SUPPORTING INFORMATION: PART A

Hydroxy-directed iridium-catalyzed enantioselective formal β-C(sp^2)–H allylic alkylation of α,β-unsaturated carbonyls

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Table of Contents

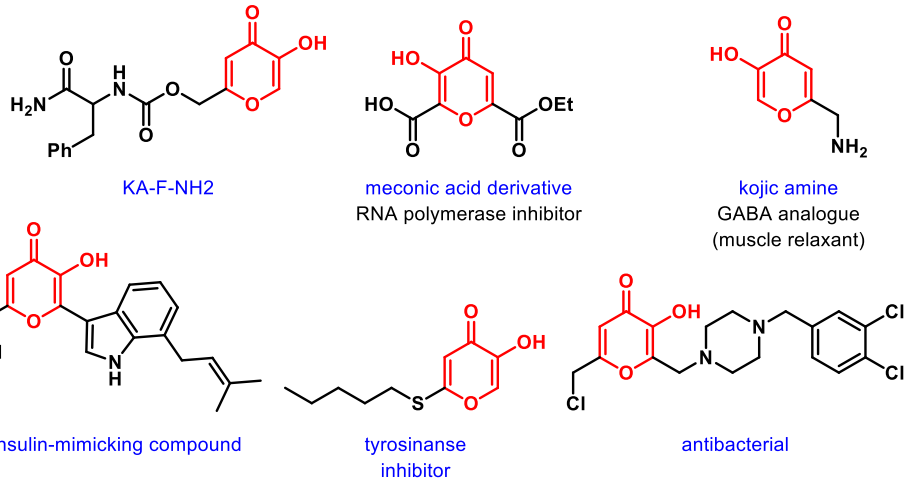
A. General information:

Infrared (FT-IR) spectra were recorded on a Bruker Alfa FT-IR, ν_{max} in cm^{-1} and the bands are characterized as broad (br), strong (s), medium (m), and weak (w). NMR spectra were recorded on Bruker Ultrashield spectrometer at 400 MHz (for ^{1}H-NMR) and 100 MHz (for ^{13}C-NMR). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard [$CDCl_3$: δ 7.26, CD_3OD: δ 3.31, $(CD_3)_2SO$: δ 2.50 for ^{1}H-NMR and $CDCl_3$: δ 77.16, CD_3OD: δ 49.00, $(CD_3)_2SO$: δ 39.52 for ^{13}C-NMR]. For ^{1}H-NMR, data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = double doublet, ddd = doublet of doublet of doublets, t = triplet, q = quartet, sep = septet, br = broad, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectrometry was performed on Waters XEVO G2-XS QTof instrument. Optical rotations were measured on a JASCO P-2000 polarimeter. Melting points were measured in open glass capillary using Büchi M-560 melting point apparatus. Enantiomeric ratios were determined by Shimadzu LC-20AD HPLC instrument and SPD-20A Diode Array Detector using stationary phase chiral columns (25 cm × 0.46 cm) in comparison with authentic racemic compounds.

Unless stated otherwise, all reactions were carried out with distilled and dried solvents under an atmosphere of nitrogen or argon in oven (120 °C) dried glassware with standard vacuum-line techniques. Organic solvents used for carrying out reactions were dried using standard methods. $[Ir(COD)Cl]_2$, (*S*)-BINOL and *rac*-BINOL were purchased from Sigma-Aldrich, iminostilbene was purchased from Combi-Blocks and used as received. All work up and purification were carried out with reagent grade solvents in air. Thin-layer chromatography was performed using Merck silica gel 60 F_{254} pre-coated plates (0.25 mm). Column chromatography was performed using silica gel (230-400 or 100-200 mesh). NMR yields were determined by using mesitylene as an internal standard. Unless otherwise noted, all reported yields of the Ir-catalyzed allylation reactions are isolated yields. Chiral ligands used in this work were prepared according to the literature procedure.[1]

[1] a) J. Y. Hamilton, D. Sarlah and E. M. Carreira, *Org. Synth*, 2015, **92**, 1-12. b) J. Y. Hamilton, D. Sarlah and E. M. Carreira, *Angew. Chem., Int. Ed.*, 2013, **52**, 7532-7535.

B. Representative bioactive natural products containing 3-hydroxypyranone:



C. Procedure for the synthesis of 3-hydroxypyranone derivatives:

Kojic acid (**1a**) and 2-hydroxynaphthaquinone (**1g**) were procured from Avra Synthesis Pvt. Ltd and Sigma-Aldrich respectively and used as received. The other 3-hydroxypyranone derivatives **1b-f**, **1h** were prepared according to the previously reported procedure and the spectral data are consistent with those described in the literature.[2]

General procedure A: **S1** was prepared according to the reported literature procedure.[3] Acyl chlorides were prepared according to the reported literature procedure.[4] 3-Hydroxypyranone derivatives **1i-j** and **1l** were prepared according to the following modified literature procedure:[5]

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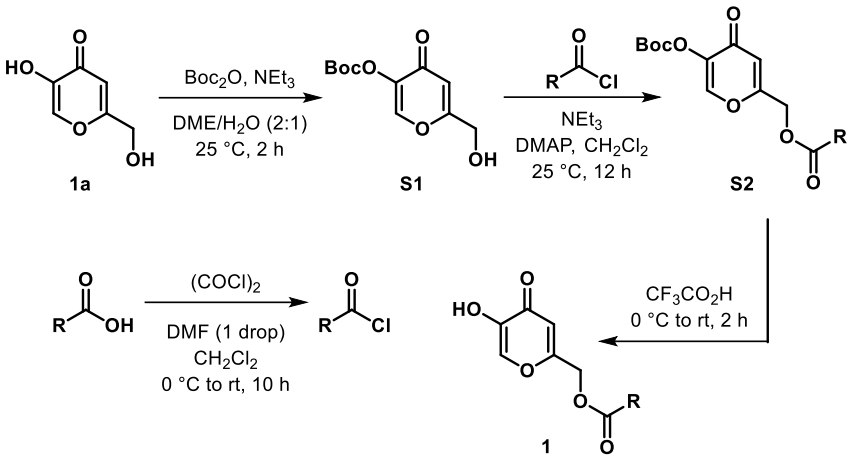
[2] (a) C. V. Credille, B. L. Dick, C. N. Morrison, R. W. Stokes, R. N. Adamek, N. C. Wu, I. A. Wilson and S. M. Cohen, *J. Med. Chem.*, 2018, **61**, 10206-10217. (b) S. M. Meier, M. Novak, W. Kandioller, M. A. Jakupec, V. B. Arion, N. Metzler-Nolte, B. K. Keppler and C. G. Hartinger, *Chem. Eur. J.*, 2013, **19**, 9297-9307. (c) H.-S. Rho, H.-S. Baek, S.-M. Ahn, M.-K. Kim, A. K. Ghimeray, D.-H. Cho and J.-S. Hwang, *Bull. Korean Chem. Soc.*, 2010, **31**, 2375-2378. (d) M. Spadafora, V. Y. Postupalenko, V. V. Shvadchak, A. S. Klymchenko, Y. Mély, A. Burger and R. Benhida, *Tetrahedron*, 2009, **65**, 7809-7816. (e) N. S. Poonia, A. k. Arora and A. V. Bajaj, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 569-570.

[3] H. Kaatz, K. Streffer, U. Wollenberger and M. G. Peter, *Naturforsch*. **1999**, *54c*, 70-74.

[4] S. K. Kariofillis, B. J. Shields, M. A. Tekle-Smith, M. J. Zacuto and A. G. Doyle, *J. Am. Chem. Soc.*, 2020, **142**, 7683-7689.

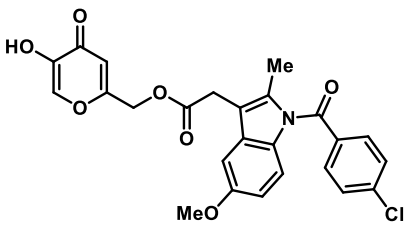
[5] S. L. Capim, G. M. Gonçalves, G. C. M. dos Santos, B. G. Marinho and M. L. A. A. Vasconcellos, *Bioorg. Med. Chem.*, 2013, **21**, 6003-6010.



In an oven-dried round-bottom flask, **S1** (1.0 equiv.) was taken along with acyl chloride (1.1 equiv.) and DMAP (0.2 equiv.) under a positive argon pressure. Then CH_2Cl_2 (9 mL/mmol of **S1**) was added, followed by dropwise addition of NEt_3 (4.0 equiv.) and the resulting mixture was stirred at 25 °C for 24 h under argon until TLC (30% EtOAc in petroleum ether) revealed complete consumption of **S1**. The reaction mixture was quenched with saturated NH_4Cl solution and diluted with CH_2Cl_2. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. Combined organic layer was washed with brine, dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain a yellow liquid. This residue was purified by silica-gel flash column chromatography (20-25% EtOAc in petroleum ether) to obtain **S2**.

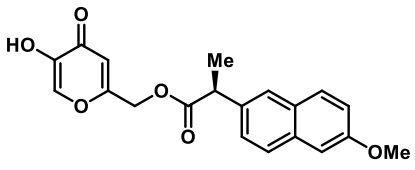
In an oven-dried round-bottom flask equipped with a magnetic stir bar, **S2** (1.0 equiv.) was taken in dry CH_2Cl_2 (6 mL/mmol of **S2**) under a positive argon pressure, followed by addition of trifluoroacetic acid (TFA) (6.0 equiv.) dropwise at 0 °C. The resulting mixture was gradually allowed to attain ambient temperature and stirred for 4-8 h under argon until TLC (30% EtOAc in petroleum ether) revealed complete consumption of **S2**. The reaction mixture was quenched with saturated $NaHCO_3$ solution and diluted with CH_2Cl_2. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. Combined organic layer was washed with brine, dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain a yellow liquid. This residue was purified by silica-gel flash column chromatography to obtain kojic acid derivative **1**.

Compound 1i: Prepared according to the general procedure A; Purified by silica-gel flash column chromatography (1-4% methanol in CH_2Cl_2); Yellow sticky liquid (205.0 mg, 0.425 mmol, 26% yield over 3 steps); **m.p.** 135-136 °C; **FT-IR (Thin film):** 3443 (br), 2956 (w), 2926 (m), 2840 (w), 1746 (s), 1681 (s), 1650 (s), 1593 (s), 1478 (m), 1457 (m), 1322 (m), 1215 (m), 1143 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.77 (s, 1H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 6.93 (d, *J* = 2.3 Hz, 1H), 6.85 (d, *J* = 9.0 Hz, 1H), 6.67 (dd, *J* = 9.0, 2.3 Hz, 1H), 6.39 (s, 1H), 4.94 (s, 2H), 3.81 (s, 3H), 3.76 (s, 2H), 2.39 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 173.9, 169.9, 168.4, 162.6, 156.2,

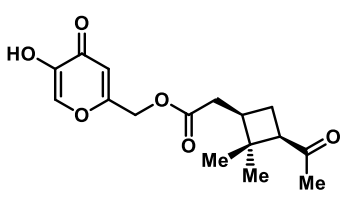


146.0, 139.5, 138.2, 136.3, 133.8, 131.3, 130.9, 130.4, 129.3, 115.1, 111.7, 111.6, 111.3, 101.4, 61.8, 55.8, 30.1, 13.4; **HRMS (ESI+):** *m/z* calcd. for $C_{25}H_{21}ClNO_7$ ($[M+H]^+$): 482.1007, Found: 482.1009.

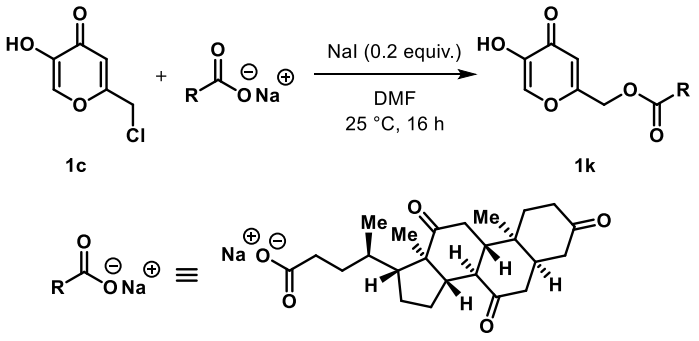
Compound 1j: Prepared according to general procedure A; Purified by silica-gel flash column chromatography (1-4% methanol in CH_2Cl_2); Yellow sticky liquid (200.0 mg, 0.570 mmol, 29% yield over 3 steps); **m.p.** 142-143 °C; **FT-IR (Thin film):** 3350 (br), 2936 (w), 1741 (s), 1620 (m), 1454 (m), 1371 (m), 1260 (m), 1167 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.73-7.69 (m, 3H), 7.66 (s, 1H), 7.39-7.37 (m, 1H), 7.17-7.12 (m, 2H), 6.37 (s, 1H), 4.95-4.86 (m, 2H), 3.97-3.92 (m, 1H), 3.92 (s, 3H), 1.62 (d, *J* = 7.1 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 173.9, 173.7, 162.9, 157.9, 145.9, 137.8, 134.7, 134.0, 129.4, 129.0, 127.5, 126.2, 126.0, 119.4, 111.1, 105.8, 61.7, 55.5, 45.3, 18.5; **HRMS (ESI+):** *m/z* calcd. for $C_{20}H_{19}O_6$ ($[M+H]^+$): 355.1182, Found: 355.1182.



Compound 1l: Prepared according to general procedure A; Purified by silica-gel flash column chromatography (35-42% EtOAc in petroleum ether); Yellow liquid (241.0 mg, 0.781 mmol, 24% yield over 3 steps); **m.p.** 82-83 °C; **FT-IR (Thin film):** 3424 (br), 2956 (m), 2923 (m), 2854 (m), 1743 (s), 1701 (s), 1651 (s), 1456 (m), 1211 (s), 1163 (s) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.82 (s, 1H), 6.45 (s, 1H), 4.86 (s, 2H), 2.93-2.82 (m, 1H), 2.42-2.29 (m, 3H), 2.03-1.99 (m, 1H), 1.99 (s, 3H), 1.90-1.86 (m, 1H), 1.26 (s, 3H), 0.81 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.4, 174.2, 171.7, 162.7, 146.1, 138.7, 111.7, 61.3, 54.1, 43.2, 37.8, 34.7, 30.2, 23.0, 17.3; **HRMS (ESI+):** *m/z* calcd. for $C_{16}H_{20}O_6Na$ ($[M+Na]^+$): 331.1158, Found: 331.1159.



General procedure B: kojic acid derivative **1k** was prepared according to the following procedure:



In an oven dried 25 mL round-bottom flask equipped with a magnetic stir bar, **1c** (200 mg, 1.245 mmol, 1.0 equiv.), sodium dehydrocholate (634 mg, 1.495 mmol, 1.2 equiv.) and NaI (37 mg, 0.249 mmol, 0.2 equiv.) were taken with 4 mL of dry DMF under a positive argon pressure. The resulting solution was then stirred at 25 °C for 16 h to obtain a grey-coloured heterogeneous solution. The resulting mixture was diluted with 10 mL of distilled water and 10 mL of diethyl ether. The organic layer was separated and washed with distilled water (10 mL × 3). The combined organic layer was

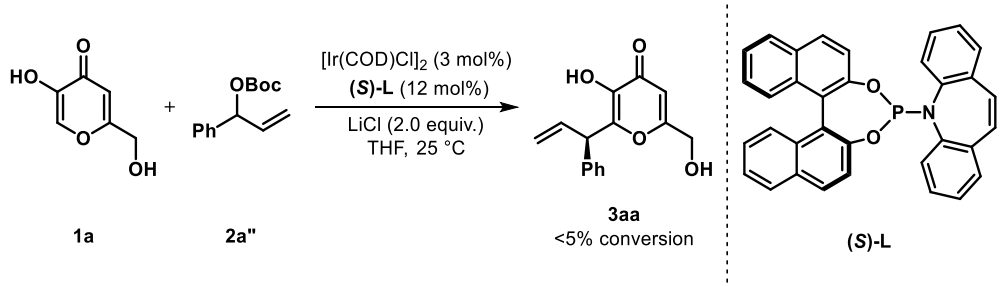
washed with brine (20 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain a yellow liquid. This residue was purified by silica-gel flash column chromatography (1-2% methanol in CH_2Cl_2) to obtain **1k** as a yellow liquid (420 mg, 0.797 mmol, 64% yield); **m.p.** 173-174 °C; **FT-IR (Thin film):** 3392 (br), 2947 (w), 2875 (w), 1703 (s), 1628 (m), 1372 (s), 1258 (m), 1166 (s) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.84 (s, 1H), 6.48 (s, 1H), 4.92 (s, 2H), 2.94-2.81 (m, 4H), 2.36-2.12 (m, 14H), 2.05-2.01 (m, 5H), 1.89-1.81 (m, 3H), 1.66-1.61 (m, 2H), 1.40 (s, 3H), 1.06 (s, 3H), 0.86 (d, *J* = 6.5 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 212.1, 209.3, 208.8, 177.8, 174.0, 173.1, 163.2, 146.0, 138.1, 111.3, 61.3, 57.0, 51.9, 49.1, 47.0, 45.7, 45.1, 42.9, 38.8, 36.6, 36.1, 35.6, 35.4, 31.2, 30.4, 27.8, 25.2, 22.0, 18.7, 12.0; **HRMS (ESI+):** *m/z* calcd. for $C_{30}H_{39}O_8$ ($[M+H]^+$): 527.2645, Found: 527.2642.

D. Procedure for the synthesis of allylic alcohols:

Allylic alcohols (**2a-r**) were prepared according to the previously reported procedure by the reaction of the corresponding aldehydes with vinyl magnesium bromide.[6]

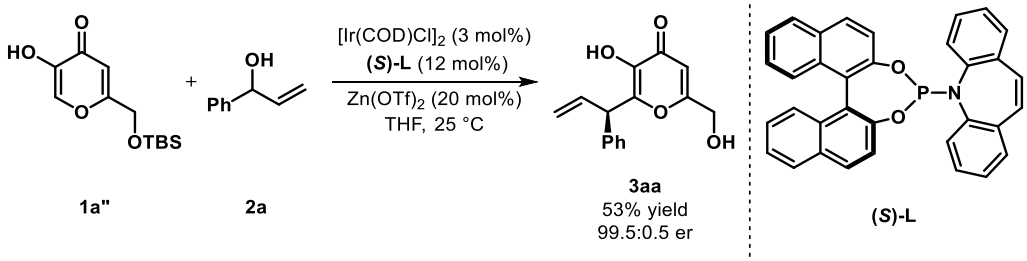
E. Preliminary studies on asymmetric allylic alkylation of kojic acid:

- Reaction with branched allylic carbonate:



1a 2a" 3aa <5% conversion (*S*)-L

- Reaction with branched allylic alcohol:

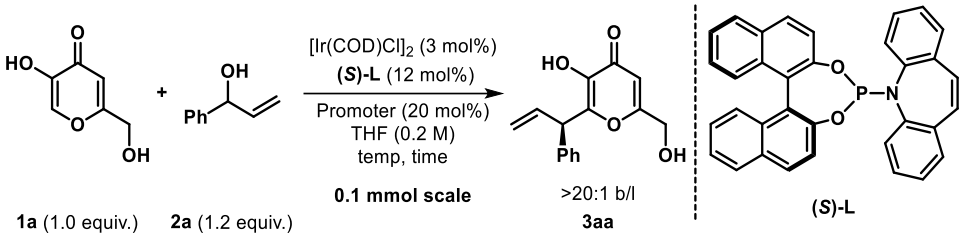


1a" 2a 3aa 53% yield 99.5:0.5 er (*S*)-L

[6] a) C. Defieber, M. A. Ariger, P. Moriel and E. M. Carreira, *Angew. Chem., Int. Ed.*, 2007, **46**, 3139-3143. b) M. Lafrance, M. Roggen and E. M. Carreira, *Angew. Chem. Int. Ed.*, 2012, **51**, 3470-3473. (c) M. Roggen and E. M. Carreira, *Angew. Chem., Int. Ed.*, 2012, **51**, 8652-8655.

F. Promoter and reaction conditions optimization for asymmetric allylic alkylation of kojic acid:

Table S1. Promoter screening and reaction conditions optimization

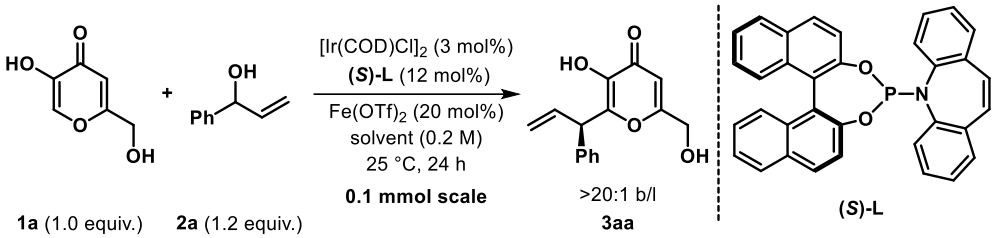


1a (1.0 equiv.) **2a** (1.2 equiv.) **3aa**

entry	promoter	temp	time (h)	yield (%)[a]	er[b]
1	-	25	24	<5	n.d.
2	$Zn(OTf)_2$	25	48	52 (50)	99.8:0.2
3	$Zn(OTf)_2$	50	24	54	99.9:0.1
4[c]	$Zn(OTf)_2$	25	36	73	99.9:0.1
5	$Sc(OTf)_3$	25	36	62	99.9:0.1
6	$Fe(OTf)_2$	25	24	81	99.9:0.1
7	$La(OTf)_3$	25	36	39	99.9:0.1
8[c]	$Fe(OTf)_2$	25	24	95 (85)	99.9:0.1
9[d]	$Fe(OTf)_2$	25	22	(91)	99.9:0.1

[a]Yields were determined by ^{1}H-NMR spectroscopy with mesitylene as the internal standard. Isolated yields are given in the parentheses. [b]Enantiomeric ratio (er) was determined by HPLC analysis on a chiral stationary phase. [c]Reaction with 2.0 equiv. of **2a**. [d]Reaction with 1.5 equiv. of **2a** on a 0.2 mmol scale. n.d. = not determined.

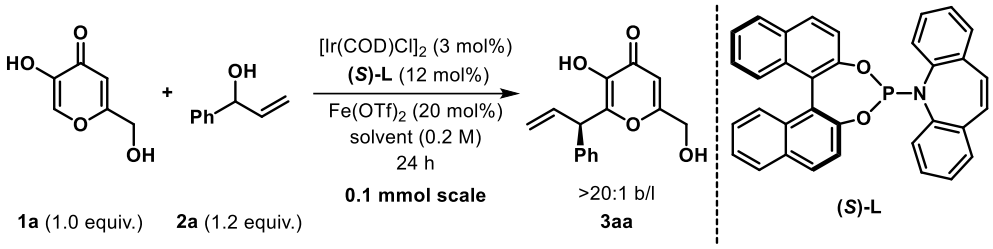
Table S2. Optimization of solvent



entry	solvent	yield (%)[a]	er[b]
1	Toluene	54 (50)	>99.5:0.5
2	1,4-dioxane	64 (62)	>99.5:0.5
3	$CHCl_3$	<10	n.d.
4	2-Me-THF	(72)	>99.9:0.1
5	THF	81	99.9:0.1
6	Acetone	75	>99.9:0.1
7	DCE	<10	n.d.

[a]Yields were determined by ^{1}H-NMR spectroscopy with mesitylene as the internal standard. Isolated yields are given in the parentheses. [b]Enantiomeric ratio (er) was determined by HPLC analysis on a chiral stationary phase. n.d. = not determined.

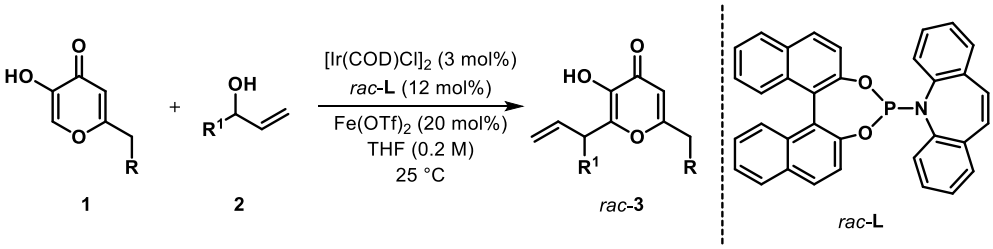
Table S3. Optimization of other reaction parameters



entry	deviation from the standard reaction conditions	yield (%)[a]	er[b]
1	$Fe(OTf)_2$ (10 mol%)	84	99.9:0.1
2	$Fe(OTf)_2$ (50 mol%)	87	>99.9:0.1
3	THF (0.1M)	81	>99.9:0.1
4	12 h instead of 24 h	87	>99.9:0.1

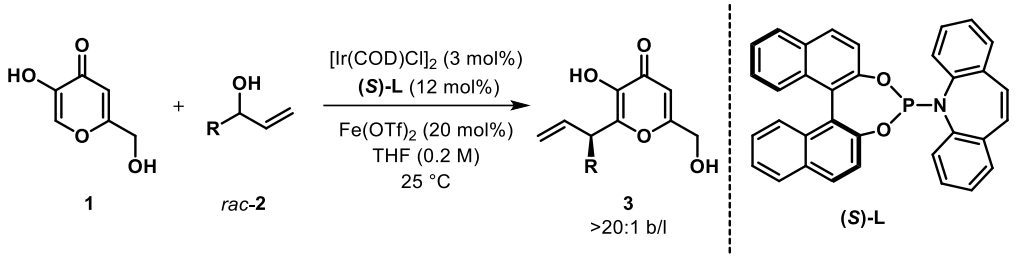
[a]Yields were determined by ^{1}H-NMR spectroscopy with mesitylene as the internal standard. [b]Enantiomeric ratio (er) was determined by HPLC analysis on a chiral stationary phase.

G. General procedure for the preparation of racemic products (*rac*-3):



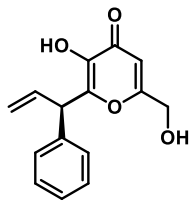
In a glass-vial $[Ir(COD)Cl]_2$ (0.003 mmol, 3 mol%) and ligand *rac*-**L** (0.012 mmol, 12 mol%) were taken with 0.1 mL of dry THF, and the resulting solution was stirred at ambient temperature for 15 min. To this solution, *rac*-**2** (0.150 mmol, 1.5 equiv.) in 0.2 mL of dry THF was added followed by addition of **1** (0.100 mmol, 1.0 equiv.) and $Fe(OTf)_2$ (0.02 mmol, 0.2 equiv.) in 0.2 mL of dry THF. The resulting suspension was stirred at 25 °C for 24-36 h. The crude reaction mixture was purified by preparative TLC (Merck silica-gel 60 F_{254} pre-coated plates of 0.25 mm thickness) to obtain the racemic β-allylic kojic acid (*rac*-**3**) samples for HPLC analysis.

H. General procedure for the Ir-catalyzed asymmetric allylic alkylation of kojic acid:

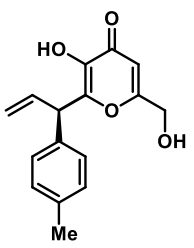


In an oven and vacuum-dried reaction tube equipped with a magnetic stir bar, $[Ir(COD)Cl]_2$ (4 mg, 0.006 mmol, 3 mol%) and (*S*)-**L** (12.2 mg, 0.024 mmol, 12 mol%) were taken with 0.3 mL of dry THF under a positive argon pressure. The solution was then stirred vigorously at 25 °C for 15 min to obtain a deep red solution. A solution of allylic alcohol *rac*-**2** (0.3 mmol, 1.5 equiv.) in 0.7 mL of dry THF was then added to this red solution and stirred at 25 °C for 5 min. Subsequently, kojic acid **1** (0.2 mmol, 1.0 equiv.) was added followed by $Fe(OTf)_2$ (14.2 mg, 0.04 mmol, 0.2 equiv.). The reaction tube was purged with argon, closed with a glass stopper, and stirred at 25 °C until TLC (5% methanol in CH_2Cl_2) revealed complete consumption of **1**. The reaction mixture was then diluted with 2 mL of CH_2Cl_2 and 2 mL of 1(N) HCl. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (4 mL × 3). Combined organic layer was washed with brine (10 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain a yellow liquid. This residue was purified by silica-gel flash column chromatography (1-3% methanol in CH_2Cl_2) to obtain β-allylic kojic acid **3**.

Compound 3aa: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1-2% methanol in CH_2Cl_2); yellow sticky liquid (47.0 mg, 0.182 mmol, 91% yield); **FT-IR (Thin film):** 3306 (w), 2923 (w), 2853 (w), 1651 (s), 1623 (s), 1580 (s), 1455 (s), 1204 (s), 1092 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.34-7.28 (m, 4H), 7.26-7.24 (m, 1H), 6.52 (s, 1H), 6.26 (ddd, *J* = 17.3, 10.1, 7.5 Hz, 1H), 5.30 (d, *J* = 10.1 Hz, 1H), 5.22 (d, *J* = 17.1 Hz, 1H), 5.08 (d, *J* = 7.3 Hz, 1H), 4.49-4.41 (m, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.5, 167.8, 150.6, 141.5, 139.0, 135.2, 128.8, 128.2, 127.4, 118.4, 108.6, 61.1, 47.8; **HRMS (ESI+):** *m/z* calcd. for $C_{15}H_{15}O_4$ ($[M+H]^+$): 259.0970, Found: 259.0968; **Optical rotation:** $[\alpha]_D^{22}$ –104.6 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 99.9:0.1 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (85:15 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 277 nm, τ_{minor} = 7.8 min, τ_{major} = 9.1 min. See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3aa** was assigned in analogy with **8**.

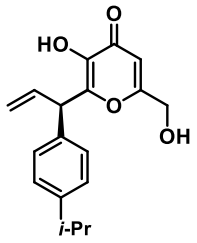


Compound 3ab: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1-3% methanol in CH_2Cl_2); Yellow liquid (51.0 mg, 0.186 mmol, 93% yield); **FT-IR (Thin film):** 3332 (br), 2958 (w), 2921 (w), 2850 (w), 1655 (s), 1622 (s), 1577 (s), 1511 (s), 1456 (m), 1204 (s), 1091 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.18 (d, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 2H), 6.54 (s, 1H), 6.28-6.20 (m, 1H), 5.27 (d, *J* = 10.0 Hz, 1H), 5.19 (d, *J* = 17.1 Hz, 1H), 5.06 (d, *J* = 7.1 Hz,

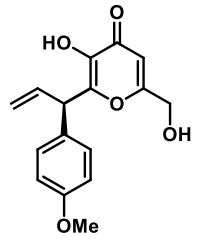


1H), 4.48-4.40 (m, 2H), 2.31 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.5, 167.9, 151.0, 141.4, 137.1, 136.0, 135.4, 129.5, 128.0, 118.2, 108.6, 61.0, 47.4, 21.1; **HRMS (ESI+):** *m/z* calcd. for $C_{16}H_{17}O_4$ ($[M+H]^+$): 273.1127, Found: 273.1130; **Optical rotation:** $[\alpha]_D^{22}$ –93.2 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with >99.9:0.1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AS-H column (90:10 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 285 nm, τ_{major} = 19.9 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ab** was assigned in analogy with **8**.

Compound 3ac: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1-3% methanol in CH_2Cl_2); Yellow liquid (56.0 mg, 0.186 mmol, 93% yield); **FT-IR (Thin film):** 3300 (br), 2961 (m), 2925 (w), 2868 (w), 1656 (s), 1623 (s), 1578 (s), 1511 (s), 1457 (m), 1202 (s), 1092 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.22 (d, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.56 (s, 1H), 6.29-6.21 (m, 1H), 5.26 (d, *J* = 10.1 Hz, 1H), 5.20 (d, *J* = 17.0 Hz, 1H), 5.07 (d, *J* = 7.4 Hz, 1H), 4.49-4.41 (m, 2H), 2.87 (sep, *J* = 6.8 Hz, 1H), 1.22 (d, *J* = 6.8 Hz, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.6, 168.0, 151.1, 148.0, 141.4, 136.3, 135.4, 128.1, 126.9, 118.2, 108.6, 61.0, 47.5, 33.8, 24.0; **HRMS (ESI+):** *m/z* calcd. for $C_{18}H_{21}O_4$ ($[M+H]^+$): 301.1440, Found: 301.1438; **Optical rotation:** $[\alpha]_D^{21}$ –96.6 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with >99.9:0.1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IH column (90:10 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 277 nm, τ_{major} = 13.8 min. See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ac** was assigned in analogy with **8**.



Compound 3ad: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1-2% methanol in CH_2Cl_2); yellow liquid (41.0 mg, 0.142 mmol, 71% yield); **FT-IR (Thin film):** 3288 (br), 2958 (s), 2919 (s), 2844 (m), 1654 (s), 1617 (s), 1579 (s), 1510 (s), 1458 (s), 1250 (s), 1032 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.20 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.52 (s, 1H), 6.22 (ddd, *J* = 17.3, 10.1, 7.4, Hz, 1H), 5.26 (d, *J* = 10.1 Hz, 1H), 5.17 (d, *J* = 17.1 Hz, 1H), 5.03 (d, *J* = 7.2 Hz, 1H), 4.48-4.39 (m, 2H), 3.77 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.4, 167.7, 158.9, 150.8, 141.3, 135.5, 131.1, 129.2, 118.1, 114.2, 108.6, 61.1, 55.4, 47.0; **HRMS (ESI+):** *m/z* calcd. for $C_{16}H_{16}O_5Na$ ($[M+Na]^+$): 311.0895, Found: 311.0899; **Optical rotation:** $[\alpha]_D^{22}$ –83.8 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 99.5:0.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IG column (85:15 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 279 nm, τ_{minor} = 22.5 min, τ_{major} = 27.2 min,). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ad** was assigned in analogy with **8**.



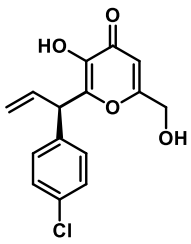
Compound 3ae: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1-2% methanol in CH_2Cl_2); Yellow sticky liquid (40.0 mg, 0.122 mmol, 61% yield); **FT-IR (Thin film):** 3363 (br), 2962 (m), 2927 (w), 2870 (w), 1735 (m), 1657 (s), 1623 (s), 1582 (m), 1457 (m), 1327 (s), 1124 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.57 (d, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 2H), 6.54 (s, 1H), 6.23 (ddd, *J* = 17.3, 9.8, 7.8, Hz, 1H), 5.34 (d, *J* = 10.1 Hz, 1H), 5.24 (d, *J* = 17.0 Hz, 1H), 5.13 (d, *J* = 7.3 Hz, 1H), 4.50-4.42 (m, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.3, 167.6, 149.5, 143.0, 141.7, 134.3, 129.7 (q, *J* = 32.5 Hz), 128.6, 125.8 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.0 Hz), 119.3, 108.8, 61.1, 47.6; **HRMS (ESI+):** *m/z* calcd. for $C_{16}H_{14}F_3O_4$ ($[M+H]^+$): 327.0844, Found: 327.0842; **Optical rotation:** $[\alpha]_D^{22}$ –80.9 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with >99.9:0.1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (95:5 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 275 nm, τ_{major} = 38.2 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ae** was assigned in analogy with **8**.

Compound 3af: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (2-4% methanol in CH_2Cl_2); white sticky liquid (23.0 mg, 0.082 mmol, 41% yield); **FT-IR (Thin film):** 3426 (br), 3297 (br), 2922 (w), 2852 (w), 1657 (m),1626 (s), 1582 (s), 1455 (m), 1204 (m), 1091 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 6.53 (s, 1H), 6.22 (ddd, *J* = 17.4, 10.1, 7.6 Hz, 1H), 5.37 (d, *J* = 10.6 Hz, 1H), 5.25 (d, *J* = 16.7 Hz, 1H), 5.11 (d, *J* = 7.6 Hz, 1H), 4.51-4.42 (m, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.1, 167.3, 148.6, 144.5, 141.8, 133.8, 132.7, 129.0, 119.8, 118.7, 111.4, 108.9, 61.2, 47.9; **HRMS (ESI+):** *m/z* calcd. for $C_{16}H_{14}NO_4$ ($[M+H]^+$): 284.0923, Found: 284.0921; **Optical rotation:** $[\alpha]_D^{21}$ –68.1 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with >99.9:0.1 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Amylose-2 column (75:25 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 254 nm, τ_{major} = 16.1 min. See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3af** was assigned in analogy with **8**.

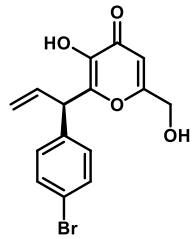
Compound 3ag: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1-2% methanol in CH_2Cl_2); pale yellow sticky liquid (48.0 mg, 0.174 mmol, 87% yield); **FT-IR (Thin film):** 3321 (br), 2921 (w), 2847 (w), 1656 (m), 1624 (s), 1579 (s), 1457 (m), 1220 (s), 1090 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.19-7.16 (m, 2H), 6.94-6.90 (m, 2H), 6.46 (s, 1H), 6.18-6.09 (m, 1H), 5.22 (d, *J* = 10.1 Hz, 1H), 5.12 (d, *J* = 17.3 Hz, 1H), 4.99 (d, *J* = 7.2 Hz, 1H), 4.42-4.33 (m, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.5, 167.8, 162.1 (d, *J* = 254.8 Hz), 150.4, 141.5, 135.0, 134.6 (d, *J* = 3.1 Hz), 129.75 (d, *J* = 8.0 Hz), 118.6, 115.7 (d, *J* = 21.5 Hz), 108.7, 61.1, 47.0; **HRMS (ESI+):** *m/z* calcd. for $C_{15}H_{14}O_4F$ ($[M+H]^+$): 277.0876, Found: 277.0874; **Optical rotation:** $[\alpha]_D^{21}$ –89.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with >99.9:0.1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H

column (85:15 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 283 nm, τ_{major} = 12.1 min. See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ag** was assigned in analogy with **8**.

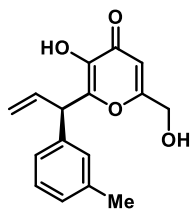
Compound 3ah: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1-2% methanol in CH_2Cl_2); pale yellow sticky liquid (51.0 mg, 0.174 mmol, 87% yield); **FT-IR (Thin film):** 3307 (br), 2923 (w), 2852 (w), 1624 (s), 1583 (s), 1454 (s), 1202 (s), 1091 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.46 (s, 1H), 6.17-6.08 (m, 1H), 5.23 (d, *J* = 8.1 Hz, 1H), 5.12 (d, *J* = 17.1 Hz, 1H), 4.98 (d, *J* = 7.4 Hz, 1H), 4.41-4.32 (m, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.5, 167.8, 150.2, 141.6, 137.5, 134.7, 133.3, 129.6, 129.0, 118.9, 108.8, 61.0, 47.2; **HRMS (ESI+):** *m/z* calcd. for $C_{15}H_{14}O_4Cl$ ($[M+H]^+$): 293.0581, Found: 293.0583; **Optical rotation:** $[\alpha]_D^{20}$ –109.3 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with >99.9:0.1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (85:15 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 282 nm, τ_{major} = 13.0 min. See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ah** was assigned in analogy with **8**.



Compound 3ai: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1-3% methanol in CH_2Cl_2); Yellow sticky liquid (59.0 mg, 0.174 mmol, 87% yield); **FT-IR (Thin film):** 3300 (br), 2959 (m), 2924 (w), 2852 (w), 1656 (s), 1623 (s), 1580 (m), 1456 (m), 1204 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.43 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.53 (s, 1H), 6.20 (ddd, *J* = 17.3, 10.0, 7.5, Hz, 1H), 5.30 (d, *J* = 10.1 Hz, 1H), 5.20 (d, *J* = 17.1 Hz, 1H), 5.03 (d, *J* = 7.3 Hz, 1H), 4.48-4.40 (m, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.4, 167.8, 150.0, 141.6, 138.0, 134.6, 131.9, 129.9, 121.4, 118.9, 108.8, 61.1, 47.2; **HRMS (ESI+):** *m/z* calcd. for $C_{15}H_{14}BrO_4$ ($[M+H]^+$): 337.0075, Found: 337.0073; **Optical rotation:** $[\alpha]_D^{22}$ –84.4 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 98.5:1.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (85:15 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 222 nm, τ_{minor} = 11.8 min τ_{major} = 13.7 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ai** was assigned in analogy with **8**.

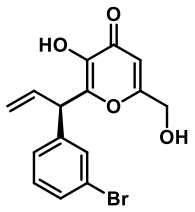


Compound 3aj: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1-2% methanol in CH_2Cl_2); pale yellow sticky liquid (50.0 mg, 0.183 mmol, 92% yield); **FT-IR (Thin film):** 3334 (br), 2920 (s), 2847 (w), 1655 (m), 1623 (s), 1579 (s), 1458 (m), 1223 (m), 1091 (w) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.22-7.18 (m, 1H), 7.10-7.05 (m, 3H), 6.53 (s, 1H), 6.25 (ddd, *J* = 17.5, 10.1, 7.5 Hz, 1H), 5.28 (d, *J* = 10.1 Hz, 1H), 5.21 (d, *J* = 17.2 Hz, 1H), 5.05 (d, *J* = 7.5 Hz, 1H), 4.49-4.40 (m, 2H), 2.32 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.6, 167.7, 150.8, 141.5, 139.0, 138.5, 135.3, 128.9, 128.7, 128.2, 125.1, 118.3, 108.6, 61.1, 47.8, 21.6; **HRMS (ESI+):**

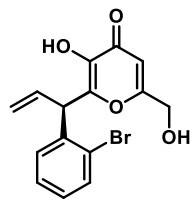


m/z calcd. for $C_{16}H_{17}O_4$ ($[M+H]^+$): 273.1127, Found: 273.1128; **Optical rotation:** $[\alpha]_D^{21}$ –86.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with >99.9:0.1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IH column (85:15 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 215 nm, τ_{major} = 10.9 min. See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3aj** was assigned in analogy with **8**.

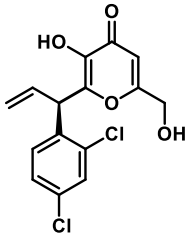
Compound 3ak: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1-2% methanol in CH_2Cl_2); pale yellow sticky liquid (54.0 mg, 0.16 mmol, 80% yield); **FT-IR (Thin film):** 3419 (br), 2921 (w), 2849 (w), 1655 (m), 1623 (s), 1581 (s), 1458 (m), 1223 (m), 1093 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.36 (s, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.15-7.08 (m, 2H), 6.48 (s, 1H), 6.13 (ddd, *J* = 17.5, 10.2, 7.5 Hz, 1H), 5.24 (d, *J* = 9.8 Hz, 1H), 5.14 (d, *J* = 17.6 Hz, 1H), 4.98 (d, *J* = 6.8 Hz, 1H), 4.43-4.34 (m, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.5, 167.9, 150.0, 141.3, 134.4, 131.2, 130.6, 130.4, 128.2, 126.9, 122.9, 119.1, 108.8, 61.0, 47.4; **HRMS (ESI+):** *m/z* calcd. for $C_{15}H_{14}O_4Br$ ($[M+H]^+$): 337.0075, Found: 337.0078; **Optical rotation:** $[\alpha]_D^{22}$ –77.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with >99.9:0.1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90:10 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 276 nm, τ_{major} = 17.6 min. See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ak** was assigned in analogy with **8**.



Compound 3al: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1-3% methanol in CH_2Cl_2); Light yellow liquid (37.0 mg, 0.110 mmol, 55% yield); **m.p.** 99-100 °C; **FT-IR (Thin film):** 3420 (br), 2922 (w), 1649 (s), 1619 (s), 1458 (m), 1219 (m), cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.57 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.39 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.32-7.29 (m, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.51 (s, 1H), 6.17 (ddd, *J* = 16.8, 10.5, 6.6 Hz, 1H), 5.47 (d, *J* = 6.2 Hz, 1H), 5.33 (d, *J* = 10.3 Hz, 1H), 5.12 (d, *J* = 17.1 Hz, 1H), 4.47-4.39 (m, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.5, 168.1, 149.0, 142.2, 138.0, 134.4, 133.2, 130.3, 129.0, 127.7, 124.6, 118.3, 108.6, 60.9, 47.4; **HRMS (ESI+):** *m/z* calcd. for $C_{15}H_{14}BrO_4$ ($[M+H]^+$): 337.0075, Found: 337.0075; **Optical rotation:** $[\alpha]_D^{22}$ –22.0 (*c* 4.0, $CHCl_3$) for an enantiomerically enriched sample with >99.9:0.1 er. The enantiomeric ratio of compound was determined by HPLC analysis using Daicel Chiralpak AD-H column (85:15 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 280 nm, τ_{minor} = 10.8 min, τ_{major} = 13.0 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3al** was assigned in analogy with **8**.



Compound 3am: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1-3% methanol in CH_2Cl_2); Yellow sticky liquid (33.0 mg, 0.100 mmol, 50% yield) [*Note*: compound **3am** is unstable in silica]; **FT-IR (Thin film):** 3414 (br), 2923 (w), 2855 (w), 1625 (s), 1588 (m), 1468 (m), 1204 (m), cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.43-7.38 (m, 1H), 7.33-7.31 (m, 1H), 7.23-7.21 (m, 1H), 6.54 (s, 1H), 6.12 (ddd, *J* = 16.9, 10.4, 6.7 Hz, 1H), 5.43 (d, *J* = 6.4 Hz, 1H),

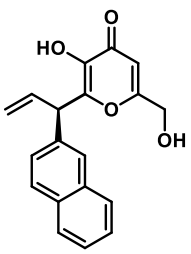


5.31 (d, *J* = 10.1 Hz, 1H), 5.10 (d, *J* = 17.1 Hz, 1H), 4.42-4.32 (m, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.3, 167.8, 148.3, 142.2, 135.0, 134.8, 134.0, 133.8, 130.9, 129.7, 127.4, 118.8, 108.7, 61.0, 44.4; **HRMS (ESI+):** *m/z* calcd. for $C_{15}H_{13}Cl_2O_4$ ($[M+H]^+$): 327.0191, Found: 327.0190; **Optical rotation:** $[\alpha]_D^{22}$ –59.3 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with >99.9:0.1 er. The enantiomeric ratio was determined by HPLC analysis using AD-H column (85:15 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 288 nm, τ_{major} = 12.4 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3am** was assigned in analogy with **8**.

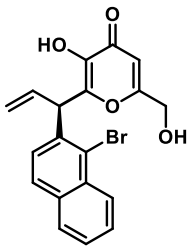
Compound 3an: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1-2% methanol in CH_2Cl_2); pale yellow sticky liquid (28.0 mg, 0.08 mmol, 40% yield) [*Note*: compound **3an** is unstable in silica]; **FT-IR (Thin film):** 3424 (br), 2923 (s), 2851 (m), 1653 (m), 1589 (s), 1461 (m), 1217 (m), 1081 (w) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.82 (s, 1H), 6.54 (s, 1H), 6.20-6.11 (m, 1H), 5.46-5.38 (m, 2H), 5.23 (d, *J* = 8.1 Hz, 1H), 4.41-4.29 (m, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.1, 173.6, 164.7, 163.8, 146.42, 146.40, 146.30, 146.27, 146.2, 145.9, 143.9, 143.85, 143.81, 143.78, 143.7, 142.8, 142.7, 142.0, 140.22, 140.16, 139.2, 139.1, 138.96, 137.8, 136.75, 136.69, 136.6, 136.4, 134.8, 133.8, 120.3, 119.7, 119.0, 110.9, 74.7, 66.6; **HRMS (ESI+):** *m/z* calcd. for $C_{15}H_9O_4F_5Na$ ($[M+Na]^+$): 371.0319, Found: 371.0321; **Optical rotation:** $[\alpha]_D^{21}$ –59.5 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with >99.9:0.1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90:10 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 241 nm, τ_{major} = 22.7 min. See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3an** was assigned in analogy with **8**.

Compound 3ao: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1-3% methanol in CH_2Cl_2); colourless sticky liquid (59.0 mg, 0.192 mmol, 96% yield); **FT-IR (Thin film):** 3407 (br), 2924 (m), 2853 (m), 1654 (s), 1622 (s), 1578 (s), 1455 (m), 1200 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.14 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.53-7.43 (m, 4H), 6.45 (s, 1H), 6.35 (ddd, *J* = 16.8, 10.2, 6.2 Hz, 1H), 5.85 (d, *J* = 6.0 Hz, 1H), 5.36 (d, *J* = 10.2 Hz, 1H), 5.16 (d, *J* = 17.2 Hz, 1H), 4.36 (d, *J* = 15.4 Hz, 1H), 4.27 (d, *J* = 15.4 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.2, 167.5, 149.5, 141.6, 135.4, 134.8, 134.0, 131.6, 129.0, 128.3, 126.8, 126.4, 126.0, 125.4, 123.2, 118.0, 108.5, 61.1, 43.3; **HRMS (ESI+):** *m/z* calcd. for $C_{19}H_{17}O_4$ ($[M+H]^+$): 309.1127, Found: 309.1127; **Optical rotation:** $[\alpha]_D^{22}$ –113.4 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with >99.9:0.1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IH column (85:15 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 281 nm, τ_{major} = 15.0 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ao** was assigned in analogy with **8**.

Compound 3ap: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1-2% methanol in CH_2Cl_2); colourless sticky liquid (58.0 mg, 0.188 mmol, 94% yield); **FT-IR (Thin film):** 3423 (br), 2922 (w), 2852 (w), 1656 (s), 1624 (s), 1586 (s), 1458 (w), 1259 (w), 1092 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.78-7.73 (m, 4H), 7.45-7.40 (m, 3H), 6.53 (s, 1H), 6.35 (ddd, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.34 (d, *J* = 10.1 Hz, 1H), 5.29-5.24 (m, 2H), 4.45-4.35 (m, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.5, 167.8, 150.7, 141.7, 136.5, 135.1, 133.5, 132.6, 128.5, 127.9, 127.7, 126.9, 126.4, 126.3, 126.1, 118.7, 108.7, 61.0, 47.9; **HRMS (ESI+):** *m/z* calcd. for $C_{19}H_{17}O_4$ ($[M+H]^+$): 309.1127, Found: 309.1125; **Optical rotation:** $[\alpha]_D^{22}$ –146.3 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with >99.9:0.1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IH column (85:15 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 221 nm, τ_{major} = 17.8 min. See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ap** was assigned in analogy with **8**.



Compound 3aq: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1-3% methanol in CH_2Cl_2); Yellow liquid (44.0 mg, 0.114 mmol, 57% yield) [*Note*: compound **3aq** is unstable in silica]; **m.p.** 114-115 °C; **FT-IR (Thin film):** 3394 (br), 2924 (m), 2853 (m), 1650 (s), 1622 (s), 1577 (s), 1457 (m), 1202 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.32 (d, *J* = 8.7 Hz, 1H), 7.80-7.76 (m, 2H), 7.60-7.56 (m, 1H), 7.52-7.49 (m, 2H), 6.52 (s, 1H), 6.24 (ddd, *J* = 16.7, 10.6, 6.6 Hz, 1H), 5.86 (d, *J* = 5.9 Hz, 1H), 5.34 (d, *J* = 10.1 Hz, 1H), 5.13 (d, *J* = 17.0 Hz, 1H), 4.45-4.35 (m, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.3, 167.7, 148.8, 142.3, 136.1, 134.6, 133.8, 132.6, 128.2, 128.0, 127.9, 127.8, 126.9, 126.8, 124.9, 118.4, 108.6, 61.1, 48.6; **HRMS (ESI+):** *m/z* calcd. for $C_{19}H_{16}BrO_4$ ($[M+H]^+$): 387.0232, Found: 387.0230; **Optical rotation:** $[\alpha]_D^{22}$ +9.5 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with >99.9:0.1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IC column (90:10 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 280 nm, τ_{minor} = 30.1 min, τ_{major} = 47.5 min,). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3aq** was assigned in analogy with **8**.



Compound 3ar: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1-3% methanol in CH_2Cl_2); Yellow sticky liquid (46.0 mg, 0.152 mmol, 76% yield); **FT-IR (Thin film):** 3332 (br), 2959 (m), 2924 (m), 2848 (m), 1656 (s), 1623 (s), 1580 (m), 1456 (m), 1251 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 6.79 (s, 1H), 6.73 (brs, 2H), 6.53 (s, 1H), 6.19 (ddd, *J* = 17.2, 9.9, 7.5 Hz, 1H), 5.91 (s, 2H), 5.25 (d, *J* = 10.0 Hz, 1H), 5.17 (d, *J* = 17.1 Hz, 1H), 4.99 (d, *J* = 7.2 Hz, 1H), 4.45 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.5, 167.9, 150.7, 148.0, 146.8, 141.3, 135.3, 132.8, 121.4, 118.3, 108.6, 108.5, 101.2, 61.0, 47.4; **HRMS (ESI+):** *m/z* calcd. for $C_{16}H_{15}O_6$ ($[M+H]^+$): 303.0869, Found: 303.0865; **Optical rotation:** $[\alpha]_D^{22}$ –82.1 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 99.5:0.5 er. The enantiomeric ratio of compound was

determined by HPLC analysis using Daicel Chiralpak AD-H column (85:15 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, I = 282 nm, τ_{minor} = 19.6 min, τ_{major} = 27.4 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ar** was assigned in analogy with **8**.

Compound 3as: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1-2% methanol in CH_2Cl_2); Yellow sticky liquid (35.0 mg, 0.132 mmol, 66% yield); **FT-IR (Thin film):** 3288 (w), 2925 (w), 2853 (w), 1660 (s), 1628 (s), 1586 (s), 1417 (m), 1121 (m), 1018 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.22 (d, *J* = 5.0 Hz, 1H), 6.97-6.95 (m, 1H), 6.93-6.92 (m, 1H), 6.53 (s, 1H), 6.22 (ddd, *J* = 17.0, 10.3, 7.5 Hz, 1H), 5.33-5.31 (m, 2H), 5.27 (d, *J* = 7.5 Hz, 1H), 4.49 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.3, 167.2, 148.9, 141.5, 141.1, 134.9, 127.1, 125.8, 125.1, 118.5, 108.7, 61.3, 43.3; **HRMS (ESI+):** *m/z* calcd. For $C_{13}H_{13}O_4S$ ($[M+H]^+$): 265.0535, Found: 265.0534; **Optical rotation:** $[\alpha]_D^{22}$ –52.9 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (85:15 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, I = 276 nm, τ_{minor} = 12.0 min, τ_{major} = 13.5 min. See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3as** was assigned in analogy with **8**.

Compound 3ba: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1% methanol in CH_2Cl_2); Yellow sticky liquid (46.0 mg, 0.190 mmol, 95% yield); **FT-IR (Thin film):** 3458 (br), 2924 (m), 2853 (m), 1654 (s), 1621 (s), 1585 (s), 1452 (m), 1344 (w), 1207 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.33-7.32 (m, 4H), 7.29-7.25 (m, 1H), 6.28 (ddd, *J* = 17.3, 10.1, 7.6 Hz, 1H), 6.21 (s, 1H), 5.30 (d, *J* = 10.2 Hz, 1H), 5.23 (d, *J* = 17.1 Hz, 1H), 5.11 (d, *J* = 7.5 Hz, 1H), 2.25 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.3, 165.4, 150.3, 141.2, 139.4, 135.5, 128.7, 128.2, 127.2, 118.1, 110.7, 47.6, 20.1; **HRMS (ESI+):** *m/z* calcd. for $C_{15}H_{15}O_3$ ($[M+H]^+$): 243.1021, Found: 243.1025; **Optical rotation:** $[\alpha]_D^{22}$ –92.0 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 99.9:0.1 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (90:10 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 276 nm, τ_{minor} = 10.4 min, τ_{major} = 14.5 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ba** was assigned in analogy with **8**.

Compound 3ca: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1% methanol in CH_2Cl_2); Yellow sticky liquid (42.0 mg, 0.152 mmol, 76% yield); **FT-IR (Thin film):** 3404 (br), 2923 (m), 2852 (m), 1632 (s), 1588 (s), 1449 (m), 1361 (w), 1208 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.35-7.33 (m, 4H), 7.29-7.26 (m, 1H), 6.48 (s, 1H), 6.28 (ddd, *J* = 17.3, 10.1, 7.5 Hz, 1H), 5.32 (d, *J* = 10.2 Hz, 1H), 5.24 (d, *J* = 17.1 Hz, 1H), 5.13 (d, *J* = 7.3 Hz, 1H), 4.30 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 173.9, 161.8, 151.0, 141.8, 139.0, 135.1, 128.9, 128.3, 127.5, 118.5, 111.4, 47.8, 41.3; **HRMS (ESI+):** *m/z* calcd. for $C_{15}H_{14}ClO_3$ ($[M+H]^+$): 277.0631, Found: 277.0630; **Optical rotation:**

$[\alpha]_D^{22}$ –60.3 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with >99.5:0.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IC column (95:5 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 305 nm, τ_{minor} = 27.7 min, τ_{major} = 32.2 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ca** was assigned in analogy with **8**.

Compound 3da: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1% methanol in CH_2Cl_2); Yellow sticky liquid (55.0 mg, 0.194 mmol, 97% yield); **FT-IR (Thin film):** 3247 (br), 3060 (m), 2923 (m), 2852 (m), 2364 (m), 2105 (s), 1646 (s), 1628 (s), 1588 (s), 1448 (m), 1201 (m), 990 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.36-7.33 (m, 4H), 7.29-7.26 (m, 1H), 6.41 (s, 2H), 6.29 (ddd, *J* = 17.3, 9.9, 7.2 Hz, 1H), 5.33 (d, *J* = 10.1 Hz, 1H), 5.24 (d, *J* = 17.0 Hz, 1H), 5.16 (d, *J* = 7.4 Hz, 1H), 4.17-4.08 (m, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 173.9, 161.7, 151.1, 141.9, 138.9, 134.9, 128.9, 128.2, 127.4, 118.5, 111.0, 51.3, 47.7; **HRMS (ESI+):** *m/z* calcd. for $C_{15}H_{14}N_3O_3$ ($[M+H]^+$): 284.1035, Found: 284.1036; **Optical rotation:** $[\alpha]_D^{22}$ –80.6 (*c* 2.5, $CHCl_3$) for an enantiomerically enriched sample with >99.9:0.1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IH column (85:15 *n*-Hexane/*i*-PrOH, flow rate = 1 mL/min, 20 °C, I = 282 nm, τ_{major} = 24.5 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3da** was assigned in analogy with **8**.

Compound 3ea: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1% methanol in CH_2Cl_2); Yellow sticky liquid (55.0 mg, 0.156 mmol, 78% yield); **FT-IR (Thin film):** 3420 (br), 2923 (w), 1621 (s), 1582 (s), 1441 (m), 1207 (m), 987 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.29-7.23 (m, 10H), 6.20-6.10 (m, 2H), 5.24 (d, *J* = 10.0 Hz, 1H), 5.17 (d, *J* = 17.0 Hz, 1H), 5.04 (d, *J* = 6.9 Hz, 1H), 3.79 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.0, 164.1, 150.8, 141.5, 139.1, 135.2, 133.5, 131.6, 129.3, 128.7, 128.2, 127.9, 127.2, 118.2, 111.0, 47.6, 37.2; **HRMS (ESI+):** *m/z* calcd. for $C_{21}H_{19}O_3S$ ($[M+H]^+$): 351.1055, Found: 351.1054; **Optical rotation:** $[\alpha]_D^{22}$ +66.0 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with >99.9:0.1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IH column (90:10 *n*-Hexane/*i*-PrOH, flow rate = 0.5 mL/min, 20 °C, I = 272 nm, τ_{major} = 48.4 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ea** was assigned in analogy with **8**.

Compound 3fa: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (5-6% EtOAc in petroleum ether); Yellow sticky liquid (40.0 mg, 0.142 mmol, 71% yield); **m.p.** 96-97 °C; **FT-IR (Thin film):** 3276 (br), 2920 (m), 2850 (m), 1605 (s), 1420 (m), 1119 (m), 1033 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.22 (d, *J* = 8.0 Hz, 1H), 7.65-7.61 (m, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.42-7.40 (m, 2H), 7.37-7.32 (m, 3H), 7.29-7.25 (m, 1H), 6.55 (br, 1H), 6.41 (ddd, *J* = 17.3, 9.6, 7.1 Hz, 1H), 5.35 (d, *J* = 10.2 Hz, 1H), 5.30 (d, *J* = 17.3 Hz, 1H), 5.28-5.19 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 173.1, 155.8, 151.0, 139.3, 138.0, 135.4, 133.3, 128.8, 128.3, 127.4, 125.6, 124.6, 121.4,

118.5, 118.4, 48.4; **HRMS (ESI+):** *m/z* calcd. for $C_{18}H_{15}O_3$ ($[M+H]^+$): 279.1021, Found: 279.1024; **Optical rotation:** $[\alpha]_D^{22}$ –24.7 (*c* 1.5, $CHCl_3$) for an enantiomerically enriched sample with >99.5:0.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IG column (95:5 *n*-Hexane/*i*-PrOH, flow rate = 1 mL/min, 20 °C, I = 233 nm, τ_{minor} = 26.0 min, τ_{major} = 33.0 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3fa** was assigned in analogy with **8**.

