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Supporting Information

Construction of Polycyclic Structures with Vicinal All-Carbon Quaternary Stereocenters via Enantioselective Photoenolization/Diels-Alder Reaction

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I. General Information

General Experimental Procedures. All reactions were carried out under nitrogen except noted. Anhydrous dichloromethane, toluene, acetonitrile and dimethylformamide were purified by the PS-MD5 (Innovative Technology) solvent purification system. Tetrahydrofuran and anhydrous diethyl ether were distilled from sodium-benzophenone ketyl. All other commercial reagents were used as received. Flash column chromatography was performed as described by Still, employing Qingdao Haiyang silica gel 60 (200-300 mesh). TLC analyses were performed on EMD 250 µm Silica Gel HSGF254 plates and visualized by quenching of UV fluorescence ($\lambda_{max} = 254$ nm), or by staining ceric ammonium molybdate, phosphomolybdic acid, or potassium permanganate. ¹H and ¹³C NMR spectra were recorded on a Bruker 500, 400 spectrometer. Chemical shifts for ¹H and ¹³C NMR spectra are reported in ppm (δ) relative to residue protium in the solvent (CDCl₃: δ 7.26, 77.0 ppm, and the multiplicities are presented as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad single. High-resolution mass spectra (HRMS) were acquired on Waters Micromass GCT Premier or Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS. Mass spectra were acquired on Agilent 5975C. The $[\alpha]_D$ was recorded using Anton Paar MCP 5500. Infrared (IR) spectra were obtained using a Shimatzu IRTracer-100 fourier transform infrared spectroscopy (FTIR). Electronic circular dichroism (ECD) spectra and corresponding ultraviolet-visual spectra were obtained on a JASCO J-815 CD spectrometer. HPLC analysis on chiral stationary phase was performed on an Agilent 1200-series instrument, employing Daicel Chiralpak OD-H, AS-H, OJ-H and IG chiral columns. The photo reactor used for this photolysis is Rayonet RPR-200 (Southern New England Ultraviolet Company). The peristaltic pump used for this flow PEDA reaction is BT 100-1F (Longer precision pump Co., Ltd.).

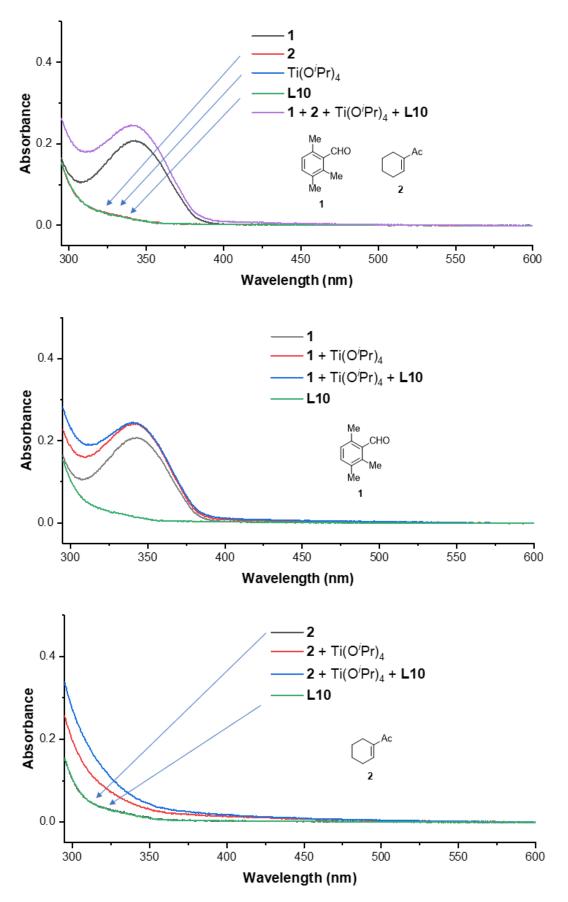
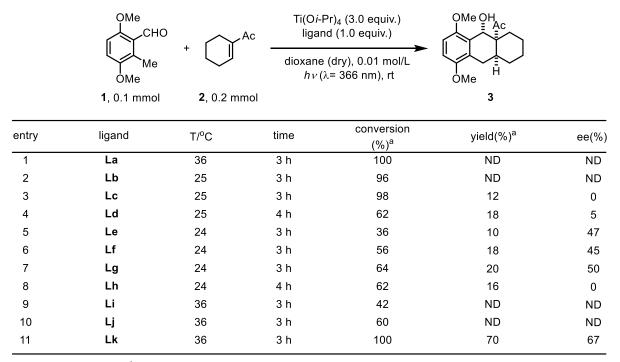


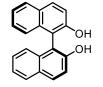
Figure S1. Absorption spectra of the reaction mixture in toluene $(5 \times 10^{-5} \text{ M})$

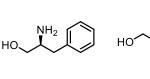
III. Control Experiments

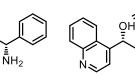
Table S1. Investigation of different kinds of ligands.

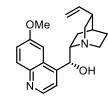


^aCrude ¹H NMR convertion and yield with 1,3,5-Trimethoxybenzene as internal standard.











La, (S)-BINOL

Lb

Et

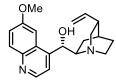
ОН

Lc Ld, cinchonine

.

Le, quinine

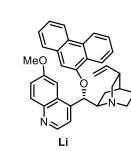
Lf, cinchonidine

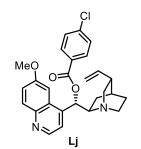


Lg, quinidine

Lh

QМе







Lk, TADDOL

Table S2. Condition optimization: solvent, dosage of Ti(Oi-Pr)4 and L10.

	OMe CHO Me OMe 1, 0.1 mmol 2,	solver	ri(O <i>i</i> -Pr) ₄ , L10 ht (dry), 0.01 mol/L, (λ= 366 nm), 2 h	Me OH Ac OMe H OMe)
entry	Ti(O <i>i</i> -Pr) ₄	L10	solvent	yield(%) ^a	ee(%)
1	3.0 equiv.	1.0 equiv.	dioxane	79	85
2	3.0 equiv.	1.0 equiv.	THF	48	72
3	3.0 equiv.	1.0 equiv.	DCM	57	90
4	3.0 equiv.	1.0 equiv.	DCE	67	90
5	3.0 equiv.	1.0 equiv.	toluene	70	91
6	2.0 equiv.	1.0 equiv.	toluene	64	93
7	1.0 equiv.	1.0 equiv.	toluene	62	91
8	1.0 equiv.	0.5 equiv.	toluene	50	89
9	0.5 equiv.	0.5 equiv.	toluene	47	82
10	0.8 equiv.	0.4 equiv.	toluene	38	85
11	0.6 equiv.	0.3 equiv.	toluene	22	78
12	0.4 equiv.	0.2 equiv.	toluene	trace	-
13	0.2 equiv.	0.1 equiv.	toluene	trace	-
14	2.0 equiv.	0.8 equiv.	toluene	54	89
15	2.0 equiv.	0.5 equiv.	toluene	48	89
16	2.0 equiv.	0.2 equiv.	toluene	45	70
17 ^b	1.0 equiv.	0.5 equiv.	toluene	78	90
18 ^c	1.0 equiv.	0.5 equiv.	toluene	72	90

^aYields determined by ¹H NMR analysis using internal standard. ^bdossage of **2** is 1.5 equiv.; ^cdossage of **2** is 1.0 equiv.

Table S3. Condition of	optimization:	additive	screening.
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OM OM OM	CHO + Ac	Ti(O <i>i</i> -Pr) ₄ , L10 , a solvent (dry), 0.0 ⁷ hν (λ= 366 nm),	1 mol/L	AC T T T T T T T T
entry	solvent	additive	yield(%) ^c	ee(%)
	toluene		70	91
2 ^b	toluene		78	90
3 ^b	toluene	Et ₃ N	64	88
4 ^b	toluene	IMD.	52	91
5 ^b	toluene	HMTA	85	88
6 ^b	toluene	DABCO	82	92
7 ^b	toluene	Quin.	89	91

^a The reaction was conducted in **1** (1.0 equiv.), **2** (2.0 equiv.), $Ti(Oi-Pr)_4$ (3.0 equiv.), **L10** (1.0 equiv.) ^b The reaction was conducted in **1** (1.0 equiv.), **2** (1.5 equiv.), $Ti(Oi-Pr)_4$ (1.0 equiv.), **L10** (0.5 equiv.)

and additive (1.0 equiv.).

^c Crude ¹H NMR yield with 1,3,5-trimethoxybenzene as internal standard.

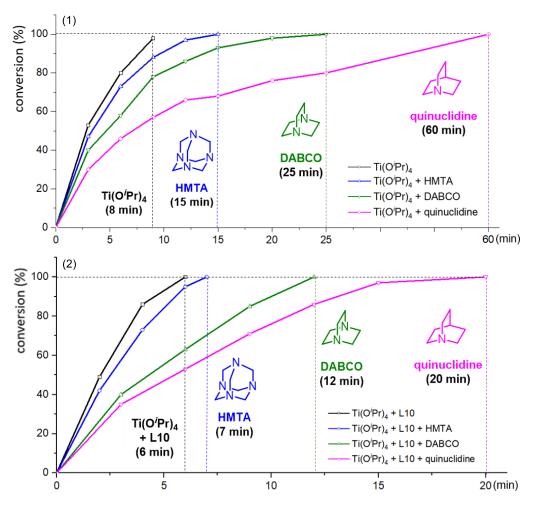
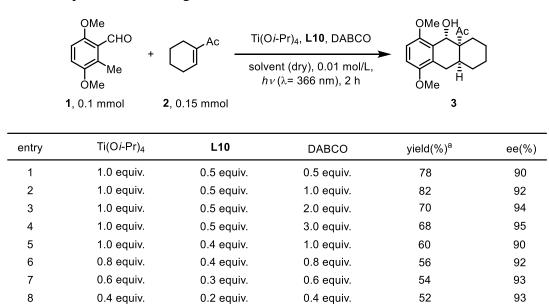


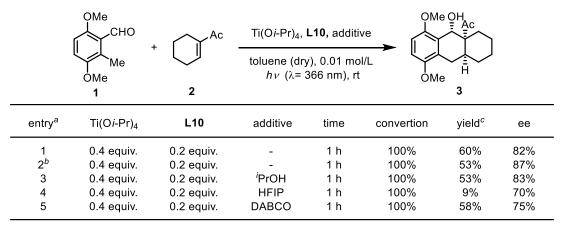
Figure S2. Dynamic studies.

Table S4. Condition optimization: dosage of DABCO.



^aYields determined by ¹H NMR analysis using internal standard.

Table S5-1. Catalytic asymmetric PEDA reaction: additive screening.



^a The reaction was conducted in 1 (1.0 equiv.), 2 (1.5 equiv.), additive (1.0 equiv.).

^b Prepared chiral catalyst (wituout [/]PrOH) was used.

^c Crude ¹H NMR yield with 1,3,5-trimethoxybenzene as internal standard.

 Table S5-2. Catalytic asymmetric PEDA reaction: wavelength screening.

	Me	+ Ac	toluene (dry	Pr) ₄ , L10 v), 0.01 mo	→ 🖒	e OH Ac	
	OMe 1	2		· , · -	OM	3	
entry ^a	Ti(O <i>i</i> -Pr) ₄	L10	<i>hν</i> (nm)	time	convertion	yield ^c	ee
1	1.0 equiv.	0.5 equiv.	300	1 h	100%	28%	77%
2	1.0 equiv.	0.5 equiv.	366	1 h	100%	78%	90%
3	0.4 equiv.	0.2 equiv.	366	1 h	100%	60%	82%
4	1.0 equiv.	0.5 equiv.	419	1 h	58%	50%	92%
5	0.4 equiv.	0.2 equiv.	419	1 h	42%	37%	91%
6 ^b	0.4 equiv.	0.2 equiv.	419	1 h	32%	22%	87%
7	1.0 equiv.	0.5 equiv.	575	1 h	48%	39%	89%
8	0.4 equiv.	0.2 equiv.	575	1 h	45%	27%	89%

^a The reaction was conducted in **1** (1.0 equiv.), **2** (1.5 equiv.).

^b Prepared chiral catalyst (wituout ⁱPrOH) was used.

^c Crude ¹H NMR yield with 1,3,5-trimethoxybenzene as internal standard.

Table S5-3. Catalytic asymmetric PEDA reaction: the ratio of titanium to ligand screening.

		ме Ме сно	Ti(O <i>i</i> -	-Pr) ₄ , L10	_		
MeO	Me	Me	•	ry), 0.01 mol/ h <i>v</i> , rt	″L MeO	L L L	
	1a	45				56 , R = CH	0
entry ^a	Ti(O <i>i</i> -Pr) ₄	L10	hν (nm)	time	convertion	yield ^c	ee
1	0.4 equiv.	0.2 equiv.	366	1.5 h	100%	49%	94%
2 ^b	0.4 equiv.	0.2 equiv.	366	1.5 h	64%	15%	92%
3	0.4 equiv.	0.2 equiv.	419/366	2+1 h	48%	23%	95%
4	0.5 equiv.	0.2 equiv.	366	1.5 h	100%	84%	96%
5	0.5 equiv.	0.2 equiv.	419/366	3+1.5 h	67%	27%	94%
6	0.6 equiv.	0.2 equiv.	366	1.5 h	100%	88%	89%
7	0.6 equiv.	0.2 equiv.	419/366	2+1 h	88%	74%	96%
8	0.6 equiv.	0.2 equiv.	419/366	2.5+1.5 h	100%	83%	93%
9	1.0 equiv.	0.2 equiv.	366	1.5 h	100%	92%	78%
10	1.0 equiv.	0.2 equiv.	419	6 h	30%	26%	84%
11	2.0 equiv.	0.2 equiv.	366	1.5 h	100%	81%	68%
12	2.0 equiv.	0.2 equiv.	419	6 h	24%	20%	78%

^a The reaction was conducted in **1a** (1.0 equiv.), **45** (1.5 equiv.). ^b Prepared chiral catalyst (wituout ⁱPrOH) was used. ^c Crude ¹H NMR yield with 1,3,5-trimethoxybenzene as internal standard. Table S5-4. Catalytic asymmetric PEDA reaction.

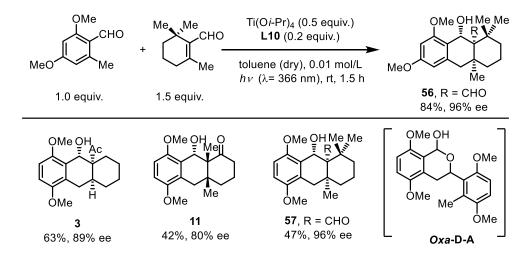
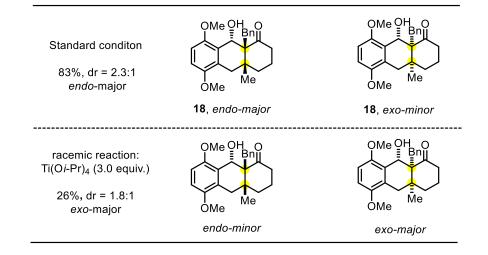


Table S6. Controlling of diastereoselectivity in PEDA reaction.



IV. Nonlinear effect of the ligand accelerated enantioselective PEDA reaction: To a solution of aromatic aldehyde (0.1 mmol, 1.0 equiv.), chiral ligand (e.e. value of ligand was calculated and regulated by mixing the racemic with chiral ligand) and 1,4-diazabicyclo[2.2.2]octane (DABCO) in anhydrous toluene (10 mL, 0.01 M) was added dienophile (0.15 mmol, 1.5 equiv.) under N₂ in quartz tube sealed with rubber plug. Then, titanium (IV) isopropoxide (Ti(O*i*-Pr)₄) was added, after homogeneous mixing, the solution was photolyzed at room temperature in a Rayonet chamber reactor (16 lamps) at λ_{max} = 366 nm for 1.5 h. Afterward, the reaction mixture was poured into saturated sodium bicarbonate and stirred over 30 min, the above mixture was extracted three times with ethyl acetate, the combined organic phases were washed twice with brine and dried over anhydrous sodium sulfate. The dried solution was filtered and the filtrate was concentrated under vacuum. The crude product was purified by PTLC to give the corresponding product for e.e. value test.

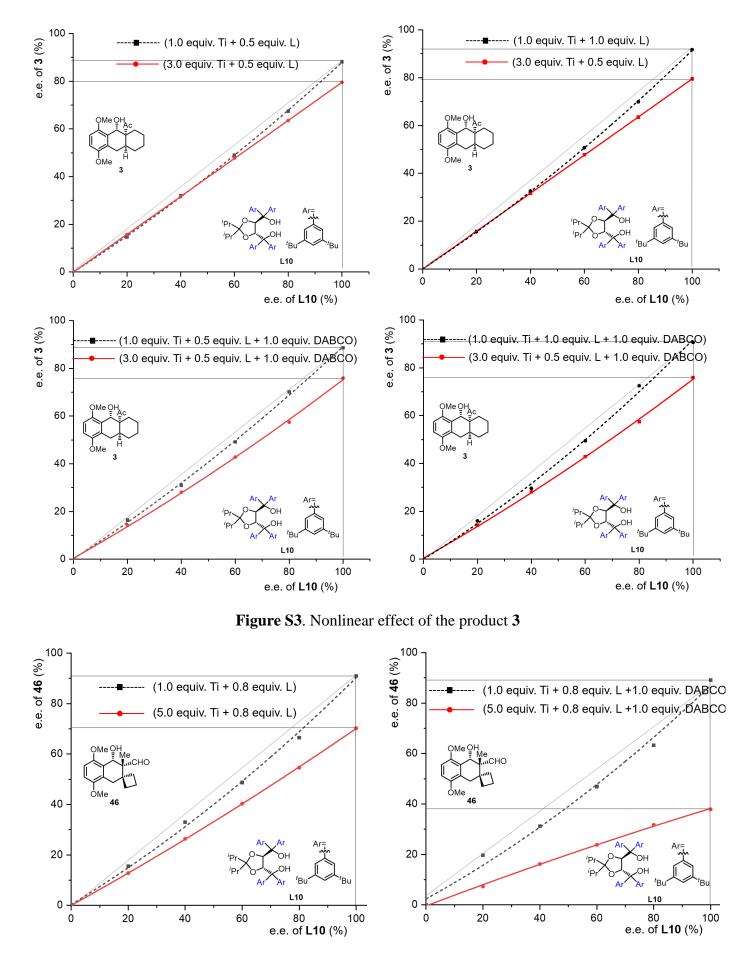
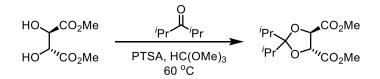


Figure S4. Nonlinear effect of the product 46

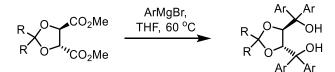
V. Preparation of TADDOL-type chiral ligands

Synthetic pathways for preparing the ketal

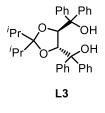


Ketal. To a 500 mL round bottom flask was added *p*-toluenesulfonic acid (PTSA, 2 g, 10.5 mmol) and trimethyl orthoformate (60 ml, 550 mmol) into a solution of dimethyl (*2R*,*3R*)-tartrate (38 g, 213 mmol) in 2,4-dimethyl-3-pentanone (180 mL, 1.27 mol). The resulting mixture was heated to 60 °C. After stirring for 24 h at the same tempreture, the reaction mixture was cooling to room temperature, then neutralized with 1 N sodium bicarbonate solution and extracted three times with ethyl acetate. The combined organic extract was washed with brine and dried over anhydrous sodium sulfate, and the solvent was removed in vacuo and the residue was purified by silica-gel chromatography (0 - 30% ethyl acetate – petroleum ether) to afford the desired ketal in 88% yield as a yellow oil: $R_f = 0.55$ (20% ethyl acetate – petroleum ether); $[\alpha]_D^{20}$ -21.1 (c 0.136, DCM); ¹H NMR (500 MHz, CDCl₃) δ 4.68 (s, 2H), 3.82 (s, 6H), 2.16 (hept, *J* = 6.8 Hz, 2H), 0.97 (d, *J* = 5.5 Hz, 6H), 0.96 (d, *J* = 5.5 Hz, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 169.0 (2C), 121.4, 78.5 (2C), 52.7 (2C), 34.2 (2C), 17.2 (2C), 17.1 (2C) ppm; IR v_{max} 3057, 1606, 1597, 1465, 1151, 1112, 1068, 1031, 866, 740 cm⁻¹; HRMS–ESI (*m/z*): [M+H]⁺ calcd for C₁₃H₂₃O₆, 275.1489; found, 275.1478.

Synthetic pathways for preparing the TADDOL-type ligands

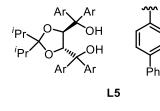


General procedure: preparation of TADDOL-type ligands. To a solution of the corresponding ketal (1.0 equiv.) in anhydrous tetrahydrofuran (0.2 M), was slowly added the corresponding Grignard reagent (1.0 M, 4.5 equiv.). The resulting mixture was heated to 60 °C and stirred for 4 h. Thereafter, the reaction was slowly quenched with saturated ammonium chloride solution and extracted twice with ethyl acetate. The combined organic extracts was washed twice with brine, and then dried over anhydrous sodium sulfate. The solvent was removed in vacuo and the residue purified by silica-gel chromatography (0 - 10% ethyl acetate – petroleum ether) to afford the desired chiral TADDOL-type ligands.



L3 (2.0 g, 85% yield) was prepared according to general procedure to afford the title compound as a white solid: $R_f = 0.8$ (10% ethyl acetate-petroleum ether); m.p. 134 – 136 °C; $[\alpha]_D^{20}$ -30.5 (c 1.16, DCM); ¹H NMR (500 MHz, CDCl₃) δ 7.49 – 7.42 (m, 8H), 7.32 – 7.26 (m, 12H), 4.77 (s, 2H), 4.38 (s, 2H), 1.69 (hept, J = 6.9 Hz, 2H), 0.79 (d, J = 6.9 Hz, 6H), 0.59 (d, J = 6.9 Hz, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 146.5 (2C), 142.4 (2C), 129.0 (4C), 128.1 (4C), 127.7 (4C), 127.5 (2C), 127.2 (2C), 127.1 (4C), 114.1, 80.2 (2C), 78.7 (2C),

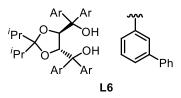
34.2 (2C), 18.3 (2C), 17.5 (2C) ppm; IR v_{max} 1421, 1267, 896, 742, 705 cm⁻¹; HRMS–ESI (*m/z*): [M+Na]⁺ calcd for C₃₅H₃₈O₄Na, 545.2662; found, 545.2662.



L5 (2.8 g, 81% yield) was prepared according to general procedure to afford the title compound as a white solid: $R_f = 0.8$ (10% ethyl acetate-petroleum ether); m.p. 161 – 163 °C; $[\alpha]_D^{20}$ -80.6 (c 0.68, DCM); ¹H NMR (500 MHz, CDCl₃) δ 7.66 – 7.55 (m, 24H), 7.44 (dt, J = 14.7, 7.6 Hz, 8H), 7.38 – 7.32 (m, 4H), 5.18 – 5.06 (m, 2H), 4.52 (d, J = 1.2 Hz, 2H), 1.80 (hept, J = 6.9 Hz, 2H), 0.86 (d, J = 6.9 Hz, 6H), 0.67 (d, J = 6.9 Hz, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 145.3 (2C), 141.4 (2C),

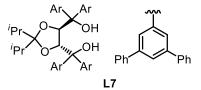
140.7 (2C), 140.6 (2C), 140.3 (2C), 139.9 (2C), 129.5 (4C), 128.8 (4C), 128.7 (4C), 128.1 (4C), 127.29 (4C), 127.26 (4C), 127.0

(4C), 126.8 (4C), 125.8 (4C), 114.3, 80.3 (2C), 78.6 (2C), 34.3 (2C), 18.4 (2C), 17.6 (2C) ppm; IR v_{max} 3055, 1421, 1267, 896, 744, 705 cm⁻¹; HRMS–ESI (*m/z*): [M+Na]⁺ calcd for C₅₉H₅₄O₄Na, 849.3914; found, 849.3915.



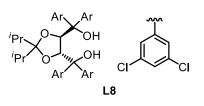
L6 (1.8 g, 72% yield) was prepared according to general procedure to afford the title compound as a white solid: $R_f = 0.8$ (10% ethyl acetate-petroleum ether); m.p. 106 – 108 °C; $[\alpha]_D^{20}$ -38.1 (c 0.72, DCM); ¹H NMR (500 MHz, CDCl₃) δ 7.82 (dt, J = 5.9, 1.9 Hz, 4H), 7.58 – 7.50 (m, 16H), 7.42 – 7.35 (m, 12H), 7.33 – 7.27 (m, 4H), 4.85 – 4.79 (m, 2H), 4.62 (s, 2H), 1.74 (hept, J = 6.9 Hz, 2H), 0.73 (d, J = 6.9 Hz, 6H), 0.58 (d, J = 6.9 Hz, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ

146.9 (2C), 142.9 (2C), 141.2 (2C), 141.2 (2C), 141.0 (2C), 140.1 (2C), 128.7 (4C), 128.7 (4C), 128.6 (2C), 128.1 (2C), 127.7 (2C), 127.7 (2C), 127.2 (6C), 127.2 (4C), 127.1 (2C), 126.7 (2C), 126.5 (2C), 126.4 (2C), 126.2 (2C), 114.4, 80.7 (2C), 78.9 (2C), 34.4 (2C), 18.2 (2C), 17.5 (2C) ppm; IR ν_{max} 3055, 1421, 1267, 896, 744, 705 cm⁻¹; HRMS–ESI (*m/z*): [M+Na]⁺ calcd for C₅₉H₅₄O₄Na, 849.3914; found, 849.3900.



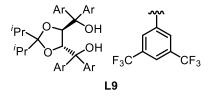
L7 (2.0 g, 76% yield) was prepared according to general procedure to afford the title compound as a white solid: $R_f = 0.7$ (10% ethyl acetate-petroleum ether); m.p. 158 – 160 °C; $[\alpha]_{D}^{20}$ -59.0 (c 0.48, DCM); ¹H NMR (500 MHz, CDCl₃) δ 7.89 (dd, J = 8.8, 1.7 Hz, 8H), 7.76 – 7.71 (m, 4H), 7.60 – 7.56 (m, 8H), 7.54 (d, J = 7.5 Hz, 8H), 7.40 – 7.28 (m, 24H), 5.07 (s,

2H), 4.87 (d, J = 2.1 Hz, 2H), 1.78 (hept, J = 6.9 Hz, 2H), 0.69 (d, J = 6.9 Hz, 6H), 0.56 (d, J = 6.9 Hz, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 147.3 (2C), 143.5 (2C), 141.6 (4C), 141.09 (4C), 141.07 (4C), 140.8 (4C), 128.68 (8C), 128.65 (8C), 127.32 (4C), 127.27 (8C), 127.25 (8C), 126.8 (4C), 125.6 (4C), 125.5 (4C), 125.4 (4C), 114.7, 81.2 (2C), 79.1 (2C), 34.5 (2C), 18.1 (2C), 17.5 (2C) ppm; IR ν_{max} 3055, 1479, 1419, 1265, 744, 705 cm⁻¹.



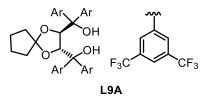
L8 (1.8 g, 72% yield) was prepared according to general procedure to afford the title compound as a yellow solid: $R_f = 0.65$ (10% ethyl acetate-petroleum ether); m.p. 122 – 124 °C; $[\alpha]_D^{20}$ -87.0 (c 0.92, DCM); ¹H NMR (500 MHz, CDCl₃) δ 7.35 (s, 6H), 7.29 (d, J = 1.9 Hz, 2H), 7.26 (s, 2H), 7.20 (d, J = 1.9 Hz, 2H), 5.69 (s, 1H), 4.17 (s, 2H), 1.85 (hept, J = 6.9 Hz, 2H), 0.97 (d, J = 6.9 Hz, 6H), 0.81 (d, J = 6.9 Hz, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ

147.0 (2C), 144.5 (2C), 135.0 (4C), 134.7 (4C), 128.4 (2C), 128.3 (4C), 126.5 (2C), 125.6 (4C), 115.7, 80.5 (2C), 77.5 (2C), 34.4 (2C), 18.4 (2C), 17.8 (2C) ppm; IR ν_{max} 3055, 1419, 1265, 896, 802, 742, 705 cm⁻¹.



L9 (5.2 g, 84% yield) was prepared according to general procedure to afford the title compound as a white solid: $R_f = 0.8$ (10% ethyl acetate-petroleum ether); m.p. 136 – 138 °C; $[\alpha]_D^{20}$ -15.3 (c 3.2, DCM); ¹H NMR (400 MHz, CDCl₃) δ 8.04 (s, 4H), 7.96 (s, 4H), 7.92 (s, 2H), 7.86 (s, 2H), 5.68 (s, 2H), 4.23 (s, 2H), 1.80 (hept, J = 6.9 Hz, 2H), 0.82 (d, J = 6.9 Hz, 6H), 0.66 (d, J = 6.9 Hz, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 146.1 (2C), 143.3 (2C),

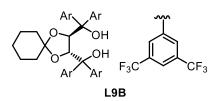
132.2 (q, J = 33.6 Hz, 4C), 131.7 (q, J = 33.6 Hz, 4C), 128.3 (q, J = 3.9 Hz, 4C), 127.4 (q, J = 3.9 Hz, 4C), 125.7 (dd, J = 272.9, 8.3 Hz, 2C), 122.7 (m, 8C), 120.3 (dd, J = 272.9, 8.3 Hz, 2C), 115.9, 80.7 (2C), 77.3 (2C), 34.5 (2C), 17.7 (2C), 17.0 (2C) ppm; IR v_{max} 1471, 1373, 1280, 1180, 1139, 900, 744, 707 cm⁻¹.



L9A (2.6 g, 86% yield) was prepared according to general procedure to afford the title compound as a white solid: $R_f = 0.8$ (10% ethyl acetate-petroleum ether); m.p. 90 – 92 °C; $[\alpha]_D^{20}$ -17.8 (c 1.4, DCM); ¹H NMR (500 MHz, CDCl₃) δ 8.08 (s, 4H), 7.95 (s, 2H), 7.87 (s, 4H), 7.85 (s, 2H), 4.79 – 4.73 (m, 2H), 4.35 (s, 2H), 1.71 – 1.62 (m, 2H), 1.62 – 1.44 (m, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 145.8 (2C), 143.5 (2C), 132.2 (q, *J* = 33.6 Hz, 4C),

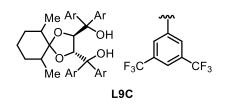
131.8 (q, J = 33.6 Hz, 4C), 128.1 (q, J = 3.6 Hz, 4C), 127.5 (q, J = 3.8 Hz, 4C), 125.2 (dd, J = 272.8, 20.7 Hz, 2C), 122.7 (m, 8C),

120.9 (dd, J = 272.8, 20.7 Hz, 2C), 120.8, 81.1 (2C), 77.1 (2C), 36.7 (2C), 22.4 (2C) ppm; IR v_{max} 1371, 1280, 1267, 1178, 1141, 900, 742, 705, 682 cm⁻¹.



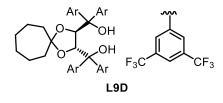
L9B (2.2 g, 85% yield) was prepared according to general procedure to afford the title compound as a white solid: $R_f = 0.8$ (10% ethyl acetate-petroleum ether); m.p. 74 – 76 °C; $[\alpha]_{D}^{20}$ -26.1 (c 8.0, DCM); ¹H NMR (500 MHz, CDCl₃) δ 8.14 (s, 4H), 7.95 (s, 2H), 7.94 (s, 4H), 7.85 (s, 2H), 5.30 (s, 2H), 4.25 (s, 2H), 1.62 – 1.48 (m, 4H), 1.44 – 1.36 (m, 4H), 1.35 – 1.28 (m, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 146.0 (2C), 143.4 (2C), 132.2 (q, *J* =

33.5 Hz, 4C), 131.7 (q, J = 33.5 Hz, 4C), 128.2 (q, J = 3.8 Hz, 4C), 127.6 (q, J = 3.9 Hz, 4C), 125.3 (dd, J = 272.7, 19.1 Hz, 2C), 122.7 (m, 8C), 121.0 (dd, J = 272.6, 19.1 Hz, 2C), 111.6, 80.9 (2C), 76.9 (2C), 36.3 (2C), 24.6, 23.7 (2C) ppm; IR v_{max} 3751, 1373, 1280, 1178, 1139, 902, 844, 744, 682 cm⁻¹.



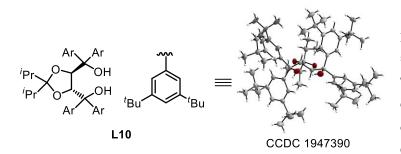
L9C (2.0 g, 76% yield) was prepared according to general procedure to afford the title compound as a white solid: $R_f = 0.8$ (10% ethyl acetate-petroleum ether); m.p. 90 – 92 °C; $[\alpha]_D^{20}$ -30.0 (c 5.4, DCM); ¹H NMR (500 MHz, CDCl₃) δ 8.10 (s, 2H), 8.05 (s, 2H), 7.96 (s, 2H), 7.94 (s, 4H), 7.87 (s, 2H), 5.07 (s, 2H), 4.29 (s, 1H), 4.25 (s, 1H), 1.81 – 1.71 (m, 1H), 1.68 – 1.55 (m, 3H), 1.50 – 1.35 (m, 3H), 1.34 – 1.23 (m, 1H), 0.68 (d, *J* = 6.5 Hz, 3H),

0.59 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 146.1 (2C), 143.3 (2C), 132.3 (q, *J* = 33.5 Hz, 4C), 131.8 (q, *J* = 33.5 Hz, 4C), 128.2 (q, *J* = 3.8 Hz, 4C), 127.4 (q, *J* = 3.9 Hz, 4C), 124.7 (dd, *J* = 272.7, 19.1 Hz, 2C), 122.7 (m, 8C), 121.5 (dd, *J* = 272.6, 19.1 Hz, 2C), 114.5, 80.7 (2C), 77.5 (2C), 35.4, 31.2 (2C), 19.3 (2C), 14.3 (2C) ppm; IR v_{max} 1373, 1280, 1267, 1178, 900, 844, 744, 707, 682 cm⁻¹.



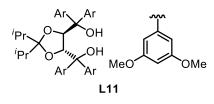
L9D (2.2 g, 78% yield) was prepared according to general procedure to afford the title compound as a white solid: $R_f = 0.8$ (10% ethyl acetate-petroleum ether); m.p. 70 – 72 °C; $[\alpha]_D^{20}$ -15.1 (c 2.2, DCM); ¹H NMR (500 MHz, CDCl₃) δ 8.11 (s, 4H), 7.93 (s, 2H), 7.86 (s, 4H), 7.83 (s, 2H), 5.10 – 5.02 (m, 2H), 4.09 (s, 2H), 1.66 – 1.56 (m, 4H), 1.53 – 1.47 (m, 4H), 1.47 – 1.35 (m, 4H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 145.6 (2C), 143.3 (2C),

132.1 (q, J = 33.5 Hz, 4C), 131.6 (q, J = 33.5 Hz, 4C), 128.0 (q, J = 3.8 Hz, 4C), 127.5 (q, J = 3.9 Hz, 4C), 125.2 (dd, J = 272.7, 19.1 Hz, 2C), 122.7 (m, 8C), 120.9 (dd, J = 272.6, 19.1 Hz, 2C), 114.6, 80.6 (2C), 76.7 (2C), 39.5 (2C), 28.1 (2C), 21.4 (2C) ppm; IR ν_{max} 1373, 1282, 1267, 1180, 1141, 900, 744, 707 cm⁻¹.



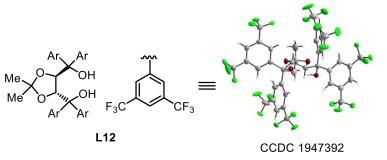
L10 (8.0 g, 82% yield) was prepared according to general procedure to afford the title compound as a white solid: $R_f = 0.8$ (10% ethyl acetate-petroleum ether); m.p. 160 – 162 °C; $[\alpha]_D^{20}$ -20.0 (c 1.48, DCM); and it was recrystallized from ethyl acetate /hexane (V/V = 1/4) at 25 °C, to obtain colorless crystals, CCDC (1947390). ¹H NMR (500 MHz, CDCl₃) δ 7.43 (s, 4H), 7.33 – 7.29 (m, 6H), 7.27 (d, *J* = 1.8

Hz, 2H), 4.65 (s, 2H), 4.57 (s, 2H), 1.77 (hept, J = 6.9 Hz, 2H), 1.29 – 1.27 (m, 36H), 1.25 – 1.23 (m, 36H), 0.59 (d, J = 6.9 Hz, 6H), 0.41 (d, J = 6.9 Hz, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 149.6 (4C), 148.8 (4C), 145.9 (2C), 142.1 (2C), 123.7 (4C), 122.0 (4C), 120.73 (2C), 120.69 (2C), 113.5, 81.3 (2C), 79.6 (2C), 35.0 (4C), 34.9 (4C), 34.8 (12C), 31.54 (12C), 31.49 (2C), 18.0 (2C), 17.2 (2C) ppm; IR v_{max} 1280, 1267, 1180, 1141, 898, 742, 705, 682 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₆₇H₁₀₂O₄Na, 993.7670; found, 993.7662.



L11 (1.6 g, 75% yield) was prepared according to general procedure to afford the title compound as a white solid: $R_f = 0.5$ (10% ethyl acetate-petroleum ether); m.p. 160 – 162 °C; $[\alpha]_D^{20}$ -45.5 (c 0.4, DCM); ¹H NMR (500 MHz, CDCl₃) δ 6.68 (d, J = 2.3 Hz, 4H), 6.65 (d, J = 2.3 Hz, 4H), 6.35 (t, J = 2.3 Hz, 2H), 6.31 (t, J = 2.3 Hz, 2H), 5.06 – 4.98 (m, 2H), 4.41 (s, 2H), 3.69 (s, 12H), 3.67 (s, 12H), 1.79 (hept, J = 7.0 Hz, 2H), 0.83 (d, J = 7.0 Hz,

6H), 0.68 (d, J = 7.0 Hz, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 160.2 (4C), 159.6 (4C), 148.2 (2C), 144.7 (2C), 113.9, 107.5 (4C), 105.8 (4C), 99.5 (2C), 99.1 (2C), 80.7 (2C), 78.6 (2C), 55.3 (4C), 55.2 (4C), 34.3 (2C), 18.3 (2C), 17.6 (2C) ppm; IR ν_{max} 1598, 1421, 1280, 1267, 1180, 1141, 898, 744, 705, 682 cm⁻¹; HRMS–ESI (m/z): [M+Na]⁺ calcd for C₄₃H₅₄O₁₂Na, 785.3507; found, 785.3502.

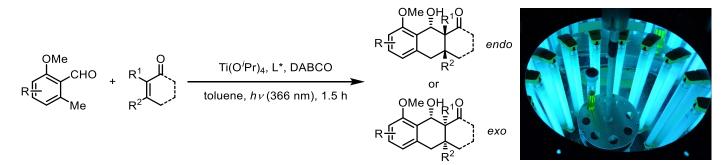


L12 was recrystallized from ethyl acetate /hexane (V/V = 1/4) at 25 °C, to obtain colorless crystals, CCDC (1947392).

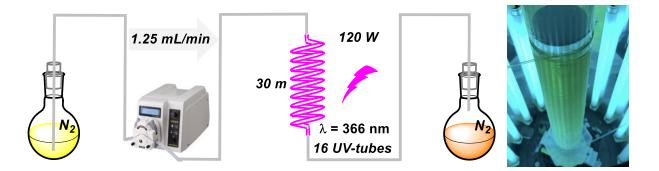
Known compound:

D.-C. A. Falk, B. S. A.-L. Göderz, H.-G. Schmalz, *Angew*. *Chem. Int. Ed.* 2013, **52**, 1576–1580.

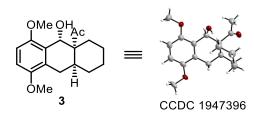
VI. General Procedures for Asymmetric Photoenolization/Diels-Alder Reaction (APEDA)



To a solution of aromatic aldehyde (0.3 mmol, 1.0 equiv.), chiral ligand (0.15 mmol, 0.5 equiv.) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (0.3 mmol, 1.0 equiv.) in anhydrous toluene (30 mL, 0.01 M) was added dienophile (0.45 mmol, 1.5 equiv.) (if the dienophile was solid, it was added before the addition of solvent) under N₂, in quartz tube sealed with rubber plug. Then, titanium (IV) isopropoxide (Ti(O*i*-Pr)₄, 0.3 mmol, 1.0 equiv.) was added, after homogeneous mixing, the solution was photolyzed at room temperature in a Rayonet chamber reactor (16 lamps) at $\lambda_{max} = 366$ nm for 1.5 h. Then the reaction mixture was poured into saturated sodium bicarbonate and stirred over 30 min, the above mixture was extracted three times with ethyl acetate, the combined organic phases were washed twice with brine and dried over anhydrous sodium sulfate. The dried solution was filtered and the filtrate was concentrated under vacuum. The residue was purified by silica gel column chromatography to give the corresponding cycloadducts, and the ligand could be recovered over 95% yield.

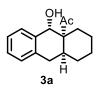


General Procedure for flow APEDA reaction: In a round-bottom flask, the aromatic aldehyde (6.0 mmol, 1.0 equiv.) and chiral ligand (3.0 mmol, 0.5 equiv.) was dissolved in anhydrous toluene (300 mL, 0.02 M) and followed by addition of titanium tetraisopropanolate (6.0 mmol, 1.0 equiv.) and dienophile (9.0 mmol, 1.5 equiv.) under nitrogen. The round-bottom flask was connected to double-ended needle and the other end of the double-ended needle was connected to the silicone tubing (1.0 mm ID, 3.0 mm OD) which was connected to peristaltic pump. The peristaltic pump was connected to FEP (fluorinated ethylene propylene) tubing (0.8 mm ID, 1.6 mm OD, 30.0 m length) wrapped around a cylinder placed in a Rayonet chamber hosting 16 UV lamps which allowed the flowing solution receive the highest photon flux. The reaction mixture was pumped through the FEP tubing wrapped around a cylinder placed in a Rayonet chamber (16 lamps) at 366 nm and collected in a round-bottom flask. The flow rate is 1.25 ml/min. When all of the reaction mixture had been pumped in to the tubing, anhydrous toluene was pumped through the tubing at the same flow rate until all solution containing the reaction mixture was collected. The reaction mixture was poured into sat. sodium bicarbonate and stirred over 30 mins, the above mixture was extracted with ethyl acetate, washed with brine and dried over anhydrous sodium sulfate, filtered, concentrated, and purified by silica gel column chromatography (10% ethyl acetate in petroleum ether), and the ligand could be recovered over 95% yield.



3 (75 mg) was prepared according to general procedure in 82% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.12$ (20% ethyl acetate-petroleum ether); m.p. 114 – 116 °C; $[\alpha]_D^{20}$ +35.8 (c 0.84, DCM); and it was recrystallized from ethyl acetate /hexane (V/V = 1/4) at 25 °C, to obtain colorless crystals, CCDC (1947396). ¹H NMR (400 MHz, CDCl₃) δ 6.72 (d, *J*

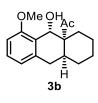
= 8.8 Hz, 1H), 6.68 (d, J = 8.8 Hz, 1H), 4.90 (s, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 2.79 (dd, J = 17.3, 6.1 Hz, 1H), 2.73 – 2.64 (m, 1H), 2.60 (dd, J = 17.2, 10.7 Hz, 1H), 2.31 (s, 3H), 2.20 (s, 1H), 2.05 – 1.91 (m, 1H), 1.80 (ddt, J = 13.4, 3.6, 1.9 Hz, 1H), 1.61 – 1.44 (m, 4H), 1.25 (td, J = 13.5, 3.0 Hz, 1H), 1.13 (tt, J = 12.9, 2.9 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 211.3, 151.6, 151.1, 125.9, 125.7, 108.8, 107.1, 68.4, 55.6 (t, J = 3.4 Hz, 2C), 54.2, 27.1, 26.6, 26.3 (d, J = 2.5 Hz, 1C), 26.2, 24.7, 22.7, 20.1 ppm; IR ν_{max} 1720, 1481, 1259, 1087, 742 cm⁻¹; HRMS–ESI (m/z): [M+Na]⁺ calcd for C₁₈H₂₄O₄Na, 327.1567; found, 327.1563; Enantiomeric excess: 92%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 240 nm): t_R = 14.419 min (major), t_R = 18.018 min (minor).



3a (35.2 mg) was prepared according to general procedure A from in 48% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a yellow oil: $R_f = 0.30$ (20% ethyl acetate-petroleum ether); $[\alpha]_D^{20} + 10.0$ (c 0.40, DCM); ¹H NMR (500 MHz, CDCl₃) δ 7.62 (d, J = 7.6 Hz, 1H), 7.22 (t, J = 7.4 Hz, 1H), 7.17 (t, J = 7.4 Hz, 1H), 7.03 (d, J = 7.5 Hz, 1H), 4.84 (d, J = 8.2 Hz, 1H), 3.22 – 3.10 (m, 1H), 2.90 (dd, J = 17.7, 6.6 Hz, 1H), 2.62 (dd, J = 17.7,

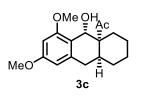
4.2 Hz, 1H), 2.54 – 2.43 (m, 1H), 2.23 (s, 3H), 2.09 – 1.97 (m, 1H), 1.82 – 1.73 (m, 1H), 1.73 – 1.33 (m, 5H) ppm; ¹³C NMR (125

MHz, CDCl₃) δ 214.7, 138.0, 133.4, 128.6, 127.3, 127.1, 126.4, 69.4, 55.3, 34.5, 32.5, 28.6, 27.4, 24.8, 24.2, 21.0 ppm; IR v_{max} 1267, 896, 744, 705, 507 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₁₆H₂₀O₂Na, 267.1356; found, 267.1351; Enantiomeric excess: 22%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 95/5, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 34.327min (major), t_R = 37.110 min (minor).



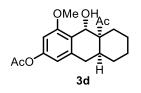
3b (65 mg) was prepared according to general procedure in 79% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.1$ (20% ethyl acetate-petroleum ether); m.p. 142 – 144 °C; $[\alpha]_D^{20}$ +24.1 (c 0.20, DCM); ¹H NMR (400 MHz, CDCl₃) δ 7.20 (t, J = 7.9 Hz, 1H), 6.77 (d, J = 7.7 Hz, 1H), 6.71 (d, J = 8.1 Hz, 1H), 4.92 (s, 1H), 3.86 (s, 3H), 2.98 – 2.85 (m, 1H), 2.81 – 2.67 (m, 2H), 2.32 (s, 3H), 2.19 (s, 1H), 2.04 –

1.91 (m, 1H), 1.83 (dt, J = 13.8, 3.4 Hz, 1H), 1.61 – 1.41 (m, 4H), 1.29 (td, J = 13.5, 3.1 Hz, 1H), 1.21 – 1.06 (m, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 211.2, 157.8, 136.9, 128.6, 124.7, 121.2, 107.3, 68.3, 55.4, 54.6, 30.0, 27.1, 26.8, 26.6, 26.3, 22.8, 20.1 ppm; IR v_{max} 2926, 1708, 1591, 1265, 1083, 740 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₁₇H₂₂O₃Na, 297.1461; found, 297.1459; Enantiomeric excess: 92%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 12.301 min (major), t_R = 13.581 min (minor).



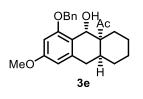
3c (72.2 mg) was prepared according to general procedure A from in 92% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a yellow oil: $R_f = 0.24$ (30% ethyl acetate-petroleum ether); $[\alpha]_D^{20}$ +17.9 (c 0.47, DCM); ¹H NMR (500 MHz, CDCl₃) δ 6.31 (d, J = 2.3 Hz, 1H), 6.27 (d, J = 2.3 Hz, 1H), 4.86 (d, J = 3.7 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 2.94 – 2.83 (m, 1H), 2.78 – 2.69 (m, 2H), 2.31 (s, 3H), 2.03 –

1.93 (m, 2H), 1.85 – 1.78 (m, 1H), 1.57 – 1.40 (m, 4H), 1.32 – 1.24 (m, 1H), 1.20 – 1.06 (m, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 211.3, 160.2, 159.0, 137.9, 117.6, 103.7, 96.4, 68.1, 55.4, 55.3, 54.8, 30.5, 27.1, 26.8, 26.6, 26.2, 22.8, 20.1 ppm; IR v_{max} 3053, 1610, 1456, 1267, 1151, 742 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₁₈H₂₄O₄Na, 327.1567; found, 327.1563; Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 21.293 min (major), t_R = 23.830 min (minor).



3d (84.6 mg) was prepared according to general procedure A from in 85% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a yellow oil: $R_f = 0.20$ (35% ethyl acetate-petroleum ether); $[\alpha]_D^{20}$ +2.9 (c 0.96, DCM); ¹H NMR (500 MHz, CDCl₃) δ 6.51 (d, J = 2.3 Hz, 1H), 6.46 (d, J = 2.1 Hz, 1H), 4.87 (s, 1H), 3.84 (s, 3H), 2.90 (dd, J = 19.7, 13.1 Hz, 1H), 2.75 (dd, J = 13.4, 6.3 Hz, 2H), 2.31 (s, 3H), 2.29 (s, 3H),

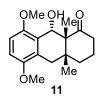
2.06 (s, 1H), 1.97 (tdd, J = 13.7, 7.8, 4.1 Hz, 1H), 1.81 (d, J = 13.9 Hz, 1H), 1.65 – 1.53 (m, 2H), 1.52 – 1.38 (m, 2H), 1.27 (td, J = 13.8, 3.6 Hz, 1H), 1.18 – 1.05 (m, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 211.0, 169.5, 158.6, 150.9, 138.0, 122.4, 113.5, 102.0, 68.0, 55.6, 54.6, 30.2, 27.0, 26.7, 26.5, 26.2, 22.7, 21.2, 20.0 ppm; IR v_{max} 1267, 1211, 1029, 744, 507 cm⁻¹; HRMS–ESI (*m/z*): [M+Na]⁺ calcd for C₁₉H₂₄O₅Na, 355.1516; found, 355.1501; Enantiomeric excess: 81%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 65/35, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 21.296 min (major), t_R = 23.696 min (minor).



3e (83.2 mg) was prepared according to general procedure A from in 73% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a yellow oil: $R_f = 0.15$ (20% ethyl acetate-petroleum ether); $[\alpha]_D^{20}$ +8.6 (c 0.96, DCM); ¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.29 (m, 5H), 6.38 (d, J = 2.3 Hz, 1H), 6.29 (d, J = 2.3 Hz, 1H), 5.12 (d, J = 12.0 Hz, 1H), 5.08 (d, J = 12.0 Hz, 1H), 4.91 (s, 1H), 3.77 (s, 3H), 2.90 (dd, J = 19.7,

13.4 Hz, 1H), 2.81 – 2.69 (m, 2H), 2.29 (s, 3H), 2.10 (s, 1H), 2.02 – 1.90 (m, 1H), 1.81 (d, *J* = 13.9 Hz, 1H), 1.61 – 1.40 (m, 3H), 1.28 (td, *J* = 13.5, 3.2 Hz, 1H), 1.19 – 1.08 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 211.3, 160.0, 158.0, 138.0, 136.6, 128.7

(2C), 128.1, 127.2 (2C), 118.1, 104.2, 97.9, 70.2, 68.34, 55.25, 54.7, 30.6, 27.01, 27.0, 26.6, 26.4, 22.7, 20.1 ppm; IR v_{max} 1606, 1267, 1151, 1072, 742 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₂₄H₂₈O₄Na, 403.1880; found, 403.1872; Enantiomeric excess: 72%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 31.923 min (major), t_R = 34.506 min (minor).



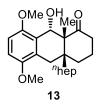
11 (70.1 mg) was prepared according to general procedure in 77% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.31$ (20% ethyl acetate-petroleum ether); m.p. 129 - 131 °C; $[\alpha]_D^{20}$ +59.9 (c 0.5, DCM); ¹H NMR (500 MHz, CDCl₃) δ 6.72 (d, J = 8.9 Hz, 1H), 6.70 (d, J = 8.9 Hz, 1H), 4.66 (d, J = 3.9 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.38 (d, J = 3.9 Hz, 1H), 2.88 – 2.80 (m, 1H), 2.77 (d, J = 18.2 Hz, 1H), 2.51

-2.44 (m, 1H), 2.42 -2.34 (m, 1H), 2.38 (d, *J* = 18.1 Hz, 1H), 2.01 -1.81 (m, 2H), 1.27 (m, 1H), 1.09 (s, 3H), 1.04 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 216.0, 151.7, 151.1, 126.0, 124.3, 108.6, 107.3, 71.2, 55.6, 55.5, 53.8, 39.4, 36.0, 34.9, 32.4, 24.8, 19.8, 16.9 ppm; IR v_{max} 2987, 1419, 1282, 1267, 1178, 742 cm⁻¹; HRMS–EI (*m*/*z*): [M]⁺ calcd for C₁₈H₂₄O₄, 304.1675; found, 304.1671; Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 8.699 min (major), t_R = 13.042 min (minor).



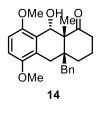
12 (88.7 mg) was prepared according to general procedure in 89% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetatepetroleum ether) as a yellow solid: $R_f = 0.36$ (20% ethyl acetate-petroleum ether); m.p. 133 - 135 °C; $[\alpha]_D^{20}$ +60.5 (c 0.75, DCM); ¹H NMR (500 MHz, CDCl₃) δ 6.72 (d, J = 8.8 Hz, 1H), 6.69 (d, J = 8.8 Hz, 1H), 4.66 (d, J = 3.6Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.31 (d, J = 3.6 Hz, 1H), 2.94 – 2.84 (m, 1H), 2.92 (d, J = 18.4 Hz, 1H), 2.51

-2.44 (m, 1H), 2.41 - 2.34 (m, 1H), 2.29 (d, J = 18.3 Hz, 1H), 1.85 - 1.73 (m, 2H), 1.45 - 1.28 (m, 5H), 1.04 (s, 3H), 0.93 (t, J = 7.0 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 216.2, 151.6, 151.2, 126.0, 124.1, 108.5, 107.1, 71.4, 55.52, 55.47, 54.5, 39.8, 38.7, 38.0, 32.0, 27.0, 19.4, 16.4, 15.9, 15.0 ppm; IR v_{max} 3055, 1691, 1282, 1178, 742 cm⁻¹; HRMS–EI (*m/z*): [M]⁺ calcd for C₂₀H₂₈O₄, 332.1988; found, 332.1986; Enantiomeric excess: 87%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 7.358 min (major), t_R = 11.298 min (minor).



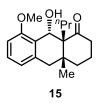
13 (87 mg) was prepared according to general procedure in 75% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.41$ (20% ethyl acetate-petroleum ether); m.p. 124 - 126 °C; $[\alpha]_D^{20}$ +49.9 (c 0.41, DCM); ¹H NMR (500 MHz, CDCl₃) δ 6.72 (d, J = 8.8 Hz, 1H), 6.69 (d, J = 8.8 Hz, 1H), 4.66 (d, J = 3.6 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.30 (d, J = 3.6 Hz, 1H), 2.95 – 2.85 (m, 1H), 2.90 (d, J = 18.0 Hz, 1H), 2.51

-2.43 (m, 1H), 2.43 -2.33 (m, 1H), 2.28 (d, J = 18.2 Hz, 1H), 1.85 -1.75 (m, 2H), 1.44 -1.38 (m, 1H), 1.34 -1.22 (m, 12H), 1.04 (s, 3H), 0.89 (t, J = 6.9 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 216.2, 151.6, 151.2, 126.0, 124.2, 108.5, 107.1, 71.5, 55.53, 55.47, 54.5, 39.8, 37.9, 36.3, 32.0, 31.9, 30.5, 29.3, 26.9, 22.6 (2C), 19.4, 16.4, 14.1 ppm; IR v_{max} 3053, 2322, 0697, 1282, 1267, 1178, 742 cm⁻¹; HRMS–ESI (m/z): [M+Na]⁺ calcd for C₂₄H₃₆O₄Na, 411.2506; found, 411.2504; Enantiomeric excess: 85%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 6.464 min (major), t_R = 7.953 min (minor).



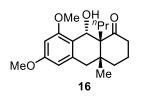
4H), 2.51 (s, 2H), 2.14 – 2.03 (m, 1H), 1.92 – 1.77 (m, 2H), 1.69 – 1.63 (m, 1H), 1.46 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ

216.7, 152.0, 151.0, 137.4, 130.7 (2C), 127.8 (2C), 126.5, 126.2, 124.3, 108.9, 108.3, 72.3, 55.8, 55.6, 54.7, 42.4, 39.6, 38.4, 29.2, 27.6, 20.7, 17.6 ppm; IR v_{max} 3055, 1691, 1280, 1267, 1139, 742, 705 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₂₄H₂₈O₄Na, 403.1880; found, 403.1872; Enantiomeric excess: 89%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 15.999 min (major), t_R = 25.205 min (minor).



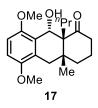
15 (86 mg) was prepared according to general procedure in 95% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.6$ (20% ethyl acetate-petroleum ether); m.p. 60 - 62 °C; $[\alpha]_D^{20}$ -110 (c 0.52, DCM); ¹H NMR (500 MHz, CDCl₃) δ 7.13 (t, J = 7.9 Hz, 1H), 6.73 (d, J = 8.2 Hz, 1H), 6.63 (d, J = 7.7 Hz, 1H), 5.39 (d, J = 3.1 Hz, 1H), 3.87 (s, 3H), 2.89 (dt, J = 3.1, 1.4 Hz, 1H), 2.84 (d, J = 16.8 Hz, 1H), 2.61 (dt,

J = 14.2, 10.9 Hz, 1H), 2.36 – 2.25 (m, 2H), 2.23 (d, J = 16.9 Hz, 1H), 2.17 (dtd, J = 14.1, 3.9, 1.3 Hz, 1H), 1.99 (tt, J = 7.3, 2.3 Hz, 2H), 1.91 (td, J = 12.7, 3.5 Hz, 1H), 1.66 – 1.53 (m, 1H), 1.35 (dtd, J = 14.1, 3.9, 1.3 Hz, 1H), 1.13 (s, 3H), 0.99 (t, J = 6.5 Hz, 3H), 0.96 – 0.89 (m, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 214.6, 157.2, 134.5, 127.7, 126.1, 121.3, 107.6, 62.0, 58.4, 55.2, 38.8, 38.6, 36.9, 33.0, 31.3, 23.5, 21.9, 17.1, 14.8 ppm; IR v_{max} 2968, 1373, 1267, 1180, 1141, 744 cm⁻¹; HRMS–ESI (*m*/*z*): [M+K]⁺ calcd for C₁₉H₂₆O₃K, 341.1514; found, 341.1504; Enantiomeric excess: 88%, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 85/15, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 6.583 min (major), t_R = 7.651 min (minor).



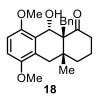
16 (71.8 mg) was prepared according to general procedure in 72% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a colorless oil; $R_f = 0.39$ (20% ethyl acetate-petroleum ether); $[\alpha]_D^{20}$ -88.0 (c 0.54, DCM); ¹H NMR (400 Hz, CDCl₃) δ 6.33 (d, J = 2.3 Hz, 1H), 6.13 (d, J = 2.3 Hz, 1H), 5.30 (s, 1H), 3.86 (s, 3H), 3.75 (s, 3H), 2.82 (d, J = 16.9 Hz, 1H), 2.70 (s, 1H), 2.65 – 2.54 (m, 1H), 2.34 – 2.21 (m,

2H), 2.21 – 2.13 (m, 2H), 2.04 – 1.95 (m, 2H), 1.89 (td, J = 12.8, 3.4 Hz, 1H), 1.62 – 1.53 (m, 1H), 1.33 (dq, J = 14.1, 2.9 Hz, 1H), 1.13 (s, 3H), 0.97 (t, J = 6.2 Hz, 3H), 0.94 – 0.85 (m, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 214.6, 159.5, 158.4, 135.3, 119.1, 104.2, 96.6, 61.9, 58.4, 55.3, 55.2, 39.2, 39.1, 37.0, 33.1, 31.4, 23.7, 22.0, 17.1, 14.9 ppm; IR v_{max} 3053, 2966, 1674, 1492, 1271, 827, 738 cm⁻¹; HRMS–EI (m/z): [M]⁺ calcd for C₂₀H₂₈O₄, 332.1988; found, 332.1990; Enantiomeric excess: 87%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 10.241 min (minor), t_R = 13.851 min (major).



