

**Organocatalytic asymmetric desymmetrization of
4,4-disubstituted cyclohexadienones
via intermolecular Diels-Alder reaction**

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General Method

All reactions involving air- and moisture-sensitive reagents were carried out under N₂. CH₂Cl₂ and benzene were distilled over CaH₂ before use. Tetrahydrofuran (THF) was distilled after refluxing over Na-benzophenone before use. Merck silica gel 60F₂₅₄ TLC aluminum sheets were used for routine monitoring of reactions. Column chromatography was performed on Kanto Chemical Silica Gel 60N (spherical, neutral 63-210 mm).

Internal references for ¹H NMR spectra were 0.0 ppm (Me₄Si) for CDCl₃. Chemical shifts for ¹³C NMR spectra were referenced to CDCl₃ (77.0 ppm). MS were recorded under electron ionization (EI; 70eV). High-resolution mass spectral (HRMS) data were recorded with a LTQ Orbitrap. Enantioselectivities were determined by high performance liquid chromatography (HPLC) analysis on Chiralpak IA, IC and IC-3 columns. Optical rotations were measured on a digital polarimeter with a 0.1 dm cell at r.t.

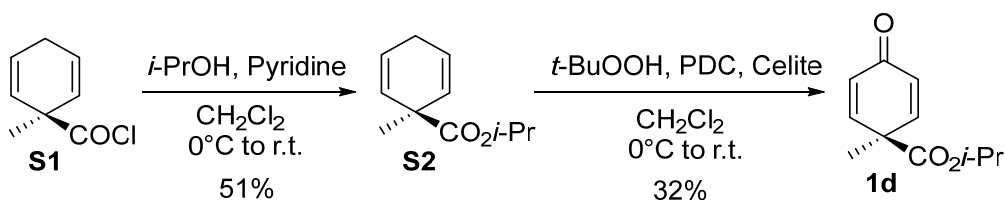
Preparation of chiral phosphoric acid 2

Chiral phosphoric acids **2a-g**¹ and H₈-**2g**² were prepared according to literature procedures.

Preparation of dienones 1a-c

Dienones **1a-c** were prepared according to literature procedure.³

Preparation of dienone 1d

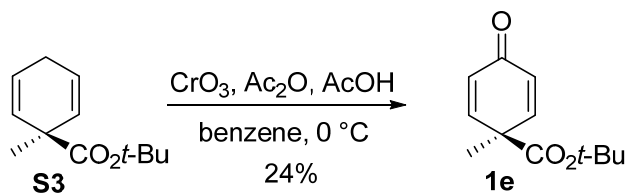


To a mixture of *i*-PrOH (0.85 mL, 11.0 mmol) and pyridine (2.90 mL, 35.9 mmol) in CH₂Cl₂ (3.0 mL) was added a solution of **S1**⁴ (670 mg, 4.29 mmol) in CH₂Cl₂ (0.6 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 3 h. After addition of water, the mixture was extracted with CH₂Cl₂. The organic layer was washed with 1 N HCl, water and brine, dried over Na₂SO₄, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 10 : 1)

to give **S2** (391 mg, 51%) as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 5.83-5.67 (m, 4 H), 4.97 (septet, $J = 6.3$ Hz, 1 H), 2.66-2.62 (m, 2 H), 1.31 (s, 3 H), 1.22 (d, $J = 6.3$ Hz, 6 H); HRMS (EI) m/z calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2$ [M^+] 180.1150, found 180.1155.

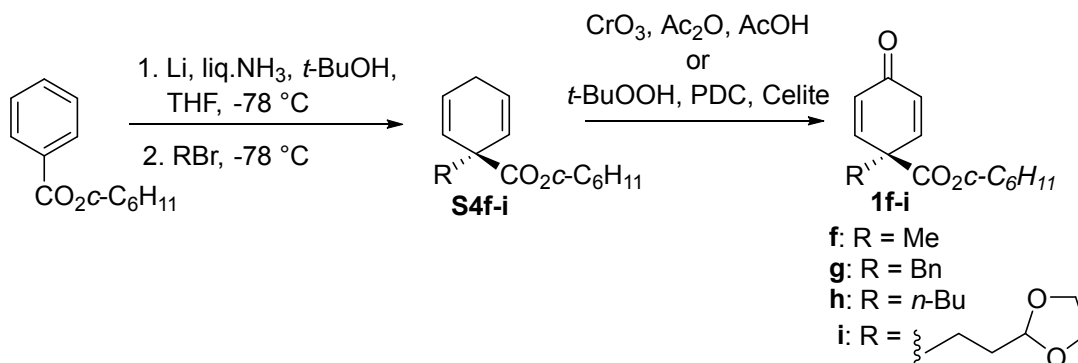
To a mixture of **S2** (291 mg, 1.62 mmol), pyridinium dichromate (PDC) (107 mg, 0.29 mmol) and Celite (300 mg) in CH_2Cl_2 (10.8 mL) was added *t*-BuOOH (70 wt% in H_2O , 0.75 mL, 5.48 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 4 h, and passed through a pad of Celite. The organic layer was washed with sat. $\text{Na}_2\text{S}_2\text{O}_3$, water, and brine, dried over MgSO_4 , and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 7 : 1) to give **1d** (99.2 mg, 32%) as a yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.04 (d, $J = 10.3$ Hz, 2 H), 6.29 (d, $J = 10.3$ Hz, 2 H), 5.03 (septet, $J = 6.2$ Hz, 1 H), 1.55 (s, 3 H), 1.24 (d, $J = 6.2$ Hz, 6 H); ^{13}C NMR (125 MHz, CDCl_3) δ 184.98, 170.06, 149.18 (x2), 128.85 (x2), 69.90, 48.23, 24.78, 21.48 (x2); HRMS (EI) m/z calcd for $\text{C}_{11}\text{H}_{14}\text{O}_3$ [M^+] 194.0943, found 194.0947.

Preparation of dienone 1e

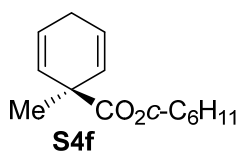


A solution of **S3**⁵ (10.4 g, 53.5 mmol), Ac_2O (50 mL), and AcOH (100 mL) was cooled to 0 °C and diluted with benzene (100 mL). CrO_3 (26.9 g, 269.3 mmol) was added to the reaction mixture. After stirring at 0 °C to r.t. for overnight, the reaction mixture was diluted with EtOAc and carefully quenched with sat. NaHCO_3 . The organic layer was washed with water and brine, dried over Na_2SO_4 , and evaporated. The residue was purified by column chromatography on silica gel (benzene/EtOAc = 40 : 1) to give **1e** (2.71 g, 24%) as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.03 (d, $J = 10.2$ Hz, 2 H), 6.29 (d, $J = 10.2$ Hz, 2 H), 1.53 (s, 3 H), 1.46 (s, 9 H); ^{13}C NMR (125 MHz, CDCl_3) δ 185.18, 169.58, 149.61 (x2), 128.70 (x2), 82.97, 49.05, 27.81 (x3), 24.79; HRMS (ESI+) m/z calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3\text{Na}$ [$\text{M}+\text{Na}$]⁺ 231.0992, found 231.0992.

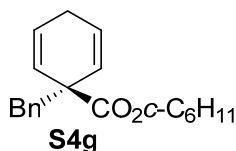
Preparation of dienones 1f-i



Typical procedure of reductive alkylation of cyclohexyl benzoate: Liquid NH₃ was added to the flask cooled to -78 °C. Lithium (1.14 g, 0.16 mmol) was added in small pieces to the stirred solution. A solution of cyclohexyl benzoate (10.3 g, 50.4 mmol) in THF (60 mL) and *t*-butyl alcohol (4.8 mL, 50.2 mmol) was added dropwise to the reaction mixture. The resulting solution was stirred at -78 °C for 2 h. MeI (5 mL, 83.3 mmol) was added dropwise to the reaction mixture. The mixture was warmed slowly to r.t. while the ammonia was removed with a stream of nitrogen. After quenched with water, the mixture was extracted with EtOAc. The organic layer was washed with water and brine, dried over Na₂SO₄, and evaporated to crude product of **S4** (9.93 g). The crude product was used for the next reaction without future purification.

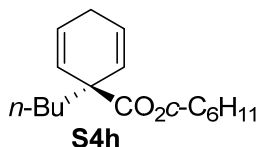


¹H NMR (500 MHz, CDCl₃) δ 5.82-5.76 (m, 4 H), 4.80-4.74 (m, 1 H), 2.66-2.63 (m, 2 H), 1.82-1.74 (m, 2 H), 1.73-1.65 (m, 2 H), 1.58-1.24 (m, 6 H), 1.32 (s, 3 H).⁵

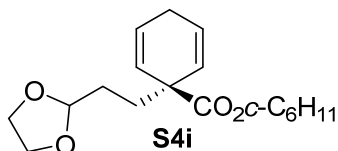


¹H NMR (500 MHz, CDCl₃) δ 7.25-7.16 (m, 3 H), 7.14-7.10 (m, 2 H), 5.86-5.76 (m, 4 H), 4.82-4.75 (m, 1 H), 2.98 (bs, 2 H), 2.58-2.49 (m, 1 H), 2.40-2.31 (m, 1 H), 1.81-1.72 (m, 2 H), 1.71-1.62 (m, 2 H), 1.54-1.23 (m, 6 H); ¹³C NMR (125

MHz, CDCl₃) δ 173.59, 136.72, 130.51 (x2), 127.63 (x2), 127.40 (x2), 126.31, 125.44 (x2), 72.80, 49.05, 64.44, 31.32 (x2), 26.05, 25.42 (x2), 23.41; HRMS (ESI+) m/z calcd for C₂₀H₂₄O₂Na [M+Na]⁺ 319.1668, found 319.1673.

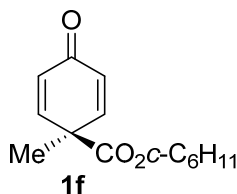


¹H NMR (500 MHz, CDCl₃) δ 6.00-5.60 (m, 4 H), 4.84-4.72 (m, 1 H), 2.75-2.56 (m, 2 H), 1.83-1.09 (m, 16 H), 0.87 (t, J = 7.2 Hz, 3 H); HRMS (ESI+) m/z calcd for C₁₇H₂₆O₂Na [M+Na]⁺ 285.1825, found 285.1829.

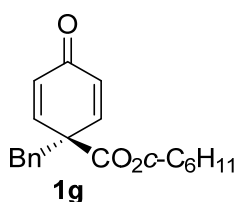


¹H NMR (500 MHz, CDCl₃) δ 5.92-5.86 (m, 2 H), 5.76-5.71 (m, 2 H), 4.84 (t, J = 4.7 Hz, 1 H), 4.81-4.73 (m, 1 H), 4.00-3.82 (m, 4 H), 2.73-2.54 (m, 2 H), 2.01-1.23 (m, 14 H); HRMS (ESI+) m/z calcd for C₁₈H₂₆O₄Na 329.1723, found 329.1724.

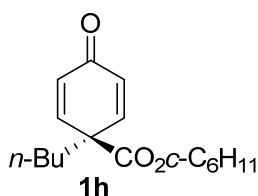
Oxidation of allylic position of S4: Oxidation of allylic position of **S4f,g** were according with the procedure for dienone **1e**. The reaction conditions for dienone **1d** were used for the preparation of **1h,i**.



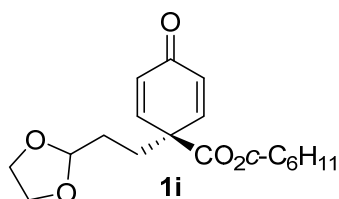
¹H NMR (500 MHz, CDCl₃) δ 7.06 (d, J = 10.4 Hz, 2 H), 6.30 (d, J = 10.4 Hz, 2 H), 4.85-4.78 (m, 1 H), 1.84-1.76 (m, 2 H), 1.73-1.64 (m, 2 H), 1.56 (s, 3 H), 1.55-1.26 (m, 6 H); ¹³C NMR (125 MHz, CDCl₃) δ 185.05, 169.99, 149.27 (x2), 128.90 (x2), 74.45, 48.42, 31.14 (x2), 25.22 (x2), 24.85, 23.31; HRMS (ESI+) m/z calcd for C₁₄H₁₈O₃Na 257.1148, found 257.1151.



^1H NMR (500 MHz, CDCl_3) δ 7.29-7.21 (m, 3 H), 7.14-7.07 (m, 4 H), 6.28 (d, J = 10.3 Hz, 2 H), 4.86-4.78 (m, 1 H), 3.21 (bs, 2 H), 1.80-1.72 (m, 2 H), 1.67-1.57 (m, 2 H), 1.54-1.20 (m, 6 H); ^{13}C NMR (125 MHz, CDCl_3) δ 185.01, 169.17, 148.00 (x2), 134.45, 130.08 (x2), 129.70 (x2), 128.23 (x2), 127.50, 74.72, 53.44, 45.34, 31.17 (x2), 25.18 (x2), 23.29; HRMS (ESI+) m/z calcd for $\text{C}_{20}\text{H}_{22}\text{O}_3\text{Na}$ 333.1461, found 333.1466.



^1H NMR (500 MHz, CDCl_3) δ 7.07 (d, J = 10.3 Hz, 2 H), 6.34 (d, J = 10.3 Hz, 2 H), 4.87-4.79 (m, 1 H), 1.97-1.90 (m, 2 H), 1.86-1.77 (m, 2 H), 1.74-1.65 (m, 2 H), 1.63-1.14 (m, 10 H), 0.87 (t, J = 7.1 Hz, 3 H), ^{13}C NMR (125 MHz, CDCl_3) δ 185.69, 170.04, 148.92 (x2), 130.17 (x2), 74.68, 52.93, 38.68, 31.52 (x2), 26.71, 25.53, 23.66, 23.00 (x2), 14.06; HRMS (ESI+) m/z calcd for $\text{C}_{17}\text{H}_{24}\text{O}_3\text{Na}$ 299.1618, found 299.1617.



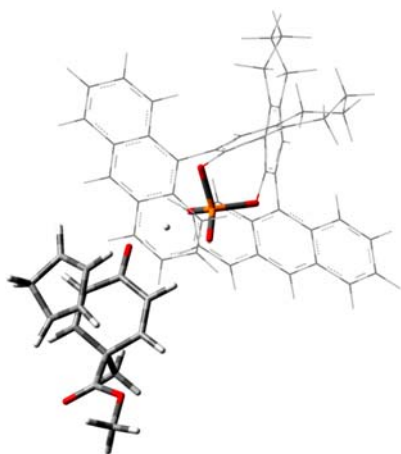
^1H NMR (500 MHz, CDCl_3) δ 7.06 (d, J = 10.3 Hz, 2 H), 6.37 (d, J = 10.3 Hz, 2 H), 4.87-4.78 (m, 2 H), 3.99-3.90 (m, 2 H), 3.89-3.80 (m, 2 H), 2.13-2.07 (m, 2 H), 1.86-1.77 (m, 2 H), 1.74-1.64 (m, 2 H), 1.61-1.24 (m, 8 H); ^{13}C NMR (125 MHz, CDCl_3) δ 185.47, 169.79, 148.32 (x2), 130.66 (x2), 103.65, 74.93, 65.32 (x2), 52.21, 32.24, 31.51 (x2), 28.73, 25.50 (x2), 23.67; HRMS (ESI+) m/z calcd for $\text{C}_{18}\text{H}_{24}\text{O}_5\text{Na}$ 343.1516, found 343.1517.

Preparation of racemic Diels-Alder adduct 3

Racemic adducts **3** were prepared by the Diels-Alder reaction of dienones **1** with cyclopentadiene in $\text{CF}_3\text{CH}_2\text{OH}$.³

Computational data: Cartesian coordinates, energies and harmonic analyses of transition states in Figure 1.⁶

TS_{r,anti}



Energy [ONIOM(B3LYP/6-31G*:HF/3-21G)] =
-3240.16139791 (Hartree/Particle)

Zero-point correction = 1.106067 (Hartree/Particle)

Thermal correction to Gibbs Free Energy = 0.954159 (Hartree/Particle)

Number of Imaginary Frequencies = 1 (-389.78)

Energy [M06-2X/6-311+G**//ONIOM(B3LYP/6-31G*:HF/3-21G)] =
-3262.09256047 (Hartree/Particle)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	-1.980289	0.529881	0.733009
2	8	0	-0.408878	-0.980452	-0.646991
3	15	0	-0.443360	0.469685	0.150952
4	8	0	-0.366975	1.433811	-1.081122
5	8	0	0.524049	0.620211	1.260591

6	6	0	3.831162	3.518245	-0.570145
7	6	0	5.170128	3.078501	-0.405348
8	6	0	5.559607	1.774464	-1.115170
9	6	0	4.409981	0.796202	-1.115275
10	6	0	3.128399	1.201542	-1.079936
11	6	0	2.768632	2.623147	-0.936671
12	8	0	1.595092	3.034484	-1.129954
13	6	0	5.905527	2.107642	-2.608775
14	6	0	3.235745	3.419085	1.947783
15	6	0	3.345825	2.042998	2.063904
16	6	0	4.695541	1.687787	1.883664
17	6	0	5.446872	2.840855	1.538284
18	6	0	4.608770	4.020910	2.013935
19	1	0	2.310939	3.981839	2.004403
20	1	0	4.746357	4.957278	1.469333
21	1	0	4.864954	4.212247	3.069190
22	1	0	3.577460	4.571454	-0.525641
23	1	0	2.515196	1.351688	2.152635
24	1	0	5.937516	3.844520	-0.502462
25	1	0	6.529186	2.860297	1.615421
26	1	0	5.064701	0.668452	1.884928
27	1	0	4.640464	-0.257019	-1.236806
28	1	0	6.174471	1.196230	-3.153827
29	1	0	5.036897	2.560232	-3.092117
30	1	0	6.748568	2.804356	-2.652783
31	6	0	6.873489	1.217251	-0.551721
32	8	0	7.823055	1.910174	-0.250020
33	8	0	6.909484	-0.131303	-0.502474
34	6	0	8.164973	-0.695486	-0.082620
35	1	0	8.025513	-1.776280	-0.119381
36	1	0	8.967740	-0.387356	-0.756965
37	1	0	8.409642	-0.371995	0.932129
38	1	0	0.440820	2.093861	-1.099915
39	1	0	2.323207	0.480087	-1.172575
40	6	0	-0.905885	-2.085608	0.051574
41	6	0	-1.918700	-4.129837	1.602810

42	6	0	-2.270326	-2.182976	0.237634
43	6	0	-0.032894	-3.034071	0.549214
44	6	0	-0.564428	-4.061445	1.302750
45	6	0	-2.785570	-3.177265	1.078253
46	1	0	0.098419	-4.811377	1.688614
47	6	0	-3.033091	0.144968	-0.103135
48	6	0	-4.979260	-0.620549	-1.903288
49	6	0	-3.915203	1.099373	-0.569896
50	6	0	-3.157711	-1.190132	-0.442277
51	6	0	-4.095834	-1.573541	-1.405828
52	6	0	-4.895987	0.688453	-1.451601
53	6	0	-3.872146	2.524248	-0.114454
54	6	0	-4.012346	5.206881	0.667059
55	6	0	-4.452544	2.862140	1.112812
56	6	0	-3.349824	3.517257	-0.946374
57	6	0	-3.435619	4.884098	-0.548723
58	6	0	-4.514611	4.228500	1.509292
59	1	0	-4.074173	6.237141	0.962719
60	6	0	1.435694	-2.999928	0.263235
61	6	0	4.189348	-3.183127	-0.206868
62	6	0	1.902076	-3.451417	-0.976367
63	6	0	2.337791	-2.616899	1.259394
64	6	0	3.738971	-2.732239	1.022131
65	6	0	3.304253	-3.532845	-1.214478
66	1	0	5.245274	-3.267214	-0.381956
67	6	0	-4.064479	-2.981483	-1.993881
68	1	0	-3.275270	-2.994946	-2.742043
69	6	0	-4.267872	-3.172829	1.444750
70	1	0	-4.582880	-2.148821	1.598157
71	1	0	-4.852999	-3.566129	0.621054
72	6	0	-2.394055	-5.241285	2.532507
73	1	0	-2.060154	-5.009973	3.540336
74	1	0	-1.920864	-6.172531	2.240155
75	6	0	-3.921423	-5.399287	2.543532
76	1	0	-4.213970	-6.054985	3.355761
77	1	0	-4.255216	-5.850990	1.614509

78	6	0	-4.563723	-4.013751	2.696907
79	1	0	-4.160038	-3.522927	3.576580
80	1	0	-5.636976	-4.097420	2.826069
81	6	0	-6.075325	-0.975453	-2.902864
82	1	0	-6.201038	-0.154262	-3.599342
83	1	0	-5.594554	1.416920	-1.814509
84	1	0	-7.010103	-1.084599	-2.358744
85	6	0	-5.794060	-2.278577	-3.665934
86	1	0	-6.677148	-2.572216	-4.222426
87	1	0	-4.989133	-2.122715	-4.376943
88	6	0	-5.005405	1.879813	2.002736
89	1	0	-4.963334	0.851686	1.713467
90	6	0	-5.112934	4.561838	2.769123
91	1	0	-5.148925	5.595800	3.053330
92	6	0	-5.559356	2.235781	3.177652
93	1	0	-5.963143	1.488474	3.831580
94	6	0	-5.615115	3.606618	3.572969
95	1	0	-6.060001	3.863156	4.513850
96	6	0	-2.714623	3.218631	-2.200601
97	1	0	-2.582444	2.194764	-2.472021
98	6	0	-2.925001	5.897542	-1.426401
99	1	0	-3.004210	6.921572	-1.116259
100	6	0	-2.246154	4.202042	-2.991409
101	1	0	-1.759791	3.962113	-3.915537
102	6	0	-2.360916	5.571963	-2.603167
103	1	0	-1.979083	6.333513	-3.253783
104	6	0	1.909813	-2.097568	2.529693
105	1	0	0.866160	-1.935756	2.687218
106	6	0	1.016783	-3.850330	-2.034532
107	1	0	-0.036683	-3.792485	-1.864275
108	6	0	1.494678	-4.280418	-3.217953
109	1	0	0.819708	-4.569021	-3.998843
110	6	0	3.768337	-3.998168	-2.489218
111	1	0	4.827322	-4.054049	-2.652382
112	6	0	2.900910	-4.356499	-3.453508
113	1	0	3.254627	-4.702640	-4.404266

114	6	0	2.802108	-1.779350	3.486559
115	1	0	2.466985	-1.383661	4.424141
116	6	0	4.652907	-2.389256	2.074020
117	1	0	5.703268	-2.506911	1.888974
118	6	0	4.203911	-1.942916	3.262247
119	1	0	4.891060	-1.697814	4.048023
120	6	0	-5.386287	-3.374000	-2.670333
121	1	0	-5.263500	-4.324950	-3.176997
122	1	0	-6.164580	-3.493756	-1.922499
123	1	0	-3.791283	-3.704027	-1.241890

TS_{r,syn}:



Energy [ONIOM(B3LYP/6-31G*:HF/3-21G)] =
-3240.16492005 (Hartree/Particle)

Zero-point correction = 1.050446 (Hartree/Particle)

Thermal correction to Gibbs Free Energy = 0.954749 (Hartree/Particle)

Number of Imaginary Frequencies = 1 (-362.06)

Energy [M06-2X/6-311+G**//ONIOM(B3LYP/6-31G*:HF/3-21G)] =
-3262.09416858 (Hartree/Particle)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

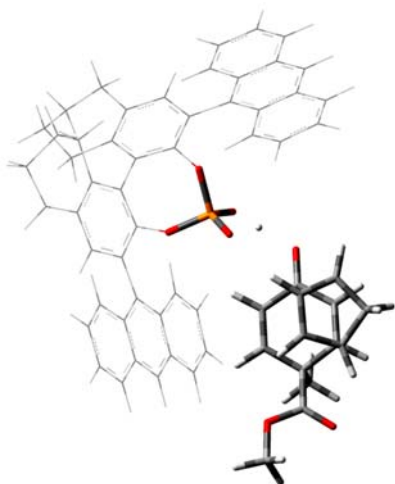
1	6	0	1.103266	-2.055452	-0.050597
2	6	0	2.469249	-2.044218	-0.259422
3	6	0	0.898456	-4.062133	-1.280290
4	6	0	3.047866	-3.007871	-1.093167
5	6	0	0.298998	-3.073200	-0.525300
6	6	0	2.248950	-4.028682	-1.598673
7	6	0	4.507934	-2.876375	-1.518314
8	1	0	0.289951	-4.864215	-1.650105
9	6	0	5.092333	-4.187131	-2.066073
10	6	0	4.149914	-4.766344	-3.130210
11	6	0	2.815542	-5.144221	-2.470693
12	6	0	3.845498	1.366079	0.542863
13	1	0	5.483217	1.822409	1.798645
14	6	0	4.852092	1.038211	1.428469
15	6	0	3.282707	-0.979307	0.407514
16	6	0	5.046884	-0.261762	1.874965
17	6	0	3.048713	0.340322	0.071281
18	6	0	4.254403	-1.285644	1.367950
19	6	0	6.157636	-0.521303	2.887144
20	6	0	5.979950	-1.847770	3.640112
21	6	0	5.702734	-2.968445	2.628591
22	6	0	4.365299	-2.704490	1.920415
23	8	0	0.532818	-0.981302	0.645111
24	8	0	1.966971	0.640597	-0.764092
25	15	0	0.444803	0.445893	-0.185903
26	8	0	0.300828	1.476054	0.984469
27	8	0	-0.533596	0.469178	-1.299163
28	1	0	5.847488	1.909773	-3.861598
29	6	0	5.385505	2.623498	-3.208672
30	1	0	4.905766	1.198934	-1.740773
31	6	0	4.863923	2.226512	-2.032037
32	6	0	4.754319	4.907007	-2.804117
33	6	0	4.235215	3.163251	-1.143145
34	6	0	5.330163	3.993467	-3.606992
35	6	0	4.186928	4.529362	-1.542452
36	6	0	3.685914	2.782392	0.085988

