Supporting Information

Asymmetric total synthesis of (+)-xestoquinone and (+)-adociaquinones A and B

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General experimental procedures

All reactions were carried out under an inert nitrogen atmosphere with dry solvents under anhydrous conditions unless otherwise noted. Anhydrous dichloromethane, tetrahydrofuran and toluene were purified by the PS-MD-5 (Innovative Technology) solvent purification system. Dimethyl sulfoxide used for IBX oxidation was purchased from commercially available anhydrous solvent. Anhydrous diethyl ether was distilled from sodium. The solvents used for condition screening of desymmetric intramolecular Michael addition are all commercially available analytical-grade solvents. TLC analyses were performed on EMD 250 μm Silica Gel $HSGF_{254}$ plates and visualized by quenching of UV fluorescence (λ_{max} = 254 nm), or by staining phosphomolybdic acid, or potassium permanganate. Flash column chromatography was performed as described by Still[1], employing SiliCycle UltraPure Silica Gels: SilicaFlash® P60 40 – 63 μm (230 – 400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker-500, 400 spectrometers. Chemical shifts for ^{1}H and ^{13}C NMR spectra are reported in ppm (δ) relative to residue protium in the solvent ($CDCl_3$: δ 7.26, 77.0 ppm; DMSO: δ 2.50, 40.4 ppm) and the multiplicities are presented as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. 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. Infrared (IR) spectra was obtained using a Shimatzu IRTracer-100 fourier transform infrared spectroscopy (FTIR). The $[\alpha]_D^{20}$was recorded at 365 nm using Anton Paar MCP 5500.

General experimental procedure A for desymmetric intramolecular Michael addition without AcOH

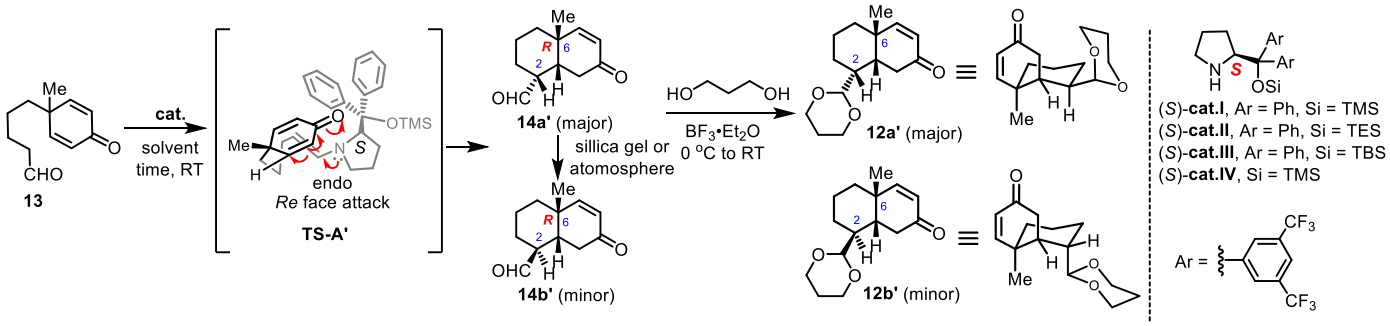
A solution of **13**, catalyst in analytical-grade solvent was stirred at room temperature for indicated time without inert nitrogen atmosphere. Then the solution was evacuated and purified by flash chromatography or preparation lamella chromatography (20% ethyl acetate – petroleum ether).

General experimental procedure B for desymmetric intramolecular Michael addition with AcOH

A solution of **13**, catalyst and additive AcOH in analytical-grade solvent was stirred at room temperature for indicated time without inert nitrogen atmosphere. Then the solution was quenched with saturated $NaHCO_3$ and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, concentrated and purified by silica gel flash chromatography or preparation lamella chromatography (20% ethyl acetate – petroleum ether).

Detail of the screening conditions of desymmetric intramolecular Michael addition

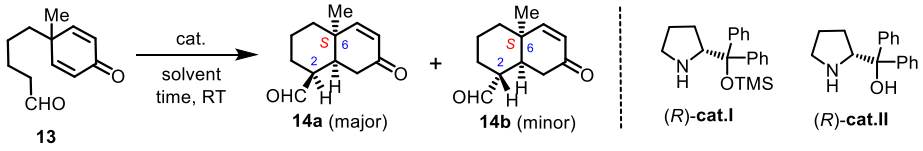
Table S1. Screening conditions of desymmetric intramolecular Michael addition to obtain **14'** using *S*-catalysts.



entry	cat. (equiv.)	solvent	time	yield/d.r. at C2[a]	e.e.[b]
1[c]	Et_2NH (10.0)	MeOH/H_2O (20:1)	6.0 h	64%	rac.
2	(*S*)-**cat.I** (0.5)	MeOH/H_2O (20:1)	10.5 h	48% / 3.0:1	**14a'**: -87%; **14b'**: -31%
3	(*S*)-**cat.II** (0.5)	MeOH/H_2O (20:1)	10.5 h	56% / 2.8:1	**14a'**: -85%; **14b'**: -5%
4	(*S*)-**cat.III** (0.5)	MeOH/H_2O (20:1)	48.0 h	trace	**14a'**: -80%; **14b'**: -15%
5	(*S*)-**cat.IV** (0.5)	MeOH/H_2O (20:1)	48.0 h	trace	**14a'**: -84%; **14b'**: -6%
6	(*S*)-**cat.I** (0.5)	MeOH	2.0 h	63% / 5.0:1	**14a'**: -85%; **14b'**: -37%
7	(*S*)-**cat.I** (0.5)	DCM	24.0 h	51% /1.1:1	**14a'**: -93%; **14b'**: -86%
8	(*S*)-**cat.I** (0.5)	Et_2O	24.0 h	50% / 2.8:1	**14a'**: -96%; **14b'**: -93%
9	(*S*)-**cat.I** (0.5)	MeCN	24.0 h	47% /1.0:1	**14a'**: -93%; **14b'**: -88%
10	(*S*)-**cat.I** (0.5)	toluene	5.5 h	42% / 22.0:1	**14a'**: -97%; **14b'**: -89%
11[c]	(*S*)-**cat.I** (0.5)	toluene	11.0 h	52% / 4.5:1	**14a'**: -97%; **14b'**: -89%
12[d]	(*S*)-**cat.I** (0.3)	toluene	16.0 h	73%[e] / 1.7:1[f]	**14a'**: -97%; **14b'**: -94%
13[g]	(*S*)-**cat.I** (0.2)	toluene	16.0 h	86%[e] / 2.0:1[f]	**14a'**: -96%; **14b'**: -89%
14[h]	(*S*)-**cat.I** (0.4)	toluene	12.0 h	62%[i] / 14.0:1[j]	**14a'**: -96%; **14b'**: -89%

All reactions were performed using **13** (5.8 mg, 0.03 mmol, 1.0 equiv., 0.05 M) and catalyst at room temperature in analytical-grade solvents, unless otherwise noted. [a]The yields and diastereoisomeric ratios (d.r.) were determined from the crude ^{1}H NMR spectrum of **14'** using CH_2Br_2 as an internal standard, unless otherwise noted. [b]The enantiomeric excess (e.e.) values were determined by chiral high-performance liquid chromatography (Chiralpak IG-H). [c]Compound **13**: 9.6 mg, 0.05 mmol, 0.1 M. [d]Compound **13**: 96 mg, 0.5 mmol, 0.1 M. [e]Isolated yield of **14a'+14b'**. [f]The d.r. values were determined from the ^{1}H NMR spectrum of purified **14'** after purification by silica gel column chromatography. [g]Compound:**13**: 1.0 g, 5.2 mmol, 0.1 M. [h]Compound **13**: 288 mg, 1.5 mmol, 0.1 M. [i]Isolated yield of **12a'+12b'**. [j]The d.r. values were determined from the crude ^{1}H NMR spectrum of **12'** obtained from the one-pot process.

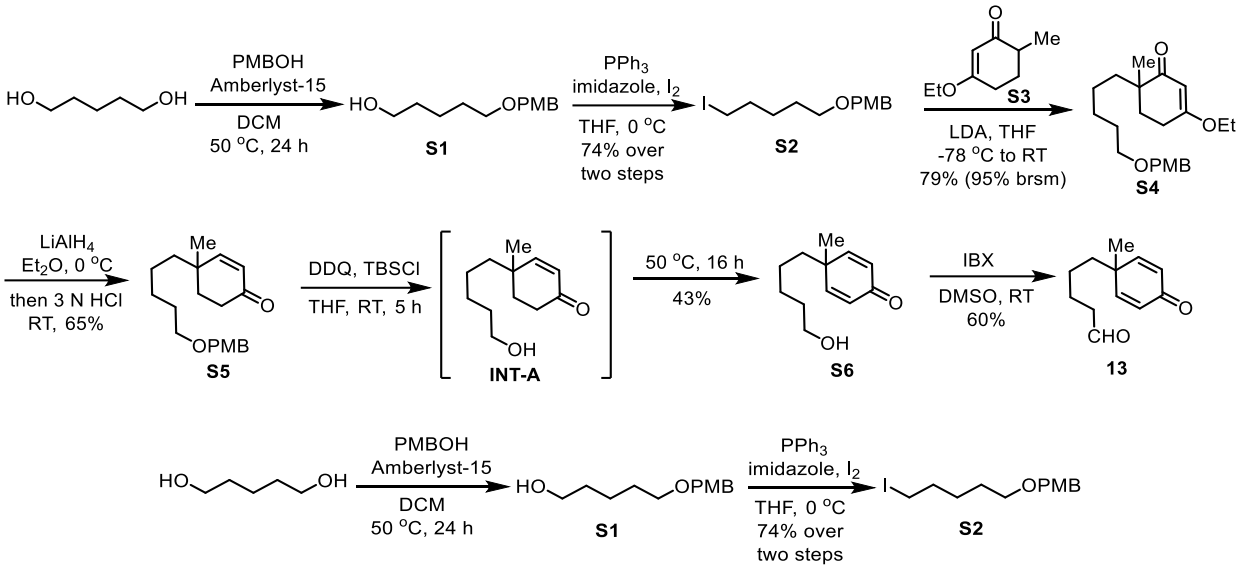
Table S2. Supplementary experiments as reviewer's suggestions.

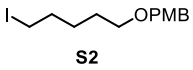


entry	condition	result
1	without **13** (*R*)-**cat.I** (0.05 mmol, 16.3 mg, 1.0 equiv.) AcOH (0.25 mmol, 15.0 mg, 5.0 equiv.) toluene (0.5 mL), RT, 9.0 h	(*R*)-**cat.I** : stable TMS group: not deprotected
2	**13** (0.05 mmol, 9.6 mg, 1.0 equiv.) (*R*)-**cat.II** (0.05 mmol, 16.3 mg, 1.0 equiv.) toluene (0.5 mL), RT, 9.0 h	N.R.
3	**13** (0.05 mmol, 9.6 mg, 1.0 equiv.) (*R*)-**cat.II** (0.05 mmol, 16.3 mg, 1.0 equiv.) AcOH (0.25 mmol, 15.0 mg, 5.0 equiv.) toluene (0.5 mL), RT, 9.0 h	N.R.

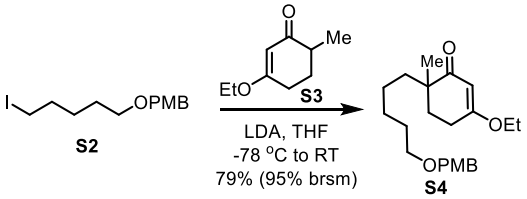
The entry 1 in **Table S2** indicate that the Hayashi–Jørgensen catalyst (*R*)-**cat.I** was stable under the stirred solution of 0.5 N AcOH/toluene for more than 9 hours. Besides, we conclude that (*R*)-**cat.I** was the effective catalyst in this desymmetrization reaction based on entries 2, 3 in **Table S2**.

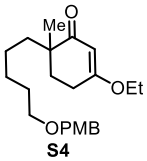
Experimental procedures and spectroscopic data





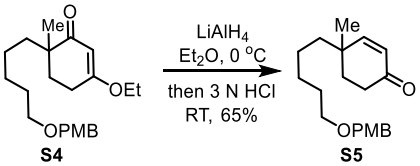
To a stirred solution of 4-methoxybenzyl alcohol (55.26 g, 49.6 mL, 0.40 mol, 1.0 equiv.) and 1,5-pentanediol (62.5 g, 62.9 mL, 0.60 mol, 1.5 equiv.) in anhydrous DCM (500 mL) at room temperature was added Amberlyst-15 resin (8.29 g, 15% w/w). The mixture was refluxed at 50 °C for 24 hours then filtered through silica gel and washed with DCM (6×50 mL). The filtrate was concentrated and the obtained crude compound **S1** was dissolved in anhydrous THF (800 mL). Then imidazole (81.7 g, 1.20 mol, 3.0 equiv.), PPh_3 (157.37 g, 0.60 mol, 1.5 equiv.), I_2 (152.29 g, 0.6 mol, 1.5 equiv.) was successively added to the solution at 0 °C. After stirred at 0 °C for 1 hour, the solution was quenched with saturated $Na_2S_2O_3$ (100 mL) then THF was evacuated. The mixture was extracted with ethyl acetate (3×200 mL). The combined organic layers were washed with water, brine, dried over anhydrous sodium sulfate, concentrated, and added 200 mL Et_2O. Then the undissolved triphenylphosphine oxide was filtered and washed with Et_2O (3×50 mL). The filtrate was concentrated and purified by silica gel flash chromatography (5% to 10% ethyl acetate – petroleum ether) to obtain **S2** as a light yellow viscous oil (98.87 g, 74% over two steps). R_f = 0.42 (10% ethyl acetate – petroleum ether). The NMR spectra of **S2** were consistent with the previous report [2].

