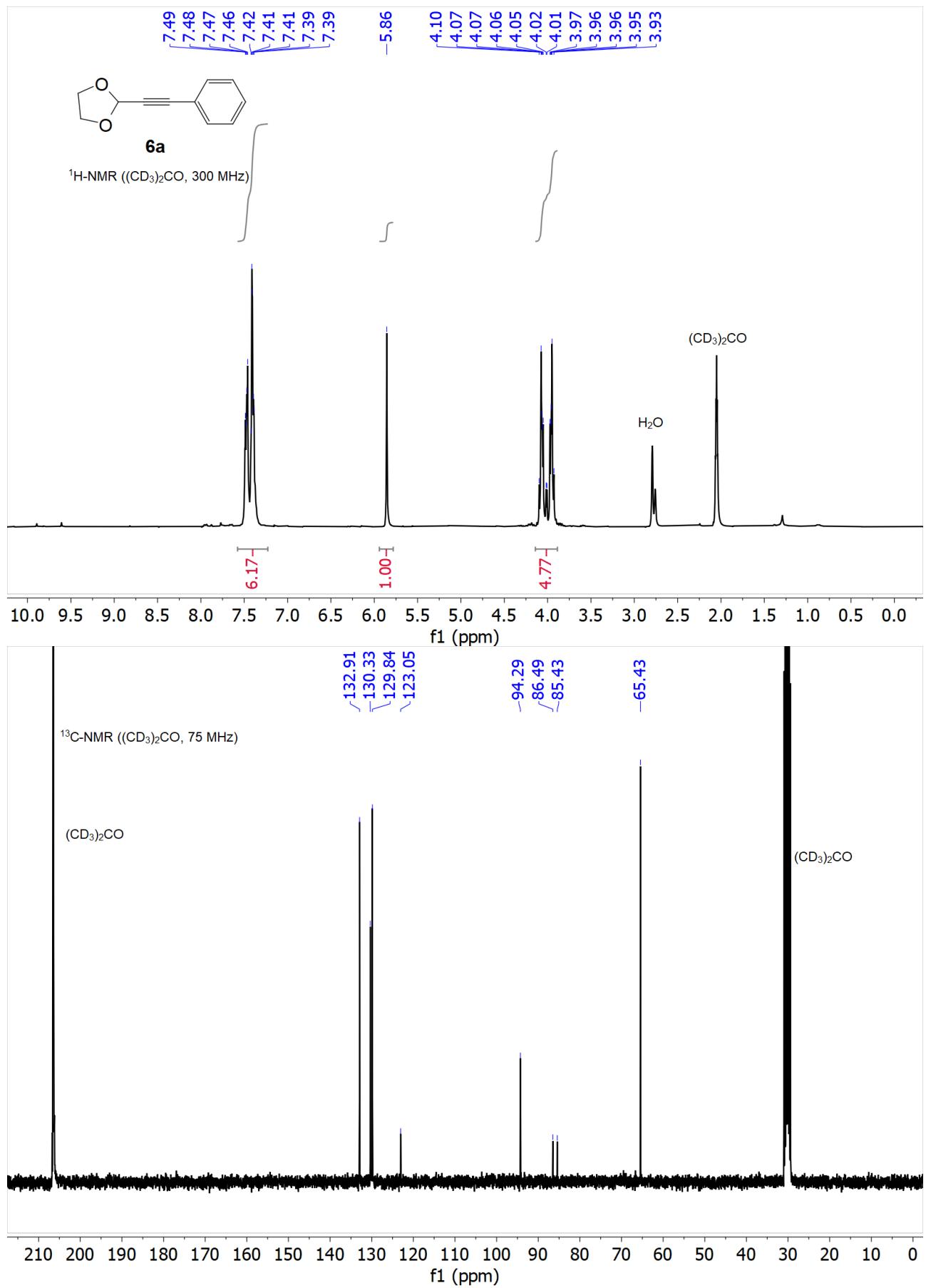


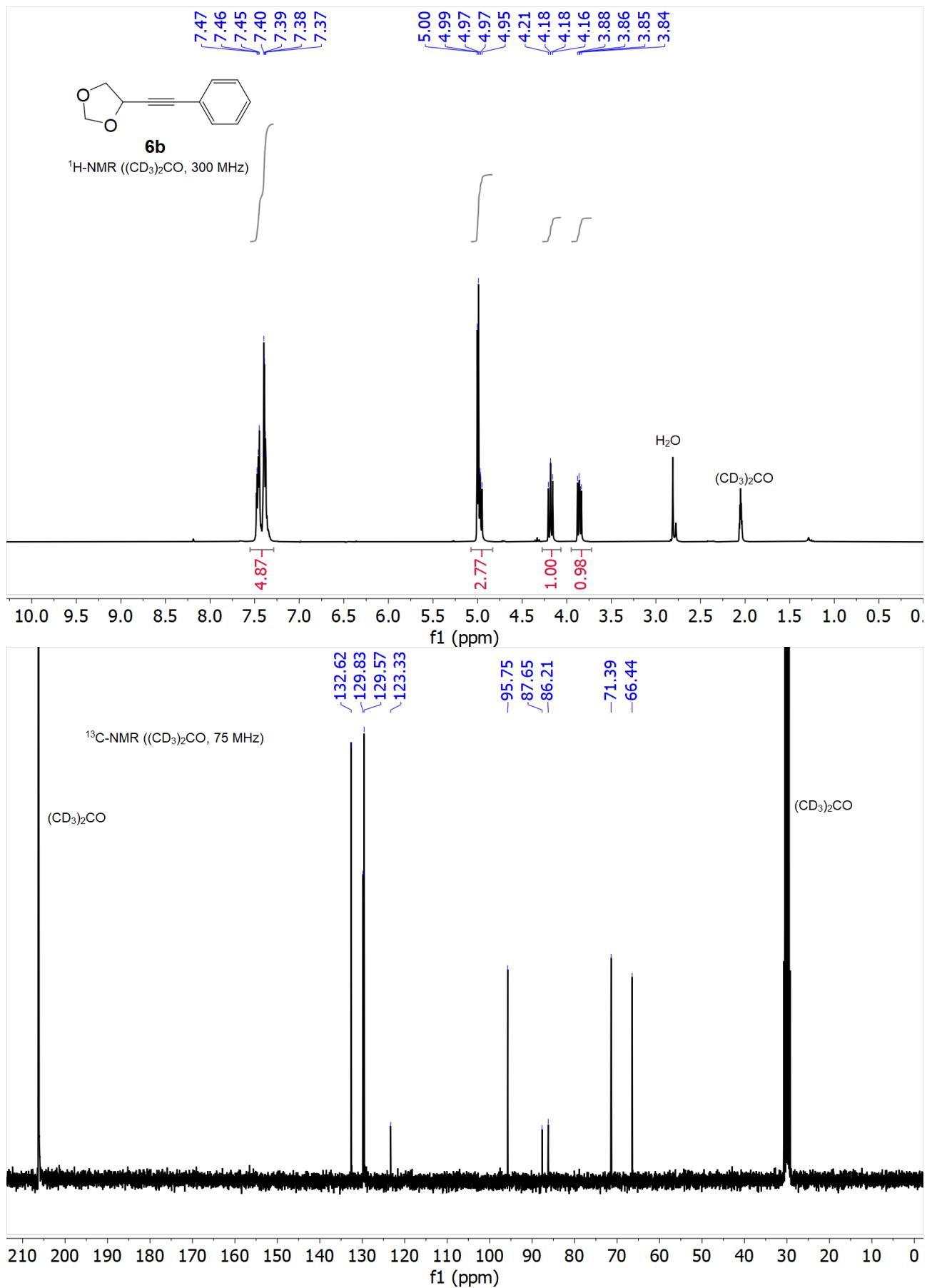
7. ^1H -, ^{13}C and ^{19}F -NMR of compounds 3-31

