**Supplementary Materials for**

**Title**

# (3*R*, 7*S*)-11-hydroxy-jasmonic acid is a major oxidative shunt product of jasmonic acid catabolism in *Arabidopsis thaliana*


**Author List**

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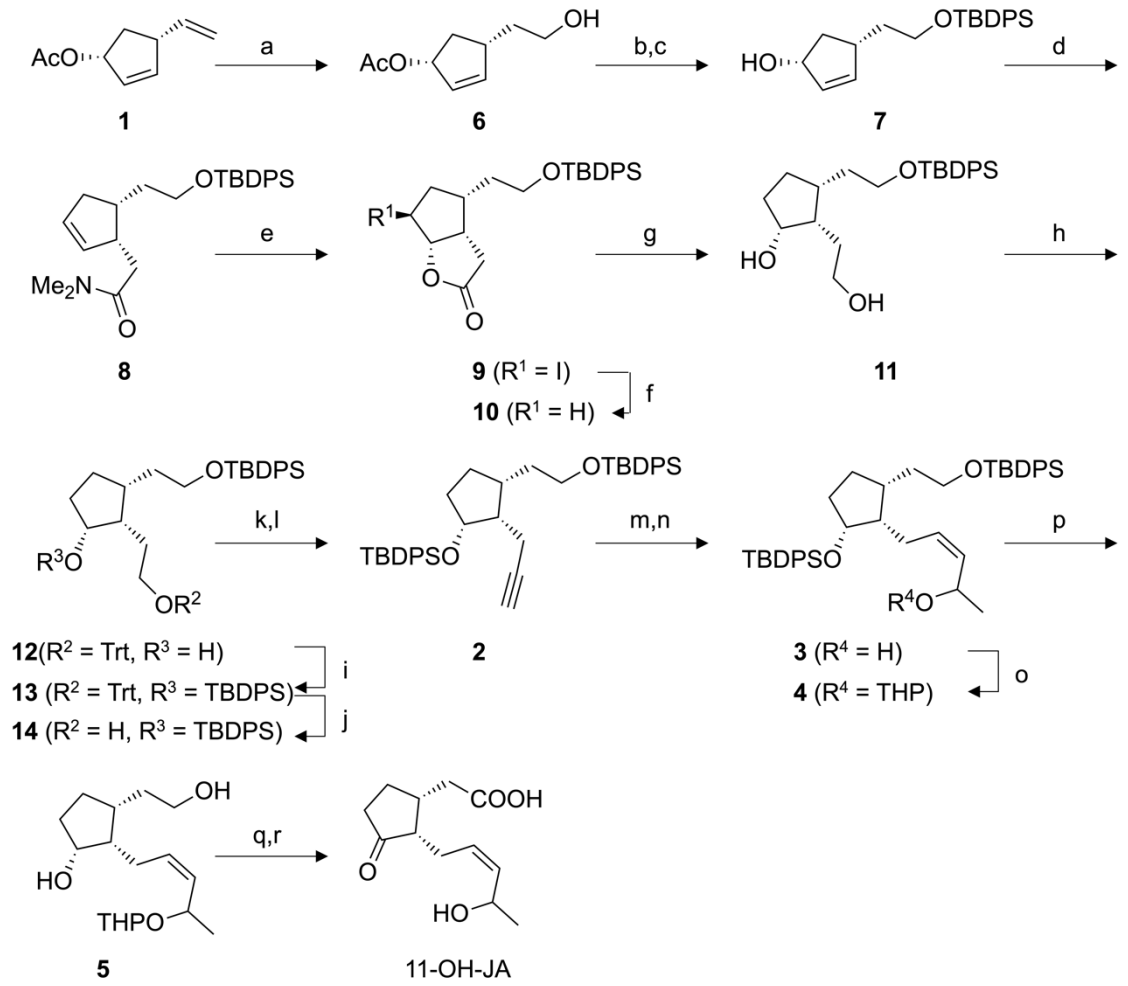
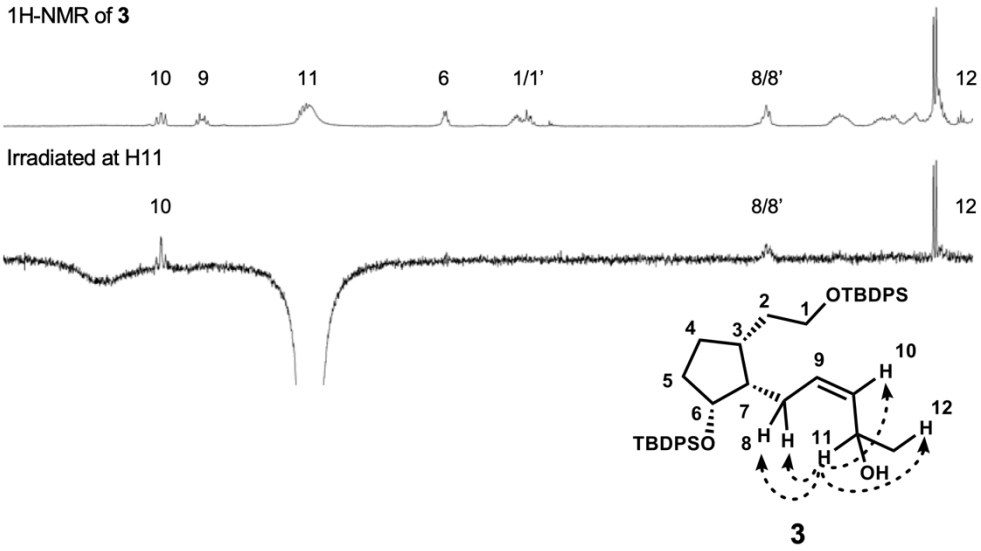
**Contents:**

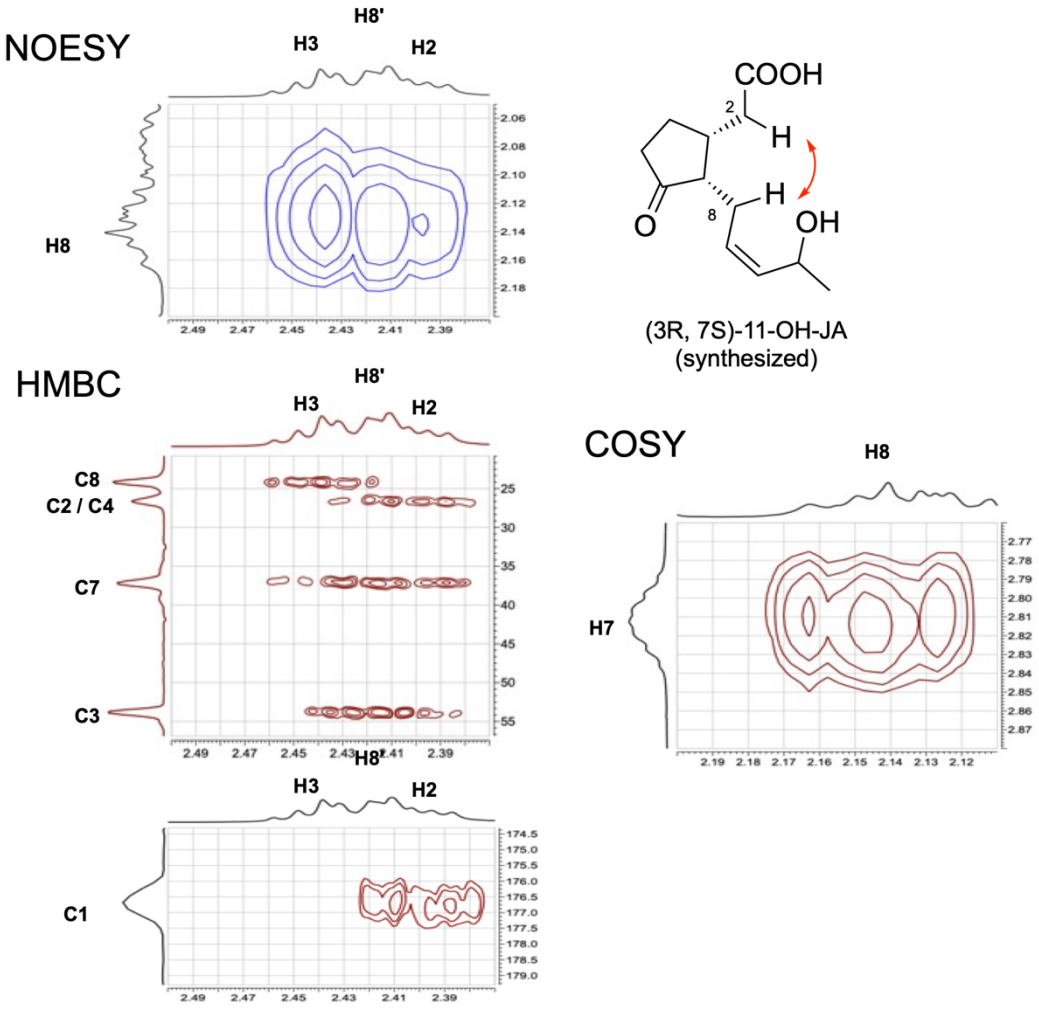



**Supplementary Fig. 1 Synthetic scheme of 11-OH-JA**: (a) $Cy_2BH$, THF, 0 ºC; $NaBO_3$, $H_2O$, 0 ºC, 60%; (b) TBDPSCl, imidazole, DMF; (c) NaOH, MeOH/$H_2O$ , 66% (2 steps); (d) $MeC(OMe)_2NMe_2$, xylene, 150 ºC, 56%; (e) $I_2$, $KH_2PO_4$, $Na_2HPO_4$, THF/$H_2O$ , 84%; (f) *n*$Bu_3SnH$, AIBN, benzene, reflux; (g) LiAlH, THF, 0 ºC, 93% (2 steps); (h) TrtCl, DMAP, $Et_3N$, $CH_2Cl_2$, 74%; (i) TBDPSCl, imidazole, DMF, 86%; (j) *p*-TsOH•$H_2O$, $CH_2Cl_2$, MeOH, 77%; (k) DMSO, $(COCl)_2$, DCM, -65 ºC; $Et_3N$, -65 ºC to rt; (l) Ohira-Bestmann reagent, $K_2CO_3$, MeOH, 69% (2 steps); (m) *n*BuLi, acetaldehyde, THF, -78 ºC, 69%; (n) $H_2$, Pd/$BaSO_4$, quinoline, MeOH, 89%; (o) DHP, *p*-TsOH•$H_2O$, $CH_2Cl_2$, 98%; (p) TBAF, THF 91%; (q) Jones reagent, acetone, -20 ºC, 96%; (r) $MgBr_2$, $Et_2O$, 38%.

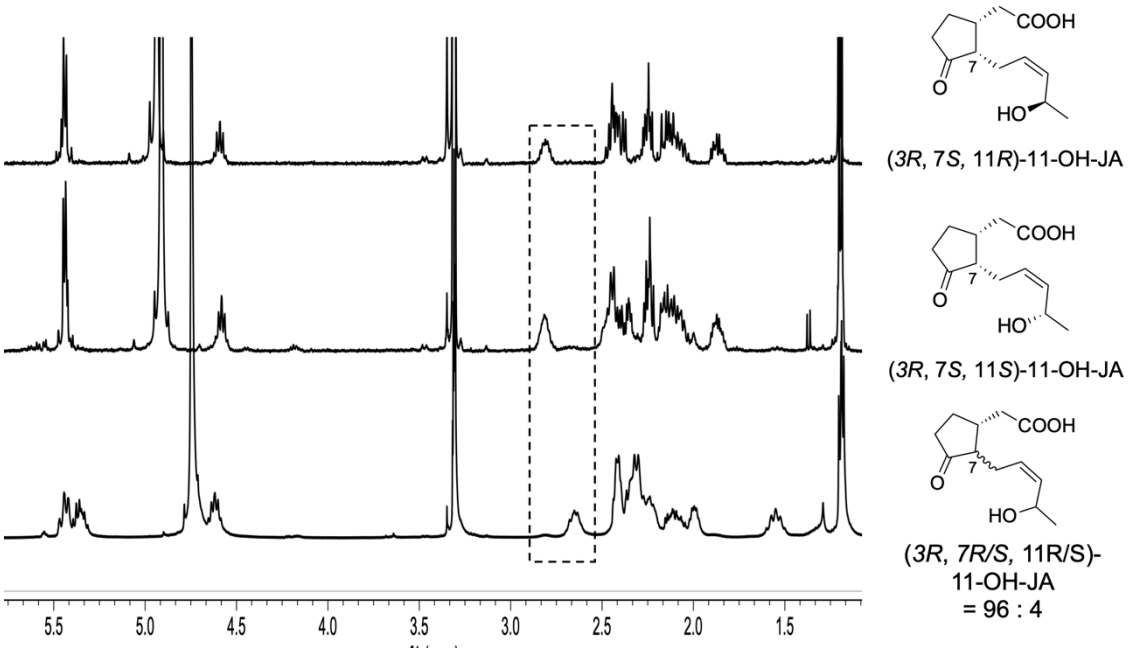
**A**


1H-NMR of 3
10
9
11
6
1/1'
8/8'
12
Irradiated at H11
10
8/8'
12
OTBDPS
TBDPSO
OH
3

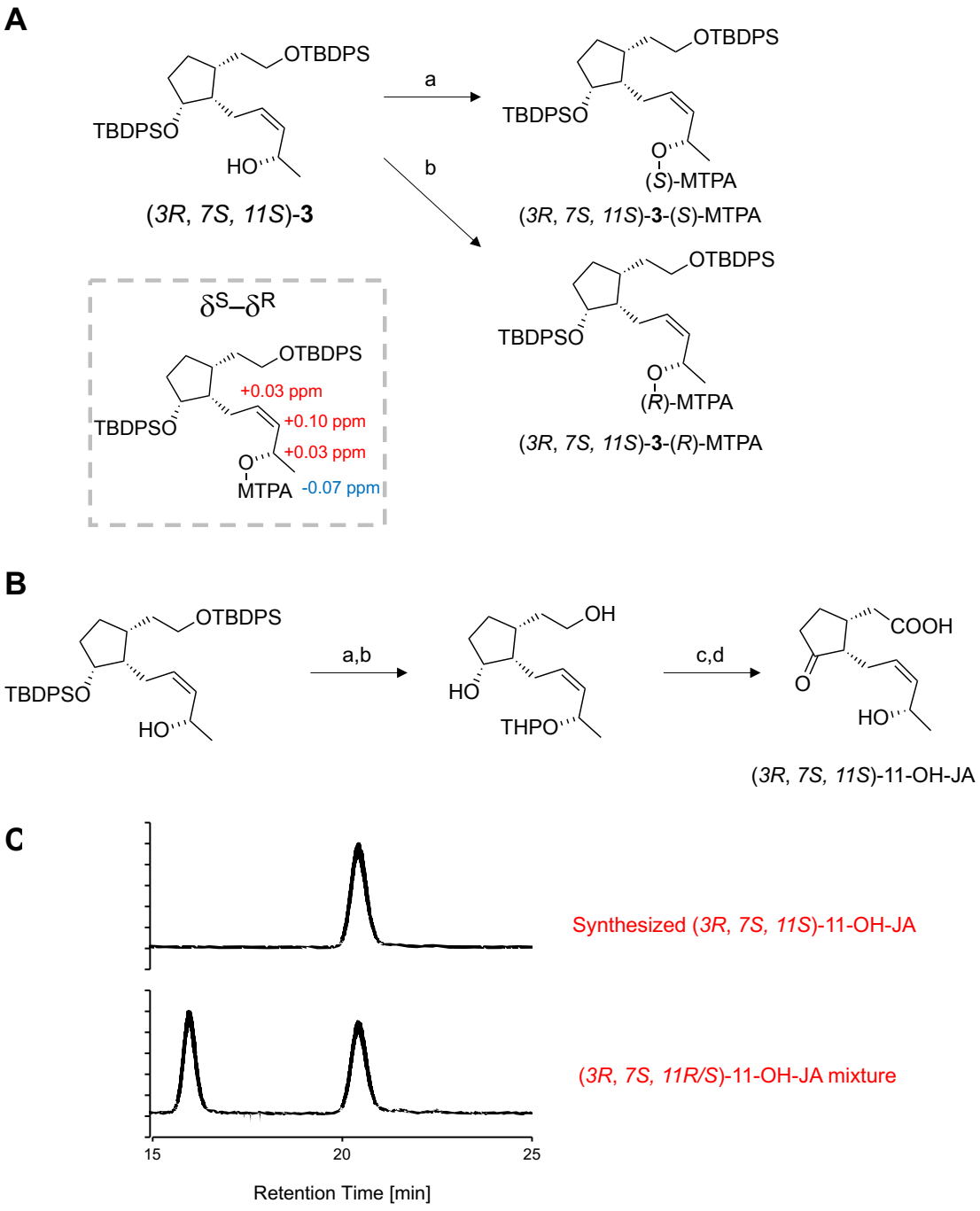
**B**


NOESY
H8'
H3
H2
H8
HMBC
C8
C2 / C4
C7
C3
C1
COOH
OH
(3R, 7S)-11-OH-JA
(synthesized)
COSY
H8
H7

**Supplementary Fig. 2** (**A**) Differential NOE experiment on intermediate **3**. 1D-differential-noe spectrum was measured in pyridine-*d5* (64 scans). H11 (δ 5.06) was selectively irradiated. The key NOE correlation between H11 and H8/H8' was 0.3%. (**B**) Expanded view of NOESY (700 MHz) cross peak of the synthesized (3*R*, 7*S*)-11-OH-JA between H2 and H8 and related HSQC and HMBC (700 MHz for $^{1}$H and 175 MHz for $^{13}$C) used to assign H2.



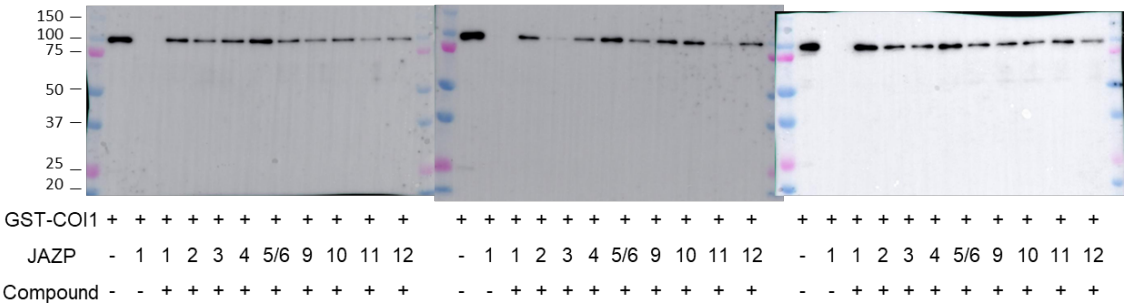

**Supplementary Fig. 3.** Comparison of $^{1}$H NMR between (3*R*, 7*S*, 11*R*)-11-OH-JA (top), (3*R*, 7*S*, 11*S*)-11-OH-JA (middle), and a separately synthesized mixture of (3*R*, 7*S*, 11*R*/11*S*)-11-OH-JA and (3*R*, 7*R*, 11*R*/11*S*)-11-OH-JA (4:96). The region within the dotted line was shown in **Fig. 1C**.



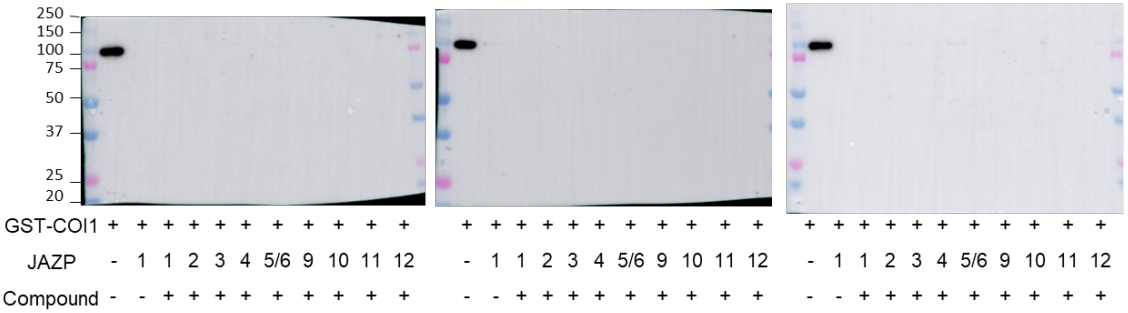

**Supplementary Fig. 4.** (**A**) Determination of the stereochemistry at the C11 position of one isolated stereoisomer of **3** by modified Mosher method : (a) (*R*)-MTPA-Cl, pyridine, DCM; (b) (*S*)-MTPA-Cl, pyridine, DCM; (B) Synthesis of (*3R, 7S, 11S*)-11-OH-JA from (*3R, 7S, 11S*)-**3** : (a) DHP, *p*-TsOH•$H_2O$, $CH_2Cl_2$, 91%; (b) TBAF, THF 89%; (c) Jones

reagent, acetone, -20 ºC, 78%; (d) $MgBr_2$, $Et_2O$ 44%; (C) Comparison of LC-MS/MS chromatogram suggested that the latter peak of (*3R*, *7S, 11R/S*)-11-OH-JA mixture was (*3R*, *7S, 11S*)-11-OH-JA isomer.