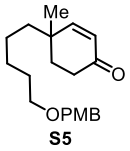




To a stirred solution of diisopropylamine (28 mL, 200 mmol, 2.0 equiv.) in anhydrous THF (300 mL) at 0 °C under nitrogen atmosphere was slowly added *n*-BuLi (80 mL, 200 mmol, 2.0 equiv., 2.5 M in hexane). After stirring at 0 °C for 30 minutes, the compound **S3** (15.4 g, 100 mmol, 1.0 equiv.) in anhydrous THF (50 mL) was slowly added at -78 °C. Then the mixture was stirred for 30 minutes at -78 °C and stirred for 30 minutes at room temperature. After that, compound **S2** (66.8 g, 200 mmol, 2.0

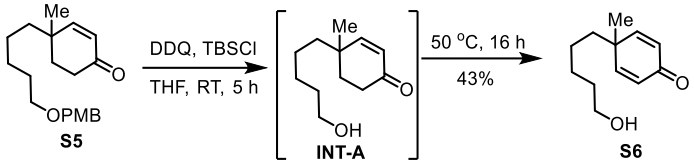
equiv.) in anhydrous THF (50 mL) was slowly added to the mixture at -78 ºC and slowly warmed to room temperature. After stirring at room temperature overnight, the mixture was quenched with water (100 mL) and extracted with ethyl acetate (3×100 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (10% to 20% ethyl acetate – petroleum ether) to obtain **S4** as a light yellow viscous oil (27.35 g, 79%) and 2.46 g recycling starting material **S3**. R_f = 0.24 (10% ethyl acetate – petroleum ether); Light yellow viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.22 (s, 1H), 4.41 (s, 2H), 3.87 (q, *J* = 7.0 Hz, 2H), 3.79 (s, 3H), 3.41 (t, *J* = 6.6 Hz, 2H), 2.48 – 2.31 (m, 2H), 1.94 – 1.82 (m, 1H), 1.70 (ddd, *J* = 13.4, 7.5, 5.7 Hz, 1H), 1.64 – 1.54 (m, 2H), 1.54 – 1.46 (m, 1H), 1.46 – 1.36 (m, 1H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.32 – 1.27 (m, 2H), 1.27 – 1.17 (m, 2H), 1.05 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.2, 175.6, 159.1, 130.8, 129.2 (2C), 113.7 (2C), 101.3, 72.5, 70.1, 64.1, 55.2, 43.2, 36.9, 32.2, 29.7, 26.9, 26.1, 23.8, 22.3, 14.2 ppm; IR ν_{max} 2935, 2858, 1653, 1608, 1512, 1458, 1375, 1359, 1246, 1190, 1099, 1035, 896, 846, 821 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{22}H_{32}O_4$, 360.2301, found, .360.2299.

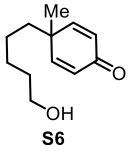




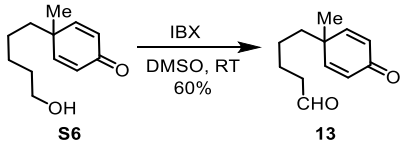
To a stirred mixture of $LiAlH_4$ (5.73 g, 151.2 mmol, 1.2 equiv.) in anhydrous Et_2O (400 mL) at 0 ºC under nitrogen atmosphere was slowly added compound **S4** (43.62 g, 126 mmol, 1.0 equiv.) in anhydrous Et_2O (100 mL). After stirred at 0 ºC for 30 minutes, 300 mL saturated NH_4Cl was slowly added to the mixture and then added 300 mL 3 N HCl at 0 ºC. The mixture was slowly warmed to room temperature and stirred for another 1 hour. Separated the Et_2O layer and washed with water, saturated $NaHCO_3$, brine. Then the separated total aqueous layer was extracted with ethyl acetate (3×100 mL) and the separated ethyl acetate layer was washed with water, saturated $NaHCO_3$, brine. The combined organic layers were dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (10% to 20% ethyl acetate – petroleum ether) to obtain **S5** as a light yellow viscous oil (26.0 g, 65%). R_f = 0.30 (10% ethyl acetate – petroleum ether); Light yellow viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 (d, J = 8.4 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.65 (d, *J* = 10.2 Hz, 1H), 5.86 (d, *J* = 10.2 Hz, 1H), 4.43 (s, 2H), 3.80 (s, 3H), 3.43 (t, *J* = 6.5 Hz, 2H), 2.47 – 2.38 (m, 2H), 1.94 (ddd, *J* = 14.5, 8.9, 5.9 Hz, 1H), 1.74 (dt, *J* = 12.8, 6.0 Hz, 1H), 1.66 – 1.58 (m, 2H), 1.50 – 1.22 (m, 6H), 1.11 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.7, 159.4, 159.1, 130.7, 129.2 (2C), 127.3, 113.8 (2C), 72.6, 69.9, 55.3, 41.0, 35.6, 34.2, 33.5, 29.7, 26.9, 24.9, 24.0 ppm; IR ν_{max} 2933, 2859, 1682, 1612, 1512, 1463, 1301, 1265, 1246, 1097, 1035, 804 cm^{-1}; HRMS–EI

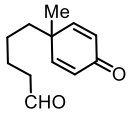
(*m/z*): $[M]^+$ calculated for $C_{20}H_{28}O_3$, 316.2038, found, 316.2034.





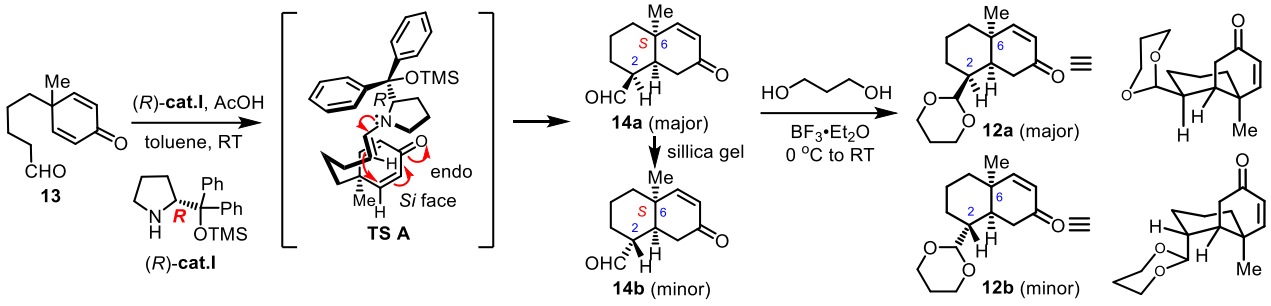
To a stirred solution of **S5** (13.0 g, 41.08 mmol, 1.0 equiv.) in anhydrous THF (400 mL) at room temperature was successively added DDQ (28.0 g, 123.24 mmol, 3.0 equiv.), TBSCl (6.81 g, 45.19 mmol, 1.1 equiv.) portion-wisely. After stirring at room temperature for 5 hours, the brown mixture was stirred at 50 °C for further 16 hours. The mixture was concentrated and diluted with ethyl acetate (150 mL) then quenched with saturated $Na_2S_2O_3$/$NaHCO_3$ (150 mL, v/v = 1:1). Separated the ethyl acetate layer and washed with water, brine. Then the separated total aqueous layer was extracted with ethyl acetate (3×100 mL). The combined organic layers were dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (30% to 60% ethyl acetate – petroleum ether) to obtain **S6** as a brown viscous oil (3.43 g, 43%). R_f = 0.20 (30% ethyl acetate – petroleum ether); Brown viscous oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.76 (d, *J* = 10.1 Hz, 2H), 6.26 (d, *J* = 10.1 Hz, 2H), 3.60 (t, *J* = 6.5 Hz, 2H), 1.66 – 1.59 (m, 2H), 1.55 – 1.47 (m, 2H), 1.47 (br s, 1H), 1.36 – 1.26 (m, 2H), 1.24 (s, 3H), 1.19 – 1.09 (m, 2H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 186.4, 155.9 (2C), 128.8 (2C), 62.7, 42.0, 40.5, 32.4, 26.1, 26.0, 24.8 ppm; IR ν_{max} 3051, 2934. 2863, 1741, 1662, 1616, 1459, 1267, 1246, 1037, 862, 704 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{12}H_{18}O_2$, 194.1307, found, 194.1305.



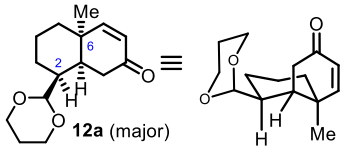


To a stirred solution of **S6** (3.30 g, 17.00 mmol, 1.0 equiv.) in anhydrous DMSO (50 mL) at room temperature was added IBX (9.52 g, 34.00 mmol, 2.0 equiv.) portion-wisely. After stirring at room temperature for 2 hours, the mixture was quenched with saturated $Na_2S_2O_3$/$NaHCO_3$ (50 mL, v/v = 1:1) and extracted with ethyl acetate (3×50 mL). The combined organic layers were washed with water, brine, then dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (30% to 40% ethyl acetate – petroleum ether) to obtain **13** as a light brown oil (1.96 g, 60%). R_f = 0.20 (20% ethyl acetate – petroleum ether); Light brown oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.69 (s, 1H), 6.72 (d, *J* = 10.0 Hz, 2H), 6.22 (d, *J* = 10.0 Hz, 2H), 2.36 (td, *J* = 7.3, 1.5 Hz, 2H), 1.63 – 1.57 (m, 2H), 1.57 – 1.49 (m, 2H), 1.21 (s, 3H), 1.16 – 1.06 (m, 2H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 202.0, 186.1, 155.5 (2C), 128.8 (2C), 43.5, 41.8, 40.2, 26.0, 24.5, 22.0 ppm; IR ν_{max} 3053, 2937, 2862, 1718, 1664, 1624,1458,

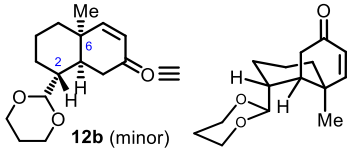
1404, 1267, 1242, 1105, 864 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{12}H_{16}O_2$, 192.1150, found, 192.1151.



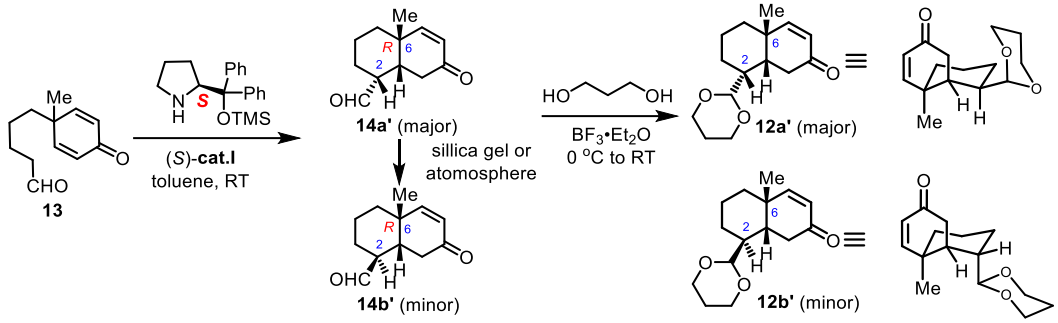
A solution of **13** (1.54 g, 8.00 mmol, 1.0 equiv.), (*R*)-**cat.I** (520 mg, 1.60 mmol, 0.2 equiv.) and AcOH (96 mg, 1.60 mmol, 0.2 equiv.) in analytical-grade toluene (80 mL) was stirred at room temperature for 9.5 hours with inert nitrogen atmosphere. Then 1,3-propanediol (2.44 g, 2.31 mL, 32.00 mol, 4.0 equiv.), 46.5% $BF_3{\cdot}Et_2O$ (1.14 g, 0.99 mL, 8.0 mmol, 1.0 equiv.) was added to the solution at 0 °C and stirred at room temperature for further 2 hours. The solution was quenched with saturated $NaHCO_3$ (50 mL) and extracted with ethyl acetate (3×50 mL). The combined organic layers were washed with brine, then dried over anhydrous sodium sulfate, concentrated and purified by flash chromatography (20% ethyl acetate – petroleum ether) to obtain pure **12a** (1.05 g), pure **12b** (0.15 g) and the mixture of **12a**+**12b** (0.40 g) all as light yellow viscous oil (total 1.6 g, total 80% for one pot synthesis, d.r. = 5.5:1).



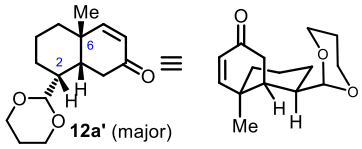
R_f = 0.30 (20% ethyl acetate – petroleum ether); Light yellow viscous oil; $[\alpha]_D^{20}$ = -10.5 (c = 1.00 in DCM); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.62 (d, *J* = 10.1 Hz, 1H), 5.84 (d, *J* = 10.1 Hz, 1H), 4.24 (d, *J* = 7.4 Hz, 1H), 4.12 – 4.02 (m, 2H), 3.76 – 3.63 (m, 2H), 2.46 – 2.35 (m, 1H), 2.30 – 2.20 (m, 2H), 2.10 – 2.02(m, 1H), 2.01 – 1.94 (m, 1H), 1.81 – 1.69 (m, 1H), 1.67 – 1.60 (m, 1H), 1.54 – 1.44 (m, 3H), 1.33 (d, *J* = 13.5 Hz, 1H), 1.16 (s, 3H), 1.14 – 1.10 (m, 1H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 200.6, 161.5, 126.0, 103.1, 67.00, 66.97, 40.1, 38.3, 36.1, 34.7, 31.3, 25.9, 24.3, 21.3, 20.3 ppm; IR ν_{max} 2937, 2860, 1676, 1614, 1375, 1267, 1240, 1143, 1114, 1086, 1014, 935, 852 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{15}H_{22}O_3$, 250.1569, found, 250.1571.