37	1	0	5.751553	4.282907	-4.549147
38	1	0	4.706912	5.939963	-3.090321
39	6	0	3.087729	3.732247	0.917260
40	6	0	3.063675	5.100826	0.516886
41	6	0	3.610001	5.466237	-0.700896
42	6	0	-2.946442	-3.865295	1.298189
43	6	0	-3.879778	-3.577916	0.315888
44	6	0	-1.561785	-3.662214	1.032301
45	1	0	-5.498053	-2.975454	-1.725810
46	6	0	-1.162158	-3.160435	-0.210972
47	6	0	-2.114904	-2.846839	-1.184348
48	6	0	-1.759859	-2.292287	-2.462029
49	6	0	-3.496981	-3.075697	-0.915943
50	6	0	-2.698848	-2.038026	-3.393904
51	1	0	-0.736141	-2.051132	-2.645416
52	1	0	-2.416903	-1.619324	-4.339286
53	6	0	-4.079459	-2.298547	-3.132481
54	1	0	-4.805134	-2.092387	-3.894207
55	6	0	-4.463079	-2.787750	-1.938245
56	1	0	3.589253	6.497640	-0.998385
57	1	0	-4.920706	-3.754470	0.511438
58	6	0	-0.623398	-3.996716	2.066923
59	1	0	0.417608	-3.847618	1.876429
60	6	0	-1.037708	-4.479773	3.253809
61	1	0	-0.324061	-4.718934	4.016889
62	6	0	-3.341980	-4.383427	2.575607
63	1	0	-4.388737	-4.530584	2.759334
64	6	0	-2.427029	-4.678131	3.517128
65	1	0	-2.729612	-5.064022	4.470217
66	6	0	2.480462	3.386868	2.173201
67	1	0	2.430547	2.356328	2.446422
68	6	0	1.937392	4.331187	2.963831
69	1	0	1.472637	4.054671	3.888790
70	6	0	2.476426	6.072429	1.394176
71	1	0	2.474818	7.099142	1.082626
72	6	0	1.942812	5.705272	2.573021

73	1	0	1.504897	6.435723	3.224115
74	6	0	-3.379319	1.099670	0.260473
75	6	0	-4.700199	0.755723	-0.126919
76	6	0	-5.827288	1.019354	0.883652
77	6	0	-5.545331	2.254810	1.702227
78	6	0	-4.292409	2.680908	1.934115
79	6	0	-3.118655	2.026677	1.327209
80	8	0	-1.977297	2.307863	1.774800
81	6	0	-5.897940	-0.200648	1.863593
82	6	0	-2.963968	2.755520	-1.631437
83	6	0	-3.910480	3.686973	-1.227813
84	6	0	-5.191051	3.128362	-1.375861
85	6	0	-5.061857	1.776376	-1.787631
86	6	0	-3.664946	1.665498	-2.382881
87	1	0	-1.887477	2.871448	-1.607539
88	1	0	-3.186353	0.687538	-2.344243
89	1	0	-3.729667	1.964266	-3.443317
90	1	0	-3.694239	4.649595	-0.777209
91	1	0	-4.801662	-0.209158	-0.618594
92	1	0	-5.896331	1.227126	-2.213183
93	1	0	-6.119611	3.610182	-1.090299
94	1	0	-6.388950	2.736254	2.187757
95	1	0	-6.671249	-0.043495	2.624451
96	1	0	-4.934559	-0.328619	2.361868
97	1	0	-6.135926	-1.109279	1.304159
98	6	0	-7.187628	1.027351	0.173003
99	8	0	-7.566976	0.133357	-0.554222
100	8	0	-7.946393	2.106084	0.464817
101	6	0	-9.256283	2.118884	-0.133331
102	1	0	-9.724250	3.040864	0.212079
103	1	0	-9.831577	1.247873	0.190025
104	1	0	-9.178670	2.109280	-1.223285
105	1	0	-4.088123	3.511204	2.604857
106	1	0	7.106669	-0.544343	2.357464
107	1	0	6.198523	0.304716	3.588038
108	1	0	6.872152	-2.061597	4.217975

109	1	0	5.146002	-1.770950	4.330299
110	1	0	6.506984	-3.005045	1.899687
111	1	0	5.661885	-3.931880	3.124686
112	1	0	3.558471	-2.833848	2.637941
113	1	0	4.205429	-3.429566	1.137879
114	1	0	4.547755	-2.121776	-2.300277
115	1	0	5.108139	-2.509309	-0.700726
116	1	0	6.073181	-3.994357	-2.486271
117	1	0	5.212657	-4.904729	-1.259845
118	1	0	3.981684	-4.024849	-3.904539
119	1	0	4.586631	-5.642187	-3.596864
120	1	0	2.969790	-6.021577	-1.847669
121	1	0	2.085346	-5.409041	-3.226999
122	1	0	-2.538499	0.560784	-0.159466
123	1	0	-0.661074	1.772693	1.238505

TS_{1,anti}



Energy [ONIOM(B3LYP/6-31G*:HF/3-21G)] =

-3240.16327498 (Hartree/Particle)

Zero-point correction = 1.051014 (Hartree/Particle)

Thermal correction to Gibbs Free Energy = 0.955546 (Hartree/Particle)

Number of Imaginary Frequencies = 1 (-376.13)

Energy [M06-2X/6-311+G**//ONIOM(B3LYP/6-31G*:HF/3-21G)] =

-3262.09364187 (Hartee/Particle)

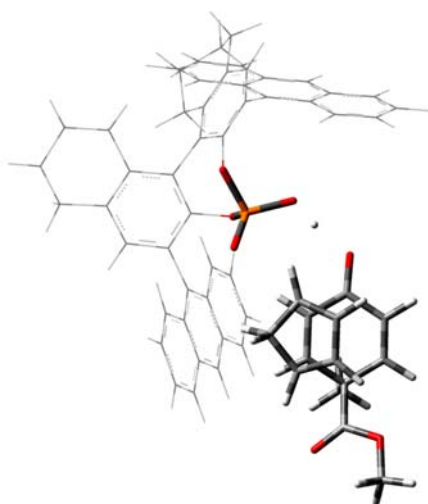
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	-1.980289	0.529881	0.733009
2	8	0	-0.408878	-0.980452	-0.646991
3	15	0	-0.443360	0.469685	0.150952
4	8	0	-0.366975	1.433811	-1.081122
5	8	0	0.524049	0.620211	1.260591
6	6	0	3.831162	3.518245	-0.570145
7	6	0	5.170128	3.078501	-0.405348
8	6	0	5.559607	1.774464	-1.115170
9	6	0	4.409981	0.796202	-1.115275
10	6	0	3.128399	1.201542	-1.079936
11	6	0	2.768632	2.623147	-0.936671
12	8	0	1.595092	3.034484	-1.129954
13	6	0	5.905527	2.107642	-2.608775
14	6	0	3.235745	3.419085	1.947783
15	6	0	3.345825	2.042998	2.063904
16	6	0	4.695541	1.687787	1.883664
17	6	0	5.446872	2.840855	1.538284
18	6	0	4.608770	4.020910	2.013935
19	1	0	2.310939	3.981839	2.004403
20	1	0	4.746357	4.957278	1.469333
21	1	0	4.864954	4.212247	3.069190
22	1	0	3.577460	4.571454	-0.525641
23	1	0	2.515196	1.351688	2.152635
24	1	0	5.937516	3.844520	-0.502462
25	1	0	6.529186	2.860297	1.615421
26	1	0	5.064701	0.668452	1.884928
27	1	0	4.640464	-0.257019	-1.236806
28	1	0	6.174471	1.196230	-3.153827
29	1	0	5.036897	2.560232	-3.092117
30	1	0	6.748568	2.804356	-2.652783
31	6	0	6.873489	1.217251	-0.551721

32	8	0	7.823055	1.910174	-0.250020
33	8	0	6.909484	-0.131303	-0.502474
34	6	0	8.164973	-0.695486	-0.082620
35	1	0	8.025513	-1.776280	-0.119381
36	1	0	8.967740	-0.387356	-0.756965
37	1	0	8.409642	-0.371995	0.932129
38	1	0	0.440820	2.093861	-1.099915
39	1	0	2.323207	0.480087	-1.172575
40	6	0	-0.905885	-2.085608	0.051574
41	6	0	-1.918700	-4.129837	1.602810
42	6	0	-2.270326	-2.182976	0.237634
43	6	0	-0.032894	-3.034071	0.549214
44	6	0	-0.564428	-4.061445	1.302750
45	6	0	-2.785570	-3.177265	1.078253
46	1	0	0.098419	-4.811377	1.688614
47	6	0	-3.033091	0.144968	-0.103135
48	6	0	-4.979260	-0.620549	-1.903288
49	6	0	-3.915203	1.099373	-0.569896
50	6	0	-3.157711	-1.190132	-0.442277
51	6	0	-4.095834	-1.573541	-1.405828
52	6	0	-4.895987	0.688453	-1.451601
53	6	0	-3.872146	2.524248	-0.114454
54	6	0	-4.012346	5.206881	0.667059
55	6	0	-4.452544	2.862140	1.112812
56	6	0	-3.349824	3.517257	-0.946374
57	6	0	-3.435619	4.884098	-0.548723
58	6	0	-4.514611	4.228500	1.509292
59	1	0	-4.074173	6.237141	0.962719
60	6	0	1.435694	-2.999928	0.263235
61	6	0	4.189348	-3.183127	-0.206868
62	6	0	1.902076	-3.451417	-0.976367
63	6	0	2.337791	-2.616899	1.259394
64	6	0	3.738971	-2.732239	1.022131
65	6	0	3.304253	-3.532845	-1.214478
66	1	0	5.245274	-3.267214	-0.381956
67	6	0	-4.064479	-2.981483	-1.993881

68	1	0	-3.275270	-2.994946	-2.742043
69	6	0	-4.267872	-3.172829	1.444750
70	1	0	-4.582880	-2.148821	1.598157
71	1	0	-4.852999	-3.566129	0.621054
72	6	0	-2.394055	-5.241285	2.532507
73	1	0	-2.060154	-5.009973	3.540336
74	1	0	-1.920864	-6.172531	2.240155
75	6	0	-3.921423	-5.399287	2.543532
76	1	0	-4.213970	-6.054985	3.355761
77	1	0	-4.255216	-5.850990	1.614509
78	6	0	-4.563723	-4.013751	2.696907
79	1	0	-4.160038	-3.522927	3.576580
80	1	0	-5.636976	-4.097420	2.826069
81	6	0	-6.075325	-0.975453	-2.902864
82	1	0	-6.201038	-0.154262	-3.599342
83	1	0	-5.594554	1.416920	-1.814509
84	1	0	-7.010103	-1.084599	-2.358744
85	6	0	-5.794060	-2.278577	-3.665934
86	1	0	-6.677148	-2.572216	-4.222426
87	1	0	-4.989133	-2.122715	-4.376943
88	6	0	-5.005405	1.879813	2.002736
89	1	0	-4.963334	0.851686	1.713467
90	6	0	-5.112934	4.561838	2.769123
91	1	0	-5.148925	5.595800	3.053330
92	6	0	-5.559356	2.235781	3.177652
93	1	0	-5.963143	1.488474	3.831580
94	6	0	-5.615115	3.606618	3.572969
95	1	0	-6.060001	3.863156	4.513850
96	6	0	-2.714623	3.218631	-2.200601
97	1	0	-2.582444	2.194764	-2.472021
98	6	0	-2.925001	5.897542	-1.426401
99	1	0	-3.004210	6.921572	-1.116259
100	6	0	-2.246154	4.202042	-2.991409
101	1	0	-1.759791	3.962113	-3.915537
102	6	0	-2.360916	5.571963	-2.603167
103	1	0	-1.979083	6.333513	-3.253783

104	6	0	1.909813	-2.097568	2.529693
105	1	0	0.866160	-1.935756	2.687218
106	6	0	1.016783	-3.850330	-2.034532
107	1	0	-0.036683	-3.792485	-1.864275
108	6	0	1.494678	-4.280418	-3.217953
109	1	0	0.819708	-4.569021	-3.998843
110	6	0	3.768337	-3.998168	-2.489218
111	1	0	4.827322	-4.054049	-2.652382
112	6	0	2.900910	-4.356499	-3.453508
113	1	0	3.254627	-4.702640	-4.404266
114	6	0	2.802108	-1.779350	3.486559
115	1	0	2.466985	-1.383661	4.424141
116	6	0	4.652907	-2.389256	2.074020
117	1	0	5.703268	-2.506911	1.888974
118	6	0	4.203911	-1.942916	3.262247
119	1	0	4.891060	-1.697814	4.048023
120	6	0	-5.386287	-3.374000	-2.670333
121	1	0	-5.263500	-4.324950	-3.176997
122	1	0	-6.164580	-3.493756	-1.922499
123	1	0	-3.791283	-3.704027	-1.241890

TS_*l,syn*:



Energy [ONIOM(B3LYP/6-31G*:HF/3-21G)] =
-3240.16570320 (Hartree/Particle)

Zero-point correction = 1.050751 (Hartee/Particle)

Thermal correction to Gibbs Free Energy = 0.955756 (Hartee/Particle)

Number of Imaginary Frequencies = 1 (-380.46)

Energy [M06-2X/6-311+G**//ONIOM(B3LYP/6-31G*:HF/3-21G)] =
-3262.09603204 (Hartee/Particle)

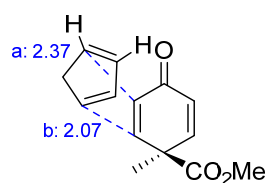
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.103266	-2.055452	-0.050597
2	6	0	2.469249	-2.044218	-0.259422
3	6	0	0.898456	-4.062133	-1.280290
4	6	0	3.047866	-3.007871	-1.093167
5	6	0	0.298998	-3.073200	-0.525300
6	6	0	2.248950	-4.028682	-1.598673
7	6	0	4.507934	-2.876375	-1.518314
8	1	0	0.289951	-4.864215	-1.650105
9	6	0	5.092333	-4.187131	-2.066073
10	6	0	4.149914	-4.766344	-3.130210
11	6	0	2.815542	-5.144221	-2.470693
12	6	0	3.845498	1.366079	0.542863
13	1	0	5.483217	1.822409	1.798645
14	6	0	4.852092	1.038211	1.428469
15	6	0	3.282707	-0.979307	0.407514
16	6	0	5.046884	-0.261762	1.874965
17	6	0	3.048713	0.340322	0.071281
18	6	0	4.254403	-1.285644	1.367950
19	6	0	6.157636	-0.521303	2.887144
20	6	0	5.979950	-1.847770	3.640112
21	6	0	5.702734	-2.968445	2.628591
22	6	0	4.365299	-2.704490	1.920415
23	8	0	0.532818	-0.981302	0.645111
24	8	0	1.966971	0.640597	-0.764092
25	15	0	0.444803	0.445893	-0.185903
26	8	0	0.300828	1.476054	0.984469
27	8	0	-0.533596	0.469178	-1.299163

28	1	0	5.847488	1.909773	-3.861598
29	6	0	5.385505	2.623498	-3.208672
30	1	0	4.905766	1.198934	-1.740773
31	6	0	4.863923	2.226512	-2.032037
32	6	0	4.754319	4.907007	-2.804117
33	6	0	4.235215	3.163251	-1.143145
34	6	0	5.330163	3.993467	-3.606992
35	6	0	4.186928	4.529362	-1.542452
36	6	0	3.685914	2.782392	0.085988
37	1	0	5.751553	4.282907	-4.549147
38	1	0	4.706912	5.939963	-3.090321
39	6	0	3.087729	3.732247	0.917260
40	6	0	3.063675	5.100826	0.516886
41	6	0	3.610001	5.466237	-0.700896
42	6	0	-2.946442	-3.865295	1.298189
43	6	0	-3.879778	-3.577916	0.315888
44	6	0	-1.561785	-3.662214	1.032301
45	1	0	-5.498053	-2.975454	-1.725810
46	6	0	-1.162158	-3.160435	-0.210972
47	6	0	-2.114904	-2.846839	-1.184348
48	6	0	-1.759859	-2.292287	-2.462029
49	6	0	-3.496981	-3.075697	-0.915943
50	6	0	-2.698848	-2.038026	-3.393904
51	1	0	-0.736141	-2.051132	-2.645416
52	1	0	-2.416903	-1.619324	-4.339286
53	6	0	-4.079459	-2.298547	-3.132481
54	1	0	-4.805134	-2.092387	-3.894207
55	6	0	-4.463079	-2.787750	-1.938245
56	1	0	3.589253	6.497640	-0.998385
57	1	0	-4.920706	-3.754470	0.511438
58	6	0	-0.623398	-3.996716	2.066923
59	1	0	0.417608	-3.847618	1.876429
60	6	0	-1.037708	-4.479773	3.253809
61	1	0	-0.324061	-4.718934	4.016889
62	6	0	-3.341980	-4.383427	2.575607
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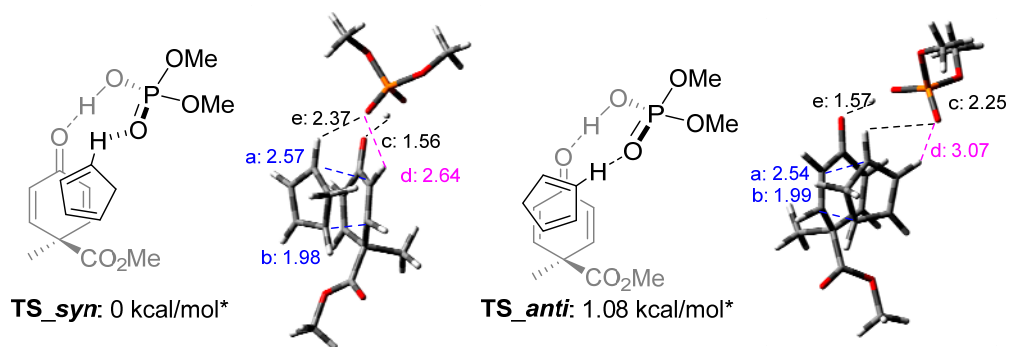
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66	6	0	2.480462	3.386868	2.173201
67	1	0	2.430547	2.356328	2.446422
68	6	0	1.937392	4.331187	2.963831
69	1	0	1.472637	4.054671	3.888790
70	6	0	2.476426	6.072429	1.394176
71	1	0	2.474818	7.099142	1.082626
72	6	0	1.942812	5.705272	2.573021
73	1	0	1.504897	6.435723	3.224115
74	6	0	-3.379319	1.099670	0.260473
75	6	0	-4.700199	0.755723	-0.126919
76	6	0	-5.827288	1.019354	0.883652
77	6	0	-5.545331	2.254810	1.702227
78	6	0	-4.292409	2.680908	1.934115
79	6	0	-3.118655	2.026677	1.327209
80	8	0	-1.977297	2.307863	1.774800
81	6	0	-5.897940	-0.200648	1.863593
82	6	0	-2.963968	2.755520	-1.631437
83	6	0	-3.910480	3.686973	-1.227813
84	6	0	-5.191051	3.128362	-1.375861
85	6	0	-5.061857	1.776376	-1.787631
86	6	0	-3.664946	1.665498	-2.382881
87	1	0	-1.887477	2.871448	-1.607539
88	1	0	-3.186353	0.687538	-2.344243
89	1	0	-3.729667	1.964266	-3.443317
90	1	0	-3.694239	4.649595	-0.777209
91	1	0	-4.801662	-0.209158	-0.618594
92	1	0	-5.896331	1.227126	-2.213183
93	1	0	-6.119611	3.610182	-1.090299
94	1	0	-6.388950	2.736254	2.187757
95	1	0	-6.671249	-0.043495	2.624451
96	1	0	-4.934559	-0.328619	2.361868
97	1	0	-6.135926	-1.109279	1.304159
98	6	0	-7.187628	1.027351	0.173003
99	8	0	-7.566976	0.133357	-0.554222

100	8	0	-7.946393	2.106084	0.464817
101	6	0	-9.256283	2.118884	-0.133331
102	1	0	-9.724250	3.040864	0.212079
103	1	0	-9.831577	1.247873	0.190025
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107	1	0	6.198523	0.304716	3.588038
108	1	0	6.872152	-2.061597	4.217975
109	1	0	5.146002	-1.770950	4.330299
110	1	0	6.506984	-3.005045	1.899687
111	1	0	5.661885	-3.931880	3.124686
112	1	0	3.558471	-2.833848	2.637941
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114	1	0	4.547755	-2.121776	-2.300277
115	1	0	5.108139	-2.509309	-0.700726
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117	1	0	5.212657	-4.904729	-1.259845
118	1	0	3.981684	-4.024849	-3.904539
119	1	0	4.586631	-5.642187	-3.596864
120	1	0	2.969790	-6.021577	-1.847669
121	1	0	2.085346	-5.409041	-3.226999
122	1	0	-2.538499	0.560784	-0.159466
123	1	0	-0.661074	1.772693	1.238505

DFT study (B3LYP/6-31G*) on transition state of thermal and (MeO)₂P(O)OH-catalyzed Diels-Alder reaction of dienone 1 with cyclopentadiene



TS of thermal DA reaction



* relative Gibbs energies at 293 K.

TS of $(\text{MeO})_2\text{P}(\text{O})\text{OH}$ -catalyzed DA reaction

TS of thermal DA reaction

Center Number	Atomic Number	Forces (Hartrees/Bohr)		
		X	Y	Z
1	6	0.000000065	-0.000000444	-0.000002093
2	6	-0.000003293	-0.000001854	0.000001906
3	6	0.000000138	-0.000001245	-0.000002734
4	6	0.000000866	0.000001217	-0.000001627
5	6	-0.000000409	-0.000000191	-0.000002127
6	6	0.000000483	-0.000000109	0.000001598
7	8	-0.000000134	-0.000000501	-0.000001123
8	6	-0.000000228	0.000001604	-0.000003396
9	6	-0.000001522	-0.000000237	0.000000435
10	8	-0.000000806	-0.000000882	-0.000000492
11	8	0.000001629	0.000001614	-0.000000688
12	6	0.000001073	0.000002270	-0.000000608
13	6	0.000000608	-0.000006867	0.000006042
14	6	0.000002160	0.000004279	0.000000846
15	6	-0.000000050	0.000001554	0.000000858
16	6	-0.000001027	-0.000005507	0.000002685

17	6	0.000001671	0.000002763	0.000002080
18	1	-0.000000349	-0.000002791	0.000000573
19	1	-0.000001430	-0.000003225	0.000000324
20	1	-0.000001074	0.000002567	-0.000002935
21	1	-0.000002490	-0.000002161	-0.000004930
22	1	0.000000459	-0.000002803	-0.000003078
23	1	-0.000001560	-0.000001839	-0.000000883
24	1	-0.000000093	0.000004021	-0.000001579
25	1	-0.000000413	0.000001683	-0.000000753
26	1	0.000000594	0.000002769	0.000000850
27	1	0.000001284	-0.000001166	0.000002776
28	1	0.000001545	0.000001870	0.000000866
29	1	0.000000785	0.000002590	0.000000499
30	1	-0.000000180	-0.000000820	0.000002401
31	1	0.000001261	-0.000000004	0.000005171
32	1	0.000000214	-0.000000013	0.000001944
33	1	0.000000221	0.000001857	-0.000002808

TS of (MeO)₂P(O)OH-catalyzed DA reaction

TS_{syn}

Energy (B3LYP/6-31G*) = -1491.46396308 (Hartee/Particle)

Zero-point correction = 0.378770 (Hartee/Particle)

Thermal correction to Gibbs Free Energy = 0.319705 (Hartee/Particle)

Number of Imaginary Frequencies = 1 (-375.23)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.346422	-0.463310	-0.160876
2	6	0	1.621430	-0.342087	-0.773263
3	6	0	2.810485	-1.016475	-0.069939
4	6	0	2.655778	-0.958845	1.429899
5	6	0	1.447888	-0.900654	2.015045
6	6	0	0.203925	-0.809100	1.228517

7	8	0	-0.891970	-1.043578	1.797070
8	6	0	2.843886	-2.523822	-0.494241
9	6	0	4.134087	-0.439499	-0.591910
10	8	0	4.395198	-0.332687	-1.771507
11	8	0	5.001837	-0.104594	0.386144
12	6	0	6.285348	0.371318	-0.063572
13	6	0	-0.026877	2.060341	0.134096
14	6	0	1.001834	2.254454	1.044108
15	6	0	2.231013	2.041225	0.396958
16	6	0	0.563607	2.035872	-1.242676
17	6	0	1.987299	1.597963	-0.929135
18	1	0	-0.559274	-0.422787	-0.754405
19	1	0	1.644399	-0.499421	-1.850154
20	1	0	3.554250	-1.070306	2.029223
21	1	0	3.666131	-3.048846	0.004997
22	1	0	1.903149	-3.004032	-0.215738
23	1	0	2.986436	-2.602454	-1.575878
24	1	0	6.852841	0.576502	0.844175
25	1	0	6.783048	-0.390426	-0.668479
26	1	0	6.167658	1.279170	-0.660214
27	1	0	-1.092838	2.101773	0.318387
28	1	0	0.877539	2.444139	2.104777
29	1	0	3.203973	2.082092	0.874168
30	1	0	0.011277	1.443517	-1.972573
31	1	0	0.605866	3.071222	-1.620768
32	1	0	2.762427	1.625716	-1.689002
33	8	0	-4.654066	0.449724	0.921476
34	8	0	-4.685020	-0.692759	-1.380233
35	15	0	-3.687546	-0.088784	-0.267542
36	8	0	-3.030392	-1.368400	0.378103
37	8	0	-2.808979	0.960479	-0.845151
38	1	0	-2.196035	-1.194399	0.947958
39	1	0	1.333492	-0.961885	3.093990
40	6	0	-5.537944	-1.803389	-1.062325
41	1	0	-4.940873	-2.689225	-0.828846
42	1	0	-6.147180	-1.986918	-1.949709

