Supporting Information

for

Effects of Silver Carbonate and *p*-Nitrobenzoic Acid for Accelerating Palladium-Catalyzed Allylic C-H Acyloxylation

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I. General Information

All reactions were performed under aerobic conditions using 4 mL vial. 7-Octenoic acid, all alkenes, and *White catalyst* were purchased and used as received. Esters **1a** and **1j**,[1] amide **1k**,[2] and ketal **1l**[3] were synthesized by following literature procedures, and ethyl 6-acetoxyoct-7-enoate (**3aa'**) was prepared by acetylation of ethyl 6-hydroxy-7-octenoate.[1] 1,4-Dioxane was distilled over benzophenone ketyl under argon atmosphere, and stored under argon before use. NMR spectra were measured on a Bruker AV400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, and 376 MHz for ^{19}F) at 303 K in 5 mm NMR tubes. ^{1}H NMR signals were reported as follows: chemical shifts in ppm (δ) with the solvent resonance as the internal standard in $CDCl_3$ at δ 7.26 and C_6D_6 at δ 7.16, multiplicity (s = singlet, d = doublet, t = triplet, q= quartet, quin = quintet, sx = sextuplet and m = multiple), coupling constant (*J*) in Hz, and integration. All ^{13}C NMR chemical shifts were reported in ppm (δ) relative to carbon resonances in $CDCl_3$ at δ 77.16 and C_6D_6 at δ 128.06. Melting points were determined using a Büchi (Model M565) automated melting point system (temperature measurement accuracy is 0.1 ºC). Column chromatography was performed with SiO_2 (Silica Flash F60, 230-400 mesh). Mass spectra and high-resolution mass spectra (HRMS) were obtained on JEOL JMS700 (double-focusing mass spectrometer) for EI and CI and on Thermo Fisher SCENTIFIC Orbitrap XL (ion trap) for ESI.

II. General Procedure for the Pd(II)-Catalyzed Allylic C-H Acyloxylation

To an oven-dried screw-capped vial, ethyl oct-7-enoate (**1a**) (51.1 mg, 0.30 mmol), *p*-nitrobenzoic acid (**2a**) (50.2 mg, 0.30 mmol), White catalyst (1.5 mg, 0.003 mmol, 1 mol%), and Ag_2CO_3 (0.9 mg, 0.003 mmol, 1 mol%) were added. 1,4-Dioxane (0.50 mL) was added to the vial, where the concentration of **1a** was 0.60 M. The mixture was stirred at 45 °C for 24 h in aluminum heating block, and then allowed to cool to room temperature. The crude product was washed with saturated aqueous solution of $NaHCO_3$ (20 mL), and the organic products were extracted with EtOAc (3 x 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, and was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (hexane/EtOAc = 8/2 as the eluent) to afford the desired product **3aa** in 89% yield (89.6 mg) as a colorless oil (Table 1, entry 14).

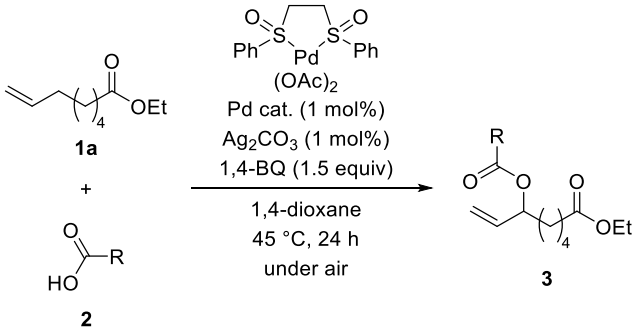
Reaction in 1 mmol scale:

To an oven-dried screw-capped vial, ethyl oct-7-enoate (**1a**) (170.3 mg, 1 mmol), *p*-nitrobenzoic acid (**2a**) (167.2 mg, 1 mmol), White catalyst (5.1 mg, 0.010 mmol, 1 mol%), and Ag_2CO_3 (2.8 mg, 0.010 mmol, 1 mol%) were added. 1,4-Dioxane (1.65 mL) was added to the vial, where the concentration of **1a** was 0.60 M. The mixture was stirred at 45 °C for 24 h in aluminum heating block, and then allowed to cool to room temperature. The mixture was taken to work-up as mentioned above. Thereafter, the residue was purified by silica-gel column chromatography (hexane/EtOAc = 8/2 as the eluent) to afford the desired product **3aa** in 84% yield (0.2828 g) as a colorless oil.

III. Screening of Carboxylic Acids for the Pd(II)-Catalyzed Allylic C-H Acyloxylation

We examined other carboxylic acids **2b-2j** for the allylic acyloxylation of **1a**, as summarized in Table S1. Arylcarboxylic acids **2b-2d** with electron-withdrawing substituents afforded the carboxylated products **3ab-3ad** in 31% to 38% yield (entries 1-3), whereas the reactions with **2e-2g** resulted in rather low yields (entries 4-6). In general, aliphatic carboxylic acids such as acetic acid are used for such allylic acyloxylation reactions of alkenes in the presence of higher loading (more than 5 mol%) of the palladium catalyst; however, both acetic acid and pivalic acid as well as more acidic trifluoroacetic acid were totally ineffective for the reaction (entries 7-9). Accordingly, we selected 4-nitrobenzoic acid (**2a**) as the best carboxylate source for this C(sp^3)-H acyloxylation reaction.

Table S1. Effect of Carboxylic Acids for the Catalytic Activity[a]



entry	R	conv. of **1a** (%)	Yield of **3** (%)	L/B ratio
1	4-$CF_3C_6H_4$ (**2b**)	44	38	7/93
2	4-ClC_6H_4 (**2c**)	36	31	3/97
3	4-FC_6H_4 (**2d**)	41	34	<1/>99
4	C_6H_5 (**2e**)	33	28	3/97
5	4-MeC_6H_4 (**2f**)	31	23	3/97
6	4-$MeOC_6H_4$ (**2g**)	27	18	<1/>99
7	CH_3 (**2h**)	<5	n.d.	-
8	^{t}Bu (**2i**)	<5	trace	-
9	CF_3 (**2j**)	<5	n.d.	-

[a]Conditions: **1a** (0.30 mmol), **2** (0.30 mmol, 1.0 equiv.), Pd cat. (1 mol%), Ag_2CO_3 (1 mol%), 1,4-BQ (1.5 equiv.) in 1,4-dioxane (0.50 mL) at 45 °C for 24 h.

IV. Synthesis of Ethyl 6,8-Dihydroxyoctanoate 5 (Scheme 2)

Hydroboration of 3aa': To a THF solution of ethyl 6-acetoxyoct-7-enoate (**3aa'**, 100.0 mg, 0.438 mmol) in an Ar-filled Schlenk tube was added 9-BBN (0.5 M in THF, 2.6 mL, 1.314 mmol) at 0 °C under argon. The reaction mixture was stirred at rt for 5 hours until the starting material was consumed (monitored by TLC). The reaction mixture was cooled to 0 °C, 2.0 M aqueous NaOH (1.0 mL) and 30% H_2O_2 (1.0 mL) were added to the reaction mixture. After stirring for 2 hours at rt, the reaction mixture extracted with ethyl acetate (3 x 10 mL). The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was

purified by silica-gel column chromatography (hexanes/EtOAc = 7/3 as the eluent) to afford ethyl 6-acetoxy-8-hydroxyoctanoate (**4**) in 45% yield (49.0 mg, 0.199 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.05 – 4.93 (m, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.69 – 3.56 (m, 1H), 3.54 – 3.46 (m, 1H), 2.46 (bs, 1H), 2.27 (t, *J* = 7.4 Hz, 2H), 2.05 (s, 3H), 1.86 – 1.74 (m, 1H), 1.70 – 1.48 (m, 5H), 1.42 – 1.26 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 172.0, 71.5, 60.4, 58.7, 37.5, 34.4, 34.2, 25.1, 24.8, 21.2, 14.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{22}O_5Na$ 269.1365; Found 269.1359.

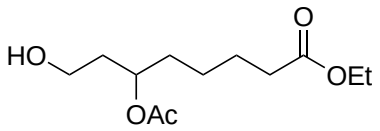
Hydrolysis of 4: Ethyl 6-acetoxy-8-hydroxyoctanoate (**4**, 100.0 mg, 0.406 mmol) was dissolved in EtOH (1.0 mL) in an Ar-filled Schlenk tube, and EtONa (0.411 mmol) in EtOH was added at rt under argon. The reaction mixture was further stirred for 2 hours until the starting material was consumed (monitored by TLC). The reaction mixture was quenched by adding saturated ammonium chloride solution (5.0 mL), and the organic product was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was purified by silica-gel column chromatography (hexanes/EtOAc = 5/5 as the eluent) to afford ethyl 6,8-dihydroxyoctanoate (**5**) in 78% yield (65.0 mg, 0.318 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.09 (q, *J* = 7.1 Hz, 2H), 3.88 – 3.71 (m, 3H), 3.15 (s, 2H), 2.28 (t, *J* = 7.4 Hz, 2H), 1.73 – 1.54 (m, 4H), 1.54 – 1.27 (m, 4H), 1.22 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 71.6, 61.6, 60.4, 38.4, 37.4, 34.3, 25.1, 24.9, 14.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{20}O_4Na$ 227.1259; Found 227.1254.

Ethyl 6-acetoxy-8-hydroxyoctanoate (4) 45% yield. Colorless oil



^{1}H NMR (400 MHz, $CDCl_3$) δ 5.00 (dddd, *J* = 11.3, 8.2, 4.9, 3.4 Hz, 1H), 4.17 – 4.04 (m, 2H), 3.66 – 3.56 (m, 1H), 3.51 (ddd, *J* = 11.6, 9.4, 4.3 Hz, 1H), 2.46 (s, 1H), 2.27 (t, *J* = 7.4 Hz, 2H), 2.05 (s, 3H), 1.87 – 1.72 (m, 1H), 1.72 – 1.48 (m, 5H), 1.42 – 1.29 (m, 2H), 1.23 (td, *J* = 7.2, 1.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 172.0, 71.5, 60.4, 58.7, 37.5, 34.3, 25.1, 24.8, 21.2, 14.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{22}O_5Na$ 269.1365; Found 269.1359.

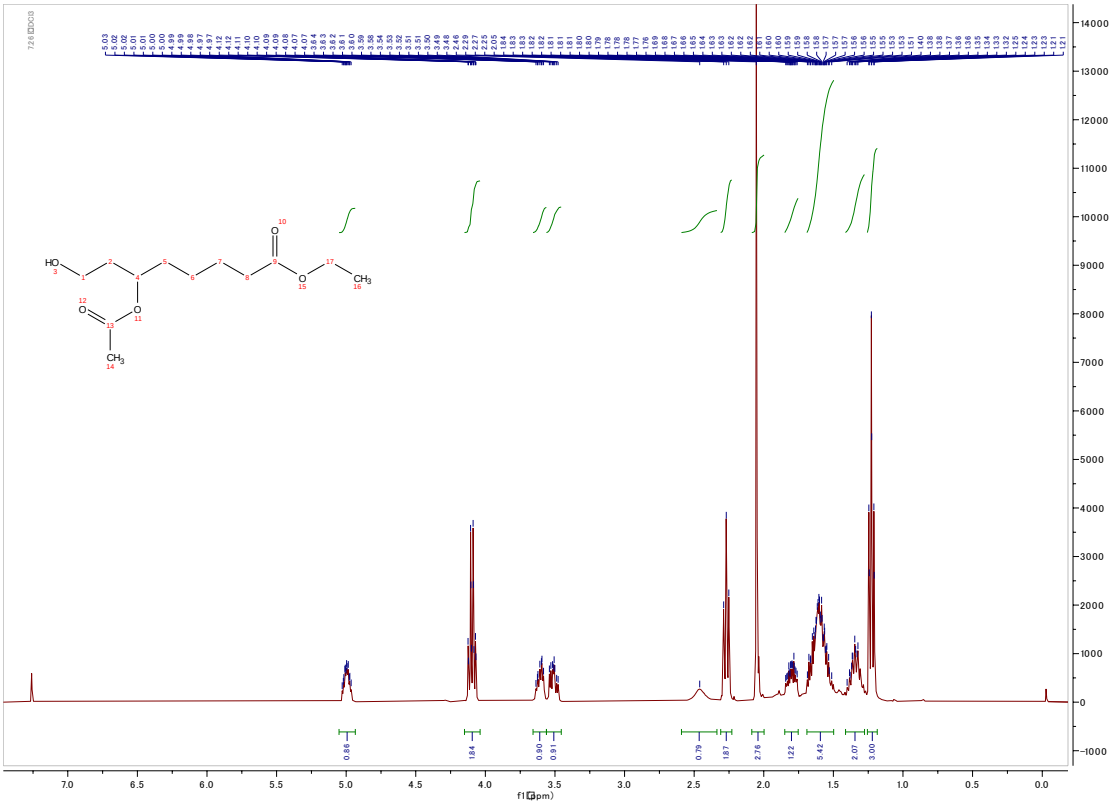


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4**.

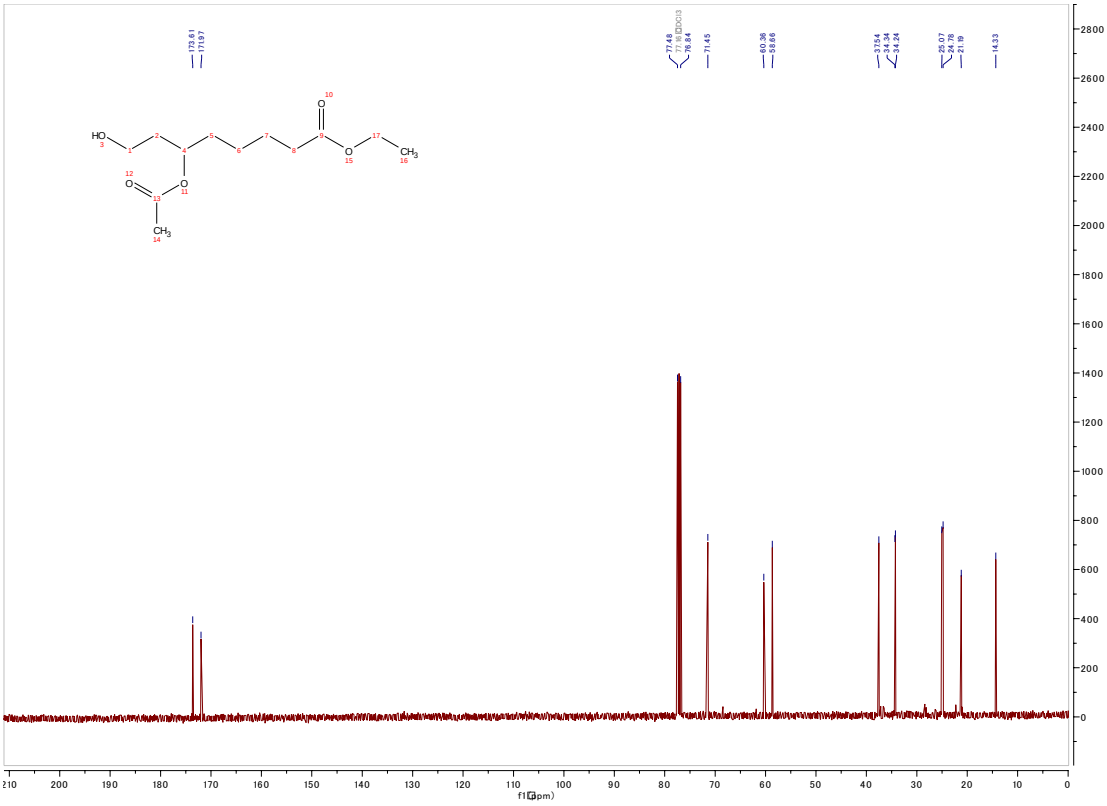
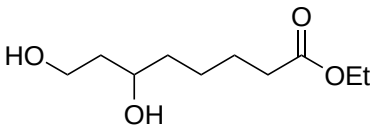


Figure S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **4**.

Ethyl 6,8-dihydroxyoctanoate (5) 78% yield. Colorless oil.



^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09 (q, *J* = 7.1 Hz, 2H), 3.80 (dtd, *J* = 18.3, 10.9, 4.8 Hz, 3H), 3.15 (s, 2H), 2.28 (t, *J* = 7.4 Hz, 2H), 1.70 – 1.55 (m, 4H), 1.53 – 1.29 (m, 4H), 1.22 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 71.6, 61.6, 60.4, 38.4, 37.4, 34.3, 25.1, 24.9, 14.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{20}O_4Na$ 227.1259; Found 227.1254.

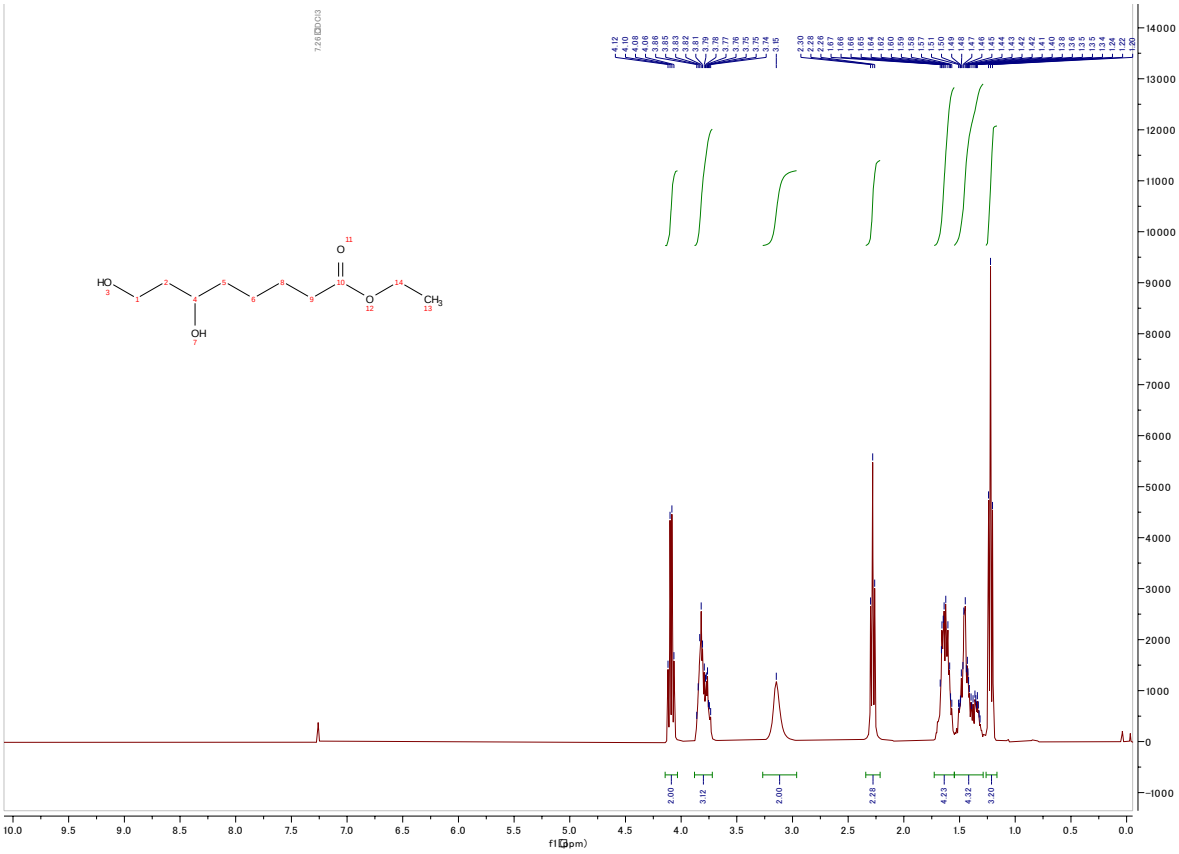


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5**.

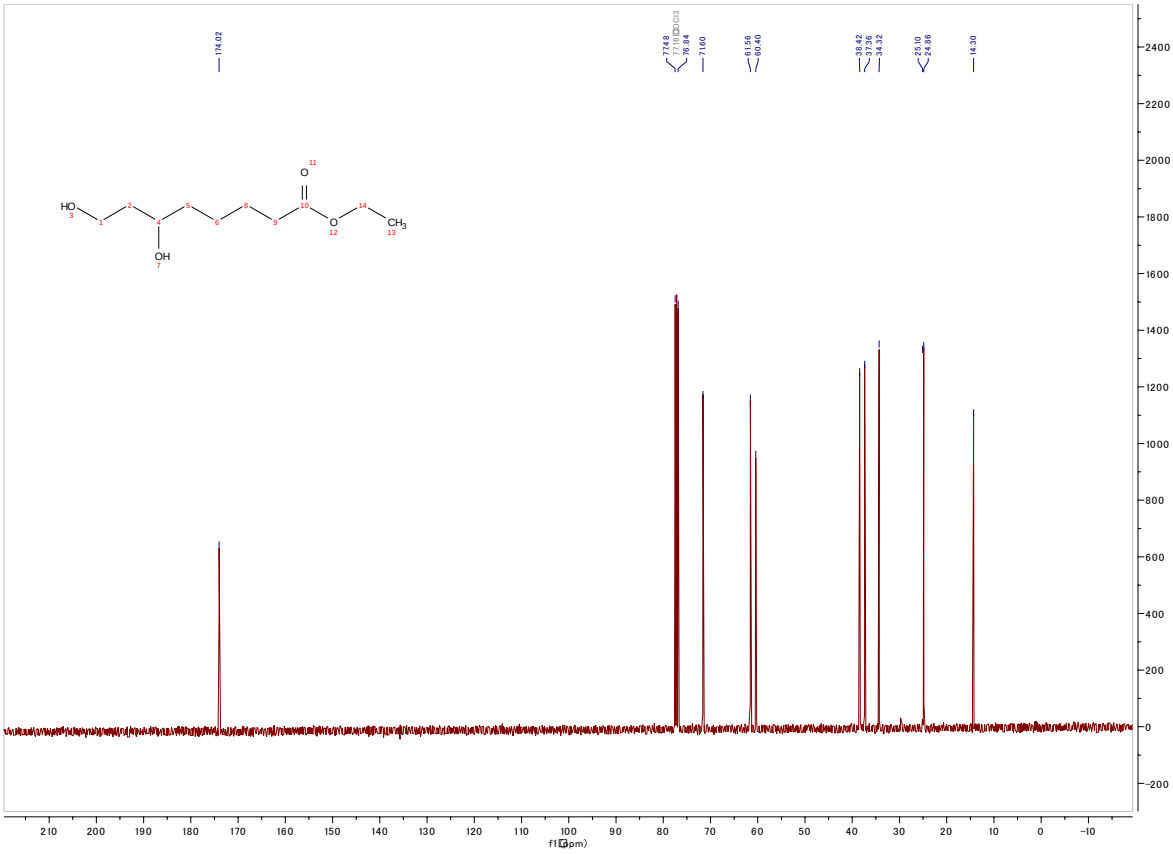


Figure S4. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **5**.

V. Kinetic Resolution for Synthesizing Chiral *O*-Acetoxy Compound (*S*)-3aa' (Scheme 3)

After hydrolysis of **3aa** with NaOEt (1 equiv) in EtOH following the similar procedure from **4** to **5**, ethyl 6-hydroxyoct-7-enoate (**6**, 90.5 mg, 0.485 mmol) was taken in an oven-dried vial, and then Novozym® 435 (22.11 mg) was added at rt under air. Vinylacetate (0.17 mL, 1.85 mmol) was added, and the reaction mixture was stirred at rt for 2 hours. The reaction was stopped by filtration with Et_2O, and the filtrate was concentrated. The crude product was purified by silica-gel column chromatography using 0% to 25% ethyl acetate in hexane as the eluent, giving (*S*)-**3aa'** in 19% isolated yield (21.1 mg, 0.092 mmol) and recovering **6** in 39% isolated yield (35.4 mg, 0.19 mmol).

Determination of the enantiomeric excess was carried out by derivatizing the recovered **6** to the corresponding Mosher's ester using (*S*)-MTPA-Cl ((*S*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride). For synthesizing the *racemic* Mosher's ester, ethyl 6-hydroxy-7-octenoate was treated with (*S*)-MTPA-Cl. The ^{1}H and ^{19}F NMR spectra of the racemic sample are shown in Figures S5 and S6.

