

Electronic Supplementary Information

Electro-oxidative coupling of Bunte salts with aryldiazonium tetrafluoroborates: A benign access to unsymmetrical sulfoxides

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Table of Contents

1. Electrochemical Apparatus / Electrode Materials	S2
2. Cyclic Voltammetry Study	S2-S3
3. Copies of ¹H, ¹⁹F, and ¹³C Spectra of the Products 3a-3t and 6a	S4-S26
4. HRMS Data of the TEMPO Adducts 4 and 5	S27
5. Crystallographic Data	S28-S29

1. Electrochemical Apparatus / Electrode Materials:

All the reactions and cyclic voltametric (CV) investigations were performed using an IKA ElectraSyn 2.0 system [Figure S1]. The graphite (SK-50) electrode (8 x 52.5 x 2 mm), platinum electrode (8 x 52.5 x 2 mm), glassy carbon electrode, and Ag/AgCl reference electrode were used as furnished in the Electrochemistry Kit by the IKA India Private Limited.



Figure S1. IKA ElectraSyn 2.0 System

2. Cyclic Voltammetry Study:

The cyclic voltammetry was recorded at room temperature using glassy carbon as working electrode, Pt as counter electrode, and Ag/AgCl as reference electrode with $n\text{-Bu}_4\text{NBF}_4$ (0.1M) as supporting electrolyte in DMF: H_2O (9:1 v/v) at a scan rate of 100 mV s^{-1} by the IKA ElectraSyn 2.0. The concentration of both the benzyl thiosulfate salt (**1a**) and 4-fluorobenzenediazonium tetrafluoroborate (**2d**) was maintained to be 10 mM for the cyclic voltammetry investigations.

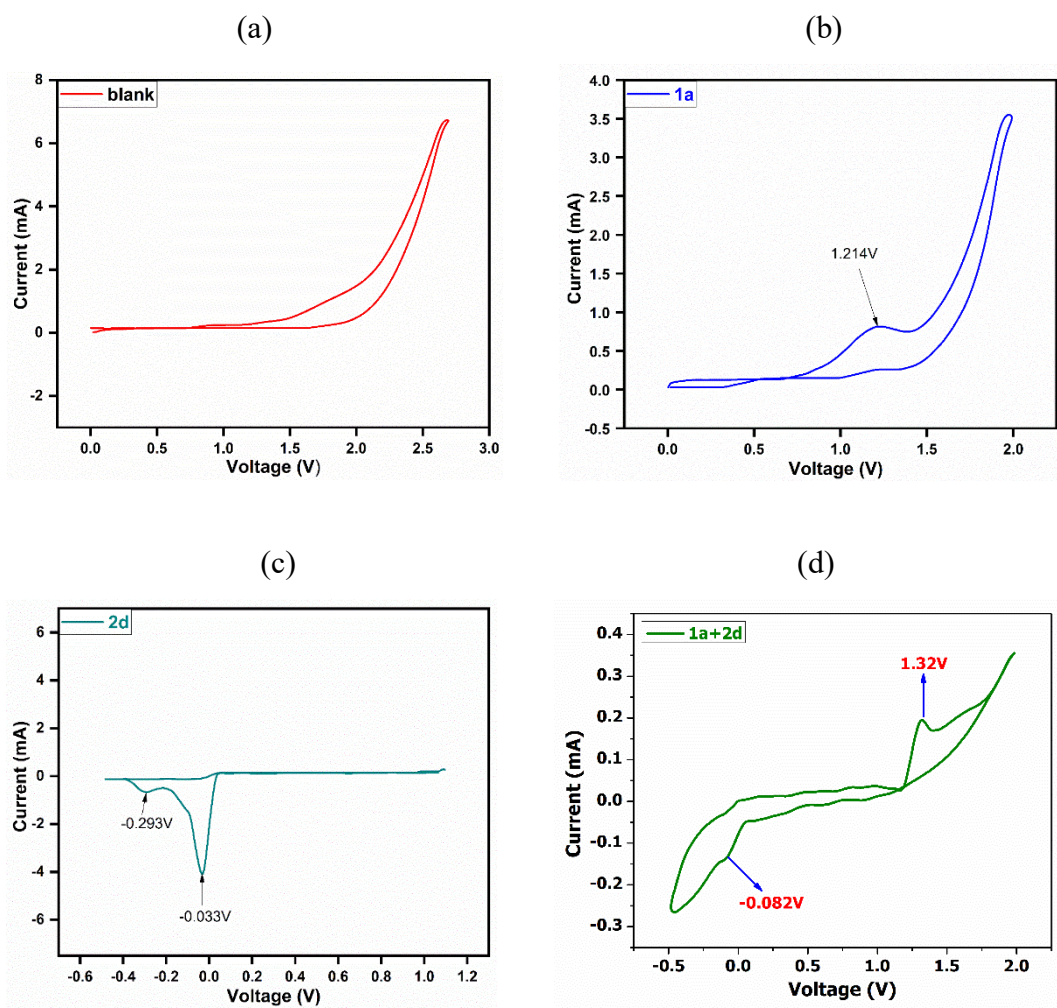
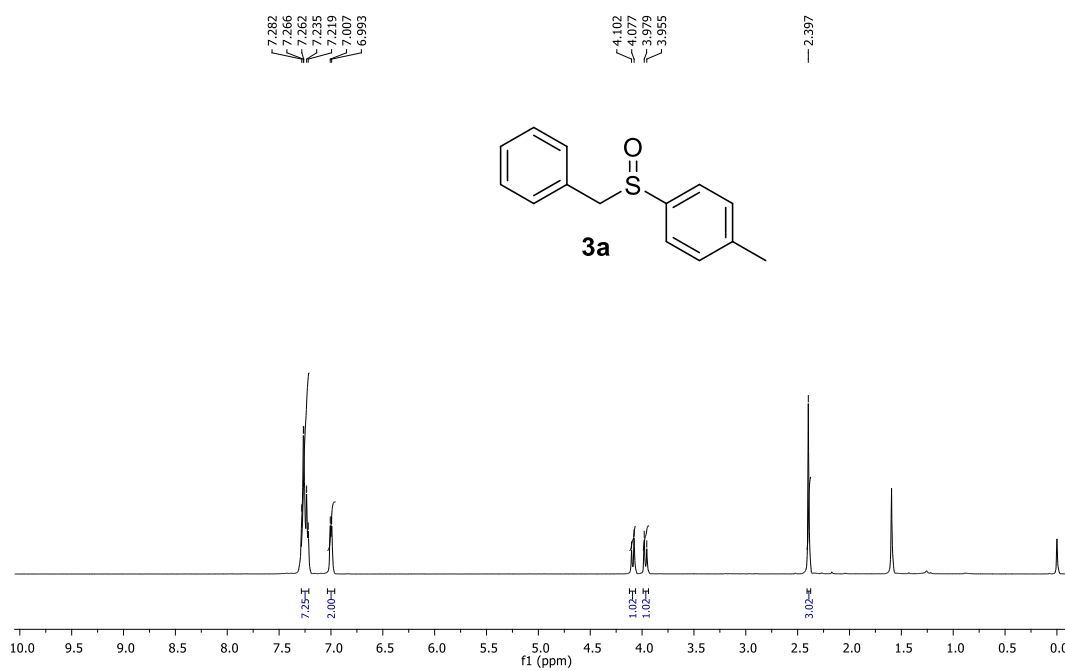


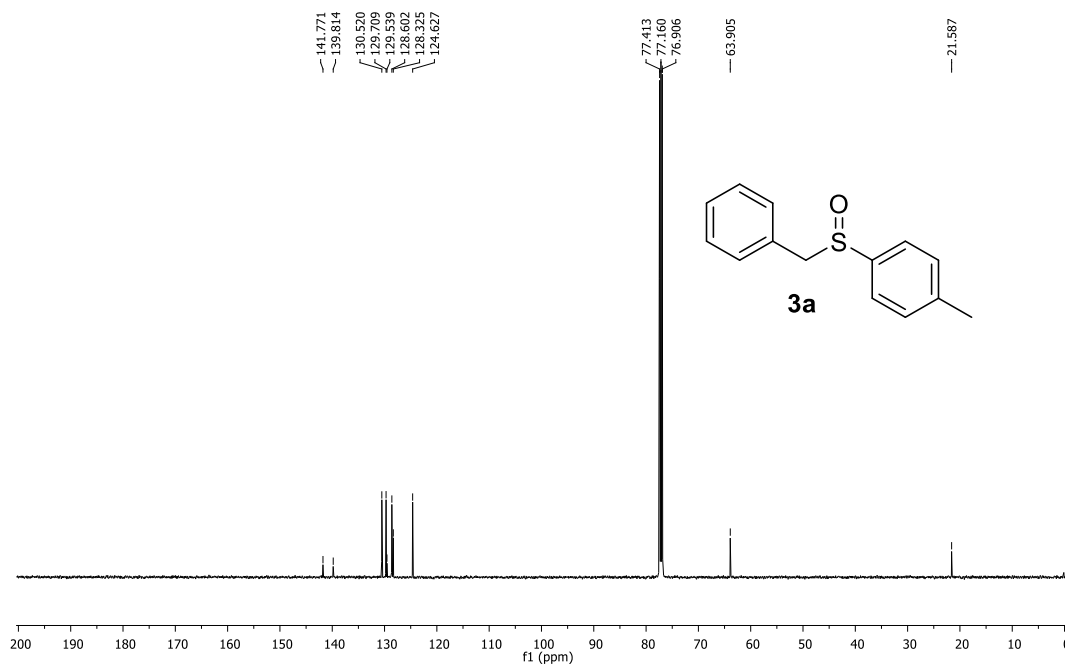
Figure S2: (a) CV of $n\text{Bu}_4\text{NBF}_4$ (0.1M) in DMF: H_2O at a scan rate of 100 mVs^{-1} vs Ag/AgCl. (b) CV of benzyl thiosulfate salt (**1a**) using 0.1M $n\text{Bu}_4\text{NBF}_4$ / DMF: H_2O at a scan rate of 100 mVs^{-1} vs Ag/AgCl. (c) CV of 4-fluorobenzenediazonium tetrafluoroborate (**2d**) in 0.1M $n\text{Bu}_4\text{NBF}_4$ / DMF: H_2O at a scan rate of 100 mVs^{-1} vs Ag/AgCl. (d) CV of the mixture of **1a** with **2d** in 0.1M $n\text{Bu}_4\text{NBF}_4$ / DMF: H_2O at a scan rate of 100 mVs^{-1} vs Ag/AgCl.

3. Copies of ^1H , ^{19}F , and ^{13}C Spectra of the Products 3

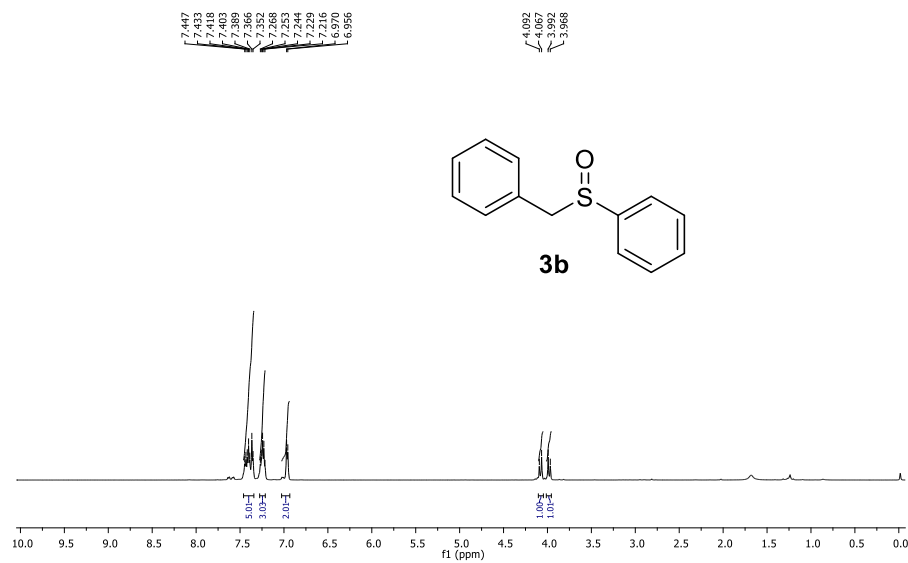
^1H NMR (500 MHz, CDCl_3)



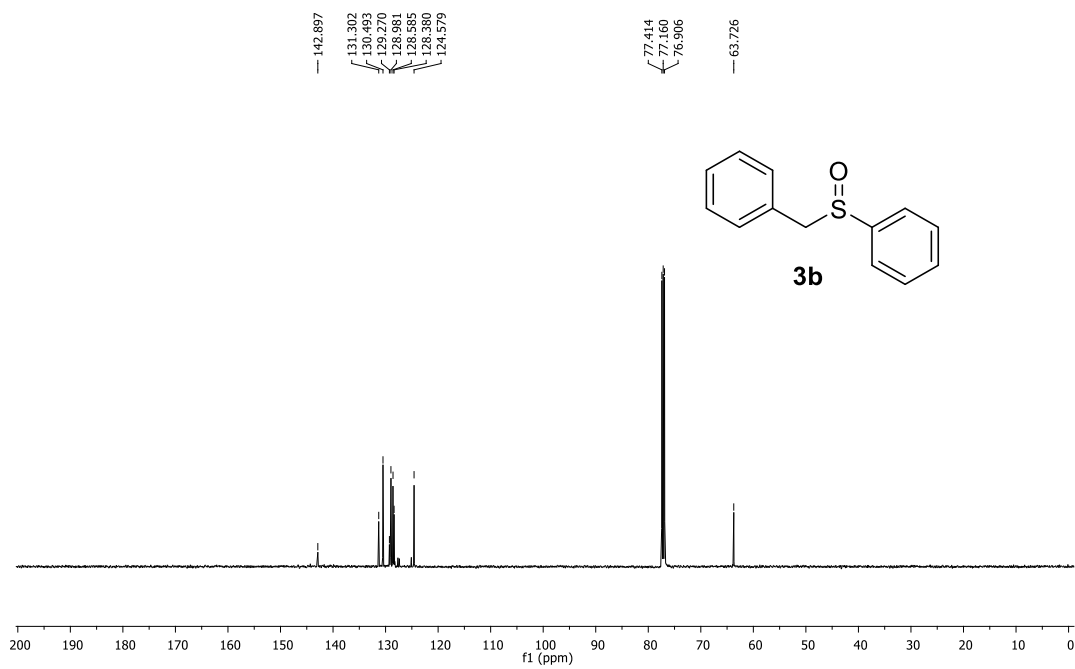
^{13}C NMR (126 MHz, CDCl_3)



