

Supporting Information

Nickel-Catalyzed Asymmetric Allylic Alkylation of β -Dicarbonyl Compounds via C–C Bond Activation of 2-Allylated Cyclic 1,3-Diketones

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1. General Remarks

All reactions and manipulations involving air- and moisture-sensitive organometallic compounds were operated using the standard Schlenk techniques under argon gas. Et₂O, DCM, THF, CH₃CN, and toluene were dried and deoxygenated by using Grubbs column (Glass Counter Solvent Dispensing System, Nikko Hansen & Co, Ltd.). Ni(cod)₂ was purchased from Sigma-Aldrich or STREM Chemicals and stored in argon-filled glove box at -20 °C under dark condition. All chiral ligands are commercially available, and we purchased these ligands from Tokyo Chemical Industry Co, Sigma-Aldrich, or STREM Chemicals. ¹H NMR (400 MHz), ¹³C{¹H} NMR (100 MHz), and ¹⁹F{¹H} NMR (376 MHz) spectra were measured on Bruker Avance III-400 spectrometers. All ¹H NMR chemical shifts were reported in ppm (δ) relative to tetramethylsilane at δ 0.00 or referenced to the chemical shifts of residual solvent resonances (DMSO-*d*₆ at δ 2.50). All ¹³C{¹H} NMR chemical shifts were reported in ppm (δ) relative to carbon resonances of CDCl₃ at δ 77.16 and DMSO-*d*₆ at δ 39.52. All ¹⁹F{¹H} NMR chemical shifts were reported in ppm (δ) relative to fluorine resonances in α,α,α-trifluorotoluene at δ -63.90. HPLC spectra were recorded on a JASCO UV-4075. Optical rotation values were recorded on Anton Paar MCP100 polarimeter at 589 nm (sodium lamp) and are given in 10⁻¹ deg cm² g⁻¹. High resolution mass spectra were obtained on JEOL JMS-700. All melting points were recorded on BUCHI Melting Point M-565. Flash column chromatography was performed using silica gel 60 (0.040-0.0663 mm, 230-400 mesh ASTM) with hexane (>95 %, KANTO CHEMICAL CO., INC.) and EtOAc (>99 %, NACALAI TESQUE, INC.). UCR-150N (Techno Sigma) was used for the AAA reactions at low temperature.

2. Experimental Section

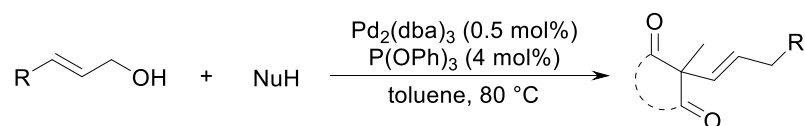
2.1. General Procedure of AAA Reaction

To a Schlenk tube with a stir bar, nucleophile **6** (0.1 mmol), allylic source **1** (0.1 mmol, 1 equiv.), (*S*)-MeO-tol-BIPHEP (**L1**: 0.012 mmol, 12 mol%), and Ni(cod)₂ (0.01 mmol, 10 mol%) were added in an argon-filled glovebox. Following removal from the glovebox, 1.0 mL of dry Et₂O was added to the Schlenk tube under argon atmosphere, and the reaction mixture was stirred at 15 °C for 40 hours. The resulting mixture was quenched under air, and Ni complex was removed through a short-pad silica-gel with EtOAc. The crude mixture was purified by silica-gel flush column chromatography (EtOAc/hexane=1/9 to 1/4) to afford the allylated compound. When the crude mixture included large amount of β-ketoester compounds **6**, the mixture was purified by PTLC instead of column chromatography for removing the β-ketoester compounds, which were widely broaden on the silica-gel column chromatography. Enantiomeric excess of the products was determined by HPLC analysis.

2.2. Preparation of Starting Materials

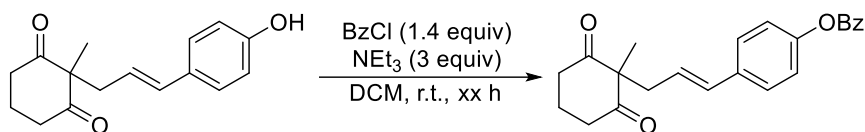
Compounds **6a-6e** were prepared through the reported procedure in our previous report.^{S1} α-Allylated-β-dicarbonyl compounds **1** and **2a-5a** were synthesized through palladium-catalyzed allylic alkylation, as shown below. β-Diester compounds **6g** and **6f** were prepared through the two-step transformation from commercially available compounds, as shown below.

2.3. Synthesis of Allylic Source (**1** and **2a-5a**)^{S2}



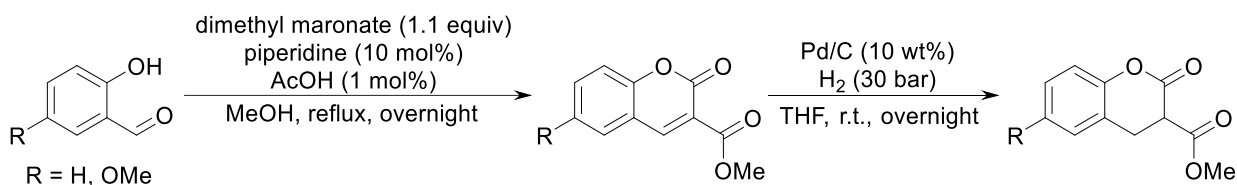
Pd₂(dba)₃ (0.5 mol%) and P(OPh)₃ (4 mol%) were dissolved in dry toluene (0.5 M) under argon atmosphere, followed by addition of nucleophile (1.0 equiv.) and allylic alcohols (1.0-2.2 equiv.) to the reaction mixture. The resulting suspension was stirred at 80 °C for several hours. After consuming of starting material, monitored by TLC, the resulting mixture was filtrated by short-pad silica-gel with EtOAc. The crude mixture was purified by silica-gel flush column chromatography (EtOAc/hexane=1/4 to 1/1) to afford the title compound in moderate yield. As the further purification, the title compound could be recrystallized from EtOH or hexane. Spectral data of the products are described in later part.

2.4. Synthesis of Allylic Source (1f)



After preparation of *(E)*-2-(3-(4-hydroxyphenyl)allyl)-2-methylcyclohexane-1,3-dione through the above method, allylic source **1f** was synthesized by benzoyl protection of the phenolic hydroxyl group. *(E)*-2-(3-(4-hydroxyphenyl)allyl)-2-methylcyclohexane-1,3-dione (4.0 mmol) was reacted with BzCl (0.95 mL, 5.6 mmol, 1.4 equiv.) in the presence of NEt₃ (0.88 mL, 12 mmol, 3.0 equiv.) in CH₂Cl₂ at room temperature for 3 days. The reaction mixture was quenched by H₂O, and the product was extracted with EtOAc. The crude mixture was purified by silica-gel flush column chromatography (EtOAc/hexane=1/9) and recrystallized from EtOH to obtain **1f** (1.08 g, 3.0 mmol, 75% yield).

2.5. Synthesis of β -Diester Compounds (**6f** and **6g**)^{S3}



2-Hydroxybenzaldehyde derivatives (20 mmol) and dimethyl malonate (22 mmol, 1.1 equiv.) were dissolved in dry MeOH (40 mL) under argon atmosphere. After addition of piperidine (2.0 mmol, 10 mol%) and acetic acid (0.2 mmol, 1 mol%), the resulting mixture was stirred overnight at reflux conditions. The reaction mixture was transferred into a round bottom flask and diluted with hot water. The solution was cooled in the fridge for several hours. The resulting precipitation was filtrated, washed with cold MeOH/water (2/3), and dried *in vacuo* to afford desired product in 80% (for R = H) and 92 % yield (for R = OMe) yield, respectively.

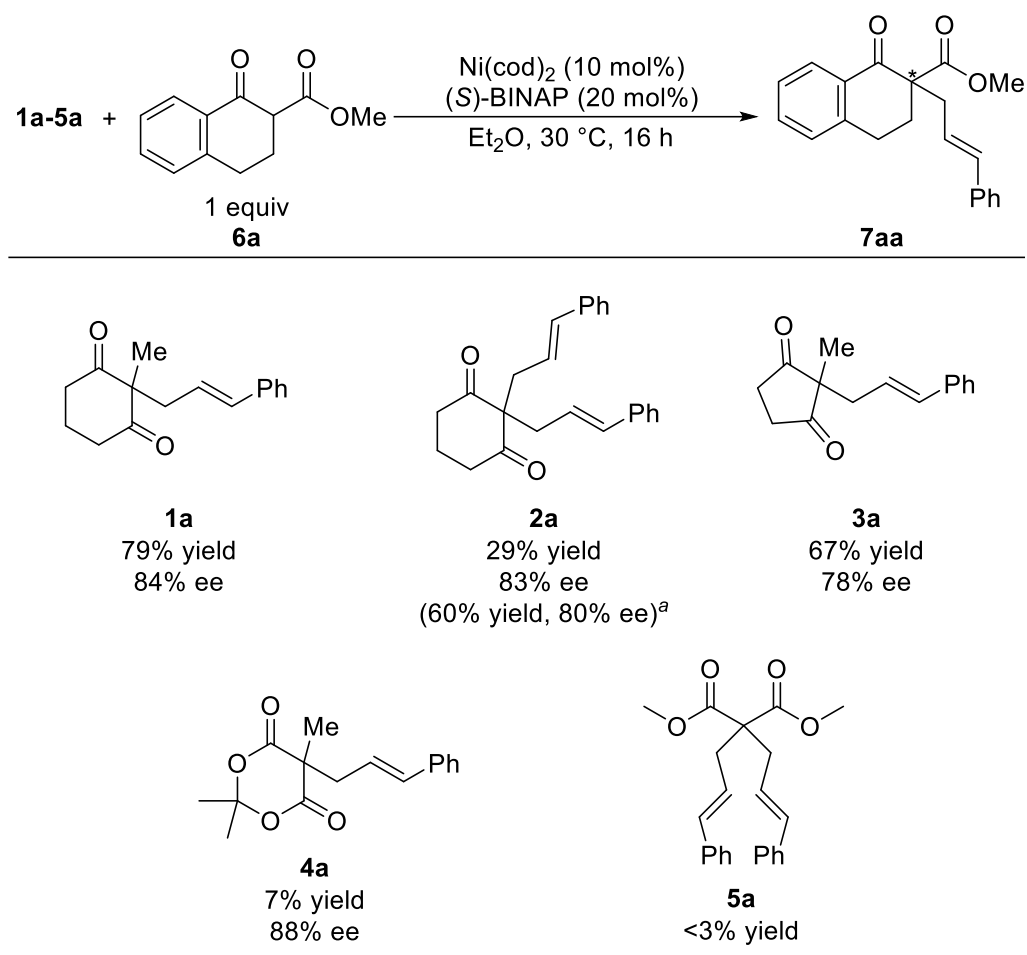
Above products (8 mmol) and Pd/C (10 wt%) were added in THF (20 mL), and the resulting mixture was pressurized with hydrogen gas (30 bar) in an autoclave. After stirring at 30 °C overnight, Pd/C was removed by filtration, and all volatile compounds were evaporated under the reduced pressure. The crude mixture was purified by recrystallization from cold EtOH to afford the desired product in 50% (for **6a**) and 86% (for **6c**) yield, respectively.

3. Additional Experimental Data

3.1. Screening of Leaving Groups with (*S*)-BINAP

Compound **1a** showed the highest reactivity in the screening of leaving groups using (*S*)-BINAP as well as (*S*)-tol-MeO-BIPHEP as ligand.

Table S1. Screening of Leaving Groups using (*S*)-BINAP as a Ligand



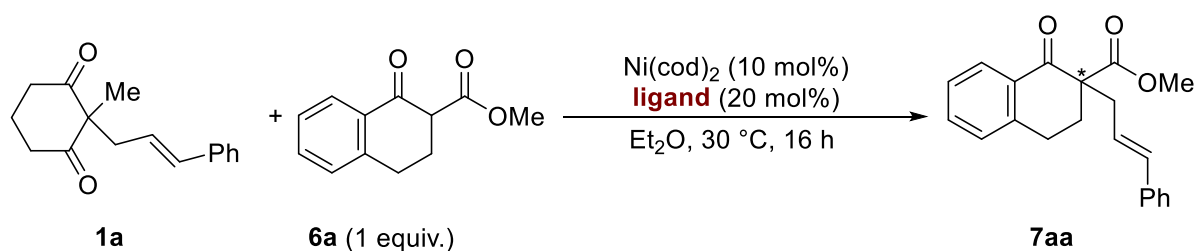
^a For 50 hours.

3.2. Screening of Solvents and Ligands

To a Schlenk tube with a stir bar, 2-cinnamyl-2-methylcyclohexane-1,3-dione (**1a**) (0.10 mmol), methyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**6a**: 0.10 mmol, 1 equiv.), ligand (0.020 mmol, 20 mol%), and Ni(cod)₂ (0.010 mmol, 10 mol%) were added in an argon-filled glovebox. Following removal from the glovebox, 1.0 mL of solvent was added to the Schlenk tube under argon atmosphere, and the reaction mixture was stirred at 30 °C for 16 hours. The resulting mixture was quenched under air, and Ph₃CH was added to the mixture as an internal standard. After removal of Ni complex through a short-pad silica-gel with EtOAc eluent, yield was determined by ¹H NMR analysis in CDCl₃, and ee was determined by HPLC analysis (Table S2).

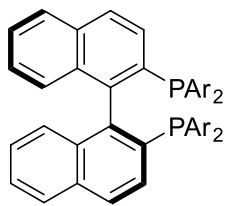
The combination of Ni(cod)₂ and (*S*)-BINAP or (*S*)-tol-BINAP afforded the desired product **7aa** in 79% yield with 84% ee (entry 1) or 85% yield with 85% ee (entry 2). The use of (*S*)-MeO-BIPHEP and (*S*)-tol-MeO-BIPHEP (**L1**) slightly increased the enantioselectivity to 87% ee and 89% ee, though yields were lower than that of (*S*)-BINAP (entries 3 and 4). When (*S*)-H₈-BINAP was used, the corresponding product was obtained in higher yield than others but the enantioselectivity was lower than that of (*S*)-tol-MeO-BIPHEP (entry 5). When (*S*)-Ph-Garphos and (*S*)-P-Phos were used, **7aa** was obtained in moderate yield and moderate enantioselectivity (entries 6 and 7). (*S*)-C₃-TunePhos, (*S*)-DIFLUORPHOS, and (*S*)-SYNPHOS reduced the catalyst activity to give **7aa** in 31%, 14%, and 54% yield, respectively, with moderate selectivity (entries 8-10). (*S*)-SEGPHOS showed higher catalytic activity but slightly lower enantioselectivity than **L1** (entry 11). The more sterically hindered (*S*)-DM-SEGPHOS and (*S*)-DTBM-SEGPHOS led to decreasing the yields, 59% and 3% yields, respectively (entries 12 and 13). When we utilized other types of chiral bisphosphine ligands or monophosphine ligand, no reaction was observed (entries 14-17). Accordingly, we selected (*S*)-tol-MeO-BIPHEP (**L1**) as the optimized chiral ligand, and then, we optimized reaction conditions.

Table S2. Screening of Ligands

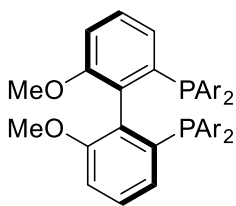


entry	ligand	yield [%]	ee [%]
1	(S)-BINAP	79	84
2	(S)-tol-BINAP	85	85
3	(S)-MeO-BIPHEP	43	87
4	(S)-tol-MeO-BIPHEP	76	89
5	(S)-H ₈ -BINAP	91	80
6	(S)-Ph-Garphos	66	87
7	(S)-P-Phos	70	87
8	(S)-C ₃ -TunePhos	31	84
9	(S)-DIFLUORPHOS	14	86
10	(S)-SYNPHOS	54	86
11	(S)-SEGPPOS	83	87
12	(S)-DM-SEGPPOS	59	78
13	(S)-DTBM-SEGPPOS	3	N/A
14	(S,S)-DIOP	no reaction	N/A
15	(S)-Phanephos	no reaction	N/A
16	(S,S,S)-Ph-SKP	no reaction	N/A
17 ^a	(S)-MONOPHOS	no reaction	N/A

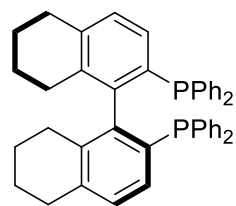
Reaction condition: **1a** (0.1 mmol), **6a** (0.1 mmol), Ni(cod)₂ (10 mol%), ligand (20 mol%) in Et₂O (1.0 mL), 30 °C, 16 h. Yield was determined by ¹H NMR analysis using Ph₃CH as an internal standard. Ee was determined by HPLC. ^a40 mol% of ligand was used.



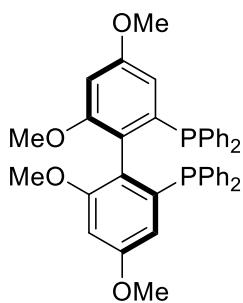
(S)-BINAP : Ar = Ph
(S)-tol-BINAP : Ar = *p*-tolyl



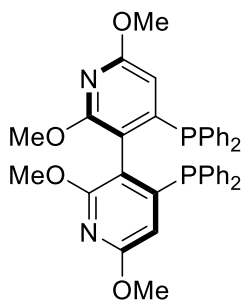
(S)-MeO-BIPHEP : Ar = Ph
(S)-tol-MeO-BIPHEP : Ar = *p*-tolyl



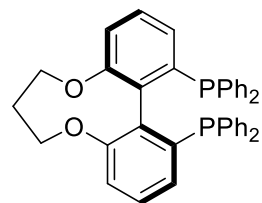
(S)-H₈-BINAP



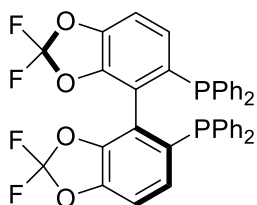
(S)-Ph-Garphos



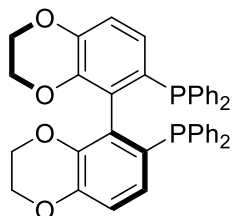
(S)-P-Phos



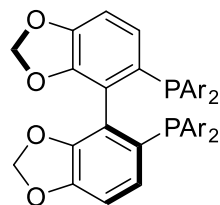
(S)-C₃-TunePhos



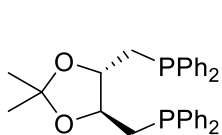
(S)-DIFLUORPHOS



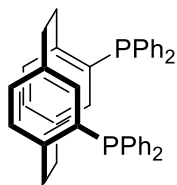
(S)-SYNPHOS



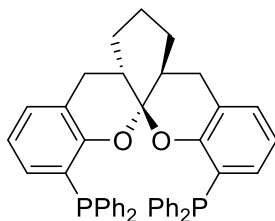
(S)-SEGPHOS : Ar = Ph
(S)-DM-SEGPHOS : Ar = 3,5-Me₂-C₆H₃
(S)-DTBM-SEGPHOS : Ar = 3,5-(^tBu)₂-4-MeOC₆H₂



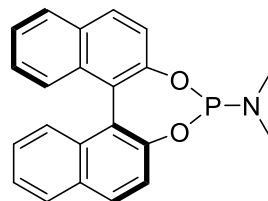
(S)-DIOP



(S)-PhanePhos



(S,S,S)-Ph-SKP

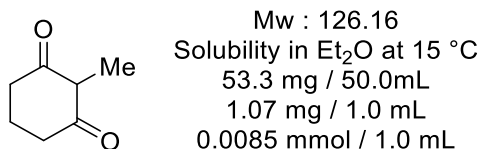


(S)-MONOPHOS

3.3. Solubility of 2-Methylcyclohexane-1,3-dione (**8**)

A large amount of 2-methylcyclohexane-1,3-dione (**8**) (purchased from Tokyo Chemical Industry Co.) was suspended to the Et₂O (70 mL) at room temperature, and the suspension was sonicated for 15 minutes. The resulting suspension was allowed to stand for 1 hour at 15 °C. 50.0 mL of supernatant was transferred to round bottom flask, and all volatiles were removed under the reduced pressure to recover 53.3 mg of **8**.

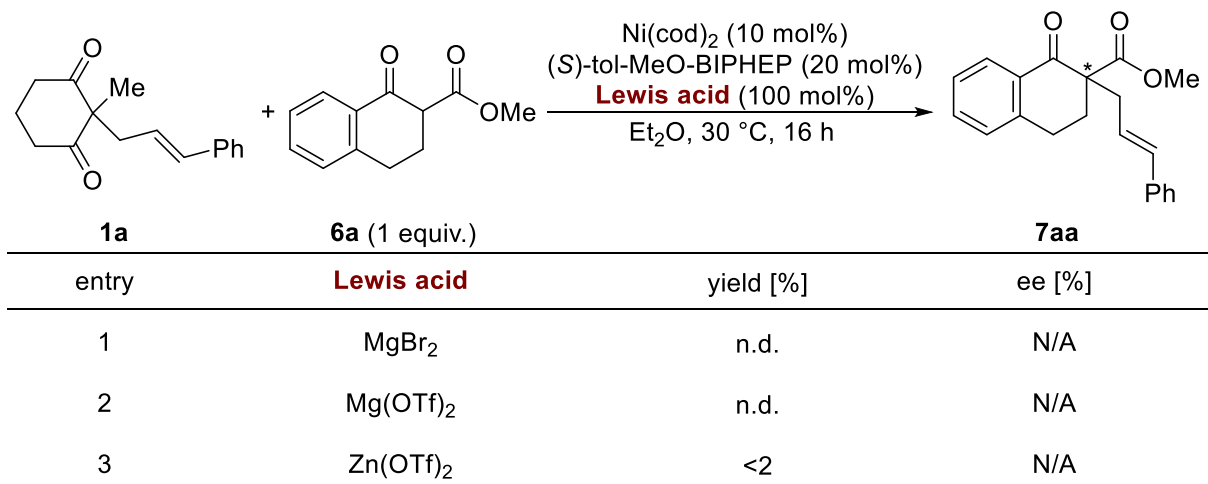
Scheme S1. Solubility of 2-Methylcyclohexane-1,3-dione



3.4. Additive Effects of Lewis Acids

Since Oshima and Yorimitsu *et al.* reported that addition of Lewis acid facilitated nickel catalyzed C–C bond transformation,^{S4} we checked the additive effects of Lewis acids (Table S3). However, addition of Lewis acids suppressed the AAA reaction.

Table S3. Screening of Additives

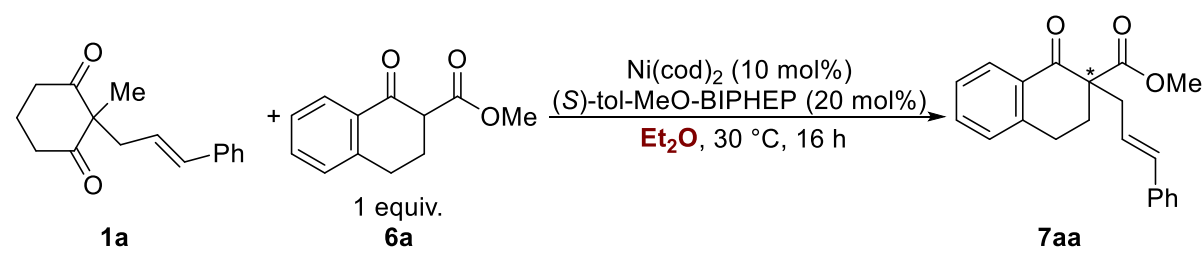


Reaction condition: **1a** (0.1 mmol), **6a** (0.1 mmol), Ni(cod)₂ (10 mol%), ligand (20 mol%), Lewis acid (100 mol%) in Et₂O (1.0 mL), 30 °C, 16 h. Yield was determined by ¹H NMR analysis using Ph₃CH as an internal standard. Ee was determined by HPLC. n.d. = not detected.

3.5. Solvent Purification

For the nickel-catalyzed AAA reaction, purification methods for dry Et₂O crucially impacted toward not only reactivity but also enantioselectivity. When we utilized absolute Et₂O purified by **Method A**, in which dry Et₂O was passed through Grubbs column including copper and molecular sieves, product **7aa** was obtained in 76% yield and 89% ee (Table S4, entry 1). On the other hand, the use of distilled Et₂O prepared through **Method B** and **C** led to decreasing both of yield and enantioselectivity (entry 2 and 4). Further addition of MS4Å was not effective for the nickel-catalyzed system (entry 3). Hence, we selected **Method A** as the purification method of Et₂O for the AAA reactions.

Table S4. Effects of Solvent Purification



entry		yield [%]	ee [%]
1	Method A	76	89
2	Method B	34	74
3	Method B + MS4Å (80 mg)	31	65
4	Method C	25	72

Yield was determined by ¹H NMR analysis using Ph₃CH as an internal standard. Ee was determined by HPLC.

Method A: Et₂O (KANTO CHEMICAL CO., INC., Purity >99.5 %, Dehydrated H₂O <50 ppm) was dried and deoxygenated by using Grubbs column (Glass Counter Solvent Dispensing System, Nikko Hansen & Co, Ltd.).

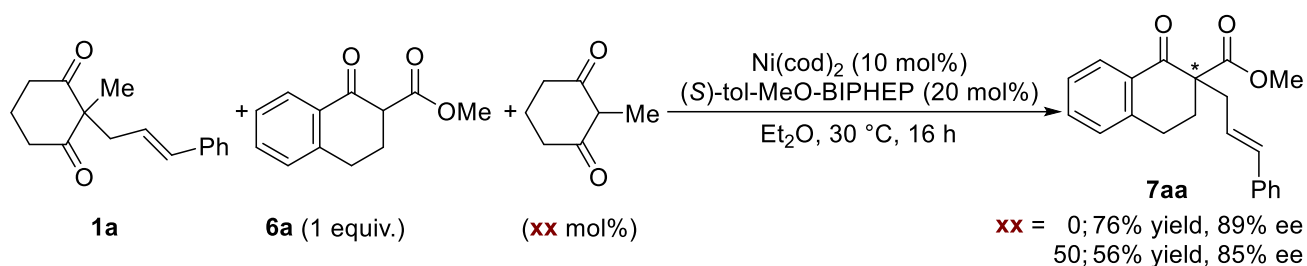
Method B: Et₂O (Nacalai tesque, INC., Purity >98 %, containing 2 ppm of BHT as a stabilizer) was distilled from sodium benzophenone ketyl under argon atmosphere.

Method C: Et₂O (Nacalai tesque, INC., Purity >98 %, containing 2 ppm of BHT as a stabilizer) was dried over CaH₂, distilled, and degassed (freeze-pump-thaw).

3.6. Control Experiments

When reaction time was extended from 16 hours to 40 hours, enantioselectivity of the product was diminished (in main manuscript; Table 3, entry 2 vs 4). For investigating the reason of diminished enantioselectivity, we tested additive effect of 2-methylcyclohexane-1,3-dione, leaving group of **1a**, on the nickel-catalyzed AAA reaction, resulting in that not only enantioselectivity but also product yield were decreased (Scheme S2). Thus, leaving group negatively impacted toward catalytic activity of nickel complex and enantioselectivity during the reaction.

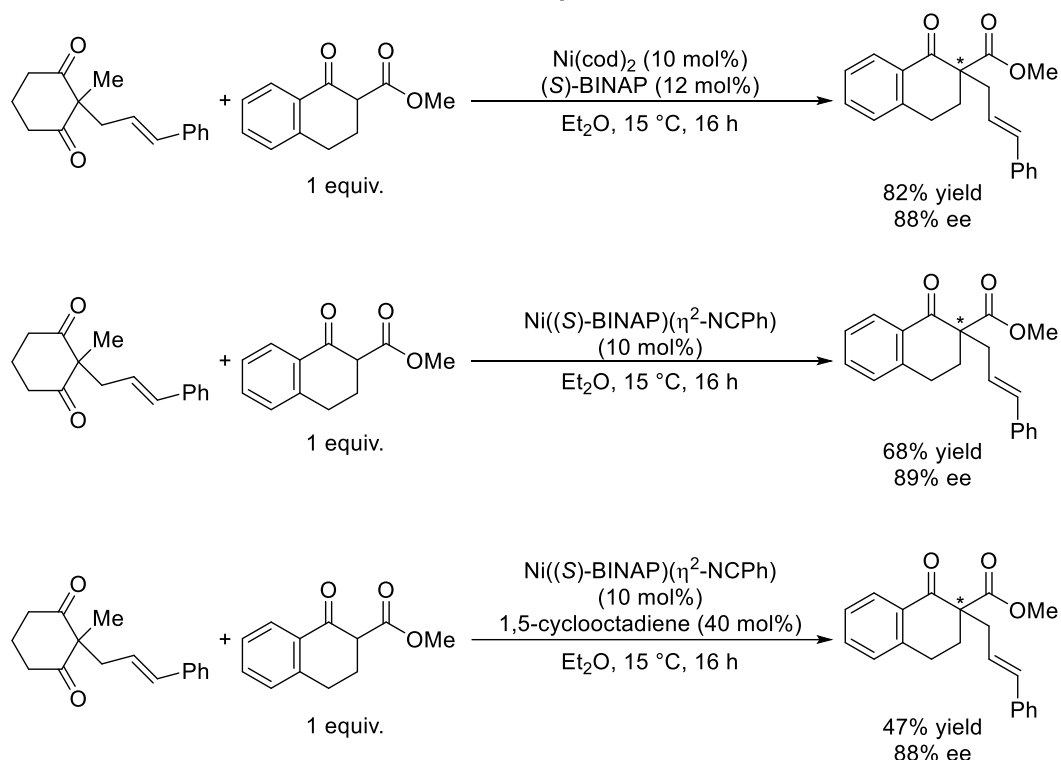
Scheme S2. Additive Effects of Leaving Group (2-Methylcyclohexane-1,3-dione)



3.7. Activity of Another Nickel(0) Precursor (Scheme S3)

Ni{(S)-BINAP}(η²-NCPH)^{S5} showed lower catalytic activity than that of the combination of Ni(cod)₂ and (S)-BINAP. The addition of 1,5-cyclooctadiene further diminished the yield.

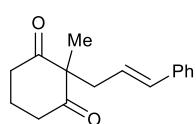
Scheme S3. Catalytic Activity of Ni{(S)-BINAP}(η²-PhCN)



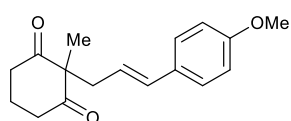
3.8. About HPLC Analysis

Enantiomeric excess was determined by comparing HPLC charts of the products with these of the racemic authentic samples or these in our previous work.^{S1} We prepared the racemic authentic samples through the allylation with allyl methyl carbonate derivatives and Pd(PPh₃)₄ or nickel-catalyzed allylic alkylation using **1** and (*rac*)-BINAP.

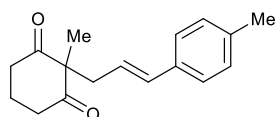
4. Spectral Data



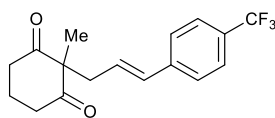
2-Cinnamyl-2-methylcyclohexane-1,3-dione (1a):^{S6} White solid (60.0 mmol scale using 1.0 equivalent of the corresponding allylic alcohol, 9.69 g, 67% yield); m.p.: 56-58 °C; IR (KBr, ν/cm^{-1}): 3397 br, 2986 w, 2968 w, 2940 w, 2918 w, 1724 s, 1697 s, 1320 m, 1031 m, 965 m; ^1H NMR (400 MHz, CDCl_3 , 30 °C): δ 7.30-7.22 (m, 4H), 7.21-7.18 (m, 1H), 6.40 (d, $J = 16.4$ Hz, 1H), 5.97 (dt, $J = 15.8, 8.0$ Hz, 1H), 2.72-2.61 (m, 6H), 2.00-1.84 (m, 2H), 1.29 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 30 °C): δ 210.2, 137.0, 134.3, 128.6, 127.6, 126.4, 123.9, 65.4, 40.4, 38.5, 20.5, 17.6; HRMS (FAB⁺) m/z calc. for $\text{C}_{16}\text{H}_{18}\text{O}_2$ 242.1307 found 242.1304.



(E)-2-(3-(4-Methoxyphenyl)allyl)-2-methylcyclohexane-1,3-dione (1b): White solid (8.0 mmol scale using 1.0 equivalent of the corresponding allylic alcohol, 1.07 g, 50% yield); m.p.: 75-76 °C; IR (KBr, ν/cm^{-1}): 3393 w, 3043 w, 3011 w, 2960 w, 2933 w, 2875 w, 2845 w, 1722 m, 1693 s, 1607 m, 1575 w, 1543 w, 1512 s, 1473 w, 1458 m, 1420 w, 1370 w, 1318 w, 1298 m, 1281 m, 1244 s, 1220 w, 1189 m, 1178 m, 1113 w, 1096 w, 1076 w, 1028 s, 975 m; ^1H NMR (400 MHz, CDCl_3 , 30 °C): δ 7.23 (d, $J = 8.7$ Hz, 2H), 6.81 (d, $J = 8.8$ Hz, 2H), 6.34 (d, $J = 15.8$ Hz, 1H), 5.81 (dt, $J = 15.7, 7.5$ Hz, 1H), 3.79 (s, 3H), 2.71-2.57 (m, 6H), 2.06-1.79 (m, 2H), 1.28 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 30 °C): δ 210.3, 159.3, 133.7, 129.8, 127.6, 121.5, 114.1, 65.6, 55.4, 40.8, 38.5, 20.1, 17.6; HRMS (FAB⁺) m/z calc. for $\text{C}_{17}\text{H}_{20}\text{O}_3$ 272.1412 found 272.1412.

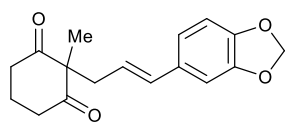


(E)-2-Methyl-2-(3-(p-tolyl)allyl)cyclohexane-1,3-dione (1c): White solid (8.0 mmol scale using 1.0 equivalent of the corresponding allylic alcohol, 1.63 g, 80% yield); m.p.: 100-101 °C; IR (KBr, ν/cm^{-1}): 3435 br, 3002 w, 2962 w, 2940 w, 1721 s, 1694 s, 1511 m, 1319 m, 1026 m, 972 m; ^1H NMR (400 MHz, CDCl_3 , 30 °C): δ 7.19 (d, $J = 7.5$ Hz, 2H), 7.08 (d, $J = 7.5$ Hz, 2H), 6.36 (d, $J = 15.7$ Hz, 1H), 5.92 (dt, $J = 15.8, 7.7$ Hz, 1H), 2.65 (m, 6H), 2.31 (s, 3H), 1.93 (m, 2H), 1.28 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 30 °C): δ 210.2, 137.5, 134.2₃, 134.1₅, 129.3, 126.3, 122.7, 65.5, 40.7, 38.5, 21.3, 20.2, 17.6; HRMS (FAB⁺) m/z calc. for $\text{C}_{17}\text{H}_{20}\text{O}_2$ 256.1463 found 256.1460.



(E)-2-Methyl-2-(3-(4-(trifluoromethyl)phenyl)allyl)cyclohexane-1,3-dione (1d): White solid (8.0 mmol scale using 1.0 equivalent of the corresponding allylic alcohol, 1.16 g, 37% yield); m.p.: 63-66 °C; IR (KBr, ν/cm^{-1}): 3404 br, 2994 w, 2963 w, 2918 w, 1726 m, 1697 s, 1613 w, 1459 w, 1419 w, 1375 w, 1324 s, 1163 m, 1122 s, 1108 s, 1066 s, 1024 m, 971 m, 955 w; ^1H NMR (400 MHz, CDCl_3 , 30 °C): δ 7.52 (d, $J = 7.51$ Hz, 2H), 7.39 (d, $J = 7.4$ Hz, 2H), 6.45 (d, $J = 6.4$ Hz, 1H), 6.09 (dt, $J = 15.7, 7.3$ Hz, 1H), 2.73-2.58 (m, 6H), 1.97-1.92 (m, 2H), 1.32 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 30 °C): δ 210.0, 140.5, 133.0, 129.4 (q, $J = 32.4$ Hz), 127.1, 126.5, 125.6 (q, $J = 3.9$ Hz), 124.3 (q, $J = 270.0$ Hz), 65.3, 39.5, 38.4, 21.3, 17.5; $^{19}\text{F}\{^1\text{H}\}$ NMR (376 Hz, CDCl_3 , 30 °C): δ -63.7; HRMS (FAB⁺) m/z

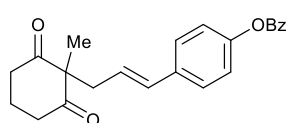
calc. for C₁₇H₁₇O₂F₃ 310.1181 found 310.1178.



(E)-2-(3-(Benzo[d][1,3]dioxol-5-yl)allyl)-2-methylcyclohexane-1,3-dione

(1e): White solid (11.5 mmol scale using 1.0 equivalent of the corresponding

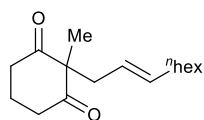
allylic alcohol, 2.62 g, 80% yield); m.p.: 86-87 °C; IR (KBr, v/cm⁻¹): 3396 br, 2998 w, 2948 w, 1722 m, 1692 s, 1491 m, 1445 m, 1252 s, 1036 m. ¹H NMR (400 MHz, CDCl₃, 30 °C): δ 6.83 (s, 1H), 6.75-6.69 (m, 2H), 6.30 (d, *J* = 15.7 Hz, 1H), 5.93-5.90 (m, 2H), 5.83-5.74 (m, 1H), 2.72-2.57 (m, 6H), 2.04-1.82 (m, 2H), 1.28 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 30 °C): δ 210.2, 148.1, 147.3, 133.8, 131.5, 122.0, 121.0, 108.3, 105.7, 101.2, 65.5, 40.5, 38.4, 20.3, 17.6; HRMS (FAB⁺) *m/z* calc. for C₁₇H₁₈O₄ 286.1205 found 286.1201.



(E)-4-(3-(1-Methyl-2,6-dioxocyclohexyl)prop-1-en-1-yl)phenyl benzoate

(1f): White solid (1.08 g, 75% yield); m.p.: 138-140 °C; IR (KBr, v/cm⁻¹):

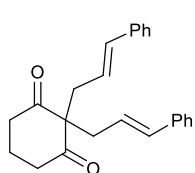
3431 br, 2992 w, 2971 w, 2939 w, 2871 w, 1728 s, 1693 s, 1600 m, 1507 s, 1454 m, 1268 s, 1202 s; ¹H NMR (400 MHz, CDCl₃, 30 °C): δ 8.19 (d, *J* = 7.3 Hz, 2H), 7.63 (t, *J* = 6.5 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.42 (d, *J* = 15.8 Hz, 1H), 5.96 (dt, *J* = 15.6, 7.5 Hz, 1H), 2.80-2.47 (m, 6H), 2.05-1.80 (m, 2H), 1.30 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 30 °C): δ 210.2, 165.3, 150.4, 134.9, 133.7, 133.3, 130.3, 129.7, 127.7, 127.4, 124.3, 121.9, 65.4, 40.2, 38.5, 20.7, 17.6; HRMS (FAB⁺) *m/z* calc. for C₂₃H₂₂O₄ 362.1518 found 362.1518.



(E)-2-Methyl-2-(non-2-en-1-yl)cyclohexane-1,3-dione (1g): Colorless liquid (5.1

mmol scale using 1.2 equivalents of the corresponding allylic alcohol, 1.07 g, 84%

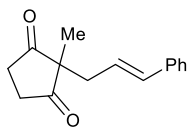
yield); IR (KBr, v/cm⁻¹): 2957 m, 2927 m, 2855 m, 1727 m, 1696 s, 1457 m, 1374 w, 1319 m, 1222 w, 1128 w, 1067 m, 1026 m; ¹H NMR (400 MHz, CDCl₃, 30 °C): δ 5.47 (dt, *J* = 15.1, 7.0 Hz, 1H), 5.17 (dt, *J* = 15.1, 7.6 Hz, 1H), 2.72-2.52 (m, 4H), 2.46 (d, *J* = 7.3 Hz, 2H), 2.08-1.76 (m, 4H), 1.35-1.22 (m, 8H), 1.21 (s, 3H), 0.88 (t, *J* = 6.8 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 30 °C): δ 210.3, 136.1, 123.4, 65.9, 41.2, 38.5, 32.7, 31.9, 29.5, 29.0, 22.9, 19.0, 17.8, 14.3; HRMS (FAB⁺) *m/z* calc. for C₁₆H₂₇O₂ 251.2011 found 251.2010.



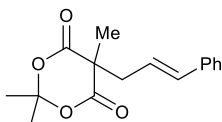
2,2-Dicinnamylcyclohexane-1,3-dione (2a):^{S7} White solid (10.0 mmol scale using

2.2 equivalents of the corresponding allylic alcohol, 2.39 g, 69% yield); m.p.: 111-

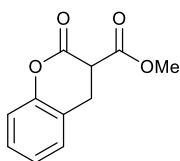
112 °C; ¹H NMR (400 MHz, CDCl₃, 30 °C): δ 7.33-7.26 (m, 8H), 7.24-7.15 (m, 2H), 6.39 (d, *J* = 15.6 Hz, 2H), 5.96 (dt, *J* = 15.6, 8.3 Hz, 2H), 2.72 (d, *J* = 7.7 Hz, 4H), 2.54 (t, *J* = 6.6 Hz, 4H), 1.86 (quint, *J* = 6.4 Hz, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 30 °C): δ 211.0, 137.0, 134.5, 128.7, 127.7, 126.4, 123.8, 68.8, 40.6, 40.4, 16.6; HRMS (FAB⁺) *m/z* calc. for C₂₄H₂₅O₂ 345.1855 found 345.1856.