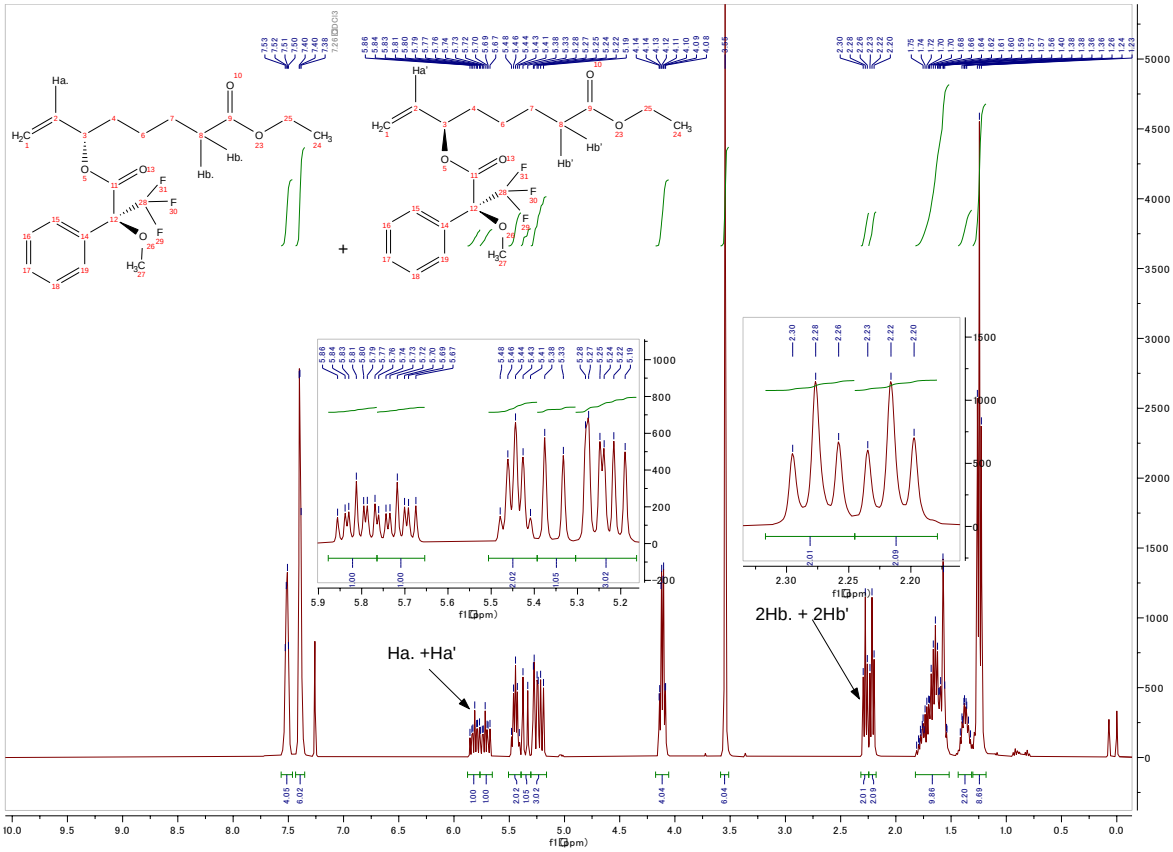
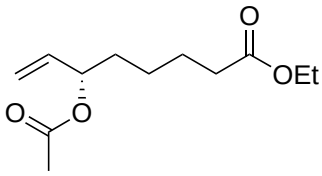


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *racemic* Mosher's ester derivative from **6**.

Figure S6. ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of *racemic* Mosher's ester derivative from **6**.

Ethyl (*S*)-6-acetoxyoct-7-enoate ((*S*)-3aa'): 19% yield. R_f = 0.41 (hexane/ EtOAc = 8/2), *ee* = 98%. Colorless oil. The NMR spectra of the Mosher's ester derivative are shown in Figures S9 and S10.



^{1}H NMR (400 MHz, $CDCl_3$): δ 5.81 – 5.71 (m, 1H), 5.26 – 5.18 (m, 2H), 5.16 (dt, *J* = 10.4, 1.2 Hz, 1H), 4.12 (q, 2H), 2.29 (t, 2H), 2.05 (s, 3H), 1.67 – 1.58 (m, 4H), 1.42 – 1.30 (m, 2H), 1.25 (t, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 170.5, 136.6, 116.9, 74.7, 60.4, 34.3, 34.0, 24.9, 24.7, 21.4, 14.4.

HRMS (CI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{21}O_4$ 229.1440; Found 229.1439.

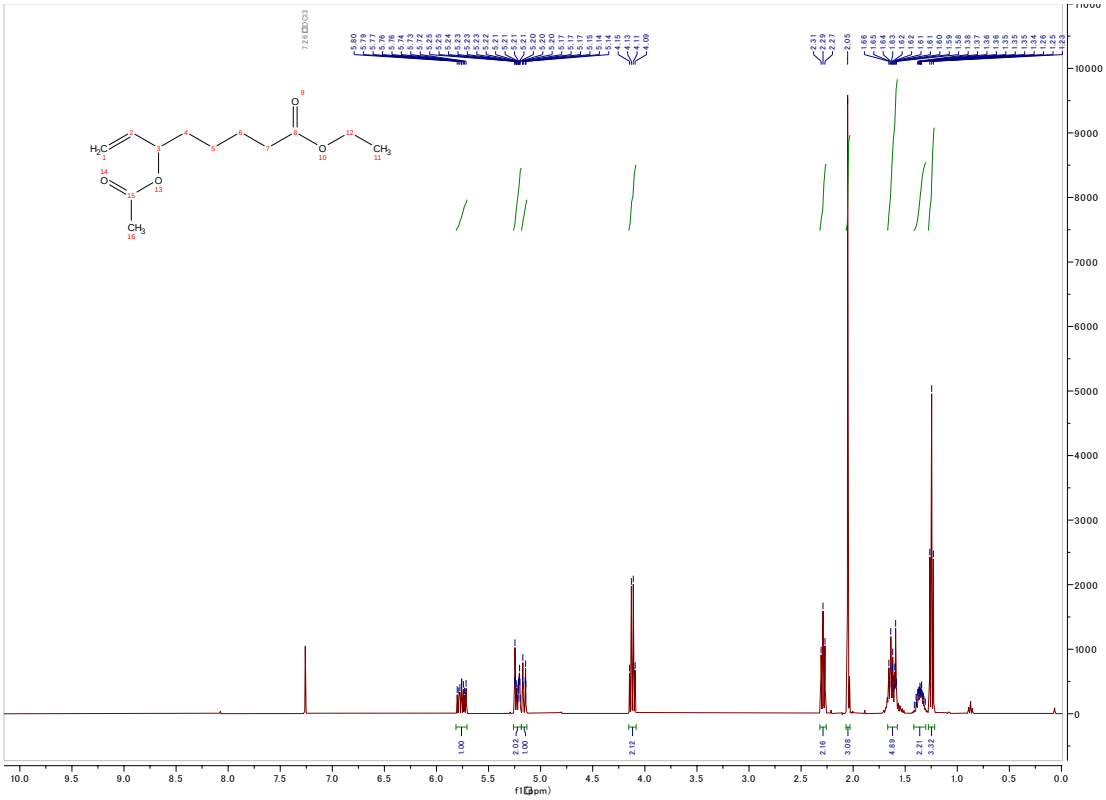


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (*S*)-**3aa'**.

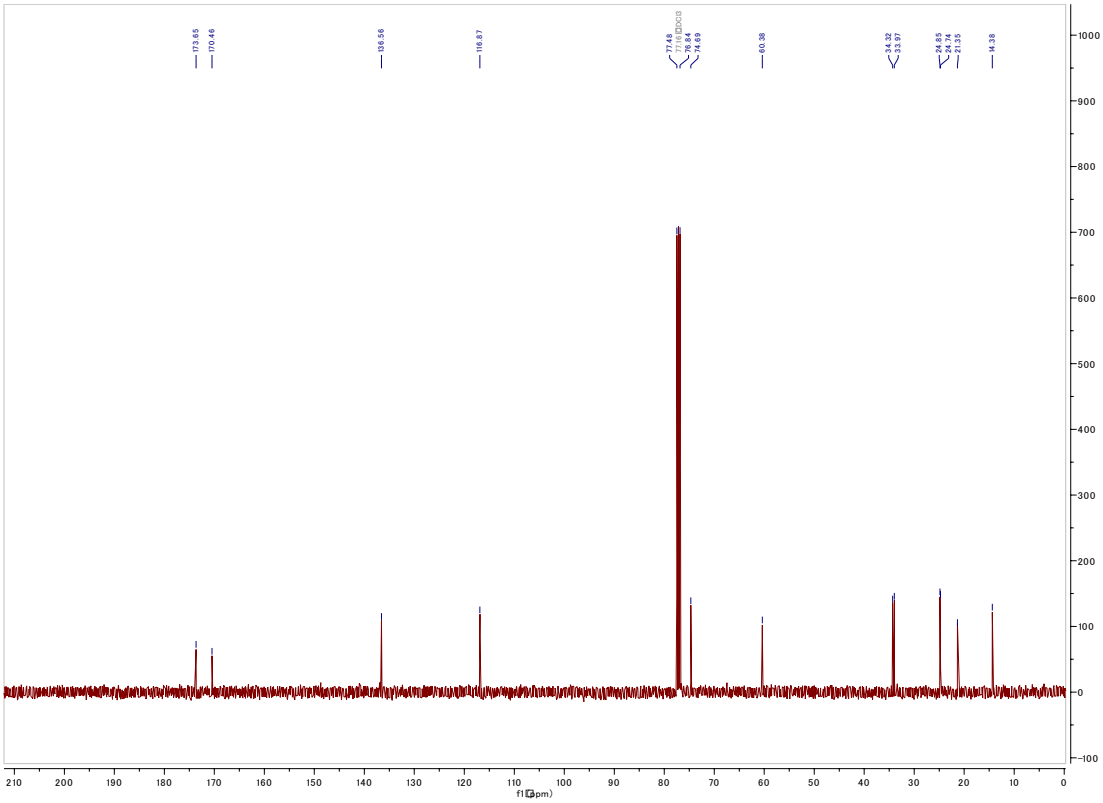


Figure S8. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (*S*)-**3aa'**.

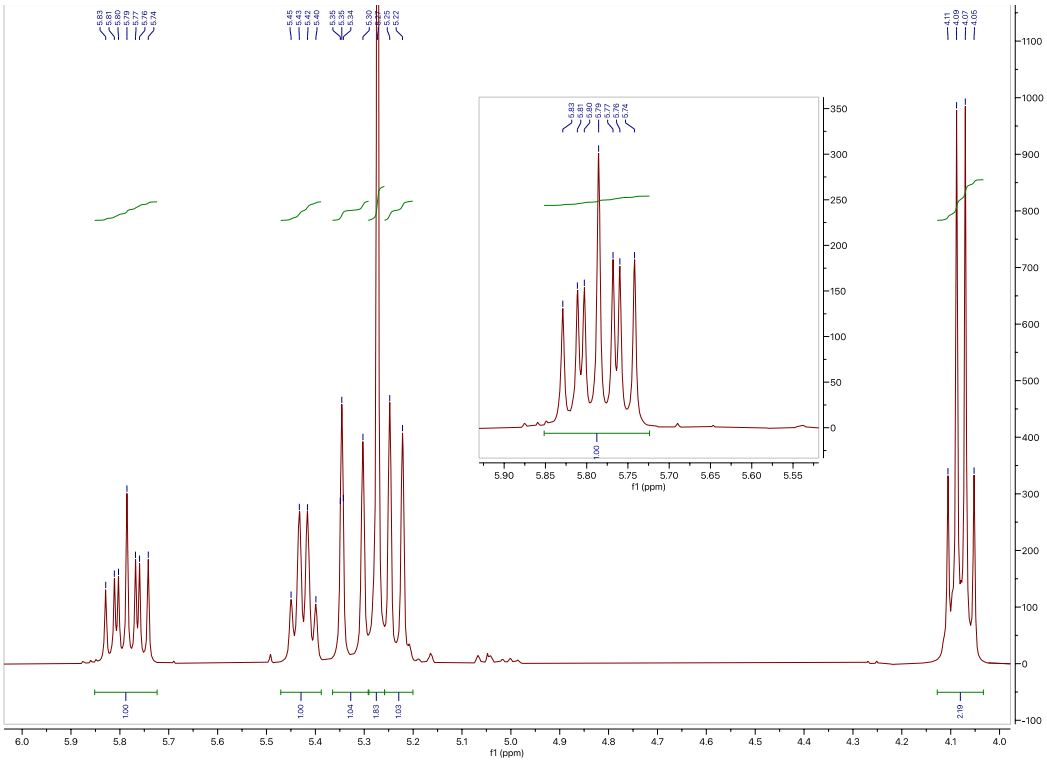


Figure S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the Mosher's ester from the hydrolyzed product of (*S*)-**3aa'**.

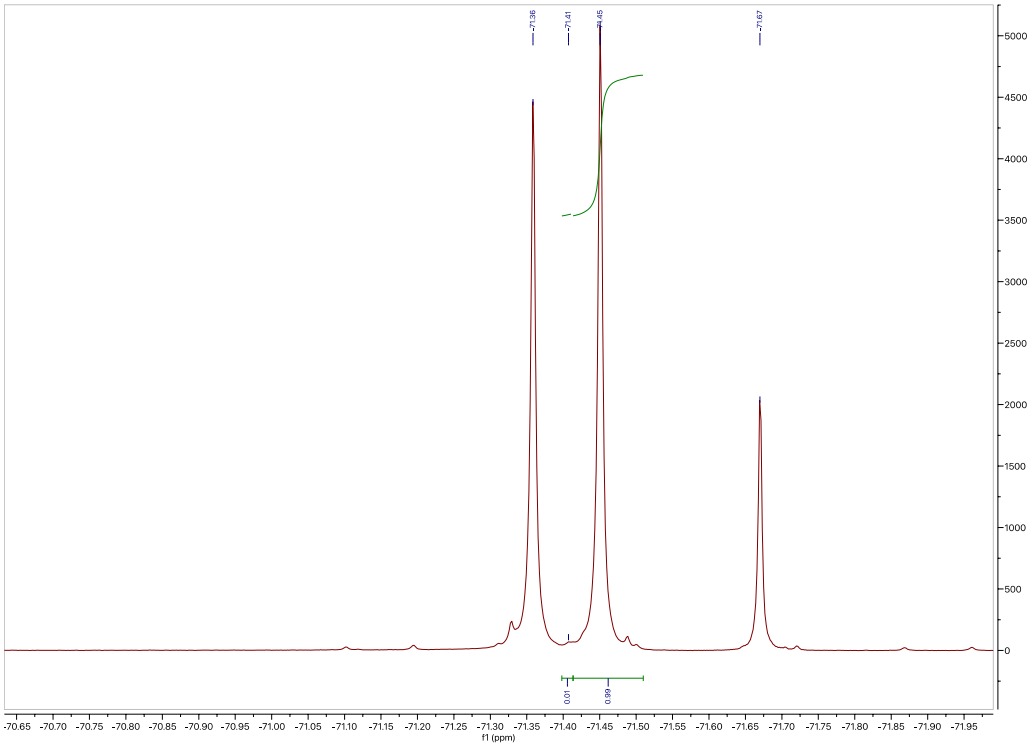
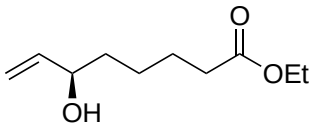


Figure S10. ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of the Mosher's ester from the hydrolyzed product of (*S*)-**3aa'**. Signals for the enantiomers, δ -71.41 and -71.46, in 1:99 ratio. Signals for δ -71.36 and -71.67 are impurities in the crude esterification mixture.

Ethyl (*R*)-6-hydroxyoct-7-enoate ((*R*)-6): 39% yield. R_f = 0.17 (hexane/ EtOAc = 8/2), *ee* = 88%. Colorless oil. The NMR spectra of the Mosher's ester derivative are shown in Figures S13 and S14.



^{1}H NMR (400 MHz, $CDCl_3$): δ 5.85 (ddd, *J* = 17.2, 10.4, 6.2 Hz, 1H), 5.21 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.09 (dt, *J* = 10.4, 1.4 Hz, 1H), 4.15 – 4.05 (m, 3H), 2.30 (t, 2H), 1.69 – 1.60 (m, 3H), 1.58 – 1.48 (m, 2H), 1.48 – 1.32 (m, 2H), 1.24 (t, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.8, 141.3, 114.8, 73.1, 60.4, 36.7, 34.4, 26.0, 25.0, 14.4.

HRMS (CI) m/z: [M + H] Calcd for $C_{10}H_{19}O_3$ 187.1334; Found 187.1341.

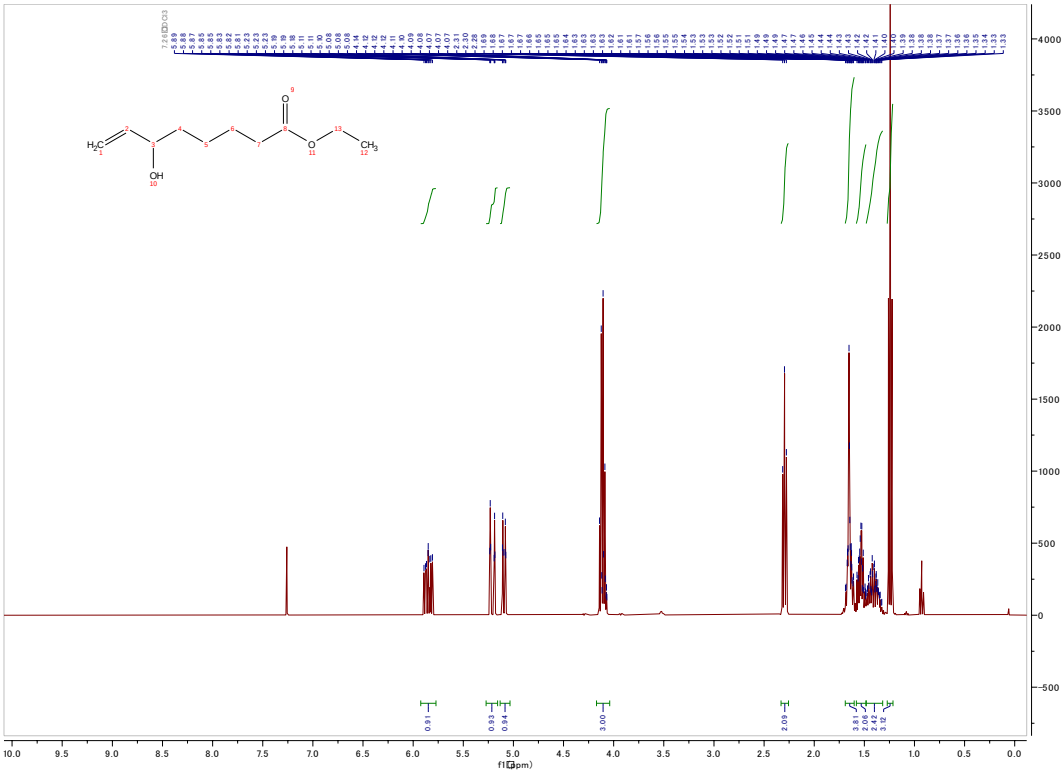


Figure S11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (*R*)-**6**.

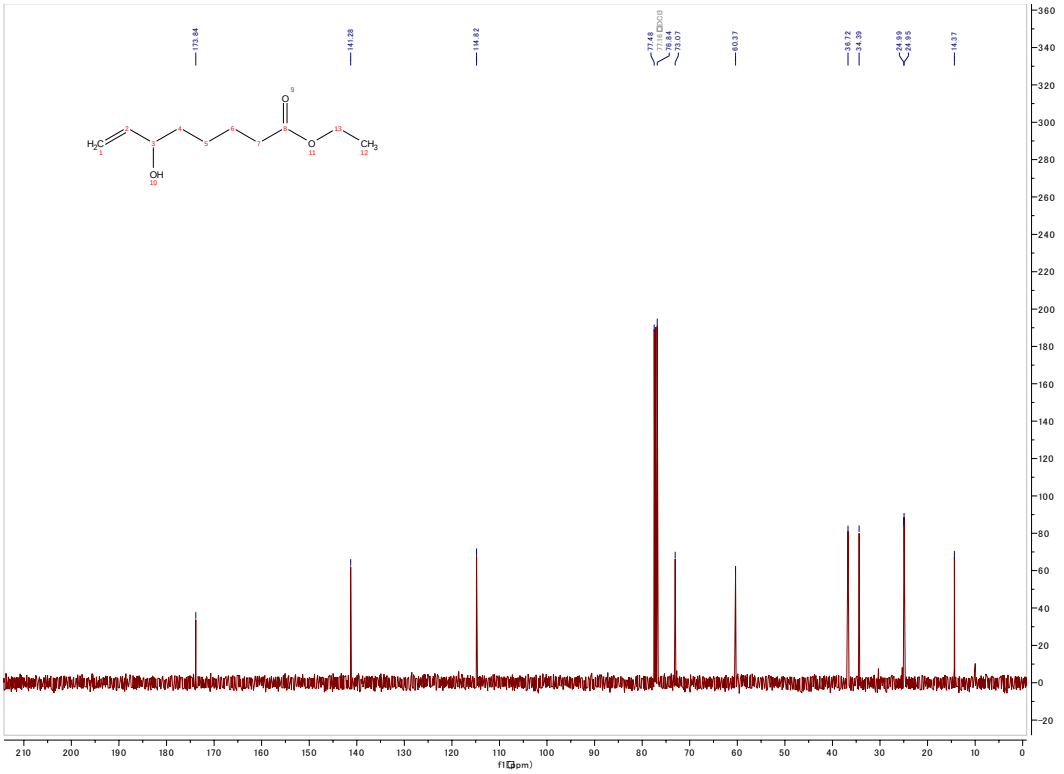


Figure S12. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (*R*)-**6**.

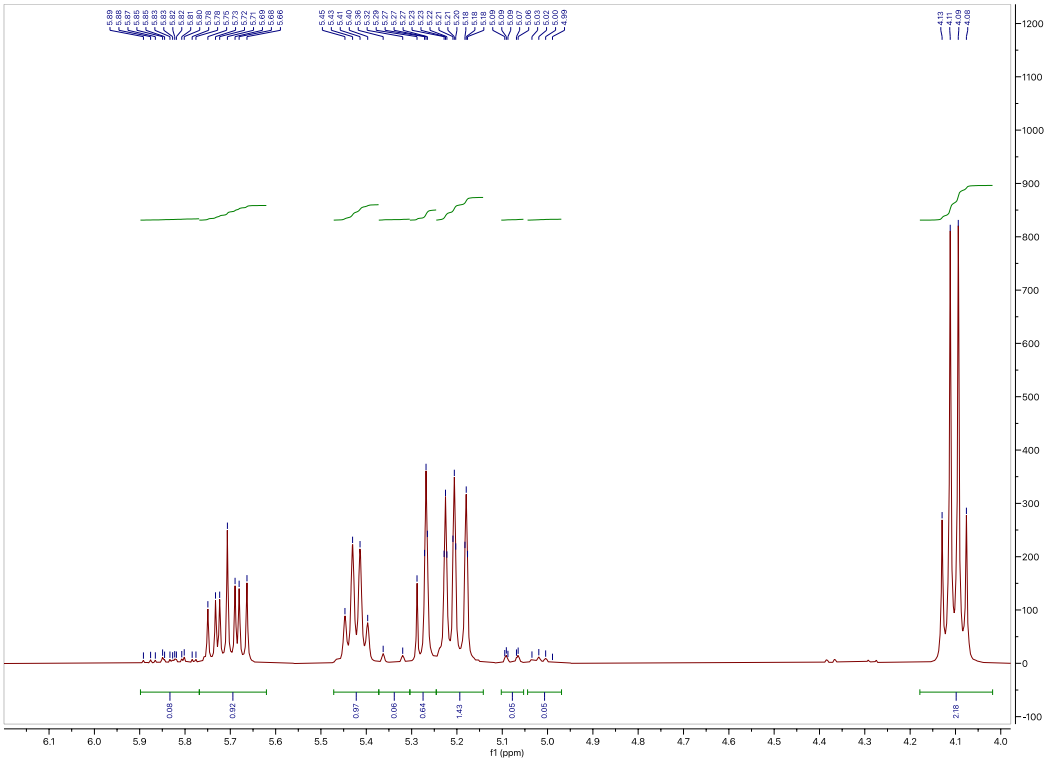


Figure S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the Mosher's ester from (*R*)-**6a**.

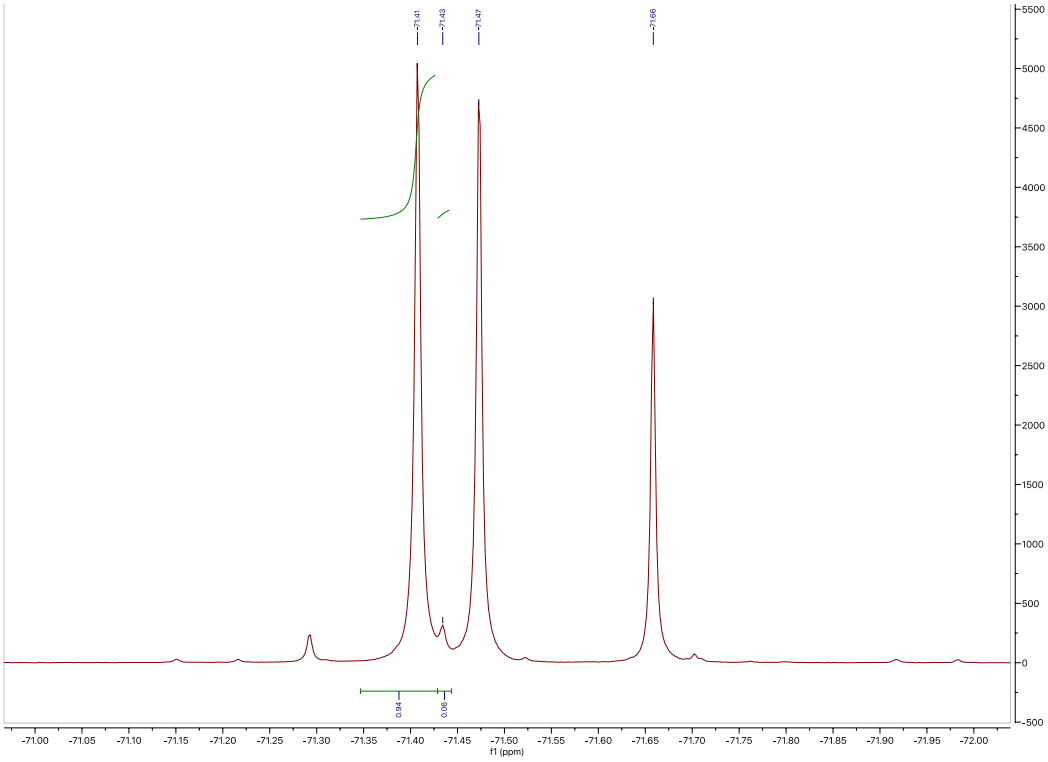
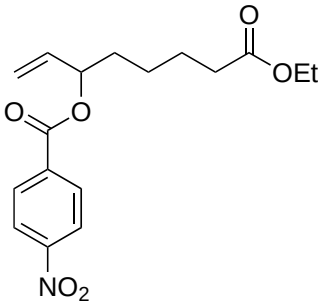


Figure S14. ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of the Mosher's ester from (*R*)-**6a**. Signals for the enantiomers, δ -71.41 and -71.43, in 94:6 ratio. Signals for δ -71.47 and -71.66 are impurities in the crude esterification mixture.

