

Electronic Supplementary Information

A regioselective synthesis of β -difluoromethoxy vinyl sulfones via *O*-difluoromethylation of β -ketosulfones using sodium chlorodifluoroacetate

Km Ishu, Neha Sharma Prabhakar, and Krishna Nand Singh*

Department of Chemistry, Institute of Science, Banaras Hindu University, Varanasi 221005,
India

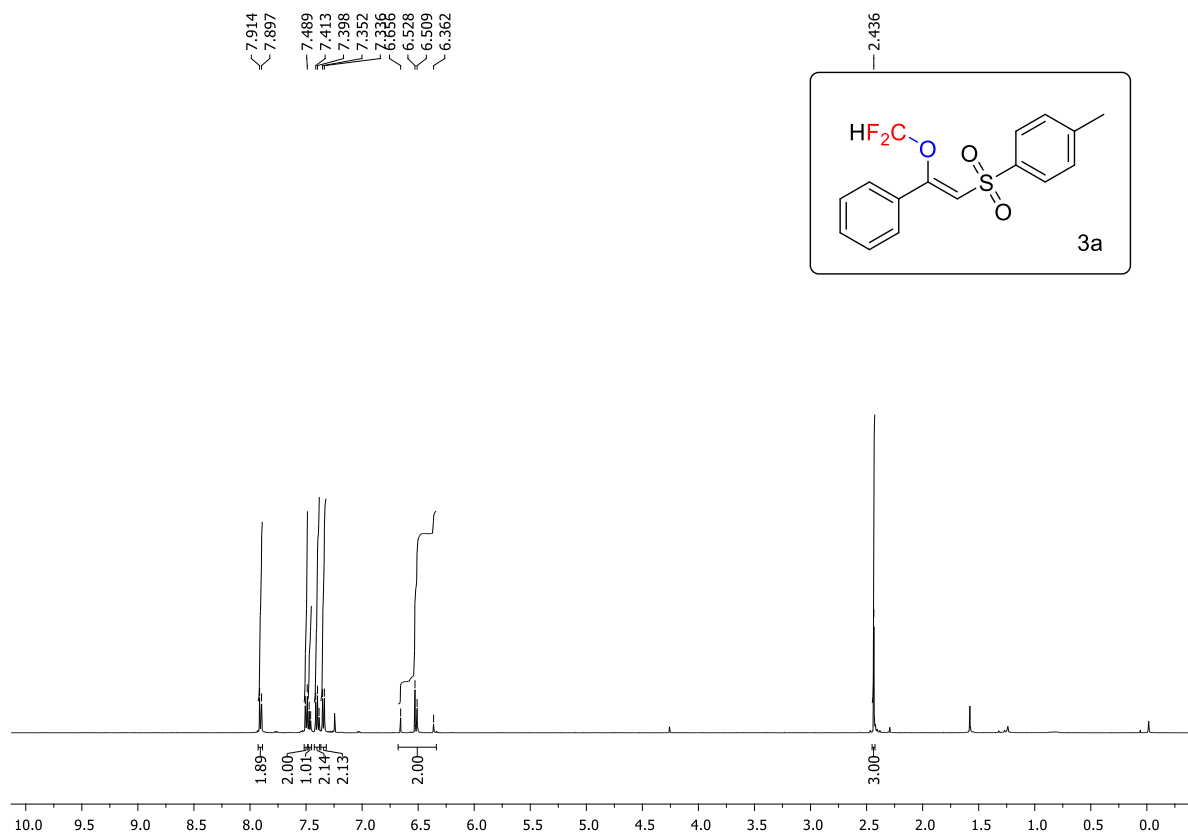
*E-mail: knsingh@bhu.ac.in; knsinghbhu@yahoo.co.in

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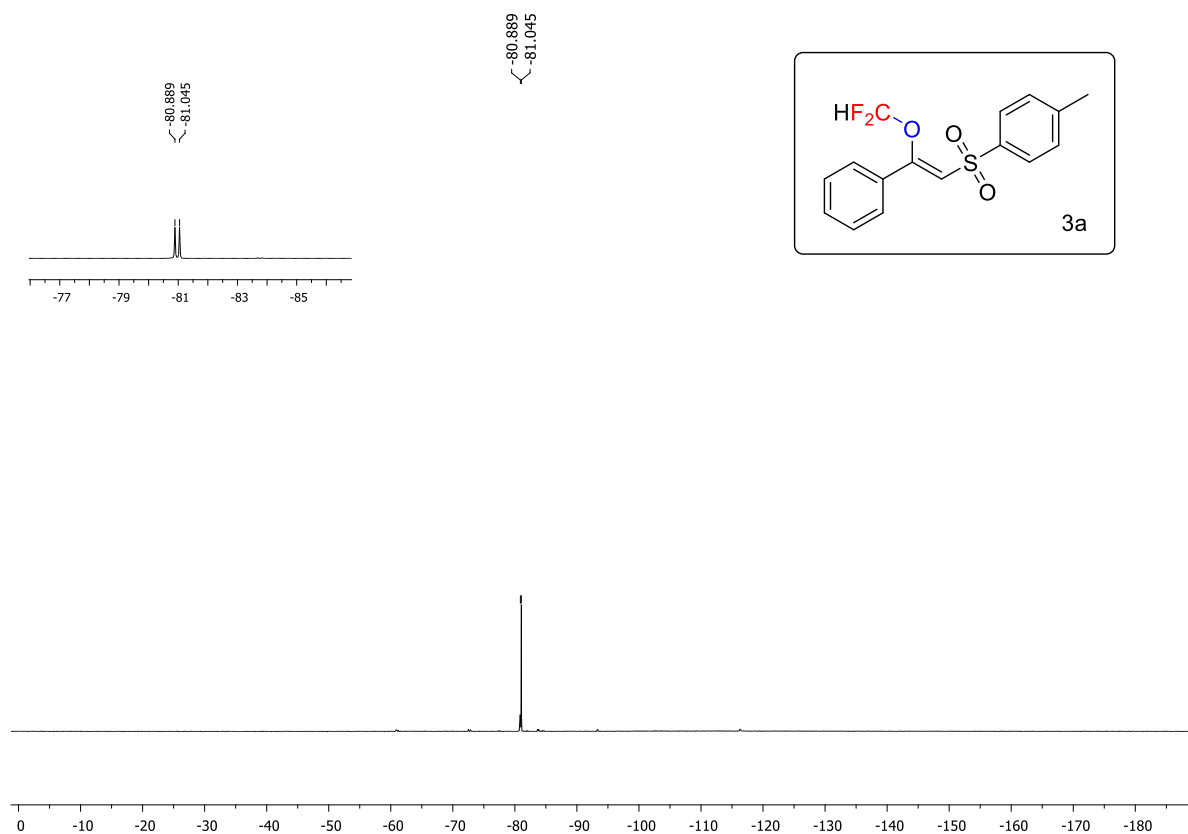
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1. Copies of ^1H , ^{19}F , and ^{13}C Spectra

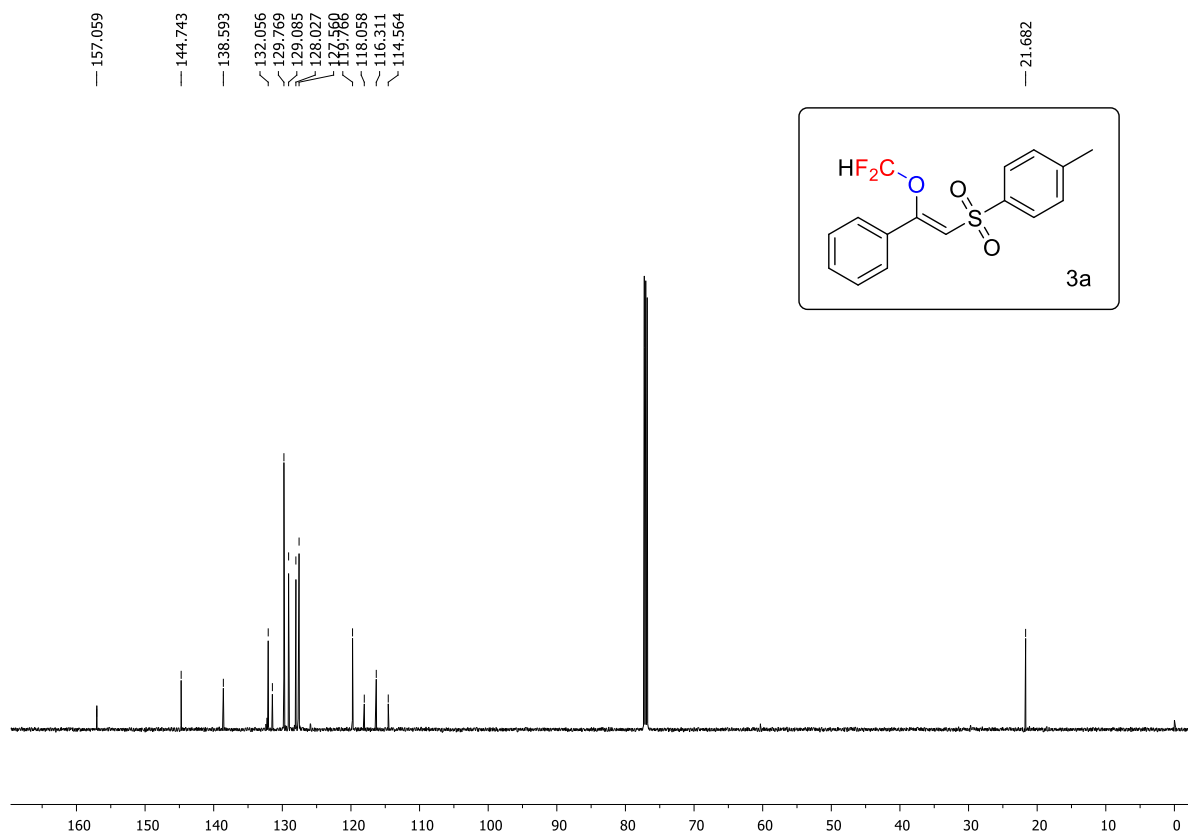
^1H NMR (500 MHz, CDCl_3)



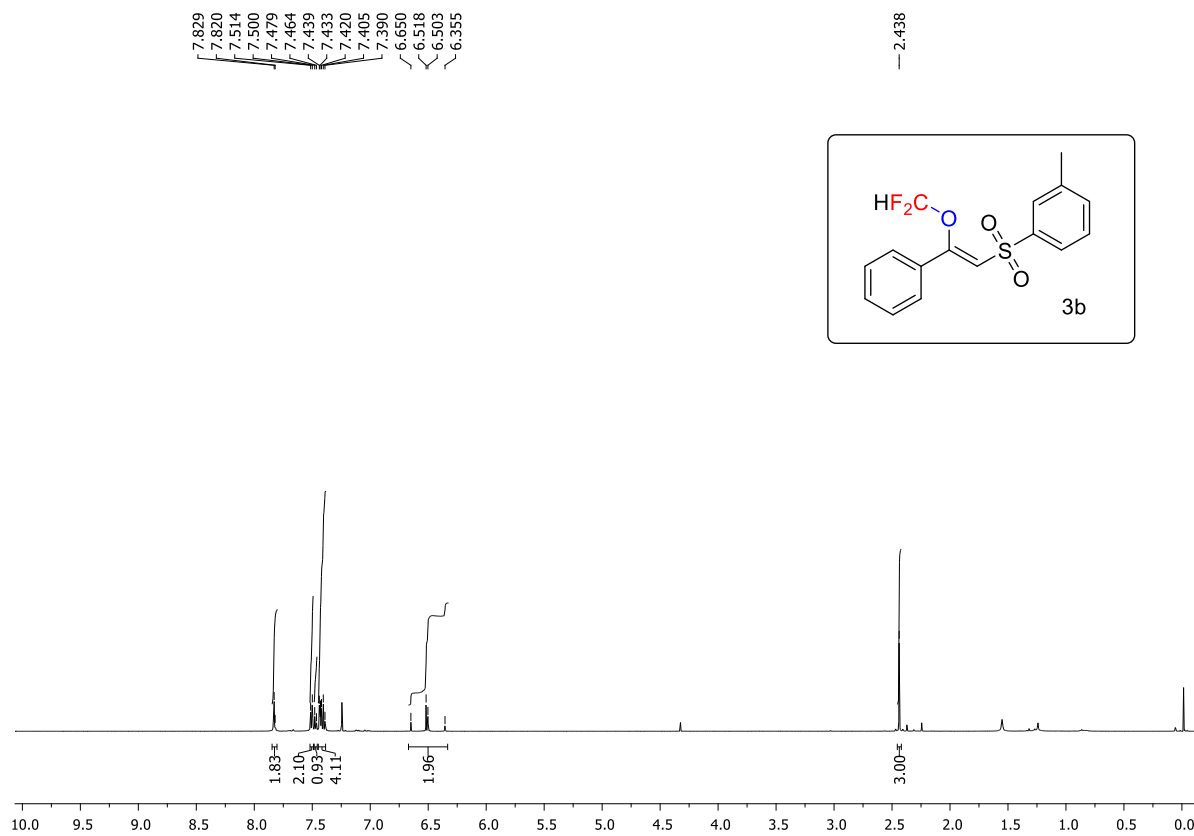
^{19}F NMR (471 MHz, CDCl_3)



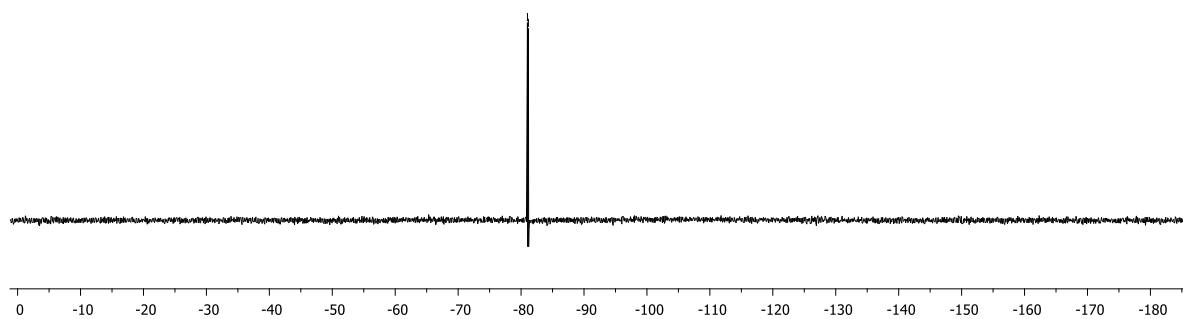
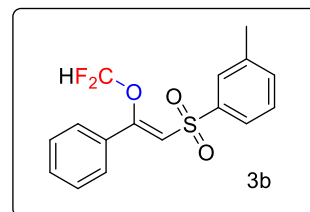
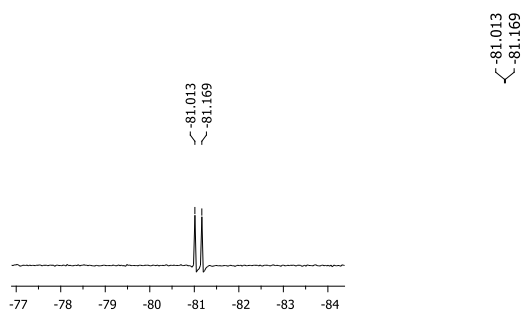
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)



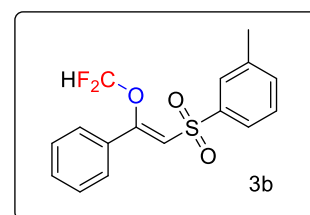
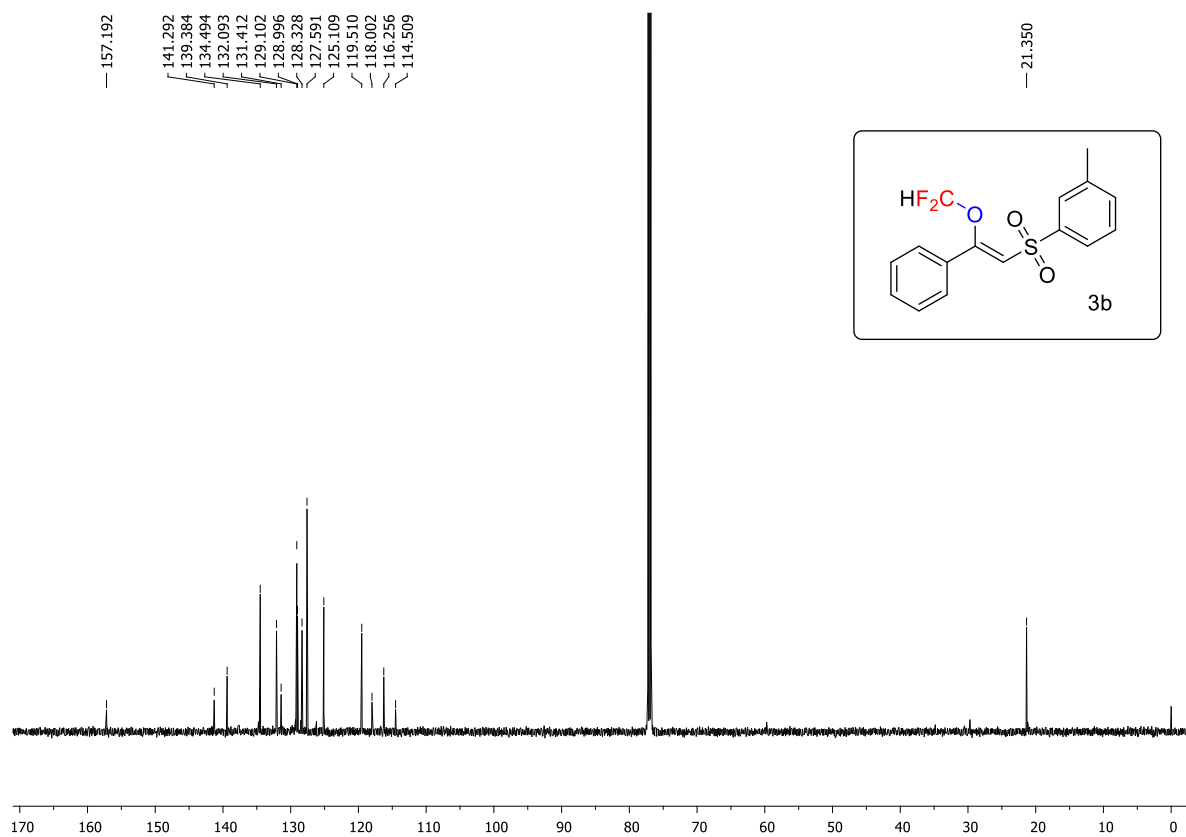
^1H NMR (500 MHz, CDCl_3)