Compound 3ga: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (1-2% methanol in CH_2Cl_2); bright yellow sticky liquid (60.0 mg, 0.2 mmol, >99% yield); **FT-IR (Thin film):** 3362 (br), 2922 (w), 2851 (w), 1661 (s), 1593 (m), 1456 (w), 1255 (s), 1076 (w) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.12 (d, *J* = 7.2 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.77-7.73 (m, 1H), 7.69-7.65 (m, 1H), 7.55 (br s, 1H), 7.41-7.39 (m, 2H), 7.31-7.28 (m, 2H), 7.22-7.18 (m, 1H), 6.67-6.59 (m, 1H), 5.29-5.23 (m, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 183.9, 181.9, 152.9, 141.6, 137.1, 135.3, 133.1, 132.9, 129.3, 128.4, 128.0, 127.2, 126.6, 126.2, 124.9, 117.3, 45.0; **HRMS (ESI+):** *m/z* calcd. for $C_{19}H_{14}O_3Na$($[M+Na]^+$): 313.0841, Found: 313.0841; **Optical rotation:** $[\alpha]_D^{22}$ –93.4 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with >99.9:0.1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IG column (90:10 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 232 nm, τ_{major} = 14.9 min. See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ga** was assigned in analogy with **8**.

Compound 3ha: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (5% EtOAc in petroleum ether); Yellow sticky liquid (55.0 mg, 0.174 mmol, 87% yield); **FT-IR (Thin film):** 3271 (br), 2924 (m), 2852 (m), 1728 (s), 1631 (s), 1593 (s), 1451 (m), 1265 (s), 1110 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.03 (d, *J* = 7.4 Hz, 2H), 7.64-7.60 (m, 1H), 7.49-7.45 (m, 2H), 7.33-7.28 (m, 3H), 7.26-7.22 (m, 2H), 6.53 (s, 1H), 6.25 (ddd, *J* = 17.2, 9.9, 7.2 Hz, 1H), 5.28 (d, *J* = 10.1 Hz, 1H), 5.22 (d, *J* = 17.1 Hz, 1H), 5.19-5.11 (m, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 173.9, 165.6, 161.8, 150.8, 141.8, 138.9, 135.1, 133.8, 129.9, 128.9, 128.8, 128.7, 128.2, 127.4, 118.4, 110.6, 61.8, 47.6; **HRMS (ESI+):** *m/z* calcd. for $C_{22}H_{19}O_5$ ($[M+H]^+$): 363.1232, Found: 363.1230; **Optical rotation:** $[\alpha]_D^{22}$ –42.1 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with >99.9:0.1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IH column (85:15 *n*-Hexane/*i*-PrOH, flow rate = 1 mL/min, 20 °C, I = 298 nm, τ_{major} = 27.5 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ha** was assigned in analogy with **8**.

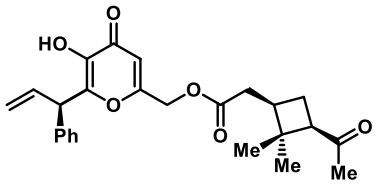
Compound 3ia: Reaction was performed on a 0.2 mmol scale; purified by silica-gel flash column chromatography (30% EtOAc in petroleum ether); Yellow sticky liquid (75.0 mg, 0.126 mmol, 63% yield); **FT-IR (Thin film):** 3266 (br), 3079 (w), 2928 (m), 1746 (s), 1680 (s), 1636 (s), 1459 (s), 1453 (m), 1318 (m), 1222 (m), 1148 (m), 1078 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.66 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.34-7.25 (m, 5H), 6.92 (d, *J* = 2.4 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.68 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.35 (s, 1H), 6.20 (ddd, *J* = 17.3, 9.9, 7.2 Hz, 1H), 5.27 (d, *J* = 10.1 Hz, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 5.09 (d, *J* = 7.5 Hz, 1H), 4.92 (s, 2H), 3.81 (s, 3H), 3.72 (s, 2H), 2.37 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 173.8, 169.8, 168.4, 161.6, 156.2, 150.8, 141.8, 139.5, 138.9, 136.3, 135.0, 133.8, 131.3, 130.9, 130.4, 129.3, 128.8, 128.2, 127.5, 118.4, 115.2, 111.8, 111.6, 110.6, 101.3, 61.8, 55.8, 47.7, 30.1, 13.4; **HRMS (ESI+):** *m/z* calcd. for $C_{34}H_{29}ClNO_7$ ($[M+H]^+$): 598.1633, Found: 598.1635; **Optical rotation:** $[\alpha]_D^{22}$ –31.4 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with >99.9:0.1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IG column (40:60 *n*-Hexane/EtOH, flow rate = 1.0 mL/min, 20 °C, I = 268 nm, τ_{minor} = 37.6 min τ_{major} = 49.9 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ia** was assigned in analogy with **8**.

Compound 3ja: Reaction was performed on a 0.2 mmol scale; **3ja** was formed with >20:1 dr as determined by ^{1}H-NMR of the crude product; purified by silica-gel flash column chromatography (25-30% EtOAc in petroleum ether); Yellow sticky liquid (86.0 mg, 0.182 mmol, 91% yield); **FT-IR (Thin film):** 3432 (br), 2978 (w), 2931 (w), 2851 (w), 1742 (m), 1632 (s), 1604 (s), 1452 (m), 1220 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.73-7.70 (m, 2H), 7.67 (s, 1H), 7.40-7.38 (m, 1H), 7.31-7.26 (m, 6H), 7.18-7.13 (m, 2H), 6.37 (s, 1H), 6.14 (ddd, *J* = 17.3, 9.8, 7.3 Hz, 1H), 5.22-5.16 (m, 2H), 5.10 (d, *J* = 7.5 Hz, 1H), 4.93-4.83 (m, 2H), 3.93-3.88 (m, 1H), 3.91 (s, 3H), 1.61 (d, *J* = 7.2 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 173.9, 173.6, 161.6, 157.9, 150.9, 141.8, 138.9, 135.0, 134.7, 133.9, 129.3, 129.0, 128.7, 128.1, 127.5, 127.3, 126.1, 126.0, 119.3, 118.3, 110.7, 105.7, 61.7, 55.4, 47.6, 45.3, 18.4; **HRMS (ESI+):** *m/z* calcd. for $C_{29}H_{27}O_6$ ($[M+H]^+$): 471.0808, Found: 471.0844; **Optical rotation:** $[\alpha]_D^{22}$ –35.5 (*c* 2.0, $CHCl_3$). The absolute stereochemistry of the product **3ja** was assigned in analogy with **8**.

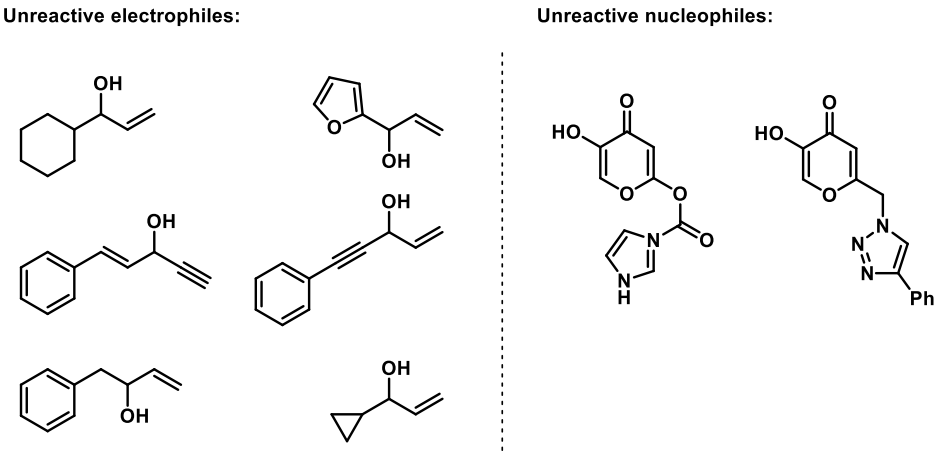
Compound 3ka: Reaction was performed on a 0.2 mmol scale; **3ka** was formed with >20:1 dr as determined by ^{1}H-NMR of the crude product; purified by silica-gel flash column chromatography (1% methanol in CH_2Cl_2); Pale yellow sticky liquid (82.0 mg, 0.128 mmol, 64% yield); **FT-IR (Thin film):** 3397 (br), 2962 (m), 2926 (m), 2876 (m), 1743 (m), 1710 (s), 1633 (s), 1591 (m), 1451 (m), 1205 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.34-7.26 (m, 4H),

7.24-7.22 (m, 1H), 6.41 (s, 1H), 6.23 (ddd, *J* = 17.3, 9.8, 7.2 Hz, 1H), 5.29 (d, *J* = 10.2 Hz, 1H), 5.21 (d, *J* = 17.2 Hz, 1H), 5.10 (d, *J* = 7.6 Hz, 1H), 4.88 (s, 2H), 2.93-2.77 (m, 4H), 2.53-2.15 (m, 11H), 2.15-2.00 (m, 6H), 1.94-1.84 (m, 4H), 1.64-1.56 (m, 1H), 1.38 (s, 3H), 1.05 (s, 3H), 0.84 (d, *J* = 6.5 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 212.1, 209.3, 208.8, 173.9, 173.0, 162.0, 150.8, 141.8, 138.9, 135.1, 128.8, 128.2, 127.4, 118.4, 110.6, 61.2, 57.0, 51.8, 49.0, 47.7, 46.9, 45.6, 45.0, 42.9, 38.7, 36.6, 36.1, 35.6, 35.3, 31.1, 30.3, 27.7, 25.2, 22.0, 18.7, 11.9; **HRMS (ESI+):** *m/z* calcd. for $C_{39}H_{47}O_8$ ($[M+H]^+$): 643.3271, Found: 643.3270; **Optical rotation:** $[\alpha]_D^{22}$ –13.7 (*c* 2.0, $CHCl_3$). The absolute stereochemistry of the product **3ka** was assigned in analogy with **8**.

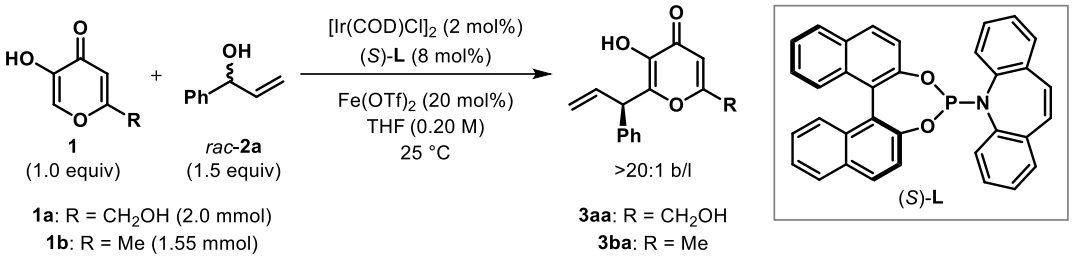
Compound 3la: Reaction was performed on a 0.2 mmol scale; **3la** was formed with >20:1 dr as determined by ^{1}H-NMR of the crude product; purified by silica-gel flash column chromatography (1% methanol in CH_2Cl_2); Yellow liquid (52.0 mg, 0.124 mmol, 62% yield); **FT-IR (Thin film):** 3272 (br), 2955 (w), 2924 (w), 2854 (w), 1744 (s), 1702 (s), 1633 (s), 1592 (s), 1451 (m), 1202 (m), 1157 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.34-7.25 (m, 5H), 6.41 (s, 1H), 6.24 (ddd, *J* = 17.3, 10.1, 7.5 Hz, 1H), 5.30 (d, *J* = 10.1 Hz, 1H), 5.21 (d, *J* = 17.2 Hz, 1H), 5.10 (d, *J* = 7.4 Hz, 1H), 4.86 (s, 2H), 2.88-2.83 (m, 1H), 2.40-2.27 (m, 3H), 2.03 (s, 3H), 1.99-1.86 (m, 2H), 1.25 (s, 3H), 0.84 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.3, 173.8, 171.7, 161.7, 150.6, 141.8, 139.0, 135.1, 128.8, 128.2, 127.4, 118.4, 110.7, 61.4, 54.2, 47.7, 43.2, 37.9, 34.7, 30.3, 29.8, 23.1, 17.5; **HRMS (ESI+):** *m/z* calcd. for $C_{25}H_{29}O_6$ ($[M+H]^+$): 425.1964, Found: 425.1963; **Optical rotation:** $[\alpha]_D^{22}$ –68.3 (*c* 2.0, $CHCl_3$). The absolute stereochemistry of the product **3la** was assigned in analogy with **8**.



I. Unsuccessful substrates for the asymmetric allylic alkylation reaction:

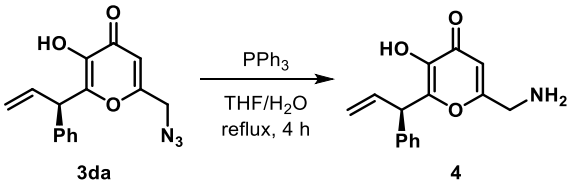


J. Large scale synthesis of 3aa and 3ba:



In an oven and vacuum-dried 50 mL round-bottom flask equipped with a magnetic stir bar, $[Ir(COD)Cl]_2$ (27.0 mg, 0.04 mmol, 2 mol%) and (*S*)-**L** (81.0 mg, 0.16 mmol, 8 mol%) were taken with 2 mL of dry THF under a positive argon pressure. The solution was stirred vigorously at 25 °C for 15 min to obtain a deep red solution. A solution of allylic alcohol *rac*-**2a** (402.0 mg, 3.0 mmol, 1.5 equiv.) in 7 mL of dry THF was then added to this red solution and stirred at 25 °C for 5 min. Kojic acid derivative **1** (2.0 mmol, 1.0 equiv.) was then added followed by $Fe(OTf)_2$ (142 mg, 0.4 mmol, 0.2 equiv.). The reaction flask was purged with argon, closed with a glass stopper, and stirred at 25 °C until TLC revealed complete consumption of **1**. The reaction mixture was then allowed to attain ambient temperature, diluted with 10 mL of CH_2Cl_2 and 10 mL of 1(N) HCl. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was washed with brine (25 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain a yellow liquid. This residue was purified by silica-gel flash column chromatography (1-3% methanol in CH_2Cl_2) to obtain β-allylic kojic acid derivatives **3aa** and **3ba** as a yellow liquid in 98% and 93% yield respectively with >99.5:0.5 er in both cases.

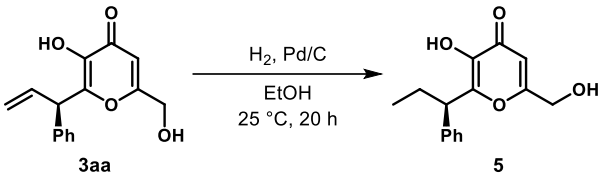
K. Procedure for the Staudinger reduction of 3da:



In an oven-dried 10 mL round-bottom flask, **3da** (50.0 mg, 0.175 mmol, 1.0 equiv.) and PPh_3 (70 mg, 0.2645 mmol, 1.5 equiv.) were taken in 3.5 mL THF followed by addition of 25 µl distilled water and allowed to reflux at 75 °C for 4 h. Then solvent was evaporated from the reaction mixture to obtain a dark yellow residue, which was purified by silica-gel flash column chromatography (3-5% methanol in CH_2Cl_2) to afford **4** as a yellow liquid (36.0 mg, 0.140 mmol, 80% yield) [*Note*: compound **4** is unstable in silica]; **FT-IR (Thin film):** 3436 (w), 2923 (m), 2852 (w), 1590 (s), 1417 (m), 1122 (s) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.35-7.26 (m, 5H), 6.40 (s, 1H), 6.26 (ddd, *J* = 17.2, 9.6, 7.2 Hz, 1H), 5.30 (d, *J* = 10.0 Hz, 1H), 5.21 (d, *J* = 16.9 Hz, 1H), 5.10 (d, *J* = 7.2 Hz, 1H), 3.69 (s, 2H), 1.42 (br, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.3, 168.8, 149.9, 141.4, 139.2, 135.3, 128.8, 128.2, 127.4, 118.3, 108.4, 47.8, 43.9; **HRMS (ESI+):** *m/z* calcd. for $C_{15}H_{16}NO_3$ ($[M+H]^+$): 258.1130, Found:

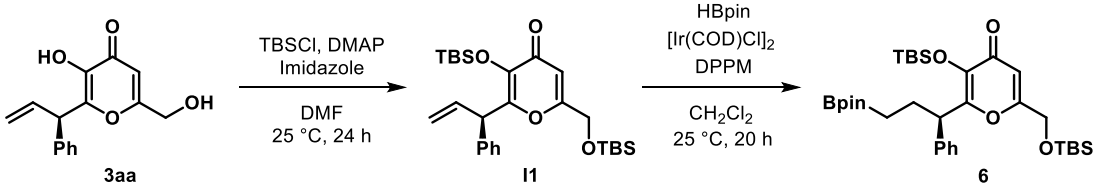
258.1129; **Optical rotation:** $[\alpha]_D^{22}$ +67.3 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with >99.9:0.1 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (70:30 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 280 nm, τ_{major} = 40.5 min). See Supporting Information: Part B for HPLC chromatograms.

L. Procedure for the selective hydrogenation of the allylic olefin of 3aa:



In an oven and vacuum-dried 10 mL two-necked round-bottom flask, a solution of **3aa** (21.0 mg, 0.081 mmol, 1.0 equiv.) in EtOH (2.0 mL) along with 10% Pd/C (4.0 mg, 0.004 mmol, 0.05 equiv.) were taken. The resulting mixture was degassed and stirred under H_2 balloon pressure for 20 h at 25 °C. The reaction mixture was filtered over Celite® and washed with ethyl acetate. The filtrate was concentrated under reduced pressure and the residue was purified by silica-gel flash column chromatography (0.5-1% methanol in CH_2Cl_2) to obtain **5** as a colorless sticky liquid (17.0 mg, 0.065 mmol, 81% yield); **FT-IR (Thin film):** 3413 (br), 2925 (m), 2866 (w), 1628 (s), 1574 (s), 1456 (m), 1210 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.35-7.21 (m, 5H), 6.49 (s, 1H), 4.51-4.43 (m, 2H), 4.22 (t, *J* = 7.9 Hz, 1H), 2.18-1.98 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.3, 167.3, 151.9, 141.6, 140.4, 128.8, 128.1, 127.3, 108.5, 61.2, 45.9, 25.5, 12.4; **HRMS (ESI+):** m/z calcd. for $C_{15}H_{17}O_4$ ($[M+H]^+$): 261.1127, Found: 261.1126; **Optical rotation:** $[\alpha]_D^{22}$ –123.3 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with >99.5:0.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90:10 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 277 nm, τ_{minor} = 13.9 min, τ_{major} = 15.9 min). See Supporting Information: Part B for HPLC chromatograms.

M. Procedure for the double silylation and hydroboration of 3aa:

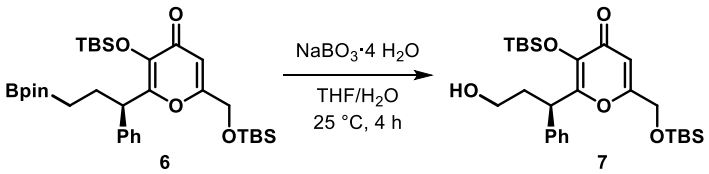


In an oven-dried 25 mL round-bottom flask, **3aa** (235.0 mg, 0.91 mmol, 1.0 equiv.) was taken along with DMAP (22.2 mg, 0.182 mmol, 0.2 equiv.) and imidazole (186.0 mg, 2.729 mmol, 3.0 equiv.) under a positive argon pressure. Then 1 mL of dry DMF was added, followed by addition of TBSCl (343 mg, 2.274 mmol, 2.5 equiv.) in 2 mL DMF and the resulting solution was stirred at 25 °C for 24 h under argon. Upon completion, the resulting mixture was diluted with 30 mL of distilled water

and 30 mL of diethyl ether. The organic layer was separated and washed with distilled water (20 mL × 3). The combined organic layer was washed with brine (25 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain a yellow liquid. This residue was purified by silica-gel flash column chromatography (2-3% EtOAc in petroleum ether) to obtain **I1** as a yellow liquid (358 mg, 0.736 mmol, 81% yield). **FT-IR (Thin film):** 3315 (br), 2935 (w), 2860 (w), 1725 (m), 1628 (s), 1581 (m), 1454 (m), 1250 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.34-7.30 (m, 2H), 7.27-7.23 (m, 3H), 6.38 (s, 1H), 6.19 (ddd, *J* = 7.4, 10.1, 17.3 Hz, 1H), 5.29 (d, *J* = 10.1 Hz, 1H), 5.24 (d, *J* = 7.4 Hz, 1H), 5.17 (d, *J* = 17.2 Hz, 1H), 4.43-4.33 (m, 2H), 0.96 (s, 9H), 0.90 (s, 9H), 0.31 (s, 3H), 0.27 (s, 3H), 0.07 (s, 3H), 0.06 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 175.3, 165.6, 155.3, 141.5, 139.4, 135.8, 128.7, 128.2, 127.2, 118.1, 110.9, 61.3, 46.9, 26.2, 25.8, 19.0, 18.3, –3.3, –3.4, –3.6, –5.4.

In an oven dried 25 mL round-bottom flask, **I1** (60.0 mg, 0.123 mmol, 1.0 equiv.) was taken along with $[Ir(COD)Cl]_2$ (2.4 mg, 0.0036 mmol, 0.03 equiv.) and bis(diphenylphosphino)methane (DPPM) (2.8 mg, 0.0072 mmol, 0.06 equiv.) under a positive argon pressure. Then 4 mL of dry CH_2Cl_2 was added, followed by addition of HBpin (36 µL, 0.246 mmol, 2.0 equiv.) and the resulting solution was stirred at 25 °C for 20 h under argon. Upon completion, the reaction mixture was quenched with 0.5 mL methanol and diluted with 4 mL of distilled water. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain a yellow oil, which was purified by silica-gel flash column chromatography (3-5% EtOAc in petroleum ether) to obtain **6** as a yellow oil (72.0 mg, 0.117 mmol, 95% yield); **FT-IR (Thin film):** 3279 (w), 2935 (m), 2861 (w), 1633 (s), 1586 (m), 1373 (m), 1215 (s) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.32-7.28 (m, 4H), 7.23-7.19 (m, 1H), 6.33 (s, 1H), 4.49-4.38 (m, 3H), 2.16-2.01 (m, 2H), 1.22 (s, 12H), 0.99 (s, 9H), 0.92 (s, 9H), 0.78-0.71 (m, 2H), 0.27 (s, 3H), 0.26 (s, 3H), 0.10 (s, 3H), 0.09 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 175.1, 165.3, 156.6, 141.7, 140.9, 128.6, 128.2, 127.0, 110.7, 83.2, 61.4, 45.6, 27.5, 26.4, 25.8, 24.9, 24.9, 19.1, 18.3, –3.1, –3.4, –5.3; **Optical rotation:** $[\alpha]_D^{22}$ –61.2 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample.

N. Procedure for the oxidation of 6:

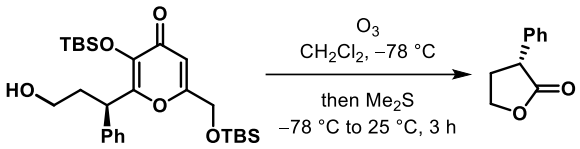


6 7

In an oven dried 10 mL round-bottom flask, **6** (38.0 mg, 0.062 mmol, 1.0 equiv.) was taken in a mixture of THF/H_2O (1:1) followed by addition of $NaBO_3 \cdot 4H_2O$ (38.0 mg, 0.247 mmol, 4.0 equiv.) and allowed to stir at 25 °C for 4 h. Upon completion, the reaction mixture was diluted with 10 mL of distilled water and 10 mL of CH_2Cl_2. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was dried over anh. Na_2SO_4 and

concentrated under reduced pressure to obtain a pale yellow residue, which was purified by silica-gel flash column chromatography (1-2% methanol in CH_2Cl_2) to afford **7** as a yellow oil (27.0 mg, 0.053 mmol, 87% yield); **FT-IR (Thin film):** 3315 (br), 2935 (w), 2860 (w), 1725 (m), 1629 (s), 1582 (m), 1455 (m), 1251 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.34-7.29 (m, 4H), 7.26-7.23 (m, 1H), 6.34 (s, 1H), 4.71 (t, *J* = 7.9 Hz, 1H), 4.46-4.37 (m, 2H), 3.63-3.60 (m, 2H), 2.28-2.23 (m, 2H), 1.00 (s, 9H), 0.91 (s, 9H), 0.30 (s, 3H), 0.27 (s, 3H), 0.09 (s, 3H), 0.09 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 175.1, 165.4, 156.1, 141.5, 140.1, 128.8, 128.1, 127.3, 110.9, 61.4, 60.7, 39.4, 35.5, 26.3, 25.8, 19.1, 18.3, –3.2, –3.3, –5.3; **HRMS (ESI+):** *m/z* calcd. for $C_{27}H_{45}O_5Si_2$ ($[M+H]^+$): 505.2806, Found: 505.2802; **Optical rotation:** $[\alpha]_D^{22}$ –92.1 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with >99.5:0.5 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (90:10 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 254 nm, τ_{minor} = 4.3 min, τ_{major} = 6.7 min). See Supporting Information: Part B for HPLC chromatograms.

O. Procedure for the ozonolysis induced cyclization of 7:

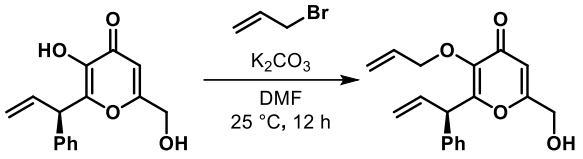


7 **8**

In an oven-dried 10 mL round-bottom flask, **7** (100.0 mg, 0.198 mmol, 1.0 equiv.) was taken in 3.5 mL CH_2Cl_2 and treated with oxygen-ozone stream for 15 min at –78 °C. After full consumption of **7**, the resulting mixture was treated with an excess of dimethyl sulfide (58 µl, 0.792 mmol, 4.0 equiv.), allowed to slowly warm to ambient temperature and stirred for 3 h. Then all the volatiles were removed under reduced pressure to obtain yellow residue, which was purified by silica-gel flash column chromatography (11-13% EtOAc in petroleum ether) to afford **8** as a yellow liquid (10.0 mg, 0.062 mmol, 31% yield); **FT-IR (Thin film):** 2958 (w), 2919 (m), 2851 (w), 1768 (s), 1597 (m), 1373 (m), 1150 (s), 1023 (s) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.39-7.36 (m, 2H), 7.32-7.28 (m, 3H), 4.48 (dt, *J* = 3.3, 8.6 Hz, 1H) 4.39-4.32 (m, 1H), 3.82 (t, *J* = 9.5 Hz, 1H), 2.76-2.68 (m, 1H), 2.50-2.40 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 177.5 136.8, 129.1, 128.0, 127.8, 66.6, 45.6, 31.7; **HRMS (ESI+):** *m/z* calcd. for $C_{10}H_{11}O_2$ ($[M+H]^+$): 163.0759, Found: 163.0760; **Optical rotation:** $[\alpha]_D^{22}$ –4.7 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er [Lit[7] $[\alpha]_D^{22}$ +3.1 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 95:5 er]. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IC column (80:20 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 210 nm, τ_{major} = 23.7 min, τ_{minor} = 26.6 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **8** was assigned by comparing its specific rotation with that reported in the literature.[7]

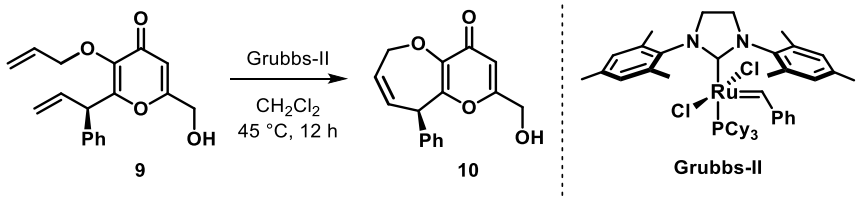
[7] N. A. Paras and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2001, **123**, 4370-4371.

P. Procedure for the selective *O*-allylation of 3aa:



In an oven-dried 10 mL round-bottom flask, **3aa** (42.0 mg, 0.163 mmol, 1.0 equiv.) and K_2CO_3 (33.7 mg, 0.243 mmol, 1.5 equiv.) were taken in 2 mL of dry DMF under argon atmosphere followed by addition of allyl bromide (17 µl, 0.195 mmol, 1.2 equiv.) and allowed to stir at 25 °C for 12 h. Upon completion, the reaction mixture was diluted with 20 mL of water and 20 mL of CH_2Cl_2. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was washed with 20 mL brine, dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain a pale yellow residue, which was purified by silica-gel flash column chromatography (1-2% Methanol in CH_2Cl_2) to afford **9** as a yellow oil (30.0 mg, 0.100 mmol, 62% yield); **FT-IR (Thin film):** 3345 (br), 3083 (w), 2922 (m), 1723 (m), 1652 (s), 1611 (s), 1424 (m), 1188 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.33-7.29 (m, 2H), 7.26-7.22 (m, 3H), 6.46 (s, 1H), 6.20 (ddd, *J* = 17.4, 10.1, 7.6, Hz, 1H), 5.98-5.88 (m, 1H), 5.31-5.27 (m, 2H), 5.20-5.13 (m, 3H), 4.59-4.48 (m, 2H), 4.41 (s, 2H), 4.10 (br, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 176.6, 167.3, 161.1, 142.6, 139.0, 135.5, 133.5, 128.9, 128.2, 127.5, 119.1, 118.6, 112.3, 73.1, 60.7, 47.7; **HRMS (ESI+):** *m/z* calcd. for $C_{18}H_{19}O_4$ ($[M+H]^+$): 299.1283, Found: 299.1281; **Optical rotation:** $[\alpha]_D^{22}$ –100.9 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with >99.5:0.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90:10 *n*-Hexane/ *i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 257 nm, τ_{minor} = 8.5 min, τ_{major} = 11.6 min). See Supporting Information: Part B for HPLC chromatograms.

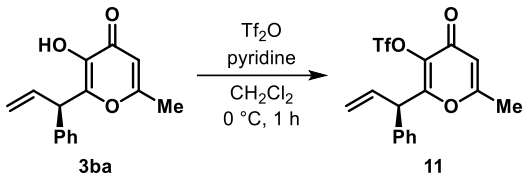
Q. Procedure for the ring closing metathesis of 9:



In an oven dried 10 mL 2-necked round-bottom flask, equipped with a reflux condenser, **9** (14.0 mg, 0.047 mmol, 1.0 equiv.) and Grubbs-II (3.2 mg, 0.00375 mmol, 0.08 equiv.) were taken in 2.5 mL of dry and degassed CH_2Cl_2 under argon. The resulting solution was heated to 45 °C for 12 h at which time starting material was completely consumed. The reaction mixture was concentrated to obtain a yellow residue. Purification by silica-gel flash column chromatography (3-4% methanol in CH_2Cl_2) afforded **10** as a light brown sticky liquid (11.0 mg, 0.047 mmol, 87% yield); **FT-IR (Thin film):** 3420 (br), 2923 (w), 2853 (w), 1653 (s), 1617 (s), 1595 (s), 1452 (m), 1272 (w) cm^{-1}; **^{1}H-NMR (400 MHz,**

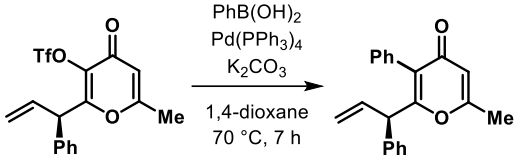
$CDCl_3$): δ 7.44-7.42 (m, 2H), 7.33-7.24 (m, 3H), 6.44 (s, 1H), 5.87-5.78 (m, 2H), 4.77-4.72 (m, 1H), 4.47-4.41 (m, 4H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 176.6, 166.9, 161.3, 144.7, 138.9, 129.1, 128.4, 128.4, 127.9, 125.4, 112.4, 69.0, 60.9, 49.9; **HRMS (ESI+):** *m/z* calcd. for $C_{16}H_{15}O_4$ ($[M+H]^+$): 271.0970, Found: 271.0968; **Optical rotation:** $[\alpha]_D^{22}$ –75.1 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with >99.5:0.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (85:15 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 259 nm, τ_{major} = 9.9 min, τ_{minor} = 13.5 min). See Supporting Information: Part B for HPLC chromatograms.

R. Procedure for the triflyl protection of 3ba:



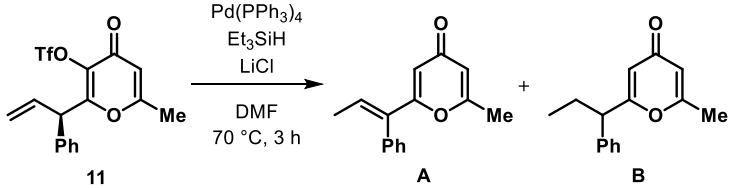
In an oven and vacuum-dried 10 mL round-bottom flask equipped with a magnetic stir bar, **3ba** (40 mg, 0.165 mmol, 1.0 equiv.) was dissolved in 1.0 mL of dry CH_2Cl_2 under a positive argon pressure and cooled to 0 °C. To this solution, pyridine (36 µl, 0.445 mmol, 2.7 equiv.) was added followed by dropwise addition of Tf_2O (36 µl, 0.214 mmol, 1.3 equiv.) and the resulting mixture was stirred at 0 °C for 1 h. Upon completion, the reaction mixture was quenched with 5 mL of 1(N) HCl solution. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (5 mL × 3). Combined organic layer was washed with brine (10 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain a dark red residue, which was purified by silica-gel flash column chromatography (CH_2Cl_2 only) to obtain **11** as yellow liquid (36.0 mg, 0.096 mmol, 58% yield); **FT-IR (Thin film):** 3072 (w), 2921 (m), 2708 (w), 1722 (m), 1667 (s), 1418 (s), 1213 (s), 1123 (s), 855 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.39-7.35 (m, 2H), 7.33-7.27 (m, 3H), 6.25 (s, 1H), 6.20 (ddd, *J* = 7.4, 10.1, 17.3 Hz, 1H), 5.41 (d, *J* = 10.2 Hz, 1H), 5.28 (d, *J* = 17.1 Hz, 1H), 5.00 (d, *J* = 7.4 Hz, 1H), 2.27 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.2, 166.1, 166.1, 162.4, 137.1, 137.0, 133.6, 129.1, 128.1, 120.0, 118.5 (q, *J* = 320.2 Hz), 114.7, 48.0, 19.7; **HRMS (ESI+):** *m/z* calcd. for $C_{16}H_{13}F_3O_5SNa$ ($[M+Na]^+$): 397.0333, Found: 397.0330; **Optical rotation:** $[\alpha]_D^{22}$ –57.8 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with >99.5:0.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IH column (90:10 *n*-Hexane/*i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 221 nm, τ_{minor} = 12.5 min, τ_{major} = 20.3 min). See Supporting Information: Part B for HPLC chromatograms.

S. Procedure for the Suzuki cross-coupling of 11 with phenyl boronic acid:



In an oven and vacuum-dried 10 mL round-bottom flask equipped with a magnetic stir bar, **11** (20 mg, 0.053 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (3.1 mg, 0.00265 mmol, 5.0 mol%), K_2CO_3 (29.3 mg, 0.212 mmol, 4.0 equiv.) and phenyl boronic acid (12.9 mg, 0.106 mmol, 2.0 equiv.) were taken in 0.6 mL of dry 1,4-dioxane under a positive argon pressure, heated to 70 °C and allowed to stir for 7 h. Upon completion, the reaction mixture was quenched with 3 mL of saturated NH_4Cl solution and diluted with 3 mL of distilled water. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 mL × 3). Combined organic layer was washed with brine (10 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain a dark brown residue, which was purified by silica-gel flash column chromatography (1% methanol in CH_2Cl_2) to obtain **12** as a yellow liquid (13.0 mg, 0.043 mmol, 85% yield); **FT-IR (Thin film):** 3446 (br), 2923 (w), 2853 (w), 1659 (s), 1623 (s), 1397 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.45-7.38 (m, 4H), 7.33-7.28 (m, 3H), 7.25-7.23 (m, 1H), 7.16-7.15 (m, 2H), 6.21 (s, 1H), 6.24-6.16 (m, 1H), 5.29 (d, *J* = 10.1 Hz, 1H), 5.09 (d, *J* = 17.0 Hz, 1H), 4.60 (d, *J* = 7.4 Hz, 1H), 2.25 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 178.9, 165.0, 164.5, 139.3, 136.2, 132.3, 130.2, 128.8, 128.7, 128.3, 128.1, 127.4, 127.2, 118.3, 113.9, 50.9, 19.8; **HRMS (ESI+):** *m/z* calcd. for $C_{21}H_{19}O_2$ ($[M+H]^+$): 303.1385, Found: 303.1384; **Optical rotation:** $[\alpha]_D^{22}$ –120.7 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with >99.5:0.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IH column (90:10 *n*-Hexane/ *i*-PrOH, flow rate = 1.0 mL/min, 20 °C, I = 224 nm, τ_{minor} = 38.9 min, τ_{major} = 43.7 min). See Supporting Information: Part B for HPLC chromatograms.

T. Attempted reductive removal of triflate in 11:



In an oven and vacuum-dried 10 mL round-bottom flask equipped with a magnetic stir bar, **11** (15 mg, 0.040 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (9.2 mg, 0.008 mmol, 20.0 mol%) and LiCl (15.0 mg, 0.35 mmol, 8.75 equiv.) were taken in 2 mL of dry DMF under a positive argon pressure. Then Et_3SiH (0.13 mL, 0.816 mmol, 20.0 equiv.) was added into it and heated to 70 °C and allowed to stir for 3 h. Upon completion, the reaction mixture was diluted with 5 mL of Et_2O and 20 mL of distilled water. The organic layer was separated, and the aqueous layer was extracted with Et_2O (5 mL × 3). Combined

organic layer was washed with brine (10 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain a dark yellow residue, which was purified by silica-gel flash column chromatography (30-40% EtOAc in Pet ether) to obtain mixture of isomerized product and hydrogenation product as an inseperable mixture (8.0 mg); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.42-7.31 (m, 6H), 7.26-7.23 (m, 4H), 7.15-7.12 (m, 2H), 6.81 (q, *J* = 7.1 Hz, 1H) [for **A**], 6.18 (d, *J* = 2.2 Hz, 1H), 6.07 (d, *J* = 1.5 Hz, 1H), 6.05 (d, *J* = 1.4 Hz, 1H), 5.75 (d, *J* = 2.1 Hz, 1H), 3.56 (t, *J* = 7.7 Hz, 1H) [for **B**], 2.32 (s, 3H) [for **A**], 2.21 (s, 3H) [for **B**], 2.13-2.07 (m, 1H), 1.99-1.90 (m, 1H) [for **B**], 1.71 (d, *J* = 7.2 Hz, 3H) [for **A**], 0.92 (t, *J* = 7.4 Hz, 3H) [for **B**]; **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 180.9, 180.6, 170.5, 165.9, 165.2, 164.1, 139.8, 135.4, 135.0, 131.4, 130.0, 128.9, 128.9, 128.2, 128.1, 127.5, 114.0, 113.8, 113.1, 113.0, 51.9, 26.2, 20.0, 19.9, 15.6, 12.3; **HRMS (ESI+):** *m/z* calcd. for $C_{15}H_{15}O_2$ ($[M+H]^+$): 227.1072, Found: 227.1069.

SUPPORTING INFORMATION: PART B

Hydroxy-directed iridium-catalyzed enantioselective formal β-C(sp^2)–H allylic alkylation of α,β-unsaturated carbonyls

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Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, INDIA

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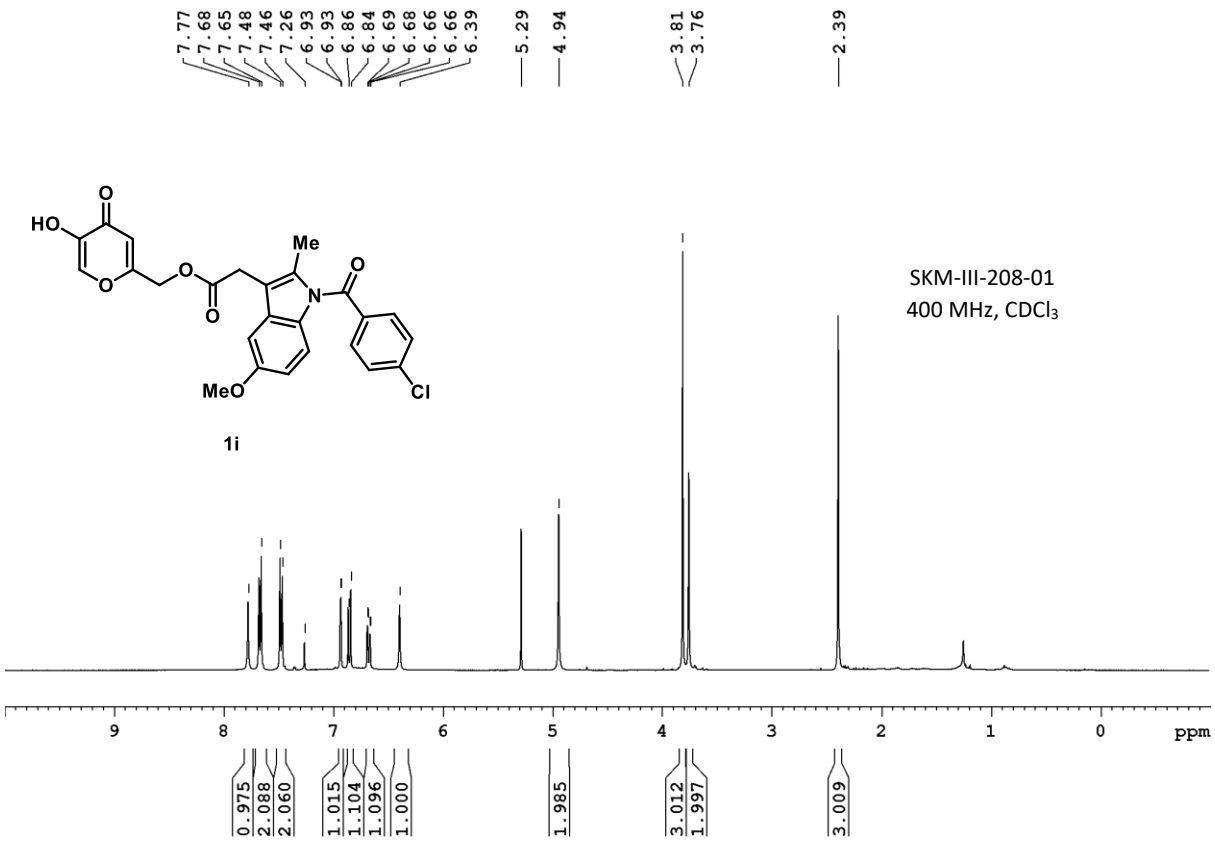
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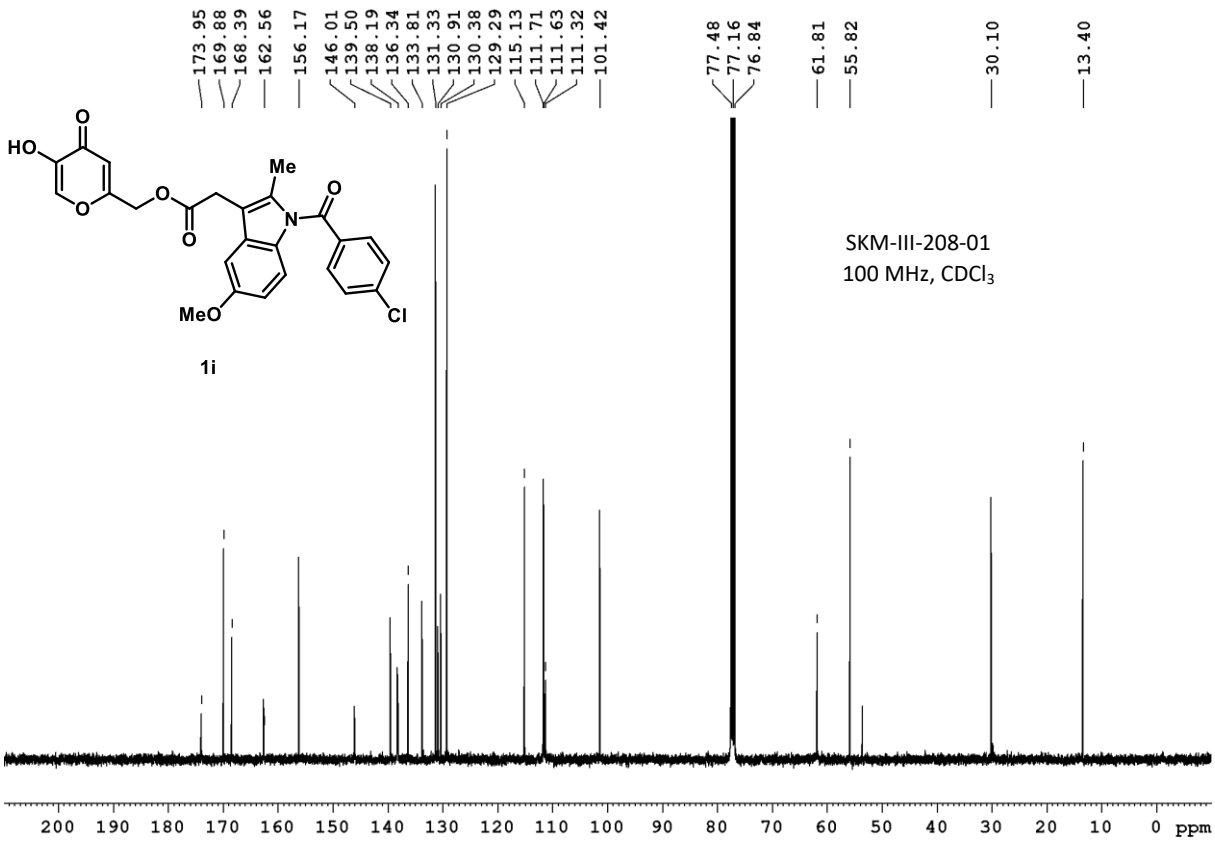
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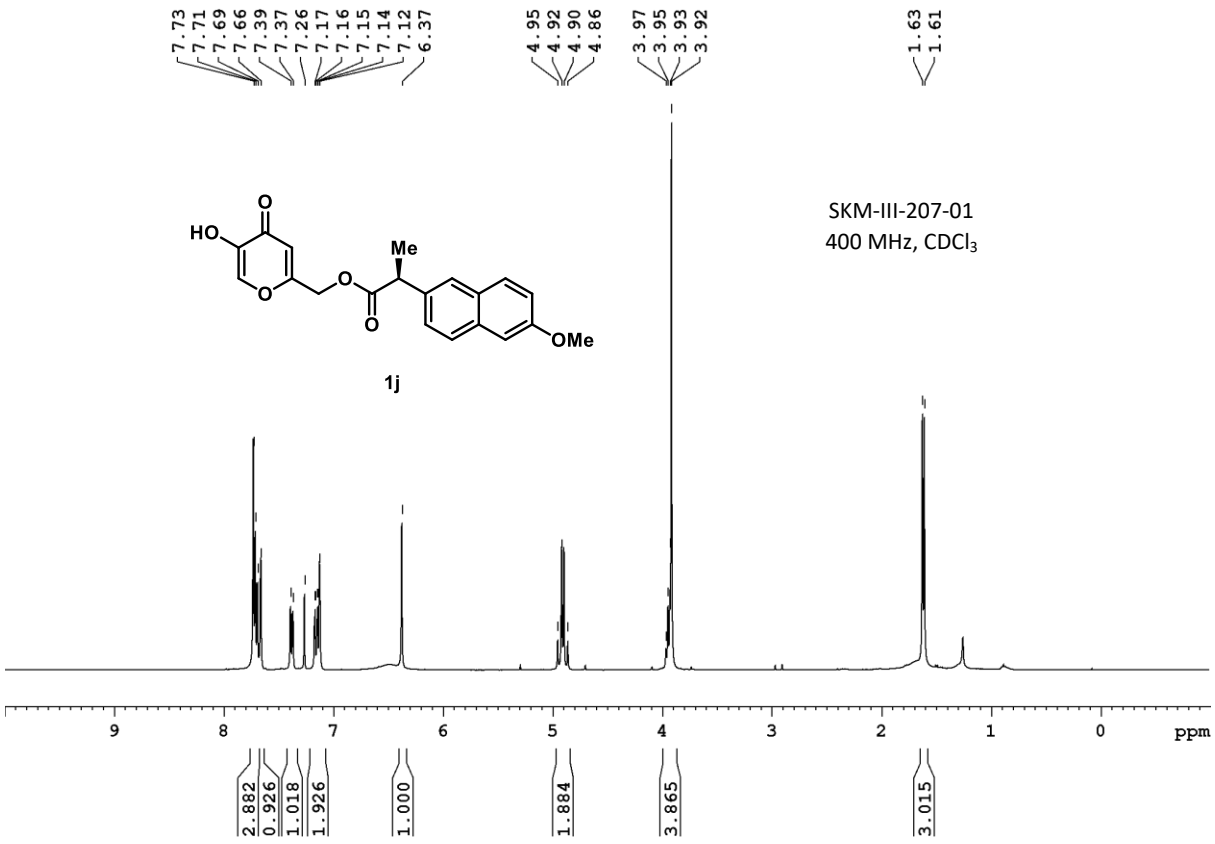
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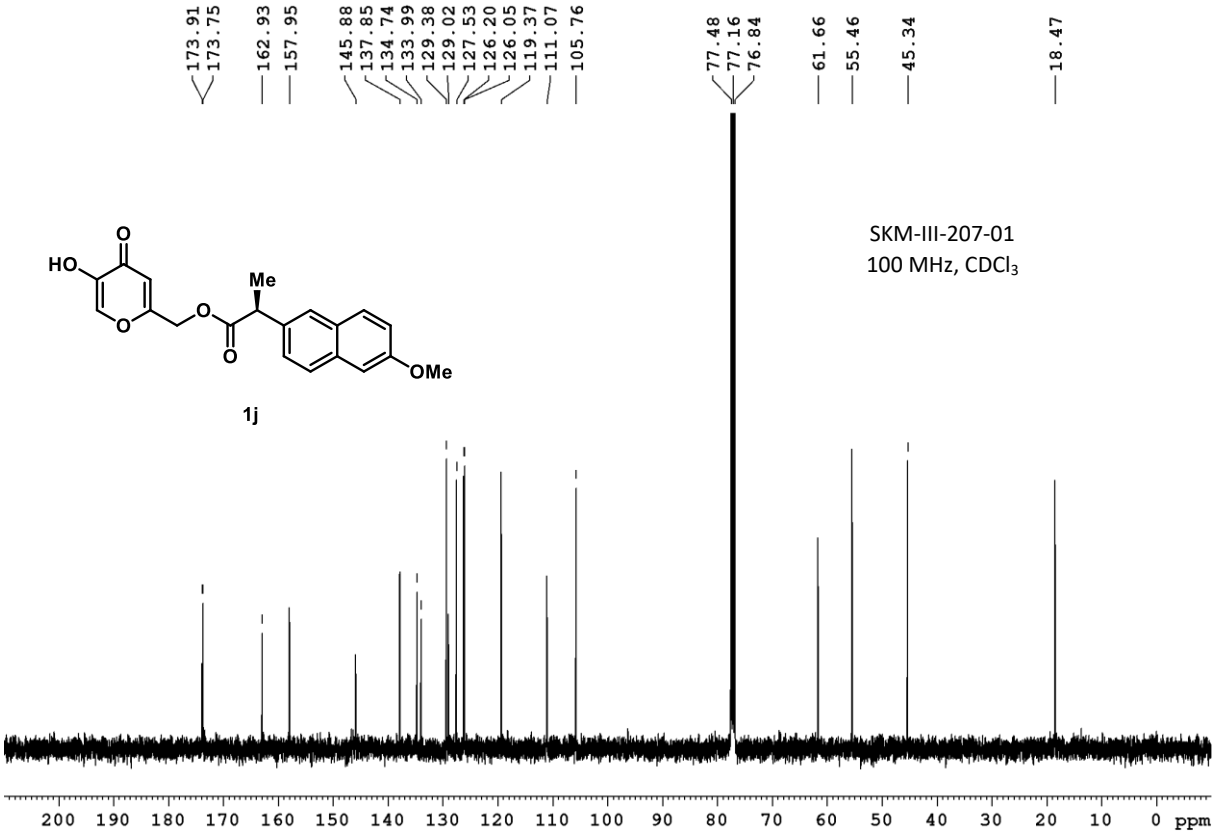
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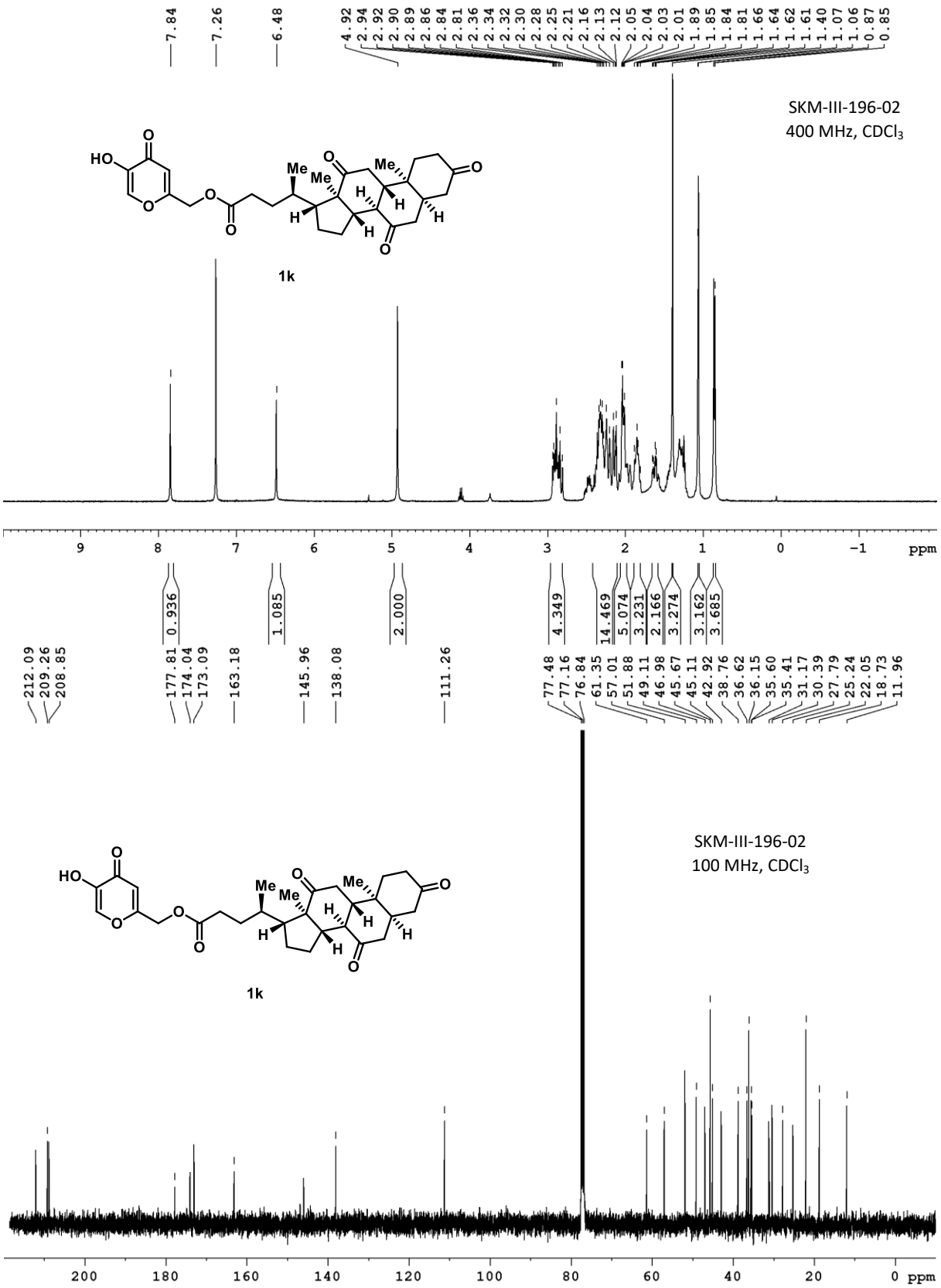
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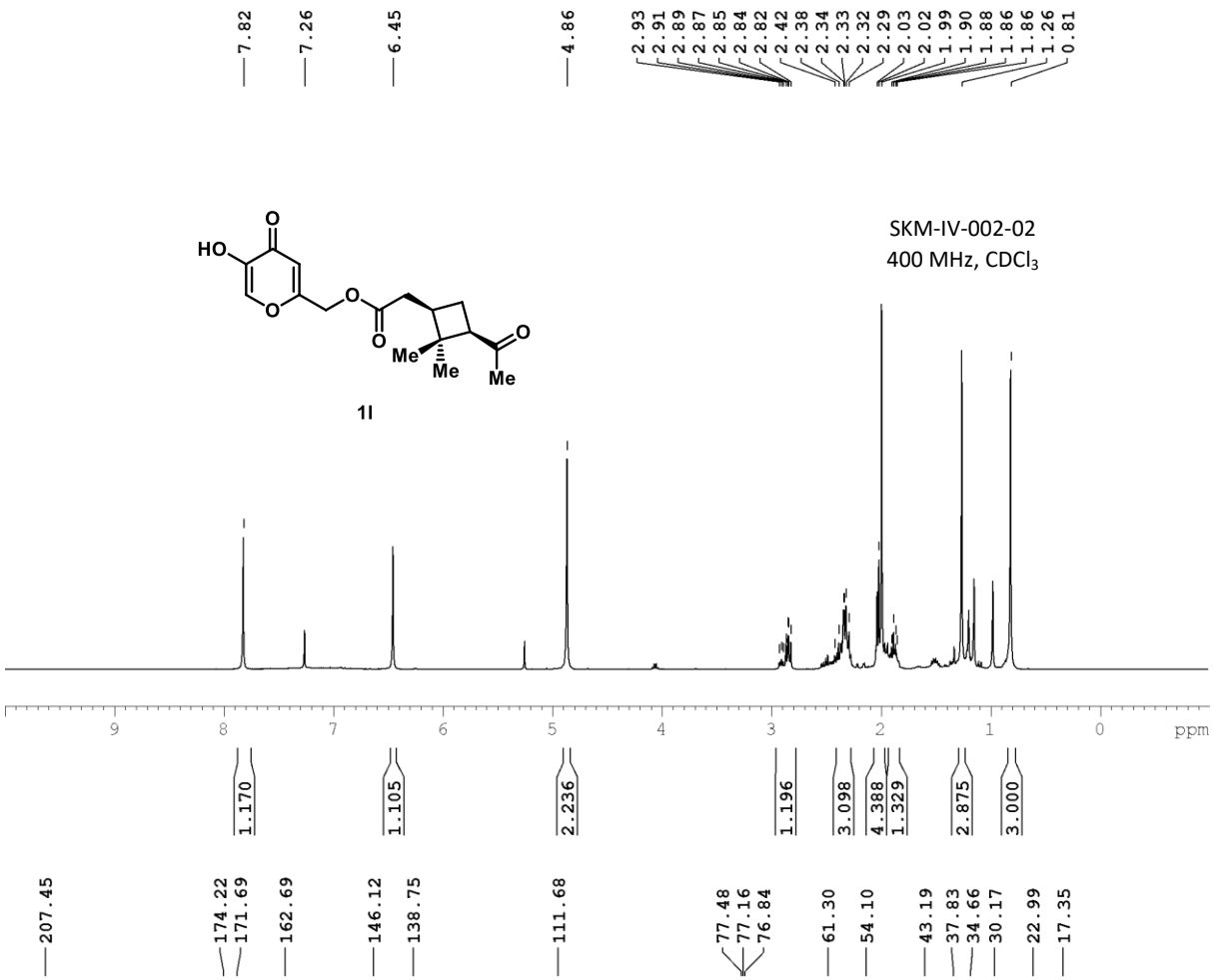
ppm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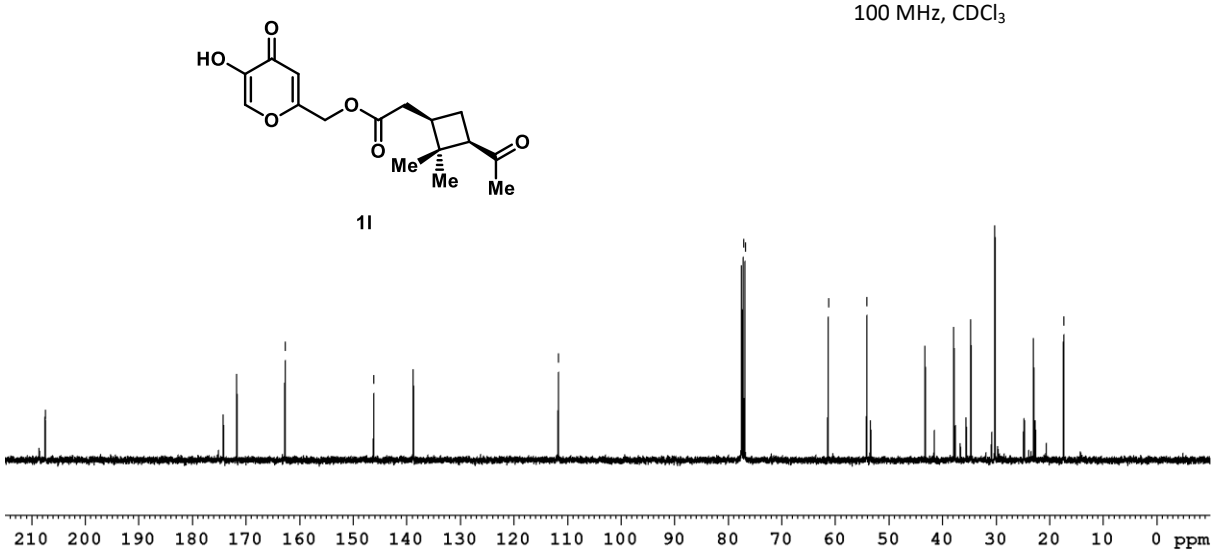
1l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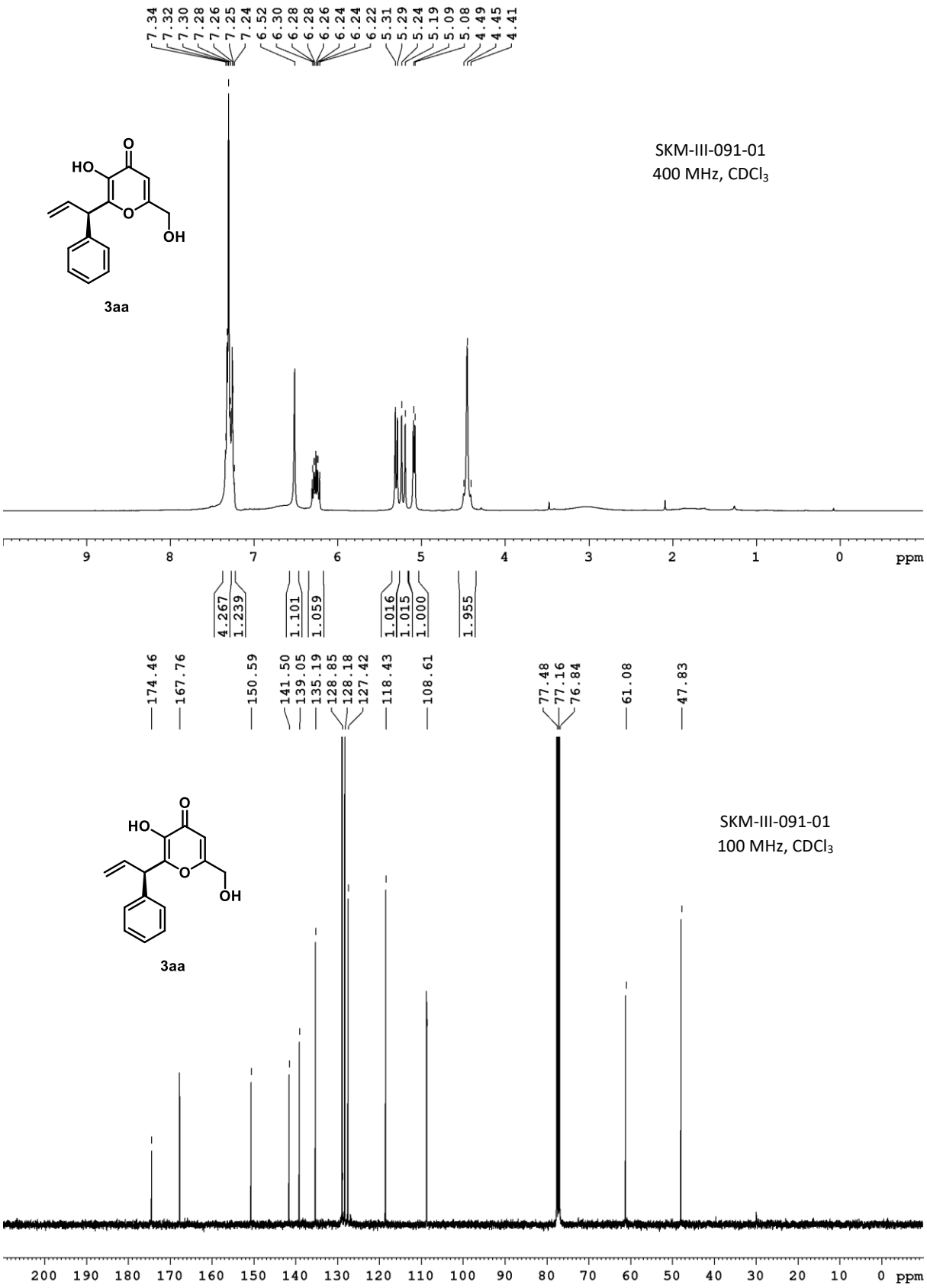
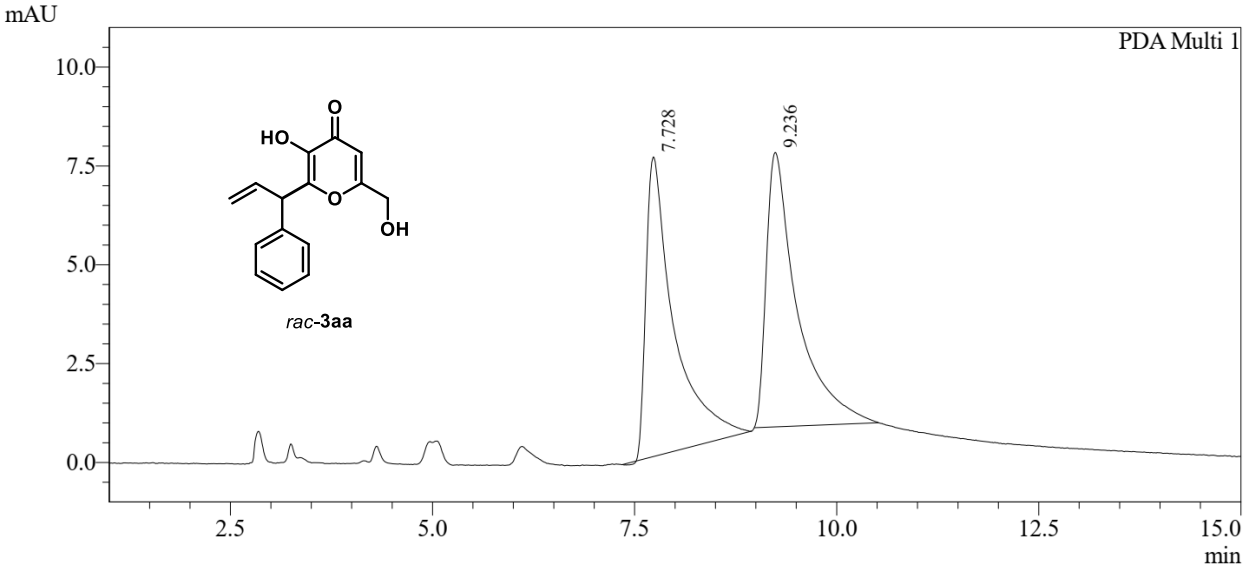
20
10
0 ppm

