Supporting Information for:

Carbonylative Cycloaddition Between two Different Alkenes Enabled by Reactive Directing Group: Expedite Construction of Bridged Polycyclic Skeletons

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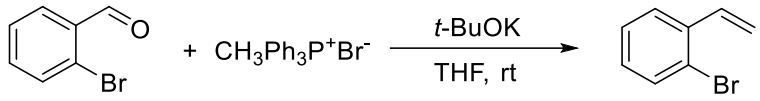
CONTENTS

1. General experiment details and materials

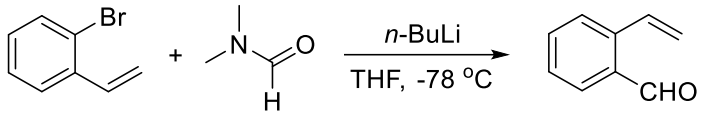
Experimental: All non-aqueous reactions and manipulations were using standard Schlenk techniques. All solvents before used were dried and degassed by standard methods and stored under nitrogen atmosphere. All reactions were monitored by TLC with silica gel-coated plates. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker 400 or 500 spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (*J*) were reported in Hz and referred to apparent peak multiplications. All the high-resolution mass spectra (HRMS) were carried out using Bruker Micro TOF-QII mass (ESI). Gas chromatographies (GC) analyses were performed on Agilent 7890B instrument with Hp-5 column. GC-MS analysis was performed with Agilent 7890B/5975B GC-MS system. Melting points were determined using a WRS-2A of shanghai INESA Physico optiacal instrument Co.,Ltd and are uncorrected. Infrared (IR) spectra were recorded on a Nicolet 6700 Fourier transform infrared spectrophotometer. All chemicals were purchased from commercial sources.

2. Preparation of *o*-alkenyl aryl aldehydes

2.1 Method A[1]:

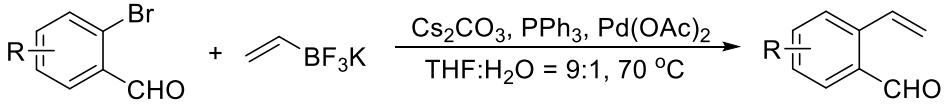


In a dry flask under N_2 atmosphere, *t*-BuOK (8.40 g, 75.0 mmol, 1.5 equiv.) was added to a suspension of methyltriphenylphosphonium bromide (23.2 g, 65.0 mmol, 1.3 equiv.) in dry THF (90 mL) at 0 ℃ and then the mixture was stirred for 30 minutes. 2-Bromobenzaldehyde (9.25 g, 50.0 mmol) was added slowly and the reaction was stirred for 5 hours at room temperature. After filtration over Celite, petroleum ether was added to the filtrate and the suspension was filtered again over Celite. The solvent was evaporated under reduced pressure to give the crude material. Purification through column chromatography (PE/EA = 50:1) gave 2-bromostyrene (8.24 g, 90% yield) as a colorless liquid.



A 200 mL round-bottom flask containing 2-bromostyrene (8.24 g, 45 mmol) in THF (80 mL) was purged with N_2 atomosphere and cooled to -78 °C in an ethyl acetate / liquid nitrogen bath. *n*-BuLi (2.5 M in hexane, 21.6 mL, 54 mmol, 1.2 equiv.) was added dropwise to the solution and then the mixture was stirred at -78 °C for 1 hour. A solution of DMF (5.22 mL, 67.5 mmol, 1.5 equiv.) in THF (5 mL) was added and then the mixture was warmed slowly to room temperature and stirred overnight. The reaction was quenched (saturated NH_4Cl) and then the aqueous phase was extracted with diethyl ether and the organic layers were dried over Na_2SO_4. The solvent was evaporated under reduced pressure to yield a crude product. Column chromatography (PE/EA = 10:1) provided *o*-alkenyl benzaldehyde (4.16 g, 70% yield). The spectral data matched those reported previously.

2.2 Method B[2]:

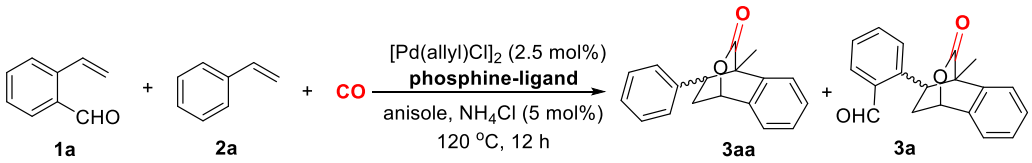


To a solution of the corresponding substituted *o*-bromobenzaldehyde (10.0 mmol, 1.0 equiv.) in THF/H_2O (9:1, 0.1 M), were successively added: $Pd(OAc)_2$ (112 mg, 0.5 mmol, 0.05 equiv.), PPh_3 (262 mg, 1.0 mmol, 0.1 equiv.), the corresponding potassium vinyltrifluoroborate (12 mmol, 1.2 equiv.) and Cs_2CO_3 (9.1 g, 30 mmol, 3.0 equiv.). After stirring for 5 minutes at room temperature in a sealed tube, the resulting solution was stirred at 70 ℃ for 4 hours. The mixture was cooled to room temperature, H_2O was added, followed by extraction with ethyl acetate. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The crude product was purified by flash chromatography employing mixtures of *n*-hexane/ethyl acetate as eluents. The spectral data matched those reported previously.

3. Optimization of the reaction conditions

In the glove box, a mixture of **1a** (66.0 mg, 0.5 mmol), **2a** (62.4 mg, 0.6 mmol), NH_4Cl (1.3 mg, 0.025 mmol, 5 mol%), [Pd] (0.025 mmol, 5 mol%), ligand (0.0275 mmol, 5.5 mol%) and solvent (1.0 mL) were added to a dry glass vessel. The glass vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (20 atm). The reaction mixture was stirred at 120 ^oC for 12 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. The yield is based on **1a** using *n*-tetradecane as the internal standard, and the ratio (*endo*-**3**/*exo*-**3**) of the crude reaction mixture was determined by ^1H NMR, GC-MS and GC analysis.

Table 1. Screening of Ligands[a]



Entry	Ligand	Yield (**3aa**)(%)	*endo*/*exo* **3aa**	Yield (**3a**)(%)
1	DPPM	0	-	0
2	DPPE	0	-	0
3	DPPP	0	-	0
4	DPPB	0	-	0
5	DPPPe	0	-	0
6	DPPH	0	-	0
7	DPPF	0	-	0
8	RuPhos	85	>20:1	<5
9	DPEPhos	Trace	-	0
10	MePhos	38	>20:1	<5
11	PCy_3	23	>20:1	<5
12	*i*-$PrPPh_2$	0	0	
13	DavePhos	64	>20:1	<5
14	XPhos	44	>20:1	<5
15	L1	0	-	-
16	L2	0	-	-
17	none	0	-	0

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), $[Pd(allyl)Cl]_2$ (0.0125 mmol, 2.5 mol%), ligand (0.0275 mmol, 5.5 mol%), NH_4Cl (0.025 mmol, 5 mol%), CO (20 atm), anisole (1.0 mL), 120 ^oC, 12 hours.

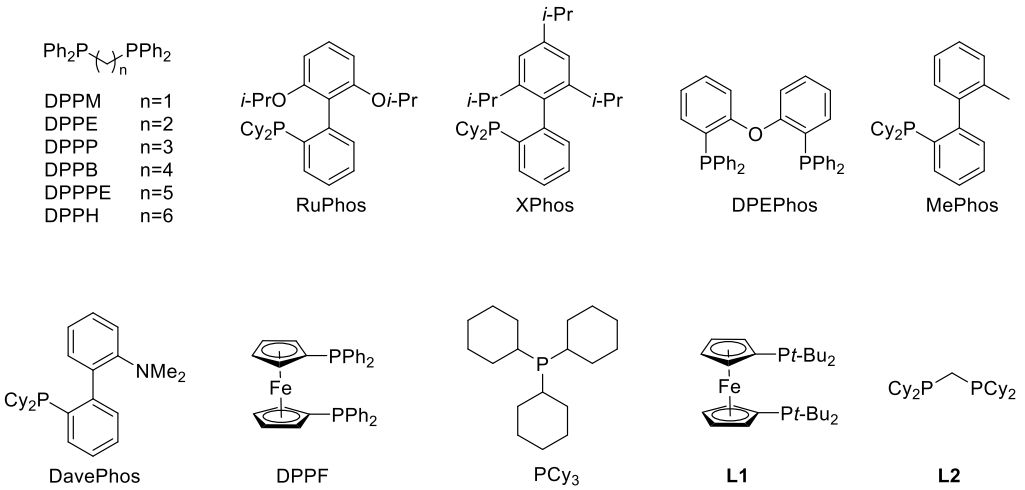
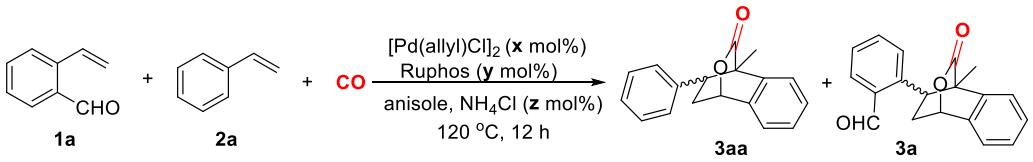


Figure S1. The structure of ligands

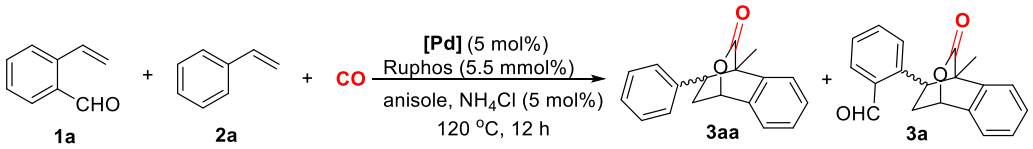
Table 2. Screening the loadings of catalyst and NH_4Cl [a]



Entry	$[Pd(allyl)Cl]_2$ **x** mol %	RuPhos **y** mol%	Yield (**3aa**) (%)	*endo*/*exo* **3aa**	Yield (**3a**) (%)
1	2.5	5.5	85	>20:1	<5
2	0	0	0	-	-
3	0.5	1.1	52	>20:1	<5
4[b]	2.5	5.5	69	>20:1	<5

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), $[Pd(allyl)Cl]_2$ (x mol%), RuPhos (y mol%), NH_4Cl (0.025 mmol, 5 mol%), CO (20 atm), anisole (1.0 mL), 120 °C, 12 hours. [b] NH_4Cl (0 mol%)

Table 3. Screening of catalyst precursors[a]

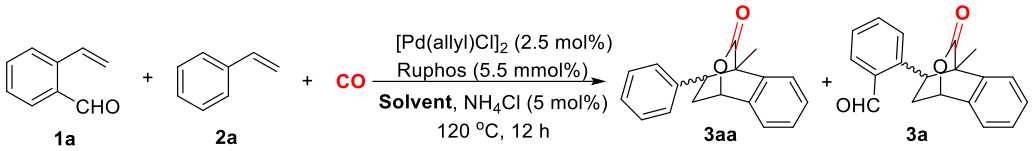


Entry	[Pd]	Yield (**3aa**)(%)	*endo*/*exo* **3aa**	Yield (**3a**)(%)
1	$PdCl_2$	48	>20:1	<5
2	$PdBr_2$	trace	-	0
3	PdI_2	0	-	0
4	$Pd(cod)Cl_2$	0	-	0
5	$Pd(MeCN)_2Cl_2$	trace	-	0
6[b]	$Pd(PPh_3)_4$	0	-	0
7[b]	$Pd(t\text{-}Bu_3P)_2$	0	-	0

8	$Pd(OAc)_2$	35	-	0
9	$Pd_2(dba)_3$	0	-	0
10	$Pd(cod)Br_2$	-	-	0
11	$[Pd(allyl)Cl]_2$	85	>20:1	<5
12[b]	$Pd(Xantphos)(CH_3CN)_2OTf_2$	trace	-	0
13	$Pd(TFA)_2$	0	-	0

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), [Pd] (0.025 mmol, 5 mol%), RuPhos (0.0275 mmol, 5.5 mol%), NH_4Cl (0.025 mmol, 5 mol%), CO (20 atm), anisole (1.0 mL), 120 °C, 12 hours. [b][Pd] (5 mol%), NH_4Cl (0.025 mmol, 5 mol%), CO (20 atm), anisole (1.0 mL), 120 °C, 12 hours.

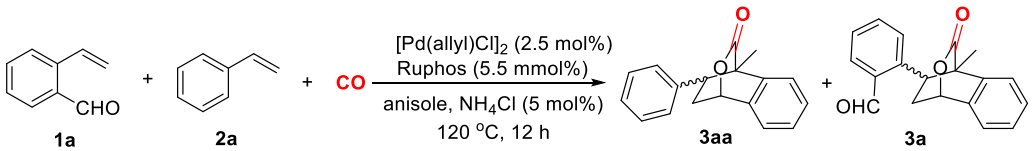
Table 4. Screening of solvents[a]



Entry	solvent	Yield (**3aa**)(%)	*endo*/*exo* **3aa**	Yield (**3a**)(%)
1	CH_3CN	30	>20:1	<5
2	MTBE	0	-	0
3	NMP	76	>20:1	<5
4	DME	75	>20:1	<5
5	anisole	85	>20:1	<5
6	1,4-dioxane	48	>20:1	<5

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), $[Pd(allyl)Cl]_2$ (0.0125 mmol, 2.5 mol%), RuPhos (0.0275 mmol, 5.5 mol%), NH_4Cl (0.025 mmol, 5 mol%), CO (20 atm), solvent (1.0 mL), 120 °C, 12 h.

Table 5. Screening of pressures of CO[a]

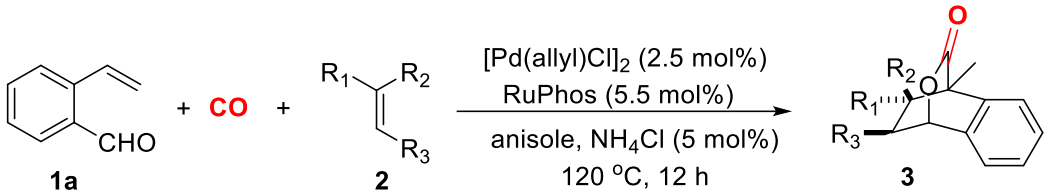


Entry	CO (atm)	Yield (**3aa**)(%)	*endo*/*exo* ***3aa***	Yield (**3a**)(%)
1	15	55	>20:1	<5
2	10	47	>20:1	<5
3	5	32	>20:1	<5
4	20	85	>20:1	<5

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), $[Pd(allyl)Cl]_2$ (0.0125 mmol, 2.5 mol%), RuPhos (0.0275 mmol, 5.5 mol%), NH_4Cl (0.025 mmol, 5 mol%), CO (x atm), anisole (1.0 mL), 120 ^oC, 12 hours.

4. General procedure for hydrocarbonylative lactonization and cycloaddition

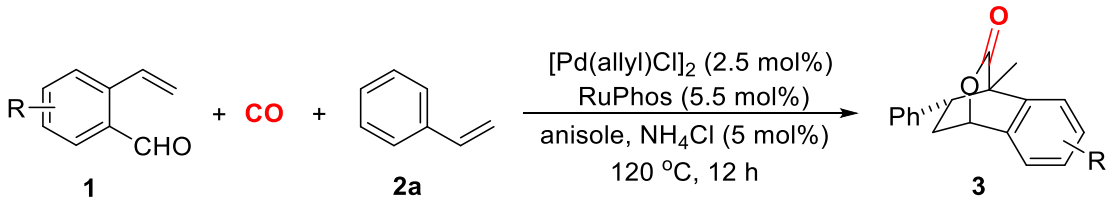
4.2 General procedure A:



1a **2** **3**

In the glove box, a mixture of 2-vinylbenzaldehyde **1a** (0.5 mmol), alkene **2** (0.6 mmol), NH_4Cl (1.3 mg, 0.025 mmol, 5 mol%), $[Pd(allyl)Cl]_2$ (4.6 mg, 0.0125 mmol, 2.5 mol%), RuPhos (12.8 mg, 0.028 mmol, 5.5 mol%) and anisole (1.0 mL) were added to a dry glass vessel. The glass vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (20 atm). The reaction mixture was stirred at 120 °C for 12 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. The ratio (***endo*/*exo***) of the crude reaction mixture was determined by ^1H NMR analysis, GC-MS, and GC analysis. The solvent was evaporated under reduced pressure and the resulting residue was purified by column chromatography on silica gel to afford the product **3**.

4.1 General procedure B:

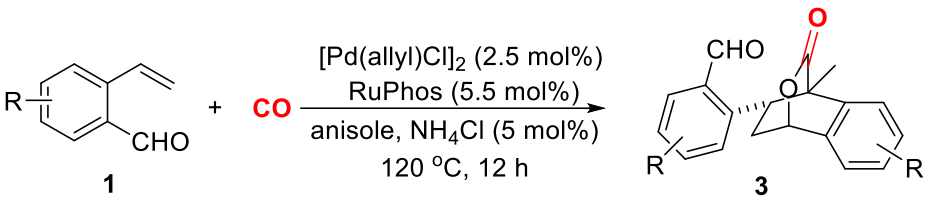


1 **2a** **3**

In the glove box, a mixture of **1** (0.5 mmol), styrene **2a** (0.6 mmol), NH_4Cl (1.3 mg, 0.025 mmol, 5 mol%), $[Pd(allyl)Cl]_2$ (4.6 mg, 0.0125 mmol, 2.5 mol%), RuPhos (12.8 mg, 0.028 mmol, 5.5 mol%) and anisole (1.0 mL) were added to a dry glass vessel. The glass vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (20 atm). The reaction mixture was stirred at 120 °C for 12 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. The ratio

(***endo*/*exo***) of the crude reaction mixture was determined by ^{1}H NMR analysis, GC-MS,and GC analysis. The solvent was evaporated under reduced pressure and the resulting residue was purified by column chromatography on silica gel to afford the product **3**.

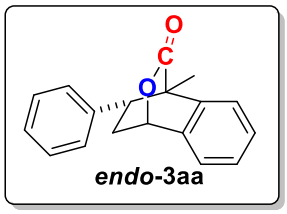
4.3 General procedure C:



In the glove box, a mixture of **1** (0.8 mmol), NH_4Cl (1.0 mg, 0.02 mmol, 5 mol%), $[Pd(allyl)Cl]_2$ (3.6 mg, 0.01 mmol, 2.5 mol%), RuPhos (10.3 mg, 0.022 mmol, 5.5 mol%) and anisole (1.0 mL) were added to a dry glass vessel. The glass vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (20 atm). The reaction mixture was stirred at 120 ^{o}C for 12 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. The ratio (***endo*/*exo***) of the crude reaction mixture was determined by ^{1}H NMR analysis, GC-MS,and GC analysis.. Then the solvent was evaporated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (PE/EA = 3:1) to afford the product **3**.

5.1 Spectral data of products

4-methyl-3-phenyl-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one



(*endo*-3aa): The title compound was prepared according to **General procedure A** and purified by column chromatography to give a light white solid (**3aa**: 111 mg, 84% yield), dr > 20:1. M.p.: 192-194 °C. IR (neat) ν(cm^{-1}): 3007, 2975, 2934, 2876, 1744. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.38 (s, 3H), 1.89 (ddd, J_1 = 14.2 Hz, J_2 = 4.5 Hz, J_3 = 1.5 Hz, 1H), 3.02 (ddd, J_1 = 14.2 Hz, J_2 = 10.2 Hz, J_3 = 4.1 Hz, 1H), 3.21 (dd, J_1 =10.4 Hz, J_2 = 4.4 Hz, 1H), 5.74 (d, J = 2.8 Hz, 1H), 6.29 (d, J = 6.8 Hz, 2H), 6.99 (m, J = 7.2 Hz, 1H), 7.06 (t, J = 8.0 Hz, 2H), 7.15 (t, J = 7.6 Hz, 1H), 7.33-7.39 (m, 1H), 7.39-7.44 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.5, 37.2, 43.8, 49.3, 76.9, 122.4, 125.0, 127.3, 127.7, 128.0, 128.4, 128.9, 136.1, 137.8, 139.8, 175.5; **HRMS** (ESI) calcd. for $C_{18}H_{16}O_2Na$ [M+Na]: 287.1048, found: 287.1049.

The compound was also confirmed by single-crystal X-ray analysis.

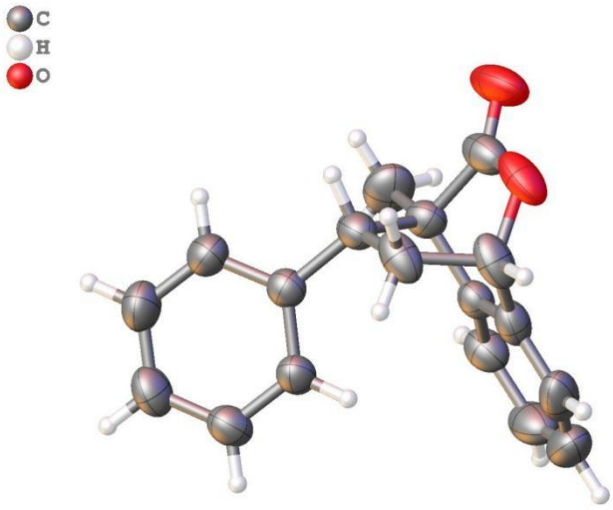
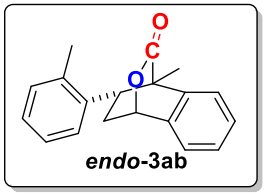


Figure S2. The structure of the product *endo*-**3aa**

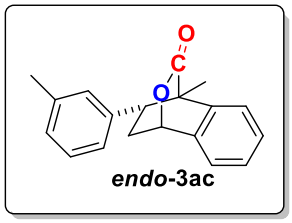
4-methyl-3-(o-tolyl)-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one



(*endo*-3ab): The title compound was prepared according to **General procedure A** and purified by column chromatography to give a light white solid (**3ab** : 89 mg, 66% yield). dr > 20:1. M. p.: 166-168 °C. IR (neat) ν(cm^{-1}): 2978, 2940, 2864, 1743, 1687, 1594. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.41 (s, 3H), 1.75 (dq, J_1 = 14.0 Hz, J_2 =

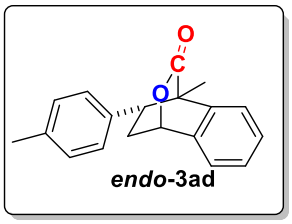
1.2 Hz, 1H), 2.40 (s, 3H), 3.02 (ddd, J_1 = 14.3 Hz, J_2 = 10,3 Hz, J_3 = 4.2 Hz, 1H), 3.64 (dd, J_1 = 10.0 Hz, J_2 = 4.4 Hz, 1H), 5.34 (d, J = 8.0 Hz, 1H), 5.73 (d, J = 4.0 Hz, 1H), 6.72 (t, J = 7.2 Hz, 1H), 6.99-7.11 (m, 3H), 7.36-7.42 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.5, 20.8, 37.1, 37.9, 50.0, 77.4, 122.4, 125.6, 126.1, 126.5, 126.9, 127.8, 129.1, 130.3, 136.4, 137.1, 138.1, 138.7, 175.9; **HRMS** (ESI) calcd. for $C_{19}H_{18}O_2Na$ [M+Na]: 301.1204, found: 301.1205.

4-methyl-3-(m-tolyl)-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one



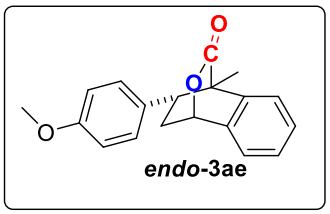
(*endo*-3ac): The title compound was prepared according to **General procedure A** and purified by column chromatography to give a light white solid (**3ac** : 105 mg, 76% yield). dr > 20:1. M. p.: 137-140 °C. IR (neat) ν(cm^{-1}): 2971, 2938, 2908, 1749. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.37 (s, 3H), 1.85 (dq, J_1 = 14.0 Hz, J_2 = 1.2 Hz, 1H), 2.13 (s, 3H), 3.00 (ddd, J_1 = 14.2 Hz, J_2 = 10.2 Hz, J_3 = 4.0 Hz, 1H), 3.17 (dd, J_1 = 10.0 Hz, J_2 = 4.4 Hz, 1H), 5.72 (dd, J_1 = 4.0 Hz, J_2 = 1.2 Hz, 1H), 6.08 (s, 2H), 6.95 (d, J = 5.2 Hz, 2H), 6.99 (d, J = 7.2 Hz, 1H), 7.33-7.37 (m, 1H), 7.39-7.44 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.6, 21.4, 37.4, 43.9, 49.4, 77.1, 122.4, 125.1, 125.5, 127.7, 128.0, 128.0, 128.9, 129.4, 136.4, 137.7, 138.0, 138.9, 175.7; **HRMS** (ESI) calcd. for $C_{19}H_{18}O_2Na$ [M+Na]: 301.1204, found: 301.1202.

4-methyl-3-(p-tolyl)-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one



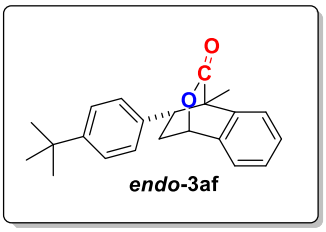
(*endo*-3ad): The title compound was prepared according to **General procedure A** and purified by column chromatography to give a light white solid (**3ad** : 101 mg, 73% yield). dr > 20:1. M. p.: 178-180 °C. IR (neat) ν(cm^{-1}): 2977, 2936, 2871, 1747, 1687. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.37 (s, 3H), 1.83 (dq, J_1 = 14.0 Hz, J_2 = 1.2 Hz, 1H), 2.23 (s, 3H), 3.00 (ddd, J_1 = 14.2 Hz, J_2 = 10.3 Hz, J_3 = 4.1 Hz, 1H), 3.17 (dd, J_1 = 10.0 Hz, J_2 = 4.4 Hz, 1H), 5.72 (dd, J_1 = 4.0 Hz, J_2 = 1.2 Hz, 1H), 6.17 (d, J = 7.2 Hz, 2H), 6.87 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 7.6 Hz, 1H), 7.32-7.43 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.5, 21.0, 37.3, 43.5, 49.4, 77.0, 122.4, 125.0, 127.7, 128.4, 128.8, 128.9, 136.3, 136.8, 137.0, 137.9, 175.7; **HRMS** (ESI) calcd. for $C_{19}H_{18}O_2Na$ [M+Na]: 301.1204, found: 301.1211.

3-(4-methoxyphenyl)-4-methyl-1,2,3,4-tetrahydro-1,4-



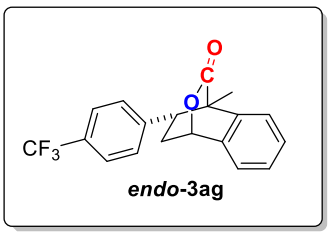
(epoxymethano)naphthalen-9-one (*endo*-3ae): The title compound was prepared according to **General procedure A** and purified by column chromatography to give a light white solid (**3ae** : 116 mg, 79% yield), dr > 20:1. M. p.: 135-137 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.37 (s, 3H), 1.81 (dq, J_1 = 14.0 Hz, J_2 = 1.2 Hz, 1H), 3.00 (ddd, J_1 = 14.2 Hz, J_2 = 10.3 Hz, J_3 = 4.0 Hz, 1H), 3.17 (dd, J_1 = 10.0 Hz, J_2 = 4.4 Hz, 1H), 3.72 (s, 3H), 5.71 (dd, J_1 = 4.0 Hz, J_2 = 1.2 Hz, 1H), 6.20 (d, J = 8.0 Hz, 2H), 6.60 (dd, J_1 =7.6 Hz, J_2 = 1.2 Hz, 2H), 6.99 (d, J = 7.4 Hz, 1H), 7.33-7.36 (m, 1H), 7.37-7.43 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.5, 37.3, 43.1, 49.5, 55.2, 77.0, 113.4, 122.4, 125.0, 127.7, 128.9, 129.4, 131.8, 136.3, 137.9, 135.8, 175.7; **HRMS** (ESI) calcd. for $C_{19}H_{18}O_3Na$ [M+Na]: 317.1154, found: 317.1157.

3-(4-(tert-butyl)phenyl)-4-methyl-1,2,3,4-tetrahydro-1,4-



(epoxymethano)naphthalen-9-one (*endo*-3af): The title compound was prepared according to **General procedure A** and purified by column chromatography to give a white solid (**3af** : 102 mg, 64% yield), dr > 20:1. M. p.: 58-61 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.23 (s, 9H), 1.38 (s, 3H), 1.83 (dq, J_1 = 14.0 Hz, J_2 = 1.2 Hz, 1H), 3.00 (ddd, J_1 = 14.2 Hz, J_2 = 10.3 Hz, J_3 = 4.1 Hz, 1H), 3.18 (dd, J_1 = 10.0 Hz, J_2 = 4.4 Hz, 1H), 5.71 (dd, J_1 = 4.0 Hz, J_2 = 1.2 Hz, 1H), 6.22 (d, J = 8.0 Hz, 2H), 7.02-7.09 (m, 3H), 7.34-7.42 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.6, 31.4, 34.5, 37.4, 43.4, 49.4, 77.1, 122.4, 125.0, 125.2, 127.7, 128.2, 129.0, 136.3, 136.8, 138.0, 150.2, 175.8; **HRMS** (ESI) calcd. for $C_{22}H_{25}O_2$ [M+H]: 321.1855, found: 321.1853.

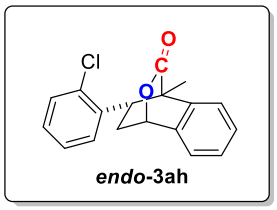
4-methyl-3-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydro-1,4-



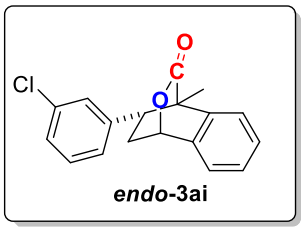
(epoxymethano)naphthalen-9-one (*endo*-3ag): The title compound was prepared according to **General procedure A** and purified by column chromatography to give yellow oil (**3ag** : 108 mg, 81% yield), dr > 20:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.38 (s, 3H), 1.85 (dq, J_1 = 14.0 Hz, J_2 = 1.2 Hz, 1H), 3.05 (ddd, J_1 = 14.3 Hz, J_2 = 10.3 Hz, J_3 = 4.0 Hz, 1H), 3.29 (dd, J_1 = 10.0 Hz,

J_2 = 4.4 Hz, 1H), 5.76 (d, J = 3.2 Hz, 1H), 6.39 (d, J = 7.2 Hz, 2H), 7.00 (d, J = 7.6 Hz, 1H), 7.33-7.37 (m, 2H), 7.38-7.42 (m, 1H), 7.43-7.46 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.5, 37.2, 43.8, 49.2, 76.8, 122.6, 125.0 (J_{C-F} = 10.0 Hz), 128.1, 128.9, 129.8, 135.8 137.8, 144.1, 175.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.6; **HRMS** (ESI) calcd. for $C_{19}H_{15}F_3O_2Na$ [M+ Na]: 355.0922, found: 355.0925.

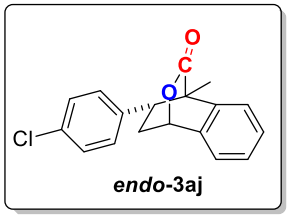
3-(2-chlorophenyl)-4-methyl-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one (*endo*-3ah): The title compound was prepared according to **General procedure A** and purified by column chromatography to give a white solid (**3ah** : 89 mg, 60% yield), dr > 20:1. M. p.: 128-130 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.46 (s, 3H), 1.74 (dq, J_1 = 14.0 Hz, J_2 = 1.2 Hz, 1H), 3.06 (ddd, J_1 = 14.3 Hz, J_2 = 10.3 Hz, J_3 = 4.1 Hz, 1H), 4.10 (dd, J_1 = 10.0 Hz, J_2 = 4.4 Hz, 1H), 5.40 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 5.74 (dd, J_1 = 4.0 Hz, J_2 = 0.8 Hz, 1H), 6.78-6.82 (m, 1H), 7.04-7.08 (m, 2H), 7.32-7.34 (m, 1H), 7.35-7.44 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.4, 37.4, 37.5, 49.8, 77.4, 122.6, 125.3, 126.7, 128.0, 128.1, 128.3, 129.1, 129.5, 135.3, 136.2, 138.0, 175.2; **HRMS** (ESI) calcd. for $C_{18}H_{16}ClO_2$ [M+H]: 299.0839, found: 299.0835.



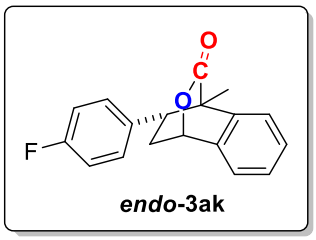
3-(3-chlorophenyl)-4-methyl-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one (*endo*-3ai): The title compound was prepared according to **General procedure A** and purified by column chromatography to give a white solid (**3ai** : 105 mg, 71% yield). dr > 20:1. M. p.: 123-126 °C. IR (neat) ν(cm^{-1}): 2977, 2936, 1752, 1614, 1589. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.39 (s, 3H), 1.81-1.86 (m, 1H), 3.02 (ddd, J_1 = 14.2 Hz, J_2 = 10.2 Hz, J_3 = 4.0 Hz, 1H), 3.19 (dd, J_1 = 10.0 Hz, J_2 = 4.4 Hz, 1H), 5.73 (dd, J_1 = 4.0 Hz, J_2 = 1.6 Hz, 1H), 6.20 (d, J = 6.4 Hz, 2H), 6.99-7.03 (m, 2H), 7.12-7.14 (m, 1H), 7.36-7.44 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.5, 37.3, 43.7, 49.3, 76.8, 122.6, 125.1, 126.8, 128.1, 128.6, 129.1, 129.3, 134.0, 135.9, 137.8, 142.1, 175.2; **HRMS** (ESI) calcd. for $C_{18}H_{16}ClO_2$ [M+H]: 299.0839, found: 299.0841.



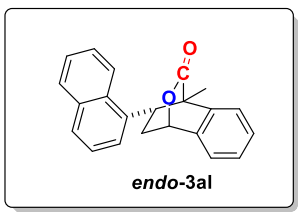
3-(2-chlorophenyl)-4-methyl-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one (*endo*-3aj): The title compound was prepared according to **General procedure A** and purified by column chromatography to give a light white solid (**3aj** : 106 mg, 71% yield), dr > 20:1. M. p.: 118-120 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.37 (s, 3H), 1.80 (dq, J_1 = 14.2 Hz, J_2 = 1.4 Hz, 1H), 3.02 (ddd, J_1 = 14.2 Hz, J_2 = 10.3 Hz, J_3 = 4.0 Hz, 1H), 3.19 (dd, J_1 = 10.4 Hz, J_2 = 4.4 Hz, 1H), 5.73 (dd, J_1 = 4.0 Hz, J_2 = 1.2 Hz, 1H), 6.20 (d, J = 7.6 Hz, 2H), 6.99 (d, J = 6.8, 1H), 7.04-7.06 (m, 2H), 7.34-7.44 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.5, 37.3, 43.3, 49.3, 76.8, 122.5, 125.1, 128.0, 128.3, 129.1, 133.3, 135.9, 137.8, 138.4, 175.3; **HRMS** (ESI) calcd. for $C_{18}H_{16}ClO_2$ [M+H]: 299.0839, found: 299.0835.



3-(4-fluorophenyl)-4-methyl-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one (*endo*-3ak): The title compound was prepared according to **General procedure A** and purified by column chromatography to give a white solid (**3ak** : 100 mg, 71% yield), dr > 20:1. M. p.: 135-137 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.37 (s, 3H), 1.81 (dd, J_1 = 14.0 Hz, J_2 = 4.0 Hz, 1H), 3.01 (ddd, J_1 = 14.2 Hz, J_2 = 10.3 Hz, J_3 = 3.9 Hz, 1H), 3.21 (dd, J_1 = 10.0 Hz, J_2 = 4.4 Hz, 1H), 5.72 (d, J = 3.6 Hz, 1H), 6.23 (t, J = 6.8 Hz, 2H), 6.74 (t, J = 8.4 Hz, 2H), 6.98 (d, J = 7.6 Hz, 1H), 7.34-7.44 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.5, 37.3, 43.1, 49.3, 76.8, 114.8 ($J_{C\text{-}F}$ = 20.0 Hz), 122.5, 125.0, 127.9, 129.0 ($J_{C\text{-}F}$ = 2.0 Hz), 129.9, 135.6 ($J_{C\text{-}F}$ = 2.0 Hz), 136.0, 137.8, 160.8 ($J_{C\text{-}F}$ = 250.0 Hz), 175.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.3; **HRMS** (ESI) calcd. for $C_{18}H_{16}FO_2$ [M+H]: 283.1134, found: 283.1138.

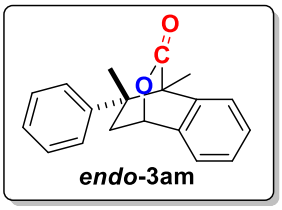


4-methyl-3-(naphthalen-1-yl)-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one (*endo*-3al): The title compound was prepared according to **General procedure A** and purified by column chromatography to a white solid (**3al** : 82 mg, 56% yield), dr > 20:1. M. p.: 132-134 °C. IR (neat) ν(cm^{-1}): 3057, 2974, 2931, 1743. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.40 (s, 3H), 1.97 (dq, J_1 = 12.8 Hz, J_2 = 4.4 Hz,



1H), 3.08 (ddd, J_1 = 14.3 Hz, J_2 = 10.3 Hz, J_3 = 4.1 Hz, 1H), 3.38 (dd, J_1 = 10.4 Hz, J_2 = 4.4 Hz, 1H), 5.78 (dd, J_1 = 3.6 Hz, J_2 = 0.8 Hz, 1H); 6.26 (d, J = 7.2 Hz, 1H), 6.85 (s, 1H), 6.95 (d, J = 7.6 Hz, 1H), 7.33-7.40 (m, 1H), 7.40-7.43 (m, 2H), 7.44-7.52 (m, 2H), 7.54-7.57 (m, 2H), 7.71-7.73 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.6, 37.4, 44.1, 49.6, 77.1, 122.6, 125.2, 126.0, 126.2, 127.6, 127.8, 127.8, 127.9, 132.6, 133.0, 136.4, 138.0, 175.6; **HRMS** (ESI) calcd. for $C_{22}H_{19}O_2Na$ [M+ Na]: 315.1385, found: 315.1387.

3,4-dimethyl-3-phenyl-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one (*endo*-3am): The title compound was prepared according to **General procedure A** and purified by column chromatography to give a white solid (**3am** : 91 mg, 66% yield), dr > 20:1. M. p.: 121-123 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.33 (s, 3H), 1.70 (s, 3H), 2.40 (dd, J_1 = 14.4 Hz, J_2 = 1.6 Hz, 1H), 2.57 (dd, J_1 = 14.0 Hz, J_2 = 4.0 Hz, 1H), 5.73 (dd, J_1 = 3.6 Hz, J_2 = 1.2 Hz, 1H), 6.38 (d, J = 7.6 Hz, 2H), 6.83 (d, J = 7.6 Hz, 1H), 7.01-7.12 (m, 3H), 7.24-7.28 (m, 1H), 7.35-7.40 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 11.2, 26.5, 42.0, 45.2, 53.8, 77.3, 122.2, 125.3, 126.7, 127.4, 127.4, 127.8, 128.9, 137.6, 138.0, 142.9, 175.5; **HRMS** (ESI) calcd. for $C_{19}H_{19}O_2$ [M+H]: 279.1385, found: 279.1388.



The compound was also confirmed by single-crystal X-ray analysis.

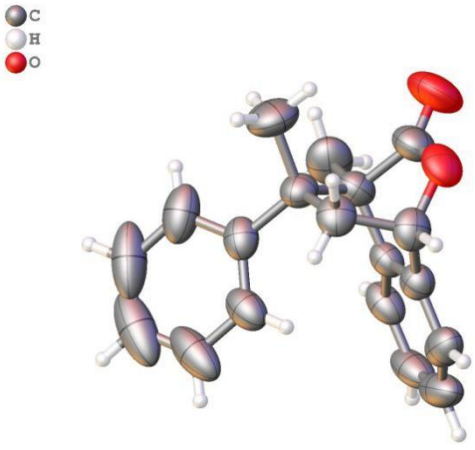
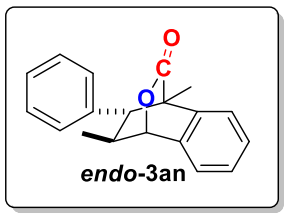


Figure S3. The structure of the product ***endo*-3am**

2,4-dimethyl-3-phenyl-1,2,3,4-tetrahydro-1,4-(epoxymethano) naphthalen-9-one (*endo*-3an): The title compound was prepared according to **General procedure A** and purified by column chromatography to give a white solid (**3an** : 83 mg, 60% yield), dr > 20:1. M. p.: 169-170 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.32 (s, 3H), 1.35 (d, J = 6.8 Hz, 3H), 2.12 (qdd, J_1 = 6.8 Hz, J_2 = 5.2 Hz, J_3 = 1.1 Hz, 1H), 2.58 (d, J = 5.2 Hz, 1H), 5.40 (s, 1H), 6.34 (d, J = 6.8 Hz, 2H), 7.04-7.17 (m, 3H), 7.15-7.19 (m, 1H), 7.35-7.42 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.5, 18.3, 44.1, 49.7, 53.3, 82.1, 122.6, 125.0, 127.4, 127.8, 128.2, 128.7, 129.0, 135.7, 138.7, 138.5, 175.5; **HRMS** (ESI) calcd. for $C_{19}H_{19}O_2$ [M+H]: 279.1385, found: 279.1385.



The compound was also confirmed by single-crystal X-ray analysis.

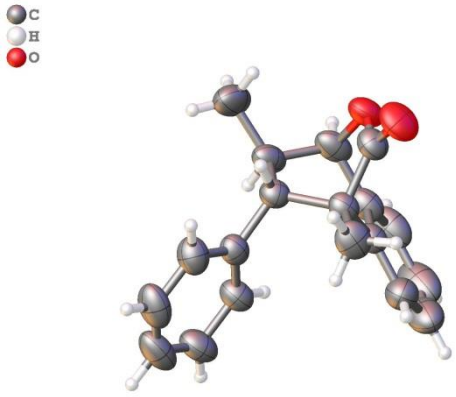
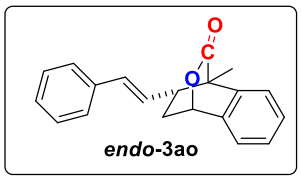
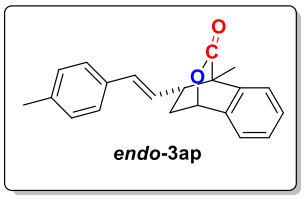


Figure S4. The structure of the product ***endo*-3an**

4-methyl-3-((E)-styryl)-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one (*endo*-3ao): The title compound was prepared according to **General procedure A** and purified by column chromatography to give yellow oil (**3ao** : 78 mg, 54% yield), dr > 20:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.56 (dd, J_1 = 11.6 Hz, J_2 = 1.2 Hz, 1H), 1.63 (s, 3H), 2.76-2.85 (m, 2H), 5.15-5.21 (m, 1H), 5.60 (t, J = 2.0 Hz, 1H), 6.34 (d, J = 14.4 Hz, 1H), 7.15-7.21 (m, 3H), 7.22-7.26 (m, 3H), 7.31-7.38 (m, 2H), 7.40-7.44 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.5, 35.3, 42.1, 48.4, 76.5, 122.8, 124.0, 126.3, 126.5, 127.6, 127.8, 128.5, 129.0, 133.0, 136.6, 137.4, 175.5; **HRMS** (ESI) calcd. for $C_{20}H_{18}O_2Na$ [M+Na]: 313.1204, found: 313.1200.

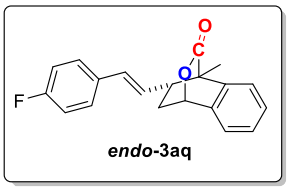


4-methyl-3-((E)-4-methylstyryl)-1,2,3,4-tetrahydro-1,4-



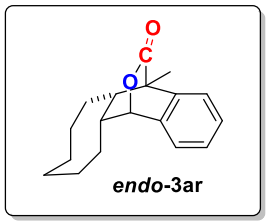
(epoxymethano)naphthalen-9-one (*endo*-3ap): The title compound was prepared according to **General procedure A** and purified by column chromatography to give oil (**3ap** : 85 mg, 56% yield), dr > 20:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.56 (dd, J_1 = 11.6 Hz, J_2 = 1.2 Hz, 1H), 1.63 (s, 3H), 2.29 (s, 3H), 2.75-2.85 (m, 2H), 5.09 (dd, J_1 = 15.6 Hz, J_2 = 9.2 Hz, 1H), 5.60 (t, J = 2.0 Hz, 1H), 6.31 (d, J = 15.6 Hz, 1H), 7.03-7.08 (m, 4H), 7.28 (s, 1H), 7.35-7.38 (m, 2H), 7.40-7.44 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.5, 21.3, 35.3, 42.2, 48.5, 76.6, 122.8, 124.1, 126.3, 127.5, 127.6, 129.0, 129.4, 132.9, 133.8, 136.7, 137.4, 137.7, 175.6; **HRMS** (ESI) calcd. for $C_{21}H_{20}O_2Na$ [M+Na]: 327.1361, found: 327.1358.

3-((E)-4-fluorostyryl)-4-methyl-1,2,3,4-tetrahydro-1,4-



(epoxymethano)naphthalen-9-one (*endo*-3aq): The title compound was prepared according to **General procedure A** and purified by column chromatography to give yellow oil (**3aq** : 46 mg, 30% yield), dr > 20:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.55-1.59 (m, 1H), 1.63 (s, 3H), 2.29 (s, 3H), 2.75-2.86 (m, 2H), 5.07 (dd, J_1 = 15.6 Hz, J_2 = 9.2 Hz, 1H), 5.61 (dd, J_1 = 3.2 Hz, J_2 = 1.2 Hz, 1H), 6.31 (d, J = 15.6 Hz, 1H), 6.90-6.95 (m, 2H), 7.10-7.15 (m, 2H), 7.27-7.29 (m, 1H), 7.34-7.39 (m, 2H), 7.42-7.45 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.6, 35.3, 42.1, 48.4, 76.5, 115.5 ($J_{C\text{-}F}$ = 20.0 Hz), 122.8, 124.0, 127.7 ($J_{C\text{-}F}$ = 9.0 Hz), 127.9, 128.2 ($J_{C\text{-}F}$ = 9.0 Hz), 129.1, 131.8, 132.7, 136.6, 137.4, 161.2 ($J_{C\text{-}F}$ = 250.0 Hz), 175.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.2; **HRMS** (ESI) calcd. for $C_{20}H_{18}O_2F$ [M+H]: 309.1291, found: 309.1296.

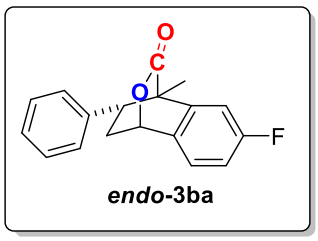
12-methyl-5,5a,6,7,8,9,10,11,11a,12-decahydro-5,12-



(epoxymethano)cycloocta[b]naphthalen-13-one (*endo*-3ar): The title compound was prepared according to **General procedure A** and purified by column chromatography to give yellow oil (**3ar** : 102.6 mg, 76% yield), dr > 20:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.56-0.60 (m, 1H), 0.82-0.89 (m, 1H), 1.17-1.64 (m, 11H), 1.70 (s, 3H), 1.94 (t, J = 9.6 Hz, 1H), 2.51-2.57 (m, 1H), 5.18 (d, J = 3.2 Hz, 1H), 7.23-7.29

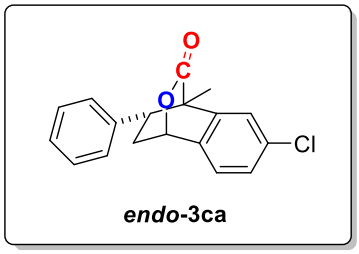
(m, 3H), 7.33-7.37 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.7, 23.3, 26.0, 26.2, 27.6, 30.7, 30.9, 43.0, 44.3, 49.6, 82.3, 123.4, 124.3, 126.8, 128.6, 135.4, 137.6, 176.2; **HRMS** (ESI) calcd. for $C_{18}H_{23}O_2Na$ [M+Na]: 293.1517, found: 293.1515.

6-fluoro-4-methyl-3-phenyl-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one (*endo*-3ba): The title compound was prepared according to **General procedure B** and purified by column chromatography to give a light white solid (**3ba** : 110 mg, 74% yield), dr > 20:1. M. p.: 182-184 °C. IR (neat) ν(cm^{-1}): 3059, 2974, 2931, 1743. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.36 (s, 3H), 1.91 (ddd, J_1 = 14.2 Hz, J_2 = 4.5 Hz, J_3 = 1.5 Hz, 1H), 3.02 (ddd, J_1 = 14.3 Hz, J_2 = 10.3 Hz, J_3 = 4.0 Hz, 1H), 3.22 (dd, J_1 =10.4 Hz, J_2 = 4.4 Hz, 1H), 5.74 (dd, J_1 = 4.0 Hz, J_2 = 1.2 Hz, 1H), 6.34 (d, J = 6.8 Hz, 2H), 6.71 (dd, J_1 =8.8 Hz, J_2 = 2.4 Hz, 1H), 7.08-7.13 (m, 3H), 7.16-7.20 (m, 1H), 7.39 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.6, 37.2, 43.7, 49.7, 76.4, 112.9 (J_{C-F} = 20.0 Hz), 114.4 (J_{C-F} = 30.0 Hz), 124.2 (J_{C-F} = 9.0 Hz), 127.6, 128.4 (J_{C-F} = 2.0 Hz), 133.8 (J_{C-F} = 9.0 Hz), 139.0, 139.1, 139.5, 162. (J_{C-F} = 25.0 Hz), 175.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.4; **HRMS** (ESI) calcd. for $C_{18}H_{16}FO_2$ [M+H]: 283.1134, found: 283.1136.



endo-3ba

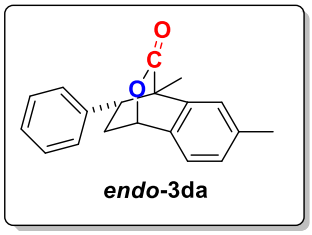
6-chloro-4-methyl-3-phenyl-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one (*endo*-3ca): The title compound was prepared according to **General procedure B** and purified by column chromatography to give a light white solid (**3ca** : 116 mg, 78% yield), dr > 20:1. M. p.: 179-181 °C. IR (neat) ν(cm^{-1}): 2982, 2960, 2920, 1749. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.36 (s, 3H), 1.91 (ddd, J_1 = 14.2 Hz, J_2 = 4.5 Hz, J_3 = 1.5 Hz, 1H), 3.03 (ddd, J_1 = 14.3 Hz, J_2 = 10.3 Hz, J_3 = 4.1 Hz, 1H), 3.22 (dd, J_1 = 10.4 Hz, J_2 = 4.4 Hz, 1H), 5.72 (dd, J_1 = 4.0 Hz, J_2 = 1.2 Hz, 1H), 6.34 (d, J = 7.2 Hz, 2H), 6.99 (d, J = 2.0 Hz, 1H), 7.10-7.17 (m, 2H), 7.17-7.21 (m, 1H), 7.36-7.42 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.5, 37.0, 43.7, 49.5, 76.4, 123.8, 125.6, 127.6, 127.9, 128.4, 128.4, 135.2, 136.4, 138.4, 139.4, 174.8; **HRMS** (ESI) calcd. for $C_{18}H_{16}ClO_2$ [M+H]: 299.0839, found:



endo-3ca

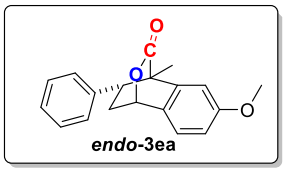
299.0839.

4,6-dimethyl-3-phenyl-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one



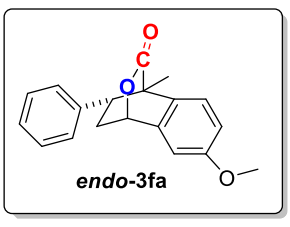
(*endo*-3da): The title compound was prepared according to **General procedure B** and purified by column chromatography to give a light white solid (**3da** : 74 mg, 53% yield), dr > 20:1. M. p.: 136-138 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.36 (s, 3H), 1.87 (ddd, J_1 = 14.2 Hz, J_2 = 4.5 Hz, J_3 = 1.5 Hz, 1H), 2.34 (s, 3H), 3.00 (ddd, J_1 = 14.2 Hz, J_2 = 10.2 Hz, J_3 = 4.0 Hz, 1H), 3.20 (dd, J_1 = 10.4 Hz, J_2 = 4.4 Hz, 1H), 5.70 (dd, J_1 = 4.0 Hz, J_2 = 1.2 Hz, 1H), 6.32 (d, J = 7.2 Hz, 1H), 6.80 (d, J = 0.6 Hz, 1H), 7.07-7.11 (m, 2H), 7.14-7.18 (m, 1H), 7.18-7.22 (m, 1H), 7.30 (d, J = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.6, 21.7, 37.4, 43.9, 49.3, 76.9, 122.3, 125.7, 127.3, 128.1, 128.2, 128.6, 135.1, 136.1, 138.9, 140.0, 175.9; **HRMS** (ESI) calcd. for $C_{19}H_{18}O_2Na$ [M+Na]: 301.1204, found: 301.1204.

6-methoxy-4-methyl-3-phenyl-1,2,3,4-tetrahydro-1,4-



(epoxymethano)naphthalen-9-one (*endo*-3ea): The title compound was prepared according to **General procedure B** and purified by column chromatography to give a light white solid (**3ea** : 93 mg, 63% yield), dr > 20:1. M. p.: 155-157 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.35 (s, 3H), 1.89 (ddd, J_1 = 14.0 Hz, J_2 = 4.5 Hz, J_3 = 1.4 Hz, 1H), 3.00 (ddd, J_1 = 14.2 Hz, J_2 = 10.3 Hz, J_3 = 4.0 Hz, 1H), 3.19 (dd, J_1 = 10.4 Hz, J_2 = 4.4 Hz, 1H), 3.77 (s, 3H), 5.69 (dd, J_1 = 4.0 Hz, J_2 = 1.2 Hz, 1H), 6.36 (d, J = 7.2 Hz, 1H), 6.54 (d, J = 2.4 Hz, 1H), 6.89 (dd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, 1H), 7.08-7.17 (m, 3H), 7.32 (d, J = 8.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.6, 37.5, 43.9, 49.7, 55.6, 76.7, 111.6, 112.4, 123.6, 127.3, 128.2, 128.6, 130.4, 137.9, 139.9, 160.5, 175.6; **HRMS** (ESI) calcd. for $C_{19}H_{18}O_3Na$ [M+Na]: 317.1154, found: 317.1155.

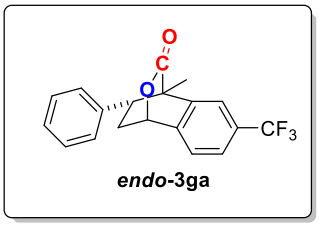
7-methoxy-4-methyl-3-phenyl-1,2,3,4-tetrahydro-1,4-



(epoxymethano)naphthalen-9-one (*endo*-3fa): The title compound was prepared according to **General procedure B** and purified by column chromatography to give yellow oil (**3fa** : 95 mg, 65% yield). dr > 20:1 **^{1}H NMR** (400 MHz,

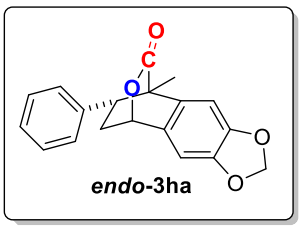
$CDCl_3$) δ 1.36 (s, 3H), 1.87 (ddd, J_1 = 14.1 Hz, J_2 = 4.5 Hz, J_3 = 1.5 Hz, 1H), 2.34 (s, 3H), 3.00 (ddd, J_1 = 14.2 Hz, J_2 = 10.2 Hz, J_3 = 4.0 Hz, 1H), 3.19 (dd, J_1 =10.4 Hz, J_2 = 3.2 Hz, 1H), 5.69 (dd, J_1 = 4.0 Hz, J_2 = 1.2 Hz, 1H), 6.32 (d, J = 7.2 Hz, 2H), 6.81 (s, 1H), 7.06-7.14 (m, 2H), 7.15-7.18 (m, 1H), 7.19-7.21 (m, 1H), 7.30 (t, J = 4.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.6, 21.7, 37.5, 44.0, 49.4, 76.9, 122.3, 125.8, 127.3, 128.1, 128.2, 128.6, 135.2, 136.2, 138.9, 140.1, 175.8; **HRMS** (ESI) calcd. for $C_{19}H_{18}O_3Na$ [M+Na]: 317.1154, found: 317.1154.

4-methyl-3-phenyl-6-(trifluoromethyl)-1,2,3,4-tetrahydro-1,4-



(epoxymethano)naphthalen-9-one (*endo*-3ga): The title compound was prepared according to **General procedure B** and purified by column chromatography to give yellow oil (**3ga** : 119 mg, 74% yield), dr > 20:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.41 (s, 3H), 1.91 (ddd, J_1 = 14.4 Hz, J_2 = 4.6 Hz, J_3 = 1.4 Hz, 1H), 3.06 (ddd, J_1 = 14.4 Hz, J_2 = 10.3 Hz, J_3 = 4.1 Hz, 1H), 3.26 (dd, J_1 = 10.4 Hz, J_2 = 4.4 Hz, 1H), 5.80 (d, J = 3.6 Hz, 1H), 6.26 (d, J = 7.2 Hz, 2H), 7.07-7.11 (m, 2H), 7.15-7.19 (m, 1H), 7.23 (s, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.4, 22.5, 35.8, 42.7, 48.6, 74.3, 121.0 ($J_{C\text{-}F}$ = 2.0 Hz), 120.0, 124.0 ($J_{C\text{-}F}$ = 2.0 Hz), 126.7, 127.3 ($J_{C\text{-}F}$ = 2.0 Hz), 129.9 ($J_{C\text{-}F}$ = 30.0 Hz), 130.9, 136.6, 138.1, 140.5, 173.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.3; **HRMS** (ESI) calcd. for $C_{19}H_{15}F_3O_2Na$ [M+Na]: 355.0922, found: 355.0922.

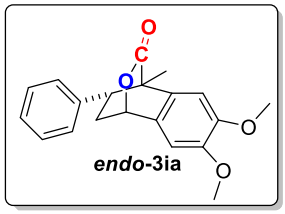
8-methyl-7-phenyl-5,6,7,8-tetrahydro-5,8-(epoxymethano)naphtho[2,3-



d][1,3]dioxol-10-one (*endo*-3ha): The title compound was prepared according to **General procedure B** and purified by column chromatography to give a light white solid (**3ha** : 112 mg, 73% yield), dr > 20:1. M. p.: 137-139 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.32 (s, 3H), 1.88 (ddd, J_1 = 14.1 Hz, J_2 = 4.5 Hz, J_3 = 1.4 Hz, 1H), 2.99 (ddd, J_1 = 14.1 Hz, J_2 = 10.1 Hz, J_3 = 4.0 Hz, 1H), 3.15 (dd, J_1 = 10.0 Hz, J_2 = 4.4 Hz, 1H), 5.63 (d, J = 3.6 Hz, 1H), 5.99 (t, J = 1.6 Hz, 1H), 6.05 (dd, J_1 = 2.2 Hz, J_2 = 1.4 Hz, 1H), 6.41 (d, J = 6.8 Hz, 2H), 6.49 (s, 1H), 6.93 (s, 1H), 7.11-7.20 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 15.0, 37.4, 43.8, 49.2, 76.9, 101.5, 104.5, 106.5, 127.4,

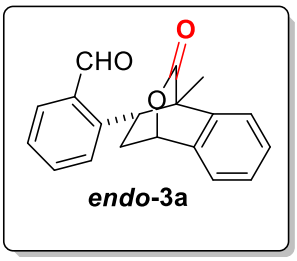
128.3, 128.6, 130.2, 131.6, 140.0, 147.1, 148.3, 175.6; **HRMS** (ESI) calcd. for $C_{19}H_{17}O_4$ [M+H]: 309.1127, found: 309.1131.

6,7-dimethoxy-4-methyl-3-phenyl-1,2,3,4-tetrahydro-1,4-



(epoxymethano)naphthalen-9-one (*endo*-3ia): The title compound was prepared according to **General procedure B** and purified by column chromatography to give a light white solid (**3ia** : 121 mg, 74% yield), dr > 20:1. M. p.: 164-166 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.35 (s, 3H), 1.87 (ddd, J_1 = 14.0 Hz, J_2 = 4.4 Hz, J_3 = 1.4 Hz, 1H), 2.99 (ddd, J_1 = 14.1 Hz, J_2 = 10.2 Hz, J_3 = 4.0 Hz, 1H), 3.17 (dd, J_1 = 10.0 Hz, J_2 = 4.4 Hz, 1H), 3.79 (s, 3H), 3.98 (s, 3H), 5.67 (d, J = 3.2 Hz, 1H), 6.34 (d, J = 6.8 Hz, 2H), 6.50 (s, 1H), 7.00 (s, 1H), 7.08-7.18 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.7, 37.5, 43.9, 49.0, 56.3, 56.3, 76.8, 106.3, 108.7, 127.3, 128.1, 128.4, 128.5, 130.4, 140.0, 148.6, 149.6, 175.8; **HRMS** (ESI) calcd. for $C_{20}H_{21}O_4$ [M+H]: 325.1440, found: 325.1441.

2-(4-Methyl-9-oxo-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-3-



yl)benzaldehyde (*endo*-3a): The title compound was prepared according to **General procedure C** and purified by column chromatography to give a white solid (**3a:** 104 mg, 85% yield), dr > 20:1. M. p.: 173-175 °C. IR (neat) ν(cm^{-1}): 2979, 2939, 2863, 2724, 1742, 1687, 1593. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.35 (s, 3H), 1.84 (ddd, J_1 = 14.2 Hz, J_2 = 4.7 Hz, J_3 = 1.4 Hz, 1H), 3.09 (ddd, J_1 = 14.3 Hz, J_2 = 10.3 Hz, J_3 = 4.1 Hz, 1H), 4.89 (dd, J_1 = 10.4 Hz, J_2 = 4.8 Hz, 1H), 5.57 (d, J = 8.0 Hz, 1H), 5.76 (d, J = 3.2 Hz, 1H), 7.01 (d, J = 7.4 Hz, 1H), 7.10-7.15 (m, 1H), 7.32-7.47 (m, 4H), 7.74 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 10.27 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.6, 34.2, 37.6, 49.5, 76.8, 122.6, 125.1, 127.5, 128.0, 128.2, 129.1, 133.3, 133.5, 135.1, 136.3, 138.1, 142.3, 175.0, 193.0; **HRMS** (ESI) calcd. for $C_{19}H_{16}O_3Na$ [M+Na]: 315.0997, found: 315.0986.