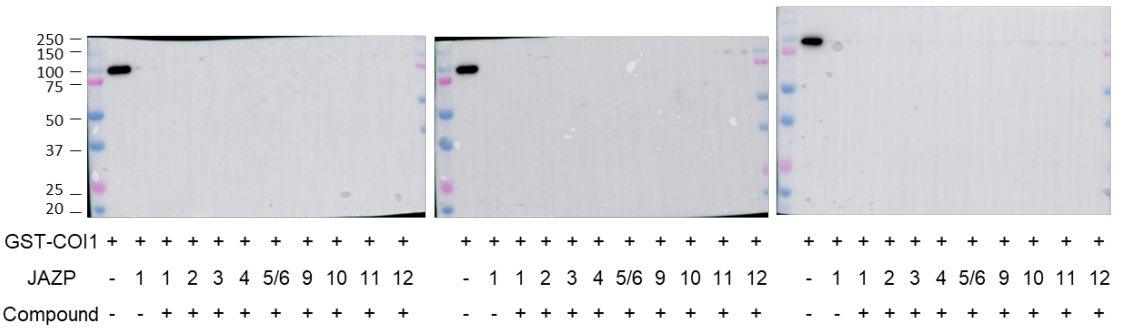
**A** (3*R*, 7*S*)-JA-Ile 1 μM



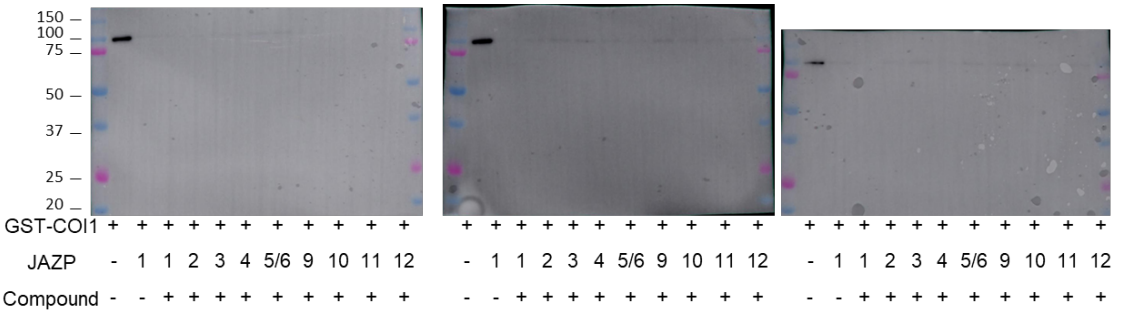

**B** (3*R*, 7*S*, 11*R*)-11-OH-JA 10 μM

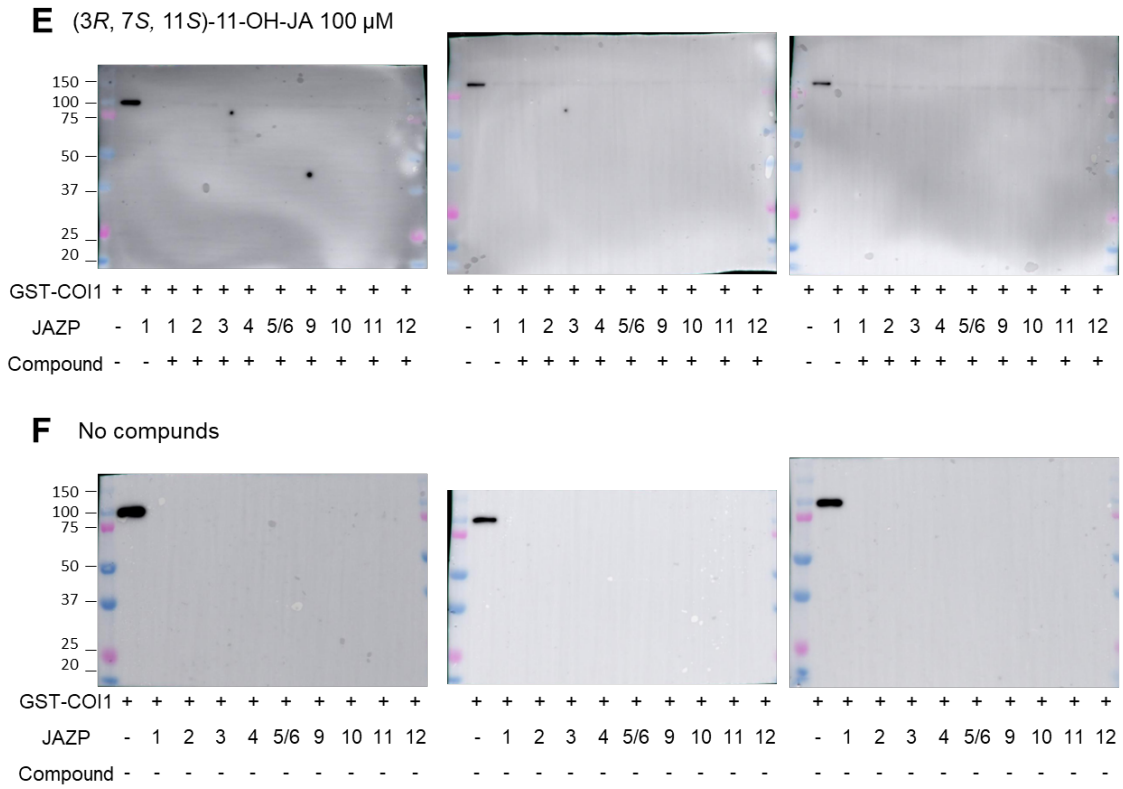



**C** (3*R*, 7*S*, 11*R*)-11-OH-JA 100 μM

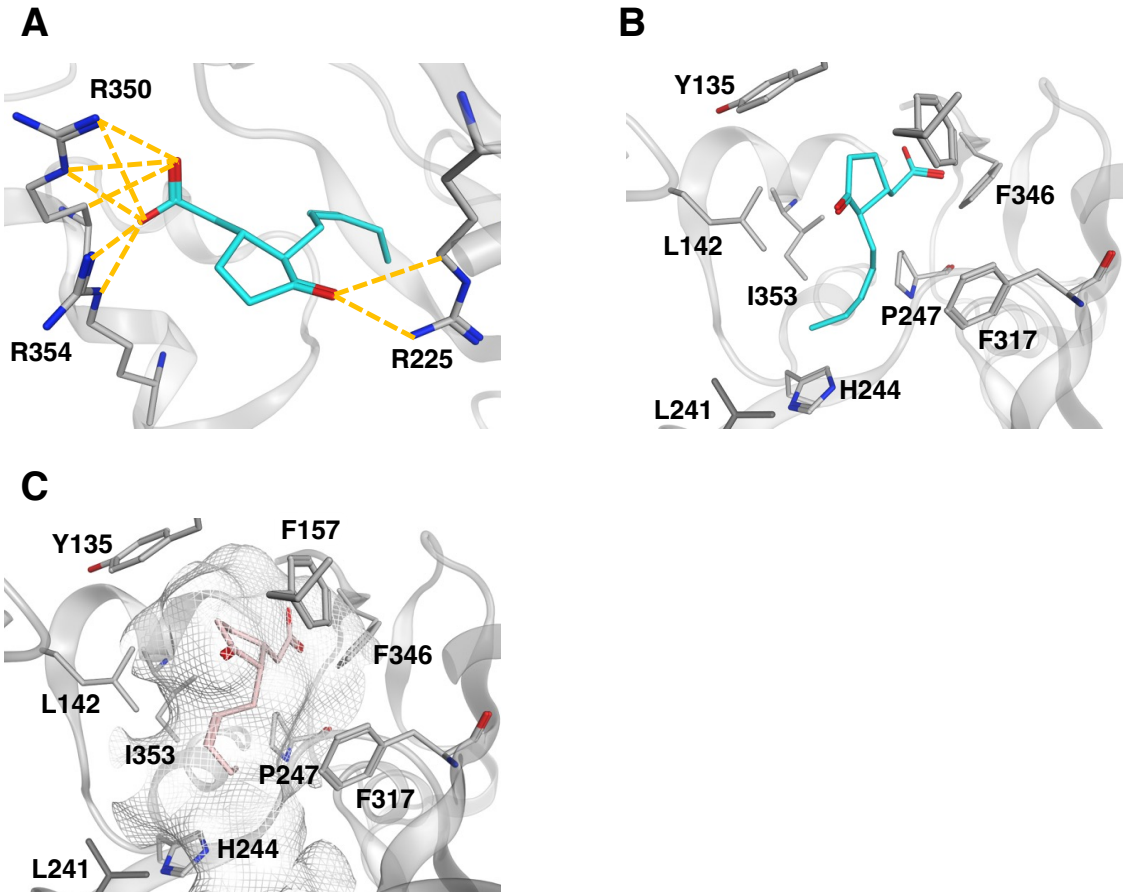



**D** (3*R*, 7*S*, 11*S*)-11-OH-JA 10 μM

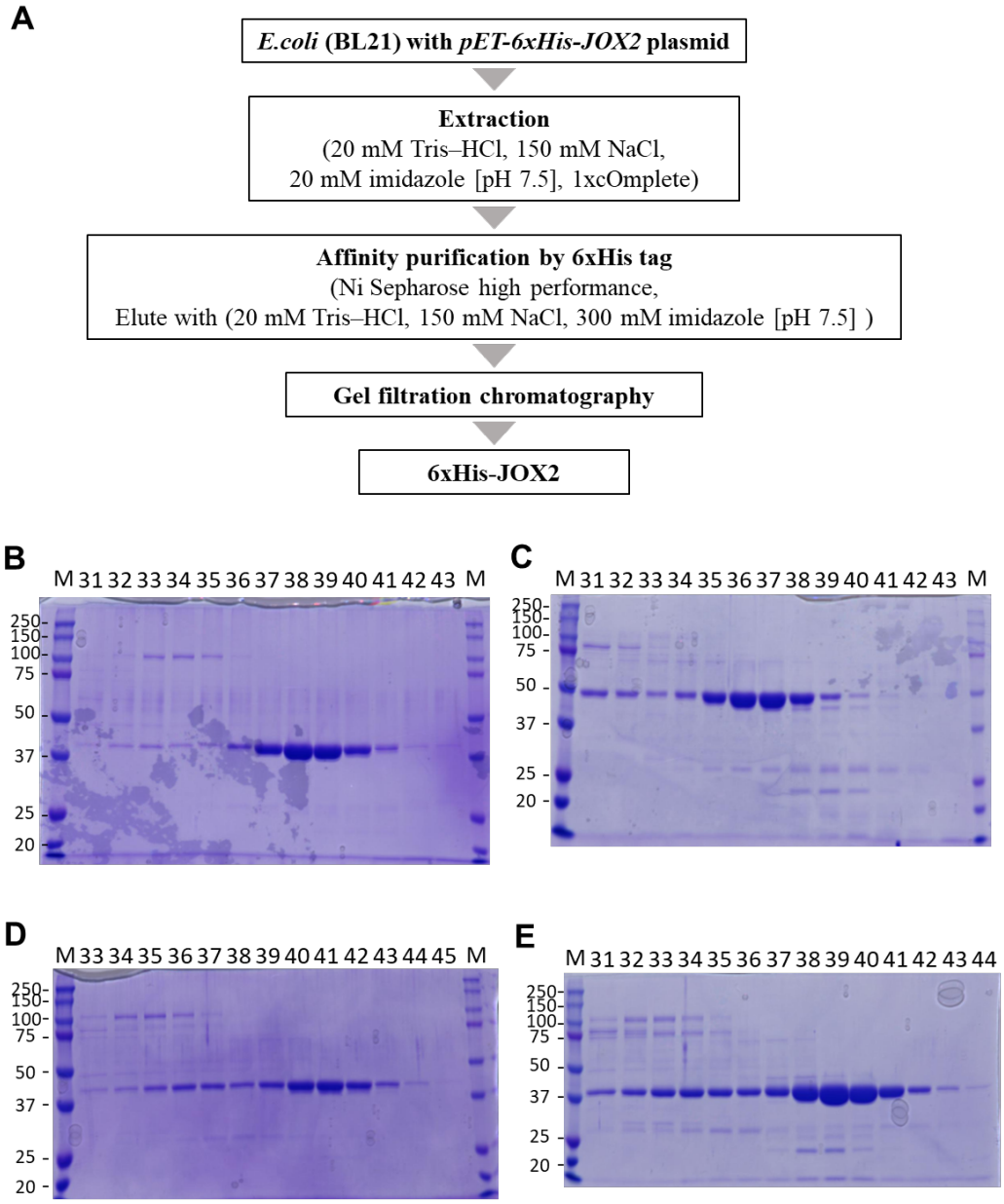





**Supplementary Fig. 5** Uncropped images and three independent pull-down results shown in Fig. 3C. Pull-down assays between GST-COI1 and Fl-JAZPs1-6/9-12 under (3*R*,7*S*)-JA-Ile (1 μM, A), (3*R*, 7*S*, 11*R*)-11-OH-JA (10/100 μM, B,C for each result), (3*R*, 7*S*, 11*S*)-11-OH-JA (10/100 μM, D,E for each result) or no compounds (F for each result). GST-COI1 which bound to JAZPs was pulled down with anti-fluorescein antibody and protein A beads. They are analyzed by immunoblotting (anti-GST-HRP conjugate for detection of GST-COI1).

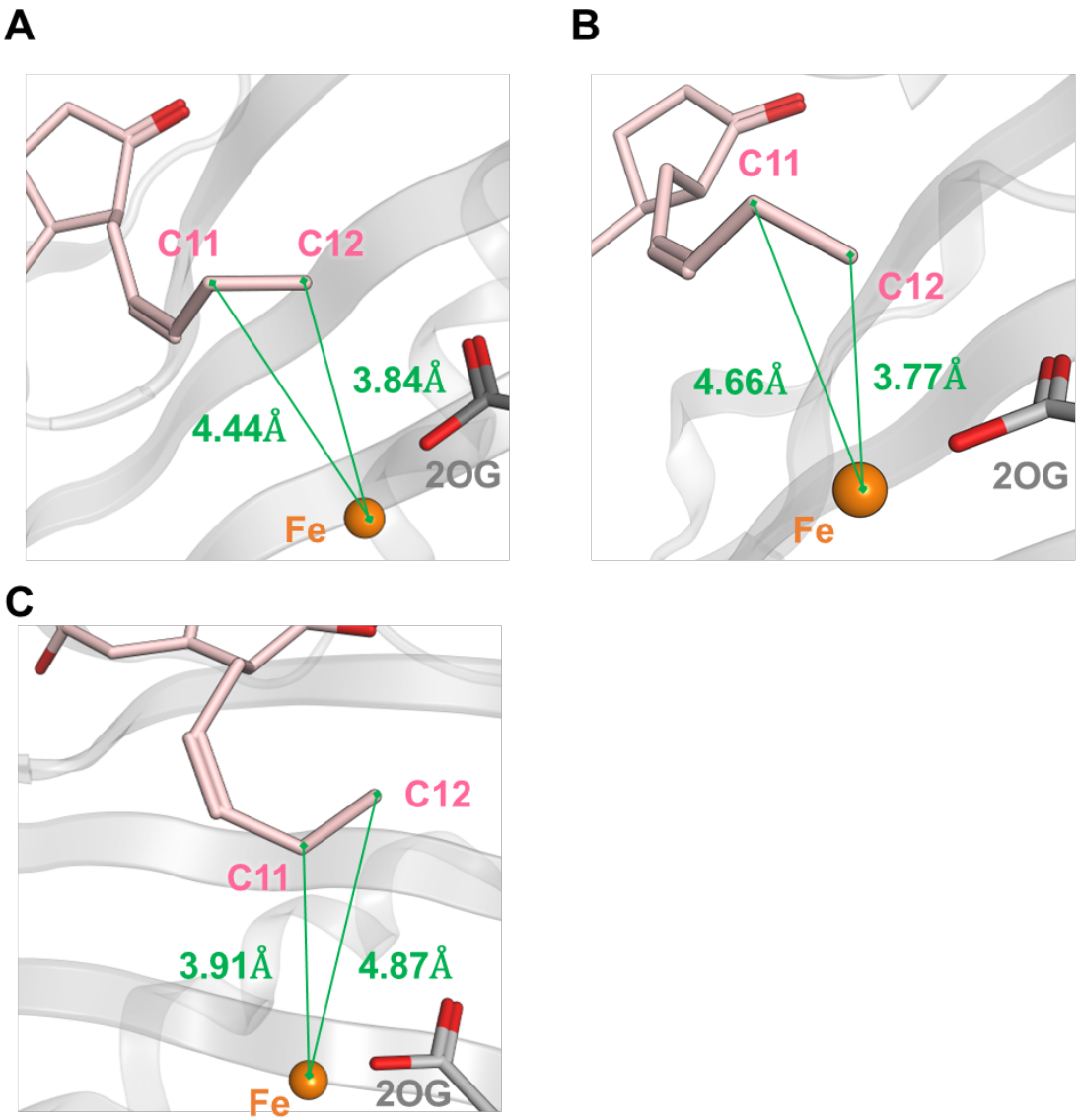



**Supplementary Fig. 6** (**A**) Hydrogen bond network and (**B**) hydrophobic interactions in the crystal structure of (3*R*, 7*R*)-JA (cyan) and JOX2 (gray) (PDB: 6LSV). (**C**) Hydrophobic residues form the ligand-binding pocket around (3*R*, 7*S*)-JA (pink) (shown in gray mesh).



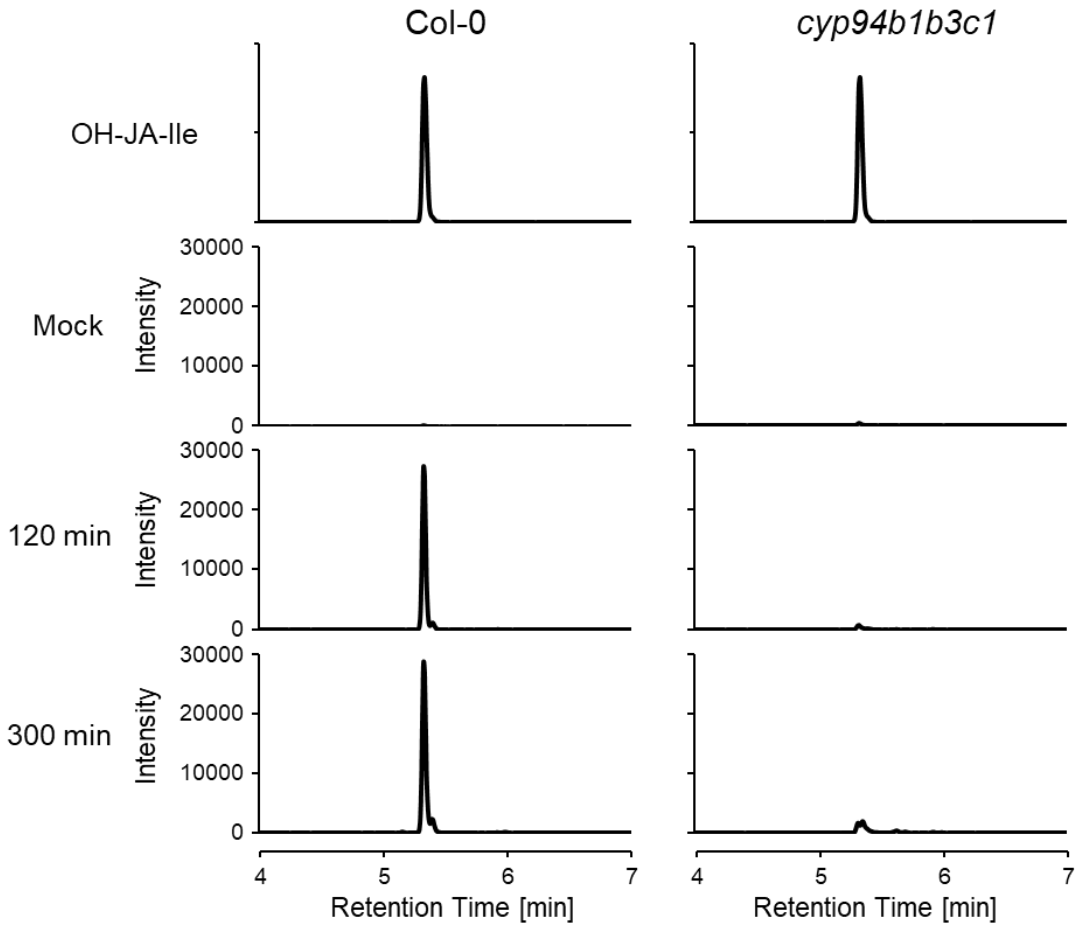

**Supplementary Fig. 7 Expression and purification of 6xHis-JOX1/2/3/4** (**A**) A schematic representation of JOX2 expression and purification. JOX1/3/4 were similarly expressed and purified. (**B**) CBB-stained SDS-PAGE analysis of 6xHis-JOX2 after gel filtration chromatography. Fractions 37-41 were collected as pure 6xHis-JOX2 protein. (**C**) CBB-stained SDS-PAGE analysis of JOX1 after gel filtration chromatography. Fractions 35-38 were collected as pure 6xHis-JOX1 protein. (**D**) CBB-stained SDS-

PAGE analysis of JOX3 after gel filtration chromatography. Fraction 37-41 were collected as pure 6xHis-JOX3 protein. (**E**) CBB-stained SDS-PAGE analysis of JOX4 after gel filtration chromatography. Fractions 37-41 were collected as pure 6xHis-JOX4 protein.



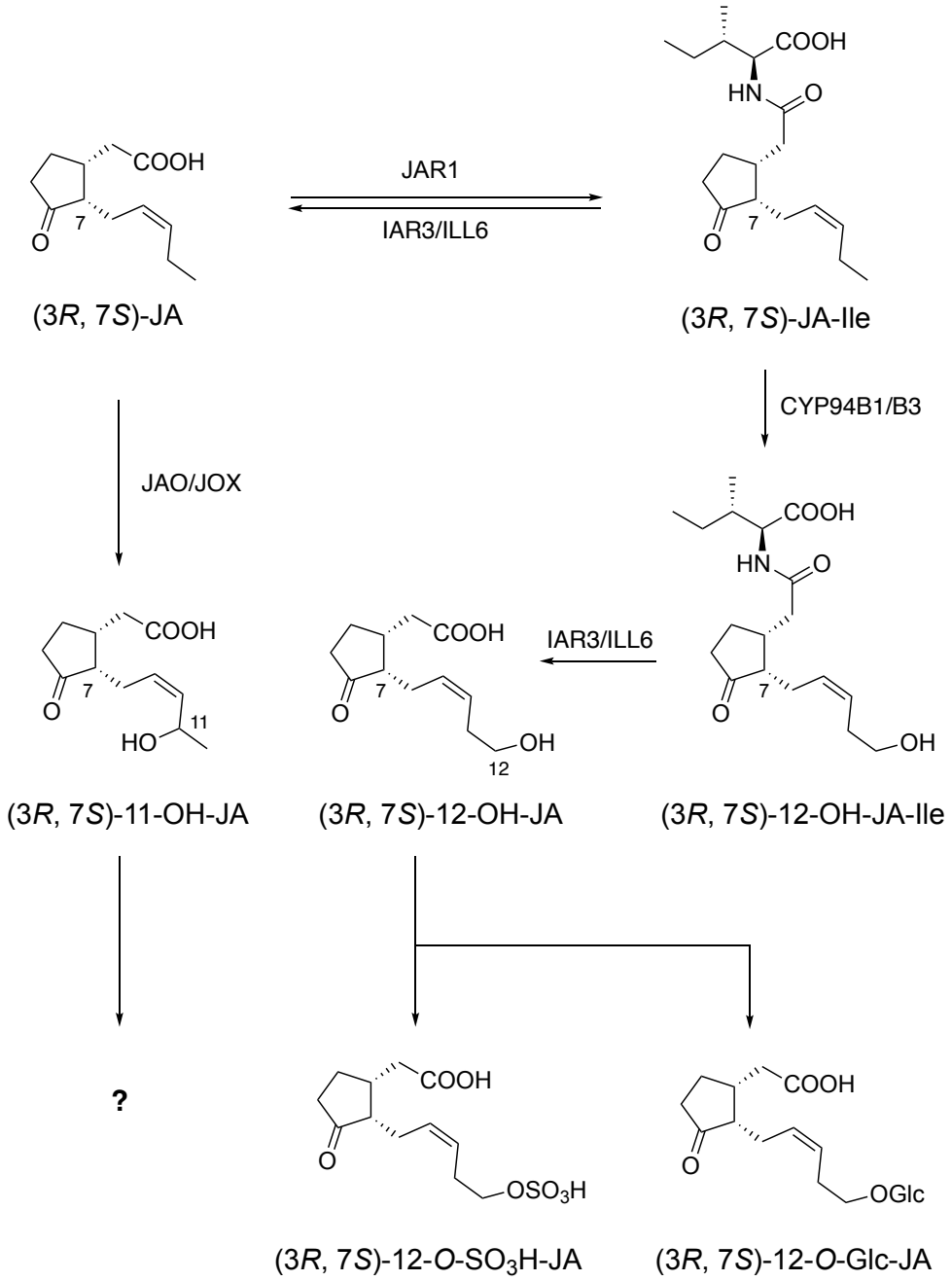

**Supplementary Fig. 8 *In silico* docking models of (A) JOX1, (B) JOX3, (C) JOX4**

Distances between the iron ion and the C12 and C11 carbon atoms of (3*R*, 7*S*)-JA (pink). (A) In the JOX1, they are 3.84 Å for C12 and 4.44 Å for C11. (B) In the JOX3, they are 3.77 Å for C12 and 4.66 Å for C11. (C) In the JOX4, they are 3.91 Å for C11 and 4.87 Å for C12. JOXs and 2OG are represented in gray. Iron ion is shown as orange sphere. Distances are marked in green.