43	1	0	-6.186806	-1.565753	-0.212610
44	6	0	-5.272066	1.734228	0.758568
45	1	0	-4.520111	2.500724	0.550400
46	1	0	-5.782339	1.954818	1.698442
47	1	0	-6.003407	1.713724	-0.057753

TS_anti

Energy (B3LYP/6-31G*) = -1491.46292958 (Hartee/Particle)

Zero-point correction = 0.378998 (Hartee/Particle)

Thermal correction to Gibbs Free Energy = 0.320389 (Hartee/Particle)

Number of Imaginary Frequencies = 1 (-384.58)

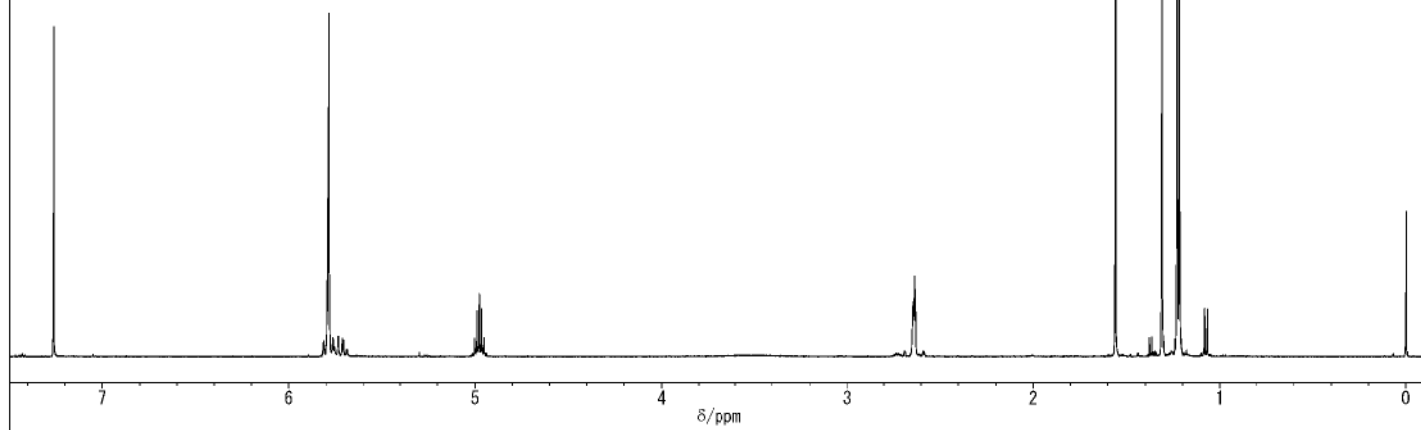
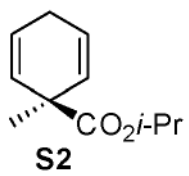
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3	15	0	-3.524110	-0.382341	-0.317021
4	8	0	-3.054037	-1.104578	1.009325
5	8	0	-2.501903	0.075968	-1.288898
6	6	0	1.155377	0.946170	1.681132
7	6	0	2.442407	0.732985	1.125199
8	6	0	2.803666	-0.707467	0.730595
9	6	0	1.592694	-1.445701	0.216036
10	6	0	0.343405	-1.126612	0.593988
11	6	0	0.072030	0.016767	1.484379
12	8	0	-1.042809	0.162148	2.043195
13	6	0	3.321052	-1.455437	2.005749
14	6	0	0.353159	2.549096	-0.125106
15	6	0	0.339615	1.623140	-1.158217
16	6	0	1.667314	1.255919	-1.439862
17	6	0	2.537566	1.874006	-0.505978
18	6	0	1.754926	3.057020	0.047076
19	1	0	-0.524407	2.997068	0.326832
20	1	0	2.025889	3.383529	1.053205

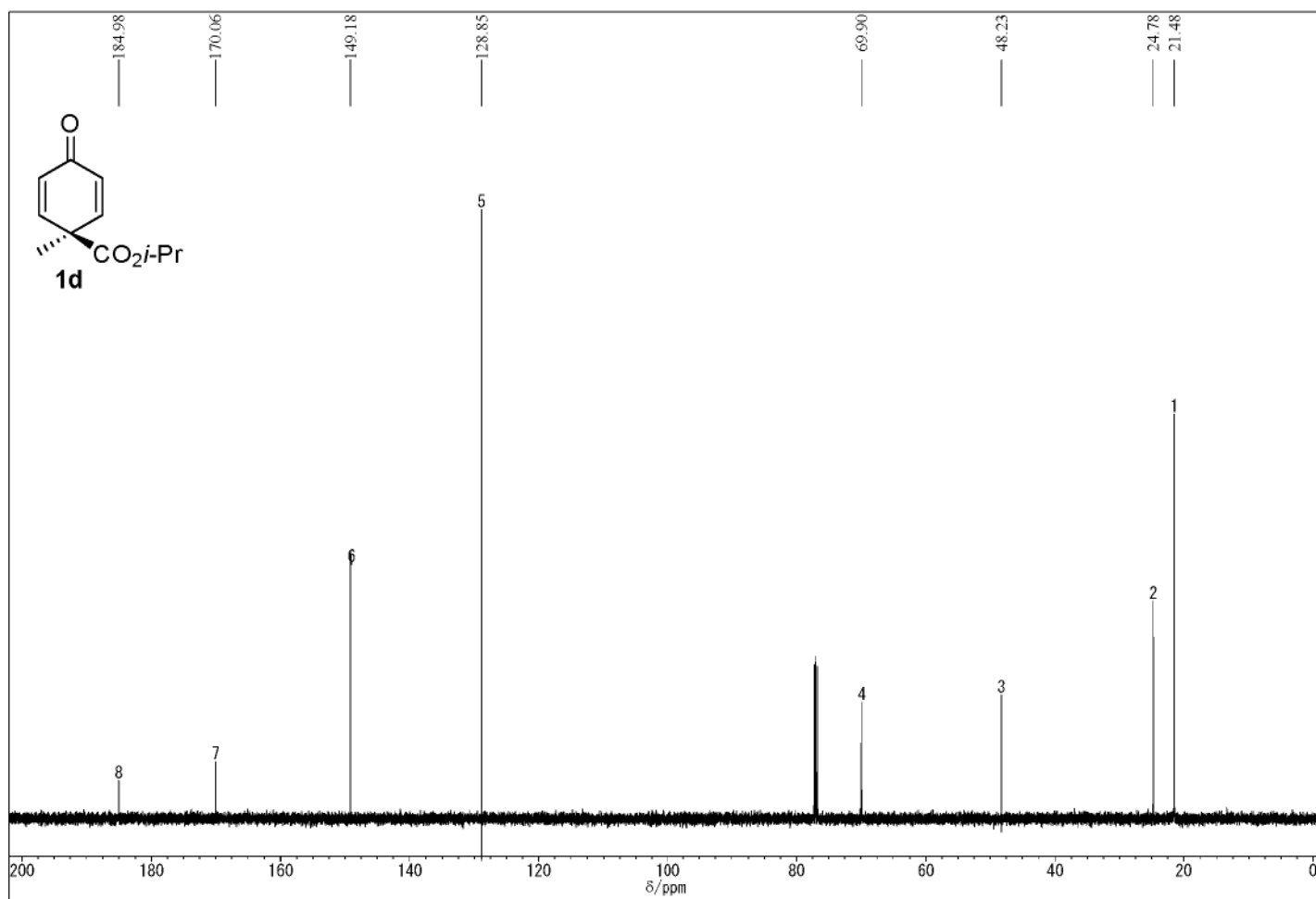
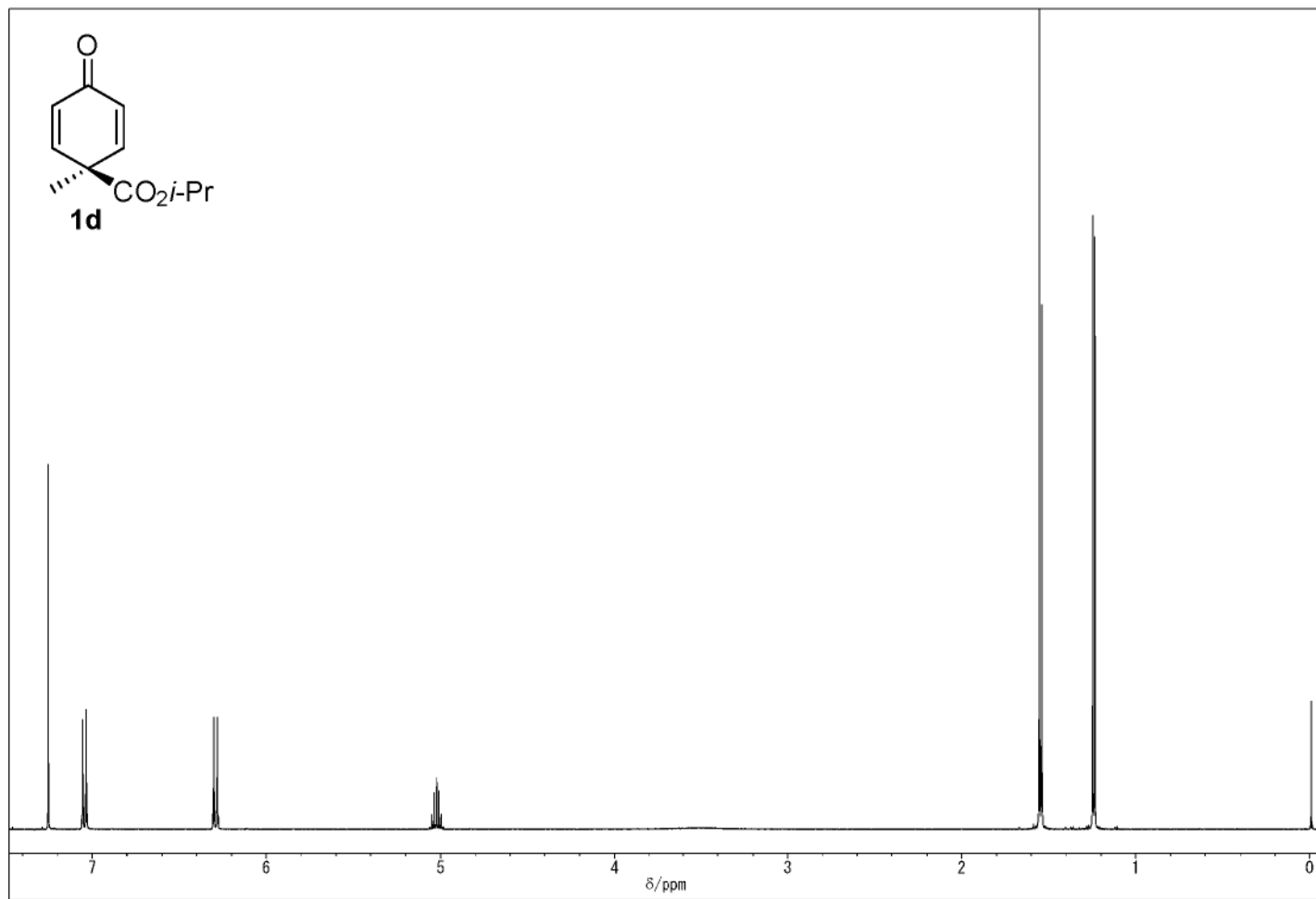
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23	1	0	-0.552954	1.167983	-1.575050
24	1	0	3.267492	1.240963	1.621326
25	1	0	3.607597	1.942717	-0.676345
26	1	0	1.963146	0.509808	-2.169208
27	1	0	1.768433	-2.314701	-0.410452
28	1	0	3.568817	-2.496340	1.769290
29	1	0	2.544966	-1.447914	2.774497
30	1	0	4.218916	-0.962287	2.389731
31	6	0	4.002180	-0.710046	-0.229696
32	8	0	5.017918	-0.078048	-0.027345
33	8	0	3.839529	-1.519778	-1.295401
34	6	0	4.969805	-1.608142	-2.184523
35	1	0	4.667912	-2.302277	-2.968719
36	1	0	5.845968	-1.983141	-1.650035
37	1	0	5.201181	-0.626298	-2.604512
38	1	0	-2.276619	-0.631742	1.476475
39	1	0	-0.509773	-1.713874	0.269589
40	6	0	-4.882343	1.836845	-0.661708
41	1	0	-4.016501	2.268200	-1.171738
42	1	0	-5.385223	2.599469	-0.063343
43	1	0	-5.580503	1.439498	-1.407626
44	6	0	-5.549304	-2.078061	-0.187685
45	1	0	-5.095499	-2.702025	0.587355
46	1	0	-6.133616	-2.698051	-0.870700
47	1	0	-6.199427	-1.330510	0.279043

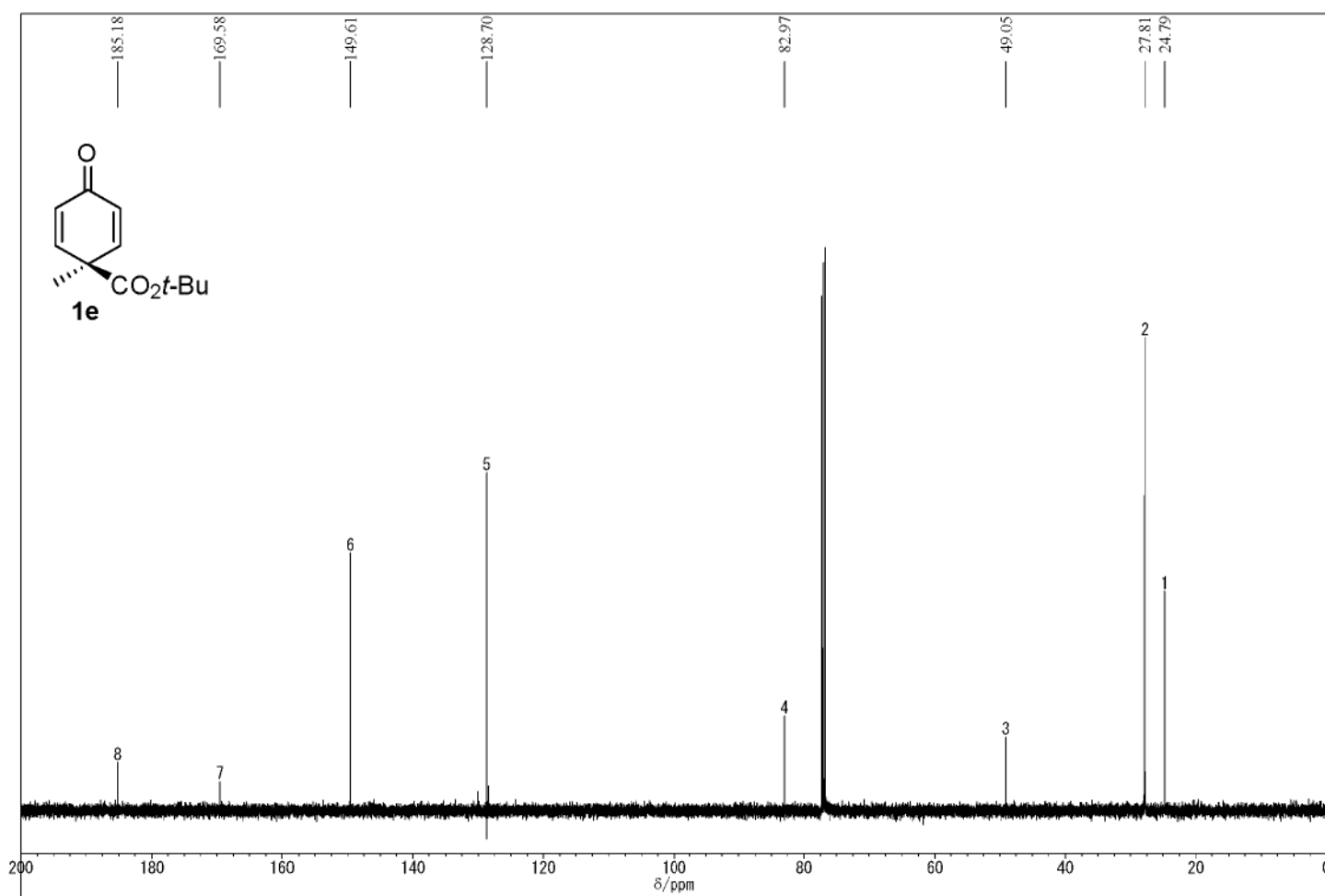
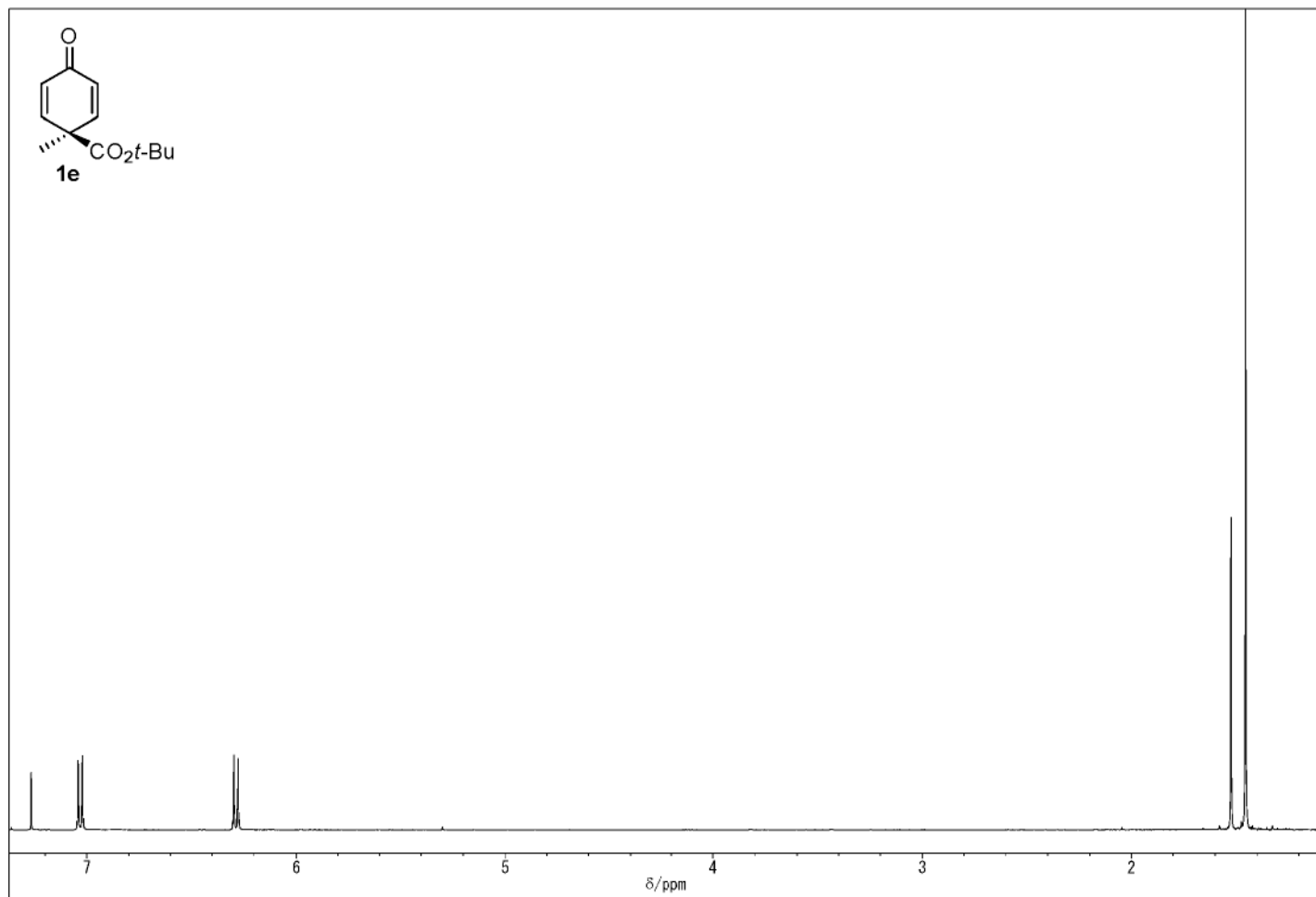
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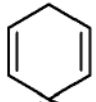
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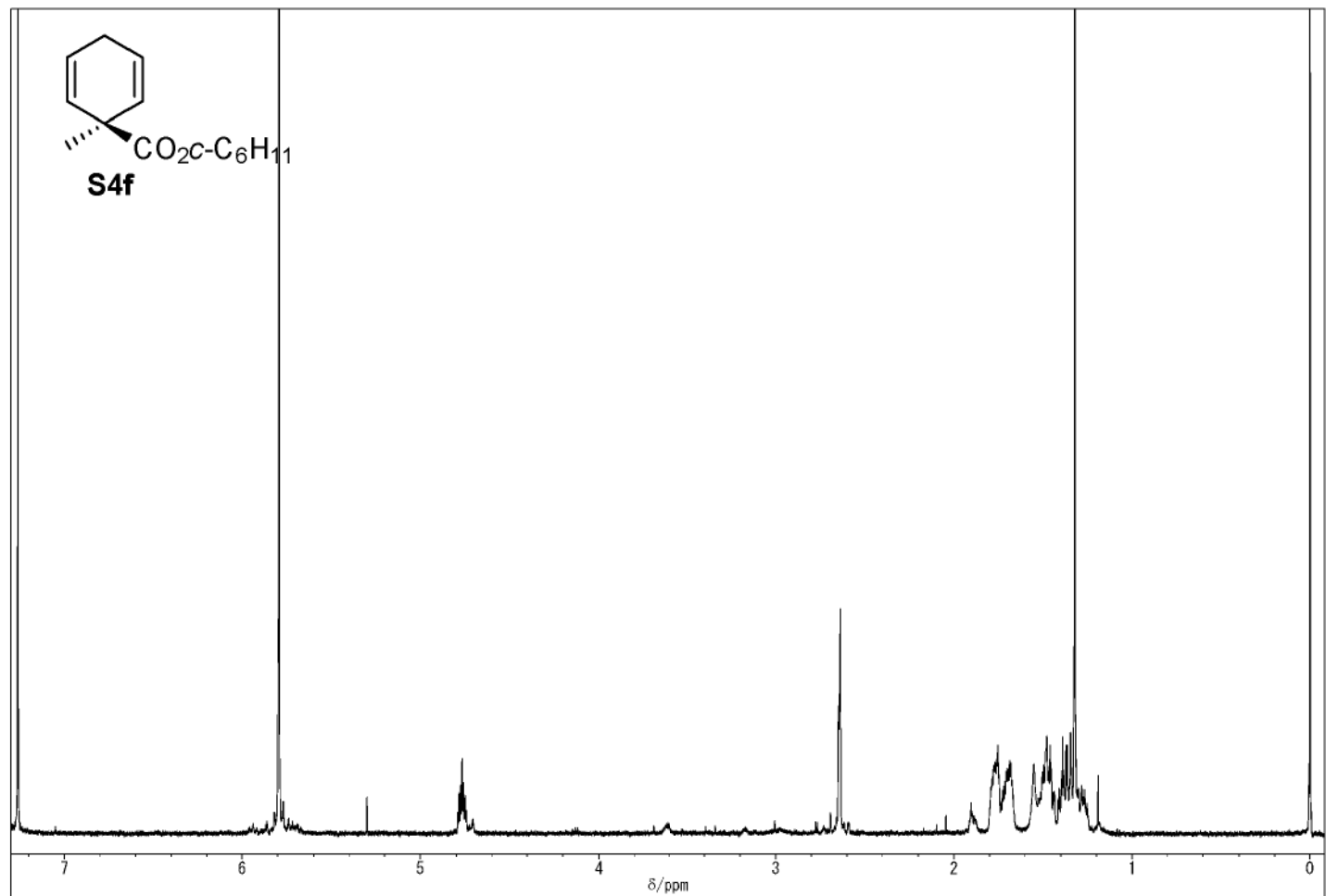