The compound was also confirmed by single-crystal X-ray analysis.

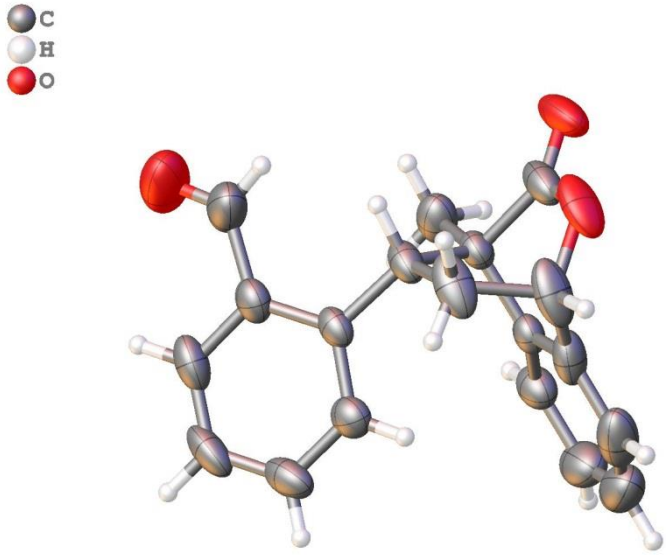
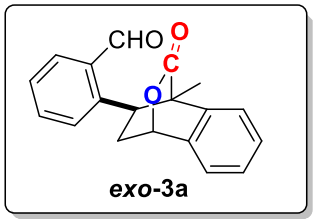


Figure S5. The structure of the product ***endo*-3a**

2-(4-Methyl-9-oxo-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-3-yl)benzaldehyde (*exo*-3a): The title compound was prepared according to **General procedure C** and purified by column chromatography to give a white solid. M. p.: 168-170 °C. IR (neat) ν(cm^{-1}): 2964, 2950, 2927, 2870, 2854, 2772, 1740, 1690, 1573. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.31 (s, 3H), 2.48-2.55 (m, 2H), 4.53 (dd, J_1 = 9.8 Hz, J_2 = 6.8 Hz, 1H), 5.75 (s, 1H), 7.32-7.33 (m, 4H), 7.47-7.54 (m, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.77 (d, J = 7.6 Hz, 1H), 10.12 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.4, 37.6, 37.8, 49.8, 76.8, 122.6, 123.0, 127.6, 127.7, 128.4, 129.2, 134.6, 135.0, 135.2, 137.7, 140.0, 143.5, 175.2, 193.7; **HRMS** (ESI) calcd. for $C_{19}H_{16}O_3Na$ [M+Na]: 315.0997, found: 315.0995.



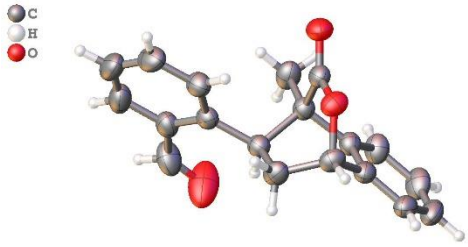
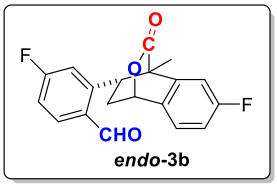


Figure S6. The structure of the product ***exo*-3a**

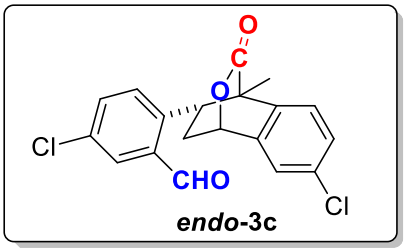
4-Fluoro-2-(6-fluoro-4-methyl-9-oxo-1,2,3,4-tetrahydro-1,4-



endo-3b

(epoxymethano)naphthalen-3-yl)benzaldehyde) (*endo*-3b): The title compound was prepared according to **General procedure C** and purified by column chromatography to give a white solid (**3b:** 108 mg, 82% yield), dr > 20:1. M. p.: 170-172 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.35 (s, 3H), 1.80 (ddd, J_1 = 14.2 Hz, J_2 = 4.7 Hz, J_3 = 1.5 Hz, 1H), 3.10 (ddd, J_1 = 14.3 Hz, J_2 = 10.3 Hz, J_3 = 4.0 Hz, 1H), 4.99-5.03 (m, 1H), 5.30 (dd, J_1 = 10.6 Hz, J_2 = 2.2 Hz, 1H), 5.76 (d, J_1 = 4.0 Hz, J_2 = 0.8 Hz, 1H), 6.78 (dd, J_1 = 8.6 Hz, J_2 = 2.4 Hz, 1H), 7.04 (dt, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.14 (dt, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.45 (dd, J_1 = 8.0 Hz, J_2 = 5.2 Hz, 1H), 7.78 (dd, J_1 = 8.4 Hz, J_2 = 6.0 Hz, 1H), 10.18 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.5, 34.0, 37.6, 49.7 (J_{C-F} = 20.0 Hz), 76.0, 113.0 (J_{C-F} = 20.0 Hz), 114.9 (J_{C-F} = 9.0 Hz), 115.3 (J_{C-F} = 9.0 Hz), 124.6 (J_{C-F} = 2.0 Hz), 129.5, 131.8 (J_{C-F} = 2.0 Hz), 133.8 (J_{C-F} = 2.0 Hz), 136.8 (J_{C-F} = 9.0 Hz), 138.7 (J_{C-F} = 9.0 Hz), 145.6 (J_{C-F} = 2.0 Hz), 162.3 (J_{C-F} = 250.0 Hz), 164.0 (J_{C-F} = 250.0 Hz), 173.9, 191.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.0, -110.6; **HRMS** (ESI) calcd. for $C_{19}H_{14}F_2O_3Na$ [M+Na]: 351.0809, found: 351.0808.

5-Chloro-2-(7-chloro-4-methyl-9-oxo-1,2,3,4-tetrahydro-1,4-



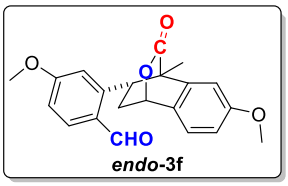
endo-3c

(epoxymethano)naphthalen-3-yl)benzaldehyde (*endo*-3c): The title compound was prepared according to **General procedure C** and purified by column chromatography to give a light solid (**3c:** 119 mg, 85% yield), dr > 20:1. M. p.: 68-70 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.33 (s, 3H), 1.80 (ddd, J_1 = 14.4 Hz, J_2 = 4.6 Hz, J_3 = 1.5 Hz, 1H), 3.09 (ddd, J_1 = 14.3 Hz, J_2 = 10.3 Hz, J_3 = 4.1 Hz, 1H), 4.94 (dd, J_1 = 10.4 Hz, J_2 = 4.4 Hz, 1H), 5.49 (d, J = 2.0 Hz, 1H), 5.76 (dd, J_1 = 4.0 Hz, J_2 = 0.8 Hz, 1H), 7.03 (d, J = 1.6 Hz, 1H), 7.28 (dd, J_1 = 10.4 Hz, J_2 = 2.0 Hz, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.47 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 10.18 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.5, 34.1, 37.4, 49.6, 76.0, 124.2, 125.7, 128.1, 128.4, 128.6, 133.4, 135.3, 135.7, 136.2, 138.2, 140.1, 143.7, 173.7, 191.7; **HRMS** (ESI) calcd. for $C_{19}H_{14}Cl_2O_3Na$ [M+Na]: 383.0218, found: 383.0216.

2-(4-methyl-9-oxo-7-(trifluoromethyl)-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-3-yl)-5-(trifluoromethyl)benzaldehyde (*endo*-3d): The title compound was prepared according to **General procedure C** and purified by column chromatography to give a light white solid (**3d:** 99 mg, 48% yield), dr > 20:1. M. p.: 67-69 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.37 (s, 3H), 1.84 (ddd, J_1 = 14.2 Hz, J_2 = 4.5 Hz, J_3 = 1.5 Hz, 1H), 3.09 (ddd, J_1 = 14.3 Hz, J_2 = 10.3 Hz, J_3 = 4.1 Hz, 1H), 5.00 (dd, J_1 = 10.4 Hz, J_2 = 4.4 Hz, 1H), 5.63 (s, 1H), 5.87 (d, J = 3.2 Hz, 1H), 7.22 (s, 1H), 7.64 (t, J = 8.0 Hz, 2H), 7.78 (d, J = 7.6 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 10.31 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.5, 34.4, 37.3, 49.7, 76.0, 122.1 (J_{C-F} = 2.0 Hz), 123.4, 124.7 (J_{C-F} = 2.0 Hz), 124.8, 124.9, 125.6 (J_{C-F} = 2.0 Hz), 132.1 (J_{C-F} = 30.0 Hz), 134.2, 134.5, 134.8, 137.3, 137.4, 141.3, 142.6, 173.3, 192.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.1, -62.8; **HRMS** (ESI) calcd. for $C_{21}H_{14}F_6O_3Na$ [M+Na]: 451.0745, found: 451.0748.

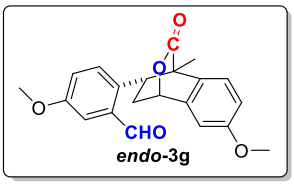
2-(4,7-dimethyl-9-oxo-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-3-yl)-5-methylbenzaldehyde (*endo*-3e): The title compound was prepared according to **General procedure C** and purified by column chromatography to give a light white solid (**3e:** 122 mg, 95% yield), dr > 20:1. M. p.: 178-180 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.30 (s, 3H), 1.79 (ddd, J_1 = 14.1 Hz, J_2 = 4.5 Hz, J_3 = 1.5 Hz, 1H), 1.98 (s, 3H), 2.36 (s, 3H), 3.03 (ddd, J_1 = 14.2 Hz, J_2 = 10.3 Hz, J_3 = 4.0 Hz, 1H), 4.87 (dd, J_1 = 10.4 Hz, J_2 = 4.4 Hz, 1H), 5.23 (s, 1H), 5.73 (dd, J_1 = 3.6 Hz, J_2 =0.8 Hz, 1H), 6.80 (s, 1H), 7.12 (dd, J_1 = 7.6 Hz, J_2 =0.8 Hz, 1H), 7.24 (dd, J_1 = 4.8 Hz, J_2 =4 Hz, 1H), 7.33-7.35 (m, 1H), 7.61 (d, J = 7.6 Hz, 1H), 10.19 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.5, 21.6, 21.7, 34.3, 37.8, 49.6, 76.7, 122.4, 125.9, 128.1, 128.3, 129.3, 132.8, 133.7, 135.3, 136.6, 138.9, 142.4, 144.1, 175.2, 192.6; **HRMS** (ESI) calcd. for $C_{21}H_{20}O_3Na$ [M+Na]: 343.1310, found: 343.1311.

4-methoxy-2-(6-methoxy-4-methyl-9-oxo-1,2,3,4-tetrahydro-1,4-



(epoxymethano)naphthalen-3-yl)benzaldehyde (*endo*-3f): The title compound was prepared according to **General procedure C** and purified by column chromatography to give a light white solid (**3f:** 125 mg, 89% yield), dr > 20:1. M. p.: 128-130 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.35 (s, 3H), 1.82 (ddd, J_1 = 14.2 Hz, J_2 = 4.5 Hz, J_3 = 1.5 Hz, 1H), 3.06 (ddd, J_1 = 14.2 Hz, J_2 = 10.3 Hz, J_3 = 4.0 Hz, 1H), 3.41 (s, 3H), 3.79 (s, 3H), 4.96 (dd, J_1 =10.0 Hz, J_2 = 4.4 Hz,1H), 5.20 (d, J = 2.4 Hz, 1H), 5.72 (d, J = 3.2 Hz, 1H), 6.62 (d, J = 2.4 Hz, 1H), 6.80 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 6.91 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.8 Hz, 1H), 10.10 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.6, 34.1, 38.0, 49.8, 55.0, 55.7, 76.4, 112.1, 112.4, 112.8, 113.9, 123.8, 128.6, 130.6, 136.2, 138.4, 145.3, 160.6, 163.2, 174.9, 191.5; **HRMS** (ESI) calcd. for $C_{21}H_{20}O_5Na$ [M+Na]: 375.1208, found: 375.1212.

5-methoxy-2-(7-methoxy-4-methyl-9-oxo-1,2,3,4-tetrahydro-1,4-

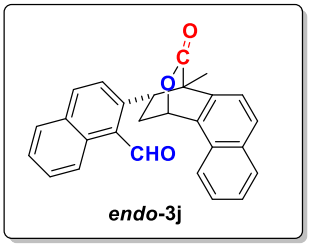


(epoxymethano)naphthalen-3-yl)benzaldehyde (*endo*-3g): The title compound was prepared according to **General procedure C** and purified by column chromatography to give a light white solid (**3g:** 130 mg, 92% yield), dr > 20:1. M. p.: 146-148 ºC. IR (neat) ν(cm^{-1}): 2987, 2957, 2938, 2910, 2833, 2753, 1747, 1494. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.30 (s, 3H), 1.81 (ddd, J_1 = 14.1 Hz, J_2 = 4.7 Hz, J_3 = 1.4 Hz, 1H), 3.04 (ddd, J_1 = 14.3 Hz, J_2 = 10.3 Hz, J_3 = 4.1 Hz, 1H), 3.80 (s, 3H), 3.89 (s, 3H), 4.59 (dd, J_1 = 10.4 Hz, J_2 = 4.8 Hz, 1H), 5.54 (d, J = 8.8 Hz, 1H), 5.68 (dd, J_1 = 4.0 Hz, J_2 = 0.8 Hz, 1H), 6.70 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H), 6.89 (t, J = 2.4 Hz, 1H), 7.01 (d, J = 2.0 Hz, 1H), 7.27 (d, J = 1.6 Hz, 1H), 10.30 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.9, 34.2, 37.6, 49.0, 55.6, 55.7, 76.9, 108.9, 113.9, 115.4, 120.2, 126.3, 128.1, 129.5, 134.5, 136.1, 139.2, 158.7 159.6, 175.3, 191.9; **HRMS** (ESI) calcd. for $C_{21}H_{20}O_5Na$ [M+Na]: 375.1208, found: 375.1211.

2-(6,7-dimethoxy-4-methyl-9-oxo-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-3-yl)-4,5-dimethoxybenzaldehyde (*endo*-3h): The title compound was prepared according to **General procedure C** and purified by column chromatography to give a yellow solid (**3h:** 138 mg, 84% yield), dr > 20:1. M. p.: 140-142 °C. IR (neat) ν(cm^{-1}): 2917, 2838, 2729, 1751, 1675, 1507. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.30 (s, 3H), 1.86 (ddd, J_1 = 14.1 Hz, J_2 = 4.4 Hz, J_3 = 1.4 Hz, 1H), 3.07 (ddd, J_1 = 14.1 Hz, J_2 = 10.1 Hz, J_3 = 4.0 Hz, 1H), 3.26 (s, 3H), 3.77 (s, 3H), 3.85 (s, 3H), 3.89 (s, 3H), 4.53 (dd, J_1 = 10.0 Hz, J_2 = 4.4 Hz, 1H), 5.06 (s, 1H), 5.67 (d, J = 3.2 Hz, 1H), 6.54 (s, 1H), 7.01 (s, 1H), 7.24 (s, 1H), 10.21 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.1, 34.2, 37.9, 49.2, 55.3, 56.0, 56.4, 56.5, 76.5, 106.6, 108.9, 109.8, 112.0, 128.5, 128.8, 130.5, 137.4, 148.0, 148.9, 149.9, 153.0, 174.9, 189.7; **HRMS** (ESI) calcd. for $C_{23}H_{24}O_7Na$ [M+Na]: 435.1420, found: 435.1421.

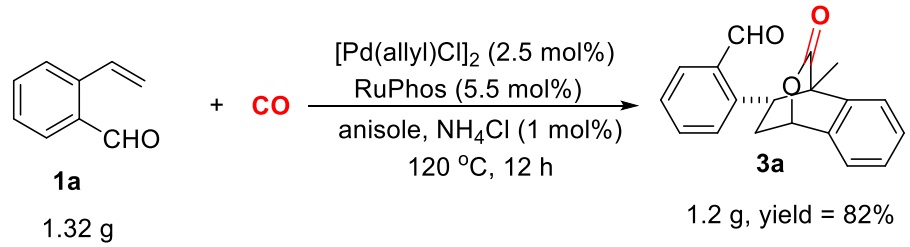
6-(8-methyl-10-oxo-5,6,7,8-tetrahydro-5,8-(epoxymethano)naphtho[2,3-d][1,3]dioxol-7-yl)benzo[d][1,3]dioxole-5-carbaldehyde (*endo*-3i): The title compound was prepared according to **General procedure C** and purified by column chromatography to give a white solid (**3i:** 111 mg, 73% yield), dr > 20:1. M. p.: 192-194 °C. IR (neat) ν(cm^{-1}): 2989, 2933, 2897, 2774, 1750, 1666, 1614, 1504, 1485. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.32 (s, 3H), 1.78 (ddd, J_1 = 14.1 Hz, J_2 = 4.7 Hz, J_3 = 1.4 Hz, 1H), 3.03 (ddd, J_1 = 14.2 Hz, J_2 = 10.1 Hz, J_3 = 4.1 Hz, 1H), 4.57 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 5.20 (s, 1H), 5.64 (d, J = 3.2 Hz, 1H), 5.96-6.06 (m, 4H), 6.58 (s, 1H), 6.95 (s, 1H), 7.26 (d, J = 3.2 Hz, 1H), 10.19 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.3, 34.4, 37.7, 49.3, 76.6, 101.7, 102.2, 104.4, 106.5, 107.6, 110.0, 129.9, 130.2, 131.6, 139.7, 147.3, 147.5, 148.6, 152.1, 174.8, 189.4; **HRMS** (ESI) calcd. for $C_{21}H_{16}O_7Na$ [M+Na]: 403.0794, found: 403.0784.

2-(1-methyl-12-oxo-1,2,3,4-tetrahydro-4,1-(epoxymethano)phenanthren-2-yl)-1-naphthaldehyde (*endo*-3j): The title compound was prepared according to **General procedure C** and purified by column chromatography to give a light white solid (**3j:** 75 mg, 48% yield), dr > 20:1. M. p.: 186-188 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.52 (s, 3H), 2.00 (ddd, J_1 = 14.2 Hz, J_2 = 5.1 Hz, J_3 = 1.3 Hz, 1H), 3.27 (ddd, J_1 = 14.3 Hz, J_2 = 10.0 Hz, J_3 = 4.3 Hz, 1H), 4.50 (q, J = 5.0 Hz, 1H), 5.54 (d, J = 8.9 Hz, 1H), 6.62 (d, J = 3.2 Hz, 1H), 7.21 (d, J = 3.2 Hz, 1H), 7.44 (d, J = 9.0 Hz, 1H), 7.49-7.52 (m, 1H), 7.59-7.65 (m, 2H), 7.93 (d, J = 8.5 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H), 8.48 (d, J = 8.7 Hz, 1H), 11.10 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 14.5, 36.6, 37.2, 49.9, 72.7, 121.9, 122.4, 124.0, 124.1, 126.6, 127.2, 127.7, 128.5, 128.6, 129.3, 129.5, 130.9, 132.3, 132.4, 132.9, 133.3, 134.2, 134.3, 140.8, 175.2, 194.3; **HRMS** (ESI) calcd. for $C_{27}H_{21}O_3Na$ [M+Na]: 415.1310, found: 415.1307.



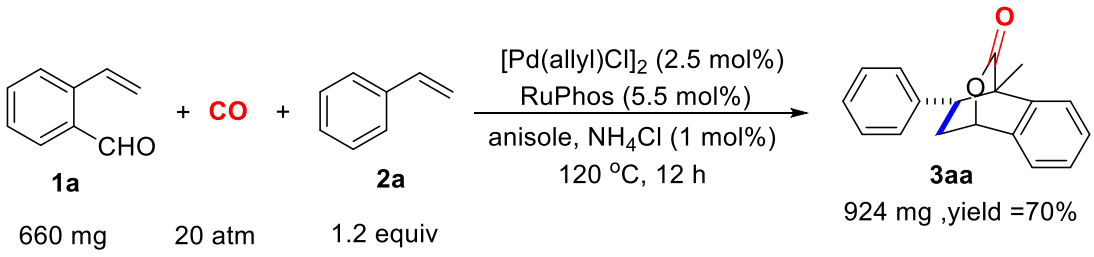
6. Synthetic Applications

6.1 Large scale synthesis of 3a



In the glove box, a mixture of 2-vinylbenzaldehyde **1a** (1.32 g, 10.0 mmol), NH_4Cl (2.7 mg, 0.05 mmol, 1 mol%), $[Pd(allyl)Cl]_2$ (46 mg, 0.125 mmol, 2.5 mol%), RuPhos (128.0 mg, 0.275 mmol, 5.5 mol%) and anisole (10.0 mL) were added to a dry glass vessel. The glass vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (20 atm). The reaction mixture was stirred at 120 °C for 12 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. The solvent was evaporated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (PE/EA = 3:1) to afford the product **3a** (1.2 g, 82% yield, *endo*/*exo* > 20/1).

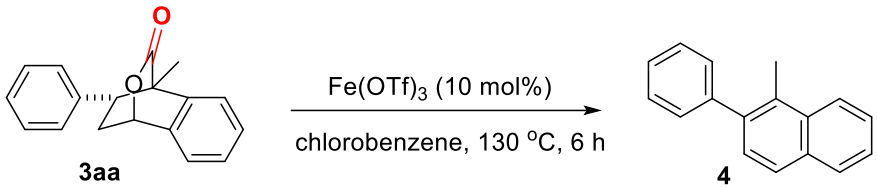
6.2 Large scale synthesis of 3aa



In the glove box, a mixture of 2-vinylbenzaldehyde **1a** (660 mg, 5.0 mmol), styrene **2a** (612 mg, 6.0 mmol), NH_4Cl (2.7 mg, 0.05 mmol, 1 mol%), $[Pd(allyl)Cl]_2$ (46 mg, 0.125 mmol, 2.5 mol%), RuPhos (128 mg, 0.275 mmol, 5.5 mol%), and anisole (10.0 mL) were added to a dry glass vessel. The glass vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (20 atm). The reaction mixture was stirred at 120 °C for 12 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in

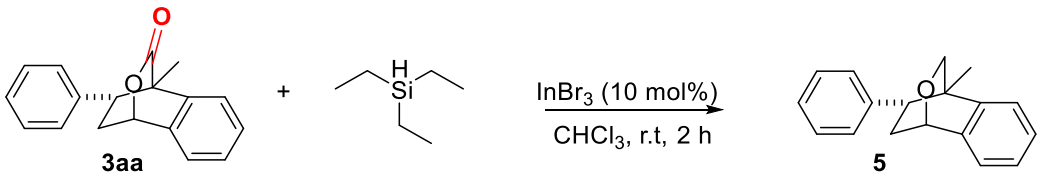
the fume hood. The solvent was evaporated under reduced pressure and the resulting residue was purified by column chromatography on silica gel to afford the product **3aa** (924 mg, 70% yield, *endo*/*exo* > 20/1).

6.3 Synthesis of 1-methyl-2-phenylnaphthalene 4



In a dry Young-type tube, $Fe(OTf)_3$ (0.076 mmol, 38 mg), **3aa** (0.76 mmol, 200 mg), and chlorobenzene (2.0 mL) were added under air atmosphere. Then the mixture was stirred at 130 °C for 6 hours. The solvent was evaporated under reduced pressure and the resulting residue was purified by column chromatography on silica gel to afford the product **4** (137 mg, 84% yield). The spectral data matched those reported previously.[3] M. p.: 85-88 °C. IR (neat) ν(cm^{-1}): 3053, 2921, 1595, 1490, 1443, 1380. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.59 (s, 3H), 7.33-7.57 (m, 7H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 16.4, 124.7, 125.6, 126.0, 126.3, 126.9, 128.2, 128.4, 128.6, 129.9, 130.9, 132.8, 133.1, 139.2, 142.8.

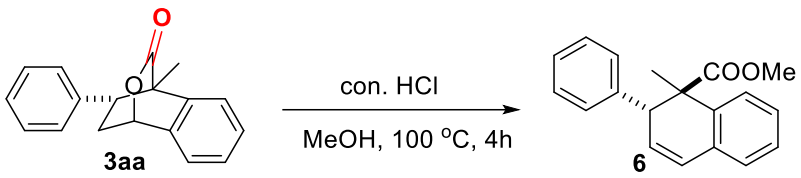
6.4 Synthesis of (1S,3S,4R)-4-methyl-3-phenyl-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalene 5 [4]



To a freshly distilled $CHCl_3$ solution (2.0 mL) in a screw-capped vial under N_2 atmosphere were added successively **3aa** (0.2 mmol, 53 mg), $InBr_3$ (0.005 mmol), triethylsilane (1.0 mmol, 116 mg), and the vial was sealed with a cap containing a PTFE septum. The reaction was monitored by GC analysis until consumption of the starting ester. After the reaction finished, H_2O (3 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (15 mL), the combined organic phase was dried over anhydrous Na_2SO_4, filtered, and then evaporated under reduced pressure. The crude product was

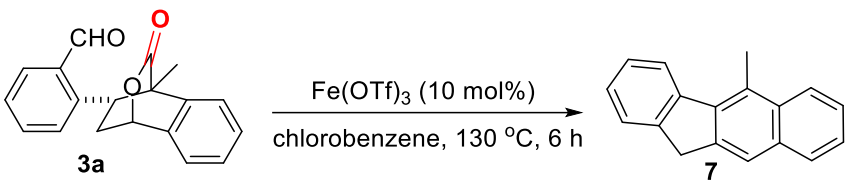
purified by flash column chromatography to give the corresponding ether **5** (35 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.07 (s, 3H), 1. 60 (ddd, J_1 = 14.3 Hz, J_2 = 4.0 Hz, J_3 = 1.5 Hz, 1H), 2.86 (ddd, J_1 = 14.2 Hz, J_2 = 10.2 Hz, J_3 = 4.0 Hz, 1H), 2.97 (dd, J = 11.8 Hz, 1H), 3.21 (d, J = 7.6 Hz, 1H), 3.84 (d, J = 7.6 Hz, 1H), 4.98 (dd, J_1 = 4.0 Hz, J_2 = 1.6 Hz, 1H), 6.31 (m, 2H), 6.95 (d, J = 7.2 Hz, 1H), 7.02-7.11 (m, 3H), 7.28-7.37 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 16.6, 38.4, 39.7, 46.6, 70.5, 73.8, 122.3, 123.6, 126.4, 126.7, 127.8, 127.9, 128.6, 140.4, 140.4, 143.8; **HRMS** (ESI) calcd. for $C_{18}H_{19}OH$ $[M+H]^+$: 251.1430, found: 251.1431.

6.5 Synthesis of methyl 1-methyl-2-phenyl-1,2-dihydronaphthalene-1-carboxylate 6 [5]



In the air atmosphere, a mixture of **3aa** (0.46 mmol, 120 mg), Concentrated hydrochloric acid (0.1 ml, 2.0 eq.), and MeOH (2.0 mL) were added to Young-type tube under air atmosphere. The reaction mixture was stirred at 100 °C for 4 hours. The solvent was evaporated under reduced pressure and the resulting residue was purified by column chromatography on silica gel to afford the product **6** (106 mg, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.26 (s, 3H), 3.70 (s, 3H), 4.40 (s, 1H), 6.09 (dd, J_1 =14.0 Hz, J_2 = 4.0 Hz, 1H), 6.60 (d, J = 9.6 Hz, 1H), 7.04-7.15 (m, 4H), 7.21-7.26 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.1, 48.4, 52.1, 52.5, 126.3, 126.6, 127.3, 127.6, 127.8, 128.2, 128.3, 129.5, 131.6, 132.8, 137.5, 139.0, 171.1; **HRMS** (ESI) calcd. for $C_{19}H_{19}O_2$ $[M+H]^+$: 279.1380, found: 279.1385.

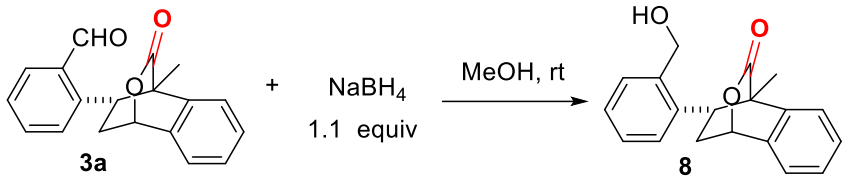
6.6 Synthesis of 5-methyl-11H-benzo[b]fluorene 7



In a dry Young-type tube, a mixture of **3a** (0.3 mmol, 88 mg), $Fe(OTf)_3$ (0.03 mmol, 17 mg) and chlorobenzene (2.0 mL) were added under air atmosphere. The reaction

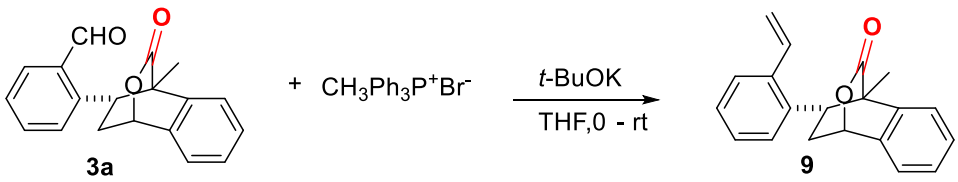
mixture was stirred at 130 °C for 6 hours. The solvent was evaporated under reduced pressure and the resulting residue was purified by column chromatography on silica gel to afford the product **7** (66 mg, 88% yield). M. p.: 166-169 °C. IR (neat) ν(cm^{-1}): 3049, 2926, 2856, 1464. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.06 (s, 3H), 4.09 (s, 2H), 7.25-7.35 (m, 1H), 7.37-7.52 (m, 3H), 7.54-7.60 (m, 1H), 7.84-7.86 (m, 2H), 8.15-8.21 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 15.4, 36.7, 121.6, 124.2, 124.5, 125.2, 125.3, 125.3, 126.9, 127.0, 128.4, 128.6, 132.6, 133.1, 138.2, 141.3, 142.6, 144.5. **HRMS** (ESI) calcd. for $C_{18}H_{15}$ [M+H]: 231.1174, found: 231.1171.

6.7 Synthesis of (1S,3S,4R)-3-(2-(hydroxymethyl)phenyl)-4-methyl-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one 8



To a stirred solution of **3a** (350 mg, 1.2 mmol) in MeOH (5.0 mL) at 0 ℃ $NaBH_4$ (50 mg, 1.1 equiv) was added. The reaction mixture was stirred at room temperature for 4 hours and then evaporated under reduced pressure. Water (3 mL) was added, then the mixture was extracted with EtOAc (3 ×5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Flash column chromatography on silica gel afforded the alcohol **8** (324 mg, 92% yield). M. p.: 163-166 °C. IR (neat) ν(cm^{-1}): 3485, 3066, 2986, 2932, 1749. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.39 (s, 3H), 1.76-1.81 (m, 2H), 3.08 (ddd, J_1 = 14.2 Hz, J_2 = 10.2 Hz, J_3 = 4.0 Hz, 1H), 3.77 (dd, J_1 = 10.4 Hz, J_2 = 4.8 Hz, 1H), 4.66 (d, J = 12.0 Hz, 1H), 4.90 (dd, J_1 = 12.0 Hz, J_2 = 3.2 Hz, 1H), 5.47 (d, J = 3.8 Hz, 1H), 5.74(d, J = 7.6 Hz, 1H), 6.86(t, J = 7.6 Hz, 1H),7.09-7.14 (m, 2H), 7.29 (d, J = 7.6 Hz, 1H), 7.37-7.43 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.9, 36.6, 38.3, 49.7, 63.9, 77.2, 122.5, 125.3, 127.1, 127.2, 127.9, 128.3, 128.8, 129.1, 136.5, 138.3, 139.4, 139.4, 175.7; **HRMS** (ESI) calcd. for $C_{19}H_{18}O_3Na$ [M+Na] $^{+}$: 317.1148, found: 317.1149.

6.8 Synthesis of (1S,3S,4R)-4-methyl-3-(2-vinylphenyl)-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalen-9-one 9[1]



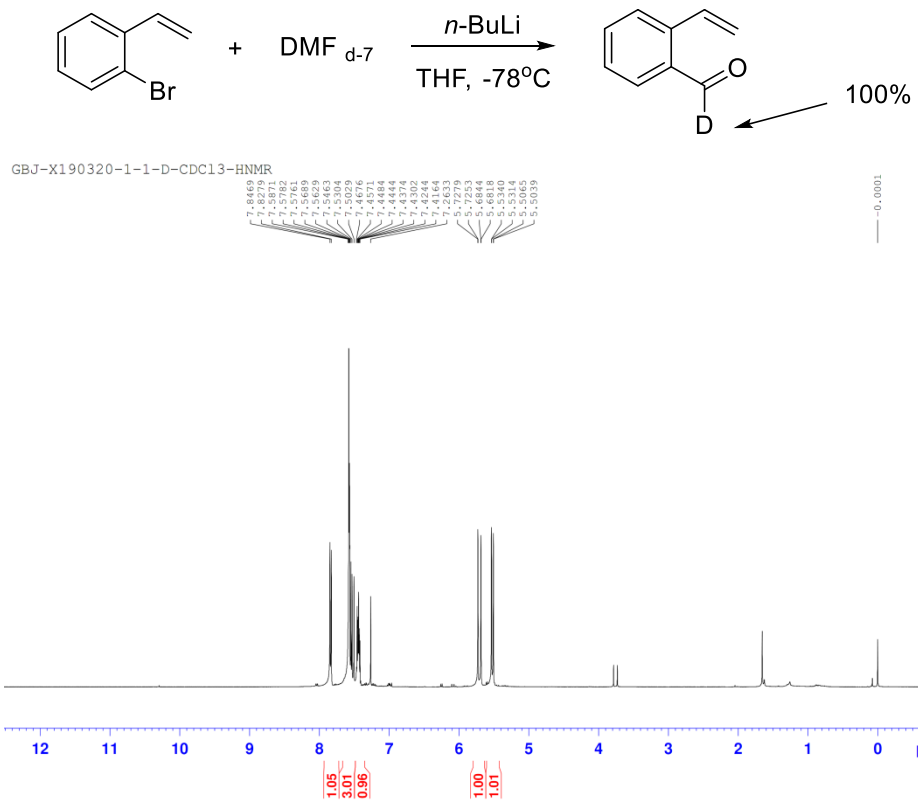
In a dry flask under N_2 atmosphere, *t*-BuOK (115 mg 1.5 equiv.) was added to a suspension of methyltriphenylphosphonium bromide (324 mg, 1.3 equiv.) in dry THF (5.0 mL) at 0 ℃ and then the mixture was stirred for 30 minutes. **3a** (0.685 mmol, 200 mg) was added slowly and the reaction was stirred for 5 hours at room temperature. After filtration over Celite, petroleum ether was added to the filtrate and the suspension was filtered again over Celite. The solvent was evaporated under reduced pressure to give the crude material. Purification through column chromatography on silica gel to afford the product **9** (180 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.36 (s, 3H), 1.79 (dd, J_1 = 14.2, J_2 = 4.8 Hz, 1H), 3.00 (ddd, J_1 = 14.0 Hz, J_2 = 10.2 Hz, J_3 = 4.2 Hz, 1H), 3.75 (dd, J_1 = 10.4 Hz, J_2 = 4.8 Hz, 1H), 5.36 (m, 2H), 5.55 (d, J = 17.2 Hz, 1H), 5.72 (d, J = 3.8 Hz, 1H), 6.80 (t, J = 7.6 Hz, 1H), 7.03 (d, J = 7.4 Hz, 1H), 7.09-7.16 (m, 2H), 7.37-7.43 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.8, 36.9, 37.7, 50.1, 77.0, 118.0, 122.4, 125.3, 126.5, 126.7, 127.2, 127.6, 127.8, 129.1, 135.4, 136.4, 137.5, 138.0, 138.9, 175.7; **HRMS** (ESI) calcd. for $C_{20}H_{18}O_2Na$ $[M+Na]^+$: 313.1199, found: 313.1220.

7. Mechanistic studies

7.1 Kinetic isotope effect experiments

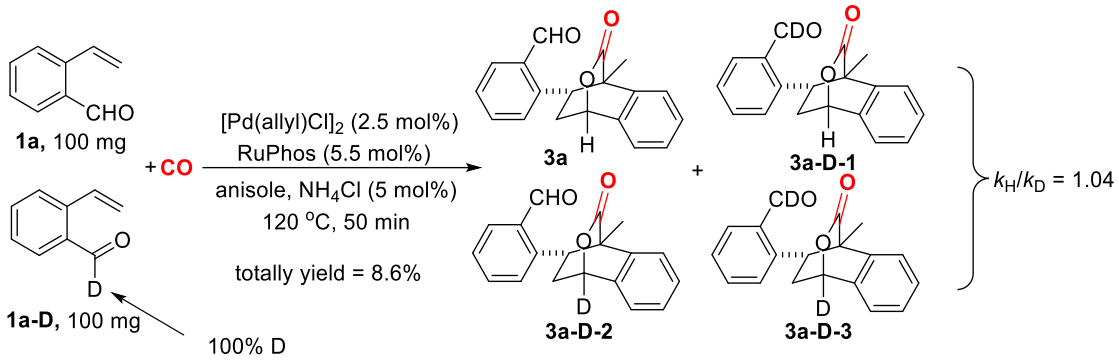
A 50 mL round-bottom flask containing 2-bromostyrene (910 mg, 5 mmol) in THF (20.0 mL) was purged with N_2 and cooled to -78 ºC in an ethyl acetate / liquid nitrogen bath. *n*-BuLi (2.5 M in hexane, 2.4 mL, 6 mmol, 1.2 equiv.) was added dropwise to the solution and then the mixture was stirred at -78 ºC for 1 hour. A solution of $DMF_{d\text{-}7}$ (1.0 mL, 5 mmol, 1.0 equiv.) in THF (5.0 mL) was added and then the mixture was warmed slowly to room temperature and stirred overnight. The reaction was quenched (saturated NH_4Cl) and then the aqueous phase was extracted with diethyl ether and the organic extracts dried (Na_2SO_4). The solvent was evaporated under reduced pressure to

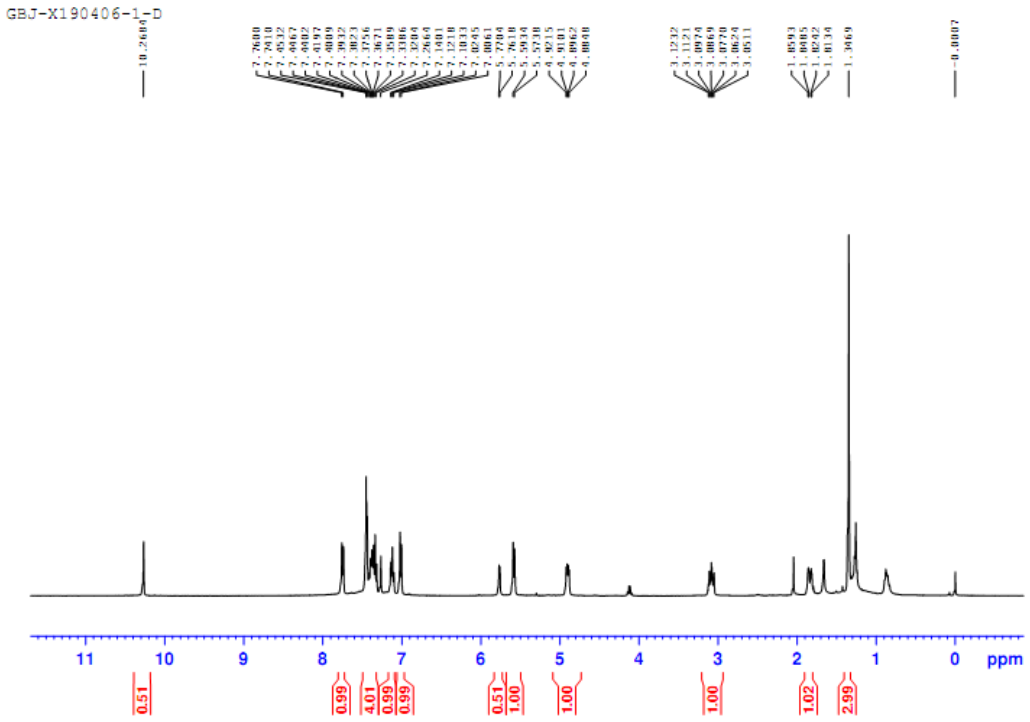
yield a crude product. Column chromatography (PE/EA = 10: 1) provided deuterium-labeling **1a-D** (460 mg, 70% yield, 100% D), The spectral data matched those reported previously.[6] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.50 (dd, J_1 = 11.0 Hz, J_2 = 1.0 Hz, 1H), 5.68 (dd, J_1 = 17.4 Hz, J_2 = 1.2 Hz, 1H), 7.42-7.47 (m, 1H), 7.50-7.59 (m, 3H), 7.83 (d, J = 7.6 Hz, 1H).



In the glove box, a mixture of 2-vinylbenzaldehyde **1a** (100 mg) and **1a-D** (100 mg), NH_4Cl (2.1 mg, 0.04 mmol, 5 mol%), $[Pd(allyl)Cl]_2$ (6.9 mg, 0.019 mmol, 2.5 mol%), RuPhos (19.4 mg, 0.082 mmol, 5.5 mol%), and anisole (4.0 mL) were added to a dry glass vessel. The glass vessel was put into an autoclave equipped with a sampler and then taken out from glove box. The autoclave was purged and charged with CO (20 atm). The reaction mixture was stirred at 120 °C for 50 minutes. After the reaction finished, the autoclave was rapidly cooled to room temperature and the pressure was carefully released in the fume hood. The solvent was evaporated under reduced pressure and the resulting residue was purified by column chromatography on silica gel to afford the product (**3a** + **3a-D-1** + **3a-D-2** + **3a-D-3**) (38.0 mg, 8.6% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.35 (s, 3H), 1.82-1.87 (m, 1H), 3.05-3.12 (m, 1H), 4.89 (dd, J_1 = 10.4 Hz, J_2 = 4.8 Hz, 1H), 5.57 (d, J = 8.0 Hz, 1H), 5.76 (d, J = 3.2 Hz, 0.51 H), 7.01 (d, J = 7.4 Hz, 1H), 7.10-7.15 (m, 1H), 7.32-7.47 (m, 4H), 7.74 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz,

1H), 10.27 (s, 0.51H).





7.2 Control experiments

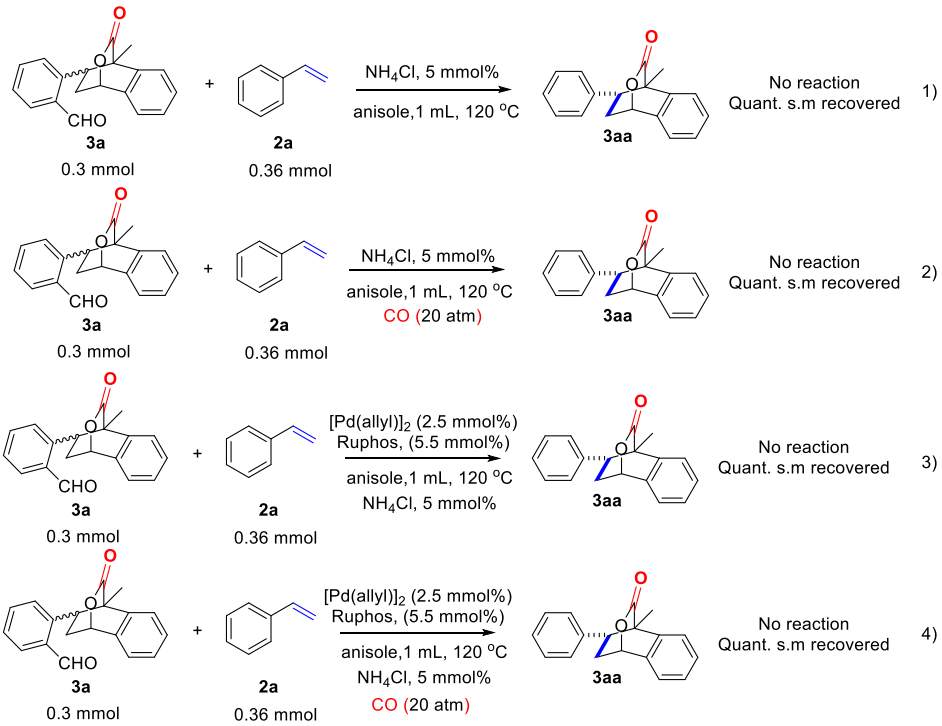
Reaction 1): In the glove box, a mixture of **3a** (0.3 mmol), styrene **2a** (0.36 mmol), NH_4Cl (0.025 mmol and anisole (1.0 mL) were added to Young-type tube under argon. The reaction mixture was stirred at 120 °C for 12 hours.

Reaction 2): In the glove box, a mixture of **3a** (0.3 mmol), styrene **2a** (0.36 mmol), NH_4Cl (0.025 mmol, 5 mol%) and anisole (1.0 mL) were added to a dry glass vessel. The glass vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (20 atm). The reaction mixture was stirred

at 120 °C for 12 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood.

Reaction 3): In the glove box, a mixture of **3a** (0.3 mmol), styrene **2a** (0.36 mmol), NH_4Cl (0.025 mmol $[Pd(allyl)Cl]_2$ (2.7 mg, 0.0075 mmol, 2.5 mol%), RuPhos (7.7 mg, 0.0165 mmol, 5.5 mol%) and anisole (1.0 mL) were added to Young-type tube under argon. The reaction mixture was stirred at 120 °C for 12 hours.

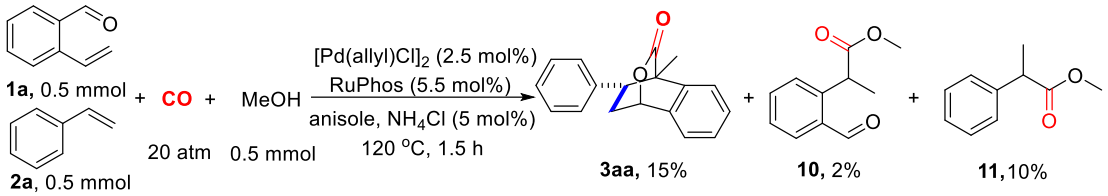
Reaction 4): In the glove box, a mixture of **3a** (0.3 mmol), styrene **2a** (0.36 mmol), NH_4Cl (0.025 mmol, 5 mol%), $[Pd(allyl)Cl]_2$ (2.7 mg, 0.0075 mmol, 2.5 mol%), RuPhos (7.7 mg, 0.0165 mmol, 5.5 mol%) and anisole (1.0 mL) were added to a dry glass vessel. The glass vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (20 atm). The reaction mixture was stirred at 120 °C for 12 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood.



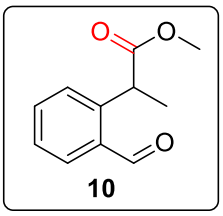
7.3 Competition experiments

In the glove box, a mixture of 2-vinylbenzaldehyde **1a** (0.5 mmol, 66 mg), styrene **2a** (0.5 mmol, 52 mg), MeOH (0.5 mmol, 16 mg), NH_4Cl (1.0 mg, 0.02 mmol, 5 mol%),

[Pd(allyl)Cl]$_2$ (4.6 mg, 0.025 mmol, 2.5 mol%), RuPhos (12.8 mg, 0.0275 mmol, 5.5 mol%), and anisole (1.0 mL) were added to a dry glass vessel. The glass vessel was put into an autoclave equipped with a sampler and then taken out from glove box. The autoclave was purged and charged with CO (20 atm). The reaction mixture was stirred at 120 °C for 1.5h. After the reaction finished, the autoclave was rapidly cooled to room temperature and the pressure was carefully released in the fume hood. The yield of **3aa**, **10** and **11** were determined by GC analysis using *n*-tetradecane as internal standard.

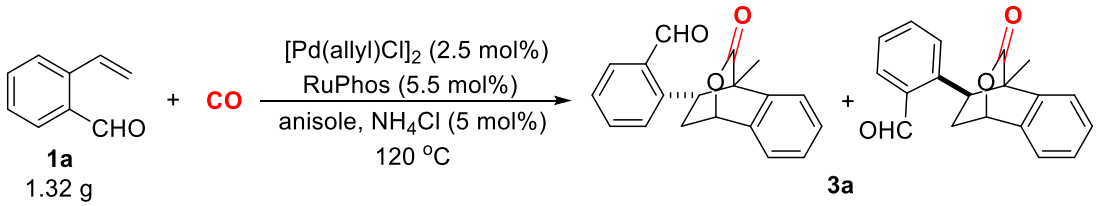


Methyl 2-(2-formylphenyl)propanoate 10:



^{1}H NMR (400 MHz, $CDCl_3$) δ 1.55 (d, J = 7.1 Hz, 3H), 3.67 (s, 3H), 4.84 (dd, J_1 = 14.1 Hz, J_2 = 7.0 Hz, 1H), 7.41-7.49 (m, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 10.19 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.3, 40.6, 52.2, 127.6, 128.7, 133.4, 134.2, 134.3, 142.4, 174.7, 193.0; **HRMS** (ESI) calcd. for $C_{11}H_{12}O_3Na$ [M+Na$^+$]: 215.0679, found: 215.0686.

7.4 Experiments for monitoring



In the glove box, a mixture of 2-vinylbenzaldehyde **1a** (1.32 g, 10.0 mmol), NH_4Cl (13 mg, 0.25 mmol, 5 mol%), [Pd(allyl)Cl]$_2$ (46 mg, 0.125 mmol, 2.5 mol%), RuPhos (128.0 mg, 0.275 mmol, 5.5 mol%), anisole (10.0 mL) and *n*-tetradecane were added to a dry glass vessel. The glass vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (20 atm). The reaction mixture was stirred at 120 °C. At each sampling time 0.2 mL reaction mixture was extracted and examined by GC. The yield of **3a** was determined using *n*-tetradecane as

internal standard by GC analysis.

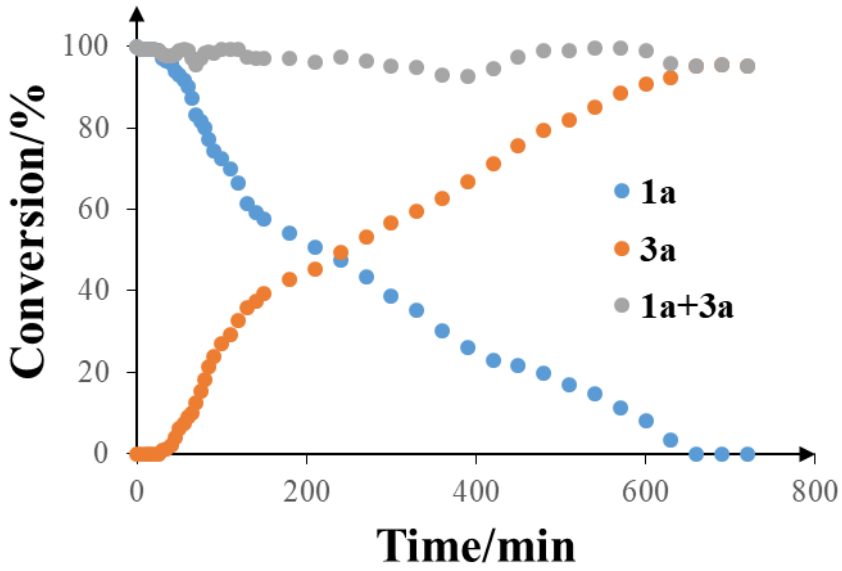
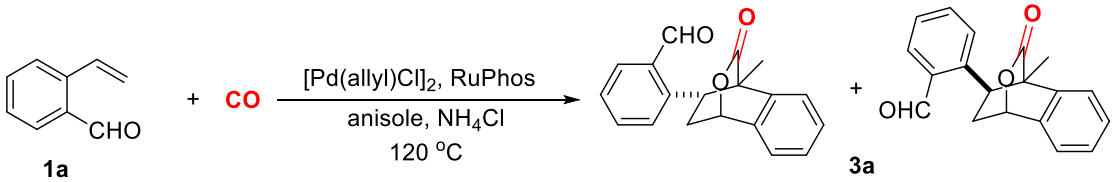


Figure S7. Reaction profiles under standard conditions.

7.5 Kinetic profiles of initial rates with 2-vinylbenzaldehyde 1a



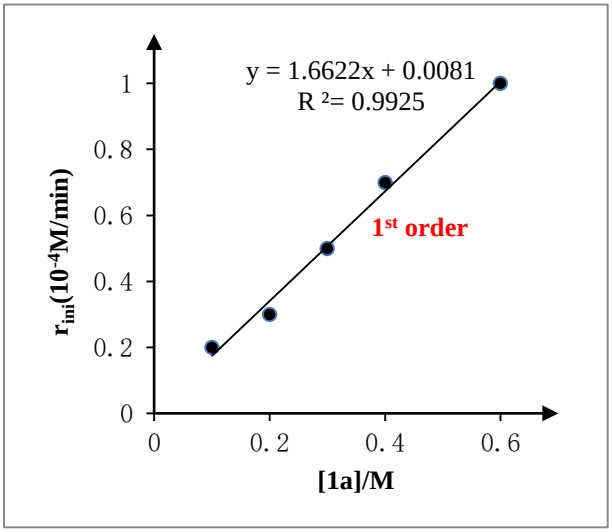


Figure S8. Plot of initial rates with respect to substrate *o*-alkenyl benzaldehyde **1a** showing first-order dependence.

Reaction conditions: 2-vinylbenzaldehyde **1a** (0.1-0.6 M), NH_4Cl (0.15 mmol), $[Pd(allyl)Cl]_2$ (0.075 mmol), RuPhos (0.165 mmol), anisole (10.0 mL), CO (20 atm), 120 °C.

Table 6. Kinetic profiles of initial rates with 2-vinylbenzaldehyde **1a**

Entry	1	2	3	4	5
1a concentration (M)	0.1	0.2	0.3	0.4	0.6
r_{ini} (10^{-4}M/min)	0.2	0.3	0.5	0.7	1.0

In the glove box, a mixture of NH_4Cl (0.15 mmol), $[Pd(allyl)Cl]_2$ (0.075 mmol), RuPhos (0.165 mmol), anisole (10.0 mL) and *n*-tetradecane were added to a dry glass vessel. Upon 2-vinylbenzaldehyde **1a** (1 mmol, 2 mmol, 3 mmol, 4 mmol, 6 mmol) was added to the tube. The glass vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (20 atm). The reaction mixture was stirred at 120 °C for designed time, take 0.2 mL from the reaction mixture, diluted with diethyl ether (2.0 mL), filtered on a silica gel, the resulting mixture was subjected to GC analysis.

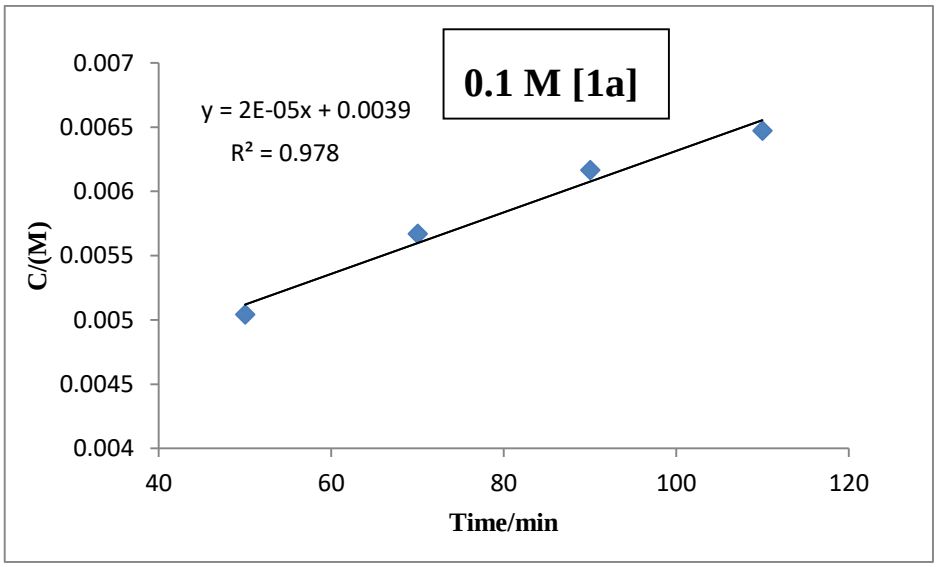


Figure S9. Kinetic profiles of initial rates with **[1a]** (0.1 M)

Reaction condition: 2-vinylbenzaldehyde **1a** (132 mg, 1.0 mmol), NH_4Cl (0.15 mmol), $[Pd(allyl)Cl]_2$ (0.075 mmol), RuPhos (0.165 mmol), anisole (10.0 mL), CO (20 atm), 120 °C.

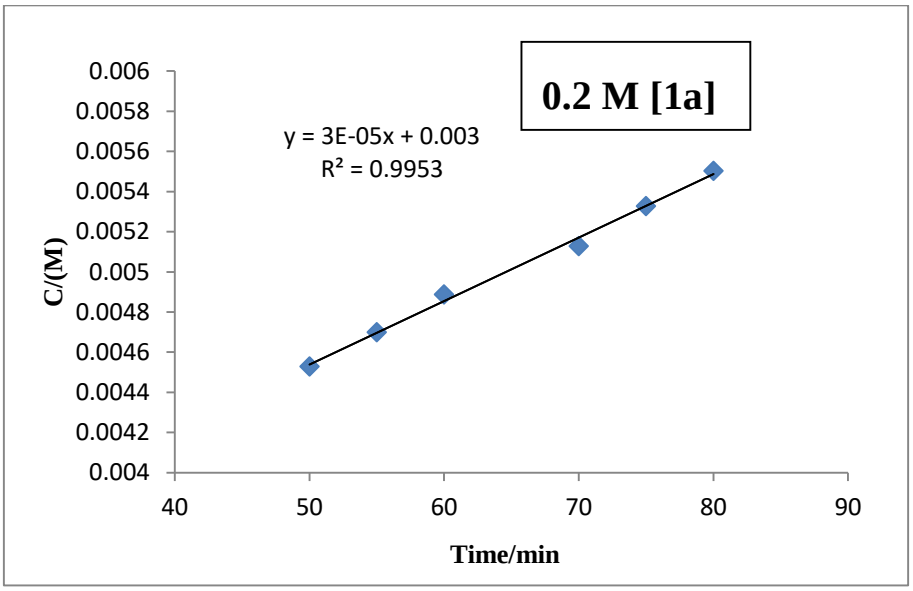


Figure S10. Kinetic profiles of initial rates with **[1a]** (0.2 M)

Reaction condition: 2-vinylbenzaldehyde **1a** (264 mg, 2 mmol), NH_4Cl (0.15 mmol), $[Pd(allyl)Cl]_2$ (0.075 mmol), RuPhos (0.165 mmol), anisole (10.0 mL), CO (20 atm), 120 °C.

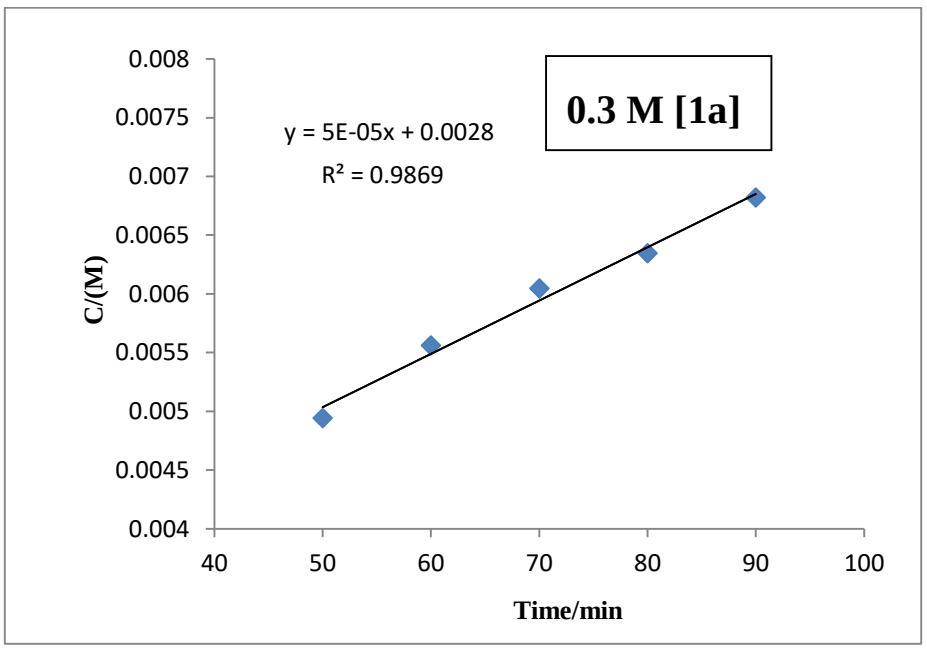


Figure S11. Kinetic profiles of initial rates with **[1a]** (0.3 M)

Reaction condition: 2-vinylbenzaldehyde **1a** (396 mg, 3 mmol), NH_4Cl (0.15 mmol), $[Pd(allyl)Cl]_2$ (0.075 mmol), RuPhos (0.165 mmol), anisole (10.0 mL), CO (20 atm), 120 °C.

