

Supporting Information

Iridium(III)-Catalyzed Asymmetric Site-Selective Carbene C–H Insertion during Late-Stage Transformation

Yuki Yamakawa,^a Takashi Ikuta,^a Hiroki, Hayashi,^b Keigo, Hashimoto,^a Ryoma Fujii,^{c,d} Kyohei Kawashima,^{c,d} Seiji Mori,^{c,d} Tatsuya Uchida,^{*,a,b,e} Tsutomu Katsuki^{e,f}

*E-mail: uchida.tatsuya.045@m.kyushu-u.ac.jp

^aDepartment of Chemistry, Graduate School of Science, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, 819-0395, Japan

^bFaculty of Arts and Science, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, 819-0395, Japan.

^cInstitute of Quantum Beam Science, Graduate School of Science and Engineering, Ibaraki University, Mito 310-8512, Japan

^dFrontier Research Center for Applied Atomic Sciences, Ibaraki University, Tokai, Ibaraki 319-1106, Japan

^eInternational Institute for Carbon-Neutral Energy Research (I2CNER), Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, 819-0395, Japan

^fHe sadly passed away on October 30, 2014.

Abstract: C–H functionalization has recently received considerable attention because C–H functionalization during the late-stage transformation is a strong and useful tool for the modification of the bioactive compounds and the creation of new active molecules. Although a carbene transfer reaction can directly convert a C–H bond to the desired C–C bond in a stereoselective manner, their application in late-stage material transformation is limited. Here, we observed that the iridium-salen complex **6** exhibited efficient catalysis in asymmetric carbene C–H insertion reactions. Under optimized conditions, benzylic, allylic, and propargylic C–H bonds were converted to desired C–C bonds in an excellent stereoselective manner. Excellent regio-selectivity was demonstrated in the reaction using not only simple substrate but also natural products, bearing multiple reaction sites. Moreover, based on the mechanistic studies, the iridium-catalyzed unique C–H insertion reaction involved rate-determining asynchronous concerted processes.

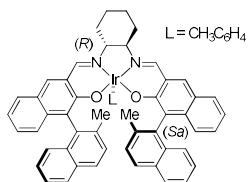
Table of Contents:

1. General Information	SI-3
2. Characterization of iridium-salen complexes	SI-3
3. The catalyst optimization	SI-5
4. Scope and limitation of α-aryl-α-diazoacetate 8	SI-5
5. General procedure for Ir-salen-catalyzed C–H insertion reaction	SI-6
6. Hammett analysis of Ir-salen 6-catalyzed competition reaction of ethylbenzene derivative 7	SI-7
7. Measurement of kinetic isotope effect	SI-7
8. Analysis data for C–H insertion products	SI-9
9. Computational Details	SI-24
10. Reference	SI-40
11. NMR spectra for C–H insertion products	SI-41

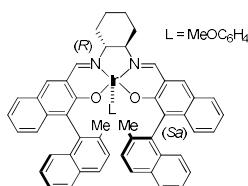
1. General

All reactions were carried out in an oven-dried glassware with magnetic stirring under nitrogen atmosphere. ^1H and ^{13}C NMR spectra were measured on a JEOL JNM-AL400 spectrometer at 400 and 100 MHz, respectively. ^{19}F NMR spectra was recorded on BRUKER ADVANCE 400 spectrometer. All chemical shifts were recorded in δ (ppm) relative to tetramethylsilane (TMS). Mass spectra were recorded on a BRUKER DALTONICS MICRO TOF-KSI focus (HR-ESI); peaks are given in m/z (% of basis peak). Infrared spectra were obtained with SHIMADZU IRAffinity-1 FTIR spectrophotometer, and only diagnostic signals are listed below. Optical rotations were recorded on an ANTON PAAR MCL-300. Enantiomeric excesses were determined by HPLC analysis using SHIMADZU HPLC Prominence equipped with a column packed with an appropriate optically active material, as described below. Column chromatography was conducted on silica gel 60N (spherical, neutral, 63–210 μm), available from Kanto Chemical Co., Inc. Preparative thin layer chromatography was performed on a silica gel 60 F₂₅₄-coated glass plate (Merck Ltd.). The iridium-salen complexes (**1** and **2**) were prepared according to the reported procedures and showed identical IR and MS spectra with the reported ones.^[1] Iridium complexes (**3–6**) were prepared in the same procedure as that of complex **1**, from the corresponding salicylaldehydes and diamines. The salicylaldehydes were synthesized according to the previous report.^[2] All the alkyl α -aryl- α -diazoacetates **8** were also prepared according to the reported procedure.^[3] Racemic or low optically active C–H insertion products were prepared using almost racemic Ir-salen complex **5** and used as a reference sample for HPLC analysis.

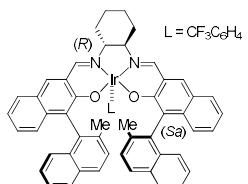
2. Characterization of iridium-salen complexes.



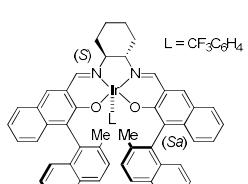
Complex 3 (Table 1), brown solid; FTIR (KBr): 3049, 2937, 2860, 1722, 1608, 1580, 1447, 1427, 1344, 1325, 1292, 1144, 1124, 1074, 808, 779, 745 cm^{-1} ; HRESI-MS (m/z) [M $^+$], calcd. for [C₅₇H₄₇IrN₂O₂] $^+$ 984.3267, found: m/z = 984.3245.



Complex 4 (Table 1), brown solid; FTIR (KBr): 3048, 2932, 2862, 1721, 1609, 1578, 1443, 1427, 1342, 1323, 1296, 1231, 1188, 1146, 1123, 1069, 1034, 953, 922, 868, 810, 779, 748, 652, 590, 571 cm^{-1} ; HRESI-MS (m/z) [M $^+$], calcd. for [C₅₇H₄₇IrN₂O₃] $^+$ 1000.3216, found: m/z = 1000.3210.



Complex 5 (Table 1), brown solid; FTIR (KBr): 3047, 2937, 2846, 1720, 1608, 1577, 1562, 1486, 1446, 1425, 1321, 1228, 1188, 1147, 1109, 1074, 808, 779, 744 cm^{-1} ; HRESI-MS (m/z) [M $^+$], calcd. for [C₅₇H₄₄F₃Ir₁N₂O₂] $^+$ 1038.2984, found: m/z = 1038.2963.; Anal. Calcd for C₅₇H₄₄F₃IrN₂O₂•0.8C₄H₈O•0.4H₂O: C, 65.55; H, 4.68; N, 2.54. Found: C, 65.53; H, 4.67; N, 2.50.



Complex 6 (Table 1) brown solid; FTIR (KBr): 3049, 2938, 2862, 1608, 1577, 1546, 1487, 1446, 1425, 1393, 1344, 1323, 1228, 1188, 1147, 1109, 1076, 810, 781, 744, 655, 594 cm^{-1} ; HRESI-MS (m/z) [M $^+$], calcd. for [C₅₇H₄₄F₃Ir₁N₂O₂] $^+$ 1038.2984, found: m/z = 1038.2994.; Anal. Calcd for C₅₇H₄₄F₃IrN₂O₂•C₄H₈O•0.6H₂O: C, 65.35; H, 4.78; N, 2.50. Found: C, 65.30; H, 4.73; N, 2.49.

X-ray analysis of 6; Single crystal of complex **6** for X-ray diffraction experiments was recrystallized from 2-propanol solution. The date was collected at 100 K on a Bruker SMART

APEX II diffractometer equipped with APEX II 4K CCD area detector, a graphite monochromator and a rotating-anode X-ray tube ($\text{Mo-K}\alpha$ radiation, $\lambda = 0.71073$) focused with Helios multilayer optics for $\text{Mo-K}\alpha$ radiation operating at 50 kV and 24 mA. Single crystals of the major product for X-ray diffraction experiments were obtained by recrystallization from 2-propanol. The data collection, the cell refinement, and the data reduction were performed by CrysAlisPro software program. The structure was solved by direct methods and refined by full-matrix least-squares based on all data using F^2 with SHELXLTL.^[4] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed from the difference map and refined with geometrical and isotropic displacement parameters. Molecular plot was obtained with ORTEP-3. Crystallographic: $\text{C}_{60}\text{H}_{54}\text{N}_2\text{O}_4\text{F}_3\text{Ir}$, red block, $0.20 \times 0.50 \times 0.50 \text{ mm}^3$, orthorhombic, $P2_12_12_1$, $a = 14.0322(12)$, $b = 17.0176(15)$, $c = 20.8620(18) \text{ \AA}$, $V = 4981.7(7) \text{ \AA}^3$, $Z = 4$, $\text{Flack} = 0.002(4)$, $R = 0.0220$ and $Rw = 0.0545$, CCDC 2153844 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

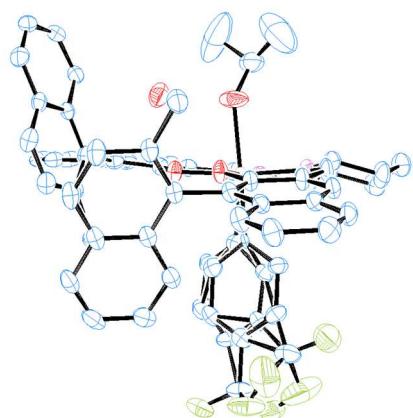


Figure S1. ORTEP view (50% probability) of complex 6.

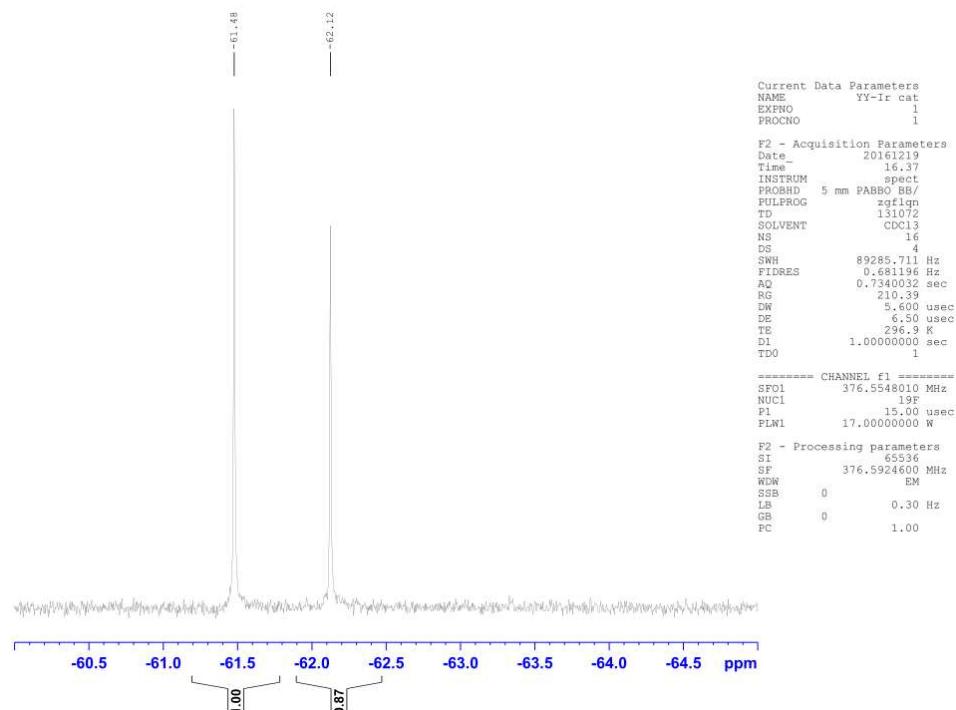
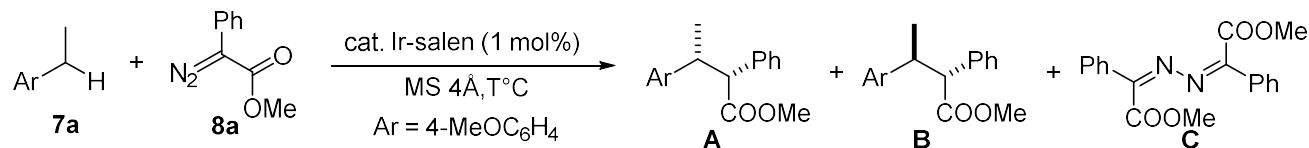


Figure S2. ^{19}F NMR spectra of complex 6.

3. The catalyst optimization.



MS 4 Å (25 mg) was placed in a Schlenk tube (10 mL), and diazo compound **8a** (0.2 mmol), 1-bromonaphthalene (0.1 mmol), and ethylanisole **7a** (1.4 mmol) were added at 25°C under nitrogen atmosphere. After stirring at the reaction temperature for 30 min, Ir-salen complexes (2 μ mol) was added and the mixture was stirred for the time shown in Tables S1. The mixture was allowed to warm to room temperature and chromatographed on silica gel to obtain C–H insertion products. The diastereomeric ratios were determined by ^1H NMR. The NMR samples were recovered, and the *e*es of the major isomers were determined by HPLC analysis after reduced with diisopropylaluminumhydride [DIBAL].

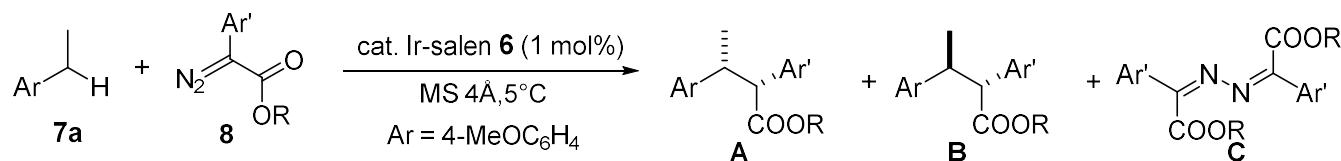
Table S1. Survey of Iridium-salen Complexes for Asymmetric Carbene C–H Insertion^a

entry	cat.	temp (°C)	time (h) ^b	yield (%) ^b	<i>ee</i> (%) ^c	A/B/C^b
1	1	25	33	nr ^d	nd ^e	nd ^e
2	2	25	4	66	-98	4.8/1/2
3	3	25	22	62	-95	12/1/3
4	<i>ent</i> - 4	25	19	58	96	12/1/4
5	5	25	5	66	-96	12/1/3
6	5	5	24	70	-99	16/1/3
7	6	5	24	77	99	20/1/3

^aReaction conditions: **7a** (1.4 mmol), **8a** (0.2 mmol), Ir-salen (2.0 μ mol), and MS 4Å (25 mg).

^bDetermined by ^1H NMR analysis using 1-bromonaphthalene as an internal standard. ^cDetermined by HPLC analysis on a chiral stationary phase column after reduced with diisopropylaluminumhydride (DIBAL). ^dNo reaction was observed. ^eNot determined.

4. Scope and limitation of α -aryl- α -diazoacetate **8**.



MS 4 Å (25 mg) was placed in a Schlenk tube (10 mL), and diazo compound **8** (0.2 mmol), 1-bromonaphthalene (0.1 mmol), and ethylanisole **7a** (1.4 mmol) were added at 5°C under nitrogen atmosphere. After stirring at the reaction temperature for 30 min, Ir-salen complex **6** (2.0 mg, 2.0 μ mol) was added to the mixture. After consumed diazo compounds, the mixture was allowed to warm to room temperature and chromatographed on silica gel to obtain C–H insertion products. The diastereomeric ratios were determined by ^1H NMR. The NMR samples were recovered, and the *e*es of the major isomers were determined by HPLC analysis after reduced with diisopropylaluminumhydride [DIBAL].

Table S2. Iridium-Catalyzed Asymmetric Carbene C–H Insertion of **7a** with **8** as the carbene source.^a

entry	diazooacetate 8		time (h) ^b	yield (%) ^b	ee (%) ^c	A/B/C ^b	
	Ar'	R					
1	Ph	Et	8b	48	66	99 ^d	>20/1/1
2	Ph	<i>t</i> Bu	8c	48	nr ^d	-	-
3	4-MeOPh	Me	8d	48	trace	-	-
4	4-MePh	Me	8e	168	96	99	>20/1/1
5	4-BrPh	Me	8f	36	86	99 (2 <i>R</i> , 3 <i>R</i>)	>20/1/1
6	4-ClPh	Me	8g	24	81	99	>20/1/2
7	3-MeOPh	Me	8h	12	84	99	>20/1/1
8	3-ClPh	Me	8i	12	87	99	>20/1/1
9	2-MeOPh	Me	8j	48	nr ^d	-	-
10	2-ClPh	Me	8k	48	nr ^d	-	-
11	2-C ₁₀ H ₇	Me	8l	8	92	99	>20/1/1
12 ^e	2-C ₁₀ H ₇	Me	8l	1	95	99	>20/1/1
13 ^{e,f}	2-C ₁₀ H ₇	Me	8l	1	95	99	>20/1/1

^aReaction conditions: **7a** (1.4 mmol), **8** (0.2 mmol), Ir-salen **6** (2.0 μ mol), and MS 4 Å (25 mg) at 5 °C, unless otherwise noted. ^bDetermined by ¹H NMR analysis using 1-bromonaphthalene as an internal standard. ^cDetermined by HPLC analysis on a chiral stationary phase column after reduction with DIBAL.

^dNo reaction was observed. ^eAbsolute ^fCarried out at 25 °C. ^fThe reaction was carried out with 1.5:1 ratio of **7a** and **8l** using 0.2 mol% of iridium complex **6**.

5. General procedure for Ir-salen-catalyzed C–H insertion reaction.

Reactions were carried out in a Schlenk tube (10 mL) under nitrogen atmosphere. MS 4 Å (25 mg) was placed in the Schlenk tube, and an alkyl α-aryl-α-diazoacetate **8l** (67.9 mg, 0.3 mmol), 1-bromonaphtharene (0.5 μ mol), and substrate (0.45 mmol) were added at 25 °C. After stirring at that temperature, complex **6** (2.0-0.2 mol%) was added and the whole mixture was stirred for the time shown in the Tables. The mixture reddish turned greenish, as the reaction proceeded. The mixture was chromatographed on silica gel (*n*-hexane/EtOAc = 1/0 to 10/1) to obtain C–H insertion products. The diastereomeric ratios were determined by ¹H NMR analysis. The mixture was re-purified on a tin-layer chromatography to obtain the major C–H insertion product. The enantiomeric excess of the product was determined by HPLC analysis on an appropriate chiral stationary phase column, after reduction with DIBAL.

6. Hammett analysis of Ir-salen 6-catalyzed competition reaction of ethylbenzene derivative 7.

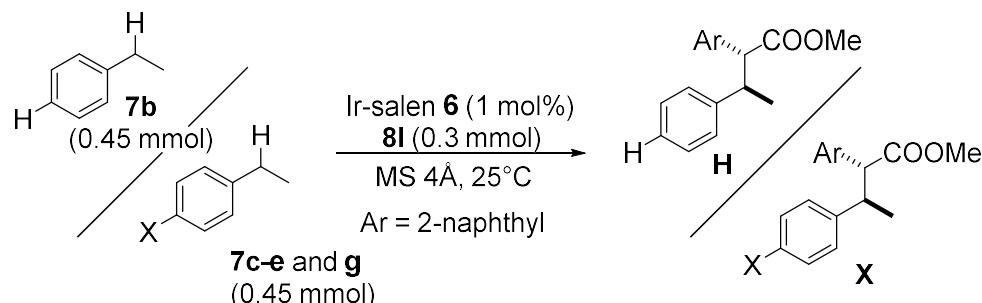


Table S3. Hammett substituent constants and molar ratio of the reactions.

entry	Sbustituent (X)	X:H (molar ratio) ^a	σ	σ^+
1	MeO	30:1	-0.27	-0.78
2	Me	7.32:1	-0.17	-0.31
3	Br	0.98:1	0.23	0.15
4	Cl	0.97:1	0.37	0.11

^aDetermined by ¹H NMR analysis

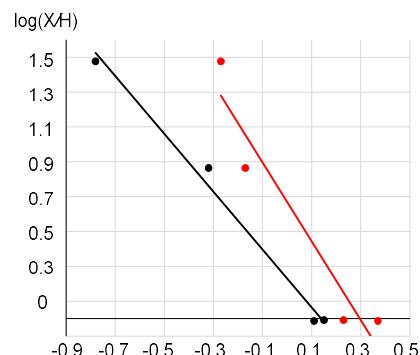
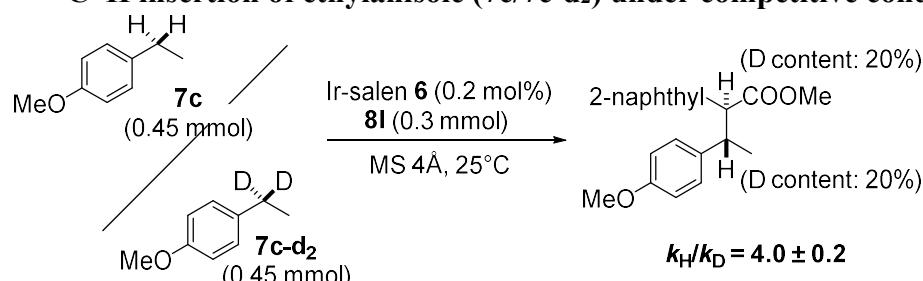


Figure S3. Plots of Hammett substituent constants vs. $\log(X/H)$.

7. Measurement of kinetic isotope effect.

7.1. Determination of intermolecular kinetic isotope effect for Ir-salen complex 6 catalyzed carbene C–H insertion of ethylanisole (**7c**/**7c-d₂**) under competitive condition.



MS 4 Å (25 mg) was placed in a Schlenk tube (10 mL), a 1:1 mixture of 4-ethylanisole **7c** and 4-(α,α -D₂-ethyl)anisole **7c-d₂** (0.45 mmol each), and diazo compound **8I** (67.9 mg, 0.3 mmol) were added at

25°C under nitrogen atmosphere. After stirring at the reaction temperature for 30 min, Ir-salen complex **6** (0.6 mg, 0.6 µmol) was added to the mixture. After stirred for 24h, the mixture was chromatographed on silica gel to obtain C–H insertion products. The H/D relative reaction ratio was determined by ¹H NMR analysis. The measurement was repeated five times. The average value and standard error were calculated based on the data.

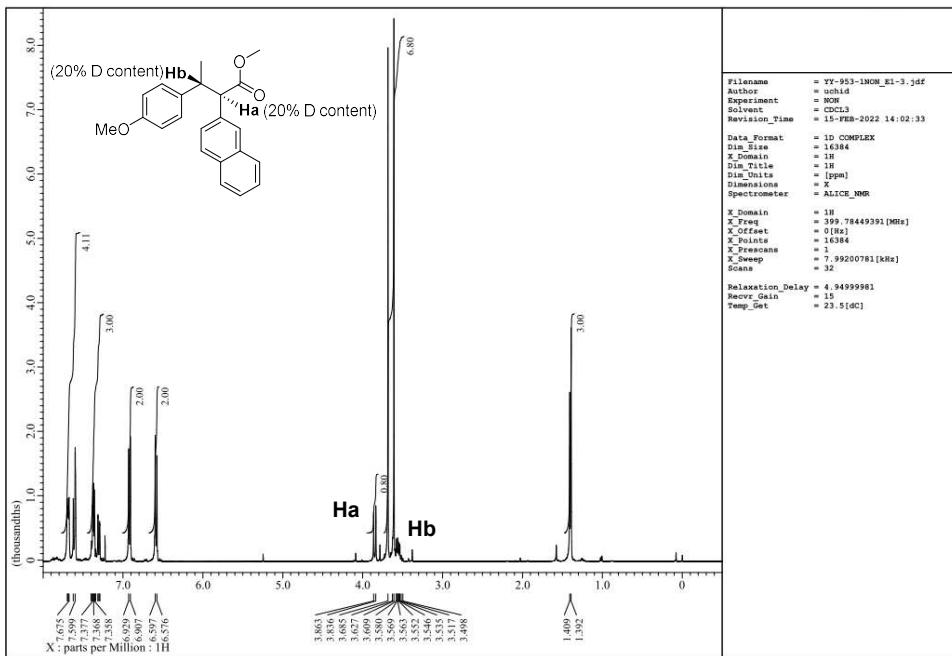


Figure S4. ^1H NMR spectra of the product under **7c** and **7c-d₂** competition conditions.

7.2.Determination of intermolecular kinetic isotope effect for Ir-salen complex 6 catalyzed carbene C–H insertion of ethylanisole (7c/7c-d₂) under independent conditions.

MS 4 Å (25 mg) was placed in a Schlenk tube (10 mL), 4-ethylanisole **7c** or 4-(α,α -D₂-ethyl)anisole **7c-d₂** (0.45 mmol), and diazo compound **8I** (67.9 mg, 0.3 mmol) were added at 25°C under nitrogen atmosphere. After stirring at the reaction temperature for 30 min, Ir-salen complex **6** (0.6 mg, 0.6 μ mol) was added to the mixture. Aliquots (20 μ L) of these solutions were taken out of the test tube at zero time and specified times. Each aliquot was passed through a short pad of silica gel to obtain reaction mixture and submitted to ¹H NMR analysis to determine the chemical yield. The measurement was repeated three times. The average value and standard error were calculated based on the data.

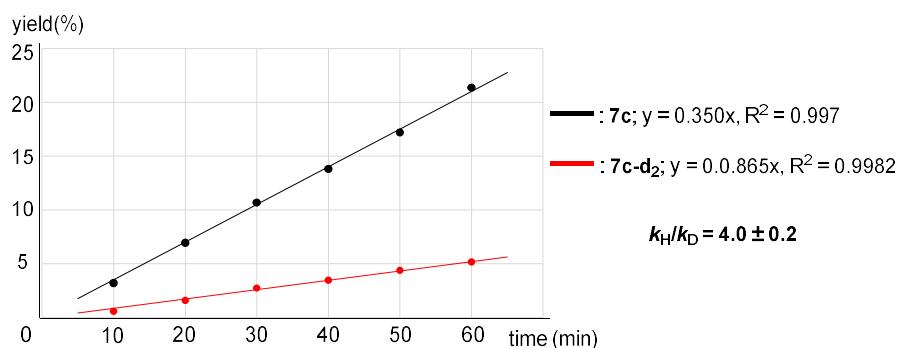
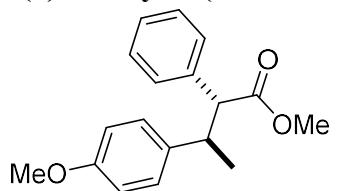


Figure S5. Initial reaction rates of **7c** and **7c-d₂** using Ir-salen complex **6** as the catalyst.

8. Analysis data for C–H insertion products.

8.1. (-)-Methyl 3-(4-methoxyphenyl)-2-phenylbutanoate



Diastereo-mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 77% yield as a colorless oil (43.7mg, d.r. = 20:1); the mixture of major and minor diastereomeric products was chromatographed on preparative TLC plates (*n*-hexane/AcOEt = 15:1) to yield the major isomer.; Mp: 40.6–40.7 °C.; $[\alpha]_D^{25} -125.0$ (*c* 1.62, CHCl₃); FTIR (neat): 3448.2, 1610.6, 1512.2, 831.3 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.14–7.09 (m, 5H), 6.88 (d, 2H, *J* = 8.8 Hz), 6.64 (d, 2H, *J* = 8.8 Hz), 3.70 (s, 3H), 3.69 (s, 3H), 3.66 (d, 1H, *J* = 11.2 Hz), 3.41 (dt, 1H, *J* = 6.8, 11.2 Hz), 1.36 (d, 3H, *J* = 6.8 Hz) ppm.; ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 174.1, 157.7, 137.6, 135.6, 128.5, 128.4, 128.1, 126.9, 113.4, 59.4, 55.0, 51.9, 43.0, 21.1 ppm.; Anal. Calcd for C₁₈H₂₀O₃: C, 76.03; H, 7.09. Found: C, 75.70; H, 7.08.; The enantiomeric excess of the major was determined to be 99% *ee* by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK IB-3 (Hexane/*i*-PrOH = 95/5, 0.75 mL/min), 25 °C, *t*_r (Major) = 16.4 min, *t*_r (Minor) = 15.3 min] after reducing with DIBAL.

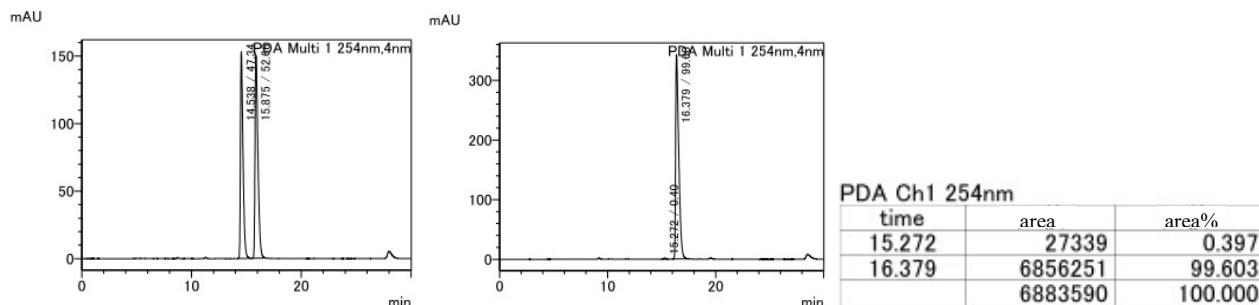
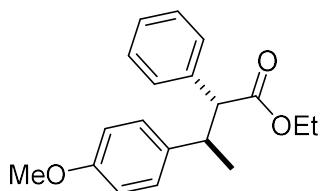


Figure S6. The chromatograms of methyl 3-(4-methoxyphenyl)-2-phenylbutanoate.

8.2. (-)-Ethyl 3-(4-methoxyphenyl)-2-phenylbutanoate



Diastereo-mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 66% yield as a colorless oil (39.4 mg, d.r. = >20:1); the mixture of major and minor diastereomeric products was chromatographed on preparative TLC plates (*n*-hexane/AcOEt = 15:1) to yield the major isomer.; $[\alpha]_D^{25} -140.2$ (*c* 0.72, CHCl₃); FTIR (neat): 3001.2, 1736.5, 1605.2, 1512.3, 1458.1, 829.5 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.15–7.06 (m, 5H), 6.89 (d, 2H, *J* = 8.5 Hz), 6.64 (d, 2H, *J* = 8.5 Hz), 4.25–4.07 (m, 2H), 3.69 (s, 3H), 3.63 (d, 1H, *J* = 11.2 Hz), 3.41 (dt, 1H, *J* = 11.2, 6.7 Hz), 1.37 (d, 3H, *J* = 6.8 Hz), 1.25 (t, 3H, *J* = 7.1 Hz) ppm.; ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 173.6, 157.7, 137.7, 135.7, 128.5, 128.4, 128.0, 126.8, 113.4, 60.7, 59.6, 55.0, 43.0, 21.0, 14.1 ppm.; [M+Na]⁺, calcd for [C₁₉H₂₂O₃Na]⁺ 321.1461; found: m/z 321.1460.; The enantiomeric excess of the major was determined to be 99% *ee* by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK IB-3 (Hexane/*i*-PrOH = 95/5, 0.75 mL/min), 25 °C, *t*_r (Major) = 16.4 min, *t*_r (Minor) = 15.3 min] after reducing with toluene solution of DIBAL.

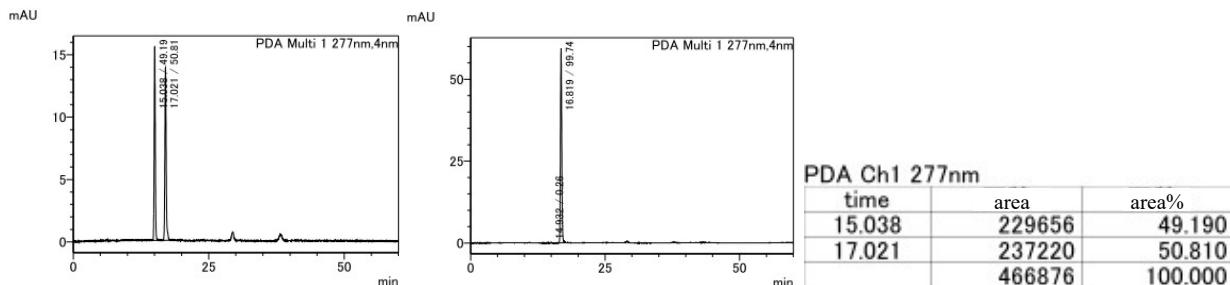
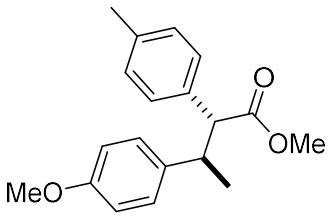


Figure S7. The chromatograms of ethyl (-)-3-(4-methoxyphenyl)-2-phenylbutanoate.

8.3. (-)-Methyl 3-(4-methoxyphenyl)-2-(4-methylphenyl)butanoate



Diastereomeric mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 96% yield as a colorless oil (57.2 mg, d.r. = >20:1); the mixture of major and minor diastereomeric products was chromatographed on preparative TLC plates (*n*-hexane/AcOEt = 15:1) to yield the major isomer.; The enantiomeric excess of the major was determined to be 99% *ee* by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK AD-3 (Hexane/*i*-PrOH = 99/1, 0.5 mL/min), 40 °C, *t_r* (Major) = 21.9 min, *t_r* (Minor) = 18.8 min]. $[\alpha]_D^{25}$ -163.7 (*c* 0.97, CHCl₃).; FTIR (neat): 2956.9, 2835.4, 1735.9, 1612.5, 1512.2, 1458.2, 1155.4, 1029.9, 827.4 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.02 (d, 2H, *J* = 8.3 Hz), 6.93 (d, 2H, *J* = 8.3 Hz), 6.89 (d, 2H, *J* = 8.8 Hz), 6.65 (d, 2H, *J* = 8.8 Hz), 3.70 (s, 3H), 3.68 (s, 3H), 3.63 (d, 1H, *J* = 11.2 Hz), 3.44–3.36 (m, 1H), 2.21 (s, 3H), 1.34 (d, 3H, *J* = 6.8 Hz) ppm.; ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 174.3, 157.7, 136.4, 135.8, 134.5, 128.8, 128.4, 128.3, 113.4, 58.9, 55.0, 51.9, 42.8, 21.2, 21.0 ppm.; Anal. Calcd for C₁₉H₂₂O₃: C, 76.48; H, 7.43. Found: C, 76.32; H, 7.41.; [M+Na]⁺, calcd for [C₁₉H₂₂O₃Na]⁺ 298.1569; found: m/z 298.1565.

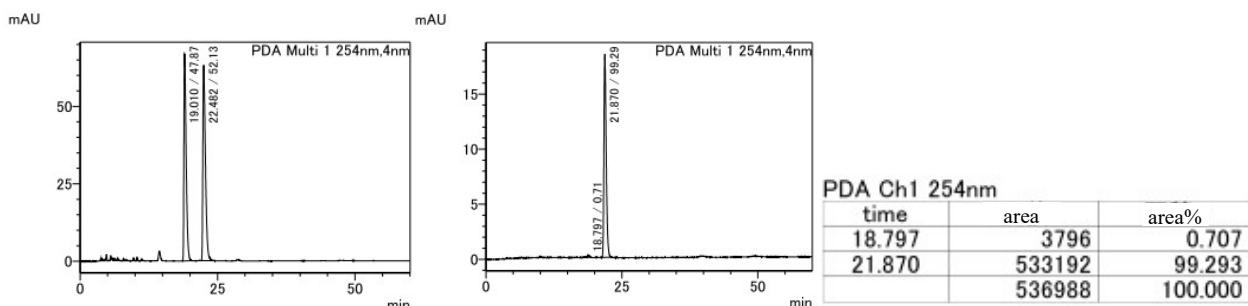
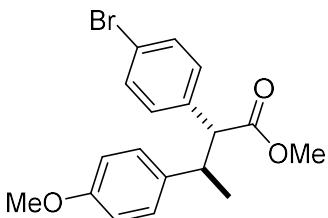


Figure S8. The chromatograms of methyl 3-(4-methoxyphenyl)-2-(4-methylphenyl)butanoate.

8.4. Methyl (2*R*,3*R*)-2-(4-bromophenyl)-3-(4-methoxyphenyl)butanoate



Diastereomeric mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 86% yield as a white solid (62.3 mg, d.r. = >20:1); the mixture of major and minor diastereomeric products was chromatographed on preparative TLC plates (*n*-hexane/AcOEt = 15:1) to yield the major isomer.; Mp: 54.1–54.3 °C.; $[\alpha]_D^{25}$ -168.1 (*c* 0.77, CHCl₃).; FTIR (neat): 2956.9, 1735.9, 1514.1, 1246.0, 1157.3, 1029.9, 827.5 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.25 (d, 2H, *J* = 8.3 Hz), 7.01 (d, 2H, *J* = 8.3 Hz), 6.87 (d, 2H, *J* = 8.8 Hz), 6.66 (d, 2H, *J* = 8.8 Hz), 3.71 (s, 3H), 3.70 (s, 3H), 3.62 (d, 1H, *J* = 11.2 Hz), 3.36 (dt, 1H, *J* = 6.8, 11.2 Hz), 1.34 (d, 3H, *J* = 6.8 Hz) ppm.; ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 173.7, 157.9, 136.6, 135.2, 131.2, 130.2, 128.4, 121.0, 113.6, 58.8, 55.1, 52.0, 43.0, 21.1 ppm.; Anal. Calcd for C₁₈H₁₉O₃Br: C, 59.52; H, 5.27. Found: C 59.31; H 5.29.; [M+Na]⁺, calcd for [C₁₈H₁₉O₃BrNa]⁺ 385.040; found: m/z 385.045.; The enantiomeric excess of the major was determined to be 99% *ee* by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK IB-3 (Hexane/*i*-PrOH = 95/5, 0.75 mL/min), 25 °C, *t_r* (Major) = 16.5 min, *t_r* (Minor) = 14.3 min] after reducing with DIBAL; corresponding alcohol $[\alpha]_D^{25}$ -23.2 (*c* 0.57, CHCl₃);^{ref.5} $[\alpha]_D^{25}$ -21.2 (*c* 2.7, CHCl₃).; FTIR (neat): 2956.9, 1734.0, 1614.4, 1514.1, 1487.1, 1458.2, 1271.1, 1246.0, 1157.3, 1070.5, 1037.7, 1010.7, 827.5, 763.8 cm⁻¹.

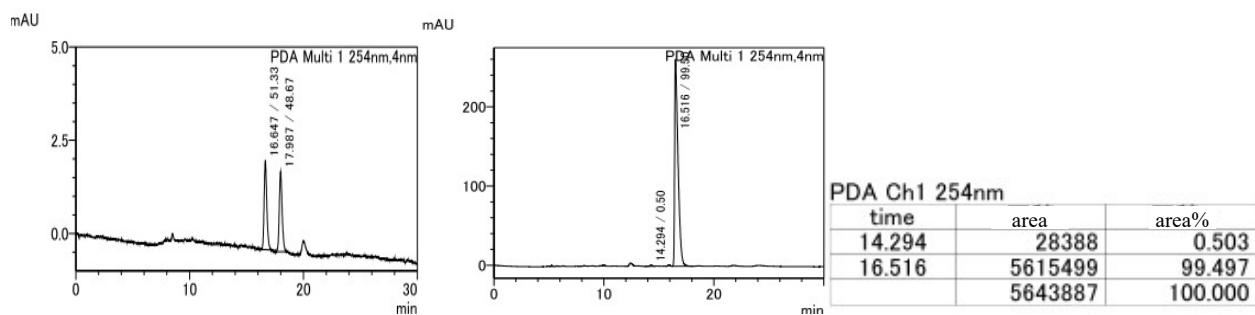


Figure S9. The chromatograms of methyl 2-(4-bromophenyl)-3-(4-methoxyphenyl)butanoate.

8.5. (-)-Methyl 2-(4-chlorophenyl)-3-(4-methoxyphenyl)butanoate

Diastereo-mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 81% yield as a white solid (51.5 mg, d.r. = >20:1); the mixture of major and minor diastereomeric products was chromatographed on preparative TLC plates (*n*-hexane/AcOEt = 15:1) to yield the major isomer.; Mp: 53.8–54.0 °C.; $[\alpha]_D^{25} -160.1$ (*c* 1.0, CHCl₃).; FTIR (neat): 2958.8, 1737.9, 1514.1, 827.5 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, the signals of the major isomer): δ 7.09 (d, 2H, *J* = 8.5 Hz), 7.06 (d, 2H, *J* = 8.5 Hz), 6.87 (d, 2H, *J* = 8.5 Hz), 6.66 (d, 2H, *J* = 8.5 Hz), 3.70 (s, 3H), 3.70 (s, 3H), 3.63 (d, 1H, *J* = 11.2 Hz), 3.36 (dt, 1H, *J* = 11.2, 6.8 Hz), 1.34 (d, 3H, *J* = 6.8 Hz) ppm.; ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 173.8, 157.9, 136.1, 135.2, 132.8, 129.8, 128.4, 128.3, 113.6, 58.8, 55.1, 52.0, 43.1, 21.1 ppm.; [M+Na]⁺, calcd for [C₁₈H₁₉O₃ClNa]⁺ 341.092; found: m/z 341.091.; The enantiomeric excess of the major was determined to be 99% ee by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK IB-3 (Hexane/*i*-PrOH = 98/2, 1.0 mL/min), 25 °C, *t*_r (Major) = 28.7 min, *t*_r (Minor) = 20.7 min] after reducing with DIBAL.