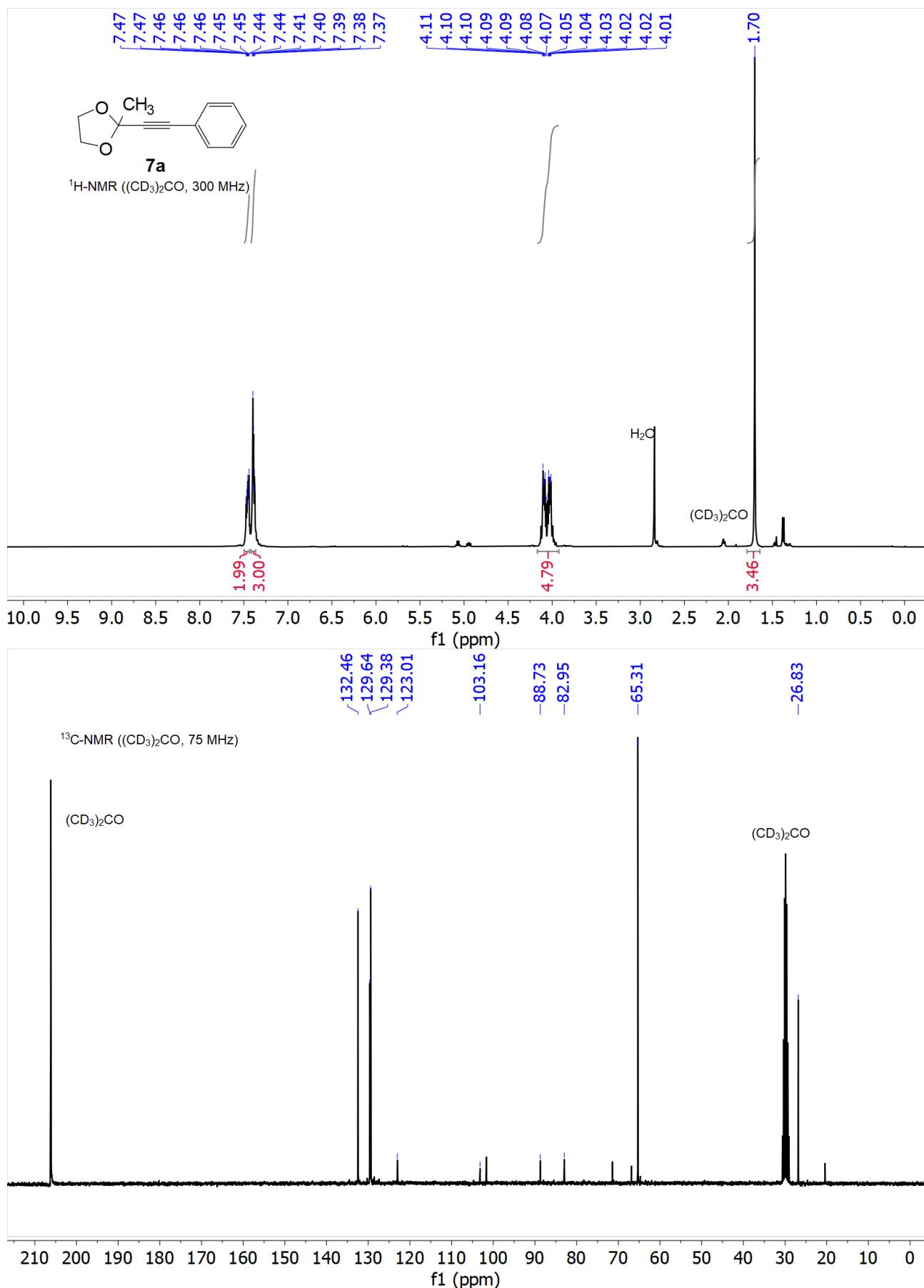


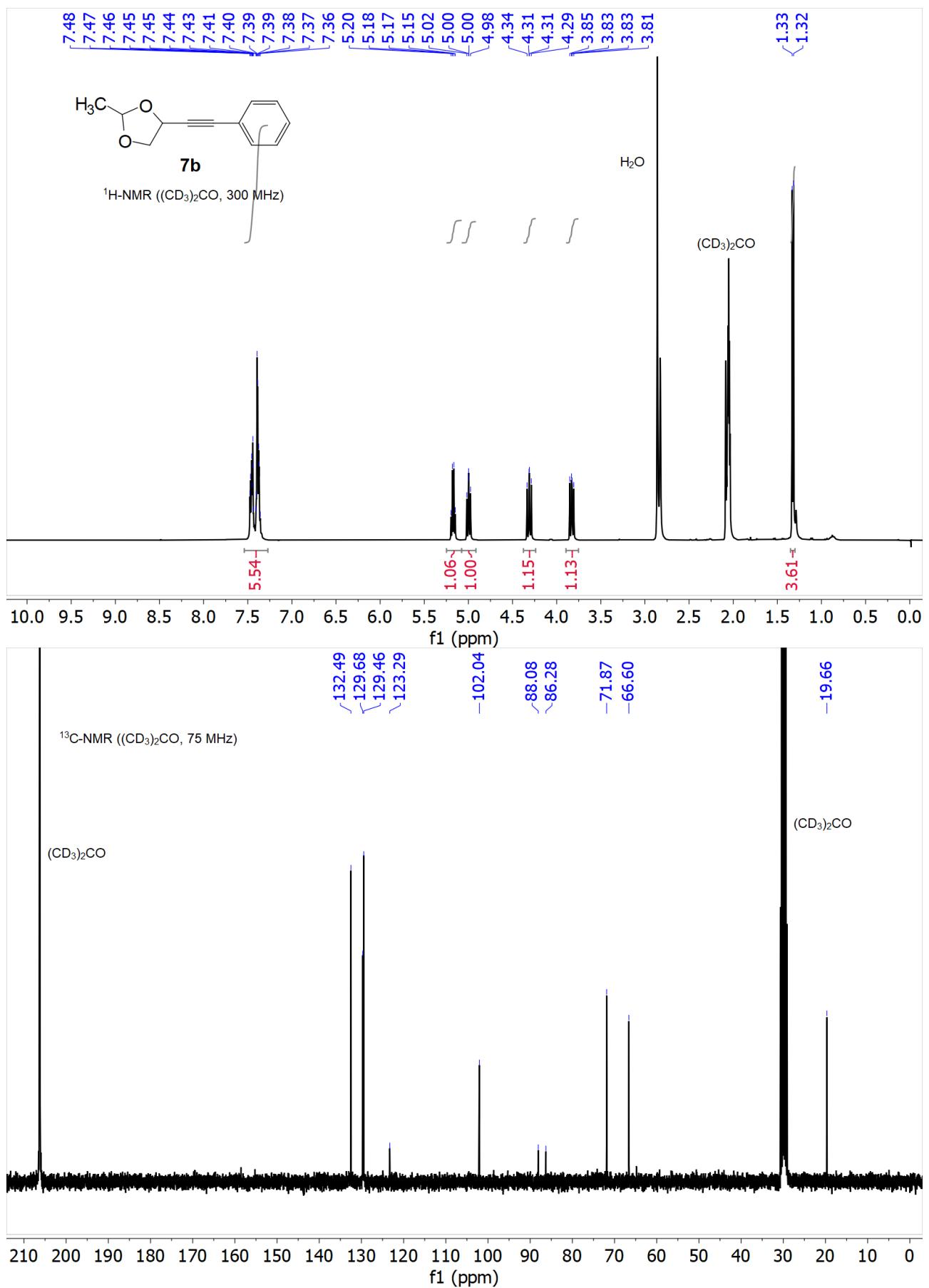


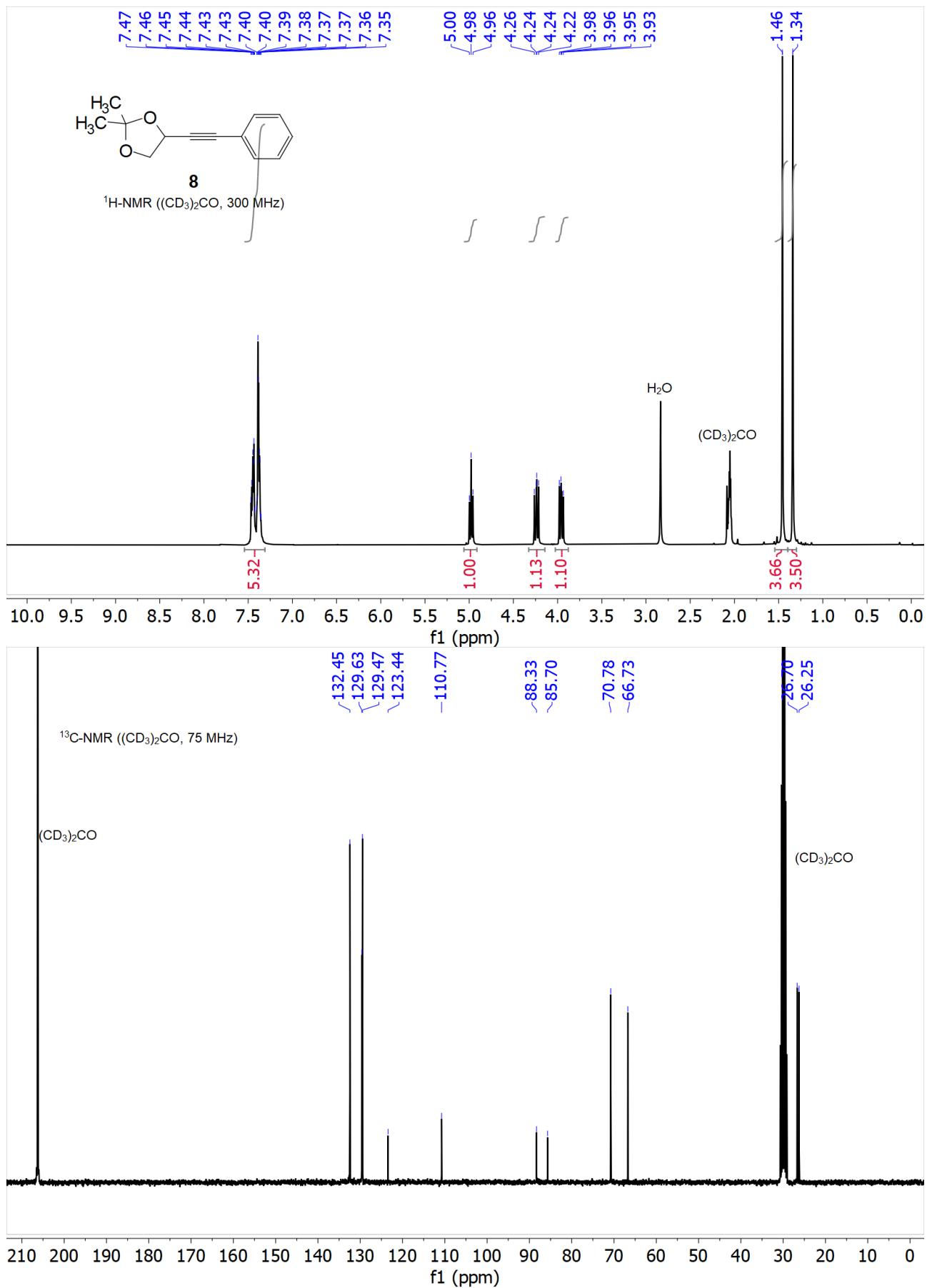


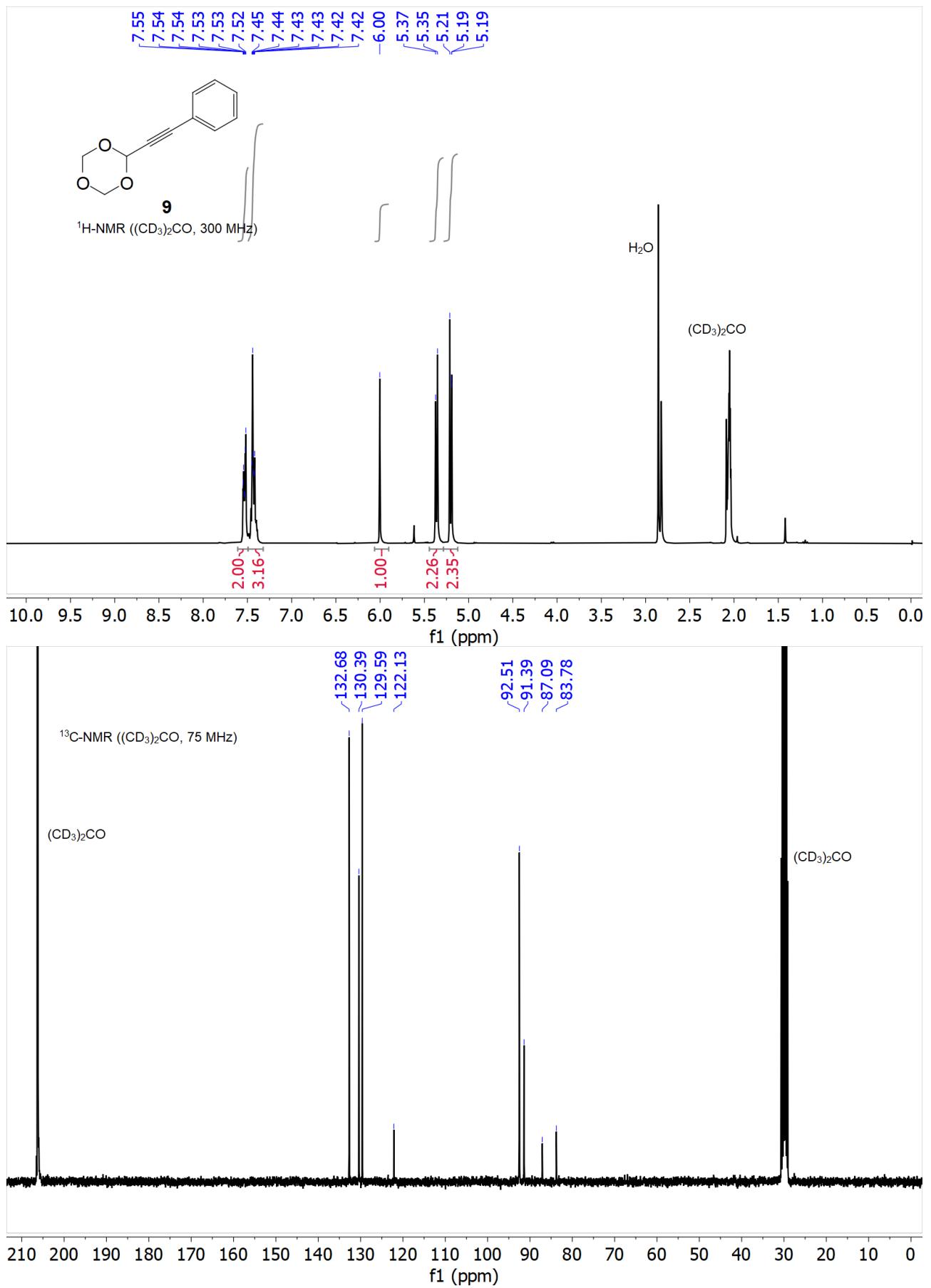