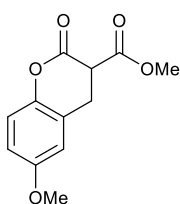
2-Cinnamyl-2-methylcyclopentane-1,3-dione (3a):^{S7} White solid (10.0 mmol scale using 1.4 equivalents of the corresponding allylic alcohol, 1.51 g, 66% yield); m.p.: 64-65 °C; IR (KBr, ν/cm^{-1}): 3460 br, 3039 w, 2988 w, 2925 w, 1759 m, 1719 s, 1493 m, 1447 m, 1319 m, 974 m; ¹H NMR (400 MHz, CDCl₃, 30 °C): δ 7.32-7.27 (m, 4H), 7.25-7.17 (m, 1H), 6.41 (d, $J = 15.8$ Hz, 1H), 5.98 (dt, $J = 15.8, 8.0$ Hz, 1H), 2.82-2.60 (m, 4H), 2.51 (d, $J = 7.8$ Hz, 2H), 1.16 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 30 °C): δ 216.4, 136.8, 134.9, 128.7, 127.8, 126.4, 122.8, 57.2, 39.3, 35.6, 19.2; HRMS (FAB⁺) m/z calc. for C₁₅H₁₆O₂ 228.1150 found 228.1147.



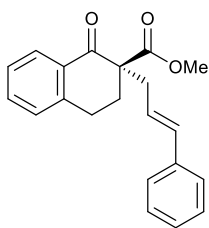
5-Cinnamyl-2,2,5-trimethyl-1,3-dioxane-4,6-dione (4a):^{S8} White solid (10 mmol scale using 1.4 equivalents of the corresponding allylic alcohol, 1.91 g, 69% yield); m.p.: 64-65 °C; IR (KBr, ν/cm^{-1}): 3496 br, 3027 w, 3006 w, 2989 w, 1778 m, 1741 s, 1452 m, 1383 m, 1324 m, 1246 m, 1205 m, 968 m; ¹H NMR (400 MHz, CDCl₃, 30 °C): δ 7.36-7.19 (m, 5H), 6.52 (d, $J = 15.8$ Hz, 1H), 6.04 (dt, $J = 15.7, 7.6$ Hz, 1H), 2.90 (d, $J = 7.5$ Hz, 2H), 1.71 (s, 3H), 1.68 (s, 3H), 1.63 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 30 °C): δ 170.1, 136.6, 136.0, 128.7, 128.0, 126.5, 122.1, 105.3, 50.5, 43.4, 29.7, 29.0, 24.5; HRMS (FAB⁺) m/z calc. for C₁₆H₁₈O₄ 274.1205 found 274.1204.



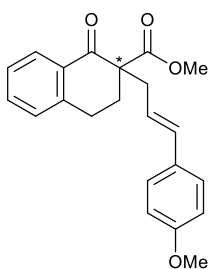
Methyl 2-oxochromane-3-carboxylate (6f):^{S9} White solid (0.70 g, 50% yield); m.p.: 97-99 °C; IR (KBr, ν/cm^{-1}): 3449 w, 2948 w, 2918 w, 2847 w, 1773 m, 1736 s, 1702 w, 1611 w, 1587 w, 1489 w, 1458 m, 1440 w, 1426 w, 1384 w, 1354 w, 1303 w, 1254 m, 1221 m, 1182 m, 1147 m, 1108 w, 1032 w, 1001 w, 945 w; ¹H NMR (400 MHz, CDCl₃, 30 °C): δ 7.32-7.26 (m, 1H), 7.24-7.19 (m, 1H), 7.16-7.10 (m, 1H), 7.10-7.05 (m, 1H), 3.78 (dd, $J = 9.0, 6.1$ Hz, 1H), 3.77 (s, 3H), 3.44 (dd, $J = 16.0, 9.0$ Hz, 1H), 3.17 (dd, $J = 16.0, 6.2$ Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 30 °C): δ 168.1, 164.8, 151.5, 128.9, 128.4, 125.0, 120.8, 117.0, 53.2, 46.4, 27.4; HRMS (FAB⁺) m/z calc. for C₁₁H₁₁O₄ 207.0657 found 207.0656.



Methyl 6-methoxy-2-oxochromane-3-carboxylate (6g): White solid (1.84 g, 86% yield); m.p.: 99-100 °C; IR (KBr, ν/cm^{-1}): 3463 w, 3045 w, 3017 w, 2981 w, 2959 w, 2939 w, 2922 w, 2839 w, 1763 s, 1739 s, 1591 w, 1496 s, 1431 m, 1362 w, 1348 w, 1304 w, 1275 s, 1235 s, 1207 s, 1169 s, 1117 w, 1025 s, 990 w; ¹H NMR (400 MHz, CDCl₃, 30 °C): δ 6.99 (d, $J = 8.9$ Hz, 1H), 6.79 (dd, $J = 8.9, 2.9$ Hz, 1H), 6.75 (d, $J = 2.9$ Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 3.75 (dd, $J = 8.8, 6.1$ Hz, 1H), 3.40 (dd, $J = 16.0, 8.8$ Hz, 1H), 3.13 (dd, $J = 16.0, 6.1$ Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 30 °C): δ 168.2, 164.9, 156.6, 145.4, 121.7, 117.8, 114.0, 113.4, 55.8, 53.2, 46.3, 27.6; HRMS (FAB⁺) m/z calc. for C₁₂H₁₃O₄ 237.0763 found 237.0761.

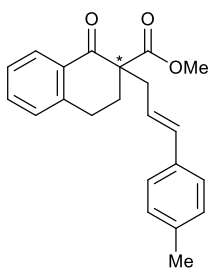


(R)-Methyl 2-cinnamyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (7aa):^{S1} White solid (31.2 mg, 97% yield); ¹H NMR (400 MHz, CDCl₃, 30 °C): δ 8.08 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.37-7.15 (m, 7H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* = 15.7, 8.0 Hz, 1H), 3.67 (s, 3H), 3.14-3.01 (m, 1H), 3.00-2.90 (m, 1H), 2.88 (d, *J* = 7.4 Hz, 2H), 2.62-2.51 (m, 1H), 2.26-2.11 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 30 °C): δ 195.1, 172.2, 143.4, 137.3, 134.1, 133.7, 132.1, 128.9, 128.6, 128.3, 127.5, 127.0, 126.4, 125.2, 58.0, 52.7, 38.2, 30.9, 26.1; HPLC (OD-3, Hexane:IPA = 95:5, 0.4 mL/min, detector: 254 nm, 30 °C): tR₁ = 22.57 min, tR₂ = 24.00 min, ee = 90%, The corresponding racemic HPLC chart was reported in our previous work;^{S1} [α]_D²⁰ = +17.6 (c = 0.720, CHCl₃) (for an ee of 90%).



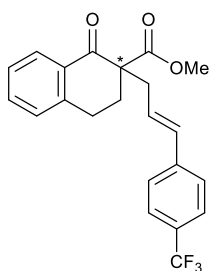
(+)-Methyl (E)-2-(3-(4-methoxyphenyl)allyl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (7ba):^{S1} Colorless oil (30.0 mg, 86% yield); ¹H NMR (400 MHz, CDCl₃, 30 °C): δ 8.07 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.46 (td, *J* = 7.5, 1.5 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 2H), 6.42 (d, *J* = 15.7 Hz, 1H), 6.08 (dt, *J* = 15.3, 7.4 Hz, 1H), 3.78 (s, 3H), 3.67 (s, 3H), 3.07 (ddd, *J* = 17.4, 10.4, 4.6 Hz, 1H), 2.93 (dt, *J* = 17.4, 5.0 Hz, 1H), 2.85 (dd, *J* = 7.6, 1.4 Hz, 2H), 2.56 (dt, *J* = 13.8, 4.8

Hz, 1H), 2.19 (ddd, *J* = 13.6, 10.4, 4.7 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 30 °C): δ 195.2, 172.2, 159.2, 143.4, 133.7, 133.4, 132.1, 130.1, 128.9, 128.2, 127.5, 126.9, 122.8, 114.0, 58.1, 55.4, 52.6, 38.2, 30.8, 26.0; HPLC (OD-3, Hexane:IPA = 95:5, 0.4 mL/min, detector: 254 nm, 30 °C): tR₁ = 43.90 min, tR₂ = 50.51 min, ee = 88%; [α]_D²⁰ = +12.8 (c = 0.880, CHCl₃) (for an ee of 89%).



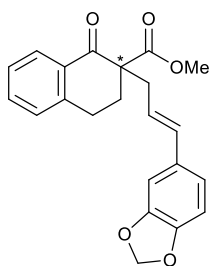
(+)-Methyl (E)-1-oxo-2-(3-(p-tolyl)allyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (7ca):^{S1} Colorless oil (27.6 mg, 83% yield); ¹H NMR (400 MHz, CDCl₃, 30 °C): δ 8.07 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.47 (td, *J* = 7.5, 1.4 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.25-7.18 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.17 (dt, *J* = 15.8, 7.4 Hz, 1H), 3.67 (s, 3H), 3.07 (ddd, *J* = 17.3, 10.4, 4.6 Hz, 1H), 2.93 (dt, *J* = 17.4, 4.9 Hz, 1H), 2.86 (dd, *J* = 7.4, 1.0 Hz, 2H), 2.56 (dt, *J* = 13.8,

4.8 Hz, 1H), 2.31 (s, 3H), 2.19 (ddd, *J* = 13.8, 10.4, 4.9 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 30 °C): δ 195.1, 172.2, 143.4, 137.2, 134.5, 133.9, 133.7, 132.1, 129.3, 128.9, 128.2, 126.9, 126.3, 124.1, 58.1, 52.6, 38.2, 30.9, 26.0, 21.3; HPLC (OD-3, Hexane:IPA = 95:5, 0.4 mL/min, detector: 254 nm, 30 °C): tR₁ = 19.19 min, tR₂ = 21.15 min, ee = 89%, The corresponding racemic HPLC chart was reported in our previous work;^{S1} [α]_D²⁰ = +10.1 (c = 0.593, CHCl₃) (for an ee of 89%).



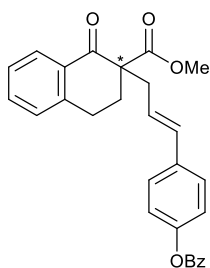
(+)-Methyl (E)-1-oxo-2-(3-(4-(trifluoromethyl)phenyl)allyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (7da):^{S1}

Colorless oil (33.4 mg, 86% yield); ¹H NMR (400 MHz, CDCl₃, 30 °C): 8.08 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.48 (td, *J* = 7.6, 1.5 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.36 (dt, *J* = 15.8, 7.4 Hz, 1H), 3.67 (s, 3H), 3.09 (ddd, *J* = 17.4, 10.7, 4.7 Hz, 1H), 2.94 (dt, *J* = 17.5, 4.8 Hz, 1H), 2.89 (d, *J* = 6.6 Hz, 2H), 2.58 (dt, *J* = 13.8, 4.7 Hz, 1H), 2.18 (ddd, *J* = 13.7, 10.7, 4.9 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 30 °C): δ 195.0, 172.1, 143.3, 140.7 (q, *J* = 1.5 Hz), 133.8, 132.7, 132.1, 129.3 (q, *J*_{C-F} = 32.3 Hz), 129.0, 128.2₇, 128.2₆, 127.0, 126.5, 125.6 (q, *J* = 4.0 Hz), 124.4 (q, *J* = 270 Hz), 58.0, 52.7, 38.3, 31.2, 26.1; ¹⁹F{¹H} NMR (376 Hz, CDCl₃, 30 °C): δ -63.6; HPLC (AD-H, Hexane:IPA = 95:5, 0.4 mL/min, detector: 254 nm, 30 °C): tR₁ = 24.53 min, tR₂ = 26.02 min, ee = 89%; [α]_D²⁰ = +23.3 (c = 1.017, CHCl₃) (for an ee of 89%).



(+)-Methyl (E)-2-(3-(benzo[d][1,3]dioxol-5-yl)allyl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (7ea):

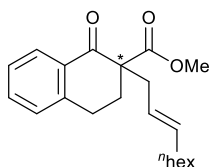
Colorless oil (34.4 mg, 94% yield); IR (KBr, v/cm⁻¹): 3448 br, 3066 w, 3028 w, 2952 w, 1734 s, 1686 s, 1602 w, 1503 m, 1490 m, 1446 m, 1349 w, 1296 w, 1251 s, 1197 m, 1124 w, 1098 w, 1038 m, 971 w; ¹H NMR (400 MHz, CDCl₃, 30 °C): δ 8.07 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 6.87 (s, 1H), 6.75 (d, *J* = 7.19 Hz, 1H), 6.70 (d, *J* = 7.19 Hz, 1H), 6.38 (d, *J* = 15.7 Hz, 1H), 6.05 (dt, *J* = 15.7, 7.3 Hz, 1H), 5.91 (s, 2H), 3.67 (s, 3H), 3.17-3.00 (m, 1H), 2.98-2.87 (m, 1H), 2.84 (d, *J* = 7.3 Hz, 2H), 2.61-2.50 (m, 1H), 2.23-2.12 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 30 °C): δ 195.1, 172.2, 148.1, 147.1, 143.4, 133.7, 133.6, 132.1, 131.8, 128.9, 128.2, 126.9, 123.3, 120.8, 108.3, 105.8, 101.1, 58.1, 52.6, 38.1, 30.9, 26.1; HPLC (OD-3, Hexane:IPA = 95:5, 0.4 mL/min, detector: 254 nm, 30 °C): tR₁ = 31.08 min, tR₂ = 34.99 min, ee = 89%; [α]_D²⁰ = +14.7 (c = 0.897, CHCl₃) (for an ee of 89%); HRMS (FAB⁺) *m/z* calcd. for C₂₂H₂₀O₅ 364.1311 found 364.1310.



(+)-Methyl (E)-2-(3-(4-(benzyloxy)phenyl)allyl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (7fa):

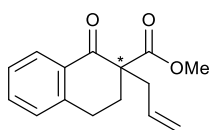
White solid (29.1 mg, 66% yield); m.p: 128-130 °C, IR (KBr, v/cm⁻¹): 3449 w, 3033 w, 2951 w, 2919 w, 2851 w, 1735 s, 1686 m, 1601 w, 1508 m, 1451 w, 1437 w, 1265 s, 1199 s, 1168 m, 1081 m, 1063 m, 1025 w, 972 w; ¹H NMR (400 MHz, CDCl₃, 30 °C): δ 8.19 (d, *J* = 7.1 Hz, 2H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.53-7.45 (m, 3H), 7.38 (d, *J* = 7.1 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* = 15.7, 7.4 Hz, 1H), 3.68 (s, 3H), 3.08 (ddd, *J* = 17.3, 10.3, 4.3 Hz, 1H), 2.94 (dt, *J* = 17.4, 4.6 Hz, 1H), 2.88 (d, *J* = 7.4 Hz, 2H), 2.58 (dt, *J* = 13.8, 4.6 Hz, 1H), 2.19 (ddd, *J* = 13.6, 10.5, 4.8 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 30 °C): δ 195.1, 172.2, 165.3, 150.3, 143.4, 135.1, 133.7₄, 132.7₀, 133.1, 132.1, 130.3, 129.7, 128.9, 128.7, 128.3, 127.3, 127.0, 125.5, 121.9, 58.0, 52.7.

38.2, 31.0, 26.1; HPLC (OD-3, Hexane:IPA = 95:5, 1.0 mL/min, detector: 254 nm, 30 °C): t_{R1} = 29.33 min, t_{R2} = 32.23 min, ee = 88%; $[\alpha]_D^{20}$ = +9.4 (c = 0.873, CHCl₃) (for an ee of 88%); $[\alpha]_D^{20}$ = +9.4 (c = 0.873, CHCl₃) (for an ee of 88%); HRMS (FAB⁺) m/z calcd. for C₂₈H₂₅O₅ 441.1702 found 441.1700.



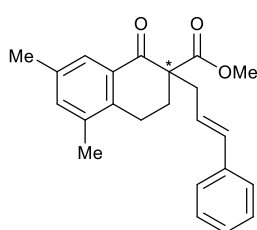
Methyl (E)-2-(non-2-en-1-yl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (7ga): The title compound was synthesized by using (*E*)-methyl non-2-en-1-yl carbonate and Pd(PPh₃)₄ as an authentic sample due to inseparable starting material on the nickel-catalyzed AAA reaction. Colorless liquid; ¹H NMR (400

MHz, CDCl₃, 30 °C): δ 8.05 (dd, J = 7.8, 1.0 Hz, 1H), 7.46 (td, J = 7.5, 1.2 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 7.6 Hz, 1H), 5.53 (dt, J = 15.2, 6.7 Hz, 1H), 5.40 (dt, J = 15.2, 7.2 Hz, 1H), 3.66 (s, 3H), 3.06 (ddd, J = 17.2, 10.2, 4.8 Hz, 1H), 2.91 (dt, J = 17.3, 5.0 Hz, 1H), 2.72-2.58 (m, 2H), 2.51 (dt, J = 13.8, 4.9 Hz, 1H), 2.14 (ddd, J = 15.0, 10.2, 4.9 Hz, 1H), 1.97 (q, J = 7.0 Hz, 2H), 1.35-1.18 (m, 8H), 0.86 (t, J = 6.8 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 30 °C): δ 195.3, 172.3, 143.5, 135.6, 133.6, 132.2, 128.9, 128.2, 126.9, 124.5, 57.9, 52.5, 37.7, 32.7, 31.8, 30.5, 29.5, 28.9, 26.0, 22.8, 14.2; HPLC (OD-3, Hexane:IPA = 98:2, 0.4 mL/min, detector: 254 nm, 30 °C): t_{R1} = 12.78 min, t_{R2} = 13.83 min, ee = 76%; HRMS (FAB⁺) m/z calcd. for C₂₁H₂₉O₃ 329.2117 found 329.2119.



(+)-Methyl 2-allyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (7ha):^{S1}

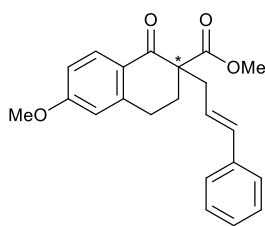
Colorless oil (15.7 mg, 64% yield); ¹H NMR (400 MHz, CDCl₃, 30 °C): δ 8.05 (d, J = 7.9 Hz, 1H), 7.47 (t, J = 7.1 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 5.88-5.75 (m, 1H), 5.14 (d, J = 16.6 Hz, 1H), 5.11 (d, J = 9.7 Hz, 1H), 3.67 (s, 3H), 3.15-3.02 (m, 1H), 2.92 (d, J = 17.4 Hz, 1H), 2.80-2.65 (m, 2H), 2.58-2.48 (m, 1H), 2.20-2.10 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 30 °C): δ 195.1, 172.1, 143.4, 133.7, 133.5, 132.1, 128.9, 128.3, 126.9, 119.1, 57.6, 52.6, 38.9, 30.7, 26.0; HPLC (OD-3, Hexane:IPA = 95:5, 0.4 mL/min, detector: 254 nm, 30 °C): t_{R1} = 13.98 min, t_{R2} = 15.34 min, ee = 69%, The corresponding racemic HPLC chart was reported in our previous work,^{S1} $[\alpha]_D^{20}$ = +30.4 (c = 0.457, CHCl₃) (for an ee of 69%).



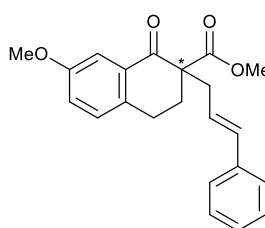
(+)-Methyl 2-cinnamyl-5,7-dimethyl-1-oxo-1,2,3,4-tetrahydronaphthalene-

2-carboxylate (7ab):^{S1} Colorless oil (34.4 mg, 99% yield); ¹H NMR (400 MHz, CDCl₃, 30 °C): δ 7.76 (s, 1H), 7.35-7.30 (m, 2H), 7.30-7.24 (m, 2H), 7.23-7.16 (m, 2H), 6.47 (d, J = 15.8 Hz, 1H), 6.24 (dt, J = 15.8, 7.5 Hz, 1H), 3.65 (s, 3H), 2.90-2.76 (m, 4H), 2.89 (dt, J = 13.9, 5.6 Hz, 1H), 2.33 (s, 3H), 2.24 (s, 3H), 2.18-2.10 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 30 °C): δ 195.6, 172.1,

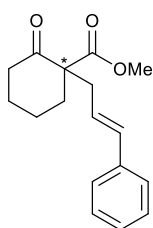
138.8, 137.3, 136.4, 136.2, 136.1, 139.9, 132.1, 128.6, 127.4, 126.4, 126.2, 125.3, 57.5, 52.6, 38.1, 30.3, 23.1, 21.0, 19.3; HPLC (AD-H, Hexane:IPA = 95:5, 0.4 mL/min, detector: 254 nm, 30 °C): t_{R1} = 20.45 min, t_{R2} = 22.20 min, ee = 85%, The corresponding racemic HPLC chart was reported in our previous work,^{S1} $[\alpha]_D^{20}$ = +14.0 (c = 0.587, CHCl₃) (for an ee of 85%).



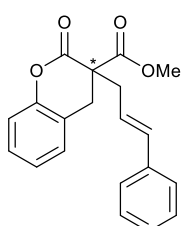
(+)-Methyl 2-cinnamyl-6-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (7ac):^{S1} Colorless oil (33.9 mg, 97% yield); ¹H NMR (400 MHz, CDCl₃, 30 °C): δ 8.05 (d, *J* = 9.0 Hz, 1H), 7.35-7.24 (m, 4H), 7.19 (tt, *J* = 7.0, 1.3 Hz, 1H), 6.84 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.65 (d, *J* = 2.6 Hz, 1H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 15.8, 7.6 Hz, 1H), 3.84 (s, 3H), 3.68 (s, 3H), 3.04 (ddd, *J* = 17.3, 10.3, 4.7 Hz, 1H), 2.94-2.83 (m, 3H), 2.54 (dt, *J* = 13.7, 5.0 Hz, 1H), 2.17 (ddd, *J* = 13.6, 10.3, 4.9 Hz, 1H); ¹³C {¹H} NMR (100 MHz, CDCl₃, 30 °C): δ 193.7, 172.4, 163.9, 145.9, 137.3, 133.9, 130.8, 128.6, 127.4, 126.4, 125.6, 125.4, 113.7, 112.6, 57.7, 55.6, 52.6, 38.3, 30.9, 26.4; HPLC (OD-3, Hexane:IPA = 95:5, 0.4 mL/min, detector: 254 nm, 30 °C): t_{R1} = 36.67 min, t_{R2} = 39.83 min, ee = 88%, The corresponding racemic HPLC chart was reported in our previous work;^{S1} [α]_D²⁰ = +17.4 (c = 0.787, CHCl₃) (for an ee of 88%).



(+)-Methyl 2-cinnamyl-7-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (7ad):^{S1} Colorless oil (34.2 mg, 98% yield); ¹H NMR (400 MHz, CDCl₃, 30 °C): δ 7.55 (d, *J* = 2.5 Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 8.6 Hz, 1H), 7.05 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* = 15.3, 7.5 Hz, 1H), 3.84 (s, 3H), 3.68 (s, 3H), 2.99 (ddd, *J* = 17.1, 10.4, 4.6 Hz, 1H), 2.92-2.80 (m, 3H), 2.55 (dt, *J* = 14.0, 4.7 Hz, 1H), 2.17 (ddd, *J* = 14.9, 10.7, 5.1 Hz, 1H); ¹³C {¹H} NMR (100 MHz, CDCl₃, 30 °C): δ 195.1, 172.2, 158.6, 137.3, 136.0, 134.1, 132.8, 130.1, 128.6, 127.5, 126.4, 125.2, 122.3, 110.0, 57.9, 55.6, 52.6, 38.2, 31.3, 25.3; HPLC (OD-3, Hexane:IPA = 95:5, 0.4 mL/min, detector: 254 nm, 30 °C): t_{R1} = 25.10 min, t_{R2} = 26.92 min, ee = 87%, The corresponding racemic HPLC chart was reported in our previous work;^{S1} [α]_D²⁰ = +12.0 (c = 0.126, CHCl₃) (for an ee of 87%).

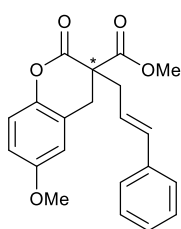


(+)-Methyl 1-cinnamyl-2-oxocyclohexane-1-carboxylate (7ae):^{S1} Colorless oil (19.1 mg, 70% yield); ¹H NMR (400 MHz, CDCl₃, 30 °C): δ 7.31 (d, *J* = 7.3 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.19 (t, *J* = 6.9 Hz, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 6.15 (dt, *J* = 15.9, 7.8 Hz, 1H), 3.69 (s, 3H), 2.75 (dd, *J* = 13.9, 7.2 Hz, 1H), 2.55-2.44 (m, 4H), 2.07-1.96 (m, 1H), 1.82-1.48 (m, 4H); ¹³C {¹H} NMR (100 MHz, CDCl₃, 30 °C): δ 207.6, 172.2, 137.4, 133.4, 128.6, 127.4, 126.3, 125.2, 61.6, 52.4, 41.3, 38.7, 36.1, 27.6, 22.6; HPLC (OD-3, Hexane:IPA = 95:5, 0.4 mL/min, detector: 254 nm, 30 °C): t_{R1} = 16.08 min, t_{R2} = 17.54 min, ee = 90%; [α]_D²⁰ = +65.9 (c = 0.513, CHCl₃) (for an ee of 90%).



(+)-Methyl 3-cinnamyl-2-oxochromane-3-carboxylate (7af): White solid (29.0 mg, 90% yield); m.p.: 96-98 °C; IR (KBr, v/cm⁻¹): 3448 w, 3082 w, 3048 w, 3025 w, 2955 w, 2917 w, 2848 w, 1772 s, 1738 s, 1686 w, 1655 w, 1611 w, 1588 w, 1560 w, 1543 w, 1509 w, 1491 m, 1458 m, 1431 w, 1346 w, 1321 w, 1303 w, 1234 m, 1214 m, 1195 m, 1167 m, 1111 w, 1052 w, 1016 w, 969 w; ¹H NMR (400 MHz, CDCl₃, 30 °C): δ 7.39-

7.26 (m, 4H), 7.26-7.20 (m, 2H), 7.17 (d, $J = 7.5$ Hz, 1H), 7.09 (t, $J = 7.5$ Hz, 1H), 7.05 (d, $J = 8.2$ Hz, 1H), 6.48 (d, $J = 15.8$ Hz, 1H), 6.28 (dt, $J = 15.5, 7.4$ Hz, 1H), 3.61 (s, 3H), 3.34 (d, $J = 16.0$ Hz, 1H), 3.09 (d, $J = 16.0$ Hz, 1H), 3.00-2.82 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 30 °C): δ 170.1, 167.1, 151.2, 136.9, 135.3, 128.8, 128.7, 128.5, 127.8, 126.5, 124.9, 123.4, 121.3, 116.7, 53.7, 53.2, 38.0, 32.5; HPLC (Daicel OD-3, temperature: 30 °C, Hexane:IPA = 95:5, flow rate 0.4 mL/min, detector: 254 nm, $t_{\text{R}1} = 26.88$ min, $t_{\text{R}2} = 35.51$ min); $[\alpha]_{\text{D}}^{20} = +23.9$ ($c = 0.913$, CHCl_3) (for an ee of 40%); HRMS (FAB⁺) m/z calc. for $\text{C}_{20}\text{H}_{19}\text{O}_4$ 323.1283 found 323.1280.



(+)-Methyl 3-cinnamyl-6-methoxy-2-oxochromane-3-carboxylate (7ag): White

solid (31.5 mg, 89% yield); m.p.: 134-135 °C; IR (KBr, v/cm^{-1}): 3449 w, 3081 w, 3025 w, 3003 w, 2961 w, 2938 w, 2917 w, 2835 w, 1760 m, 1737 s, 1593 w, 1496 m, 1449 w, 1435 m, 1334 w, 1281 w, 1243 m, 1216 m, 1200 s, 1159 m, 1122 w, 1085 w, 1067 w, 1052 w, 1041 w, 1020 w, 977 w; ^1H NMR (400 MHz, CDCl_3 , 30 °C): δ 7.35 (d, $J = 7.5$ Hz, 2H), 7.30 (t, $J = 7.4$ Hz, 2H), 7.22 (t, $J = 6.9$ Hz, 2H), 6.97 (d, $J = 8.8$ Hz,

1H), 6.77 (dd, $J = 8.9, 2.9$ Hz, 1H), 6.69 (d, $J = 2.9$ Hz, 1H), 6.48 (d, $J = 15.8$ Hz, 1H), 6.27 (dt, $J = 15.4, 7.4$ Hz, 1H), 3.77 (s, 3H), 3.62 (s, 3H), 3.29 (d, $J = 16.0$ Hz, 1H), 3.06 (d, $J = 15.9$ Hz, 1H), 2.97-2.83 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 30 °C): δ 170.2, 167.2, 156.5, 145.1, 136.9, 135.3, 128.7, 127.8, 126.5, 123.4, 122.2, 117.4, 114.0, 113.4, 55.7, 53.6, 53.2, 38.0, 32.8; HPLC (Daicel OD-3, temperature: 30 °C, Hexane:IPA = 95:5, flow rate 0.4 mL/min, detector: 254 nm, $t_{\text{R}1} = 46.57$ min, $t_{\text{R}2} = 51.17$ min); $[\alpha]_{\text{D}}^{20} = +31.1$ ($c = 1.013$, CHCl_3) (for an ee of 48%); HRMS (FAB⁺) m/z calc. for $\text{C}_{21}\text{H}_{21}\text{O}_5$ 353.1389 found 353.1392.

5. DFT Studies

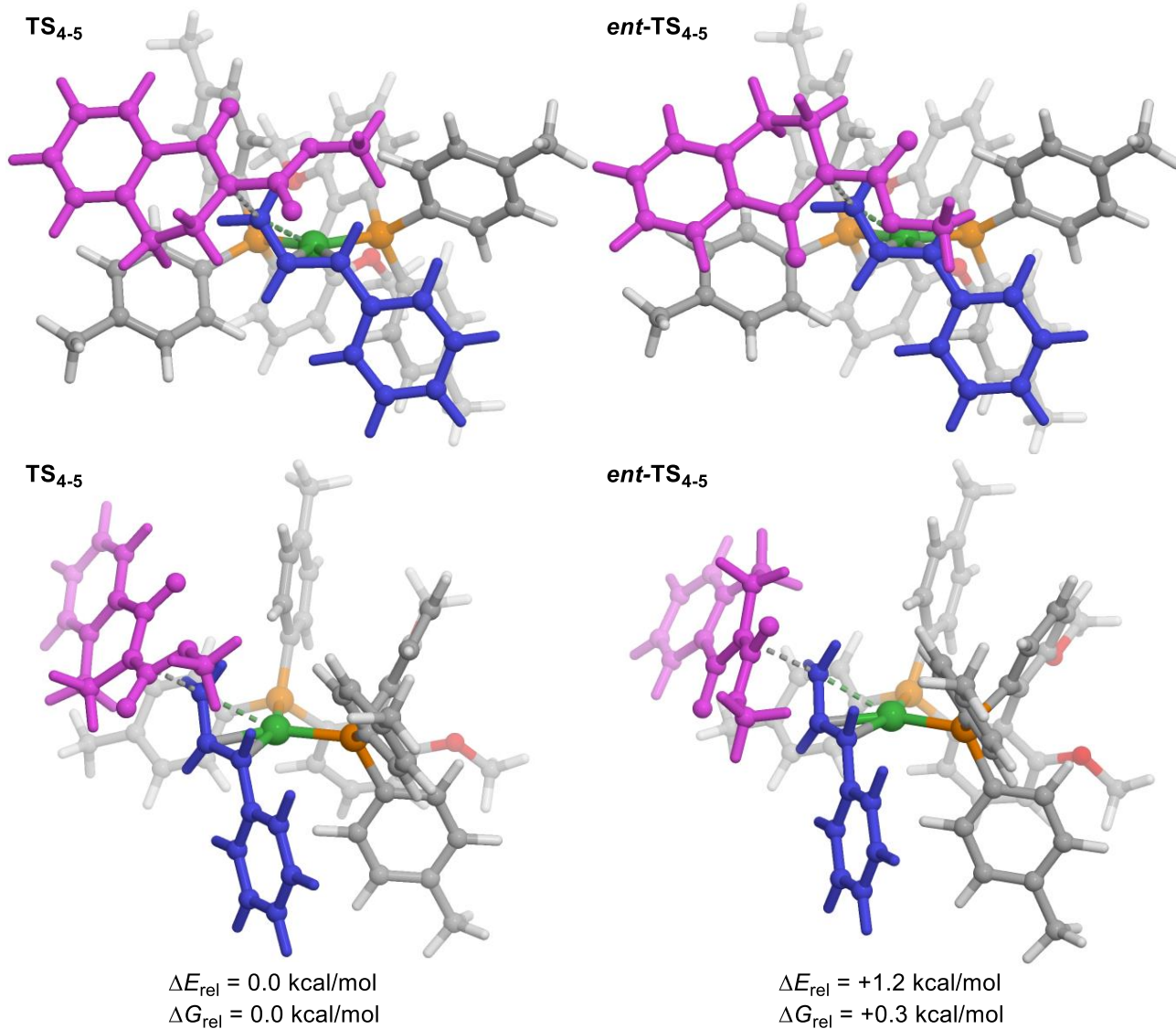
5.1. General Procedure

All geometry optimizations and single-point calculations were performed by Gaussian 16 package.^{S10} The geometry optimizations were conducted at the M06 functional^{S11} in conjunction with the lanl2dz (for Ni) and 6-31+G(d) (for other) basis set using SMD (Et₂O)^{S12} as a solvation model. Frequency analyses were performed at the same level of theory for geometry optimizations, in which the thermal free energy corrections were provided. The single imaginary frequency was confirmed for each transition states, which were traced with intrinsic reaction coordinate (IRC) analyses to describe the reaction pathway. Additional single-point calculations were performed at the M06 functional in conjunction with the SDD (for Ni) and 6-311+G(2d,p) (for other) basis set with SMD (Et₂O) as a solvation model, based on geometries obtained through the method described as above. The solution phase Gibbs free energies (G_{sol}) at 298.15 K (25 °C) were obtained from $G_{\text{sol}} = E + G_{\text{corr}}$, wherein the solvation electronic energies (E) were given from single-point energy calculations at the M06/SDD,6-311+G(2d,p)/SMD level of theory and thermal free energy corrections (G_{corr}) were given from frequency analyses at the M06/lanl2dz,6-31+G(d)/SMD level of theory. Relative Gibbs free energies (ΔG_{sol}) were calculated from $\Delta G_{\text{sol}} = \Sigma G_{\text{sol}}(\text{for products}) - \Sigma G_{\text{sol}}(\text{for reactants})$.

5.2. Summary of Energies

Structure Name	Electronic Energy (E) [Hartree]	Thermal Free Energy Correction (G_{corr}) [Hartree]	Gibbs Free Energy (E + G_{corr}) [Hartree]
Int-1	-2939.785528	0.792784	-2938.992744
Int-2	-3398.595105	0.902037	-3397.693068
TS₂₋₃	-3398.561649	0.898651	-3397.662998
Int-3	-3398.575423	0.899042	-3397.676381
Int-4	-3665.439101	0.952678	-3664.486423
TS₄₋₅	-3665.428961	0.953485	-3664.475476
Int-5	-3665.471454	0.953714	-3664.517740
<i>ent</i> - TS₄₋₅	-3665.427070	0.952006	-3664.475064
1a	-770.663204	0.254690	-770.408514
6a	-689.953128	0.179059	-689.774069
8	-423.079180	0.126139	-422.953041
COD	-311.867458	0.147551	-311.719907

5.3. Structures of TS₄₋₅ and *ent*-TS₄₋₅



5.4. Cartesian Coordinates (xyz file format)

107				H	-0.11094000	-4.14446100	3.46422200
Int-1				C	1.44583700	-2.47585700	-3.22348100
P	-1.65823100	0.28635500	0.15017100	H	0.11092000	-4.14442000	-3.46421900
C	-1.28379400	-1.23610500	1.14483000	H	2.65089200	-0.77290400	-2.75844600
C	-2.24429900	-0.49327800	-1.41920100	C	3.23256800	0.94560700	-0.85806900
C	-3.23255300	0.94559400	0.85808600	C	2.24429700	-0.49322000	1.41921400
C	-0.29275600	-2.12541100	0.68916800	H	1.91021000	-2.61941100	-4.19915300
C	-1.85963300	-1.43202600	2.40812900	C	4.40683200	1.08224300	-0.11151700
C	-3.18386400	-1.52985200	-1.41225500	C	3.20868900	1.52243300	-2.13900600
C	-1.73232600	-0.07159500	-2.64896300	C	3.18384800	-1.52980600	1.41228300
C	-3.20863700	1.52244800	2.13901000	C	1.73235700	-0.07148400	2.64897200
C	-4.40682600	1.08224900	0.11155200	C	5.51775200	1.74810200	-0.63188800
C	0.29278500	-2.12540700	-0.68914400	H	4.46518400	0.68025900	0.89977400
C	0.12788700	-3.16776400	1.54606600	C	4.32168400	2.16658600	-2.66157300
C	-1.44585100	-2.47589000	3.22348300	H	2.29530300	1.47908900	-2.73471500
H	-2.65090300	-0.77293600	2.75844300	C	3.59992700	-2.12099700	2.60058600
C	-3.59993800	-2.12106800	-2.60054800	H	3.59069300	-1.88822900	0.46423300
H	-3.59072900	-1.88824300	-0.46420200	C	2.14610700	-0.66676800	3.83698300
C	-2.14606900	-0.66690500	-3.83696400	H	0.97549400	0.71446200	2.67359300
H	-0.97543800	0.71432600	-2.67359500	C	5.50109800	2.29353500	-1.91519000
C	-4.32160500	2.16664200	2.66158400	H	6.41730300	1.84320600	-0.02102900
H	-2.29524000	1.47909500	2.73470200	H	4.27391300	2.59617200	-3.66443700
C	-5.51771900	1.74814800	0.63192900	C	3.08181800	-1.70565100	3.83196000
H	-4.46520400	0.68025800	-0.89973500	H	4.33120900	-2.93176100	2.57267700
C	-0.12787700	-3.16774800	-1.54604500	H	1.72121200	-0.33280200	4.78574800
C	1.28380900	-1.23608900	-1.14481600	O	-1.10403900	-3.97308000	-1.06237400
C	-0.43901500	-3.34119900	2.80841400	O	1.10405400	-3.97310400	1.06242400
H	-1.91023900	-2.61945400	4.19914700	C	-1.61668200	-4.98722400	-1.89624100
C	-3.08180400	-1.70576500	-3.83192600	H	-2.41764300	-5.47133700	-1.32910200
H	-4.33123500	-2.93181800	-2.57262600	H	-2.03645900	-4.57377100	-2.82722200
H	-1.72115000	-0.33297700	-4.78573100	H	-0.84819000	-5.73567500	-2.14223300
C	-5.50102800	2.29360900	1.91521900	C	1.61662200	-4.98726400	1.89631800
H	-4.27380300	2.59625000	3.66443700	H	2.41761900	-5.47138300	1.32923500
H	-6.41727800	1.84327000	0.02108300	H	2.03633000	-4.57382400	2.82733600
C	0.43900300	-3.34116700	-2.80840600	H	0.84810100	-5.73570700	2.14224500
C	1.85963000	-1.43200000	-2.40812500	C	-3.47517000	-2.38763600	-5.10755200
P	1.65823200	0.28638400	-0.15017100	H	-3.63536700	-1.66726900	-5.92108700

H	-2.68429100	-3.07620800	-5.44377700	P	1.76333700	-0.75999200	0.63800400
H	-4.39385600	-2.97610400	-4.98708900	C	2.16158400	0.82537600	1.50574700
C	-6.69525200	2.99342100	2.49001000	C	3.06235000	-0.88821800	-0.64448300
H	-7.49040400	3.11524600	1.74377900	C	2.20350700	-2.06795500	1.85354200
H	-7.11658300	2.43246500	3.33687000	C	2.07035600	2.03742600	0.79822900
H	-6.43217300	3.99072100	2.86930800	C	2.38816100	0.84325300	2.88816400
C	6.69535400	2.99329600	-2.48997700	C	4.39435200	-0.52251400	-0.41387600
H	7.49050400	3.11509900	-1.74374000	C	2.70666300	-1.38114900	-1.90162900
H	7.11667100	2.43231700	-3.33682900	C	1.29960400	-2.30098200	2.90221500
H	6.43231600	3.99060300	-2.86928600	C	3.30029200	-2.92188900	1.72775200
C	3.47518100	-2.38750100	5.10759700	C	1.95595500	2.13753400	-0.68976100
H	3.63545900	-1.66711400	5.92109900	C	2.18415500	3.24940000	1.51153700
H	2.68426400	-3.07600200	5.44387700	C	2.50939400	2.04803500	3.56790700
H	4.39382000	-2.97603800	4.98712400	H	2.47622900	-0.09022600	3.44103800
Ni	-0.00001300	1.74434200	-0.00001800	C	5.34145900	-0.65051500	-1.42186900
C	1.13950900	3.12998300	1.16426200	H	4.69100600	-0.13017300	0.56090400
H	1.79693700	2.52962000	1.80023800	C	3.66013200	-1.50409800	-2.91045700
C	-0.18382400	3.25197300	1.54849300	H	1.67039700	-1.67219800	-2.09493600
H	-0.49839200	2.70751400	2.44270700	C	1.50507600	-3.33227400	3.80769400
C	-1.09250800	4.36669700	1.07851800	H	0.41583300	-1.66441000	3.00323800
H	-0.49800600	5.28230800	0.93644400	C	3.49473900	-3.96881800	2.63085200
H	-1.81370700	4.60698200	1.87416400	H	4.00710500	-2.79233400	0.90768600
C	-1.86980600	4.03592200	-0.20435700	C	3.12444200	2.49506000	-1.39572100
H	-2.81097000	3.53741900	0.07248100	C	0.75660400	1.97948700	-1.40567300
H	-2.16782600	4.97227800	-0.71323900	C	2.39852500	3.25746900	2.89067100
C	-1.13957500	3.12991400	-1.16435700	H	2.69113300	2.04892500	4.64243100
H	-1.79699100	2.52951100	-1.80030800	C	4.98870500	-1.13541500	-2.68881100
C	0.18375400	3.25191200	-1.54859500	H	6.37798500	-0.36315300	-1.23019100
H	0.49832600	2.70742200	-2.44278900	H	3.36353500	-1.89077400	-3.88716300
C	1.09242000	4.36667100	-1.07866800	C	2.60841700	-4.18921600	3.68539800
H	0.49790300	5.28228000	-0.93664500	H	0.79185000	-3.49042200	4.61903600
H	1.81362000	4.60692900	-1.87432200	H	4.35474200	-4.62930100	2.50738400
C	1.86971700	4.03597700	0.20423100	C	3.09922400	2.69642900	-2.77670800
H	2.81090400	3.53750000	-0.07257300	C	0.73792700	2.19538000	-2.79001500
H	2.16769400	4.97236700	0.71307600	P	-0.71828300	1.26297300	-0.55084000
				H	2.48489400	4.19343900	3.43794400
				C	1.89859700	2.55223400	-3.46307700
				H	4.00156200	2.96840400	-3.31941400