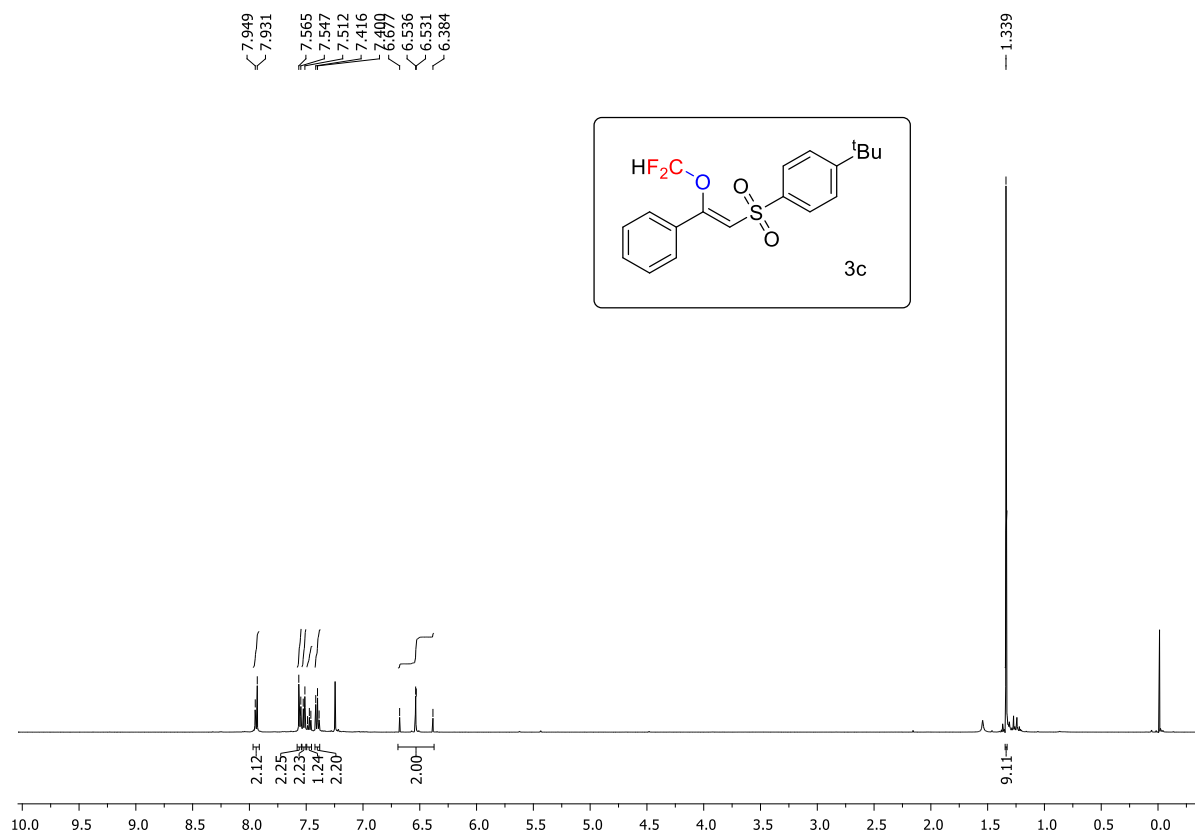
^{19}F NMR (471 MHz, CDCl_3)



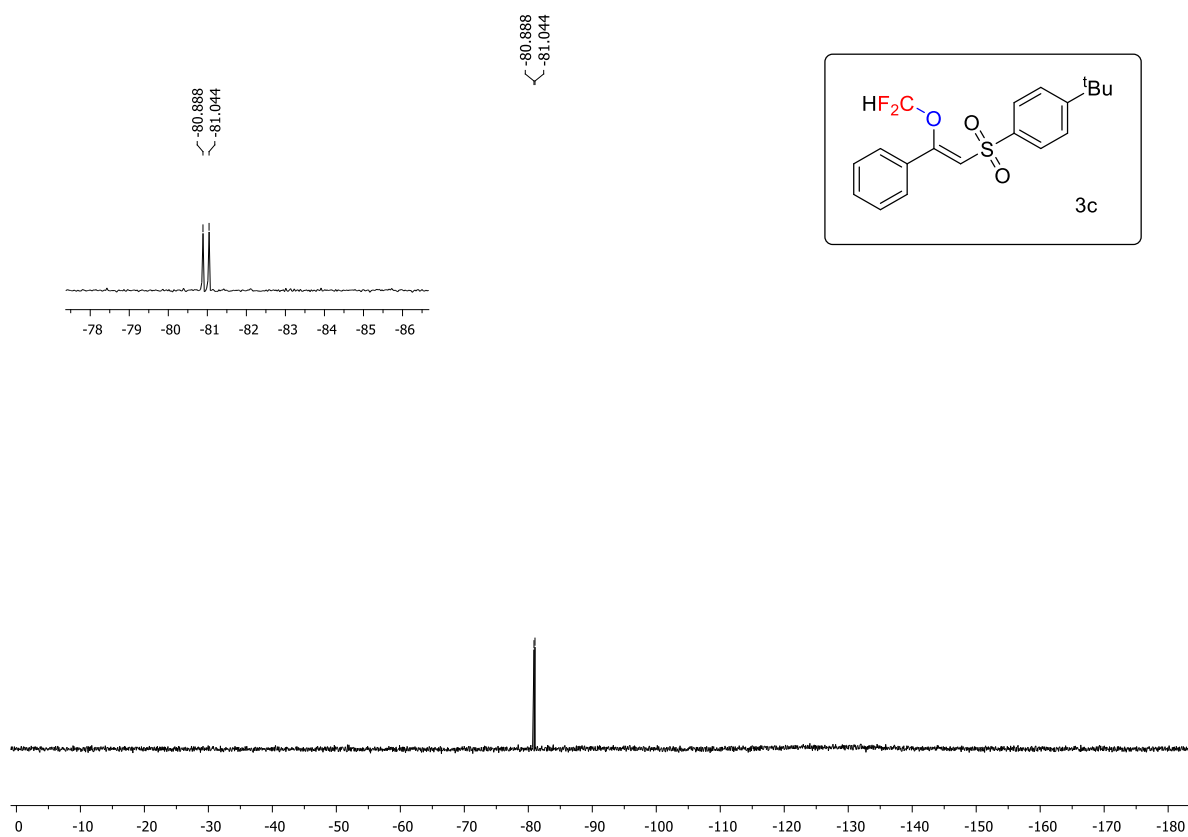
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)



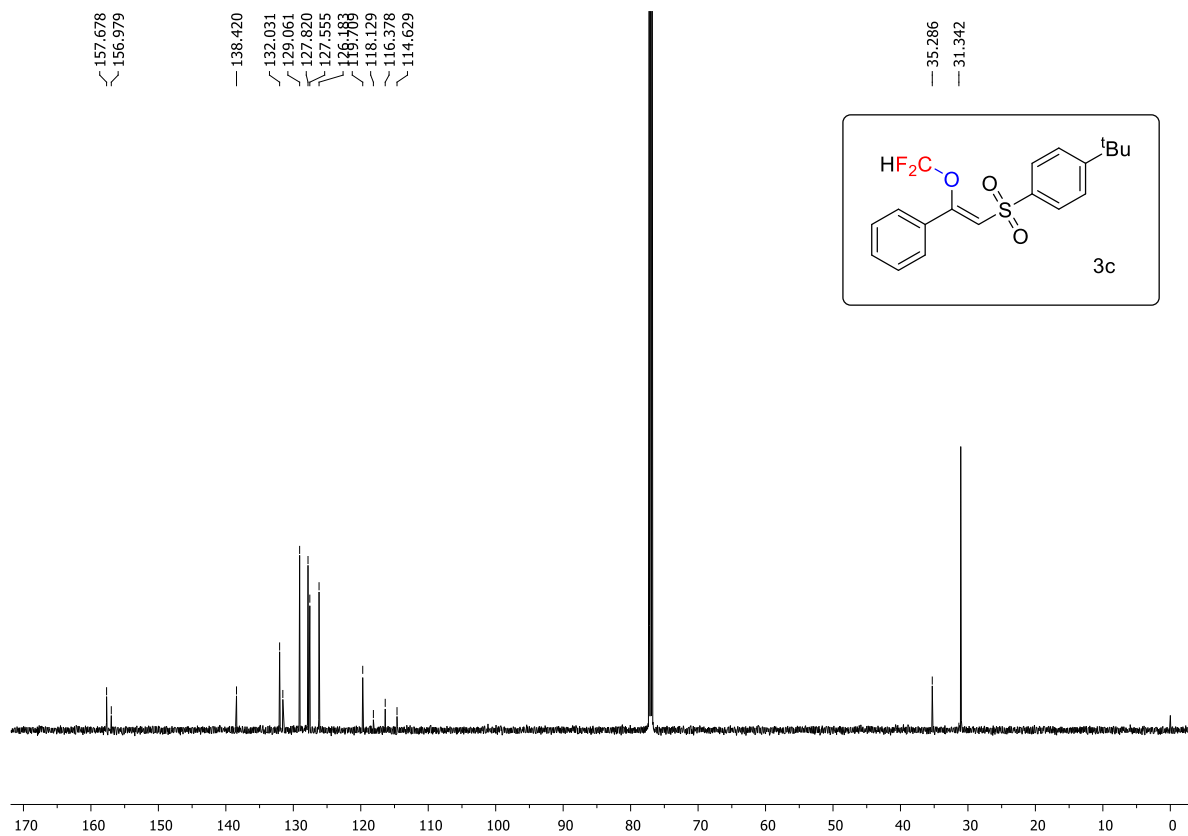
^1H NMR (500 MHz, CDCl_3)



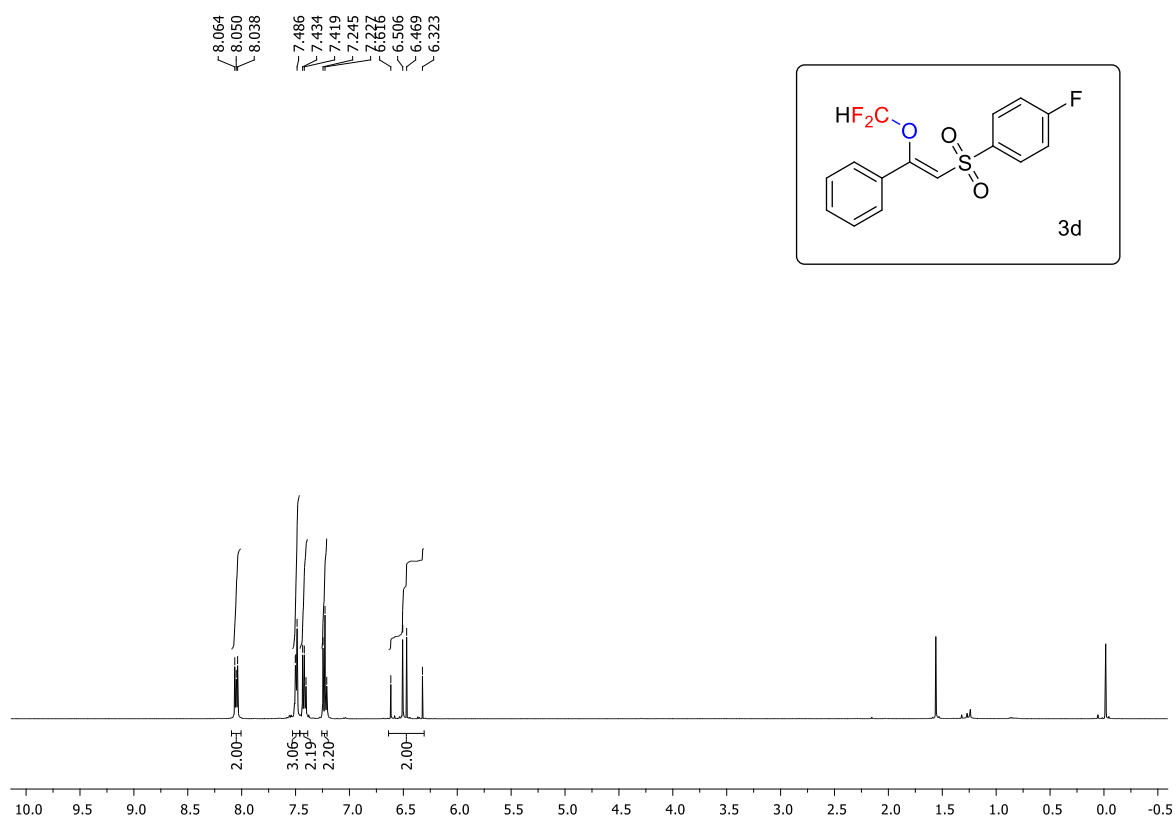
^{19}F NMR (471 MHz, CDCl_3)



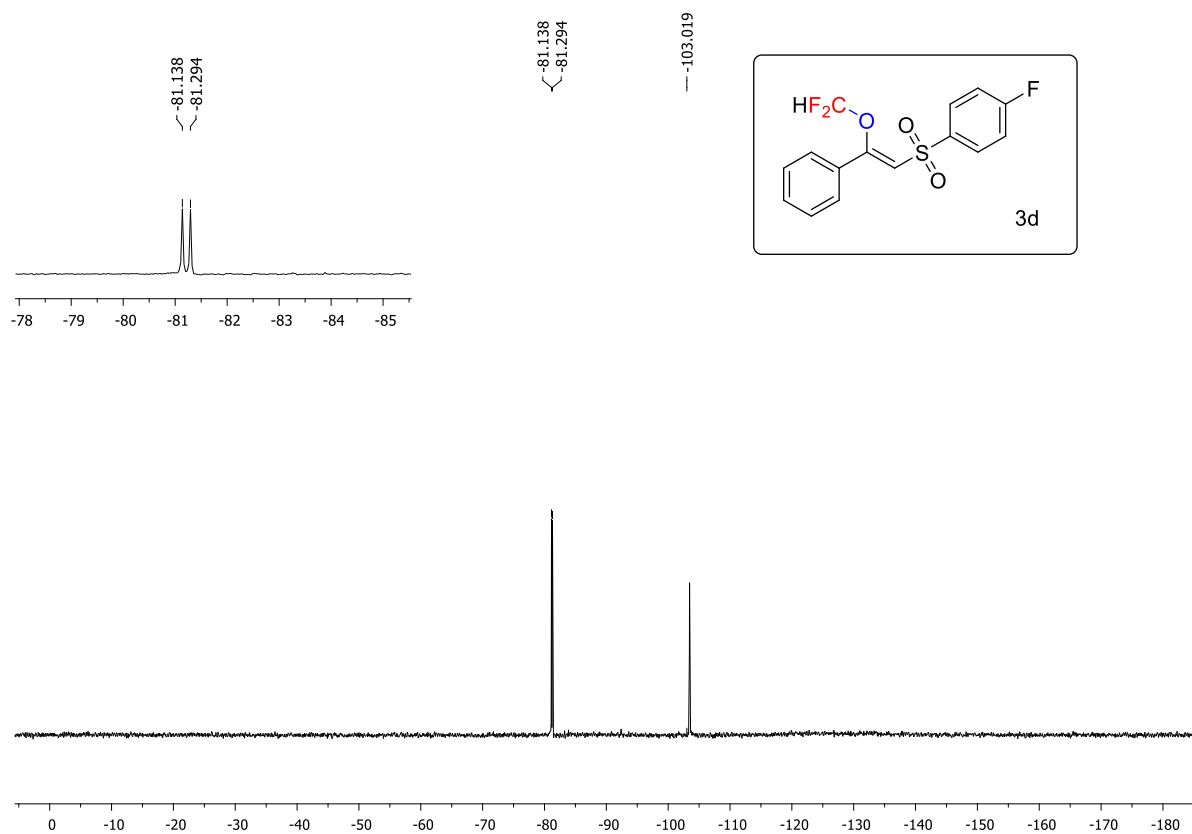
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)



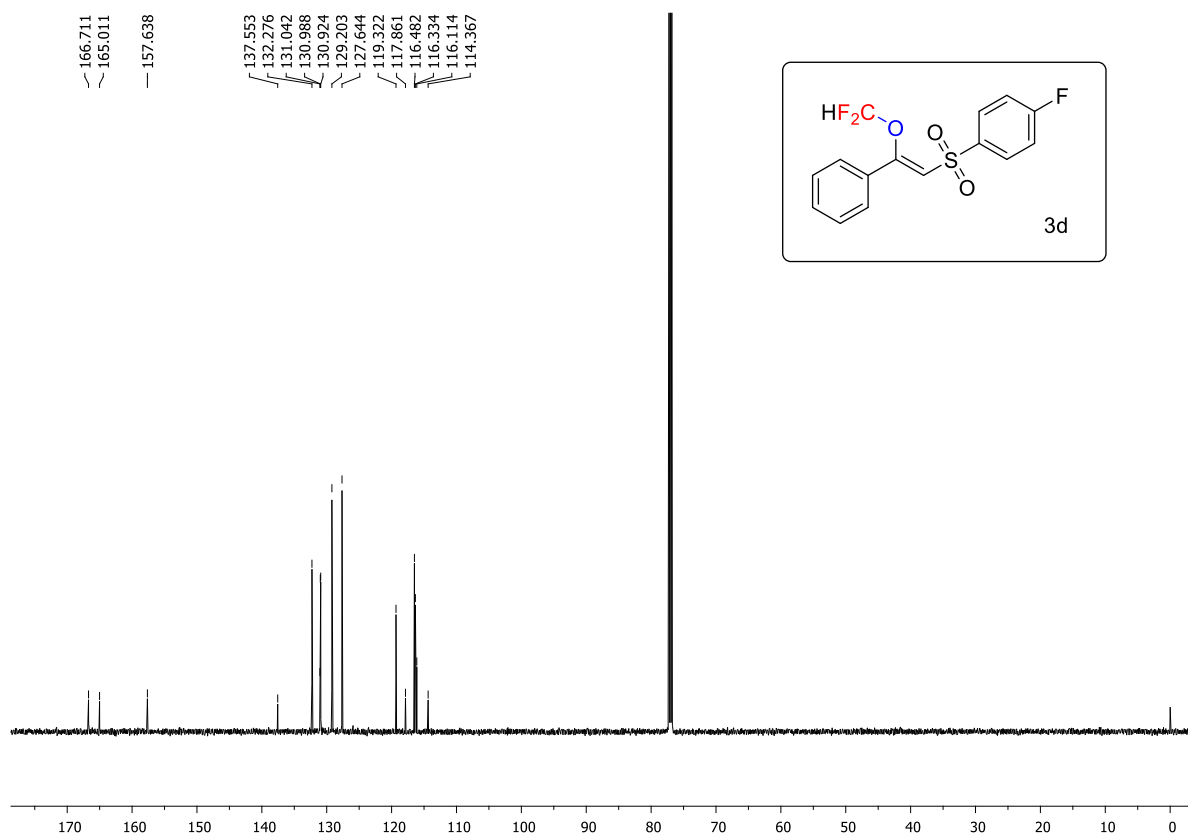
^1H NMR (500 MHz, CDCl_3)