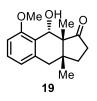
17 (77 mg) was prepared according to general procedure in 77% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.3$ (20% ethyl acetate-petroleum ether); m.p. 104-106 °C; $[\alpha]_D^{20}$ -72.8 (c 0.25, DCM); ¹H NMR (400 MHz, CDCl₃) δ 6.71 (d, J = 8.9 Hz, 1H), 6.69 (d, J = 8.9 Hz, 1H), 4.94 (d, J = 7.6 Hz, 1H), 4.25 (d, J = 7.6 Hz, 1H), 3.84 (s, 3H), 3.76 (s, 3H), 2.69 (d, J = 17.8 Hz, 1H), 2.62 – 2.44 (m, 2H), 2.40

(d, J = 17.8 Hz, 1H), 2.12 – 1.94 (m, 3H), 1.93 – 1.73 (m, 3H), 1.58 – 1.51 (m, 1H), 1.36 – 1.21 (m, 1H), 0.94 (s, 3H), 0.90 (t, J = 7.2 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 218.1, 152.0, 150.8, 127.7, 124.6, 108.7, 108.4, 71.3, 57.1, 56.0, 55.6, 40.8, 39.4, 37.0, 33.9, 33.5, 22.9, 21.8, 19.2, 15.4 ppm; IR v_{max} 3055, 1691, 1280, 1267, 1178, 742 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₂₀H₂₈O₄Na, 355.1880; found, 355.1876; Enantiomeric excess: 99%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 11.047 min (major), t_R = 22.223 min (minor).



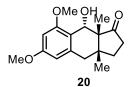
18 (94.6 mg, d.r. = 2.3:1) was prepared according to general procedure in 83% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a colorless oil: $R_f = 0.38$ (20% ethyl acetate-petroleum ether); $[\alpha]_D^{20}$ +59.2 (c 0.10, DCM); ¹H NMR (400 MHz, CDCl₃) δ 7.12 – 7.01 (m, 5H), 6.75 (d, J = 8.8 Hz, 1H), 6.69 (d, J = 8.8 Hz, 1H), 4.69 (d, J = 3.6 Hz, 1H), 3.82 (s, 3H), 3.65 (s, 3H), 3.31 (d, J = 13.9 Hz, 1H), 3.09 – 2.96 (m, 2H), 2.79 (d, J = 3.6 Hz, 1H), 3.82 (s, 3H), 3.65 (s, 3H), 3.81 (d, J = 13.9 Hz, 1H), 3.09 – 2.96 (m, 2H), 2.79 (d, J = 3.6 Hz, 1H), 3.82 (s, 3H), 3.65 (s, 3H), 3.81 (d, J = 13.9 Hz, 1H), 3.09 – 2.96 (m, 2H), 2.79 (d, J = 3.6 Hz, 1H), 3.82 (s, 3H), 3.65 (s, 3H), 3.81 (s, 3

18.6 Hz, 1H), 2.64 (d, J = 18.6 Hz, 1H), 2.60 (dt, J = 18.6, 5.8 Hz, 1H), 2.49 (d, J = 13.9 Hz, 1H), 2.53 – 2.43 (m, 1H), 2.05 – 1.82 (m, 2H), 1.33 – 1.27 (m, 1H), 1.09 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 216.1, 151.5, 151.2, 139.3, 131.5 (2C), 127.5 (2C), 126.4, 125.7, 124.5, 108.8, 107.8, 67.0, 58.2, 55.7, 55.6, 40.6, 37.9, 36.6, 35.8, 33.8, 24.4, 20.3 ppm; IR v_{max} 3055, 1697, 1282, 1267, 1178, 705 cm⁻¹; HRMS–ESI (m/z): [M+Na]⁺ calcd for C₂₄H₂₈O₄Na, 403.1880; found, 403.1875; Enantiomeric excess: 99%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 7.432 min (major), t_R = 13.839 min (minor).



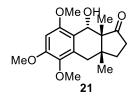
19 (66.2 mg, d.r. = 12:1) was prepared according to general procedure in 85% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.2$ (20% ethyl acetate-petroleum ether); m.p. 110 – 112 °C; $[\alpha]_D^{20}$ +89.4 (c 0.48, DCM); ¹H NMR (400 MHz, CDCl₃) δ 7.21 (t, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.74 (d, *J*

 $= 8.2 \text{ Hz}, 1\text{H}, 4.88 \text{ (d, } J = 3.0 \text{ Hz}, 1\text{H}, 3.83 \text{ (s, 3H)}, 2.96 \text{ (d, } J = 16.8 \text{ Hz}, 1\text{H}, 2.75 \text{ (d, } J = 3.5 \text{ Hz}, 1\text{H}), 2.67 \text{ (d, } J = 16.8 \text{ Hz}, 1\text{H}), 2.46 - 2.36 \text{ (m, 1H)}, 2.27 \text{ (q, } J = 9.9, 9.2 \text{ Hz}, 1\text{H}), 2.23 - 2.14 \text{ (m, 1H)}, 1.63 - 1.55 \text{ (m, 1H)}, 0.95 \text{ (s, 3H)}, 0.93 \text{ (s, 3H)} \text{ ppm;}^{13}\text{C NMR} (100 \text{ MHz}, \text{CDCl}_3) \delta 221.7, 157.6, 136.6, 128.6, 124.6, 121.3, 107.9, 69.6, 55.4 \text{ (d, } J = 3.0 \text{ Hz}), 54.2, 40.0, 38.9, 37.2, 32.5, 25.9, 16.6 \text{ ppm;} \text{ IR } v_{\text{max}} 2308, 1531, 1492, 1398, 1267, 904, 798, 748, 698, 653 \text{ cm}^{-1}; \text{ HRMS}-\text{ESI } (m/z): [M+Na]^+ \text{ calcd for } C_{16}\text{H}_{20}\text{O}_3\text{Na}, 283.1305; \text{ found, } 283.1301; \text{ Enantiomeric excess: } 98\%, \text{ determined by HPLC (Daicel Chiralpak AS-H, hexane/isopropanol = 90/10, flow rate 0.8 \text{ mL/min, } \text{T} = 25 \text{ °C}, 230 \text{ nm}): \text{t}_{\text{R}} = 32.496 \text{ min (minor)}, \text{t}_{\text{R}} = 44.993 \text{ min (major)}.$



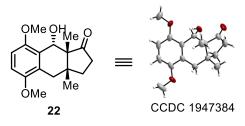
20 (81.7 mg, d.r. = 5:1) was prepared according to general procedure in 94% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.17$ (20% ethyl acetate-petroleum ether); m.p. 132 - 134 °C; $[\alpha]_{p}^{20}$ +95.9 (c 0.28, DCM); ¹H NMR (400 MHz, CDCl₃) δ 6.33 (d, J = 2.3 Hz, 1H), 6.29 (d,

J = 2.4 Hz, 1H), 4.82 (d, J = 2.8 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 2.92 (d, J = 16.8 Hz, 1H), 2.64 (d, J = 16.8 Hz, 1H), 2.58 (d, J = 3.6 Hz, 1H), 2.47 – 2.34 (m, 1H), 2.32 – 2.14 (m, 3H), 0.95 (s, 3H), 0.92 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 221.8, 160.2, 158.7, 137.4, 117.3, 104.4, 96.5, 69.4, 55.4, 55.3, 54.3, 40.1, 39.4, 37.3, 32.6, 25.9, 16.6 ppm; IR v_{max} 2306, 1735, 1305, 1267, 1122, 744 cm⁻¹; HRMS–ESI (m/z): [M+Na]⁺ calcd for C₁₇H₂₂O₄Na, 313.1410; found, 313.1408; Enantiomeric excess: 97%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 29.535 min (minor), t_R = 60.764 min (major).



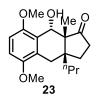
21 (61.5 mg) was prepared according to general procedure in 64% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.11$ (20% ethyl acetate-petroleum ether); m.p. 128 - 130 °C; $[\alpha]_{D}^{20}$ +85.4 (c 1.13, DCM); ¹H NMR (400 MHz, CDCl₃) δ 6.40 (s, 1H), 4.84 (d, *J* = 3.4 Hz, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 3.77 (s, 3H), 3.00 (d, *J* = 17.2 Hz, 1H), 2.61 (d, *J* = 17.2 Hz, 1H), 2.61 (d, *J* = 3.5 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 3H), 3.00 (d, *J* = 17.2 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 3H), 3.00 (d, *J* = 17.2 Hz, 1H), 2.61 (d, *J* = 17.2 Hz, 1H), 2.61 (d, *J* = 3.5 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 3H), 3.00 (s, 3H), 3.0

1H), 2.44 – 2.34 (m, 1H), 2.32 – 2.10 (m, 2H), 1.65 – 1.57 (m, 1H), 0.96 (s, 3H), 0.90 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 222.0, 154.1, 152.5, 140.2, 130.4, 117.1, 94.6, 69.5, 60.4, 55.9, 55.7, 54.0, 39.8, 37.3, 32.9, 32.7, 26.1, 16.7 ppm; IR v_{max} 3055, 1734, 1492, 1236, 1074, 738 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₁₈H₂₄O₅Na, 343.1516; found, 343.1510; Enantiomeric excess: 92%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 13.698 min (major), t_R = 19.137 min (minor).



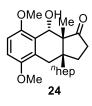
22 (69.1 mg) was prepared according to general procedure in 79% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.18$ (20% ethyl acetate-petroleum ether); m.p. 147 – 149 °C; $[\alpha]_D^{20}$ +75.5 (c 0.55, DCM); and it was recrystallized from ethyl acetate /hexane (V/V = 1/5) at 25 °C, to obtain colorless crystals, CCDC (1947384). ¹H NMR (500 MHz, CDCl₃) δ 6.74 (d, *J*

= 8.8 Hz, 1H), 6.69 (d, J = 8.8 Hz, 1H), 4.81 (d, J = 3.6 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 2.95 (d, J = 18.2 Hz, 1H), 2.88 (d, J = 3.6 Hz, 1H), 2.47 (d, J = 18.2 Hz, 1H), 2.41 – 2.33 (m, 1H), 2.27 – 2.15 (m, 2H), 1.60 – 1.52 (m, 1H), 0.99 (s, 3H), 0.93 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 221.8, 151.6, 151.1, 125.5, 124.8, 109.0, 107.2, 69.7, 55.7, 55.5, 53.4, 39.0, 37.1, 32.3, 32.2, 26.2, 16.0 ppm; IR ν_{max} 3053, 1735, 1267, 1180, 1139, 740 cm⁻¹; HRMS–EI (m/z): [M]⁺ calcd for C₁₇H₂₂O₄, 290.1518; found, 290.1514; Enantiomeric excess: 95%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 10.883 min (major), t_R = 17.052 min (minor).



23 (78.4 mg) was prepared according to general procedure in 82% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.18$ (20% ethyl acetate-petroleum ether); m.p. 110 – 112 °C; $[\alpha]_D^{20}$ +73.9 (c 0.68, DCM); ¹H NMR (500 MHz, CDCl₃) δ 6.74 (d, *J* = 8.8 Hz, 1H), 6.68 (d, *J* = 8.8 Hz, 1H), 4.80 (d, *J* = 3.3 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.02 (d, *J* = 18.2 Hz, 1H), 3.01 (s, 1H), 2.45 (d, *J* = 18.2 Hz, 1H), 2.38 – 2.29 (m, 1H),

2.20 – 2.10 (m, 1H), 2.09 – 2.00 (m, 1H), 1.85 – 1.77 (m, 1H), 1.52 – 1.35 (m, 2H), 1.27 – 1.09 (m, 2H), 0.95 (s, 3H), 0.92 (t, J = 7.2 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 222.2, 151.6, 151.2, 125.5, 124.8, 108.9, 107.3, 70.0, 55.62, 55.56, 54.3, 41.8, 39.8, 36.7, 29.6, 27.0, 16.8, 15.7, 15.0 ppm; IR v_{max} 3061, 1735, 1267, 1171, 1060, 742 cm⁻¹; HRMS–EI (*m/z*): [M]⁺ calcd for C₁₉H₂₆O₄, 318.1831; found, 318.1834; Enantiomeric excess: 93%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 11.074 min (major), t_R = 14.873 min (minor).



24 (95.5 mg) was prepared according to general procedure in 85% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.29$ (20% ethyl acetate-petroleum ether); m.p. 114 – 116 °C; $[\alpha]_D^{20}$ +58.6 (c 0.40, DCM); ¹H NMR (500 MHz, CDCl₃) δ 6.74 (d, *J* = 8.8 Hz, 1H), 6.69 (d, *J* = 8.8 Hz, 1H), 4.80 (d, *J* = 2.7 Hz, 1H),

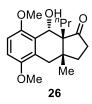
3.81 (s, 3H), 3.80 (s, 3H), 3.00 (d, J = 18.2 Hz, 1H), 2.96 (d, J = 3.6 Hz, 1H), 2.41 (d, J = 18.2 Hz, 1H), 2.37 - 2.30 (m, 1H), 2.14 (m, 1H), 2.09 - 2.00 (m, 1H), 1.85 - 1.77 (m, 1H), 1.48 - 1.23 (m, 10H), 1.21 - 1.08 (m, 2H), 0.95 (s, 3H), 0.89 (t, J = 6.9 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 222.2, 151.6, 151.2, 125.5, 124.8, 108.9, 107.3, 70.0, 55.61, 55.56, 54.4, 41.8, 37.3, 36.8, 31.9, 30.5, 29.5, 29.3, 27.0, 23.6, 22.6, 15.7, 14.1 ppm; IR v_{max} 3062, 1735, 1267, 1171, 1139, 740 cm⁻¹; HRMS-ESI (*m*/*z*): [M+Na]⁺ calcd for C₂₃H₃₄O₄Na, 397.2349; found, 397.2344; Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 8.896 min (major), t_R = 10.430 min (minor).



25 (94.5 mg) was prepared according to general procedure in 86% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.21$ (20% ethyl acetate-petroleum ether); m.p. 184 – 186 °C; $[\alpha]_D^{20}$ +70.7 (c 0.58, DCM); ¹H NMR (500 MHz, CDCl₃) δ 7.38 – 7.30 (m, 2H), 7.31 – 7.25 (m, 1H), 7.23 – 7.17 (m, 2H), 6.74 (d, *J*

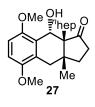
 $= 8.8 \text{ Hz}, 1\text{H}, 6.70 \text{ (d, } J = 8.8 \text{ Hz}, 1\text{H}), 4.87 \text{ (d, } J = 3.8 \text{ Hz}, 1\text{H}), 3.82 \text{ (s, } 3\text{H}), 3.79 \text{ (s, } 3\text{H}), 3.13 \text{ (d, } J = 3.8 \text{ Hz}, 1\text{H}), 2.88 \text{ (d, } J = 18.0 \text{ Hz}, 1\text{H}), 2.64 \text{ (d, } J = 18.0 \text{ Hz}, 1\text{H}), 2.57 \text{ (d, } J = 12.7 \text{ Hz}, 1\text{H}), 2.48 - 2.28 \text{ (m, } 3\text{H}), 1.94 - 1.83 \text{ (m, } 1\text{H}), 1.77 - 1.65 \text{ (m, } 1\text{H}), 1.12 \text{ (s, } 3\text{H}) \text{ ppm}; {}^{13}\text{C} \text{ NMR} (125 \text{ MHz}, \text{CDCl}_3) \delta 221.4, 151.5, 151.2, 137.8, 130.4 (2C), 128.1 (2C), 126.4, 125.4, 124.3, 109.0, 107.4, 70.3, 55.62, 55.59, 54.7, 43.2, 42.6, 36.8, 29.3, 26.5, 15.8 \text{ ppm}; \text{IR } v_{\text{max}} 3651, 1735, 1479, 1265, 1012, 742 \text{ cm}^{-1}; \text{HRMS-EI } (m/z): [M]^+ \text{ calcd for } C_{23}\text{H}_26\text{O}_4, 366.1831; \text{ found}, 366.1826; \text{Enantiomeric excess: } 95\%, \text{ determined by HPLC} \text{ (Daicel } 1.25\%,$

Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 11.349$ min (major), $t_R = 15.958$ min (minor).



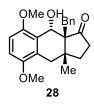
26 (74.4 mg) was prepared according to general procedure in 78% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.26$ (20% ethyl acetate-petroleum ether); m.p. 124 – 126 °C; $[\alpha]_D^{20}$ +72.2 (c 0.22, DCM); ¹H NMR (500 MHz, CDCl₃) δ 6.73 (d, J = 8.8 Hz, 1H), 6.69 (d, J = 8.8 Hz, 1H), 4.94 (s, 1H), 3.81 (s,

3H), 3.81 (s, 3H), 3.01 (d, J = 3.4 Hz, 1H), 2.93 (d, J = 18.4 Hz, 1H), 2.55 (d, J = 18.4 Hz, 1H), 2.38 – 2.28 (m, 1H), 2.27 – 2.07 (m, 2H), 1.77 (td, J = 13.9, 3.9 Hz, 1H), 1.54 – 1.47 (m, 1H), 1.36 (td, J = 13.9, 3.9 Hz, 1H), 1.18 – 1.09 (m, 1H), 1.06 (s, 3H), 0.99 – 0.88 (m, 1H), 0.78 (t, J = 7.2 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 221.6, 151.1, 150.9, 126.8, 124.8, 108.6, 107.1, 68.0, 55.8, 55.54, 55.48, 39.4, 36.8, 35.3, 34.3, 33.1, 25.6, 16.6, 15.2 ppm; IR v_{max} 3053, 1735, 1282, 1267, 1139, 742 cm⁻¹; HRMS–EI (*m*/*z*): [M]⁺ calcd for C₁₉H₂₆O₄, 318.1831; found, 366.1826; Enantiomeric excess: 90%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 11.404 min (major), t_R = 14.586 min (minor).



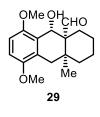
27 (84.9 mg) was prepared according to general procedure in 76% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.32$ (20% ethyl acetate-petroleum ether); m.p. 100 – 102 °C; $[\alpha]_D^{20}$ +67.1 (c 0.31, DCM); ¹H NMR (500 MHz, CDCl₃) δ 6.74 (d, *J* = 8.8 Hz, 1H), 6.69 (d, *J* = 8.8 Hz, 1H), 4.93 (s, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 3.04 (d, *J* = 3.4 Hz, 1H), 2.93 (d, *J* = 18.4 Hz, 1H), 2.55 (d, *J* = 18.4 Hz, 1H), 2.37 – 2.28 (m,

1H), 2.26 – 2.07 (m, 2H), 1.83 – 1.73 (m, 1H), 1.50 (m, 1H), 1.43 – 1.35 (m, 1H), 1.26 – 1.09 (m, 9H), 1.06 (s, 3H), 1.00 – 0.87 (m, 1H), 0.82 (t, J = 7.2 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 221.7, 151.1, 150.9, 126.9, 124.9, 108.7, 107.1, 68.1, 55.7, 55.6, 55.5, 39.5, 36.8, 34.2, 33.0, 32.9, 31.8, 30.6, 28.7, 25.5, 22.9, 22.5, 14.0 ppm; IR v_{max} 3053, 1735, 1282, 1267, 1139, 742 cm⁻¹; HRMS–ESI (m/z): [M+Na]⁺ calcd for C₂₃H₃₄O₄Na, 397.2349; found, 397.2345; Enantiomeric excess: 93%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 10.097 min (major), t_R = 11.136 min (minor).



28 (93.7 mg) was prepared according to general procedure in 85% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.26$ (20% ethyl acetate-petroleum ether); m.p. 129 - 131 °C; $[\alpha]_D^{20}$ +101 (c 0.44, DCM); ¹H NMR (400 MHz, CDCl₃) δ 7.12 – 7.07 (m, 2H), 7.05 – 6.99 (m, 3H), 6.64 (d, J = 8.8 Hz, 1H), 6.60 (d, J = 8.8 Hz, 1H), 5.11 (d, J = 3.4 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.11 (d, J = 14.3 Hz, 1H), 2.82 (d, J = 8.8 Hz, 1H), 2.82 (d, J = 8.8 Hz, 1H), 5.11 (d, J = 3.4 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.11 (d, J = 14.3 Hz, 1H), 2.82 (d, J = 8.8 Hz, 1H), 5.82 (d, J = 8.8 Hz, 1H), 5.83 (d, J = 8.8 Hz,

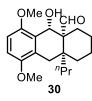
18.5 Hz, 1H), 2.76 (d, J = 3.9 Hz, 1H), 2.55 (d, J = 14.3 Hz, 1H), 2.44 – 2.18 (m, 4H), 1.56 – 1.49 (m, 1H), 1.20 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 220.9, 151.12, 151.06, 137.6, 130.5 (2C), 127.5 (2C), 126.0, 125.8, 124.9, 109.0, 107.3, 66.5, 57.0, 55.72, 55.66, 39.9, 36.99, 36.98, 33.2, 32.9, 25.9 ppm; IR v_{max} 3055, 1421, 1267, 1178, 1139, 742 cm⁻¹; HRMS–ESI (*m/z*): [M+Na]⁺ calcd for C₂₃H₂₆O₄Na, 389.1723; found, 389.1718; Enantiomeric excess: 89%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 10.963 min (major), t_R = 18.918 min (minor).



29 (86 mg) was prepared according to general procedure in 94% yield. Ligand **L10** (0.24 mmol, 0.8 equiv.) was used. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.32$ (20% ethyl acetate-petroleum ether); m.p. 85 – 87 °C; $[\alpha]_D^{20}$ +23.3 (c 0.88, DCM); ¹H NMR (400 MHz, CDCl₃) δ 9.84 (s, 1H), 6.75 (d, J = 8.9 Hz, 1H), 6.72 (d, J = 8.9 Hz, 1H), 5.13 (s, 1H), 3.86 (s, 3H), 3.80 (s, 3H), 3.63 (s, 1H), 2.76 (d, J = 8.9 Hz, 1H), 5.16 (s, 20% ethyl acetate-petroleum ether) as a solution of the solid is the solid is

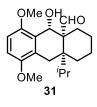
18.3 Hz, 1H), 2.55 (d, *J* = 18.3 Hz, 1H), 1.88 (dt, *J* = 17.2, 5.7 Hz, 1H), 1.66 (s, 1H), 1.57 – 1.40 (m, 6H), 1.16 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 205.8, 151.7, 151.3, 125.4, 124.8, 108.7, 107.3, 68.3, 55.6, 55.5, 53.9, 35.0, 34.7, 33.7, 24.1, 20.8, 20.6

ppm; IR v_{max} 1373, 1282, 1267, 1180, 1141, 800, 744, 707 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₁₈H₂₄O₄Na, 327.1567; found, 327.1556; Enantiomeric excess: 93%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 13.622 min (major), t_R = 22.610 min (minor).



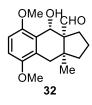
30 (94 mg) was prepared according to general procedure in 94% yield. Ligand **L10** (0.24 mmol, 0.8 equiv.) was used. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.35$ (20% ethyl acetate-petroleum ether); m.p. 116 – 118 °C; $[\alpha]_D^{20}$ +35.6 (c 1.44, DCM); ¹H NMR (400 MHz, CDCl₃) δ 9.81 (s, 1H), 6.75 (d, J = 8.8 Hz, 1H), 6.72 (d, J = 8.8 Hz, 1H), 5.21 (s, 1H), 3.96 (s, 1H), 3.86 (s, 3H), 3.80 (s, 3H), 2.80 (d,

J = 18.4 Hz, 1H), 2.63 (d, J = 18.4 Hz, 1H), 2.05 – 1.86 (m, 2H), 1.73 (d, J = 14.6 Hz, 1H), 1.66 – 1.45 (m, 5H), 1.37 – 1.24 (m, 3H), 1.14 (s, 1H), 0.89 (t, J = 7.2 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 205.7, 151.8, 151.4, 125.4, 124.9, 108.7, 107.4, 67.6, 55.6 (dd, J = 12.1, 5.2 Hz, 2C), 54.7, 36.9, 36.8, 31.7, 29.7, 22.5, 20.5, 20.3, 15.8, 14.9 ppm; IR v_{max} 2954, 1724, 1479, 1255, 1082, 800, 742, 705 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₂₀H₂₈O₄Na, 355.1880; found, 355.1866; Enantiomeric excess: 93%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 10.734 min (major), t_R = 12.232 min (minor).



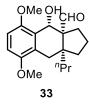
31 (56 mg) was prepared according to general procedure in 56% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a colorless oil: $R_f = 0.3$ (20% ethyl acetate-petroleum ether); $[\alpha]_D^{20}$ +61.3 (c 0.90, DCM); ¹H NMR (500 MHz, CDCl₃) δ 10.02 (s, 1H), 6.74 (d, J = 8.9 Hz, 1H), 6.71 (d, J = 8.9 Hz, 1H), 5.27 (s, 1H), 4.02 (s, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 2.94 (d, J = 18.4 Hz, 1H), 2.59 (d, J = 18.4 Hz, 1H), 2.41 (hept, J = 6.8 Hz,

1H), 1.97 - 1.86 (m, 1H), 1.86 - 1.76 (m, 1H), 1.70 - 1.60 (m, 3H), 1.56 - 1.49 (m, 2H), 1.48 - 1.35 (m, 1H), 0.92 (d, J = 6.8 Hz, 3H), 0.87 (d, J = 6.8 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 207.2, 151.7, 151.5, 125.1, 125.0, 108.6, 107.4, 67.9, 55.6, 55.5, 54.4, 40.5, 29.0, 28.8, 26.2, 20.0, 19.4, 19.2(2C), 18.2 ppm; IR v_{max} 1396, 1267, 1051, 904, 746, 698, 651 cm⁻¹; HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₂₀H₂₈O₄Na, 355.1880; found, 355.1867; Enantiomeric excess: 94%, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 85/15, flow rate 0.8 mL/min, T = 25 °C, 230 nm): tR = 14.467min (major), tR = 18.503 min (minor).



32 (41.4 mg) was prepared according to general procedure in 48% yield. Ligand **L10** (0.24 mmol, 0.8 equiv.) was used. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a yellow oil: $R_f = 0.42$ (20% ethyl acetate-petroleum ether); $[\alpha]_{D}^{20}$ +8.4 (c 0.12, DCM); ¹H NMR (400 MHz, CDCl₃) δ 9.83 (s, 1H), 6.77 (d, *J* = 8.9 Hz, 1H), 6.72 (d, *J* = 8.9 Hz, 1H), 5.17 (d, *J* = 2.1 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 2.80 (d, *J* = 16.6 Hz, 1H), 2.72 (d, *J*

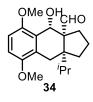
= 16.6 Hz, 1H), 2.19 – 2.08 (m, 1H), 1.71 – 1.57 (m, 3H), 1.53 – 1.37 (m, 2H), 1.22 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 206.2, 151.38, 151.33, 126.5, 125.8, 109.9, 108.3, 68.4, 61.2, 55.98, 55.96, 43.7, 41.1, 34.3, 31.3, 25.0, 21.5 ppm; IR v_{max} 2985, 1697, 1280, 1267, 742 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₁₇H₂₂O₄Na, 313.1410; found, 313.1406; Enantiomeric excess: 93%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 10.239 min (major), t_R = 11.706 min (minor).



33 (88 mg) was prepared according to general procedure in 92% yield. Ligand **L10** (0.24 mmol, 0.8 equiv.) was used. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a colorless oil: $R_f = 0.35$ (20% ethyl acetate-petroleum ether); $[\alpha]_{D}^{20}$ +14.3 (c 0.96, DCM); ¹H NMR (400 MHz, CDCl₃) δ 9.83 (s, 1H), 6.77 (d, *J* = 8.9 Hz, 1H), 6.71 (d, *J* = 8.9 Hz, 1H), 5.20 (d, *J* = 1.8 Hz, 1H), 3.84 (d, *J* = 1.8 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 2.94

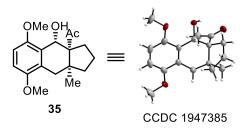
 $(d, J = 16.4 \text{ Hz}, 1\text{H}), 2.62 (d, J = 16.4 \text{ Hz}, 1\text{H}), 2.85 - 1.99 (m, 1\text{H}), 1.83 - 1.73 (m, 1\text{H}), 1.70 - 1.58 (m, 2\text{H}), 1.57 - 1.52 (m, 1\text{H}), 1.51 - 1.45 (m, 3\text{H}), 1.44 - 1.28 (m, 2\text{H}), 0.88 (t, J = 6.5 \text{ Hz}, 3\text{H}) \text{ ppm}; {}^{13}\text{C} \text{ NMR} (100 \text{ MHz}, \text{CDCl}_3) \delta 206.7, 151.5, 151.4, 126.9, 1.51 - 1.45 (m, 2\text{H}), 1.44 - 1.28 (m, 2\text{H}), 0.88 (t, J = 6.5 \text{ Hz}, 3\text{H}) \text{ ppm}; {}^{13}\text{C} \text{ NMR} (100 \text{ MHz}, \text{CDCl}_3) \delta 206.7, 151.5, 151.4, 126.9, 1.51 - 1.5$

125.9, 110.2, 108.5, 68.2 (d, J = 3.0 Hz), 62.3, 56.2 (t, J = 3.0 Hz, 2C), 48.1, 40.1, 38.6, 31.6, 30.7, 22.1, 18.5, 15.0 ppm; IR v_{max} 2956, 1714, 1489, 1265, 1085, 742 cm⁻¹; HRMS–ESI (m/z): [M+Na]⁺ calcd for C₁₉H₂₆O₄Na, 341.1723; found, 341.1714; Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 9.717 min (minor), t_R = 13.171 min (major).



34 (75 mg) was prepared according to general procedure A from **7** (0.3 mmol) and **16** in 79% yield. Ligand **L10** (0.24 mmol, 0.8 equiv.) was used. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a yellow oil: $R_f = 0.55$ (20% ethyl acetate-petroleum ether); $[\alpha]_D^{20}$ +3.79 (c 1.52, DCM); ¹H NMR (500 MHz, CDCl₃) δ 9.95 (s, 1H), 6.77 (d, J = 8.9 Hz, 1H), 6.70 (d, J = 8.8 Hz, 1H), 5.34 (s, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.53 (s, 1H), 2.95 (d, J = 8.9 Hz, 1H), 6.70 (d, J = 8.8 Hz, 1H), 5.34 (s, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.53 (s, 1H), 2.95 (d, J = 8.9 Hz, 1H), 5.34 (s, 1H), 5.34 (s, 1H), 5.34 (s, 20% s) (s, 20\% s) (s, 20\% s

15.5 Hz, 1H), 2.65 (d, J = 15.5 Hz, 1H), 2.14 (hept, J = 6.8 Hz, 1H), 1.94 (dt, J = 13.7, 7.4 Hz, 1H), 1.89 – 1.83 (m, 1H), 1.65 – 1.57 (m, 1H), 1.56 – 1.47 (m, 1H), 1.35 – 1.27 (m, 1H), 1.16 – 1.07 (m, 1H), 1.02 (d, J = 6.7 Hz, 3H), 0.95 (d, J = 6.7 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 207.0, 151.12, 151.09, 128.6, 125.9, 110.6, 108.4, 66.8, 62.1, 56.2, 56.1, 53.1, 41.9, 34.6, 32.7, 26.5, 23.4, 19.6, 19.5 ppm; IR v_{max} 2956, 1265, 1207, 1151, 1068, 1031, 740, 704 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₁₉H₂₆O₄Na, 341.1723; found, 341.1709; Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 92/8, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 20.294 min (major), t_R = 23.006 min (minor).



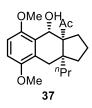
35 (72.1 mg) was prepared according to general procedure in 79% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a yellow solid: $R_f = 0.26$ (20% ethyl acetate-petroleum ether); m.p. 76 - 78 °C; $[\alpha]_D^{20}$ +47.3 (c 0.50, DCM); and it was recrystallized from ethyl acetate /hexane (V/V = 1/4) at 25 °C, to obtain colorless crystals, CCDC (1947385). ¹H NMR (500 MHz, CDCl₃) δ 6.75 (d, *J*

= 8.9 Hz, 1H), 6.73 (d, J = 8.8 Hz, 1H), 4.98 (s, 1H), 4.36 (d, J = 1.8 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 2.81 (d, J = 18.1 Hz, 1H), 2.71 (d, J = 18.1 Hz, 1H), 2.55 – 2.45 (m, 1H), 2.14 (s, 3H), 2.04 – 1.94 (m, 1H), 1.83 – 1.72 (m, 1H), 1.71 – 1.56 (m, 3H), 1.05 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 210.8, 151.6, 151.2, 126.3, 125.7, 108.6, 107.7, 70.6, 63.2, 55.61, 55.57, 42.8, 38.9, 33.3, 31.9, 29.7, 24.7, 18.9 ppm; IR v_{max} 3053, 1697, 1421, 1267, 742 cm⁻¹; HRMS–EI (m/z): [M]⁺ calcd for C₁₈H₂₄O₄, 304.1675; found, 304.1679; Enantiomeric excess: 88%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 11.803 min (major), t_R = 14.162 min (minor).



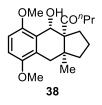
36 (77 mg, d.r. = 16 :1) was prepared according to general procedure in 85% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.4$ (20% ethyl acetate-petroleum ether); m.p. 100 - 102 °C; $[\alpha]_{D}^{20}$ +98.4 (c 0.30, DCM); ¹H NMR (500 MHz, CDCl₃) δ 7.18 (t, J = 7.9 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 6.74 (d,

J = 8.5 Hz, 1H), 5.10 (s, 1H), 4.28 (d, J = 1.9 Hz, 1H), 3.86 (s, 3H), 3.06 (d, J = 16.6 Hz, 1H), 2.66 (d, J = 16.6 Hz, 1H), 2.38 – 2.29 (m, 1H), 2.18 (s, 3H), 1.84 (ddd, J = 11.9, 8.6, 5.4 Hz, 1H), 1.76 (ddd, J = 13.5, 9.4, 3.6 Hz, 1H), 1.72 – 1.60 (m, 1H), 1.53 – 1.43 (m, 3H), 1.39 – 1.17 (m, 3H), 0.90 (t, J = 6.9 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 212.7, 157.3, 137.9, 128.3, 124.8, 121.5, 108.1, 70.2, 64.6, 55.4, 47.6, 39.3, 37.6, 35.9, 32.6, 30.2, 20.4, 17.6, 15.0 ppm; IR v_{max} 2956, 1591, 1471, 1375, 1280, 1180, 744, 744 cm⁻¹; HRMS–ESI (m/z): [M+Na]⁺ calcd for C₁₉H₂₆O₃Na, 325.1774; found, 325.1762; Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 8.839 min (minor), t_R = 11.127 min (major).



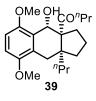
37 (74.3 mg) was prepared according to general procedure in 75% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.36$ (20% ethyl acetate-petroleum ether); m.p. 94 - 96 °C; $[\alpha]_D^{20}$ +43.7 (c 0.36, DCM); ¹H NMR (500 MHz, CDCl₃) δ 6.73 (d, J = 9.0 Hz, 1H), 6.70 (d, J = 9.0 Hz, 1H), 4.99 (s, 1H), 4.31 (d, J = 1.9

Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 2.79 (d, J = 18.0 Hz, 1H), 2.69 (d, J = 18.0 Hz, 1H), 2.49 – 2.38 (m, 1H), 2.13 (s, 3H), 1.94 – 1.79 (m, 2H), 1.75 – 1.64 (m, 1H), 1.61 – 1.56 (m, 1H), 1.51 – 1.42 (m, 3H), 1.38 – 1.30 (m, 1H), 1.19 – 1.09 (m, 1H), 0.90 (t, J = 6.8 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 211.3, 151.5, 151.3, 126.1, 125.9, 108.7, 107.6, 70.6, 64.1, 55.7, 55.6, 46.2, 38.5, 34.6, 31.9, 30.3, 29.9, 19.2, 17.3, 15.0 ppm; IR v_{max} 3055, 1697, 1241, 1267, 1105, 804 cm⁻¹; HRMS–EI (*m*/*z*): [M]⁺ calcd for C₂₀H₂₈O₄, 332.1988; found, 332.1982; Enantiomeric excess: 94%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 9.967 min (minor), t_R = 12.793 min (major).



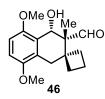
38 (72.1 mg) was prepared according to general procedure in 72% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a yellow solid: $R_f = 0.52$ (20% ethyl acetate-petroleum ether); m.p. 79 - 81 °C; $[\alpha]_D^{20}$ +55.4 (c 0.14, DCM); ¹H NMR (500 MHz, CDCl₃) δ 6.72 (d, J = 8.9 Hz, 1H), 6.69 (d, J = 8.9 Hz, 1H), 4.93 (s, 1H), 4.32 (d, J = 1.8 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 2.74 (d, J = 2.1 Hz, 2H), 2.53 - 2.44 (m, 2H), 2.44 - 2.35

(m, 1H), 2.01 (m, 1H), 1.82 - 1.71 (m, 1H), 1.70 - 1.63 (m, 1H), 1.58 - 1.53 (m, 3H), 1.23 (d, J = 17.6 Hz, 1H), 1.02 (s, 3H), 0.86 (t, J = 7.4 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 213.1, 151.5, 151.3, 126.3, 126.1, 108.6, 107.6, 71.0, 62.6, 55.7, 55.6, 43.9, 43.1, 38.7, 33.4, 31.8, 24.7, 19.1, 17.0, 13.9 ppm; IR v_{max} 3736, 3055, 1697, 1421, 1267, 1107 cm⁻¹; HRMS–EI (*m/z*): [M]⁺ calcd for C₂₀H₂₈O₄, 332.1988; found, 332.1990; Enantiomeric excess: 94%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 8.652 min (minor), t_R = 11.045 min (major).



39 (52 mg) was prepared according to general procedure in 46% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a colorless oil: $R_f = 0.55$ (20% ethyl acetate-petroleum ether); $[\alpha]_D^{20}$ +48.5 (c 0.20, DCM); ¹H NMR (500 MHz, CDCl₃) δ 6.71 (d, J = 8.9 Hz, 1H), 6.68 (d, J = 8.9 Hz, 1H), 4.97 (d, J = 1.7 Hz, 1H), 4.30 (d, J = 1.8 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 2.76 (d, J = 18.0 Hz, 1H), 2.71 (d, J = 18.0 Hz, 1H), 2.53 – 2.45

(m, 1H), 2.41 (ddt, J = 11.1, 8.4, 5.7 Hz, 2H), 1.98 – 1.90 (m, 1H), 1.86 – 1.77 (m, 1H), 1.74 – 1.66 (m, 1H), 1.64 – 1.54 (m, 3H), 1.48 – 1.39 (m, 3H), 1.38 – 1.30 (m, 1H), 1.17 – 1.09 (m, 1H), 0.89 (t, J = 6.9 Hz, 3H), 0.86 (t, J = 7.4 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 213.6, 151.4, 151.3, 126.04, 125.99, 108.6, 107.4, 70.8, 63.4, 55.6, 55.5, 46.4, 44.0, 38.3, 34.2, 31.7, 30.2, 19.3, 17.2, 17.0, 15.0, 13.8 ppm; IR v_{max} 1701, 1465, 1371, 1180, 1141, 744, 701 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₂₂H₃₂O₄Na, 383.2193; found, 383.2178; Enantiomeric excess: 88%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 85/15, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 12.014 min (minor), t_R = 13.248 min (major).



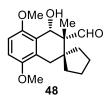
46 (48 mg, d.r. = 9:1) was prepared according to general procedure in 55% yield. Ligand **L10** (0.24 mmol, 0.8 equiv.) was used. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.35$ (20% ethyl acetate-petroleum ether); m.p. 100 - 102 °C; $[\alpha]_D^{20}$ +16.6 (c 0.32, DCM); ¹H NMR (500 MHz, CDCl₃) δ 10.07

(s, 1H), 6.74 (d, J = 8.9 Hz, 1H), 6.72 (d, J = 9.1 Hz, 1H), 4.88 (d, J = 1.8 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.54 (d, J = 2.4 Hz, 1H), 2.99 (d, J = 18.0 Hz, 1H), 2.85 (d, J = 18.0 Hz, 1H), 2.64 (dt, J = 11.9, 9.1 Hz, 1H), 2.26 (dt, J = 11.9, 9.1 Hz, 1H), 2.26 (dt, J = 11.9, 9.1 Hz, 1H), 2.11 – 2.01 (m, 1H), 1.93 – 1.83 (m, 1H), 1.71 – 1.63 (m, 1H), 1.61 – 1.53 (m, 1H), 1.14 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 207.4, 151.63, 151.59, 126.5, 124.9, 108.8, 107.8, 70.7, 55.6, 55.5, 52.2, 40.9, 34.5, 29.3, 28.5, 15.6, 13.8 ppm; IR v_{max}.2966, 1722, 1456, 1267, 744, 704 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₁₇H₂₂O₄Na, 313.1410; found, 313.1407; Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 85/15, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 15.752 min (major), t_R = 21.974 min (minor).



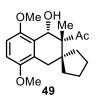
47 (68 mg, d.r. = 6:1) was prepared according to general procedure in 75% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.2$ (20% ethyl acetate-petroleum ether); m.p. 152 - 154 °C; $[\alpha]_{2^{\circ}}^{2^{\circ}}$ +12.9 (c 0.32, DCM); ¹H NMR (500 MHz, CDCl₃) δ 6.73 (d, J = 9.0 Hz 1H), 6.71 (d, J = 9.0 Hz 1H), 4.94 (d, J= 2.4 Hz, 1H), 3.84 (s 3H), 3.81 (s, 3H), 3.32 (d, J = 3.5 Hz, 1H), 2.97 (d, J = 18.1 Hz, 1H), 2.73 (d, J = 18.1 Hz, 1Hz, 1H), 2. 1H), 2.70 (ddd, J = 11.9, 9.9, 8.1 Hz, 1H), 2.56 (ddd, J = 11.9, 9.9, 8.1 Hz, 1H), 2.25 (s, 3H), 2.09 – 1.94 (m, 2H), 1.54 – 1.45 (m, 2H), 1.54 – 1.54 (m, 2H), 1.54

2H), 1.18 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) & 211.5, 151.6, 151.5, 126.8, 125.2, 108.7, 107.8, 70.8, 55.62, 55.58, 54.8, 40.6, 35.4, 29.3, 29.0, 28.1, 16.5, 15.3 ppm; IR v_{max} 2958, 1722, 1469, 1265, 1085, 1014, 746 cm⁻¹; HRMS–ESI (*m/z*): [M+Na]⁺ calcd for C18H24O4Na, 327.1567; found, 327.1563; Enantiomeric excess: 89%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 95/5, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 30.903 min (major), t_R = 32.791 min (minor).



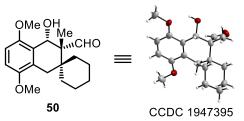
48 (55 mg) was prepared according to general procedure in 60% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetatepetroleum ether) as a colorless oil: $R_f = 0.4$ (20% ethyl acetate-petroleum ether); $[\alpha]_{D}^{20} + 19.0$ (c 0.20, DCM); ¹H NMR (400 MHz, CDCl₃) δ 9.91 (s, 1H), 6.73 (s, 2H), 4.88 (d, J = 2.1 Hz, 1H), 3.91 (d, J = 2.1 Hz, 1H), 3.85 (s, 3H), 3.78 (s, 3H), 2.66 (d, J = 18.1 Hz, 1H), 2.57 (d, J = 18.1 Hz, 1H), 2.06 (ddd, J = 13.3, 8.3, 6.8 Hz,

1H), 1.75 – 1.56 (m, 5H), 1.37 – 1.25 (m, 2H), 1.20 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 207.4, 151.7, 151.5, 126.8, 125.8, 108.7, 107.8, 72.1, 55.6, 55.52, 55.49, 53.3, 45.9, 34.7, 34.4, 25.6, 24.8, 14.3 ppm; IR v_{max} 1701, 1371, 1282, 1267, 1180, 1141, 902, 844, 744, 707 cm⁻¹; HRMS–ESI (m/z): [M+Na]⁺ calcd for C₁₈H₂₄O₄Na, 327.1567; found, 327.1561; Enantiomeric excess: 92%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 12.605$ min (major), $t_R = 14.471$ min (minor).



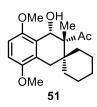
49 (90 mg, d.r. = 10:1) was prepared according to general procedure in 94% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.3$ (20% ethyl acetate-petroleum ether); m.p. 132 – 134 °C; $[\alpha]_{2^{D}}^{D}$ +12.9 (c 0.32, DCM); ¹H NMR (400 MHz, CDCl₃) δ 6.71 (s, 2H), 5.00 (d, J = 3.2 Hz, 1H), 3.86 (s, 3H), 3.78 (s, 3H), 3.24 (d, J = 3.2 Hz, 1H), 2.70 (d, J = 18.1 Hz, 1H), 2.40 (d, J = 18.1 Hz, 1H), 2.26 (s, 3H), 2.13 - 1.99 (m,

2H), 1.84 – 1.60 (m, 5H), 1.30 – 1.25 (m, 1H), 1.23 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 210.9, 151.7, 151.4, 126.7, 126.3, 108.6, 107.3, 71.6, 55.8, 55.6, 55.5, 45.2, 36.3, 35.6, 34.2, 28.2, 26.0, 25.0, 18.6 ppm; IR v_{max} 2964, 1701, 1371, 1282, 1265, 1180, 1141, 902, 802, 744, 707 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₁₉H₂₆O₄Na, 341.1723; found, 341.1720; Enantiomeric excess: 90%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 95/5, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 28.209$ min (minor), $t_R = 30.850$ min (major).



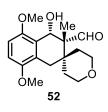
50 (88 mg, d.r. = 10:1) was prepared according to general procedure in 92% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white foam: $R_f = 0.4$ (20% ethyl acetate-petroleum ether); $[\alpha]_D^{20} + 5.71$ (c 0.80, DCM); and it was recrystallized from DCM /hexane (V/V = 1/4) at 25 °C, to obtain colorless crystals, CCDC (1947395). ¹H NMR (400 MHz, CDCl₃) δ 9.84 (s, 1H), 6.76 (d, J =

8.8 Hz, 1H), 6.74 (d, J = 8.8 Hz, 1H), 4.86 (s, 1H), 4.15 (d, J = 1.7 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 3.26 (d, J = 18.5 Hz, 1H), 2.34 (d, J = 18.8 Hz, 1H), 1.70 - 1.63 (m, 2H), 1.54 (dt, J = 10.1, 3.1 Hz, 2H), 1.45 - 1.33 (m, 5H), 1.26 (s, 3H), 1.18 - 1.06 (m, 2H), 1.26 (s, 2H), 1.26 (s, 2H), 1.26 (s, 2H), 1.26 (s, 2H), 1.18 - 1.06 (m, 2H), 1.26 (s, 2H), 1.26 (1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 207.3, 151.7, 151.5, 126.3, 125.3, 108.9, 107.9, 71.7, 55.7, 55.5, 54.9, 37.9, 32.1, 28.8, 27.9, 26.0, 21.1, 21.0, 12.2 ppm; IR v_{max} 2935, 1722, 1479, 1265, 1082, 1024, 744 cm⁻¹; HRMS–ESI (*m/z*): [M+Na]⁺ calcd for C19H26O4Na, 341.1723; found, 341.1720; Enantiomeric excess: 95%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 84/16, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 19.210 min (minor), t_R = 20.349 min (major).



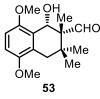
51 (46 mg, d.r. = 5.2:1) was prepared according to general procedure in 46% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.35$ (20% ethyl acetate-petroleum ether); ¹H NMR (500 MHz, CDCl₃) δ 6.73 (d, *J* = 8.9 Hz, 1H), 6.71 (d, *J* = 9.0 Hz, 1H), 4.90 (d, *J* = 1.7 Hz, 1H), 3.99 (d, *J* = 2.2 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 2.99 (d, *J* = 18.3 Hz, 1H), 2.54 (d, *J* = 18.3 Hz, 1H), 2.16 (s, 3H), 1.85 – 1.74 (m, 1H),

1.70 - 1.65 (m, 2H), 1.55 - 1.50 (m, 2H), 1.48 - 1.43 (m, 2H), 1.38 (s, 3H), 1.34 (d, J = 2.7 Hz, 1H), 1.28 - 1.23 (m, 1H), 1.22 - 1.13 (m, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 212.1, 151.42, 151.37, 126.8, 126.0, 108.7, 107.5, 72.6, 57.2, 55.7, 55.5, 37.6, 31.4, 30.7, 29.6, 27.9, 25.9, 21.63, 21.55, 17.6 ppm; IR v_{max}.2937, 1602, 1465, 1265, 1255, 1141, 1093, 742, 705 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₂₀H₂₈O₄Na, 355.1880; found, 355.1873; Enantiomeric excess: 83%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 95/5, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 34.910 min (minor), t_R = 38.588 min (major).



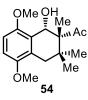
52 (85 mg) was prepared according to general procedure in 89% yield. Ligand **L10** (0.24 mmol, 0.8 equiv.) was used. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.4$ (20% ethyl acetate-petroleum ether); m.p. 82 - 84 °C; $[\alpha]_D^{20}$ +6.61 (c 1.15, DCM); ¹H NMR (400 MHz, CDCl₃) δ 9.91 (s, 1H), 6.76 (s, 2H), 4.87 (d, J = 1.4 Hz, 1H), 4.02 (d, J = 2.0 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 3.78 - 3.59 (m, 4H), 3.24

(d, J = 18.5 Hz, 1H), 2.58 (d, J = 18.4 Hz, 1H), 2.15 (ddd, J = 14.0, 12.6, 5.3 Hz, 1H), 1.89 (ddd, J = 14.0, 12.6, 5.3 Hz, 1H), 1.29 – 1.14 (m, 5H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 206.7, 151.7, 151.4, 126.0, 124.3, 109.0, 108.1, 71.2, 63.3, 62.9, 55.6, 54.0, 35.5, 31.7, 29.7, 27.5, 12.5 ppm; IR v_{max} 1718, 1481, 1390, 1257, 1083, 798, 744, 698, 651 cm⁻¹; HRMS–ESI (*m/z*): [M+Na]⁺ calcd for C₁₈H₂₄O₅Na, 343.1516; found, 343.1512; Enantiomeric excess: 88%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 18.671min (major), t_R = 21.838 min (minor).



53 (47 mg) was prepared according to general procedure in 56% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetatepetroleum ether) as a white solid: $R_f = 0.35$ (20% ethyl acetate-petroleum ether); m.p. 78 – 80 °C; $[\alpha]_D^{20}$ +9.68 (c 0.28, DCM); ¹H NMR (500 MHz, CDCl₃) δ 9.81 (s, 1H), 6.75 (s, 2H), 4.88 (s, 1H), 4.20 (d, *J* = 1.7 Hz, 1H),

 $3.87 (s, 3H), 3.80 (s, 3H), 2.65 (d, J = 18.2 Hz, 1H), 2.56 (d, J = 18.2 Hz, 1H), 1.24 (s, 3H), 1.04 (s, 3H), 0.94 (s, 3H) ppm; {}^{13}C NMR (100 MHz, CDCl₃) <math>\delta$ 207.0, 151.8, 151.4, 126.3, 125.7, 108.8, 108.0, 72.1, 55.62, 55.57, 54.1, 36.2, 35.1, 25.4, 24.3, 13.0 ppm; IR v_{max} 1730, 1602, 1477, 1371, 1280, 1180, 1141, 742, 705 cm⁻¹; HRMS–ESI (*m/z*): [M+Na]⁺ calcd for C₁₆H₂₂O₄Na, 301.1410; found, 301.1401; Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 10.040 min (major), t_R = 14.544 min (minor).



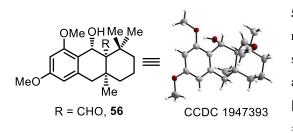
54 (22 mg, d.r. = 10:1) was prepared according to general procedure in 25% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.35$ (20% ethyl acetate-petroleum ether); m.p. 105 – 107 °C; [α] $^{20}_{D}$ +33.6 (c 0.32, DCM); ¹H NMR (400 MHz, CDCl₃) δ 6.72 (s, 2H), 4.95 (d, *J* = 1.6 Hz, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 2.57 (d, *J* = 18.0 Hz, 1H), 2.50 (d, *J* = 18.0 Hz, 1H), 2.20 (s, 3H), 1.31 (s, 3H), 1.11 (s, 3H), 1.07 (s, 3H)

ppm; ¹³C NMR (100 MHz, CDCl₃) δ 211.5, 151.6, 151.2, 126.5, 126.2, 108.7, 107.4, 72.5, 55.9, 55.6, 55.5, 37.3, 34.4, 29.6, 25.6, 25.4, 18.3 ppm; IR v_{max} 2358, 2330, 1274, 1267, 763, 748, 705 cm⁻¹; HRMS–ESI (*m/z*): [M+Na]⁺ calcd for C₁₇H₂₄O₄Na, 315.1567; found, 315.1568; Enantiomeric excess: 89%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): tR = 9.179 min (major), tR = 10.041 min (minor).



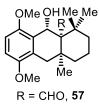
55 (74 mg) was prepared according to general procedure in 82% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetatepetroleum ether) as a white solid: $R_f = 0.25$ (20% ethyl acetate-petroleum ether); m.p. 115 – 117 °C; $[\alpha]_{D}^{20} + 1.40$ (c 0.88, DCM); ¹H NMR (400 MHz, CDCl₃) δ 10.09 (s, 1H), 7.19 (t, J = 7.9 Hz, 1H), 6.74 (d, J = 8.3 Hz, 1H), 6.72 (d, J = 7.9 Hz, 1H), 5.51 (d, J = 3.2 Hz, 1H), 3.91 (s, 3H), 3.29 (d, J = 18.1 Hz, 1H), 3.12 (d, J = 3.3 Hz, 1H), 2.37 (d, J = 17.8 Hz, 1H), 2.30 – 2.36 (m, 1H), 1.80 – 1.68 (m, 1H), 1.64 – 1.53 (m, 2H), 1.35 – 1.28 (m, 1H), 1.28 – 1.20 (m, 1H), 1.17 (s, 3H), 1.12 (s, 3H), 0.72 (s, 3H) ppm; 13 C NMR (100 MHz, CDCl₃) δ 207.1 (d, J = 2.0 Hz, 1C), 156.9, 136.6, 128.2, 126.4, 121.4, 107.5, 64.6 (d, J = 4.7 Hz, 2C), 57.3, 55.5 (d, J = 5.5 Hz, 2C), 41.7, 38.2, 36.8, 36.7, 33.8, 28.7, 28.7, 25.8, 18.5 ppm; IR v_{max} 2958, 1716, 1595, 1265, 744 cm⁻¹; HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₁₉H₂₆O₃Na, 325.1774; found, 325.1765;

Enantiomeric excess: 97%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 9.100 \text{ min (major)}, t_R = 9.998 \text{ min (minor)}.$



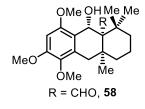
56 (90 mg) was prepared according to general procedure in 90% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.25$ (20% ethyl acetate-petroleum ether); m.p. 47 - 49 °C; $[\alpha]_{D}^{20}$ +4.78 (c 0.74, DCM); and it was recrystallized from DCM /hexane (V/V = 1/4) at 25 °C, to obtain colorless crystals, CCDC (1947393). ¹H NMR (400

MHz, CDCl₃) δ 10.07 (s, 1H), 6.33 (d, J = 2.3 Hz, 1H), 6.21 (d, J = 2.3 Hz, 1H), 5.44 (s, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 3.26 (d, J = 2.3 Hz, 1H), 5.44 (s, 1H), 3.88 (s, 2H), 3.78 (s, 3H), 3.26 (d, J = 2.3 Hz, 1H), 5.44 (s, 1H), 5.44 (s, 1H), 5.44 (s, 2H), 5.44 = 18.1 Hz, 1H), 2.97 (s, 1H), 2.40 - 2.28 (m, 2H), 1.73 (d, J = 13.4 Hz, 1H), 1.60 (dd, J = 6.9, 3.3 Hz, 1H), 1.29 (dt, J = 14.5, 3.5 Hz, 1H), 1.29 (dt, J = 14.5, 3. Hz, 1H), 1.25 – 1.20 (m, 1H), 1.17 (s, 3H), 1.10 (s, 3H), 0.72 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 207.2, 159.8, 158.1, 137.4, 119.4, 104.0, 96.5, 64.4, 57.4, 55.5, 55.2, 42.3, 38.2, 36.8, 36.7, 33.9, 28.9, 28.7, 25.8, 18.5 ppm; IR v_{max} 1371, 1282, 1180, 1141, 904, 844, 746, 707 cm⁻¹; HRMS–ESI (*m/z*): [M+Na]⁺ calcd for C₂₀H₂₈O₄Na, 355.1880; found, 355.1869; Enantiomeric excess: 98%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 12.526 min (major), $t_R = 16.350$ min (minor).



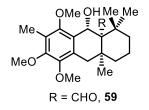
57 (77 mg) was prepared according to general procedure in 77% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetatepetroleum ether) as a vellow solid: $R_f = 0.45$ (20% ethyl acetate-petroleum ether); m.p. 109 – 111 °C; $[\alpha]_{D}^{20}$ +10.2 (c 0.87, DCM); ¹H NMR (400 MHz, CDCl₃) δ 10.09 (s, 1H), 6.70 (s, 2H), 5.49 (d, J = 3.1 Hz, 1H), 3.87 (s, 3H), 3.79 (s, 3H), 3.18 (d, J = 3.3 Hz, 1H), 2.95 (d, J = 18.9 Hz, 1H), 2.43 (d, J = 18.9 Hz, 1H), 2.36 (td, J = 13.5, 4.1 Hz, 1H), 1.85 - 1.71 (m, 1H), 1.63 - 1.53 (m, 2H), 1.39 (dt, J = 13.7, 3.2 Hz, 1H), 1.26 - 1.19 (m, 1H), 1.15 (s, 3H),

1.09 (s, 3H), 0.67 (s, 3H) ppm; 13 C NMR (100 MHz, CDCl₃) δ 207.3 (d, J = 2.0 Hz, 1C), 151.2, 150.8, 127.5, 125.6, 108.4, 107.2, 64.6 (d, J = 3.0 Hz, 1C), 56.9, 55.7 (d, J = 3.3 Hz, 1C), 55.5 (d, J = 3.1 Hz, 1C), 38.2, 36.83, 36.78, 36.4, 33.2, 29.1, 28.6, 25.8, 18.6 ppm; IR v_{max} 1529, 1456, 1396, 1265, 1051, 904, 798, 748, 698, 651 cm⁻¹; HRMS–ESI (*m/z*): [M+Na]⁺ calcd for C₂₀H₂₈O₄Na, 355.1880; found, 355.1868; Enantiomeric excess: 99%, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 8.289 \text{ min (minor)}, t_R = 9.444 \text{ min (major)}.$



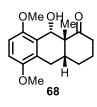
58 (72 mg) was prepared according to general procedure in 66% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.2$ (20% ethyl acetate-petroleum ether); m.p. 75 – 77 °C; [α]²⁰₂₀ -3.5 (c 0.16, DCM); ¹H NMR (500 MHz, CDCl₃) δ 10.08 (s, 1H), 6.42 (s, 1H), 5.45 (s, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.74 (s, 3H), 3.09 (s, 1H), 3.06 (d, J = 18.7 Hz, 1H), 2.47 (d, J = 18.7 Hz, 1H),

2.34 (td, J = 13.6, 4.3 Hz, 1H), 1.76 (ddd, J = 14.6, 10.3, 7.2 Hz, 1H), 1.61 – 1.56 (m, 2H), 1.38 (dt, J = 14.2, 3.2 Hz, 1H), 1.27 – 1.19 (m, 1H), 1.16 (s, 3H), 1.08 (s, 3H), 0.69 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) & 207.4, 153.4, 152.0, 140.1, 130.5, 119.1, 94.6, 64.4, 60.1, 57.0, 55.9, 55.8, 38.3, 36.8, 36.7, 36.5, 33.4, 29.1, 28.7, 25.9, 18.5 ppm; IR v_{max} 1371, 1282, 1267, 1180, 1141, 900, 844, 744, 707 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₂₁H₃₀O₅Na, 385.1985; found, 385.1967; Enantiomeric excess: 97%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 13.596 min (major), t_R = 15.106 min (minor).



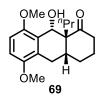
59 (82 mg) was prepared according to general procedure in 73% yield. Ligand **L12** (0.15 mmol, 0.5 equiv.) was used instead of **L10**. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a colorless oil: $R_f = 0.4$ (20% ethyl acetate-petroleum ether); $[\alpha]_D^{20}$ -14.3 (c 1.28, DCM); ¹H NMR (500 MHz, CDCl₃) δ 10.14 (s, 1H), 5.43 (d, J = 2.8 Hz, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 3.78 (s, 3H), 3.36 (d,

J = 3.2 Hz, 1H), 3.03 (d, J = 18.5 Hz, 1H), 2.49 (d, J = 18.5 Hz, 1H), 2.28 (td, J = 13.7, 4.3 Hz, 1H), 2.20 (s, 3H), 1.81 (dd, J = 13.4, 3.9 Hz, 1H), 1.69 – 1.61 (m, 2H), 1.48 – 1.40 (m, 1H), 1.30 – 1.22 (m, 1H), 1.18 (s, 3H), 1.05 (s, 3H), 0.68 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 208.4, 152.6, 151.3, 146.8, 127.3, 127.2, 123.1, 64.7, 61.3, 60.1, 59.8, 57.5, 38.7, 37.1, 36.5, 36.1, 33.2, 29.7, 28.8, 26.2, 18.6, 9.5 ppm; IR v_{max} 2360, 1463, 1267, 1078, 748, 705 cm⁻¹; HRMS–ESI (*m/z*): [M+Na]⁺ calcd for C₂₂H₃₂O₅Na, 399.2142; found, 399.2125; Enantiomeric excess: 85%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 6.816 min (major), t_R = 8.958 min (minor).