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H	-0.18903900	2.08734800	-3.35024900	H	3.69888900	-5.90420200	4.41391900
C	-2.07861700	1.45250200	-1.77660800	H	2.94072400	-4.92481900	5.68503600
C	-1.11196900	2.49146700	0.74865400	C	-5.33539400	1.43348900	-4.63098400
H	1.87190400	2.72058500	-4.53942300	H	-5.92027700	2.36141900	-4.60130300
C	-3.09487100	2.40800300	-1.70586800	H	-4.98907600	1.27972100	-5.66191900
C	-2.13954700	0.49930200	-2.80559000	H	-6.01892900	0.60280000	-4.39778100
C	-1.05971600	3.87303900	0.52648000	C	-2.00654800	5.27450400	3.92856900
C	-1.47356200	2.02773600	2.01626800	H	-2.50963800	4.79258500	4.77616000
C	-4.13529200	2.41123500	-2.63705500	H	-1.07175700	5.71444700	4.30855400
H	-3.09320500	3.15676300	-0.91311900	H	-2.63497300	6.10772400	3.58603500
C	-3.16843500	0.51299800	-3.73723900	Ni	-0.35213000	-0.81239300	0.03613300
H	-1.36127200	-0.26523700	-2.87510500	C	-1.04025600	-2.67431800	0.15832500
C	-1.37011900	4.76144700	1.54851900	C	-2.07460600	-1.75085300	-0.12643700
H	-0.76409200	4.25679500	-0.45205300	C	-0.32068200	-3.47237400	-0.84387000
C	-1.78107700	2.92258900	3.03916600	H	-0.94849900	-3.04358800	1.18724600
H	-1.49391100	0.95209600	2.20952400	C	-3.06655900	-1.34121500	0.92685000
C	-4.19187400	1.46786700	-3.66404200	H	-2.43850700	-1.66348900	-1.15745200
H	-4.92420500	3.16138400	-2.55501300	C	-0.56344500	-3.37668600	-2.22637300
H	-3.19372100	-0.24055000	-4.52673400	C	0.68224800	-4.36566400	-0.42373700
C	-1.72854100	4.30177900	2.82284700	H	-2.65351200	-1.52767400	1.93211500
H	-1.32493100	5.83687300	1.36212700	H	-3.26250000	-0.25969000	0.86501800
H	-2.05291800	2.54352000	4.02560000	C	0.18032600	-4.11784000	-3.14082000
O	4.24745400	2.62524700	-0.65039500	H	-1.35304700	-2.71886000	-2.59295400
O	2.07423100	4.38016400	0.77405300	C	1.43009900	-5.09987700	-1.33692000
C	5.45627500	2.94126000	-1.30489400	H	0.88215200	-4.46545600	0.64552500
H	6.23004900	2.94237500	-0.53108400	C	1.18856800	-4.97862100	-2.70647300
H	5.71229700	2.19064200	-2.06868800	H	-0.03424300	-4.02382300	-4.20600200
H	5.41267900	3.93685300	-1.77161500	H	2.20811400	-5.77334000	-0.97511100
C	2.11097300	5.62329100	1.43921300	H	1.77228500	-5.55358400	-3.42478700
H	1.95032400	6.38485300	0.67001800	C	-4.43846400	-2.11341900	0.86168500
H	1.31382300	5.70196200	2.19537400	C	-5.06410500	-1.80697400	-0.49046300
H	3.08665100	5.79633200	1.91765100	C	-5.27937400	-1.53154500	2.00139900
C	6.01796000	-1.22919700	-3.77444200	C	-4.21958400	-3.60469400	1.05750600
H	6.91669800	-1.76122500	-3.43287200	C	-5.56220300	-0.40192800	-0.74129700
H	5.62930400	-1.75171800	-4.65737300	O	-5.13419100	-2.64775100	-1.37108200
H	6.34397800	-0.22887000	-4.09763700	C	-6.28975900	-0.46642400	1.66029300
C	2.81245700	-5.30730900	4.66233600	O	-5.12216500	-1.91979200	3.14543700
H	1.94606400	-5.98339200	4.68304500	H	-3.60773300	-4.01414100	0.24629000

H	-3.71201300	-3.79051800	2.01131000	C	5.08770400	-0.97343600	-2.53163800
H	-5.17450800	-4.14750800	1.06552000	H	6.38985000	-0.14757900	-1.02272200
C	-5.84469000	0.42785900	0.50960600	H	3.53632500	-1.77666300	-3.79480600
H	-6.46233700	-0.50188000	-1.36568100	C	2.56051400	-3.90810400	3.86522400
H	-4.81029100	0.08906200	-1.38112500	H	0.66030800	-3.27712900	4.67312400
H	-6.52563400	0.09640500	2.57168600	H	4.38698400	-4.29939100	2.79573900
H	-7.21151600	-1.00346700	1.36863000	C	3.03848700	2.76677000	-2.82262600
H	-6.62573300	1.16801900	0.29238000	C	0.69116000	2.20078500	-2.87257600
H	-4.95801100	1.00520200	0.81168700	P	-0.77034500	1.30459500	-0.62974100
				H	2.18338000	4.40572000	3.33679700
123				C	1.85598200	2.57541600	-3.52933800
TS₂₋₃				H	3.94348100	3.05082400	-3.35452700
P	1.72720300	-0.63953000	0.65311300	H	-0.22366400	2.05613800	-3.44444800
C	2.02181000	0.98144900	1.48952700	C	-2.14319000	1.35214100	-1.84549300
C	3.06705900	-0.75095700	-0.58068600	C	-1.23523100	2.53713100	0.63124600
C	2.13751100	-1.89485600	1.92447700	H	1.84714700	2.72089300	-4.60909600
C	1.93879900	2.17012200	0.74414400	C	-3.28499800	2.13876100	-1.68149000
C	2.18367400	1.04024000	2.87987400	C	-2.13092000	0.40677800	-2.88383400
C	4.37725100	-0.34733100	-0.29387200	C	-1.23070800	3.91024100	0.35578600
C	2.77829200	-1.26161000	-1.84747000	C	-1.63494100	2.10094200	1.89620500
C	1.19245500	-2.13191200	2.93483100	C	-4.38186200	1.98346700	-2.53057500
C	3.28325600	-2.69037500	1.88814000	H	-3.34277700	2.86714800	-0.87205200
C	1.87145000	2.22658800	-0.74744900	C	-3.22124600	0.26124200	-3.72845500
C	1.99134700	3.40413200	1.42636300	H	-1.25720700	-0.23620600	-3.02024600
C	2.24829200	2.26635200	3.52852200	C	-1.62091200	4.81970300	1.32942100
H	2.26620700	0.12530500	3.46308400	H	-0.91755600	4.26763400	-0.62717600
C	5.37089000	-0.46383500	-1.25687400	C	-2.02459900	3.01888200	2.86965700
H	4.61936100	0.06626300	0.68709800	H	-1.63115800	1.03337100	2.12936700
C	3.77894900	-1.37400700	-2.80991200	C	-4.37292300	1.04302800	-3.56019900
H	1.75881400	-1.57347200	-2.08583000	H	-5.27160100	2.59550200	-2.37098600
C	1.40597300	-3.11253400	3.89328200	H	-3.19561900	-0.48865800	-4.52110000
H	0.27425900	-1.53872100	2.96945800	C	-2.01802900	4.39005600	2.60345100
C	3.48745600	-3.68372100	2.84660900	H	-1.61429400	5.88860200	1.10485500
H	4.02154000	-2.55867700	1.09700300	H	-2.33029400	2.66381200	3.85488600
C	3.04463000	2.59761200	-1.43683100	O	4.14690300	2.77149700	-0.67263100
C	0.69373800	2.02007800	-1.48408500	O	1.88335700	4.50931300	0.65340500
C	2.14297400	3.45368200	2.81276000	C	5.36416500	3.09558000	-1.30982500
H	2.38016600	2.30092300	4.60951200	H	6.11971700	3.13469200	-0.51935800

H	5.65177700	2.32862700	-2.04566800	H	0.84781000	-4.48056800	-4.02061900
H	5.30976200	4.07647800	-1.80492800	H	2.61467700	-5.91641000	-0.36736600
C	1.86980300	5.77248100	1.28356100	H	2.51699200	-5.92091100	-2.86107600
H	1.71566900	6.50722400	0.48762800	C	-4.61630500	-2.41844300	0.75433900
H	1.04774400	5.85196400	2.01185900	C	-5.26502000	-1.99855600	-0.46735700
H	2.82570600	5.98109600	1.78656000	C	-4.91873300	-1.76921800	2.00908600
C	6.16741600	-1.05836400	-3.56733900	C	-4.03477800	-3.79810400	0.80175400
H	7.06554200	-1.55256000	-3.17215700	C	-6.08507100	-0.72018100	-0.46339400
H	5.83623400	-1.61297500	-4.45389200	O	-5.17951700	-2.64058200	-1.52710600
H	6.47628500	-0.05561100	-3.89944300	C	-5.75158200	-0.49992400	2.00328000
C	2.77600900	-4.96661500	4.90347400	O	-4.52419100	-2.20700100	3.10378900
H	1.93134000	-5.66863300	4.93915400	H	-3.52174400	-4.04625300	-0.13607800
H	3.68792000	-5.54446200	4.70865300	H	-3.32407900	-3.89789700	1.63206400
H	2.86515600	-4.52651200	5.90694500	H	-4.81729700	-4.56072300	0.95102600
C	-5.56382100	0.83539200	-4.44366700	C	-5.77325100	0.23727600	0.67489400
H	-6.38006900	1.52369900	-4.19085400	H	-7.14298000	-1.03260000	-0.40497100
H	-5.31027800	0.98462600	-5.50274400	H	-5.96274300	-0.24137400	-1.44695700
H	-5.94613600	-0.19145700	-4.34929800	H	-5.39310100	0.13990600	2.82261500
C	-2.40021800	5.39100900	3.65099000	H	-6.77794900	-0.80107700	2.27913600
H	-2.82369900	4.90699000	4.53953800	H	-6.51445900	1.04978300	0.70103900
H	-1.52554800	5.97475300	3.97526300	H	-4.80079900	0.72716400	0.50303400
H	-3.13831400	6.10987000	3.26963800				
Ni	-0.35829800	-0.79804200	-0.05792300	123			
C	-0.75208300	-2.76749900	0.02114400	Int-3			
C	-1.85984600	-2.04008800	-0.49372300	P	1.70907100	0.32620800	-0.50960200
C	0.09745700	-3.64460700	-0.79522300	C	1.16586000	-0.82169900	-1.85254200
H	-0.74752600	-2.99241300	1.09410500	C	3.09721300	-0.53907500	0.29349400
C	-2.66383200	-1.23739800	0.33453300	C	2.44157200	1.75489500	-1.38626300
H	-2.09961700	-2.06153200	-1.55949700	C	0.73925200	-2.11784400	-1.52164300
C	0.05115200	-3.66498400	-2.19970900	C	1.04428800	-0.36426500	-3.17053700
C	1.02758600	-4.48212200	-0.15919800	C	4.12141900	-1.12856500	-0.45665500
H	-2.47831300	-1.19700800	1.41007400	C	3.13227100	-0.64170000	1.68575900
H	-3.22272000	-0.41634100	-0.10540200	C	1.57964800	2.62042400	-2.07574600
C	0.90821100	-4.47968600	-2.93209000	C	3.80279000	2.06126600	-1.34771700
H	-0.66231600	-3.03514600	-2.73286800	C	0.92776500	-2.74756400	-0.18242300
C	1.89575200	-5.28564400	-0.89109900	C	0.15515300	-2.91965500	-2.52490800
H	1.06965300	-4.48975200	0.93137300	C	0.47822400	-1.17527700	-4.14522600
C	1.84208100	-5.28937900	-2.28435800	H	1.39154000	0.62751600	-3.44841500

C	5.15844000	-1.79776000	0.18121500	C	-3.20553000	-0.61096700	-2.58408500
H	4.10251500	-1.07322100	-1.54675900	H	-1.94906700	0.60567700	-1.33247800
C	4.16866300	-1.31999100	2.31876100	C	-3.63312100	-1.17853500	4.73813700
H	2.32933800	-0.19970300	2.27904600	H	-5.28058200	-1.69982600	3.45609500
C	2.07254700	3.73848000	-2.73428900	H	-1.78749300	-0.63987500	5.71903100
H	0.50672400	2.41523300	-2.10638400	C	-3.80437700	-1.85784800	-2.78250800
C	4.29004700	3.19067600	-2.00349200	H	-4.04633500	-3.84647200	-1.97883900
H	4.49674200	1.43180000	-0.79062200	H	-3.38550500	0.20857600	-3.28310900
C	1.94331500	-3.71941300	-0.06295200	O	2.71358700	-3.90198900	-1.15812600
C	0.10606700	-2.48993300	0.92511900	O	-0.25391300	-4.14749500	-2.13273900
C	0.01723100	-2.44771400	-3.83030600	C	3.77526600	-4.83113000	-1.09057500
H	0.38577800	-0.80728700	-5.16627000	H	4.27830500	-4.78704200	-2.06089800
C	5.19397400	-1.91316700	1.57628200	H	4.49477200	-4.56558700	-0.30005300
H	5.95311500	-2.25235600	-0.41356900	H	3.40458900	-5.85321100	-0.92305000
H	4.17673700	-1.40253900	3.40681000	C	-0.90076400	-4.97442200	-3.07767500
C	3.43956200	4.04443600	-2.70729400	H	-1.18366800	-5.88454000	-2.54073500
H	1.38363700	4.39300600	-3.27109700	H	-1.80784900	-4.49581700	-3.47812800
H	5.35651500	3.41727400	-1.95502500	H	-0.22822100	-5.23882900	-3.90706000
C	2.12022700	-4.42734300	1.12669600	C	6.27654300	-2.69952600	2.24939400
C	0.27719000	-3.21637600	2.11050500	H	7.22146400	-2.64732400	1.69337800
P	-1.06843800	-1.07241700	0.86157300	H	6.45857900	-2.34730000	3.27258200
H	-0.44045300	-3.06276200	-4.60196600	H	5.99947400	-3.76319000	2.31795300
C	1.27343900	-4.17952800	2.20107200	C	3.95898000	5.28262300	-3.37118200
H	2.90443900	-5.17518500	1.22075700	H	3.79725600	6.16485400	-2.73316100
H	-0.37170200	-3.04080400	2.96547200	H	5.03625100	5.21487600	-3.56841500
C	-2.08822300	-1.23102200	2.37226000	H	3.44602600	5.47790300	-4.32195700
C	-2.16282400	-1.39955100	-0.54774600	C	-4.44259200	-1.13828700	5.99767400
H	1.39710900	-4.74503900	3.12403800	H	-5.48885800	-1.41104200	5.81397600
C	-3.45323400	-1.51406200	2.33646800	H	-4.03999900	-1.82799500	6.75274300
C	-1.50324800	-0.90605000	3.60640000	H	-4.43071200	-0.13421600	6.44461800
C	-2.75766900	-2.65244700	-0.73989500	C	-4.64022400	-2.12106300	-3.99740100
C	-2.40011700	-0.38043100	-1.47366200	H	-5.06318000	-1.19370000	-4.40462200
C	-4.21221500	-1.48529700	3.50739100	H	-4.03429300	-2.57823000	-4.79550100
H	-3.94616000	-1.74166700	1.39141900	H	-5.46487000	-2.81309300	-3.78152500
C	-2.26025600	-0.89216300	4.76816200	Ni	-0.01748000	0.87967200	0.79661100
H	-0.44177000	-0.64826400	3.65510100	C	0.50209900	2.87581800	1.14865700
C	-3.57832500	-2.86974500	-1.83916600	C	-0.46956400	2.42227900	2.06181500
H	-2.57241300	-3.46168700	-0.03058900	C	1.83982900	3.33420700	1.54722400

H	0.13277000	3.27440000	0.19610000	C	3.54533600	0.21266900	0.46085100
C	-1.63806700	1.84043800	1.56189800	C	2.39788500	1.77914100	-1.73125300
H	-0.20860400	2.29077300	3.11605900	C	1.87879200	-2.34594500	-1.04798800
C	2.54616100	2.75146100	2.60954600	C	2.02846000	-0.95192400	-3.03002700
C	2.43729100	4.39473900	0.85425500	C	4.75016900	-0.25887400	-0.07655200
H	-2.04121000	2.15378700	0.59063600	C	3.48433000	0.51984800	1.82091900
H	-2.35911100	1.38520900	2.24034300	C	1.33794300	2.23925600	-2.52756100
C	3.81533600	3.20255200	2.95350900	C	3.64395200	2.39291800	-1.85756300
H	2.10258500	1.92139500	3.16253000	C	1.95793800	-2.59672200	0.42051500
C	3.70404900	4.85361000	1.20181700	C	1.72026700	-3.47030100	-1.88486600
H	1.89604500	4.86167200	0.03007700	C	1.89139100	-2.07469100	-3.83515000
C	4.40176700	4.25511500	2.24874300	H	2.14778200	0.02334600	-3.49654200
H	4.35331300	2.72670900	3.77332100	C	5.86747200	-0.40031400	0.73508200
H	4.15058900	5.67790000	0.64505400	H	4.81065000	-0.52649500	-1.13317500
H	5.39798100	4.60519600	2.51669600	C	4.60879600	0.37553400	2.62969800
C	-3.82173000	3.25953400	-0.81568100	H	2.54540700	0.87028100	2.25462900
C	-4.40497400	3.26920400	0.48293900	C	1.53433100	3.26303200	-3.44400200
C	-4.36497600	2.49890500	-1.88476900	H	0.34592600	1.78645300	-2.43920600
C	-2.64623000	4.14561500	-1.10658700	C	3.83097800	3.43138900	-2.76999200
C	-5.55846300	2.31753400	0.77067600	H	4.47972600	2.08160400	-1.23063900
O	-4.02974700	4.01427900	1.41923200	C	3.13888300	-3.19116500	0.91260100
C	-5.58354100	1.63019300	-1.61326100	C	0.90110000	-2.35276500	1.31246600
O	-3.90655100	2.52780100	-3.05437000	C	1.72846700	-3.33584600	-3.27361500
H	-2.29694500	4.62975400	-0.18493400	H	1.90610700	-1.96730000	-4.91908500
H	-1.80481000	3.58433300	-1.55193800	C	5.81570000	-0.08657500	2.10049500
H	-2.88353900	4.93981800	-1.83413700	H	6.80201000	-0.77029000	0.30773600
C	-5.63325200	1.13492100	-0.17906900	H	4.54483300	0.62073100	3.69111100
H	-6.49486800	2.90131300	0.71220100	C	2.78710400	3.87772500	-3.58189800
H	-5.46320000	1.99854300	1.81977200	H	0.70028700	3.59732700	-4.06372300
H	-5.57866300	0.80148100	-2.33682000	H	4.81129800	3.90395600	-2.84911900
H	-6.48621600	2.22963400	-1.83054700	C	3.25383600	-3.55055200	2.25642300
H	-6.54464100	0.54435800	0.00331100	C	1.01785500	-2.72944000	2.65636500
H	-4.77610300	0.45932000	-0.00079500	P	-0.54548900	-1.36255700	0.74624500
				H	1.61042400	-4.20212000	-3.92026200
131				C	2.18410800	-3.32721900	3.11589000
Int-4				H	4.16315700	-4.01111500	2.63544100
P	2.04980200	0.41895900	-0.55806000	H	0.19419100	-2.56947400	3.34843500
C	2.01748500	-1.07929700	-1.63515100	C	-1.79448300	-1.47224200	2.08084000

C	-1.26783200	-2.26414200	-0.65476400	C	-4.92407300	-1.10039500	5.04189400
H	2.26421400	-3.62469000	4.16088600	H	-5.27407400	-2.08205600	5.39126500
C	-3.06092500	-2.02188000	1.86066100	H	-4.60079400	-0.52589900	5.91860200
C	-1.55840700	-0.79972800	3.28775900	H	-5.79487900	-0.58918000	4.60586200
C	-1.41553600	-3.65541500	-0.62451500	C	-3.11832700	-4.31303000	-3.96324200
C	-1.74005900	-1.54483300	-1.75616200	H	-2.45398400	-4.31132100	-4.84007500
C	-4.05612000	-1.90768300	2.82736500	H	-3.35065200	-5.35834500	-3.72371100
H	-3.29422500	-2.51803900	0.91820600	H	-4.05002100	-3.81786500	-4.27069800
C	-2.55518500	-0.69496700	4.25082400	Ni	0.10804300	0.73960300	0.48590500
H	-0.58981500	-0.32526500	3.46809300	C	0.22101800	2.80906800	0.72755400
C	-2.02545100	-4.31363900	-1.68601100	C	-0.86358000	2.26796500	1.44943900
H	-1.05624200	-4.22692100	0.23367900	C	1.36545800	3.48708800	1.34714900
C	-2.33053500	-2.21685800	-2.82150000	H	0.03385900	3.06479200	-0.32113400
H	-1.68418000	-0.45346800	-1.78096300	C	-1.77147600	1.45590600	0.76794400
C	-3.82581100	-1.24037200	4.03284300	H	-0.85429200	2.26341500	2.54245400
H	-5.04177900	-2.33335400	2.63046000	C	1.67668600	3.35984100	2.71072700
H	-2.35190900	-0.16286700	5.18147100	C	2.19832400	4.28587800	0.55108500
C	-2.48298300	-3.60621800	-2.80475900	H	-1.93785000	1.58963200	-0.30882000
H	-2.14831700	-5.39777300	-1.64974600	H	-2.54200700	0.90958400	1.31110700
H	-2.69341700	-1.64628000	-3.67867800	C	2.78344100	4.00228800	3.25229000
O	4.12213100	-3.38370700	0.00558400	H	1.05430700	2.73876900	3.35714300
O	1.56214600	-4.65551400	-1.25374600	C	3.31580100	4.91745800	1.08869000
C	5.35230200	-3.91861200	0.44667400	H	1.96240200	4.40610300	-0.50746000
H	6.00730400	-3.93452700	-0.42954200	C	3.61463100	4.77818800	2.44241000
H	5.80937300	-3.28992400	1.22670900	H	3.00564800	3.89051300	4.31348300
H	5.23175500	-4.94434500	0.82533600	H	3.95260200	5.52430800	0.44474300
C	1.32510300	-5.80823200	-2.03524200	H	4.48716300	5.27325500	2.86702400
H	1.15891700	-6.62547500	-1.32733000	C	-4.36635300	2.87158000	-0.49841300
H	0.43175700	-5.69004700	-2.66712200	C	-4.18547400	1.64758700	-1.18637100
H	2.19232200	-6.05058800	-2.66714300	C	-5.55476500	3.02554200	0.42633500
C	7.03141200	-0.25670000	2.95967300	C	-3.52113700	4.02705300	-0.61459600
H	7.85781500	0.37851700	2.61070300	C	-5.12888500	0.52908000	-0.80197800
H	6.82728700	0.00141800	4.00602100	O	-3.30261700	1.36915800	-2.03985700
H	7.39658000	-1.29376600	2.93345000	C	-5.78098000	1.77702300	1.26396800
C	2.98501200	4.97839800	-4.57860600	H	-5.39357700	3.89203500	1.07935400
H	2.25410300	5.78578900	-4.43319700	H	-6.48454100	3.23897000	-0.13726300
H	3.98980100	5.41283100	-4.50748800	O	-3.71983700	5.10819900	-0.04848100
H	2.85006000	4.61059700	-5.60576800	O	-2.40554200	3.87968200	-1.39513400

C	-5.87950900	0.56511800	0.38624100	C	4.03064000	3.65878400	-2.44277800
C	-5.19601500	-0.60814700	-1.61214300	H	4.55864600	2.24107400	-0.91820700
H	-6.68546600	1.86899100	1.88541100	C	3.25455100	-3.11590000	0.92563600
H	-4.93159700	1.65219000	1.96282700	C	0.98136500	-2.34951400	1.25429500
C	-1.56687000	5.01672300	-1.46024400	C	1.96185000	-3.23519500	-3.31182700
C	-6.67157600	-0.53269300	0.73145100	H	2.16541700	-1.84731300	-4.93819300
C	-5.98826900	-1.69815200	-1.26491000	C	5.69992600	0.07369500	2.35901800
H	-4.59621100	-0.61870300	-2.52107400	H	6.80937800	-0.64122000	0.65241100
H	-0.71990600	4.73196700	-2.09621900	H	4.32496600	0.82655300	3.83927400
H	-2.08333000	5.87647300	-1.90802500	C	3.06652900	4.11783500	-3.34095400
H	-1.20094800	5.31460500	-0.46708700	H	1.06117200	3.79811900	-4.07064400
C	-6.73140700	-1.66079500	-0.08442800	H	4.99359800	4.16857100	-2.38335700
H	-7.25002500	-0.49798200	1.65822500	C	3.32973300	-3.49419400	2.26729900
H	-6.02497600	-2.57524400	-1.91289600	C	1.05805000	-2.74343500	2.59586100
H	-7.35863100	-2.50680300	0.19856200	P	-0.46476600	-1.39435500	0.63462600
				H	1.86685100	-4.09588600	-3.96973000
131				C	2.22366200	-3.31332200	3.09080600
TS₄₋₅				H	4.23690500	-3.93630600	2.67260900
P	2.11637300	0.50246200	-0.55915100	H	0.20347100	-2.61406800	3.25724400
C	2.18768800	-0.99198500	-1.64171200	C	-1.75068100	-1.50683100	1.93856200
C	3.54099300	0.31234800	0.56444100	C	-1.13406300	-2.38488800	-0.74116300
C	2.55954700	1.89586600	-1.66554000	H	2.27524500	-3.62355100	4.13399200
C	2.04551100	-2.26798200	-1.06993900	C	-2.98610700	-2.12454000	1.73098500
C	2.23411600	-0.85229300	-3.03475000	C	-1.55959800	-0.78262400	3.12675400
C	4.78254000	-0.16049800	0.12117400	C	-1.22170300	-3.78079900	-0.66447500
C	3.39027100	0.66128300	1.90775100	C	-1.61555300	-1.73599700	-1.87949600
C	1.57771100	2.36959300	-2.55008700	C	-3.99467500	-2.03307100	2.69074600
C	3.78519600	2.56144000	-1.61663400	H	-3.18753800	-2.66593900	0.80593900
C	2.07867000	-2.54241100	0.39877500	C	-2.56365100	-0.70335900	4.08145000
C	1.92538400	-3.38429800	-1.92476100	H	-0.61233400	-0.26435000	3.29928200
C	2.12574200	-1.96654700	-3.85598000	C	-1.77809200	-4.50324500	-1.71102500
H	2.35813900	0.13003600	-3.48593100	H	-0.85100100	-4.30372200	0.21941700
C	5.84501700	-0.27195800	1.00839200	C	-2.17249200	-2.46757900	-2.92630900
H	4.91682400	-0.44807000	-0.92338100	H	-1.55582900	-0.64875300	-1.95860300
C	4.45933500	0.54635200	2.79303900	C	-3.80486400	-1.32335100	3.87612400
H	2.42559000	1.02643300	2.26728000	H	-4.95380200	-2.51807700	2.50251100
C	1.83312300	3.45210300	-3.38057400	H	-2.39346500	-0.13734500	4.99941700
H	0.60066700	1.87869100	-2.59361100	C	-2.25603000	-3.85975800	-2.86141900

H	-1.84364200	-5.59140500	-1.64193600	H	-2.74464500	0.58155000	0.49622200
H	-2.54857100	-1.94343600	-3.80606800	C	1.92550800	3.83866600	3.54741700
O	4.27682200	-3.26854100	0.05358800	H	0.24160100	2.53839200	3.26892300
O	1.77160600	-4.58082700	-1.31238400	C	2.80310500	4.89798700	1.57185200
C	5.49223900	-3.80592300	0.52919000	H	1.77281300	4.45743800	-0.26809600
H	6.18493600	-3.78693700	-0.31754000	C	2.86349700	4.68031000	2.94754100
H	5.90814400	-3.20100200	1.34941500	H	1.95755500	3.66605900	4.62340000
H	5.36599100	-4.84475400	0.86887000	H	3.52426900	5.55719200	1.08799400
C	1.56943700	-5.72668300	-2.11206900	H	3.63126400	5.16538900	3.54928400
H	1.40429600	-6.55573900	-1.41739800	C	-3.97985400	2.61594300	-0.42622300
H	0.68506700	-5.61770500	-2.75932800	C	-4.43069600	1.54139400	-1.27028400
H	2.45202200	-5.94649800	-2.73100200	C	-4.68540100	2.87830800	0.88469500
C	6.84842100	-0.08946700	3.30745500	C	-3.21669800	3.75519500	-0.90447300
H	7.77255500	0.34110700	2.89828800	C	-5.43529900	0.59258000	-0.66645700
H	6.64765400	0.38976700	4.27353500	O	-4.01953300	1.29724100	-2.41930000
H	7.05147700	-1.15359900	3.50163800	C	-5.11027800	1.60914800	1.60609500
C	3.32562100	5.28679000	-4.24155900	H	-4.02482800	3.46791400	1.53611300
H	2.56694000	6.07047600	-4.10788700	H	-5.57467800	3.51602200	0.71993800
H	4.30948900	5.73322200	-4.05155800	O	-3.14082700	4.82528300	-0.30408600
H	3.29059500	4.98850200	-5.29905900	O	-2.52181400	3.56161200	-2.05339500
C	-4.89823100	-1.19177200	4.89187800	C	-5.78726500	0.63248600	0.69307100
H	-5.76402500	-1.81532300	4.63562500	C	-6.01384600	-0.37557800	-1.49537100
H	-4.55486100	-1.48290400	5.89440800	H	-5.76870000	1.85255200	2.45344800
H	-5.24590500	-0.15046000	4.96566400	H	-4.22491200	1.11506700	2.05059600
C	-2.82321500	-4.66271100	-3.99236400	C	-1.75700700	4.67026600	-2.49652100
H	-3.58705300	-5.36923700	-3.63941600	C	-6.72183800	-0.28346500	1.18392300
H	-3.28015300	-4.02123300	-4.75576500	C	-6.93924800	-1.28532500	-0.99810600
H	-2.04012500	-5.25949200	-4.48403500	H	-5.71695000	-0.39411400	-2.54315200
Ni	0.10849400	0.72458200	0.33178400	H	-1.29793700	4.35668000	-3.43955600
C	-0.08707200	2.72324700	0.53217100	H	-2.39022900	5.54949800	-2.67032100
C	-1.23738900	2.04339200	1.01416300	H	-0.97726900	4.94213000	-1.77004500
C	0.88292200	3.41134200	1.39173300	C	-7.29884800	-1.23623400	0.34970700
H	-0.10560000	3.06765200	-0.50808600	H	-6.99360600	-0.24602900	2.24161400
C	-2.08296100	1.35962300	0.12374800	H	-7.38489700	-2.02906900	-1.65841200
H	-1.44395500	1.97540300	2.08520000	H	-8.02979500	-1.93968500	0.74896500
C	0.95166900	3.20811000	2.78042400				
C	1.81917100	4.27847400	0.80784300				
H	-1.90571400	1.38473000	-0.95262700				

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P	2.08860400	0.78170600	-0.57917500	H	0.58869600	-2.62223800	3.17721600
C	2.49452600	-0.66927900	-1.65157400	C	-1.47214300	-1.92194800	1.78818900
C	3.49457400	0.85371200	0.58976900	C	-0.60125900	-2.59914100	-0.87655700
C	2.33773200	2.23880800	-1.67273100	H	2.76665700	-3.23877700	4.14435700
C	2.52758500	-1.95263200	-1.07825400	C	-2.51715200	-2.82072800	1.56506700
C	2.61169000	-0.52428700	-3.04008200	C	-1.47546800	-1.19197600	2.98878800
C	4.81509200	0.59983500	0.20051300	C	-0.45825500	-3.99110200	-0.81444500
C	3.23498000	1.18032400	1.92277100	C	-1.08994000	-2.02446300	-2.05164100
C	1.32935500	2.52996700	-2.60564900	C	-3.51834400	-3.00286800	2.52125200
C	3.40110600	3.13444500	-1.55169900	H	-2.56878500	-3.38623200	0.63443900
C	2.53022100	-2.21887000	0.39377600	C	-2.46415700	-1.38767300	3.94310900
C	2.65977900	-3.07173400	-1.92698500	H	-0.68540600	-0.46002900	3.17524900
C	2.74777100	-1.63973300	-3.85593100	C	-0.80152700	-4.78143500	-1.90342800
H	2.60121900	0.46671400	-3.49054400	H	-0.06961100	-4.45879800	0.09249300
C	5.84654000	0.67533200	1.12824800	C	-1.43192400	-2.82183400	-3.14259400
H	5.03701100	0.33488800	-0.83530300	H	-1.19092500	-0.93831500	-2.11819600
C	4.27242500	1.25046600	2.84985800	C	-3.50685700	-2.29976900	3.72550600
H	2.20778600	1.38120400	2.23929900	H	-4.32473400	-3.71075200	2.32060800
C	1.40663600	3.65788900	-3.41115600	H	-2.43900900	-0.81536400	4.87277400
H	0.46874900	1.86065500	-2.69823300	C	-1.28852000	-4.20981600	-3.08711800
C	3.46410200	4.27874000	-2.34891200	H	-0.68441400	-5.86595700	-1.84337700
H	4.18639600	2.95949700	-0.81591900	H	-1.80754000	-2.35679700	-4.05533200
C	3.76780400	-2.56950100	0.97409900	O	4.83878600	-2.53621000	0.14596000
C	1.37915800	-2.22292900	1.20190900	O	2.67745700	-4.27860700	-1.31293300
C	2.76531600	-2.91879200	-3.31033000	C	6.11451100	-2.80603100	0.68393500
H	2.84197900	-1.51489700	-4.93444800	H	6.82599100	-2.66558800	-0.13569700
C	5.59140500	0.99201200	2.46927400	H	6.36539500	-2.11030000	1.50029900
H	6.87352300	0.47737200	0.81266200	H	6.18711800	-3.84125200	1.04986900
H	4.05104300	1.50717100	3.88747400	C	2.76088200	-5.43807800	-2.11174900
C	2.47686500	4.55668000	-3.29440800	H	2.69489900	-6.28672100	-1.42411100
H	0.61970900	3.85536600	-4.14178100	H	1.93127000	-5.49373400	-2.83342400
H	4.30091900	4.96908400	-2.22955400	H	3.71808000	-5.48617300	-2.65249900
C	3.85777200	-2.92523800	2.32069900	C	6.70965600	1.01684000	3.46706700
C	1.47662200	-2.59777000	2.54837000	H	7.60377500	1.50818400	3.06010200
P	-0.19067800	-1.50657200	0.53334800	H	6.42105100	1.54039400	4.38718000
H	2.86526400	-3.78303400	-3.96283600	H	7.00717800	-0.00451100	3.75067500
C	2.70388800	-2.94670000	3.09631600	C	2.54392700	5.77401800	-4.16610800
H	4.81374500	-3.19062100	2.76627600	H	1.63260100	6.38185400	-4.07676600

H	3.39967000	6.40990400	-3.90716800	O	-4.13500300	4.41869600	0.13904900
H	2.63953300	5.49961800	-5.22654600	O	-2.94250300	3.60182200	-1.57136100
C	-4.57874500	-2.48793300	4.75610000	C	-5.81566200	-0.16830400	0.62358100
H	-5.30509100	-3.25154200	4.44996900	C	-6.66398100	-0.36653600	-1.64844700
H	-4.15529800	-2.79568300	5.72268300	H	-5.49652000	0.52674600	2.61827200
H	-5.12933700	-1.55289500	4.93667000	H	-4.05231200	-0.06417800	1.81640300
C	-1.61686600	-5.07680700	-4.26472900	C	-2.52792400	4.93161900	-1.87933700
H	-2.26875900	-5.91400700	-3.97944000	C	-6.57270200	-1.29198000	0.96875600
H	-2.11919600	-4.50983800	-5.05827800	C	-7.40012700	-1.48566800	-1.29323600
H	-0.70528700	-5.51639600	-4.69727100	H	-6.68673200	0.01693700	-2.66749900
Ni	0.04465900	0.63896800	0.21078100	H	-1.88835500	4.84839000	-2.76146900
C	-0.71117000	2.46957400	0.38890300	H	-3.39222100	5.56828500	-2.09928300
C	-1.67970900	1.47003800	0.65618200	H	-1.96330300	5.36032200	-1.04130300
C	0.06467900	3.19656400	1.40256800	C	-7.35345700	-1.94809500	0.02480900
H	-0.71705300	2.94206100	-0.59921700	H	-6.55138000	-1.64593600	2.00132600
C	-2.76977900	1.13582800	-0.32900800	H	-8.01302200	-1.99741200	-2.03383500
H	-1.93122100	1.25034500	1.70042400	H	-7.93643300	-2.82125000	0.31677400
C	-0.02085000	2.93304200	2.78185900				
C	0.96669000	4.19504900	0.99052000	131			
H	-2.40777900	1.24840000	-1.36130700	ent-TS₄₋₅			
H	-3.06348200	0.08016600	-0.21703200	P	-2.11245400	0.68358600	0.53417200
C	0.77656100	3.61584200	3.69632900	C	-2.58697800	-0.85472700	1.43741900
H	-0.72487200	2.18335000	3.14641100	C	-3.38407400	0.85320900	-0.76289700
C	1.76980400	4.87069100	1.90217900	C	-2.44970300	2.03681600	1.72431500
H	1.04276200	4.42573300	-0.07491200	C	-2.57895800	-2.08569600	0.75981300
C	1.68476400	4.58347800	3.26546800	C	-2.81151800	-0.81851800	2.81972100
H	0.68594200	3.38955100	4.75941600	C	-4.73530300	0.57304400	-0.52394200
H	2.46742800	5.62891100	1.54422900	C	-2.99652000	1.28443900	-2.03288100
H	2.31179400	5.11187100	3.98297200	C	-1.50611600	2.26674200	2.73782300
C	-4.04704200	2.01935000	-0.16944200	C	-3.53600900	2.90614700	1.62044500
C	-5.09367700	1.48640400	-1.14555300	C	-2.43852500	-2.22493100	-0.72117200
C	-4.62415200	1.94906500	1.25044800	C	-2.77883700	-3.26906700	1.50135300
C	-3.72955700	3.47149100	-0.50297000	C	-3.01527700	-1.99541900	3.52804400
C	-5.86703500	0.29461800	-0.70287000	H	-2.83340400	0.13234500	3.34876500
O	-5.27004200	1.98595400	-2.24650900	C	-5.67126900	0.73099500	-1.53768000
C	-4.97122000	0.52606800	1.65162400	H	-5.05557800	0.22401100	0.45968600
H	-3.91139400	2.39098500	1.95986000	C	-3.93978600	1.43834600	-3.04601900
H	-5.52790700	2.57506200	1.29273600	H	-1.94507600	1.50186400	-2.23424300

