

Supporting Information

Synthesis of Nitrosobenzene Derivatives via Nitrosodesilylation Reaction

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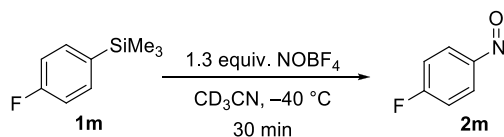
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Table of content

NMR analysis of the nitrosodesilylation	S-1
NMR Spectra	S-9

NMR analysis of the nitrosodesilylation

^1H , ^{19}F and ^{29}Si NMR analysis of the reaction mixture



Scheme S1: Reaction conditions for examination of the mechanism by NMR analysis.

A round bottom flask was charged with acetonitrile (8.3 mL, 0.03 M), and (4-fluorophenyl)trimethylsilane **1m** (42.1 mg, 0.25 mmol, 1.0 equiv.) and cooled to $-40\text{ }^\circ\text{C}$. After adding NOBF_4 (38.0 mg, 0.33 mmol, 1.3 equiv.) the reaction mixture was stirred for 30 min. Then, the NMR probe was prepared and ^1H NMR, ^{19}F NMR and $^{29}\text{Si}\{^1\text{H}\}$ INEPT spectra were recorded. After that a small amount of water was added to the NMR tube and once again ^1H NMR, ^{19}F NMR and $^{29}\text{Si}\{^1\text{H}\}$ INEPT spectra were recorded.

Resolved signals of Me_3SiF :

^1H NMR (500 MHz, CD_3CN , ppm): $\delta = 0.22$ (d, $J = 7.4$ Hz, 9H).

^{19}F NMR (470 MHz, CD_3CN , ppm): $\delta = -158.0$.

$^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR (99 MHz, CD_3CN , ppm): $\delta = 33.6$ (d, $J = 272.6$ Hz).

The analytic data are in accordance with the literature.^[1]

Spectra of the reaction mixture

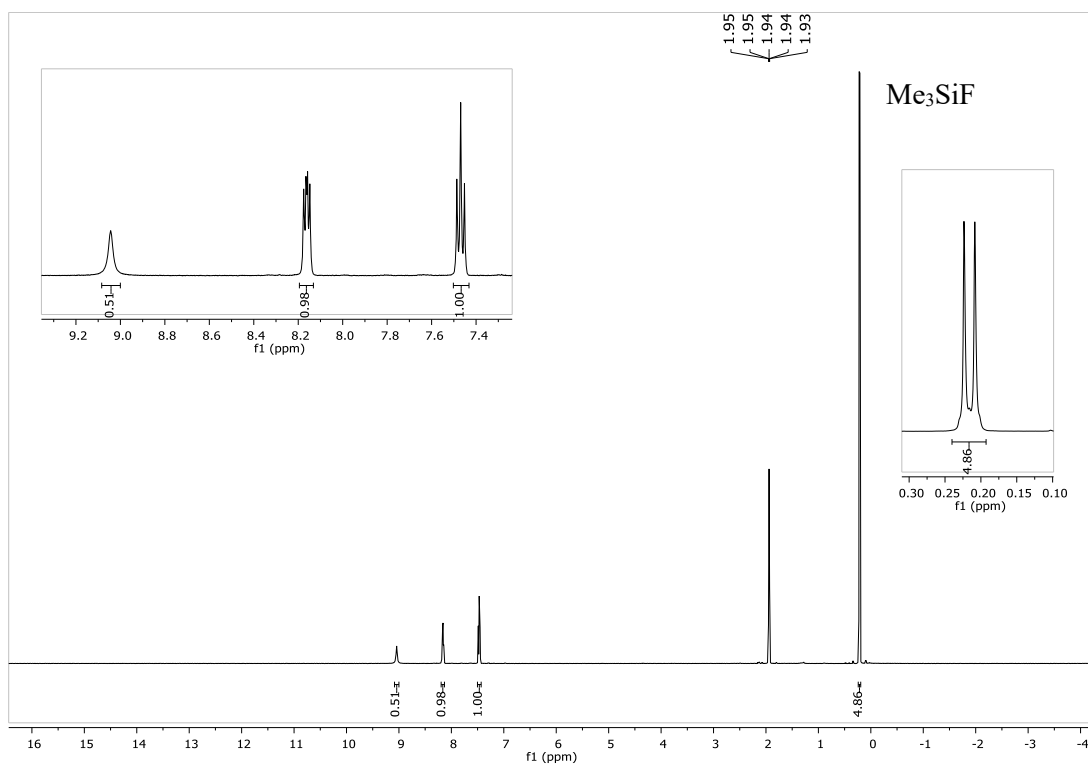


Figure S1: ¹H NMR spectrum (CD₃CN, 500 MHz) of the reaction mixture.

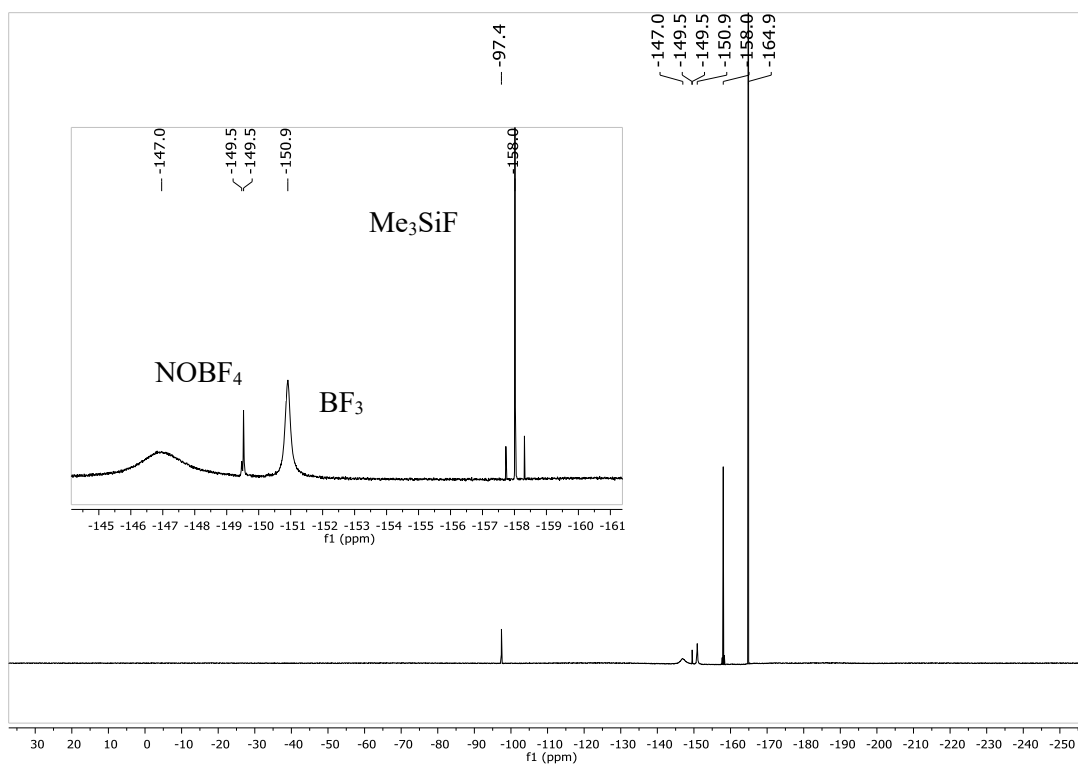


Figure S2: ¹⁹F NMR spectrum (CD₃CN, 470 MHz) of the reaction mixture. C₆F₆ ($\delta(^{19}\text{F}) = -164.9$ ppm) was used as internal standard.

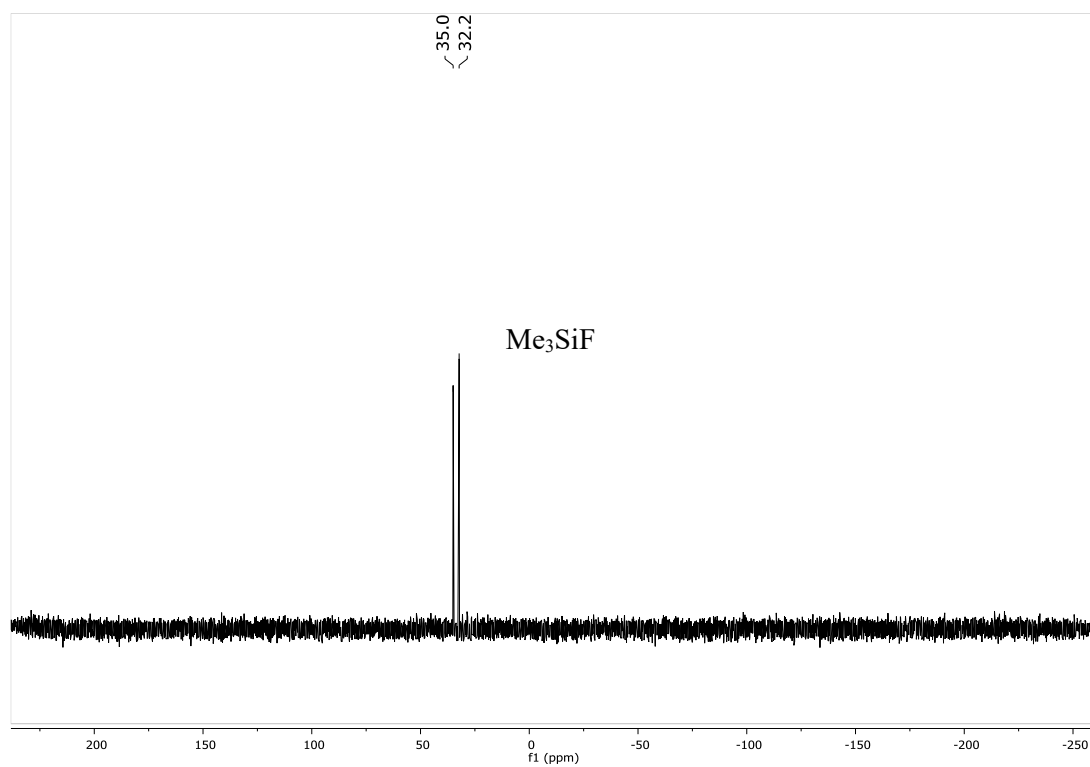


Figure S3: $^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR spectrum (CD_3CN , 99 MHz) of the reaction mixture.