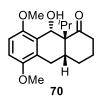
68 (52.2 mg) was prepared according to general procedure in 60% yield. Ligand **L10** (0.24 mmol, 0.8 equiv.) was used. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.46$ (20% ethyl acetate-petroleum ether); m.p. 137 - 139 °C; $[\alpha]_D^{20}$ +96.8 (c 0.47, DCM); ¹H NMR (400 MHz, CDCl₃) δ 6.74 (d, J = 8.8 Hz, 1H), 6.70 (d, J = 8.8 Hz, 1H), 4.69 (d, J = 3.0 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 2.96 (d, J = 3.2 Hz, 1H),

2.88 – 2.72 (m, 3H), 2.59 – 2.48 (m, 1H), 2.26 – 2.14 (m, 1H), 2.13 – 1.95 (m, 2H), 1.84 – 1.70 (m, 1H), 1.57 – 1.49 (m, 1H), 1.09 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 215.3, 151.7, 151.4, 126.1, 123.8, 108.8, 107.3, 68.6, 55.6, 55.5, 50.3, 41.2, 38.9, 27.8, 26.5, 23.7, 20.9 ppm; IR v_{max} 3055, 1697, 1423, 1265, 1107, 808 cm⁻¹; HRMS–EI (*m/z*): [M]⁺ calcd for C₁₇H₂₂O₄, 290.1518; found, 290.1522; Enantiomeric excess: 88%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 8.785 min (major), t_R = 11.375 min (minor).



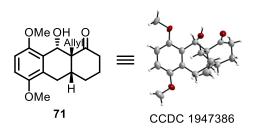
69 (69 mg) was prepared according to general procedure in 72% yield. Ligand **L10** (0.24 mmol, 0.8 equiv.) was used. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.5$ (20% ethyl acetate-petroleum ether); m.p. 116 - 118 °C; $[\alpha]_D^{20}$ +90.9 (c 0.18, DCM); ¹H NMR (500 MHz, CDCl₃) δ 6.75 (d, J = 8.8 Hz, 1H), 6.71 (d, J = 8.8 Hz, 1H), 4.70 (d, J = 3.3 Hz, 1H), 3.82 (s, 6H), 2.93 (d, J = 3.4 Hz, 1H), 2.86 – 2.80

(m, 1H), 2.73 - 2.65 (m, 2H), 2.55 - 2.47 (m, 1H), 2.41 - 2.33 (m, 1H), 2.25 - 2.12 (m, 1H), 2.04 - 1.96 (m, 1H), 1.95 - 1.87 (m, 1H), 1.86 - 1.75 (m, 1H), 1.64 - 1.55 (m, 1H), 1.36 - 1.24 (m, 1H), 1.22 - 1.12 (m, 1H), 1.11 - 1.03 (m, 1H), 0.84 (t, J = 7.2 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 215.4, 151.6, 151.3, 126.3, 124.1, 108.7, 107.2, 69.4, 55.6, 55.5, 53.7, 41.2, 35.8, 33.1, 27.0, 26.1, 22.5, 18.3, 14.7 ppm; IR v_{max} 3738, 3055, 1697, 1267, 1105, 802, 742 cm⁻¹; HRMS–EI (*m*/*z*): [M]⁺ calcd for C₁₉H₂₆O₄, 318.1831; found, 318.1829; Enantiomeric excess: 98%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 9.407 min (major), t_R = 10.959 min (minor).



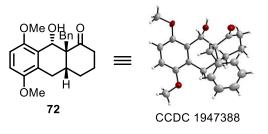
70 (52.3 mg) was prepared according to general procedure in 55% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a yellow solid: $R_f = 0.29$ (20% ethyl acetate-petroleum ether); m.p. 85 - 87 °C; $[\alpha]_D^{20}$ +59.6 (c 0.05, DCM); ¹H NMR (400 MHz, CDCl₃) δ 6.74 (d, J = 8.8 Hz, 1H), 6.68 (d, J = 8.8 Hz, 1H), 5.41 (d, J = 3.5 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.01 (dd, J = 16.9, 7.0 Hz, 1H), 2.68 (dd, J = 16.9, 6.7 Hz, 1H), 2.55 - 2.46

(m, 3H), 2.40 – 2.29 (m, 1H), 2.00 – 1.78 (m, 5H), 0.86 (d, J = 6.8 Hz, 3H), 0.77 (d, J = 7.0 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 217.6, 150.80, 150.76, 127.4, 126.5, 109.8, 107.9, 67.4, 57.7, 55.9, 55.8, 41.3, 34.5, 34.2, 30.0, 27.0, 20.8, 18.6, 18.5 ppm; IR ν_{max} 3055, 2306, 1697, 1267, 1105, 802, 742 cm⁻¹; HRMS–EI (m/z): [M]⁺ calcd for C₁₉H₂₆O₄, 318.1831; found, 318.1836; Enantiomeric excess: 95%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 11.371 min (major), t_R = 21.511 min (minor).



71 (72.5 mg) was prepared according to general procedure in 76% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.5$ (20% ethyl acetate-petroleum ether); m.p. 121 - 123 °C; $[\alpha]_D^{20}$ +57.1 (c 0.44, DCM); and it was recrystallized from DCM /hexane (V/V = 1/4) at 25 °C, to obtain colorless crystals, CCDC (1947386). ¹H NMR (500 MHz, CDCl₃) δ 6.74 (d, *J* = 8.8

Hz, 1H), 6.69 (d, J = 8.8 Hz, 1H), 5.72 – 5.59 (m, 1H), 5.04 – 5.01 (m, 1H), 5.00 (d, J = 1.5 Hz, 1H), 4.69 (d, J = 3.1 Hz, 1H), 3.81 (s, 6H), 2.94 (d, J = 3.3 Hz, 1H), 2.85 – 2.65 (m, 4H), 2.54 – 2.45 (m, 1H), 2.35 – 2.25 (m, 1H), 2.23 – 2.13 (m, 1H), 2.01 – 1.91 (m, 1H), 1.81 – 1.72 (m, 2H), 1.59 – 1.51 (m, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 214.8, 151.8, 151.6, 135.0, 126.2, 124.3, 117.8, 109.0, 107.4, 68.9, 55.9, 55.7, 53.8, 41.7, 38.2, 33.5, 27.3, 25.7, 23.0 ppm; IR v_{max} 3055, 1697, 1267, 1105, 742 cm⁻¹; HRMS– EI (*m*/*z*): [M]⁺ calcd for C₁₉H₂₄O₄, 316.1675; found, 316.1673; Enantiomeric excess: 87%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 9.109 min (major), t_R = 12.277 min (minor).



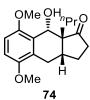
72 (80.5 mg) was prepared according to general procedure in 73% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a yellow solid: $R_f = 0.36$ (20% ethyl acetate-petroleum ether); m.p. 145 - 147 °C; $[\alpha]_D^{20}$ +58.9 (c 0.12, DCM); and it was recrystallized from DCM /hexane (V/V = 1/4) at 25 °C, to obtain colorless crystals, CCDC (1947388). ¹H NMR (500 MHz,

CDCl₃) δ 7.25 – 7.16 (m, 3H), 7.16 – 7.10 (m, 2H), 6.77 (d, *J* = 8.8 Hz, 1H), 6.73 (d, *J* = 8.8 Hz, 1H), 4.91 (d, *J* = 3.5 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.58 (d, *J* = 13.7 Hz, 1H), 2.91 – 2.84 (m, 2H), 2.75 (d, *J* = 18.2 Hz, 1H), 2.59 (ddd, *J* = 16.6, 9.4, 7.0 Hz, 1H), 2.41 – 2.32 (m, 1H), 2.21 (d, *J* = 13.7 Hz, 1H), 2.15 – 2.04 (m, 2H), 1.92 – 1.83 (m, 1H), 1.66 – 1.59 (m, 1H), 1.52 – 1.46 (m, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 216.1, 151.6, 151.4, 138.2, 130.1 (2C), 128.2 (2C), 126.3, 125.8, 123.9, 108.9, 107.3, 69.0, 55.7, 55.5, 55.0, 41.2, 39.3, 31.5, 26.8, 25.9, 21.2 ppm; IR v_{max} 3691, 3055, 1697, 1267, 1105, 804 cm⁻¹; HRMS–EI (*m/z*): [M]⁺ calcd for C₂₃H₂₆O₄, 366.1831; found, 366.1826; Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 10.404 min (major), t_R = 13.115 min (minor).



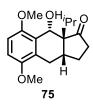
73 (76.2 mg) was prepared according to general procedure in 92% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.18$ (20% ethyl acetate-petroleum ether); m.p. 122 - 124 °C; $[\alpha]_D^{20}$ +104

⁷³ (c 0.23, DCM); ¹H NMR (400 MHz, CDCl₃) δ 6.77 (d, J = 8.8 Hz, 1H), 6.70 (d, J = 8.8 Hz, 1H), 4.95 (d, J = 2.5 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 2.99 (dd, J = 17.8, 7.6 Hz, 1H), 2.86 (dd, J = 17.8, 4.0 Hz, 1H), 2.51 – 2.41 (m, 1H), 2.38 (d, J = 3.3 Hz, 1H), 2.30 – 2.16 (m, 2H), 2.06 – 1.93 (m, 2H), 0.96 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 222.4, 151.6, 151.3, 126.2, 124.9, 109.7, 107.7, 67.6, 55.81, 55.76, 50.1, 40.3, 38.7, 26.7, 24.0, 21.2 ppm; IR v_{max} 3736, 3055, 1697, 1421, 1267, 1107 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₁₆H₂₀O₄Na, 299.1254; found, 299.1251; Enantiomeric excess: 86%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 11.862 min (major), t_R = 15.564 min (minor).



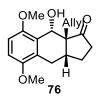
74 (87 mg) was prepared according to general procedure in 95% yield. Ligand **L10** (0.24 mmol, 0.8 equiv.) was used. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a colorless oil: $R_f = 0.2$ (20% ethyl acetate-petroleum ether); $[\alpha]_D^{20}$ +91.8 (c 0.84, DCM); ¹H NMR (400 MHz, CDCl₃) δ 6.76 (d, *J* = 8.9 Hz, 1H), 6.68 (d, *J* = 8.9 Hz, 1H), 5.00 (s, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.01 (dd, *J* = 17.2, 7.6 Hz, 1H), 2.80 (dd, *J* = 17.2, 5.1 Hz,

1H), 2.50 – 2.38 (m, 2H), 2.29 (s, 1H), 2.25 – 2.12 (m, 1H), 2.08 – 1.90 (m, 2H), 1.65 – 1.56 (m, 1H), 1.18 (ddt, J = 15.1, 7.8, 3.6 Hz, 1H), 1.10 – 1.00 (m, 2H), 0.78 (t, J = 7.0 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 222.3, 151.3, 151.1, 126.8, 125.6, 109.8, 107.8, 67.9, 55.8 (t, J = 3.0 Hz, 2C), 54.6, 39.6, 37.0, 36.5, 26.7, 24.6, 17.8, 14.6 ppm; IR ν_{max} 1481, 1394, 1265, 1085, 904, 798, 744, 698, 651 cm⁻¹; HRMS–ESI (m/z): [M+Na]⁺ calcd for C₁₈H₂₄O₄Na, 327.1567; found, 327.1562; Enantiomeric excess: 92%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 11.261 min (major), t_R = 13.630 min (minor).



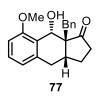
75 (55.1 mg) was prepared according to general procedure in 60% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.19$ (20% ethyl acetate-petroleum ether); m.p. 121 - 123 °C; $[\alpha]_D^{20}$ +153 (c 0.25, DCM); ¹H NMR (400 MHz, CDCl₃) δ 6.75 (d, J = 8.8 Hz, 1H), 6.68 (d, J = 8.8 Hz, 1H), 5.21 (d, J = 3.1 Hz, 1H), 3.80 (s, 6H), 3.11 (dd, J = 16.4, 7.3 Hz, 1H), 2.73 (dd, J = 16.4, 7.3 Hz, 1H), 2.51 – 2.38 (m, 2H), 2.27

-2.14 (m, 2H), 2.12 - 1.98 (m, 2H), 1.94 - 1.83 (m, 1H), 0.80 (d, J = 6.8 Hz, 3H), 0.55 (d, J = 7.0 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 223.0, 150.9, 150.4, 128.0, 126.8, 110.0, 108.0, 67.3, 58.7, 55.9, 55.8, 39.8, 35.0, 33.8, 27.2, 26.0, 19.0, 17.8 ppm; IR ν_{max} 3055, 1691, 1489, 1267, 1105, 744 cm⁻¹; HRMS–ESI (m/z): [M+Na]⁺ calcd for C₁₈H₂₄O₄Na, 327.1572; found, 327.1562; Enantiomeric excess: 93%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 13.622 min (major), t_R = 15.511 min (minor).



76 (86 mg) was prepared according to general procedure in 95% yield. Ligand **L10** (0.24 mmol, 0.8 equiv.) was used. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.2$ (20% ethyl acetate-petroleum ether); m.p. 85 - 87 °C; $[\alpha]_D^{20}$ +87.2 (c 0.36, DCM); ¹H NMR (500 MHz, CDCl₃) δ 6.77 (d, *J* = 8.9 Hz,

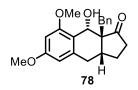
1H), 6.69 (d, J = 8.9 Hz, 1H), 5.61 – 5.50 (m, 1H), 5.00 (d, J = 2.5 Hz, 1H), 4.97 (d, J = 1.3 Hz, 1H), 4.96 – 4.92 (m, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 2.95 (dd, J = 17.5, 7.6 Hz, 1H), 2.81 (dd, J = 17.5, 4.6 Hz, 1H), 2.50 – 2.40 (m, 3H), 2.38 (d, J = 3.5 Hz, 1H), 2.15 (ddd, J = 18.2, 9.6, 8.5 Hz, 1H), 2.02 – 1.93 (m, 2H), 1.83 (dd, J = 13.7, 8.7 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 221.5, 151.3, 151.2, 133.8, 126.2, 125.3, 118.2, 109.7, 107.7, 67.3, 55.8, 55.7, 54.2, 39.4, 38.9, 36.0, 26.6, 24.0 ppm; IR v_{max} 2358, 2330, 2108, 1504, 1456, 744, 624 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₁₈H₂₂O₄Na, 325.1410; found, 325.1404; Enantiomeric excess: 99.5%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 11.144 min (major), t_R = 16.277 min (minor).



77 (98 mg, d.r. = 10:1) was prepared according to general procedure in 98% yield. Ligand **L10** (0.24 mmol, 0.8 equiv.) was used. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.3$ (20% ethyl acetate-petroleum ether); ¹H NMR (500 MHz, CDCl₃) δ 7.25 – 7.22 (m, 1H), 7.22 – 7.15 (m, 3H), 7.03 – 6.99 (m, 2H), 6.84 (d, J = 7.6 Hz, 1H), 6.77 (d, J = 8.3 Hz, 1H), 5.23 (s, 1H), 3.84 (s, 3H), 3.27 (d, J = 13.3 Hz, 1H), 2.95 (t, J

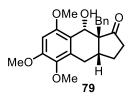
= 6.1 Hz, 2H), 2.37 (ddd, J = 17.8, 8.4, 4.6 Hz, 1H), 2.33 – 2.23 (m, 2H), 2.10 (d, J = 13.3 Hz, 1H), 1.89 (dt, J = 17.5, 8.6 Hz, 1H), 1.83 – 1.76 (m, 1H), 1.61 (ddt, J = 11.8, 7.9, 3.8 Hz, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 222.2, 157.3, 137.5, 137.4, 130.1 (2C), 129.0, 128.1 (2C), 126.4, 125.1, 121.1, 108.2, 67.7, 57.0, 55.4, 40.7, 39.8, 36.0, 31.4, 26.5 ppm; IR v_{max} 1732, 1589, 1280, 1340, 786, 736, 702, 682 cm⁻¹; HRMS–ESI (m/z): [M+Na]⁺ calcd for C₂₁H₂₂O₃Na, 345.1461; found, 345.1455; Enantiomeric excess:

97%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 8.952$ min (major), $t_R = 10.329$ min (minor).



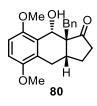
78 (98.8 mg, d.r. = 5:1) was prepared according to general procedure in 94% yield. Ligand **L10** (0.24 mmol, 0.8 equiv.) was used. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid; R_f = 0.46 (30% ethyl acetate-petroleum ether); ¹H NMR (500 Hz, CDCl₃) δ 7.21 – 7.15 (m, 3H), 7.02 (d, *J* = 6.9 Hz, 2H), 6.36 (d, *J* = 2.3 Hz, 1H), 6.35 (d, *J* = 2.3 Hz, 1H), 5.14 (s, 1H), 3.83 (s, 3H), 3.82 (s, 3H),

3.26 (d, J = 13.4 Hz, 1H), 2.95 – 2.89 (m, 2H), 2.42 – 2.32 (m, 1H), 2.30 – 2.21 (m, 1H), 2.16 (s, 1H), 2.11 (d, J = 13.3 Hz, 1H), 1.93 – 1.76 (m, 2H), 1.64 – 1.57 (m, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 222.3, 160.4, 158.5, 138.5, 137.5, 130.1 (2C), 128.2 (2C), 126.4, 117.9, 104.6, 96.3, 67.6, 57.1, 55.5, 55.3, 40.7, 39.8, 36.0, 31.8, 26.6 ppm; IR v_{max} 2966, 1741, 1492, 1265, 1095, 813, 746 cm⁻¹; HRMS–EI (m/z): [M]⁺ calcd for C₂₂H₂₄O₄, 352.1675; found, 352.1678; Enantiomeric excess: 98% (major), determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 13.803 min (minor), t_R = 18.339 min (major); Enantiomeric excess: 96% (minor), determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 13.803 min (minor).



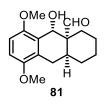
79 (98.6 mg, d.r. = 9:1) was prepared according to general procedure in 86% yield. Ligand **L10** (0.24 mmol, 0.8 equiv.) was used. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid; R_f = 0.28 (30% ethyl acetate-petroleum ether); ¹H NMR (400 Hz, CDCl₃) δ 7.22 – 7.14 (m, 3H), 7.03 – 6.97 (m, 2H), 6.42 (s, 1H), 5.17 (d, *J* = 2.4 Hz, 1H), 3.91 (s, 3H), 3.85 (s, 3H), 3.78 (s, 3H), 3.23 (d, *J* = 13.3

Hz, 1H), 3.17 - 3.08 (m, 1H), 2.79 (dd, J = 16.7, 6.3 Hz, 1H), 2.42 - 2.31 (m, 1H), 2.31 - 2.21 (m, 1H), 2.10 (d, J = 13.3 Hz, 2H), 1.95 - 1.76 (m, 2H), 1.67 - 1.60 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 222.4, 154.0, 153.0, 140.3, 137.4, 131.1, 130.1 (2C), 128.2 (2C), 126.5, 117.7, 94.7, 67.8, 60.7, 56.8, 56.0, 40.9, 39.8, 35.8, 26.9, 25.0 ppm; IR v_{max} 2962, 1734, 1489, 1259, 1095, 796, 744 cm⁻¹; HRMS-EI (*m*/*z*): [M]⁺ calcd for C₂₃H₂₆O₅, 382.1780; found, 382.1777; Enantiomeric excess: 97% (major), determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 7.685 min (major), t_R = 9.340 min (minor).



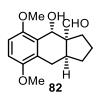
80 (101 mg) was prepared according to general procedure in 96% yield. Ligand **L10** (0.24 mmol, 0.8 equiv.) was used. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.3$ (20% ethyl acetate-petroleum ether); m.p. 108 – 110 °C; $[\alpha]_D^{20}$ +62.4 (c 0.76, DCM); ¹H NMR (400 MHz, CDCl₃) δ 7.23 – 7.15 (m, 3H), 7.08 – 7.02 (m, 2H), 6.79 (d, J = 8.8 Hz, 1H), 6.72 (d, J = 8.8 Hz, 1H), 5.08 (d, J = 2.7 Hz, 1H), 3.83 (s,

3H), 3.82 (s, 3H), 3.33 (d, J = 13.4 Hz, 1H), 2.96 (dd, J = 18.0, 7.8 Hz, 1H), 2.80 (dd, J = 18.0, 3.7 Hz, 1H), 2.44 (d, J = 3.5 Hz, 1H), 2.40 – 2.31 (m, 1H), 2.24 – 2.13 (m, 2H), 1.95 – 1.82 (m, 2H), 1.74 – 1.65 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 221.9, 151.6, 151.3 137.7, 130.1 (2C), 128.2 (2C), 126.4, 126.0, 125.0, 109.7, 107.7, 67.63, 67.61, 55.8 (dd, J = 5.3, 3.2 Hz, 1C), 55.7, 39.7, 39.6, 34.5, 26.5, 23.9 ppm; IR v_{max} 1720, 1481, 1265, 1089, 744 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₂₂H₂₄O₄Na, 375.1567; found, 375.1561; Enantiomeric excess: 97%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 11.387 min (major), t_R = 14.498 min (minor).



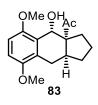
81 (73 mg) was prepared according to general procedure in 84% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a colorless oil: $R_f = 0.25$ (20% ethyl acetate-petroleum ether); $[\alpha]_D^{20}$ +40.9 (c 0.70, DCM); ¹H NMR (400 MHz, CDCl₃) δ 9.86 (s, 1H), 6.73 (d, J = 8.9 Hz, 1H), 6.70 (d, J = 8.8 Hz, 1H), 5.05 (s, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 2.96 (s, 1H), 2.84 (dd, J = 18.7, 6.9 Hz, 1H), 2.63 (dd, J = 18.7, 7.9 Hz, 1H), 2.54 – 2.46

(m, 1H), 1.75 - 1.66 (m, 2H), 1.65 - 1.57 (m, 1H), 1.55 - 1.36 (m, 5H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 207.7, 151.7, 151.3, 125.8, 125.7, 108.9, 107.4, 67.59, 67.57, 55.59, 55.56, 51.3, 29.8, 27.2, 25.7, 25.1, 21.6 ppm; IR v_{max} 1720, 1481, 1259, 1087, 904, 798, 744 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₁₇H₂₂O₄Na, 313.1410; found, 313.1406; Enantiomeric excess: 88%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 240 nm): t_R = 16.842 min (major), t_R = 20.397 min (minor).



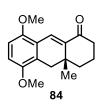
82 (56 mg) was prepared according to general procedure in 68% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.25$ (20% ethyl acetate-petroleum ether); m.p. 46 – 48 °C; $[\alpha]_D^{20}$ -10.3 (c 0.68, DCM); ¹H NMR (500 MHz, CDCl₃) δ 9.79 (s, 1H), 6.79 (d, J = 8.8 Hz, 1H), 6.71 (d, J = 8.9 Hz, 1H), 5.44 (s, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 2.99 – 2.92 (m, 1H), 2.86 (t, J = 4.6 Hz, 2H), 2.43 (s, 1H), 1.99 – 1.90 (m,

2H), 1.41 (ddd, J = 13.3, 6.4, 3.4 Hz, 1H), 1.31 – 1.21 (m, 1H), 1.13 – 1.05 (m, 2H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 203.9, 151.7, 151.3, 128.2, 126.4, 111.0, 108.5, 65.9, 61.4, 56.2, 56.0, 34.3, 34.0, 33.0, 24.5, 23.6 ppm; IR v_{max} 2949, 1718, 1489, 1257, 1082, 740 cm⁻¹; HRMS–ESI (*m*/*z*): [M+Na]⁺ calcd for C₁₆H₂₀O₄Na, 299.1254; found, 299.1250; Enantiomeric excess: 86%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 92/8, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 35.280 min (major), t_R = 37.406 min (minor).



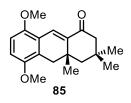
83 (83 mg) was prepared according to general procedure in 95% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a colorless oil: $R_f = 0.2$ (20% ethyl acetate-petroleum ether); $[\alpha]_D^{20}$ -21.1 (c 0.92, DCM); ¹H NMR (500 MHz, CDCl₃) δ 6.78 (d, J = 8.9 Hz, 1H), 6.69 (d, J = 8.9 Hz, 1H), 5.52 (s, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.30 – 3.23 (m, 1H), 2.86 (dd, J = 15.7, 3.0 Hz, 1H), 2.80 (dd, J = 15.7, 6.4 Hz, 1H), 2.38 (s, 3H), 2.04 (s,

1H), 1.96 - 1.87 (m, 2H), 1.34 - 1.25 (m, 1H), 1.23 - 1.09 (m, 2H), 1.05 - 0.94 (m, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 210.7, 151.7, 151.3, 128.3, 126.8, 111.0, 108.2, 66.2, 63.6, 56.2, 55.9, 35.6, 34.4, 33.9, 26.1, 24.9, 23.9 ppm; IR ν_{max} 3068, 1255, 705 cm⁻¹; HRMS–ESI (*m/z*): [M+Na]⁺ calcd for C₁₇H₂₂O₄Na, 313.1410; found, 313.1408; Enantiomeric excess: 84%, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 85/15, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 11.026 min (minor), t_R = 13.877 min (major).



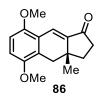
84 (80 mg) was prepared according to general procedure in 87% yield. The reaction was quenched with hydrochloric acid (HCl, 1 N) instead of saturated sodium bicarbonate. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a yellow solid: $R_f = 0.35$ (20% ethyl acetate-petroleum ether); m.p. 126 – 128 °C; $[\alpha]_D^{20}$ -30.4 (c 0.12, DCM); ¹H NMR (500 MHz, CDCl₃) δ 7.77 (s, 1H), 6.83 (d, J = 8.9 Hz, 1H), 6.67 (d, J = 8.9 Hz, 1H),

3.80 (d, J = 3.4 Hz, 6H), 3.09 (d, J = 16.4 Hz, 1H), 2.61 (ddd, J = 17.6, 4.7, 2.3 Hz, 1H), 2.50 (d, J = 16.3 Hz, 1H), 2.38 (ddd, J = 17.6, 12.3, 7.4 Hz, 1H), 2.06 – 1.91 (m, 2H), 1.91 – 1.82 (m, 1H), 1.77 (dd, J = 13.0, 4.1 Hz, 1H), 0.99 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 199.9, 151.9, 150.7, 139.8, 126.7, 125.8, 122.2, 113.0, 108.6, 56.1, 55.8, 39.9, 37.9, 37.1, 33.9, 23.3, 18.7 ppm; IR v_{max} 1672, 1483, 1261, 1099, 910, 732 cm⁻¹; HRMS–ESI (m/z): [M+H]⁺ calcd for C₁₇H₂₁O₃, 273.1485; found, 273.1479; Enantiomeric excess: 66%, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 85/15, flow rate 1.0 mL/min, T = 25 °C, 230 nm): t_R = 7.072 min (major), t_R = 8.418 min (minor).



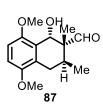
85 (63 mg) was prepared according to general procedure in 66% yield. The reaction was quenched with hydrochloric acid (HCl, 1 N) instead of saturated sodium bicarbonate. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a yellow oil: $R_f = 0.55$ (20% ethyl acetate-petroleum ether); $[\alpha]_{D}^{20}$ -50.2 (c 0.52, DCM); ¹H NMR (400 MHz, CDCl₃) δ 7.75 (s, 1H), 6.81 (d, J = 9.0 Hz, 1H), 6.67 (d, J = 8.9 Hz, 1H), 3.79

(d, J = 4.1 Hz, 6H), 3.04 (d, J = 16.5 Hz, 1H), 2.61 (d, J = 16.5 Hz, 1H), 2.36 (d, J = 16.3 Hz, 1H), 2.29 (d, J = 16.3 Hz, 1H), 1.76 (d, J = 12.0 Hz, 1H), 1.72 (d, J = 12.0 Hz, 1H), 1.08 (s, 3H), 1.06 (s, 3H), 1.05 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 200.6, 151.9, 150.8, 139.0, 126.6, 125.9, 122.3, 113.0, 108.6, 56.1, 55.8, 52.7, 51.3, 38.5, 32.7, 32.2, 30.9, 29.7, 27.6 ppm; IR v_{max} 1678, 1485, 1261, 1190, 1097, 910, 796, 732 cm⁻¹; HRMS–ESI (*m*/*z*): [M+H]⁺ calcd for C₁₉H₂₅O₃, 301.1798; found, 301.1791; Enantiomeric excess: 75%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 15.053 min (major), t_R = 17.159 min (minor).



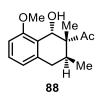
86 (33 mg) was prepared according to general procedure in 43% yield. The reaction was quenched with hydrochloric acid (HCl, 1 N) instead of saturated sodium bicarbonate. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a yellow solid: $R_f = 0.4$ (20% ethyl acetate-petroleum ether); m.p. 104 – 106 °C; $[\alpha]_D^{20}$ -65.8

(c 0.60, DCM); ¹H NMR (500 MHz, CDCl₃) δ 7.61 (s, 1H), 6.85 (d, *J* = 8.9 Hz, 1H), 6.69 (d, *J* = 9.0 Hz, 1H), 3.799 (s, 3H), 3.796 (s, 3H), 3.34 (d, *J* = 16.3 Hz, 1H), 2.55 – 2.39 (m, 3H), 2.09 (ddd, *J* = 12.5, 8.2, 1.6 Hz, 1H), 1.81 (td, *J* = 12.2, 8.7 Hz, 1H), 1.01 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 206.6, 152.5, 151.1, 142.7, 125.5, 122.9, 122.3, 113.5, 109.0, 56.2, 56.0, 37.3, 37.0, 35.9, 35.5, 22.4 ppm; IR v_{max} 1705, 1629, 1483, 1261, 1226, 1109, 1091, 910, 798, 732 cm⁻¹; HRMS–ESI (*m*/*z*): [M+H]⁺ calcd for C₁₆H₁₉O₃, 259.1329; found, 259.1325; Enantiomeric excess: 82%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 9.967 min (minor), t_R = 11.633 min (major).



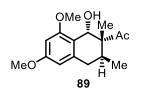
87 (58.1 mg) was prepared according to general procedure in 81% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.22$ (20% ethyl acetate-petroleum ether); m.p. 75 - 77 °C; $[\alpha]_D^{20}$ +99.6 (c 0.67, DCM); ¹H NMR (400 MHz, CDCl₃) δ 9.93 (s, 1H), 6.74 (d, J = 8.9 Hz, 1H), 6.69 (d, J = 8.9 Hz, 1H), 4.92 (s, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 2.96 (dd, J = 18.3, 5.6 Hz, 1H), 2.82 – 2.70 (m, 1H), 2.49 (s, 1H), 2.18

(dd, J = 18.3, 11.5 Hz, 1H), 1.04 (d, J = 6.8 Hz, 3H), 0.85 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 208.9, 151.6, 150.8, 126.2, 125.9, 109.0, 107.4, 70.0, 55.56, 55.55, 50.5, 28.6, 25.9, 15.8, 10.6 ppm; IR v_{max} 3055, 1718, 1483, 1625, 1085, 744 cm⁻¹; HRMS–ESI (m/z): [M+Na]⁺ calcd for C₁₅H₂₀O₄Na, 287.1254; found, 287.1251; Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 25.834 min (major), t_R = 31.518 min (minor).



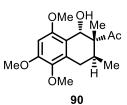
88 (66 mg) was prepared according to general procedure in 89% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.2$ (20% ethyl acetate-petroleum ether); m.p. 88 – 90 °C; $[\alpha]_D^{20}$ +51.2 (c 0.64, DCM); ¹H NMR (500 MHz, CDCl₃) δ 7.19 (t, J = 7.9 Hz, 1H), 6.74 (d, J = 7.8 Hz, 1H), 6.72 (d, J = 8.2 Hz, 1H), 4.92 (s, 1H), 3.85 (s, 3H), 2.86 (dd, J = 17.7, 5.8 Hz, 1H), 2.75 – 2.66 (m, 1H), 2.51 – 2.40 (m, 2H),

2.32 (s, 3H), 1.03 (d, J = 6.5 Hz, 3H), 0.99 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 212.6, 158.0, 137.2, 128.5, 124.8, 120.9, 107.6, 69.2, 55.4, 53.5, 34.8, 27.6, 26.6, 17.0, 13.2 ppm; IR v_{max} 2956, 1710, 1589, 1469, 1259, 1099, 740, 561 cm⁻¹; HRMS–ESI (m/z): [M+Na]⁺ calcd for C₁₅H₂₀O₃Na, 271.1305; found, 271.1301; Enantiomeric excess: 94%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 20.782 min (major), t_R = 21.418 min (minor).



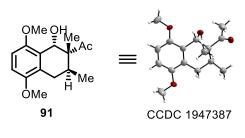
89 (70.1 mg) was prepared according to general procedure in 84% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.23$ (30% ethyl acetate-petroleum ether); m.p. 97 - 99 °C; $[\alpha]_{D}^{20}$ +49.6 (c 0.36, DCM); ¹H NMR (500 MHz, CDCl₃) δ 6.31 (d, J = 2.3 Hz, 1H), 6.23 (d, J = 2.3 Hz, 1H), 4.86 (s, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 2.82 (dd, J = 17.7, 5.8 Hz, 1H), 2.75 – 2.63 (m, 1H), 2.41 (dd,

J = 17.7, 11.9 Hz, 1H), 2.30 (s, 3H), 1.02 (d, J = 6.5 Hz, 3H), 0.98 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 212.5, 160.1, 159.1, 138.1, 117.7, 103.6, 96.5, 69.1, 55.4, 55.3, 53.6, 35.3, 27.4, 26.7, 17.0, 13.2 ppm; IR v_{max} 3053, 2304, 1610, 1267, 1149, 941, 740 cm⁻¹; HRMS–EI (m/z): [M]⁺ calcd for C₁₆H₂₂O₄, 278.1518; found, 278.1522; Enantiomeric excess: 90%, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 80/20, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 9.037 min (minor), t_R = 11.962 min (major).



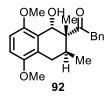
90 (46.1 mg) was prepared according to general procedure in 50% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.15$ (30% ethyl acetate-petroleum ether); m.p. 117 - 119 °C; $[\alpha]_D^{20}$ +39.6 (c 0.28, DCM); ¹H NMR (500 MHz, CDCl₃) δ 6.41 (s, 1H), 4.87 (s, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.76 (s, 3H), 2.98 (dd, J = 18.4, 5.9 Hz, 1H), 2.75 – 2.53 (m, 1H), 2.42 (s, 1H), 2.31 (s, 3H), 2.22

(dd, J = 18.4, 11.9 Hz, 1H), 1.06 (d, J = 6.6 Hz, 3H), 0.96 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 213.0, 154.5, 152.3, 139.7, 131.0, 117.4, 94.7, 69.2, 60.1, 55.9, 55.7, 53.3, 29.5, 27.7, 26.3, 17.1, 13.2 ppm; IR ν_{max} 3053, 1708, 1492, 1236, 1124, 738 cm⁻¹; HRMS–ESI (m/z): [M+Na]⁺ calcd for C₁₇H₂₄O₅Na, 331.1516; found, 331.1515; Enantiomeric excess: 90%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 17.420 min (minor), t_R = 22.880 min (major).



91 (73.5 mg) was prepared according to general procedure in 88% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.15$ (20% ethyl acetate-petroleum ether); m.p. 111 - 113 °C; $[\alpha]_D^{20}$ +77.6 (c 0.74, DCM); and it was recrystallized from DCM /hexane (V/V = 1/4) at 25 °C, to obtain colorless crystals, CCDC (1947387). ¹H NMR (400 MHz, CDCl₃) δ 6.72 (d, *J* = 8.9

Hz, 1H), 6.69 (d, J = 8.9 Hz, 1H), 4.90 (s, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 2.93 (dd, J = 18.6, 6.0 Hz, 1H), 2.69 – 2.60 (m, 1H), 2.54 (s, 1H), 2.31 (s, 3H), 2.12 (dd, J = 18.5, 11.7 Hz, 1H), 1.06 (d, J = 6.5 Hz, 3H), 0.97 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 212.9, 151.7, 150.8, 126.2, 125.9, 108.9, 107.4, 69.4, 55.6, 55.5, 53.1, 29.4, 27.6, 26.1, 17.1, 13.2 ppm; IR v_{max} 3055, 1710, 1265, 1105, 744, 677 cm⁻¹; HRMS–ESI (m/z): [M+Na]⁺ calcd for C₁₆H₂₂O₄Na, 301.1410; found, 301.1409; Enantiomeric excess: 92%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 10.622 min (major), t_R = 13.047 min (minor).



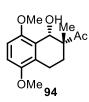
92 (73.4 mg) was prepared according to general procedure in 69% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a colorless oil: $R_f = 0.21$ (20% ethyl acetate-petroleum ether); $[\alpha]_D^{20} + 21.9$ (c 0.22, DCM); ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.26 (m, 4H), 7.26 – 7.21 (m, 1H), 6.74 (d, *J* = 8.9 Hz, 1H), 6.71 (d, *J* = 8.9 Hz, 1H), 5.03 (s, 1H), 4.05 (d, *J* = 16.5 Hz, 1H), 3.98 (d, *J* = 16.5 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 2.97

(dd, J = 18.6, 6.0 Hz, 1H), 2.80 – 2.68 (m, 1H), 2.55 (s, 1H), 2.16 (dd, J = 18.6, 11.7 Hz, 1H), 1.10 (d, J = 6.6 Hz, 3H), 1.04 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 211.4, 151.8, 150.9, 135.3, 130.0 (2C), 128.2 (2C), 126.5, 126.2, 126.0, 109.0, 107.5, 69.7, 55.7, 55.6, 53.6, 45.6, 29.5, 26.2, 17.3, 13.2 ppm; IR v_{max} 3055, 1710, 1483, 1317, 1267, 1107, 744, 677 cm⁻¹; HRMS–ESI (*m/z*): [M+Na]⁺ calcd for C₂₂H₂₆O₄Na, 377.1729; found, 377.1717; Enantiomeric excess: 88%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 14.045 min (major), t_R = 15.956 min (minor).



93 (59.9 mg) was prepared according to general procedure in 83% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetatepetroleum ether) as a colorless oil: $R_f = 0.18$ (20% ethyl acetate-petroleum ether); $[\alpha]_D^{20}$ +34.9 (c 0.37, DCM); ¹H NMR (400 MHz, CDCl₃) δ 9.81 (s, 1H), 6.74 (d, J = 8.8 Hz, 1H), 6.71 (d, J = 8.8 Hz, 1H), 5.04 (s, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 2.99 – 2.88 (m, 1H), 2.65 (s, 1H), 2.56 – 2.45 (m, 1H), 2.20 – 2.09 (m, 1H), 1.82 – 1.73

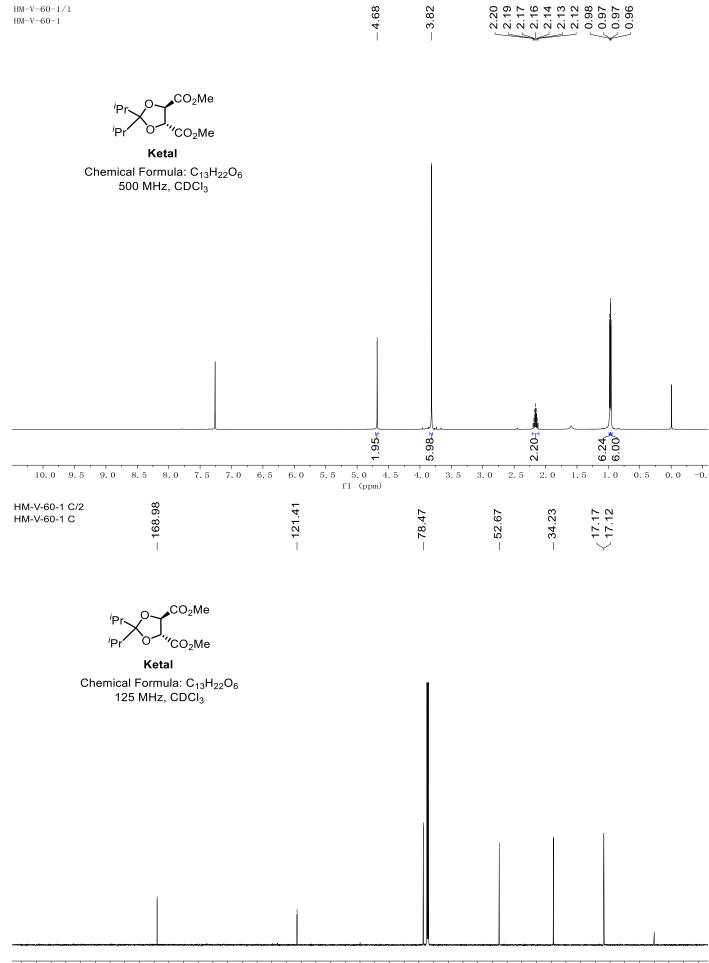
(m, 1H), 0.99 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 205.6, 151.9, 151.3, 126.4, 125.8, 109.1, 107.6, 67.3, 55.7, 55.6, 48.1, 21.9, 19.4, 16.3 ppm; IR v_{max} 3055, 1697, 1280, 1265, 1105, 742 cm⁻¹; HRMS–EI (*m*/*z*): [M]⁺ calcd for C₁₄H₁₈O₄, 250.1205; found, 250.1208; Enantiomeric excess: 85%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 85/15, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 23.790 min (major), t_R = 25.744 min (minor).



94 (28.5 mg) was prepared according to general procedure in 36% yield. The reaction time was 90 min under 366 nm light. The product was isolated through silica gel column chromatography (6% to 20% ethyl acetate-petroleum ether) as a white solid: $R_f = 0.12$ (20% ethyl acetate-petroleum ether); m.p. 103 - 105; $[\alpha]_D^{20}$ +89.3 (c 0.18, DCM); ¹H NMR (400 MHz, CDCl₃) δ 6.73 (d, J = 8.8 Hz, 1H), 6.70 (d, J = 8.8 Hz, 1H), 5.90 (d, J = 1.9 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 2.95 (ddd, J = 18.6, 6.2, 1.6 Hz, 1H), 2.54 – 2.41 (m, 2H), 2.33 (s, 3H), 2.11

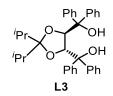
(m, 1H), 1.95 - 1.84 (m, 1H), 1.00 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 212.7, 152.0, 151.2, 126.2, 126.0, 109.0, 107.6, 67.4, 55.7, 55.6, 49.9, 25.6, 22.3, 20.1, 18.2 ppm; IR v_{max} 3055, 1697, 1483, 1265, 1107, 743 cm⁻¹; HRMS–EI (*m/z*): [M]⁺ calcd for C₁₅H₂₀O₄, 264.1362; found, 264.1357; Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 80/20, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 20.123 min (major), t_R = 21.728 min (minor).

VII. NMR and HPLC Spectra

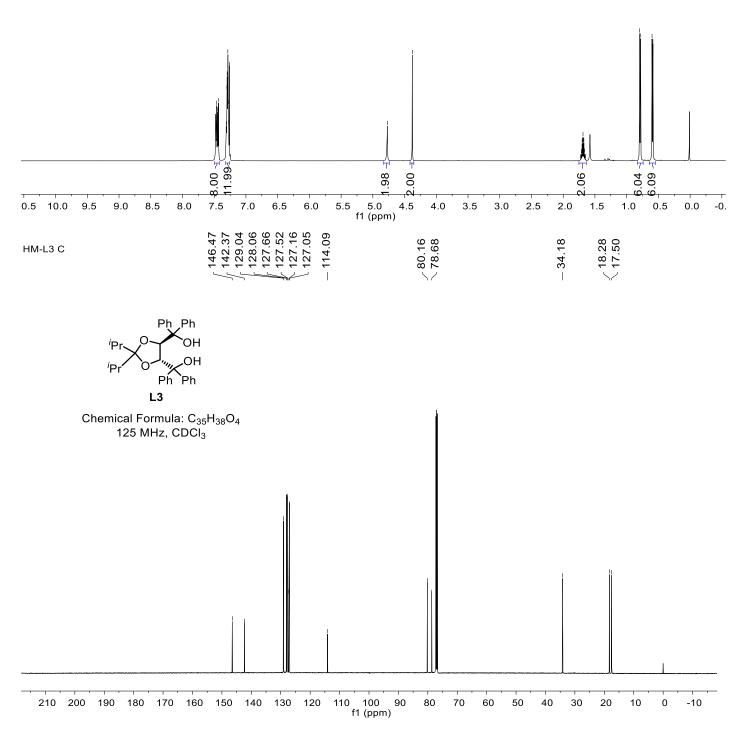


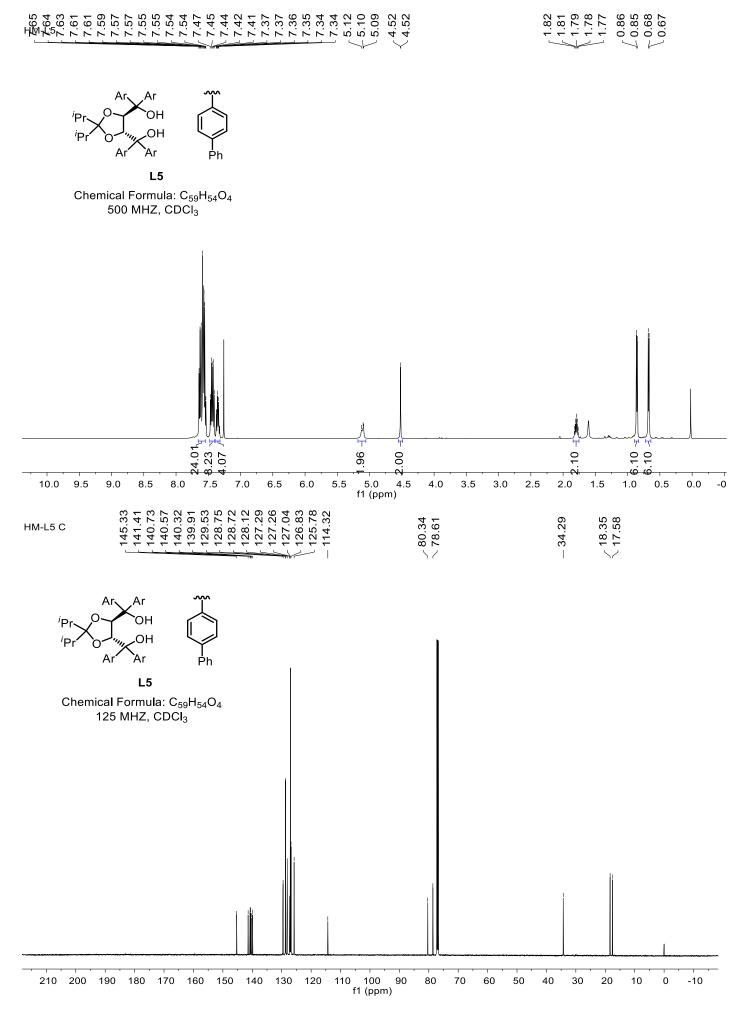
210 200 190 180 170 160 150 -10 f1 (ppm)

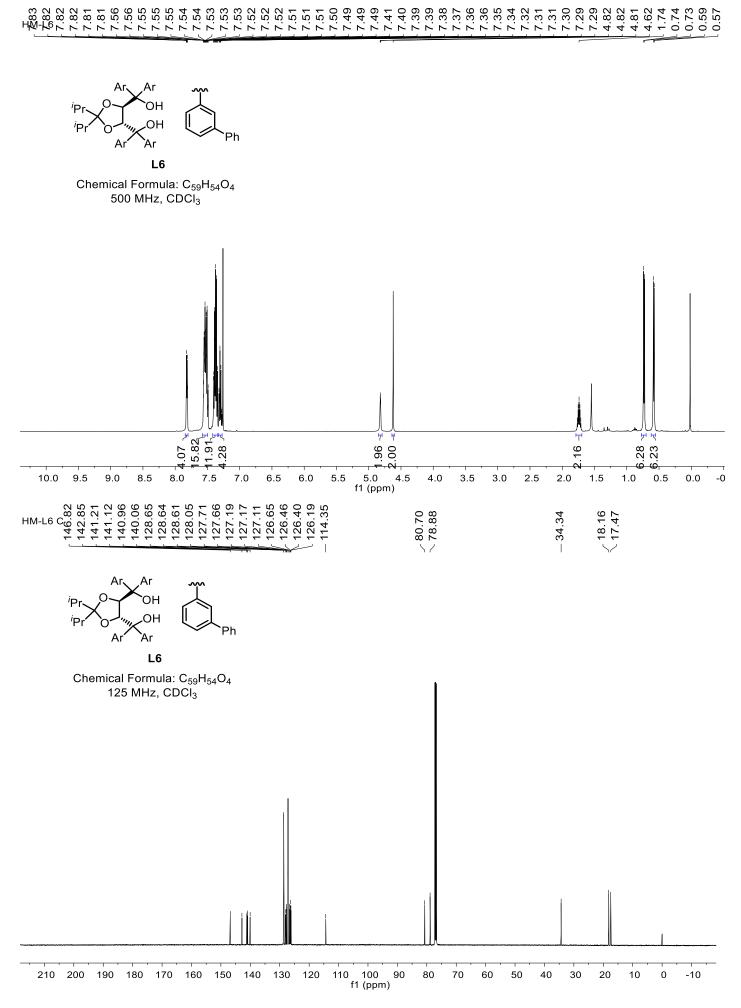
HM-L3	7.28 7.28 7.47 7.45 7.45 7.45 7.45 7.45 7.33 7.33 7.33 7.33 7.33 7.33 7.33 7.3	4.77	4.38	1.73 1.72 1.65 1.65 1.65 0.79 0.79 0.79

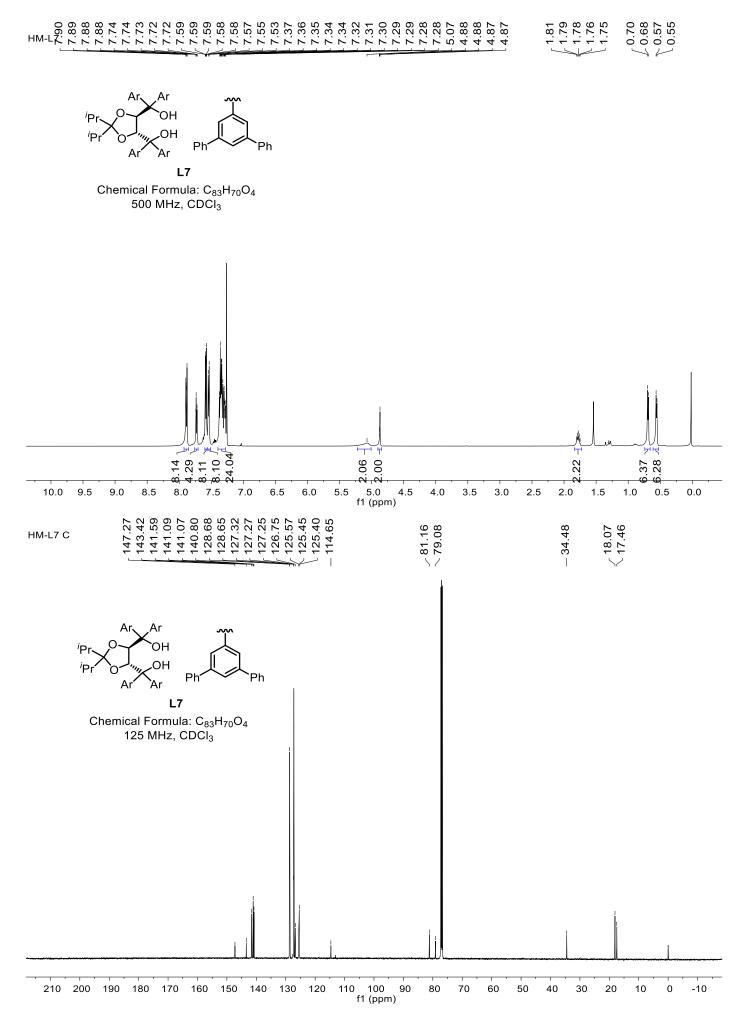


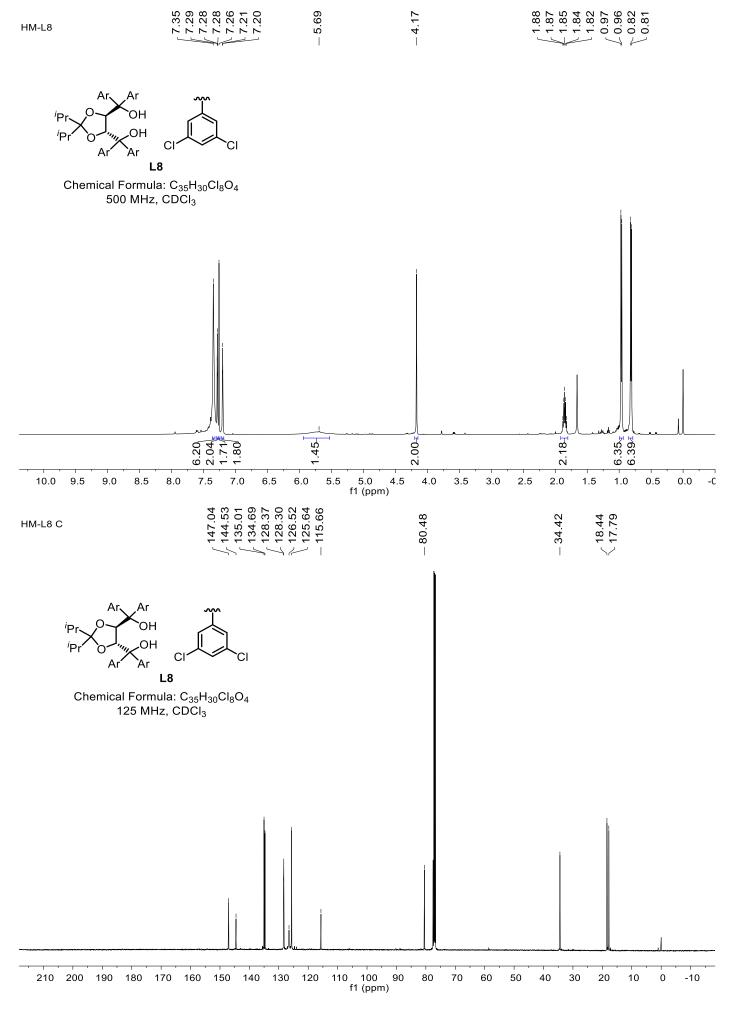
 $\begin{array}{c} \mbox{Chemical Formula: } C_{35} H_{38} O_4 \\ 500 \mbox{ MHz, } \mbox{CDCI}_3 \end{array}$

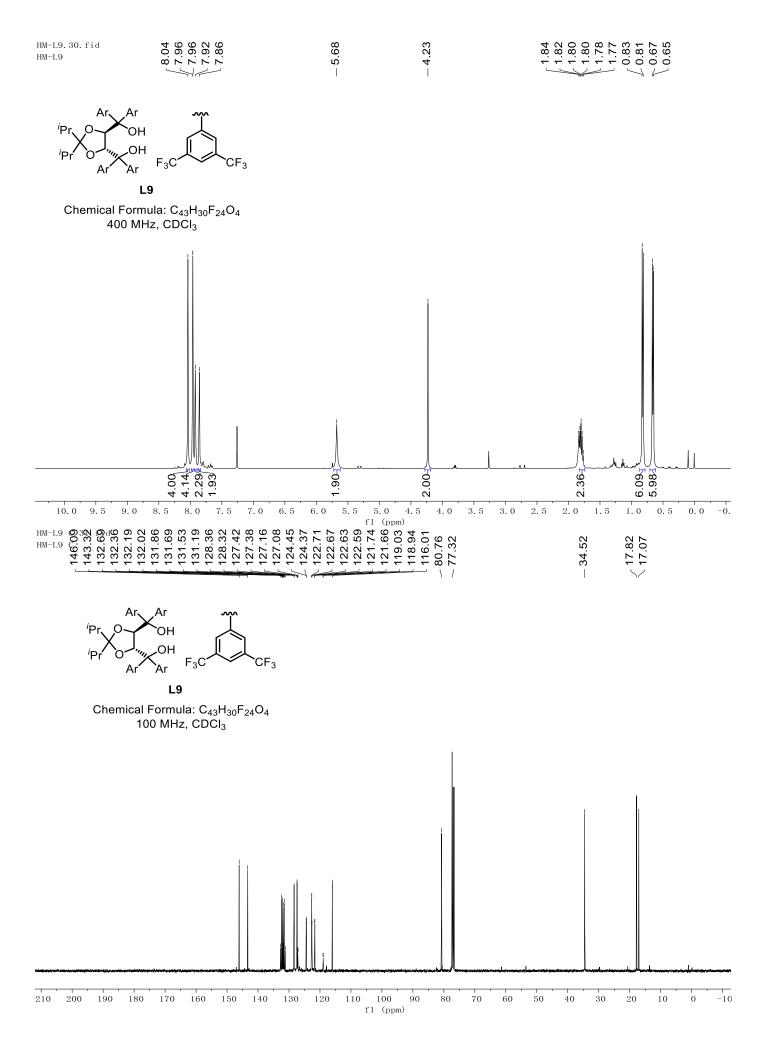




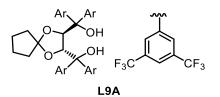




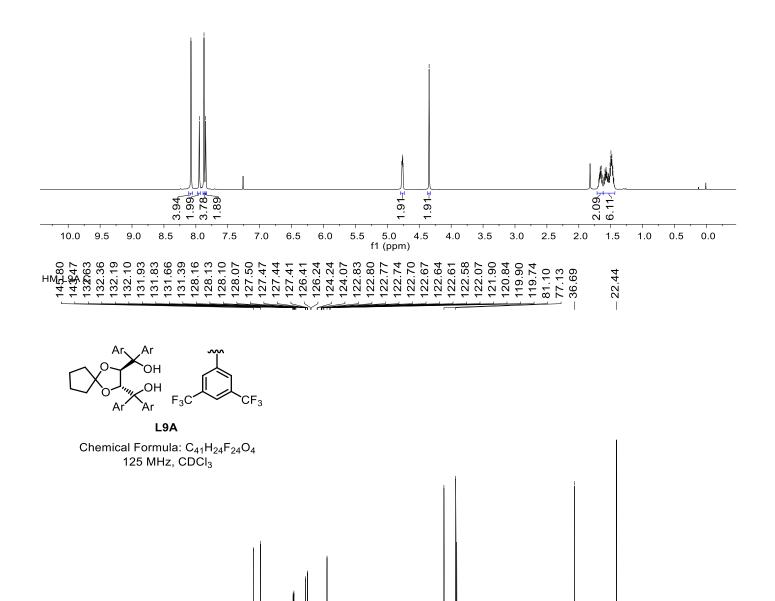


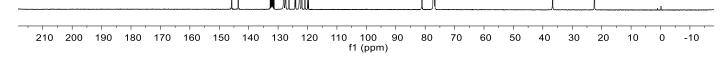


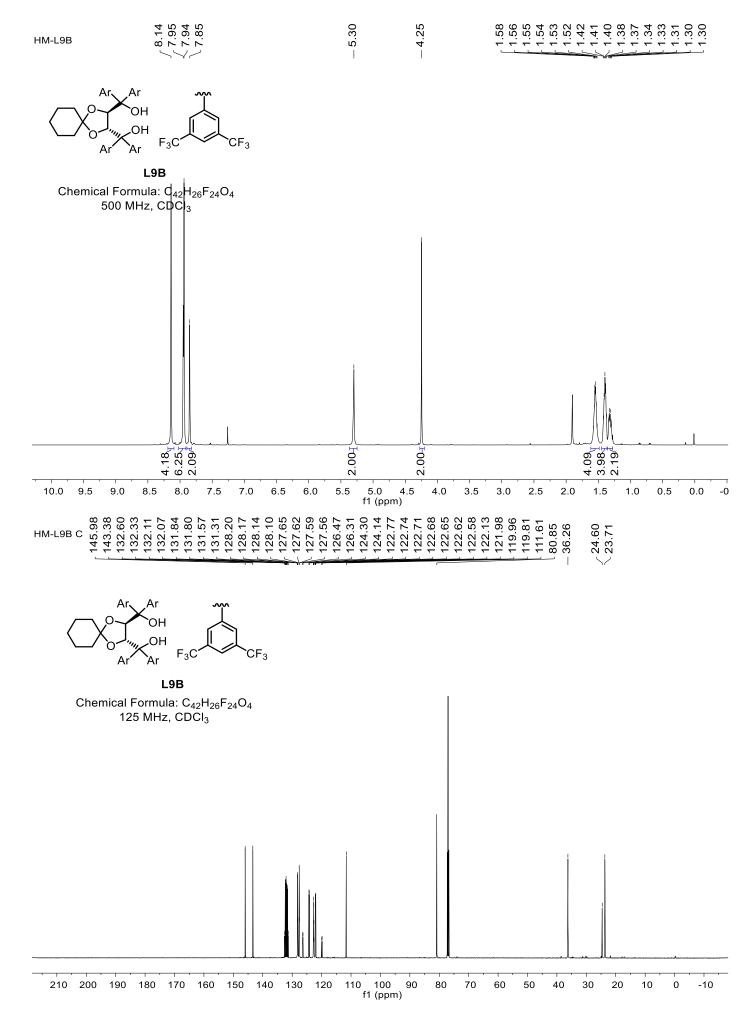
 	 .55 .55 .55 .55 .55 .55 .55 .55 .55 .55