C	-1.65910000	3.32004400	3.62828500	H	3.07060300	-0.25747800	-4.33222000
H	-0.63511900	1.61160700	2.82910400	C	0.96080700	-4.54507100	2.97790600
C	-3.68207200	3.96859500	2.51329400	H	0.58429800	-6.08099600	1.51015200
H	-4.27153700	2.77596900	0.82618900	H	1.28128500	-2.78703700	4.18191000
C	-3.60256300	-2.52010500	-1.46055000	O	-4.75451400	-2.56365100	-0.75292000
C	-1.20927700	-2.15489600	-1.39764500	O	-2.74528400	-4.42044400	0.79221400
C	-2.99049800	-3.22546400	2.88038700	C	-5.96281400	-2.79641200	-1.44489900
H	-3.19383200	-1.95788100	4.60224300	H	-6.75797200	-2.73642600	-0.69563400
C	-5.28895100	1.16019700	-2.81607000	H	-6.14021100	-2.03310300	-2.21889500
H	-6.72316400	0.51205600	-1.34072900	H	-5.97639300	-3.79561200	-1.90495700
H	-3.61950300	1.77856900	-4.03231200	C	-2.91738200	-5.64046000	1.48110000
C	-2.75315000	4.19210600	3.53048900	H	-2.80069200	-6.43083100	0.73372500
H	-0.91234400	3.48037600	4.40809900	H	-2.15807400	-5.77290300	2.26701400
H	-4.53552000	4.64070600	2.41021800	H	-3.92068500	-5.71057100	1.92719000
C	-3.53920900	-2.74755900	-2.83658800	C	-6.30962100	1.28847300	-3.90571000
C	-1.15079100	-2.39237700	-2.77629000	H	-7.19063000	1.85117000	-3.56797700
P	0.27021200	-1.53878000	-0.48986900	H	-5.89933700	1.79551800	-4.78772800
H	-3.14271500	-4.13841900	3.45157100	H	-6.66826500	0.29954600	-4.22924300
C	-2.30903100	-2.68972600	-3.48275800	C	-2.90467900	5.32721600	4.49656900
H	-4.43732200	-2.97273700	-3.40718800	H	-3.03179600	4.95897400	5.52458400
H	-0.19845100	-2.35201600	-3.30190800	H	-2.01415000	5.97104200	4.49872400
C	1.69986600	-1.79391900	-1.60970600	H	-3.77338800	5.95172900	4.25415100
C	0.52046100	-2.73777800	0.86152000	C	5.23161600	-1.88382400	-4.10921100
H	-2.25693900	-2.87908700	-4.55448600	H	5.97452400	-2.60572800	-3.74766200
C	2.73650100	-2.69024400	-1.34191900	H	4.97394500	-2.15315300	-5.14392200
C	1.84409900	-0.91664800	-2.69663800	H	5.70990400	-0.89462000	-4.14668700
C	0.43068300	-4.11867200	0.64594600	C	1.15083100	-5.51509800	4.10394000
C	0.82874600	-2.27130400	2.14093600	H	1.63491200	-5.04369100	4.96821600
C	3.87396300	-2.72209400	-2.15007300	H	0.18332500	-5.91375600	4.44563700
H	2.67663000	-3.36615100	-0.48859700	H	1.75994200	-6.37579000	3.79686000
C	2.97617800	-0.95399300	-3.49713400	Ni	0.00678900	0.61977000	-0.07918400
H	1.06036800	-0.18487600	-2.90984000	C	0.51468400	2.57090600	-0.10213300
C	0.65408700	-5.00607700	1.69025100	C	1.60514700	1.75373500	-0.49663800
H	0.18128700	-4.50017600	-0.34620700	C	-0.21086700	3.46270400	-1.01519900
C	1.04729100	-3.16635900	3.18607100	H	0.44645700	2.84768700	0.95596300
H	0.88634300	-1.19614100	2.32745600	C	2.25279100	0.91899200	0.42527400
C	4.01405000	-1.86017300	-3.23741000	H	1.93663800	1.71537200	-1.53579800
H	4.67509000	-3.42596600	-1.91884000	C	-0.07823000	3.39899900	-2.41244200

C	-1.10618500	4.40469000	-0.48425800
H	1.97973300	0.92324400	1.48294400
H	2.84793900	0.08242400	0.06573800
C	-0.82321800	4.23281200	-3.24001700
H	0.61277900	2.68493200	-2.86250700
C	-1.86131000	5.23019100	-1.31107800
H	-1.21463300	4.47656200	0.59976100
C	-1.72591900	5.14766600	-2.69637200
H	-0.69924400	4.16589700	-4.32103700
H	-2.55691900	5.94374400	-0.86845700
H	-2.31350800	5.79401700	-3.34750900
C	4.25739000	1.94247200	1.14353500
C	4.66215100	1.07826100	2.31798800
C	4.90512900	1.74851700	-0.12929200
C	3.56951800	3.16081600	1.52816000
C	4.96234200	-0.36213200	1.93472700
H	3.86731100	1.10041900	3.07643600
H	5.55192400	1.50743300	2.81801000
C	5.82219200	0.55356400	-0.23570800
O	4.74831300	2.44816100	-1.14394800
O	3.17502000	3.38842700	2.67493900
O	3.33686900	4.04247200	0.53292900
H	4.02280800	-0.89295900	1.69738600
H	5.40026200	-0.90166800	2.78751200
C	5.87674400	-0.44533700	0.75008800
C	6.64360600	0.44635900	-1.36346300
C	2.60101600	5.19879900	0.89486000
C	6.75564500	-1.51949200	0.58897000
C	7.52009700	-0.62206700	-1.51355500
H	6.57634100	1.22857900	-2.11923400
H	2.42383500	5.74430100	-0.03735500
H	1.64089900	4.93825800	1.36114800
H	3.16793600	5.82855600	1.59325600
C	7.57747500	-1.61116700	-0.53074100
H	6.79469600	-2.29166200	1.36008000
H	8.16087500	-0.68483000	-2.39346000
H	8.26562500	-2.45027200	-0.63504600

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compound 1a

O	-2.33227100	1.66169900	-1.64916400
C	-2.45812500	1.07076800	-0.59140300
C	-2.90593900	1.77921000	0.65755000
C	-2.21596300	-0.44104400	-0.52970700
C	-2.13347600	1.29769200	1.87767600
H	-3.98024600	1.56559600	0.79801200
H	-2.81019300	2.85852300	0.48973700
C	-1.96413600	-1.00911400	0.87435500
C	-3.53616300	-1.08707800	-1.00520600
C	-1.07425000	-0.84856800	-1.47878400
C	-2.35617500	-0.19251900	2.07728100
H	-2.45367600	1.85036000	2.76946000
H	-1.05887000	1.50424900	1.74839600
O	-1.51697000	-2.13466300	0.99603000
H	-3.77781200	-0.73486200	-2.01634600
H	-3.42347200	-2.17846400	-1.03003200
H	-4.37982300	-0.84362100	-0.34422500
H	-0.98244200	-1.94213900	-1.44950900
H	-1.37505500	-0.56518200	-2.49777300
C	0.23253600	-0.20833800	-1.13386600
H	-1.81756100	-0.59183200	2.94521500
H	-3.43010400	-0.38114800	2.25549800
C	1.29851500	-0.87939100	-0.67542000
H	0.28856500	0.87587800	-1.27203800
H	1.20761400	-1.96322300	-0.54874900
C	2.60568100	-0.32336500	-0.31130500
C	2.92157900	1.03953700	-0.42775800
C	3.59374300	-1.18899400	0.17845400
C	4.17637900	1.51309300	-0.06585300
H	2.17871100	1.73984300	-0.80943000
C	4.85177400	-0.71640400	0.54168900
H	3.36405300	-2.25122700	0.27501400
C	5.14911500	0.63840800	0.42136400
H	4.40003800	2.57479300	-0.16596400
H	5.60149700	-1.41047700	0.92002600
H	6.13212700	1.01329400	0.70337200

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compound 6a

C	-3.12069200	1.26423000	0.04763500
C	-1.77451800	0.92382300	0.15114900
C	-1.40471600	-0.42844100	0.03263600
C	-2.38080300	-1.40944500	-0.17440300
C	-3.72005900	-1.05271000	-0.27776400
C	-4.08992800	0.28668300	-0.16872300
H	-3.41181400	2.31136500	0.14050200
H	-2.08111500	-2.45184800	-0.26242500
H	-4.47519200	-1.81887400	-0.44602700
H	-5.13791100	0.57205800	-0.25200700
C	0.01352000	-0.78329100	0.12307600
C	0.99397500	0.16987400	0.00411600
C	0.60342300	1.60553300	-0.23933700
C	-0.71149600	1.94056800	0.44899100
H	-1.05435700	2.94411200	0.16327100
H	-0.54668600	1.96390500	1.54060300
H	1.38930300	2.27645700	0.12599100
H	0.51729000	1.79562400	-1.32390500
O	0.25475100	-2.08411200	0.28922000
C	2.37784300	-0.25413600	0.01105900
O	2.75780700	-1.41914000	0.18424800
O	3.25051500	0.73848500	-0.19948300
C	4.63214600	0.37437500	-0.21237500
H	5.17936100	1.30195300	-0.39452600
H	4.92831900	-0.05585500	0.75047500
H	4.83510900	-0.34663800	-1.01166900
H	1.24092400	-2.19651000	0.30148200

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compound 8

O	-0.70100300	2.17177800	-0.51522400
C	-0.11172600	1.25307500	0.01917000
C	1.37440000	1.26317700	0.26151800
C	-0.84499100	-0.00000800	0.49238100
C	2.02354400	0.00005200	-0.30324300

H	1.54322700	1.30213900	1.35089500
H	1.79880600	2.17289600	-0.17848400
C	-0.11169500	-1.25313600	0.01931200
C	1.37447500	-1.26313700	0.26146800
H	3.09581000	0.00008300	-0.07224400
H	1.93716800	0.00007700	-1.40035900
O	-0.70092400	-2.17176400	-0.51525900
H	1.79888500	-2.17280200	-0.17864200
H	1.54340200	-1.30219400	1.35082600
H	-0.68822100	0.00003400	1.58937600
C	-2.32210100	-0.00004900	0.17022300
H	-2.80752500	0.89009600	0.58542900
H	-2.49006800	-0.00013700	-0.91348600
H	-2.80750200	-0.89014100	0.58556800

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COD

C	-1.17366400	1.25258800	-0.49681700
H	-1.75658400	1.87640200	-1.18148800
C	0.06178000	1.68626700	-0.21410700
H	0.37231000	2.60919200	-0.71290200
C	1.11014900	1.06542600	0.66923200
H	0.68239000	0.68815700	1.60512800
H	1.81897500	1.85091600	0.96812600
C	1.91415000	-0.03611100	-0.02734200
H	2.42049900	0.40317300	-0.90360600
H	2.73385100	-0.35624700	0.63894500
C	1.17366400	-1.25258800	-0.49681700
H	1.75658400	-1.87640200	-1.18148800
C	-0.06178000	-1.68626700	-0.21410700
H	-0.37231000	-2.60919200	-0.71290200
C	-1.11014900	-1.06542600	0.66923300
H	-0.68239000	-0.68815700	1.60512800
H	-1.81897500	-1.85091600	0.96812600
C	-1.91415000	0.03611200	-0.02734200
H	-2.42049900	-0.40317300	-0.90360500
H	-2.73385100	0.35624800	0.63894500

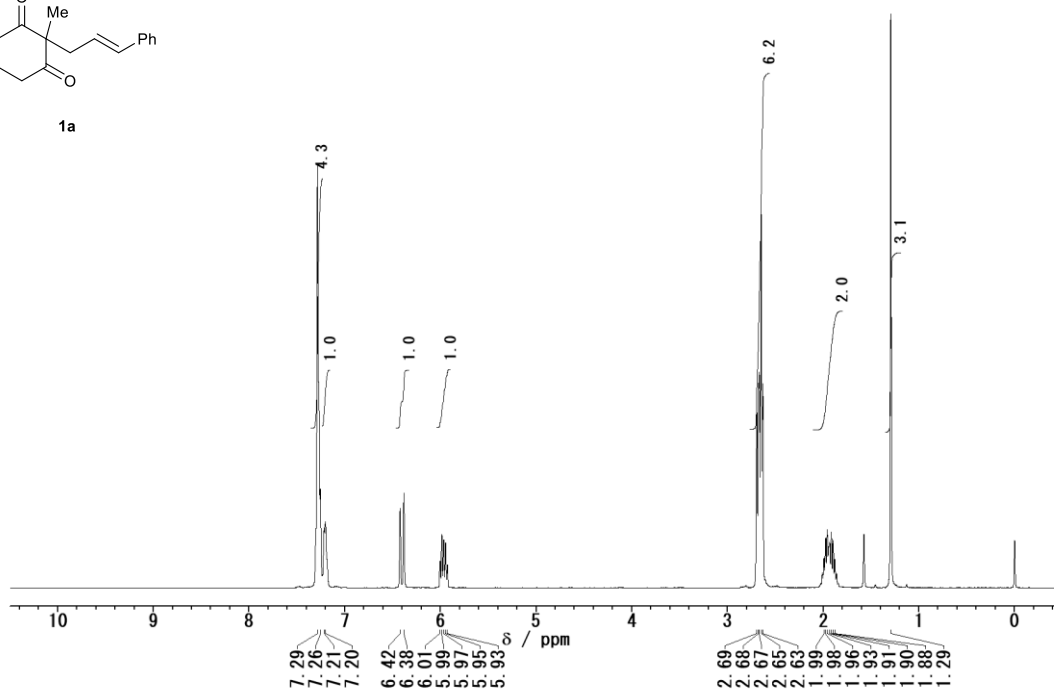
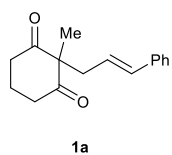
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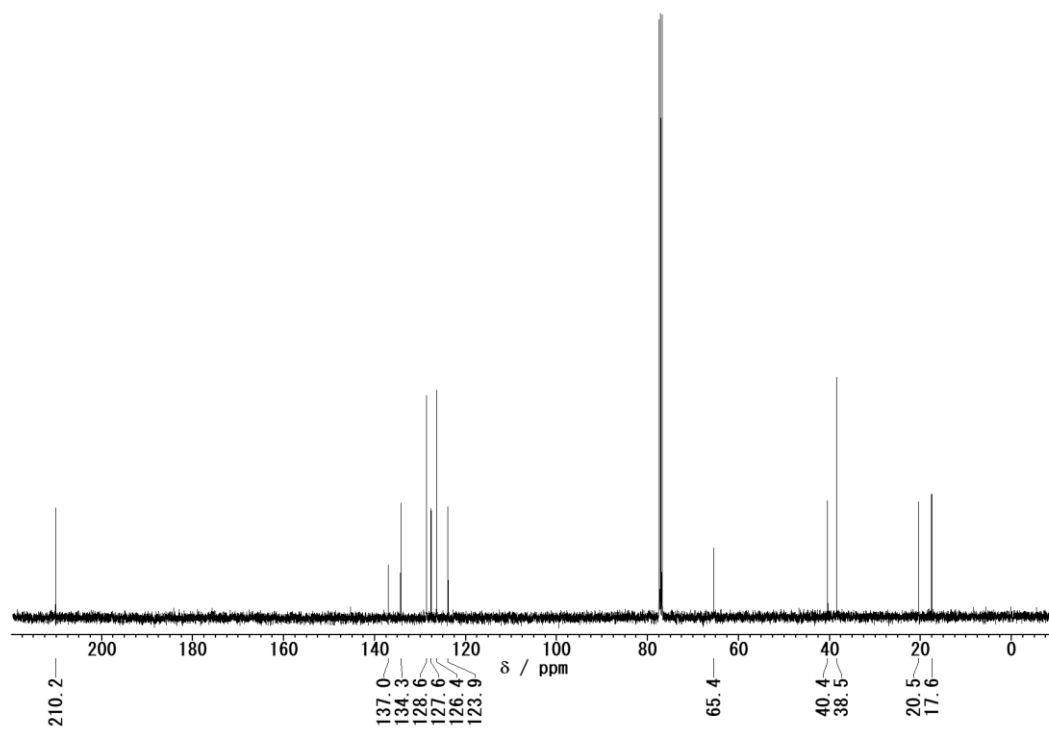
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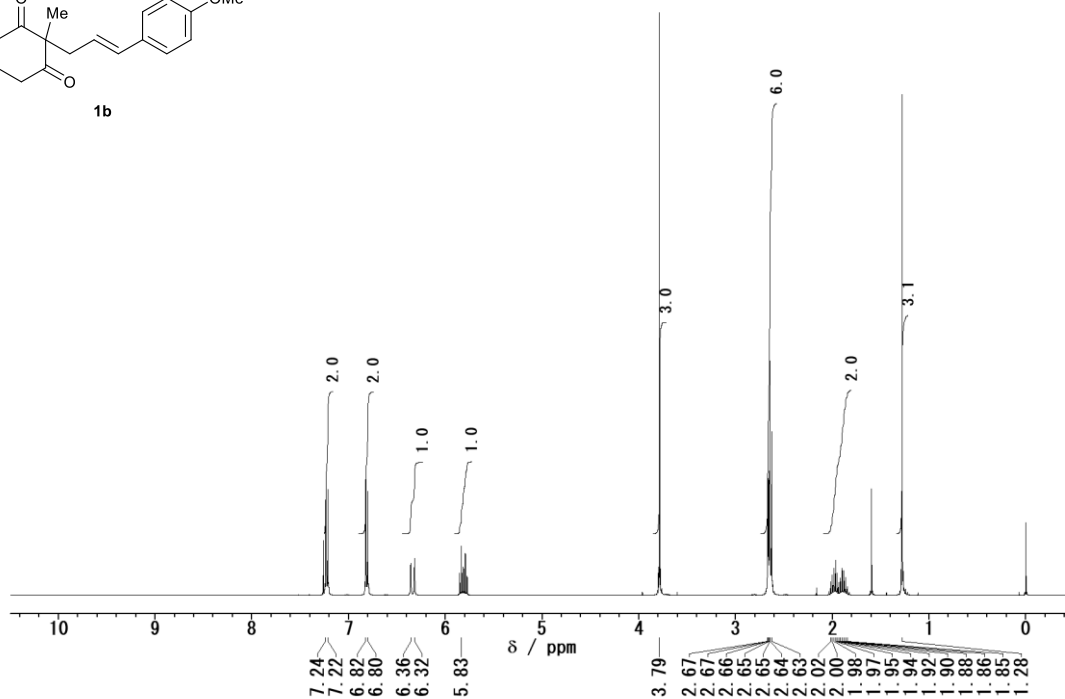
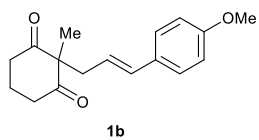
^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR Charts



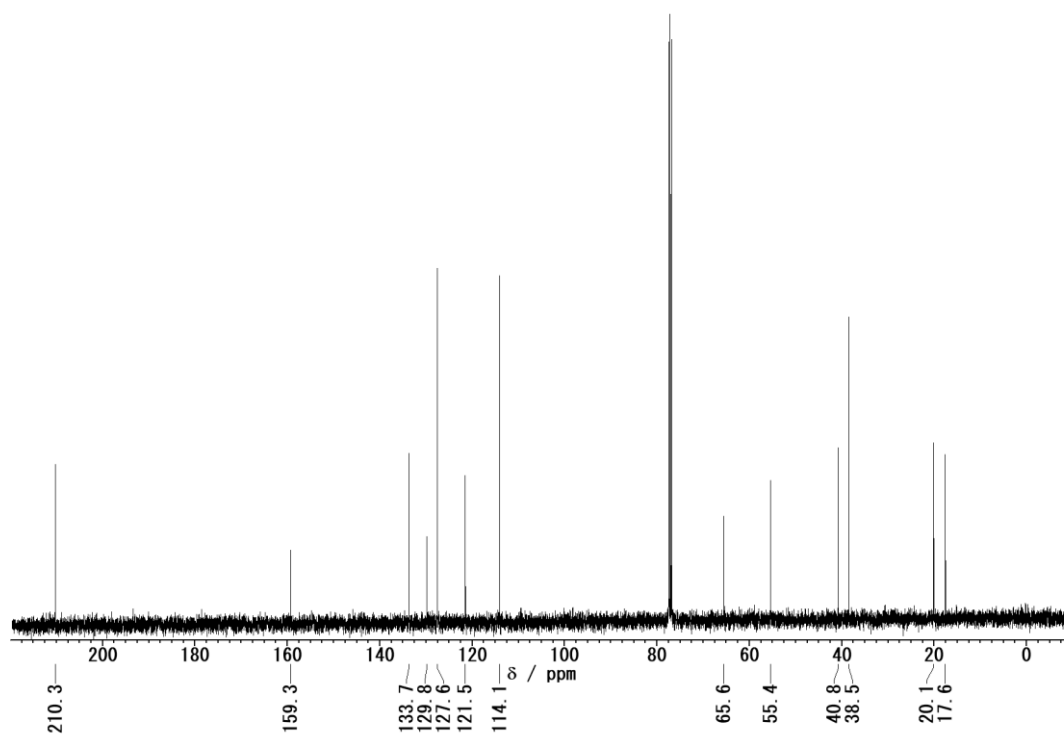
^1H NMR spectrum of **1a**



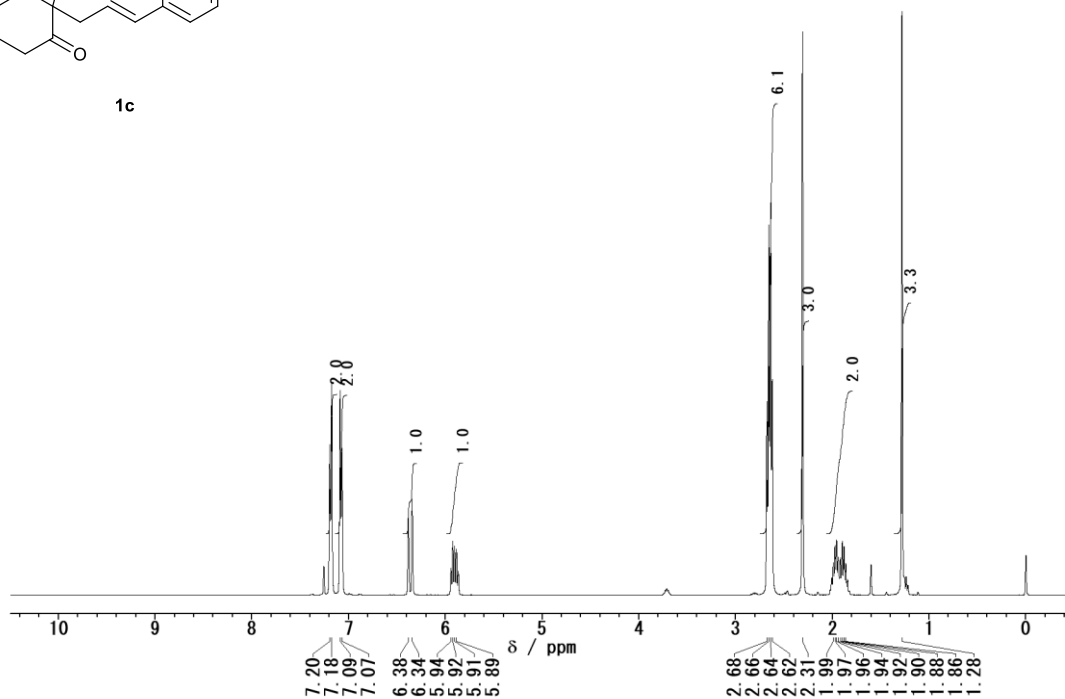
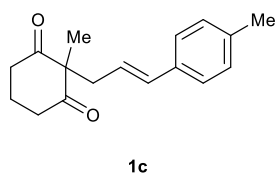
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1a**



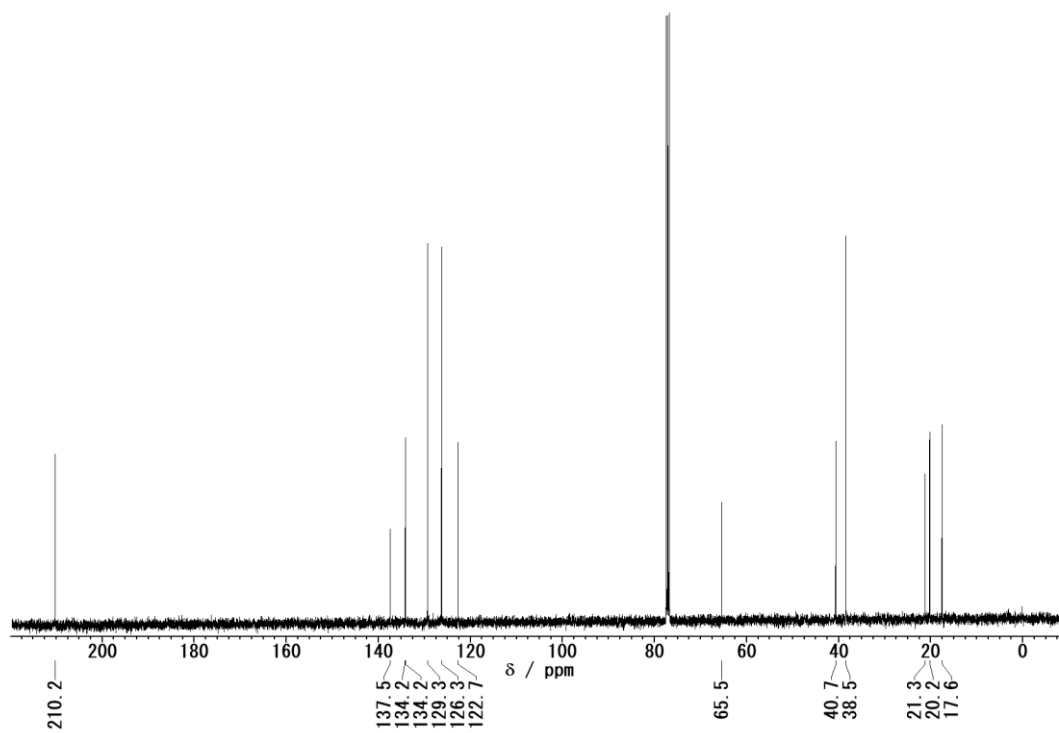
^1H NMR spectrum of **1b**



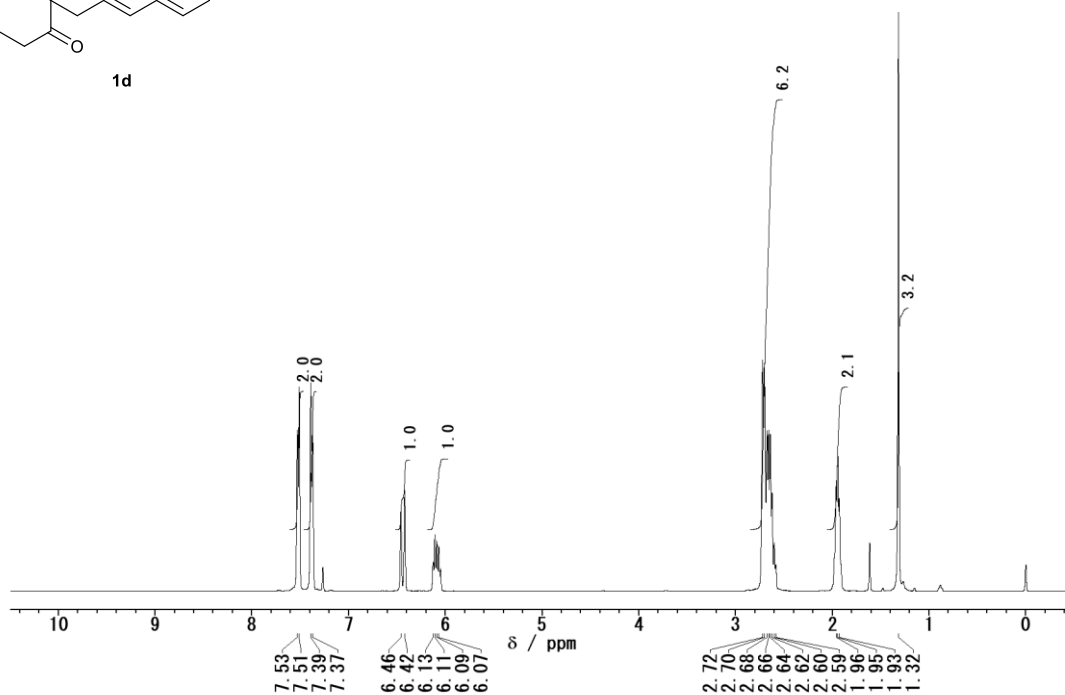
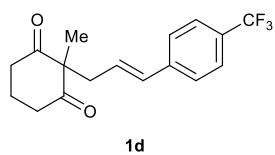
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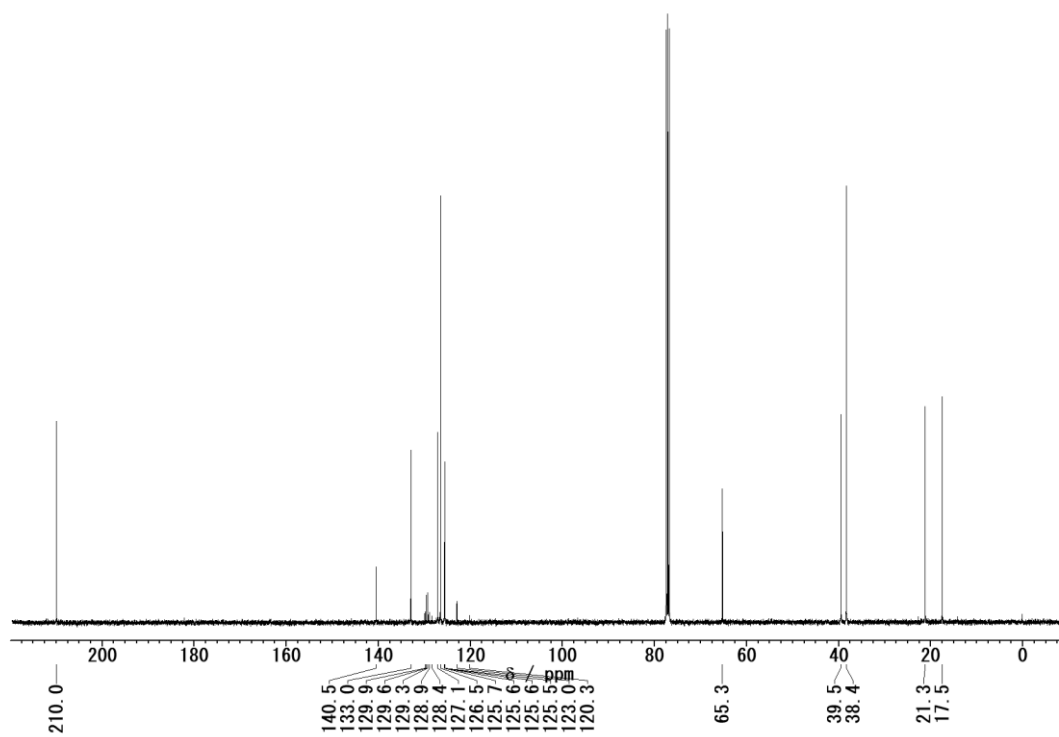
^1H NMR spectrum of **1c**



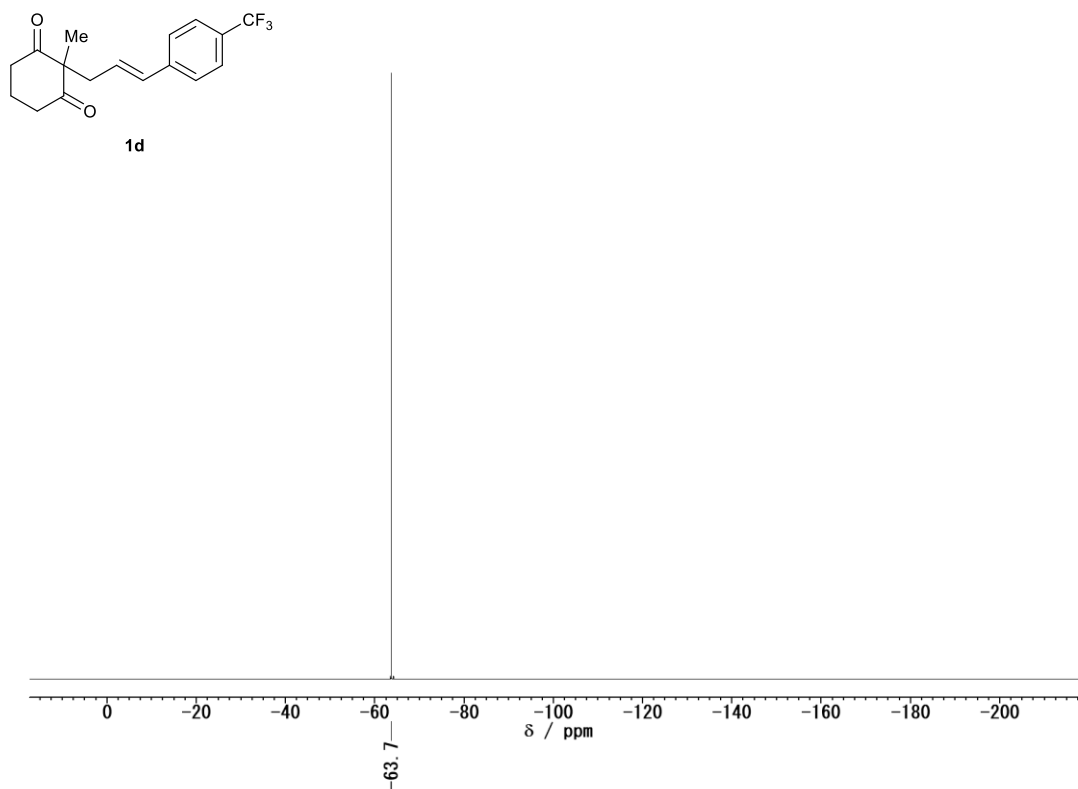
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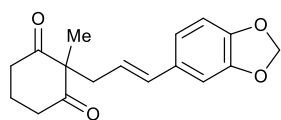
^1H NMR spectrum of **1d**



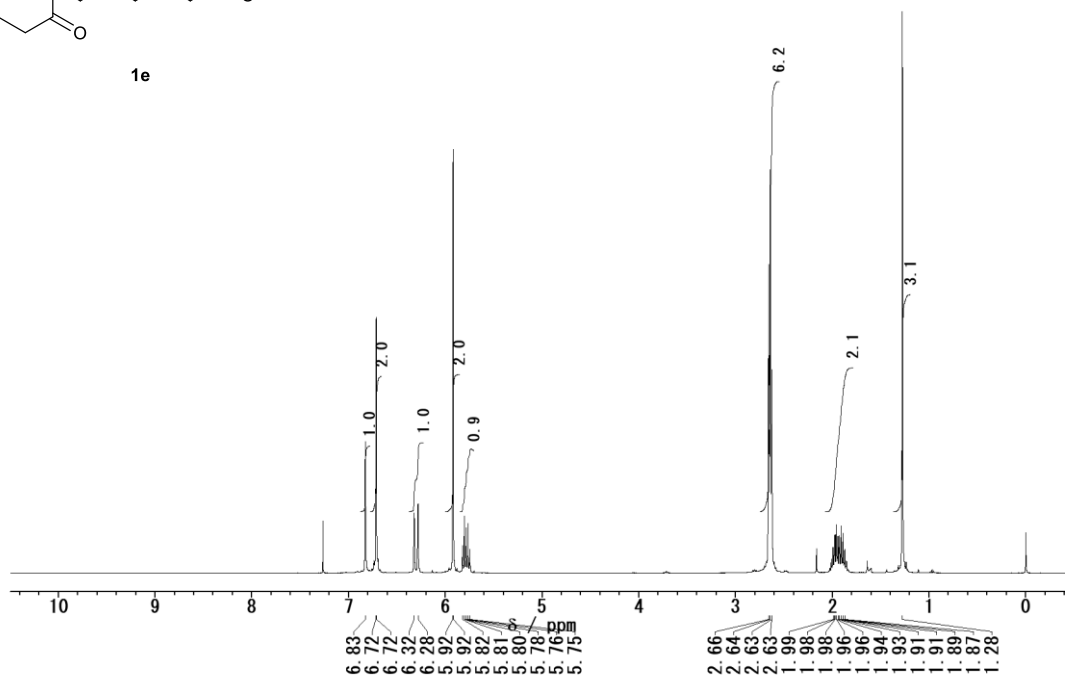
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1d**



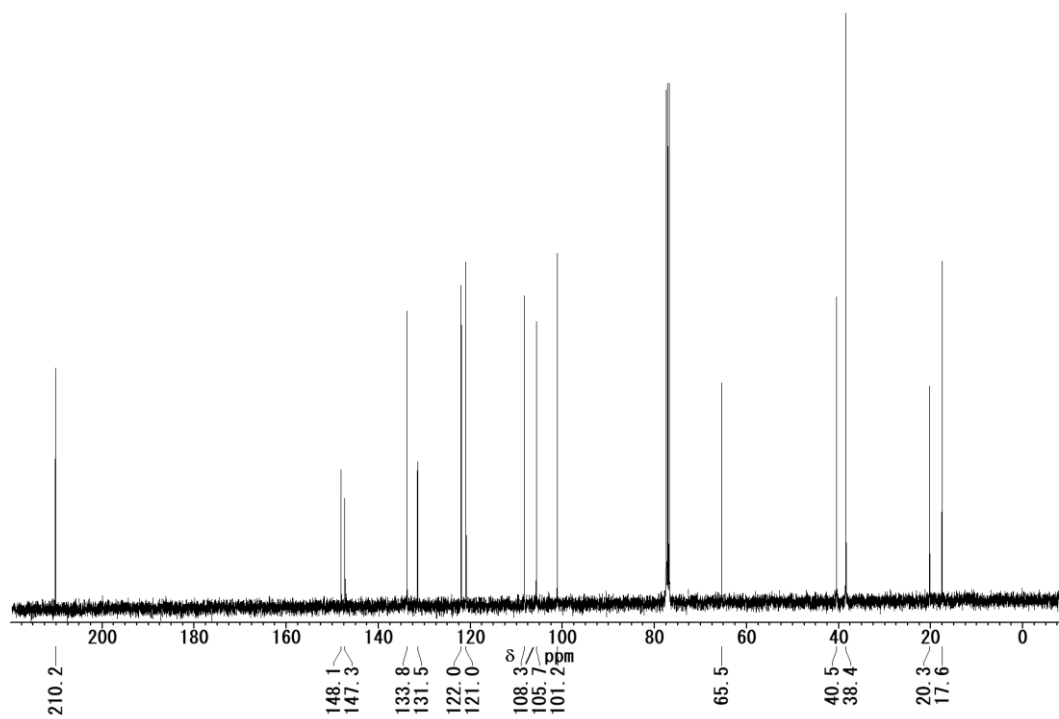
$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **1d**



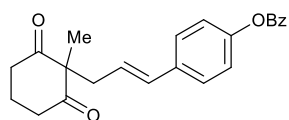
1e



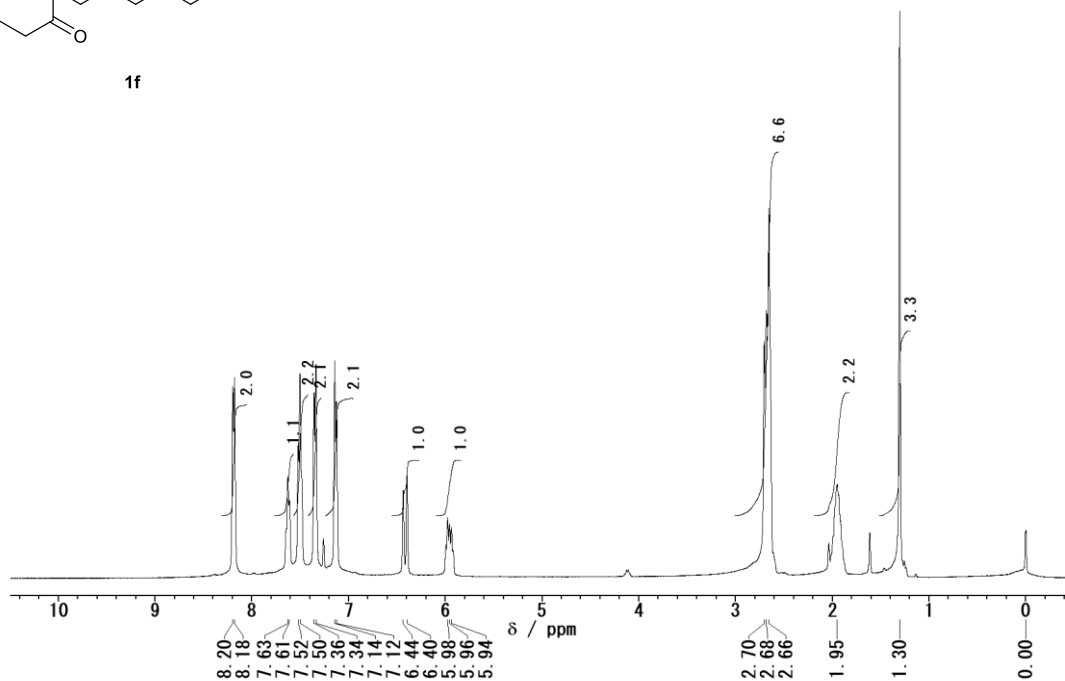
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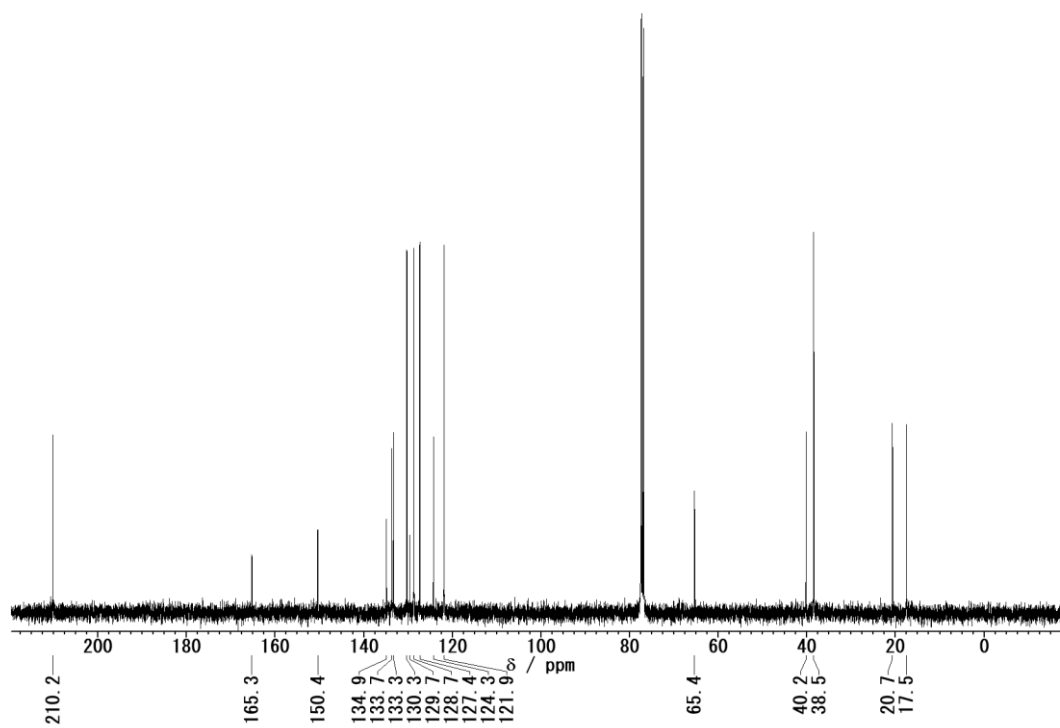
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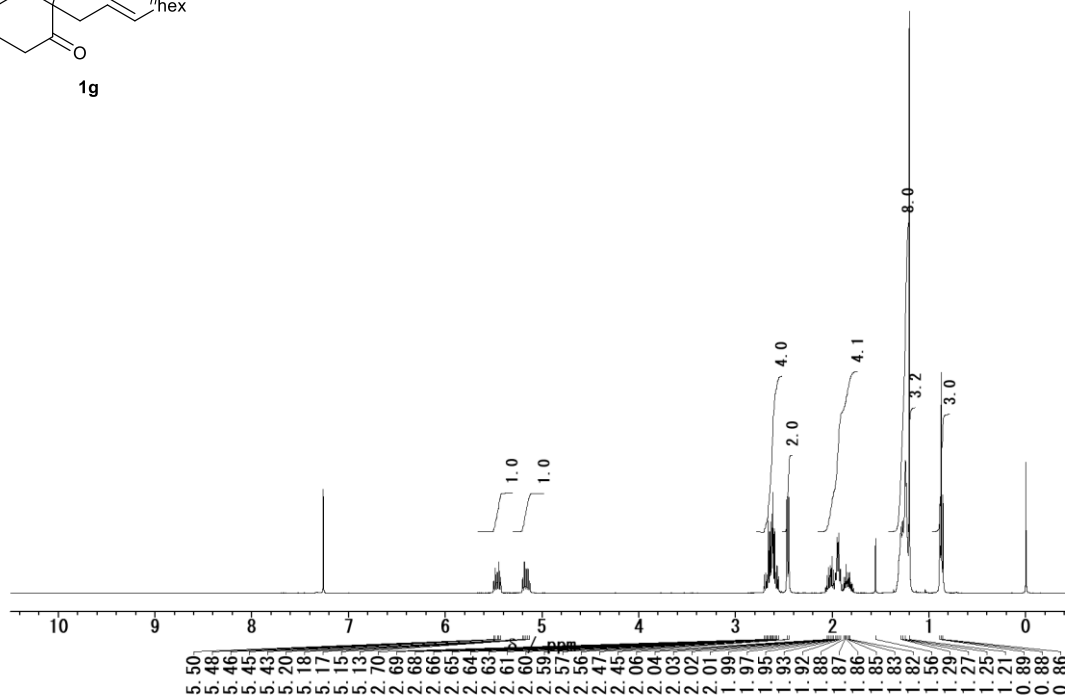
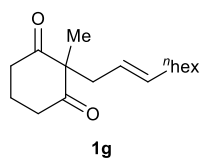
1f