Spectra after the addition of a slightly amount of water

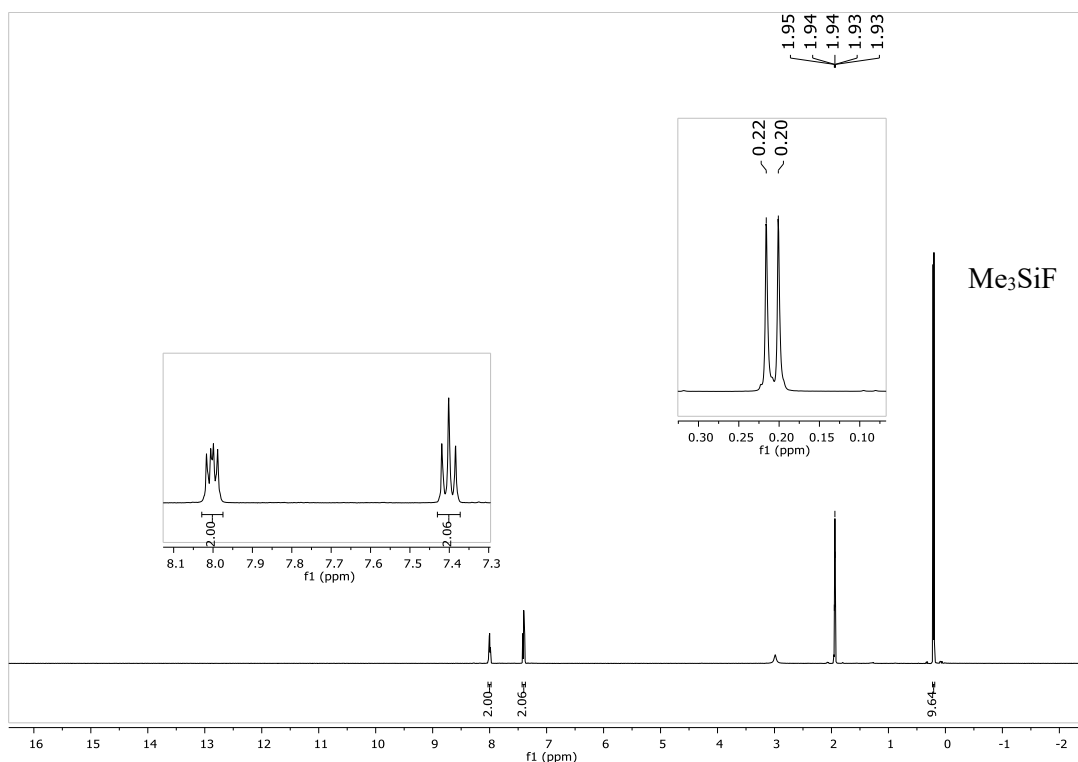


Figure S4: ^1H NMR spectrum (CD_3CN , 500 MHz) after the addition of water. C_6F_6 ($\delta(^{19}\text{F}) = -164.9$ ppm) was used as internal standard.

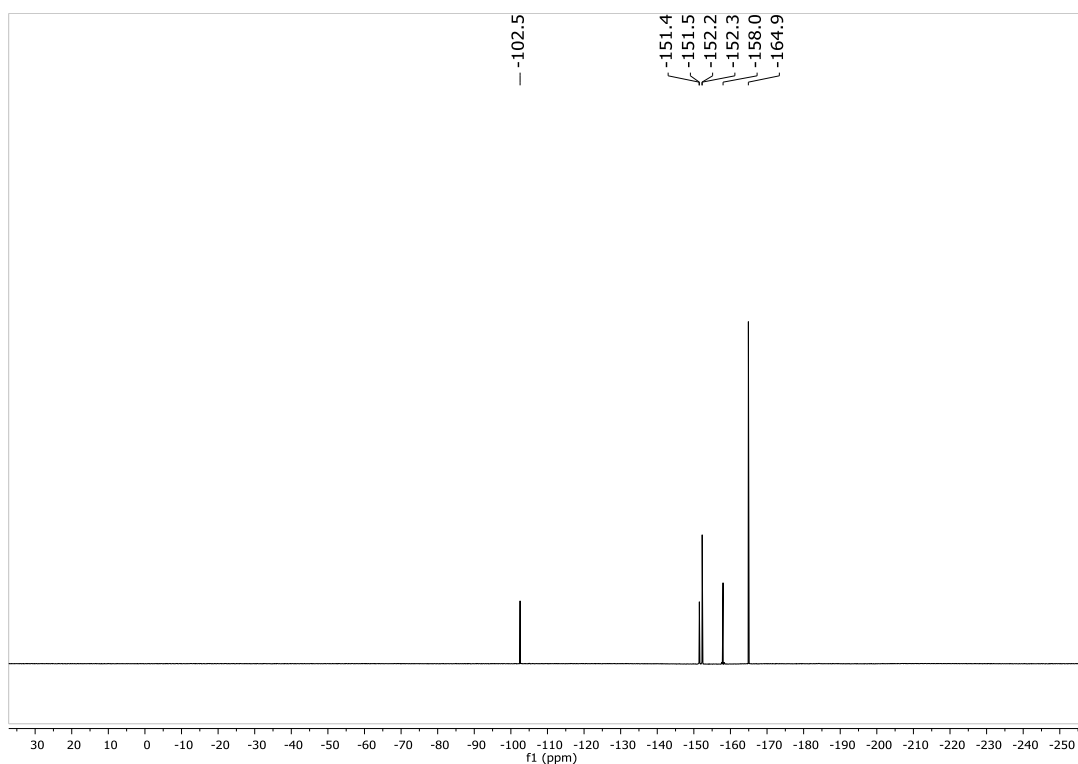


Figure S5: ^{19}F NMR spectrum (CD_3CN , 470 MHz) after the addition of water. C_6F_6 ($\delta(^{19}\text{F}) = -164.9$ ppm) was used as internal standard.

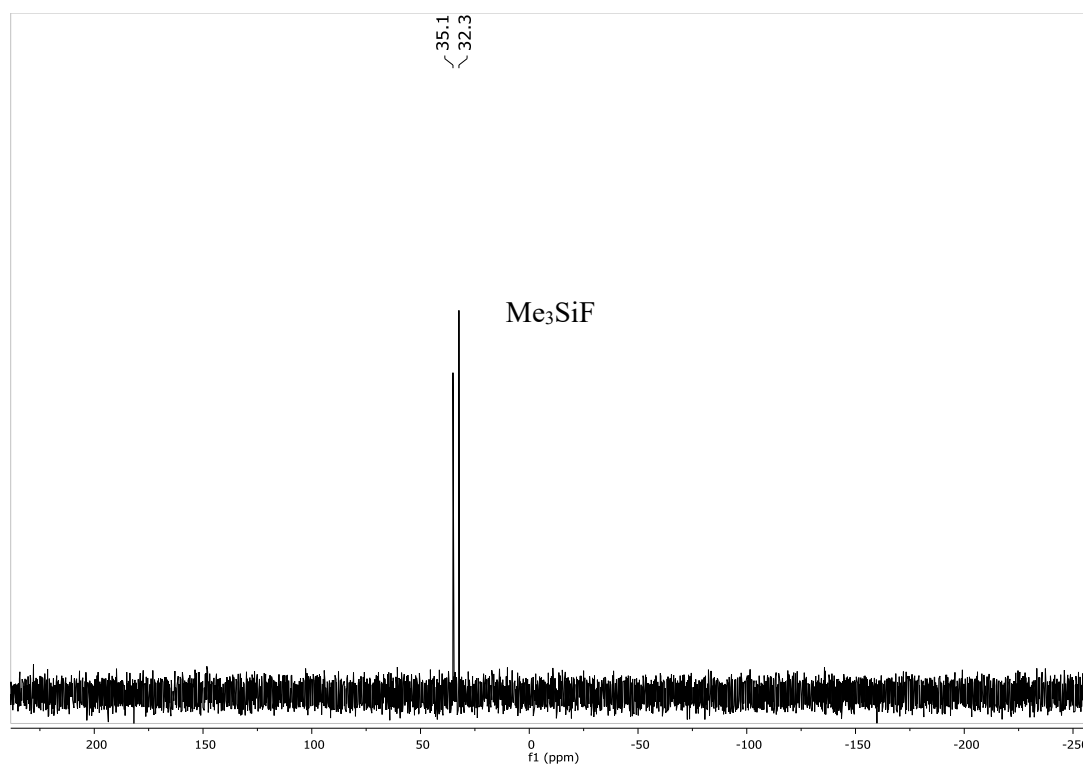
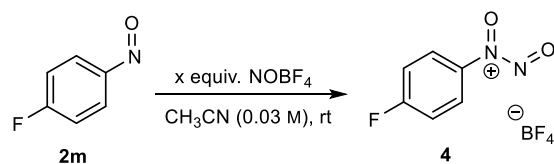


Figure S6: $^{29}\text{Si}\{^1\text{H}\}$ NMR INEPT spectrum (CD_3CN , 99 MHz) after the addition of a small amount of water.

Influence of NOBF₄ to the shift of the nitrosoarene **2m**



A round bottom flask was charged with acetonitrile (8.3 mL, 0.03 M), 1-fluoro-4-nitrosobenzene **2n** (52.2 mg, 0.42 mmol, 1.0 equiv.) and NOBF₄ (14.6 mg, 0.13 mmol, 0.3 equiv.) were added. A ¹⁹F NMR spectrum of the reaction mixture was recorded and again NOBF₄ (14.6 mg, 0.13 mmol, 0.3 equiv.) was added. Once more a ¹⁹F NMR spectrum of the reaction mixture was recorded. Slowly the amount of NOBF₄ was increased up to 35.0 equiv. (see Figure S8).