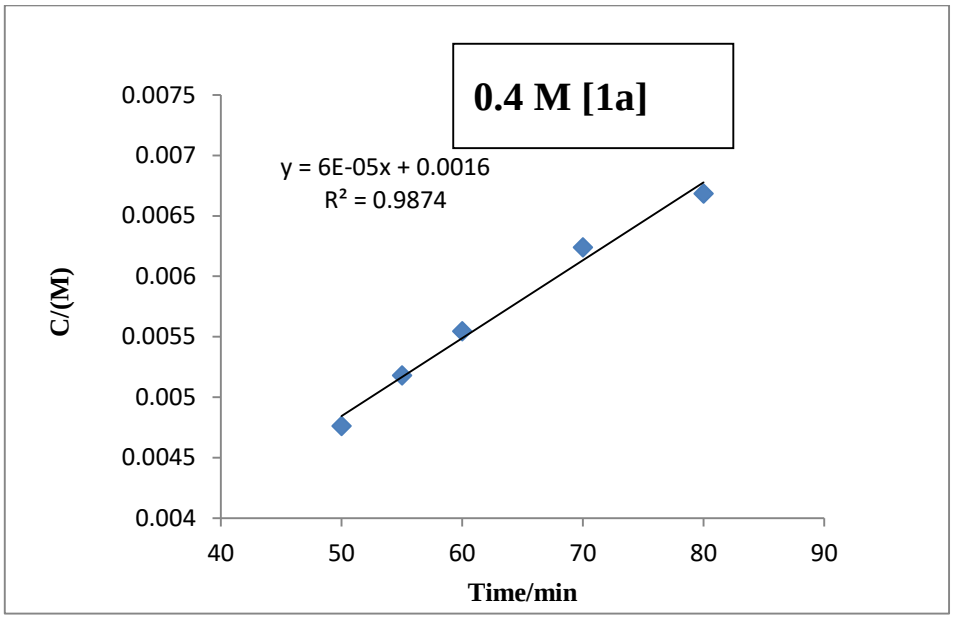


Figure S12. Kinetic profiles of initial rates with **[1a]** (0.4 M)

Reaction condition: 2-vinylbenzaldehyde **1a** (528 mg, 4 mmol), NH_4Cl (0.15 mmol), $[Pd(allyl)Cl]_2$ (0.075 mmol), RuPhos (0.165 mmol), anisole (10.0 mL), CO (20 atm), 120 °C.

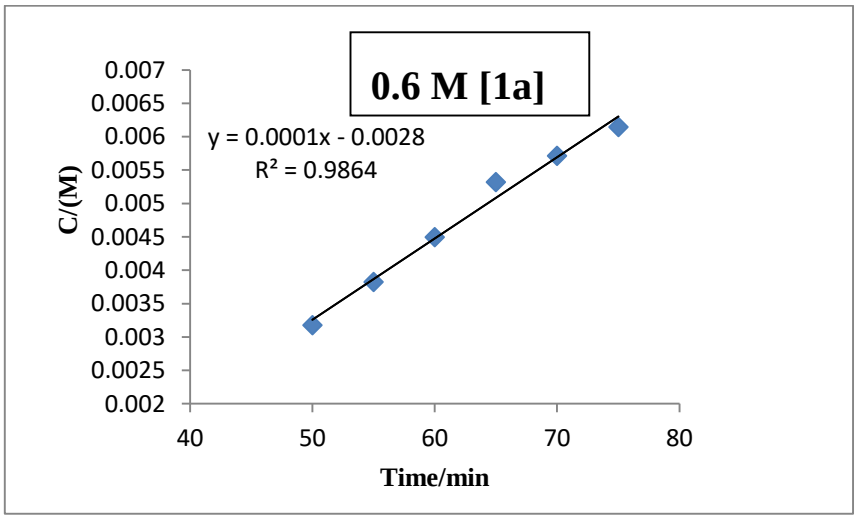
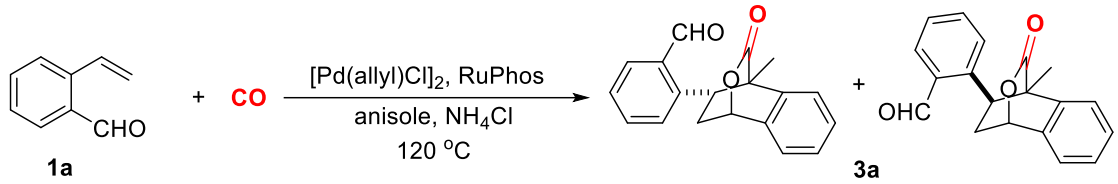


Figure S13. Kinetic profiles of initial rates with **[1a]** (0.6 M)

Reaction condition: 2-vinylbenzaldehyde **1a** (792 mg, 6 mmol), NH_4Cl (0.15 mmol), $[Pd(allyl)Cl]_2$ (0.075 mmol), RuPhos (0.165 mmol), anisole (10.0 mL), CO (20 atm), 120 °C.

7.6 Kinetic profiles of initial rates with [Pd]



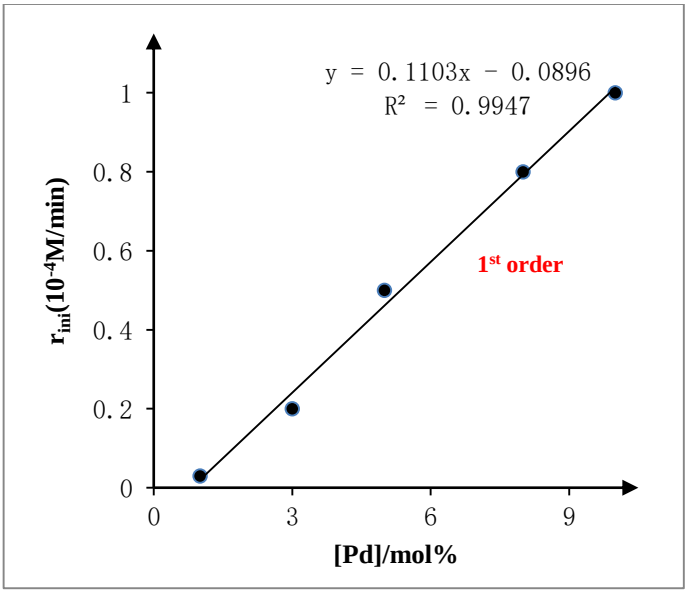


Figure S14. Plot of initial rates with respect to **[Pd]** showing first-order dependence. Reaction conditions: 2-vinylbenzaldehyde **1a** (4 mmol), NH_4Cl (0.02-0.2 mmol), $[Pd(allyl)Cl]_2$ (0.01-0.1 mmol), RuPhos (0.022-0.22 mmol), anisole (10.0 mL), CO (20 atm), 120 °C.

Table 7. Kinetic profiles of initial rates with **[Pd]**

Entry	1	2	3	4	5
Pd loading (mol%)	1	3	5	8	10
r_{ini} (10^{-4}M/min)	0.03	0.2	0.5	0.8	1.0

In the glove box, a mixture of 2-vinylbenzaldehyde **1a** (528 mg, 4 mmol), NH_4Cl (x mol%), [Pd] (x mol%), RuPhos (1.1x mol%) and anisole (10.0 mL) were added to a

dry glass vessel. The glass vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (20 atm), the time was started. The reaction mixture was stirred at 120 °C for designed time, take 0.2 mL from the reaction mixture, diluted with diethyl ether (2.0 mL), filtered on a silica gel, the resulting mixture was subjected to GC analysis.

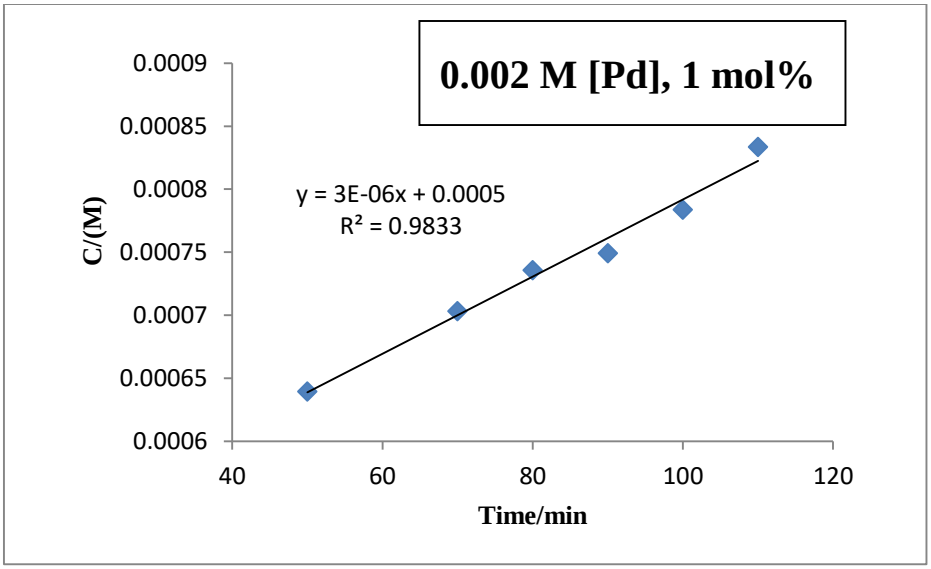


Figure S15. Kinetic profiles of initial rates with **[Pd]** (0.002 M, 1 mol%)

Reaction condition: $[Pd(allyl)Cl]_2$ (0.01 mmol, 0.5 mol%), RuPhos (0.022 mmol, 1.1 mol%), 2-vinylbenzaldehyde **1a** (4 mmol), NH_4Cl (0.02 mmol), anisole (10.0 mL), CO (20 atm), 120 °C.

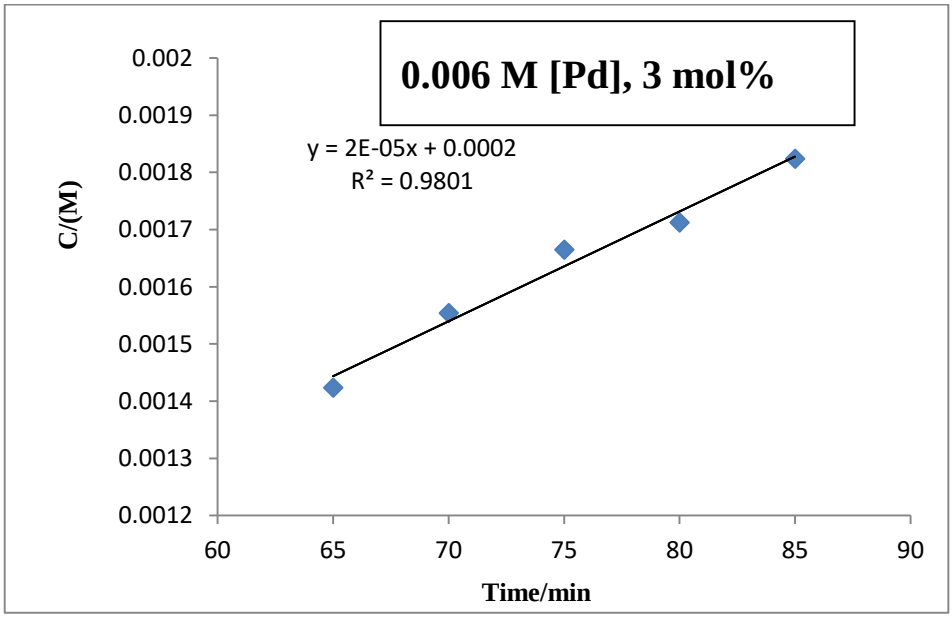


Figure S16. Kinetic profiles of initial rates with **[Pd]** (0.006 M, 3 mol%)

Reaction condition: $[Pd(allyl)Cl]_2$ (0.03 mmol, 1.5 mol%), RuPhos (0.07 mmol, 3.3 mol%), 2-vinylbenzaldehyde **1a** (4 mmol), NH_4Cl (0.06 mmol), anisole (10.0 mL), CO (20 atm), 120 °C.

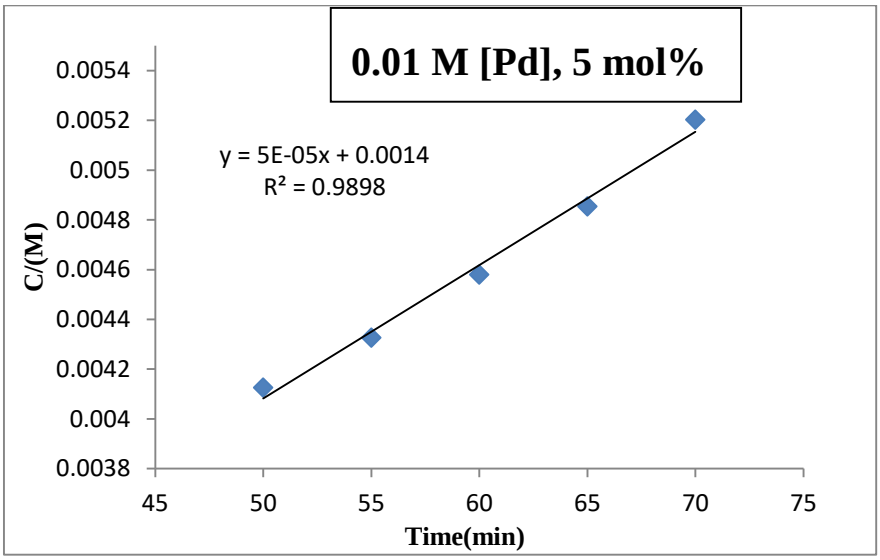


Figure S17. Kinetic profiles of initial rates with **[Pd]** (0.01 M, 5 mol%)

Reaction condition: $[Pd(allyl)Cl]_2$ (0.05 mmol, 2.5 mol%), RuPhos (0.11 mmol, 5.5 mol%), 2-vinylbenzaldehyde **1a** (4 mmol), NH_4Cl (0.1 mmol), anisole (10.0 mL), CO (20 atm), 120 °C.

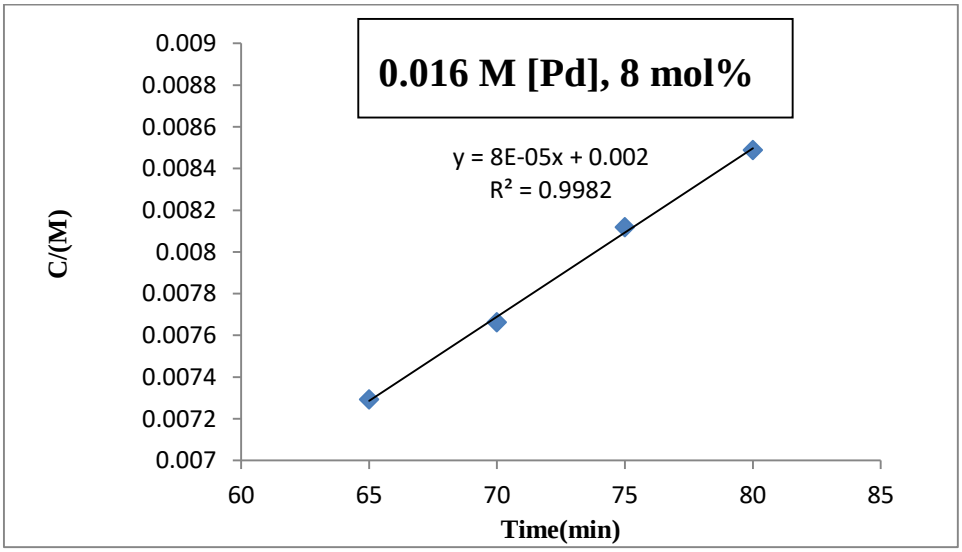


Figure S18. Kinetic profiles of initial rates with **[Pd]** (0.016 M, 8 mol%)

Reaction condition: $[Pd(allyl)Cl]_2$ (0.08 mmol, 4 mol%), RuPhos (0.18 mmol, 8.8 mol%), 2-vinylbenzaldehyde **1a** (4 mmol), NH_4Cl (0.16 mmol), anisole (10.0 mL), CO (20 atm), 120 °C.

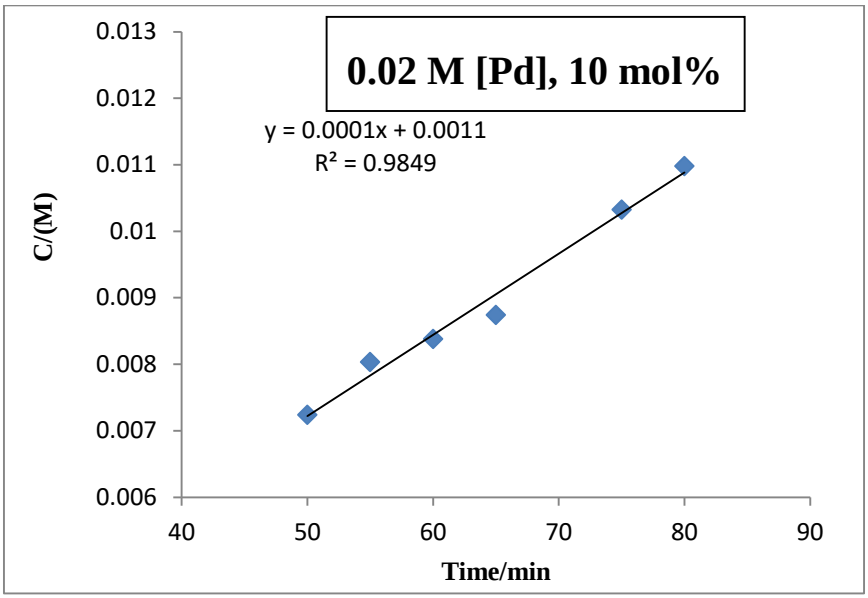
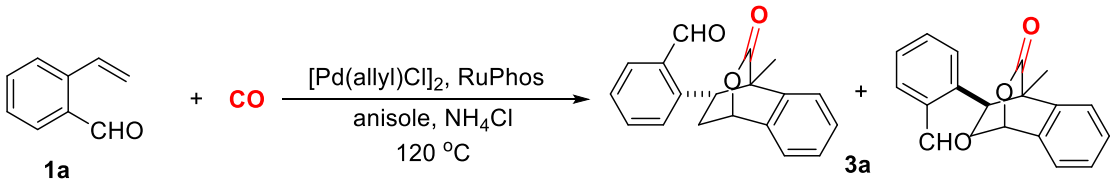


Figure S19. Kinetic profiles of initial rates with **[Pd]** (0.02 M, 10 mol%)

Reaction condition: $[Pd(allyl)Cl]_2$ (0.1 mmol, 5 mol%), RuPhos (0.22 mmol, 11 mol%), 2-vinylbenzaldehyde **1a** (4 mmol), NH_4Cl (0.2 mmol), anisole (10.0 mL), CO (20 atm), 120 °C.

7.7 Kinetic profiles of initial rates with CO



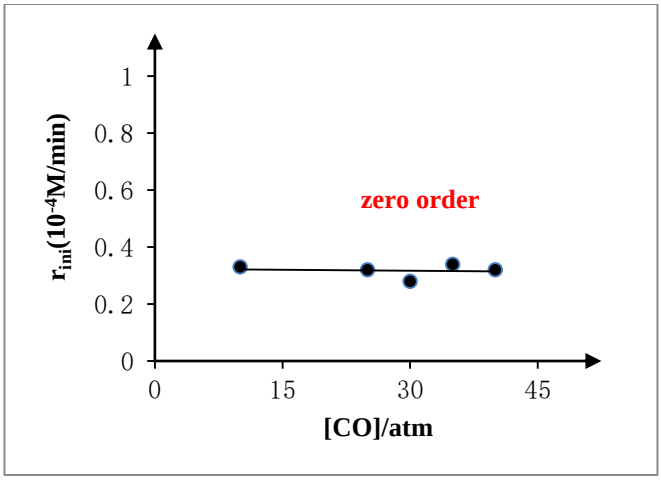


Figure S20. Plot of initial rates with respect to **[CO]** showing zero order dependence. Reaction conditions: CO (10-40 atm), 2-vinylbenzaldehyde **1a** (3 mmol), $[Pd(allyl)Cl]_2$ (0.0375 mmol, 2.5 mol%), RuPhos (0.083 mmol, 5.5 mol%), NH_4Cl (0.075 mmol, 5 mol%), anisole (10.0 mL), 120 °C.

Table 8. Kinetic profiles of initial rates with **[CO]**

Entry	1	2	3	4	5
CO loading (atm)	10	25	30	35	40
r_{ini} (10^{-4}M/min)	0.33	0.32	0.28	0.34	0.32

In the glove box, a mixture of 2-vinylbenzaldehyde **1a** (396 mg, 3 mmol), NH_4Cl (0.075 mmol, 5 mol%), $[Pd(allyl)Cl]_2$ (0.0375 mmol, 2.5 mol%), RuPhos (0.083 mmol, 5.5 mol%) and anisole (10.0 mL) were added to a dry glass vessel. The glass vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (10, 25, 30, 35, 40 atm), the time was started. The reaction mixture was stirred at 120 °C for designed time, take 0.2 mL from the reaction mixture, diluted with diethyl ether (2.0 mL), filtered on a silica gel, the resulting mixture was subjected to GC analysis.

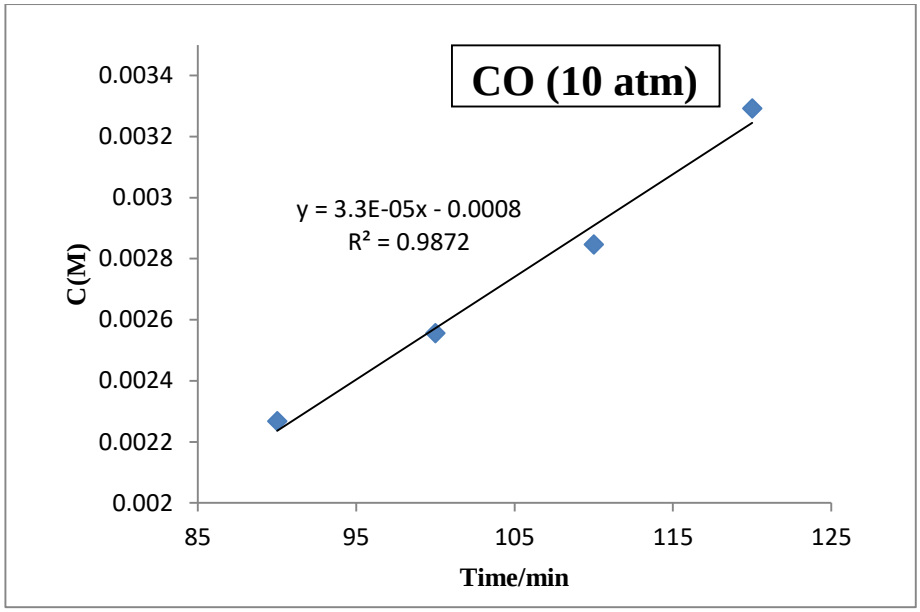


Figure S21. Kinetic profiles of initial rates with **CO** (10 atm)

Reaction condition: CO (10 atm), 2-vinylbenzaldehyde **1a** (3 mmol), $[Pd(allyl)Cl]_2$ (0.0375 mmol, 2.5 mol%), RuPhos (0.083 mmol, 5.5 mol%), NH_4Cl (0.075 mmol, 5 mol%), anisole (10.0 mL), 120 °C.

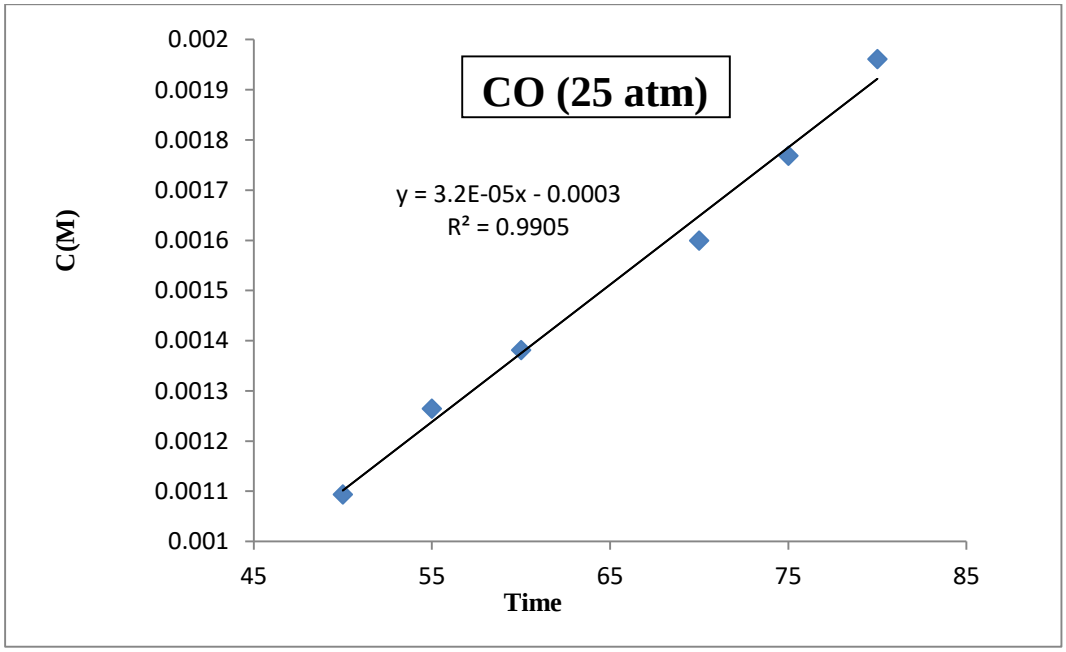


Figure S22. Kinetic profiles of initial rates with **CO** (25 atm)

Reaction condition: CO (25 atm), 2-vinylbenzaldehyde **1a** (3 mmol), $[Pd(allyl)Cl]_2$ (0.0375 mmol, 2.5 mol%), RuPhos (0.083 mmol, 5.5 mol%), NH_4Cl (0.075 mmol, 5 mol%), anisole (10.0 mL), 120 °C.

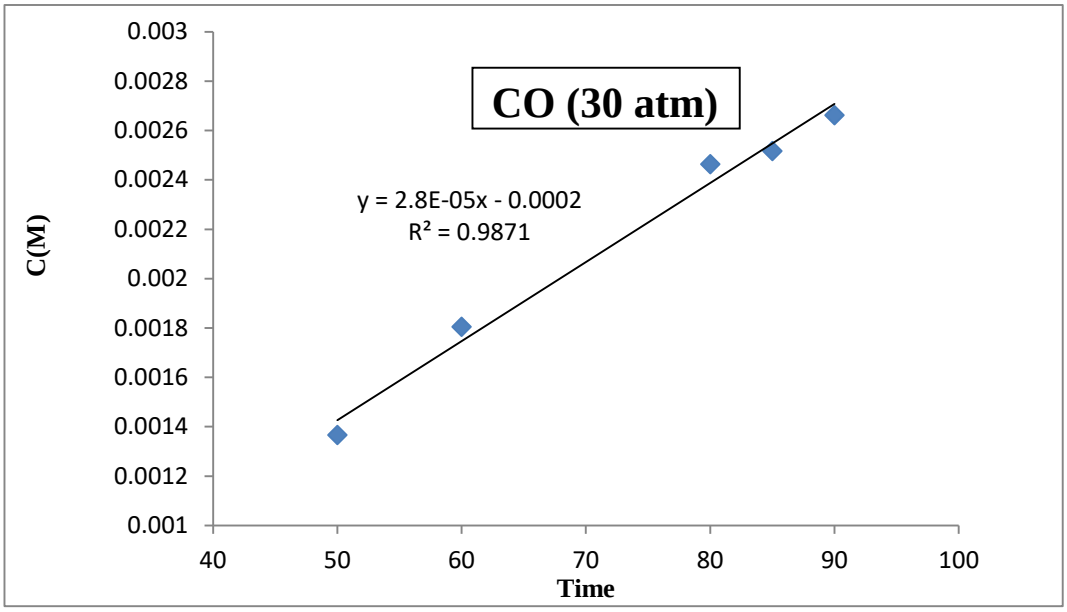


Figure S23. Kinetic profiles of initial rates with **CO** (30 atm)

Reaction condition: CO (30 atm), 2-vinylbenzaldehyde **1a** (3 mmol), $[Pd(allyl)Cl]_2$ (0.0375 mmol, 2.5 mol%), RuPhos (0.083 mmol, 5.5 mol%), NH_4Cl (0.075 mmol, 5 mol%), anisole (10.0 mL), 120 °C.

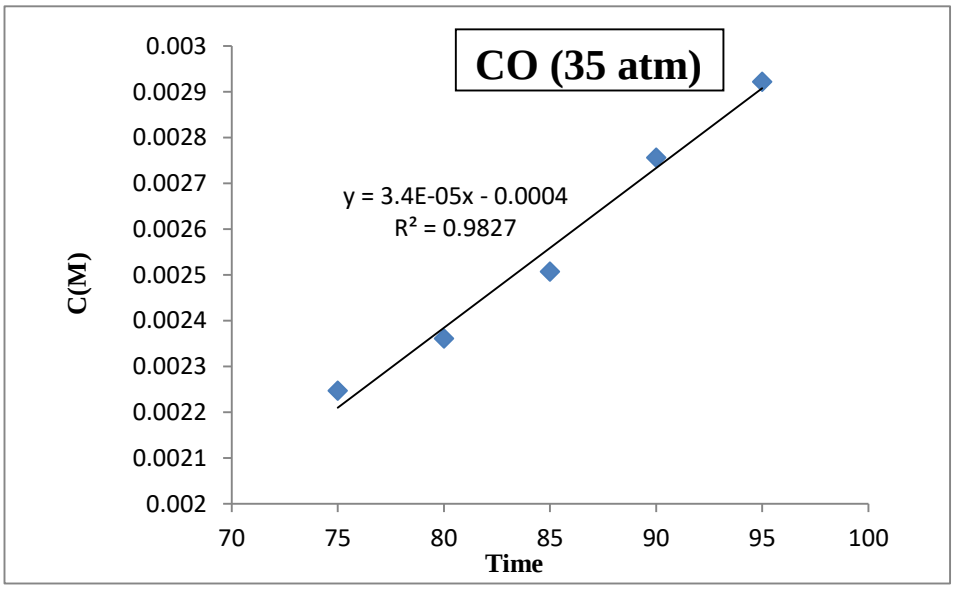


Figure S24. Kinetic profiles of initial rates with **CO** (35 atm)

Reaction condition: CO (35 atm), 2-vinylbenzaldehyde **1a** (3 mmol), $[Pd(allyl)Cl]_2$ (0.0375 mmol, 2.5 mol%), RuPhos (0.083 mmol, 5.5 mol%), NH_4Cl (0.075 mmol, 5 mol%), anisole (10.0 mL), 120 °C.

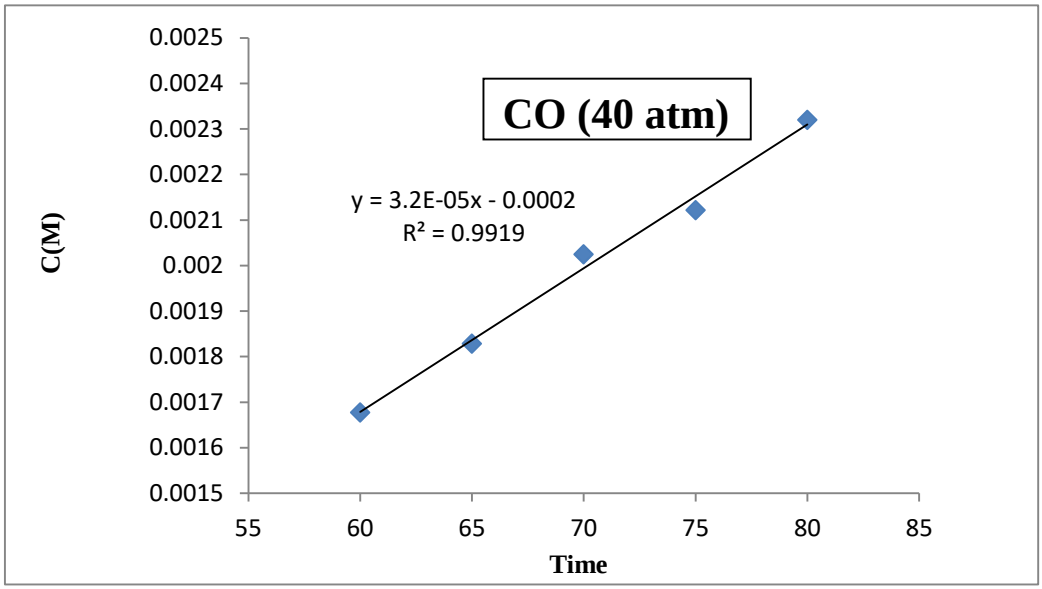
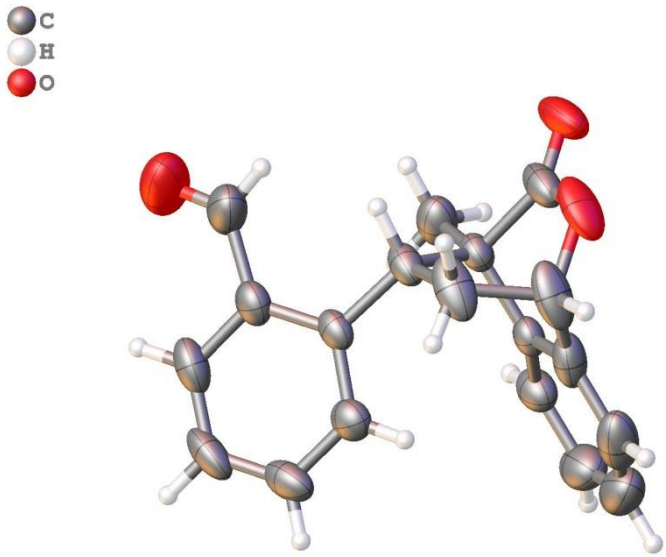


Figure S25. Kinetic profiles of initial rates with **CO** (40 atm)

Reaction condition: CO (40 atm), 2-vinylbenzaldehyde **1a** (3 mmol), $[Pd(allyl)Cl]_2$ (0.0375 mmol, 2.5 mol%), RuPhos (0.083 mmol, 5.5 mol%), NH_4Cl (0.075 mmol, 5 mol%), anisole (10.0 mL), 120 ^oC.

8. X-ray crystallographic data

Table 9. Crystal data and structure refinement for product *endo*-**3a**

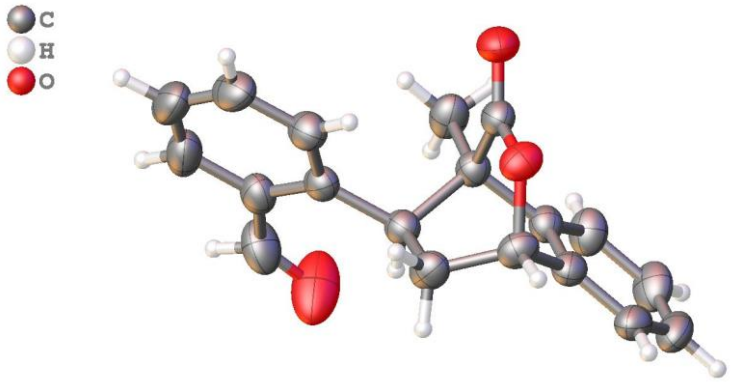


endo-**3a**

Identification code	GBJ-X190911-BZ
Empirical formula	$C_{19}H_{16}O_3$
Formula weight	292.32
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.03400(10)
b/Å	16.0025(2)
c/Å	13.2355(2)
α/°	90
β/°	100.3580(10)
γ/°	90
Volume/Å^3	1465.53(4)
Z	4
ρ_{calc}g/cm^3	1.325
μ/mm^{-1}	0.718
F(000)	616.0
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.756 to 146.36
Index ranges	-8 ≤ h ≤ 8, -19 ≤ k ≤ 19, -14 ≤ 1 ≤ 16

Reflections collected	5804
Independent reflections	2851 [R_{int} = 0.0212, R_{sigma} = 0.0248]
Data/restraints/parameters	2851/2/200
Goodness-of-fit on F^2	1.101
Final R indexes [I>=2σ (I)]	R_1 = 0.0936, wR_2 = 0.2227
Final R indexes [all data]	R_1 = 0.0978, wR_2 = 0.2285
Largest diff. peak/hole / e $Å^{-3}$	0.50/-0.63

Table 10. Crystal data and structure refinement for product *exo*-**3a**

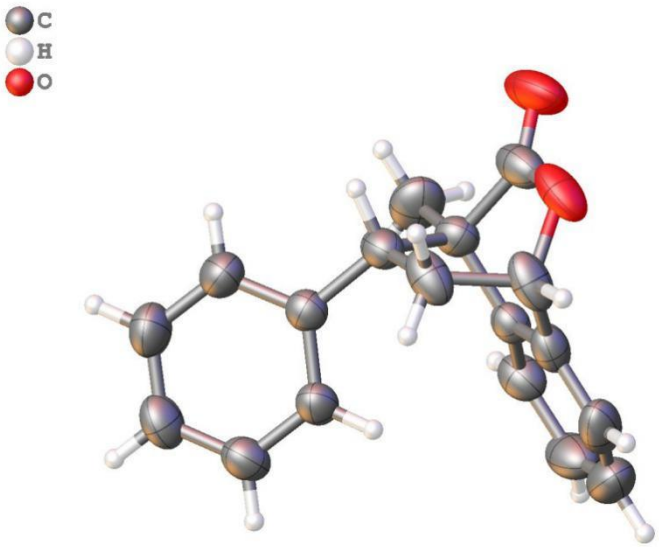


exo-**3a**

Identification code	Platon-tw
Empirical formula	$C_{38}H_{32}O_6$
Formula weight	584.63
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	20.5228(5)
b/Å	8.2219(2)
c/Å	17.4215(3)
α/°	90
β/°	96.111(2)
γ/°	90
Volume/$Å^3$	2922.94(11)
Z	4
$\rho_{calc}g/cm^3$	1.329

μ/mm^{-1}	0.720
F(000)	1232.0
Crystal size/mm^3	0.12 × 0.11 × 0.04
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.666 to 133.174
Index ranges	-24 ≤ h ≤ 24, -9 ≤ k ≤ 9, -20 ≤ 1 ≤ 20
Reflections collected	5160
Independent reflections	5160 [R_{int} = 0.0253, R_{sigma} = 0.0242]
Data/restraints/parameters	5160/0/400
Goodness-of-fit on F^2	1.110
Final R indexes [I>=2σ (I)]	R_1 = 0.0482, wR_2 = 0.1391
Final R indexes [all data]	R_1 = 0.0551, wR_2 = 0.1458
Largest diff. peak/hole / e Å^{-3}	0.19/-0.23

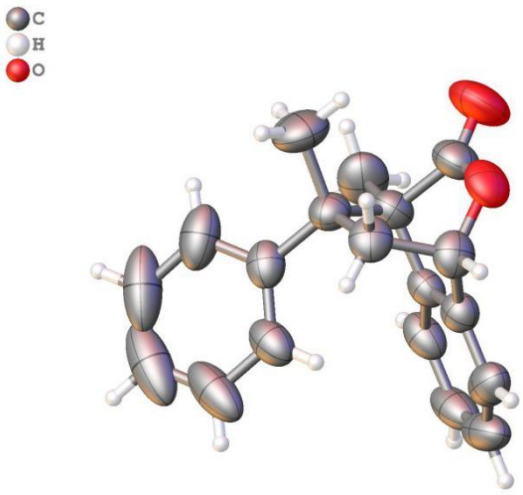
Table 11. Crystal data and structure refinement for product *endo*-**3aa**



	endo-**3aa**
Identification code	GBJ-X190308
Empirical formula	$C_{18}H_{16}O_2$
Formula weight	264.31
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.6891(4)
b/Å	7.0857(2)

c/Å	14.1959(5)
α/°	90
β/°	91.491(3)
γ/°	90
Volume/Å^3	1376.49(7)
Z	4
ρ_{calc}g/cm^3	1.275
μ/mm^{-1}	0.650
F(000)	560.0
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.86 to 147.318
Index ranges	-16 ≤ h ≤ 16, -5 ≤ k ≤ 8, -17 ≤ l ≤ 16
Reflections collected	4942
Independent reflections	2709 [R_{int} = 0.0186, R_{sigma} = 0.0250]
Data/restraints/parameters	2709/0/182
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0475, wR_2 = 0.1287
Final R indexes [all data]	R_1 = 0.0545, wR_2 = 0.1374
Largest diff. peak/hole / e Å^{-3}	0.17/-0.20

Table 12. Crystal data and structure refinement for product *endo*-**3am**

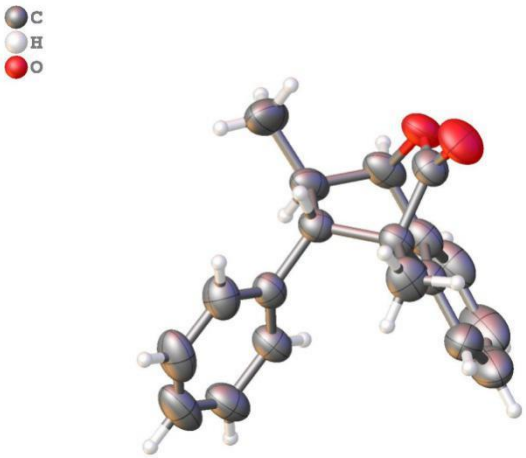


endo-**3am**

Identification code	GBJ-X190318
Empirical formula	$C_{19}H_{18}O_2$

Formula weight	278.33
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	7.2898(2)
b/Å	15.8113(4)
c/Å	25.4414(9)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	2932.41(15)
Z	8
$\rho_{calc}g/cm^3$	1.261
μ/mm^{-1}	0.635
F(000)	1184.0
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.948 to 147.6
Index ranges	$-5 \leq h \leq 8$, $-19 \leq k \leq 19$, $-30 \leq l \leq 15$
Reflections collected	6277
Independent reflections	2876 [R_{int} = 0.0210, R_{sigma} = 0.0218]
Data/restraints/parameters	2876/0/192
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0659, wR_2 = 0.1652
Final R indexes [all data]	R_1 = 0.0737, wR_2 = 0.1764
Largest diff. peak/hole / e $Å^{-3}$	0.23/-0.42

Table 13. Crystal data and structure refinement for product *endo*-**3an**



endo-**3an**

Identification code	GBJ-X18Z20-1-8
Empirical formula	$C_{19}H_{18}O_2$
Formula weight	278.33
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.4303(2)
b/Å	7.16982(9)
c/Å	14.45517(18)
α/°	90
β/°	90.2129(13)
γ/°	90
Volume/Å^3	1495.55(3)
Z	4
ρ_{calc}g/cm^3	1.236
μ/mm^{-1}	0.623
F(000)	592.0
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.642 to 147.728
Index ranges	$-17 \le h \le 17$, $-8 \le k \le 8$, $-17 \le l \le 18$
Reflections collected	12756
Independent reflections	2918 [R_{int} = 0.0315, R_{sigma} = 0.0186]
Data/restraints/parameters	2918/0/192
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0469, wR_2 = 0.1302

Final R indexes [all data]	R_1 = 0.0530, wR_2 = 0.1357
Largest diff. peak/hole / e $Å^{-3}$	0.13/-0.20

9. References

(1) A. Abengózar, P. García-García, D. Sucunza, A. Pérez-Redondo, and J. J. Vaquero, *Chem. Commun*. 2018, **54**, 2467.

(2) L. Jarrige, A. Carboni, G. Dagousset, G. Levitre, E. Magnier, and G. Masson. *Org. Lett*. 2016, **18**, 2906.

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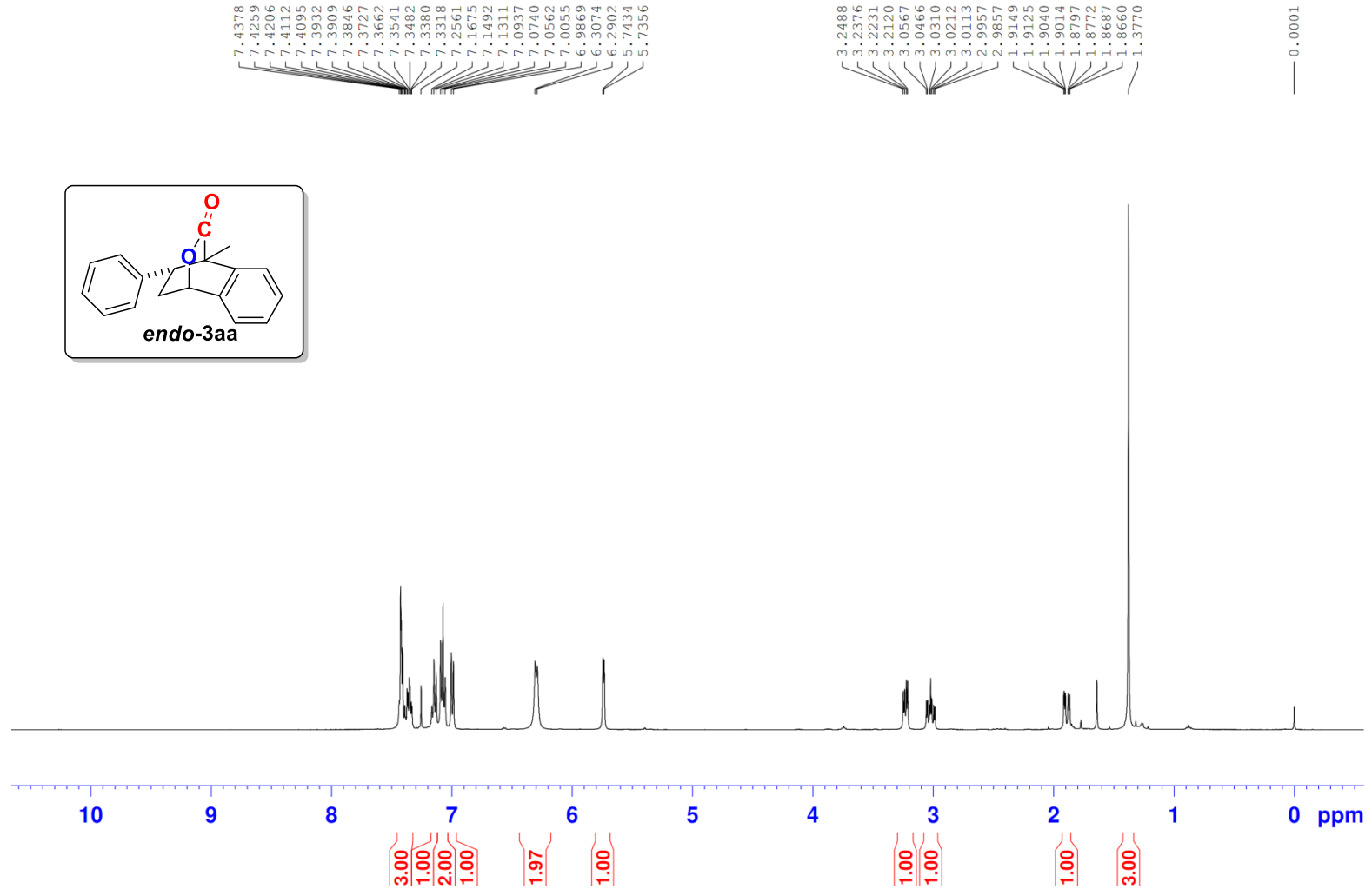
(4) N. Sakai, T. Moriya, and T. Konakahara, *J. Org. Chem*. 2007, **72**, 5920.

(5) D. A. Bleasdale, and D. W. Jones. *J. Chem. Soc., Chem. Commun*. 1985, 1027.

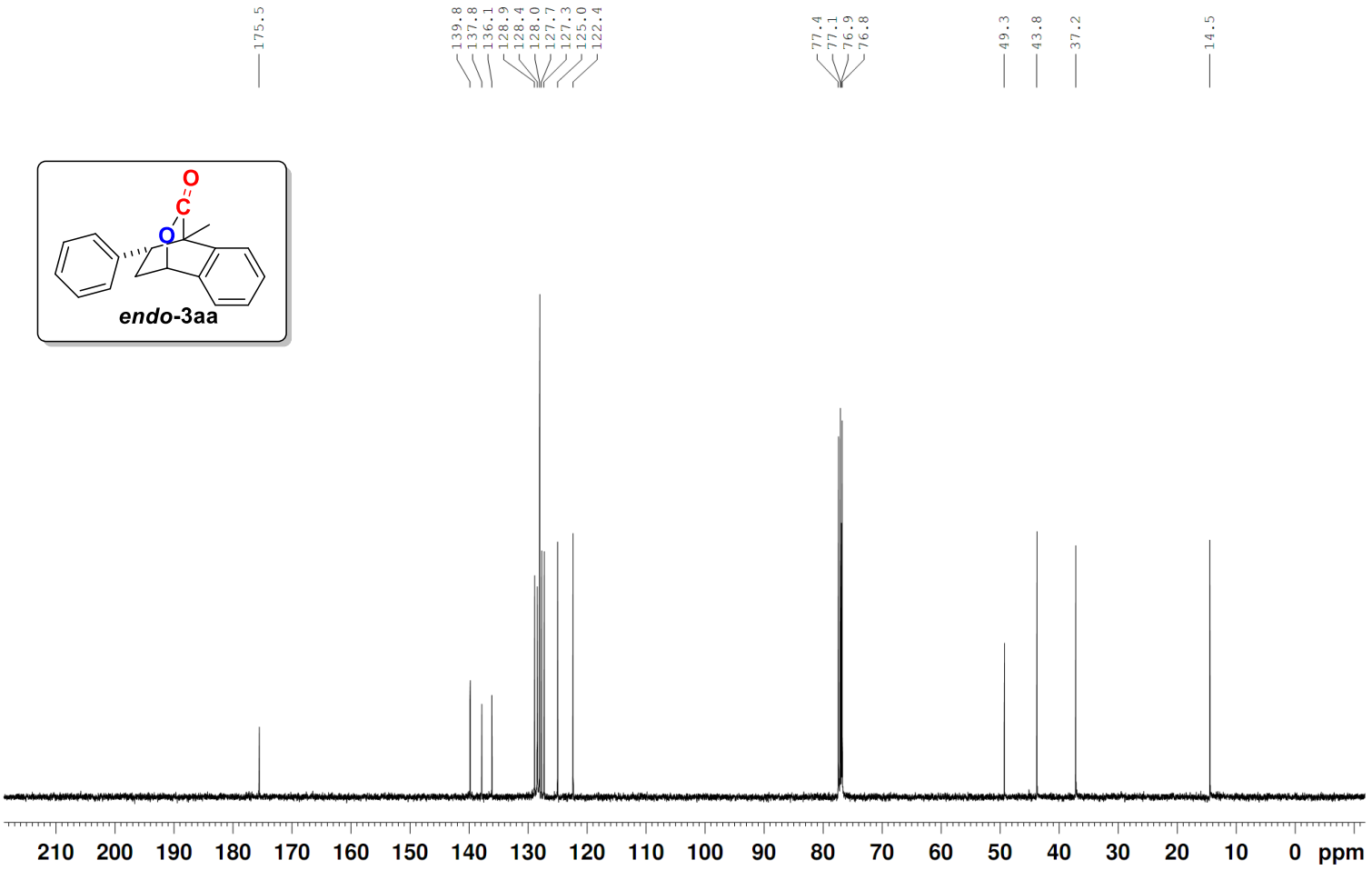
(6) M. A. O'Leary, D. Wege. *Tetrahedron 1981*, **37**, 801.

10. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR of the products

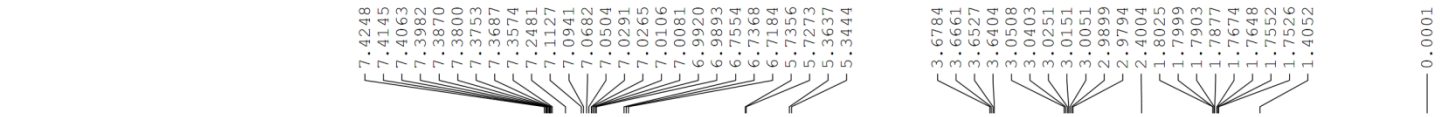
GBJ-X190105-2-5-HNMR

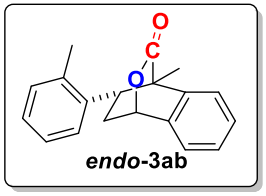


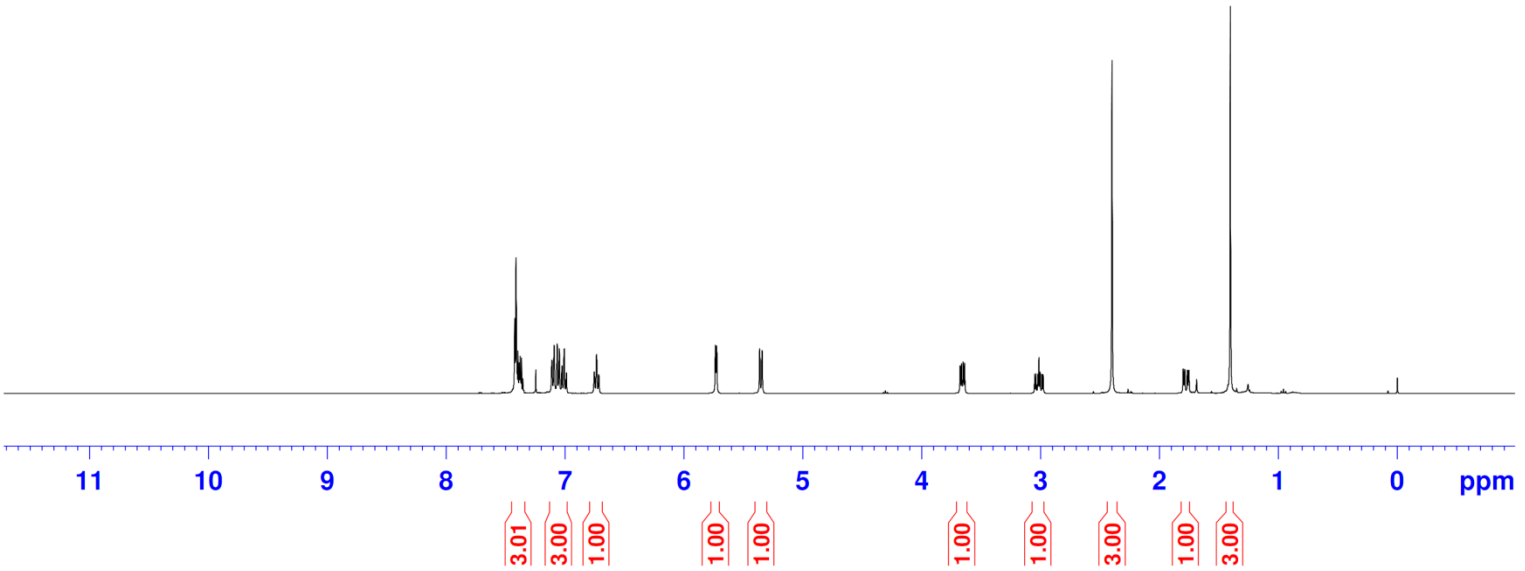
GBJ-X190105-2-5-C



GBJ-X190123-2-1-H







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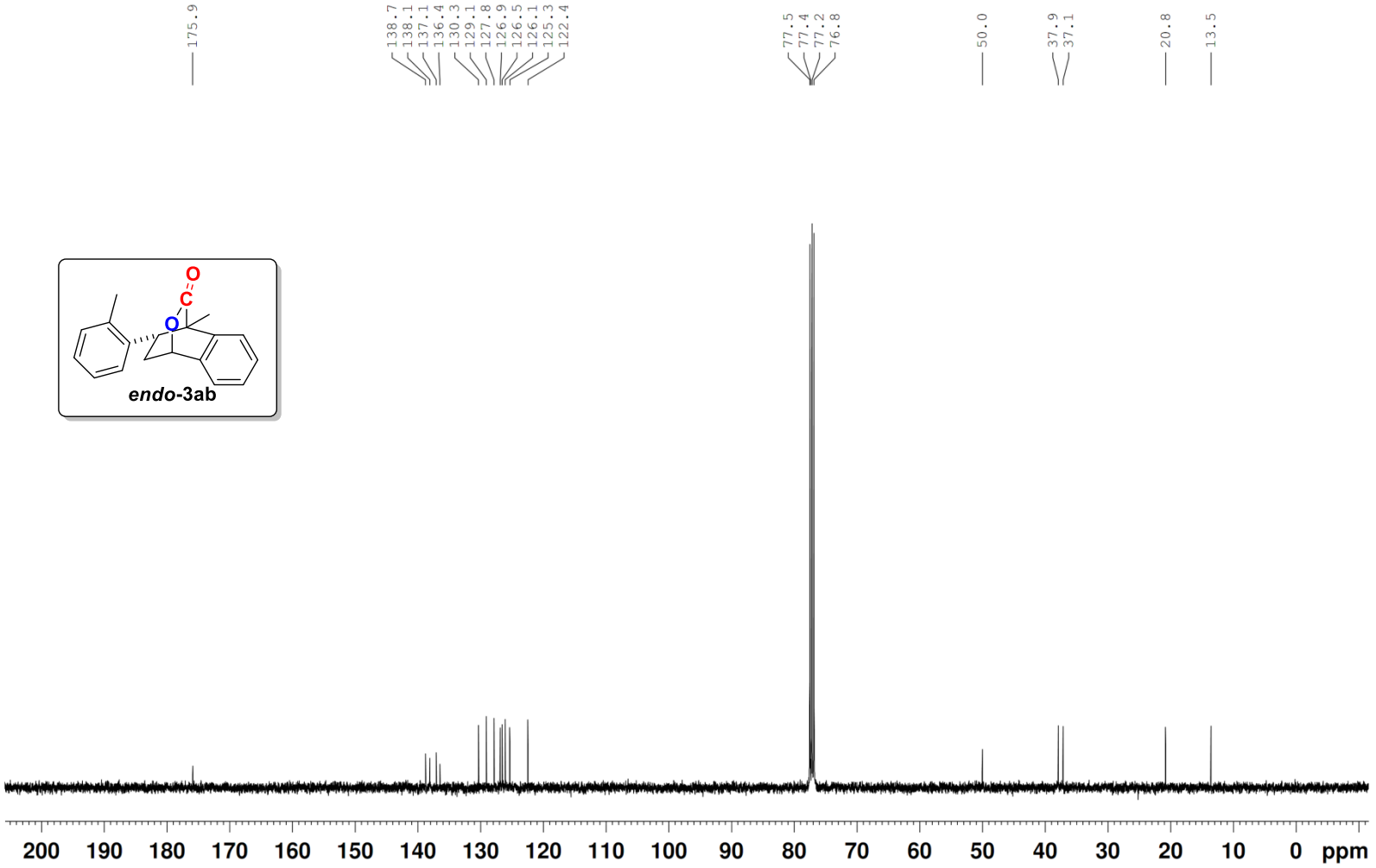

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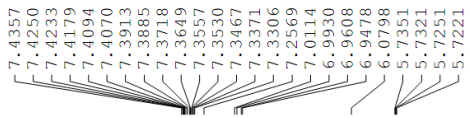

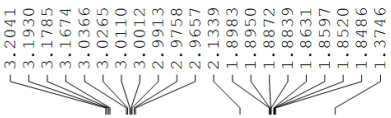

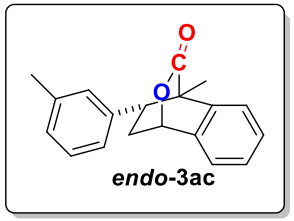

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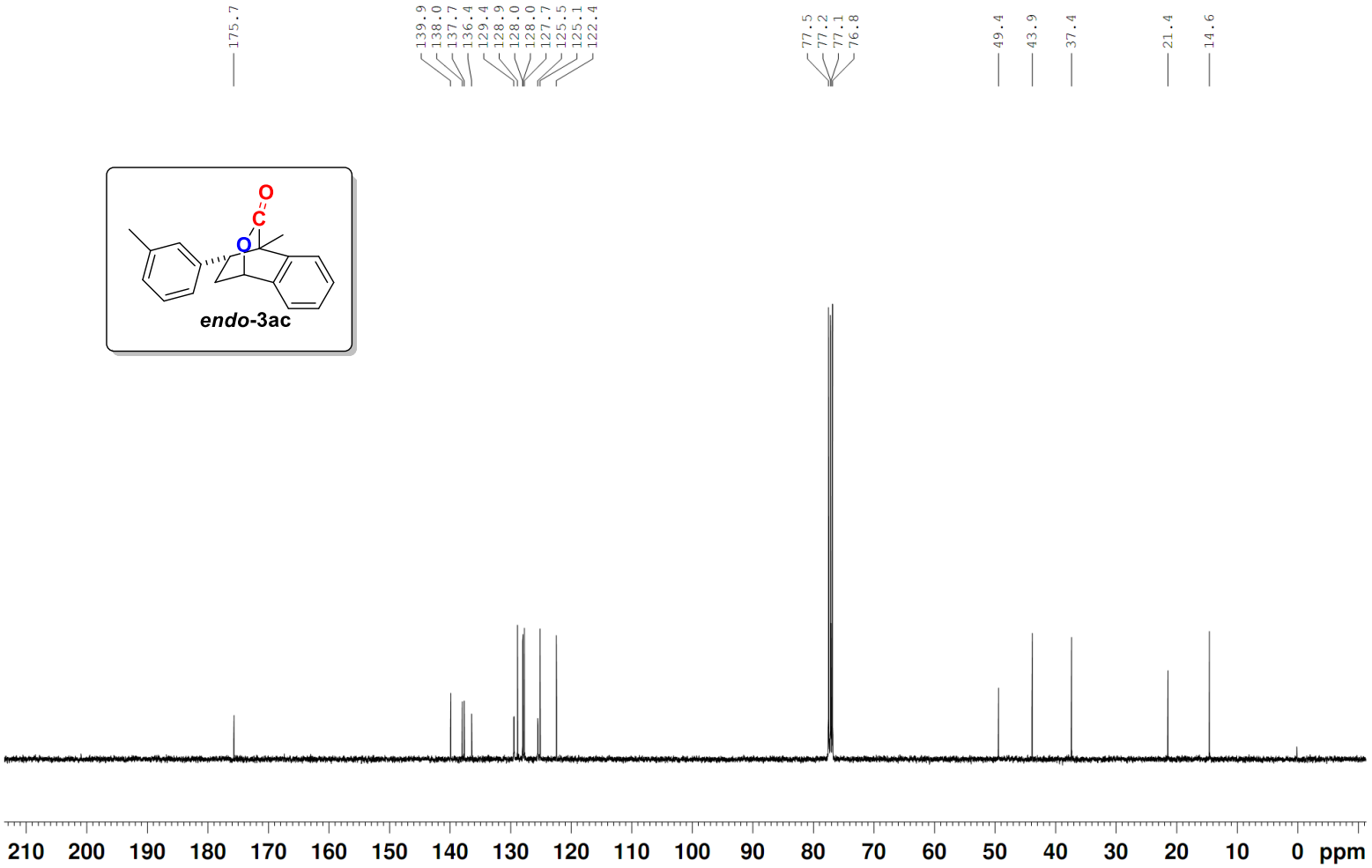
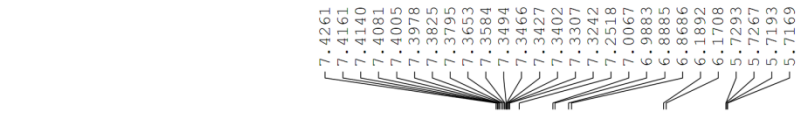
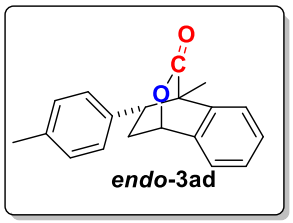
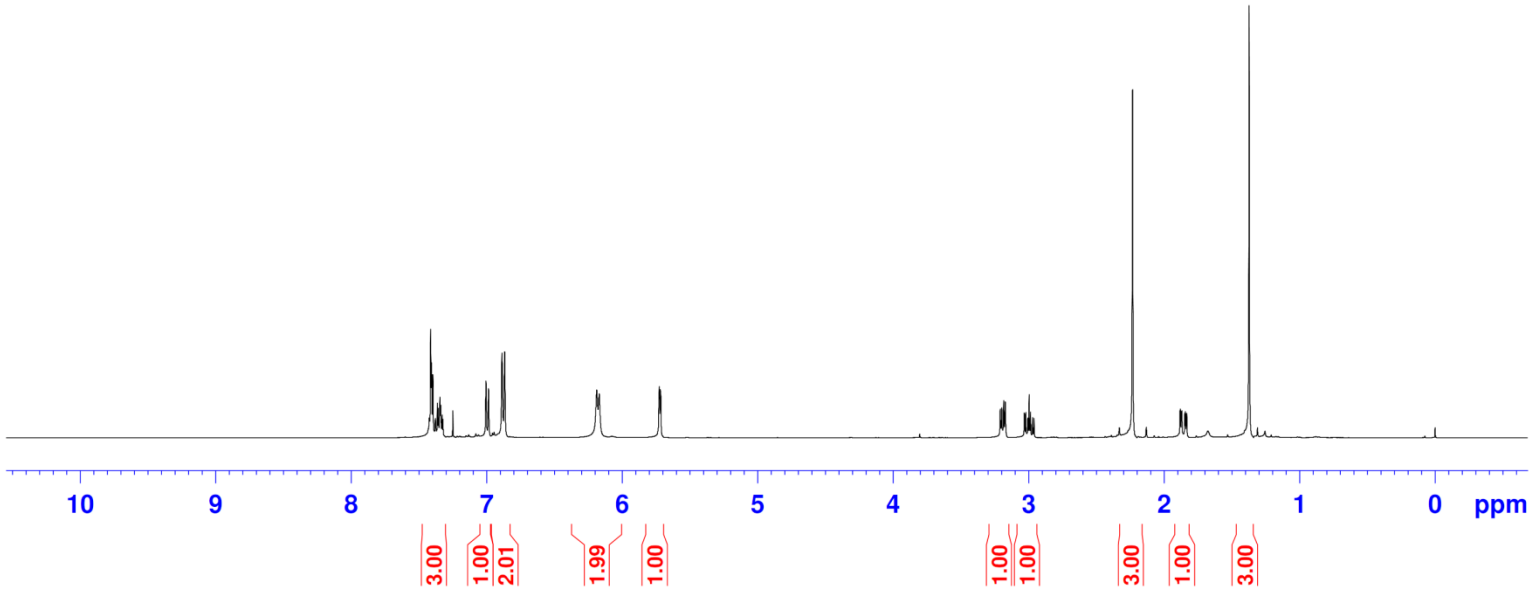