1l


7.34
7.32
7.30
7.28
7.26
7.25
7.24
6.52
6.30
6.28
6.28
6.26
6.24
6.24
6.22
5.31
5.29
5.24
5.19
5.09
5.08
4.49
4.45
4.41
HO
O
O
OH
3aa
SKM-III-091-01
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
4.267
1.239
1.101
1.059
1.016
1.015
1.000
1.955
174.46
167.76
150.59
141.50
139.05
135.19
128.85
128.18
127.42
118.43
108.61
77.48
77.16
76.84
61.08
47.83
HO
O
O
OH
3aa
SKM-III-091-01
100 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



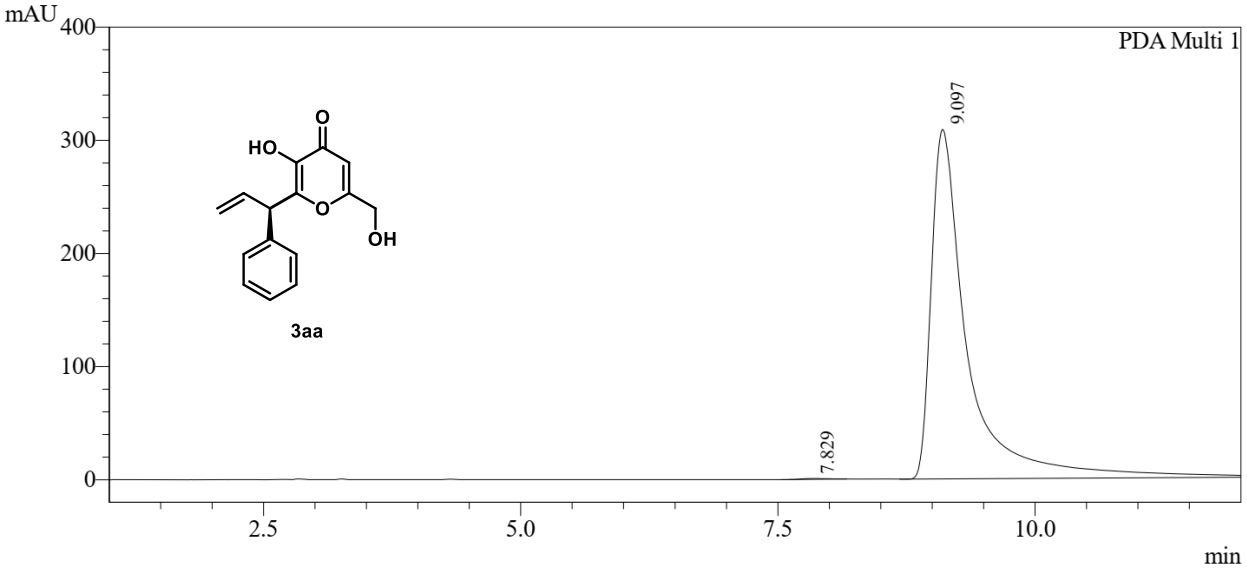
rac-**3aa**

PeakTable

PDA Ch1 277nm 4nm

Peak#	Ret. Time	Area	Area %
1	7.728	181481	49.623
2	9.236	184241	50.377
Total		365722	100.000

Phenomenex Cellulose-1 column (85:15 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

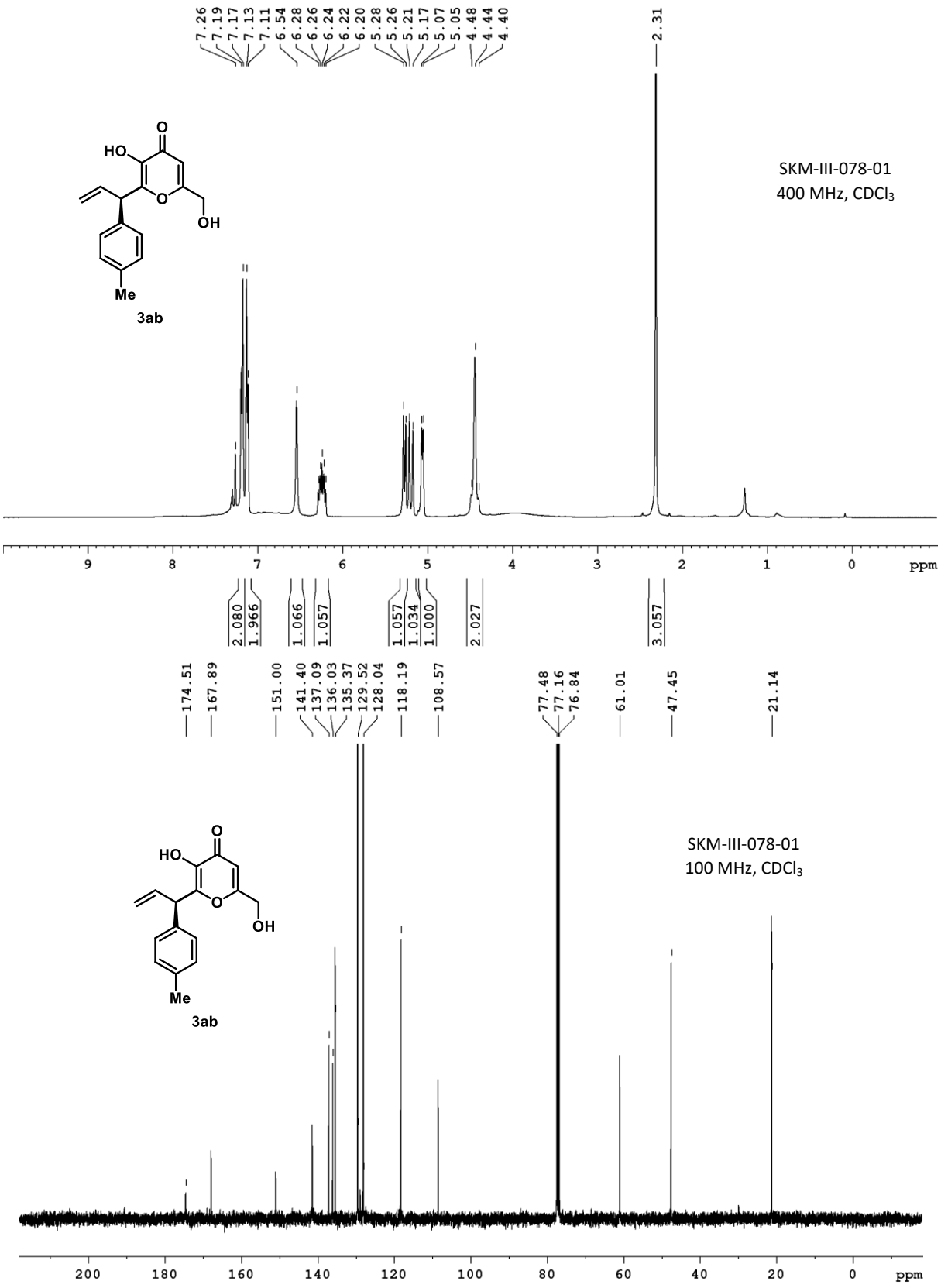


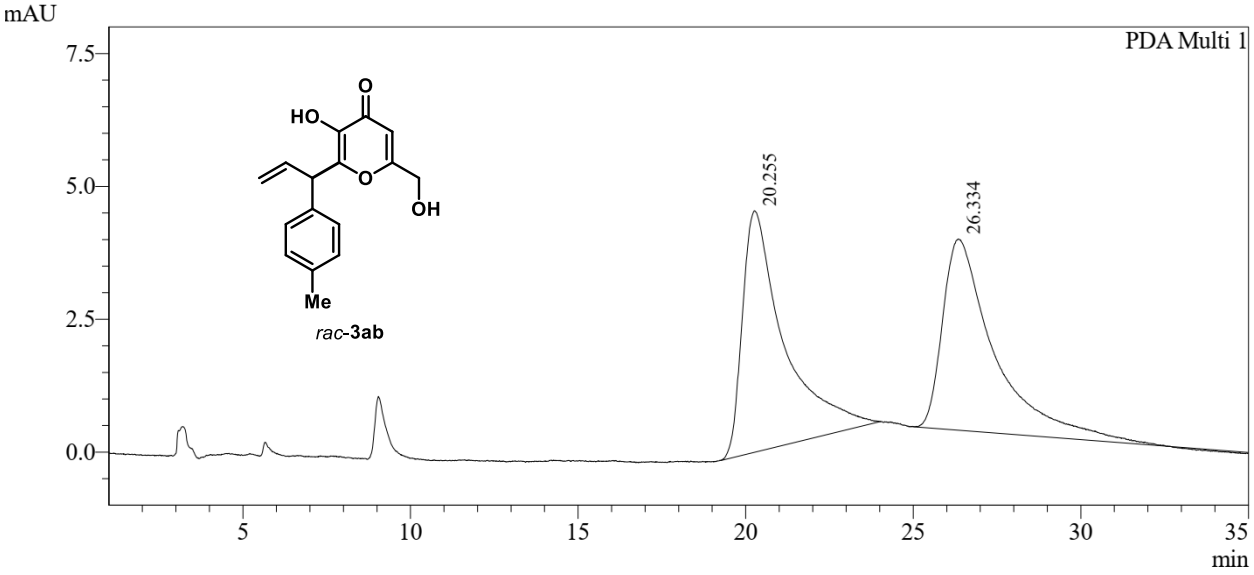
3aa

PeakTable

PDA Ch1 277nm 4nm

Peak#	Ret. Time	Area	Area %
1	7.829	12326	0.160
2	9.097	7715447	99.840
Total		7727773	100.000


7.26
7.19
7.17
7.13
7.11
6.54
6.28
6.26
6.24
6.22
6.20
5.28
5.26
5.21
5.17
5.07
5.05
4.48
4.44
4.40
2.31
HO
O
O
OH
Me
3ab
SKM-III-078-01
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
2.080
1.966
1.066
1.057
1.057
1.034
1.000
2.027
3.057
174.51
167.89
151.00
141.40
137.09
136.03
135.37
129.52
128.04
118.19
108.57
77.48
77.16
76.84
61.01
47.45
21.14
SKM-III-078-01
100 MHz, CDCl3
200
180
160
140
120
100
80
60
40
20
0
ppm

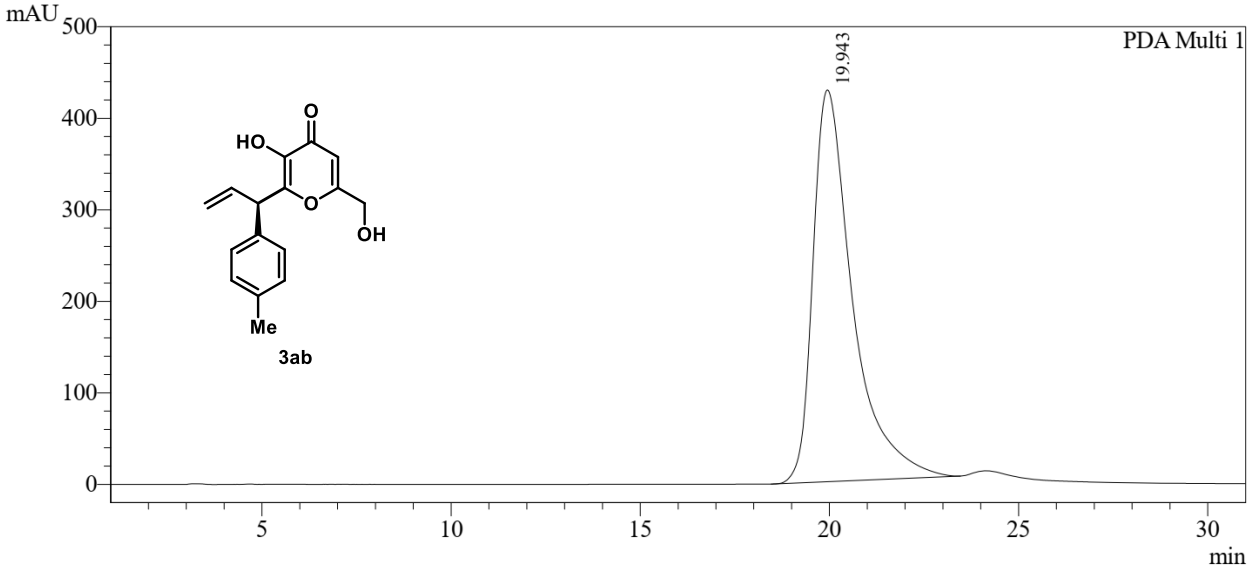


PeakTable

PDA Ch1 285nm 4nm

Peak#	Ret. Time	Area	Area %
1	20.255	392668	50.512
2	26.334	384715	49.488
Total		777383	100.000

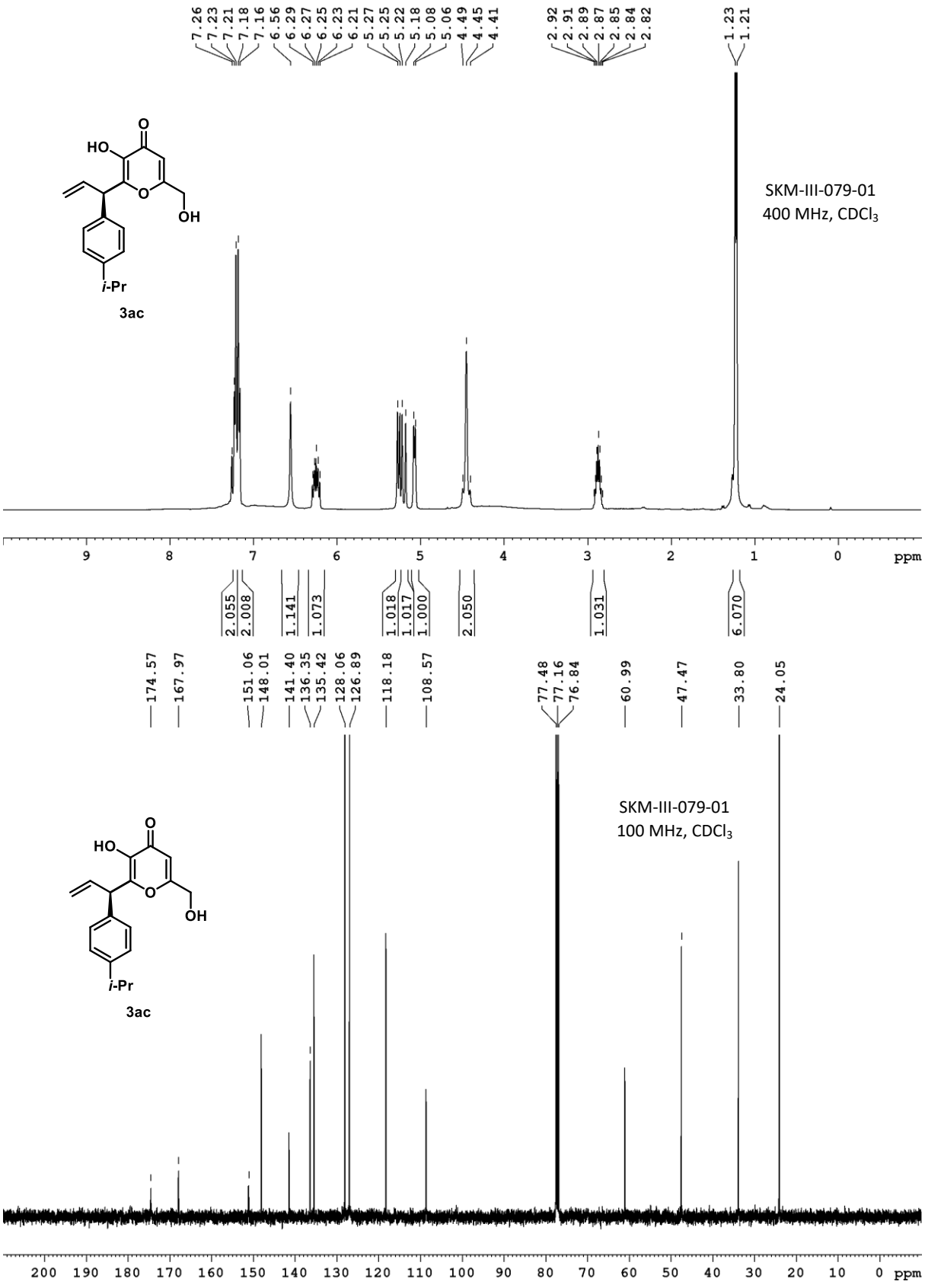
Daicel Chiralpak AS-H column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

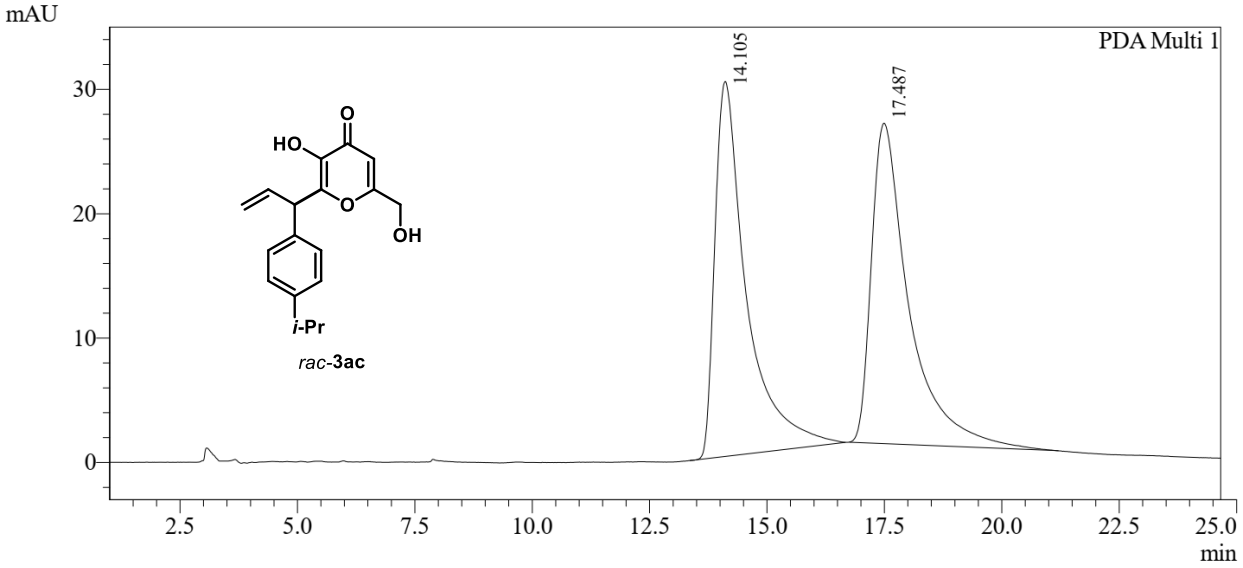


PeakTable

PDA Ch1 285nm 4nm

Peak#	Ret. Time	Area	Area %
1	19.943	31150645	100.000
Total		31150645	100.000


7.26
7.23
7.21
7.18
7.16
6.56
6.29
6.27
6.25
6.23
6.21
5.27
5.25
5.22
5.18
5.08
5.06
4.49
4.45
4.41
2.92
2.91
2.89
2.87
2.85
2.84
2.82
1.23
1.21
HO
O
OH
i-Pr
3ac
SKM-III-079-01
400 MHz, CDCl3
ppm
2.055
2.008
1.141
1.073
1.018
1.017
1.000
2.050
1.031
6.070
174.57
167.97
151.06
148.01
141.40
136.35
135.42
128.06
126.89
118.18
108.57
77.48
77.16
76.84
60.99
47.47
33.80
24.05
SKM-III-079-01
100 MHz, CDCl3
ppm

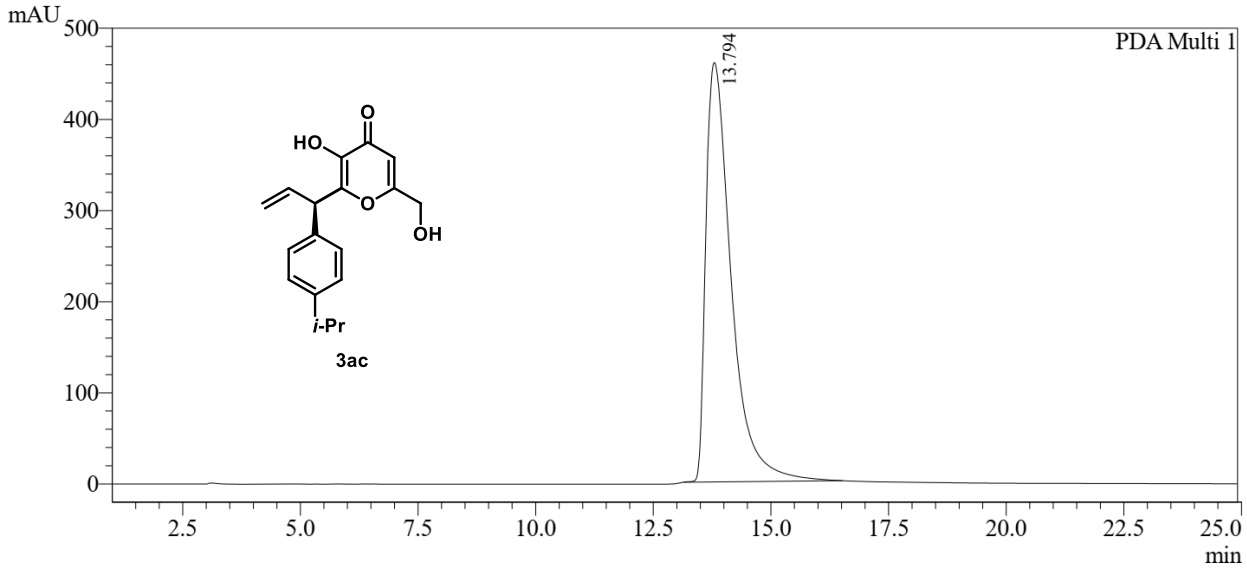


PeakTable

PDA Ch1 277nm 4nm

Peak#	Ret. Time	Area	Area %
1	14.105	1408829	49.574
2	17.487	1433019	50.426
Total		2841847	100.000

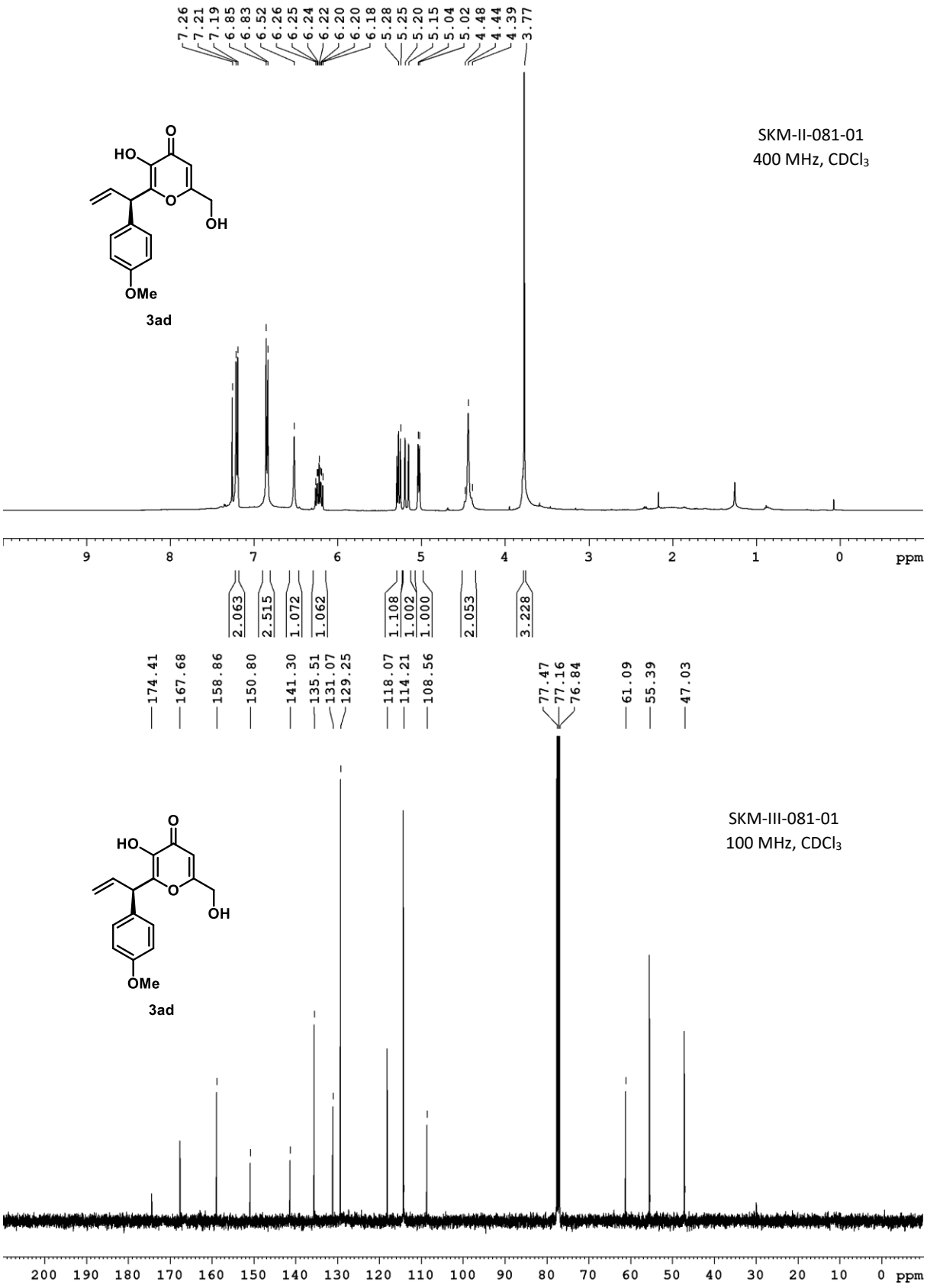
Daicel Chiralpak IH column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

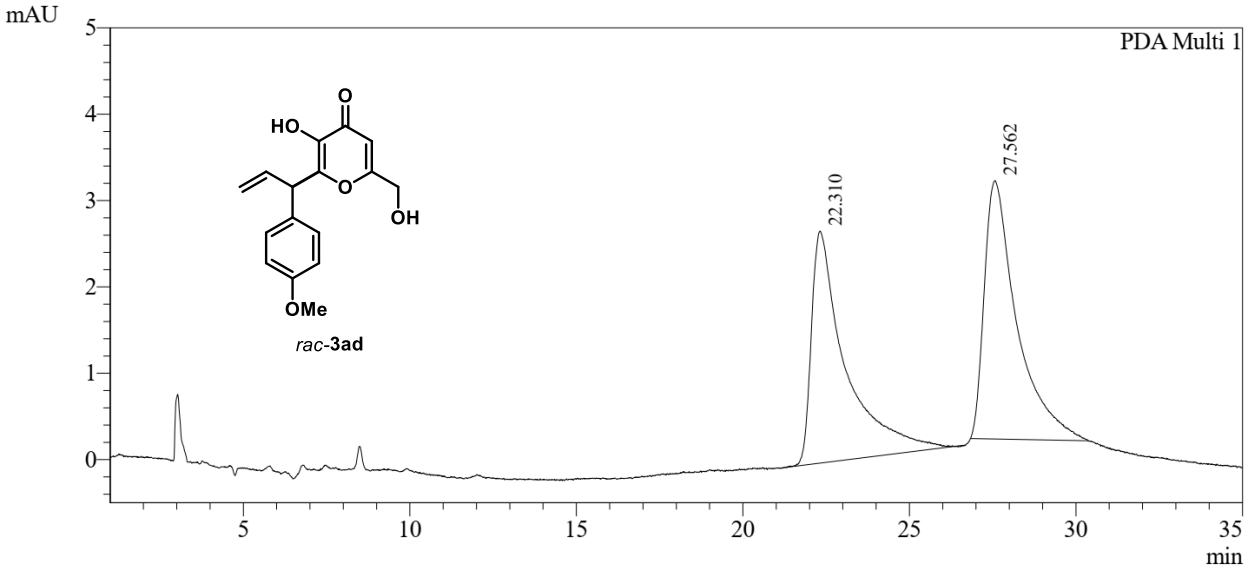


PeakTable

PDA Ch1 277nm 4nm

Peak#	Ret. Time	Area	Area %
1	13.794	17289900	100.000
Total		17289900	100.000


7.26
7.21
7.19
6.85
6.83
6.52
6.26
6.25
6.24
6.22
6.20
6.20
6.18
5.28
5.25
5.20
5.15
5.04
5.02
4.48
4.44
4.39
3.77
HO
O
O
OH
OMe
3ad
SKM-II-081-01
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
2.063
2.515
1.072
1.062
1.108
1.002
1.000
2.053
3.228
174.41
167.68
158.86
150.80
141.30
135.51
131.07
129.25
118.07
114.21
108.56
77.47
77.16
76.84
61.09
55.39
47.03
HO
O
O
OH
OMe
3ad
SKM-III-081-01
100 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

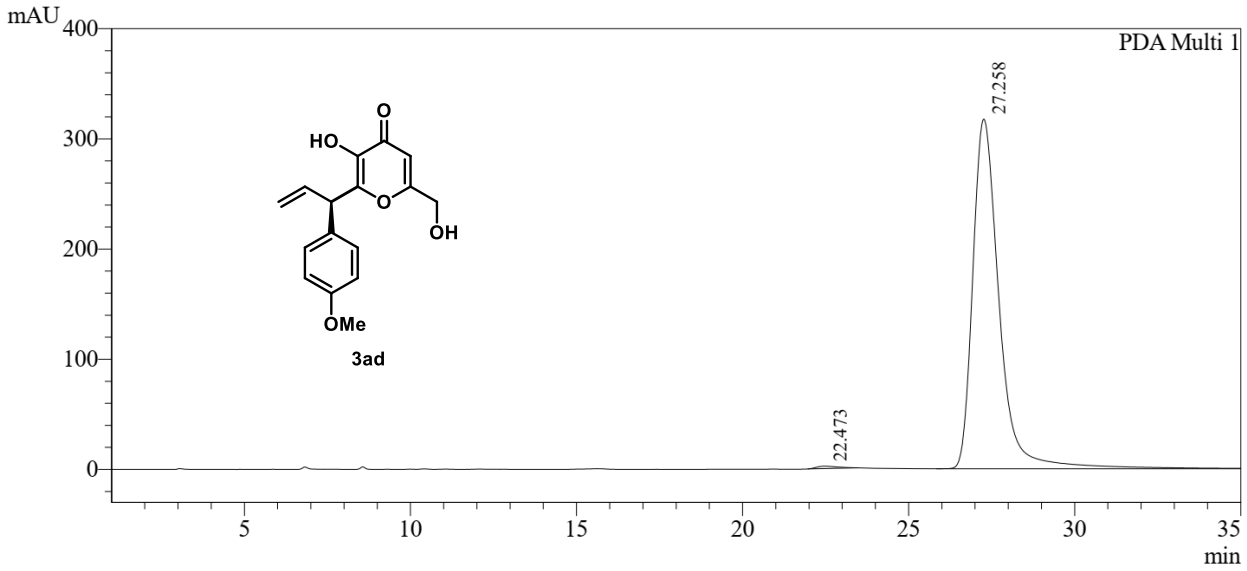


PeakTable

PDA Ch1 279nm 4nm

Peak#	Ret. Time	Area	Area %
1	22.310	191486	48.511
2	27.562	203241	51.489
Total		394727	100.000

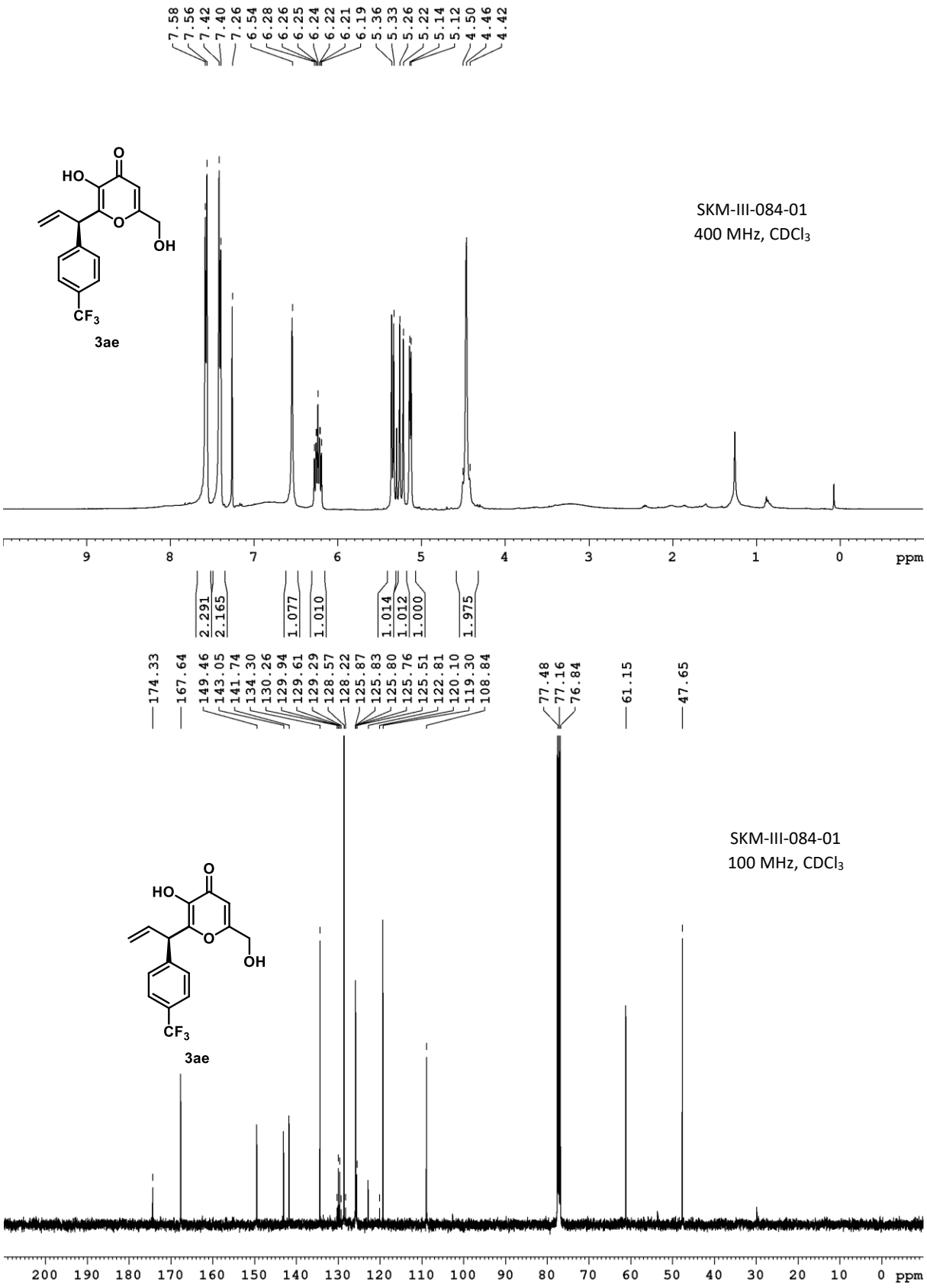
Daicel Chiralpak IG column (85:15 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

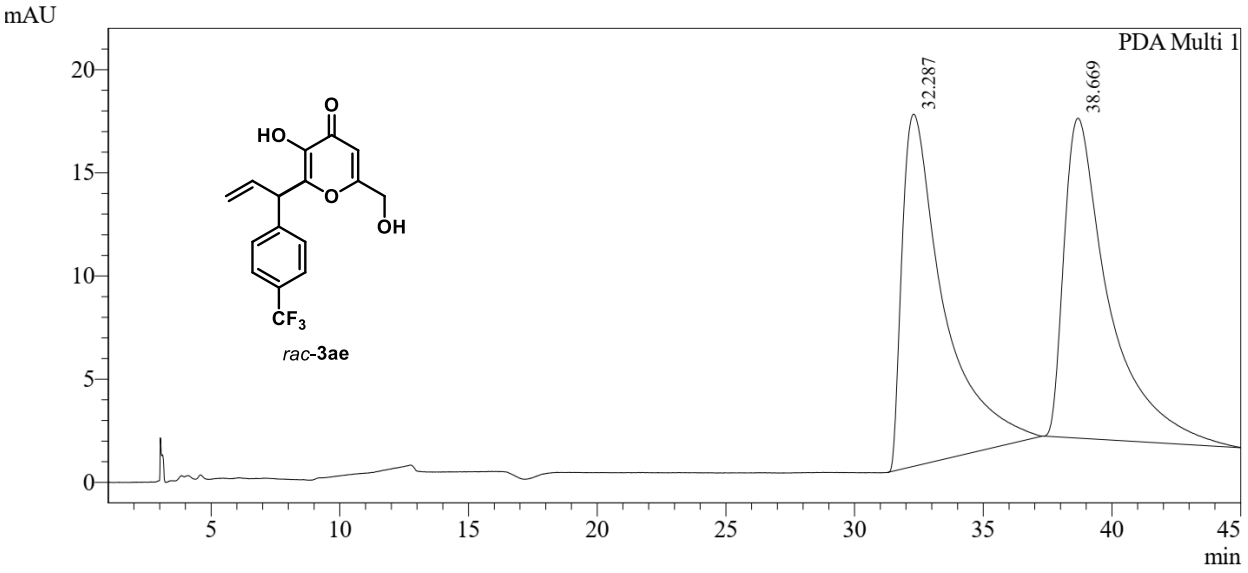


PeakTable

PDA Ch1 279nm 4nm

Peak#	Ret. Time	Area	Area %
1	22.473	100159	0.566
2	27.258	17597829	99.434
Total		17697988	100.000


7.58
7.56
7.42
7.40
7.26
6.54
6.28
6.26
6.25
6.24
6.22
6.21
6.19
5.36
5.33
5.26
5.22
5.14
5.12
4.50
4.46
4.42
HO
O
O
OH
CF3
3ae
SKM-III-084-01
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
2.291
2.165
1.077
1.010
1.014
1.012
1.000
1.975
174.33
167.64
149.46
143.05
141.74
134.30
130.26
129.94
129.61
129.29
128.57
128.22
125.87
125.83
125.80
125.76
125.51
122.81
120.10
119.30
108.84
77.48
77.16
76.84
61.15
47.65
SKM-III-084-01
100 MHz, CDCl3
HO
O
O
OH
CF3
3ae
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

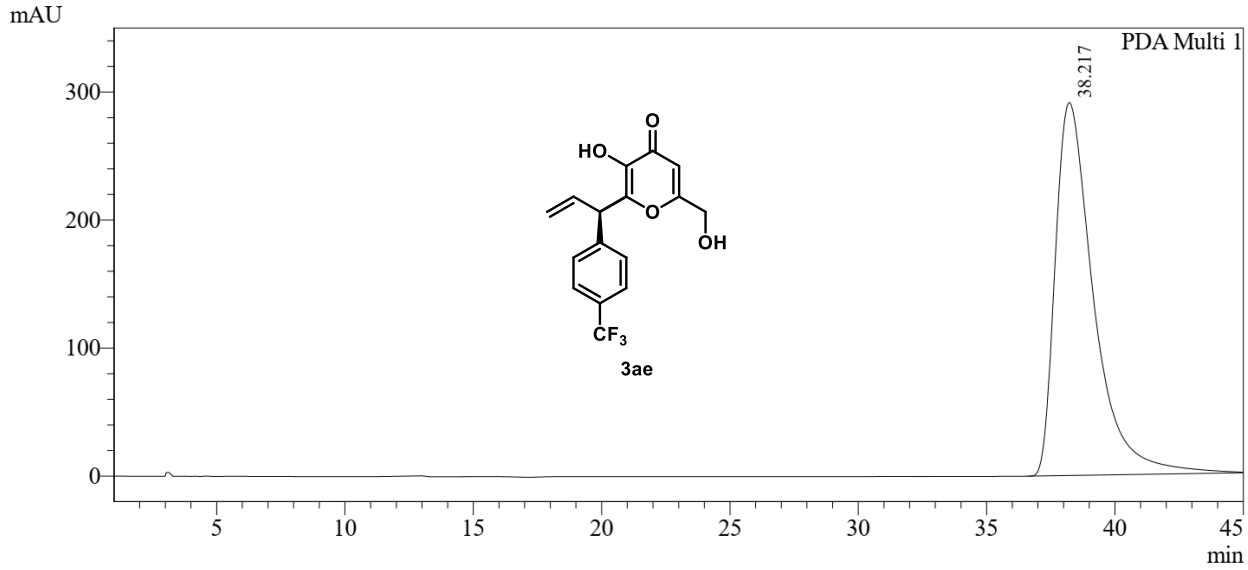


PeakTable

PDA Ch1 275nm 4nm

Peak#	Ret. Time	Area	Area %
1	32.287	1921425	50.558
2	38.669	1878982	49.442
Total		3800407	100.000

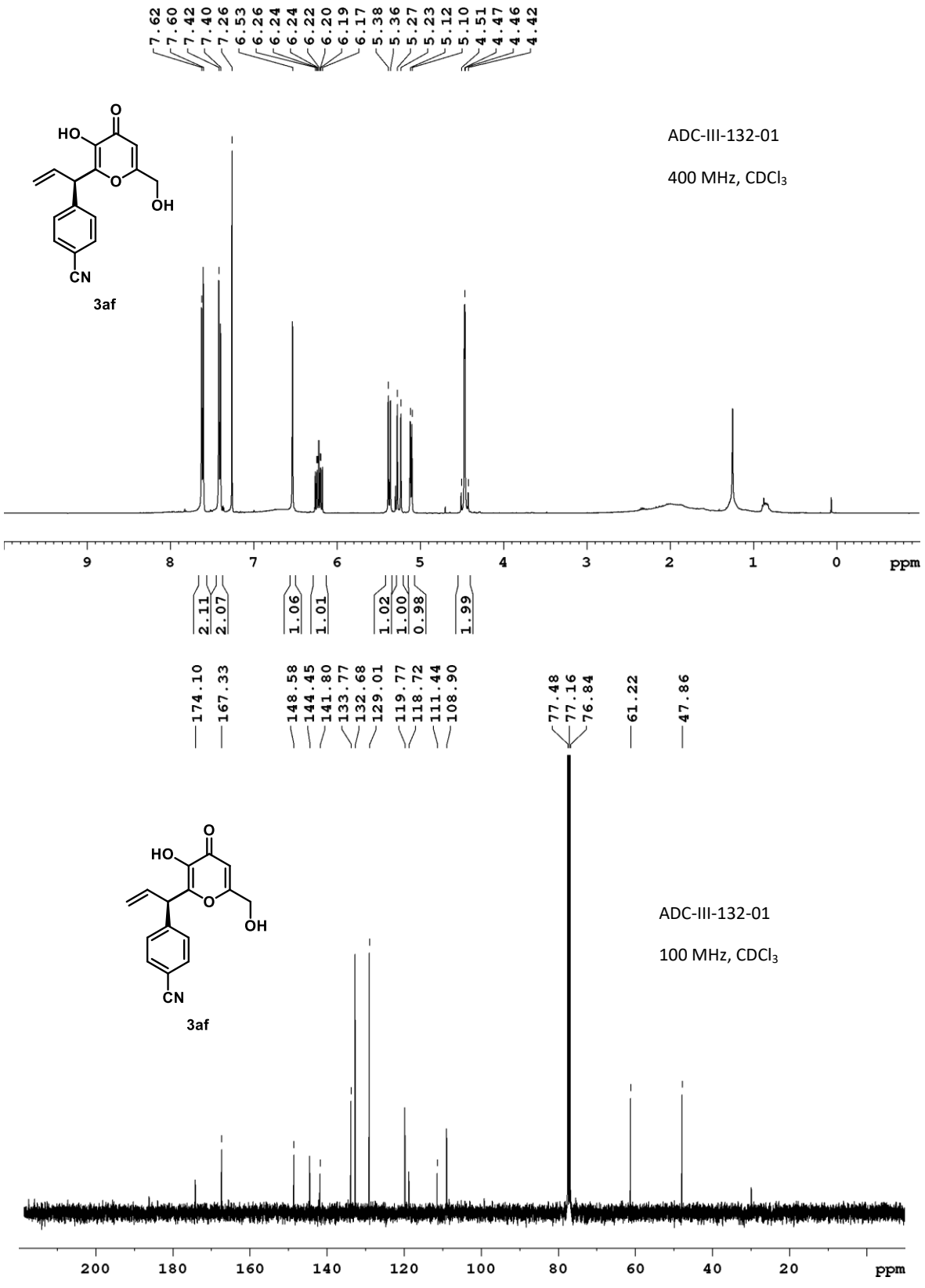
Daicel Chiralpak AD-H column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

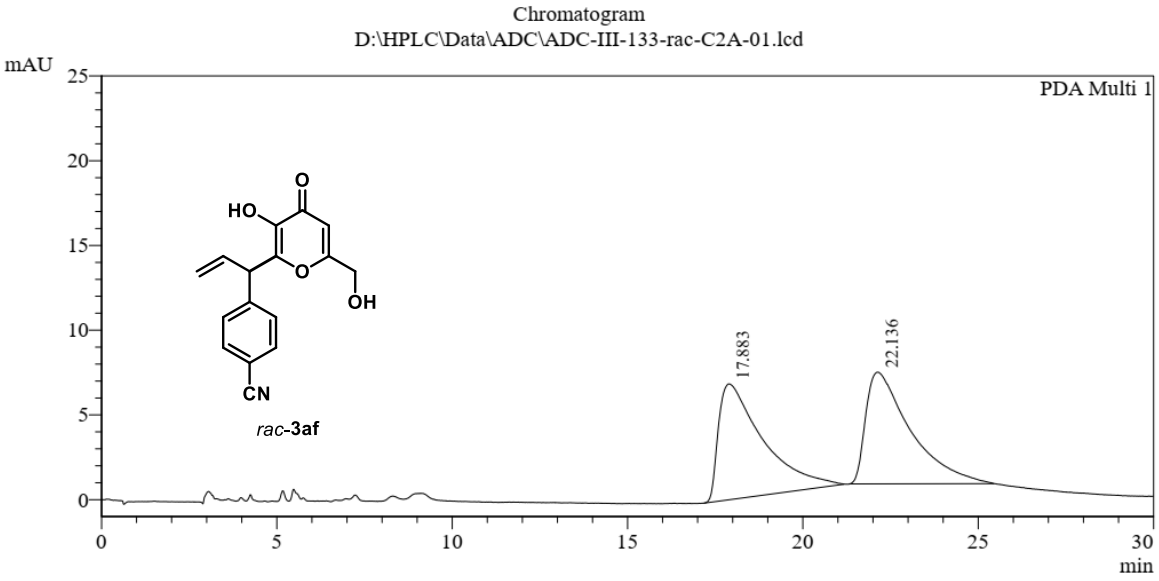


PeakTable

PDA Ch1 275nm 4nm

Peak#	Ret. Time	Area	Area %
1	38.217	30361885	100.000
Total		30361885	100.000


7.62
7.60
7.42
7.40
7.26
6.53
6.26
6.24
6.24
6.22
6.20
6.19
6.17
5.38
5.36
5.27
5.23
5.12
5.10
4.51
4.47
4.46
4.42
HO
O
O
OH
CN
3af
ADC-III-132-01
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
2.11
2.07
1.06
1.01
1.02
1.00
0.98
1.99
174.10
167.33
148.58
144.45
141.80
133.77
132.68
129.01
119.77
118.72
111.44
108.90
77.48
77.16
76.84
61.22
47.86
HO
O
O
OH
CN
3af
ADC-III-132-01
100 MHz, CDCl3
200
180
160
140
120
100
80
60
40
20
ppm

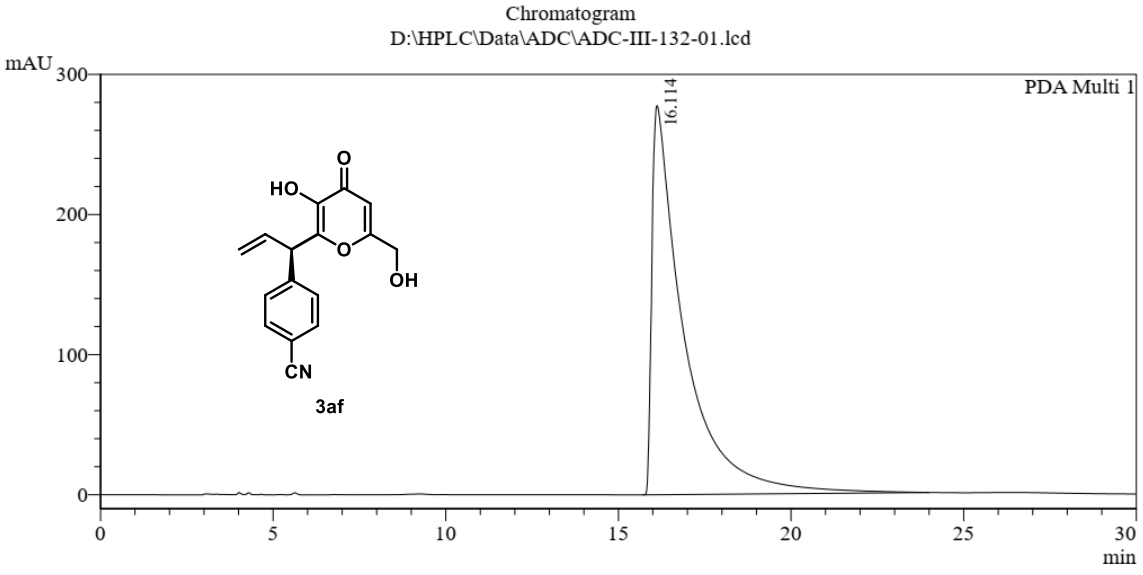


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	17.883	600801	50.724
2	22.136	583654	49.276
Total		1184455	100.000

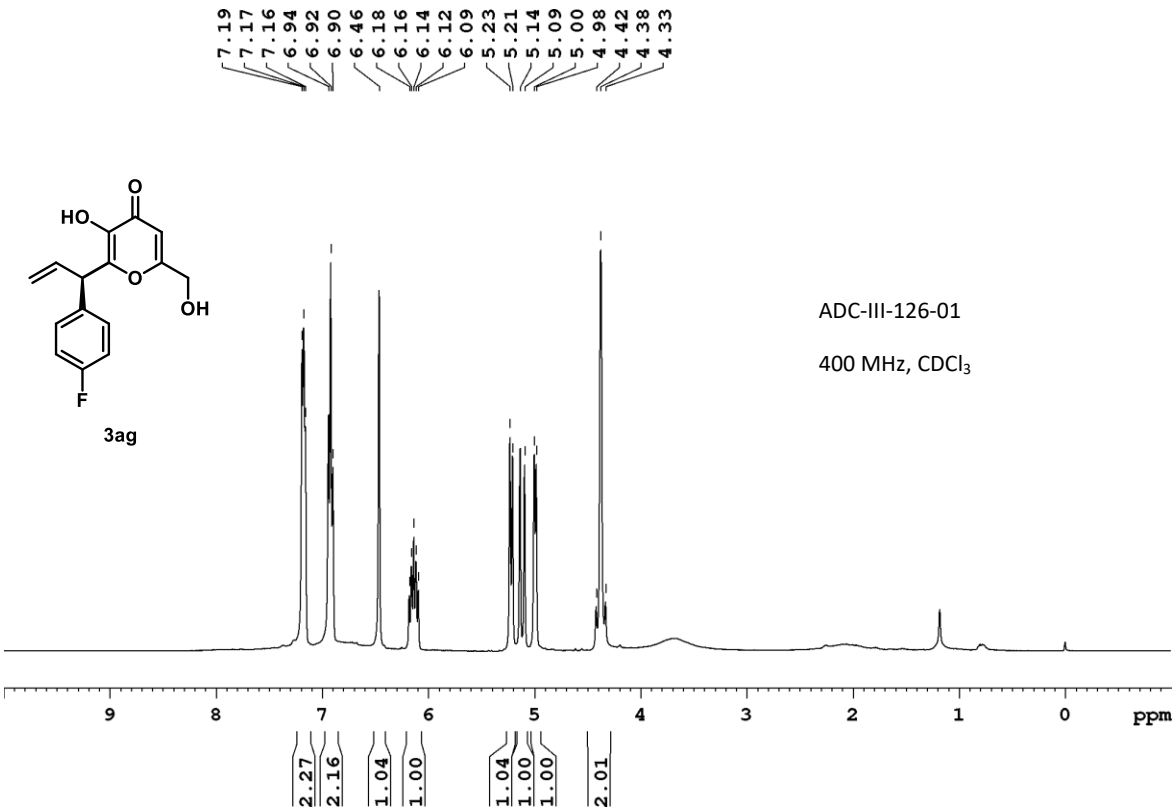
Phenomenex Amylose-2 column (75:25 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