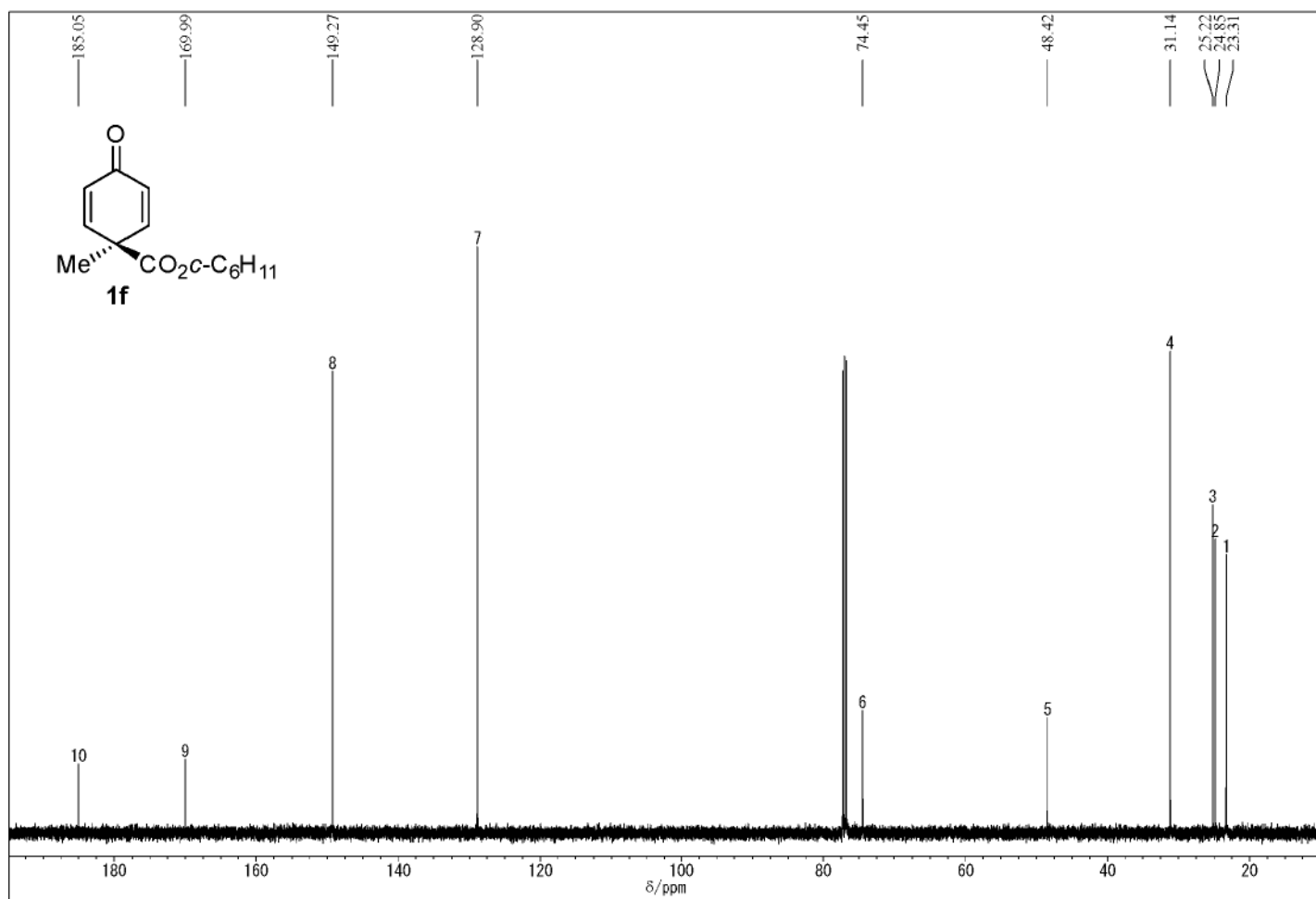
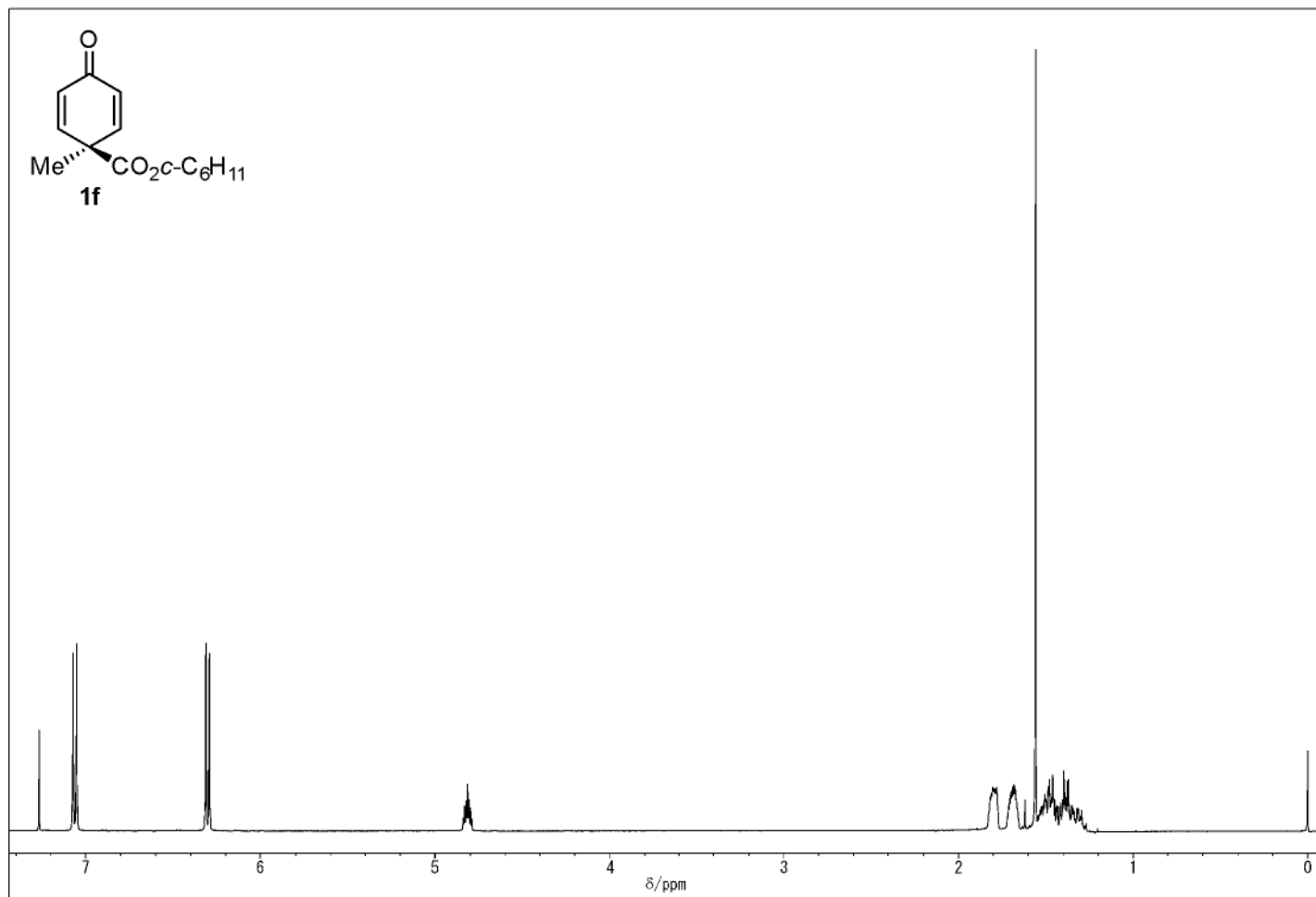


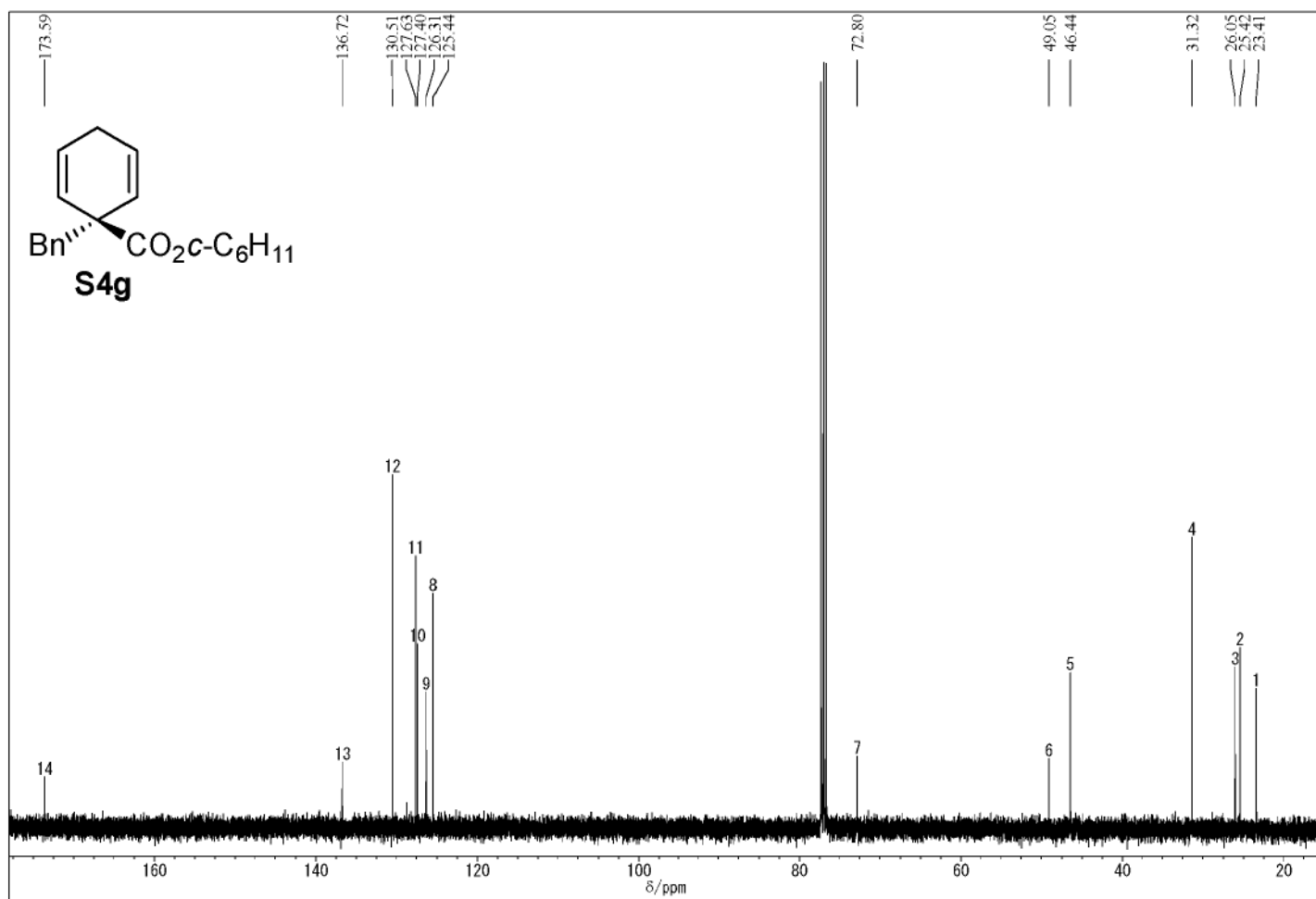
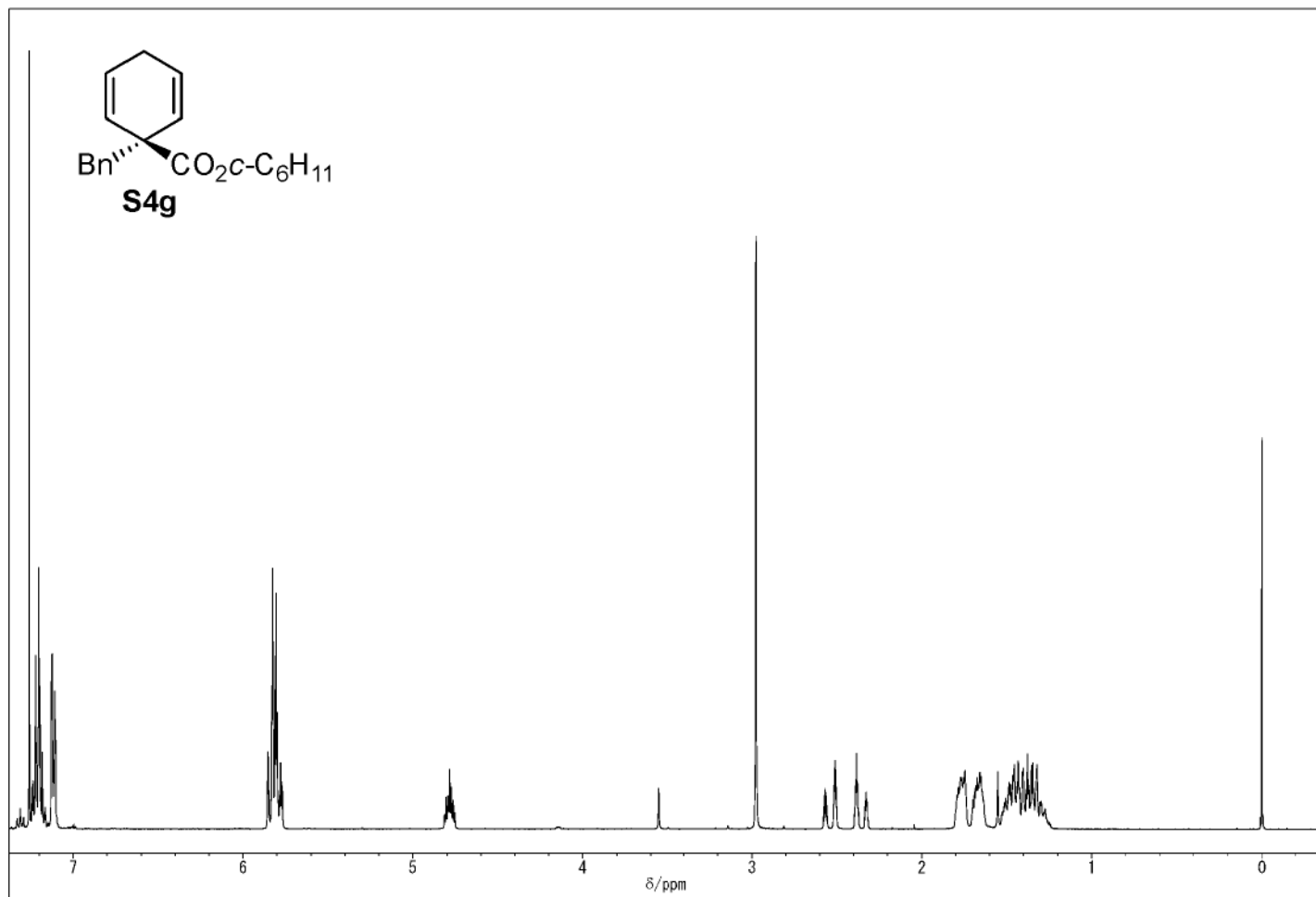


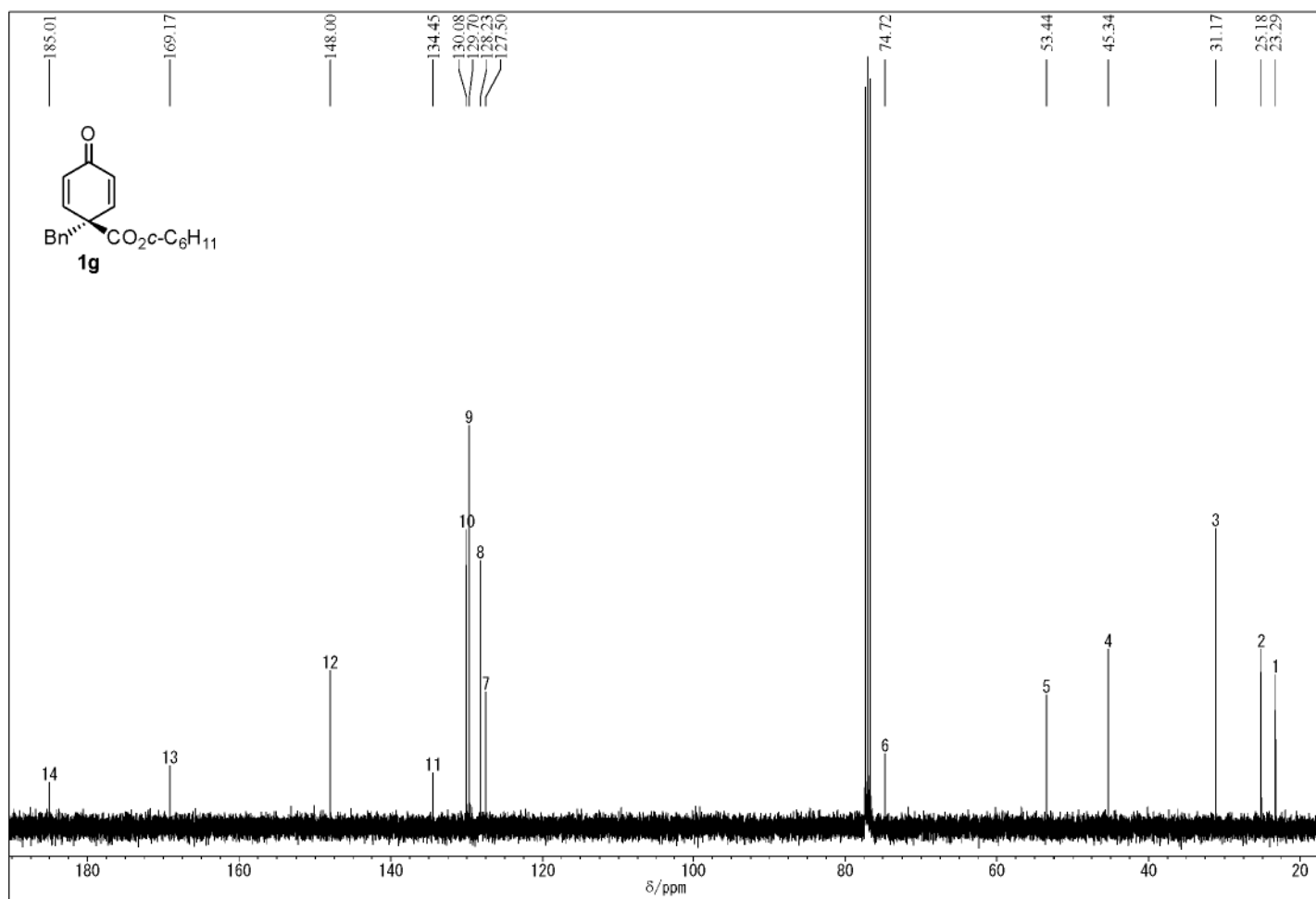
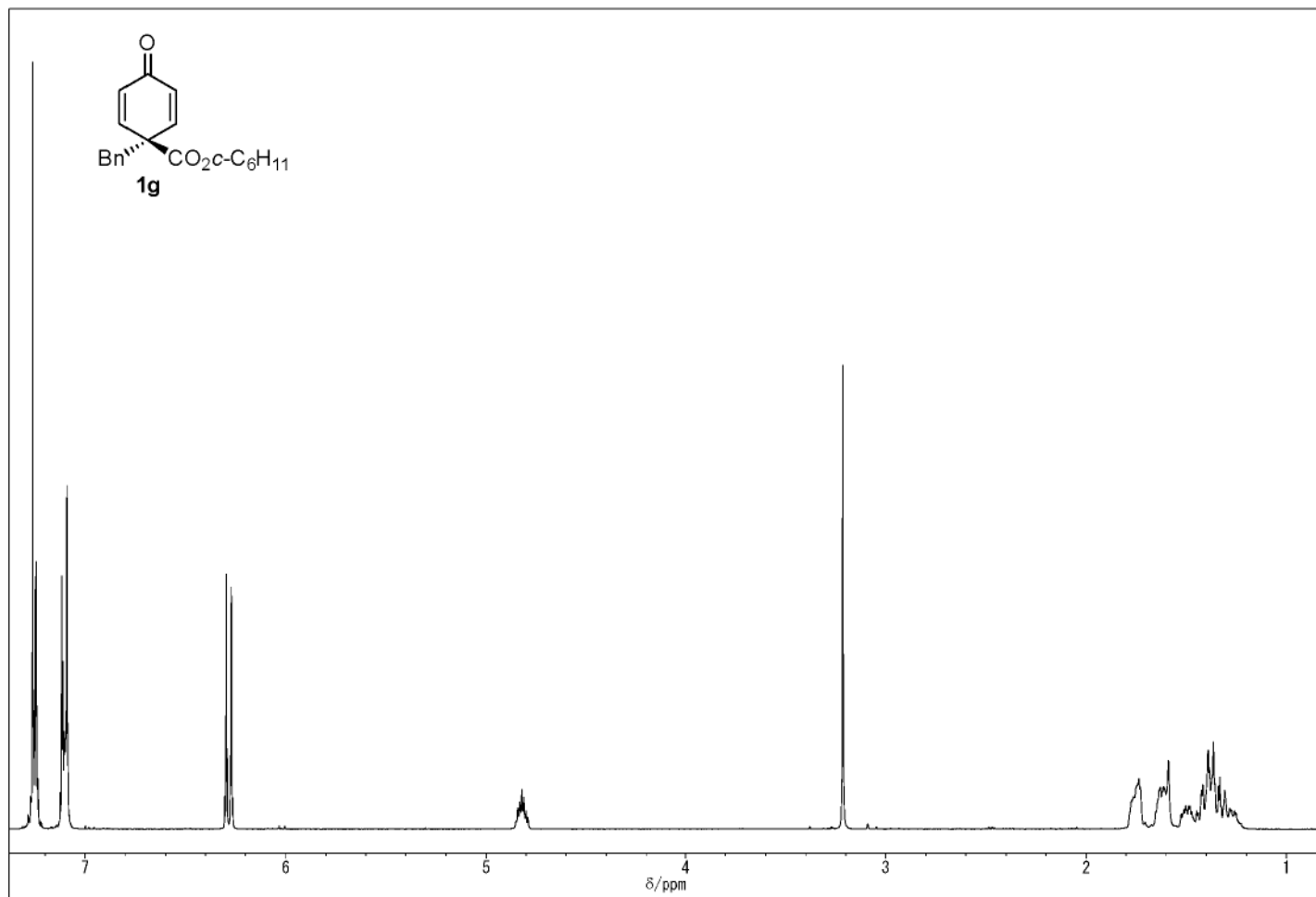
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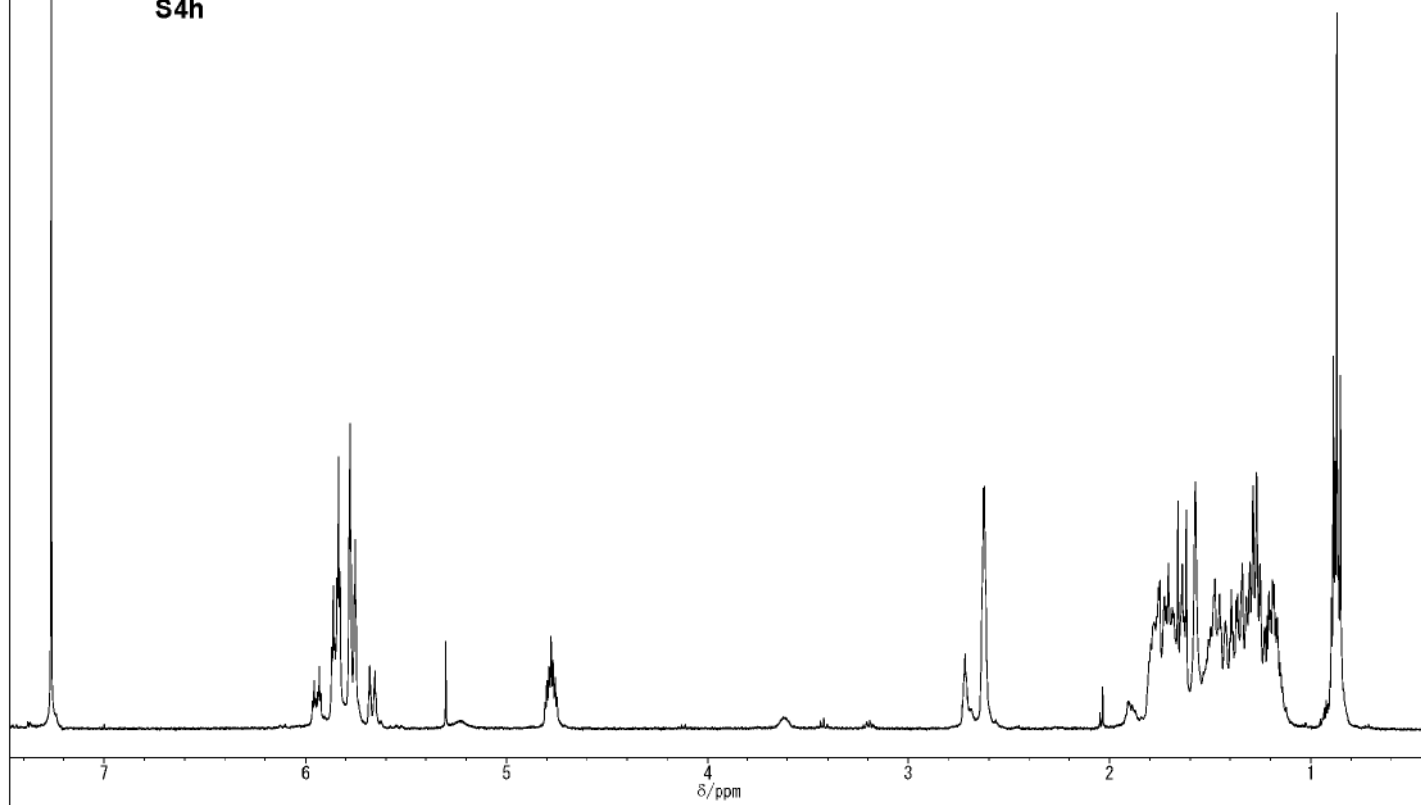
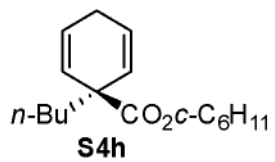
S4f