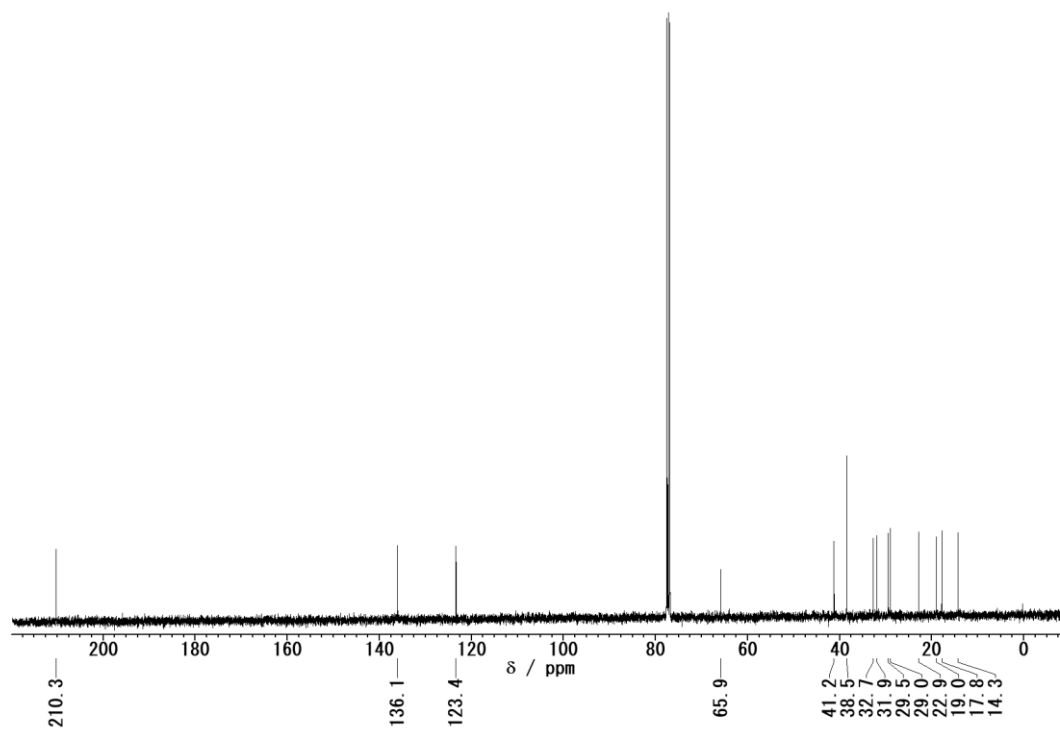
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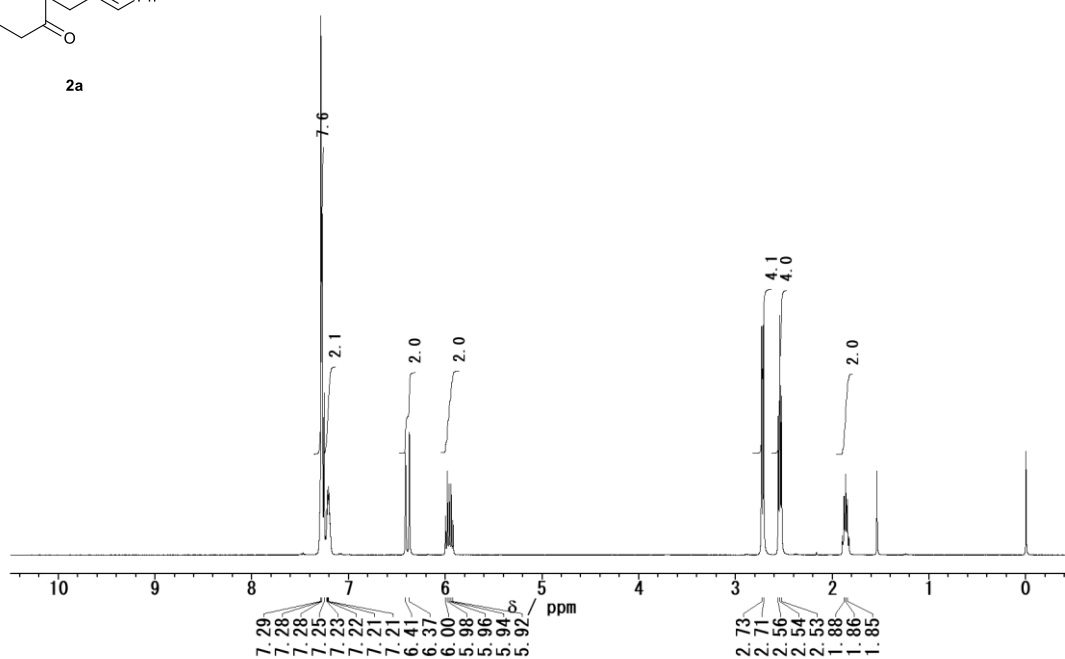
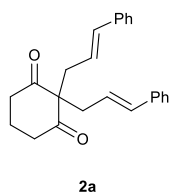
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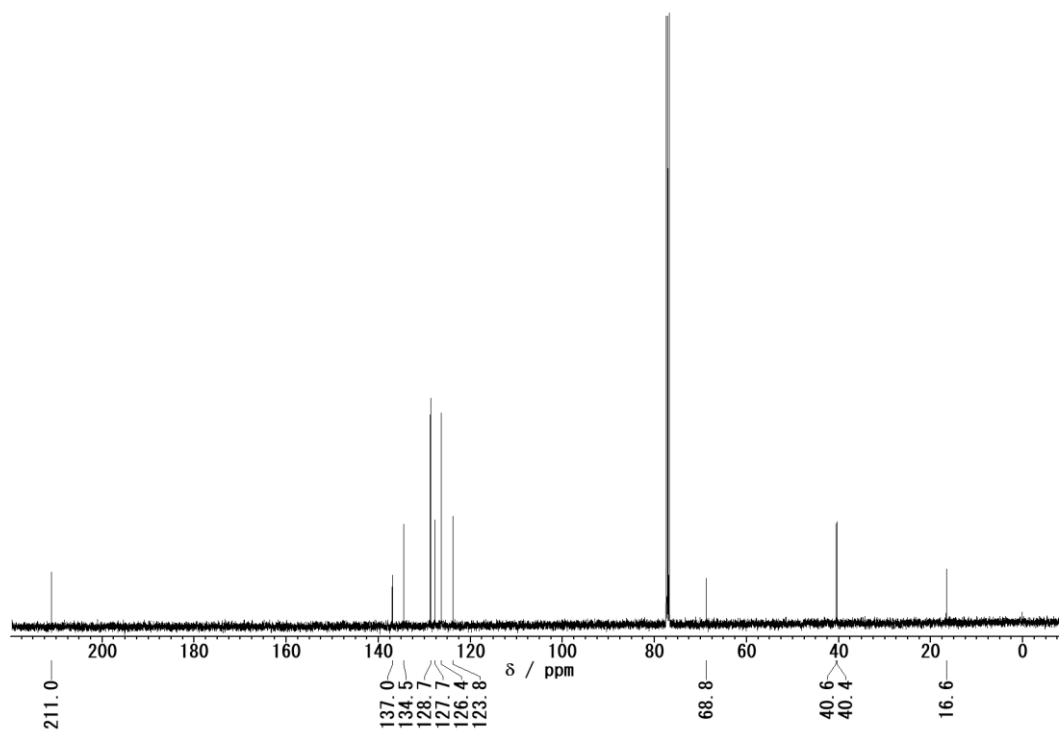
¹H NMR spectrum of **1g**



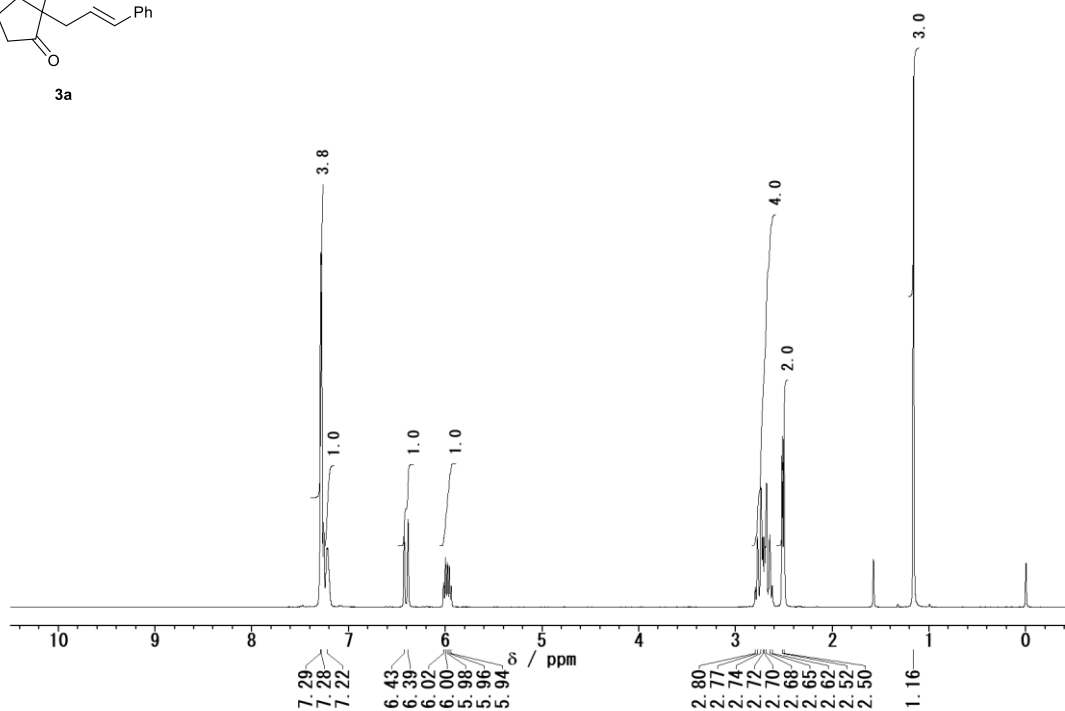
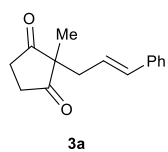
¹³C{¹H} NMR spectrum of **1g**



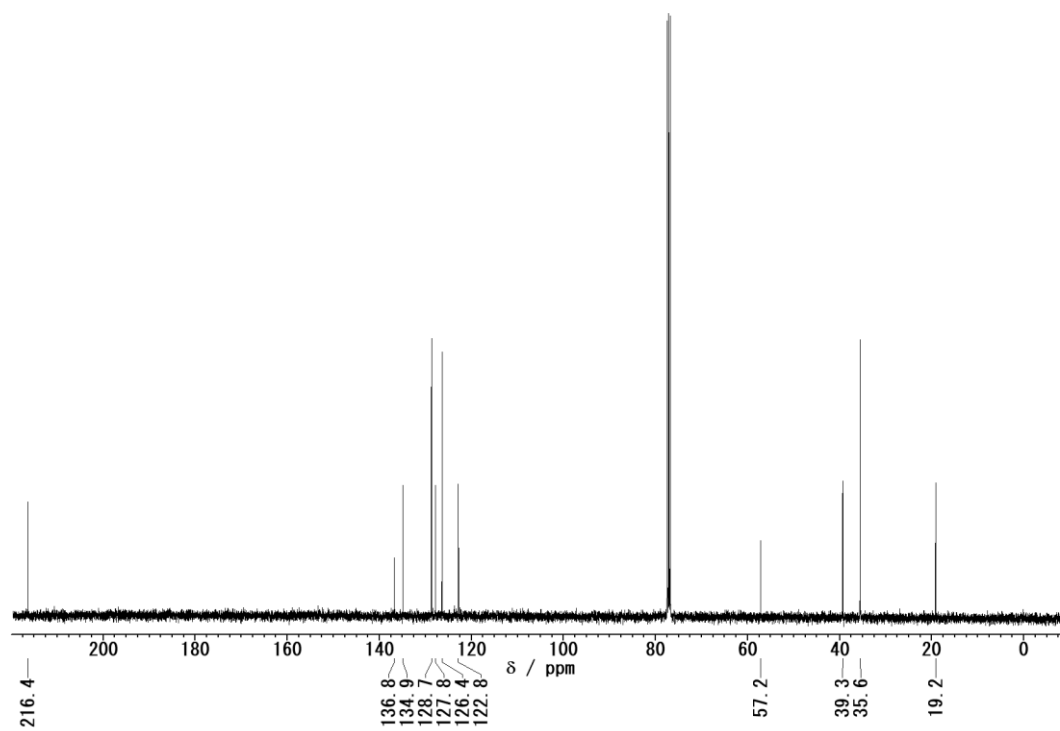
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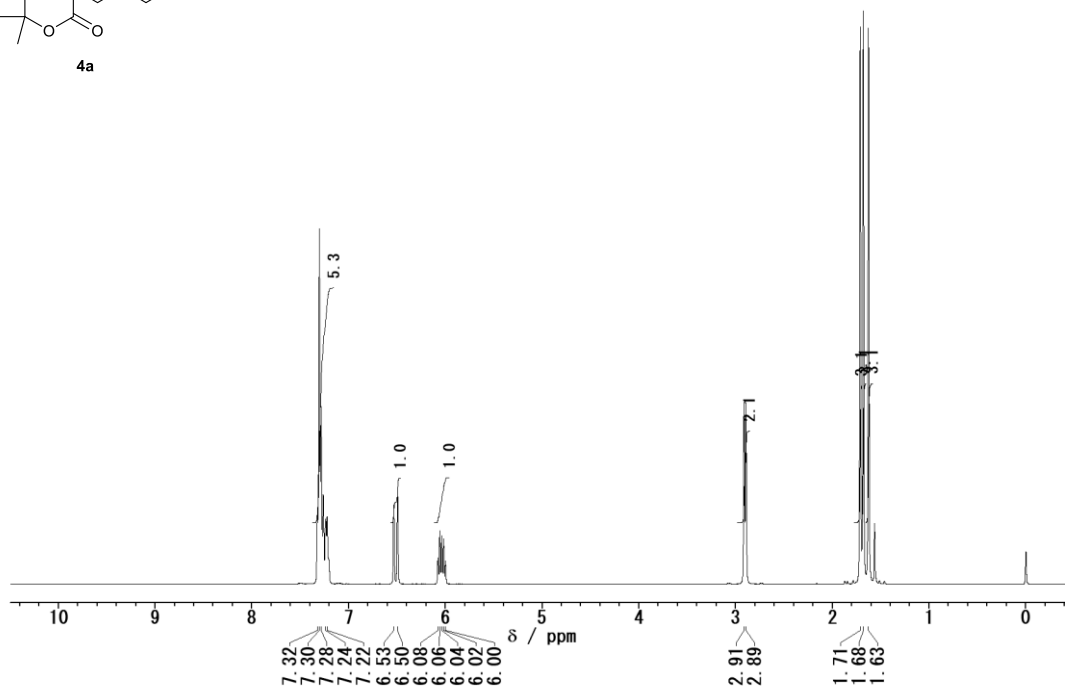
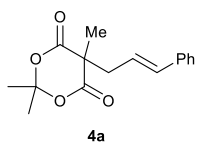
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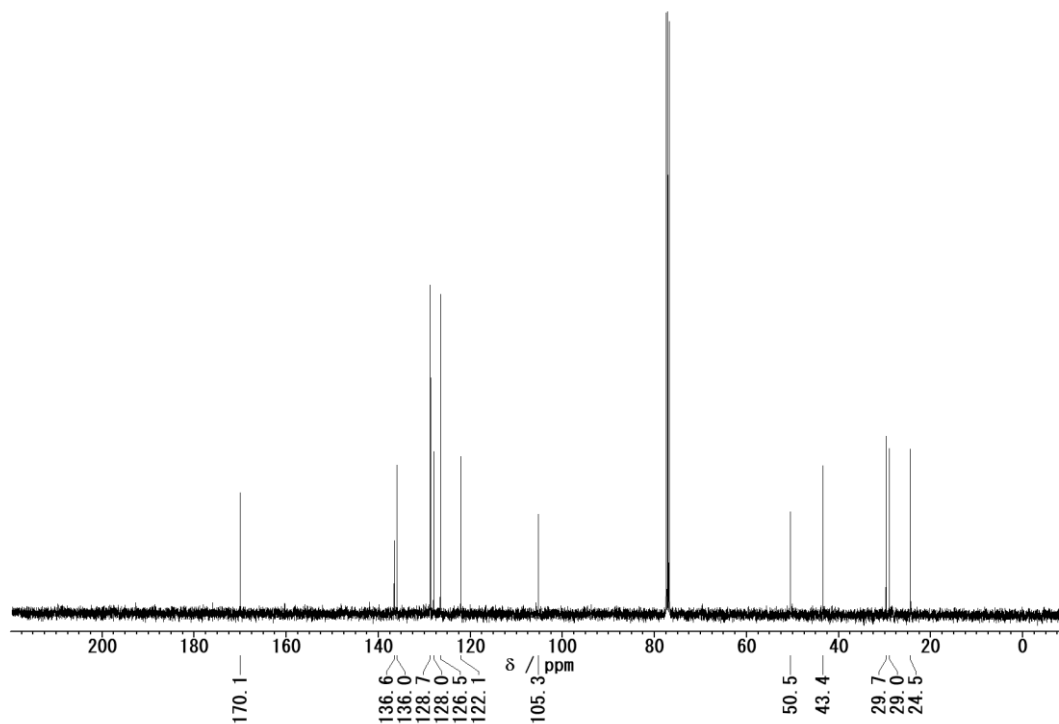
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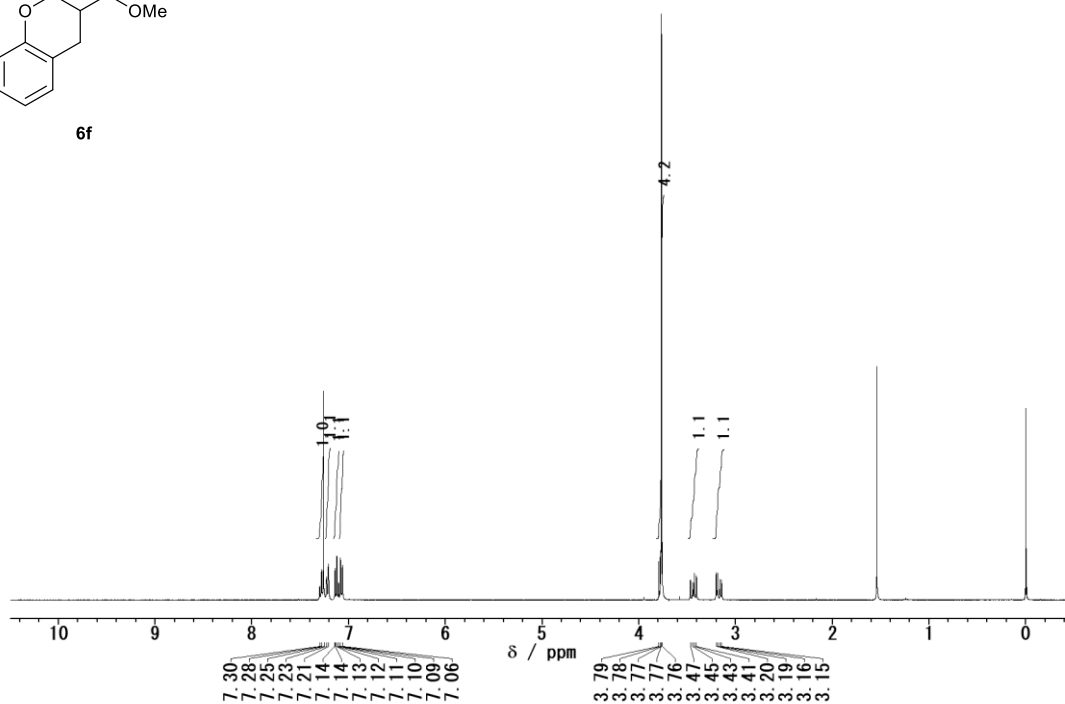
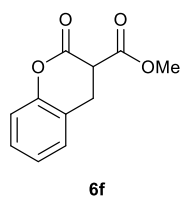
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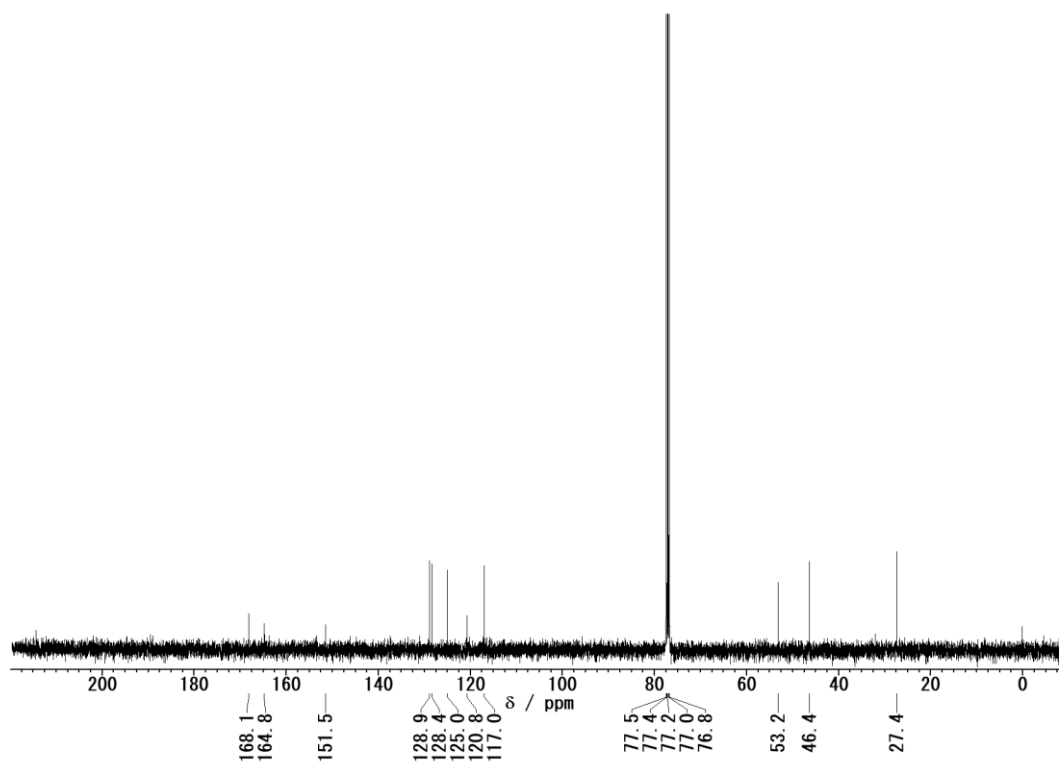
^1H NMR spectrum of **4a**



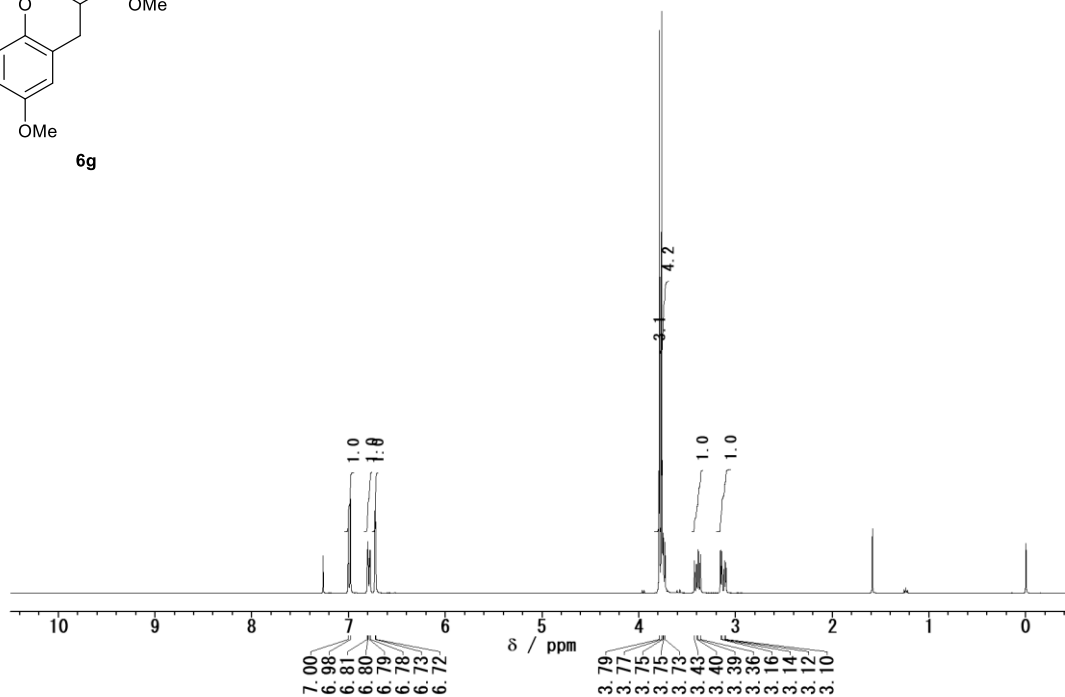
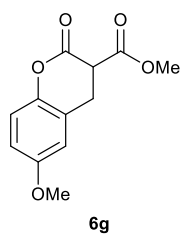
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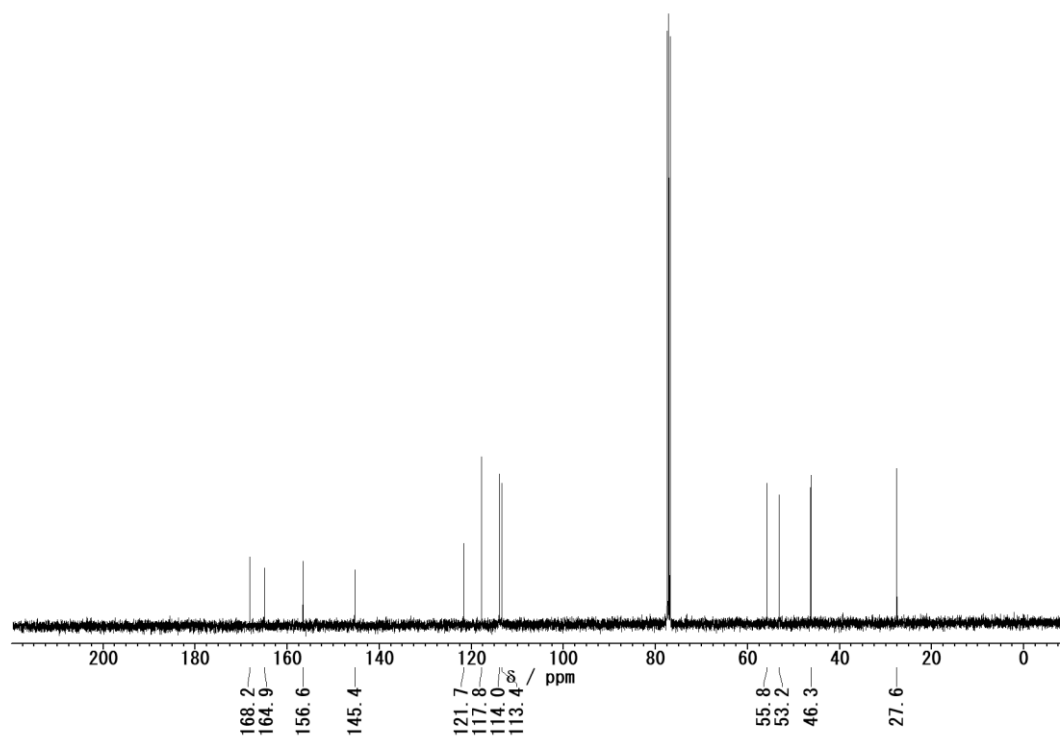
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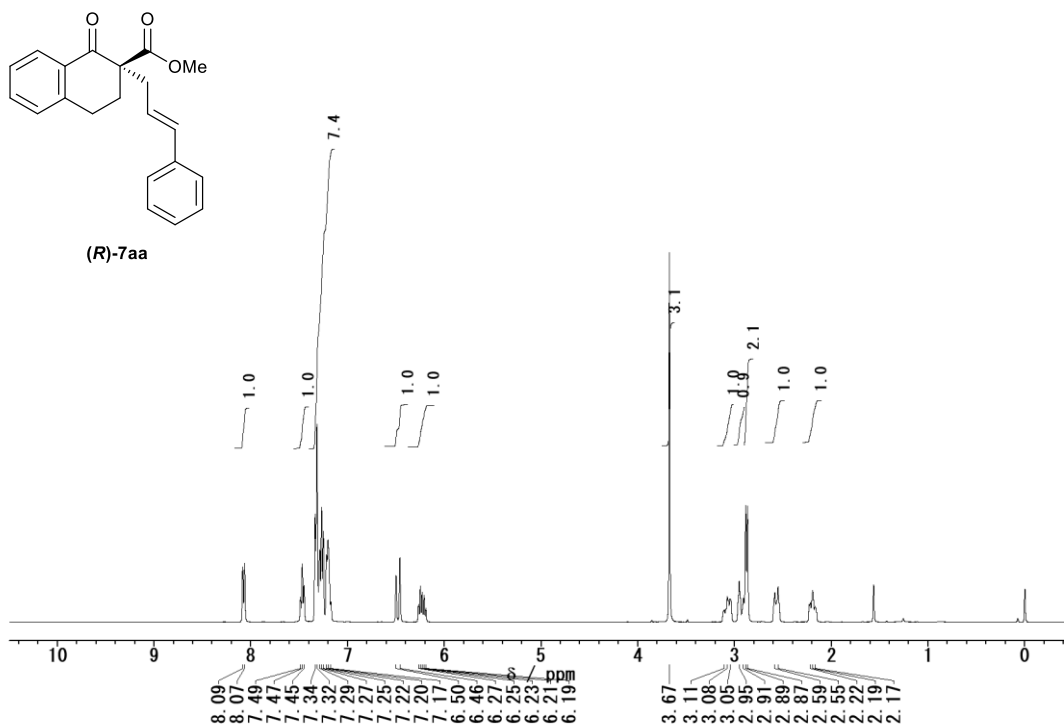
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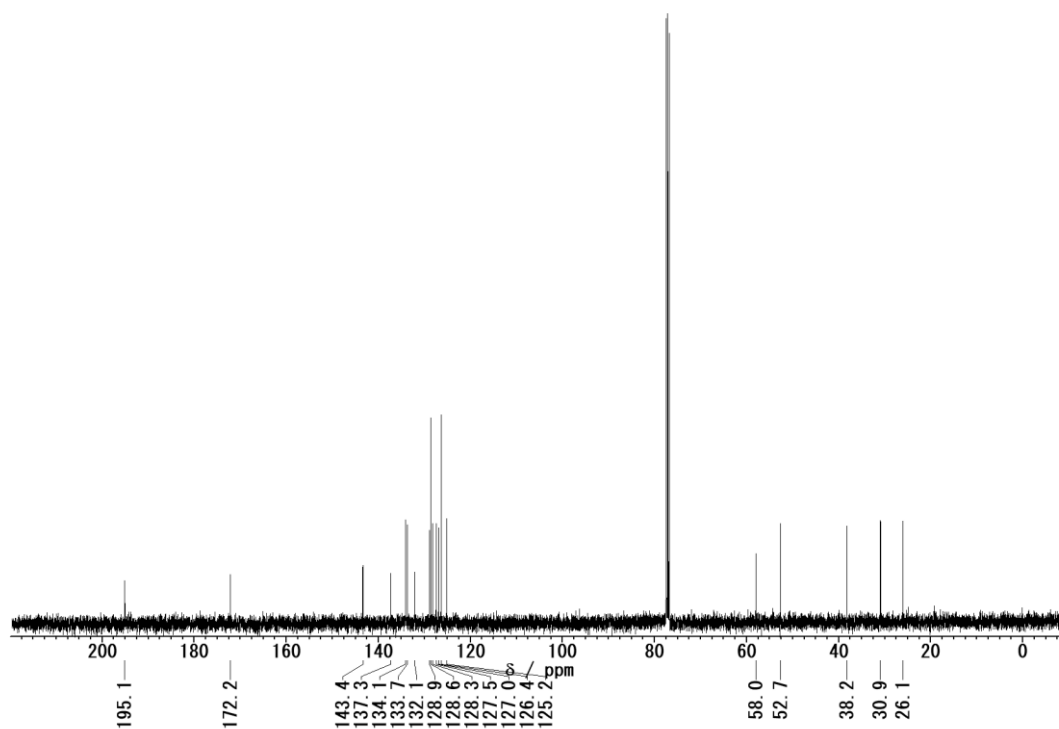
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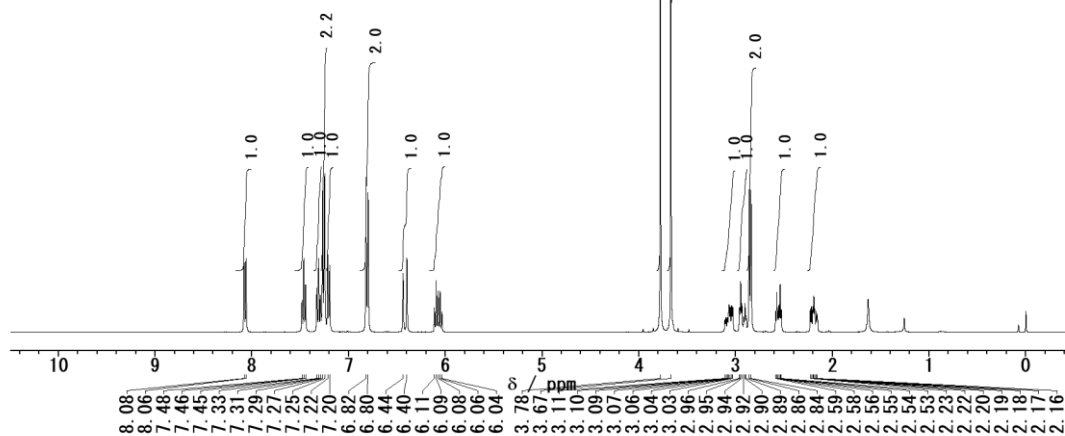
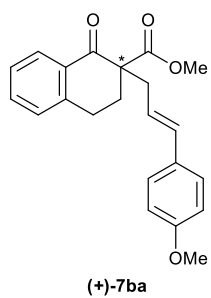
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6g**



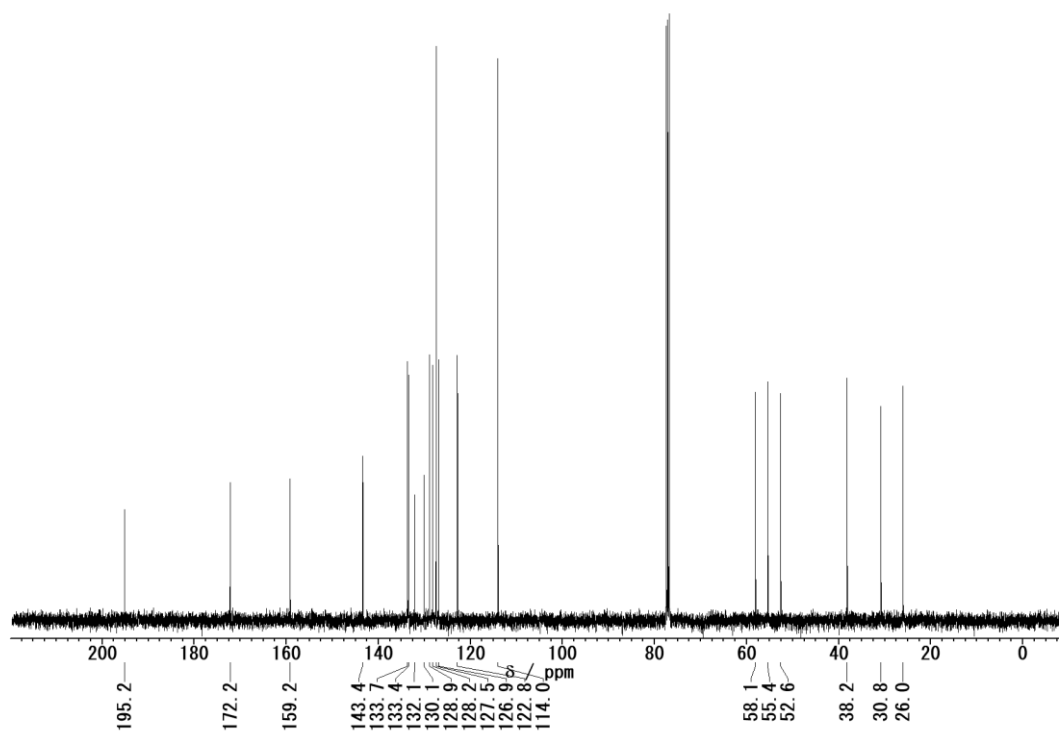
^1H NMR spectrum of **(R)-7aa**



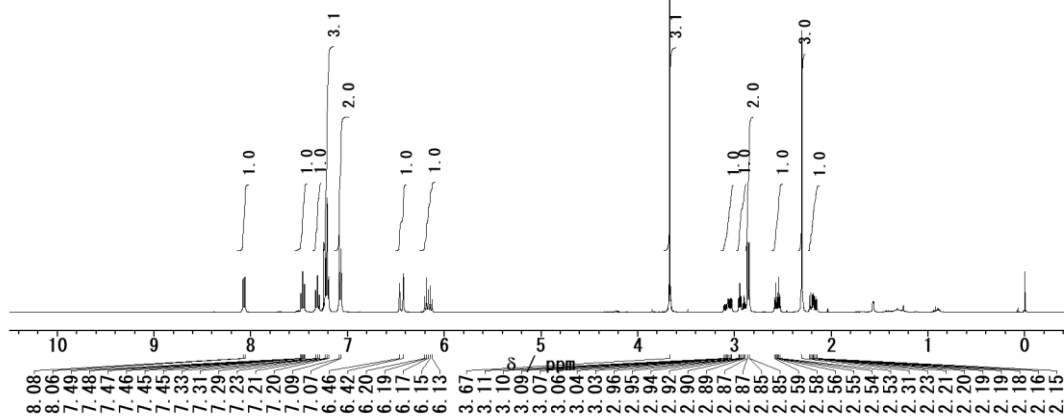
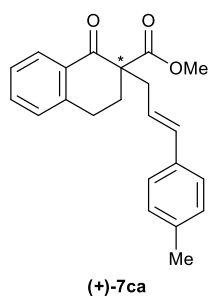
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **(R)-7aa**



