Supporting Information

2nd generation Julia reaction-based 1,3-diene synthesis: Aldehyde dependent (*E*,*E*/*E*,*Z*)-selectivity

François Billiard, Raphaël Robiette and Jiří Pospíšil*

Institute of Condensed Matter and Nanosciences – Molecules, Solids and Reactivity (IMCN/MOST), Université catholique de Louvain, Bâtiment Lavoisier, Place Louis Pasteur 1, bte L4.01.02, B-1348 Louvain-la-Neuve, Belgium

jiri.pospisil@uclouvain.be

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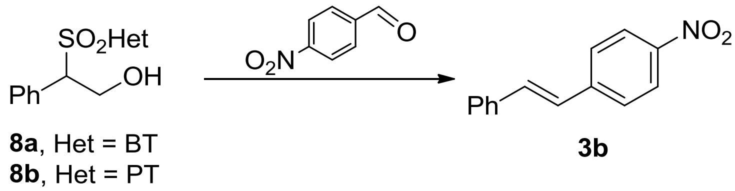
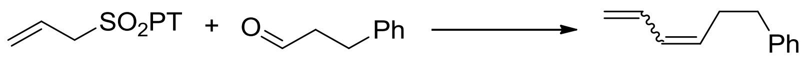
Table S-1. Hydroxy sulfone 8 retroaddition reaction evaluation.



Entry	Hydroxy sulfone	Conditions	Reversibility[a] [%][b]
1	**8a**	$LiN(TMS)_2$ (1.2 equiv), toluene, -75°C	<5
2	**8a**	$LiN(TMS)_2$ (1.2 equiv), THF, -78°C	<5
3	**8a**	$LiN(TMS)_2$ (1.2 equiv), 12-crown-6 (2.2 equiv), THF, -78°C	<5
4	**8a**	$LiN(TMS)_2$ (1.2 equiv), THF/HMPA = 6:1, -78°C	<5
5	**8a**	$LiN(TMS)_2$ (1.2 equiv), DMF, -55°C	<5
6	**8a**	$LiN(TMS)_2$ (1.2 equiv), DMF/HMPA = 3:1, -60°C	<5
7	**8a**	$KN(TMS)_2$ (1.2 equiv), THF, -78°C	<5
8	**8a**	$KN(TMS)_2$ (1.2 equiv), 18-crown-6 (2.5 equiv), THF, -78°C	<5
9	**8a**	$KN(TMS)_2$ (1.2 equiv), DMF, -55°C	<5
10	**8a**	$KN(TMS)_2$ (1.2 equiv), 18-crown-6 (2.5 equiv), DMF, -55°C	32
11	**8a**	$KN(TMS)_2$ (1.2 equiv), DMF/TDA-1 = 3:1, -60°C	56
12	**8b**	$LiN(TMS)_2$ (1.2 equiv), toluene, -75°C	<5
13	**8b**	$LiN(TMS)_2$ (1.2 equiv), THF, -78°C	<5
14	**8b**	$LiN(TMS)_2$ (1.2 equiv), 12-crown-4 (2.2 equiv), THF, -78°C	<5
15	**8b**	$LiN(TMS)_2$ (1.2 equiv), THF/HMPA = 6:1, -78°C	<5
16	**8b**	$LiN(TMS)_2$ (1.2 equiv), DMF, -55°C	31
17	**8b**	$LiN(TMS)_2$ (1.2 equiv), DMF/HMPA = 3:1, -60°C	48
18	**8b**	$KN(TMS)_2$ (1.2 equiv), THF, -78°C	<5
19	**8b**	$KN(TMS)_2$ (1.2 equiv), 18-crown-6 (2.5 equiv), THF, -78°C	8
20	**8b**	$KN(TMS)_2$ (1.2 equiv), DMF, -55°C	34
21	**8b**	$KN(TMS)_2$ (1.2 equiv), 18-crown-6 (2.5 equiv), DMF, -55°C	70 (65)[c]
22	**8b**	$KN(TMS)_2$ (1.2 equiv), DMF/TDA-1 = 3:1, -60°C	>98 (93)[c]

[a] Reversibility is determined as the amount of detected crossover adduct **3b**. [b] Based on crude ^{1}H-NMR and HPLC analysis. [c] Isolated yield.

Table S-2. Reaction between allyl sulfone 1a and dihydrocinnamaldehyde 2c.



1a, Het = PT
1b, Het = BT
2c
3c

Entry	Sulfone	Conditions[a]	Yield[b] [%]	*E*/*Z*[c] [%]
1	**1a**	$KN(TMS)_2$ added to a solution of **1a** and **2c** in toluene at -70°C	n.d.	61:39
2	**1a**	$LiN(TMS)_2$ added to a solution of **1a** and **2c** in THF at -78°C	n.d.	45:55
3	**1a**	$KN(TMS)_2$ added to a solution of **1a** and **2c** in THF at -78°C	n.d.	68:32
4	**1a**	$KN(TMS)_2$ added to a solution of **1a** and **2c** in DMF at -55°C	65	58:42
5	**1a**	$KN(TMS)_2$ added to a solution of **1a**, **2c** and 18-crown-6 in DMF at -55°C	73	35:65
6	**1a**	$KN(TMS)_2$ added to a solution of **1a** in DMF at -55°C, stirred for 30 min, aldehyde **2c** added at -55°C	64	25:75
7	**1a**	$KN(TMS)_2$ added to a solution of **1a** and 18-crown-6 in DMF at -55°C, stirred for 30 min, aldehyde **2c** added at -55°C	17	16:84
8	**1a**	$KN(TMS)_2$ added to a solution of **1a** and 18-crown-6 in DMF at -55°C, stirred for 20 min, aldehyde **2c** added at -55°C	48	15:85
9	**1a**	$KN(TMS)_2$ added to a solution of **1a** and 18-crown-6 in DMF at -55°C, stirred for 2 min, aldehyde **2c** added at -55°C	74	15:85
10	**1a**	$KN(TMS)_2$ added to a solution of **1a** and 18-crown-6 in DMF at -55°C, stirred for 1 min, aldehyde **2c** added at -55°C	79	23:77
11	**1a**	$KN(TMS)_2$ added to a solution of **1a** in DMF/TDA-1 = 5:1 (V/V) at -60°C, stirred for 2 min, aldehyde **2c** added at -60°C	n.d.	21:79
12	**1a**	$KN(TMS)_2$ added to a solution of **1a** in DMF/TDA-1 = 3:1 (V/V) at -60°C, stirred for 2 min[d], aldehyde **2c** added at -60°C	78	14:86
13	**1a**	$KN(TMS)_2$ added to a solution of **1a** in DMF/TDA-1 = 2:1 (V/V) at -60°C, stirred for 2 min, aldehyde **2c** added at -60°C	n.d.	20:80
14	**1a**	$KN(TMS)_2$ added to a solution of **1a** in DMF/TDA-1 = 1:1 (V/V) at -60°C, stirred for 2 min, aldehyde **2c** added at -60°C	n.d.	38:62
15	**1a**	$LiN(TMS)_2$ added to a solution of **1a** in DMF/DMPU = 5:1 (V/V) at -45°C, stirred for 2 min, aldehyde **2c** added at -45°C	n.d.	24:76
16	**1a**	$LiN(TMS)_2$ added to a solution of **1a** in DMF/HMPA = 1:1 (V/V) at -60°C, stirred for 2 min, aldehyde **2c** added at -60°C	n.d.	23:77
15	**1b**	$KN(TMS)_2$ added to a solution of **1b** and **2c** in DMF at -55°C	53	57:43
16	**1b**	$KN(TMS)_2$ added to a solution of **1b** and 18-crown-6 in DMF at -55°C, stirred for 10 min, aldehyde **2c** added at -55°C	37	25:75
17	**1b**	$KN(TMS)_2$ added to a solution of **1b** and 18-crown-6 in DMF at -55°C, stirred for 2 min, aldehyde **2c** added at -55°C	49	29:71
18	**1b**	$KN(TMS)_2$ added to a solution of **1b** in DMF/TDA-1 = 3:1 (V/V) at -60°C, stirred for 2 min, aldehyde **2c** added at -60°C	52	16:84

[a] The following quantities of given reagents were used: sulfone **1a** or **1b** (1.0 equiv), Li or $KN(TMS)_2$ (1.1 equiv), aldehyde **2c** (1.1 equiv) and 18-crown-6 (2.3 equiv). [b] Average of two runs. Refers to pure isolated compounds. [c] Average of two runs. Based on GC analysis. [d] Extended stirring time (10 min or 20 min) had no influence on the (*E/Z*)-ratio of the product.

Experimental Part

General Information. All compounds were used as received. THF was distilled under argon from sodium benzophenone ketyl. DMF was distilled from CaH_2 under argon and reduced pressure (70°C/100 mbar). Flash chromatography was performed on silica gel 60 (40-63 μm). ^1H and ^{13}C-NMR spectra were recorded on a standard spectrometer operating at 300 MHz or 500 MHz for ^1H at ambient temperature in $CDCl_3$. Proton and carbon chemical shifts (s) are reported in ppm downfield from internal reference of residual $CHCl_3$ peak in $CDCl_3$ (for ^1H-NMR; calibrated to 7.27 ppm) and the middle peak of the triplet in $CDCl_3$ (for ^{13}C-NMR; calibrated to 77.23 ppm). Coupling constants (*J*) are reported in Hertz (Hz), and the following abbreviations are used: singlet (s), doublet (d), doublet of doublet (dd), triplet (t), doublet of triplet (dt), multiplet (m). HRMS measurement were performed using orbitrap Q exactive mass analyzer. All reactions were carried out under an atmosphere of argon in flame-dried apparatus with magnetic stirring, unless otherwise indicated. Analysis and assignments were made by comparison with literature spectroscopic data or using 2D-COSY, HSQC, HMBC, 2D-NOESY and NOEdiff experiments: **3b**[1]. GC and HPLC data of **3b**[2] and **3c**[3].

[1] For (*E*)-nitrostilben (*E*)-**3b** see Luo, F.; Pan C.; Wang, W.; Ye, Z.; Cheng, J. *Tetrahedron* **2010**, *66*, 1399-1403. For (*Z*)-nitrostilben (*Z*)-**3b** see Dong, D.-J.; Li, H.-H.; Tian, S.-K. *J. Am. Chem. Soc.* **2010**, *132*, 5018-5020.

[2] The conversion of **3b** (Table 1) was determined by chiral HPLC using ChromSep SS 100x4.6MM column (MeOH:H_2O = 70:30, 1 mL/min, $\tau_{(Z)\text{-}\mathbf{3b}}$ = 14.10 min, $\tau_{(E)-\mathbf{3b}}$ = 15.58 min).

[3] The (*E*/*Z*)-ration of **3c** in Table 2 was determined by chiral GC using γ-TA column (90°C (2min) -> 2°C/min till 120°C -> 120°C (10 min), $\tau_{(Z)\text{-}\mathbf{3c}}$ = 18.12 min, $\tau_{(E)-\mathbf{3c}}$ = 18.37 min).

Copy of ¹H and ¹³C NMR spectra

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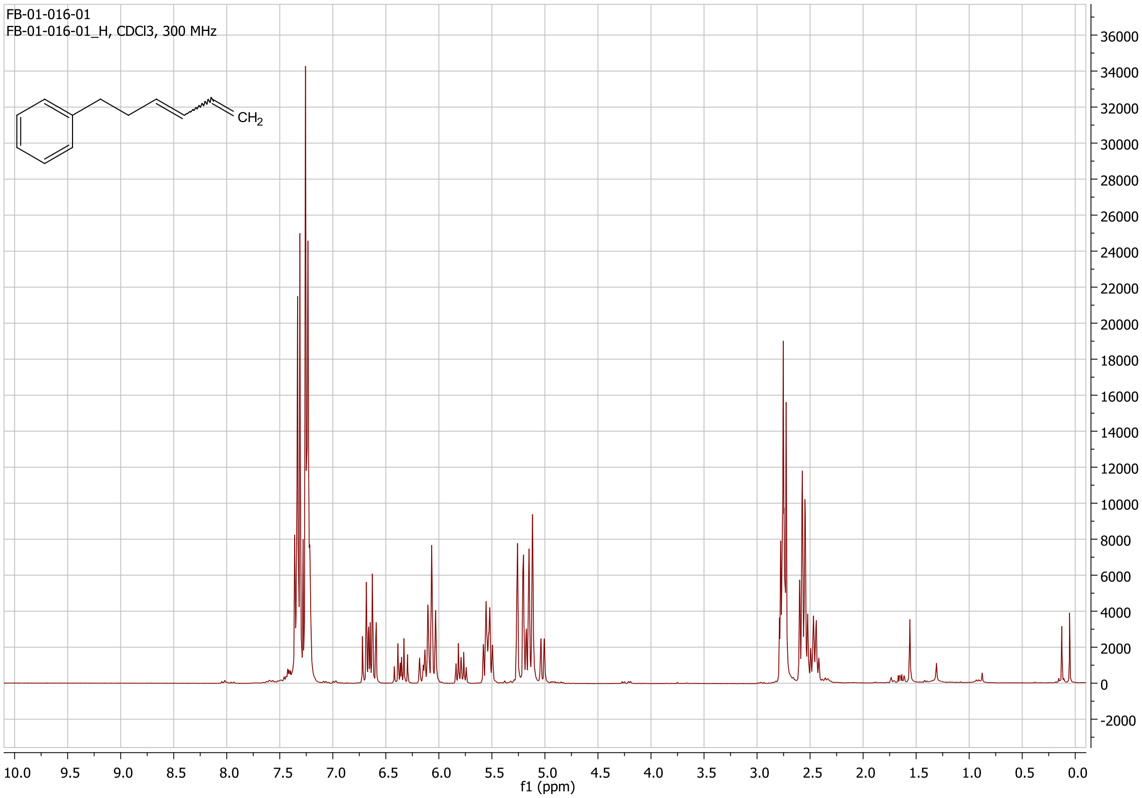