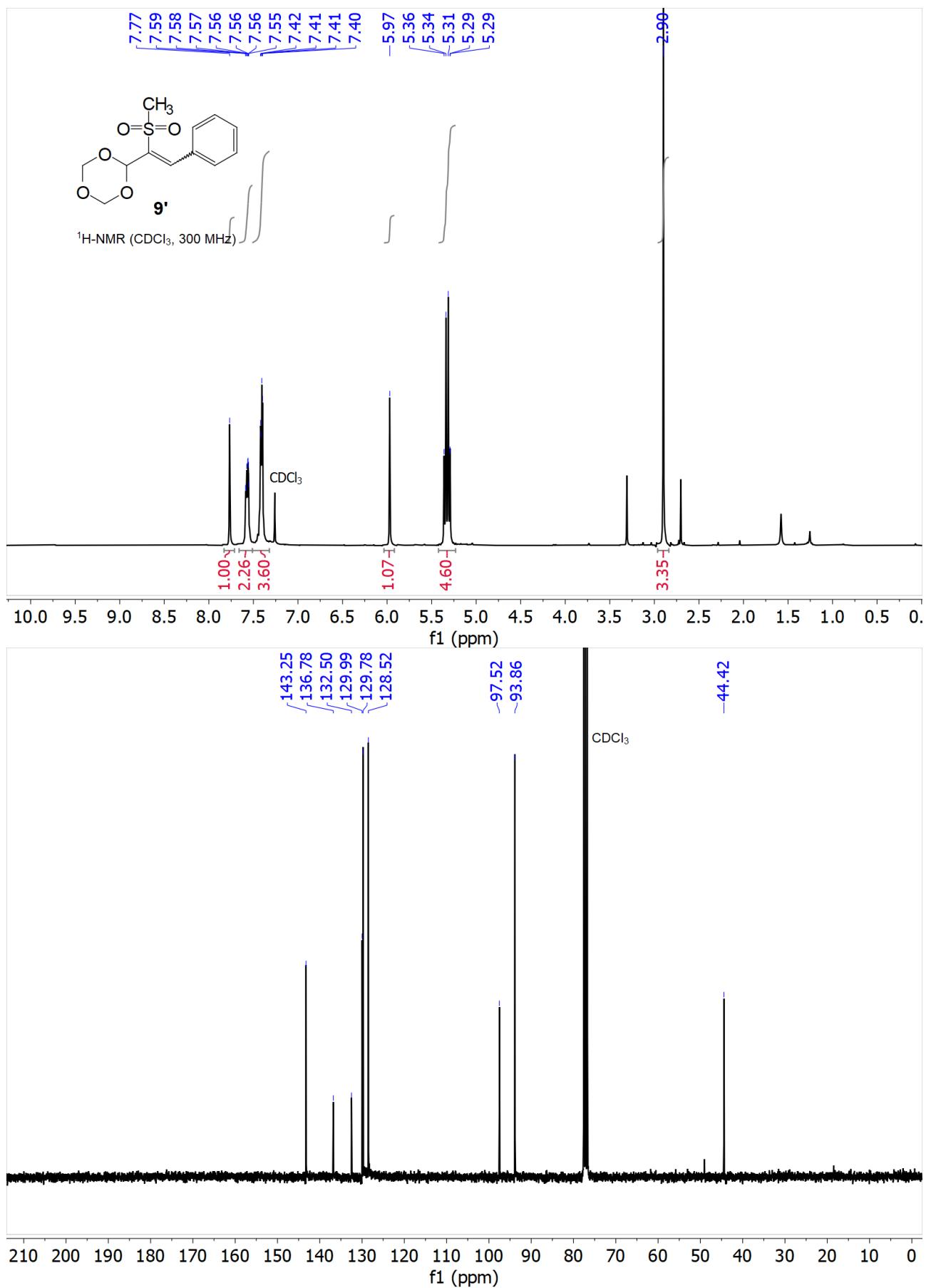


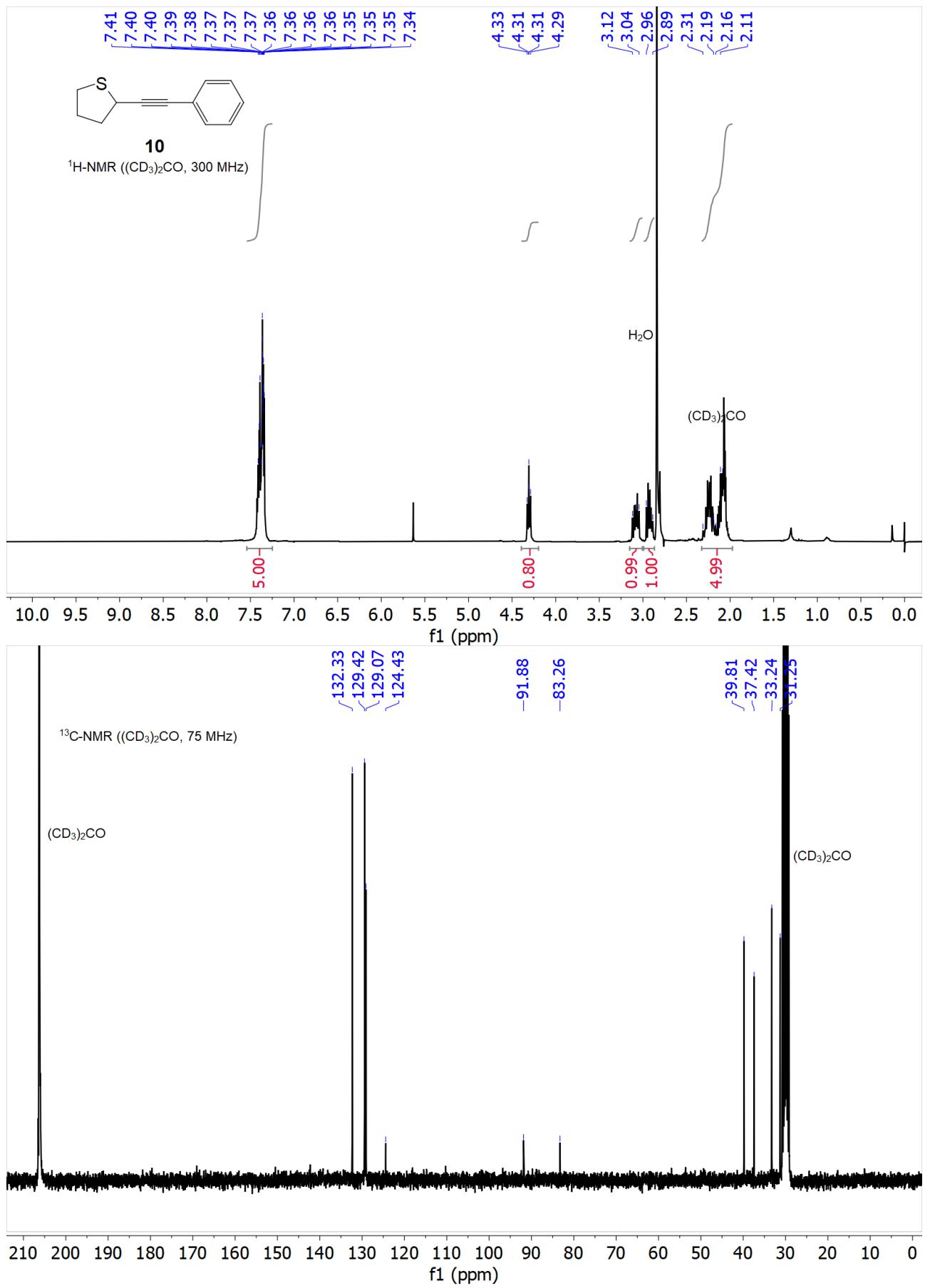


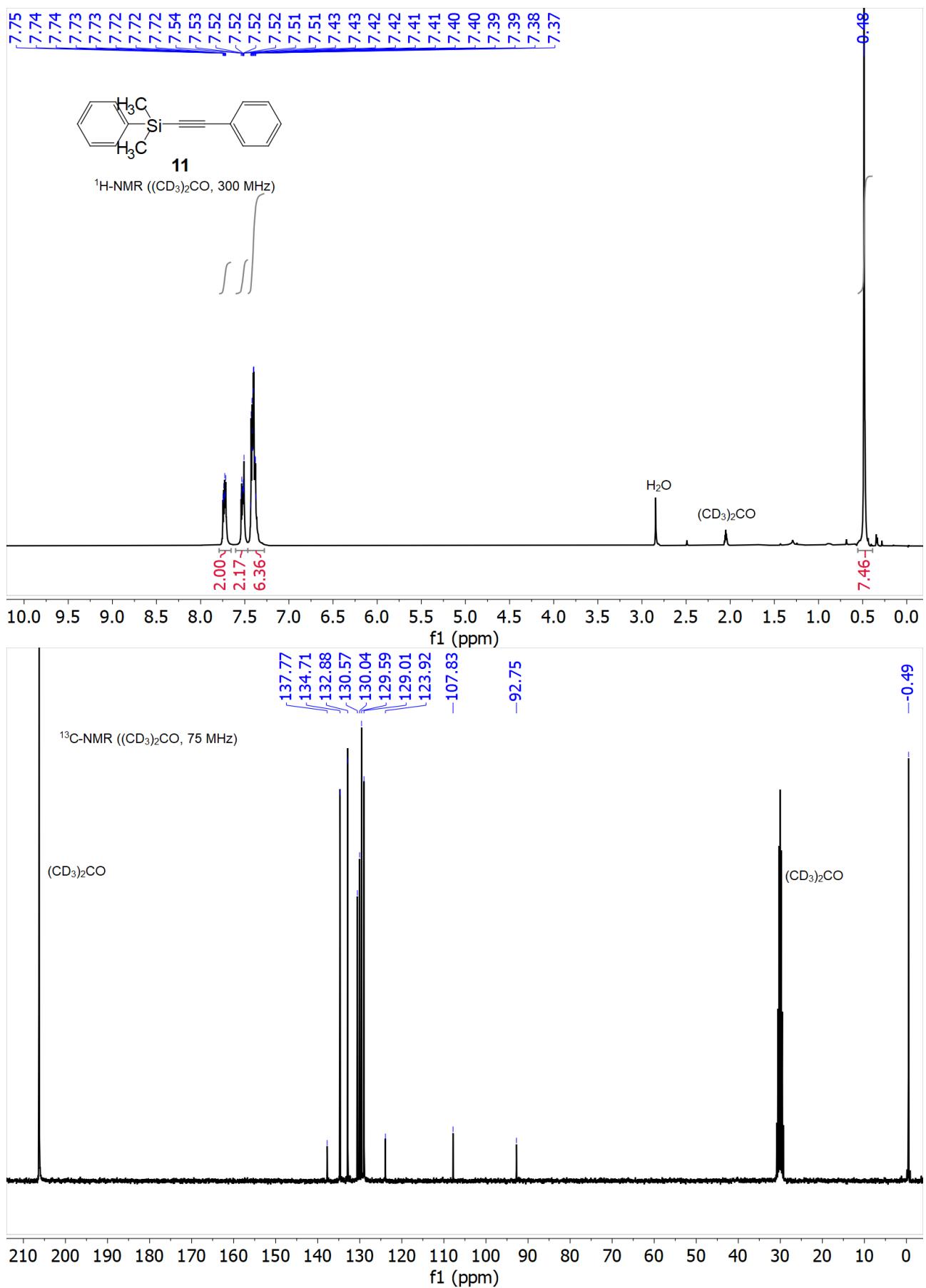


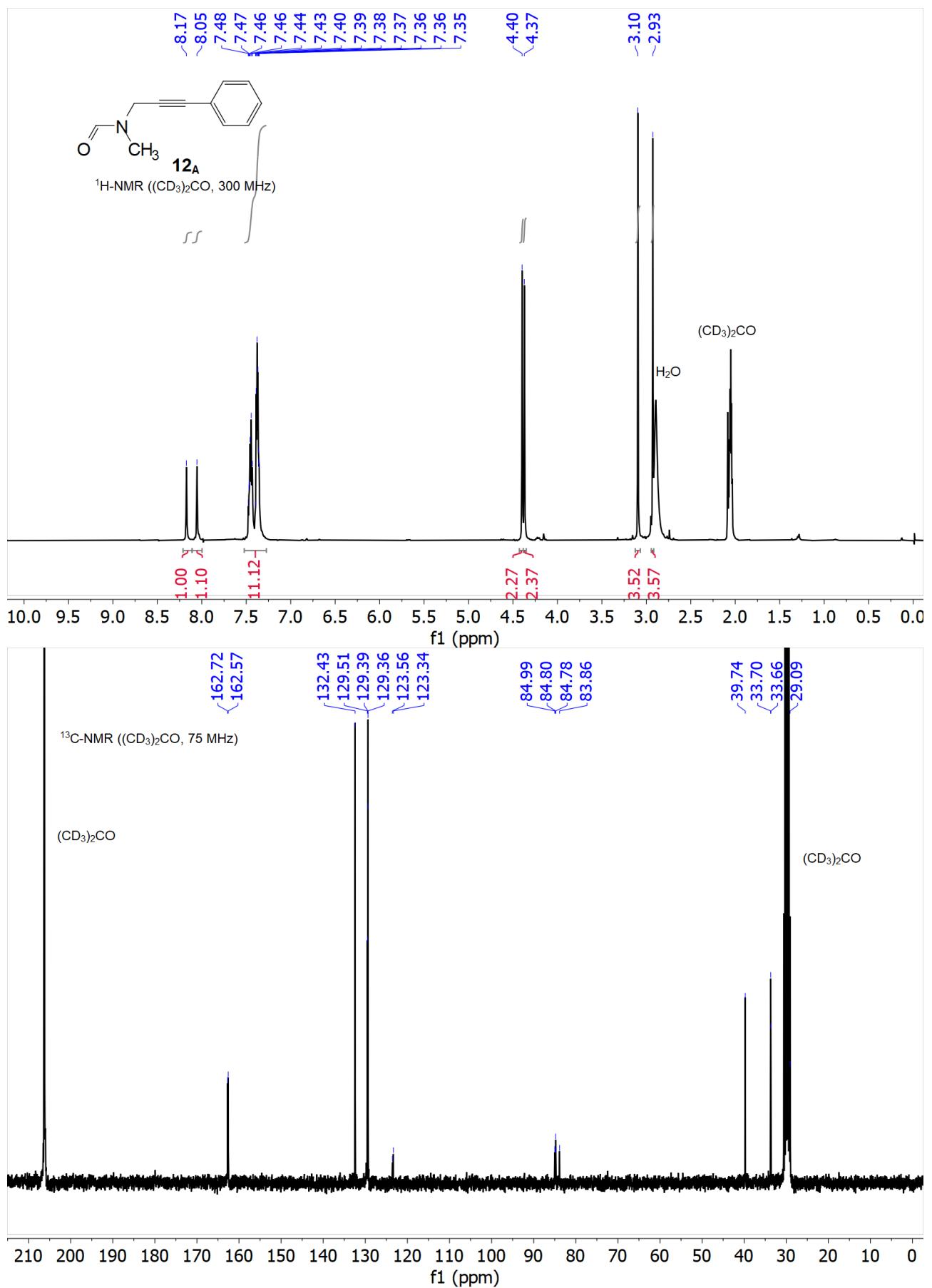