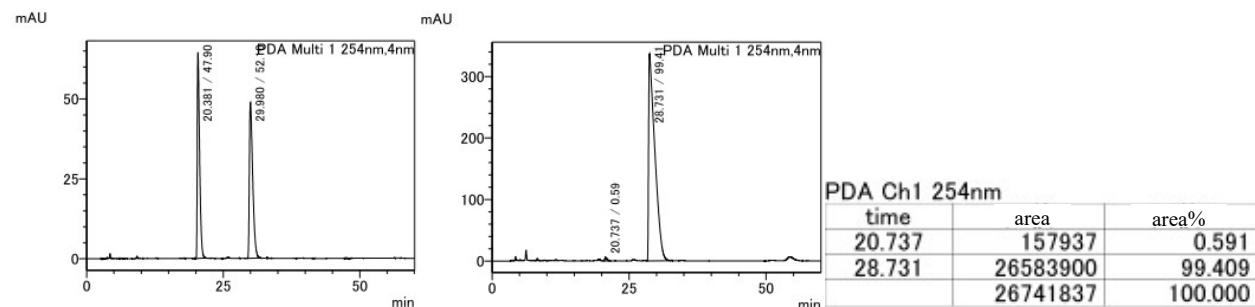


Figure S10. The chromatograms of methyl 2-(4-chlorophenyl)-3-(4-methoxyphenyl)butanoate

8.6. (-)-Methyl 2-(3-methoxyphenyl)-3-(4-methoxyphenyl)butanoate

Diastereo-mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 84% yield as a colorless oil (52.7 mg, d.r. = >20:1); the mixture of major and minor diastereomeric products was chromatographed on preparative TLC plates (*n*-hexane/AcOEt = 5:1) to yield the major isomer.; $[\alpha]_D^{25} -140.2$ (*c* 0.72, CHCl₃).; FTIR (PTFE): 2999.3, 2956.9, 2837.3, 1734.0, 1606.7, 1512.2, 1459.4, 1239.3, 1155.4, 1041.6, 831.3, 692.4 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.03 (pseud-t, 1H, *J* = 7.8 Hz), 6.90 (d, 2H, *J* = 8.8 Hz), 6.72–6.62 (m, 5H), 3.70 (s, 3H), 3.69 (s, 3H), 3.68 (s, 3H), 3.63 (d, 1H, *J* = 10.7 Hz), 3.40 (dt, 1H, *J* = 10.7, 6.8 Hz), 1.35 (d, 3H, *J* = 6.8 Hz) ppm.; ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 174.0, 159.2, 157.8, 139.0, 135.6, 129.0, 128.4, 121.0, 114.1, 113.4, 112.5, 59.3, 55.0, 51.9, 42.9, 21.1 ppm.; Anal. Calcd for C₁₉H₂₂O₄: C, 72.59; H, 7.05. Found: C, 72.52, H, 7.01.; The enantiomeric excess of the major was determined to be 99% ee by HPLC

analysis using a chiral stationary phase [DAICEL CHIRALPAK IB-3 (Hexane/*i*-PrOH = 98/2, 1.0 mL/min), 25 °C, t_r (Major) = 39.6 min, t_r (Minor) = 50.2 min] after reducing with DIBAL.

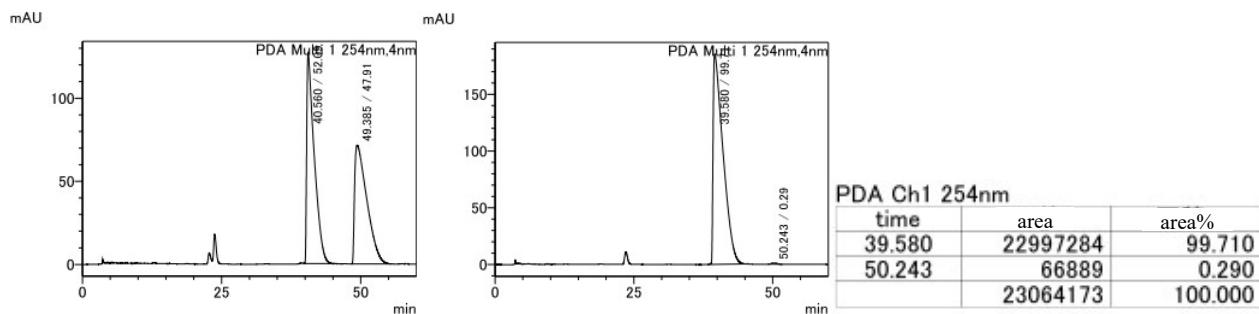


Figure S11. The chromatograms of methyl 2-(3-methoxyphenyl)-3-(4-methoxyphenyl)butanoate.

8.7. (-)-Methyl 2-(3-chlorophenyl)-3-(4-methoxyphenyl)butanoate

Diastereo-mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 87% yield as a colorless oil (55.3 mg, d.r. = >20:1); the mixture of major and minor diastereomeric products was chromatographed on preparative TLC plates (*n*-hexane/AcOEt = 15:1) to yield the major isomer.; Mp: 53.7–53.6 °C.; $[\alpha]_D^{25} -134.9$ (*c* 0.60, CHCl₃); FTIR (PTFE): 2998.8, 2837.3, 1728.2, 1215.2, 1155.4, 815.9, 634.6 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.18 (broad-s, 1H), 7.08–7.02 (m, 2H), 6.97 (broad-d, 1H, *J* = 7.3 Hz), 6.88 (d, 2H, *J* = 8.8 Hz), 6.67 (d, 2H, *J* = 8.8 Hz), 3.71 (s, 3H), 3.70 (s, 3H), 3.63 (d, 1H, *J* = 10.7 Hz), 3.42–3.34 (m, 1H), 1.35 (d, 3H, *J* = 6.8 Hz) ppm.; ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 173.6, 157.9, 139.6, 135.1, 133.9, 129.3, 128.5, 128.3, 127.2, 126.9, 113.6, 59.0, 55.1, 52.1, 43.0, 21.0 ppm.; Anal. Calcd for C₁₈H₁₉ClO₃: C, 67.82; H, 6.01. Found: C, 67.60; H, 5.96.; [M+Na]⁺, calcd for [C₁₈H₁₉O₃ClNa]⁺ 341.092; found: m/z 341.085.; The enantiomeric excess of the major isomer was determined to be 99% ee by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK IB-3 (Hexane/*i*-PrOH = 95/5, 0.75 mL/min), 25 °C, t_r (Major) = 16.8 min, t_r (Minor) = 15.5 min] after reducing with DIBAL.

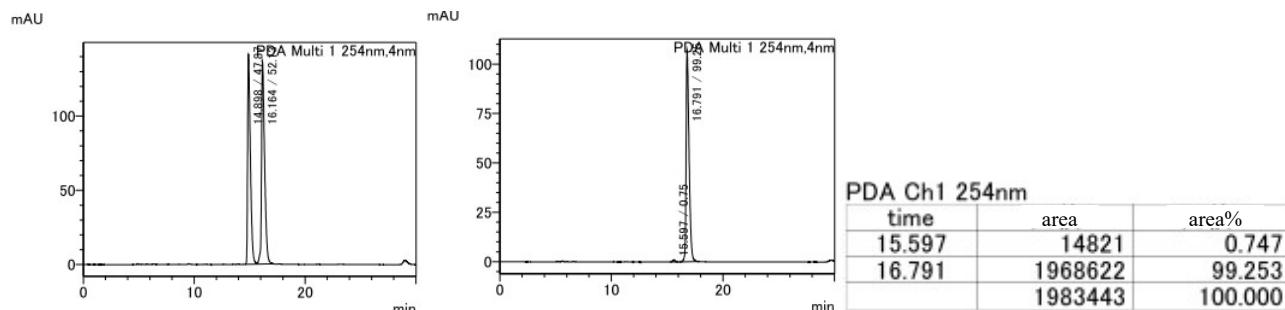


Figure S12. The chromatograms of methyl 2-(3-chlorophenyl)-3-(4-methoxyphenyl)butanoate.

8.8. (-)-Methyl 2-(2-naphthyl)-3-(4-methoxyphenyl)butanoate

Diastereo-mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 95% yield as a colorless oil (63.5 mg, d.r. = >20:1); the mixture of major and minor diastereomeric products was chromatographed on preparative TLC plates (*n*-hexane/AcOEt = 15:1) to yield the major isomer.; Mp: 57.8–57.9 °C.; $[\alpha]_D^{25} -191.1$ (*c* 1.21, CHCl₃).; FTIR (neat): 3059.1, 2962.7, 2837.3, 1732.1, 1608.6, 1512.2, 1444.7, 1157.3, 1028.1, 823.6, cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.70 (pseudo-q, 2H, *J* = 4.1 Hz), 7.62 (d, 1H, *J* = 8.8 Hz), 7.60 (s, 1H), 7.41–7.36 (m, 2H), 7.30 (d, 1H, *J* = 8.3 Hz), 6.92 (d, 2H, *J* = 8.8 Hz), 6.60 (d, 2H, *J* = 8.8 Hz), 3.85 (d, 1H, *J* = 11.2 Hz), 3.70 (s, 3H), 3.64 (s, 3H), 3.56 (dt, 1H, *J* = 11.2, 6.8 Hz), 1.40 (d, 3H, *J* = 6.8 Hz) ppm.; ¹³C{¹H}

NMR (100 MHz, CDCl₃): δ 174.1, 157.8, 135.6, 135.1, 133.1, 132.4, 128.4, 127.8, 127.7, 127.6, 127.5, 126.5, 125.8, 125.6, 113.5, 59.4, 55.0, 52.0, 42.8, 21.3 ppm.; [M+Na]⁺, calcd for [C₂₂H₂₂O₃Na]⁺ 357.1461; found: m/z 357.1461.; The enantiomeric excess of the major isomer was determined to be 99% ee by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK IB-3 (Hexane/i-PrOH = 95/5, 0.75 mL/min), 25 °C, *t*_r (Major) = 25.5 min, *t*_r (Minor) = 21.4 min] after reducing with DIBAL.

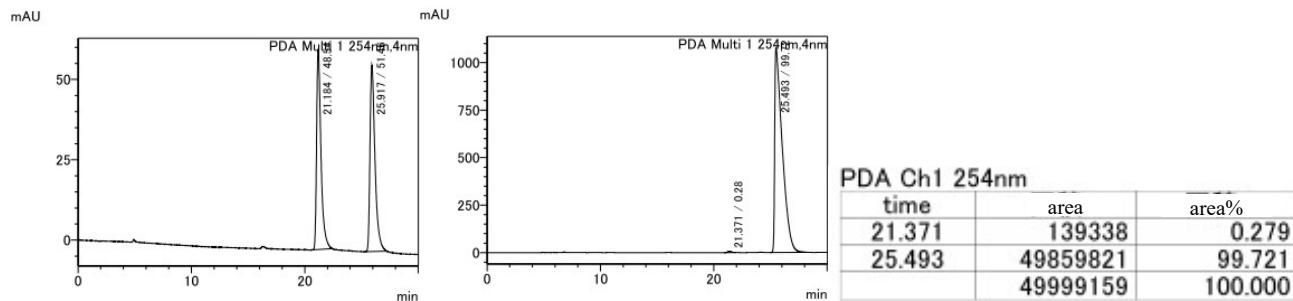
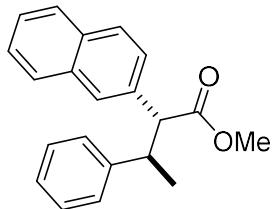


Figure S13. The chromatograms of methyl (2*R*,3*R*)-2-(2-naphthyl)-3-(4-methoxyphenyl)butanoate.

8.9. Methyl 2-(2-naphthyl)-3-phenylbutanoate



Diastereo-mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 75% yield as a white solid (45.6 mg, d.r. = >20:1); major isomer: Mp: 93.0–93.2 °C.; ¹H NMR (400 MHz, CDCl₃): δ 7.69 (pseudo-q, 2H, *J* = 4.4 Hz), 7.61 (pseud-d, 2H, *J* = 9.3 Hz), 7.41–7.34 (m, 2H), 7.30 (dd, 1H, *J* = 8.5, 1.7 Hz), 7.08–6.96 (m, 5H), 3.90 (d, 1H, *J* = 11.2 Hz), 3.71 (s, 3H), 3.60 (dt, 1H, *J* = 11.2, 6.8 Hz), 1.43 (d, 3H, *J* = 6.8 Hz) ppm.; ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 174.0, 143.5, 135.0, 133.1, 132.4, 128.1, 127.8, 127.7, 127.5, 127.4, 126.4, 126.2, 125.8, 125.6, 59.2, 52.0, 43.7, 21.2 ppm.; Anal. Calcd for C₂₁H₂₀O₂: C, 82.86; H, 6.62. Found: C, 82.64; H, 6.61.; [M+Na]⁺, calcd for [C₂₁H₂₀O₂Na]⁺ 327.1356; found: m/z 327.1355.; The enantiomeric excess of the major isomer was determined to be 99% ee by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK IB-3 (Hexane/i-PrOH = 95/5, 0.75 mL/min), 25 °C, *t*_r (Major) = 17.1 min, *t*_r (Minor) = 19.3 min] after reducing with DIBAL.; Corresponding alcohol: $[\alpha]$ _D²⁵ –37.6 (*c* 0.43, CHCl₃).; FTIR (neat): 3294.4, 3053.3, 2960.7, 2881.7, 1504.5, 1454.3, 817.8, 748.4, 702.1 cm⁻¹.

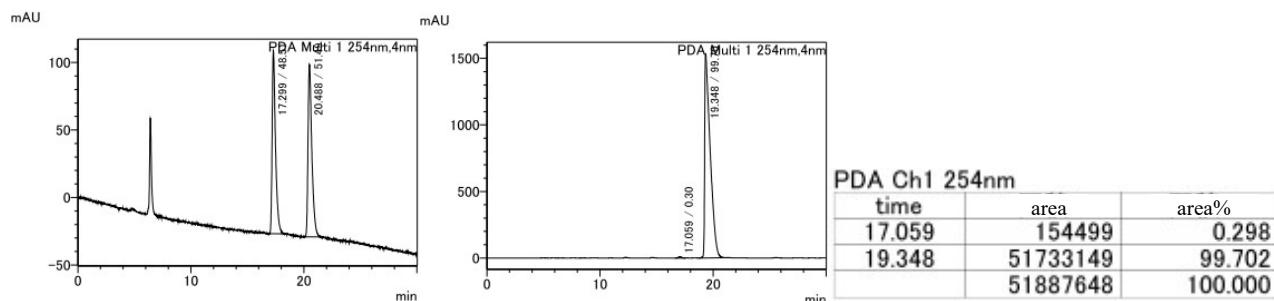
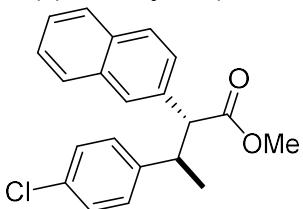


Figure S14. The chromatograms of methyl 2-(2-naphthyl)-3-phenylbutanoate.

8.10. (–)-Methyl 3-(4-chlorophenyl)-2-(2-naphthyl)butanoate



Diastereo-mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 27% yield as a white solid (18.3 mg, d.r. = >20:1); the mixture of major and minor diastereomeric products was chromatographed on preparative TLC plates (*n*-hexane/AcOEt = 15:1) to yield the major isomer.; Mp: 120.2–120.4 °C.; $[\alpha]$ _D²⁵ –196.0 (*c* 0.98, CHCl₃).; FTIR (neat): 3057.2, 2330.0, 1735.9, 1492.9,

1163.08, 1012.6, 827.5 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.70 (pseud-q, 2H, *J* = 6.1 Hz), 7.63 (d, 1H, *J* = 8.3 Hz), 7.58 (s, 1H), 7.42–7.37 (m, 2H), 7.28 (dd, 1H, *J* = 8.8 Hz, 1.7 Hz), 7.02 (d, 2H, *J* = 8.8 Hz), 6.94 (d, 2H, *J* = 8.8 Hz), 3.84 (d, 1H, *J* = 11.2 Hz), 3.70 (s, 3H), 3.56 (dt, 1H, *J* = 11.2, 6.8 Hz), 1.41 (d, 3H, *J* = 6.8 Hz) ppm.; ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 173.8, 142.0, 134.6, 133.1, 132.5, 131.8, 128.8, 128.3, 127.9, 127.8, 127.5, 127.5, 126.2, 126.0, 125.8, 59.1, 52.1, 43.0, 21.1 ppm.; [M+Na]⁺, calcd for [C₂₁H₁₉O₂ClNa]⁺ 361.0967; found: m/z 361.0960.; The enantiomeric excess of the major isomer was determined to be 99% ee by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK IB-3 (Hexane/i-PrOH = 95/5, 0.75 mL/min), 25 °C, *t*_r (Major) = 23.8 min, *t*_r (Minor) = 19.6 min] after reducing with DIBAL.

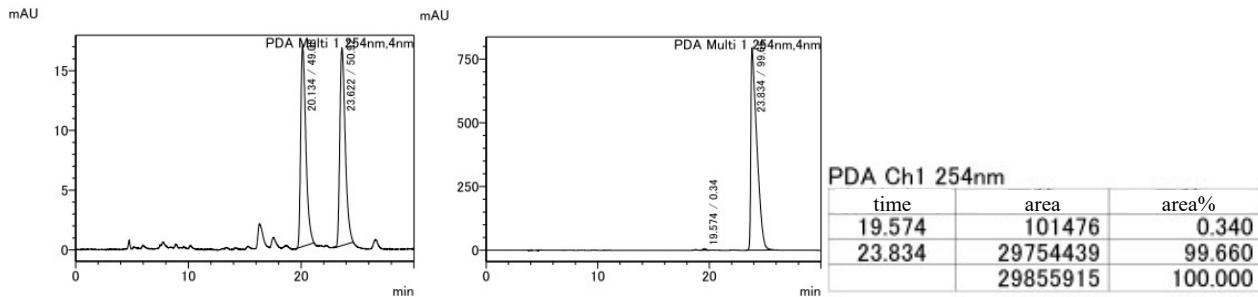


Figure S15. The chromatograms of methyl 3-(4-chlorophenyl)-2-(2-naphthyl)butanoate.

8.11. (-)-Methyl (2*R*,3*R*)-3-(4-bromophenyl)-2-(2-naphthyl)butanoate

Diastereomeric mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 67% yield as a white solid (51.2 mg, d.r. = >20:1); the mixture of major and minor diastereomeric products was chromatographed on preparative TLC plates (*n*-hexane/AcOEt = 15:1) to yield the major isomer. The enantiomeric excess of the major isomer was determined to be 98% ee by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK IB-3 (Hexane/i-PrOH = 95/5, 0.75 mL/min), 25 °C, *t*_r (Major) = 25.0 min, *t*_r (Minor) = 20.1 min] after reducing with DIBAL.; Mp: 120.2–120.4 °C.; [α]_D²⁵ -195.0 (*c* 0.87, CHCl₃).; FTIR (PTFE): 2956.9, 2835.4, 1734.0, 1610.6, 1512.2, 1247.9, 1157.3, 1012.6, 827.5, 763.8 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.71 (pseud-q, 2H, *J* = 6.1 Hz), 7.63 (d, 1H, *J* = 8.8 Hz), 7.58 (s, 1H), 7.43–7.38 (m, 2H), 7.28 (d, 1H, *J* = 8.3 Hz), 7.18 (d, 2H, *J* = 8.3 Hz), 6.89 (d, 2H, *J* = 8.3 Hz), 3.85 (d, 1H, *J* = 11.2 Hz), 3.70 (s, 3H), 3.58 (dt, 1H, *J* = 11.2, 6.8 Hz), 1.40 (d, 3H, *J* = 6.8 Hz) ppm.; ¹³C NMR (100 MHz, CDCl₃): δ 173.7, 142.5, 134.6, 133.1, 132.5, 131.2, 129.3, 128.0, 127.8, 127.5, 126.2, 126.0, 125.8, 119.9, 59.0, 52.1, 43.1, 21.1 ppm.; Anal. Calcd for C₂₁H₁₉O₂Br: C, 65.81; H, 5.00. Found: C, 65.79; H, 5.04.; [M+Na]⁺, calcd for [C₂₁H₁₉O₂BrNa]⁺ 405.0461; found: m/z 405.0462.

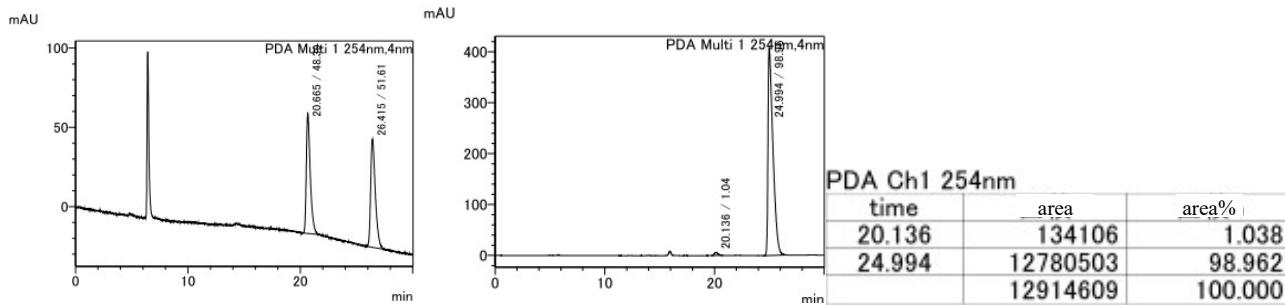


Figure S16. The chromatograms of methyl 3-(4-bromophenyl)-2-(2-naphthyl)butanoate.

X-ray analysis of major product; Single crystals of the major product for X-ray diffraction experiments were obtained by recrystallization from hexane. The data were collected at 120 K on a Rigaku XtaLAB diffractometer equipped with CCD area detector, a mirror monochromator and a

rotating-anode X-ray tube (Mo- $K\alpha$ radiation, $\lambda = 0.71073$) focused with Helios multilayer optics for Mo- $K\alpha$ radiation operating at 50 kV and 16 mA. The data collection, the cell refinement, and the data reduction were performed by CrysAlisPro software program. The structure was solved by direct methods and refined by full-matrix least-squares based on all data using F^2 with SHELXLTL.^[4] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed from the difference map and refined with geometrical and isotropic displacement parameters. Molecular plot was obtained with ORTEP-3. Crystallographic: $C_{21}H_{19}BrO_2$, colourless block, $0.20 \times 0.09 \times 0.09$ mm 3 , orthorhombic, $P2_12_12_1$, $a = 10.0700(5)$, $b = 10.3224(14)$, $c = 34.083(2)$ Å, $V = 3542.8(2)$ Å 3 , $Z = 8$, $Flack = 0.019(7)$, $R = 0.0523$ and $Rw = 0.1078$, CCDC 2119506 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

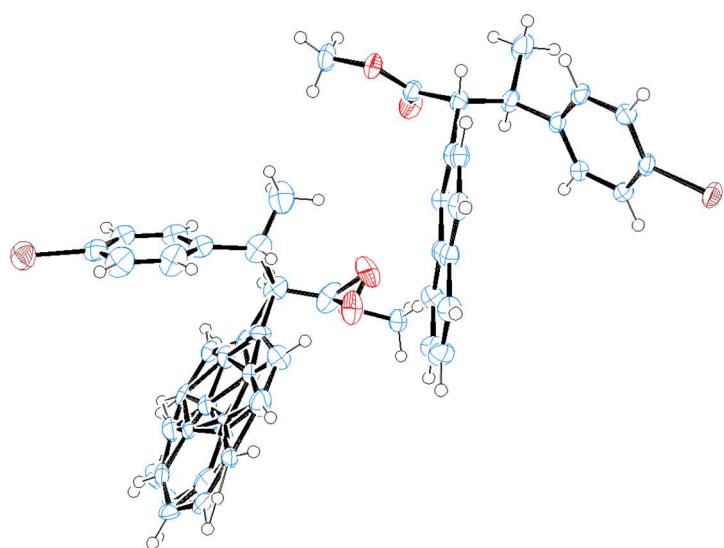
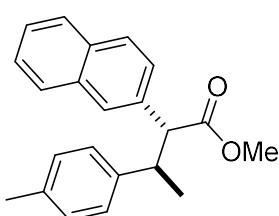


Figure S17. ORTEP view (50% probability) of (-)-Methyl (2*R*,3*R*)-3-(4-bromophenyl)-2-(2-naphthyl)butanoate.

ECD analysis of (-)-Methyl (2*R*,3*R*)-3-(4-bromophenyl)-2-(2-naphthyl)butanoate see Section 7.

8.12. (-)-Methyl 3-(4-methylphenyl)-2-(2-naphthyl)butanoate



Diastereo-mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 81% yield as a white solid (51.5 mg, d.r. = >20:1); the mixture of major and minor diastereomeric products was chromatographed on preparative TLC plates (*n*-hexane/AcOEt = 15:1) to yield the major isomer.; Mp: 104.7–104.9 °C.; $[\alpha]_D^{25} -161.8$ (*c* 0.24, CHCl₃).; FTIR (PTFE): 3053.3, 3020.5, 2956.9, 2872.0, 1732.1, 1213.2, 1155.4, 1016.5.0, 814.0, 750.3 cm $^{-1}$; ¹H NMR (400 MHz, CDCl₃): δ 7.70–7.68 (m, 2H), 7.61 (comb-d and s, 2H, *J* = 8.3 Hz), 7.38–7.32 (m, 3H), 6.91 (d, 2H, *J* = 8.0 Hz), 6.66 (d, 2H, *J* = 8.0 Hz), 3.89 (d, 1H, *J* = 10.7 Hz), 3.69 (s, 3H), 3.58 (dt, 1H, *J* = 10.8, 6.8 Hz), 2.14 (s, 3H), 1.40 (d, 3H, *J* = 6.8 Hz) ppm.; ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 174.1, 140.4, 135.6, 135.1, 133.2, 132.5, 128.8, 127.8, 127.7, 127.6, 127.5, 127.3, 126.5, 125.7, 125.6, 59.2, 52.0, 43.1, 21.3, 20.9 ppm.; [M+Na] $^+$, calcd for [C₂₂H₂₂O₂Na] $^+$ 341.1512; found: m/z 341.1515.; The enantiomeric excess of the major isomer was determined to be 99% ee by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK IB-3 (Hexane/*i*-PrOH = 95/5, 0.75 mL/min), 25 °C, *t*_r (Major) = 17.9 min, *t*_r (Minor) = 15.7 min] after reducing with DIBAL.

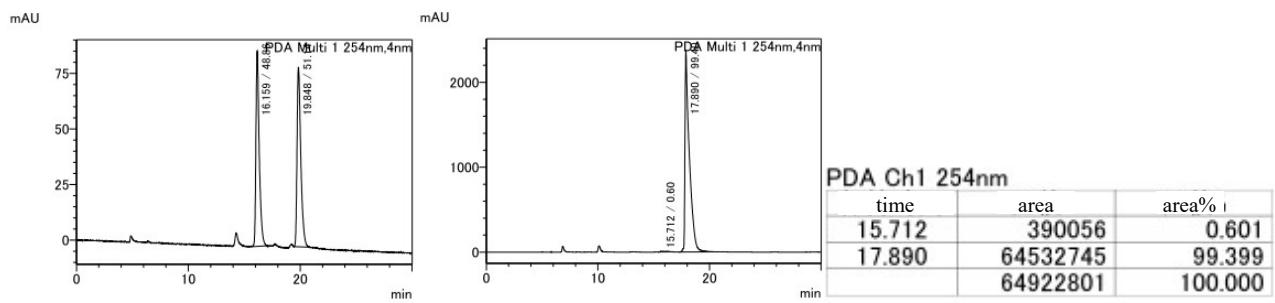
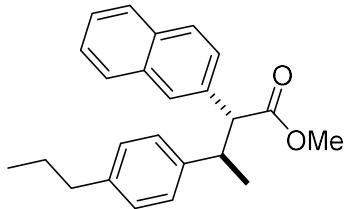


Figure S18. The chromatograms of methyl 3-(4-methylphenyl)-2-(2-naphthyl)butanoate.

8.13. Methyl 2-(2-naphthyl)-3-(4-*n*-propylphenyl)butanoate



Diastereomeric mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 87% yield as a colorless oil (60.2 mg, d.r. = >20:1); major isomer: ¹H NMR (400 MHz, CDCl₃): δ 7.68 (pseud-dd, 2H, *J* = 9.3, 5.9 Hz), 7.61 (d, 1H, *J* = 8.8 Hz), 7.58 (s, 1H), 7.39–7.34 (m, 2H), 7.30 (d, 1H, *J* = 8.3 Hz), 6.90 (d, 2H, *J* = 7.8 Hz), 6.85 (d, 2H, *J* = 7.8 Hz), 3.88 (d, 1H, *J* = 11.2 Hz), 3.69 (s, 3H), 3.60–3.50 (m, 1H), 2.37 (t, 2H, *J* = 7.6 Hz), 1.47 (pseud-q, 2H, *J* = 7.5 Hz), 1.42 (d, 3H, *J* = 6.8 Hz), 0.79 (t, 3H, *J* = 7.3 Hz) ppm.; ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 174.1, 140.6, 140.4, 135.1, 133.1, 132.4, 128.1, 127.8, 127.6, 127.6, 127.4, 127.3, 126.4, 125.7, 125.5, 59.3, 52.0, 43.3, 24.2, 21.1, 13.7 ppm.; [M+Na]⁺, calcd for [C₂₄H₂₆O₂Na]⁺ 369.1825; found: m/z 369.1825.; The enantiomeric excess of the major isomer was determined to be 99% ee by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK IB-3 (Hexane/*i*-PrOH = 95/5, 0.75 mL/min), 25 °C, *t*_r (Major) = 16.6 min, *t*_r (Minor) = 14.7 min] after reducing with DIBAL.; corresponding alcohol: [α]_D²⁵ –23.1 (*c* 1.13, CHCl₃).; FTIR (neat): 3302.1, 2982.7, 2927.9, 2872.0, 1510.3, 1373.3, 1060.4, 1022.3, 819.8, cm^{–1}.

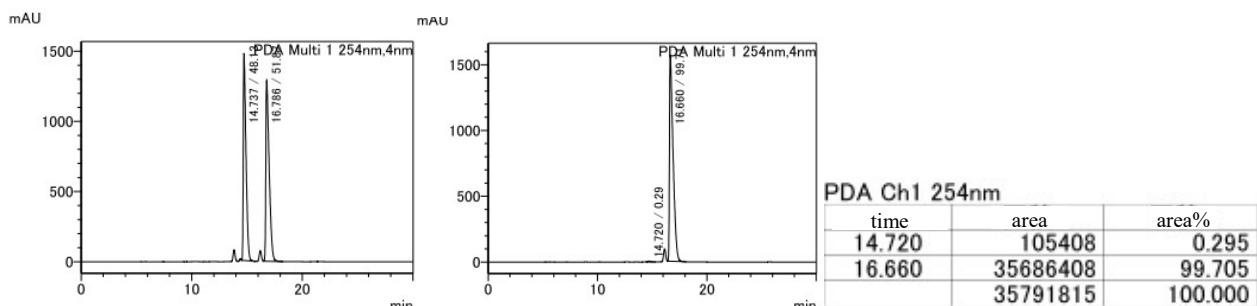
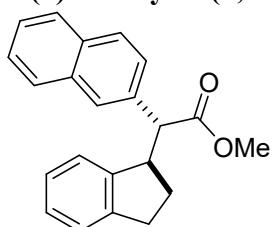


Figure S19. The chromatograms of methyl 2-(2-naphthyl)-3-(4-*n*-propylphenyl)butanoate.

8.14. (–)-Methyl 2-(2,3-dihydro-1*H*-inden-1-yl)-2-(2-naphthyl)acetate



Diastereomeric mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 78% yield as a white solid (49.3 mg, d.r. = >20:1); the mixture of major and minor diastereomeric products was chromatographed on preparative TLC plates (*n*-hexane/AcOEt = 15:1) to yield the major isomer. The enantiomeric excess of the major isomer was determined to be 99% ee by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK ID-3 (Hexane/*i*-PrOH = 95/5, 0.75 mL/min), 25 °C, *t*_r (Major) = 14.4 min, *t*_r (Minor) = 16.7 min] after reducing with DIBAL.; Mp: 127.7–127.9 °C.; [α]_D²⁵ –157.8 (*c* = 1.72, CHCl₃); FTIR (neat): 2949.2, 1732.1, 1294.2, 1192.0, 1165.0, 1145.7, 814.0, cm^{–1}; ¹H NMR (400 MHz, CDCl₃): δ 7.84–7.74 (m, 4H), 7.51–7.45 (m, 3H), 7.18 (d, 1H, *J* = 7.3 Hz), 7.05 (t, 1H, *J* = 7.3 Hz), 6.72 (t, 1H, *J* = 7.8 Hz), 6.15 (d, 1H, *J* = 7.8 Hz), 4.07–4.01 (m, 1H), 3.78 (d, 1H, *J* = 10.7 Hz), 3.68 (s, 3H), 3.03–2.95 (m, 2H), 2.90–2.83 (m, 1H), 1.99–1.91 (m, 1H) ppm.; ¹³C{¹H}

NMR (100 MHz, CDCl₃): δ 173.8, 144.3, 143.8, 135.2, 133.3, 132.8, 128.2, 128.0, 127.9, 127.6, 126.7, 126.1, 125.9, 125.5, 125.2, 124.4, 56.8, 52.0, 47.9, 31.4, 30.8 ppm.; [M+Na]⁺, calcd for [C₂₂H₂₀O₂Na]⁺ 339.1356; found: m/z 339.1356.

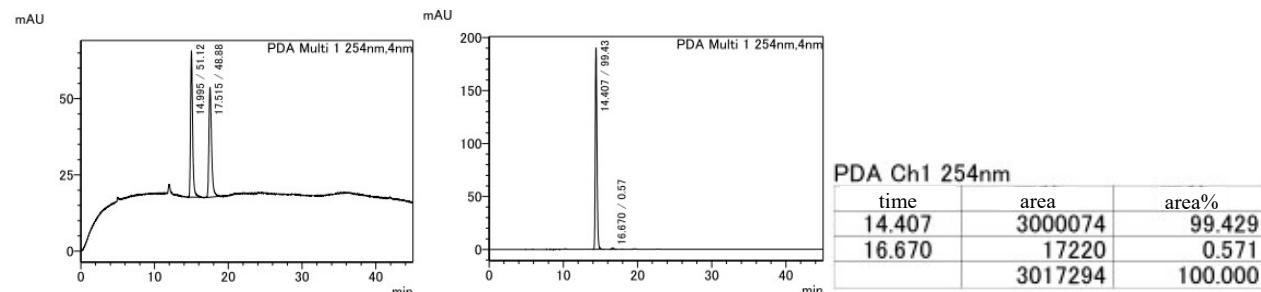


Figure S20. The chromatograms of methyl 2-(2,3-dihydro-1*H*-inden-1-yl)-2-(2-naphthyl)acetate.

8.15. (-)-Methyl 2-(2,3-dihydrobenzofuran-3-yl)-2-(2-naphthyl)acetate

Diastereomeric mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 77% yield as a white solid (49.0 mg, d.r. = >20:1); the mixture of major and minor diastereomeric products was chromatographed on preparative TLC plates (*n*-hexane/AcOEt = 15:1) to yield the major isomer.; Mp: 108.5–108.7 °C.; [α]_D²⁵ –238.2 (*c* = 1.61, CHCl₃); FTIR (neat): 2951.1, 1734.0, 1483.3, 1240.2, 1163.1, 1147.7, 974.1, 814.0 cm^{–1}; ¹H NMR (400 MHz, CDCl₃): δ 7.87–7.77 (m, 3H), 7.69 (s, 1H), 7.51–7.47 (m, 2H), 7.41 (dd, 1H, *J* = 8.5, 1.7 Hz), 7.03 (t, 1H, *J* = 7.8 Hz), 6.77 (d, 1H, *J* = 7.8 Hz), 6.42 (t, 1H, *J* = 7.6 Hz), 5.93 (d, 1H, *J* = 7.3 Hz), 4.79 (t, 1H, *J* = 9.3 Hz), 4.38 (q, 1H, *J* = 4.7 Hz), 4.30–4.24 (m, 1H), 3.87 (d, 1H, *J* = 11.2 Hz), 3.68 (s, 3H) ppm.; ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 173.4, 160.2, 134.0, 133.3, 132.9, 128.7, 128.6, 128.1, 128.0, 127.7, 127.2, 126.4, 126.2, 126.2, 125.7, 119.9, 109.5, 76.0, 56.6, 52.3, 44.9 ppm.; [M+Na]⁺, calcd for [C₂₁H₁₈O₃Na]⁺ 341.1148; found: m/z 341.1149.; The enantiomeric excess of the major isomer was determined to be 99% ee by HPLC analysis using a chiral stationary phase [(R,R)-WHRLK01 (Hexane/*i*-PrOH = 70/30, 0.75 mL/min), 25 °C, *t*_r (Major) = 41.6 min, *t*_r (Minor) = 33.1 min] after reducing with DIBAL.

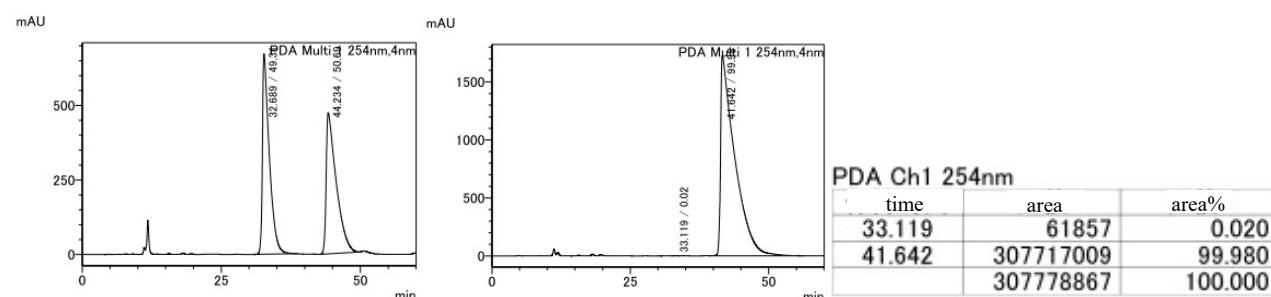
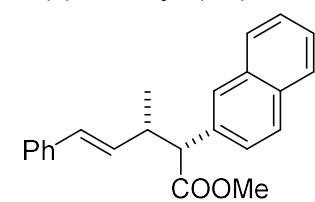


Figure S21. The chromatograms of methyl 2-(2,3-dihydrobenzofuran-3-yl)-2-(2-naphthyl) acetate

8.16. (-)-Methyl (4E)-3-methyl-2-(2-naphthyl)-5-phenylpent-4-enoate

Diastereomeric mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 83% yield as a colorless oil (54.8 mg, d.r. = 7:1); the mixture of major and minor diastereomeric products was chromatographed on preparative TLC plates (*n*-hexane/AcOEt = 15:1) to yield the major isomer.; [α]_D²⁵ –171.8 (*c* = 1.27, CHCl₃); FTIR (neat): 3057.2, 3024.4, 2960.7, 1500.6, 1440.8, 1159.2, 966.3, 750.3 cm^{–1}; ¹H NMR (400 MHz, CDCl₃): δ 7.80–7.76 (m, 4H), 7.49–7.41 (m, 3H), 7.18–7.09 (m, 5H), 6.25 (d, 1H, *J* = 16.1 Hz), 5.91 (dd, 1H, *J* = 16.1, 7.8 Hz), 3.68 (s, 3H), 3.64 (d, 1H, *J* = 10.2 Hz), 3.29–3.19 (m, 1H), 1.27 (d, 3H, *J* = 6.8 Hz) ppm.; ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 173.8,



137.4, 134.9, 133.3, 132.7, 132.3, 130.2, 128.3, 128.1, 127.9, 127.7, 127.6, 127.0, 126.6, 126.0, 125.8, 58.4, 52.0, 40.1, 19.1 ppm.; $[M+Na]^+$, calcd for $[C_{23}H_{22}O_2Na]^+$ 353.1512; found: m/z 353.1513.; The enantiomeric excess of the major isomer was determined to be 99% ee by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK IB-3 (Hexane/i-PrOH = 95/5, 0.75 mL/min), 25 °C, t_r (Major) = 25.3 min, t_r (Minor) = 19.1 min] after reducing with DIBAL.

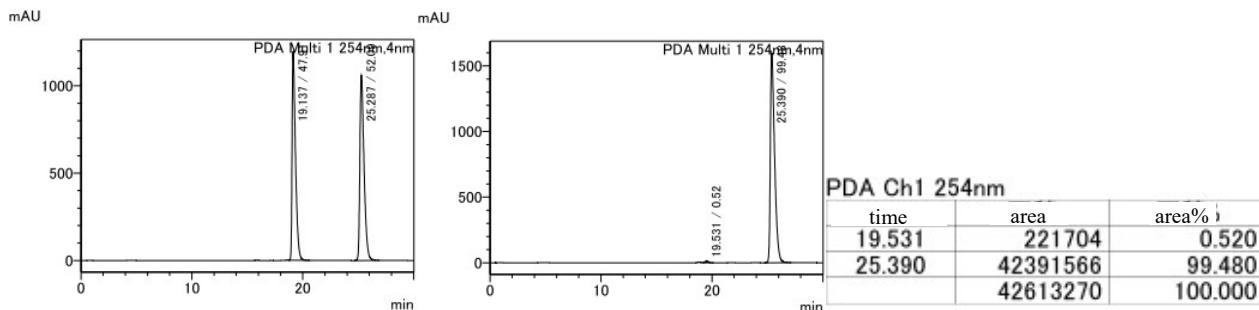
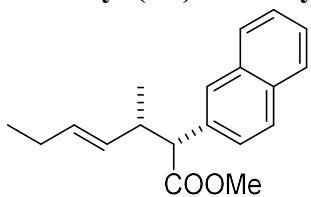


Figure S22. The chromatograms of methyl (4E)-3-methyl-2-(2-naphthyl)-5-phenylpent-4-enoate.