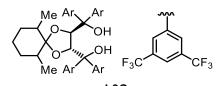
Chemical Formula: C₄₁H₂₄F₂₄O₄ 500 MHz, CDCl₃



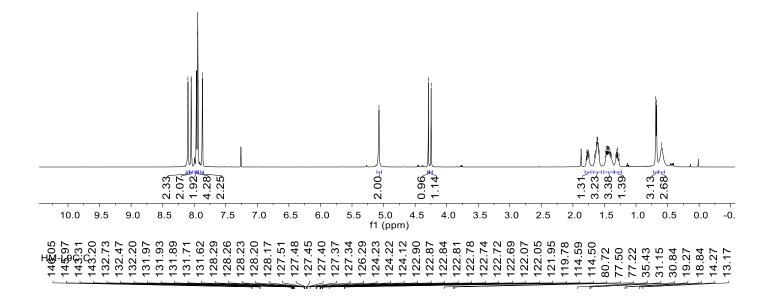


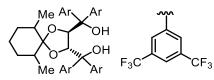




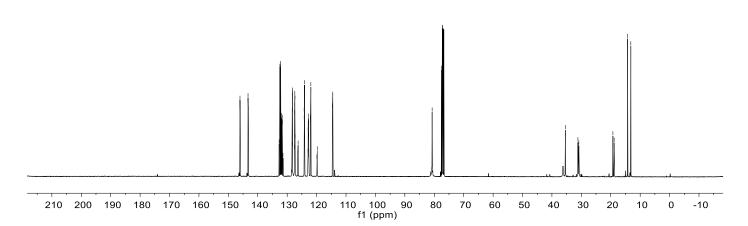


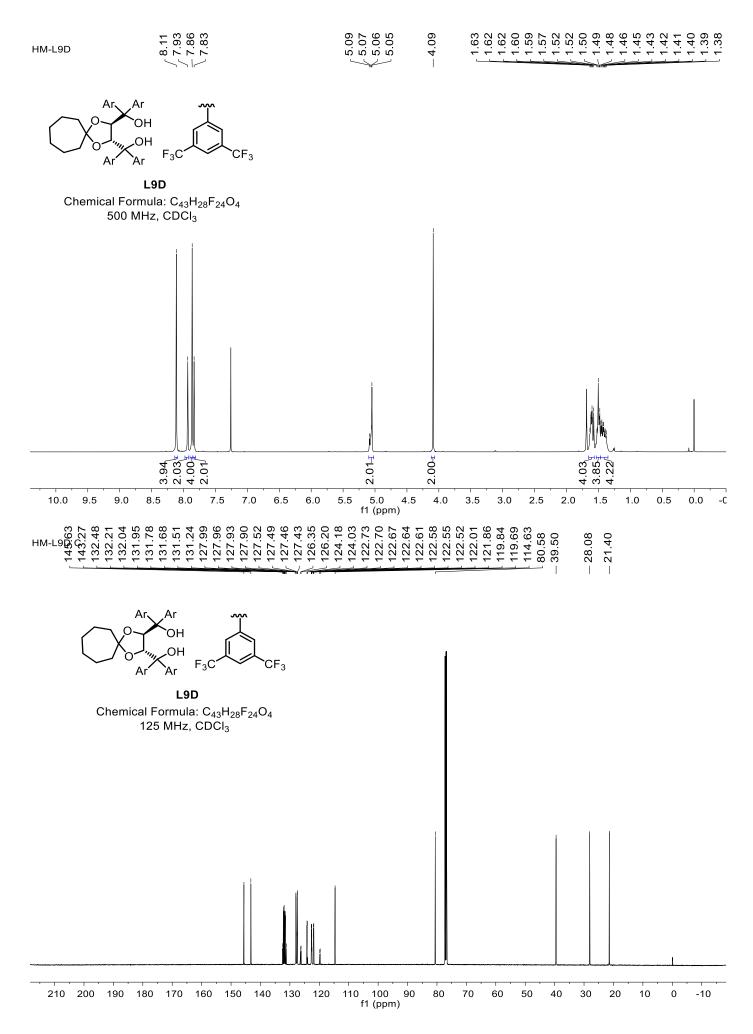
L9C Chemical Formula: C₄₄H₃₀F₂₄O₄ 500 MHz, CDCl₃

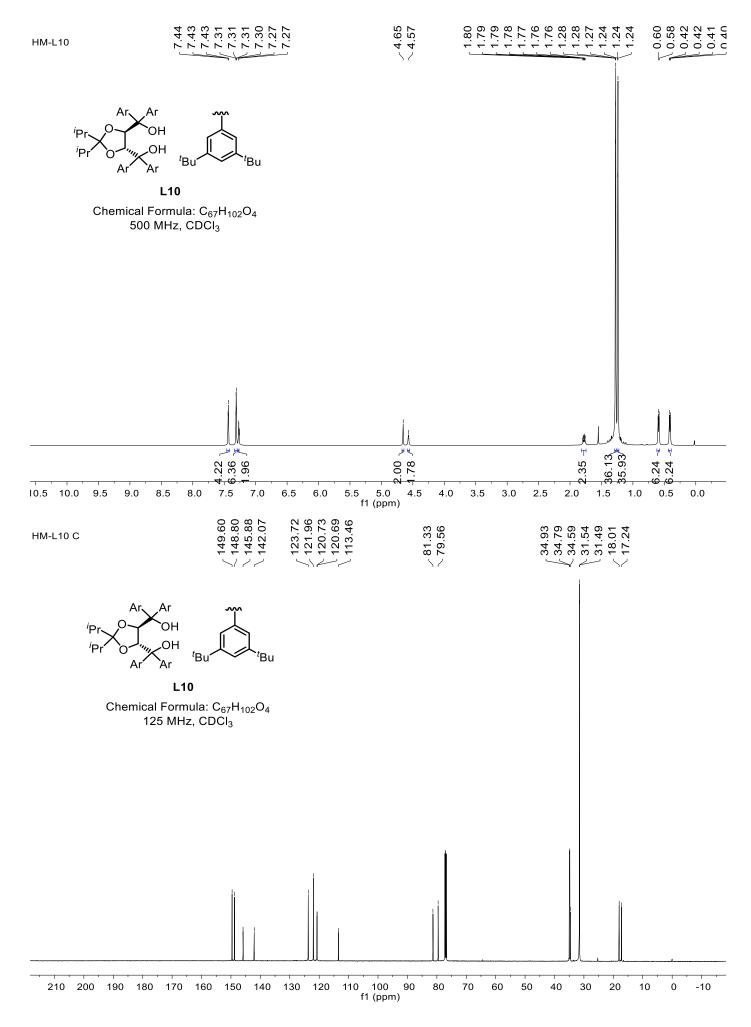


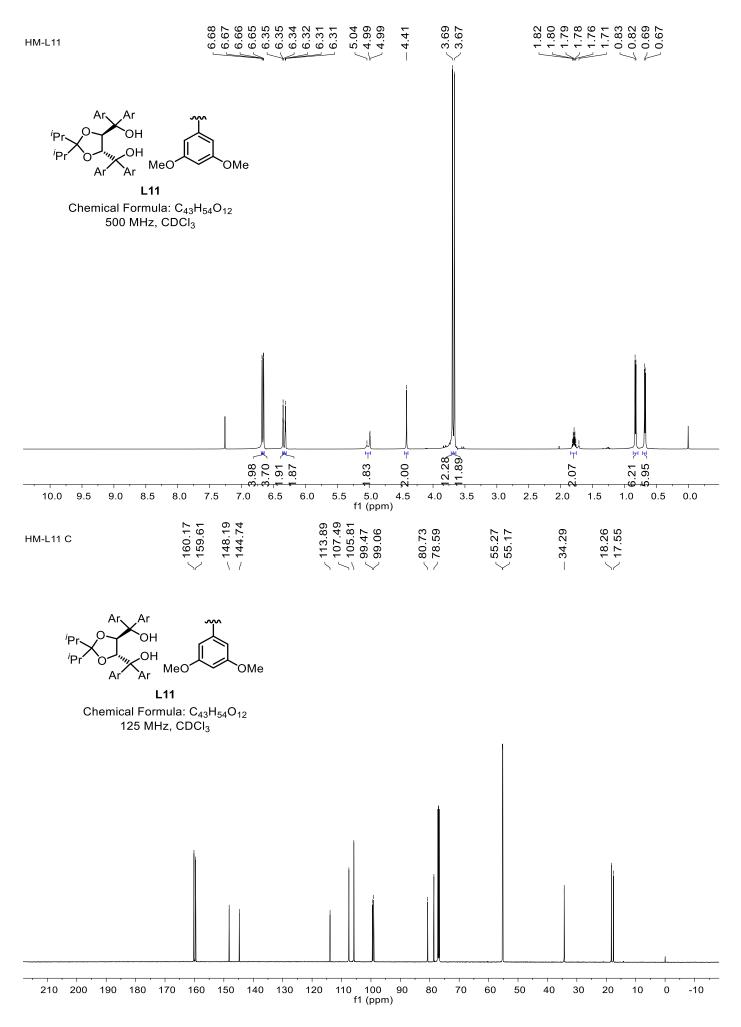


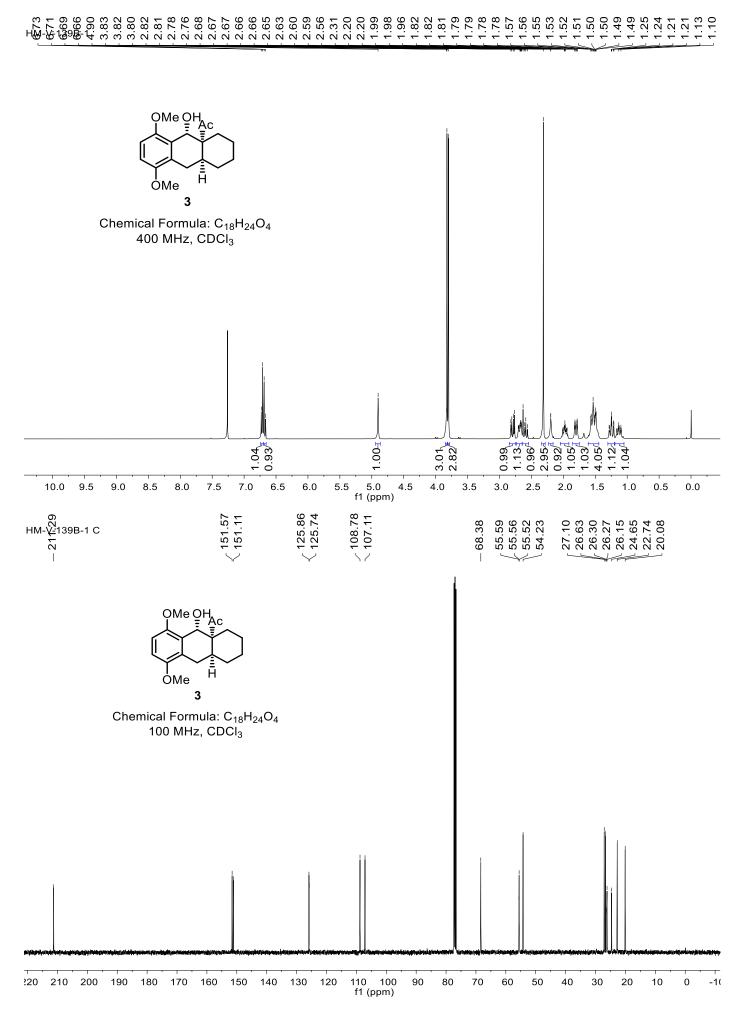
 $\begin{array}{c} \textbf{L9C}\\ \textbf{Chemical Formula: } C_{44}H_{30}F_{24}O_{4}\\ \textbf{125 MHz, CDCI}_{3} \end{array}$

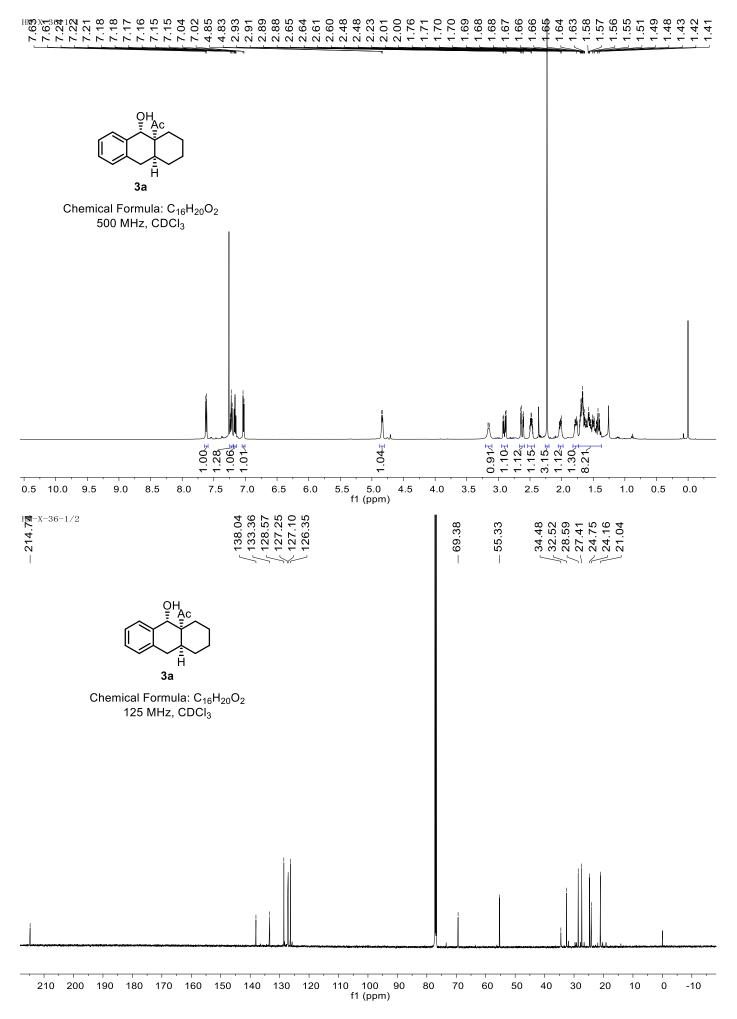


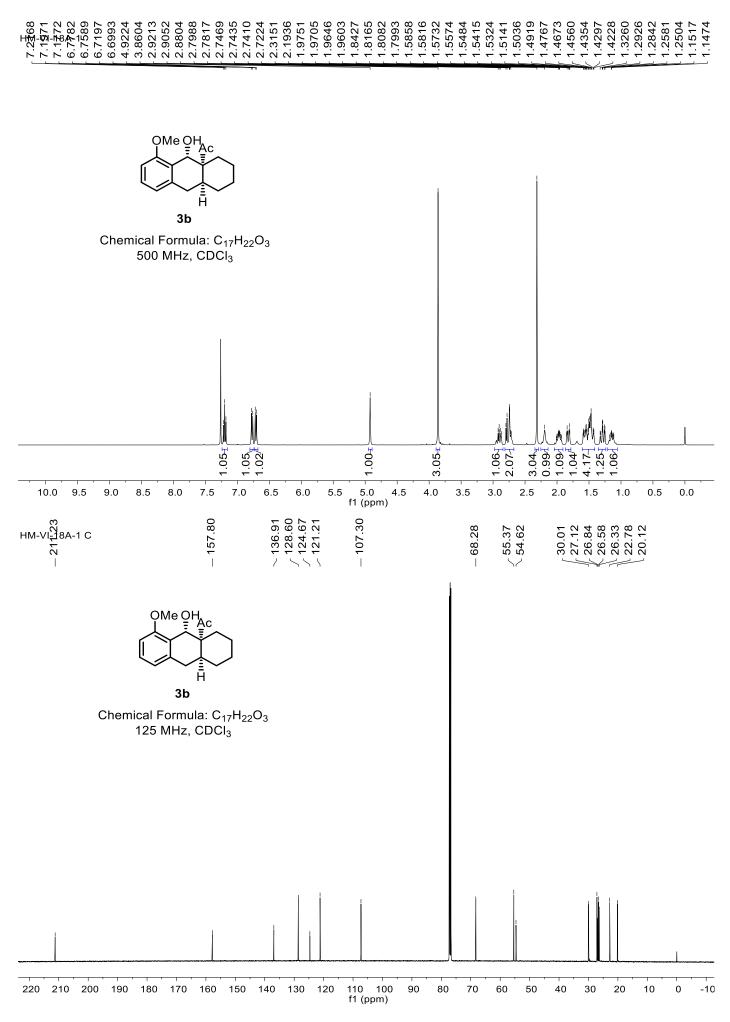


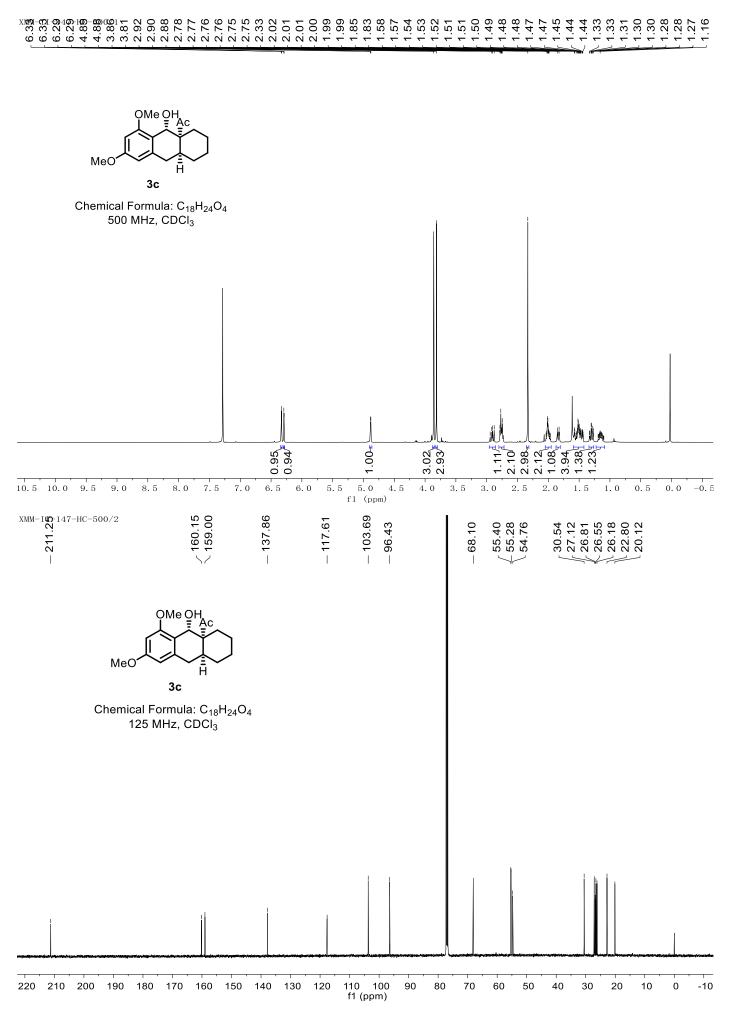


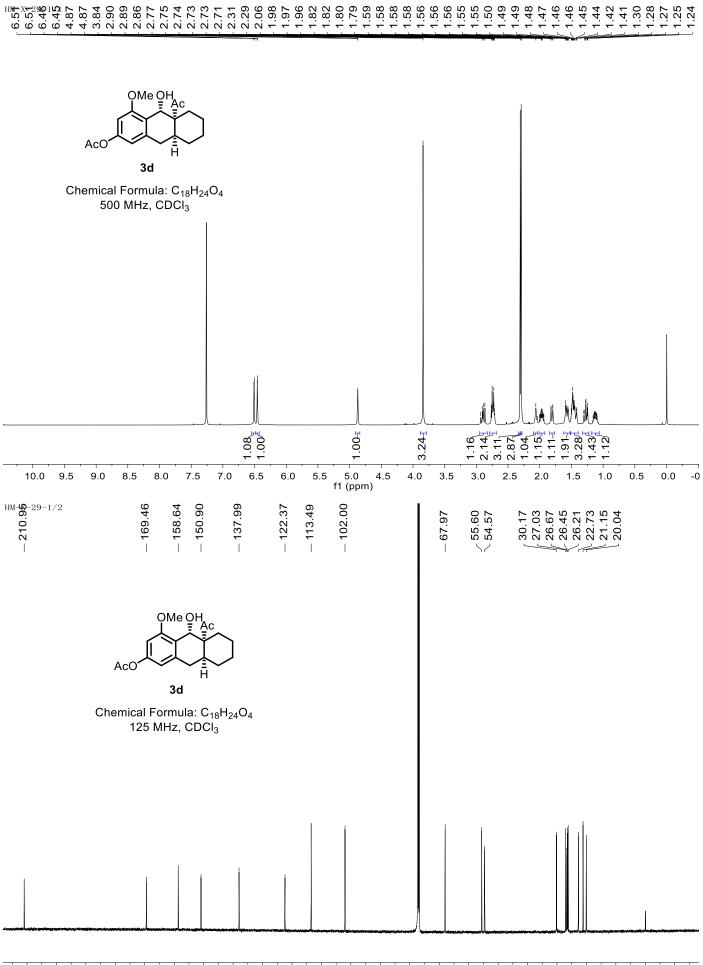




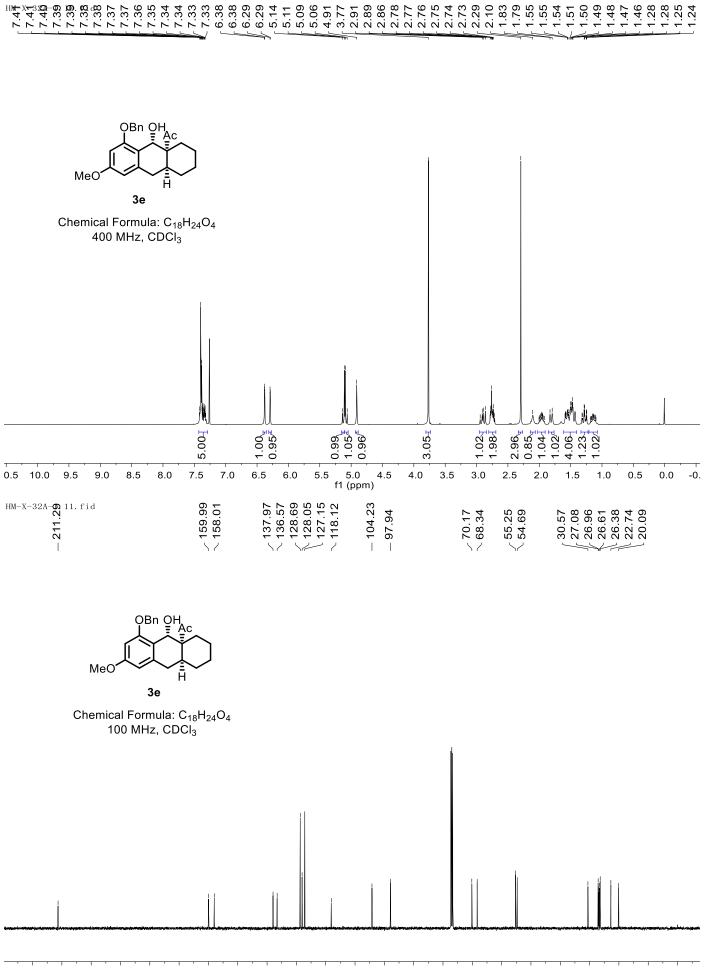




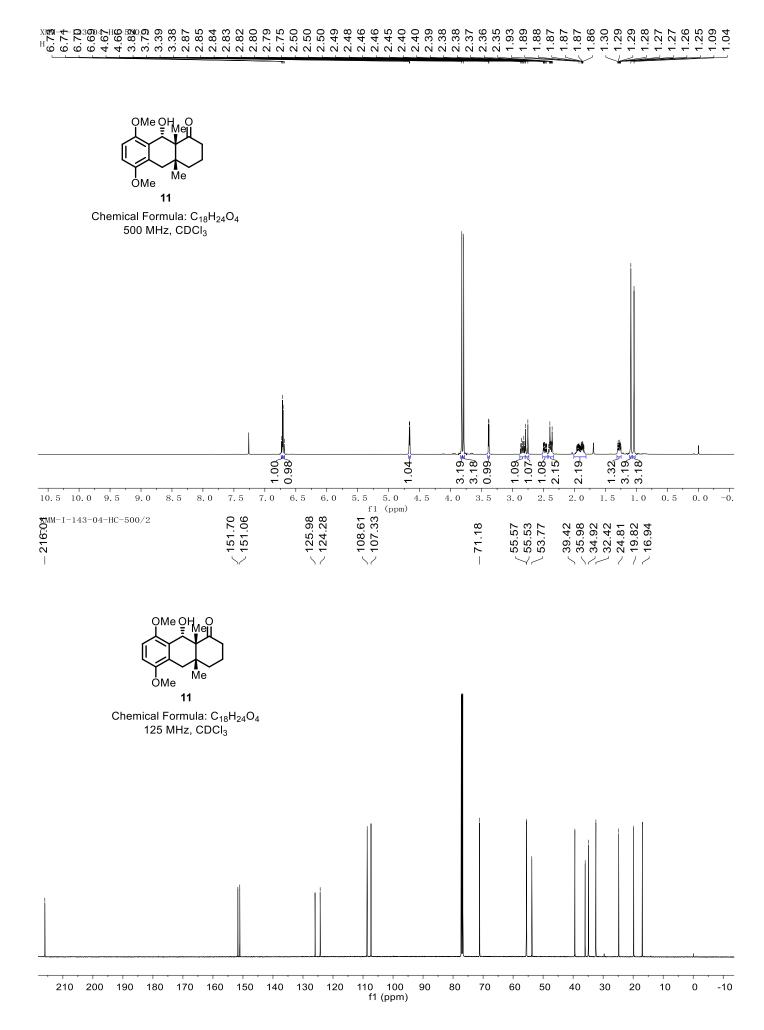


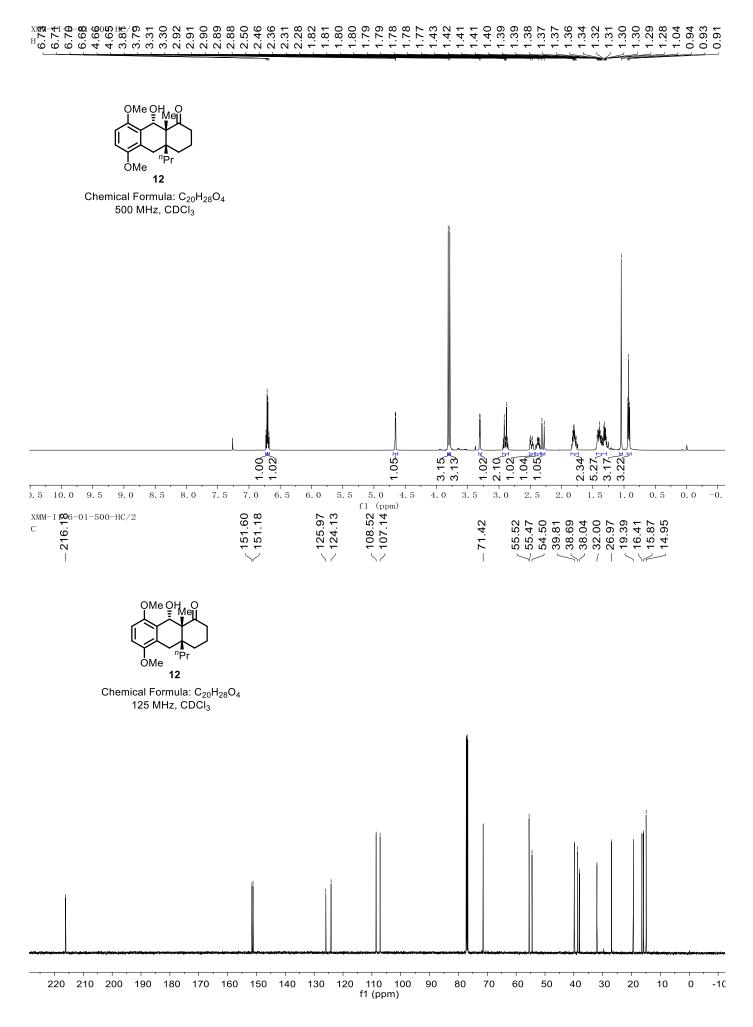


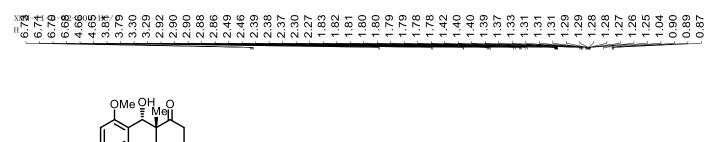
-10 f1 (ppm)



---120 11υ f1 (ppm)

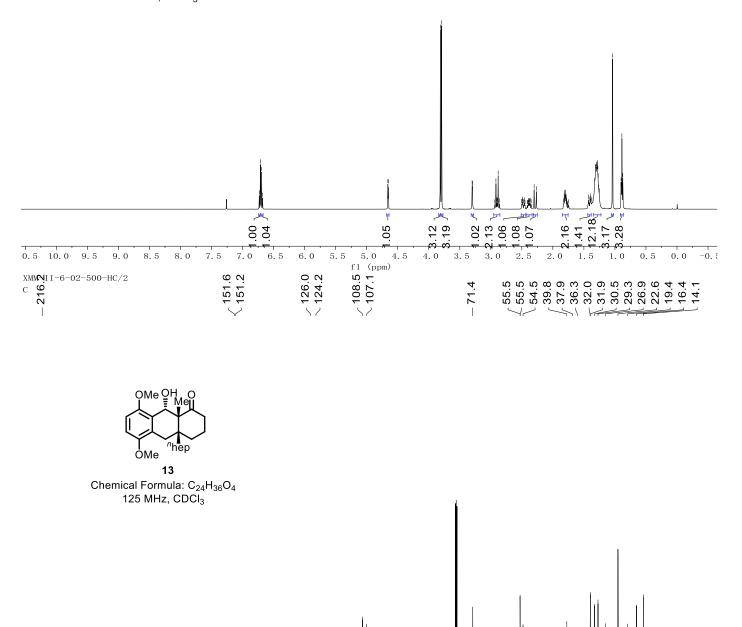


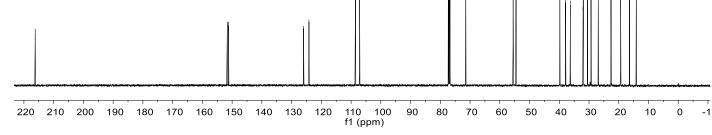


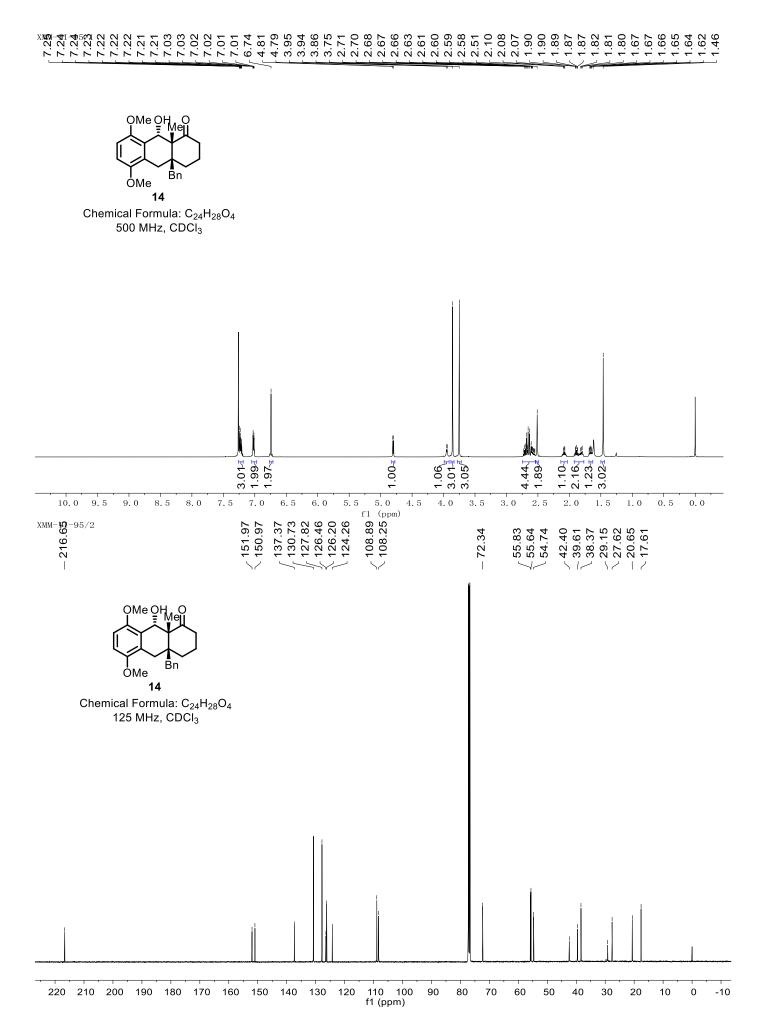


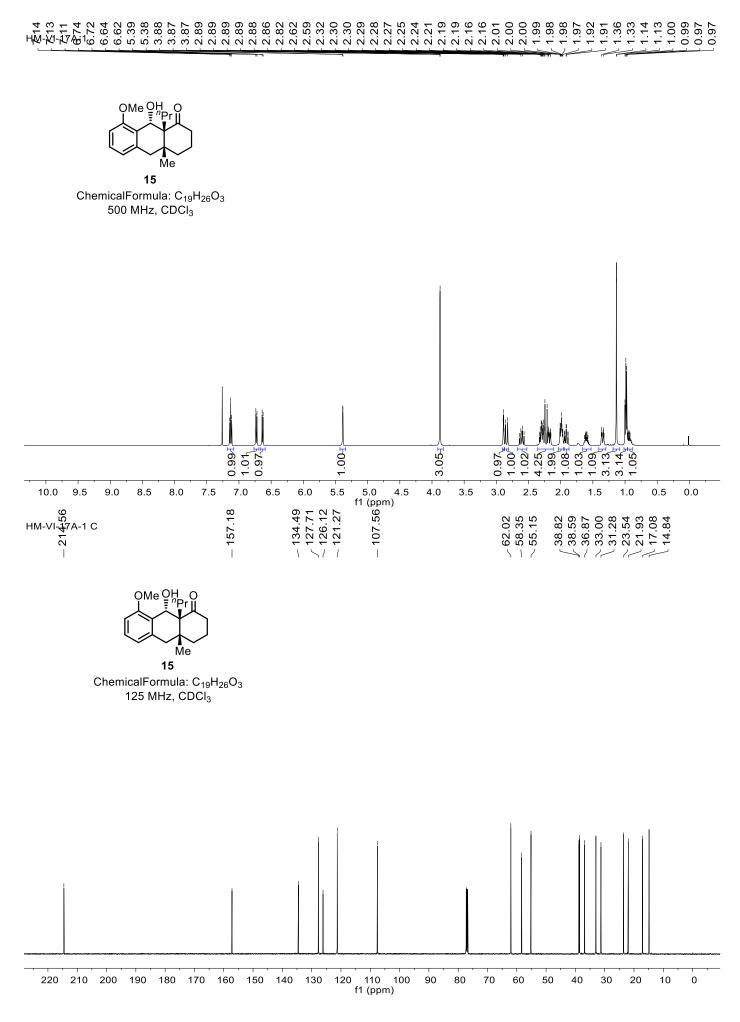


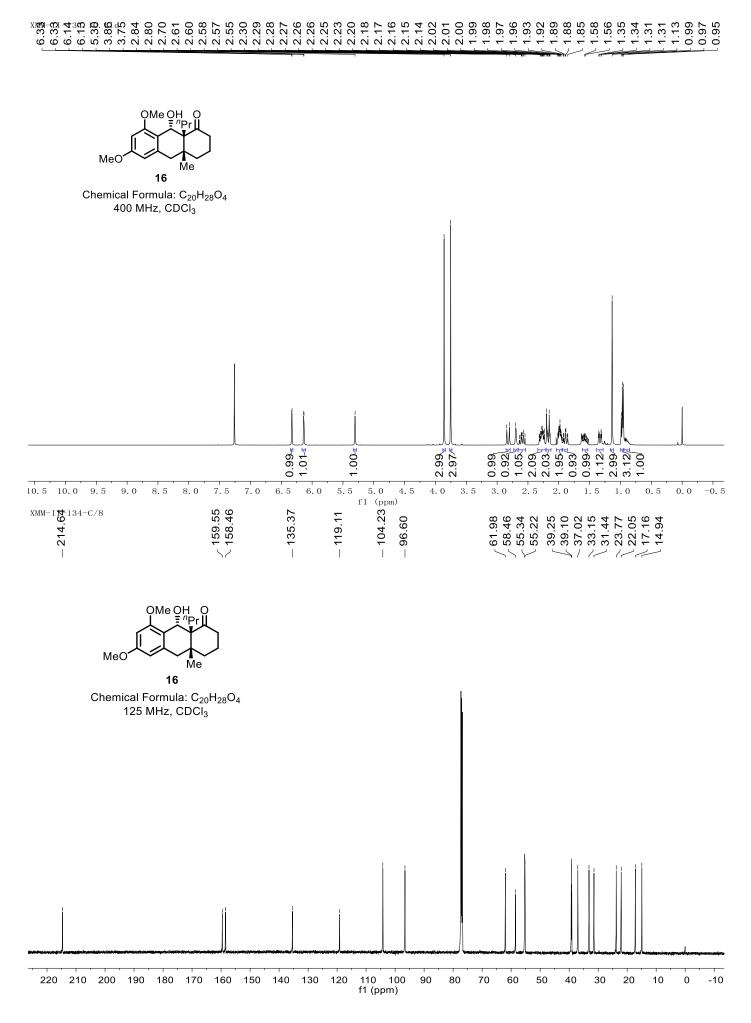
 $\begin{array}{c} \mbox{Chemical Formula: } C_{24} H_{36} O_4 \\ 500 \mbox{ MHz, } \mbox{CDCI}_3 \end{array}$

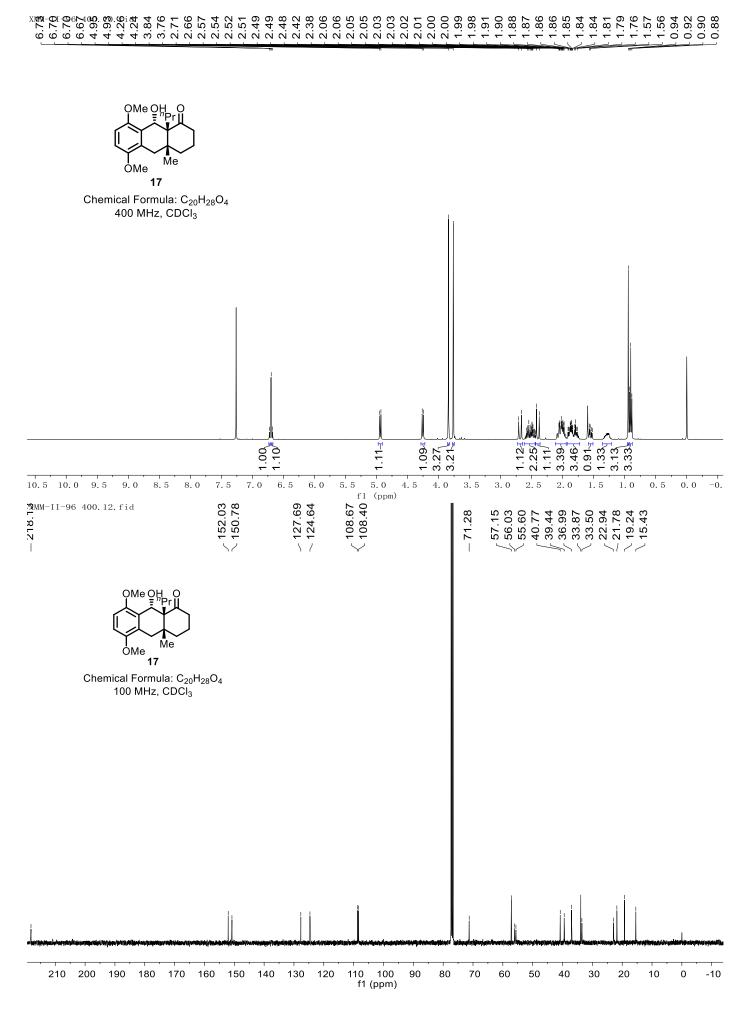


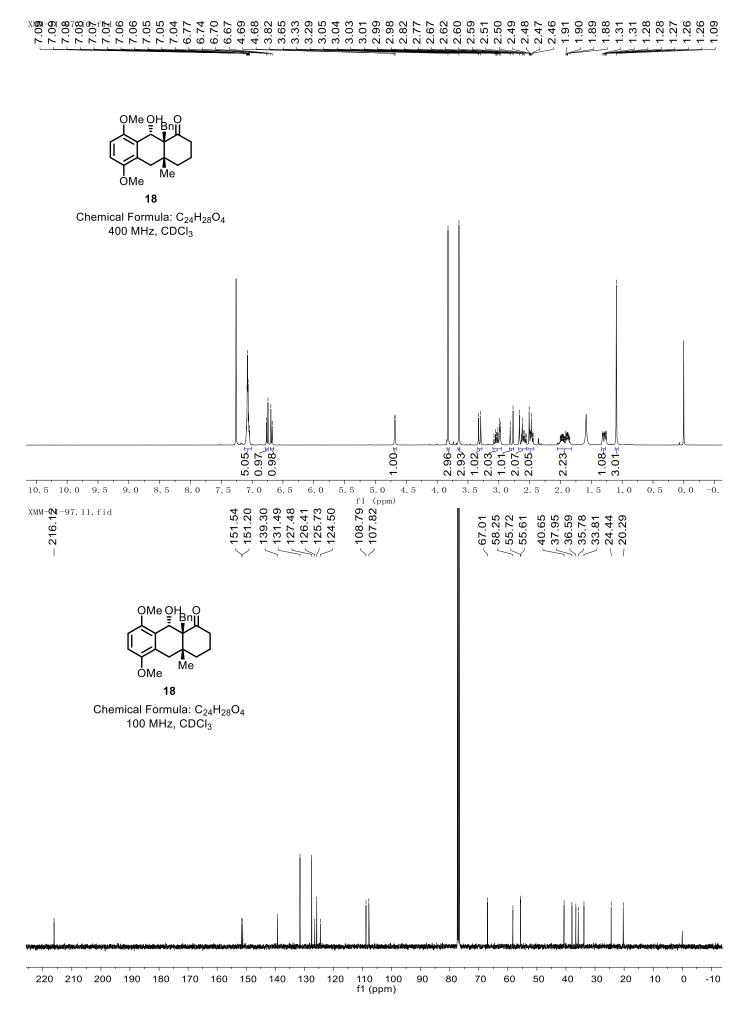


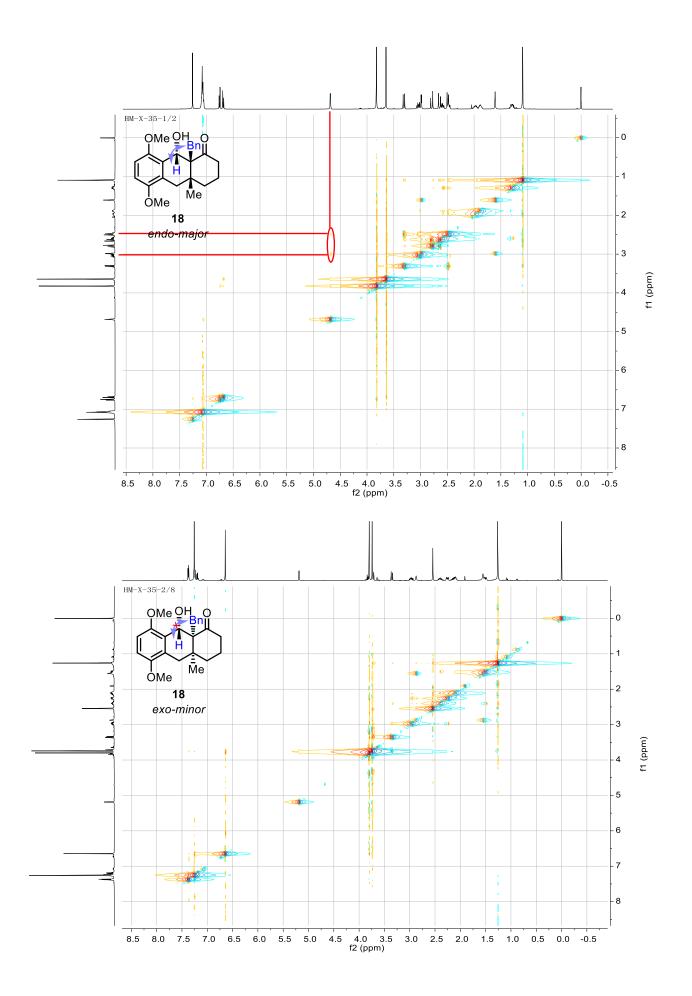






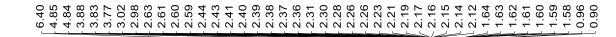


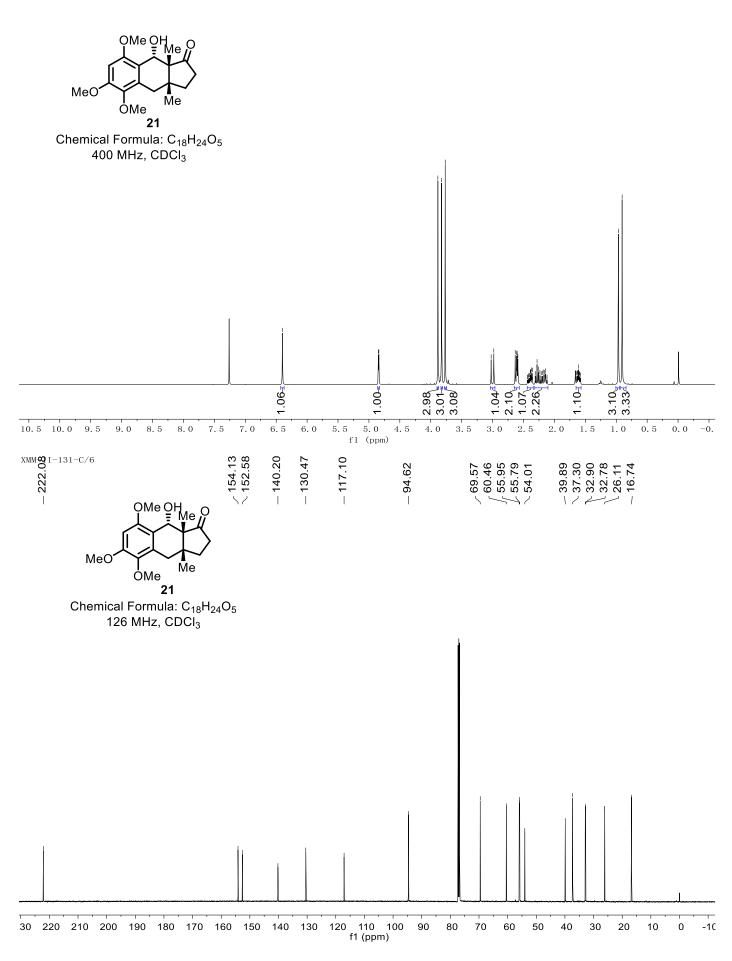


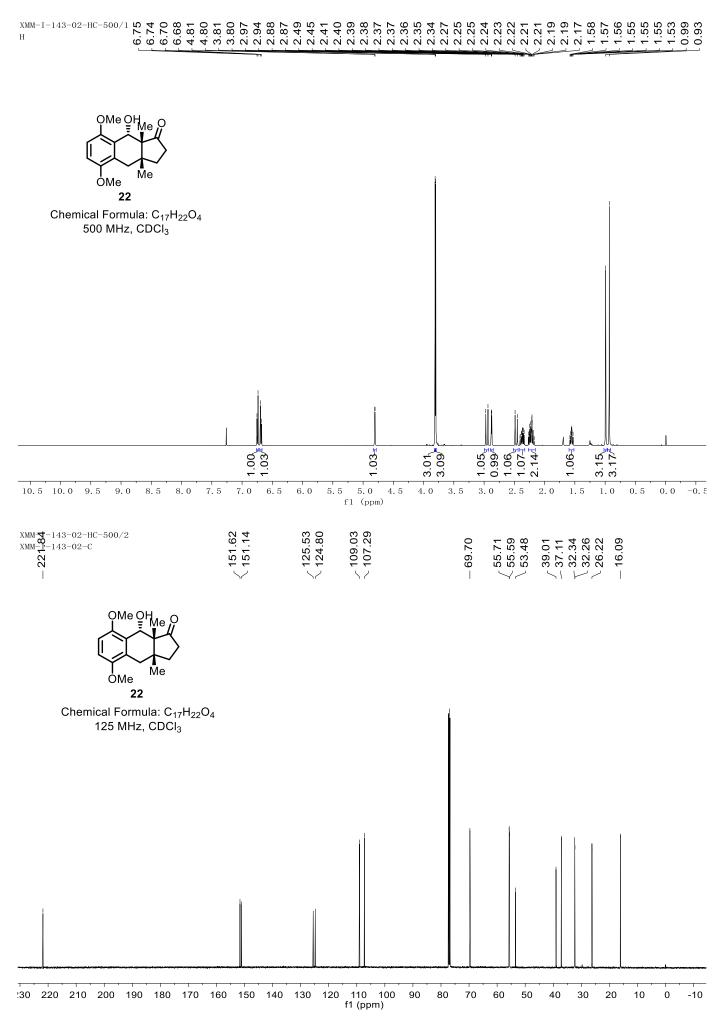


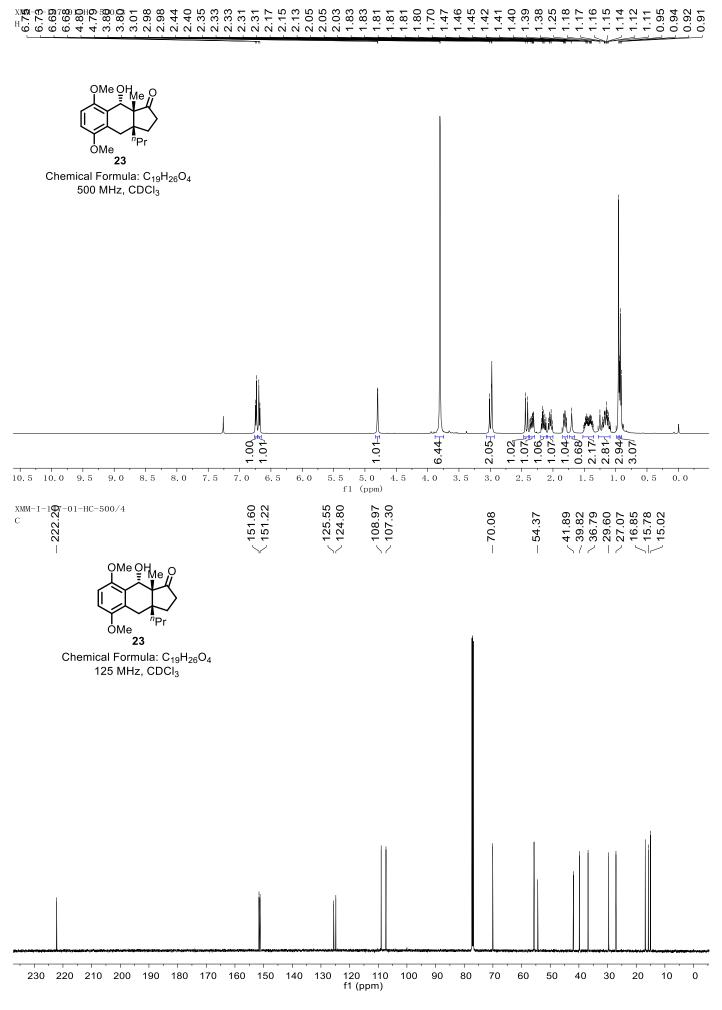
HM-IV-17B-1 QMe QH Ţ_Me C Ŵе 19 Chemical Formula: C₁₆H₂₀O₃ 400 MHz, CDCl₃ 1.031 1.03 1.00-3.15₁ 1.05 0.99 .011 3.02 3.01 1.05 0.91 00. f1 (ppm) 3.0 4.0 2.5 2.0 1.0 10.0 9.5 7.0 6.0 5.5 3.5 1.5 0.5 9.0 8.5 8.0 7.5 6.5 4.5 0.5 0.0 -0 - 136.58 7 128.68 7 124.63 - 121.31 -40.02
38.97
38.97
37.26
32.56
25.95
16.62 157.61 00 HM-IV-17₿-1 C 55.44 55.41 54.26 69.61 22 1 I L QMe QH ≣ Me 0 Ŵе 19 Chemical Formula: C₁₆H₂₀O₃ 100 MHz, CDCl₃ <u>240 230 220 210 200 190 180 170 160 150 140 130 120 110 100</u> 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

