Supporting Information

Brønsted Acid-Controlled [3+2] Coupling Reaction of Quinone Monoacetals with Alkene Nucleophiles: A Catalytic System of Perfluorinated Acids and Hydrogen Bond Donor for the Construction of Benzofurans

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E-mail: kita@ph.ritsumei.ac.jp

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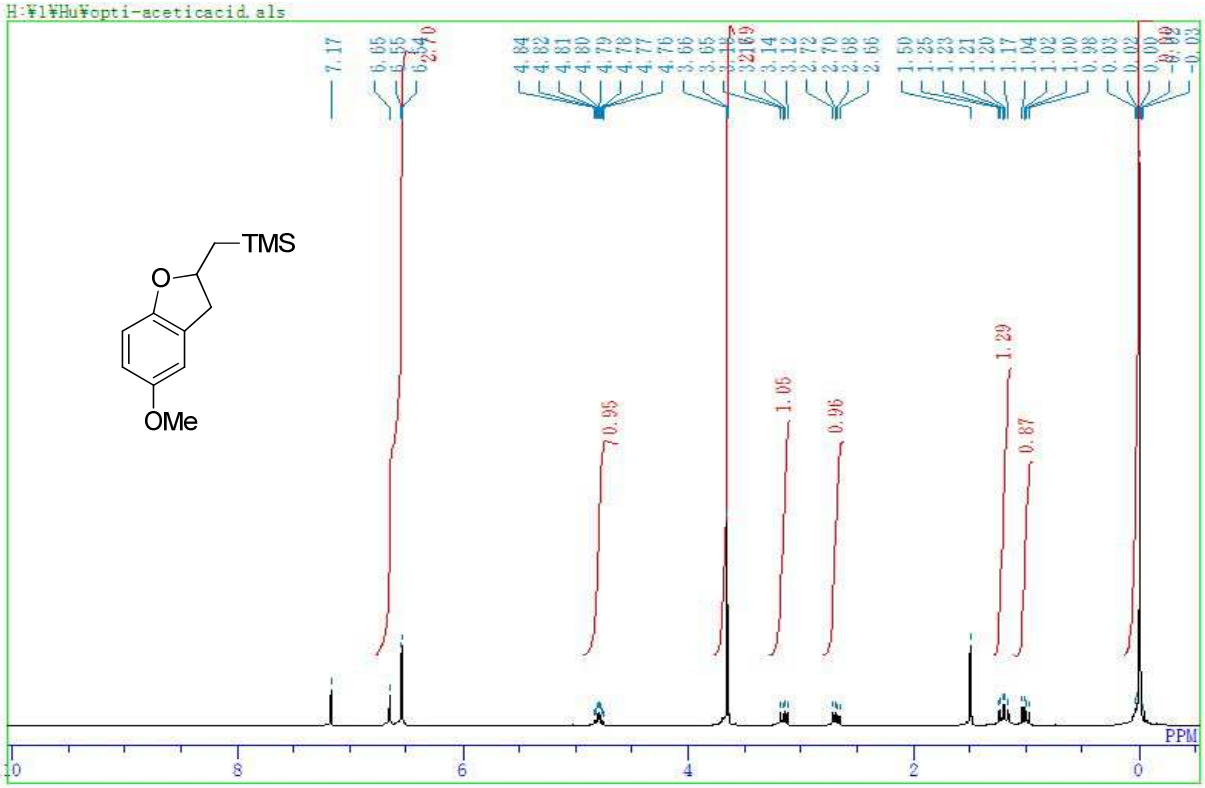
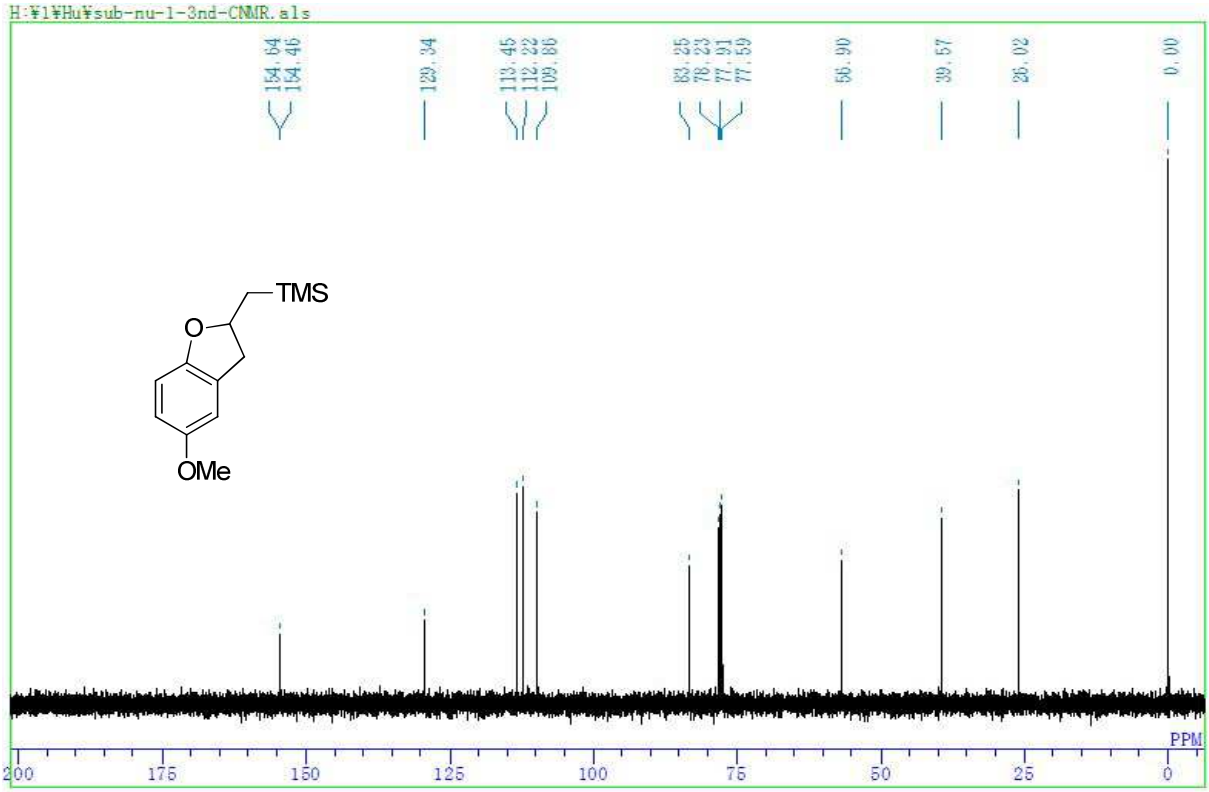
1. ^{1}H and ^{13}C NMR spectra of the products

(3aa)