8.17. Methyl (4E)-3-methyl-2-(2-naphthyl)hept-4-enoate



Diastereo-mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 86% yield a colorless oil (48.5 mg, d.r. = 6:1); major isomer: 1H NMR (400 MHz, $CDCl_3$): δ 7.80–7.71 (m, 4H), 7.47–7.41 (m, 3H), 5.26 (dt, 1H, J = 15.6, 6.0 Hz), 5.07 (dd, 1H, J = 15.6, 7.8 Hz), 3.66 (s, 3H), 3.49 (d, 1H, J = 10.7 Hz), 3.03–2.92 (m, 1H), 1.79–1.68 (m, 2H), 1.14 (d, 3H, 6.8 Hz), 0.65 (t, 3H, J = 7.7 Hz) ppm.; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.0, 135.4, 133.3, 132.9, 132.6, 130.9, 127.8, 127.5, 126.8, 125.9, 125.6, 58.6, 51.8, 40.0, 25.4, 19.3, 13.6 ppm.; $[M+Na]^+$, calcd for $[C_{19}H_{22}O_2Na]^+$ 305.1512; found: m/z 305.1516.; The enantiomeric excess of the major isomer was determined to be 96% ee by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK IA-3 (Hexane/i-PrOH = 80/20, 0.75 mL/min), 25 °C, t_r (Major) = 36.2 min, t_r (Minor) = 30.9 min] after reducing with DIBAL.; corresponding alcohol: $[\alpha]_D^{25}$ +37.2 (c 0.44, $CHCl_3$).; FTIR (neat): 3282.8, 3057.2, 2962.7, 1512.2, 1458.2, 1371.4, 1064.7, 1012.7, 979.8, 819.8, 748.4 cm^{-1} .

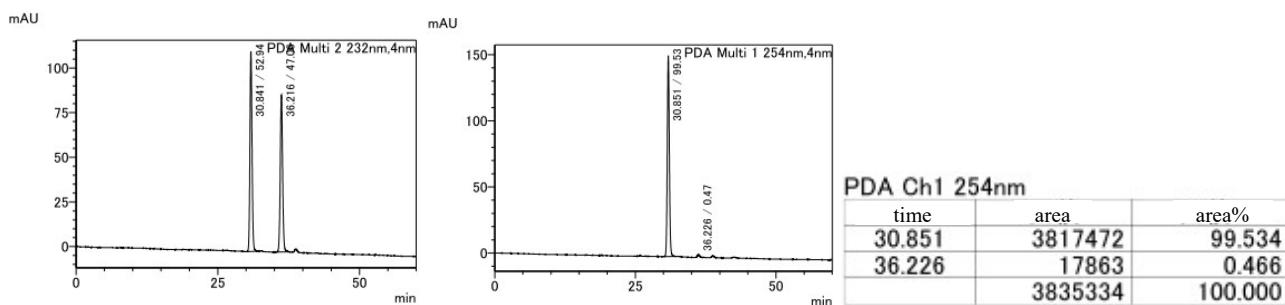
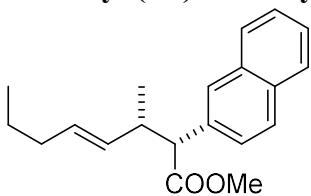


Figure S23. The chromatograms of methyl (4E)-3-methyl-2-(2-naphthyl)hept-4-enoate.

8.18. Methyl (4E)-3-methyl-2-(2-naphthyl)oct-4-enoate



Diastereo-mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 77% yield a colorless oil (45.6 mg, d.r. = 7:1); major isomer: 1H NMR (400 MHz, $CDCl_3$): δ 7.82–7.71 (m, 4H), 7.46–7.43 (m, 3H), 5.25–5.18 (m, 1H), 5.08 (dd, 1H, J = 11.6, 7.8 Hz) 3.66 (s, 3H), 3.50 (d, 1H, J = 10.2 Hz), 3.04–2.93 (m, 1H), 1.78–1.63 (m, 2H), 1.14 (d, 3H, J = 6.8 Hz), 1.04 (td, 2H, J = 14.3, 7.0 Hz), 0.54 (t, 3H, J = 7.3 Hz) ppm.; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.1, 135.4, 133.3, 132.6, 132.1, 131.1, 127.8, 127.8, 127.5, 126.7, 125.9, 125.6, 58.6, 51.9, 40.1, 34.4,

22.3, 19.4, 13.1 ppm.; $[M+Na]^+$, calcd for $[C_{20}H_{24}O_2Na]^+$ 319.1669; found: m/z 319.1670.; The enantiomeric excess of the major isomer was determined to be 99% ee by HPLC analysis using a chiral stationary phase [(R,R)-WHRLK01 (Hexane/i-PrOH = 70/30, 0.75 mL/min), 25 °C, t_r (Major) = 26.2 min, t_r (Minor) = 19.1 min] after reducing with DIBAL.; corresponding alcohol: $[\alpha]_D^{25} +41.6$ (c 0.98, CHCl₃); FTIR (neat): 3295.4, 3055.2, 2958.8, 1454.3, 1064.7, 1014.6, 821.7, 746.5 cm⁻¹.

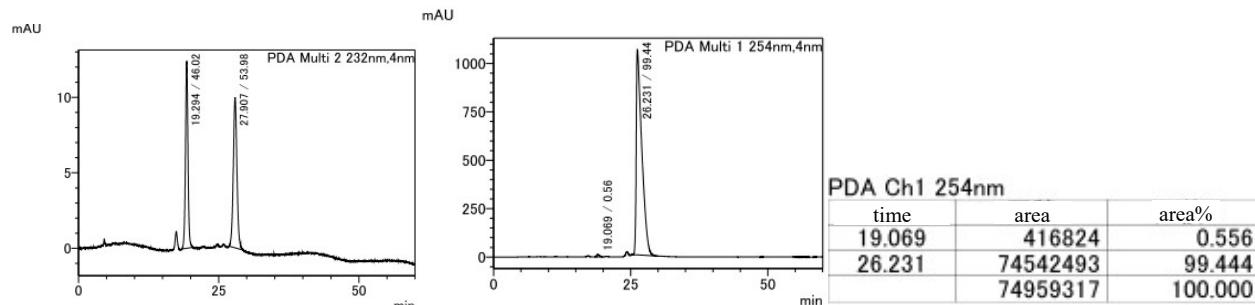


Figure S24. The chromatograms of methyl (4E)-3-methyl-2-(2-naphthyl)oct-4-enoate.

8.19. Methyl (4E)-3-methyl-2-(2-naphthyl)non-4-enoate

Diastereo-mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 67% yield as a white solid (41.5 mg, d.r. = 7:1); the mixture of major and minor diastereomeric products was chromatographed on preparative TLC plates (*n*-hexane/AcOEt = 15:1) to yield the major isomer.; $[\alpha]_D^{25} -102.4$ (c = 1.45, CHCl₃); FTIR (neat): 3057.2, 2962.7, 2922.2, 2856.6, 2374.4, 2314.6, 1739.8, 1687.7, 1645.3, 1548.8, 1514.1, 1460.1, 1012.6, 958.3, 854.5, 814.0, 748.4 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.78 (pseud-t, 3H, J = 8.8 Hz), 7.70 (s, 1H), 7.46–7.40 (m, 3H), 5.23–5.14 (m, 1H), 5.06 (dd, 1H, J = 15.2, 7.6 Hz), 3.66 (s, 3H), 3.48 (d, 1H, J = 10.7 Hz), 3.03–2.94 (m, 1H), 1.80–1.64 (m, 2H), 1.14 (d, 3H, J = 6.8 Hz), 1.01–0.91 (m, 2H), 0.90–0.79 (m, 2H), 0.57 (t, 3H, J = 7.3 Hz) ppm.; ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 174.1, 135.5, 133.3, 132.6, 132.0, 131.4, 127.8, 127.8, 127.5, 126.7, 125.9, 125.6, 58.6, 51.8, 40.3, 32.0, 31.3, 21.6, 19.5, 13.6 ppm.; $[M+Na]^+$, calcd for $[C_{21}H_{26}O_2Na]^+$ 333.1825; found: m/z 333.1827.; The enantiomeric excess of the major isomer was determined to be 99% ee by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK IB-3 (Hexane/i-PrOH = 95/5, 0.75 mL/min), 25 °C, t_r (Major) = 13.1 min, t_r (Minor) = 11.7 min] after reducing with DIBAL.

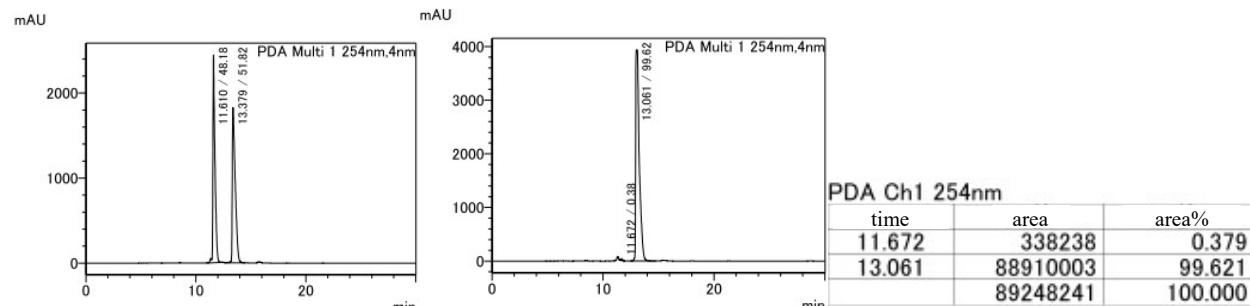
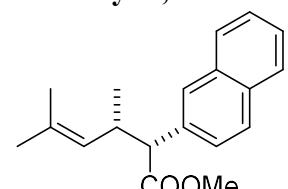


Figure S25. The chromatograms of methyl (4E)-3-methyl-2-(2-naphthyl)non-4-enoate.

8.20. Methyl 3,5-dimethyl-2-(2-naphthyl)hex-4-enoate

Diastereo-mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 79% yield as a white solid (44.6 mg, d.r. = >20:1); major isomer: Mp: 32.1–32.3 °C.; FTIR (PTFE): 3053.3, 2962.7, 2870.1, 1734.0, 1444.7, 1215.2, 1155.4, 812.0, 750.3 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.79–7.72 (m, 4H), 7.44–7.42 (m, 3H),



4.77 (d, 1H, $J = 9.6$ Hz), 3.66 (s, 3H), 3.49 (d, 1H, $J = 10.2$ Hz), 3.29–3.19 (m, 1H), 1.41 (s, 3H), 1.35 (s, 3H), 1.09 (d, 3H, $J = 6.3$ Hz) ppm.; $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 174.2, 135.7, 133.2, 132.5, 132.0, 128.8, 127.6, 127.5, 127.2, 126.7, 125.8, 125.6, 58.6, 51.8, 36.3, 25.6, 20.1, 17.8 ppm.; $[\text{M}+\text{Na}]^+$, calcd for $[\text{C}_{19}\text{H}_{22}\text{O}_2\text{Na}]^+$ 305.1512; found: m/z 305.1510.; The enantiomeric excess of the major isomer was determined to be 98% ee by HPLC analysis using a chiral stationary phase [(R,R)-WHRLK01 (Hexane/*i*-PrOH = 70/30, 0.75 mL/min), 25 °C, t_r (Major) = 27.1 min, t_r (Minor) = 23.0 min] after reducing with DIBAL.; corresponding alcohol: $[\alpha]_D^{25} +67.6$ (c 0.33, CHCl_3).

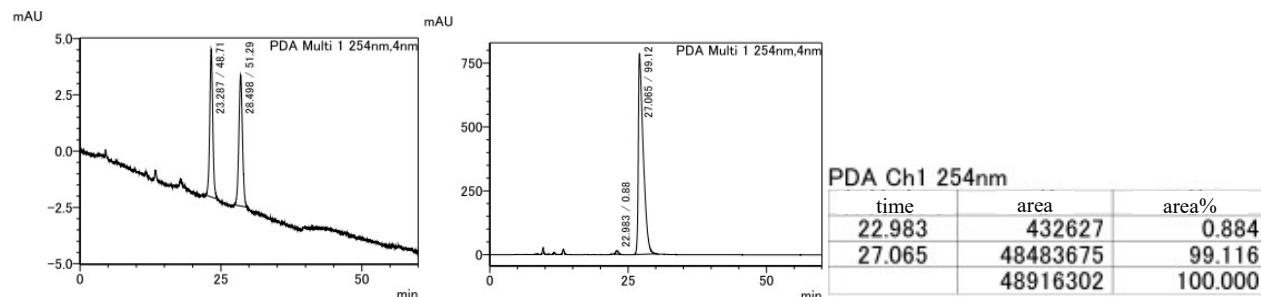
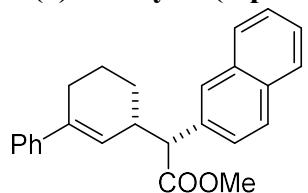


Figure S26. The chromatograms of methyl 3,5-dimethyl-2-(2-naphthyl)hex-4-enoate.

8.21. (-)-Methyl 2-(3-phenylcyclohex-2-en-1-yl)-2-(2-naphthyl)acetate



Diastereo-mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 87% yield as a white solid (62.0 mg, d.r. = >20:1); the mixture of major and minor diastereomeric products was chromatographed on preparative TLC plates (*n*-hexane/AcOEt = 15:1) to yield the major isomer.; Mp: 100.3–100.5 °C.; $[\alpha]_D^{25} -110.4$ (c = 1.27, CHCl_3); FTIR (neat): 3055.2, 2935.7, 2858.5, 1735.9, 1512.2, 1155.4, 815.9, 752.2 cm⁻¹; ^1H NMR (400 MHz, CDCl_3): δ 7.85–7.81 (m, 4H), 7.55 (d, 1H, $J = 8.3$ Hz), 7.50–7.45 (m, 2H), 7.20–7.11 (m, 5H), 5.60 (s, 1H), 3.68 (s, 3H), 3.59 (d, 1H, $J = 11.2$ Hz), 3.22–3.15 (m, 1H), 2.43–2.40 (m, 2H), 2.04–1.94 (m, 2H), 1.82–1.71 (m, 1H), 1.48–1.30 (m, 1H) ppm.; $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 173.9, 142.1, 138.5, 134.8, 133.4, 132.8, 128.3, 128.1, 127.9, 127.9, 127.6, 126.8, 125.6, 125.1, 125.1, 57.6, 51.9, 39.2, 27.6, 21.6 ppm.; $[\text{M}+\text{Na}]^+$, calcd for $[\text{C}_{25}\text{H}_{24}\text{O}_2\text{Na}]^+$ 379.1669; found: m/z 379.1671.; The enantiomeric excess of the major isomer was determined to be 96% ee by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK IA-3 (Hexane/*i*-PrOH = 90/10, 0.6 mL/min), 25 °C, t_r (Major) = 39.1 min, t_r (Minor) = 36.5 min] after reducing with DIBAL.

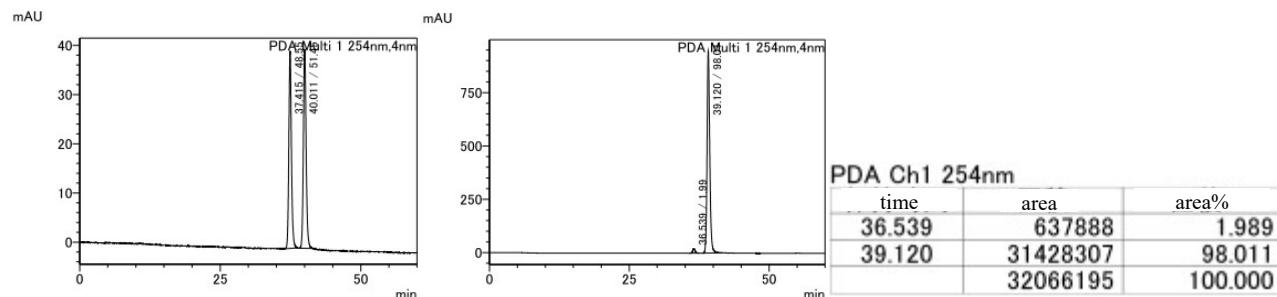
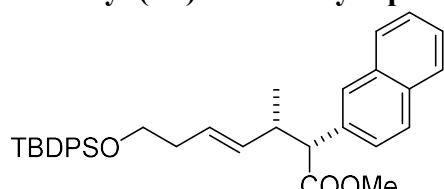


Figure S27. The chromatograms of methyl 2-(3-phenylcyclohex-2-en-1-yl)-2-(2-naphthyl) acetate.

8.22. Methyl (4*E*)-7-*tert*-butyldiphenylsilyloxy-3-methyl-2-(2-naphthyl)hept-4-enoate



Diastereo-mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 77% yield as a colorless oil (82.6 mg, d.r. = 7:1); the mixture of major and minor diastereomeric products was chromatographed on preparative TLC plates (*n*-hexane/AcOEt =

15:1) to yield the major isomer.; $[\alpha]_D^{25} -56.6$ ($c = 1.07$, CHCl_3).; FTIR (neat): 3061.0, 2956.9, 2858.5, 1512.2, 1464.0, 1427.3, 1105.2, 819.8, 702.1 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.76–7.67 (m, 4H), 7.58–7.55 (m, 3H), 7.44–7.30 (m, 10H), 5.24 (m, 1H), 5.13 (dd, 1H, $J = 15.2, 7.6$ Hz), 3.65 (s, 3H), 3.46 (d, 1H, $J = 9.6$ Hz), 3.36 (t, 2H, $J = 6.3$ Hz), 3.03–2.92 (m, 1H), 2.06–1.93 (m, 2H), 1.13 (d, 3H, $J = 6.3$ Hz), 0.97 (s, 9H) ppm.; $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 174.0, 135.5, 135.2, 134.0, 133.2, 132.6, 129.5, 127.9, 127.8, 127.7, 127.3, 126.7, 125.9, 125.7, 63.7, 58.5, 51.9, 40.0, 35.8, 26.8, 19.1, 19.1 ppm.; $[\text{M}+\text{Na}]^+$, calcd for $[\text{C}_{35}\text{H}_{40}\text{O}_3\text{SiNa}]^+$ 559.2639; found: m/z 559.2639.; The enantiomeric excess of the major isomer was determined to be 99% ee by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK ID-3 (Hexane/*i*-PrOH = 98/2, 0.75 mL/min), 25 °C, t_r (Major) = 12.9 min, t_r (Minor) = 14.0 min] after reducing with DIBAL.

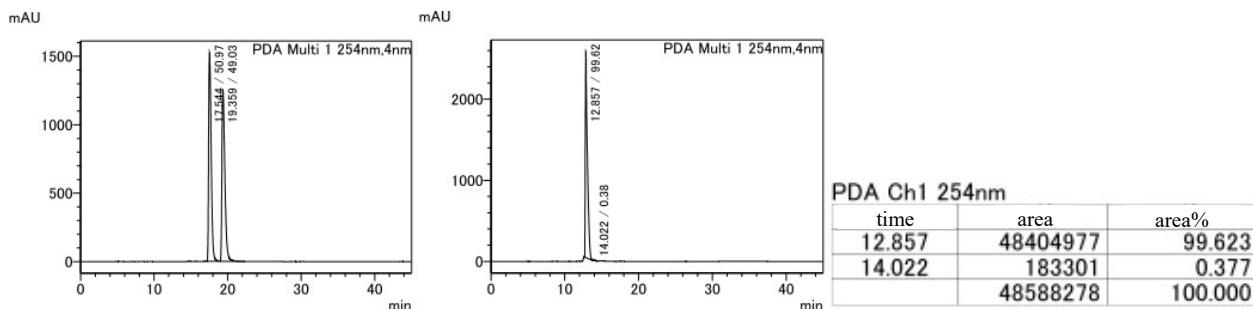


Figure S28. The chromatograms of methyl (4*E*)-7-*tert*-butyldiphenylsilyloxy-3-methyl-2-(2-naphthyl)hept-4-enoate.

8.23. Methyl (4*E*)-6-*tert*-butyldimethylsilyloxy-3-methyl-2-(2-naphthyl)hept-4-enoate

Diastereo-mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 86% yield as a colorless oil (61.0 mg, d.r. = 6:1); major isomer: ^1H NMR (400 MHz, CDCl_3): δ 7.82–7.71 (m, 4H), 7.46–7.41 (m, 3H), 5.42–5.31 (m, 2H), 3.88 (d, 2H, $J = 3.9$ Hz), 3.66 (s, 3H), 3.51 (d, 1H, $J = 10.7$ Hz), 3.12–3.02 (m, 1H), 1.17 (d, 3H, $J = 6.8$ Hz), 0.72 (s, 9H), -0.16 (s, 3H), -0.19 (s, 3H) ppm.; $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 173.9, 135.1, 133.4, 132.7, 132.1, 130.0, 128.0, 127.9, 127.8, 127.5, 126.5, 125.9, 125.7, 63.5, 58.4, 51.9, 39.4, 25.7, 19.0, 18.2, -5.4 ppm.; $[\text{M}+\text{Na}]^+$, calcd for $[\text{C}_{24}\text{H}_{34}\text{O}_3\text{SiNa}]^+$ 421.2169; found: m/z 421.2169. The enantiomeric excess of the major isomer was determined to be 99% ee by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK OD-3 (Hexane/*i*-PrOH = 98/2, 1.0 mL/min), 25 °C, t_r (Major) = 20.2 min, t_r (Minor) = 18.0 min] after reducing with DIBAL.; $[\alpha]_D^{25} +15.8$ ($c = 0.64$, CHCl_3).; FTIR (neat): 3279.0, 2958.8, 2856.6, 2385.9, 2328.1, 1736.0, 1703.1, 1371.4, 1253.8, 837.1, 777.3 cm^{-1} .

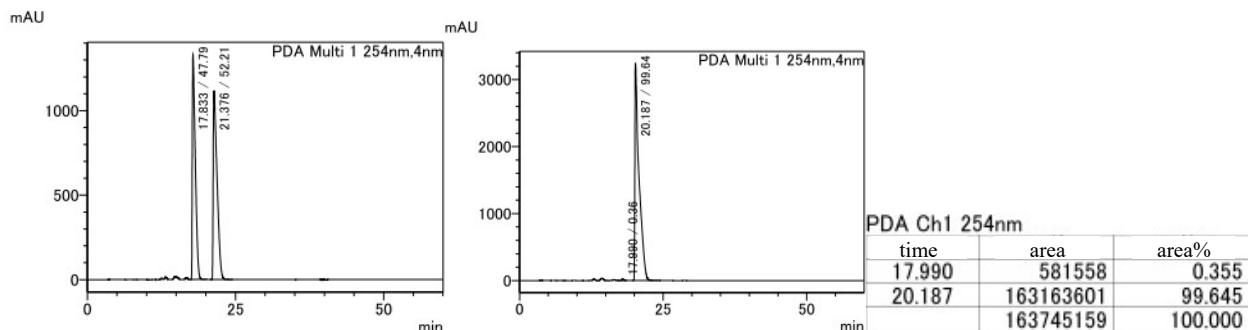
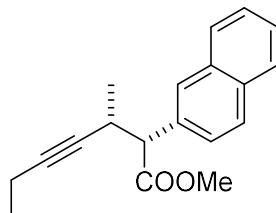


Figure S29. The chromatograms of methyl (4*E*)-6-*tert*-butylidimethylsilyloxy-3-methyl-2-(2-naphthyl)hept-4-enoate.

8.24. (−)-Methyl 3-methyl-2-(2-naphthyl)hept-4-yoate



Diastereo-mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 57% yield as a white solid (31.9 mg, d.r. = >20:1); the mixture of major and minor diastereomeric products was chromatographed on preparative TLC plates (*n*-hexane/AcOEt = 15:1) to yield the major isomer.; Mp: 69.4–69.6 °C.; $[\alpha]_D^{25}$ –87.8 ($c = 0.44$, CHCl₃); FTIR (neat): 1728.0 1514.1, 1460.1, 1427.3, 1344.4, 1282.7, 1155.4, 814.0, 756.1 cm^{–1}; ¹H NMR (400 MHz, CDCl₃): δ 7.81 (pseud-t, 4H, $J = 9.0$ Hz), 7.52–7.43 (m, 3H), 3.68 (s, 3H), 3.64 (d, 1H, $J = 9.6$ Hz), 3.30–3.26 (m, 1H), 1.92 (m, 2H), 1.27 (d, 3H, $J = 6.8$ Hz), 0.84 (t, 3H, $J = 7.6$ Hz) ppm.; ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 173.1, 135.0, 133.2, 132.8, 127.9, 127.7, 127.7, 126.6, 125.9, 125.7, 84.5, 80.9, 57.8, 52.0, 30.3, 20.3, 14.0, 12.2 ppm.; [M+Na]⁺, calcd for [C₁₉H₂₀O₂Na]⁺ 303.1356; found: m/z 303.1355.; The enantiomeric excess of the major isomer was determined to be 99% ee by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK IB-3 (Hexane/*i*-PrOH = 99/1, 1.0 mL/min), 25 °C, t_r (Major) = 29.8 min, t_r (Minor) = 35.2 min] after reducing with DIBAL.

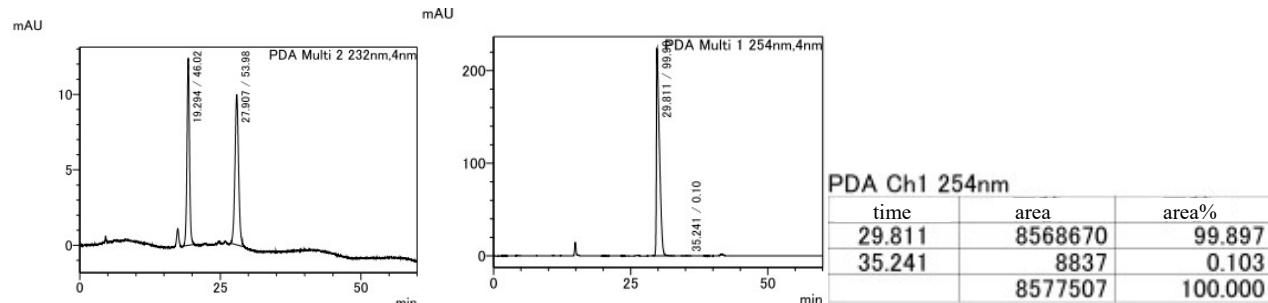
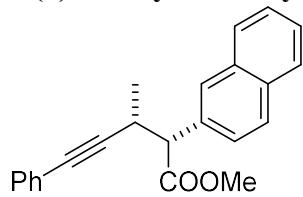


Figure S30. The chromatograms of methyl (2*R*,3*R*)-3-methyl-2-(2-naphthyl)hept-4-ynoate.

8.25. (–)-Methyl 3-methyl-2-(2-naphthyl)-5-phenylpent-4-ynoate



Diastereo-mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 57% yield as a white solid (37.4 mg, d.r. = >20:1); the mixture of major and minor diastereomeric products was chromatographed on preparative TLC plates (*n*-hexane/AcOEt = 15:1) to yield the major isomer.; Mp: 93.4–93.6 °C.; $[\alpha]_D^{25}$ –148.6 ($c = 0.23$, CHCl₃); FTIR (neat): 3053.3, 1732.1, 1290.4, 1157.3, 812.0, 752.2 cm^{–1}; ¹H NMR (400 MHz, CDCl₃): δ 7.87–7.82 (m, 4H), 7.57 (d, 1H, $J = 6.8$ Hz), 7.49–7.44 (m, 2H), 7.17–7.12 (m, 3H), 7.06 (d, 2H, $J = 8.3$ Hz), 3.77 (d, 1H, $J = 9.8$ Hz), 3.71 (s, 3H), 3.55 (dt, 1H, $J = 9.8, 6.8$ Hz), 1.40 (d, 3H, $J = 6.8$ Hz) ppm.; ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 172.9, 134.8, 133.3, 132.9, 131.4, 131.4, 128.0, 127.9, 127.7, 127.6, 126.6, 126.0, 125.9, 123.4, 91.4, 83.2, 57.6, 52.2, 30.9, 20.0 ppm.; [M+Na]⁺, calcd for [C₂₃H₂₀O₂Na]⁺ 351.1356; found: m/z 351.1360.; The enantiomeric excess of the major isomer was determined to be 99% ee by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK ID-3 (Hexane/*i*-PrOH = 98/2, 0.75 mL/min), 25 °C, t_r (Major) = 17.6 min, t_r (Minor) = 19.6 min] after reducing with DIBAL.

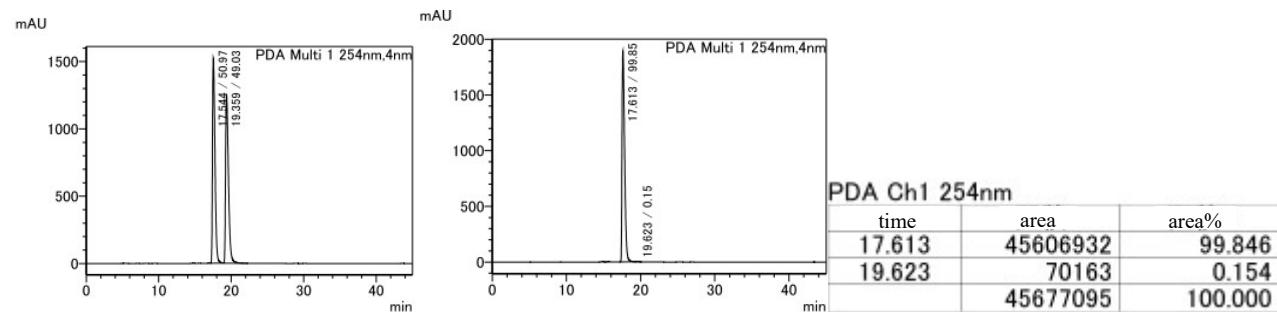
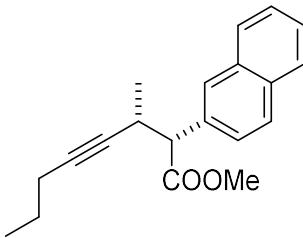


Figure S31. The chromatograms of methyl (2*R*,3*R*)-3-methyl-2-(2-naphthyl)-5-phenylpent-4-ynoate.

8.26. Methyl 3-methyl-2-(2-naphthyl)oct-4-ynoate



Diastereo-mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 57% yield as a white solid (33.5 mg, d.r. = >20:1); ^1H NMR (400 MHz, CDCl_3): δ 7.82–7.78 (m, 4H), 7.52 (d, 1H, J = 8.0 Hz), 7.48–7.43 (m, 2H), 3.67 (s, 3H), 3.64 (d, 1H, J = 10.4 Hz), 3.35–3.27 (m, 1H), 1.94–1.85 (m, 2H), 1.28 (d, 3H, J = 6.8 Hz), 1.24–1.16 (m, 2H), 0.63 (t, 3H, J = 7.3 Hz) ppm.; $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 173.1, 135.0, 133.3, 132.8, 127.9, 127.8, 127.8, 127.5, 126.5, 125.9, 125.7, 83.0, 81.7, 57.9, 52.0, 30.3, 22.1, 20.5, 20.3, 13.0 ppm.; $[\text{M}+\text{Na}]^+$, calcd for $[\text{C}_{20}\text{H}_{22}\text{O}_2\text{Na}]^+$ 317.1512; found: m/z 317.1516. The enantiomeric excess of the major isomer was determined to be 99% ee by HPLC analysis using a chiral stationary phase [DAICEL CHIRALPAK IB-3 (Hexane/i-PrOH = 95/5, 0.75 mL/min), 25 °C, t_r (Major) = 12.8 min, t_r (Minor) = 11.5 min] after reducing with DIBAL.

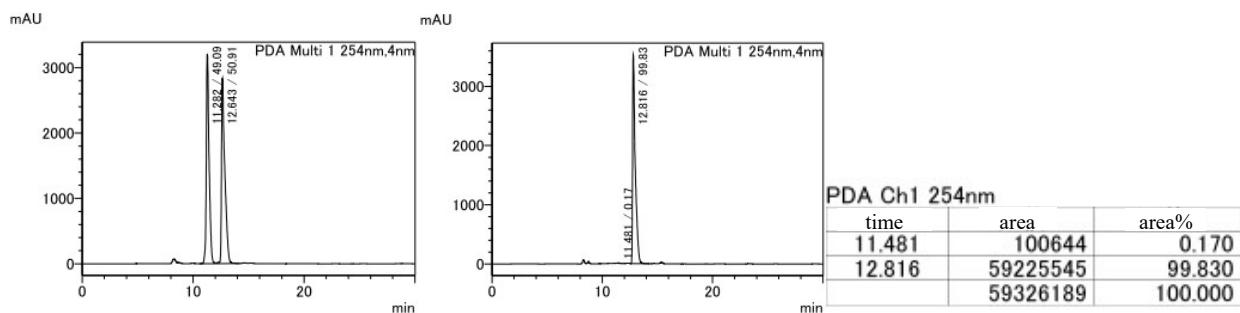
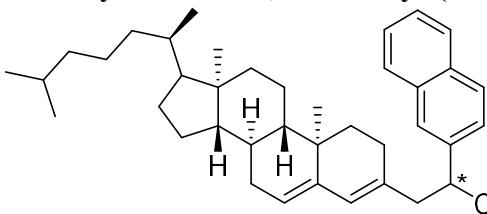


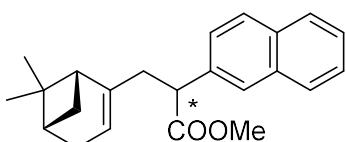
Figure S32. The chromatograms of methyl 3-methyl-2-(2-naphthyl)oct-4-ynoate.

8.27. Methyl cholesta-3,5-dien-3-yl-(2-naphthyl)-ethanoate



Diastereo-mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 71% yield as a white solid (20.1 mg); Mp: 86.5–86.7 °C.; $[\alpha]_D^{25}$ –127.0 (c = 1.80, CHCl_3).; FTIR (neat): 2945.3, 2854.7, 1730.2, 1556.6, 1452.4, 1375.3, 1151.5, 821.7, 744.5 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.79–7.77 (m, 3H), 7.74 (s, 1H), 7.47–7.41 (m, 3H), 5.70 (s, 1H), 5.26 (q, 1H, J = 2.3 Hz), 3.97 (t, 1H, J = 8.0 Hz), 3.65 (s, 3H), 2.89 (dd, 1H, J = 14.1, 8.0 Hz), 2.59 (dd, 1H, J = 14.4, 7.3 Hz), 2.18–2.05 (m, 3H), 2.01–1.94 (m, 3H), 1.85–1.74 (m, 3H), 1.63 (broad-d, 2H, J = 10.8 Hz), 1.55–1.49 (m, 3H), 1.41–1.39 (m, 4H), 1.24 (broad-d, 2H, J = 9.6 Hz), 1.20–1.06 (m, 3H), 1.04–0.94 (m, 3H), 0.91 (d, 3H, J = 6.4 Hz), 0.86 (dd, 6H, J = 6.4, 0.8 Hz), 0.71 (s, 3H), 0.66 (s, 3H) ppm.; $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 174.2, 141.4, 136.1, 133.4, 133.0, 132.6, 128.2, 127.8, 127.6, 126.8, 126.5, 126.0, 125.9, 125.7, 122.3, 56.9, 56.1, 52.1, 50.3, 48.2, 42.4, 41.1, 39.8, 39.5, 36.2, 35.8, 34.7, 34.1, 31.7, 28.2, 28.0, 26.3, 24.2, 23.8, 22.8, 22.6, 21.0, 18.7, 18.6, 11.9 ppm.; $[\text{M}+\text{Na}]^+$, calcd for $[\text{C}_{41}\text{H}_{56}\text{O}_2\text{Na}]^+$ 603.4176; found: m/z 603.4173.

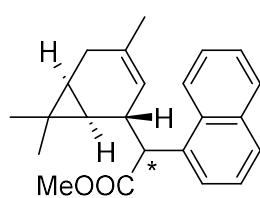
8.28. Methyl 6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-((2-naphthyl)acetate)



Diastereo-mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 74% yield as a white solid (23.7 mg); Mp: 82.7–82.9 °C.; $[\alpha]_D^{25}$ –51.2 (c = 1.74, CHCl_3).; FTIR (neat): 3047.5, 2918.3, 2829.6, 1728.2, 1552.7, 1431.2, 1369.5, 1329.0, 1207.4, 1150.0, 950.9, 827.5, 740.7 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.81–7.77 (m, 4H), 7.50–7.42 (m, 3H), 5.31 (s, 1H), 3.91 (q, 1H, J = 5.0 Hz), 3.65 (s, 3H), 2.91 (dd, 1H, J = 14.4, 10.0 Hz), 2.44 (dq, 1H, J = 14.4, 2.4 Hz), 2.34 (dt, 1H, J = 8.8, 5.2 Hz), 2.19 (q, 2H, J = 17.6), 2.06 (d, 2H, J = 4.9 Hz), 1.26 (s, 3H), 1.10 (d, 1H, J = 8.3 Hz), 0.76 (s, 3H) ppm.; $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 174.1, 145.4, 136.5, 133.4, 132.6, 128.2,

127.8, 127.6, 126.7, 126.1, 126.0, 125.8, 118.4, 51.9, 50.0, 45.9, 40.7, 40.7, 38.0, 31.7, 31.3, 26.3, 21.0 ppm.; $[M+Na]^+$, calcd for $[C_{23}H_{26}O_2Na]^+$ 357.1825; found: m/z 357.1825.

8.29. Methyl 3-Carene-5-((2-naphthyl)acetate)



Diastereomeric mixture of this compound was purified by column chromatography on silica gel (hexane/ethyl acetate, 1/0 to 20/1) to give 67% yield as a white solid (22.4 mg); Mp: 82.7–82.9 °C.; $[\alpha]_D^{25} -44.6$ ($c = 1.22, CHCl_3$); FTIR (neat): 3055.2, 2983.9, 2945.3, 2910.6, 2831.5, 1734.0, 1599.0, 1435.0, 1371.4, 1332.8, 1273.0, 1207.4, 1153.4, 1024.2, 954.8, 893.0, 858.3, 817.9, 746.4 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$): δ 7.83–7.790 (m, 4H), 7.51 (dd, 1H, $J = 8.4, 0.8$ Hz), 7.49–7.43 (m, 2H), 4.80 (s, 1H), 3.70 (d, 1H, $J = 10.2$ Hz), 3.68 (s, 3H), 2.93 (d, 1H, $J = 10.3$ Hz), 2.14 (dd, 1H, $J = 18.8, 7.6$ Hz), 1.77 (dd, 1H, $J = 18.8, 3.3$ Hz), 1.45 (s, 3H), 1.05 (s, 3H), 0.84 (s, 3H), 0.76 (dd, 1H, $J = 8.8, 7.6$ Hz), 0.41 (d, 1H, $J = 8.8$ Hz) ppm.; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $CDCl_3$): δ 174.2, 135.2, 133.9, 133.4, 132.7, 128.0, 127.9, 127.8, 127.6, 126.7, 126.0, 125.7, 120.6, 58.6, 51.9, 34.8, 28.5, 25.4, 23.6, 22.7, 19.0, 17.0, 13.7 ppm.; $[M+Na]^+$, calcd for $[C_{23}H_{26}O_2Na]^+$ 357.1825; found: m/z 357.1825.

9. Computational Details

9.1. Computational methods

Geometry and transition state optimizations for all candidate structures were carried out using the M06-L^[6] density functional, with the def2-SVP^[7] basis set for all atoms. All optimized geometries were verified by frequency computations as minima (zero imaginary frequencies) or transition structures (a single imaginary frequency). To obtain more accurate energies, M06-L(SMD)/def2-TZVPP level was used for single-point calculation. To account for the solvent polarity effects of the ethylbenzene ($\epsilon = 2.4339$), solvation model density (SMD)^[7] method was used for single-point calculation. Accordingly, thermal corrections are estimated at the reaction temperature $T = 298.15$ K and at normal pressure $p = 1.0$ atm. All quantum chemical computations were performed using Gaussian 16 rev. A 03.