**Supplementary Fig. 9 MS/MS (MRM) signal corresponding to 12- or 11-OH-JA-Ile in *cyp94b1b3c1* triple mutant**

UPLC-MS/MS chromatogram (*m*/*z* 338 > 130) of a mixture of 12- or 11-OH-JA-Ile. ZORBAX RRHD Eclipse Plus C18 1.8 μm (ϕ2.1 × 50 mm; Agilent Technologies) was used at 40 °C and a flow rate of 0.350 mL/min. The elution was performed using a gradient of water (solvent A) and MeCN (solvent B), both containing 0.1% formic acid (v/v). The proportion of solvent B in the eluent was 5% for 2 min and was increased linearly from 5% to 100% for 10 min, followed by a flow of 100% B for 2 min. The column was then re-equilibrated with 5% solvent B for 3 min.




**Supplementary Fig. 10** Current understanding of JA catabolism in *A. thaliana*. Further conversion of (3*R*, 7*S*)-11-OH-JA remains unknown.

## Supplementary Materials and Methods

### Chemical Syntheses

### General materials and methods

All chemical reagents and solvents were obtained from commercial suppliers (Kanto Chemical Co. Ltd., Wako Pure Chemical Industries Co. Ltd., Nacalai Tesque Co. Ltd., Tokyo Chemical Industry Co. Ltd., Sigma-Aldrich Co. LLC., GE Healthcare) and used without further purification. All anhydrous solvents were either dried by standard techniques and freshly distilled before use or purchased in anhydrous form and used as supplied. Reversed-phase high–performance liquid chromatography (HPLC) was carried out on a PU–4180 plus pump equipped with UV–4075 and MD–4010 detectors (JASCO, Tokyo, Japan). $^{1}$H and $^{13}$C NMR spectra were recorded on a JNM–ECS–400 spectrometer (JEOL, Tokyo, Japan). HMBC/HSQC and NOESY experiments were carried out on a Bruker AVANCE NEO700 spectrometer equipped with cryoprobe (Bruker BioSpin Inc., Billerica, MA, US). Chemical shifts are denoted in δ (ppm) relative to TMS or residual solvent peaks as internal standard (TMS, $^{1}$H δ 0.00; $CDCl_3$, $^{13}$C δ 77.0; $CD_3OD$, $^{1}$H δ 3.31, $^{13}$C δ 49.0; pyridine-*d5*, $^{1}$H δ 8.74, $^{13}$C δ 150.4). Fourier transforms infrared (FT/IR) spectra were recorded on an FT/IR–4100 (JASCO, Tokyo, Japan). High–resolution (HR) electrospray ionization (ESI)–mass spectrometry (MS) analyses were conducted using a microTOF II (Bruker Daltonics Inc., Billerica, MA, US). Optical rotations were measured using a JASCO P–2200 polarimeter (JASCO, Tokyo, Japan). Flash chromatography was performed on an Isolera system (Biotage Ltd., North Carolina, US). TLC analyses were performed on Silica gel F254 (0.25 mm or 0.5 mm, MERCK, Germany) or RP–18F254S (0.25 mm, MERCK). All reactions were carried out under air unless stated otherwise.

**Synthesis of (*3R*, *7S*)-11-OH-JA and (*3R*, *7S*)-11-OH-JA-Ile**

**Synthesis of alcohol 6**

To a solution of $BH_3$·THF (63 mL, 0.91 M in THF, 57.3 mmol) in THF (100 mL) was added cyclohexene (11.8 mL, 116 mmol) at 0 °C under an argon atmosphere. The solution was stirred at 0 °C for 2 hours, and the supernatant was removed. The mixture was added to a solution of **1** (2.24 g, 14.7 mmol) which was prepared by previous method (27) in THF (50 mL). After stirring at 0 °C for 1 h, the reaction mixture was added $NaBO_3$·$4H_2O$ (29.4 g, 191 mmol) and $H_2O$ (150 mL) . After stirring at room temperature for 3 h, the reaction mixture was quenched with saturated aqueous $NH_4Cl$ and extracted with EtOAc. The organic layer was washed with saturated aqueous NaCl, dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel medium-pressure chromatography (*n*-hexane/EtOAc = 88/12 to 0/100) to give **6** (1.33 g, 60%) as a colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$ 6.04 (d, *J* = 5.5 Hz, 1H), 5.81 (dt, *J* = 5.5, 2.3 Hz, 1H), 5.66-5.52 (m, 1H), 3.75 (dt, *J* = 10.6, 6.4 Hz, 1H), 3.70 (dt, *J* = 10.6, 6.4 Hz, 1H), 2.77 (brt, *J* = 6.4 Hz, 1H), 2.55 (dt, *J* = 14.2, 7.8 Hz, 1H), 2.03 (s, 3H), 1.78 (q, *J* = 6.4 Hz, 1H), 1.65 (q, *J* = 6.4 Hz, 1H), 1.47 (dt, *J* = 14.2, 4.6 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$: 170.9, 140.6, 129.2, 79.7, 61.4, 40.95, 38.9, 36.4, 21.3; IR (neat) $cm^{-1}$: 3423, 2933, 2878, 1734, 1716, 1244; HRMS (ESI, positive) *m*/*z* $[M+Na]^+$ Calcd. for $C_9H_{14}NaO_3$: 193.0835, Found : 193.0834.

**Synthesis of alcohol 7**

To a solution of **6** (1.33 g, 7.79 mmol) in DMF (60 mL) was added imidazole (1.60 g, 23.5 mmol) and TBDPSCl (3.0 mL, 11.6 mmol) under an argon atmosphere. After

being stirred at room temperature (rt) for 23 h, the reaction mixture was added MeOH and $H_2O$ and stirred 30 min. The solution was extracted with *n*-hexane, then organic layer was washed with brine, dried over $Na_2SO_4$, and concentrated under reduced pressure to afford a TBDPS-protected intermediate, which was used for the following reaction without further purification.

To a solution of above intermediate in MeOH (10 mL) was added NaOH (3 M in $H_2O$, 10 mL, 30 mmol). After being stirred at room temperature for 15 h, the reaction mixture was extracted with ether. The organic layer was washed with brine, dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel medium-pressure chromatography (*n*-hexane/EtOAc = 93/7 to 40/60) to give **7** (1.87 g, 66% in 2 steps) as a yellow oil: $[\alpha]_D^{28}$ = -2 (*c* 1.02, $CHCl_3$); $^1$H NMR (400 MHz, $CD_3OD$) $\delta_H$: 7.67 (dt, *J* = 7.8, 1.4 Hz, 4H), 7.38-7.45 (m, 6H), 5.81 (dt, *J* = 5.5, 1.8 Hz, 1H), 5.71 (dt, *J* = 5.5, 1.8 Hz, 1H), 4.72 (ddt, *J* = 7.8, 5.5, 1.8 Hz, 1H), 3.75 (dt, *J* = 10.1, 6.4 Hz, 1H), 3.72 (dt, *J* = 10.1, 6.4 Hz, 1H), 2.71 (*J* = 6.0, 1.8 Hz, 1H), 2.39 (dt, *J* = 13.3, 7.8 Hz, 1H), 1.79 (dt, *J* = 19.7, 6.4 Hz, 1H), 1.58 (dt, *J* = 19.7, 7.8 Hz, 1H), 1.19 (dt, *J* = 13.3, 6.0 Hz, 1H), 1.04 (s, 9H); $^{13}$C NMR (100 MHz, $CD_3OD$) $\delta_C$: 138.7, 136.7 (4C), 135.0 (2C), 134.3, 130.9 (2C), 128.8(4C), 77.7, 63.8, 42.4, 41.1, 40.6, 27.4 (3C), 20.0; IR (neat) $cm^{-1}$: 3335, 2930, 2858, 1428, 1111, 705; HRMS (ESI, positive) *m/z* $[M+Na]^+$ Calcd. for $C_{23}H_{30}NaO_2Si$: 389.1913, Found : 389.1900.

**Synthesis of dimethylamide 8**

To a solution of **7** (1.87 g, 5.10 mmol) in xylene (18 mL) was added $MeC(OMe)_2NMe_2$ (3.8 mL, 26.0 mmol) under an argon atmosphere. The mixture was stirred at 150 °C, and MeOH was removed in a Dean Stark apparatus with MS4A. After

16 h, the reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel medium-pressure chromatography (*n*-hexane/EtOAc = 93/7 to 40/60) to give **8** (1.24 g, 56%) as a brown oil: $[\alpha]_D^{28}$ = -62 (*c* 1.19, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta_H$: 7.65-7.68 (m, 4H), 7.36-7.44 (m, 6H), 5.79-5.82 (m, 1H), 5.68-5.71 (m, 1H), 3.64-3.74 (m, 2H), 3.04-3.11 (m, 1H), 2.95 (s, 3H), 2.94 (s, 3H), 2.36-2.46 (m, 1H), 2.29-2.35 (m, 1H), 2.28 (dd, *J* = 14.7, 5.0 Hz, 1H), 2.07(dd, *J* = 14.7, 10.1 Hz, 1H), 1.92 (ddq, *J* = 16.0, 8.2, 2.3 Hz, 1H), 1.71-1.80 (m, 1H), 1.51 (dddd, *J* = 12.9, 9.7, 7.0, 5.0 Hz, 1H), 1.04 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta_C$: 172.5, 135.6 (4C), 135.5, 134.0 (2C), 130.2, 129.6 (2C), 127.6 (4C), 63.4, 43.6, 37.8, 37.4, 37.1, 35.4, 33.6, 33.4, 26.9 (3C), 19.2; IR (neat) $cm^{-1}$: 3049, 2931, 1651, 1394, 1111, 705; HRMS (ESI, positive) *m*/*z* $[M+Na]^+$ Calcd. for $C_{27}H_{37}NNaO_2Si$: 458.2486, Found : 458.2502.

**Synthesis of iodolactone 9**

To a solution of **8** (1.24 g, 2.86 mmol) in THF/$H_2O$ (6.4 mL, 1:1, v/v) was added $KH_2PO_4$ (511 mg, 3.75 mmol), $Na_2HPO_4 \cdot 4H_2O$ (138 mg, 773 μmol) and $I_2$ (1.45 g, 5.73 mmol). The solution was stirred room temperature for 26 h. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ and extracted with EtOAc. The organic layer was washed with brine, dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel medium-pressure chromatography (*n*-hexane/EtOAc = 95/5 to 60/40) to give dimethylamide **9** (1.29 g, 84%) as a yellow oil: $[\alpha]_D^{28}$ = +5 (*c* 1.15, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta_H$: 7.65-7.68 (m, 4H), 7.38-7.47 (m, 6H), 5.24 (d, *J* = 6.4 Hz, 1H), 4.43 (d, *J* = 5.0 Hz, 1H), 3.68 (dt, *J* = 10.1, 6.4 Hz, 1H), 3.64 (dt, *J* = 10.1, 6.4 Hz, 1H), 2.97-3.04 (m, 1H), 2.85-2.95 (m, 1H), 2.47 (dd, *J* = 18.8, 10.1 Hz, 1H), 2.38 (dd, *J* = 18.8, 4.1 Hz, 1H), 2.08 (dd, *J* = 14.7, 5.5 Hz, 1H), 1.58-1.74 (m, 3H), 1.06

(s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$: 176.4, 135.6 (4C), 133.5, 133.4, 129.8 (2C), 127.8 (4C), 92.7, 62.4, 40.1, 38.9, 37.1, 32.6, 28.9, 28.0, 26.9 (3C), 19.1; IR (neat) cm$^{-1}$: 2930, 2857, 1784, 1427, 1111, 704; HRMS (ESI, positive) *m*/*z* $[M+Na]^+$ Calcd. for $C_{25}H_{31}INaO_3Si$: 557.0979, Found : 557.0967.

**Synthesis of diol 11**

To a solution of **9** (3.08 g, 5.75 mmol) in benzene (35 mL) was added *n*-$Bu_3SnH$ (4.65 mL, 17.3 mmol), AIBN (188 mg, 1.14 mmol). The mixture was stirred at 90 °C for 40 min, then cooled to rt. The reaction mixture was diluted with $CH_2Cl_2$ and quenched with 1M NaOHaq. , then was extracted with $CH_2Cl_2$. The organic layer was washed with saturated aqueous $NH_4Cl$, brine, dried over $Na_2SO_4$, and concentrated under reduced pressure to afford **10**, which was used for the following reaction without further purification.

To a solution of crude **10** in THF (60 mL) was added $LiAlH_4$ (658.2 mg, 17.3 mmol) at -20 ºC. After being stirred at 0 ºC for 40 min, the reaction mixture was re-cooled to -20 ºC and then a homogeneous mixture of $SiO_2$ (68 g) and $H_2O$ (20 mL) was added. The mixture was stirred for 40 min and the solids were removed by filtration and washed thoroughly with EtOAc and concentrated under reduced pressure. The residue was purified by Silica gel medium-pressure chromatography (*n*-hexane/EtOAc = 88/12 to 0/100) to give diol **11** (2.20 g, 93%) as a colorless oil: $[\alpha]_D^{22} = +11$ (*c* 1.56, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$: 7.68-7.65 (m, 4H), 7.45-7.35 (m, 6H), 4.27-4.22 (m, 1H), 3.81 (dt, *J* = 10.1, 5.0 Hz, 1H), 3.69 (ddd, *J* = 10.1, 7.3, 5.0 Hz, 1H), 3.65-3.57 (m, 2H), 2.10-2.00 (m, 1H), 1.91-1.81 (m, 2H), 1.79-1.67 (m, 2H), 1.66-1.53 (m, 3H), 1.52-1.36 (m, 2H), 1.04 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$: 135.6 (4C), 134.0 (2C), 129.5

(2C), 127.6 (4C), 77.2, 74.6, 63.1, 63.0, 46.3, 36.8, 34.1, 32.7, 27.3, 26.9 (3C), 19.2; IR (neat) $cm^{-1}$: 3335, 2932, 2858, 1428, 1111, 823, 739, 703; HRMS (ESI, positive) *m*/*z* $[M+Na]^+$ Calcd. for $C_{25}H_{36}NaO_3Si$: 435.2331, Found : 435.2323.

**Synthesis of 12**

To a solution of **11** (2.20 g, 5.33 mmol) in $CH_2Cl_2$ (30 mL) was added DMAP (65.2 mg, 0.534 mmol), Trt-Cl (1.56 g, 5.60 mmol) and $Et_3N$ (1.48 mL, 10.7 mmol). The solution was stirred at rt for 11 h. The reaction mixture was quenched with saturated aqueous $NH_4Cl$ and extracted with $CH_2Cl_2$. The organic layer was washed with brine, dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel medium-pressure chromatography (*n*-hexane/EtOAc = 98/2 to 80/20) to give **12** (2.59 g, 74%) as a pale yellow oil: $[\alpha]_D^{26} = +23$ (*c* 0.95, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta_H$: 7.67-7.63 (m, 4H), 7.45-7.33 (m, 11H), 7.32-7.19 (m, 10H), 4.10 (m, 1H), 3.65 (ddd, *J* = 10.1, 7.8, 5.0 Hz, 1H), 3.55 (dt, *J* = 10.1, 7.3 Hz, 1H), 3.34 (dt, *J* = 9.2, 5.0 Hz, 1H), 3.04 (ddd, *J* = 9.2, 7.8, 5.0 Hz, 1H), 2.29 (d, *J* = 3.2 Hz, 1H), 1.99-1.89 (m, 1H), 1.88-1.53 (m, 8H), 1.49-1.37 (m, 2H), 1.03 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta_C$: 144.0 (3C),135.6 (4C), 134.1 (2C), 129.5 (2C), 129.4, 128.7 (2C), 128.6 (2C), 129.9 (2C), 127.8 (2C), 127.7 (2C), 127.6 (2C), 127.5 (2C), 127.1, 126.9 (3C), 87.3, 74.3, 63.2, 46.4, 36.8, 34.2, 32.9, 28.9, 26.9 (3C), 25.3, 19.2; IR (neat) $cm^{-1}$: 3474, 2933, 1959, 1890, 1823, 1735, 1596, 1490, 701; HRMS (ESI, positive) *m*/*z* $[M+Na]^+$ Calcd. for $C_{44}H_{50}NaO_3Si$: 677.3421, Found : 677.3427.

**Synthesis of 13**

To a solution of **12** (2.59 g, 3.95 mmol) in DMF (20 mL) was added imidazole

(802 mg, 11.8 mmol) and TBDPSCl (2.00 mL, 7.79 mmol). The solution was stirred at rt for 19 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with hexane. The organic layer was washed with brine, dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel medium-pressure chromatography (*n*-hexane/EtOAc = 100/0 to 94/6) to give **13** (3.04 g, 86%) as a pale yellow oil: $[\alpha]_D^{26}$ = +6.4 (*c* 1.89, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$: 7.65-7.61 (m, 4H), 7.60-7.54 (m, 4H), 7.42-7.27 (m, 19H), 7.25-7.15 (m, 8H), 4.00 (m, 1H), 3.58 (ddd, *J* = 9.6, 7.3, 4.8 Hz, 1H), 3.50 (dt, *J* = 10.1, 6.9 Hz, 1H), 3.11-3.04 (m, 1H), 3.03-2.96 (m, 1H), 1.99-1.87 (m, 1H), 1.86-1.74 (m, 1H), 1.73-1.60 (m, 3H), 1.53-1.30 (m, 3H), 1.01 (s, 9H), 1.00 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$: 144.6 (3C), 135.9 (4C), 135.5 (4C), 134.8, 134.2, 134.1 (2C), 129.5 (2C), 129.4 (2C), 128.7 (6C), 127.6 (6C), 127.5 (4C), 127.4 (2C), 127.3 (2C), 126.7 (3C), 86.3, 77.2, 63.4, 63.3, 44.6, 35.9, 34.5, 32.9, 28.2, 27.1 (3C), 26.9 (3C), 25.3, 19.2 (2C); IR (neat) $cm^{-1}$: 2856, 1959, 1890, 1824, 1590, 1490, 1110; HRMS (ESI, positive) *m/z* $[M+Na]^+$ Calcd. for $C_{60}H_{68}NaO_3Si_2$: 915.4599, Found : 915.4617.

**Synthesis of 14**

To a solution of **13** (3.04 g, 3.40 mmol) in $CH_2Cl_2$ (10 mL) and MeOH (10 mL) was added *p*-TsOH·$H_2O$ (194.1mg, 1.02 mmol). The solution was stirred at rt for 15 min. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with $CH_2Cl_2$. The organic layer was washed with brine, dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel medium-pressure chromatography (*n*-hexane/EtOAc = 98/2 to 80/20) to give **14** (1.70 g, 77%) as a colorless oil: $[\alpha]_D^{25}$ = +7.9 (*c* 0.93, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$: 7.68-7.63 (m, 8H),

7.44-7.33 (m, 12H), 4.14 (m, 1H), 3.68 (ddd, $J$ = 10.1, 7.3, 5.0 Hz, 1H), 3.63-3.49 (m, 3H), 1.96-1.85 (m, 1H), 1.83-1.69 (m, 3H), 1.65-1.30 (m, 6H), 1.06 (s, 9H), 1.04 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$: 136.0 (2C), 135.9 (2C), 135.6 (4C), 134.4, 134.1, 134.0, 133.8, 129.7, 129.6, 129.5 (2C), 127.6 (6C), 127.5 (2C), 77.2, 76.9, 63.1, 62.6, 44.6, 36.0, 34.4, 32.3, 28.0, 27.1 (3C), 26.9 (3C), 19.2 (2C); IR (neat) cm$^{-1}$: 3397, 3071, 2932, 1739, 1589, 1472, 1427, 1390, 1241, 1108; HRMS (ESI, positive) $m/z$ $[M+Na]^+$ Calcd. for $C_{41}H_{54}NaO_3Si_2$: 673.3504, Found : 673.3483.

**Synthesis of 2**

To a solution of DMSO (0.56 mL, 7.88 mmol) in $CH_2Cl_2$ (5.0 mL) was added oxalyl chloride (0.40 mL, 4.66 mmol) at -78 °C under an argon atmosphere. After the reaction mixture was stirred at -78 °C for 40 min, a solution of **14** (463 mg, 0.711 mmol) in $CH_2Cl_2$ (14 mL) was slowly added. After the reaction mixture was stirred at -65 °C for 2 h, $Et_3N$ (0.99 mL, 7.14 mmol) was slowly added. The mixture was gradually warmed to room temperature for 1 h with stirring. The reaction mixture was quenched with saturated aqueous $NH_4Cl$. The mixture was extracted with *n*-hexane. The organic layer was washed with saturated aqueous NaCl, dried over $Na_2SO_4$, and filtered. The reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel medium-pressure chromatography (*n*-hexane/EtOAc = 95/5) to give aldehyde intermediate (410 mg, 89%) as a pale yellow oil and was used for the next reaction immediately.