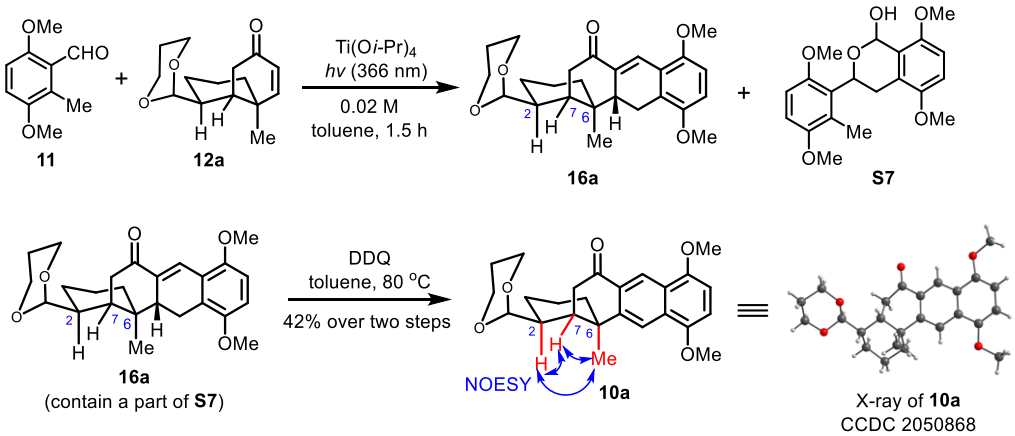
R_f = 0.34 (20% ethyl acetate – petroleum ether); Light yellow viscous oil; $[\alpha]_D^{20}$ = -64.9 (c = 0.60 in DCM); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.53 (dd, *J* = 10.1, 2.1 Hz, 1H), 5.88 (d, *J* = 10.1 Hz, 1H), 4.57 (d, *J* = 2.4 Hz, 1H), 4.09 – 4.01 (m, 2H), 3.77 – 3.62 (m, 2H), 2.77 – 2.60 (m, 2H), 2.06 – 1.92 (m, 2H), 1.89 – 1.79 (m, 1H), 1.69 – 1.58 (m, 3H), 1.35 – 1.25 (m, 2H), 1.22 (s, 3H), 1.21 – 1.11 (m, 2H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 199.4, 159.1, 128.3, 102.2, 67.1, 67.0, 42.0, 40.9, 40.2, 37.53, 37.52, 27.8, 25.8, 25.3, 22.6 ppm; IR ν_{max} 2936, 2858, 1676, 1610, 1377, 1238, 1151, 1122, 1101, 1016, 997, 941, 893 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{15}H_{22}O_3$, 250.1569, found, 250.1567.



A solution of **13** (288 mg, 1.50 mmol, 1.0 equiv.), (*S*)-**cat.I** (195 mg, 0.60 mmol, 0.4 equiv.) in analytical-grade toluene (15 mL) was stirred at room temperature for 12 hours with inert nitrogen atmosphere. Then 1,3-propanediol (457 mg, 0.43 mL, 6.00 mol, 4.0 equiv.), 46.5% $BF_3{\cdot}Et_2O$ (213 mg, 0.185 mL, 1.5 mmol, 1.0 equiv.) was added to the solution at 0 °C and stirred at room temperature for further 2 hours. The solution was quenched with saturated $NaHCO_3$ (10 mL).and extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with brine, then dried over anhydrous sodium sulfate, concentrated and purified by flash chromatography (20% ethyl acetate – petroleum ether) to obtain pure **12a'** as a light yellow viscous oil (233 mg, 62% for one pot synthesis, d.r. = 14.0:1).



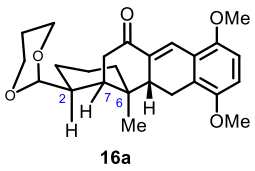
R_f = 0.30 (20% ethyl acetate – petroleum ether); Light yellow viscous oil; $[\alpha]_D^{20}$ = +9.4 (c = 0.60 in DCM); ^{1}H NMR: the same to compound **12a**; ^{13}C NMR: the same to compound **12a**; IR ν_{max} 2928, 2863, 1684, 1676, 1376, 1275, 1240, 1145, 1116, 1015, 934, 852, 764 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{15}H_{22}O_3$, 250.1569, found, 250.1571.



To a solution of dienophile **12a** (2.00 g, 8.00 mmol, 1.0 equiv.), aromatic aldehyde **11** (2.16 g, 12.0 mmol, 1.5 equiv.) in anhydrous and degassed toluene (400 mL) (concentration for dienophile **12a** is 0.02 M) was added titanium(IV) isopropoxide (6.82 g, 7.10 mL, 24.0 mmol, 3.0 equiv.) under N_2. After homogeneous mixing, the solution was divided into 10 parallel reactions in 10 quartz tubes (10×40 mL). 5 parallel reactions were conducted with 5 quartz tubes once. The solution was photolyzed at room temperature in a Rayonet chamber reactor (16 lamps) at λ_{max} = 366 nm for 1.5 hours (**Note**: the atmosphere temperature among quartz tubes was 35 to 40 °C). After the above 5 parallel reactions were over, the reaction mixture was quenched with

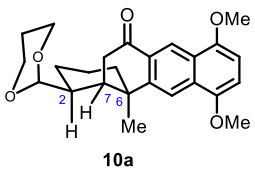
saturated $NaHCO_3$ (50 mL). Then another 5 parallel reactions were conducted for another 1.5 hours, the reaction mixture was also quenched with saturated $NaHCO_3$ (50 mL). The total mixture was filtered through silica gel and washed with ethyl acetate (6×50 mL). The combined organic layers were washed with brine, then dried over anhydrous sodium sulfate, concentrated and purified by flash chromatography (10% to 30% ethyl acetate – petroleum ether) to obtain 1.80 g **16a** (contain ~ 9% **S7**) as a yellow viscous oil.

To a solution of above obtained 1.80 g **16a** (contain ~ 9% **S7**) in anhydrous toluene (40 mL) was added DDQ (1.97 g, 8.69 mmol, 2.0 equiv.) at room temperature. After stirred at 80 ºC for 3 hours, the mixture was quenched with saturated $Na_2S_2O_3$/$NaHCO_3$ (40 mL, v/v = 1:1) and extracted with ethyl acetate (3×50 mL). The combined organic layers were washed with water, brine, then dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (20% ethyl acetate – petroleum ether) to obtain pure **10a** as a yellow foam solid (1.38 g, 42% over two steps).



16a

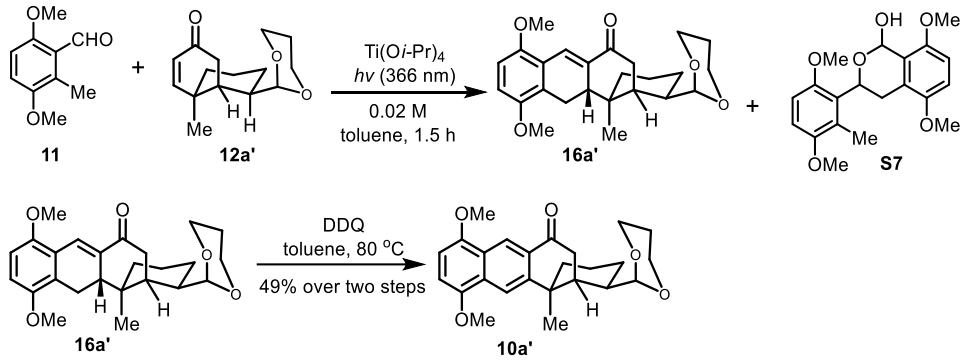
R_f = 0.36 (30% ethyl acetate – petroleum ether); Yellow viscous oil; $[\alpha]_D^{20}$ = +179.0 (c = 1.10 in DCM); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 2.4 Hz, 1H), 6.79 (d, *J* = 8.9 Hz, 1H), 6.65 (d, *J* = 8.9 Hz, 1H), 4.41 (d, *J* = 7.6 Hz, 1H), 4.02 (dd, *J* = 11.4, 5.0 Hz, 1H), 3.92 (dd, *J* = 11.5, 5.0 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.64 (td, *J* = 12.3, 2.6 Hz, 1H), 3.41 (td, *J* = 12.0, 2.6 Hz, 1H), 2.99 (dd, *J* = 15.7, 6.9 Hz, 1H), 2.72 (ddd, *J* = 11.5, 6.9, 2.5 Hz, 1H), 2.66 – 2.60 (m, 1H), 2.57 (d, *J* = 7.1 Hz, 1H), 2.49 (dd, *J* = 17.6, 5.7 Hz, 1H), 2.04 – 1.88 (m, 3H), 1.76 (ddd, *J* = 13.8, 7.0, 3.0 Hz, 1H), 1.57 – 1.50 (m, 3H), 1.47 – 1.35 (m, 2H), 1.28 – 1.21 (m, 1H), 0.96 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.5, 151.7, 150.0, 134.5, 127.0, 126.4, 122.4, 112.5, 108.6, 103.6, 66.9, 66.0, 55.93, 55.91, 41.7, 40.6, 39.1, 38.3, 35.8, 35.5, 25.6, 24.8, 24.0, 21.8, 19.4 ppm; IR ν_{max} 2957, 2925, 2863, 1675, 1599, 1576, 1484, 1465, 1275, 1267, 1110, 1098, 1003, 763, 759 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{25}H_{32}O_5$, 412.2250, found, 412.2255.



10a

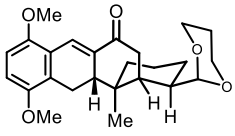
R_f = 0.42 (30% ethyl acetate – petroleum ether); Yellow foam solid, m.p. 110-112 ºC; Compound **10a** was recrystallized from dichloromethane at room temperature to obtain yellow crystals, CCDC 2050868; $[\alpha]_D^{20}$ = +1.5 (c = 1.00 in DCM); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.93 (s, 1H), 8.23 (s, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 6.57 (d, *J* = 8.3 Hz, 1H), 4.30 (d, *J* = 7.3 Hz, 1H), 4.14 – 4.04 (m, 2H), 3.912 (s, 3H), 3.908 (s, 3H), 3.77 – 3.64 (m, 2H), 2.78 (dd, *J* = 16.6, 13.9 Hz, 1H), 2.62 (dd, *J* = 16.7, 4.2 Hz, 1H), 2.49 (dt, *J* = 13.9, 4.2 Hz, 1H), 2.29 – 2.19 (m, 1H), 2.11 – 1.98 (m, 1H), 1.80 – 1.69 (m, 2H), 1.69 – 1.61 (m, 3H), 1.60 (s, 3H), 1.36 – 1.20 (m, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.9, 150.8, 148.9, 148.6, 129.1, 128.6, 124.2, 122.5, 119.4, 105.6, 103.4, 102.7, 66.93, 66.91, 55.6, 55.5, 40.0, 38.2, 37.7, 35.9, 35.8, 25.9, 25.2, 21.4, 21.2 ppm; IR ν_{max} 3055, 2937, 2862, 2837,

1684, 1626, 1589, 1458, 1267, 1240, 1143, 1103, 1091, 1008, 985 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{25}H_{30}O_5$, 410.2093, found, 410.2089.



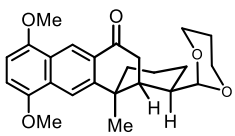
To a solution of dienophile **12a'** (200 mg, 0.80 mmol, 1.0 equiv.), aromatic aldehyde **11** (216 mg, 1.20 mmol, 1.5 equiv.) in anhydrous and degassed toluene (40 mL) (concentration for dienophile **12a'** is 0.02 M) was added titanium(IV) isopropoxide (682 mg, 0.71 mL, 2.40 mmol, 3.0 equiv.) under N_2. 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 hours (**Note**: the atmosphere temperature among quartz tubes was 35 to 40 °C). After that, the mixture was quenched with saturated $NaHCO_3$ (10 mL) and filtered through silica gel and washed with ethyl acetate (6×10 mL). The combined organic layers were washed with brine, then dried over anhydrous sodium sulfate, concentrated and purified by flash chromatography (10% to 30% ethyl acetate – petroleum ether) to obtain 190 mg **16a'** as a yellow viscous oil.

To a solution of above obtained **16a'** (190 mg, 0.46 mmol, 1.0 equiv.) in anhydrous toluene (10 mL) was added DDQ (218 mg, 0.96 mmol, 2.0 equiv.) at room temperature. After stirred at 80 °C for 3 hours, the mixture was quenched with saturated $Na_2S_2O_3$/$NaHCO_3$ (10 mL, v/v = 1:1) and extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with water, brine, then dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (20% ethyl acetate – petroleum ether) to obtain **10a'** as a yellow foam solid (161 mg, 49 % over two steps).



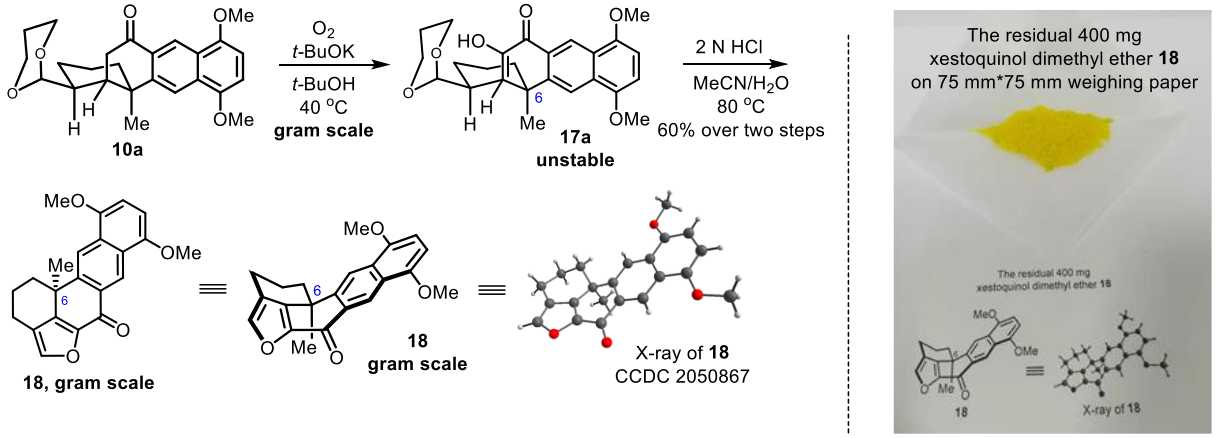
16a'

R_f = 0.36 (30% ethyl acetate – petroleum ether); Yellow viscous oil; $[\alpha]_D^{20}$ = -144.9 (c = 0.40 in DCM); ^{1}H NMR: the same to **16a**; ^{13}C NMR: the same to **16a**; IR ν_{max} 2960, 2925, 2857, 1691, 1675, 1598, 1570, 1483, 1464, 1275, 1260, 1144, 1096, 1016, 802, 799 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{25}H_{32}O_5$, 412.2250, found, 412.2248.