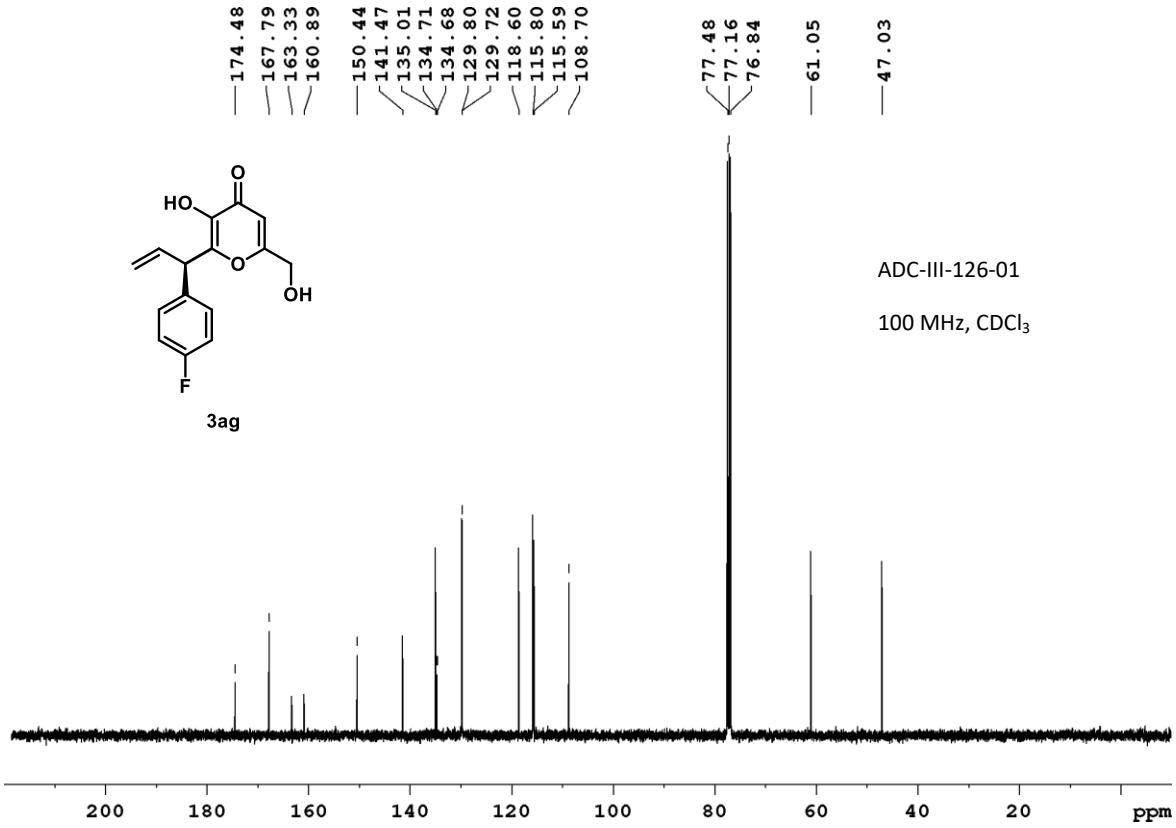


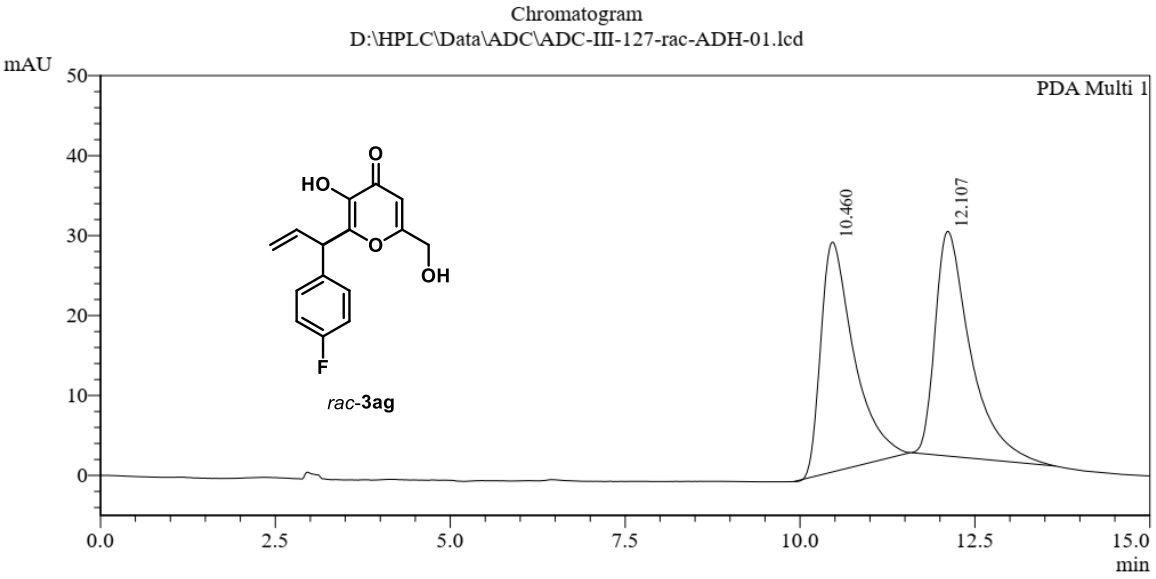
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	16.114	17964377	100.000
Total		17964377	100.000


7.19
7.17
7.16
6.94
6.92
6.90
6.46
6.18
6.16
6.14
6.12
6.09
5.23
5.21
5.14
5.09
5.00
4.98
4.42
4.38
4.33
HO
O
O
OH
F
3ag
ADC-III-126-01
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
2.27
2.16
1.04
1.00
1.04
1.00
1.00
2.01


174.48
167.79
163.33
160.89
150.44
141.47
135.01
134.71
134.68
129.80
129.72
118.60
115.80
115.59
108.70
77.48
77.16
76.84
61.05
47.03
HO
O
O
OH
F
3ag
ADC-III-126-01
100 MHz, CDCl3
200
180
160
140
120
100
80
60
40
20
ppm



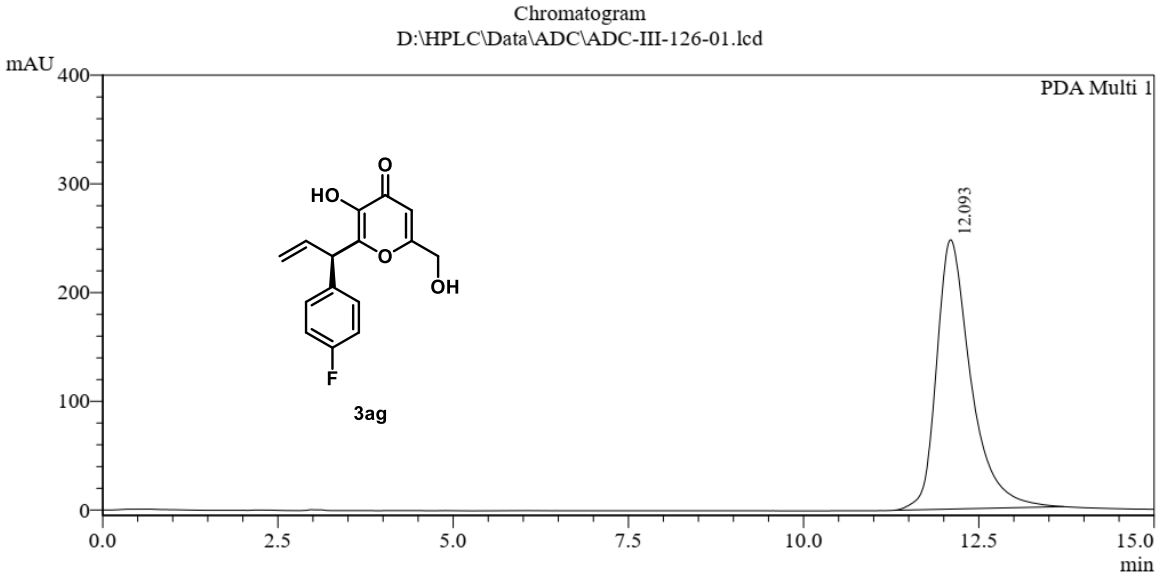
PeakTable

PDA Ch1 283nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.460	949262	48.929
2	12.107	990827	51.071
Total		1940089	100.000

Da

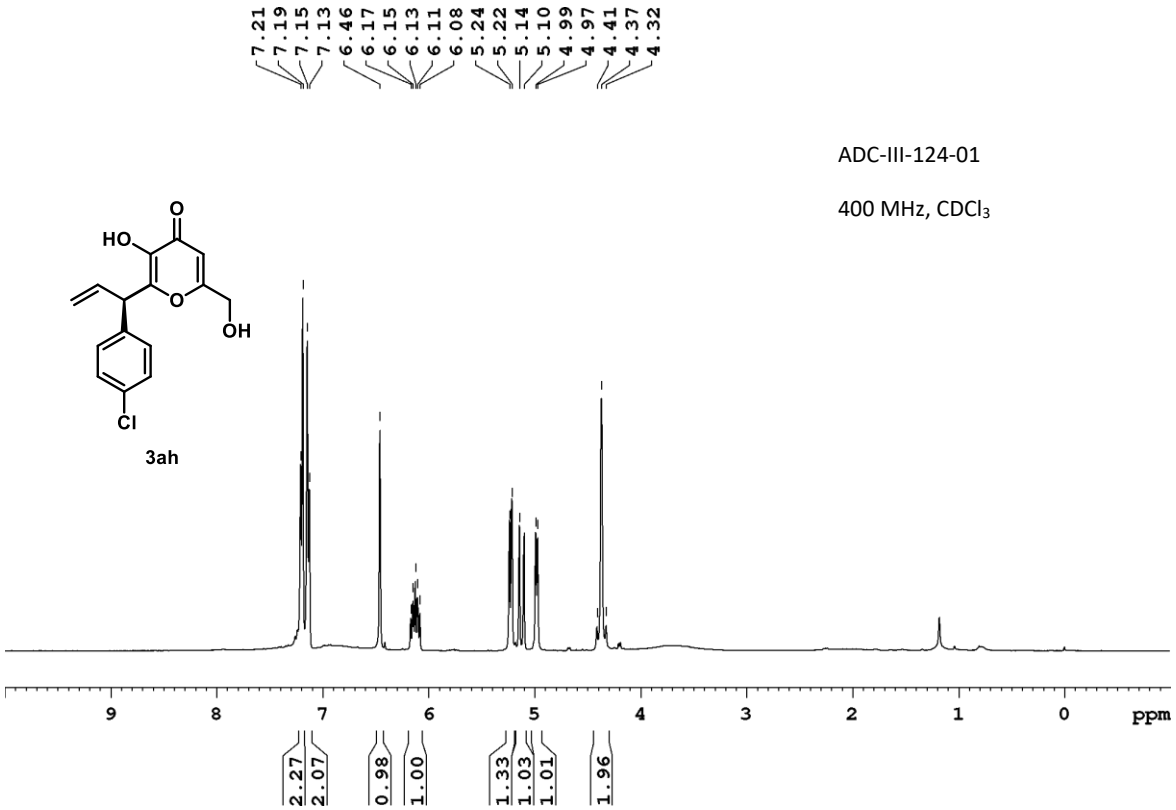
icel Chiralpak AD-H column (85:15 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

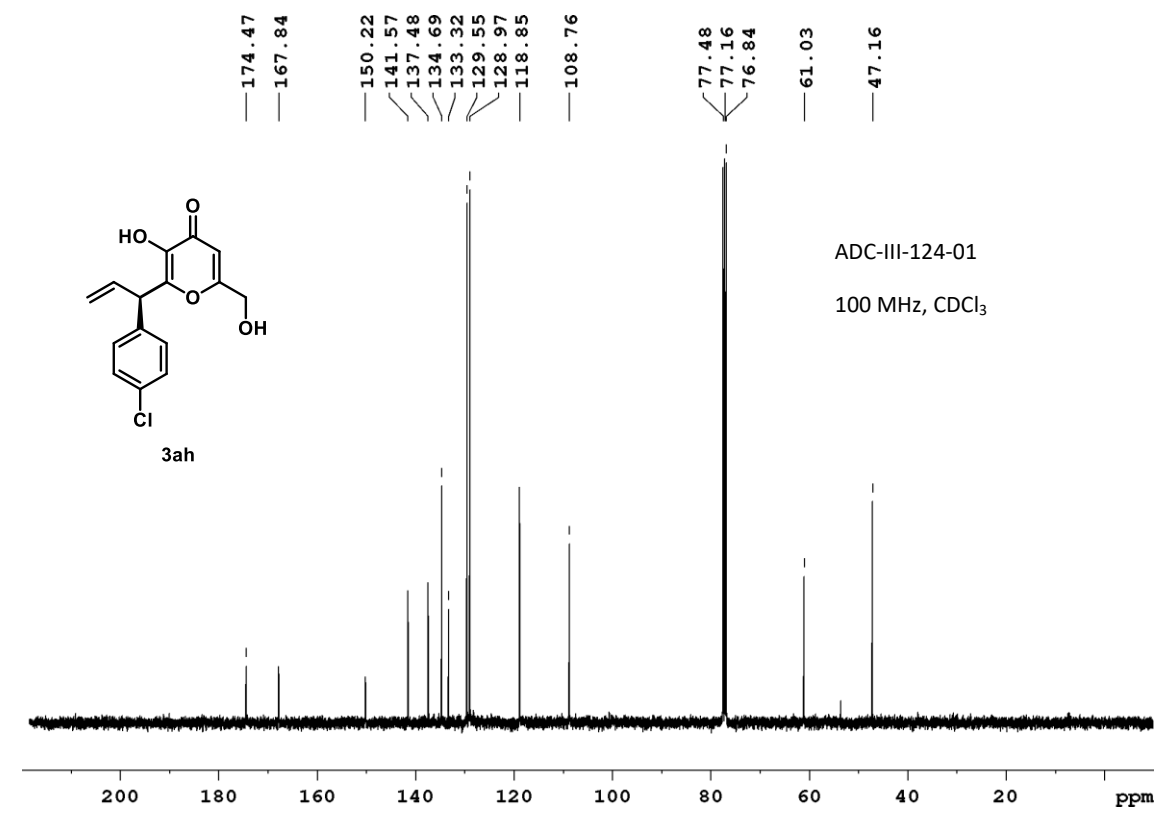


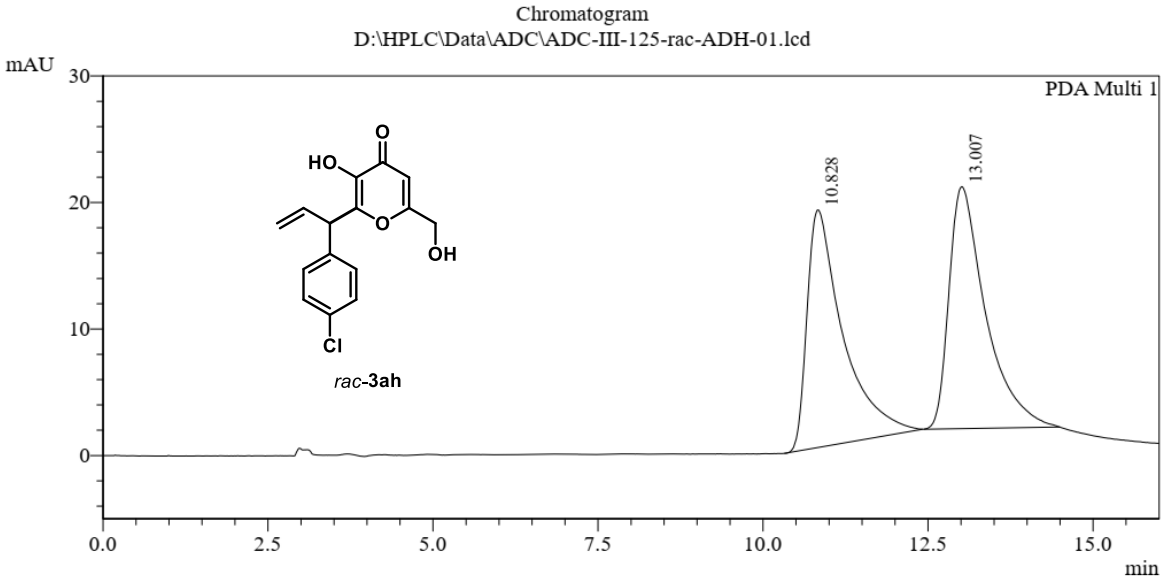
PeakTable

PDA Ch1 283nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.093	8457622	100.000
Total		8457622	100.000


7.21
7.19
7.15
7.13
6.46
6.17
6.15
6.13
6.11
6.08
5.24
5.22
5.14
5.10
4.99
4.97
4.41
4.37
4.32
ADC-III-124-01
400 MHz, CDCl3
HO
O
O
OH
Cl
3ah
9
8
7
6
5
4
3
2
1
0
ppm
2.27
2.07
0.98
1.00
1.33
1.03
1.01
1.96


174.47
167.84
150.22
141.57
137.48
134.69
133.32
129.55
128.97
118.85
108.76
77.48
77.16
76.84
61.03
47.16
ADC-III-124-01
100 MHz, CDCl3
HO
O
O
OH
Cl
3ah
200
180
160
140
120
100
80
60
40
20
ppm

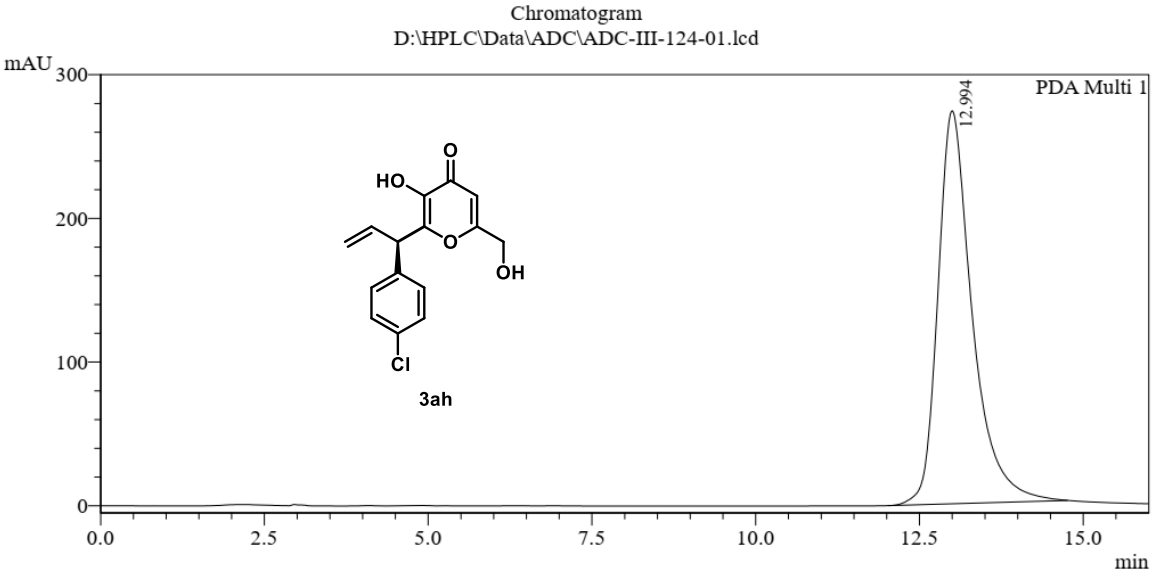


PeakTable

PDA Ch1 282nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.828	710118	49.015
2	13.007	738662	50.985
Total		1448780	100.000

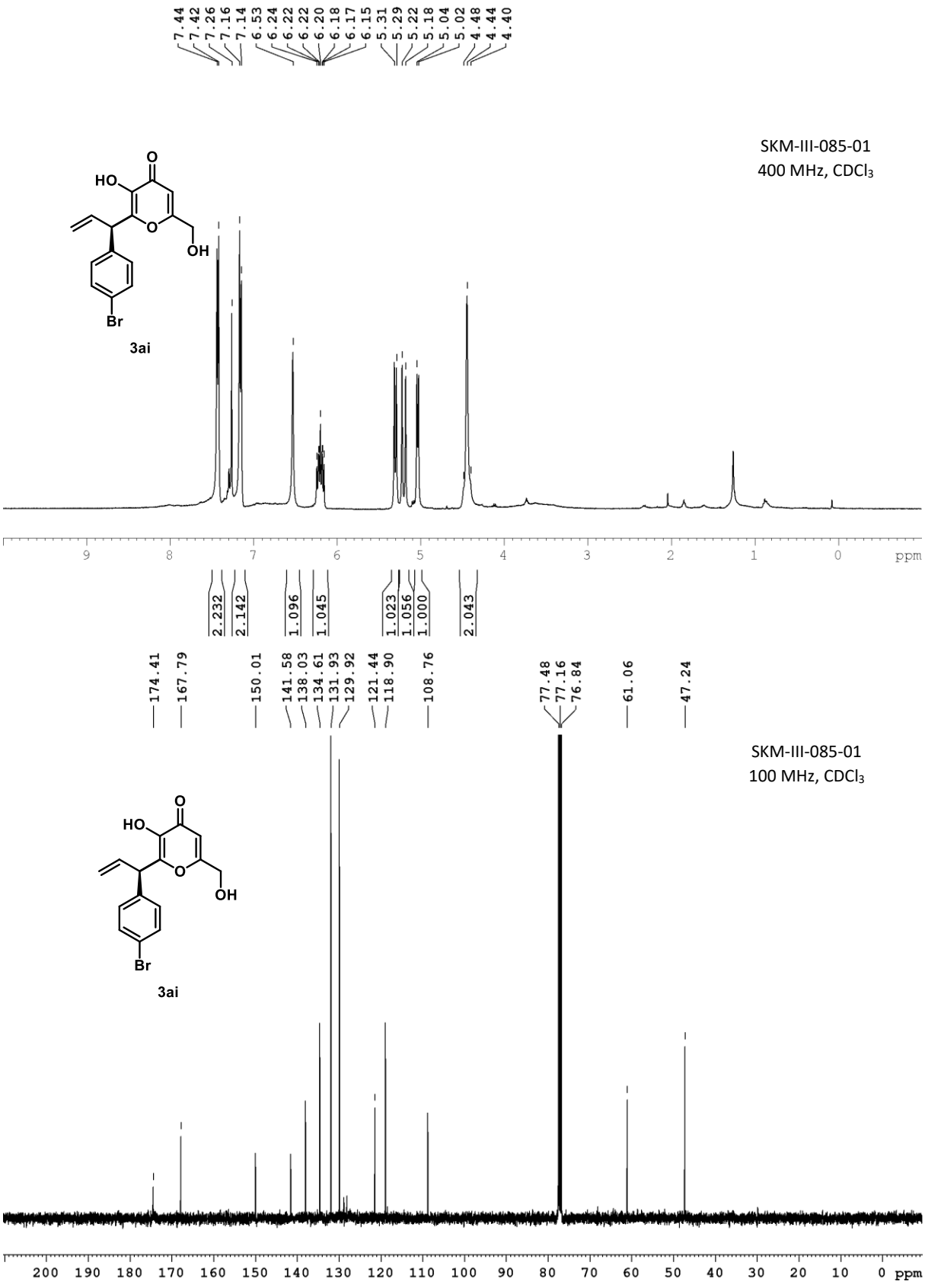
Daicel Chiralpak AD-H column (85:15 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

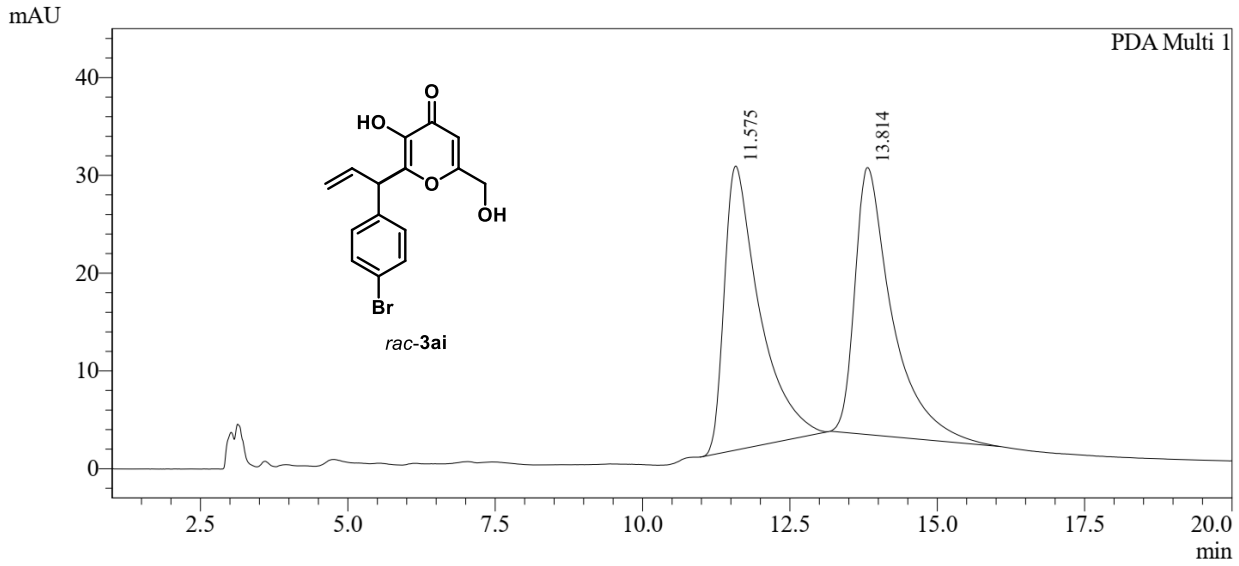


PeakTable

PDA Ch1 282nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.994	9983031	100.000
Total		9983031	100.000


7.44
7.42
7.26
7.16
7.14
6.53
6.24
6.22
6.22
6.20
6.18
6.17
6.15
5.31
5.29
5.22
5.18
5.04
5.02
4.48
4.44
4.40
SKM-III-085-01
400 MHz, CDCl3
HO
O
O
OH
Br
3ai
9
8
7
6
5
4
3
2
1
0
ppm
2.232
2.142
1.096
1.045
1.023
1.056
1.000
2.043
174.41
167.79
150.01
141.58
138.03
134.61
131.93
129.92
121.44
118.90
108.76
77.48
77.16
76.84
61.06
47.24
SKM-III-085-01
100 MHz, CDCl3
HO
O
O
OH
Br
3ai
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm



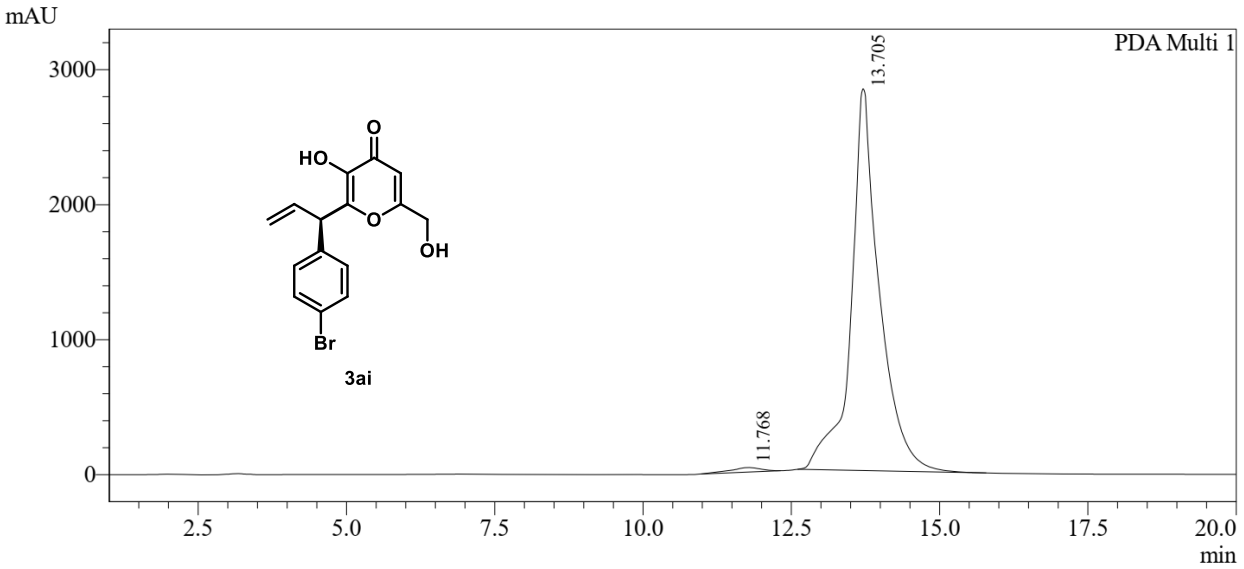
rac-**3ai**

PeakTable

PDA Ch1 222nm 4nm

Peak#	Ret. Time	Area	Area %
1	11.575	1208357	50.125
2	13.814	1202307	49.875
Total		2410664	100.000

Daicel Chiralpak AD-H column (85:15 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

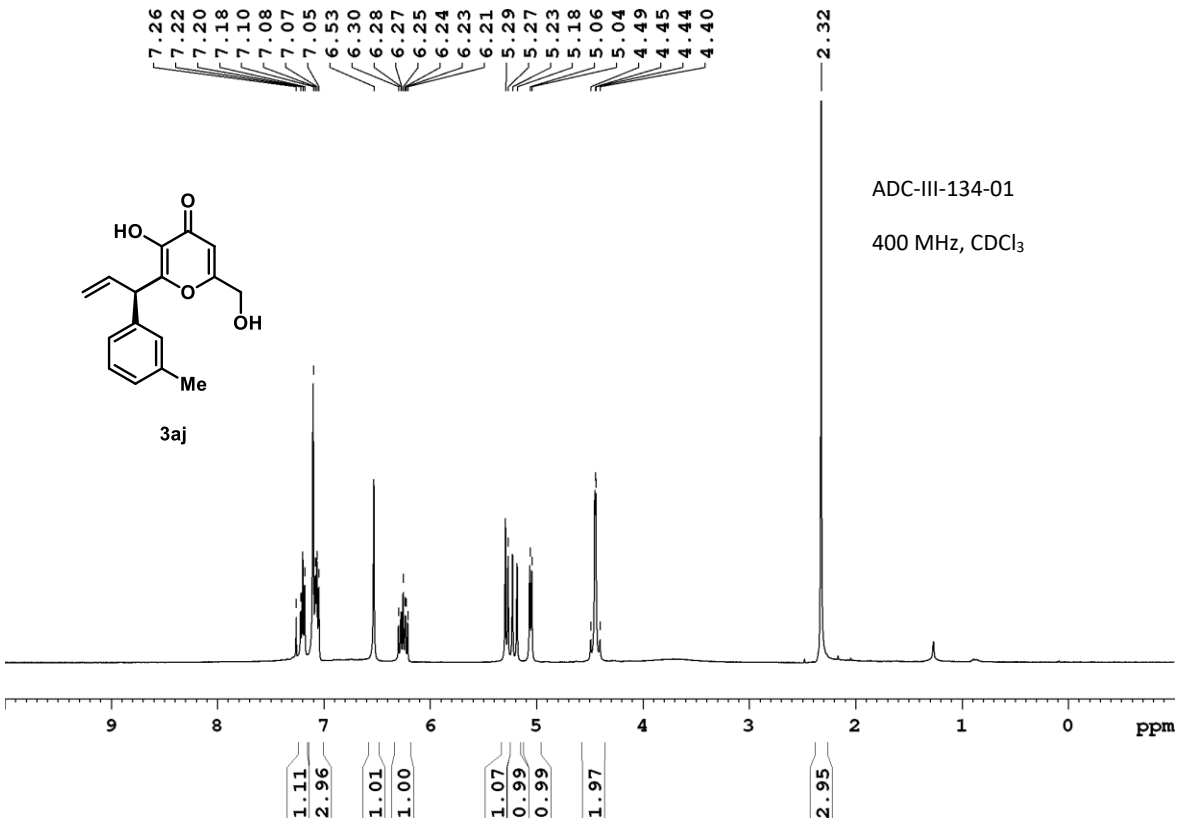


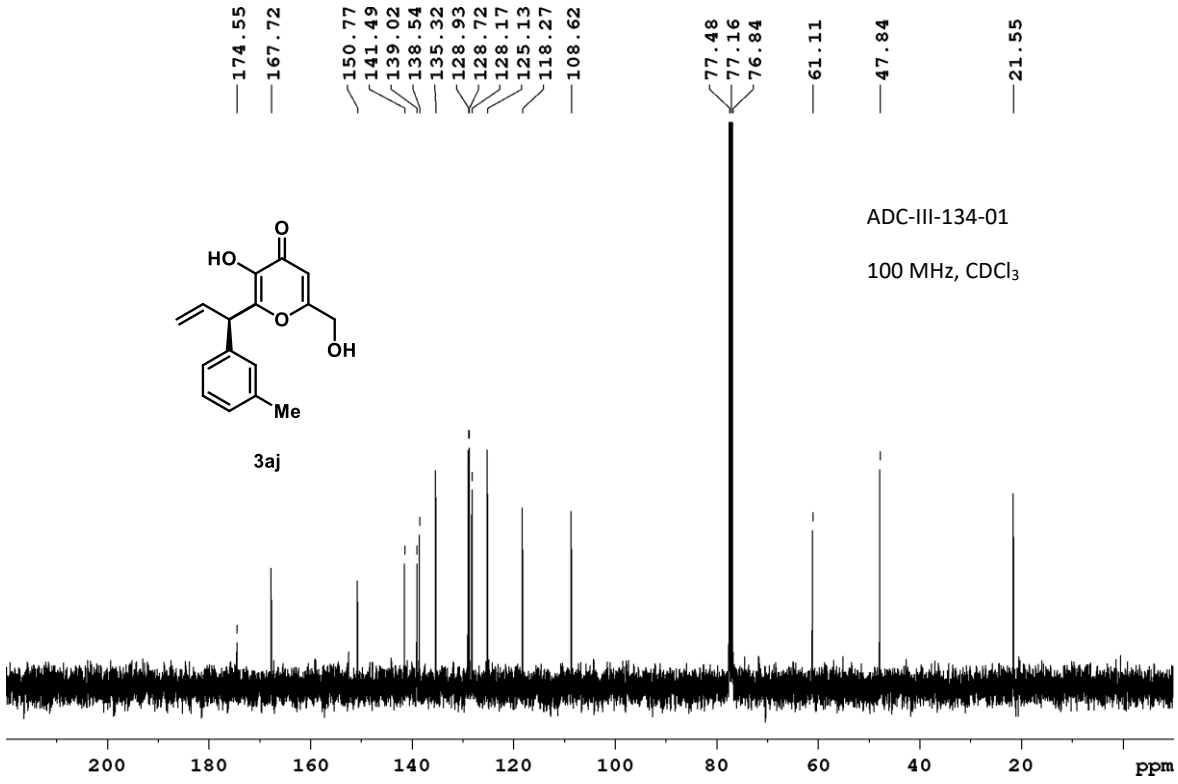
3ai

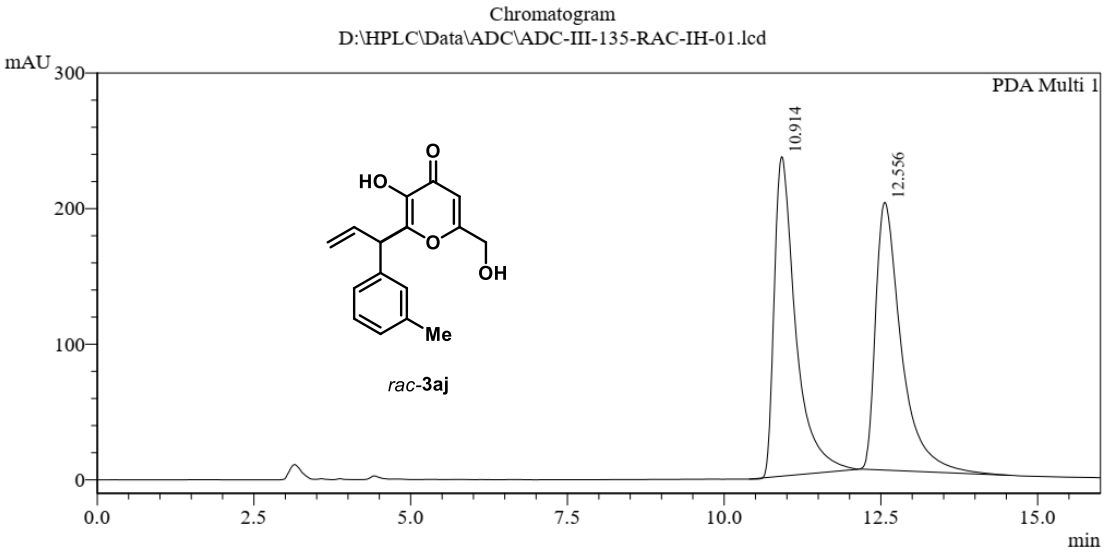
PeakTable

PDA Ch1 222nm 4nm

Peak#	Ret. Time	Area	Area %
1	11.768	1242475	1.301
2	13.705	94281879	98.699
Total		95524354	100.000


7.26
7.22
7.20
7.18
7.10
7.08
7.07
7.05
6.53
6.30
6.28
6.27
6.25
6.24
6.23
6.21
5.29
5.27
5.23
5.18
5.06
5.04
4.49
4.45
4.44
4.40
2.32
ADC-III-134-01
400 MHz, CDCl3
HO
O
O
OH
Me
3aj
9
8
7
6
5
4
3
2
1
0
ppm
1.11
2.96
1.01
1.00
1.07
0.99
0.99
1.97
2.95


174.55
167.72
150.77
141.49
139.02
138.54
135.32
128.93
128.72
128.17
125.13
118.27
108.62
77.48
77.16
76.84
61.11
47.84
21.55
ADC-III-134-01
100 MHz, CDCl3
HO
O
O
OH
Me
3aj
200
180
160
140
120
100
80
60
40
20
ppm

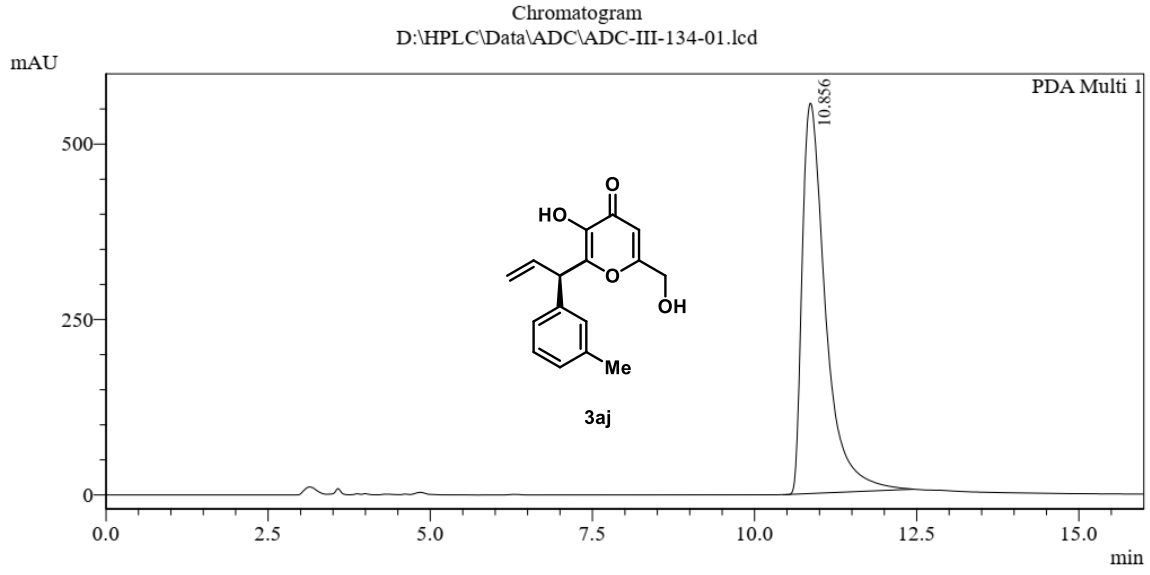


PeakTable

PDA Ch1 215nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.914	5618243	49.850
2	12.556	5652037	50.150
Total		11270280	100.000

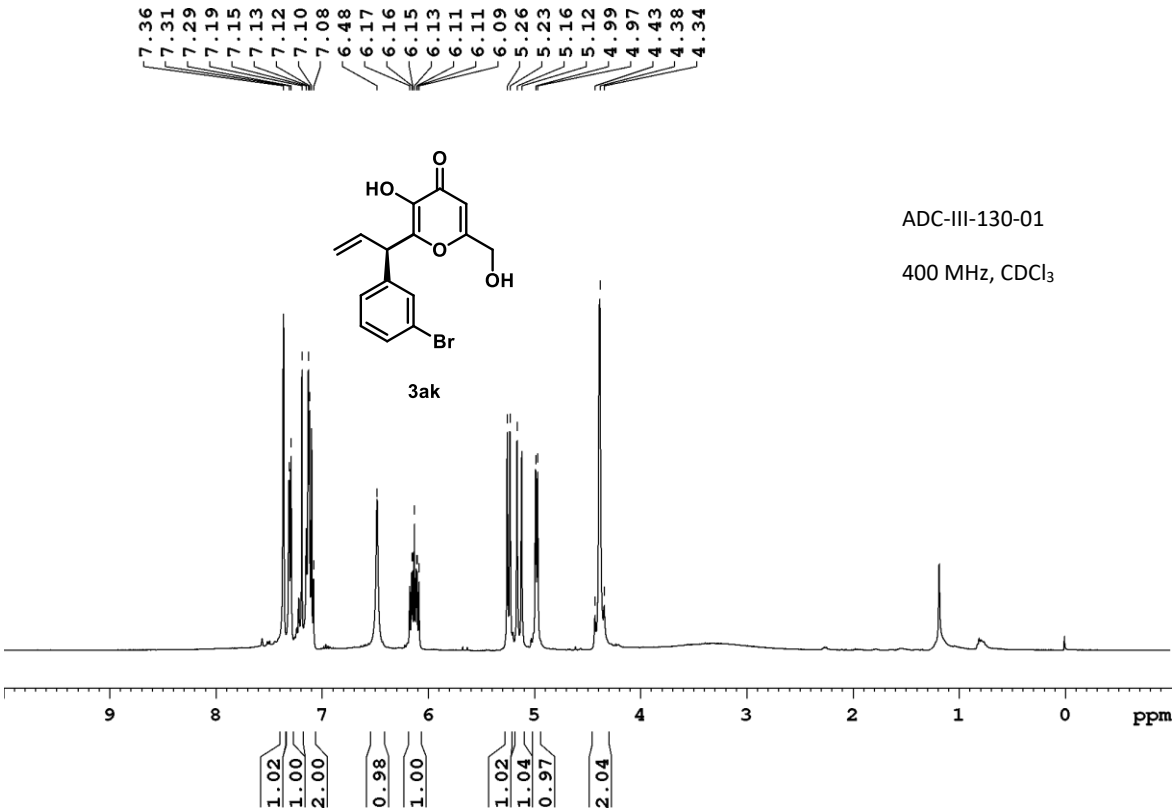
Daicel Chiralpak IH column (85:15 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

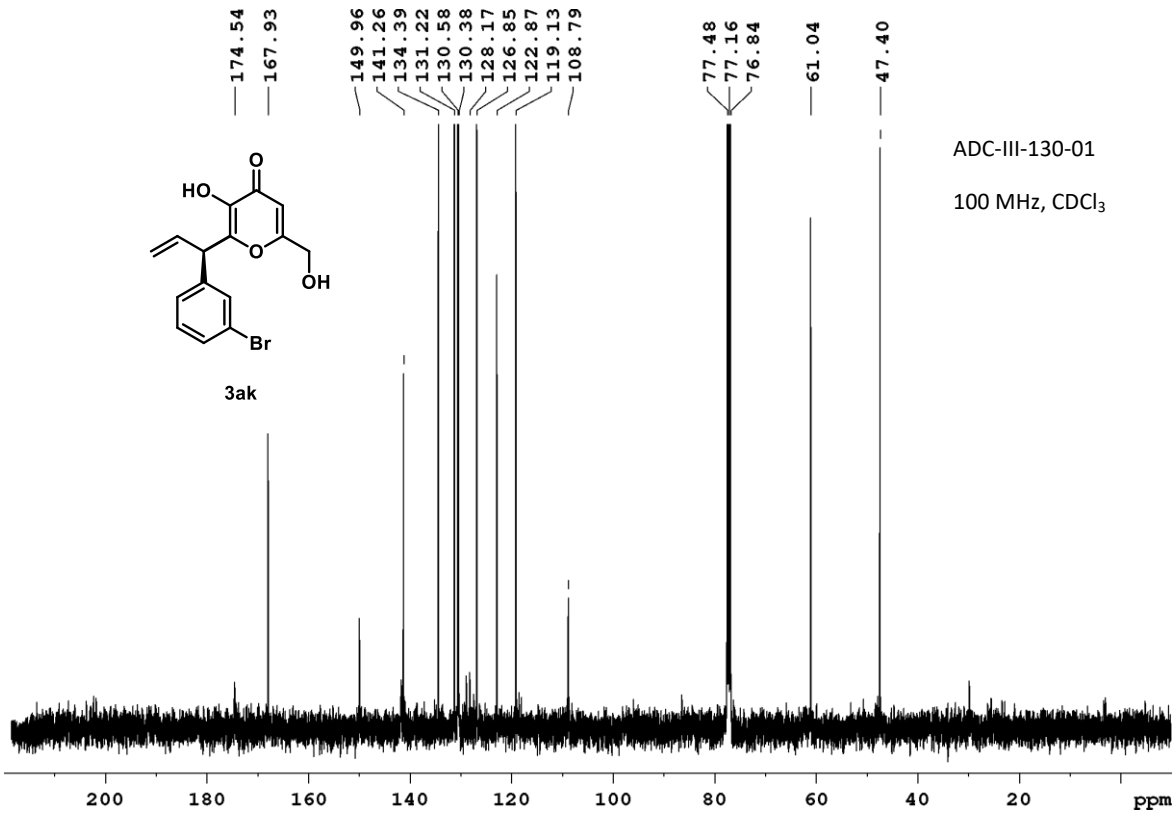


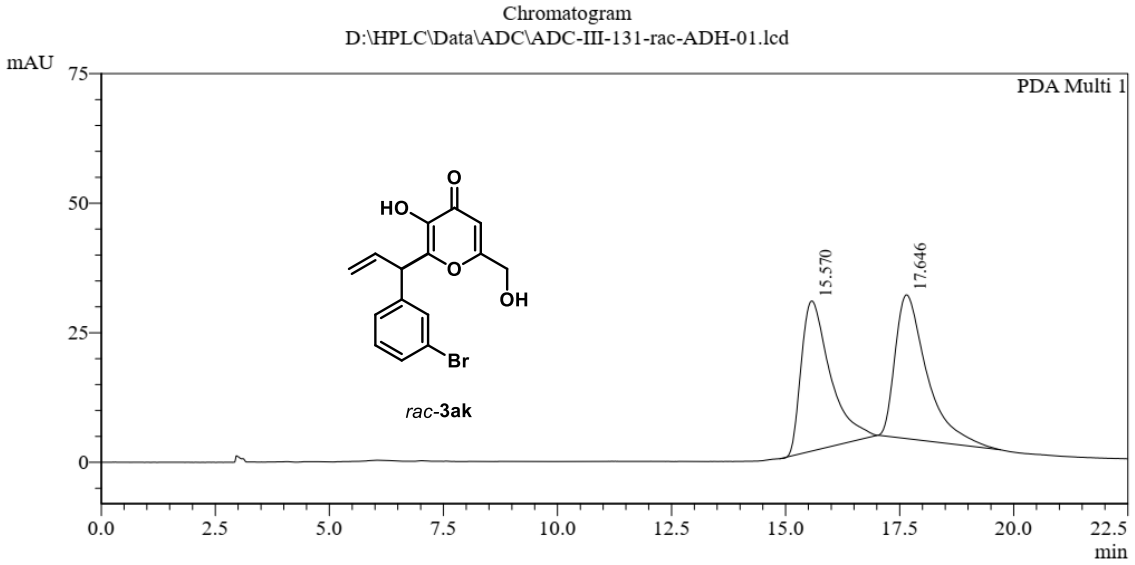
PeakTable

PDA Ch1 215nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.856	14000208	100.000
Total		14000208	100.000


7.36
7.31
7.29
7.19
7.15
7.13
7.12
7.10
7.08
6.48
6.17
6.16
6.15
6.13
6.11
6.11
6.09
5.26
5.23
5.16
5.12
4.99
4.97
4.43
4.38
4.34
HO
O
O
OH
Br
3ak
ADC-III-130-01
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.00
2.00
0.98
1.00
1.02
1.04
0.97
2.04


174.54
167.93
149.96
141.26
134.39
131.22
130.58
130.38
128.17
126.85
122.87
119.13
108.79
77.48
77.16
76.84
61.04
47.40
HO
O
O
OH
Br
3ak
ADC-III-130-01
100 MHz, CDCl3
200
180
160
140
120
100
80
60
40
20
ppm

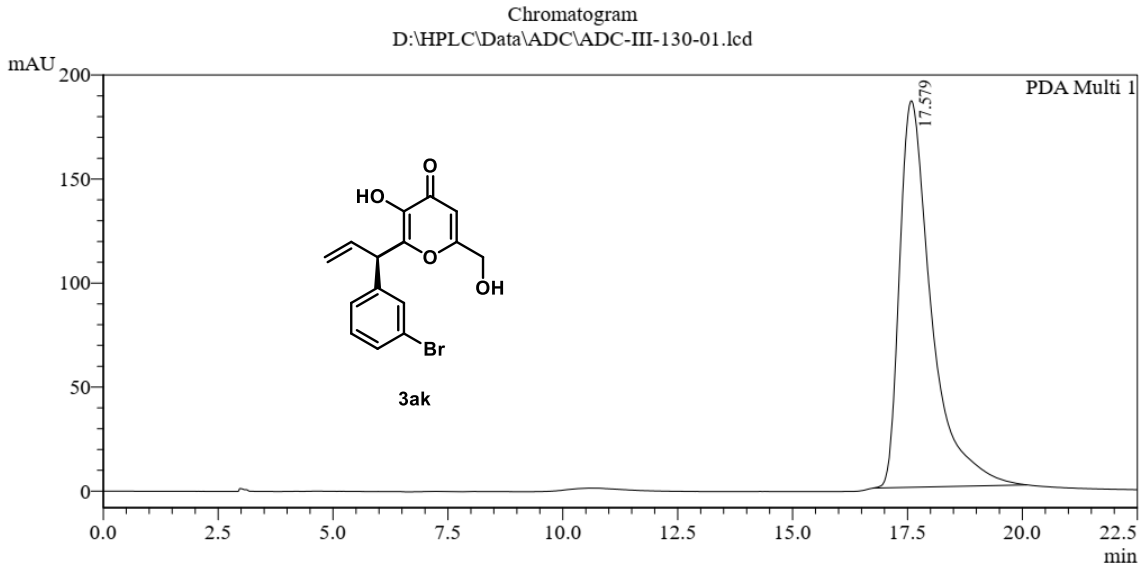


PeakTable

PDA Ch1 276nm 4nm

Peak#	Ret. Time	Area	Area %
1	15.570	1280722	48.752
2	17.646	1346295	51.248
Total		2627017	100.000

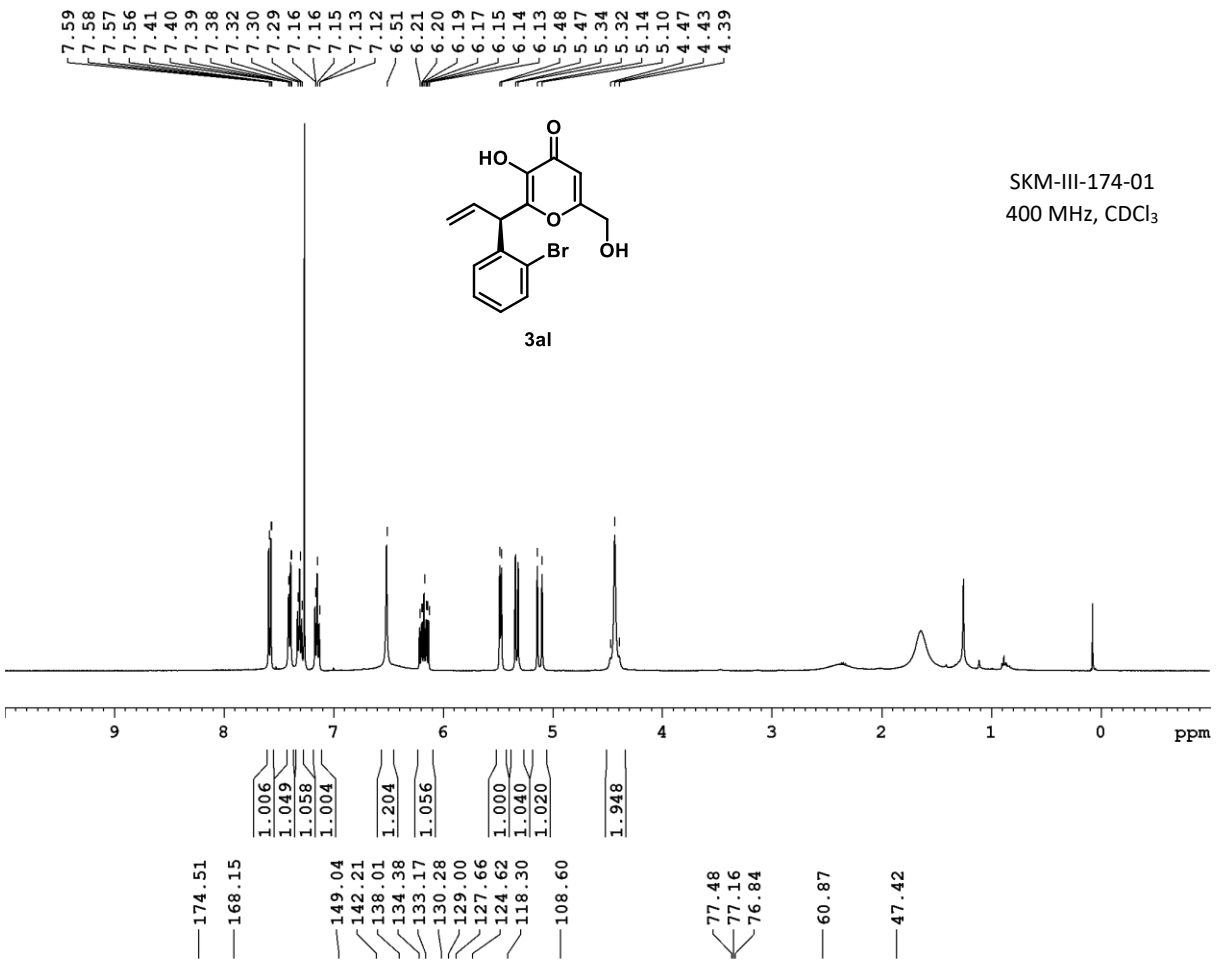
Daicel Chiralpak AD-H column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

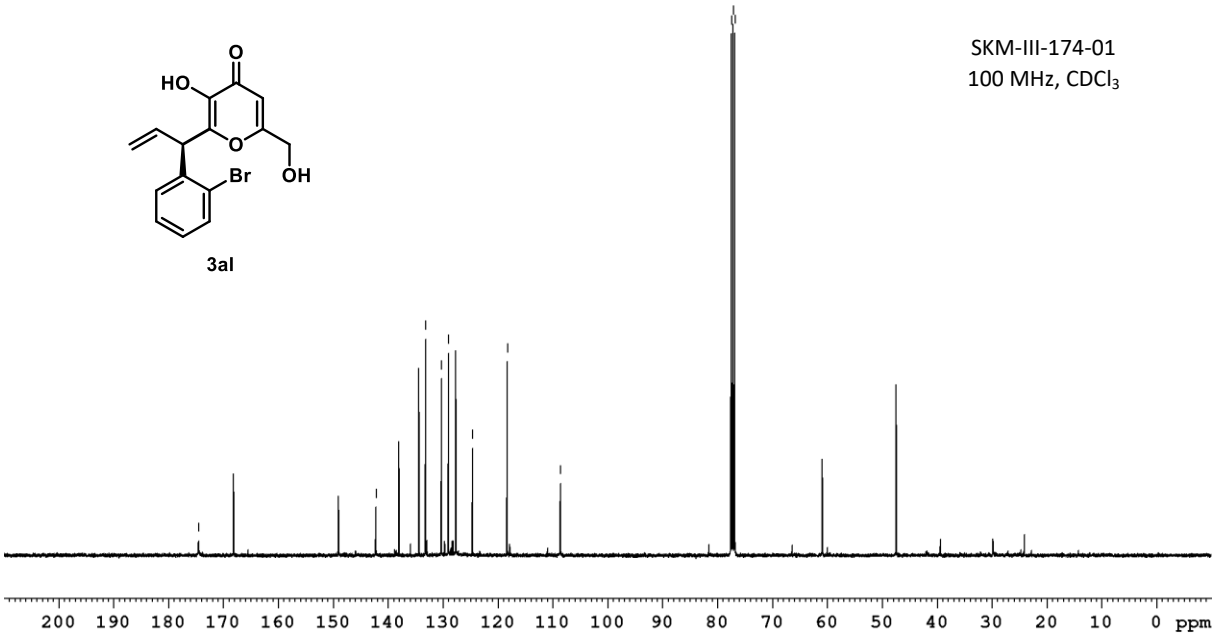


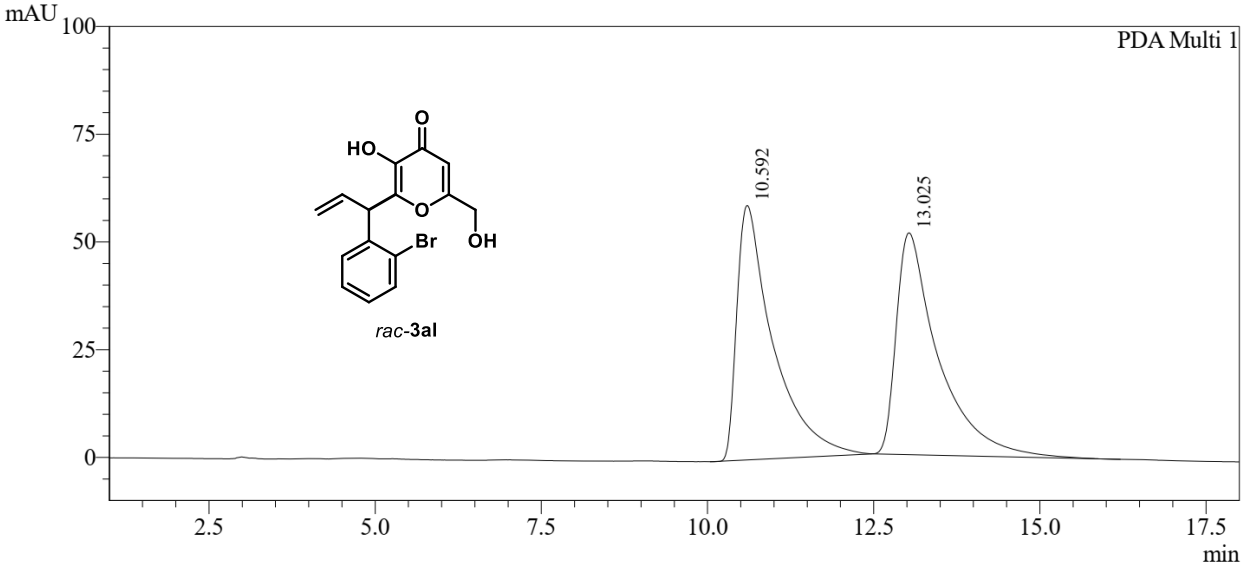
PeakTable

PDA Ch1 276nm 4nm

Peak#	Ret. Time	Area	Area %
1	17.579	8950689	100.000
Total		8950689	100.000


7.59
7.58
7.57
7.56
7.41
7.40
7.39
7.38
7.32
7.30
7.29
7.16
7.16
7.15
7.13
7.12
6.51
6.21
6.20
6.19
6.17
6.15
6.14
6.13
5.48
5.47
5.34
5.32
5.14
5.10
4.47
4.43
4.39
HO
O
O
Br
OH
3aI
SKM-III-174-01
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
1.006
1.049
1.058
1.004
1.204
1.056
1.000
1.040
1.020
1.948
174.51
168.15
149.04
142.21
138.01
134.38
133.17
130.28
129.00
127.66
124.62
118.30
108.60
77.48
77.16
76.84
60.87
47.42


HO
O
O
Br
OH
3aI
SKM-III-174-01
100 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

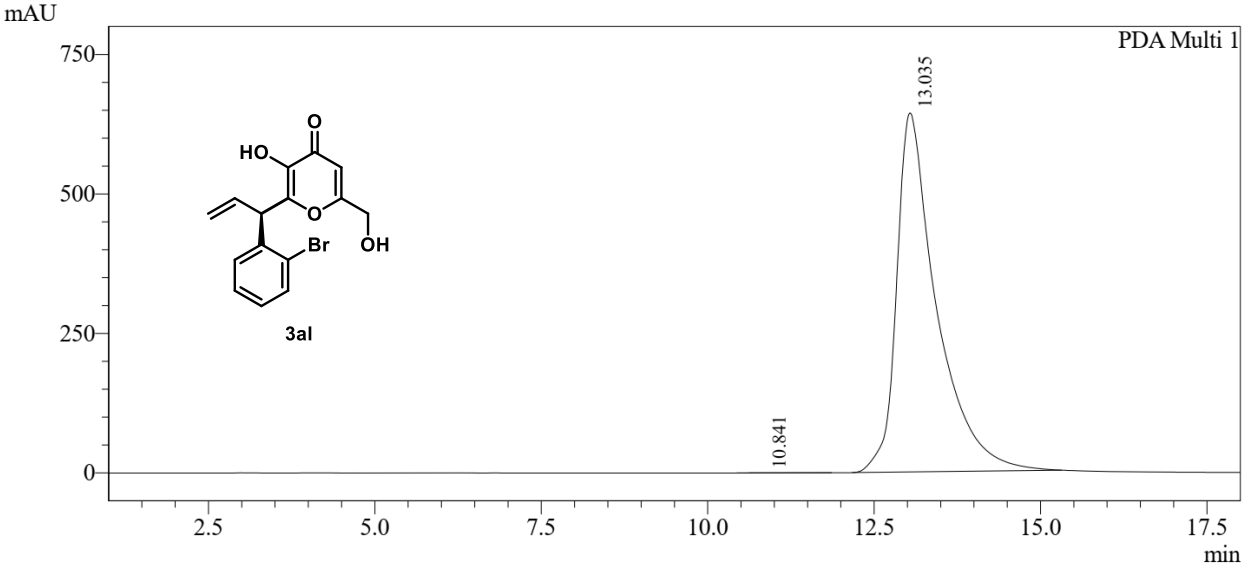


PeakTable

PDA Ch1 280nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.592	2237312	49.770
2	13.025	2257984	50.230
Total		4495297	100.000