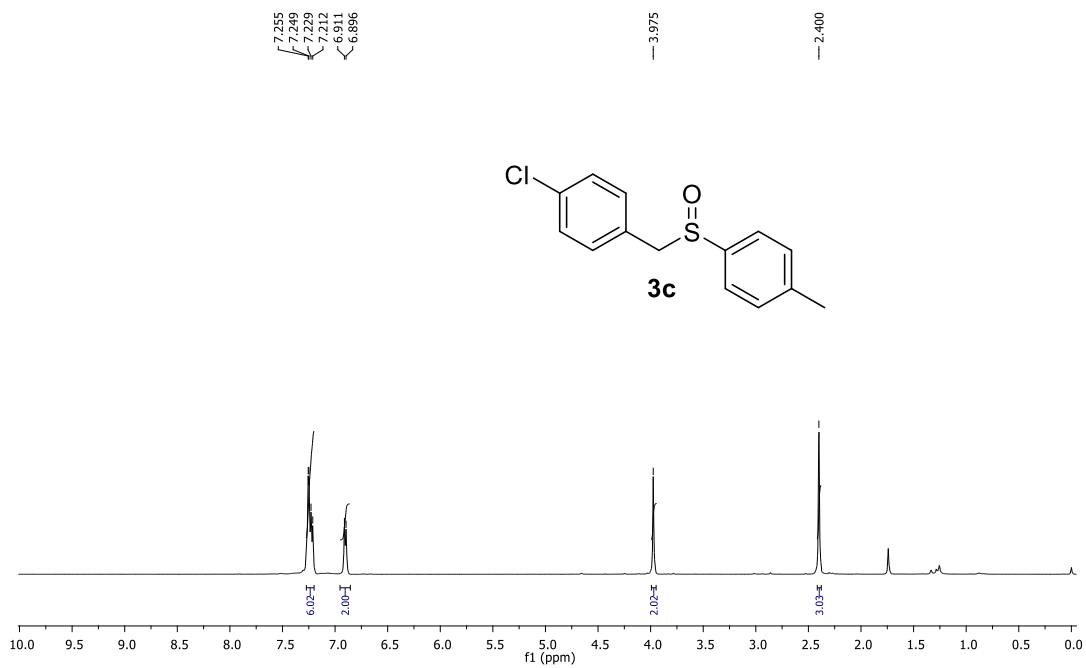
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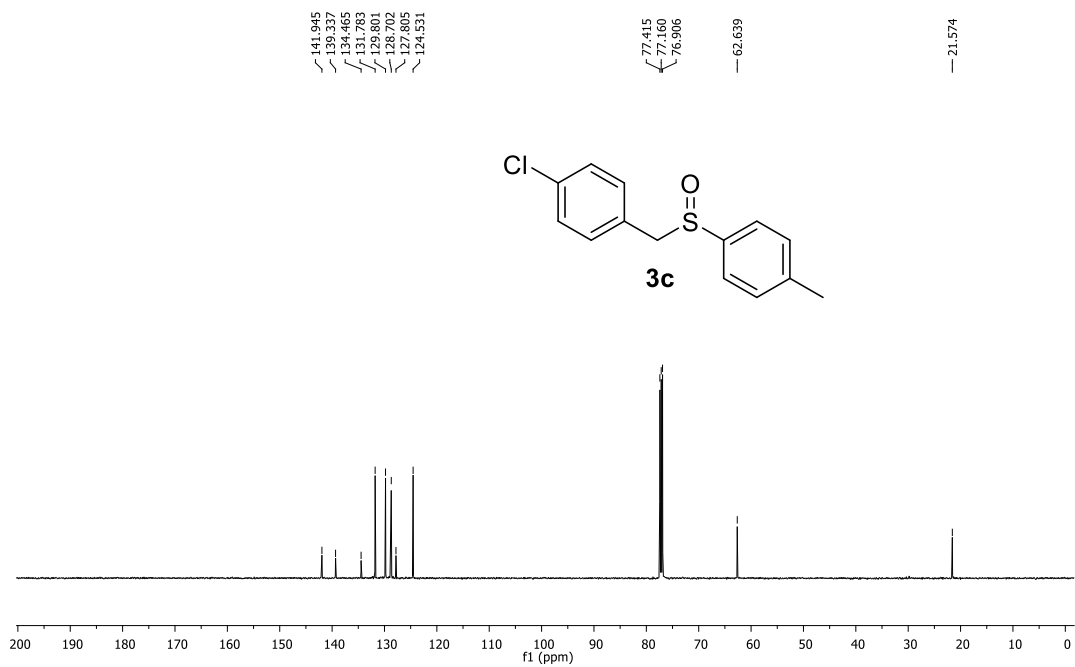
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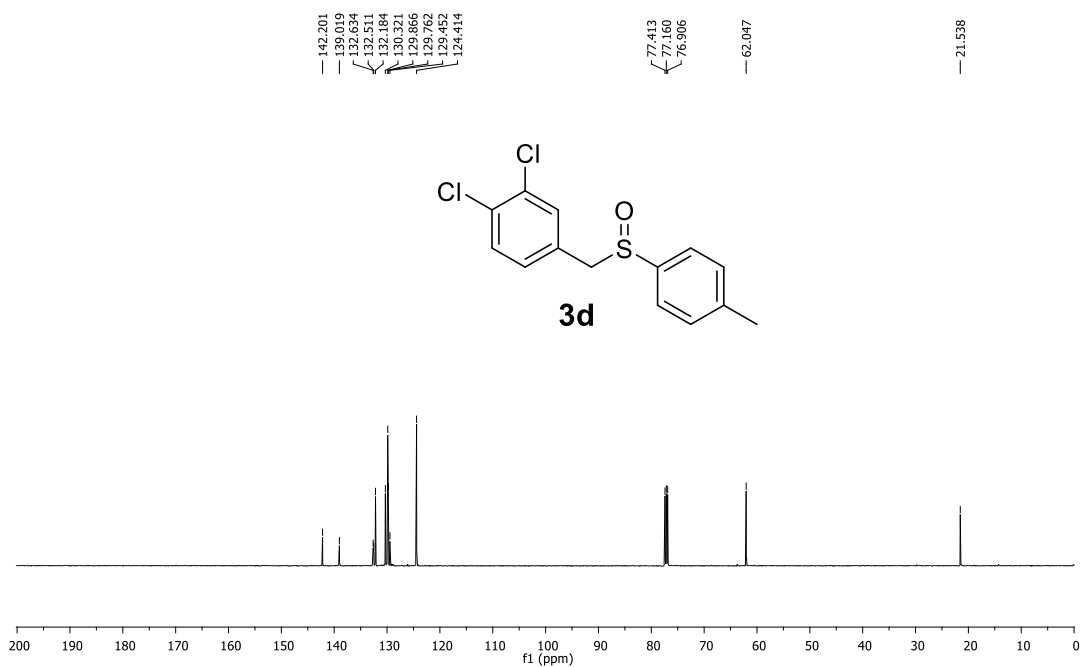
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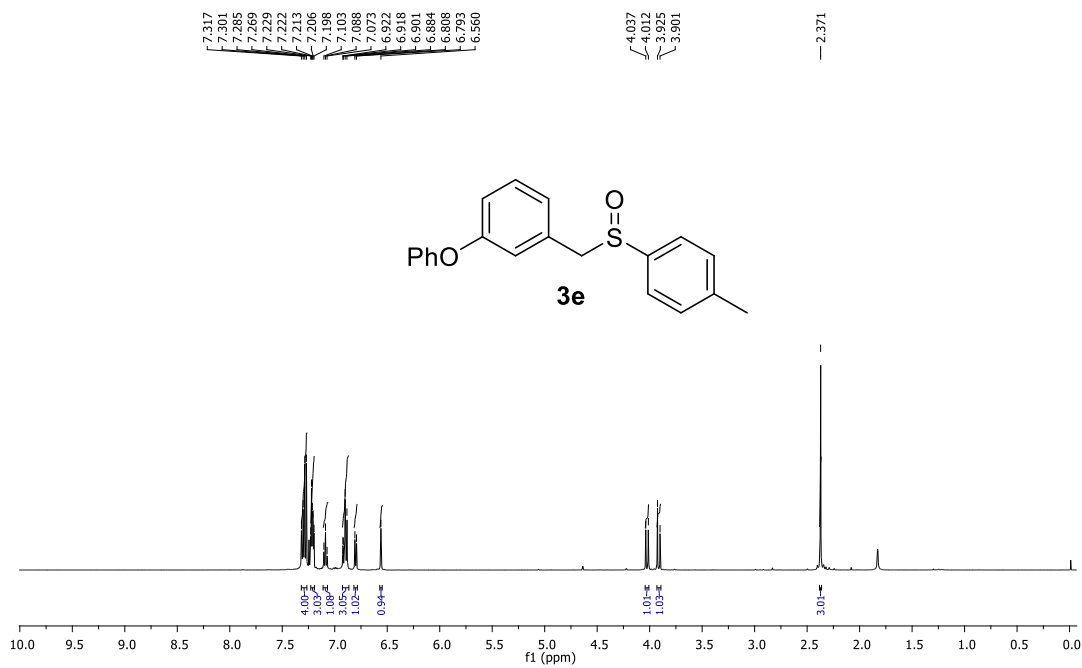
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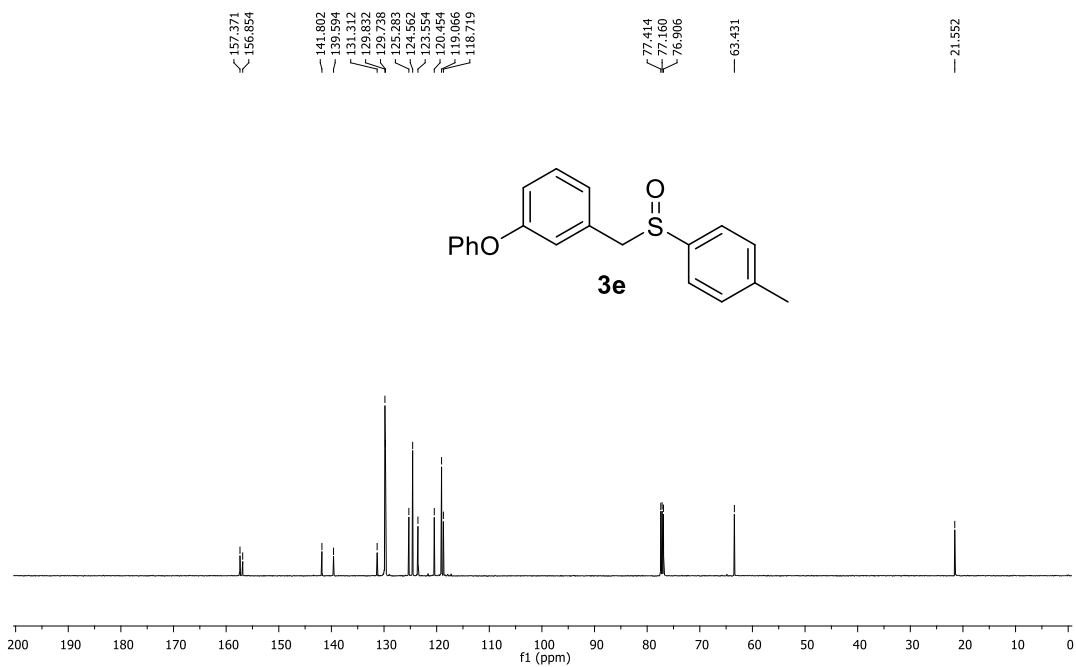
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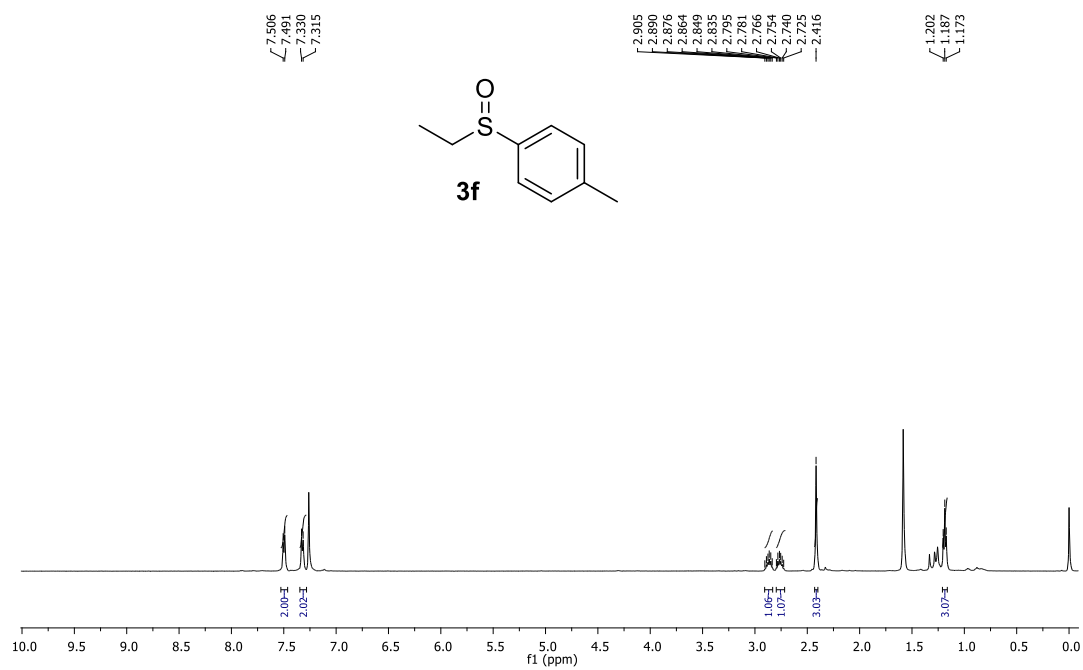
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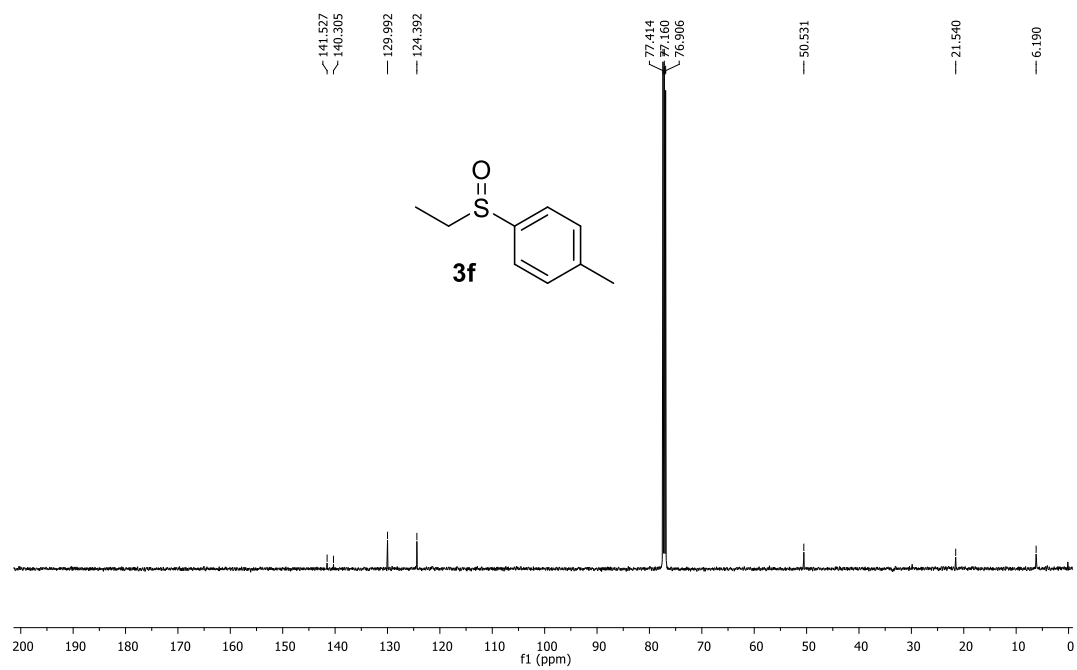
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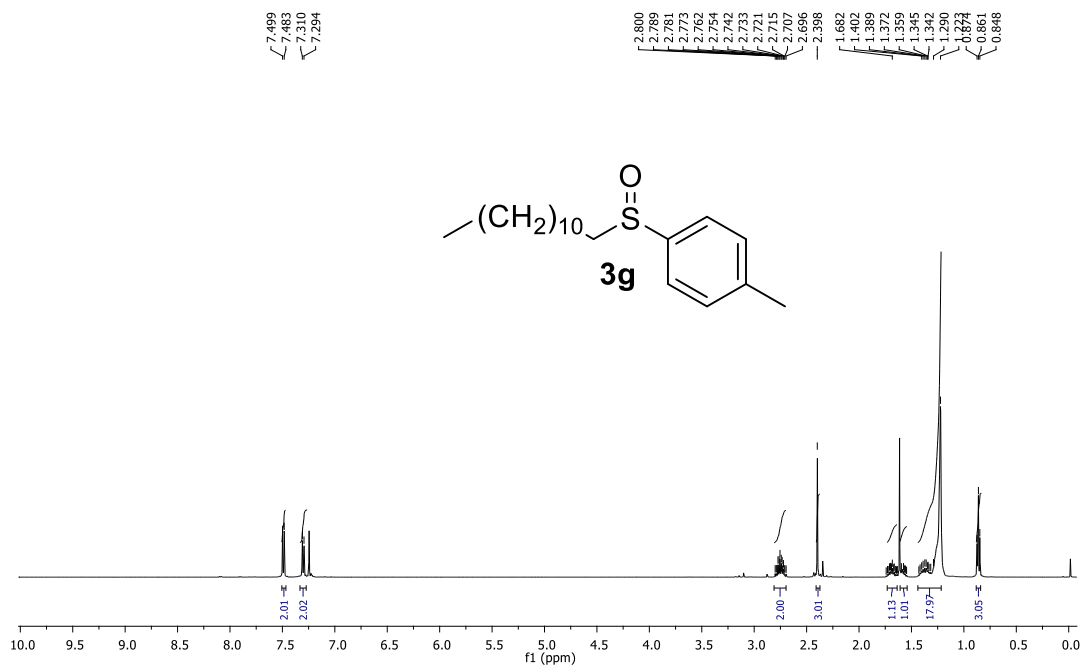
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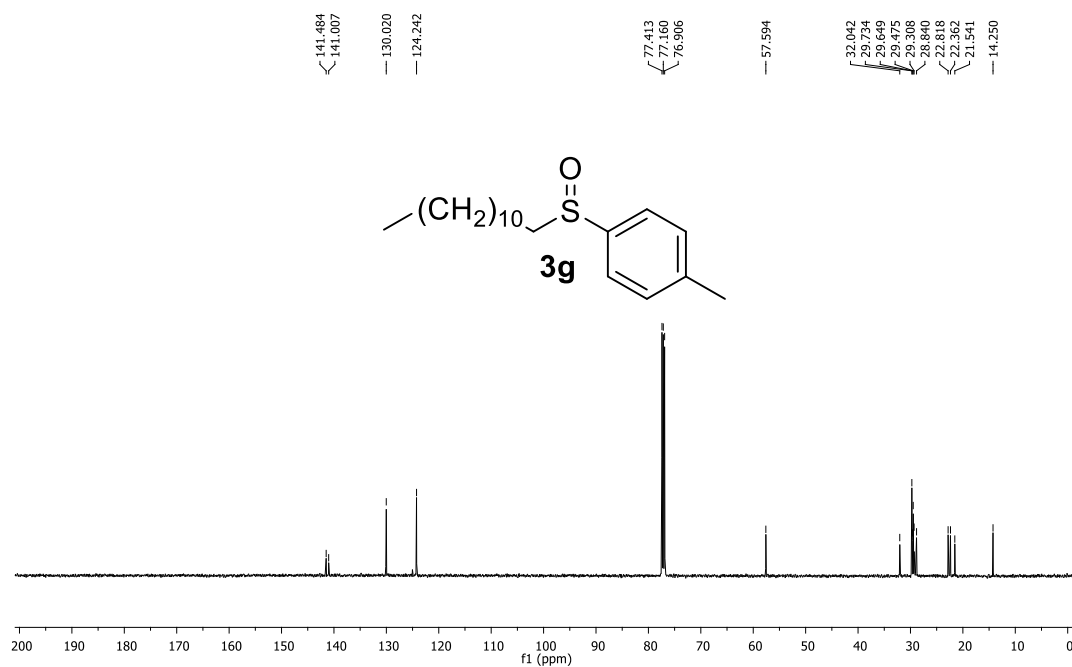
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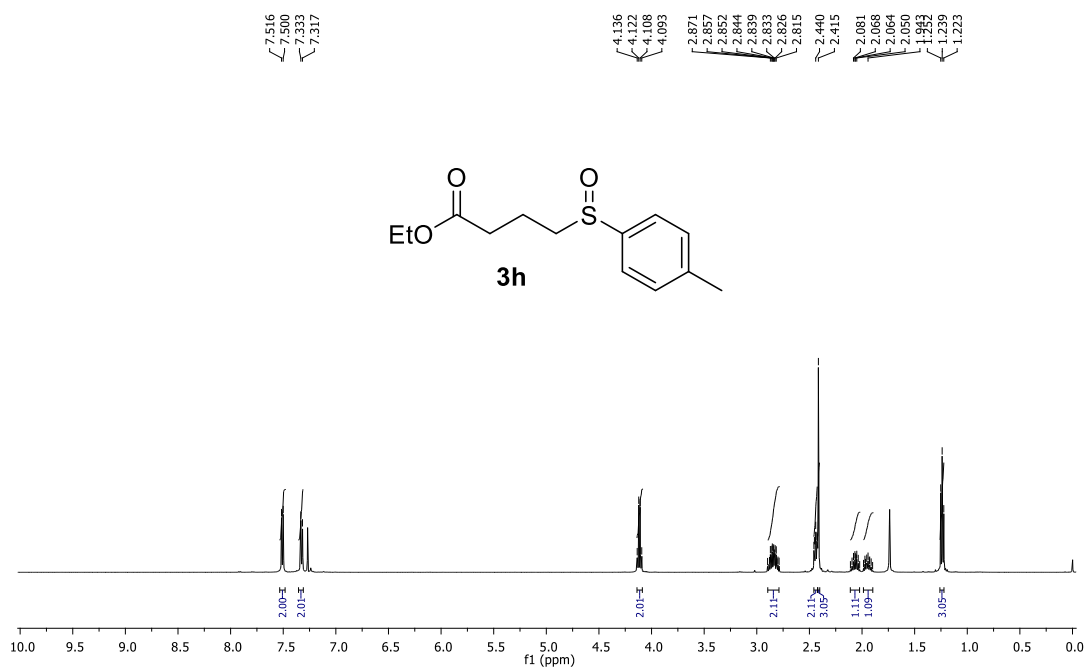
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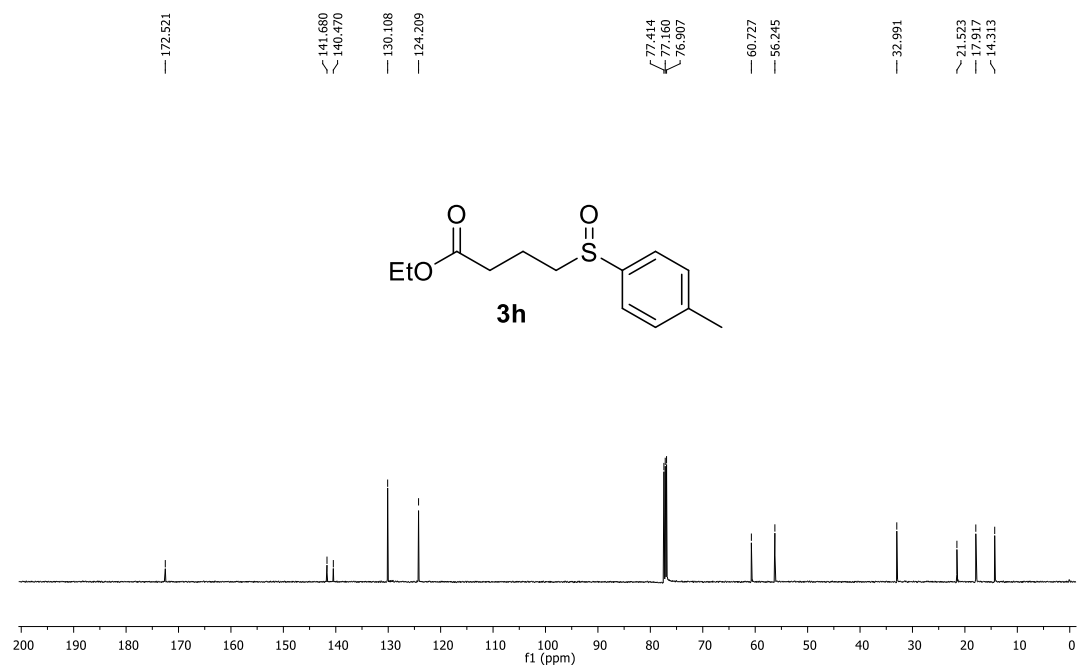
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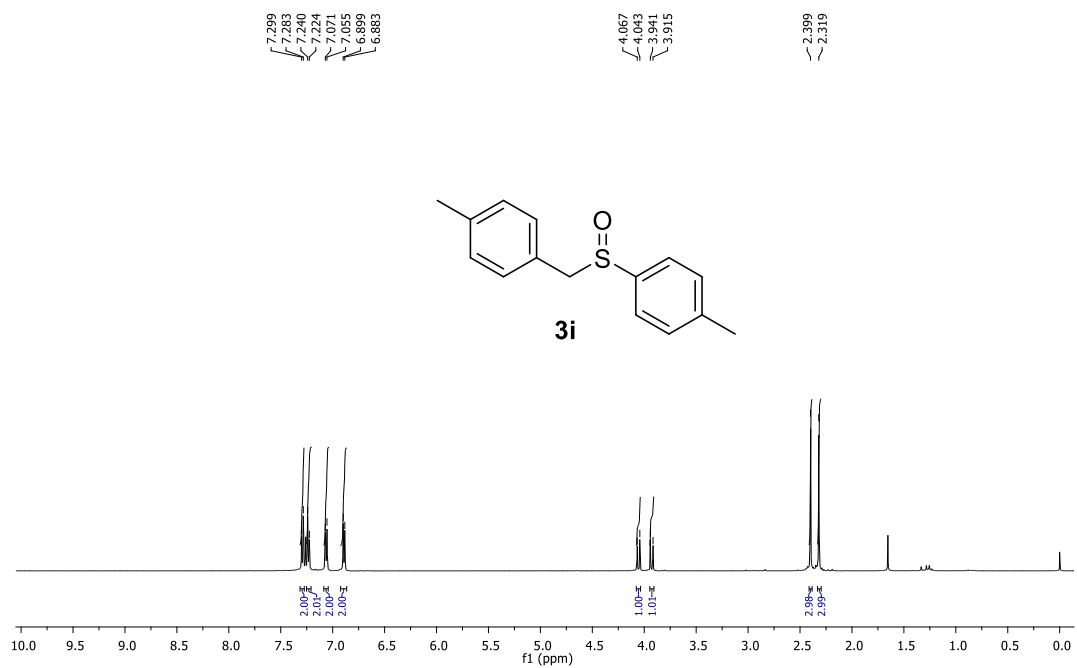
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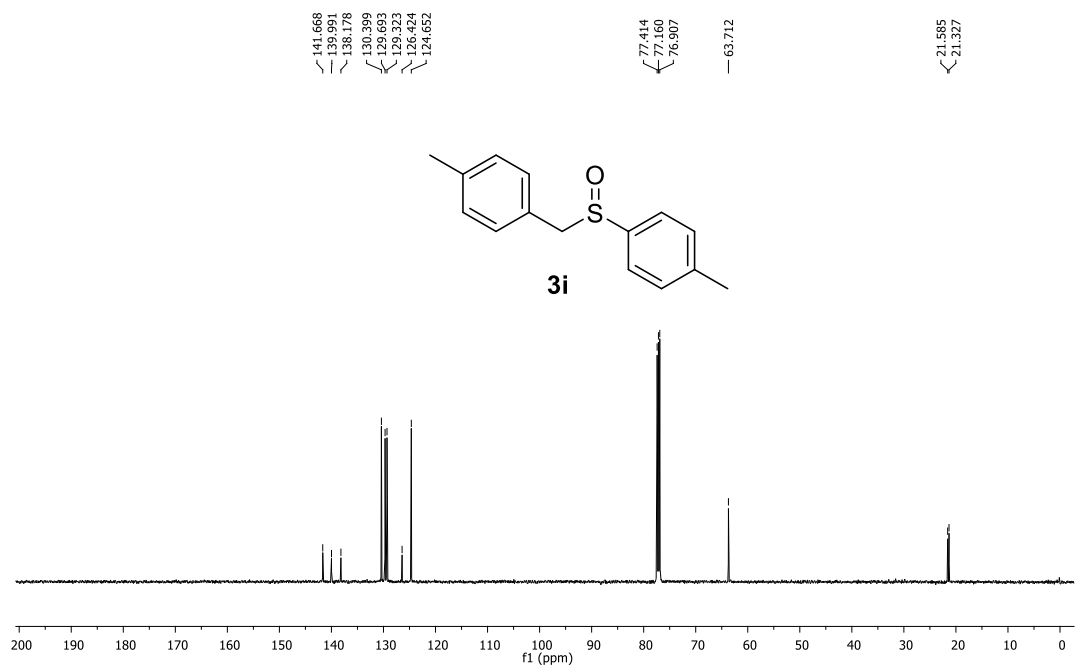
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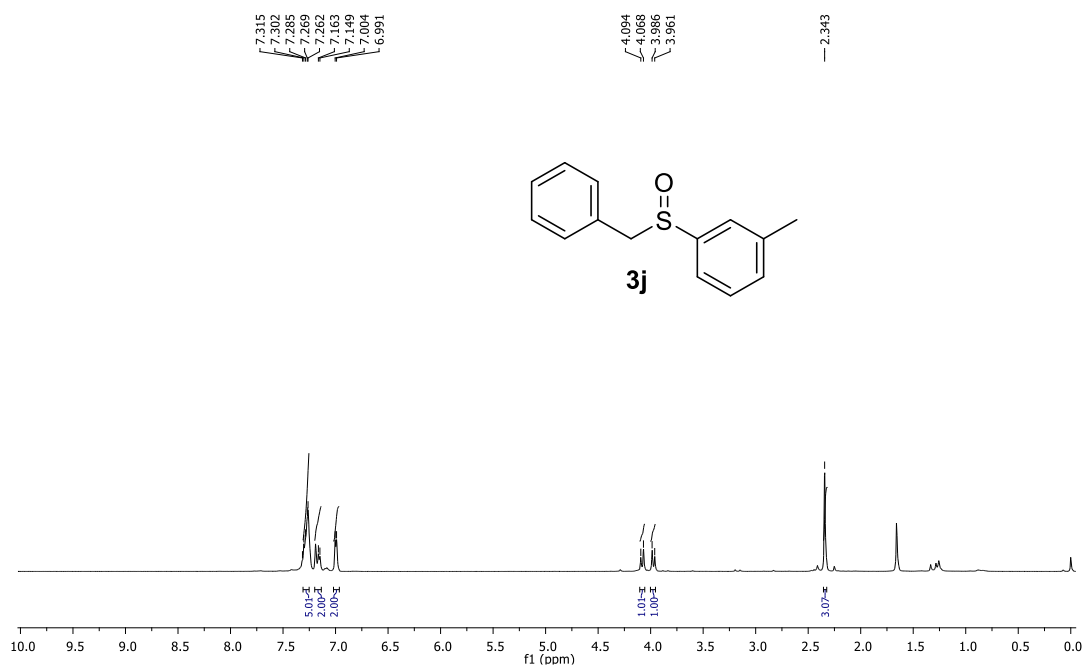
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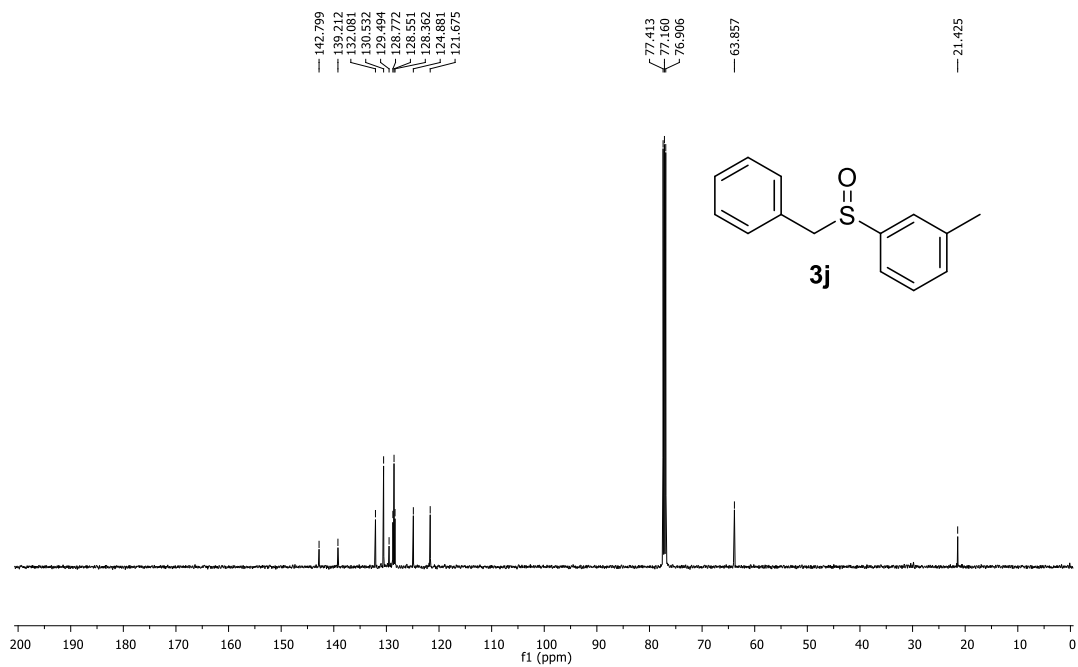
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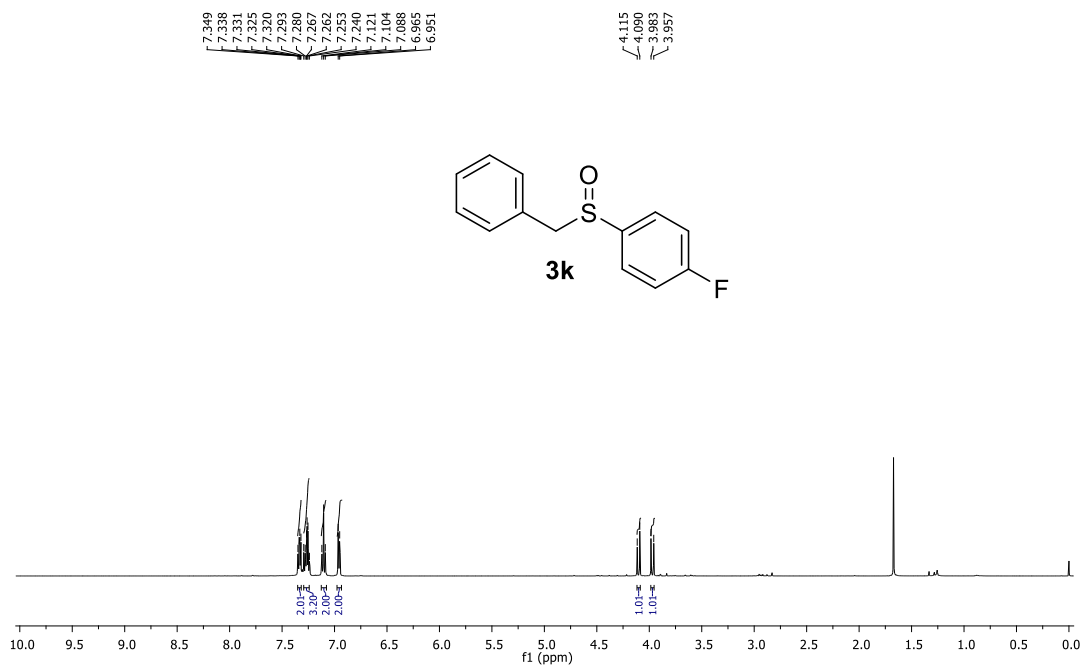
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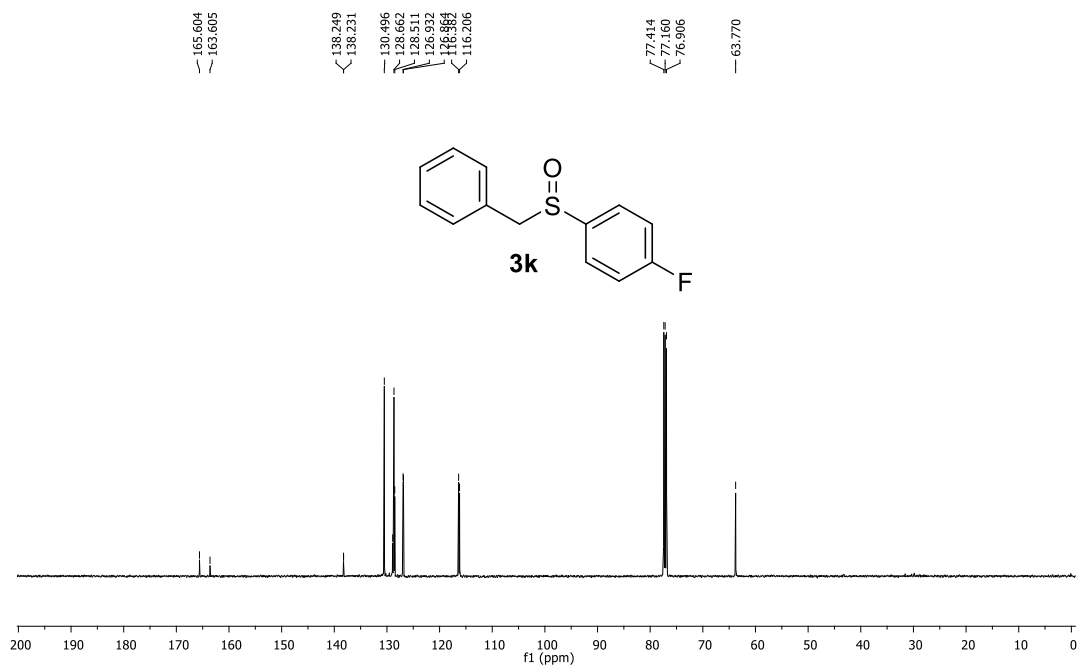
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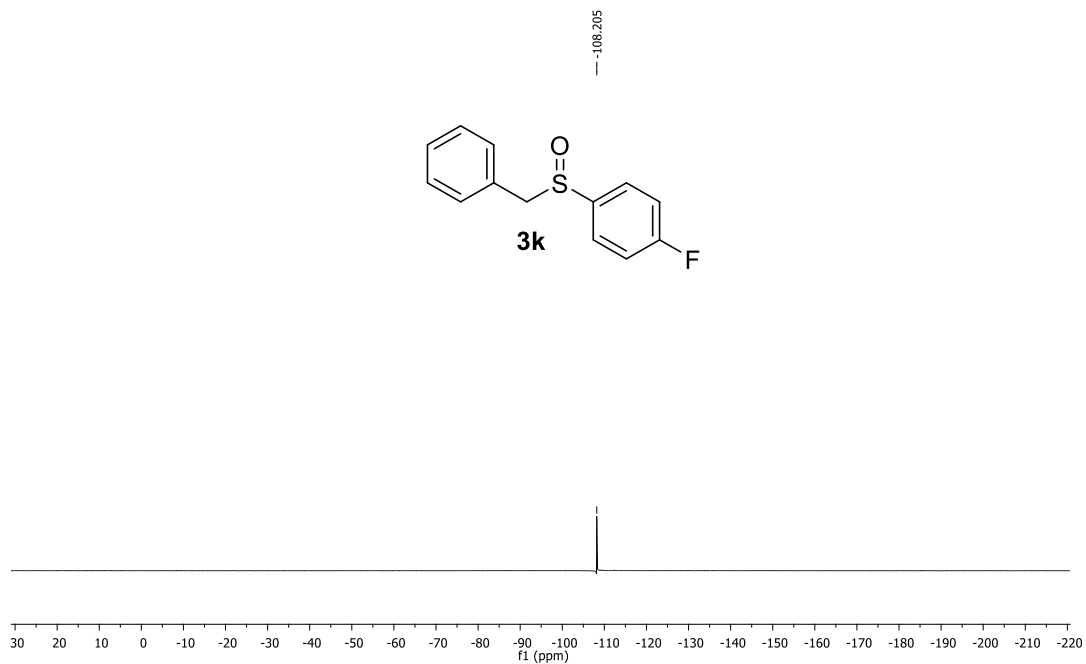
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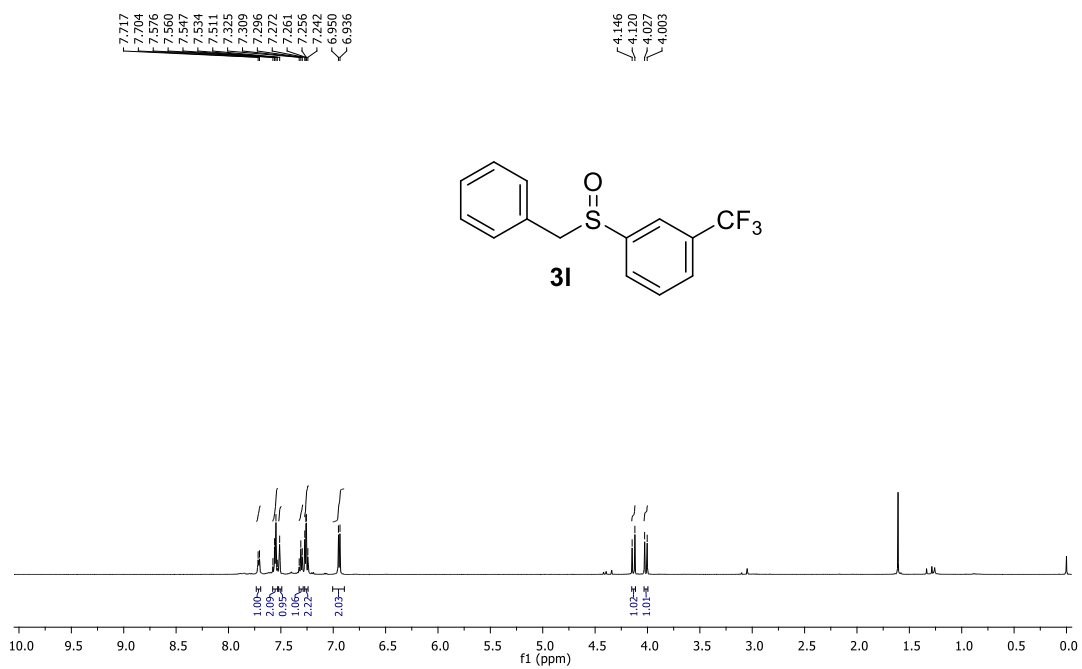
^{13}C NMR (126 MHz, CDCl_3)