VI. Characterization of C-H Acyloxylation Products

8-Ethoxy-8-oxooct-1-en-3-yl 4-nitrobenzoate (3aa)



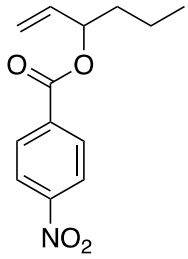
89% yield (89.5 mg, 0.267 mmol). R_f = 0.52 (hexane/ EtOAc = 8/2). Pale colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 9.1 Hz, 2H), 8.20 (d, *J* = 9.1 Hz, 2H), 5.88 (ddd, *J* = 17.1, 10.5, 6.5 Hz, 1H), 5.55 – 5.45 (m, 1H), 5.34 (dt, *J* = 17.1, 1.2 Hz, 1H), 5.25 (dt, *J* = 10.5, 1.2 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.30 (t, *J* = 8.0 Hz, 2H), 1.91 – 1.61 (m, 4H), 1.52 – 1.36 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 164.0, 150.7, 136.7, 136.0, 135.9, 130.8, 123.7, 117.8, 60.4, 34.2, 34.0, 24.8, 24.7, 14.4.

HRMS (CI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{22}NO_6$ 336.1447; Found 336.1455.

Hex-1-en-3-yl 4-nitrobenzoate (3ba)



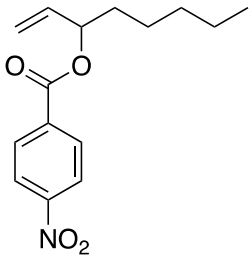
91% yield (68.1 mg, 0.273 mmol). R_f = 0.64 (hexane/ EtOAc = 8/2). White solid. Mp, 52.5-55.8 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.6 Hz, 2H), 8.22 (d, *J* = 8.6 Hz, 2H), 5.89 (ddd, *J* = 17.3, 10.5, 6.6 Hz, 1H), 5.60 – 5.45 (m, 1H), 5.34 (dt, *J* = 17.3, 1.3 Hz, 1H), 5.24 (dt, *J* = 10.5, 1.3 Hz, 1H), 1.89 – 1.66 (m, 2H), 1.51 – 1.37 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 150.7, 136.2, 136.1, 130.8, 123.7, 117.5, 77.6, 36.5, 18.5, 14.0

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{13}H_{15}NO_4$ 249.1001; Found 249.1003.

Oct-1-en-3-yl 4-nitrobenzoate (3ca)



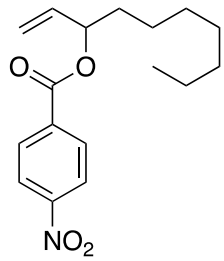
92% yield (76.5 mg, 0.276 mmol). R_f = 0.67 (hexane/ EtOAc = 8/2). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.8 Hz, 2H), 8.21 (d, *J* = 8.8 Hz, 2H), 5.89 (ddd, *J* = 17.1, 10.5, 6.5 Hz, 1H), 5.55 – 5.45 (m, 1H), 5.33 (d, *J* = 17.1 Hz, 1H), 5.24 (d, *J* = 10.5 Hz, 1H), 1.89 – 1.67 (m, 2H), 1.45 – 1.27 (m, 6H), 0.89 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 150.7, 136.2 (2C), 130.8, 123.7, 117.6, 76.8, 34.3, 31.7, 24.9, 22.6, 14.1.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{19}NO_4$ 277.1314; Found 277.1314.

Dec-1-en-3-yl 4-nitrobenzoate (3da)



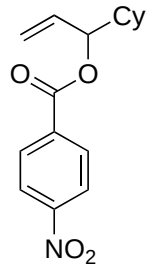
95% yield (87.0 mg, 0.285 mmol). R_f = 0.7 (hexane/ EtOAc = 8/2). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.8 Hz, 2H), 8.22 (d, *J* = 8.8 Hz, 2H), 5.89 (ddd, *J* = 17.1, 10.5, 6.6 Hz, 1H), 5.55 – 5.45 (m, 1H), 5.34 (d, *J* = 17.1 Hz, 1H), 5.24 (d, *J* = 10.5 Hz, 1H), 1.89 – 1.67 (m, 2H), 1.46 – 1.17 (m, 11H), 0.86 (t, *J* = 7.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 150.7, 136.2, 136.2, 130.8, 123.7, 117.6, 76.9, 34.4, 31.9, 29.5, 29.3, 25.2, 22.7, 14.2.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{23}NO_4$ 305.1627; Found 305.1628.

1-Cyclohexylallyl 4-nitrobenzoate (3ea)



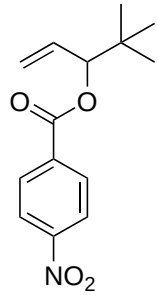
72% yield (62.5 mg, 0.216 mmol). R_f = 0.61 (hexane/ EtOAc = 8/2). White solid. Mp, 59.4-61.8 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.8 Hz, 2H), 8.22 (d, *J* = 8.8 Hz, 2H), 5.87 (ddd, *J* = 17.4, 10.5, 6.9 Hz, 1H), 5.39 – 5.29 (m, 2H), 5.27 (d, *J* = 10.5 Hz, 1H), 1.90 – 1.64 (m, 6H), 1.34 – 1.0 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 150.7, 136.2, 134.6, 130.8, 123.7, 118.4, 80.8, 41.8, 28.8, 28.6, 26.5, 26.1, 26.0.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{19}NO_4$ 289.1314; Found 289.1310.

4,4-Dimethylpent-1-en-3-yl 4-nitrobenzoate (3fa)



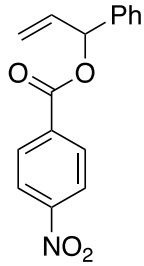
57% yield (45.5 mg, 0.171 mmol). R_f = 0.6 (hexane/ EtOAc = 8/2). White solid. Mp, 56.6-58.9 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.9 Hz, 1H), 8.22 (d, *J* = 8.9 Hz, 1H), 5.91 (ddd, *J* = 17.4, 10.5, 7.1 Hz, 1H), 5.37 – 5.22 (m, 3H), 1.03 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.0, 150.7, 136.2, 133.1, 130.8, 123.7, 119.2, 83.9, 34.7, 26.0.

HRMS (CI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{17}NO_4$ 264.1236; Found 264.1236.

1-Phenylallyl 4-nitrobenzoate (3ga)



49% yield (branch and linear isomers) (41.6 mg, 0.147 mmol). R_f = 0.57 (hexane/ EtOAc = 8/2). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 8.9 Hz, 2H), 8.23 (d, *J* = 8.9 Hz, 2H), 7.5-7.3 (m, 5H), 6.53 (d, *J* = 5.9 Hz, 1H), 6.06 (ddd, *J* = 17.1, 10.5, 5.9 Hz, 1H), 5.73 (d, *J* = 17.1 Hz, 1H), 5.56 (d, *J* = 10.5 Hz, 1H).

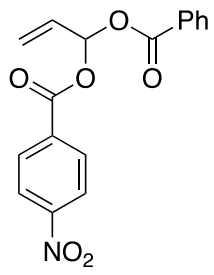
^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8, 150.8, 138.4, 135.8_5, 135.8_3, 131.0, 128.9, 128.7, 127.4, 123.7, 118.0, 78.0.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{13}NO_4$ 283.0845; Found 283.0844.

Linear isomer of **3ga**: R_f = 0.48 (hexane/ EtOAc = 8/2). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 9.0 Hz, 2H), 8.25 (d, *J* = 9.0 Hz, 2H), 7.46 – 7.40 (m, 2H), 7.34 – 7.25 (m, 3H), 6.77 (d, *J* = 15.8 Hz, 1H), 6.41 (dt, *J* = 15.8, 6.6 Hz, 1H), 5.03 (dd, *J* = 6.6, 1.3 Hz, 2H).

1-(Benzoyloxy)allyl 4-nitrobenzoate (3ha)



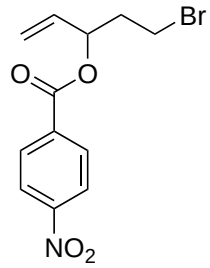
63% yield (61.8 mg, 0.189 mmol). R_f = 0.45 (hexane/ EtOAc = 8/2). White solid. Mp, 75.2-76.7 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 9.0 Hz, 2H), 8.25 (d, *J* = 9.0 Hz, 2H), 8.09 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.67 (d, *J* = 5.6 Hz, 1H), 7.67 – 7.56 (m, 1H), 7.49 – 7.45 (m, 2H), 6.18 (ddd, *J* = 17.2, 10.6, 5.6 Hz, 1H), 5.78 (d, *J* = 17.2 Hz, 1H), 5.57 (d, *J* = 10.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 162.7, 151.0, 134.7, 133.9, 131.2, 131.0, 130.2, 129.0, 128.7, 123.7, 121.6, 90.8.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{13}NO_6$ 327.0743; Found 327.0745.

5-Bromopent-1-en-3-yl 4-nitrobenzoate (3ia)



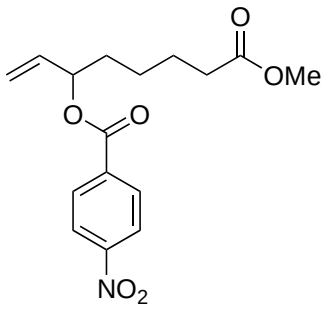
72% yield (67.9 mg, 0.216 mmol). R_f = 0.55 (hexane/ EtOAc = 8/2). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.8 Hz, 2H), 8.22 (d, *J* = 8.8 Hz, 2H), 5.90 (ddd, *J* = 17.1, 10.5, 6.6 Hz, 1H), 5.75 – 5.65 (m, 1H), 5.44 (d, *J* = 17.1 Hz, 1H), 5.34 (d, *J* = 10.5 Hz, 1H), 3.5 – 3.4 (m, 2H), 2.47 – 2.26 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 150.8, 135.6, 134.7, 130.9, 123.8, 118.9, 74.9, 37.2, 27.9.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{12}H_{12}{}^{79}BrNO_4$ 312.9950; Found 312.9936. $[M]^+$ Calcd for $C_{12}H_{12}{}^{81}BrNO_4$ 314.9929; Found 314.9919.

8-Methoxy-8-oxooct-1-en-3-yl 4-nitrobenzoate (3ja)



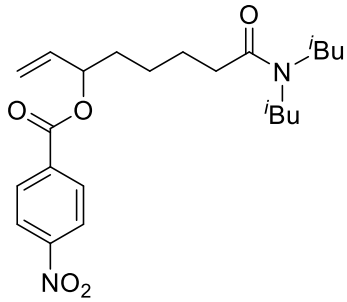
76% yield (73.3 mg, 0.228 mmol). R_f = 0.37 (hexane/ EtOAc = 8/2). Pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, *J* = 9.0 Hz, 2H), 8.20 (d, *J* = 9.0 Hz, 2H), 5.87 (ddd, J = 17.2, 10.5, 6.6 Hz, 1H), 5.55 – 5.45 (m, 1H), 5.33 (dt, J = 17.2, 1.2 Hz, 1H), 5.24 (dt, J = 10.5, 1.2 Hz, 1H), 3.64 (s, 3H), 2.32 (t, *J* = 7.9 Hz, 2H), 1.91 – 1.71 (m, 2H), 1.71 – 1.63 (m, 2H), 1.51 – 1.37 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.9, 164.0, 150.7, 136.0, 135.8, 130.8, 123.7, 117.8, 76.5, 51.6, 34.0, 34.0, 24.7, 24.7.

HRMS (CI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{20}NO_6$ 322.1291; Found 321.1292.

8-(Diisobutylamino)-8-oxooct-1-en-3-yl 4-nitrobenzoate (3ka)



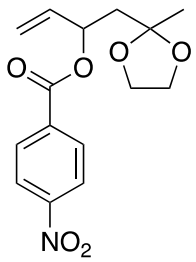
86% yield (108.0 mg, 0.258 mmol). R_f = 0.19 (hexane/ EtOAc = 8/2). Light brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, *J* = 8.9 Hz, 2H), 8.20 (d, *J* = 8.9 Hz, 2H), 5.88 (ddd, *J* = 17.2, 10.5, 6.4 Hz, 1H), 5.55 – 5.45 (m, 1H), 5.32 (dt, *J* = 17.2, 1.2 Hz, 1H), 5.23 (dt, *J* = 10.5, 1.2 Hz, 1H), 3.16 (d, *J* = 7.5 Hz, 2H), 3.05 (d, *J* = 7.6 Hz, 2H), 2.32 (t, *J* = 7.4 Hz, 2H), 2.02 – 1.60 (m, 6H), 1.49 – 1.37 (m, 2H), 0.88 (d, *J* = 6.6 Hz, 6H), 0.83 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0, 164.0, 150.7, 136.1, 135.9, 130.8, 123.6, 117.7, 76.7, 55.6, 53.2, 34.3, 33.3, 28.0, 26.6, 25.5, 25.1, 20.3, 20.2.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{23}H_{34}N_2O_5$ 418.2468; Found 418.2460.

1-(2-Methyl-1,3-dioxolan-2-yl)but-3-en-2-yl 4-nitrobenzoate (3la)



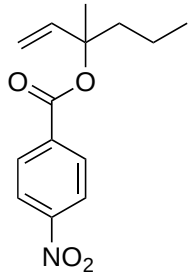
78% yield (71.9 mg, 0.237 mmol). R_f = 0.31 (hexane/ EtOAc = 8/2). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.8 Hz, 2H), 8.22 (d, *J* = 8.8 Hz, 2H), 5.94 (ddd, *J* = 17.0, 10.4, 6.1 Hz, 1H), 5.85 – 5.75 (m, 1H), 5.33 (dt, *J* = 17.0, 1.3 Hz, 1H), 5.21 (dt, *J* = 10.4, 1.3 Hz, 1H), 3.97 – 3.83 (m, 4H), 2.28 (dd, *J* = 15.0, 8.2 Hz, 1H), 2.09 (dd, *J* = 15.0, 4.0 Hz, 1H), 1.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 136.5, 136.2, 130.9, 123.7, 116.8, 108.6, 72.7, 64.8, 64.7, 43.2, 24.7.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{17}NO_6$ 307.1056; Found 307.1052.

3-Methylhex-1-en-3-yl 4-nitrobenzoate (3ma)



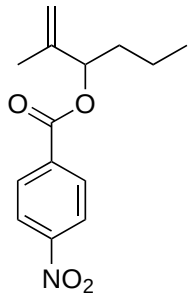
21% yield (16.6 mg, 0.063 mmol). R_f = 0.61 (hexane/ EtOAc = 8/2). White solid. Mp, 41.7-43.4 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.8 Hz, 2H), 8.16 (d, *J* = 8.8 Hz, 2H), 6.09 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.26 (d, *J* = 17.5 Hz, 1H), 5.22 (d, *J* = 11.0 Hz, 1H), 2.0 – 1.9 (m, 2H), 1.69 (s, 3H), 1.50 – 1.35 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 141.4, 137.3, 130.7, 123.6, 123.6, 114.0, 85.5, 42.5, 23.7, 17.2, 14.5.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{17}NO_4$ 263.1158; Found 263.1154.

2-Methylhex-1-en-3-yl 4-nitrobenzoate (3na)



51% yield (40.3 mg, 0.153 mmol). R_f = 0.54 (hexane/ Et_2O= 8/2). Colorless oil.

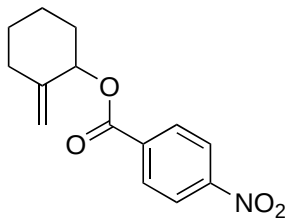
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.7 Hz, 2H), 8.22 (d, *J* = 8.7 Hz, 2H), 5.47 (t, *J* = 6.8 Hz, 1H), 5.04 (s, 1H), 4.97 (s, 1H), 1.81 (s, 3H), 1.85 – 1.68 (m, 2H), 1.45 – 1.34 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 150.7, 142.8, 136.2, 130.8, 123.7, 113.5, 79.2, 34.9, 18.8, 18.2, 14.0.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{17}NO_4$ 263.1158; Found 263.1159.

Some signals for the minor isomer, 2-methylenehexyl 4-nitrobenzoate (**3na'**), were detected: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.13 (s, 1H), 4.82 (s, 2H), 2.15 (t, *J* = 7.9 Hz, 2H). From the ratio of intensities for **3na** and **3na'** in the isolated sample, the regioselectivity is approximately 5:1 ratio.

2-Methylenecyclohexyl 4-nitrobenzoate (3oa)



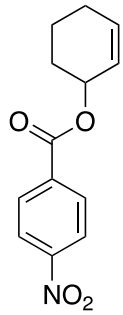
75% yield (58.8 mg, 0.225 mmol). R_f = 0.62 (hexane/ EtOAc = 8/2). White solid. Mp, 53.6-55.1 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.8 Hz, 2H), 8.24 (d, *J* = 8.8 Hz, 2H), 5.55 – 5.45 (m, 1H), 4.92 (s, 1H), 4.86 (s, 1H), 2.47 – 2.41 (m, 1H), 2.22 – 2.17 (m, 1H), 2.08 – 1.97 (m, 1H), 1.9 – 1.75 (m, 2H), 1.7 – 1.55 (3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.9, 150.7, 146.1, 136.3, 130.9, 123.7, 108.5, 76.2, 33.4, 33.4, 27.5, 23.2.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{15}NO_4$ 261.1001; Found 261.1000.

Cyclohex-2-en-1-yl 4-nitrobenzoate (3pa)



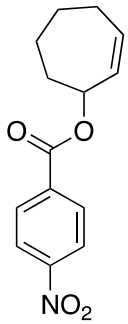
90% yield (66.8 mg, 0.27 mmol). R_f = 0.52 (hexane/ EtOAc = 8/2). White solid. Mp, 75.3-77.6 ºC

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.9 Hz, 2H), 8.23 (d, *J* = 8.9 Hz, 2H), 6.11 – 6.02 (m, 1H), 5.94 – 5.81 (m, 1H), 5.57 – 5.54 (m, 1H), 2.25 – 1.75 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 150.6, 136.4, 133.7, 130.8, 125.1, 123.6, 70.0, 28.4, 25.0, 19.0.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{13}H_{13}NO_4$ 247.0845; Found 247.0843.

Cyclohept-2-en-1-yl 4-nitrobenzoate (3qa)



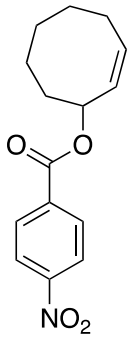
93% yield (72.9 mg, 0.279 mmol). R_f = 0.55 (hexane/ EtOAc = 8/2). White solid. Mp, 50.7-52.7 ºC

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.9 Hz, 2H), 8.22 (d, *J* = 8.9 Hz, 2H), 5.95 – 5.88 (m, 1H), 5.82 – 5.74 (m, 1H), 5.72 – 5.63 (m, 1H), 2.29 – 2.12 (m, 2H), 2.07 – 1.94 (m, 2H), 1.92 – 1.82 (m, 1H), 1.79 – 1.70 (m, 2H), 1.56 – 1.45 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 150.6, 136.3, 132.8, 132.7, 130.8, 123.6, 76.0, 32.8, 28.6, 26.7, 26.5.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{15}NO_4$ 261.1001; Found 261.1001.

(*Z*)-Cyclooct-2-en-1-yl 4-nitrobenzoate (3ra)



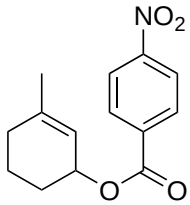
96% yield (79.3 mg, 0.288 mmol). R_f = 0.61 (hexane/ EtOAc = 8/2). White solid. Mp, 102.3-104.7 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, *J* = 8.7 Hz, 2H), 8.21 (d, *J* = 8.7 Hz, 2H), 5.98 – 5.88 (m, 1H), 5.82 – 5.73 (m, 1H), 5.63 – 5.59 (m, 1H), 2.40 – 2.26 (m, 1H), 2.22 – 2.15 (m, 1H), 2.08 – 2.04 (m, 1H), 1.77 – 1.51 (m, 6H), 1.52 – 1.37 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 150.6, 136.3, 130.8, 130.6, 130.0, 123.6, 74.3, 35.2, 28.9, 26.6, 26.0, 23.5.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{17}NO_4$ 275.1158; Found 275.1159.

3-Methylcyclohex-2-en-1-yl 4-nitrobenzoate (3sa)



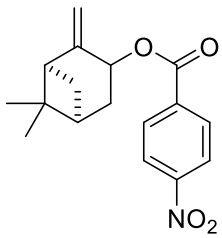
47% yield (36.8 mg, 0.14 mmol). R_f = 0.61 (hexane/ EtOAc = 8/2). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.8 Hz, 2H), 8.22 (d, *J* = 8.8 Hz, 2H), 5.80 – 5.75 (m, 1H), 5.55 – 5.45 (m, 1H), 2.20 – 2.08 (m, 1H), 2.08 – 1.97 (m, 1H), 1.95 – 1.86 (m, 2H), 1.75 – 1.62 (m, 2H), 1.72 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 150.6, 136.3, 131.4, 130.8, 128.8, 123.6, 72.8, 29.1, 25.3, 20.7, 18.6.

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{15}NO_4$ 261.1001; Found 261.1002.

(1*S*,5*S*)-6,6-dimethyl-2-methylenebicyclo[3.1.1]heptan-3-yl 4-nitrobenzoate (3ta)



58% yield (52.4 mg, 0.174 mmol). R_f = 0.65 (hexane/ EtOAc = 8/2). Light yellow Solid. Mp, 68.8-70.7 ºC

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.9 Hz, 2H), 8.20 (d, *J* = 8.9 Hz, 2H), 5.85 (d, *J* = 7.9 Hz, 1H), 5.16 (m, 1H), 4.96 (m, 1H), 2.65 – 2.45 (m, 3H), 2.11 – 2.02 (m, 1H), 2.00 – 1.92 (m, 1H), 1.72 (d, *J* = 10.1 Hz, 1H), 1.33 (s, 3H), 0.75 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 150.7, 149.8, 136.5, 130.8, 123.7, 115.2, 70.6, 50.9, 40.8, 39.7, 33.4, 28.2, 26.0, 22.2.

HRMS (CI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{20}NO_4$ 302.1392; Found 302.1385.

VII. ^{1}H and ^{13}C NMR Spectra

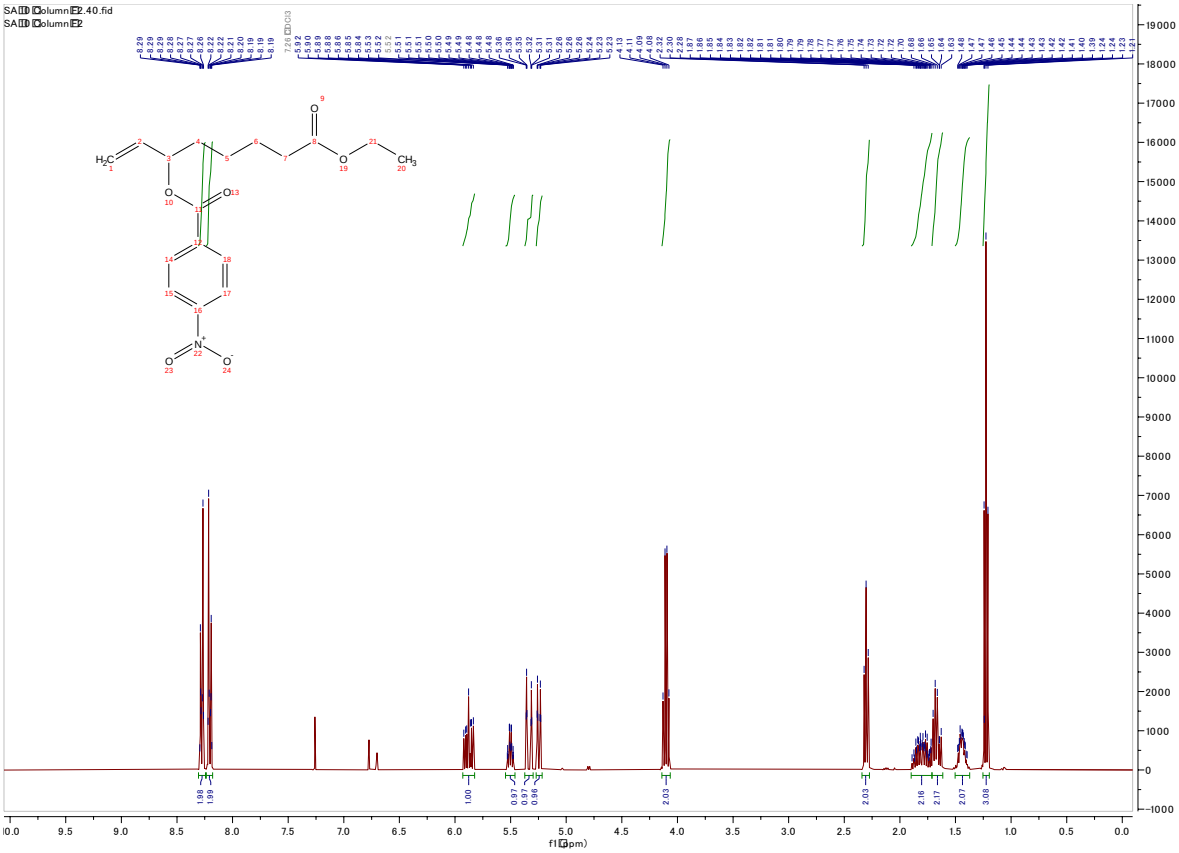


Figure S15. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3aa**.