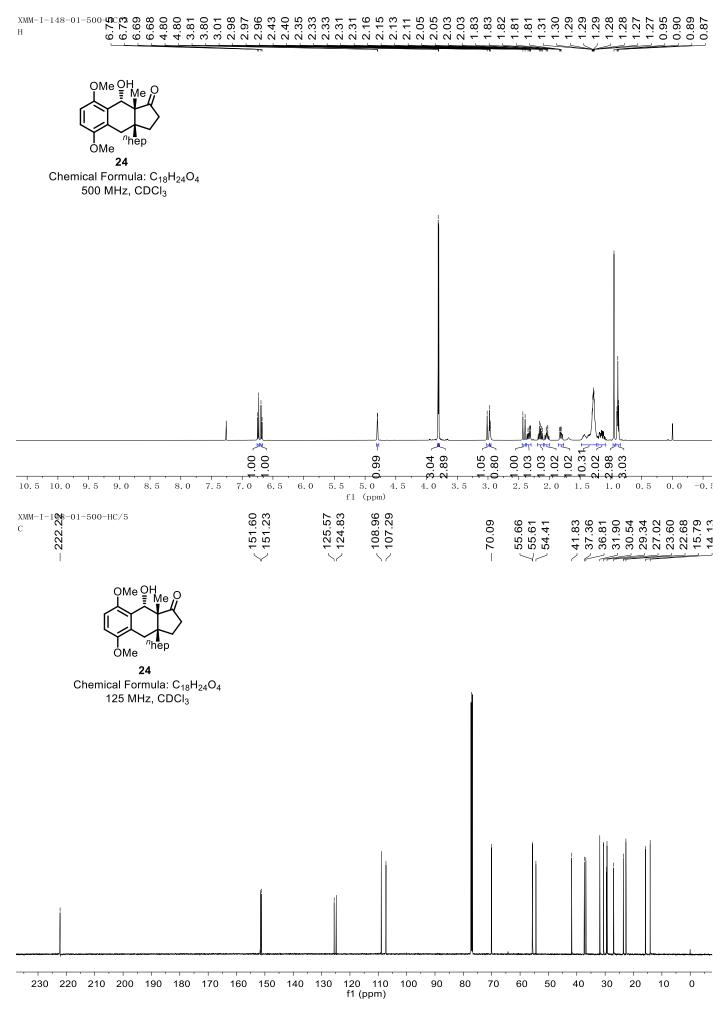


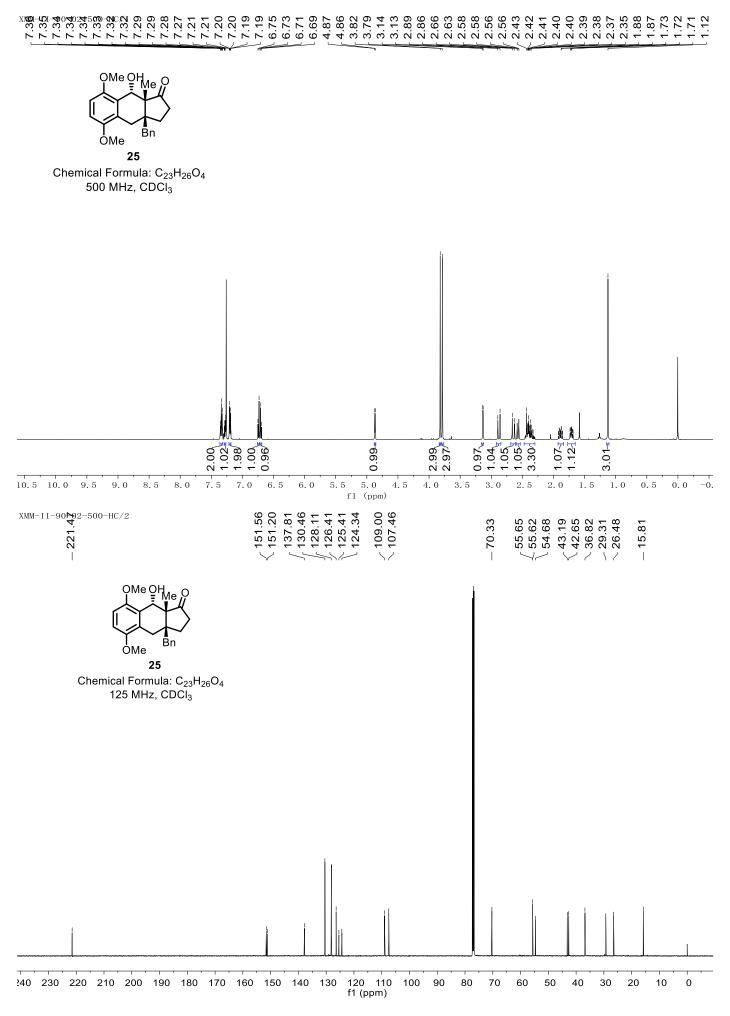


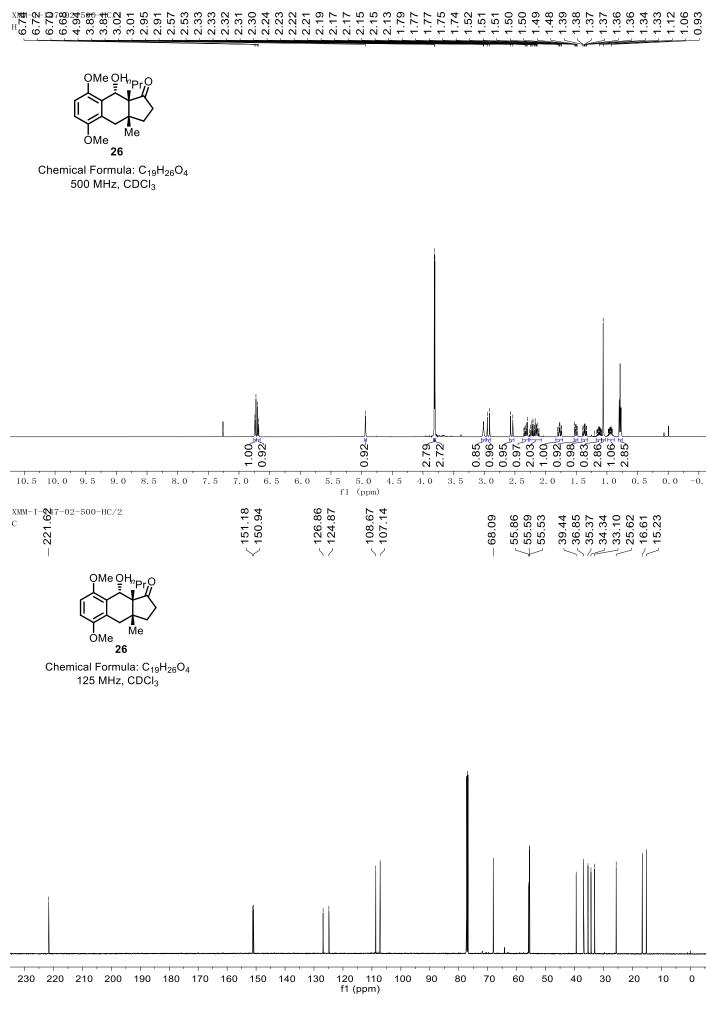


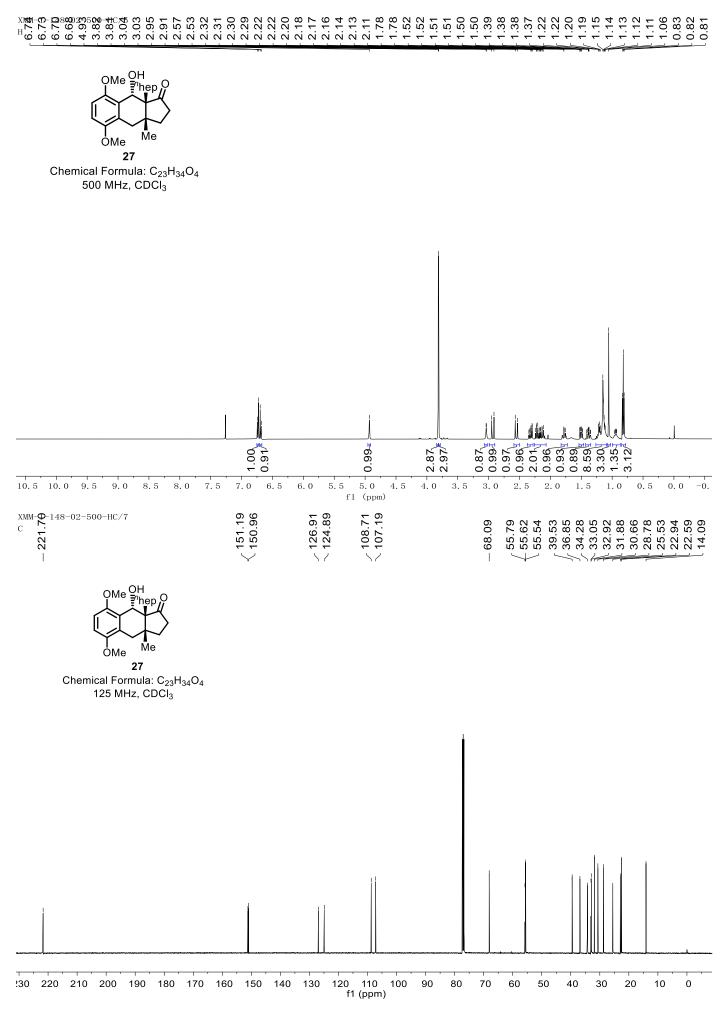


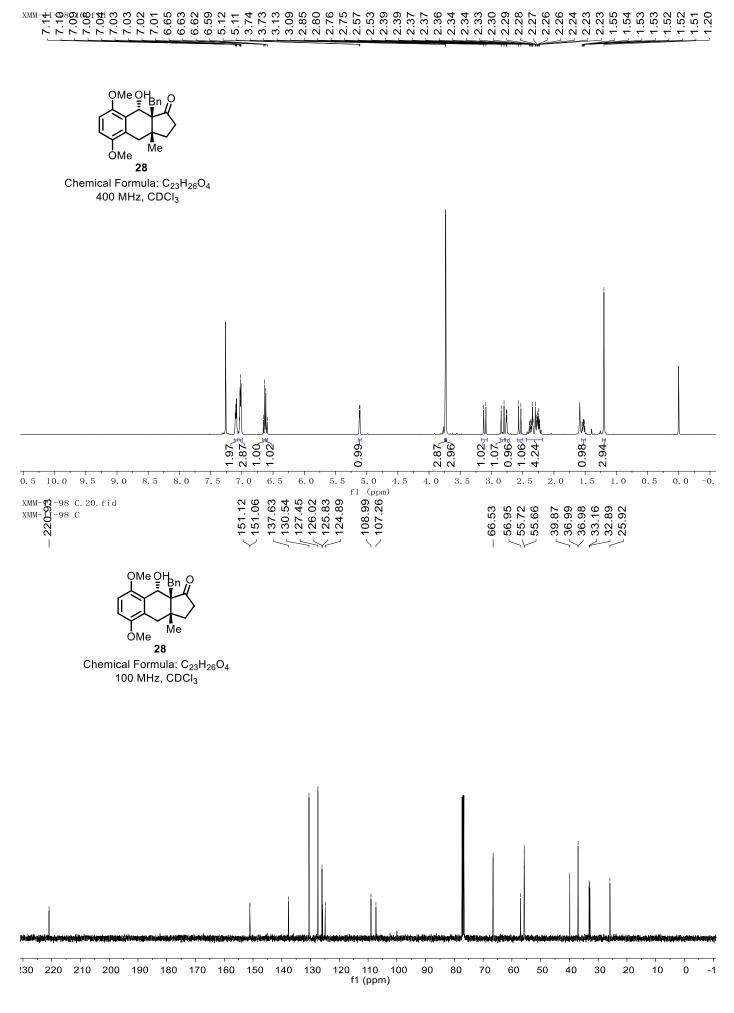


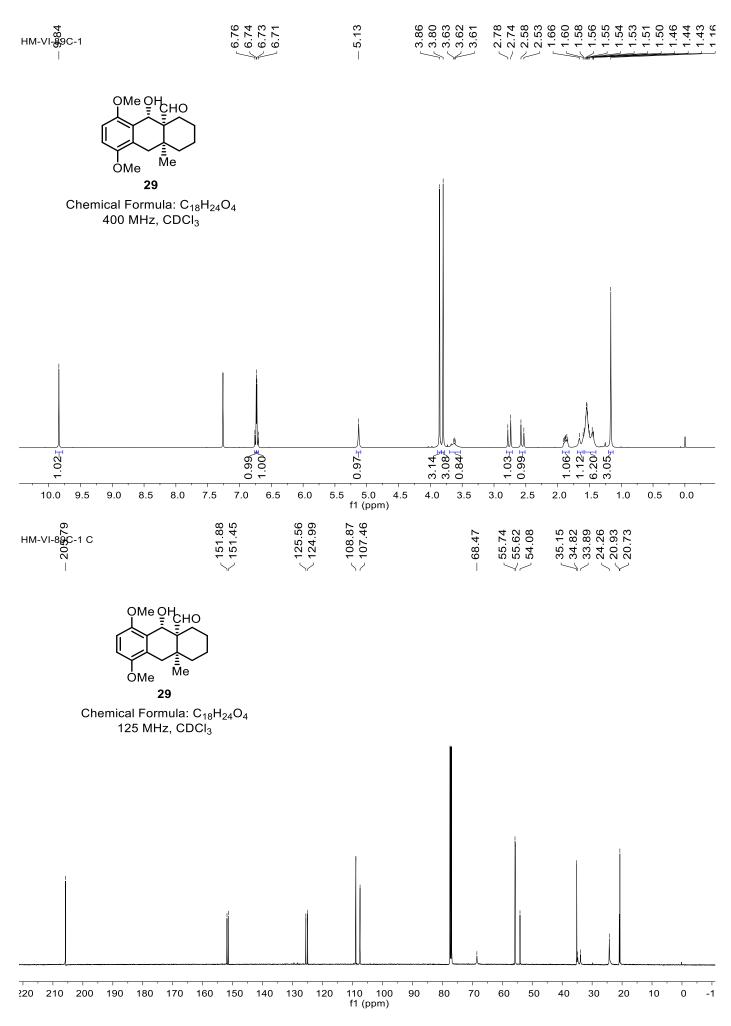


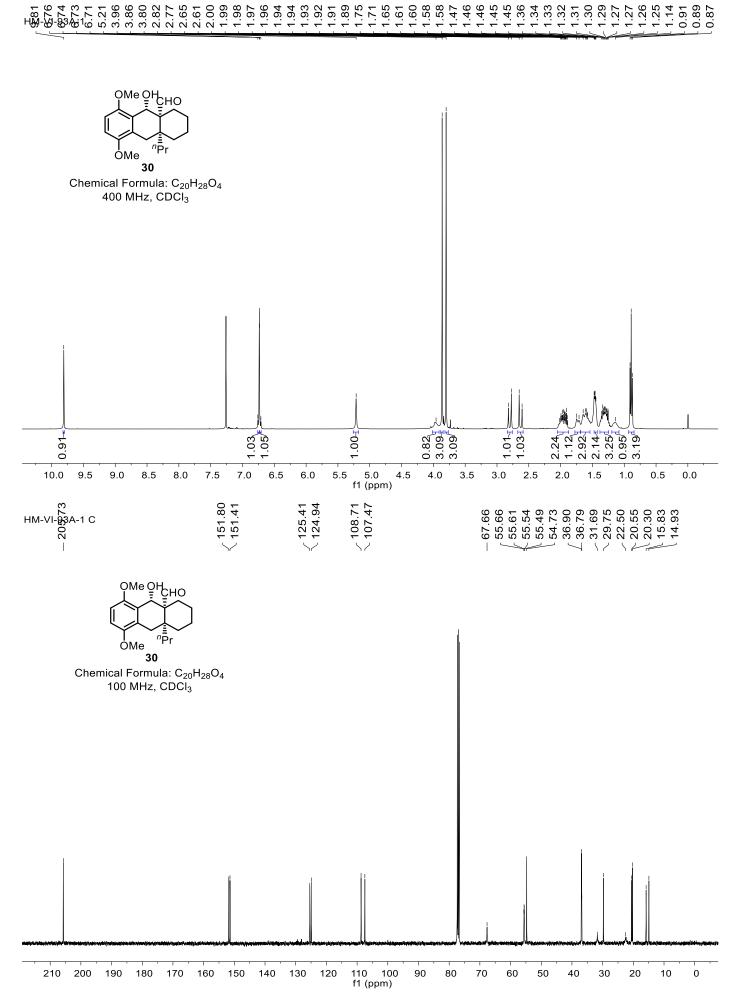


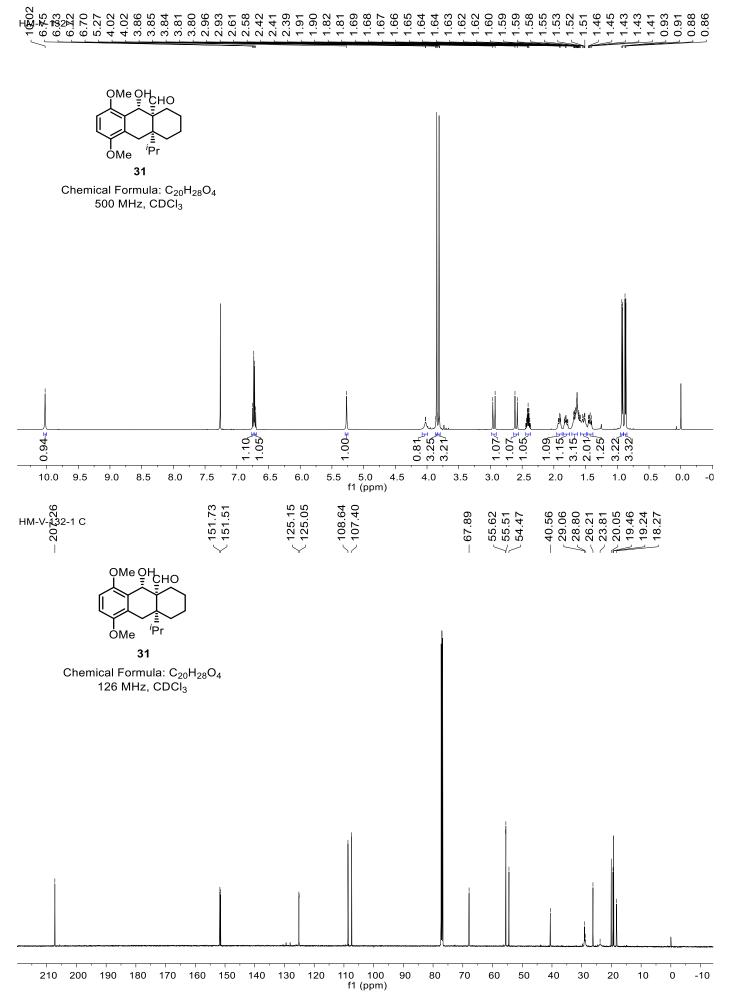


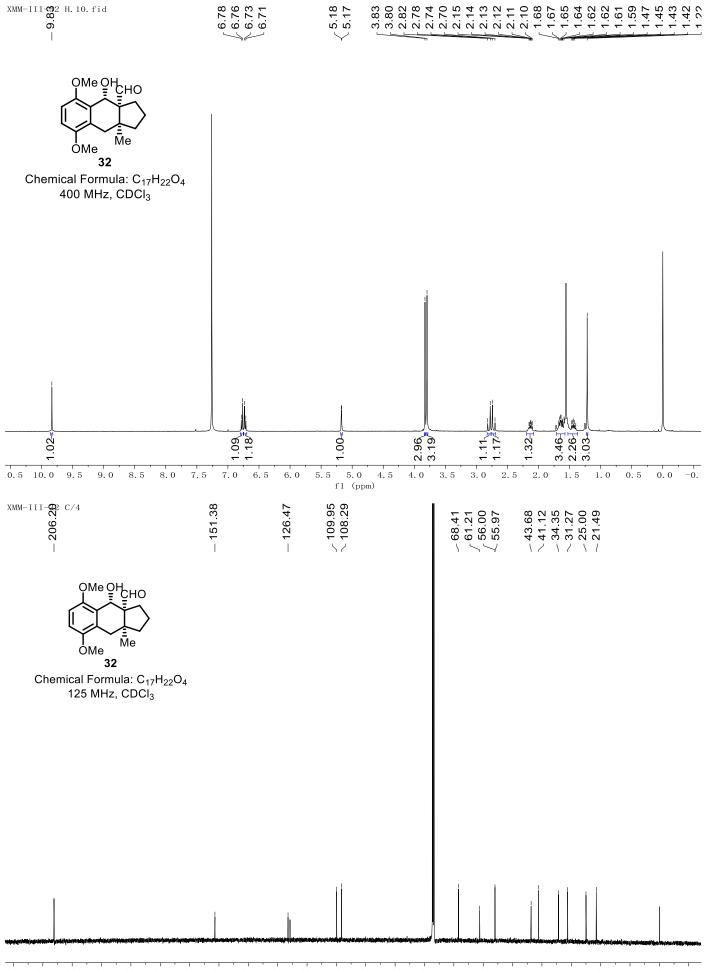




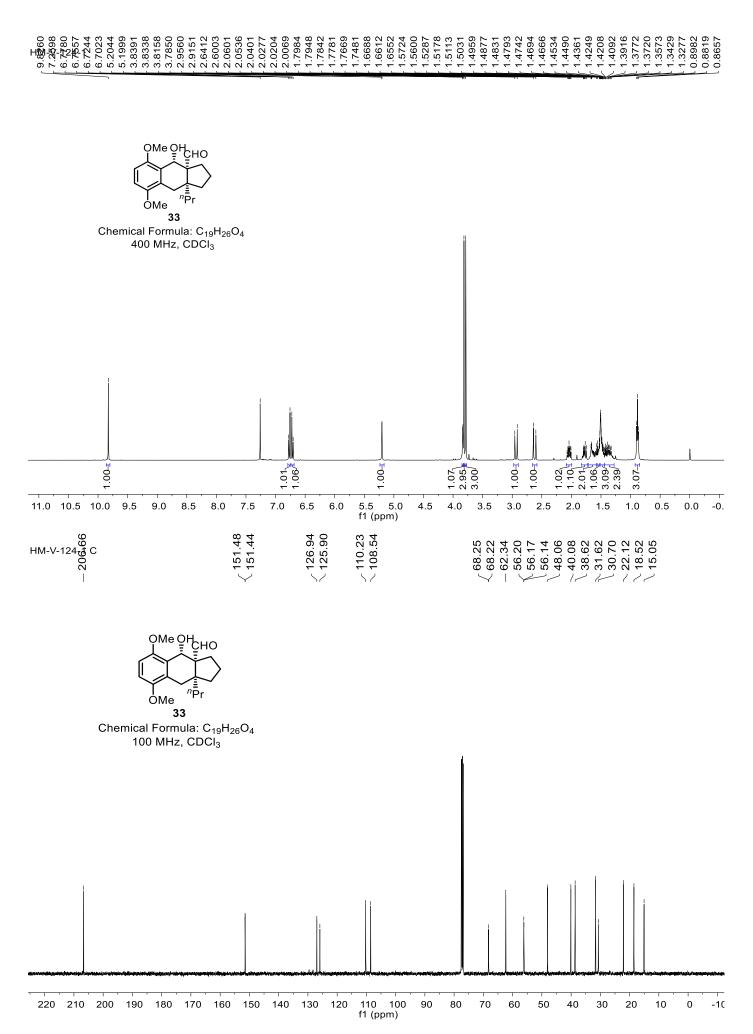


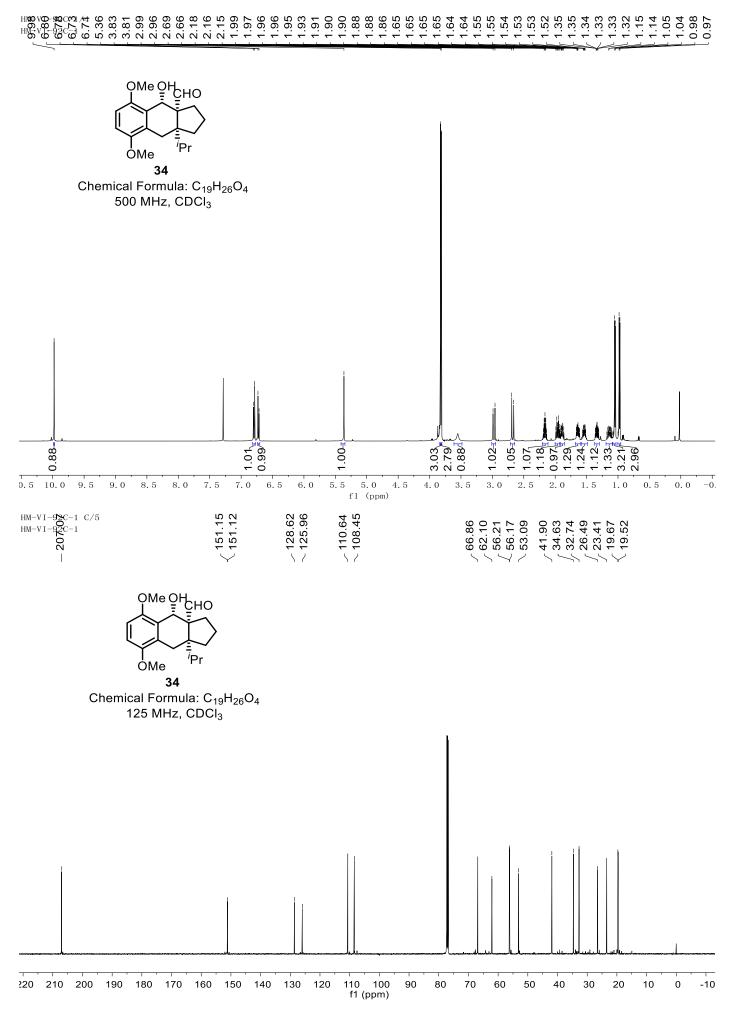


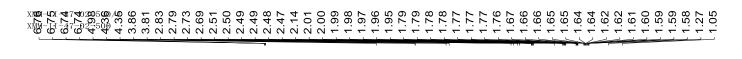


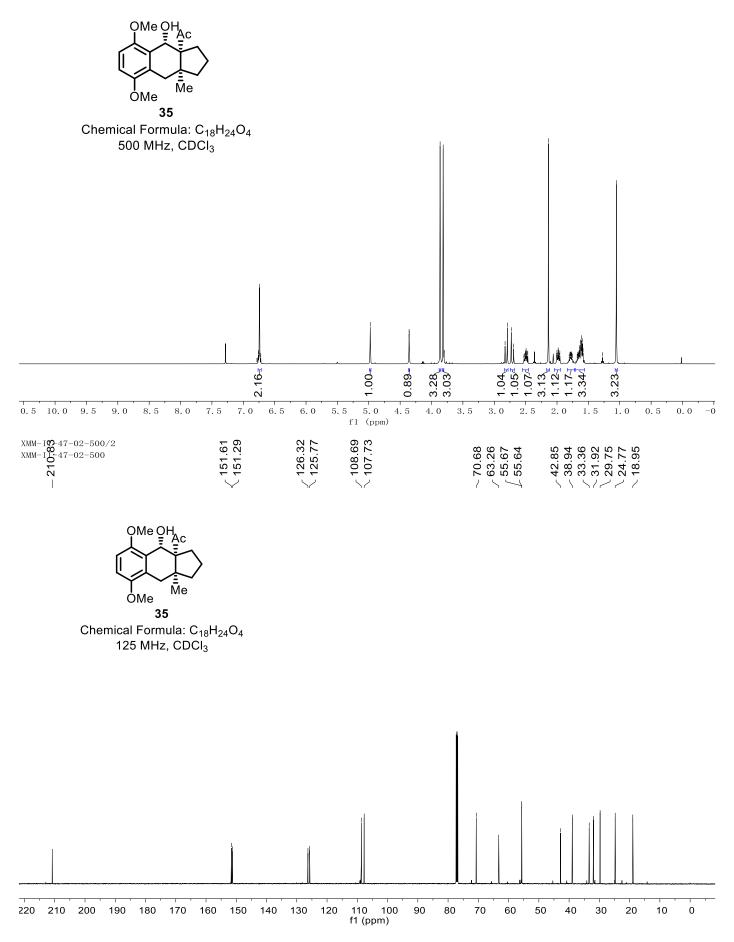


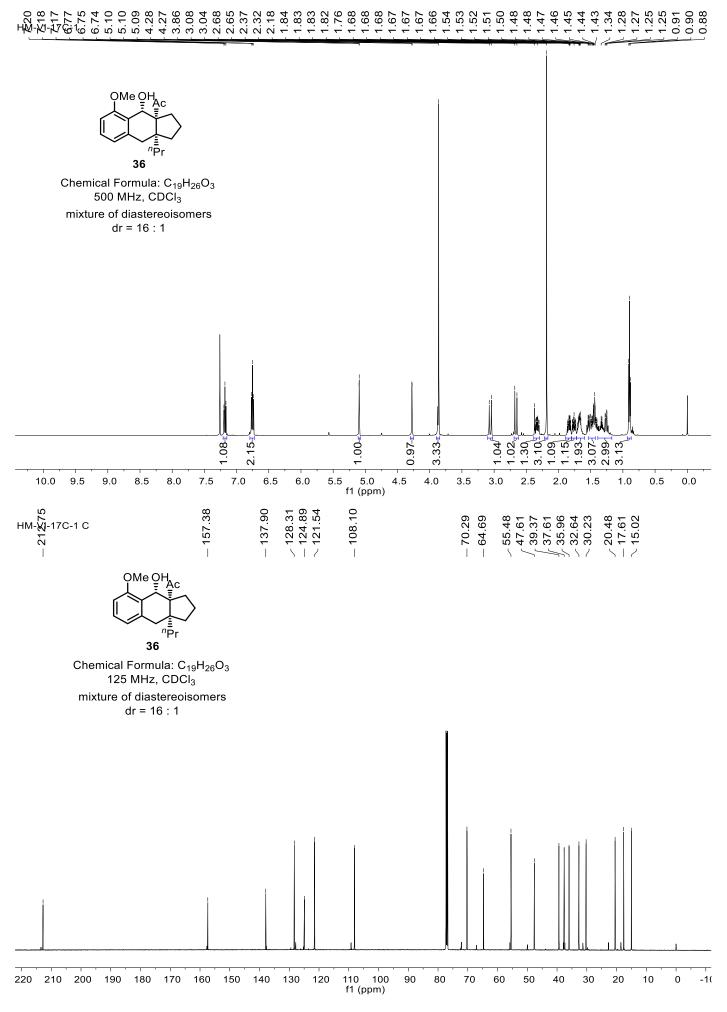
210 200 110 100 -10 f1 (ppm)

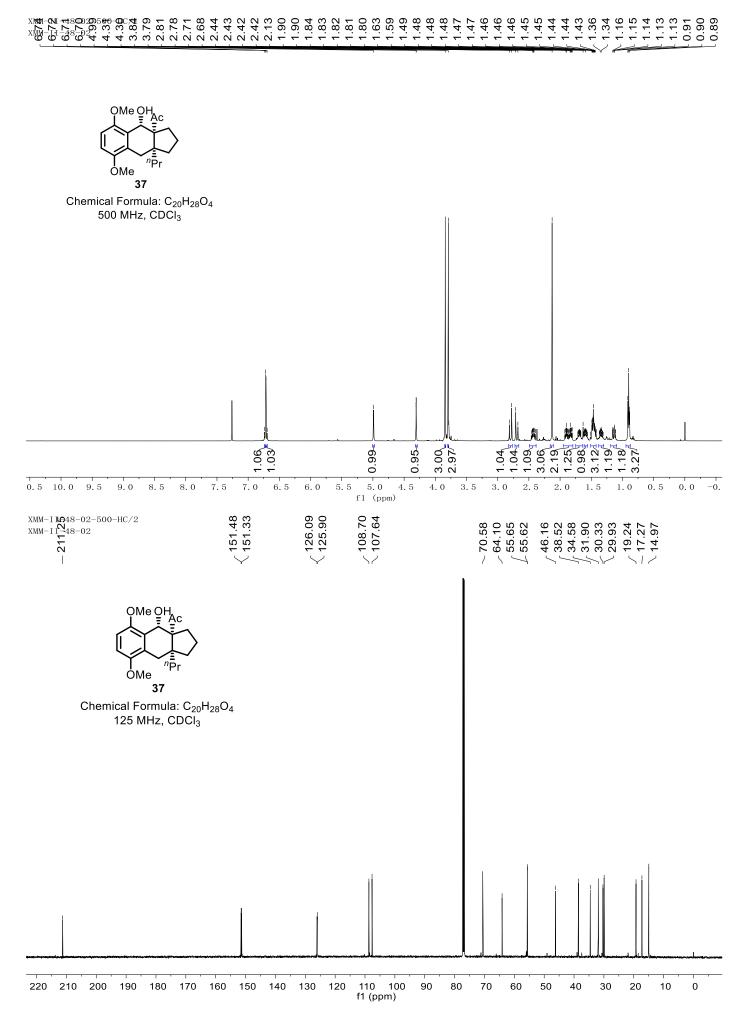


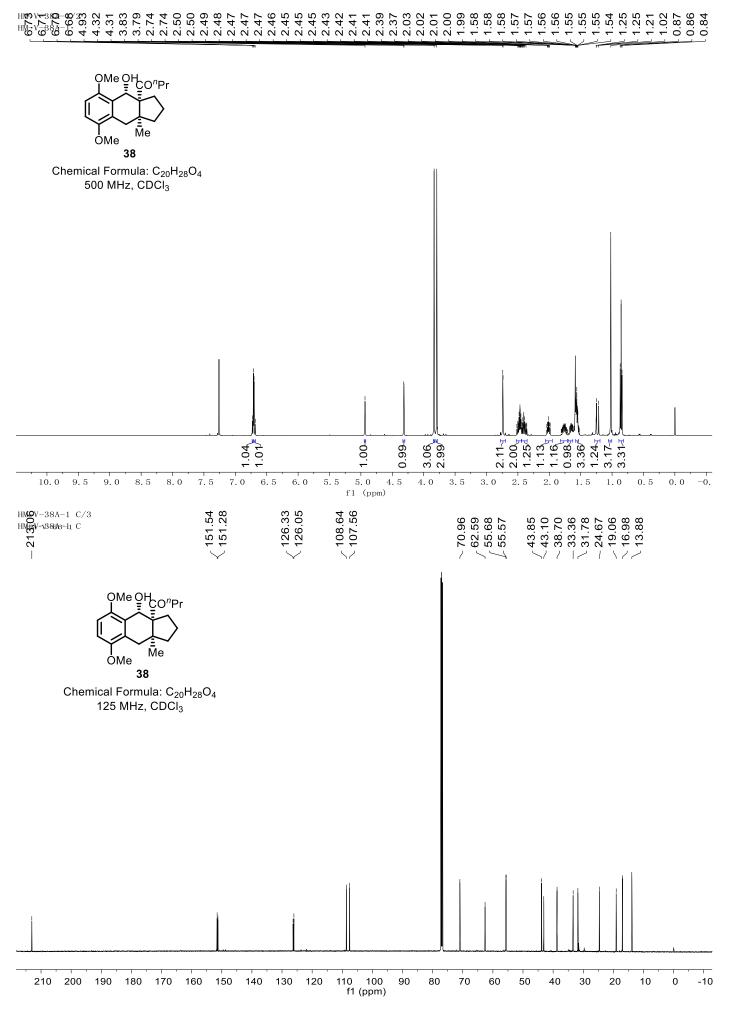


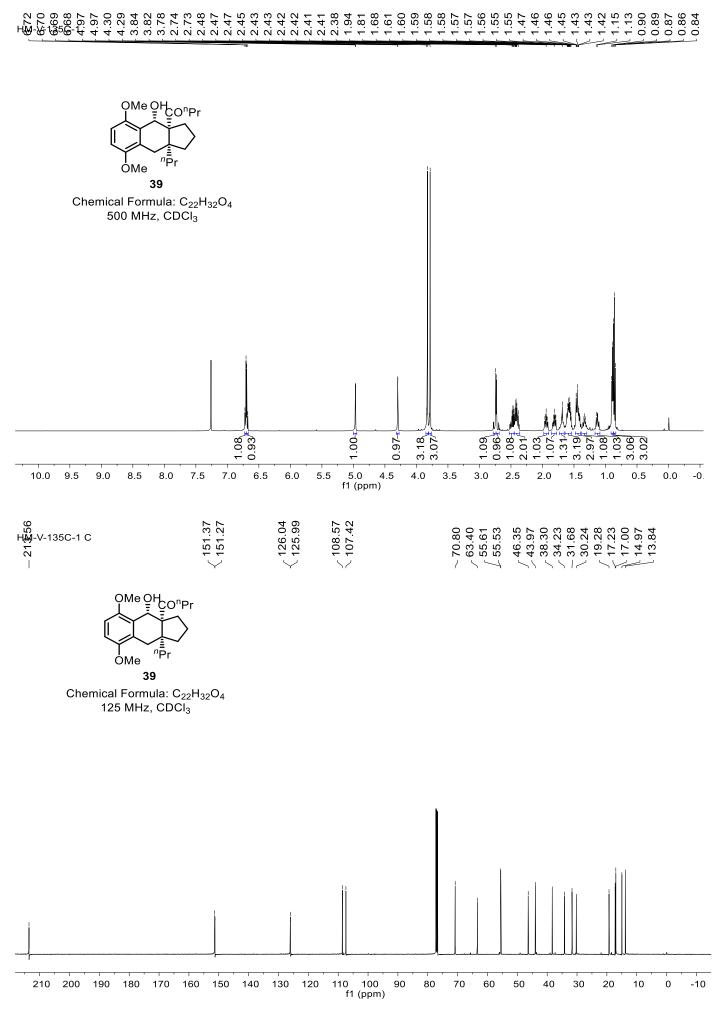


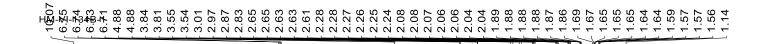


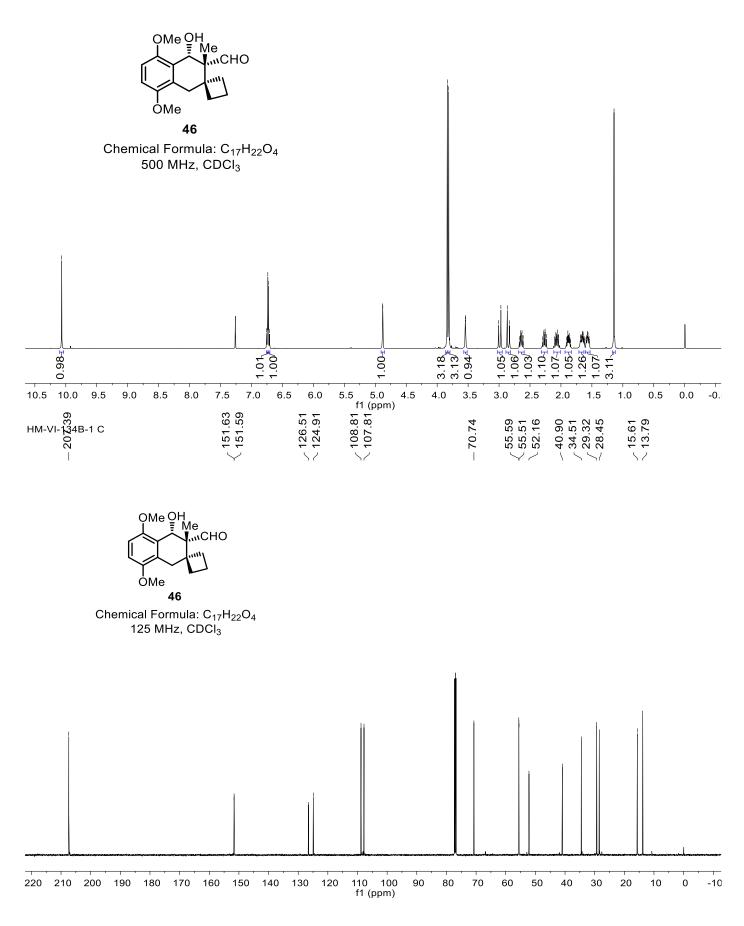




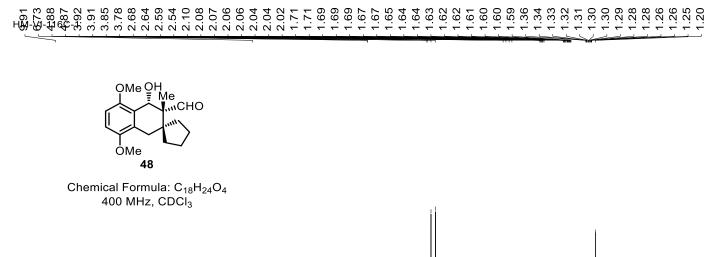


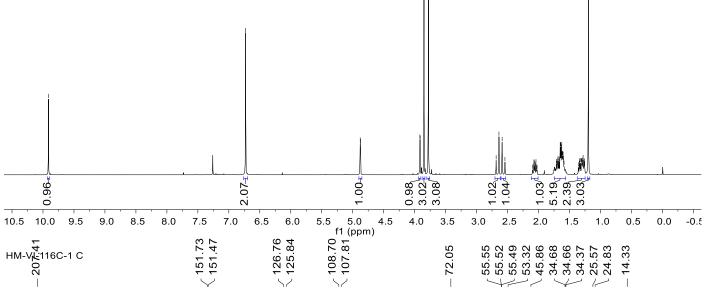


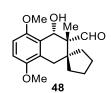




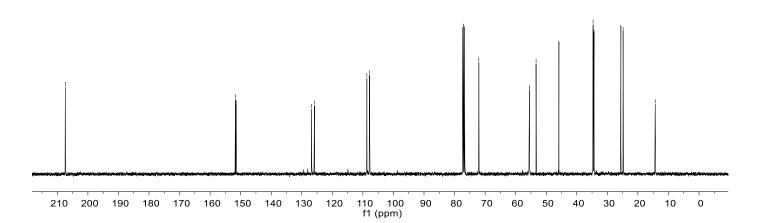


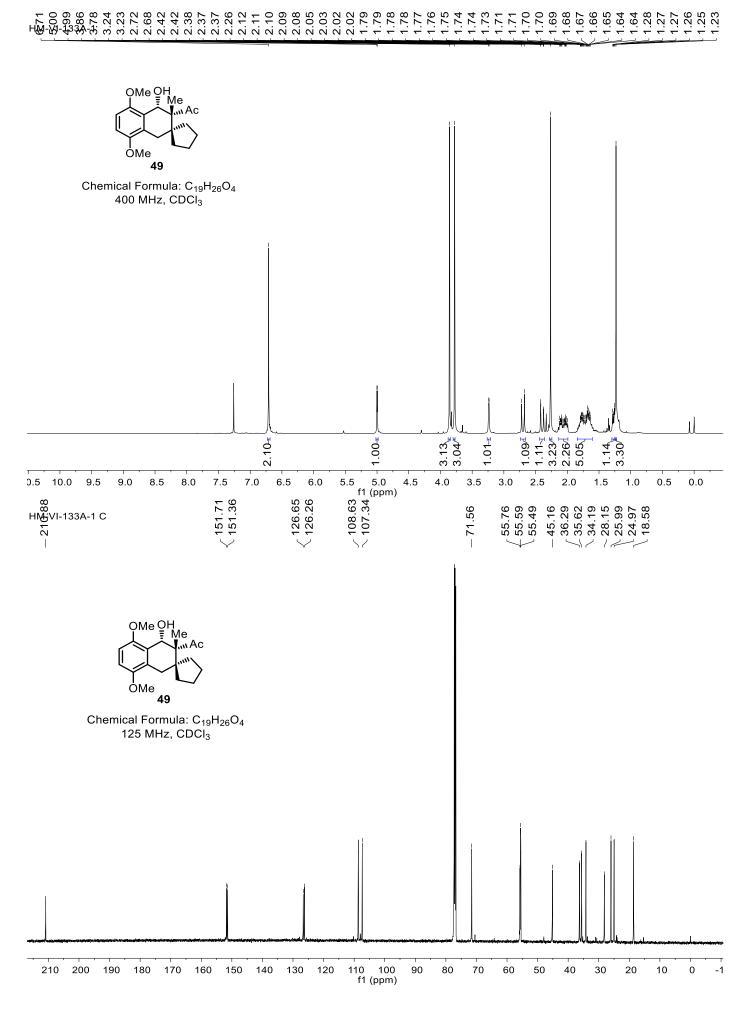


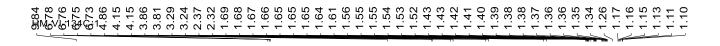


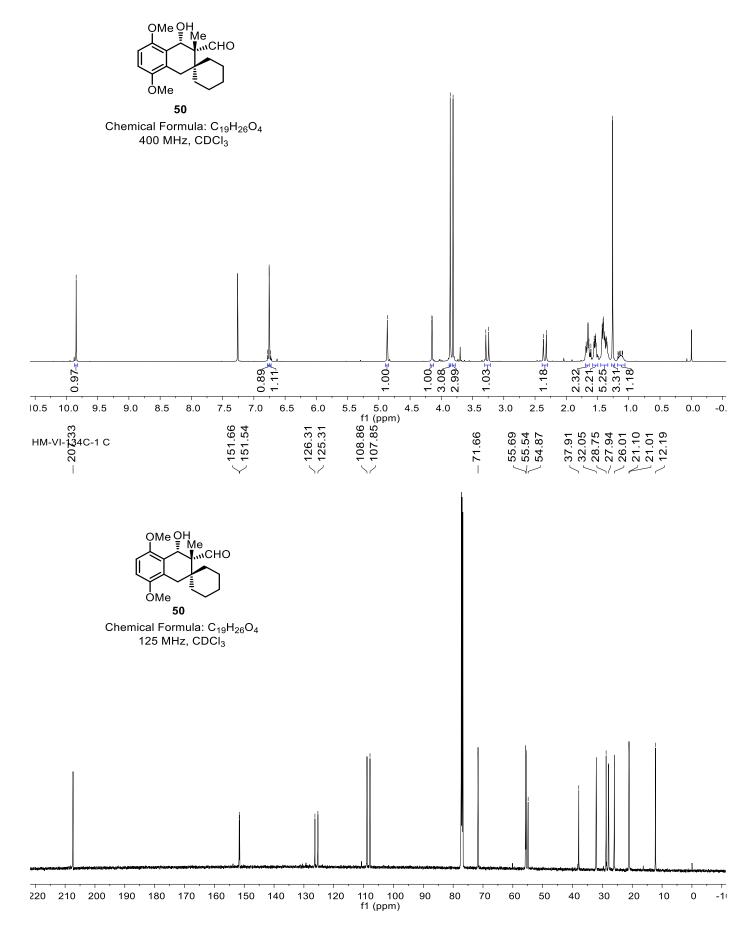


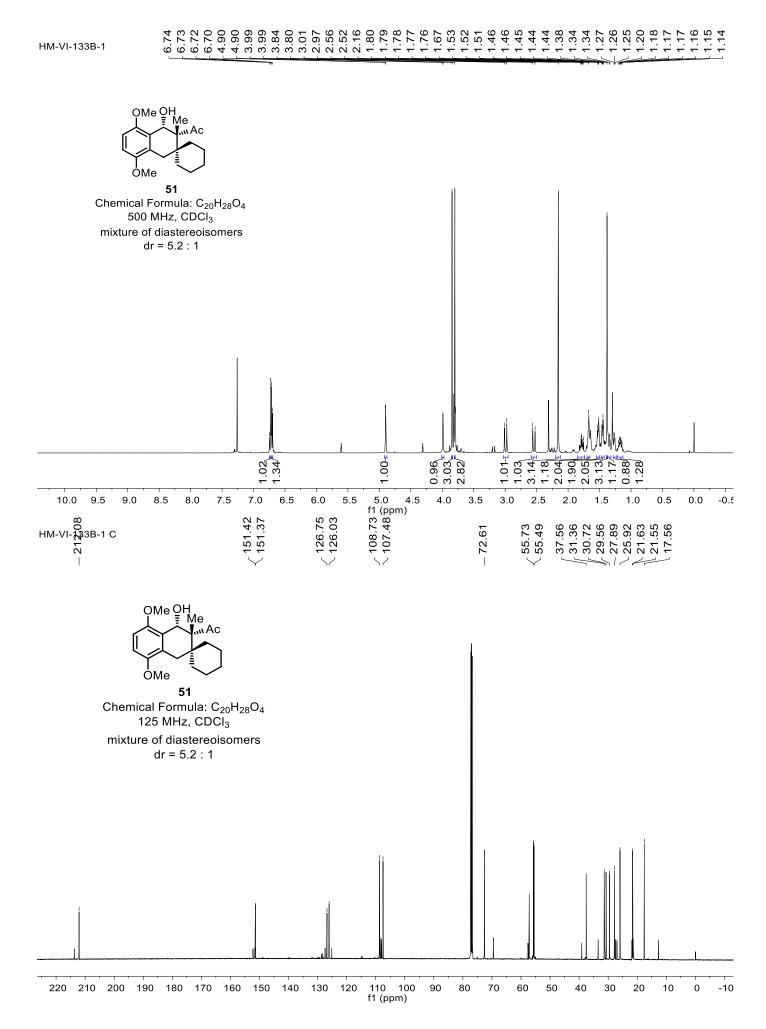
Chemical Formula: C₁₈H₂₄O₄ 100 MHz, CDCl₃