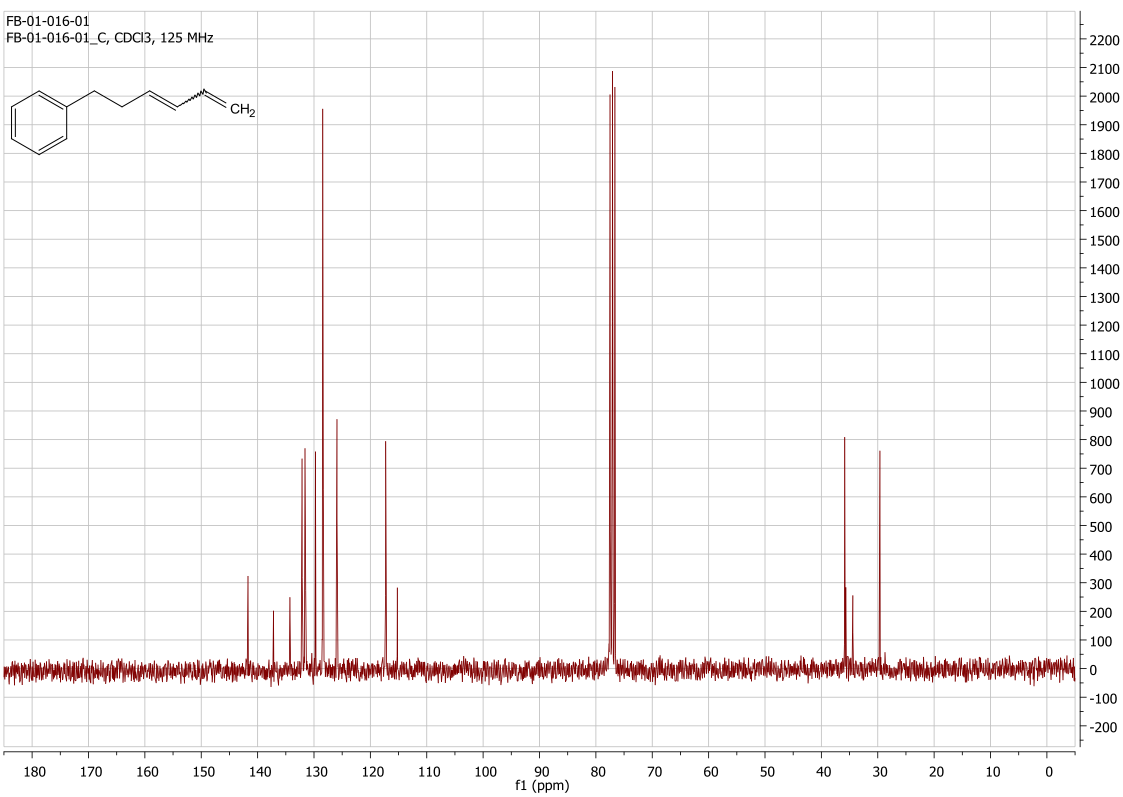

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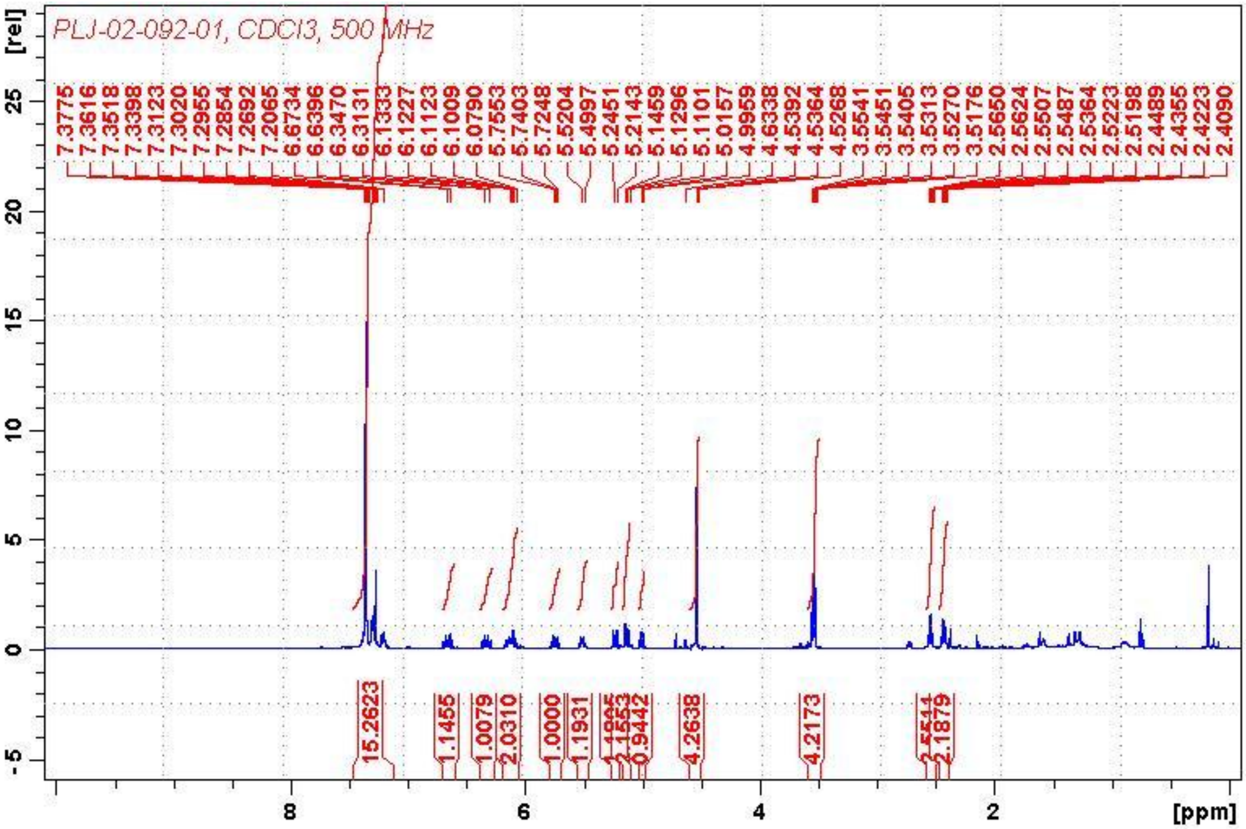
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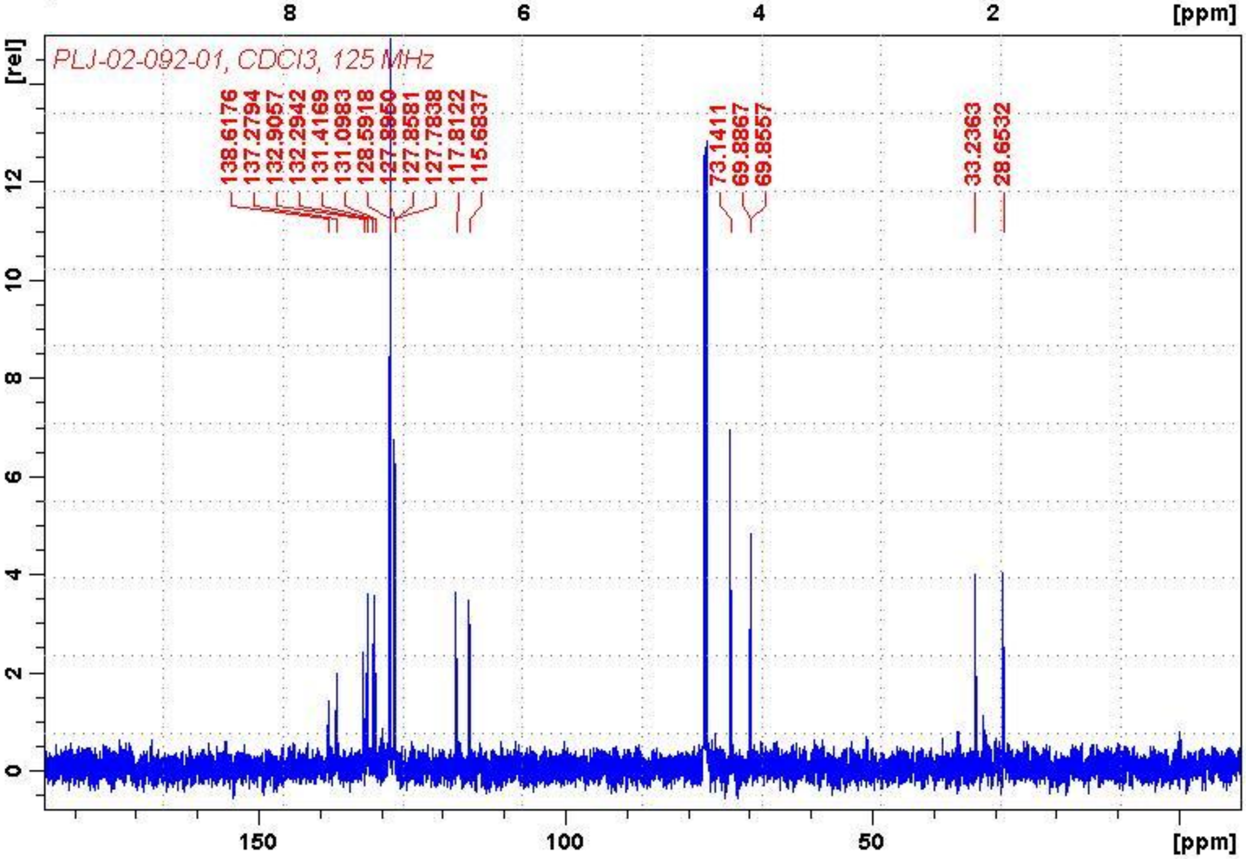
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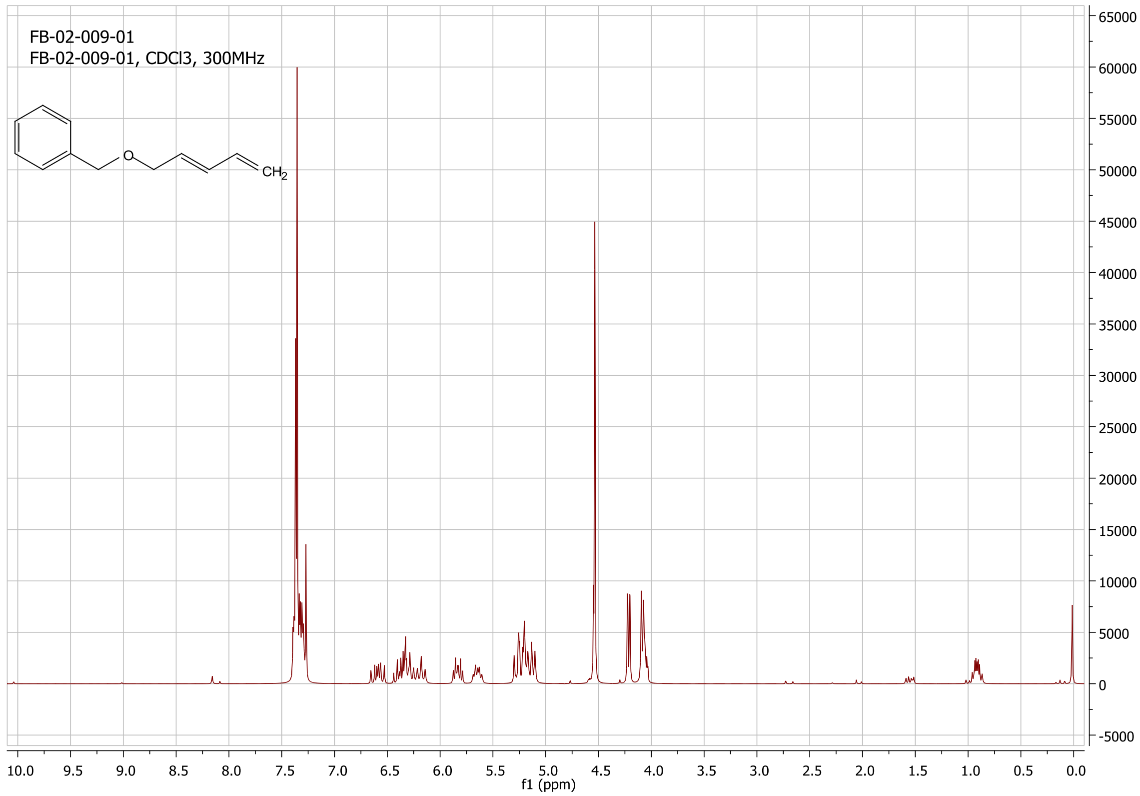
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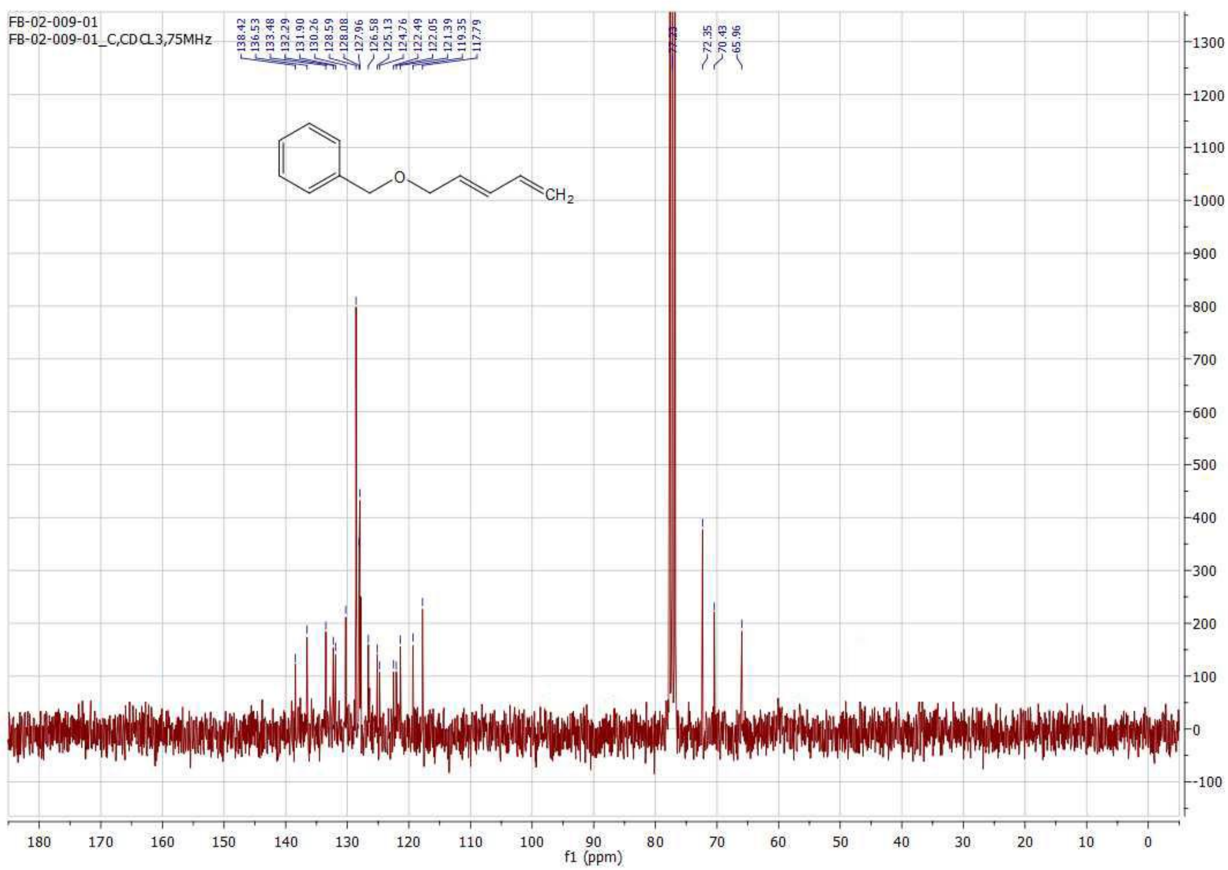
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f1 (ppm)