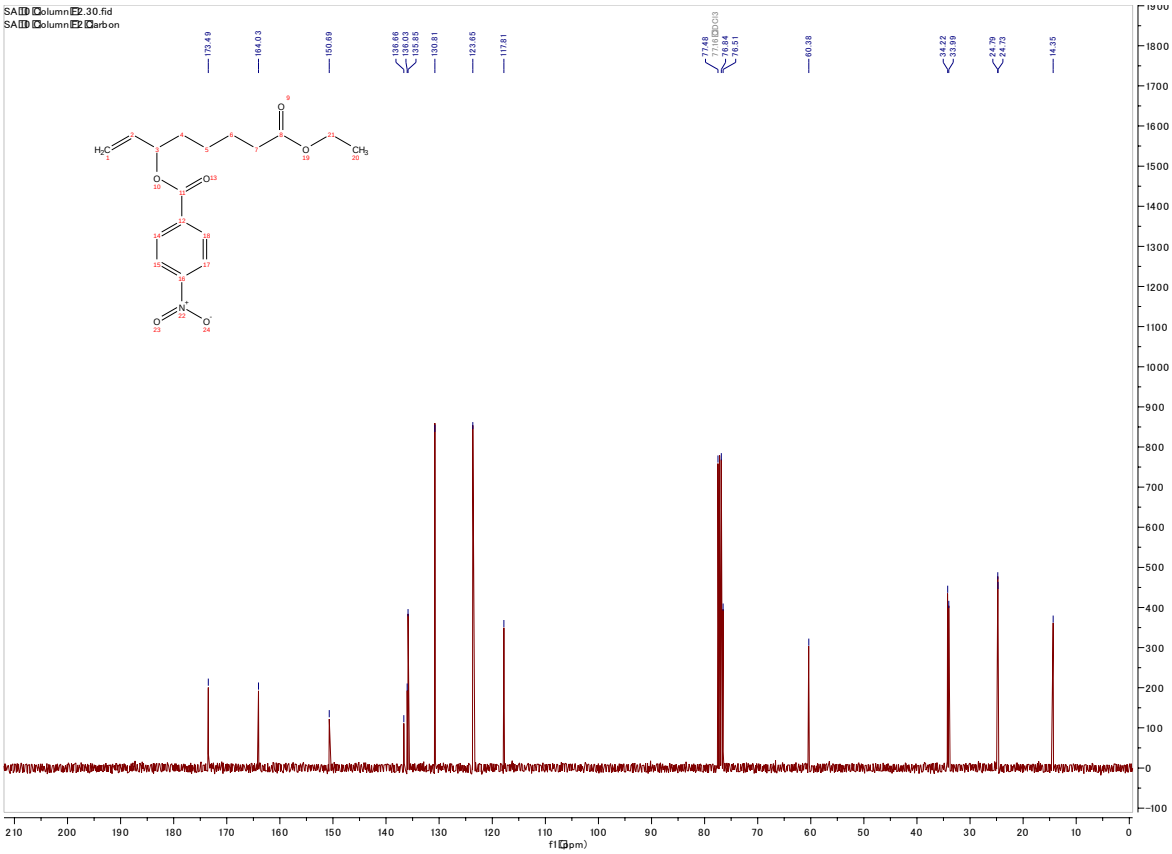


Figure S16. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3aa**.

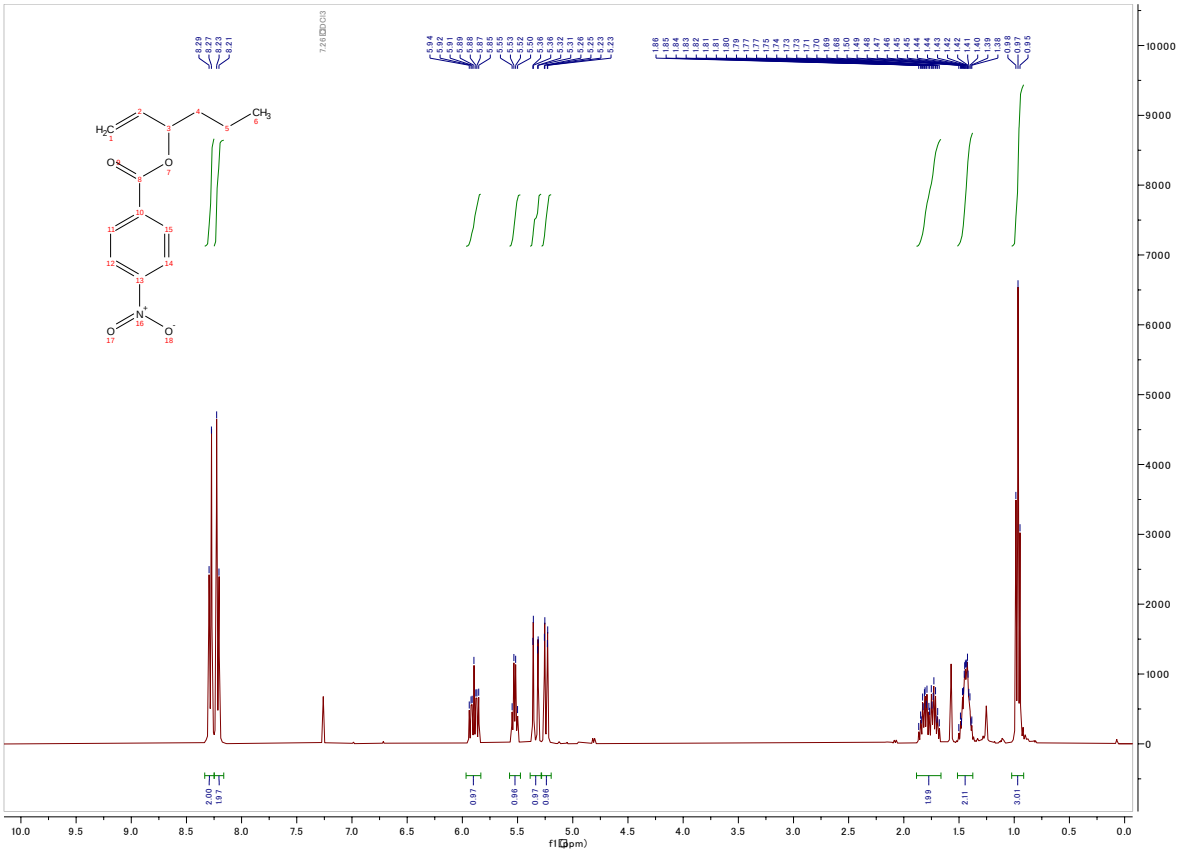


Figure S17. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3ba**.

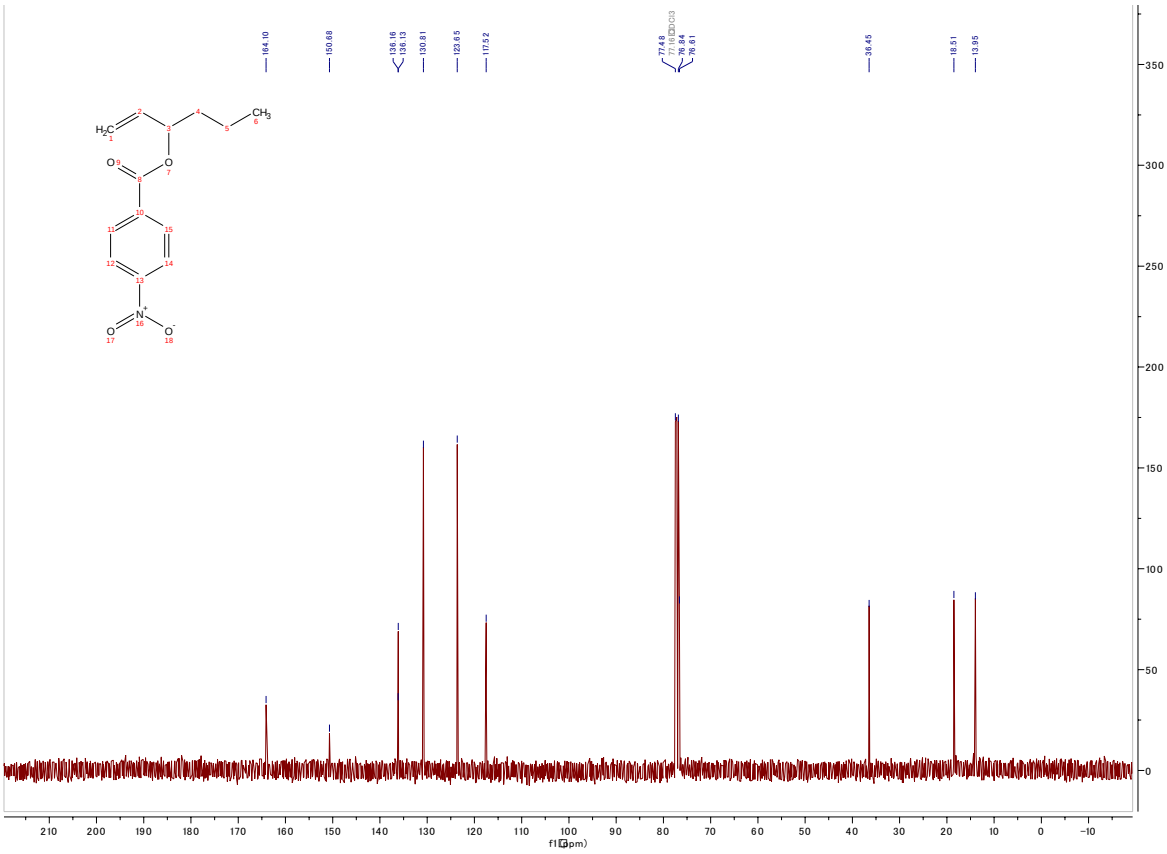


Figure S18. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3ba**.

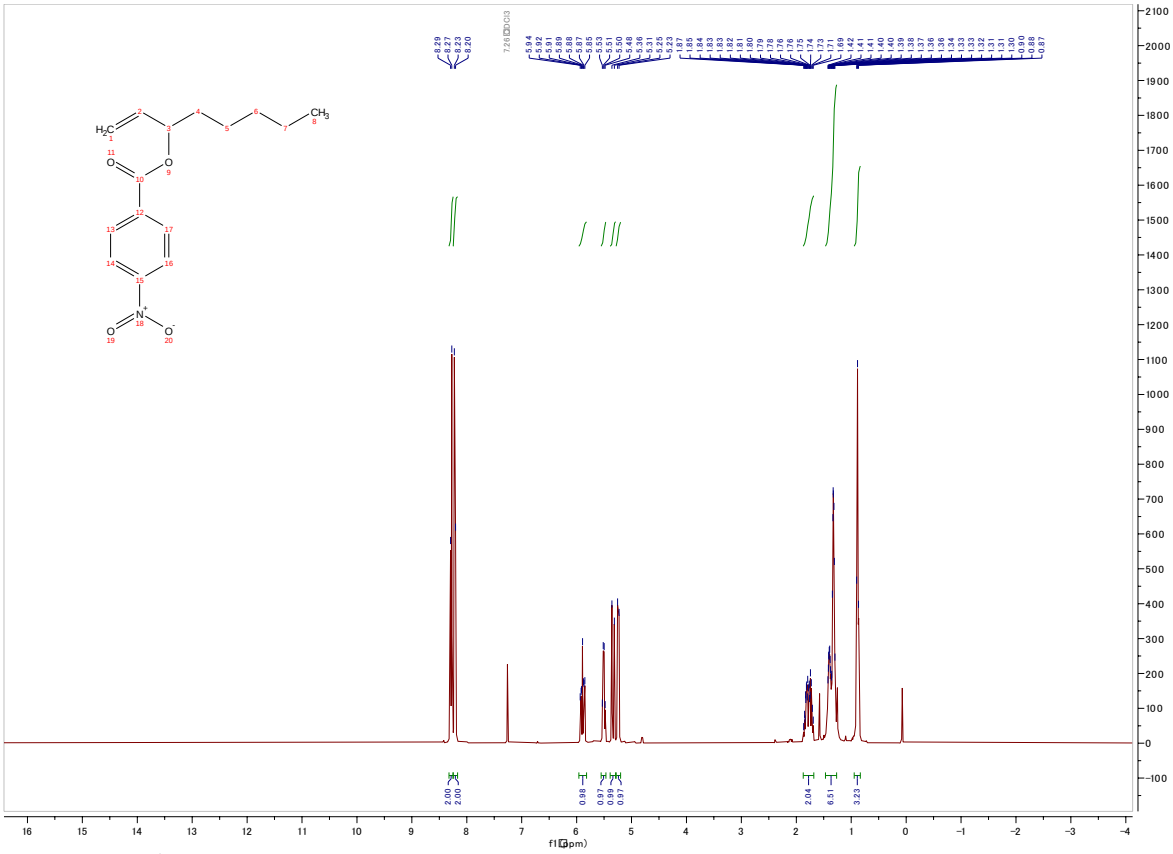


Figure S19. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3ca**.

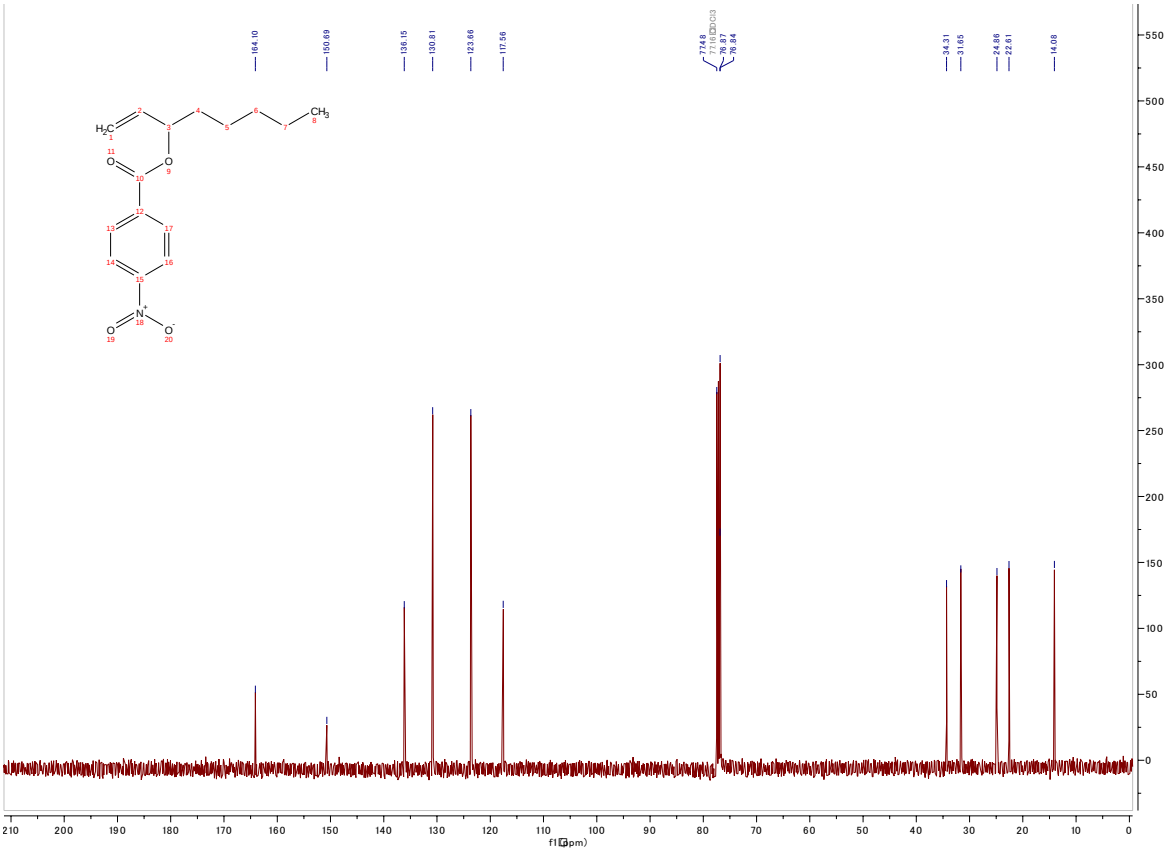


Figure S20. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3ca**.

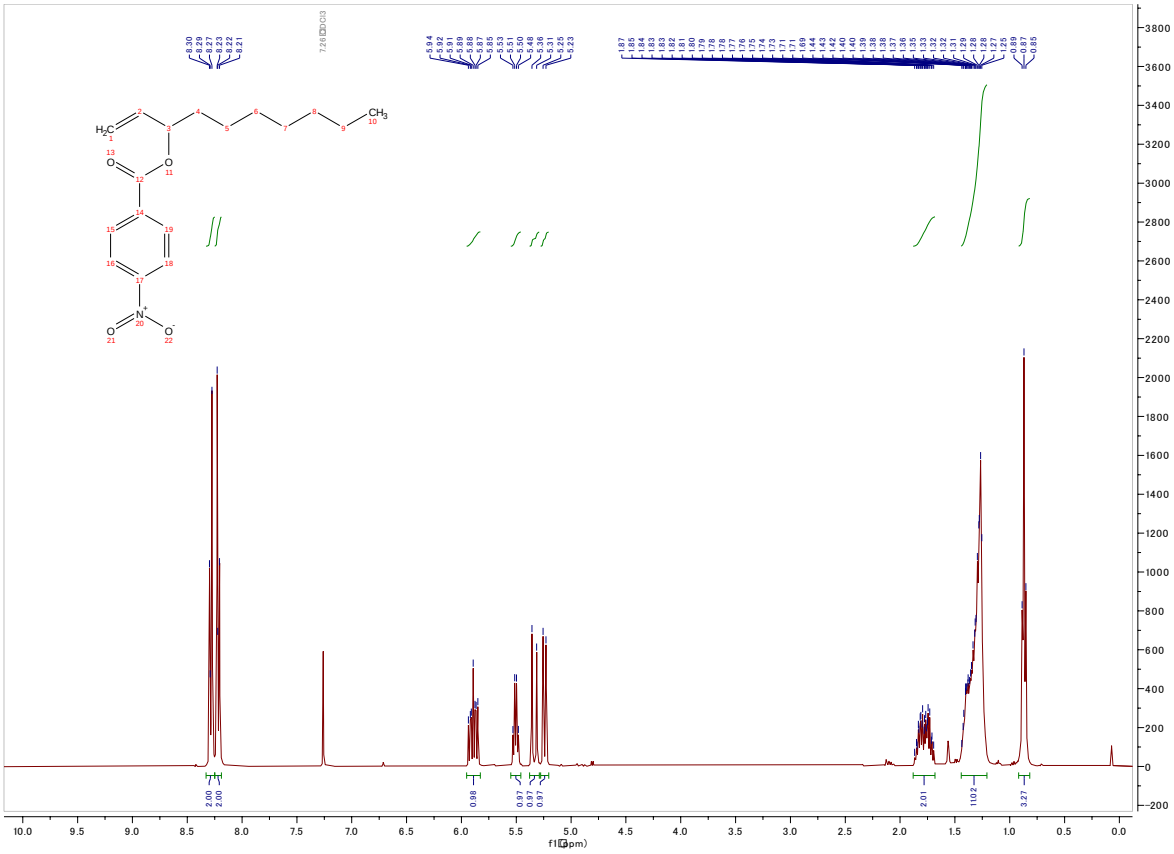


Figure S21. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3da**.

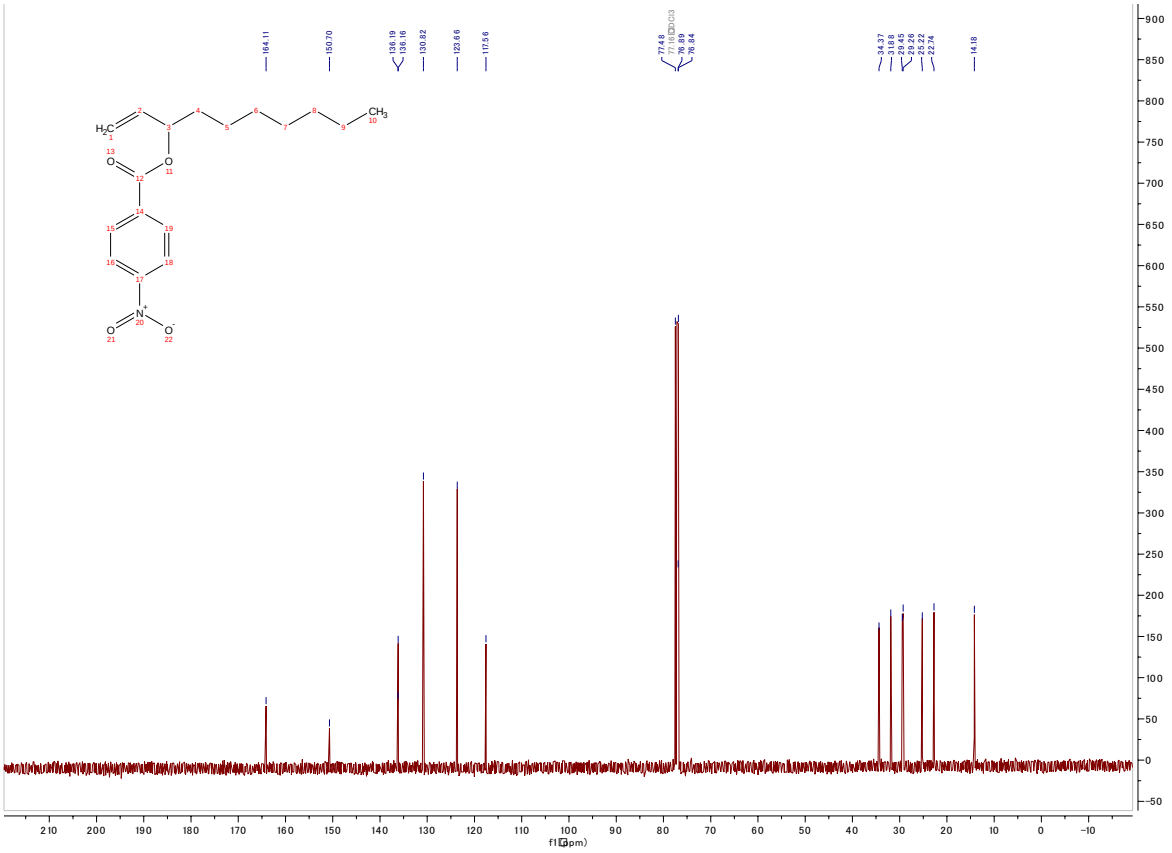


Figure S22. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3da**.