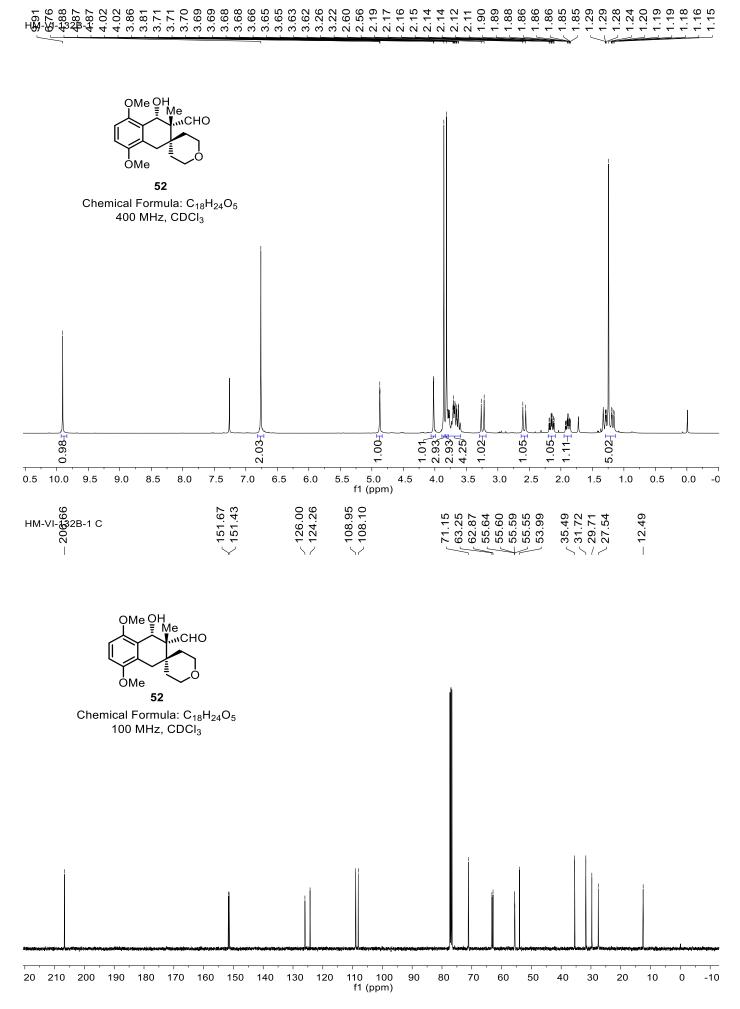


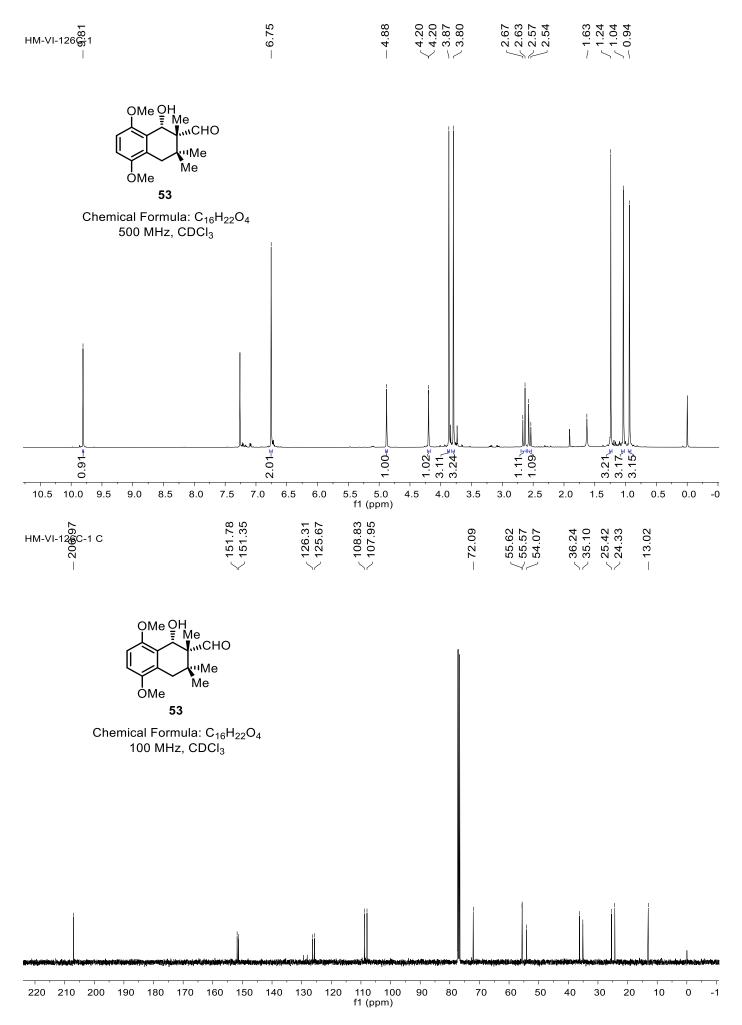


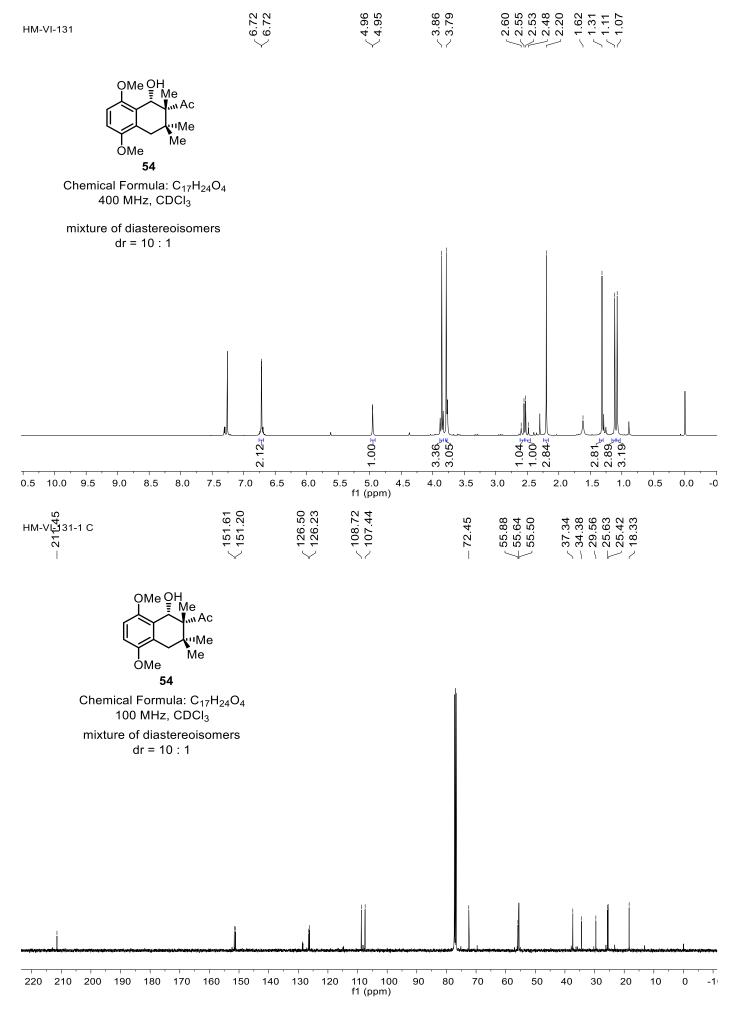


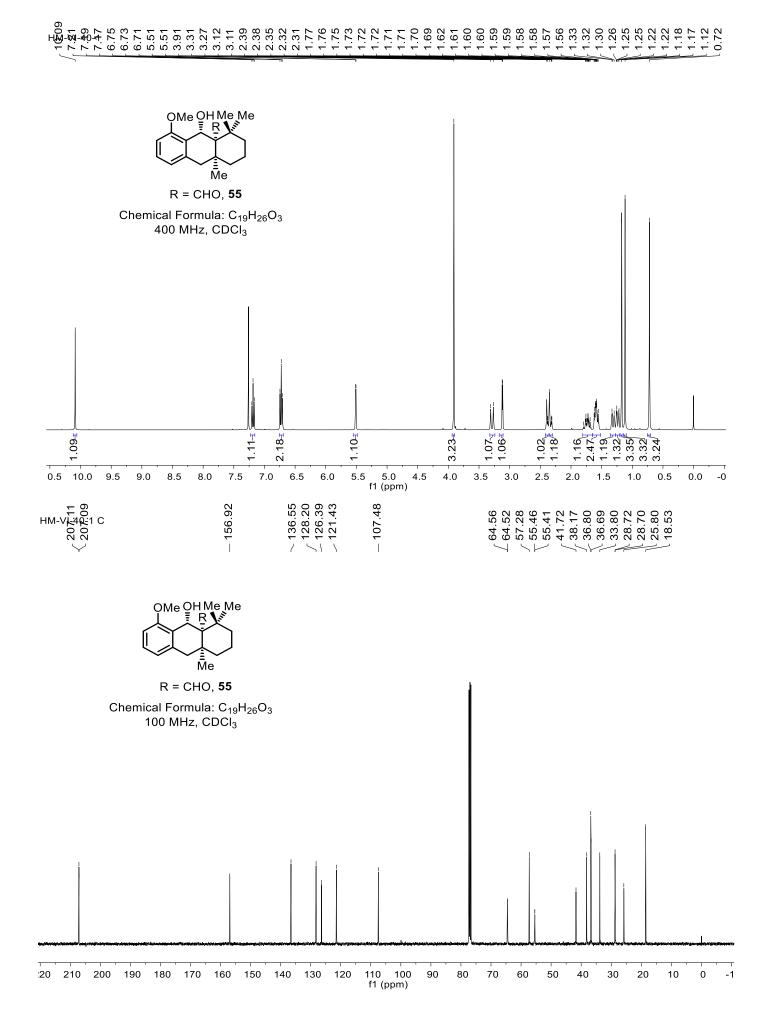


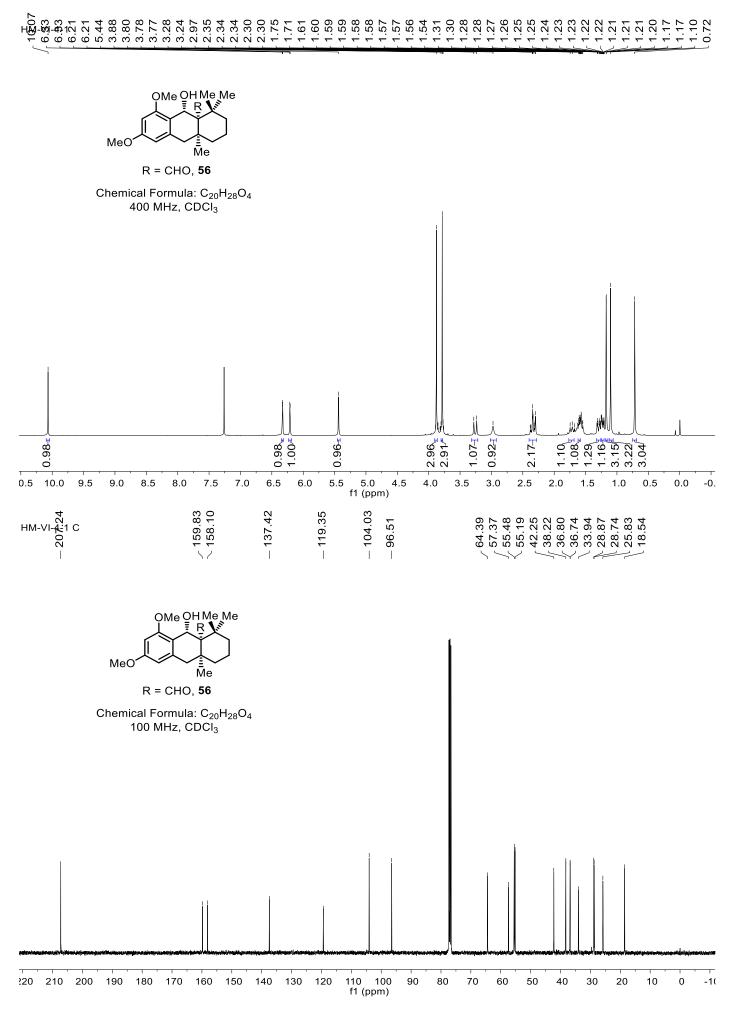


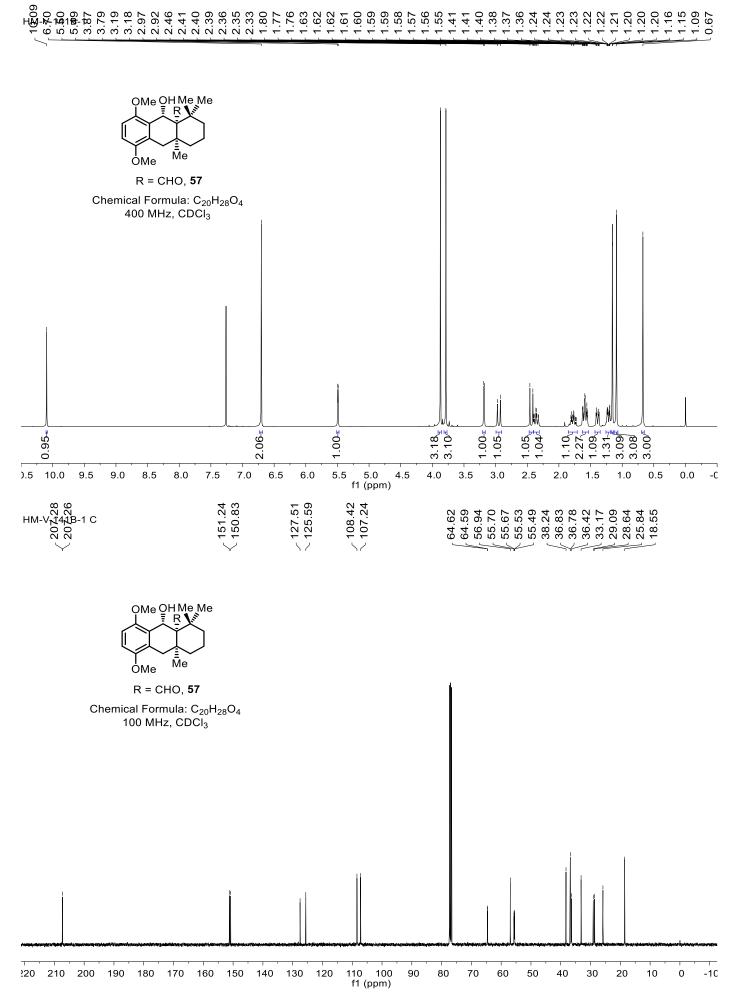


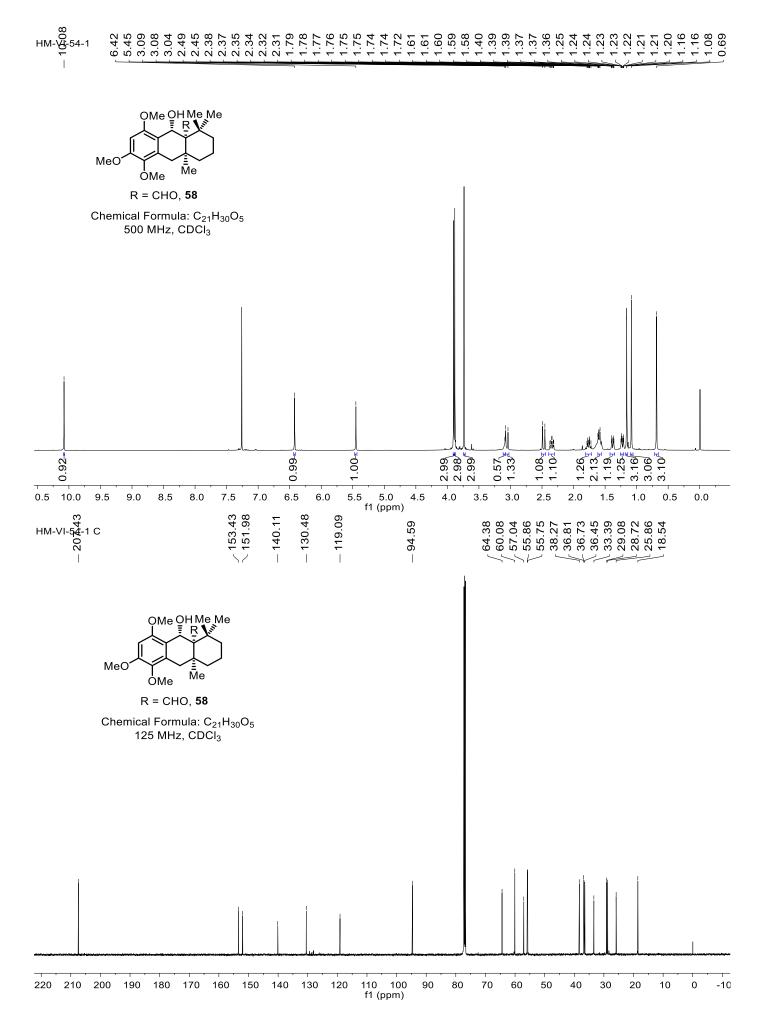


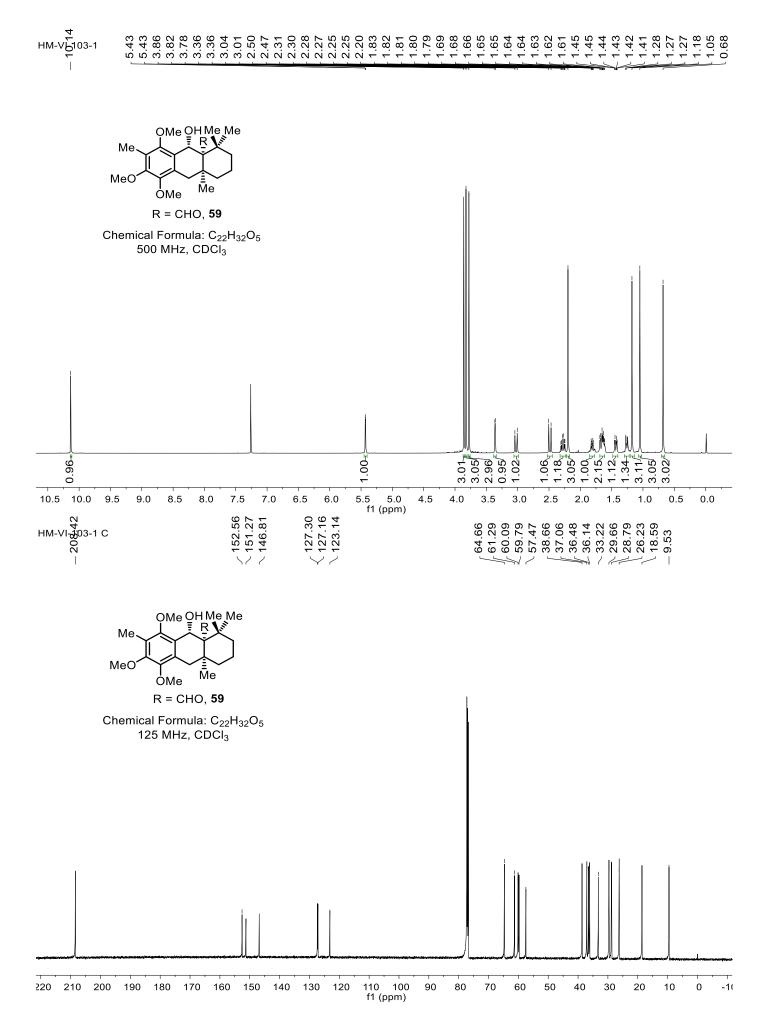


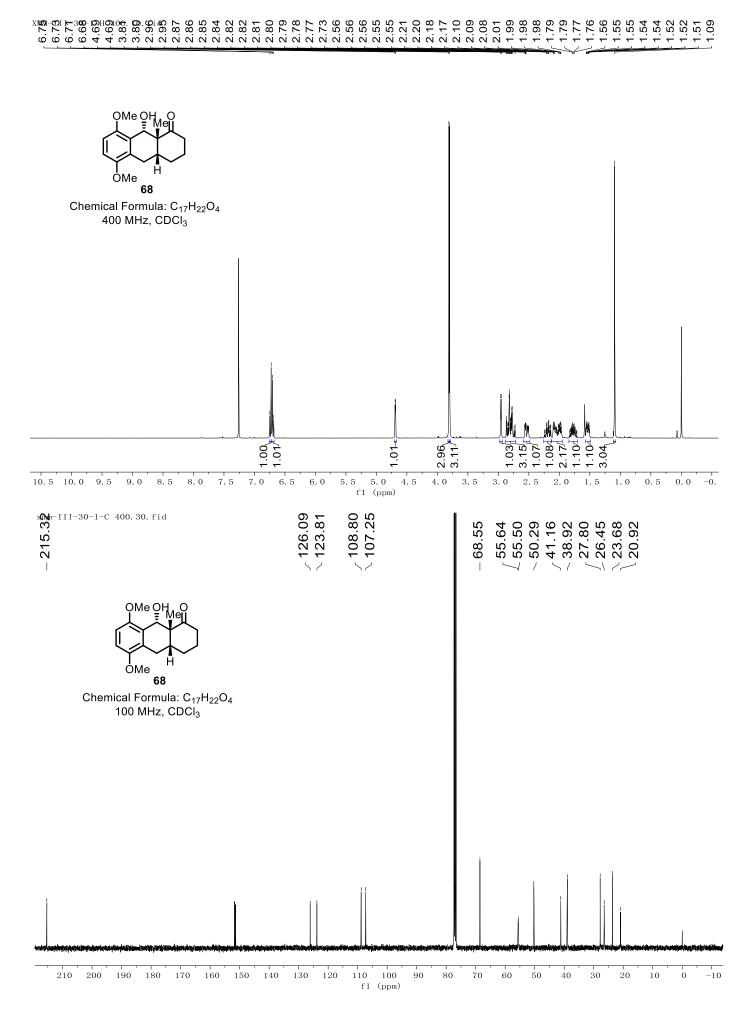


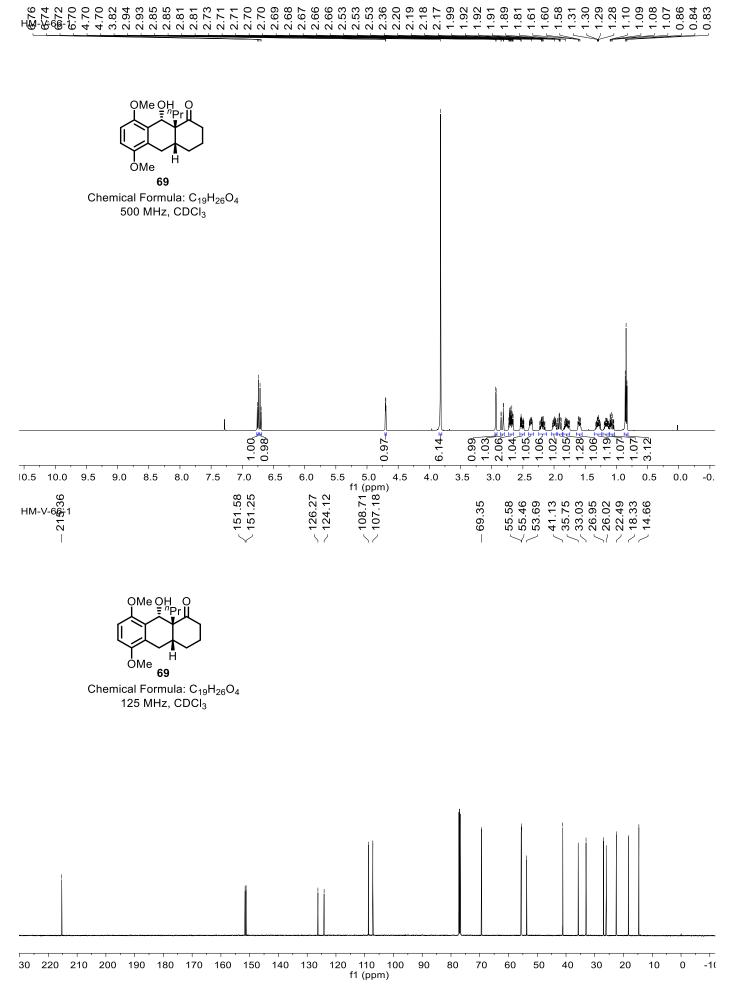


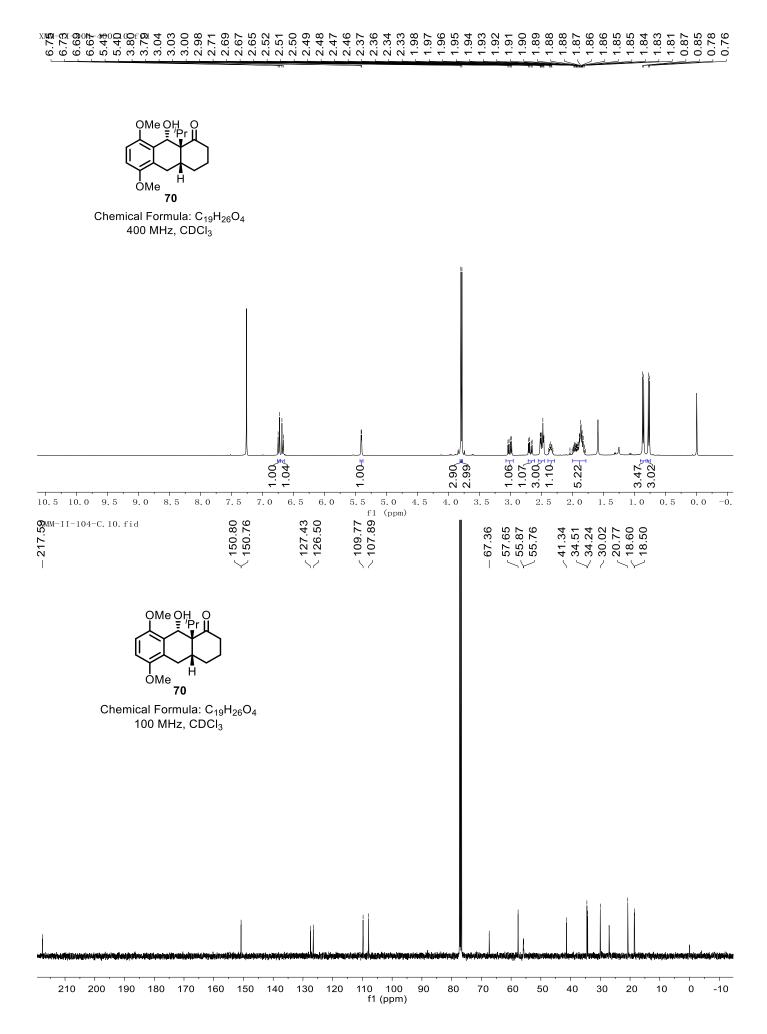


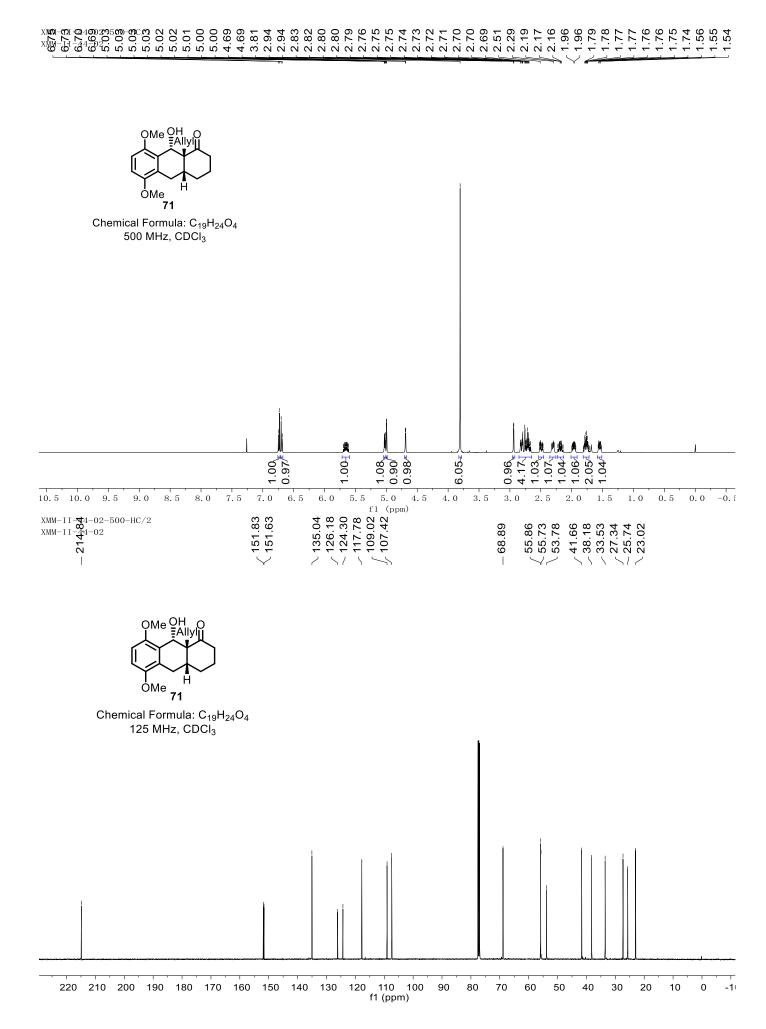


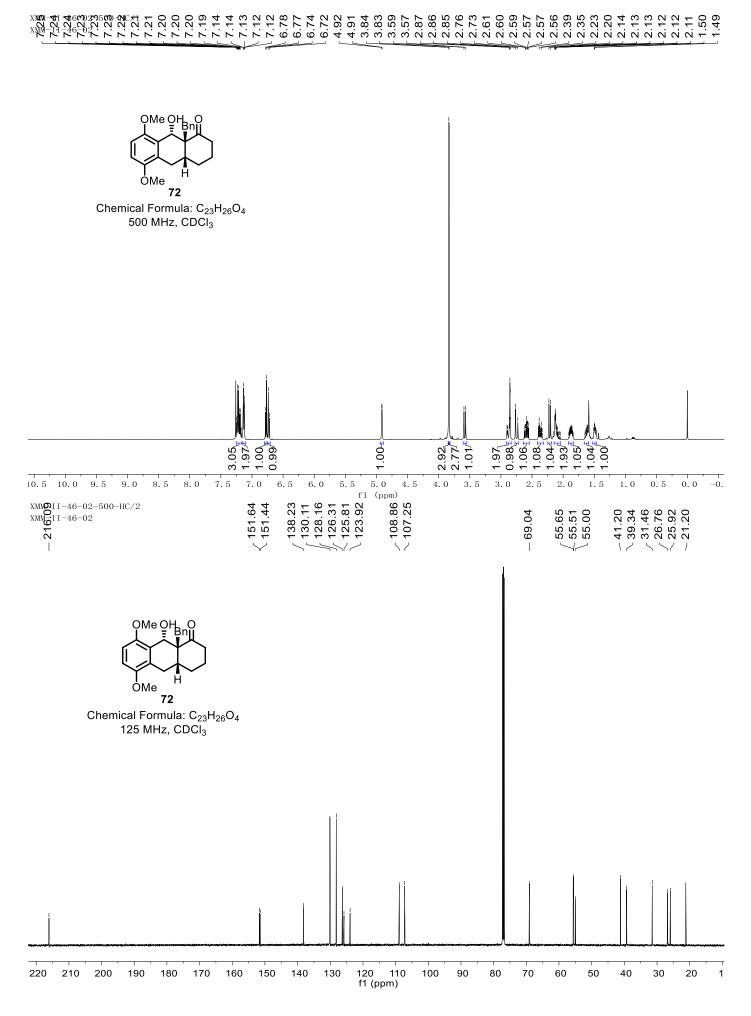


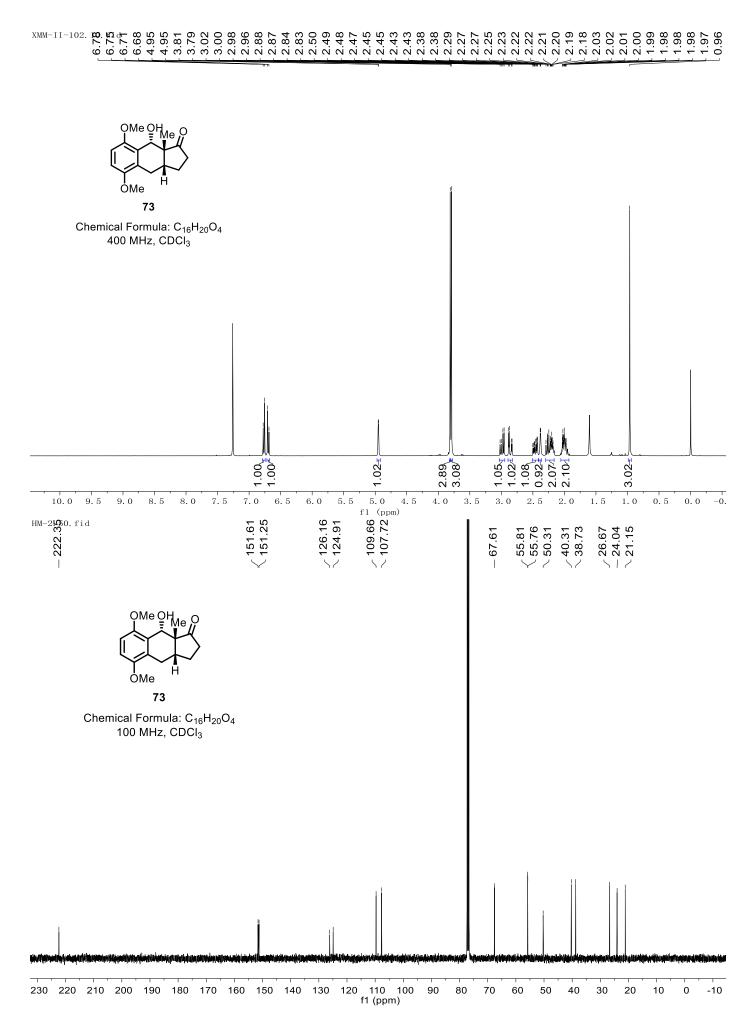


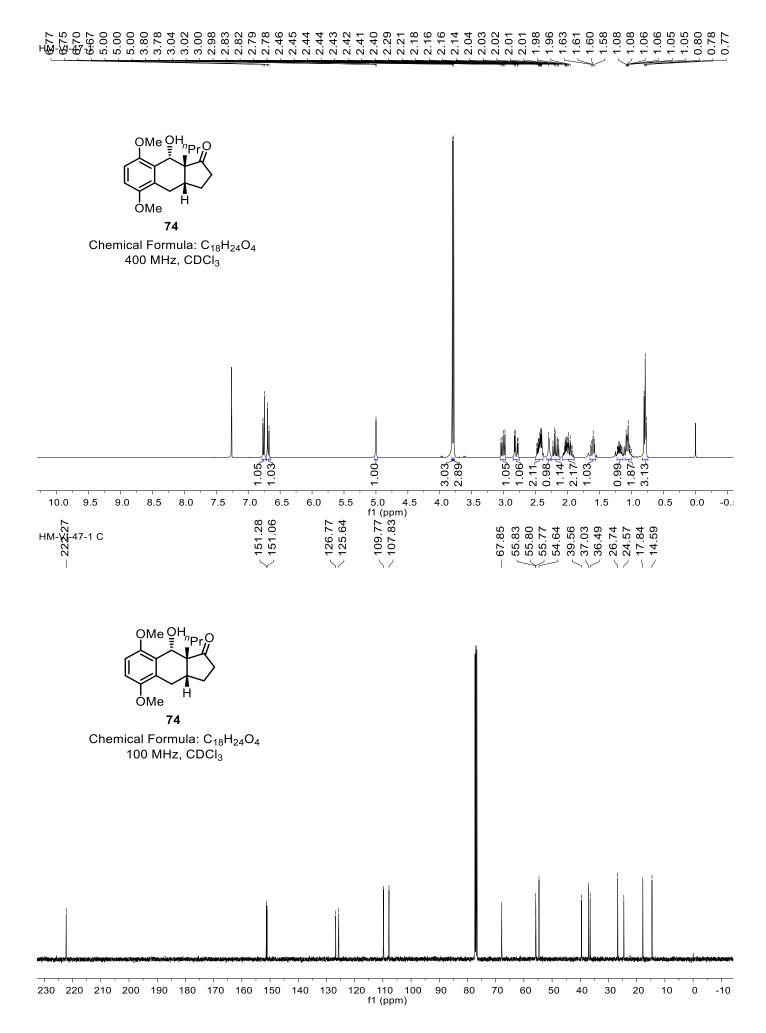


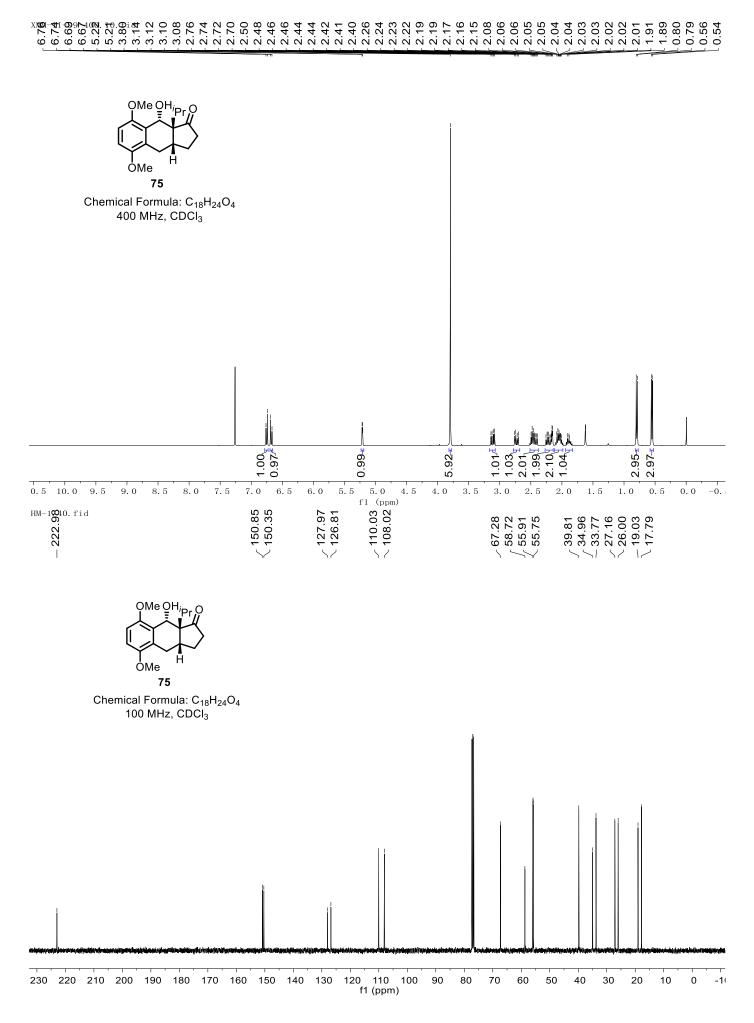


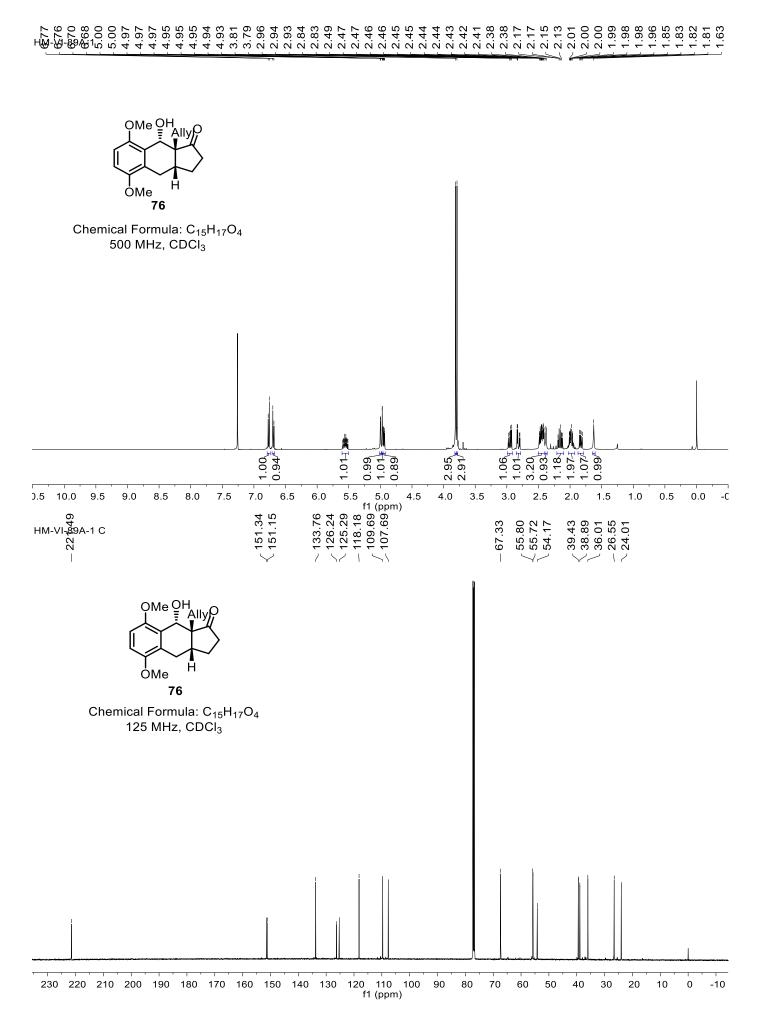


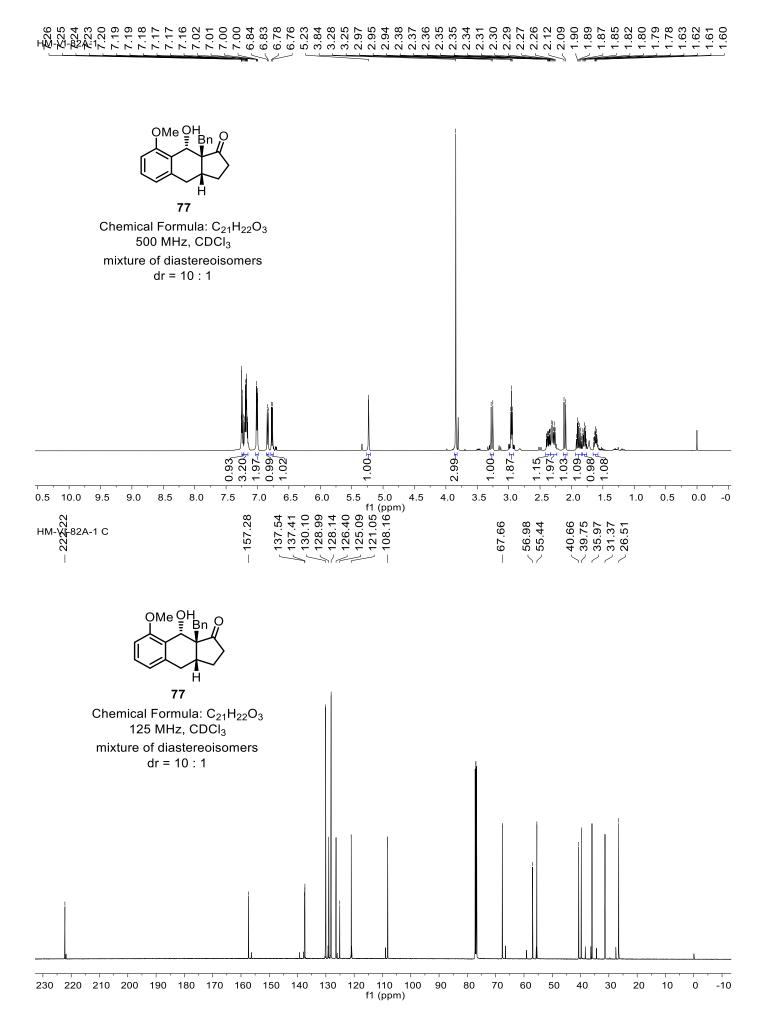


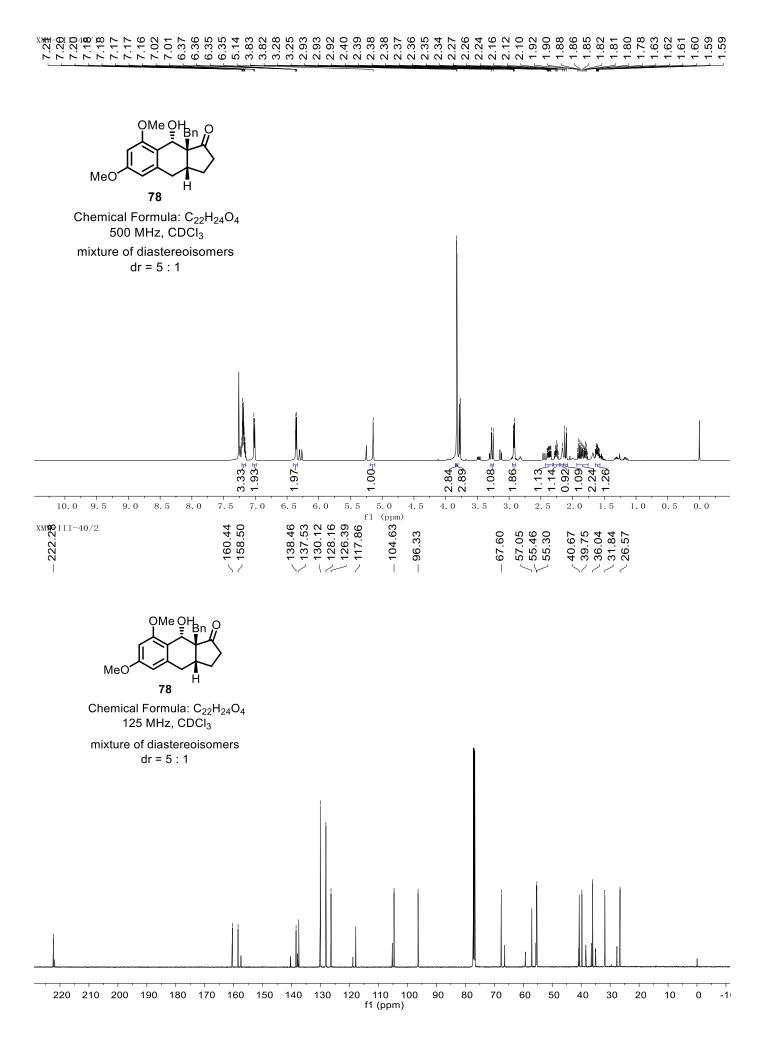


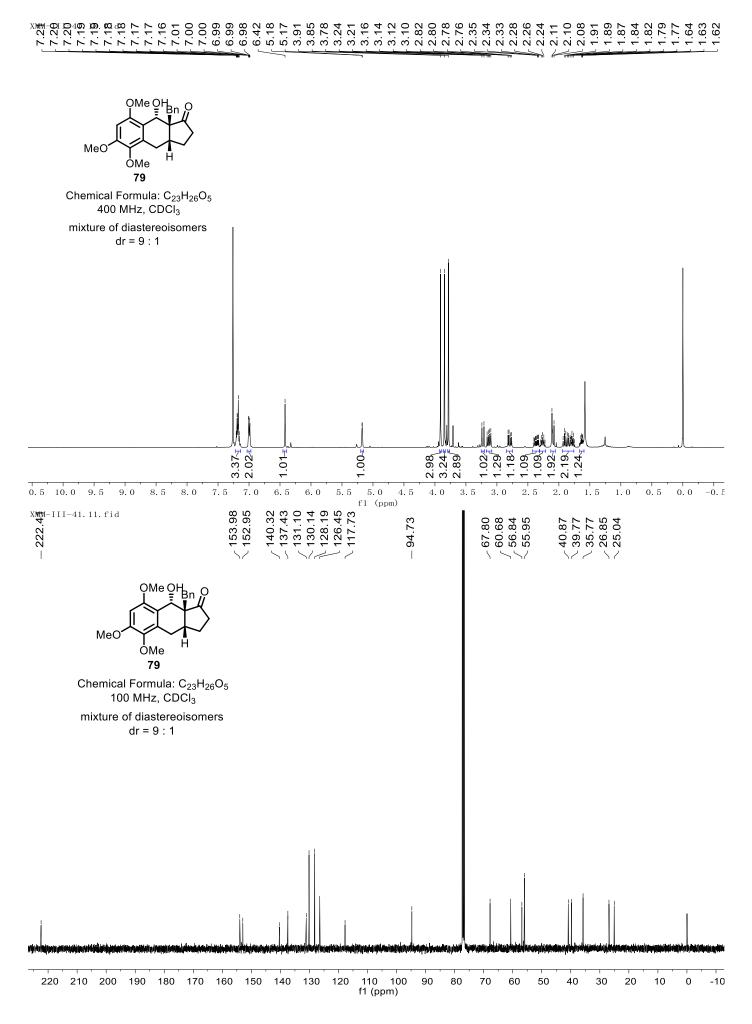


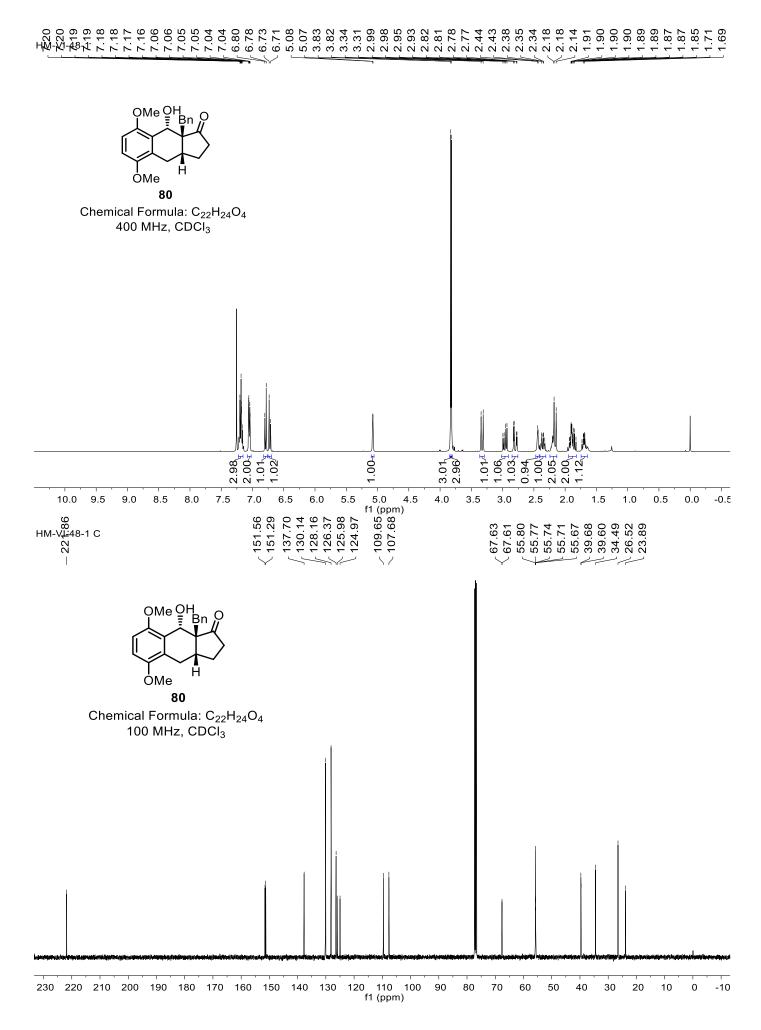




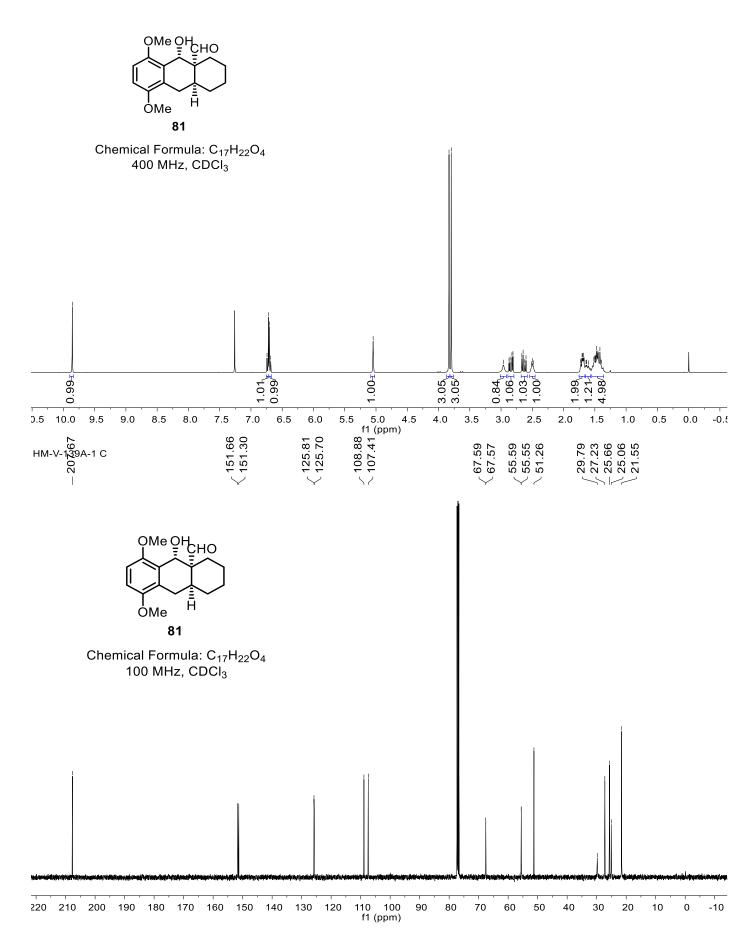


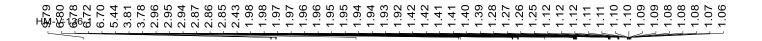


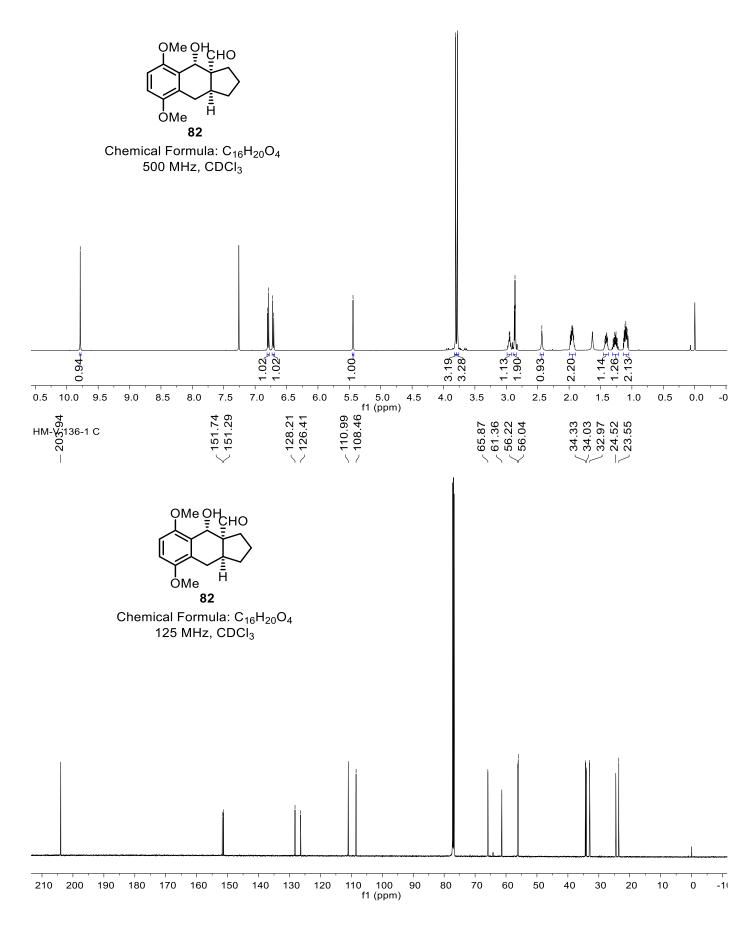


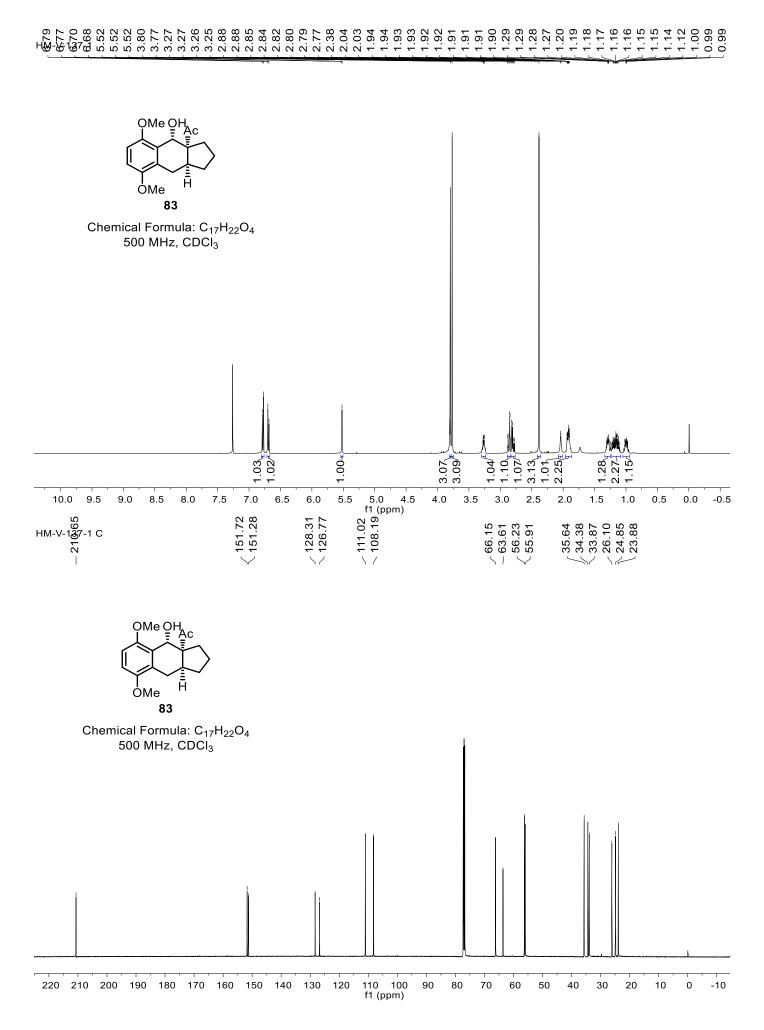


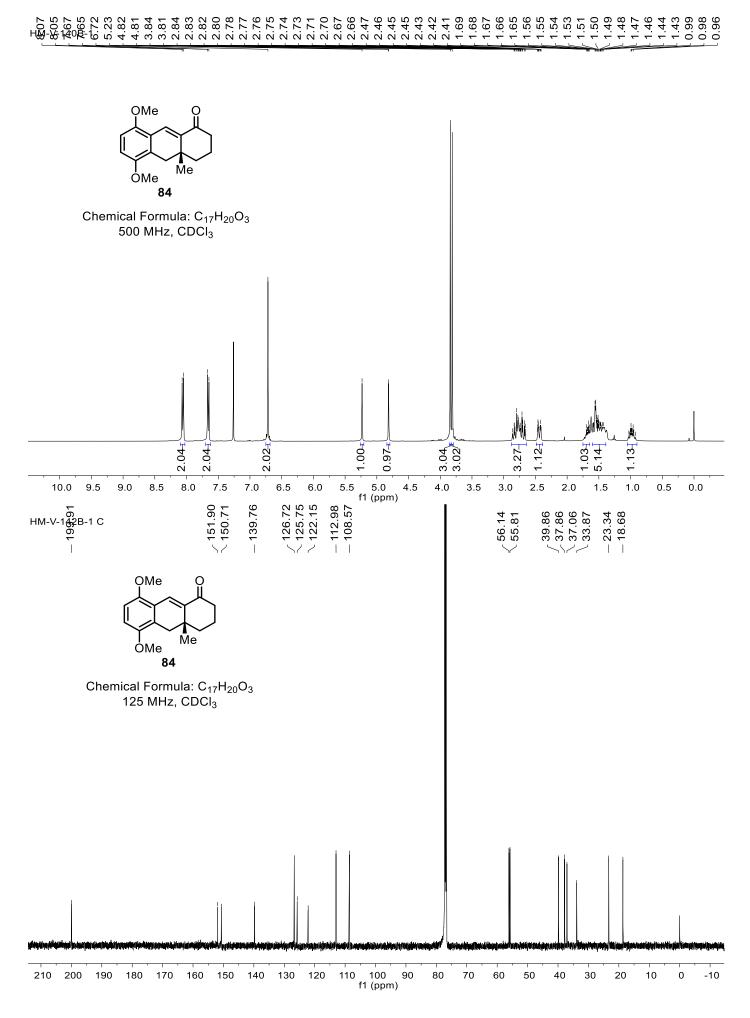


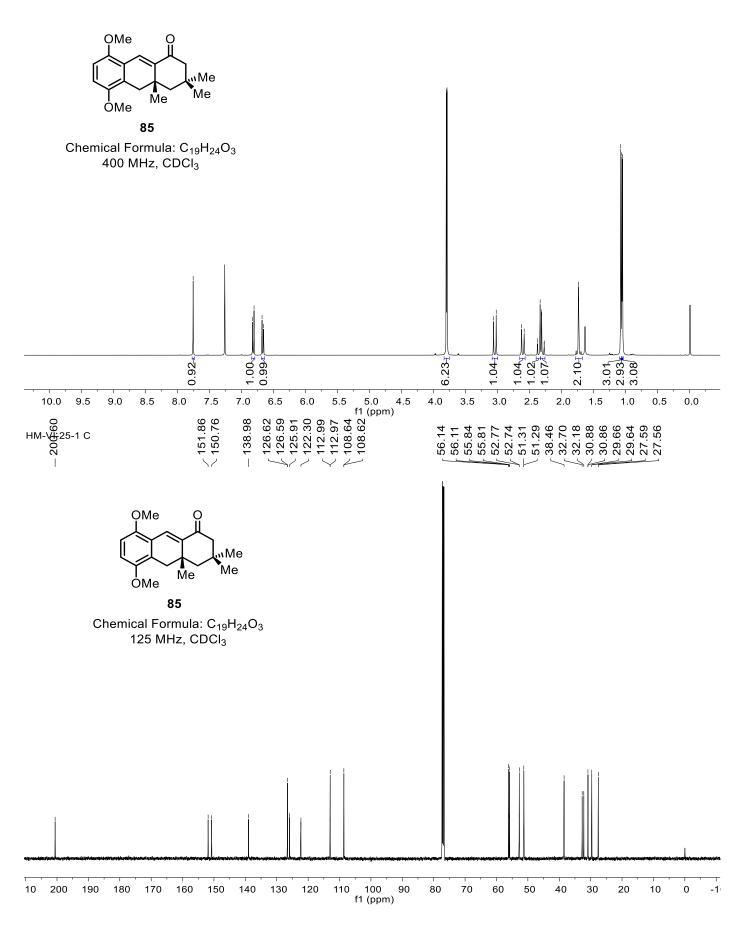


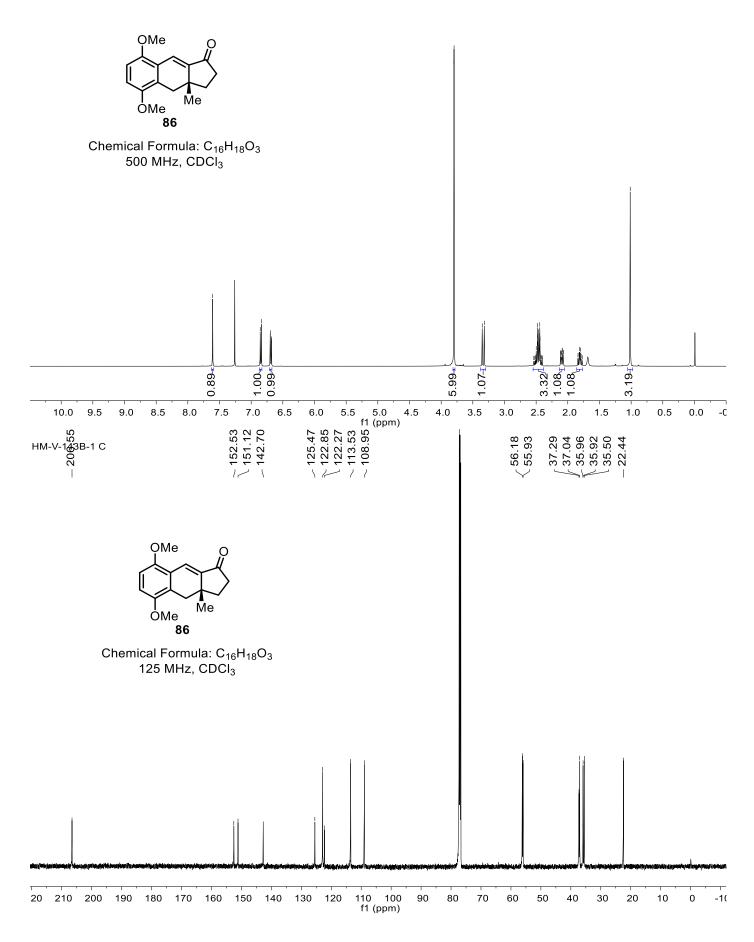


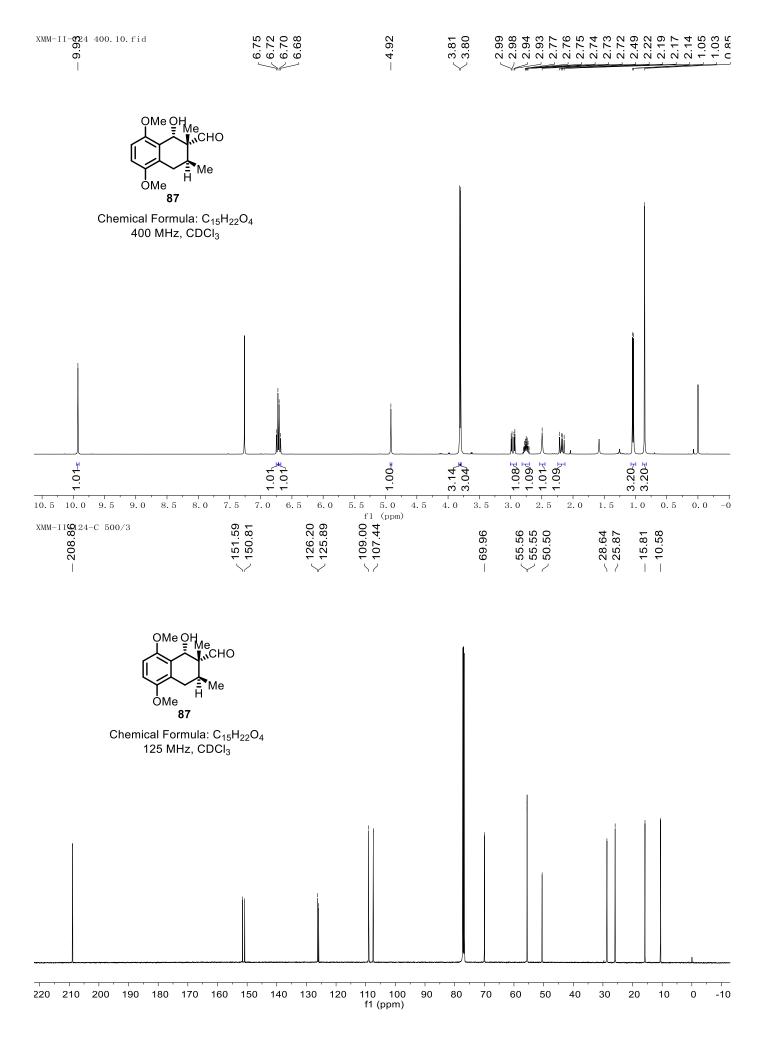


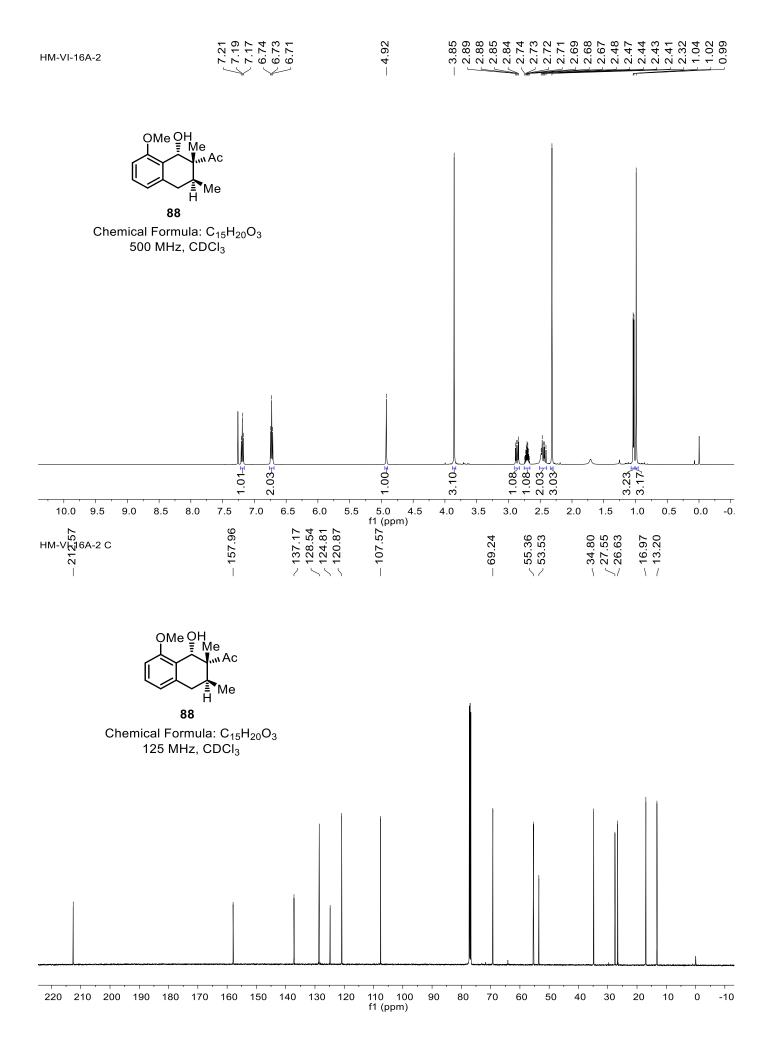




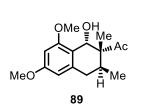






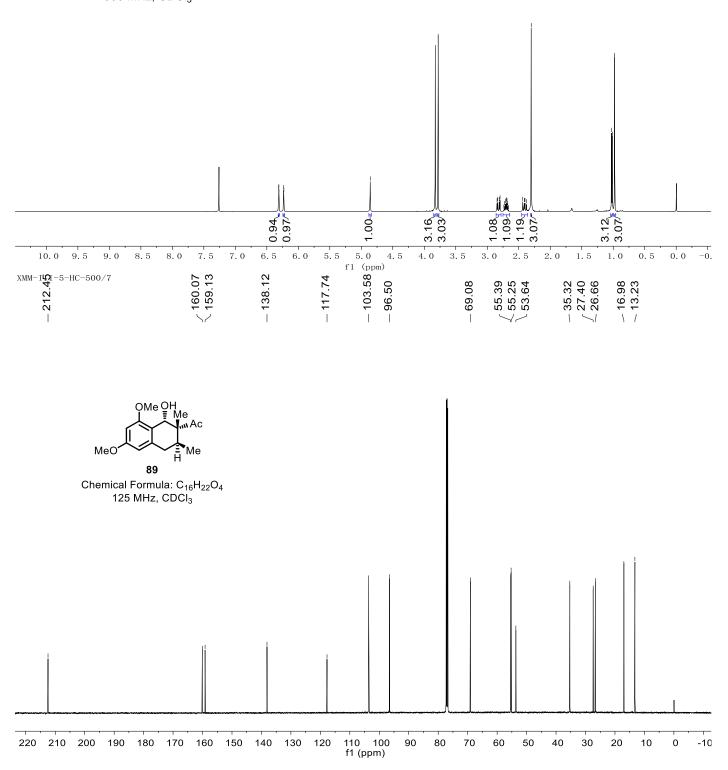


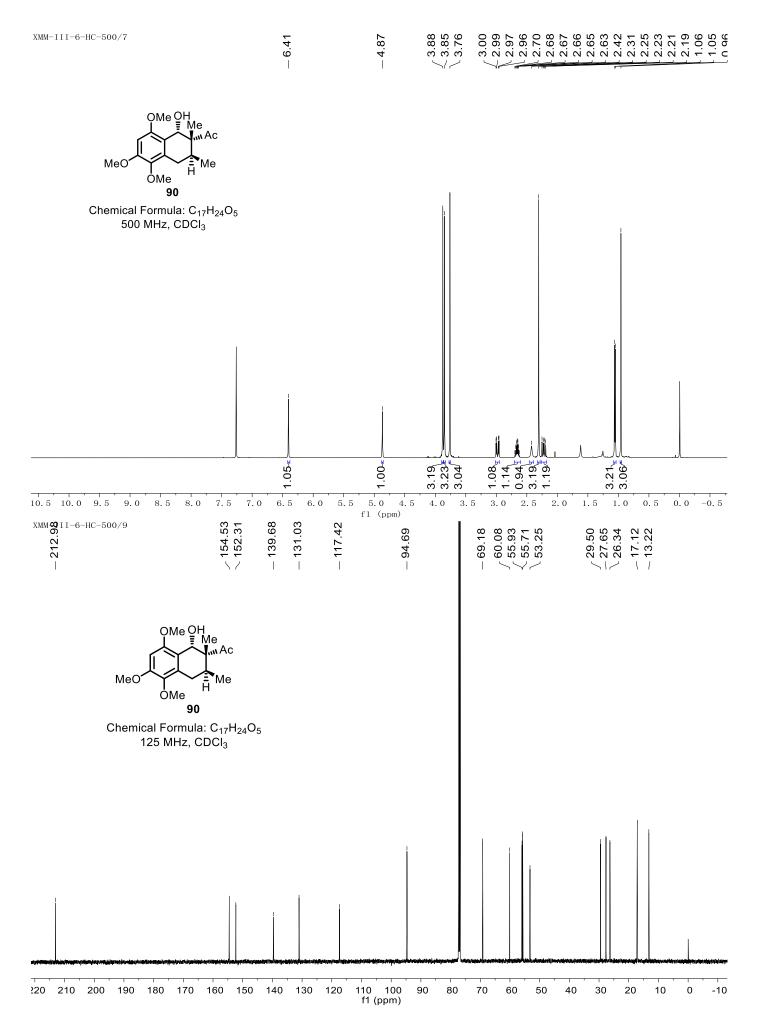
6.23	4.86	3.3.3.3.3.3.3.3.3.3.3.3.3.3.3.3.3.3.3.
12		



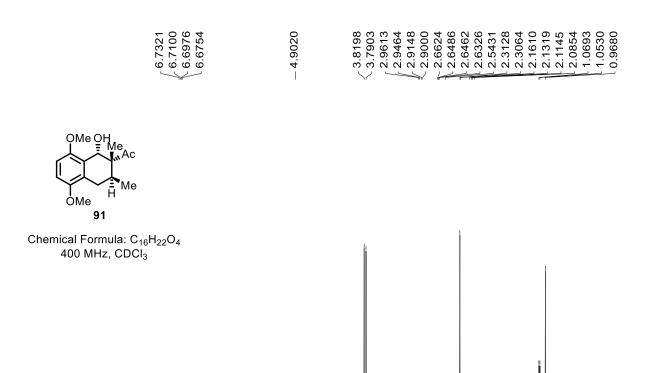
 $\int_{0.31}^{6.31}$

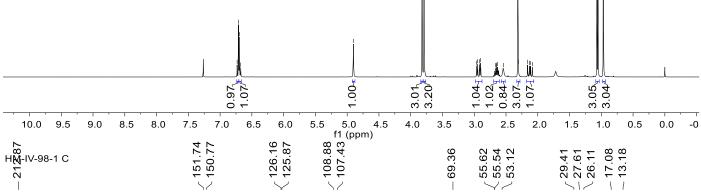
Chemical Formula: C₁₆H₂₂O₄ 500 MHz, CDCl₃



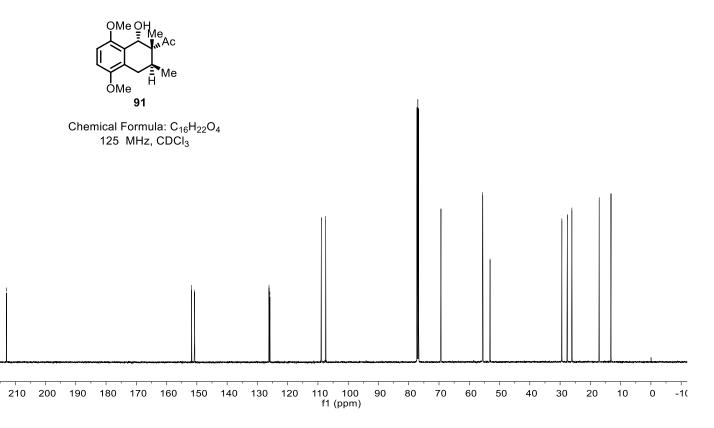


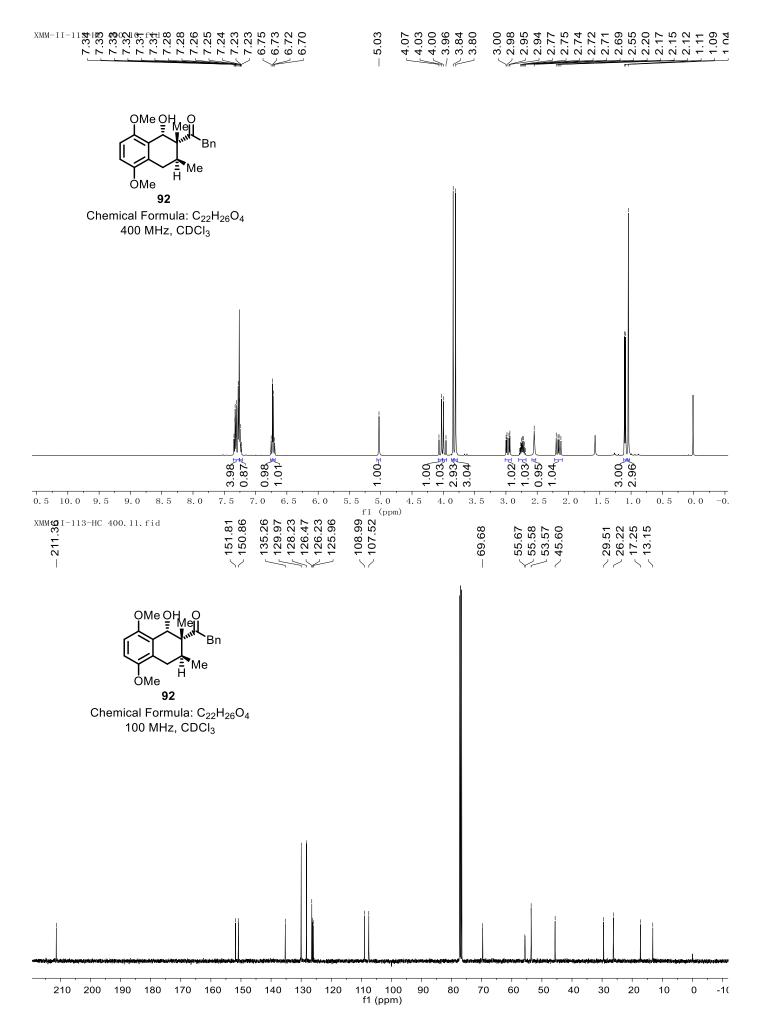
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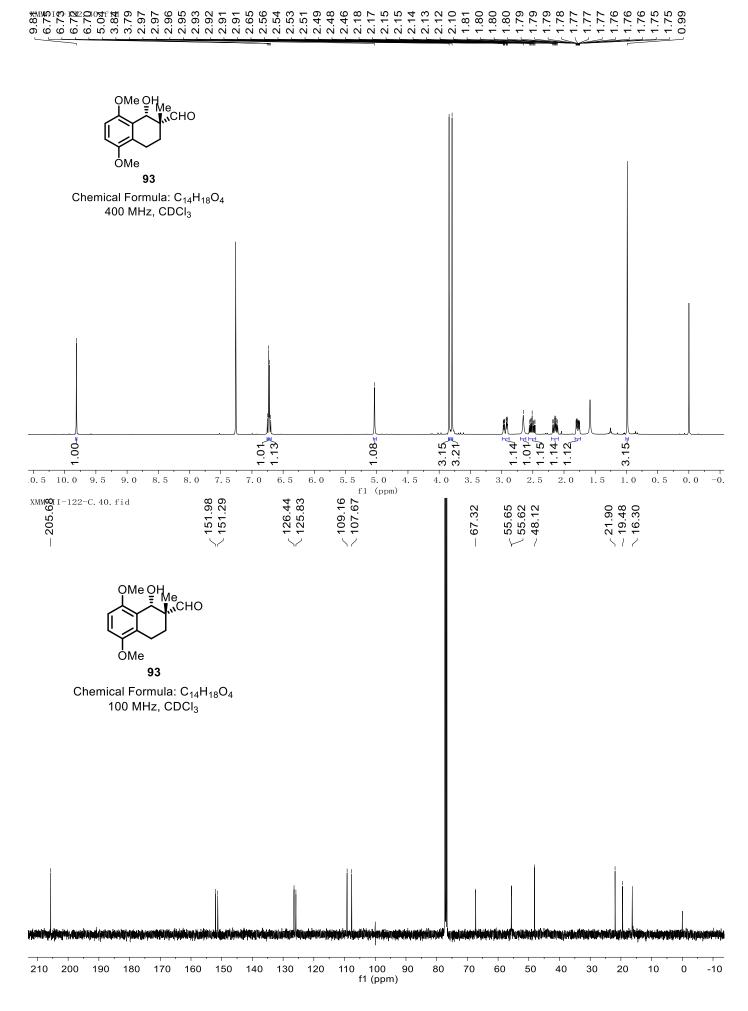