9.2. ECD calculations

Conformational searches for (−)-Methyl (2*R*,3*R*)-3-(4-bromophenyl)-2-(2-naphthyl)butanoate were performed by Spartan'18 by using the Merck Molecular Force Field (MMFF).^[8] And then, all structures were optimized by DFT at M06-2X^[5]/def2-SVP level. All optimized structures were confirmed to be local minima (no imaginary frequencies) by calculating the harmonic frequencies at the same level of theory. To account for the solvent polarity effects of the acetonitrile ($\epsilon = 35.688$), solvation model density (SMD) was incorporated into the M06-2X functional. Accordingly, thermal corrections are estimated at the reaction temperature $T = 298.15$ K and at normal pressure $p = 1.0$ atm. We screened low-energy conformations, based on Boltzmann distributions, which are higher than 1%

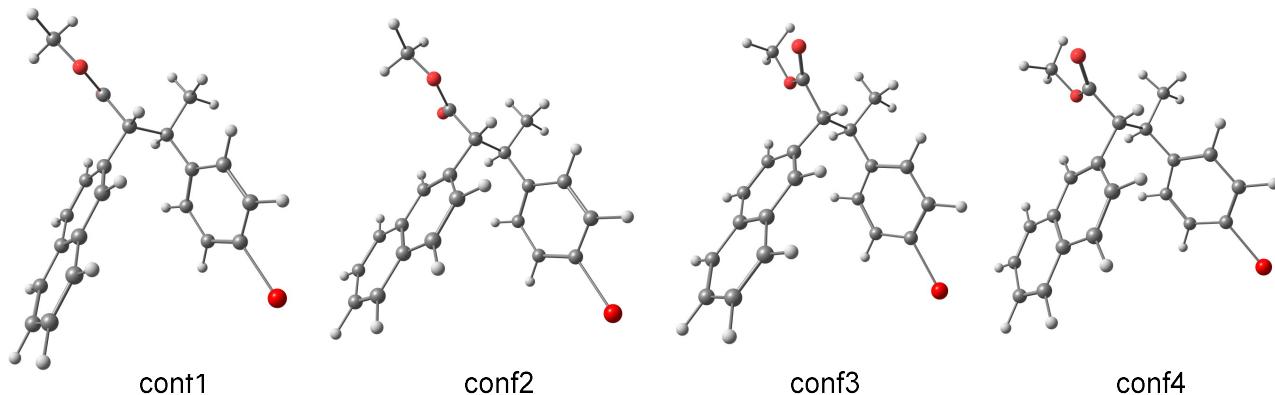


Figure S33. Conformers of (−)-Methyl (2*R*,3*R*)-3-(4-bromophenyl)-2-(2-naphthyl)butanoate.

Table S4. Total electronic energies and Boltzmann distribution at the M06-2X(SMD)/def2-TZVPP//M06-2X/def2-SVP level.

conf	total electronic energy (a.u.) (M06-2X(SMD)/def2-TZVPP)	Gibbs free energy (M06-2X/def2-SVP)	ΔG (kJ/mol)	distribution
1	-3536.339895	0.294752	0	0.57
2	-3536.339675	0.295547	2.66	0.19
3	-3536.338898	0.294846	2.86	0.18
4	-3536.338494	0.295579	5.85	0.05

These screened structures were subjected to TD-DFT calculations at the B3LYP+D3BJ(SMD)/def2-TZVPP level.^[6,9-11] ECD and UV-vis spectra of all conformers were Boltzmann distribution by their total electronic energies. The σ values of the simulated CD curve and the simulated UV-vis curve are 0.4 eV, which corresponds to a half of the bandwidth at 1/e of peak height in energy units. The theoretical molar difference of the absorption coefficients for left and right circularly polarized light ($\Delta\epsilon$ in $M^{-1} cm^{-1}$) was converted from the rotational strength (in cgs unit) with a Gaussian-approximation modified formula by Stephens and Harada,^[12,13] which is expressed as follows,

$$\Delta(\epsilon) = \frac{1}{2.297 \times 10^{-39}} \times \frac{1}{\sqrt{\pi}\sigma} \Delta E_i R_i e^{-\left(\frac{(E - \Delta E_i)}{\sigma}\right)^2}$$

where E , ΔE_i , and R_i refer to the energy in arbitrary wavelength, excitation energy, and rotational strength for transition i , respectively.

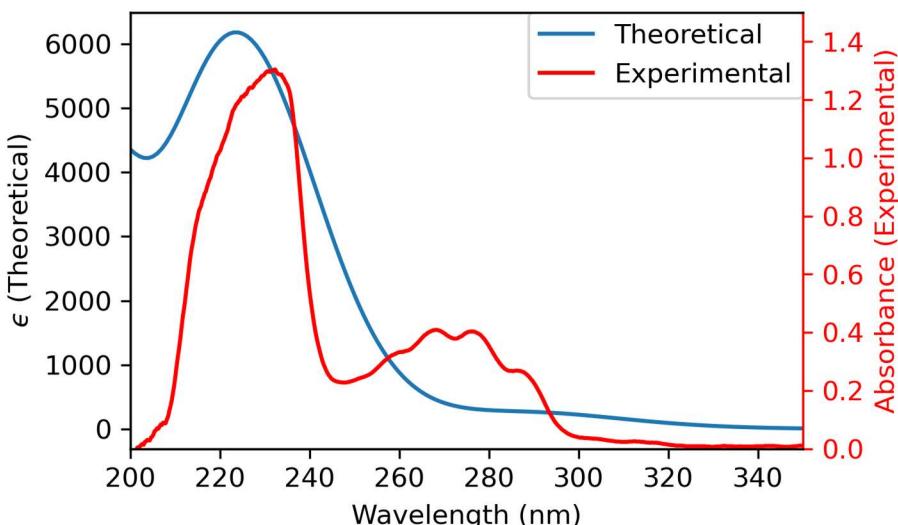


Figure S34. Experimental and theoretical UV-Vis spectra.

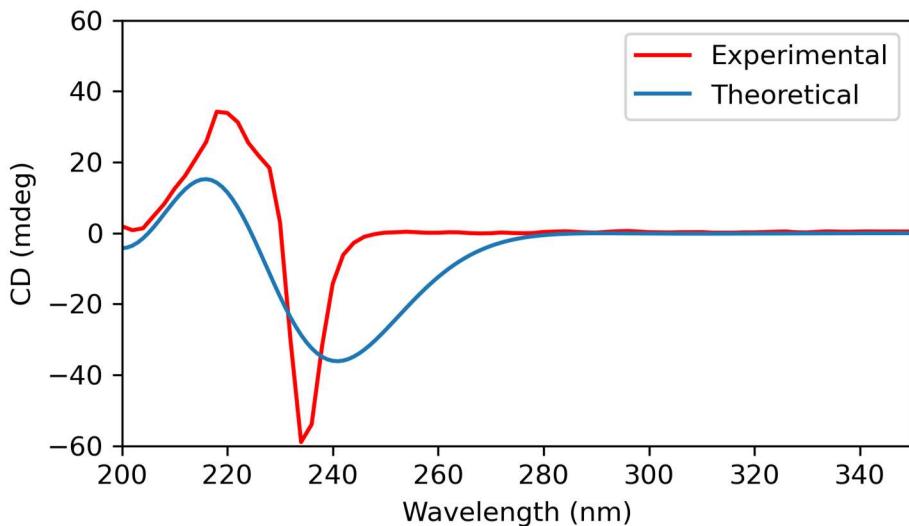


Figure S35. Experimental and theoretical ECD spectra

9.3. Cartesian Coordinates, absolute electronic and Gibbs free energies of optimized structures

Table S5. Total electronic and Gibbs free energies at the M06-L(SMD)/def2-TZVPP// M06-L/def2-SVP level.

	total electronic energy (a.u.) (M06-L(SMD)/def2-TZVPP)	Gibbs free energy (a.u.) (M06-L/def2-SVP)
A	-3178.20614943	0.959546
B	-3178.18910802	0.959984
C	-3178.19115253	0.960359
D	-3178.18842782	0.959870
³ A	-3178.17688097	0.958828
³ B	-3178.16540792	0.955732
³ C	-3178.16721711	0.953865
³ D	-3178.16447704	0.960195
TS	-1909.41829713	0.579729

9.3.1. Conformer 1: (-)-Methyl (2*R*,3*R*)-3-(4-bromophenyl)-2-(2-naphthyl)butanoate

6	-2.149434	-1.042306	-0.305564	1	0.926509	5.916214	0.314178
1	-1.935781	-1.269628	-1.360601	6	-0.301068	4.276349	0.933423
6	-1.727954	0.389507	-0.027445	6	-3.648112	-1.161033	-0.100898
1	-0.554349	0.569472	-1.810099	8	-4.180768	-1.40915	0.949061
6	-0.882362	1.052022	-0.88569	8	-4.324501	-0.911916	-1.223054
6	-1.675033	2.277921	1.499759	6	-5.740345	-0.915988	-1.10531
6	-0.392243	2.351288	-0.584263	1	-6.066588	-0.154741	-0.384192
6	-2.128176	1.021753	1.183784	1	-6.094891	-1.896833	-0.761482
6	-0.793646	2.977767	0.630624	1	-6.132457	-0.693212	-2.101999
6	0.49493	3.041724	-1.454872	6	-1.3911	-2.047535	0.598061
1	-2.804607	0.493623	1.85989	1	-1.670829	-1.80851	1.636144
1	-0.614043	4.752447	1.865031	6	0.100918	-1.829364	0.448763
1	-1.987505	2.758228	2.42945	6	2.823358	-1.275946	0.102672
6	0.956521	4.294861	-1.135035	6	0.80138	-1.0554	1.37971
1	0.804931	2.555201	-2.381871	6	0.798392	-2.321943	-0.65937
1	1.638372	4.814705	-1.809546	6	2.153781	-2.052356	-0.839733
6	0.553144	4.920155	0.072038	6	2.155781	-0.773579	1.216865

1 0.271331 -0.64768 2.243537
 1 0.281004 -2.927298 -1.406633
 1 2.689337 -2.441472 -1.705784
 1 2.689763 -0.164613 1.946314
 6 -1.820214 -3.486443 0.307162

1 -1.692396 -3.738578 -0.756531
 1 -2.877527 -3.630135 0.566732
 1 -1.222557 -4.194581 0.897197
 35 4.664666 -0.90208 -0.13531

9.3.2. Conformer 2: (-)-Methyl (2*R*,3*R*)-3-(4-bromophenyl)-2-(2-naphthyl)butanoate

6 1.676235 -1.579121 0.294466
 1 1.388984 -2.068799 1.237351
 6 1.528982 -0.075877 0.469011
 1 2.775988 0.426072 -1.202351
 6 2.125621 0.802412 -0.407632
 6 0.442875 1.775786 1.606691
 6 1.904319 2.203323 -0.310429
 6 0.679607 0.429846 1.490834
 6 1.045228 2.701261 0.711091
 6 2.510686 3.123873 -1.20923
 1 0.199831 -0.271825 2.176484
 1 0.159181 4.47709 1.586484
 1 -0.217484 2.153797 2.389724
 6 2.273048 4.471923 -1.098236
 1 3.16898 2.737741 -1.990231
 1 2.743043 5.168905 -1.793641
 6 1.417444 4.966889 -0.081466
 1 1.236602 6.039938 -0.003913
 6 0.818932 4.101831 0.801441
 6 3.13385 -1.903859 0.032677
 8 3.646797 -1.933095 -1.055353
 8 3.807764 -2.113086 1.164548

6 5.204207 -2.331302 1.020977
 1 5.680745 -1.461213 0.549825
 1 5.39374 -3.21402 0.395855
 1 5.597145 -2.4834 2.030551
 6 0.782549 -2.111406 -0.853505
 1 1.168944 -1.654035 -1.777732
 6 -0.641334 -1.634264 -0.651398
 6 -3.207679 -0.6275 -0.164645
 6 -1.113695 -0.508903 -1.334611
 6 -1.488705 -2.247593 0.277727
 6 -2.768216 -1.753945 0.526489
 6 -2.388396 0.000649 -1.09929
 1 -0.462446 -0.007213 -2.053814
 1 -1.15029 -3.127417 0.829261
 1 -3.421506 -2.23831 1.252493
 1 -2.743051 0.882139 -1.633248
 6 0.896328 -3.6304 -0.985607
 1 0.643417 -4.138324 -0.042614
 1 1.920887 -3.914377 -1.261582
 1 0.216262 -4.002781 -1.763897
 35 -4.940765 0.057821 0.171123

9.3.3. Conformer 3: (-)-Methyl (2*R*,3*R*)-3-(4-bromophenyl)-2-(2-naphthyl)butanoate

6 -2.07854 -0.982887 -0.588747
 1 -1.729359 -1.172815 -1.614012
 6 -1.725289 0.446271 -0.223177
 1 -0.498052 0.736613 -1.954
 6 -0.87536 1.172213 -1.025191
 6 -1.797038 2.283372 1.36699
 6 -0.448044 2.478894 -0.664853
 6 -2.189129 1.022297 0.994238
 6 -0.916156 3.047854 0.553828
 6 0.438664 3.233178 -1.481152
 1 -2.865322 0.448562 1.629556
 1 -0.852049 4.785559 1.85089
 1 -2.15913 2.718309 2.301061
 6 0.837073 4.492473 -1.10488
 1 0.79849 2.791654 -2.412643
 1 1.518481 5.062081 -1.738386
 6 0.367928 5.059922 0.106826
 1 0.691453 6.061466 0.393866
 6 -0.488018 4.353845 0.916221
 6 -3.581394 -1.193727 -0.650567

8 -4.220738 -1.280215 -1.660795
 8 -4.135451 -1.282904 0.569911
 6 -5.543894 -1.468384 0.592217
 1 -5.832022 -1.519425 1.646587
 1 -5.815308 -2.397608 0.073338
 1 -6.049481 -0.63076 0.093938
 6 -1.395873 -2.005804 0.359482
 1 -1.737177 -1.776397 1.381007
 6 0.104505 -1.799022 0.314001
 6 2.851891 -1.28187 0.170582
 6 0.875516 -2.302534 -0.739278
 6 0.74307 -1.029355 1.291851
 6 2.109382 -0.766037 1.229776
 6 2.244107 -2.051502 -0.818255
 1 0.407434 -2.903374 -1.521859
 1 0.15586 -0.612105 2.113118
 1 2.595595 -0.161573 1.995351
 1 2.83724 -2.450335 -1.641355
 6 -1.818168 -3.435717 0.019423
 1 -1.642541 -3.667382 -1.041704

1	-2.88983	-3.578732	0.217885	35	4.710938	-0.934526	0.074648
1	-1.258998	-4.161269	0.625743				

9.3.4. Conformer 4: (-)-Methyl (2*R*,3*R*)-3-(4-bromophenyl)-2-(2-naphthyl)butanoate

6	1.569006	-1.584919	0.603612	6	4.922895	-2.425102	-0.692661
1	1.138033	-1.98781	1.532024	1	5.24091	-2.263937	-1.727163
6	1.510586	-0.068403	0.672307	1	4.98692	-3.489932	-0.431439
1	2.875722	0.279856	-0.944409	1	5.558825	-1.858055	-0.000035
6	2.205253	0.73002	-0.209293	6	0.7509	-2.133835	-0.596283
6	0.470096	1.901158	1.649262	1	1.207455	-1.716033	-1.506878
6	2.060762	2.144273	-0.193968	6	-0.669853	-1.614428	-0.508535
6	0.634421	0.540076	1.613479	6	-3.238166	-0.53533	-0.236846
6	1.176204	2.743441	0.748117	6	-1.595947	-2.179627	0.374974
6	2.769858	2.981026	-1.099688	6	-1.06278	-0.498053	-1.253925
1	0.075551	-0.096043	2.30317	6	-2.338209	0.046877	-1.125959
1	0.34857	4.609972	1.480367	6	-2.877195	-1.649948	0.516245
1	-0.211215	2.355085	2.37162	1	-1.319981	-3.049639	0.97472
6	2.60653	4.344178	-1.070379	1	-0.348927	-0.031813	-1.93674
1	3.447876	2.518314	-1.81994	1	-2.631499	0.920373	-1.708167
1	3.155683	4.975843	-1.77016	1	-3.59235	-2.09746	1.206641
6	1.725577	4.93968	-0.132031	6	0.832563	-3.658844	-0.666646
1	1.60469	6.023812	-0.11855	1	0.519107	-4.12465	0.279506
6	1.028214	4.157385	0.755382	1	1.863666	-3.980818	-0.870807
6	2.997606	-2.097292	0.593874	1	0.188973	-4.04618	-1.468268
8	3.564151	-2.565631	1.540762	35	-4.974517	0.197215	-0.049129
8	3.577119	-1.976545	-0.612288				

9.3.5. Singlet conformer A: Ir-carbene intermediate

7	0.338426	3.273072	0.184729	6	1.621106	1.831118	-1.893534
7	2.537649	1.921988	0.912547	6	2.961471	1.586429	-2.233279
8	-0.951151	0.85711	-0.895723	6	0.806515	2.395869	-2.887501
6	-2.01208	1.603754	-0.832567	6	3.466612	1.886494	-3.50134
6	-2.000537	3.013255	-0.463256	1	3.642736	1.13221	-1.503179
6	-0.835927	3.756299	-0.065177	6	1.300241	2.698487	-4.158615
6	3.542495	1.140387	1.163468	1	-0.250994	2.596164	-2.678366
6	3.657733	-0.253685	0.829954	6	2.635983	2.446243	-4.471707
6	2.664418	-1.027866	0.100756	1	4.515382	1.676013	-3.733199
8	1.521804	-0.568311	-0.300134	1	0.634833	3.131818	-4.911428
6	-3.255018	1.011828	-1.167784	1	3.025716	2.681419	-5.465605
6	-4.436723	1.792283	-1.256245	6	3.581804	5.466632	1.994101
6	-4.403691	3.193958	-0.930641	6	3.803326	4.046245	1.491433
6	-3.184325	3.75216	-0.532995	6	2.473896	3.322944	1.356494
6	4.851638	-0.872865	1.216315	6	1.530678	4.094061	0.420617
6	5.144699	-2.208443	0.920577	6	1.289036	5.498317	0.945937
6	4.174255	-2.974662	0.180167	6	2.611181	6.235228	1.113073
6	2.951292	-2.380693	-0.205637	1	4.543643	5.995422	2.065475
77	0.830137	1.336083	0.030983	1	3.184788	5.424117	3.02427
1	-0.981207	4.839833	0.038058	1	4.468831	3.511307	2.184715
1	4.41248	1.568422	1.679888	1	4.310763	4.052165	0.510082
1	-3.15513	4.813858	-0.267484	1	1.987002	3.313736	2.351028
1	5.592877	-0.283481	1.766075	1	2.039964	4.156986	-0.563577

1	0.640604	6.06013	0.25821	1	-0.424876	-3.923562	-4.858872
1	0.750223	5.43521	1.908701	6	-5.592295	3.969945	-1.012684
1	2.433467	7.241441	1.520065	1	-5.538236	5.031598	-0.755426
1	3.064805	6.388231	0.118407	6	-6.779222	3.404092	-1.407316
6	-3.313706	-0.45572	-1.39168	1	-7.687702	4.006802	-1.469497
6	-2.67267	-1.057091	-2.474908	6	-6.81644	2.028494	-1.744584
6	-2.818755	-2.455198	-2.671719	1	-7.757658	1.581546	-2.074128
6	-3.57411	-3.235788	-1.832239	6	-5.68707	1.247555	-1.671685
6	-4.209828	-2.666319	-0.703074	1	-5.738564	0.192715	-1.947837
6	-4.057435	-1.260944	-0.464301	6	6.368882	-2.815237	1.315224
6	-4.626731	-0.728715	0.724258	1	7.088495	-2.215037	1.879369
6	-5.331576	-1.523335	1.603029	6	6.647246	-4.120626	0.993643
6	-5.519032	-2.895968	1.335994	1	7.590455	-4.577642	1.300007
6	-4.961815	-3.452089	0.206366	6	5.704869	-4.873254	0.248365
1	-2.319975	-2.907763	-3.53347	1	5.936424	-5.906597	-0.021686
1	-3.685345	-4.308258	-2.019122	6	4.509919	-4.321035	-0.147521
1	-5.078415	-4.520029	-0.00278	1	3.799543	-4.910088	-0.732871
1	-6.084358	-3.516315	2.03593	6	-0.05195	0.775206	1.798813
1	-5.744336	-1.087119	2.516353	6	-0.82475	-0.405753	2.030399
1	-4.48356	0.329787	0.953348	6	-1.423986	-0.633794	3.287954
6	-1.830907	-0.288858	-3.440864	6	-0.952872	-1.431734	1.030991
1	-2.100963	0.775027	-3.478881	1	-0.533023	-1.27289	0.039735
1	-0.768482	-0.331576	-3.148219	1	-1.368599	0.138895	4.061382
1	-1.905098	-0.703596	-4.456159	6	-2.087119	-1.830925	3.595777
1	2.494205	-0.747262	-4.834585	6	-2.14071	-2.866549	2.599981
6	1.978436	-1.56206	-4.320569	6	-1.573309	-2.618523	1.324956
1	0.763226	-2.093275	-6.043143	1	-1.639073	-3.3953	0.558006
6	0.996665	-2.31646	-4.999217	6	0.110246	1.70555	2.923044
6	2.287736	-1.841429	-3.008057	8	-0.520231	2.73107	3.079636
1	3.054951	-1.254033	-2.499239	8	1.126329	1.334925	3.740434
6	1.617324	-2.868327	-2.293735	1	1.643326	3.21902	4.486882
6	1.906154	-3.158249	-0.922064	6	1.38233	2.206351	4.831061
6	1.18752	-4.145985	-0.250037	1	2.220567	1.774118	5.385606
6	1.419476	-4.435239	1.201891	1	0.50399	2.292829	5.485562
1	1.53894	-3.512776	1.789271	6	-2.690162	-2.060392	4.864303
1	2.334607	-5.027482	1.368048	1	-2.655777	-1.264798	5.61336
1	0.584855	-5.00373	1.63547	6	-3.298353	-3.260791	5.144948
1	-0.362661	-5.649927	-0.413493	1	-3.757065	-3.42887	6.121738
6	0.1973	-4.879421	-0.953624	6	-3.324595	-4.289155	4.172355
6	-0.080708	-4.634892	-2.276721	1	-3.802715	-5.242237	4.41092
1	-0.853251	-5.208615	-2.797355	6	-2.761341	-4.094602	2.929919
6	0.613254	-3.622455	-2.982259	1	-2.795506	-4.882815	2.172654
6	0.334641	-3.328769	-4.341911				

9.3.6. Singlet conformer B: Ir-carbene intermediate

7	0.603167	2.882656	0.757014	6	1.767167	2.80188	1.328844
7	-1.862228	2.672673	-0.319912	6	-3.068571	2.410857	-0.710347
8	1.010217	-0.044462	0.672498	6	-3.684969	1.109489	-0.777719
6	2.181347	0.269228	1.111255	6	-3.031585	-0.156209	-0.461032
6	2.58413	1.626557	1.478445	8	-1.78091	-0.289863	-0.149986

6	3.130467	-0.779613	1.261788	1	3.221822	-5.760329	-2.01427
6	4.414644	-0.524147	1.798645	1	5.103949	-4.681699	-3.227661
6	4.800839	0.819025	2.156763	1	5.863824	-2.397851	-2.544515
6	3.868019	1.84693	1.989123	1	4.758259	-1.209897	-0.708591
6	-5.027269	1.107144	-1.171325	6	0.934216	-2.180386	2.677432
6	-5.793951	-0.060666	-1.25513	1	1.505576	-1.385265	3.174476
6	-5.169786	-1.309279	-0.898983	1	-0.010527	-1.729833	2.328253
6	-3.808972	-1.337458	-0.513335	1	0.667794	-2.934689	3.431658
77	-0.495365	1.296932	0.179176	1	-3.217971	-1.579278	4.373697
1	2.208811	3.727587	1.724304	6	-2.992875	-2.315571	3.598296
1	-3.707169	3.249733	-1.018803	1	-2.246192	-3.798271	5.002038
1	4.157063	2.868008	2.260873	6	-2.439689	-3.565792	3.951957
1	-5.501484	2.063586	-1.41675	6	-3.244988	-2.012549	2.278498
6	-1.189299	1.25655	2.19109	1	-3.676127	-1.043079	2.018563
6	-2.544227	1.459129	2.510965	6	-2.93875	-2.930412	1.240172
6	-0.318889	1.04674	3.274563	6	-3.160024	-2.624144	-0.138117
6	-3.005305	1.454294	3.829314	6	-2.784337	-3.534603	-1.122349
1	-3.283186	1.615881	1.718776	6	-2.920011	-3.193612	-2.573801
6	-0.766772	1.036491	4.596754	1	-2.321172	-2.301557	-2.813368
1	0.745792	0.87203	3.097598	1	-3.960399	-2.964887	-2.854806
6	-2.115819	1.243883	4.88222	1	-2.574339	-4.013348	-3.216925
1	-4.068887	1.61168	4.03315	1	-1.949746	-5.490506	-1.527373
1	-0.055351	0.860993	5.409149	6	-2.234214	-4.783897	-0.742109
1	-2.471527	1.237107	5.915977	6	-2.04665	-5.115947	0.57778
6	-1.455528	6.500456	-0.380605	1	-1.618552	-6.085059	0.851654
6	-2.214073	5.181305	-0.333753	6	-2.373862	-4.197008	1.603002
6	-1.250577	4.008272	-0.367877	6	-2.143306	-4.48668	2.972229
6	-0.221783	4.103835	0.772756	1	-1.713409	-5.458571	3.234143
6	0.539925	5.416974	0.705967	6	6.10593	1.069278	2.665376
6	-0.422421	6.596397	0.729253	1	6.37405	2.097925	2.923583
1	-2.161076	7.342508	-0.327502	6	7.006164	0.047655	2.835681
1	-0.951736	6.590328	-1.358741	1	8.005635	0.248205	3.227182
1	-2.909018	5.125634	-1.184191	6	6.62284	-1.279945	2.515466
1	-2.828102	5.120674	0.58314	1	7.332722	-2.095921	2.671911
1	-0.690586	4.036366	-1.324989	6	5.372606	-1.558847	2.018883
1	-0.792805	4.063348	1.724161	1	5.095621	-2.58903	1.787265
1	1.244675	5.499564	1.546024	6	-7.157377	-0.040677	-1.65691
1	1.147283	5.433903	-0.216823	1	-7.607148	0.920463	-1.92257
1	0.137796	7.540283	0.658162	6	-7.896981	-1.197018	-1.707104
1	-0.935048	6.622963	1.706734	1	-8.94402	-1.172785	-2.016086
6	2.70905	-2.149356	0.85849	6	-7.292958	-2.426728	-1.344909
6	1.672587	-2.796025	1.534618	1	-7.885547	-3.344611	-1.373991
6	1.276948	-4.093694	1.122426	6	-5.976382	-2.483935	-0.951412
6	1.870623	-4.73438	0.065393	1	-5.529869	-3.440236	-0.668365
6	2.923751	-4.113217	-0.646347	6	0.092349	1.115912	-1.811051
6	3.350813	-2.80188	-0.247946	6	1.371704	0.750693	-2.351042
6	4.415883	-2.210645	-0.980136	6	2.532182	1.25323	-1.753091
6	5.034904	-2.876035	-2.017251	6	1.518436	-0.045171	-3.537593
6	4.608615	-4.164029	-2.402576	1	0.62501	-0.464253	-4.004674
6	3.5676	-4.762387	-1.729537	1	2.432726	1.91362	-0.895294
1	0.470777	-4.582784	1.675493	6	3.814432	1.015348	-2.281602
1	1.541963	-5.733326	-0.236242	6	3.938665	0.207977	-3.458981

6 2.757075 -0.318175 -4.052988
 1 2.856345 -0.950322 -4.939261
 6 -0.979403 1.298423 -2.806614
 8 -1.237895 2.408198 -3.232992
 8 -1.652141 0.194127 -3.147989
 1 -3.411699 1.193974 -3.652949
 6 -2.764594 0.387283 -4.020873
 1 -3.315306 -0.558328 -4.031658
 1 -2.42346 0.641407 -5.033493

6 4.984049 1.526251 -1.65959
 1 4.876011 2.120598 -0.747665
 6 6.229019 1.252439 -2.179997
 1 7.125827 1.634895 -1.68795
 6 6.349199 0.474966 -3.353598
 1 7.341051 0.269656 -3.763332
 6 5.229115 -0.035131 -3.979168
 1 5.32886 -0.650106 -4.877458

9.3.7. Singlet conformer C: Ir-carbene intermediate

7 1.017577 -2.616537 -1.244266
 7 -1.62354 -2.207257 -0.862089
 8 1.672631 0.115649 -0.308833
 6 2.882399 -0.344435 -0.363804
 6 3.238246 -1.676902 -0.837197
 6 2.307195 -2.682684 -1.285084
 6 -2.854382 -1.814675 -0.800546
 6 -3.315139 -0.455198 -0.632847
 6 -2.460018 0.708206 -0.417897
 8 -1.176759 0.658078 -0.217859
 6 3.927552 0.518994 0.050137
 6 5.285379 0.125325 -0.045063
 6 5.626513 -1.189665 -0.523383
 6 4.585252 -2.046335 -0.900739
 6 -4.699507 -0.28675 -0.683839
 6 -5.318776 0.966229 -0.57071
 6 -4.481114 2.125923 -0.414146
 6 -3.074392 1.978516 -0.335078
 77 -0.021453 -1.018876 -0.589555
 1 2.764893 -3.59904 -1.681559
 1 -3.64864 -2.566176 -0.914707
 1 4.836684 -3.047615 -1.266156
 1 -5.330492 -1.171389 -0.819935
 6 -0.088343 -0.487399 -2.655642
 6 -1.271021 -0.380161 -3.406186
 6 1.113348 -0.222205 -3.335304
 6 -1.261306 -0.008037 -4.753068
 1 -2.243894 -0.575292 -2.944128
 6 1.135883 0.155912 -4.678644
 1 2.068725 -0.291661 -2.805865
 6 -0.054838 0.262875 -5.396953
 1 -2.205083 0.072363 -5.300928
 1 2.091744 0.368395 -5.166602
 1 -0.042347 0.553642 -6.450755
 6 -1.654453 -5.970624 -1.673499
 6 -2.221767 -4.56021 -1.591822
 6 -1.199311 -3.609196 -0.996933
 6 0.117076 -3.635343 -1.799837
 6 0.67964 -5.044429 -1.868207
 6 -0.347854 -6.006485 -2.448061
 1 -2.39389 -6.647687 -2.125896

1 -1.484027 -6.348598 -0.650319
 1 -3.139104 -4.564371 -0.984501
 1 -2.509238 -4.200095 -2.59639
 1 -0.943711 -3.952333 0.027758
 1 -0.131326 -3.28761 -2.824502
 1 1.589201 -5.062762 -2.486115
 1 0.979614 -5.353614 -0.851731
 1 0.062156 -7.026904 -2.467825
 1 -0.540462 -5.738837 -3.501884
 6 3.551778 1.853152 0.589767
 6 2.980022 2.821644 -0.234597
 6 2.640493 4.084405 0.314525
 6 2.837115 4.378549 1.640514
 6 3.39591 3.414245 2.512383
 6 3.758075 2.132773 1.980417
 6 4.303583 1.177021 2.878465
 6 4.49035 1.464684 4.212887
 6 4.139417 2.730909 4.728306
 6 3.602431 3.681363 3.889546
 1 2.206632 4.834811 -0.352443
 1 2.561272 5.358872 2.040195
 1 3.321364 4.665764 4.274854
 1 4.29135 2.951706 5.787502
 1 4.912716 0.70667 4.878172
 1 4.579126 0.193872 2.493436
 6 2.683145 2.574927 -1.67748
 1 3.329143 1.801039 -2.114647
 1 1.642964 2.229106 -1.800732
 1 2.790424 3.492099 -2.273702
 1 -0.79559 3.12017 -4.55061
 6 -0.767089 3.61418 -3.576386
 1 0.593479 5.177643 -4.232454
 6 0.020447 4.772116 -3.395011
 6 -1.49697 3.09635 -2.529317
 1 -2.102579 2.200157 -2.683219
 6 -1.465957 3.695296 -1.243025
 6 -2.198906 3.165255 -0.137151
 6 -2.096783 3.757743 1.118625
 6 -2.799629 3.174326 2.305782
 1 -2.480987 2.135106 2.484729
 1 -3.893556 3.150186 2.175778

1 -2.588613 3.741925 3.221034
 1 -1.219587 5.367995 2.269482
 6 -1.29239 4.913652 1.277114
 6 -0.603912 5.46144 0.221807
 1 0.014006 6.352952 0.365155
 6 -0.659863 4.866025 -1.060669
 6 0.067051 5.384473 -2.162729
 1 0.674994 6.281786 -2.010556
 6 6.99027 -1.582337 -0.605443
 1 7.220877 -2.587153 -0.971138
 6 7.996575 -0.722145 -0.239469
 1 9.041881 -1.030737 -0.306568
 6 7.668966 0.578183 0.21827
 1 8.470441 1.266835 0.497097
 6 6.360469 0.990934 0.312089
 1 6.130305 2.000095 0.659798
 6 -6.730287 1.115898 -0.612674
 1 -7.346028 0.219245 -0.728144
 6 -7.312489 2.357554 -0.515636
 1 -8.398731 2.463974 -0.549647
 6 -6.492849 3.504453 -0.380753
 1 -6.956919 4.491796 -0.317168
 6 -5.121933 3.395698 -0.333609
 1 -4.502583 4.290429 -0.233725
 6 0.059978 -1.782978 1.35049

6 -1.075104 -2.044269 2.197895
 6 -2.135603 -1.130813 2.199973
 6 -1.185805 -3.1969 3.049823
 1 -0.370429 -3.923768 3.067543
 1 -2.020512 -0.214508 1.626391
 6 -3.301663 -1.328275 2.96278
 6 -3.410579 -2.507126 3.771465
 6 -2.314904 -3.417071 3.794593
 1 -2.393444 -4.310702 4.419891
 6 1.281927 -2.521468 1.716827
 8 1.467346 -3.685184 1.403025
 8 2.154733 -1.770383 2.389789
 1 3.272672 -3.433007 2.977238
 6 3.400341 -2.372397 2.727924
 1 3.791504 -1.820199 3.587663
 1 4.099297 -2.284955 1.881877
 6 -4.385652 -0.412323 2.90917
 1 -4.291176 0.474328 2.274386
 6 -5.536178 -0.652504 3.62715
 1 -6.371002 0.049686 3.574049
 6 -5.639487 -1.808621 4.432455
 1 -6.554361 -1.986367 5.002635
 6 -4.600508 -2.716327 4.504251
 1 -4.689541 -3.61015 5.127213

9.3.8. Singlet conformer D: Ir-carbene intermediate

7 -0.664134 2.447783 1.40002
 7 -2.6293 0.710102 0.882237
 8 1.420964 0.548116 0.446218
 6 2.188437 1.584095 0.606015
 6 1.731513 2.875039 1.108255
 6 0.391745 3.192741 1.514412
 6 -3.447623 -0.271663 0.668116
 6 -3.102366 -1.603101 0.243321
 6 -1.749348 -2.108397 0.043058
 8 -0.66323 -1.411836 0.177262
 6 3.56141 1.441113 0.283326
 6 4.481766 2.492048 0.525963
 6 4.021104 3.759415 1.031897
 6 2.658664 3.908169 1.295853
 6 -4.187155 -2.468593 0.053904
 6 -4.035328 -3.810685 -0.307273
 6 -2.699895 -4.323092 -0.480986
 6 -1.587414 -3.46818 -0.313741
 77 -0.638366 0.582313 0.642196
 1 0.27042 4.178237 1.985611
 1 -4.522324 -0.089488 0.809294
 1 2.300975 4.868021 1.682432
 1 -5.19912 -2.078723 0.20676
 6 -0.444292 -0.072074 2.680204
 6 -1.356918 -0.954487 3.279518

6 0.639969 0.349232 3.465853
 6 -1.1959 -1.400618 4.593854
 1 -2.216057 -1.333309 2.714074
 6 0.81085 -0.090238 4.780669
 1 1.389722 1.03106 3.049417
 6 -0.108638 -0.96884 5.352454
 1 -1.923612 -2.095269 5.024697
 1 1.673054 0.253611 5.359823
 1 0.022952 -1.316661 6.380348
 6 -4.728831 3.706899 2.065224
 6 -4.418114 2.232229 1.84731
 6 -3.055327 2.080136 1.19745
 6 -1.955986 2.752475 2.030227
 6 -2.26735 4.225893 2.230966
 6 -3.639992 4.400043 2.867412
 1 -5.705076 3.818259 2.559167
 1 -4.830803 4.198202 1.080643
 1 -5.196972 1.784816 1.21187
 1 -4.431899 1.68173 2.805349
 1 -3.080656 2.61756 0.228056
 1 -1.932834 2.244453 3.016919
 1 -1.503717 4.700696 2.864174
 1 -2.229428 4.737572 1.251666
 1 -3.866221 5.470018 2.984045
 1 -3.617452 3.983896 3.889701

6	4.02762	0.173037	-0.336991	1	4.567365	5.767605	1.638898
6	3.990645	-1.034154	0.362647	6	6.286536	4.643364	1.013337
6	4.50644	-2.203832	-0.253665	1	6.992988	5.456816	1.190955
6	5.033876	-2.189746	-1.521047	6	6.751203	3.391559	0.536101
6	5.059183	-0.991067	-2.272862	1	7.81988	3.248371	0.358337
6	4.538563	0.205943	-1.678955	6	5.883339	2.352516	0.29977
6	4.517283	1.382187	-2.475999	1	6.268586	1.395876	-0.057149
6	4.999019	1.383359	-3.766956	6	-5.151259	-4.674213	-0.486499
6	5.533173	0.207527	-4.336917	1	-6.155228	-4.26198	-0.350816
6	5.556594	-0.955383	-3.600583	6	-4.976238	-5.995086	-0.816608
1	4.484922	-3.136052	0.317404	1	-5.83835	-6.651636	-0.95071
1	5.432767	-3.105131	-1.968262	6	-3.663934	-6.508607	-0.974644
1	5.953764	-1.879026	-4.031556	1	-3.527394	-7.563714	-1.224404
1	5.915857	0.22063	-5.360282	6	-2.562036	-5.703346	-0.81141
1	4.957058	2.301563	-4.35767	1	-1.557169	-6.116863	-0.927269
1	4.077529	2.292416	-2.066352	6	-0.720224	1.12175	-1.296825
6	3.427107	-1.153667	1.740794	6	-1.738001	1.956636	-1.909496
1	3.458738	-0.204046	2.291772	6	-3.039542	1.507187	-2.099775
1	2.368011	-1.460193	1.702136	6	-1.414866	3.310603	-2.233335
1	3.962726	-1.912704	2.328319	1	-0.382094	3.644532	-2.108113
1	0.724632	-3.865558	4.021784	1	-3.283928	0.461078	-1.897429
6	1.065587	-4.113659	3.013704	6	-4.058227	2.375359	-2.55448
1	3.016031	-4.809794	3.675226	6	-3.740196	3.748977	-2.819141
6	2.361476	-4.63937	2.816981	6	-2.39603	4.174514	-2.657642
6	0.227848	-3.906099	1.94062	1	-2.143523	5.214602	-2.882202
1	-0.774106	-3.503988	2.107183	6	0.474807	0.792539	-2.095519
6	0.646041	-4.187539	0.613493	8	1.326291	1.631873	-2.304437
6	-0.200666	-3.965584	-0.516355	8	0.496353	-0.480512	-2.458969
6	0.271995	-4.20498	-1.804829	1	2.343891	-0.268775	-3.420722
6	-0.578151	-3.919904	-3.005444	6	1.727618	-1.03262	-2.929909
1	-0.9537	-2.884861	-2.995038	1	1.470913	-1.830546	-3.634619
1	-1.466476	-4.569554	-3.052314	1	2.266136	-1.45921	-2.070554
1	-0.01946	-4.068172	-3.939439	6	-5.39962	1.940239	-2.718822
1	1.950201	-4.884761	-2.99373	1	-5.638808	0.891267	-2.520397
6	1.588317	-4.703675	-1.976804	6	-6.382248	2.81932	-3.117138
6	2.410104	-4.9559	-0.904347	1	-7.410528	2.470693	-3.237447
1	3.422082	-5.341877	-1.059157	6	-6.068048	4.172324	-3.377719
6	1.968331	-4.70226	0.416291	1	-6.855078	4.858444	-3.698272
6	2.798017	-4.930182	1.544237	6	-4.774169	4.624366	-3.232892
1	3.80052	-5.337668	1.380436	1	-4.526358	5.669417	-3.437791
6	4.948063	4.815275	1.258988				

9.3.9. triplet conformer A: Ir-carbene intermediate

7	0.530144	3.238222	-0.2373	8	-1.669834	-0.111445	0.047903
7	-1.787516	2.434374	-1.311796	6	3.205914	0.109544	1.419264
8	0.96768	0.66473	1.091593	6	4.56954	0.491787	1.501299
6	2.208716	1.042741	1.04538	6	4.967021	1.83254	1.160571
6	2.631773	2.380292	0.648686	6	3.978359	2.732067	0.741885
6	1.759749	3.400397	0.130107	6	-4.825241	0.453234	-1.701639
6	-2.949035	1.970148	-1.665647	6	-5.53125	-0.702413	-1.328067
6	-3.535646	0.724361	-1.250667	6	-4.89634	-1.650798	-0.449609
6	-2.876537	-0.247044	-0.391771	6	-3.570098	-1.426133	-0.010663