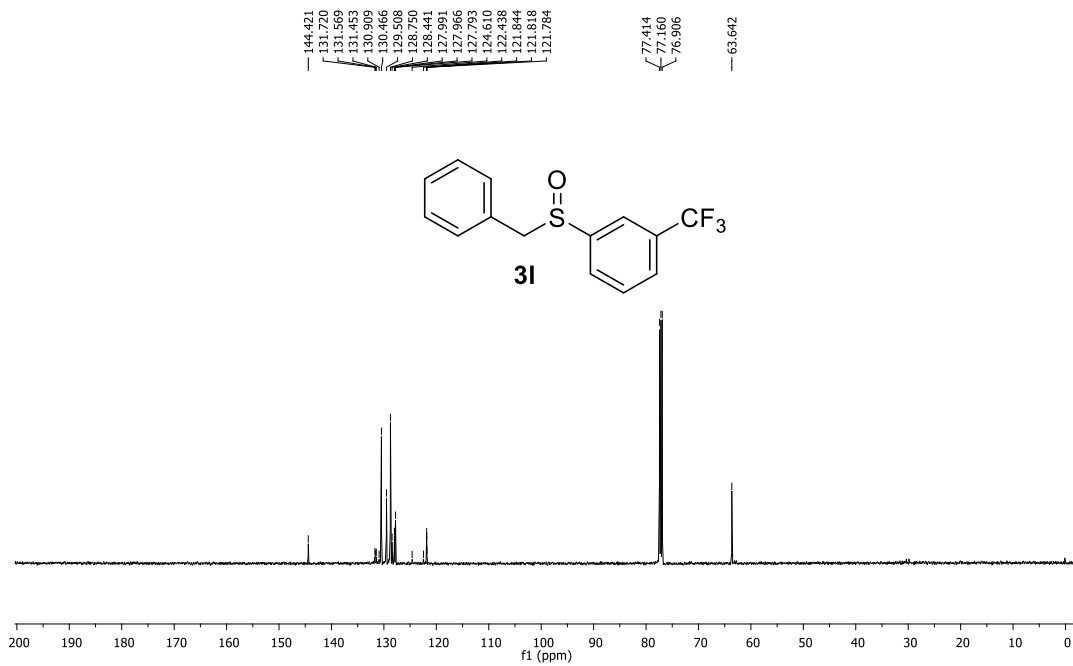
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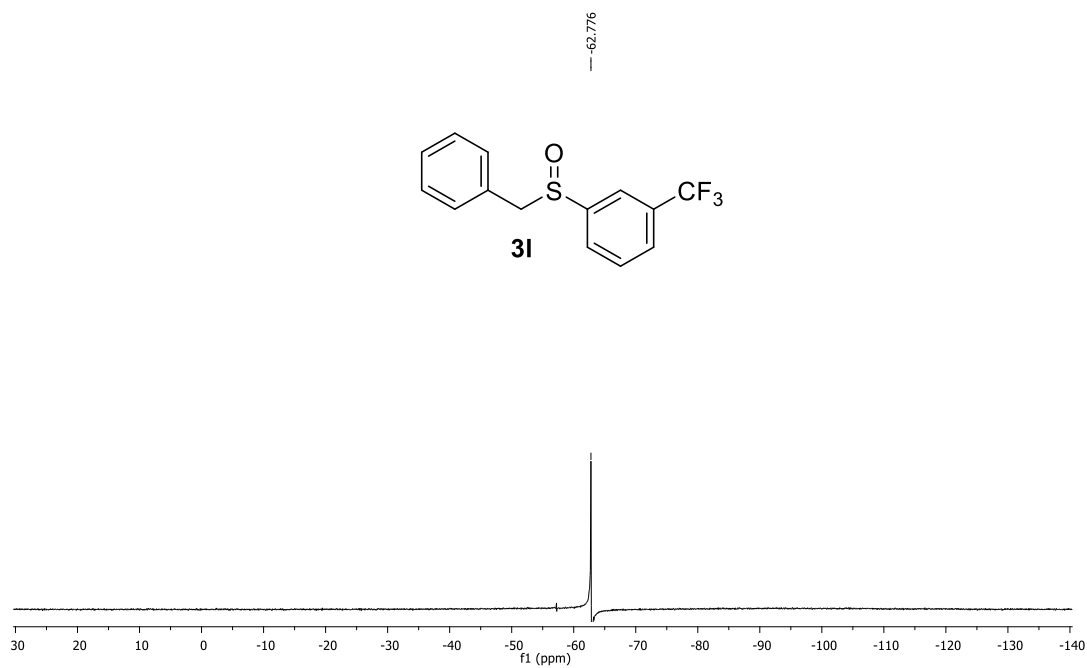
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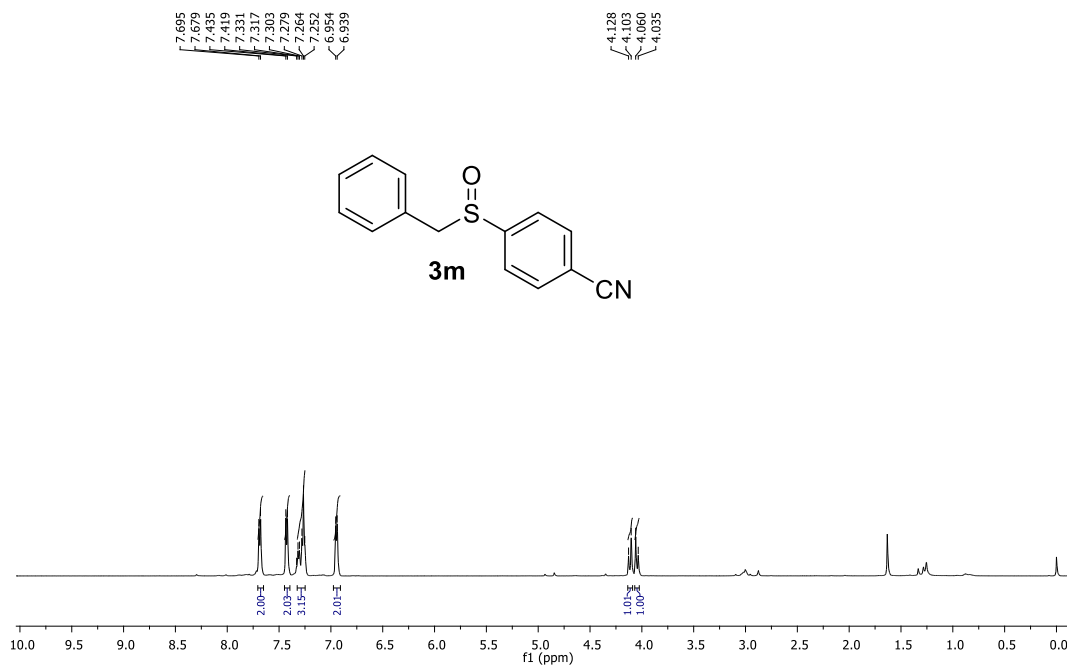
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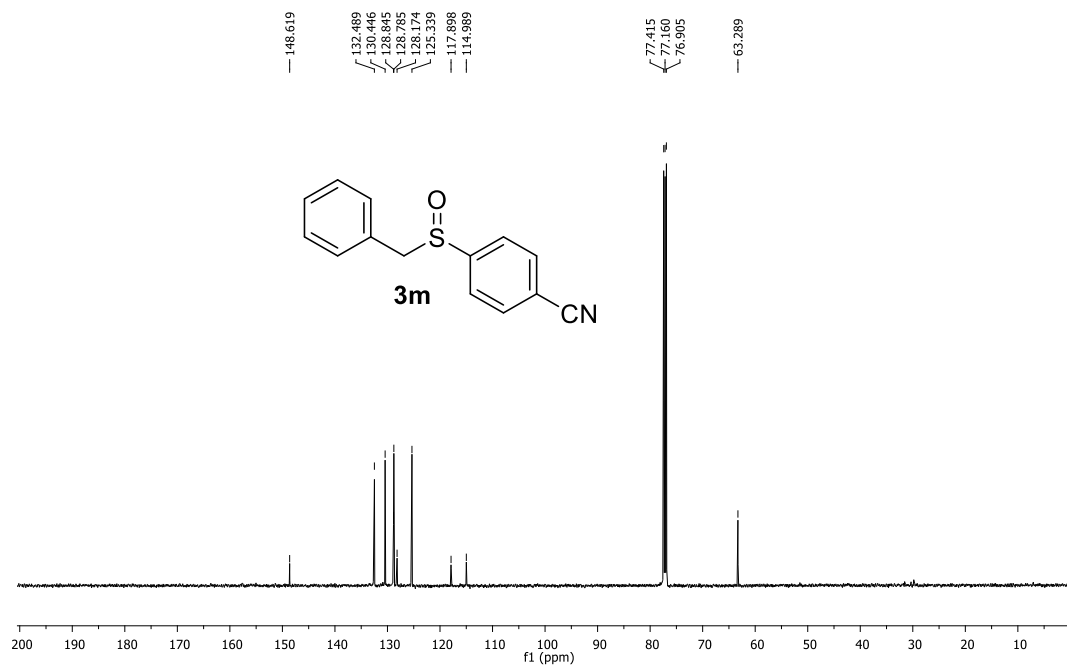
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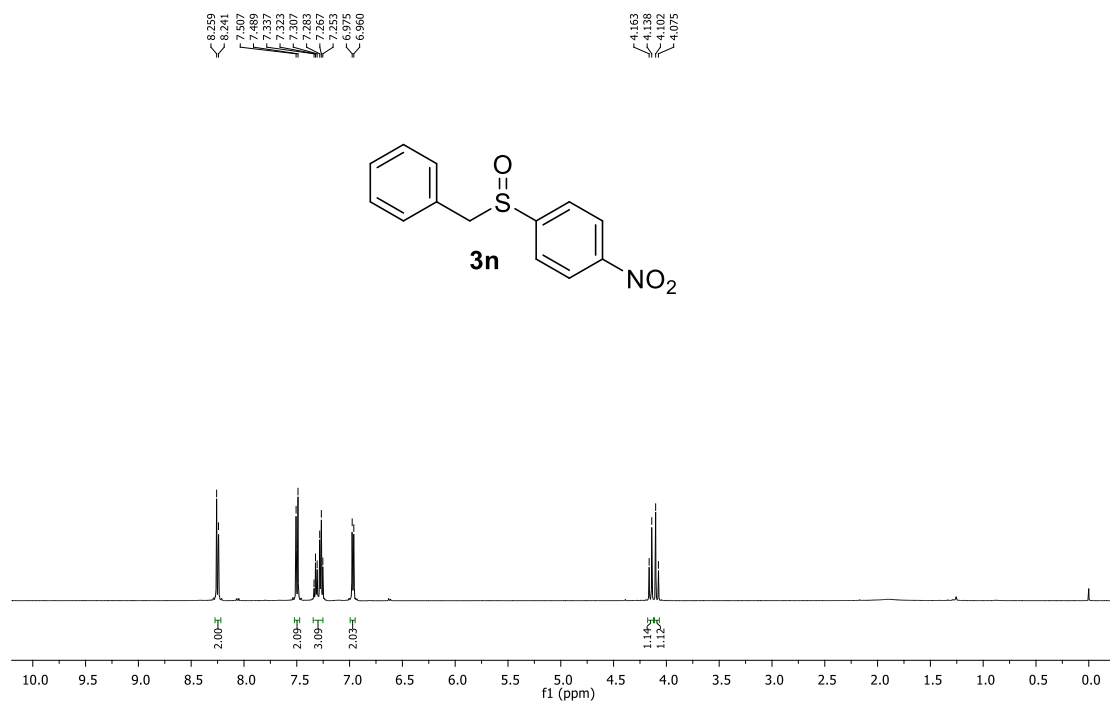
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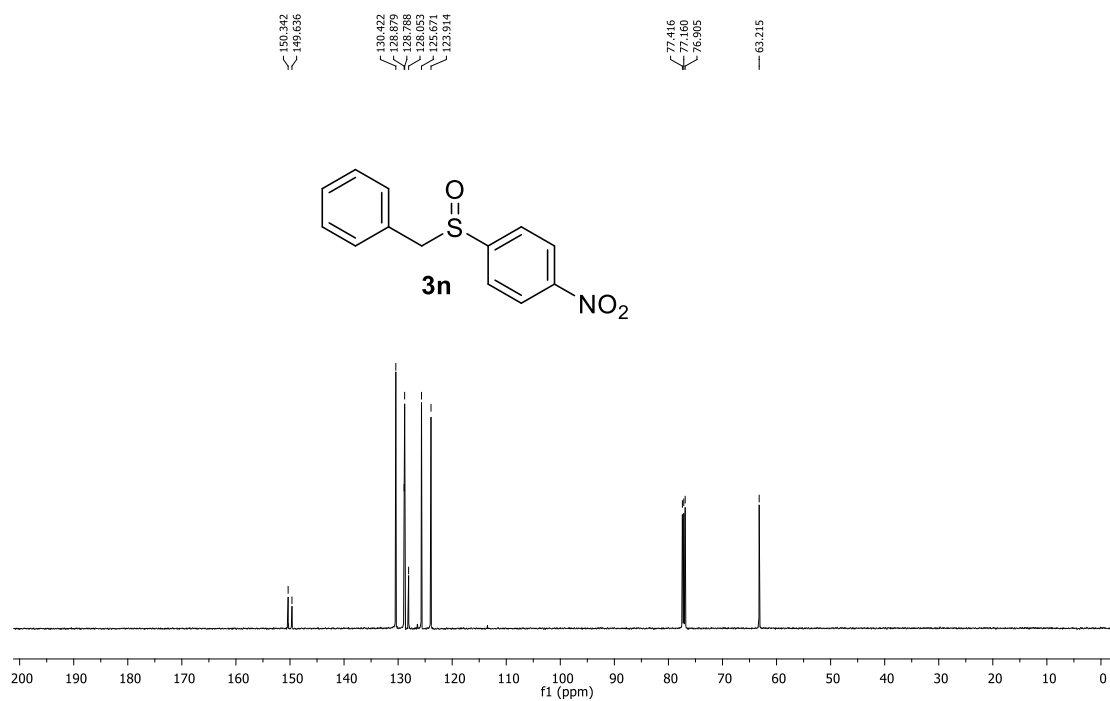
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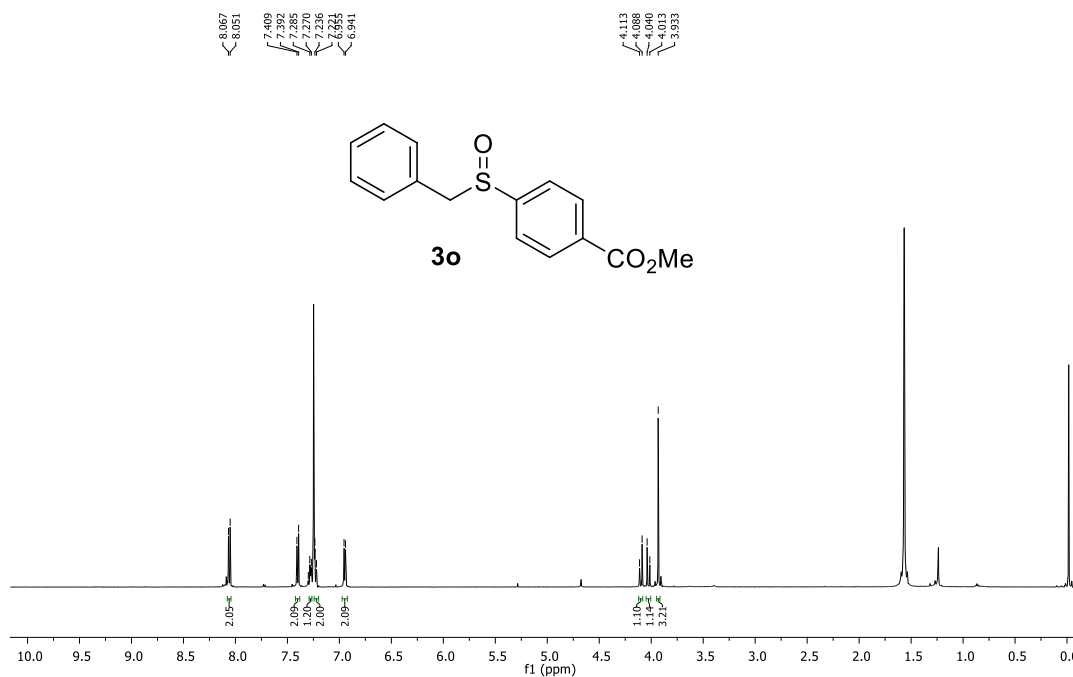
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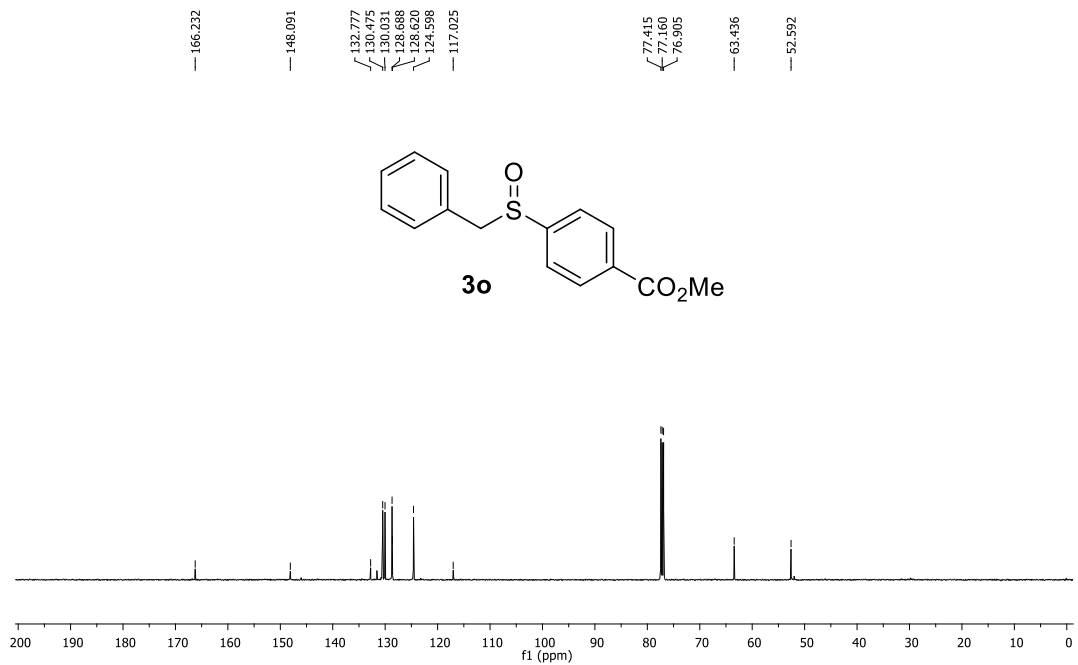
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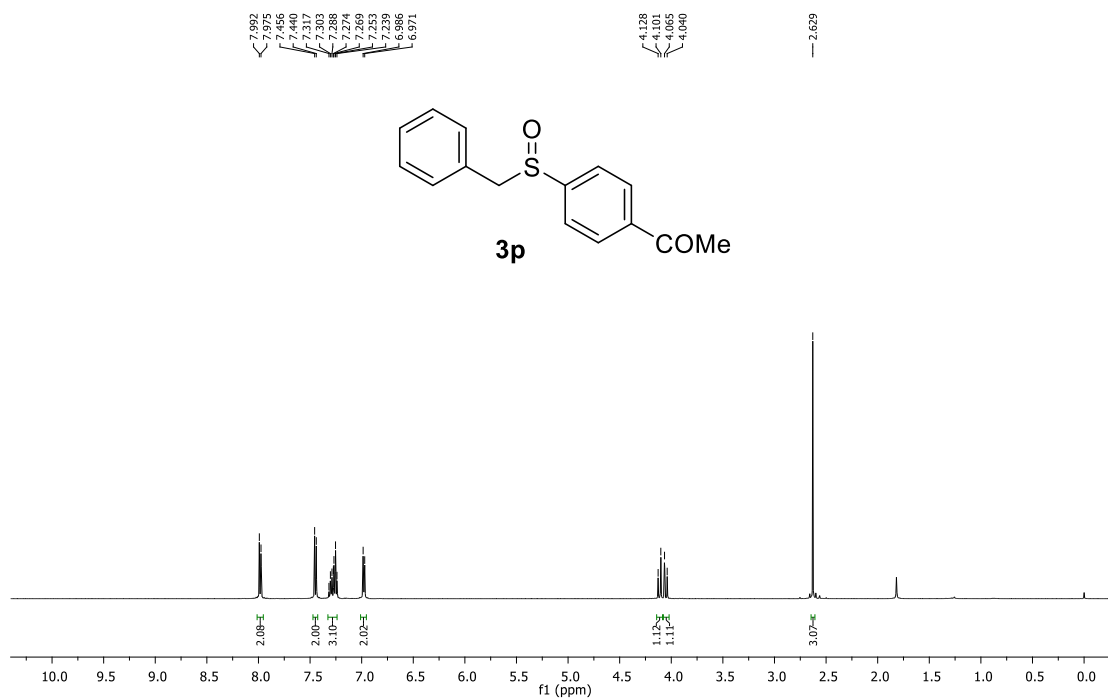
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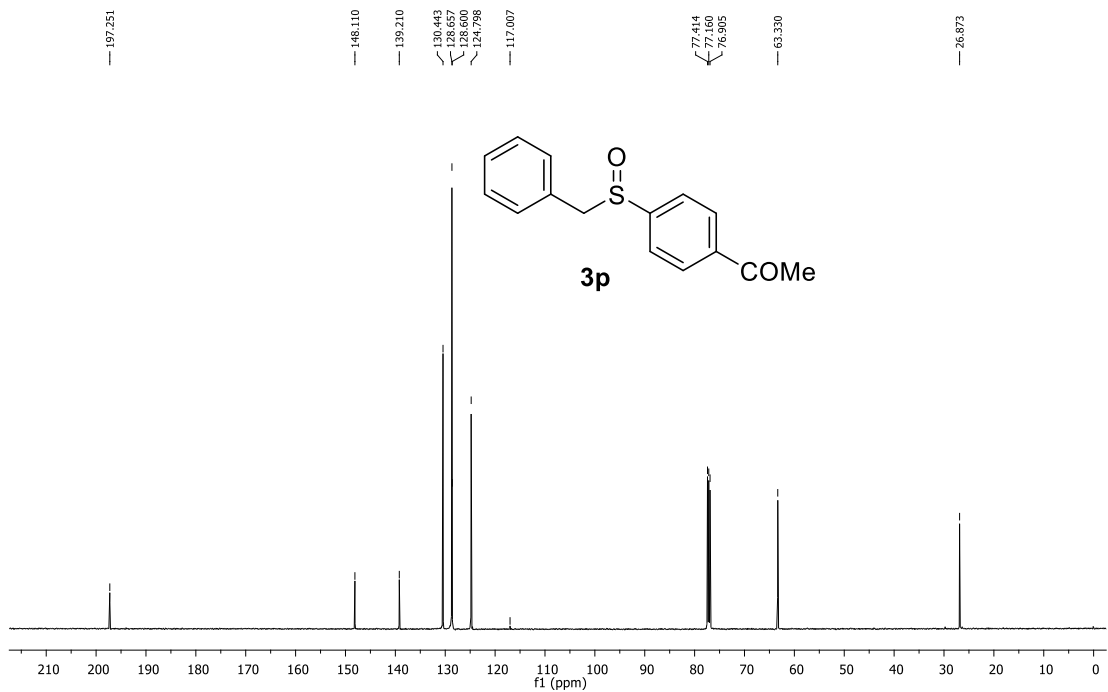
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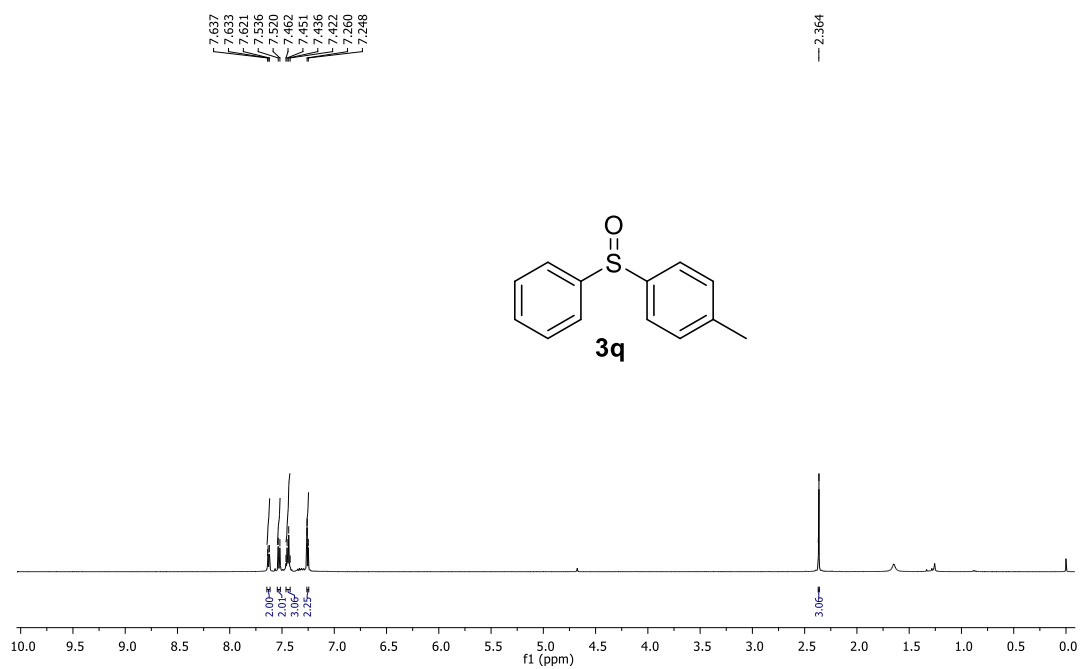
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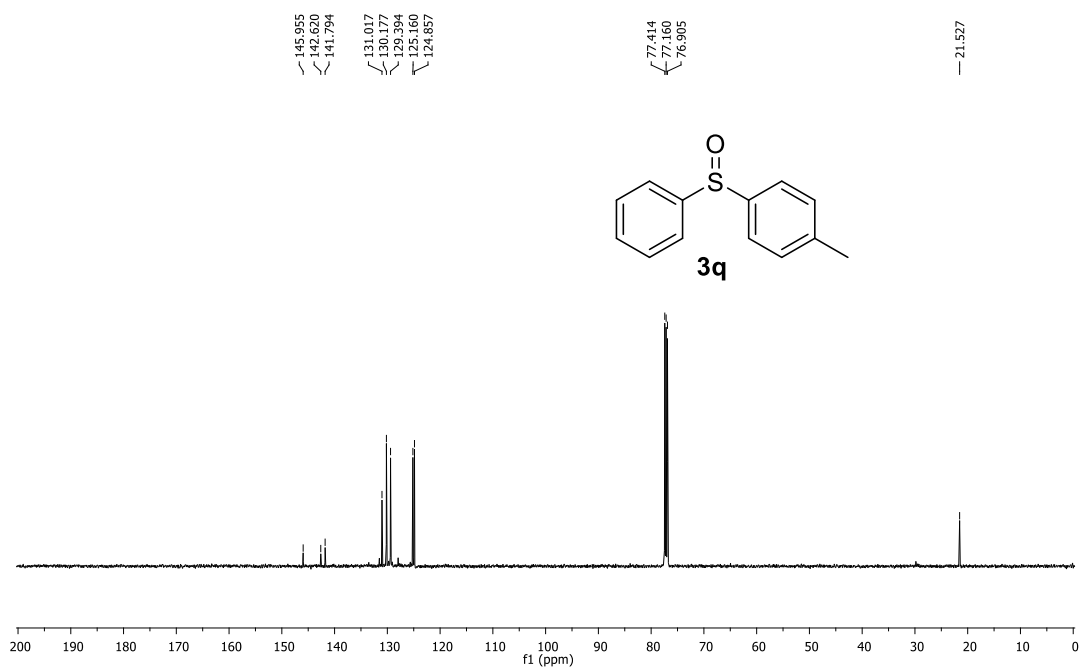
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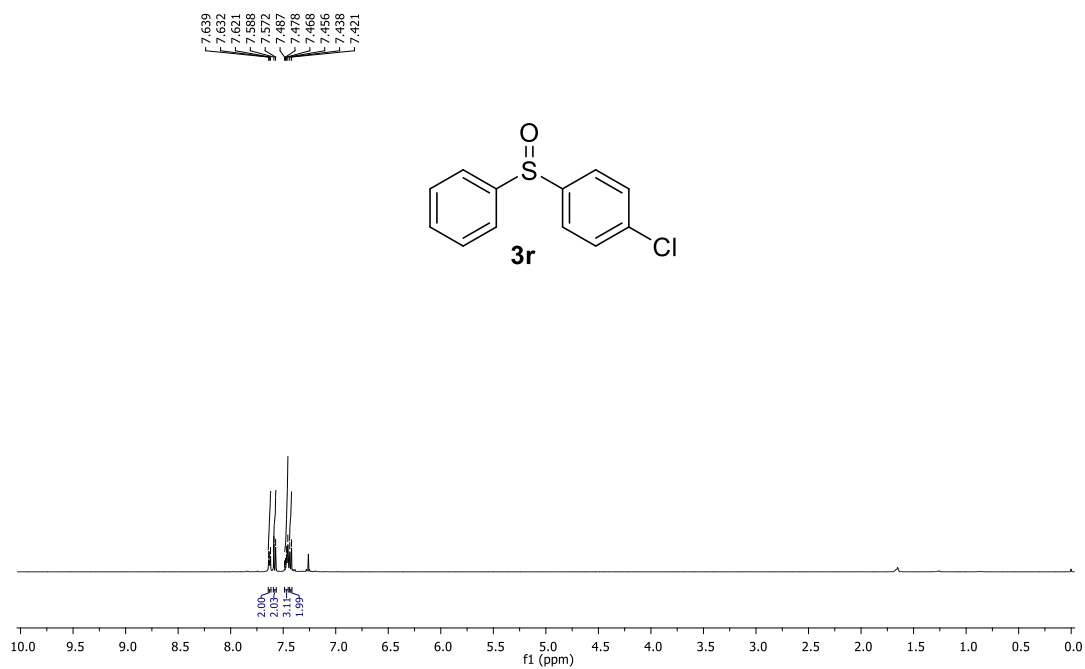
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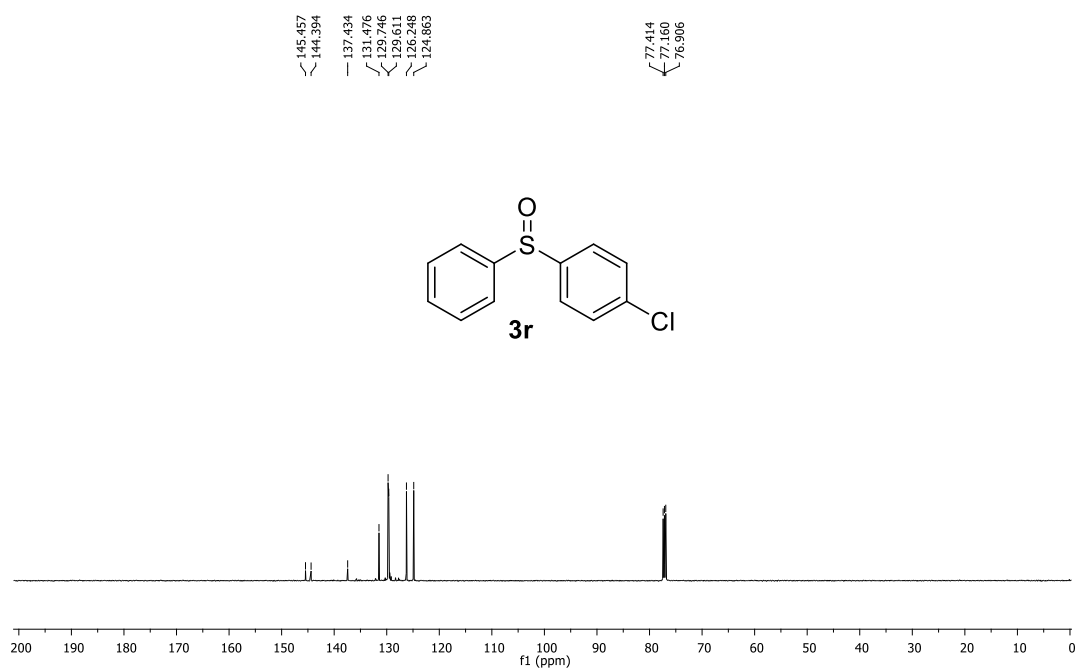
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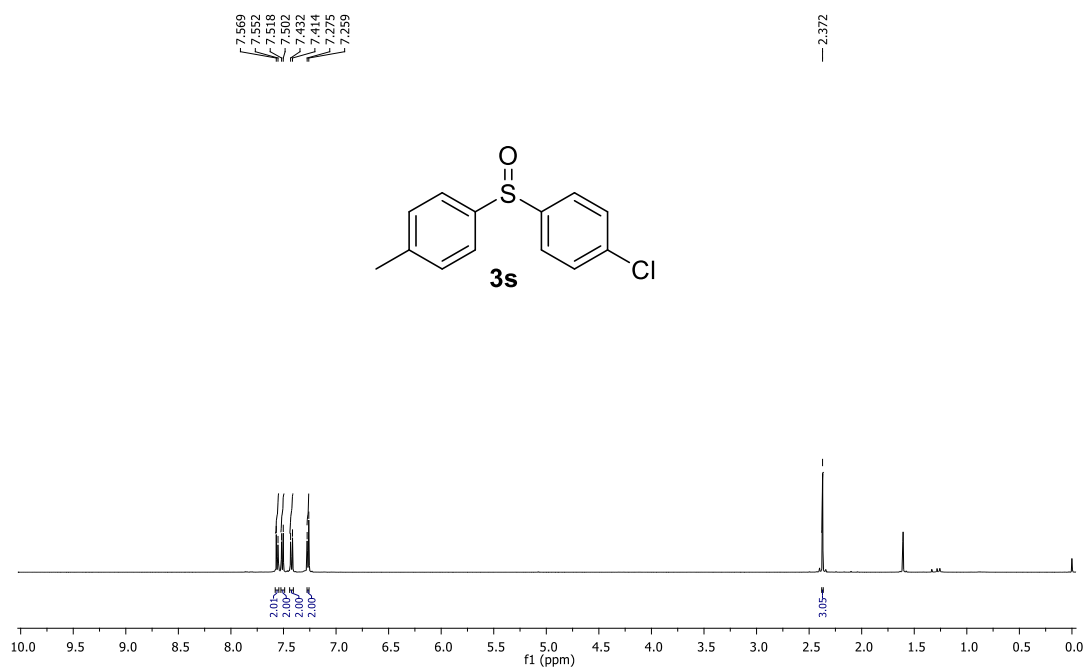
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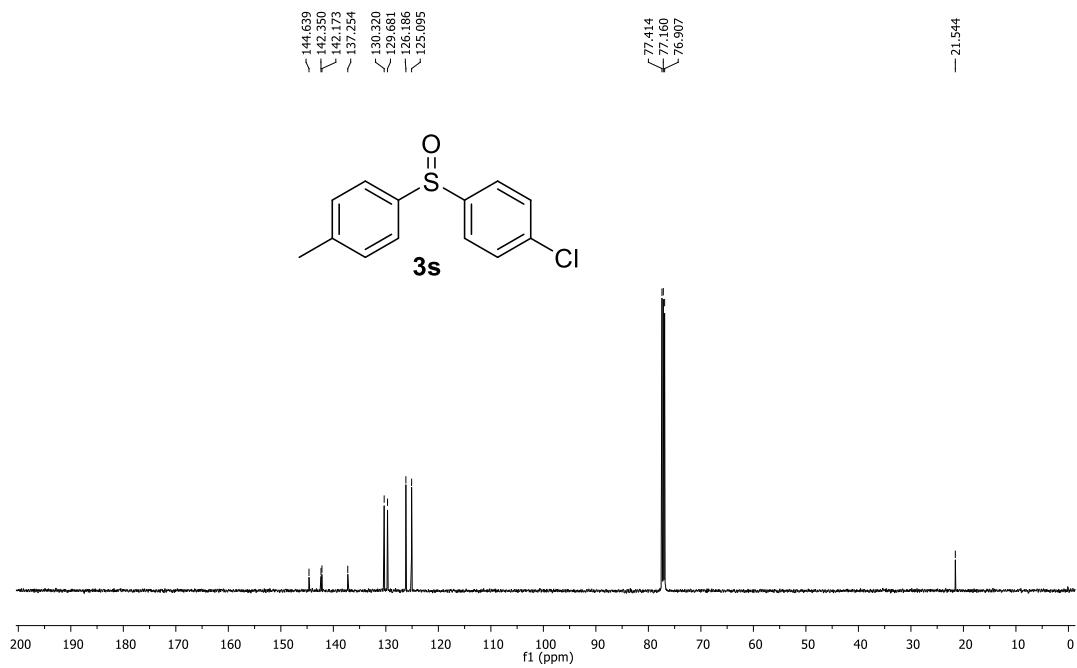
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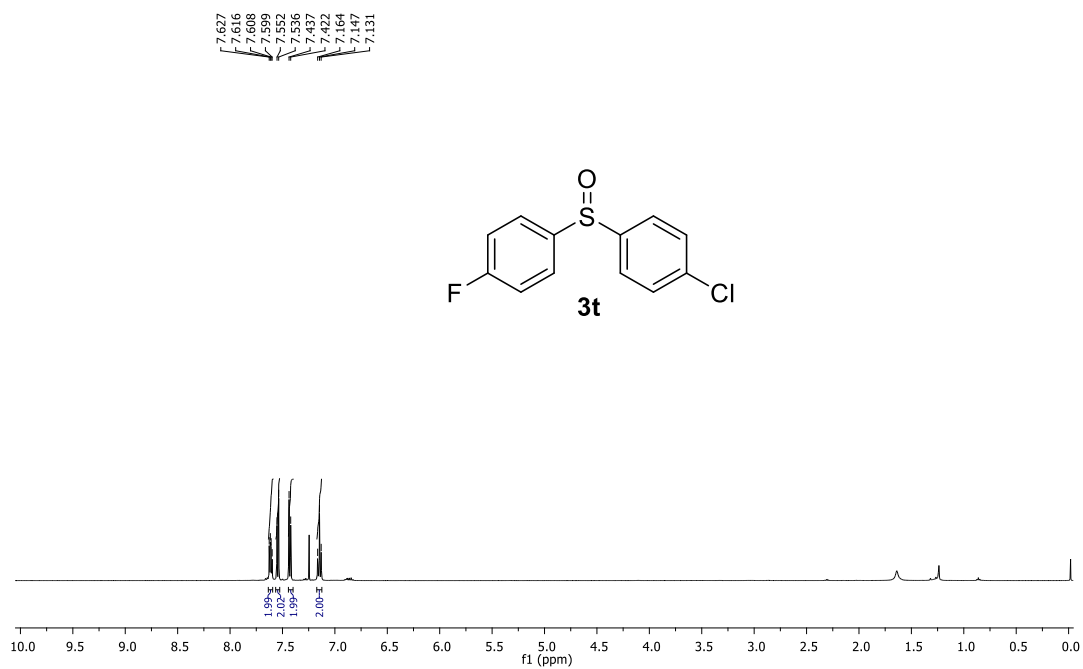
^1H NMR (500 MHz, CDCl_3)