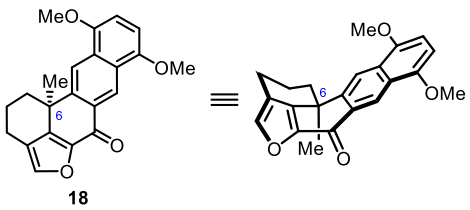
10a'

R_f = 0.42 (30% ethyl acetate – petroleum ether); Yellow foam solid, m.p. 57-59 °C; $[\alpha]_D^{20}$ = -4.4 (c = 0.60 in DCM); ^{1}H NMR: the same to **10a**; ^{13}C NMR: the same to **10a**; IR ν_{max} 2954, 2930, 2927, 2857, 1683, 1627, 1590, 1458, 1435, 1343, 1333, 1268, 1239, 1142, 1119, 1104, 1092, 1009, 934 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{25}H_{30}O_5$, 410.2093, found, 410.2097.

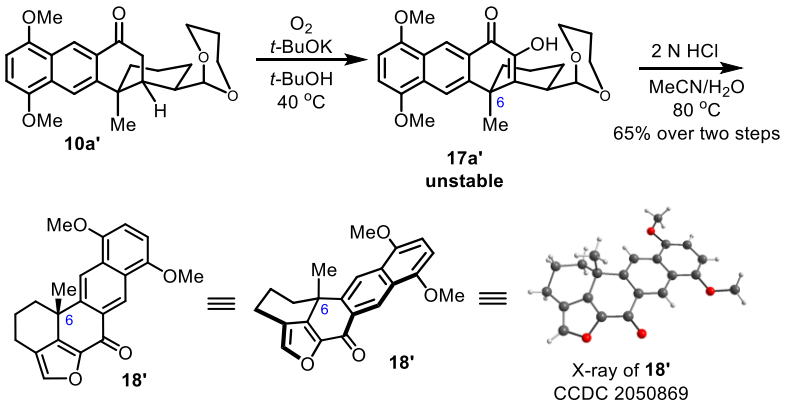


To a solution of **10a** (1.31 g, 3.2 mmol, 1.0 equiv.) in analytical-grade *t*-BuOH (60 mL) was added *t*-BuOK (3.60 g, 32.0 mmol, 10.0 equiv.). Then the mixture was stirred with bubbling O_2 into the mixture at 40 °C for 3 hours. After that, *t*-BuOH was evacuated and the mixture was diluted with ethyl acetate (50 mL).and water (30 mL). Separated the organic layer and the aqueous layer was washed with ethyl acetate (3×50 mL). The combined organic layers were washed with water, brine, dried over anhydrous sodium sulfate, then concentrated to obtain 1.12 g crude **17a** as a yellow foam solid for the next step without further purification.

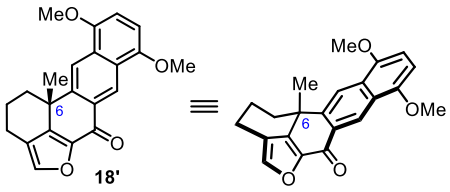
To a solution of above obtained crude **17a** in analytical-grade MeCN (60 mL) was added 2 N HCl (10 mL) at room temperature. Then the solution was stirred at 80 °C for 5 hours and quenched with saturated $NaHCO_3$ (50 mL). The mixture was extracted with DCM (3×60 mL) and washed with brine. The combined organic layers were dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (20% to 30% ethyl acetate – petroleum ether) to obtain **18** as a yellow solid (668 mg, 60% over two steps). **Note**: The xestoquinol dimethyl ether **18** was easier to dissolve in DCM than ethyl acetate.



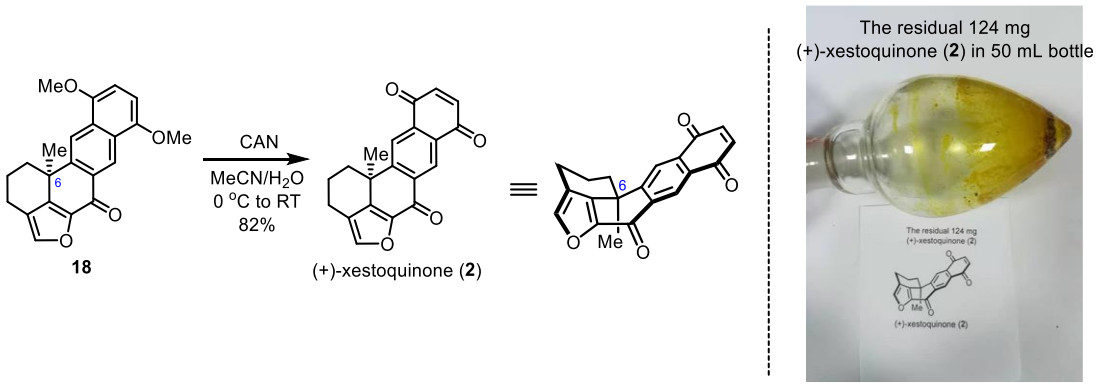
R_f = 0.38 (30% ethyl acetate – petroleum ether); Yellow solid, m.p. 243-245 °C; Compound **18** was recrystallized from THF/hexane (v/v = 1/2) at room temperature to obtain yellow crystals, CCDC 2050867; $[\alpha]_D^{20}$ = +99.6 (c = 1.00 in DCM); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.23 (s, 1H), 8.23 (s, 1H), 7.42 (t, *J* = 1.4 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 2.81 (ddt, *J* = 16.9, 7.8, 1.7 Hz, 1H), 2.61 – 2.50 (m, 2H), 2.29 – 2.14 (m, 1H), 2.13 – 2.02 (m, 1H), 1.76 (td, *J* = 13.2, 4.3 Hz, 1H), 1.49 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.7, 150.6, 148.6, 146.7, 146.6, 144.6, 143.6, 131.2, 127.2, 124.5, 123.9, 121.2, 117.4, 105.9, 103.2, 55.6, 55.5, 36.2, 33.6, 31.9, 18.6, 17.1 ppm; IR ν_{max} 2938, 2835, 1670, 1614, 1541, 1471, 1465, 1423, 1356, 1267, 1244, 1192, 1144, 1091, 1043, 904, 862, 806 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{22}H_{20}O_4$, 348.1362, found, 348.1360.



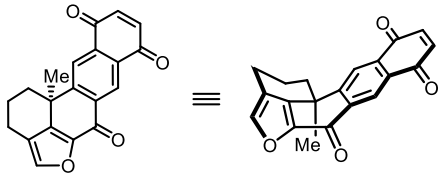
The enantiomer compound **18'** (136 mg, 65% over two steps) was synthesized according to the above similar procedures using **10a'** (246 mg, 0.60 mmol, 1.0 equiv.) as starting material. **Note**: The xestoquinol dimethyl ether **18'** was easier to dissolve in DCM than ethyl acetate.



R_f = 0.38 (30% ethyl acetate – petroleum ether); Yellow solid, m.p. 248-250 °C; Compound **18'** was recrystallized from THF/hexane (v/v = 1/2) at room temperature to obtain yellow crystals, CCDC 2050869; $[\alpha]_D^{20}$ = -95.4 (c = 1.00 in DCM); ^{1}H NMR: the same to **18**; ^{13}C NMR: the same to **18**; IR ν_{max} 3102, 2944, 2836, 1666, 1628, 1613, 1533, 1464, 1423, 1357, 1267, 1245, 1190, 1145, 1089, 1044, 905, 865, 802 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{22}H_{20}O_4$, 348.1362, found, 348.1360.

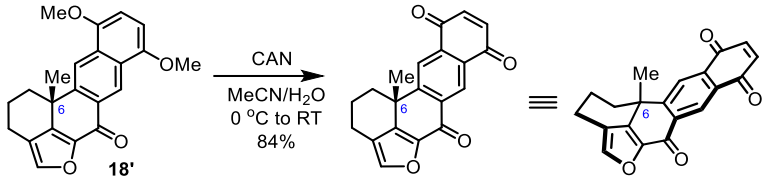


To stirred solution of **18** (208 mg, 0.6 mmol, 1.0 equiv.) in MeCN/H_2O (50 mL, v/v = 4:1) was added CAN (987 mg, 1.8 mmol, 3.0 equiv.) at 0 °C. Then the solution was stirred at room temperature for 1 hours After that, the mixture was extracted with ethyl acetate (3×30 mL). The combined organic layers were washed with water, brine, dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (30% ethyl acetate – petroleum ether) to obtain (+)-xestoquinone (**2**) as a yellow-brown solid (156 mg, 82%).



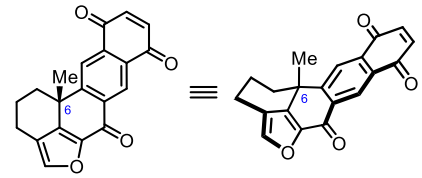
(+)-xestoquinone (**2**)

R_f = 0.26 (30% ethyl acetate – petroleum ether); Yellow-brown solid, m.p. 213-216 °C; $[\alpha]_D^{20}$ = +11.2 (c = 1.00 in DCM); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.98 (s, 1H), 8.22 (s, 1H), 7.54 (br t, *J* = 1.5 Hz, 1H), 7.05 (d, *J* = 10.0 Hz, 1H), 7.02 (d, *J* = 10.0 Hz, 1H), 2.89 (ddt, *J* = 17.1, 8.0, 1.8 Hz, 1H), 2.66 (dddd, *J* = 17.0, 10.0, 8.5, 1.5 Hz, 1H), 2.58 (dt, *J* = 12.9, 3.6 Hz, 1H), 2.35 – 2.24 (m, 1H), 2.23 – 2.15 (m, 1H), 1.76 (td, *J* = 13.1, 4.4 Hz, 1H), 1.53 (s, 3H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 184.6, 183.8, 170.1, 156.2, 147.3, 145.0, 144.0, 139.3, 138.7, 137.9, 133.2, 130.3, 126.9, 123.2, 121.6, 37.4, 32.6, 31.2, 18.4, 16.9 ppm; IR ν_{max} 3105, 2862, 1670, 1614, 1456, 1444, 1319, 1267, 1238, 1134, 1095, 898, 846, 796 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{20}H_{14}O_4$, 318.0892, found, 318.0889.



(-)-xestoquinone (**2'**)

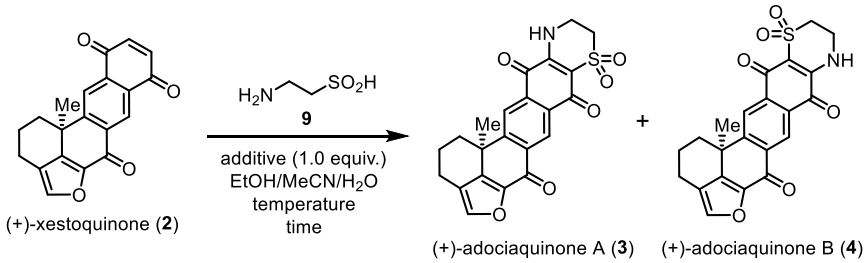
The (-)-xestoquinone (**2'**) (40 mg, 84%) was synthesized according to the above similar procedures using **18'** (52 mg, 0.15 mmol, 1.0 equiv.) as starting material.



(-)-xestoquinone (**2'**)

R_f = 0.26 (30% ethyl acetate – petroleum ether); Yellow-brown solid, m.p. 96 - 98 °C; $[\alpha]_D^{20}$ = -8.2 (c = 1.00 in DCM); ^{1}H NMR: the same to **2**; ^{13}C NMR: the same to **2**; IR ν_{max} 2953, 2926, 2856, 1669, 1602, 1539, 1444, 1430, 1318, 1274, 1236, 1134, 1092, 1058, 986, 845, 764 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{20}H_{14}O_4$, 318.0892, found, 318.0894.

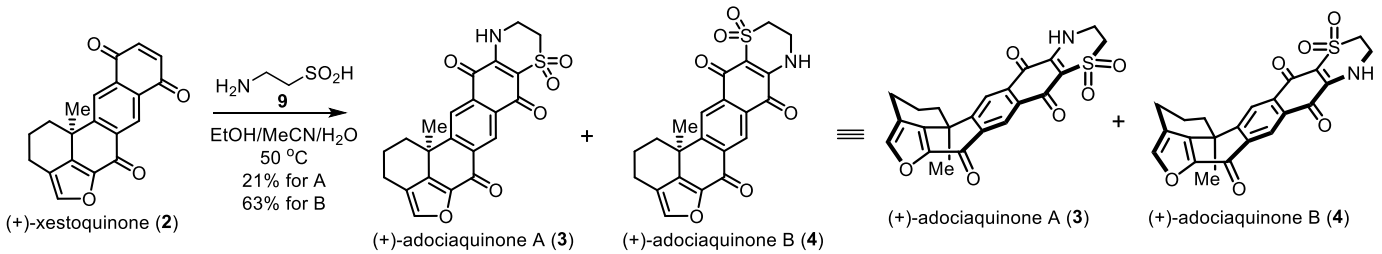
Table S3. Screening conditions of the late-stage cyclization.