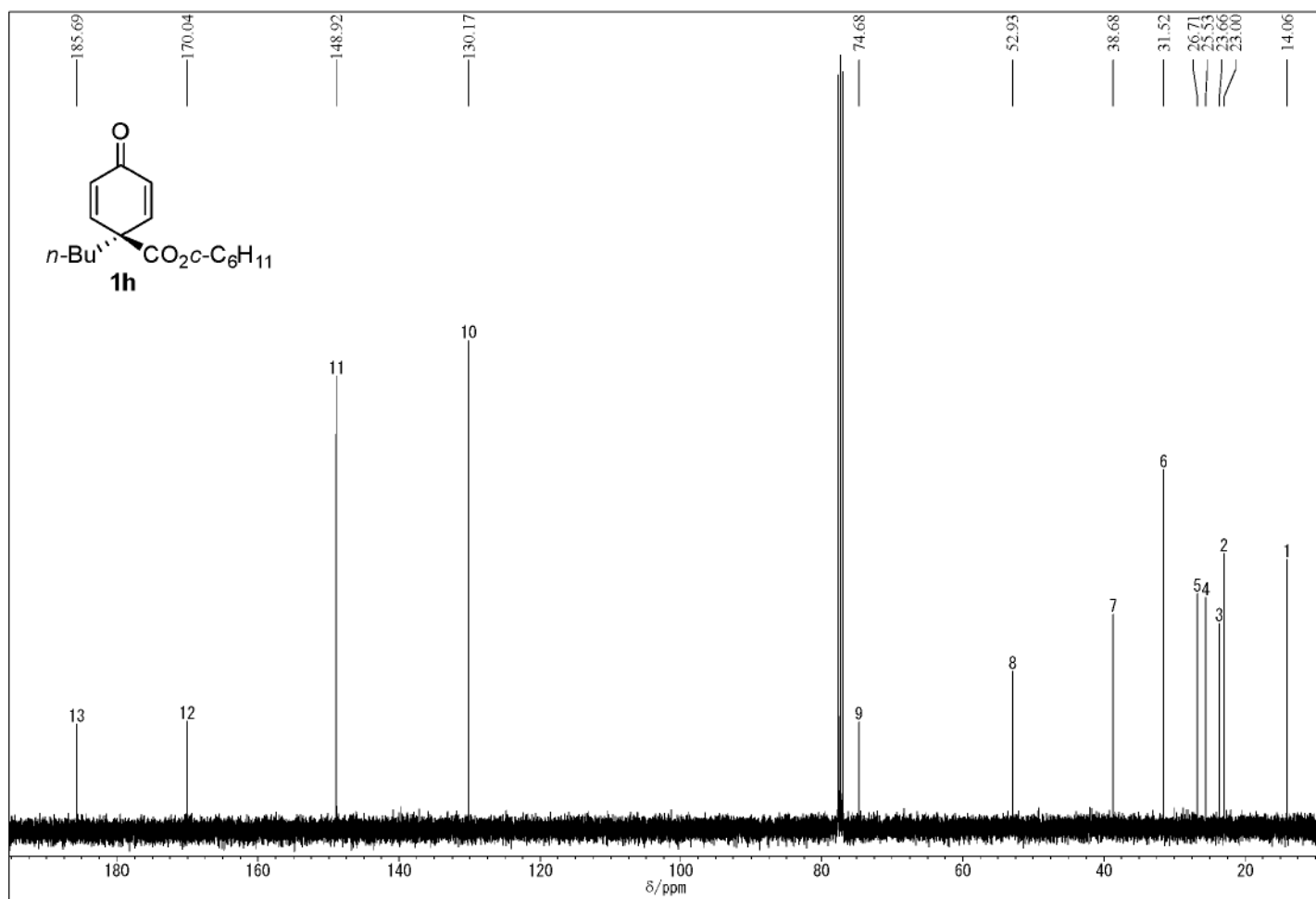
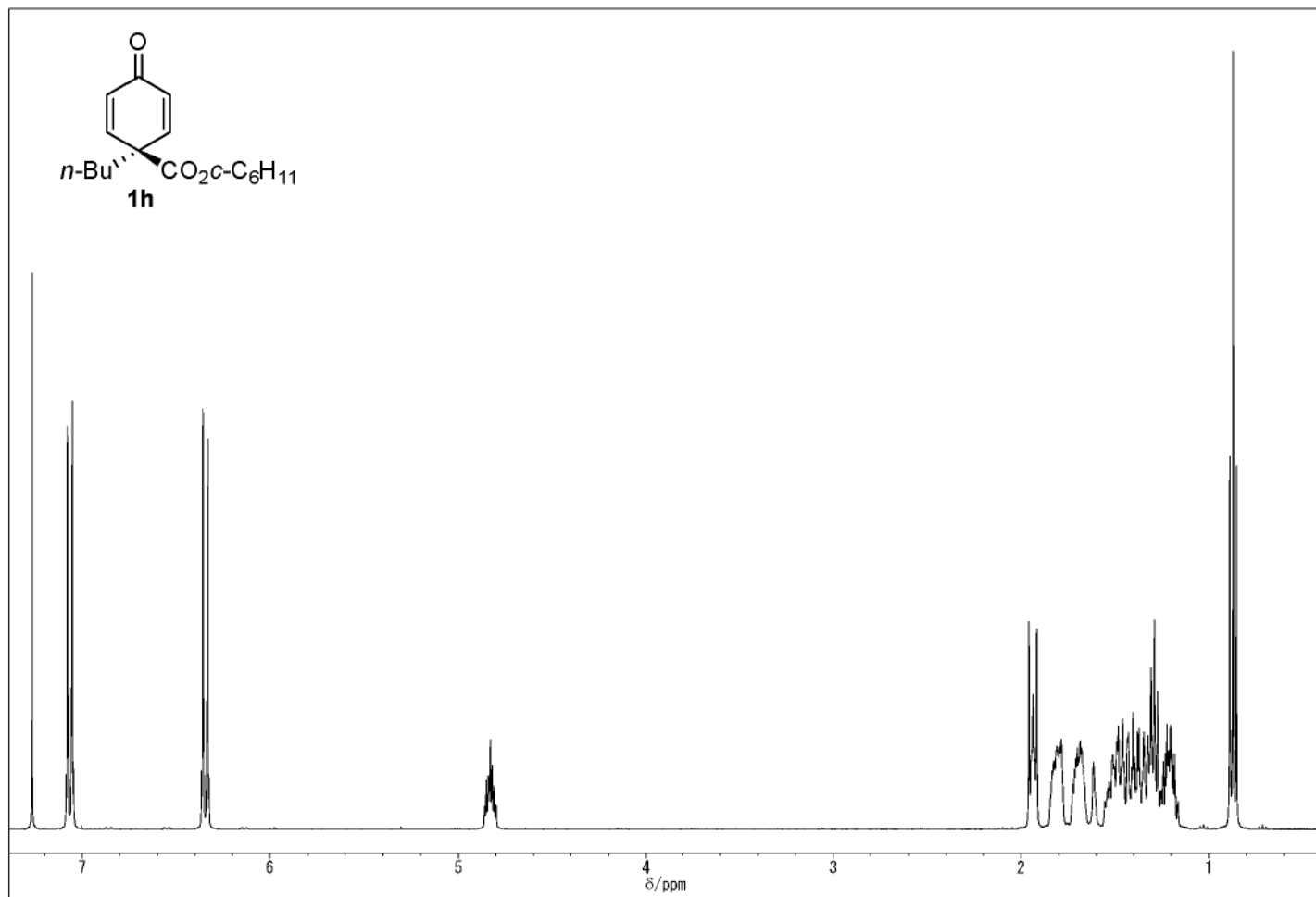


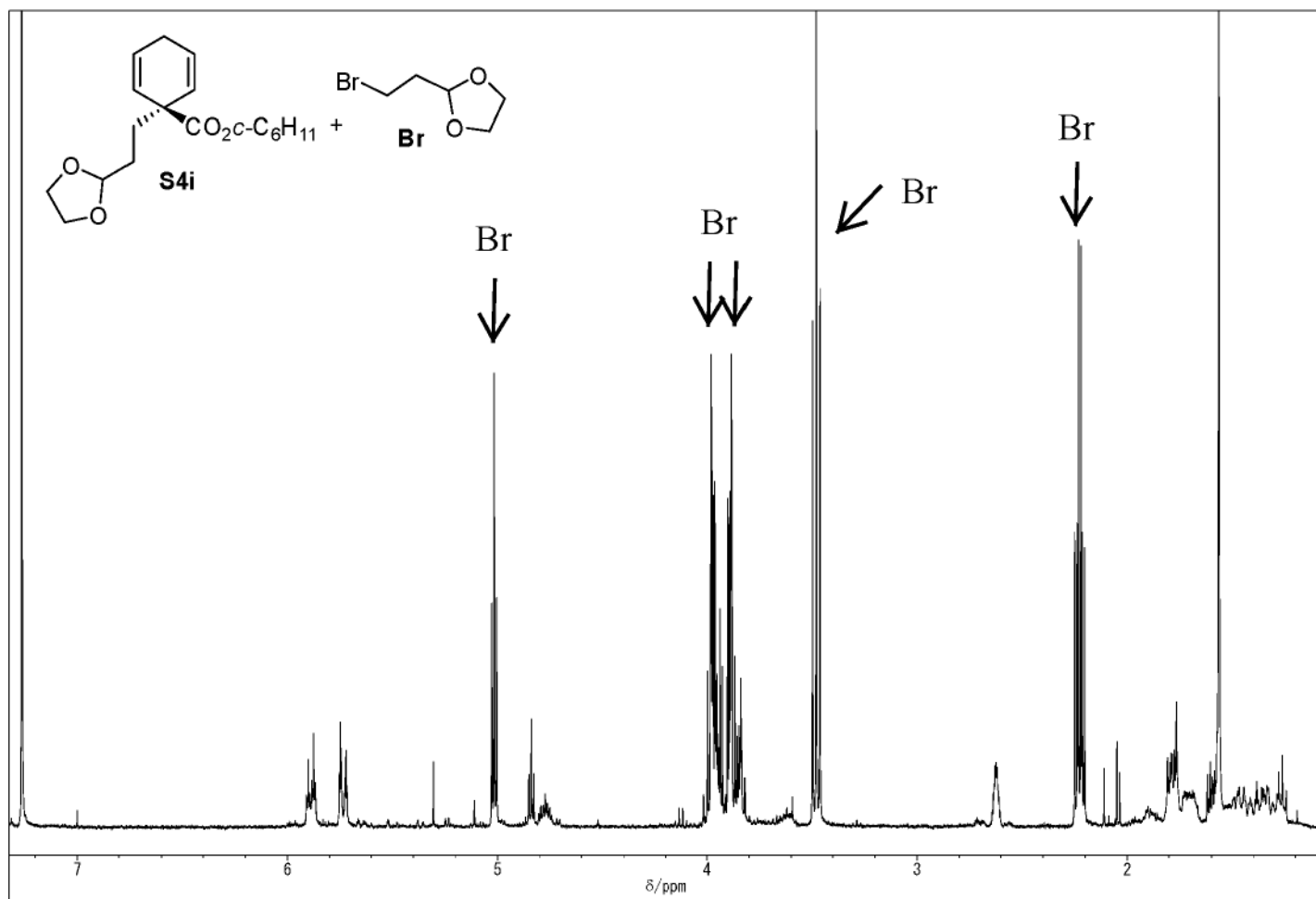


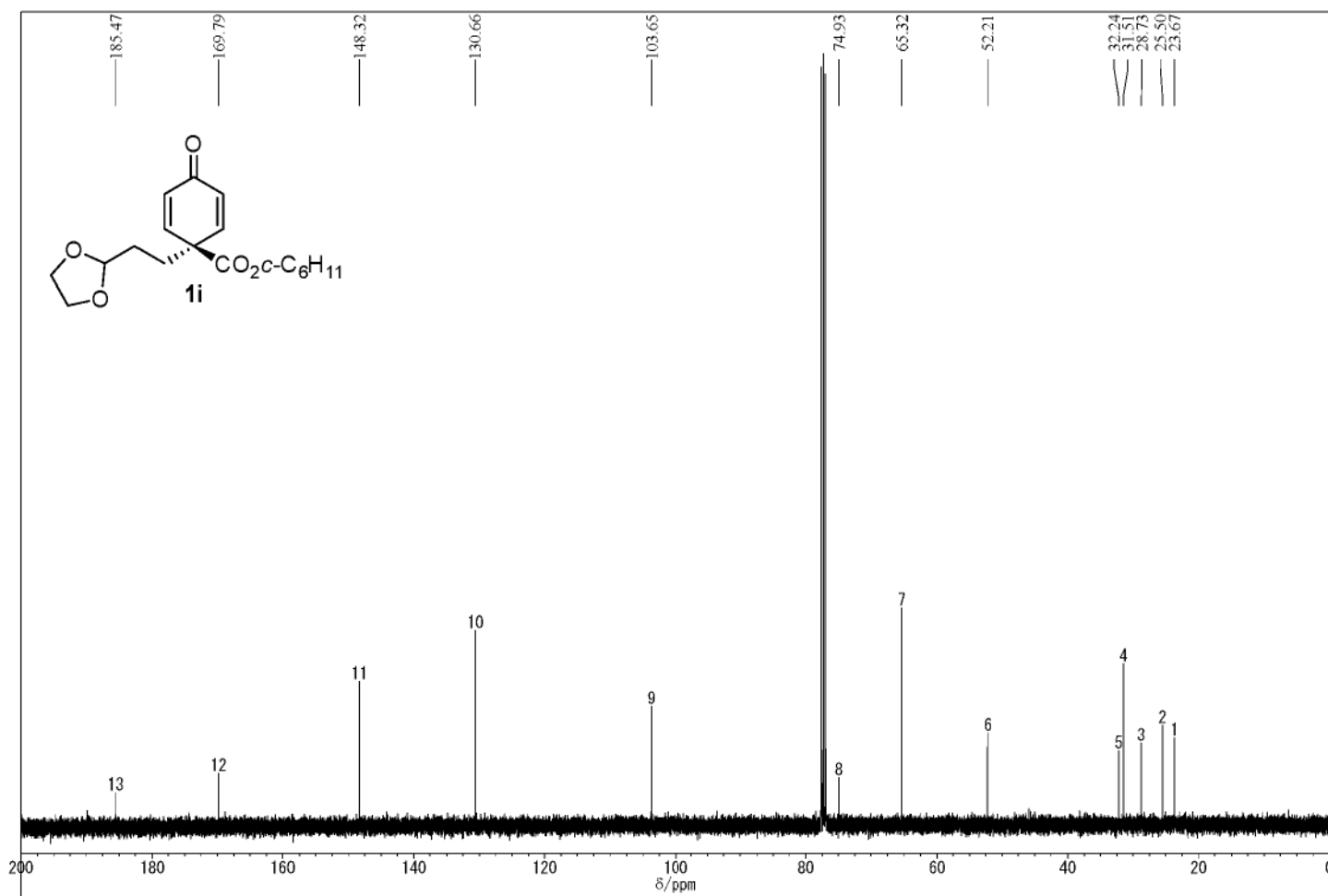
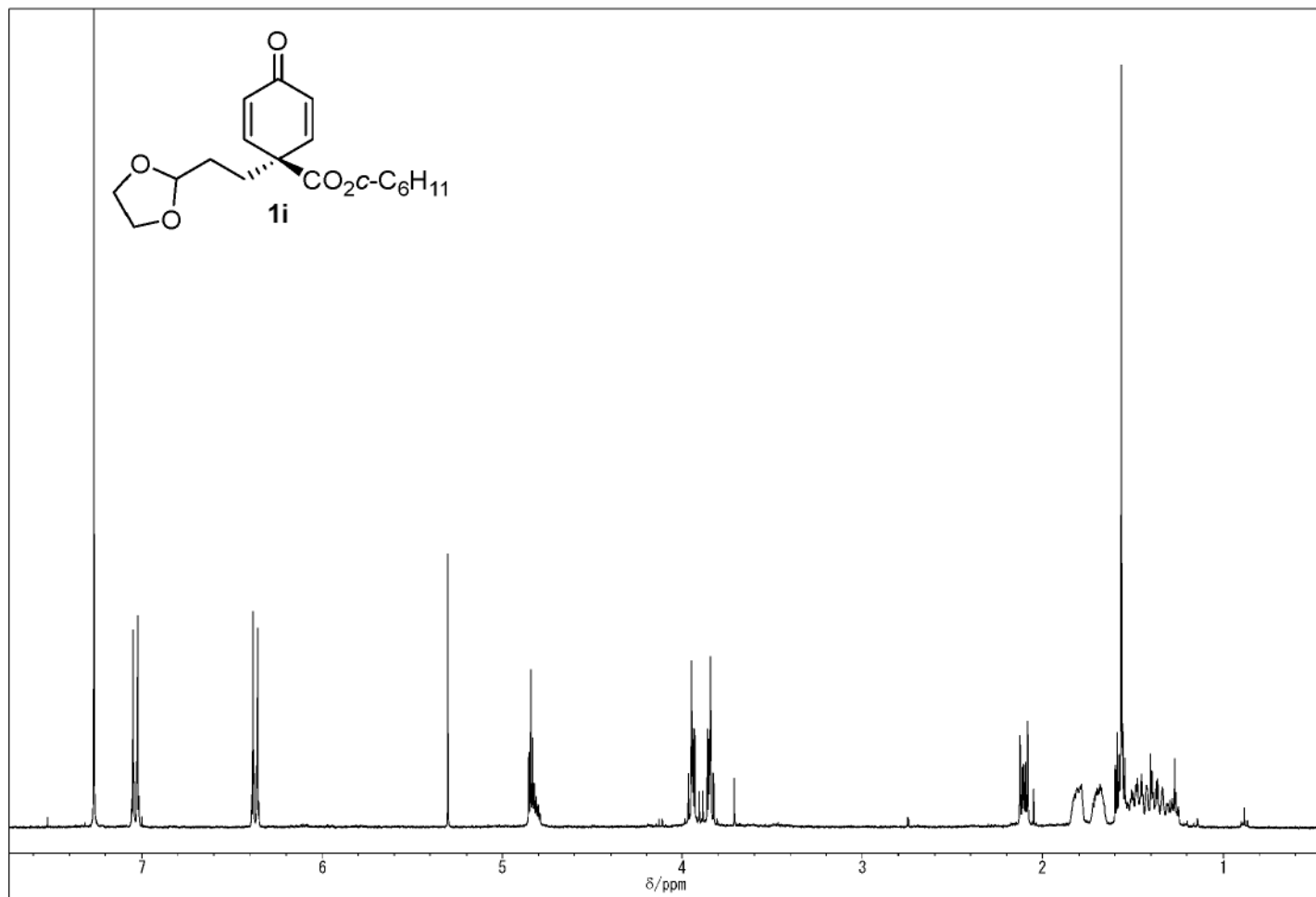


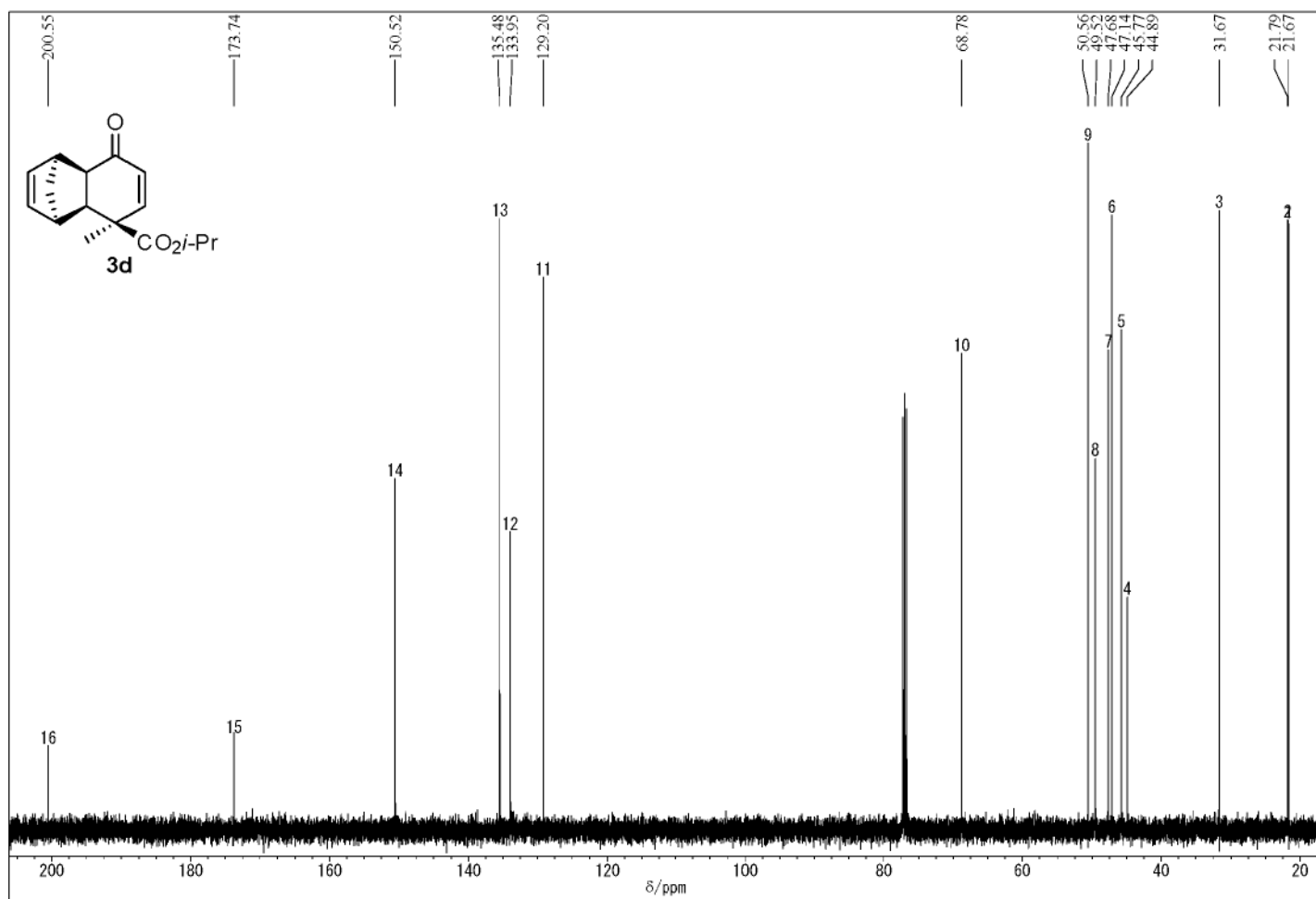
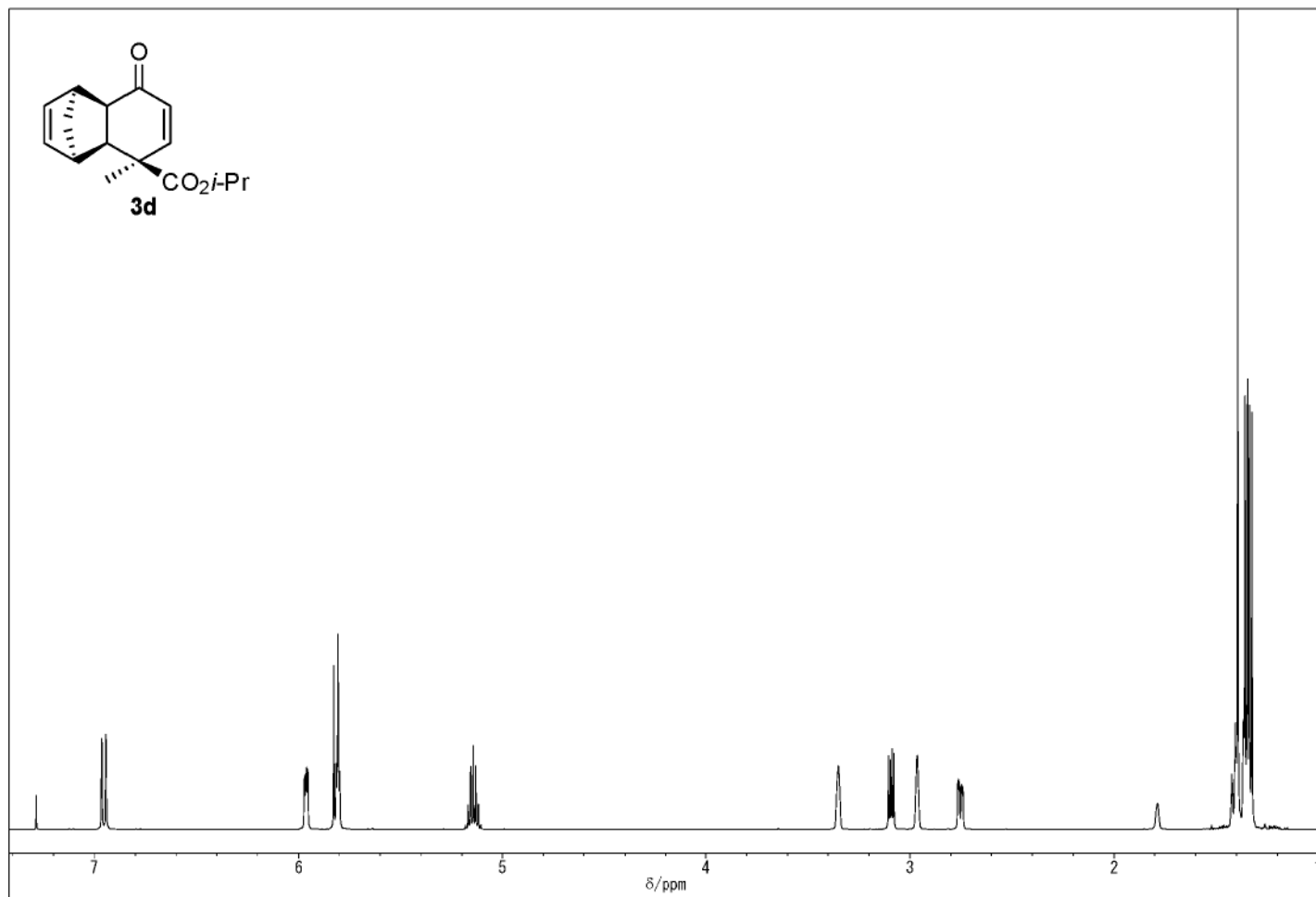