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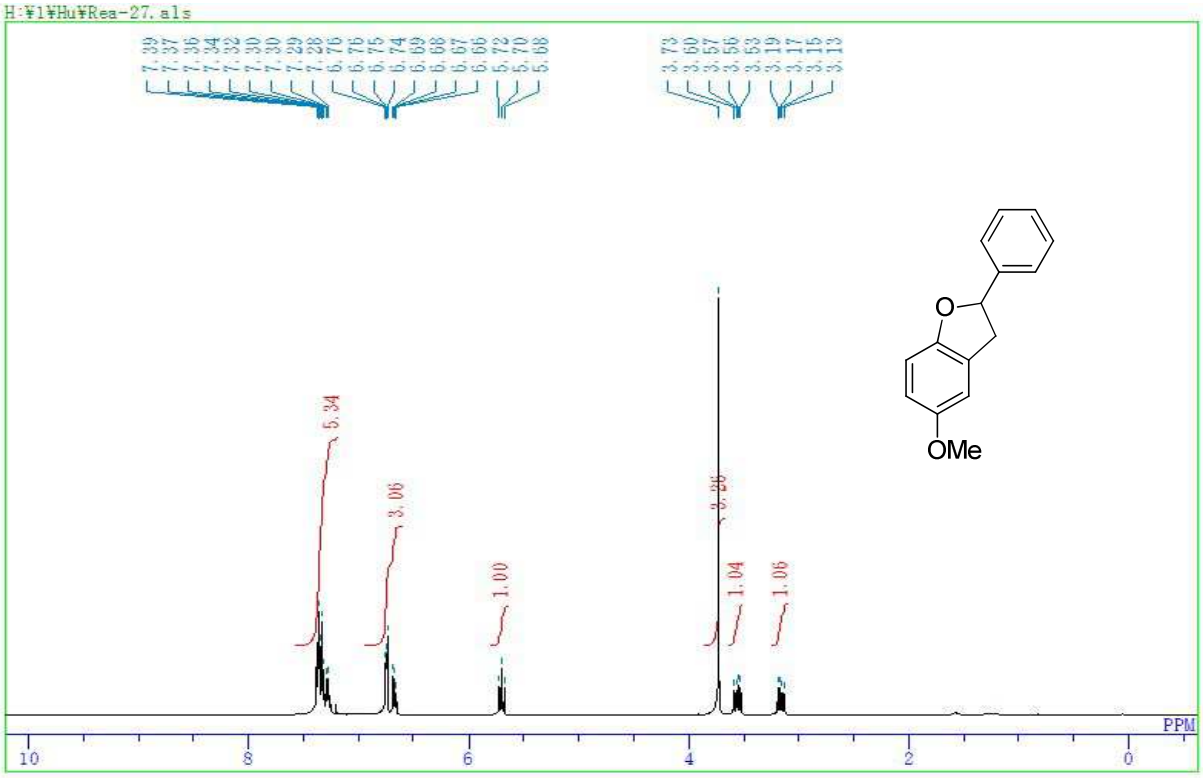
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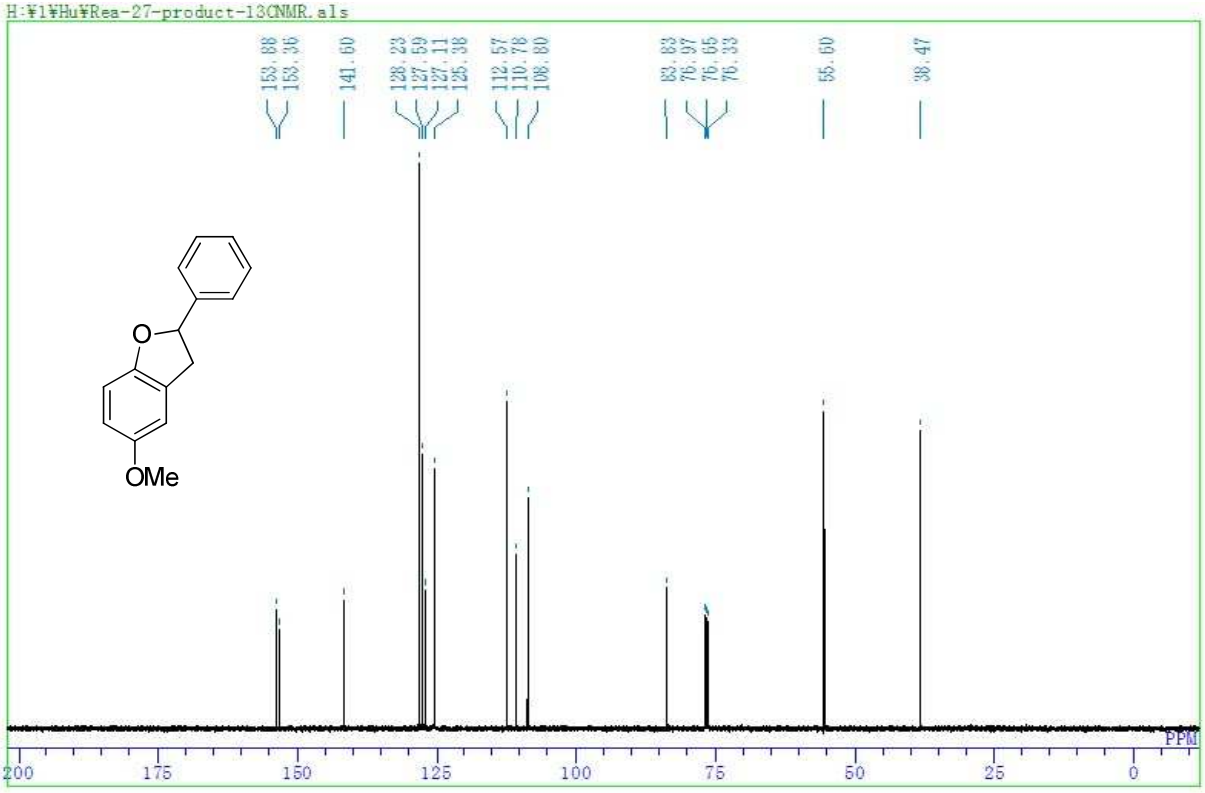
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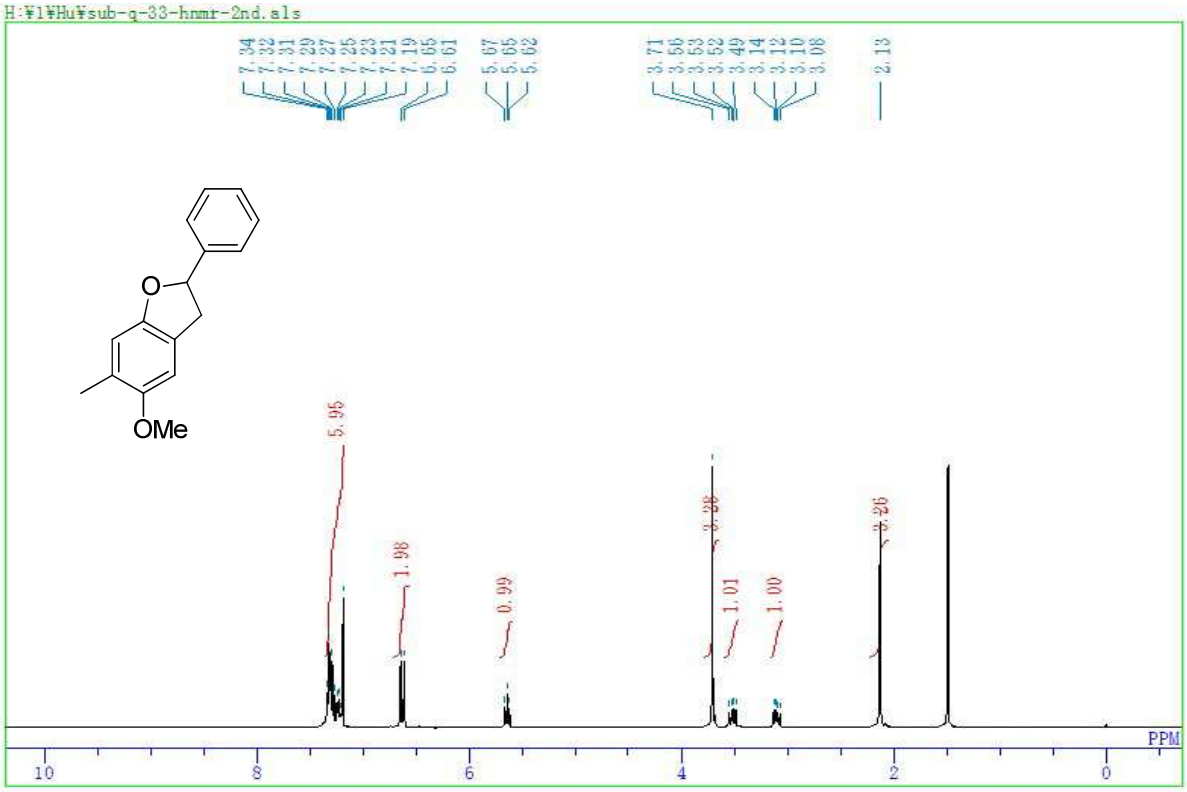
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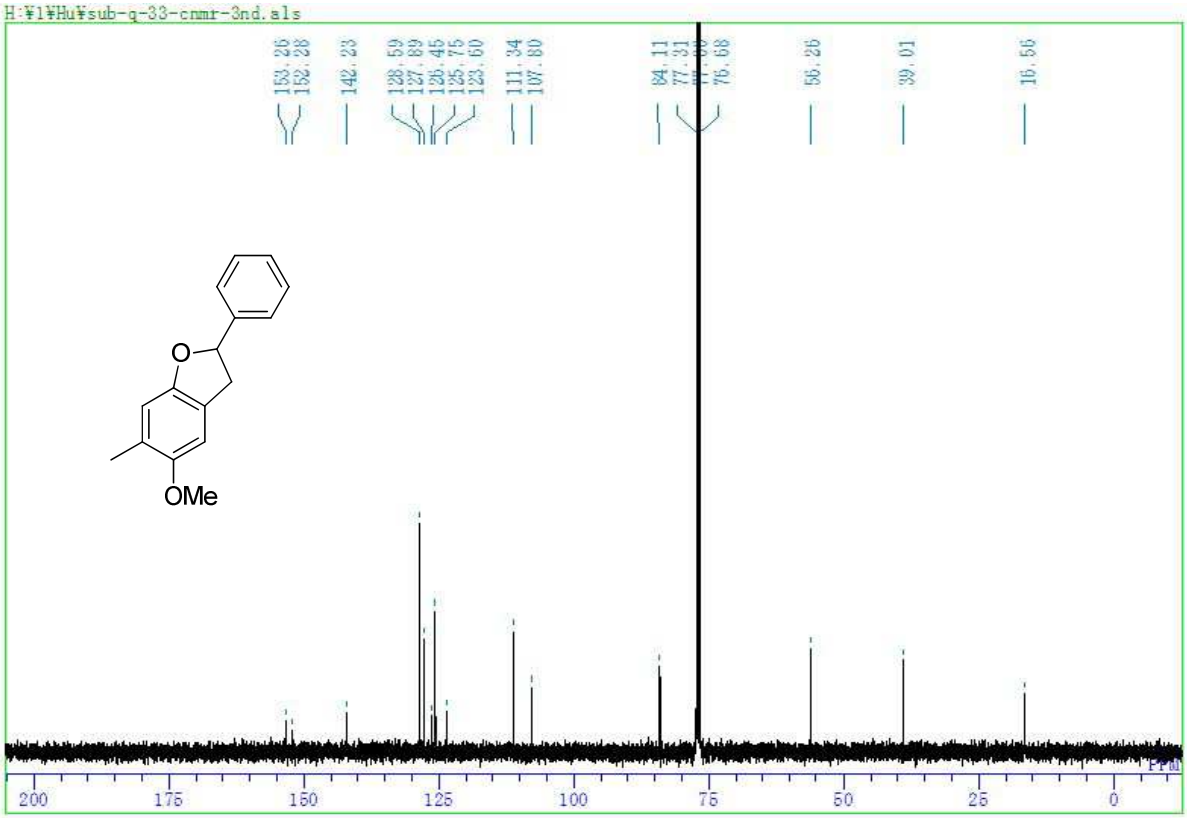
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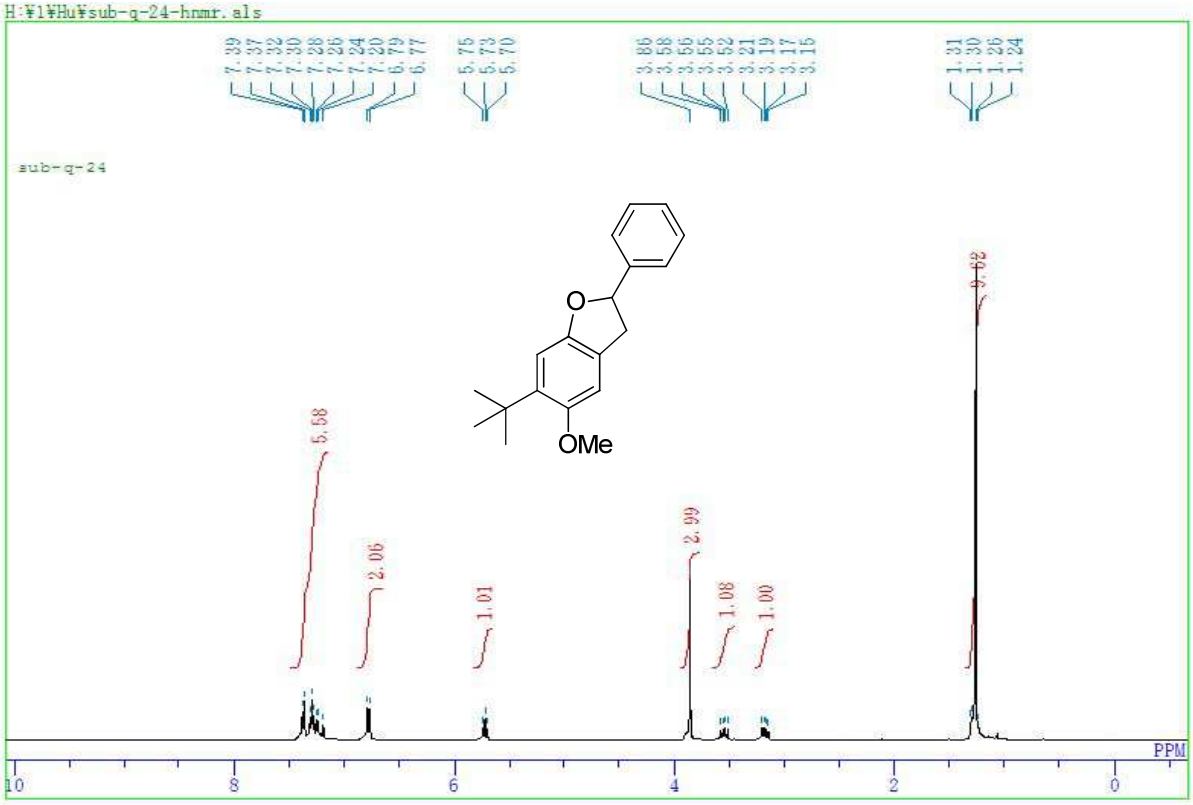
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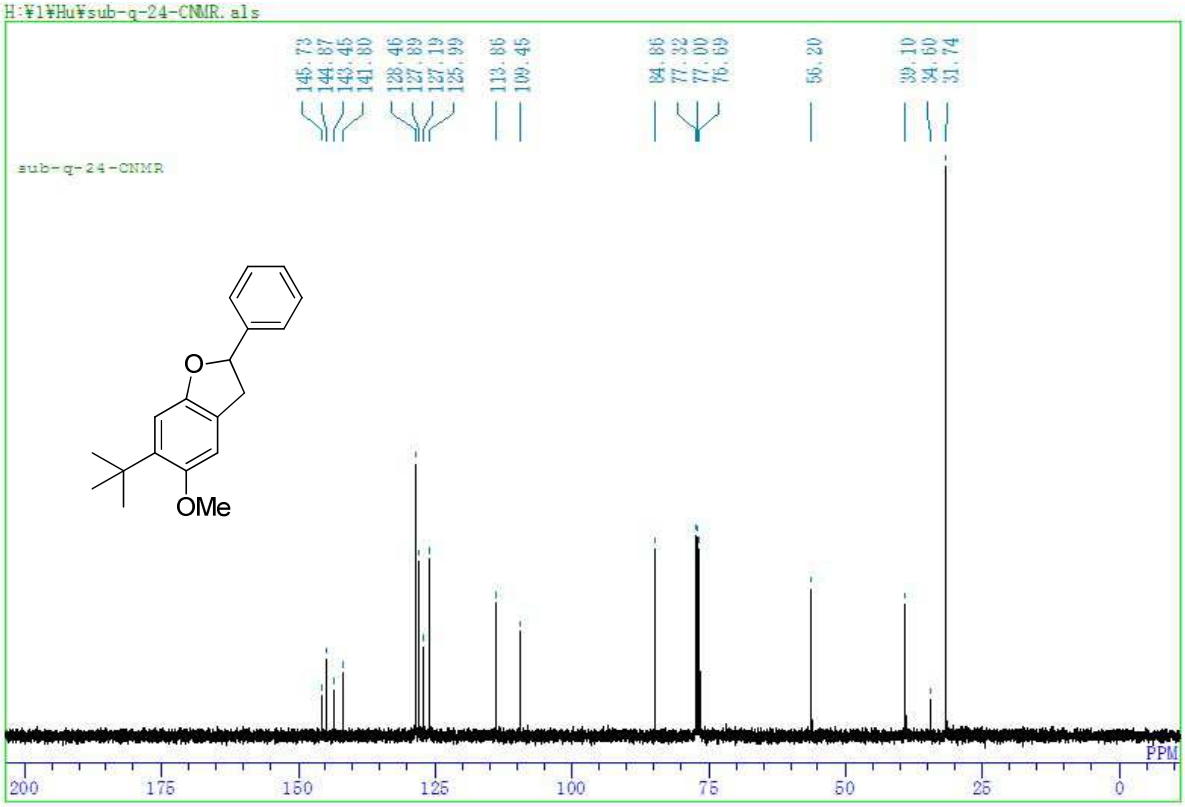
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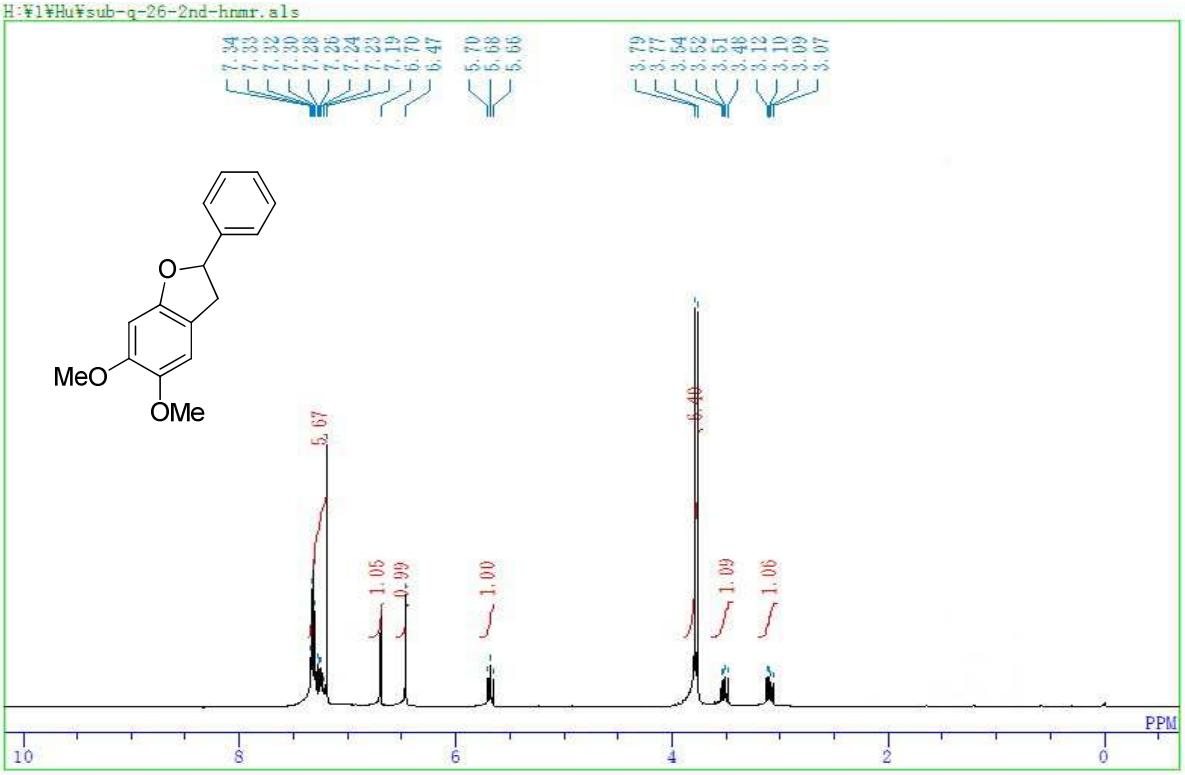
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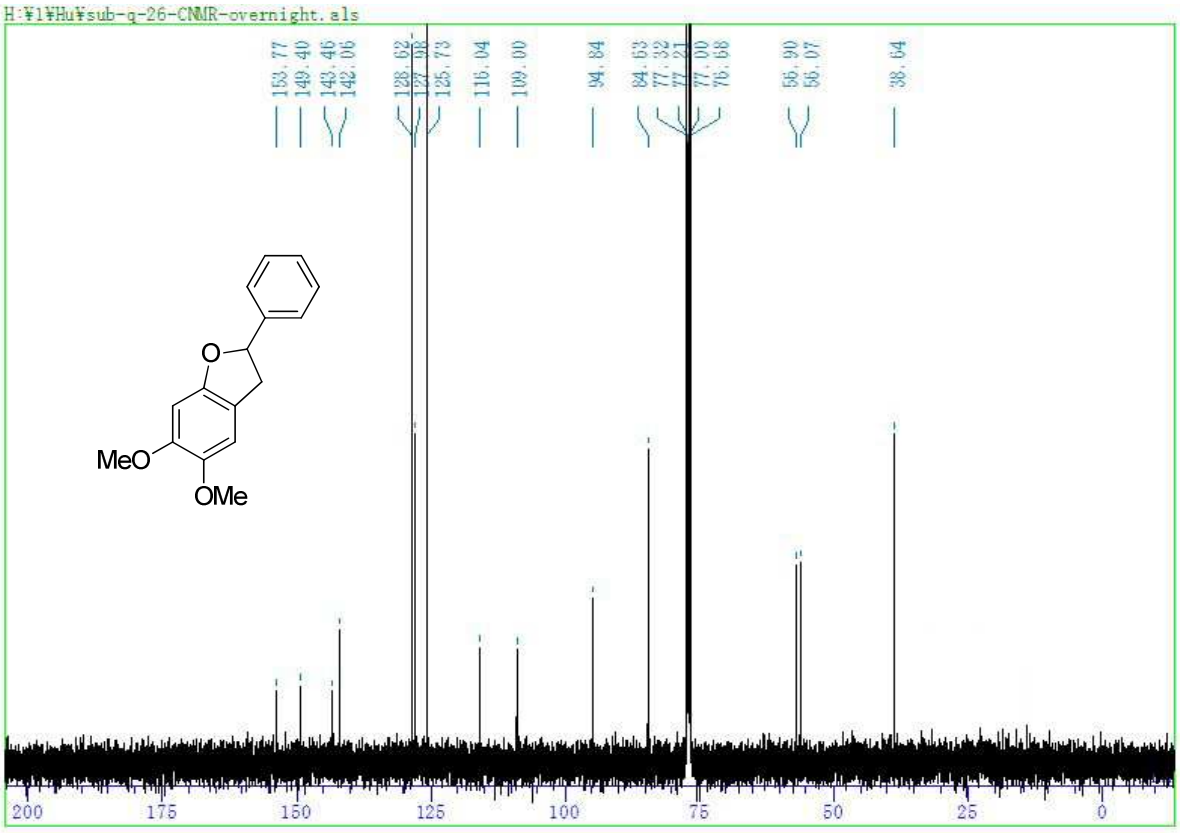
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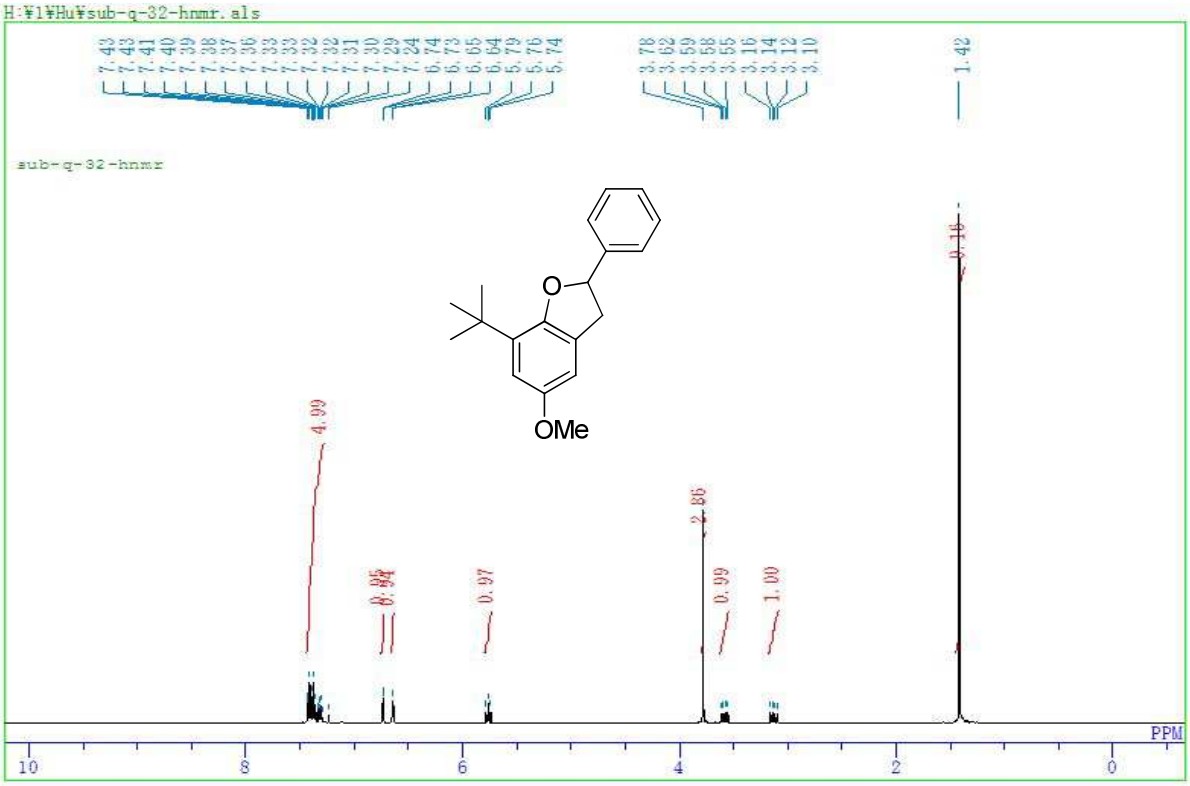
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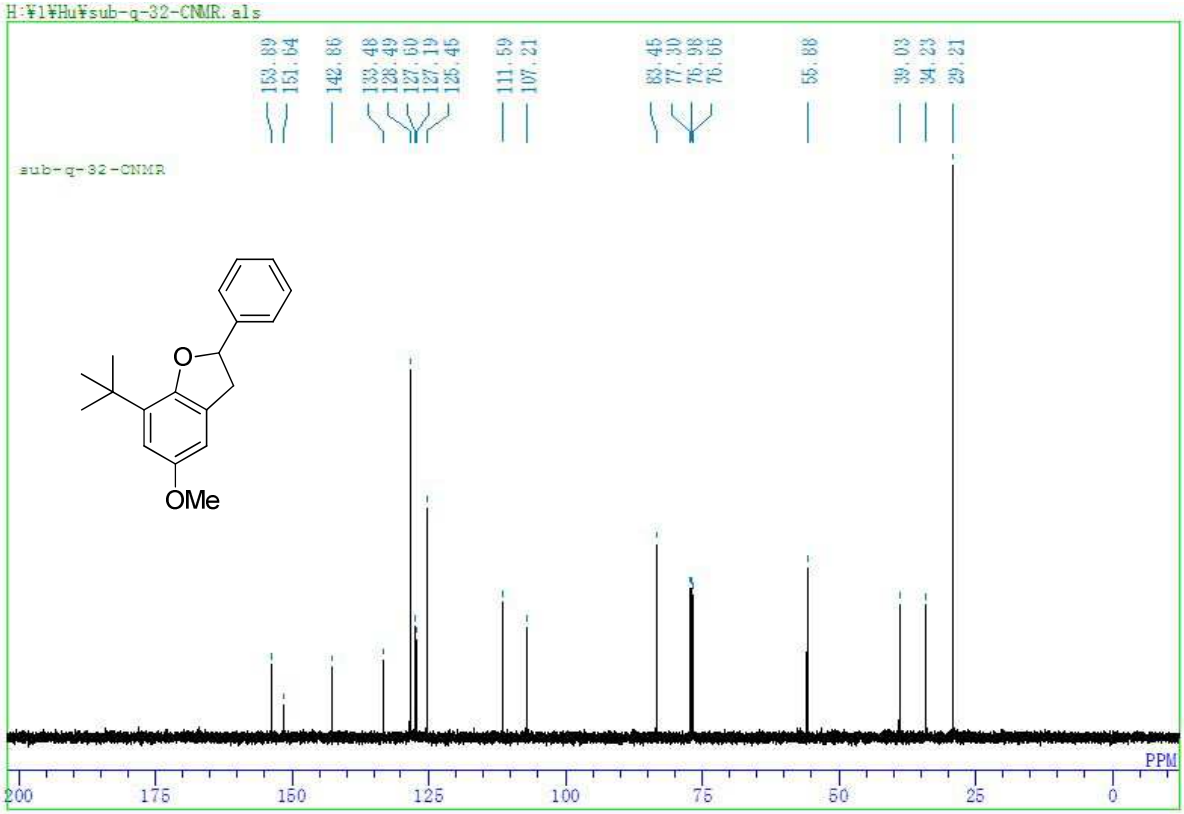
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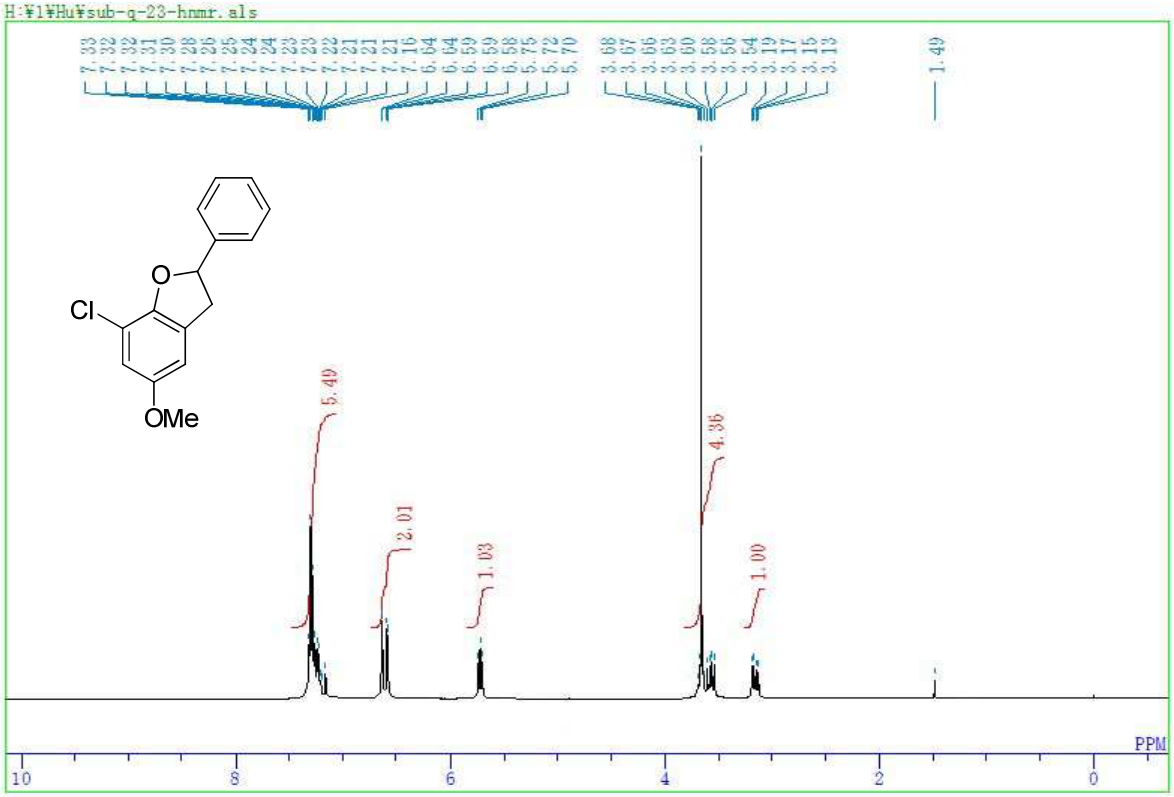
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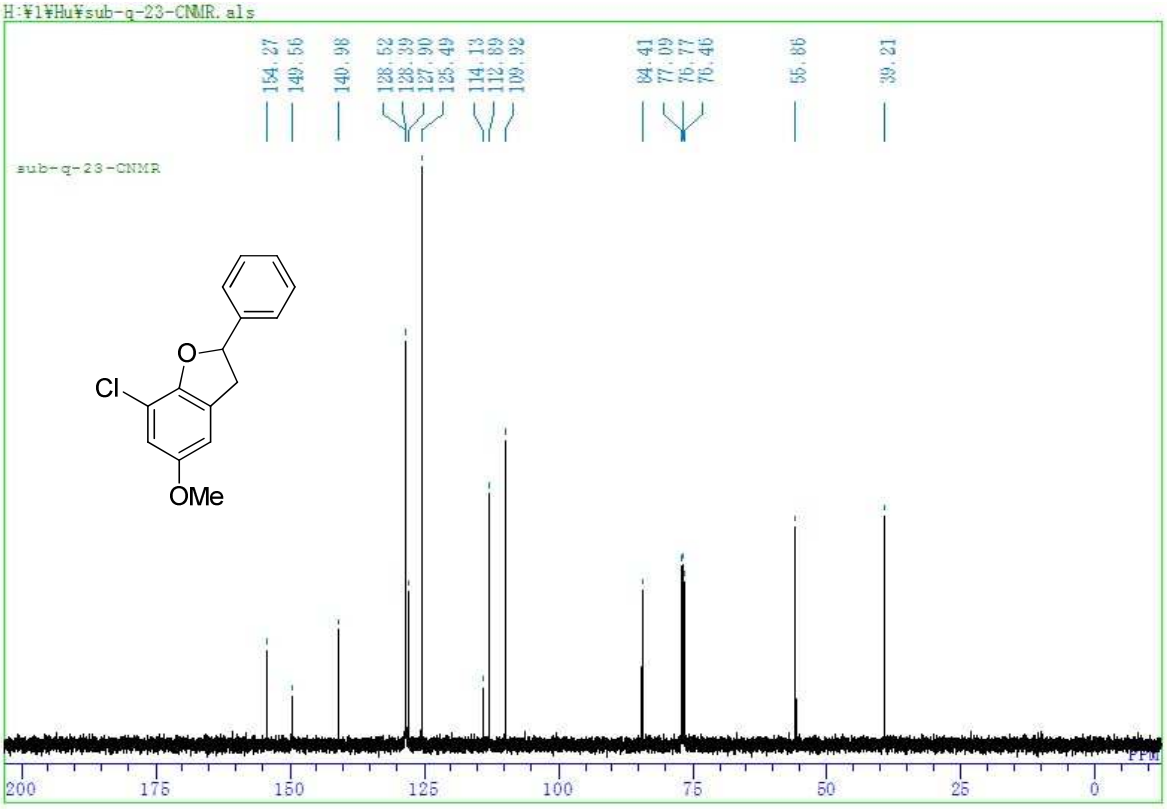
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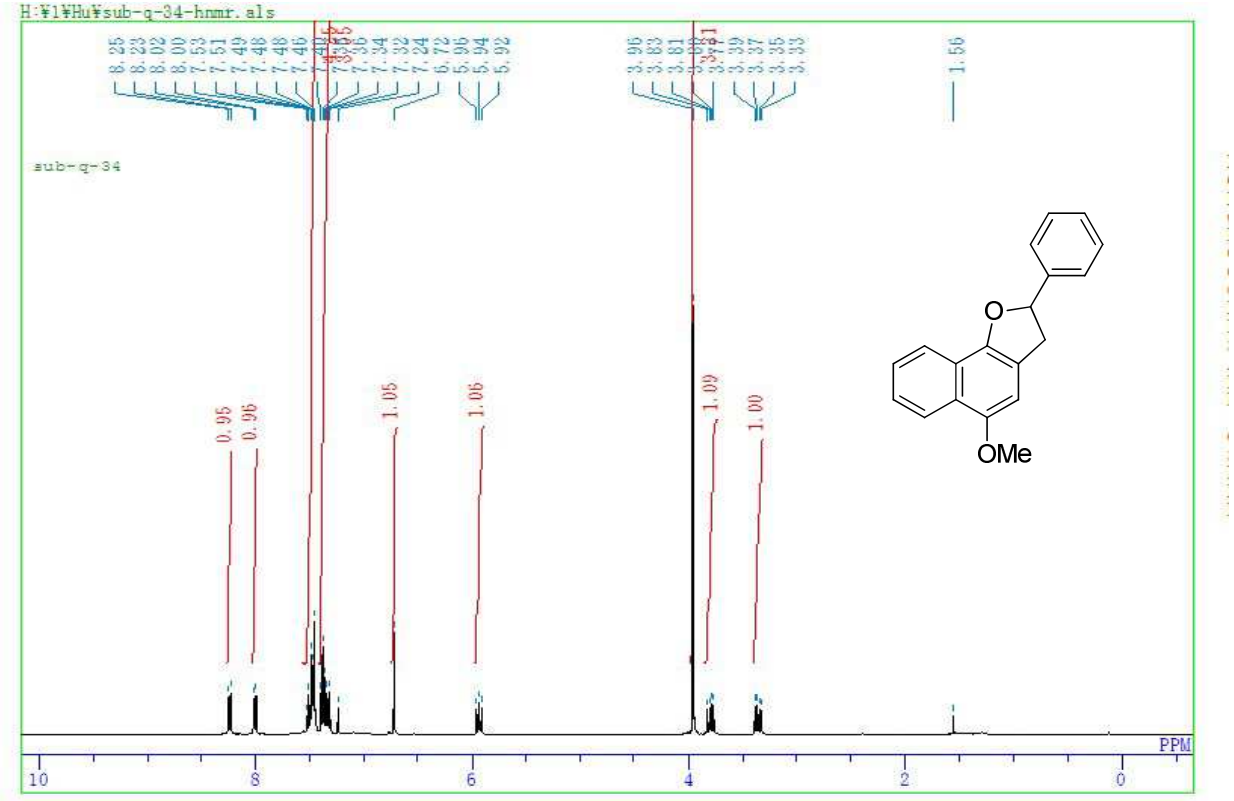