77	-0.485017	1.525592	-0.113672		1	-2.912014	0.411686	4.51959
1	2.214711	4.390478	-0.007012		6	-2.633083	-0.560209	4.10499
1	-3.567897	2.579761	-2.335939		1	-1.742169	-1.275122	5.954212
1	4.277686	3.746467	0.457424		6	-1.969432	-1.509808	4.911535
1	-5.316083	1.175783	-2.361131		6	-2.930868	-0.848302	2.791437
6	-1.340717	2.352576	1.648806		1	-3.456042	-0.105273	2.187392
6	-2.722304	2.565592	1.763524		6	-2.565263	-2.088118	2.206358
6	-0.535641	2.690047	2.744736		6	-2.859635	-2.410899	0.842833
6	-3.282368	3.076962	2.938364		6	-2.468221	-3.637315	0.307947
1	-3.397919	2.313958	0.937107		6	-2.71918	-3.988347	-1.126874
6	-1.088202	3.206336	3.918559		1	-2.536451	-3.135869	-1.797038
1	0.547332	2.534024	2.696127		1	-3.759866	-4.3082	-1.301558
6	-2.46583	3.402371	4.020547		1	-2.071924	-4.812353	-1.455489
1	-4.365091	3.220548	3.004673		1	-1.47221	-5.517651	0.70631
1	-0.436453	3.455212	4.761091		6	-1.789906	-4.564304	1.140299
1	-2.900426	3.807117	4.938129		6	-1.509255	-4.285244	2.4558
6	-1.579703	5.987471	-2.788271		1	-0.978313	-5.013128	3.07616
6	-2.277359	4.730563	-2.284127		6	-1.886383	-3.045935	3.026566
6	-1.251599	3.710486	-1.824065		6	-1.610005	-2.727996	4.380776
6	-0.332874	4.30866	-0.743437		1	-1.102407	-3.475188	4.99832
6	0.373726	5.548066	-1.261105		6	6.33513	2.207212	1.240901
6	-0.642955	6.572645	-1.7452		1	6.610624	3.23172	0.97484
1	-2.326888	6.73198	-3.100437		6	7.291375	1.307077	1.644597
1	-1.003876	5.735839	-3.695606		1	8.340779	1.603297	1.704286
1	-2.903271	4.316843	-3.088433		6	6.906516	-0.010768	1.992535
1	-2.957609	4.973335	-1.446826		1	7.666059	-0.722404	2.325159
1	-0.589049	3.433027	-2.664408		6	5.591455	-0.407332	1.924342
1	-0.982395	4.589399	0.112497		1	5.315154	-1.425228	2.20576
1	0.994739	5.992407	-0.469115		6	-6.854469	-0.946236	-1.778833
1	1.053307	5.251432	-2.078794		1	-7.319399	-0.219589	-2.450501
1	-0.125184	7.45727	-2.144162		6	-7.543422	-2.066826	-1.376566
1	-1.232845	6.931724	-0.883471		1	-8.561977	-2.242754	-1.728756
6	2.809446	-1.29813	1.676665		6	-6.934073	-2.988732	-0.492016
6	2.040506	-1.643073	2.786977		1	-7.493252	-3.866415	-0.159841
6	1.745178	-3.010926	3.018766		6	-5.650794	-2.78722	-0.039735
6	2.189295	-4.00392	2.179976		1	-5.192363	-3.496961	0.652972
6	2.934634	-3.685118	1.020192		6	0.796042	0.680523	-1.689685
6	3.232648	-2.309534	0.752035		6	0.868458	-0.732986	-1.94603
6	3.889099	-1.99807	-0.469683		6	1.311219	-1.210014	-3.19705
6	4.256708	-2.987148	-1.355833		6	0.490261	-1.7219	-0.974968
6	4.004677	-4.344615	-1.063105		1	0.206345	-1.404018	0.028212
6	3.35266	-4.681296	0.101353		1	1.610637	-0.494125	-3.96836
1	1.155759	-3.269476	3.903374		6	1.385551	-2.583473	-3.50857
1	1.959151	-5.053013	2.389706		6	0.984665	-3.542878	-2.522792
1	3.122992	-5.727163	0.327488		6	0.552762	-3.060478	-1.257814
1	4.298865	-5.119558	-1.775259		1	0.293798	-3.785453	-0.480314
1	4.731618	-2.716325	-2.302411		6	1.697401	1.575575	-2.401411
1	4.063323	-0.951228	-0.729225		8	1.433342	2.673746	-2.87646
6	1.503654	-0.620429	3.735849		8	2.981364	1.110492	-2.42114
1	2.125154	0.285196	3.770916		1	3.750448	2.177152	-4.039965
1	0.496195	-0.297655	3.424943		6	3.943096	1.984	-2.974475
1	1.417825	-1.021086	4.755802		1	4.916094	1.495632	-2.852591

1 3.948467 2.953472 -2.452903
 6 1.854027 -3.054108 -4.763963
 1 2.164687 -2.323145 -5.515965
 6 1.923601 -4.40494 -5.033489
 1 2.290843 -4.750586 -6.002806

6 1.521103 -5.346489 -4.061715
 1 1.579527 -6.414598 -4.284493
 6 1.060883 -4.918256 -2.830921
 1 0.763809 -5.643194 -2.066376

9.3.10. triplet conformer B: Ir-carbene intermediate

7 -0.499937 3.024001 -0.684086
 7 1.867865 2.619858 0.510818
 8 -0.999121 0.172212 -0.869104
 6 -2.135234 0.542381 -1.349023
 6 -2.489121 1.934981 -1.607799
 6 -1.641584 3.060625 -1.309294
 6 3.026278 2.273083 0.975533
 6 3.583556 0.945866 0.98589
 6 2.893308 -0.257447 0.531232
 8 1.668228 -0.286787 0.12664
 6 -3.072854 -0.48706 -1.638367
 6 -4.336962 -0.166314 -2.190532
 6 -4.678339 1.208329 -2.449136
 6 -3.739024 2.212741 -2.150558
 6 4.884197 0.836958 1.477556
 6 5.579491 -0.380036 1.526053
 6 4.926666 -1.56285 1.025753
 6 3.60267 -1.486594 0.5364
 77 0.495964 1.373889 -0.208419
 1 -2.033174 4.039003 -1.61639
 1 3.659549 3.051652 1.418525
 1 -4.009774 3.254861 -2.347402
 1 5.386813 1.741435 1.834929
 6 1.378034 1.476909 -2.146157
 6 2.760764 1.605683 -2.351467
 6 0.570238 1.430471 -3.293402
 6 3.311108 1.677206 -3.633535
 1 3.448263 1.644474 -1.50064
 6 1.110826 1.494911 -4.579961
 1 -0.51618 1.326559 -3.202712
 6 2.487527 1.620756 -4.757021
 1 4.394666 1.773301 -3.752679
 1 0.44773 1.443845 -5.448726
 1 2.915052 1.672443 -5.761643
 6 1.503105 6.405315 1.091578
 6 2.254019 5.093354 0.910623
 6 1.279143 3.95006 0.70025
 6 0.337495 4.223687 -0.483008
 6 -0.415833 5.528038 -0.284492
 6 0.557498 6.678604 -0.066003
 1 2.215732 7.234054 1.213392
 1 0.927286 6.361656 2.032119
 1 2.874229 4.897847 1.797413
 1 2.939981 5.156187 0.046352
 1 0.65224 3.844014 1.610343

1 0.968053 4.299423 -1.393256
 1 -1.053976 5.746159 -1.153105
 1 -1.090209 5.423372 0.584367
 1 0.001404 7.613051 0.099107
 1 1.142368 6.835059 -0.989442
 6 -2.679961 -1.886722 -1.341977
 6 -1.677396 -2.508093 -2.086946
 6 -1.347202 -3.855919 -1.801835
 6 -1.955127 -4.553403 -0.787771
 6 -2.944581 -3.939966 0.016066
 6 -3.319003 -2.584566 -0.265342
 6 -4.294239 -1.978851 0.570115
 6 -4.873414 -2.669819 1.612185
 6 -4.507232 -4.005522 1.879125
 6 -3.561246 -4.624281 1.09359
 1 -0.579886 -4.337373 -2.413599
 1 -1.673674 -5.590355 -0.58205
 1 -3.25954 -5.656379 1.293605
 1 -4.967899 -4.538915 2.714201
 1 -5.608735 -2.171316 2.248144
 1 -4.574822 -0.936741 0.398448
 6 -0.914298 -1.804449 -3.162295
 1 -1.483278 -0.987528 -3.627815
 1 0.00737 -1.358156 -2.750703
 1 -0.602586 -2.498136 -3.955325
 1 3.532683 -1.31364 -4.385775
 6 3.189496 -2.093296 -3.701447
 1 2.532297 -3.420346 -5.29294
 6 2.619728 -3.27983 -4.212835
 6 3.310101 -1.907083 -2.34197
 1 3.755176 -0.985032 -1.960439
 6 2.848029 -2.882954 -1.420621
 6 2.929909 -2.697865 -0.006026
 6 2.405396 -3.656286 0.857086
 6 2.387462 -3.427504 2.335562
 1 1.753508 -2.560333 2.577011
 1 3.388796 -3.210226 2.738815
 1 1.989521 -4.296129 2.87585
 1 1.439048 -5.586492 1.008382
 6 1.843067 -4.839963 0.318376
 6 1.788592 -5.059839 -1.036788
 1 1.349563 -5.980694 -1.43274
 6 2.268348 -4.085202 -1.943533
 6 2.175779 -4.255579 -3.348518
 1 1.733608 -5.179926 -3.73328

6	-5.947291	1.518905	-3.000097	1	-1.107905	-0.642592	3.817059
1	-6.192919	2.56743	-3.188799	6	-3.23022	-0.262789	3.732976
6	-6.852819	0.524671	-3.295191	6	-4.284806	0.480244	3.103728
1	-7.82715	0.776935	-3.719019	6	-3.93307	1.374307	2.056733
6	-6.516866	-0.828501	-3.056547	1	-4.723191	1.957085	1.571807
1	-7.235011	-1.6138	-3.302595	6	0.874913	1.023899	2.87161
6	-5.294365	-1.166178	-2.522745	8	1.484793	2.00289	3.272261
1	-5.040685	-2.213683	-2.348137	8	1.190805	-0.222255	3.307278
6	6.903593	-0.468048	2.030368	1	3.222905	-0.049168	3.734916
1	7.379332	0.441802	2.406939	6	2.269659	-0.293188	4.229456
6	7.577465	-1.666469	2.043223	1	2.30133	-1.323979	4.597212
1	8.595806	-1.723606	2.433206	1	2.126453	0.403817	5.065586
6	6.94675	-2.830368	1.539358	6	-3.574901	-1.173892	4.767275
1	7.489127	-3.778933	1.541229	1	-2.776915	-1.752781	5.240355
6	5.664989	-2.78264	1.043281	6	-4.883084	-1.329345	5.17285
1	5.19307	-3.687028	0.652049	1	-5.126098	-2.034262	5.971864
6	-0.193544	1.087007	1.87487	6	-5.913973	-0.578882	4.565577
6	-1.547916	0.820868	2.288094	1	-6.946692	-0.702838	4.900209
6	-1.892801	-0.067058	3.321682	6	-5.615157	0.305859	3.547629
6	-2.629662	1.524877	1.663091	1	-6.409159	0.885566	3.06738
1	-2.382323	2.258713	0.89776				

9.3.11. triplet conformer C: Ir-carbene intermediate

7	1.181292	-2.484901	-1.368232	1	2.093534	0.060055	-2.838605
7	-1.472152	-2.260289	-1.032066	6	-0.017031	0.590303	-5.4432
8	1.643127	0.191437	-0.330162	1	-2.146304	0.227416	-5.405828
6	2.87986	-0.147019	-0.404272	1	2.110911	0.83737	-5.156638
6	3.342489	-1.414246	-0.964049	1	-0.00693	0.940511	-6.478616
6	2.478464	-2.464516	-1.432614	6	-1.24143	-6.018383	-1.833343
6	-2.732228	-1.95435	-1.024039	6	-1.908296	-4.652429	-1.750343
6	-3.289056	-0.638535	-0.846779	6	-0.957873	-3.632172	-1.151556
6	-2.512538	0.553772	-0.51638	6	0.361239	-3.565505	-1.9436
8	-1.245845	0.549367	-0.259419	6	1.02131	-4.931297	-2.019135
6	3.836437	0.785743	0.089538	6	0.063932	-5.958223	-2.608019
6	5.222077	0.511751	-0.010875	1	-1.929581	-6.746096	-2.287581
6	5.668883	-0.72867	-0.588124	1	-1.04475	-6.385001	-0.810968
6	4.709011	-1.651911	-1.041311	1	-2.822776	-4.722864	-1.143303
6	-4.67086	-0.531736	-0.991938	1	-2.219951	-4.315407	-2.755851
6	-5.354872	0.687059	-0.866606	1	-0.690799	-3.938125	-0.119078
6	-4.593353	1.874469	-0.575763	1	0.105144	-3.223978	-2.968514
6	-3.193311	1.79077	-0.399297	1	1.933832	-4.886322	-2.631453
77	0.034699	-0.996645	-0.724725	1	1.330968	-5.230496	-1.002711
1	2.989482	-3.33381	-1.867207	1	0.545375	-6.946732	-2.635311
1	-3.462196	-2.758761	-1.184106	1	-0.145328	-5.695887	-3.659959
1	5.056836	-2.599773	-1.464778	6	3.345152	2.026352	0.733925
1	-5.24742	-1.435068	-1.215443	6	2.726567	3.024547	-0.017685
6	-0.04685	-0.308128	-2.741791	6	2.341375	4.226088	0.627839
6	-1.217596	-0.25173	-3.51614	6	2.53679	4.423995	1.972369
6	1.142339	0.08601	-3.380186	6	3.122495	3.413641	2.772032
6	-1.209481	0.192433	-4.841445	6	3.523289	2.187717	2.147462
1	-2.181382	-0.549696	-3.093178	6	4.057932	1.161652	2.971008
6	1.163151	0.531434	-4.703447	6	4.222811	1.350622	4.326024

6	3.857934	2.571618	4.932014	1	8.292595	1.874536	0.660643
6	3.312075	3.577816	4.167206	6	6.212344	1.436846	0.427743
1	1.882304	5.010881	0.020576	1	5.890371	2.390396	0.850555
1	2.233183	5.363074	2.444263	6	-6.762586	0.777603	-1.022628
1	3.005112	4.521697	4.62647	1	-7.323255	-0.135825	-1.239539
1	3.994195	2.70945	6.007203	6	-7.410408	1.985122	-0.906016
1	4.626382	0.540932	4.93842	1	-8.493965	2.043962	-1.027678
1	4.308569	0.196587	2.526601	6	-6.665619	3.157958	-0.631537
6	2.443773	2.879299	-1.477928	1	-7.183683	4.116275	-0.54804
1	3.119379	2.169853	-1.975458	6	-5.300354	3.107669	-0.472942
1	1.416414	2.509087	-1.638205	1	-4.735553	4.019758	-0.265629
1	2.516787	3.843507	-2.000023	6	0.135734	-1.78923	1.348557
1	-0.86671	3.443661	-4.415389	6	-0.874401	-1.987024	2.331685
6	-0.899702	3.848136	-3.400908	6	-2.138053	-1.37026	2.243409
1	0.362379	5.555	-3.869437	6	-0.662427	-2.823807	3.490842
6	-0.201222	5.035633	-3.09047	1	0.30896	-3.307341	3.621955
6	-1.621152	3.189974	-2.429151	1	-2.324712	-0.677636	1.4294
1	-2.15782	2.272218	-2.682212	6	-3.163795	-1.57224	3.187716
6	-1.666286	3.670844	-1.094265	6	-2.927245	-2.433999	4.309542
6	-2.395453	2.999811	-0.066416	6	-1.640279	-3.036858	4.423068
6	-2.368012	3.47271	1.242679	1	-1.441733	-3.681798	5.284375
6	-3.068513	2.733295	2.34013	6	1.444869	-2.393136	1.594508
1	-2.691159	1.702376	2.429308	8	2.471975	-1.819539	1.894621
1	-4.152786	2.653028	2.16358	8	1.445901	-3.7516	1.366937
1	-2.926766	3.220039	3.313139	1	3.453316	-4.004321	0.84418
1	-1.622513	5.01548	2.564914	6	2.699588	-4.385342	1.551792
6	-1.64059	4.653857	1.532872	1	2.541566	-5.457059	1.386829
6	-0.961794	5.340859	0.554859	1	3.087375	-4.219162	2.56685
1	-0.409277	6.25291	0.800223	6	-4.433892	-0.945367	3.066376
6	-0.944872	4.868315	-0.779154	1	-4.611637	-0.283278	2.212354
6	-0.228225	5.533391	-1.806683	6	-5.422506	-1.164248	4.002324
1	0.311093	6.452264	-1.555853	1	-6.393568	-0.674811	3.894386
6	7.057645	-0.993791	-0.68454	6	-5.187076	-2.016362	5.10285
1	7.379756	-1.941928	-1.123477	1	-5.97612	-2.181955	5.840157
6	7.985156	-0.079186	-0.237816	6	-3.959405	-2.63671	5.24986
1	9.052718	-0.295017	-0.317399	1	-3.771729	-3.293613	6.104222
6	7.553049	1.147312	0.318311				

9.3.12. triplet conformer D: Ir-carbene intermediate

7	-1.431674	-2.296248	0.739744	6	-4.22346	-0.070418	1.340362
7	0.873223	-3.001868	-0.437327	6	4.31929	-2.691907	-1.521257
8	-0.651062	0.55972	0.760599	6	5.470504	-1.890616	-1.613094
6	-1.921949	0.728043	0.952136	6	5.383569	-0.519243	-1.194192
6	-2.874888	-0.36312	1.134976	6	4.143352	0.004455	-0.745821
6	-2.563328	-1.769819	1.083568	77	0.182202	-1.239222	0.200316
6	2.048685	-3.196444	-0.944086	1	-3.394095	-2.44319	1.339181
6	3.103539	-2.218347	-1.039958	1	2.299509	-4.19673	-1.320924
6	2.991319	-0.815744	-0.659695	1	-4.932253	-0.900068	1.442557
8	1.897961	-0.254135	-0.242702	1	4.389715	-3.740642	-1.826684
6	-2.409326	2.06097	0.995843	6	0.810736	-1.590945	2.162324
6	-3.77917	2.326089	1.259055	6	2.023149	-2.244059	2.422811
6	-4.71273	1.240869	1.403514	6	0.04235	-1.155542	3.249384

6	2.468719	-2.431708	3.734409	6	4.096708	2.418044	-1.346377
1	2.655308	-2.598543	1.600781	6	4.198585	2.061135	-2.798359
6	0.485049	-1.343664	4.559738	1	3.572421	1.192711	-3.052093
1	-0.909198	-0.640887	3.080336	1	5.23005	1.800151	-3.087834
6	1.699443	-1.984638	4.807713	1	3.892121	2.900522	-3.437353
1	3.425021	-2.931803	3.913938	1	4.079168	4.547052	-1.741931
1	-0.124269	-0.982853	5.393113	6	4.045051	3.781787	-0.960687
1	2.043865	-2.135835	5.833788	6	3.947431	4.154844	0.358171
6	-0.868887	-6.436664	-0.286056	1	3.909895	5.212917	0.634038
6	0.31211	-5.475923	-0.332153	6	3.87233	3.179121	1.380869
6	-0.173494	-4.038109	-0.401914	6	3.755872	3.532586	2.749606
6	-1.115867	-3.725512	0.77761	1	3.738748	4.594397	3.013768
6	-2.295508	-4.679729	0.817202	6	-6.092526	1.511344	1.602839
6	-1.811113	-6.122101	0.863949	1	-6.779243	0.664113	1.690082
1	-0.506792	-7.472968	-0.218574	6	-6.554933	2.803247	1.683995
1	-1.421147	-6.373082	-1.240378	1	-7.6173	3.004291	1.837114
1	0.946731	-5.713875	-1.198042	6	-5.637073	3.876636	1.584128
1	0.944967	-5.597577	0.565571	1	-5.999396	4.903852	1.672925
1	-0.756253	-3.902159	-1.335432	6	-4.2953	3.648796	1.380604
1	-0.514694	-3.87108	1.69975	1	-3.60572	4.492413	1.310595
1	-2.925552	-4.466899	1.693508	6	6.704869	-2.406158	-2.080965
1	-2.932876	-4.51525	-0.069777	1	6.747419	-3.450749	-2.401214
1	-2.670132	-6.808837	0.860004	6	7.830009	-1.613679	-2.126022
1	-1.290404	-6.296516	1.821639	1	8.777064	-2.020389	-2.486606
6	-1.451982	3.165824	0.716538	6	7.758005	-0.270659	-1.691311
6	-0.360243	3.403885	1.553378	1	8.656338	0.350764	-1.710912
6	0.53273	4.46243	1.24595	6	6.572043	0.262183	-1.236726
6	0.375579	5.252467	0.135584	1	6.532759	1.298778	-0.894163
6	-0.70609	5.032016	-0.748669	6	-0.856653	-0.877474	-1.768214
6	-1.633656	3.978209	-0.455398	6	-2.283578	-0.847329	-1.944903
6	-2.698344	3.774113	-1.373859	6	-3.055089	-2.013211	-1.844681
6	-2.837974	4.544692	-2.50764	6	-2.99627	0.387498	-2.127757
6	-1.92185	5.581066	-2.787054	1	-2.417724	1.301143	-2.255579
6	-0.880745	5.816723	-1.917482	1	-2.54978	-2.979221	-1.754514
1	1.36961	4.64125	1.92673	6	-4.46616	-1.991631	-1.792232
1	1.082959	6.058447	-0.080498	6	-5.147392	-0.732894	-1.879462
1	-0.160642	6.615725	-2.116941	6	-4.364682	0.436079	-2.083934
1	-2.040431	6.19042	-3.686068	1	-4.880196	1.397484	-2.183793
1	-3.665836	4.350591	-3.194693	6	0.10693	-0.004933	-2.45547
1	-3.420183	2.982443	-1.174472	8	1.101153	-0.394304	-3.037057
6	-0.072249	2.58419	2.769041	8	-0.211425	1.296963	-2.3046
1	-0.958472	2.053773	3.142031	1	1.528939	2.331844	-1.903973
1	0.688991	1.819191	2.543575	6	0.757153	2.26019	-2.686709
1	0.326103	3.206771	3.583311	1	0.231981	3.218466	-2.768406
1	3.603818	0.433716	4.143799	1	1.226738	1.9974	-3.643876
6	3.686681	1.201487	3.370562	6	-5.238858	-3.168872	-1.607668
1	3.561557	2.855244	4.77618	1	-4.725079	-4.134474	-1.564404
6	3.659226	2.567646	3.726625	6	-6.610706	-3.105824	-1.48391
6	3.816113	0.827746	2.051325	1	-7.188741	-4.02129	-1.336922
1	3.844265	-0.23317	1.793289	6	-7.275356	-1.861887	-1.551157
6	3.904669	1.794648	1.016155	1	-8.362357	-1.821782	-1.450392
6	4.03551	1.433945	-0.361319	6	-6.554391	-0.701225	-1.753125

1 -7.06366 0.265102 -1.810195

9.3.12. Transition state model

TS (imaginary frequencies: 783.2321*i* cm⁻¹)

7 1.917720 -0.309557 0.509630
7 -0.396941 -1.649668 0.591100
8 0.827731 1.739370 -1.328336
6 1.972111 2.292653 -1.076444
6 2.996820 1.763841 -0.203447
6 2.936538 0.496020 0.466307
6 -1.614031 -2.104527 0.605995
6 -2.724477 -1.622424 -0.158658
6 -2.669611 -0.563115 -1.142800
8 -1.634405 0.154959 -1.428085
6 2.239498 3.545986 -1.696172
6 3.406588 4.245709 -1.470281
6 4.401060 3.735074 -0.615511
6 4.185425 2.514132 -0.012077
6 -3.962710 -2.278594 0.070277
6 -5.114441 -1.949267 -0.609395
6 -5.052640 -0.937009 -1.587280
6 -3.872649 -0.276660 -1.850024
77 0.160934 0.005771 -0.403631
1 3.862281 0.185552 0.970963
1 -1.836912 -2.946346 1.276183
1 4.952480 2.090496 0.644172
1 -3.984173 -3.073235 0.822692
6 0.838952 -1.183089 -1.959262
6 0.093550 -2.268020 -2.445217
6 2.078874 -0.922451 -2.564657
6 0.569480 -3.064947 -3.488155
1 -0.886406 -2.499645 -2.014962
6 2.557383 -1.716829 -3.608993
1 2.688313 -0.075014 -2.232307
6 1.806158 -2.795368 -4.073810
1 -0.036279 -3.901252 -3.849065
1 3.523843 -1.484591 -4.065928
1 2.178433 -3.417415 -4.891657
6 1.752683 -4.025269 2.714881
6 0.654674 -3.658230 1.725732
6 0.649298 -2.155698 1.489807
6 2.015892 -1.705349 0.960311
6 3.110930 -2.033339 1.960304
6 3.115583 -3.527312 2.261194

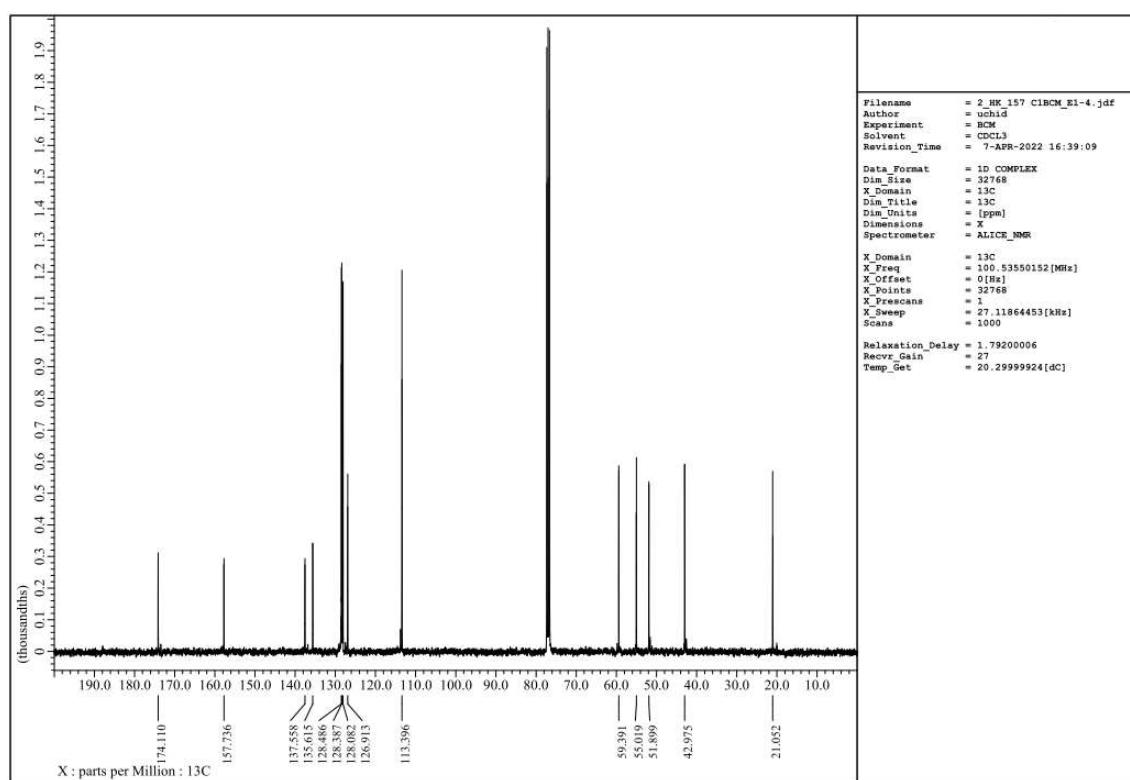
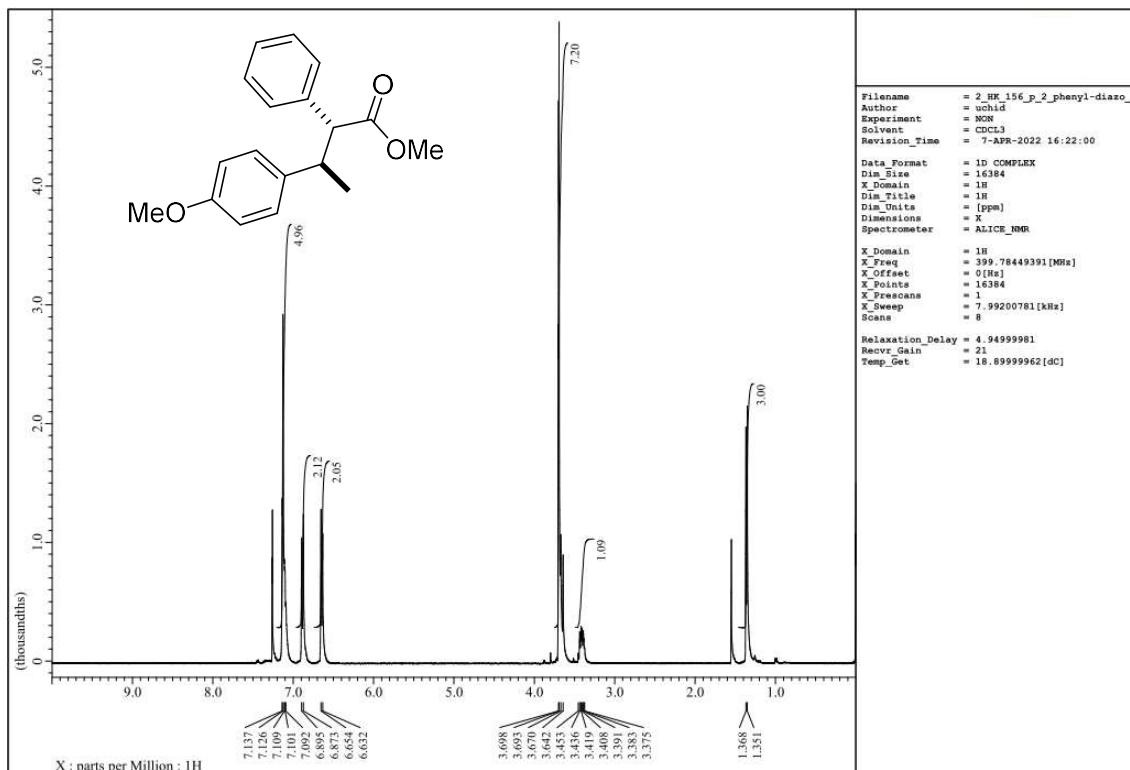
1 1.773451 -5.113614 2.873626
1 1.509963 -3.583129 3.698109
1 -0.318015 -3.995691 2.110658
1 0.806529 -4.173012 0.760208
1 0.491352 -1.663149 2.470202
1 2.204501 -2.286945 0.033697
1 4.095488 -1.736109 1.570763
1 2.950968 -1.449712 2.885519
1 3.883690 -3.758630 3.014079
1 3.415609 -4.070805 1.348530
6 -0.774357 1.295755 1.199956
6 -2.100393 1.850642 0.891137
6 -2.261481 2.577335 -0.308059
6 -3.232380 1.639618 1.702942
1 -3.138314 1.059836 2.621208
1 -1.392863 2.720449 -0.955722
6 -3.502455 3.079187 -0.673507
6 -4.620831 2.840146 0.128677
6 -4.480534 2.115088 1.311426
1 -5.352574 1.916294 1.938716
6 -0.535516 0.732101 2.538600
8 -1.238424 -0.119166 3.049004
8 0.620933 1.146337 3.109231
1 0.133536 0.752685 5.097738
6 0.924347 0.555716 4.361187
1 1.866308 1.002248 4.694498
1 1.039386 -0.535365 4.275106
1 0.063608 2.209815 1.034949
6 0.395569 3.373471 1.388090
1 0.152573 3.948568 0.489208
1 -0.179811 3.667326 2.268306
1 1.467799 3.261351 1.576861
1 -5.602247 3.214915 -0.172008
1 -3.605563 3.640543 -1.605082
1 -3.816994 0.511562 -2.603143
1 -5.953021 -0.667267 -2.146438
1 -6.051238 -2.469188 -0.402885
1 5.326494 4.286463 -0.442838
1 3.559131 5.207130 -1.968274
1 1.467209 3.933215 -2.364145

10. References

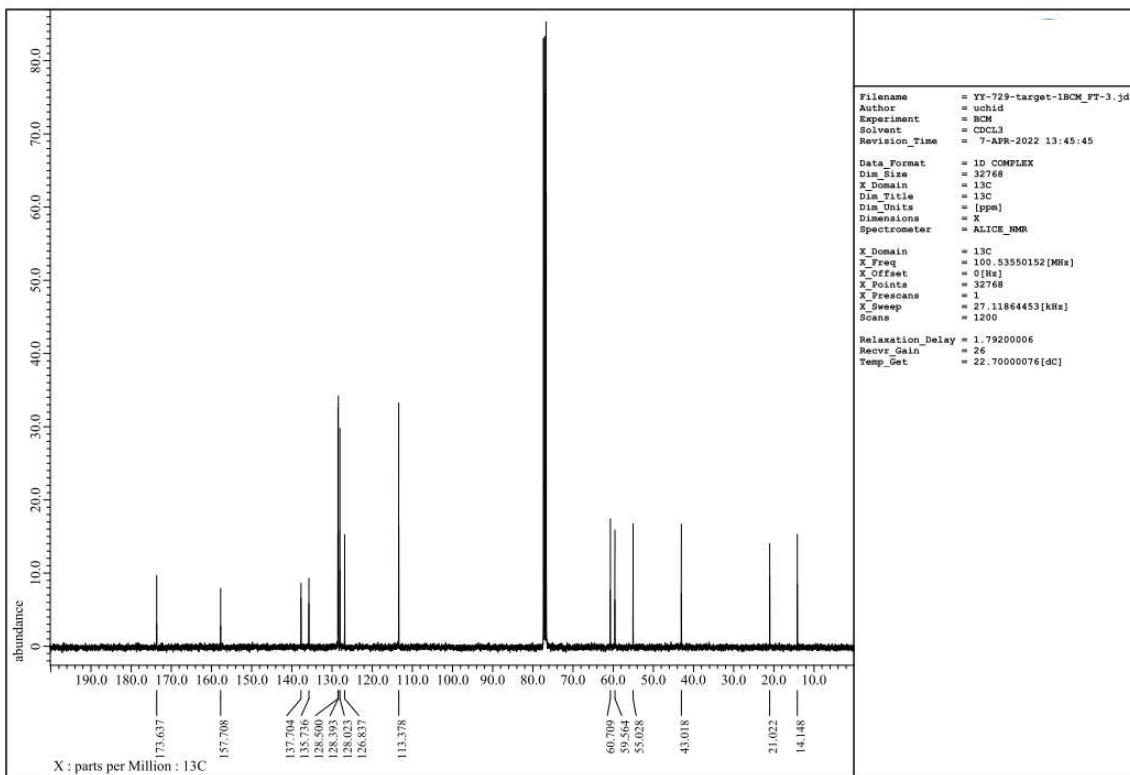
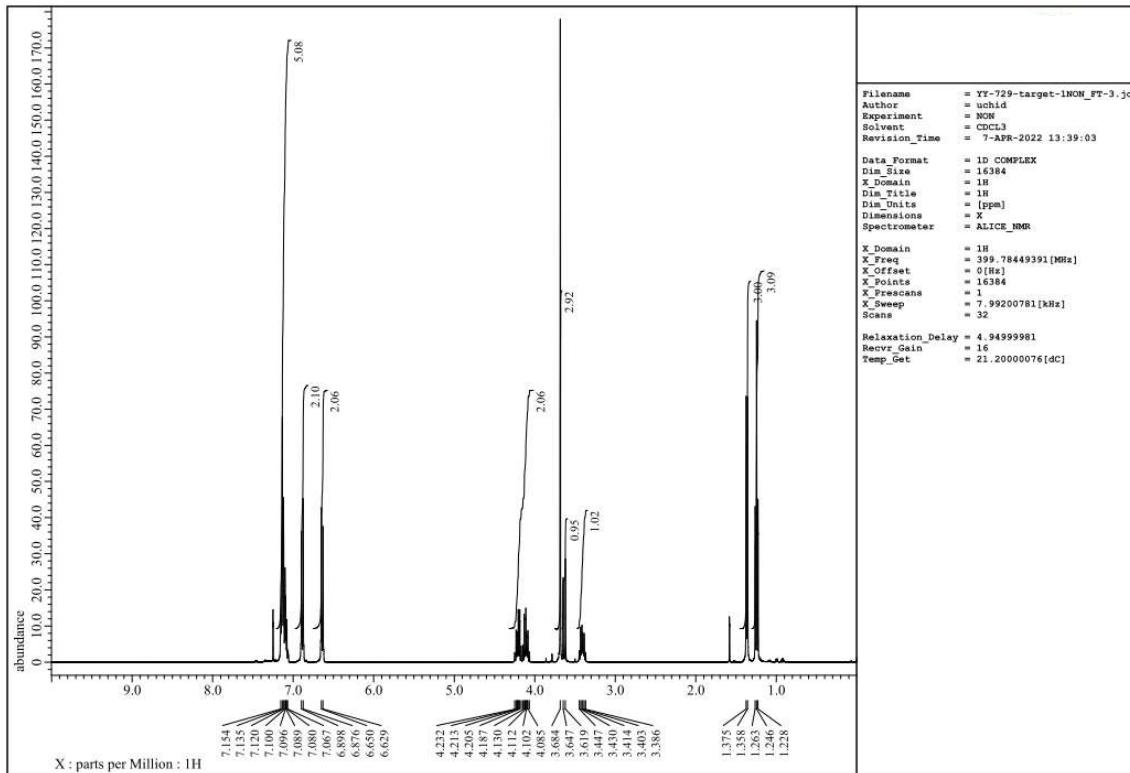
- [1] For the synthesis of complexes **1** and **2**, see: Suematsu, H.; Katsuki, T. “Iridium(III)Catalyzed Diastereo- and Enantioselective C–H Bond Functionalization”, *J. Am. Chem. Soc.* **2009**, *131*, 14218–14219.
- [2] (a) Ichinose, M.; Suematsu, H.; Yasutomi, Y.; Nishioka, Y.; Uchida, T.; Katsuki, T. “Enantioselective Intermolecular Benzylic C–H Bond Amination: Efficient Synthesis of Optically Active Benzosultams”, *Angew. Chem. Int. Ed.* **2011**, *50*, 9884–9887. (b) Hosoya, N.; Hatayama, A.; Irie, R.; Sasaki, H.; Katsuki, T. “Rational Design of Mn-Salen Catalysts: Preliminary Results”, *Tetrahedron* **1994**, *50*, 4311–4322.
- [3] Davies, H. M. L.; Hansen, T. “Asymmetric Intermolecular, Carbenoid C–H Insertions Catalyzed by Rhodium(II) (*S*)-*N*-(*p*-Dodecylphenyl)sulfonylproline”, *J. Am. Chem. Soc.* **1997**, *119*, 9075–9076.
- [4] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. “Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions”, *J. Phys. Chem. B* **2009**, *113*, 6378–6396.
- [5] Davies, H. M. L.; Jin, Q.; Ren, P.; Kovalevsky, A. Y. “Catalytic Asymmetric Benzylic C–H Activation by Means of Carbenoid-Induced C–H Insertions”, *J. Org. Chem.* **2002**, *67*, 4165–4169.
- [6] Zhao, Y.; Truhlar, D. G. “The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-classfunctionals and 12 other functionals”, *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- [7] Weigend, F.; Ahlrichs, R. “Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy”, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
- [8] Spartan’18 Parallel Suite, Wavefunction Inc. Irvine, CA, 2018.
- [9] Becke, A. D. “Density-functional exchange-energy approximation with correct asymptotic behavior”, *Phys. Rev. A* **1988**, *38*, 3098–3100.
- [10] Lee, C.; Yang, W.; Parr, R. G. “Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density”, *Phys. Rev. B* **1988**, *37*, 785–789.
- [11] Becke, A. D.; Johnson, E. R. “A density-functional model of the dispersion interaction”, *J. Chem. Phys.* **2005**, *123*, 154101.
- [12] Stephens, P. J.; Harada, N. “ECD Cotton Effect Approximated by the Gaussian Curve and Other Methods”, *Chirality* **2009**, *22*, 229–233.
- [13] Polavarapu, P. L. Chiroptical Spectroscopy Fundamentals and Applications, CRC Press, Boca Raton, FL 2017.
- Full citation of Gaussian 16**
Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

11.NMR spectra for C–H insertion products.