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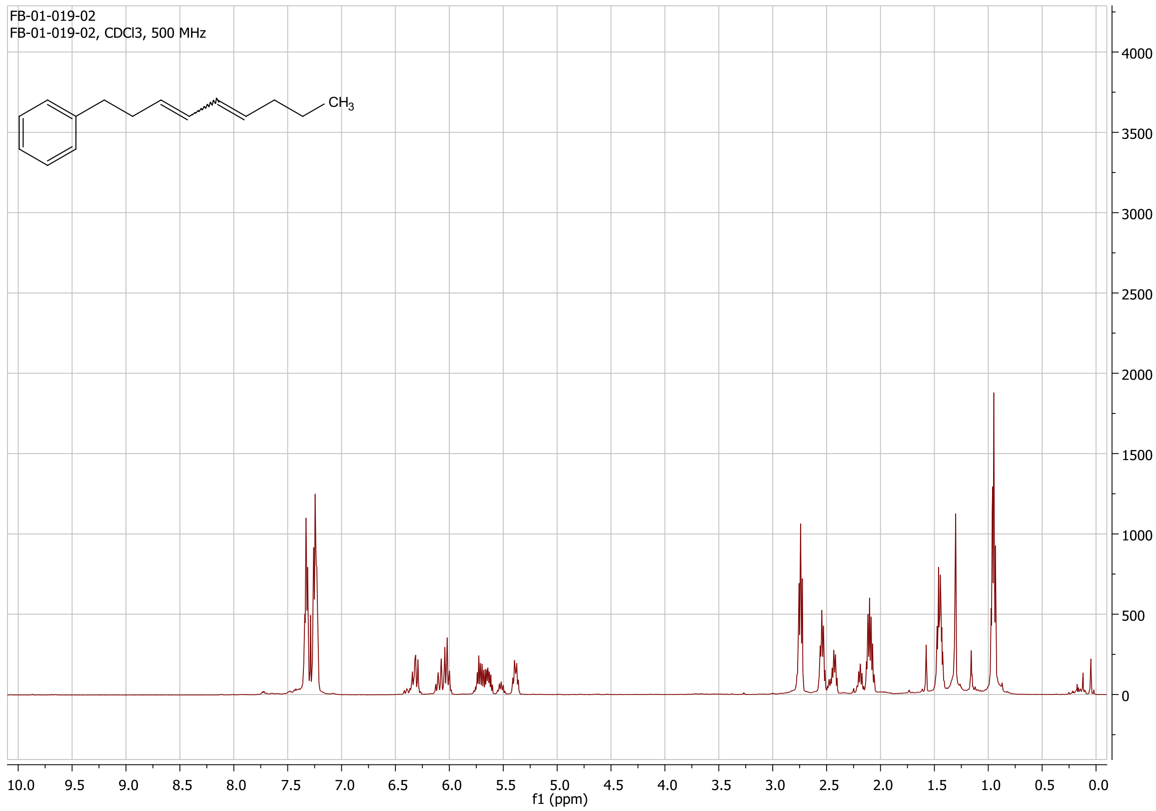
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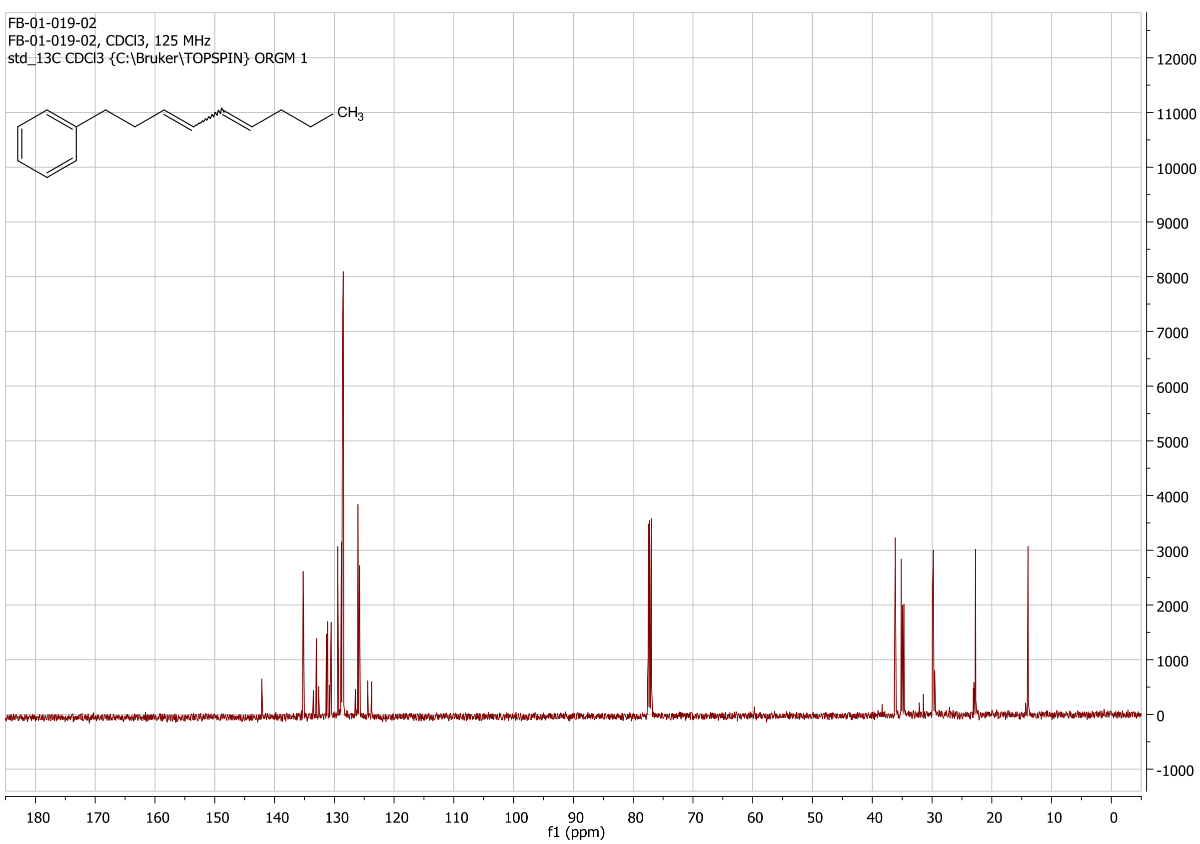
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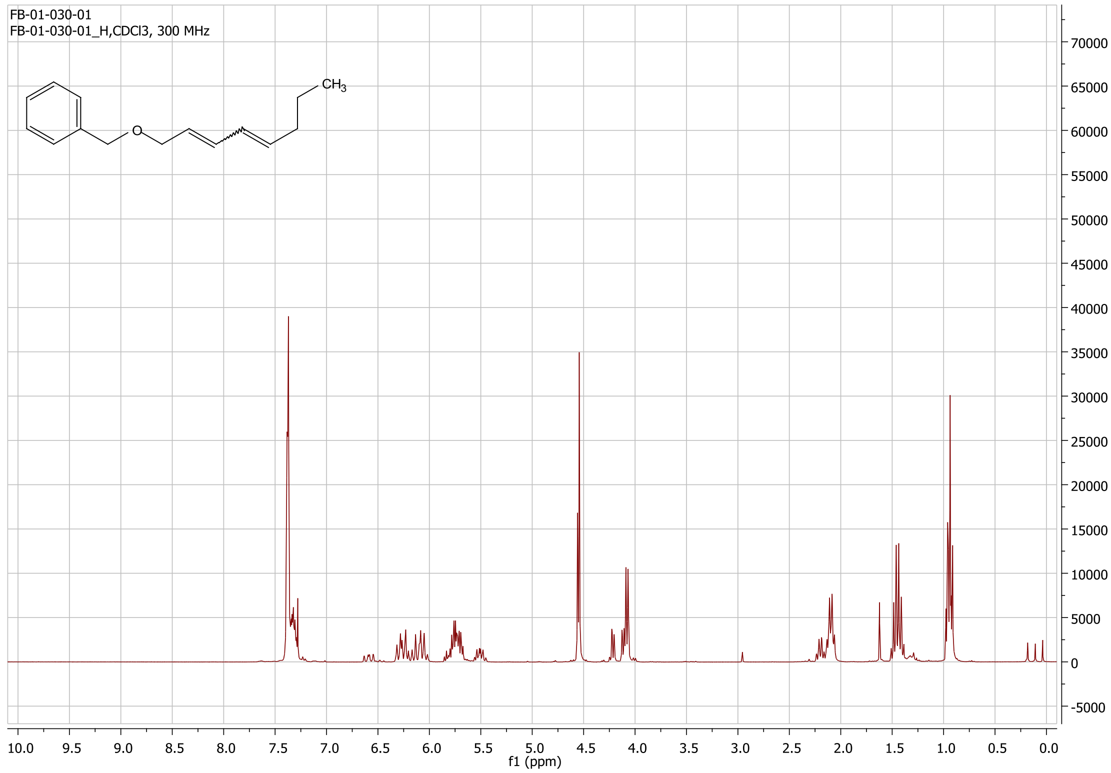
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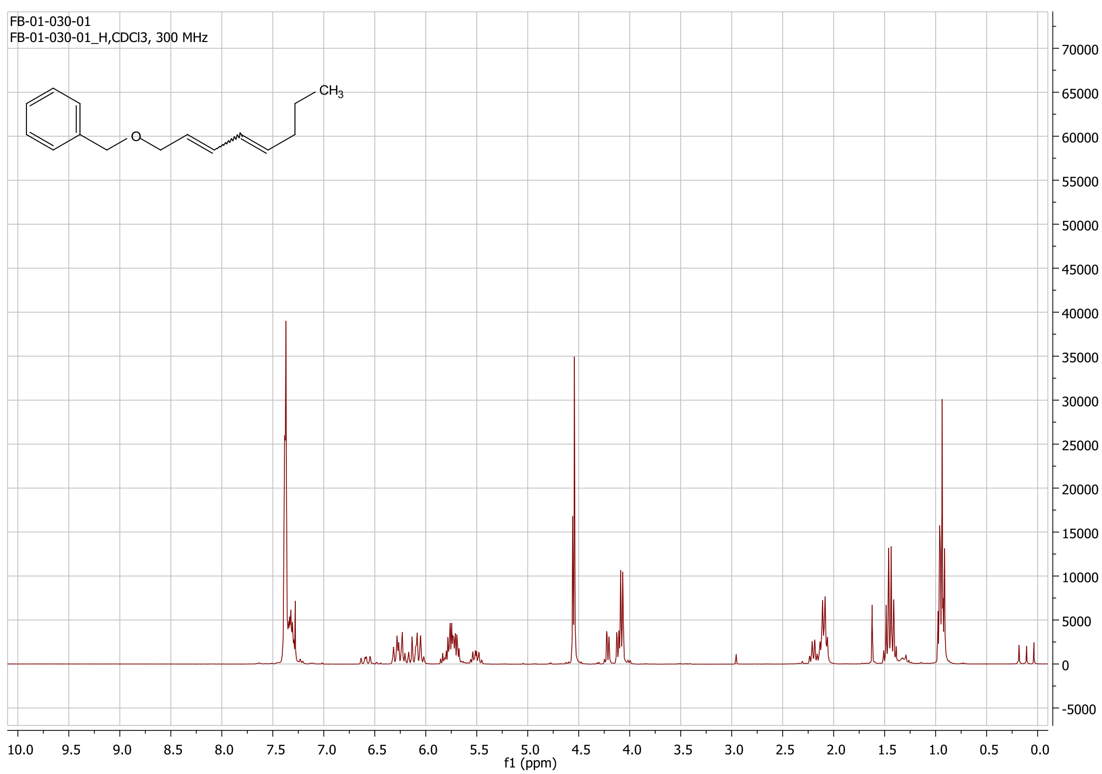
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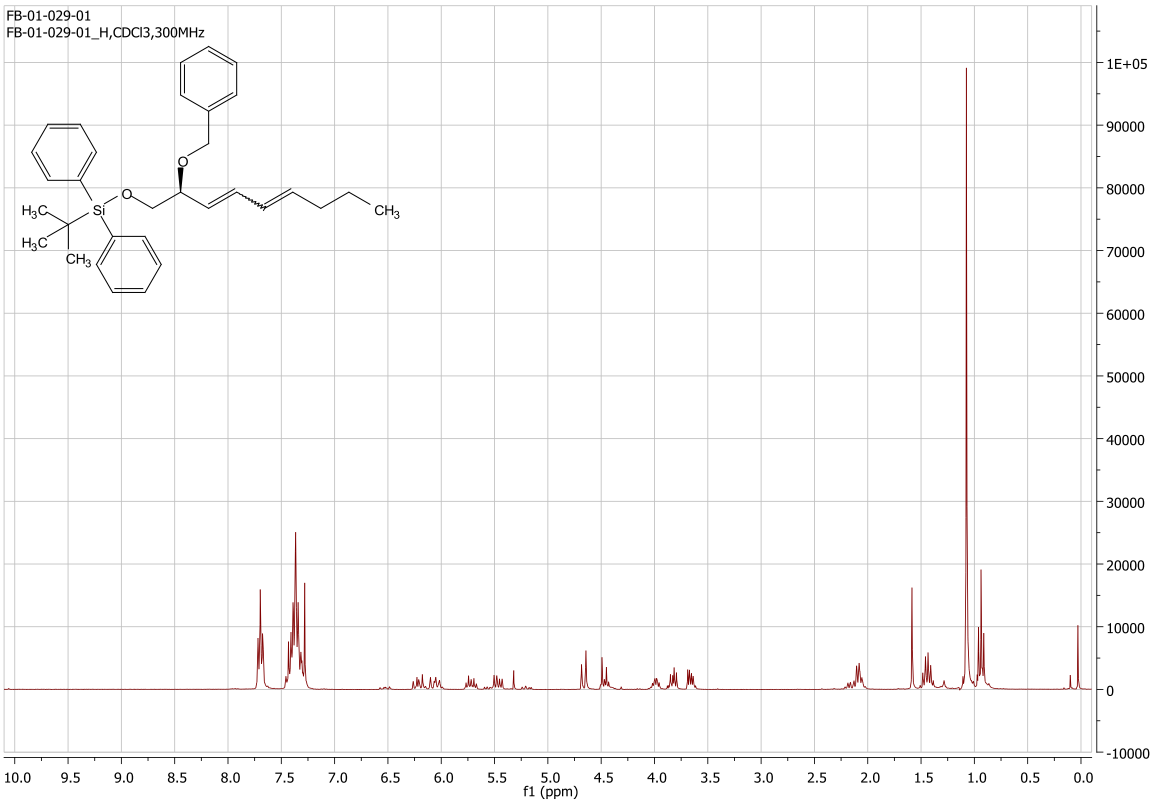
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70000
60000
50000
40000
30000
20000
10000
0
-10000
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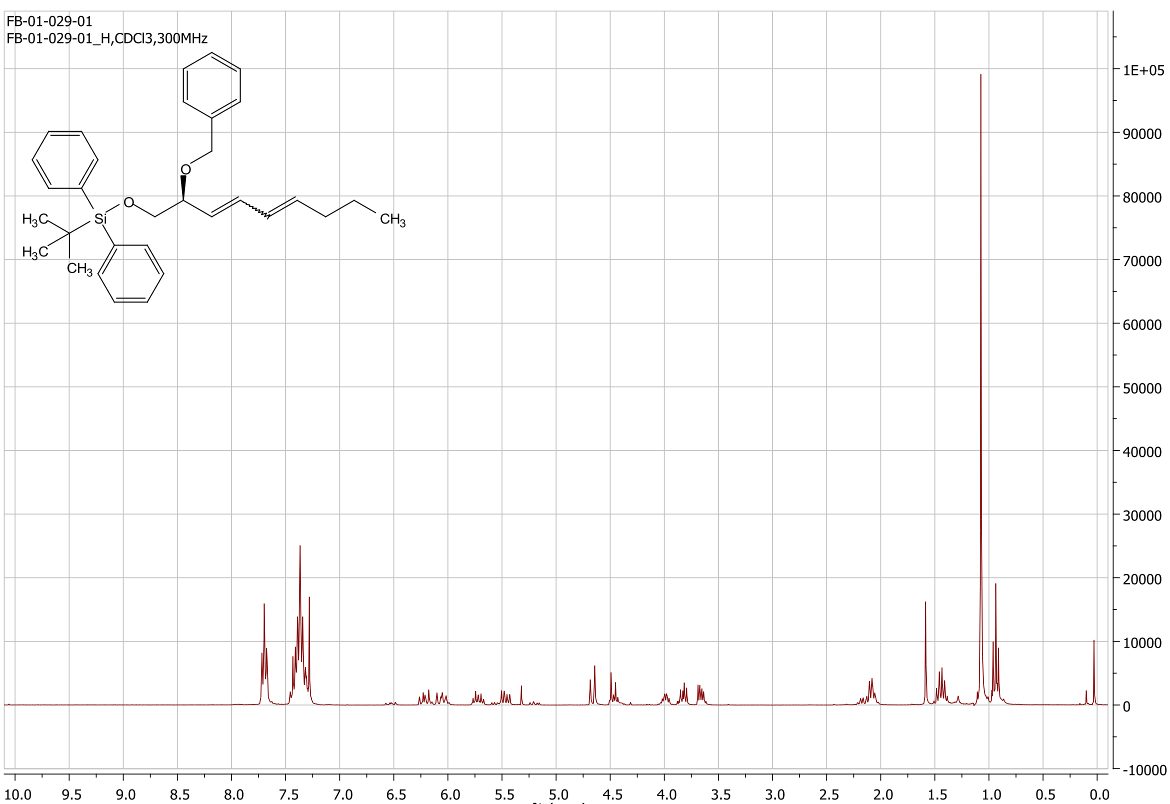
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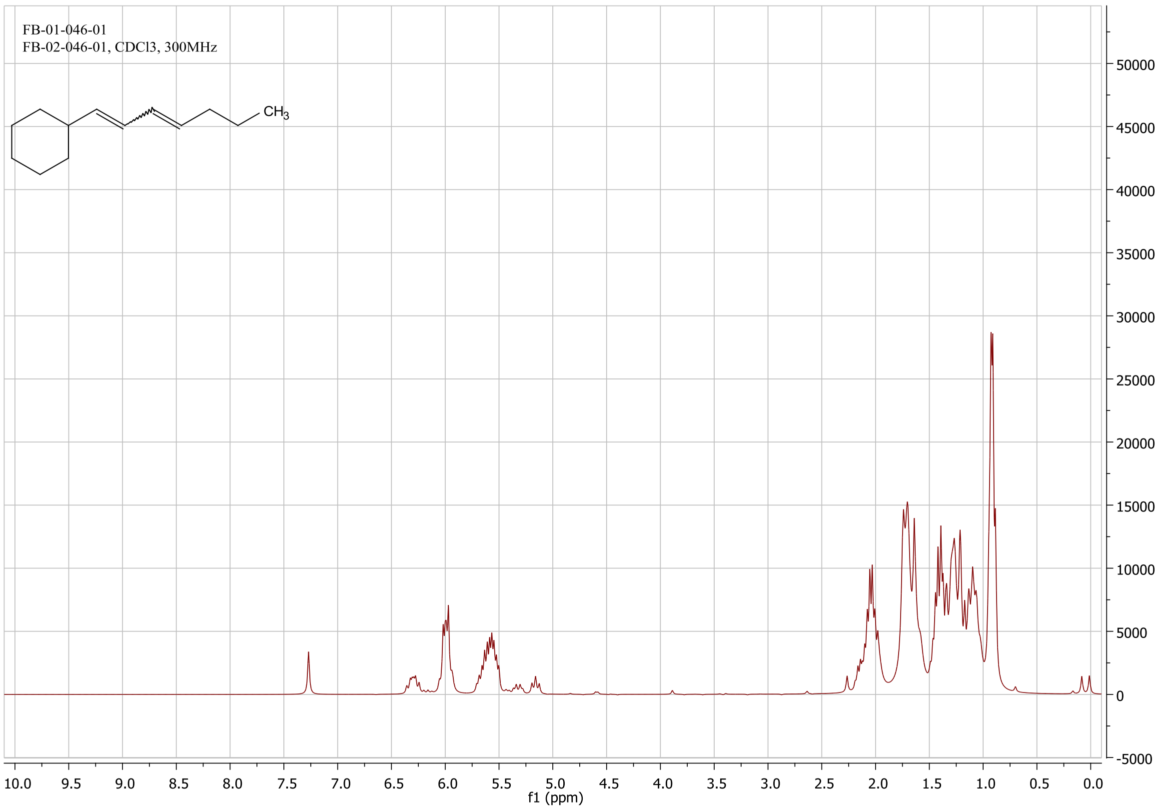
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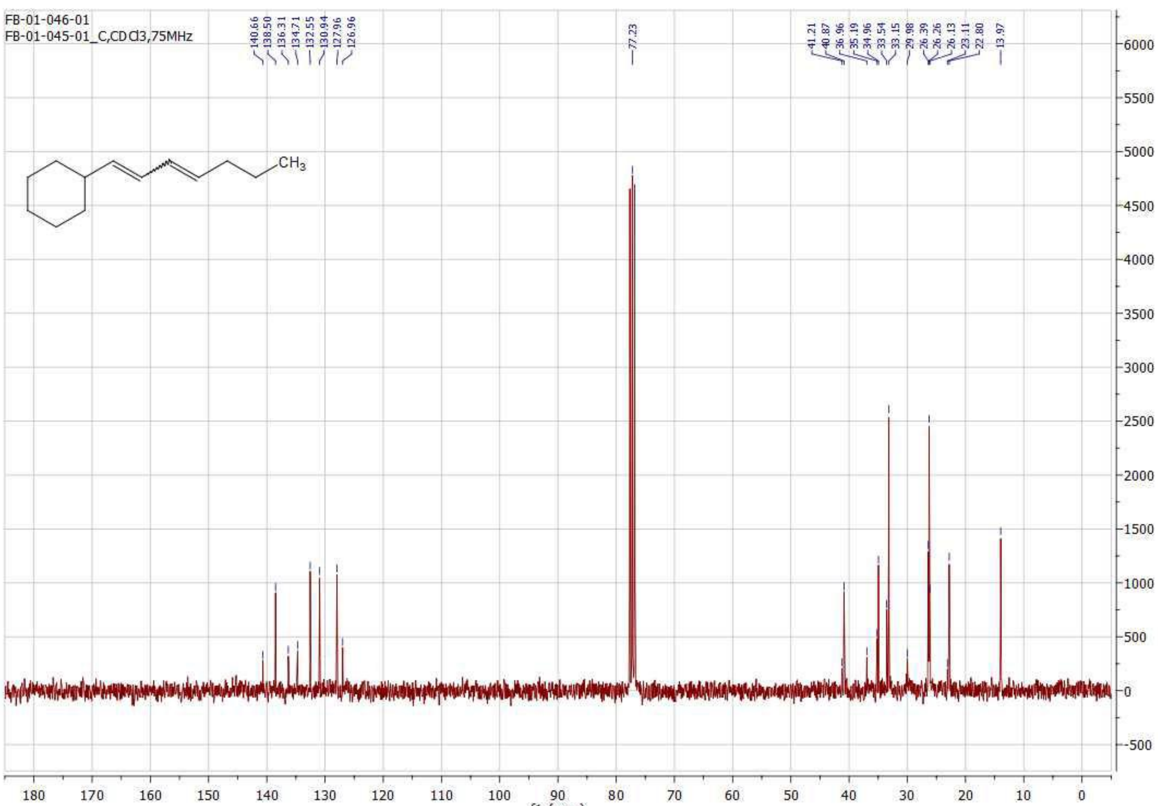
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f1 (ppm)