To a solution of aldehyde intermediate in anhydrous MeOH (9.0 mL) was added $K_2CO_3$ (171 mg, 1.24 mmol) and Ohira-Bestmann reagent (290 μL, 1.93 mmol). The mixture was stirred for 6 h. The reaction mixture was quenched with saturated aqueous

$NaHCO_3$ and extracted with *n*-hexane. The organic layer was washed with brine, dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel medium-pressure chromatography (*n*-hexane/EtOAc = 98/2) to give **2** (313 mg, 77%) as a pale yellow oil: $[\alpha]_D^{29}$ = +11.0 (*c* 0.97, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$: 7.71-7.61 (m, 8H), 7.44-7.32 (m, 12H), 4.19 (q, *J* = 5.0 Hz, 1H), 3.77-3.60 (m, 2H), 2.46 (ddd, *J* = 16.9, 5.5, 2.8 Hz, 1H), 2.24 (ddd, *J* = 16.9, 8.7, 2.3 Hz, 1H), 2.14-2.03 (m, 1H), 2.01-1.92 (m, 2H), 1.85 (t, *J* = 2.8 Hz, 1H), 1.68-1.36 (m, 5H), 1.06 (s, 9H), 1.04 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$: 136.0 (2C), 135.9 (2C), 135.6 (4C), 134.6, 134.2, 134.1, 133.8, 129.5 (4C), 127.6 (8C), 85.1, 76.1, 68.2, 63.1, 62.6, 47.5, 35.8, 34.3, 32.8, 29.7, 28.1, 27.0 (3C), 26.9 (3C), 26.8, 19.3, 19.2; IR (neat) $cm^{-1}$: 3309, 3071, 2998, 2857, 2117, 1959, 1889, 1824, 1732, 1471, 1427; HRMS (ESI, positive) *m*/*z* $[M+Na]^+$ Calcd. for $C_{42}H_{52}NaO_2Si_2$: 667.3398, Found: 673.3405.

**Synthesis of 3**

To a solution of **2** (313 mg, 0.485 mmol) in THF (10 mL) was added *n*BuLi (0.76 mL, 1.22 mmol, 1.6 M in hexane) at -78 °C under an argon atmosphere. The reaction mixture was warmed to 0 ºC and stirred for 1.5 h. The reaction mixture was re-cooled to -78 ºC. After the reaction mixture was stirred at -78 °C for 30 min, a solution of acetaldehyde (141 μL, 2.52 mmol) in THF (1.27 mL) was slowly added. The reaction mixture was warmed to room temperature and stirred for 6 h. The reaction mixture was quenched with saturated aqueous $NH_4Cl$. The mixture was extracted with $CH_2Cl_2$. The organic layer was washed with saturated aqueous NaCl, dried over $Na_2SO_4$, and filtered. The residue was purified by silica gel medium-pressure chromatography (*n*-hexane/EtOAc = 98/2 to 80/20) to give alkyne intermediate (231 mg, 69%) as a yellow

oil.

To a solution of alkyne intermediate (47.3 mg, 68.6 mmol) in anhydrous MeOH (2.0 mL) was added quinoline (8.2 μL, 69.2 mmol) and Pd/$BaSO_4$ (4.3 mg, 9 wt%) under an argon atmosphere. The reaction vessel was evacuated and recharged with $H_2$. After being stirred at room temperature for 10 min under $H_2$ atmosphere, the reaction mixture was filtered through a pad of Celite with EtOAc. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel medium-pressure chromatography (*n*-hexane/EtOAc = 98/2 to 80/20) to give **12** (42.4 mg, 89%) as a colorless oil. **3** was obtained as the stereoisomer mixture at C-11 position: $[\alpha]_D^{22} = +20.2$ (*c* 0.75, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$: 7.60-7.69 (m, 8H), 7.32-7.46 (m, 12H), 5.30-5.44 (m, 2H), 4.65 (quin, *J* = 6.2 Hz, 0.5H), 4.57 (quin, *J* = 6.4 Hz, 0.5H), 4.15 (q, *J* = 5.0 Hz, 1H), 3.68 (dtd, *J* = 10.1, 5.0, 2.3 1H), 3.60 (dt, *J* = 10.1, 6.9 Hz, 1H), 2.08-2.31 (m, 2H), 1.90-2.02 (m, 1H), 1.75-1.88 (m, 1H), 1.63-1.71 (m, 1H), 1.30-1.63 (m, 5H), 1.22 (d, *J* = 6.4 Hz, 1.5H), 1.22 (d, *J* = 6.2 Hz, 1.5H), 1.07 (s, 4.5H), 1.06 (s, 4.5H), 1.04 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$: 135.9, 135.5, 134.6, 134.5, 134.2, 134.1 (2C), 133.9 (2C), 133.5, 133.3, 131.5, 131.0, 129.5, 127.6, 127.5, 127.4, 77.2, 76.6, 63.9, 63.8, 63.1 (2C), 48.5, 48.4, 35.8, 35.7, 34.5, 34.2, 32.9, 28.1, 27.0 (3C), 26.8 (3C), 23.3, 23.2, 23.0 (2C), 19.2 (2C); IR (neat) $cm^{-1}$: 3368, 3072, 2931, 2858, 1471, 1428, 1390, 1110, 822, 740; HRMS (ESI, positive) *m/z* $[M+Na]^+$ Calcd. for $C_{44}H_{58}NaO_3Si_2$: 713.3817, Found : 713.3825.

**Synthesis of 4**

To a solution of **3** (202 mg, 0.292 mmol) in $CH_2Cl_2$ (10 mL) was added DHP (40 μL, 0.44 mmol) and *p*-TsOH·$H_2O$ (0.7 mg, 5 μmol) at 0 ºC. The solution was stirred at

0 ºC for 2 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with $CH_2Cl_2$. The organic layer was washed with brine, dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel medium-pressure chromatography (*n*-hexane/EtOAc = 98/2 to 90/10) to give **4** (221 mg, 98%) as a pale yellow oil. **4** was obtained as the stereoisomer mixture at C-11 and THP position: $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$: 7.59-7.72 (m, 8H), 7.30-7.46 (m, 12H), 5.12-5.61 (m, 2H), 4.46-4.77 (m, 2H), 4.09-4.28 (m, 1H), 3.78-3.94 (m, 1H), 3.56-3.74(m, 2H), 3.35-3.51 (m, 1H), 2.14-2.35 (m, 2H), 1.936-2.05 (m, 1H), 1.75-1.91 (m, 2H), 1.36-1.74 (m, 11H), 1.25 (d, $J$ = 6.4 Hz, 0.75H), 1.22 (d, $J$ = 6.9 Hz, 0.75H), 1.19 (d, $J$ = 6.0 Hz, 0.75H), 1.16 (d, $J$ = 6.4 Hz, 0.75H), 1.07 (s, 9H), 1.04 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$: 136.1, 135.7, 133.4, 132.9, 132.4, 132.1, 131.5, 131.0, 130.5, 130.1, 129.6, 127.7, 96.7, 96.5, 96.3, 96.0, 76.7, 68.3, 68.2, 66.9, 66.7, 63.4, 63.3, 63.2,62.6, 62.5, 48.9, 48.8, 48.6, 36.1, 36.0, 35.8, 34.6(2C), 34.5, 33.1, 31.3, 31.2, 31.1, 28.3, 27.2, 27.0, 25.7, 25.6, 25.6, 23.4, 23.3, 23.1(2C), 21.7(2C), 20.5(2C), 19.9, 19.8, 19.4, 19.3; IR (neat) cm$^{-1}$: 3072, 2932, 2859, 1428, 1389, 1111, 822, 740; HRMS (ESI, positive) *m*/*z* $[M+Na]^+$ Calcd. for $C_{49}H_{66}NaO_4Si_2$: 797.4392, Found : 797.4379.

**Synthesis of 5**

To a solution of **4** (111 mg, 0.144 mmol) in anhydrous THF (10 mL) was added TBAF (0.72 mL, 0.72 mmol, 1.0 M in THF) under an argon atmosphere. The reaction mixture was stirred for 2 h under reflux condition. The reaction mixture was cooled to rt. The reaction mixture was quenched with saturated aqueous $NH_4Cl$. The mixture was extracted with EtOAc. The organic layer was washed with brine, dried over $Na_2SO_4$, and filtered. The residue was purified by silica gel medium-pressure chromatography (*n*-

hexane/EtOAc = 90/10 to 0/100) to give **5** (38.9 mg, 91%) as a pale yellow oil. **5** was obtained as the stereoisomer mixture at C-11 and THP position: $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta_H$: 5.15-5.65 (m, 2H), 4.60-4.84 (m, 2H), 4.09-4.28 (m, 1H), 4.04-4.24 (m, 1H), 3.42-3.96(m, 4H), 2.45-2.61(m, 0.5H), 2.17-2.33(m, 1H), 1.47-2.12(m, 14.5H), 1.27 (d, *J* = 6.4 Hz, 1.5H), 1.22 (d, *J* = 6.0 Hz, 1.5H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta_C$: 133.5, 132.8, 132.7, 132.3, 132.2, 131.2, 129.7, 129.6, 98.5, 97.6, 94.6, 93.6, 75.3, 75.2, 73.6(2C), 70.2, 69.4, 66.5, 65.6, 63.2(2C), 62.3, 62.2(2C), 61.8, 60.9, 48.7, 48.3, 48.2, 48.0, 36.3(2C), 35.9(2C), 35.5, 35.3, 35.0, 34.7, 33.7, 33.6, 33.4, 33.3, 31.3, 31.2, 30.8, 30.2, 29.2, 29.0, 28.9, 28.8, 25.7, 25.5(2C), 25.4, 23.8, 23.7, 23.6, 23.5, 21.8, 21.7, 21.4, 20.8, 20.1, 19.9, 19.1, 18.4; IR (neat) cm$^{-1}$: 3409, 2930, 1728, 1442, 1022, 899, 868, 809, 754; HRMS (ESI, positive) *m/z* $[M+Na]^+$ Calcd. for $C_{17}H_{30}NaO_4$: 321.2036, Found :321.2036.

**Determination of Stereochemistry of (3*R*, 7*S*, 11*R*)-11-OH-JA and (3*R*,7*S*, 11*S*)-11-OH-JA by modified Mosher's method**

**Isolation of a single stereoisomer of 3**

Single stereoisomer of **3** was isolated from a mixture of (3*R,* 7*S,* 11*R/S*)-**3** by multiple silica gel medium-pressure chromatography. From a mixture of (3*R,* 7*S,* 11*R/S*)-**3** (39.2 mg), (3*R,* 7*S,* 11*R*)-**3** (14.2 mg) and (3*R,* 7*S,* 11*S*)-**3** (17.5 mg) were isolated.

**Synthesis of (3*R,* 7*S,* 11*S*)-3-(*S*)-MTPA ester**

To solution of (3*R,* 7*S,* 11*S*)-**3** (2.2 mg, 3.2 μmol) in DCM (2.0 mL) and pyridine (0.10 mL) was added (*R*)-MTPA-Cl (4.0 μL, 21 μmol). The solution was stirred at rt for 2 h. The reaction mixture was quenched with 1M aqueous HCl and extracted with $CHCl_3$.

The organic layer was washed with brine, dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was roughly purified by silica gel chromatography (*n*-hexane/EtOAc = 98/2 to 95/5) to give (3*R,* 7*S,* 11*S*)-**3**-(*S*)-MTPA ester (0.5 mg) as a pale yellow amorphous solid: $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$: 7.68-7.31 (m, 25H), 5.88 (dq, *J* = 9.2, 6.4 Hz, 1H), 5.55 (dt, *J* = 11.0, 6.9 Hz, 1H), 5.34 (dd, *J* = 11.0, 9.2 Hz, 1H), 4.19-4.14 (m, 1H), 3.71-3.55 (m, 2H), 3.51 (s, 3H), 2.44-2.31 (m, 2H), 2.30-2.20 (m, 1H), 2.05-1.95 (m, 2H), 1.85-1.75 (m, 1H), 1.72-1.63 (m, 1H), 1.61-1.47 (m, 3H), 1.26 (d, *J* = 6.4 Hz, 3H), 1.06 (s, 9H), 1.03 (s, 9H); HRMS (ESI, positive) *m*/*z* $[M+Na]^+$ Calcd. for $C_{54}H_{65}F_3NaO_5Si_2$: 929.4215, Found : 929.4242.

**Synthesis of (3*R,* 7*S,* 11*S*)-3-(*R*)-MTPA ester**

To solution of (3*R,* 7*S,* 11*S*)-**3** (2.3 mg, 3.3 μmol) in DCM (2.0 mL) and pyridine (0.10 mL) was added (*S*)-MTPA-Cl (4.0 μL, 21 μmol). The solution was stirred at rt for 1 h. The reaction mixture was quenched with 1M aqueous HCl and extracted with $CHCl_3$. The organic layer was washed with brine, dried over $Na_2SO_4$, and concentrated under reduced pressure to give crude (3*R,* 7*S,* 11*S*)-**3**-(*R*)-MTPA ester (1.2 mg) as a pale yellow amorphous solid: $^1$H NMR (400 MHz, $CDCl_3$) $\delta_H$: 7.68-7.31 (m, 25H), 5.85 (dq, *J* = 8.7, 6.4 Hz, 1H), 5.52 (dt, *J* = 11.0, 7.3 Hz, 1H), 5.24 (dd, *J* = 11.0, 9.2 Hz, 1H), 4.17 (q, *J* = 5.0 Hz, 1H), 3.71-3.58 (m, 2H), 3.53 (s, 3H), 2.45-2.35 (m, 2H), 2.28-2.17 (m, 1H), 2.05-1.95 (m, 2H), 1.85-1.75 (m, 1H), 1.72-1.64 (m, 1H), 1.61-1.47 (m, 3H), 1.33 (d, *J* = 6.0 Hz, 3H), 1.06 (s, 9H), 1.03 (s, 9H); HRMS (ESI, positive) *m*/*z* $[M+Na]^+$ Calcd. for $C_{54}H_{65}F_3NaO_5Si_2$: 929.4215, Found : 929.4233.

**Synthesis of (3*R,* 7*S,* 11*S*)-11-OH-JA from (3*R,* 7*S,* 11*S*)-3 (Supplementary**

**Fig. 3B)**

**Synthesis of (3*R*, 7*S*, 11*S*)-5**

To a solution of (3*R,* 7*S,* 11*S*)-**3** (12 mg, 17 μmol) in $CH_2Cl_2$ (4.0 mL) was added DHP (6.0 μL, 67 μmol) and *p*-TsOH·$H_2O$ (0.16 mg, 1 μmol) at 0 ºC. The solution was stirred at 0 ºC for 1 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with $CH_2Cl_2$. The organic layer was washed with brine, dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (*n*-hexane/EtOAc = 95/5) to give (3*R,* 7*S,* 11*S*)-**4** (12 mg, 91%) as a pale yellow oil. (3*R,* 7*S,* 11*S*)-**4** was obtained as the stereoisomer mixture at THP position and directly used for the next reaction.

To a solution of (3*R,* 7*S,* 11*S*)-**4** (12 mg, 16 μmol) in anhydrous THF (6.0 mL) was added TBAF (0.10 mL, 0.10 mmol, 1.0 M in THF) under an argon atmosphere. The reaction mixture was stirred for 16 h at rt. The reaction mixture was quenched with saturated aqueous $NH_4Cl$. The mixture was extracted with EtOAc. The organic layer was washed with brine, dried over $Na_2SO_4$, and filtered. The residue was purified by silica gel chromatography (*n*-hexane/EtOAc = 50/50 to 40/60) to give (3*R,* 7*S,* 11*S*)-**5** (4.2 mg, 89%) as a yellow oil. (3*R,* 7*S,* 11*S*)-**5** was obtained as the stereoisomer mixture at THP position and directly used for the synthesis of (3*R,* 7*S,* 11*S*)-11-OH-JA.

**Synthesis of (3*R*, 7*S*, 11*S*)-11-OH-JA**

To a solution of (3*R,* 7*S,* 11*S*)-**5** (4.2 mg, 14 umol) in acetone (10 mL) was added Jones reagent (4.0 M solution, 90 uL, 0.36 mmol) at -20 ºC. After 1 h of stirring at -20 ºC, *i*-PrOH (1.4 mL) was added to quench the remaining reagent. After 1 h of stirring at -20 ºC, EtOAc/*n*-hexane (1/1, 10 mL) and $H_2O$ (15 mL) were added, and the aqueous

layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (*n*-hexane/0.1%AcOH/EtOAc+0.1%AcOH = 40/60) to give a carboxylic acid intermediate (3.4 mg, 78%) as a colorless oil.

To a solution of the carboxylic acid intermediate (3.4 mg) in $Et_2O$ (1.4 mL) was added $MgBr_2$•$OEt_2$ (4.2 mg, 16 μmol). The resulting white suspension was stirred at room temperature for 3 h and dried under reduced pressure. The residue was dissolved with 30% aq. MeOH containing 0.1% AcOH and syringe-filtered through PTFE membrane. The crude product was directly purified by RP-HPLC (ODS-HG-5 ϕ4.6x250, 210 nm, 0.6 mL/min, eluent: 30% aq. MeOH + 0.1%AcOH) to give (3*R*, 7*S*, 11*S*)-OH-JA ($t_R$ = 21 min, 1.1 mg, 44%) as a colorless amorphous solid. The synthesized (3*R*, 7*S*, 11*S*)-OH-JA was the same as the latter isomer of (3*R*, 7*S*, 11*R/S*)-11-OH-JA in UPLC-MS/MS analysis (**Supplementary Fig. 3C**).

**Pull-down experiments using fluorescein-tagged JAZ peptides**

For the pulldown experiment with Fl-JAZPs, purified GST-COI1 (5 nM), Fl-JAZPs (10 nM) and the ligands (1 - 100 μM) in 350 μL of incubation buffer (50 mM Tis-HCl, 100mM NaCl, 10% glycerol, 0.1% Polyoxyethylene (20) Sorbitan Monolaurate, pH 7.8) were combined with anti-fluorescein antibody (ab19491; Abcam, Cambridge, UK ; 0.1 μL) and incubated for 10–15 h at 4 °C with rotation. After incubation, the samples were combined with SureBeads Protein A (10 μL in incubation buffer slurry; Cytiva, USA; 10 mg beads/ml). After 1.5 h of incubation at 4 °C with rotation, the samples were washed three times with 350 μL of Dulbecco's phosphate-buffered saline containing 0.1% Polyoxyethylene (20) Sorbitan Monolaurate. The washed beads were resuspended in 35

μL of SDS-PAGE loading buffer containing dithiothreitol (100 mM). After heating for 10 min at 60 °C, the samples were subjected to SDS-PAGE and analyzed by western blotting. The bound GST-COI1 was detected using anti-GST HRP conjugate (RPN1236; Cytiva ; 10000-fold dilution in blocking buffer).

**Plasmid constructions for JOX1/2/3/4 expression**

The coding sequence of *JOX1/2/3/4* (At5g05600, At3g55970, At2g38240, respectively) was obtained from TAIR database and JOX2/3/4 genes were amplified from an *A. thaliana* cDNA library using primers (JOX2-forward, 5′-ATGAACAAGAACAAGATTGATGTTAAGATCGAG-3′; JOX2-reverse, 5′-TCAACGAGGAGAAATATGAGATTCAACATG-3′, JOX3-forward, 5′-CATCATCATCATCACATGAATATCTTCCAAGACTGGC-3′; JOX3-reverse, 5′-TTAGCAGCCGGATCCCTATCGAGGGGATTTAAGTTCG-3′, JOX4-forward, 5′-CATCATCATCATCACATGGCTACATGCTGGCCTGAGC-3′; JOX4-reverse, 5′-TTAGCAGCCGGATCCTTATCTAGTTAATAACAGTG-3′). In the case of JOX1, we ordered Eurofins genomics to synthesis sequence and amplified them using primers (JOX1-forward, 5′- ATGAACAACCTAGACGAGATCAAGATCG-3′; JOX1-reverse, 5′- TCACCAATCTTTTGGAATCTCTAGGTAGTTC-3′). Using the In-Fusion HD Cloning kit (Takara Bio, Shiga, Japan), the PCR-amplified *JOX1-4* coding sequence was cloned into pET-*6xHis*-vector linearized with primers (JOX1-forward, 5′-CCAAAAGATTGGTGAGGATCCGGCTGCTAACAAAGCC -3′; JOX1-reverse, 5′-GTCTAGGTTGTTCATGTGATGATGATGATGATGGCCCATATG-3′, JOX2-forward, 5′- ATTTCTCCTCGTTGAGGATCCGGCTGCTAACAAAGC -3′; JOX2-reverse, 5′-CTTGTTCTTGTTCATGTGATGATGATGATGATGGCCCATATG-3′, JOX3/4-

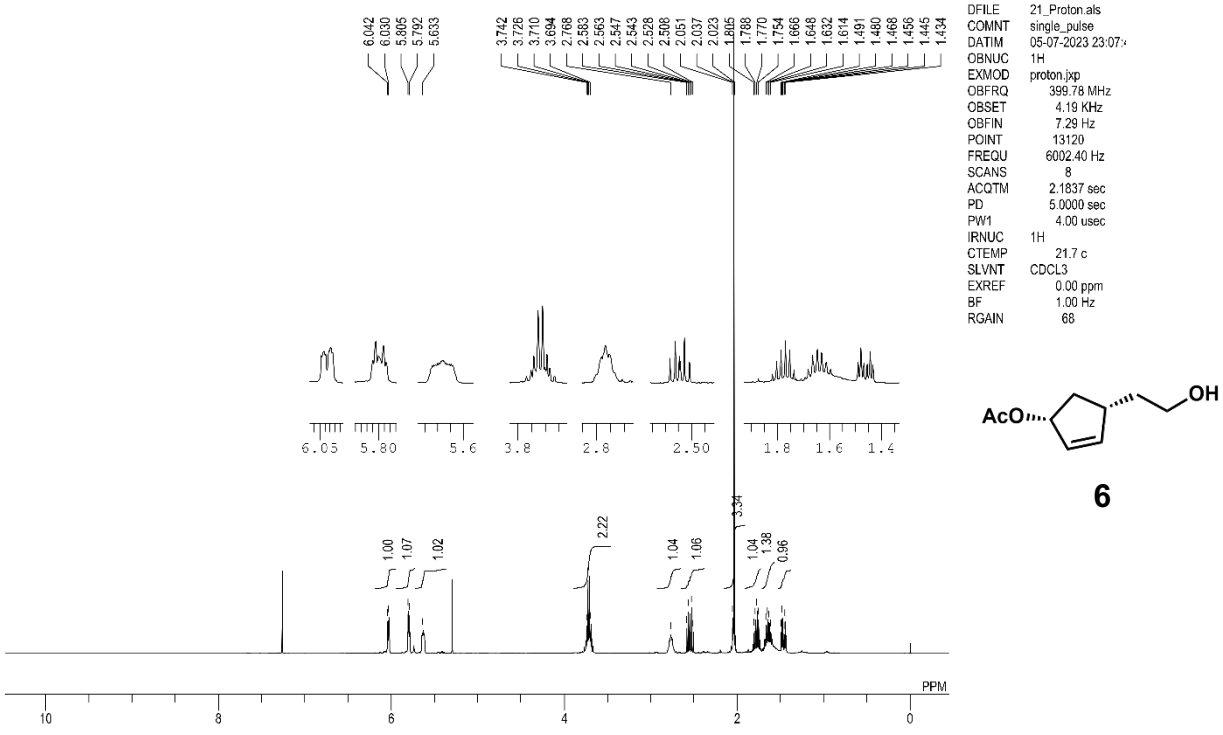
forward, 5′- GGATCCGGCTGCTAACAAAGCCC -3′; JOX3/4-reverse, 5′- GTGATGATGATGATGATGGCCCATATG -3′).