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

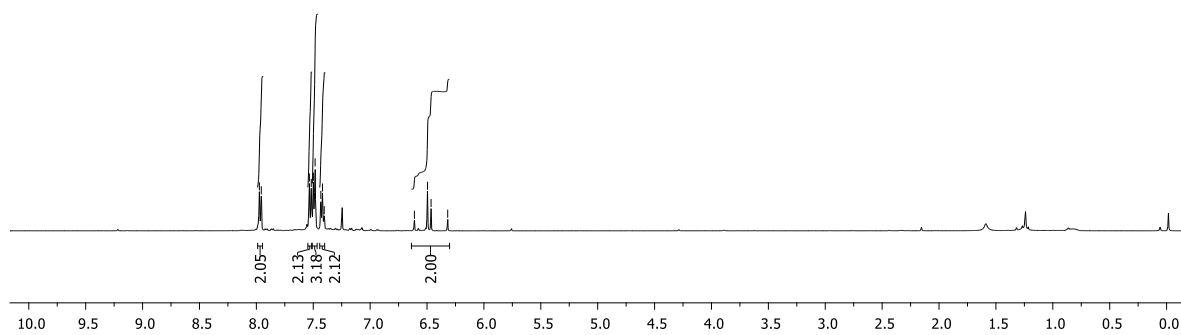
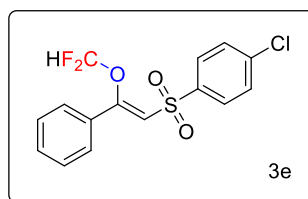


$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)



¹H NMR (500 MHz, CDCl₃)

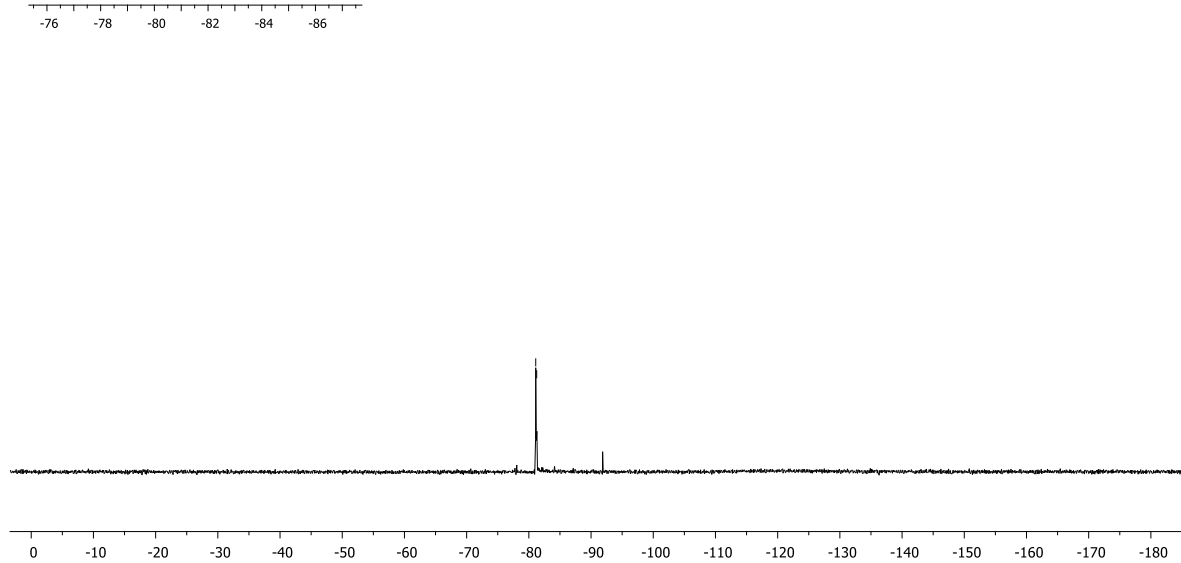
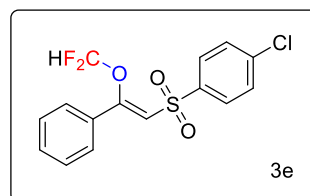
7.973
7.957
7.534
7.518
7.499
7.484
7.433
6.811
6.496
6.465
6.318



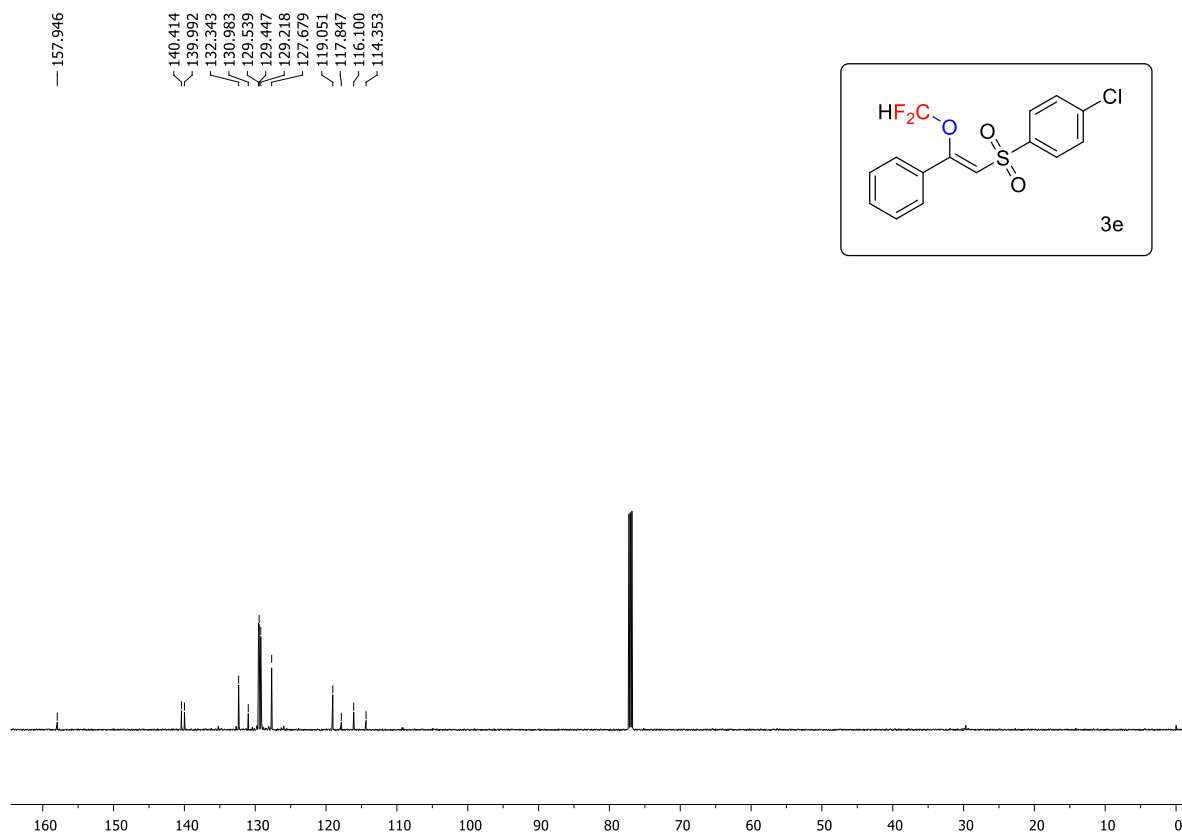
¹⁹F NMR (471 MHz, CDCl₃)

-81.109
-81.262

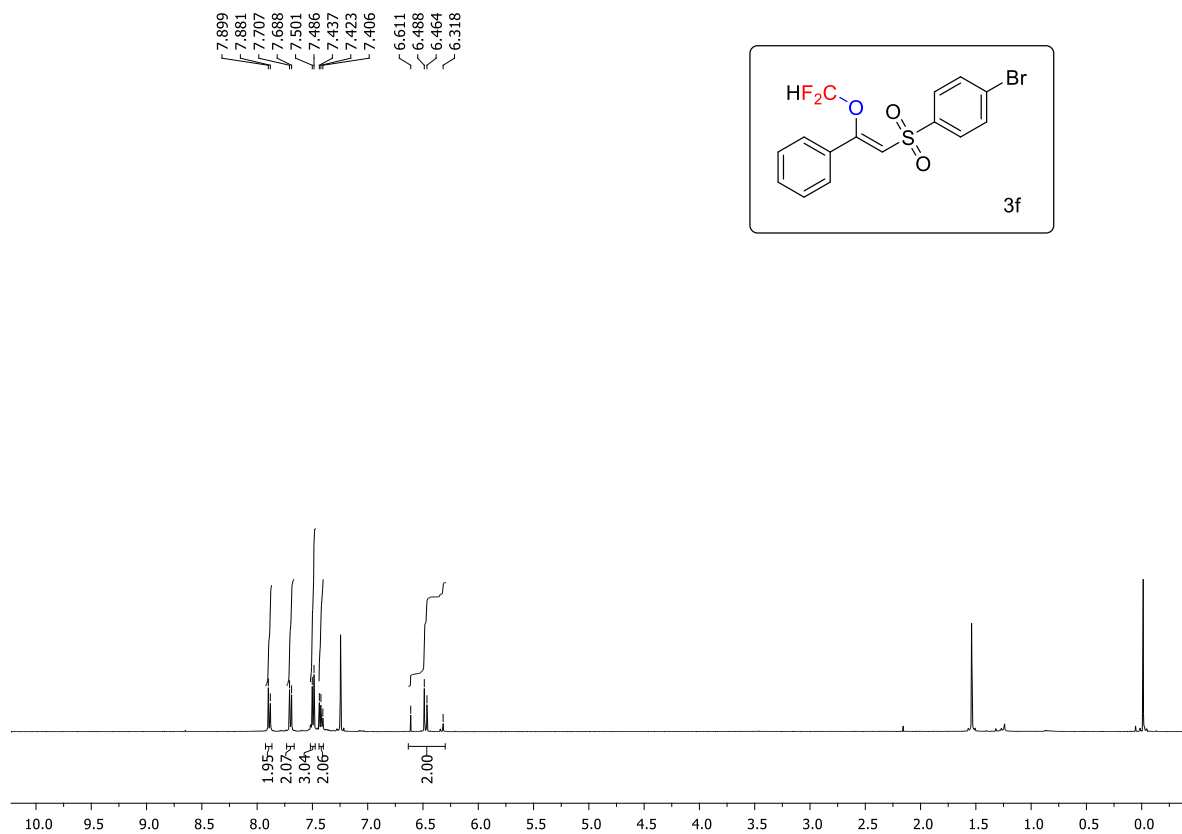
-81.109
-81.262



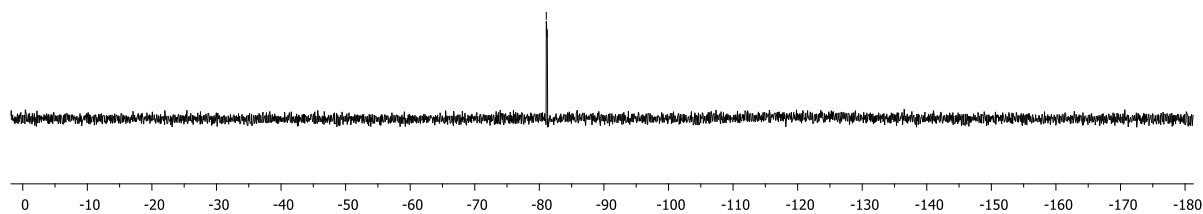
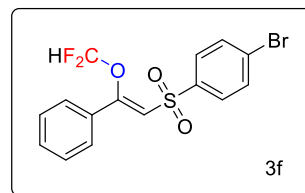
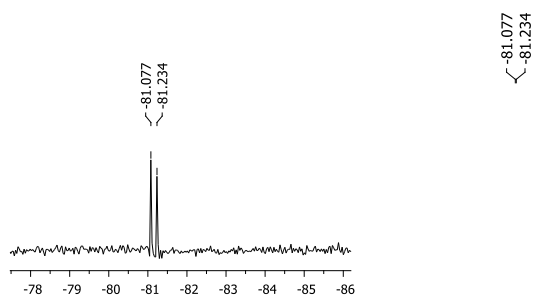
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)



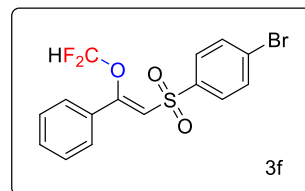
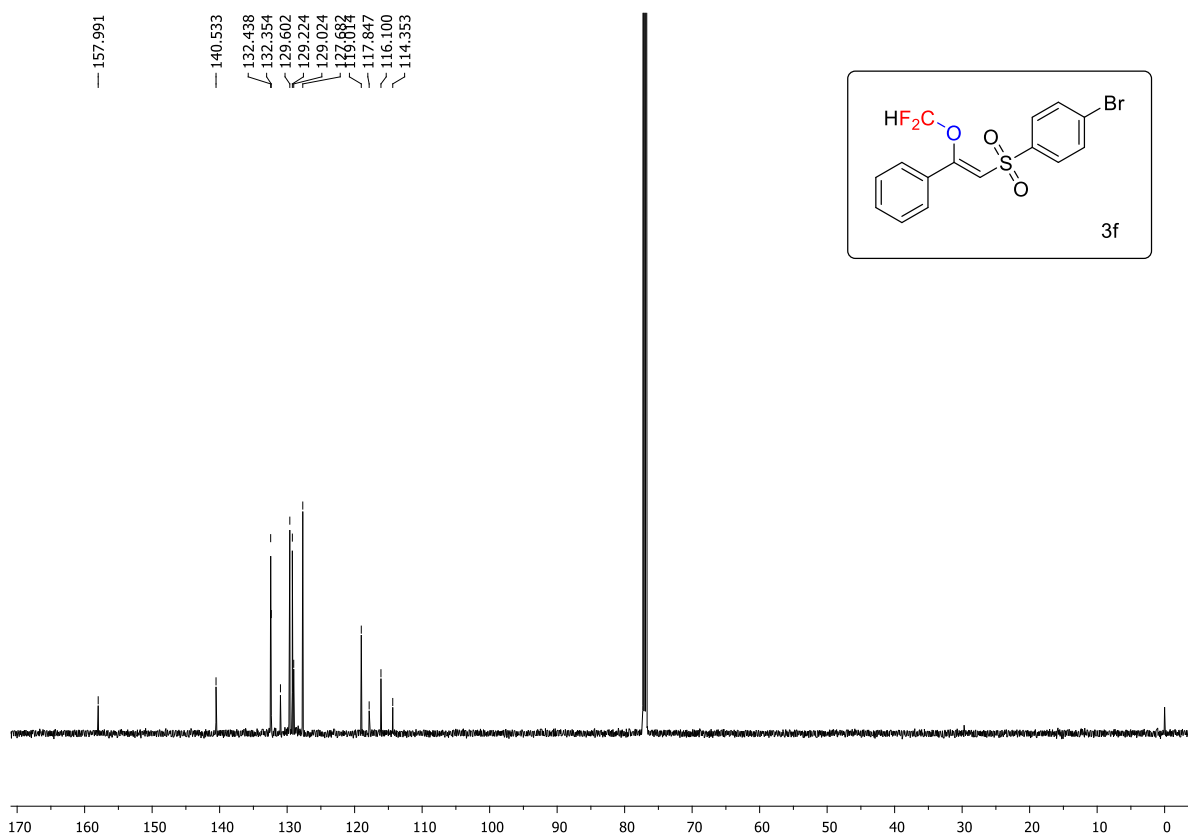
^1H NMR (500 MHz, CDCl_3)



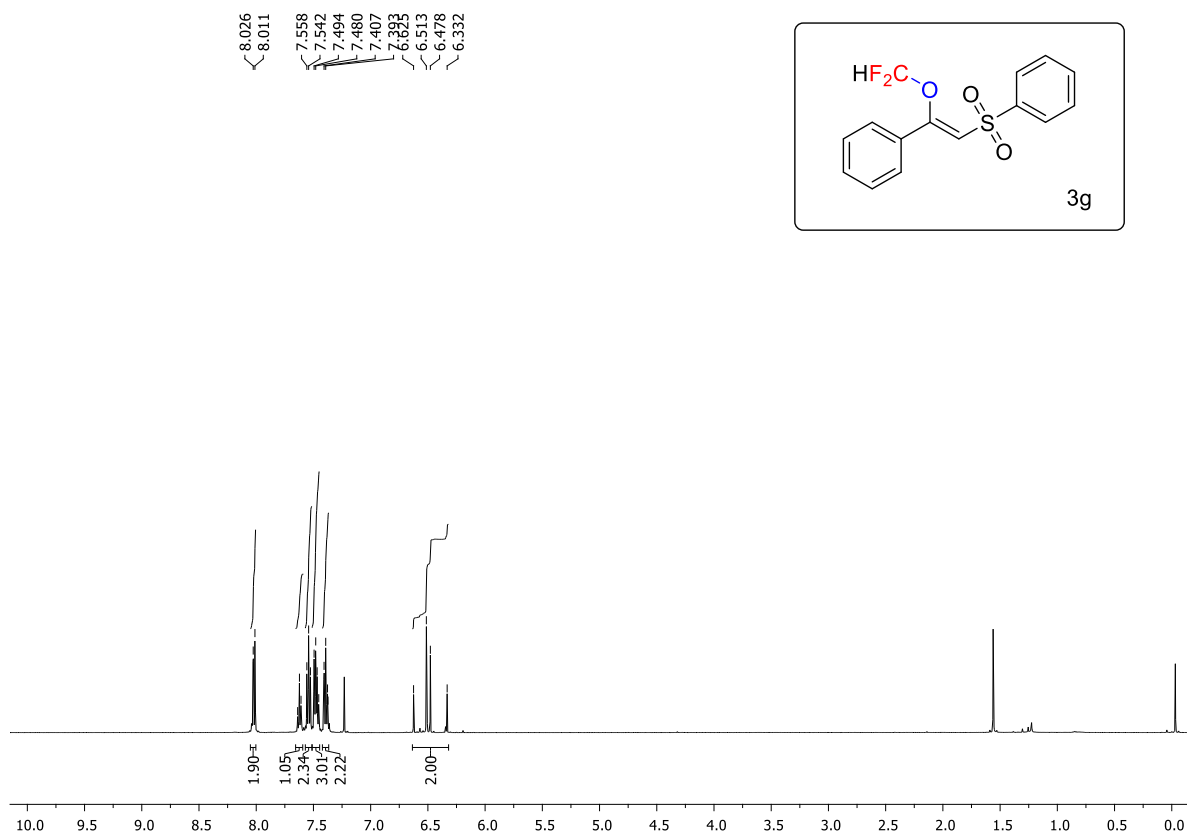
^{19}F NMR (471 MHz, CDCl_3)