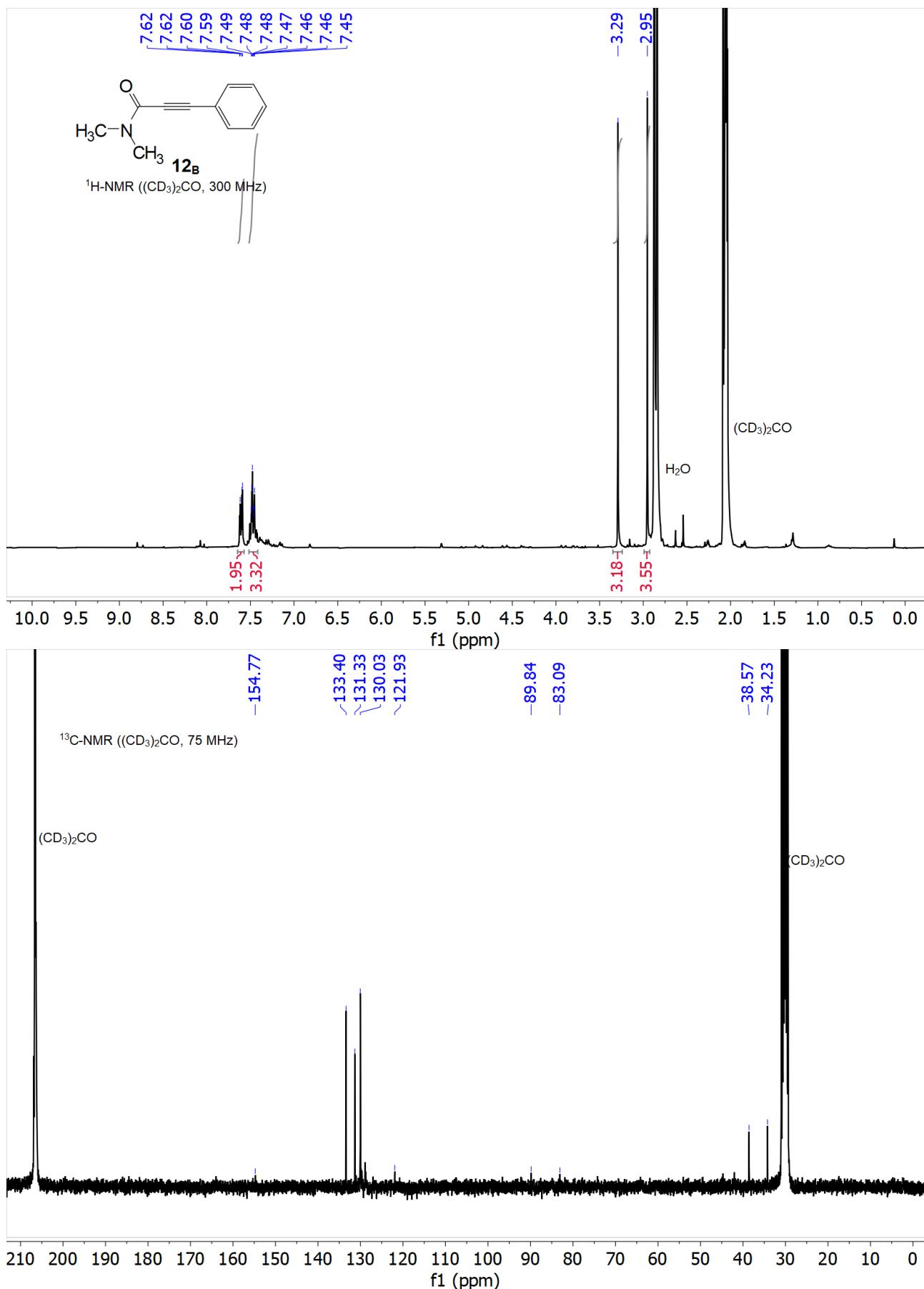


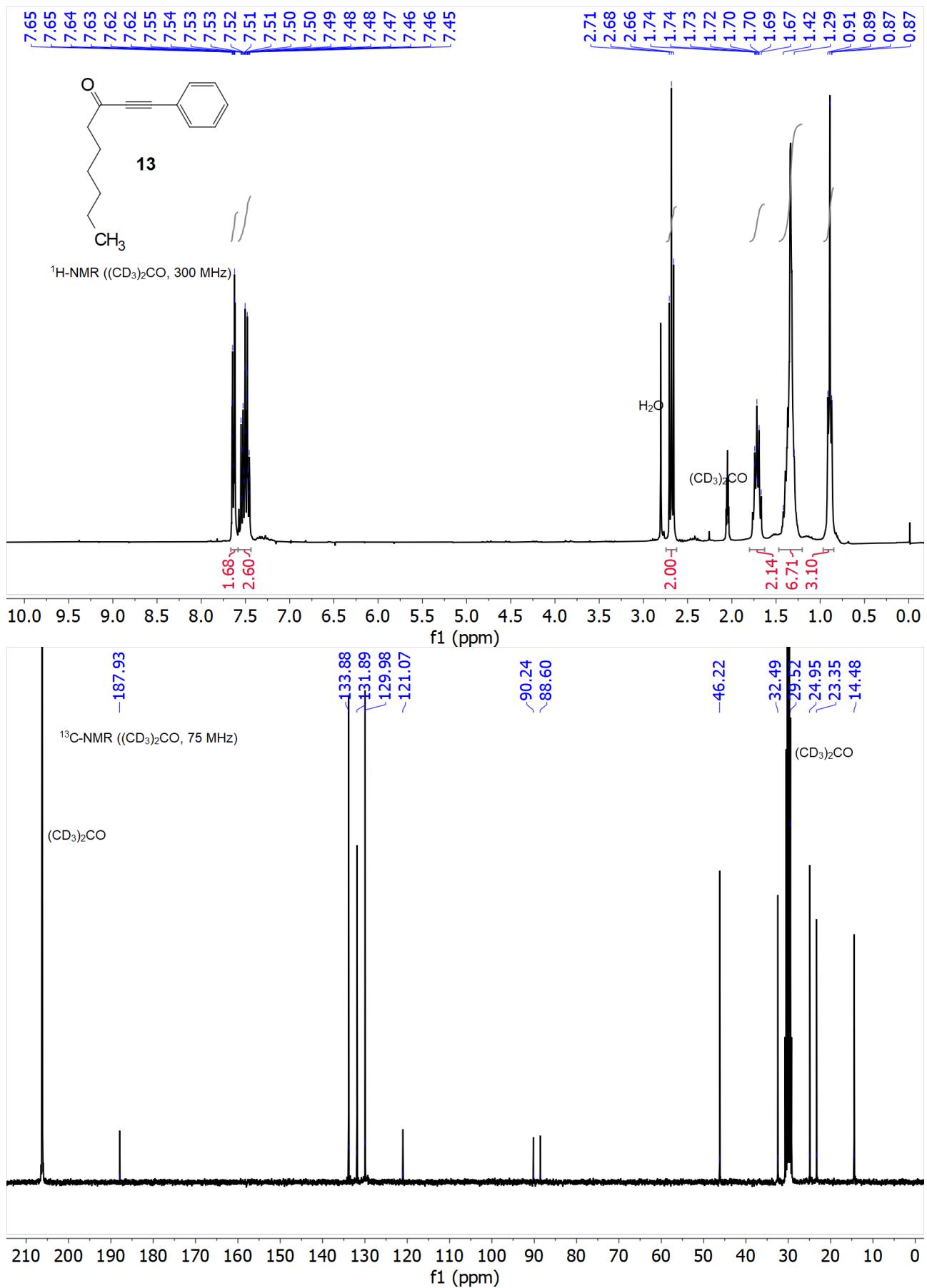


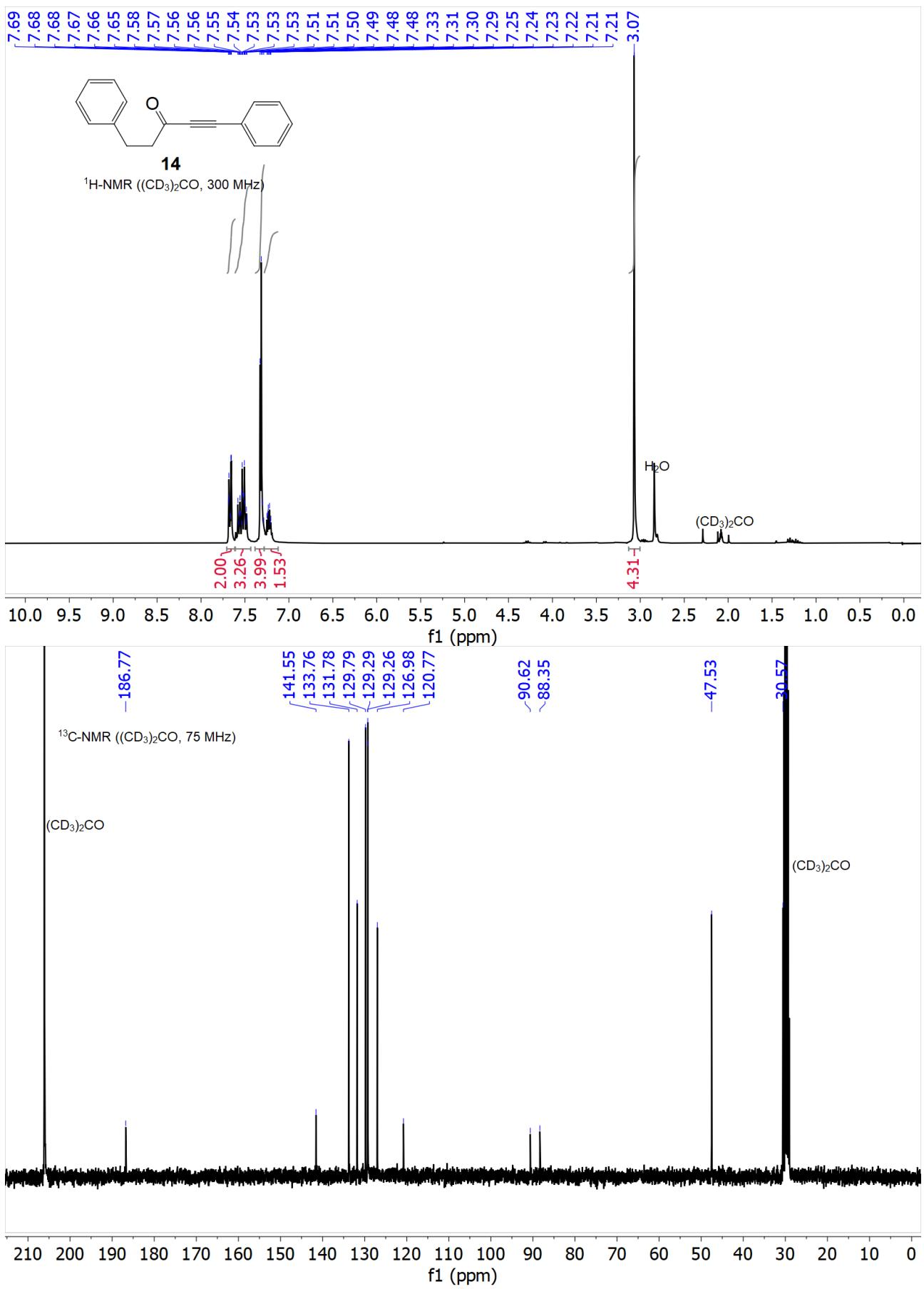


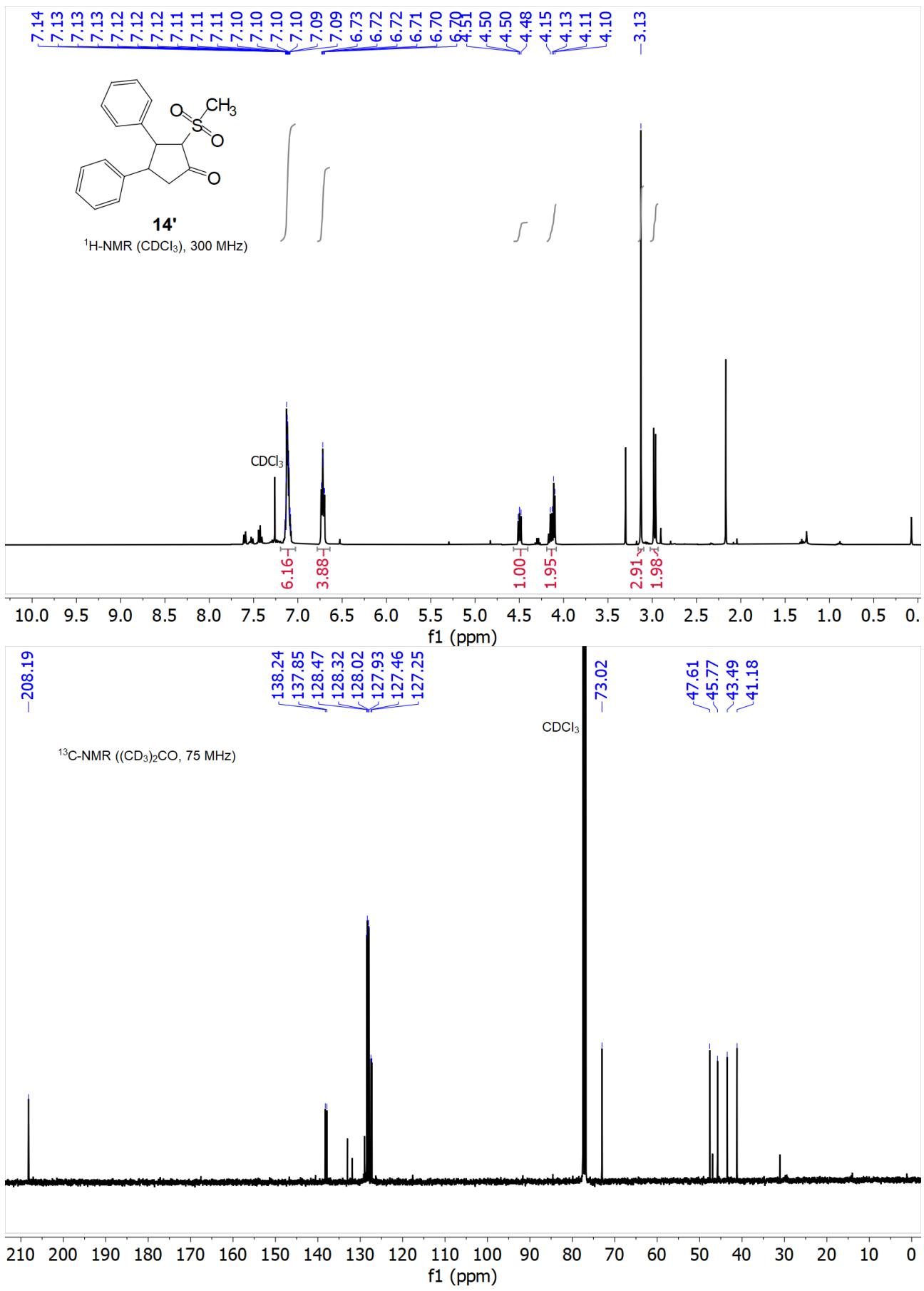