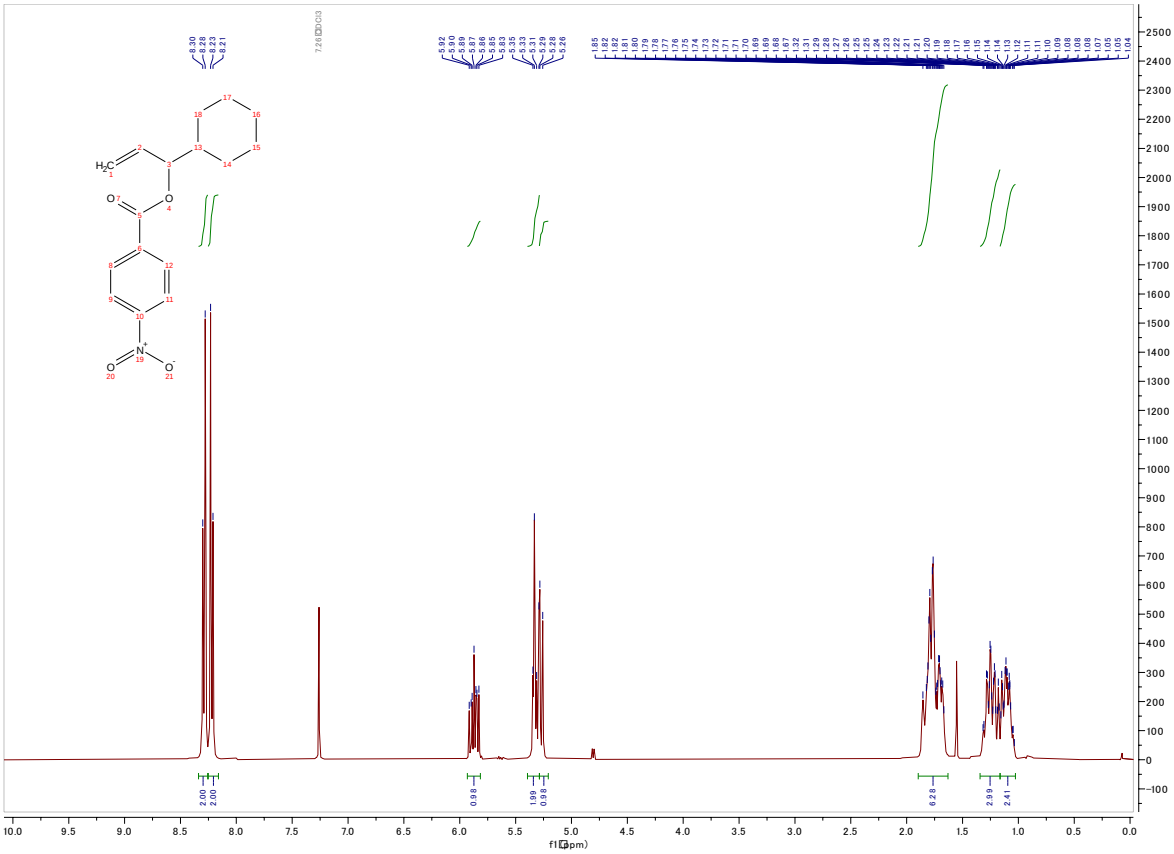


Figure S23. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3ea**.

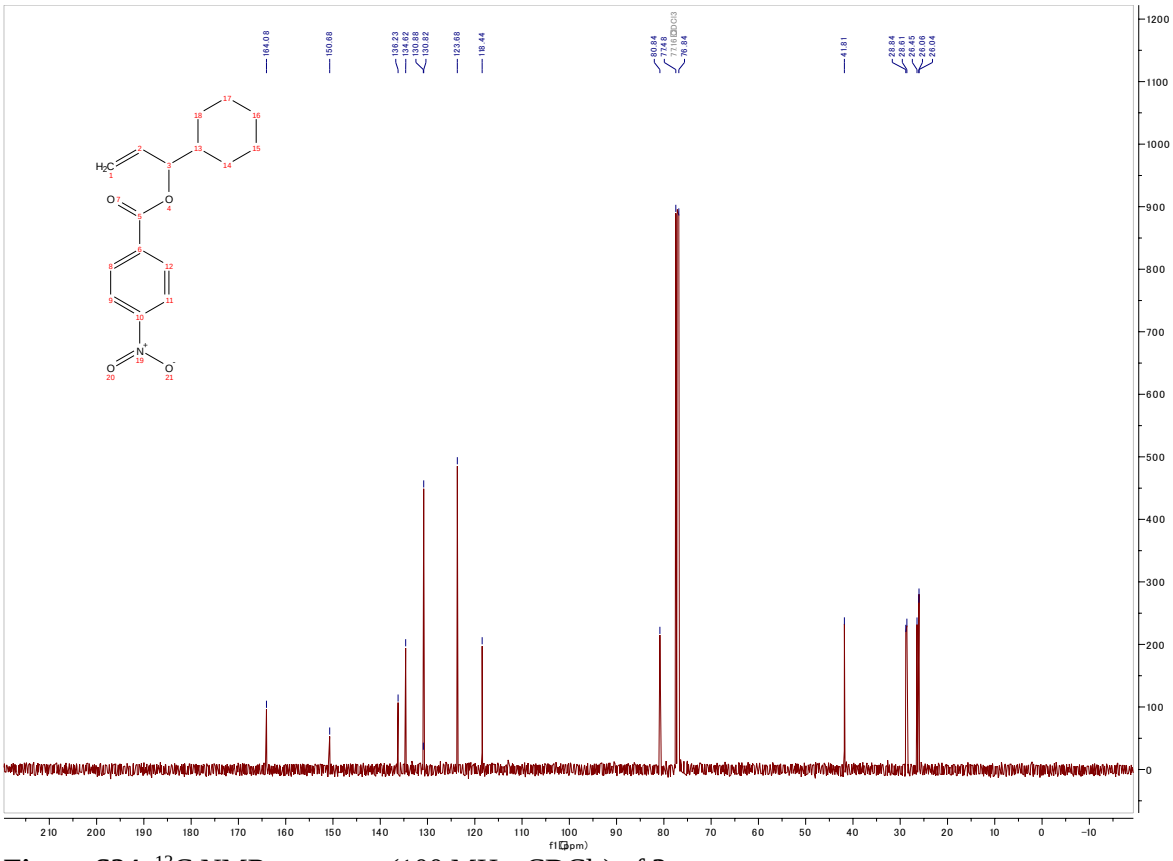


Figure S24. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3ea**.

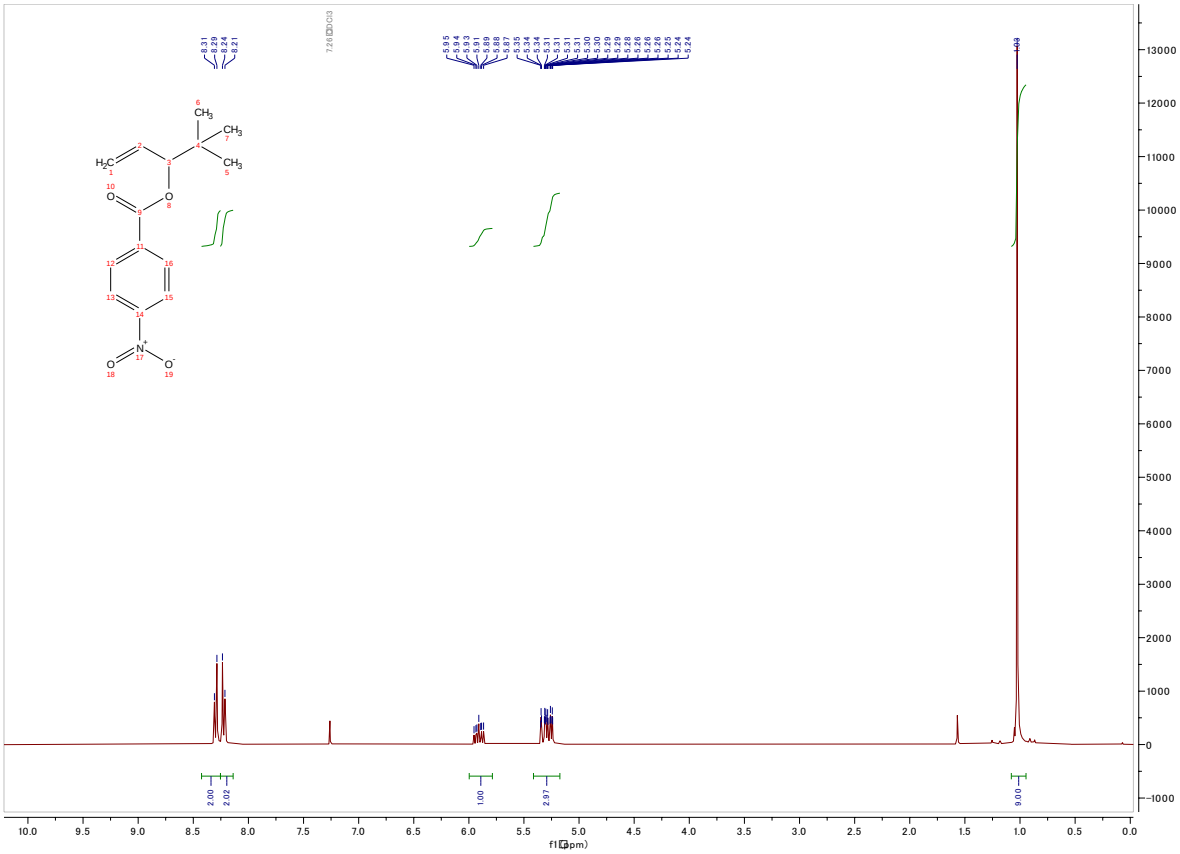


Figure S25. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3fa**.

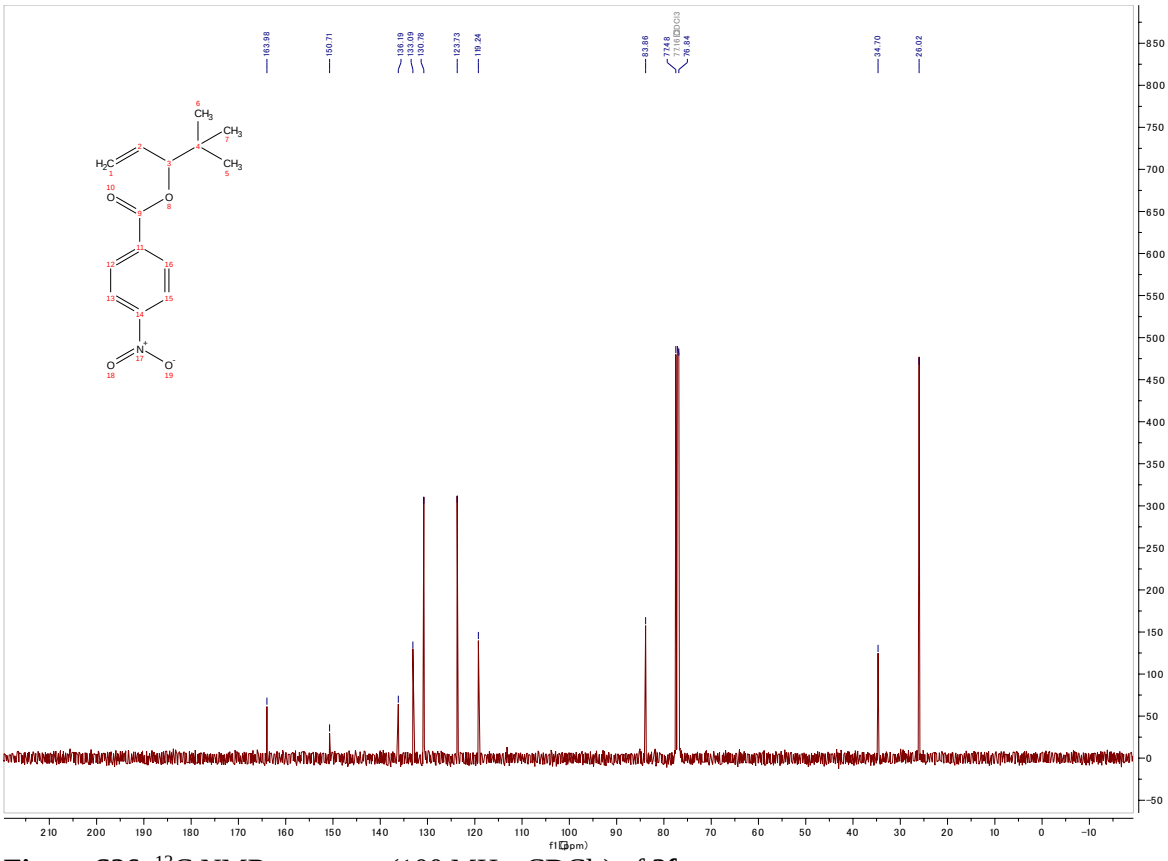


Figure S26. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3fa**.

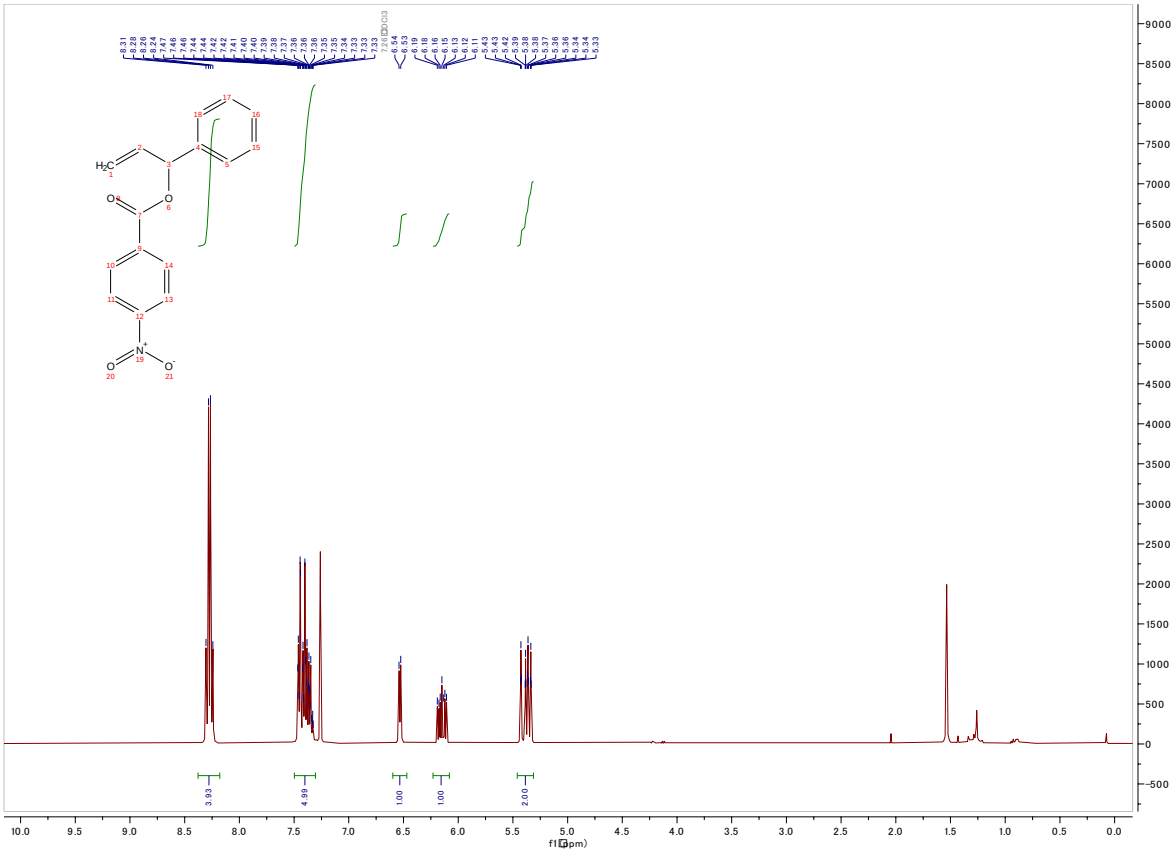


Figure S27. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3ga**.

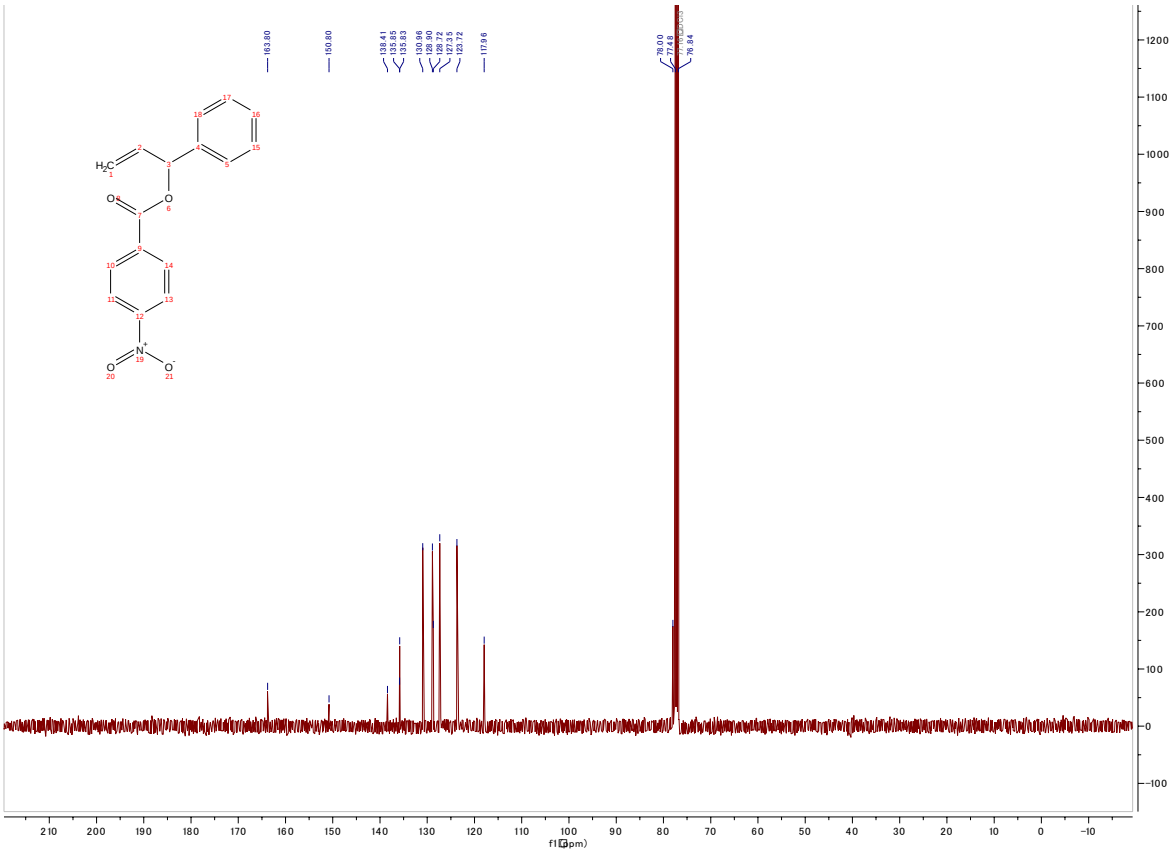


Figure S28. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3ga**.

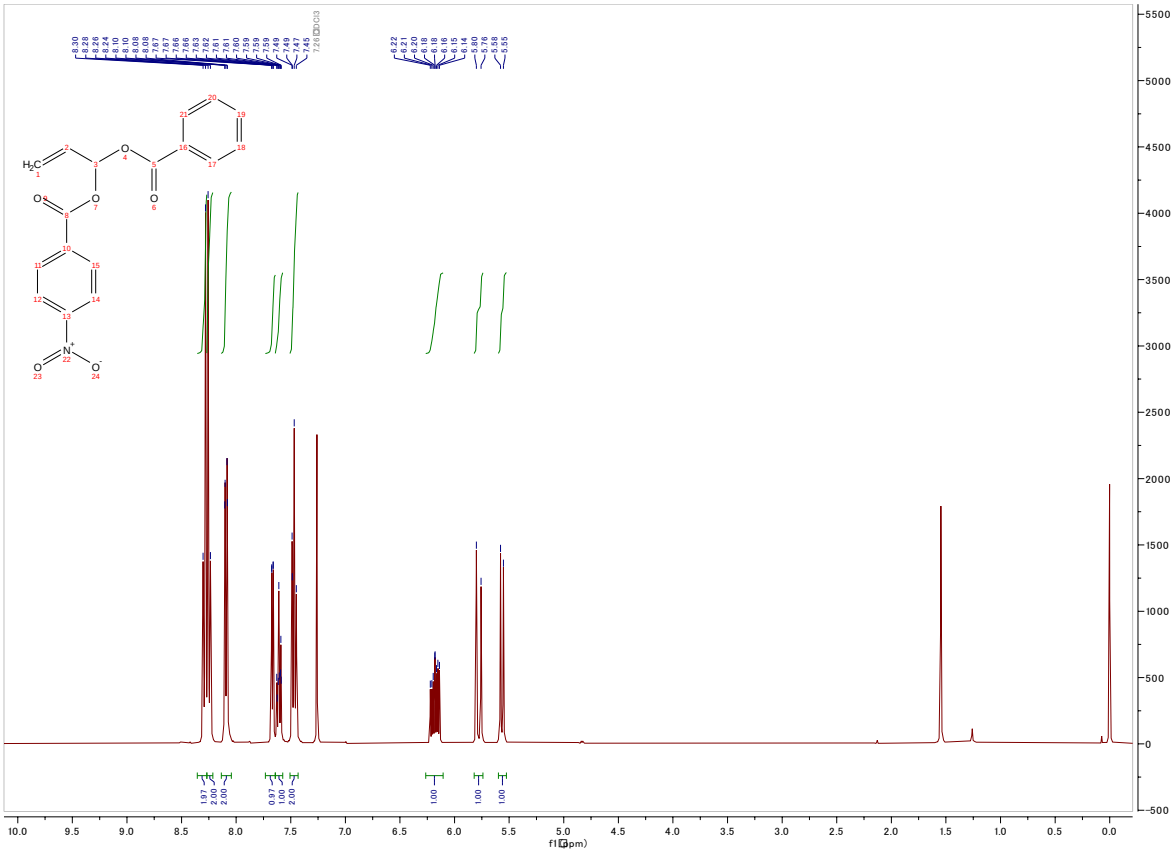


Figure S29. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3ha**.

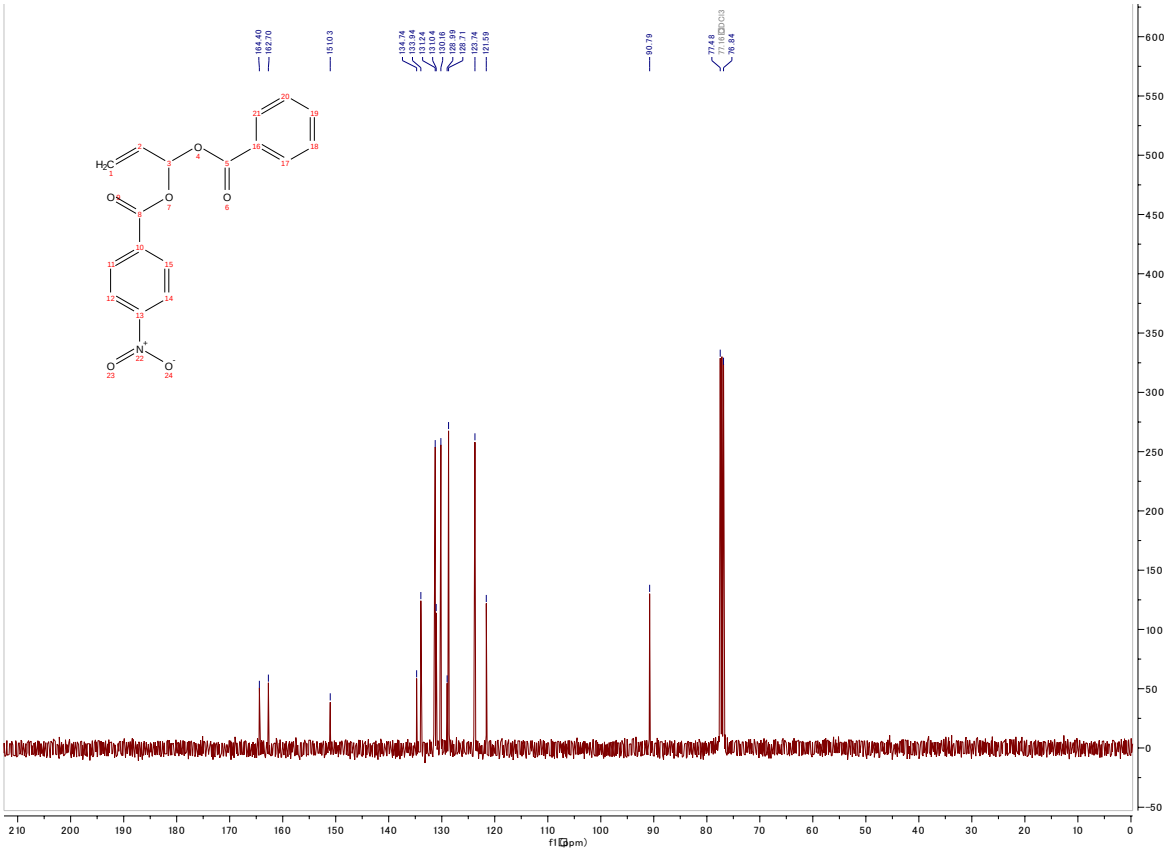


Figure S30. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3ha**.