GBJ-X191107-1-HNMR







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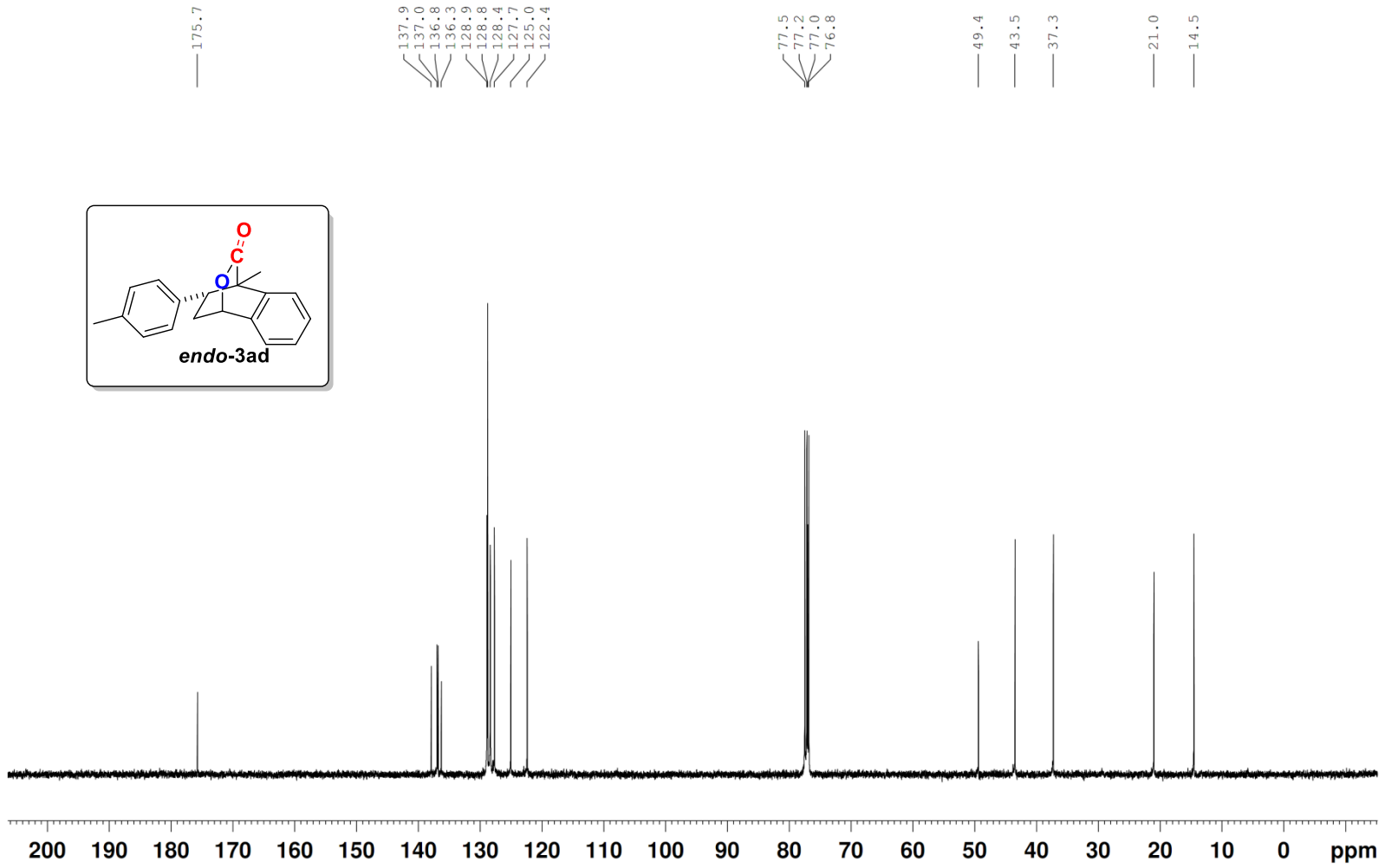

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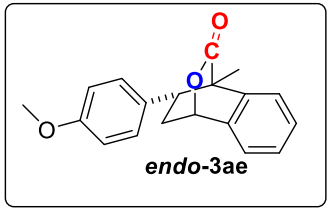

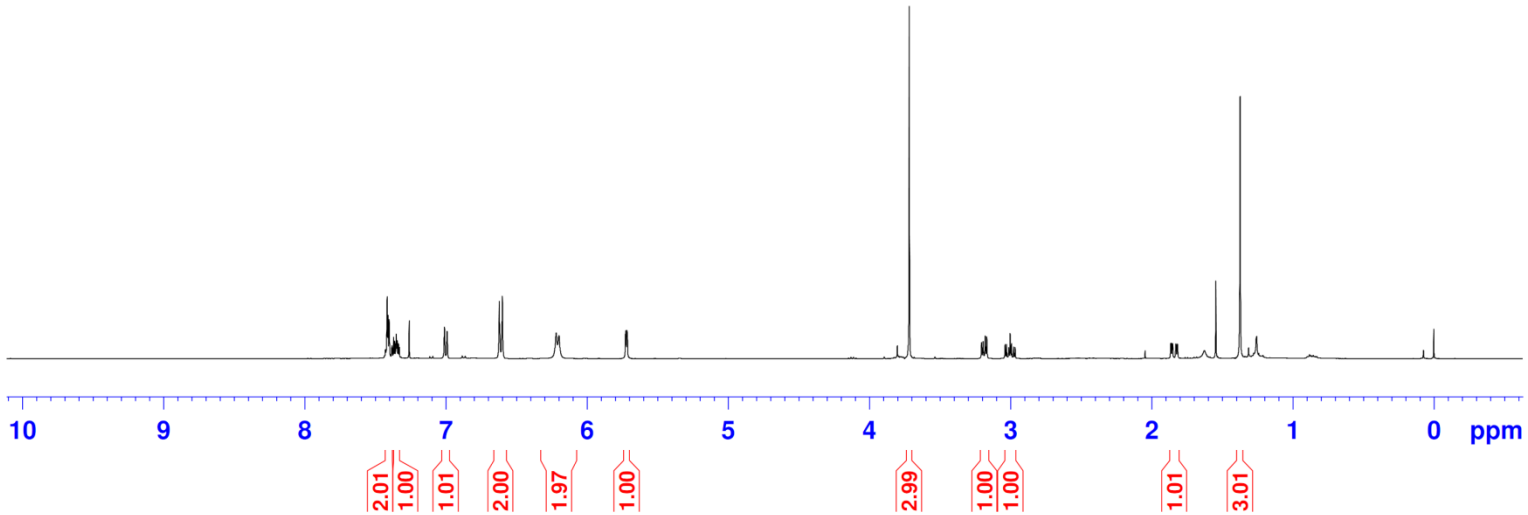

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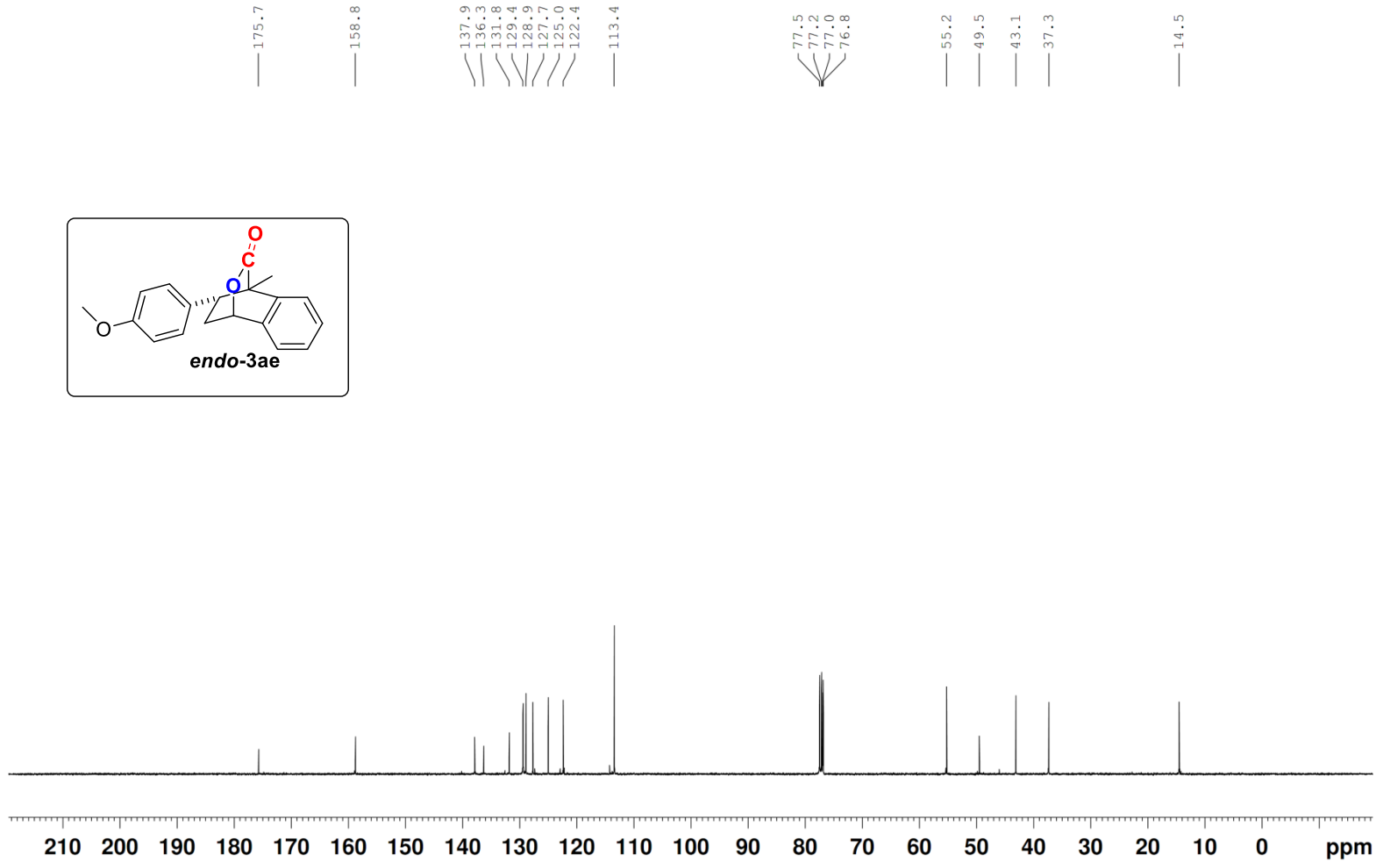

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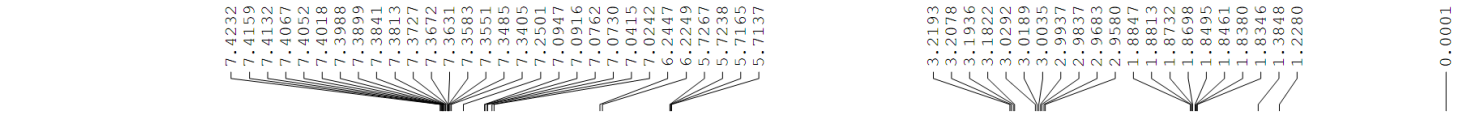

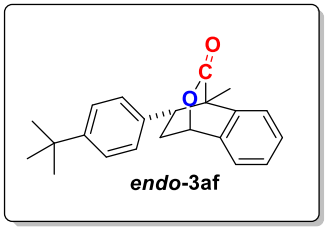

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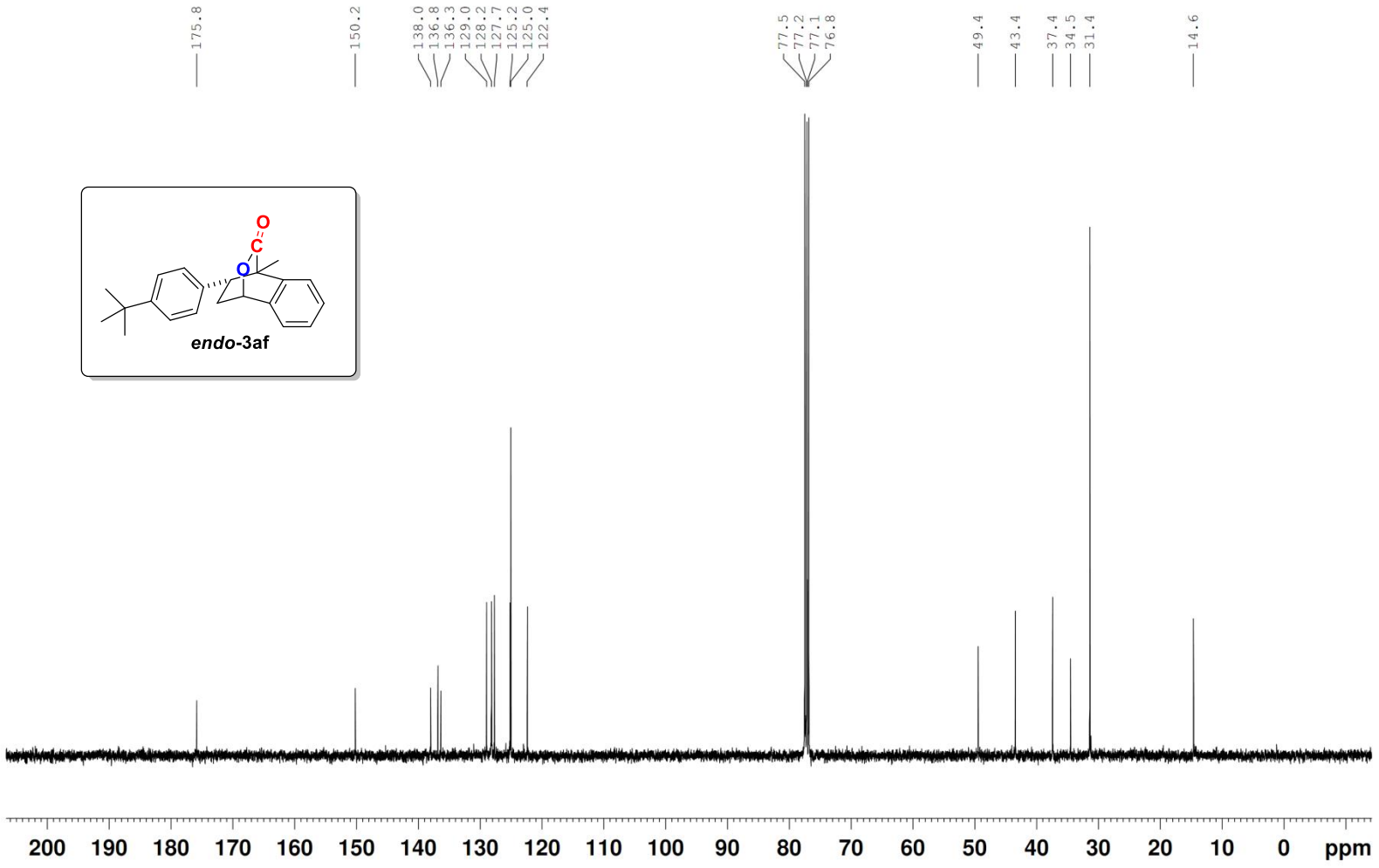
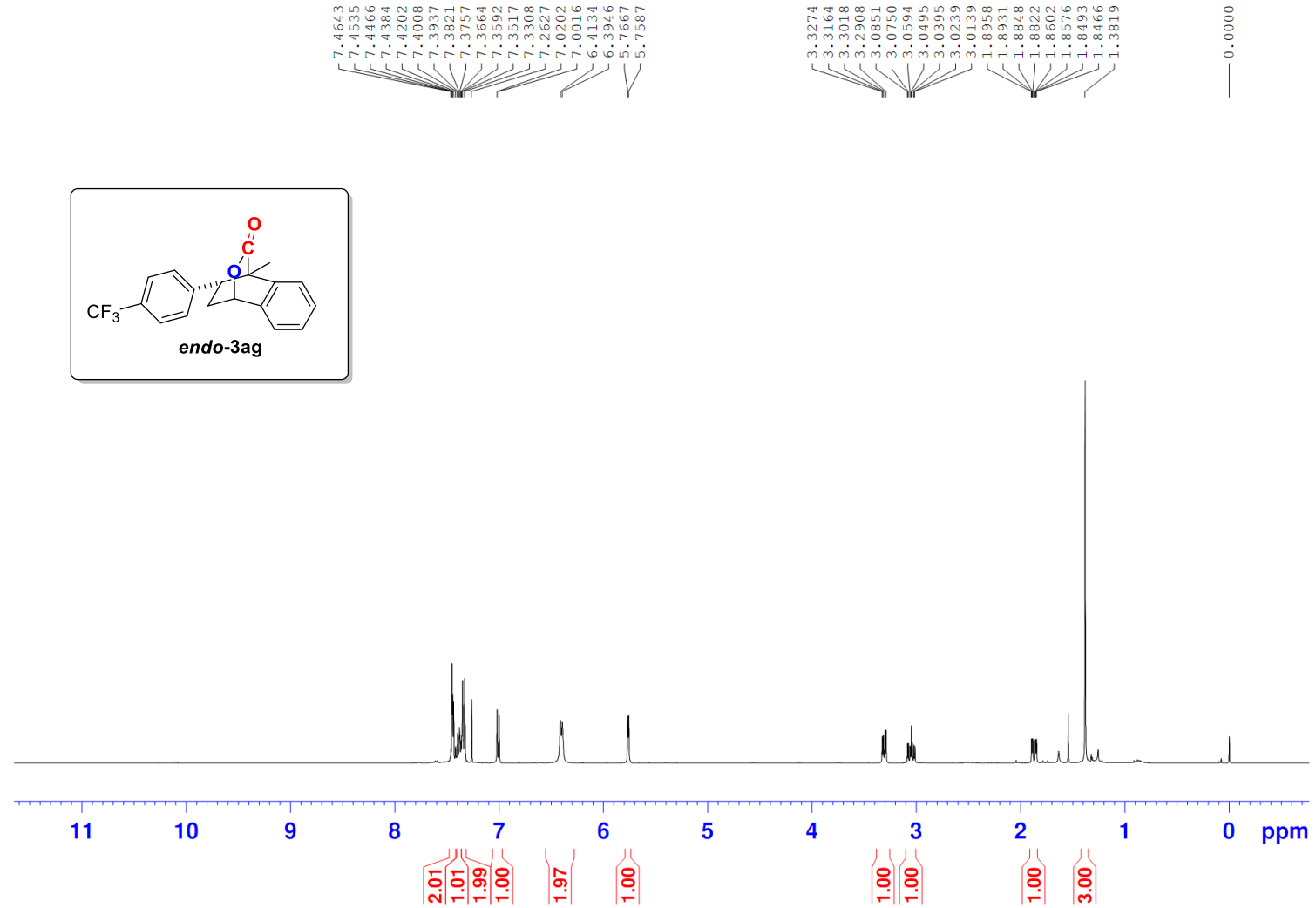


GBJ-X190220-1-2-H



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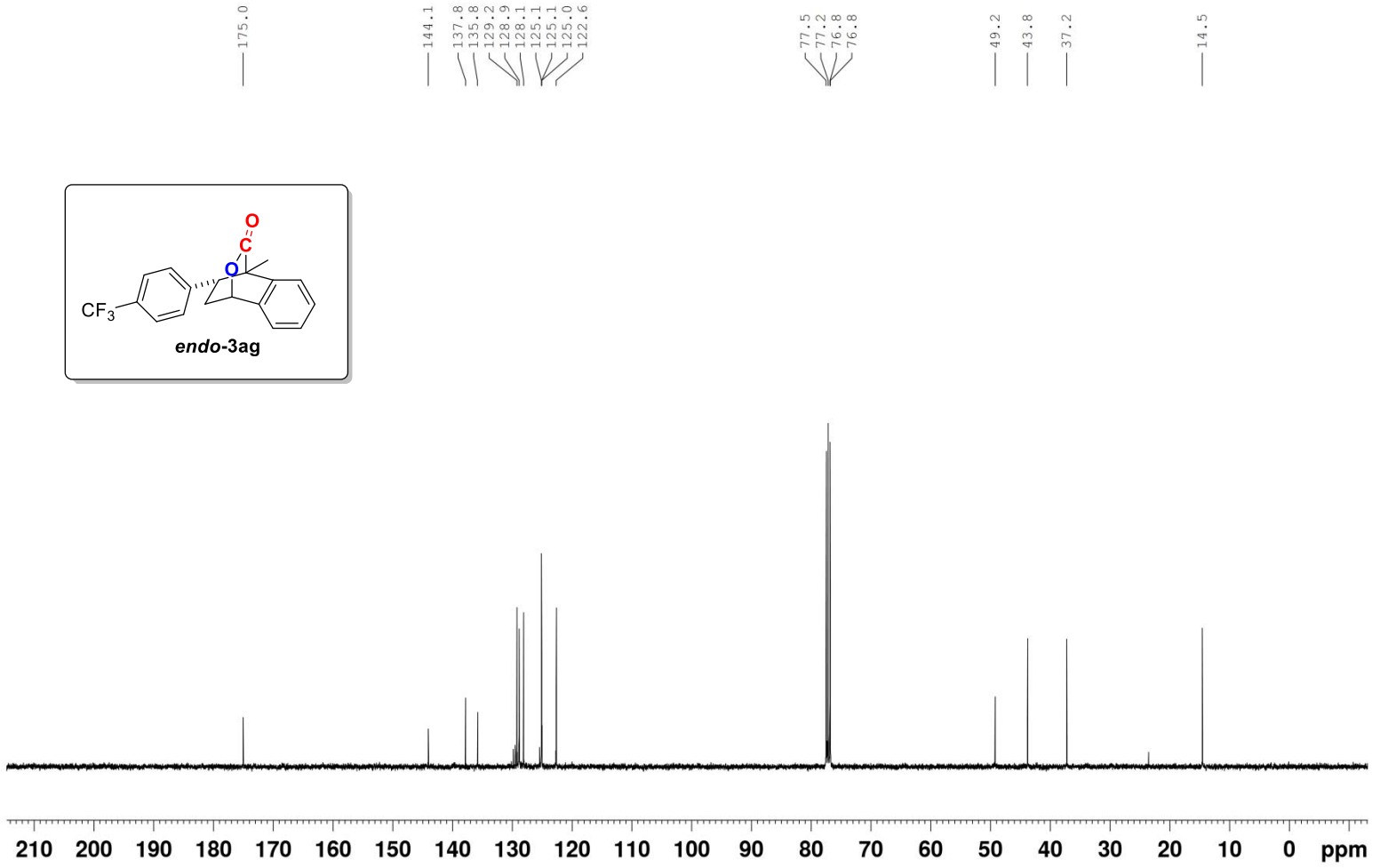

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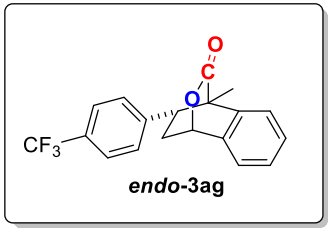
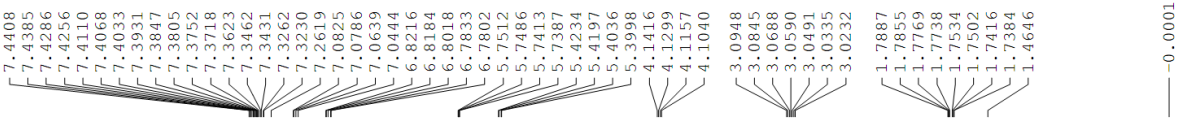
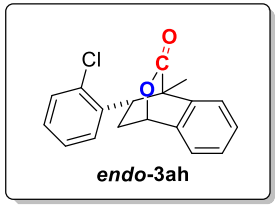
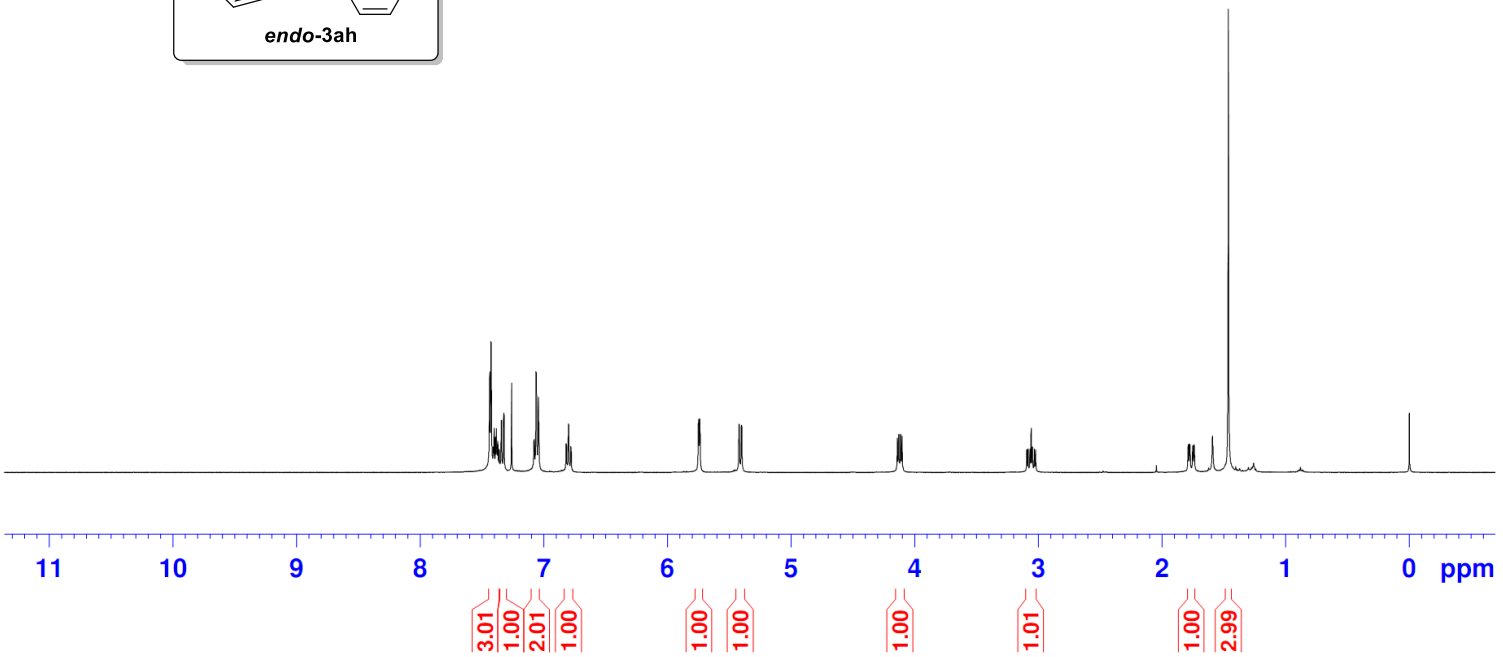


endo-3ag

GBJ-X190123-2-5-H







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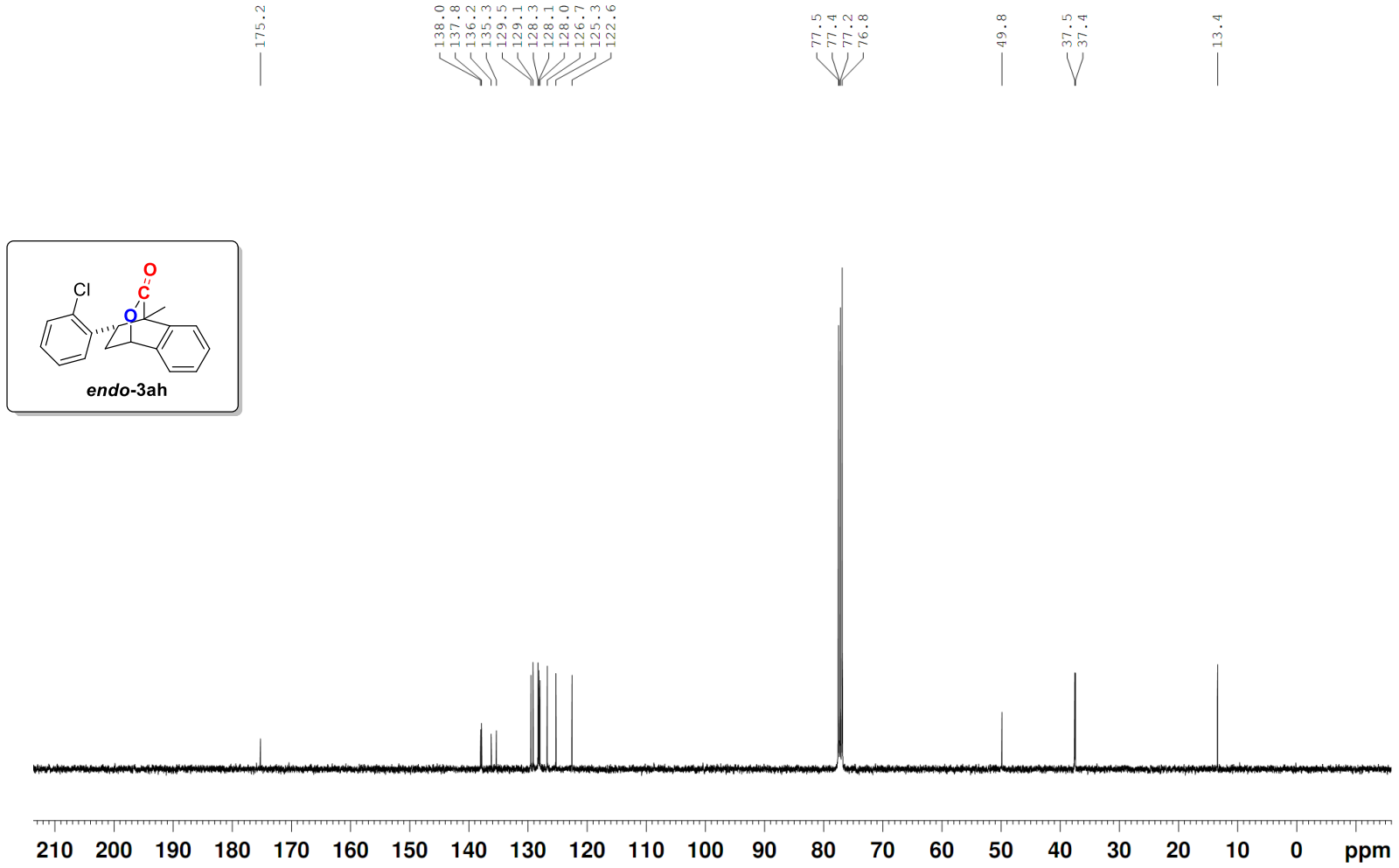
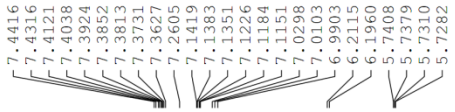
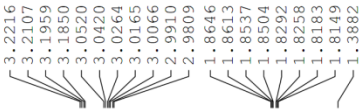
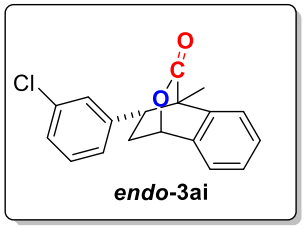
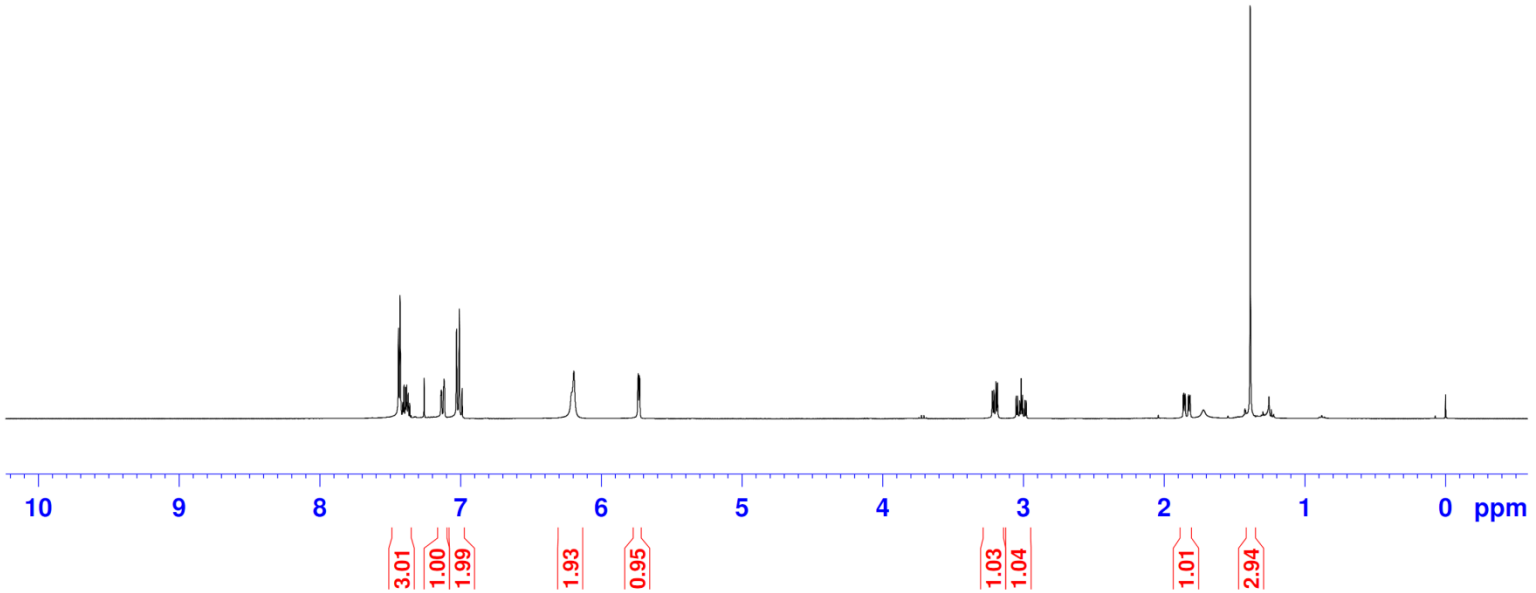


GBJ-X190902--1-11-HNMR









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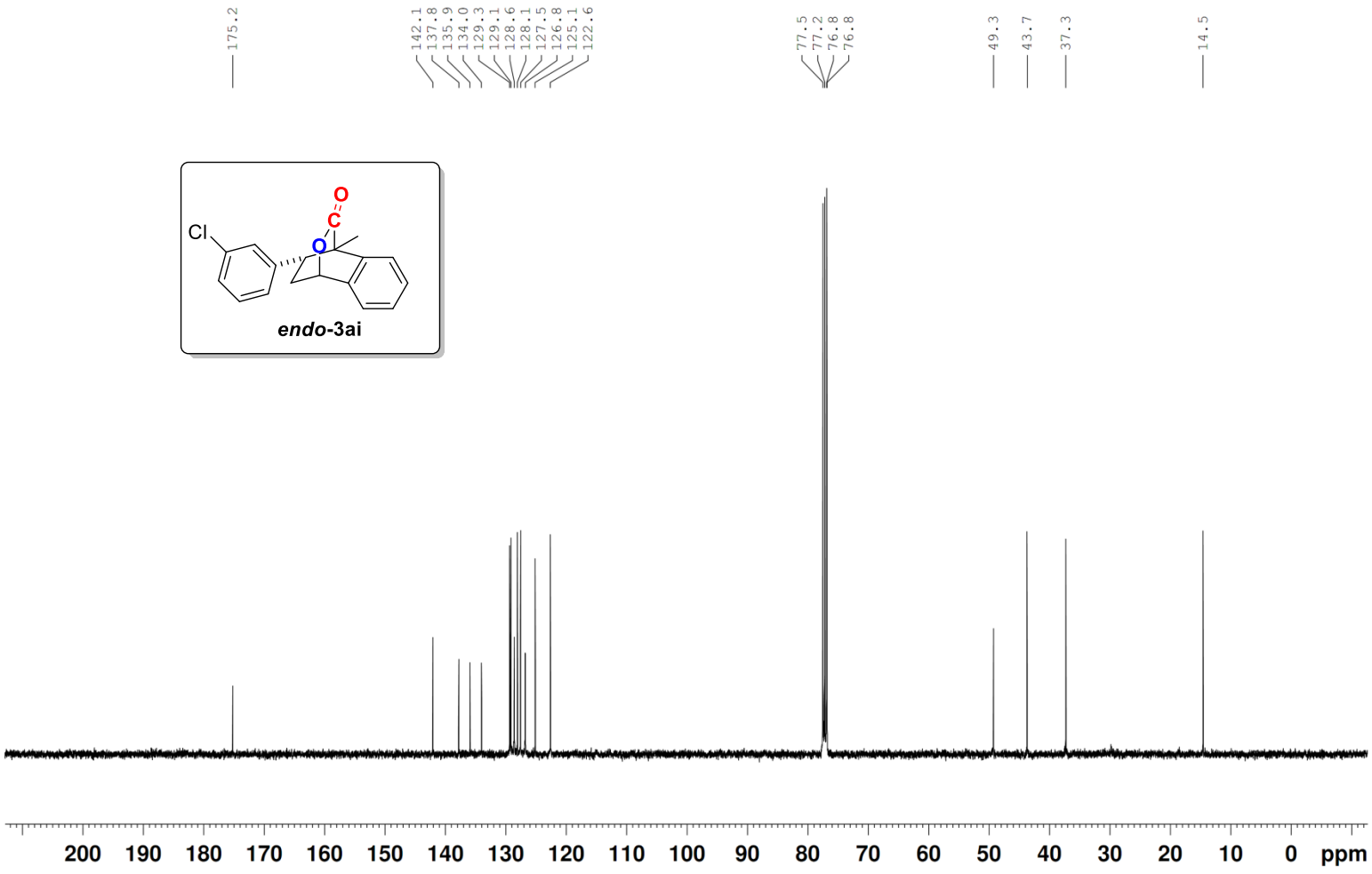

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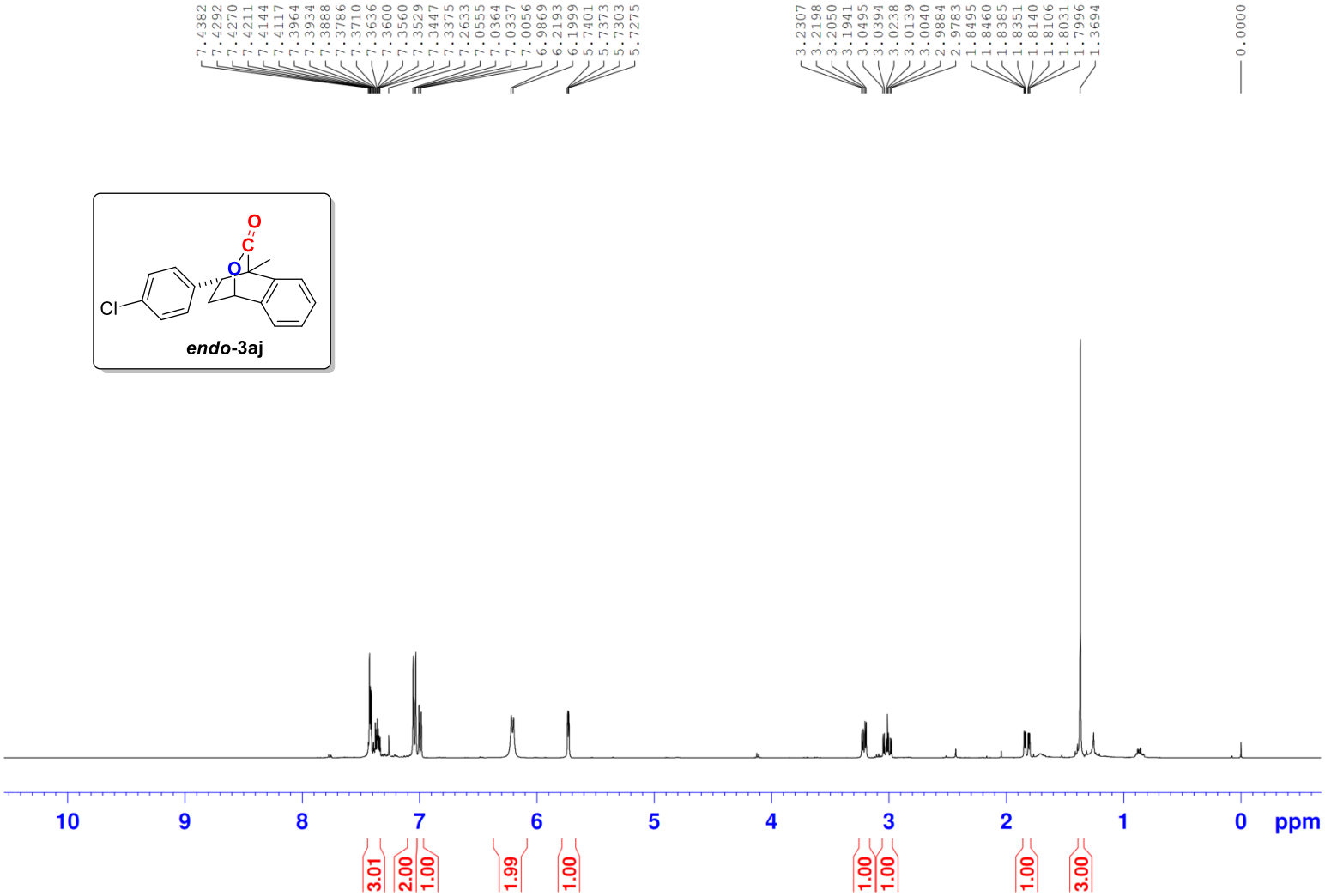

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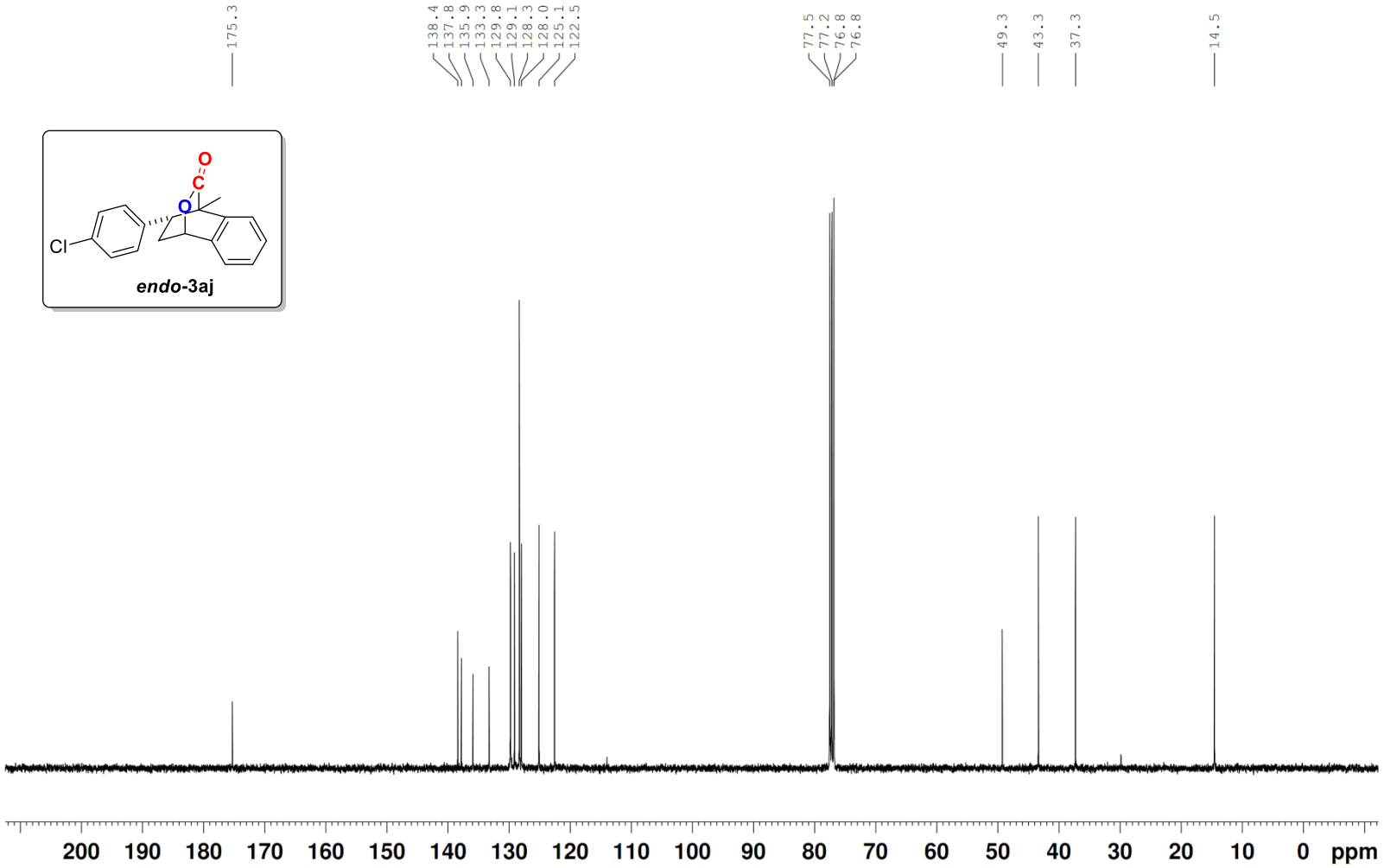

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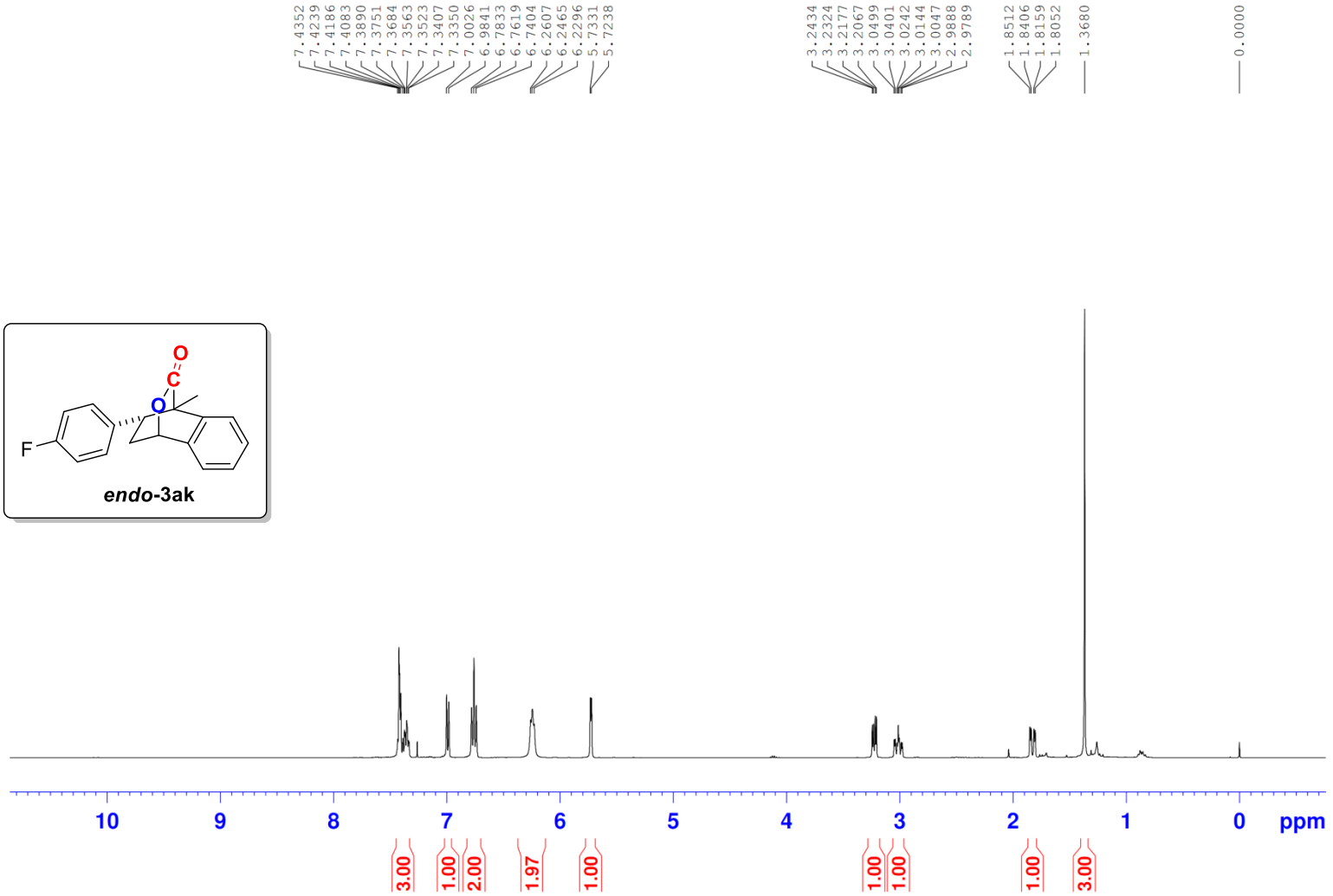

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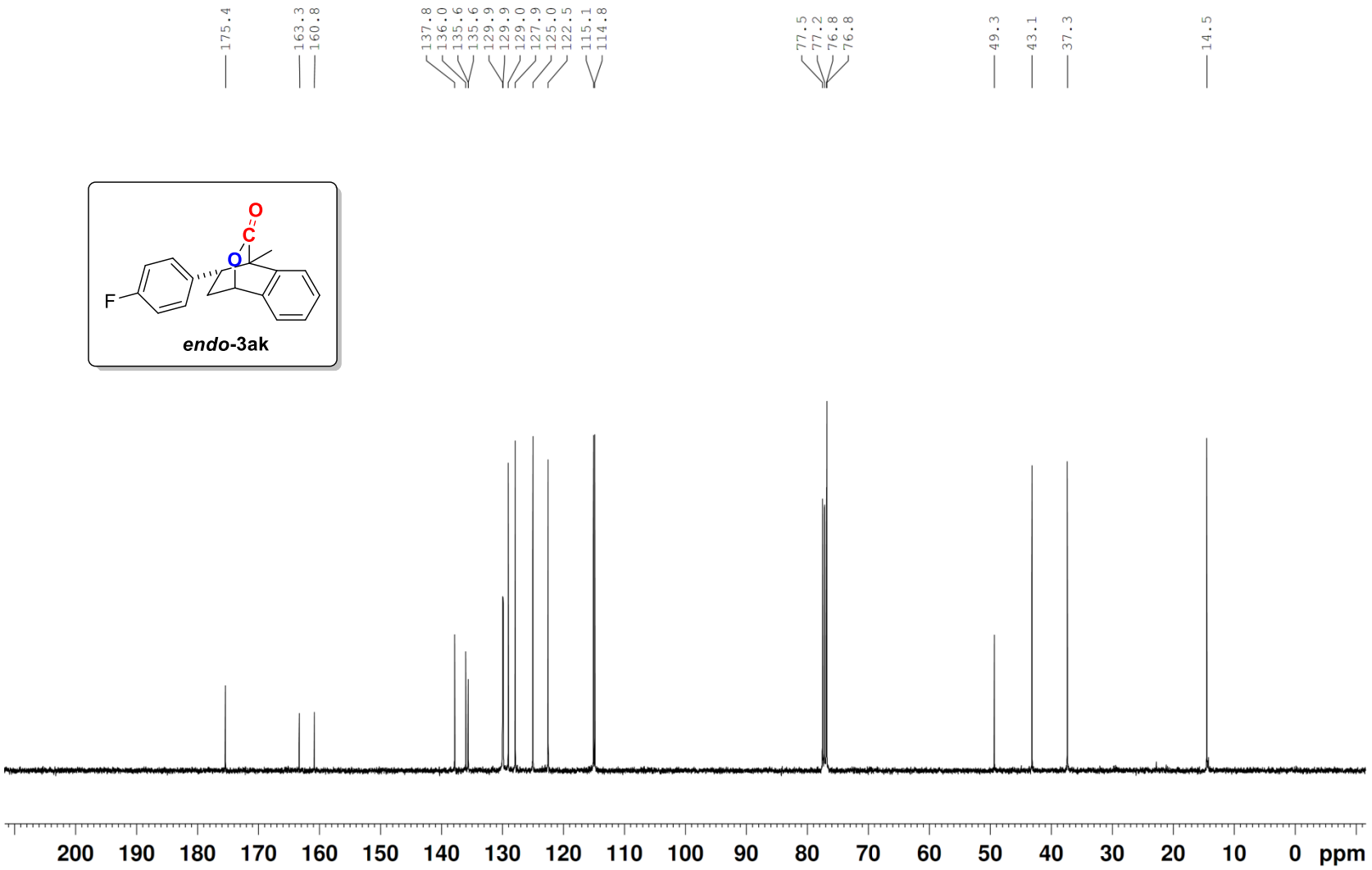

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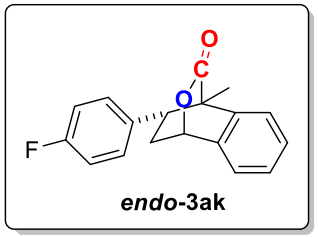

endo-3ak

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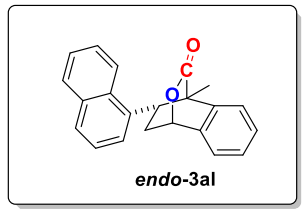
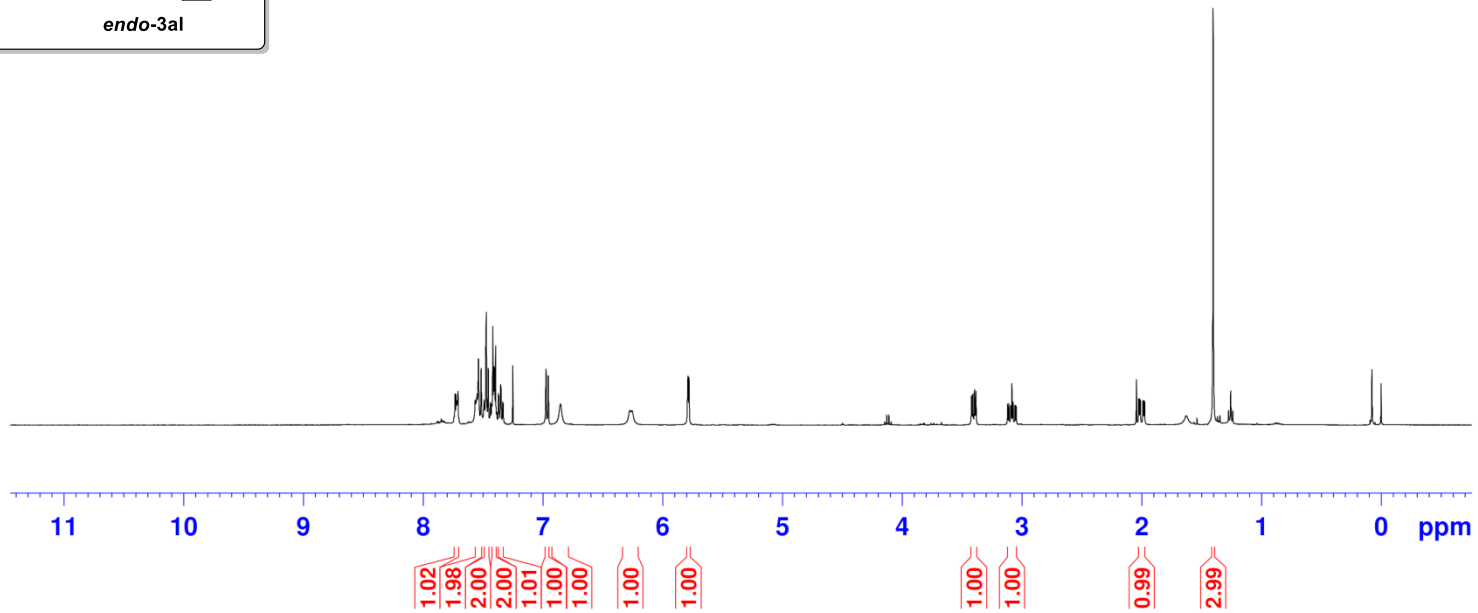


endo-3al



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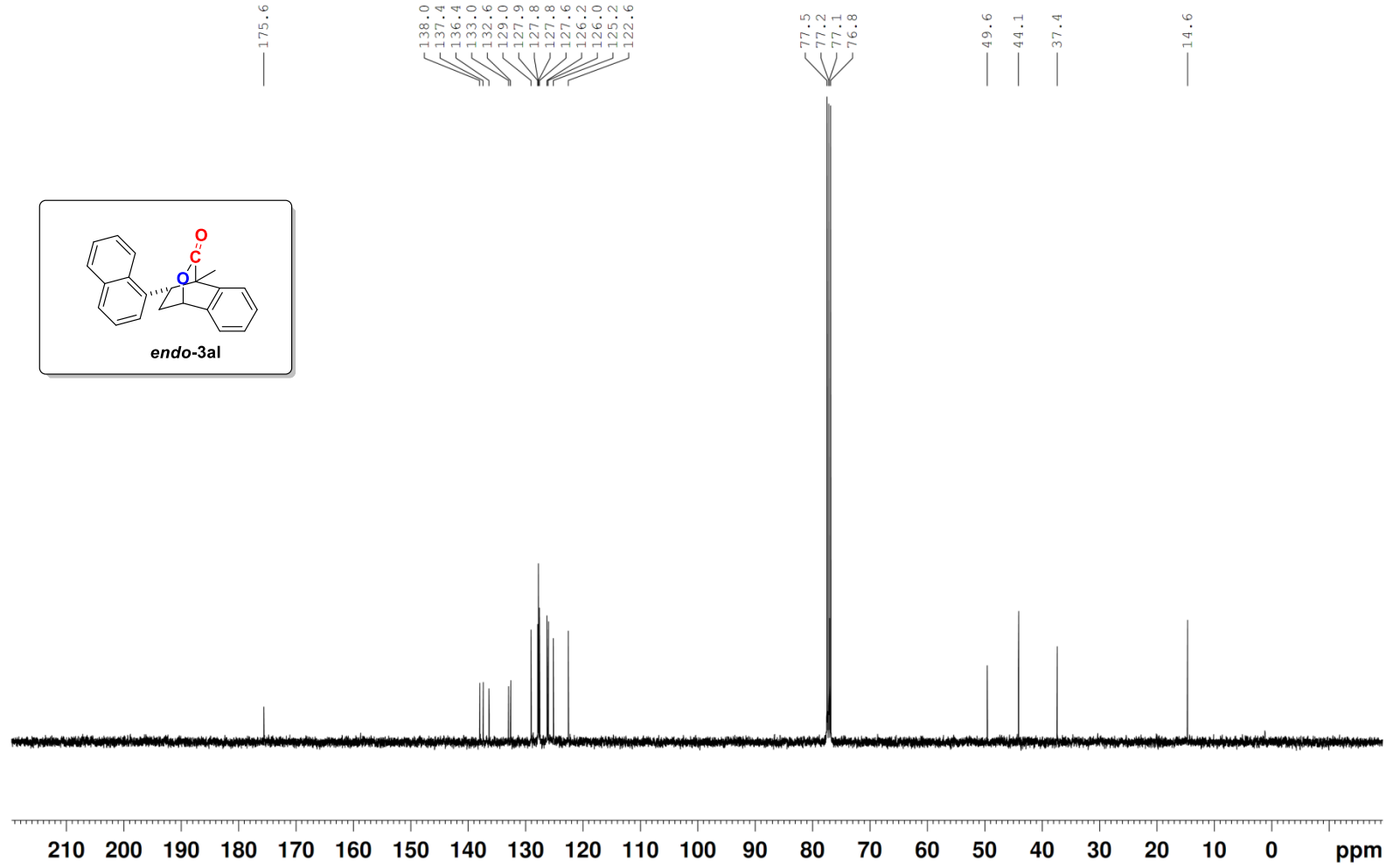