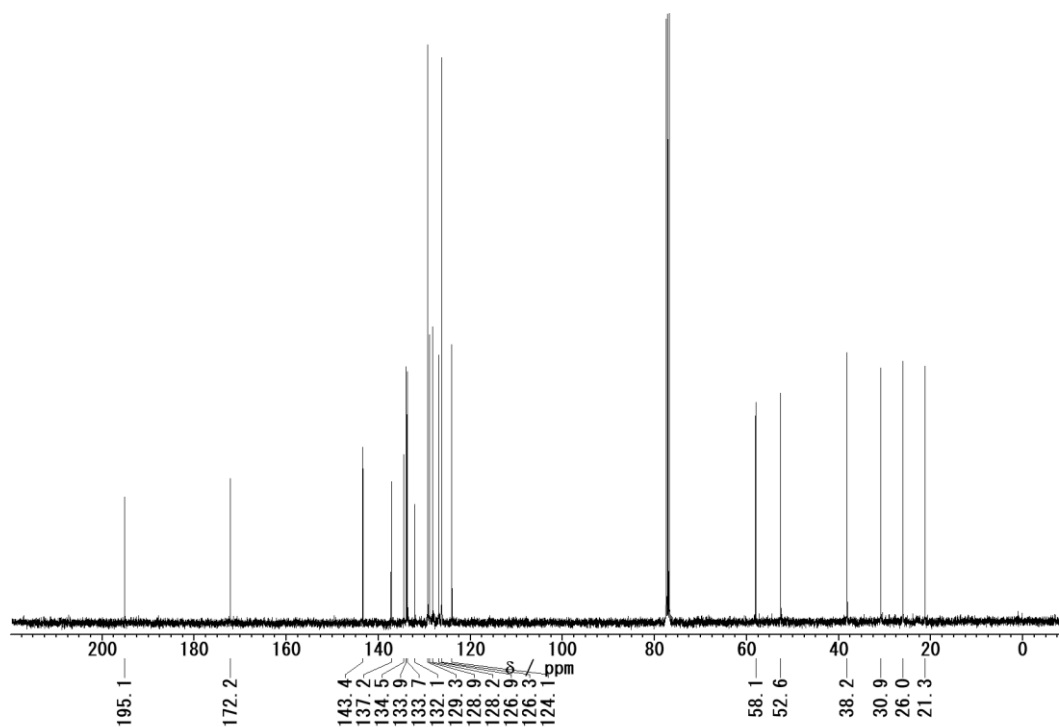
^1H NMR spectrum of (+)-7ba



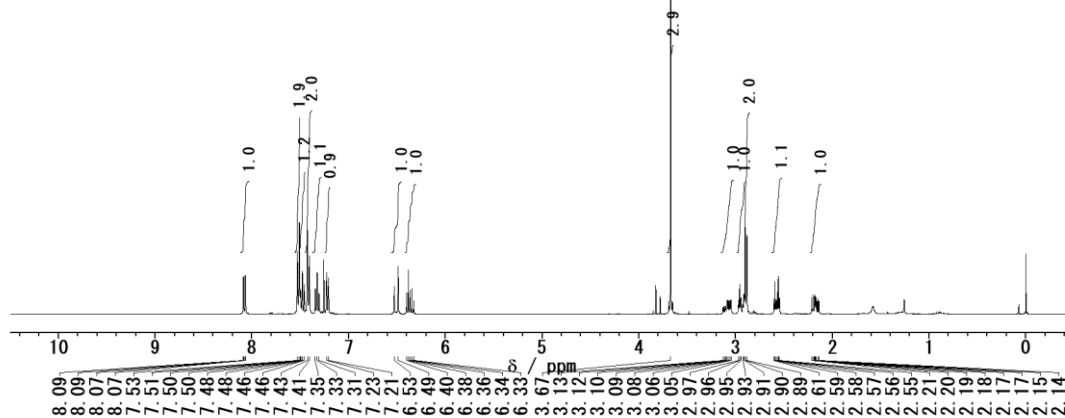
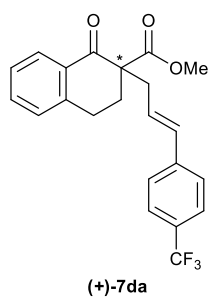
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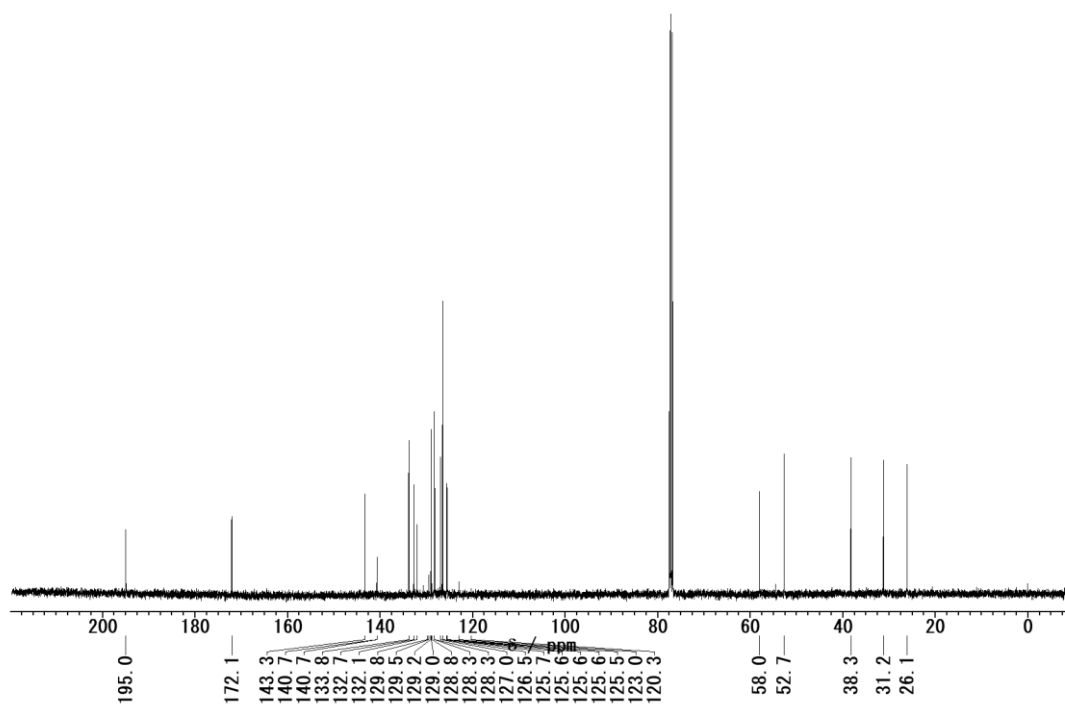
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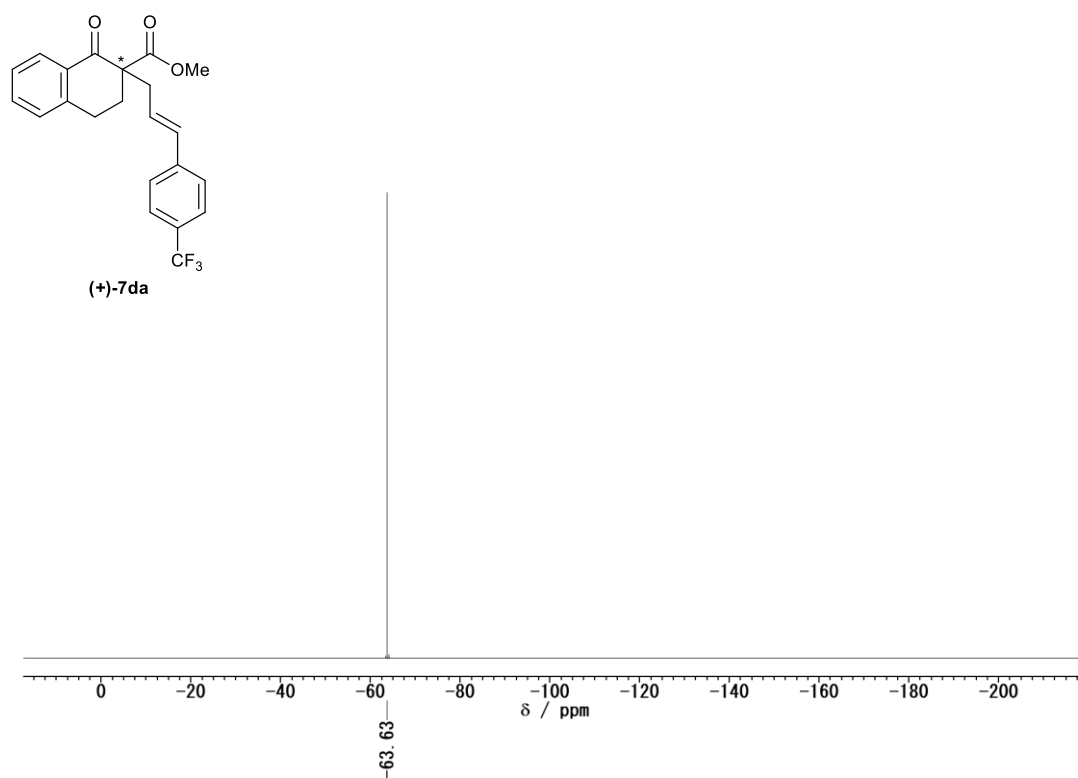
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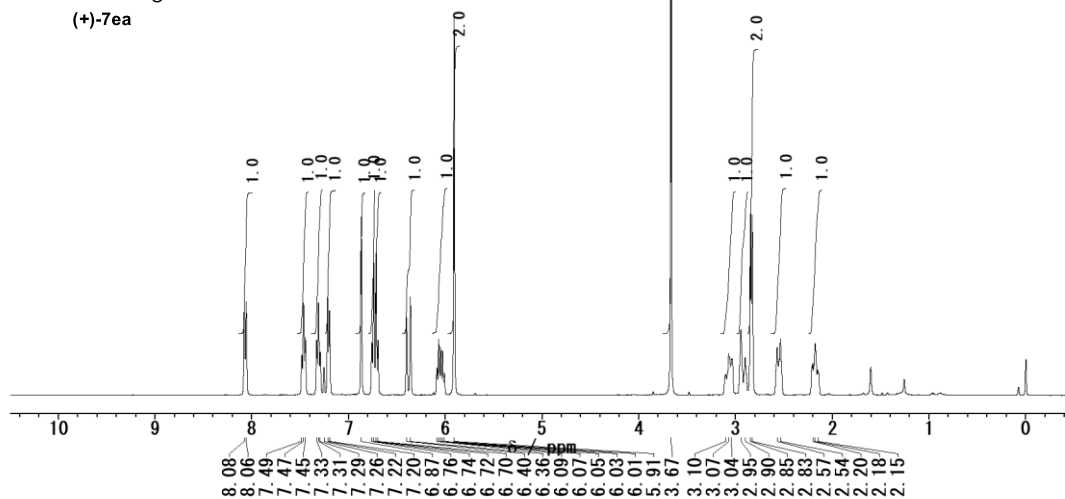
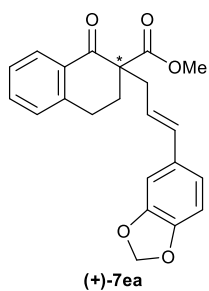
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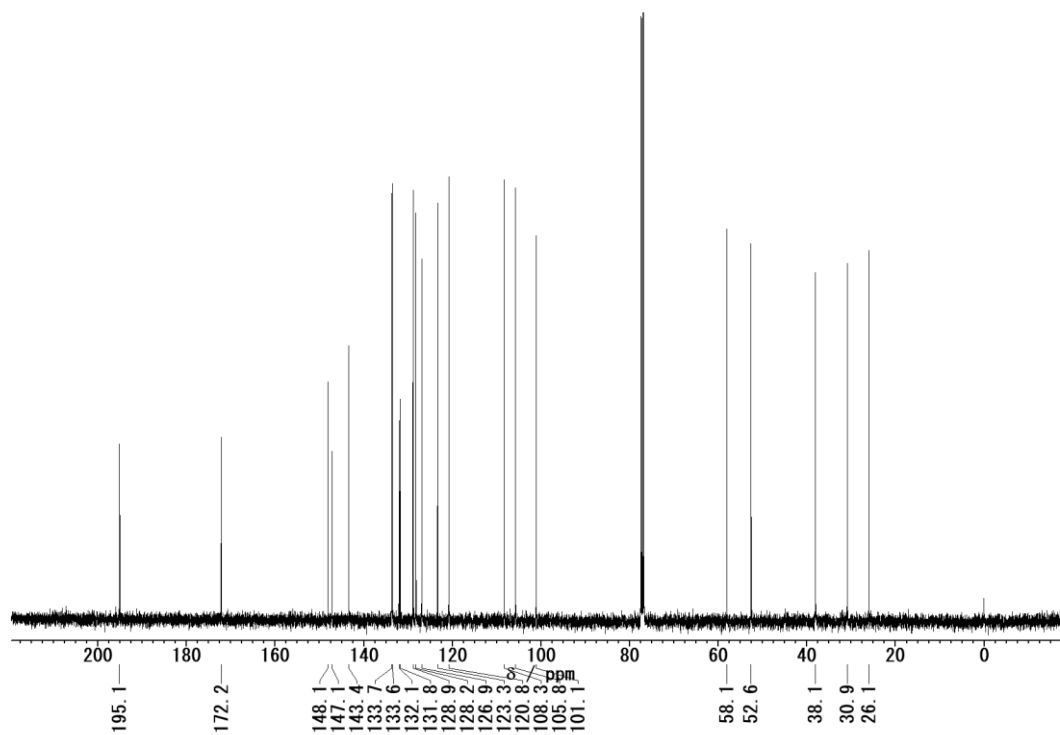
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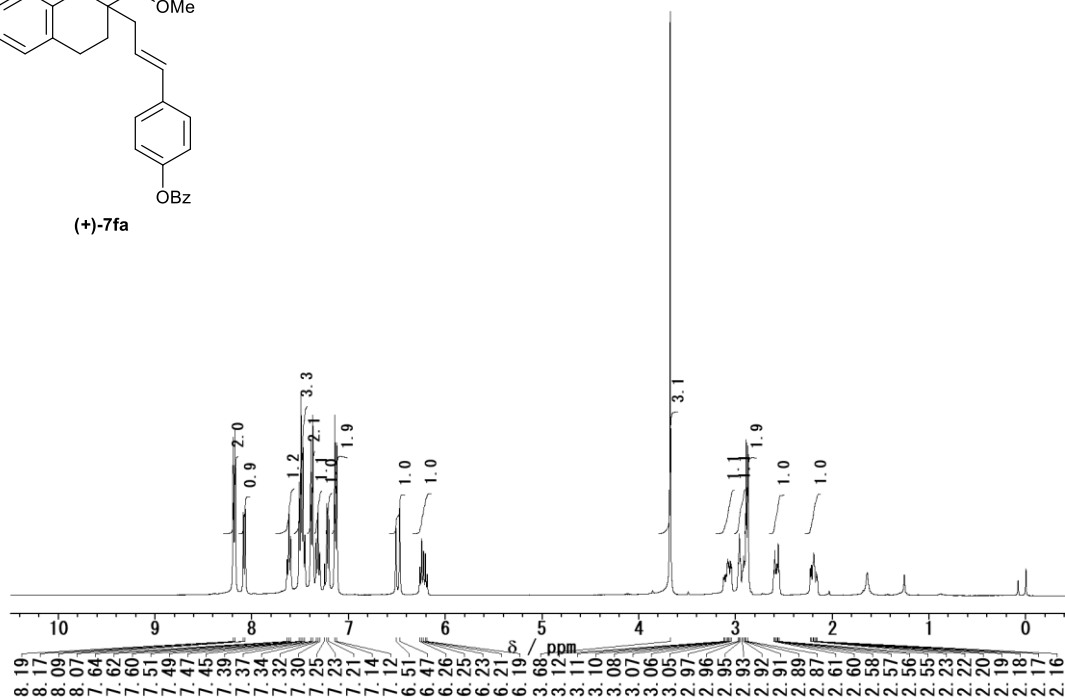
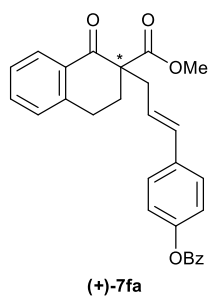
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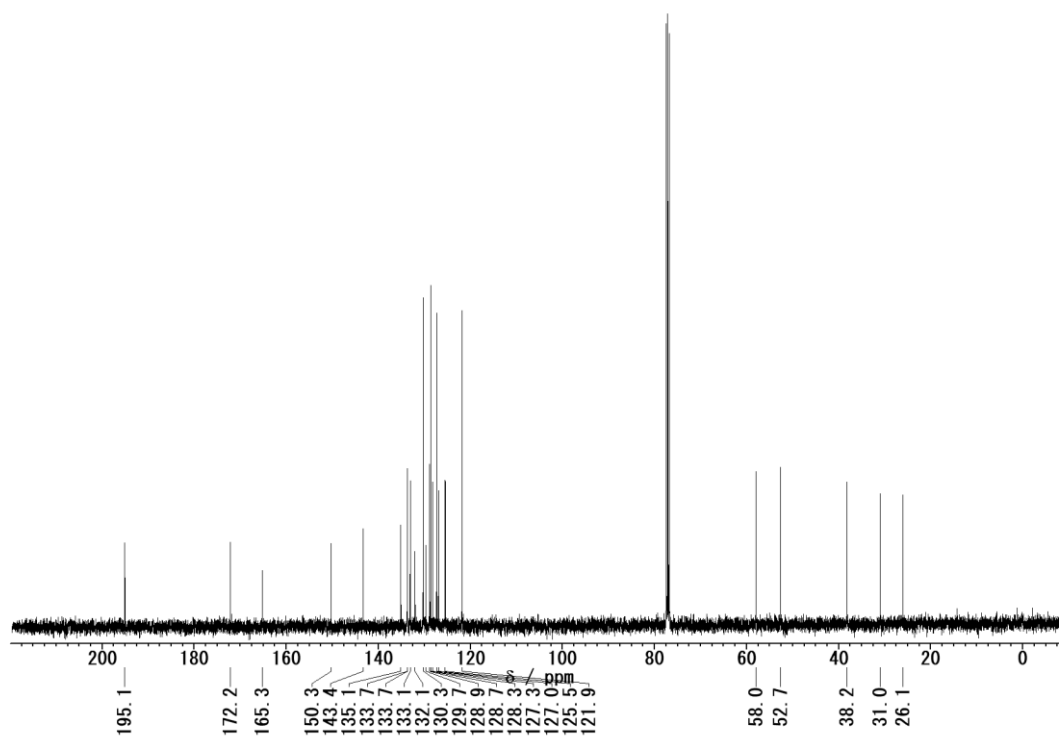
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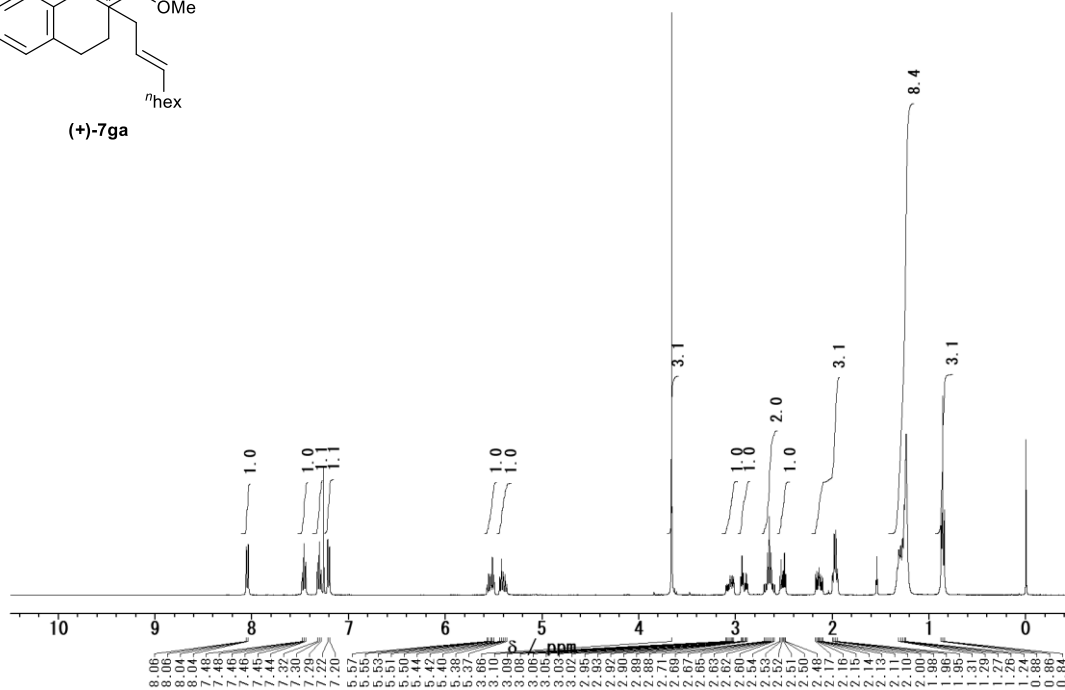
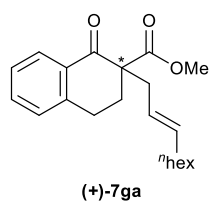
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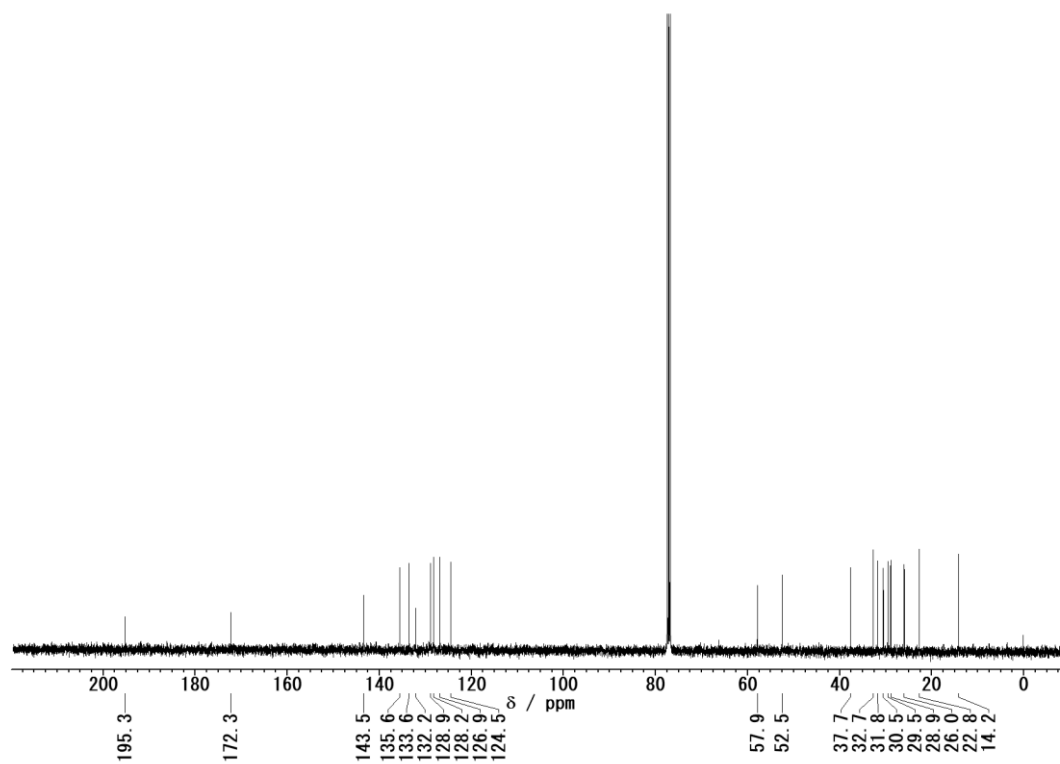
¹H NMR spectrum of (+)-7fa



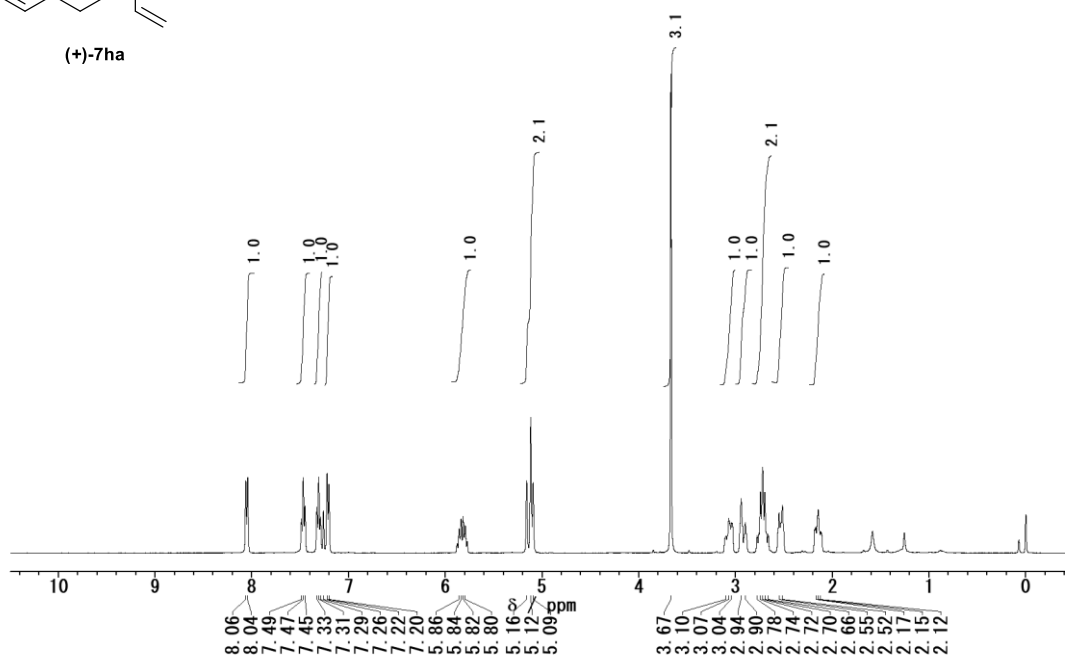
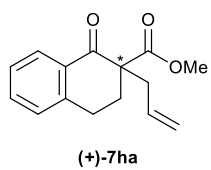
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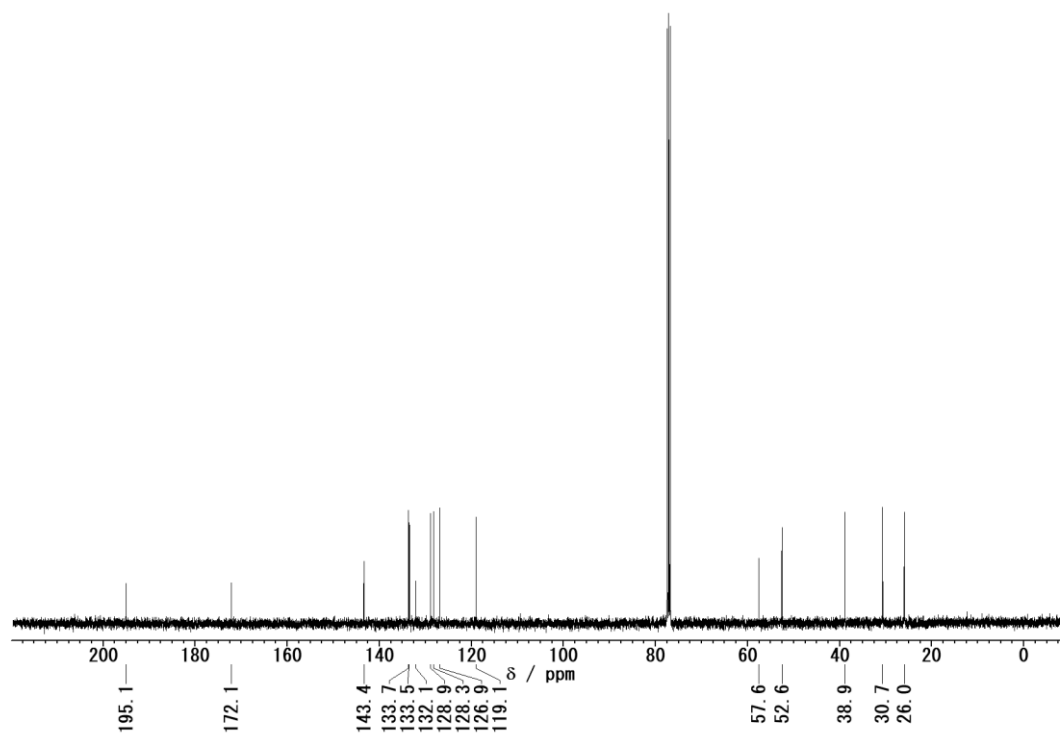
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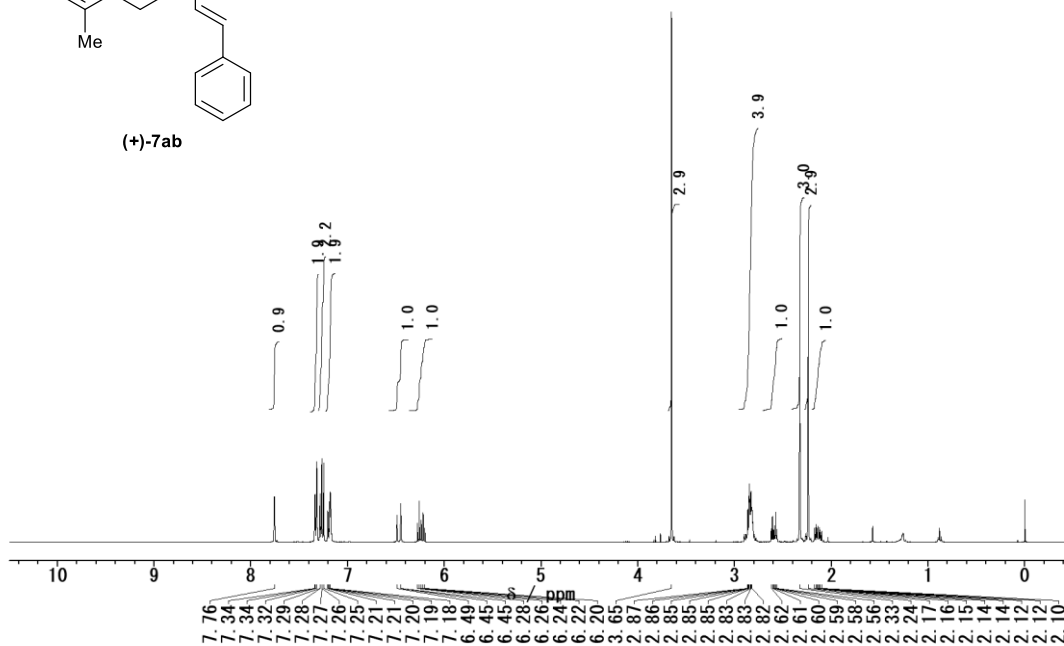
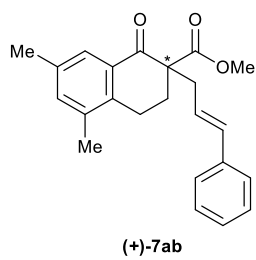
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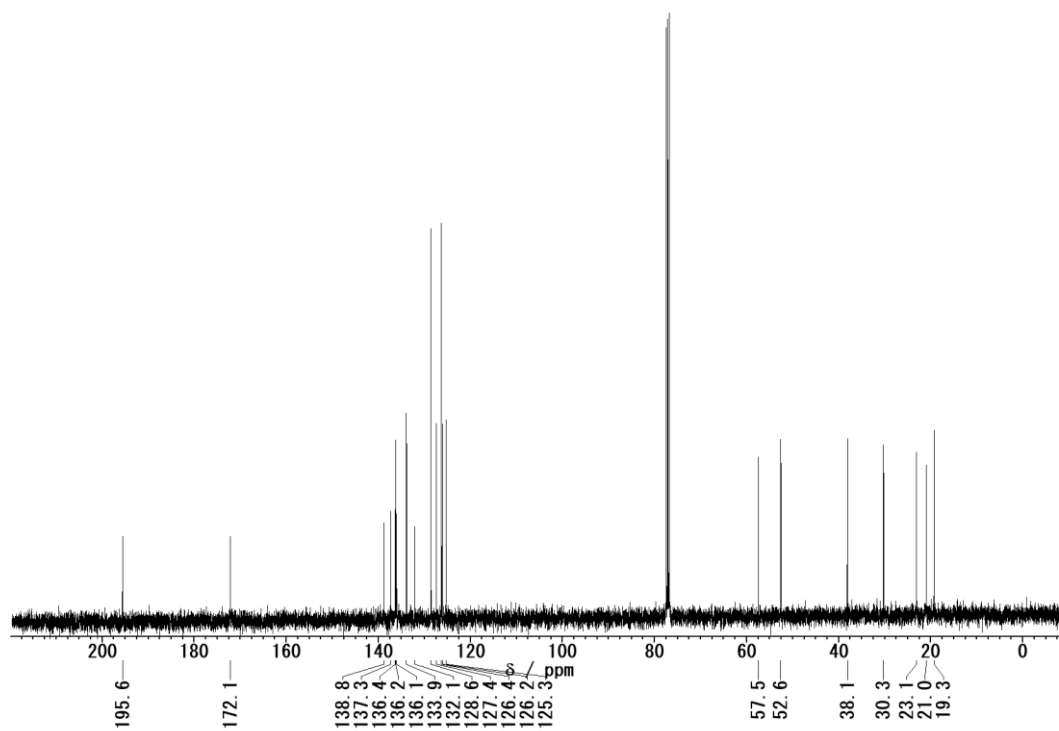
^1H NMR spectrum of (+)-7ha



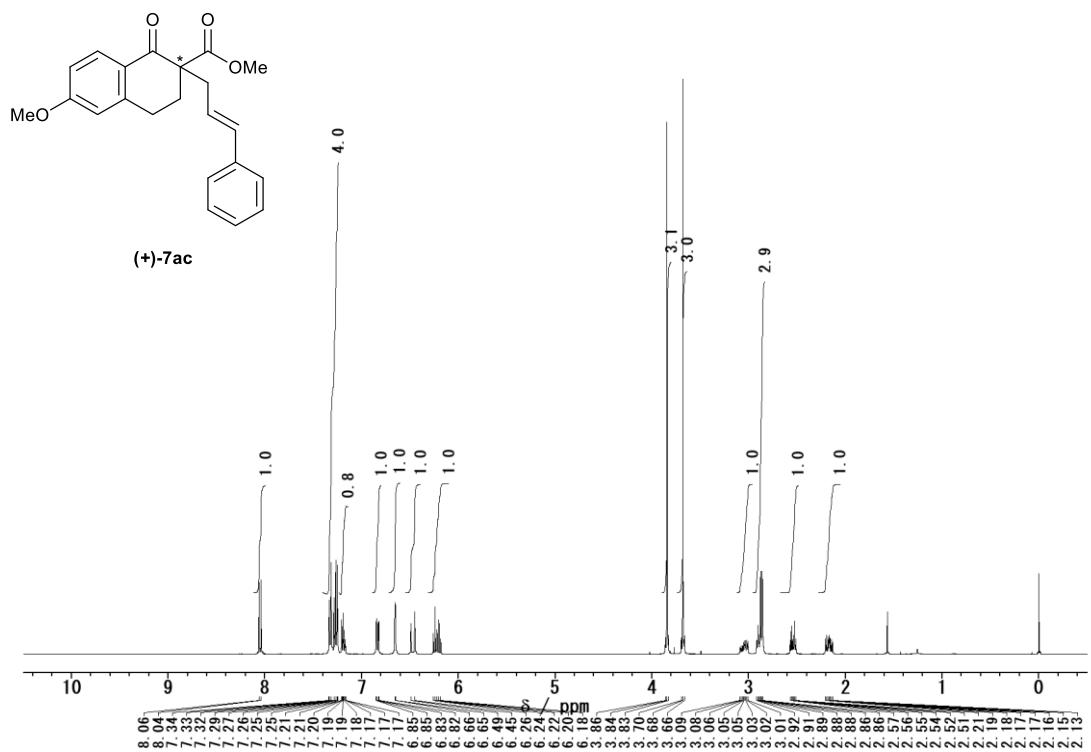
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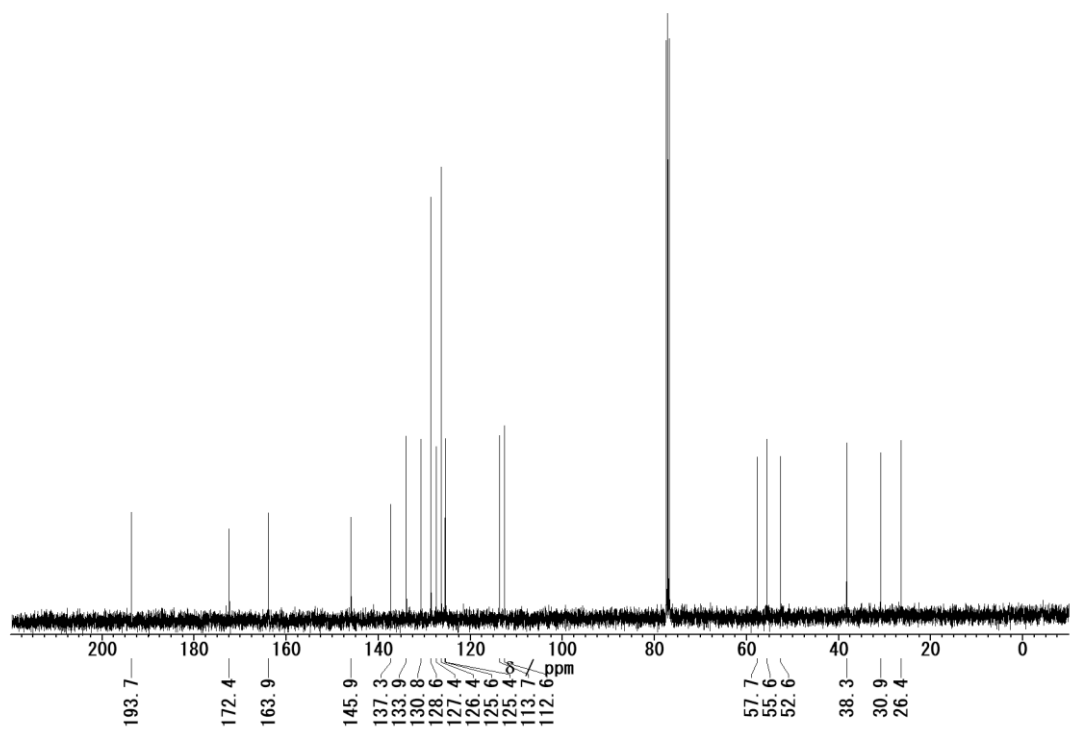
¹H NMR spectrum of (+)-7ab