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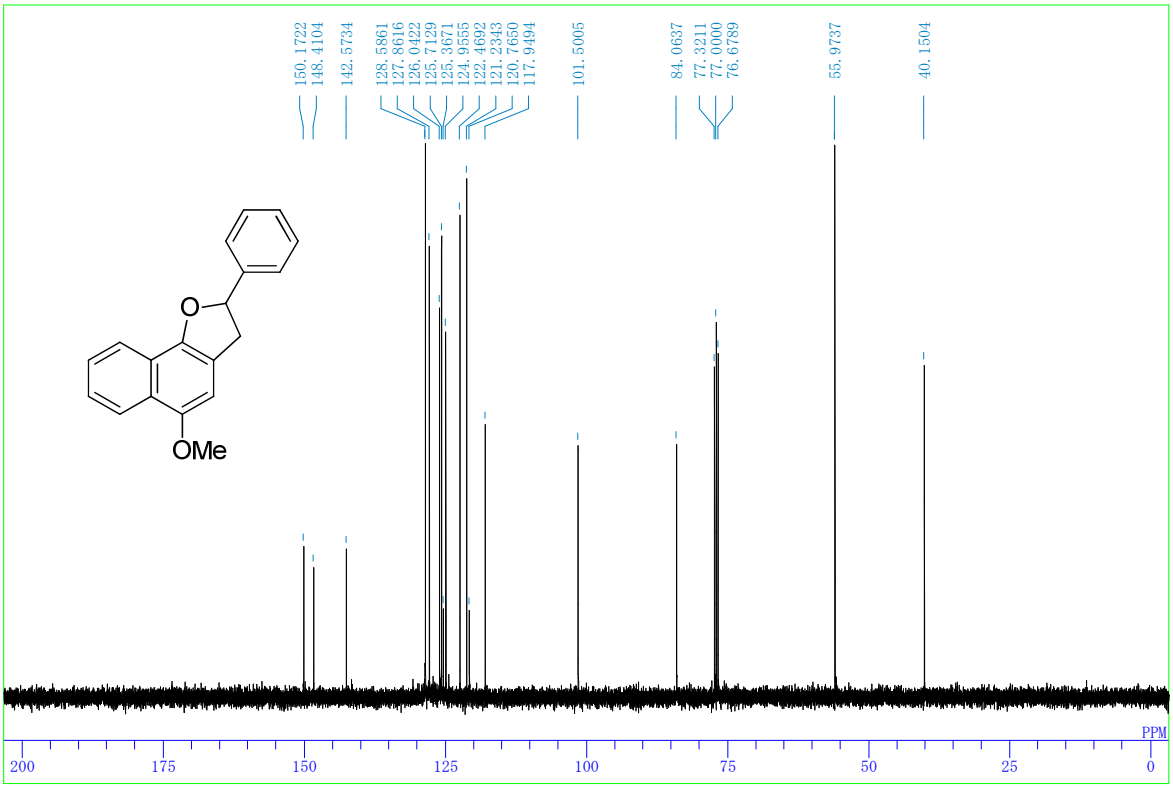