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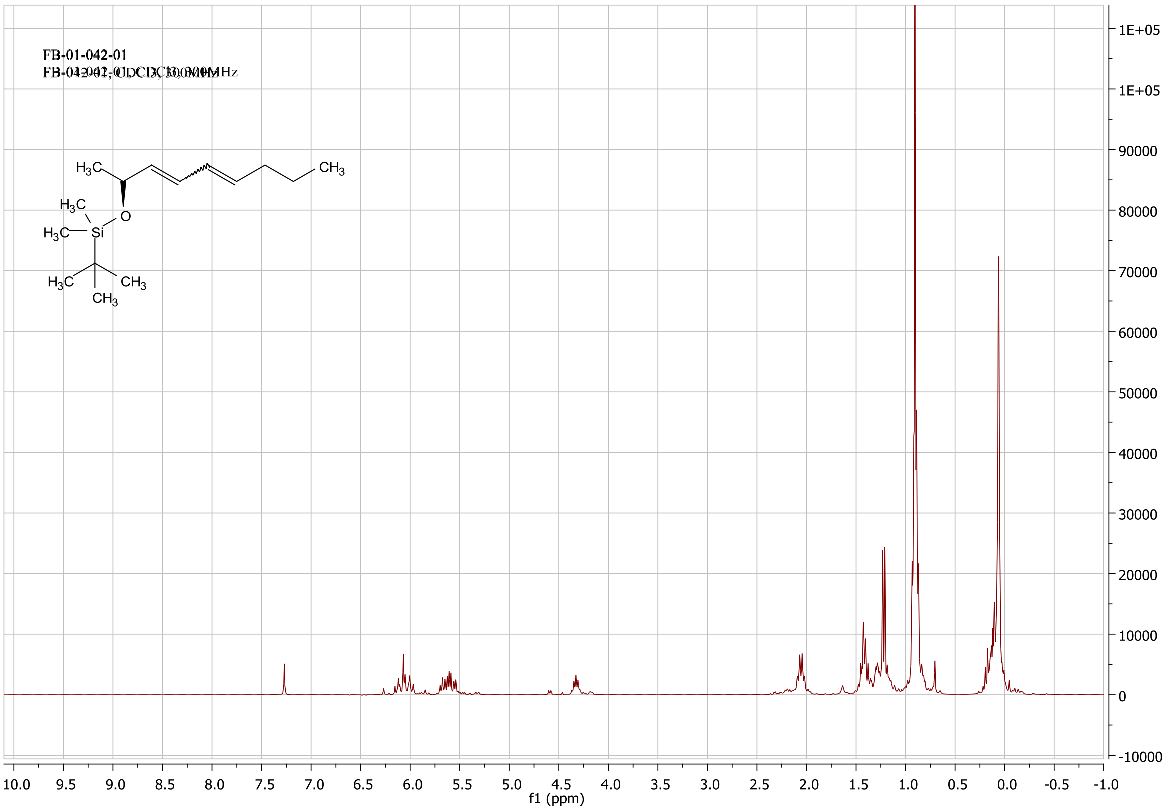
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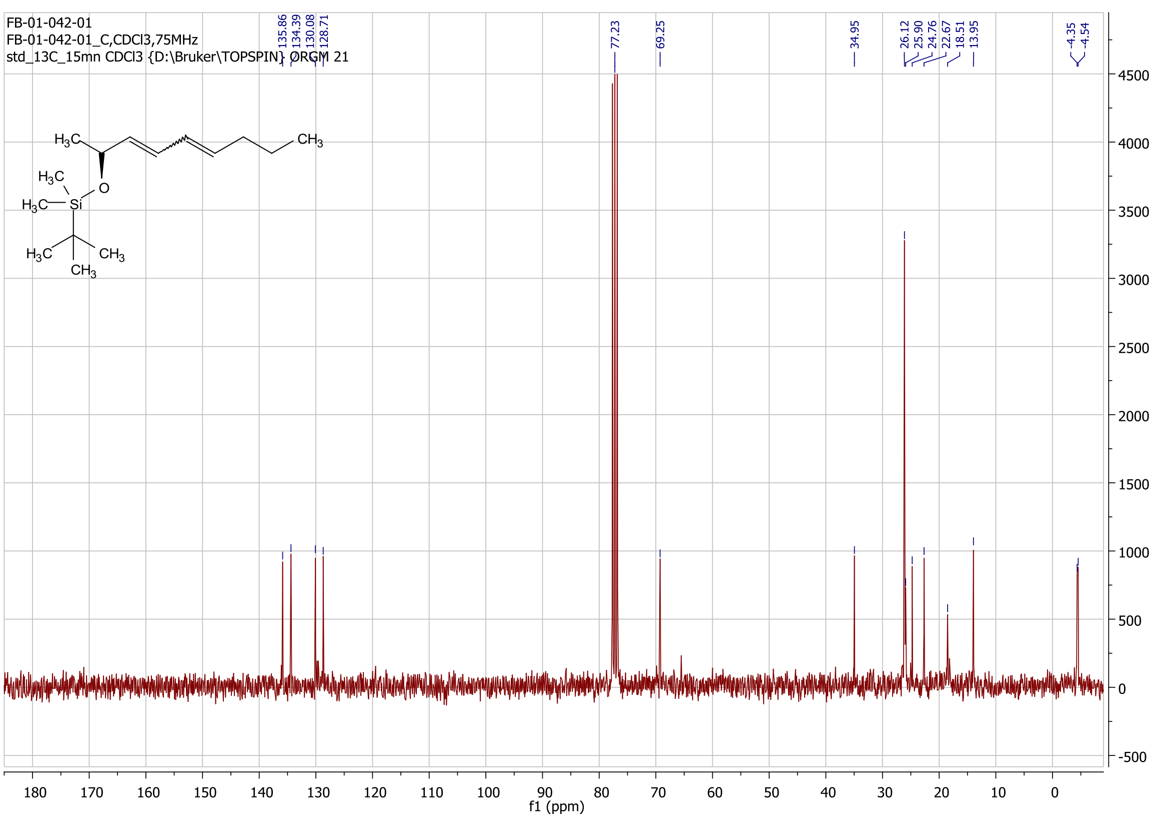
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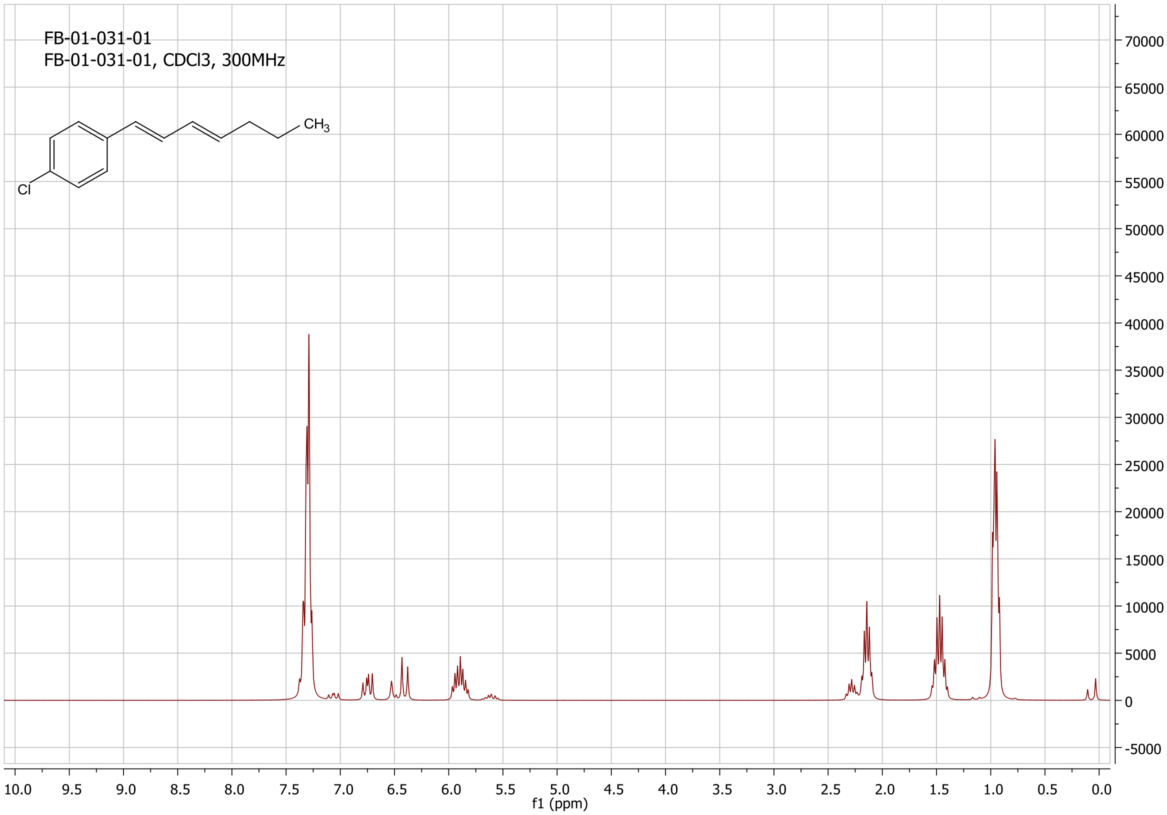
Olefin 3k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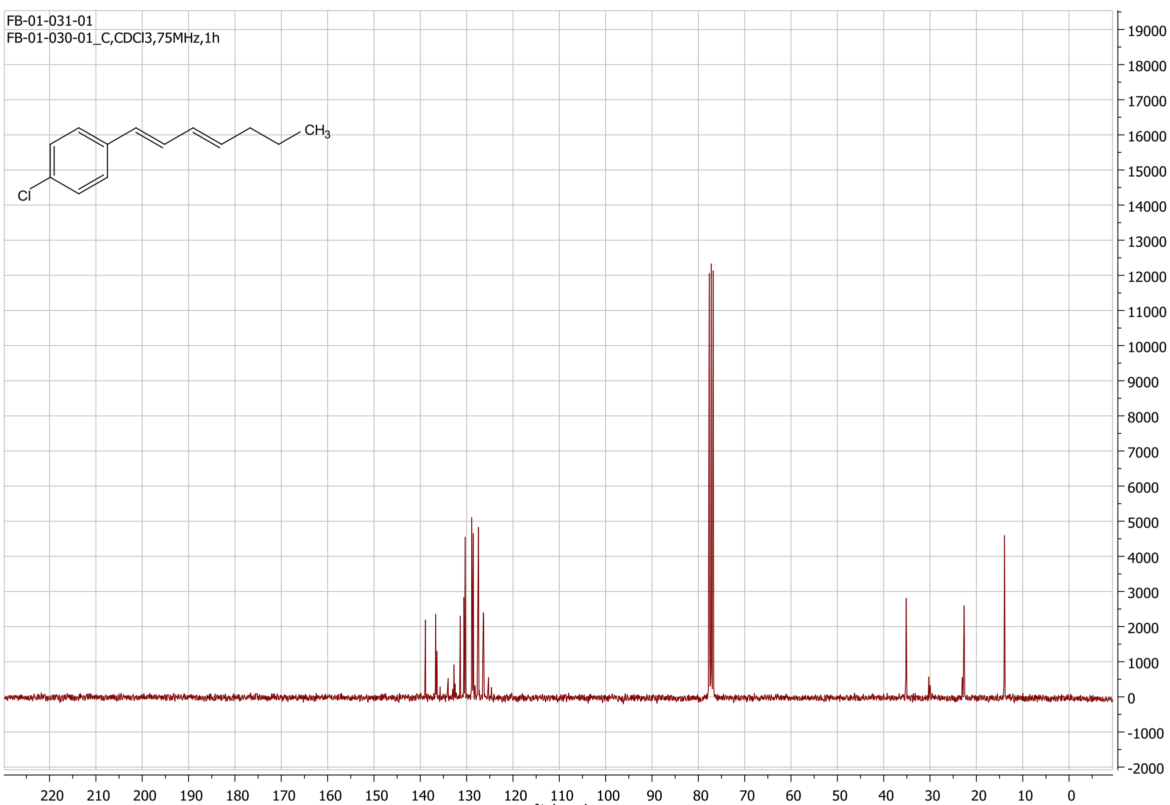
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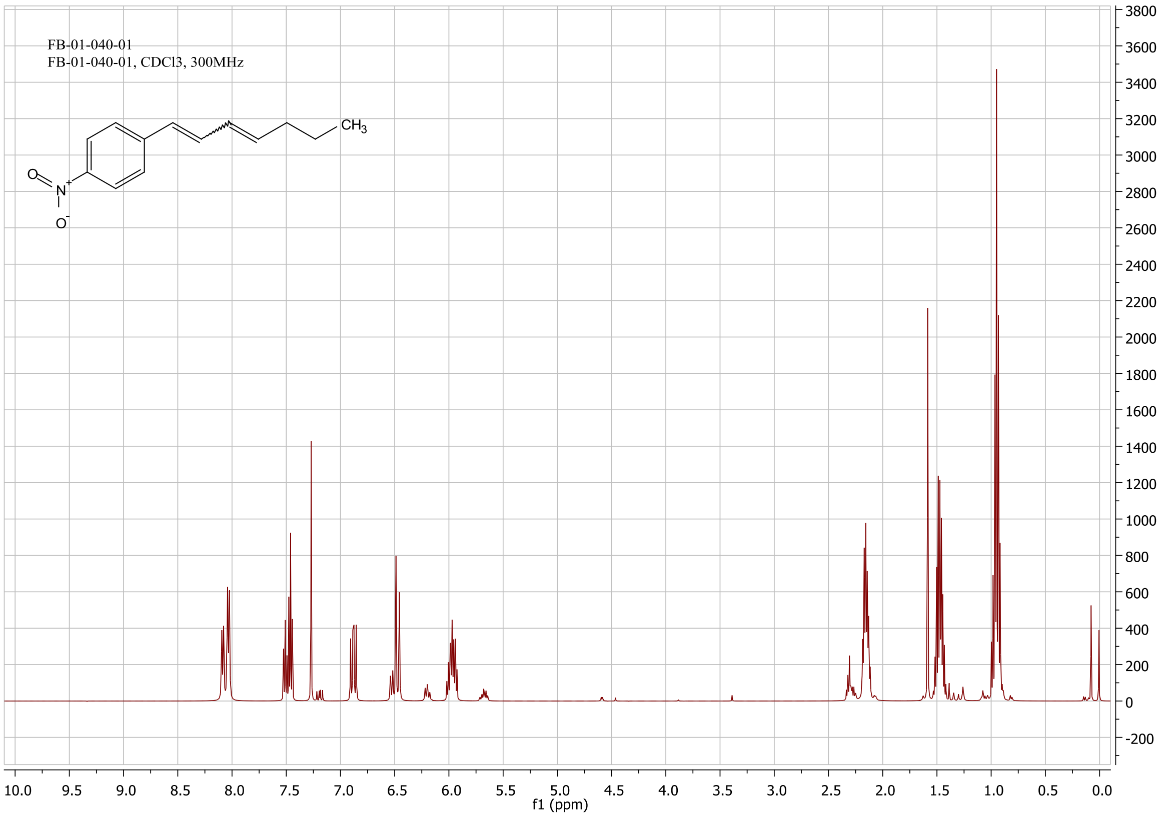
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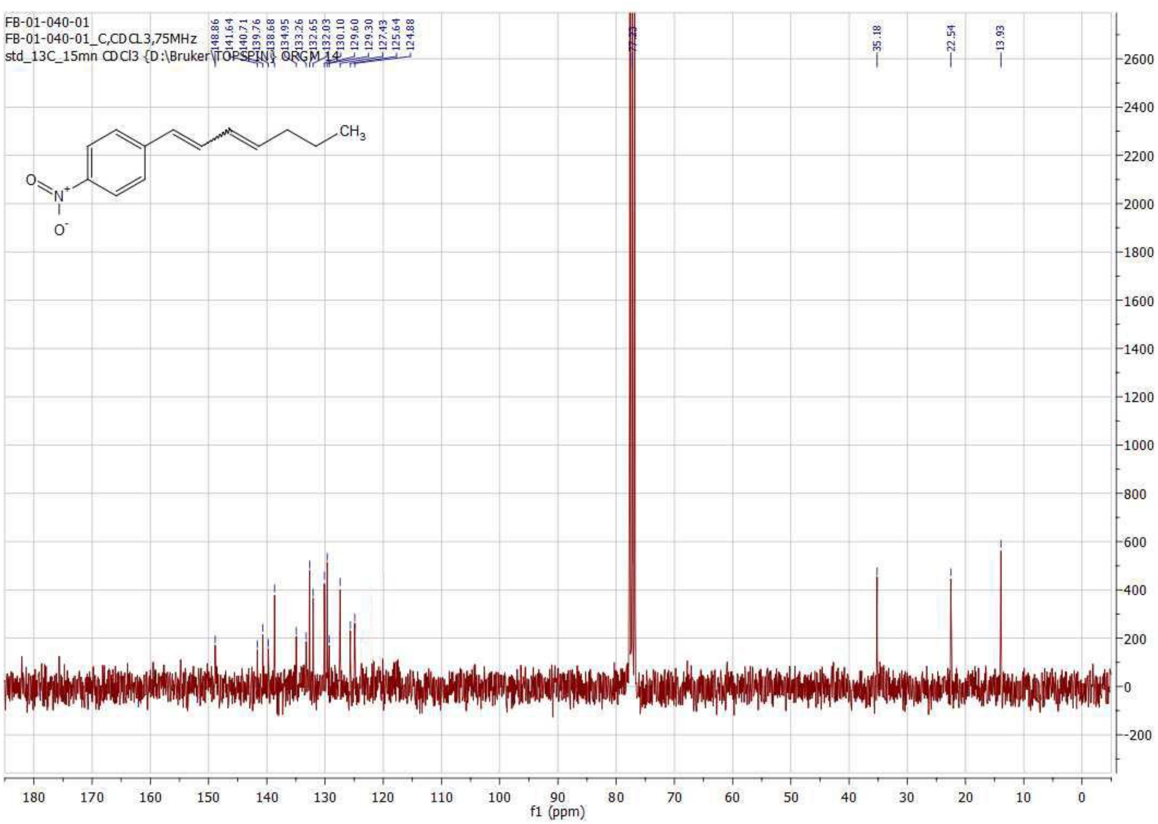
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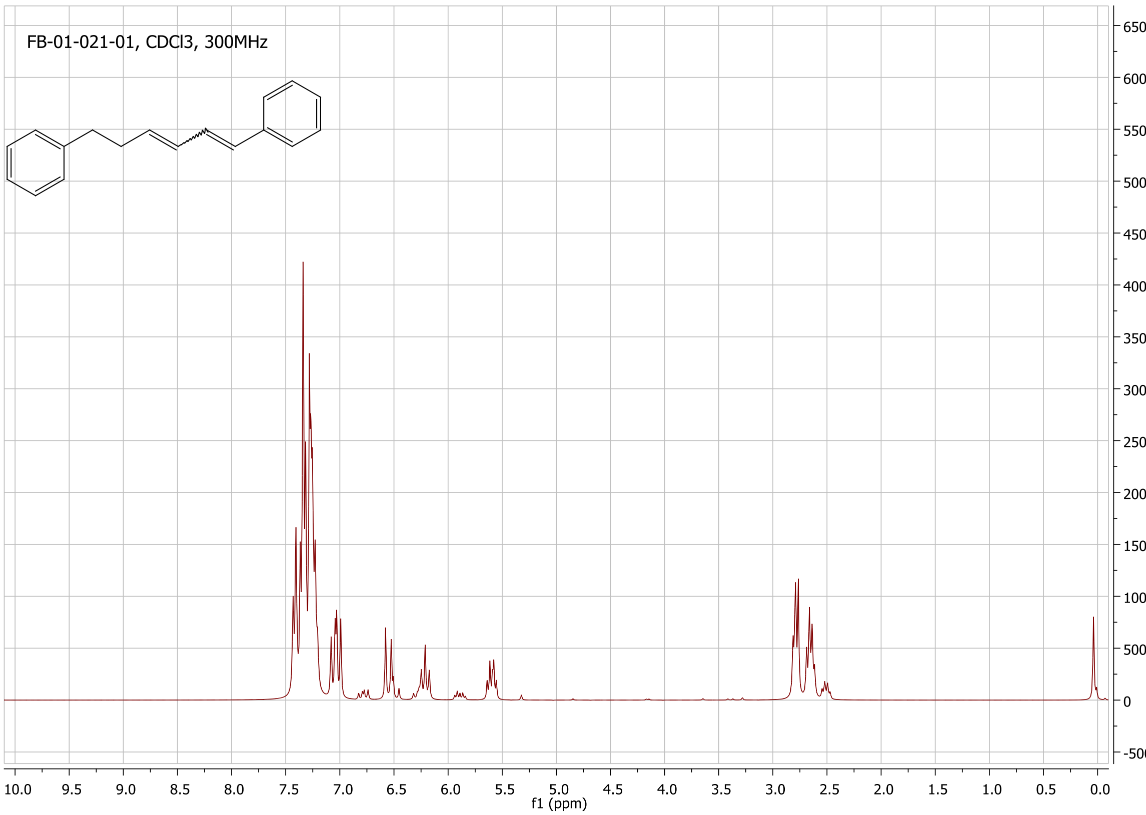
Olefin 3m