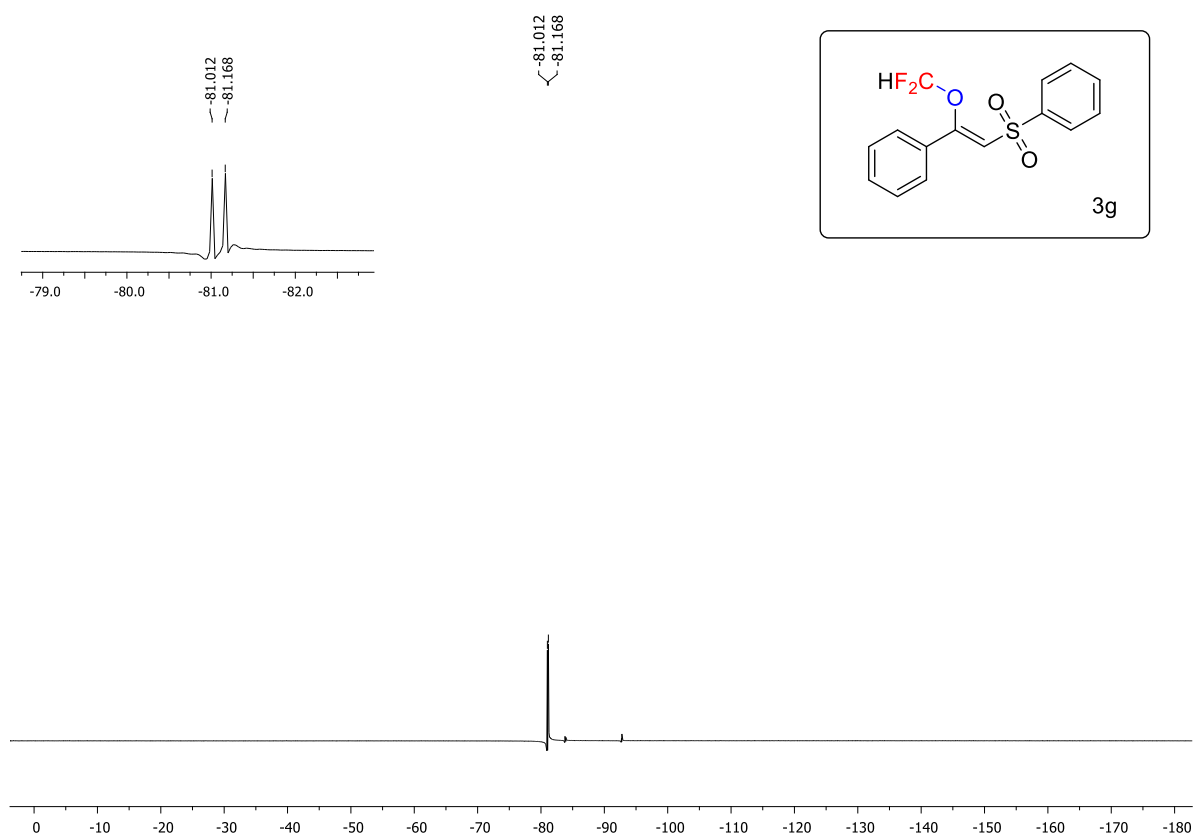
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)



^1H NMR (500 MHz, CDCl_3)

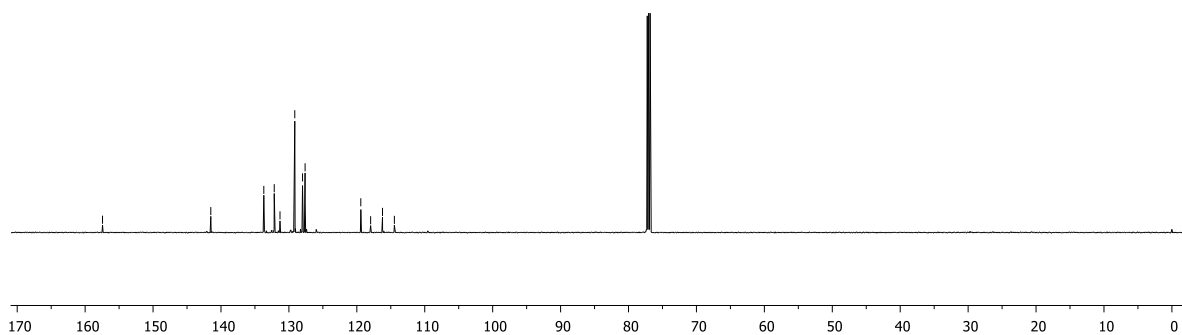
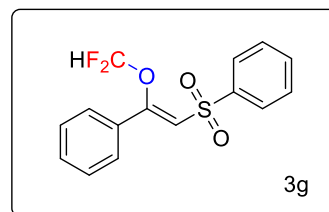


^{19}F NMR (471 MHz, CDCl_3)



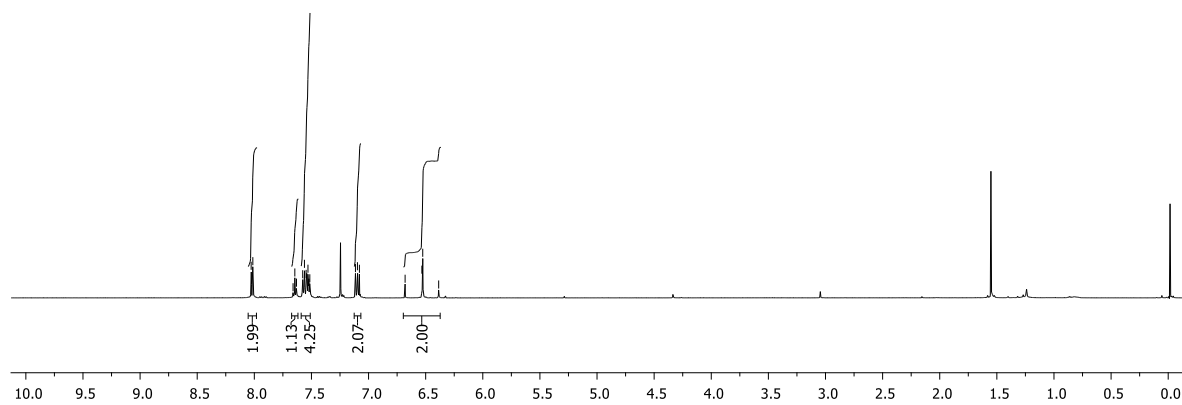
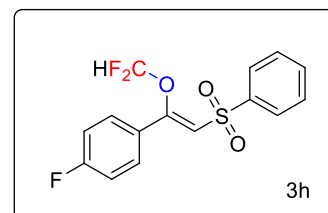
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)

— 157.439
— 141.499
/ 133.694
/ 132.159
/ 131.312
— 129.133
— 127.991
— 127.617
/ 119.413
/ 117.966
— 116.219
— 114.472

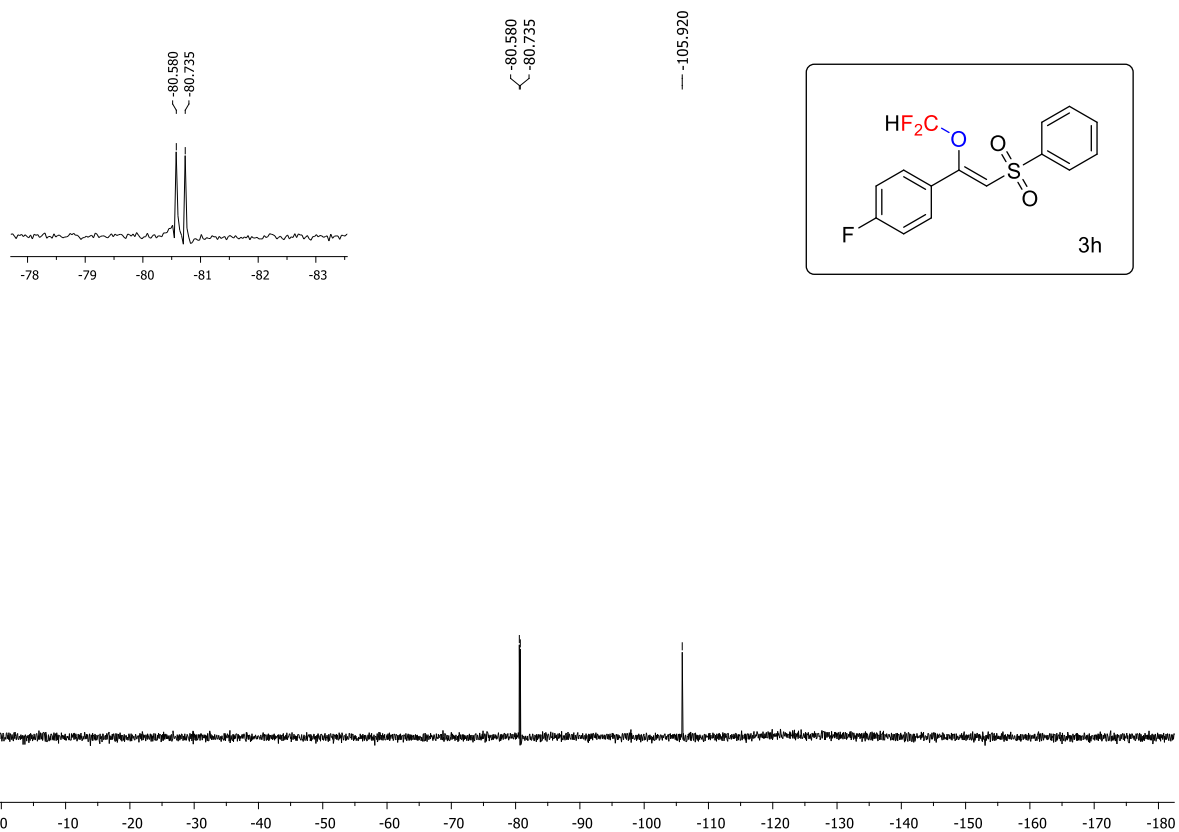


^1H NMR (500 MHz, CDCl_3)

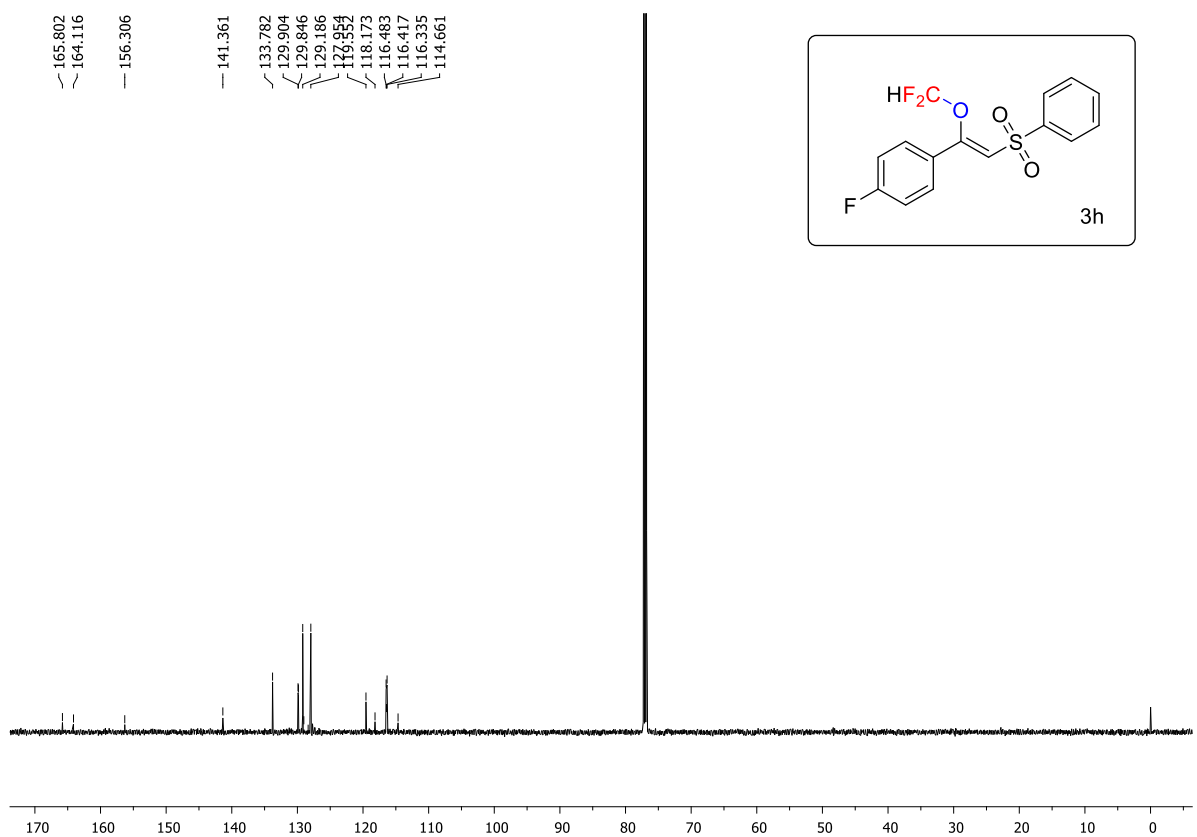
< 8.028
< 8.013
— 7.645
— 7.561
— 7.530
— 7.115
/ 6.986
/ 6.887
— 6.533
— 6.526
— 6.386



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

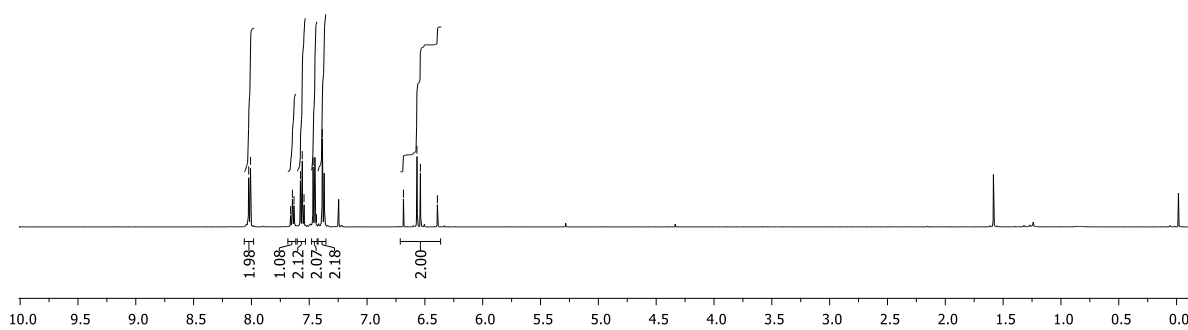
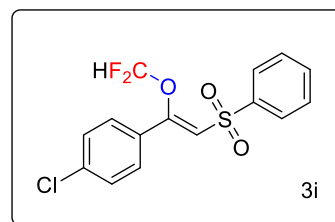


$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)



¹H NMR (500 MHz, CDCl₃)

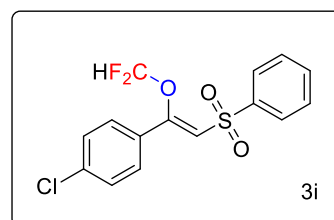
8.023
8.007
7.646
7.576
7.560
7.545
7.467
7.385
6.569
6.539
6.392



¹⁹F NMR (471 MHz, CDCl₃)

-80.514
-80.670

-80.514
-80.670

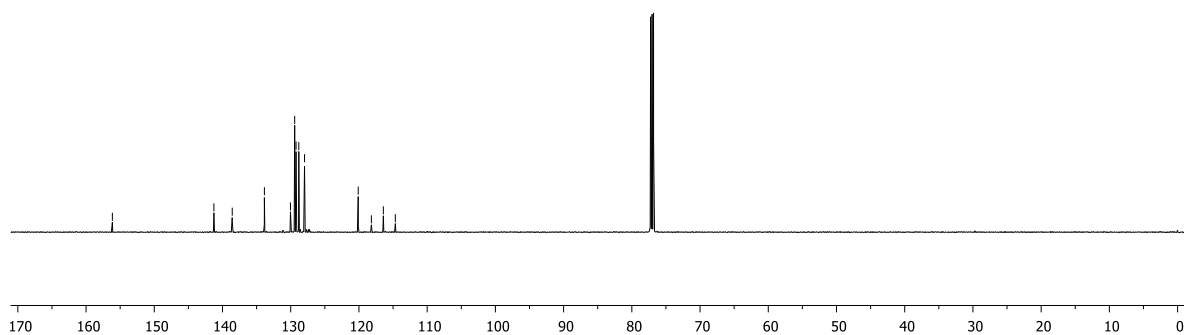
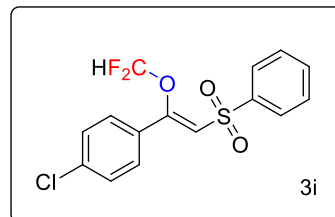


-78
-79
-80
-81
-82
-83
-84

0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180

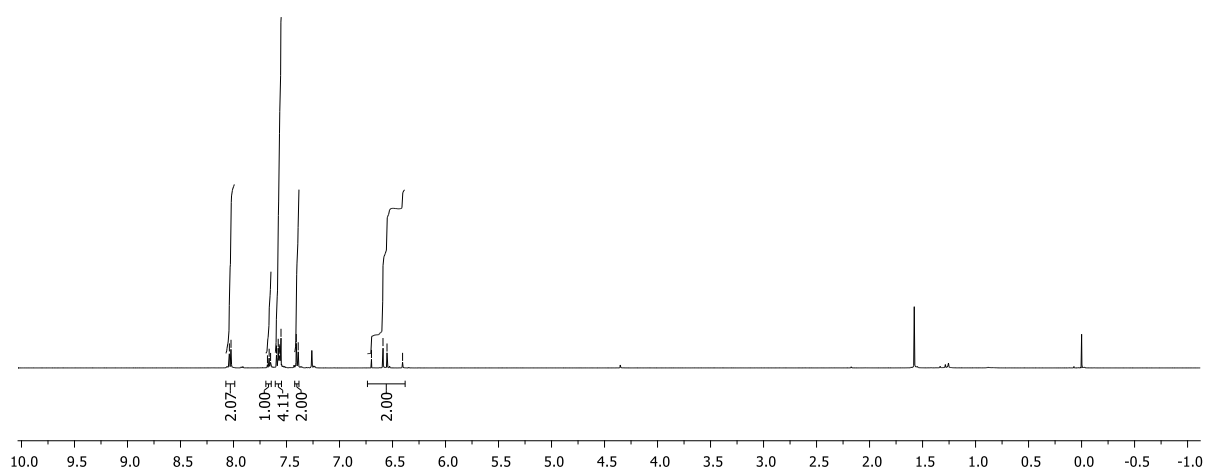
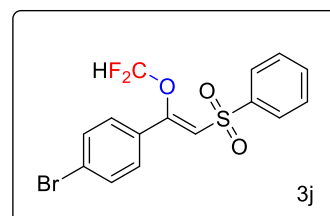
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)