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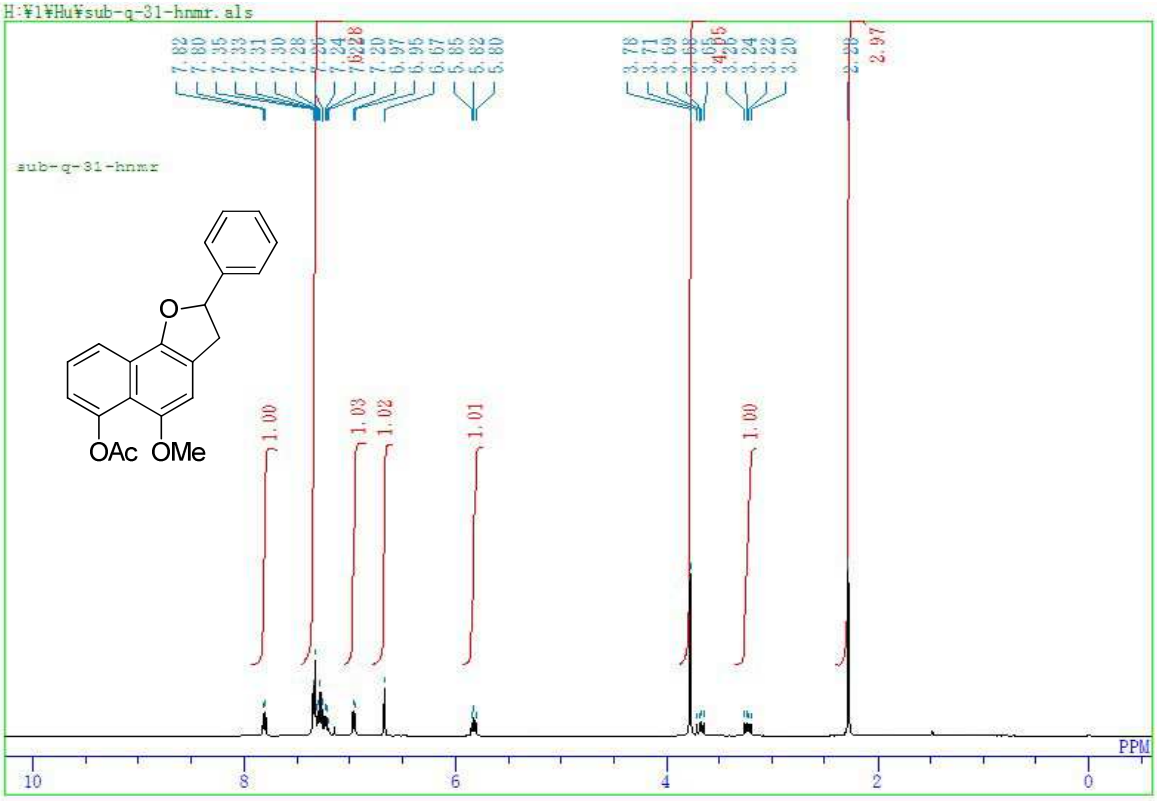
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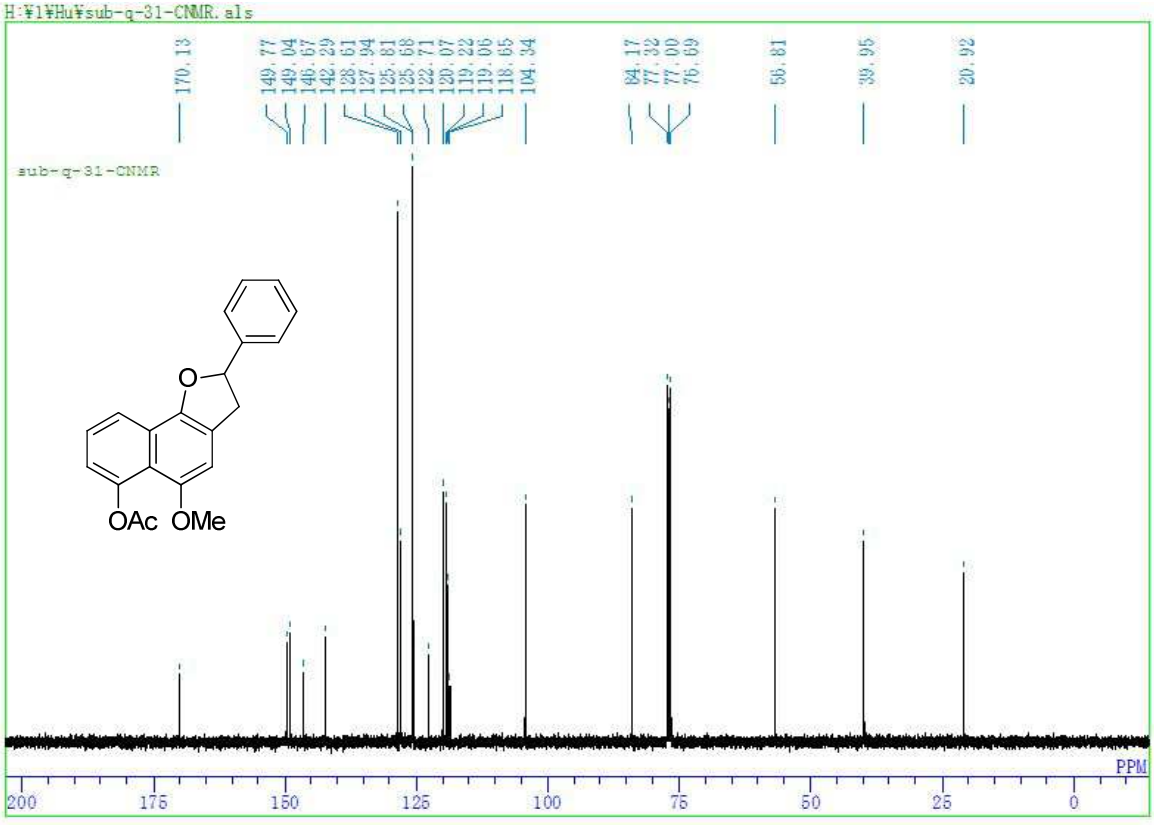
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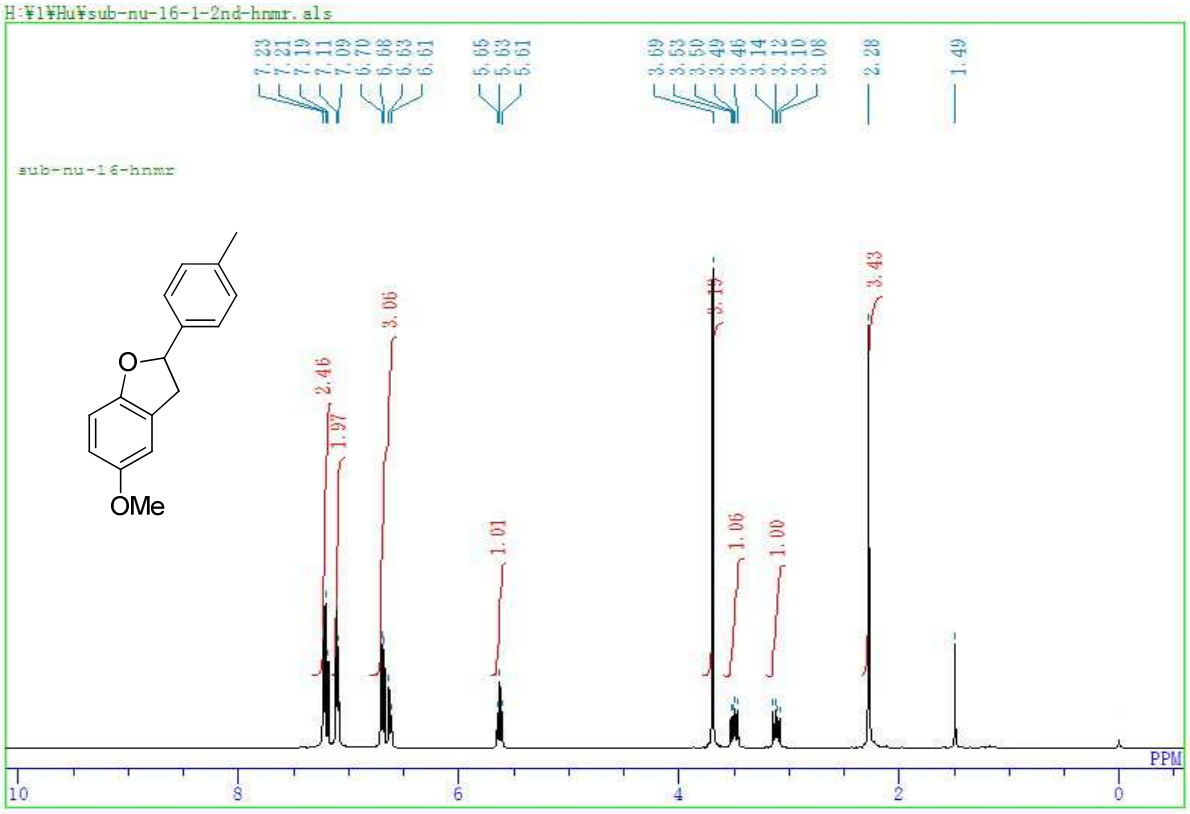
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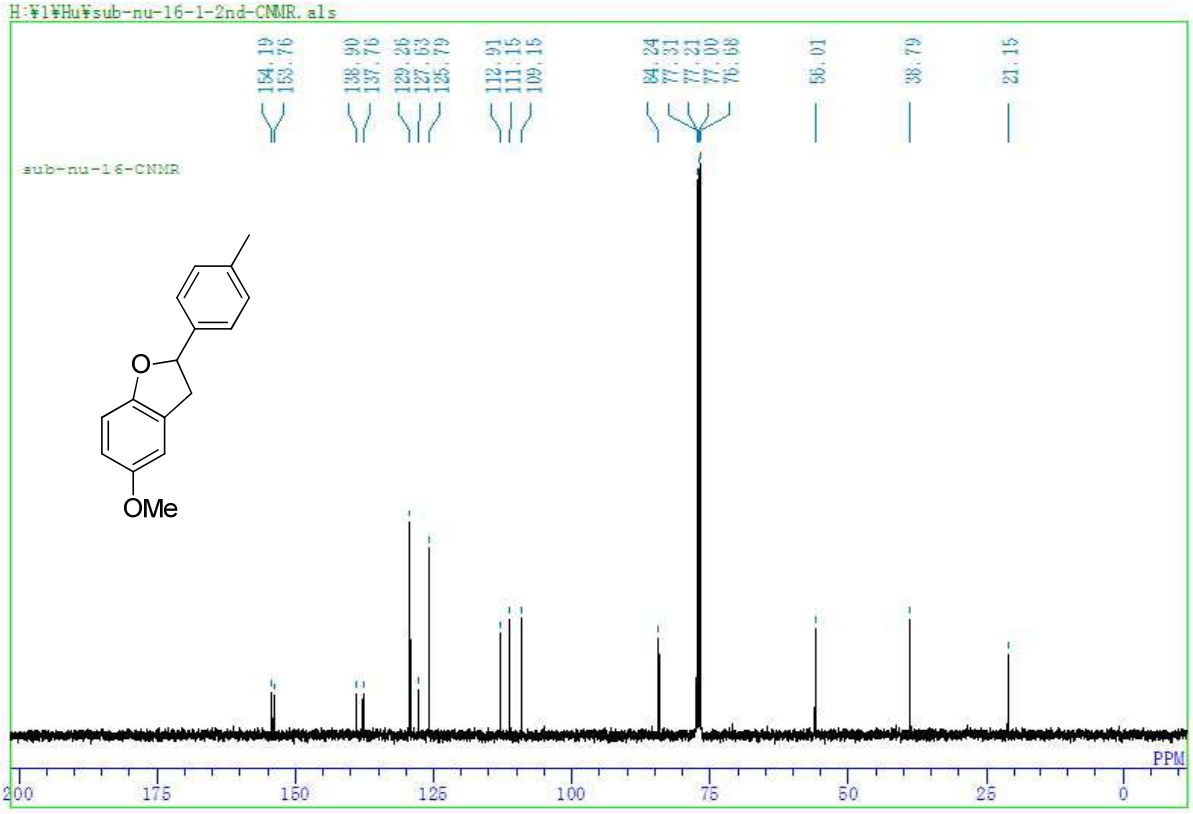
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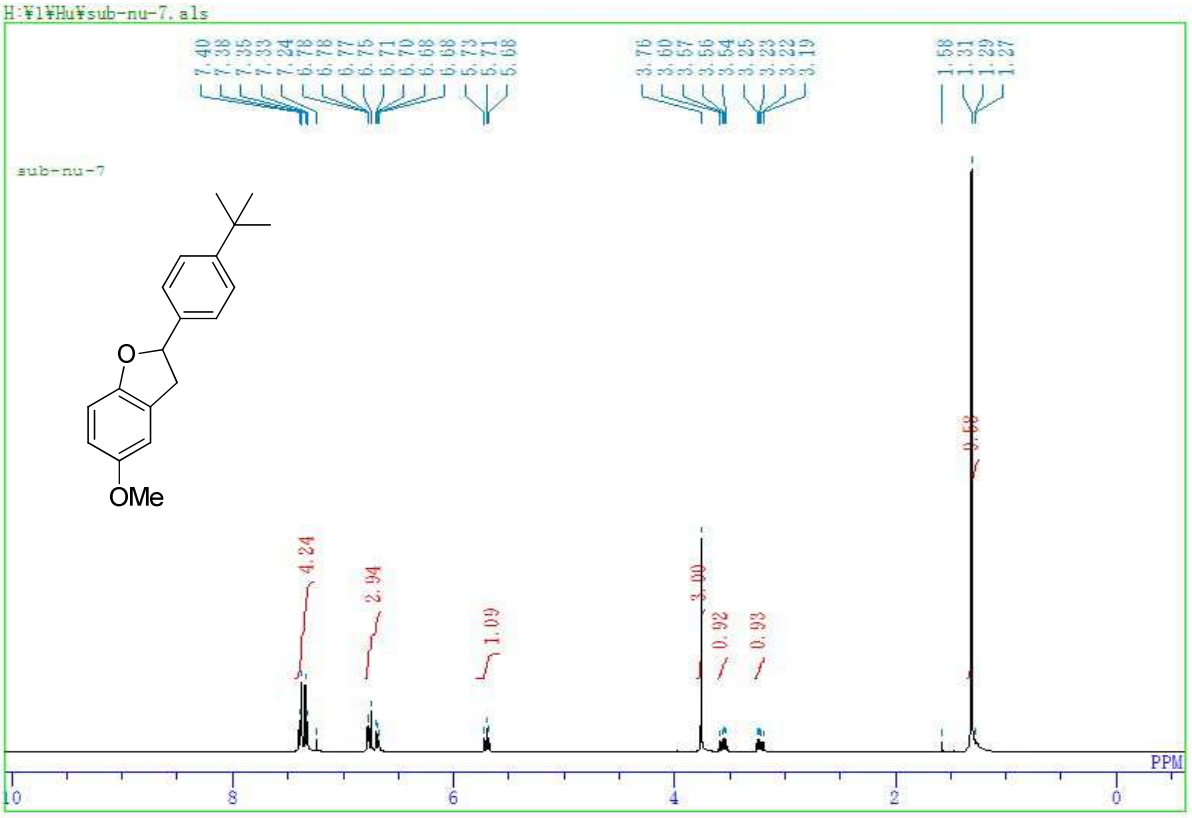
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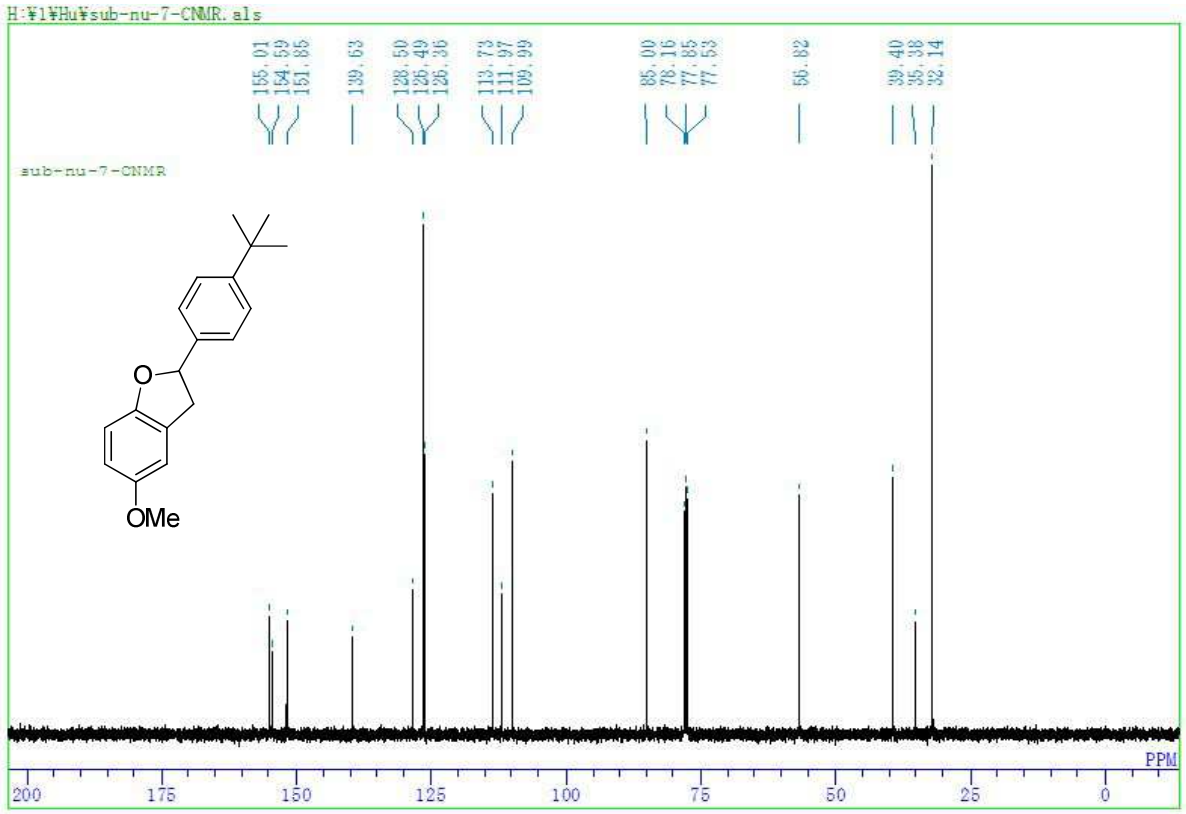
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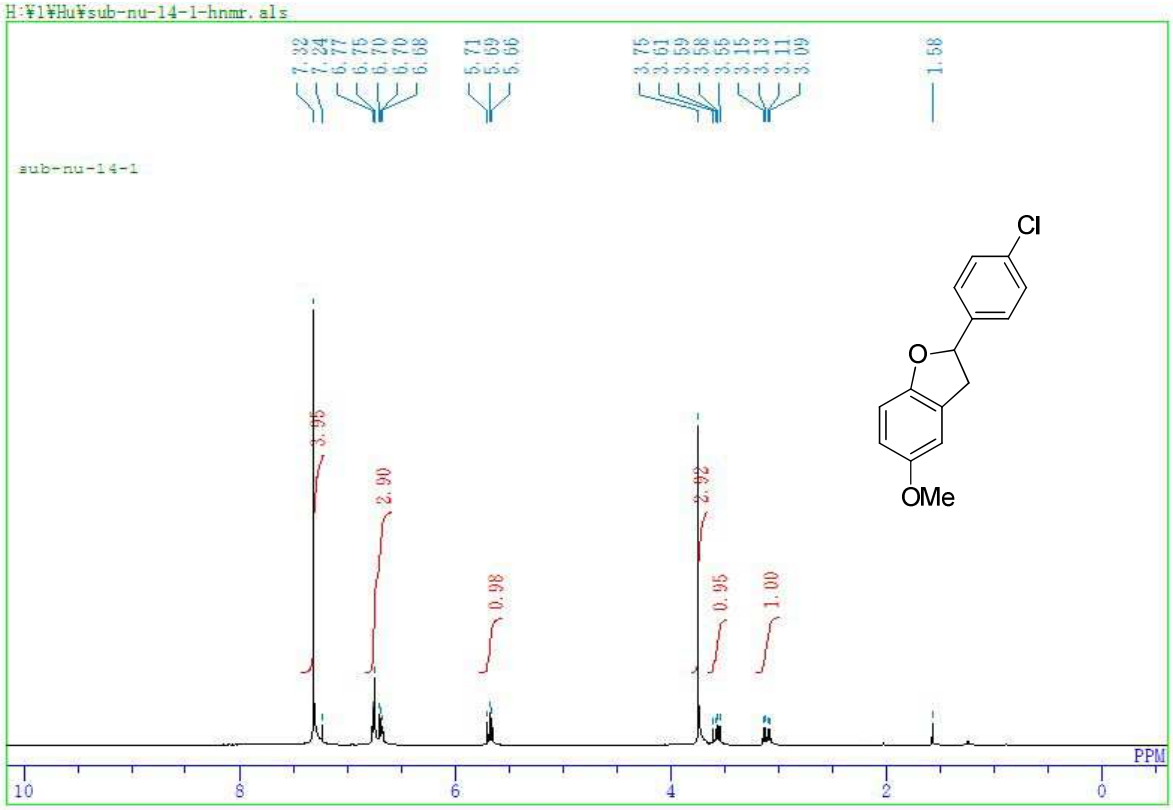
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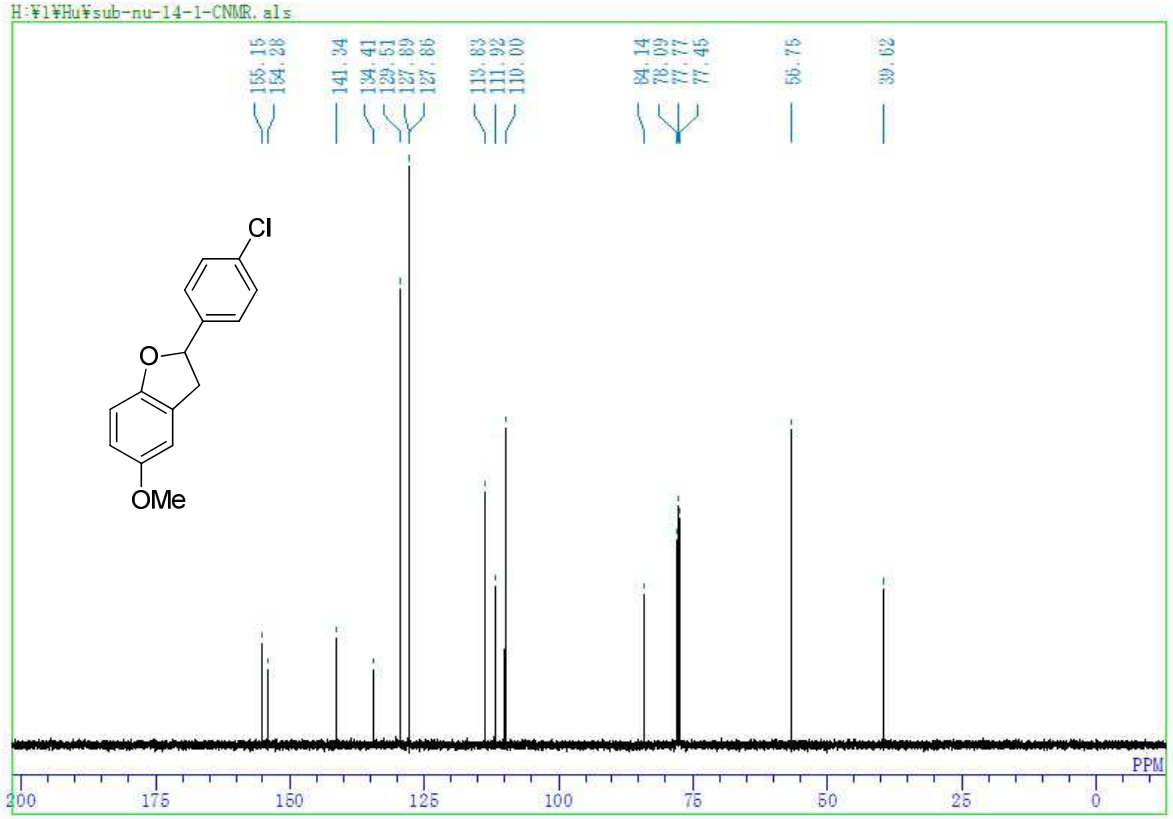