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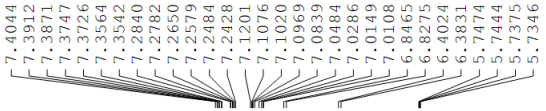

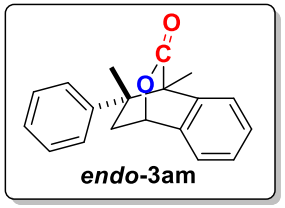

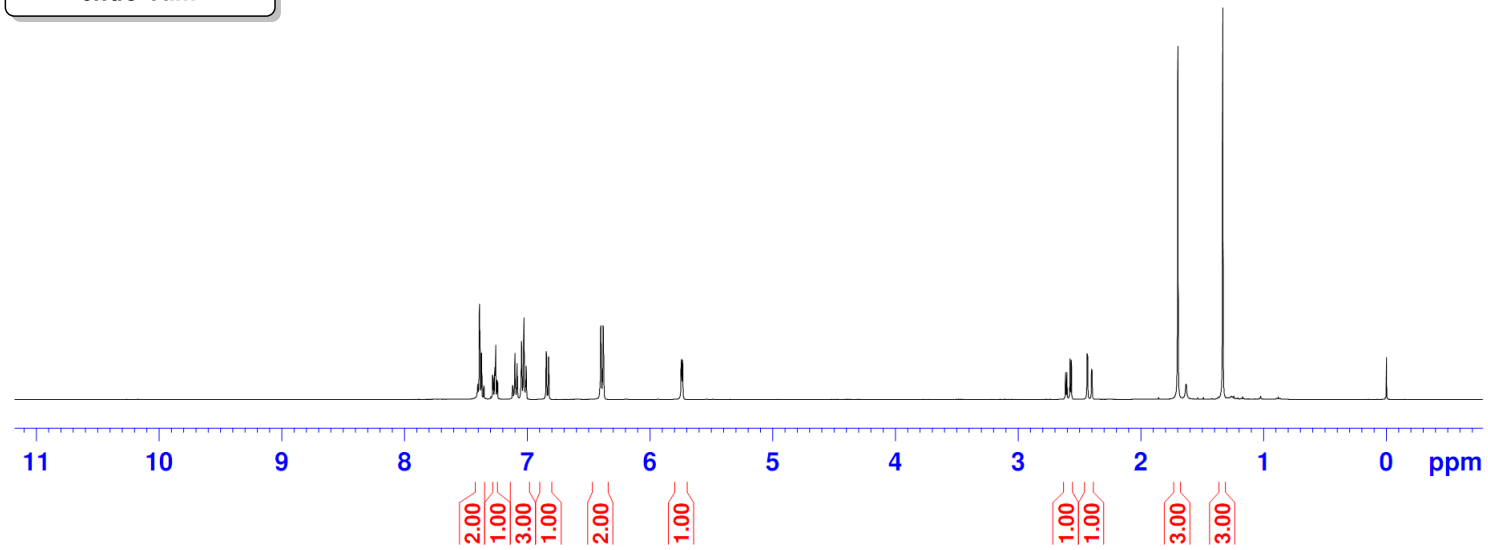

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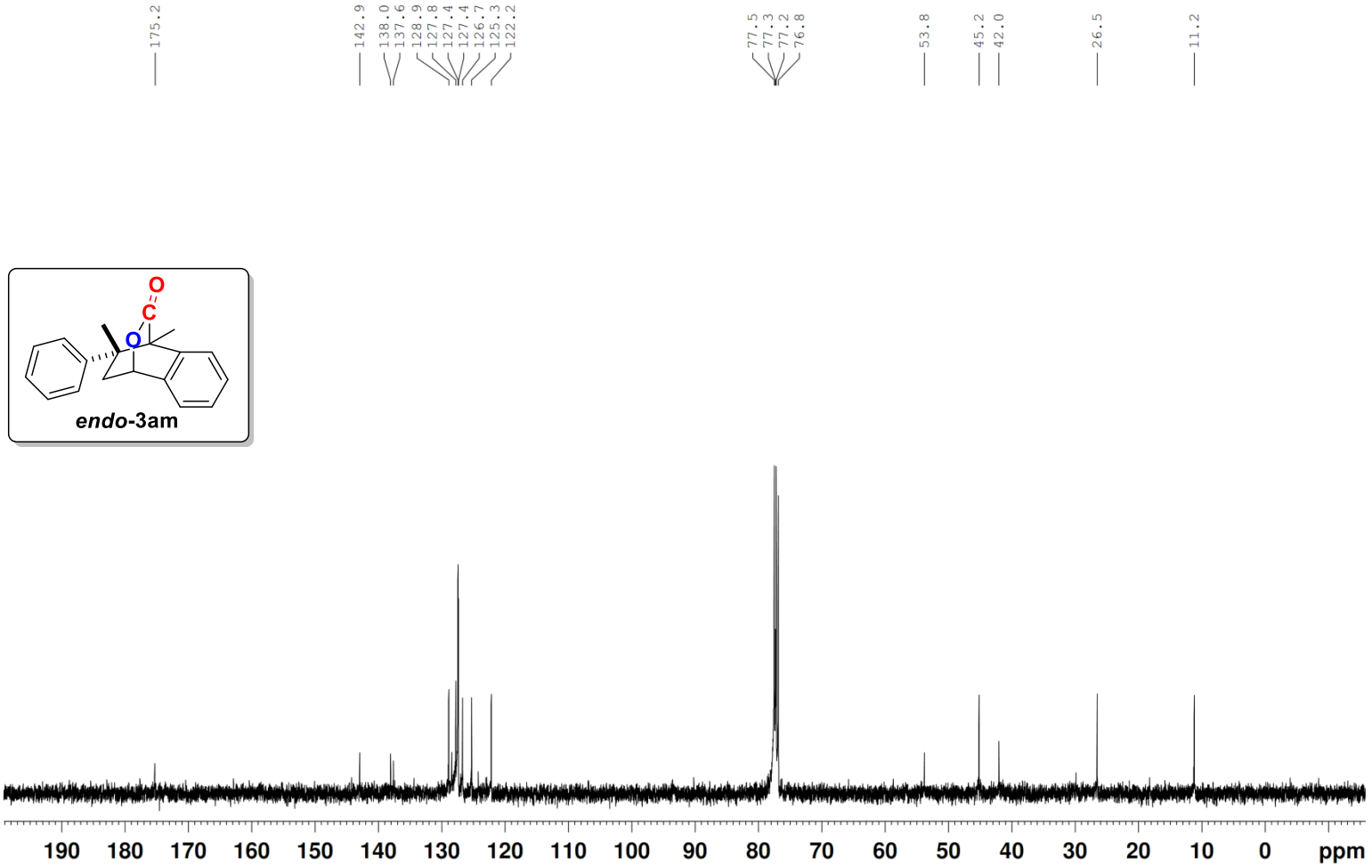

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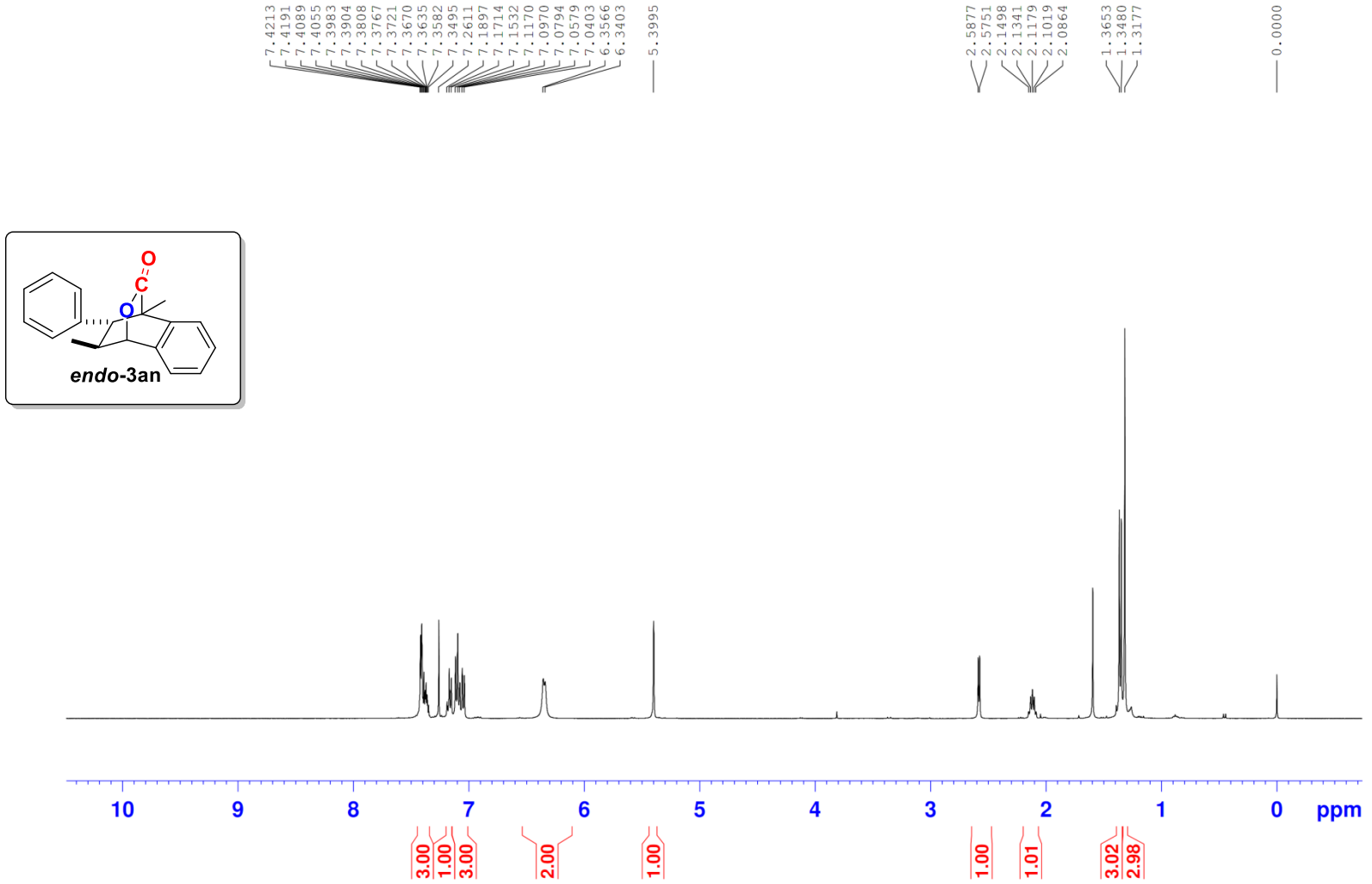

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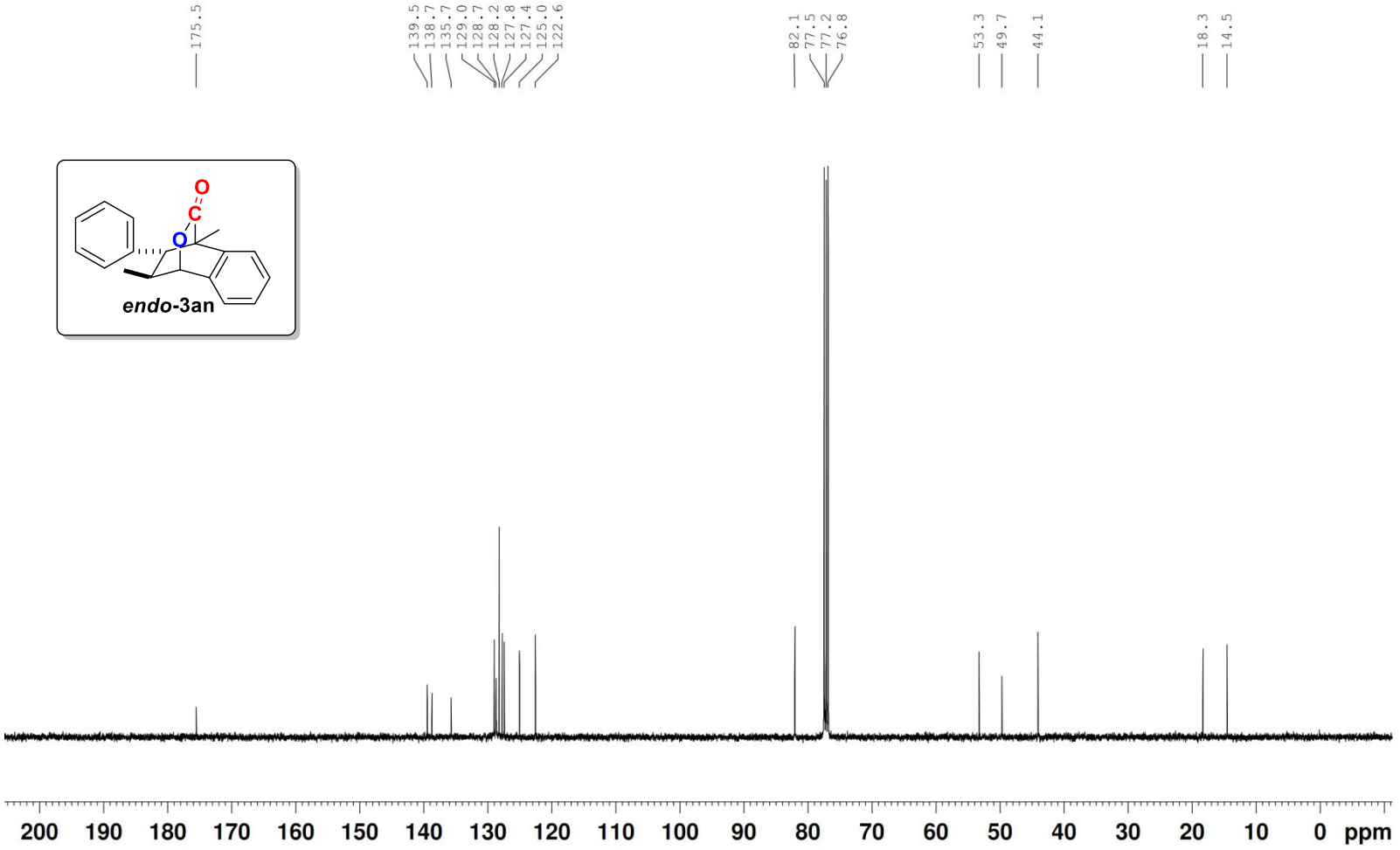

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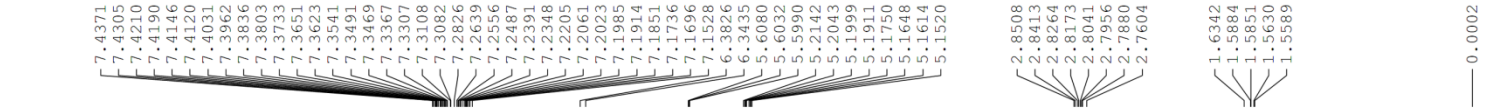

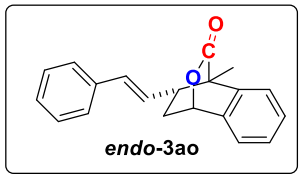

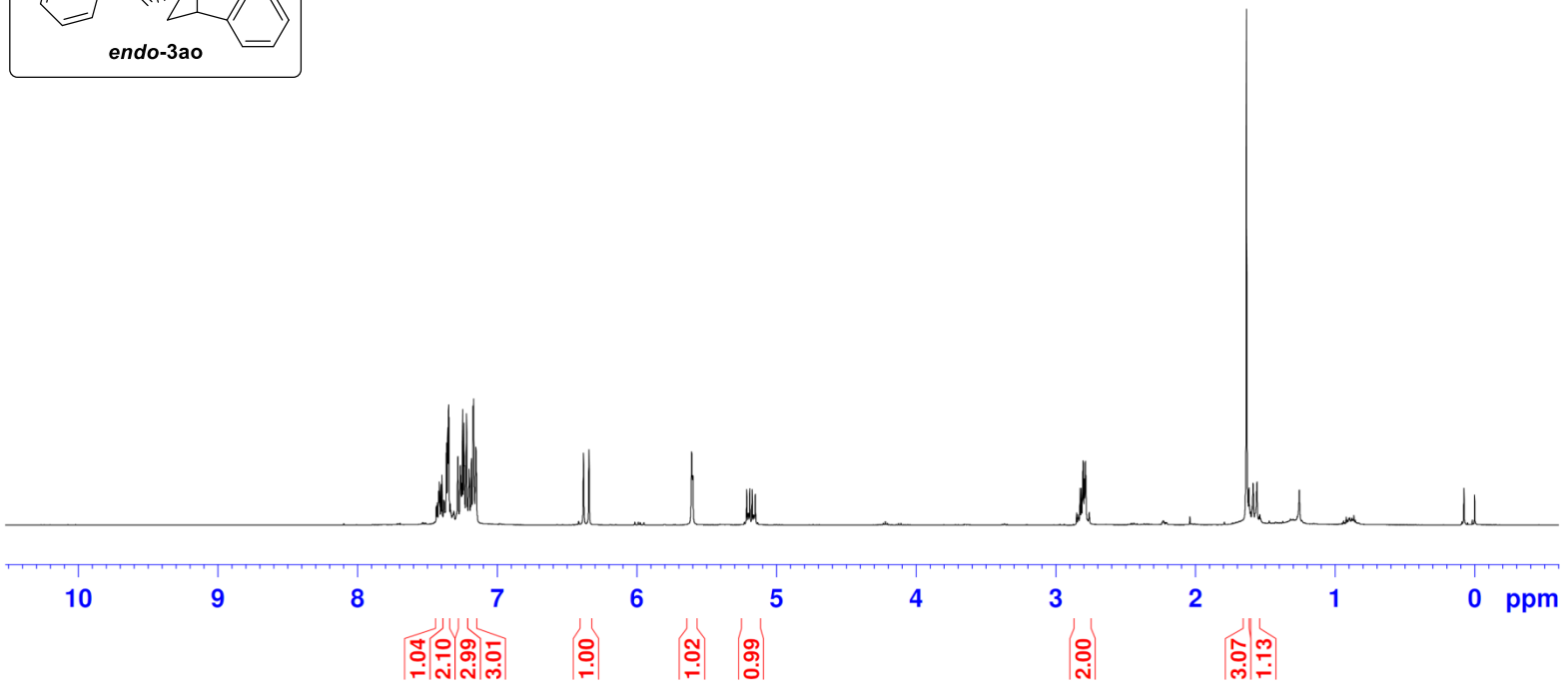

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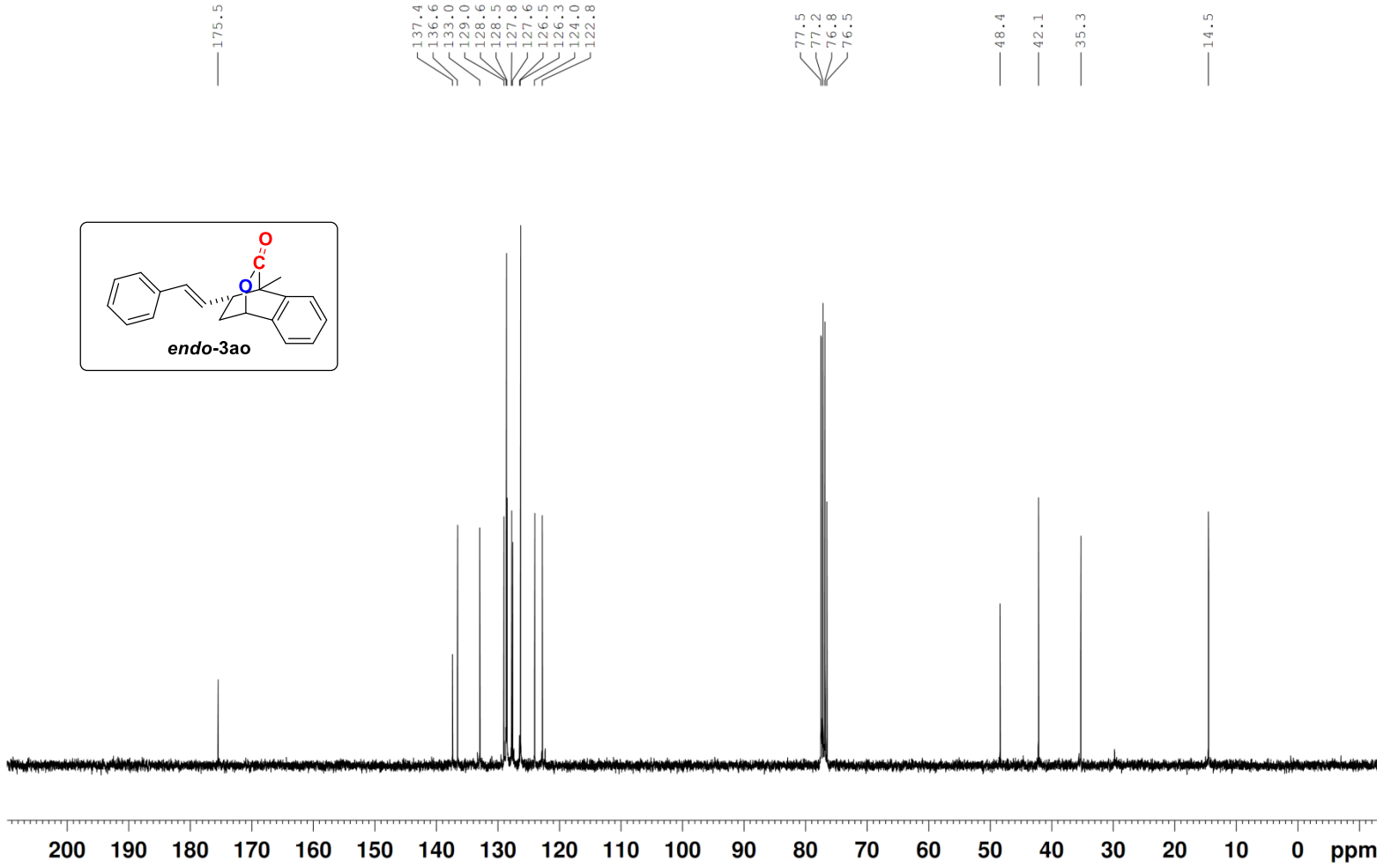

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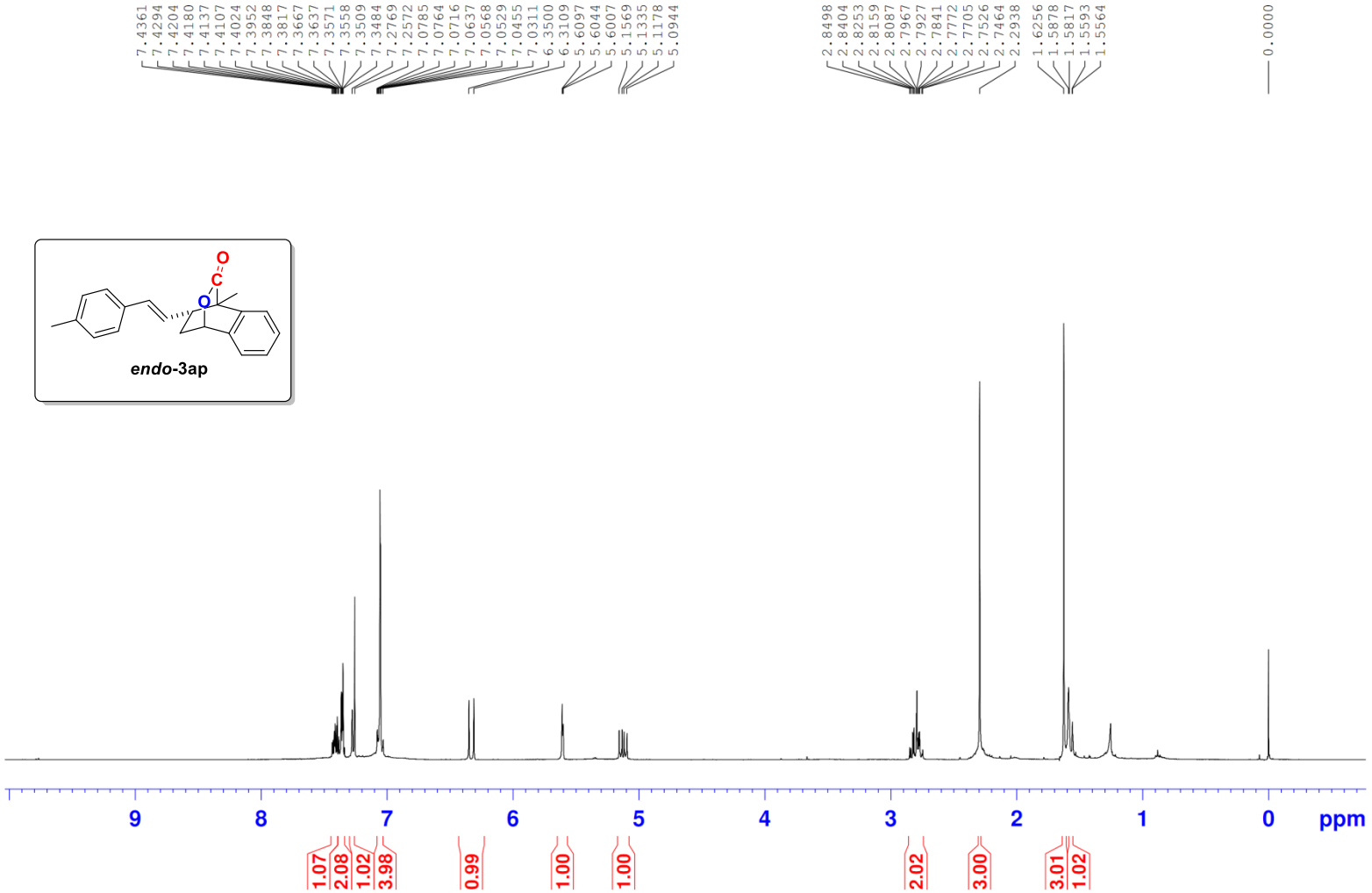

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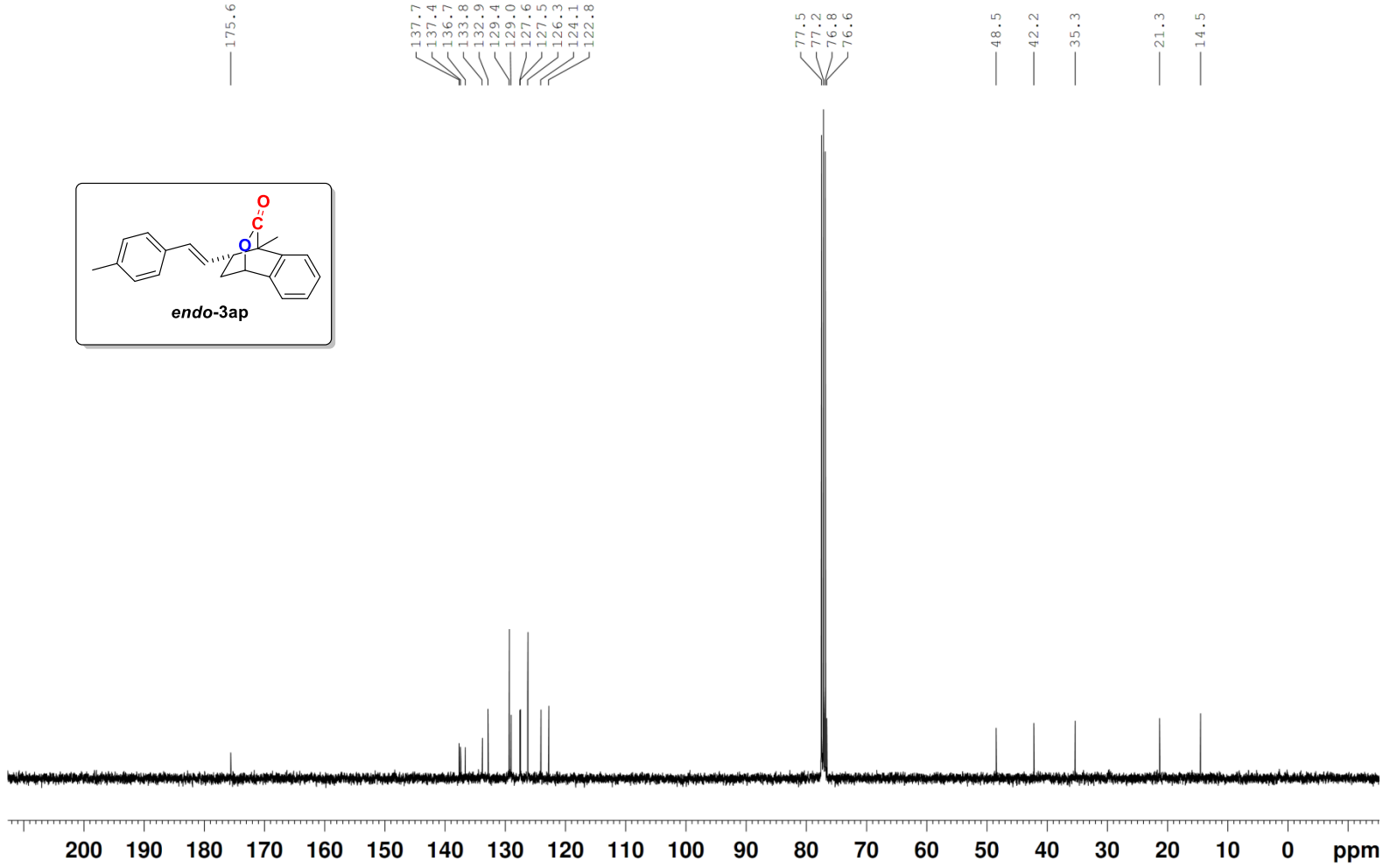

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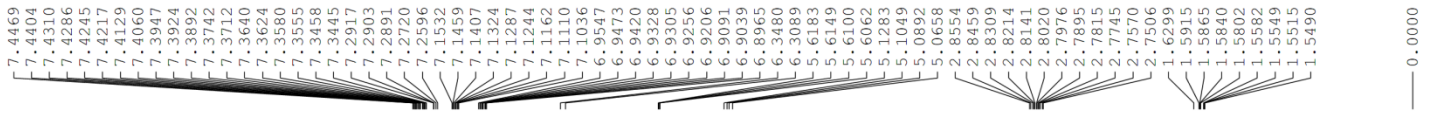
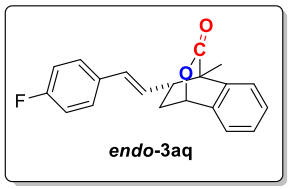
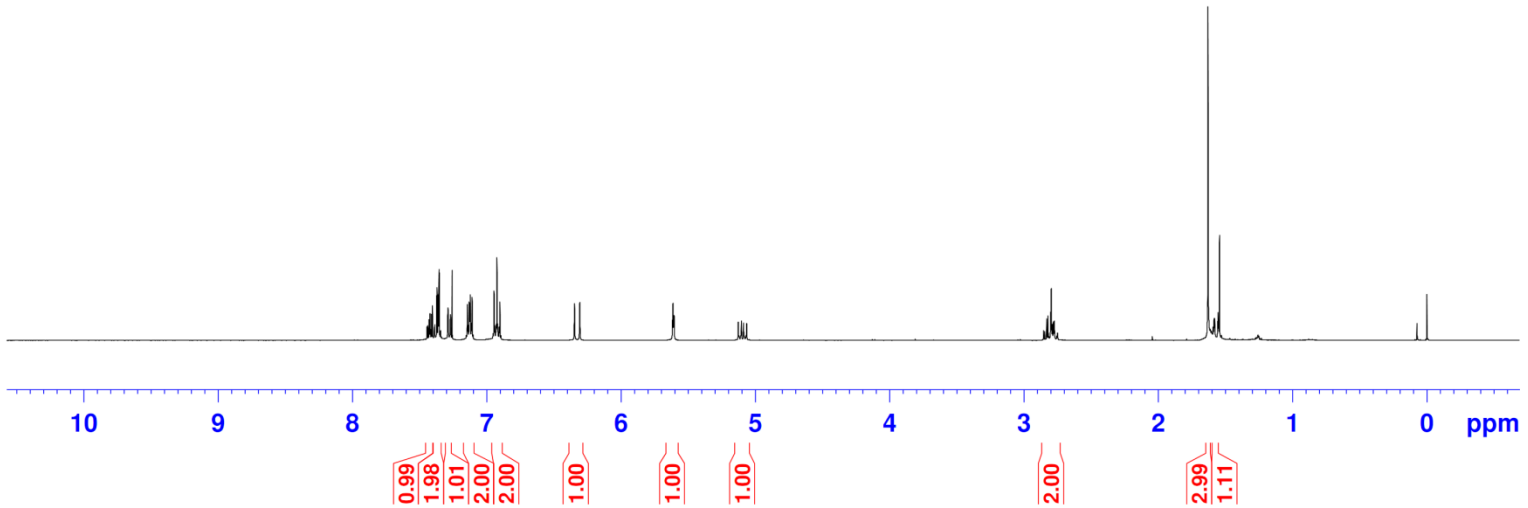




***endo*-3aq**



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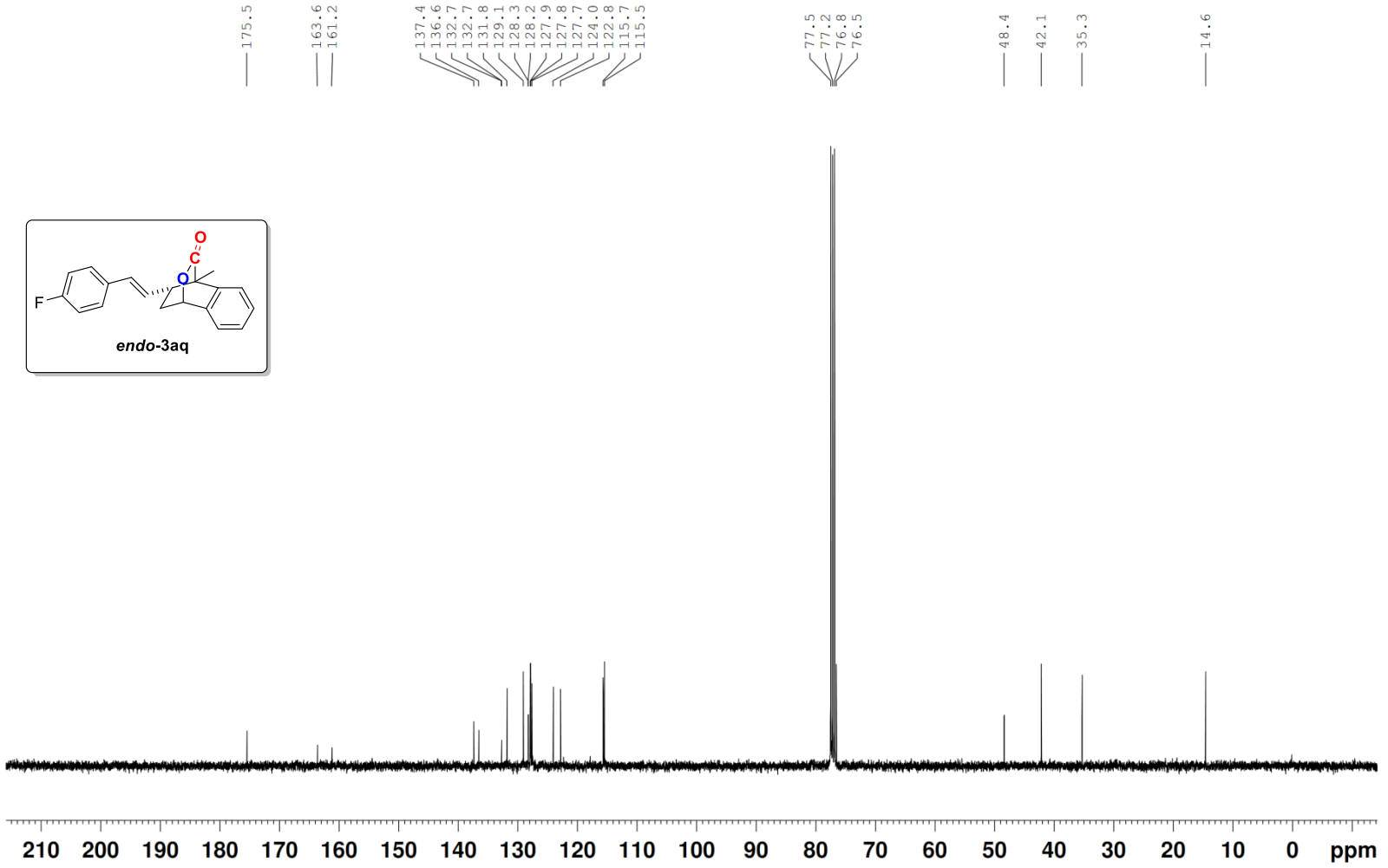

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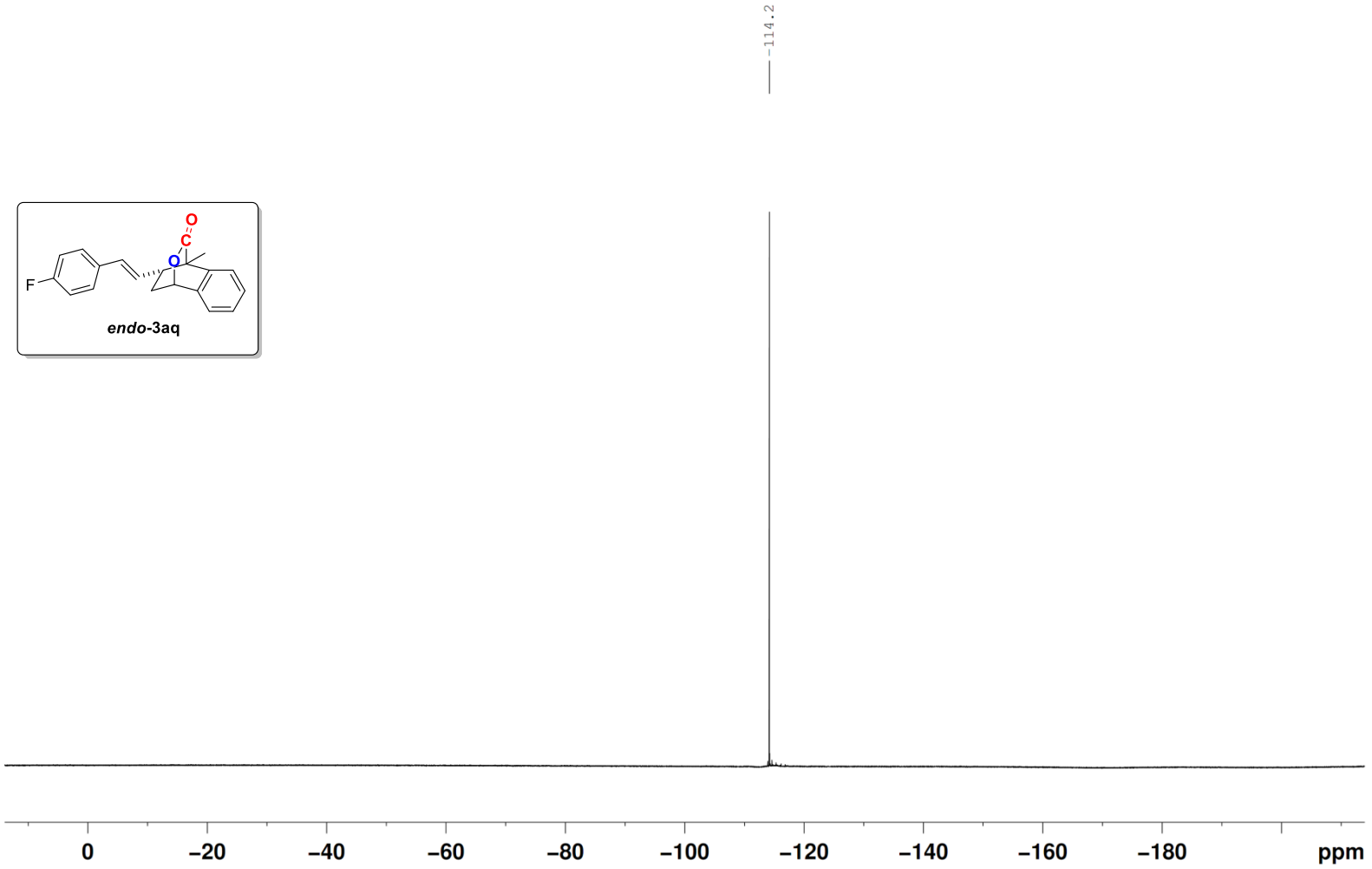

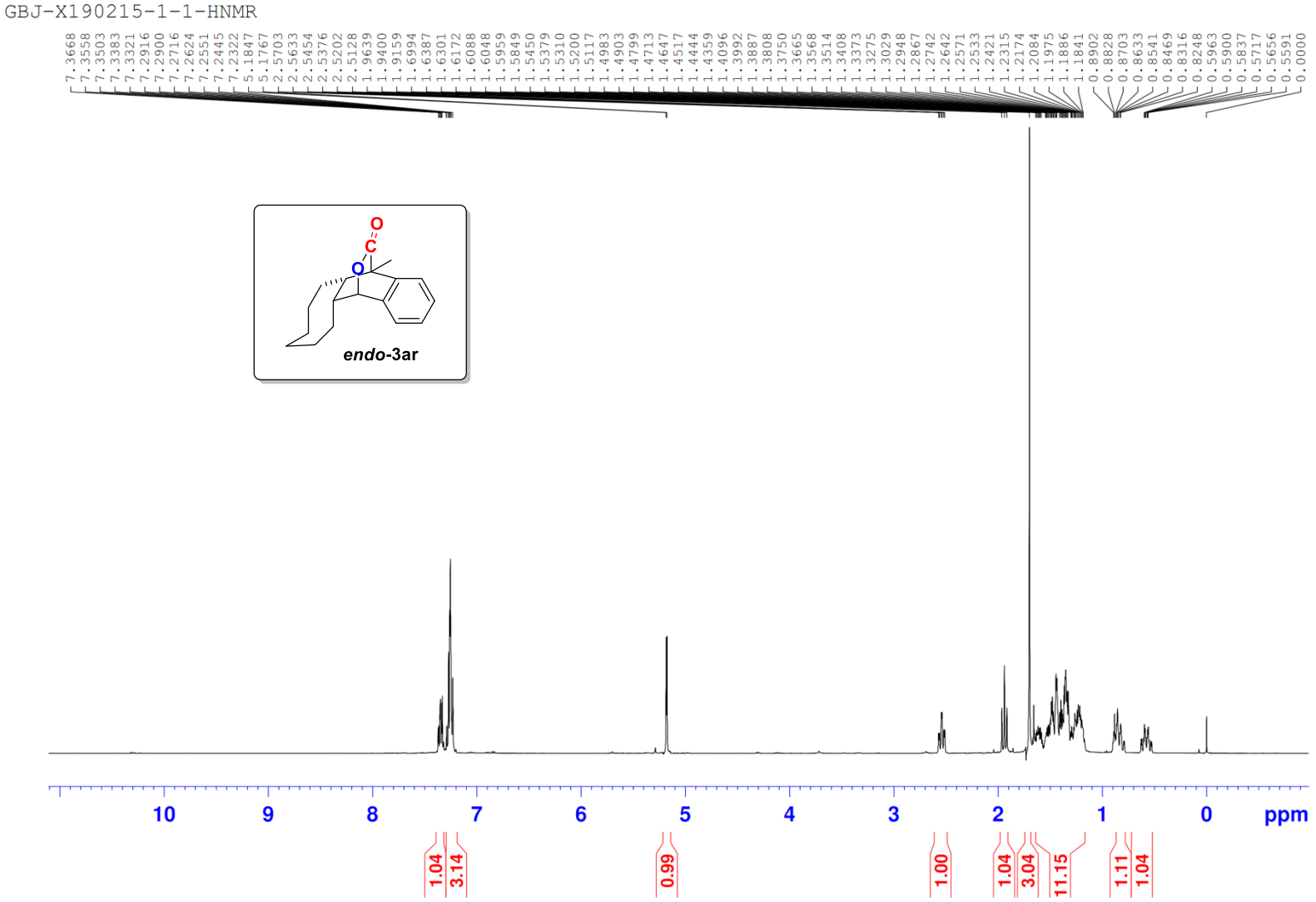
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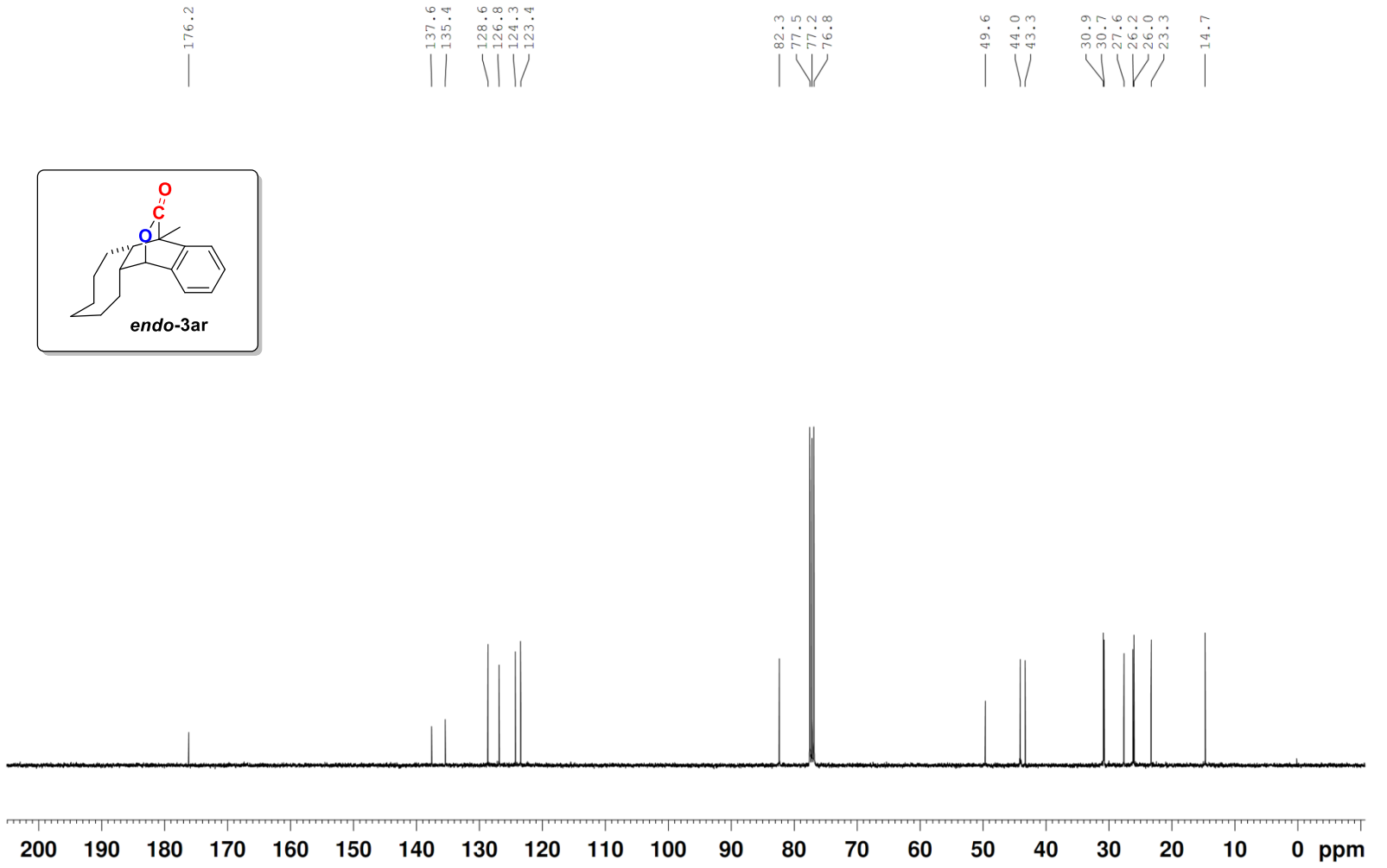
GBJ-X190215-1-1-CNMR



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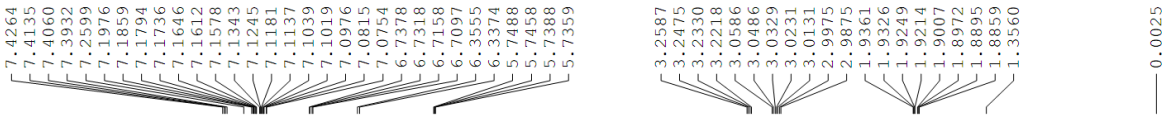
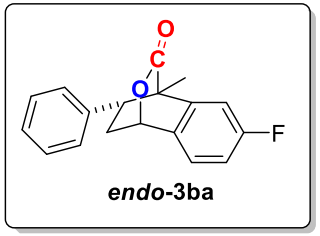
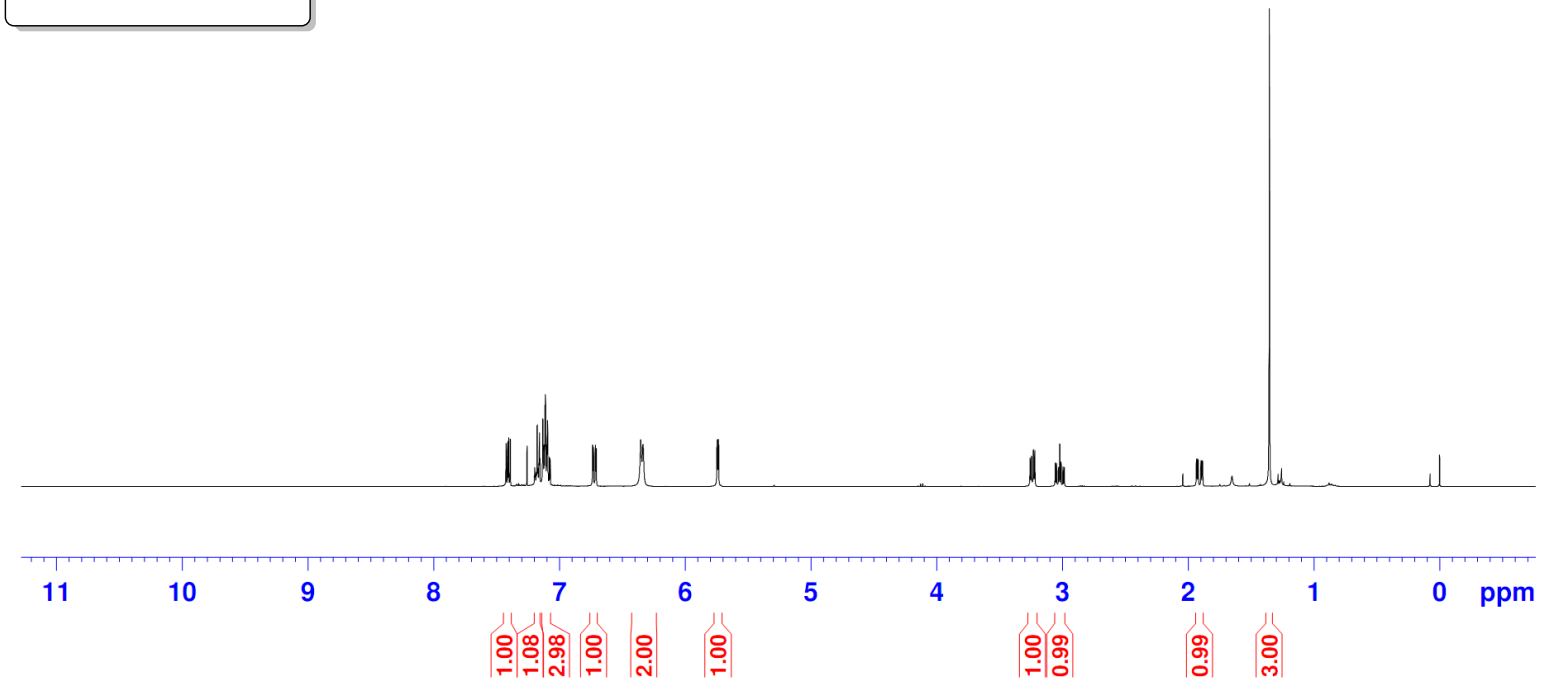




***endo*-3ba**



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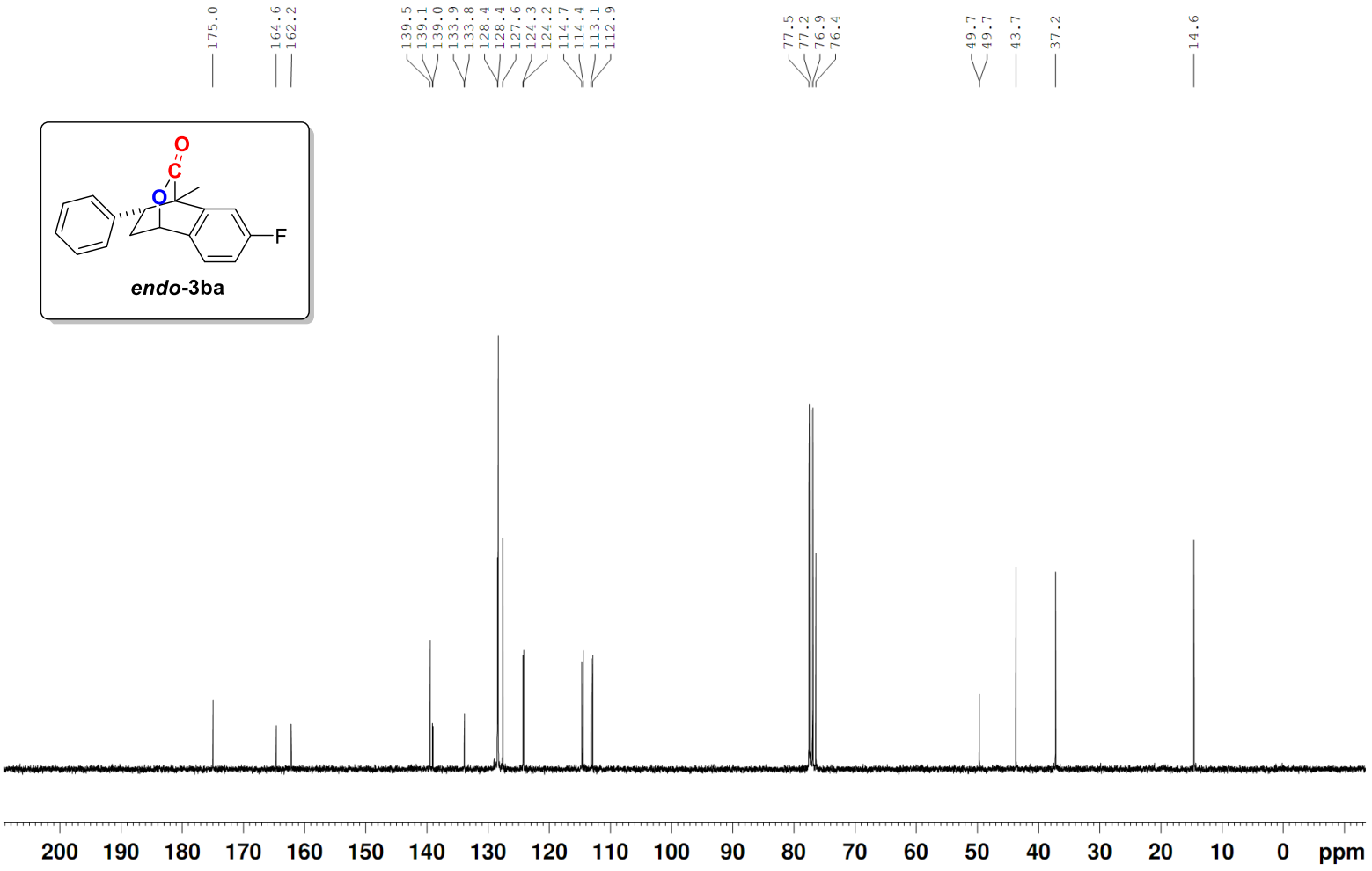

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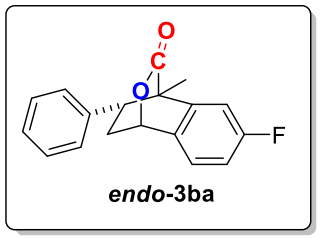
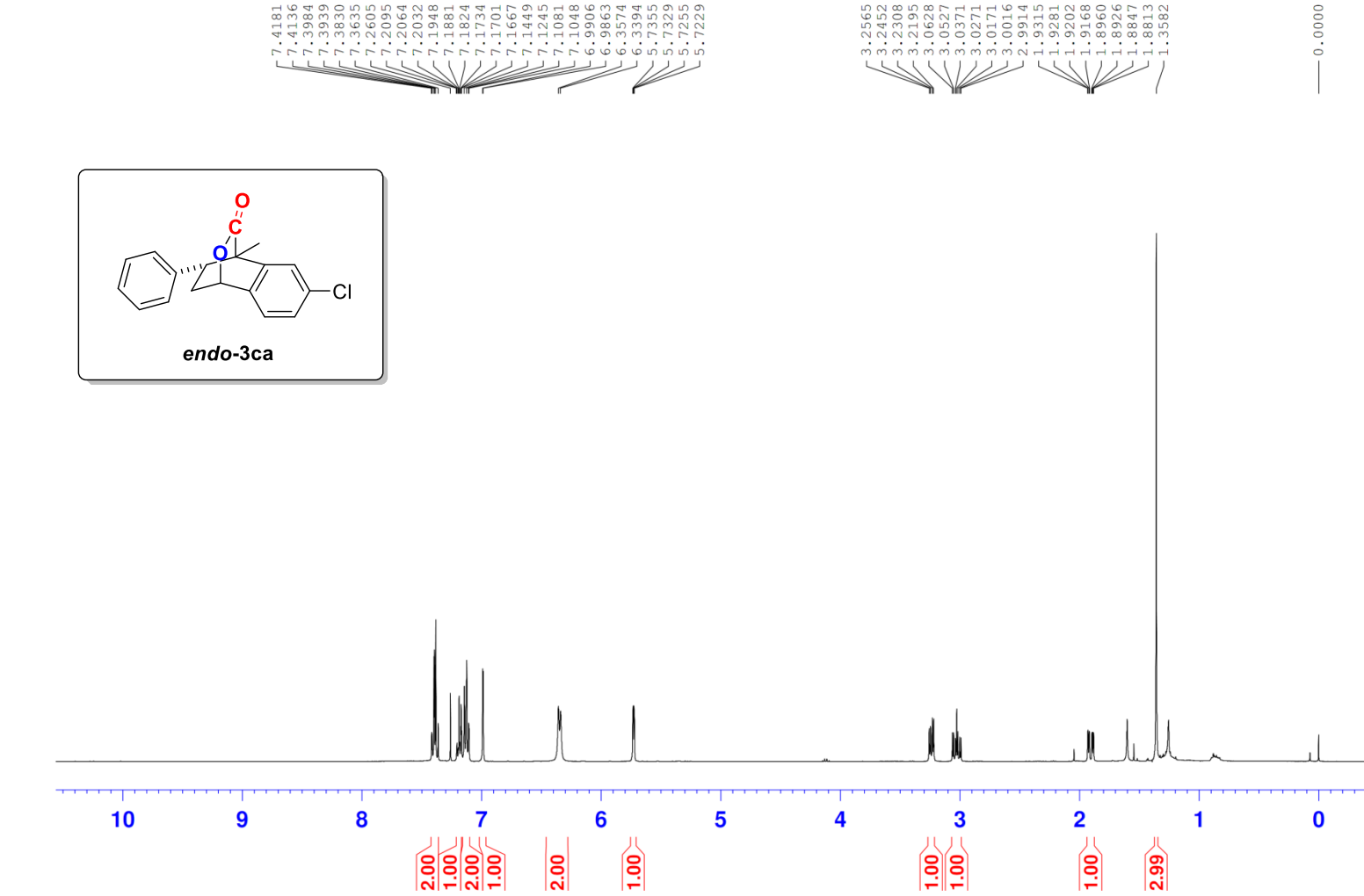