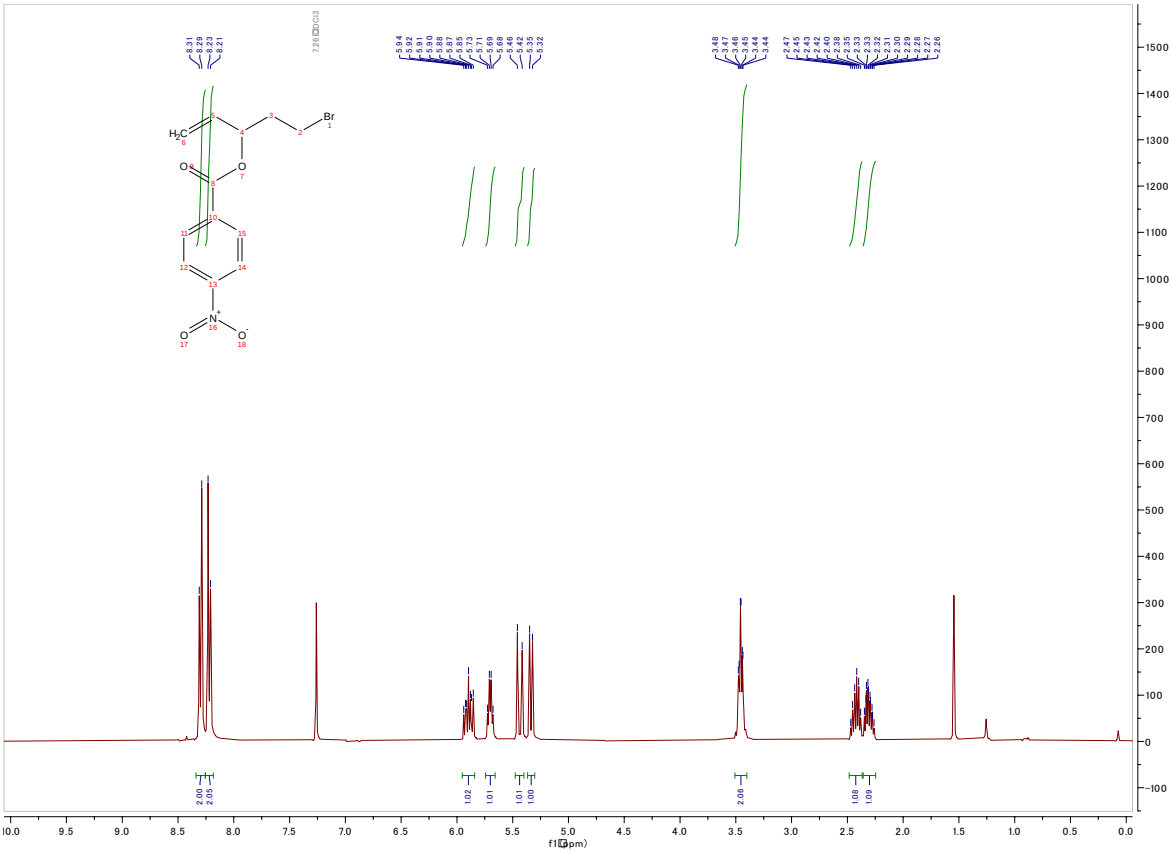


Figure S31. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3ia**.

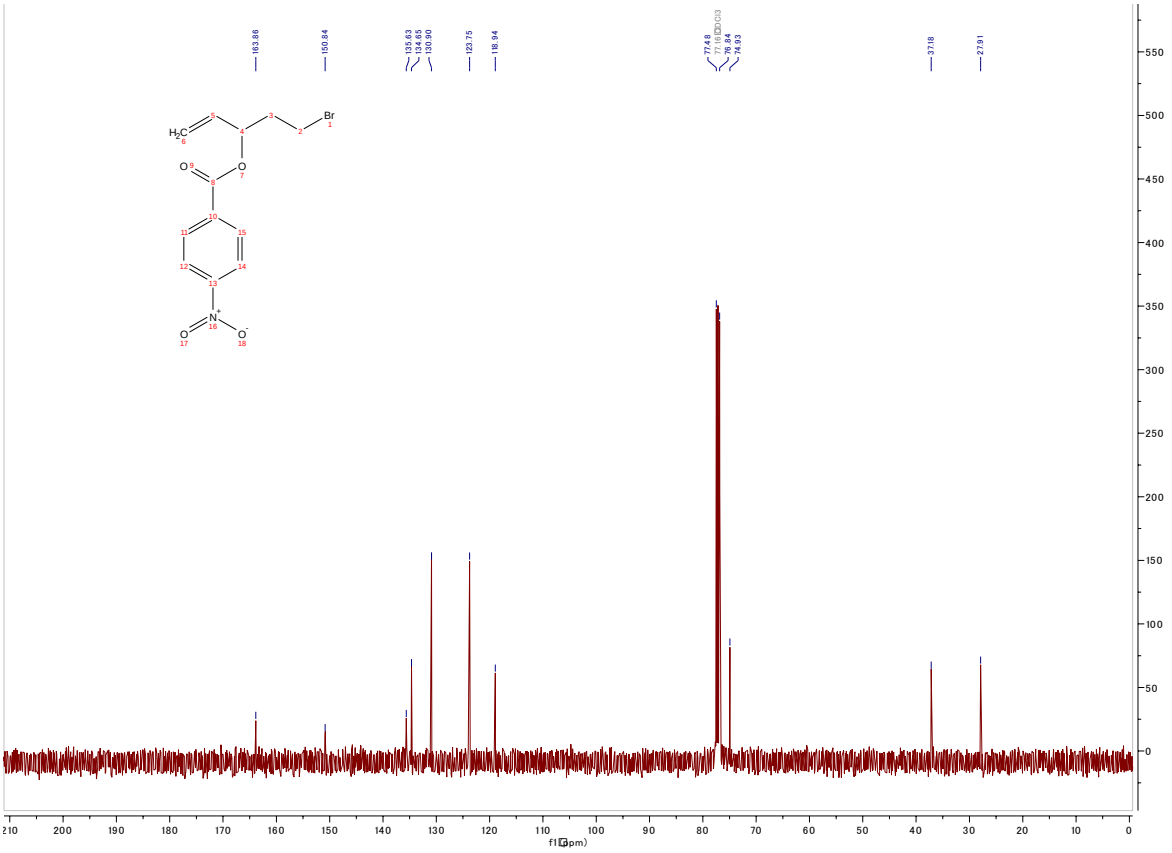


Figure S32. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3ia**.

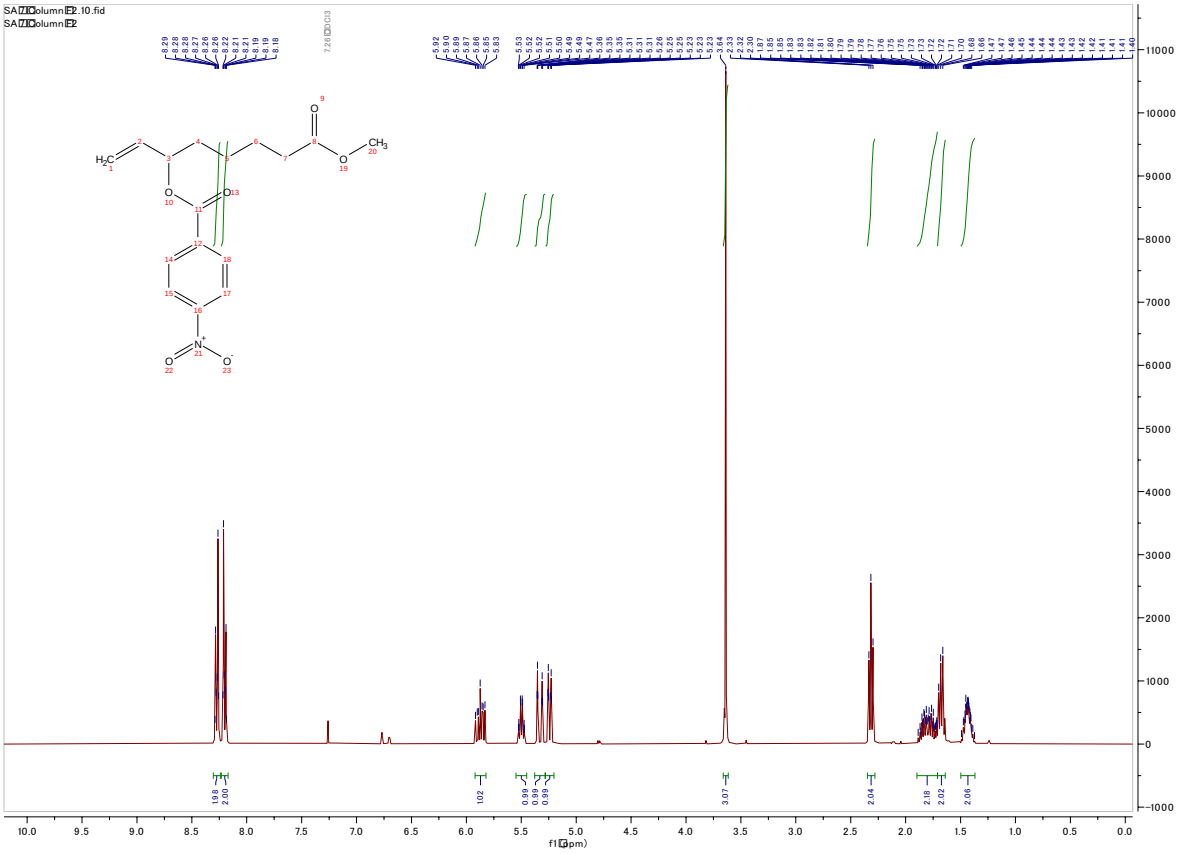


Figure S33. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3ja**.

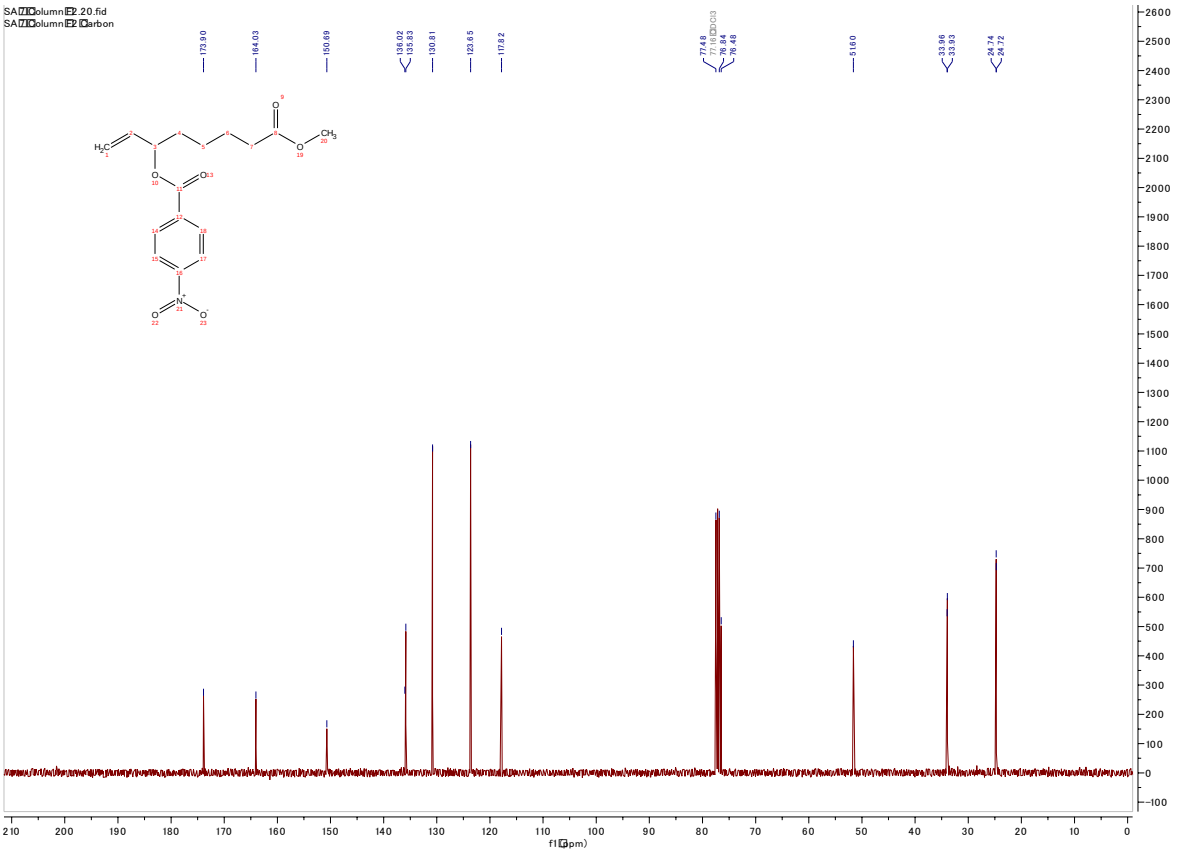


Figure S34. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3ja**.

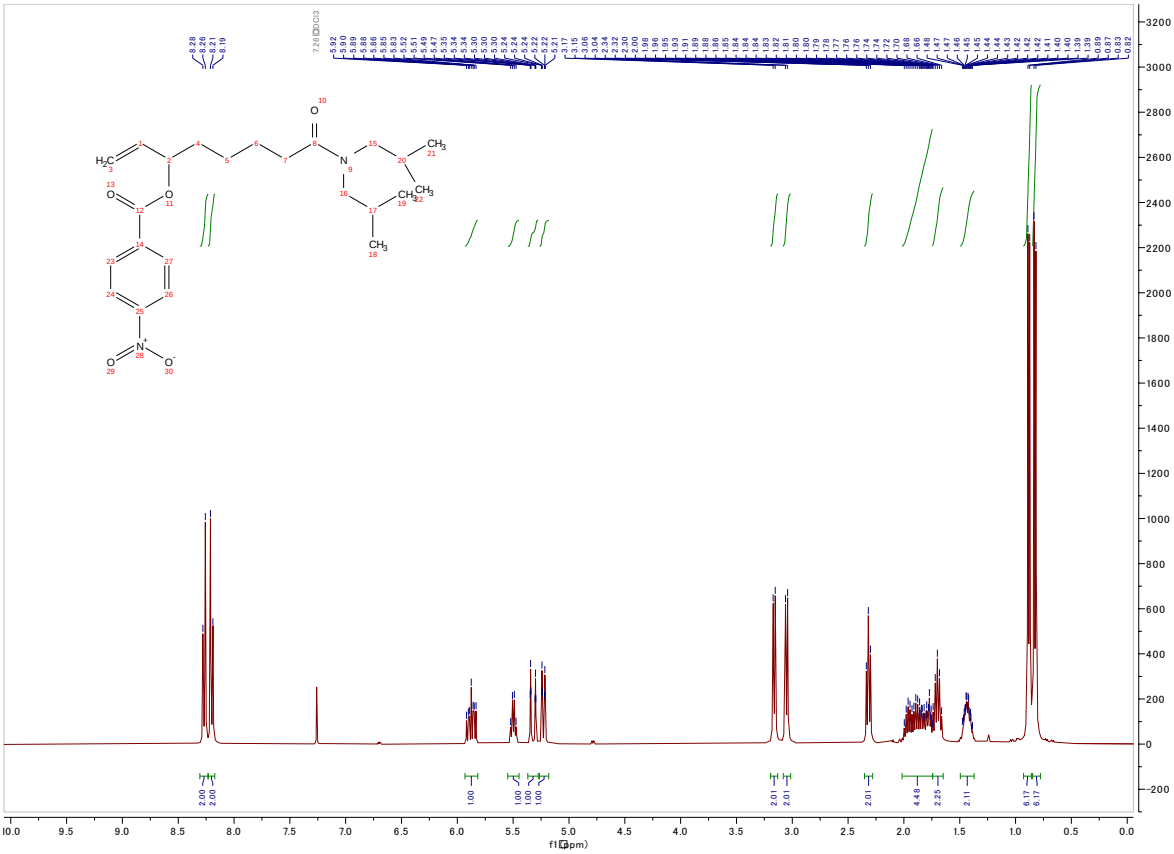


Figure S35. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3ka**.

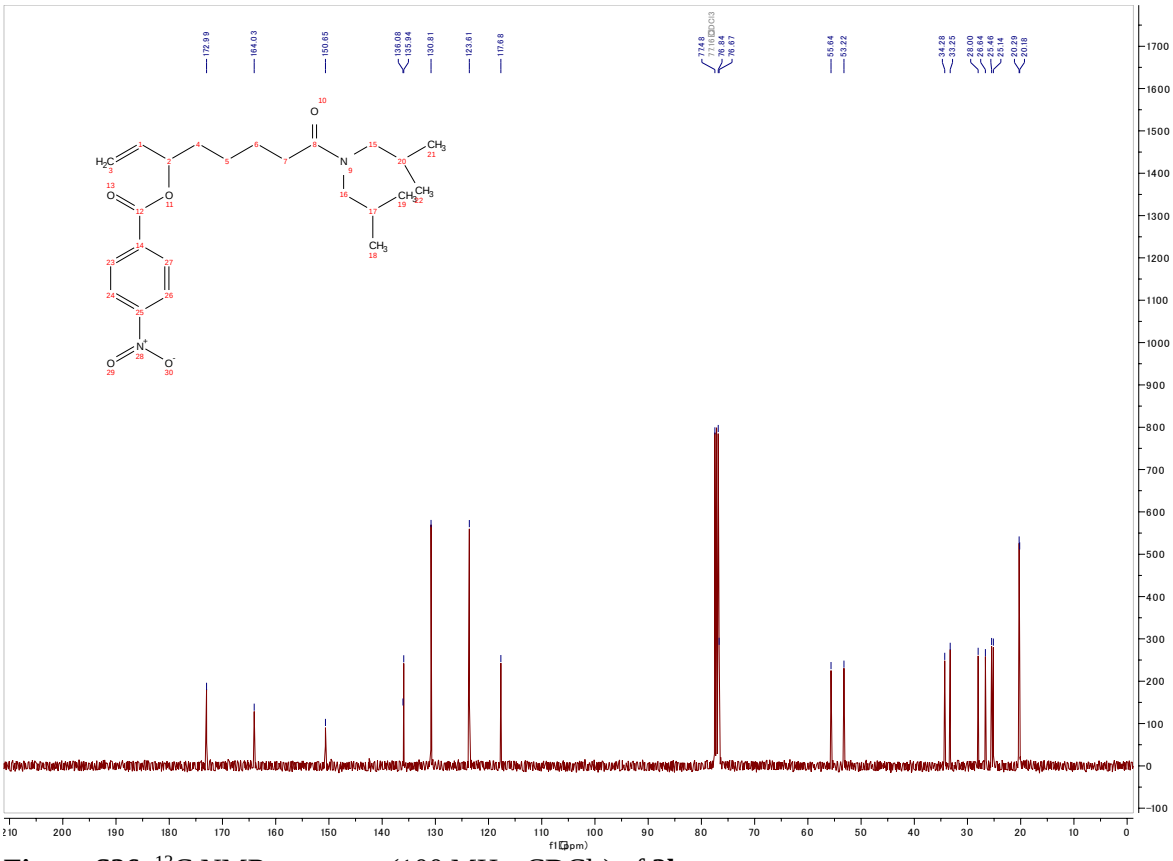


Figure S36. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3ka**.

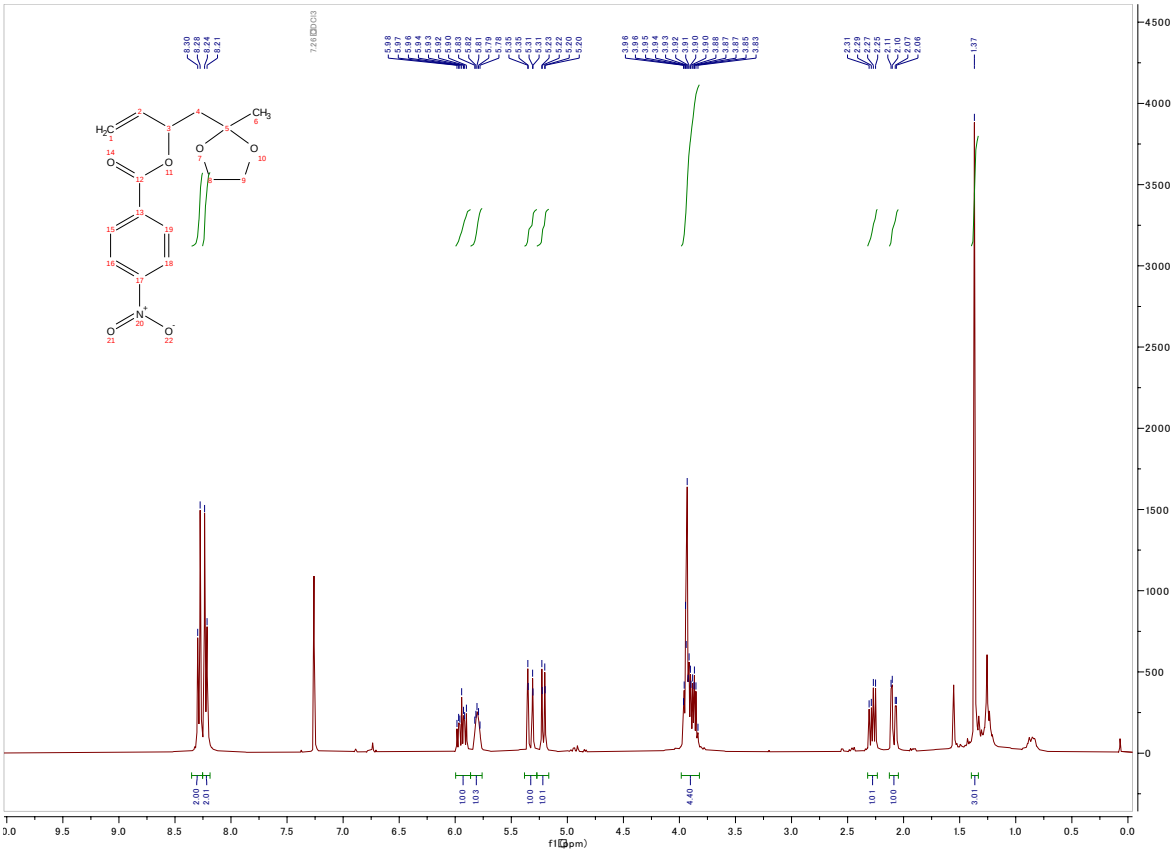


Figure S37. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3la**.

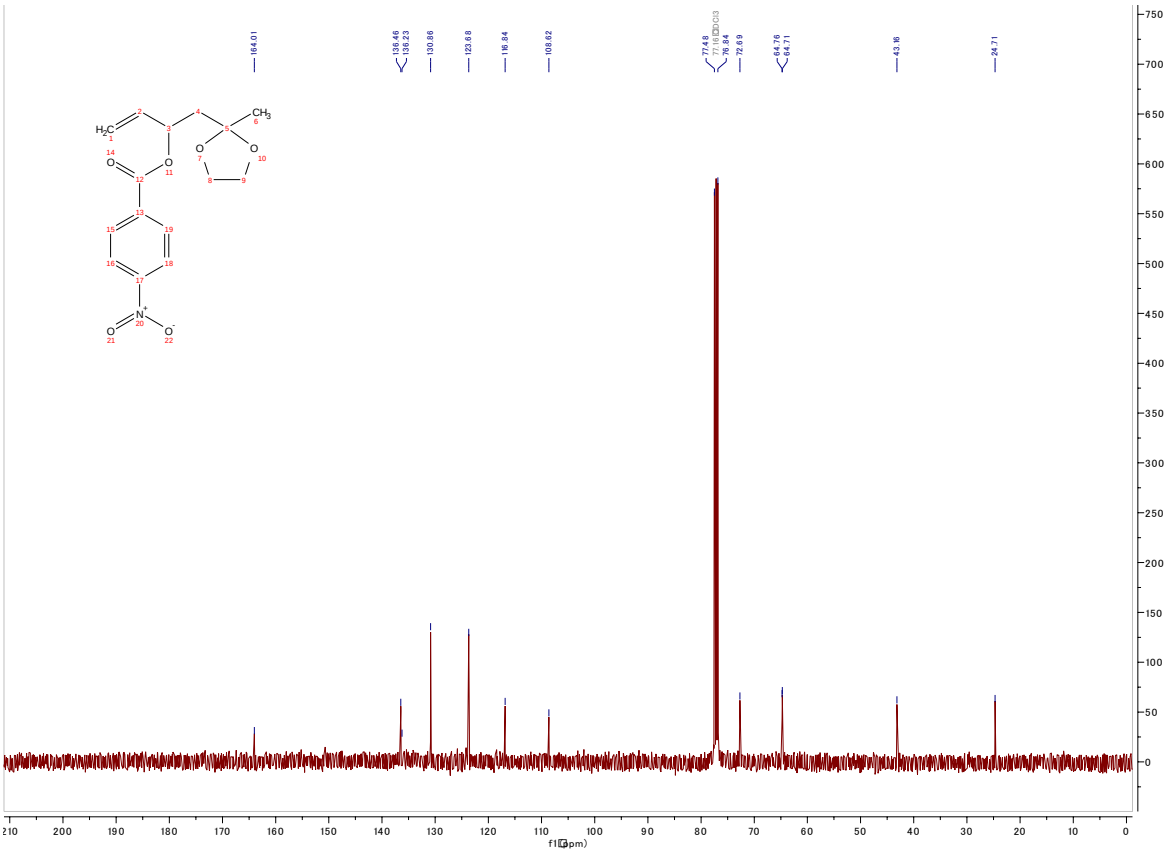


Figure S38. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3la**.