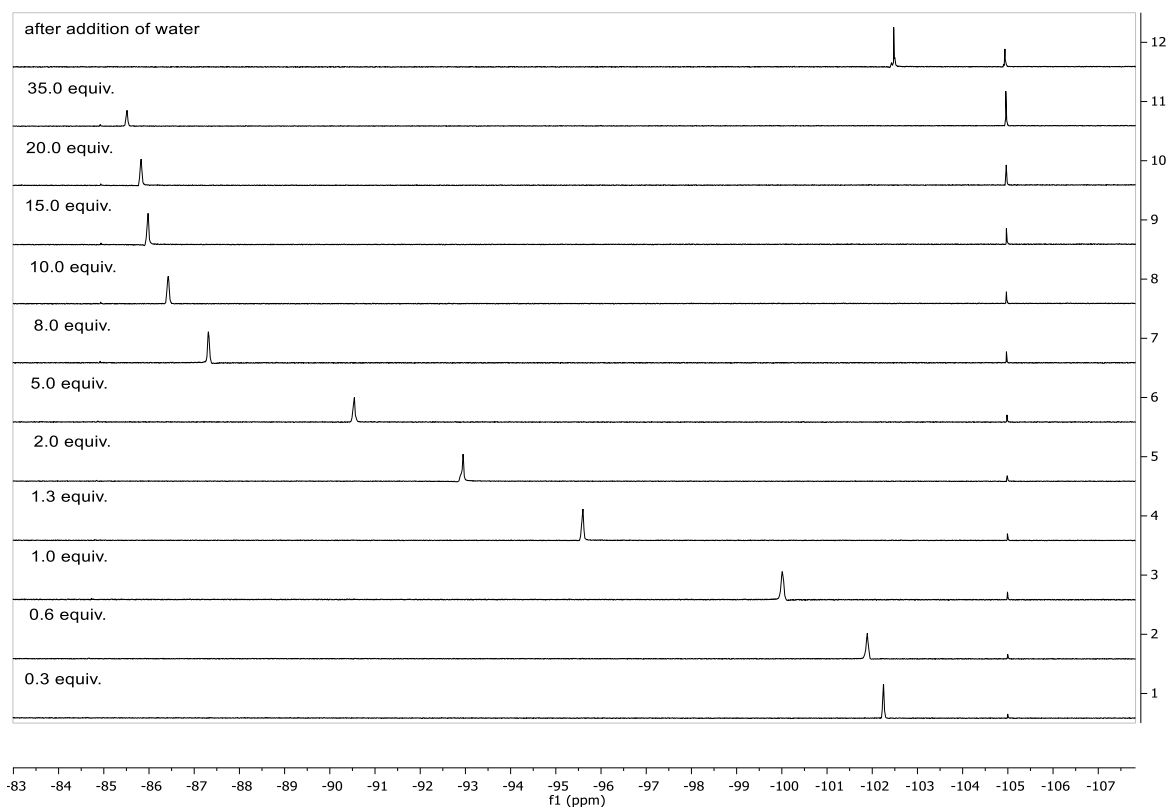


Figure S7: ¹⁹F NMR shift of the nitrosoarene by increasing the amount of NOBF₄. C₆F₆ was used as internal standard ($\delta(^{19}\text{F}) = -164.9$ ppm).

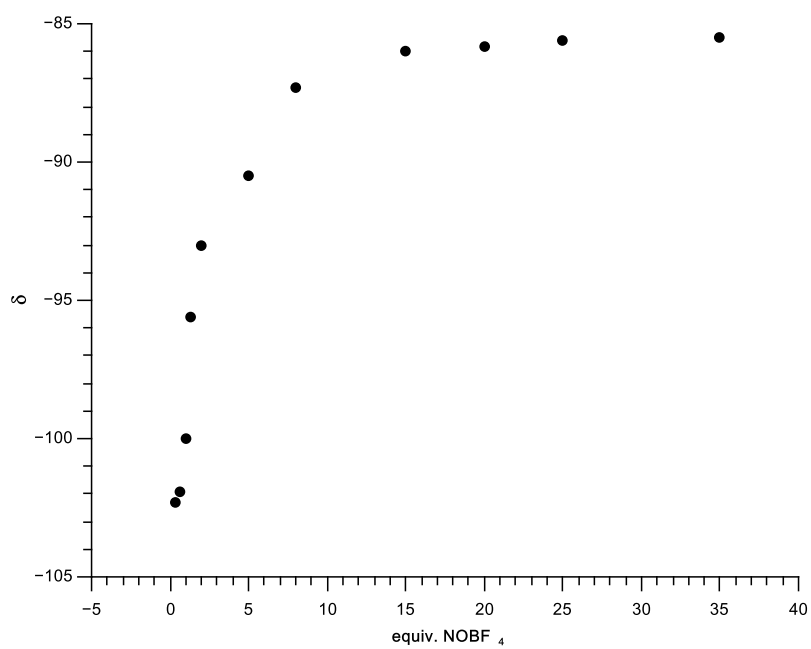
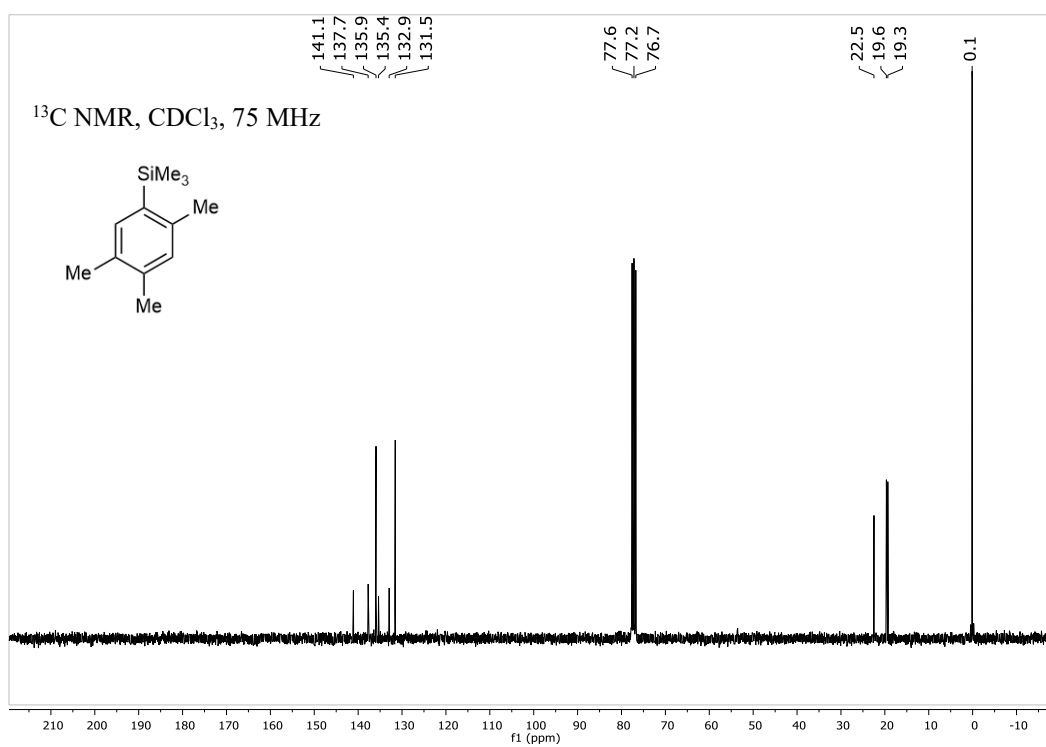
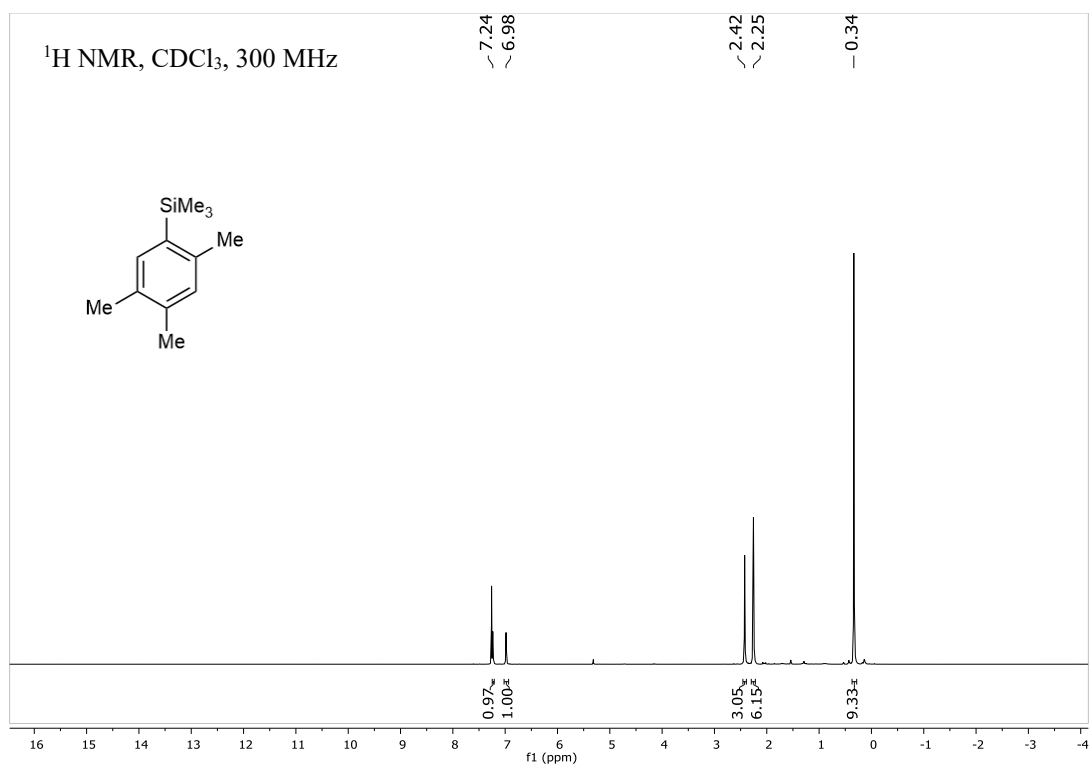