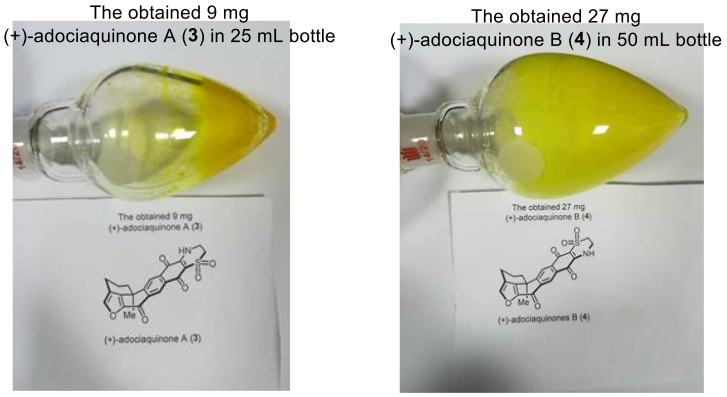


(+)-xestoquinone (**2**) (+)-adociaquinone A (**3**) (+)-adociaquinone B (**4**)

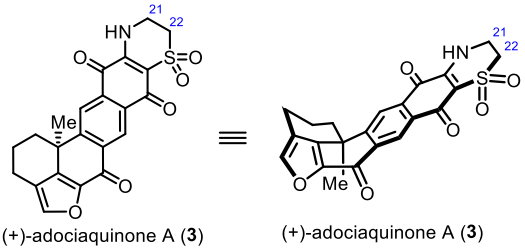
entry	additive	temperature/time	ratio of **3**:**4** [a]	combined yield [a]
1	--	-20 °C / 6 h	1:2.5	28%
2	--	0 °C / 3 h	1:2.2	28%
3	--	20 °C / 1 h	1:2.3	33%
4[b]	--	50 °C /3 h	1:3.0	84%[c]
5	$CeCl_3$•$7H_2O$	50 °C /1 h	1:2.2	52%
6	TFA	50 °C /1 h	1:1.1	13%
7	Cs_2CO_3	50 °C /1 h	--	messy, N.D.
8	NEt_3	50 °C /1 h	1:2.5	18%

All reactions were performed using (+)-xestoquinone (**2**) (3.2 mg, 0.01 mmol, 1.0 equiv.) and hypotaurine **9** (1.7 mg, 0.015 mmol 1.5 equiv.) as starting materials in EtOH/MeCN/H_2O (0.5 mL, v/v/v = 2:2:1), unless otherwise noted. [a]The ratios of **3**:**4** and combined yields were determined from crude ^{1}H NMR spectrum of **3+4** using CH_2Br_2 as an internal standard, [b] (+)-xestoquinone (**2**) (32 mg, 0.1 mmol, 1.0 equiv.) and hypotaurine **9** (17 mg, 0.15 mmol, 1.5 equiv) in EtOH/MeCN/H_2O (5 mL, v/v/v = 2:2:1); [c] isolated combined yield of **3+4**.

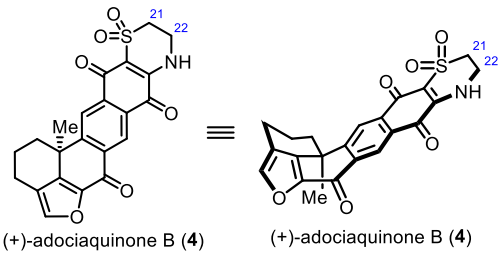




To a stirred solution of (+)-xestoquinone (**2**) (32 mg, 0.1 mmol, 1.0 equiv.) in EtOH/MeCN/H_2O (5 mL, v/v/v = 2:2:1) was added hypotaurine **9** (17 mg, 0.15 mmol, 1.5 equiv.) at room temperature. Then the solution was stirred at 50 °C for 3 hours. TLC analysis showed all (+)-xestoquinone (**2**) was consumed. The solvent was evacuated under vacuum, and the residue was purified by preparation lamella chromatography (7% MeOH-DCM, washed with 10% MeOH-DCM) directly to afford yellow solid (+)-adociaquinone A (**3**) (9.0 mg, 21%), (+)-adociaquinone B (**4**) (27.0 mg, 63%).



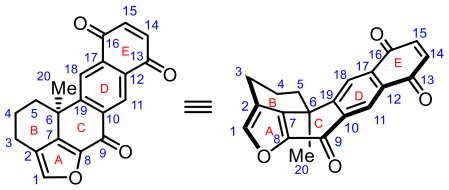
R_f = 0.52 (10% methanol-dichloromethane); Yellow solid, m.p. >320 °C (decomposed); $[\alpha]_D^{20}$ = +65.2 (c = 0.1 in chloroform-methanol (v/v = 2:1)); ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.35 (br s, 1H, NH), 8.68 (s, 1H), 8.26 (s, 1H), 8.00 (s, 1H), 3.88 (t, *J* = 6.0 Hz, 2H), 3.40 (t, *J* = 6.0 Hz, 2H), 2.84 (dd, *J* = 17.0, 8.0 Hz, 1H), 2.64 – 2.60 (m, 1H), 2.60 – 2.57 (m, 1H), 2.30 – 2.16 (m, 1H), 2.13 – 2.03 (m, 1H), 1.65 (td, *J* = 13.0, 4.4 Hz, 1H), 1.50 (s, 3H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ 177.9, 173.8, 169.4, 157.4, 147.8, 147.2, 146.2, 143.0, 136.0, 134.4, 128.6, 125.4, 123.0, 121.7, 111.7, 48.2, 39.4 (C21, buried in the peak of DMSO-d_6), 37.2, 31.8, 30.3, 17.9, 16.3 ppm; IR ν_{max} 3270, 2928, 2858, 1668, 1655, 1589, 1508, 1458, 1344, 1282, 1238, 1116, 1028, 864 cm^{-1}; HRMS–ESI (*m/z*): $[M+Na]^+$ calculated for $C_{22}H_{17}NO_6SNa^+$, 446.0669, found, 446.0663.



R_f = 0.48 (10% methanol-dichloromethane); Yellow solid, m.p. >320 ºC (decomposed); $[\alpha]_D^{20}$ = +100.4 (c = 0.05 in chloroform-methanol (v/v = 2:1)); ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.24 (br s, 1H, NH), 8.72 (s, 1H), 8.28 (s, 1H), 8.00 (s, 1H), 3.88 (t, *J* = 5.9 Hz, 2H), 3.40 (t, *J* = 5.9 Hz, 2H), 2.84 (dd, *J* = 17.1, 7.9 Hz, 1H), 2.65 (dd, *J* = 13.2, 4.1 Hz, 1H), 2.59 (dd, *J* = 17.4, 8.9 Hz, 1H), 2.28 – 2.15 (m, 1H), 2.12 – 2.01 (m, 1H), 1.63 (td, *J* = 12.9, 4.3 Hz, 1H), 1.50 (s, 3H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ 178.3, 173.7, 169.4, 154.6, 147.9, 147.1, 146.2, 143.0, 137.9, 131.8, 130.8, 124.7, 123.4, 121.6, 111.3, 48.2, 39.3 (C22, buried in the peak of DMSO-d_6), 36.8, 31.6, 30.3, 17.8, 16.2 ppm; IR ν_{max} 3274, 2935, 2862, 1716, 1664, 1616, 1541, 1508, 1458, 1267, 1240, 1143, 935, 864, 806 cm^{-1}; HRMS–ESI (*m/z*): $[M+Na]^+$ calculated for $C_{22}H_{17}NO_6SNa^+$, 446.0669, found, 446.0662.

Note: The (+)-adociaquinones A (**3**) and B (**4**) were uneasy to dissolve in organic solution, especially for the major product (+)-adociaquinone B (**4**), which was uneasy to dissolve in DMSO-d_6.

Comparison of NMR spectroscopic data of natural and synthetic (+)-xestoquinone (2), (+)-adociaquinones A (3) and B (4)



(+)-xestoquinone (**2**)

Natural product (+)-xestoquinone: $[\alpha]_D^{25}$ = +17.2 (c = 1.16 in DCM) [3]

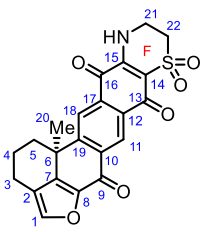
Our Synthetic (+)-xestoquinone: $[\alpha]_D^{20}$ = +11.2 (c = 1.00 in DCM)

Table S4. Comparison of ^{1}H NMR spectroscopic data of natural [4] and synthetic [5] (+)-xestoquinone with this synthetic work.

position	**natural (a) (Laurent's work)** δ ^{1}H [ppm; mult; *J* (Hz)], 300 MHz, Chloroform-*d*	**synthetic (b) (Harada's work)** δ ^{1}H [ppm; mult; *J* (Hz)], 400 MHz, Chloroform-*d*	**synthetic (c) (this work)** δ^{1}H [ppm; mult; *J* (Hz)], 500 MHz, Chloroform-*d*	**deviation (a-c; b-c)** Δδ (ppm)
1	7.54; t; 1.5	7.54; br t; 1.5	7.54; br t; 1.5	0.00; 0.00
3a	2.64; dddd; 17.1, 9.8, 8.4, 1.5	2.64; dddd; 17.0, 9.9, 8.4, 1.5	2.66; dddd; 17.0, 10.0, 8.5, 1.5	-0.02; -0.02
3b	2.88; dddd; 17.1, 8.0, 2.5, 1.5	2.88; dddd; 17.0, 8.0, 2.2, 1.5	2.89; ddt; 17.1, 8.0, 1.8	-0.01; -0.01
4	2.22; m, 2H	2.28; m, 1H 2.19; m, 1H	2.29; m, 1H 2.19; m, 1H	-0.07, 0.03; -0.01, 0.00
5a	1.75; ddd; 13.0, 13.0, 4.7	1.76; ddd; 13.0, 13.0, 4.5	1.76; td; 13.1, 4.4	-0.01; 0.00
5b	2.57; ddd; 12.8, 3.6, 3.6	2.58; ddd; 13.0, 4.1, 3.0	2.58; dt; 12.9, 3.6	-0.01; 0.00
11	9.03; s	9.05; s	8.98; s	0.05; 0.07
14	7.02; s, 2H	7.06; d; 10.4	7.05; d; 10.0	-0.03, 0.00;
15		7.03; d; 10.4	7.02; d; 10.0	0.01, 0.01
18	8.23; s	8.25; s	8.22; s	0.01; 0.03
20	1.53; s	1.54; s	1.53; s	0.00; 0.01

Table S5. Comparison of ^{13}C NMR spectroscopic data of natural [4] (+)-xestoquinone with this synthetic work.

position	**natural (a)** **(Laurent's work)** δ ^{13}C [ppm], 75 MHz, Chloroform-*d*	**synthetic (b)** **(this work)** δ ^{13}C [ppm], 125 MHz, Chloroform-*d*	**deviation** **(a-b)** $\Delta\delta$ (ppm)
1	145.0	145.0	0.0
2	121.5	121.6	-0.1
3	16.9	16.9	0.0
4	18.4	18.4	0.0
5	31.2	31.2	0.0
6	37.4	37.4	0.0
7	147.3	147.3	0.0
8	144.0	144.0	0.0
9	170.3	170.1	0.2
10	137.9	137.9	0.0
11	127.0	126.9	0.1
12	130.3	130.3	0.0
13	183.9	183.8	0.1
14	139.4	139.3	0.1
15	138.7	138.7	0.0
16	184.7	184.6	0.1
17	133.2	133.2	0.0
18	123.2	123.2	0.0
19	156.2	156.2	0.0
20	32.6	32.6	0.0



(+)-adociaquinone A (**3**)

Natural product (+)-adociaquinone A: $[\alpha]_D$ = +31.7 (c = 4.66 in MeCN) [6]

Harada's Synthetic (+)-adociaquinone A: $[\alpha]_D^{20}$ = +70 (c = 0.107 in chloroform -methanol (v/v = 2:1)) [7]

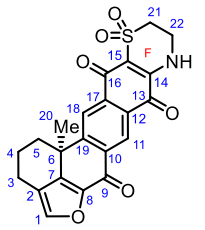
Our Synthetic (+)-adociaquinone A: $[\alpha]_D^{20}$ = +65.2 (c = 0.1 in chloroform -methanol (v/v = 2:1))

Table S6. Comparison of ^{1}H NMR spectroscopic data of natural [6] and synthetic [7] (+)-adociaquinone A with this synthetic work.

position	**natural (a) (Ireland's work)** δ^1H [ppm; mult; *J* (Hz)], 500 MHz, DMSO-d_6	**synthetic (b) (Harada's work)** δ^1H [ppm; mult; *J* (Hz)], 500 MHz, DMSO-d_6	**synthetic (c) (this work)** δ^1H [ppm; mult; *J* (Hz)], 500 MHz, DMSO-d_6	**deviation (a-c; b-c)** Δδ (ppm)
1	7.97; s	8.00; s	8.00; s	-0.03; 0.00
3a	2.56; dd; 17.0, 9.0	2.60; m	2.59; m	-0.03; 0.01
3b	2.82; dd; 17.0, 8.5	2.84; dd; 17.4, 8.2,	2.84; dd; 17.0, 8.0	-0.02; 0.00
4a	2.06; m	2.08; m	2.08; m	-0.02; 0.00
4b	2.21; m	2.23; m	2.22; m	-0.01; 0.01
5a	1.63; dt; 13.0, 4.5	1.66; ddd; 12.9, 12.9, 4.2	1.65; td; 13.0, 4.4	-0.02; 0.01
5b	2.60; m	2.60; m	2.61; m	-0.01; -0.01
11	8.65; s	8.69; s	8.68; s	-0.03; 0.01
18	8.24; s	8.26; s	8.26; s	-0.02; 0.00
20	1.48; s	1.50; s	1.50; s	-0.02; 0.00
21	3.87; m	3.88; br s	3.88; t; 6.0	-0.01; 0.00
22	3.39; t; 6.0	3.40; t; 6.0	3.40; t; 6.0	-0.01; 0.00
NH	9.33; br s	9.34; br s	9.35; br s	-0.02; -0.01

Table S7. Comparison of ^{13}C NMR spectroscopic data of natural [6] and synthetic [7] (+)-adociaquinone A with this synthetic work.

position	**natural (a) (Ireland's work)** δ ^{13}C [ppm], 125 MHz, DMSO-d_6	**synthetic (b) (Harada's work)** δ ^{13}C [ppm], 125 MHz, DMSO-d_6	**synthetic (c) (this work)** δ ^{13}C [ppm], 125 MHz, DMSO-d_6	**deviation (a-c)** Δδ (ppm)
1	146.2	--	146.2	0.0
2	121.6	--	121.7	-0.1
3	16.3	--	16.3	0.0
4	17.8	--	17.9	-0.1
5	30.3	--	30.3	0.0
6	37.2	--	37.2	0.0
7	147.7	--	147.8	-0.1
8	143.0	--	143.0	0.0
9	169.3	--	169.4	-0.1
10	135.9	--	136.0	-0.1
11	125.4	--	125.4	0.0
12	128.6	--	128.6	0.0
13	173.7	--	173.8	-0.1
14	111.7	--	111.7	0.0
15	147.2	--	147.2	0.0
16	177.9	--	177.9	0.0
17	134.4	--	134.4	0.0
18	122.9	--	123.0	-0.1
19	157.3	--	157.4	-0.1
20	31.8	--	31.8	0.0
21	39.4	--	39.4, buried in the peak of DMSO-d_6	0.0
22	48.2	--	48.2	0.0



(+)-adociaquinone B (**4**)