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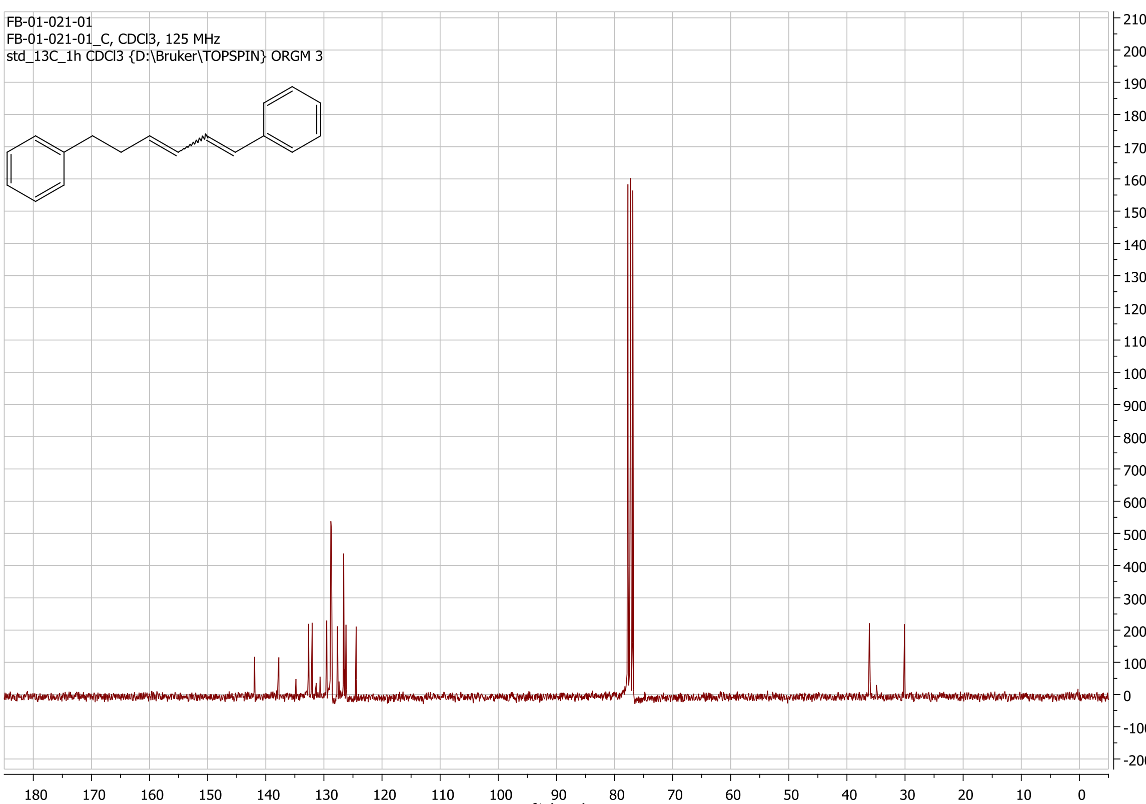

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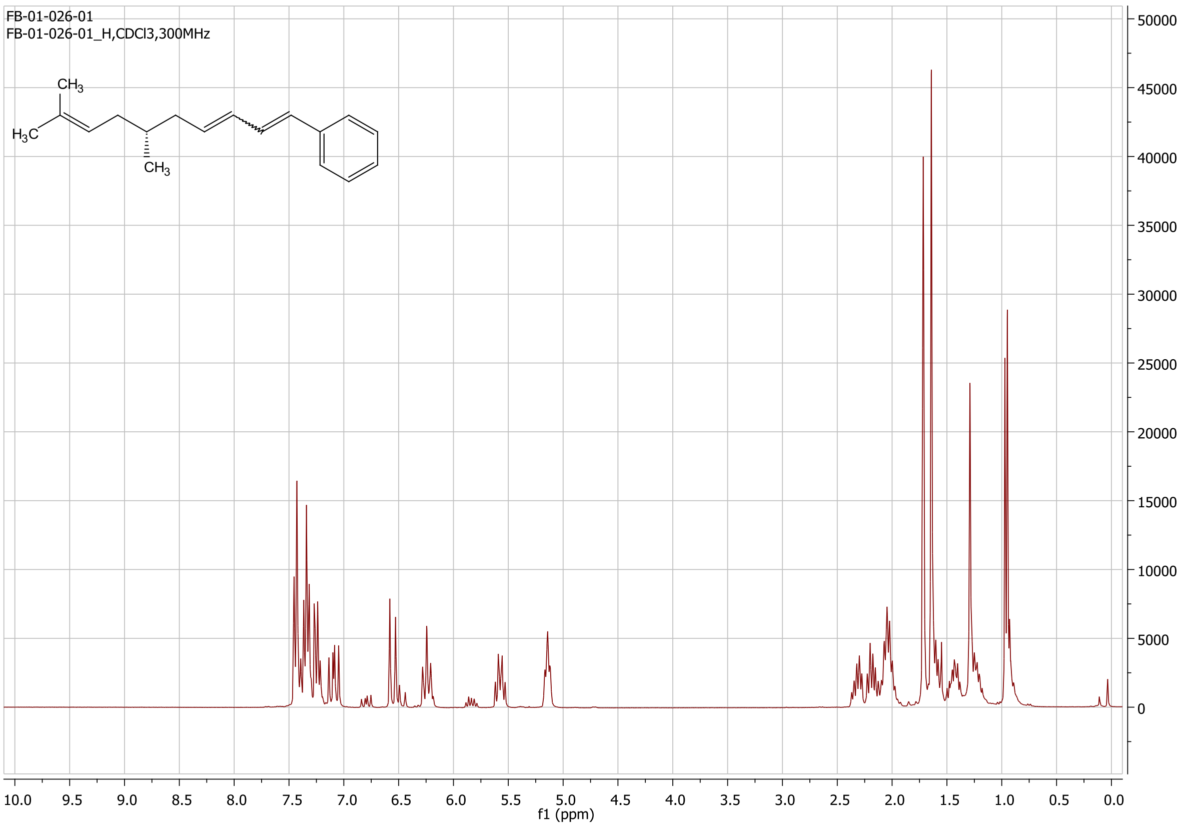
Olefin 3n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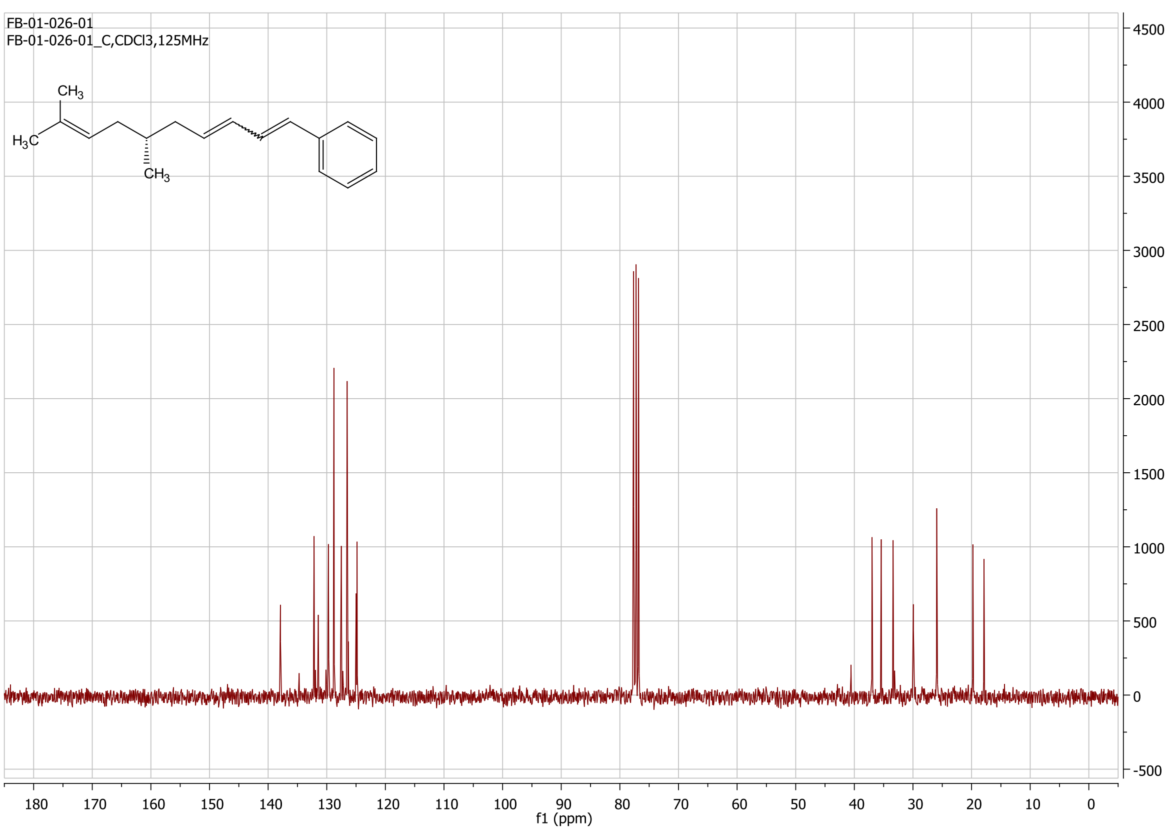
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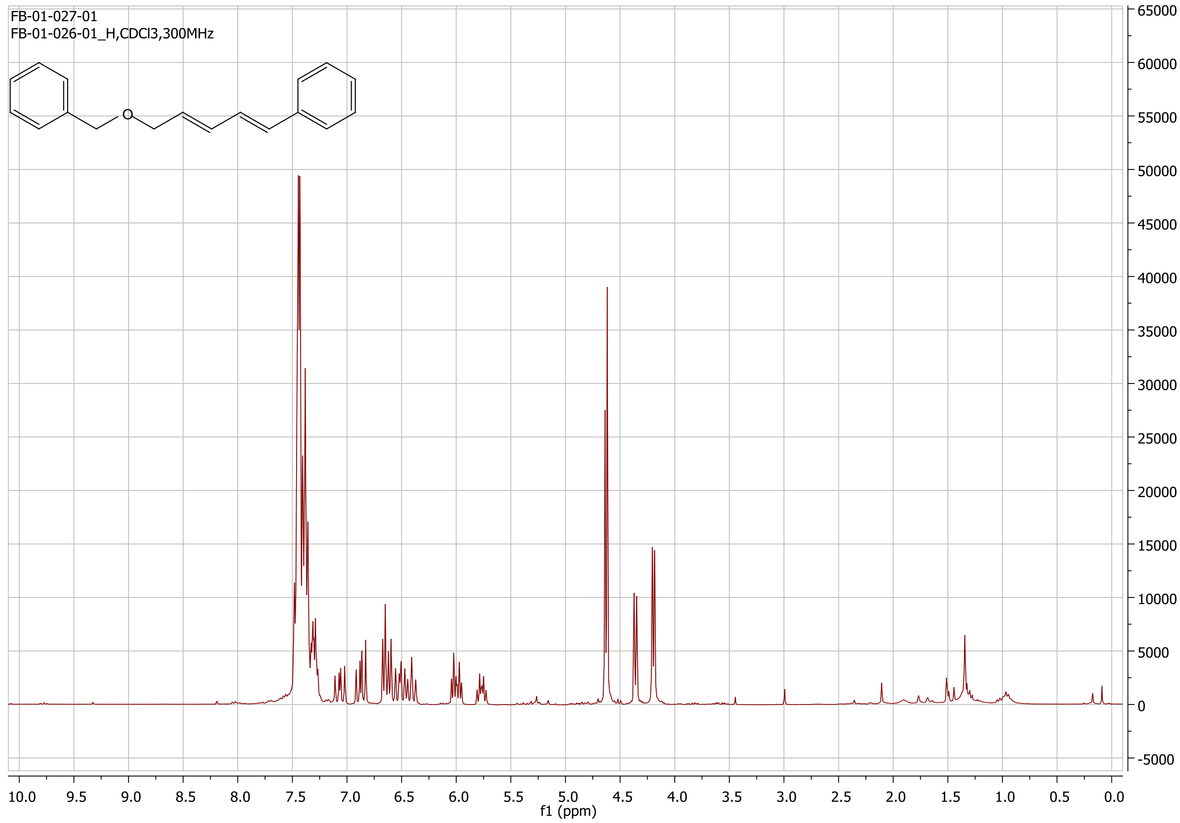
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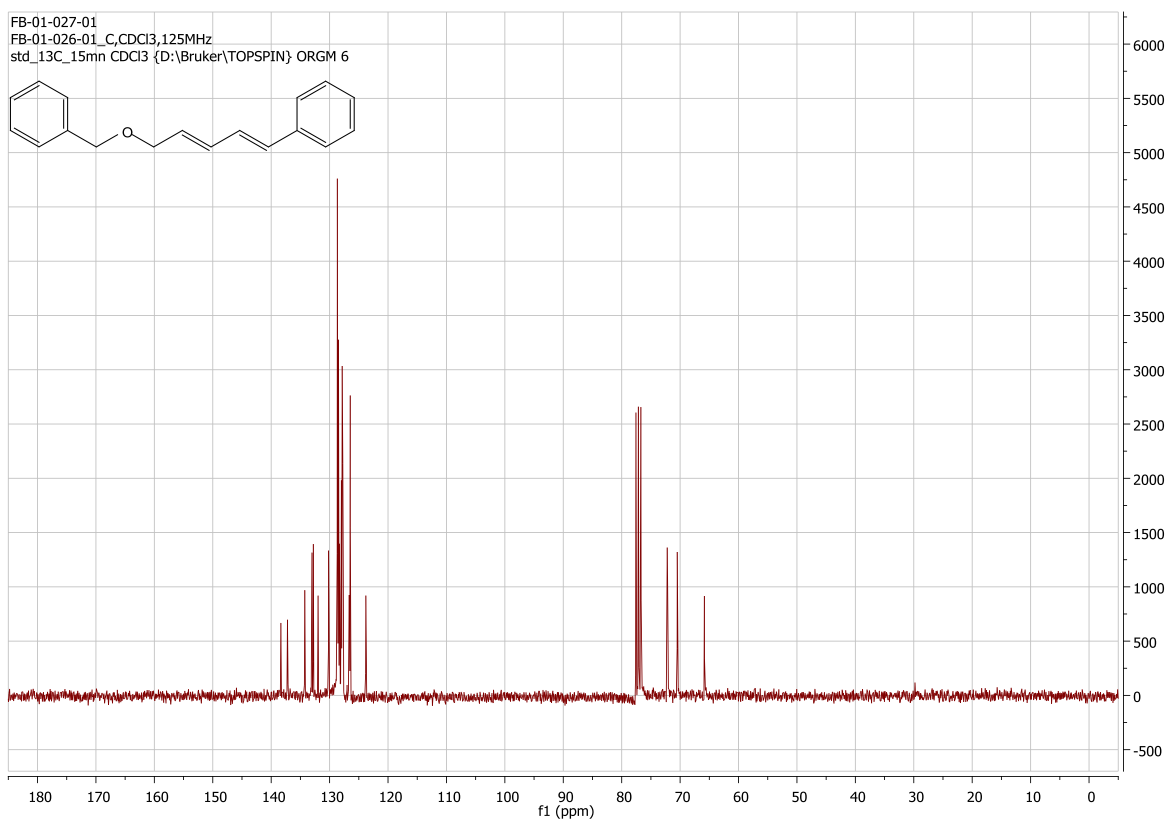
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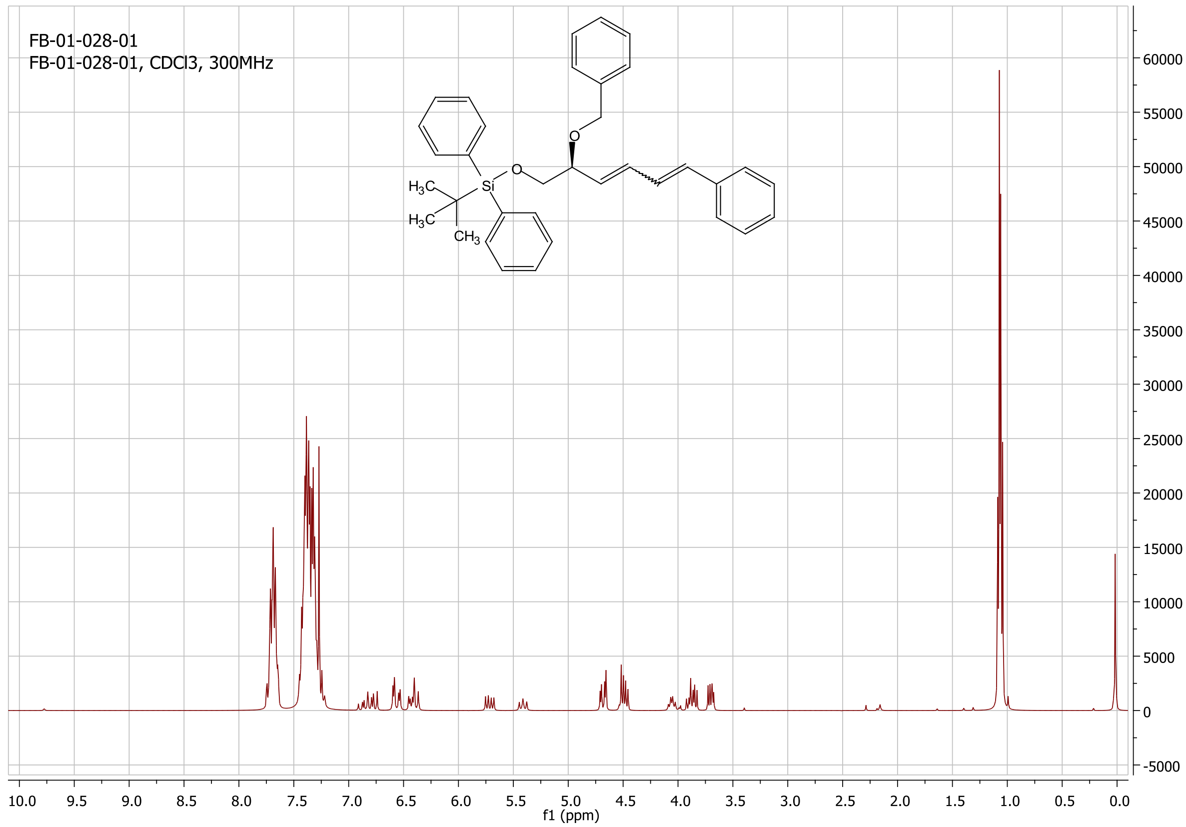