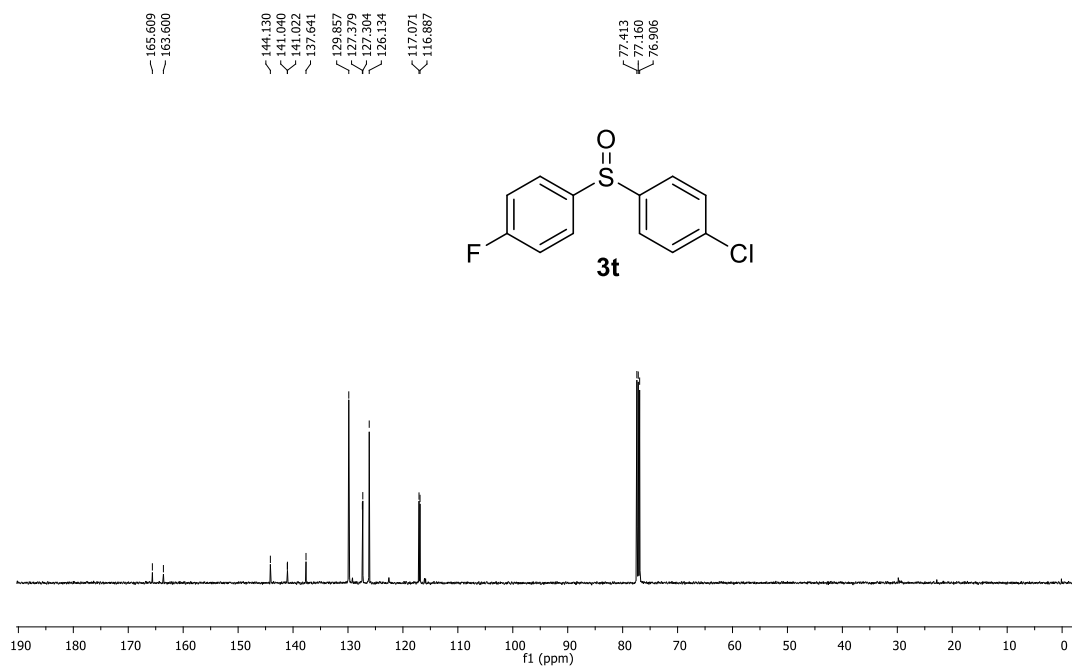
^{13}C NMR (126 MHz, CDCl_3)