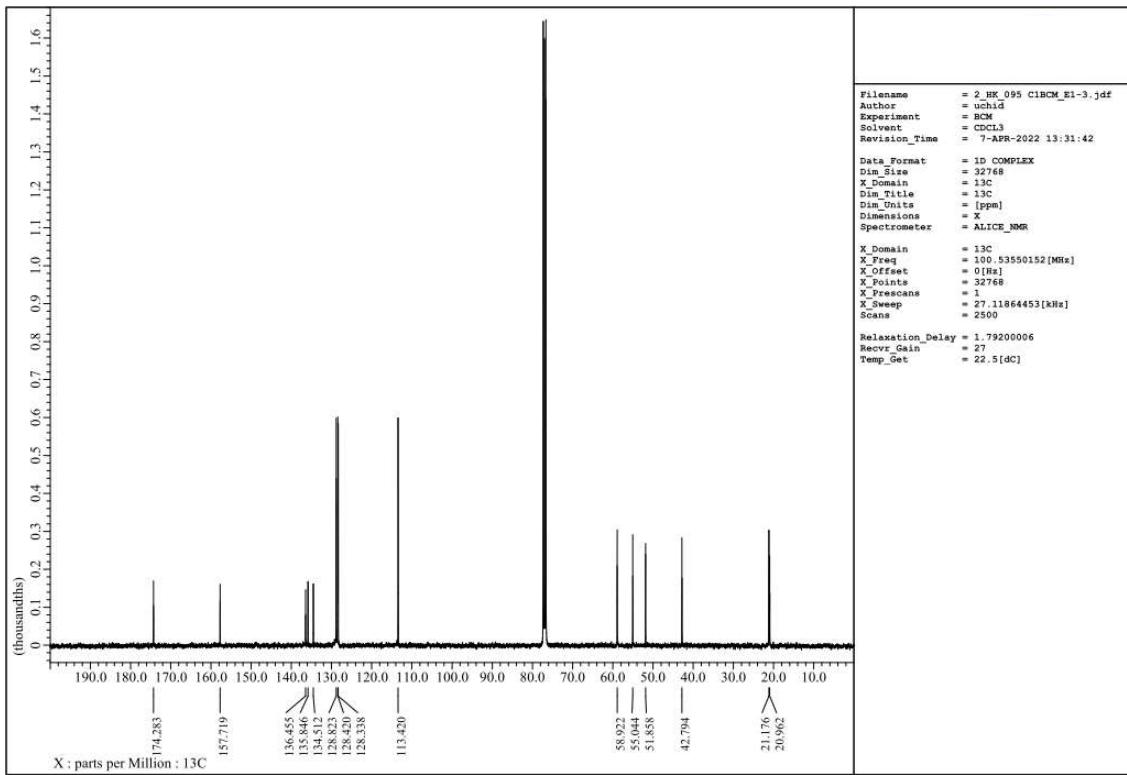
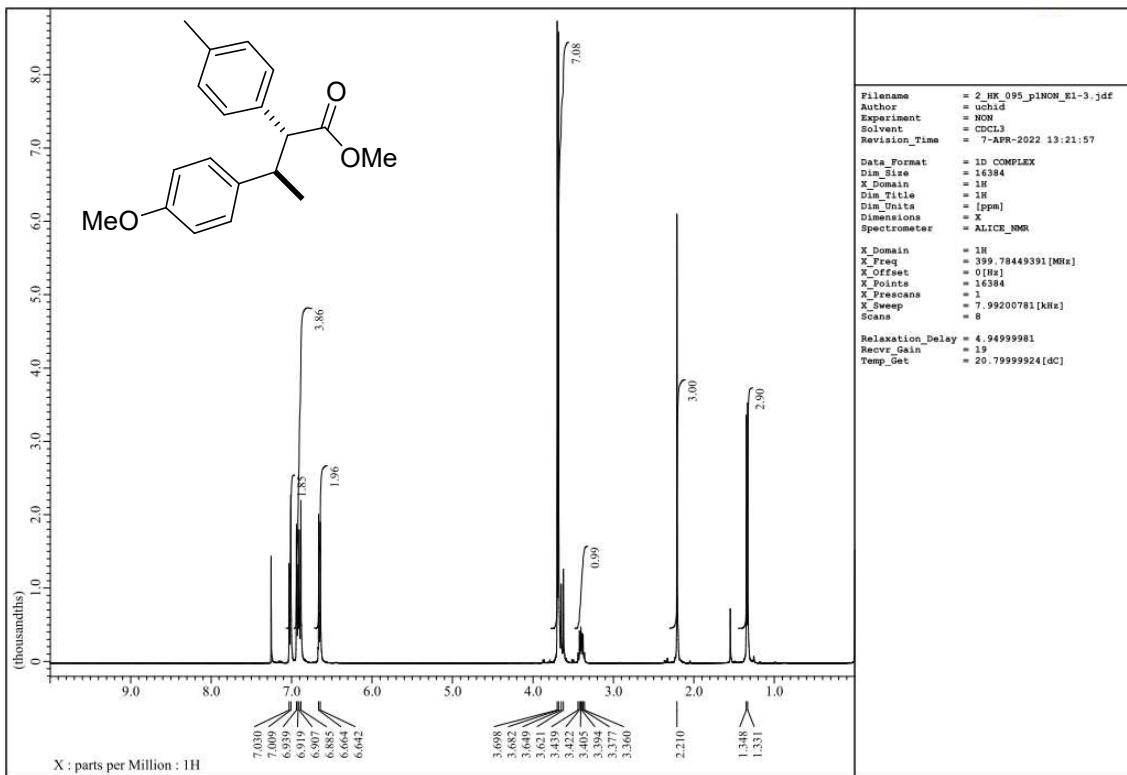
11.1. Methyl (2*R*^{*,3*R*^{*})-3-(4-methoxyphenyl)-2-phenylbutanoate}



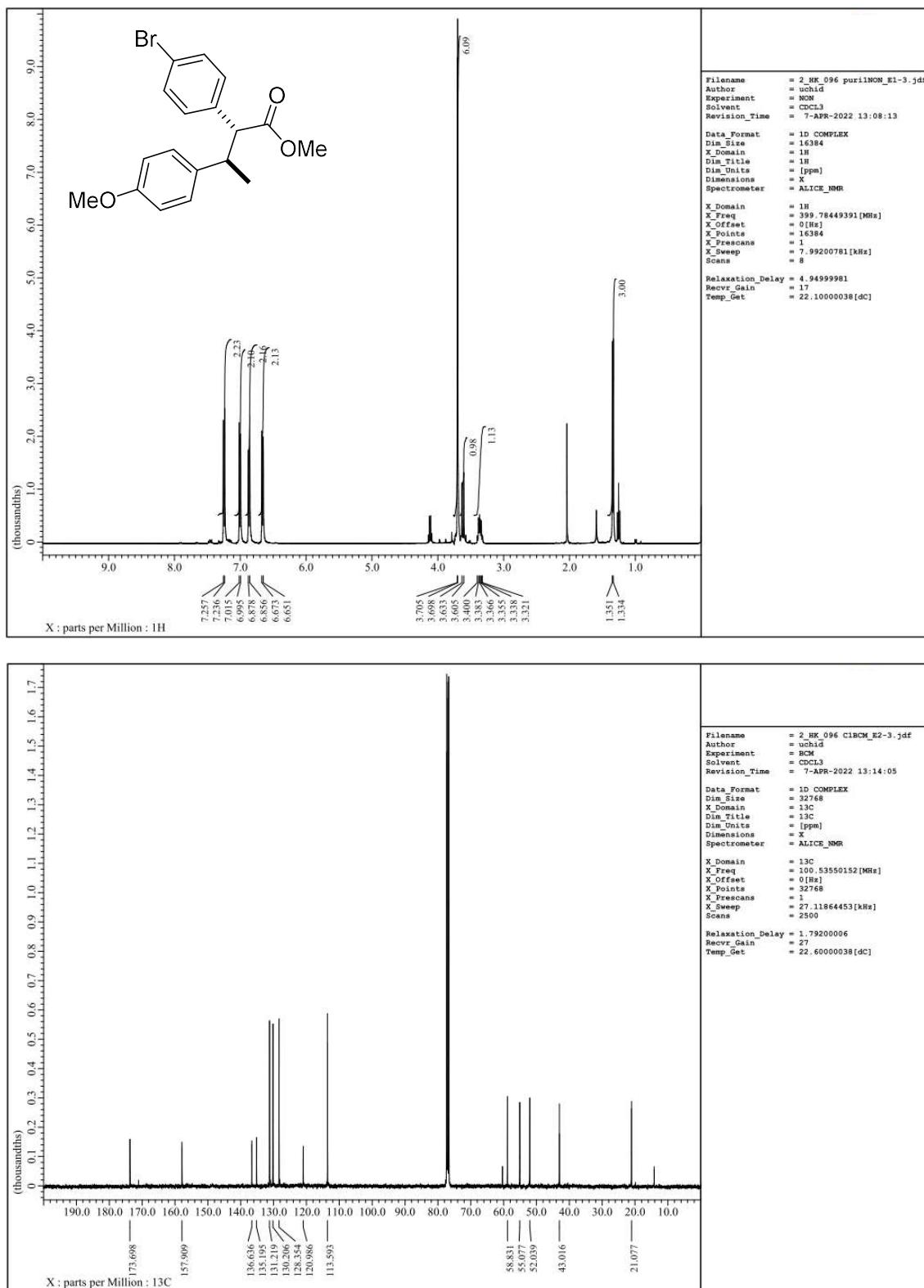
11.2. Ethyl (2*R*^{*},3*R*^{*})-3-(4-methoxyphenyl)-2-phenylbutanoate



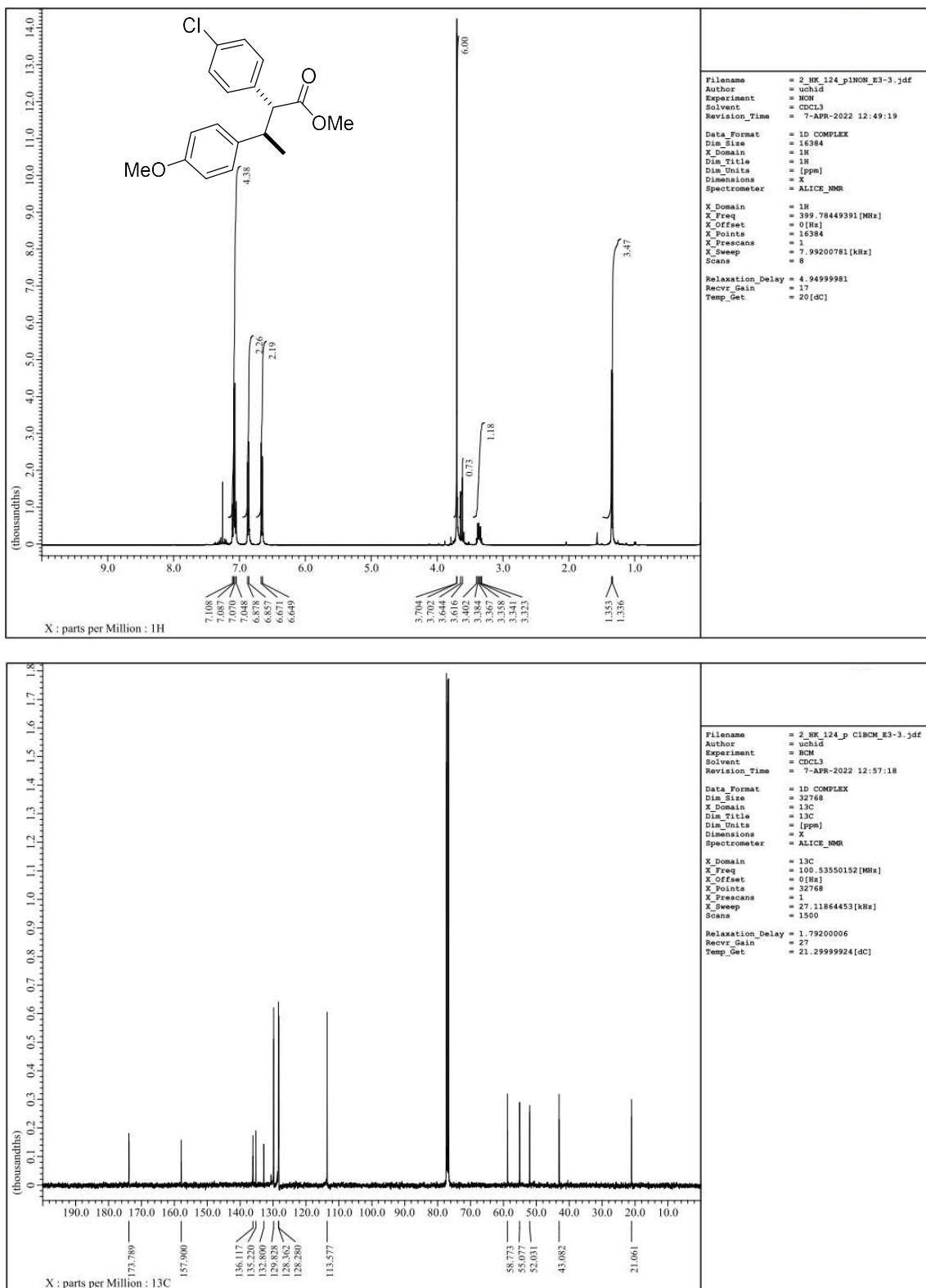
11.3. Methyl (2*R*^{*,3*R*^{*})-3-(4-methoxyphenyl)-2-(4-methylphenyl)butanoate}



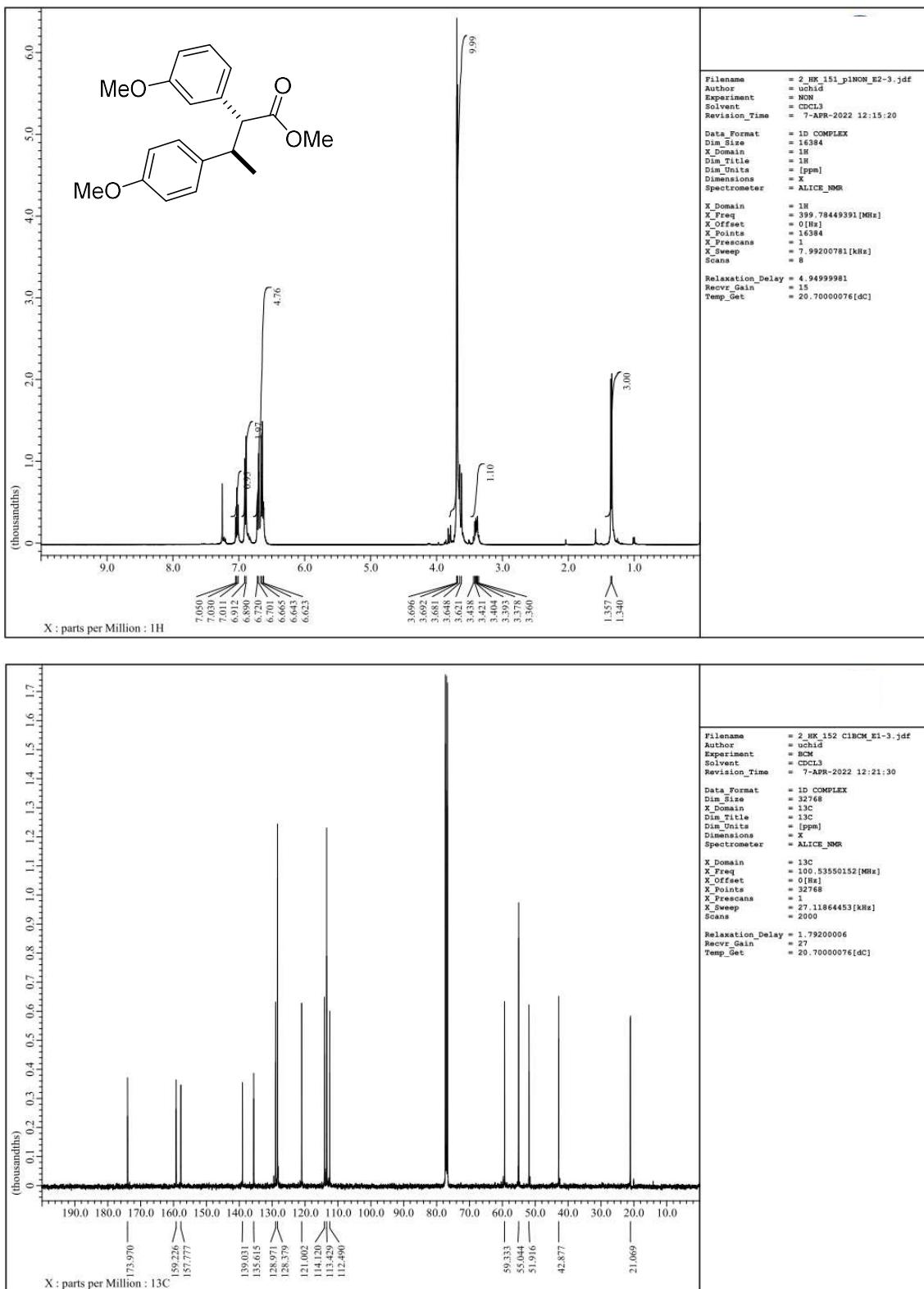
11.4. Methyl (2*R*^{*,3*R*^{*})-2-(4-bromophenyl)-3-(4-methoxyphenyl)butanoate}



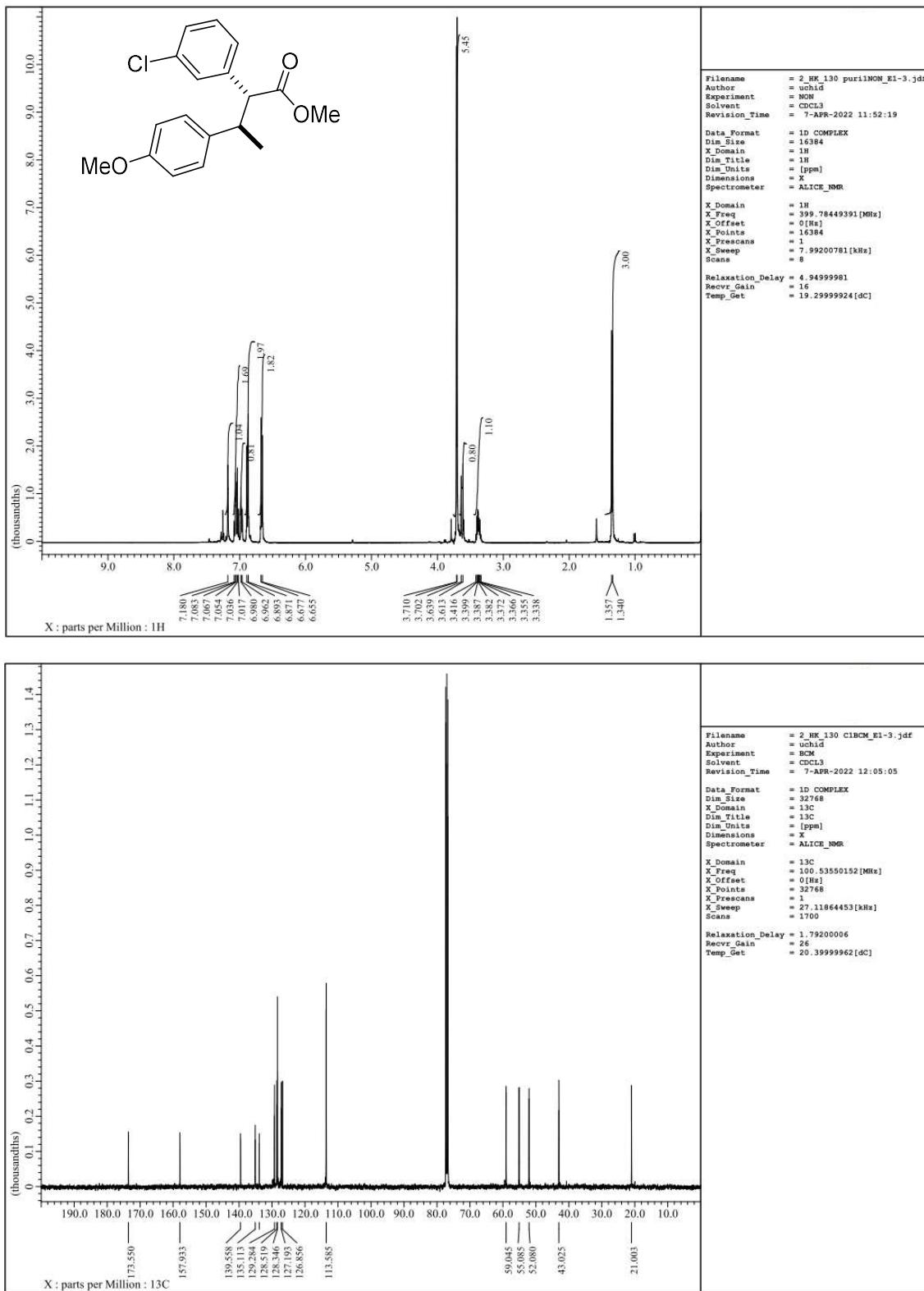
11.5. Methyl (2*R,3*R**)-2-(4-chlorophenyl)-3-(4-methoxyphenyl)butanoate**



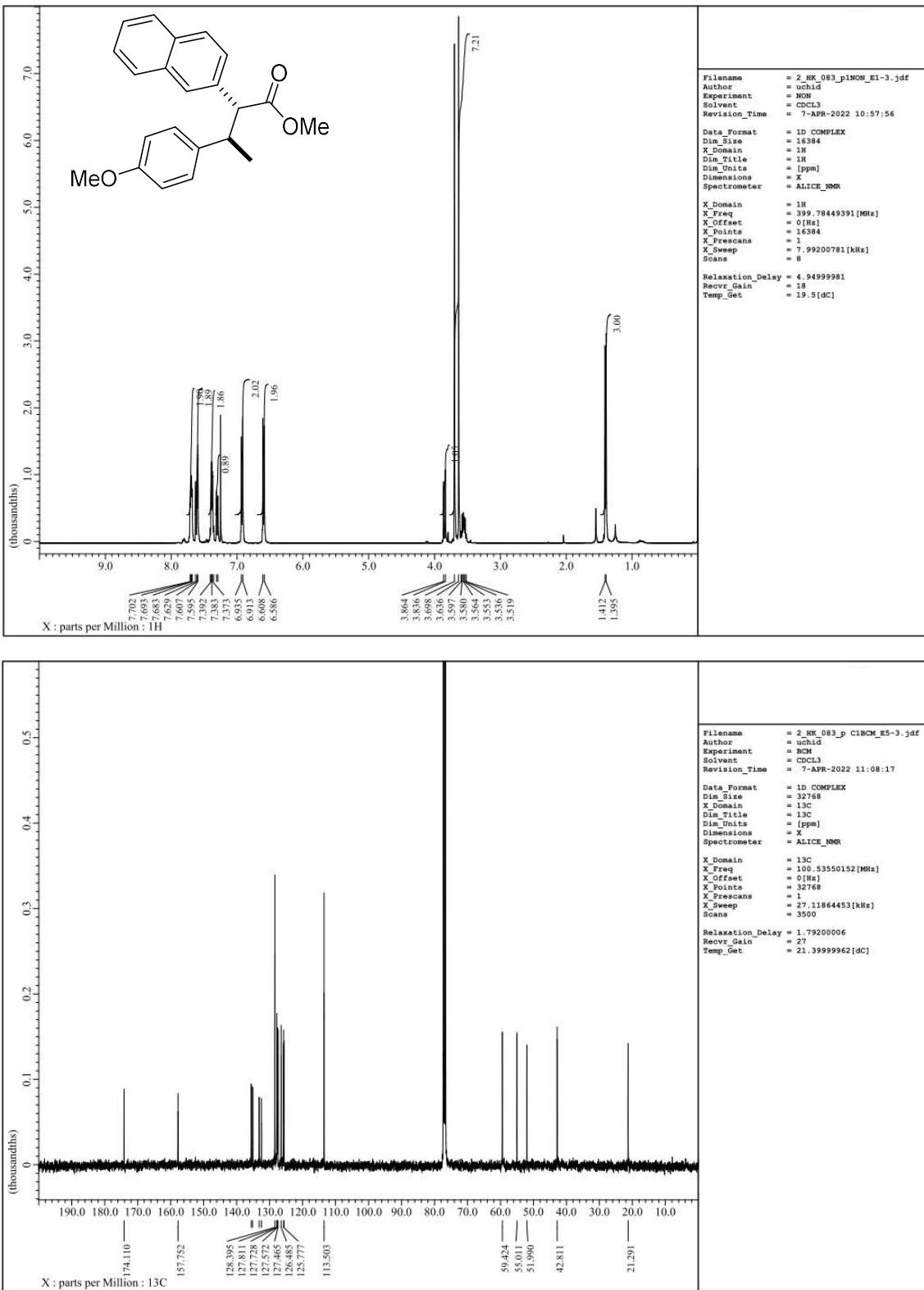
11.6. Methyl (2*R*^{*,3*R*^{*})-2-(3-methoxyphenyl)-3-(4-methoxyphenyl)butanoate}



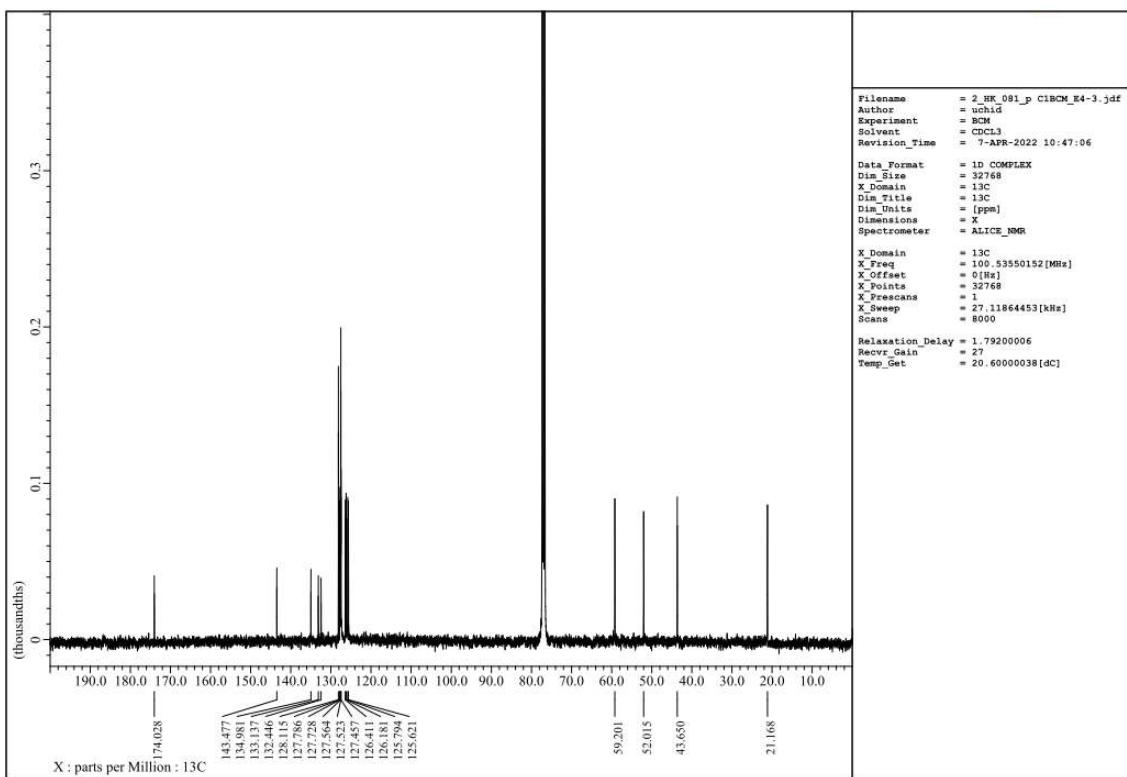
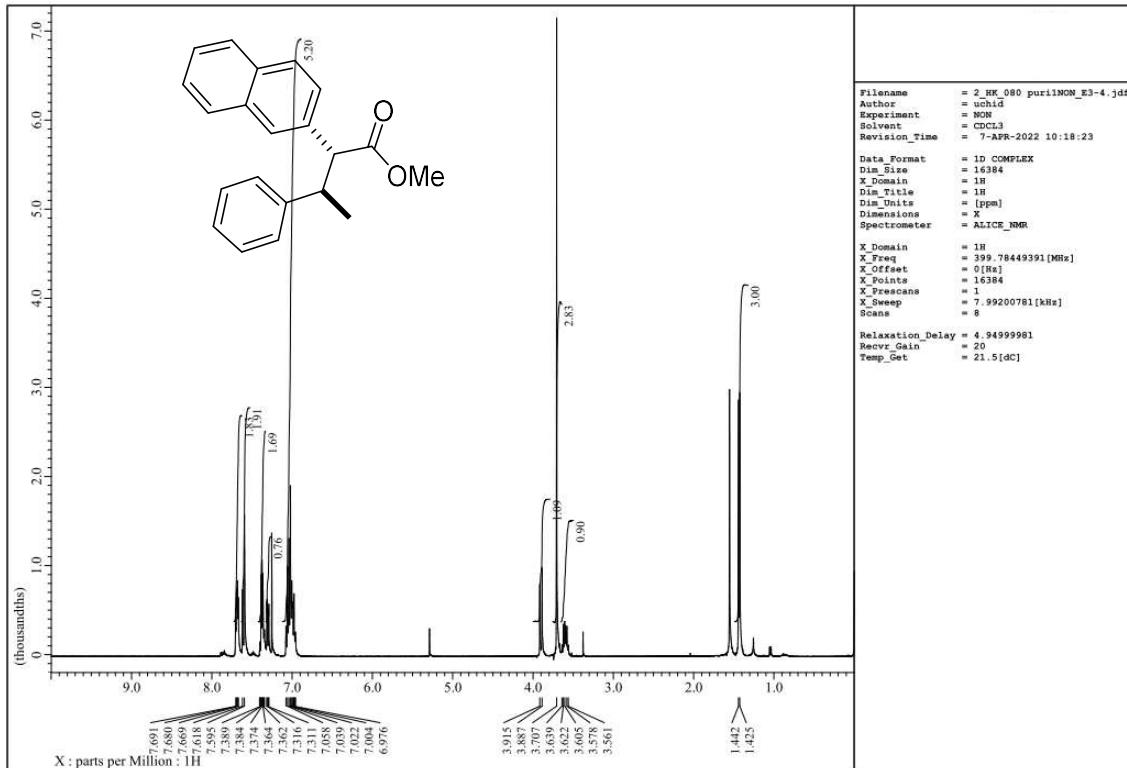
11.7. Methyl (2*R*^{*},3*R*^{*})-2-(3-chlorophenyl)-3-(4-methoxyphenyl)butanoate



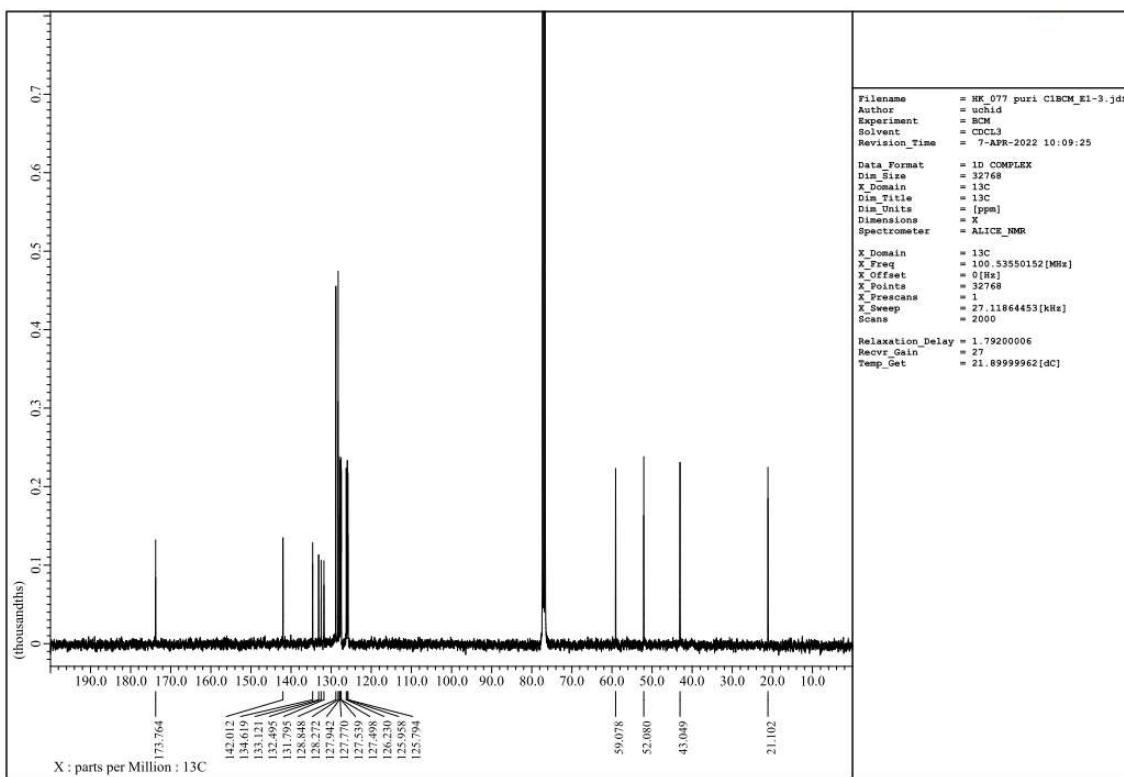
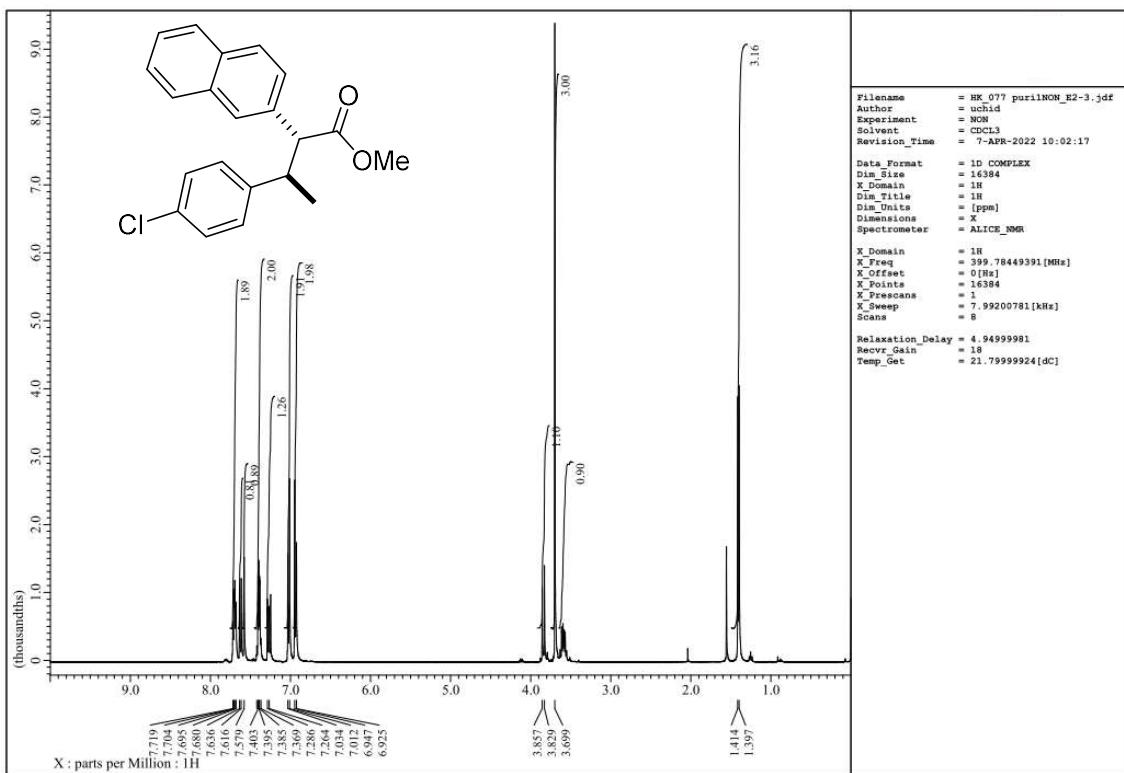
11.8. Methyl (2*R*^{*},3*R*^{*})-2-(2-naphthyl)-3-(4-methoxyphenyl)butanoate



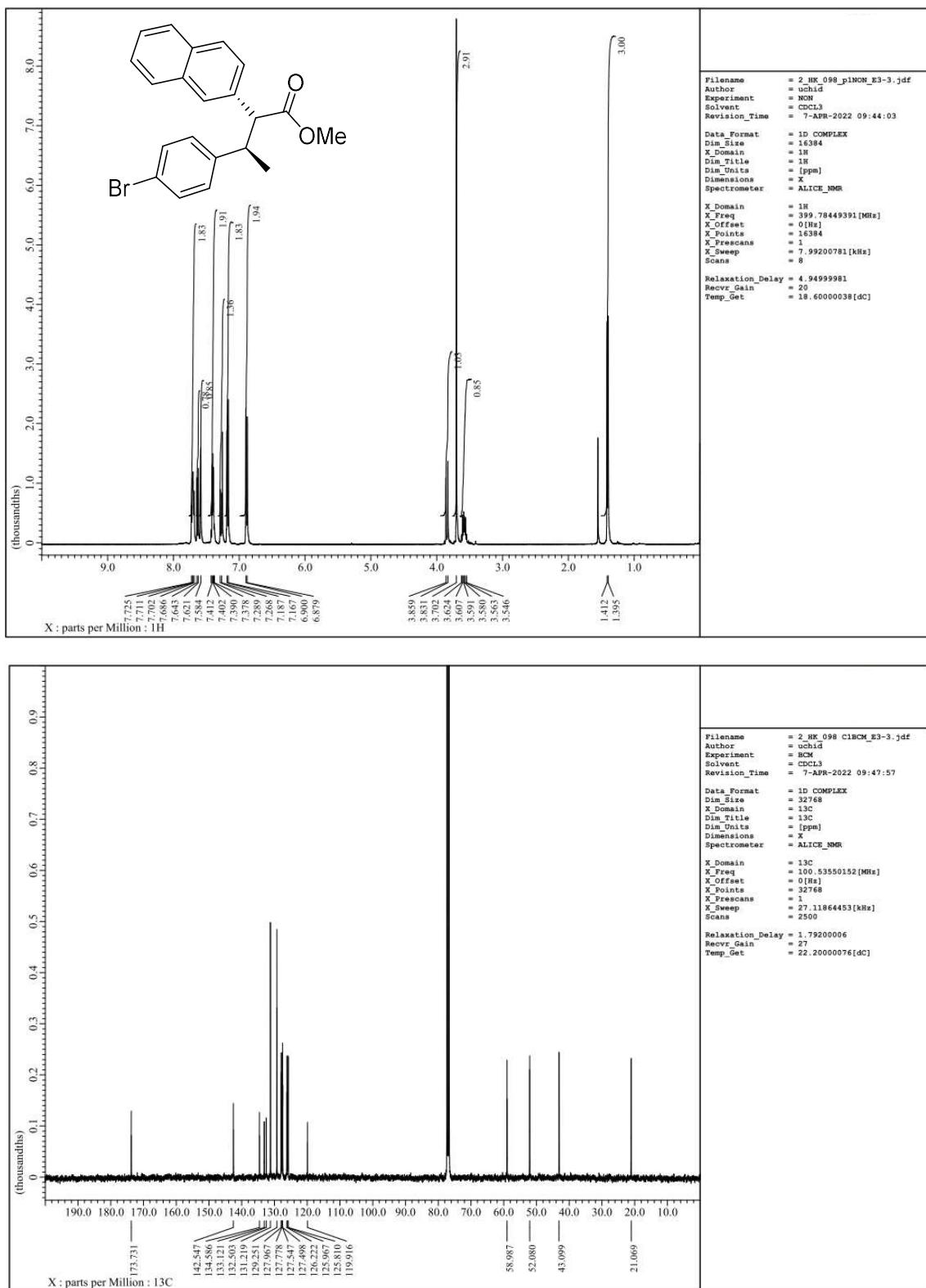
11.9. Methyl (2*R*^{*,3*R*^{*})-2-(2-naphthyl)-3-phenylbutanoate}



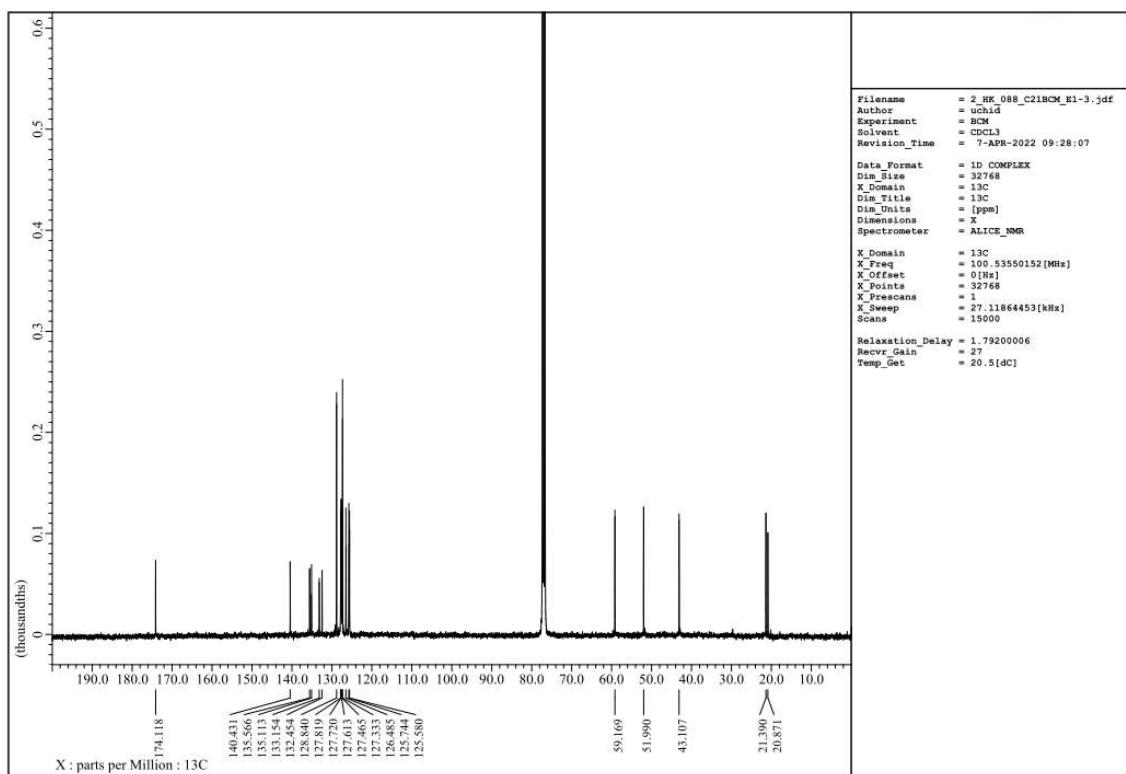
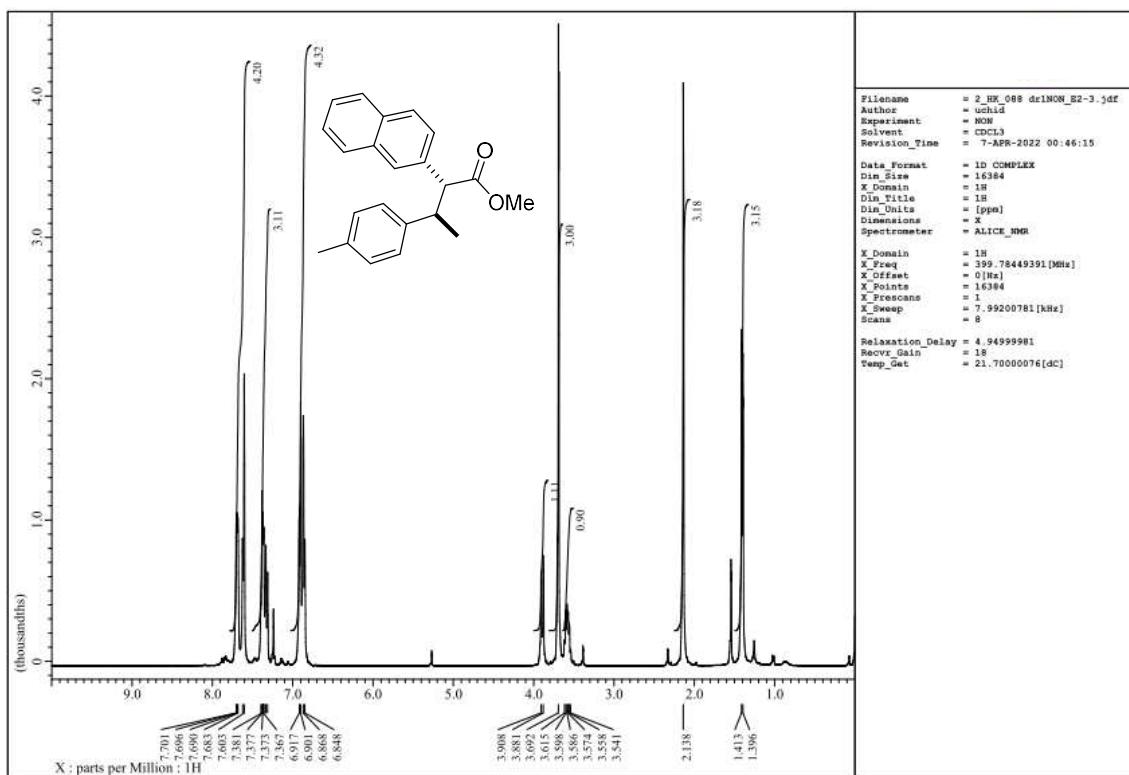
11.10. Methyl (2*R*^{*},3*R*^{*})-3-(4-chlorophenyl)-2-(2-naphthyl)butanoate