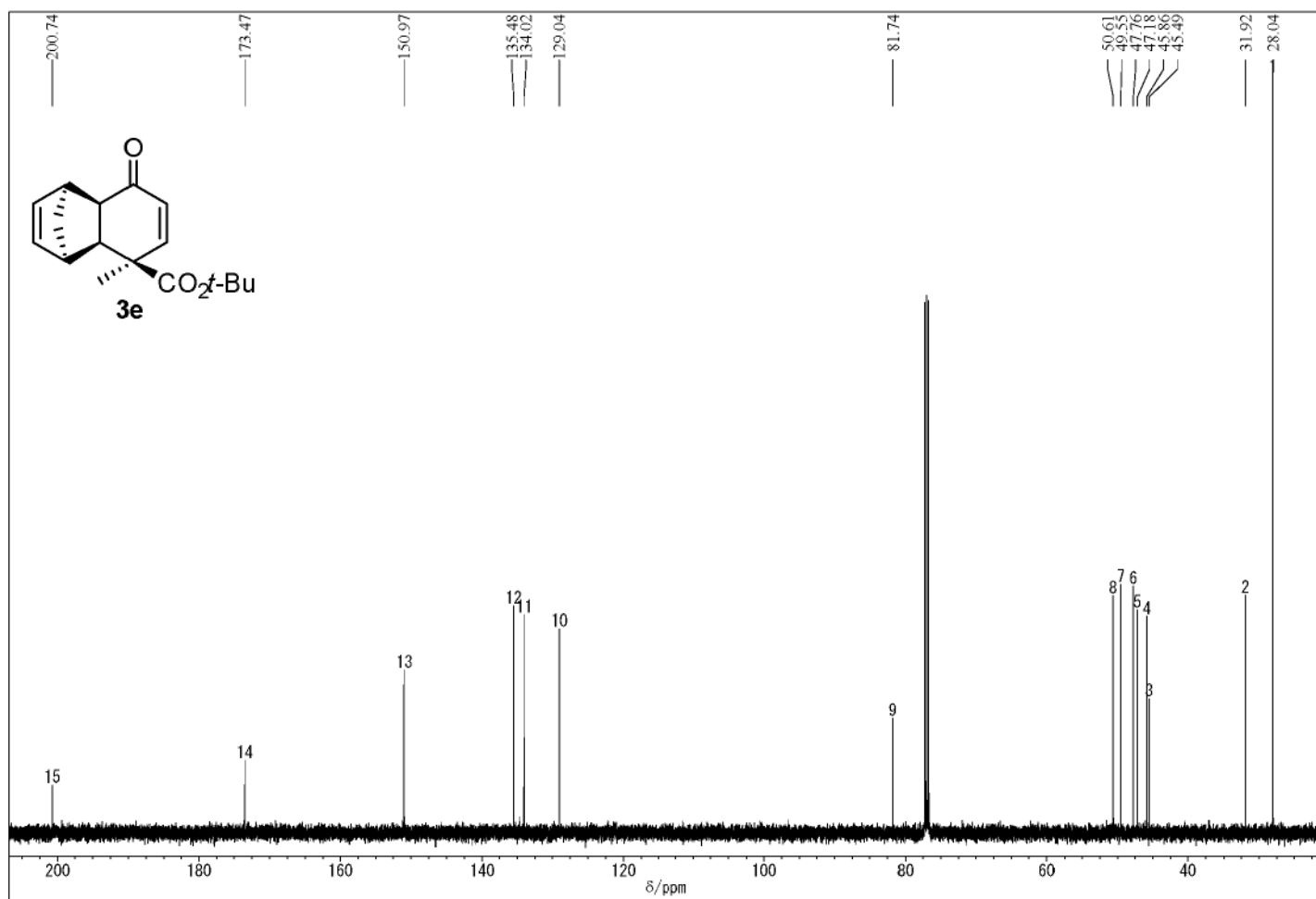
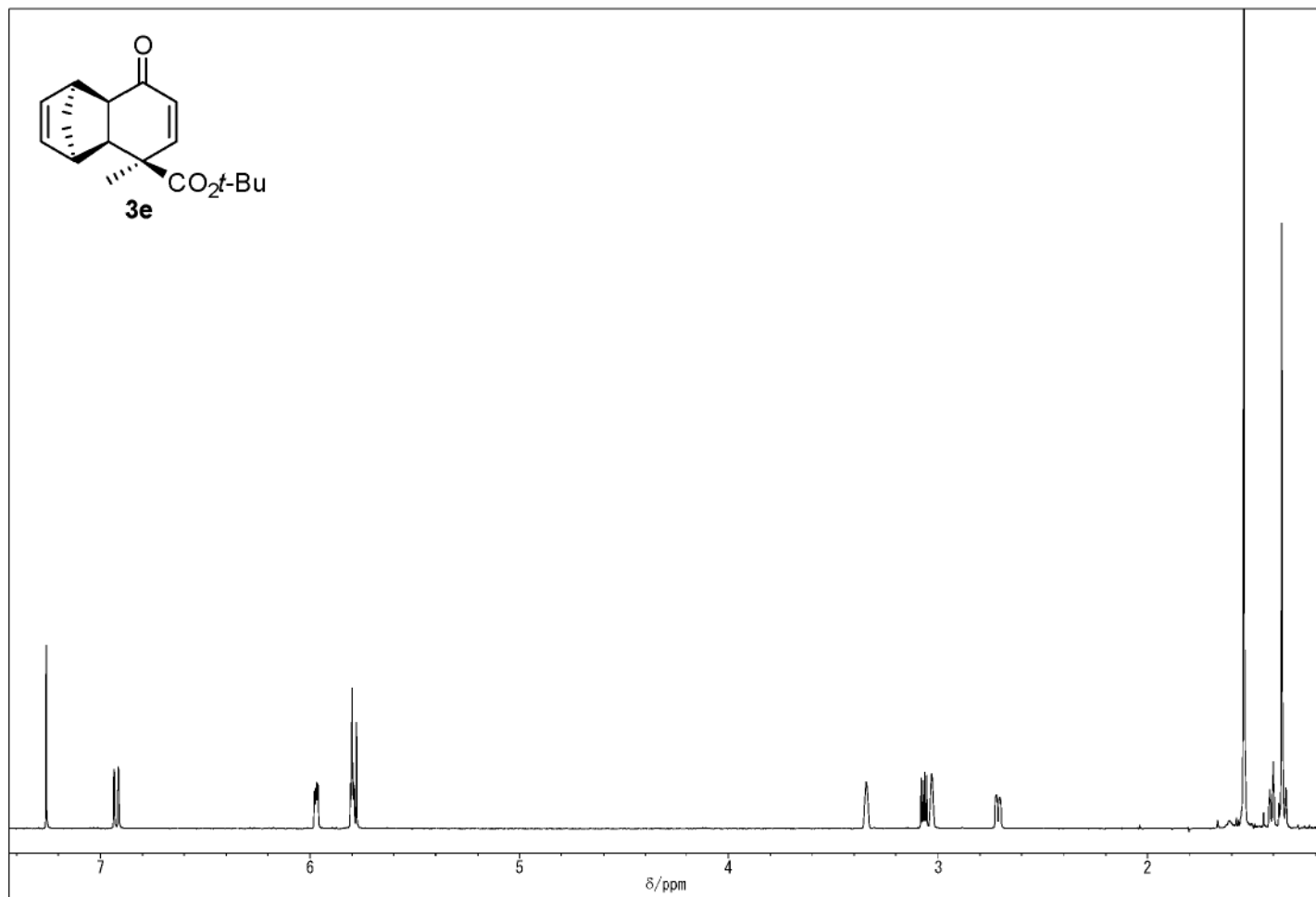


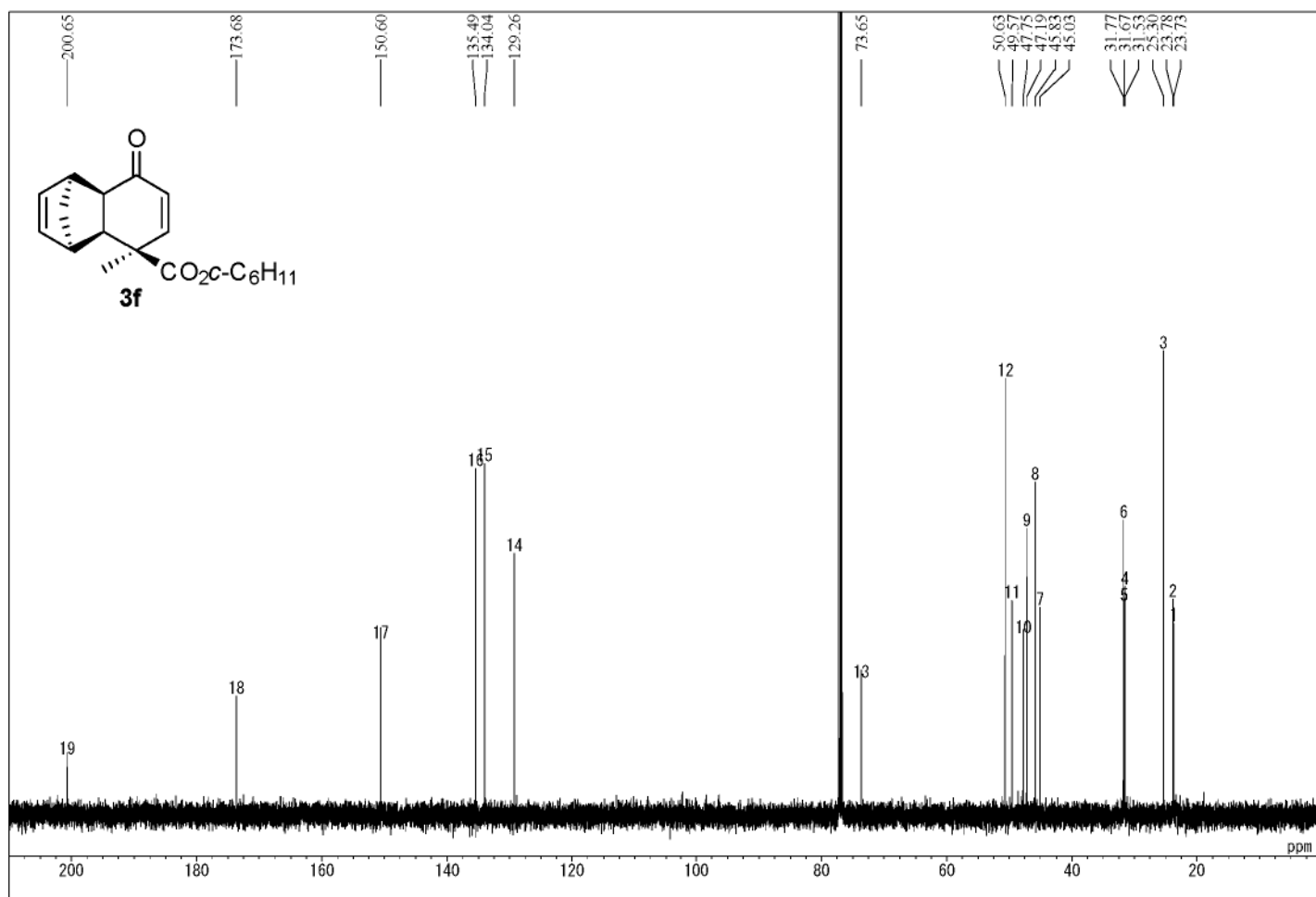
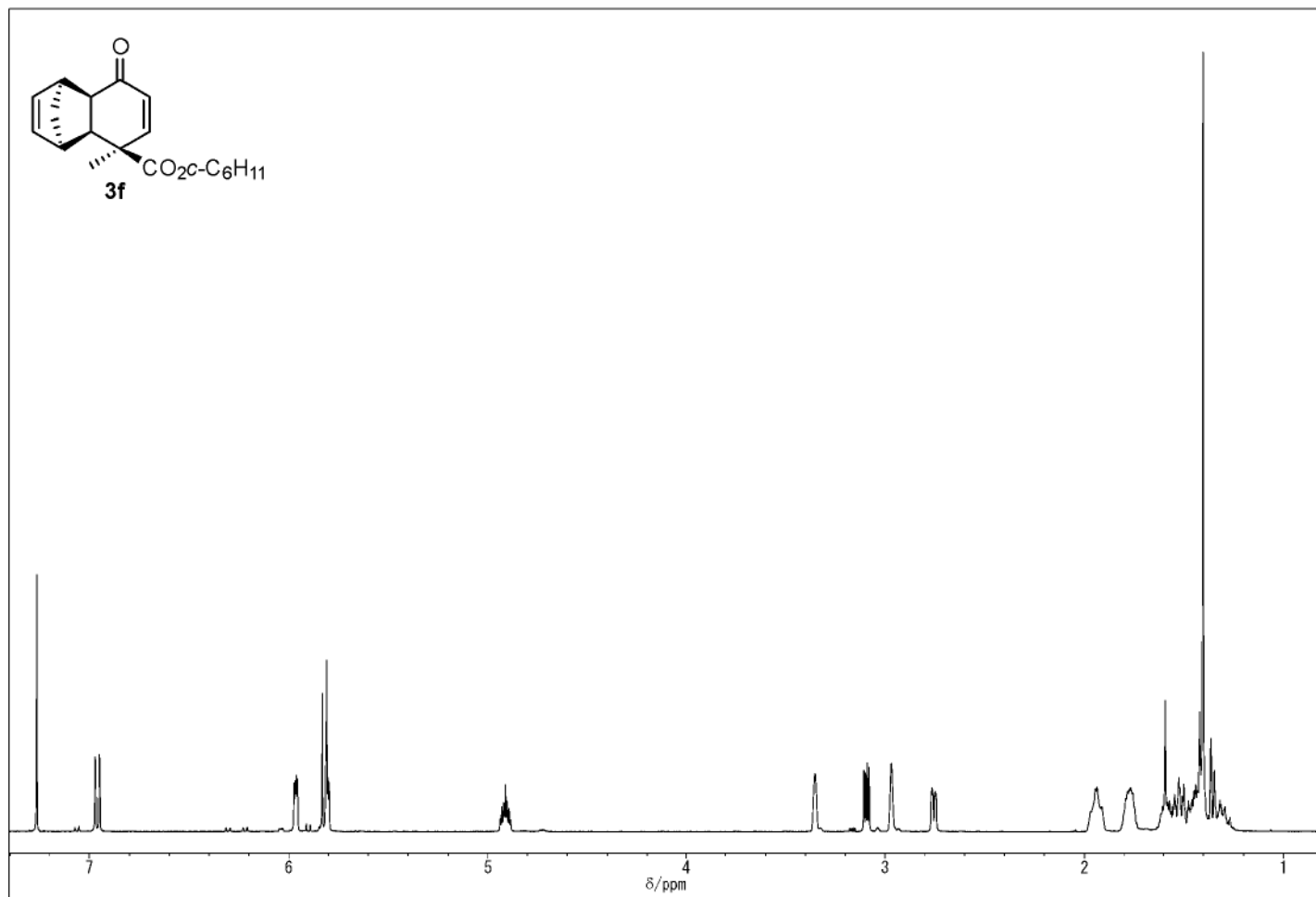


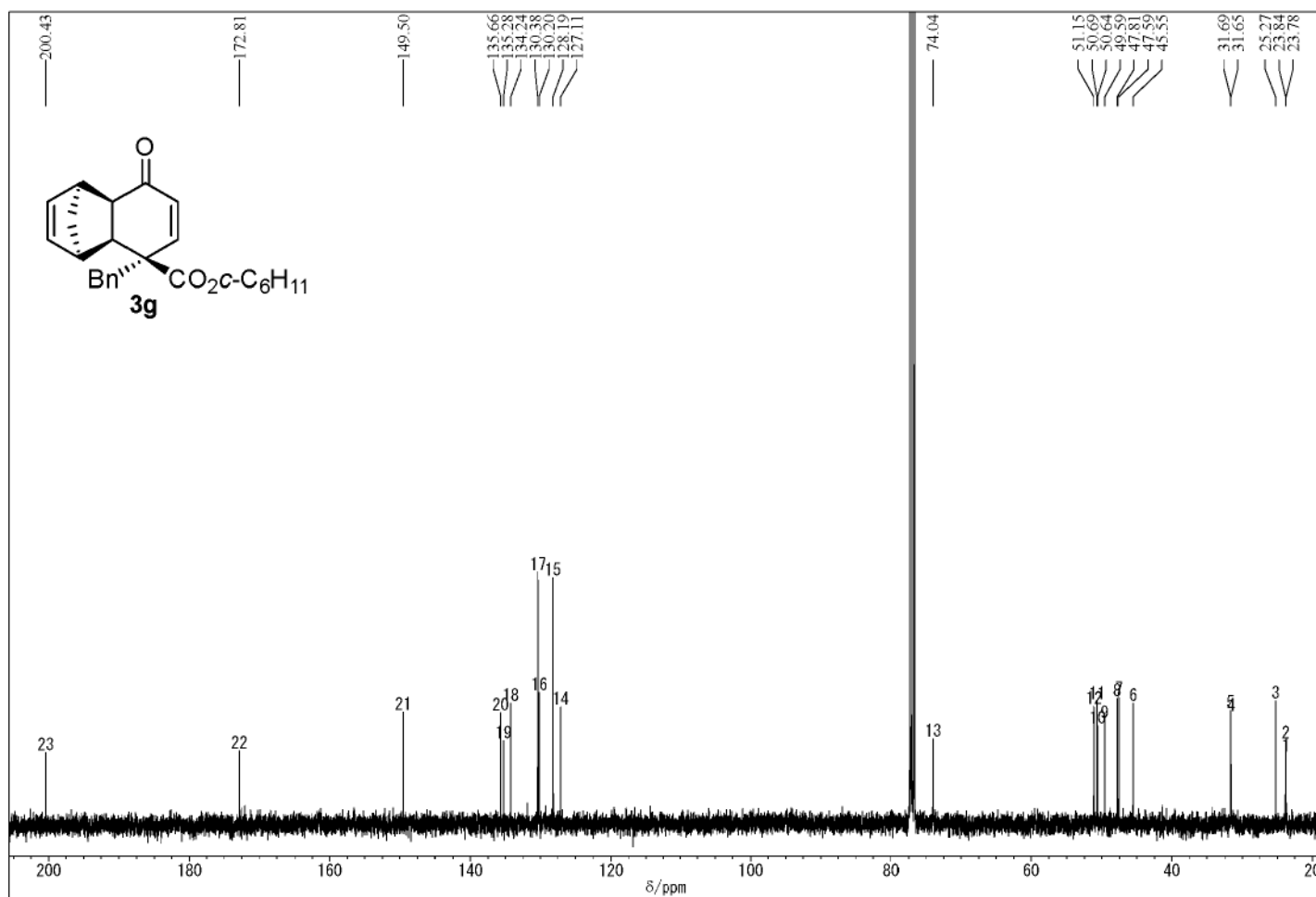
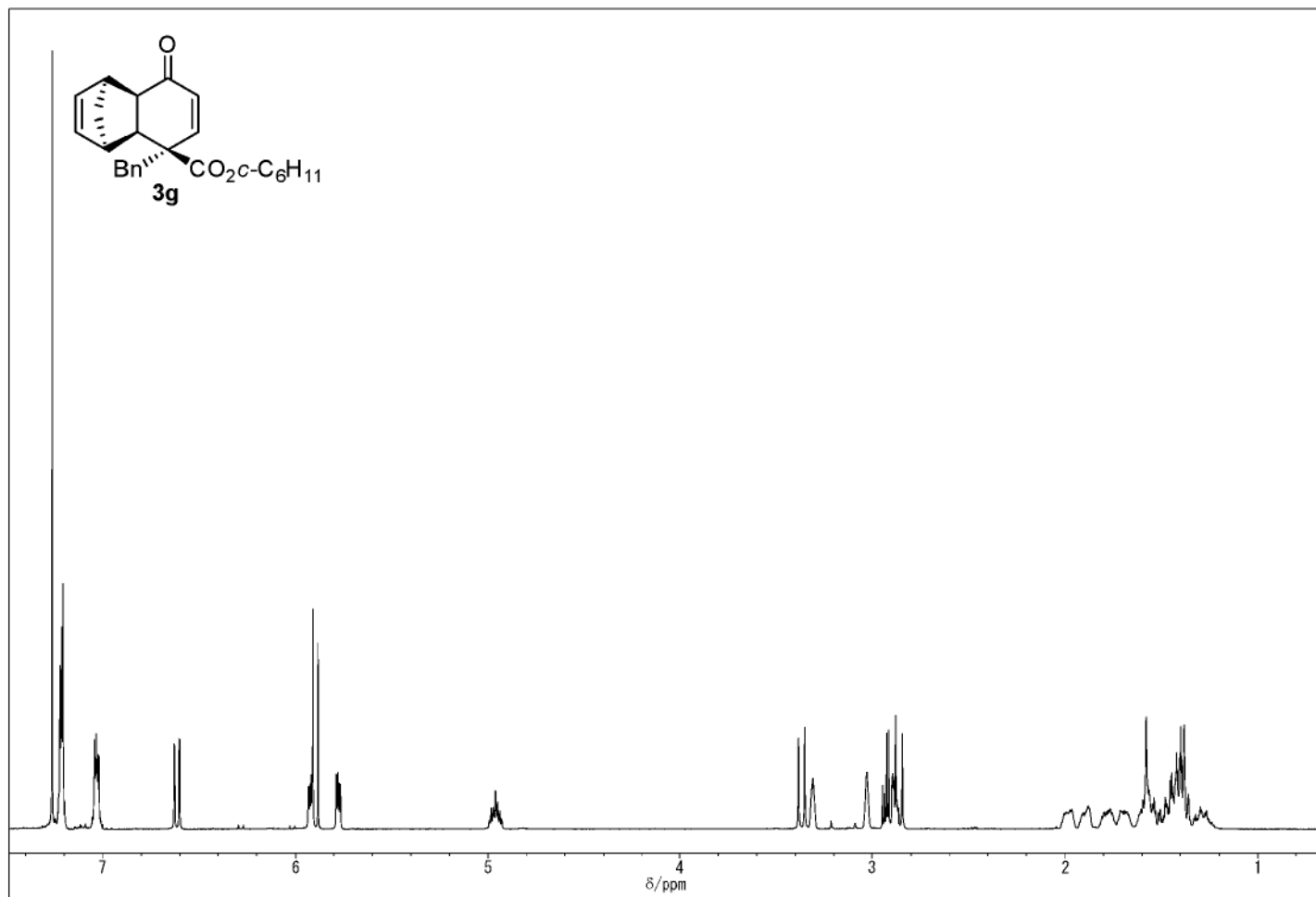