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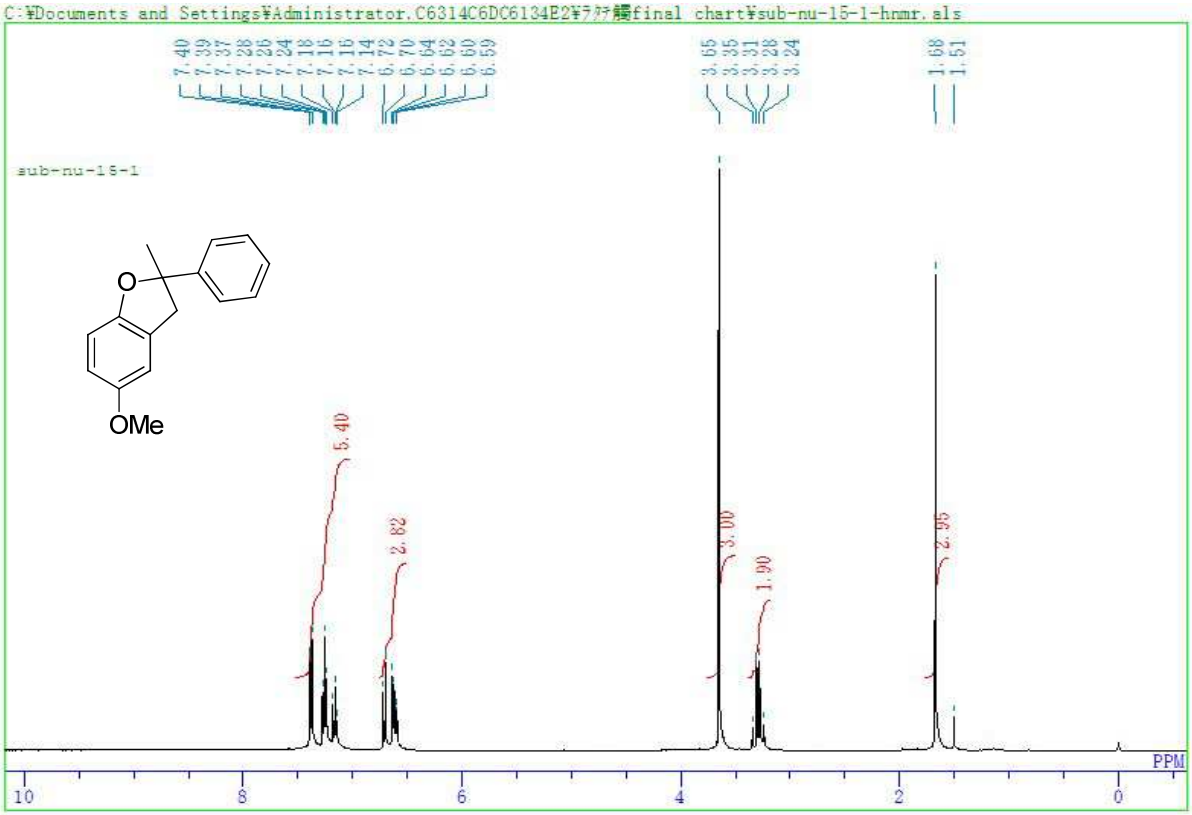
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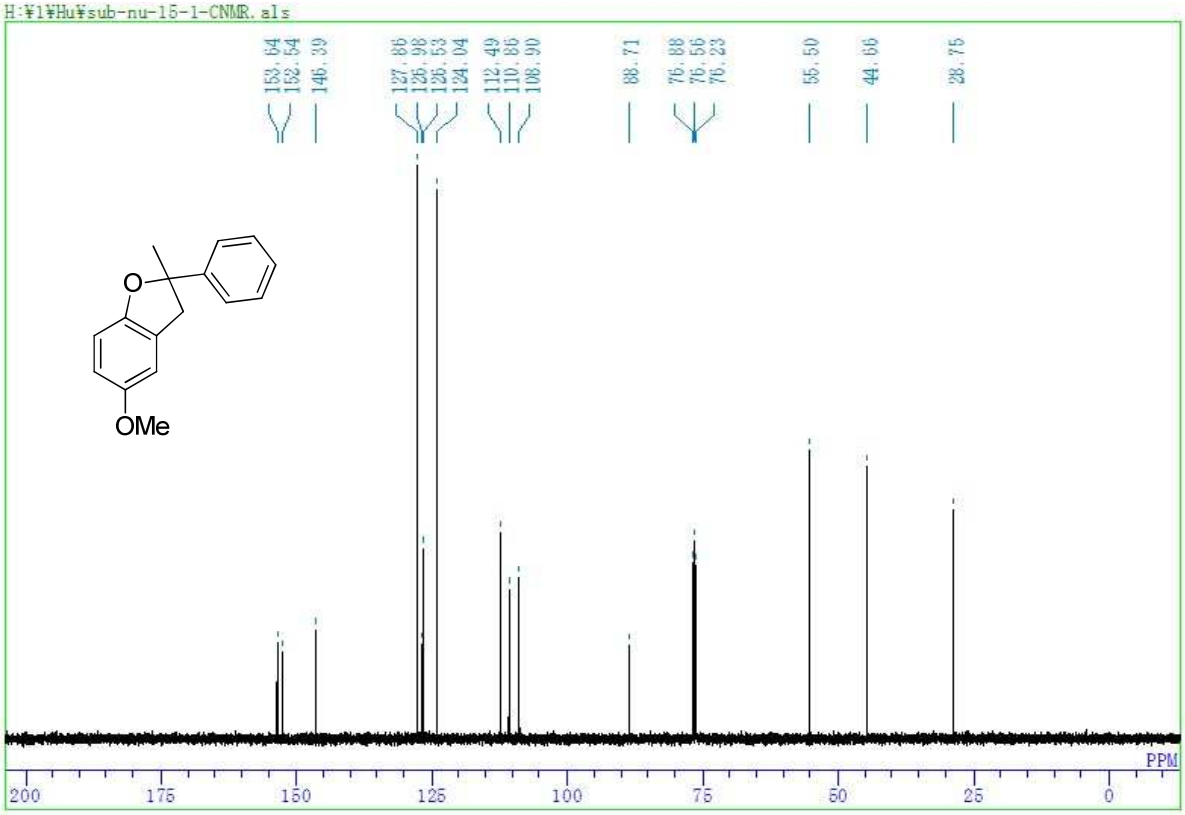
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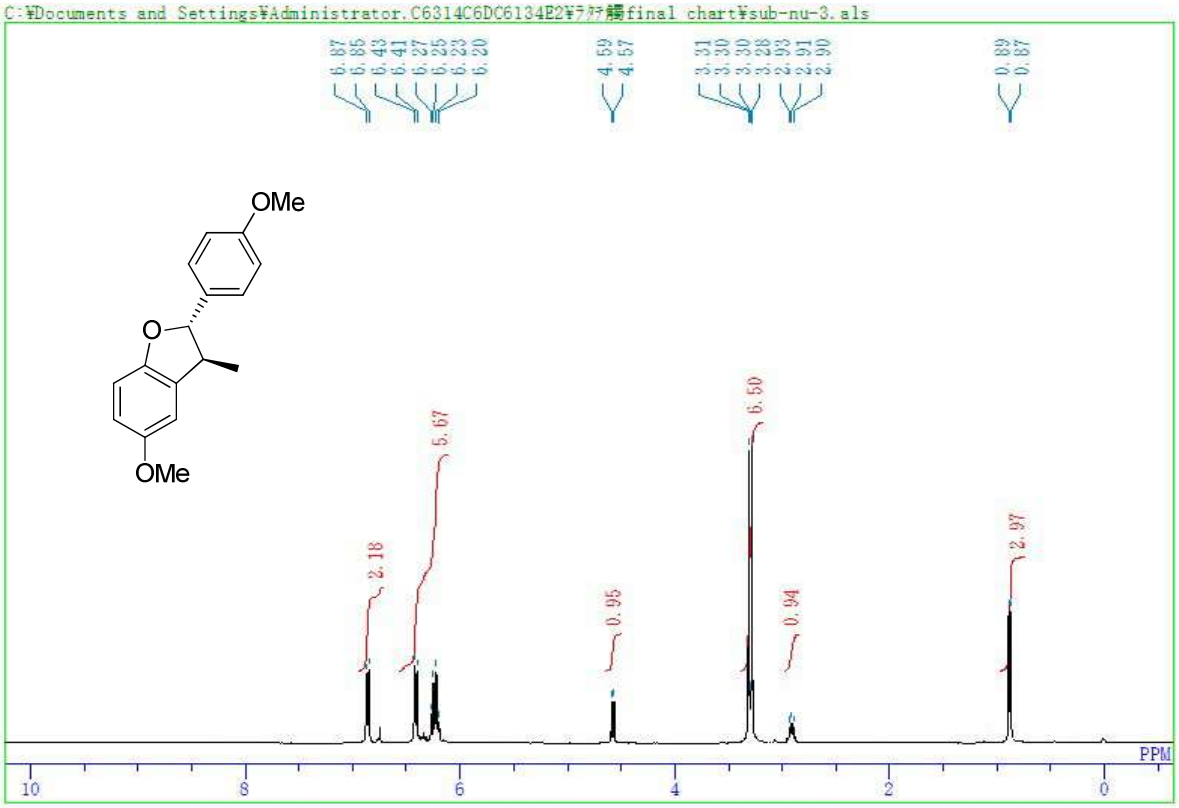
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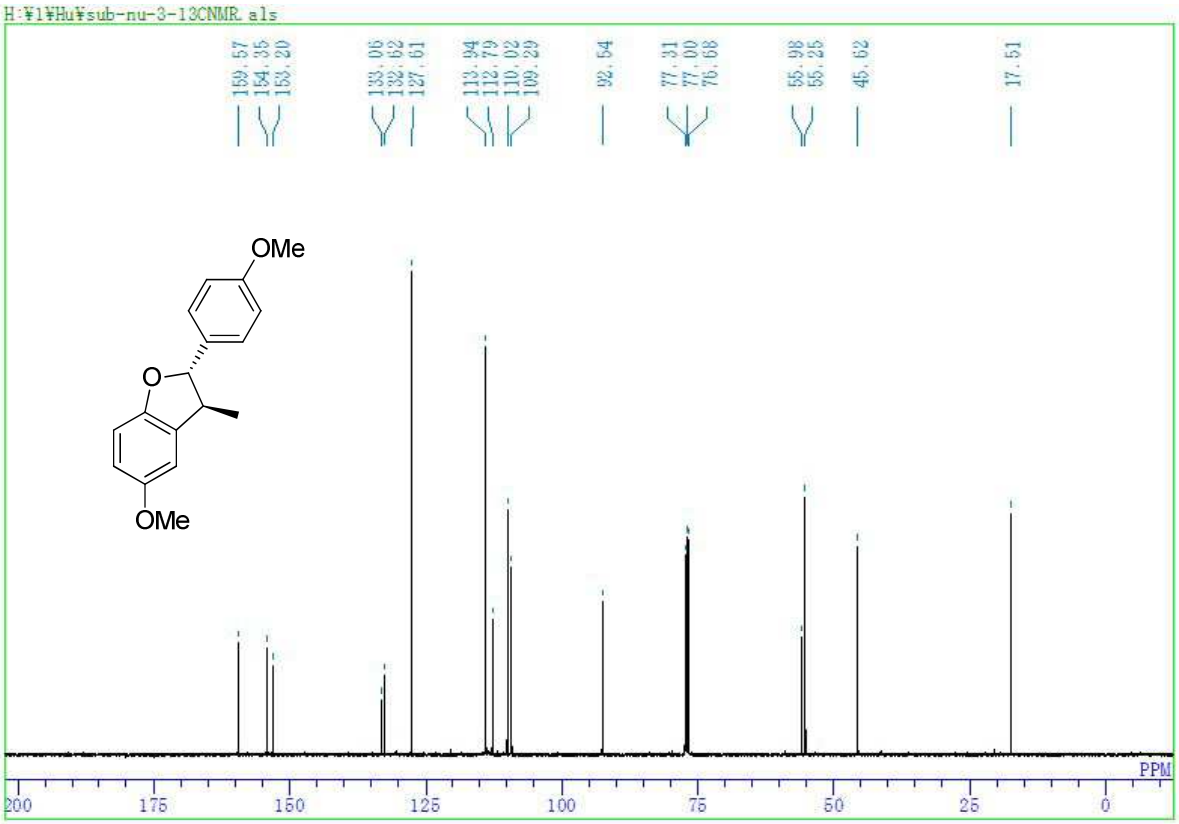
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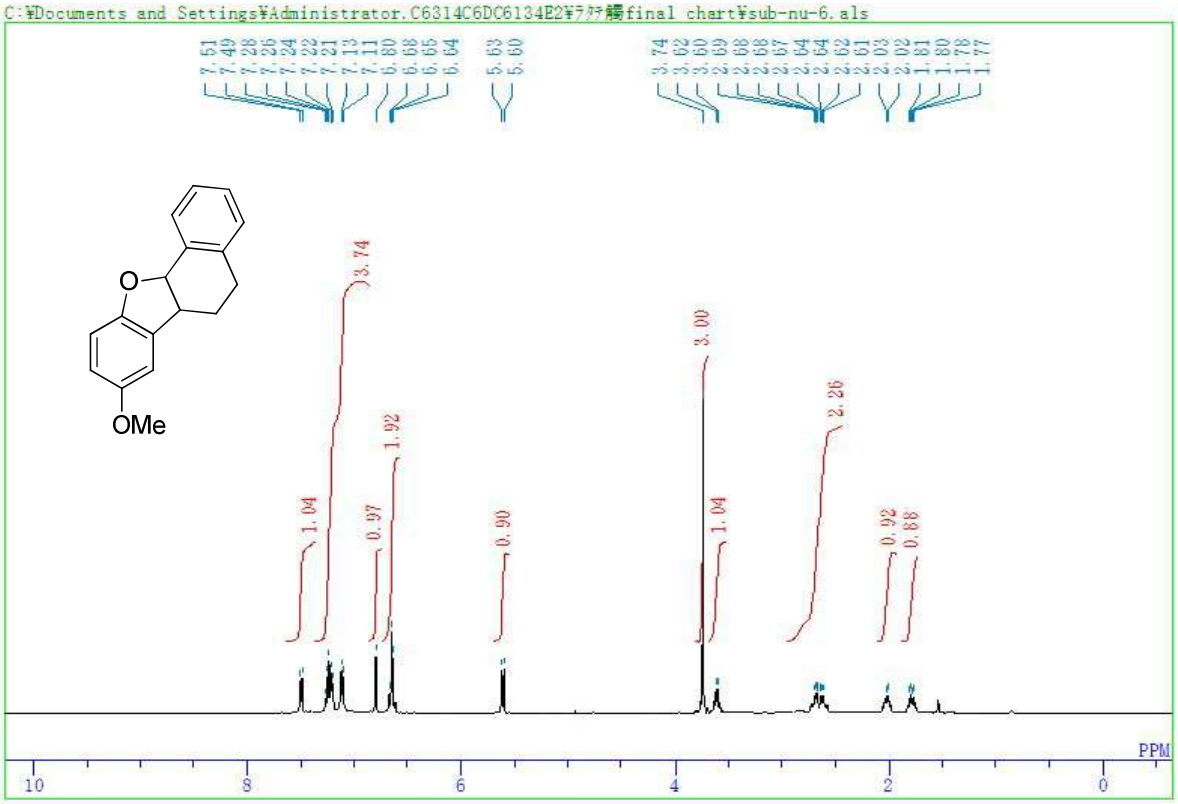
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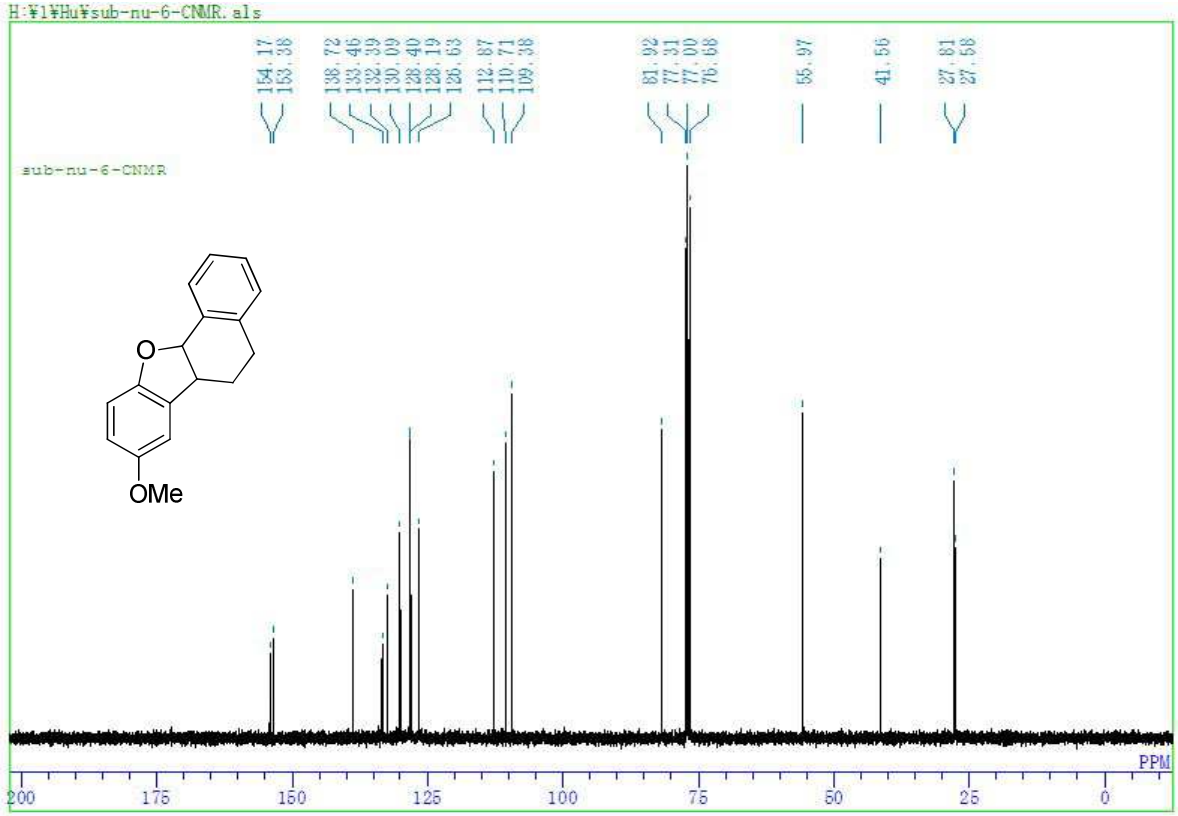
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OMe
PPM
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(3ai)