***endo*-3ba**

GBJ-X191107-3-HNMR



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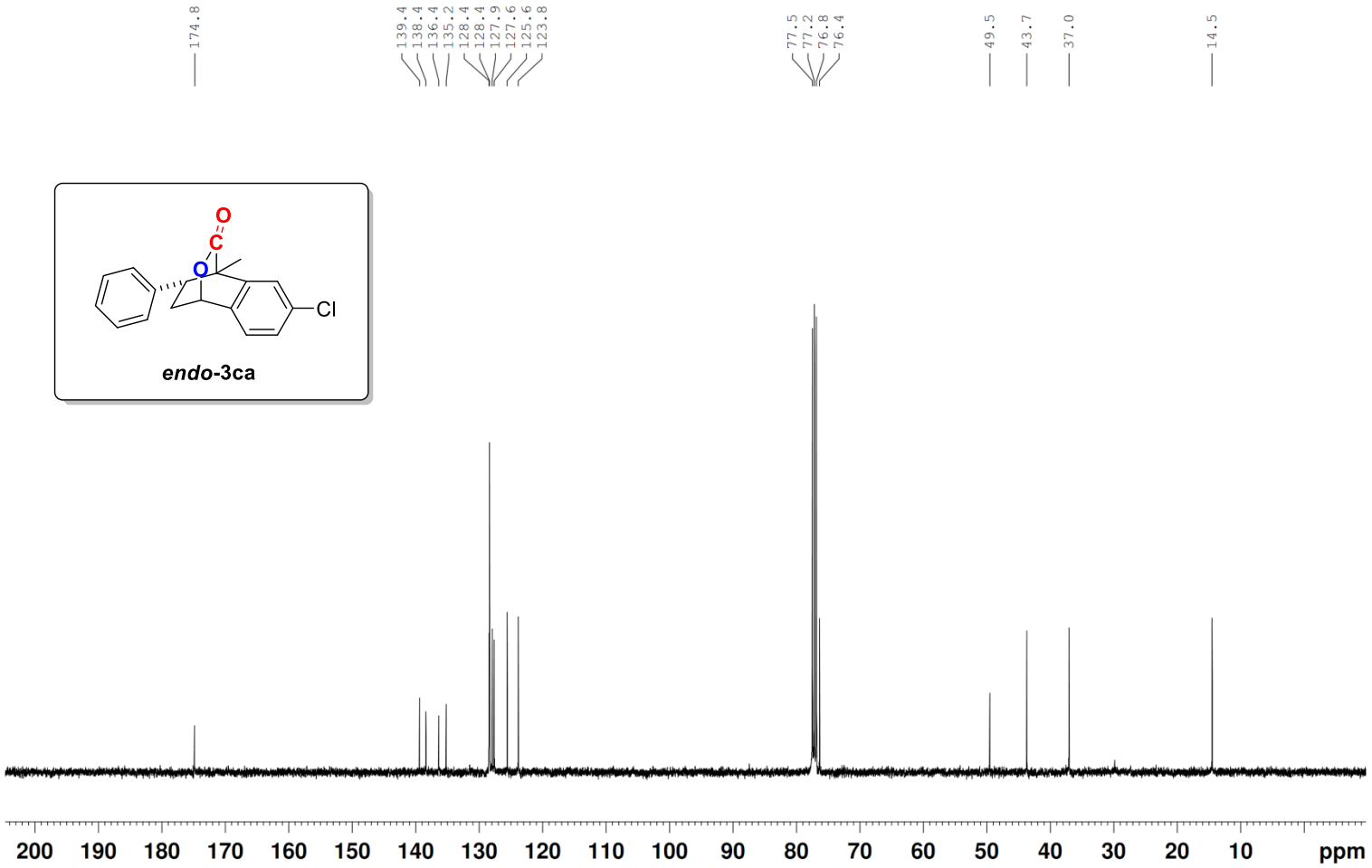

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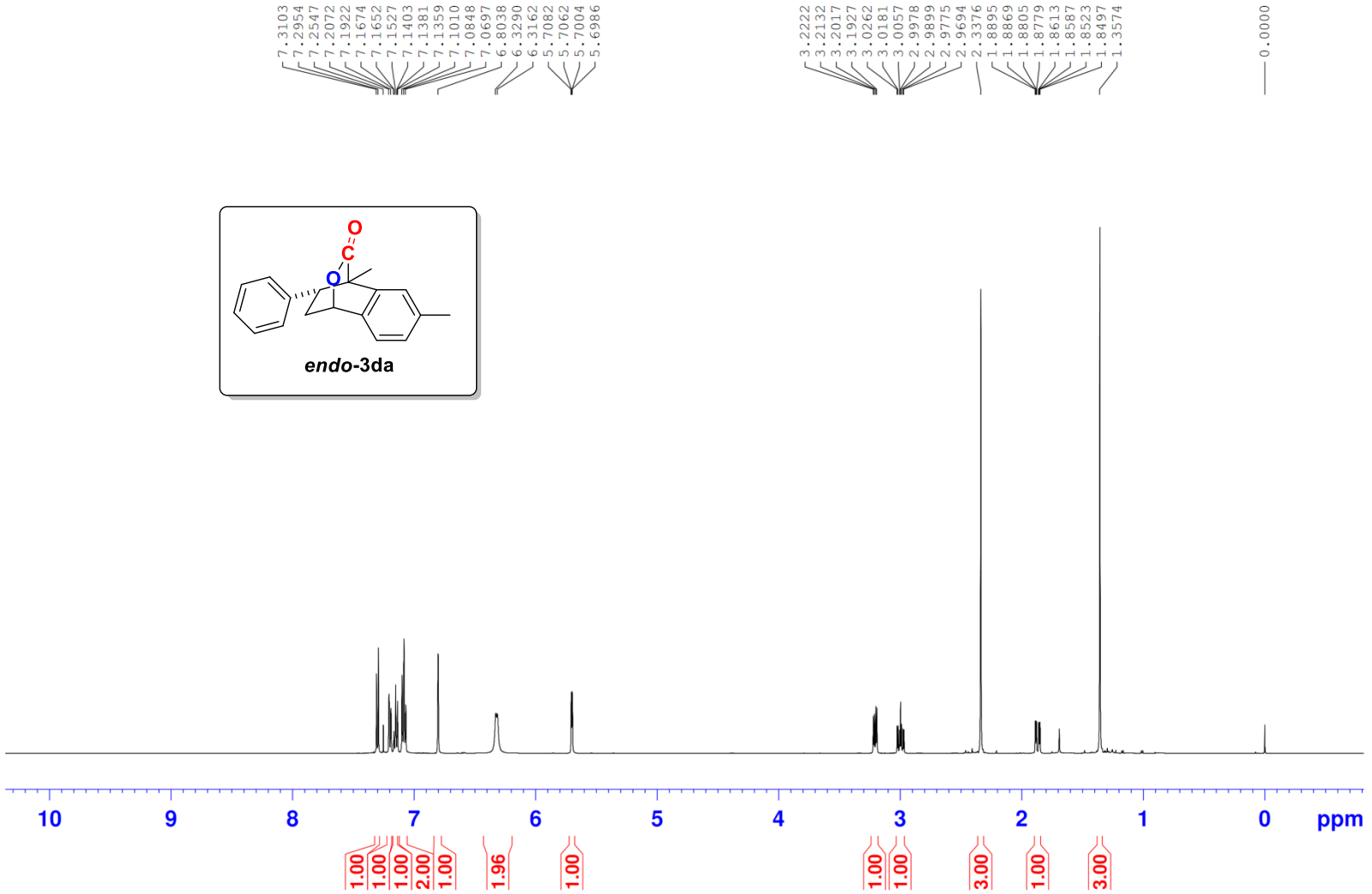

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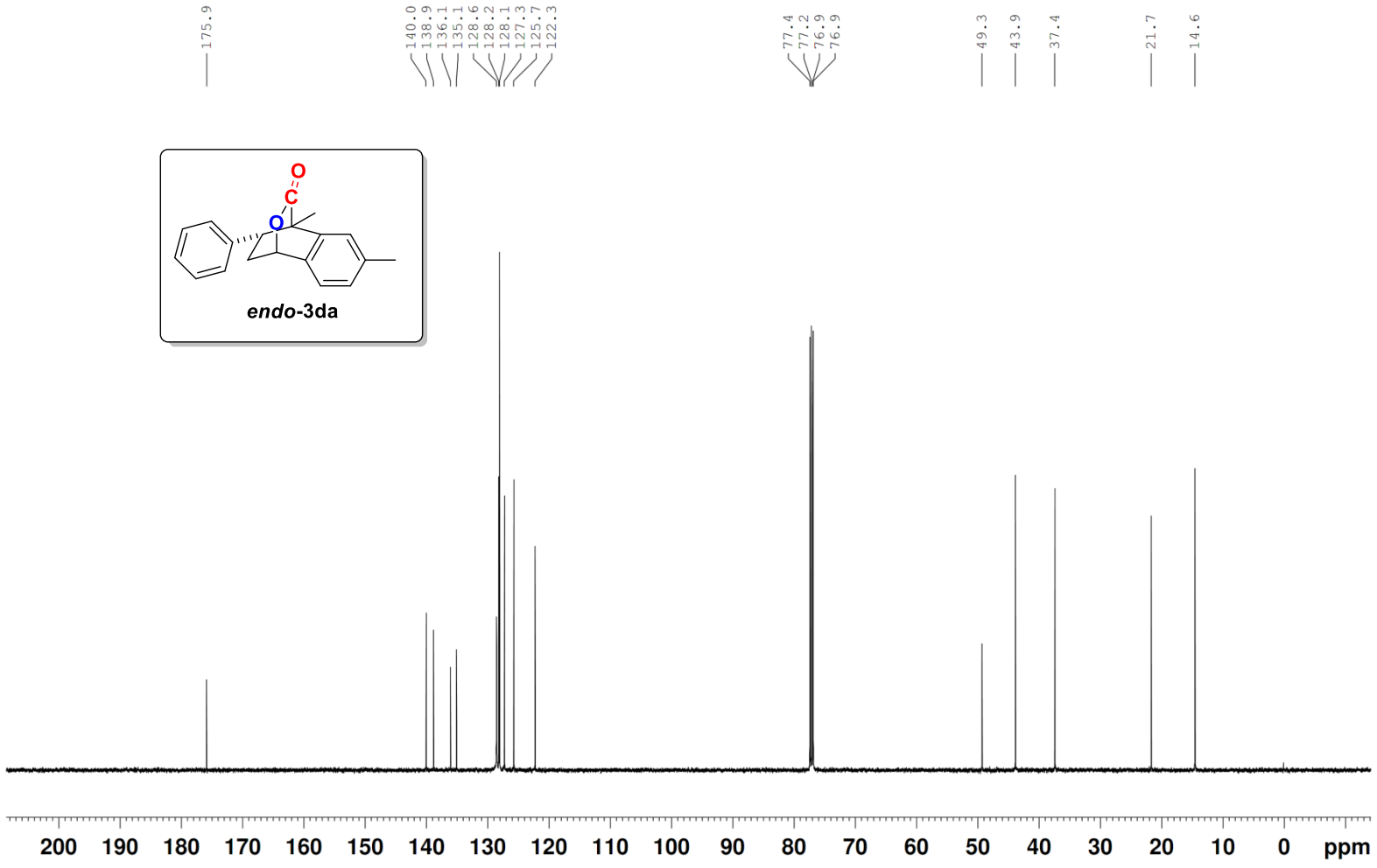
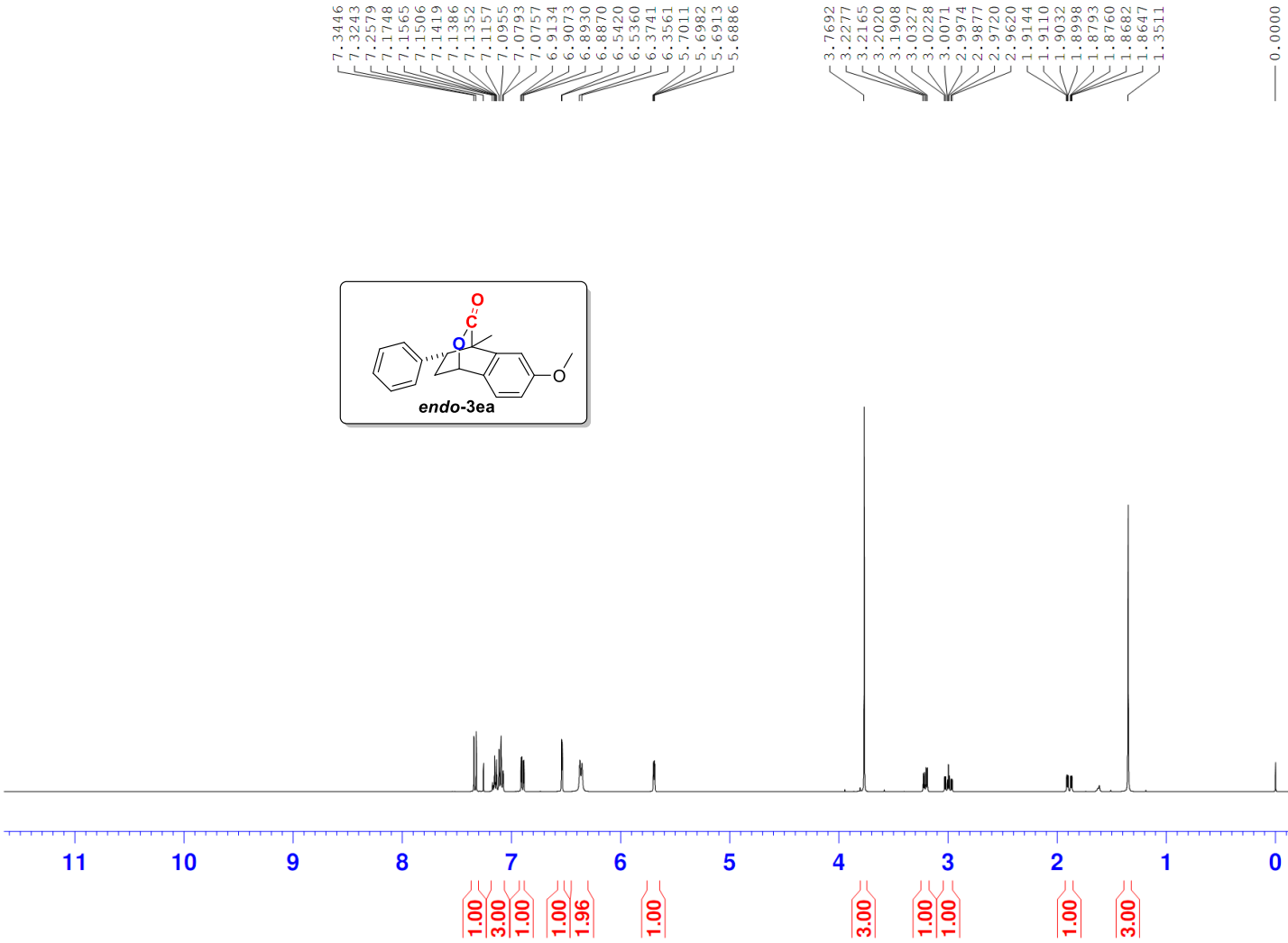
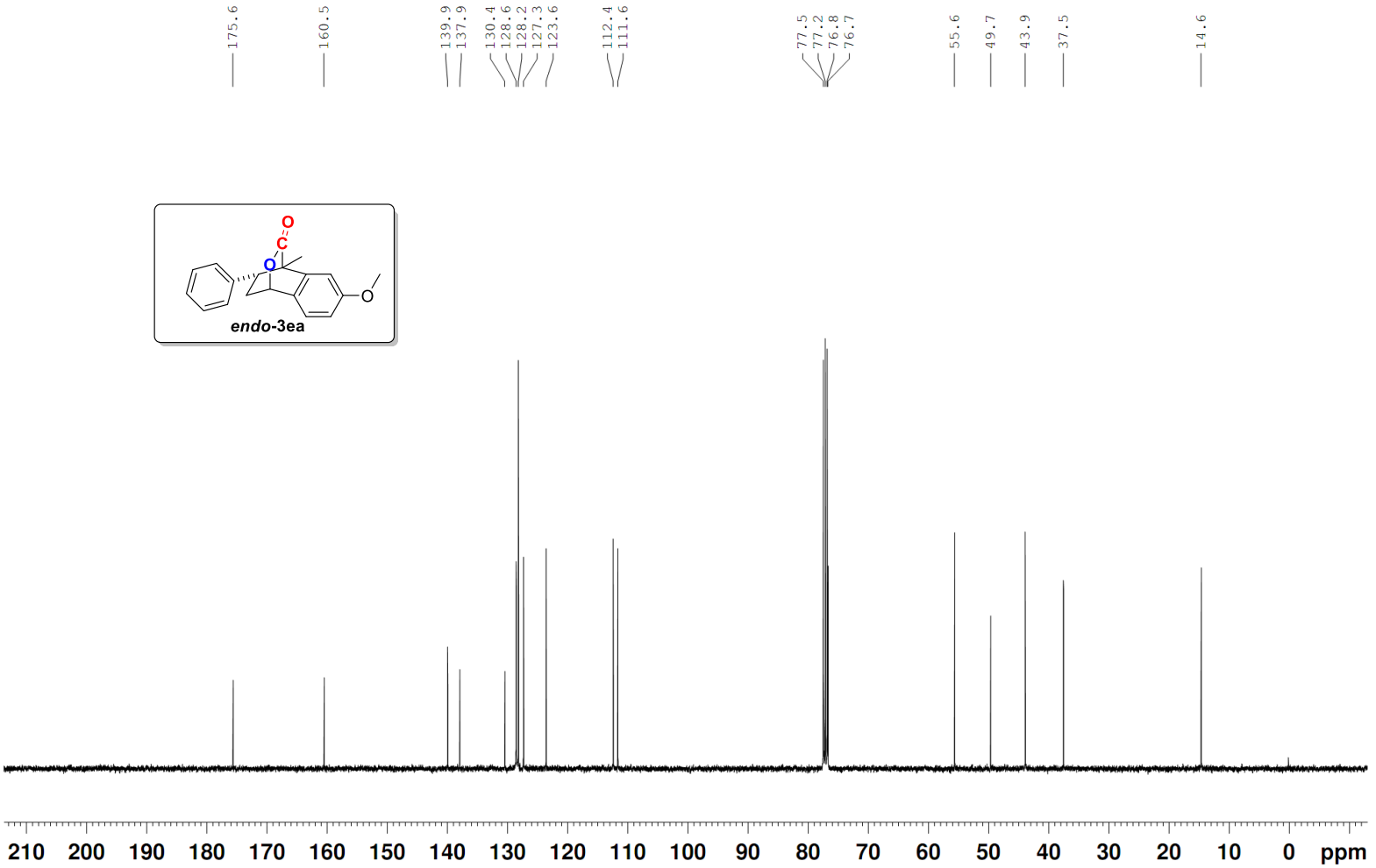


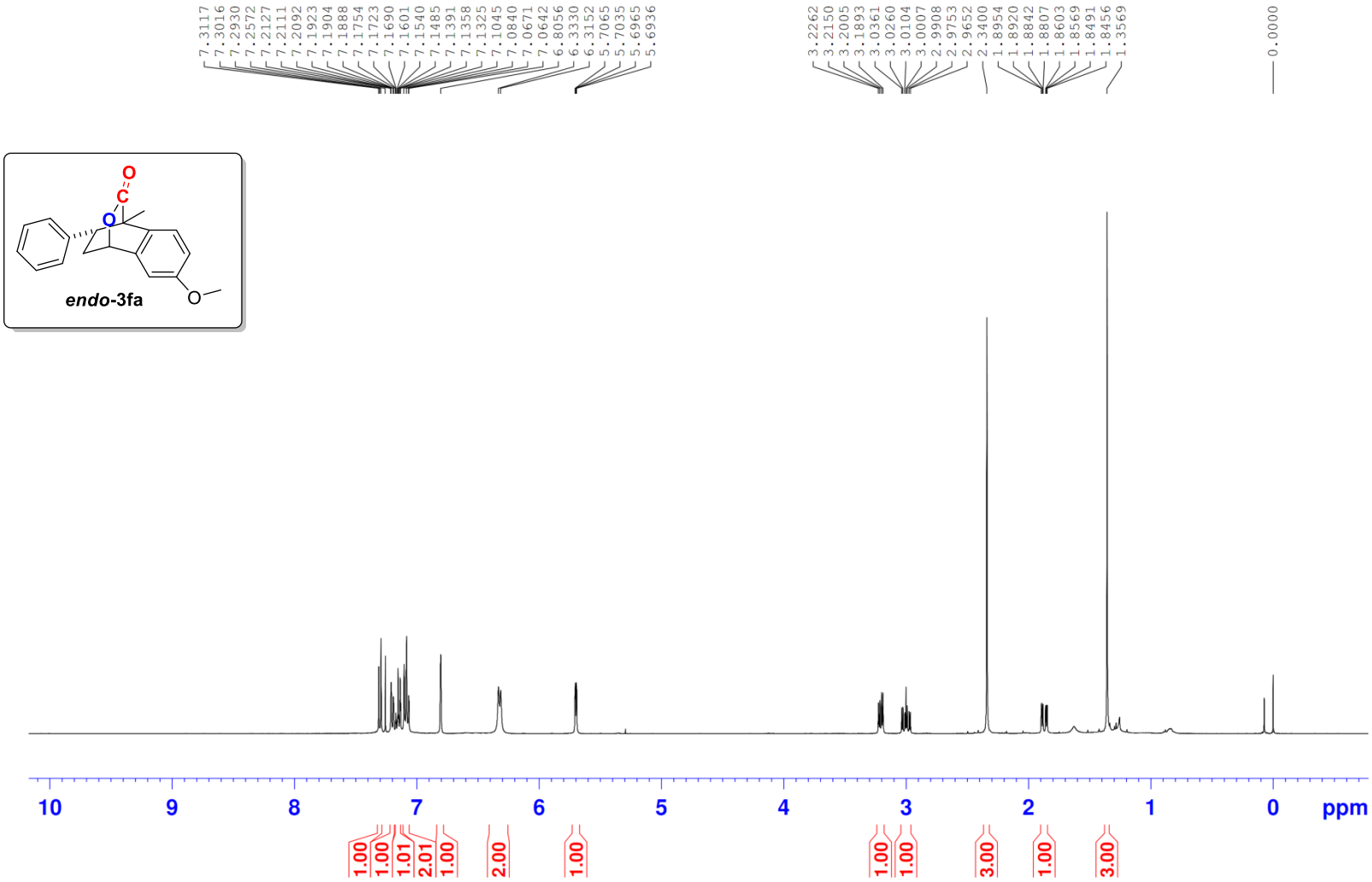
GBJ-X19O227-1-8-H



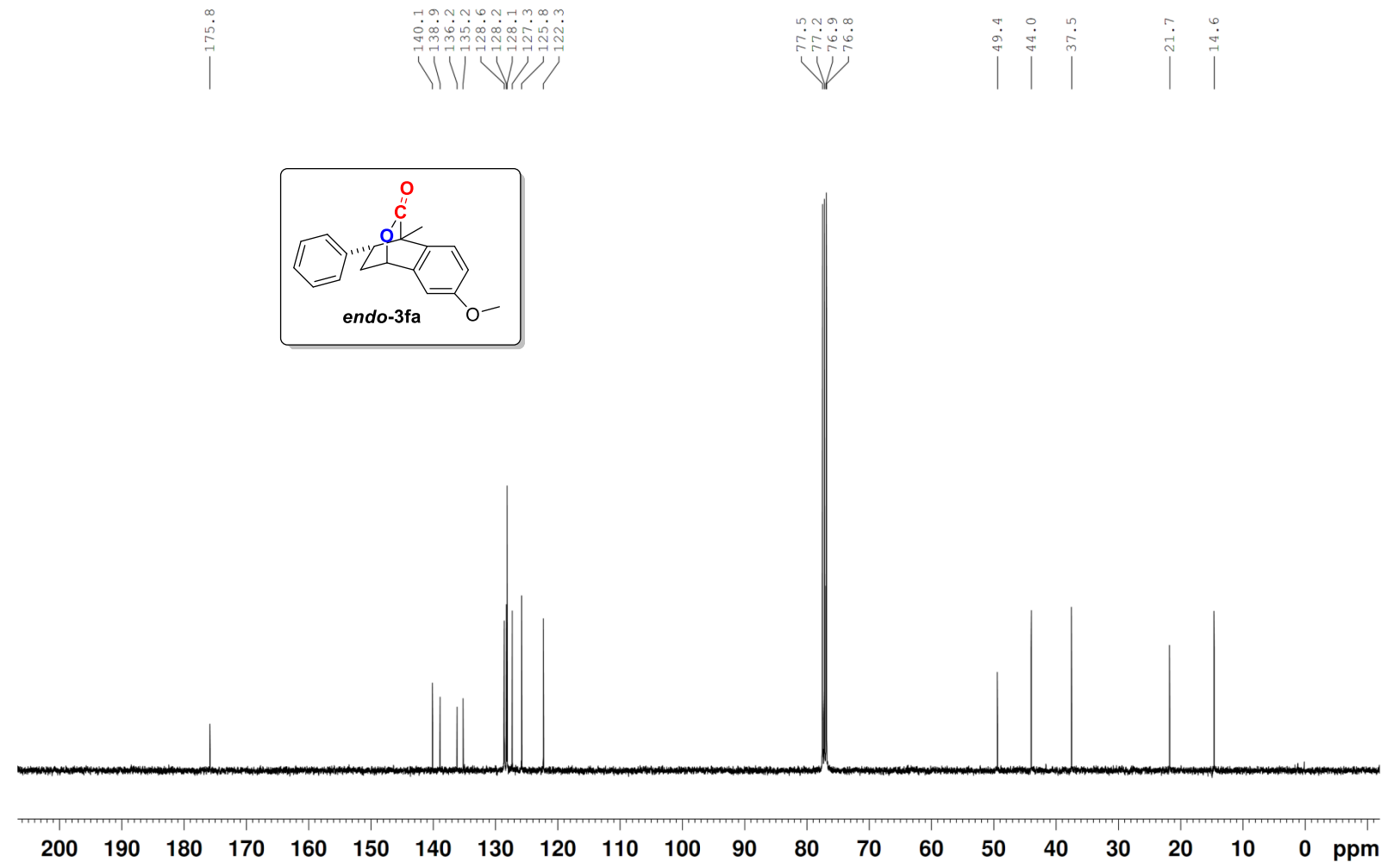
GBJ-X190227-1-8-C



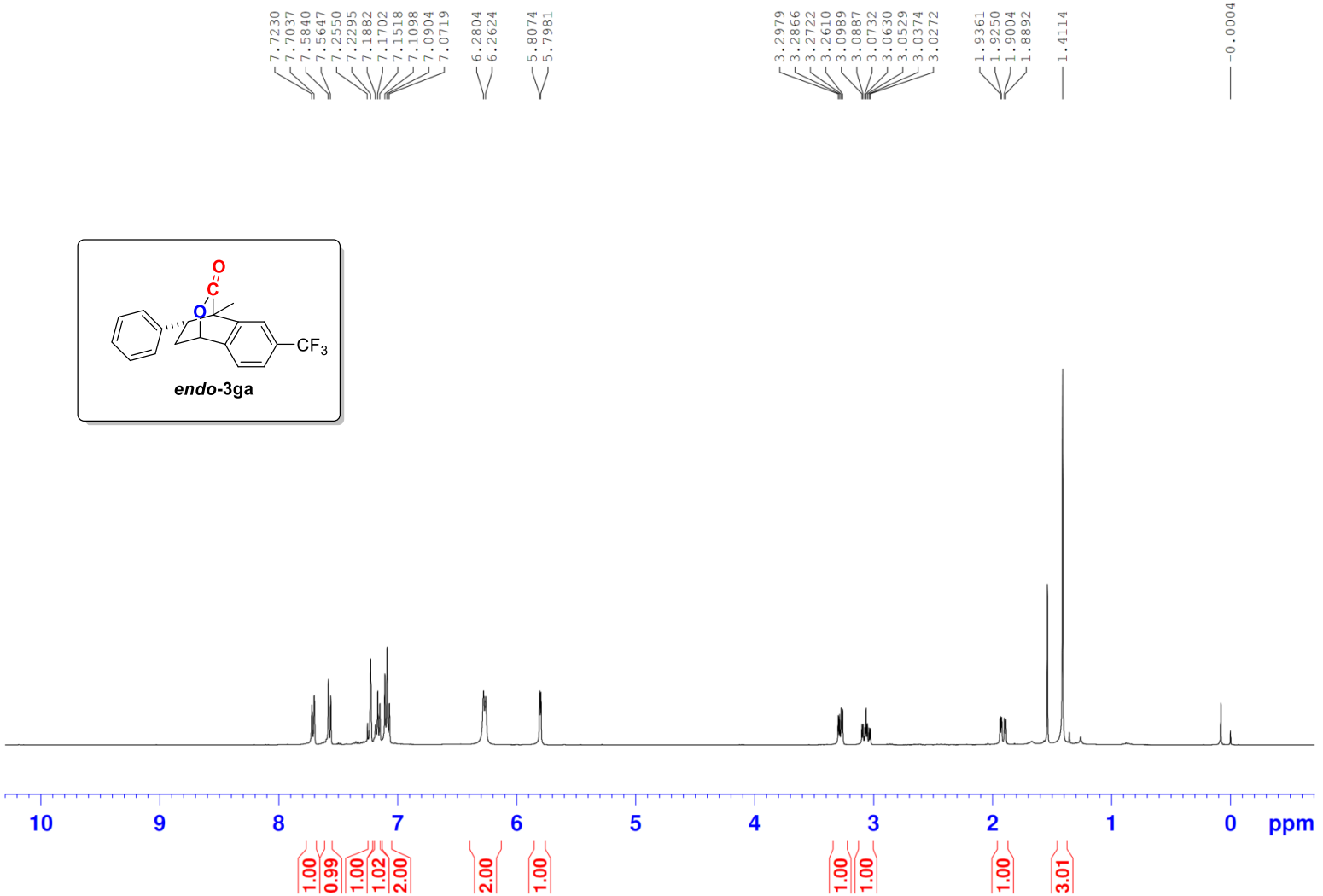
GBJ-X191213-1-HNMR



GBJ-X191213-1-CNMR



GBJ-X190227-1-5-HNMR



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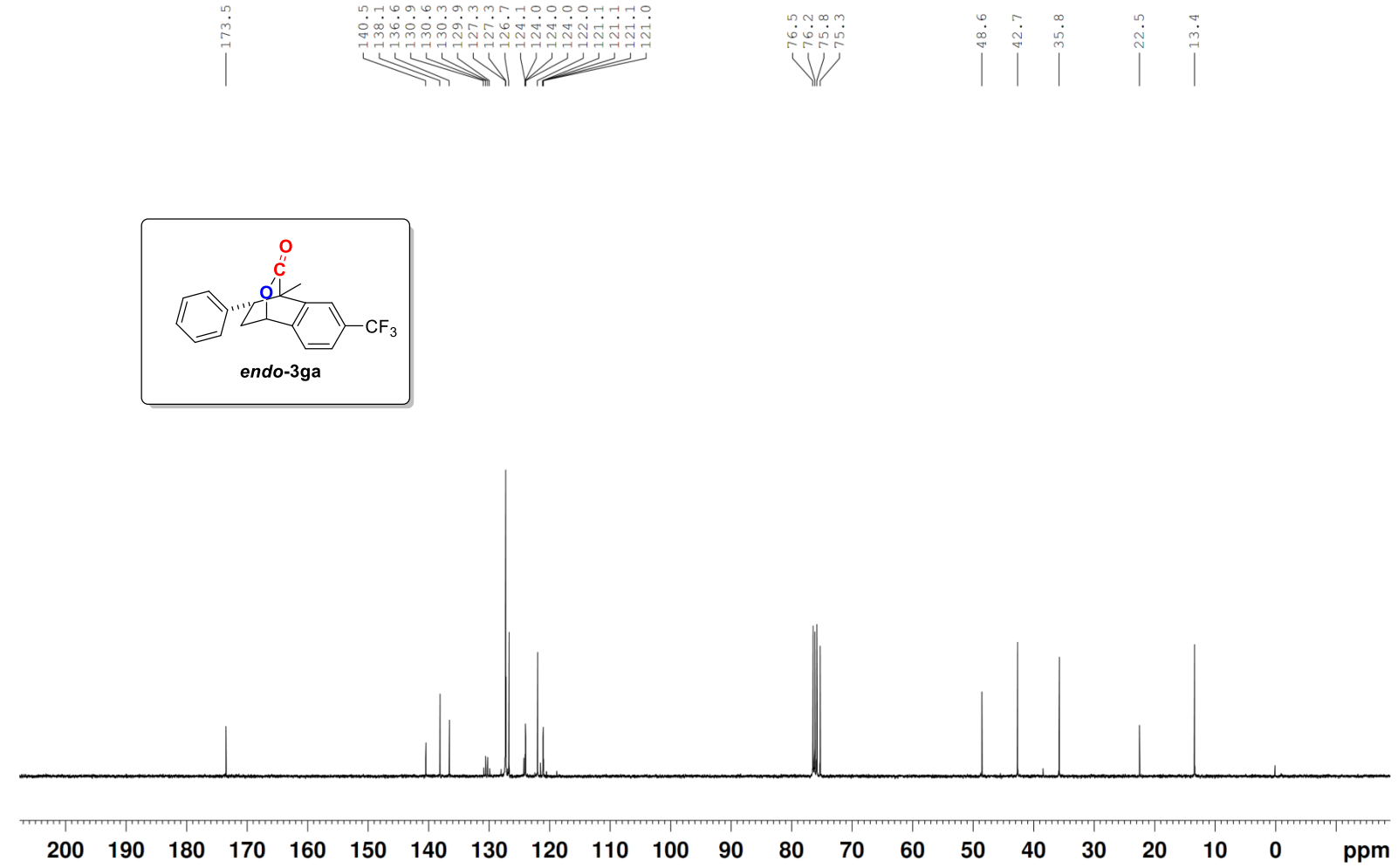
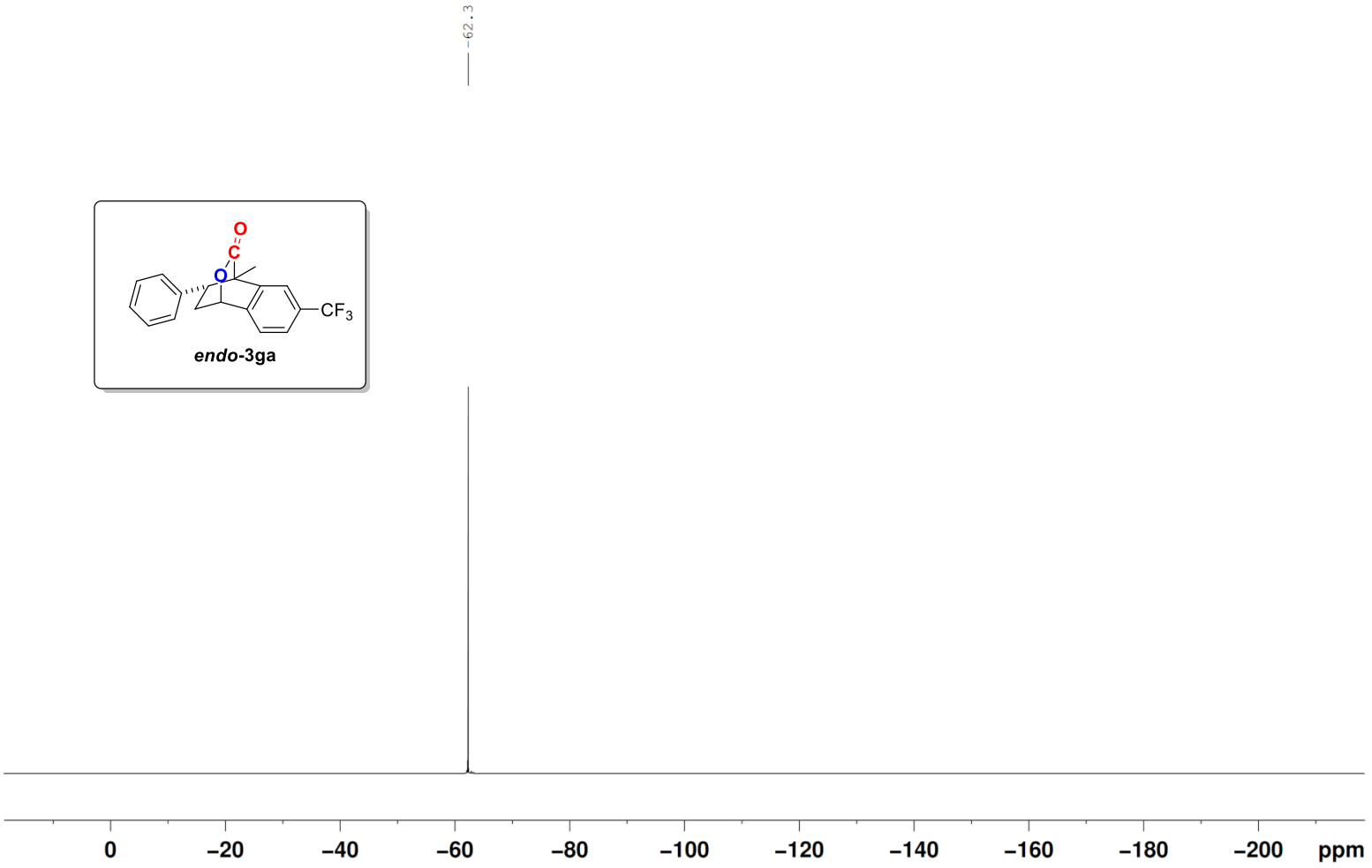


GBJ-X190227-1-5-FNMR



GBJ-X190311-1-1-HNMR

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7.1934
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6.4299
6.4125
6.0569
6.0537
5.9970
5.9938
5.6427
5.6353
5.6331

3.1928
3.1817
3.1674
3.1563
3.0232
3.0132
2.9978
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2.9781
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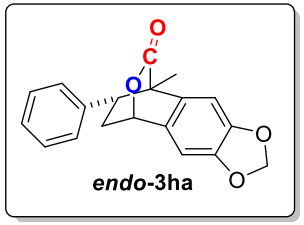
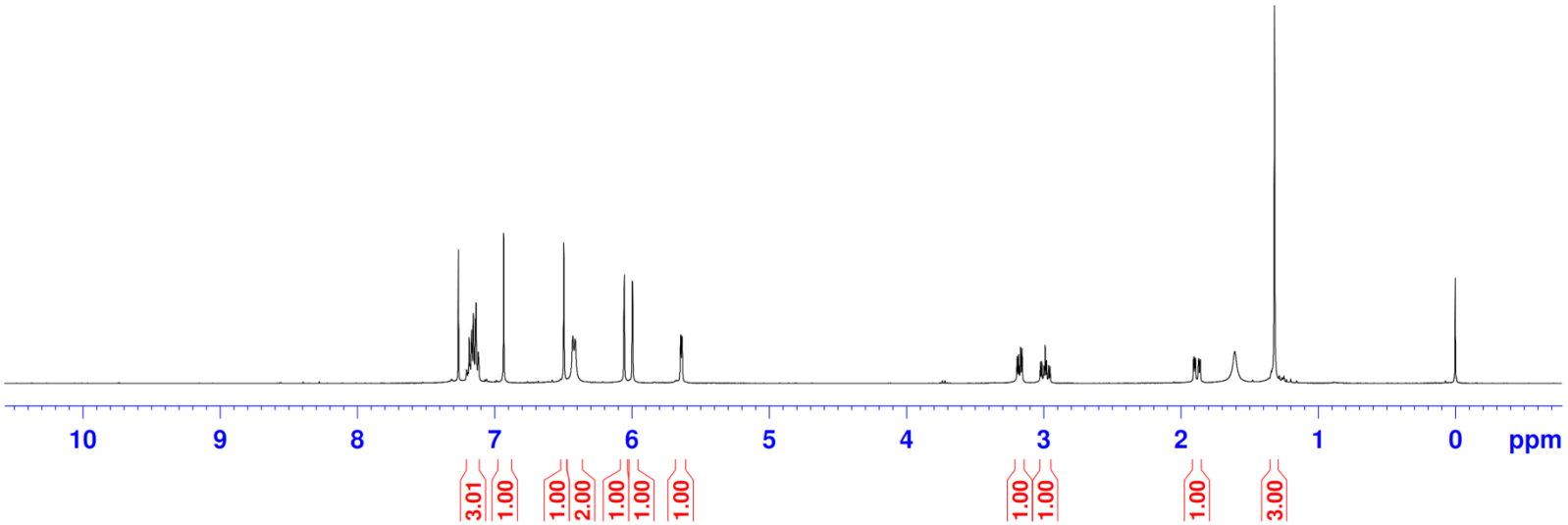
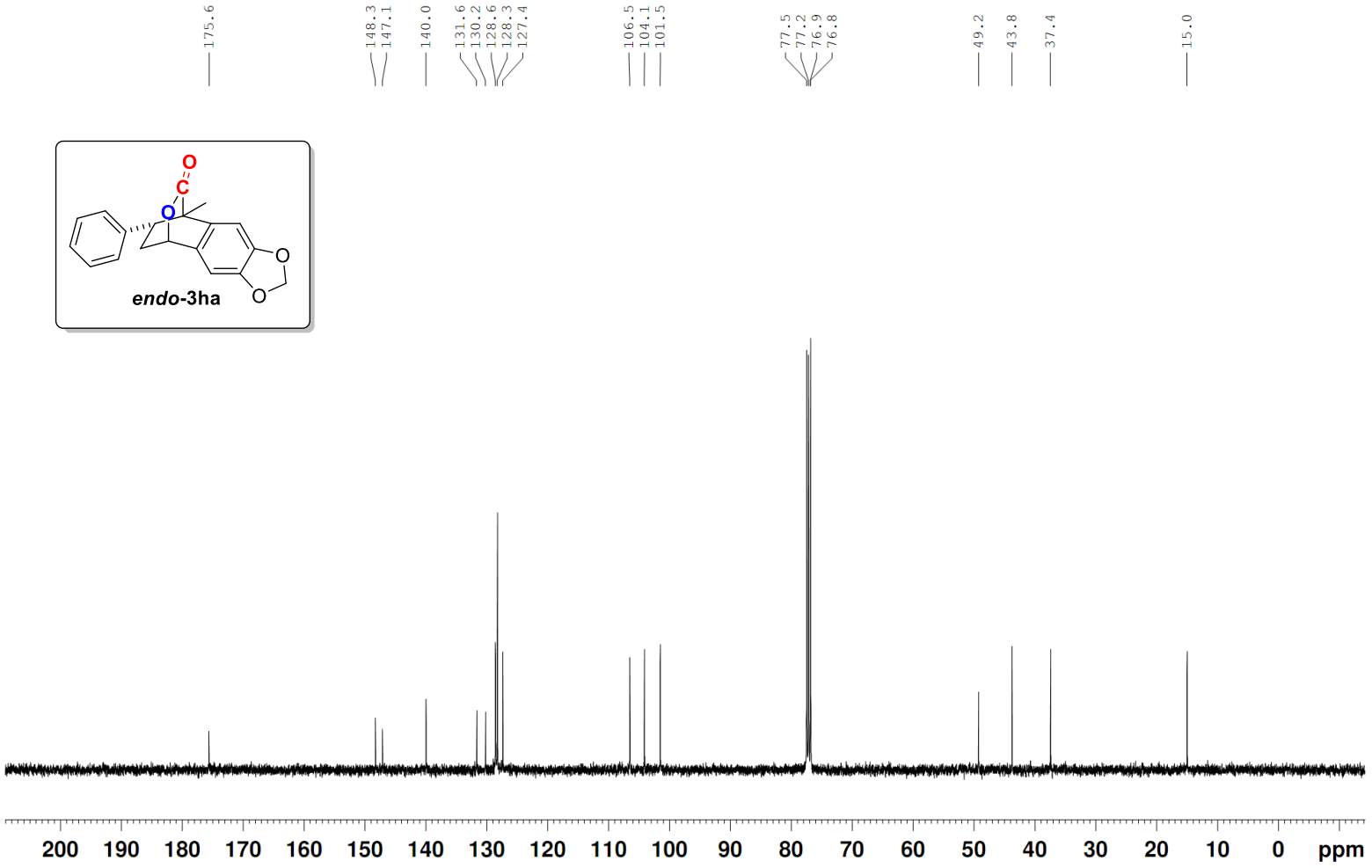
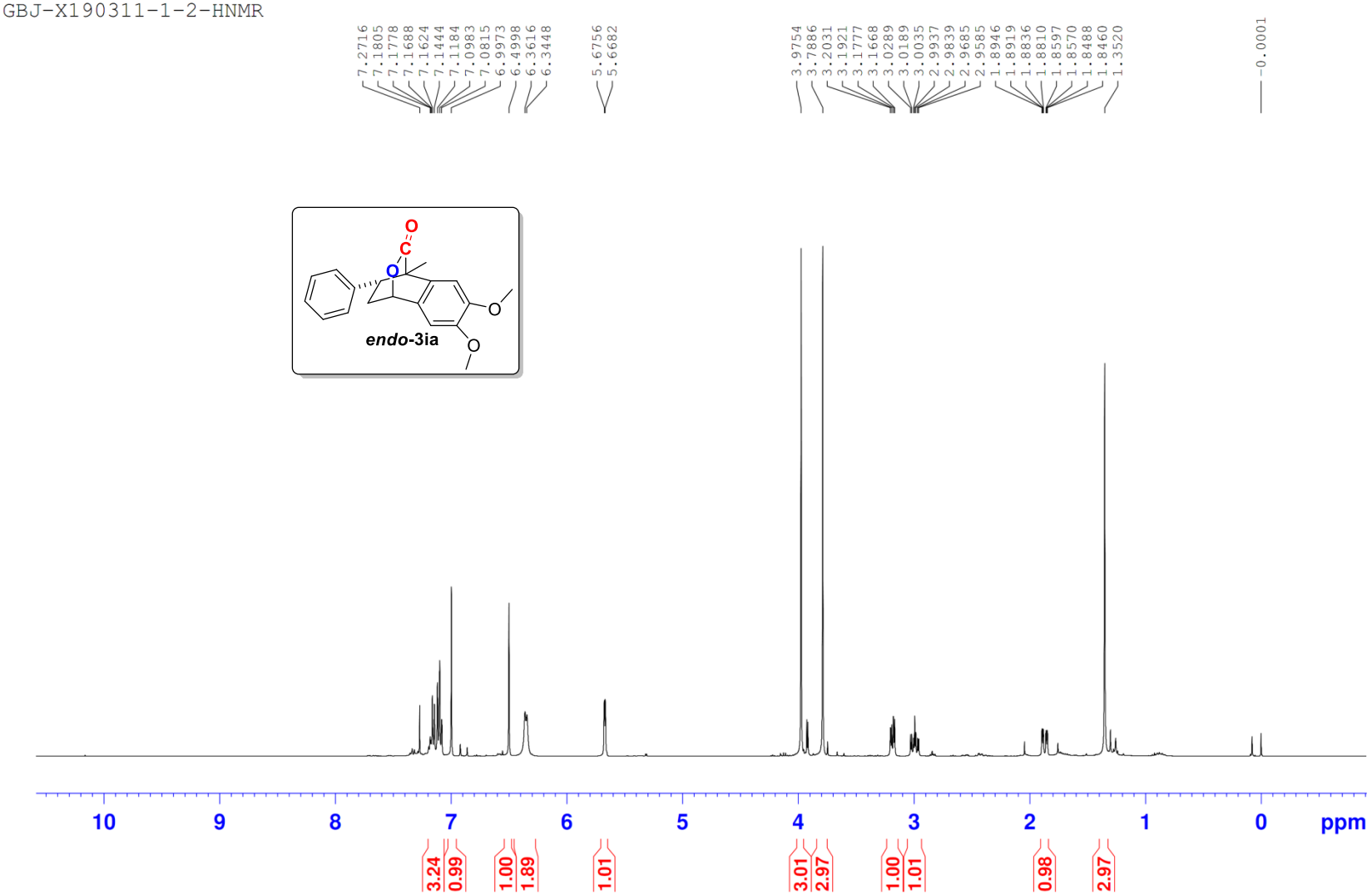




GBJ-X190311-1-1



GBJ-X190311-1-2-HNMR



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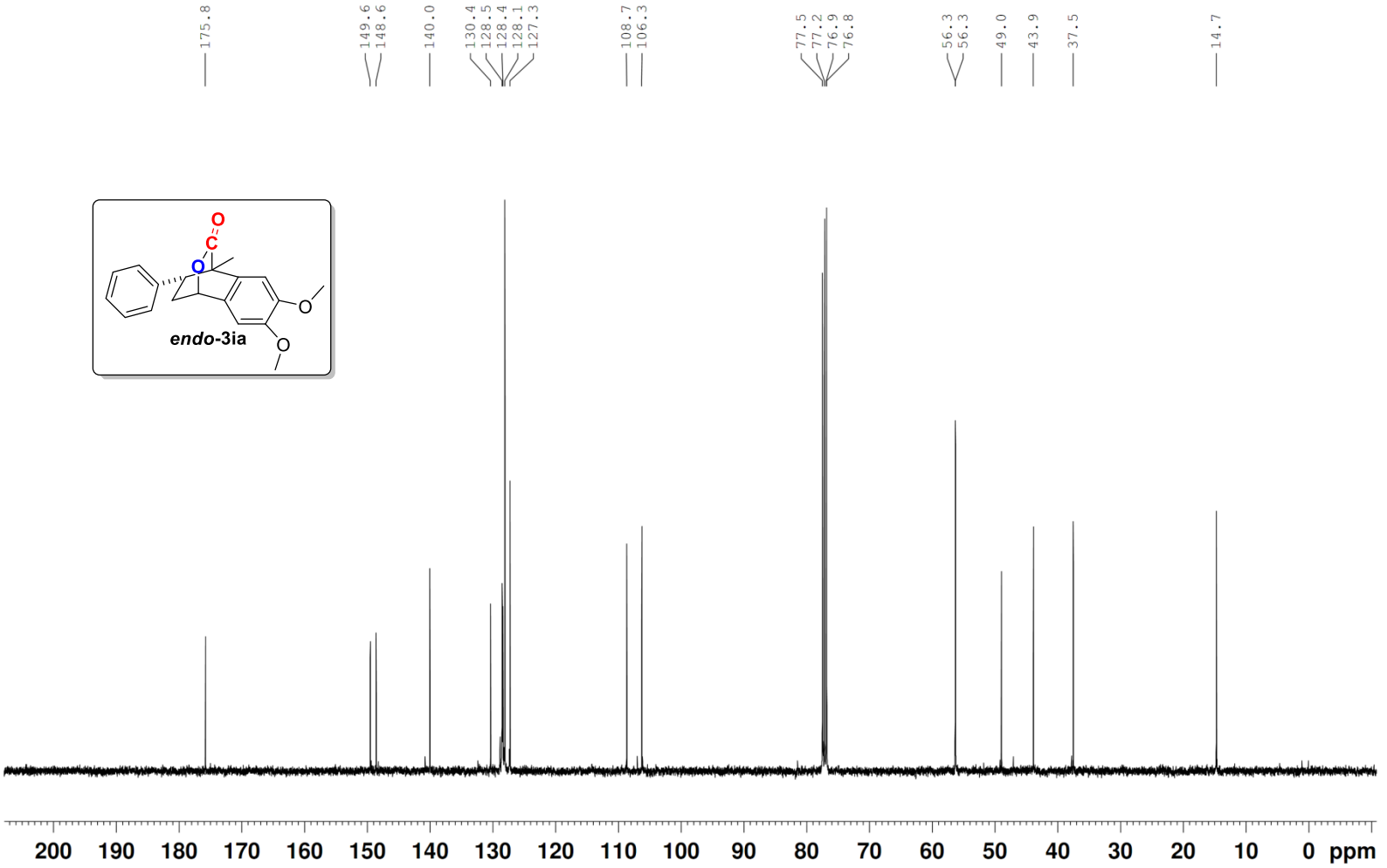
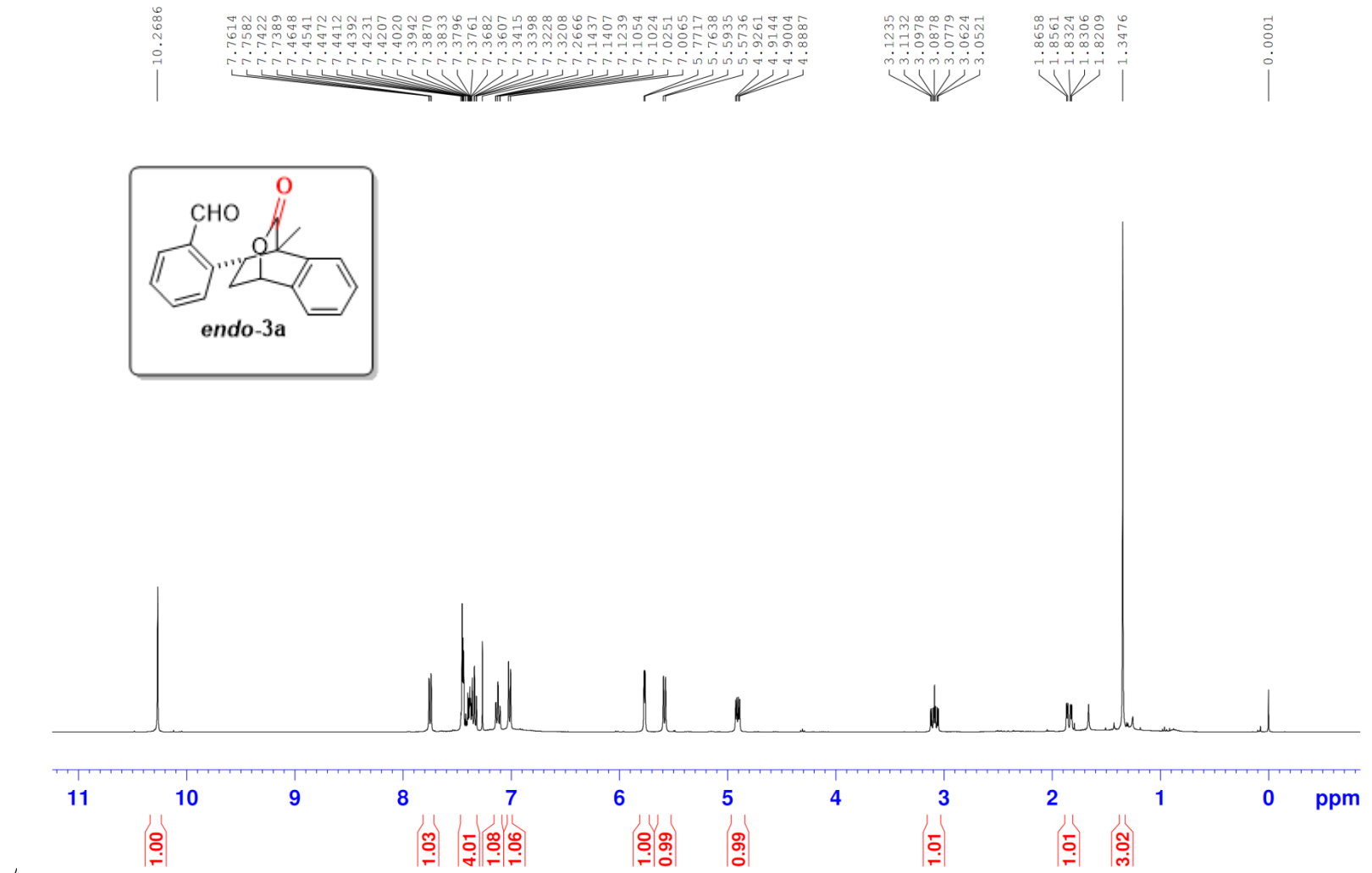


GBJ-X200104-HNMR



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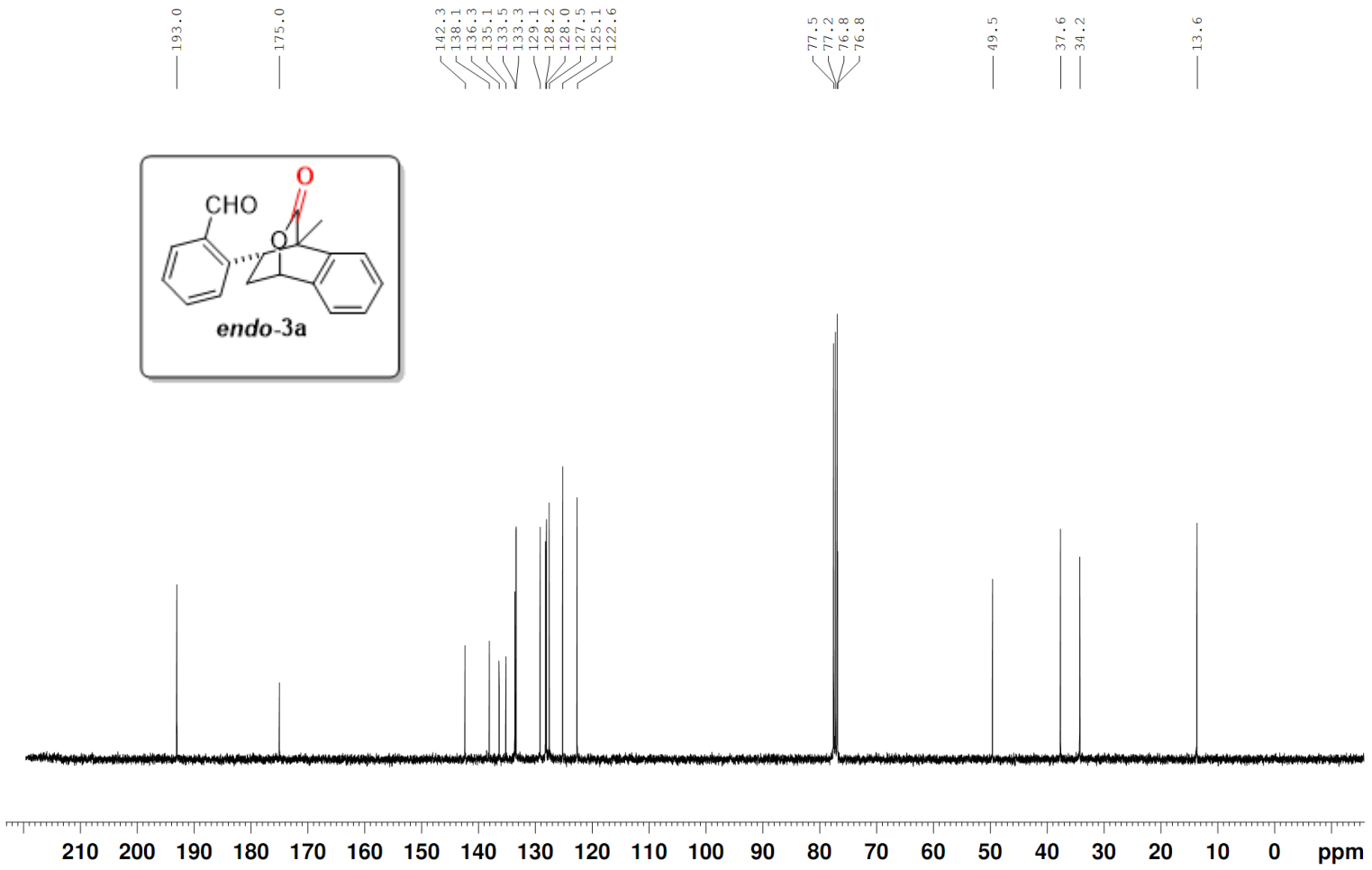
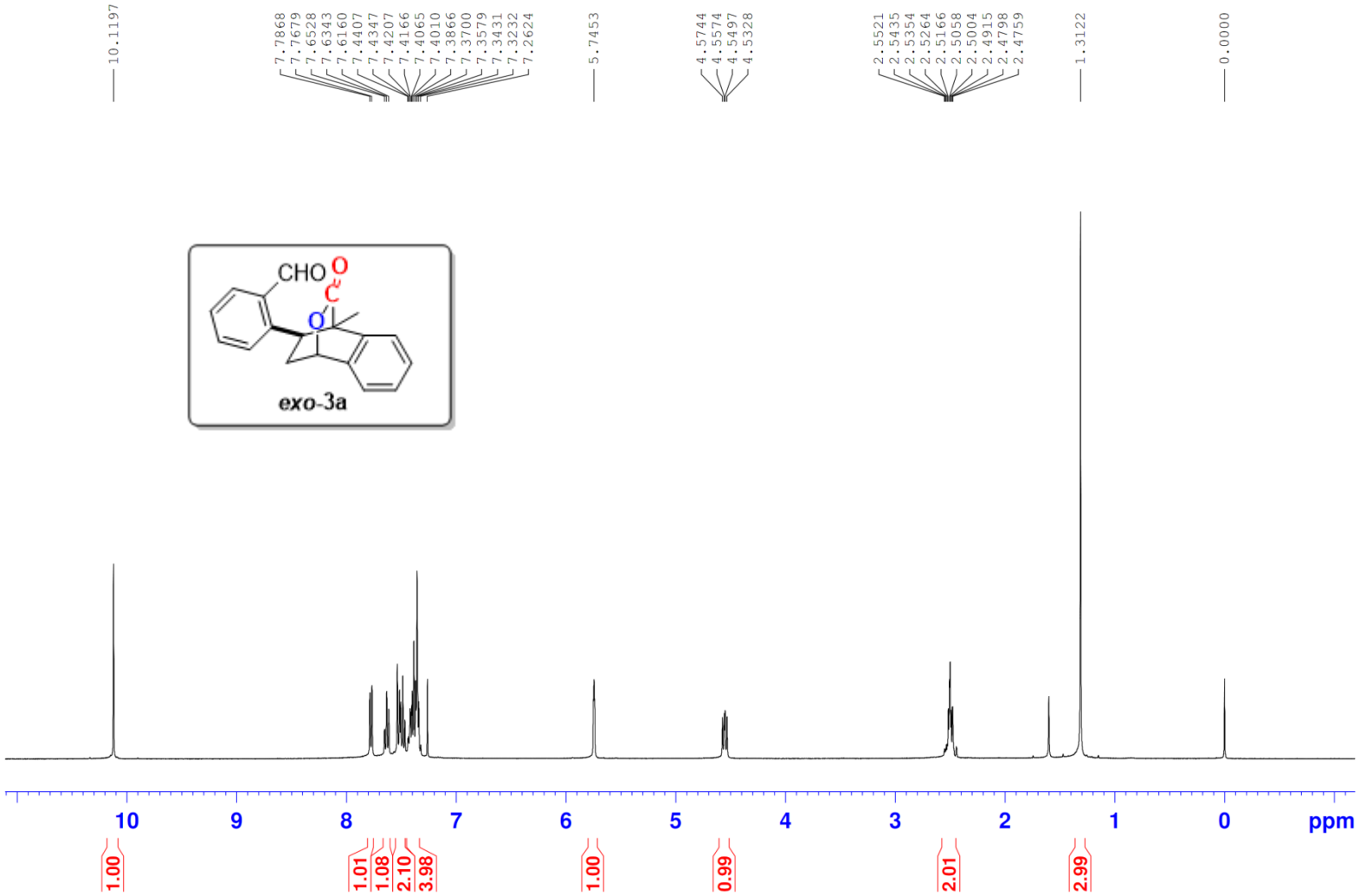
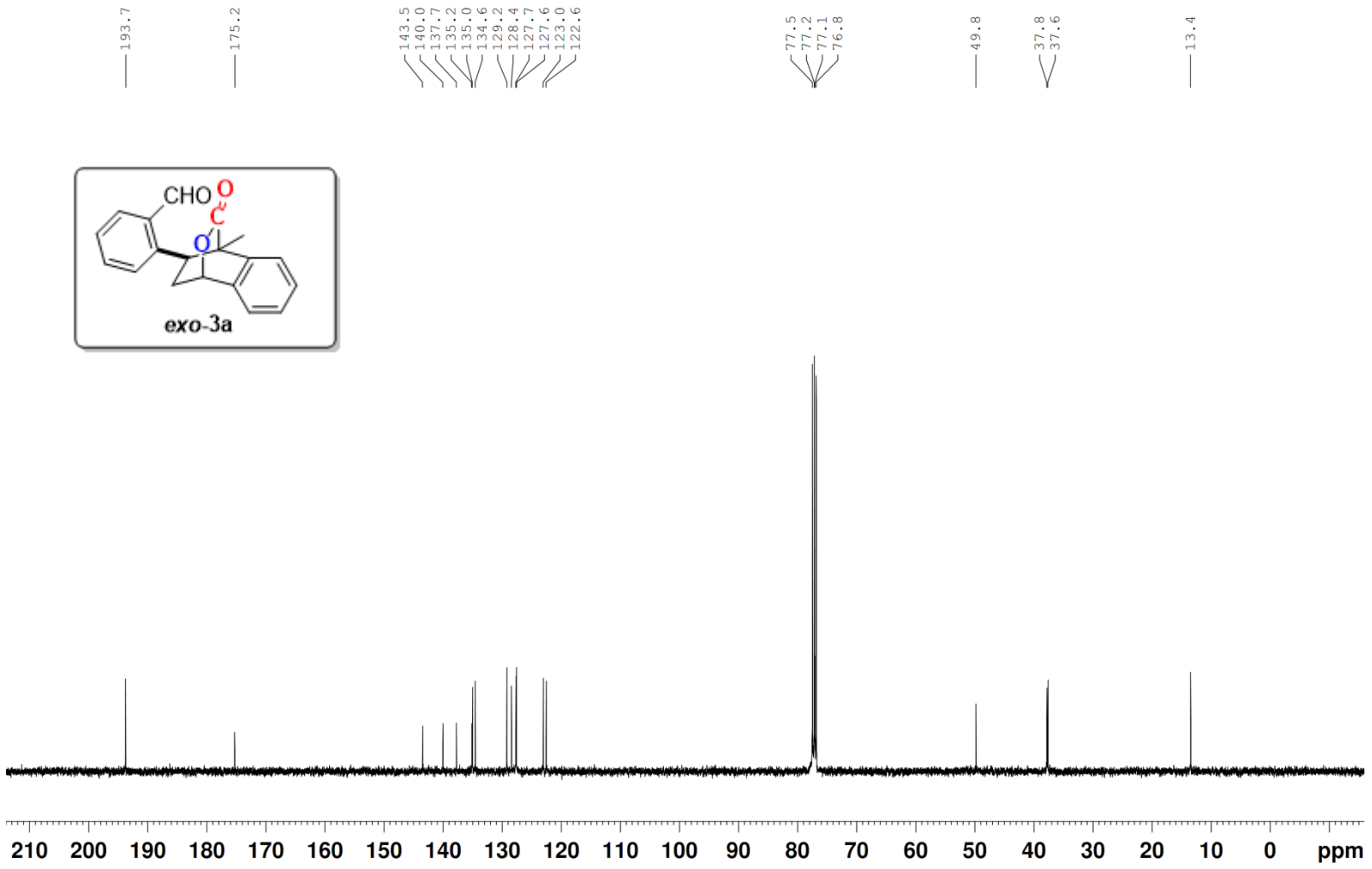
GBJ-X191104-CNMR