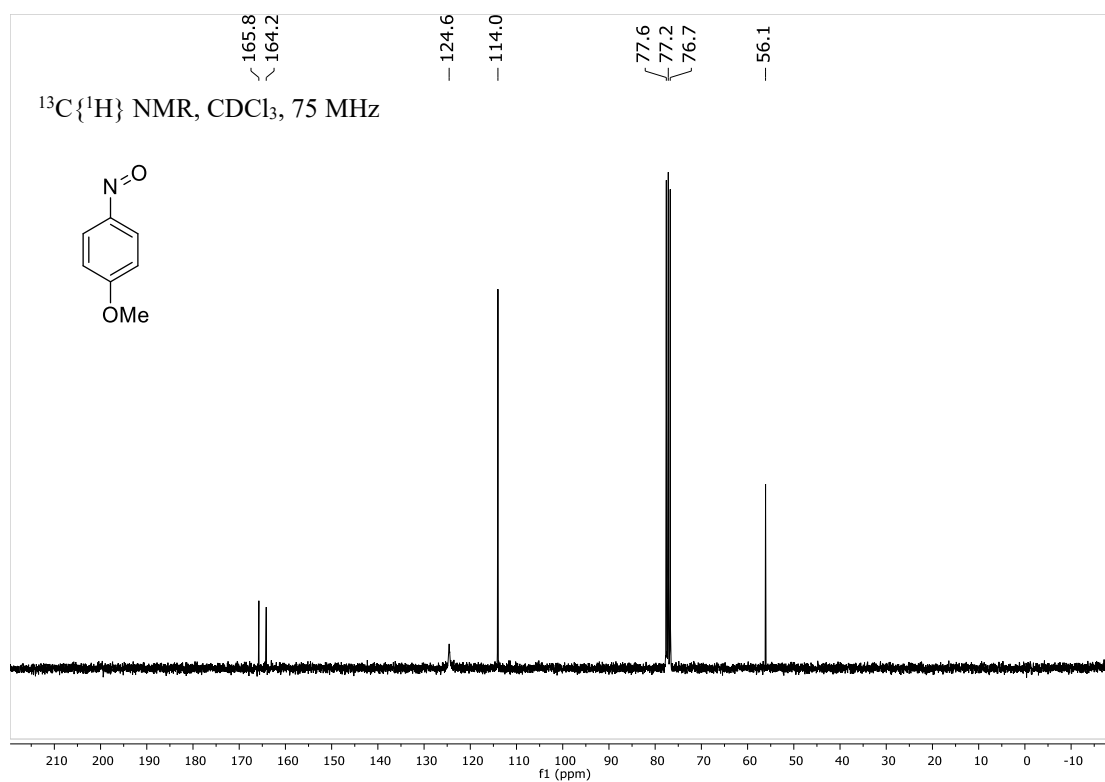
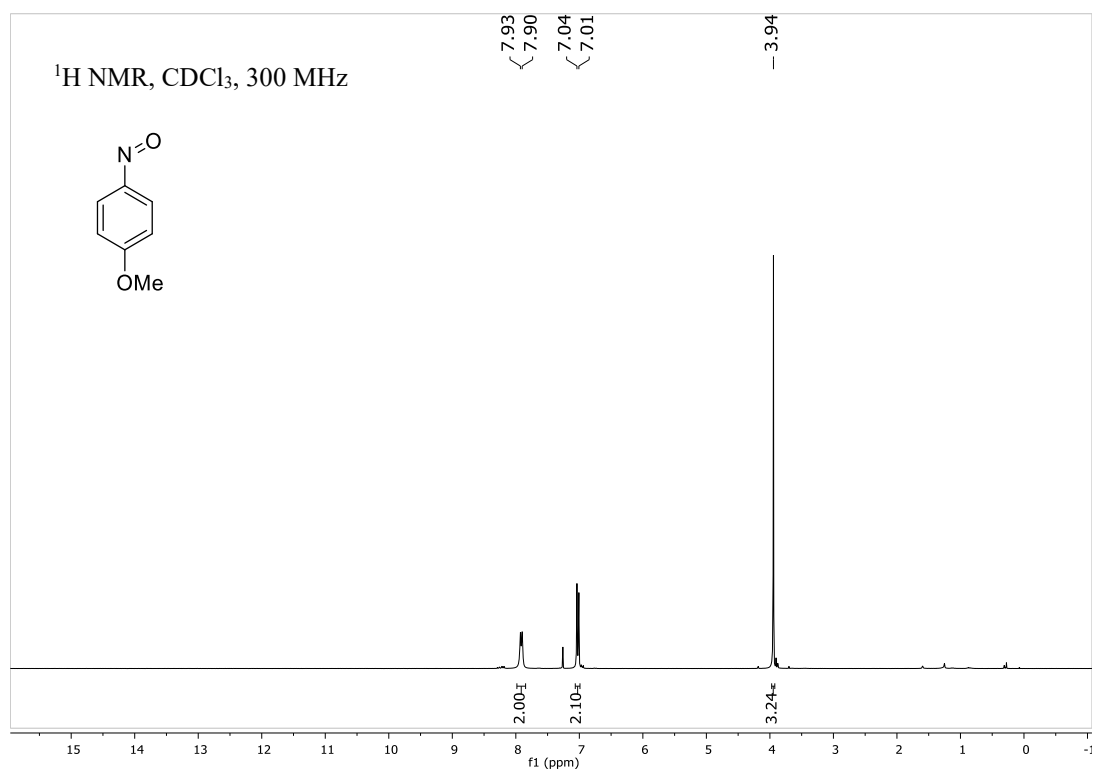
Figure S8: Plot of the chemical shift of the ^{19}F NMR while increasing the amount of NOBF_4 .

NMR spectra

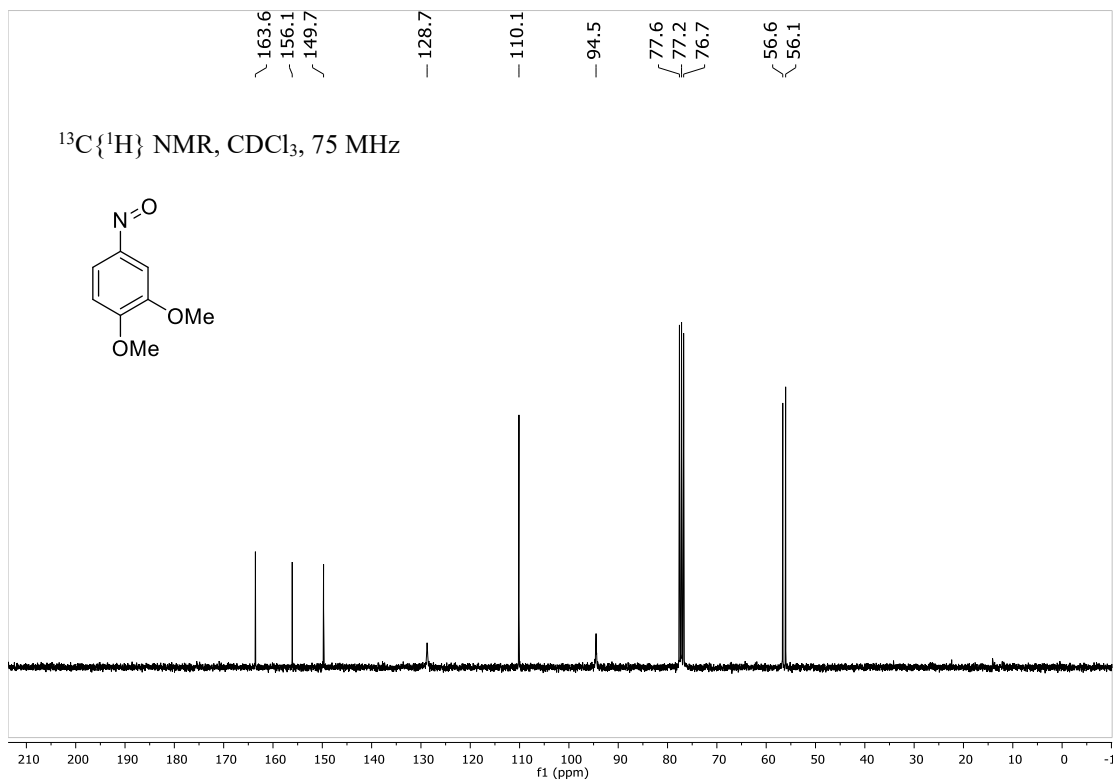
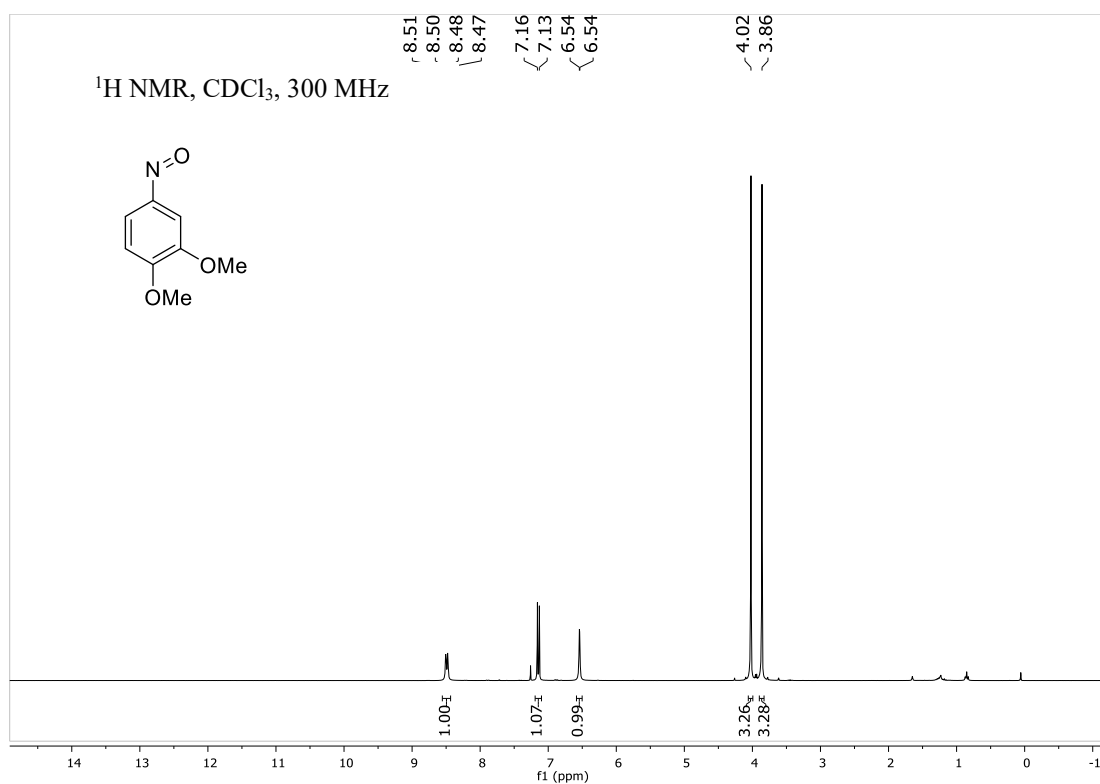
Trimethyl(2,4,5-trimethylphenyl)silane (1e)