— 156.143
/ 141.260
/ 138.573
/ 133.858
/ 130.036
/ 129.420
/ 128.218
/ 127.974
/ 120.106
/ 118.178
/ 116.422
/ 114.666

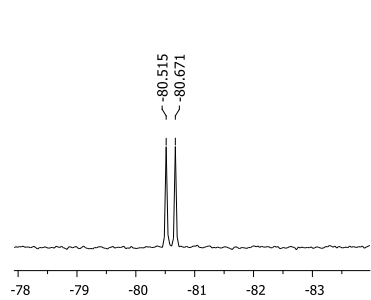


^1H NMR (500 MHz, CDCl_3)

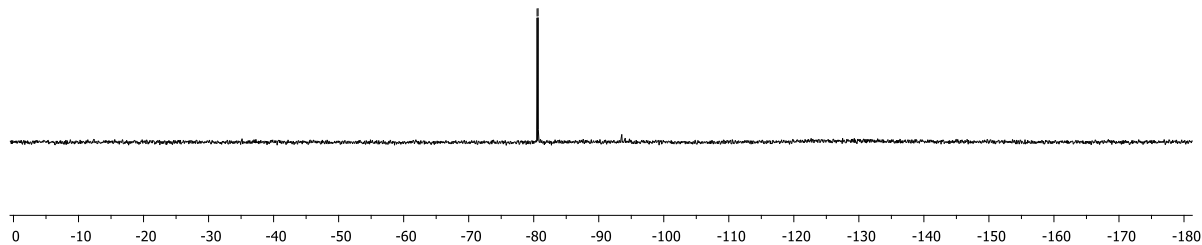
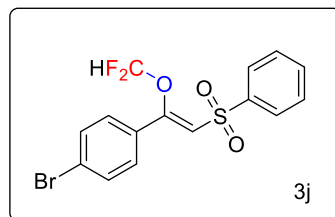
8.039
8.024
7.680
7.664
7.650
7.594
7.578
7.570
7.564
7.552
7.408
7.390
6.699
6.590
6.552
6.405



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

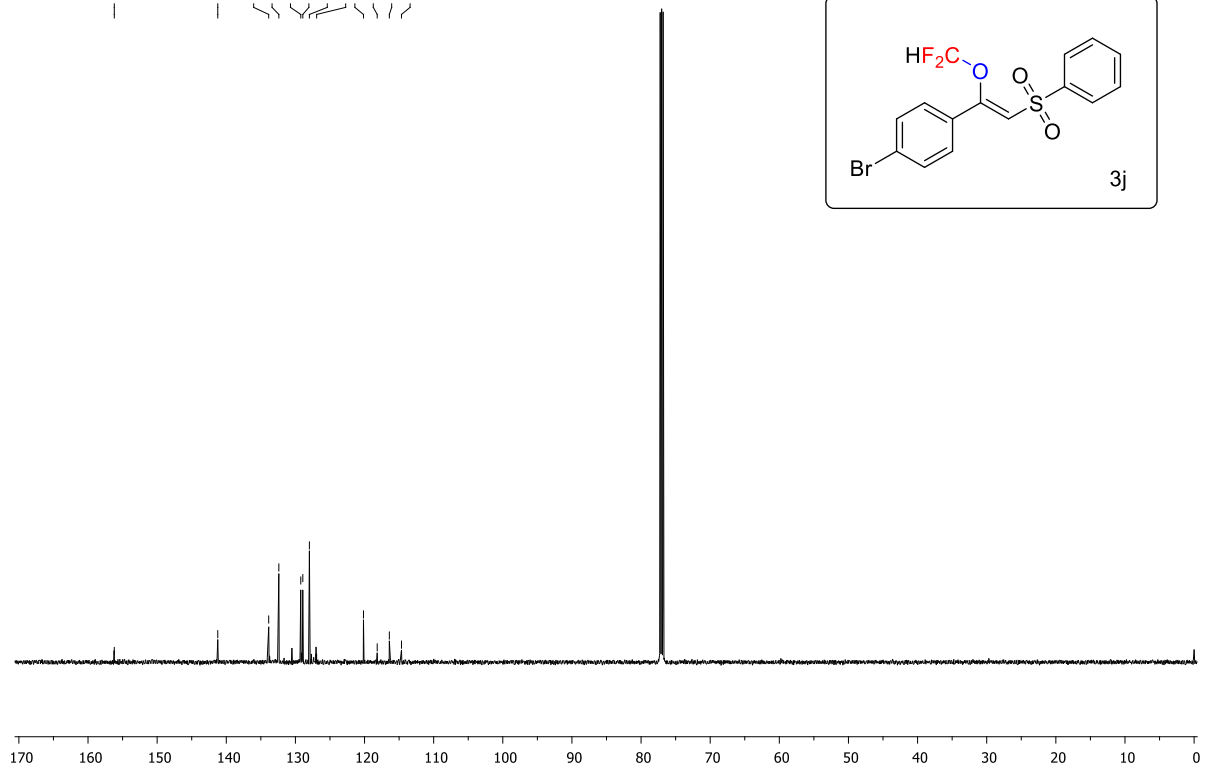
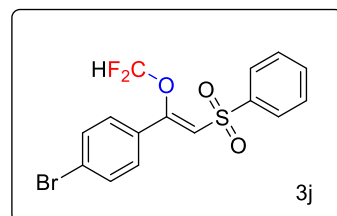


-80.515
-80.671

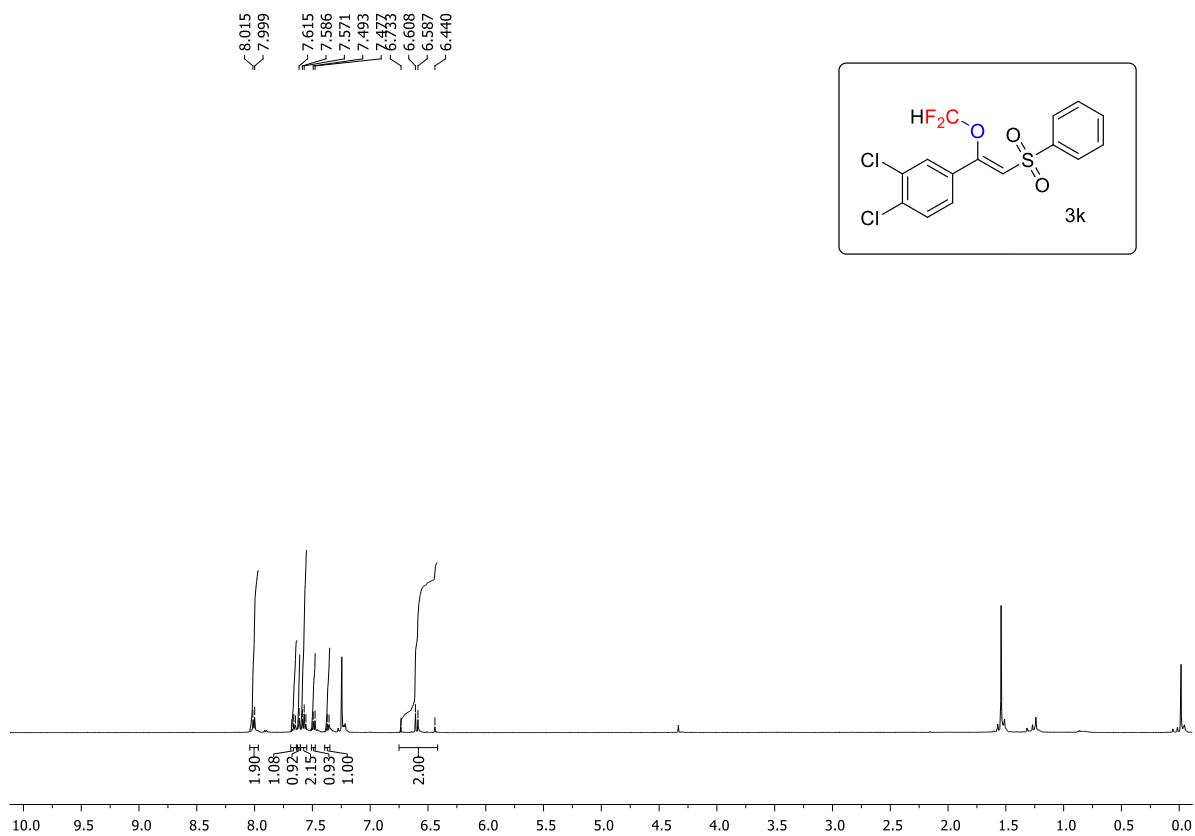


$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)

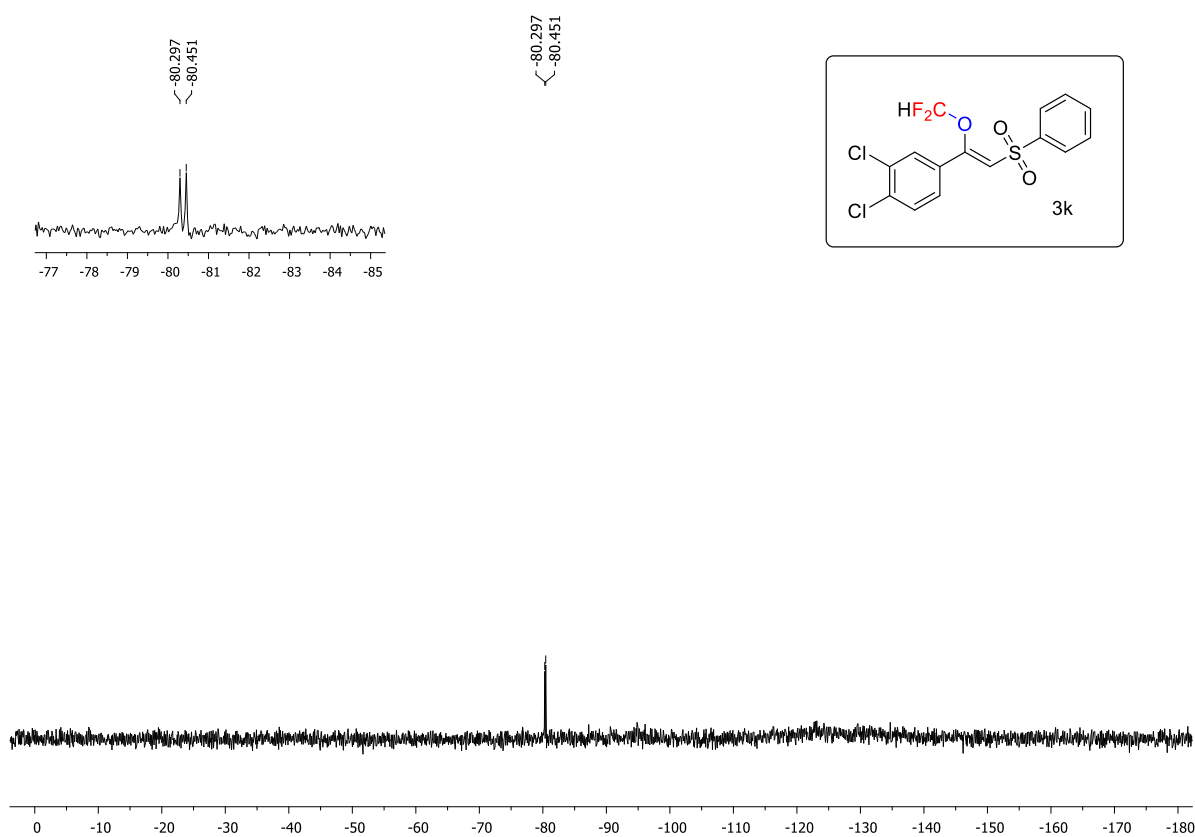
-156.199
-141.232
-133.863
-132.397
-129.223
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-114.656



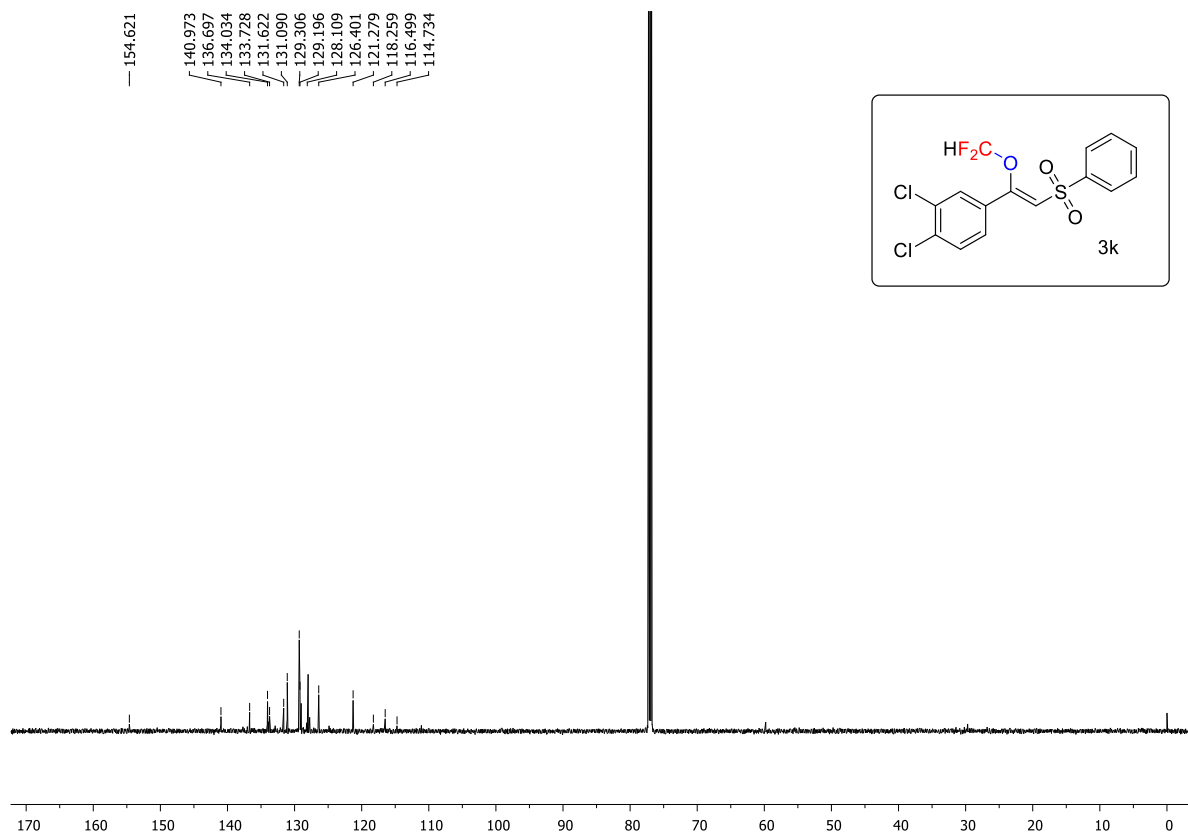
¹H NMR (500 MHz, CDCl₃)



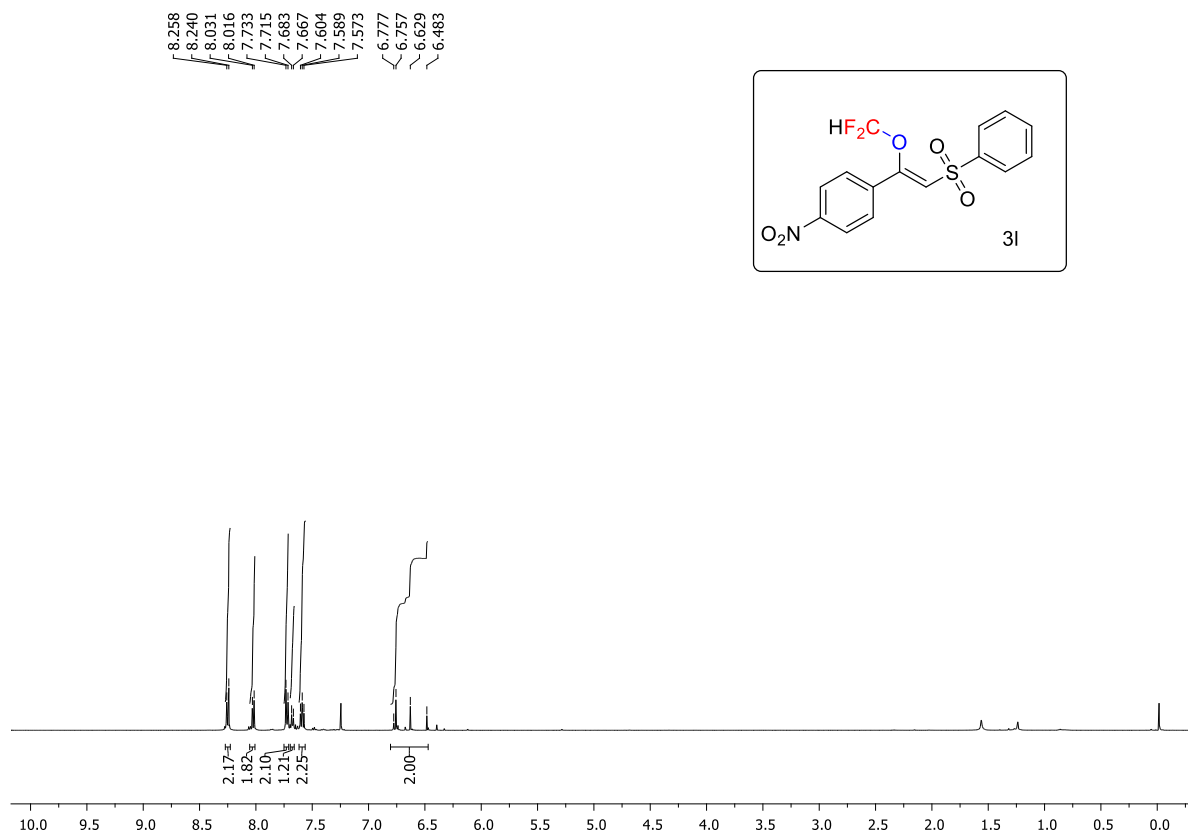
¹⁹F NMR (471 MHz, CDCl₃)



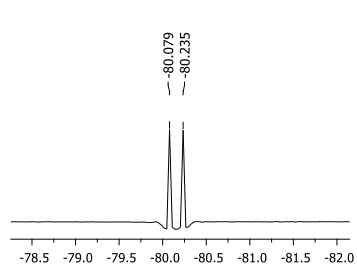
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)



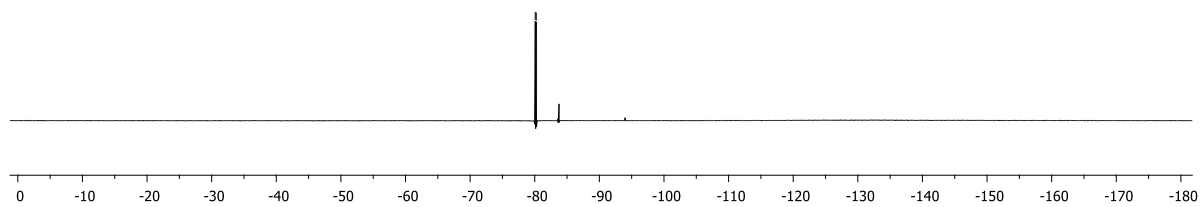
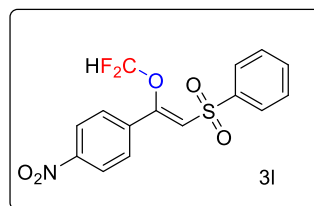
^1H NMR (500 MHz, CDCl_3)