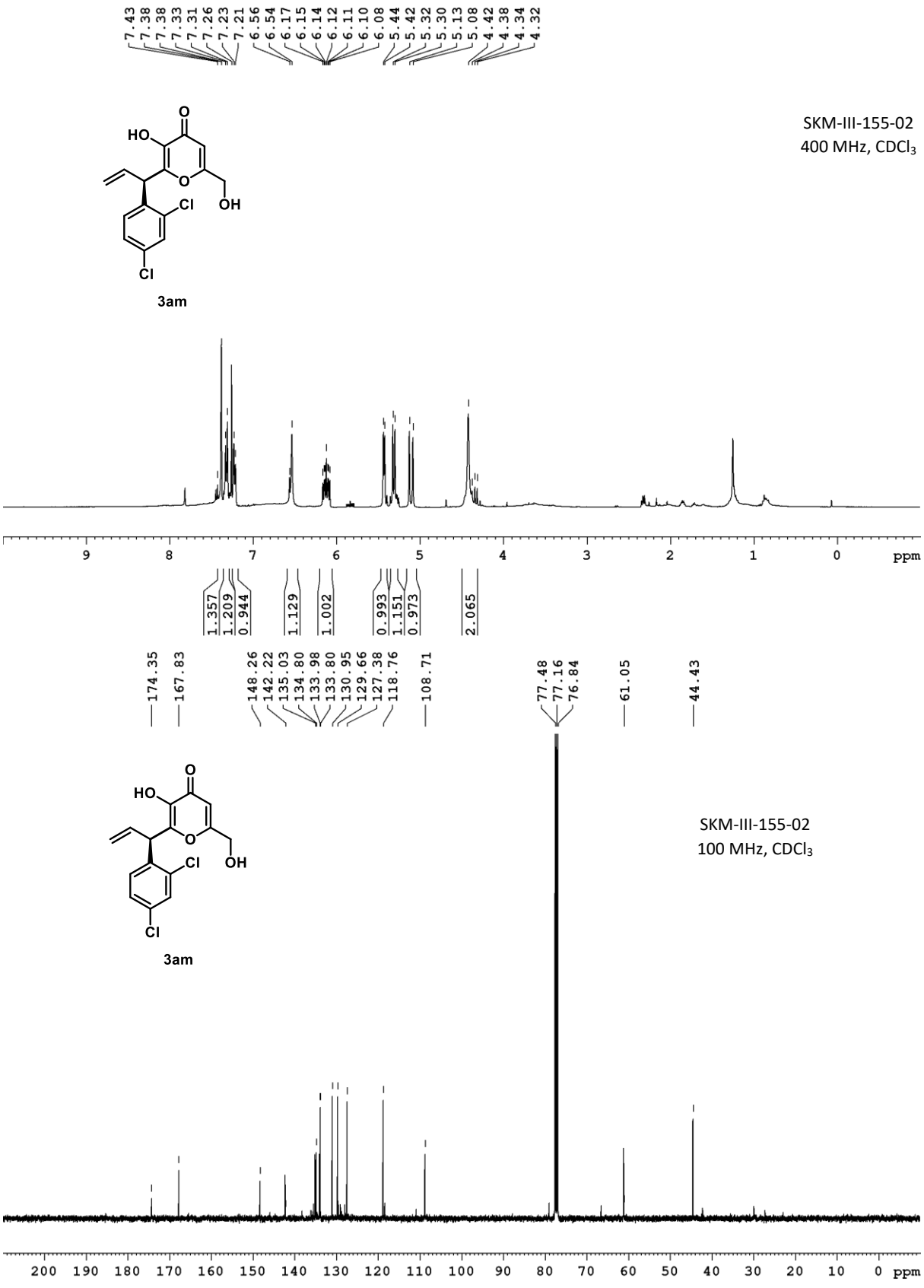
Daicel Chiralpak AD-H column (85:15 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

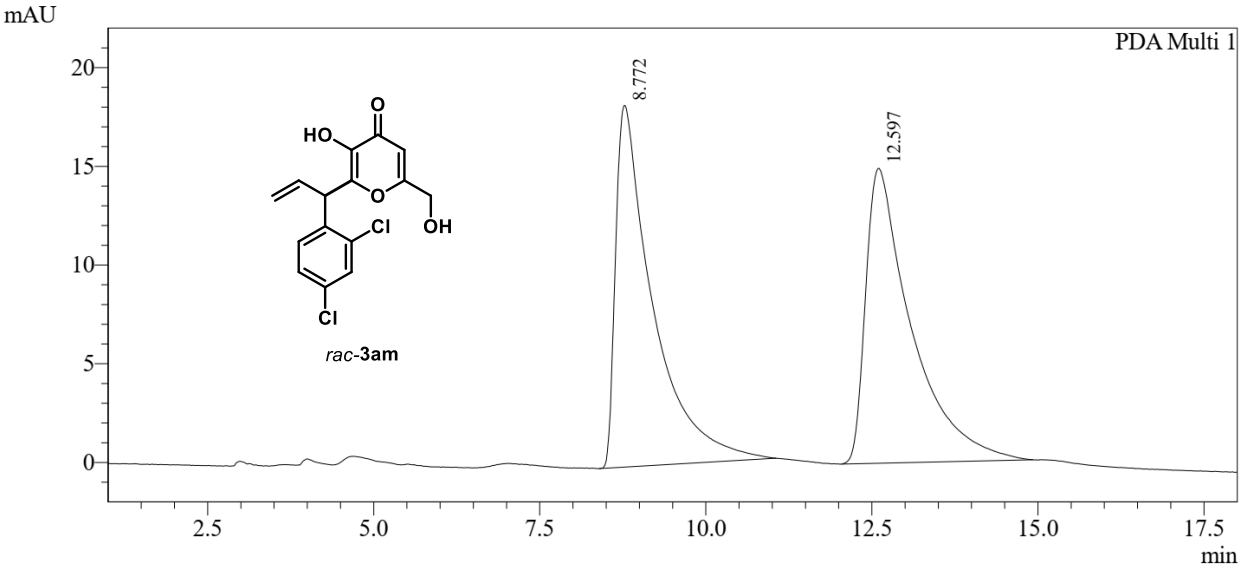


PeakTable

PDA Ch1 280nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.841	20520	0.076
2	13.035	26844750	99.924
Total		26865270	100.000


7.43
7.38
7.38
7.33
7.31
7.26
7.23
7.21
6.56
6.54
6.17
6.15
6.14
6.12
6.11
6.10
6.08
5.44
5.42
5.32
5.30
5.13
5.08
4.42
4.38
4.34
4.32
HO
O
O
Cl
OH
Cl
3am
SKM-III-155-02
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
1.357
1.209
0.944
1.129
1.002
0.993
1.151
0.973
2.065
174.35
167.83
148.26
142.22
135.03
134.80
133.98
133.80
130.95
129.66
127.38
118.76
108.71
77.48
77.16
76.84
61.05
44.43
HO
O
O
Cl
OH
Cl
3am
SKM-III-155-02
100 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

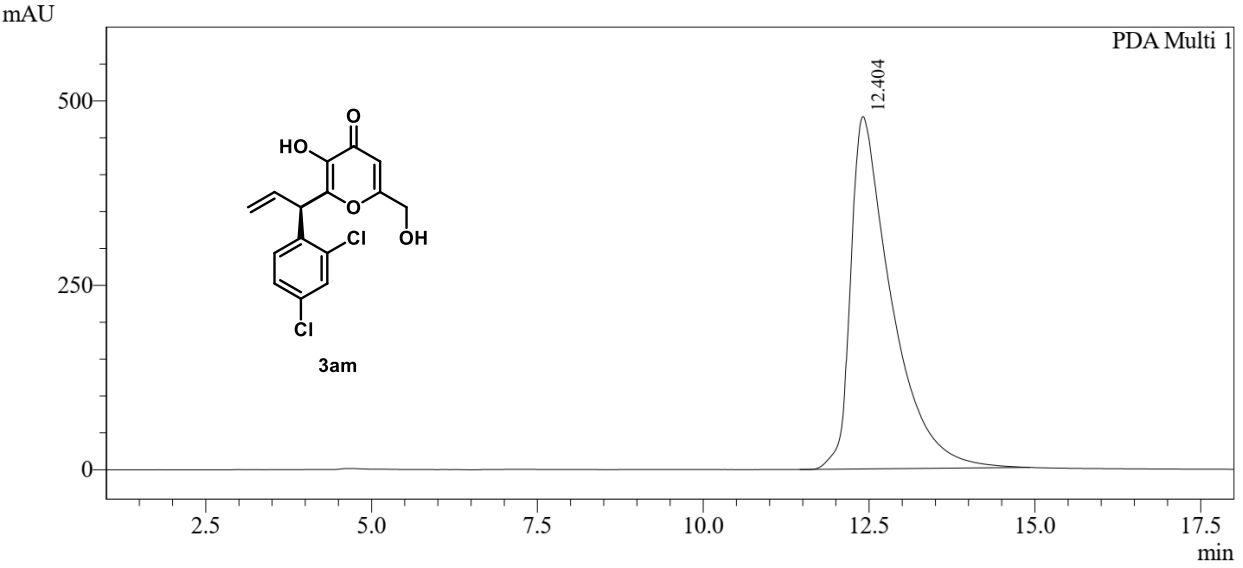


PeakTable

PDA Ch1 288nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.772	713810	50.023
2	12.597	713143	49.977
Total		1426953	100.000

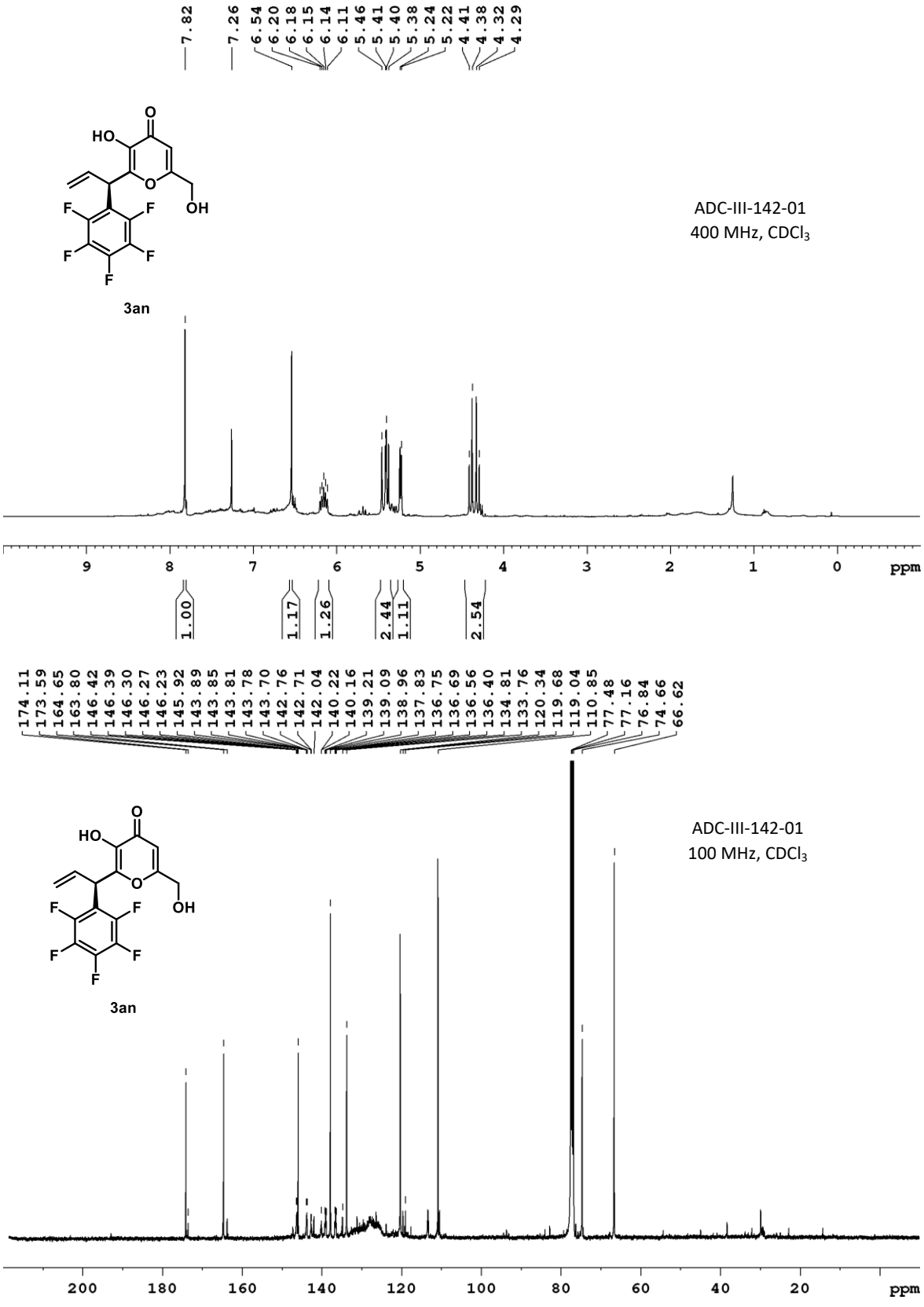
Daicel Chiralpak AD-H column (85:15 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

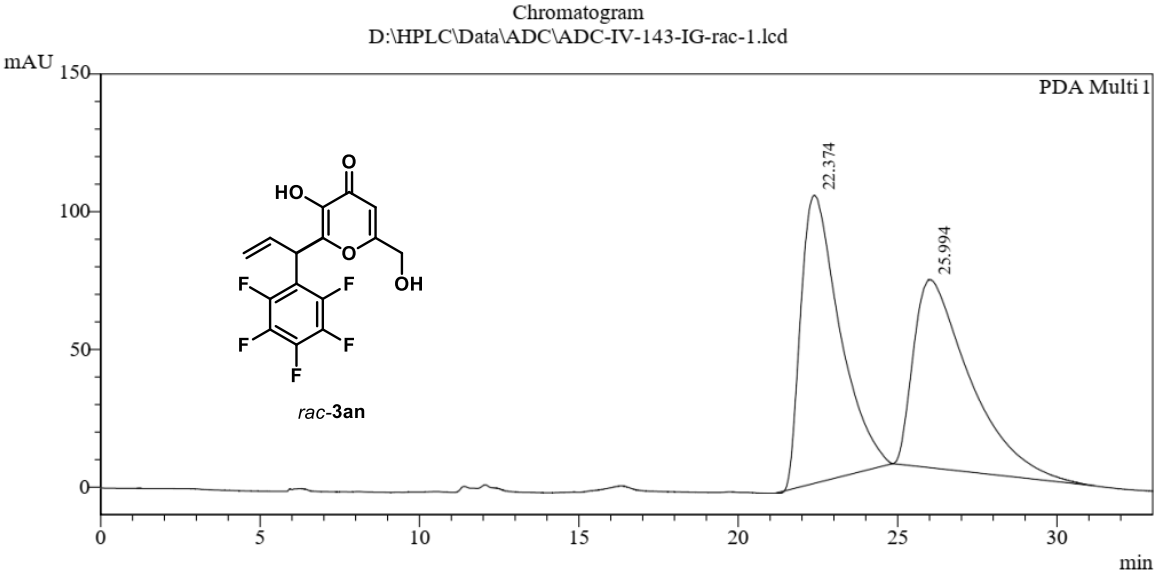


PeakTable

PDA Ch1 288nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.404	20547043	100.000
Total		20547043	100.000


7.82
7.26
6.54
6.20
6.18
6.15
6.14
6.11
5.46
5.41
5.40
5.38
5.24
5.22
4.41
4.38
4.32
4.29
HO
O
O
OH
F
F
F
F
F
3an
ADC-III-142-01
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.17
1.26
2.44
1.11
2.54
174.11
173.59
164.65
163.80
146.42
146.39
146.30
146.27
146.23
145.92
143.89
143.85
143.81
143.78
143.70
142.76
142.71
142.04
140.22
140.16
139.21
139.09
138.96
137.83
136.75
136.69
136.56
136.40
134.81
133.76
120.34
119.68
119.04
110.85
77.48
77.16
76.84
74.66
66.62
HO
O
O
OH
F
F
F
F
F
3an
ADC-III-142-01
100 MHz, CDCl3
200
180
160
140
120
100
80
60
40
20
ppm

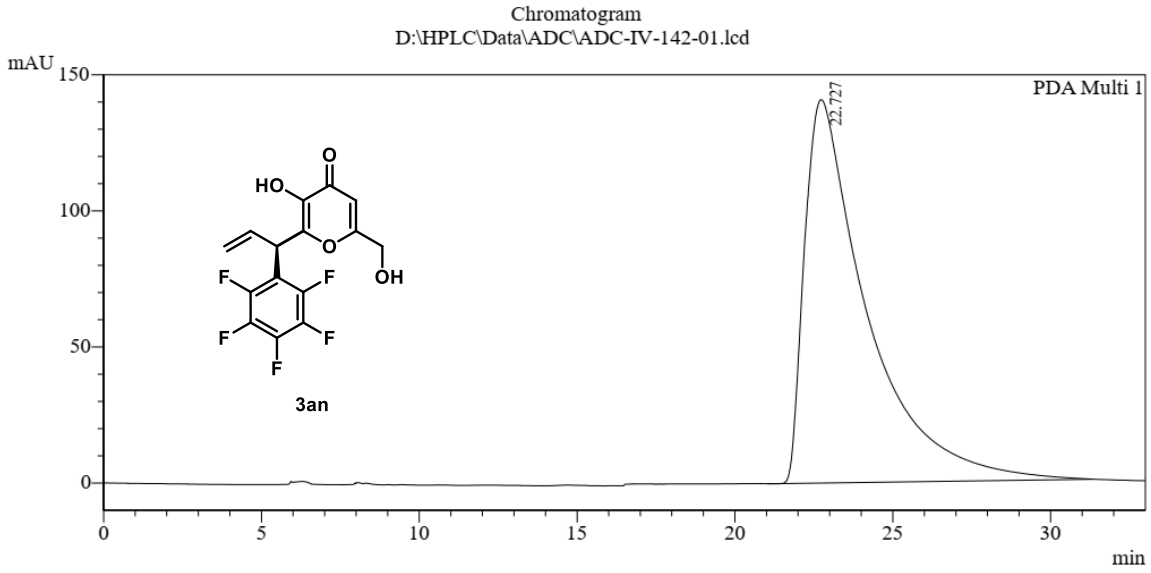


PeakTable

PDA Ch1 241nm 4nm

Peak#	Ret. Time	Area	Area %
1	22.374	8825292	51.310
2	25.994	8374509	48.690
Total		17199800	100.000

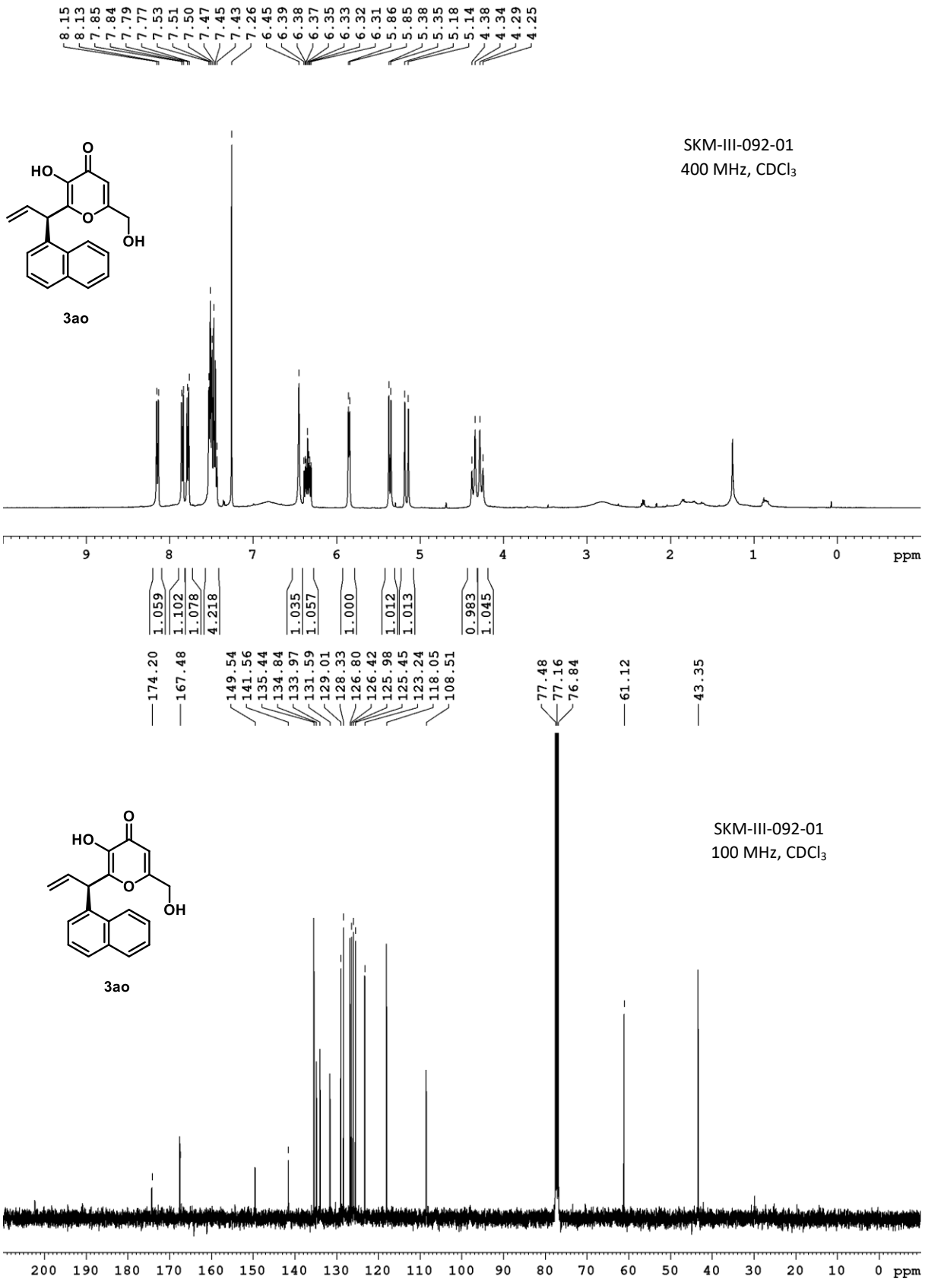
Daicel Chiralpak AD-H column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

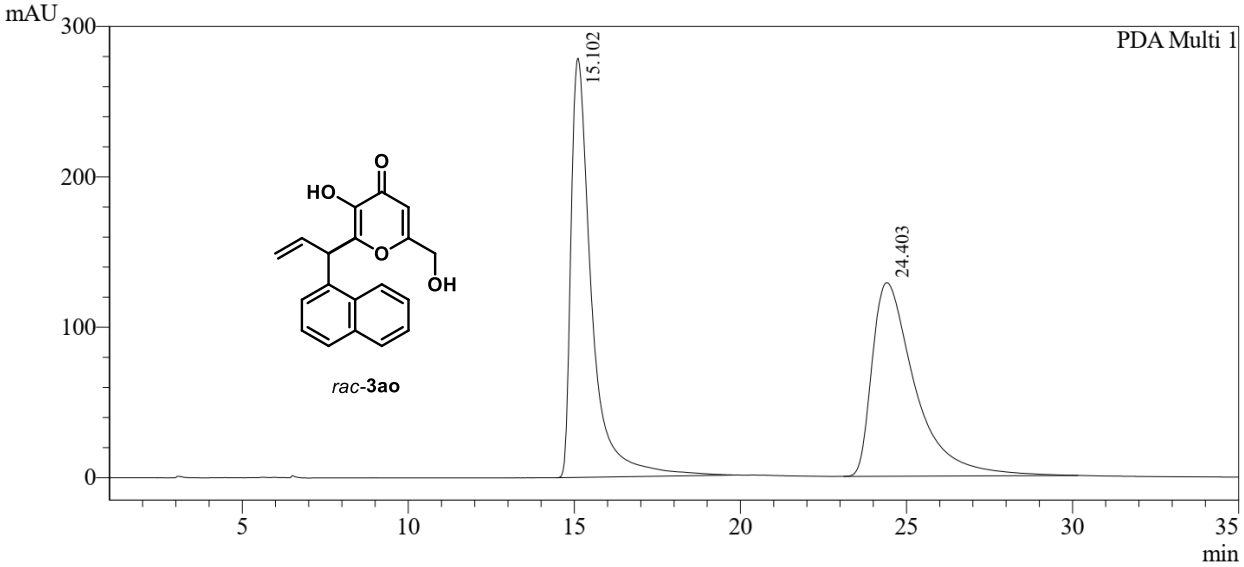


PeakTable

PDA Ch1 241nm 4nm

Peak#	Ret. Time	Area	Area %
1	22.727	19376672	100.000
Total		19376672	100.000


8.15
8.13
7.85
7.84
7.79
7.77
7.53
7.51
7.50
7.47
7.45
7.43
7.26
6.45
6.39
6.38
6.37
6.35
6.33
6.32
6.31
5.86
5.85
5.38
5.35
5.18
5.14
4.38
4.34
4.29
4.25
HO
O
O
OH
3ao
SKM-III-092-01
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
1.059
1.102
1.078
4.218
1.035
1.057
1.000
1.012
1.013
0.983
1.045
174.20
167.48
149.54
141.56
135.44
134.84
133.97
131.59
129.01
128.33
126.80
126.42
125.98
125.45
123.24
118.05
108.51
77.48
77.16
76.84
61.12
43.35
HO
O
O
OH
3ao
SKM-III-092-01
100 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

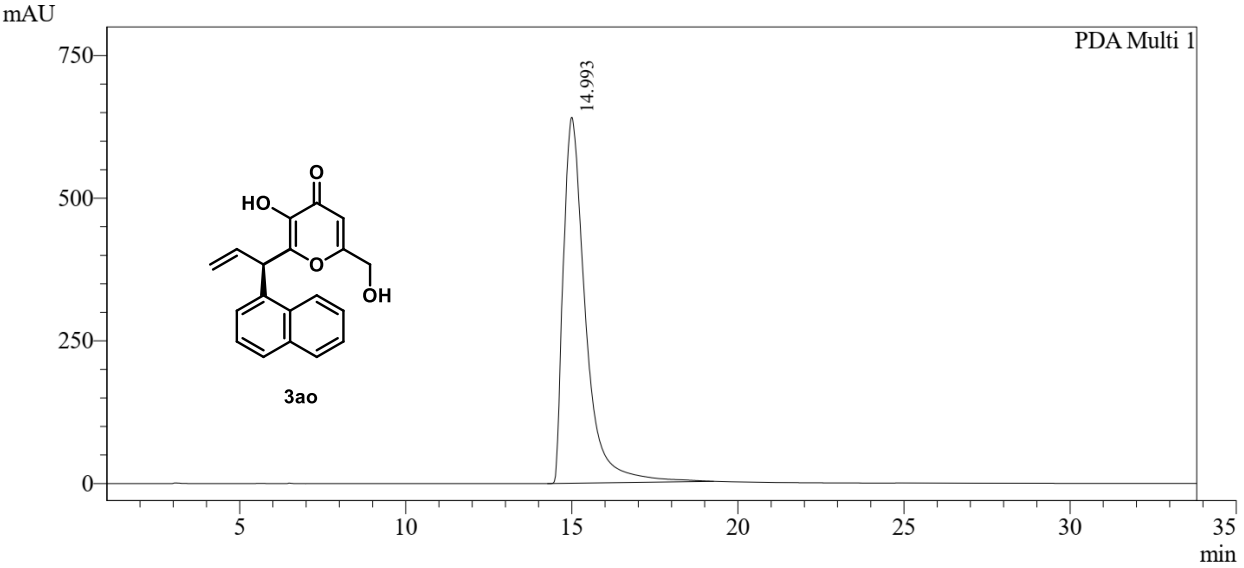


PeakTable

PDA Ch1 281nm 4nm

Peak#	Ret. Time	Area	Area %
1	15.102	12043561	50.903
2	24.403	11616314	49.097
Total		23659874	100.000

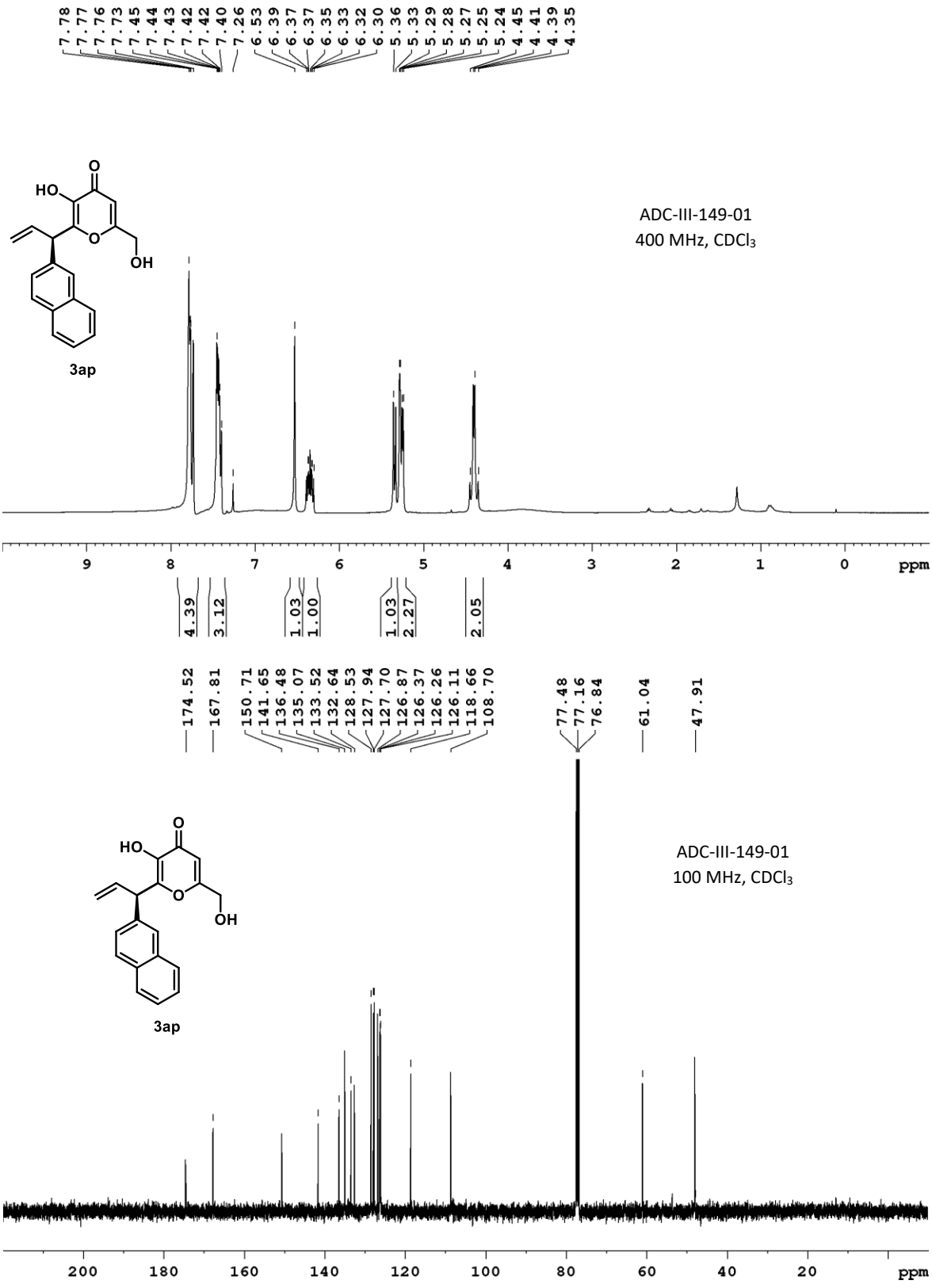
Daicel Chiralpak IH column (85:15 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

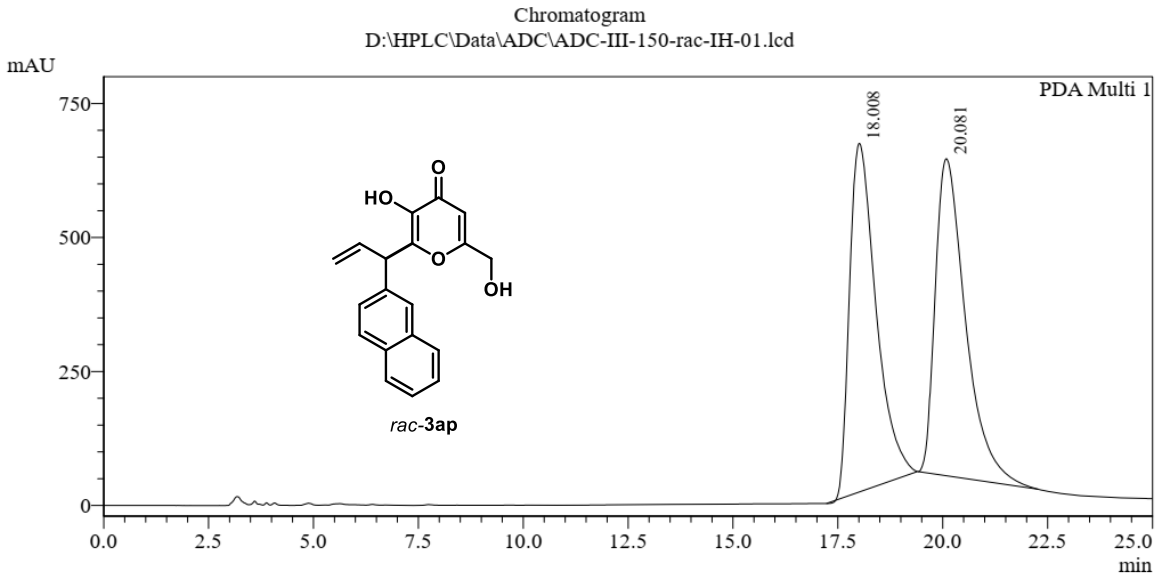


PeakTable

PDA Ch1 281nm 4nm

Peak#	Ret. Time	Area	Area %
1	14.993	29763637	100.000
Total		29763637	100.000


7.78
7.77
7.76
7.73
7.45
7.44
7.43
7.42
7.42
7.40
7.26
6.53
6.39
6.37
6.37
6.35
6.33
6.32
6.30
5.36
5.33
5.29
5.28
5.27
5.25
5.24
4.45
4.41
4.39
4.35
HO
O
O
OH
3ap
ADC-III-149-01
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
4.39
3.12
1.03
1.00
1.03
2.27
2.05
174.52
167.81
150.71
141.65
136.48
135.07
133.52
132.64
128.53
127.94
127.70
126.87
126.37
126.26
126.11
118.66
108.70
77.48
77.16
76.84
61.04
47.91
HO
O
O
OH
3ap
ADC-III-149-01
100 MHz, CDCl3
200
180
160
140
120
100
80
60
40
20
ppm

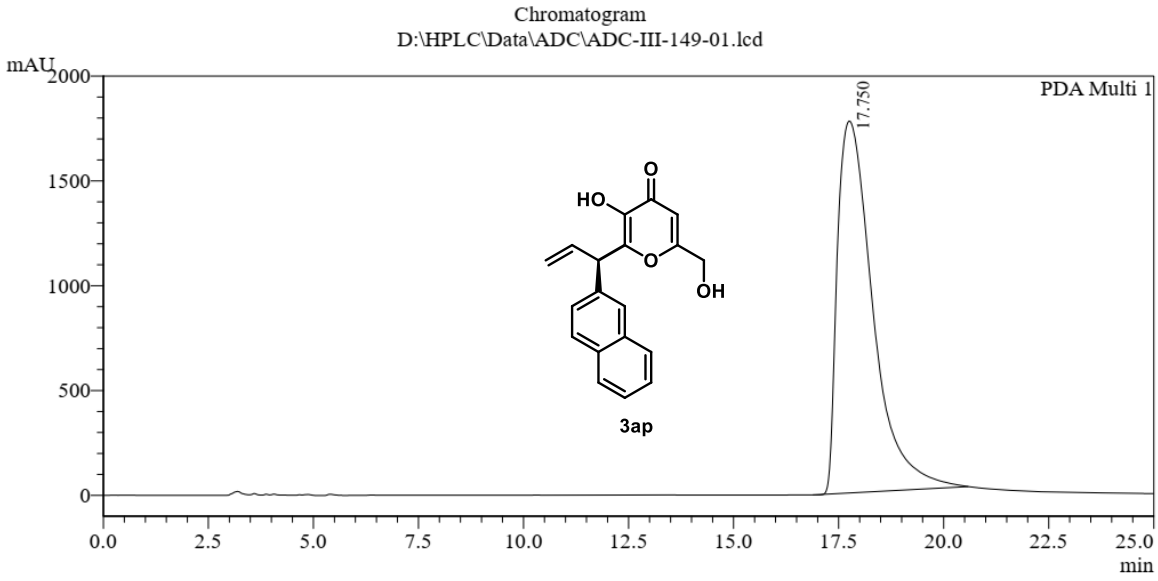


PeakTable

PDA Ch1 221nm 4nm

Peak#	Ret. Time	Area	Area %
1	18.008	28636919	49.075
2	20.081	29716098	50.925
Total		58353016	100.000

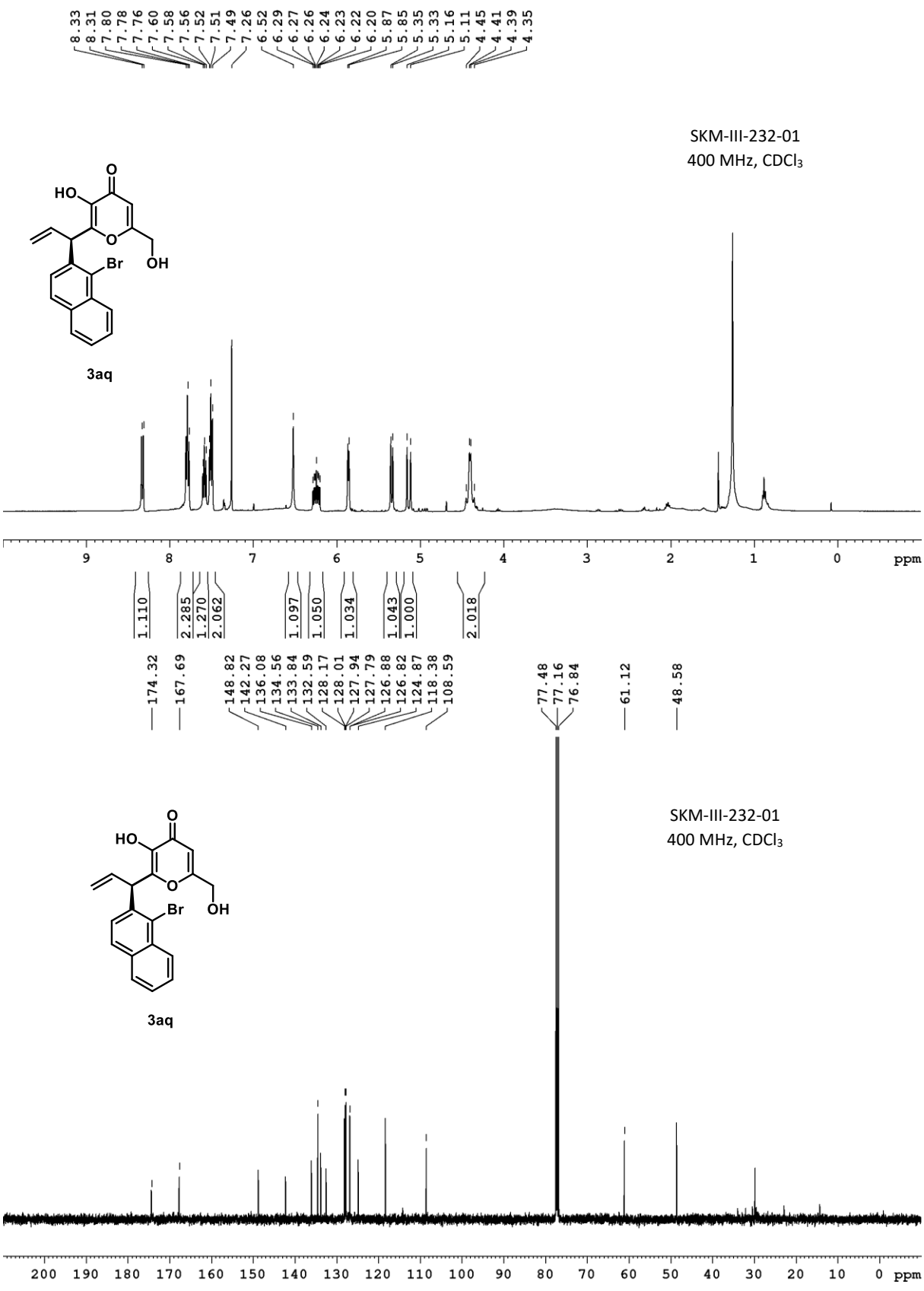
Daicel Chiralpak IH column (85:15 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

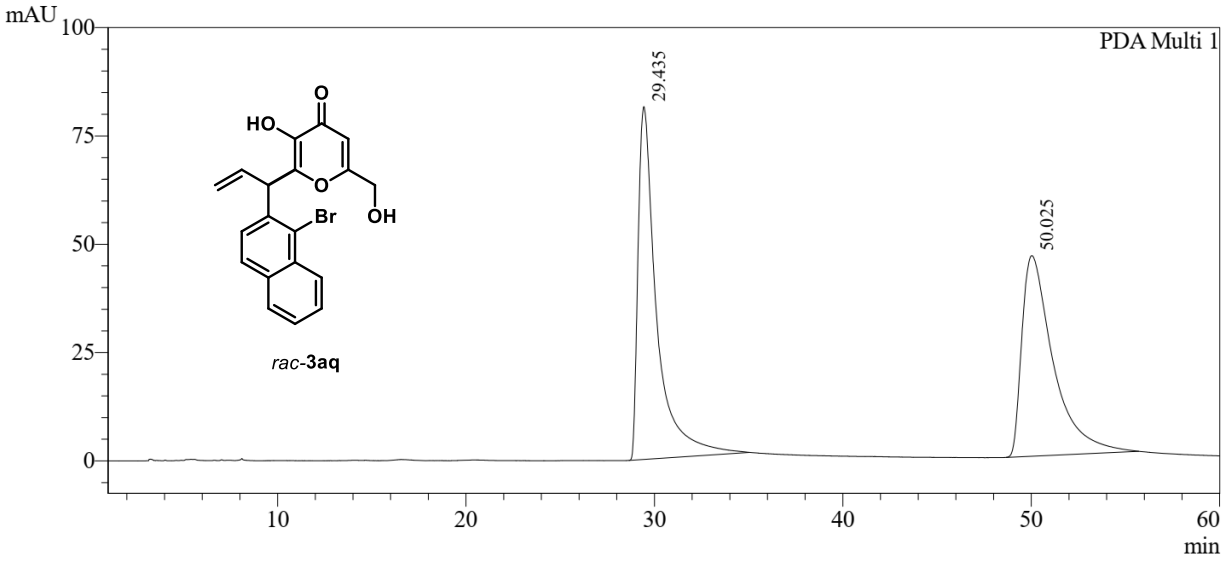


PeakTable

PDA Ch1 221nm 4nm

Peak#	Ret. Time	Area	Area %
1	17.750	104515516	100.000
Total		104515516	100.000


8.33
8.31
7.80
7.78
7.76
7.60
7.58
7.56
7.52
7.51
7.49
7.26
6.52
6.29
6.27
6.26
6.24
6.23
6.22
6.20
5.87
5.85
5.35
5.33
5.16
5.11
4.45
4.41
4.39
4.35
SKM-III-232-01
400 MHz, CDCl3
HO
O
O
Br
OH
3aq
9
8
7
6
5
4
3
2
1
0
ppm
1.110
2.285
1.270
2.062
1.097
1.050
1.034
1.043
1.000
2.018
174.32
167.69
148.82
142.27
136.08
134.56
133.84
132.59
128.17
128.01
127.94
127.79
126.88
126.82
124.87
118.38
108.59
77.48
77.16
76.84
61.12
48.58
SKM-III-232-01
400 MHz, CDCl3
HO
O
O
Br
OH
3aq
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

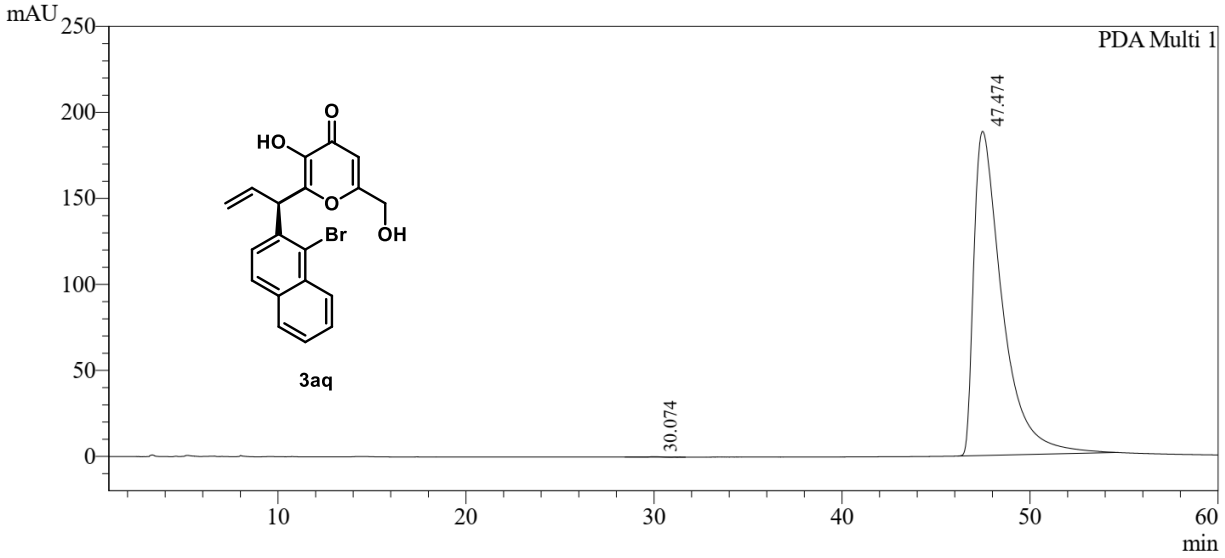


PeakTable

PDA Ch1 280nm 4nm

Peak#	Ret. Time	Area	Area %
1	29.435	5600391	51.069
2	50.025	5365901	48.931
Total		10966292	100.000

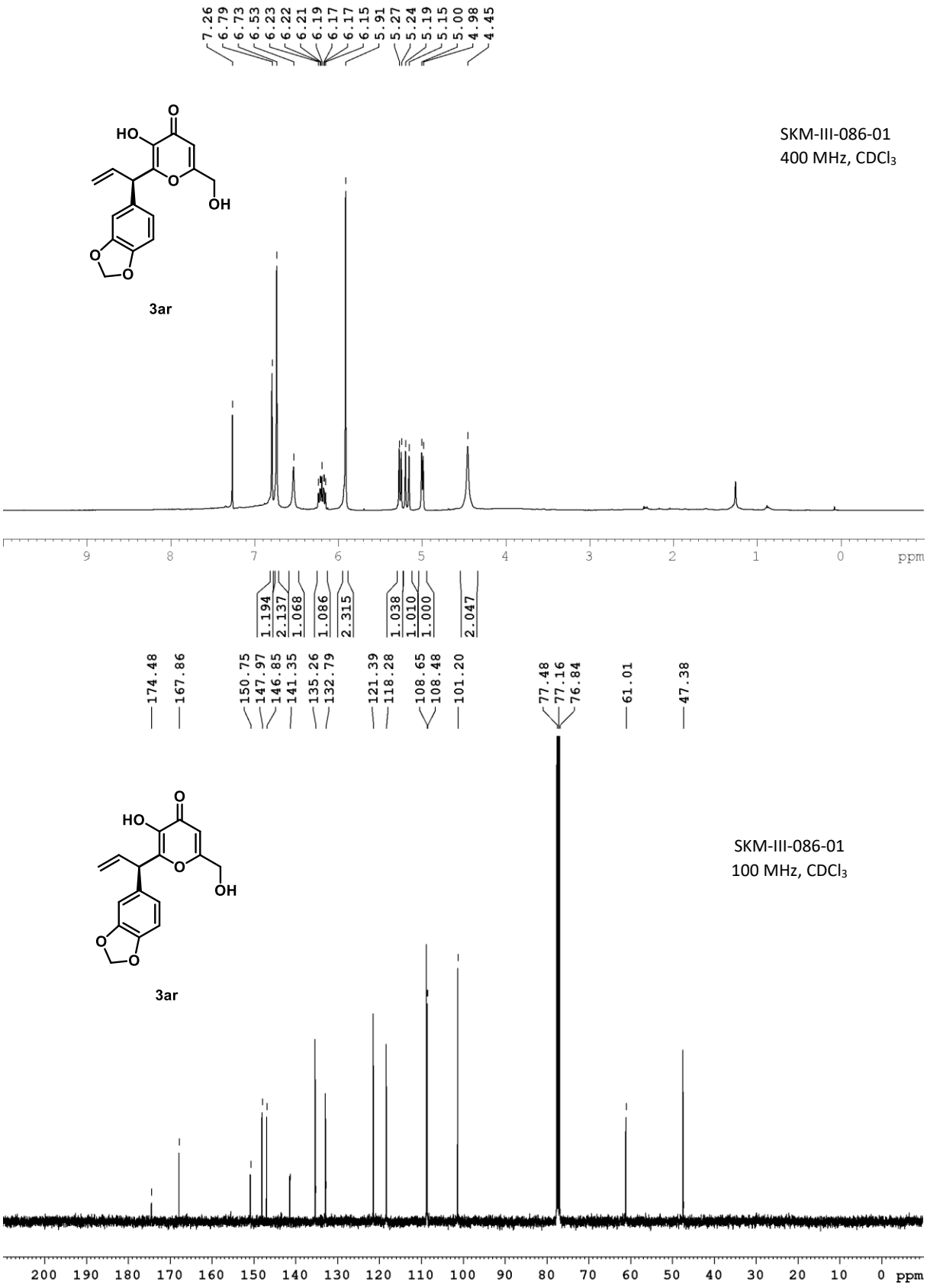
Daicel Chiralpak IC column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

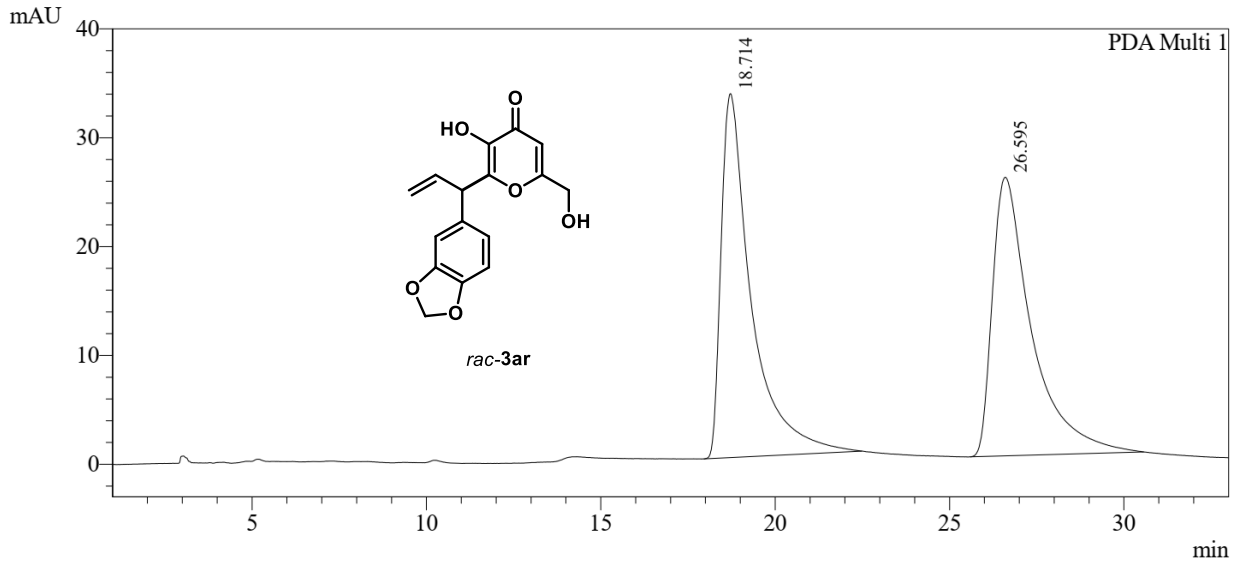


PeakTable

PDA Ch1 280nm 4nm

Peak#	Ret. Time	Area	Area %
1	30.074	8815	0.044
2	47.474	19841047	99.956
Total		19849862	100.000


7.26
6.79
6.73
6.53
6.23
6.22
6.21
6.19
6.17
6.17
6.15
5.91
5.27
5.24
5.19
5.15
5.00
4.98
4.45
HO
O
O
OH
O
O
3ar
SKM-III-086-01
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
1.194
2.137
1.068
1.086
2.315
1.038
1.010
1.000
2.047
174.48
167.86
150.75
147.97
146.85
141.35
135.26
132.79
121.39
118.28
108.65
108.48
101.20
77.48
77.16
76.84
61.01
47.38
HO
O
O
OH
O
O
3ar
SKM-III-086-01
100 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

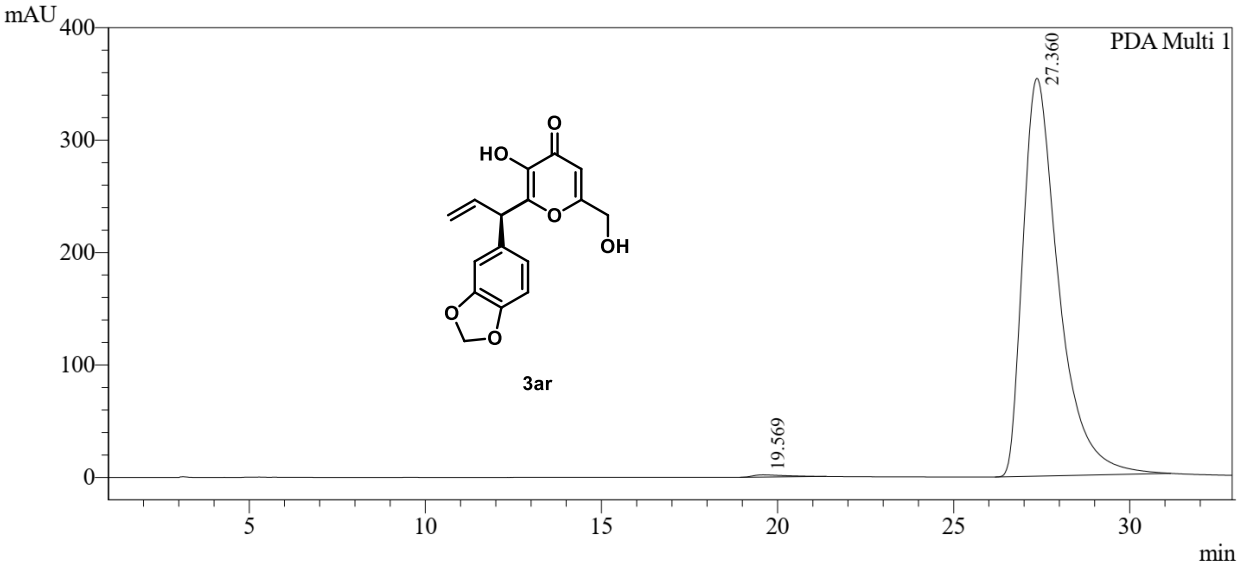


PeakTable

PDA Ch1 282nm 4nm

Peak#	Ret. Time	Area	Area %
1	18.714	2013359	50.194
2	26.595	1997831	49.806
Total		4011190	100.000

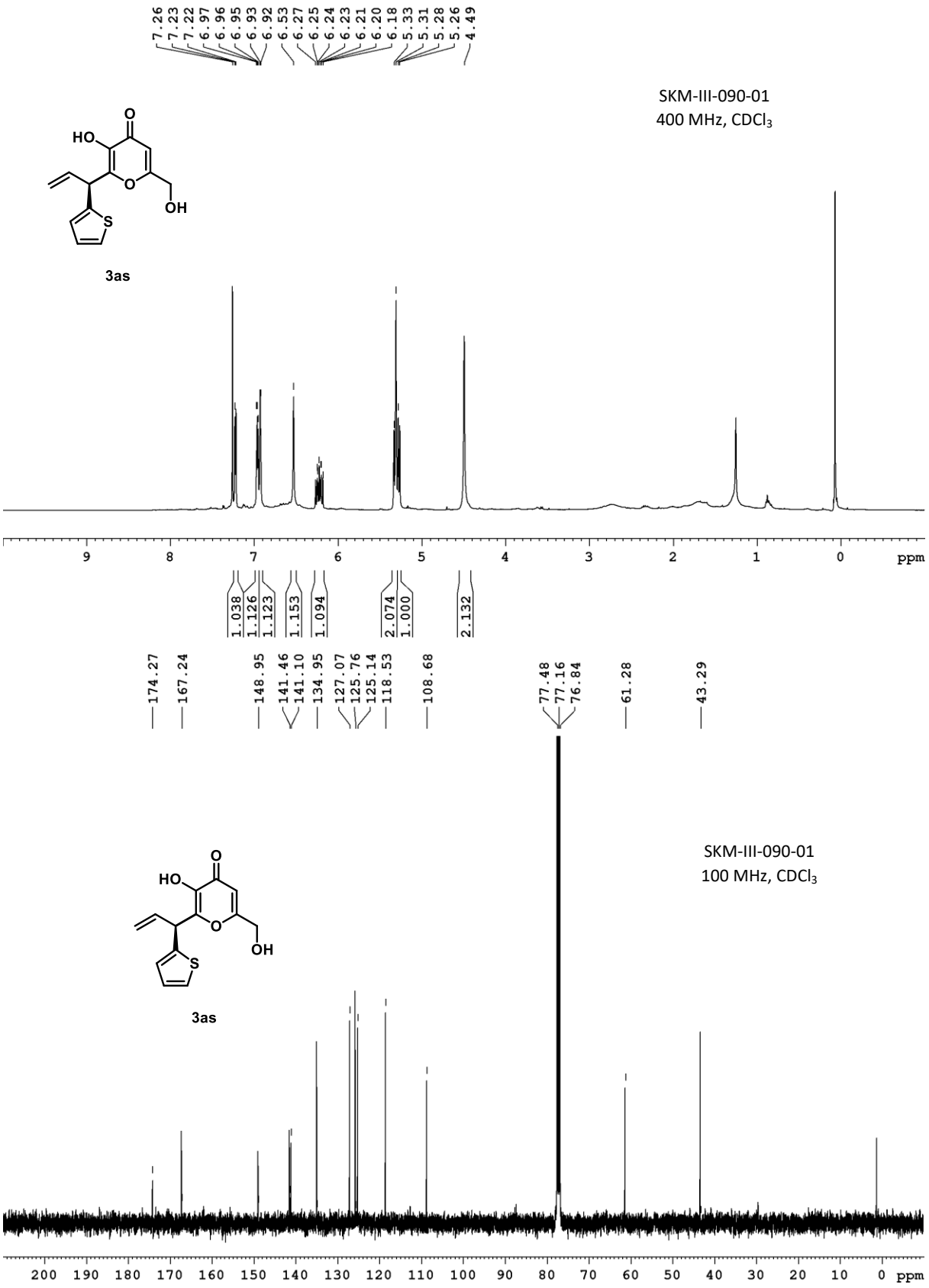
Daicel Chiralpak AD-H column (85:15 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

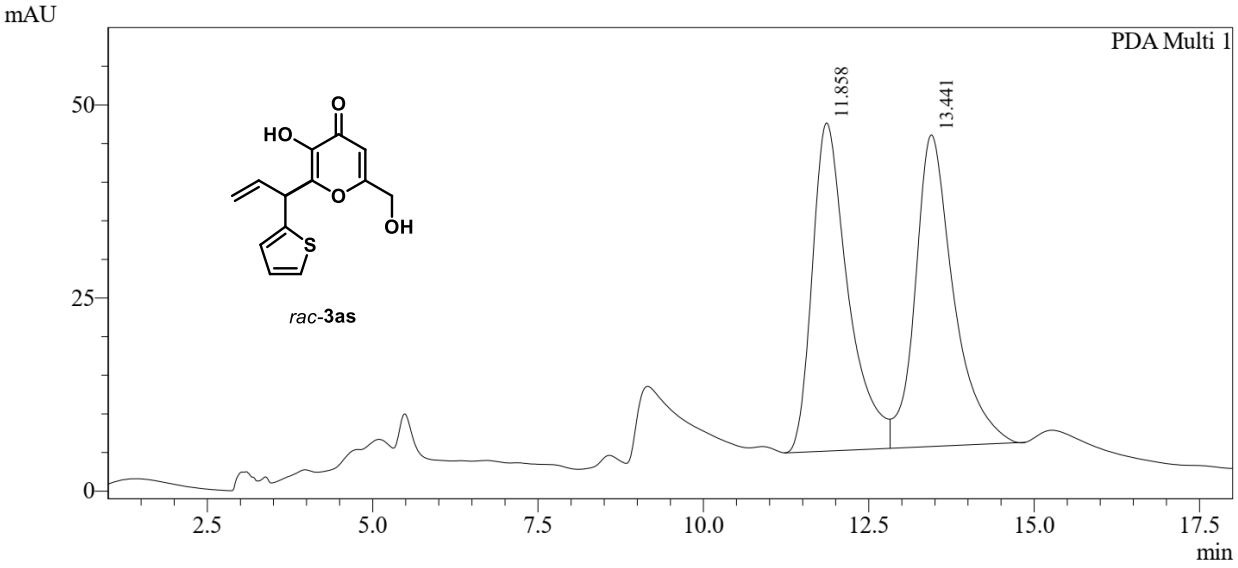


PeakTable

PDA Ch1 282nm 4nm

Peak#	Ret. Time	Area	Area %
1	19.569	130860	0.521
2	27.360	24983661	99.479
Total		25114520	100.000