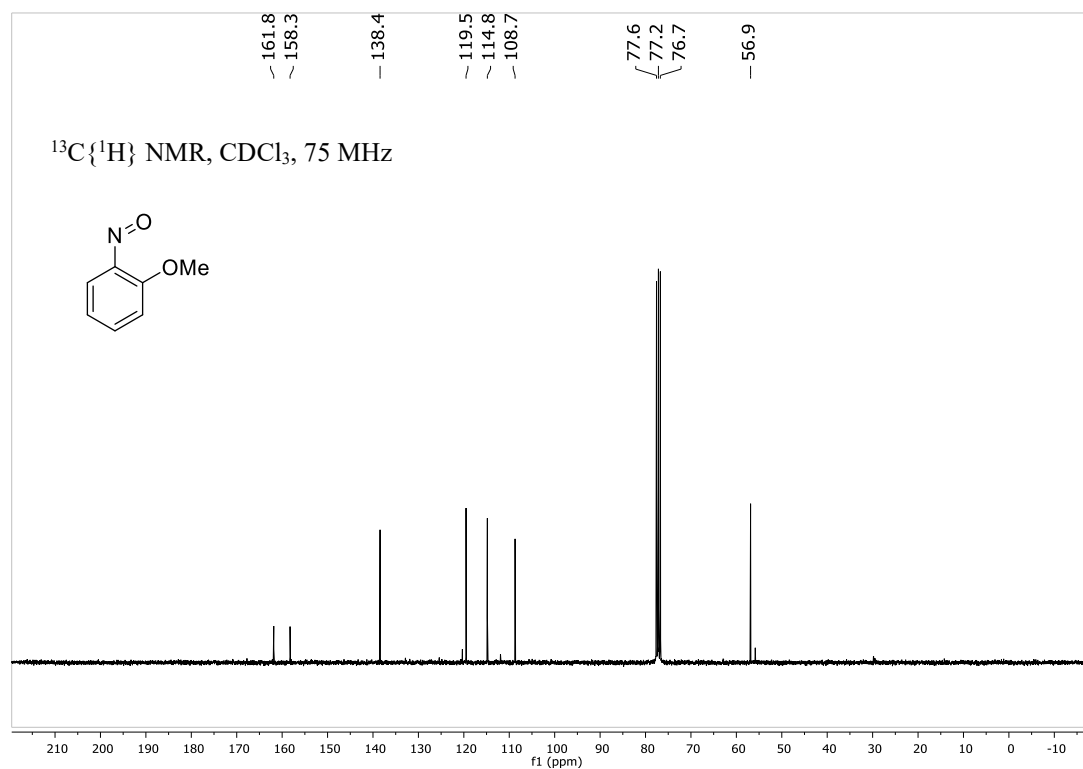
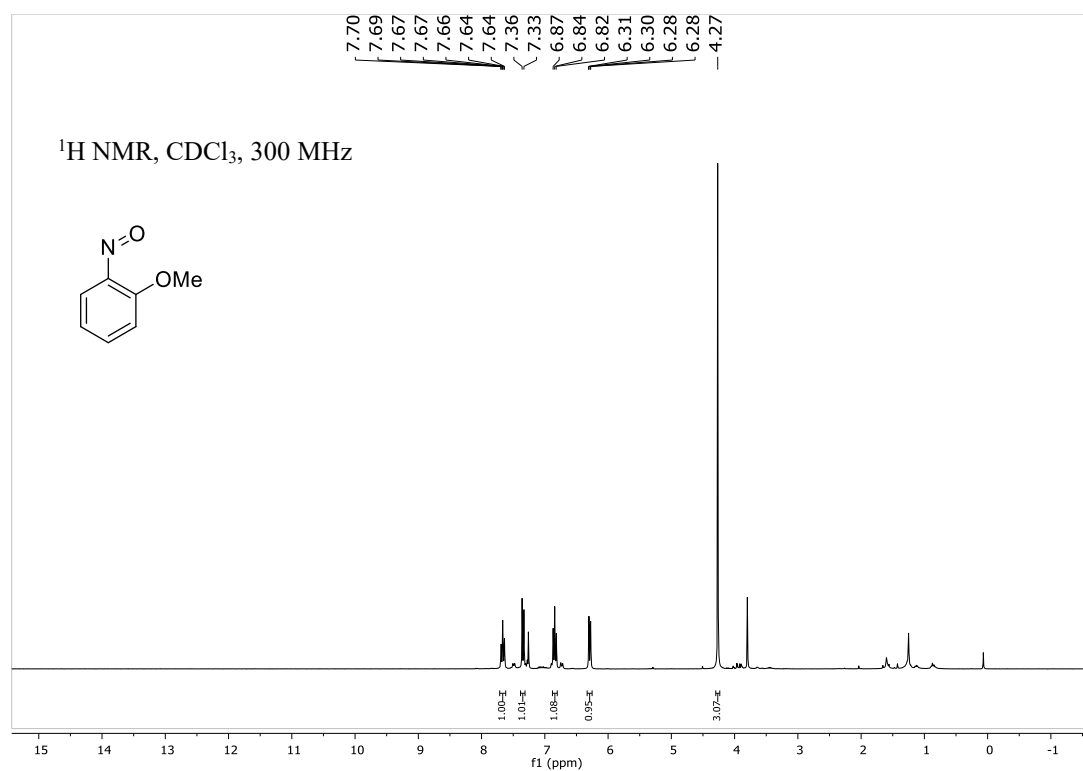
1-Methoxy-4-nitrosobenzene (2a)



1,2-Dimethoxy-4-nitrosobenzene (2b)

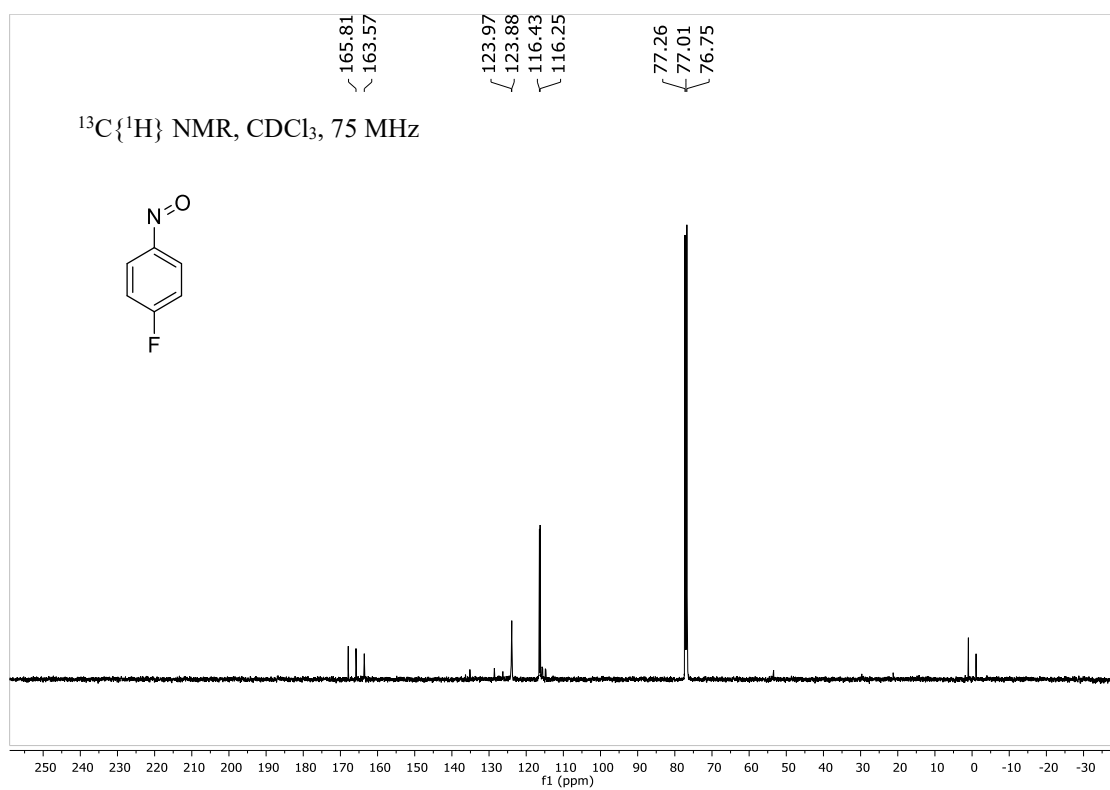
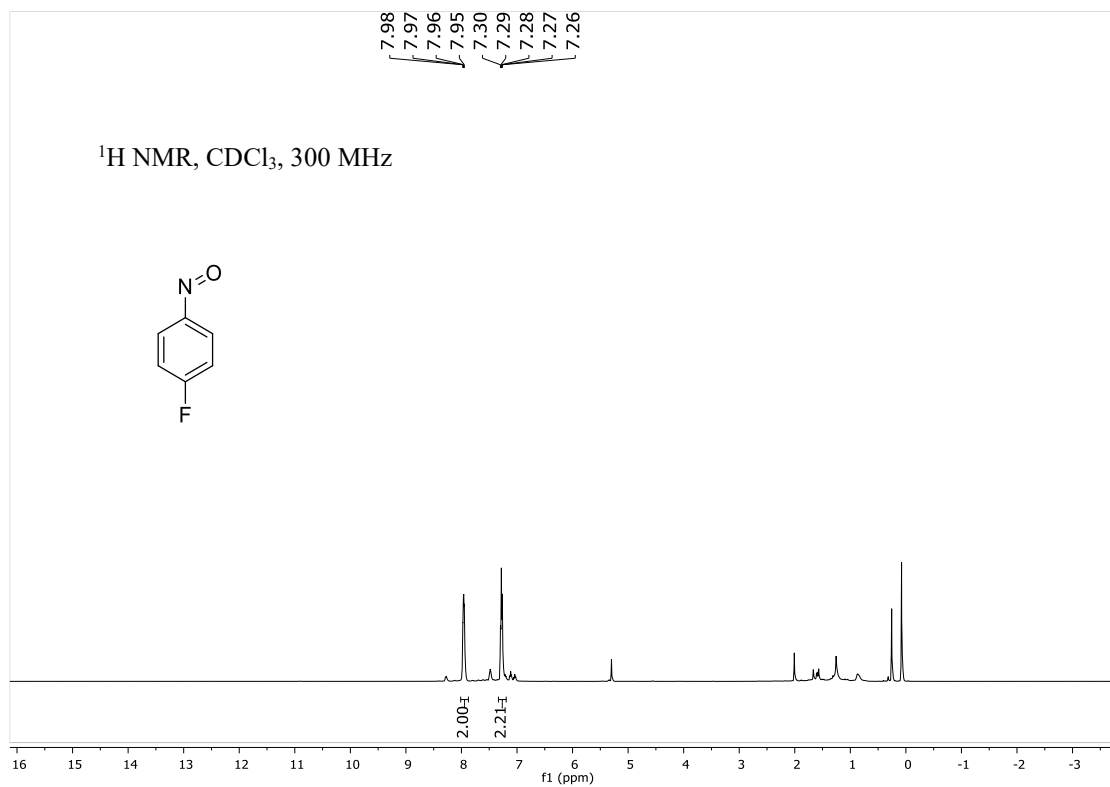


1-Methoxy-2-nitrosobenzene (2c)