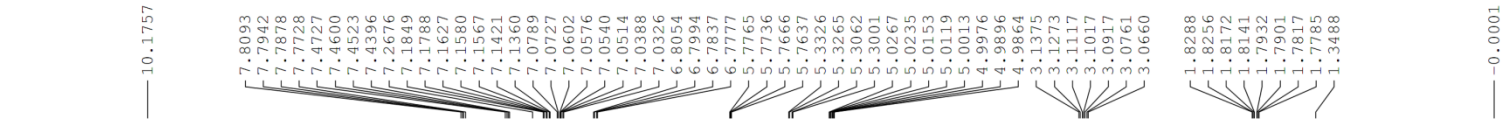
GBJ-X190312-1-H

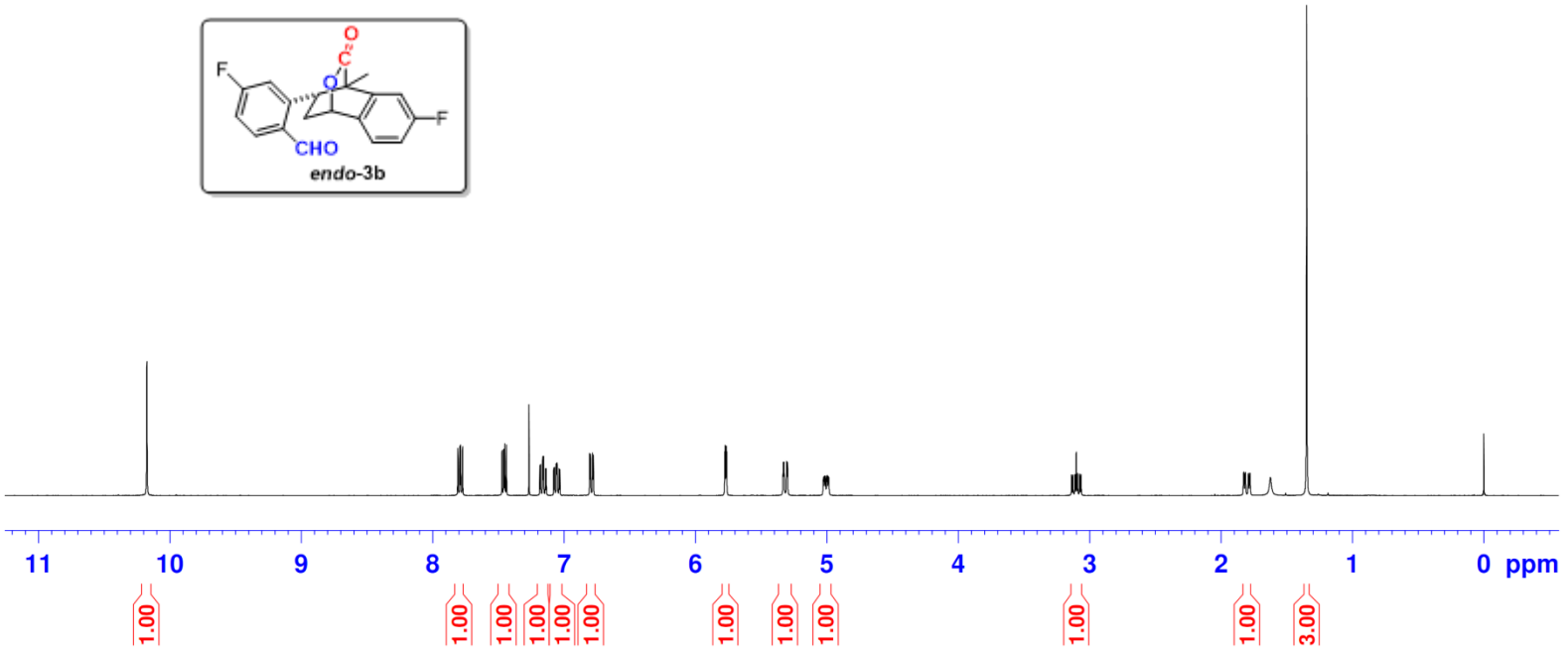


GBJ-X190312-1-C



GBJ-X190119-1-8-HNMR,





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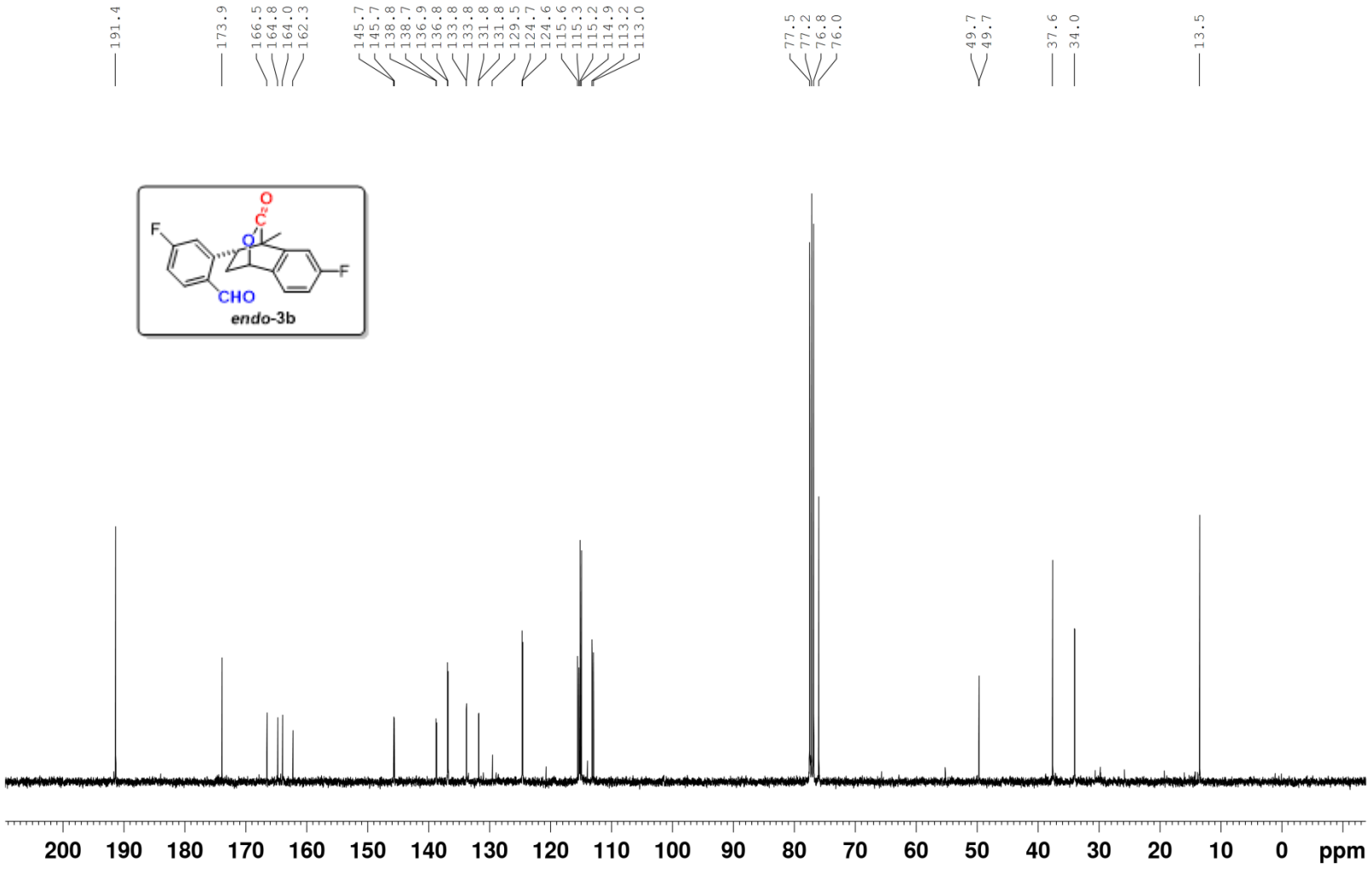

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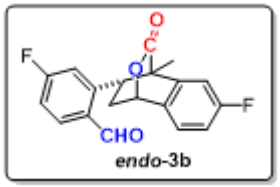
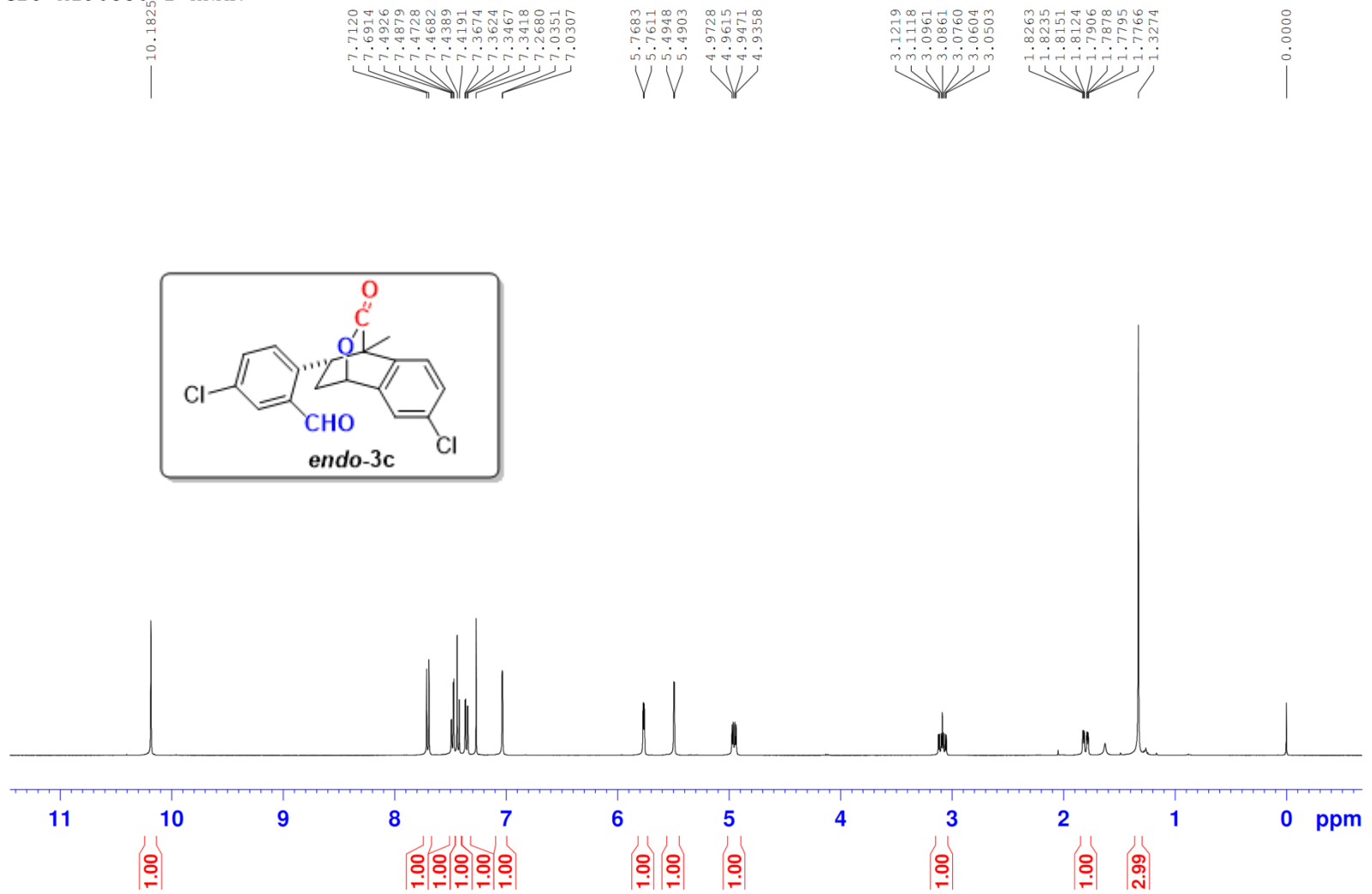


GBJ-X190330-1-HNMR



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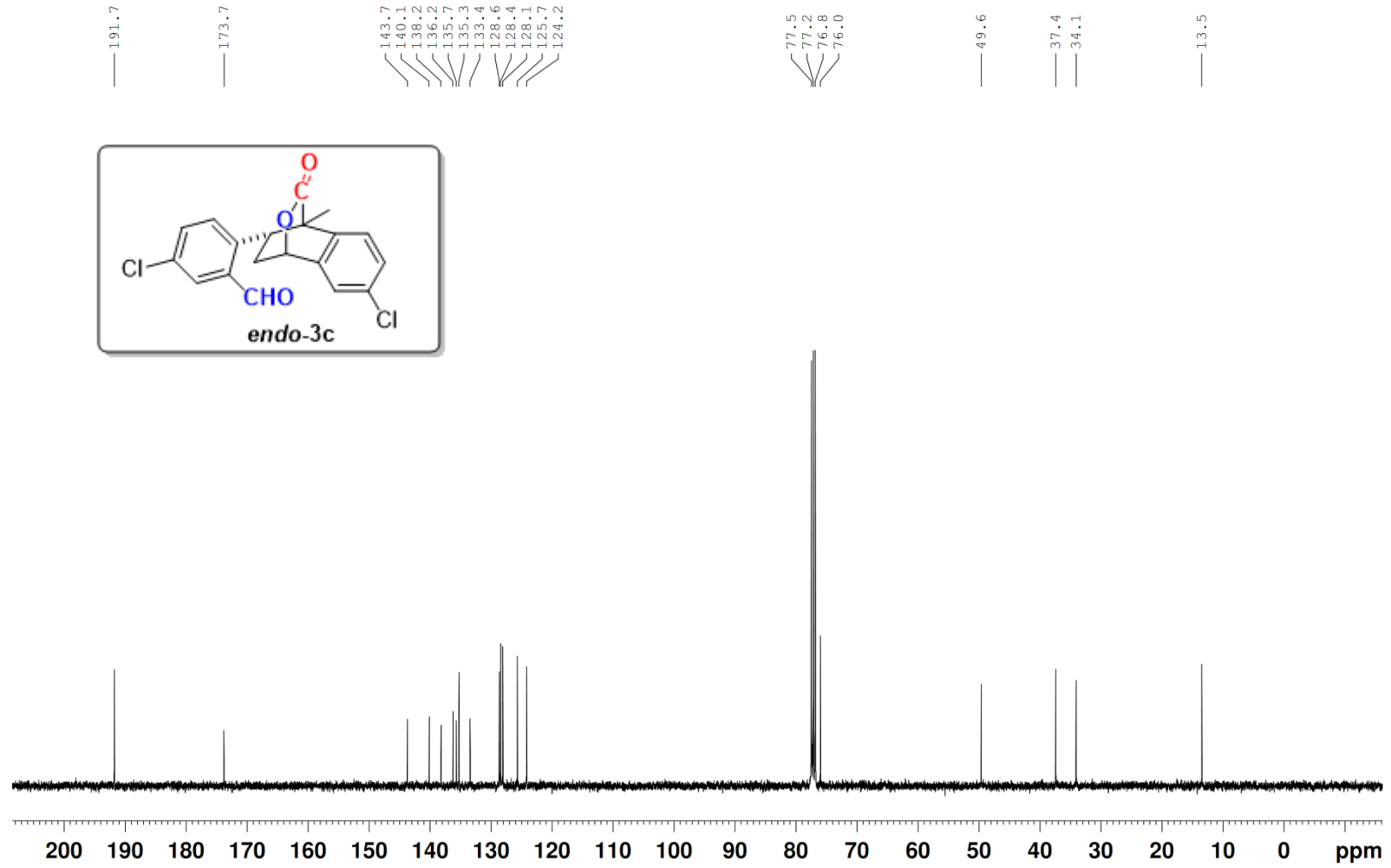
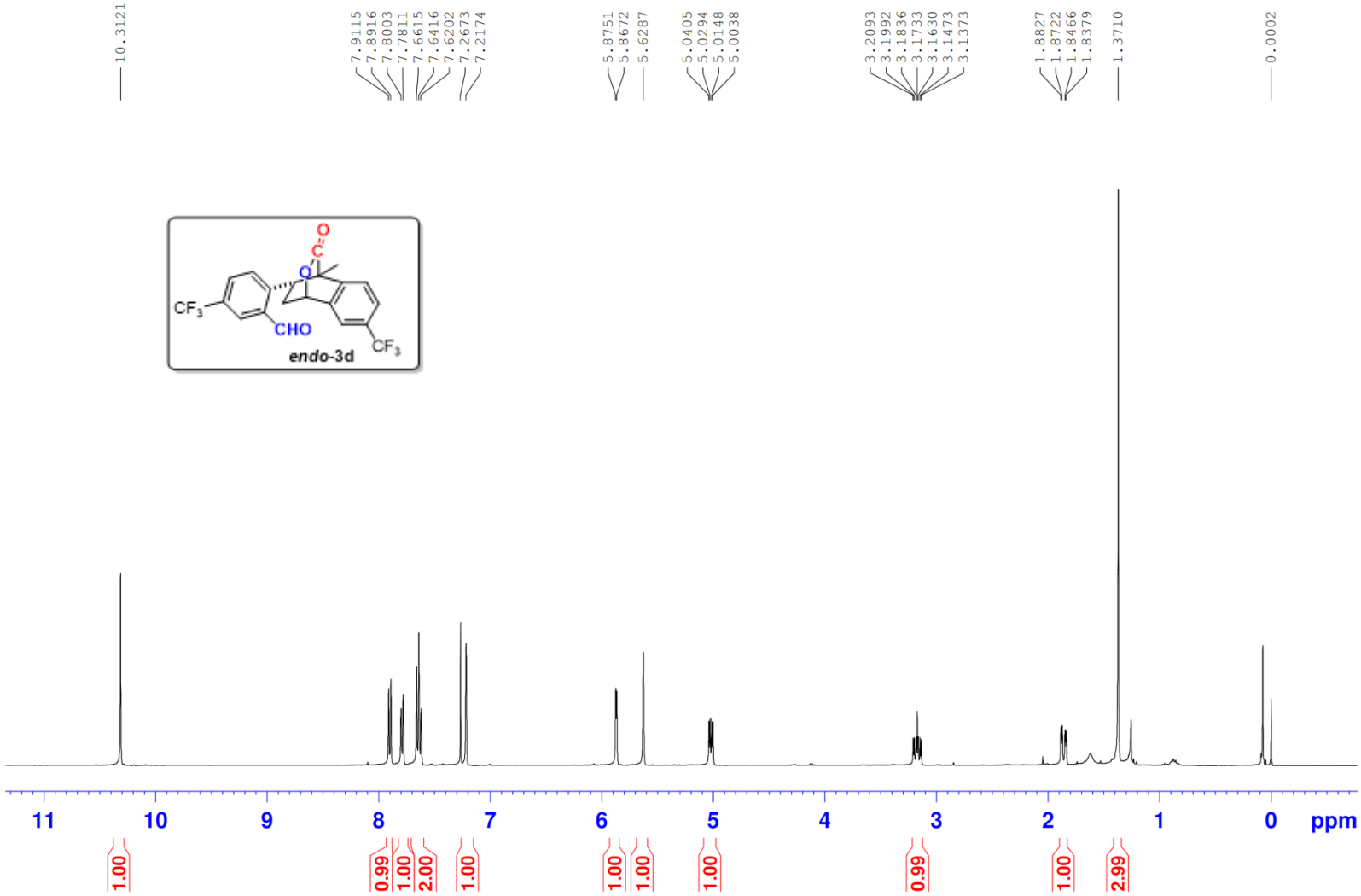


GBJ-X190119-1-3-HNMR



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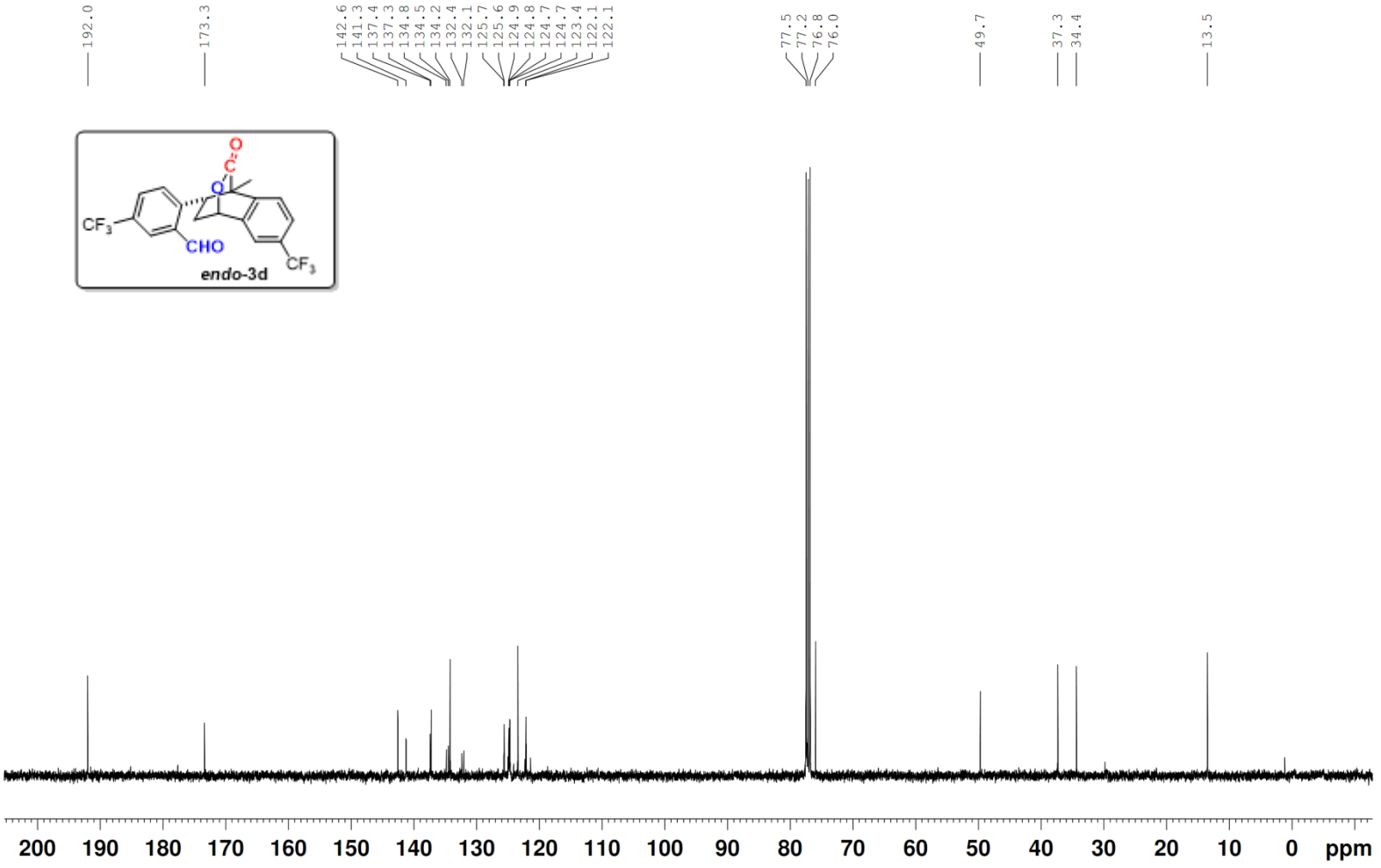
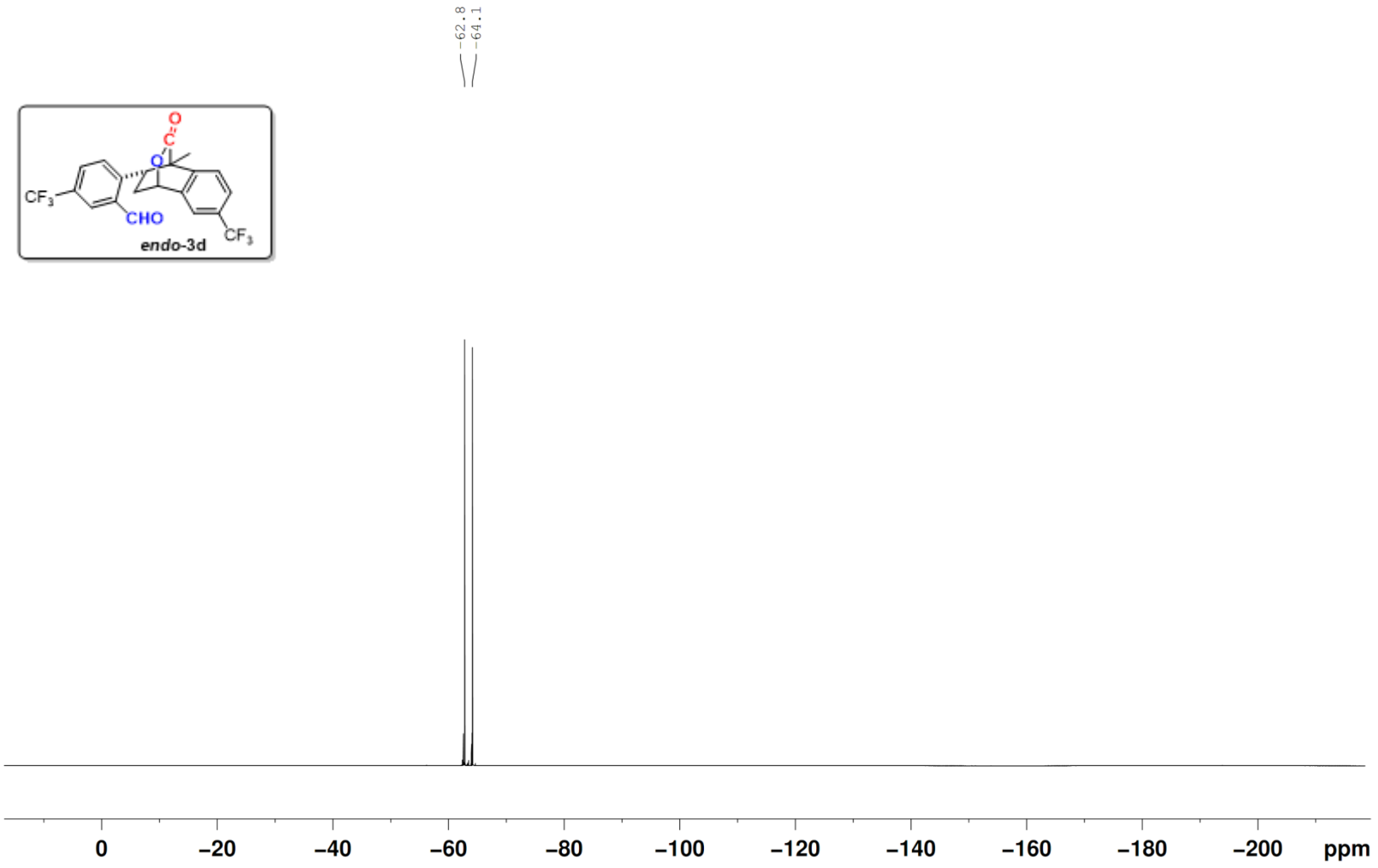
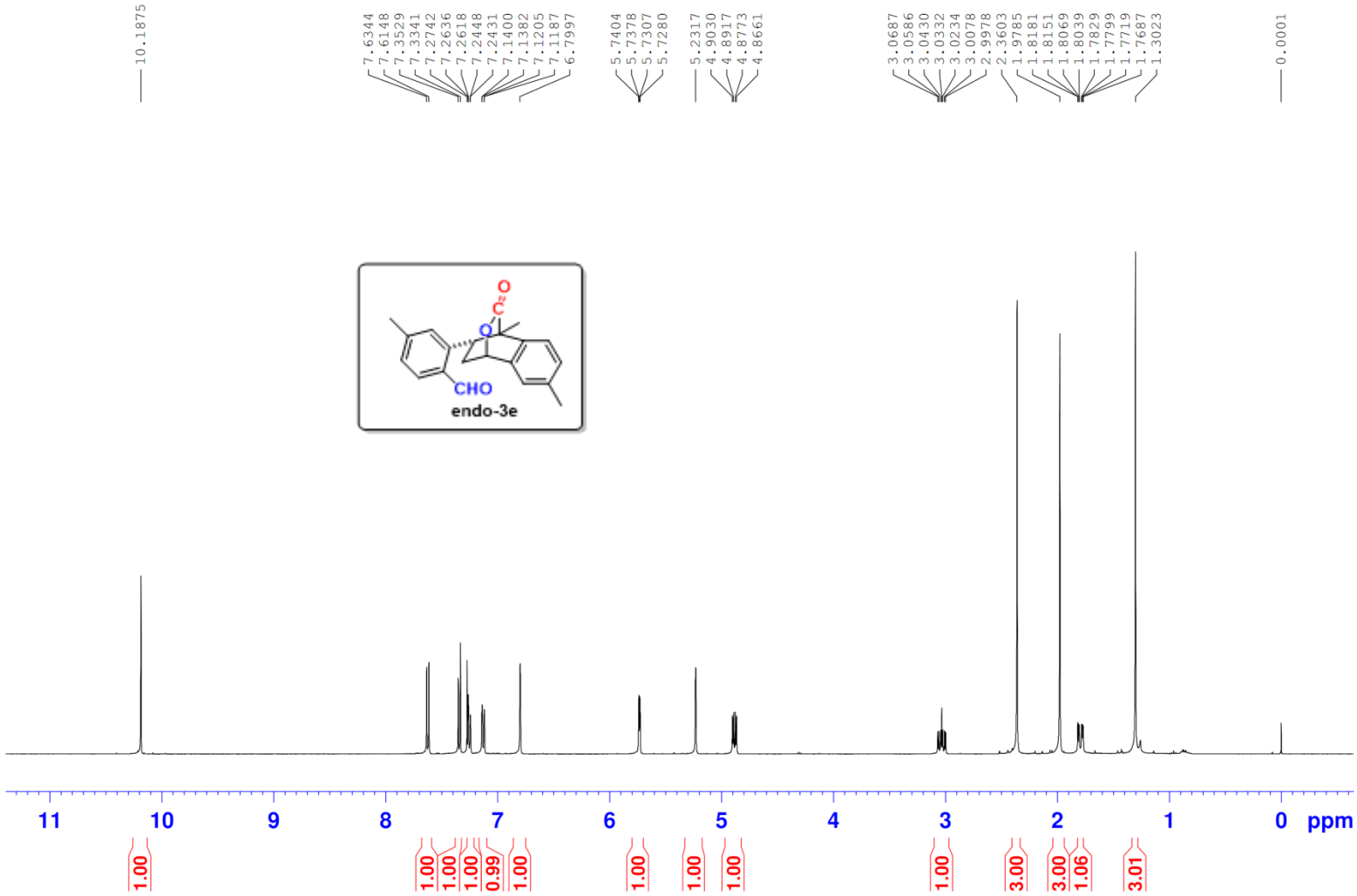


GBJ-X190228-1-9-FNMR



GBJ-X190105-1-2-HNMR



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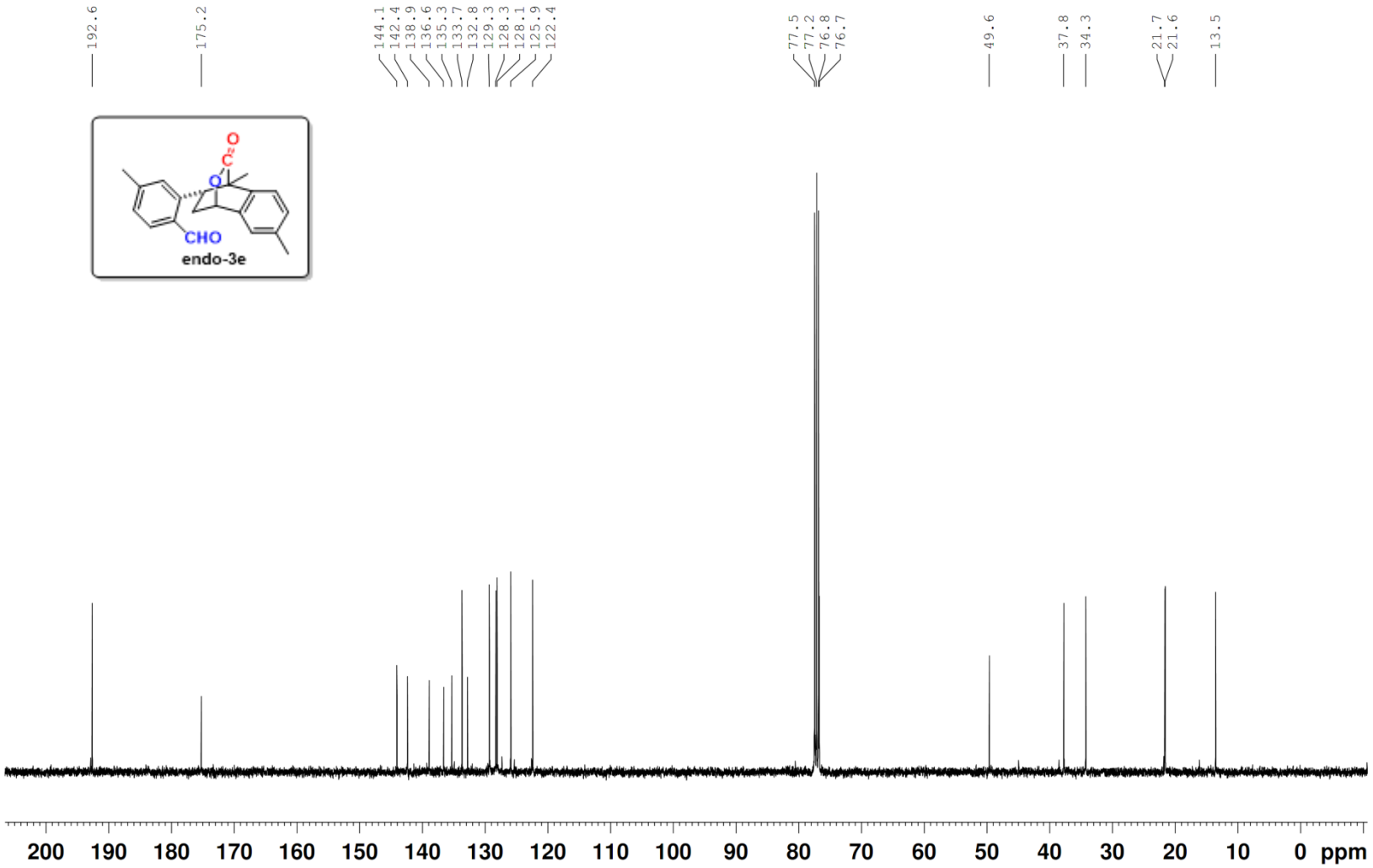
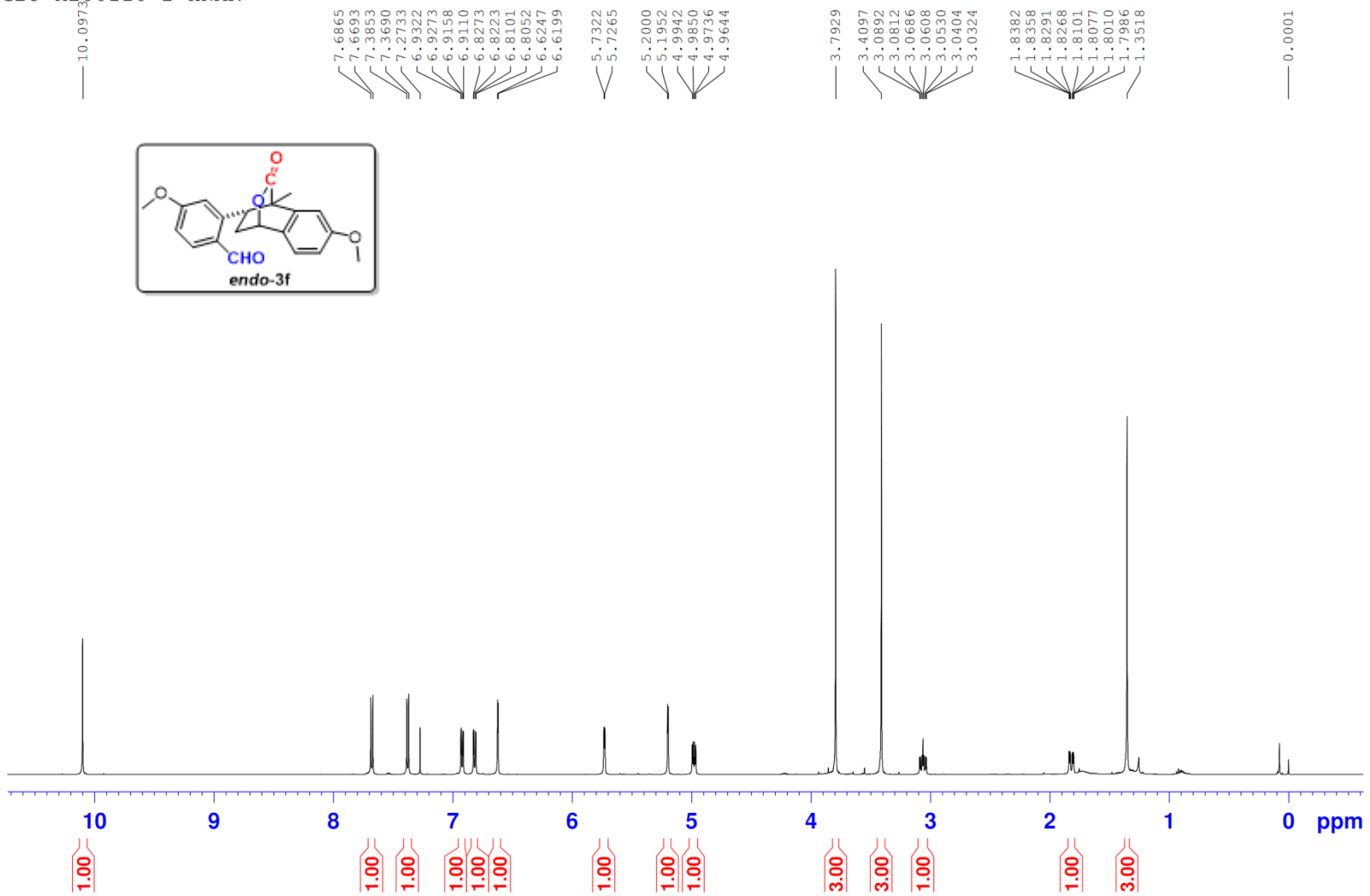


GBJ-X200110-2-HNMR



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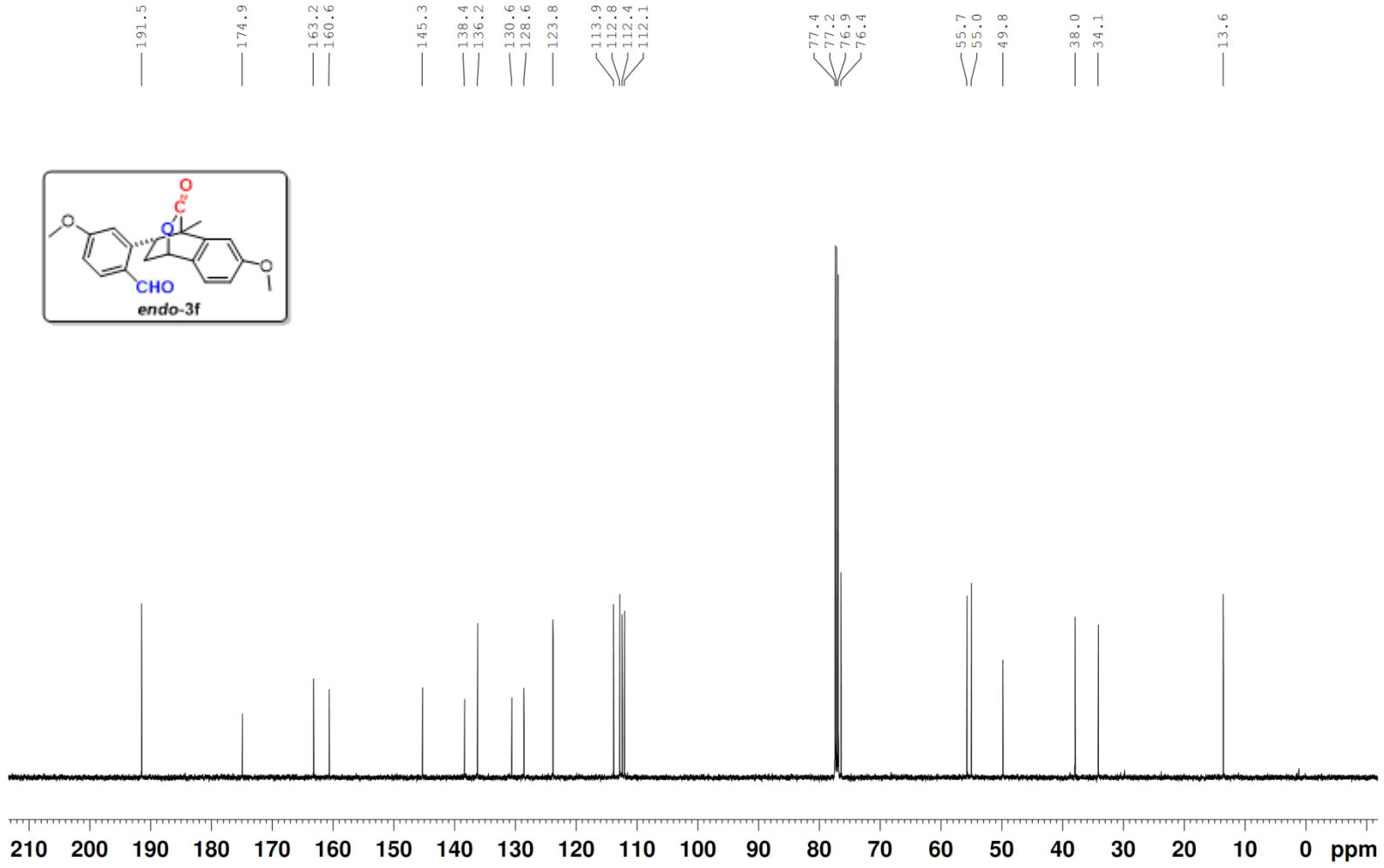
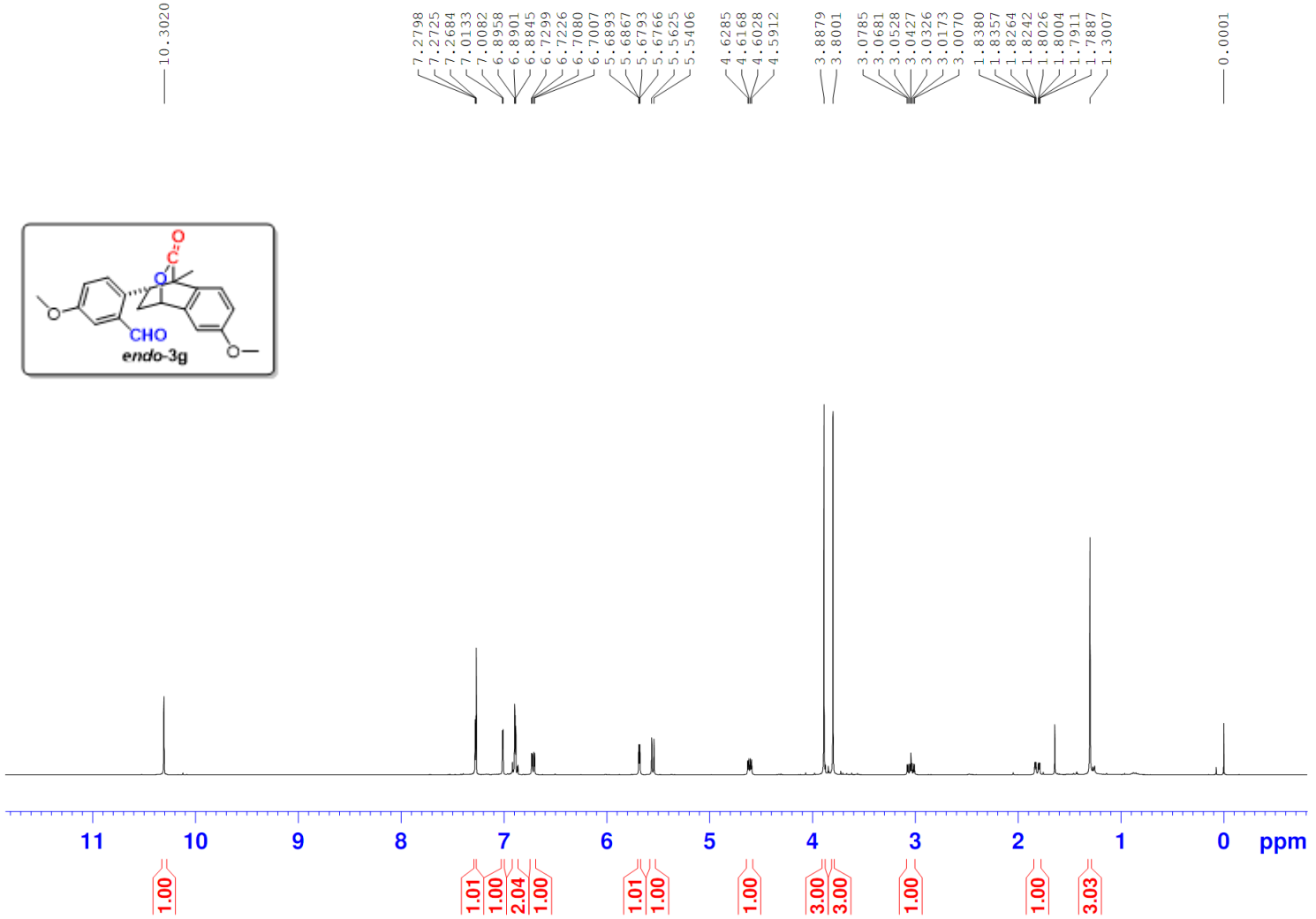


GBJ-X190115-1-5-H



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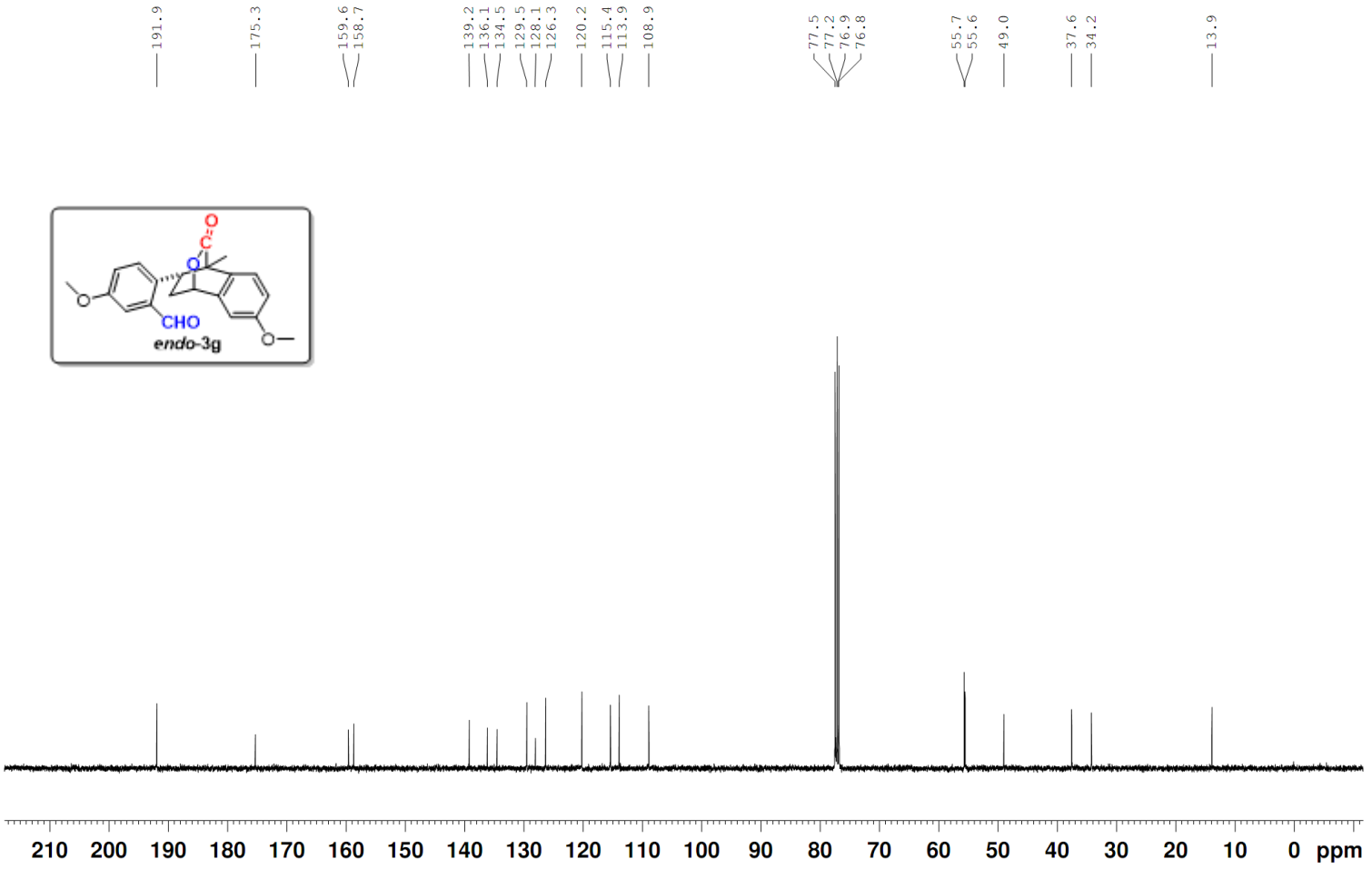

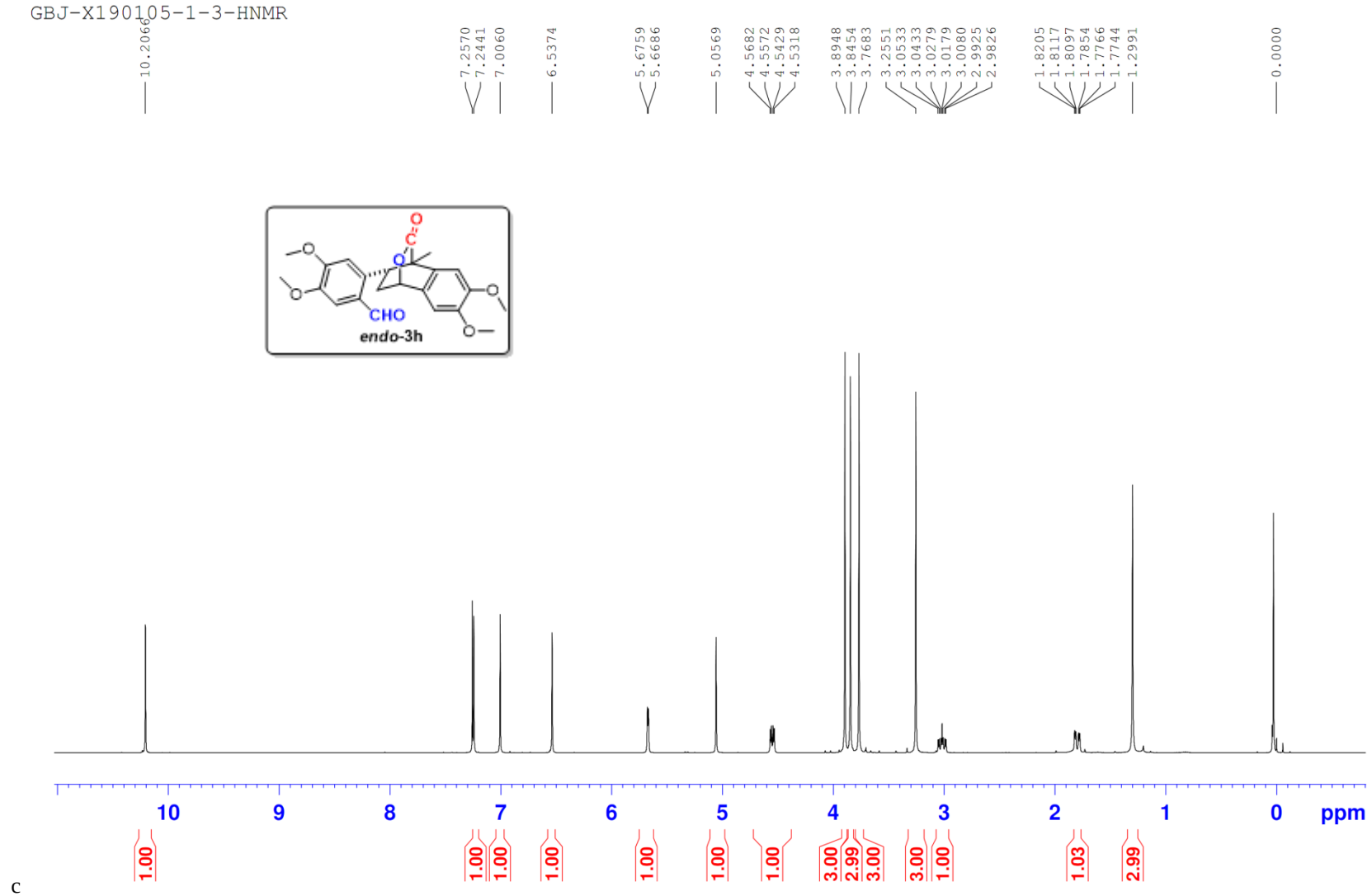
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4.5572
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4.5318
3.8948
3.8454
3.7683
3.2551
3.0533
3.0433
3.0279
3.0179
3.0080
2.9925
2.9826
1.8205
1.8117
1.8097
1.7854
1.7766
1.7744
1.2991
0.0000
O
C=
O
CHO
endo-3h
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.00
1.00
1.00
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3.00
3.00
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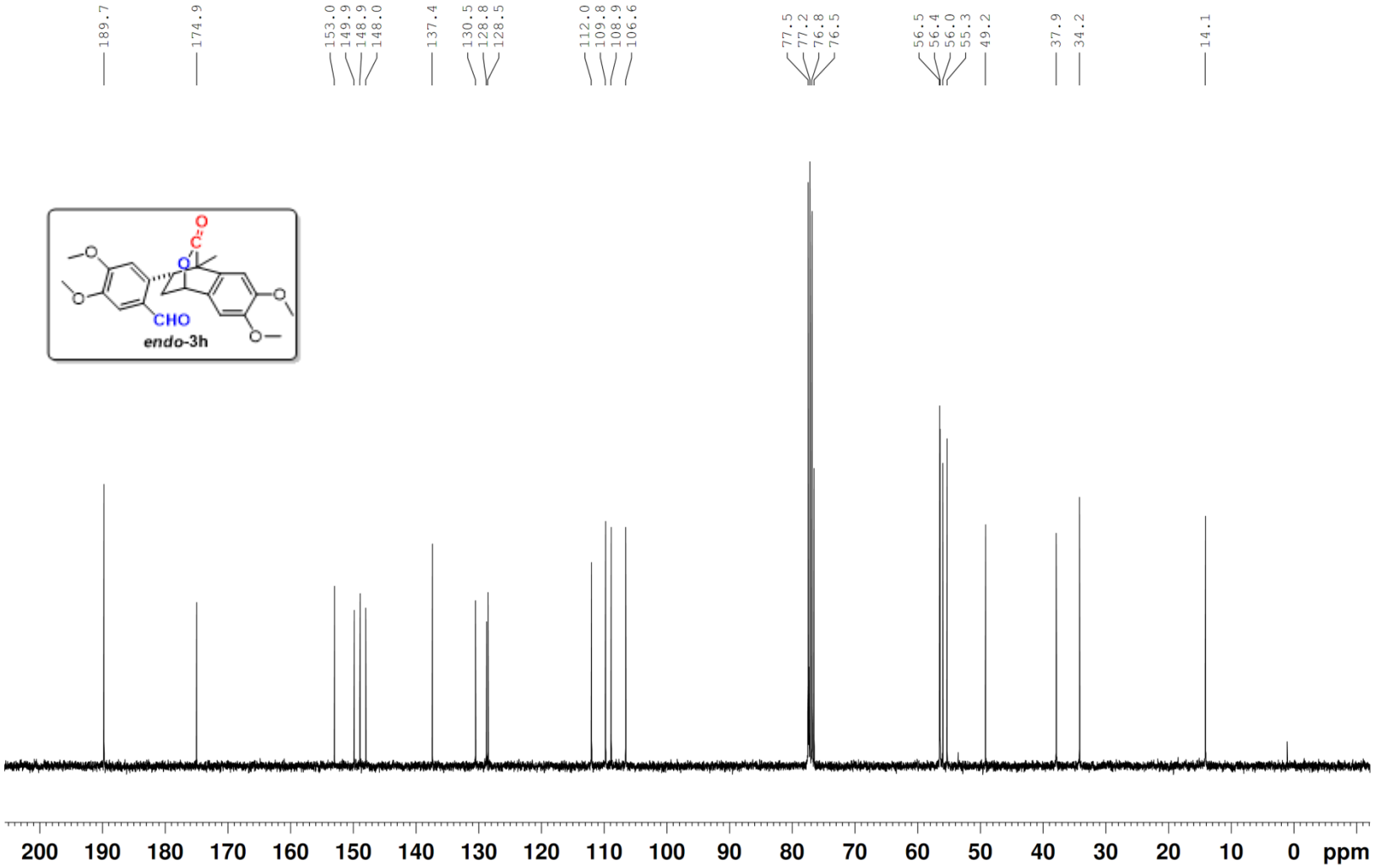
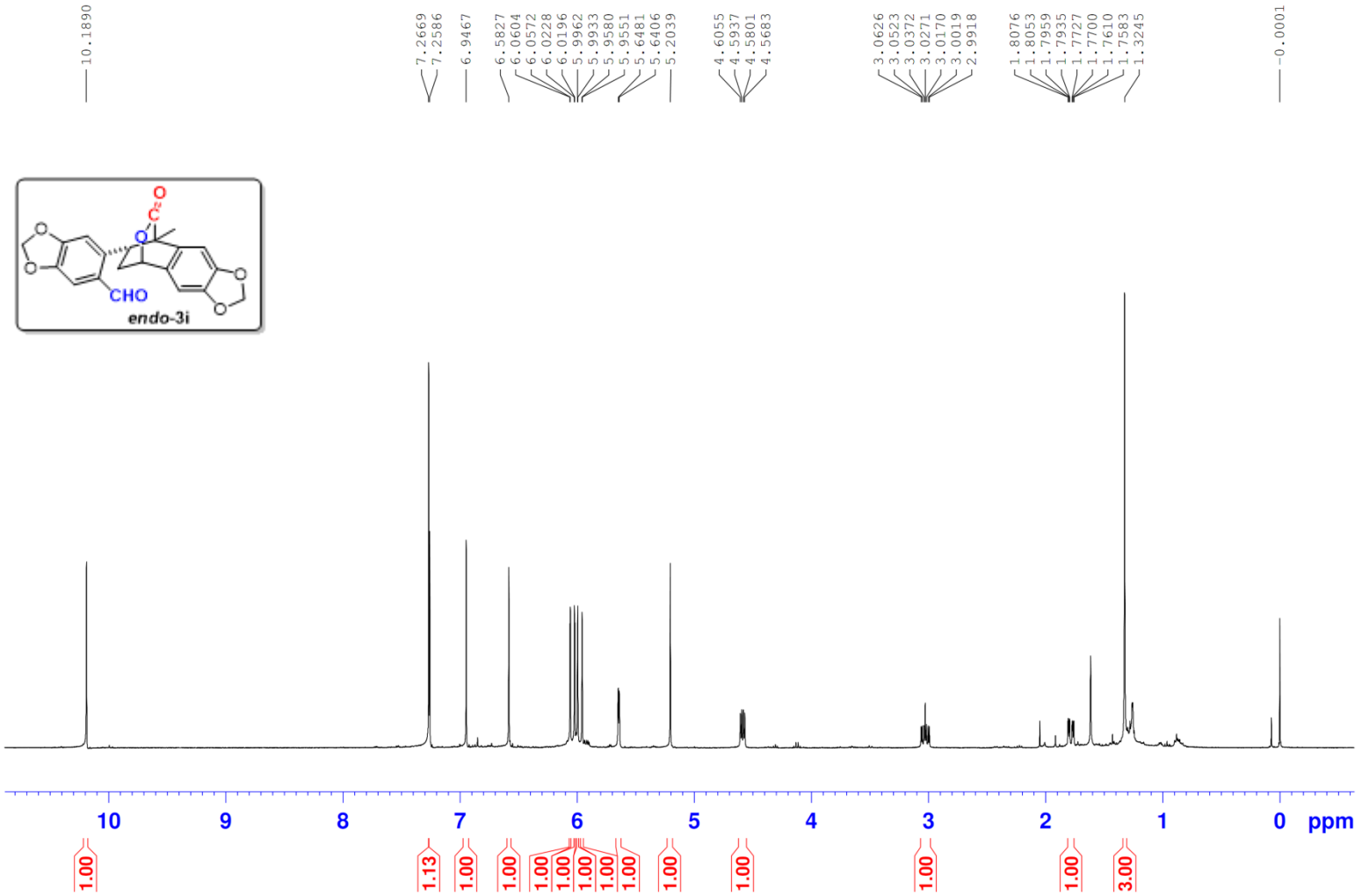
2.99

c

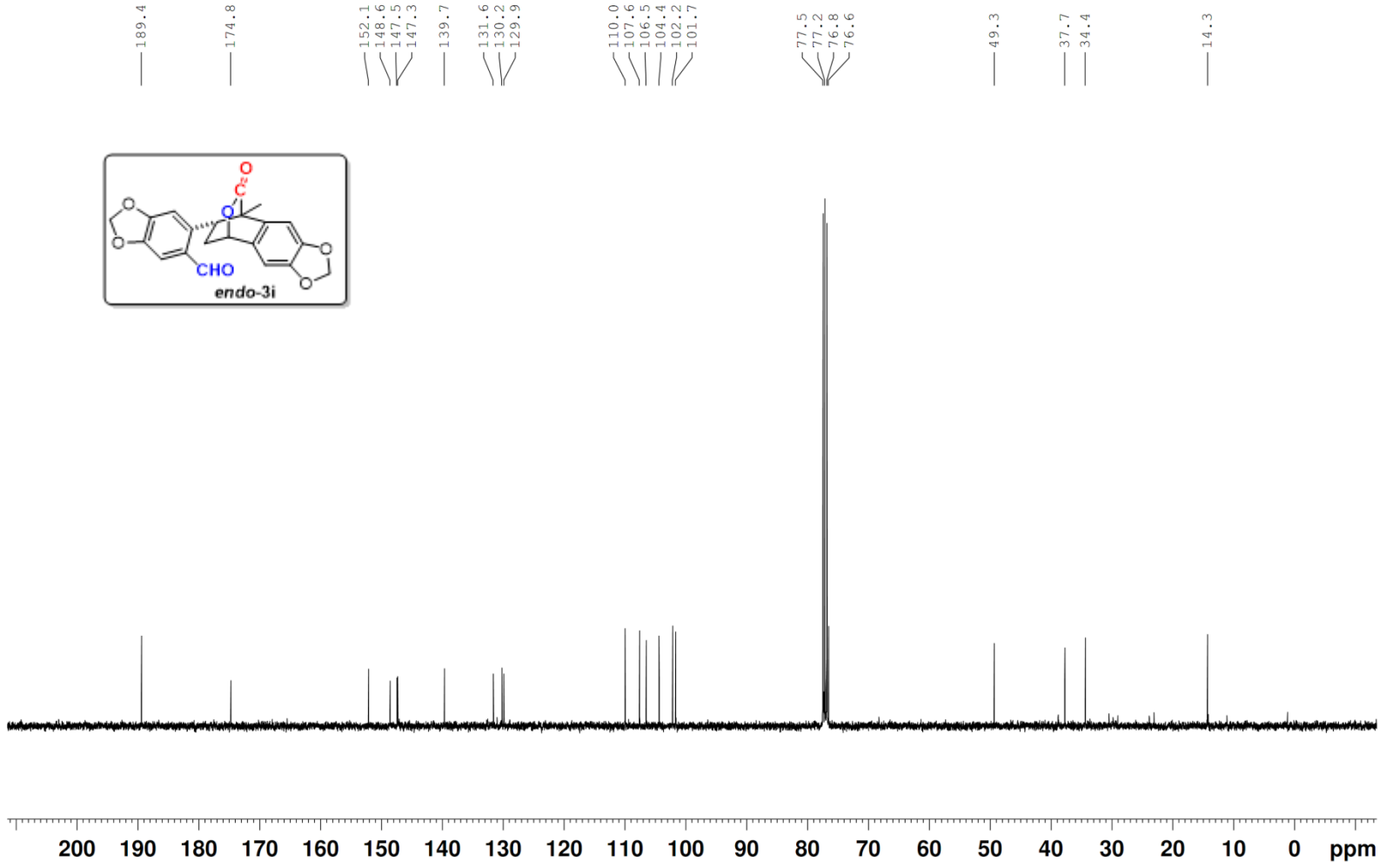
GBJ-X191129-3-CNMR



GBJ-X190105-1-4-HNMR



GBJ-X190105-1-4-CNMR



GBJ-X191102-1-NAI(500MHz)