7.26
7.23
7.22
6.97
6.96
6.95
6.93
6.92
6.53
6.27
6.25
6.24
6.23
6.21
6.20
6.18
5.33
5.31
5.28
5.26
4.49
SKM-III-090-01
400 MHz, CDCl3
HO
O
O
OH
S
3as
9
8
7
6
5
4
3
2
1
0
ppm
1.038
1.126
1.123
1.153
1.094
2.074
1.000
2.132
174.27
167.24
148.95
141.46
141.10
134.95
127.07
125.76
125.14
118.53
108.68
77.48
77.16
76.84
61.28
43.29
SKM-III-090-01
100 MHz, CDCl3
HO
O
O
OH
S
3as
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



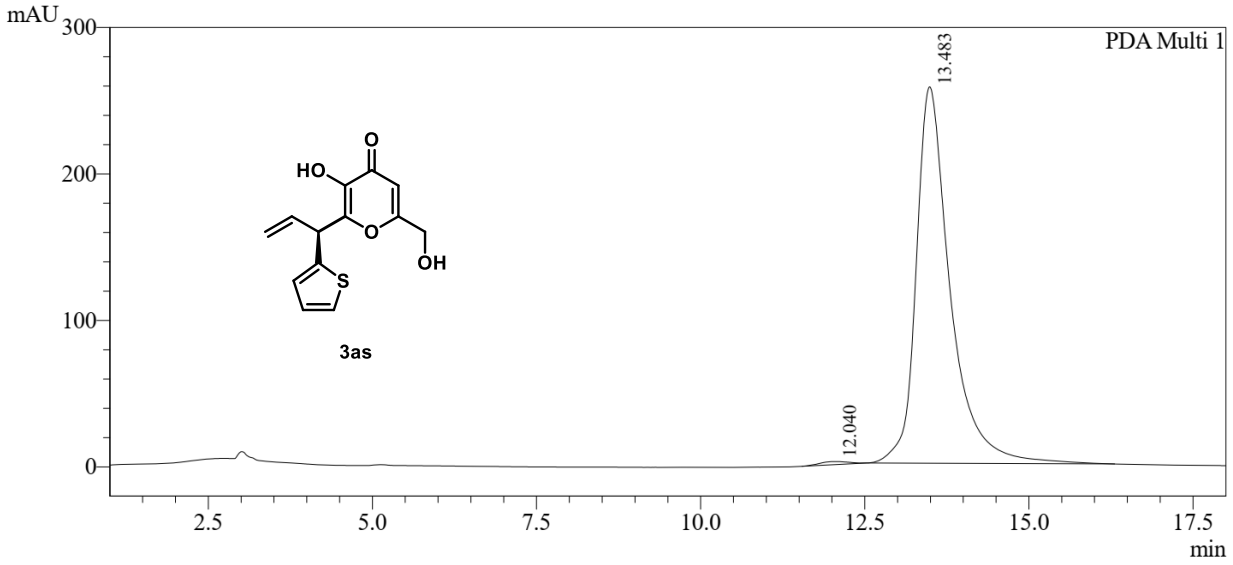
rac-**3as**

PeakTable

PDA Ch1 276nm 4nm

Peak#	Ret. Time	Area	Area %
1	11.858	1601446	49.606
2	13.441	1626908	50.394
Total		3228354	100.000

Daicel Chiralpak AD-H column (85:15 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

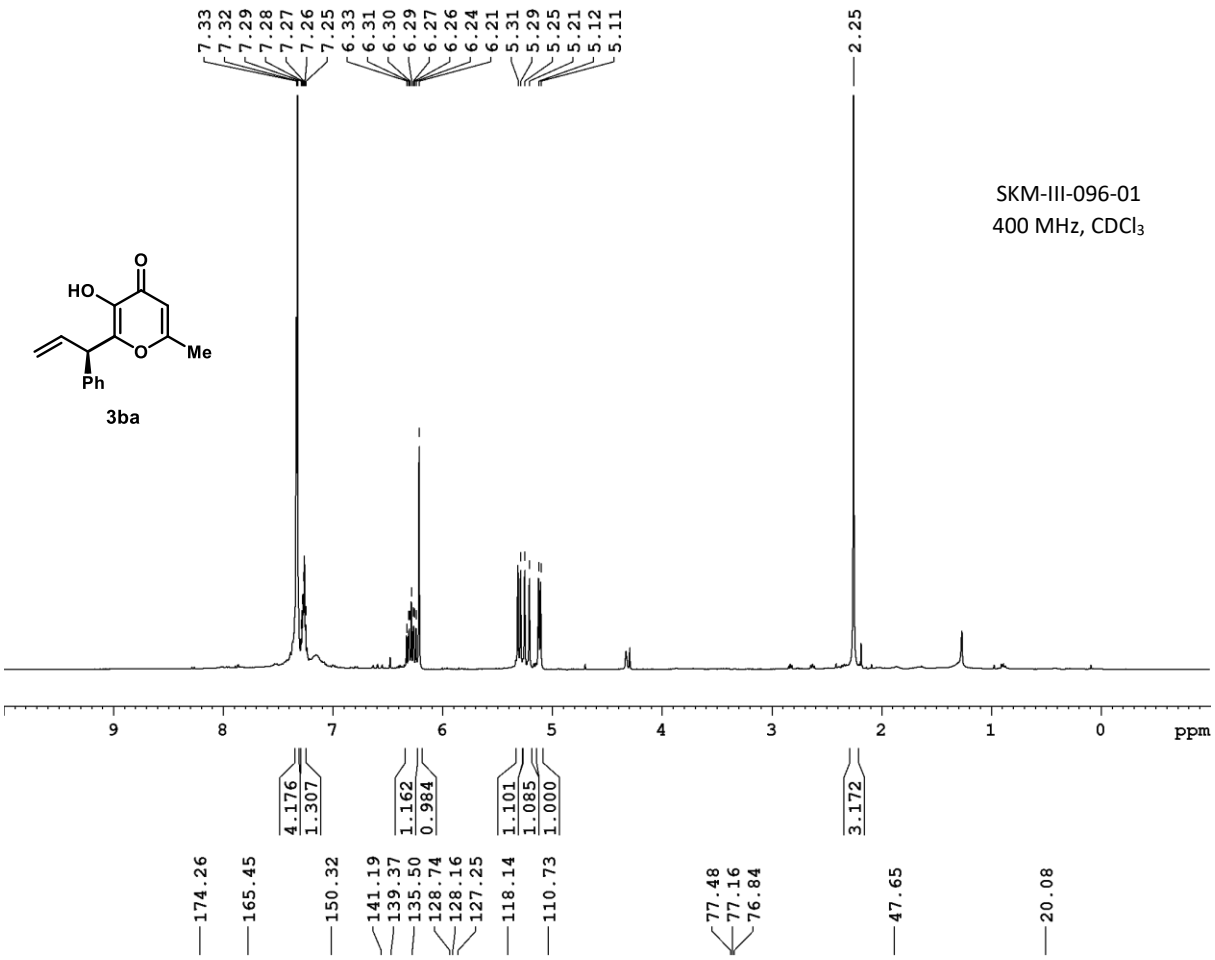


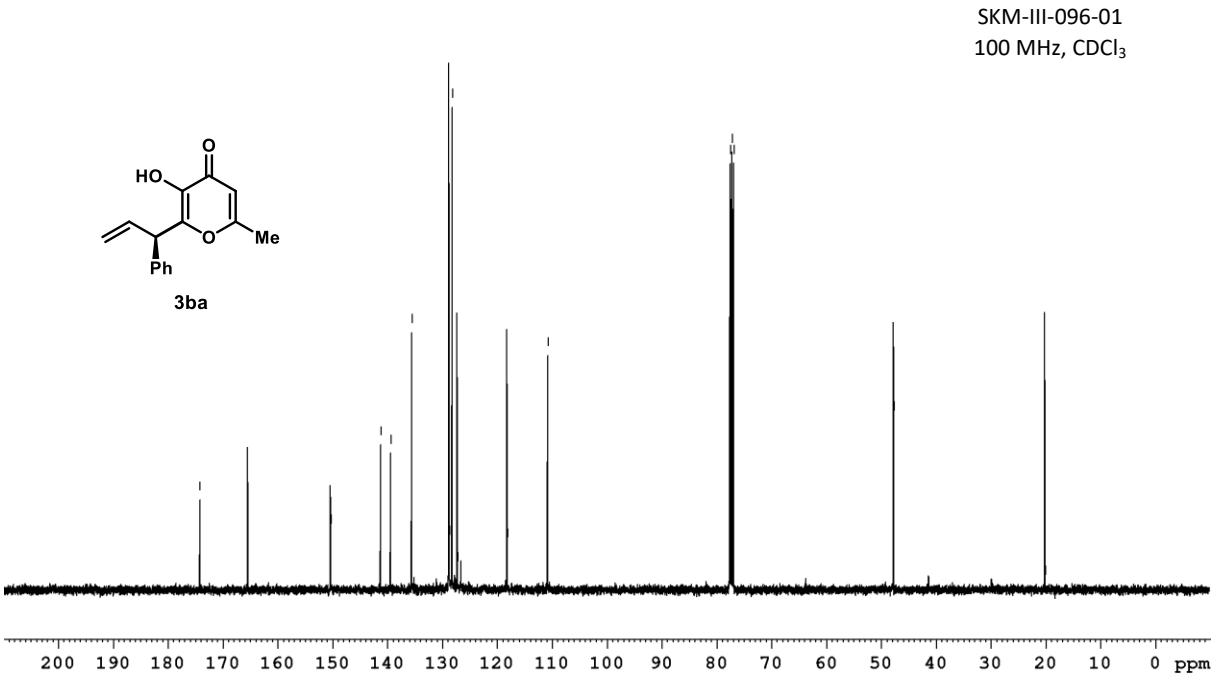
3as

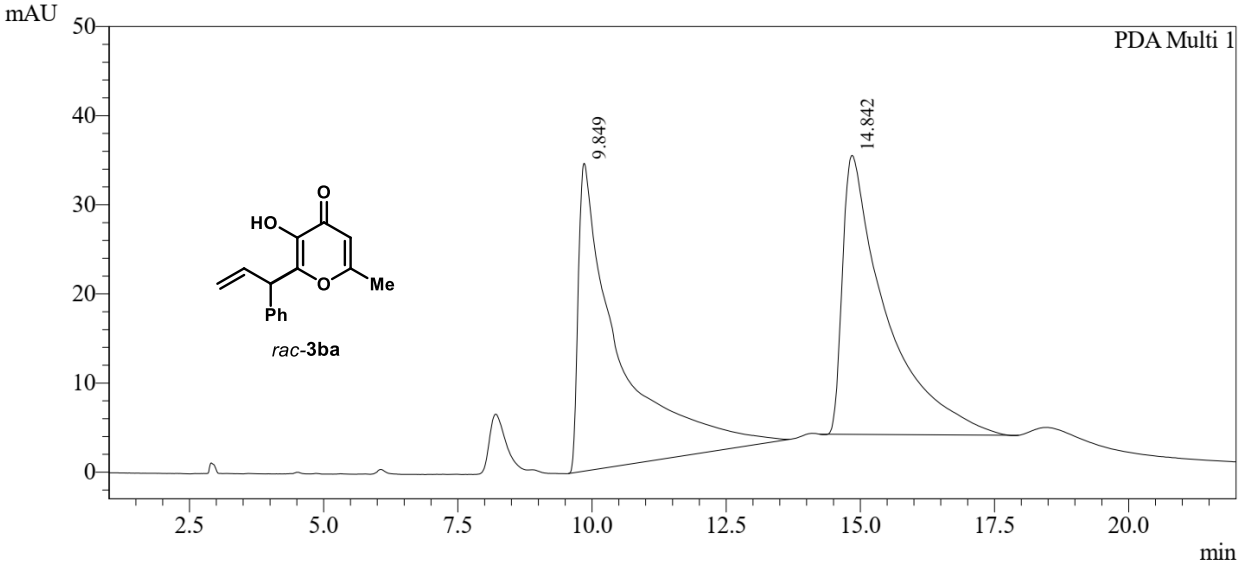
PeakTable

PDA Ch1 276nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.040	65842	0.704
2	13.483	9288585	99.296
Total		9354427	100.000


7.33
7.32
7.29
7.28
7.27
7.26
7.25
6.33
6.31
6.30
6.29
6.27
6.26
6.24
6.21
5.31
5.29
5.25
5.21
5.12
5.11
2.25
SKM-III-096-01
400 MHz, CDCl3
HO
O
O
Me
Ph
3ba
9
8
7
6
5
4
3
2
1
0
ppm
4.176
1.307
1.162
0.984
1.101
1.085
1.000
3.172
174.26
165.45
150.32
141.19
139.37
135.50
128.74
128.16
127.25
118.14
110.73
77.48
77.16
76.84
47.65
20.08


SKM-III-096-01
100 MHz, CDCl3
HO
O
O
Me
Ph
3ba
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

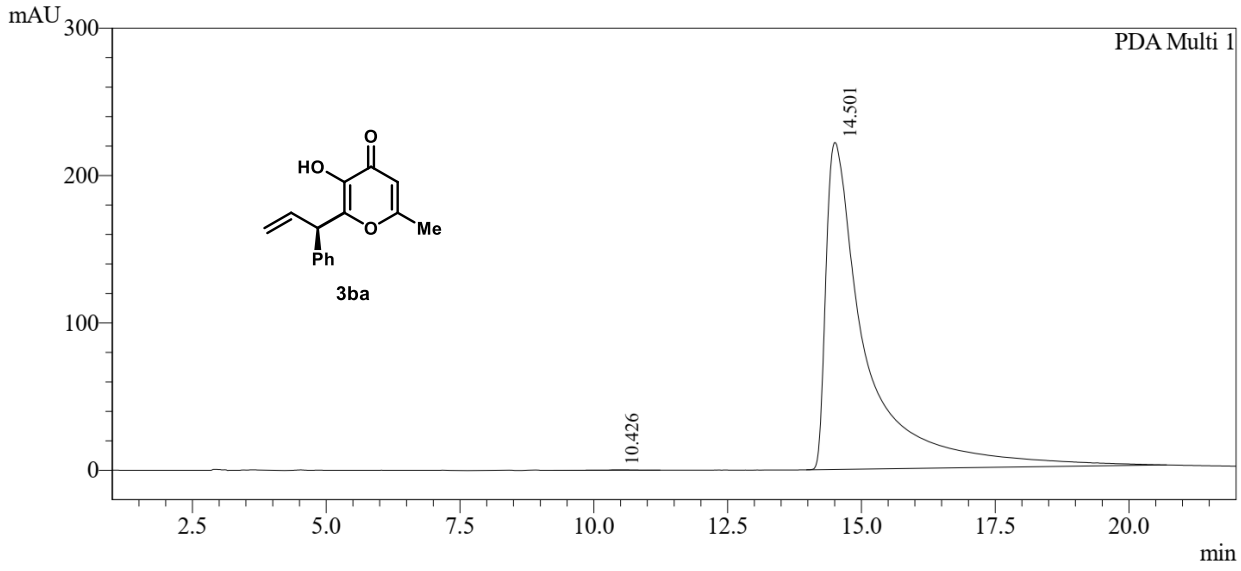


PeakTable

PDA Ch1 276nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.849	1834843	50.987
2	14.842	1763816	49.013
Total		3598659	100.000

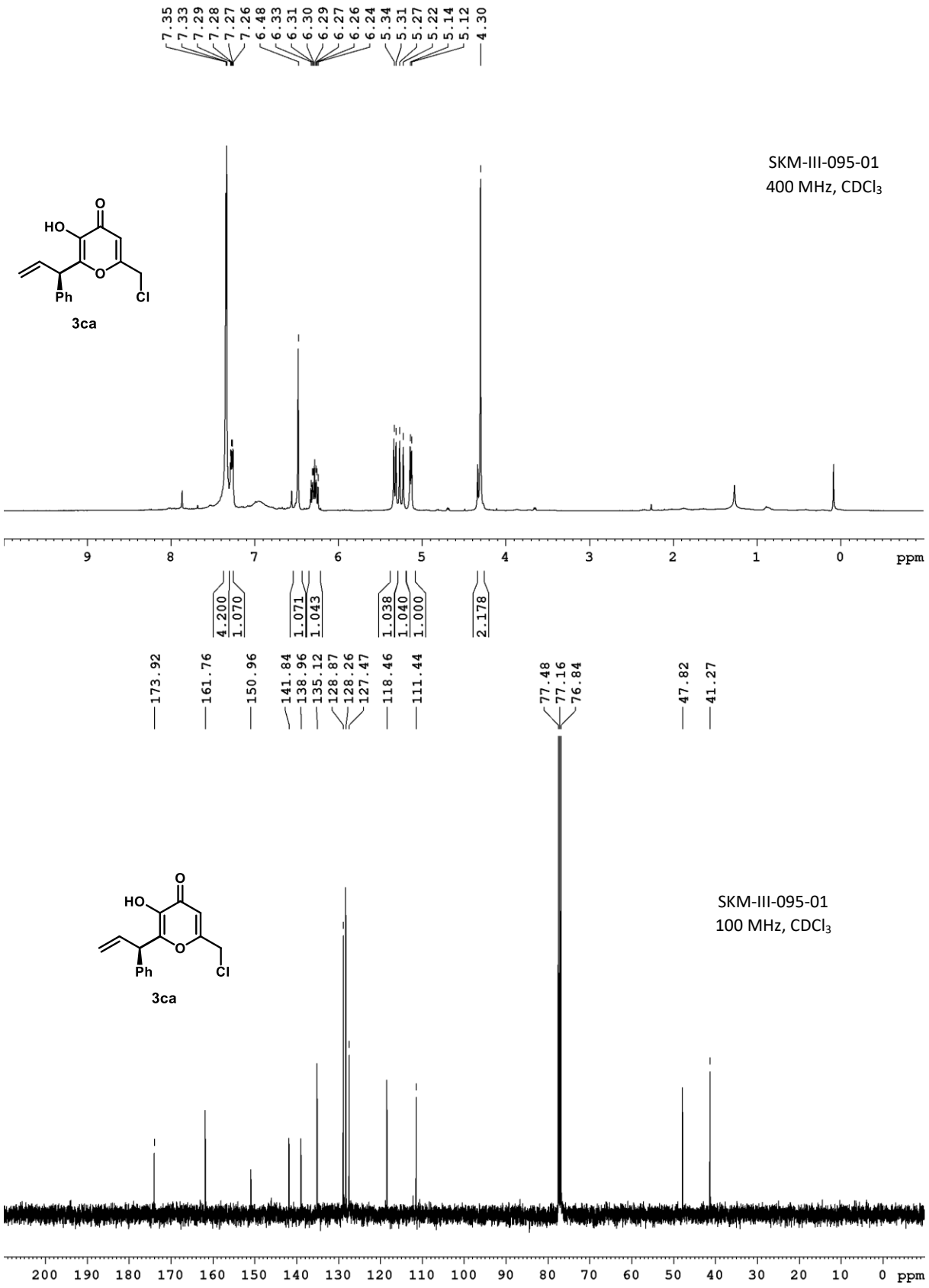
Phenomenex Cellulose-1 column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

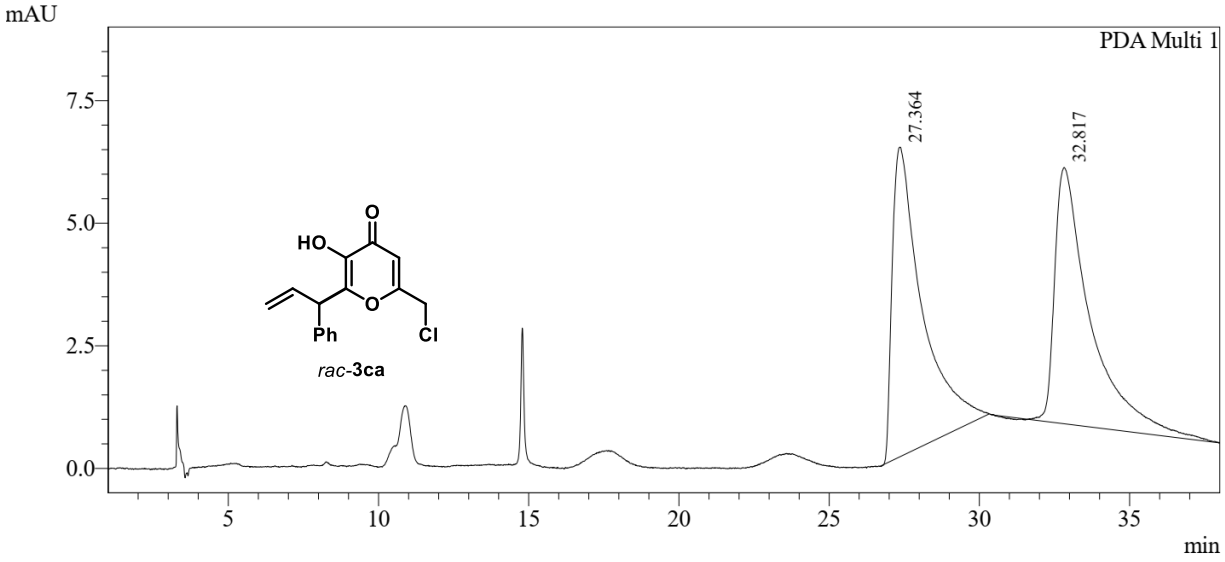


PeakTable

PDA Ch1 276nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.426	9511	0.081
2	14.501	11693298	99.919
Total		11702809	100.000


7.35
7.33
7.29
7.28
7.27
7.26
6.48
6.33
6.31
6.30
6.29
6.27
6.26
6.24
5.34
5.31
5.27
5.22
5.14
5.12
4.30
SKM-III-095-01
400 MHz, CDCl3
HO
O
Ph
Cl
3ca
9
8
7
6
5
4
3
2
1
0
ppm
4.200
1.070
1.071
1.043
1.038
1.040
1.000
2.178
173.92
161.76
150.96
141.84
138.96
135.12
128.87
128.26
127.47
118.46
111.44
77.48
77.16
76.84
47.82
41.27
SKM-III-095-01
100 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

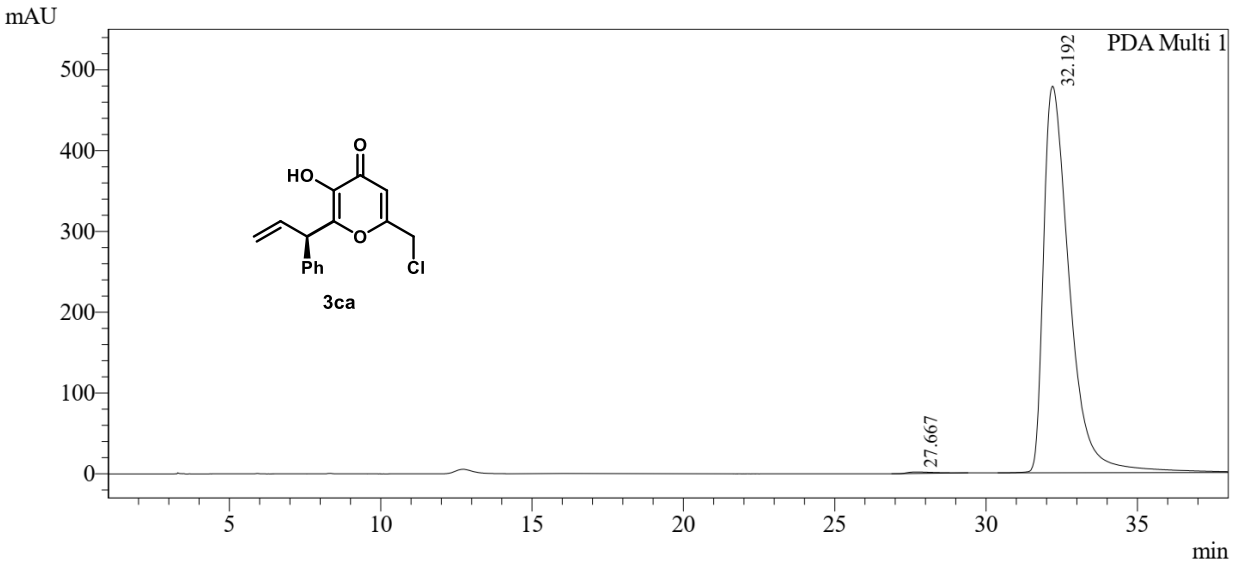


PeakTable

PDA Ch1 305nm 4nm

Peak#	Ret. Time	Area	Area %
1	27.364	437310	50.573
2	32.817	427404	49.427
Total		864714	100.000

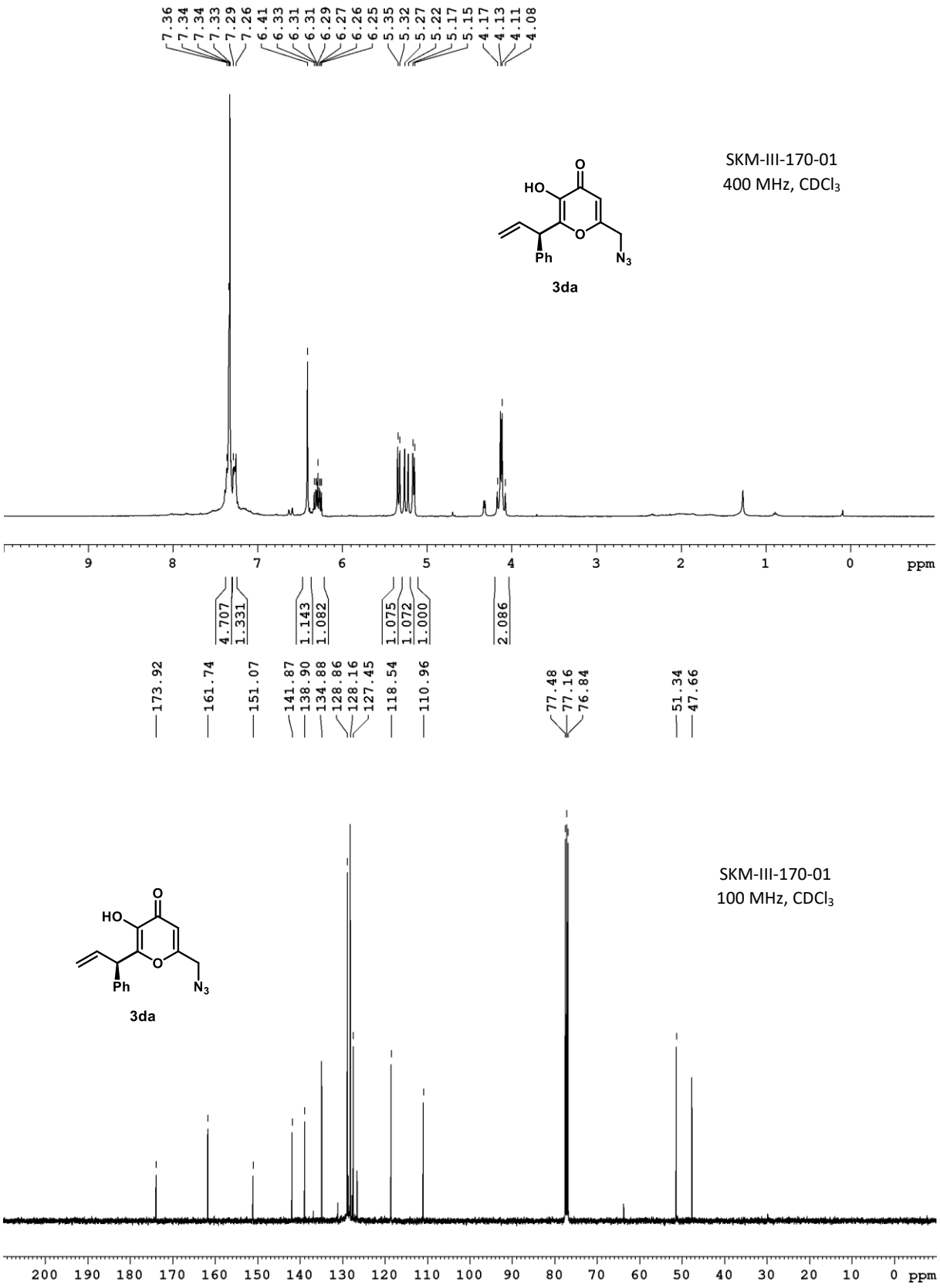
Daicel Chiralpak IC column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

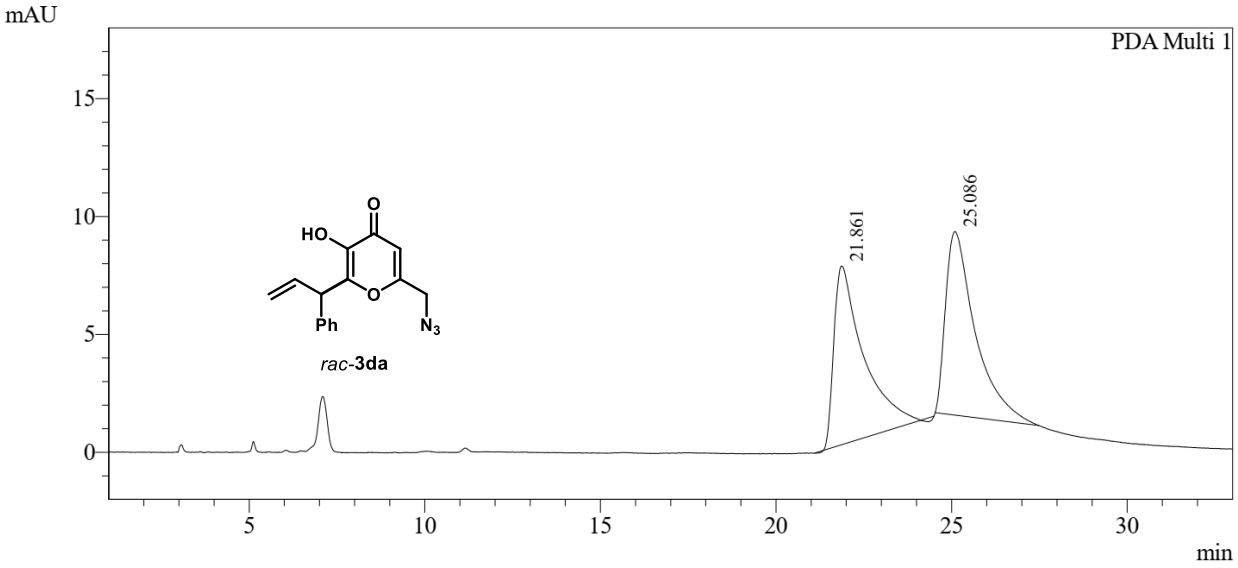


PeakTable

PDA Ch1 305nm 4nm

Peak#	Ret. Time	Area	Area %
1	27.667	115094	0.400
2	32.192	28681963	99.600
Total		28797057	100.000


7.36
7.34
7.34
7.33
7.29
7.26
6.41
6.33
6.31
6.31
6.29
6.27
6.26
6.25
5.35
5.32
5.27
5.22
5.17
5.15
4.17
4.13
4.11
4.08
SKM-III-170-01
400 MHz, CDCl3
HO
O
Ph
N3
3da
ppm
4.707
1.331
1.143
1.082
1.075
1.072
1.000
2.086
173.92
161.74
151.07
141.87
138.90
134.88
128.86
128.16
127.45
118.54
110.96
77.48
77.16
76.84
51.34
47.66
SKM-III-170-01
100 MHz, CDCl3
3da
ppm

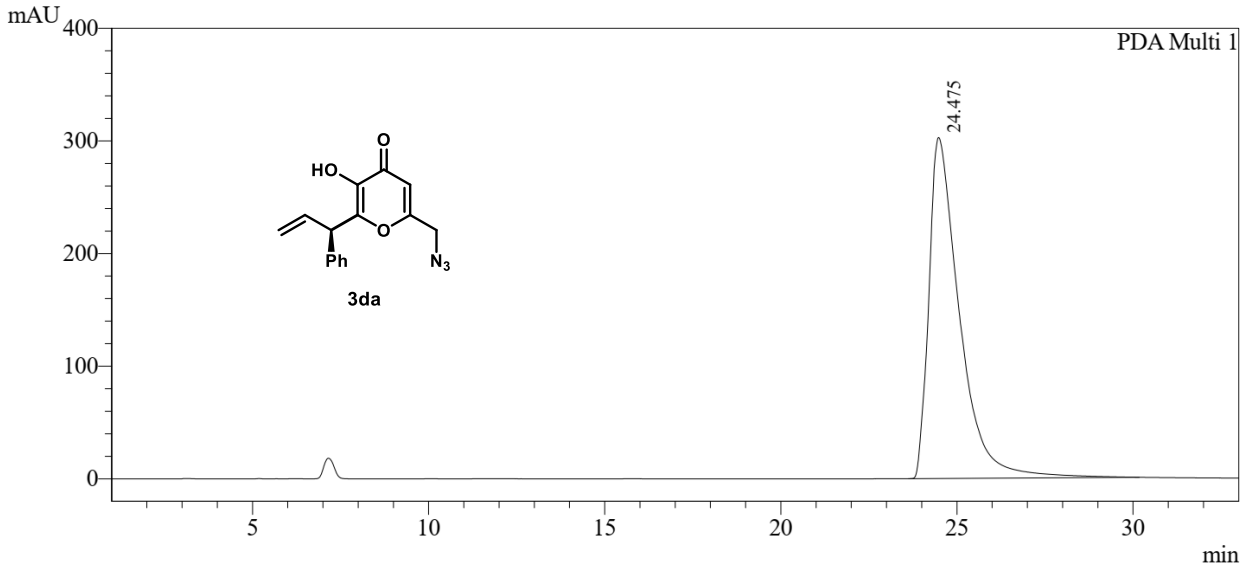


PeakTable

PDA Ch1 282nm 4nm

Peak#	Ret. Time	Area	Area %
1	21.861	444060	49.171
2	25.086	459030	50.829
Total		903090	100.000

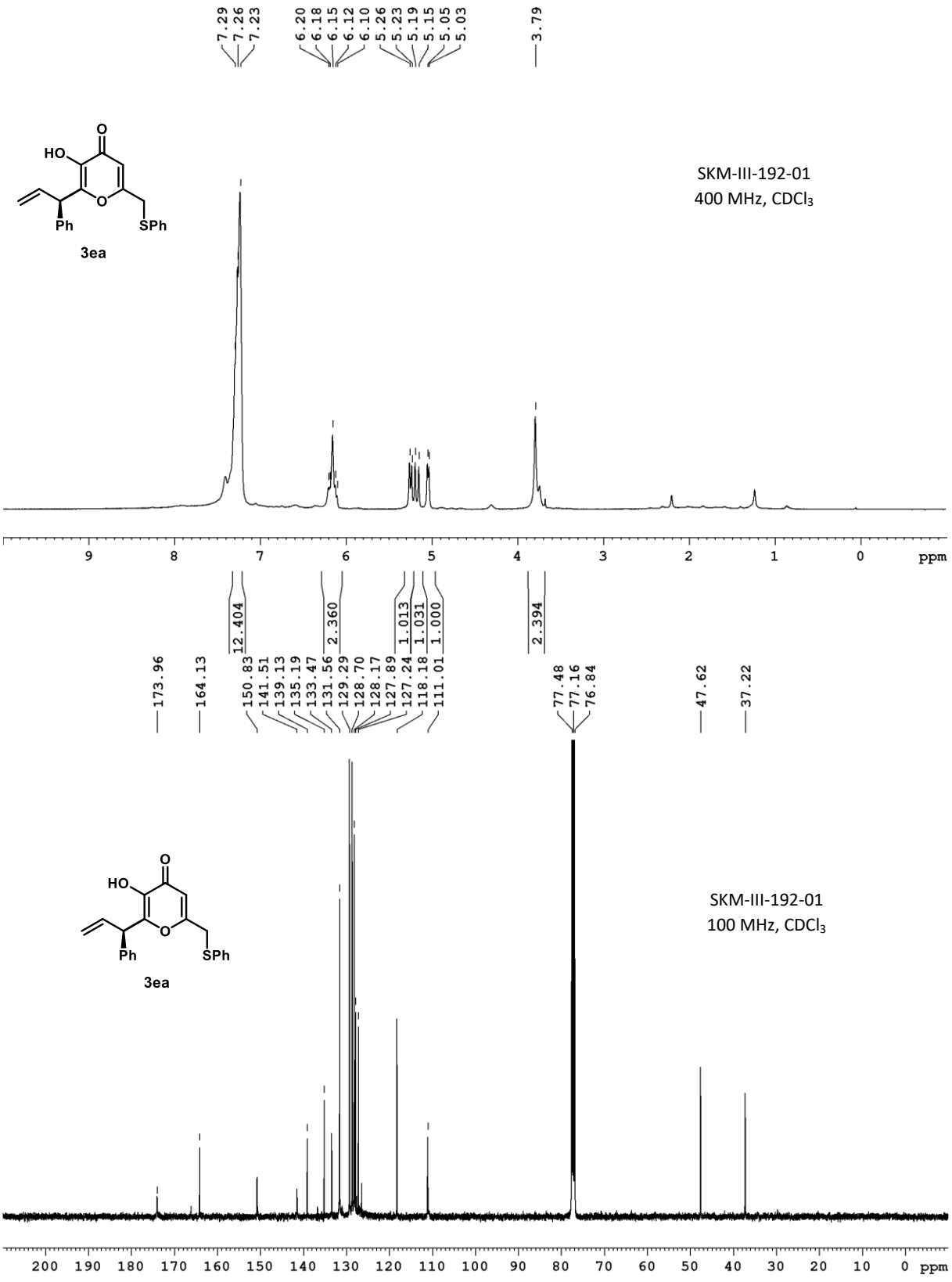
Daicel Chiralpak IH column (85:15 *n*-Hexane/*i*-PrOH, 1mL/min, 20 °C)

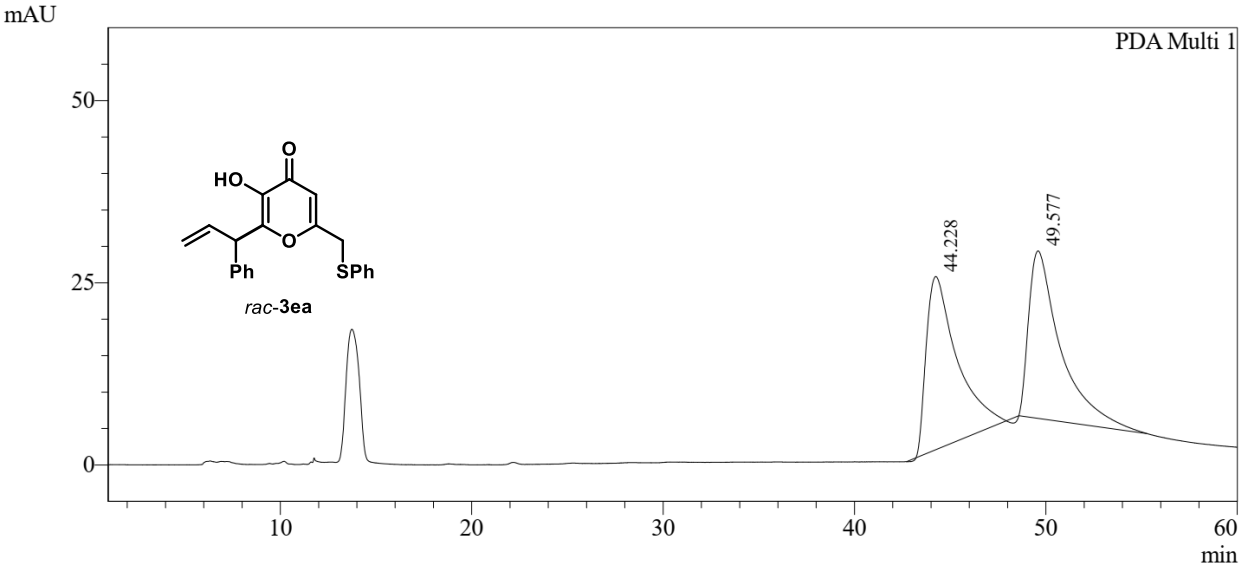


PeakTable

PDA Ch1 282nm 4nm

Peak#	Ret. Time	Area	Area %
1	24.475	18302946	100.000
Total		18302946	100.000


7.29
7.26
7.23
6.20
6.18
6.15
6.12
6.10
5.26
5.23
5.19
5.15
5.05
5.03
3.79
HO
O
O
Ph
SPh
3ea
SKM-III-192-01
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
12.404
2.360
1.013
1.031
1.000
2.394
173.96
164.13
150.83
141.51
139.13
135.19
133.47
131.56
129.29
128.70
128.17
127.89
127.24
118.18
111.01
77.48
77.16
76.84
47.62
37.22
HO
O
O
Ph
SPh
3ea
SKM-III-192-01
100 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

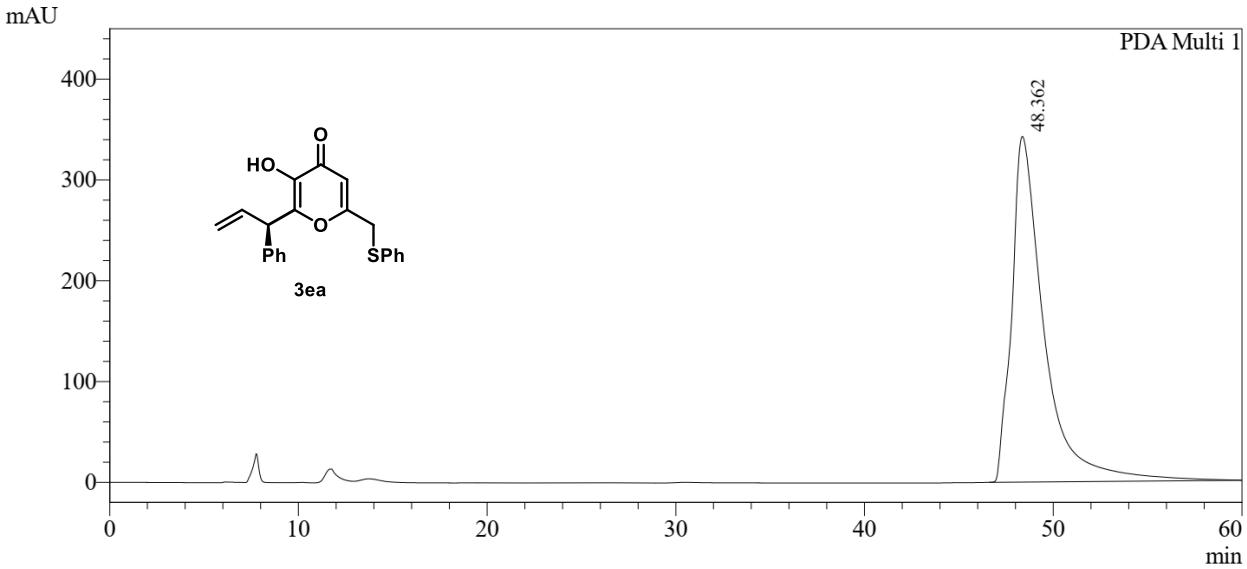


PeakTable

PDA Ch1 272nm 4nm

Peak#	Ret. Time	Area	Area %
1	44.228	2643491	49.769
2	49.577	2667996	50.231
Total		5311487	100.000

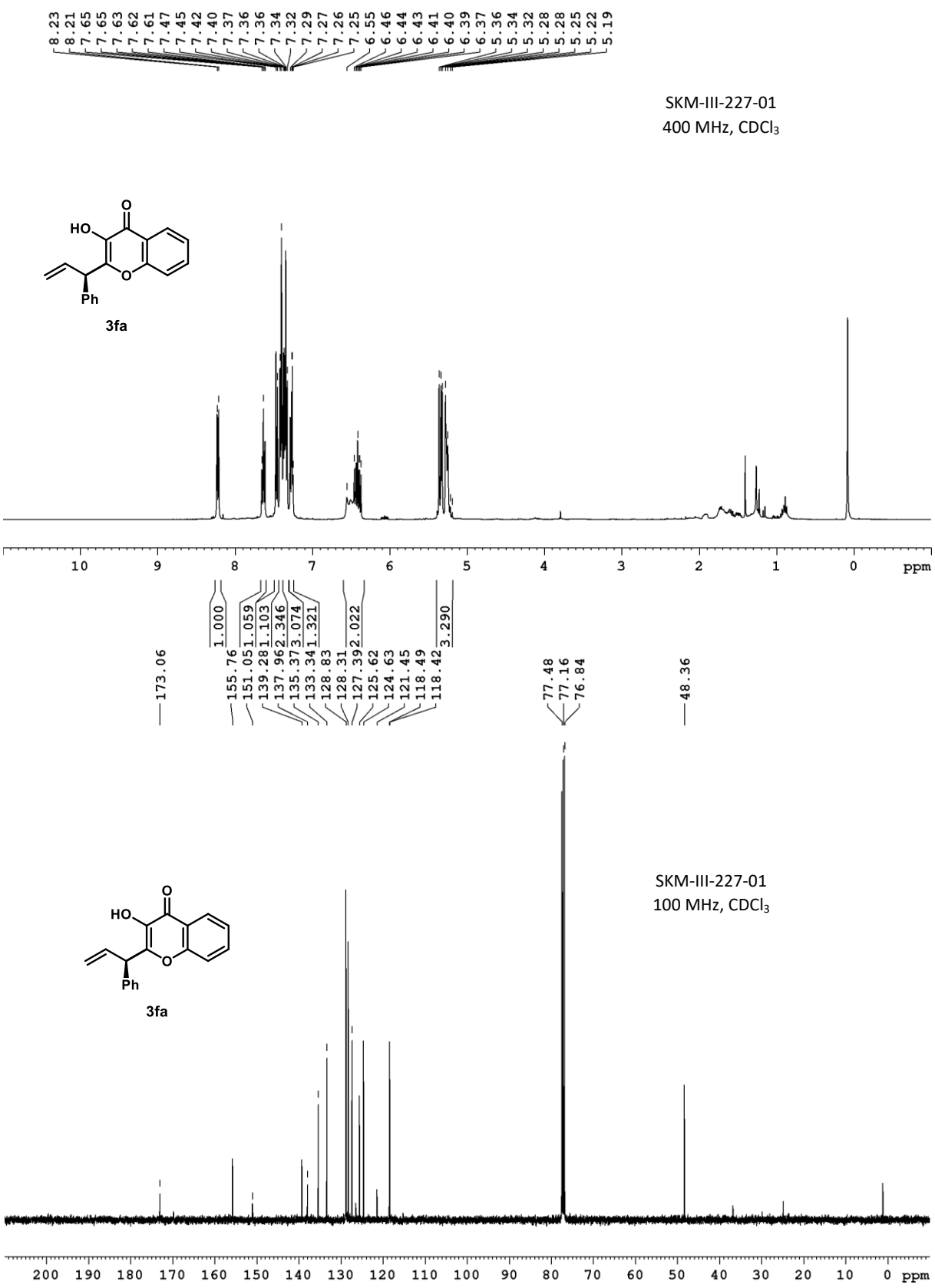
Daicel Chiralpak IH column (90:10 *n*-Hexane/*i*-PrOH, 0.5 mL/min, 20 °C)

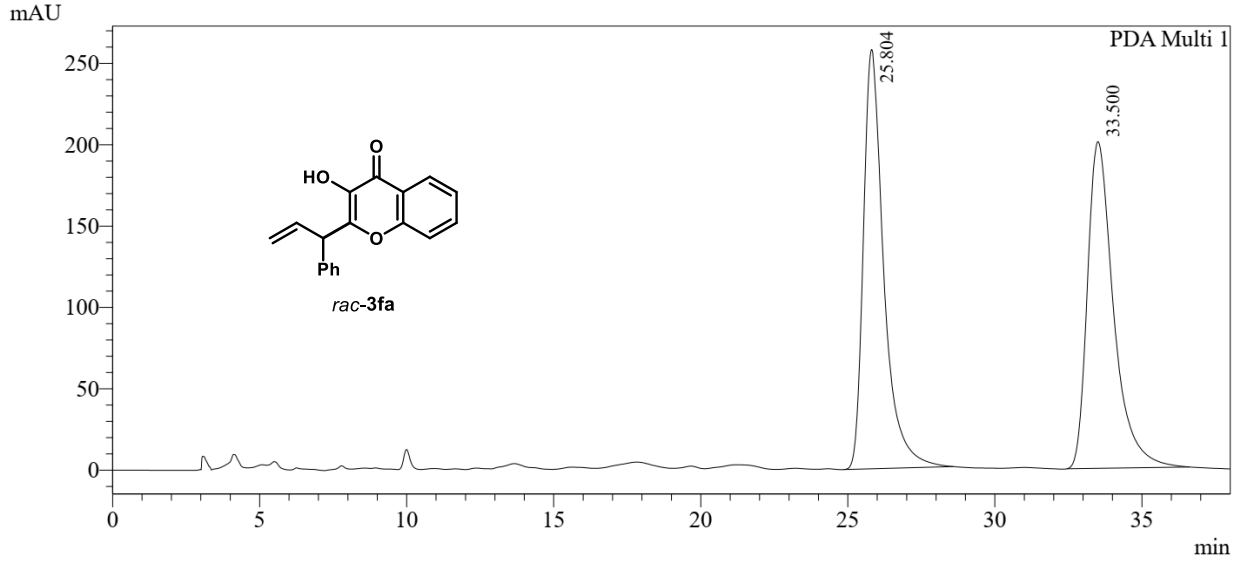


PeakTable

PDA Ch1 272nm 4nm

Peak#	Ret. Time	Area	Area %
1	48.362	40998998	100.000
Total		40998998	100.000


8.23
8.21
7.65
7.65
7.63
7.62
7.61
7.47
7.45
7.42
7.40
7.37
7.36
7.36
7.34
7.32
7.29
7.27
7.26
7.25
6.55
6.46
6.44
6.43
6.41
6.40
6.39
6.37
5.36
5.34
5.32
5.28
5.28
5.25
5.22
5.19
SKM-III-227-01
400 MHz, CDCl3
HO
O
O
Ph
3fa
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.059
1.103
2.346
3.074
1.321
2.022
3.290
173.06
155.76
151.05
139.28
137.96
135.37
133.34
128.83
128.31
127.39
125.62
124.63
121.45
118.49
118.42
77.48
77.16
76.84
48.36
SKM-III-227-01
100 MHz, CDCl3
HO
O
O
Ph
3fa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

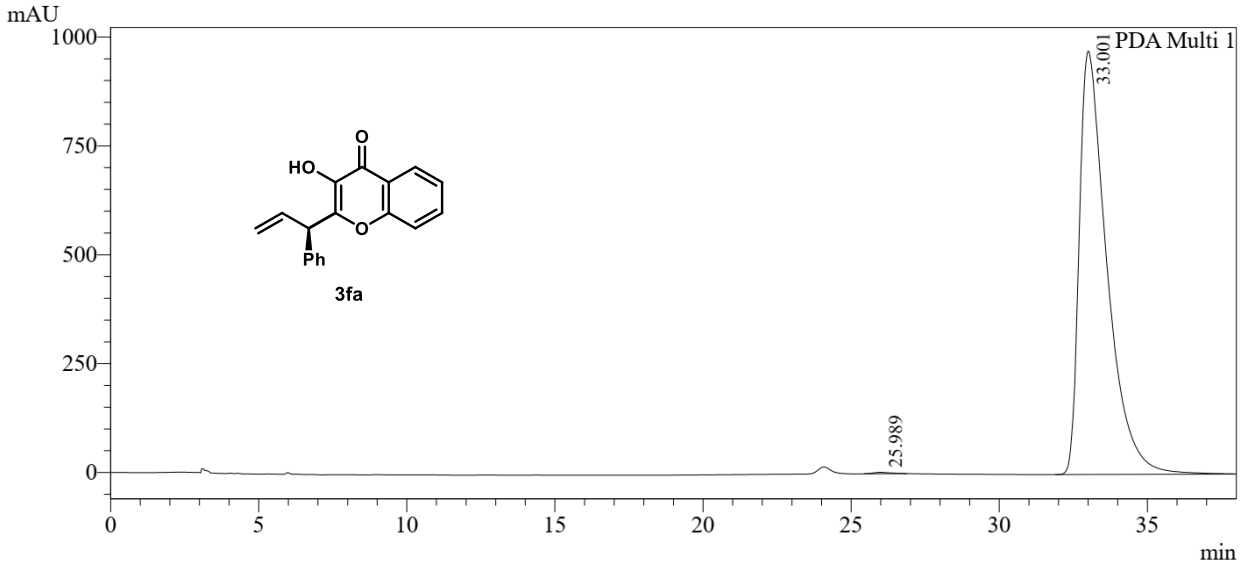


PeakTable

PDA Ch1 233nm 4nm

Peak#	Ret. Time	Area	Area %
1	25.804	12421526	50.005
2	33.500	12418942	49.995
Total		24840468	100.000

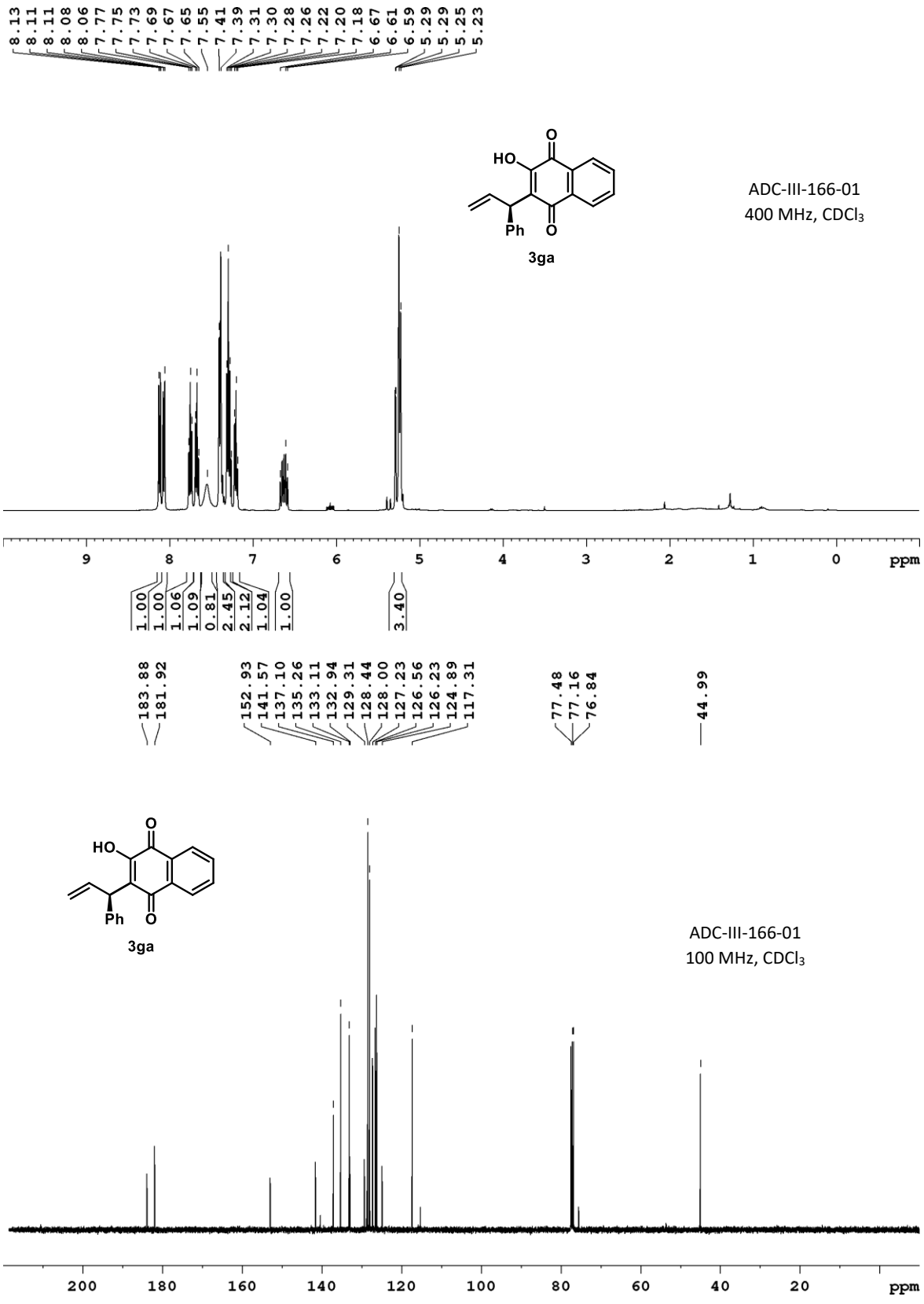
Daicel Chiralpak IG column (95:5 *n*-Hexane/*i*-PrOH, 1 mL/min, 20 °C)

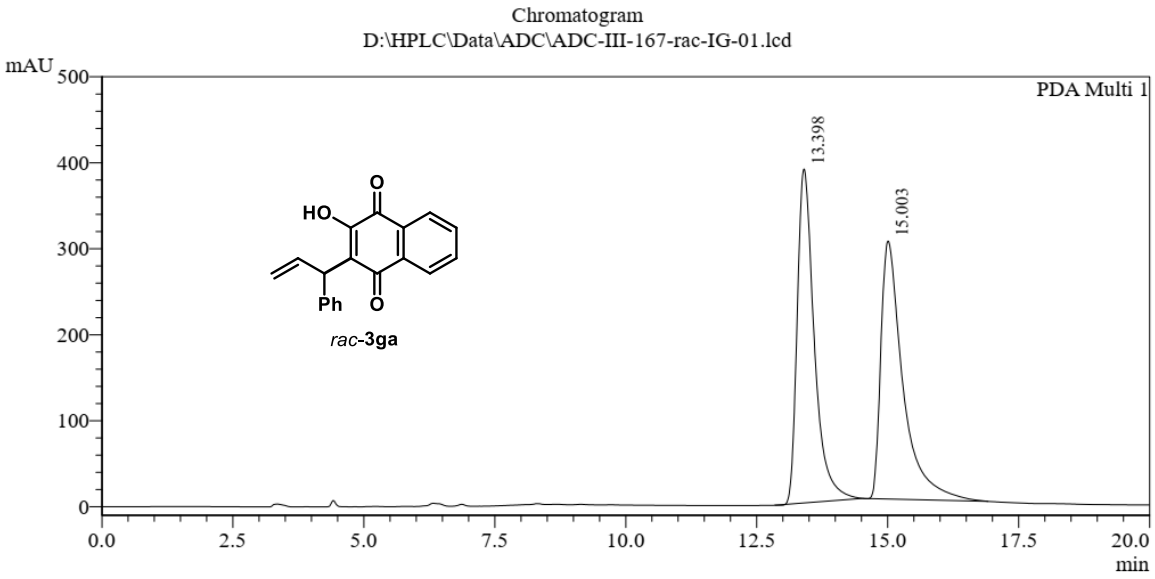


PeakTable

PDA Ch1 233nm 4nm

Peak#	Ret. Time	Area	Area %
1	25.989	132196	0.209
2	33.001	63141661	99.791
Total		63273857	100.000


8.13
8.11
8.11
8.08
8.06
7.77
7.75
7.73
7.69
7.67
7.65
7.55
7.41
7.39
7.31
7.30
7.28
7.26
7.22
7.20
7.18
6.67
6.61
6.59
5.29
5.29
5.25
5.23
HO
O
Ph
O
3ga
ADC-III-166-01
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.06
1.09
0.81
2.45
2.12
1.04
1.00
3.40
183.88
181.92
152.93
141.57
137.10
135.26
133.11
132.94
129.31
128.44
128.00
127.23
126.56
126.23
124.89
117.31
77.48
77.16
76.84
44.99
HO
O
Ph
O
3ga
ADC-III-166-01
100 MHz, CDCl3
200
180
160
140
120
100
80
60
40
20
ppm

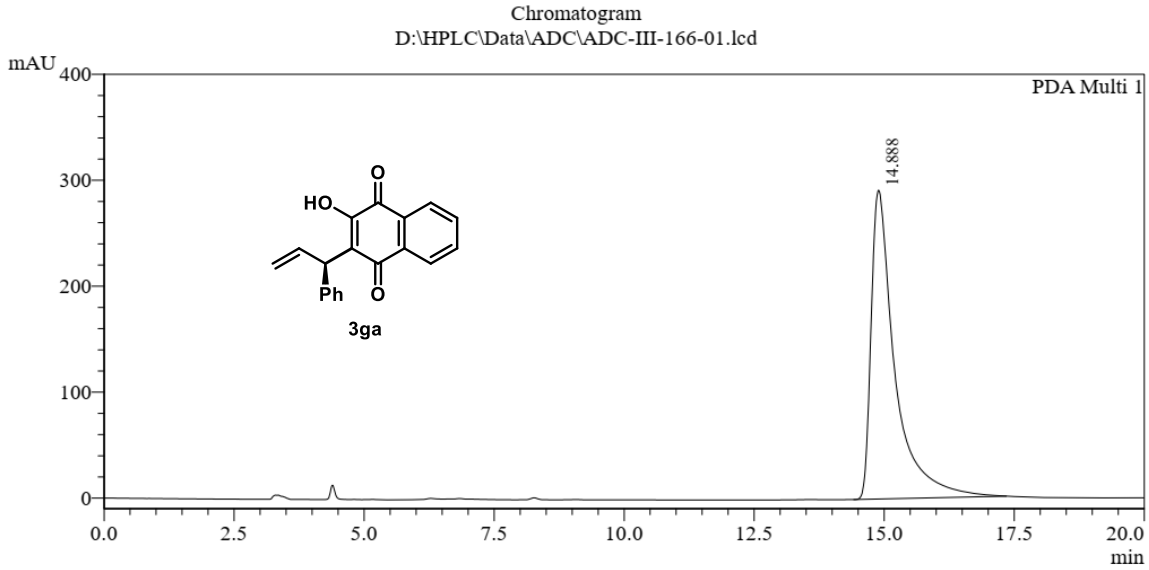


PeakTable

PDA Ch1 232nm 4nm

Peak#	Ret. Time	Area	Area %
1	13.398	8806755	50.008
2	15.003	8803947	49.992
Total		17610702	100.000