Natural product (+)-adociaquinone B: $[\alpha]_D$ = +21.5 (c = 1.86 in MeCN) [6]

Harada's Synthetic (+)-adociaquinone B: $[\alpha]_D^{20}$ = +74 (c = 0.0668 in chloroform -methanol (v/v = 2:1)) [7]

Our Synthetic (+)-adociaquinone B: $[\alpha]_D^{20}$ = +100.4 (c = 0.05 in chloroform -methanol (v/v = 2:1))

Table S8. Comparison of ^{1}H NMR spectroscopic data of natural [6] and synthetic [7] (+)-adociaquinone B with this synthetic work.

position	**natural (a) (Ireland's work)** δ ^{1}H [ppm; mult; *J* (Hz)], 500 MHz, DMSO-d_6	**synthetic (b) (Harada's work)** δ ^{1}H [ppm; mult; *J* (Hz)], 500 MHz, DMSO-d_6	**synthetic (c) (this work)** δ^{1}H [ppm; mult; *J* (Hz)], 500 MHz, DMSO-d_6	**deviation (a-c; b-c)** Δδ (ppm)
1	7.99; s	8.00; s	8.00; s	-0.01; 0.00
3a	2.58; dd; 16.5, 8.5	2.59; dd; 16.9, 9.0	2.59; dd; 17.4, 8.9	-0.01; 0.00
3b	2.83; dd; 16.5, 7.5	2.84; dd; 16.9, 7.7	2.84; dd; 17.1, 7.9	-0.01; 0.00
4a	2.05; m	2.07; m	2.07; m	-0.02; 0.00
4b	2.20; m	2.21; m	2.21; m	-0.01; 0.00
5a	1.62; dt; 13.0, 4.0	1.63; ddd; 12.8, 12.8, 4.2	1.63; td; 12.9, 4.3	-0.01; 0.00
5b	2.64; m	2.65; ddd; 12.8, 3.0, 3.0	2.65; dd; 13.2, 4.1	-0.01; 0.00
11	8.70; s	8.72; s	8.72; s	-0.02; 0.00
18	8.26; s	8.28; s	8.28; s	-0.02; 0.00
20	1.49; s	1.50; s	1.50; s	-0.01; 0.00
21	3.38; t; 6.0	3.40; buried in the peak of water	3.40; t; 5.9	-0.02; 0.00
22	3.86; m	3.88; t; 5.9	3.88; t; 5.9	-0.02; 0.00
NH	9.23; br s	8.90; br s	9.24; br s	-0.01; -0.34

Table S9. Comparison of ^{13}C NMR spectroscopic data of natural [6] and synthetic [7] (+)-adociaquinone B with this synthetic work.

position	**natural (a) (Ireland's work)** δ ^{13}C [ppm], 125 MHz, DMSO-d_6	**synthetic (b) (Harada's work)** δ ^{13}C [ppm], 125 MHz, DMSO-d_6	**synthetic (c) (this work)** δ ^{13}C [ppm], 125 MHz, DMSO-d_6	**deviation (a-c; b-c)** Δδ (ppm)
1	146.2	146.1	146.2	0.0; -0.1
2	121.6	121.6	121.6	0.0; 0.0
3	16.2	16.2	16.2	0.0; 0.0
4	17.8	17.8	17.8	0.0; 0.0
5	30.3	30.3	30.3	0.0; 0.0
6	36.8	36.8	36.8	0.0; 0.0
7	147.9	147.9	147.9	0.0; 0.0
8	143.1	143.1	143.0	0.1; 0.1
9	169.4	169.4	169.4	0.0; 0.0
10	137.9	137.9	137.9	0.0; 0.0
11	124.7	124.8	124.7	0.0; 0.1
12	130.9	130.9	130.8	0.1; 0.1
13	173.7	173.7	173.7	0.0; 0.0
14	147.1	147.1	147.1	0.0; 0.0
15	111.3	111.4	111.3	0.0; 0.1
16	178.3	178.3	178.3	0.0; 0.0
17	131.8	131.8	131.8	0.0; 0.0
18	123.4	123.4	123.4	0.0; 0.0
19	154.6	154.6	154.6	0.0; 0.0
20	31.6	31.6	31.6	0.0; 0.0
21	48.2	48.3	48.2	0.0; 0.1
22	39.3	around 40, buried in the peak of DMSO-d_6	39.3, buried in the peak of DMSO-d_6	0.0; 0.7

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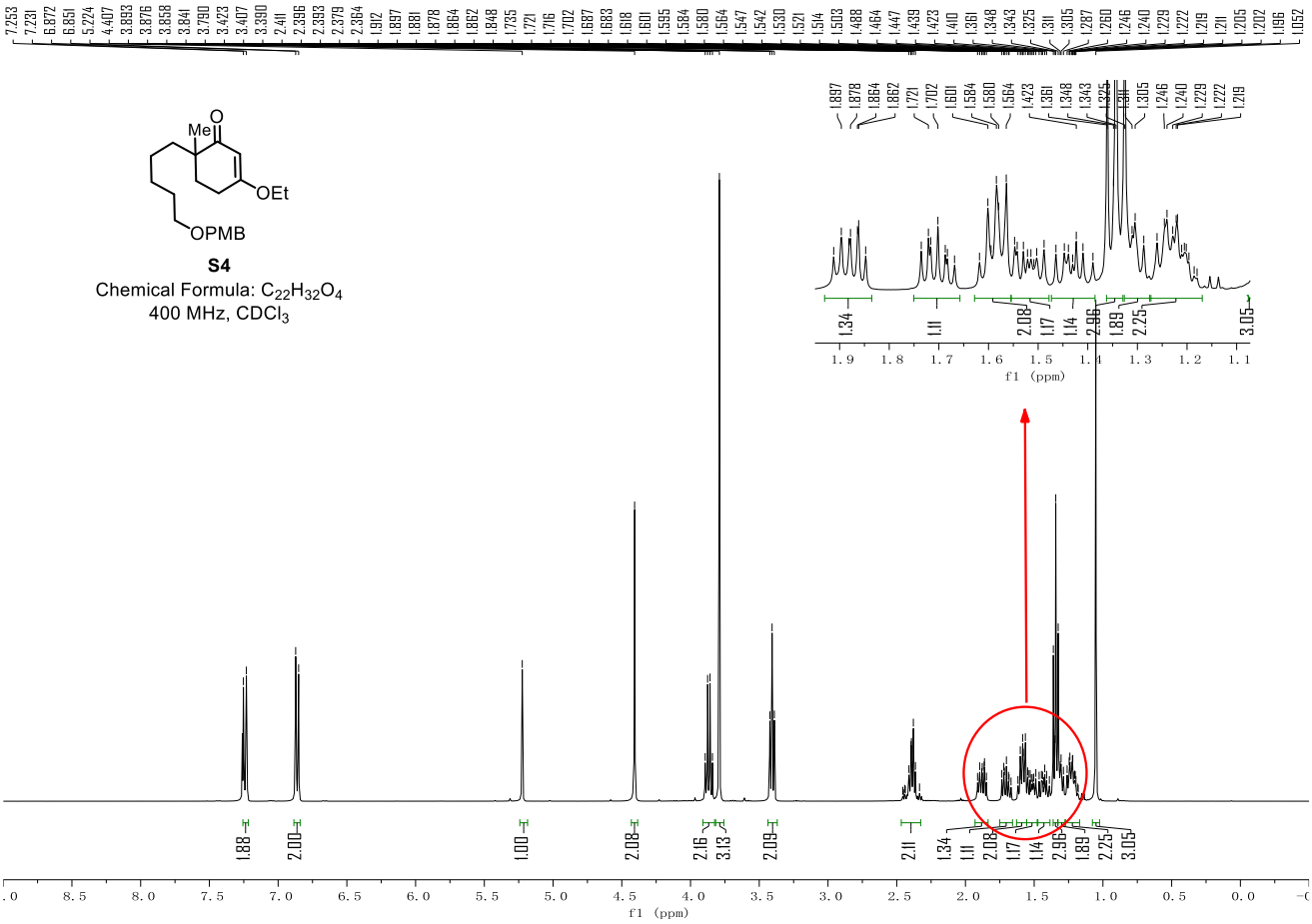
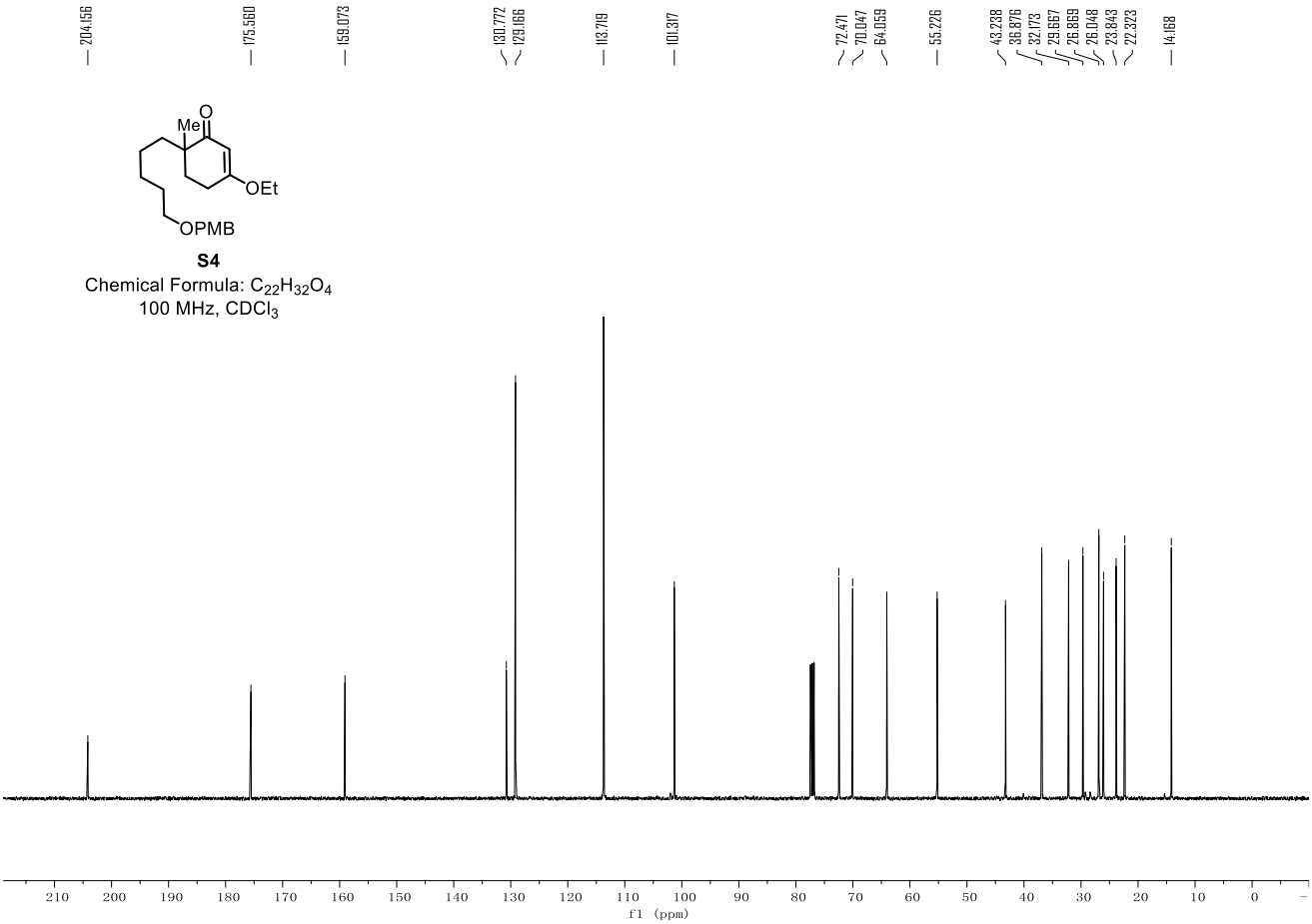
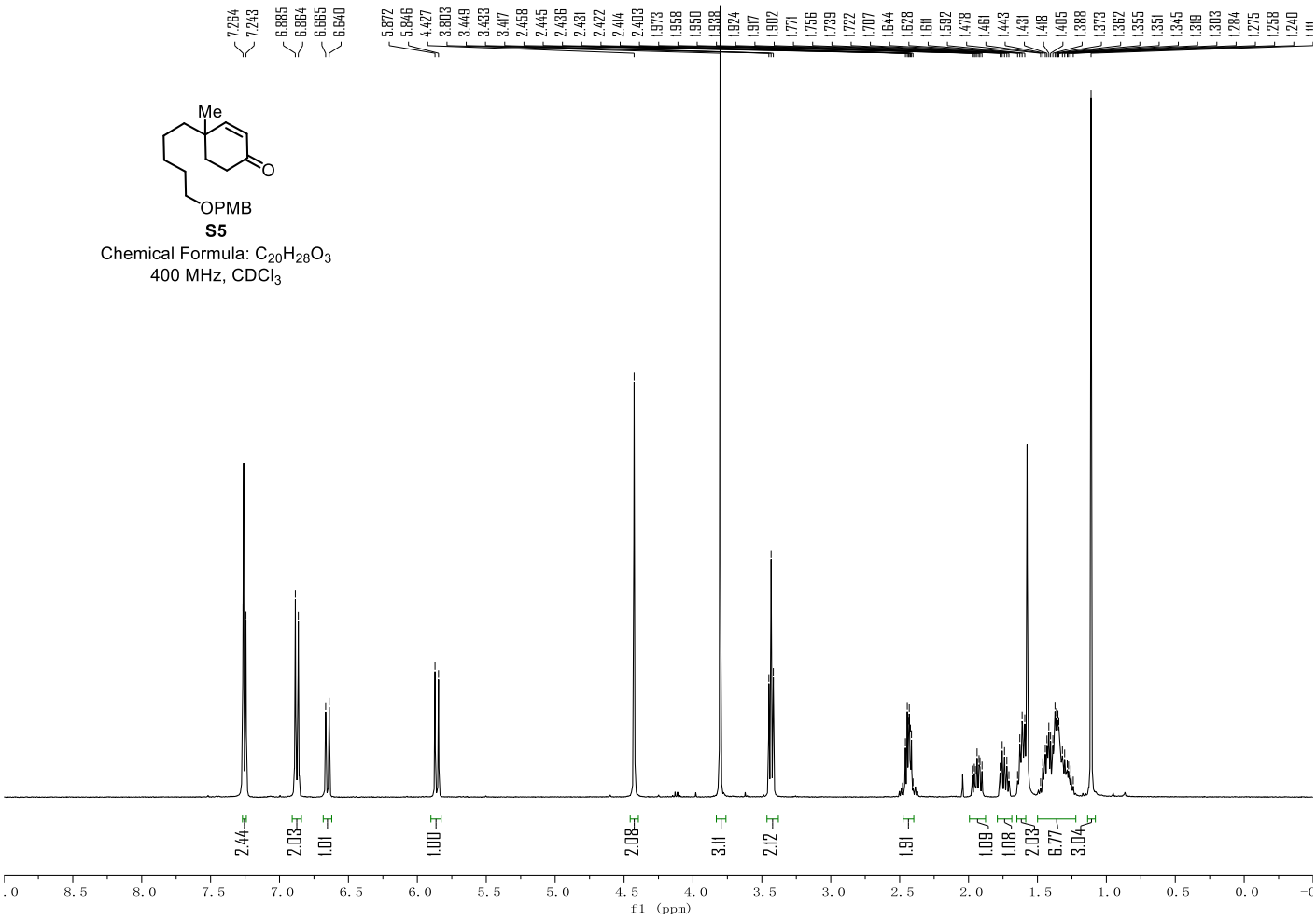
^{1}H and ^{13}C NMR, HPLC spectra of the synthetic intermediates and products