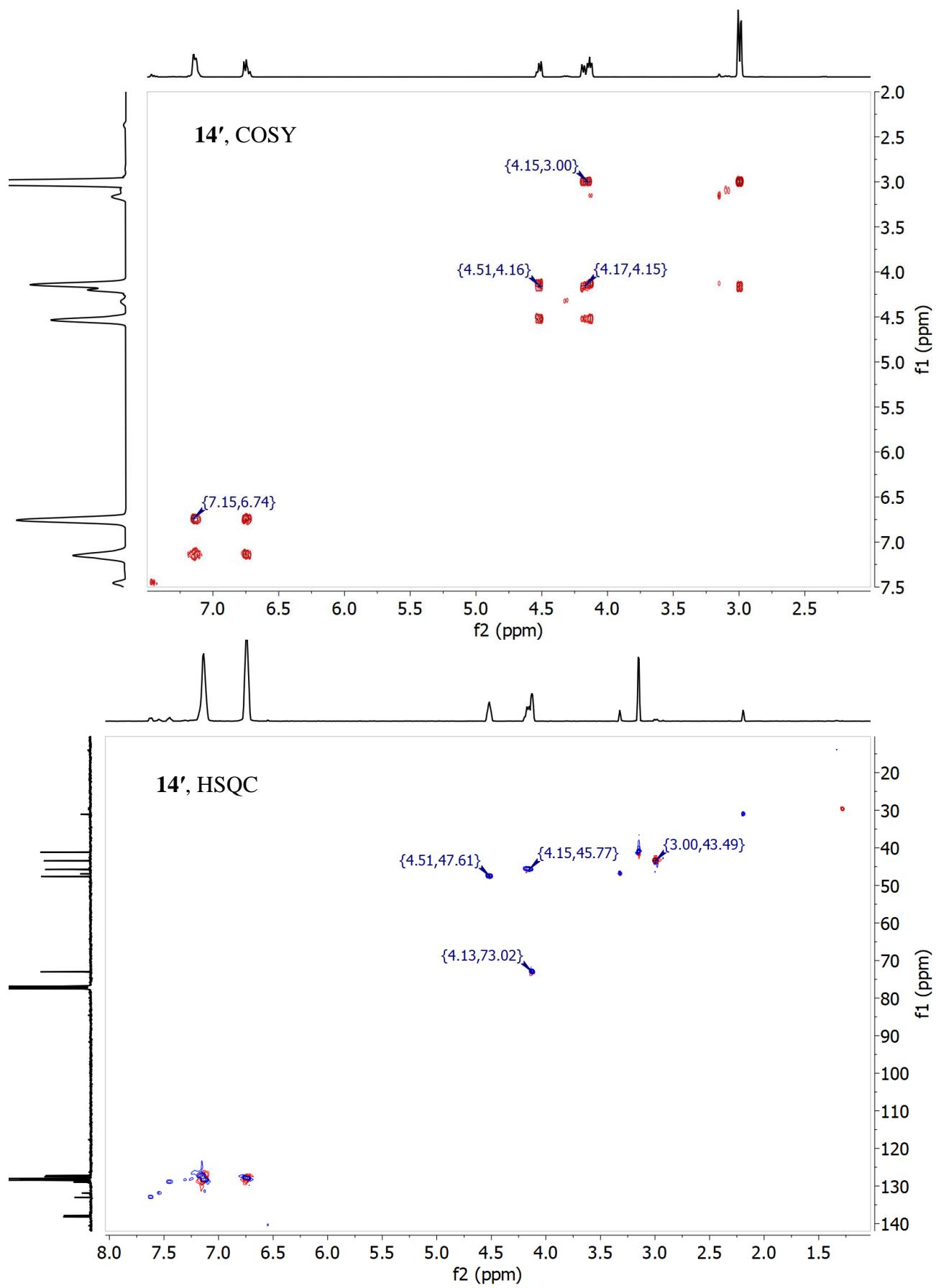


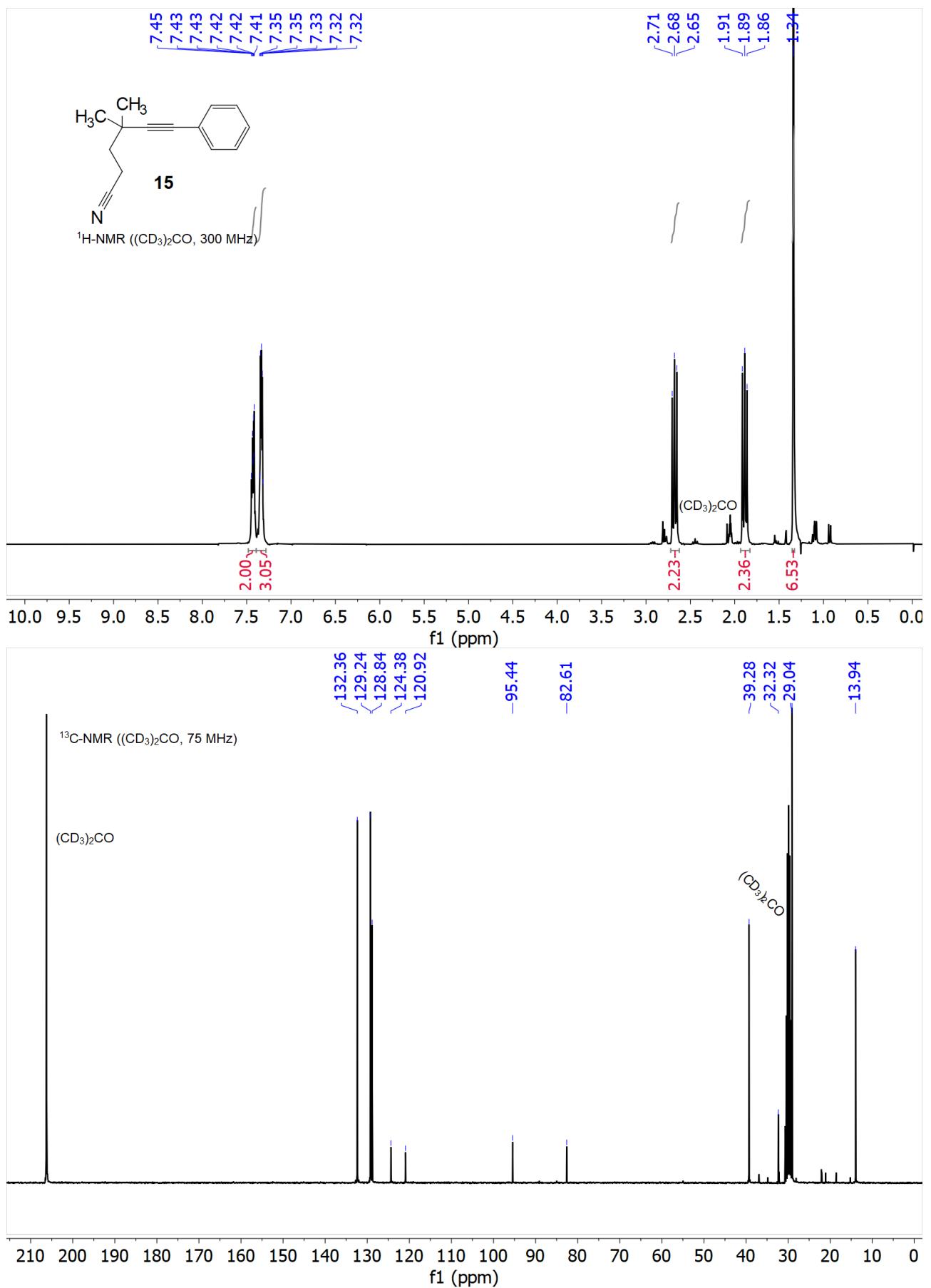


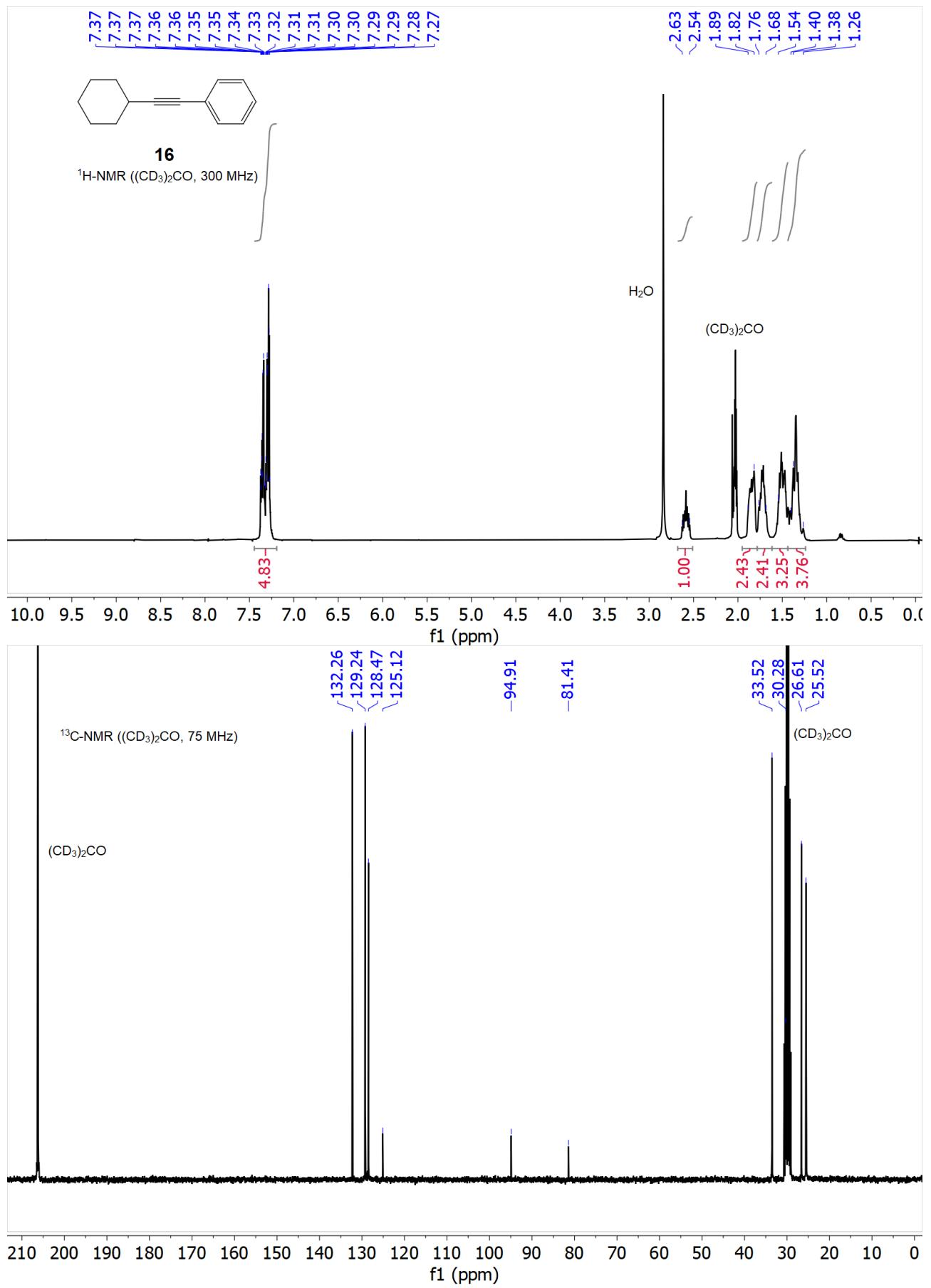


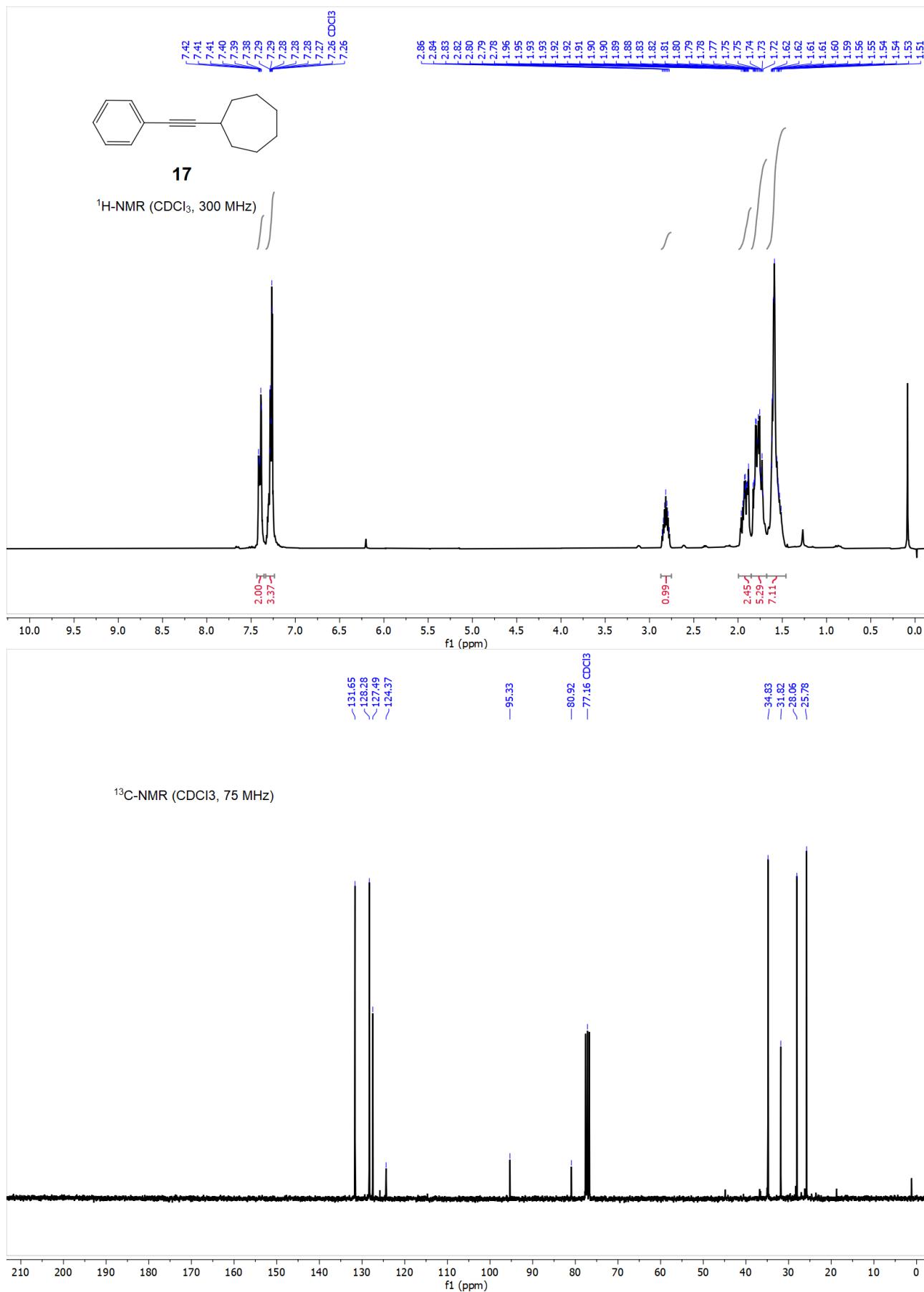