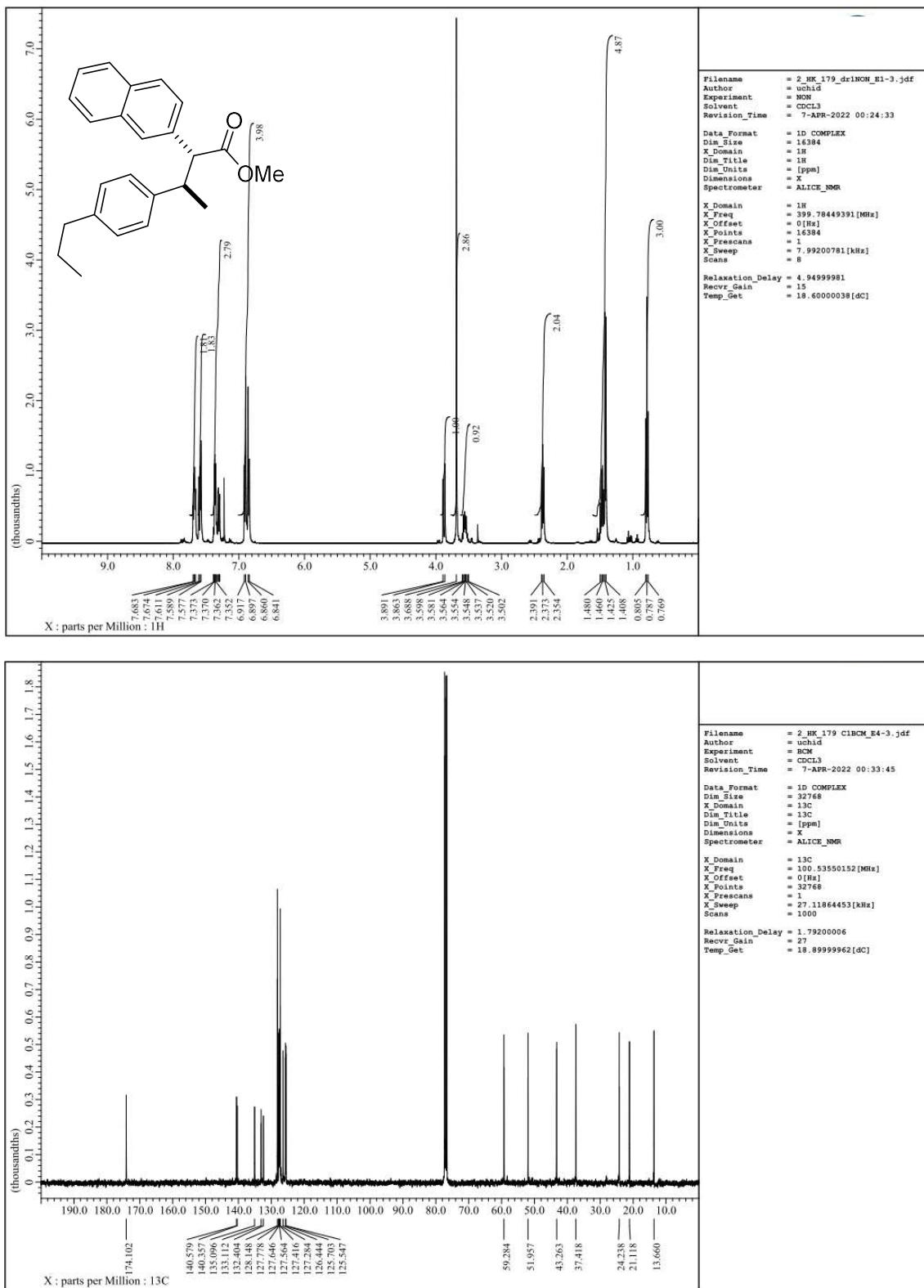
11.11. Methyl (2*R*,3*R*)-3-(4-bromophenyl)-2-(2-naphthyl)butanoate



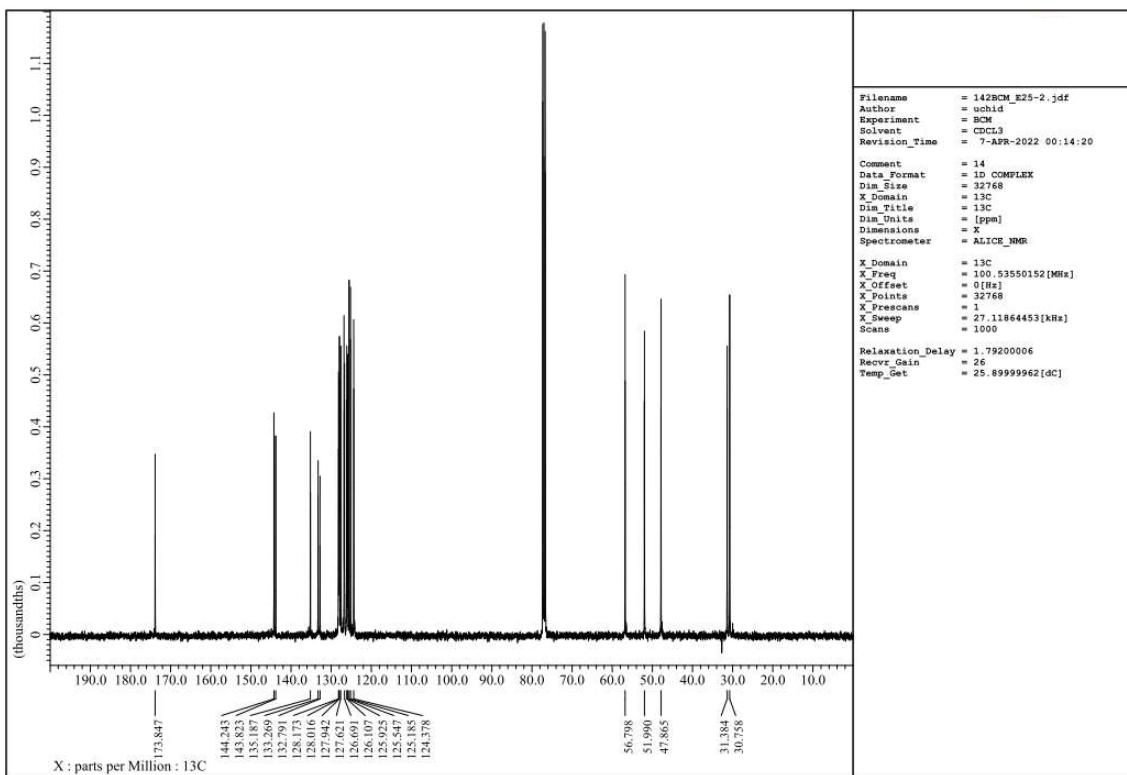
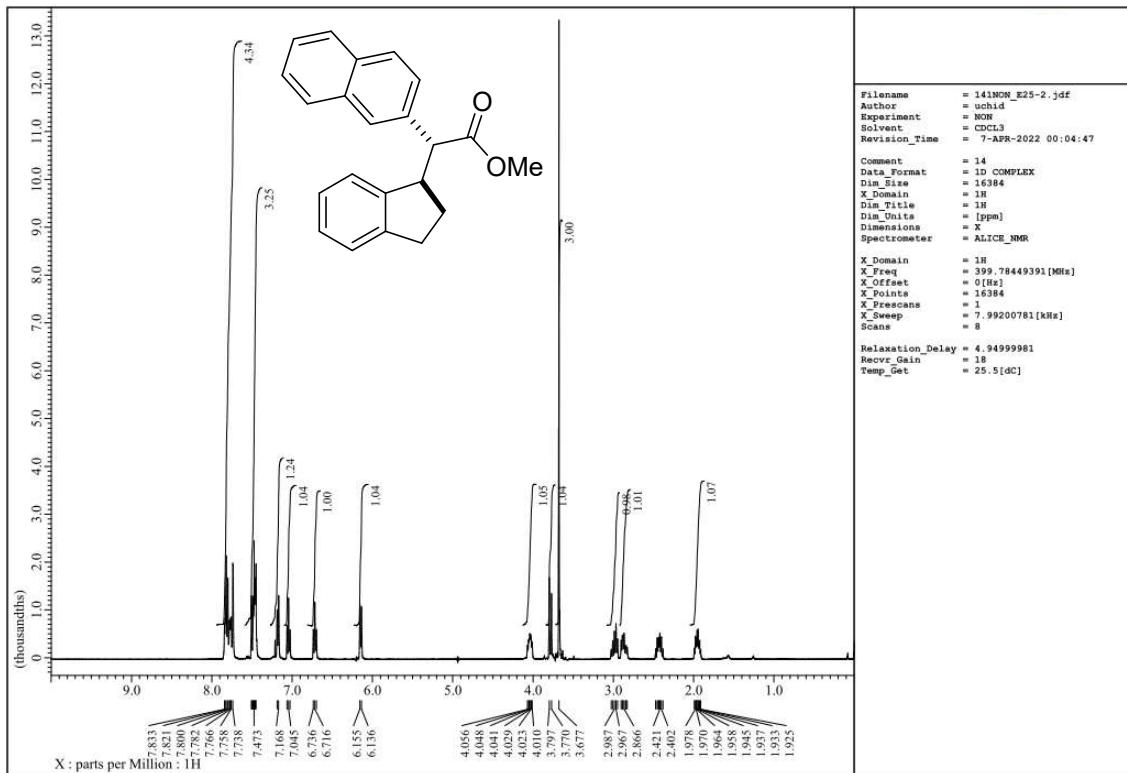
11.12. Methyl (*2R*^{*},*3R*^{*})-3-(4-methylphenyl)-2-(2-naphthyl)butanoate



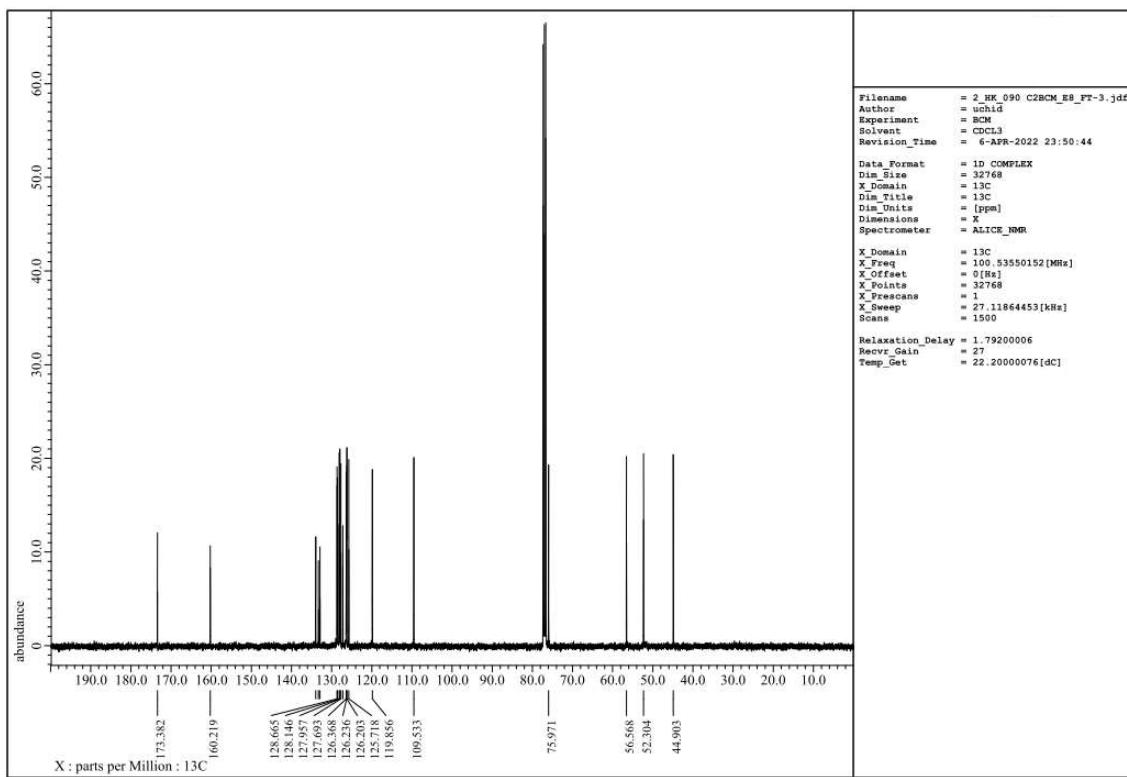
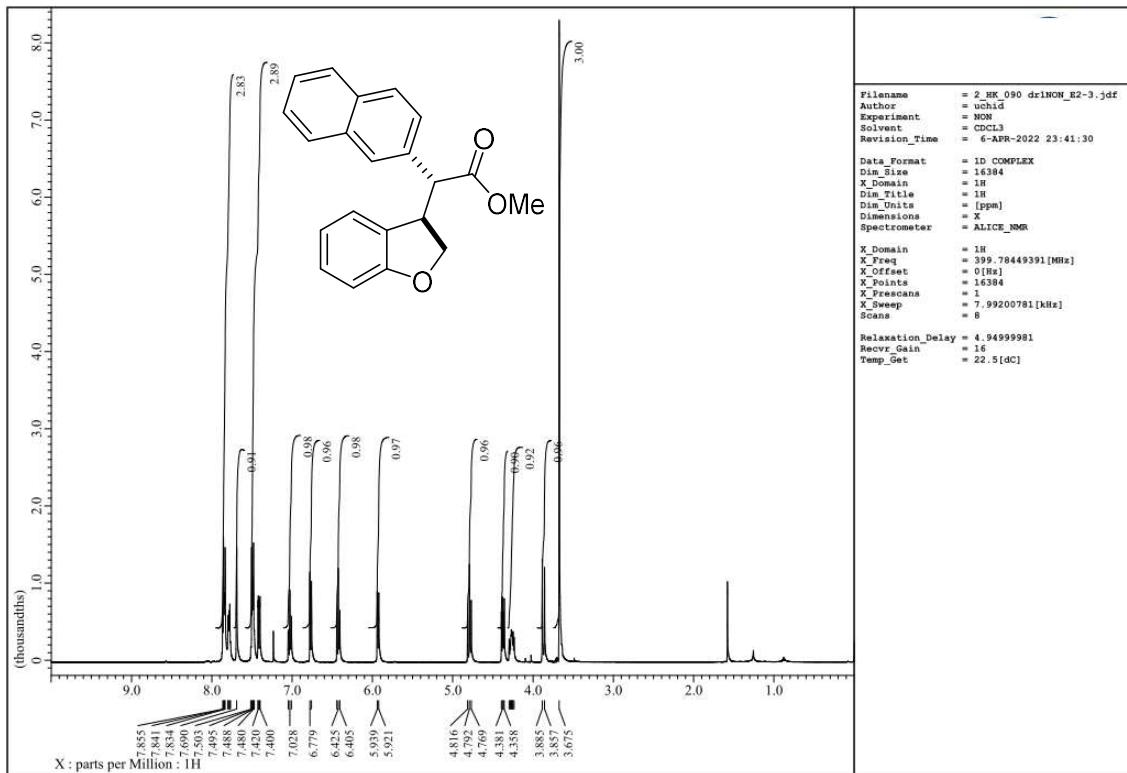
11.13. Methyl (2*R*^{*},3*R*^{*})-2-(2-naphthyl)-3-(4-*n*-propylphenyl)butanoate



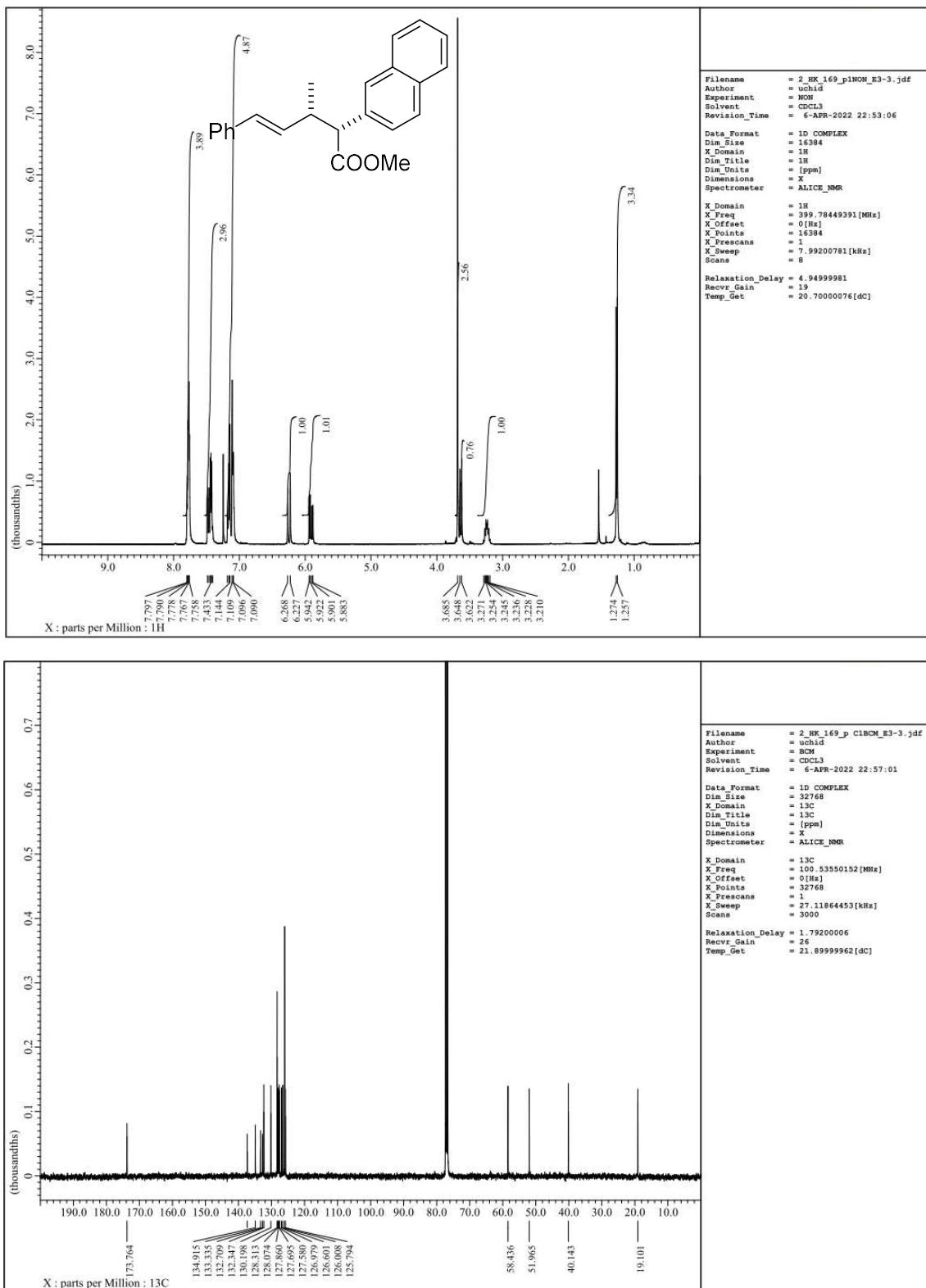
11.14. Methyl (*R*^{*})-2-((*R*^{*})-2,3-dihydro-1*H*-inden-1-yl)-2-(2-naphthyl)acetate



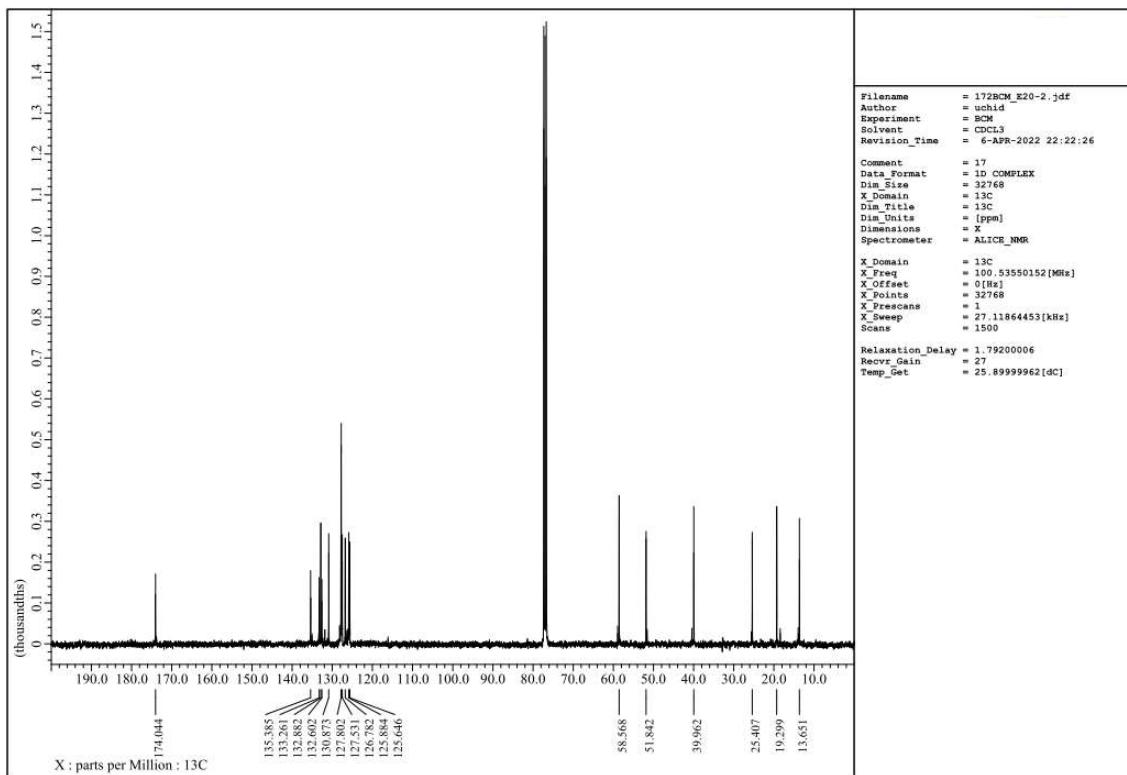
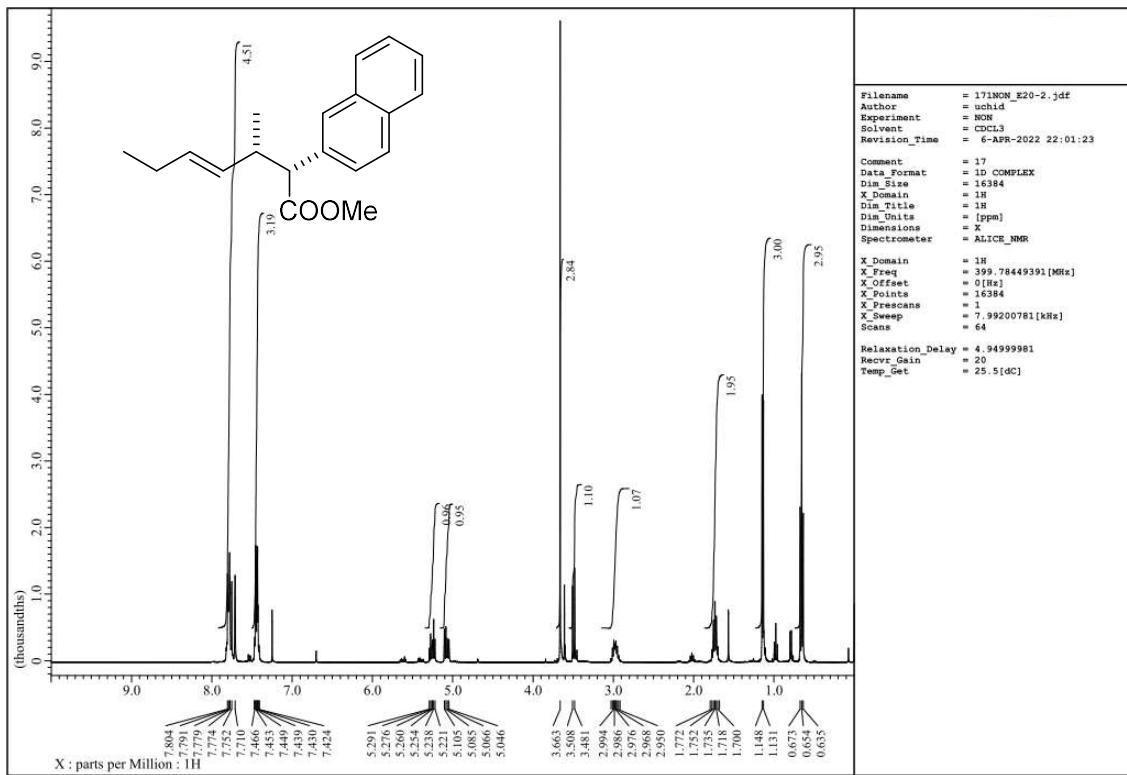
11.15. Methyl (*R*^{*})-2-((*R*^{*})-2,3-dihydrobenzofuran-3-yl)-2-(2-naphthyl)acetate



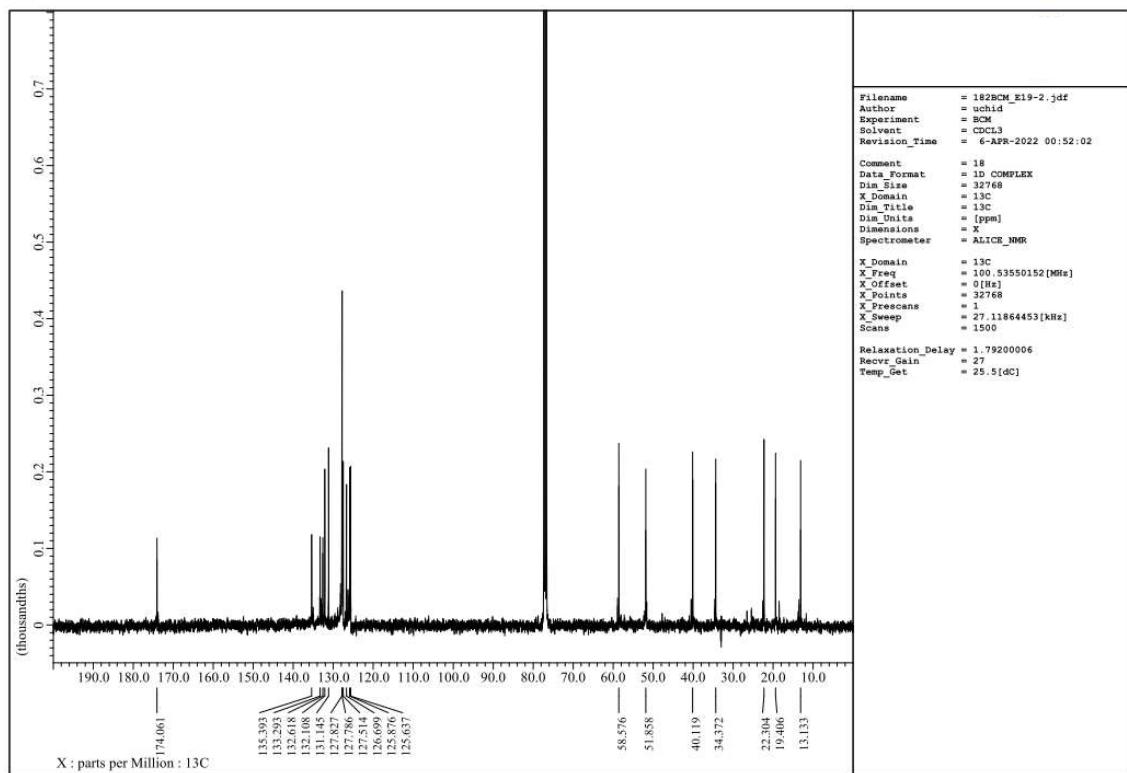
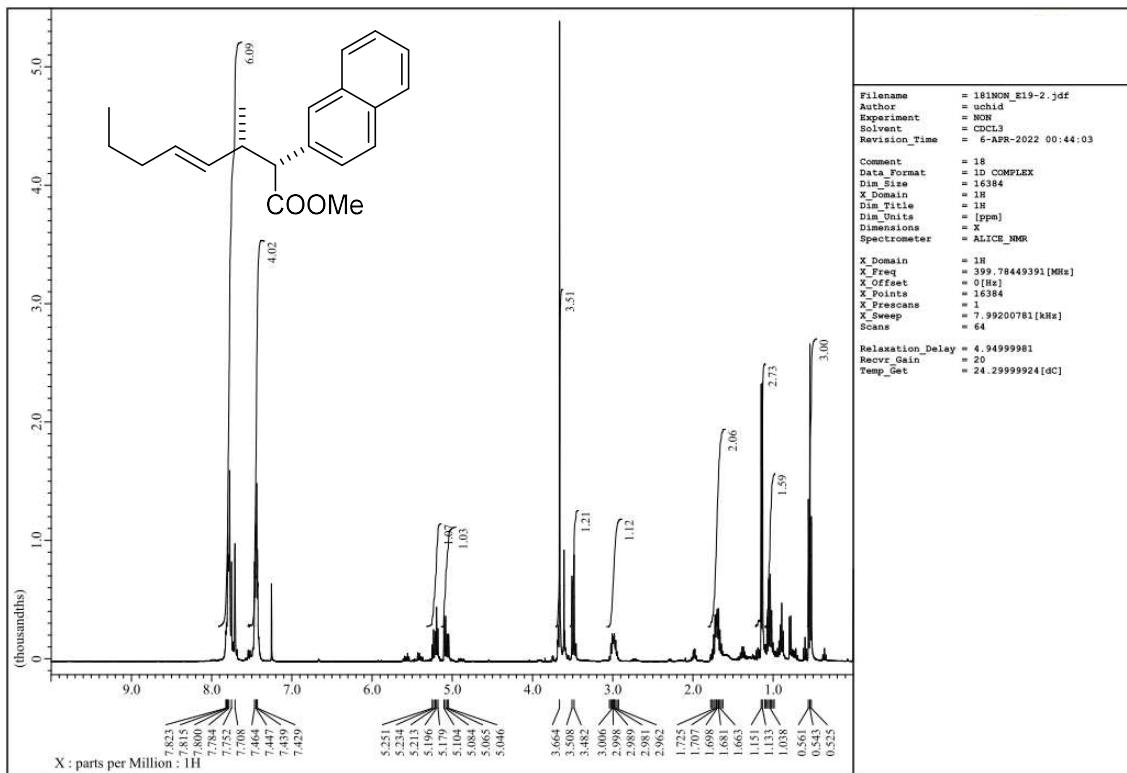
11.16. Methyl (2*R*^{*},3*R*^{*},4*E*)-3-methyl-2-(2-naphthyl)-5-phenylpent-4-enoate



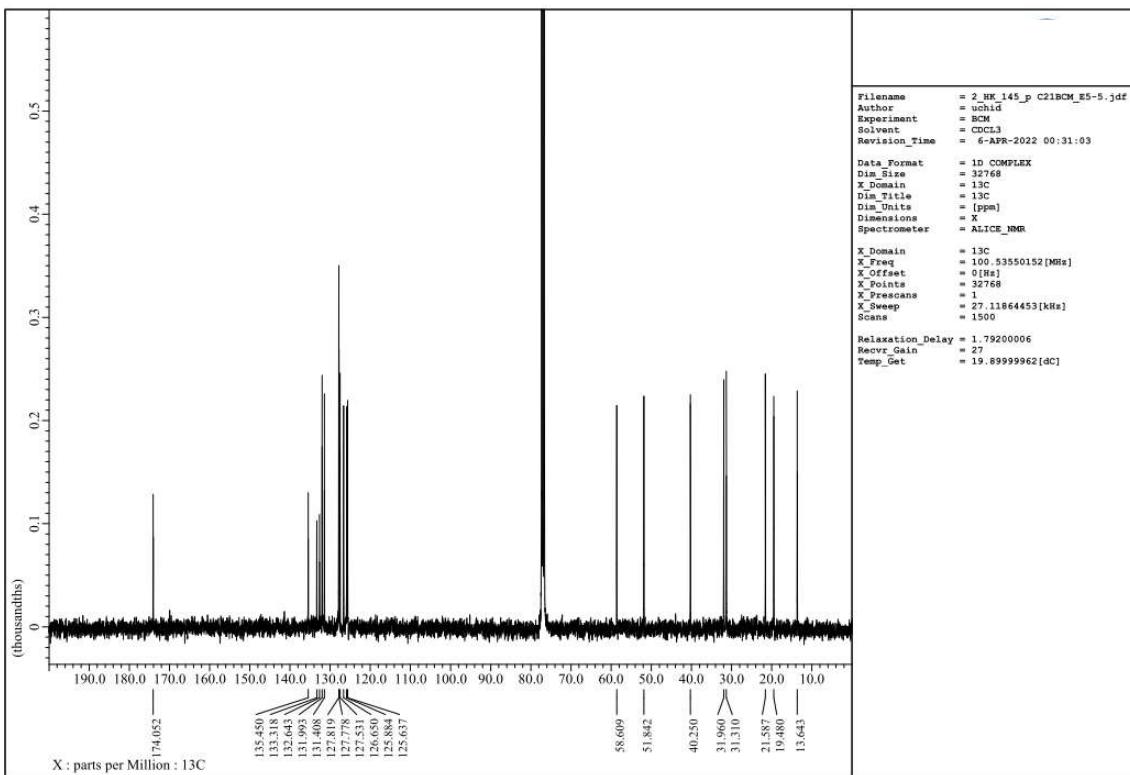
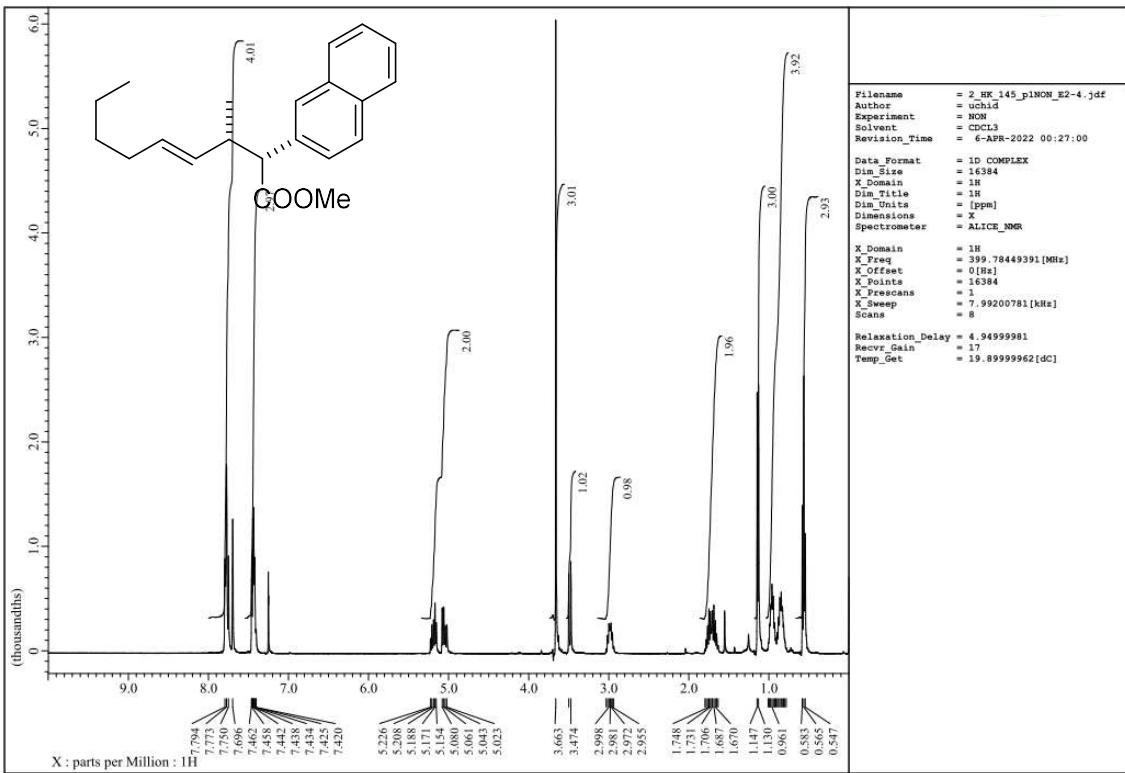
11.17. Methyl (2*R*^{*},3*R*^{*},4*E*)-3-methyl-2-(2-naphthyl)hept-4-enoate



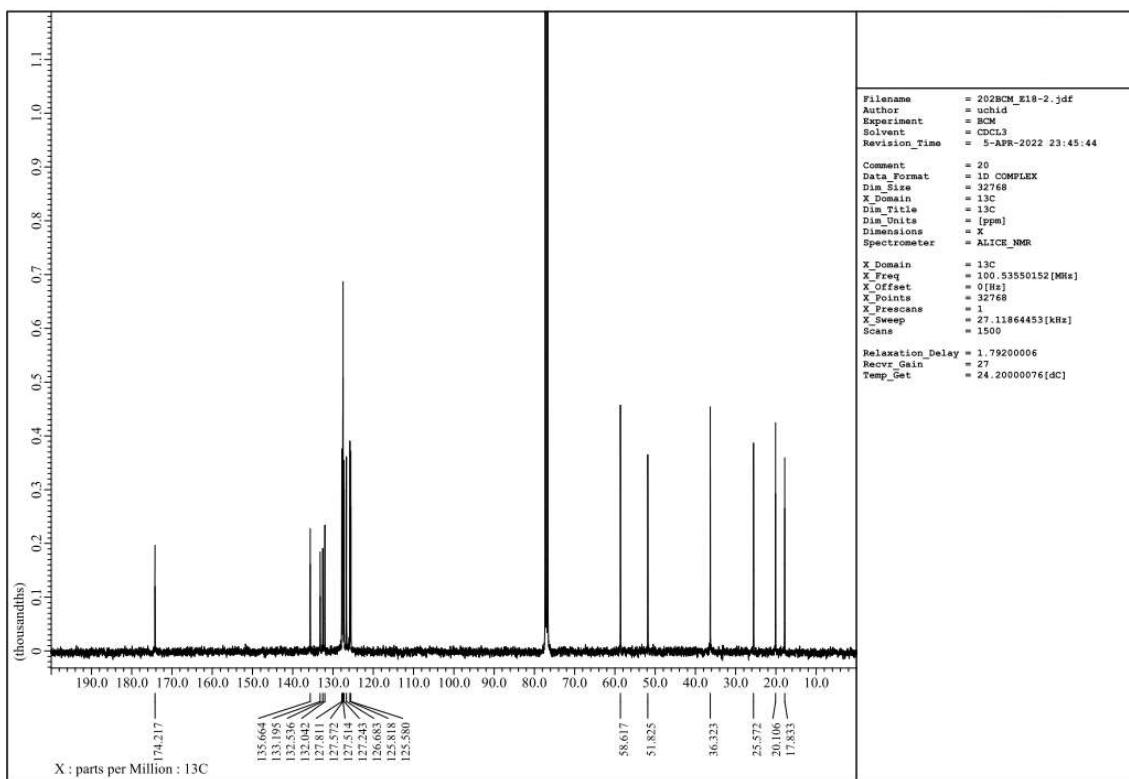
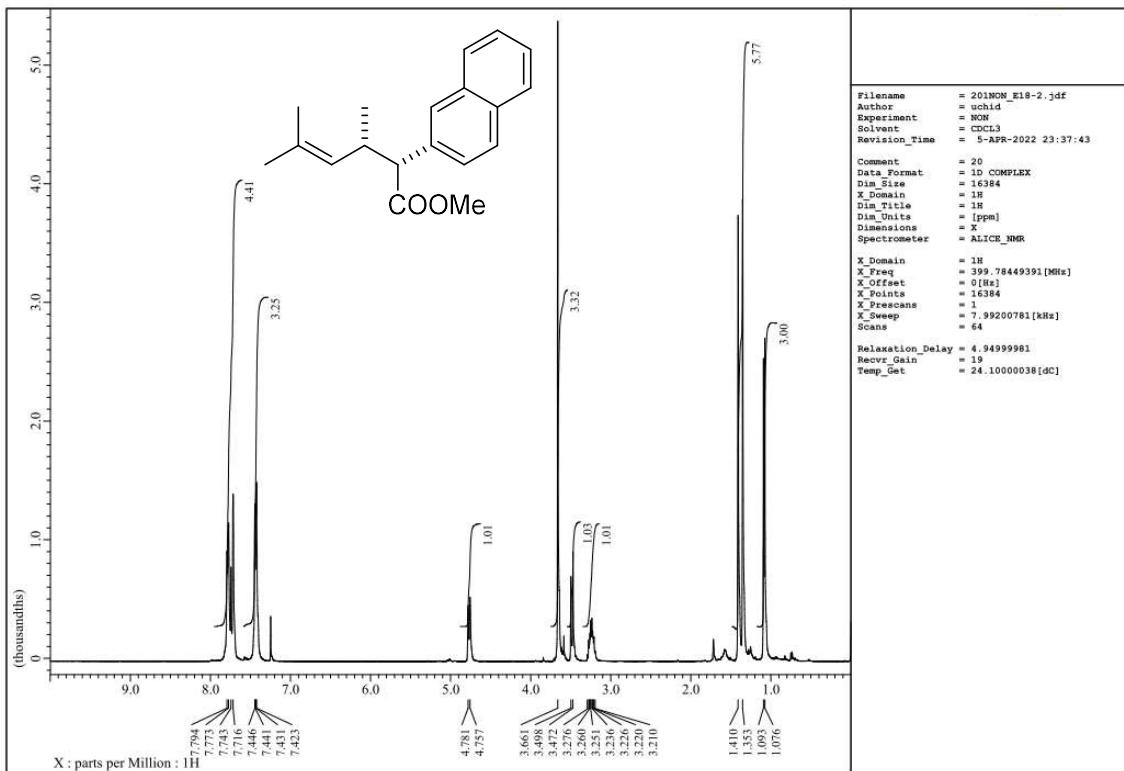
11.18. Methyl (2*R*^{*},3*R*^{*},4*E*)-3-methyl-2-(2-naphthyl)oct-4-enoate