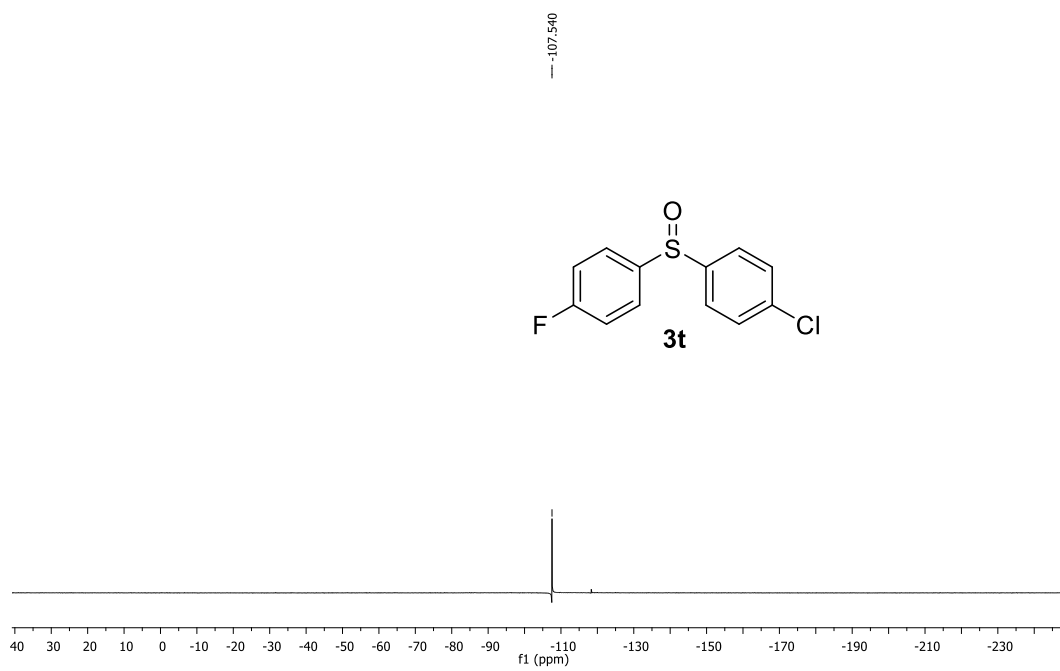
^1H NMR (500 MHz, CDCl_3)