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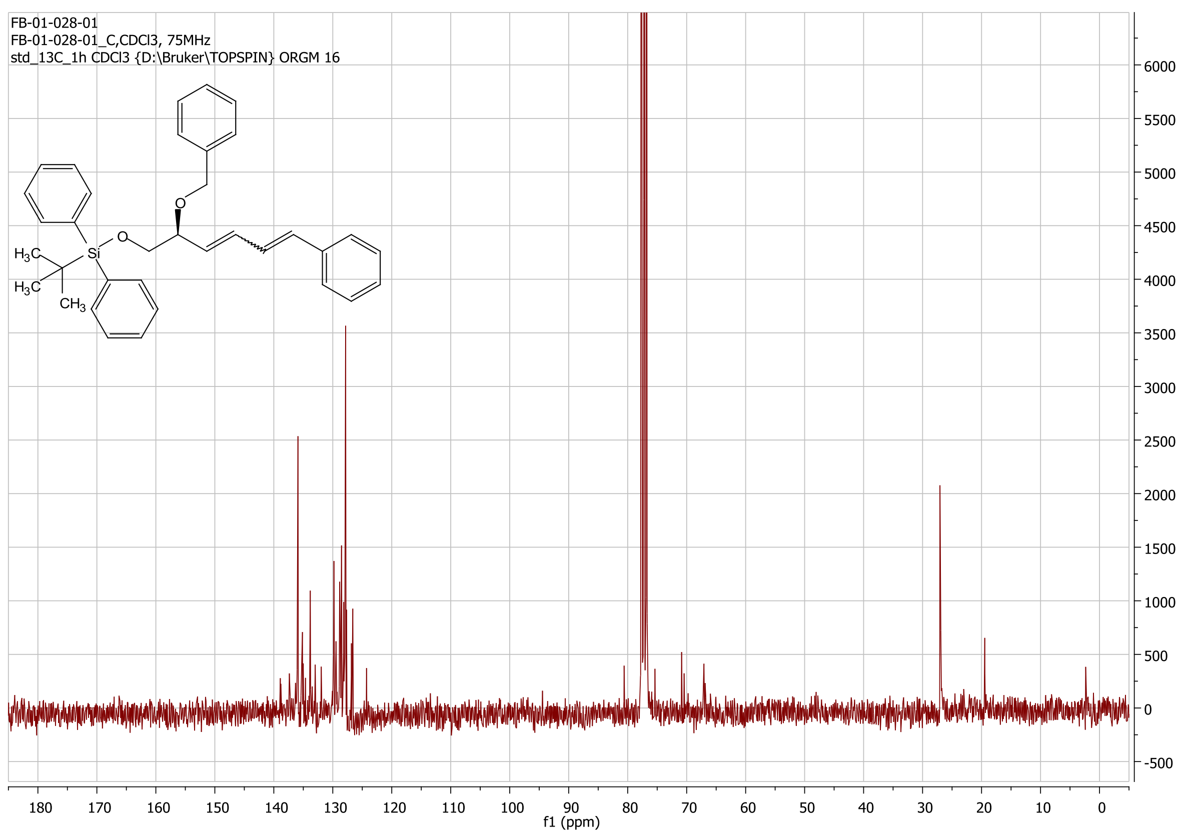

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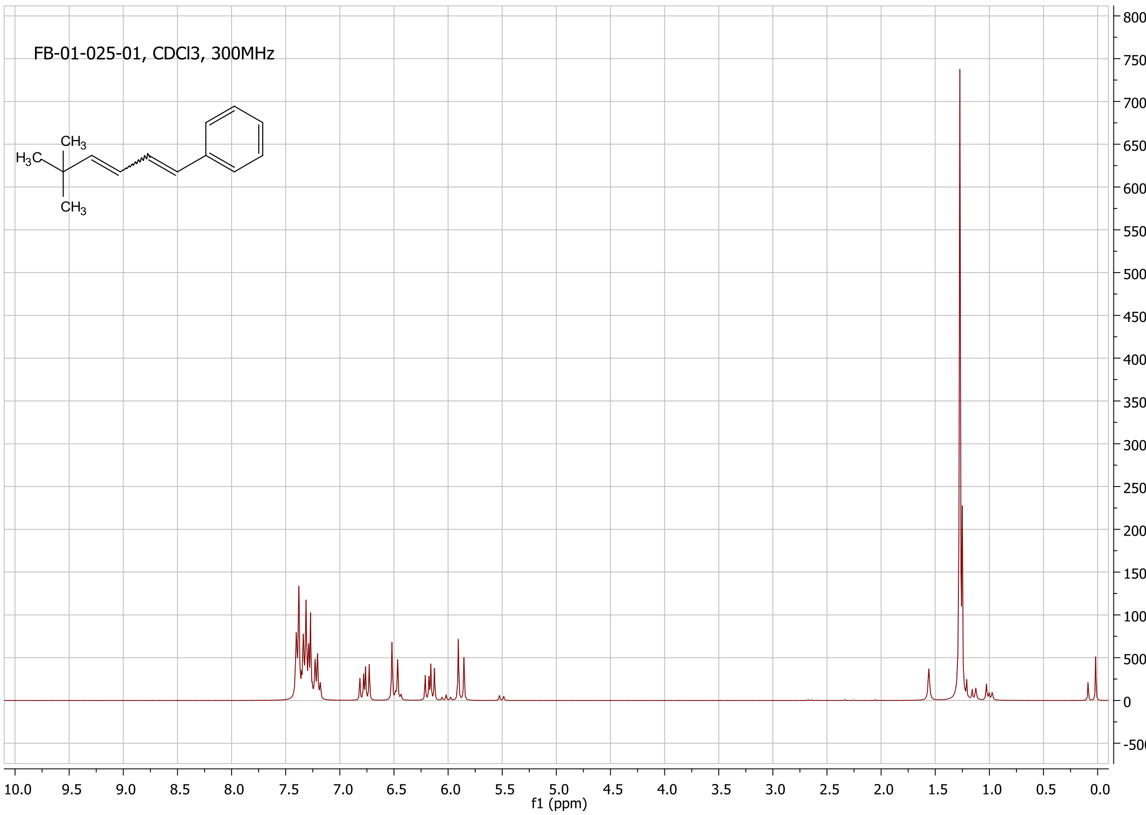
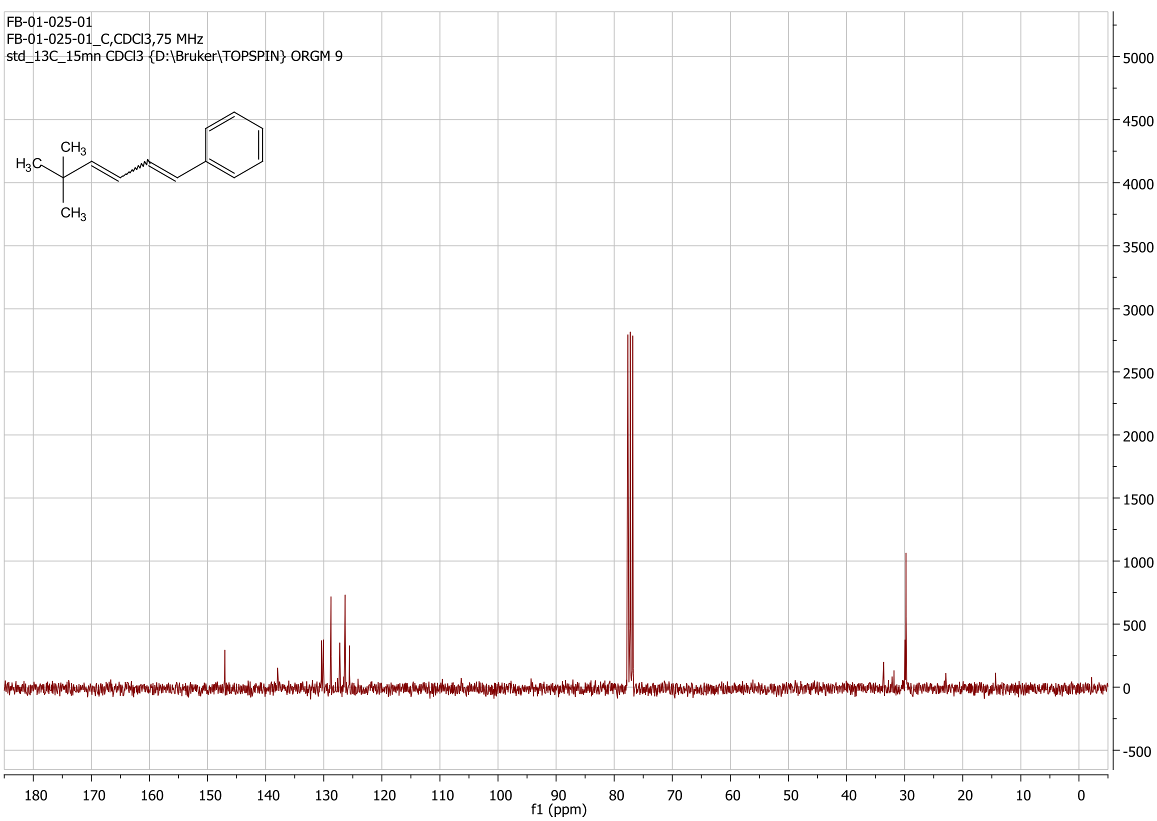
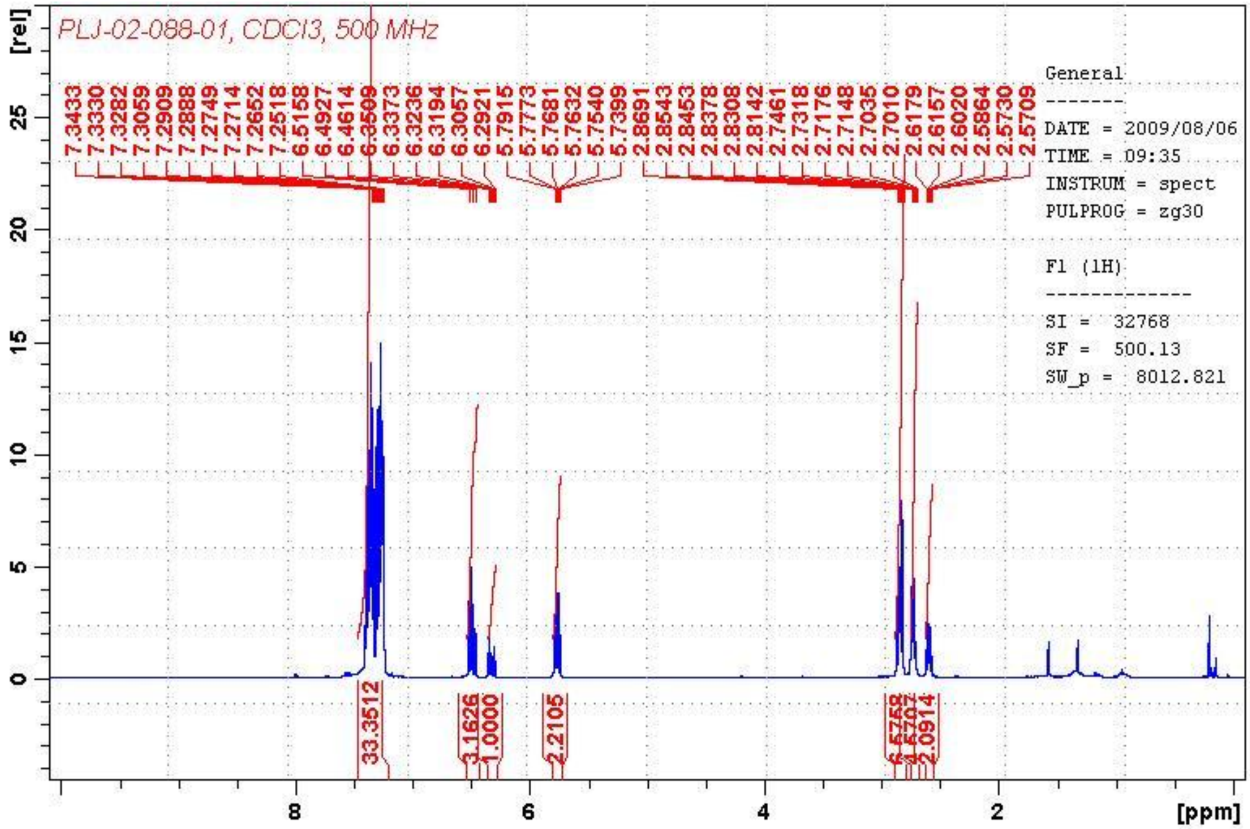
f1 (ppm)