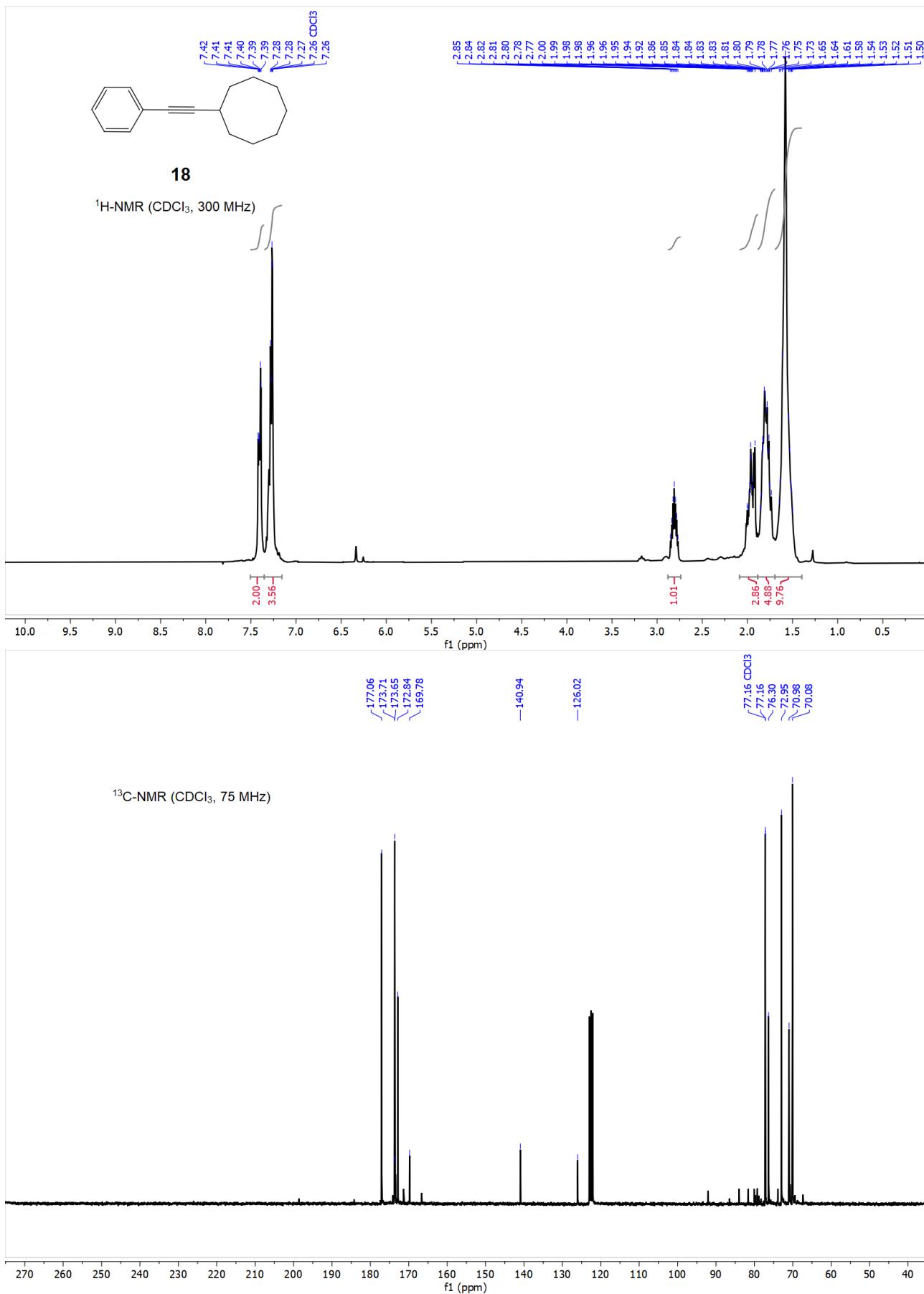


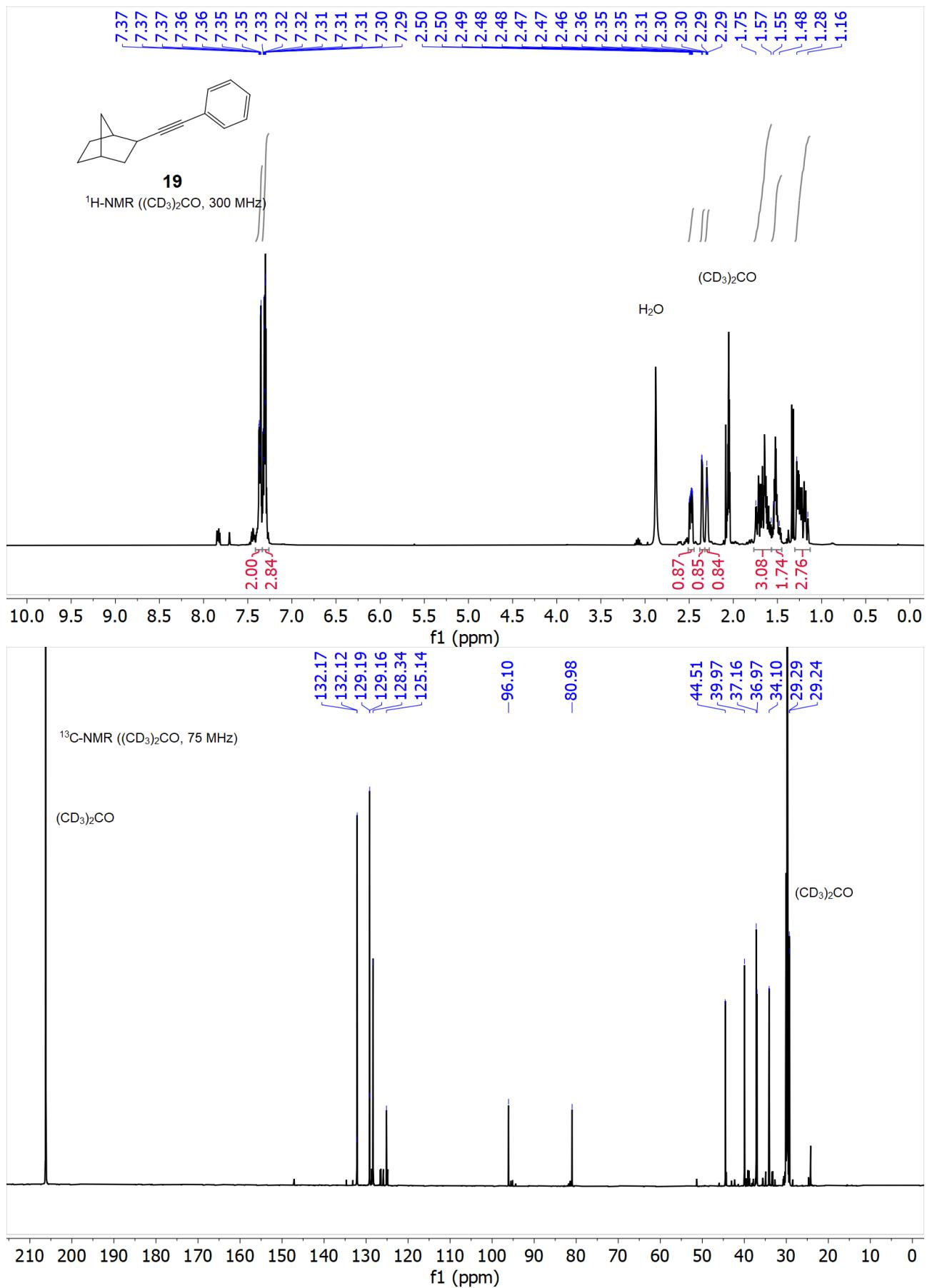


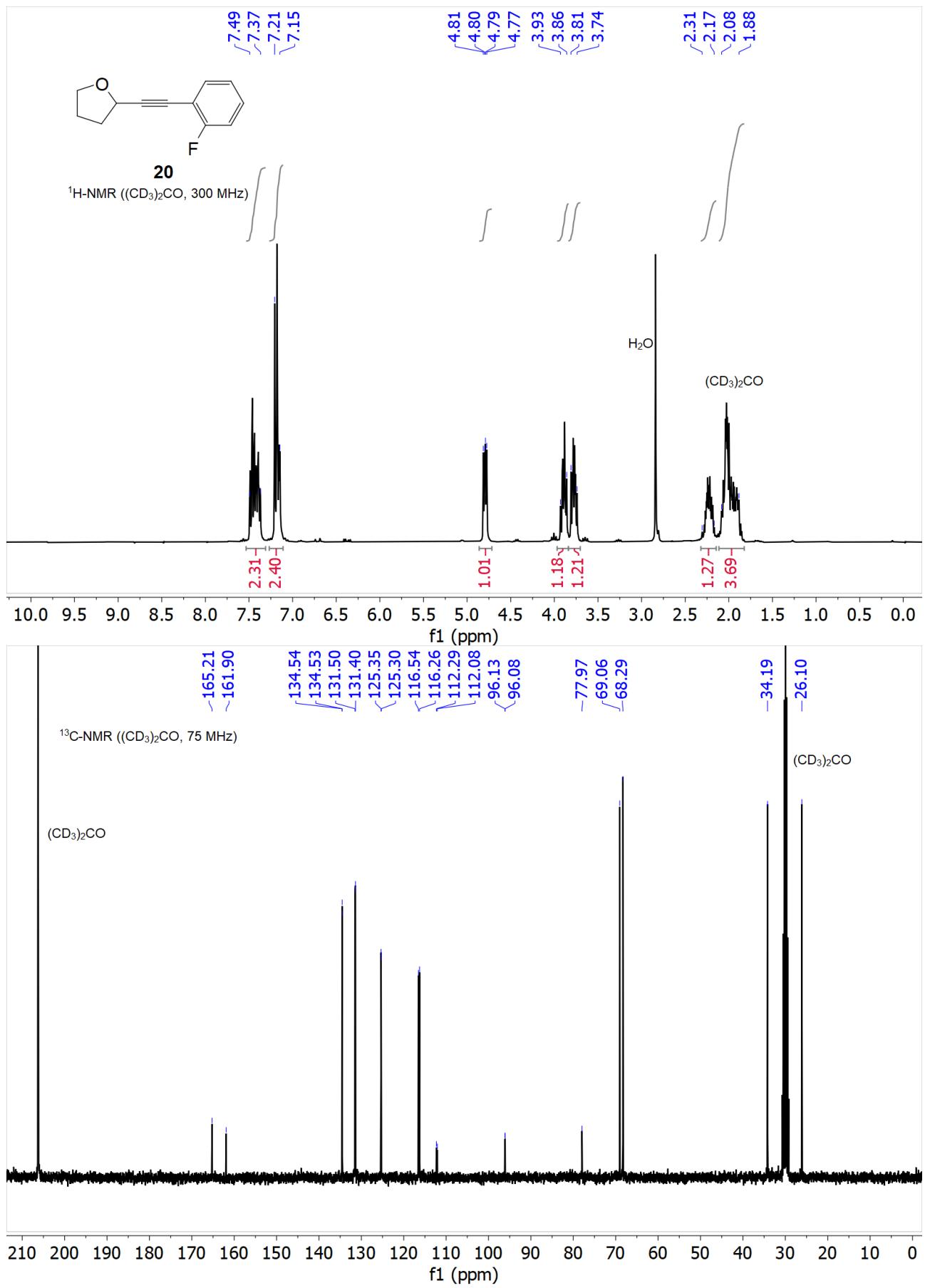


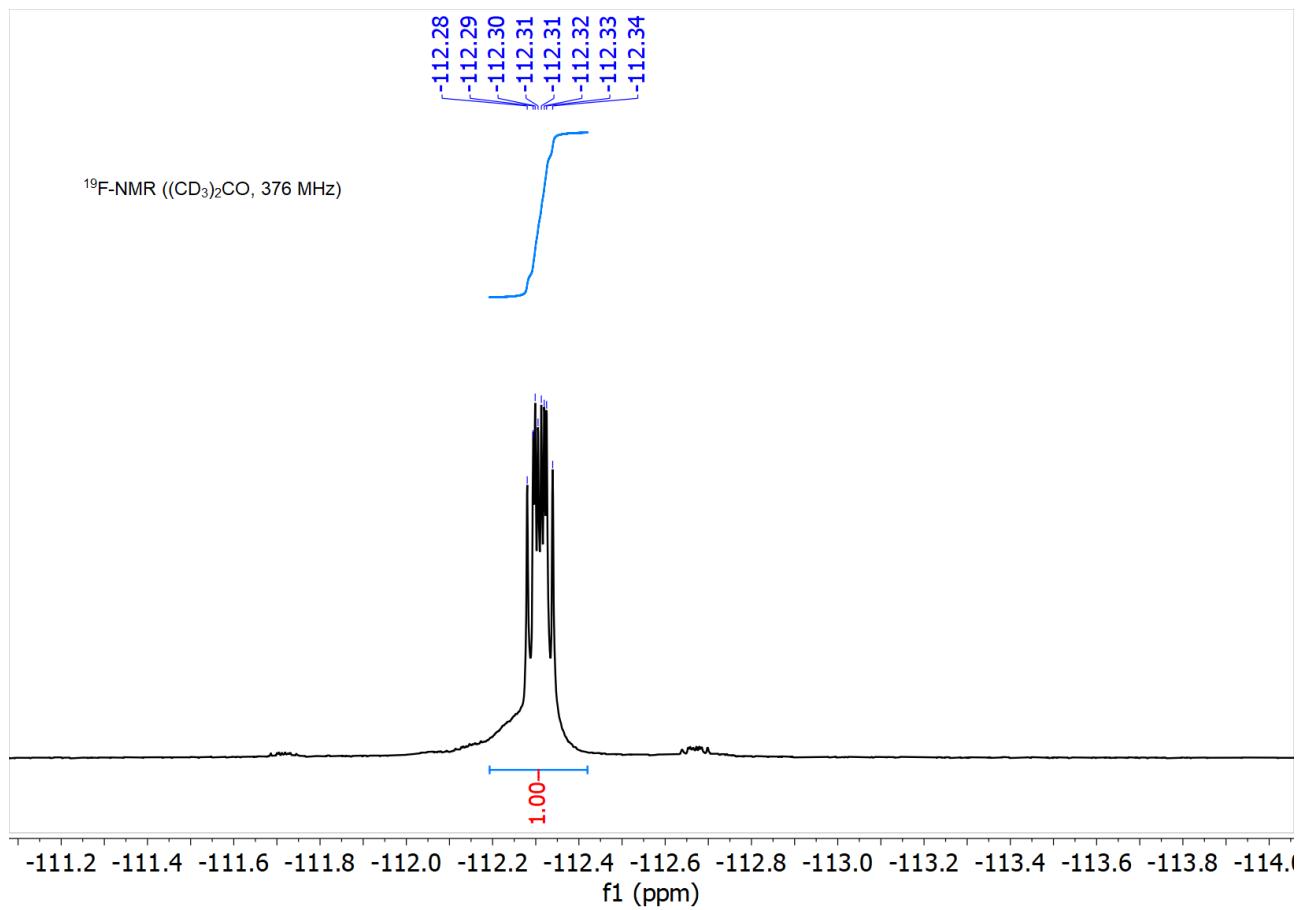