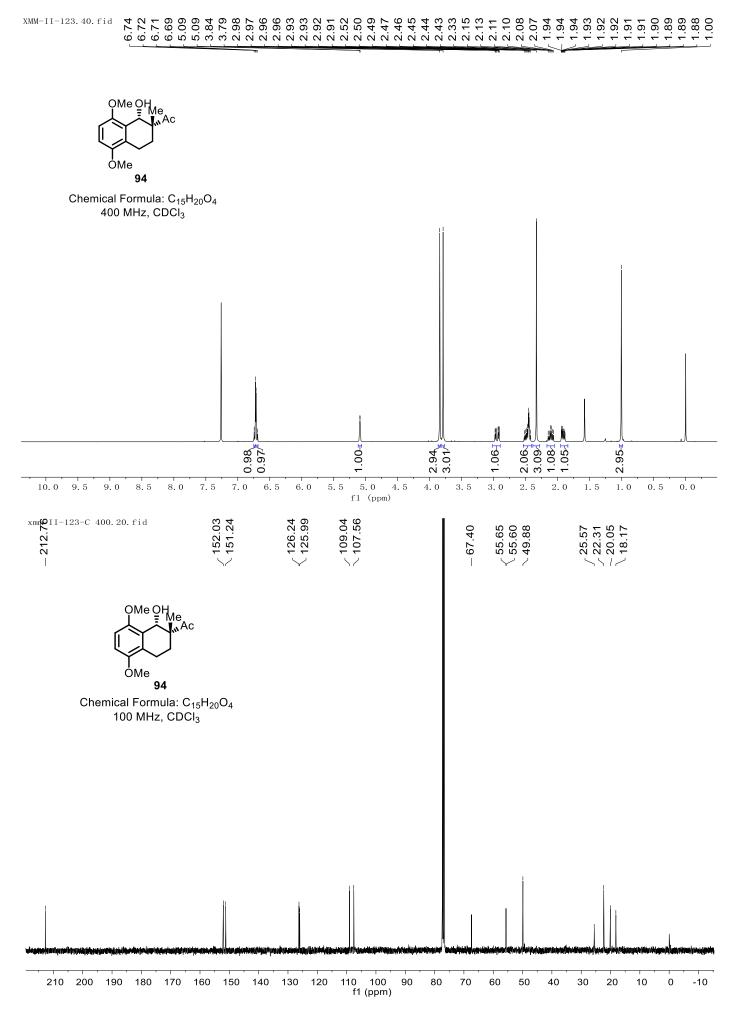


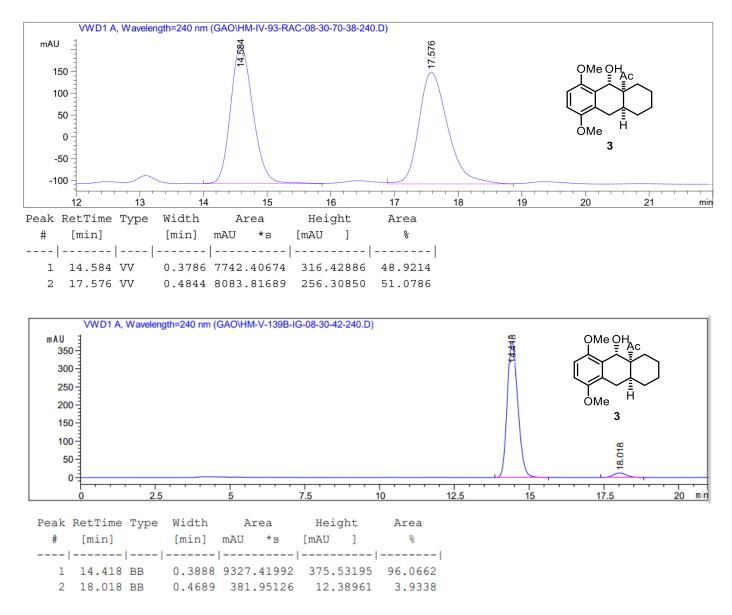
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 1.0
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 \] - 126.16 - 125.87 151.74
150.77 - 69.36 55.62 55.54 53.12



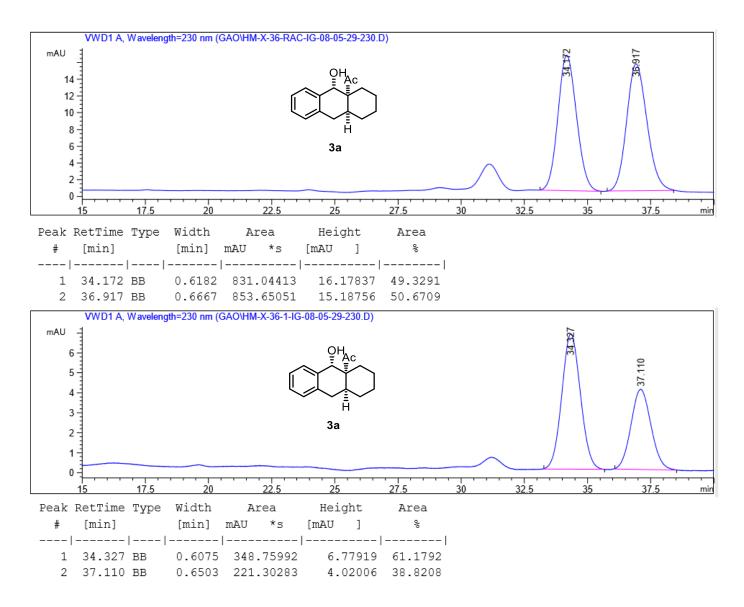




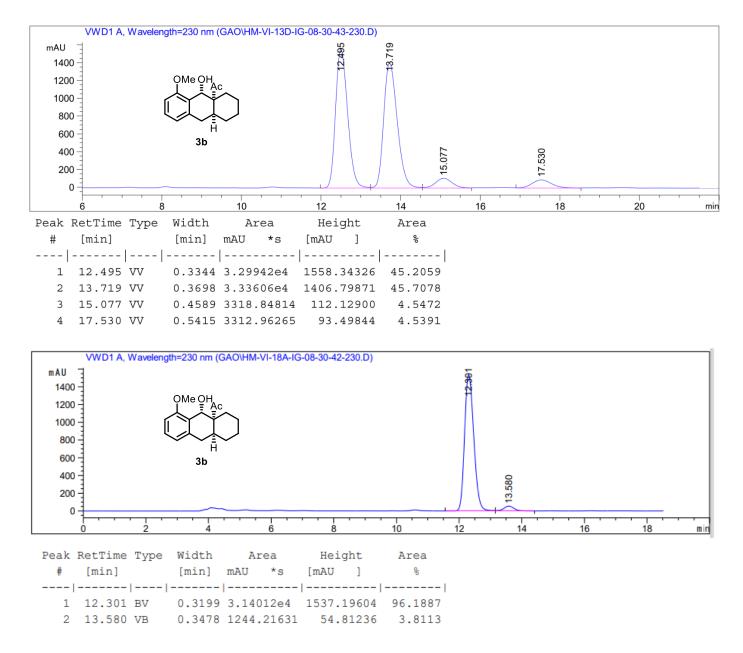




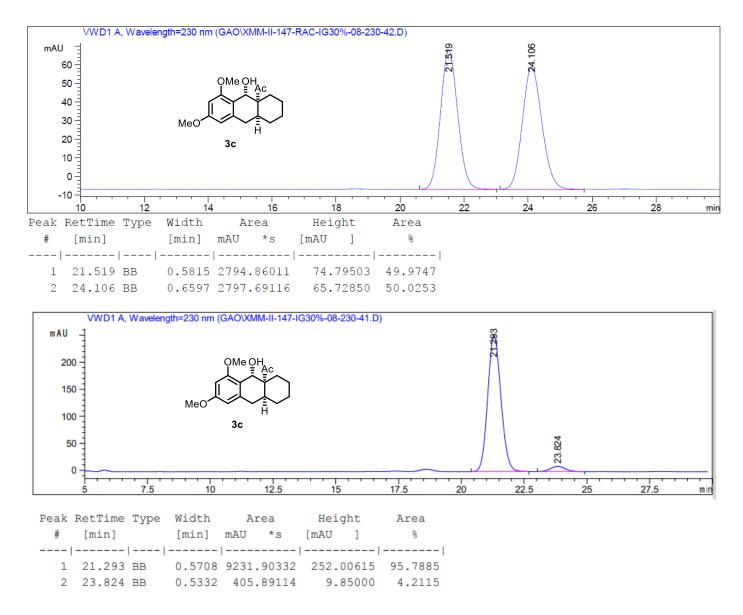
Enantiomeric excess: 92%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 240 nm): $t_R = 14.419$ min (major), $t_R = 18.018$ min (minor).



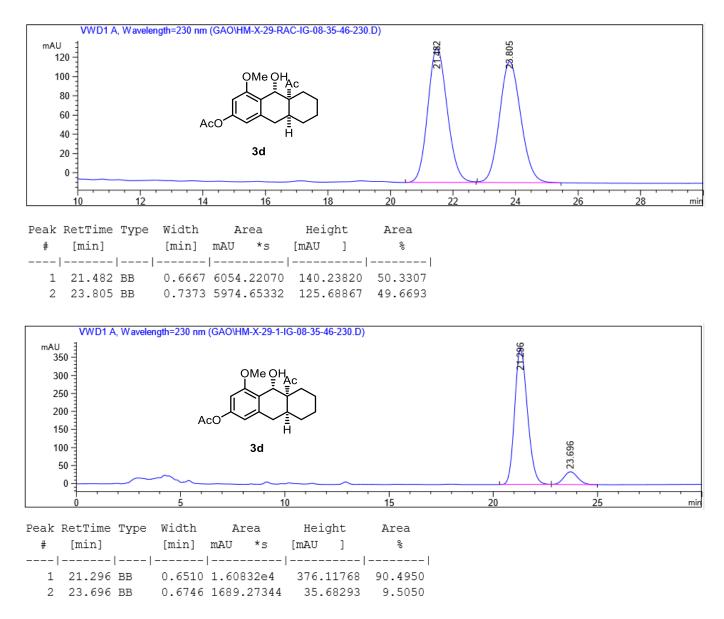
Enantiomeric excess: 22%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 95/5, flow rate 0.8 mL/min, T = 25 °C, 240 nm): $t_R = 34.327$ min (major), $t_R = 37.110$ min (minor).



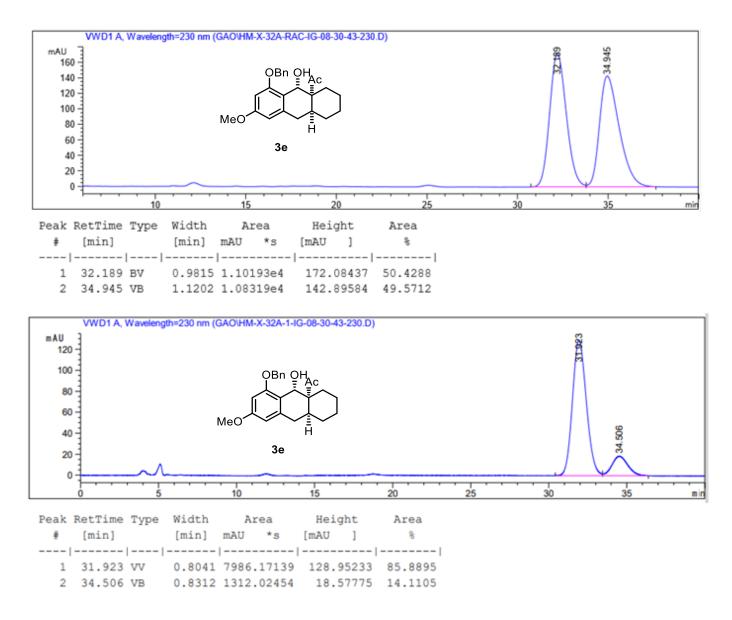
Enantiomeric excess: 92%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 12.301min (major), t_R = 13.580 min (minor).



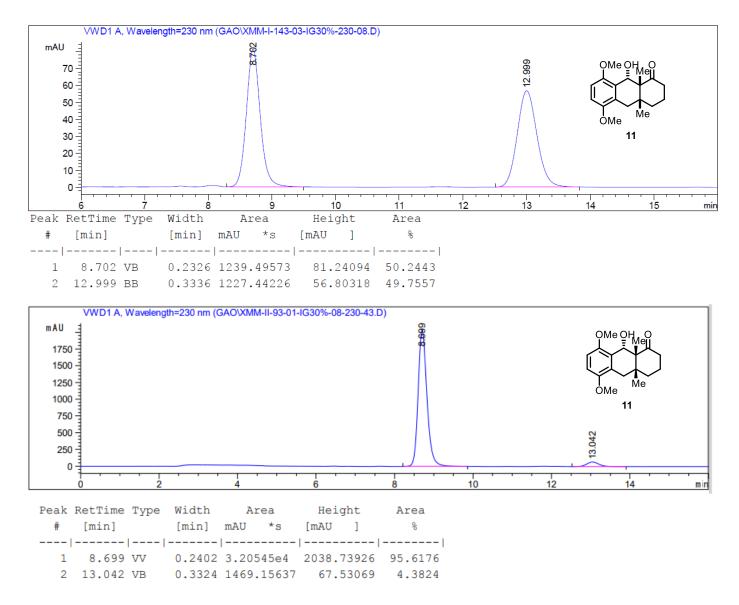
Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 21.293$ min (major), $t_R = 23.830$ min (minor).



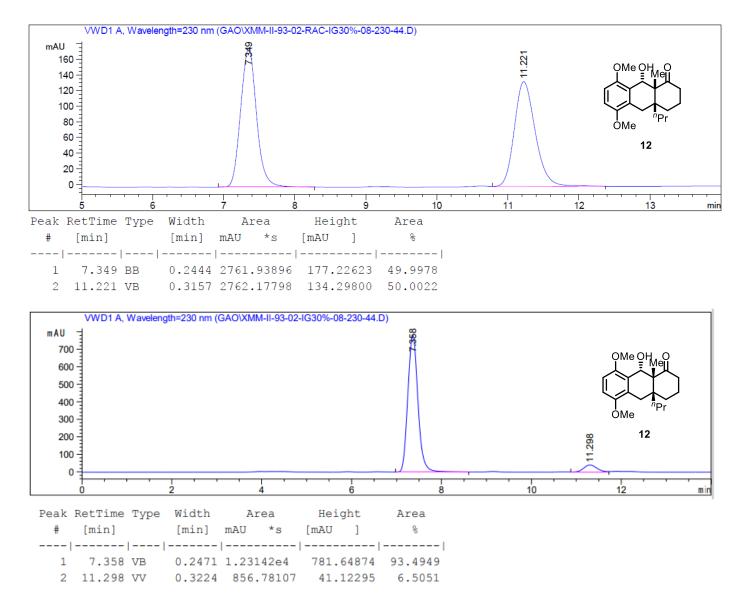
Enantiomeric excess: 81%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 65/35, flow rate 0.8 mL/min, T = 25 °C, 240 nm): $t_R = 21.296$ min (major), $t_R = 23.696$ min (minor).



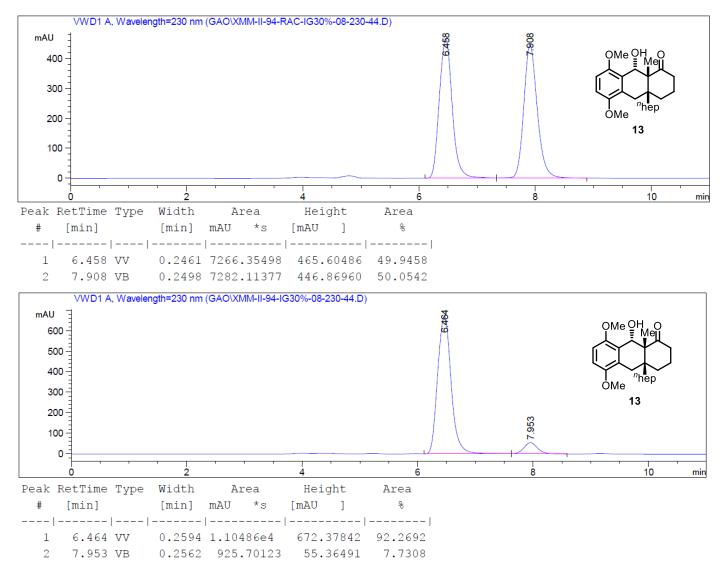
Enantiomeric excess: 72%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 31.923 min (major), t_R = 34.506 min (minor).



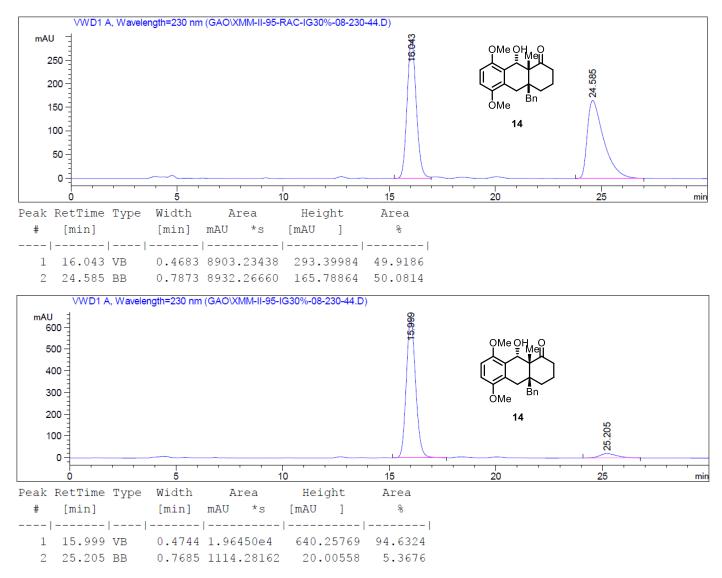
Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 8.699 \text{ min (major)}, t_R = 13.042 \text{ min (minor)}.$



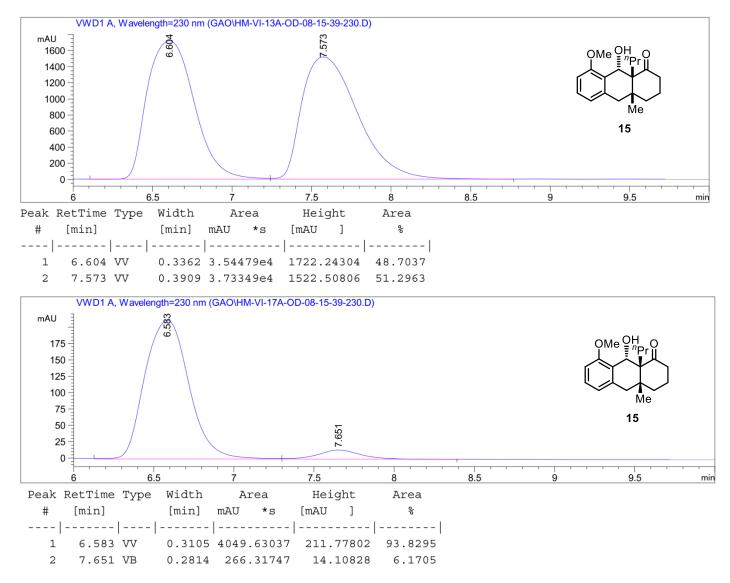
Enantiomeric excess: 87%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 7.358 min (major), t_R = 11.298 min (minor).



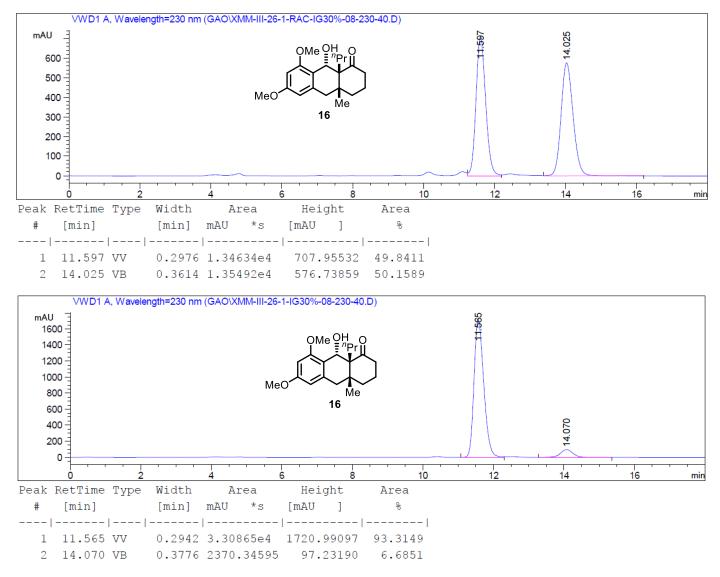
Enantiomeric excess: 85%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 6.464 \text{ min (major)}, t_R = 7.953 \text{ min (minor)}.$



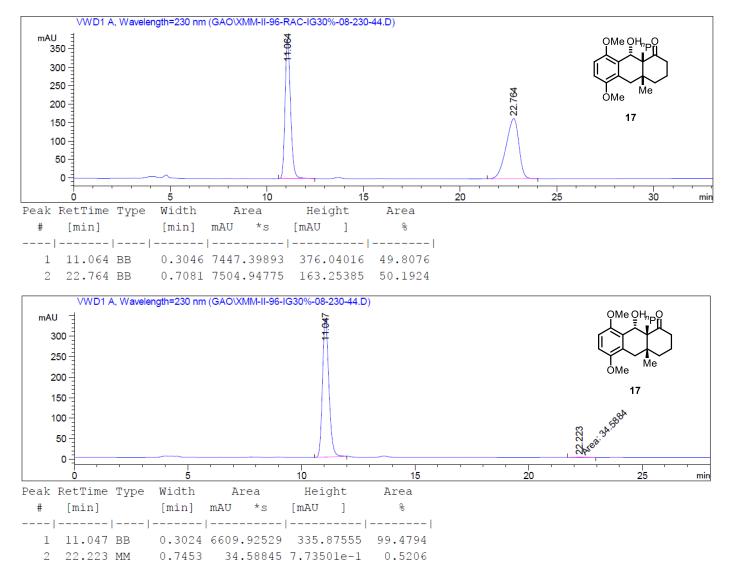
Enantiomeric excess: 89%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 15.999$ min (major), $t_R = 25.205$ min (minor).



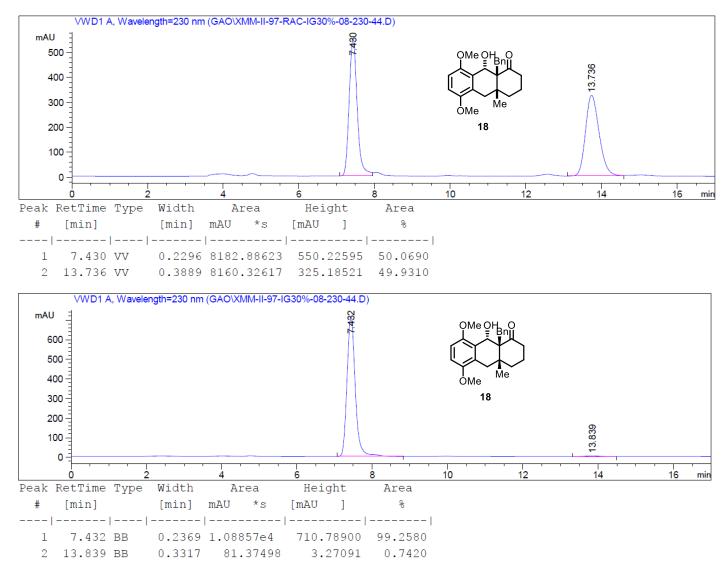
Enantiomeric excess: 88%, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 85/15, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 6.583$ min (major), $t_R = 7.651$ min (minor).



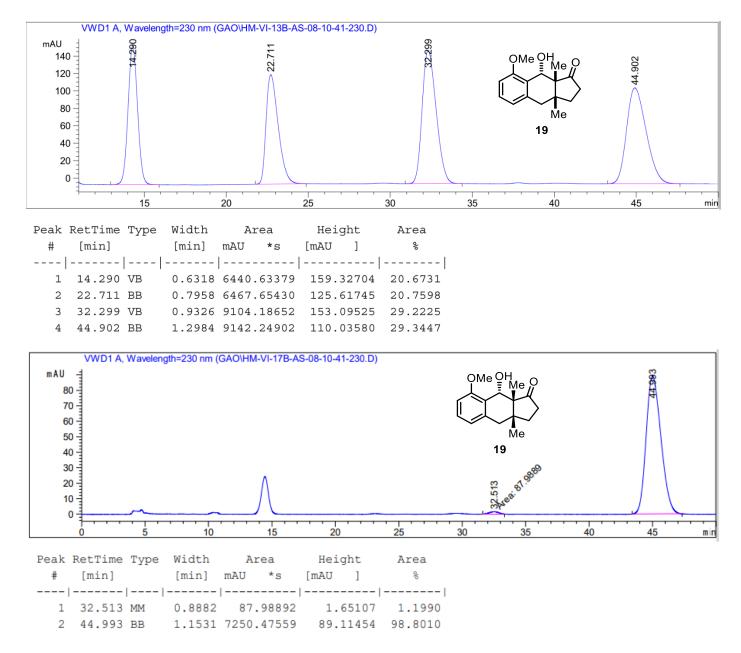
Enantiomeric excess: 87%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 10.241 \text{ min (minor)}, t_R = 13.851 \text{ min (major)}.$



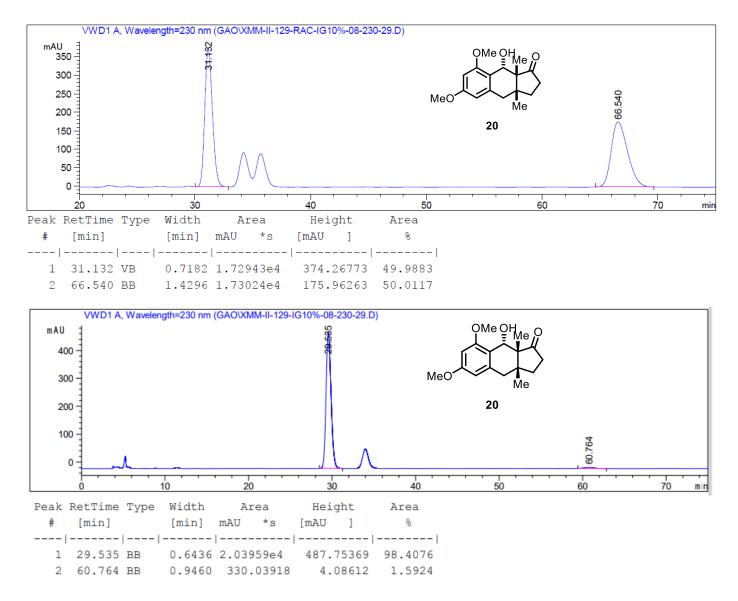
Enantiomeric excess: 99%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 11.047$ min (major), $t_R = 22.223$ min (minor).



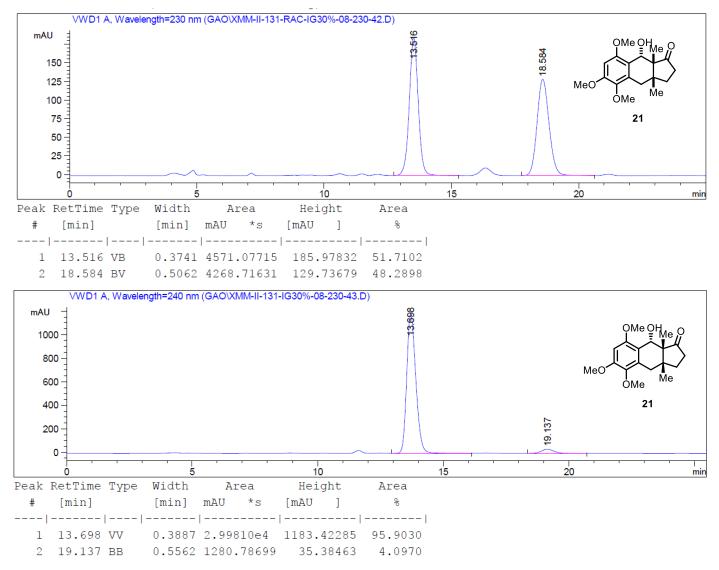
Enantiomeric excess: 99%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 7.432 min (major), t_R = 13.839 min (minor).



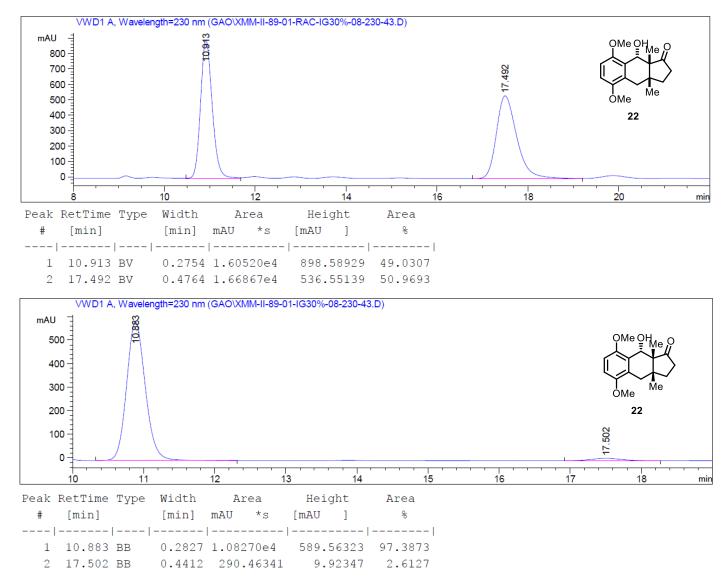
Enantiomeric excess: 98%, determined by HPLC (Daicel Chiralpak AS-H, hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 32.496 min (minor), t_R = 44.993 min (major).



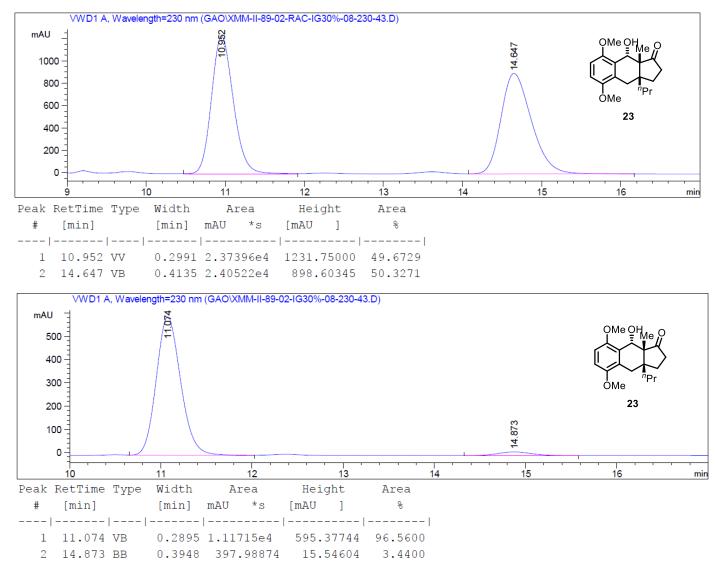
Enantiomeric excess: 97%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 29.535$ min (minor), $t_R = 60.764$ min (major).



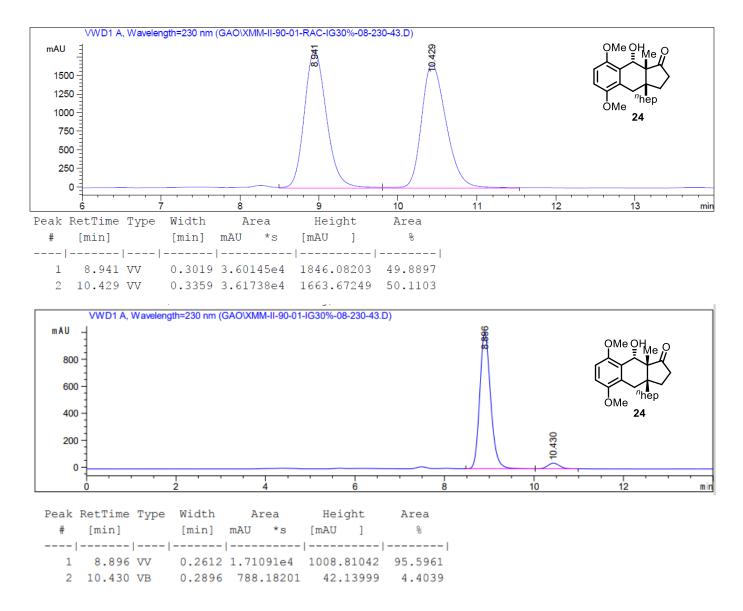
Enantiomeric excess: 92%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 13.698 min (major), t_R = 19.137 min (minor).



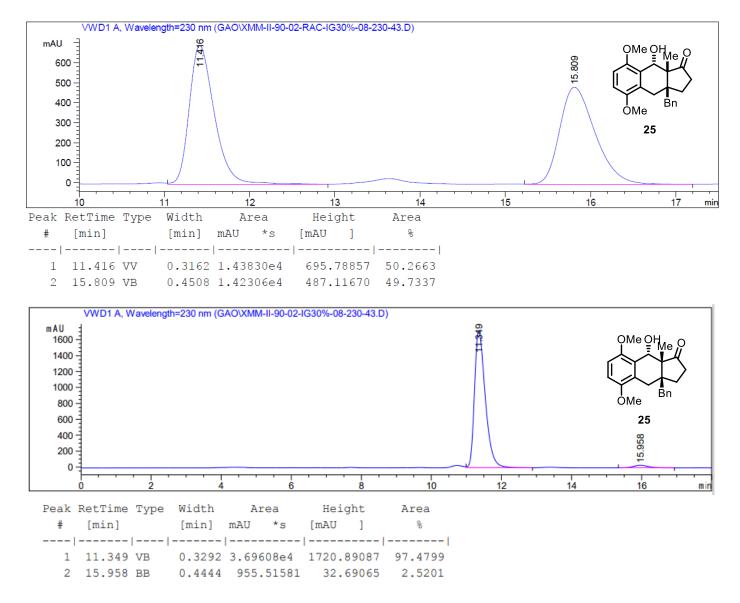
Enantiomeric excess: 95%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 10.883$ min (major), $t_R = 17.052$ min (minor).



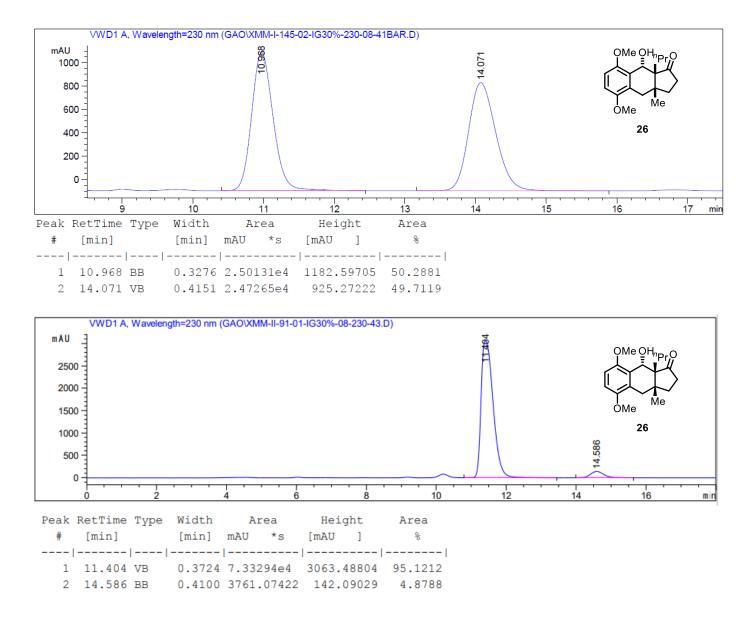
Enantiomeric excess: 93%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 11.074$ min (major), $t_R = 14.873$ min (minor).



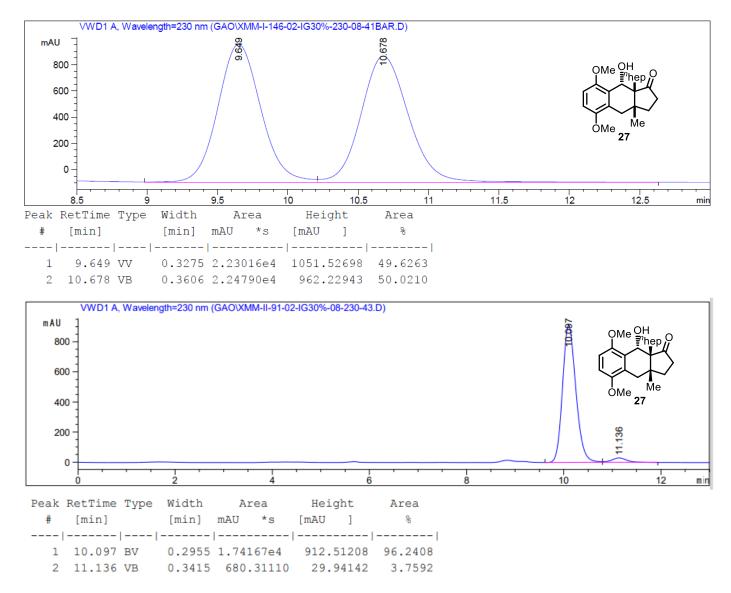
Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 8.896$ min (major), $t_R = 10.430$ min (minor).



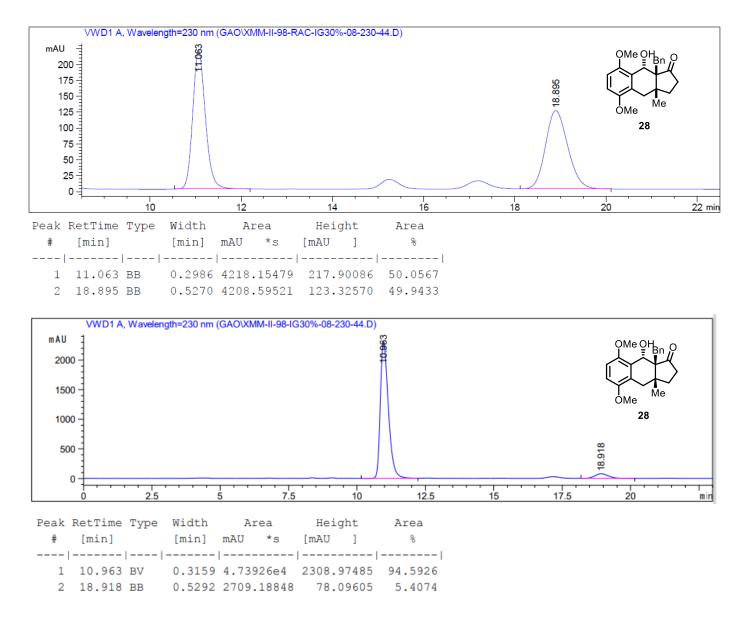
Enantiomeric excess: 95%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 11.349$ min (major), $t_R = 15.958$ min (minor).



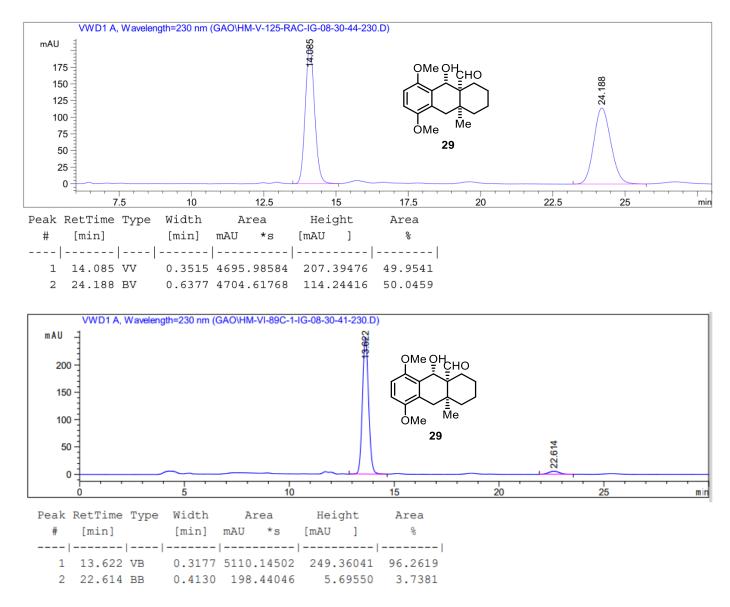
Enantiomeric excess: 90%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 11.404$ min (major), $t_R = 14.586$ min (minor).



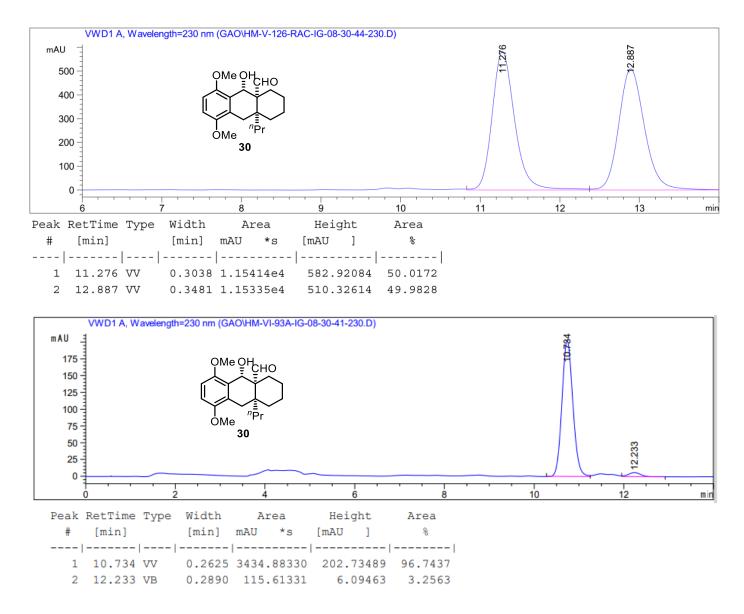
Enantiomeric excess: 93%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 10.097$ min (major), $t_R = 11.136$ min (minor).



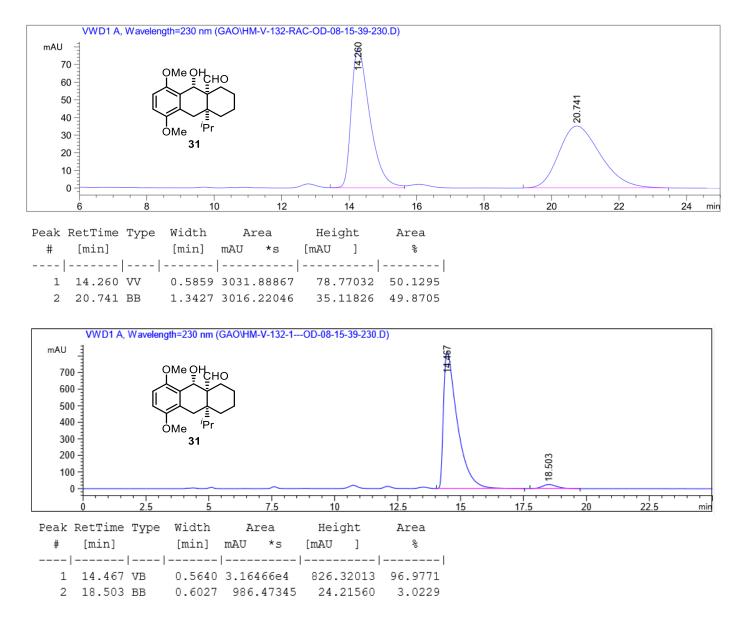
Enantiomeric excess: 89%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 10.963 \text{ min (major)}, t_R = 18.918 \text{ min (minor)}.$



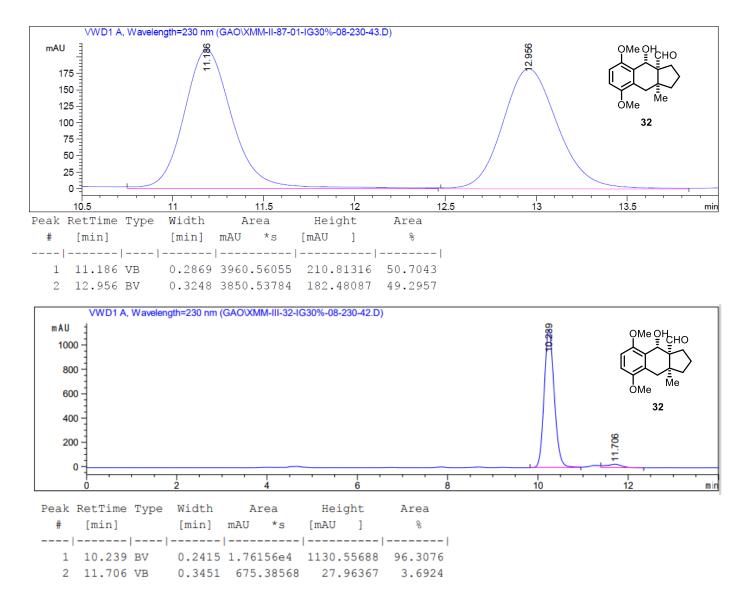
Enantiomeric excess: 93%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 13.622min$ (major), $t_R = 22.610 min$ (minor).



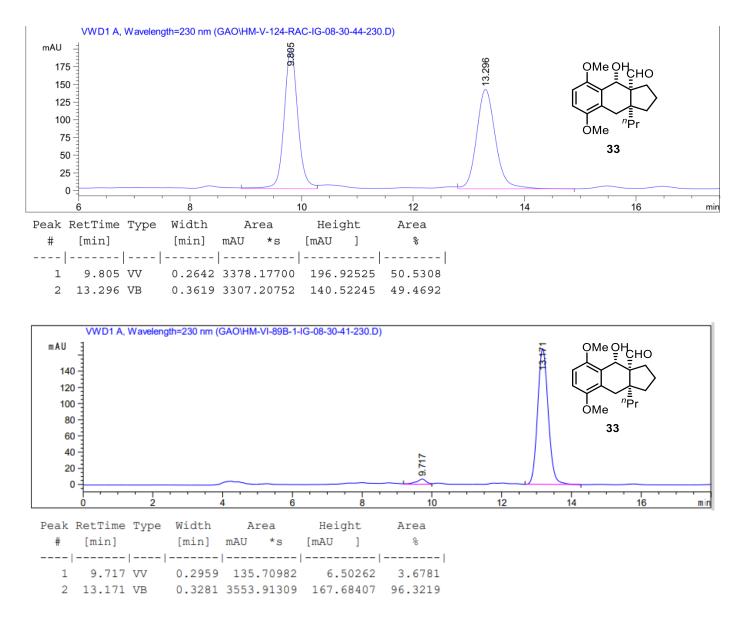
Enantiomeric excess: 93%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 10.734$ min (major), $t_R = 12.232$ min (minor).



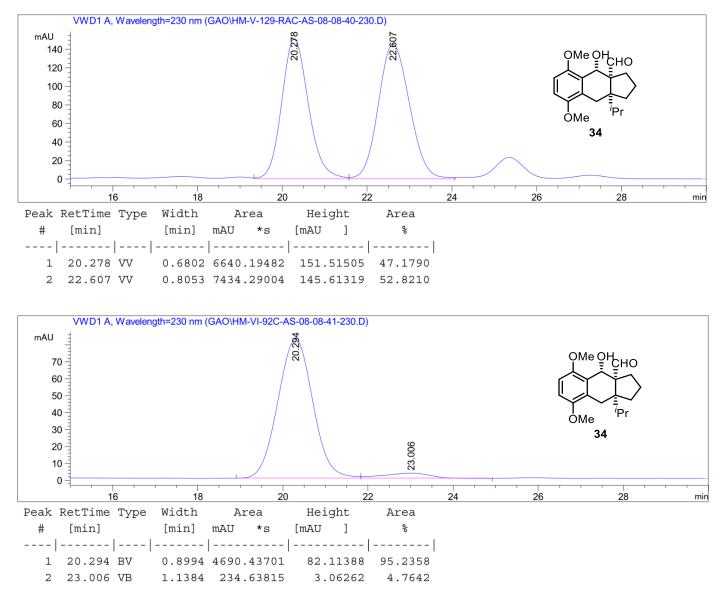
Enantiomeric excess: 94%, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 85/15, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 14.467$ min (major), $t_R = 18.503$ min (minor).



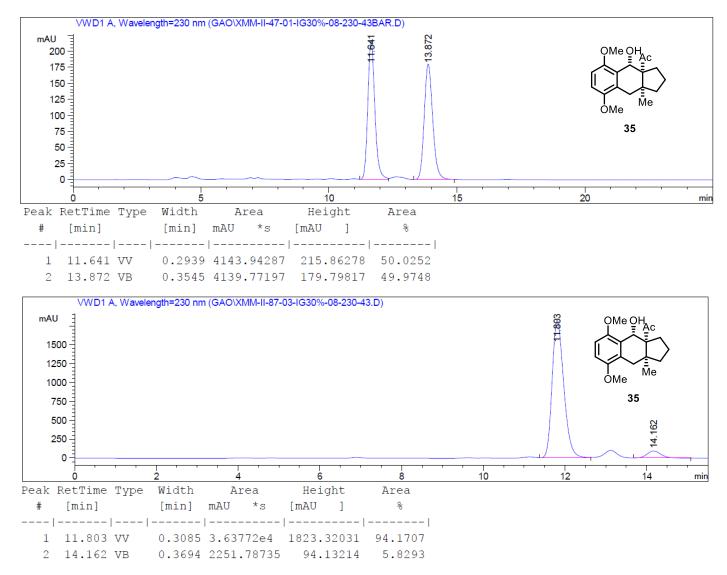
Enantiomeric excess: 93%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 10.239$ min (major), $t_R = 11.706$ min (minor).



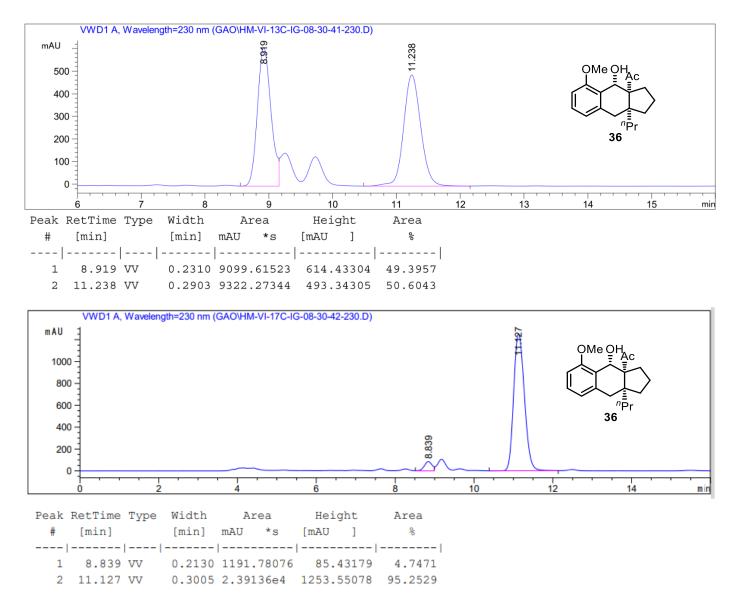
Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 9.717min (minor), t_R = 13.171 min (major).



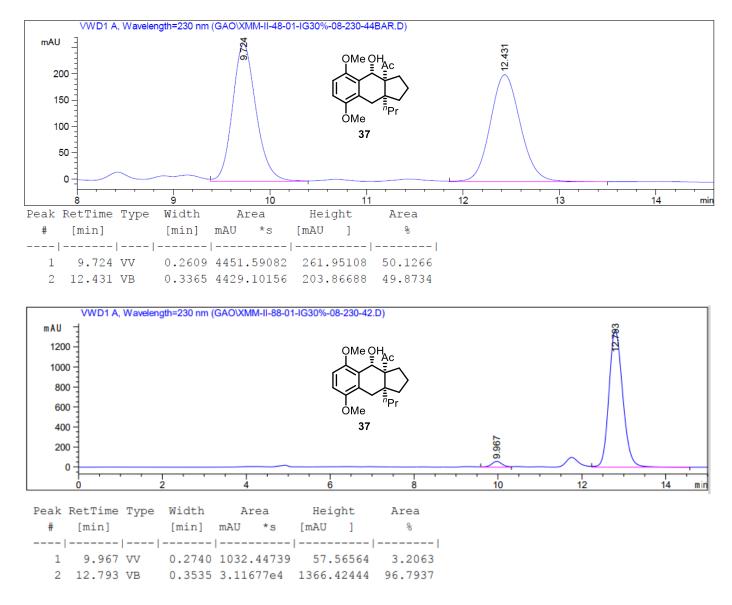
Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 92/8, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 20.294$ min (major), $t_R = 23.006$ min (minor).



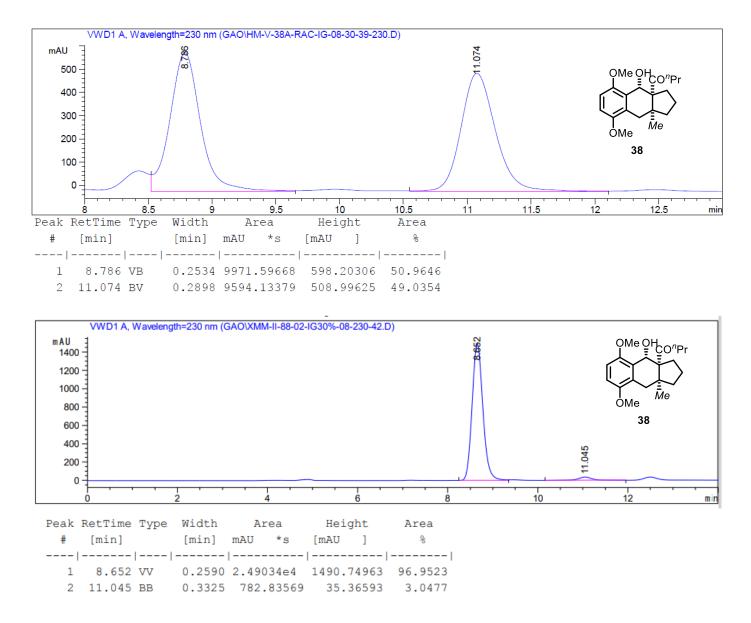
Enantiomeric excess: 88%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 11.803$ min (major), $t_R = 14.162$ min (minor).



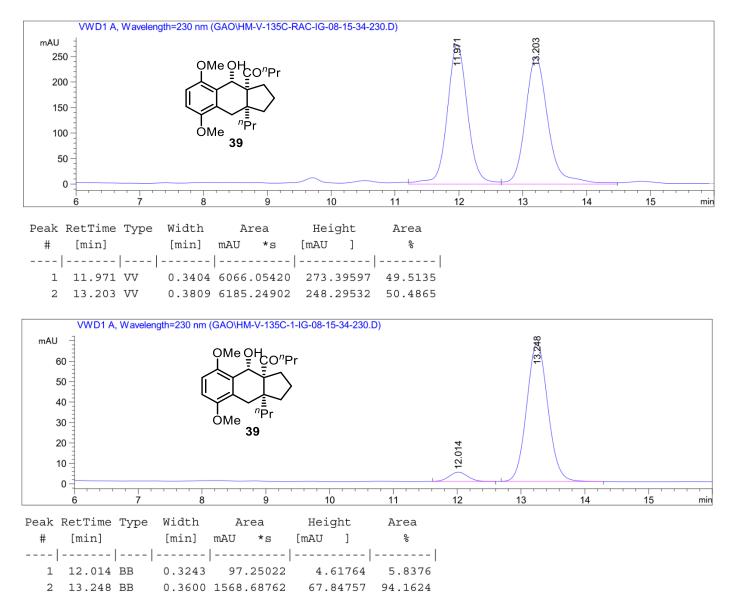
Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 8.839$ min (minor), $t_R = 11.127$ min (major).



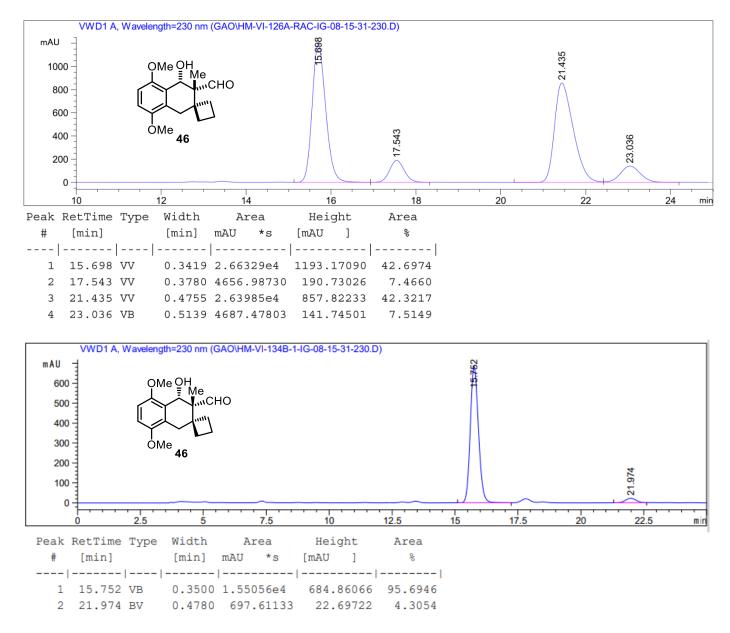
Enantiomeric excess: 94%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 9.967 min (minor), t_R = 12.793 min (major).