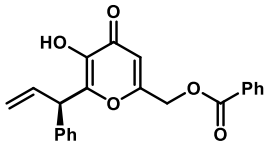
Daicel Chiralpak IG column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)



PeakTable

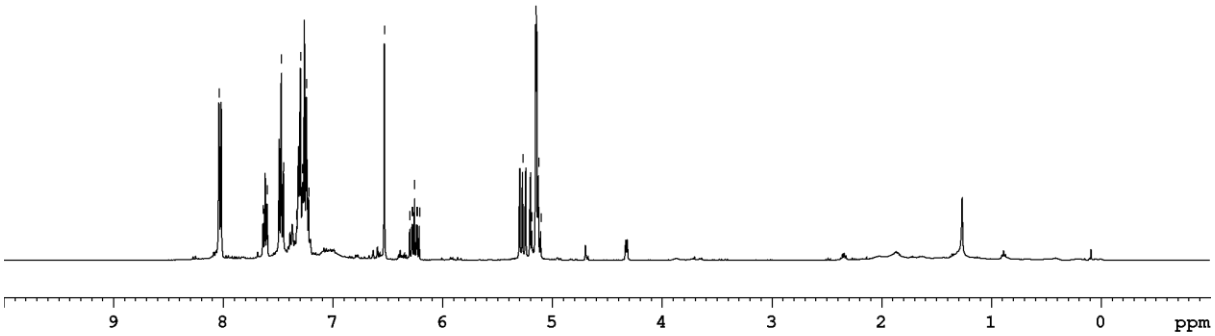
PDA Ch1 232nm 4nm

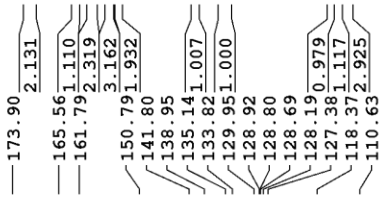
Peak#	Ret. Time	Area	Area %
1	14.888	9263135	100.000
Total		9263135	100.000

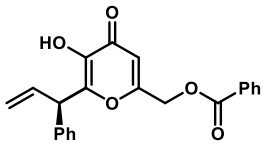


3ha

SKM-III-165-01
400 MHz, $CDCl_3$

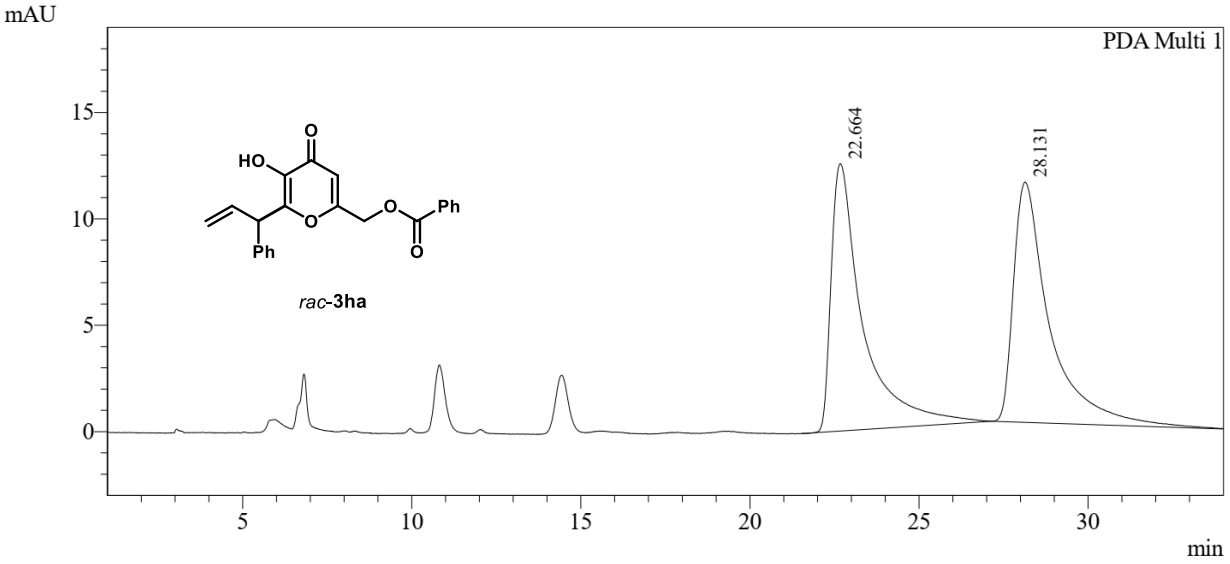






3ha

SKM-III-165-01
100 MHz, $CDCl_3$

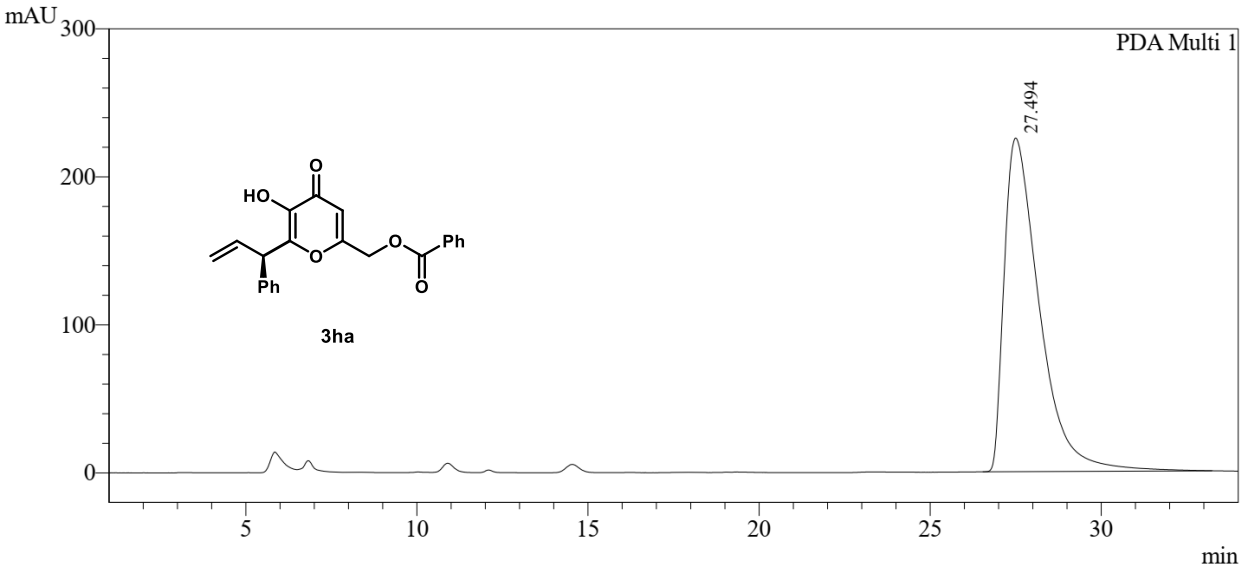


PeakTable

PDA Ch1 298nm 4nm

Peak#	Ret. Time	Area	Area %
1	22.664	820498	49.374
2	28.131	841299	50.626
Total		1661797	100.000

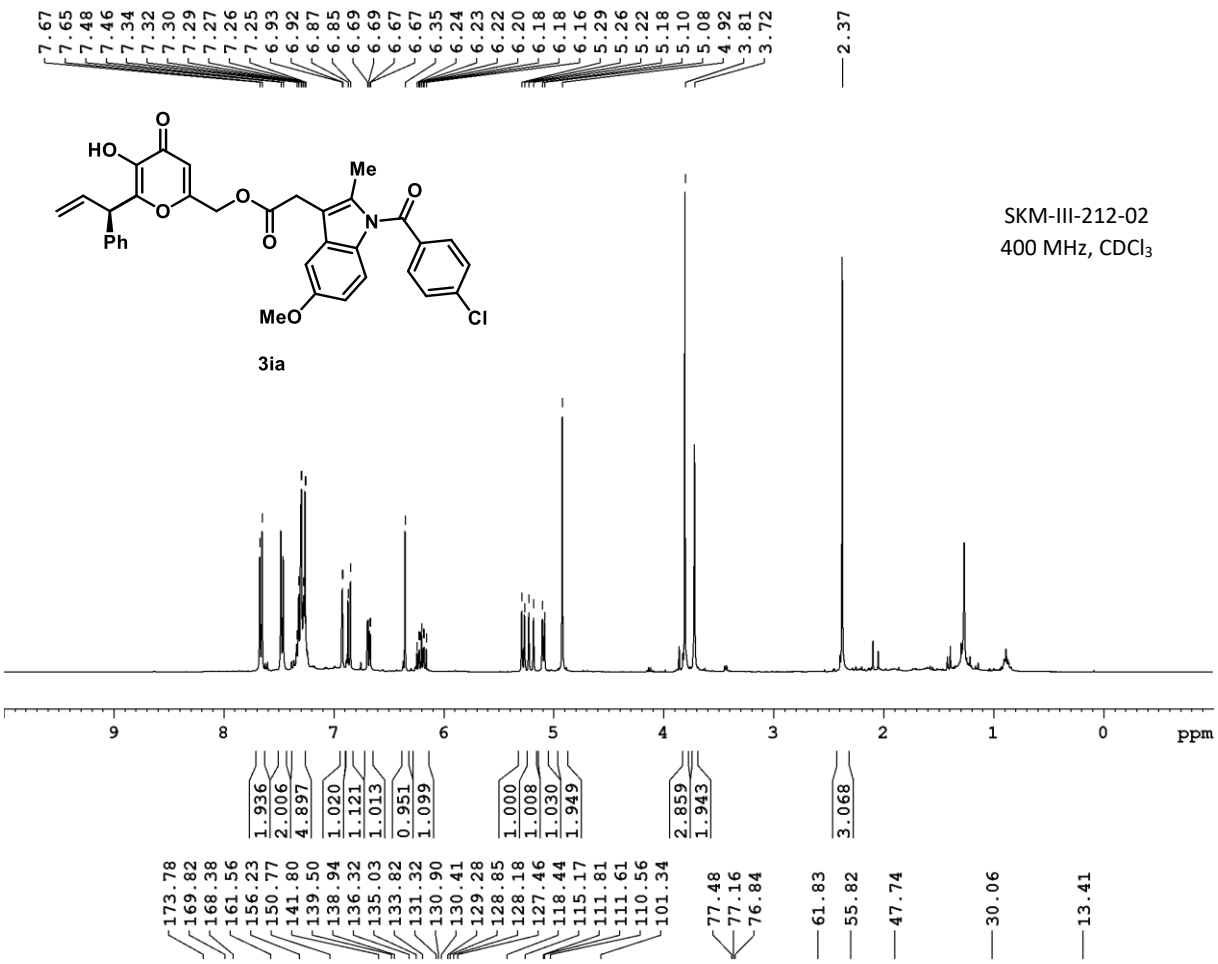
Daicel Chiralpak IH column (85:15 *n*-Hexane/*i*-PrOH, 1 mL/min, 20 °C)

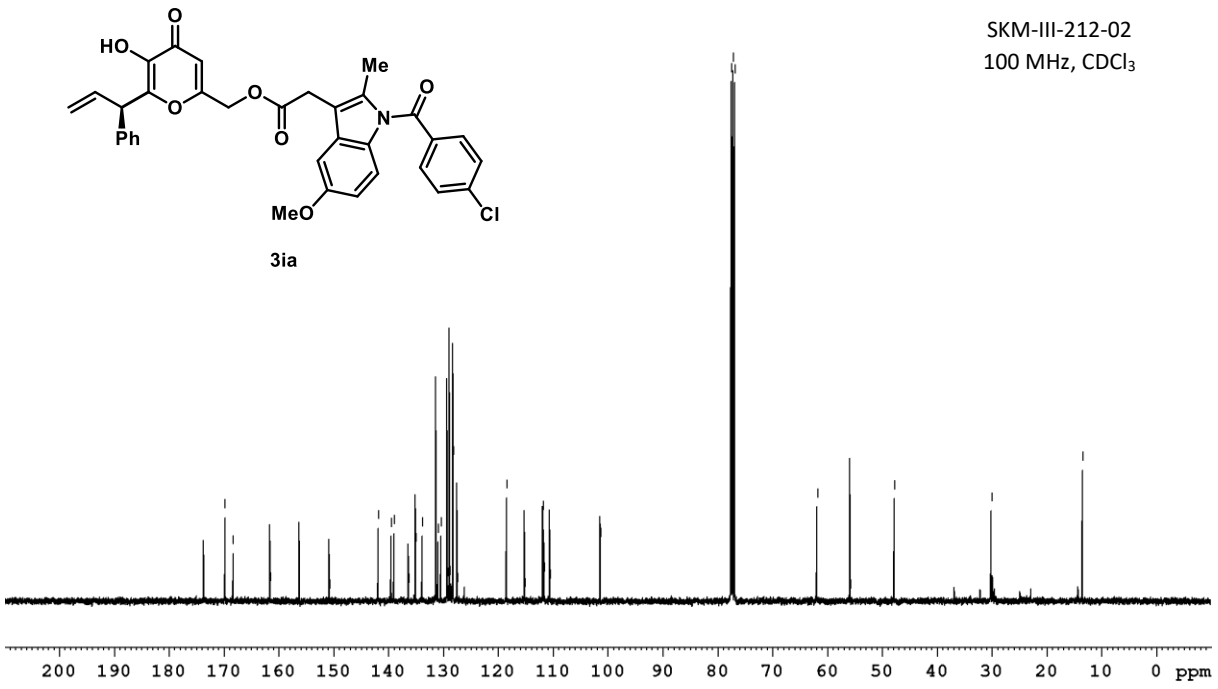


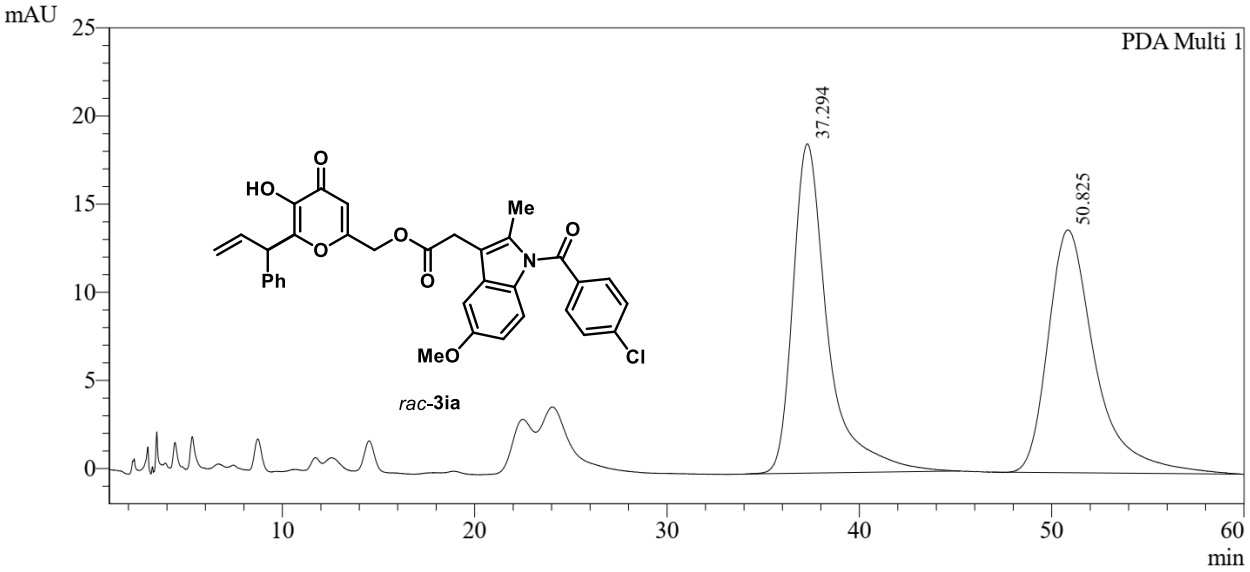
PeakTable

PDA Ch1 298nm 4nm

Peak#	Ret. Time	Area	Area %
1	27.494	16145576	100.000
Total		16145576	100.000


7.67 7.65 7.48 7.46 7.34 7.32 7.30 7.29 7.27 7.26 7.25 6.93 6.92 6.87 6.85 6.69 6.69 6.67 6.67 6.35 6.24 6.23 6.22 6.20 6.18 6.18 6.16 5.29 5.26 5.22 5.18 5.10 5.08 4.92 3.81 3.72
2.37
HO
Me
Ph
MeO
Cl
3ia
SKM-III-212-02
400 MHz, CDCl3
9 8 7 6 5 4 3 2 1 0 ppm
1.936 2.006 4.897 1.020 1.121 1.013 0.951 1.099 1.000 1.008 1.030 1.949 2.859 1.943 3.068


173.78 169.82 168.38 161.56 156.23 150.77 141.80 139.50 138.94 136.32 135.03 133.82 131.32 130.90 130.41 129.28 128.85 128.18 127.46 118.44 115.17 111.81 111.61 110.56 101.34
77.48 77.16 76.84
61.83 55.82 47.74 30.06 13.41
HO
Me
Ph
MeO
Cl
3ia
SKM-III-212-02
100 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

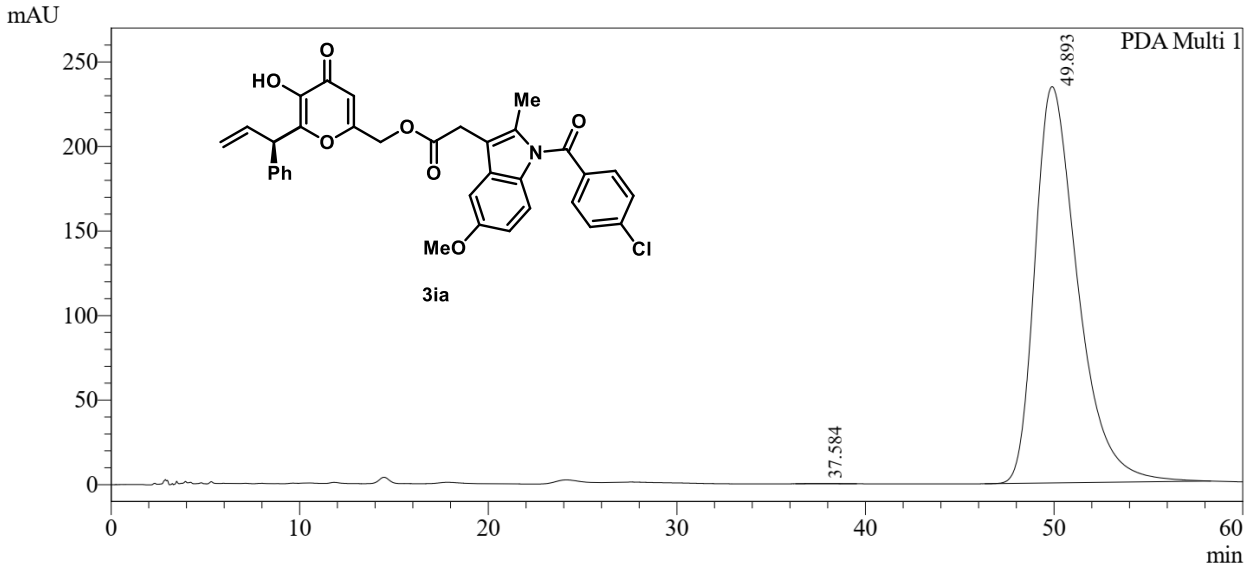


PeakTable

PDA Ch1 268nm 4nm

Peak#	Ret. Time	Area	Area %
1	37.294	2349354	50.040
2	50.825	2345638	49.960
Total		4694992	100.000

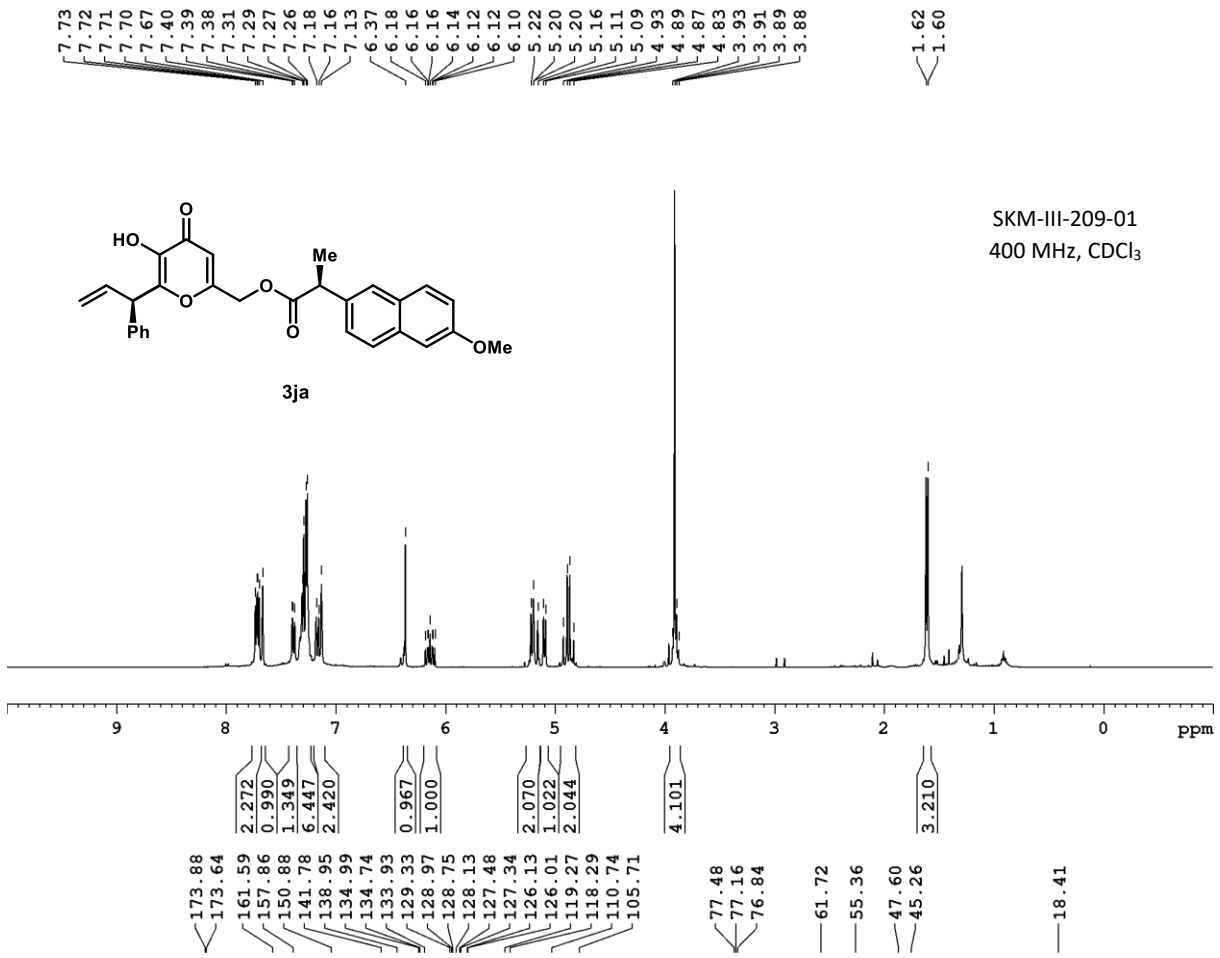
Daicel Chiralpak IG column (40:60 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C)

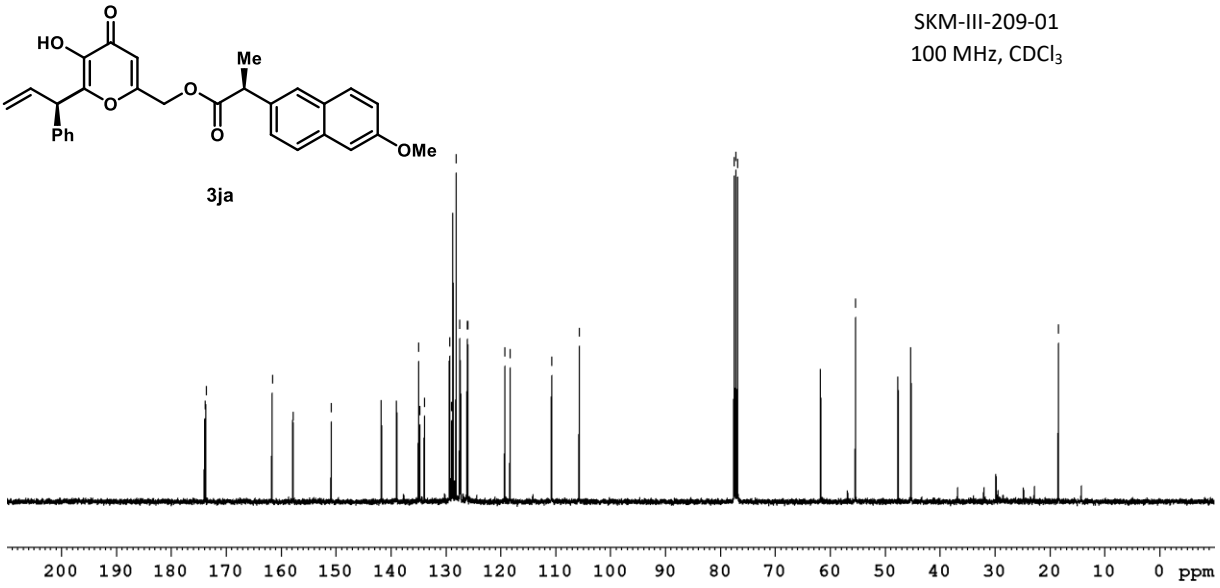


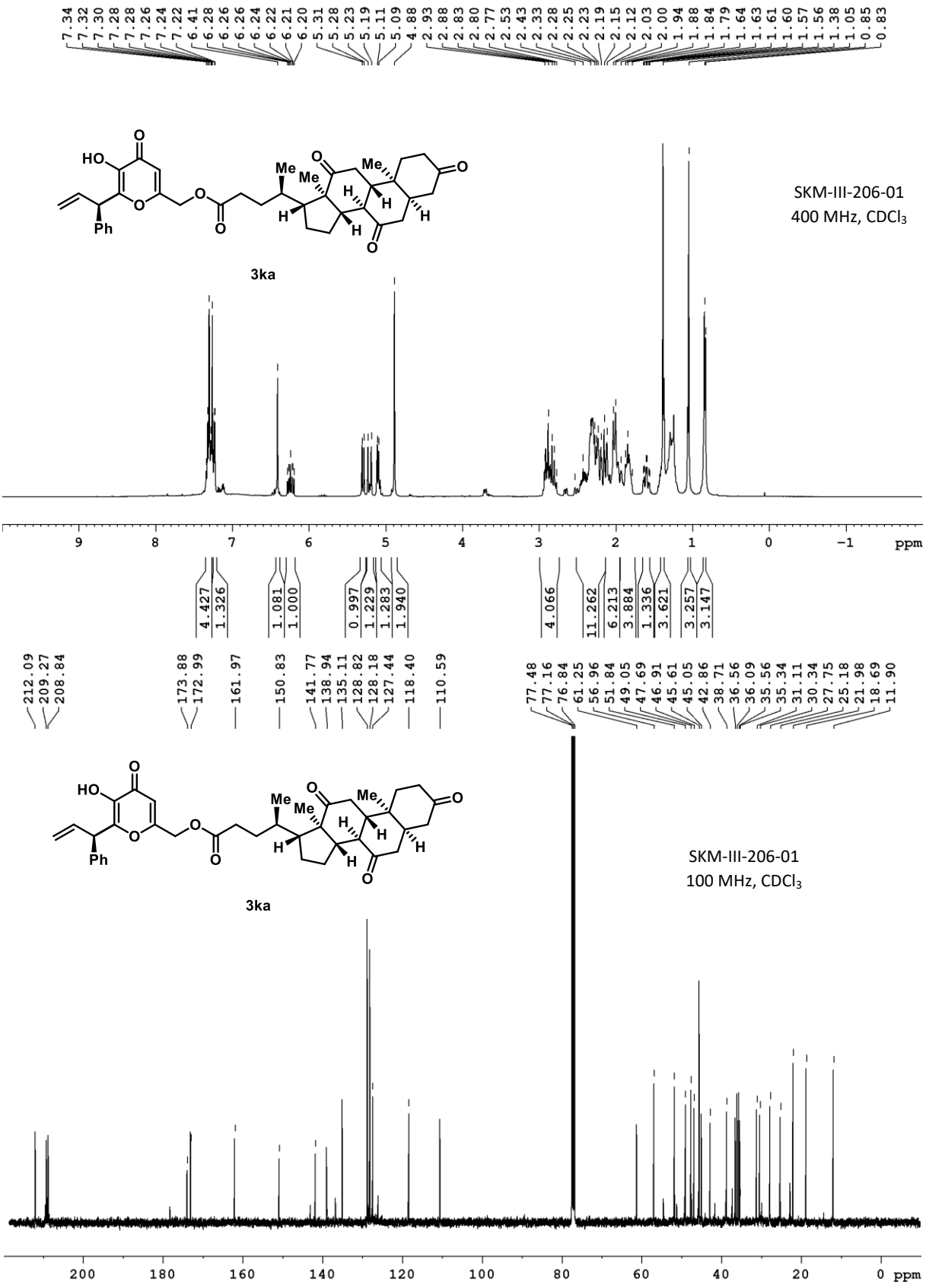
PeakTable

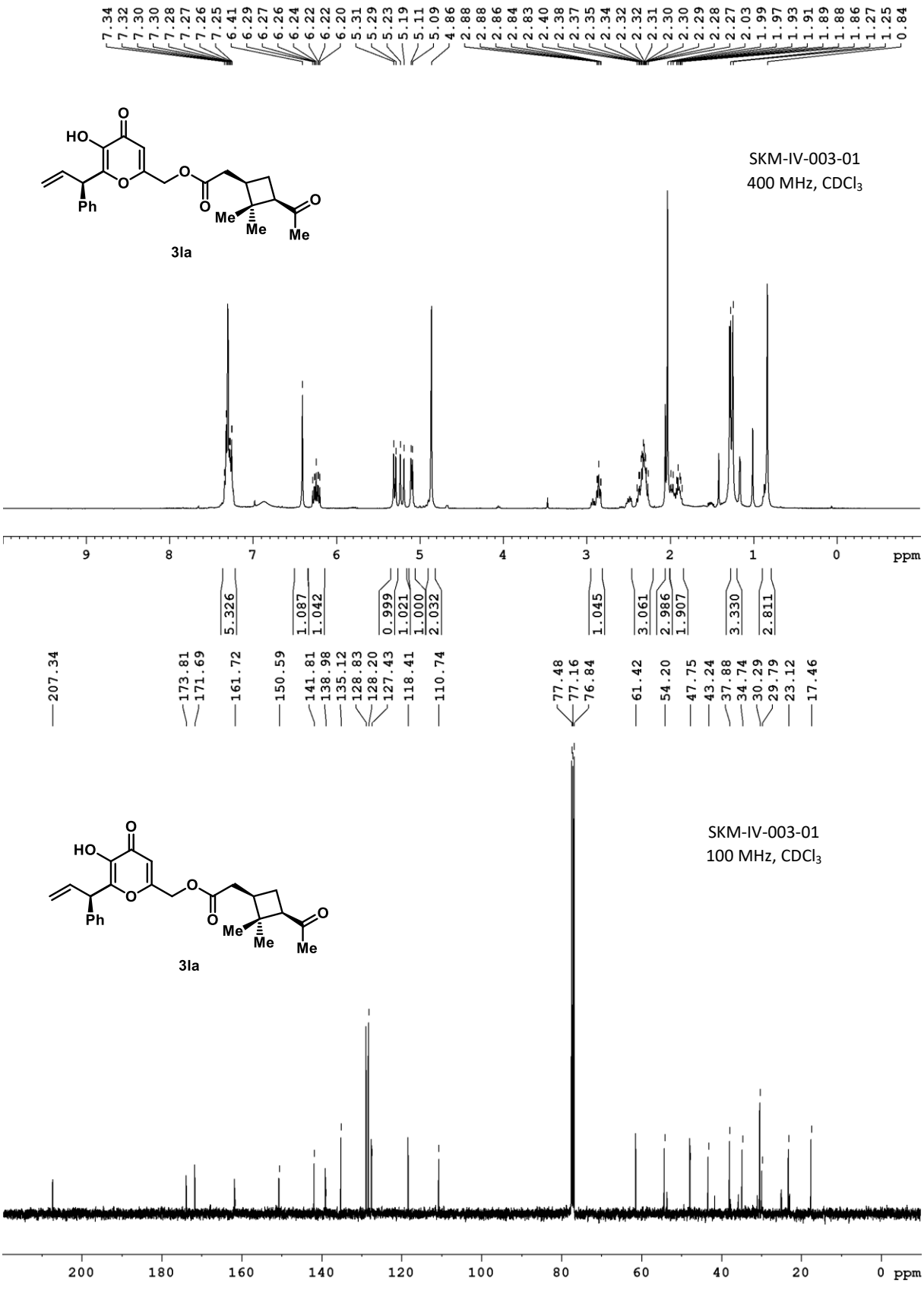
PDA Ch1 268nm 4nm

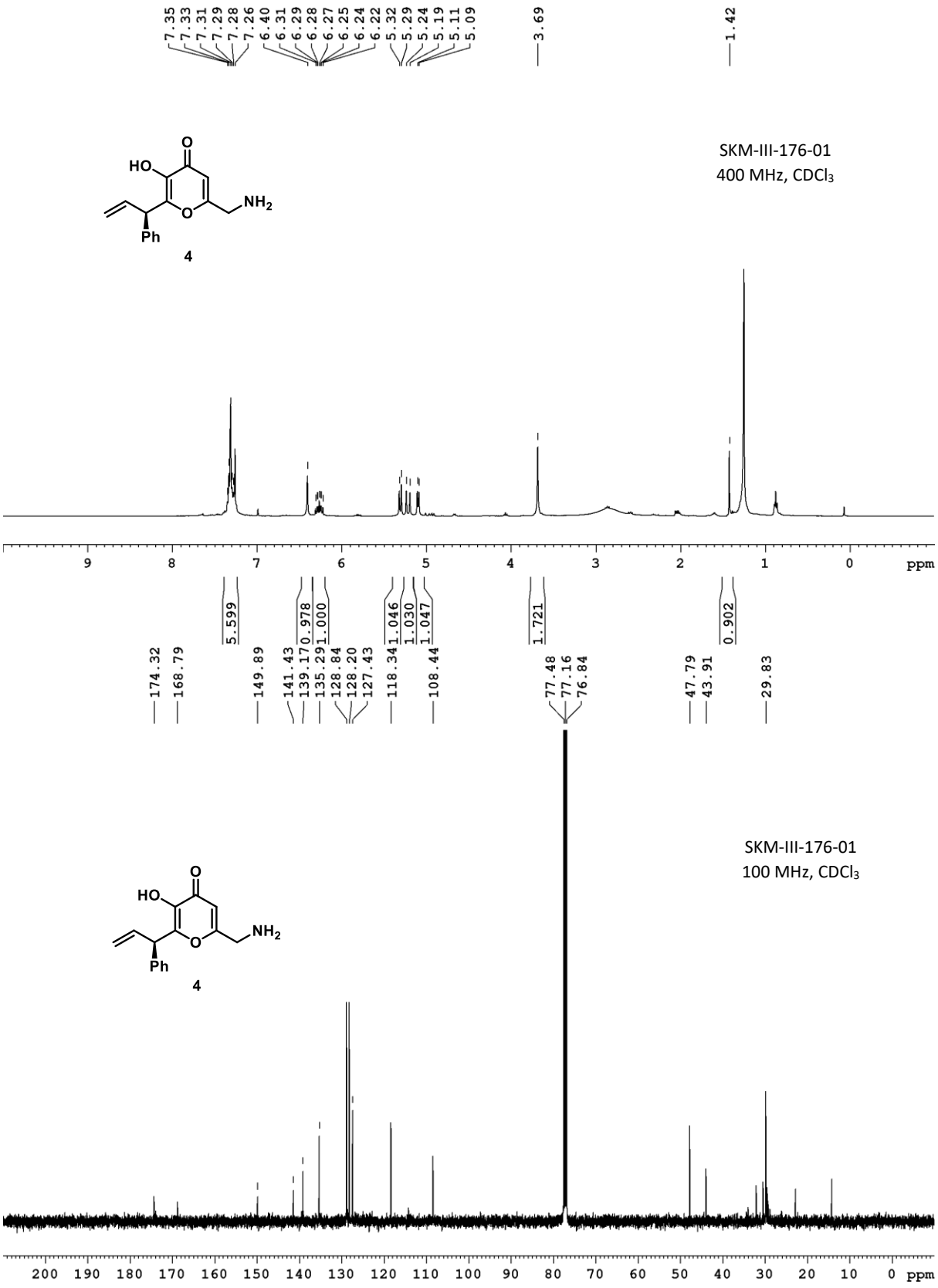
Peak#	Ret. Time	Area	Area %
1	37.584	15292	0.041
2	49.893	37000103	99.959
Total		37015395	100.000

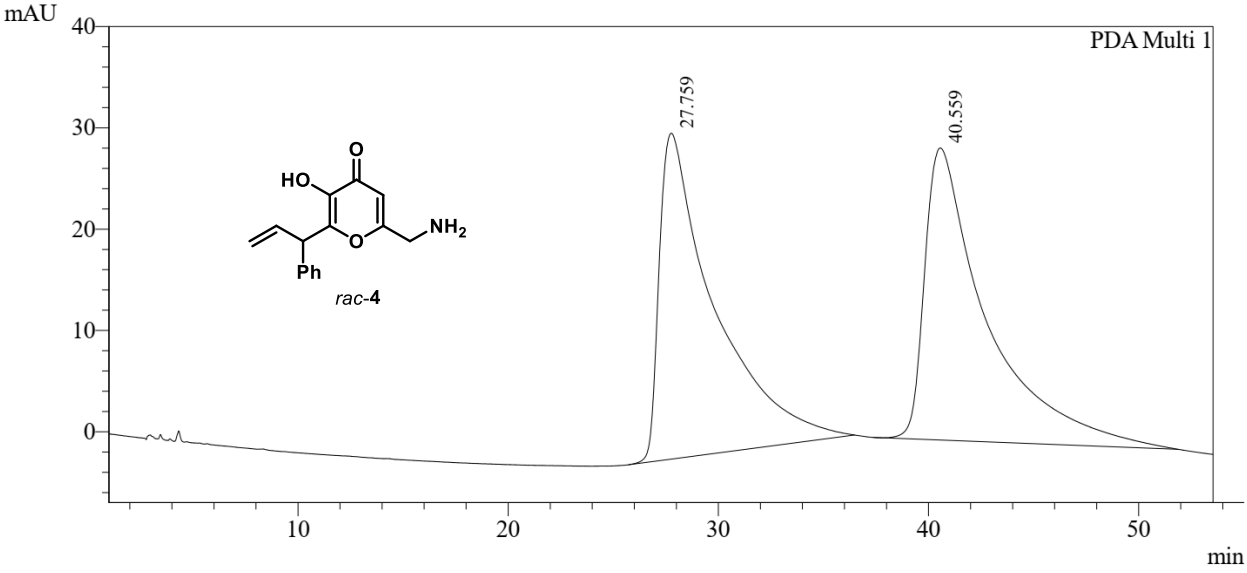

7.73
7.72
7.71
7.70
7.67
7.40
7.39
7.38
7.31
7.29
7.27
7.26
7.18
7.16
7.13
6.37
6.18
6.16
6.16
6.14
6.12
6.12
6.10
5.22
5.20
5.20
5.16
5.11
5.09
4.93
4.89
4.87
4.83
3.93
3.91
3.89
3.88
1.62
1.60
HO
O
Me
Ph
OMe
3ja
SKM-III-209-01
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
2.272
0.990
1.349
6.447
2.420
0.967
1.000
2.070
1.022
2.044
4.101
3.210
173.88
173.64
161.59
157.86
150.88
141.78
138.95
134.99
134.74
133.93
129.33
128.97
128.75
128.13
127.48
127.34
126.13
126.01
119.27
118.29
110.74
105.71
77.48
77.16
76.84
61.72
55.36
47.60
45.26
18.41


HO
O
Me
Ph
OMe
3ja
SKM-III-209-01
100 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


SKM-III-206-01
400 MHz, CDCl3
3ka
ppm
SKM-III-206-01
100 MHz, CDCl3
3ka
ppm


7.34 7.32 7.30 7.30 7.28 7.27 7.26 7.25 6.41 6.29 6.27 6.26 6.24 6.22 6.22 6.20 5.31 5.29 5.23 5.19 5.11 5.09 4.86 2.88 2.88 2.86 2.84 2.83 2.40 2.38 2.37 2.35 2.34 2.32 2.32 2.31 2.30 2.30 2.29 2.28 2.27 2.03 1.99 1.97 1.93 1.91 1.89 1.88 1.86 1.27 1.25 0.84
HO
O
O
O
Ph
Me
Me
Me
O
3Ia
SKM-IV-003-01
400 MHz, CDCl3
9 8 7 6 5 4 3 2 1 0 ppm
5.326 1.087 1.042 0.999 1.021 1.000 2.032 1.045 3.061 2.986 1.907 3.330 2.811
207.34 173.81 171.69 161.72 150.59 141.81 138.98 135.12 128.83 128.20 127.43 118.41 110.74 77.48 77.16 76.84 61.42 54.20 47.75 43.24 37.88 34.74 30.29 29.79 23.12 17.46
HO
O
O
O
Ph
Me
Me
Me
O
3Ia
SKM-IV-003-01
100 MHz, CDCl3
200 180 160 140 120 100 80 60 40 20 0 ppm


7.35
7.33
7.31
7.29
7.28
7.26
6.40
6.31
6.29
6.28
6.27
6.25
6.24
6.22
5.32
5.29
5.24
5.19
5.11
5.09
3.69
1.42
HO
O
NH2
Ph
4
SKM-III-176-01
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
5.599
0.978
1.000
1.046
1.030
1.047
1.721
0.902
174.32
168.79
149.89
141.43
139.17
135.29
128.84
128.20
127.43
118.34
108.44
77.48
77.16
76.84
47.79
43.91
29.83
SKM-III-176-01
100 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

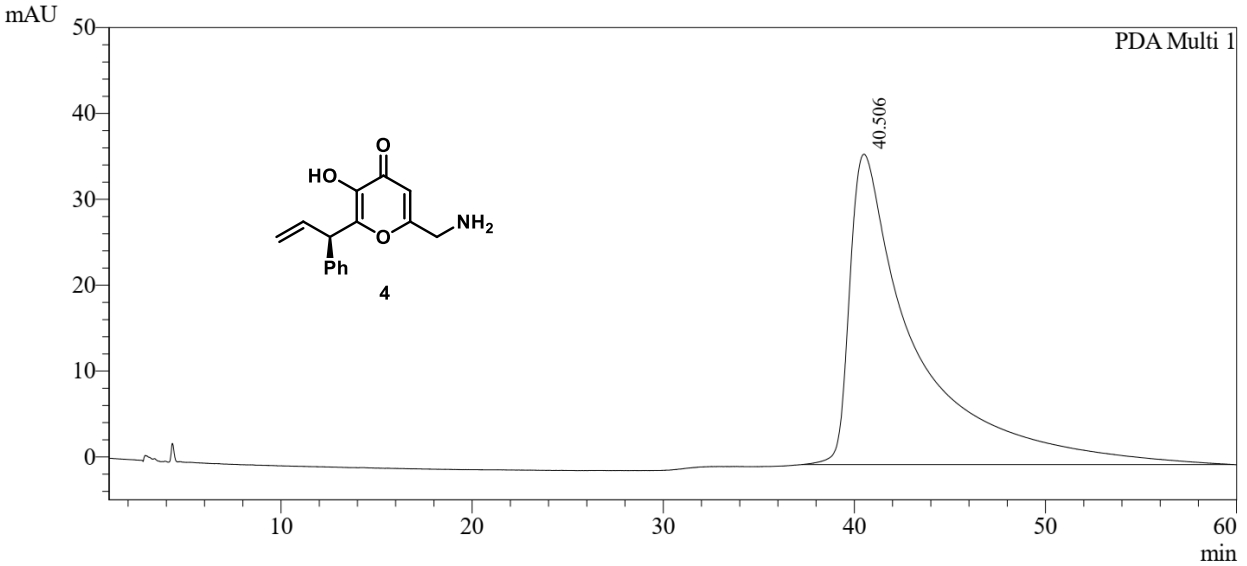


PeakTable

PDA Ch1 280nm 4nm

Peak#	Ret. Time	Area	Area %
1	27.759	5901396	50.050
2	40.559	5889578	49.950
Total		11790973	100.000

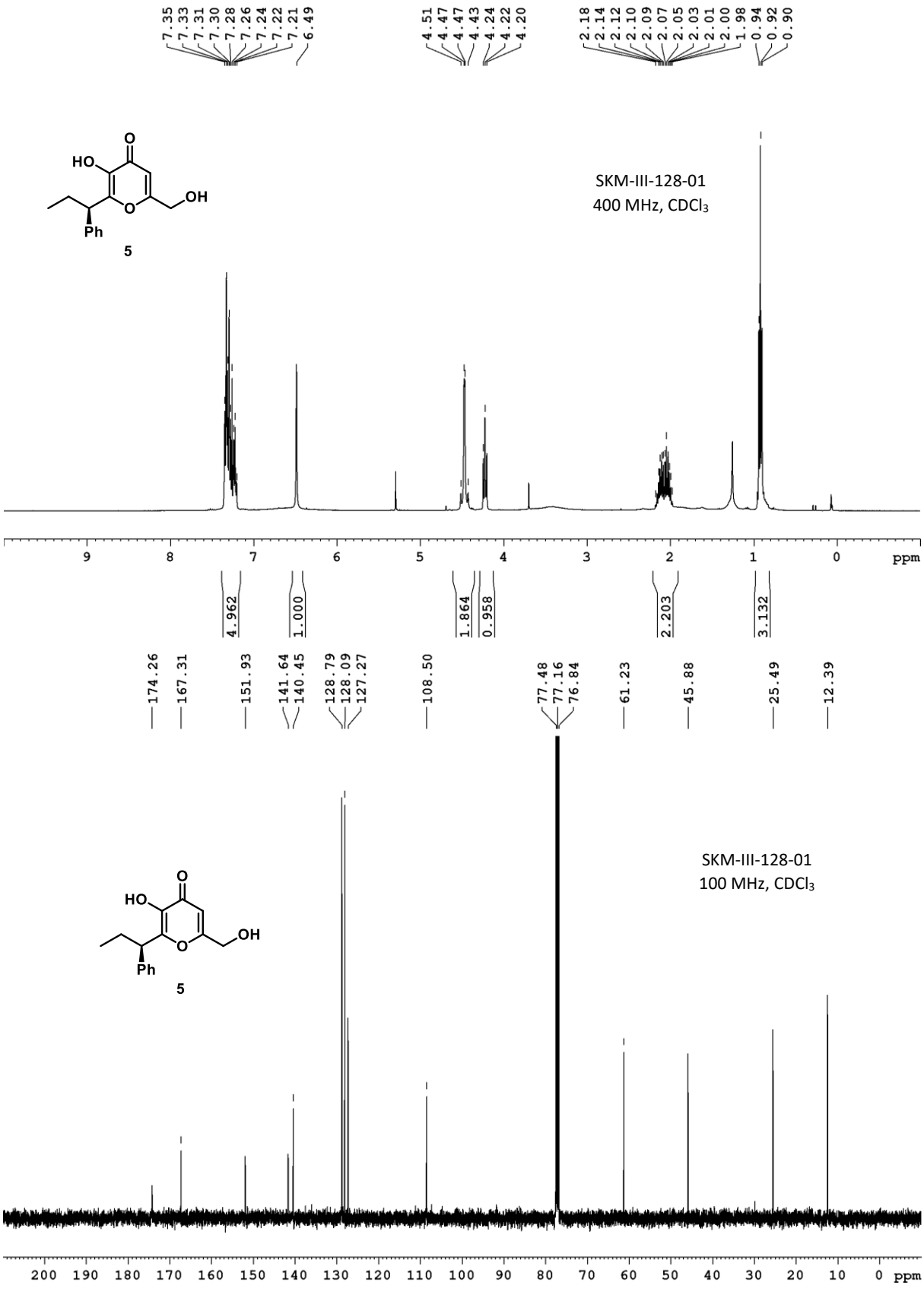
Phenomenex Cellulose-2 column (70:30 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

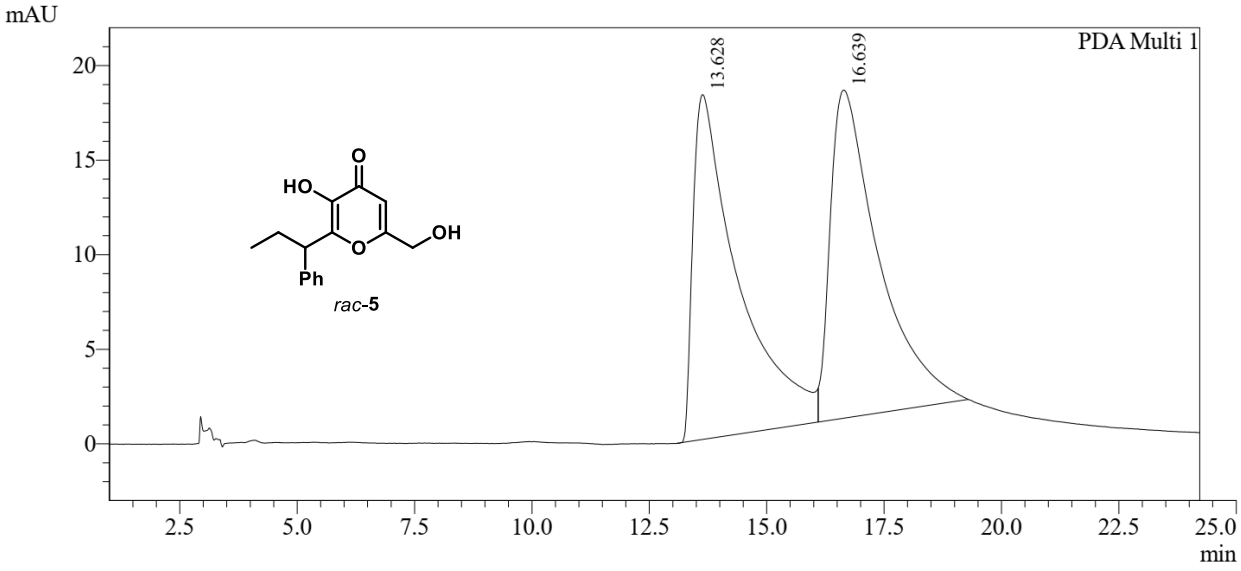


PeakTable

PDA Ch1 280nm 4nm

Peak#	Ret. Time	Area	Area %
1	40.506	8762993	100.000
Total		8762993	100.000


7.35
7.33
7.31
7.30
7.28
7.26
7.24
7.22
7.21
6.49
4.51
4.47
4.47
4.43
4.24
4.22
4.20
2.18
2.14
2.12
2.10
2.09
2.07
2.05
2.03
2.01
2.00
1.98
0.94
0.92
0.90
HO
O
OH
Ph
5
SKM-III-128-01
400 MHz, CDCl3
ppm
4.962
1.000
1.864
0.958
2.203
3.132
174.26
167.31
151.93
141.64
140.45
128.79
128.09
127.27
108.50
77.48
77.16
76.84
61.23
45.88
25.49
12.39
SKM-III-128-01
100 MHz, CDCl3
ppm

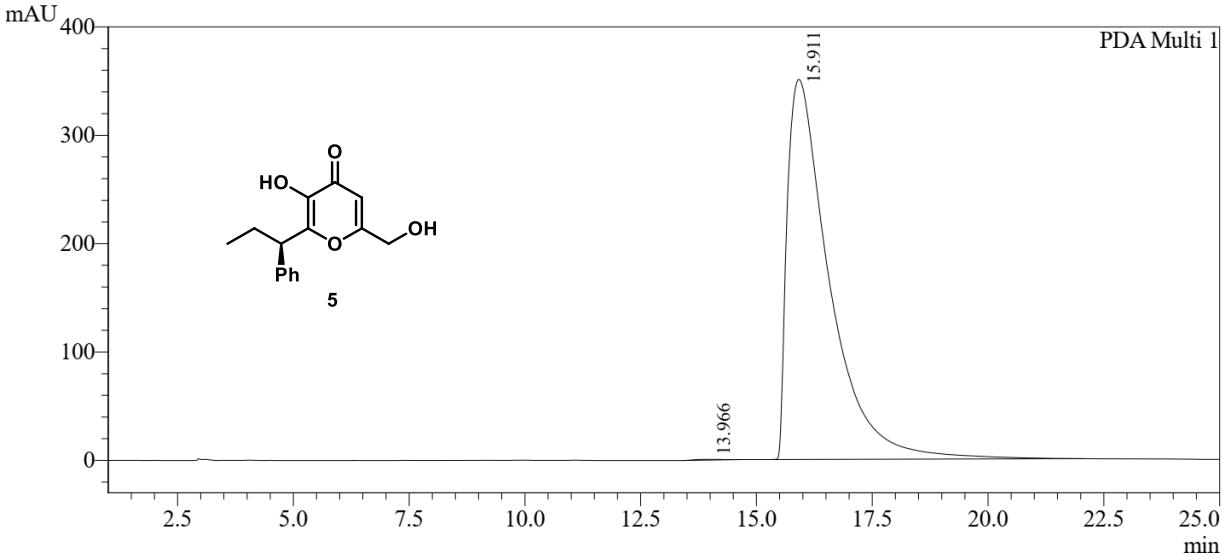


PeakTable

PDA Ch1 277nm 4nm

Peak#	Ret. Time	Area	Area %
1	13.628	1220477	49.572
2	16.639	1241534	50.428
Total		2462011	100.000

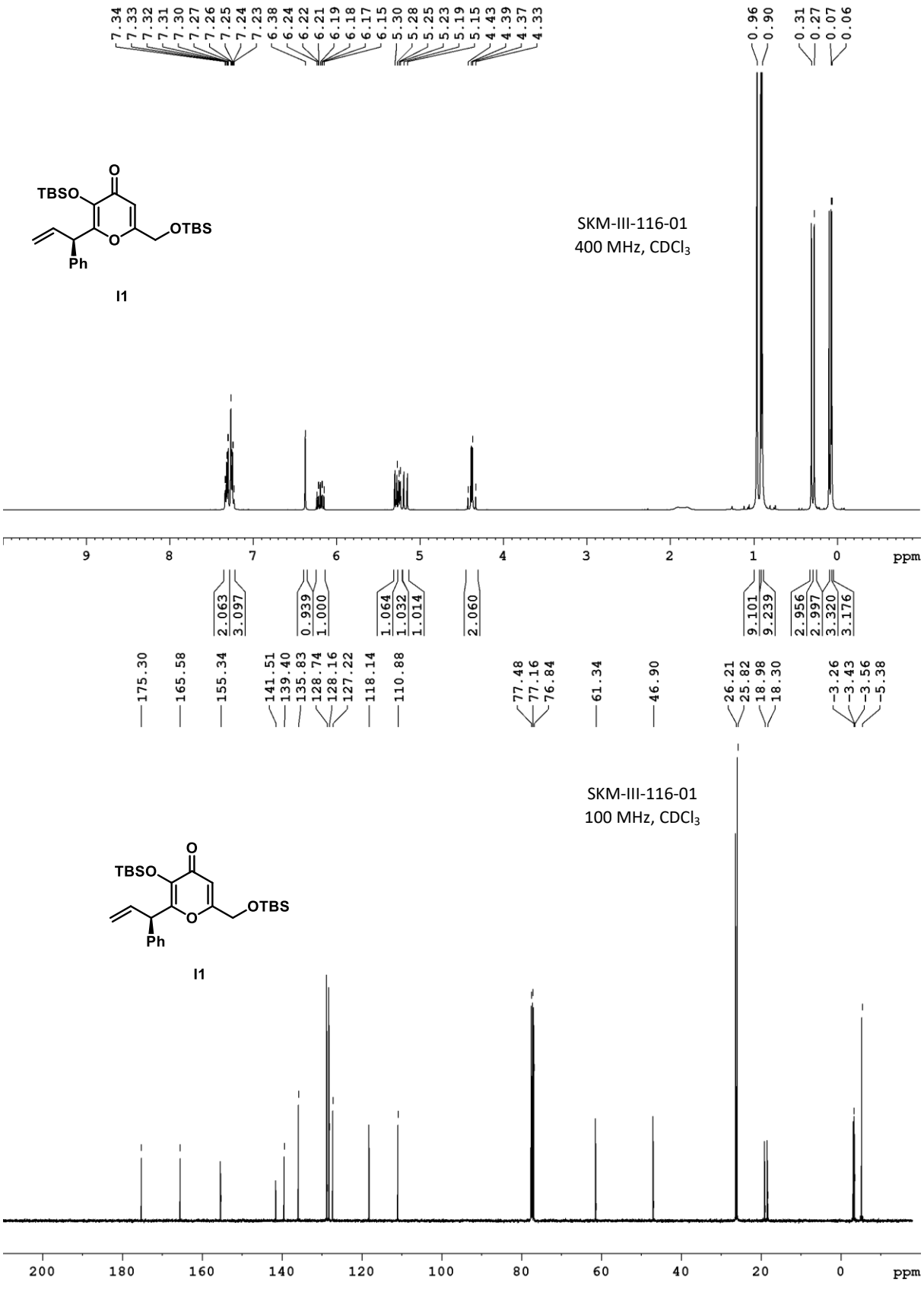
Daicel Chiralpak AD-H column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