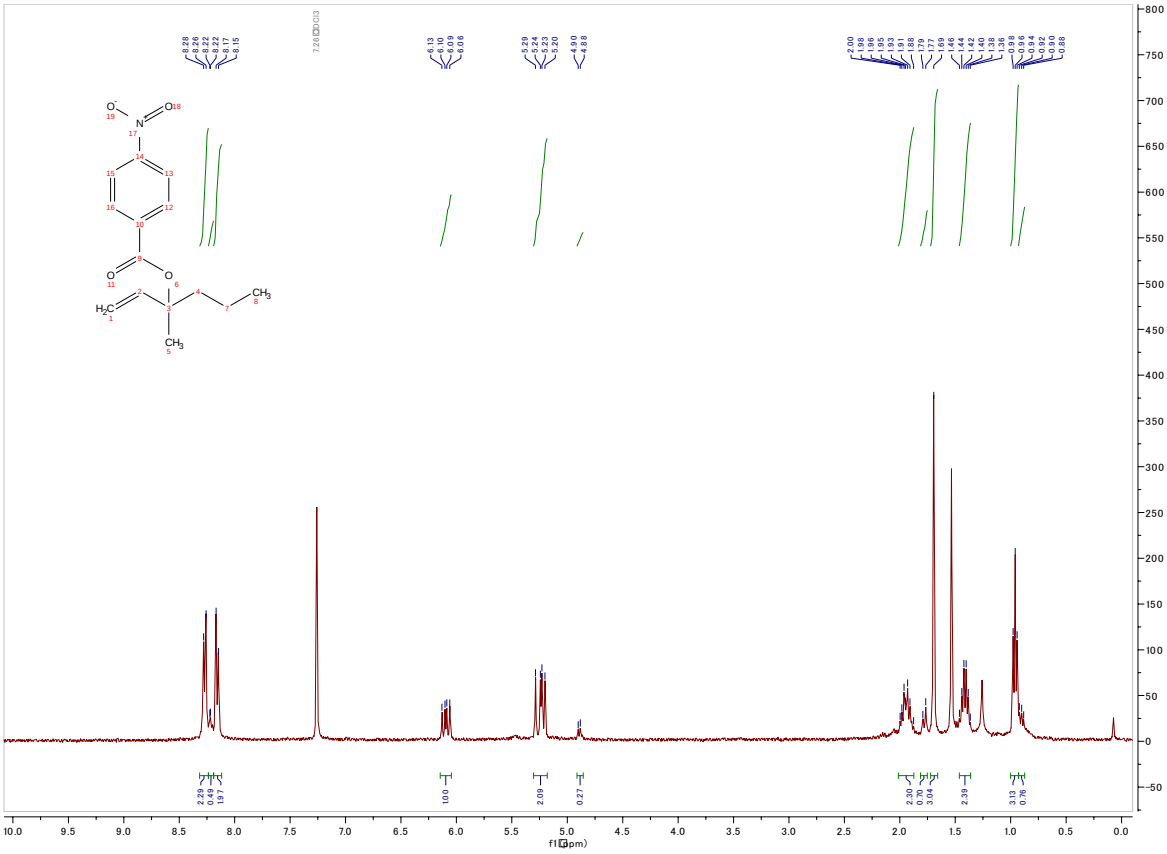


Figure S39. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3ma**.

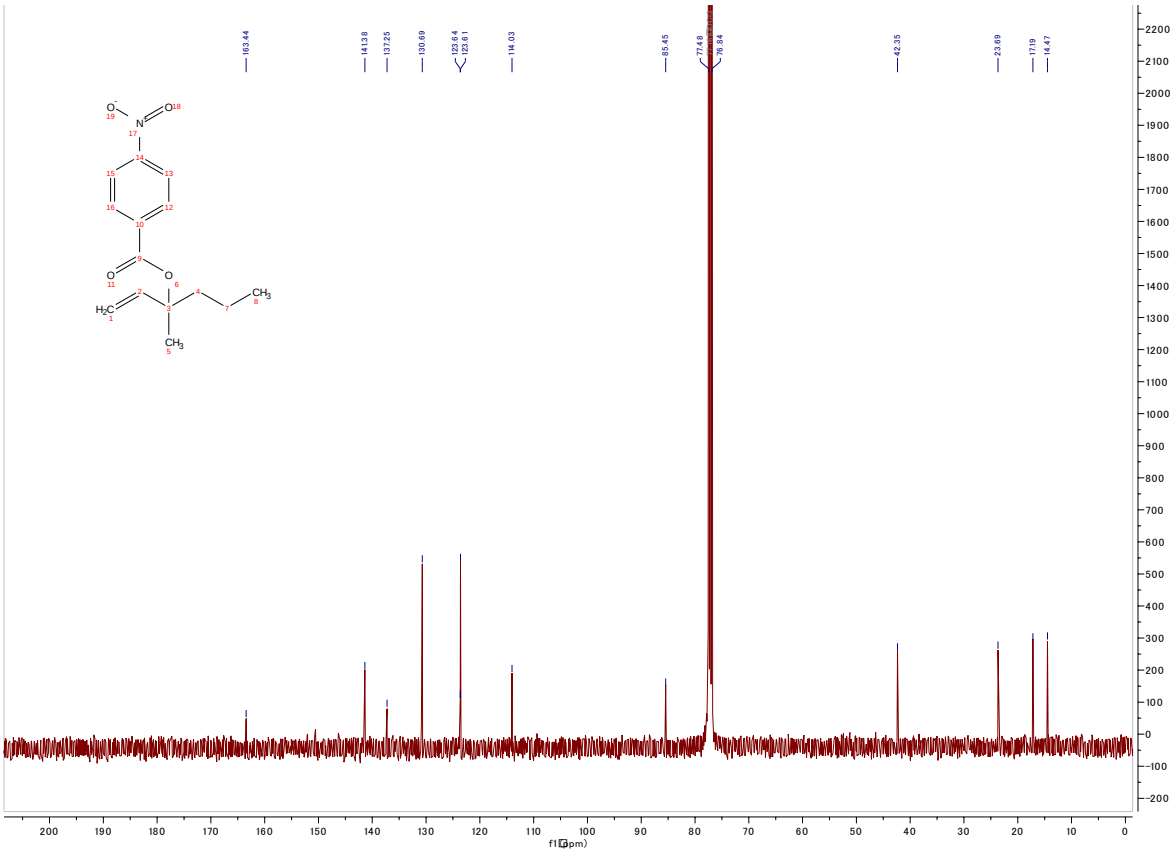


Figure S40. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3ma**.

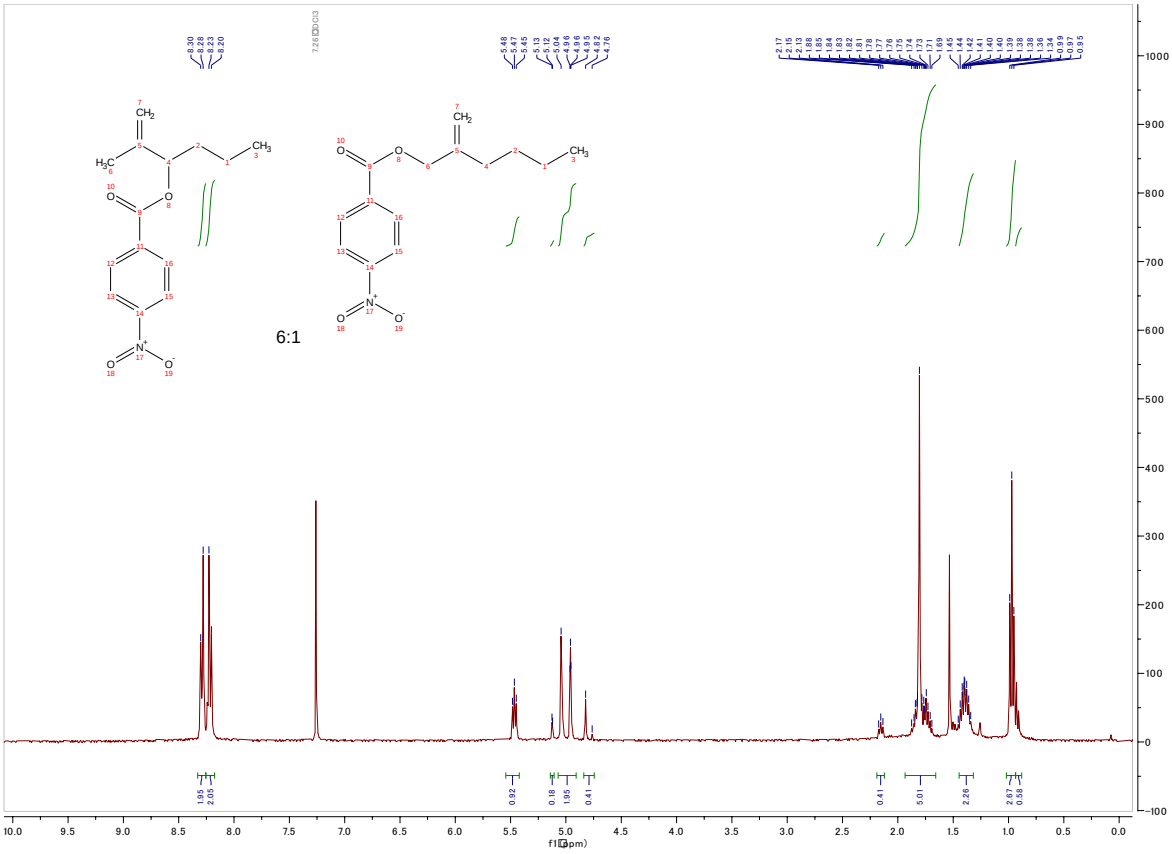


Figure S41. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3na**.

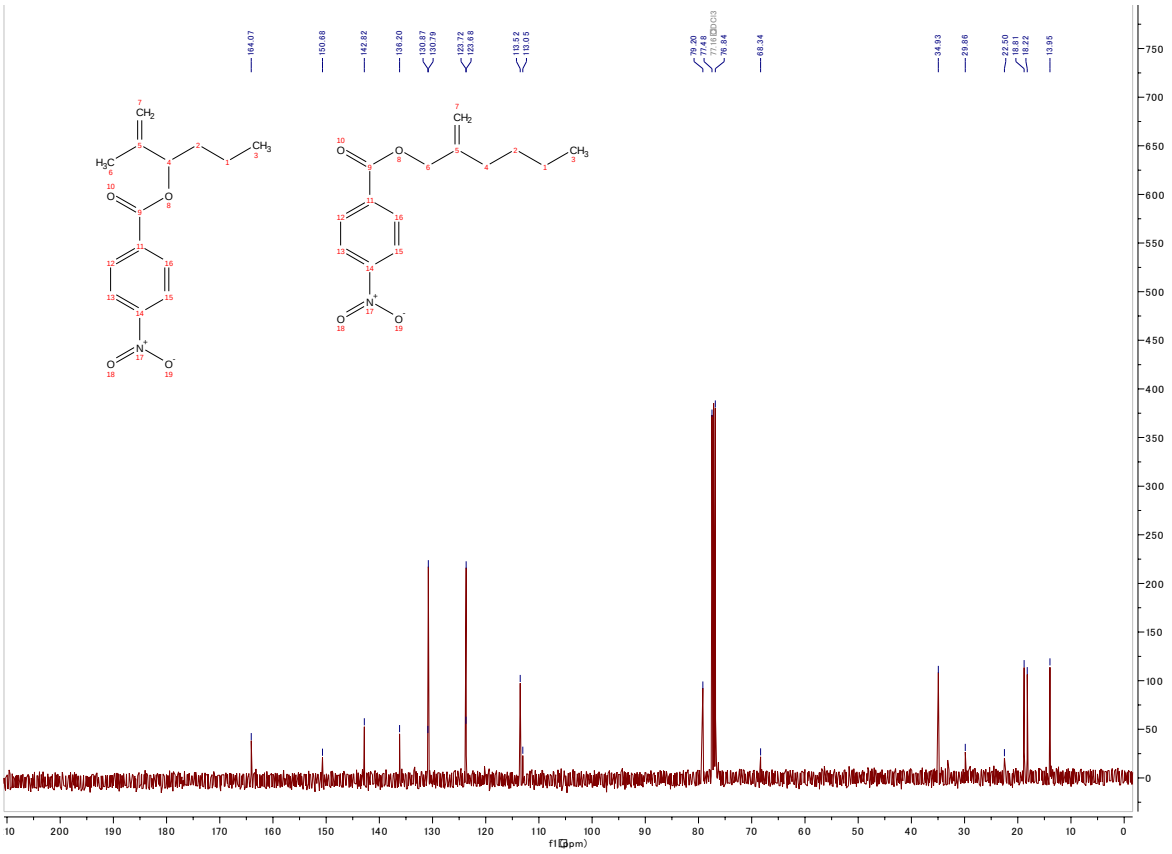


Figure S42. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3na**.

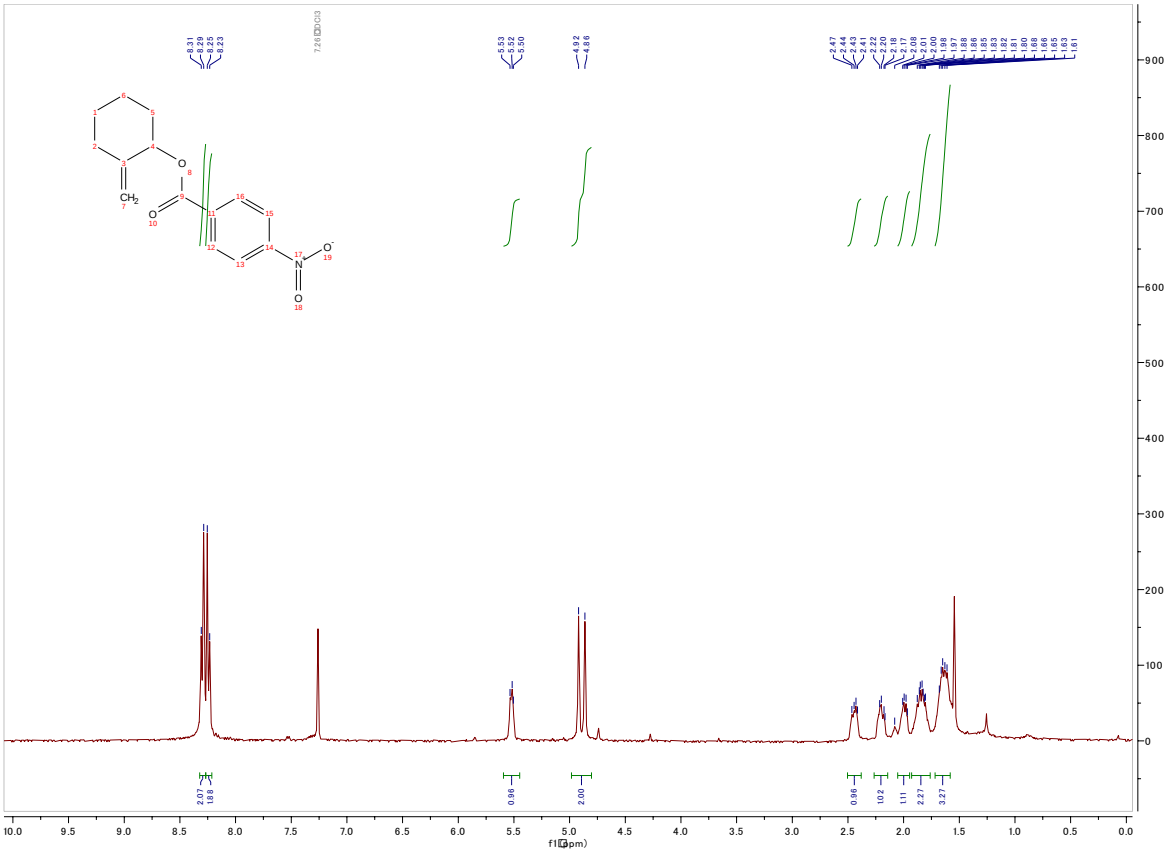


Figure S43. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3oa**.

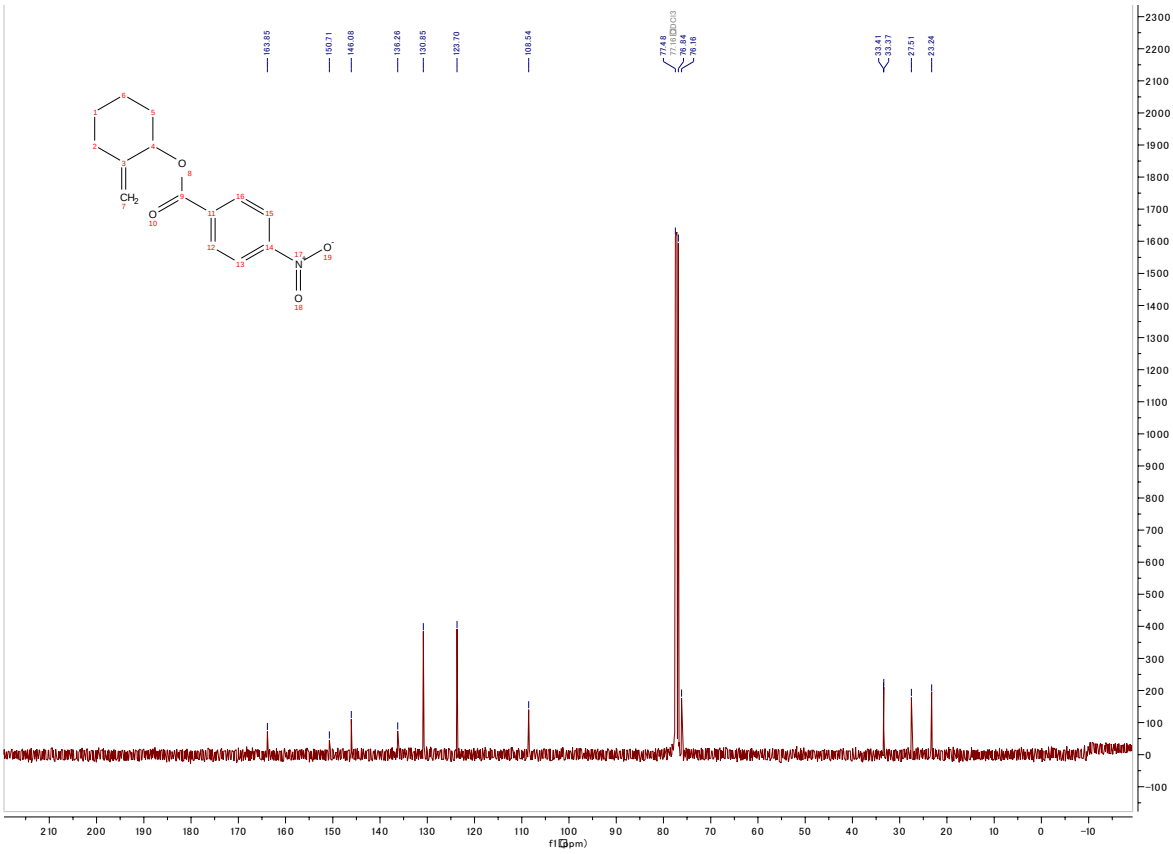


Figure S44. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3oa**.

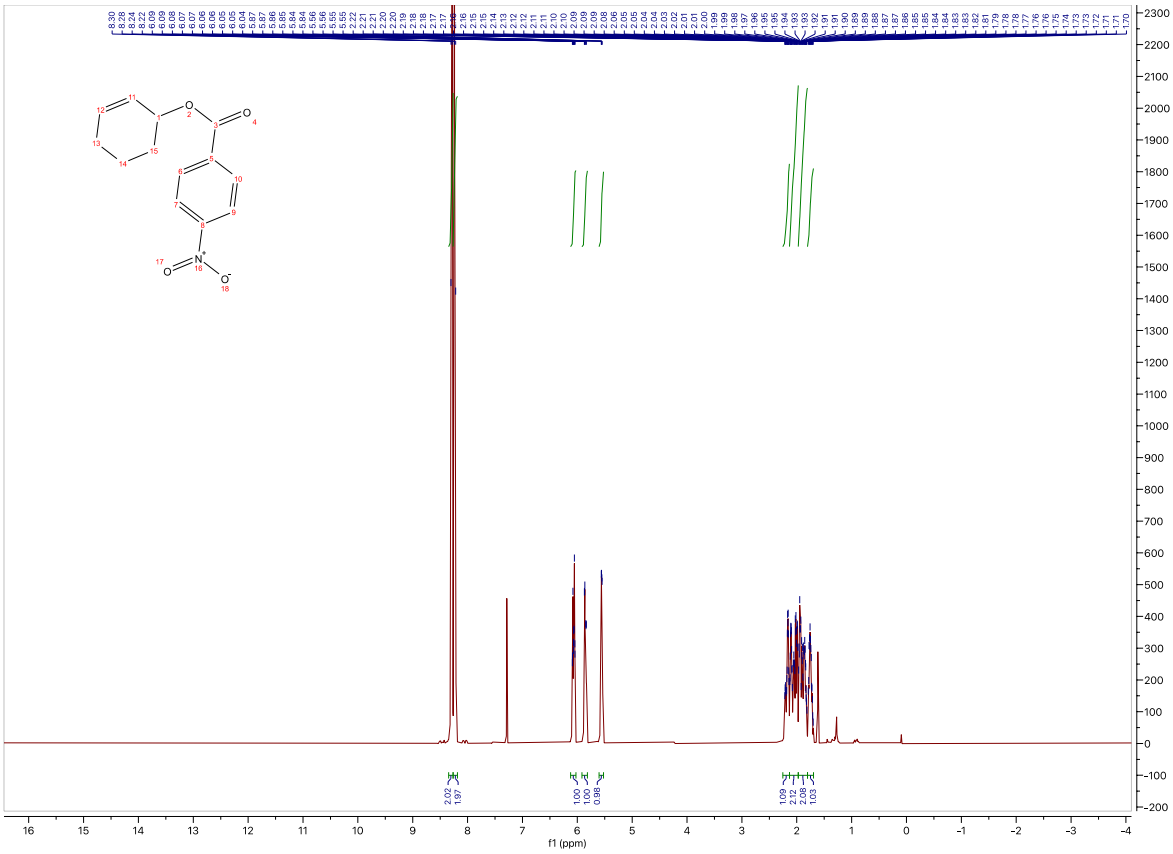


Figure S45. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3pa**.

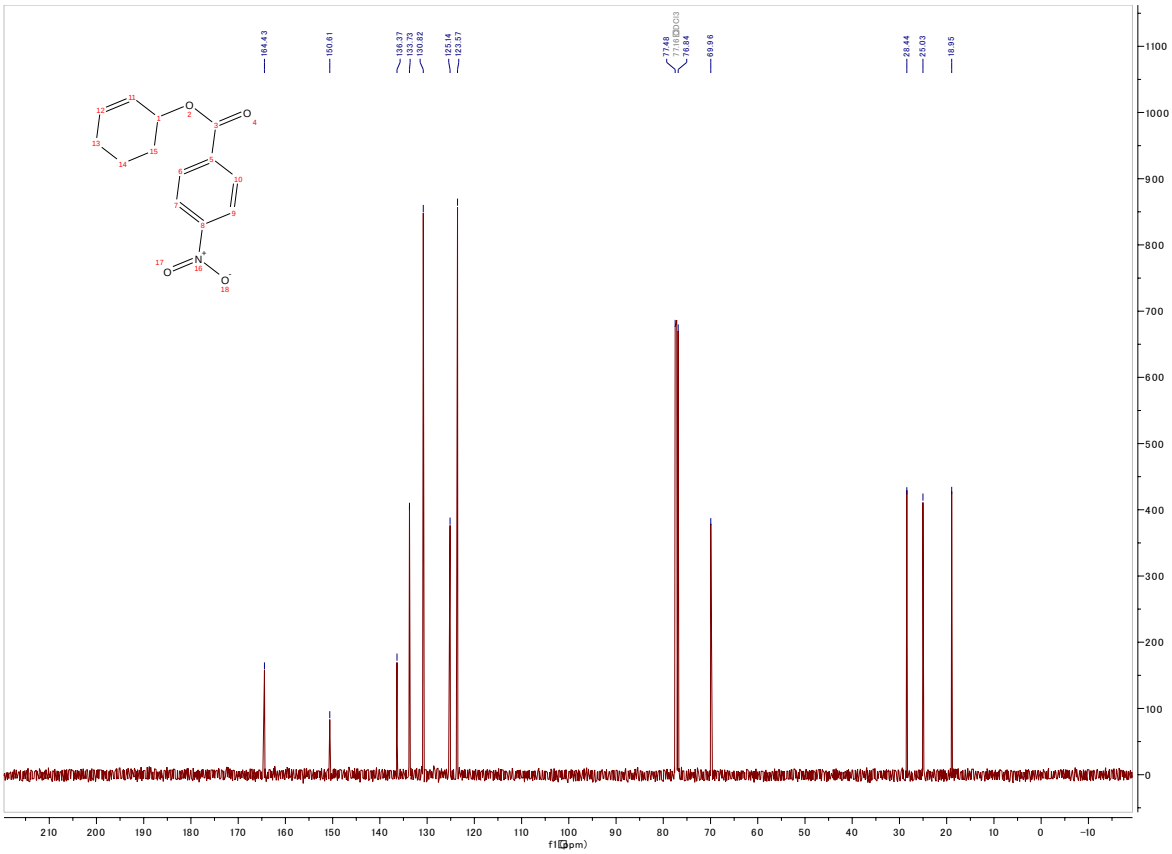


Figure S46. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3pa**.