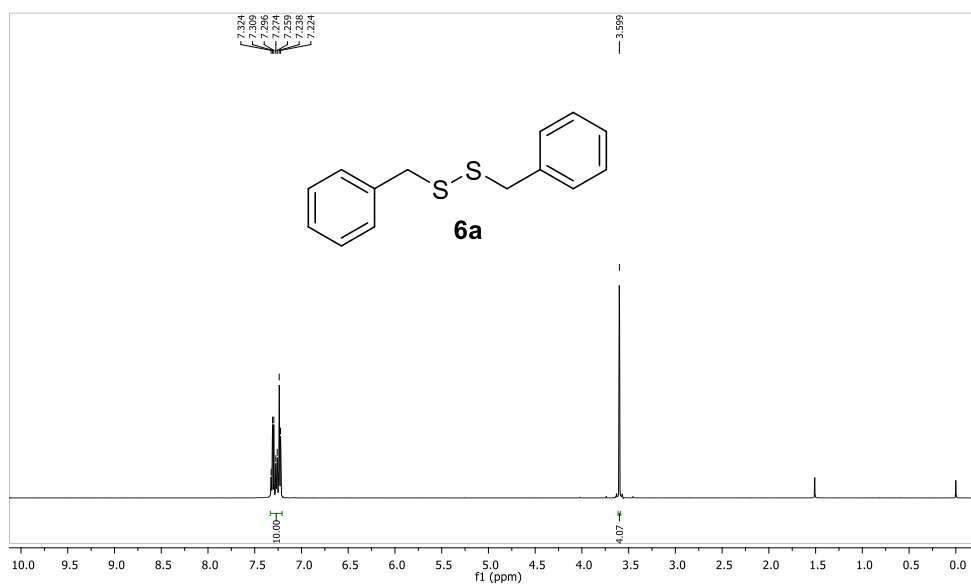
^{13}C NMR (126 MHz, CDCl_3)