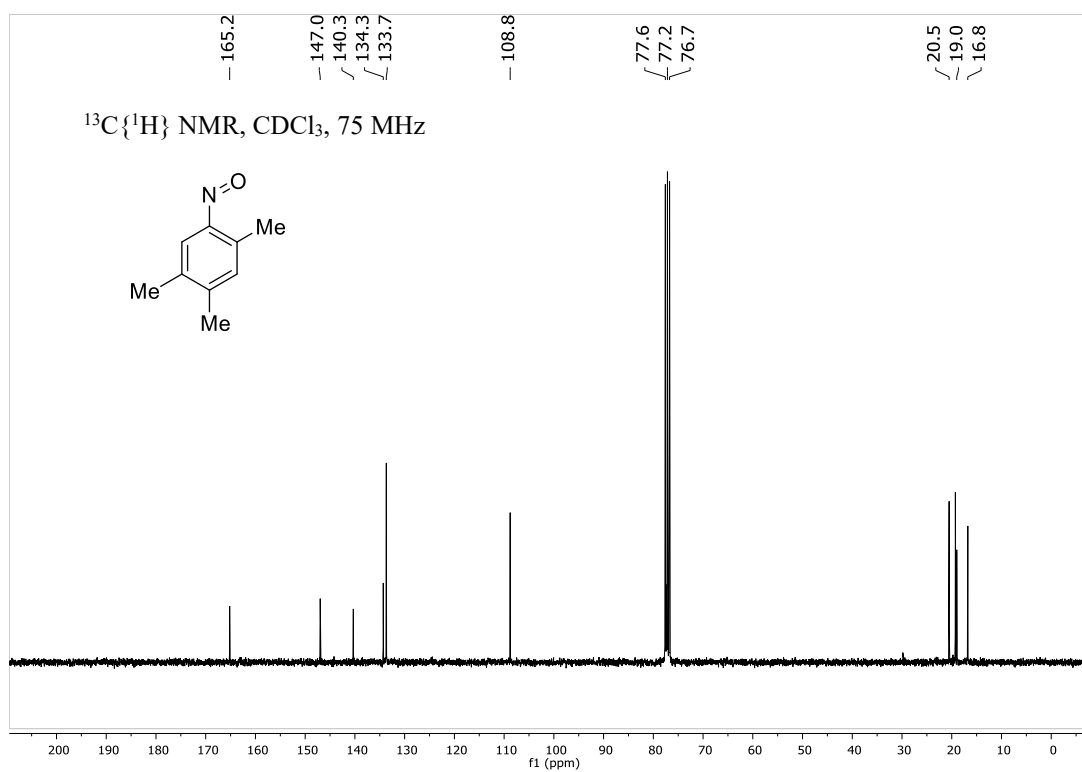
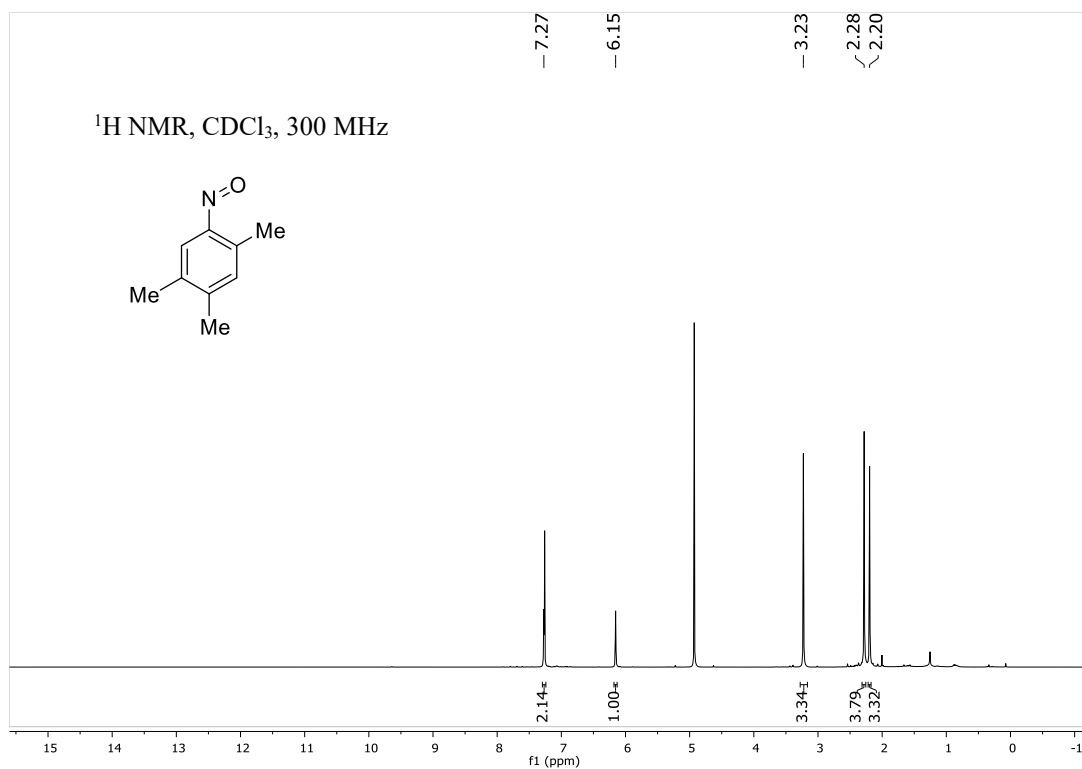


(4-Fluorophenyl)trimethylsilane (2d)

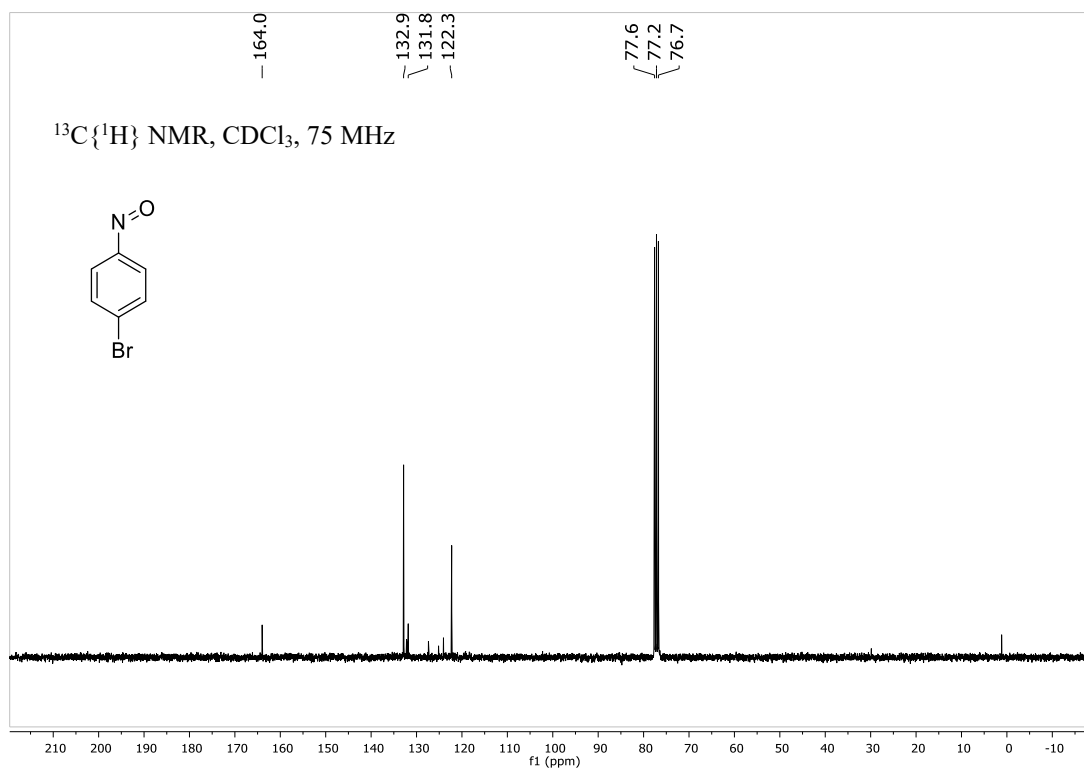
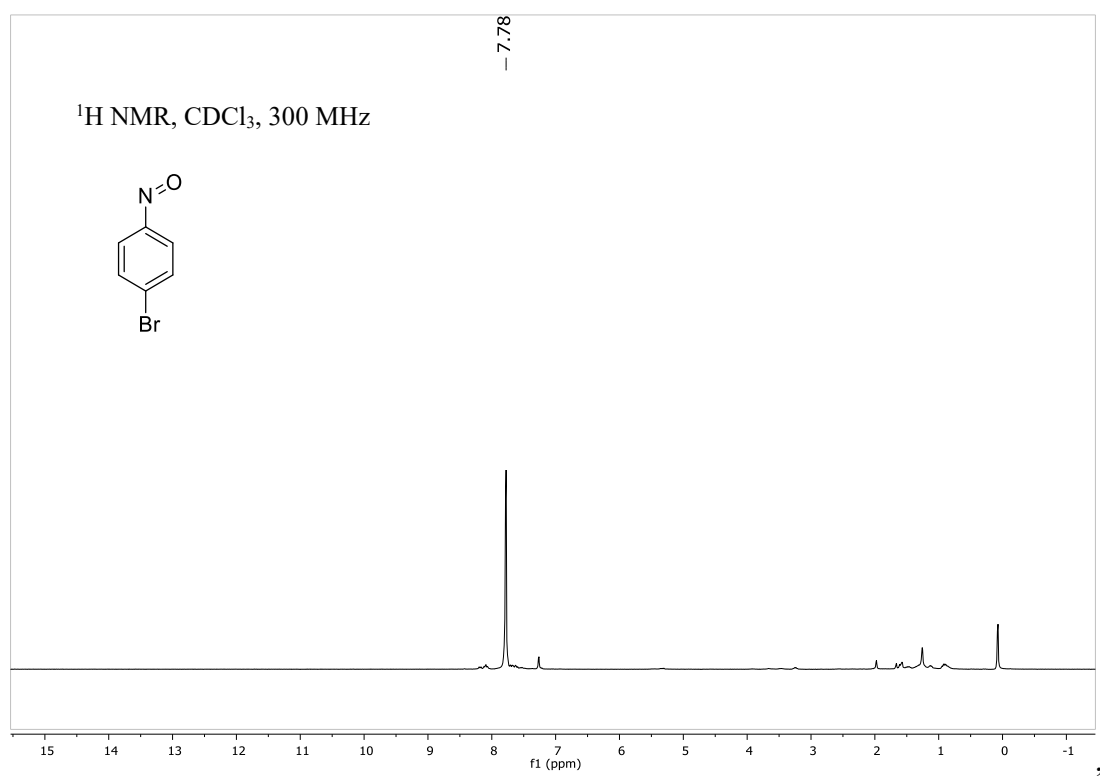
The product contains 5% of 1-fluoro-4-nitrobenzene **3d**.