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

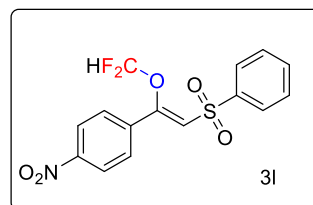
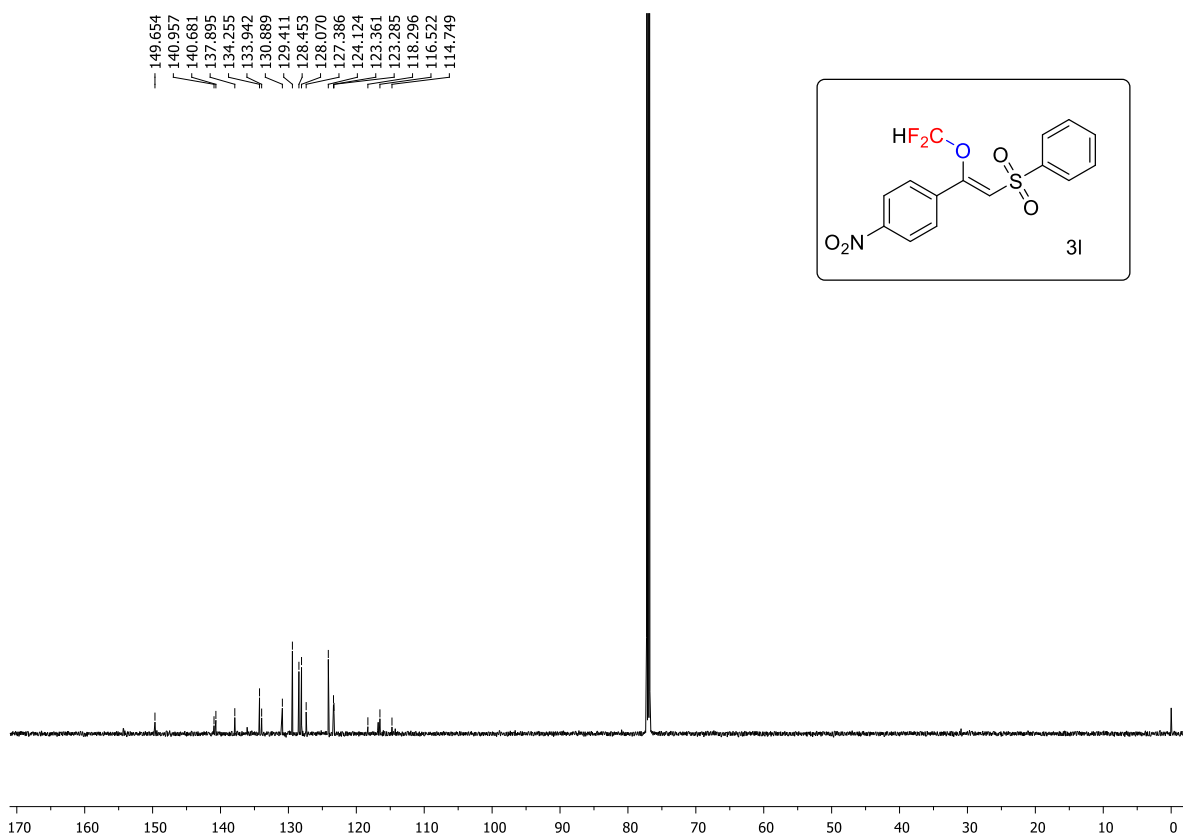


δ -80.079
 δ -80.235



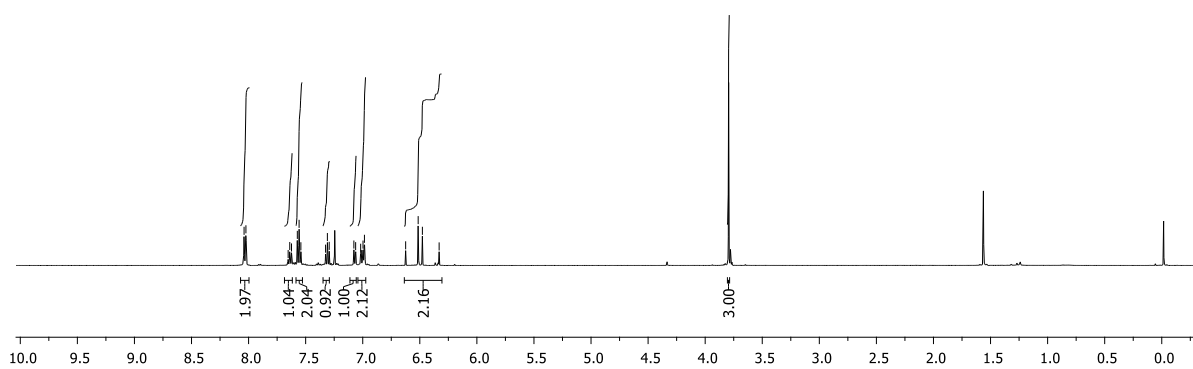
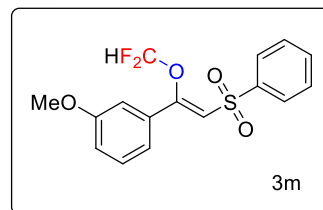
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)

149.654
140.957
140.681
137.895
134.255
133.942
130.889
129.411
128.453
128.070
127.386
124.124
123.361
123.285
118.296
116.522
114.749



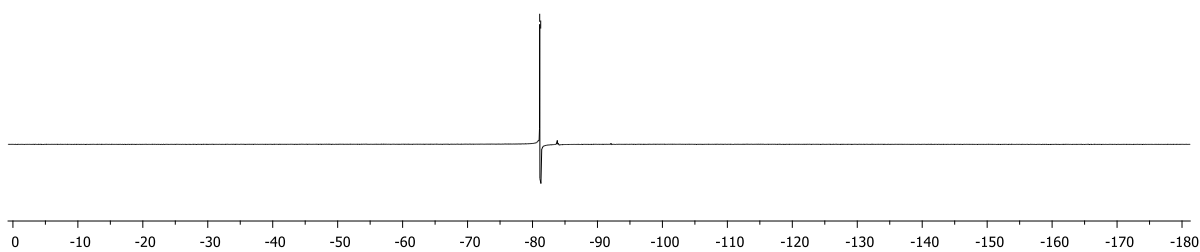
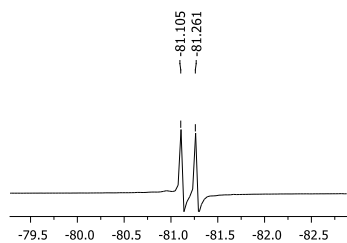
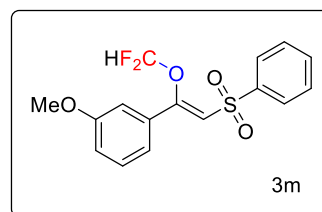
¹H NMR (500 MHz, CDCl₃)

8.040
8.023
7.573
7.558
7.310
7.078
6.998
6.824
6.514
6.477
6.331

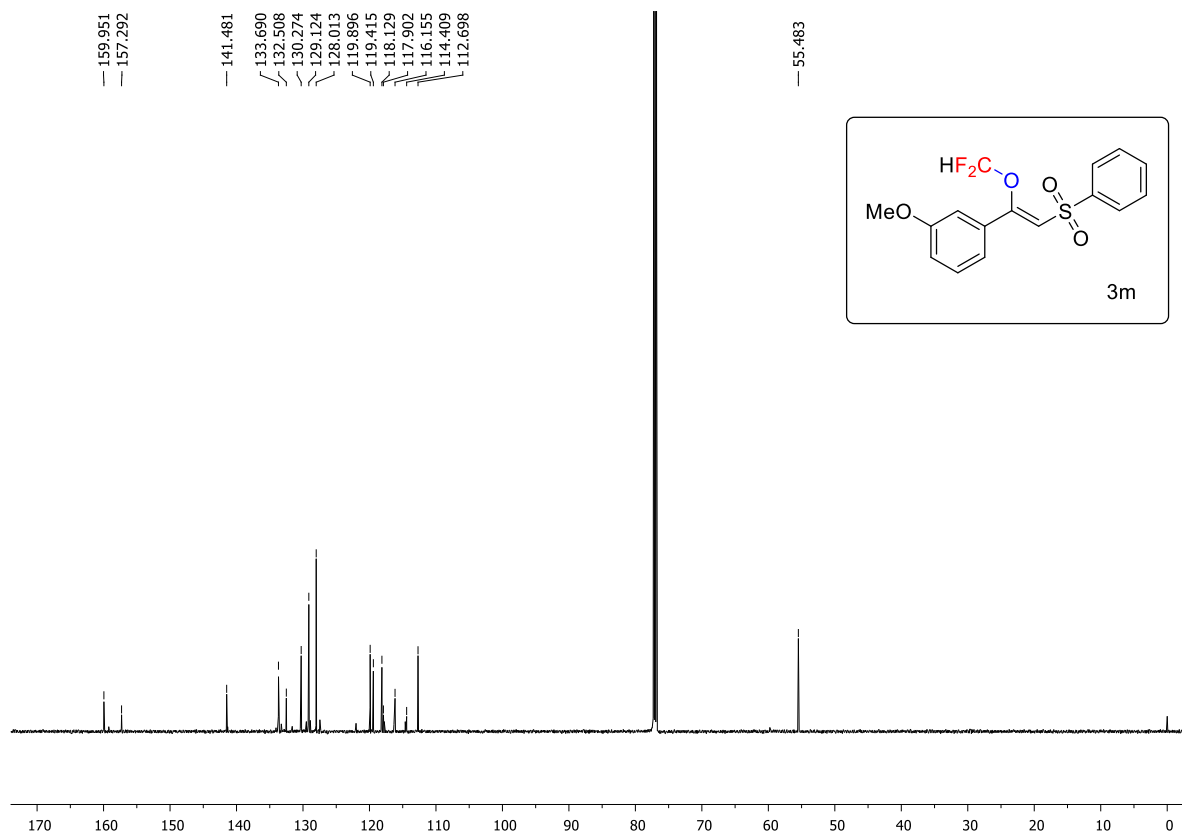


¹⁹F NMR (471 MHz, CDCl₃)

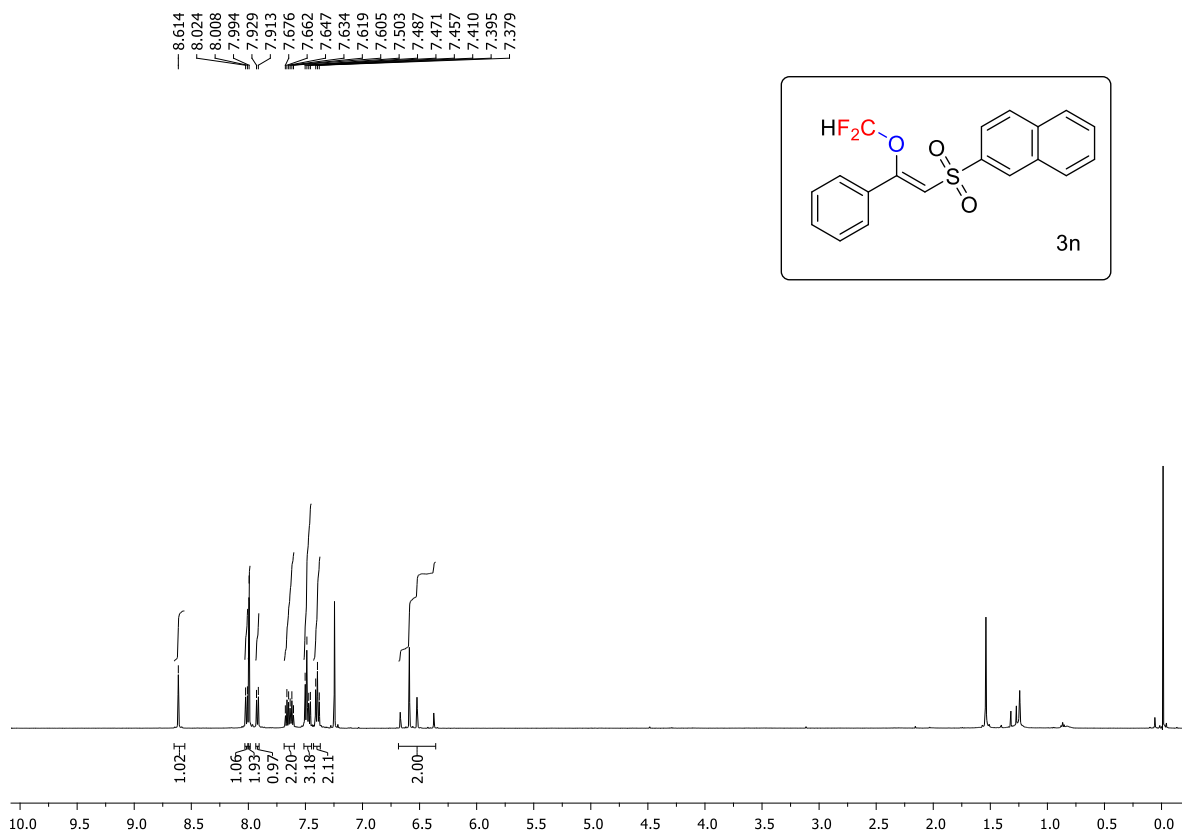
-81.105
-81.261



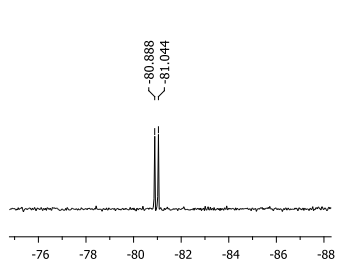
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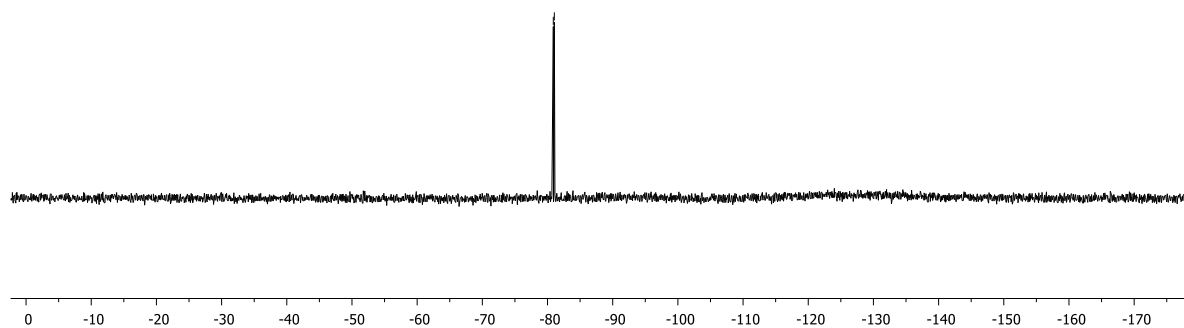
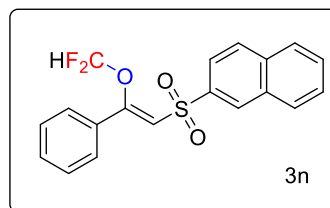
^1H NMR (500 MHz, CDCl_3)



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

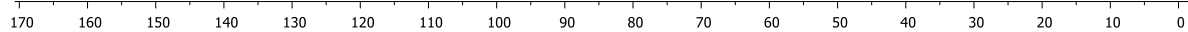
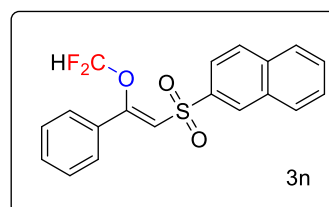


-80.888
-81.044

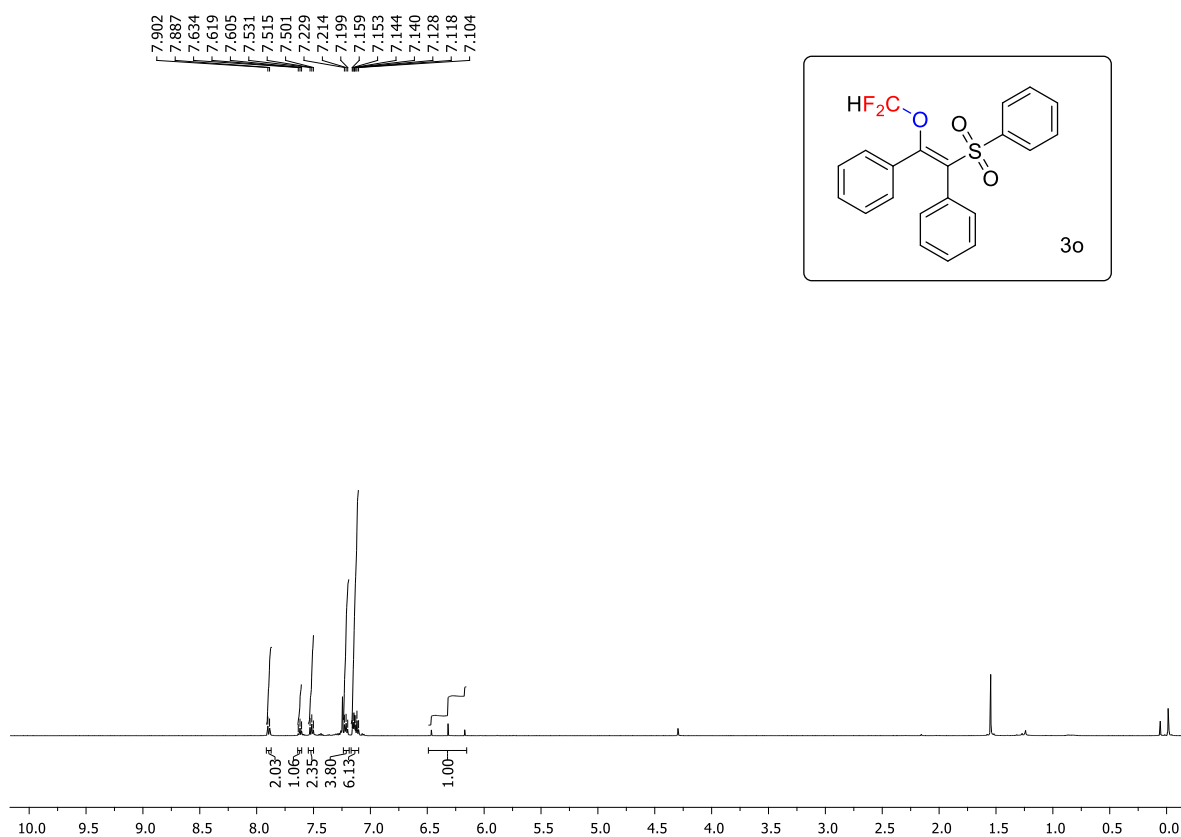


$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)