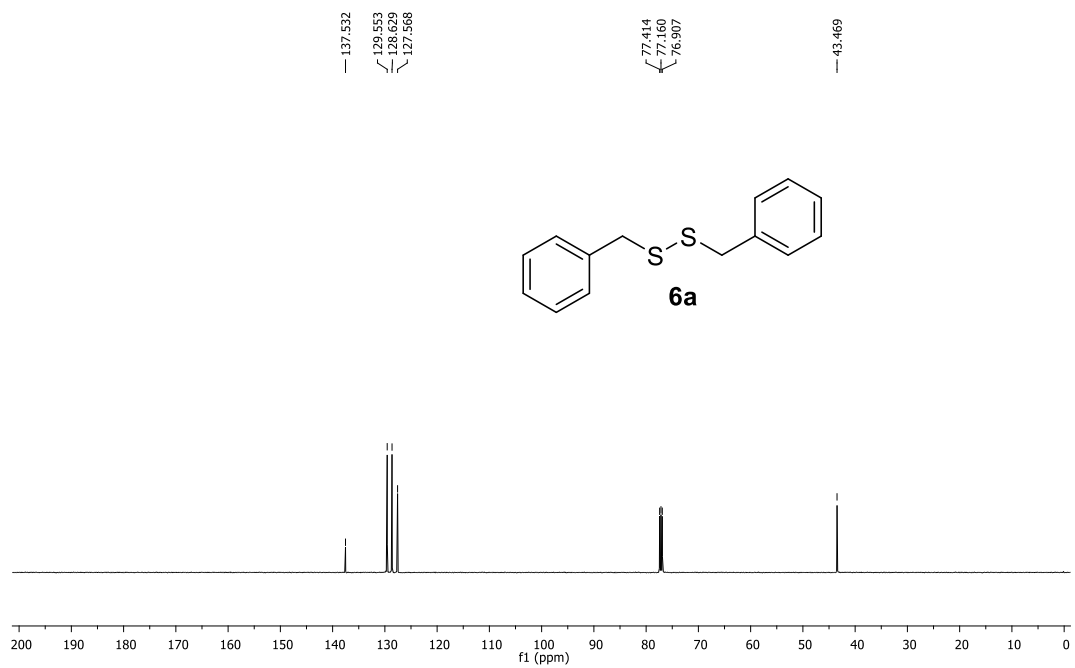
^{19}F NMR (471 MHz, CDCl_3)