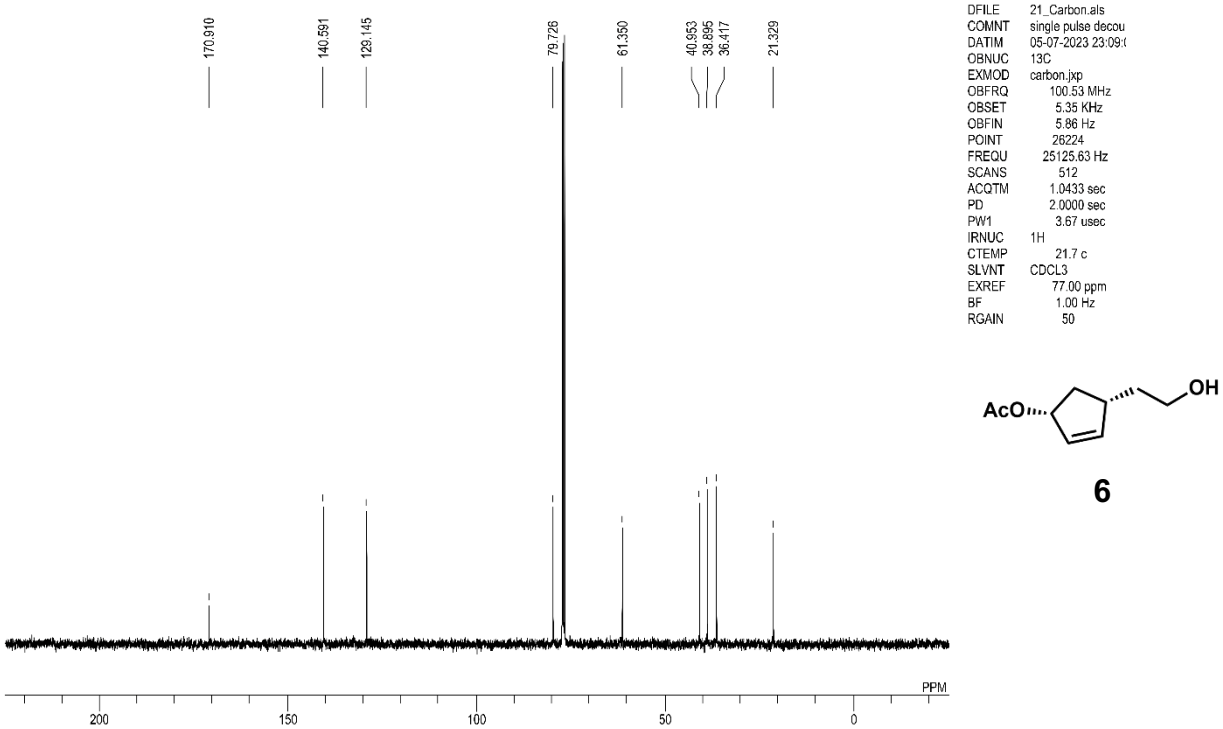
**Protein expression and purification**

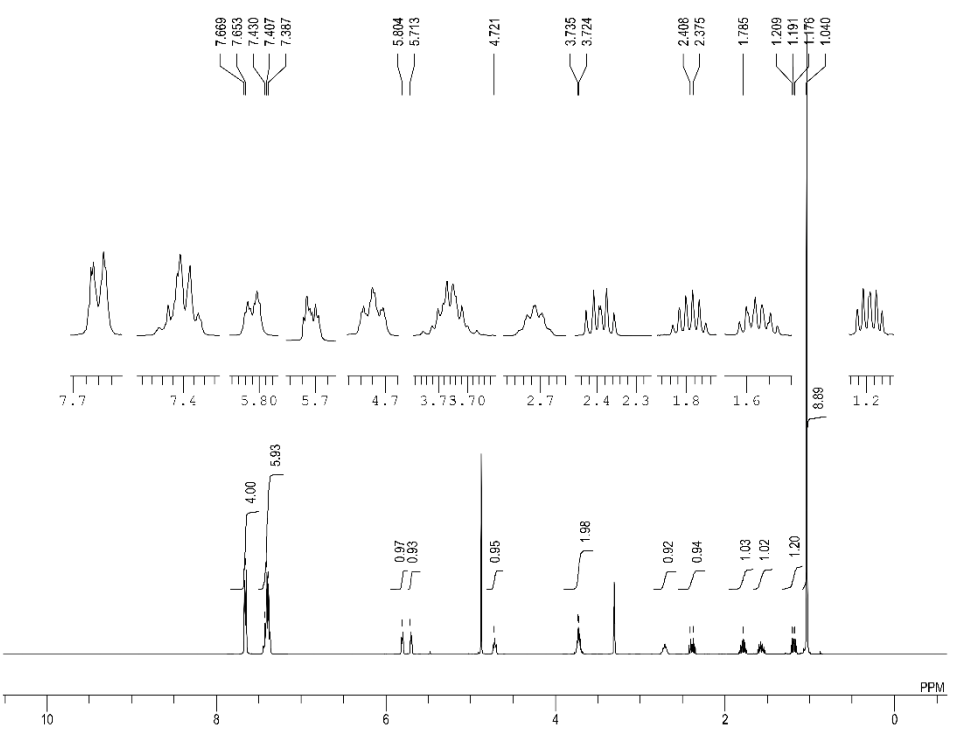
The *6xHis-JOX1/2/3/4* genes in pET vector was expressed in *E. coli* BL21 (DE3) strain. *E. coli was* grown in LB medium supplemented with 50 μg/ml ampicillin and protein expression was induced by the addition of 0.2 mM isopropyl-β-D-thiogalactopyranoside with shaking at 16 °C for 16 h when optical density at 600 nm got 0.6. Cells were collected by centrifugation and lysed by sonication with lysis buffer (20 mM Tris–HCl, 150 mM NaCl, 20 mM imidazole [pH 7.5]). Recombinant protein was collected from Ni Sepharose$^{TM}$ High Performance (Cytiva) using elution buffer (20 mM Tris–HCl, 150 mM NaCl, 300 mM imidazole [pH 7.5])

The obtained crude fraction of *6xHis*-JOX was concentrated. The concentrated fraction was purified by gel filtration chromatography on the AKTA system (Amersham Pharmacia Biotech, column: Hiload 16/60 Superdex 200 prepgrade (1CV=120mL), elution buffer: 10 mM HEPES, 150 mM NaCl, pH 7.4, flowrate: 0.50 mL/min, detection: 280, 254, and 220nm, fraction volume: 2.0 mL, equilibration: 1.1 CV, elution 1.2 CV). The fractions of pure 6xHis-JOX1-4 were collected, and the concentration was determined by UV absorption at 280 nm using NanoPhotometerN60 (IMPLEN GmbH, Germany).

$^{1}H$, $^{13}C$ NMR spectra



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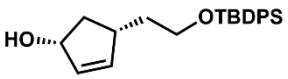


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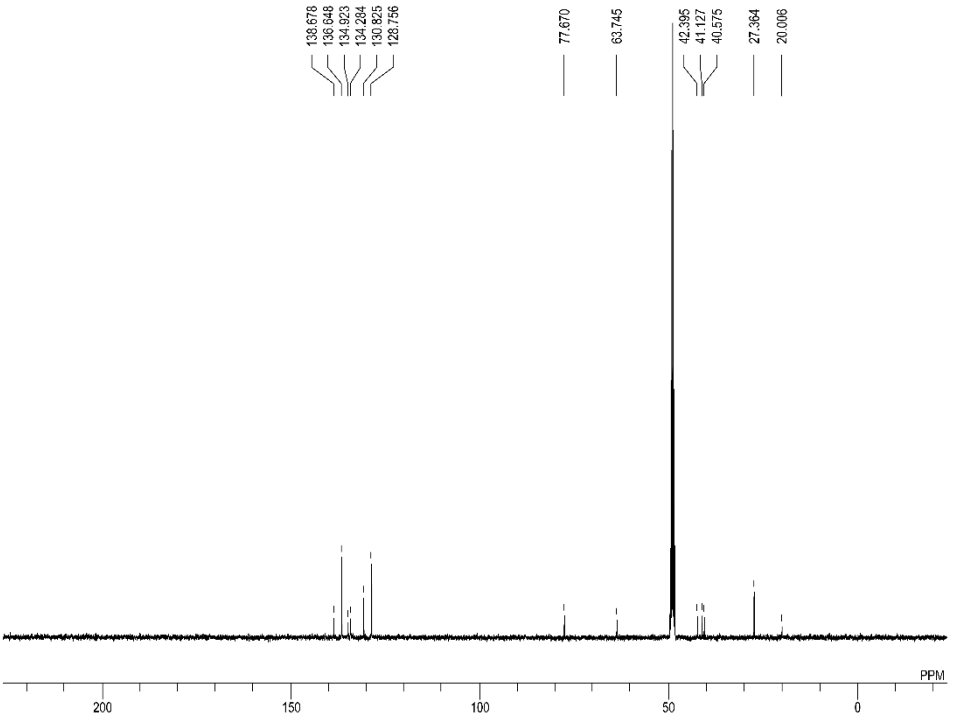


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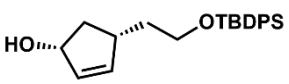
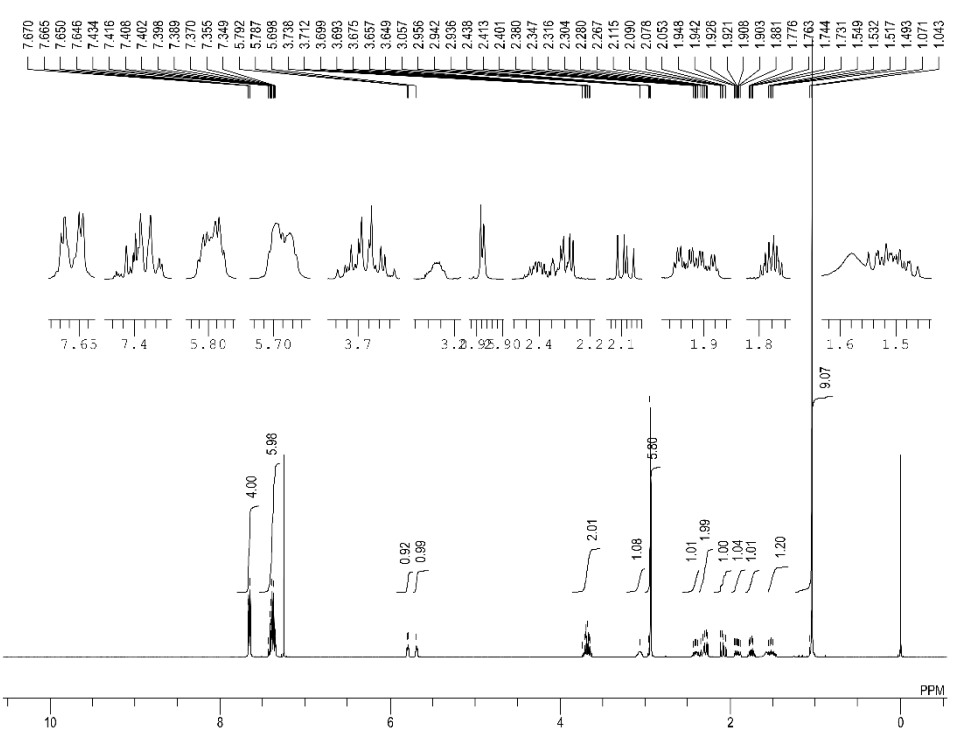



**7**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PD 5.0000 sec
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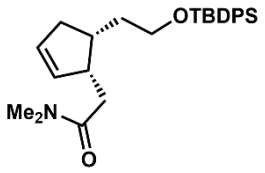
RGAIN 74
PPM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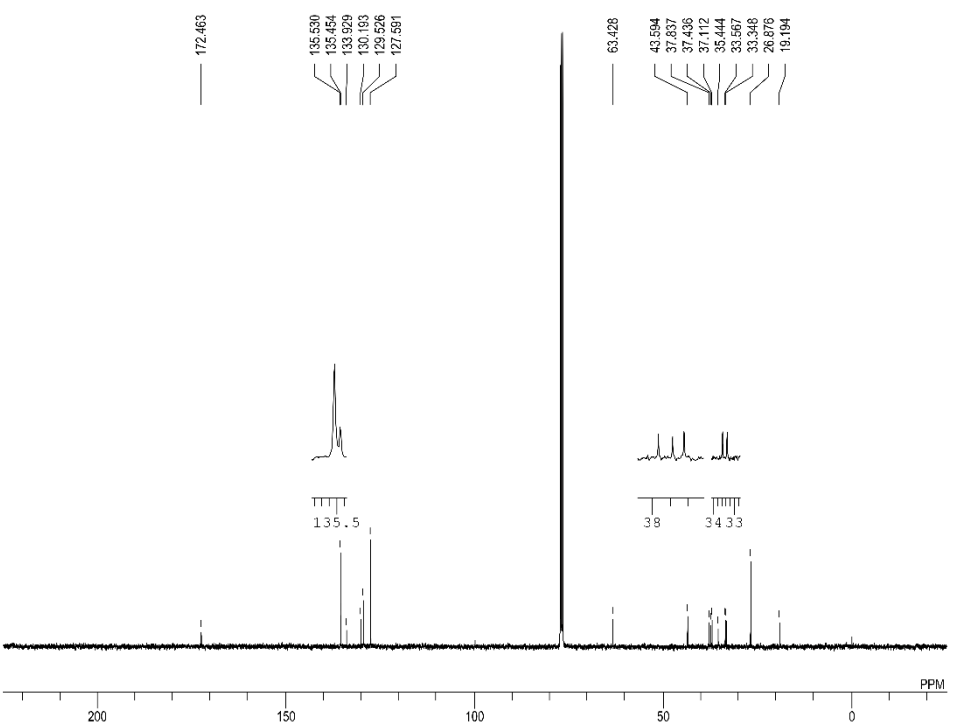
**8**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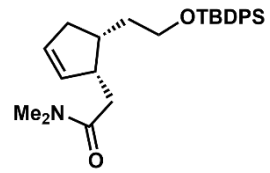
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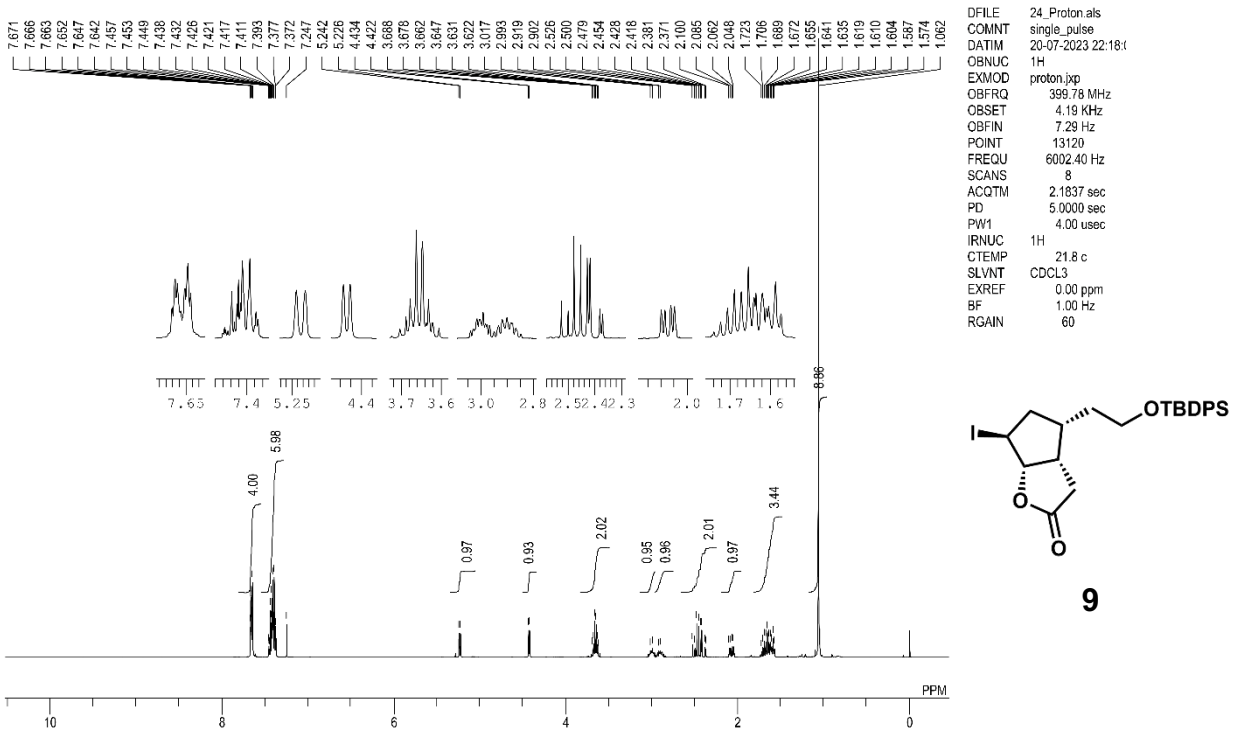
O