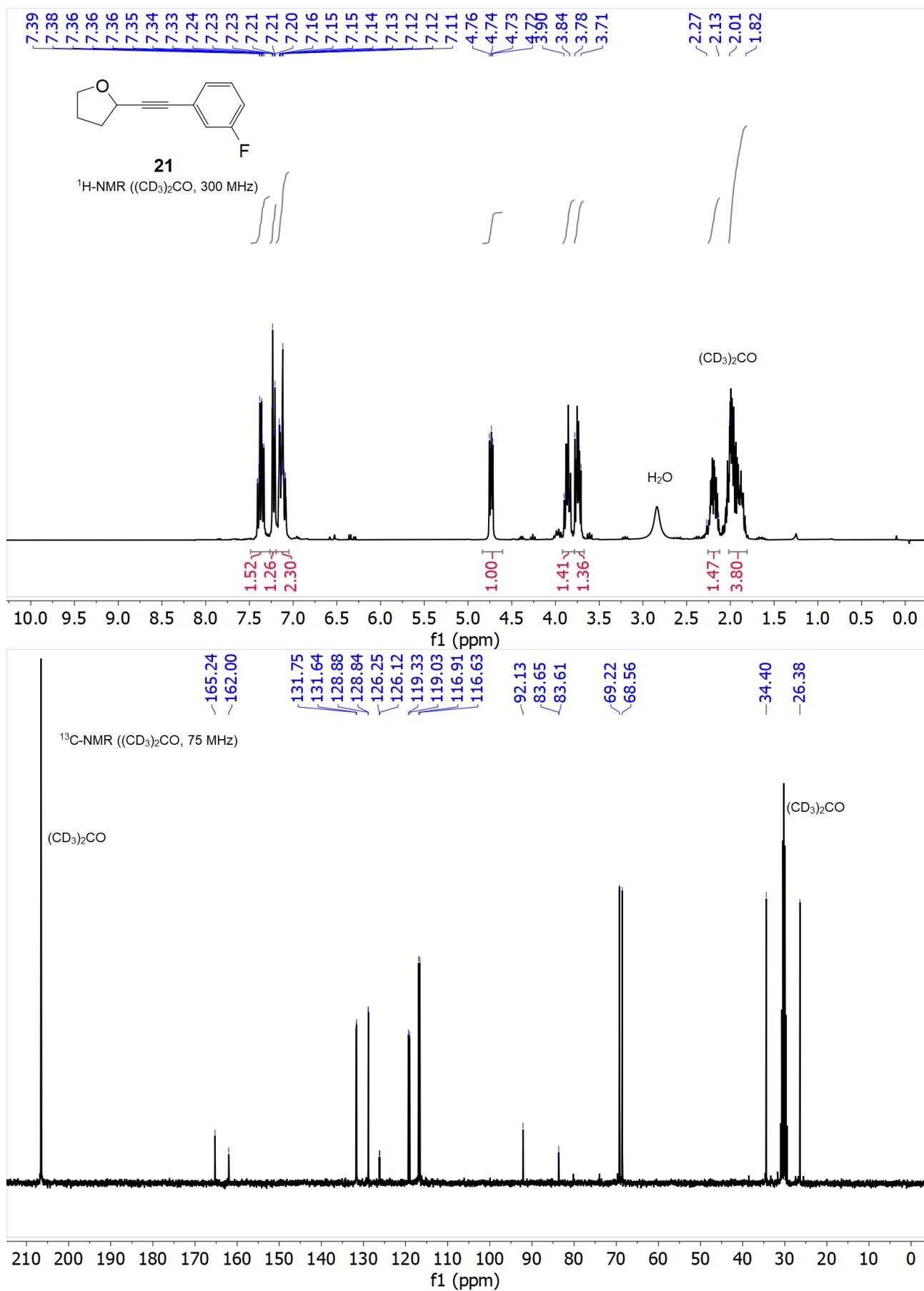


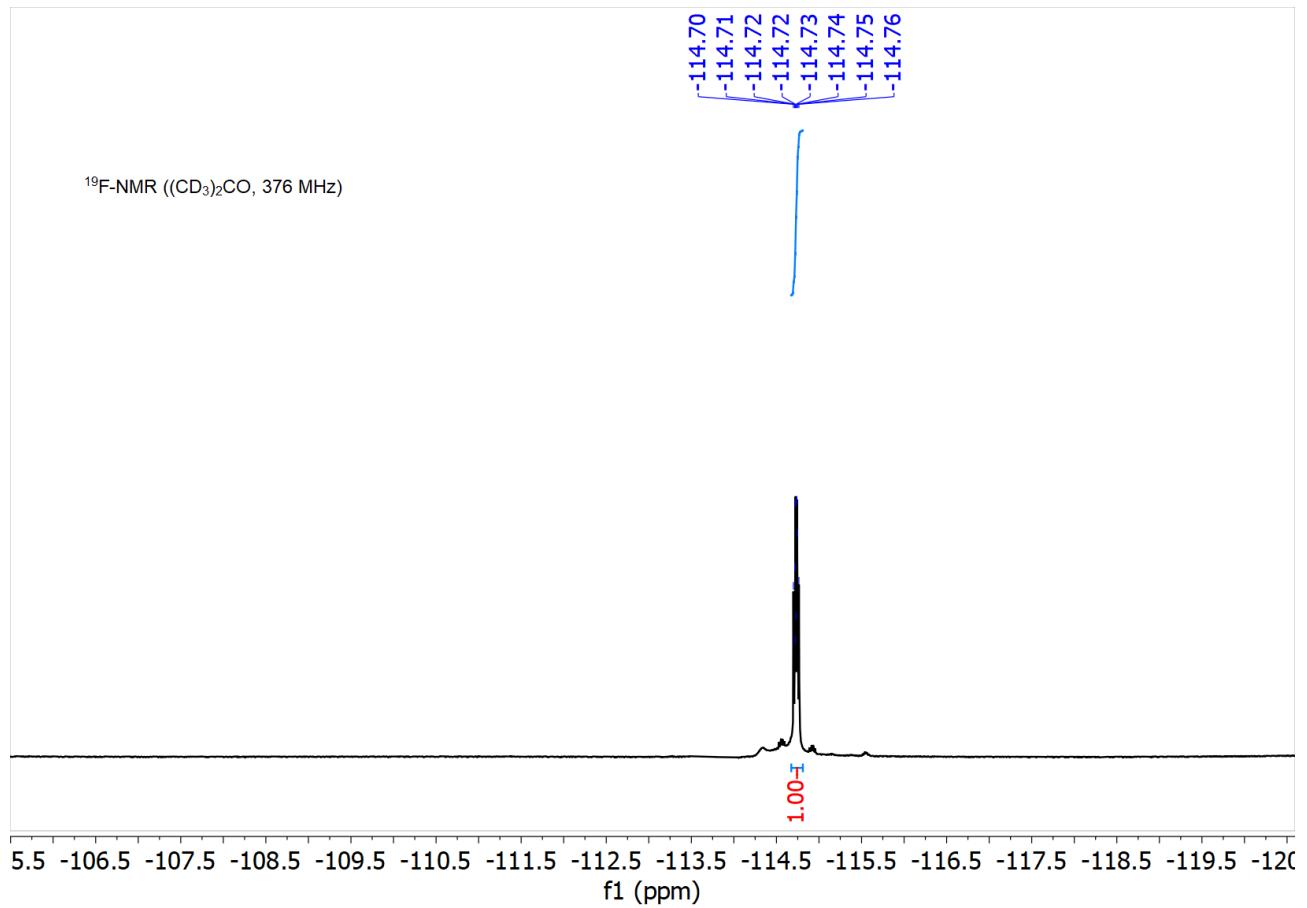


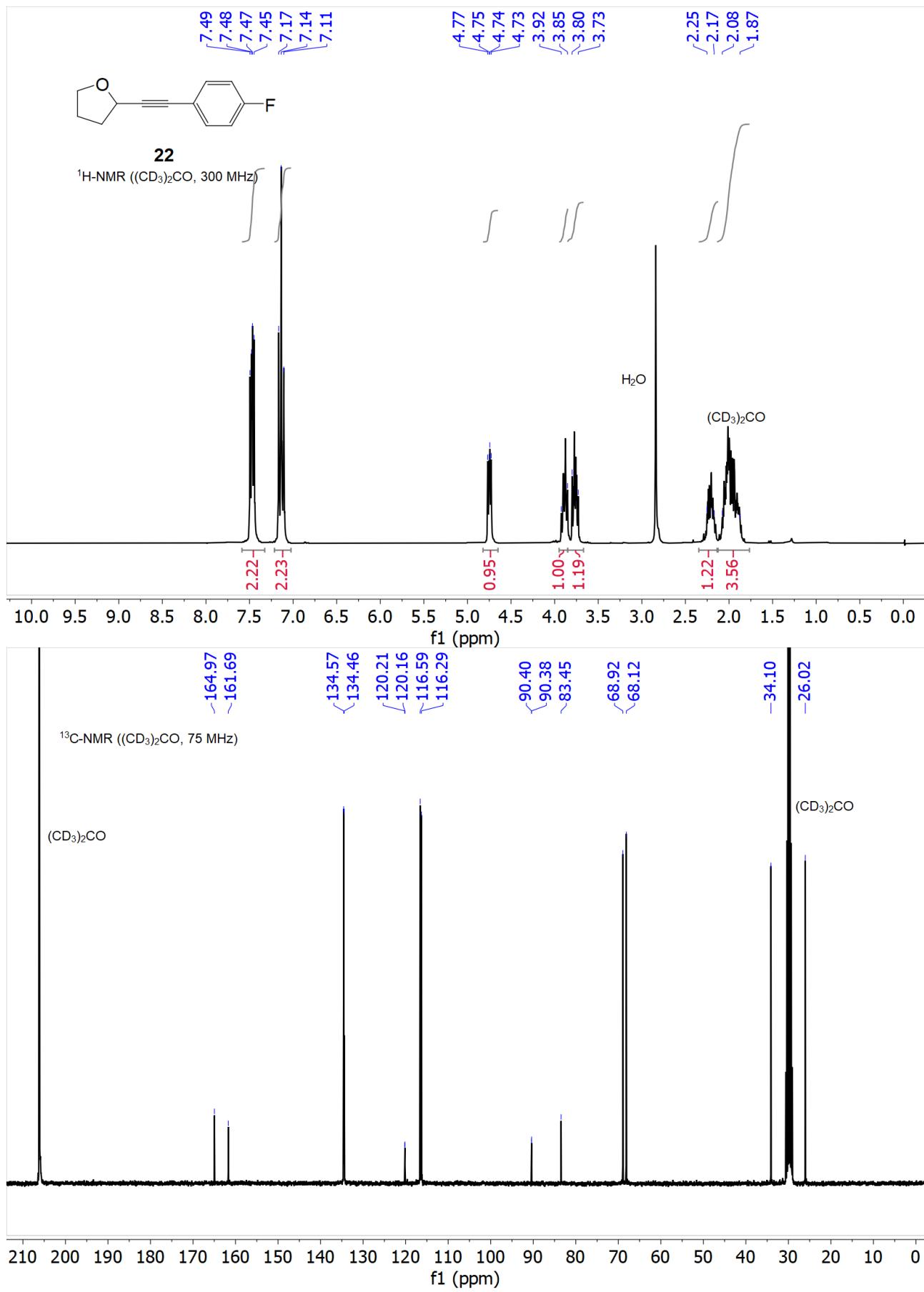


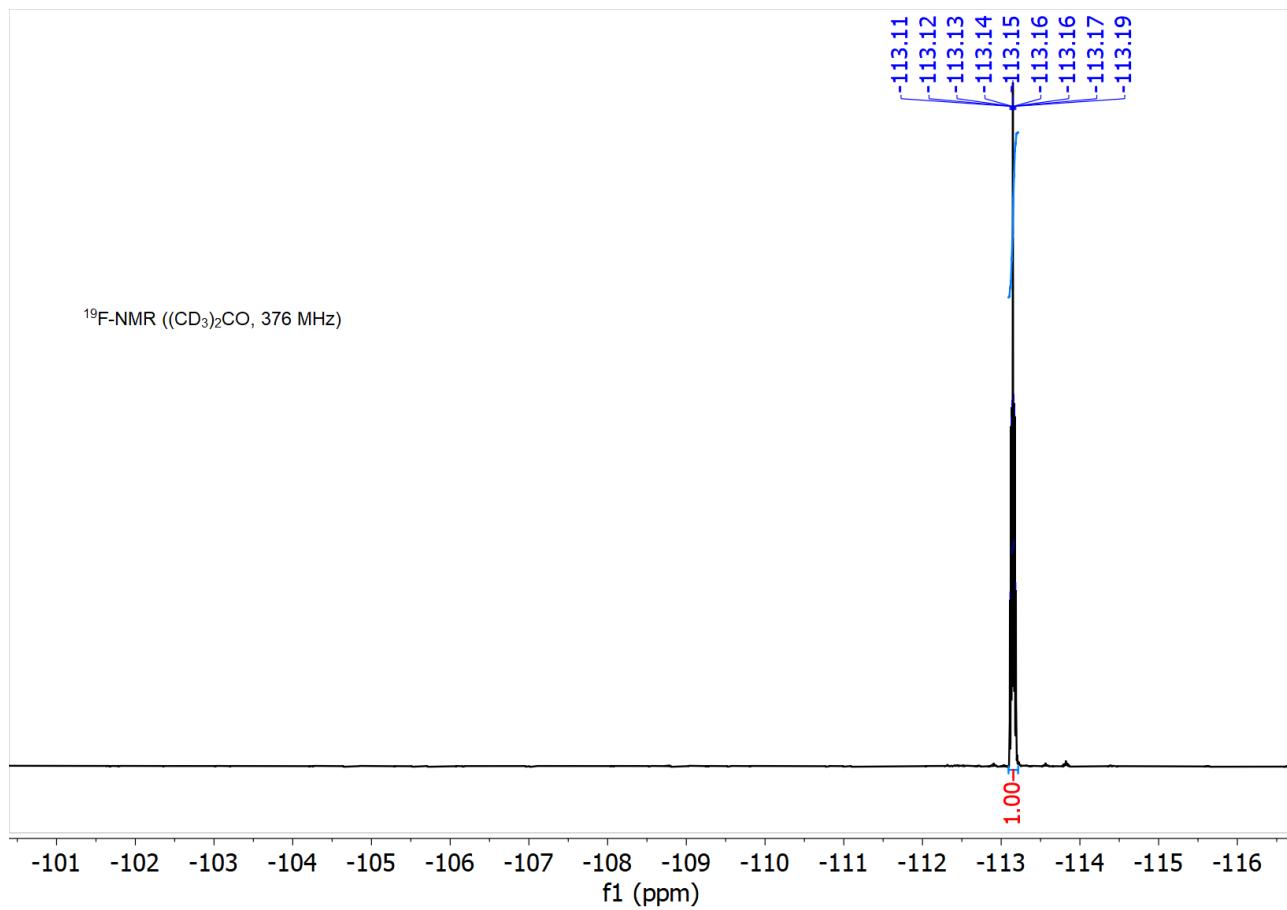