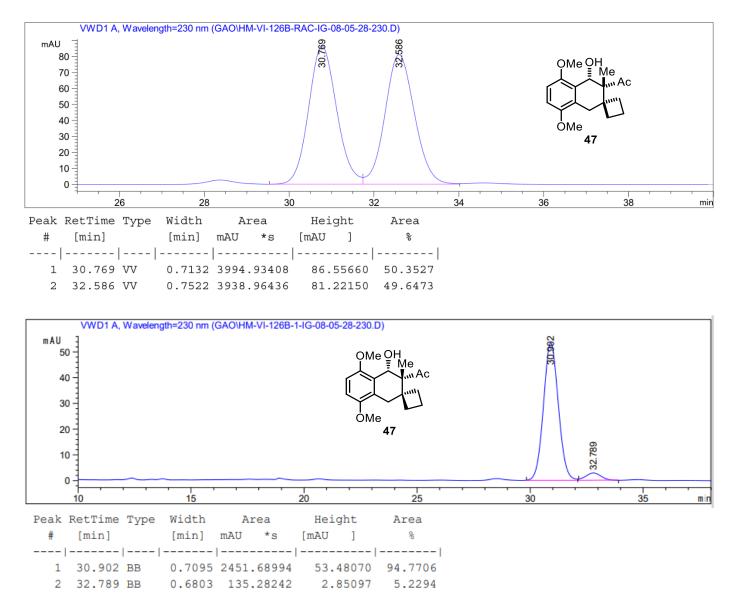
Enantiomeric excess: 94%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 8.652 \text{ min}$ (minor), $t_R = 11.045 \text{ min}$ (major).



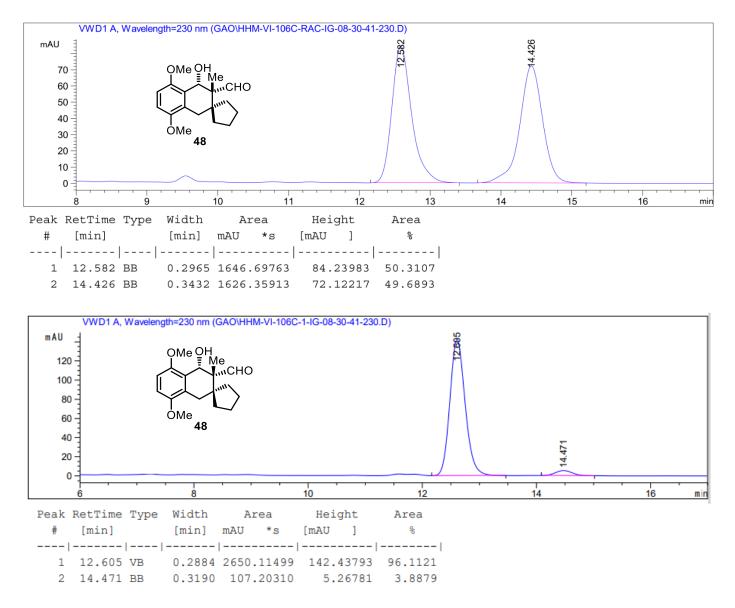
Enantiomeric excess: 88%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 85/15, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 12.014$ min (minor), $t_R = 13.248$ min (major).



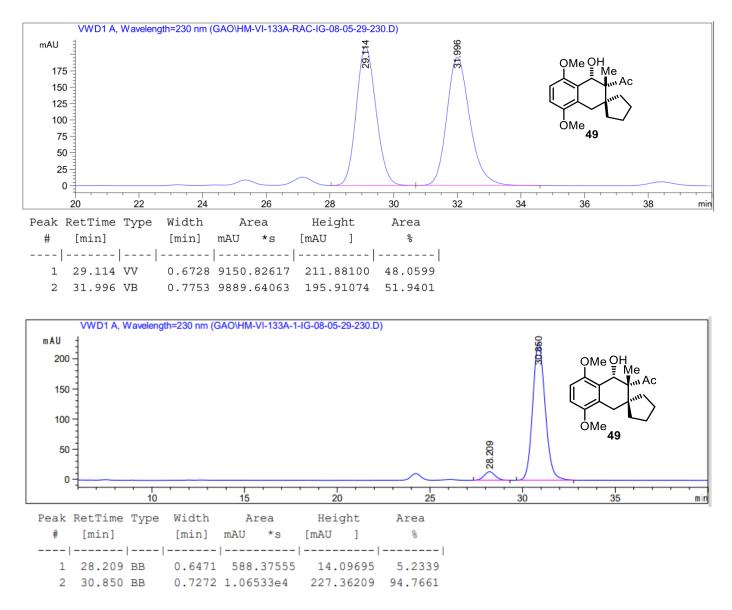
Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 85/15, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 15.752min$ (major), $t_R = 21.974 min$ (minor).



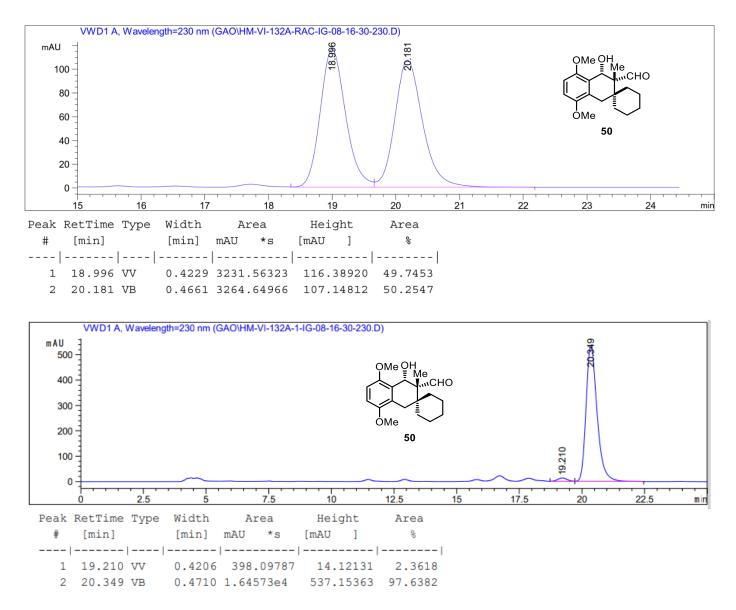
Enantiomeric excess: 89%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 95/5, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 30.903min (major), t_R = 32.791 min (minor).



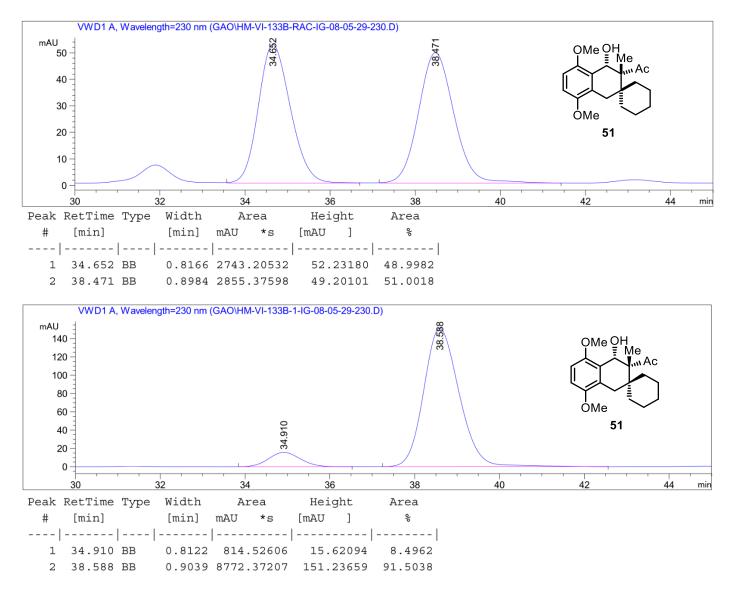
Enantiomeric excess: 92%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 12.605 \text{min}$ (major), $t_R = 14.471 \text{ min}$ (minor).



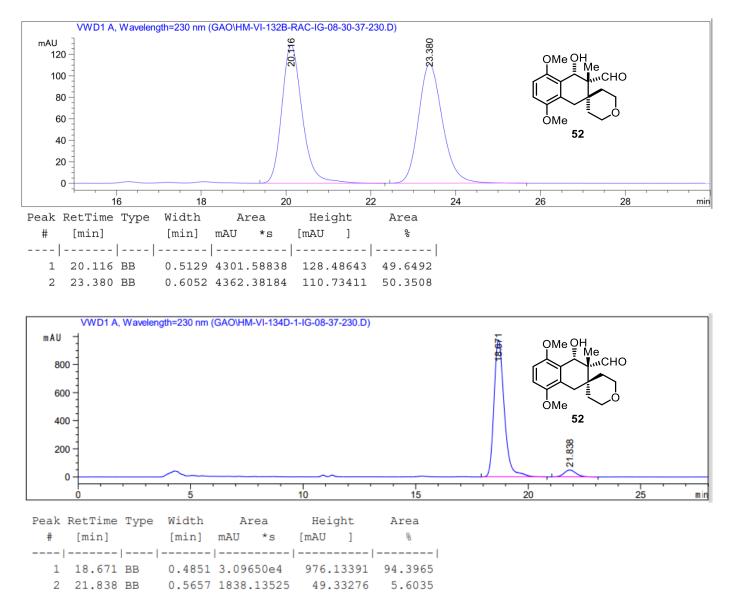
Enantiomeric excess: 90%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 95/5, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 28.209$ min (minor), $t_R = 30.850$ min (major).



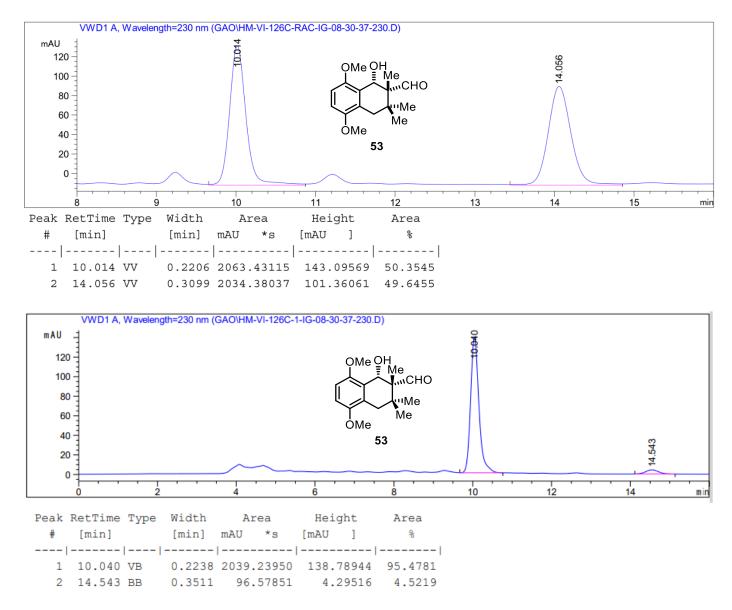
Enantiomeric excess: 95%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 84/ 16, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 19.210min$ (minor), $t_R = 20.349 min$ (major).



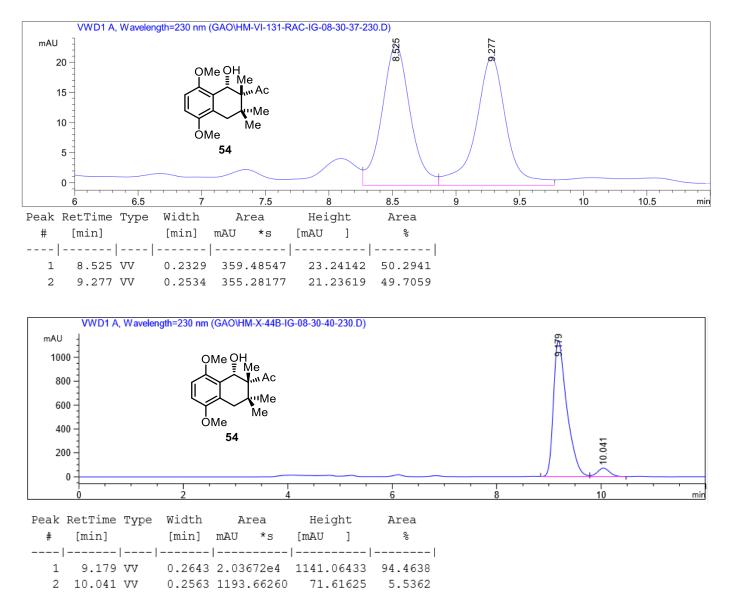
Enantiomeric excess: 83%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 95/5, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 34.910 min (minor), t_R = 38.588 min (major).



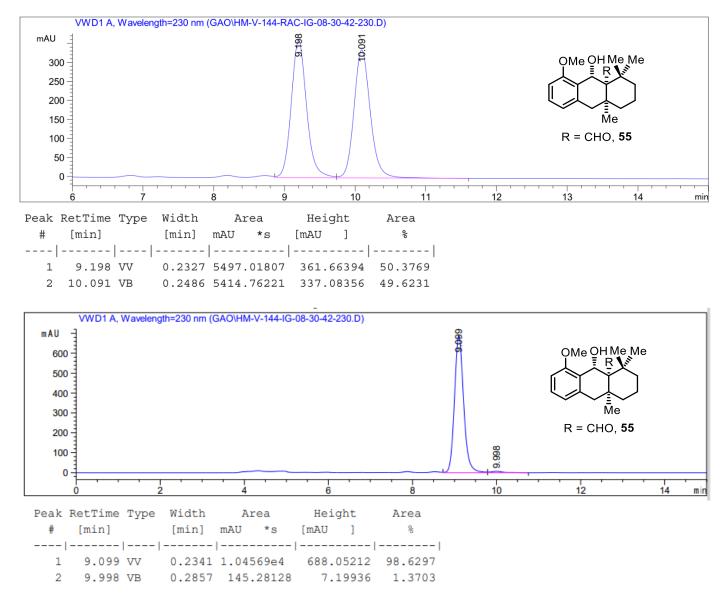
Enantiomeric excess: 88%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 18.671$ min (major), $t_R = 21.838$ min (minor).



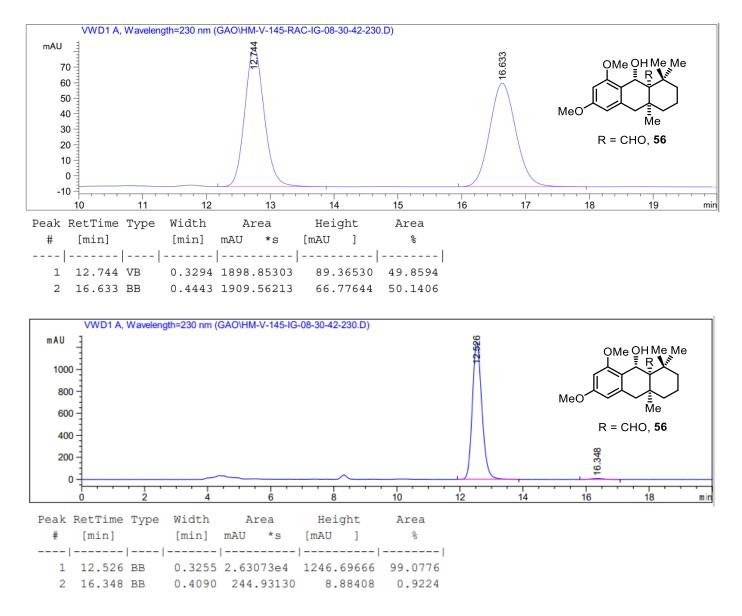
Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 10.040$ min (major), $t_R = 14.544$ min (minor).



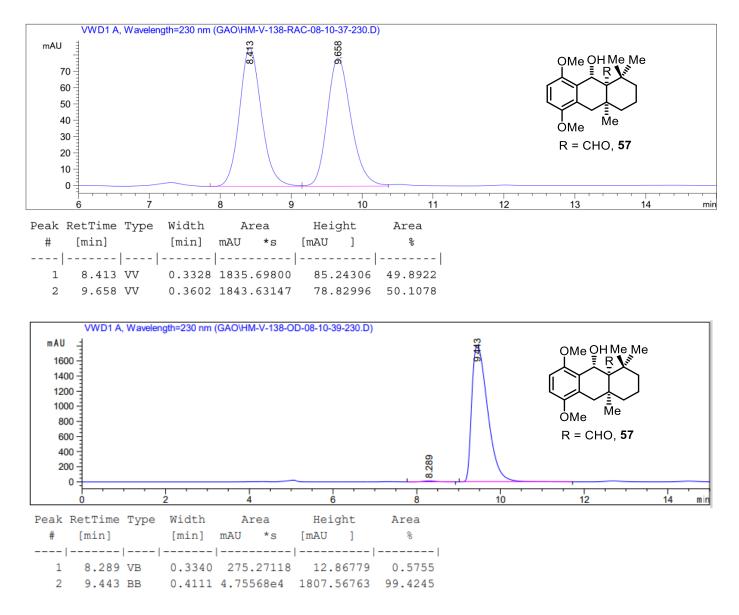
Enantiomeric excess: 89%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 9.179 min (major), t_R = 10.041 min (minor).



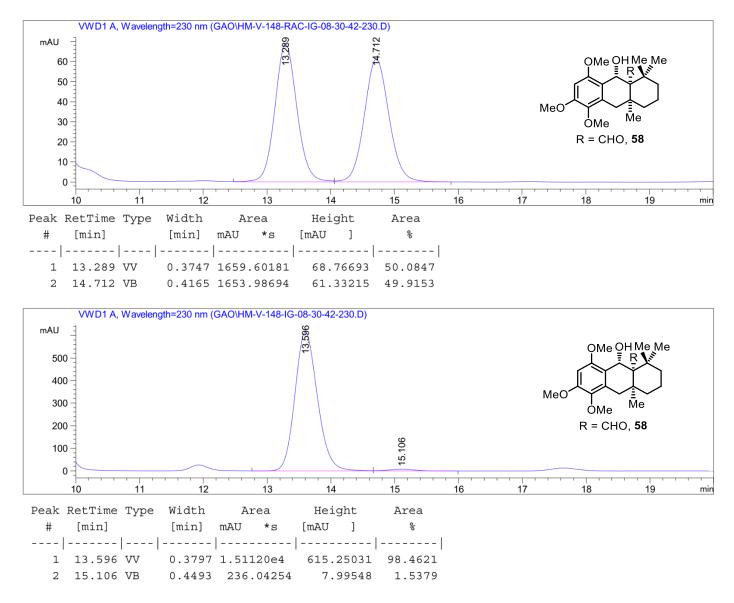
Enantiomeric excess: 97%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 9.100min (major), t_R = 9.998 min (minor).



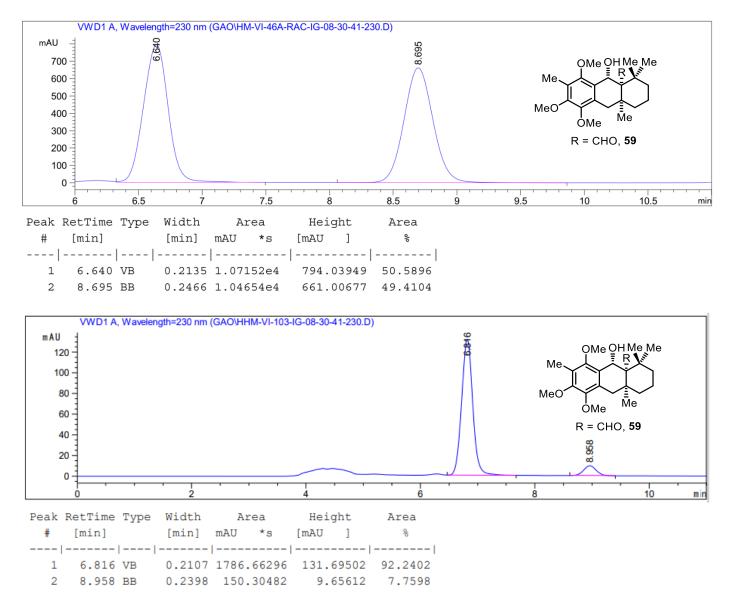
Enantiomeric excess: 98%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 12.526$ min (major), $t_R = 16.350$ min (minor).



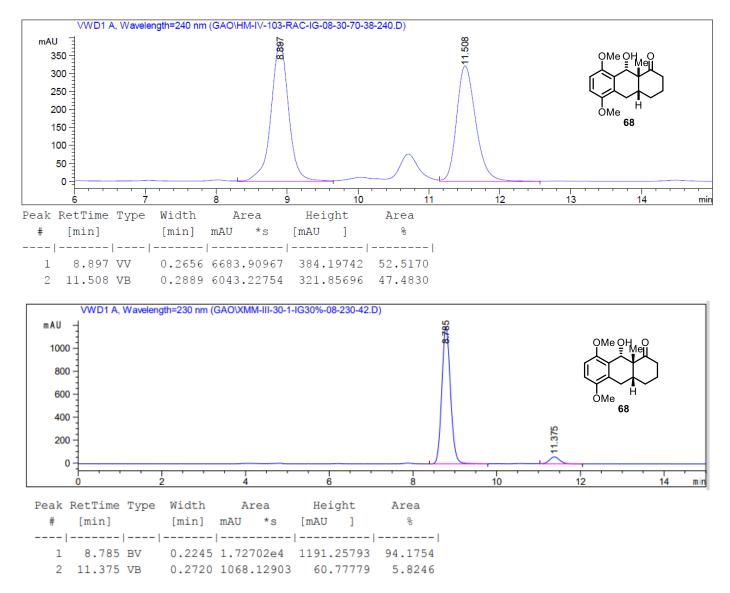
Enantiomeric excess: 99%, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 8.289$ min (minor), $t_R = 9.444$ min (major).



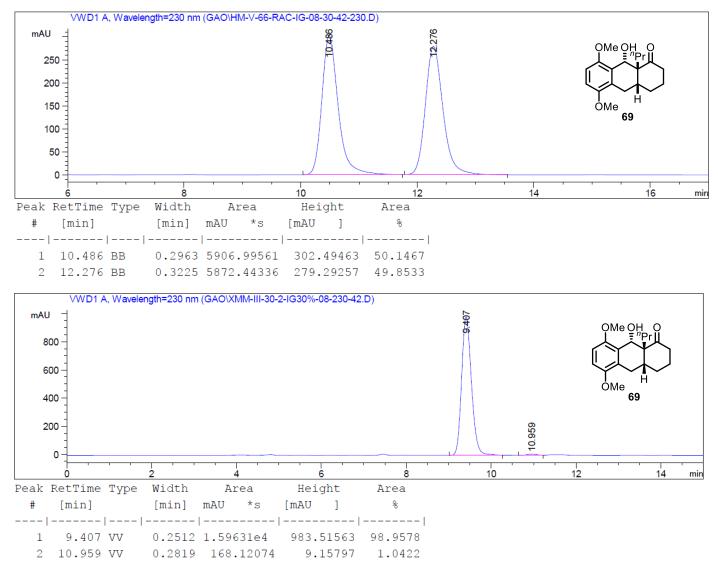
Enantiomeric excess: 97%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 13.596$ min (major), $t_R = 15.106$ min (minor).



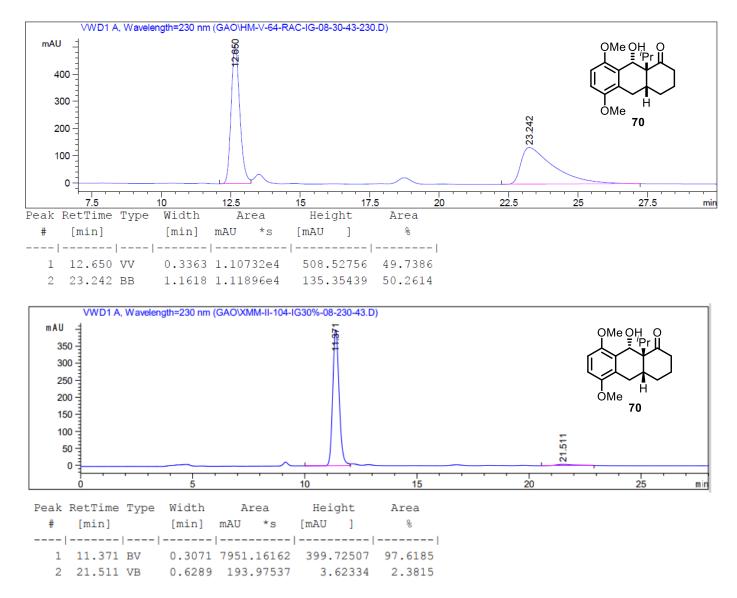
Enantiomeric excess: 85%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 6.816$ min (major), $t_R = 8.958$ min (minor).



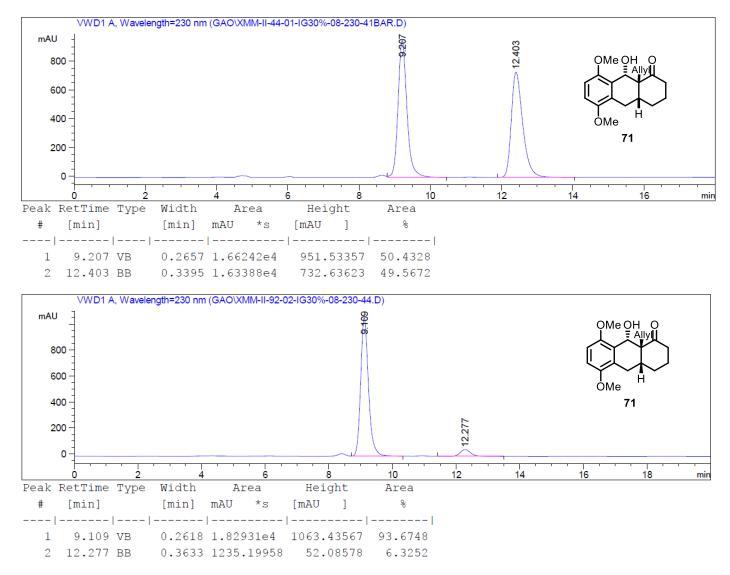
Enantiomeric excess: 88%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 8.785 \text{ min (major)}, t_R = 11.375 \text{ min (minor)}.$



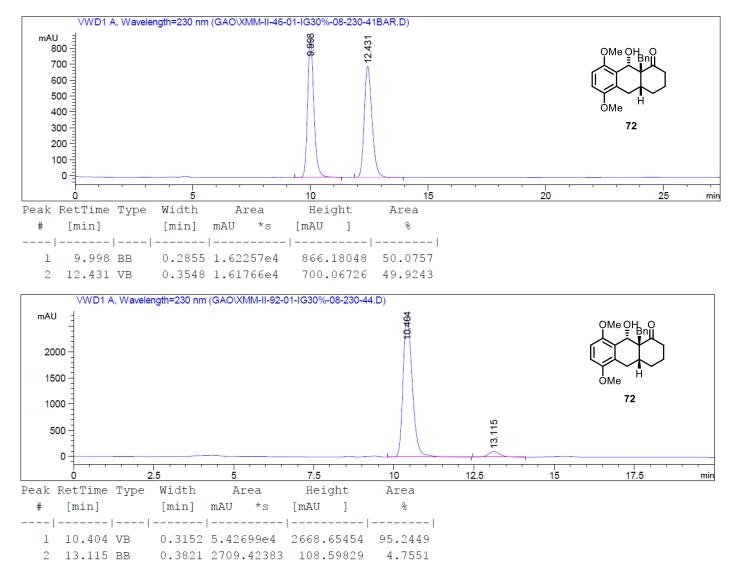
Enantiomeric excess: 98%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 9.407 min (major), t_R = 10.959 min (minor).



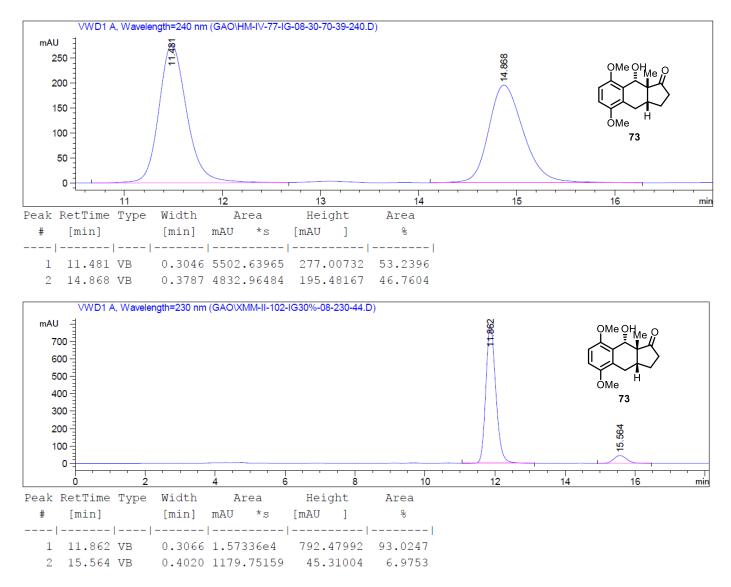
Enantiomeric excess: 95%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 11.371 \text{ min (major)}, t_R = 21.511 \text{ min (minor)}.$



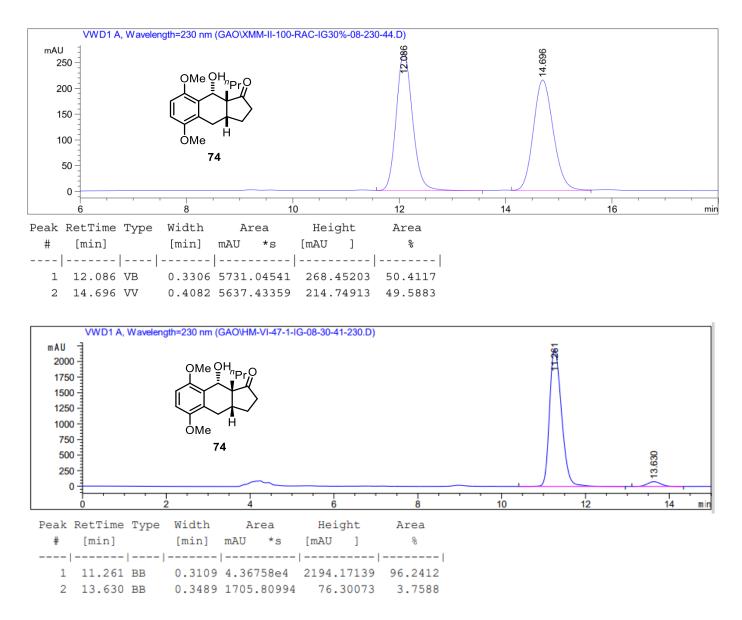
Enantiomeric excess: 87%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 9.109 min (major), t_R = 12.277 min (minor).



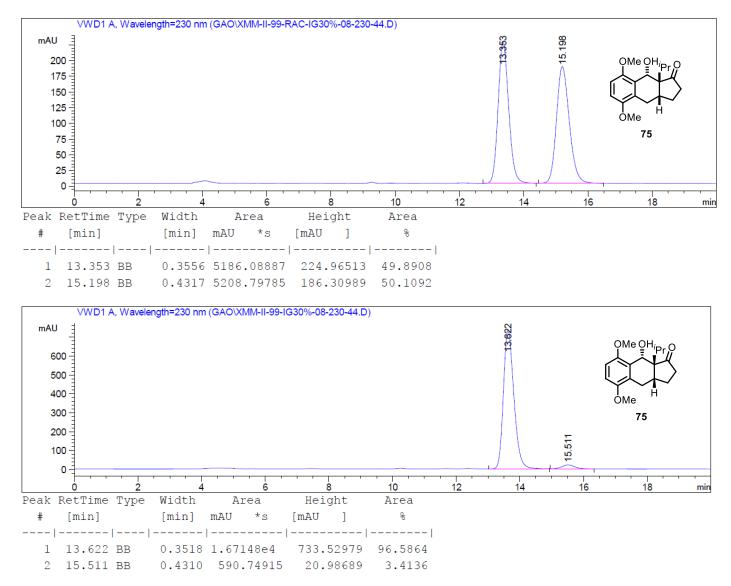
Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 10.404$ min (major), $t_R = 13.115$ min (minor).



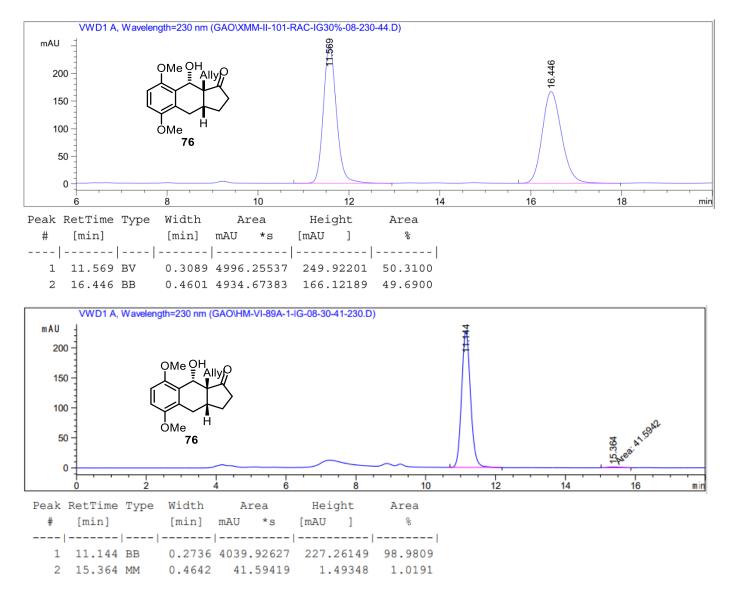
Enantiomeric excess: 86%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 11.862 \text{ min (major)}, t_R = 15.564 \text{ min (minor)}.$



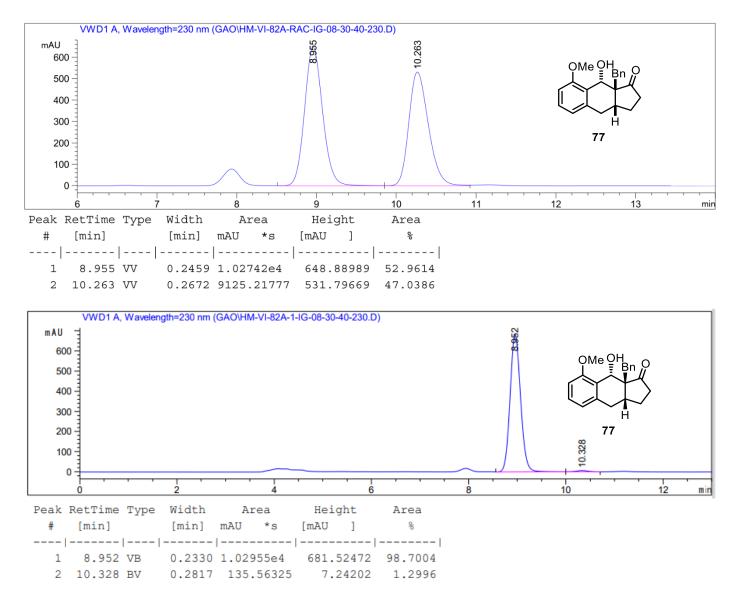
Enantiomeric excess: 92%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 11.261$ min (major), $t_R = 13.630$ min (minor).



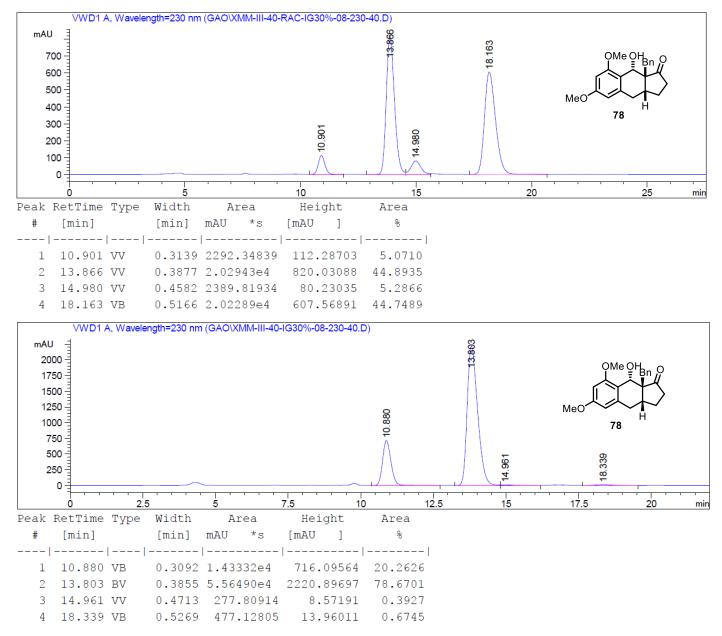
Enantiomeric excess: 93%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 13.622 \text{ min (major)}, t_R = 15.511 \text{ min (minor)}.$



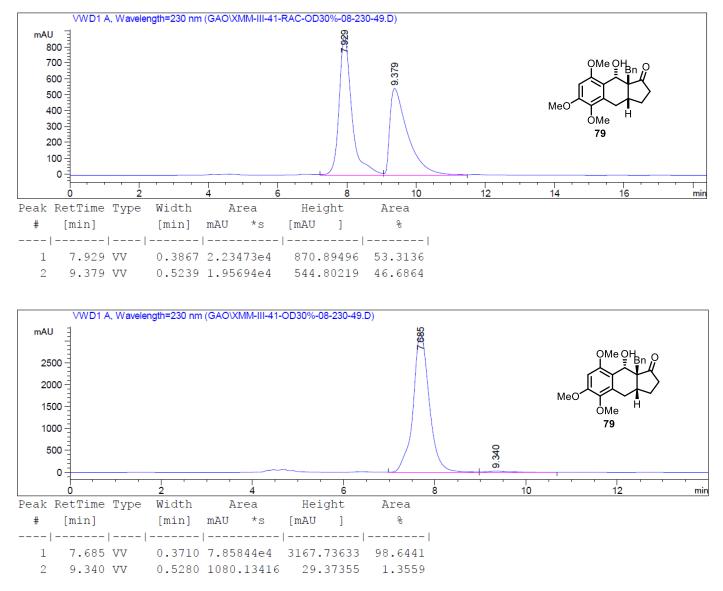
Enantiomeric excess: 99.5%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 11.144$ min (major), $t_R = 16.277$ min (minor).



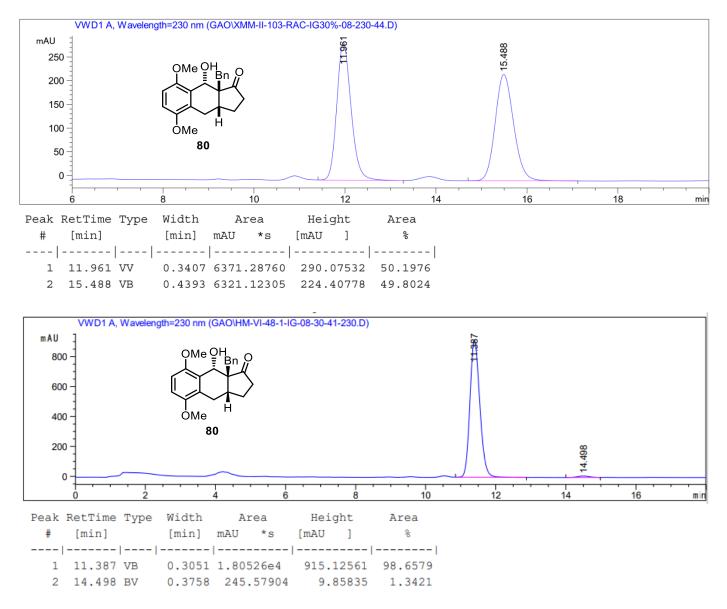
Enantiomeric excess: 97%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 8.952 \text{ min (major)}, t_R = 10.329 \text{ min (minor)}.$



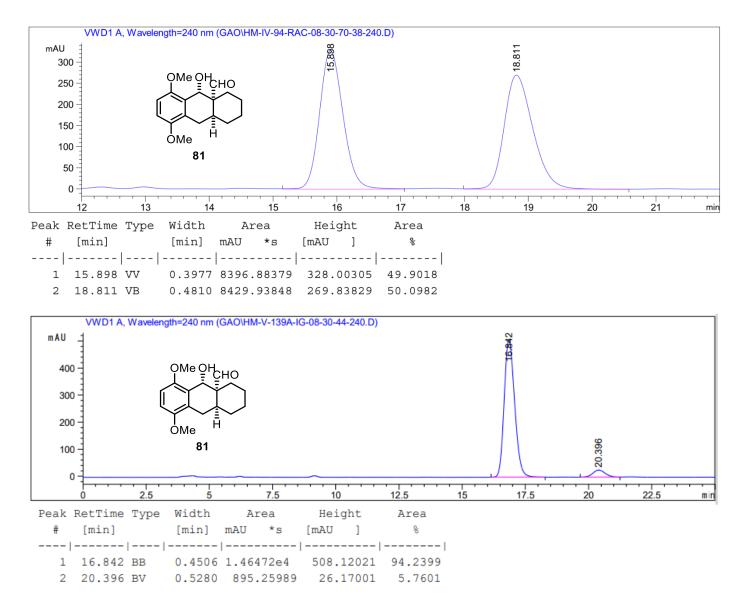
Enantiomeric excess: 96% (minor), determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 10.880 \text{ min (major)}, t_R = 14.961 \text{ min (minor)}.$



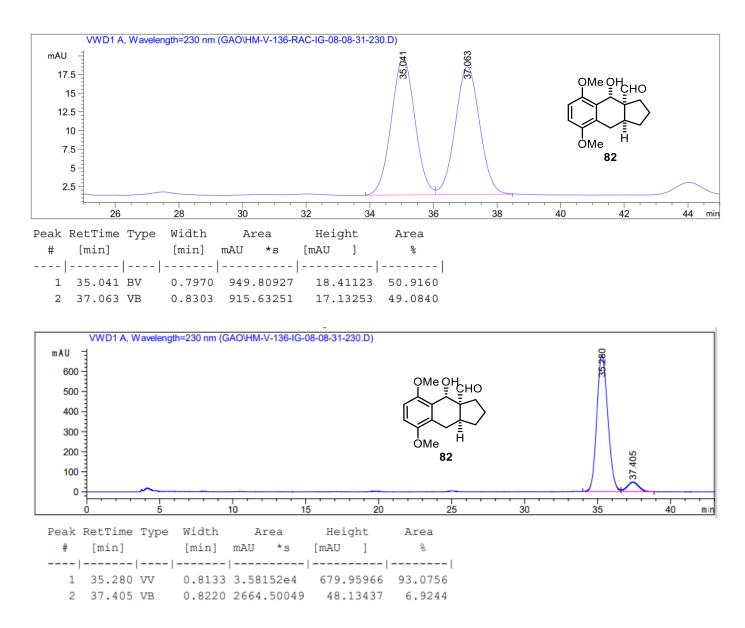
Enantiomeric excess: 97% (major), determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 7.685 \text{ min (major)}, t_R = 9.340 \text{ min (minor)}.$



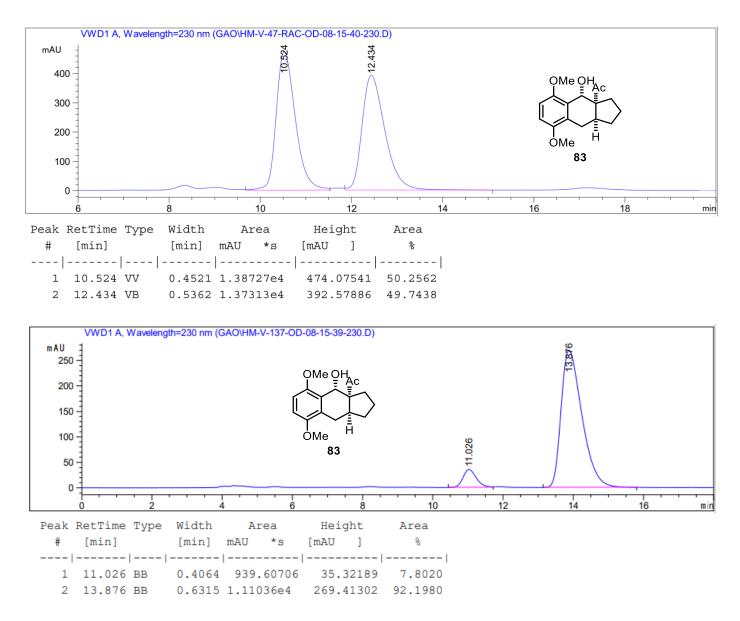
Enantiomeric excess: 97%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 11.387$ min (major), $t_R = 14.498$ min (minor).



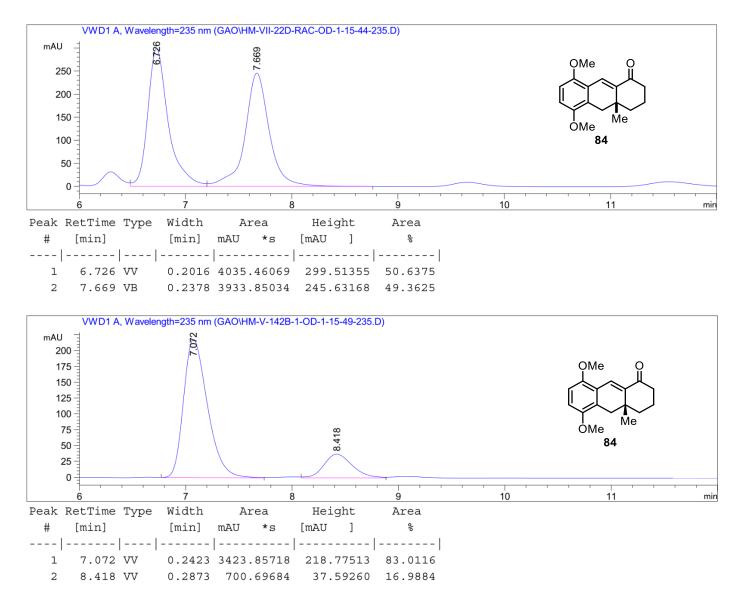
Enantiomeric excess: 88%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 240 nm): $t_R = 16.842min$ (major), $t_R = 20.397 min$ (minor).



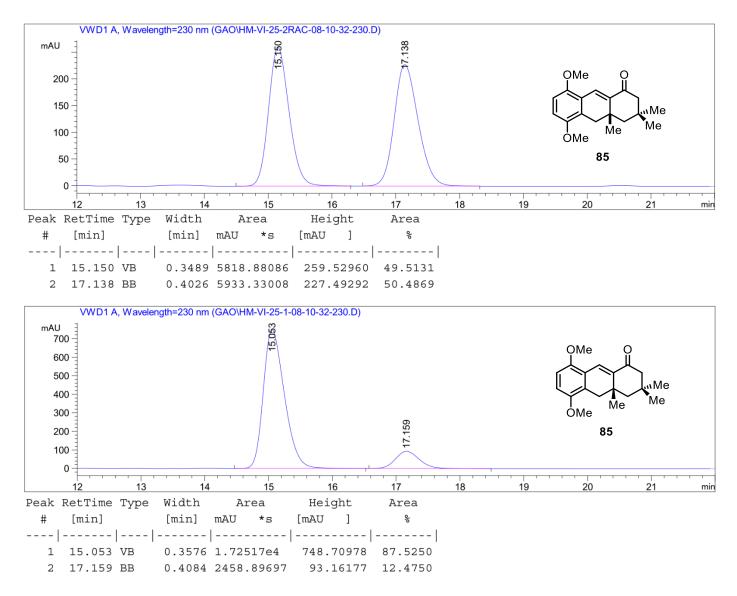
Enantiomeric excess: 86%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 92/ 8, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 35.280$ min (major), $t_R = 37.406$ min (minor).



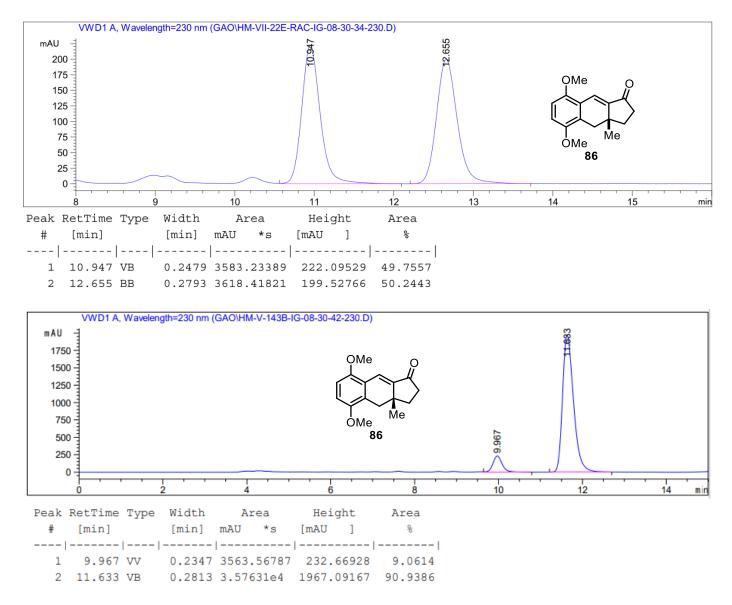
Enantiomeric excess: 84%, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 85/15, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 11.026min$ (minor), $t_R = 13.877$ min (major).



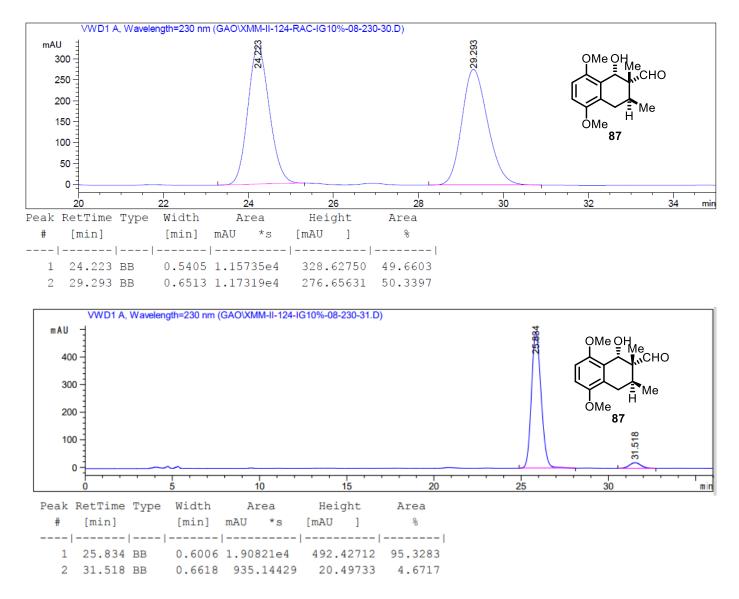
Enantiomeric excess: 66%, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 85/15, flow rate 1.0 mL/min, T = 25 °C, 230 nm): $t_R = 7.072 \text{ min (major)}, t_R = 8.418 \text{ min (minor)}.$



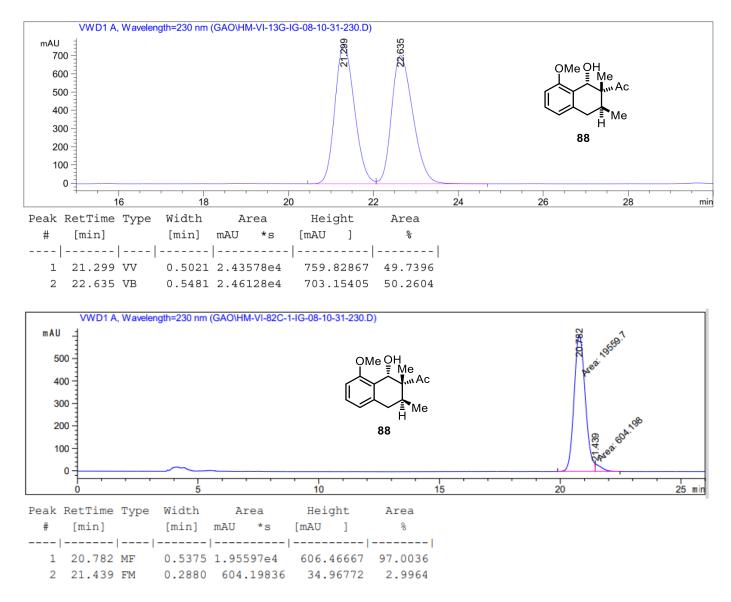
Enantiomeric excess: 75%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 15.053$ min (major), $t_R = 17.159$ min (minor).



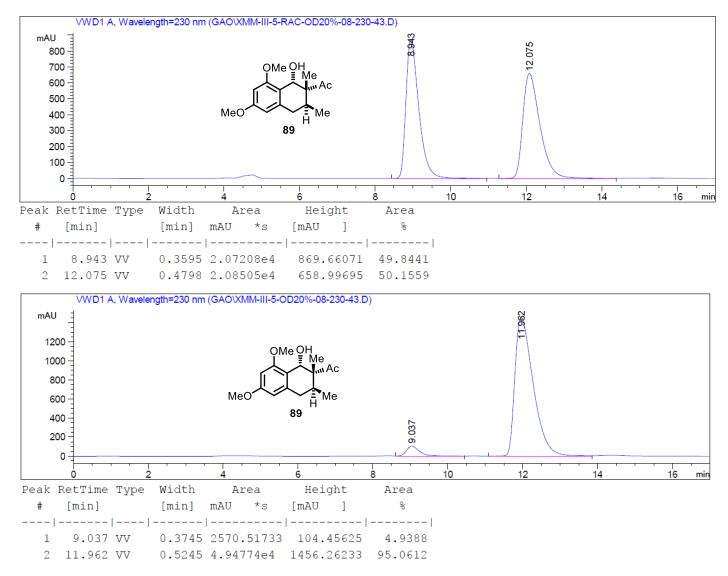
Enantiomeric excess: 82%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 9.967 min (minor), t_R = 11.633 min (major).



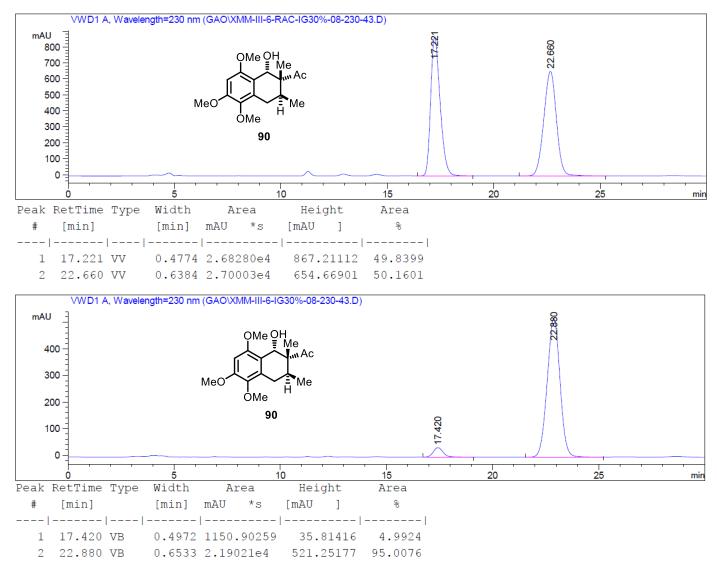
Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 25.834$ min (major), $t_R = 31.518$ min (minor).



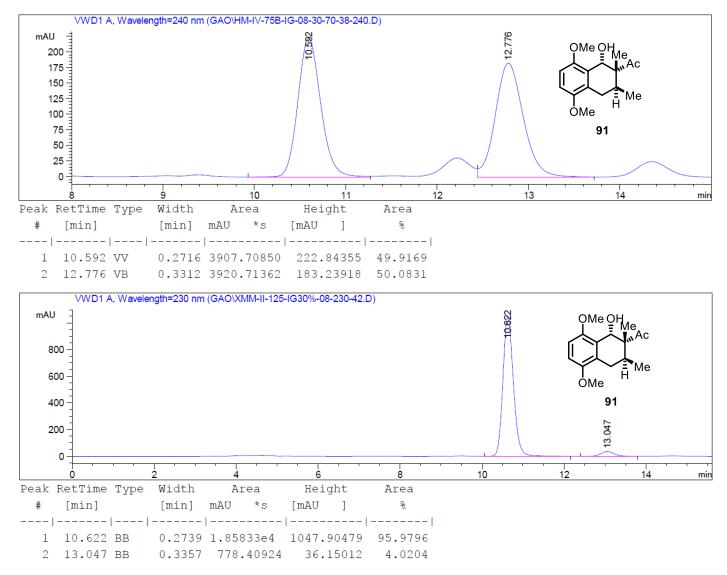
Enantiomeric excess: 94%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 20.782min$ (major), $t_R = 21.418 min$ (minor).



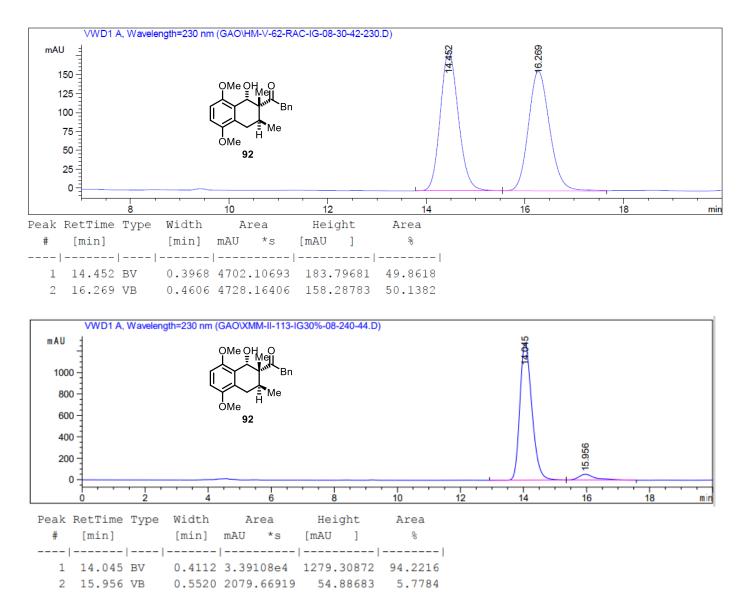
Enantiomeric excess: 90%, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 80/ 20, flow rate 0.8 mL/min, T = 25 °C, 230 nm): t_R = 9.037 min (minor), t_R = 11.962 min (major).



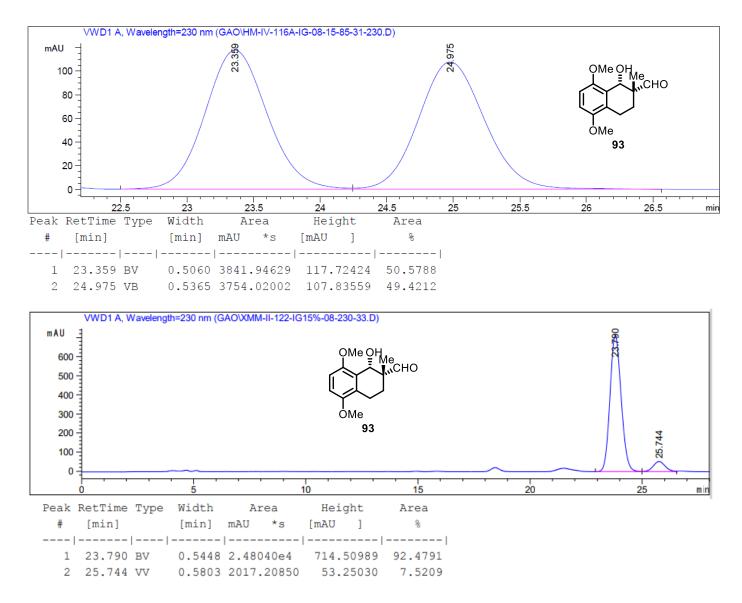
Enantiomeric excess: 90%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 17.420$ min (minor), $t_R = 22.880$ min (major).



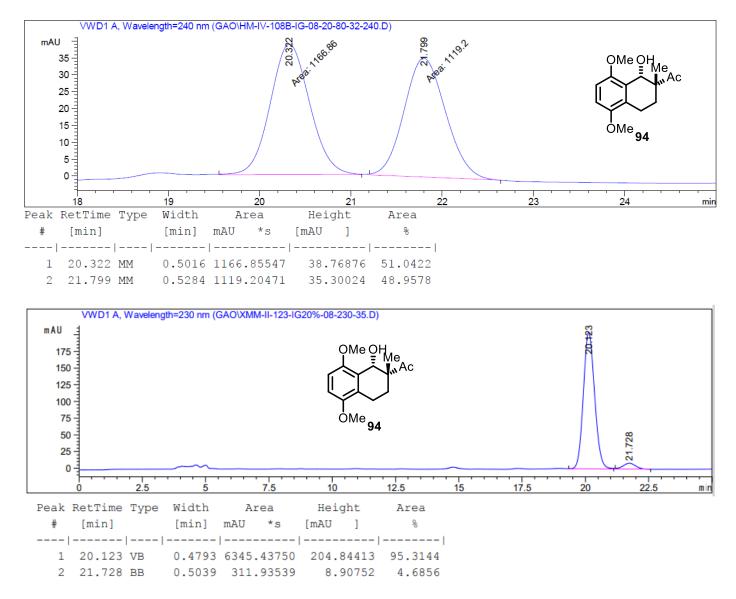
Enantiomeric excess: 92%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 10.622 \text{ min (major)}, t_R = 13.047 \text{ min (minor)}.$



Enantiomeric excess: 88%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 70/30, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 14.045$ min (major), $t_R = 15.956$ min (minor).



Enantiomeric excess: 85%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 85/15, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 23.790 \text{ min (major)}, t_R = 25.744 \text{ min (minor)}.$



Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 80/ 20, flow rate 0.8 mL/min, T = 25 °C, 230 nm): $t_R = 20.123 \text{ min (major)}, t_R = 21.728 \text{ min (minor)}.$