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7.7048
7.6919
7.6884
7.6475
7.6456
7.6314
7.6223
7.6194
7.6177
7.6086
7.6058
7.5913
7.5889
7.5187
7.5171
7.5029
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7.4871
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7.2585
7.2315
7.2146
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6.6184
5.5558
5.5382
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4.5180
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3.2832
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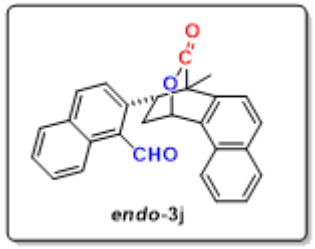
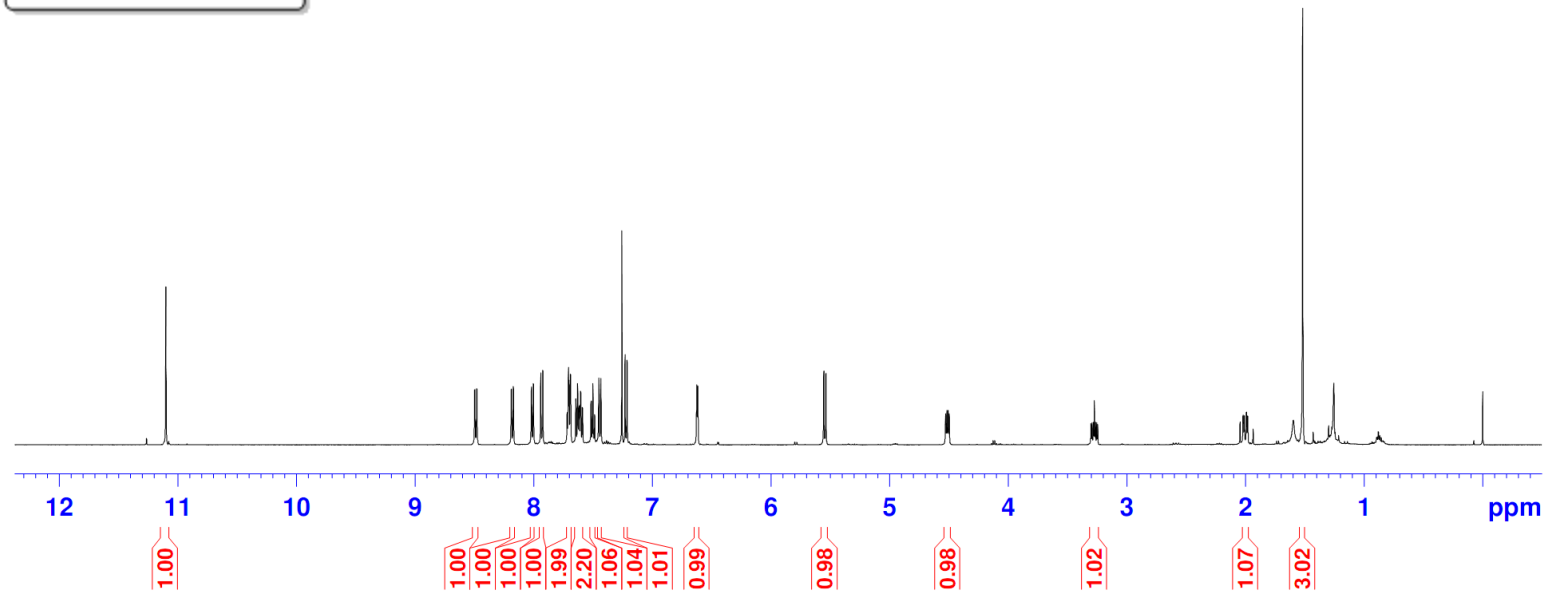
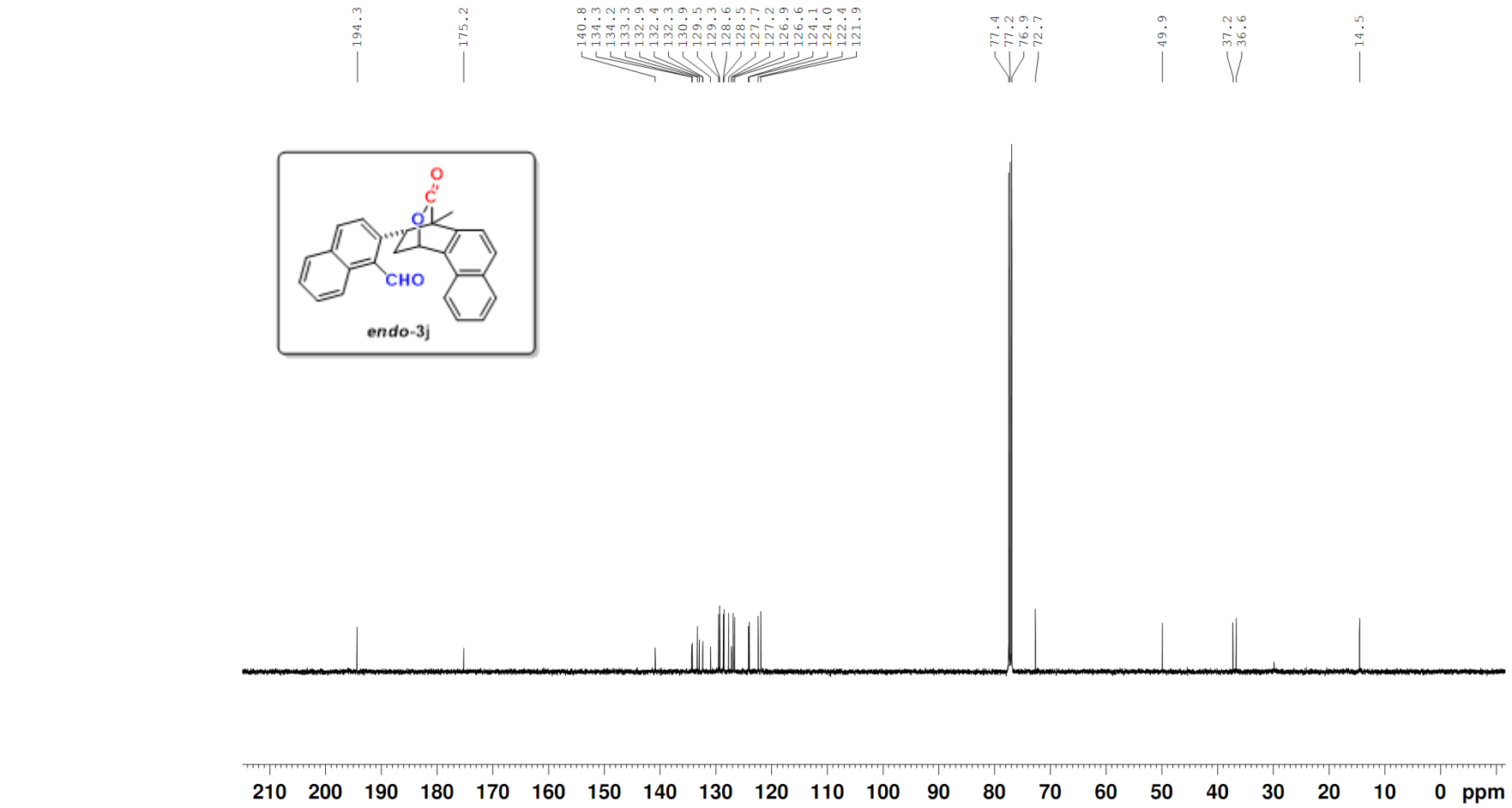
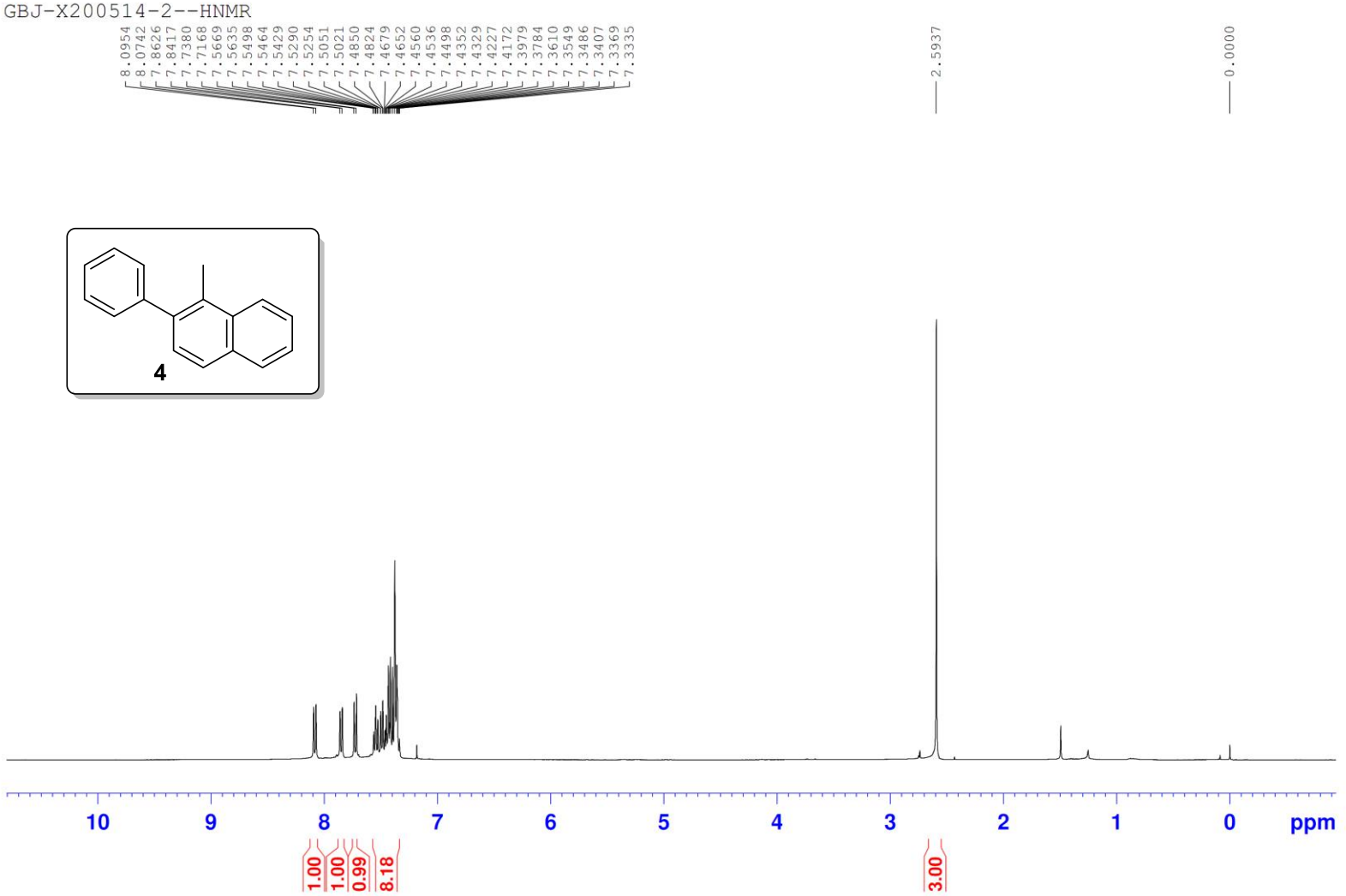


endo-3j



GBJ-X191102-1-C-NAI(500MHz)




GBJ-X200514-2--HNMR
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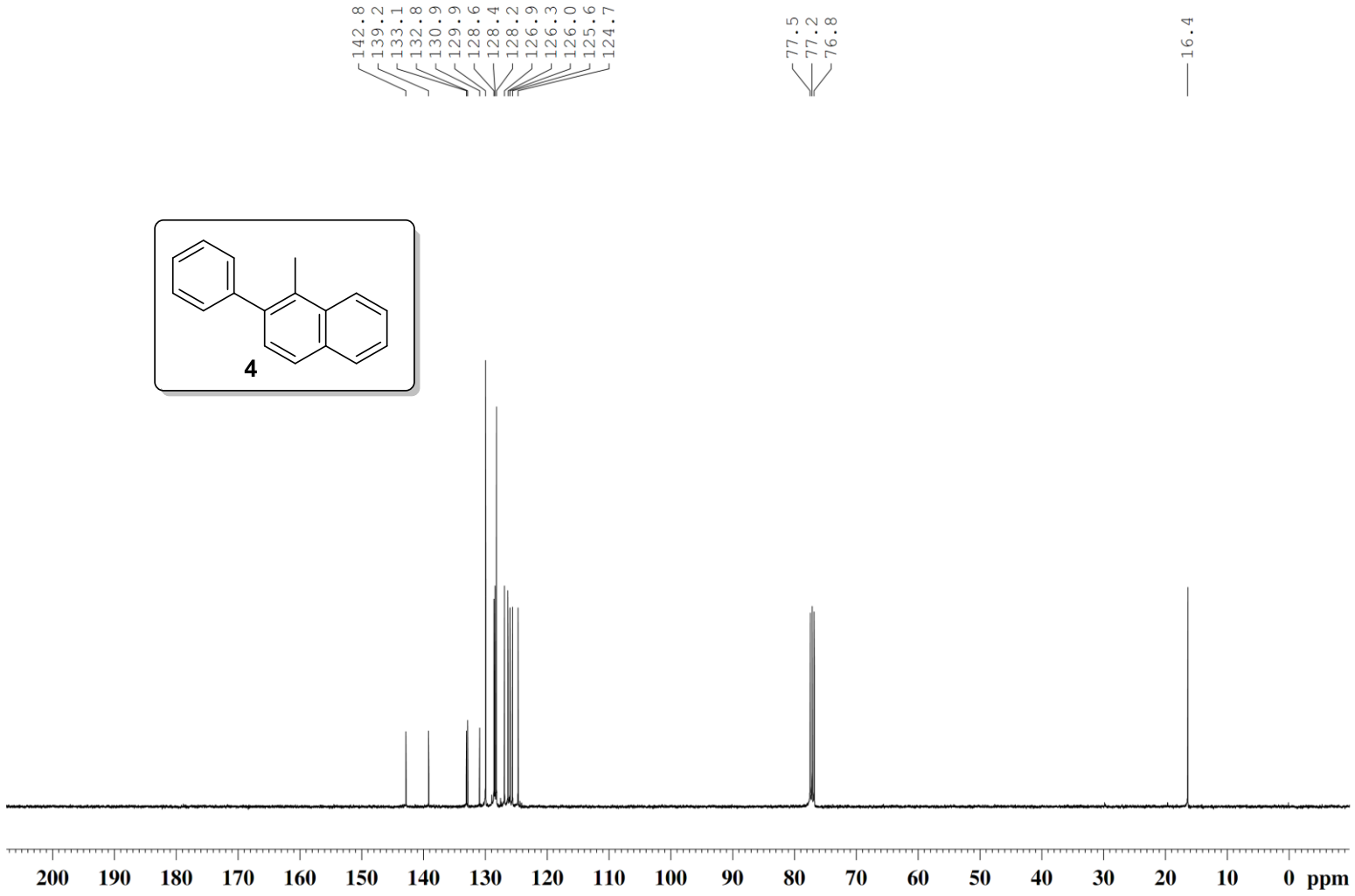
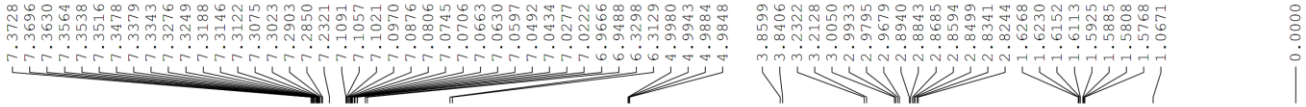
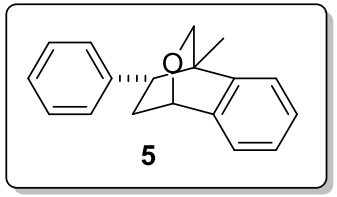
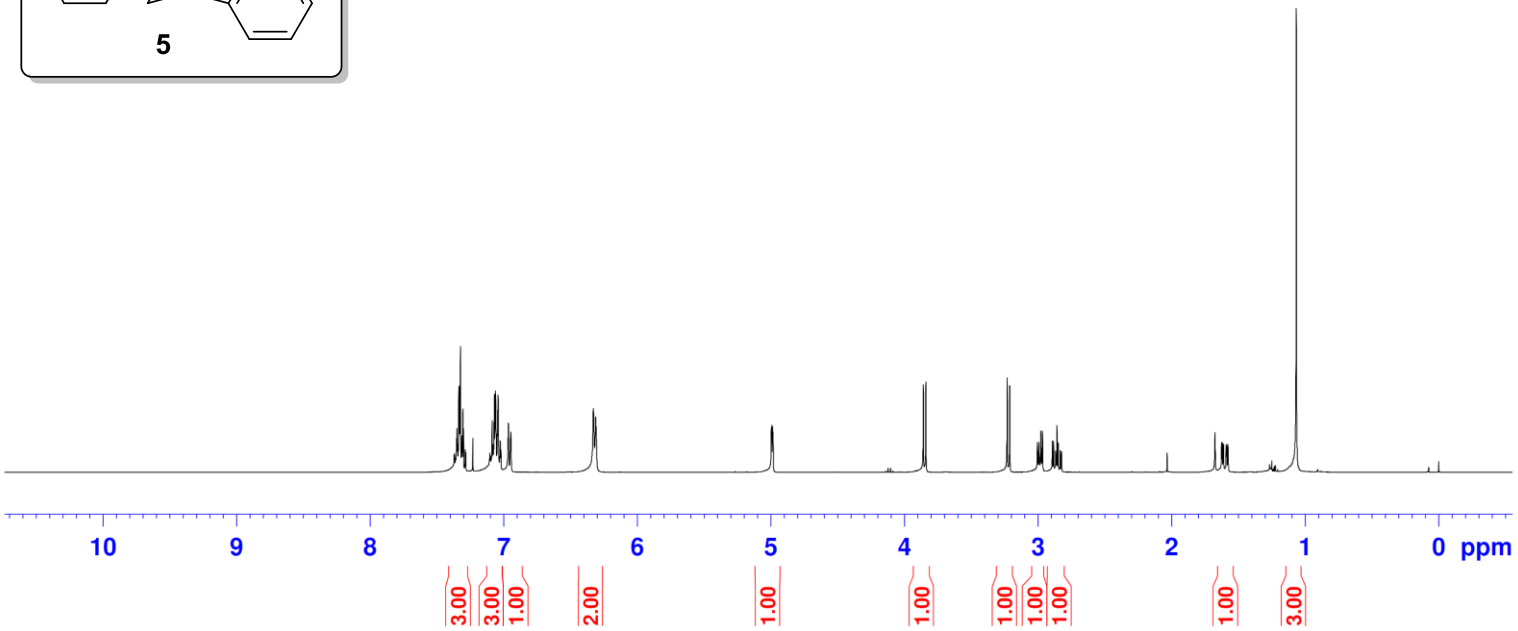
GBJ-X200514-2-CNMR



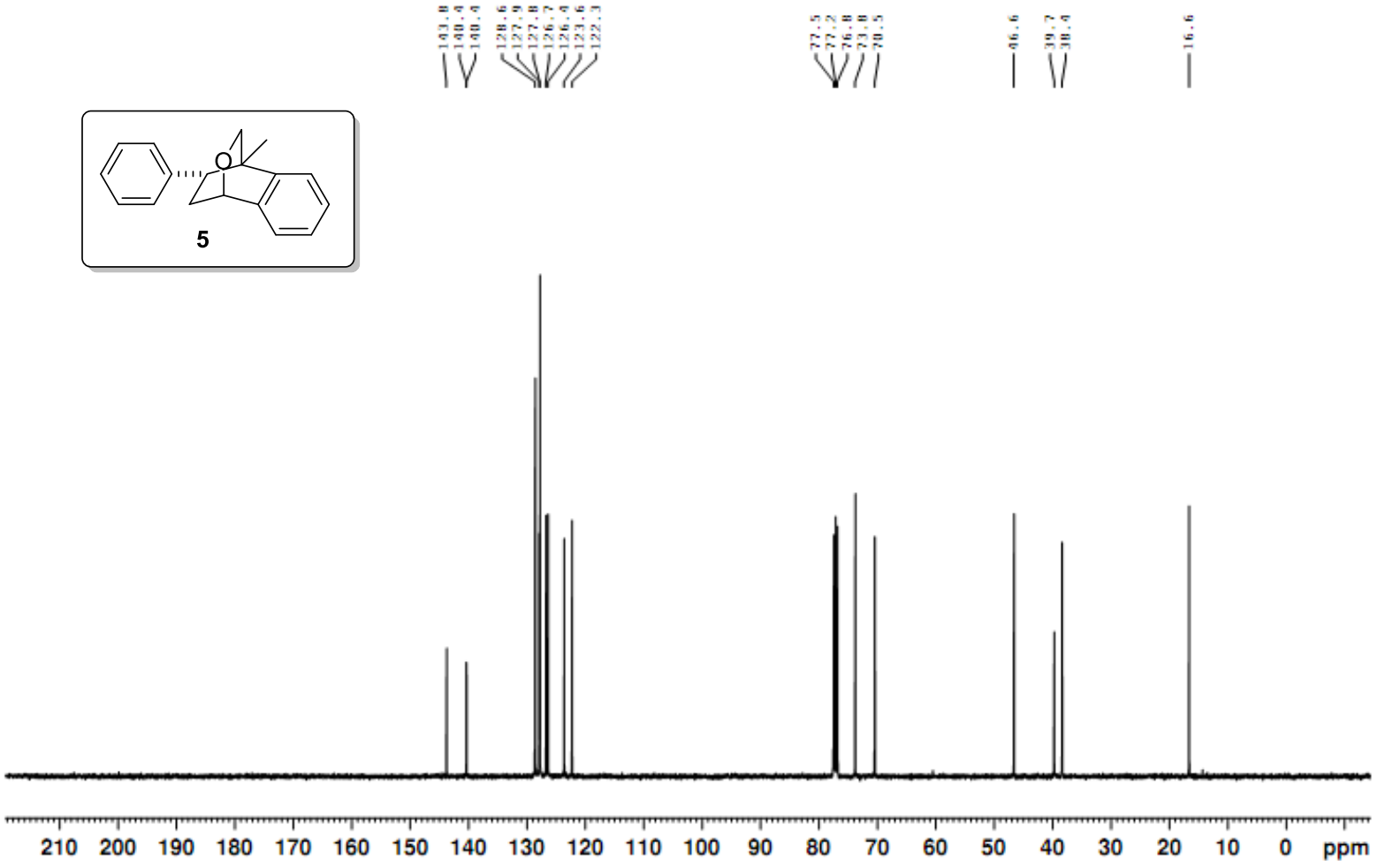
GBJ-X190911-1-HNMR



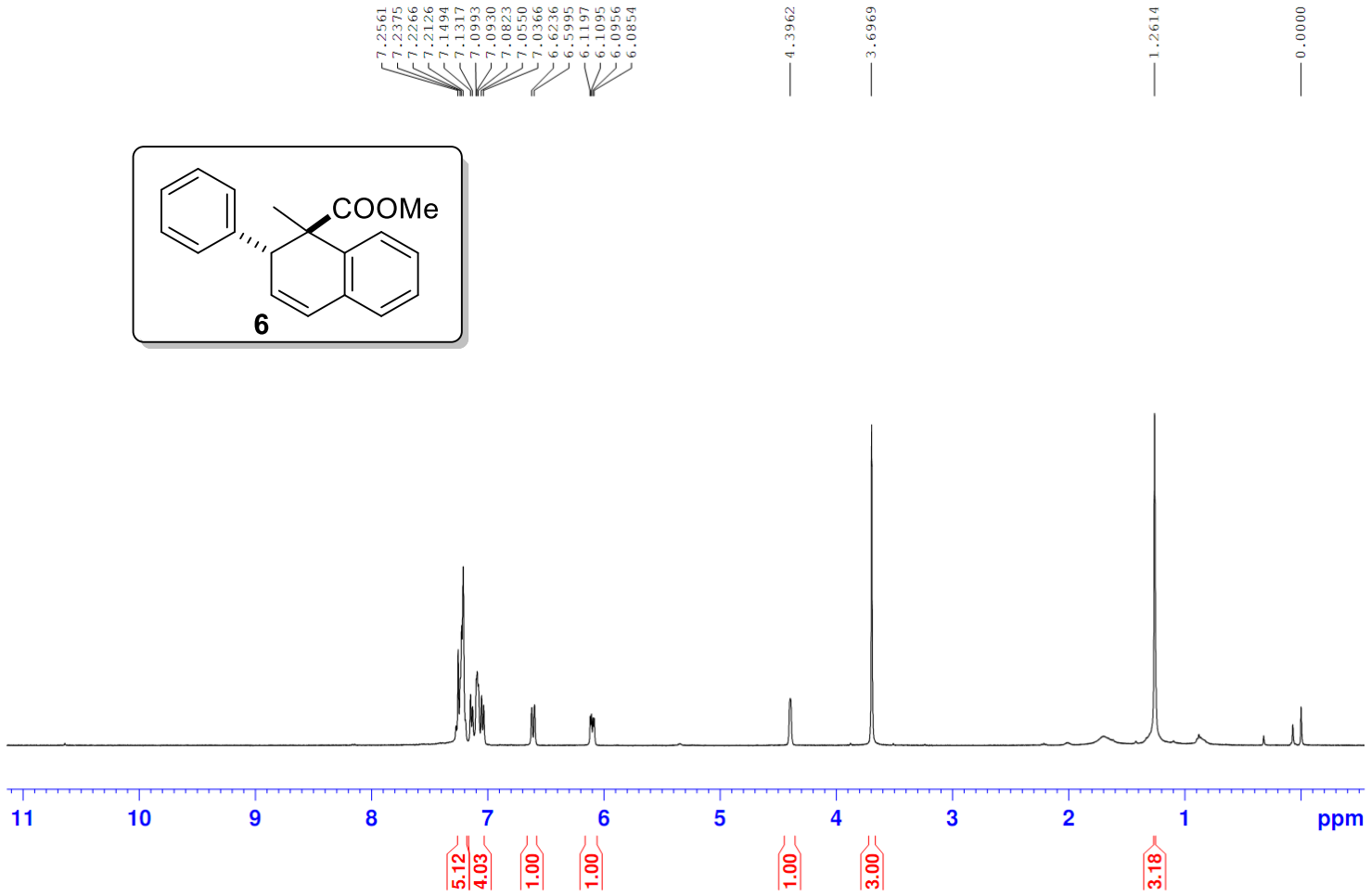




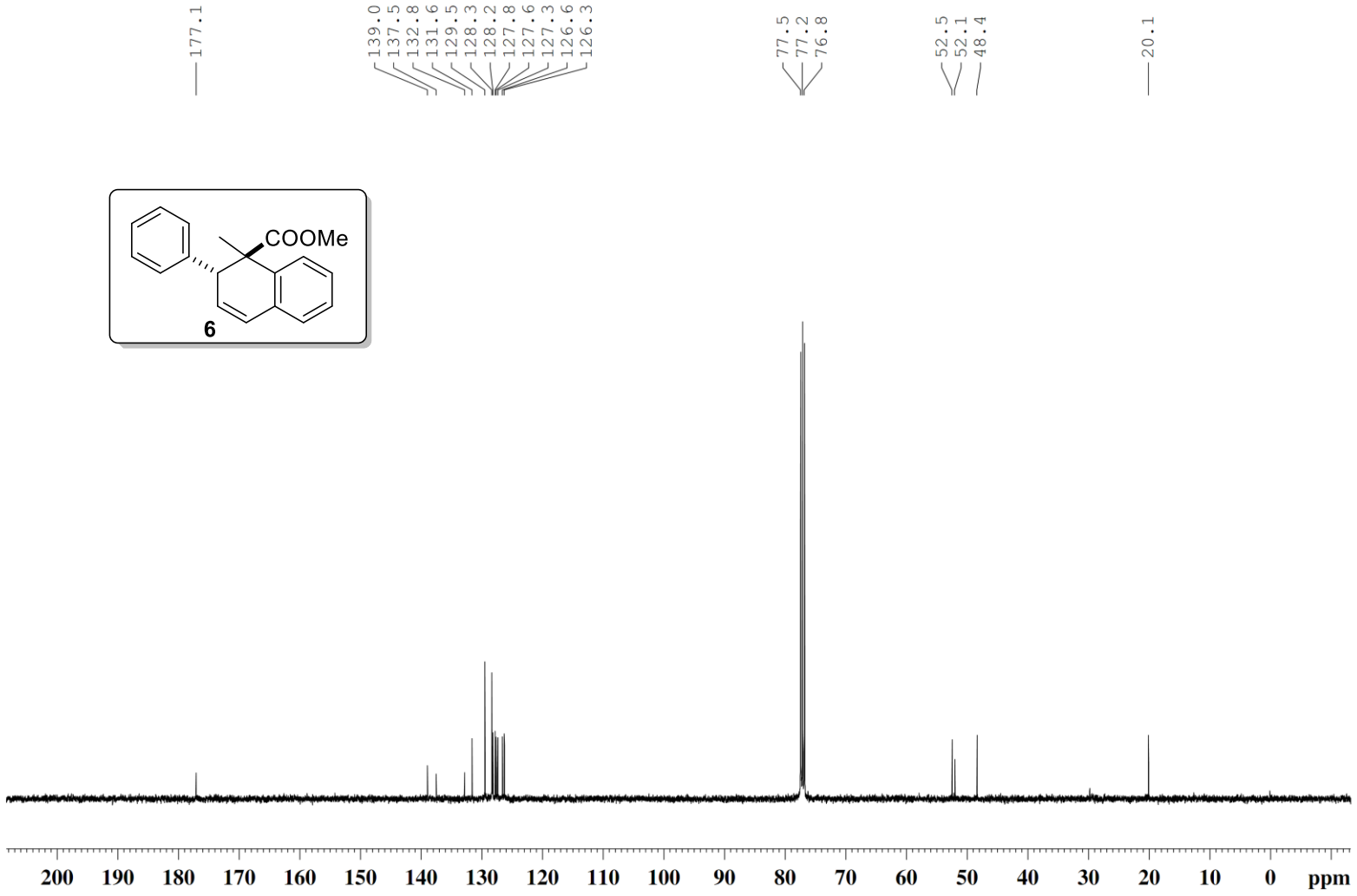
GBJ-X190911-1-CNMR



GBJ-X200513-1-HNMR



GBJ-X200513-2-CNMR



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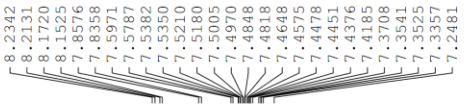

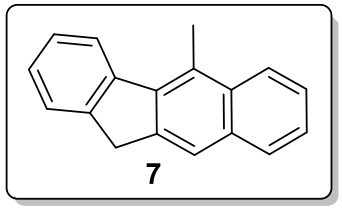

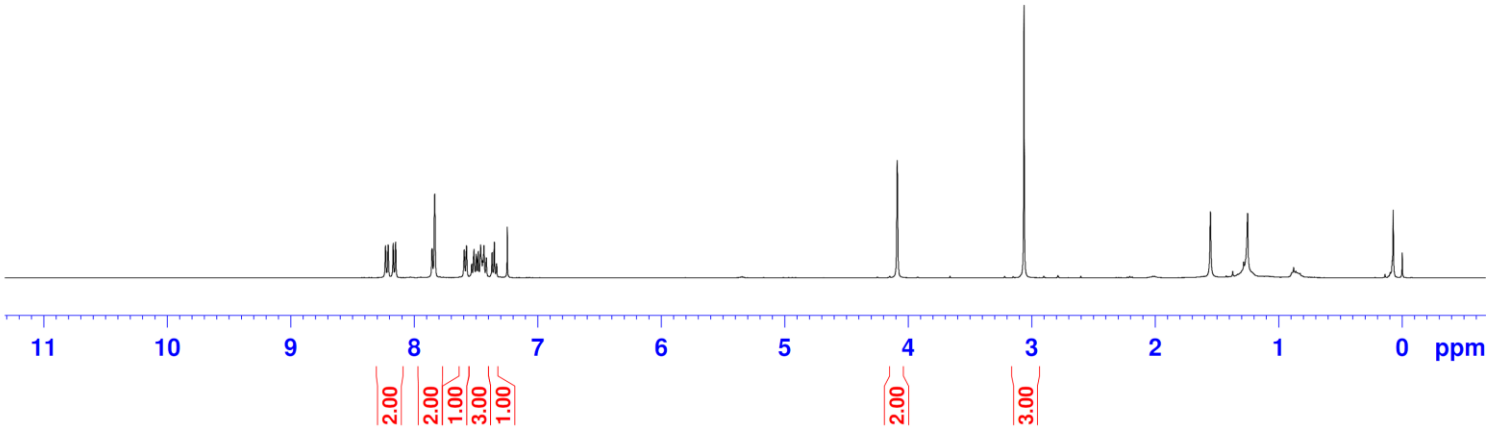

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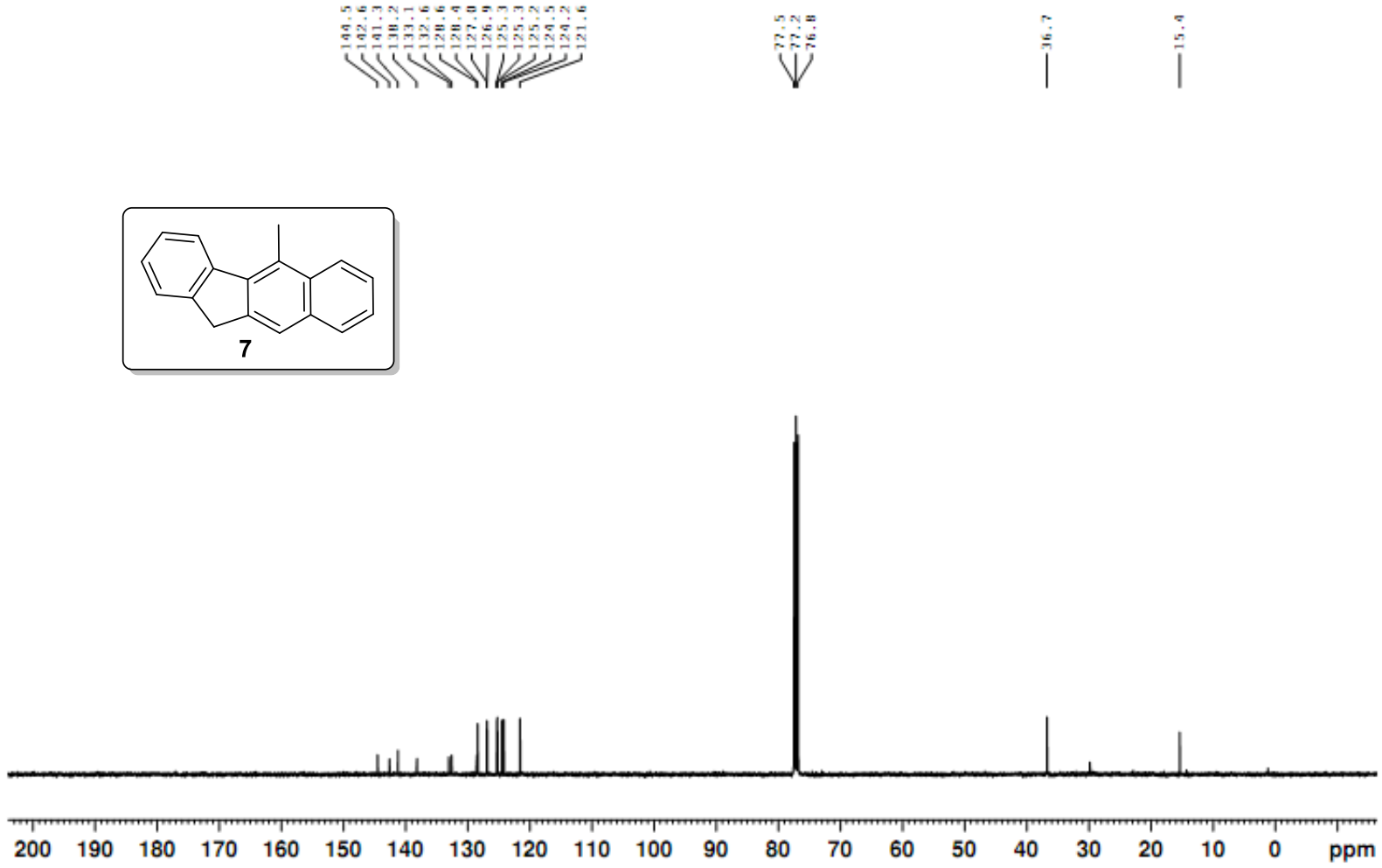
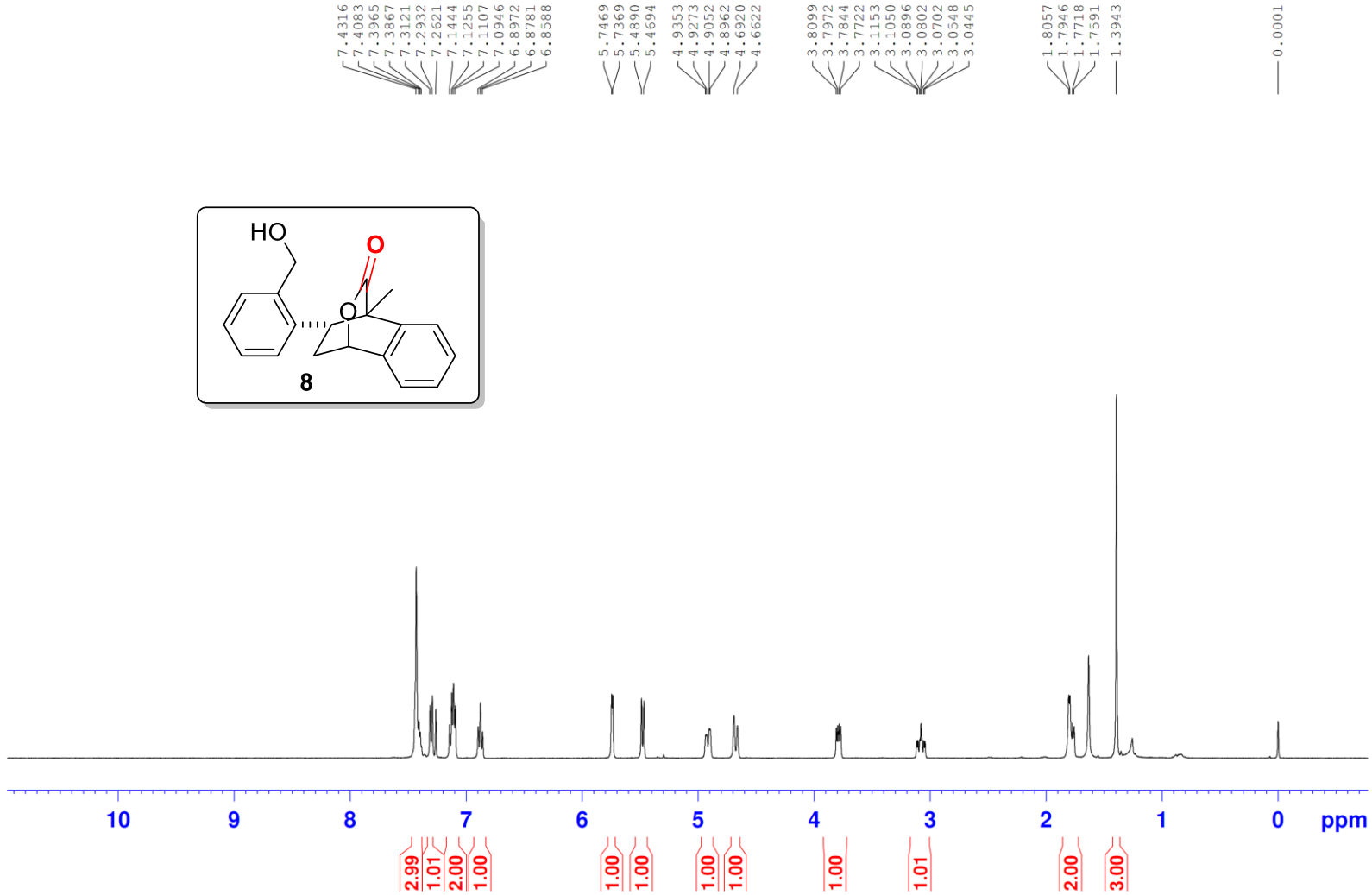


GBJ-X200510-2-HNMR



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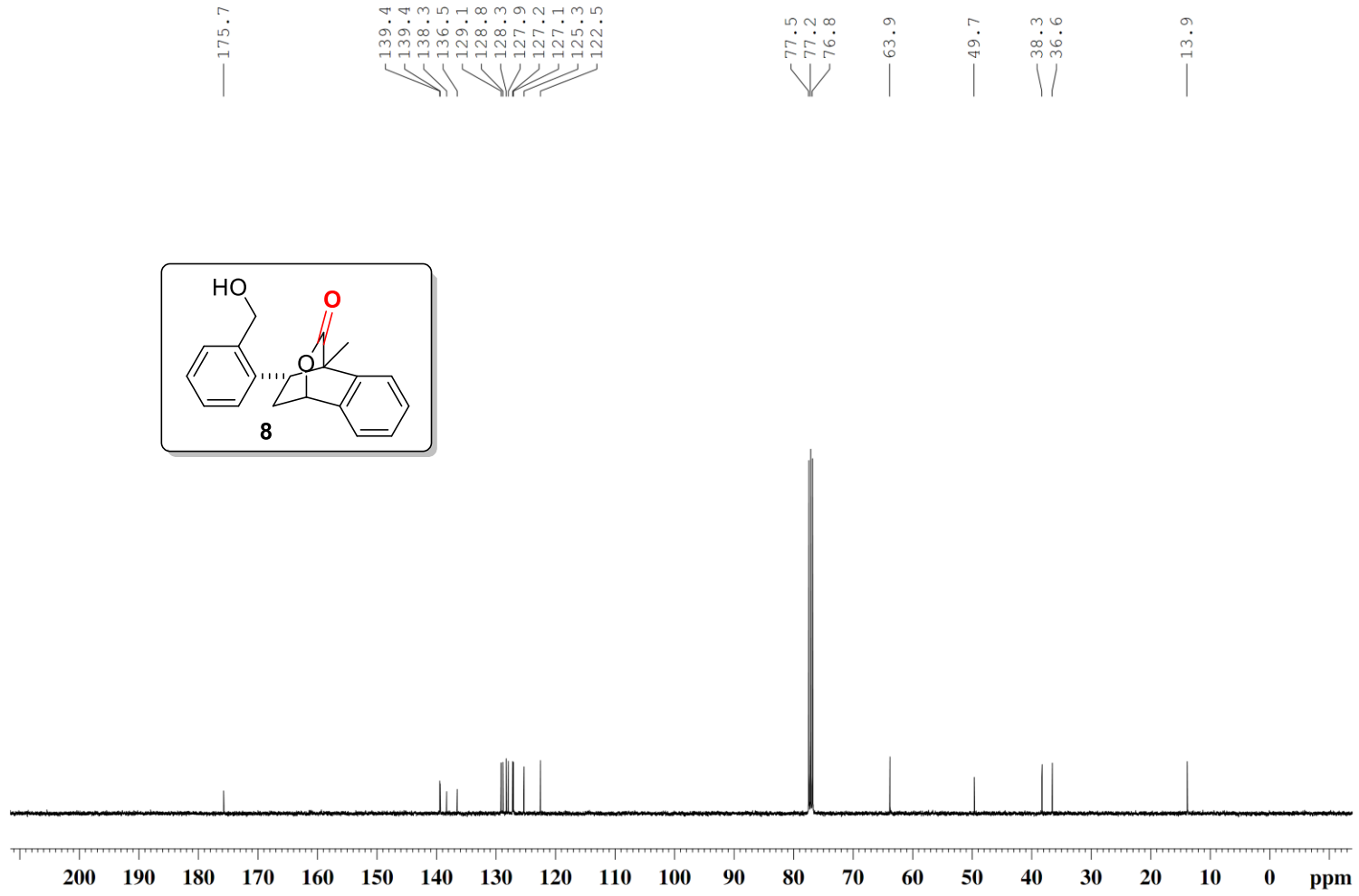

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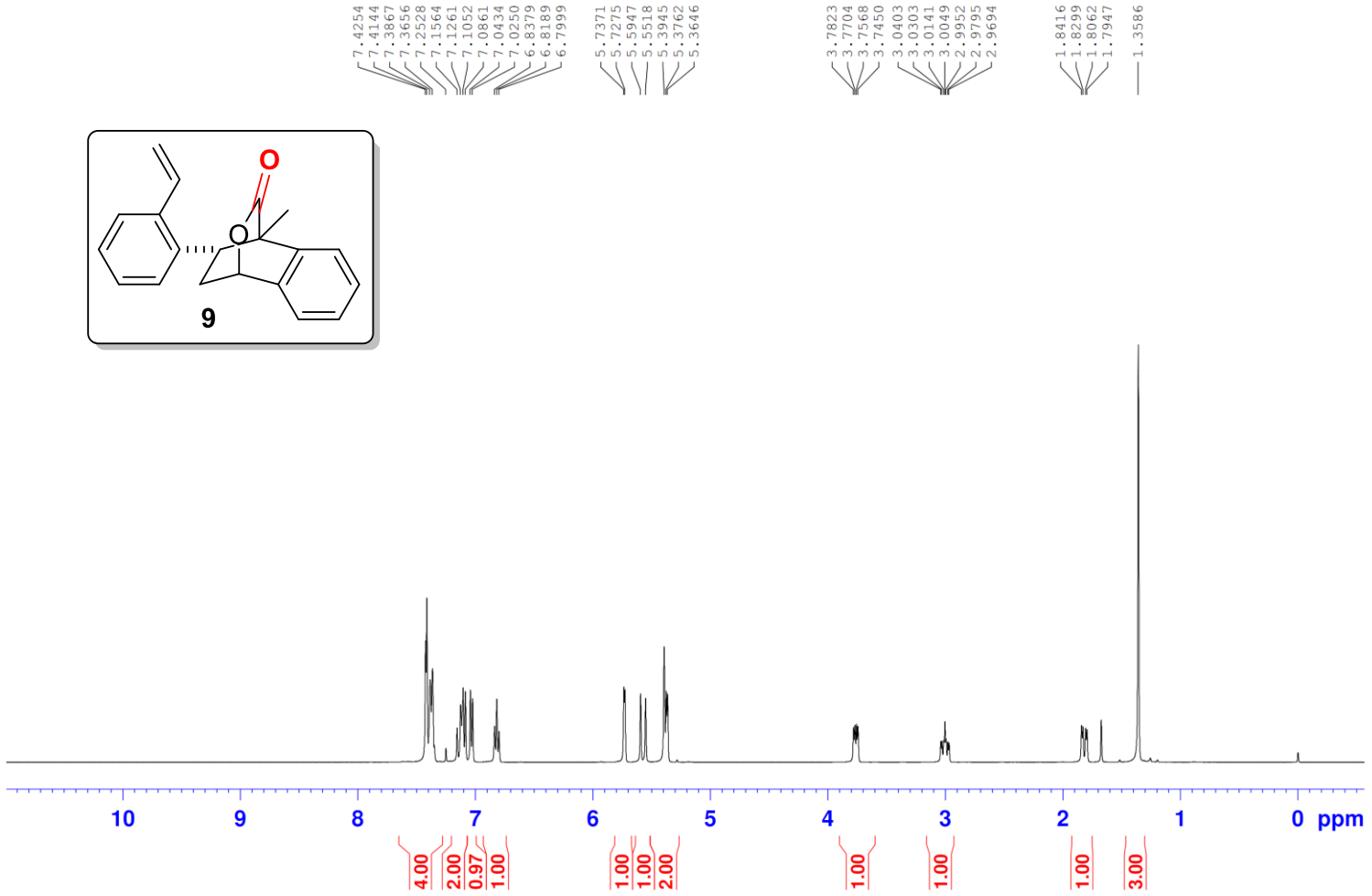

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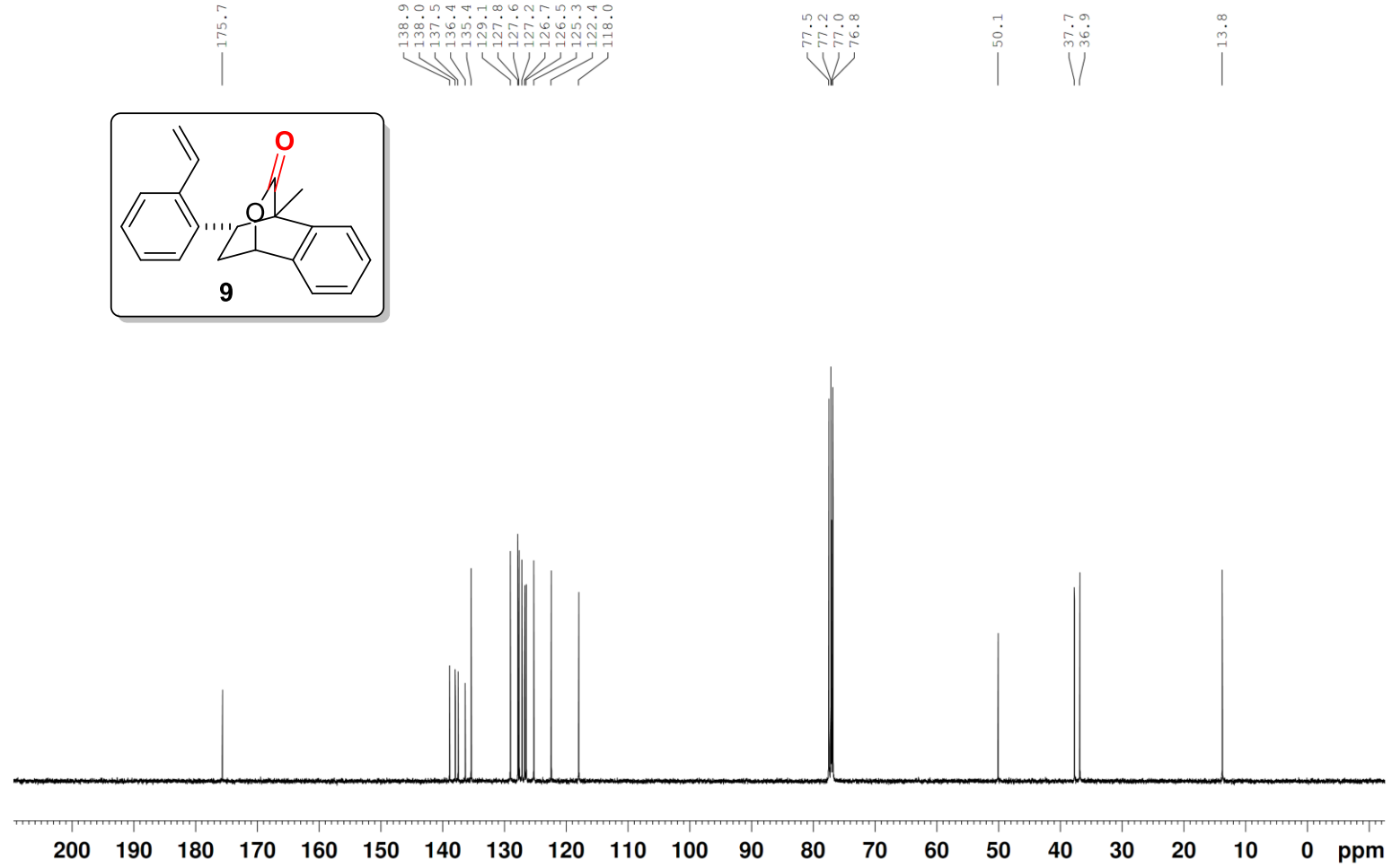

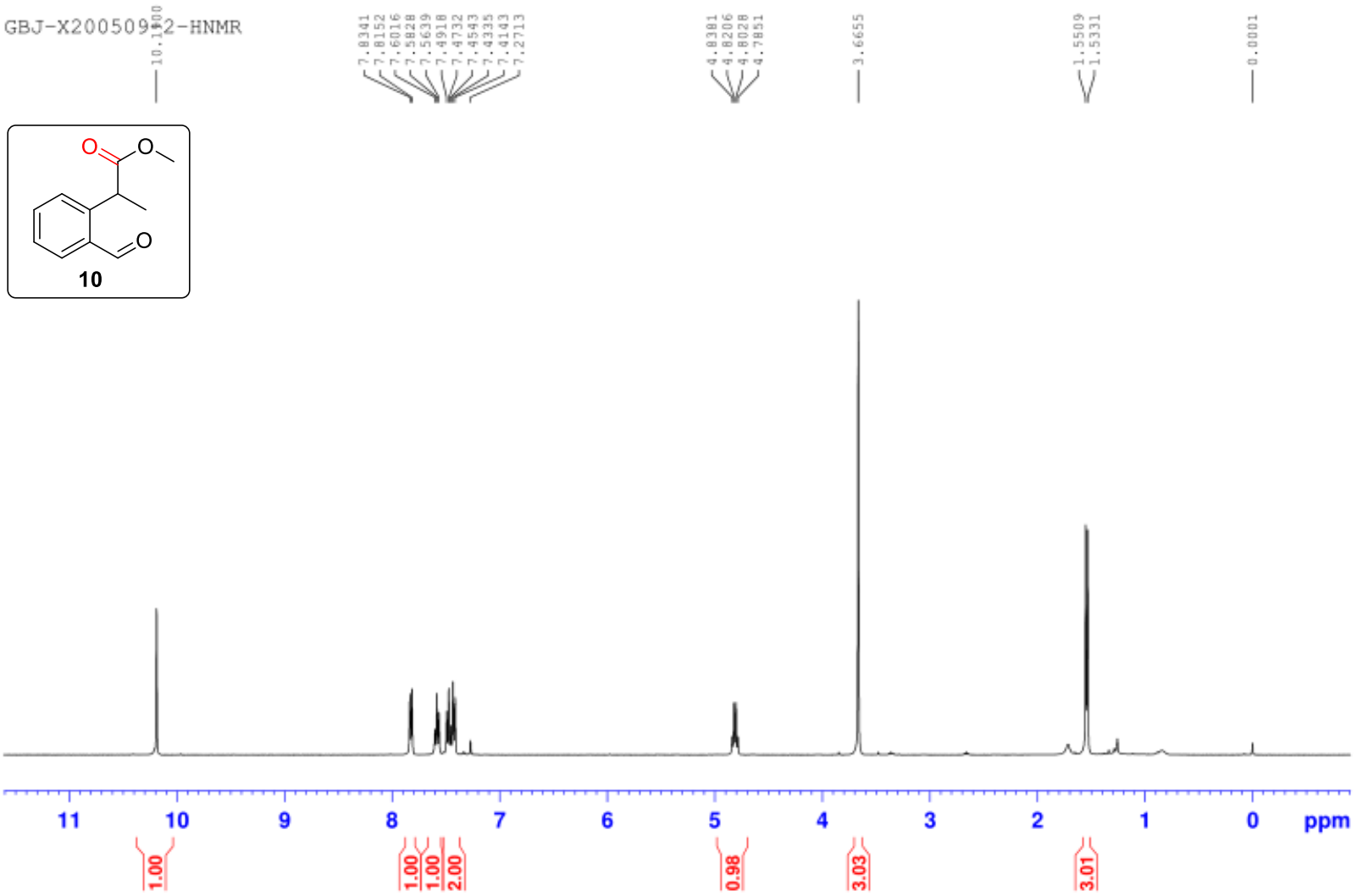
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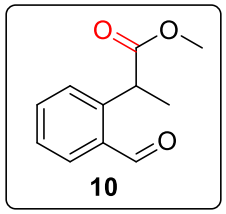
7.8341
7.8152
7.6016
7.5828
7.5639
7.4918
7.4732
7.4543
7.4335
7.4143
7.2713
4.8381
4.8206
4.8028
4.7851
3.6655
1.5509
1.5331
0.0001
O
O
O
10
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.00
2.00
0.98
3.03
3.01

GBJ-X200509-2-CNMR

193.0
174.7
142.4
134.3
134.2
133.4
128.7
127.6
77.5
77.2
76.8
52.2
40.6
18.3



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