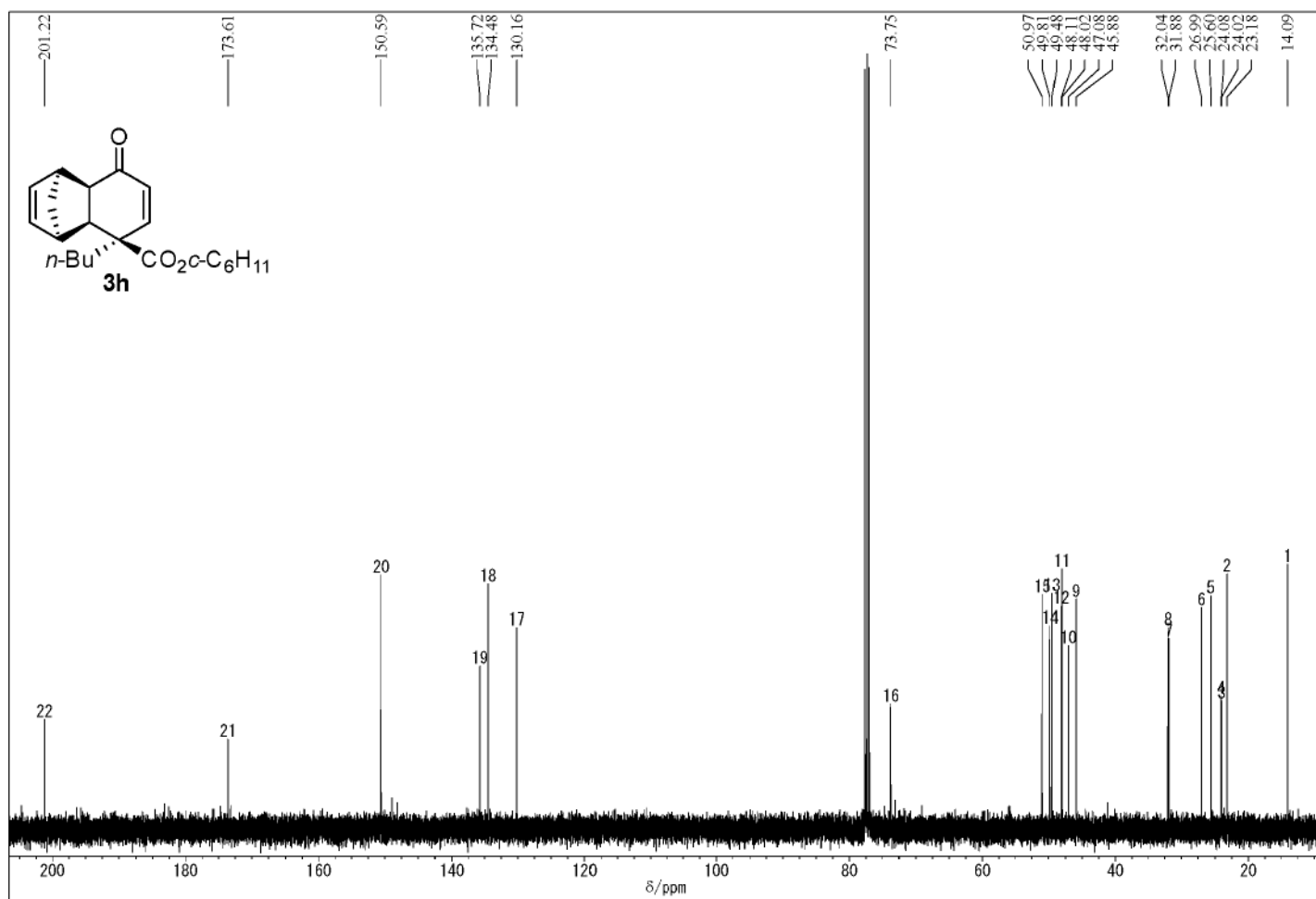
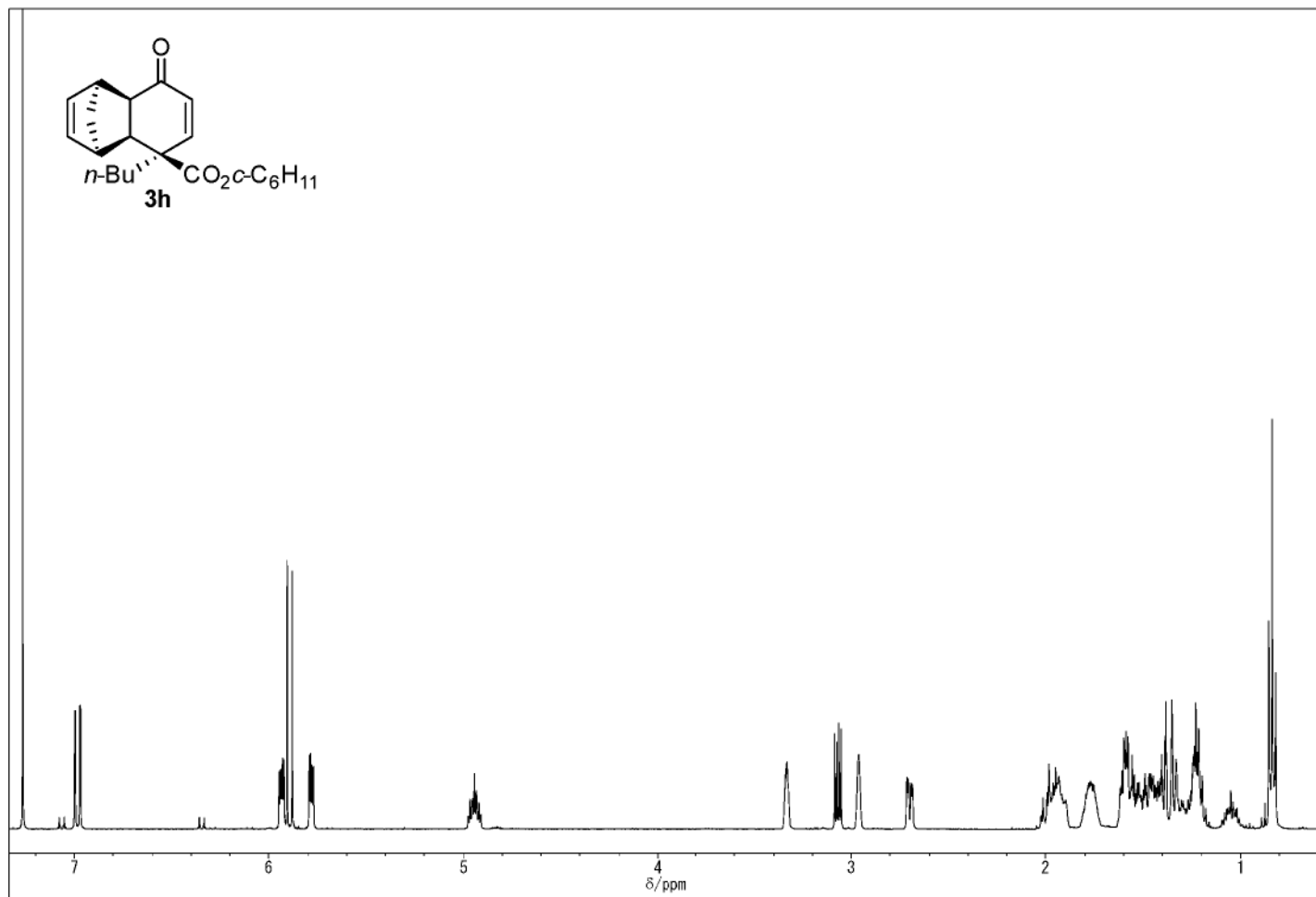


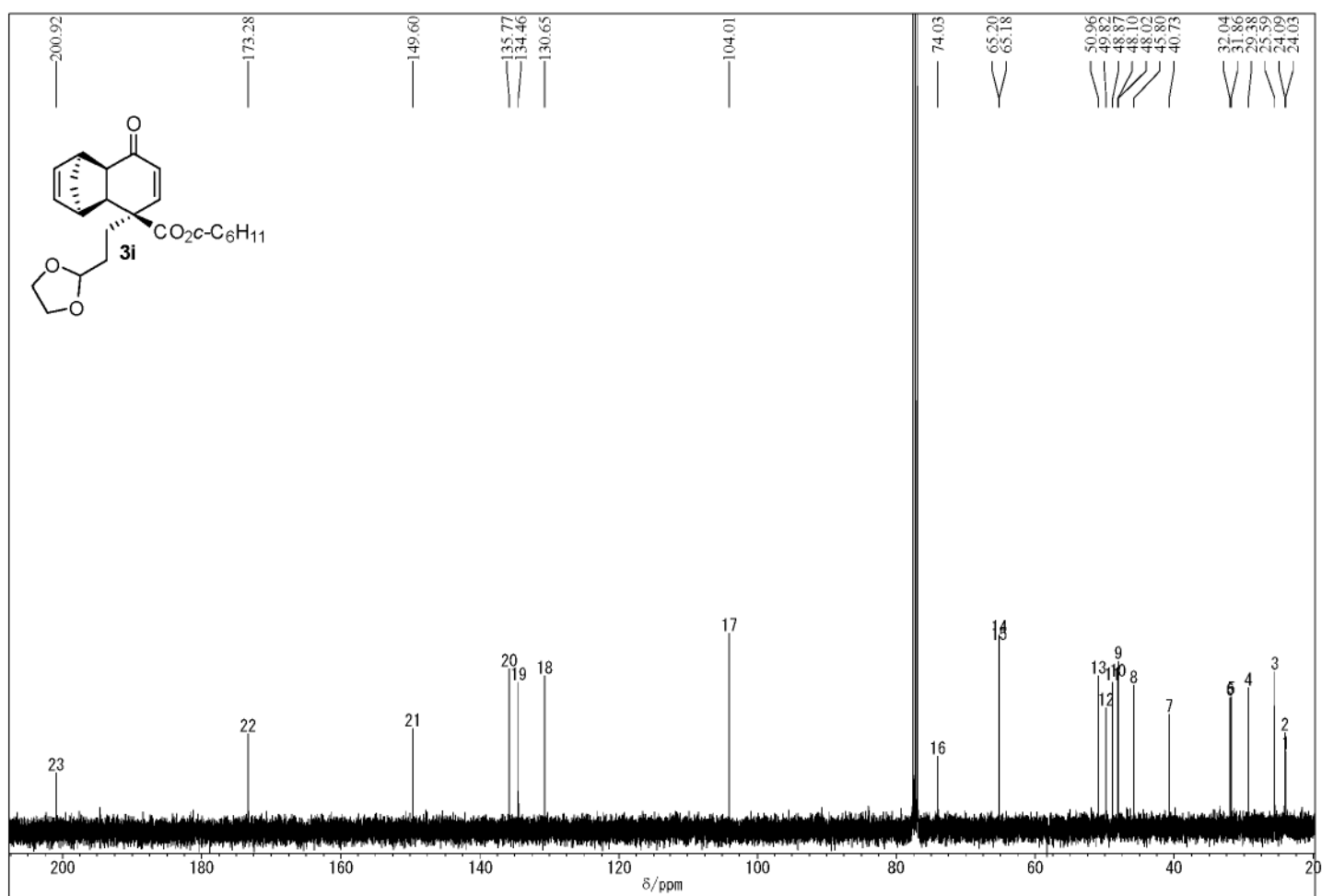
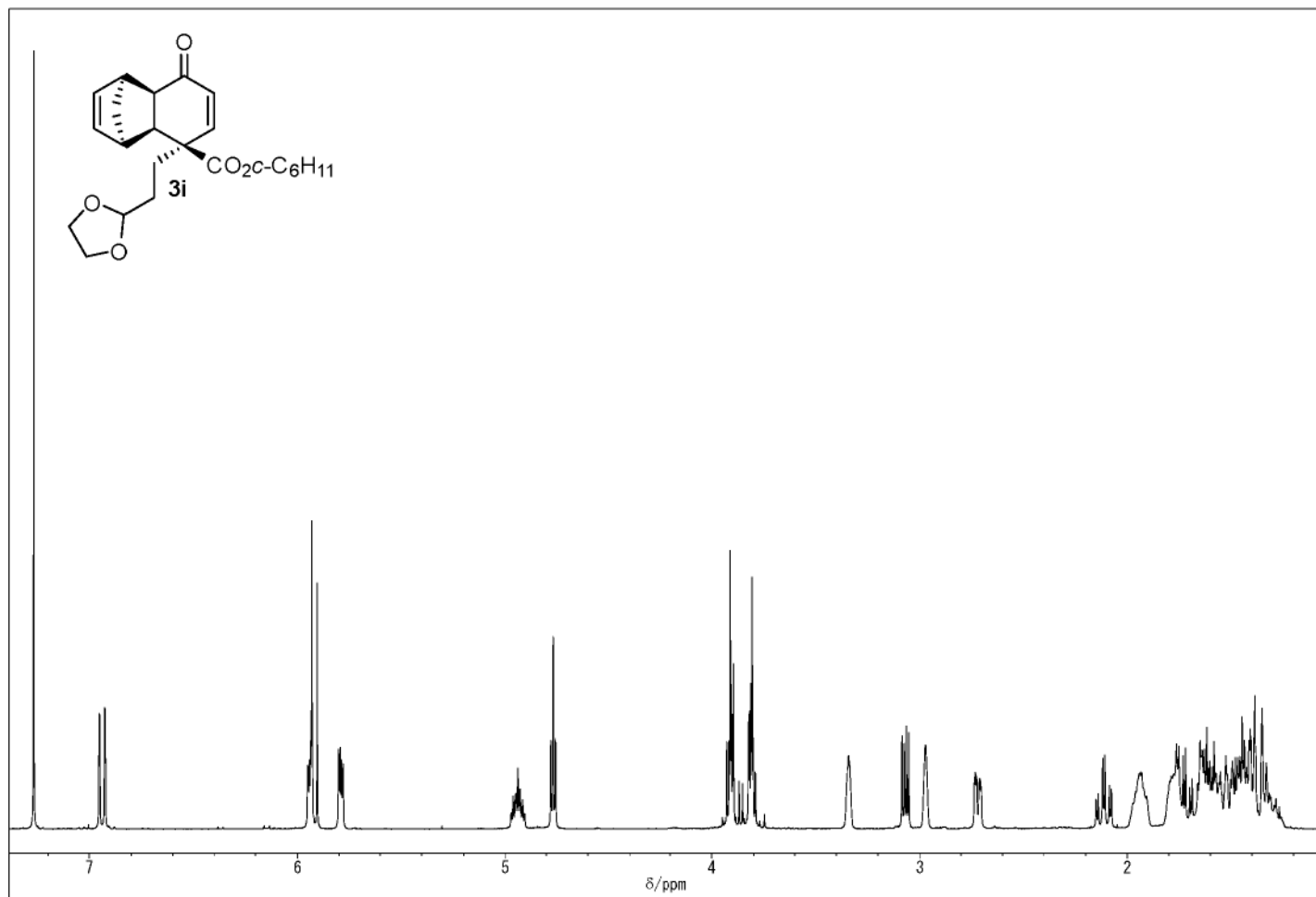


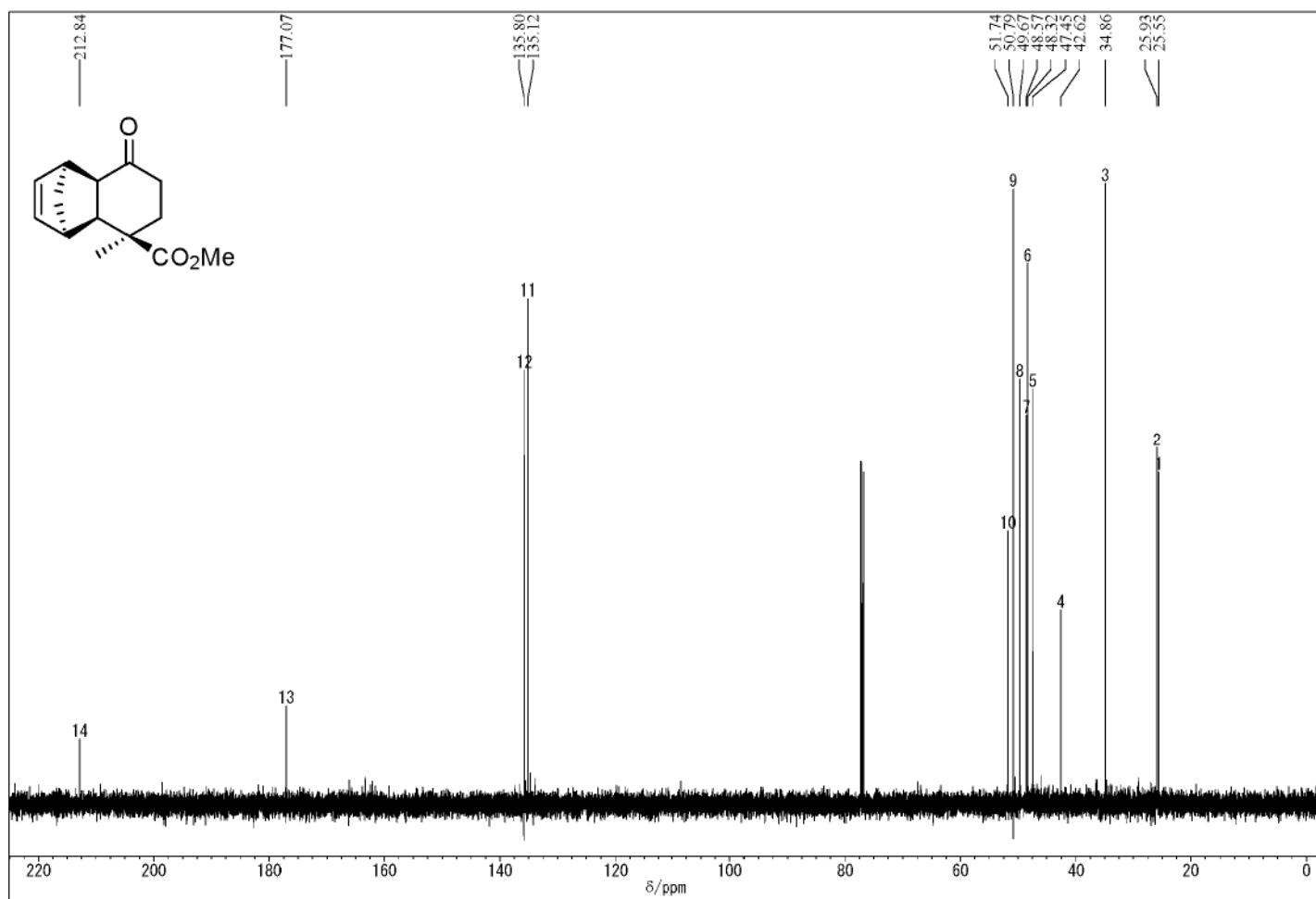
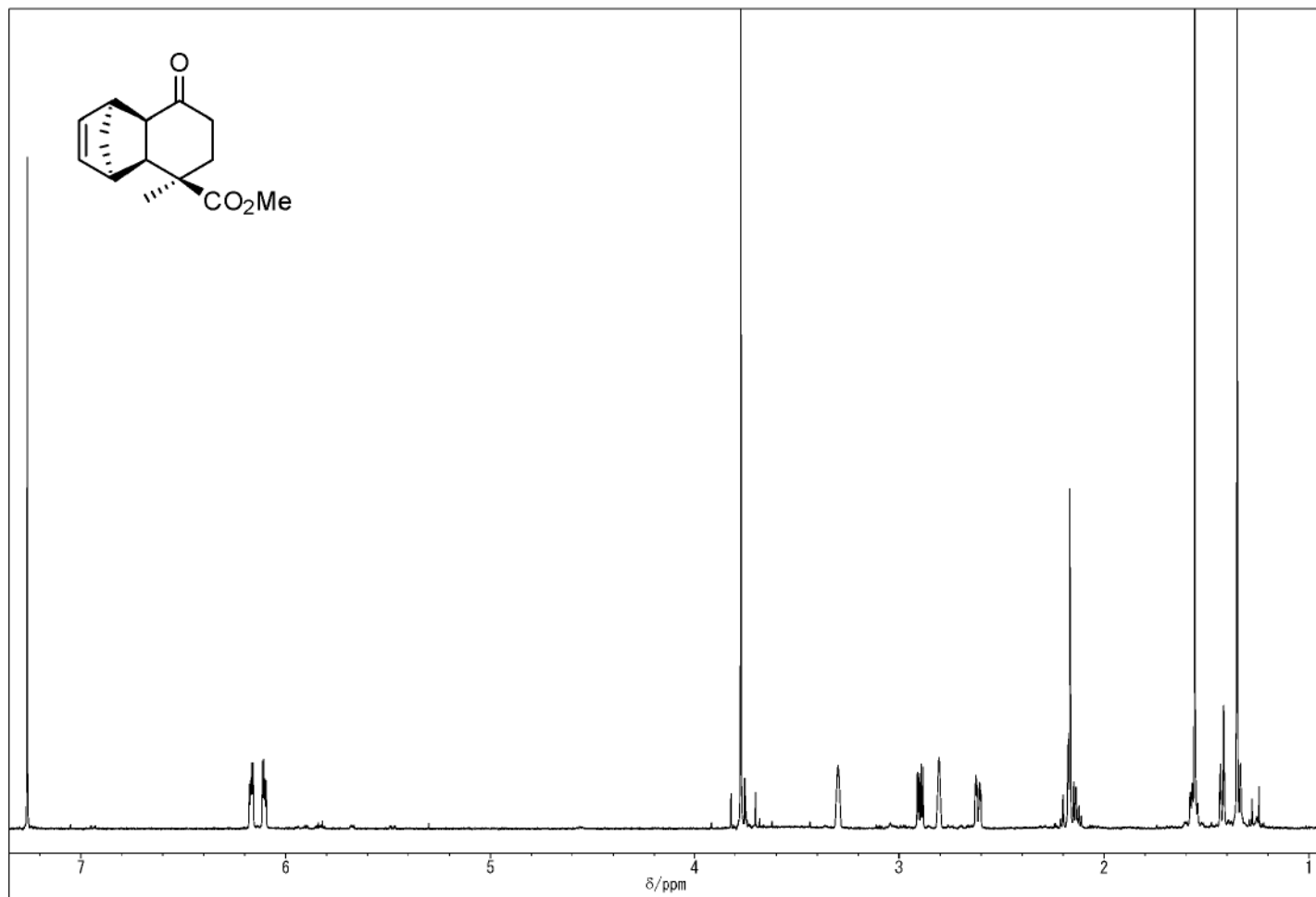