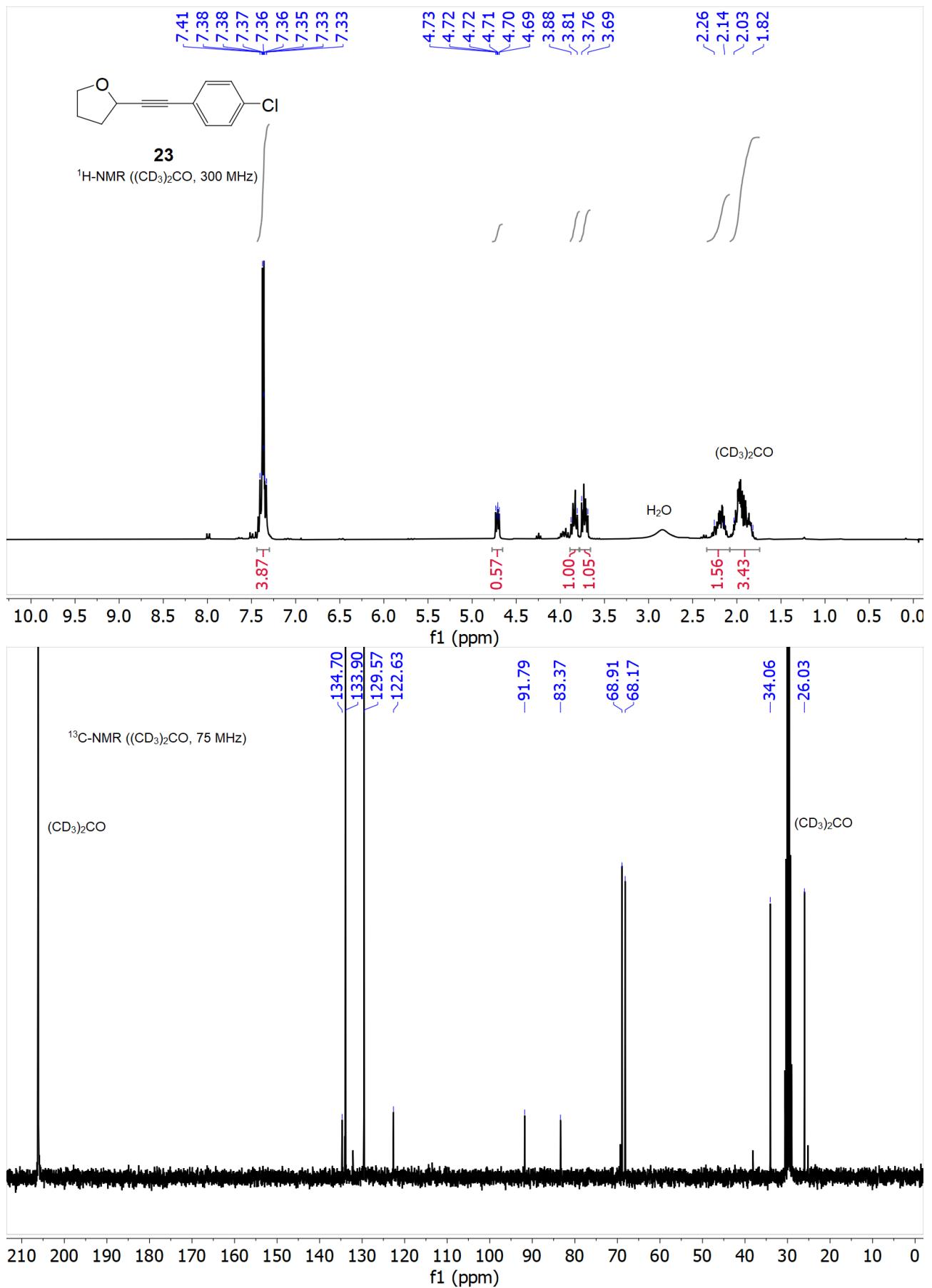


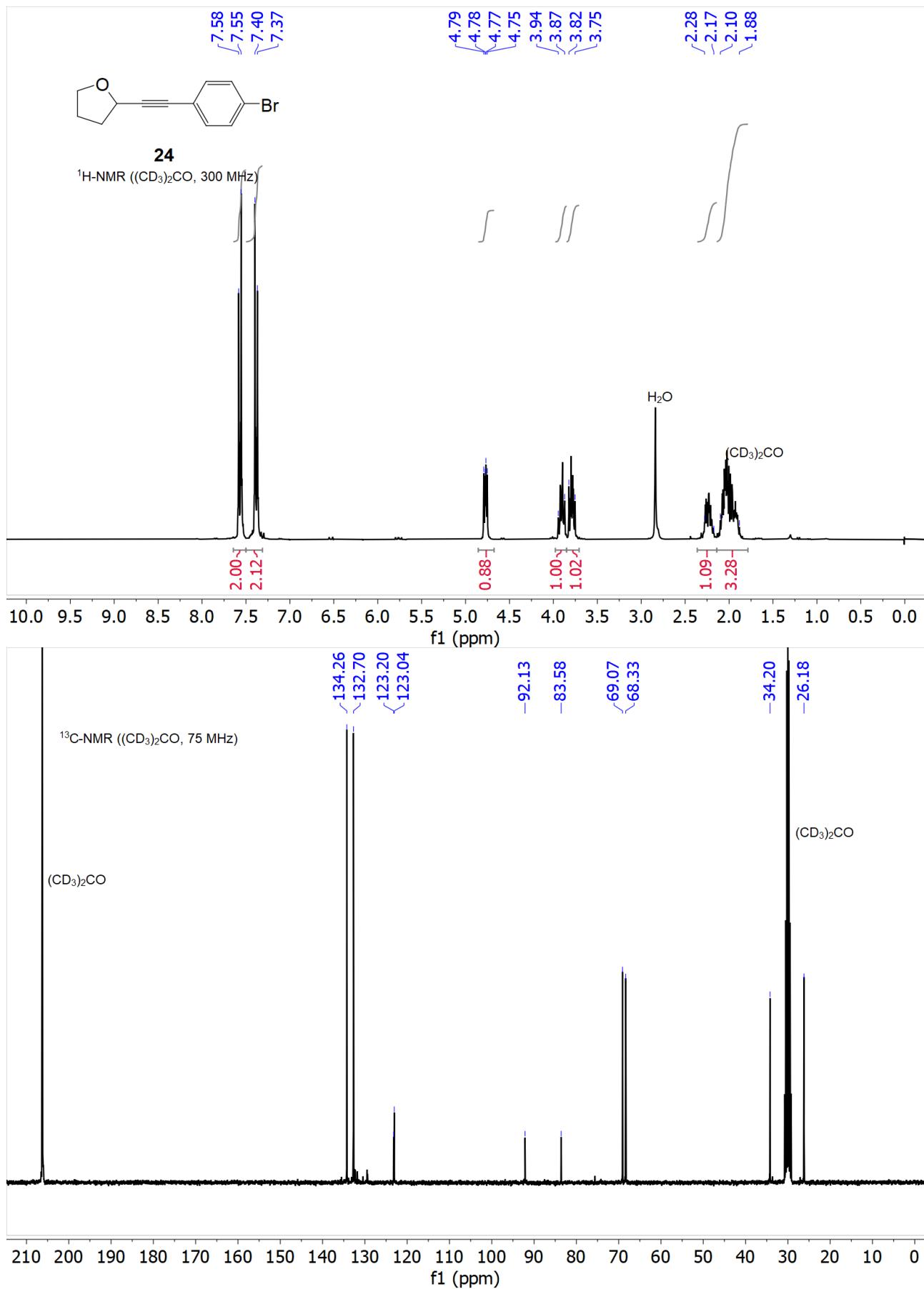


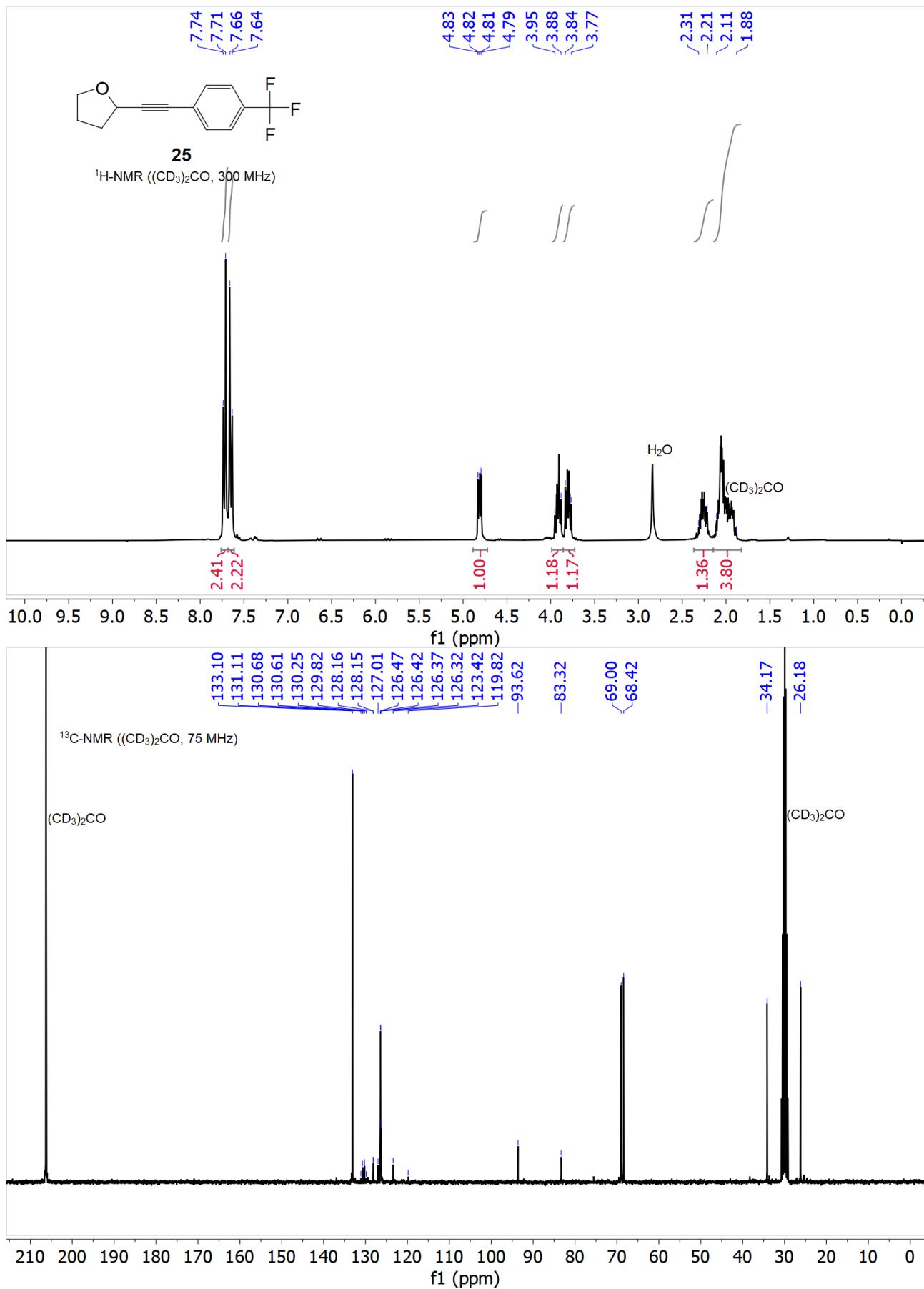












¹⁹F-NMR ((CD₃)₂CO, 376 MHz)