**8**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PD 5.0000 sec
PW1 4.00 usec
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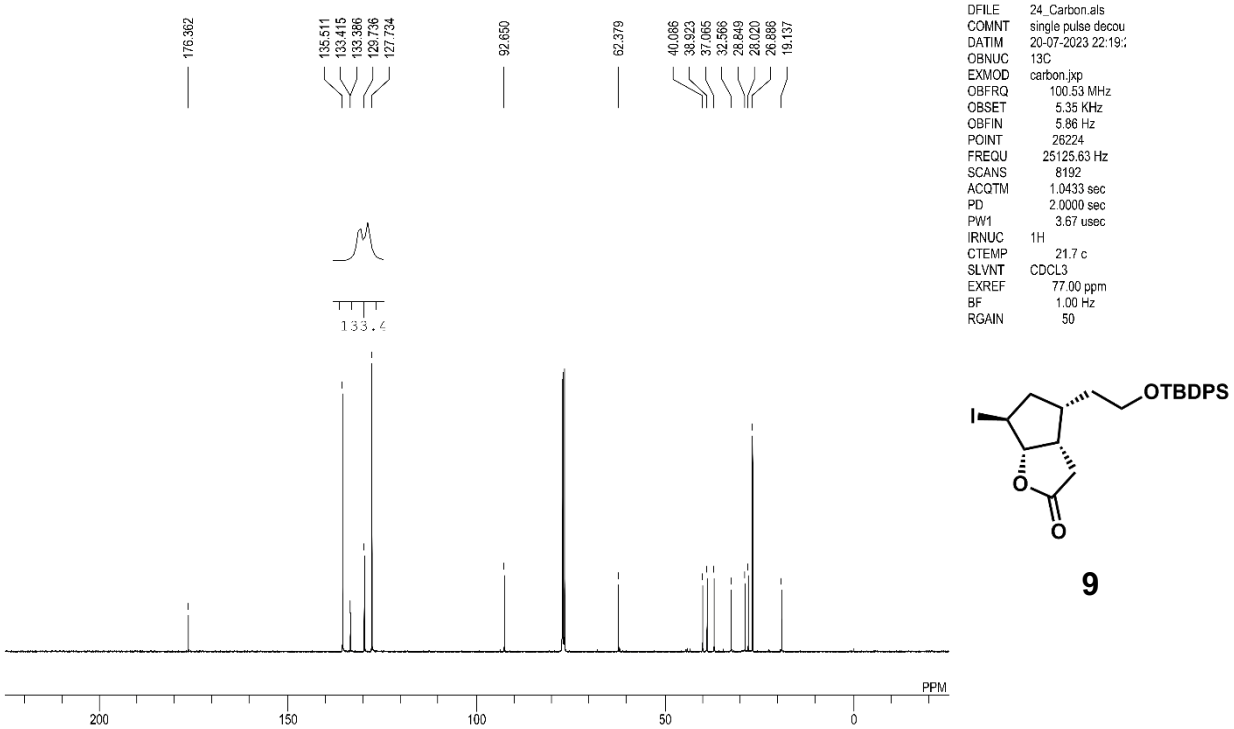
OTBDPS
9
PPM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PD 2.0000 sec
PW1 3.67 usec
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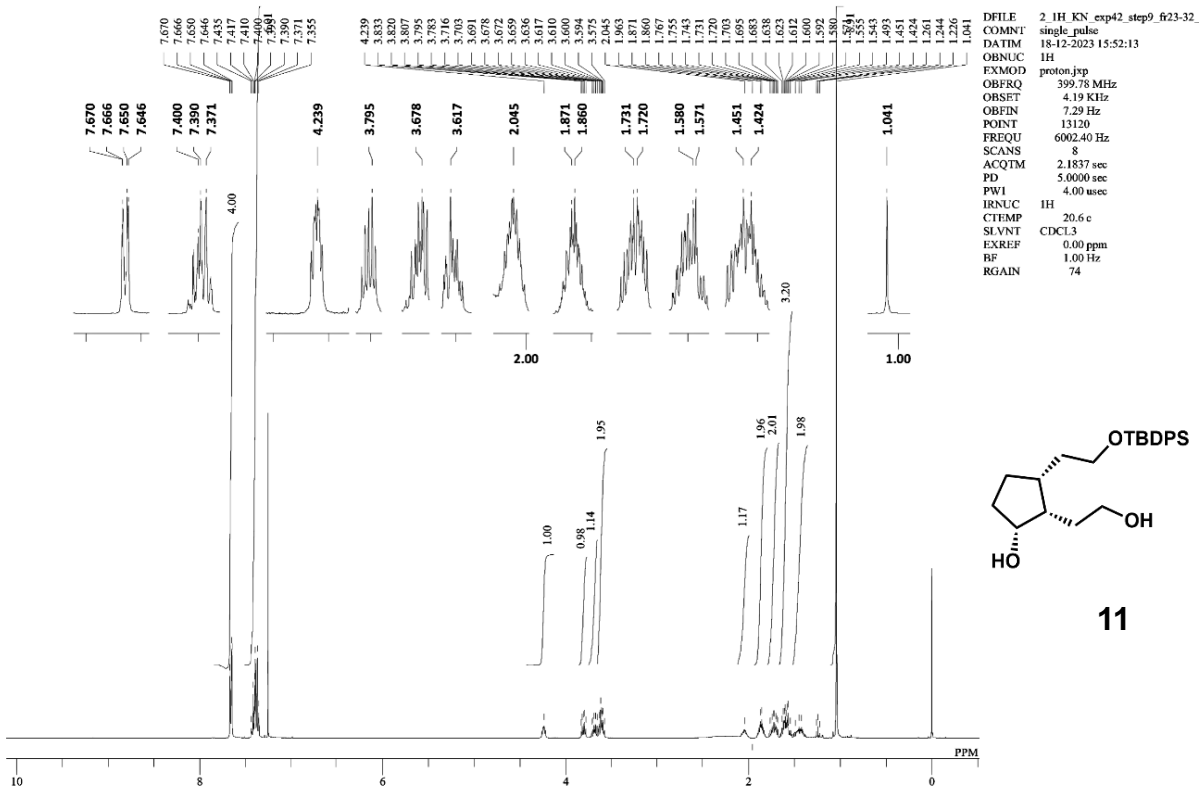
RGAIN 50
OTBDPS
9
PPM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OBFIN 7.29 Hz
POINT 13120
FREQU 6002.40 Hz
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PD 5.0000 sec
PW1 4.00 usec
IRNUC 1H
CTEMP 20.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.00 Hz
RGAIN 74
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7.666
7.650
7.646
7.400
7.390
7.371
4.239
3.795
3.678
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1.731
1.720
1.580
1.571
1.451
1.424
1.041
4.00
2.00
1.00
3.20
1.00
0.98
1.14
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1.17
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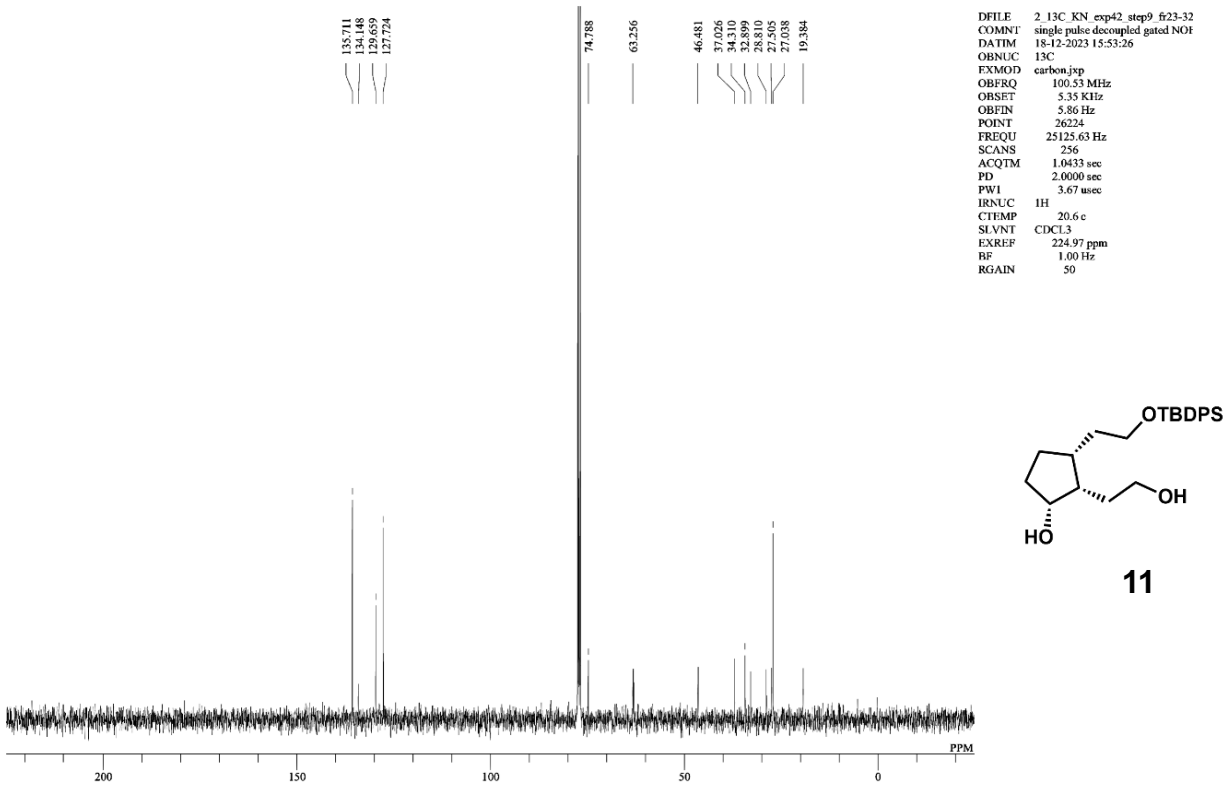
2.01
1.98
PPM
10
8
6
4
2
0


OTBDPS
OH
HO

**11**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OBFIN 5.86 Hz
POINT 26224
FREQU 25125.63 Hz
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PD 2.0000 sec
PW1 3.67 usec
IRNUC 1H
CTEMP 20.6 c
SLVNT CDCL3
EXREF 224.97 ppm
BF 1.00 Hz
RGAIN 50
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134.148
129.659
127.724
74.788
63.256
46.481
37.026
34.310
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27.038
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PPM
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100
50
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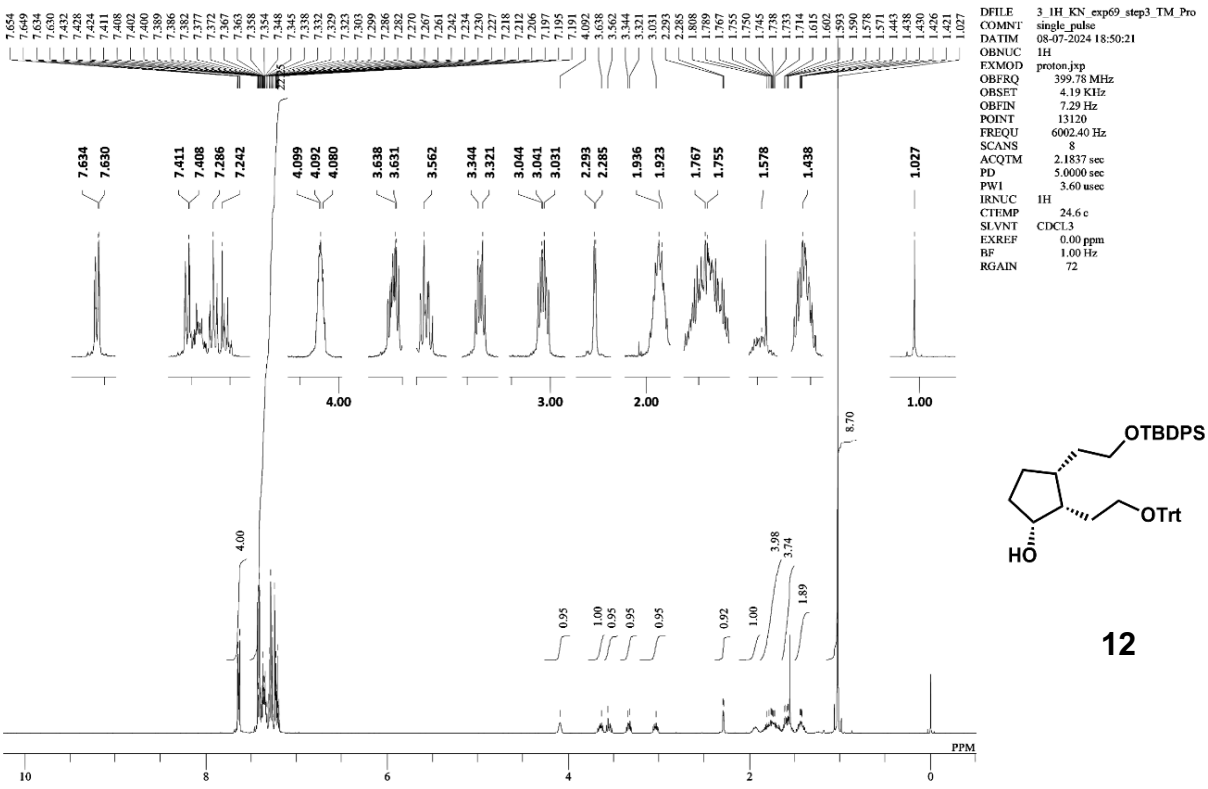
OTBDPS
OH
HO

**11**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OBFIN 7.29 Hz
POINT 13120
FREQU 6002.40 Hz
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ACQTM 2.1837 sec
PD 5.0000 sec
PWI 3.60 usec
IRNUC 1H
CTEMP 24.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.00 Hz
RGAIN 72
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7.630
7.411
7.408
7.286
7.242
4.099
4.092
4.080
3.638
3.631
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3.344
3.321
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1.755
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3.00
2.00
1.00
8.70
4.00
0.95
1.00
0.95
0.95
0.95
0.92
1.00
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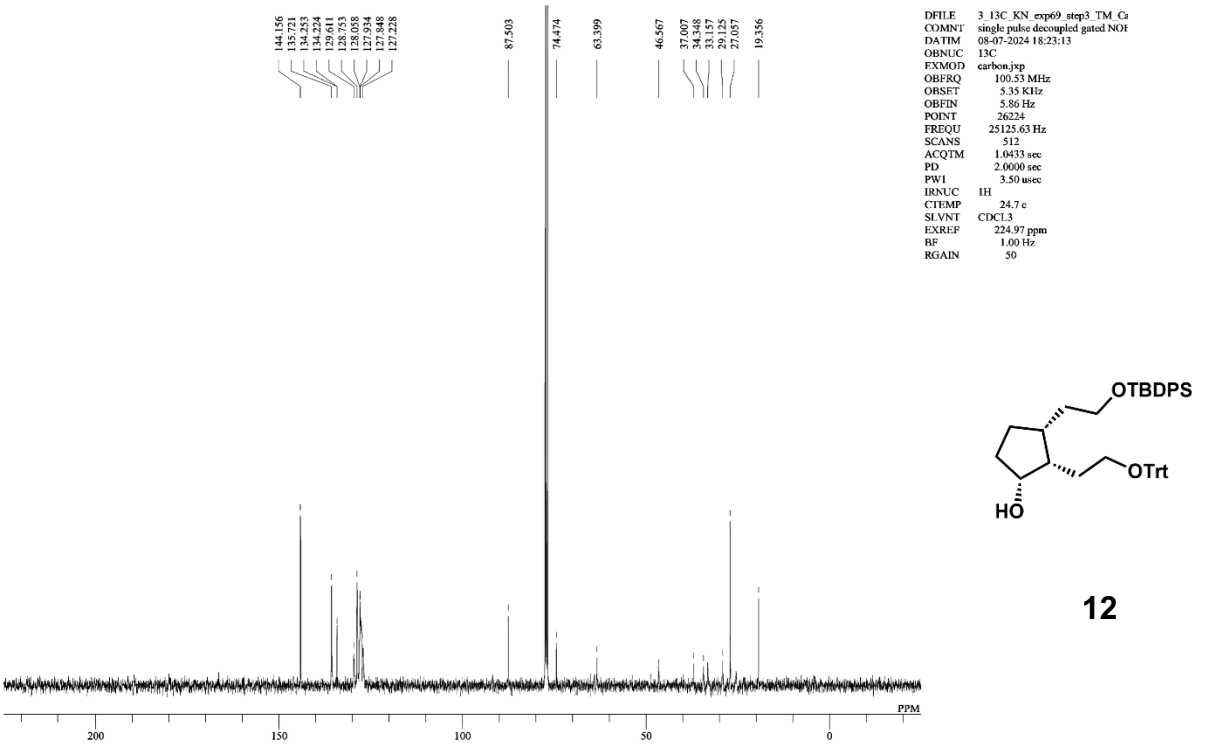
PPM
10
8
6
4
2
0


OTBDPS
OTrt
HO

**12**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37.007
34.348
33.157
29.125
27.057
19.356
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OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26224
FREQU 25125.63 Hz
SCANS 512
ACQTM 1.0433 sec
PD 2.0000 sec
PWI 3.50 usec
IRNUC 1H
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SLVNT CDCL3
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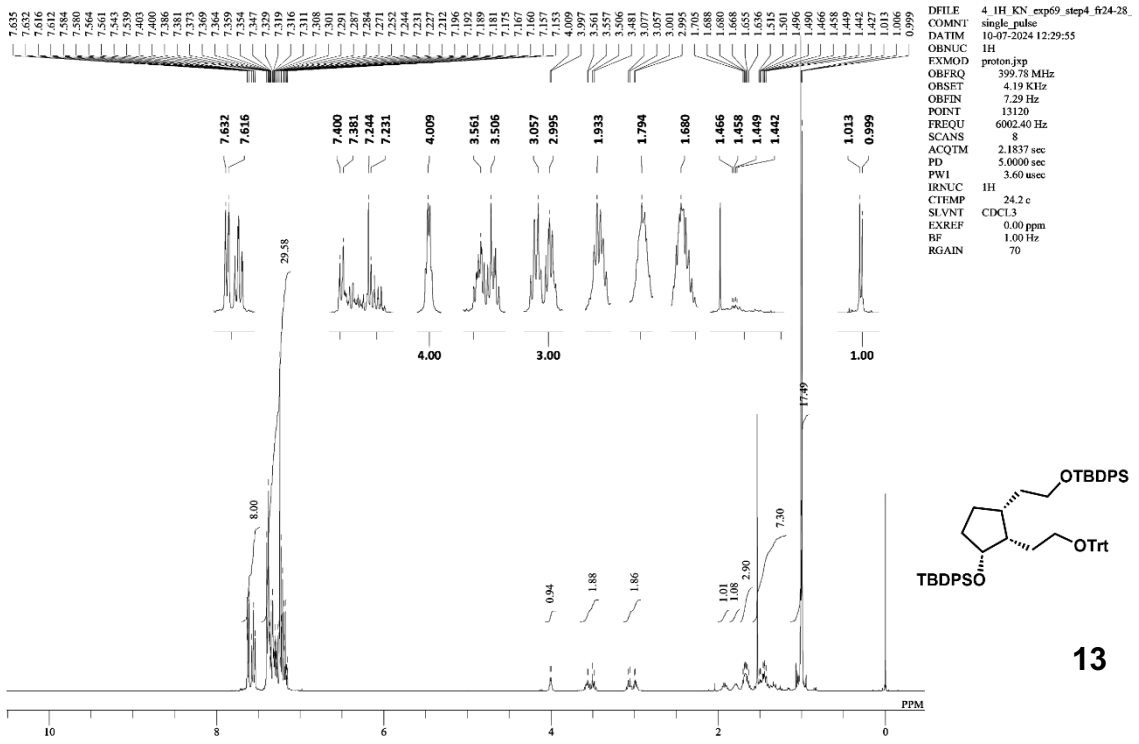
PPM
200
150
100
50
0


OTBDPS
OTrt
HO

**12**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POINT 13120
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 3.60 usec
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CTEMP 24.2 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 1.00 Hz
RGAIN 70
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7.616
7.400
7.381
7.244
7.231
4.009
3.561
3.506
3.057
2.995
1.933
1.794
1.680
1.466
1.458
1.449
1.442
1.013
0.999
4.00
3.00
1.00
29.58
17.49
8.00
7.30
2.90
1.88
1.86
1.01
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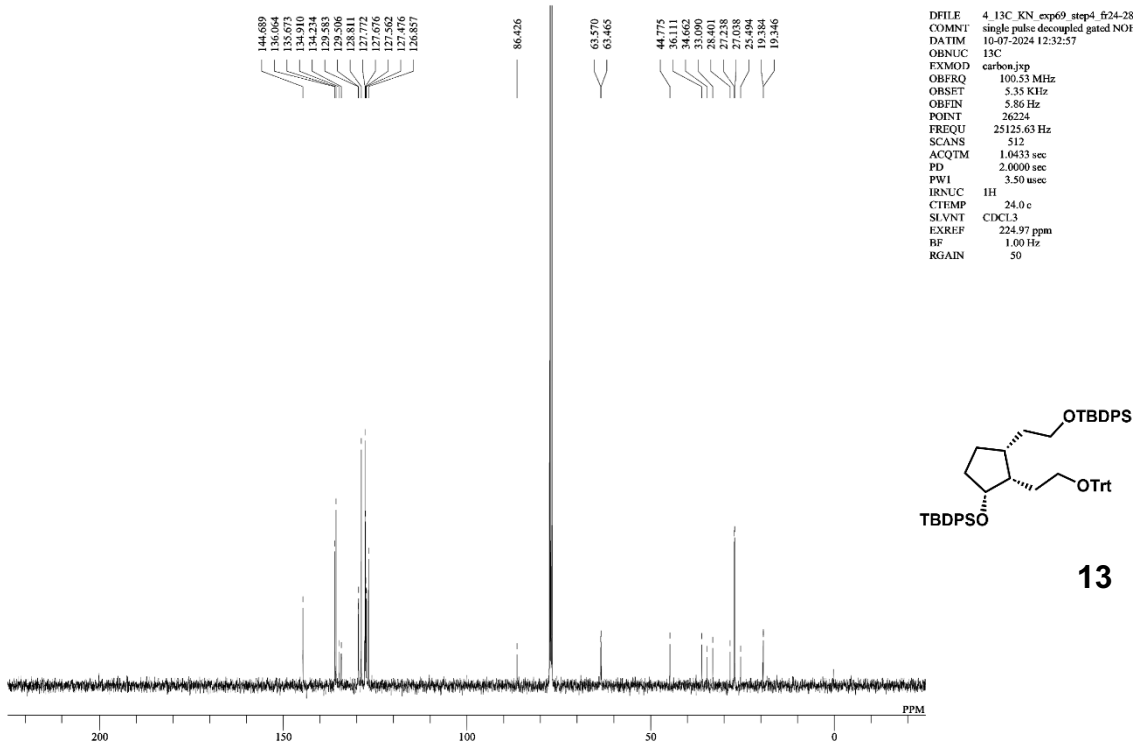
0.94
PPM
10
8
6
4
2
0


OTBDPS
OTrt
TBDPSO

**13**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SCANS 512
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PD 2.0000 sec
PW1 3.50 usec
IRNUC 1H
CTEMP 24.0 c
SLVNT CDCl3
EXREF 224.97 ppm
BF 1.00 Hz
RGAIN 50
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135.677
134.910
134.234
129.583
129.506
128.811
127.772
127.676
127.562
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33.090
28.401
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PPM
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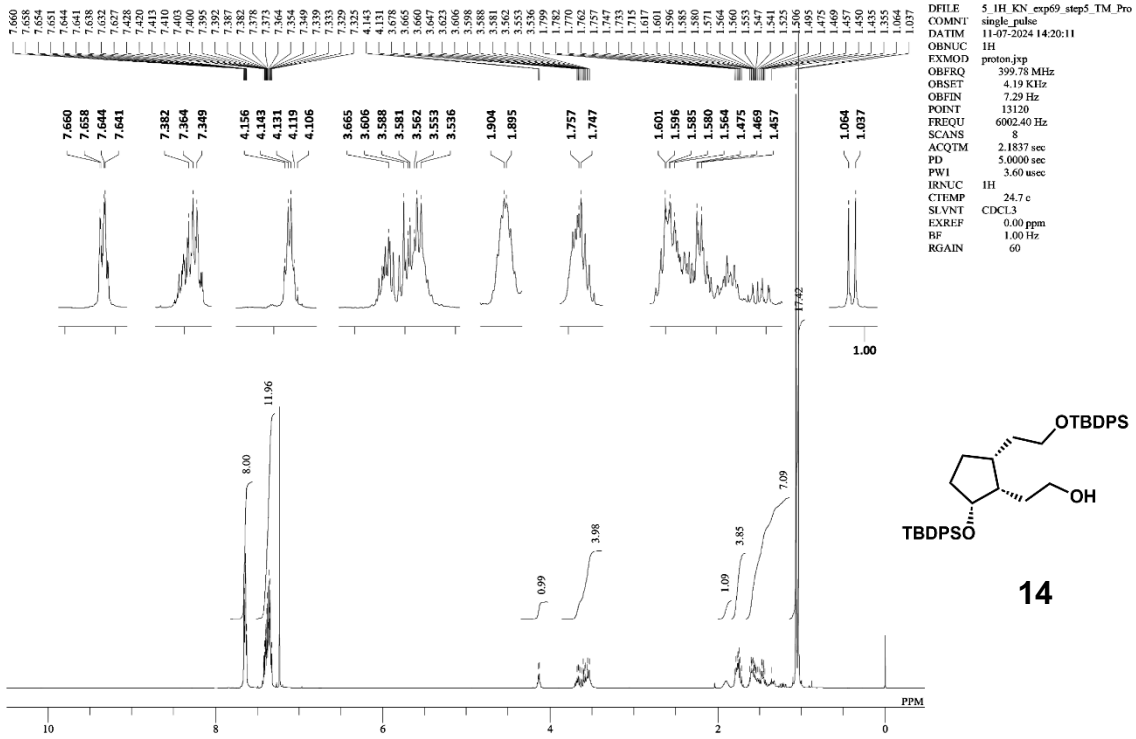
50
0