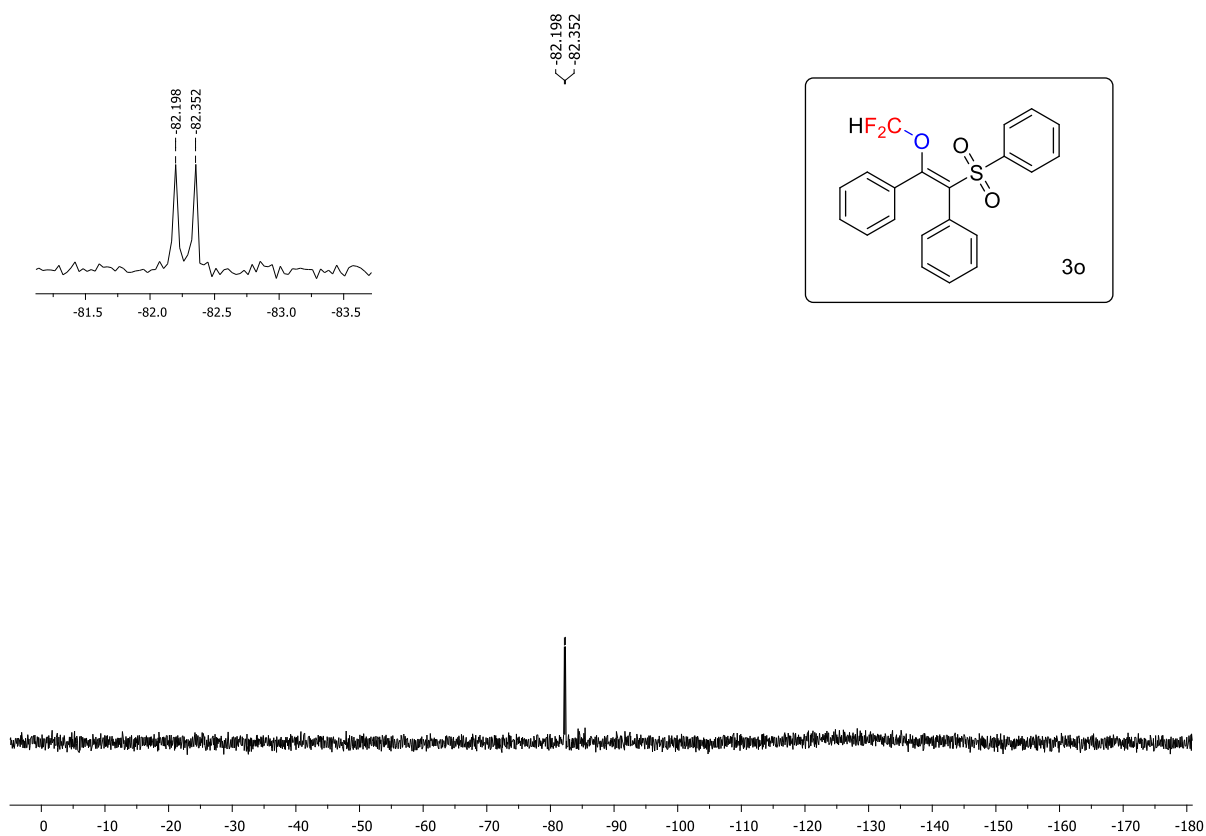
157.491
138.333
135.382
132.201
132.137
131.329
129.830
129.615
129.423
129.260
129.112
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127.616
127.595
122.778
119.402
118.009
116.262
114.515



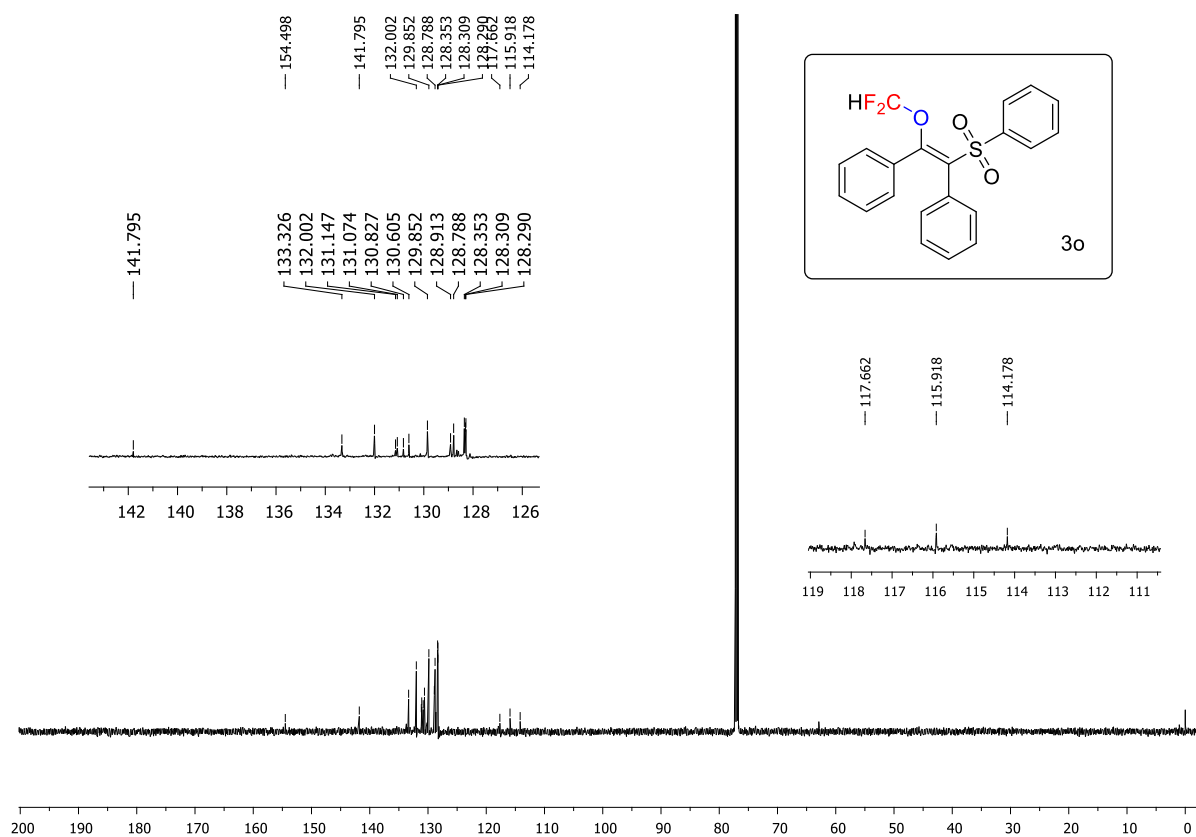
¹H NMR (500 MHz, CDCl₃)



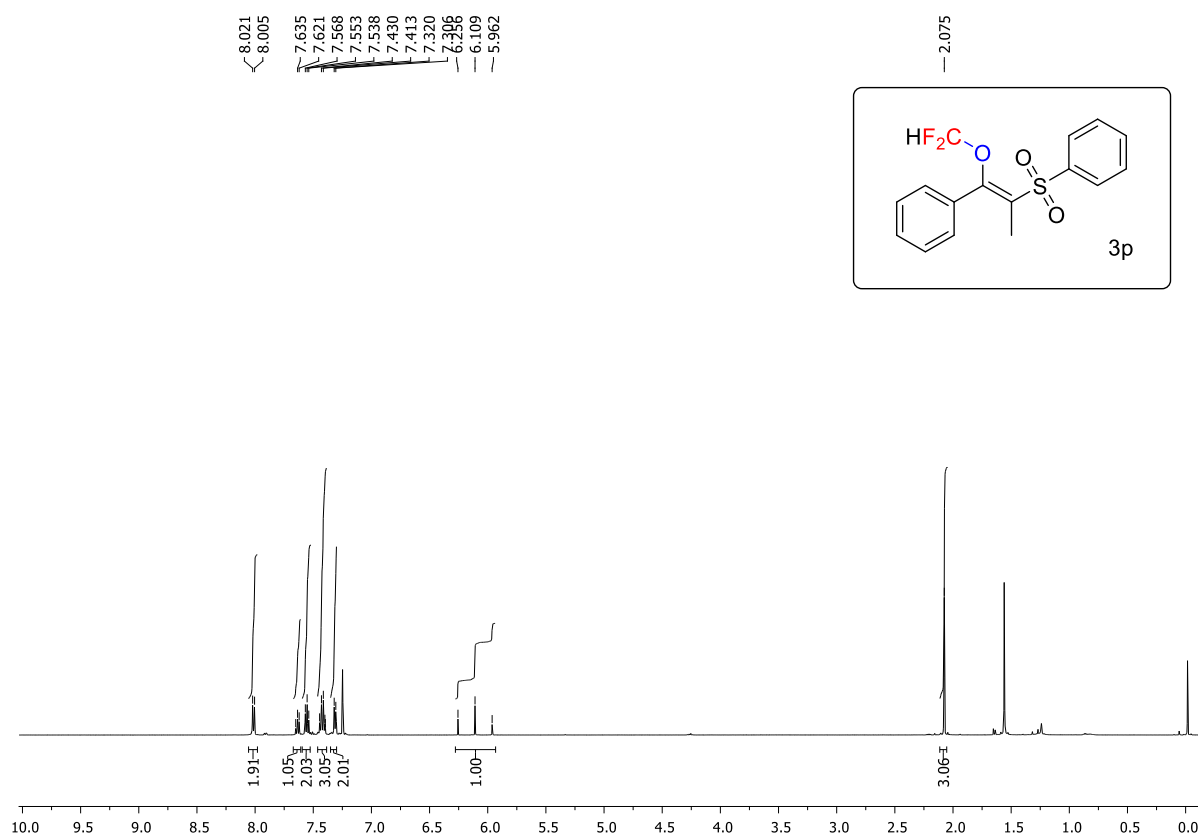
¹⁹F NMR (471 MHz, CDCl₃)



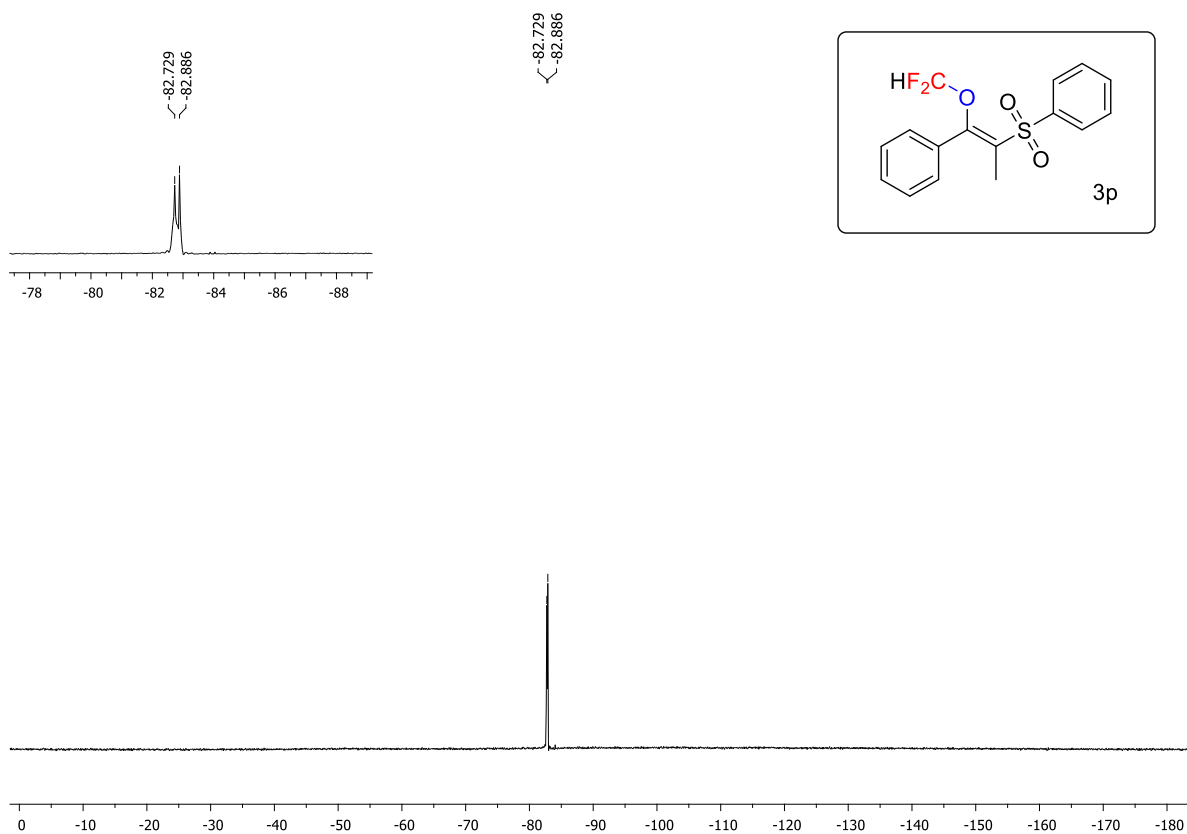
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)



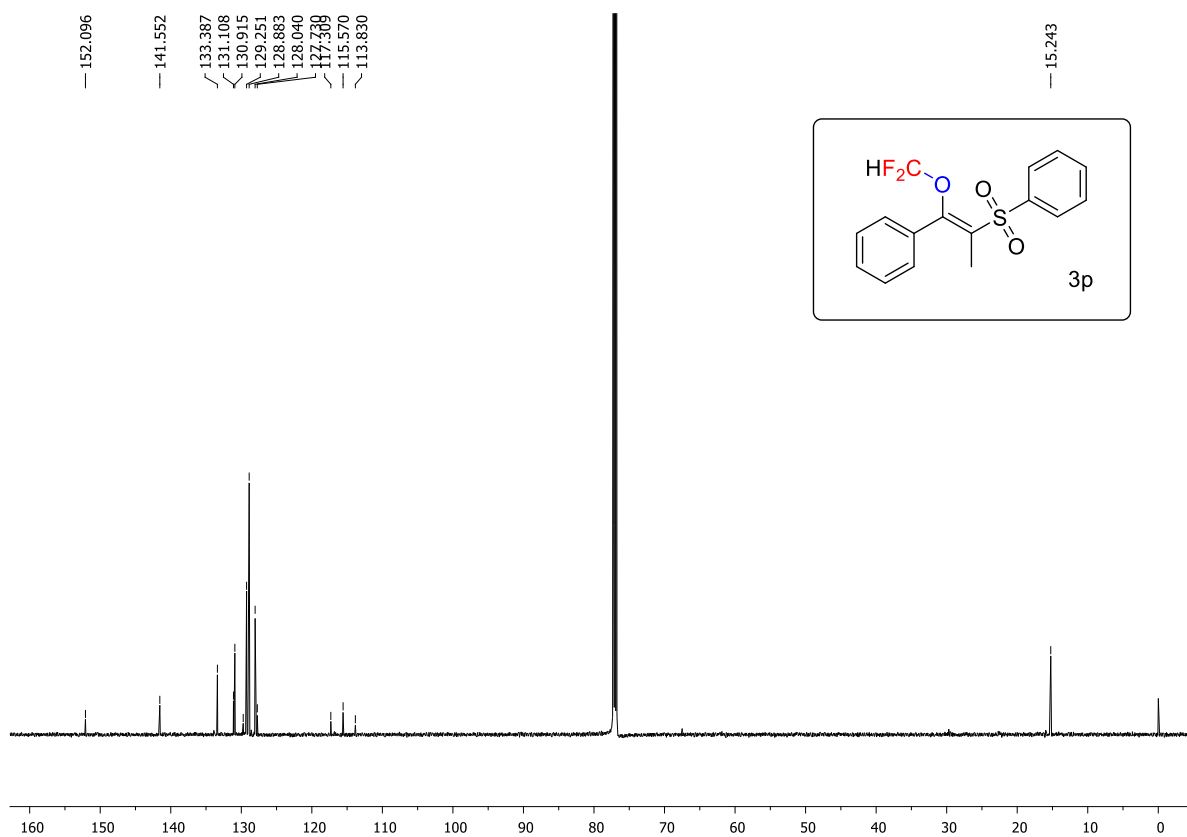
^1H NMR (500 MHz, CDCl_3)



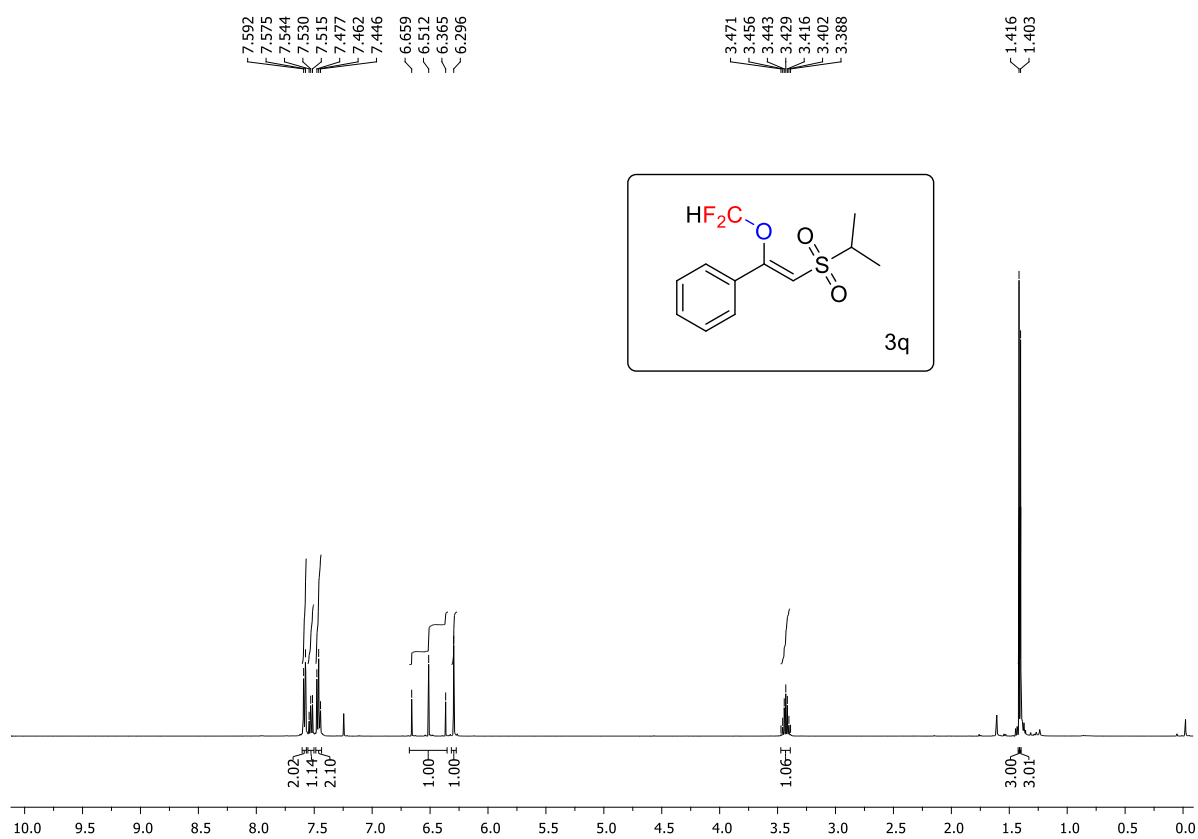
^{19}F NMR (471 MHz, CDCl_3)