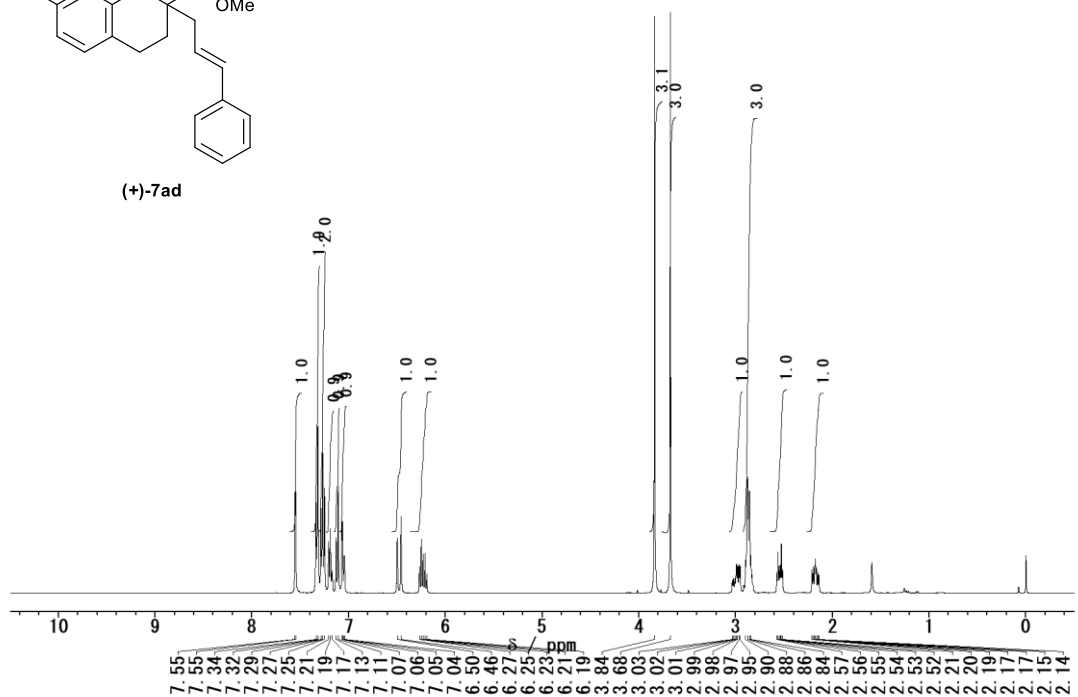
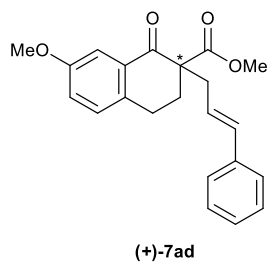
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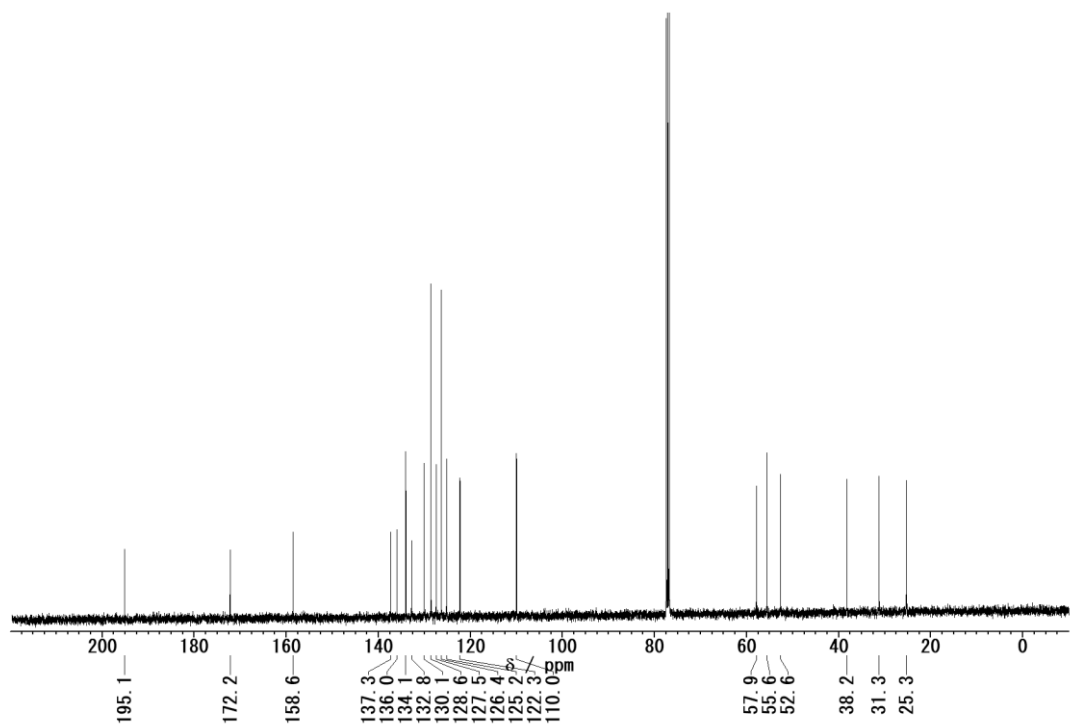
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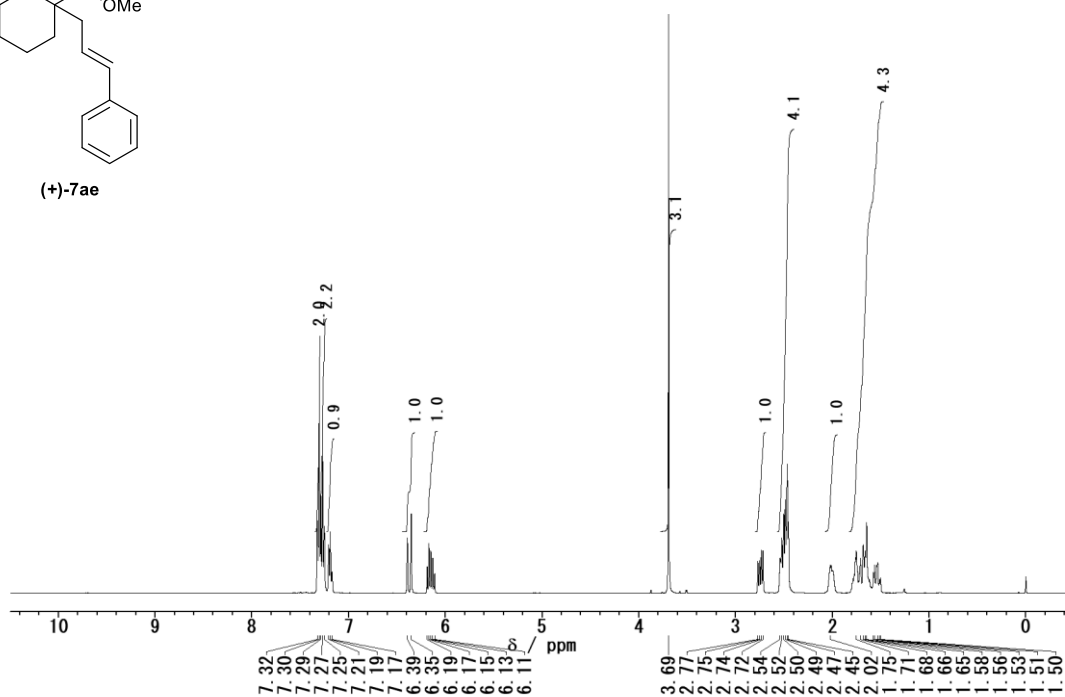
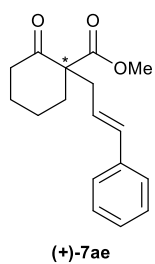
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (+)-7ac



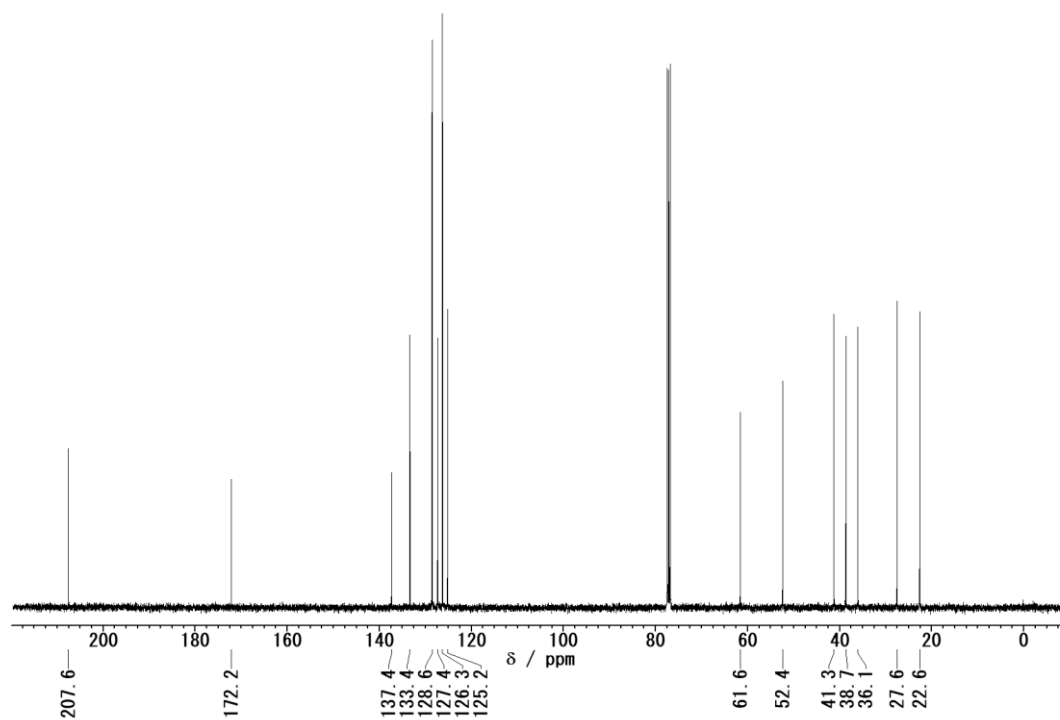
^1H NMR spectrum of (+)-7ad



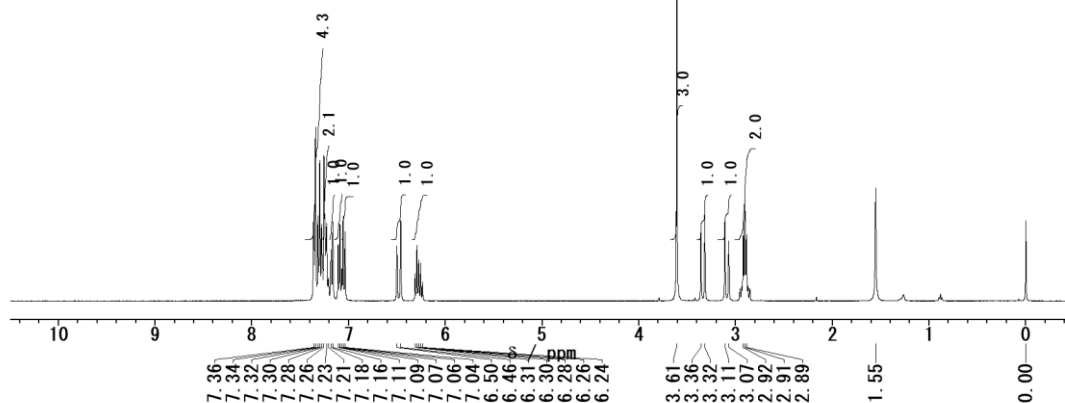
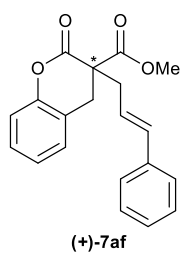
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (+)-7ad



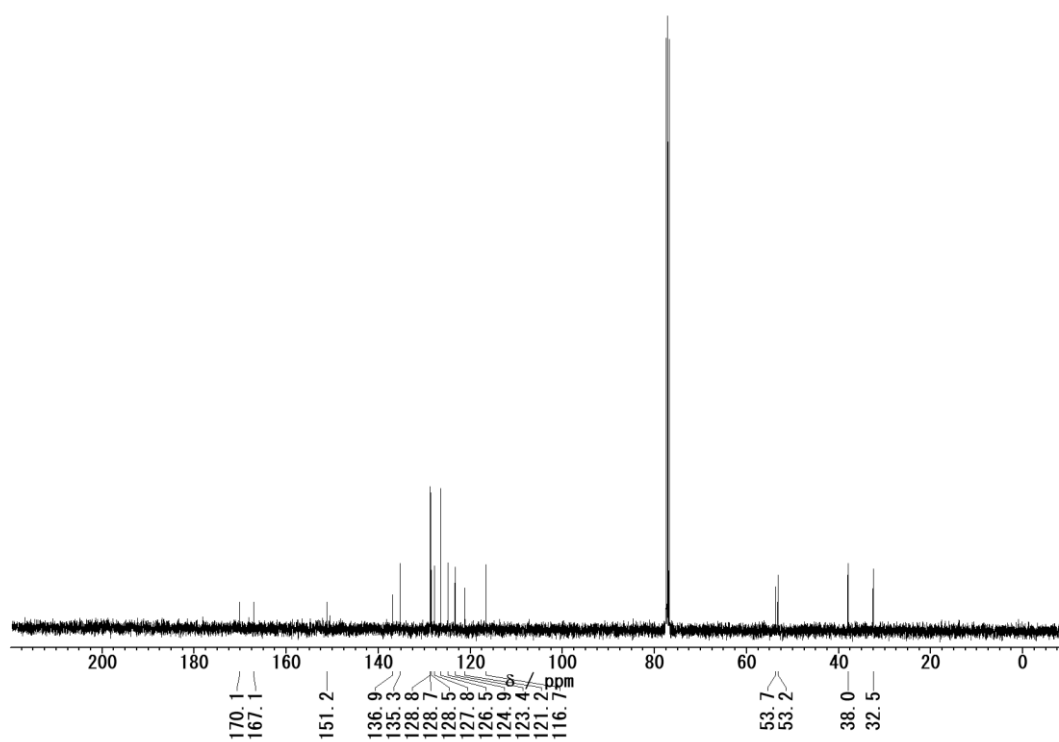
^1H NMR spectrum of (+)-7ae



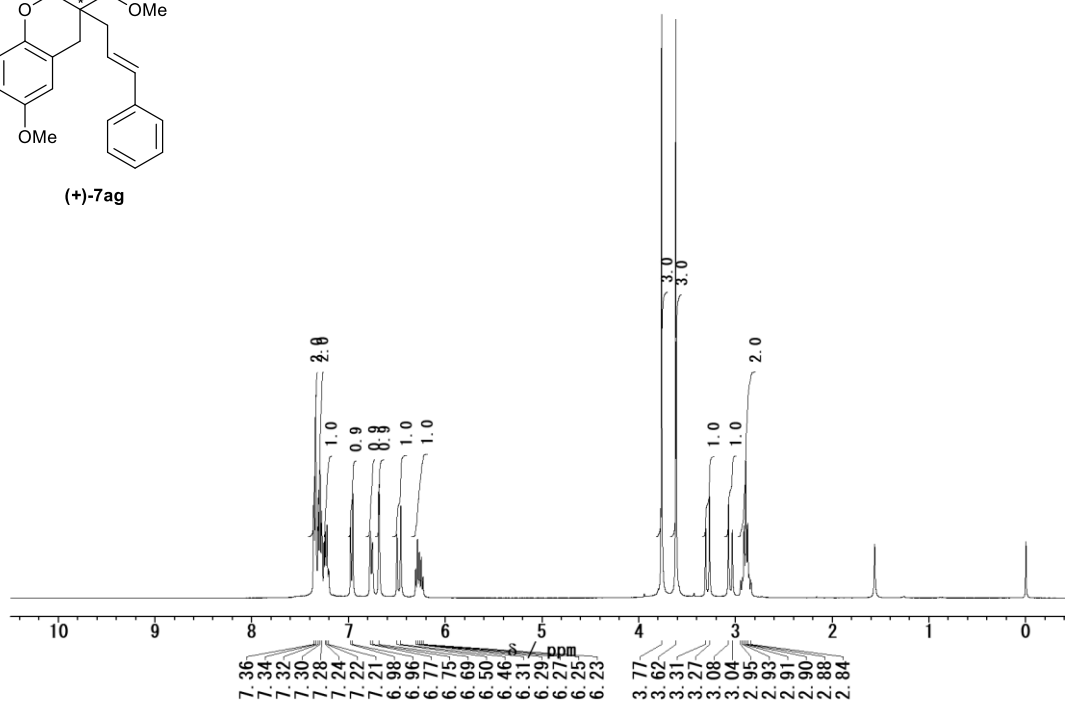
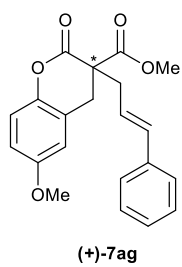
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (+)-7ae



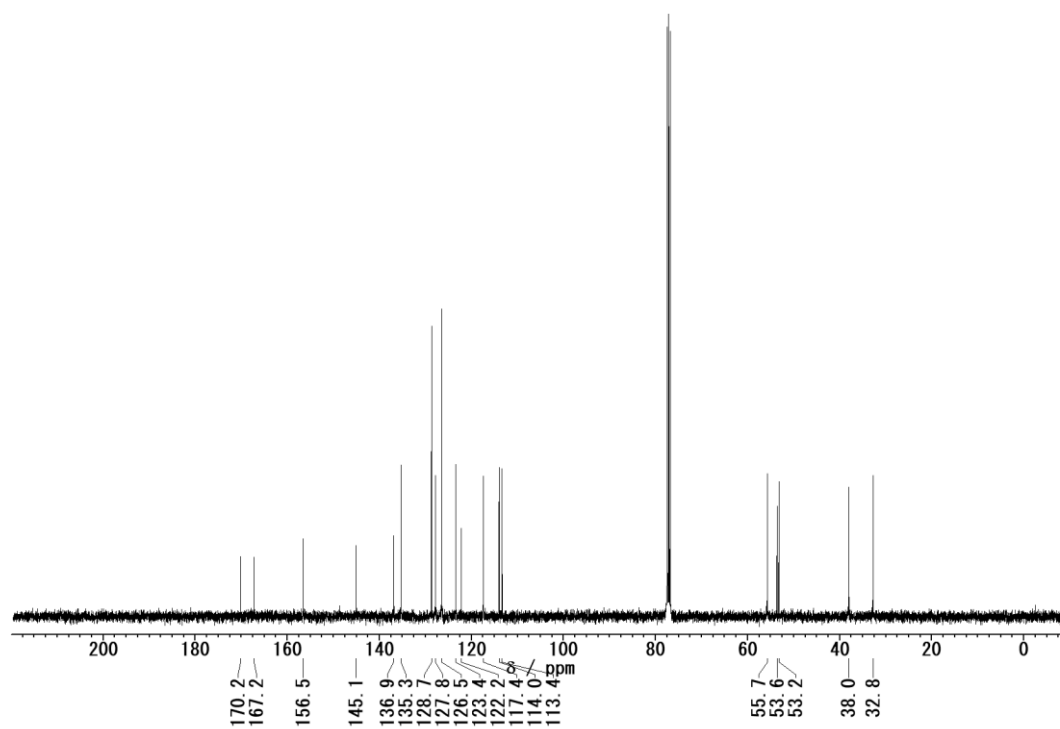
^1H NMR spectrum of (+)-7af



$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (+)-7af

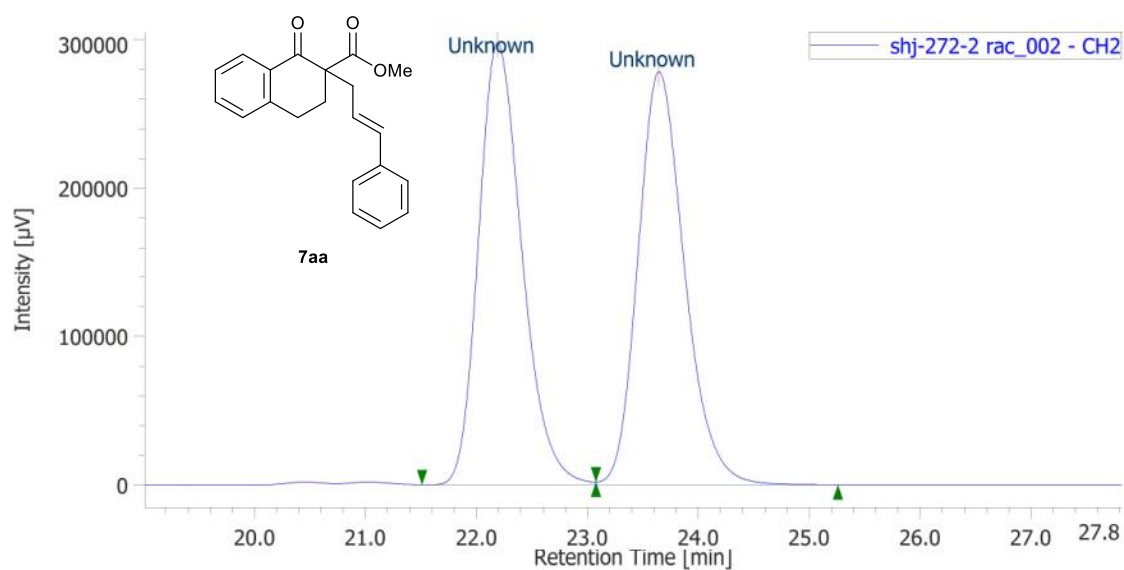


^1H NMR spectrum of (+)-7ag

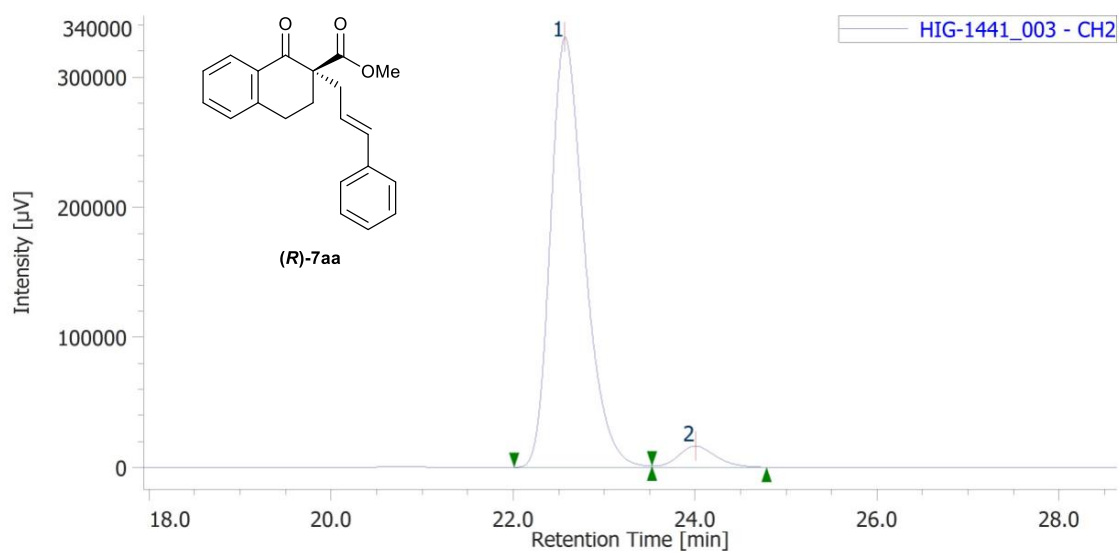


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (+)-7ag

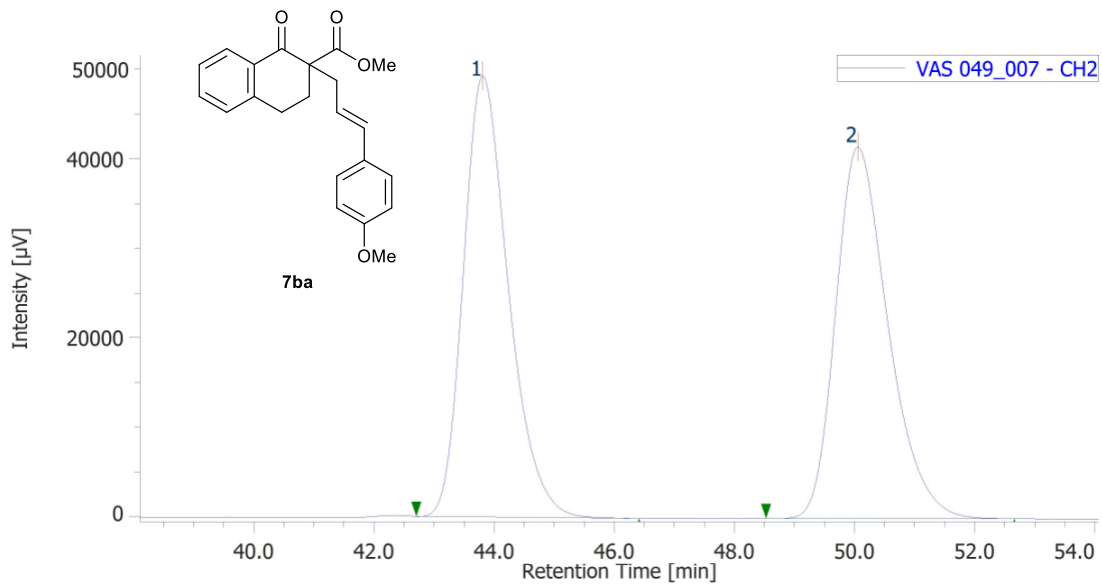
HPLC Charts



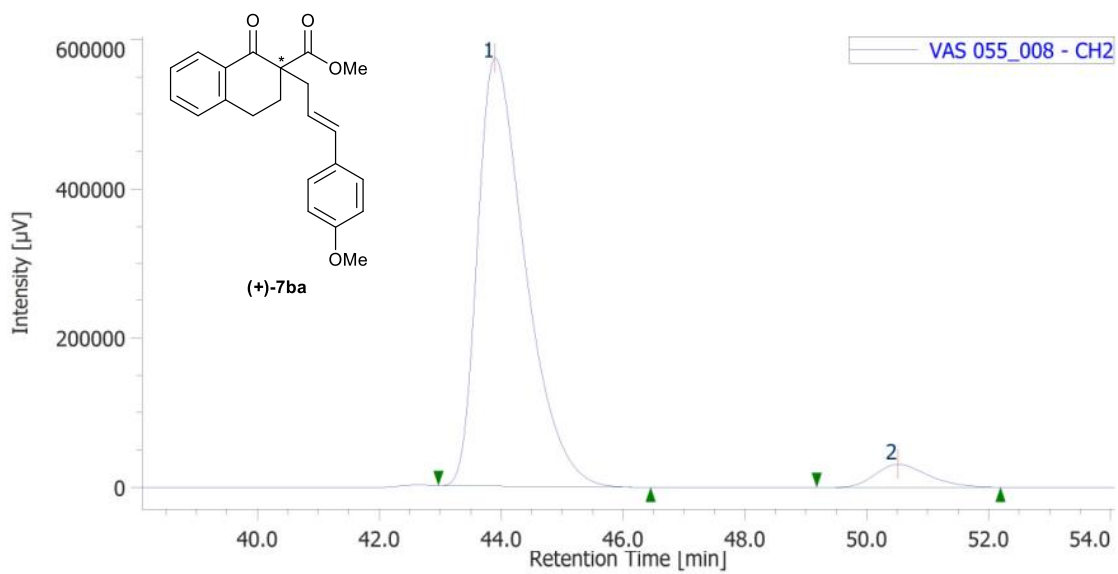
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	22.192	8061470	297187	49.906	51.673	N/A	15865	1.996	1.250	
2	Unknown	2	23.642	8091865	277941	50.094	48.327	N/A	15807	N/A	1.232	



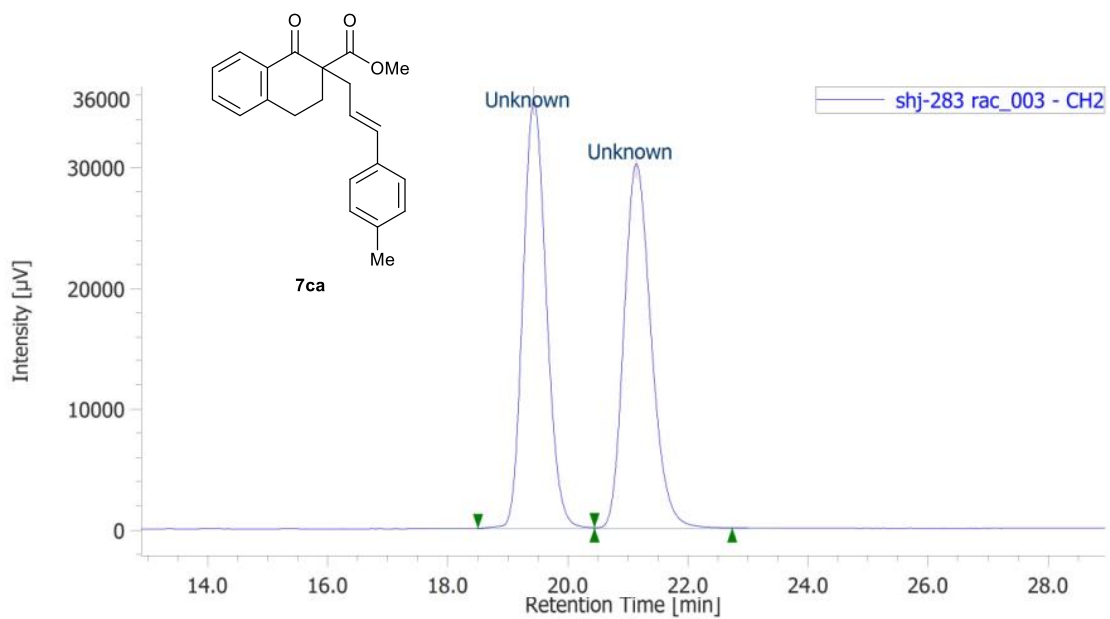
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	22.567	8553386	330259	94.858	95.307	N/A	18338	2.050	1.322	
2	Unknown	2	24.000	463661	16262	5.142	4.693	N/A	17047	N/A	N/A	



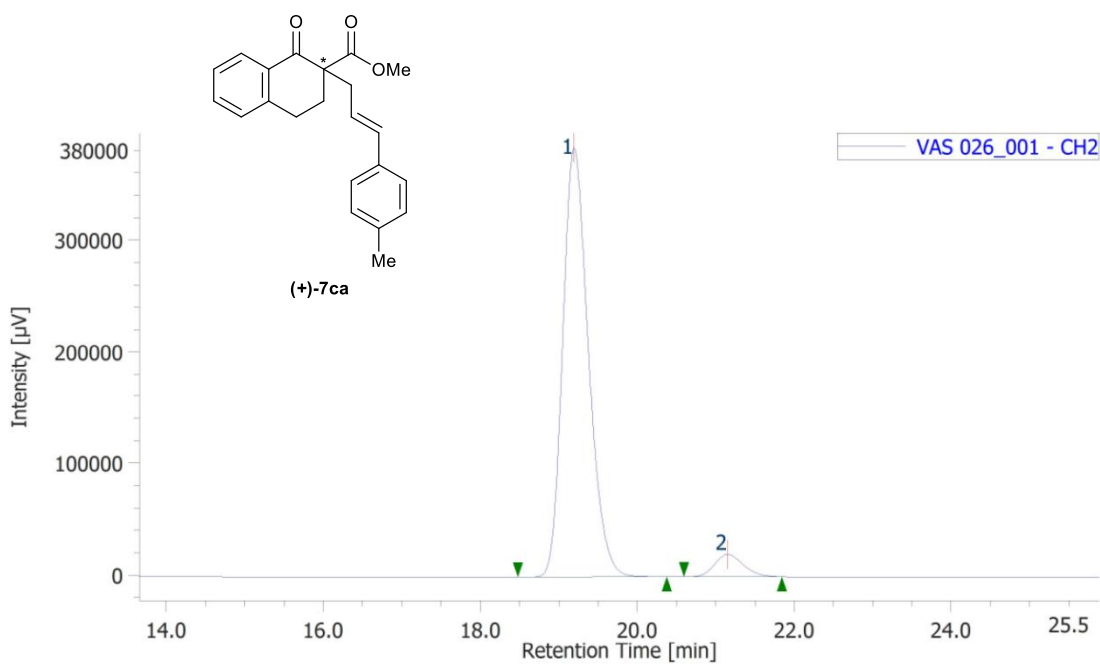
#	Peak Name	CH	tR [min]	Area [$\mu\text{V}\cdot\text{sec}$]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	43.808	2564643	49244	50.494	54.261	N/A	16884	4.295	1.295	
2	Unknown	2	50.050	2514422	41510	49.506	45.739	N/A	16356	N/A	1.325	



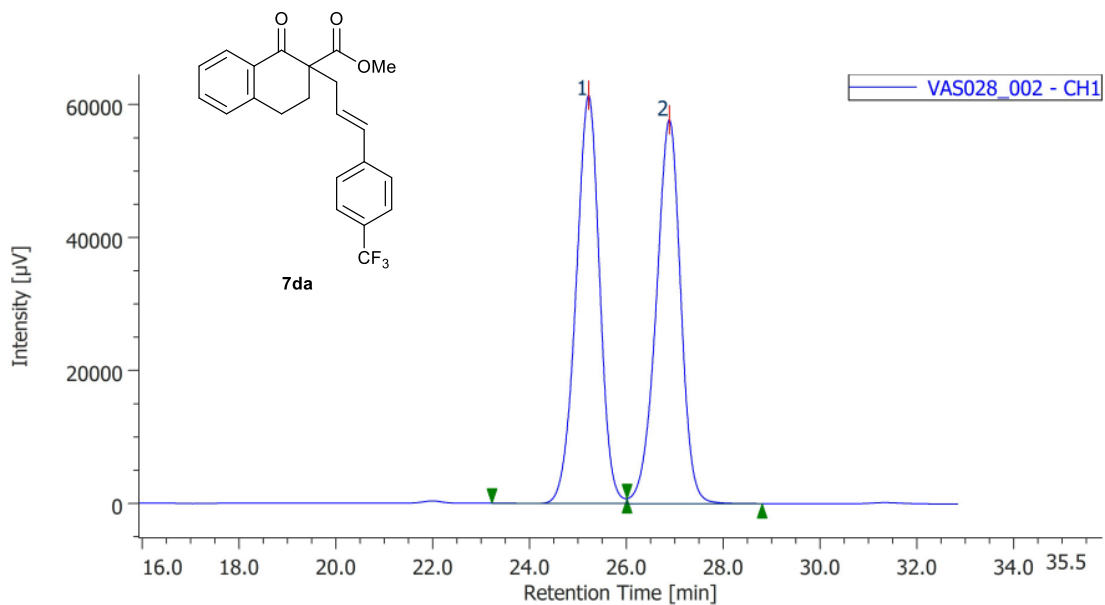
#	Peak Name	CH	tR [min]	Area [$\mu\text{V}\cdot\text{sec}$]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	43.900	31178566	572955	94.384	94.902	N/A	15547	4.450	1.582	
2	Unknown	2	50.508	1855146	30778	5.616	5.098	N/A	16564	N/A	1.281	



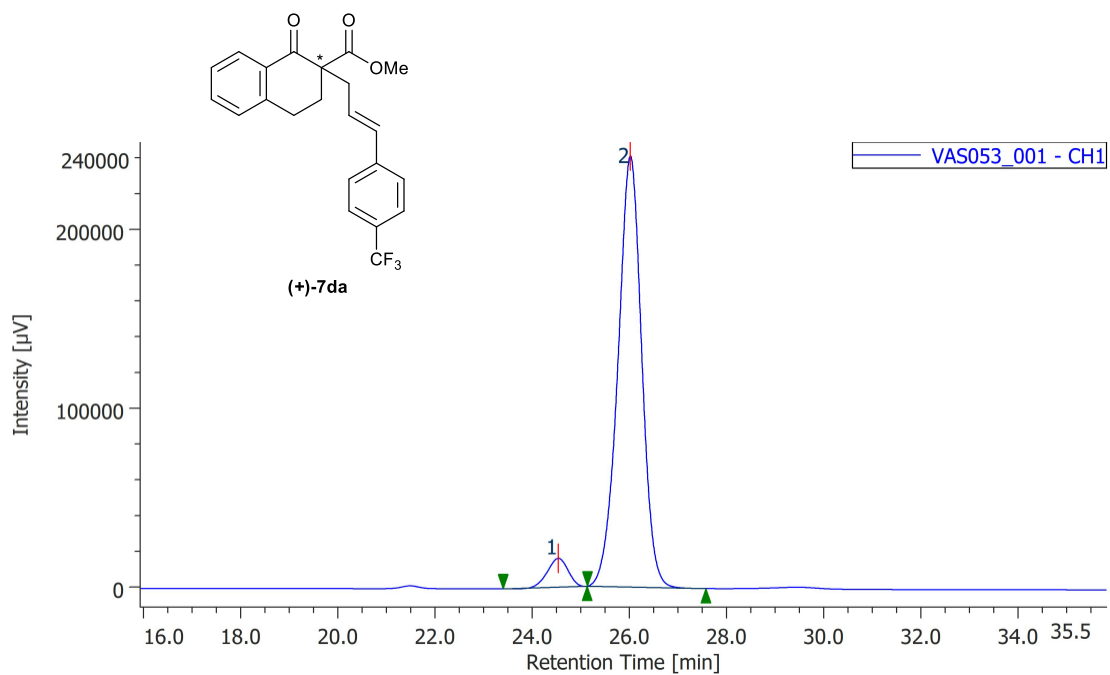
#	Peak Name	CH	tR [min]	Area [$\mu\text{V}\cdot\text{sec}$]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	19.433	960740	35408	50.179	53.990	N/A	11907	2.233	1.147	
2	Unknown	2	21.142	953874	30175	49.821	46.010	N/A	10586	N/A	1.203	



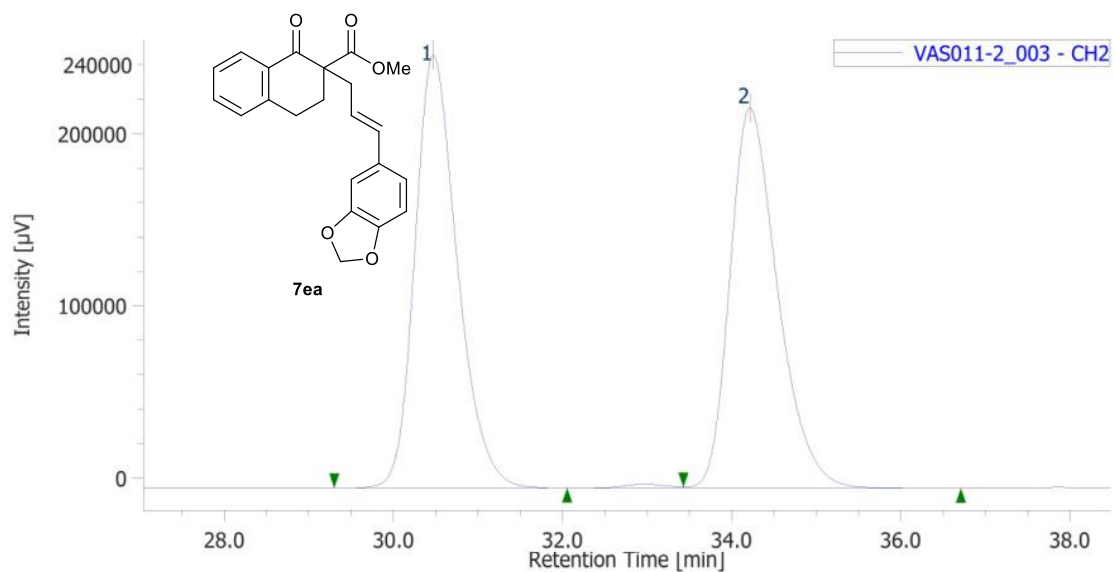
#	Peak Name	CH	tR [min]	Area [$\mu\text{V}\cdot\text{sec}$]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	19.192	8698685	383263	94.496	95.063	N/A	16925	3.118	1.244	
2	Unknown	2	21.150	506681	19903	5.504	4.937	N/A	15972	N/A	1.187	



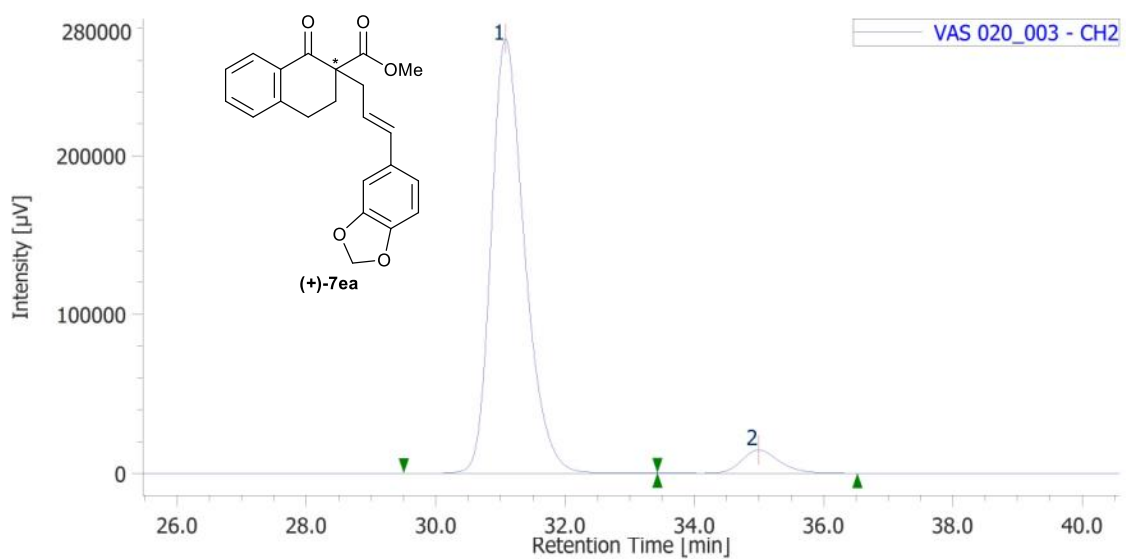
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	25.217	2074447	61355	50.469	51.525	N/A	13087	1.866	0.942	
2	Unknown	1	26.883	2035859	57722	49.531	48.475	N/A	13980	N/A	0.925	



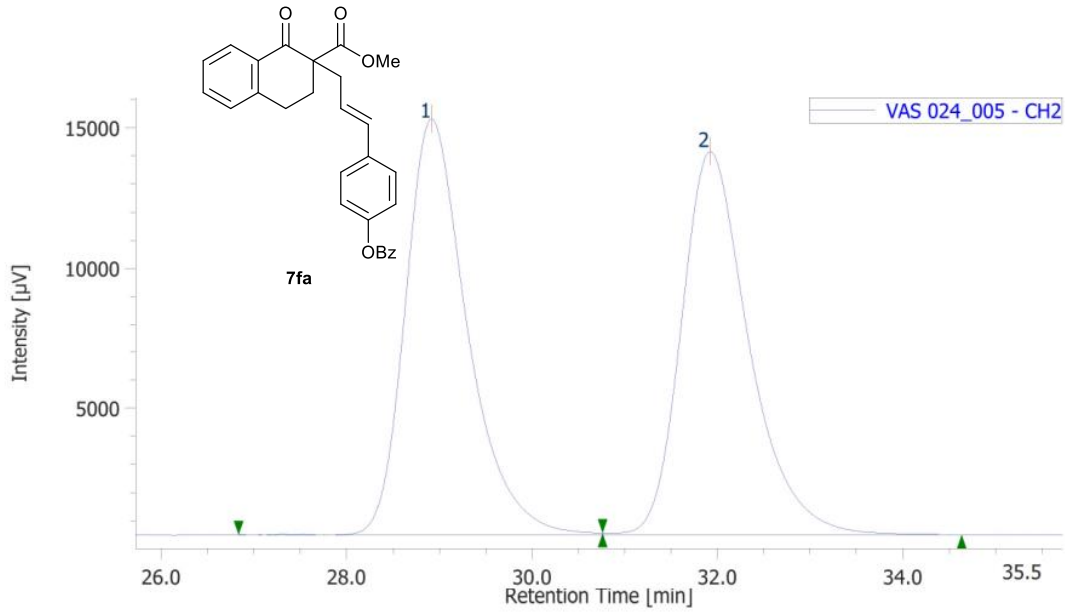
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	24.533	477232	16138	5.517	6.277	N/A	15258	1.781	0.926	
2	Unknown	1	26.017	8172755	240944	94.483	93.723	N/A	14129	N/A	0.950	