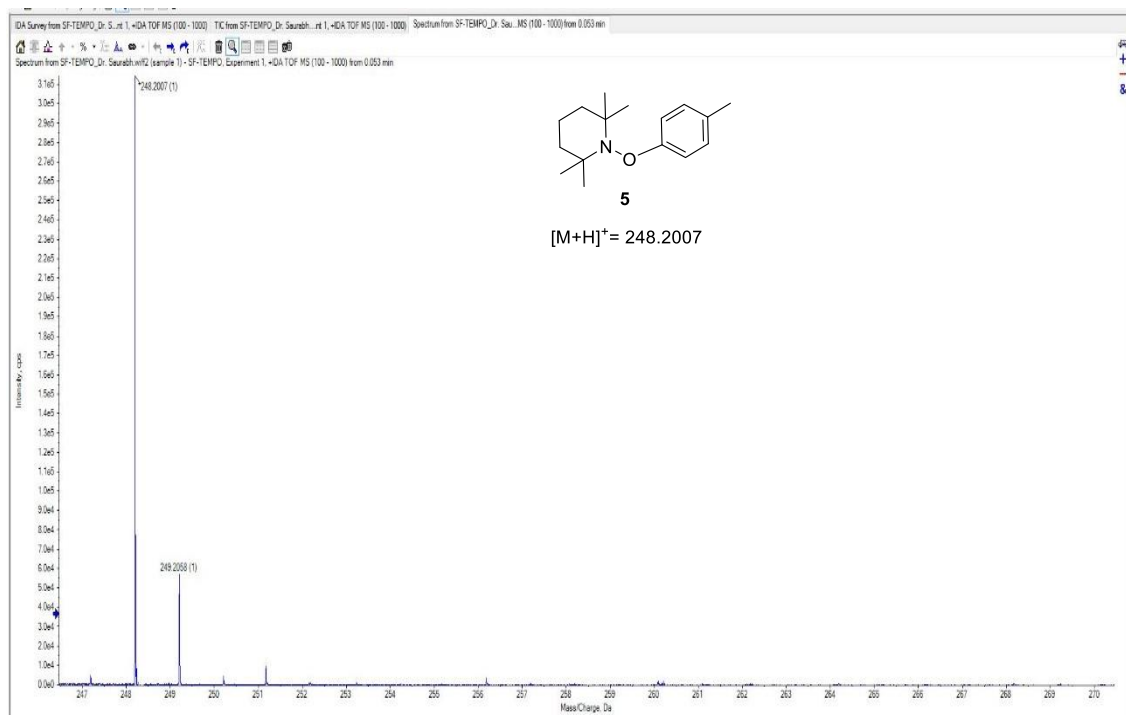
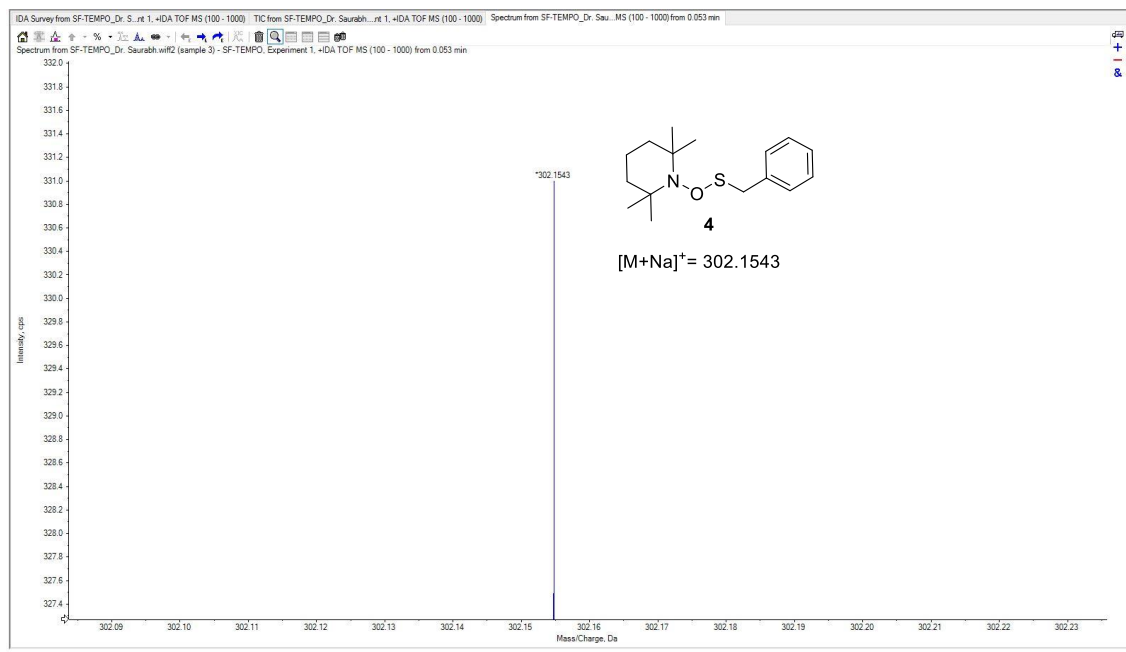
^1H NMR (500 MHz, CDCl_3)



^{13}C NMR (126 MHz, CDCl_3)



4. HRMS Data of TEMPO Adduct 4 and 5:



5. Crystallographic Data.

Crystal of compound **3d** was grown by slow evaporation of a solution of the compound in CHCl_3 . All the measurements were obtained on Oxford Xcalibur Diffractometer system (model of the instrument – XcaliburTM E).

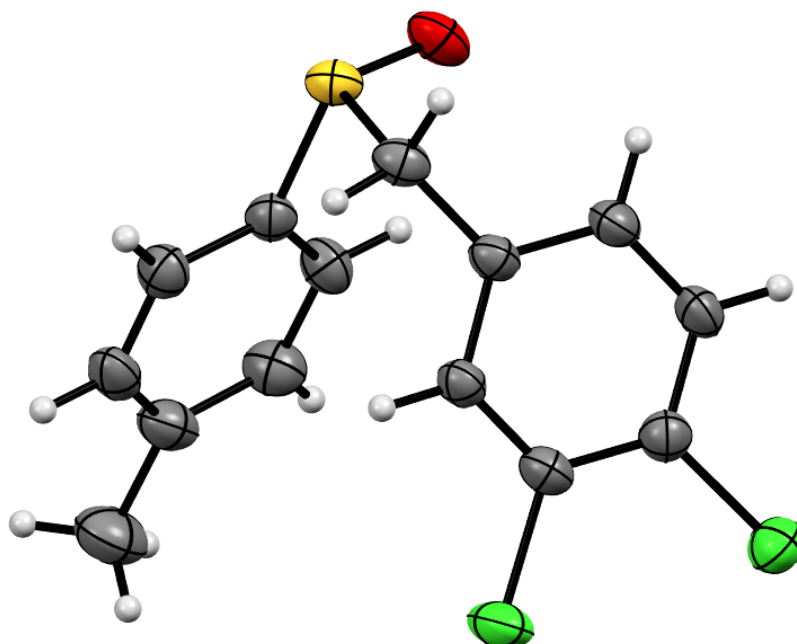
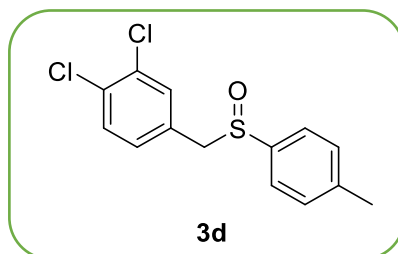


Figure S3. View of the molecular structure of **3d**.

Table T1. Crystallographic data for compound **3d**.

Crystallized from	CHCl ₃
Empirical formula	C ₁₄ H ₁₂ Cl ₂ OS
Formula weight [g mol ⁻¹]	299.20
Crystal colour, habit	White, block
Crystal dimensions (mm)	0.41 × 0.38 × 0.36
Temperature [K]	293(2)
Crystal system	Monoclinic
Space group	<i>P2₁/n</i>
<i>a</i> /Å	5.7326(5)
<i>b</i> /Å	16.7916(19)
<i>c</i> /Å	14.3441(12)
α /°	90
β /°	92.205(9)
γ /°	90
<i>V</i> [Å ³]	1379.7(2)
<i>Z</i>	4
<i>D_x</i> [g/cm ³]	1.4404
μ (MoK α) [mm ⁻¹]	5.515
<i>F</i> (000)	621.6
Radiation	Cu K α (λ = 1.54184)
2 θ range for data collection/°	8.12 to 144.66
Index ranges	-6 ≤ <i>h</i> ≤ 7, -18 ≤ <i>k</i> ≤ 20, -17 ≤ <i>l</i> ≤ 14
Reflections collected	5008
Independent reflections	2644 [<i>R</i> _{int} = 0.0538, <i>R</i> _{sigma} = 0.0769]
Data/restraints/parameters	2644/0/164
Goodness-of-fit on <i>F</i> ²	1.017
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0749, <i>wR</i> ₂ = 0.1869
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1063, <i>wR</i> ₂ = 0.2285
Largest diff. peak/hole / e Å ⁻³	0.74/-0.46