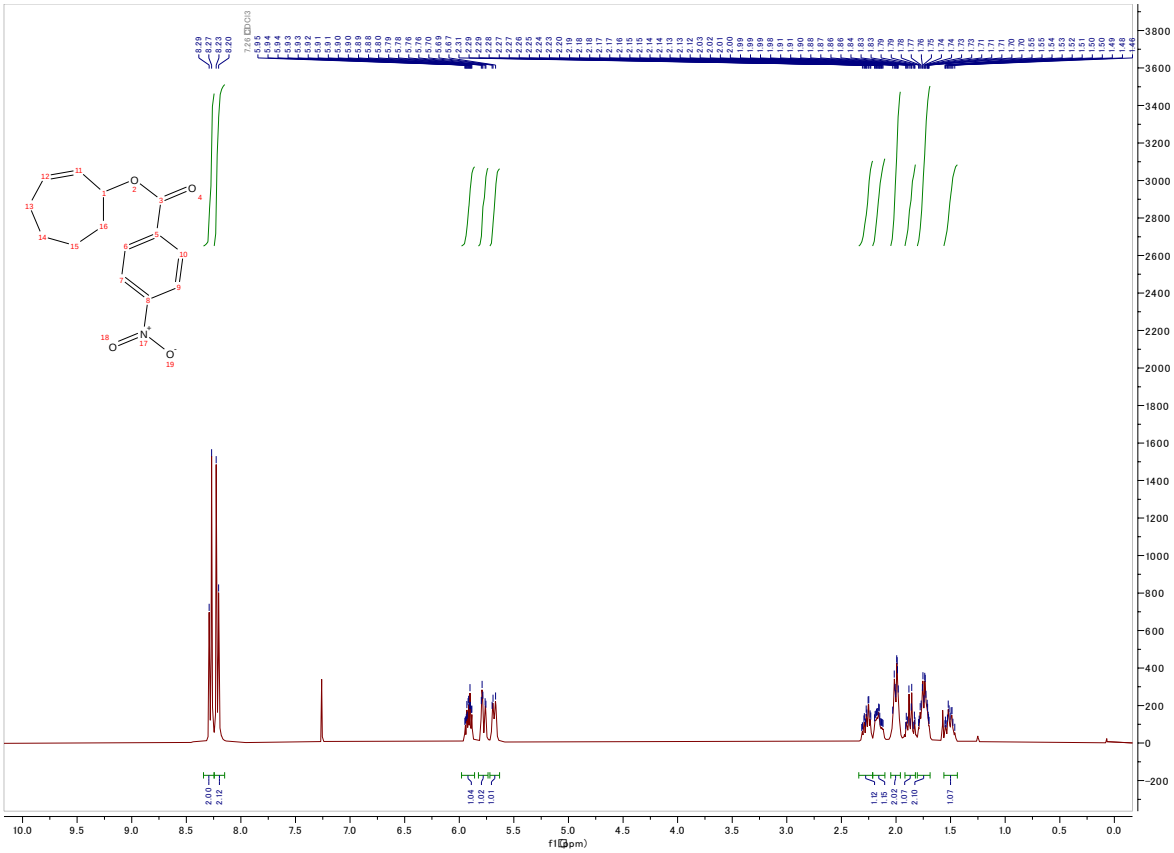


Figure S47. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3qa**.

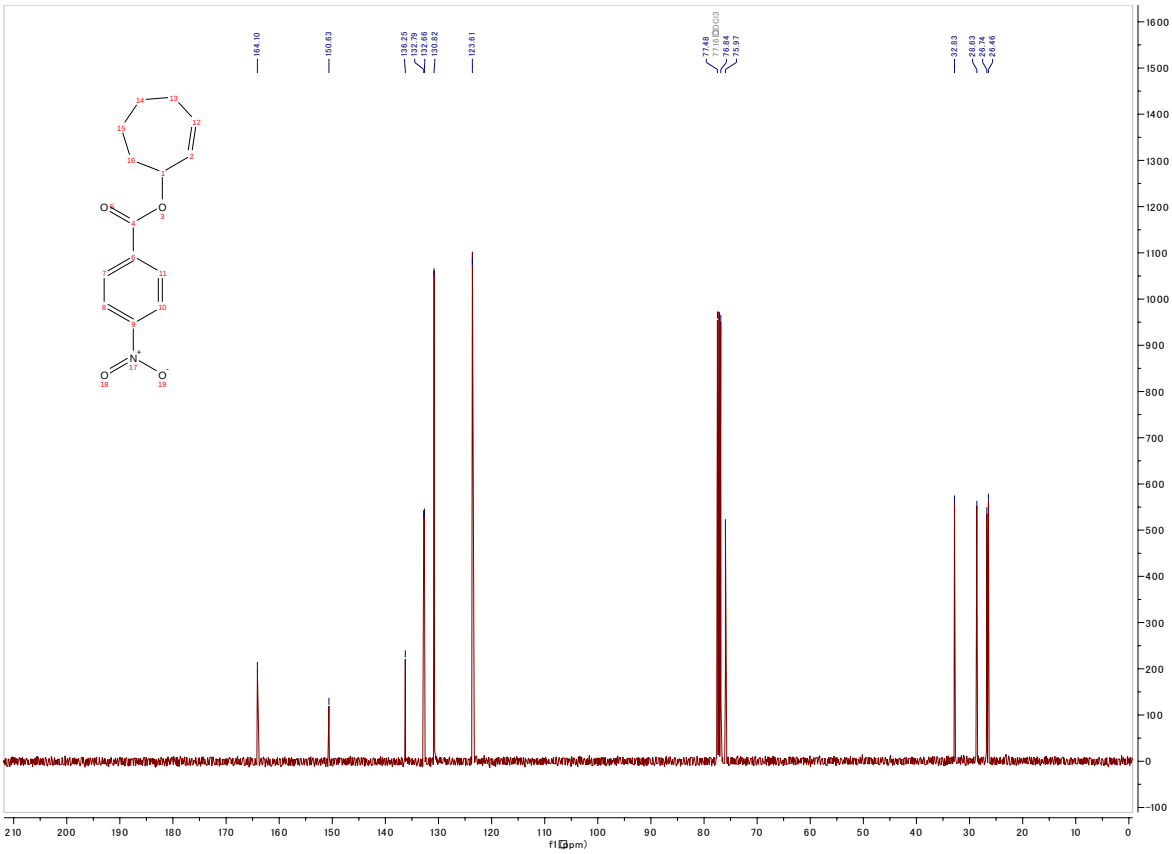


Figure S48. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3qa**.

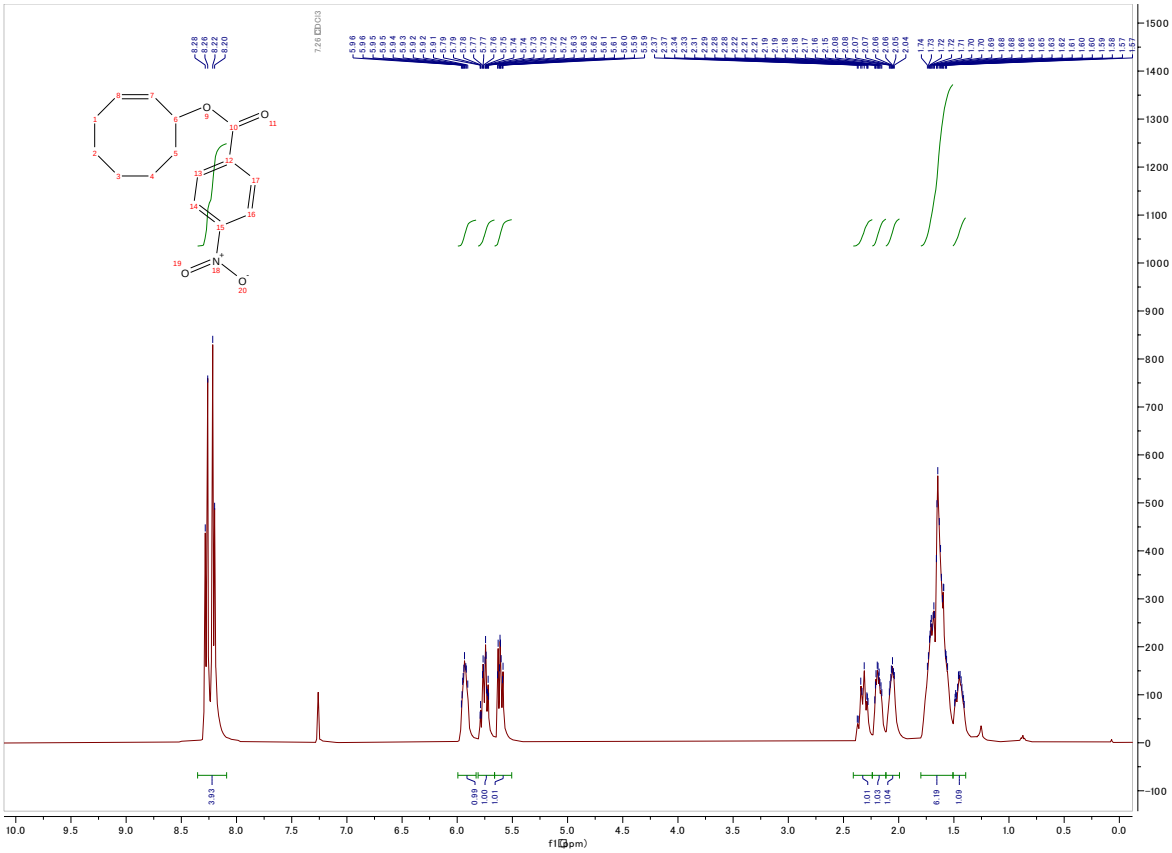


Figure S49. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3ra**.

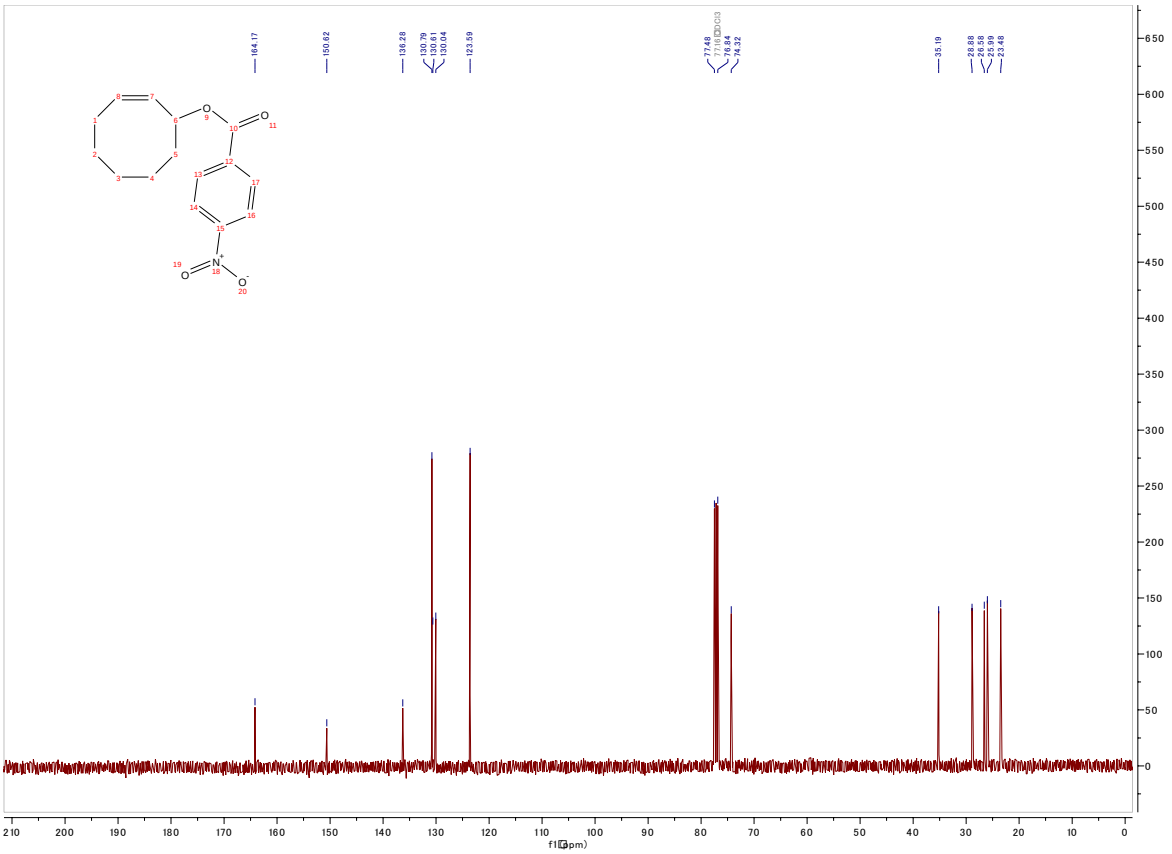


Figure S50. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3ra**.

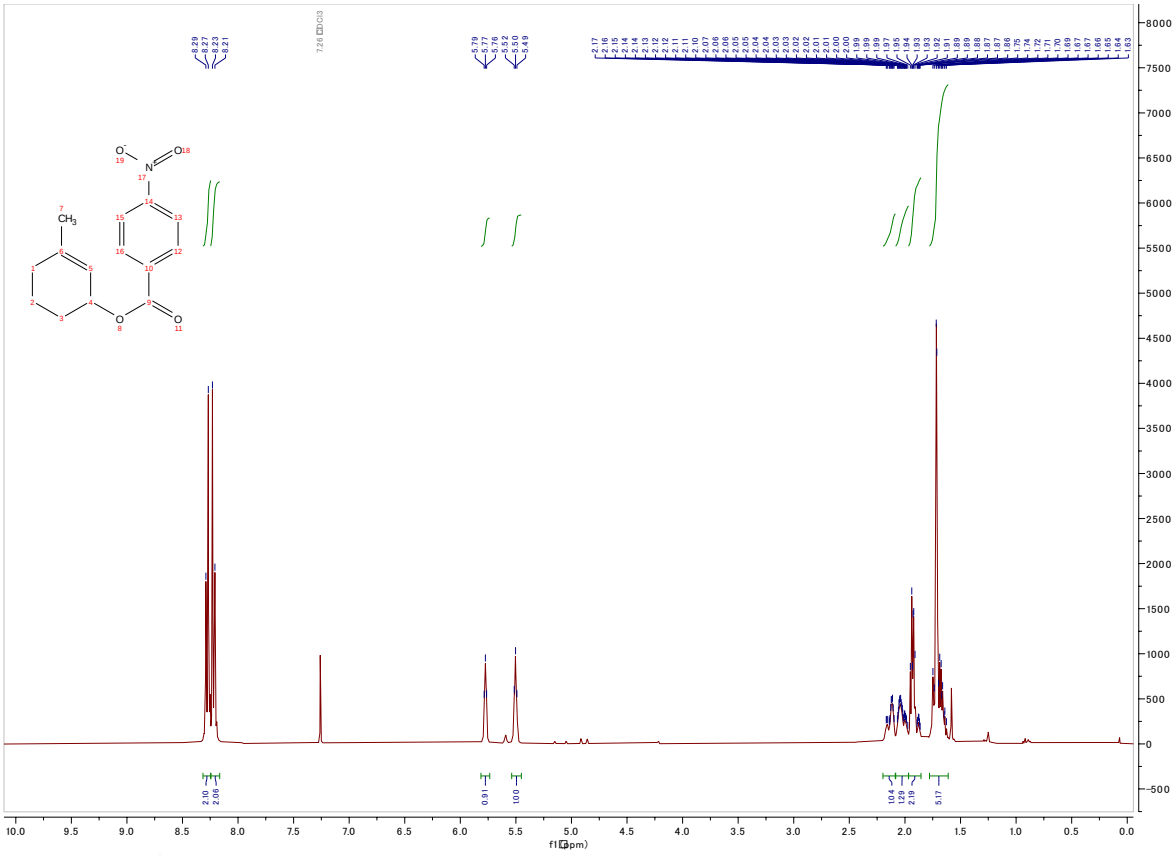


Figure S51. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3sa**.

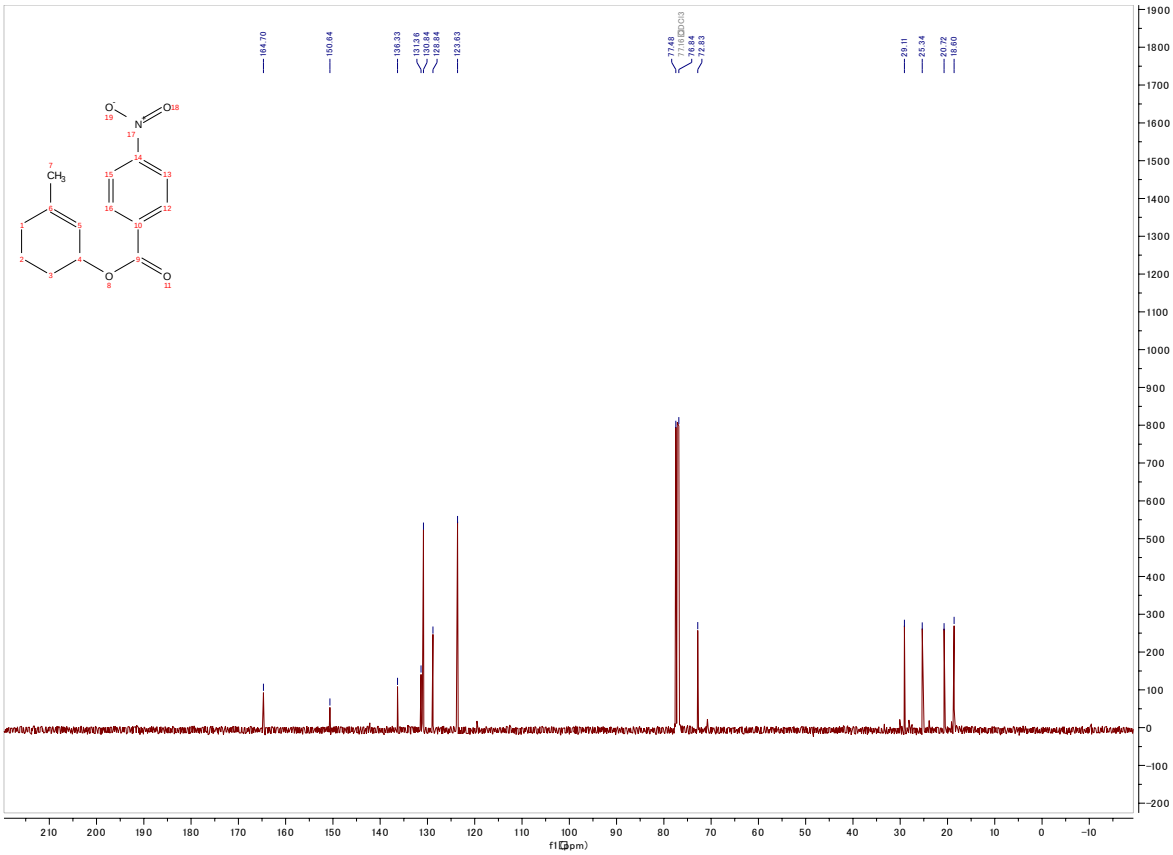


Figure S52. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3sa**.

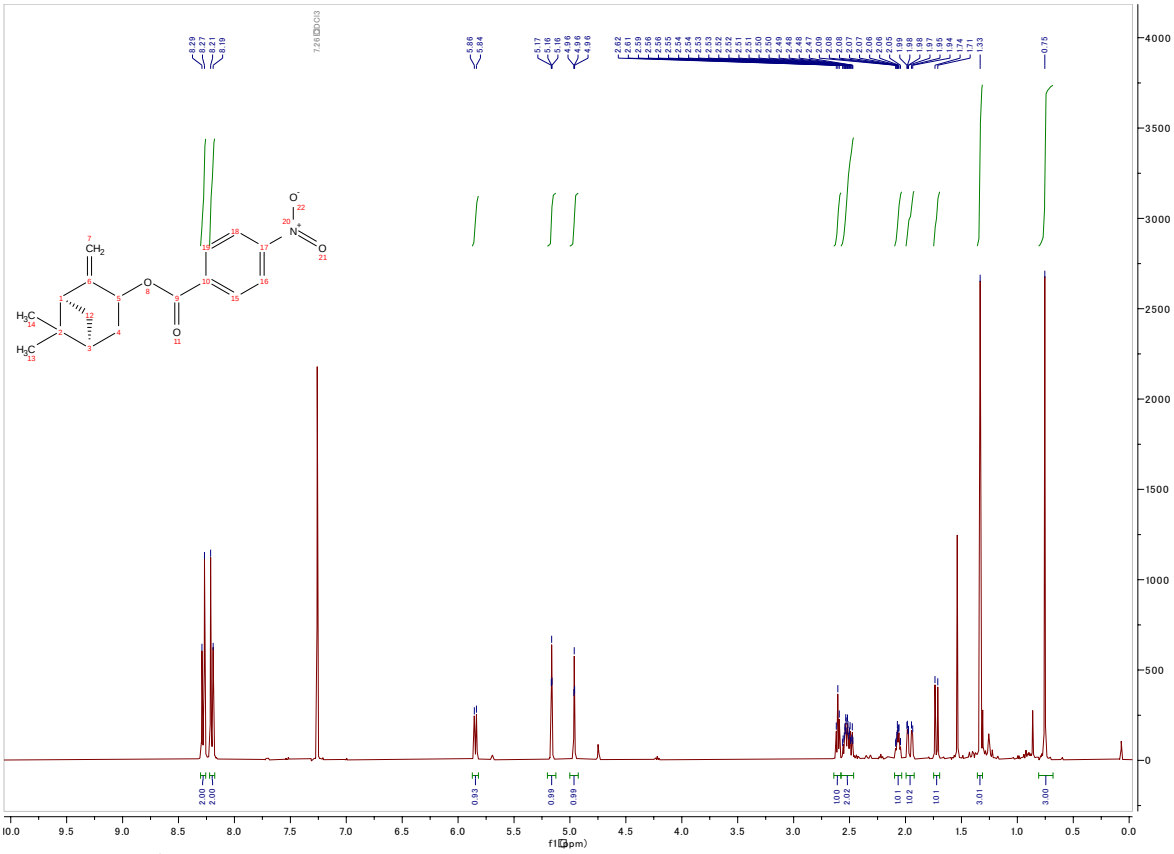


Figure S53. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3ta**.

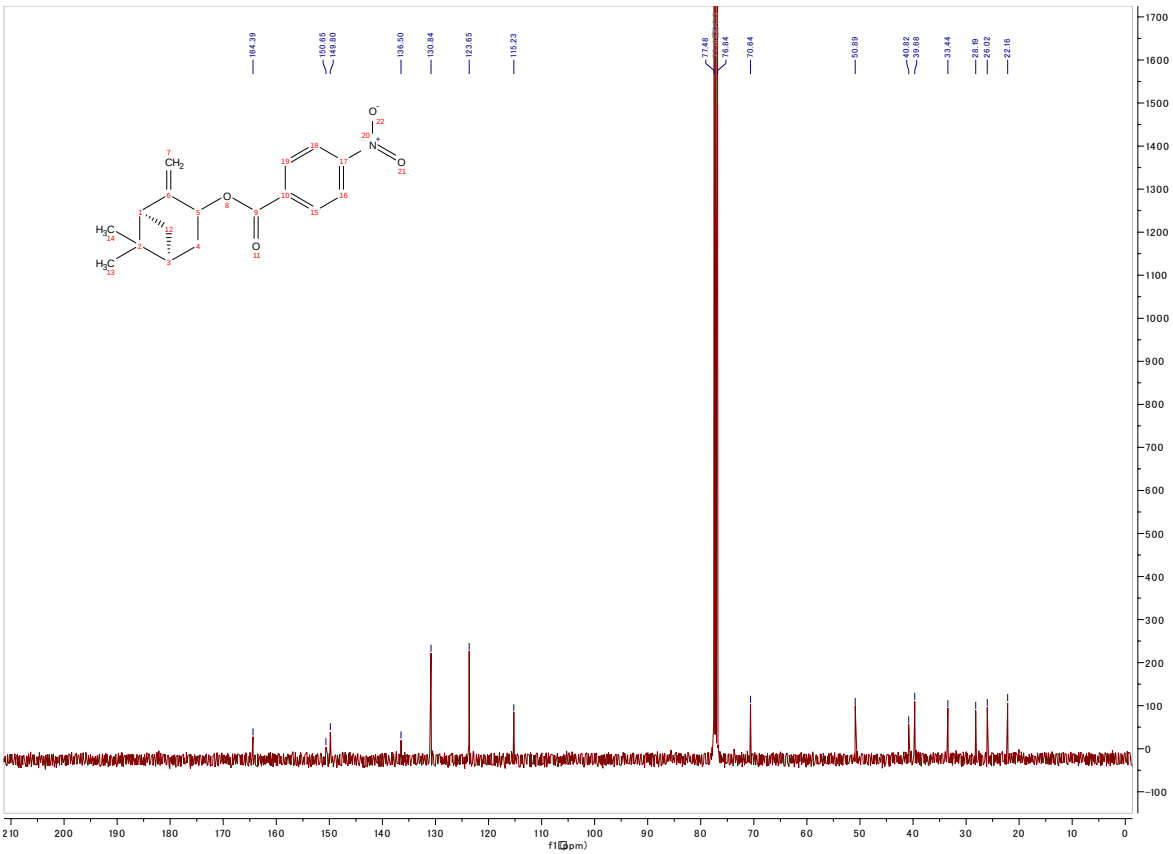


Figure S54. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3ta**.

VIII. References:

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