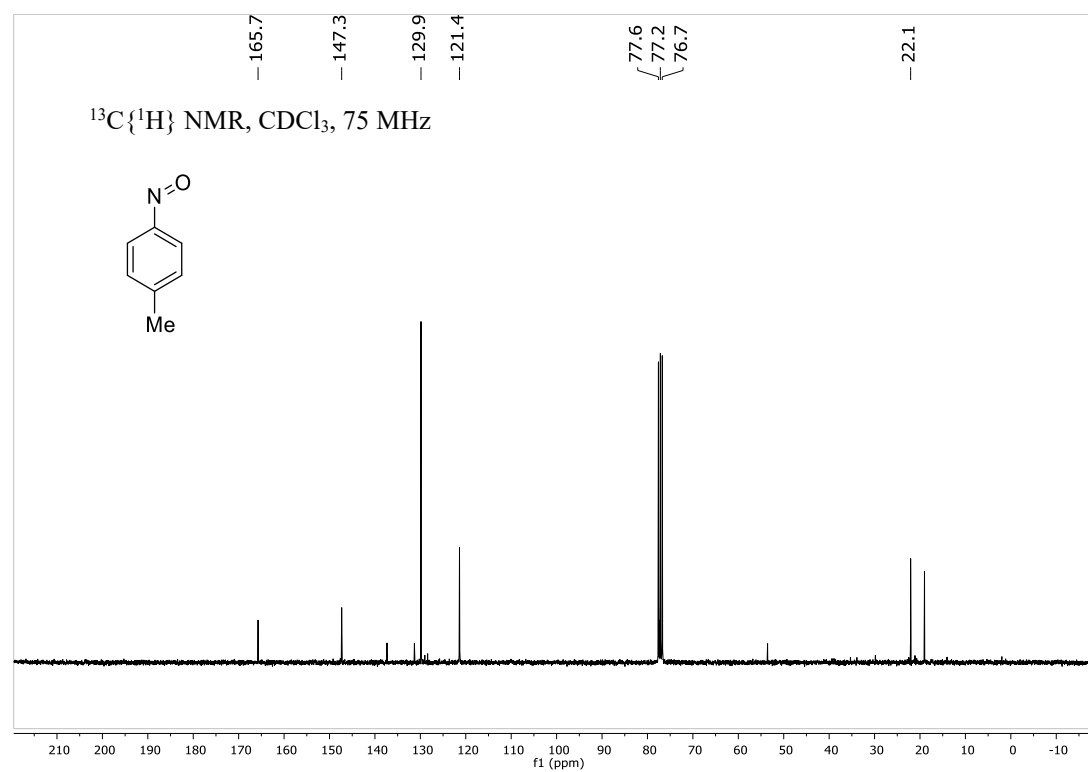
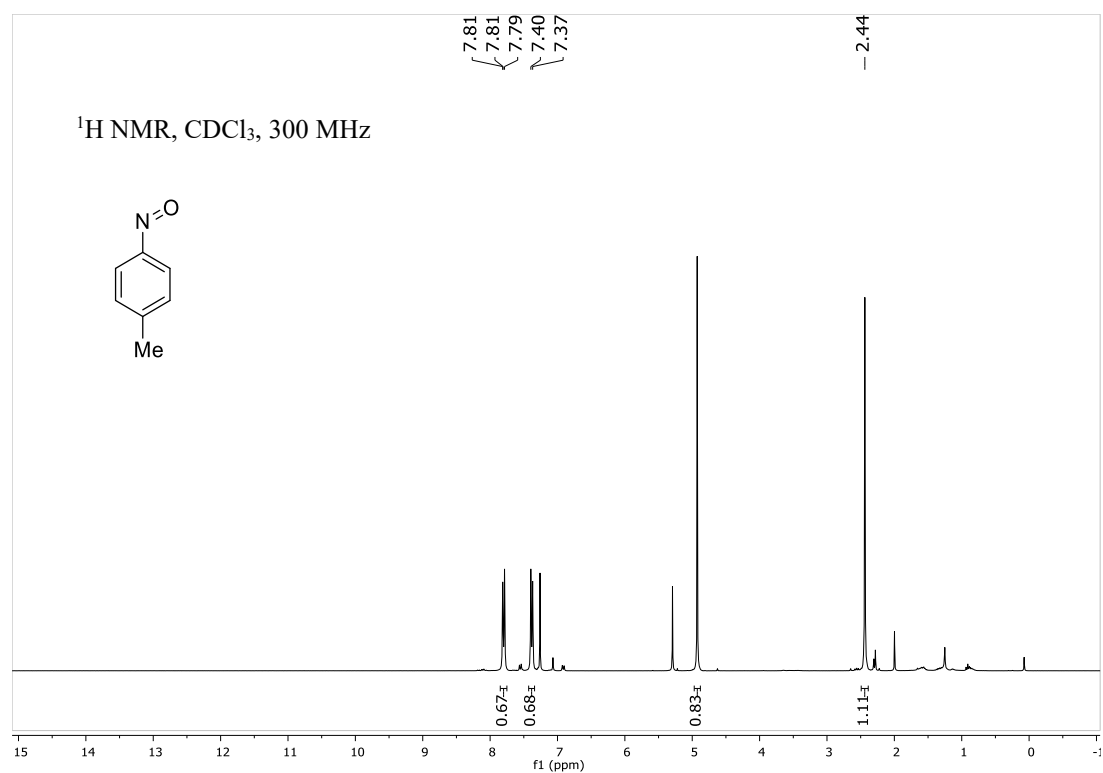
1,2,4-Trimethyl-5-nitrosobenzene (2f)



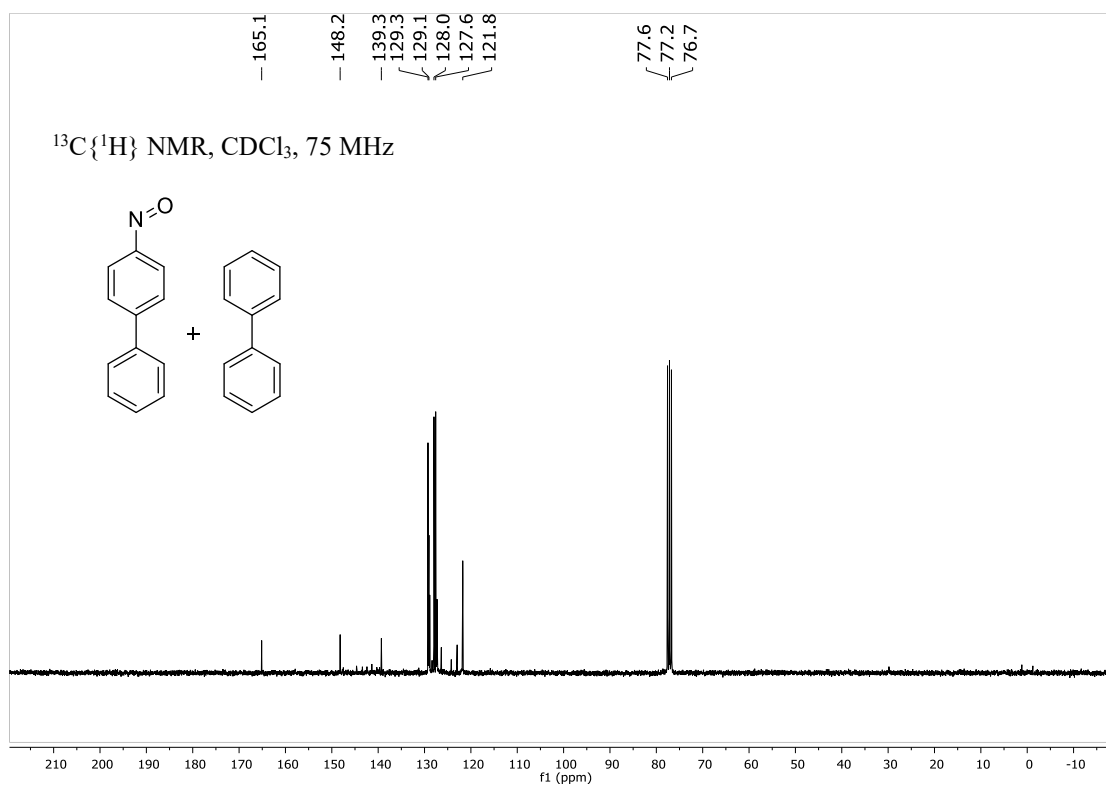
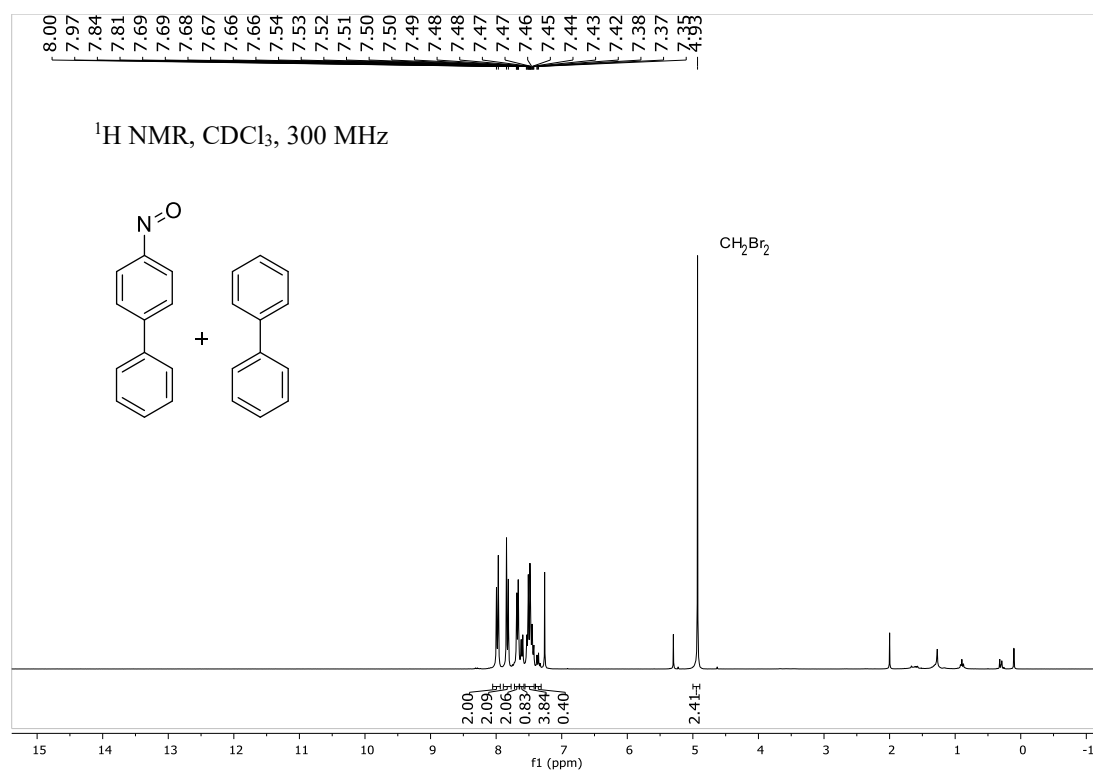
1-Bromo-4-nitrosobenzene (2g)