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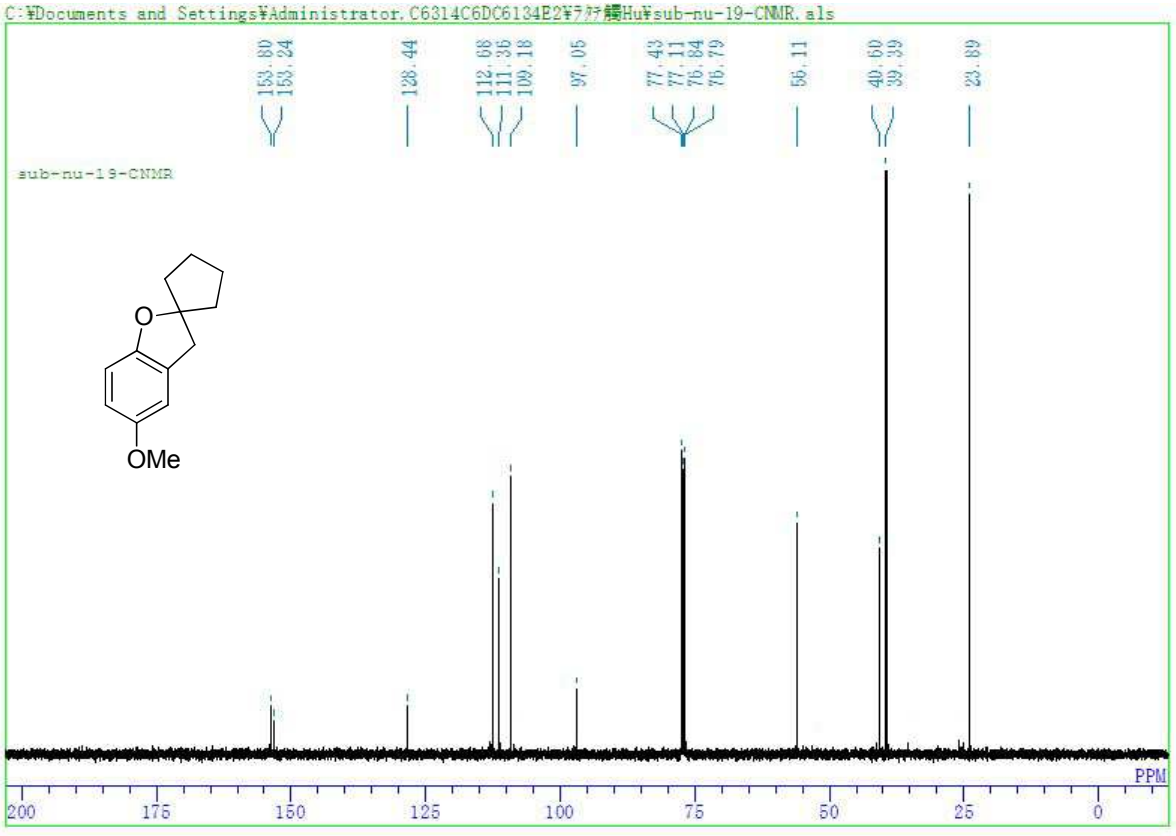
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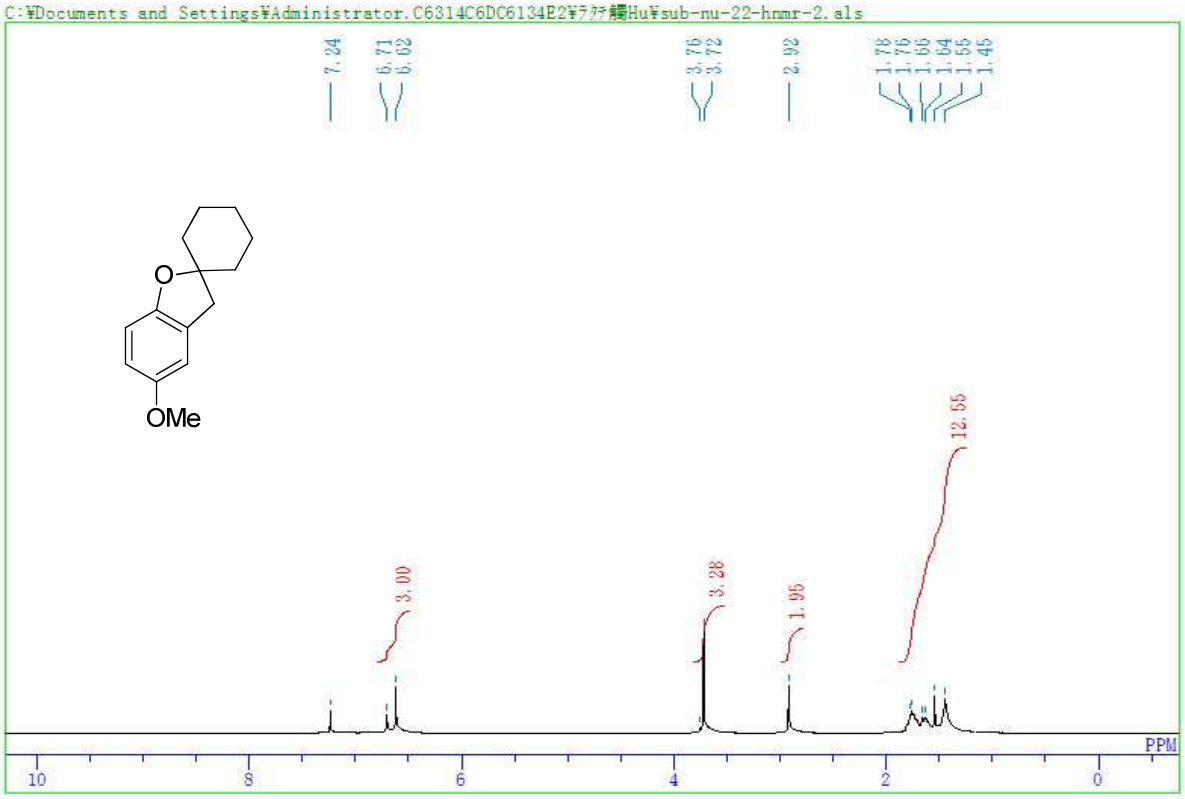
(3aj)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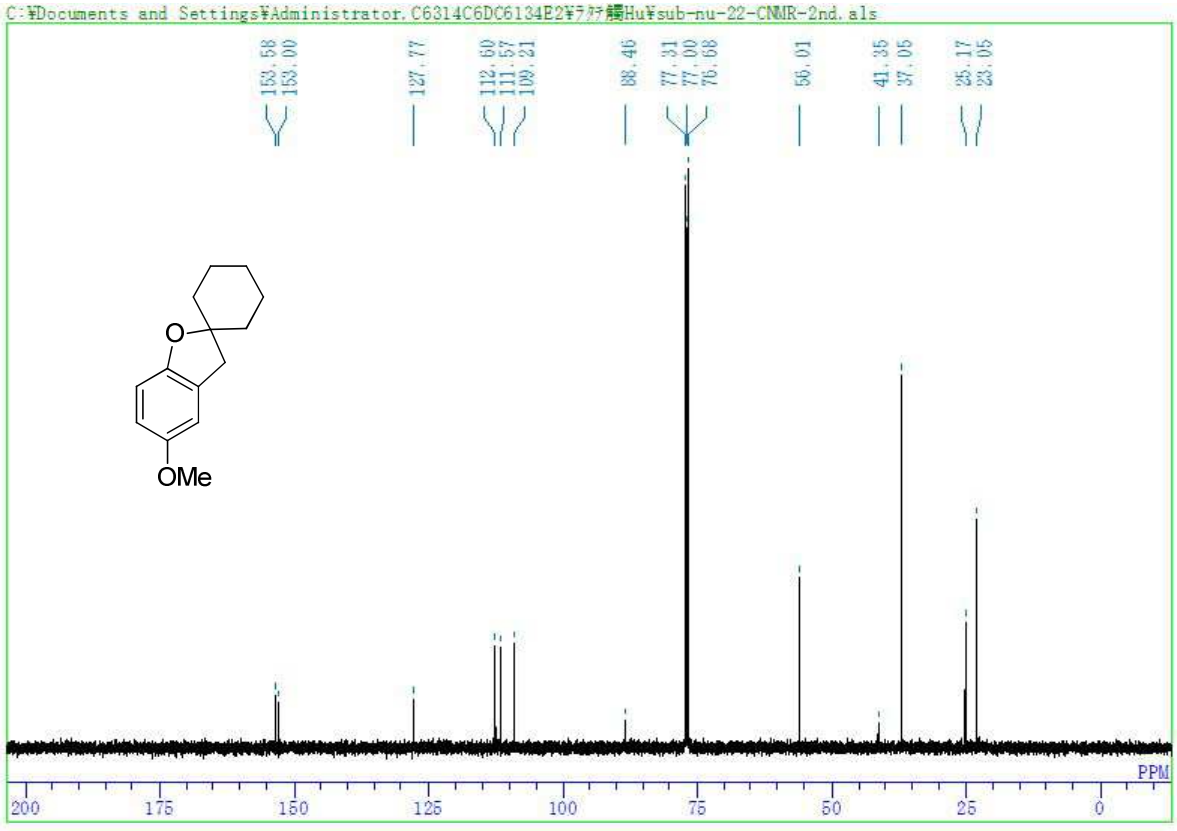
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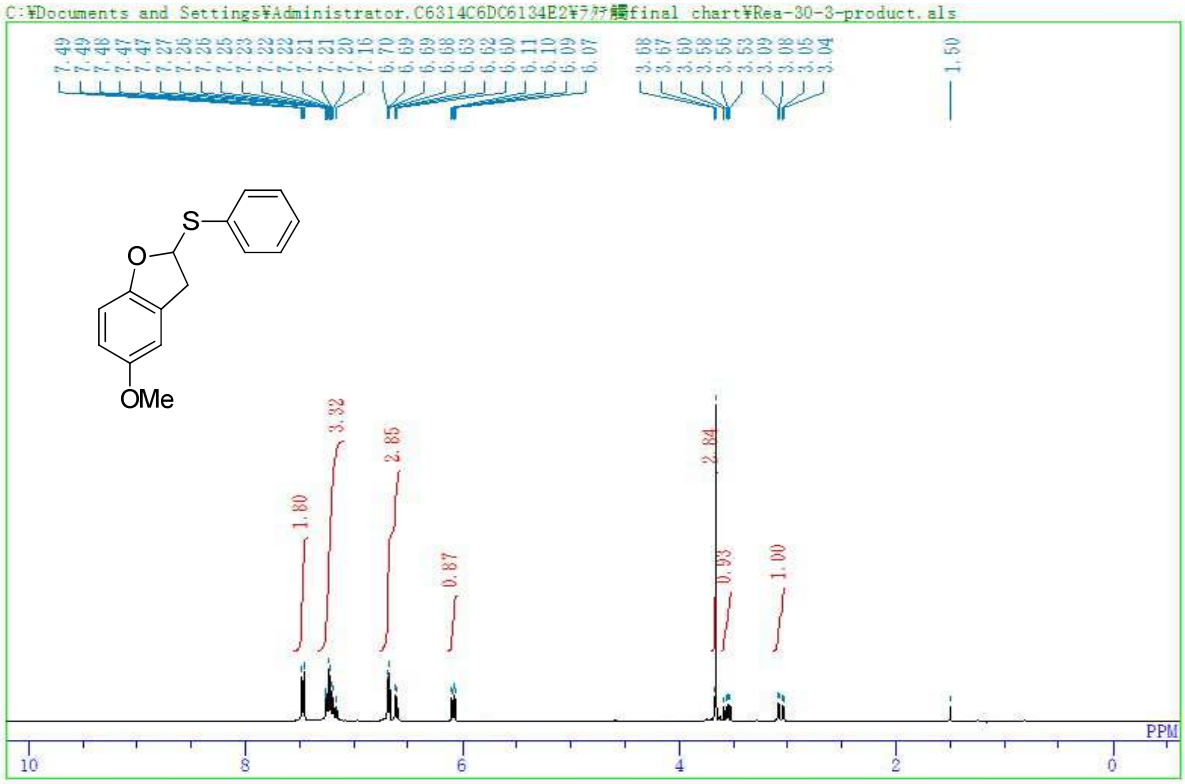
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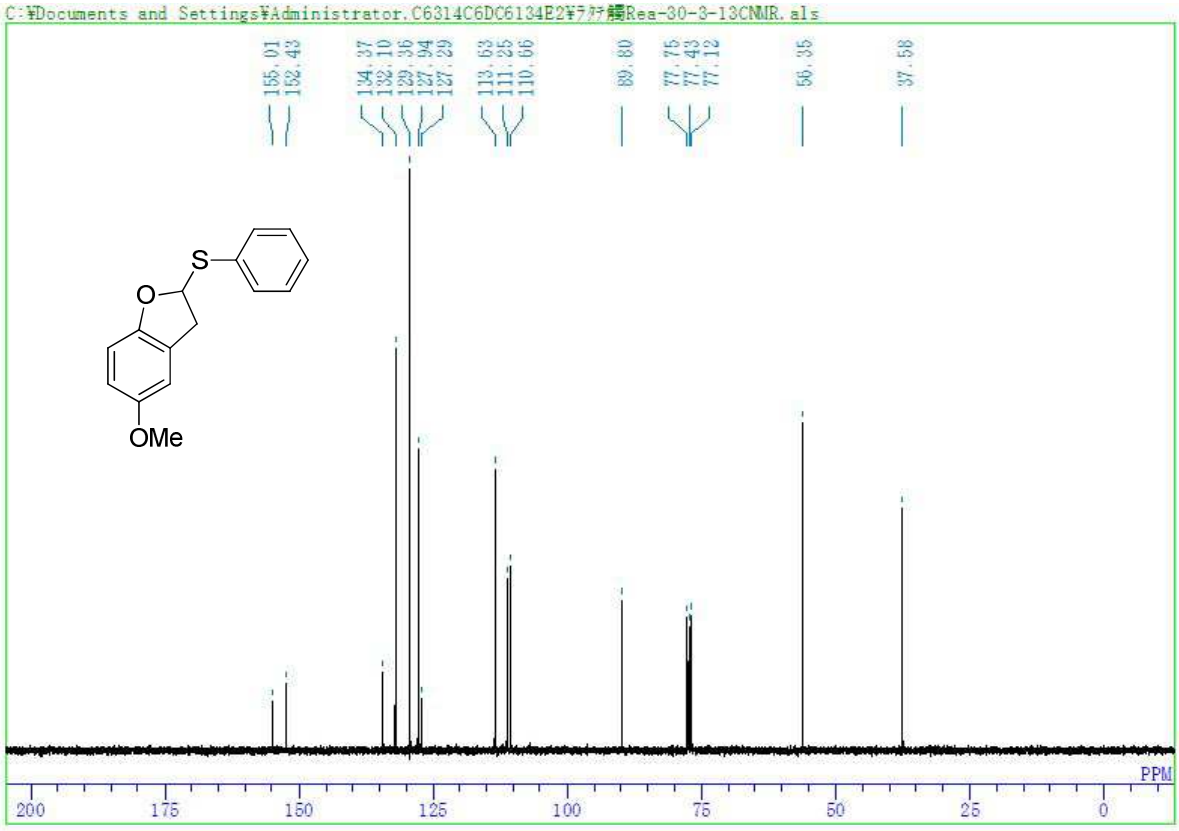
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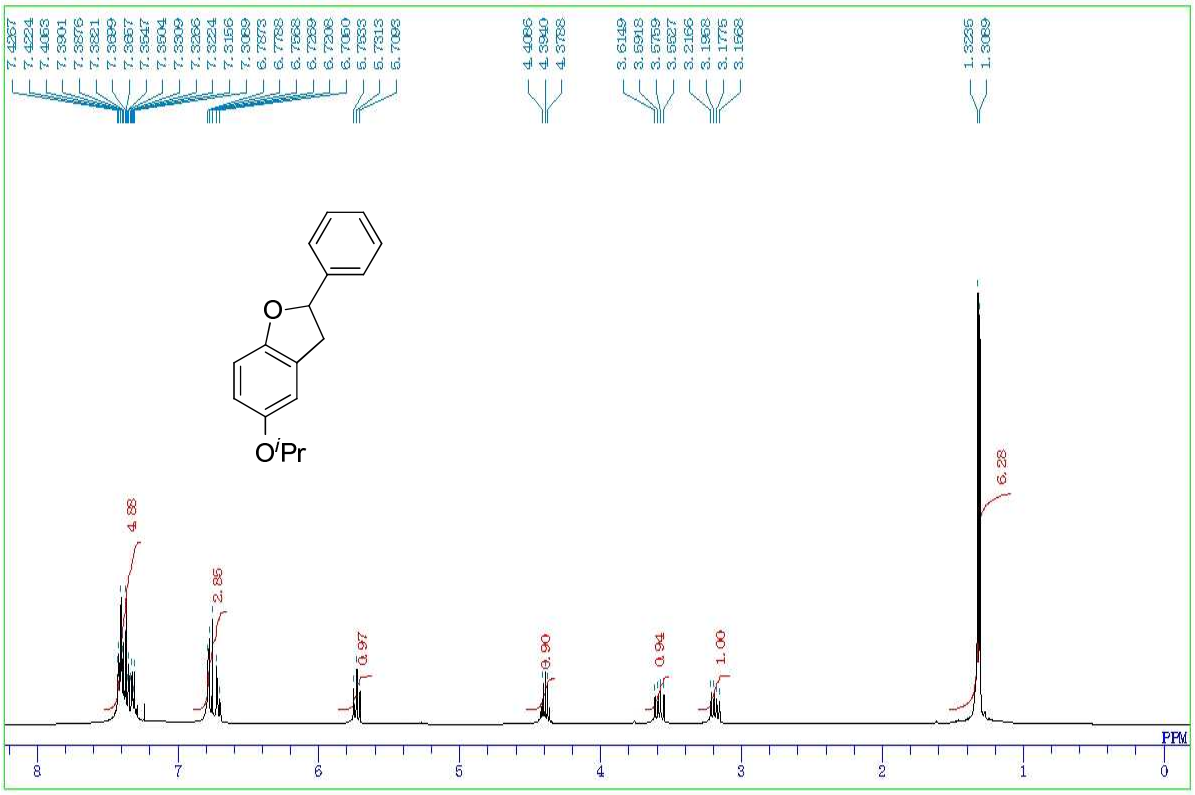
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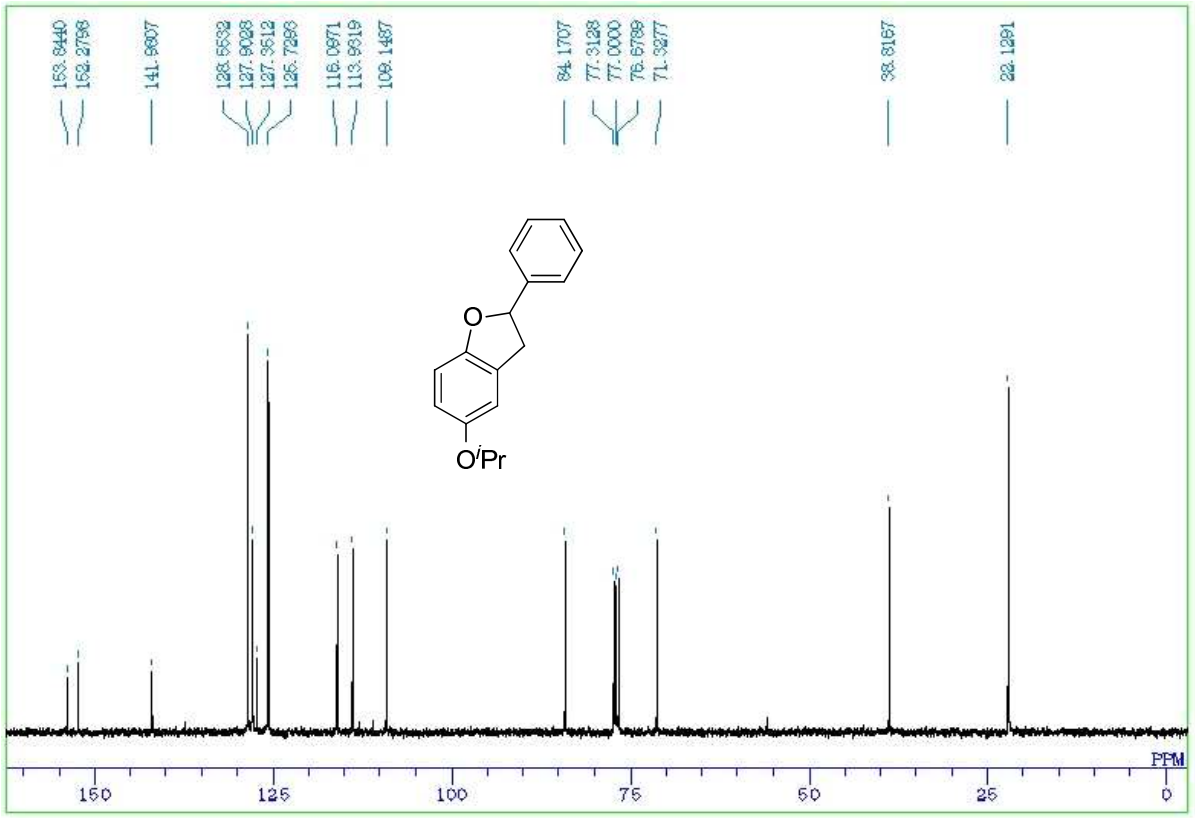
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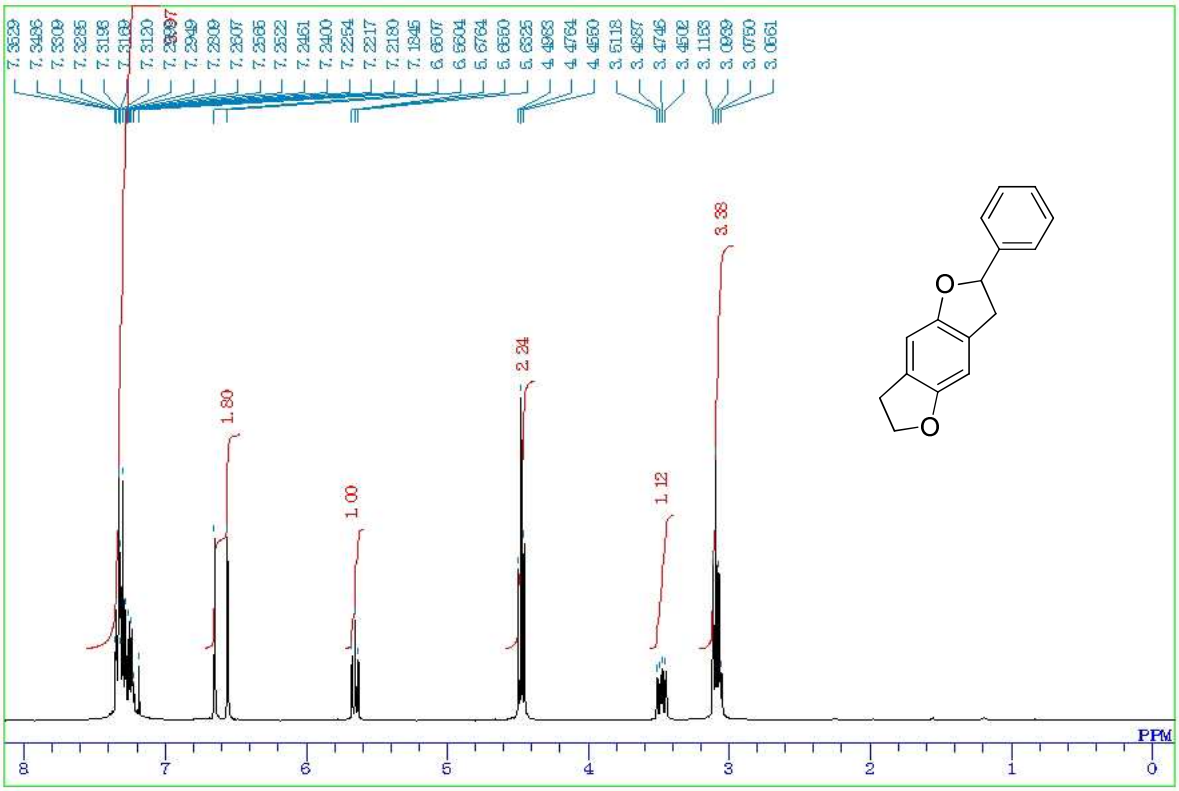
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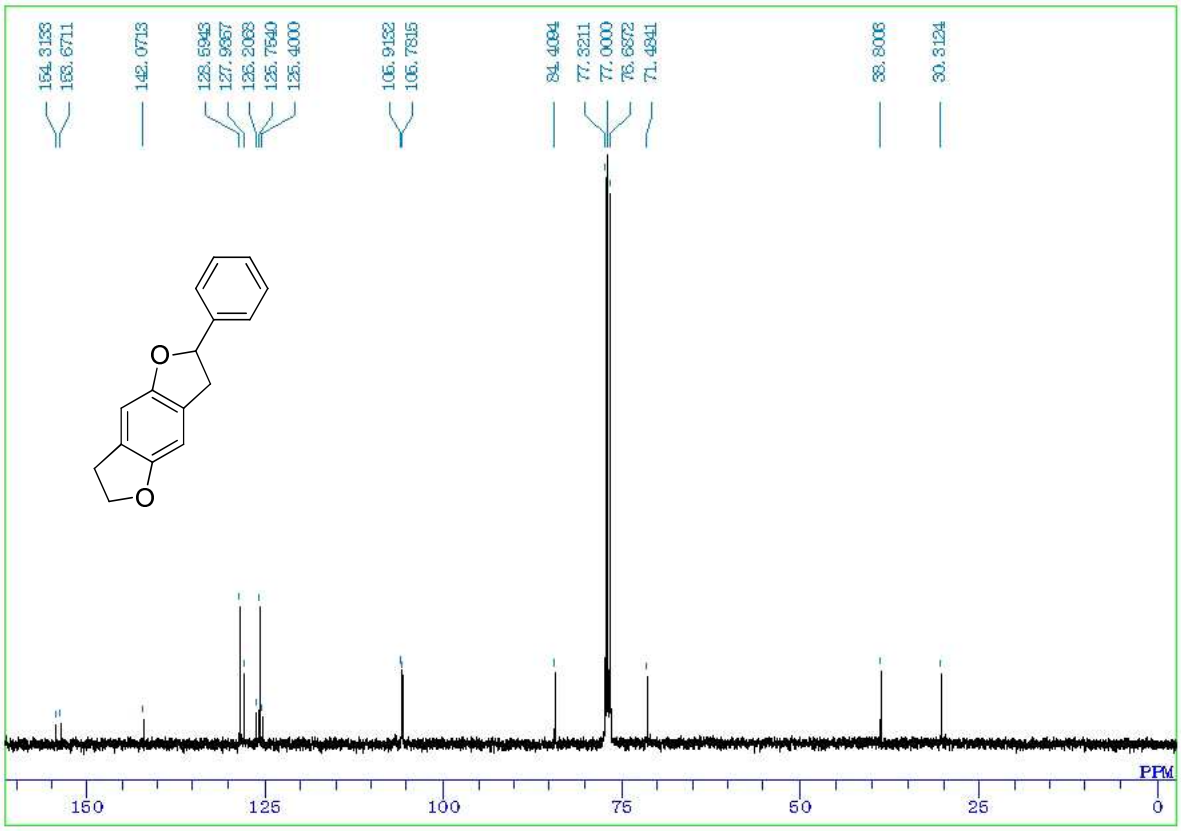
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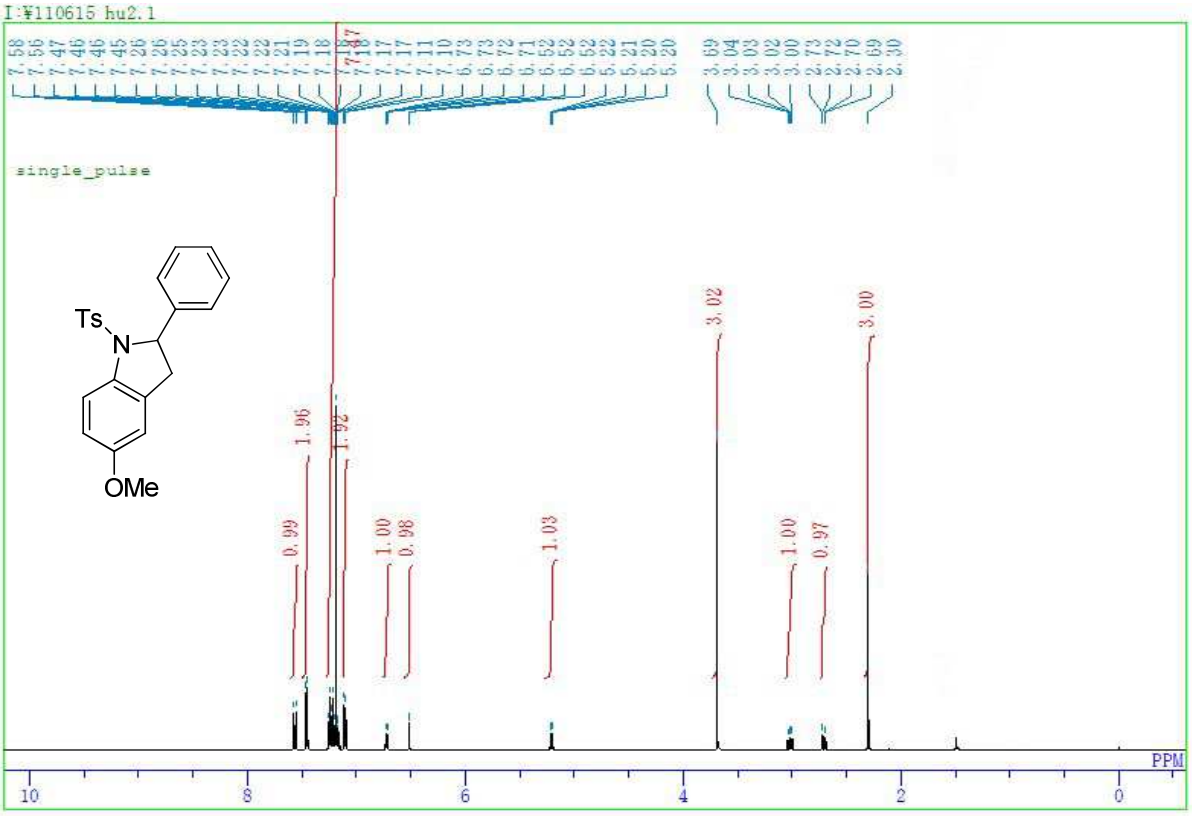
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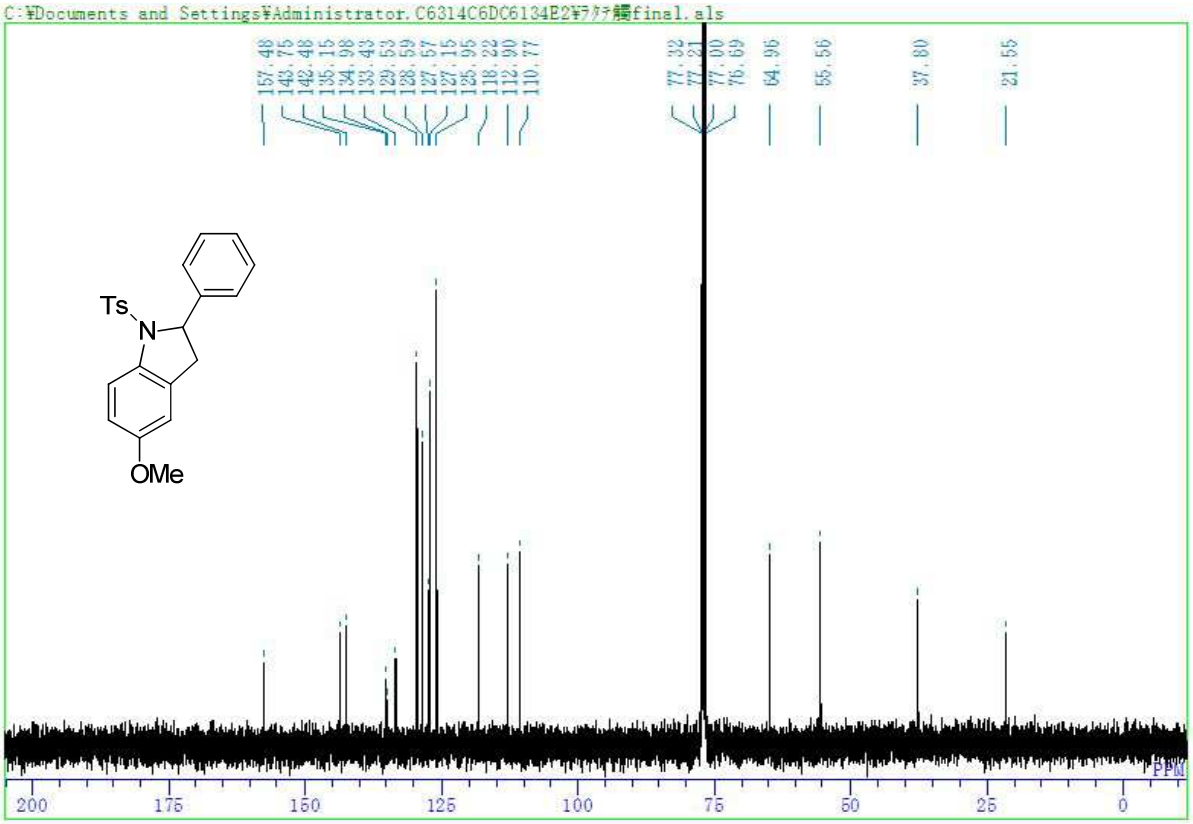
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Ts
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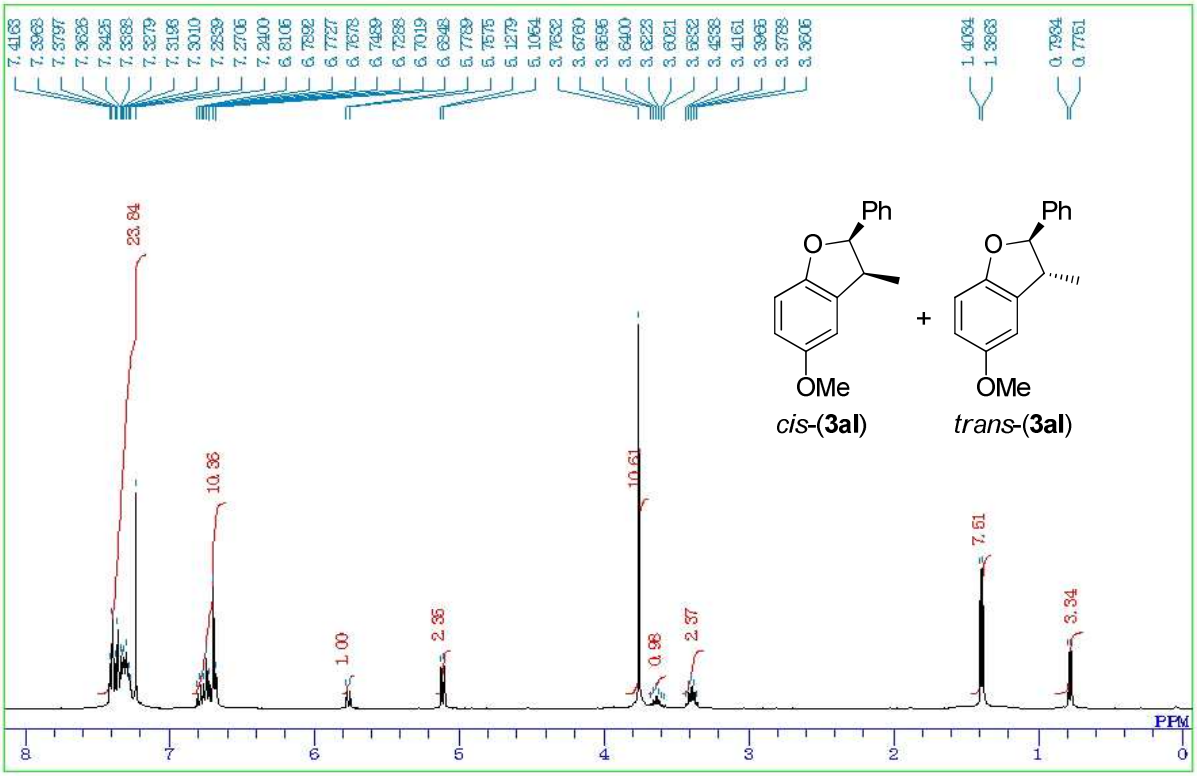
PPM