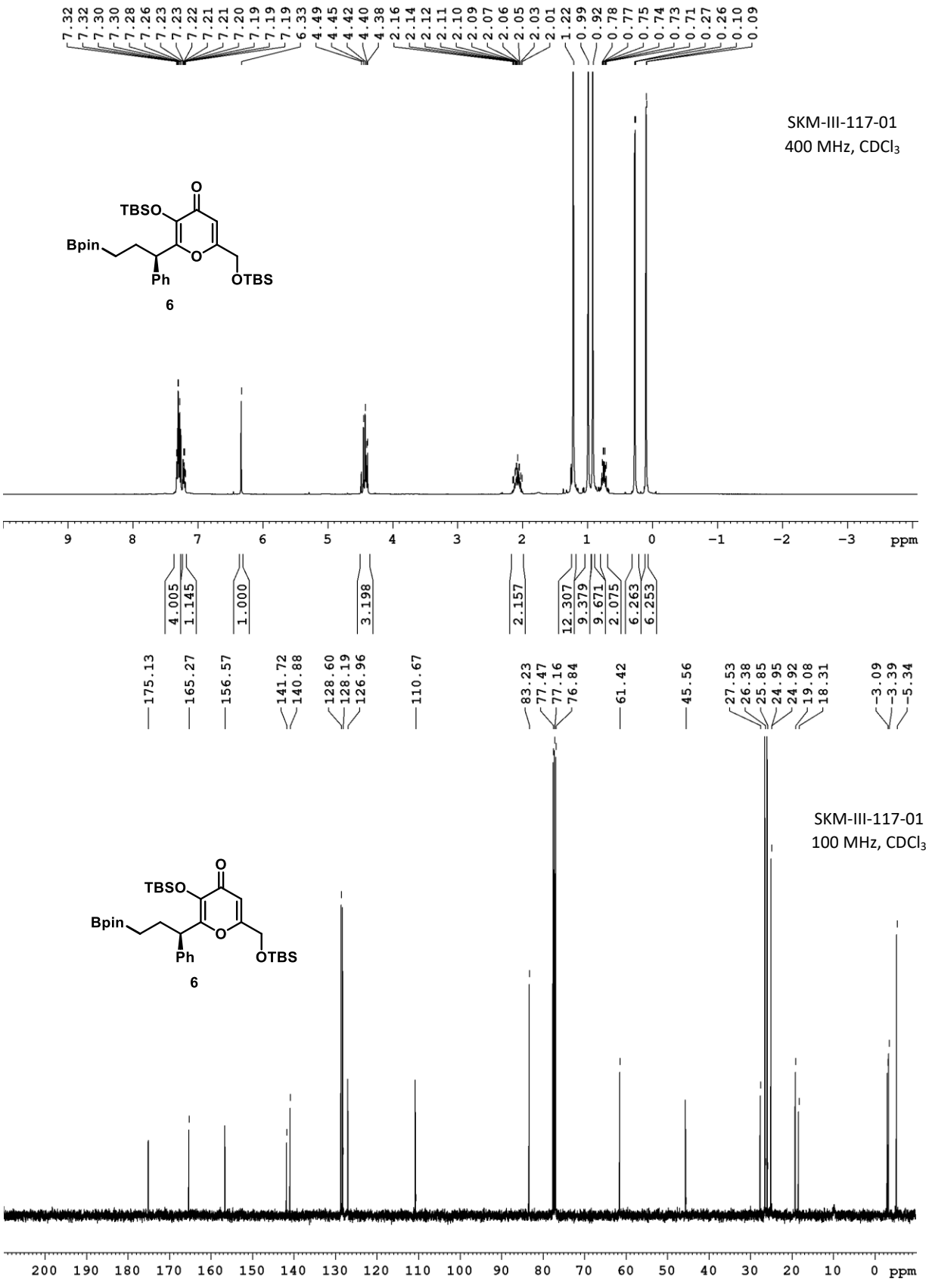


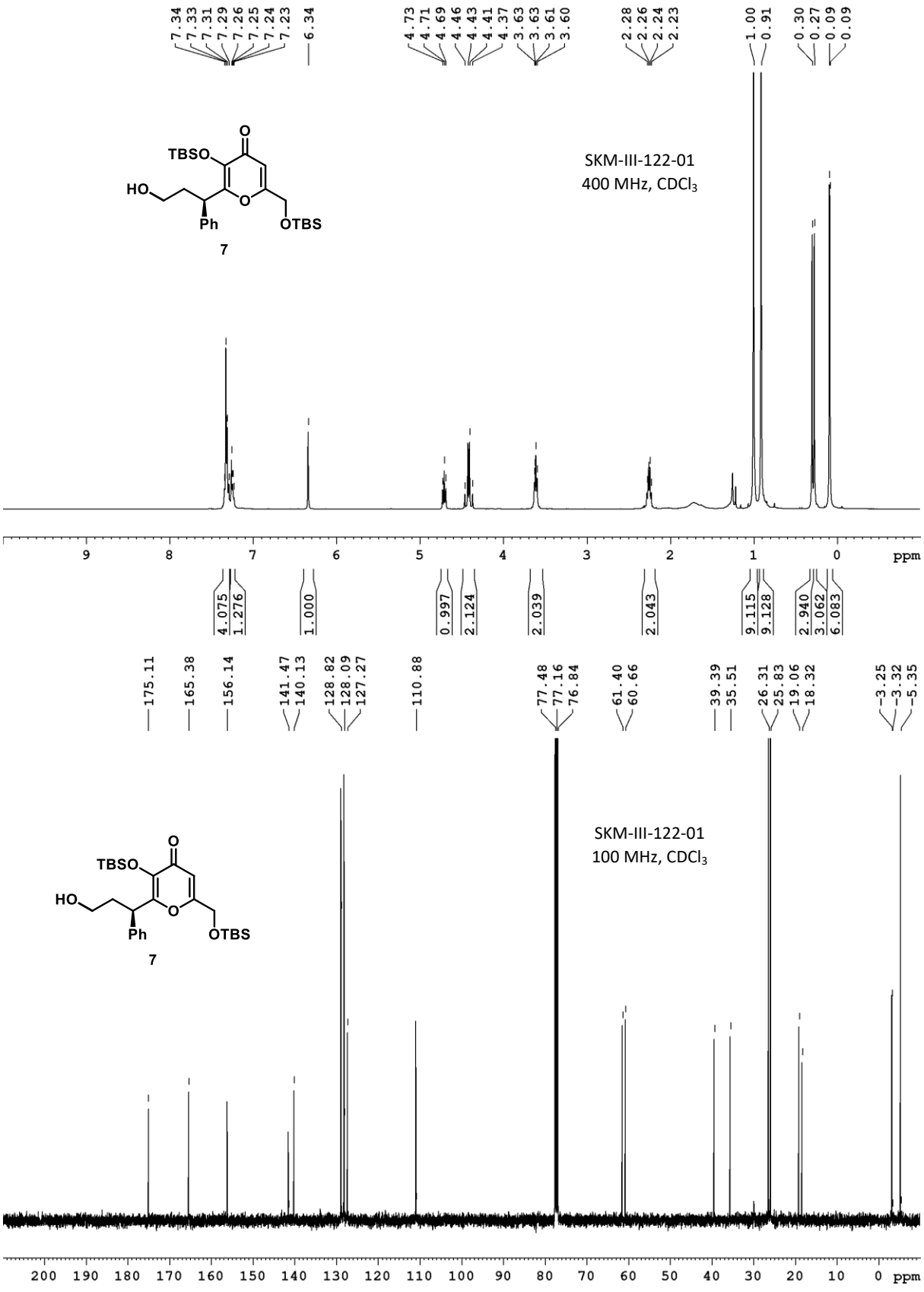
PeakTable

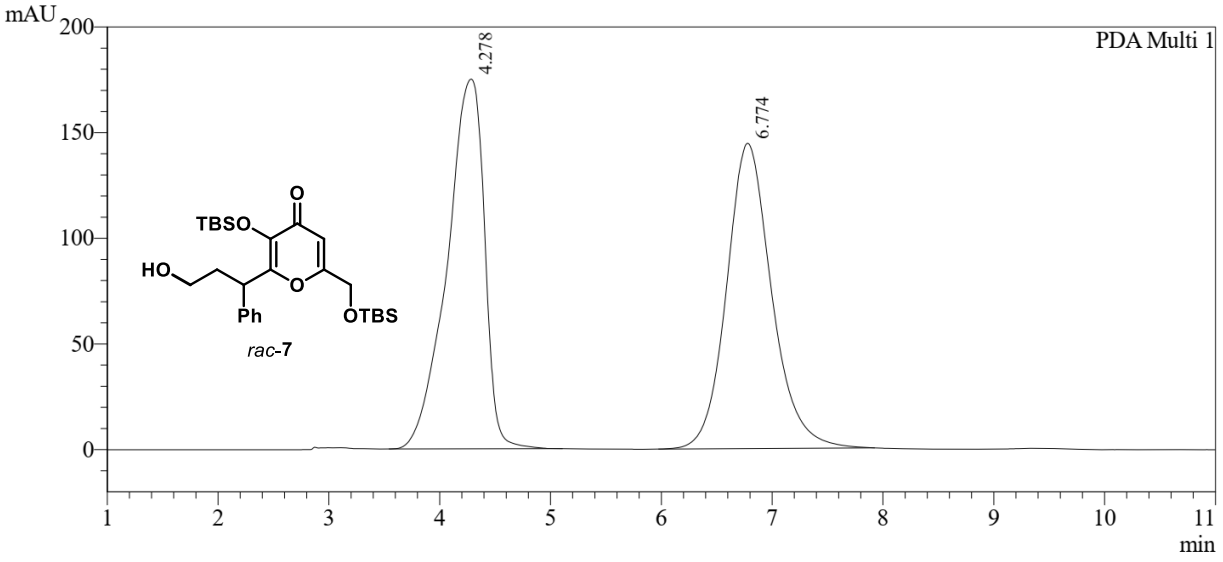
PDA Ch1 277nm 4nm

Peak#	Ret. Time	Area	Area %
1	13.966	29563	0.132
2	15.911	22298420	99.868
Total		22327983	100.000


7.34
7.33
7.32
7.31
7.30
7.27
7.26
7.25
7.24
7.23
6.38
6.24
6.22
6.21
6.19
6.18
6.17
6.15
5.30
5.28
5.25
5.23
5.19
5.15
4.43
4.39
4.37
4.33
0.96
0.90
0.31
0.27
0.07
0.06
TBSO
OTBS
Ph
O
I1
SKM-III-116-01
400 MHz, CDCl3
ppm
2.063
3.097
0.939
1.000
1.064
1.032
1.014
2.060
9.101
9.239
2.956
2.997
3.320
3.176
175.30
165.58
155.34
141.51
139.40
135.83
128.74
128.16
127.22
118.14
110.88
77.48
77.16
76.84
61.34
46.90
26.21
25.82
18.98
18.30
-3.26
-3.43
-3.56
-5.38
SKM-III-116-01
100 MHz, CDCl3
I1
ppm


SKM-III-117-01
400 MHz, CDCl3
TBSO
Bpin
Ph
OTBS
6
ppm
SKM-III-117-01
100 MHz, CDCl3
TBSO
Bpin
Ph
OTBS
6
ppm


7.34
7.33
7.31
7.29
7.26
7.25
7.24
7.23
6.34
4.73
4.71
4.69
4.46
4.43
4.41
4.37
3.63
3.63
3.61
3.60
2.28
2.26
2.24
2.23
1.00
0.91
0.30
0.27
0.09
0.09
TBSO
HO
Ph
OTBS
7
SKM-III-122-01
400 MHz, CDCl3
ppm
4.075
1.276
1.000
0.997
2.124
2.039
2.043
9.115
9.128
2.940
3.062
6.083
175.11
165.38
156.14
141.47
140.13
128.82
128.09
127.27
110.88
77.48
77.16
76.84
61.40
60.66
39.39
35.51
26.31
25.83
19.06
18.32
-3.25
-3.32
-5.35
SKM-III-122-01
100 MHz, CDCl3
ppm

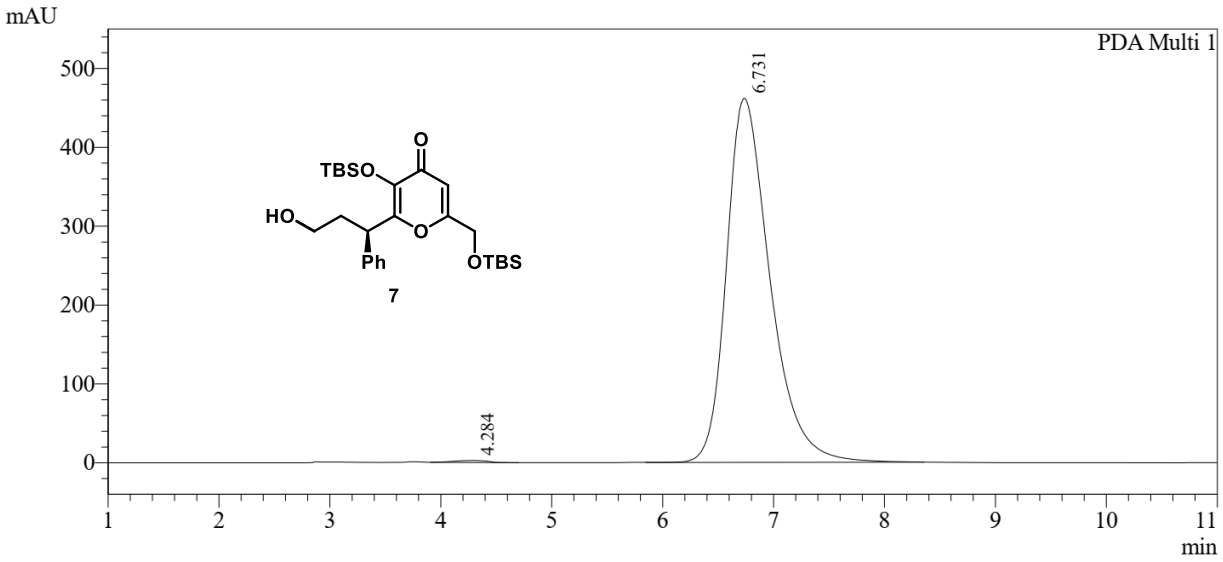


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	4.278	4105388	50.124
2	6.774	4085006	49.876
Total		8190394	100.000

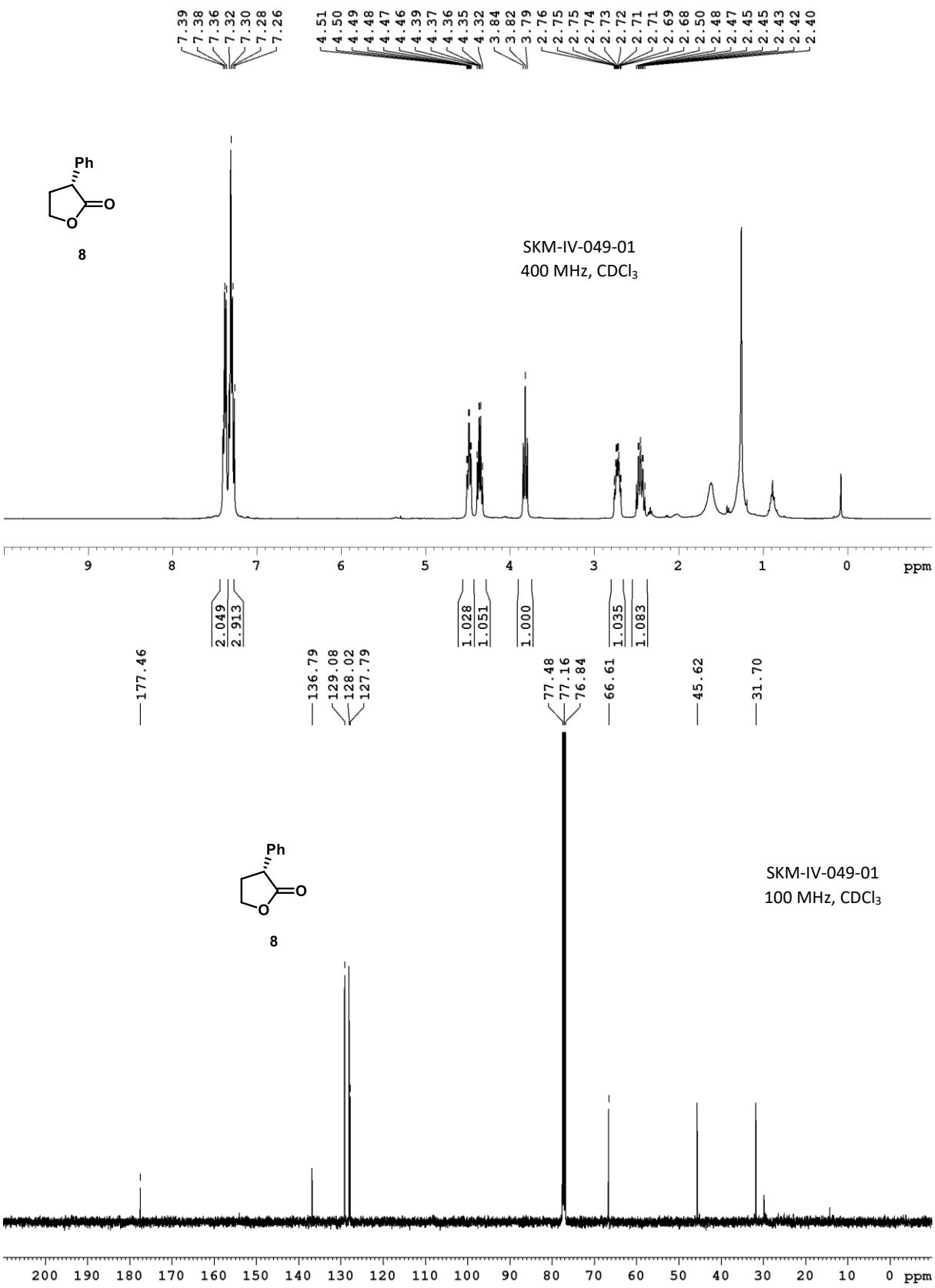
Phenomenex Cellulose-2 column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

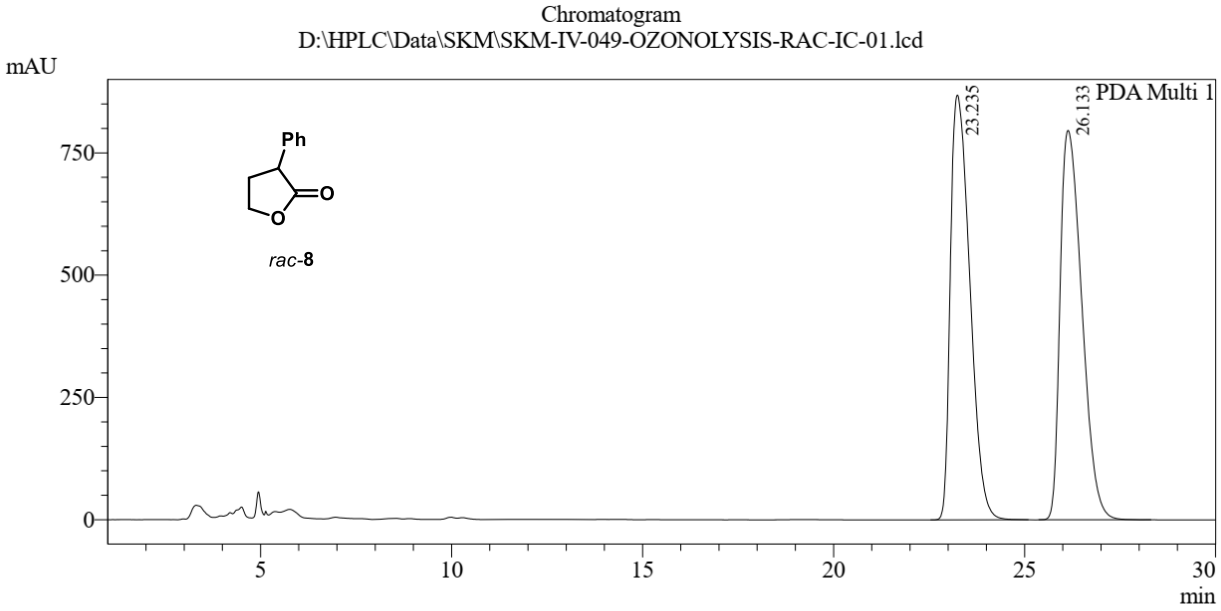


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	4.284	50508	0.399
2	6.731	12601482	99.601
Total		12651990	100.000


7.39
7.38
7.36
7.32
7.30
7.28
7.26
4.51
4.50
4.49
4.48
4.47
4.46
4.39
4.37
4.36
4.35
4.32
3.84
3.82
3.79
2.76
2.75
2.75
2.74
2.73
2.72
2.71
2.71
2.69
2.68
2.50
2.48
2.47
2.45
2.45
2.43
2.42
2.40
Ph
O
O
8
SKM-IV-049-01
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
2.049
2.913
1.028
1.051
1.000
1.035
1.083
177.46
136.79
129.08
128.02
127.79
77.48
77.16
76.84
66.61
45.62
31.70
Ph
O
O
8
SKM-IV-049-01
100 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

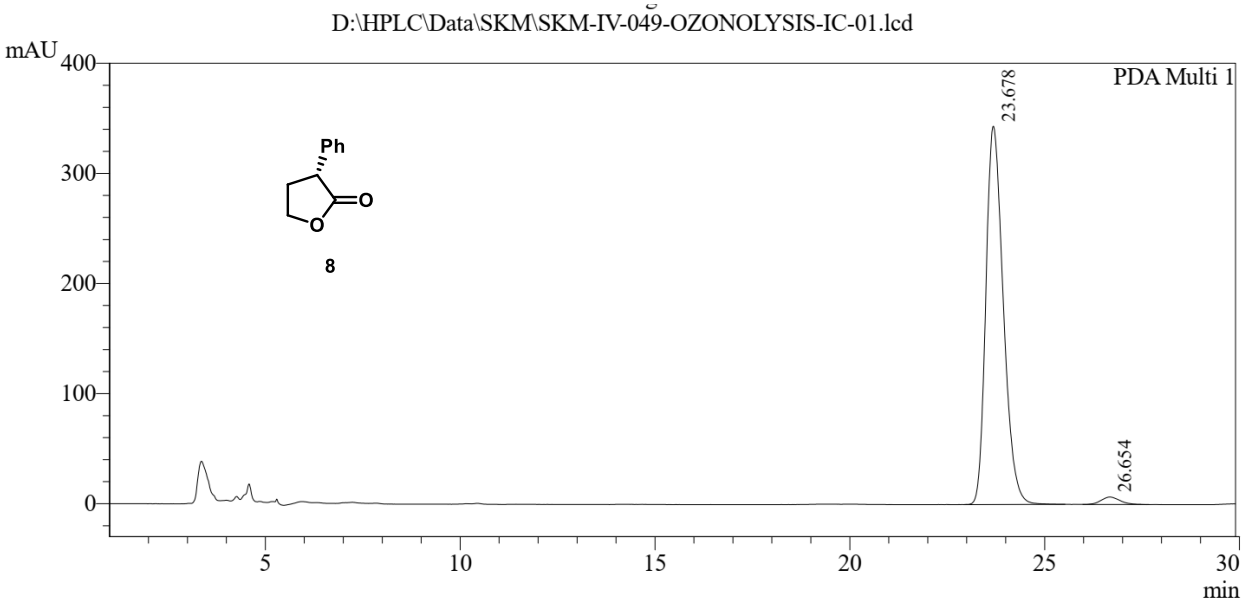


PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Area %
1	23.235	30815757	49.504
2	26.133	31433433	50.496
Total		62249190	100.000

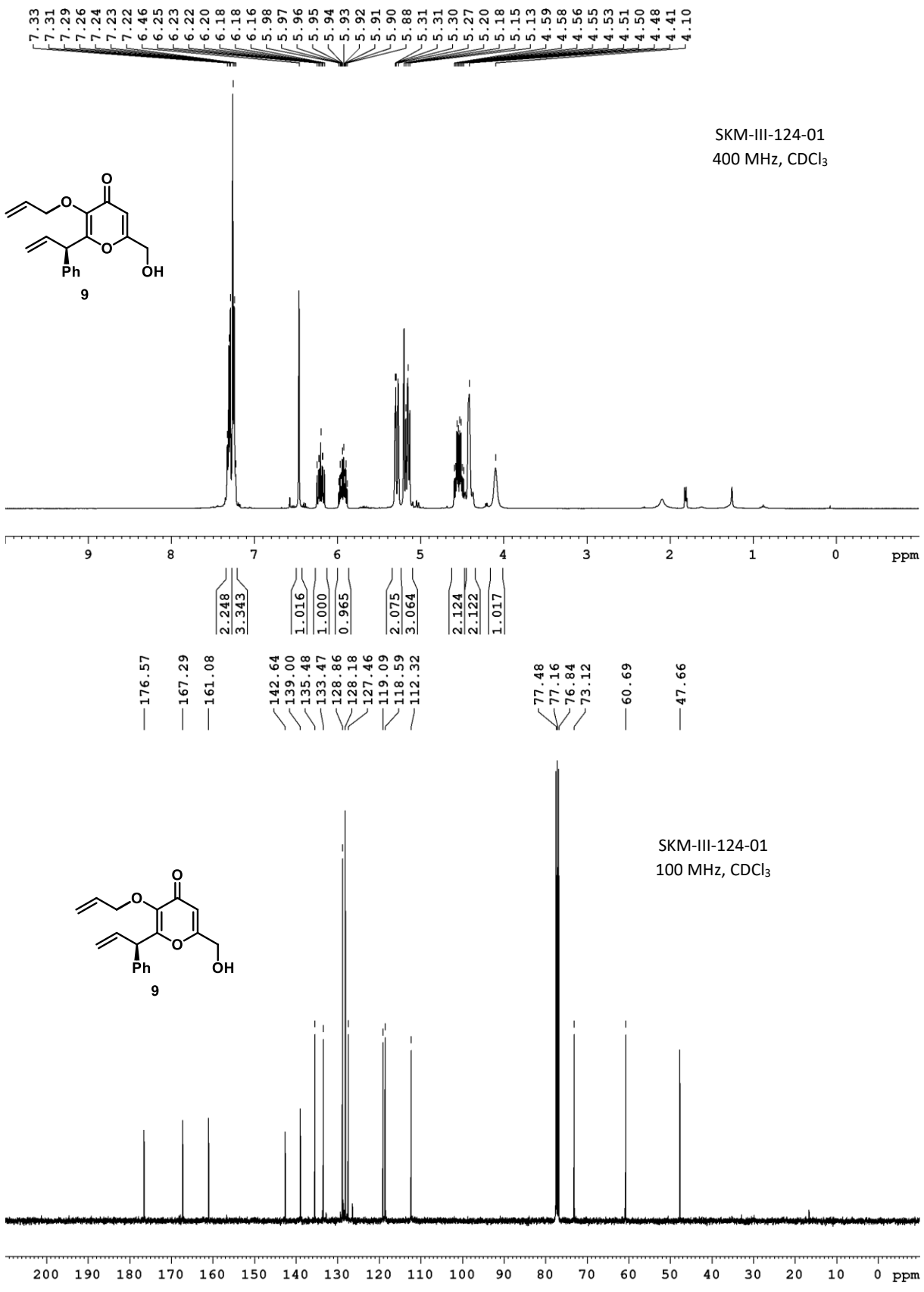
Daicel Chiralpak IC column (80:20 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

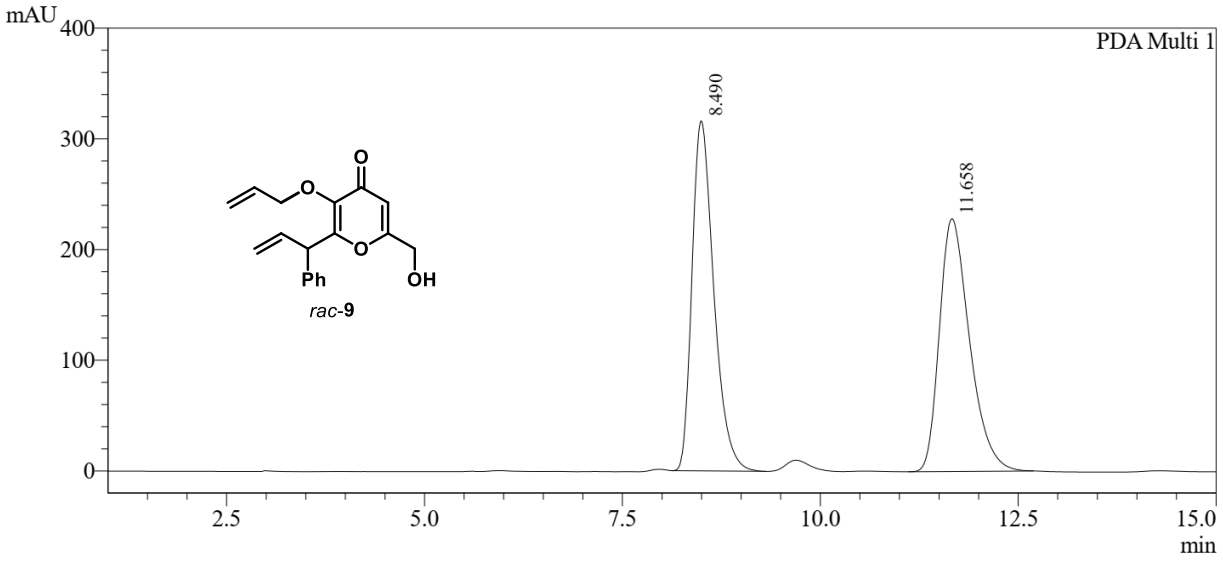


PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Area %
1	23.678	10699807	97.936
2	26.654	225476	2.064
Total		10925283	100.000


SKM-III-124-01
400 MHz, CDCl3
9
SKM-III-124-01
100 MHz, CDCl3
9

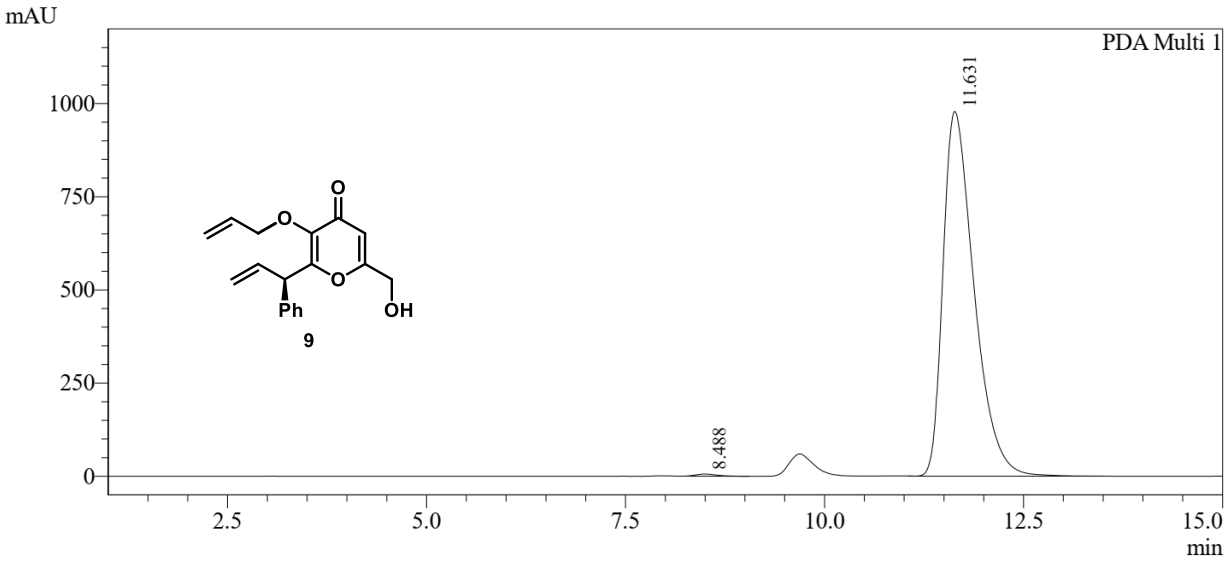


PeakTable

PDA Ch1 257nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.490	6054124	50.012
2	11.658	6051216	49.988
Total		12105340	100.000

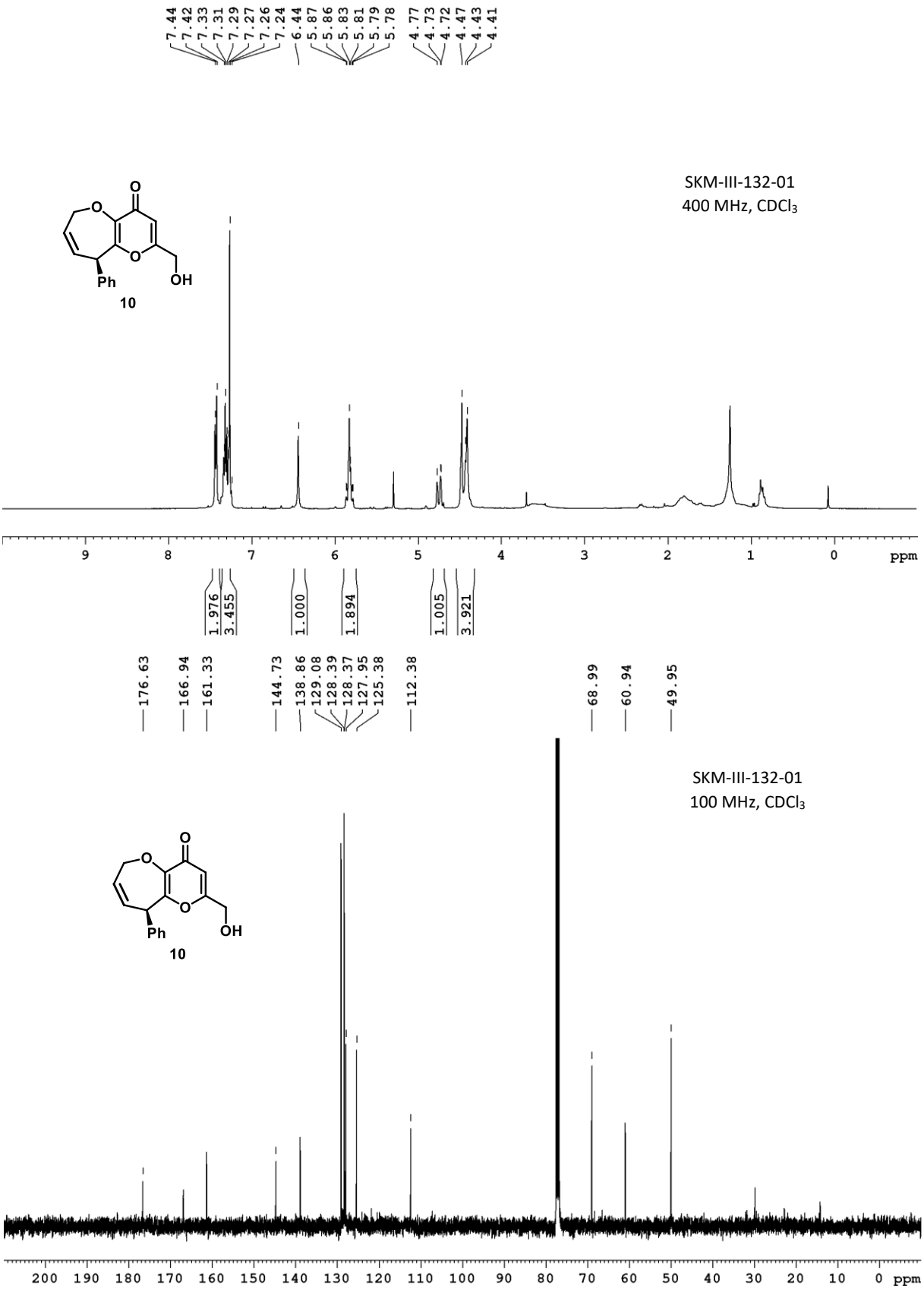
Daicel Chiralpak AD-H column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

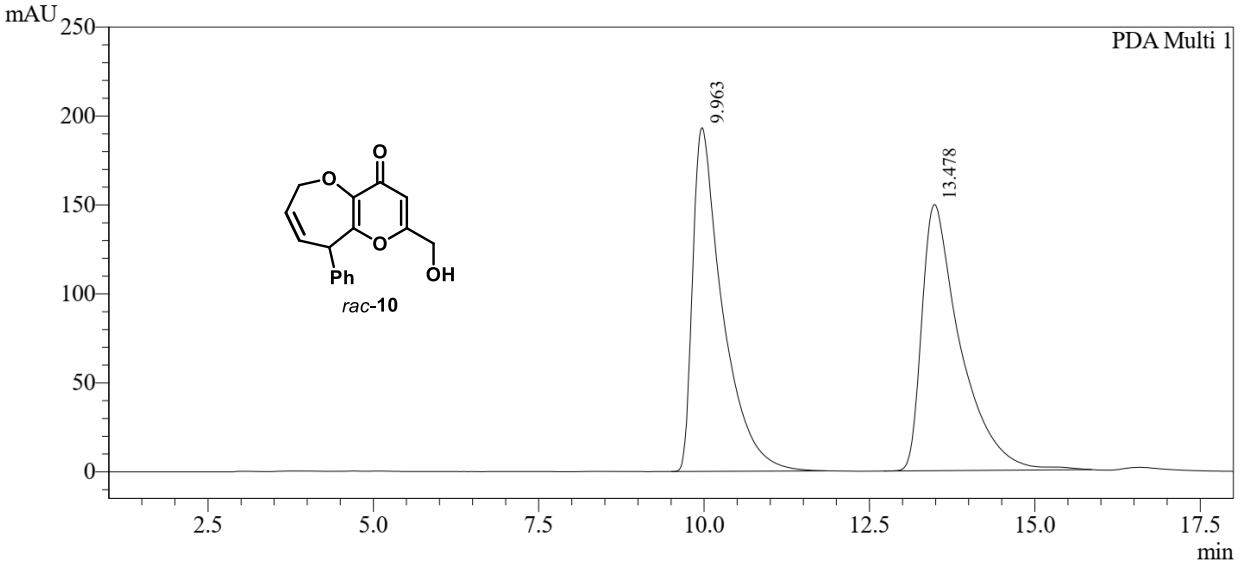


PeakTable

PDA Ch1 257nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.488	105566	0.396
2	11.631	26577259	99.604
Total		26682824	100.000


7.44
7.42
7.33
7.31
7.29
7.27
7.26
7.24
6.44
5.87
5.86
5.83
5.81
5.79
5.78
4.77
4.73
4.72
4.47
4.43
4.41
SKM-III-132-01
400 MHz, CDCl3
Ph
OH
10
9
8
7
6
5
4
3
2
1
0
ppm
1.976
3.455
1.000
1.894
1.005
3.921
176.63
166.94
161.33
144.73
138.86
129.08
128.39
128.37
127.95
125.38
112.38
68.99
60.94
49.95
SKM-III-132-01
100 MHz, CDCl3
Ph
OH
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

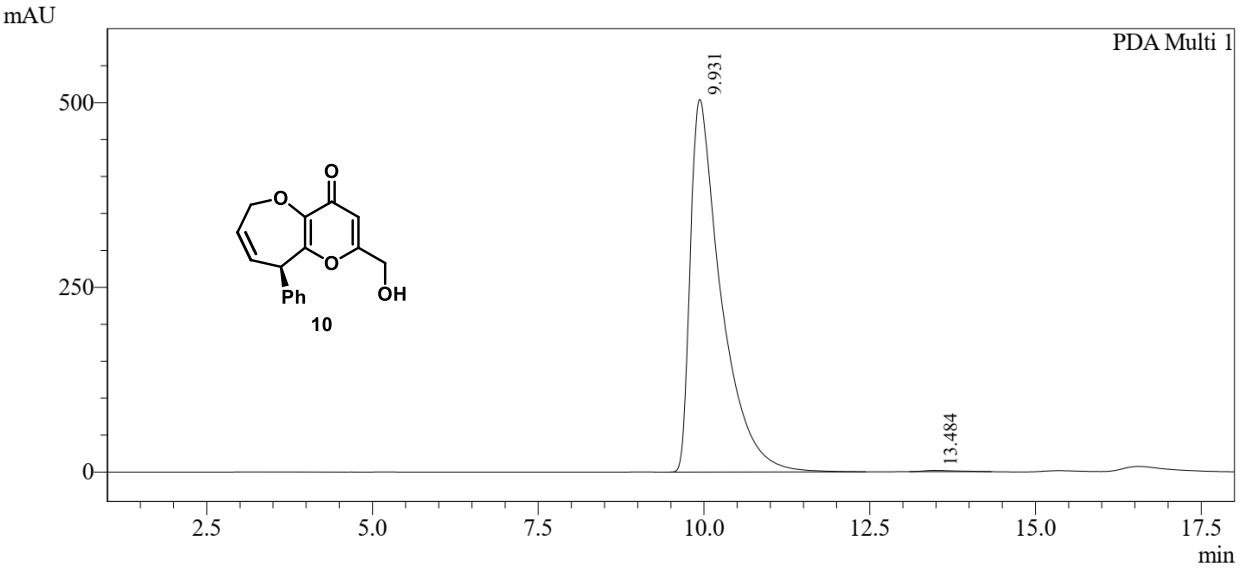


PeakTable

PDA Ch1 259nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.963	6078716	50.015
2	13.478	6074964	49.985
Total		12153680	100.000

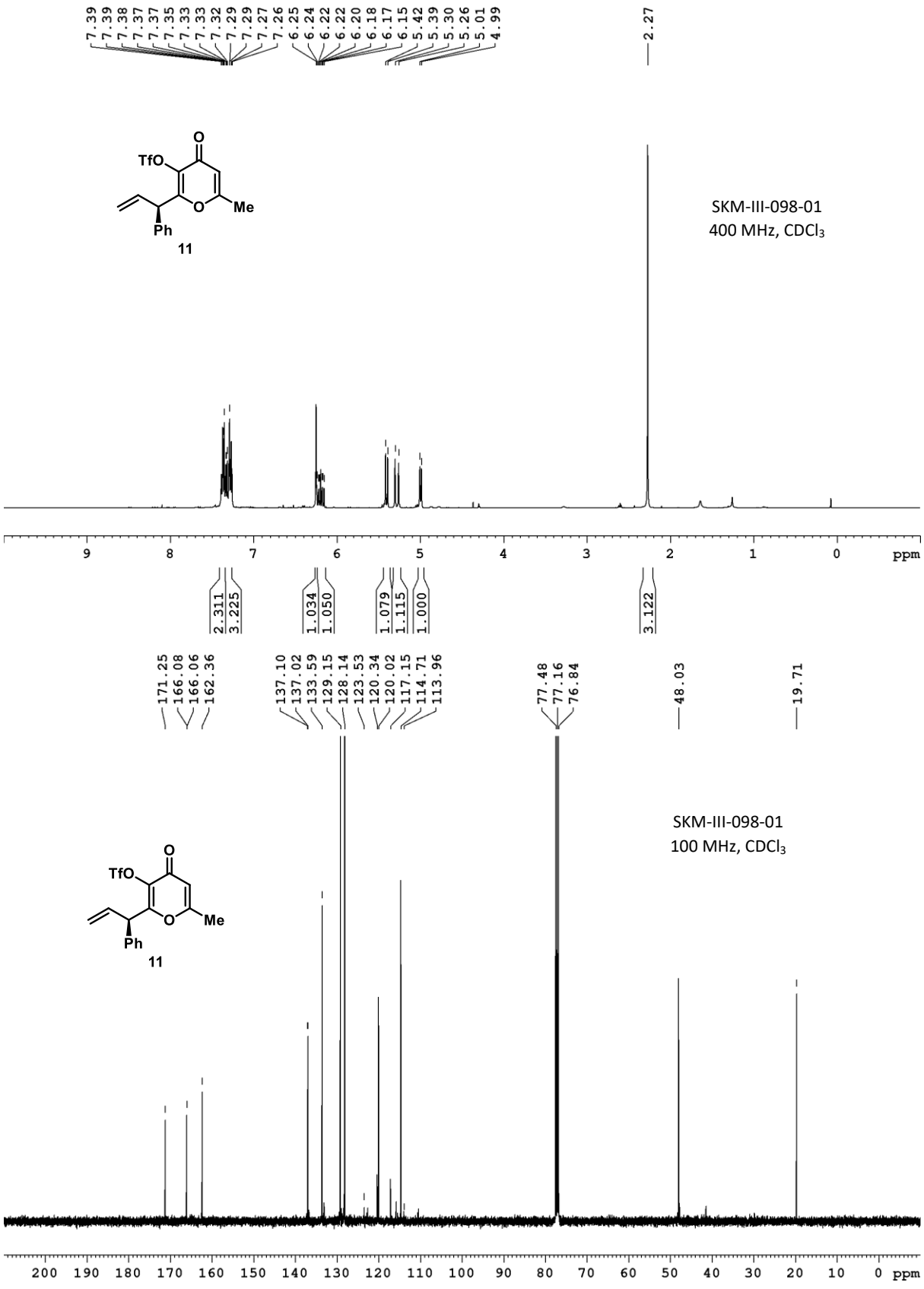
Daicel Chiralpak AD-H column (85:15 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

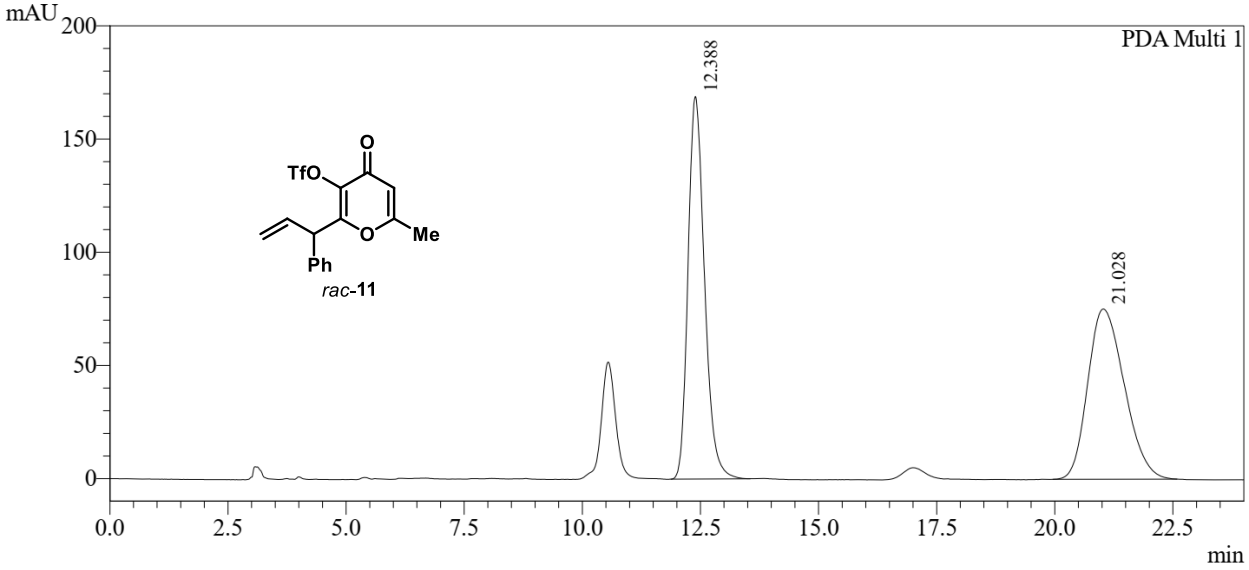


PeakTable

PDA Ch1 259nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.931	16347226	99.635
2	13.484	59866	0.365
Total		16407092	100.000


7.39
7.39
7.38
7.37
7.37
7.35
7.33
7.33
7.32
7.29
7.29
7.27
7.26
6.25
6.24
6.22
6.22
6.20
6.18
6.17
6.15
5.42
5.39
5.30
5.26
5.01
4.99
2.27
TfO
O
Me
Ph
11
SKM-III-098-01
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
2.311
3.225
1.034
1.050
1.079
1.115
1.000
3.122
171.25
166.08
166.06
162.36
137.10
137.02
133.59
129.15
128.14
123.53
120.34
120.02
117.15
114.71
113.96
77.48
77.16
76.84
48.03
19.71
SKM-III-098-01
100 MHz, CDCl3
TfO
O
Me
Ph
11
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

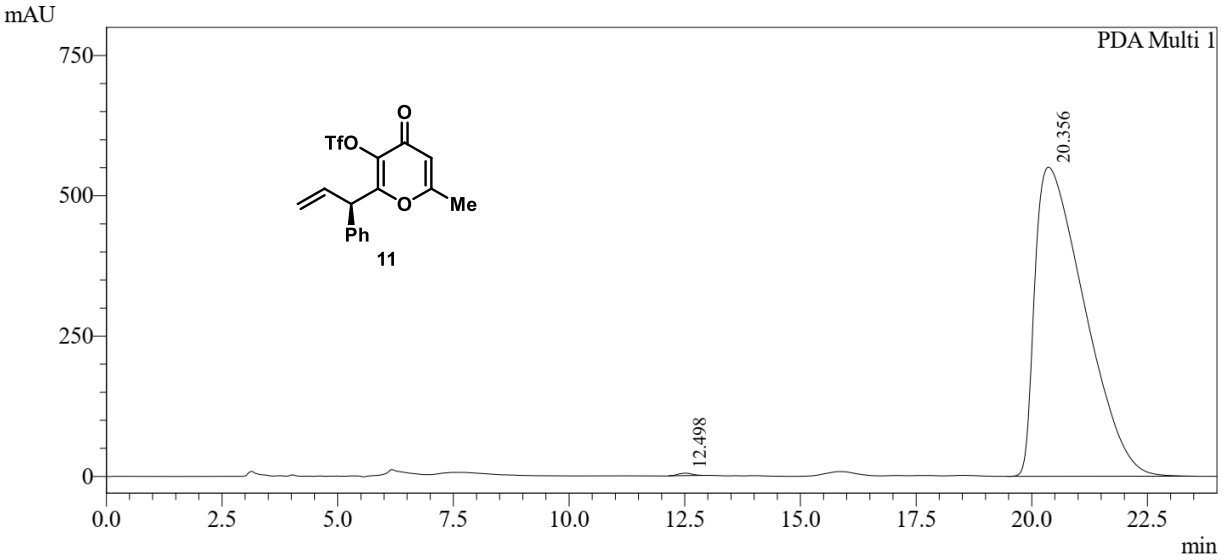


PeakTable

PDA Ch1 221nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.388	4101190	50.301
2	21.028	4052139	49.699
Total		8153329	100.000

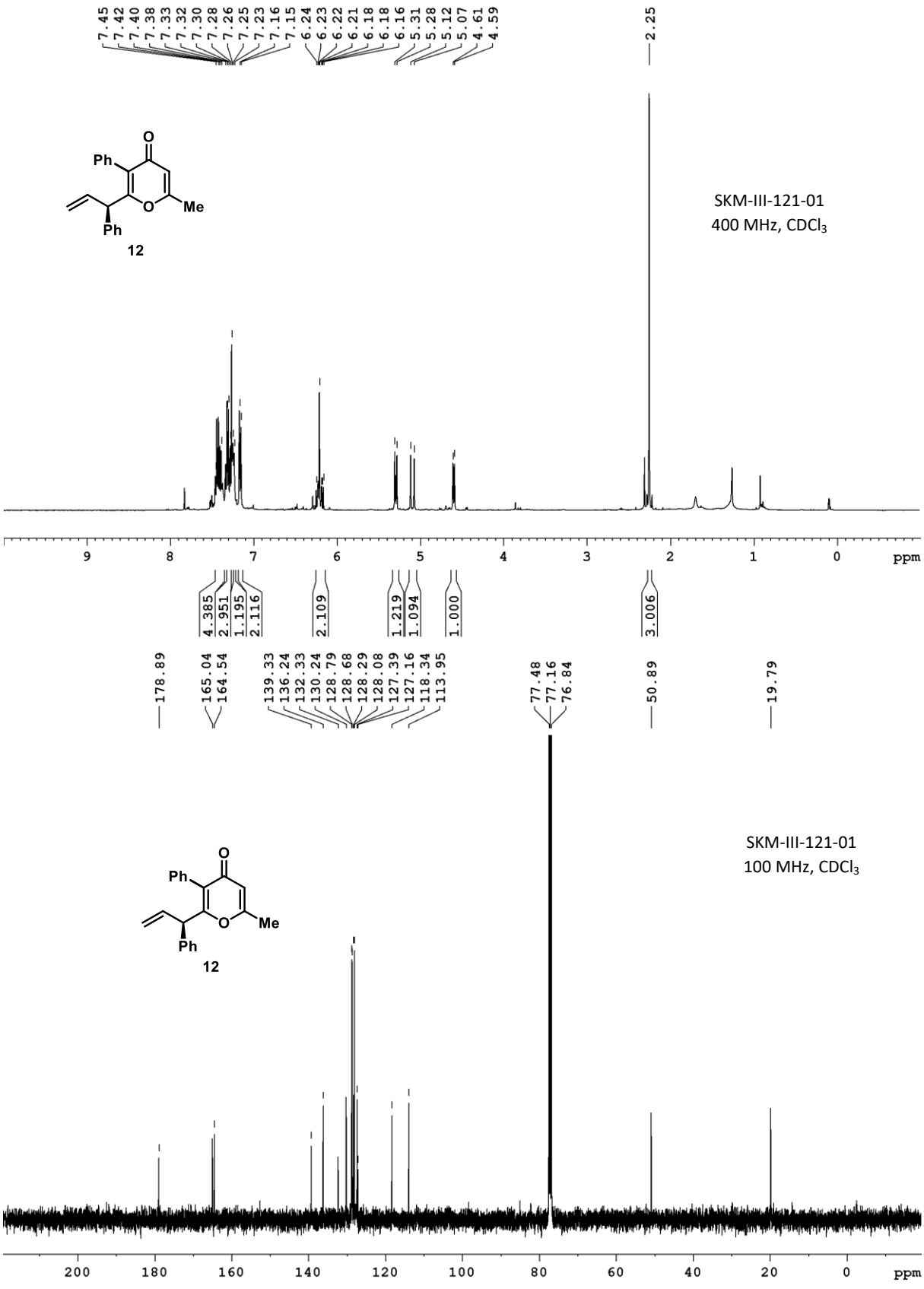
Daicel Chiralpak IH column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C)

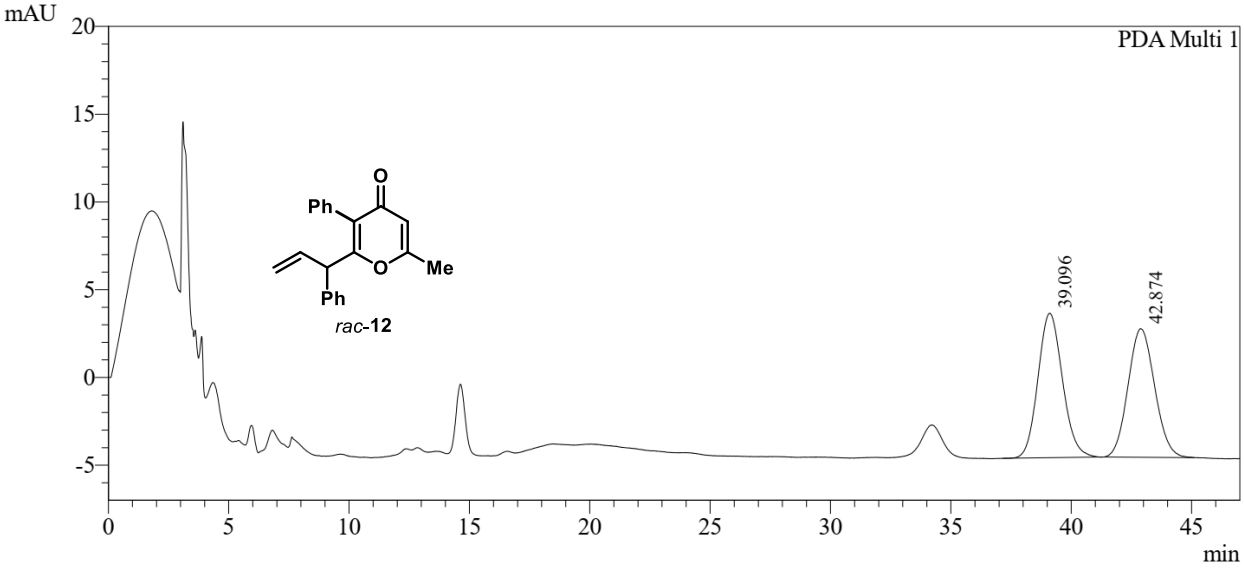


PeakTable

PDA Ch1 221nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.498	93484	0.227
2	20.356	41076107	99.773
Total		41169591	100.000


7.45
7.42
7.40
7.38
7.33
7.32
7.30
7.28
7.26
7.25
7.23
7.16
7.15
6.24
6.23
6.22
6.21
6.18
6.18
6.16
5.31
5.28
5.12
5.07
4.61
4.59
2.25
Ph
O
Me
O
Ph
12
SKM-III-121-01
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
4.385
2.951
1.195
2.116
2.109
1.219
1.094
1.000
3.006
178.89
165.04
164.54
139.33
136.24
132.33
130.24
128.79
128.68
128.29
128.08
127.39
127.16
118.34
113.95
77.48
77.16
76.84
50.89
19.79
SKM-III-121-01
100 MHz, CDCl3
200
180
160
140
120
100
80
60
40
20
0
ppm

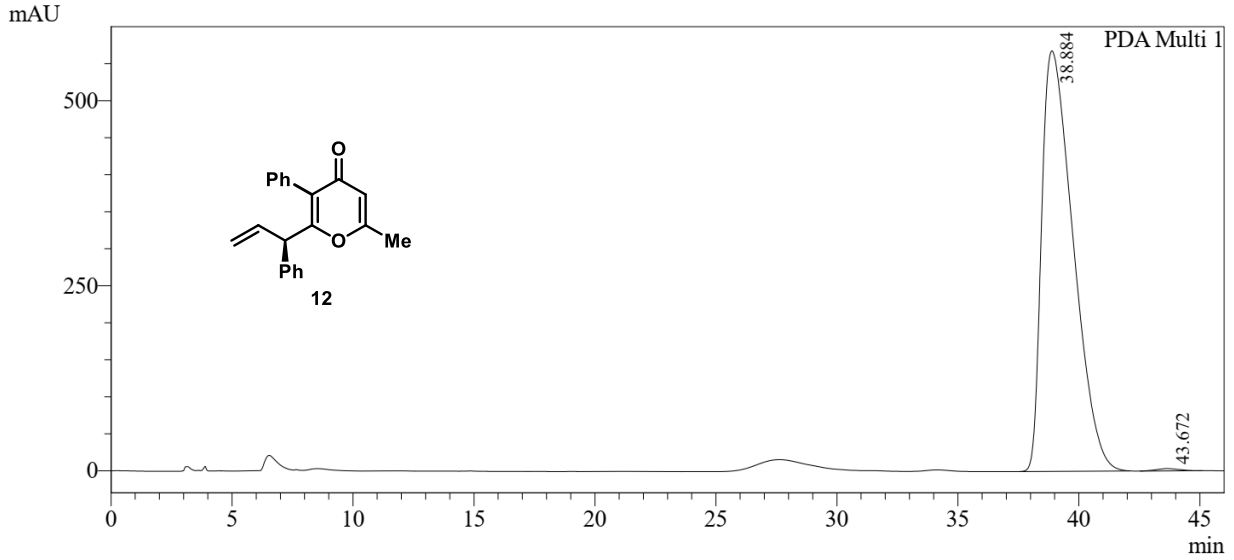


PeakTable

PDA Ch1 224nm 4nm

Peak#	Ret. Time	Area	Area %
1	39.096	582139	50.828
2	42.874	563179	49.172
Total		1145317	100.000

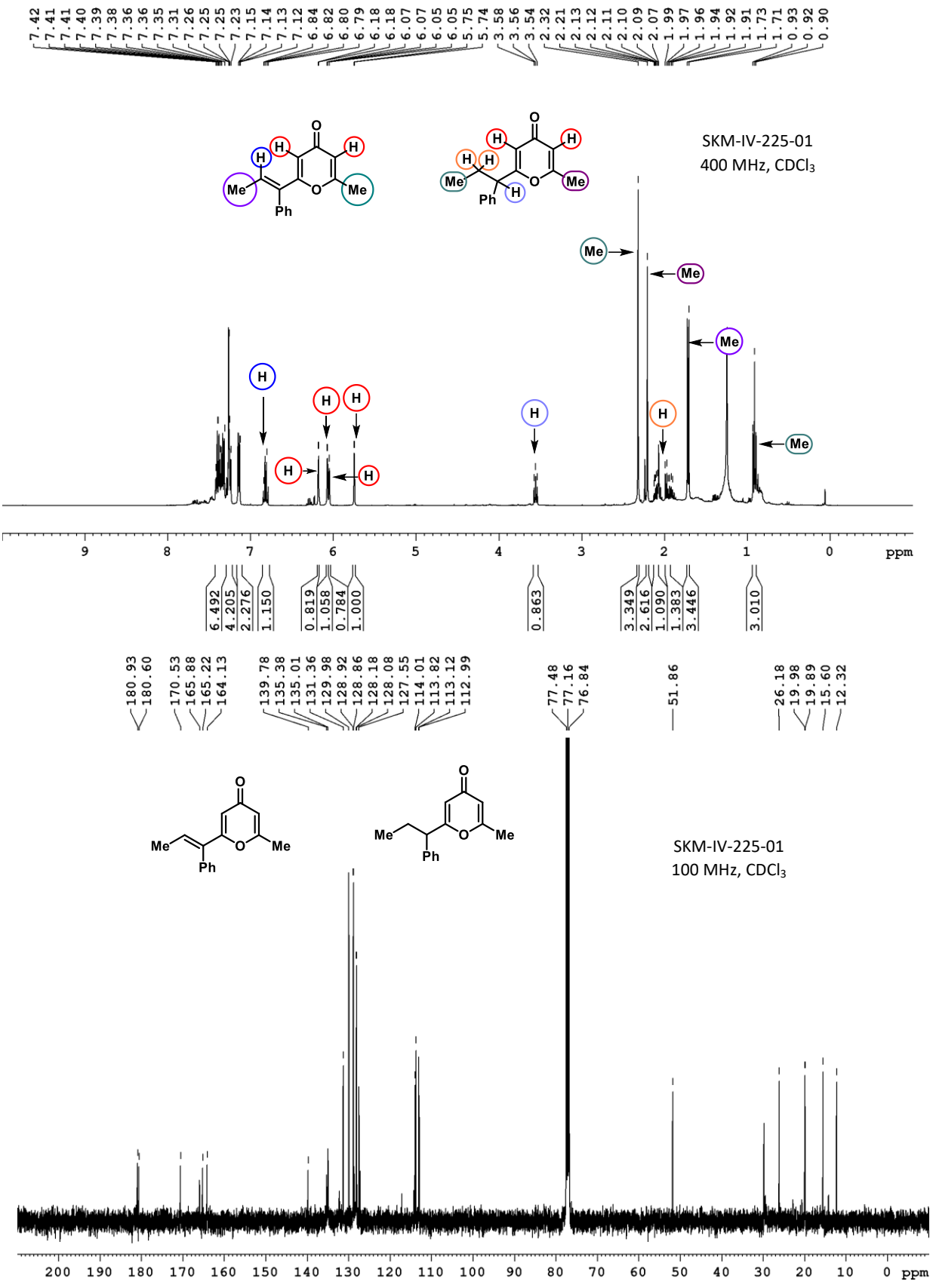
Daicel Chiralpak IH column (90:10 *n*-Hexane/*i*-PrOH, 1 mL/min, 20 °C)



PeakTable

PDA Ch1 224nm 4nm

Peak#	Ret. Time	Area	Area %
1	38.884	51435075	99.604
2	43.672	204439	0.396
Total		51639513	100.000


SKM-IV-225-01
400 MHz, CDCl3
SKM-IV-225-01
100 MHz, CDCl3
ppm