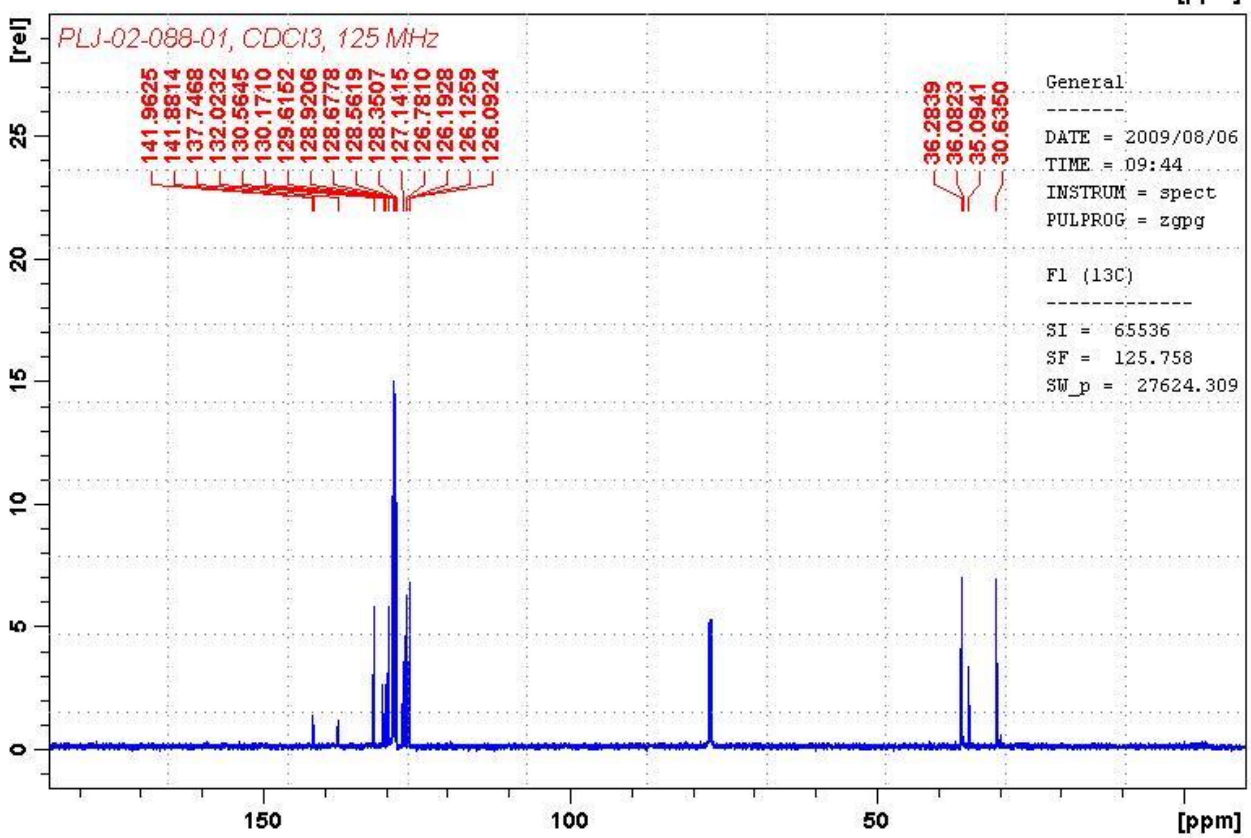
Olefin 3q


FB-01-025-01, CDCl3, 300MHz
CH_3
H_3C
CH_3
f1 (ppm)

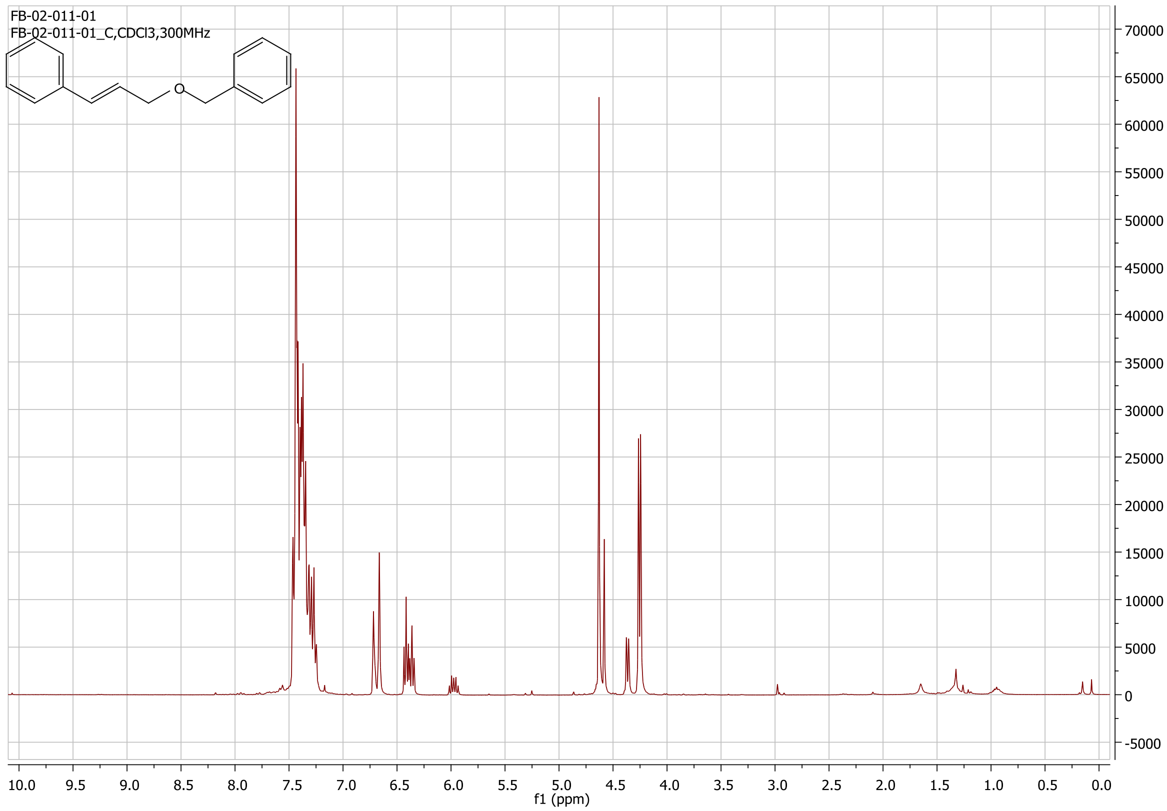

FB-01-025-01
FB-01-025-01_C,CDCl3,75 MHz
std_13C_15mn CDCl3 {D:\Bruker\TOPSPIN} ORGM 9
CH_3
H_3C
CH_3
f1 (ppm)

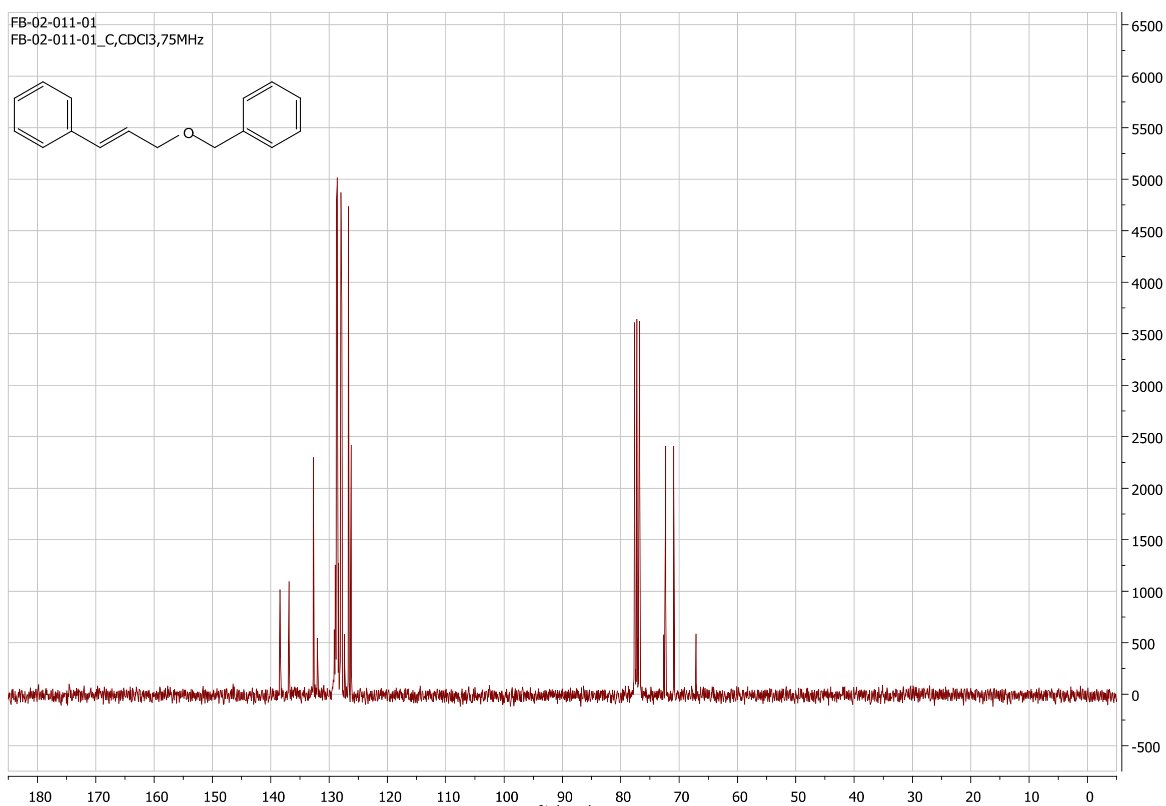
Olefin 3r


PLJ-02-088-01, CDCl3, 500 MHz
7.3433
7.3330
7.3282
7.3059
7.2909
7.2888
7.2749
7.2714
7.2652
7.2518
6.5158
6.4927
6.4614
6.3509
6.3373
6.3236
6.3194
6.3057
6.2921
5.7915
5.7773
5.7681
5.7632
5.7540
5.7399
2.8691
2.8543
2.8453
2.8378
2.8308
2.8142
2.7461
2.7318
2.7176
2.7148
2.7035
2.7010
2.6179
2.6157
2.6020
2.5864
2.5730
2.5709
General
DATE = 2009/08/06
TIME = 09:35
INSTRUM = spect
PULPROG = zg30
F1 (1H)
SI = 32768
SF = 500.13
SW_p = 8012.821
33.3512
3.1626
1.0000
2.2105
2.0914
[rel]
[ppm]

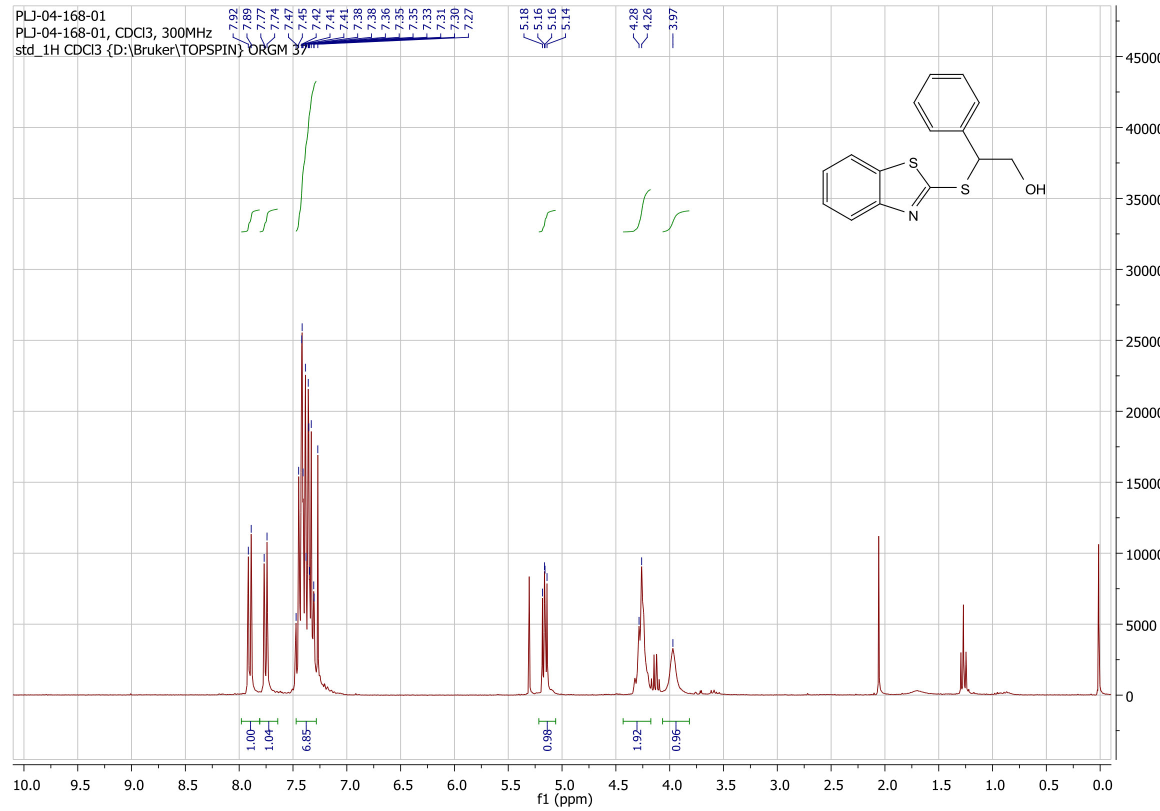

PLJ-02-088-01, CDCl3, 125 MHz
141.9625
141.8814
137.7468
132.0232
130.5645
130.1710
129.6152
128.9206
128.6778
128.5619
128.3507
127.1415
126.7810
126.1928
126.1259
126.0924
36.2839
36.0823
35.0941
30.6350
General
DATE = 2009/08/06
TIME = 09:44
INSTRUM = spect
PULPROG = zgpg
F1 (13C)
SI = 65536
SF = 125.758
SW_p = 27624.309
[rel]
[ppm]

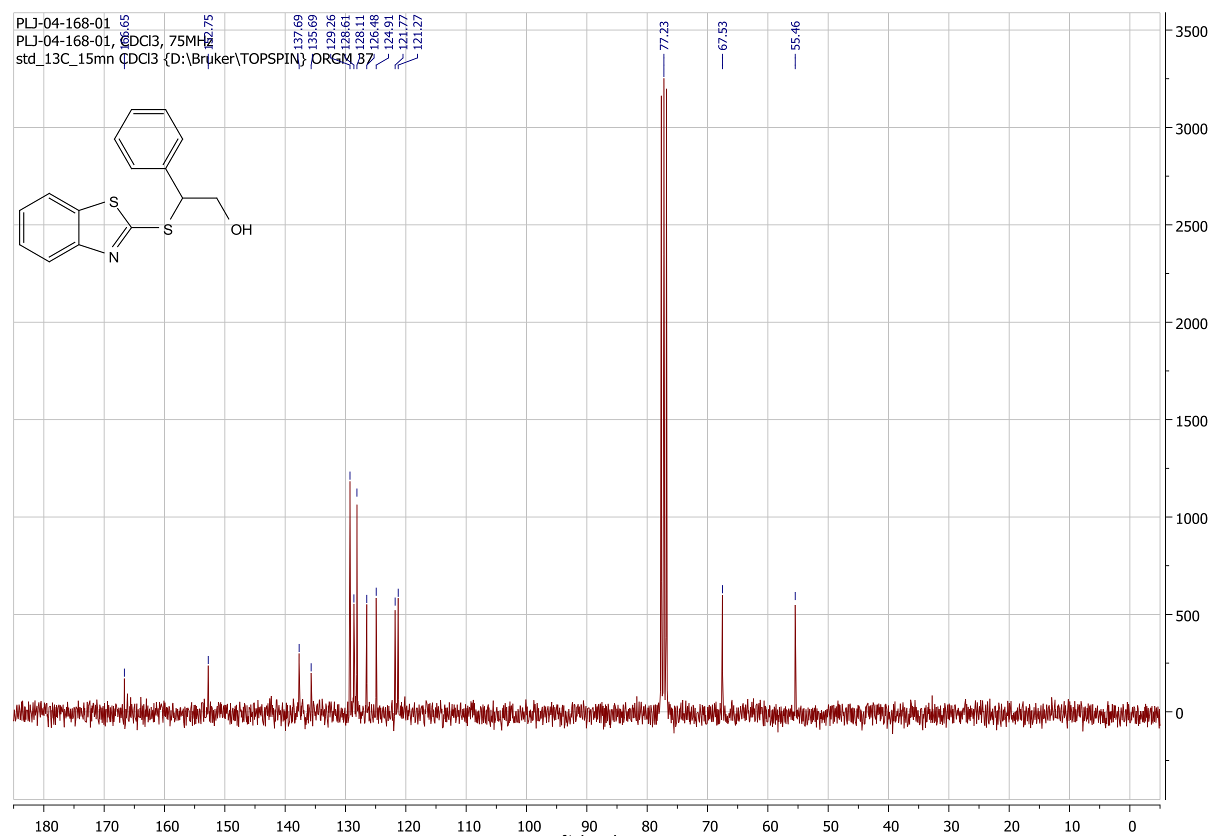
Olefin 3s


FB-02-011-01
FB-02-011-01_C,CDCl3,300MHz
O
f1 (ppm)

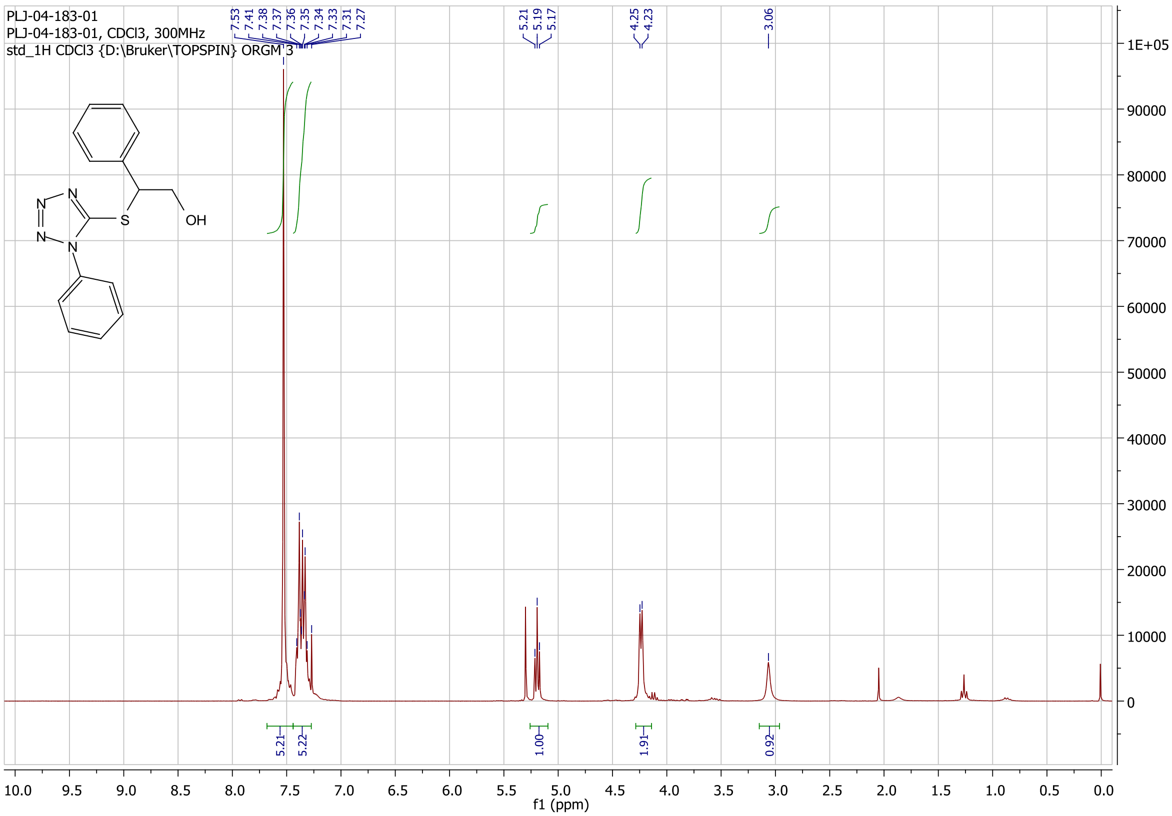

FB-02-011-01
FB-02-011-01_C,CDCl3,75MHz
O
f1 (ppm)