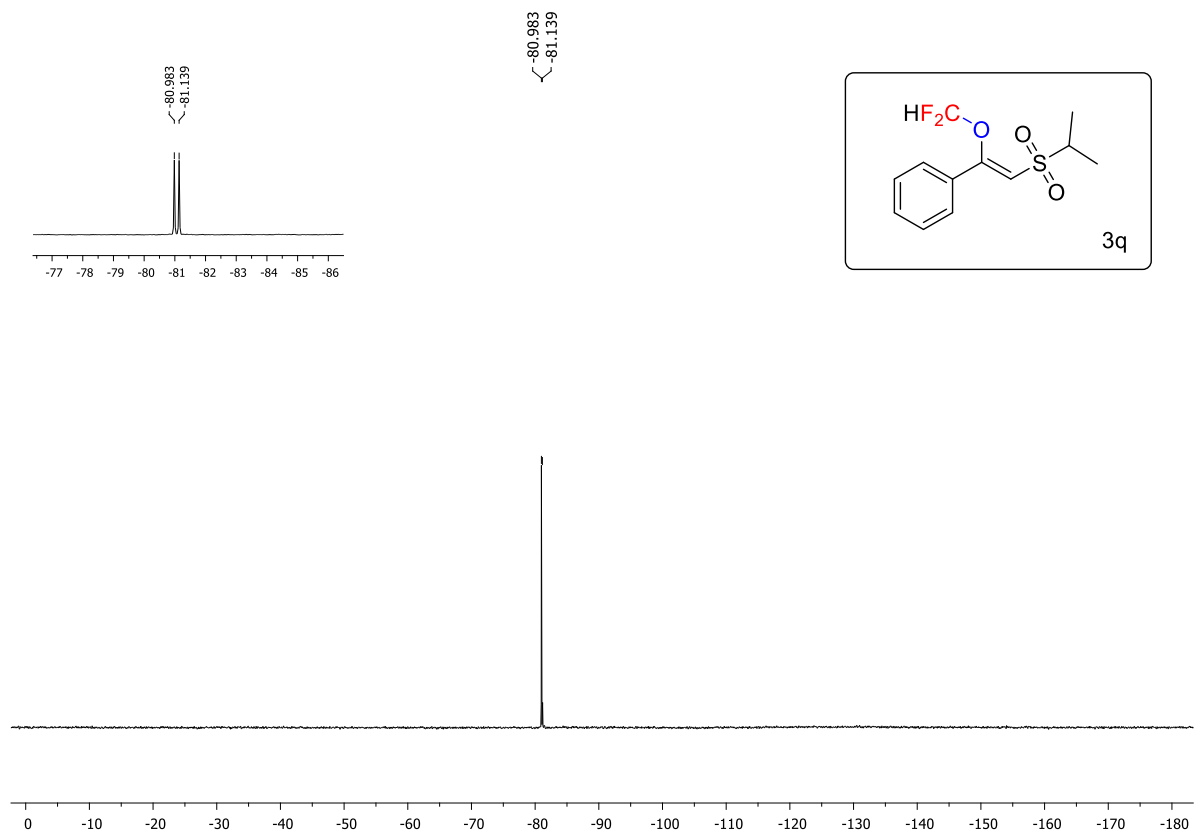
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)



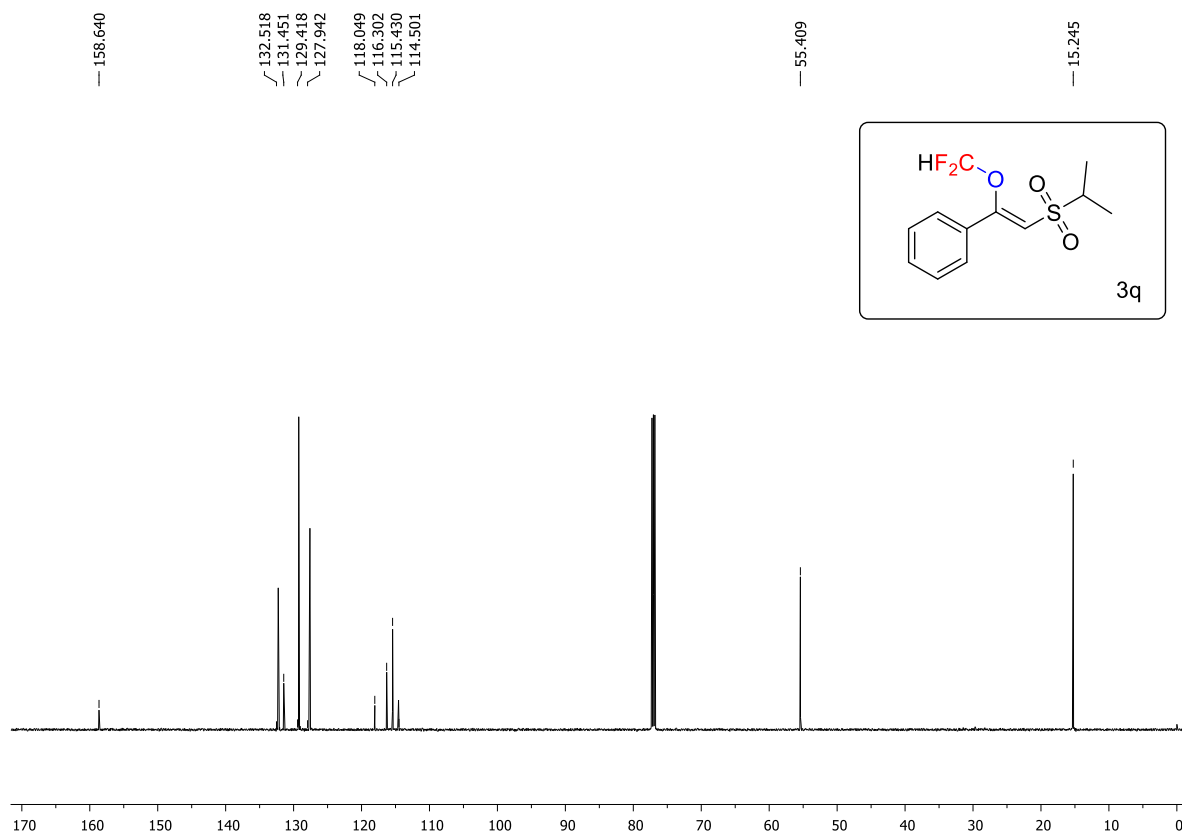
¹H NMR (500 MHz, CDCl₃)



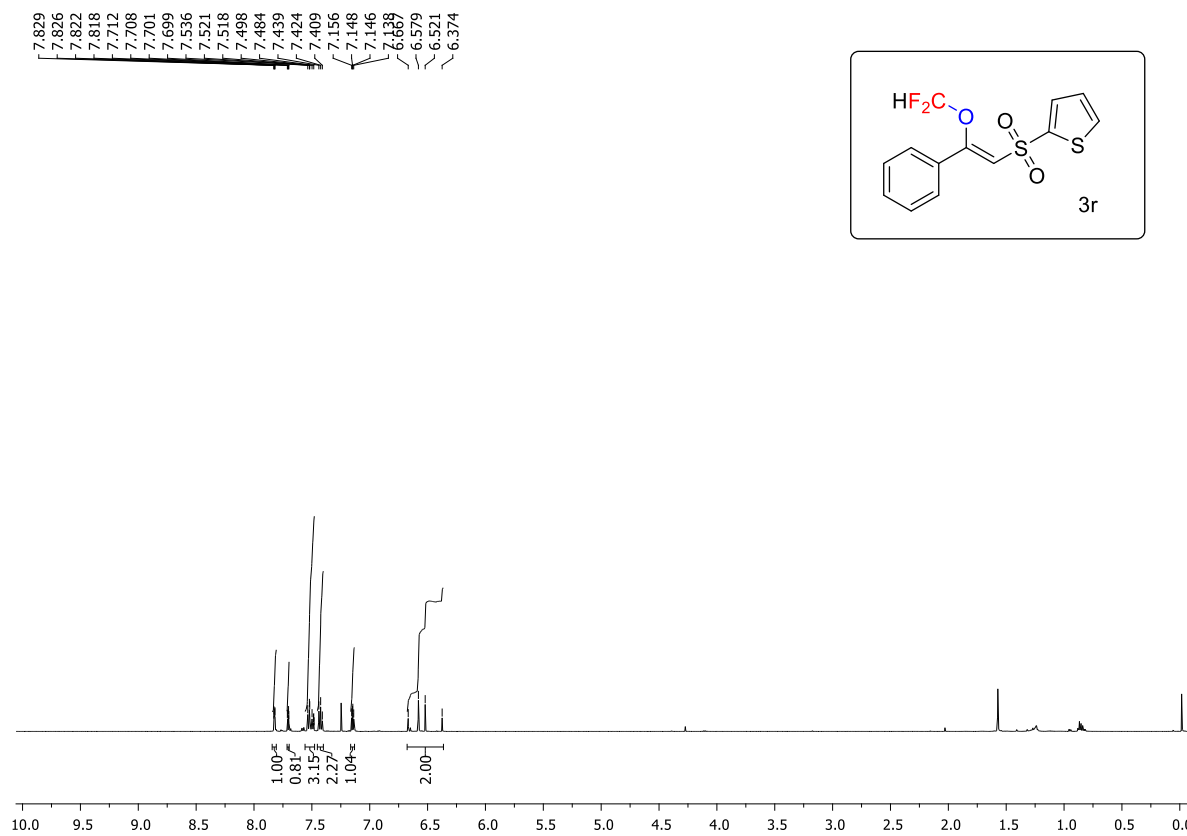
¹⁹F NMR (471 MHz, CDCl₃)



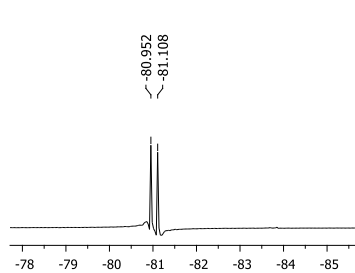
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)



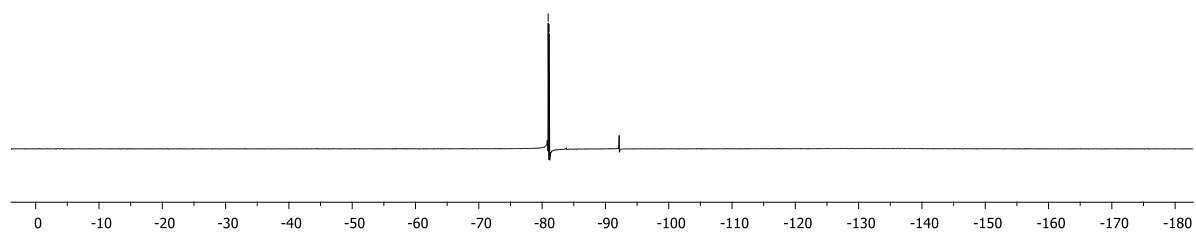
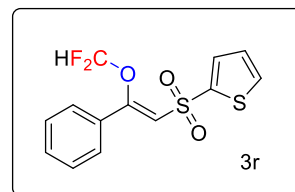
^1H NMR (500 MHz, CDCl_3)



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

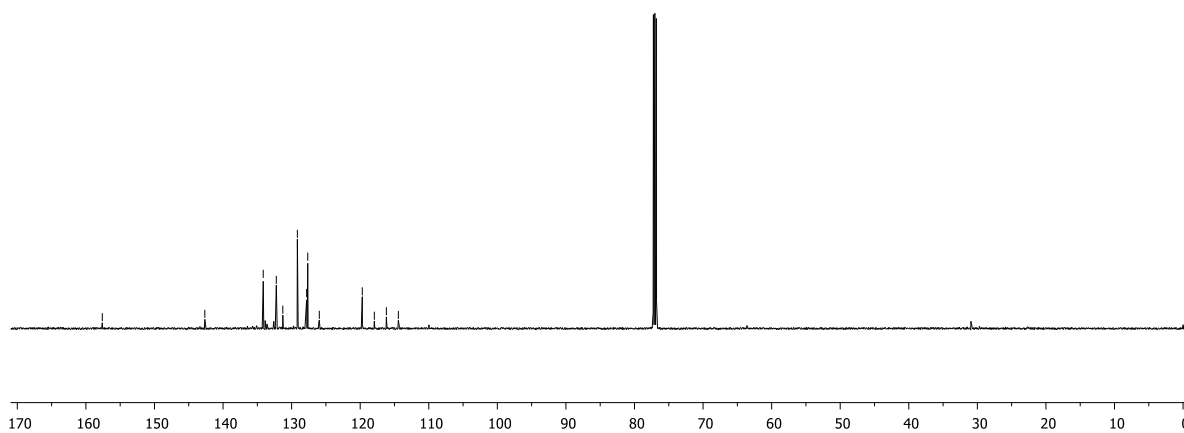
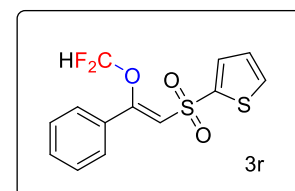


δ -80.952
 δ -81.108

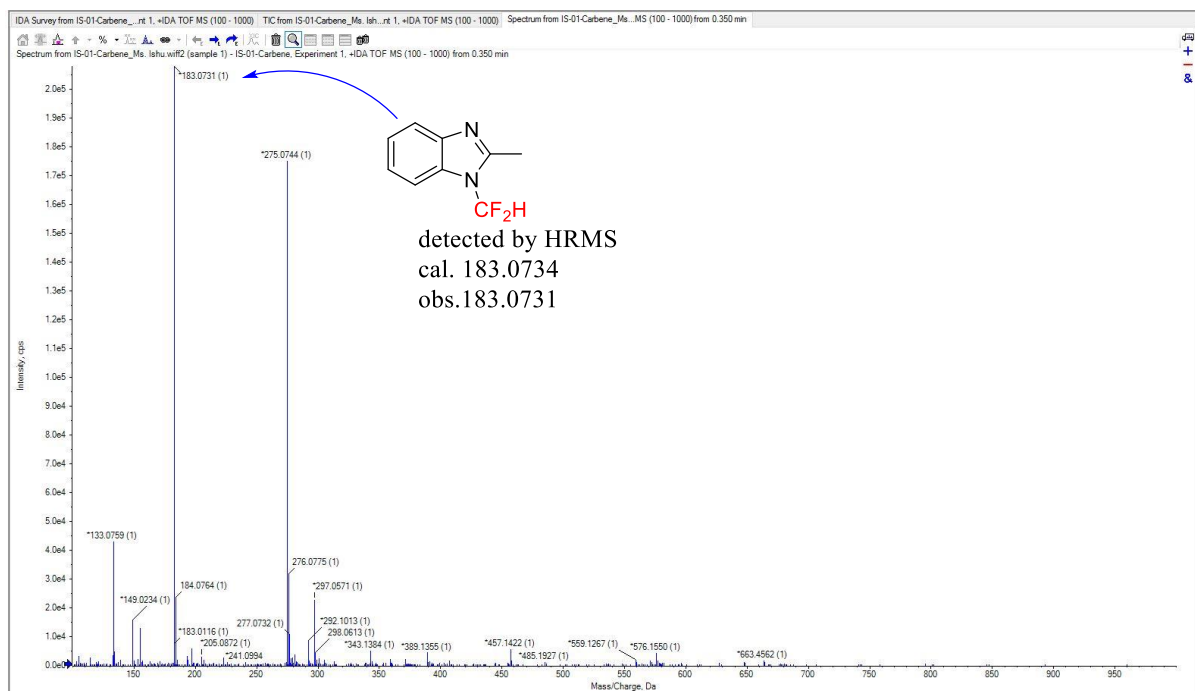


$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3)

δ 157.608
 δ 142.656
 δ 134.138
 δ 132.232
 δ 131.285
 δ 129.162
 δ 127.807
 δ 127.647
 δ 125.964
 δ 119.694
 δ 117.937
 δ 116.184
 δ 114.436



HRMS of the adduct 5



2. Crystallographic Data of the Product 3c:

Crystal of the product **3c** was grown by slow evaporation of a solution of the compound in EtOH/hexane.

Specification: Crystallographic data measurements were obtained on Rigaku XtaLAB Synergy-i dualflex X-ray diffractometer using graphite monochromated Cu-K α radiation ($\lambda = 1.54184 \text{ \AA}$) based diffraction at 285 K. The extracted data was evaluated using CrysAlisPro CCD software. The crystal structure was solved by direct methods using SHELXT 2018/2, and was refined by the full-matrix least-squares methods through Olex2.

X-ray Crystallographic Data of the Product 3c

Empirical formula	C ₁₉ H ₂₀ F ₂ O ₃ S
Formula weight	366.432
Temperature/K	285.15
Crystal system	monoclinic
Space group	I2/a
a/Å	21.1418(11)
b/Å	6.3999(3)
c/Å	27.7760(13)
α /°	90
β /°	96.557(4)
γ /°	90
Volume/Å ³	3733.7(3)
Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.304
μ/mm^{-1}	1.843
F(000)	1544.1
Crystal size/mm ³	0.2 × 0.1 × 0.1
Radiation	Cu K α ($\lambda = 1.54184$)
2 Θ range for data collection/°	6.4 to 143.7
Index ranges	-26 ≤ h ≤ 26, -7 ≤ k ≤ 7, -34 ≤ l ≤ 33
Reflections collected	12895
Independent reflections	3590 [$R_{\text{int}} = 0.0887$, $R_{\text{sigma}} = 0.0918$]
Data/restraints/parameters	3590/18/227
Goodness-of-fit on F ²	1.041
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.1050$, $wR_2 = 0.2711$
Final R indexes [all data]	$R_1 = 0.1538$, $wR_2 = 0.3266$
Largest diff. peak/hole / e Å ⁻³	0.89/-0.44

ORTEP Diagram of the Product 3c

ORTEP with 50% thermal ellipsoid probability level