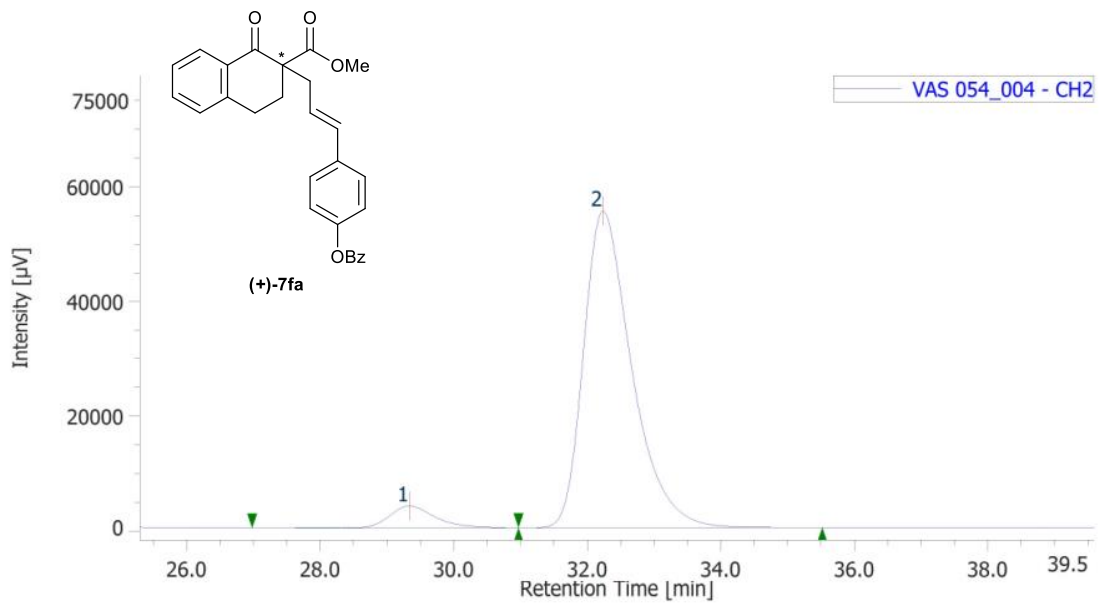
#	Peak Name	CH	tR [min]	Area [$\mu\text{V}\cdot\text{sec}$]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	30.467	8759140	251104	50.286	53.229	N/A	18325	3.927	1.269	
2	Unknown	2	34.217	8659520	220642	49.714	46.771	N/A	18197	N/A	1.325	



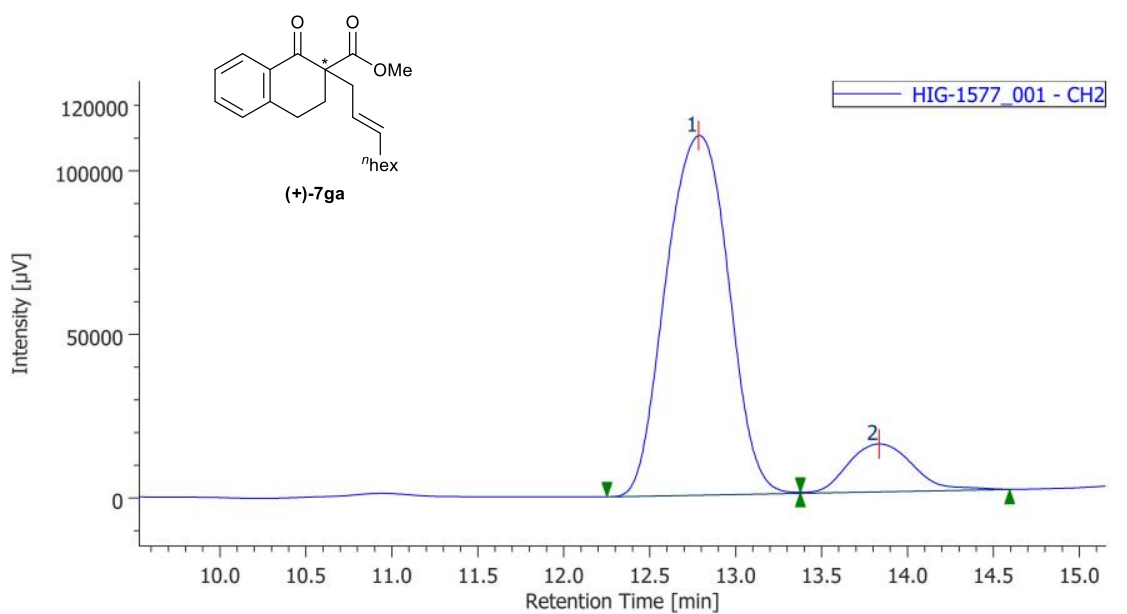
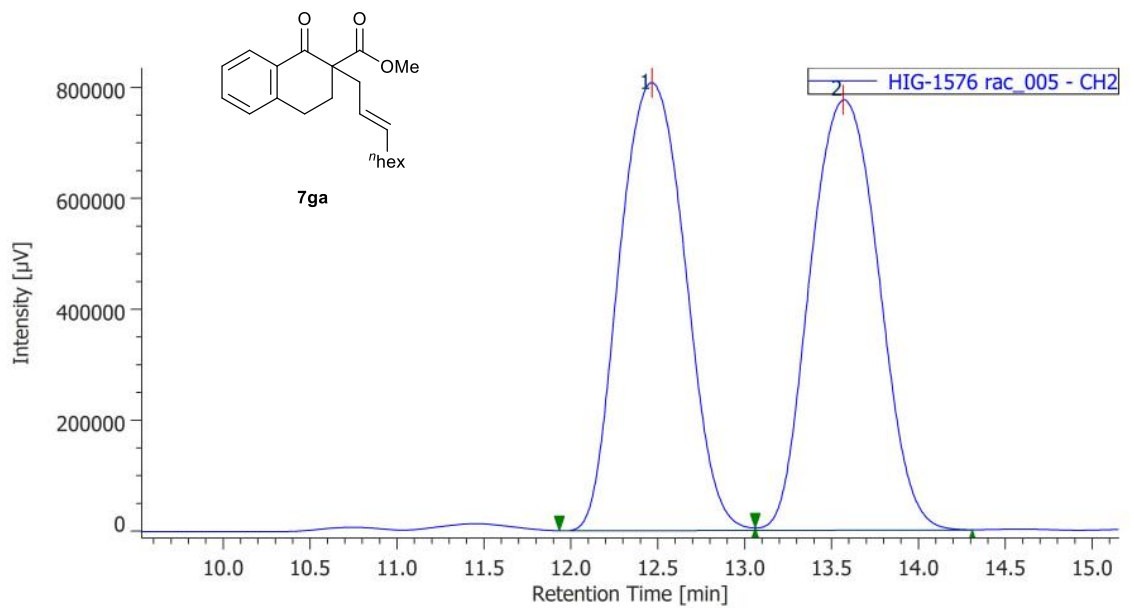
#	Peak Name	CH	tR [min]	Area [$\mu\text{V}\cdot\text{sec}$]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	31.075	9800309	273146	94.325	94.949	N/A	18189	4.011	1.297	
2	Unknown	2	34.992	589681	14531	5.675	5.051	N/A	18233	N/A	1.227	

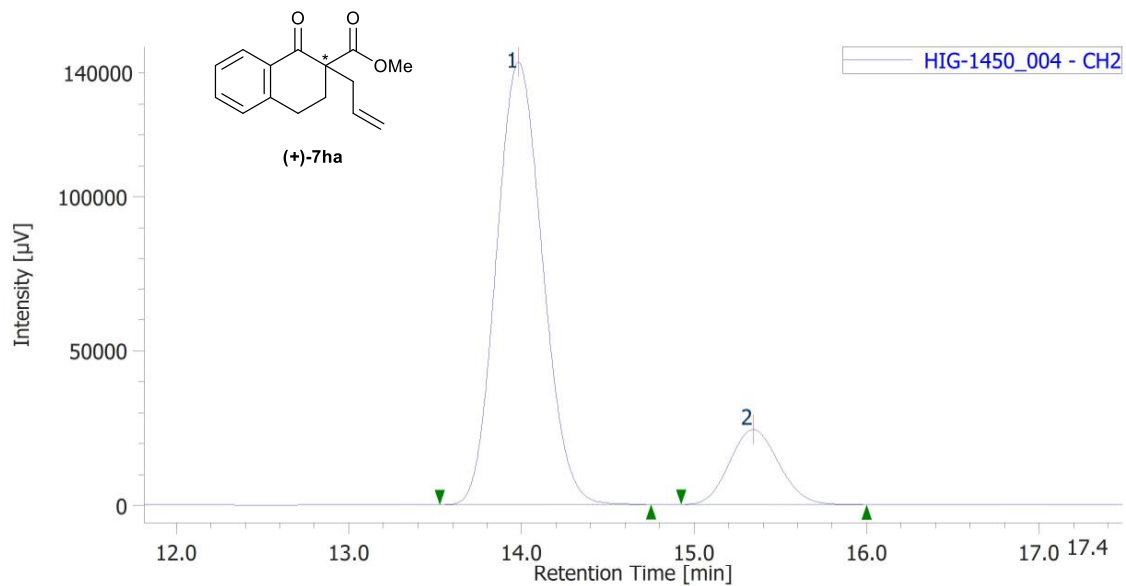
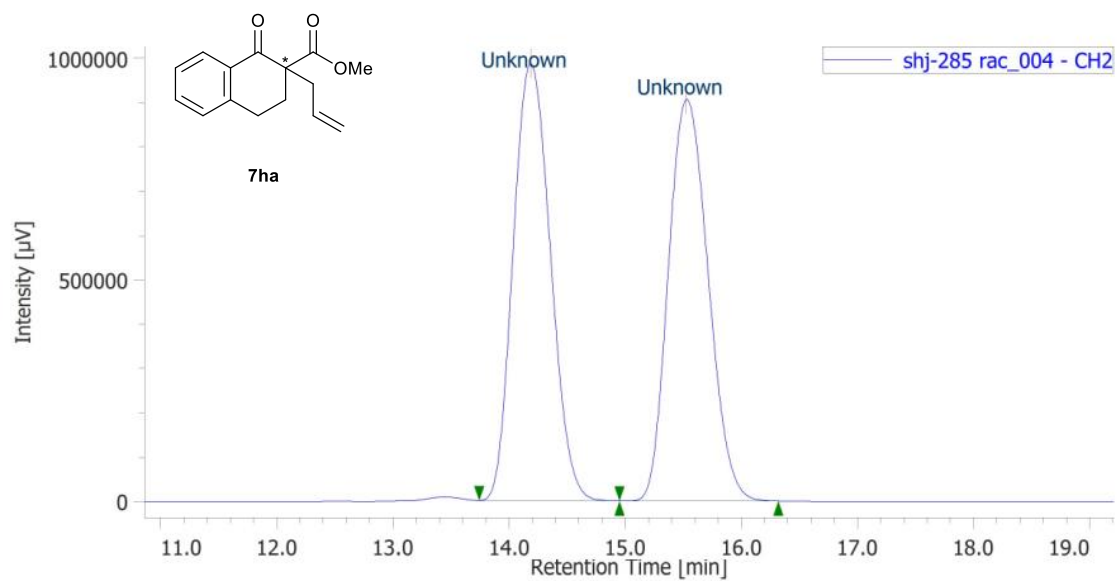


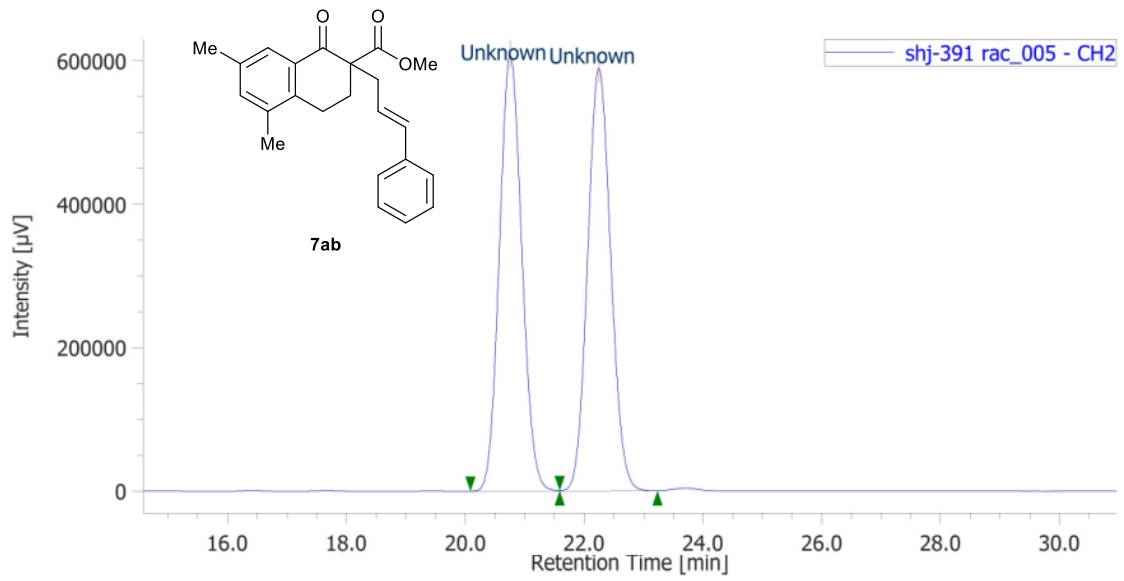
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	28.917	686632	14811	49.886	52.056	N/A	9704	2.452	1.353	
2	Unknown	2	31.917	689766	13641	50.114	47.944	N/A	9957	N/A	1.341	



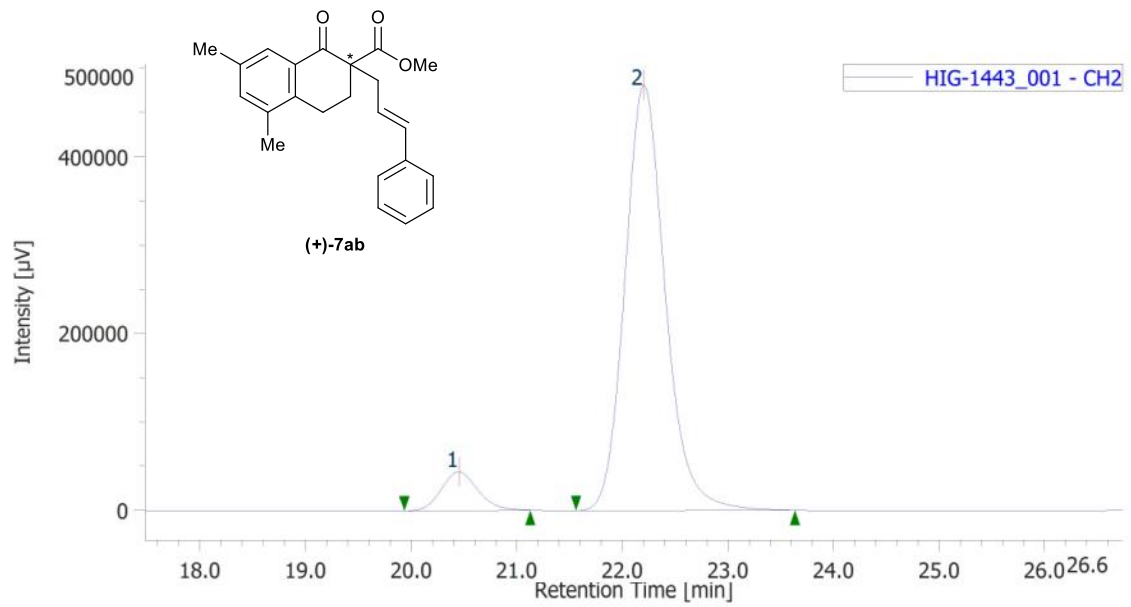
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	29.333	175285	3772	5.973	6.404	N/A	9807	2.367	1.302	
2	Unknown	2	32.233	2759251	55127	94.027	93.596	N/A	10282	N/A	1.439	



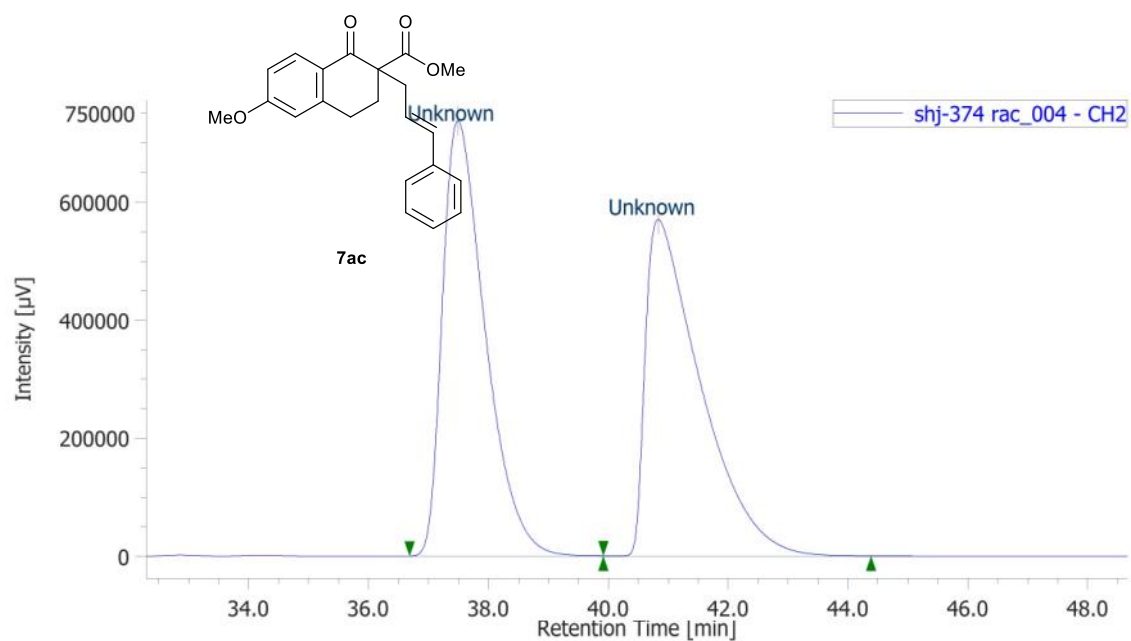




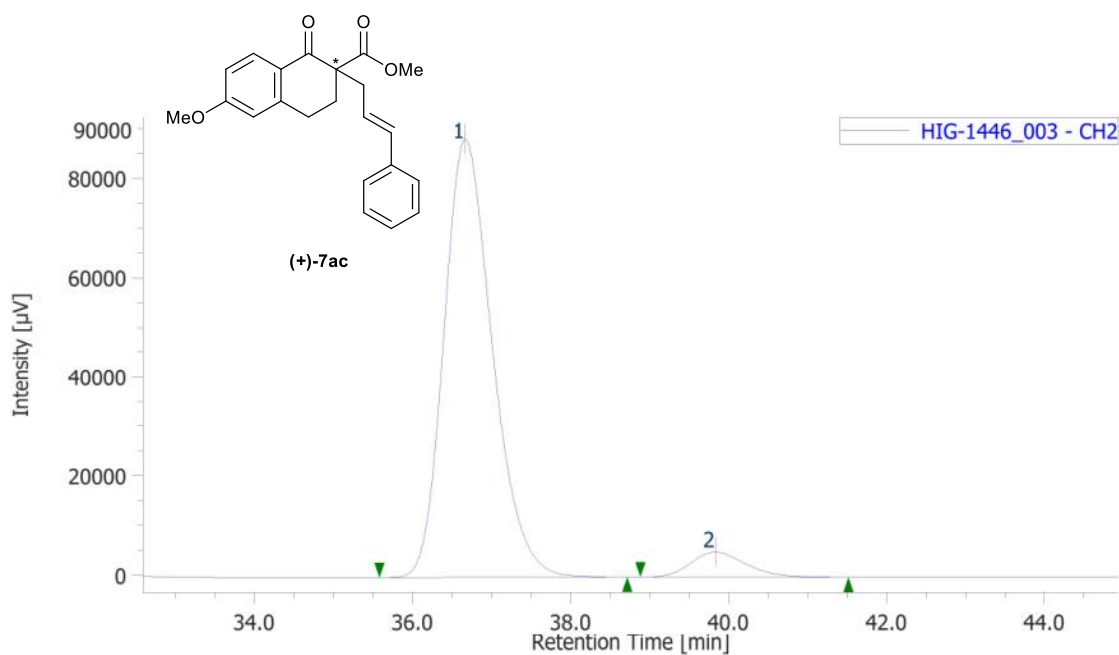
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	20.750	15944302	607696	50.020	50.783	N/A	14136	2.113	1.094	
2	Unknown	2	22.242	15931270	588962	49.980	49.217	N/A	15359	N/A	1.087	



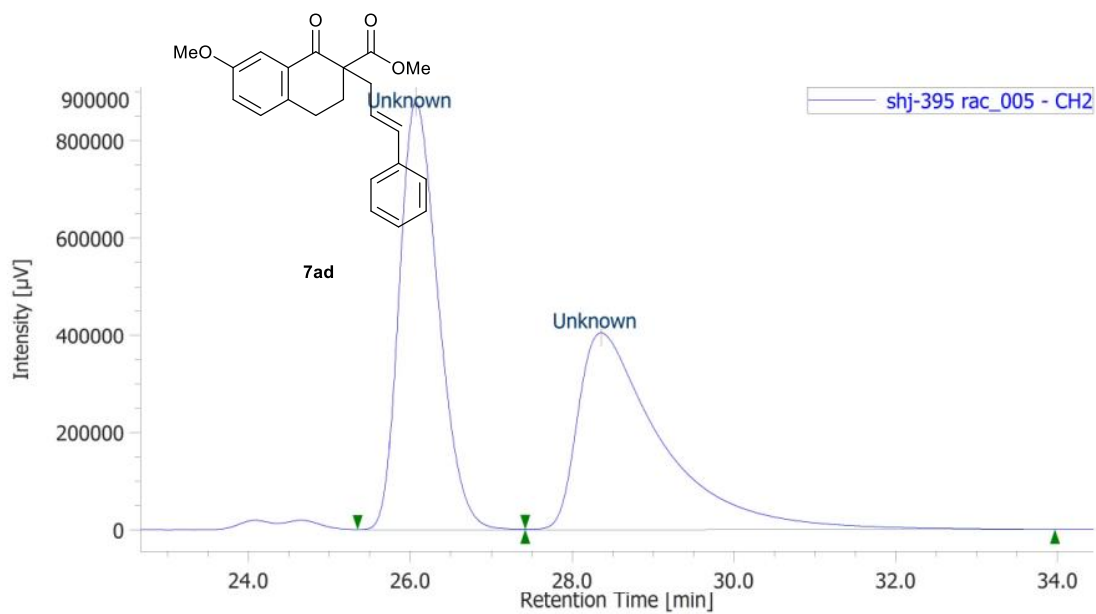
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	20.450	1051003	43765	7.606	8.335	N/A	17117	2.696	1.134	
2	Unknown	2	22.200	12767485	481319	92.394	91.665	N/A	17238	N/A	1.172	



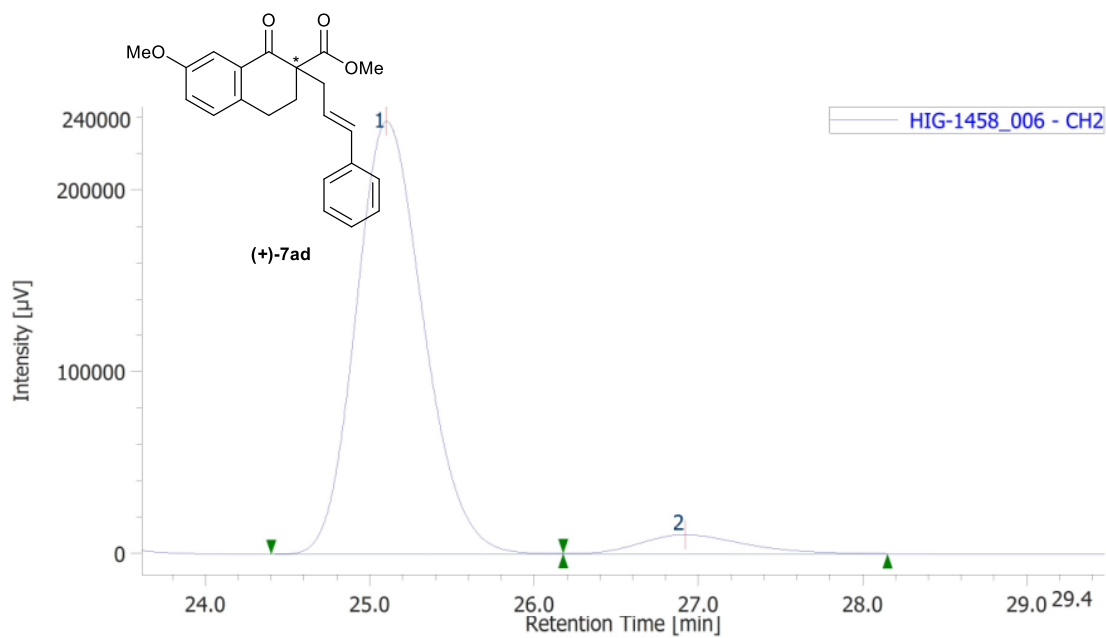
#	Peak Name	CH	tR [min]	Area [$\mu\text{V}\cdot\text{sec}$]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	37.483	36543173	736728	49.980	56.388	N/A	13531	2.291	1.657	
2	Unknown	2	40.833	36572593	569806	50.020	43.612	N/A	9883	N/A	2.888	



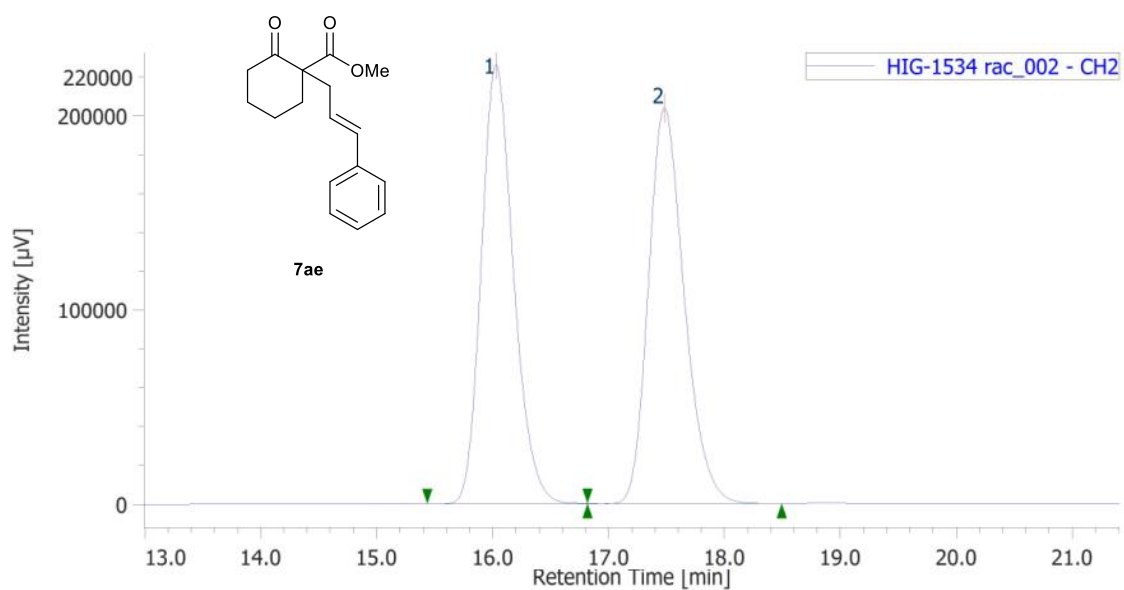
#	Peak Name	CH	tR [min]	Area [$\mu\text{V}\cdot\text{sec}$]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	36.667	3754415	88218	93.909	94.611	N/A	17568	2.676	1.247	
2	Unknown	2	39.833	243495	5025	6.091	5.389	N/A	15834	N/A	1.224	



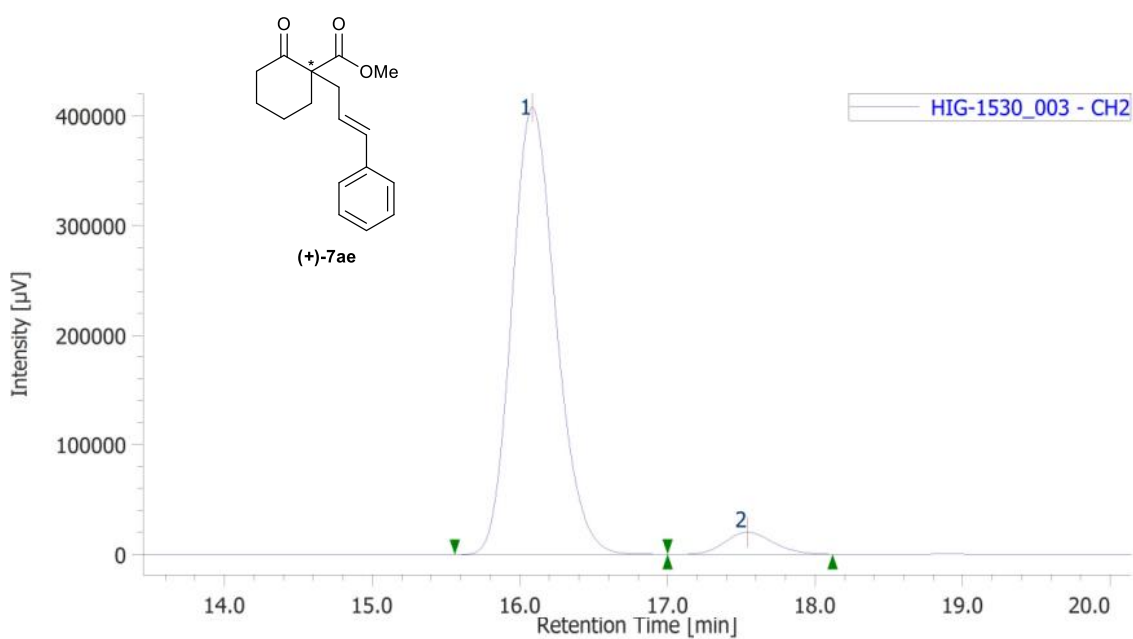
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	26.067	29247758	878378	50.185	68.470	N/A	13981	1.795	1.285	
2	Unknown	2	28.358	29031890	404487	49.815	31.530	N/A	4569	N/A	2.563	



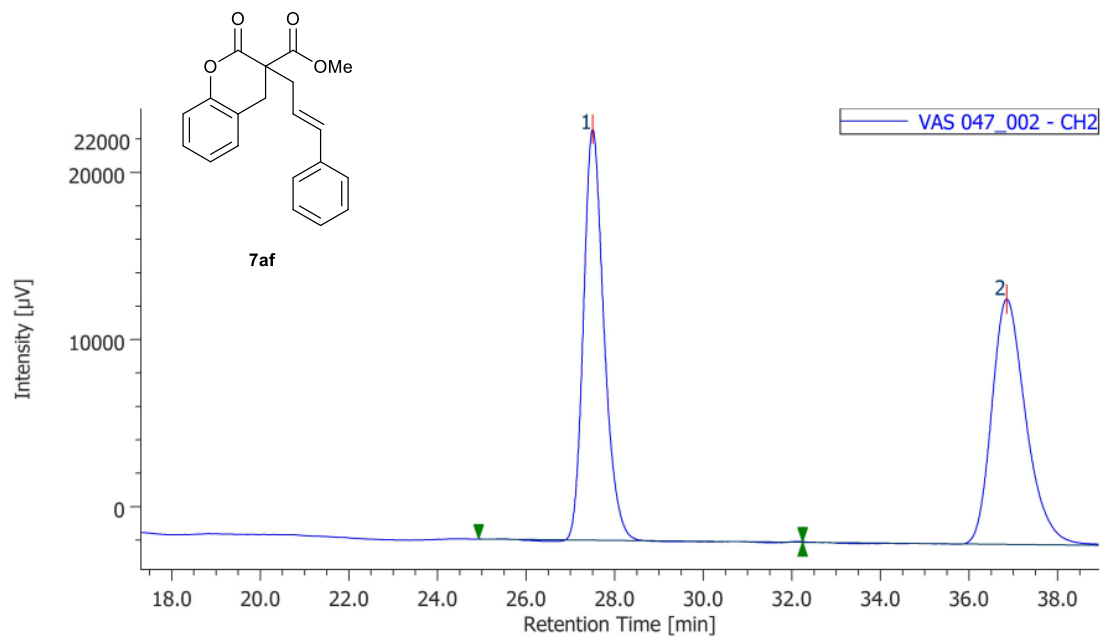
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	25.100	6794709	238006	93.625	95.773	N/A	17856	1.920	1.182	
2	Unknown	2	26.917	462656	10504	6.375	4.227	N/A	8821	N/A	1.289	



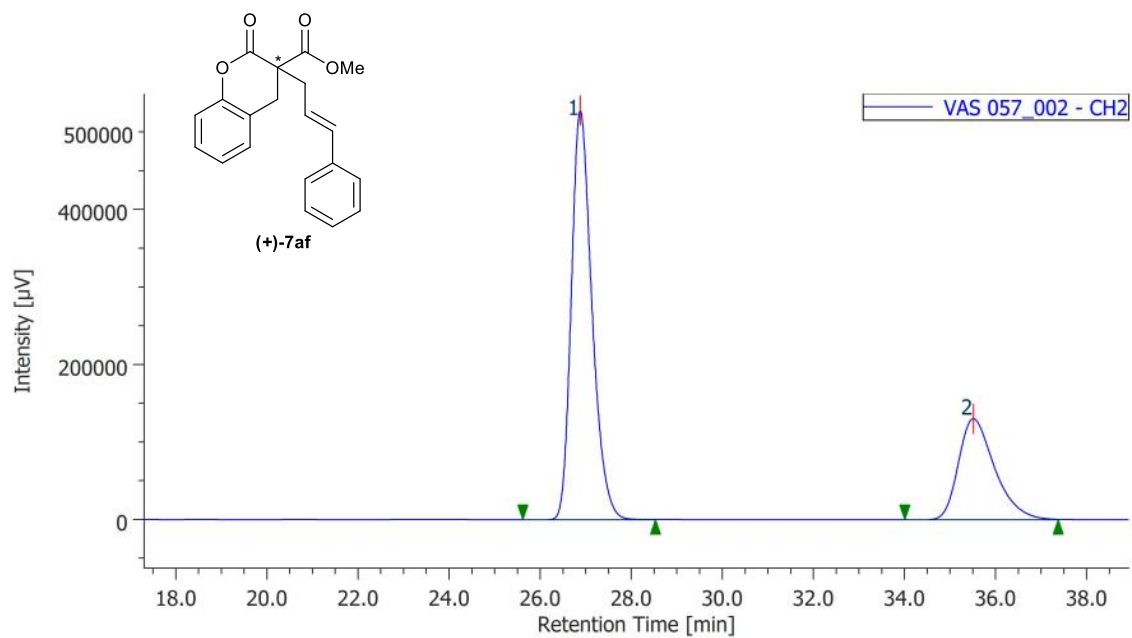
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	16.025	4365098	226051	49.979	52.620	N/A	16449	2.763	1.216	
2	Unknown	2	17.483	4368801	203544	50.021	47.380	N/A	15670	N/A	1.227	



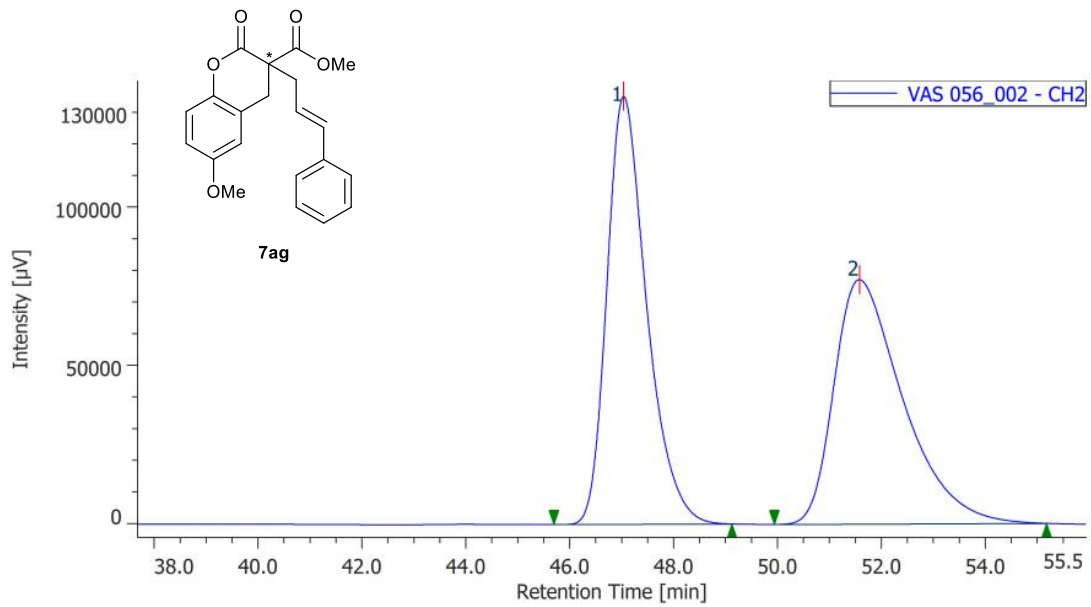
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	16.083	8446593	407661	94.906	95.317	N/A	14067	2.568	1.173	
2	Unknown	2	17.542	453387	20028	5.094	4.683	N/A	13840	N/A	1.148	



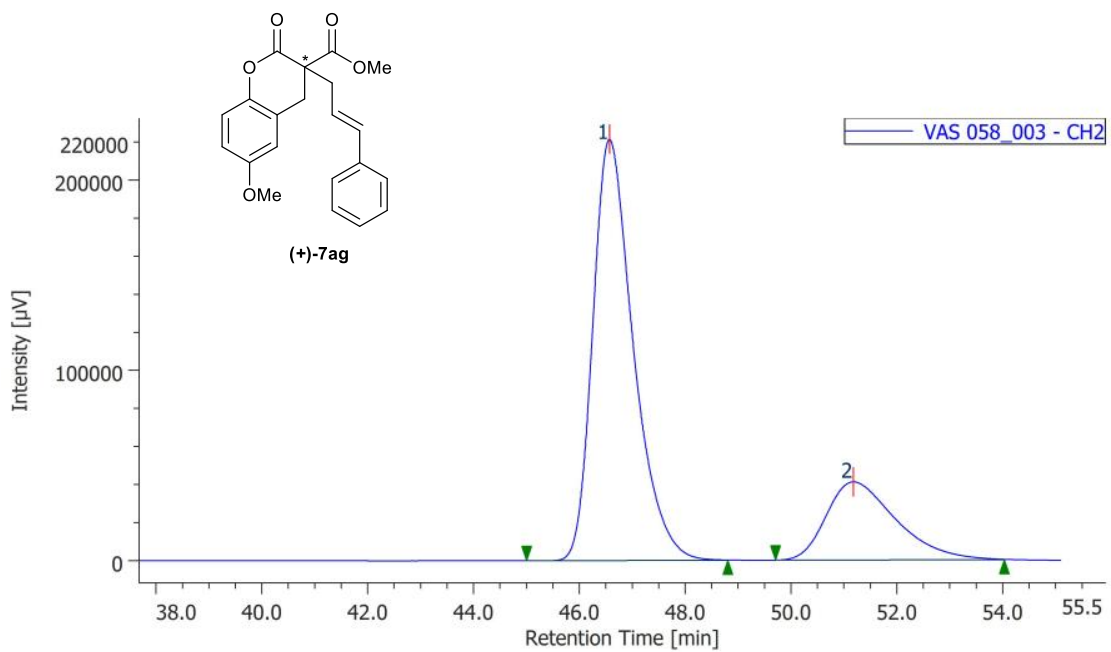
#	Peak Name	CH	tR [min]	Area [$\mu\text{V}\cdot\text{sec}$]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	27.500	787130	24567	50.020	62.620	N/A	17765	8.527	1.232	
2	Unknown	2	36.842	786497	14665	49.980	37.380	N/A	11542	N/A	1.292	



#	Peak Name	CH	tR [min]	Area [$\mu\text{V}\cdot\text{sec}$]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	26.875	16606298	527802	69.801	80.207	N/A	17432	7.751	1.286	
2	Unknown	2	35.508	7184507	130248	30.199	19.793	N/A	10012	N/A	1.375	



#	Peak Name	CH	tR [min]	Area [$\mu\text{V}\cdot\text{sec}$]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	47.033	7202617	135214	50.301	63.640	N/A	19057	2.447	1.349	
2	Unknown	2	51.575	7116430	77253	49.699	36.360	N/A	7651	N/A	1.588	



#	Peak Name	CH	tR [min]	Area [$\mu\text{V}\cdot\text{sec}$]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	2	46.567	11746683	221214	75.850	84.358	N/A	18810	2.478	1.381	
2	Unknown	2	51.175	3740024	41019	24.150	15.642	N/A	7452	N/A	1.453	