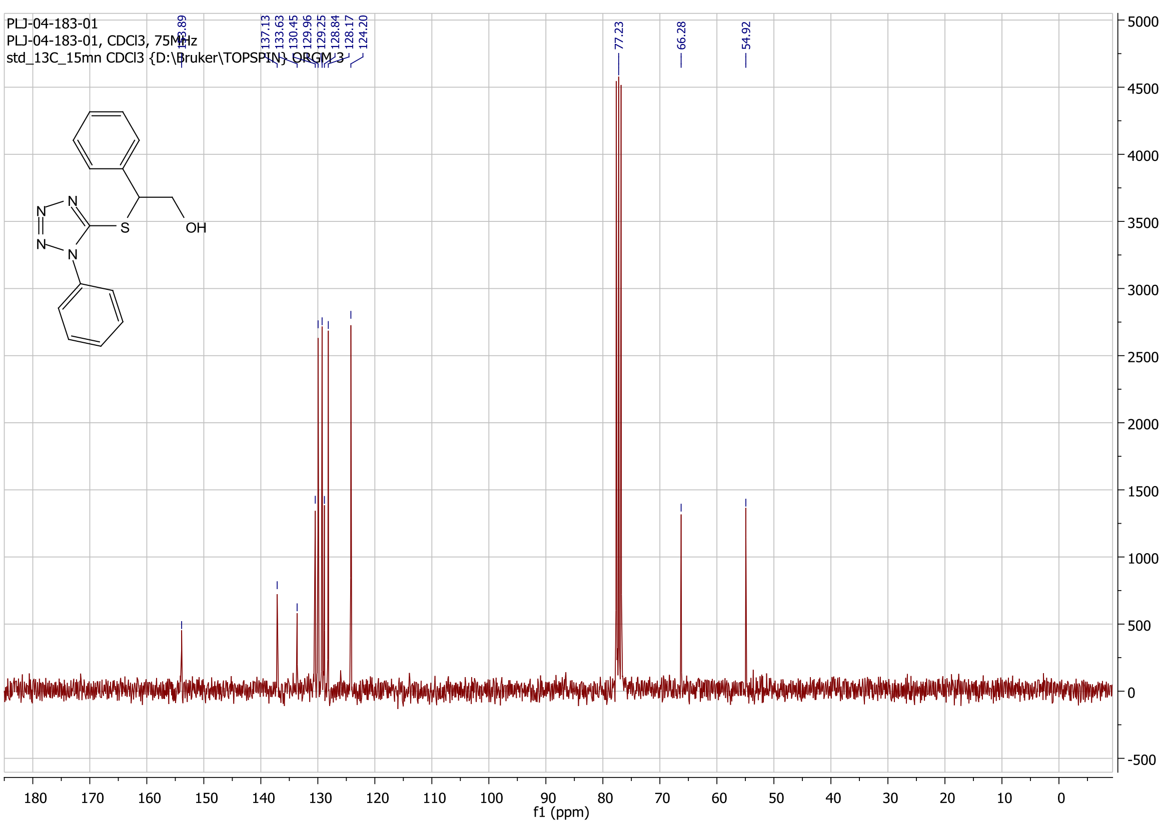
Hydroxy BT-sulfide



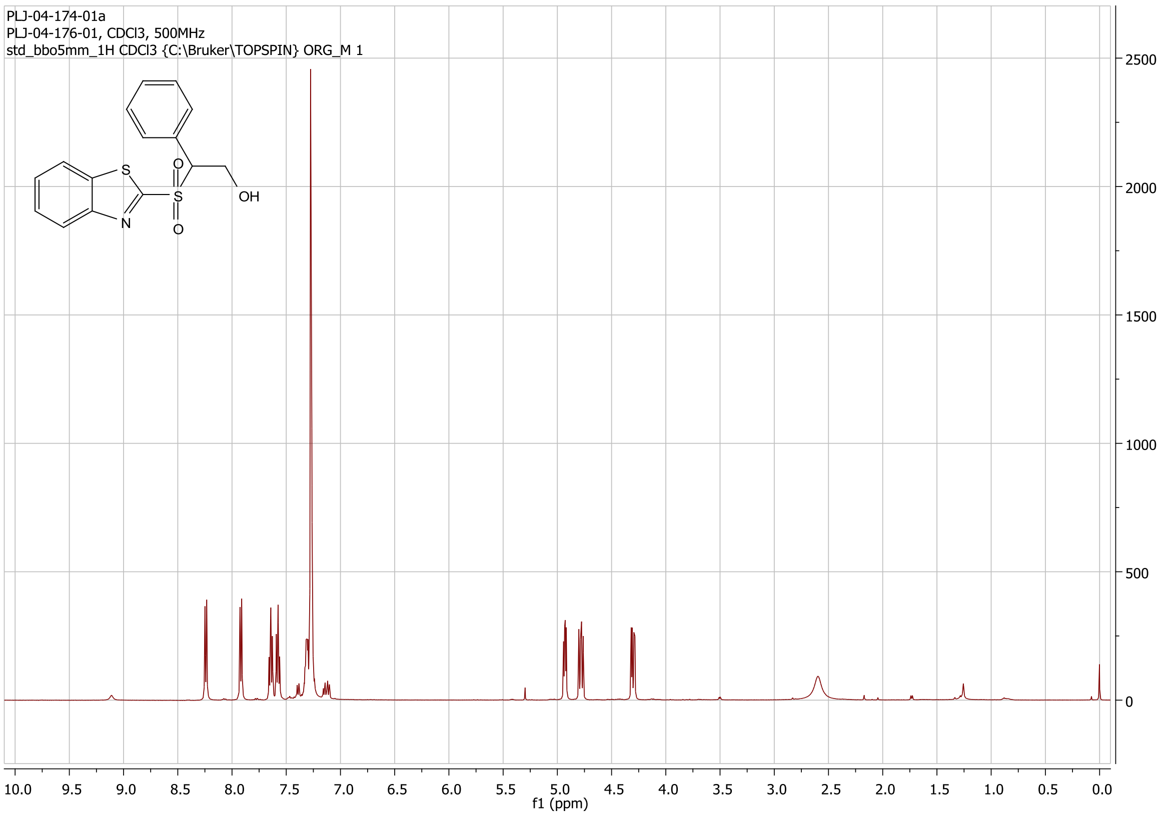


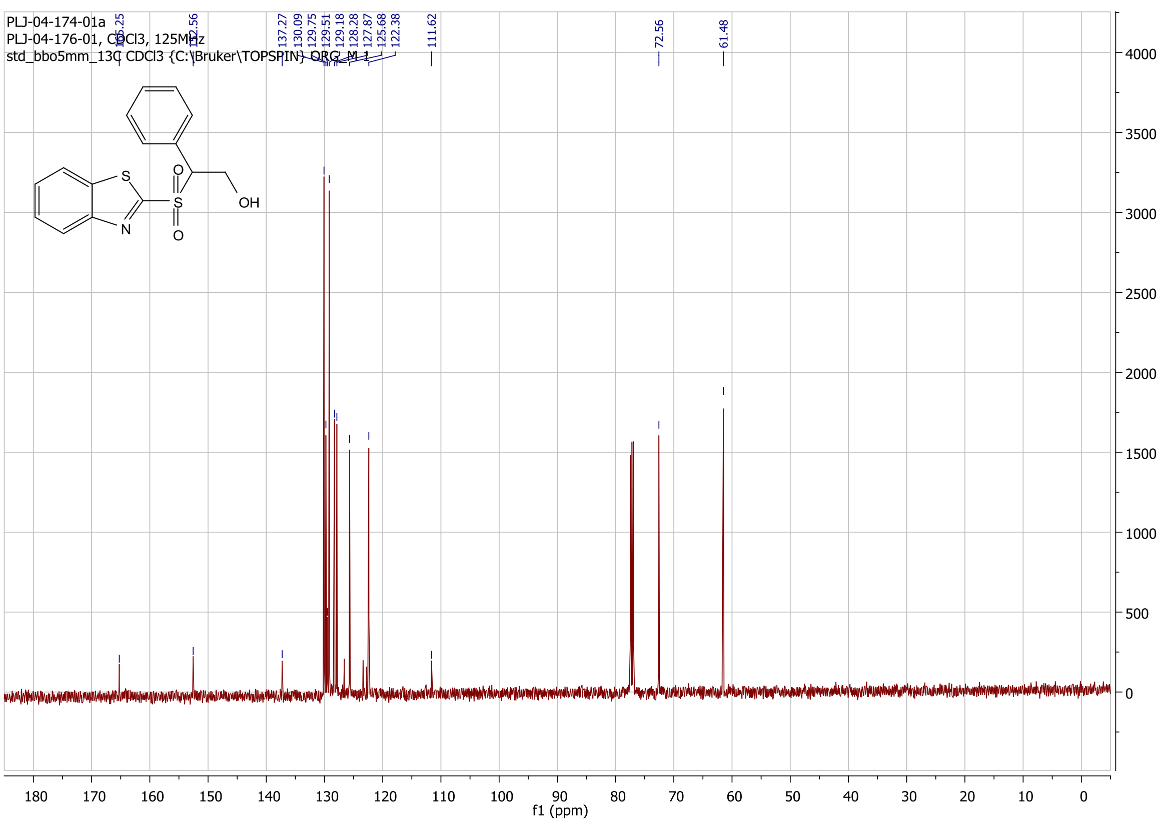
Hydroxy PT-sulfide



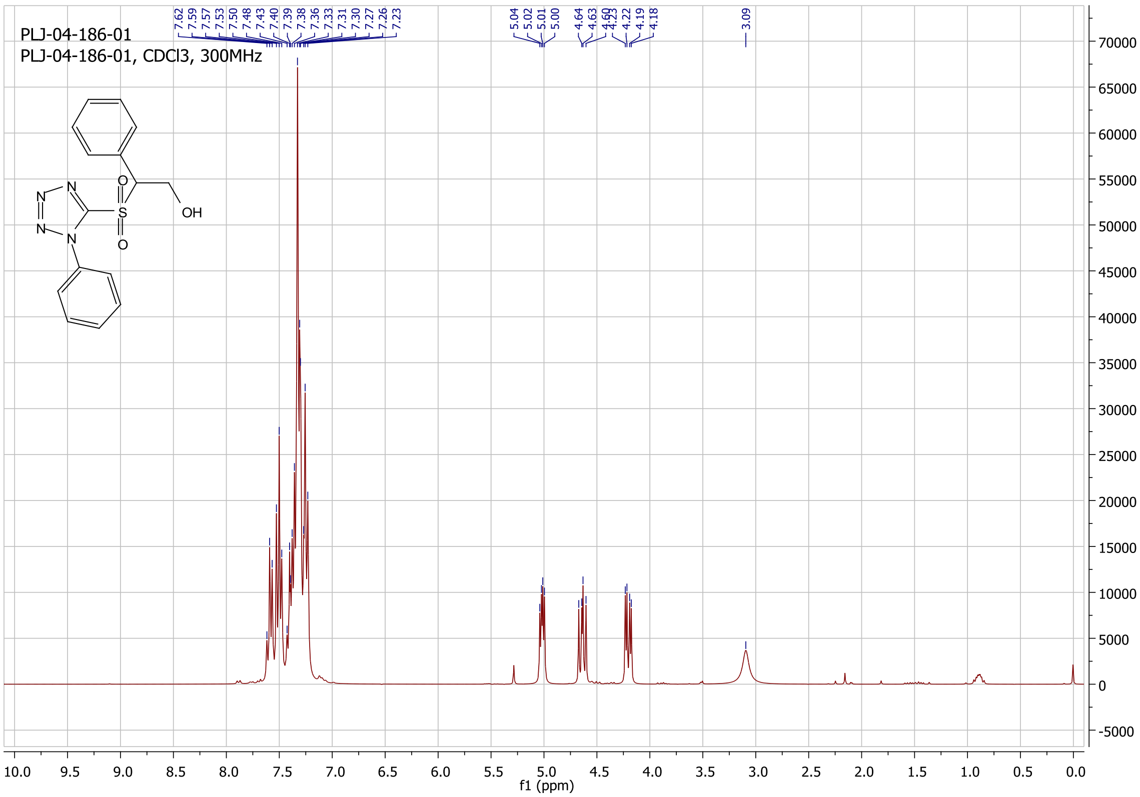


Sulfone 8a

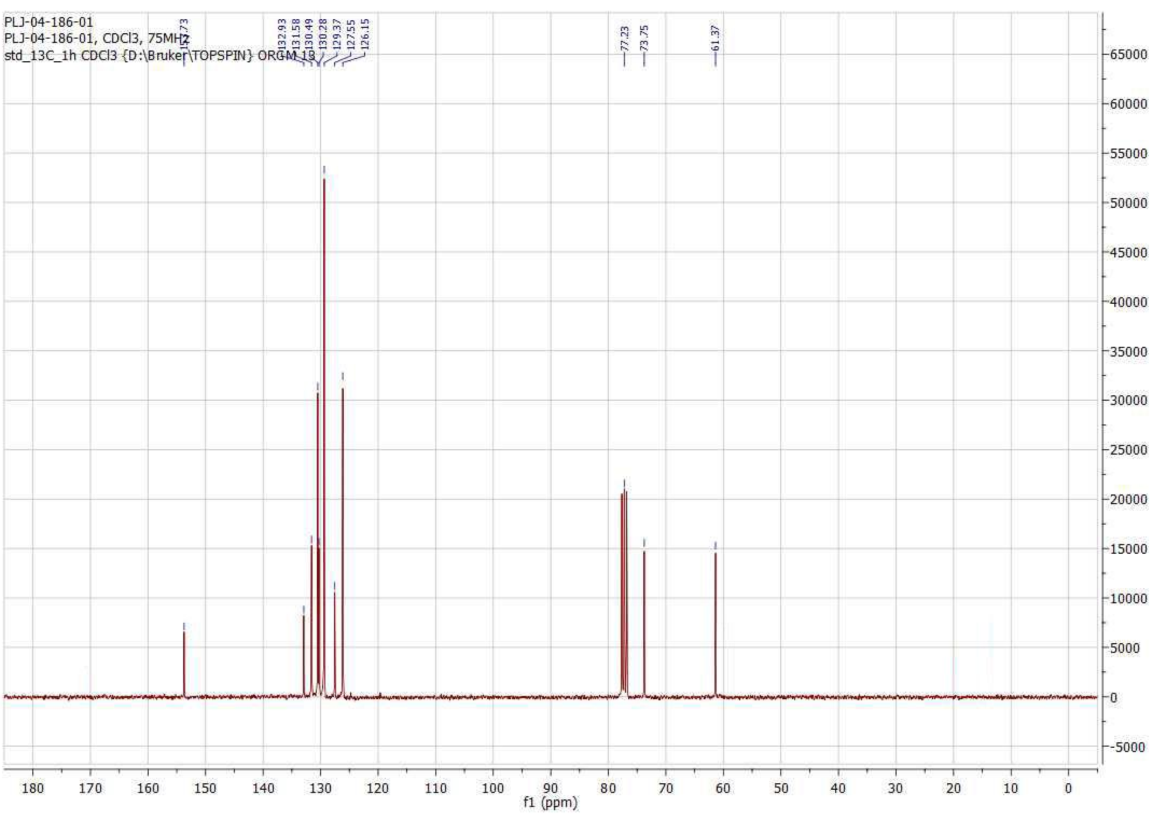

PLJ-04-174-01a
PLJ-04-176-01, CDCl3, 500MHz
std_bbo5mm_1H CDCl3 {C:\Bruker\TOPSPIN} ORG_M 1
S
O
S
OH
N
O
f1 (ppm)


PLJ-04-174-01a
PLJ-04-176-01, CDCl3, 125MHz
std_bbo5mm_13C CDCl3 {C:\Bruker\TOPSPIN} ORG_M 1
137.27
130.09
129.75
129.51
129.18
128.28
127.87
125.68
122.38
111.62
72.56
61.48
S
O
S
OH
N
O
f1 (ppm)

Sulfone 8b



PLJ-04-186-01
PLJ-04-186-01, CDCl3, 300MHz
7.62 7.59 7.57 7.53 7.50 7.48 7.43 7.40 7.39 7.38 7.36 7.33 7.31 7.30 7.27 7.26 7.23
5.04 5.02 5.01 5.00
4.64 4.63
4.22 4.19 4.18
3.09
OH
f1 (ppm)



PLJ-04-186-01
PLJ-04-186-01, CDCl3, 75MHz
std_13C_1h CDCl3 {D:\Bruker\TOPSPIN} ORGM 18
132.93 131.58 130.49 130.28 129.37 127.55 126.15
77.23
73.75
61.37
f1 (ppm)