(3al)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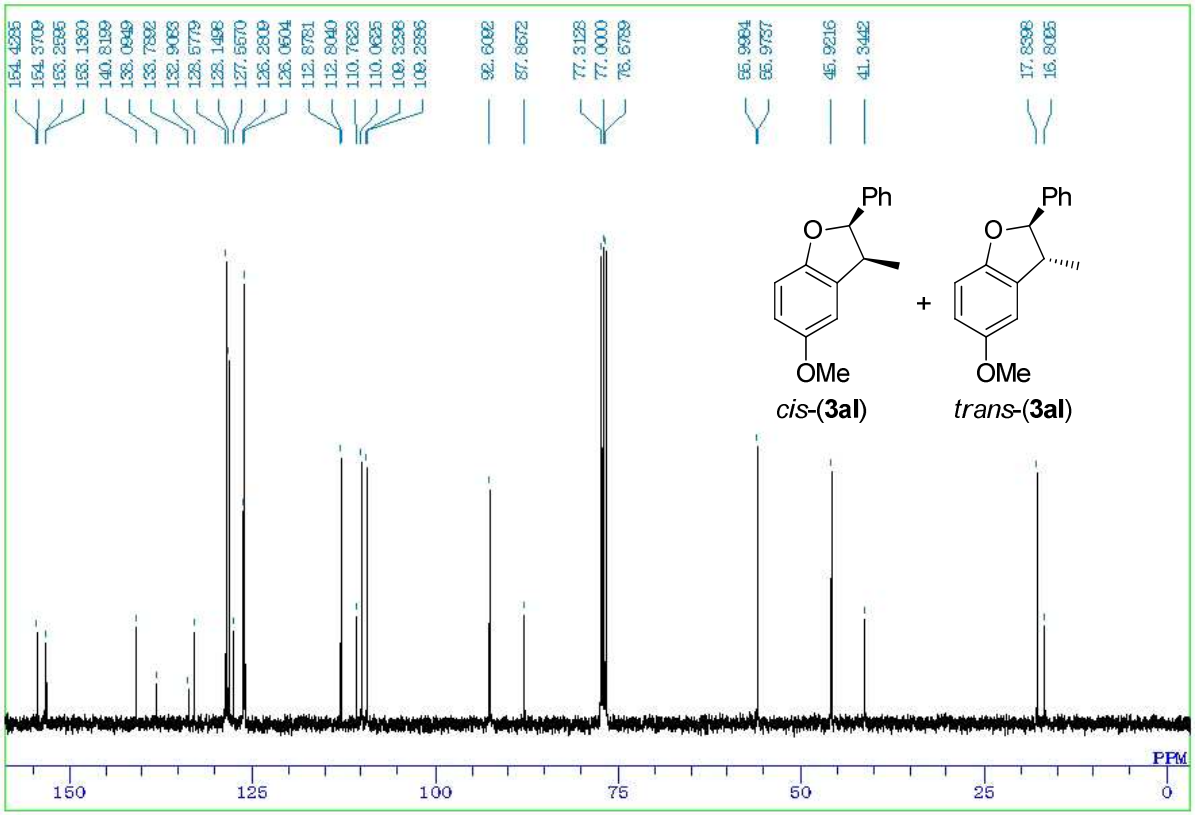
+
Ph
O
OMe
trans-(3al)
PPM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+
Ph
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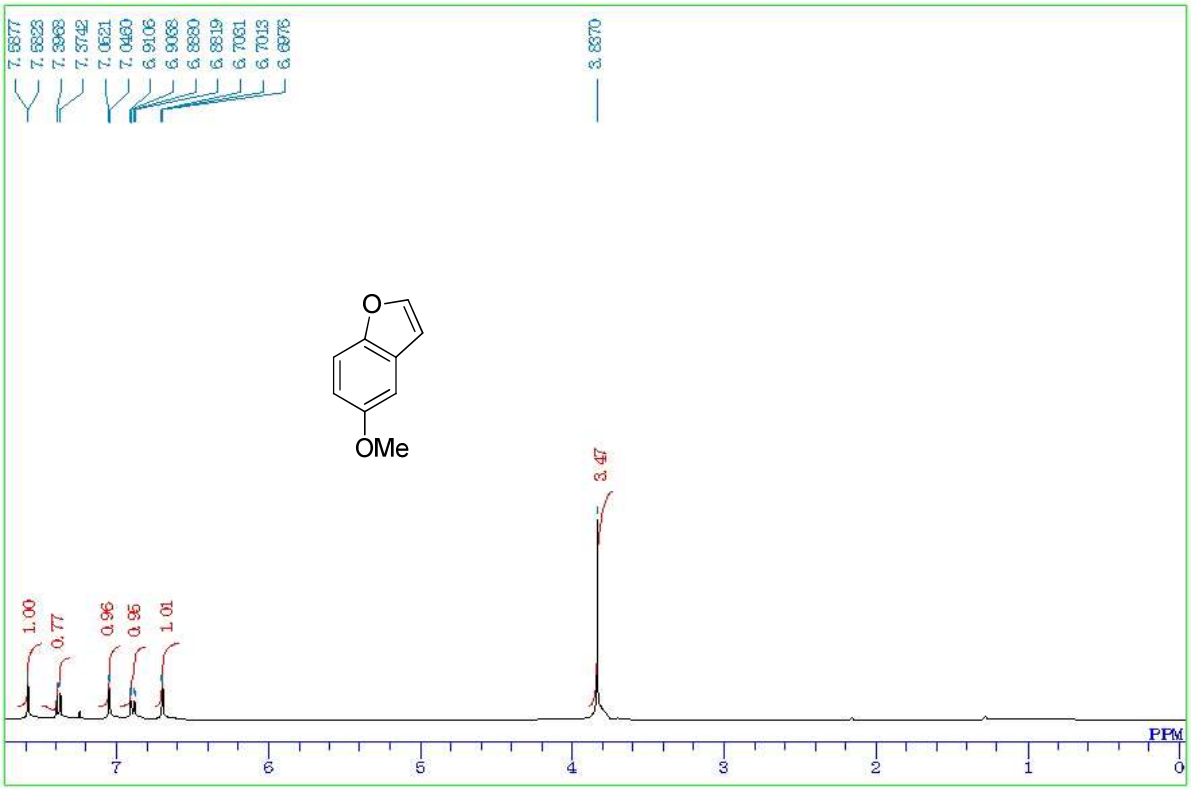
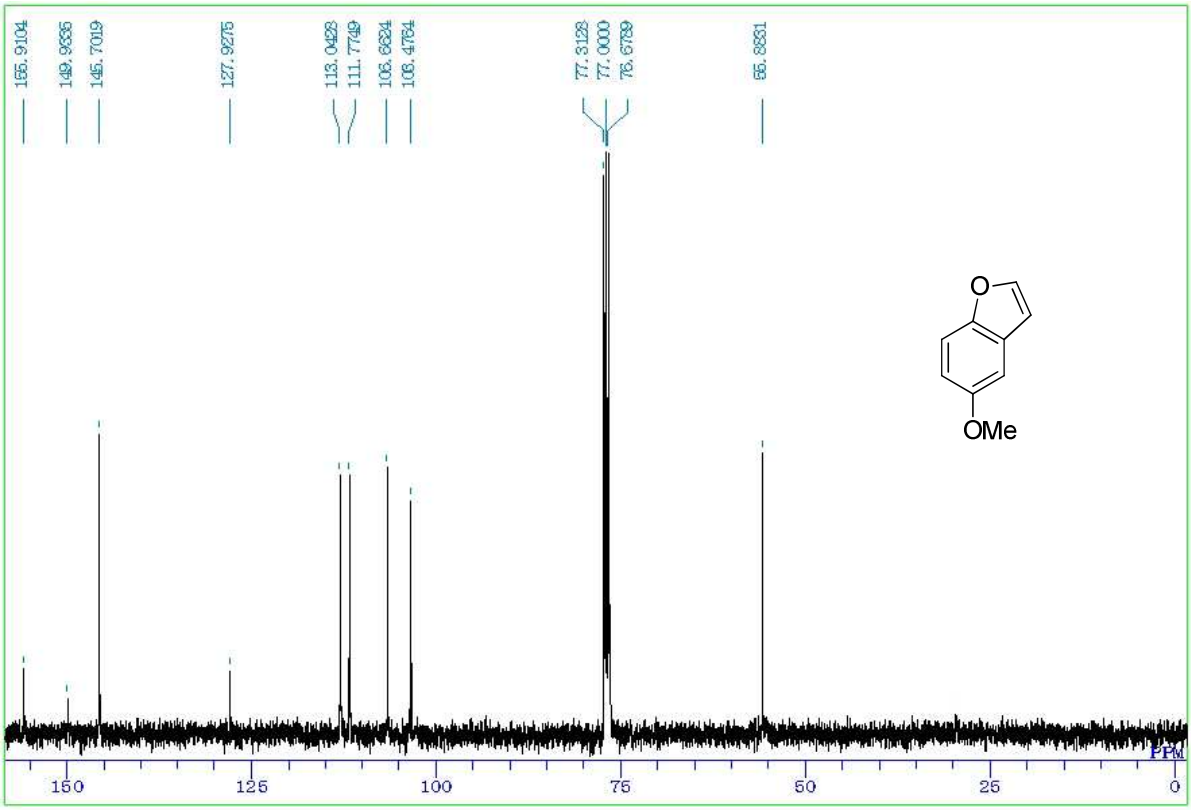
5-Methoxybenzofuran (4)