OTBDPS
OTrt
TBDPSO

**13**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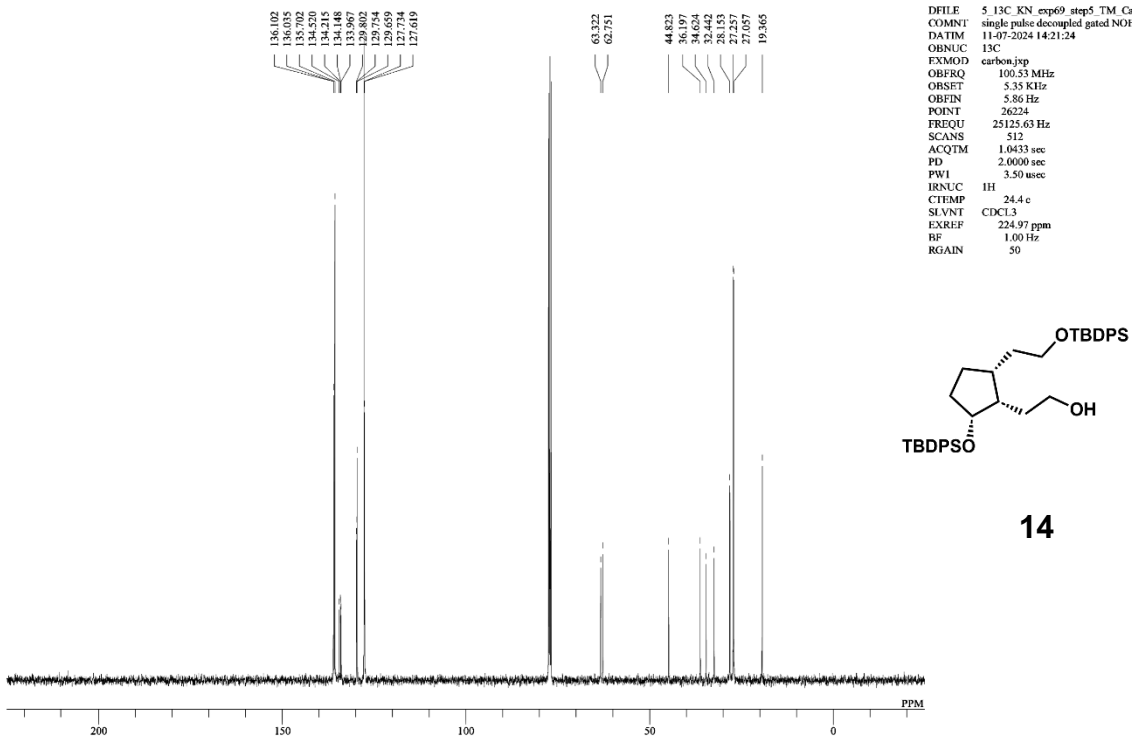
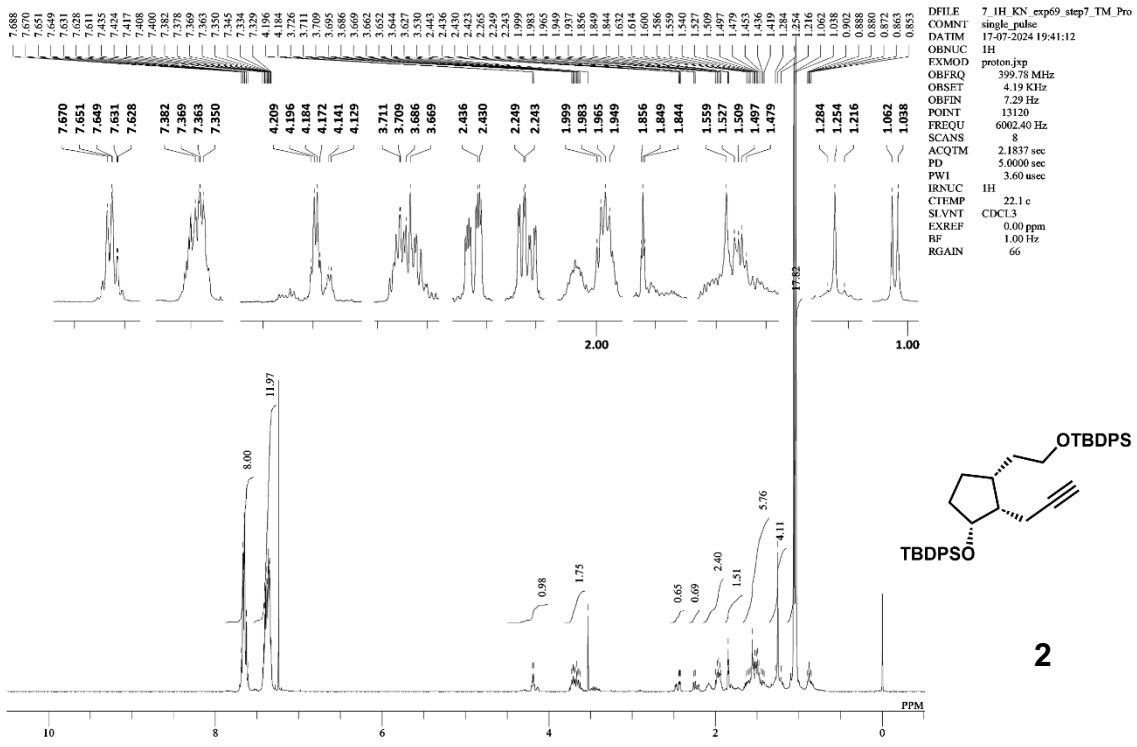
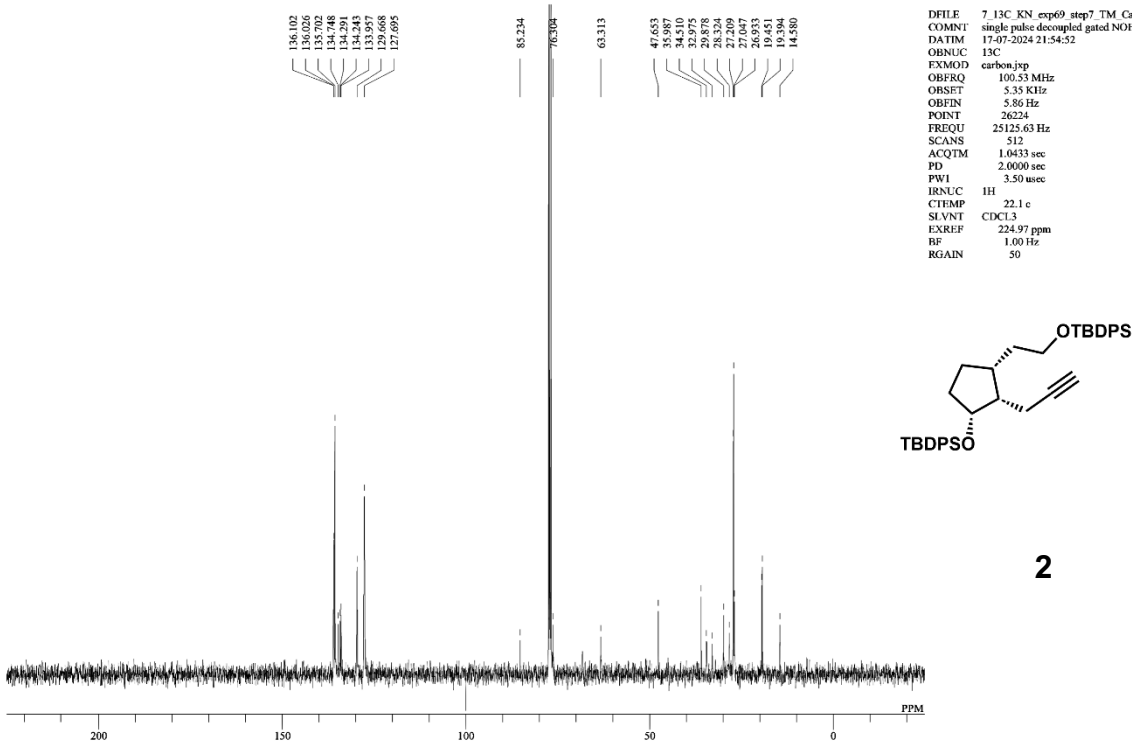
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13120
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 3.60 usec
IRNUC 1H
CTEMP 24.7 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 1.00 Hz
RGAIN 60
7.660 7.658 7.644 7.641 7.382 7.364 7.349 4.156 4.143 4.131 4.119 4.106 3.665 3.606 3.588 3.581 3.562 3.553 3.536 1.904 1.895 1.757 1.747 1.601 1.596 1.585 1.580 1.564 1.475 1.469 1.457 1.064 1.037
17.42
1.00
11.96
8.00
0.99
3.98
1.09
3.85
7.09
PPM
10
8
6
4
2
0
OTBDPS
OH
TBDPSO
14

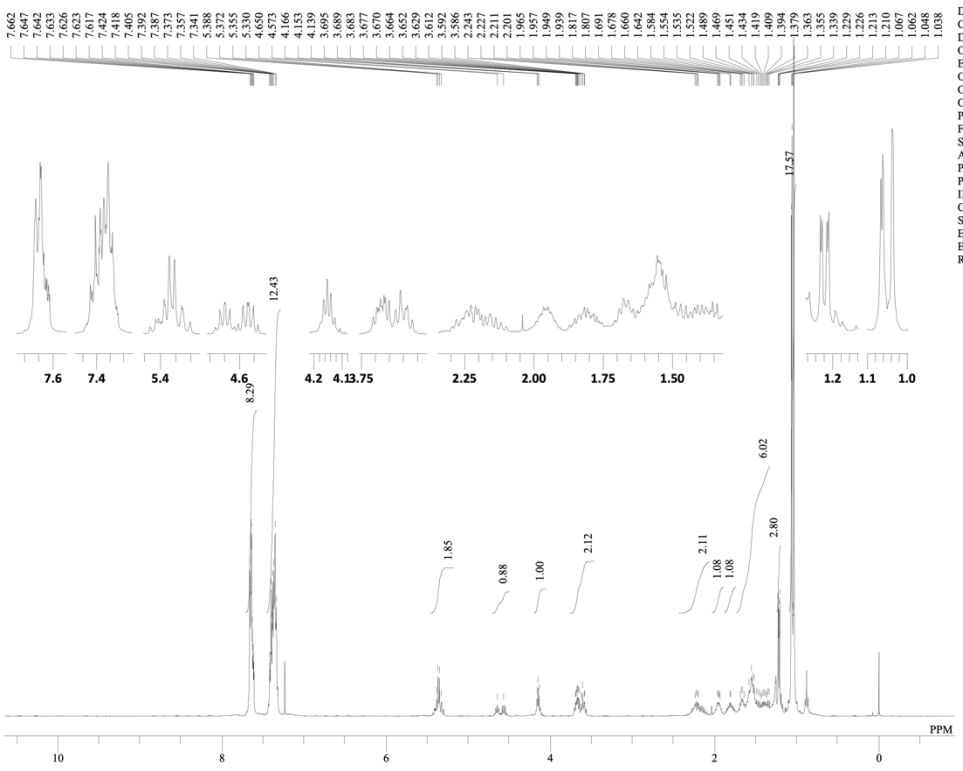

DFILE 5_13C_KN_exp69_step5_TM_Ca
COMNT single pulse decoupled gated NOE
DATIM 11-07-2024 14:21:24
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26224
FREQU 25125.63 Hz
SCANS 512
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.50 usec
IRNUC 1H
CTEMP 24.4 c
SLVNT CDCl3
EXREF 224.97 ppm
BF 1.00 Hz
RGAIN 50
136.102 136.035 135.702 134.520 134.215 134.148 133.967 129.802 129.754 129.659 127.734 127.619
63.322 62.751
44.823 36.197 34.624 32.442 28.155 27.257 27.057 19.365
PPM
200
150
100
50
0
OTBDPS
OH
TBDPSO
14

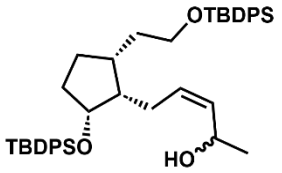

DFILE 7_1H_KN_exp69_step7_TM_Pro
COMNT single_pulse
DATIM 17-07-2024 19:41:12
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13120
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 3.60 usec
IRNUC 1H
CTEMP 22.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.00 Hz
RGAIN 66
7.670 7.651 7.649 7.631 7.628 7.382 7.369 7.363 7.350 4.209 4.196 4.184 4.172 4.141 4.129 3.711 3.709 3.686 3.669 2.436 2.430 2.249 2.243 1.999 1.983 1.965 1.949 1.856 1.849 1.844 1.559 1.527 1.509 1.497 1.479 1.284 1.254 1.216 1.062 1.038
17.82
2.00
1.00
11.97
8.00
0.98
1.75
0.65
0.69
2.40
1.51
5.76
4.11
PPM
10
8
6
4
2
0
OTBDPS
TBDPSO

**2**

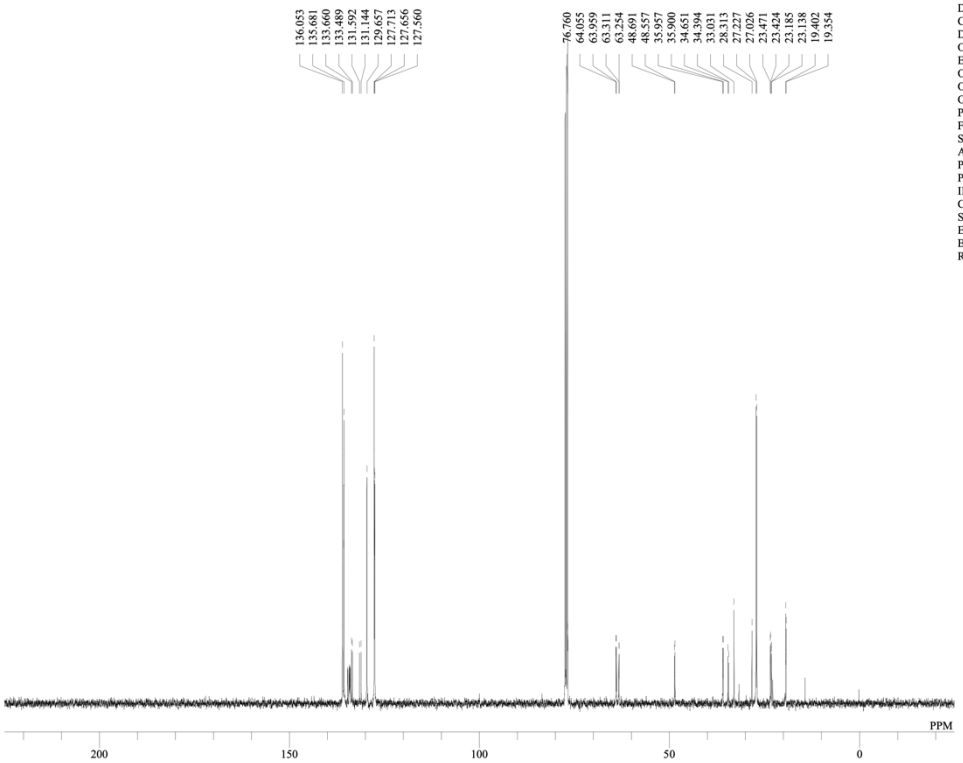

DFILE 7_13C_KN_exp69_step7_TM_Ca
COMNT single pulse decoupled gated NOE
DATIM 17-07-2024 21:54:52
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26224
FREQU 25125.63 Hz
SCANS 512
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.50 usec
IRNUC 1H
CTEMP 22.1 c
SLVNT CDCL3
EXREF 224.97 ppm
BF 1.00 Hz
RGAIN 50
136.102 136.026 135.702 134.748 134.701 134.243 133.957 129.668 127.695
85.234
76.304
63.313
47.653 39.587 34.410 32.975 29.878 28.324 27.209 27.047 26.933 19.451 19.394 14.580
PPM
200
150
100
50
0
OTBDPS
TBDPSO

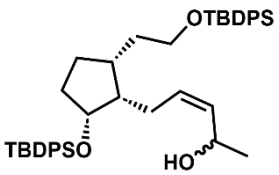
**2**


DFILE TO-ex11-st2_Proton-6-1.als
COMNT single_pulse
DATIM 15-11-2024 22:02:15
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13120
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 3.60 usec
IRNUC 1H
CTEMP 20.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.00 Hz
RGAIN 60
PPM

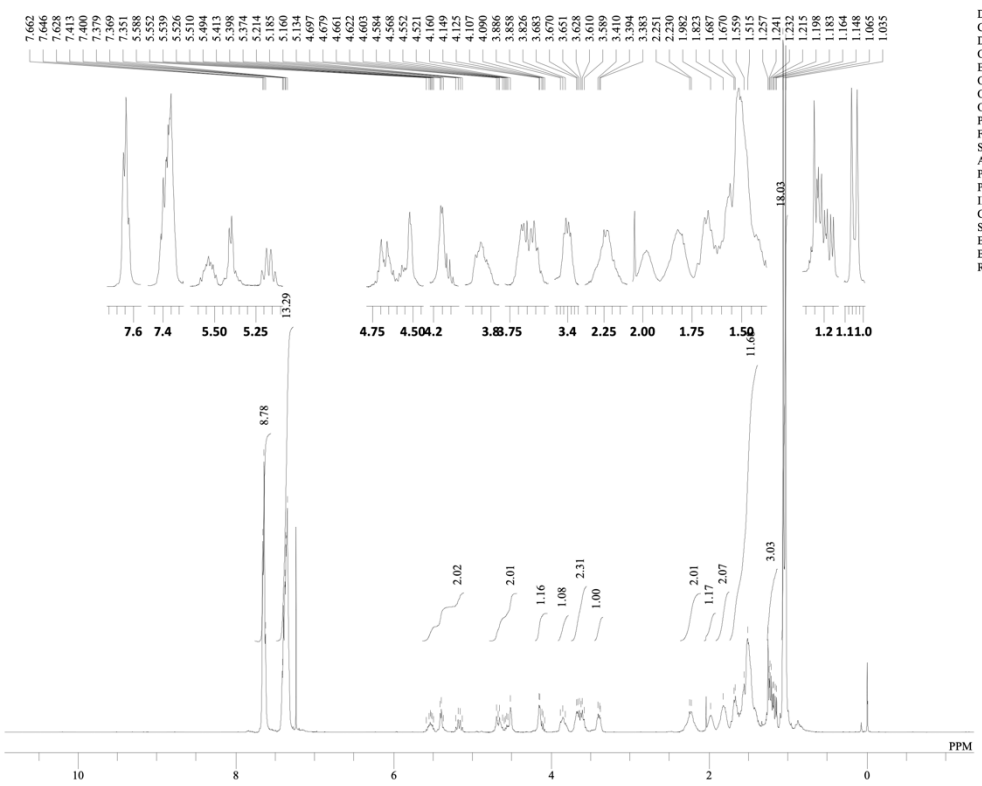

OTBDPS
TBDPSO
HO

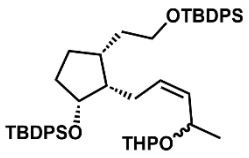
**3**


DFILE TO-ex11-st2_Carbon-2-1.als
COMNT single pulse decoupled gated NOE
DATIM 15-11-2024 21:30:40
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26224
FREQU 25125.63 Hz
SCANS 601
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.50 usec
IRNUC 1H
CTEMP 20.8 c
SLVNT CDCL3
EXREF 77.16 ppm
BF 1.00 Hz
RGAIN 50
PPM

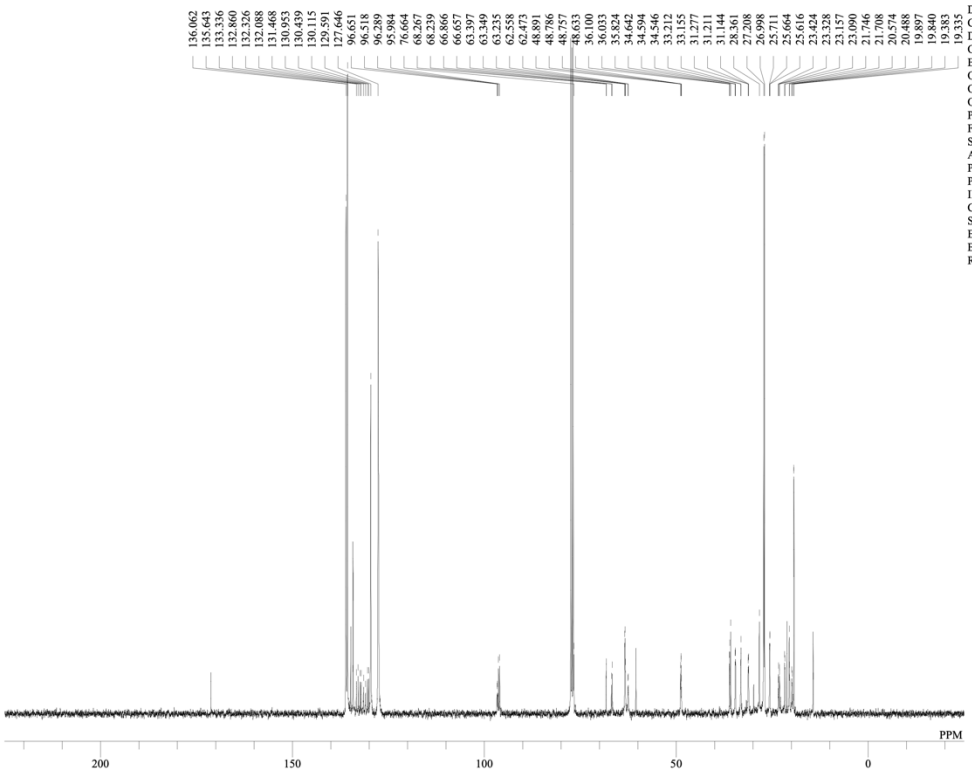

OTBDPS
TBDPSO
HO

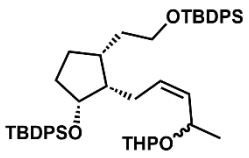
**3**


DFILE TO-ex12-st1_Proton-4-1.als
COMNT single_pulse
DATIM 22-11-2024 16:23:50
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13120
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 3.60 usec
IRNUC 1H
CTEMP 20.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.00 Hz
RGAIN 68
PPM