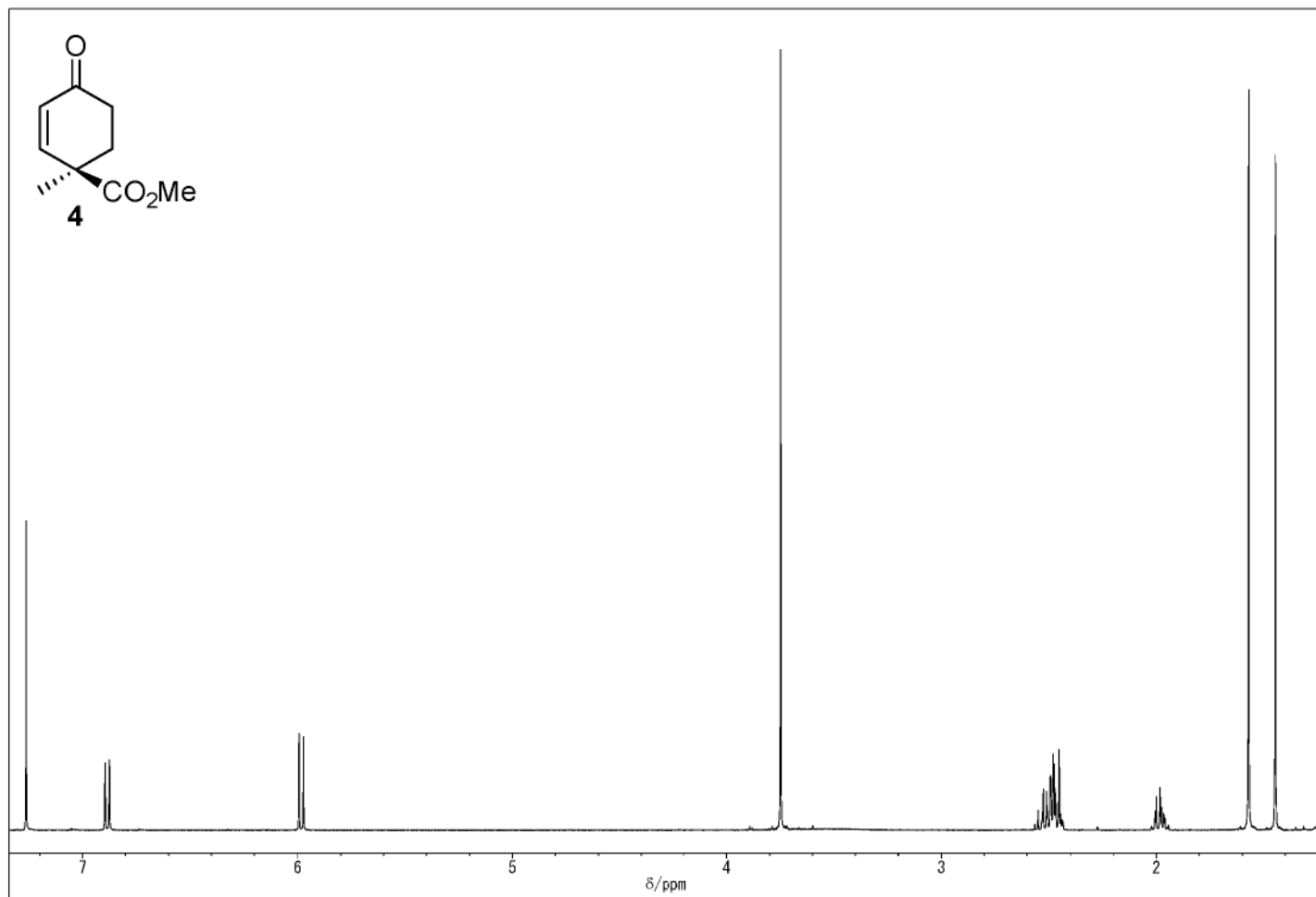


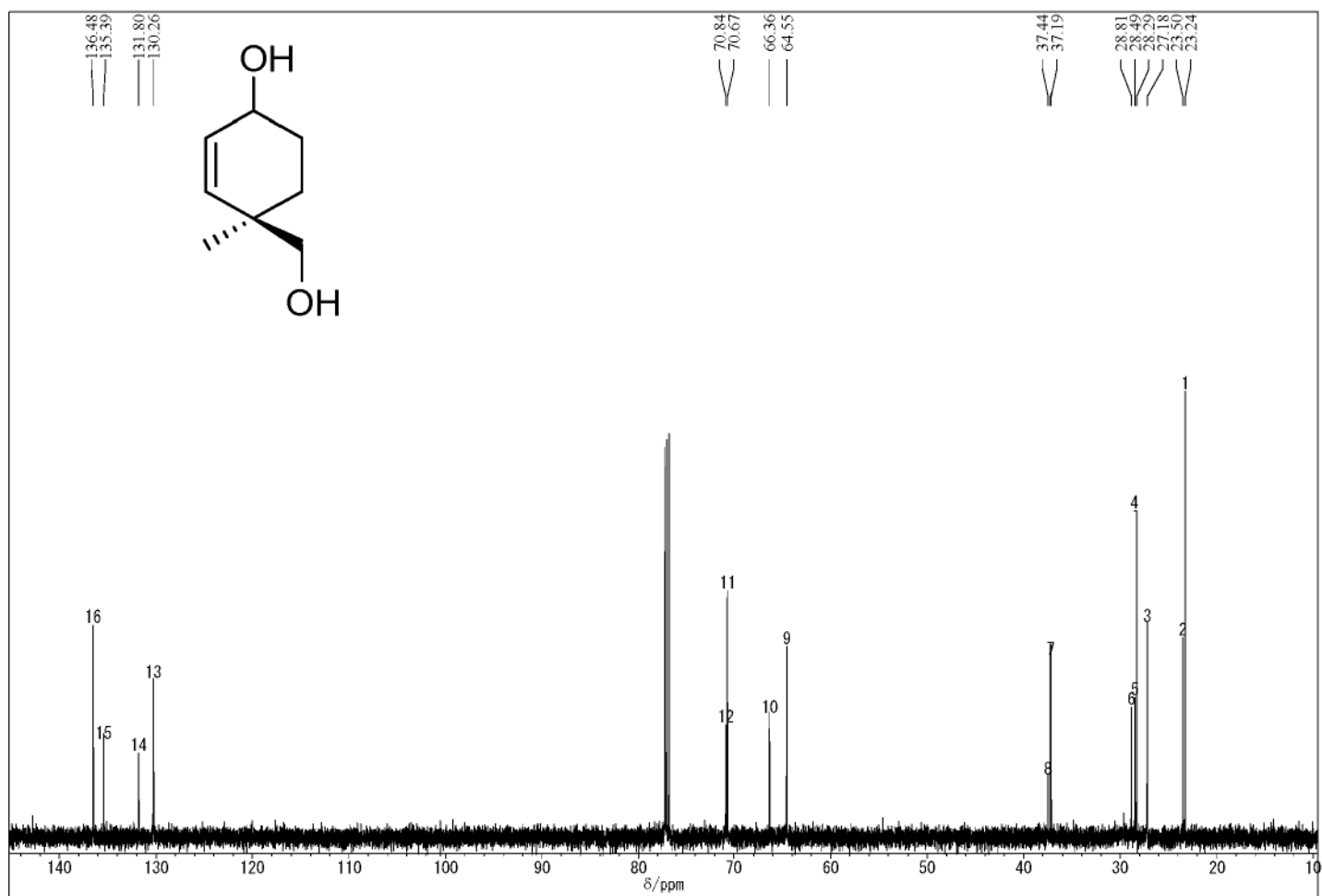
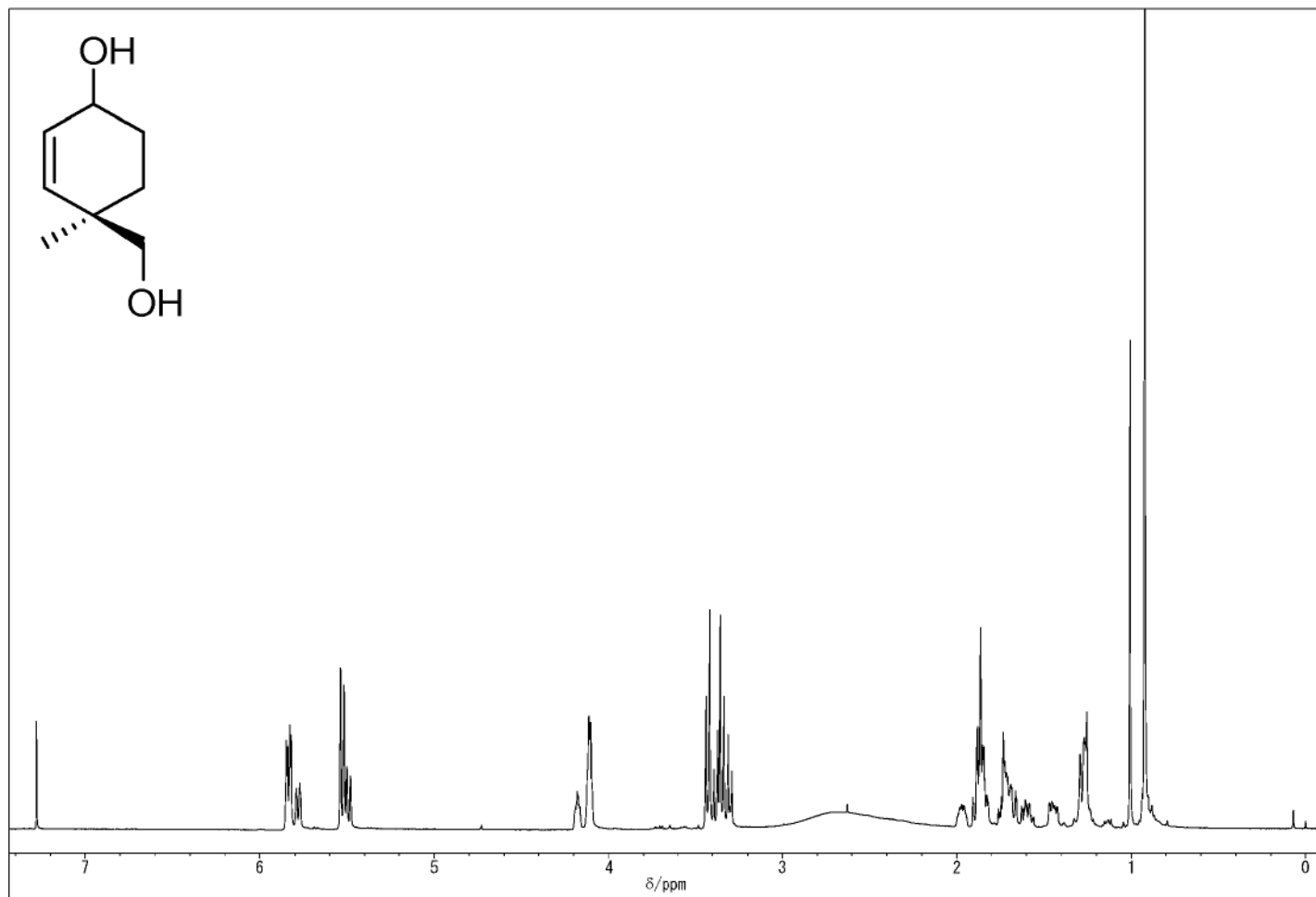


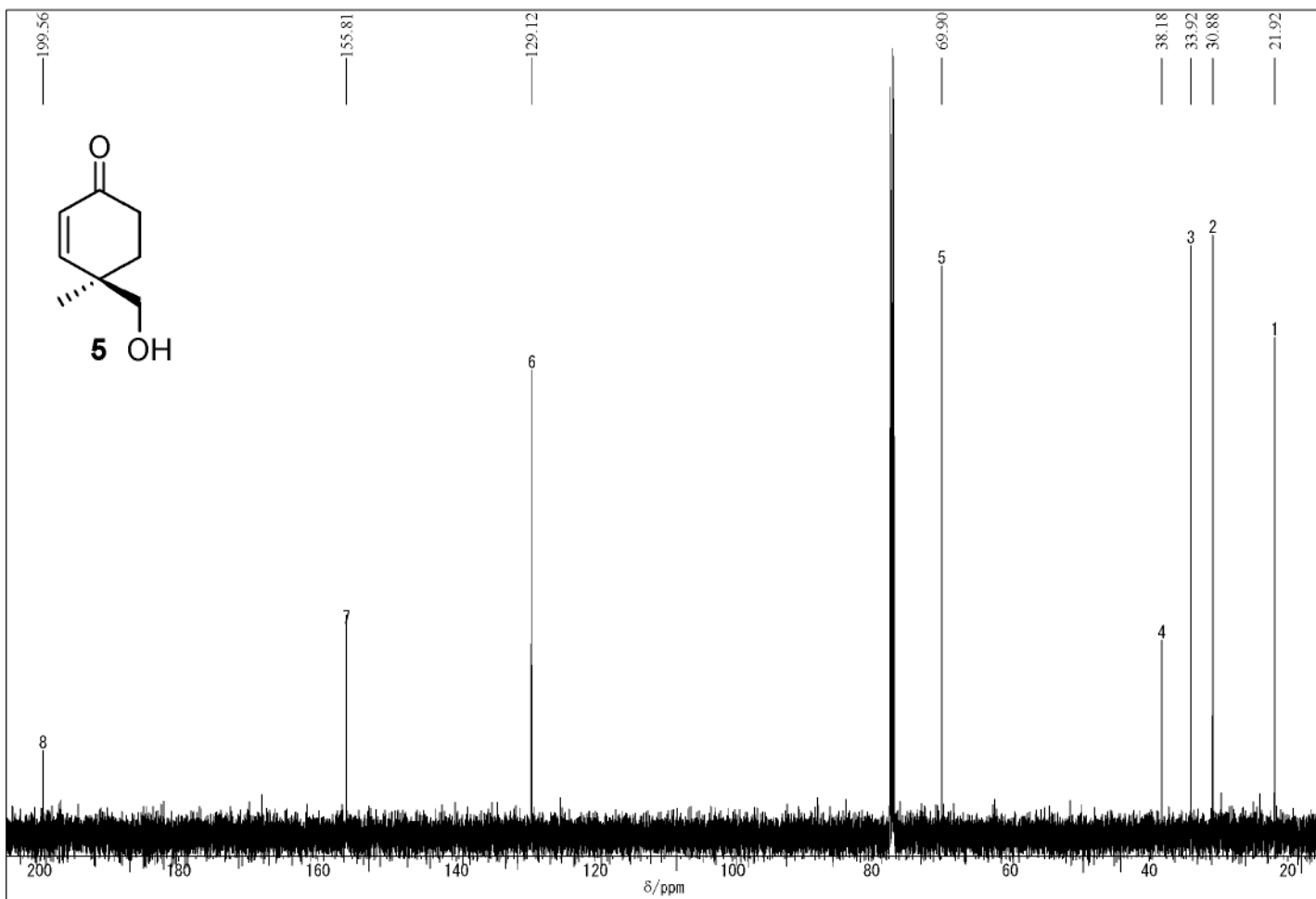
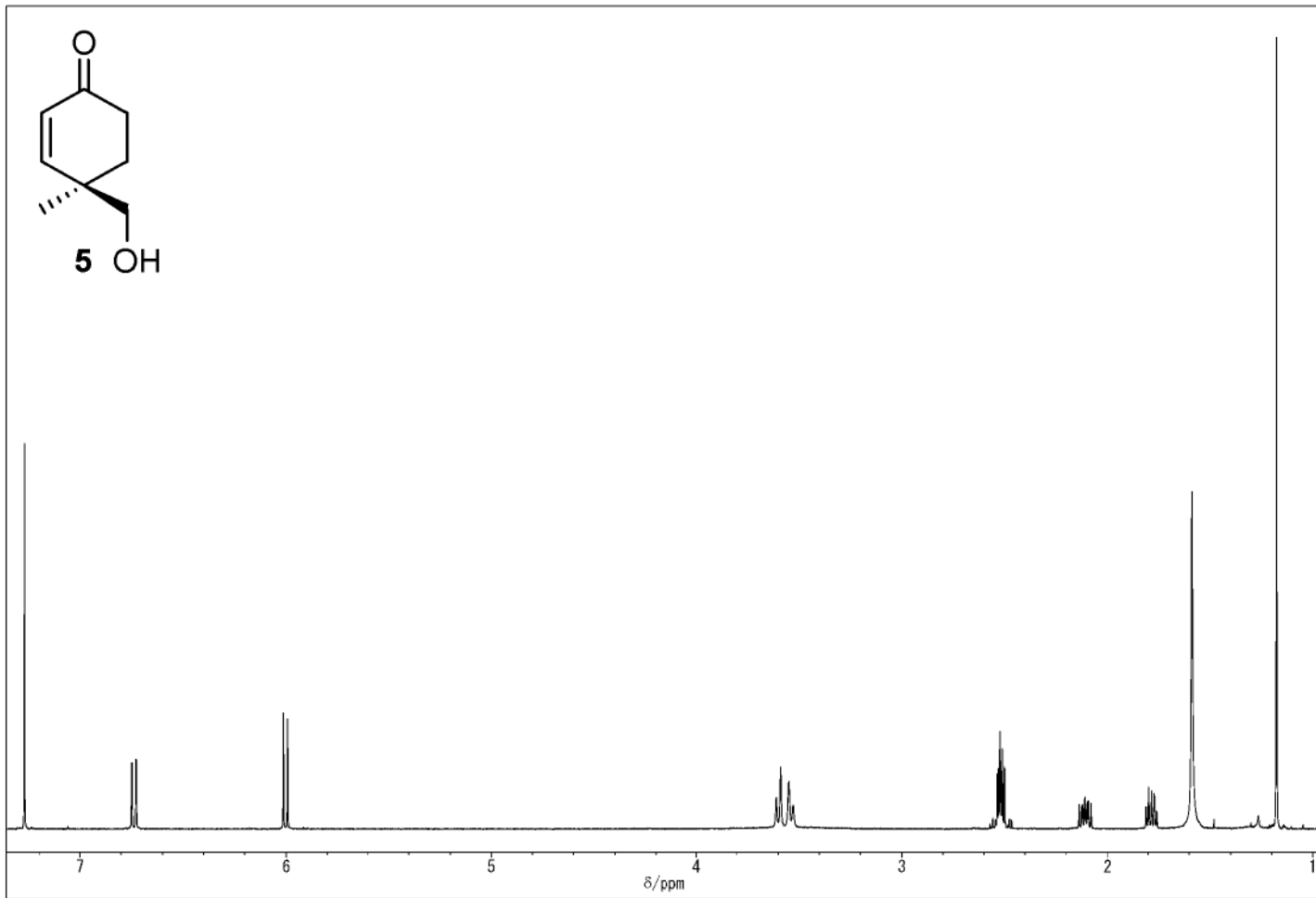












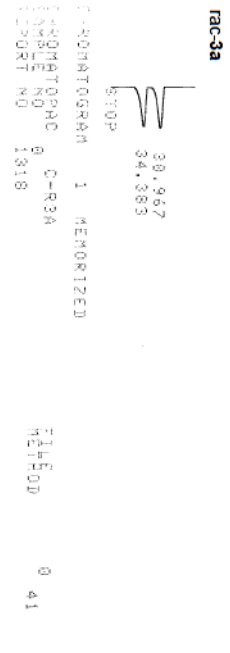
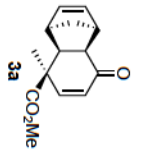


Table 1, entry 6

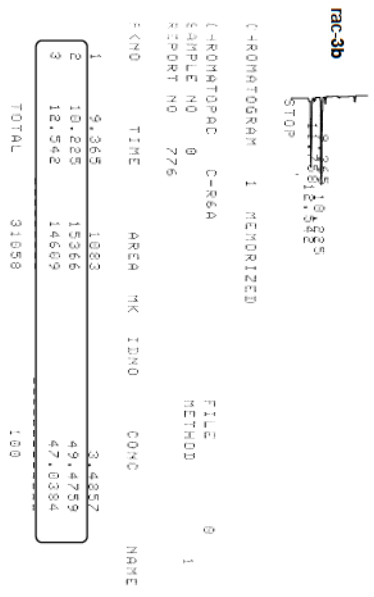
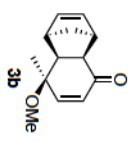
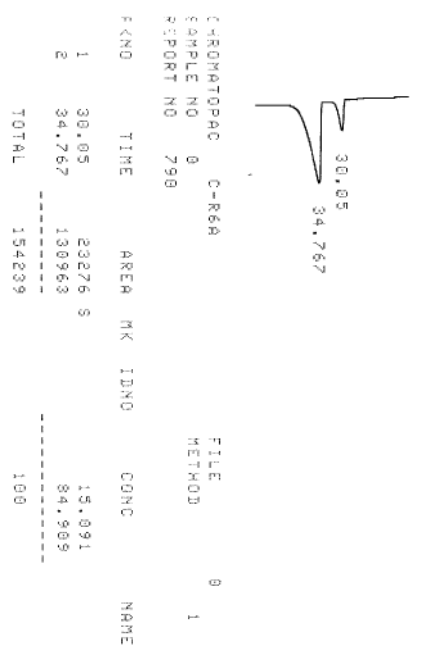
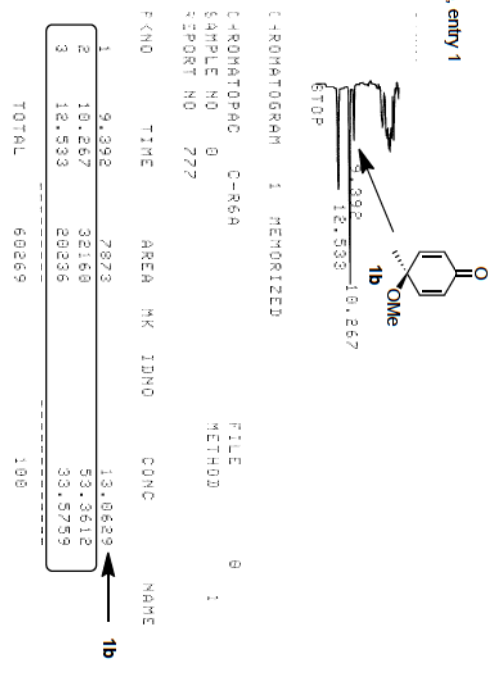
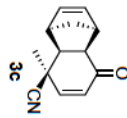
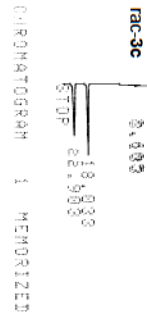


Table 3, entry 1





rac-3c



CHROMATOGRAM 1 MEMORIZED

CHROMATOPAC 0-R6A
 SAMPLE NO 0
 REPORT NO 6645

RUN	TIME	AREA	NK	IDNO	CONC	NAME
1	18.817	16186			49.6507	
2	22.902	16416			50.9493	
TOTAL		32599			100	

FILE 0
 METHOD 41

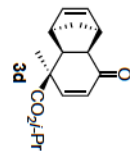
Table 3, entry 2

CHROMATOGRAM 1 MEMORIZED

CHROMATOPAC 0-R6A
 SAMPLE NO 0
 REPORT NO 5627

RUN	TIME	AREA	NK	IDNO	CONC	NAME
1	18.817	44550			43.8956	
2	22.98	57147			56.1964	
TOTAL		101698			100	

FILE 2
 METHOD 41



rac-3d



CHROMATOGRAM 1 MEMORIZED

CHROMATOPAC 0-R6A
 SAMPLE NO 0
 REPORT NO 8146

RUN	TIME	AREA	NK	IDNO	CONC	NAME
1	15.108	111356			54.1413	
2	18.057	116478			49.8588	
3	21.527	111356			54.1413	
TOTAL		339190			100	

FILE 0
 METHOD 1

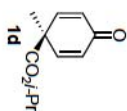
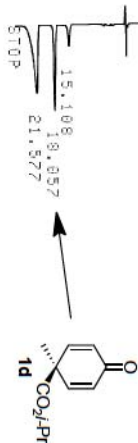
Table 3, entry 3

CHROMATOGRAM 1 MEMORIZED

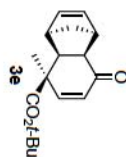
CHROMATOPAC 0-R6A
 SAMPLE NO 0
 REPORT NO 779

RUN	TIME	AREA	NK	IDNO	CONC	NAME
1	15.108	5451			6.8503	
2	18.057	24192			30.4021	
3	21.527	49930			62.7476	
TOTAL		79572			100	

FILE 0
 METHOD 1



1d



CHROMATOGRAM 1 MEMORIZED
 CHROMATOGRAPH C-REB FILE 0
 SAMPLE NO 0 METHOD 41
 REPORT NO 6658

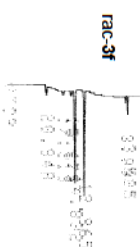
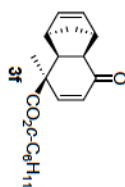
PKNO	TIME	AREA	WK	DNNO	CONC	NAME
1	9.447	1138			1.5445	
2	7.817	39137	Y		46.737	
3	9.817	39937			48.4284	
4	10.138	4078			5.9237	
TOTAL		88645			100	

Table 4, entry 4



CHROMATOGRAM 1 MEMORIZED
 CHROMATOGRAPH C-REB FILE 0
 SAMPLE NO 0 METHOD 41
 REPORT NO 6659

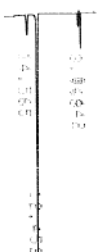
PKNO	TIME	AREA	WK	DNNO	CONC	NAME
1	9.533	1138			1.5445	
2	7.245	1863	Y		1.645	
3	7.48	11916			25.75969	
4	6.432	2797			3.17738	



CHROMATOGRAM 1 MEMORIZED

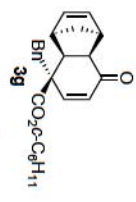
PKNO	TIME	AREA	WK	DNNO	CONC	NAME
1	9.996	1811			9.6137	
2	9.92	241			1.4338	
3	10.965	18932			2.3111	
4	10.928	1863	Y		2.0299	
5	12.113	1138			1.4338	
6	9.918	333			4.9364	
7	9.918	333			4.9364	
TOTAL		44584			100	

Table 3, entry 5



CHROMATOGRAM 1 MEMORIZED
 CHROMATOGRAPH C-REB FILE 0
 SAMPLE NO 0 METHOD 41
 REPORT NO 6636

PKNO	TIME	AREA	WK	DNNO	CONC	NAME
1	9.442	4936			4.6883	
2	9.963	1927			1.8363	
3	10.452	45442			41.9567	
4	14.555	447			4.2377	

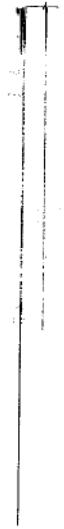


CHROMATOGRAM 1 MEMORIZED

CHROMATOPAC C-R6A FILE 0
 SAMPLE NO 0 METHOD 41
 REPORT NO 6749

PKNO	TIME	AREA	NK	IDNO	CONC	NAME
1	11.113	94133	Y		44.118	
2	11.113	94133	Y		44.118	
3	11.113	94133	Y		44.118	
4	11.113	94133	Y		44.118	
5	11.113	94133	Y		44.118	
6	11.113	94133	Y		44.118	
7	11.113	94133	Y		44.118	
8	11.113	94133	Y		44.118	
9	11.113	94133	Y		44.118	
TOTAL		213066			100	

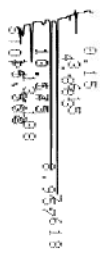
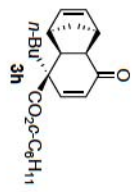
Table 4, entry 1



CHROMATOGRAM 1 MEMORIZED

CHROMATOPAC C-R6A FILE 0
 SAMPLE NO 0 METHOD 41
 REPORT NO 6749

PKNO	TIME	AREA	NK	IDNO	CONC	NAME
1	11.113	94133	Y		44.118	
2	11.113	94133	Y		44.118	
3	11.113	94133	Y		44.118	
4	11.113	94133	Y		44.118	
5	11.113	94133	Y		44.118	
6	11.113	94133	Y		44.118	
7	11.113	94133	Y		44.118	
8	11.113	94133	Y		44.118	
9	11.113	94133	Y		44.118	
TOTAL		213066			100	



CHROMATOGRAM 1 MEMORIZED

CHROMATOPAC C-R6A FILE 0
 SAMPLE NO 0 METHOD 41
 REPORT NO 6749

PKNO	TIME	AREA	NK	IDNO	CONC	NAME
1	7.608	23236	Y		36.2372	
2	7.608	23236	Y		36.2372	
3	7.608	23236	Y		36.2372	
4	7.608	23236	Y		36.2372	
5	7.608	23236	Y		36.2372	
6	7.608	23236	Y		36.2372	
7	7.608	23236	Y		36.2372	
8	7.608	23236	Y		36.2372	
TOTAL		65192			100	

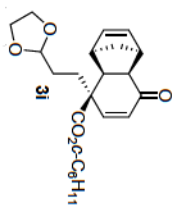
Table 4, entry 2



CHROMATOGRAM 1 MEMORIZED

CHROMATOPAC C-R6A FILE 0
 SAMPLE NO 0 METHOD 41
 REPORT NO 6749

PKNO	TIME	AREA	NK	IDNO	CONC	NAME
1	7.608	23236	Y		36.2372	
2	7.608	23236	Y		36.2372	
3	7.608	23236	Y		36.2372	
4	7.608	23236	Y		36.2372	
5	7.608	23236	Y		36.2372	
6	7.608	23236	Y		36.2372	
7	7.608	23236	Y		36.2372	
8	7.608	23236	Y		36.2372	
TOTAL		65192			100	



1-ROH470894M 1 MET091289 3i
 1-ROH470894M 0-ROH
 1-ROH470894M 0-ROH
 1-ROH470894M 0-ROH

PK NO	TIME	AREA	%	CONC	NAME
1	9.74	4845	100	48.45	3i
2	11.75	3213	6.6	3.21	
3	9.74	4845	100	48.45	3i
4	11.75	3213	6.6	3.21	
5	9.74	4845	100	48.45	3i
6	11.75	3213	6.6	3.21	
7	9.74	4845	100	48.45	3i
8	11.75	3213	6.6	3.21	
9	9.74	4845	100	48.45	3i
10	11.75	3213	6.6	3.21	
11	9.74	4845	100	48.45	3i
12	11.75	3213	6.6	3.21	
13	9.74	4845	100	48.45	3i
14	11.75	3213	6.6	3.21	
15	9.74	4845	100	48.45	3i
16	11.75	3213	6.6	3.21	
17	9.74	4845	100	48.45	3i
18	11.75	3213	6.6	3.21	
19	9.74	4845	100	48.45	3i
20	11.75	3213	6.6	3.21	
21	9.74	4845	100	48.45	3i
22	11.75	3213	6.6	3.21	
23	9.74	4845	100	48.45	3i
24	11.75	3213	6.6	3.21	
25	9.74	4845	100	48.45	3i
26	11.75	3213	6.6	3.21	
27	9.74	4845	100	48.45	3i
28	11.75	3213	6.6	3.21	
29	9.74	4845	100	48.45	3i
30	11.75	3213	6.6	3.21	
31	9.74	4845	100	48.45	3i
32	11.75	3213	6.6	3.21	
33	9.74	4845	100	48.45	3i
34	11.75	3213	6.6	3.21	
35	9.74	4845	100	48.45	3i
36	11.75	3213	6.6	3.21	
37	9.74	4845	100	48.45	3i
38	11.75	3213	6.6	3.21	
39	9.74	4845	100	48.45	3i
40	11.75	3213	6.6	3.21	
41	9.74	4845	100	48.45	3i
42	11.75	3213	6.6	3.21	
43	9.74	4845	100	48.45	3i
44	11.75	3213	6.6	3.21	
45	9.74	4845	100	48.45	3i
46	11.75	3213	6.6	3.21	
47	9.74	4845	100	48.45	3i
48	11.75	3213	6.6	3.21	
49	9.74	4845	100	48.45	3i
50	11.75	3213	6.6	3.21	

Table 4, entry 3



CHROMATOGRAM 1 MEMORIZED
 CHROMATOPAC C-R6A
 SAMPLE NO 0
 REPORT NO 6762
 FILE 0
 METHOD 41
 NAME
 PK NO TIME AREA MK IDNO CONC
 1 9.74 4845 48.45
 2 11.75 3213 3.21