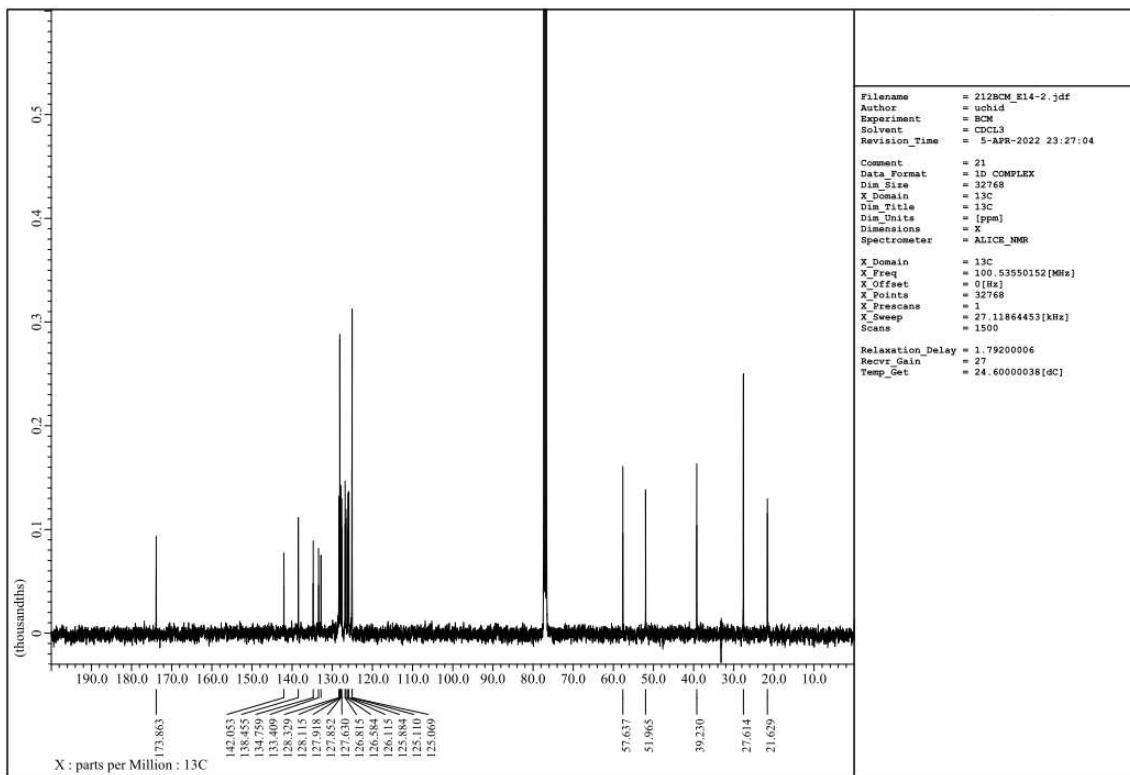
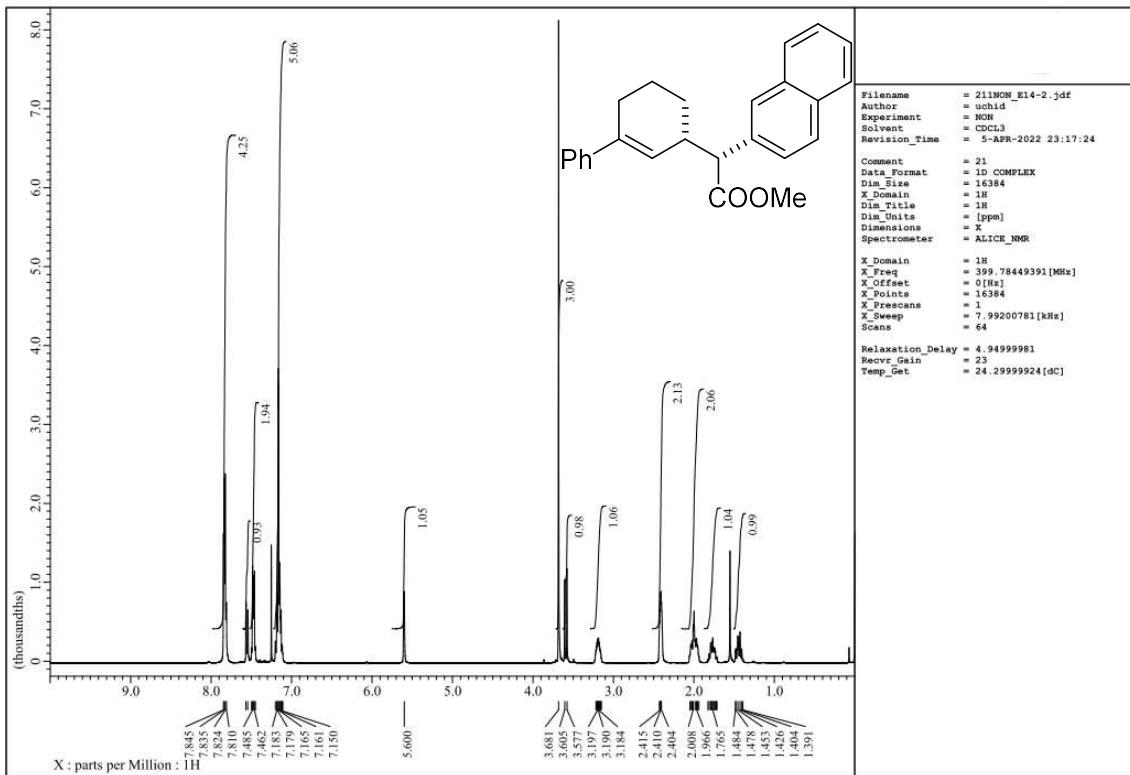
11.19. Methyl (*2R*^{*},*3R*^{*},*4E*)-3-methyl-2-(2-naphthyl)non-4-enoate



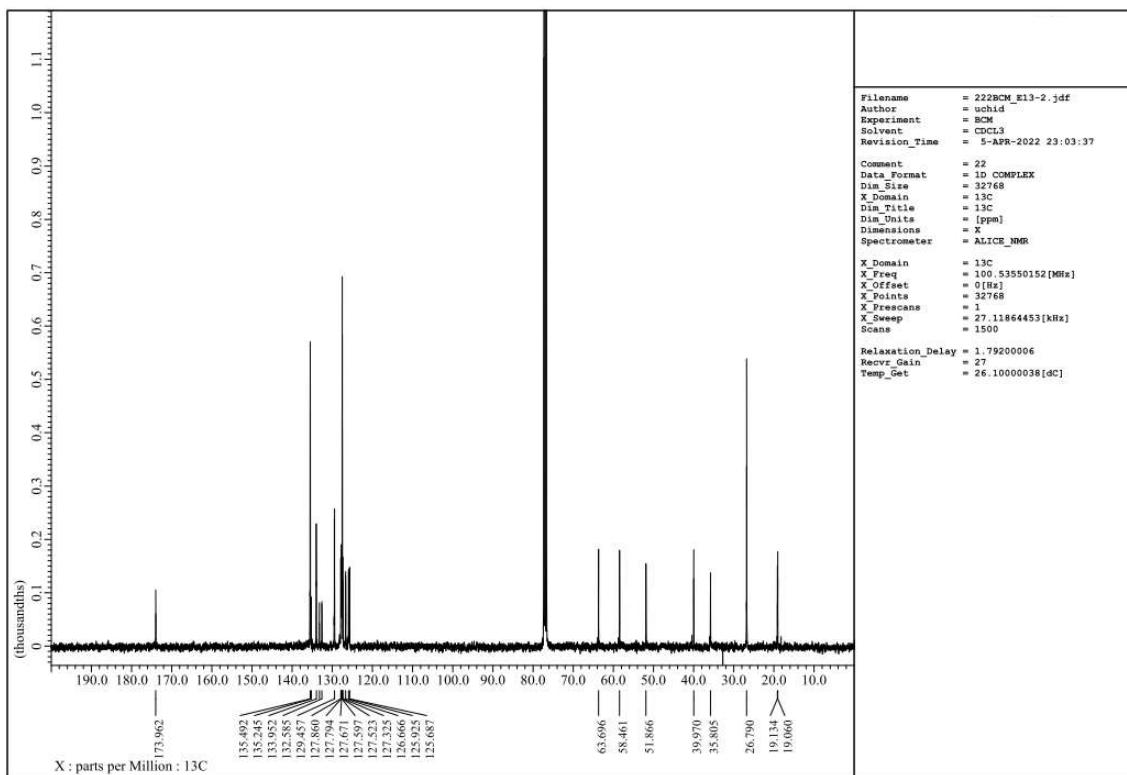
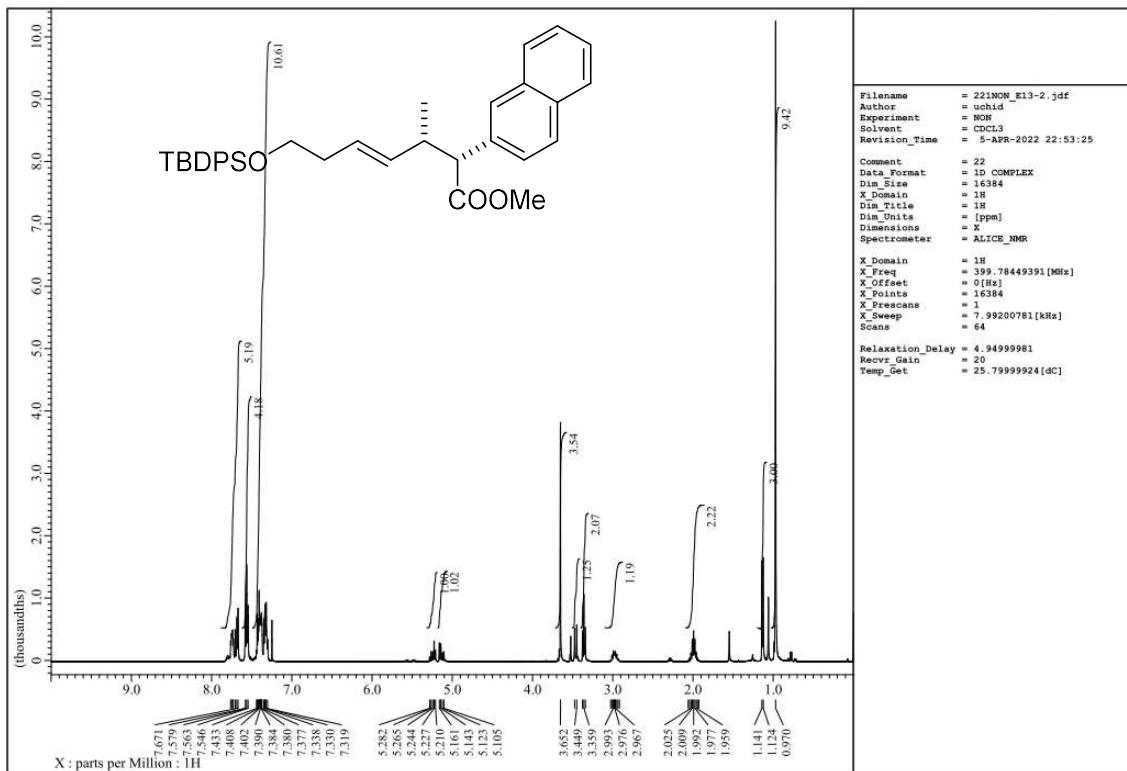
11.20. Methyl (*2R*^{*},*3R*^{*})-3,5-dimethyl-2-(2-naphthyl)hex-4-enoate



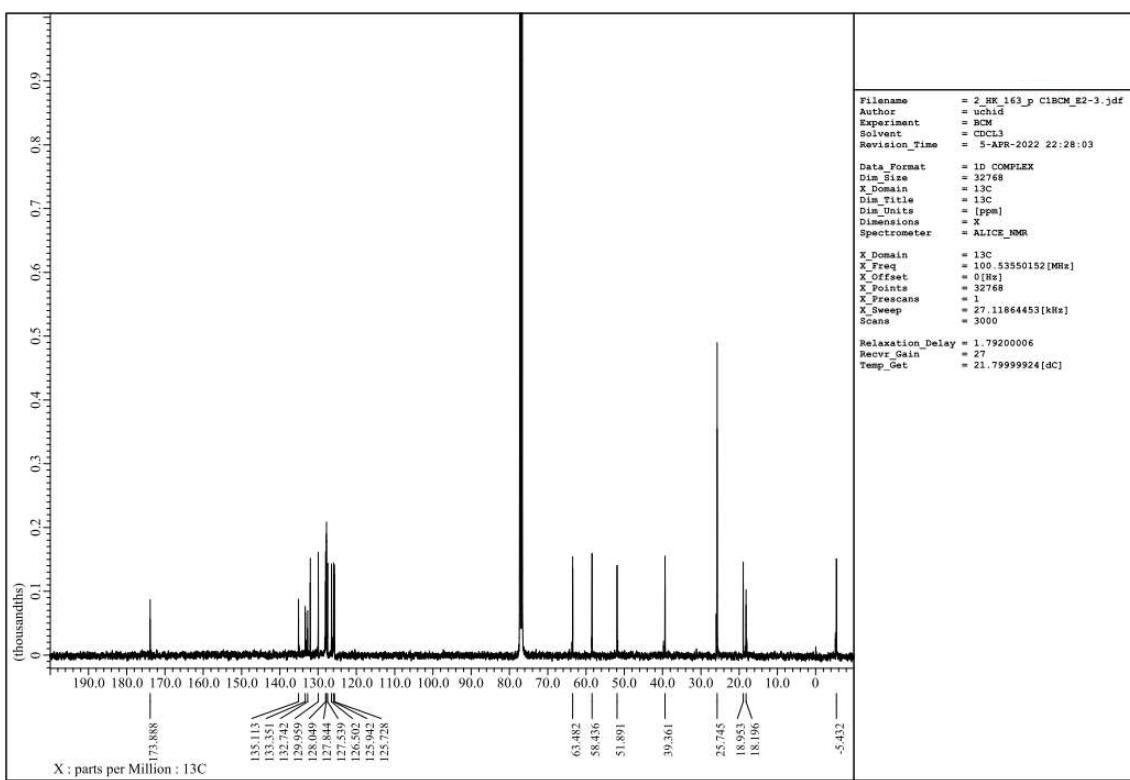
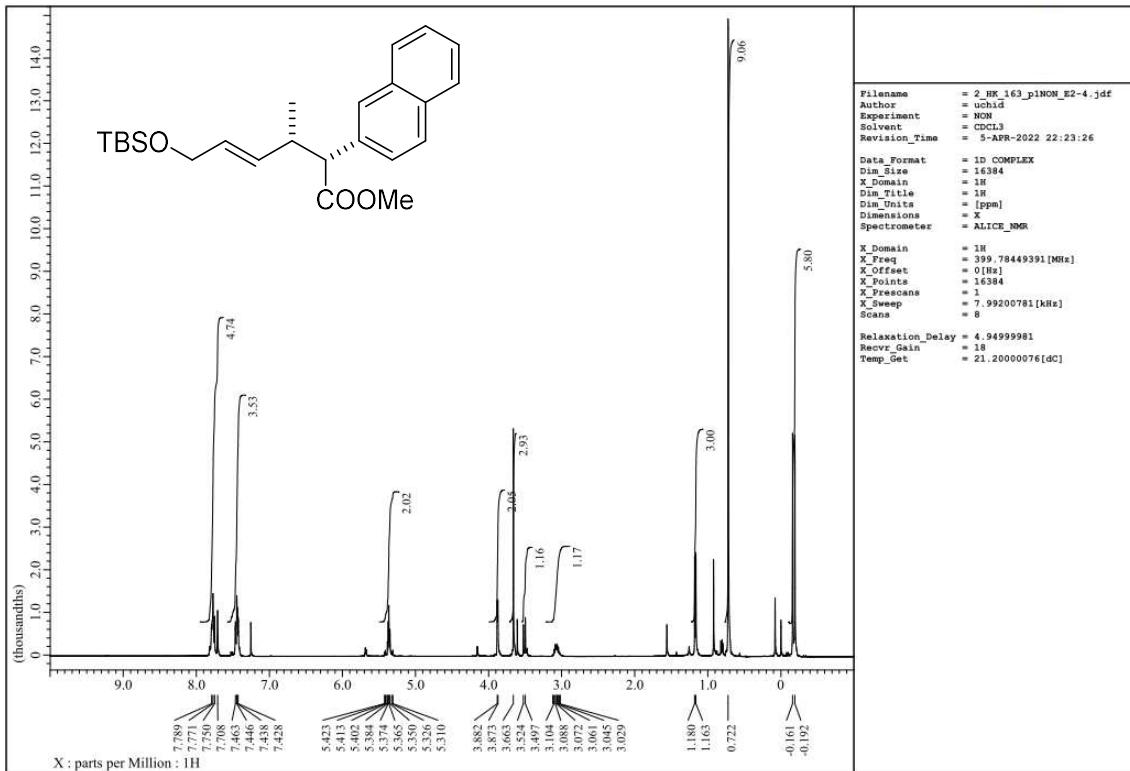
11.21. Methyl (2*R*^{*}-2-((*R*^{*})-3-phenylcyclohex-2-en-1-yl)-2-(2-naphthyl)acetate



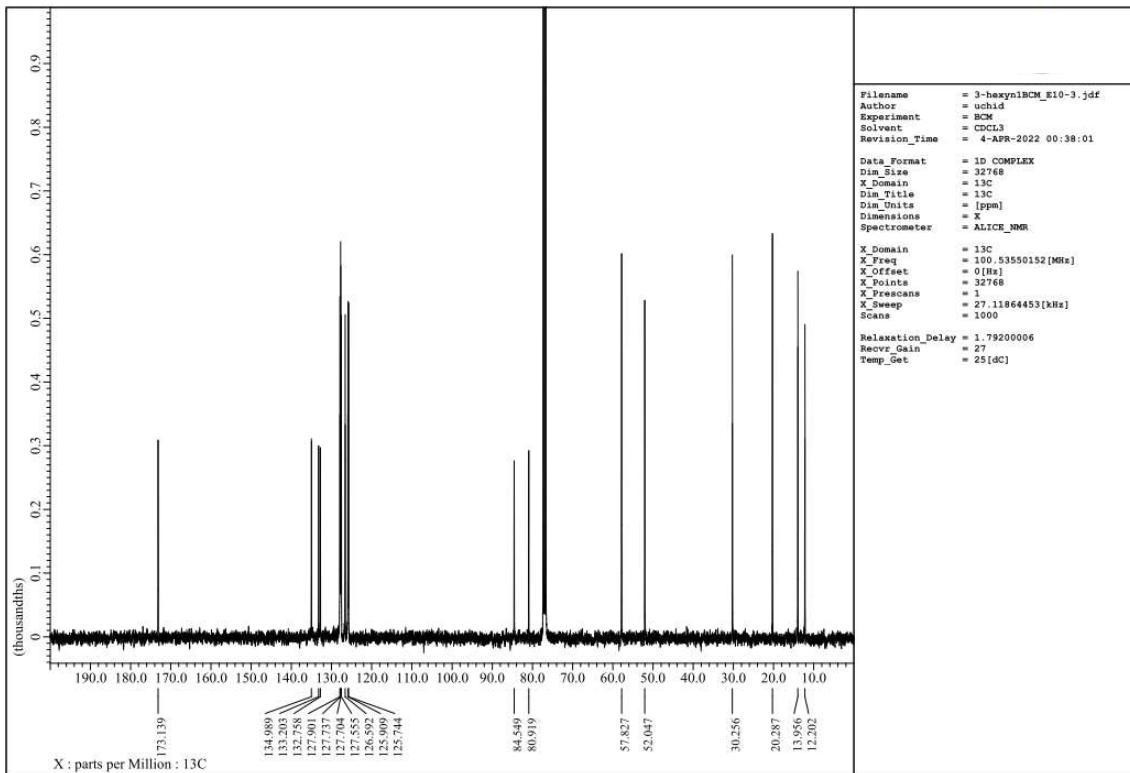
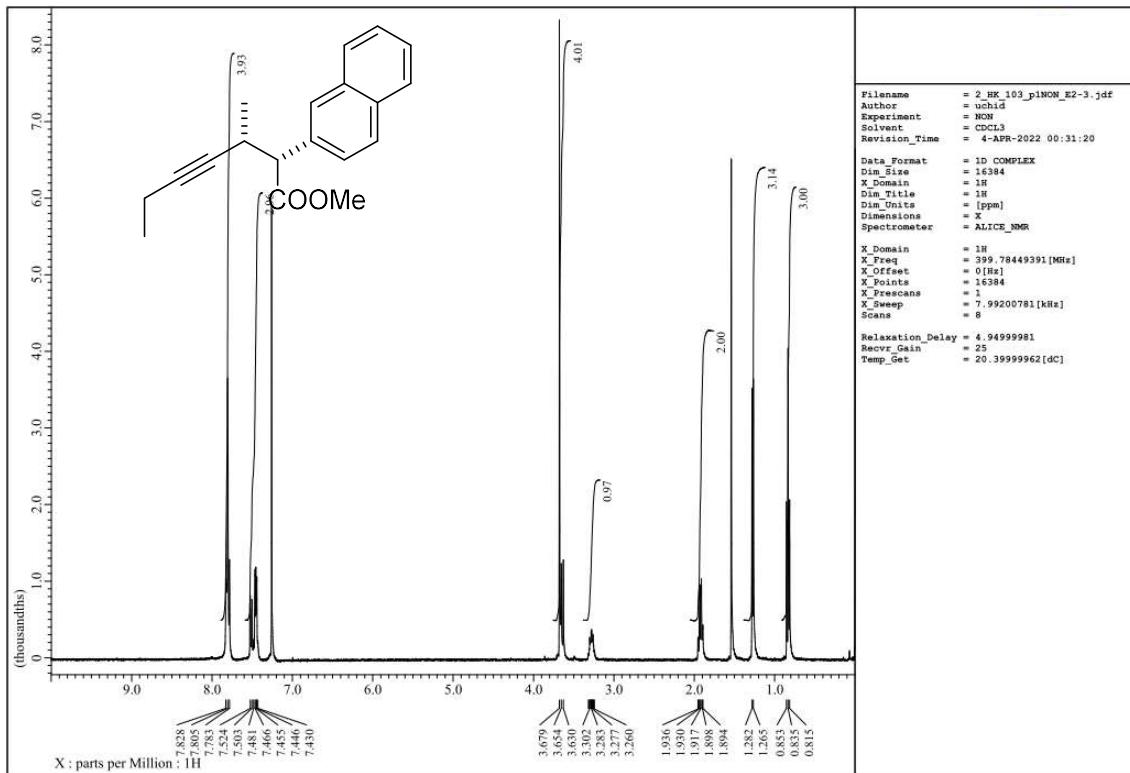
11.22. Methyl (2*R*^{*,3*R*^{*,4*E*})-7-*tert*-butyldiphenylsilyloxy-3-methyl-2-(2-naphthyl)he-pt-4-enoate}



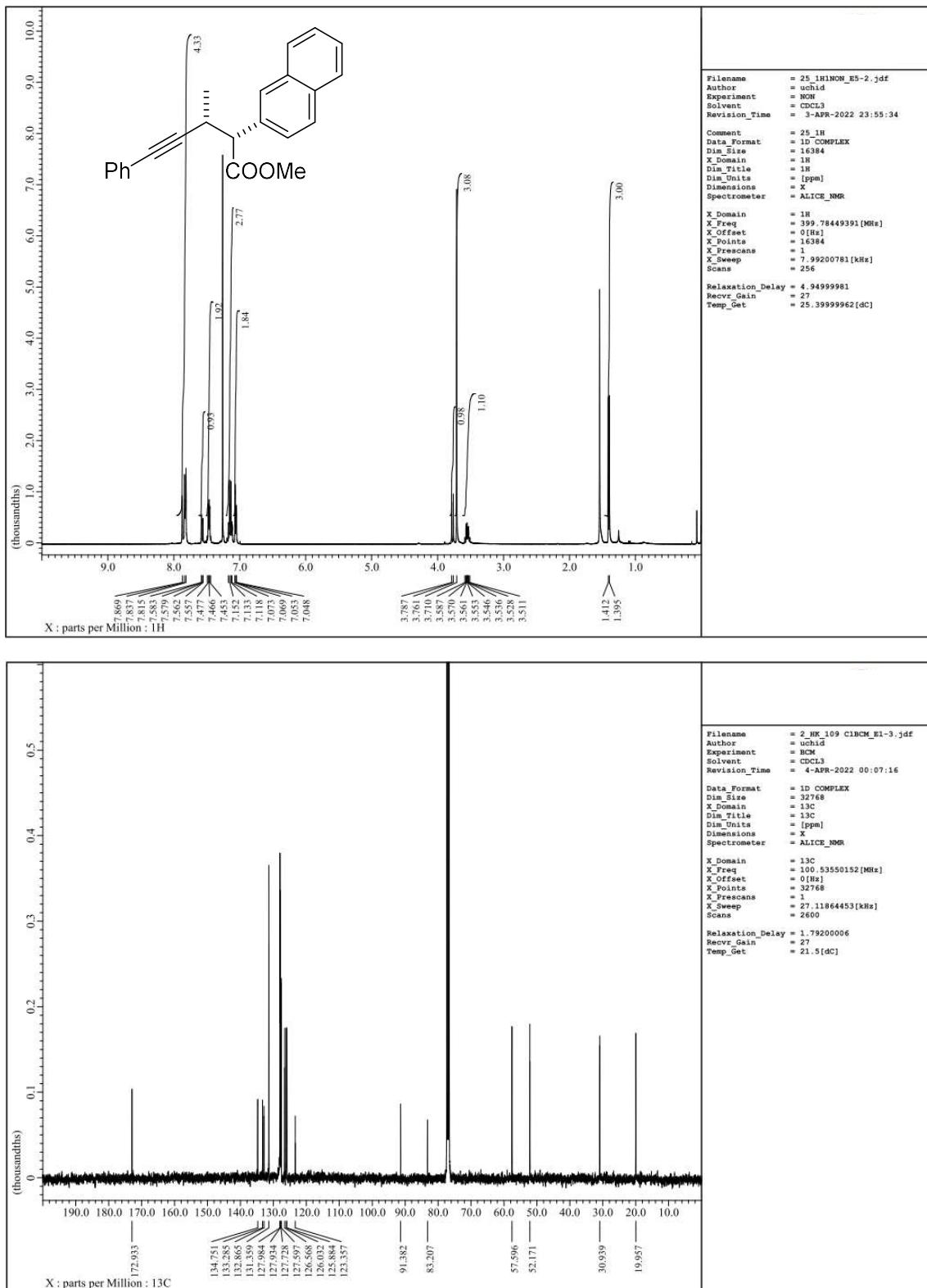
11.23. Methyl (2*R*^{*,3*R*^{*,4*E*})-6-*tert*-butyldimethylsilyloxy-3-methyl-2-(2-naphthyl)hept-4-enoate}



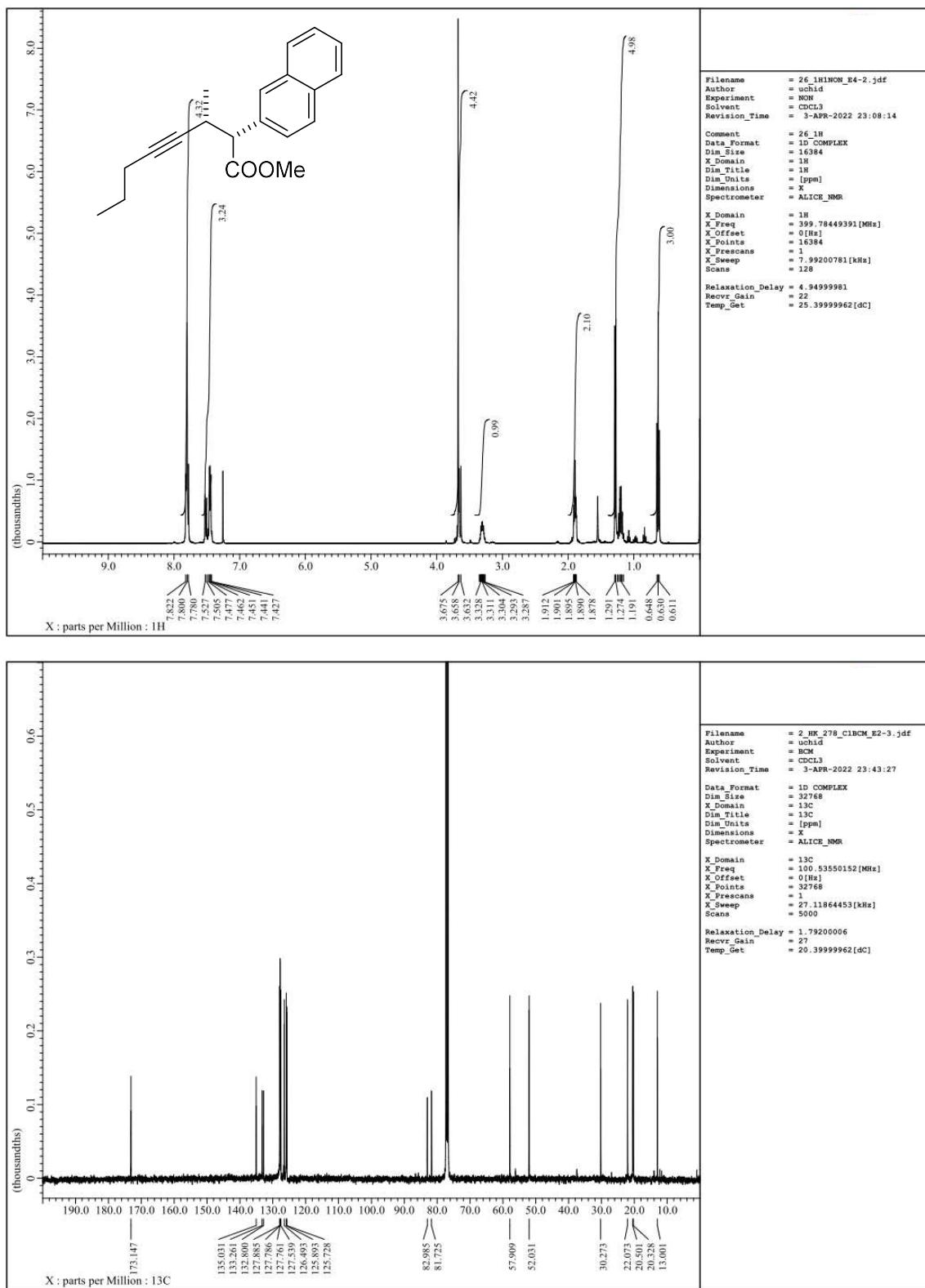
11.24. Methyl (2*R*^{*},3*R*^{*})-3-methyl-2-(2-naphthyl)hept-4-ynoate



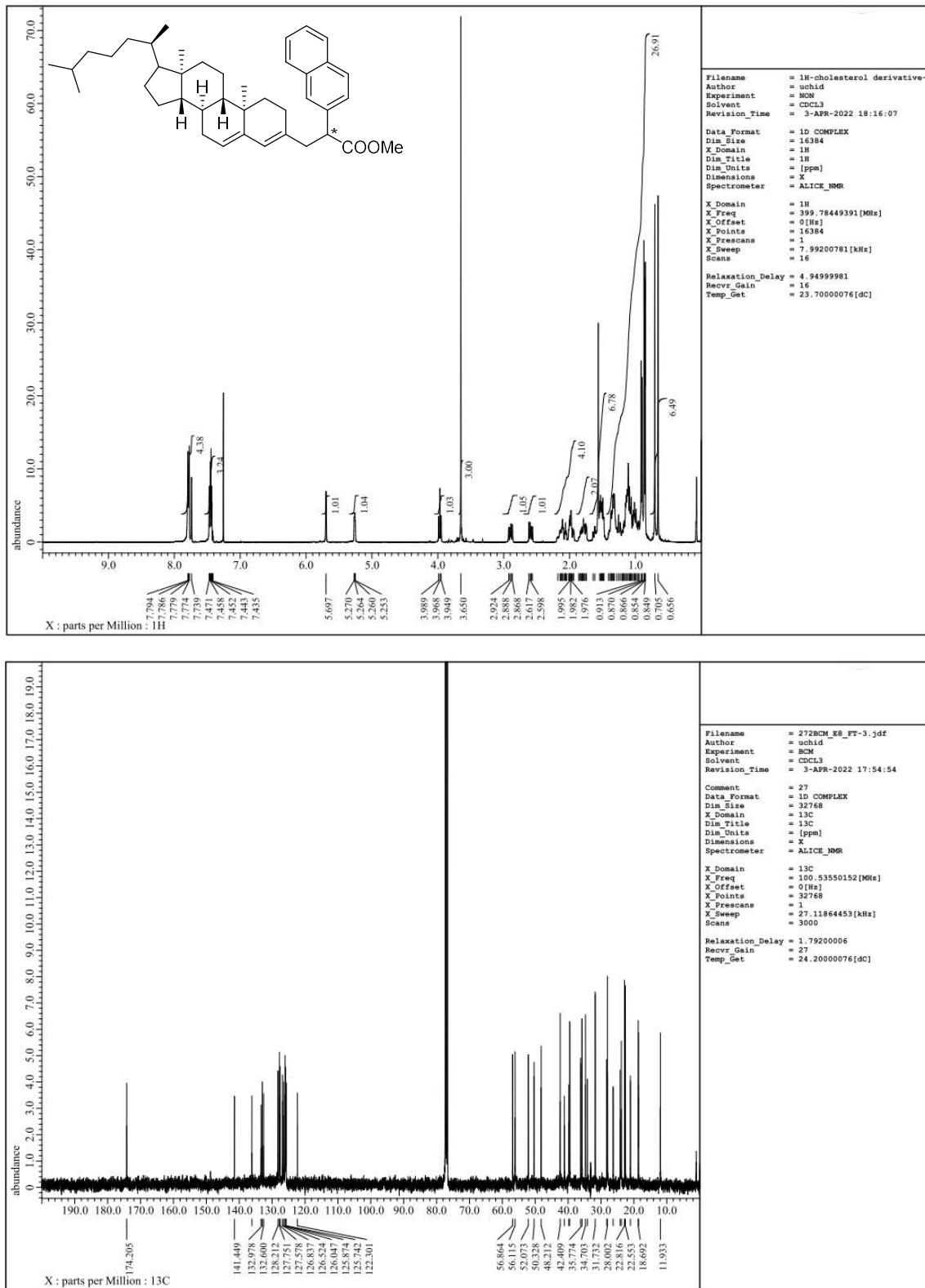
11.25. Methyl (2*R*^{*},3*R*^{*})-3-methyl-2-(2-naphthyl)-5-phenylpent-4-ynoate



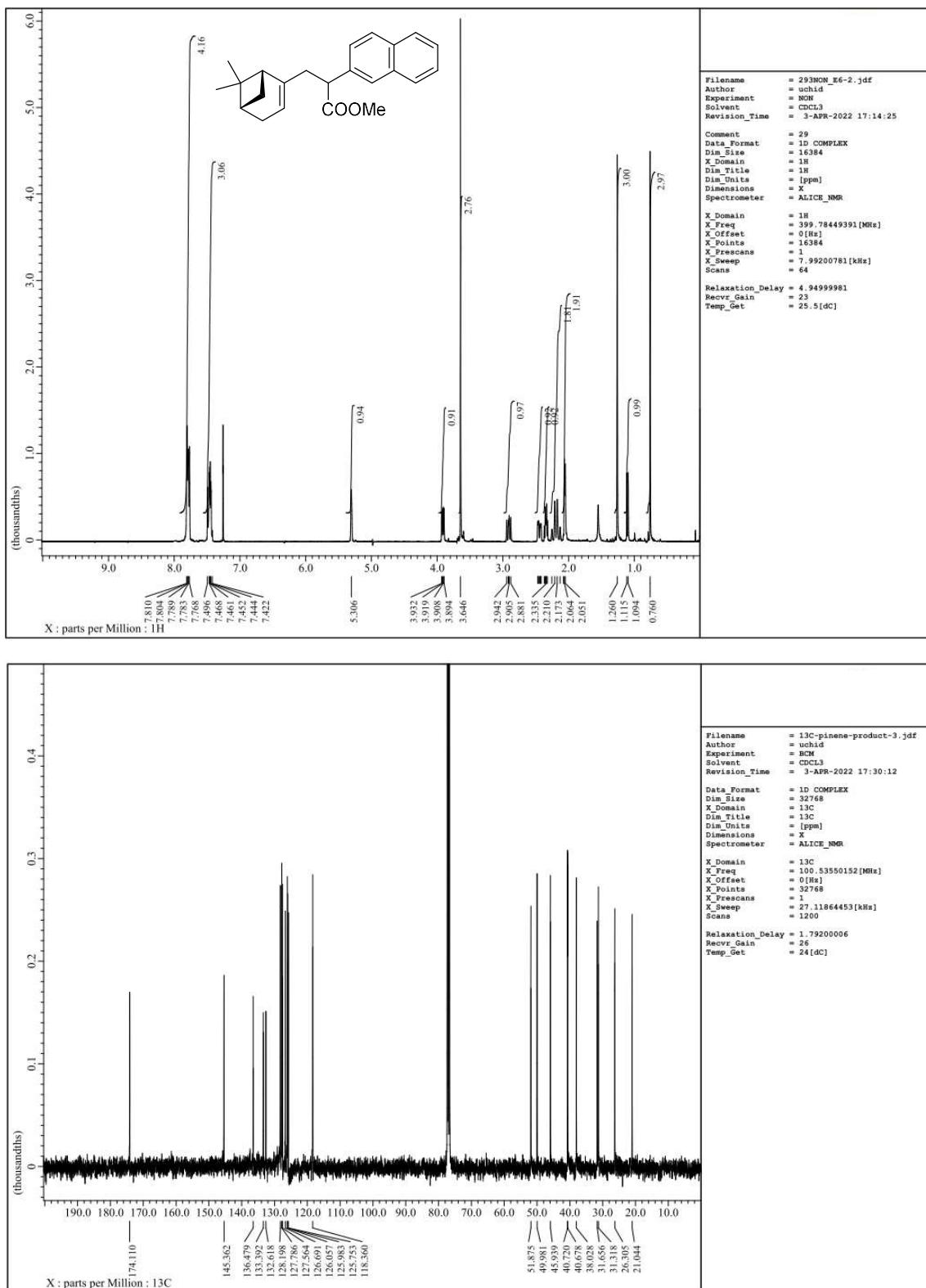
11.26. Methyl (2*R*^{*},3*R*^{*})-3-methyl-2-(2-naphthyl)oct-4-ynoate



11.27. Methyl cholesta-3,5-dien-3-yl-(2-naphthyl)-ethanoate



11.28. Methyl 6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-((2-naphthyl)acetate)



11.29. Methyl Carene-5-((2-naphthyl)acetate)