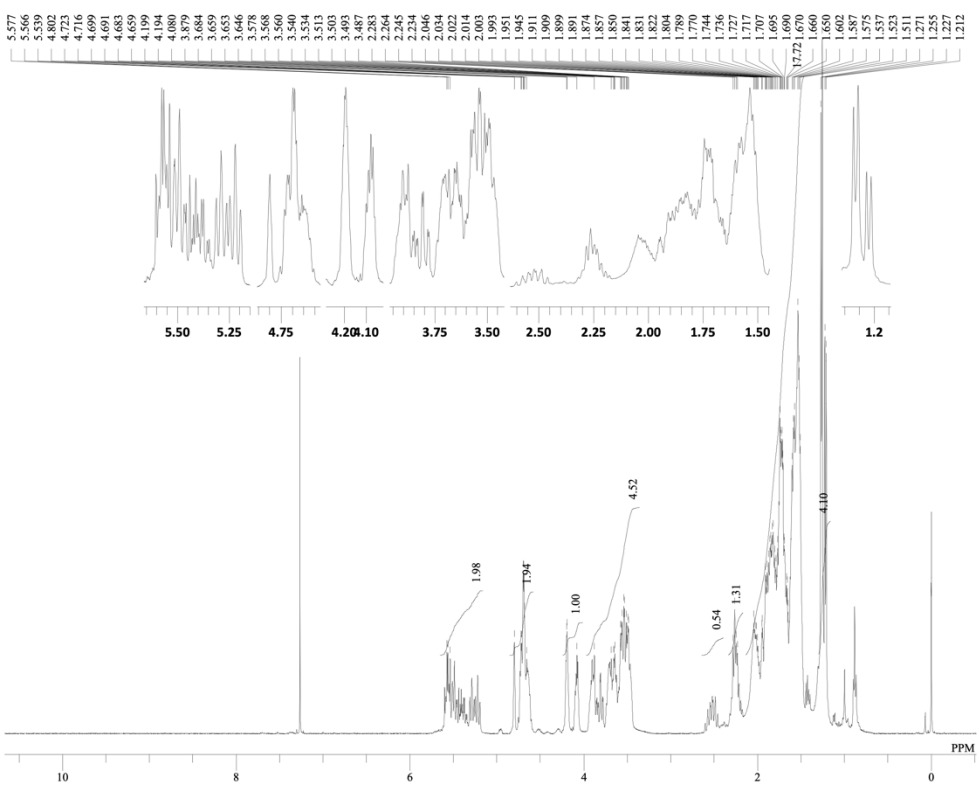

OTBDPS
TBDPSO
THPO

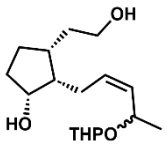
**4**


DFILE TO-ex12-st1_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 21-11-2024 21:26:26
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26224
FREQU 25125.63 Hz
SCANS 1024
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.50 usec
IRNUC 1H
CTEMP 20.7 c
SLVNT CDCL3
EXREF 77.16 ppm
BF 1.00 Hz
RGAIN 50
PPM

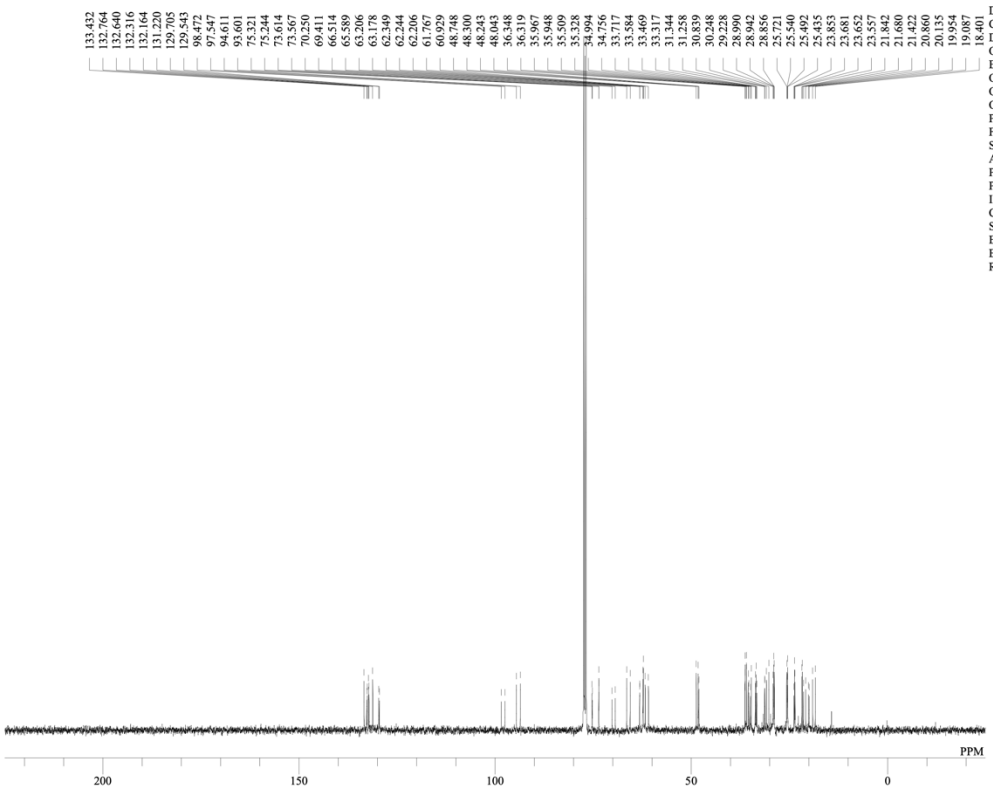

OTBDPS
TBDPSO
THPO

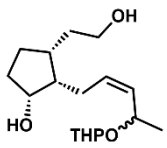
**4**


DFILE TO-ex12-st2_Proton-3-1.als
COMNT single_pulse
DATIM 27-11-2024 15:12:02
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13120
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 3.60 usec
IRNUC 1H
CTEMP 20.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.00 Hz
RGAIN 68
1.98
1.94
1.00
4.52
0.54
1.31
4.10
PPM

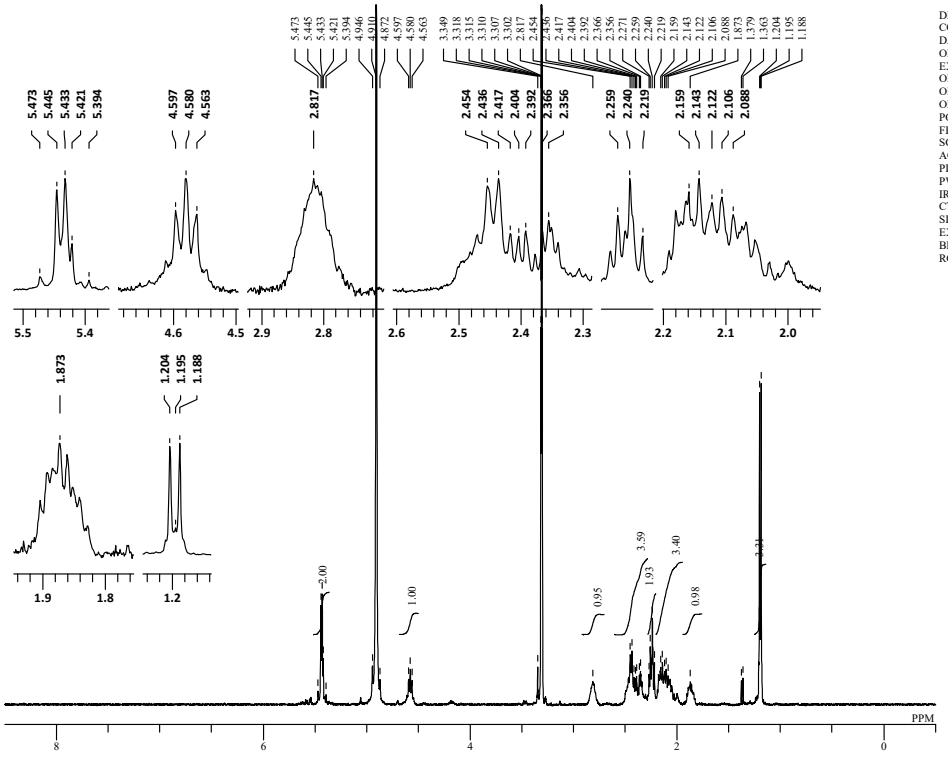

OH
HO
THPO

**5**

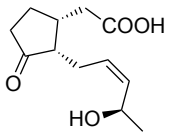

DFILE To-ex12-st2_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 27-11-2024 12:49:10
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26224
FREQU 25125.63 Hz
SCANS 1024
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.50 usec
IRNUC 1H
CTEMP 21.0 c
SLVNT CDCL3
EXREF 77.16 ppm
BF 1.00 Hz
RGAIN 50
PPM


OH
HO
THPO

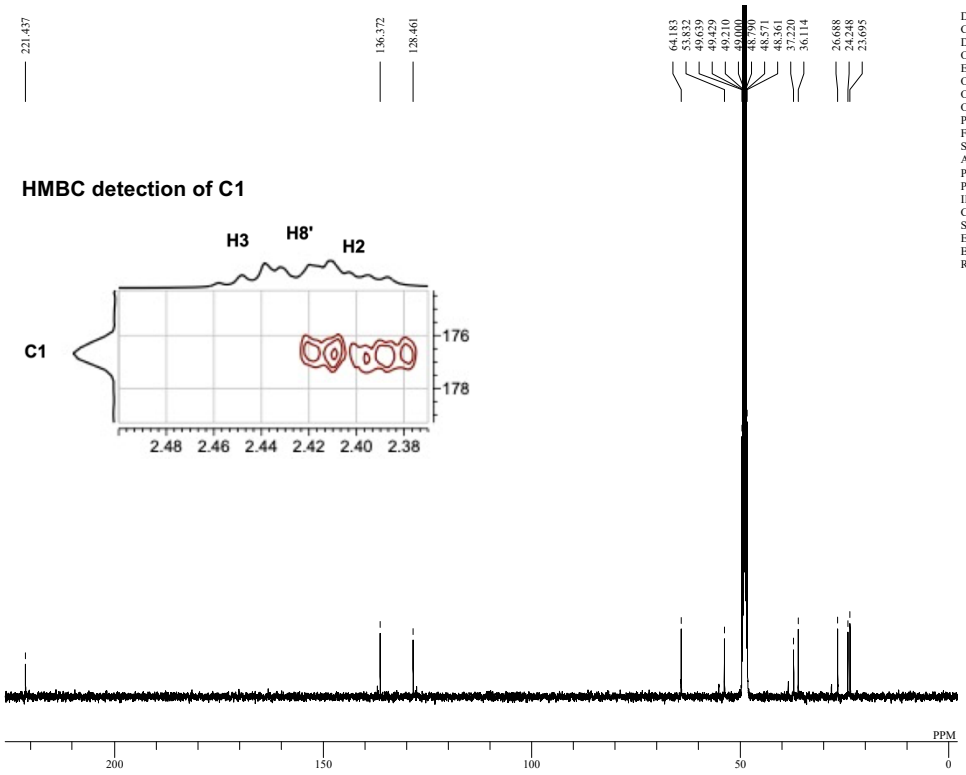
**5**



DFILE TK04198-11S-OH-JA_Proton-1-1
COMNT single_pulse
DATIM 10-03-2025 23:11:05
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16400
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 3.60 usec
IRNUC 1H
CTEMP 18.7 c
SLVNT CD3OD
EXREF 3.31 ppm
BF 1.00 Hz
RGAIN 86



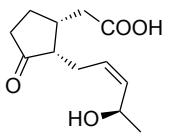
(*3R,7S,11R*)-11-OH-JA



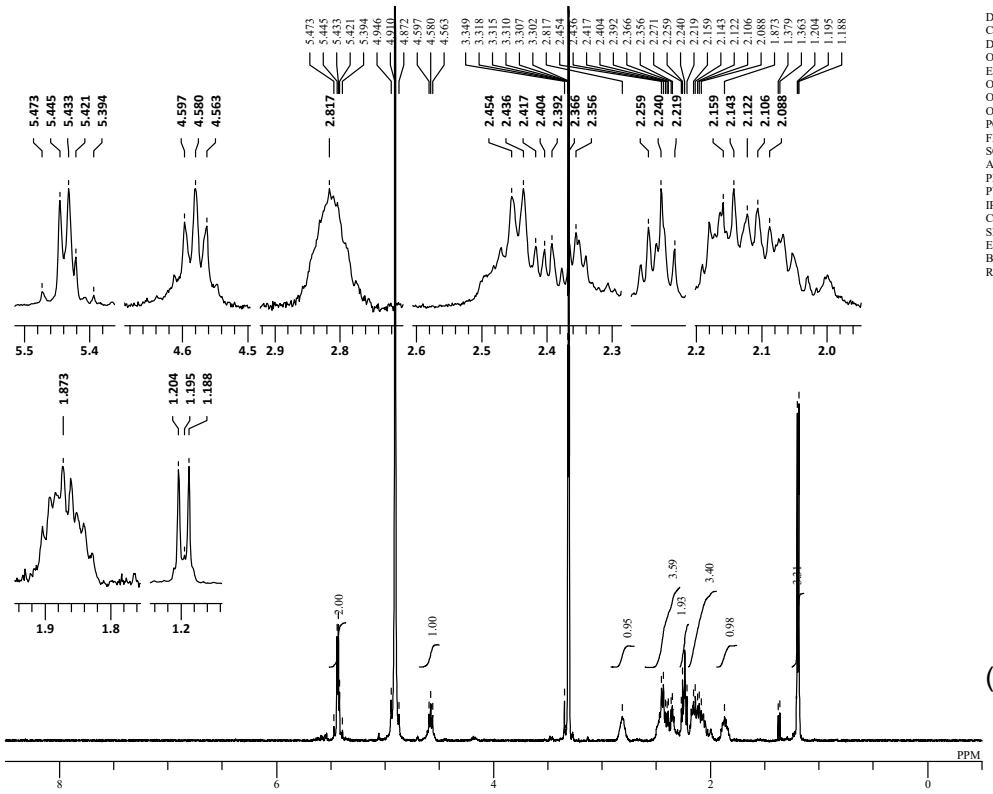
**HMBC detection of C1**



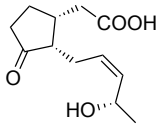
DFILE TK04178-LC1st-P1_Carbon-1-3.
COMNT single pulse decoupled gated NOE
DATIM 14-01-2025 23:10:59
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26224
FREQU 25125.63 Hz
SCANS 4000
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.50 usec
IRNUC 1H
CTEMP 35.0 c
SLVNT CD3OD
EXREF 49.00 ppm
BF 1.00 Hz
RGAIN 50



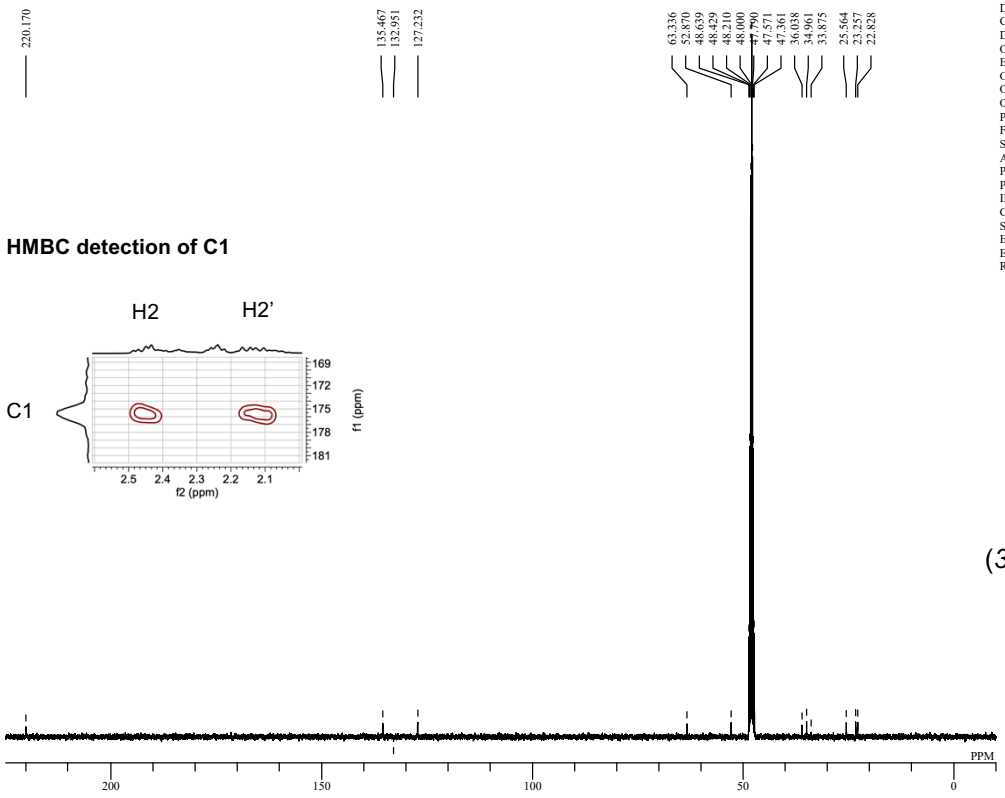
(*3R,7S,11R*)-11-OH-JA



DFILE TK04198-11S-OH-JA_Proton-1-1
COMNT single_pulse
DATIM 10-03-2025 23:11:05
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16400
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 3.60 usec
IRNUC 1H
CTEMP 18.7 c
SLVNT CD3OD
EXREF 3.31 ppm
BF 1.00 Hz
RGAIN 86



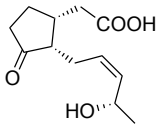
(*3R,7S,11S*)-11-OH-JA



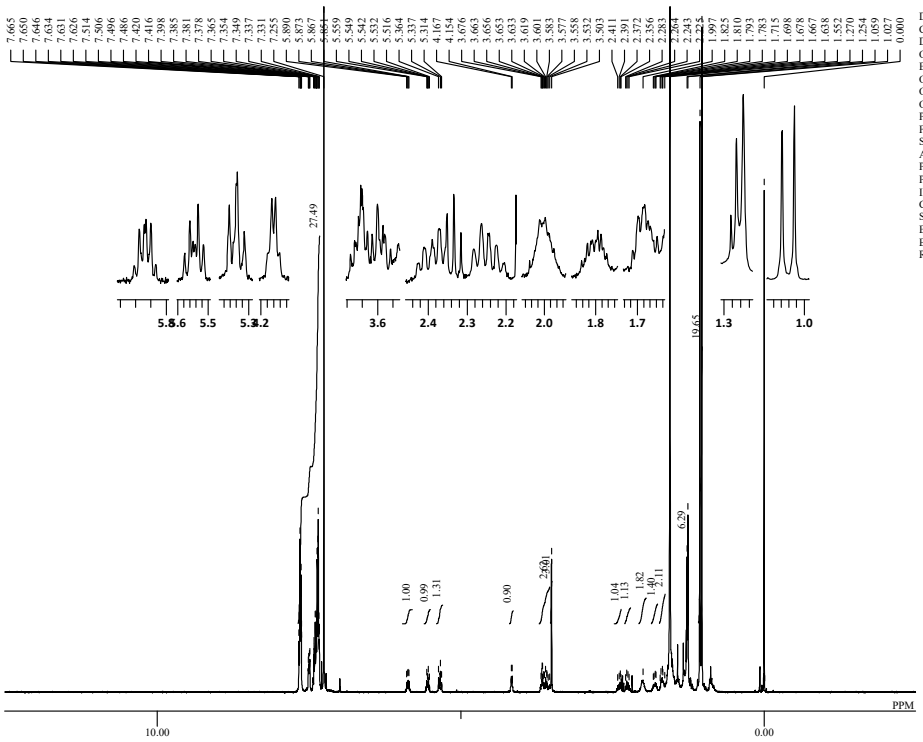
DFILE 3R7S11S-11OH-JA_Carbon-1-1.a
COMNT single pulse decoupled gated NOE
DATIM 14-07-2025 20:51:59
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26224
FREQU 25125.63 Hz
SCANS 481
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.50 usec
IRNUC 1H
CTEMP 21.5 c
SLVNT CD3OD
EXREF 48.00 ppm
BF 1.00 Hz
RGAIN 50

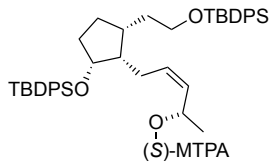
**HMBC detection of C1**



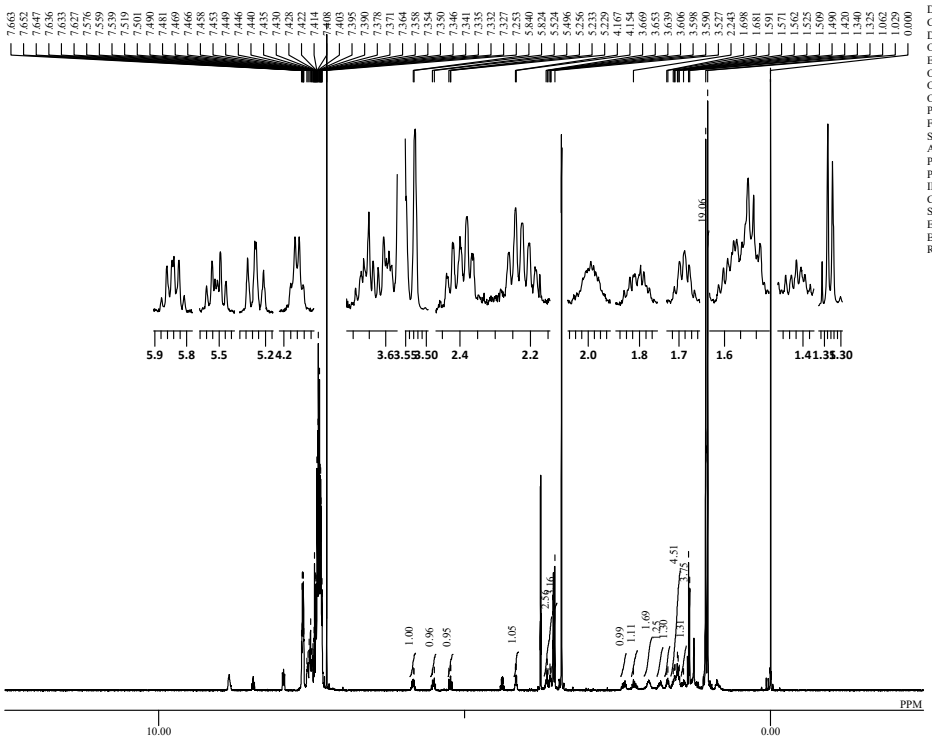



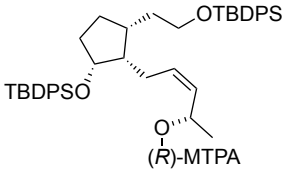
(*3R,7S,11S*)-11-OH-JA




**3**-(*S*)-MTPA




**3**-(*R*)-MTPA