2. Additional Data for Optimization of [3+2] Coupling Reactions of QMAs

2.1. Screening and Optimization of Stoichiometric Acids

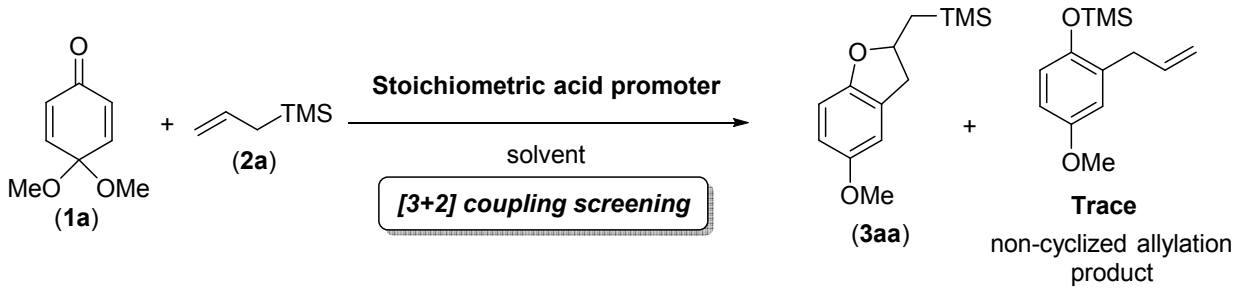


Table S-1. Screening and Optimization of Acid Promoters for Stoichiometric [3+2] Coupling of QMA **1a** with Allyltrimethylsilane **2a**.

Further Screening of Acid Promoters [a]

entry	acid (equiv)	Solvent (ratio)	conc.	Time	yield of **3aa**[b]
1	MK-SF[c]	HFIP/DCM (10/1)	0.1	3 days	68%
2	Al-Clay[c]	HFIP/DCM (10/1)	0.1	1 days	61%
3	HMK-10[c]	HFIP/DCM (10/1)	0.1	3 days	23%
4	Bentonite[c]	HFIP/DCM (10/1)	0.1	2 days	n.d.
5	$H_3[PW_{12}O_{40}]\cdot xH_2O$[d]	HFIP/DCM (10/1)	0.1	3 days	24%
6	$H_3[PMo_{12}O_{40}]$[d]	HFIP/DCM (10/1)	0.1	3 days	30%
7	$(NH_4)_3PMo_{12}O_{40}\cdot xH_2O$[d]	HFIP/DCM (10/1)	0.1	1 day	n.d.

8	TMS Triflimide	HFIP/DCM (10/1)	0.1	1 day	n.d.
9	$B(C_6F_5)_3$	HFIP/DCM (10/1)	0.1	1 day	n.d.

Solvent, Substrate Concentration, Temperature, Reagent and Substrate Stoichiometry

entry	**2a** (equiv.)	$C_6F_5CO_2H$ (equiv.)	solvent (ratio)	temp.	conc.[e]	time	yield of **3aa**[b]
10	1.5	1.0	HFIP/DCM (10/1)	r.t.	0.1 M	1 h	71%
11	2.0	1.0	HFIP/DCM (10/1)	r.t.	0.1 M	1 h	75%
12	3.0	1.0	HFIP/DCM (10/1)	r.t.	0.1 M	1 h	72%
13	2.0	2.0	HFIP/DCM (10/1)	r.t.	0.1 M	1 h	76%
14	2.0	0.5	HFIP/DCM (10/1)	r.t.	0.1 M	1 h	70%
15	**2.0**	**1.0**	**HFIP/DCM (10/1)**	**r.t.**	**0.2 M**	1 h	**86%**
16	2.0	1.0	HFIP/DCM (10/1)	r.t.	0.5 M	1 h	78%
17	**2.0**	**1.0**	**HFIP/DCM (10/1)**	**0 °C**	**0.2 M**	1 h	**90%**
18	2.0	1.0	HFIP/DCM (10/1)	10 °C	0.2 M	1 h	86%

19	2.0	1.0	HFIP/DCM (1/1)	r.t.	0.2 M	1 h	83%
20	2.0	1.0	HFIP/DCM (5/1)	r.t.	0.2 M	1 h	78%
21	2.0	1.0	HFIP/DCM (1/5)	r.t.	0.2 M	1 h	67%
22	2.0	1.0	$MeNO_2$/DCM (10/1)	r.t.	0.2 M	1 h	n.d.
23	2.0	1.0	HFIP/$CHCl_3$ (10/1)	r.t.	0.2 M	1 h	73%
24	2.0	1.0	HFIP/toluene (10/1)	r.t.	0.2 M	1 h	79%
25	2.0	1.0	HFIP/THF (10/1)	r.t.	0.2 M	1 h	64%
26	2.0	1.0	HFIP/DMF (10/1)	r.t.	0.2 M	1 h	43%

[a] Unless otherwise noted, the screenings were carried out with 2 equiv. of acids in HFIP/DCM (10/1 v/v, 0.1 M of QMA **1a**) at room temperature. 5 equiv. of allyltrimethylsilane **2a** was used for the reactions. [b] Isolated yields after purification. Formation of very small amounts of non-cyclized allylation product was observed. [c] 25 mg relative to 1 mL of the solvent. [d] 2 mg relative to 1 mL of the solvent. [e] Concentration of QMA **1a** in solvent.

DCM = dichloromethane. THF = tetrahydrofuran. DMF = *N*,*N*-dimethylformamide.

n.d. = not determined due to < 3% formation of the product.

2.2 Screening and Optimization for Catalytic [3+2] Coupling Reaction of 1a and 2a.

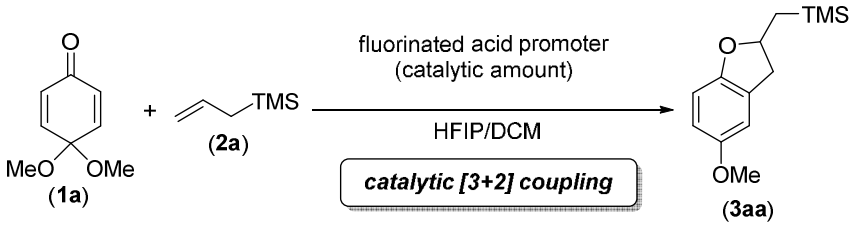


Table S-2. Screening and Optimization for Catalytic [3+2] Coupling Reaction of QMA **1a** with Allyltrimethylsilane **2a** in the Presence of Fluorinated Acid Catalyst.[a]

Catalyst Loading, Substrate Stoichiometry, Solvent Ratio, and Temperature						
entry	loading of acid catalyst **h**	**2a** (equiv.) [b]	temp.	time	HFIP/DCM ratio	yield of **3aa**[c]
1	1 mol%	1.2	r.t.	1 h	1/1	45%
2	2 mol%	1.2	r.t.	1 h	1/1	24%
3	5 mol%	1.2	r.t.	1 h	1/1	15%
4	5 mol%	1.0	r.t.	1 h	1/1	27%
5	5 mol%	1.2	r.t.	1 h	5/1	18%
6	5 mol%	1.2	r.t.	1 h	2/1	41%
7	5 mol%	1.2	r.t.	1 h	1/2	61%

8	5 mol%	1.2	r.t.	1 h	1/5	72%
9[d]	**5 mol%**	**1.2**	**0 °C**	3 h	**1/1**	**84%**

[a] Unless otherwise noted, reactions were examined in HFIP/DCM (1/1 v/v, 0.2 M) at room temperature for 1 hour. [b] Relative to QMA **1a**. [c] Isolated yields after purification. Formation of very small amounts of non-cyclized allylation product was observed. [d] Performed at 0 °C.