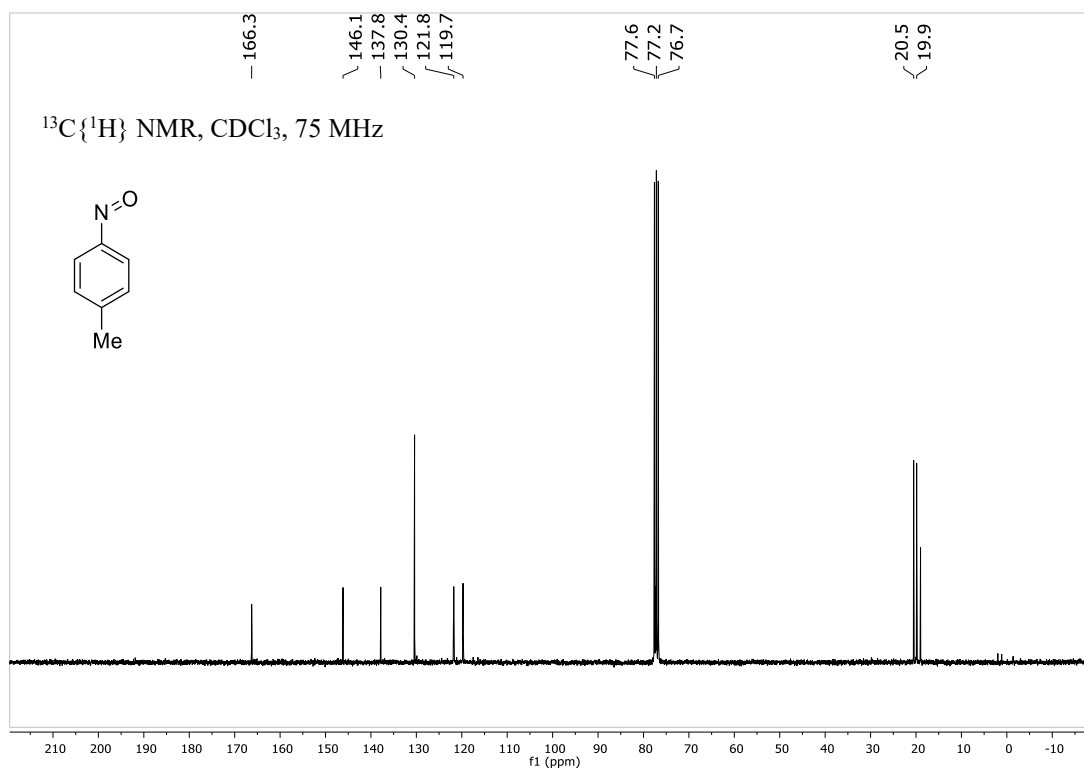
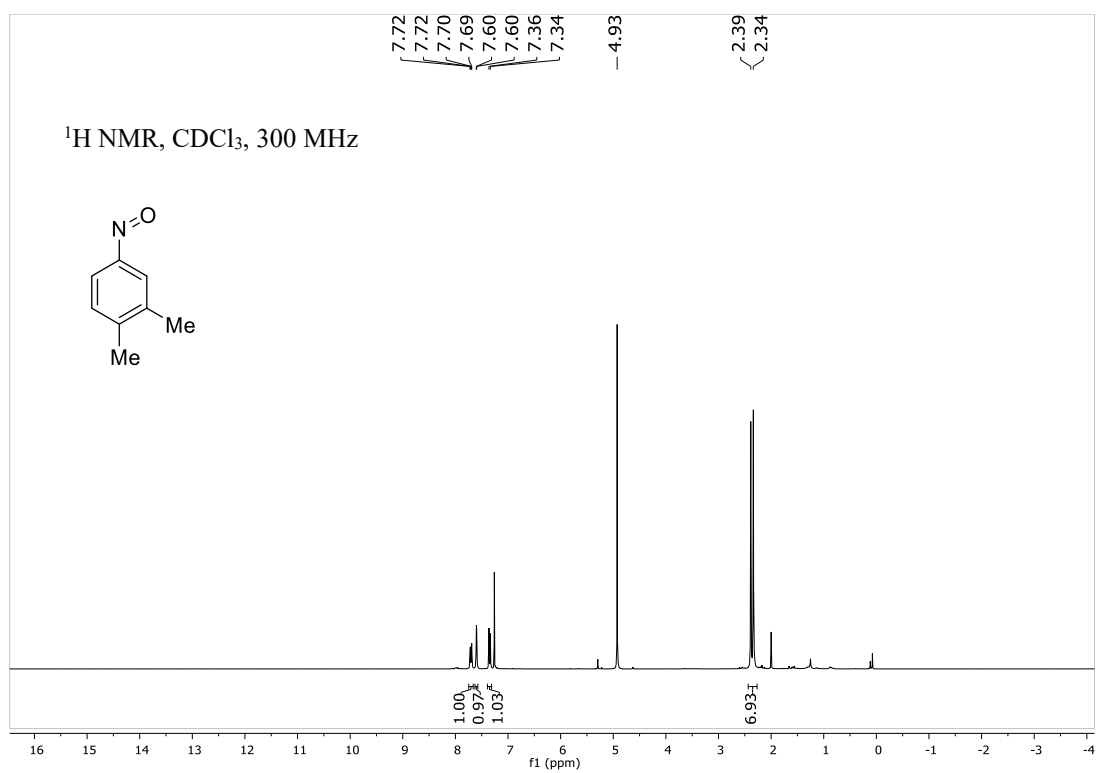
1-Methyl-4-nitrosobenzene (2h)



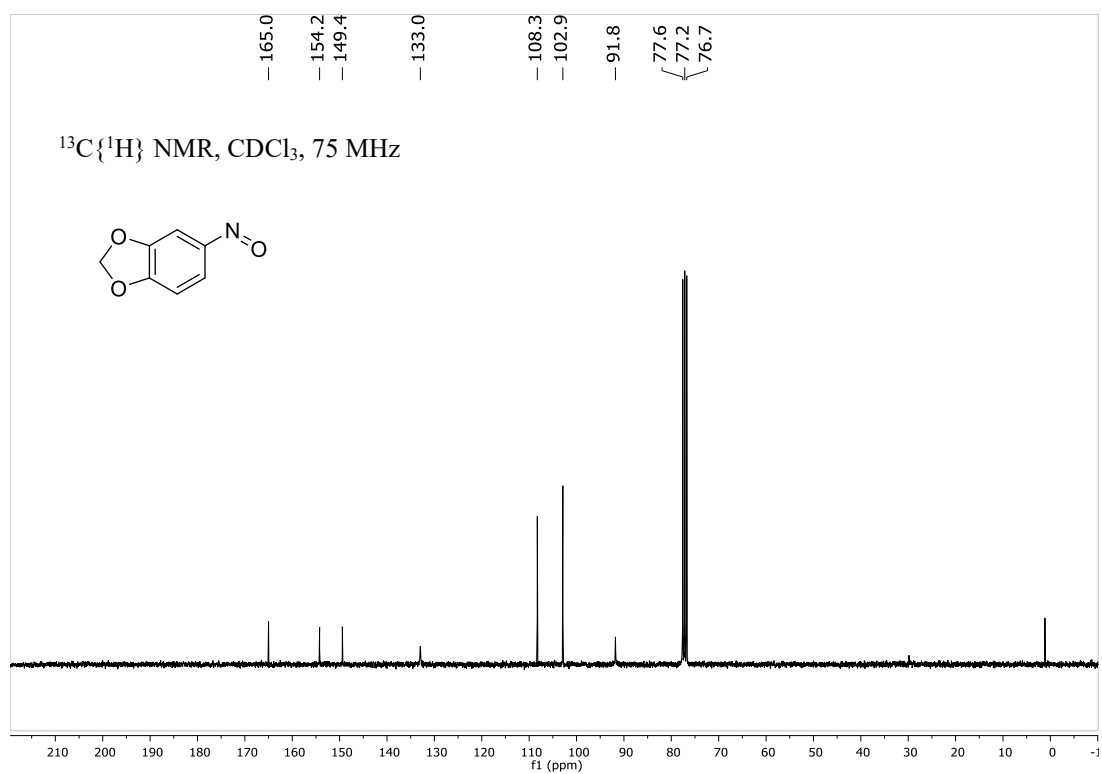
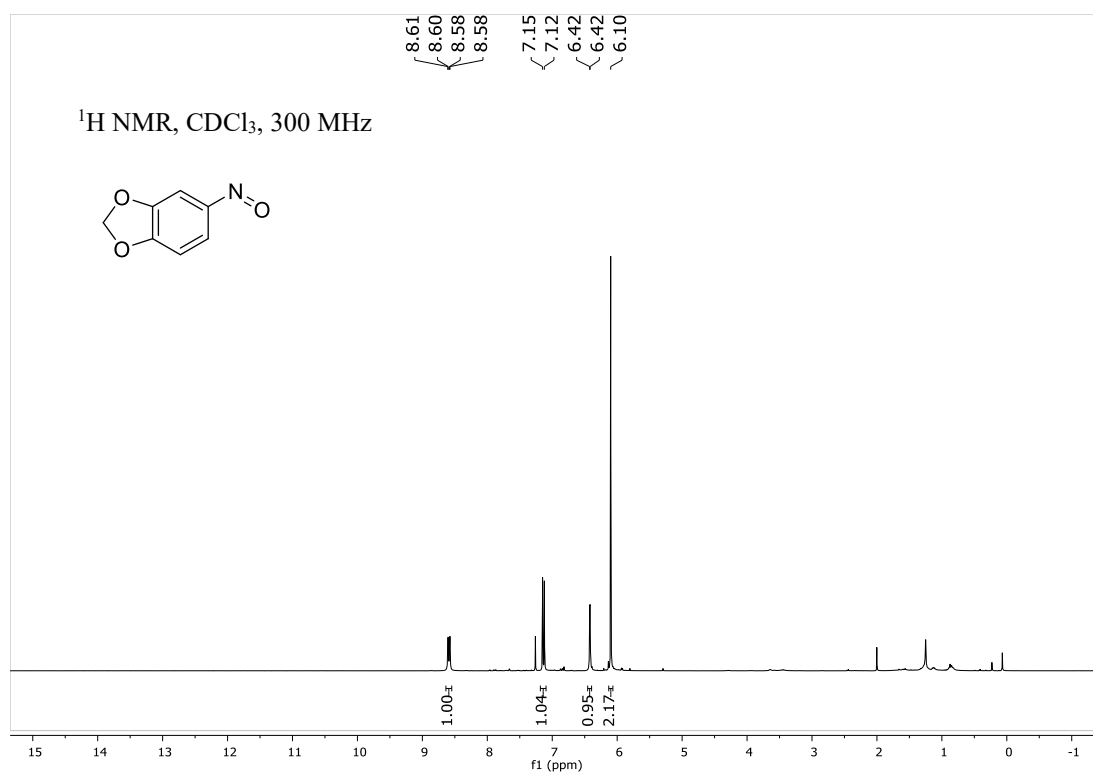
4-Nitroso-1,1'-biphenyl (2i)



1,2-Dimethyl-4-nitrosobenzene (2j)



5-Nitrosobenzo[d][1,3]dioxole (2k):



References

- [1] Lehmann, M.; Schulz, A.; Villinger, A. *Angew. Chem. Int. Ed.* **2009**, *48*, 7444–7447.