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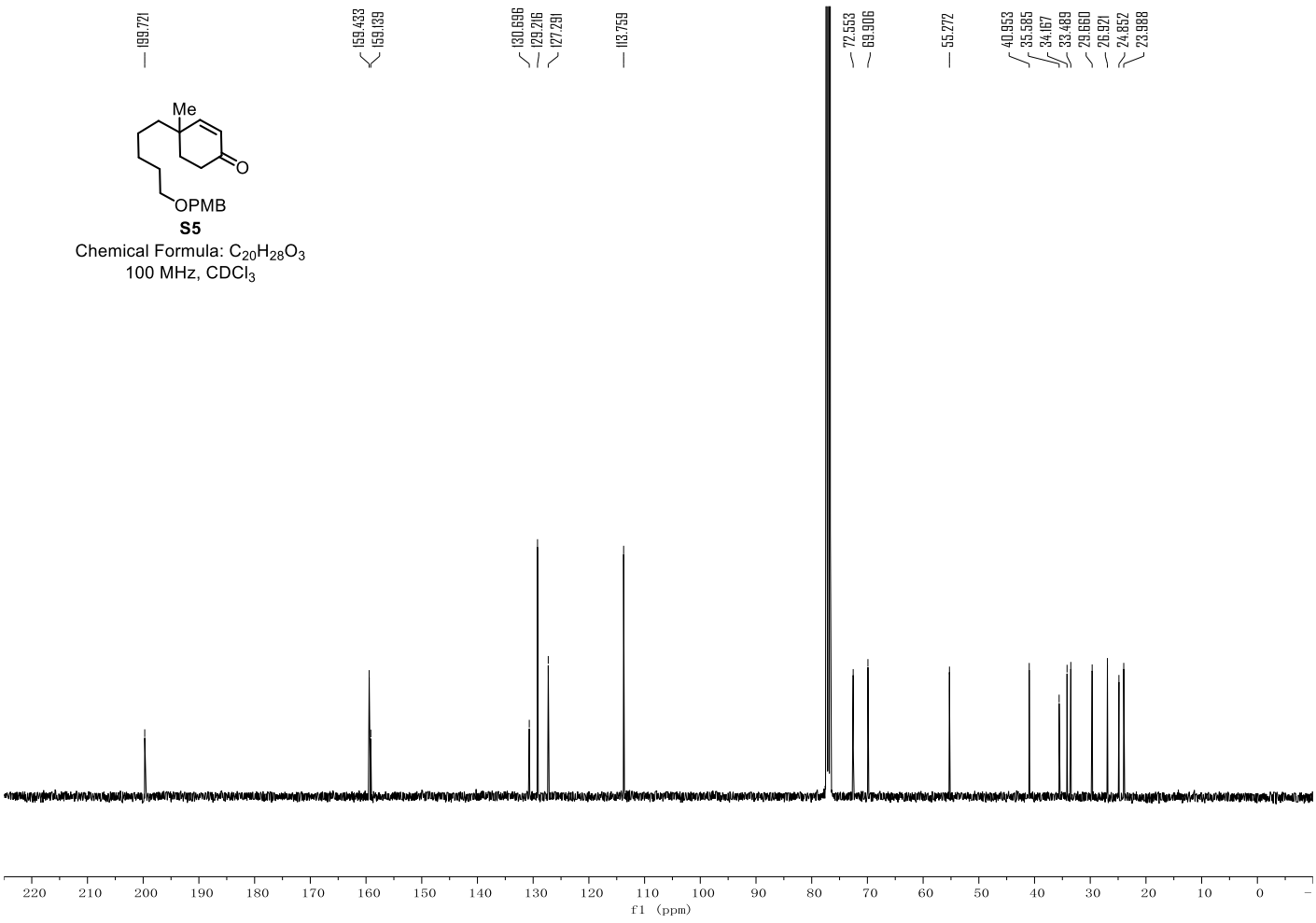
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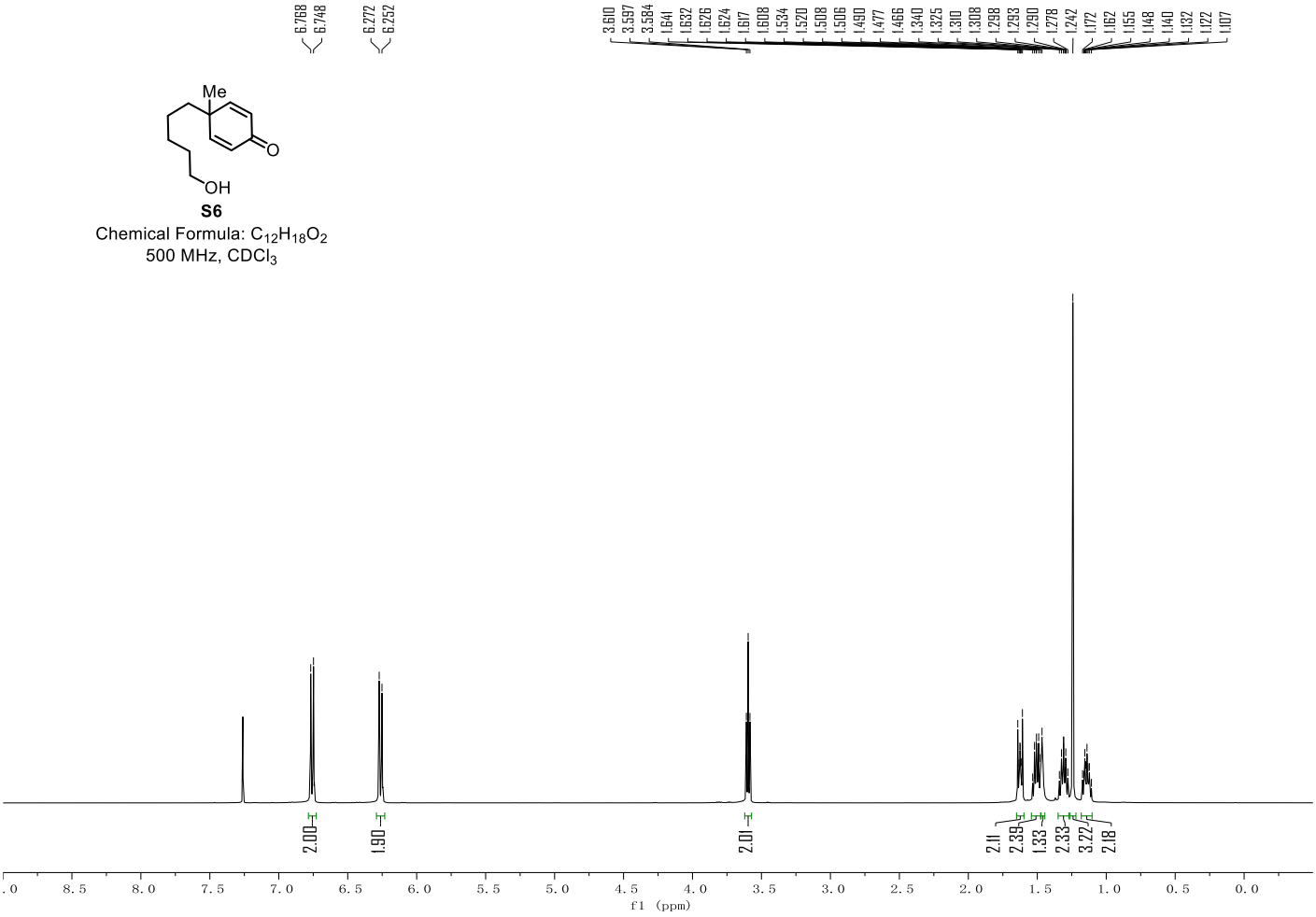
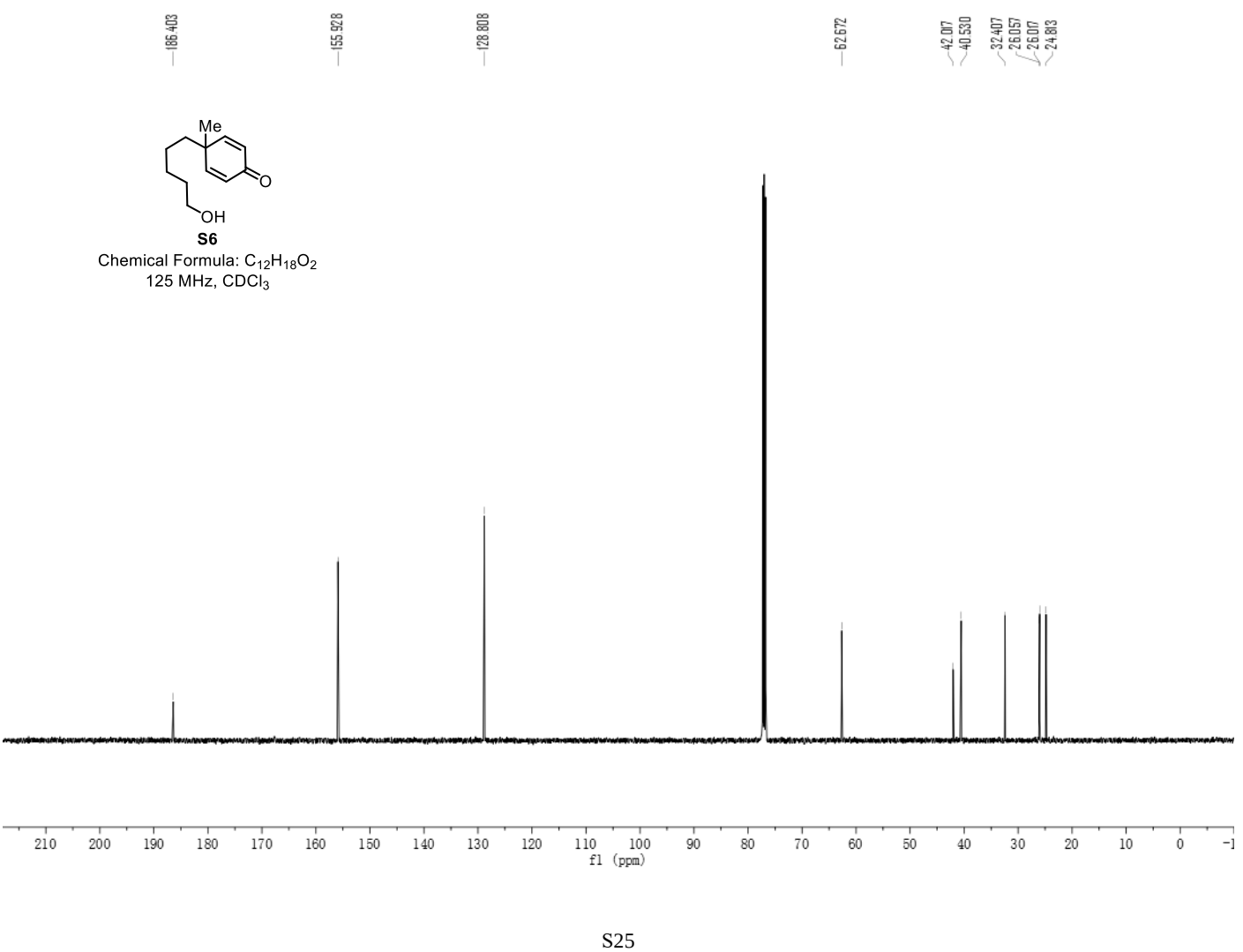
100 MHz, $CDCl_3$
f1 (ppm)



S6

Chemical Formula: $C_{12}H_{18}O_2$

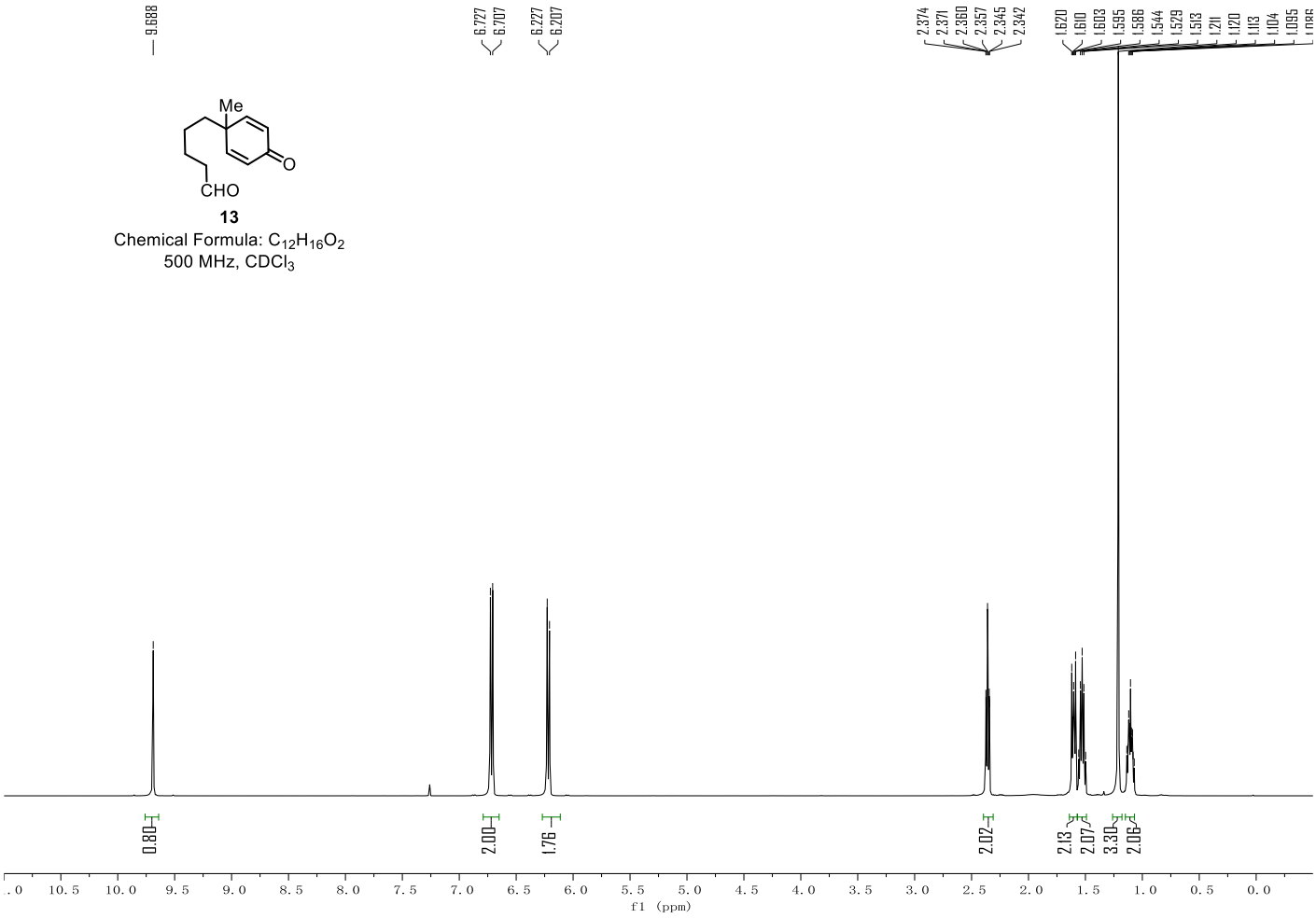
500 MHz, $CDCl_3$



S6

Chemical Formula: $C_{12}H_{18}O_2$

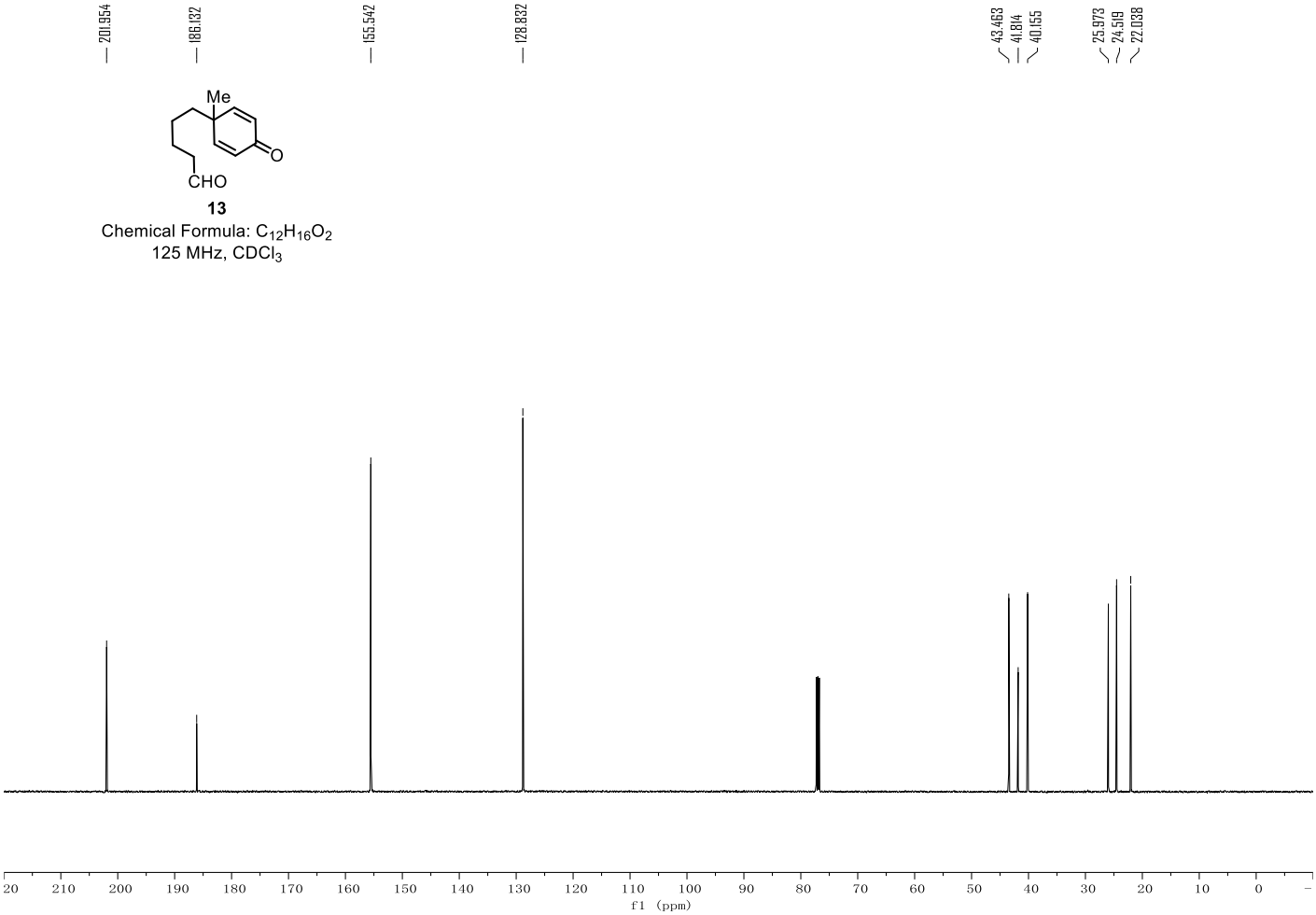
125 MHz, $CDCl_3$



13

Chemical Formula: $C_{12}H_{16}O_2$

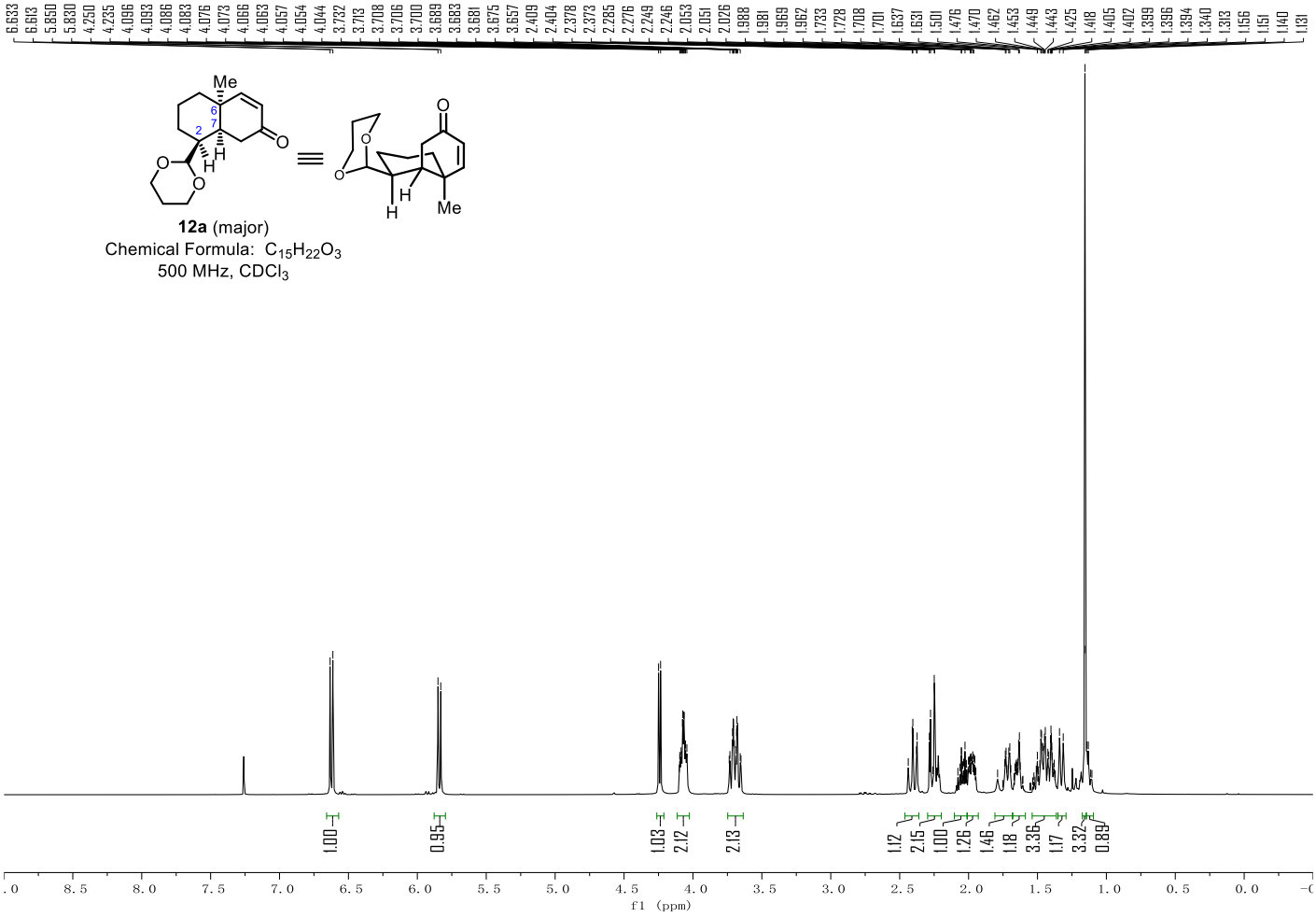
500 MHz, $CDCl_3$

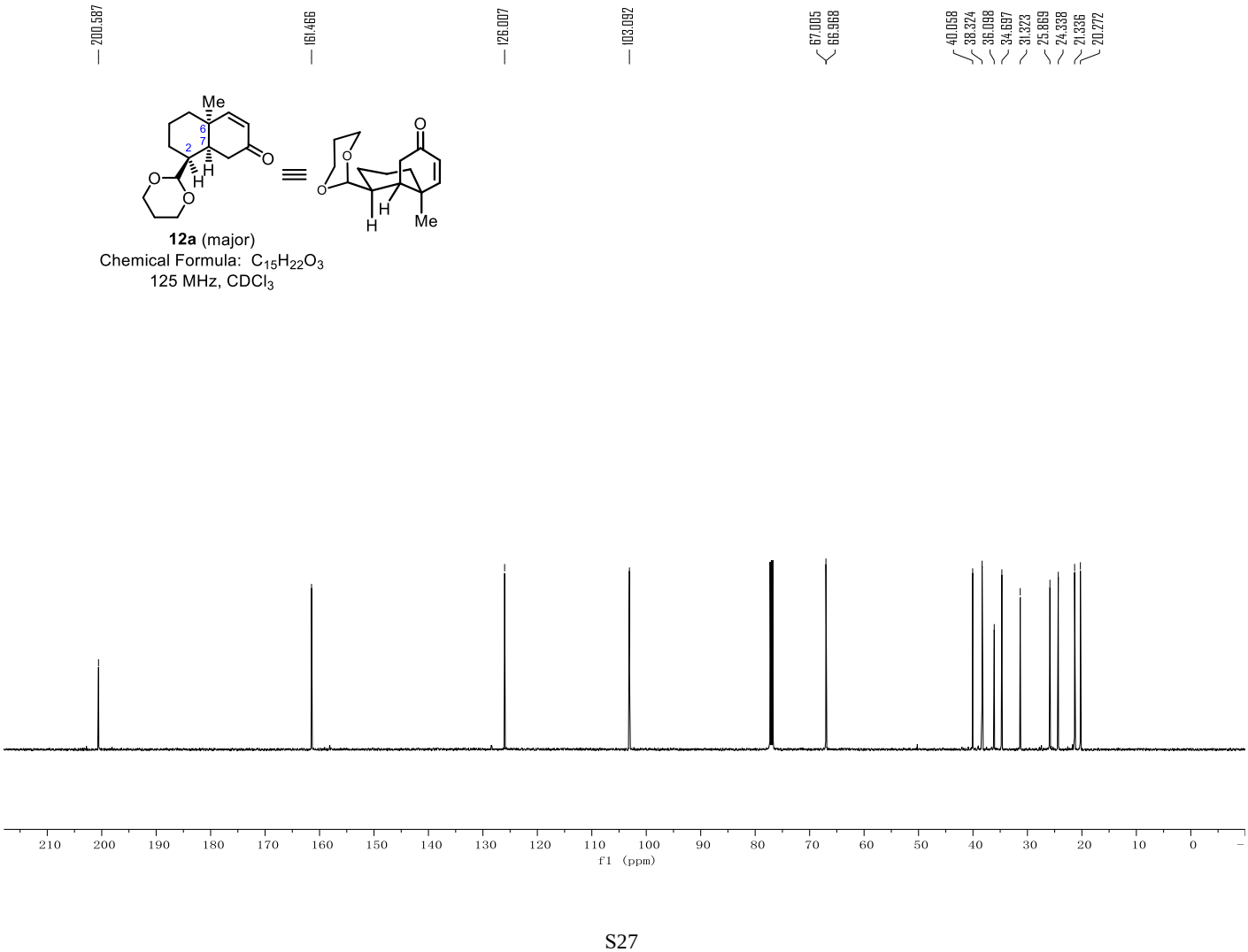


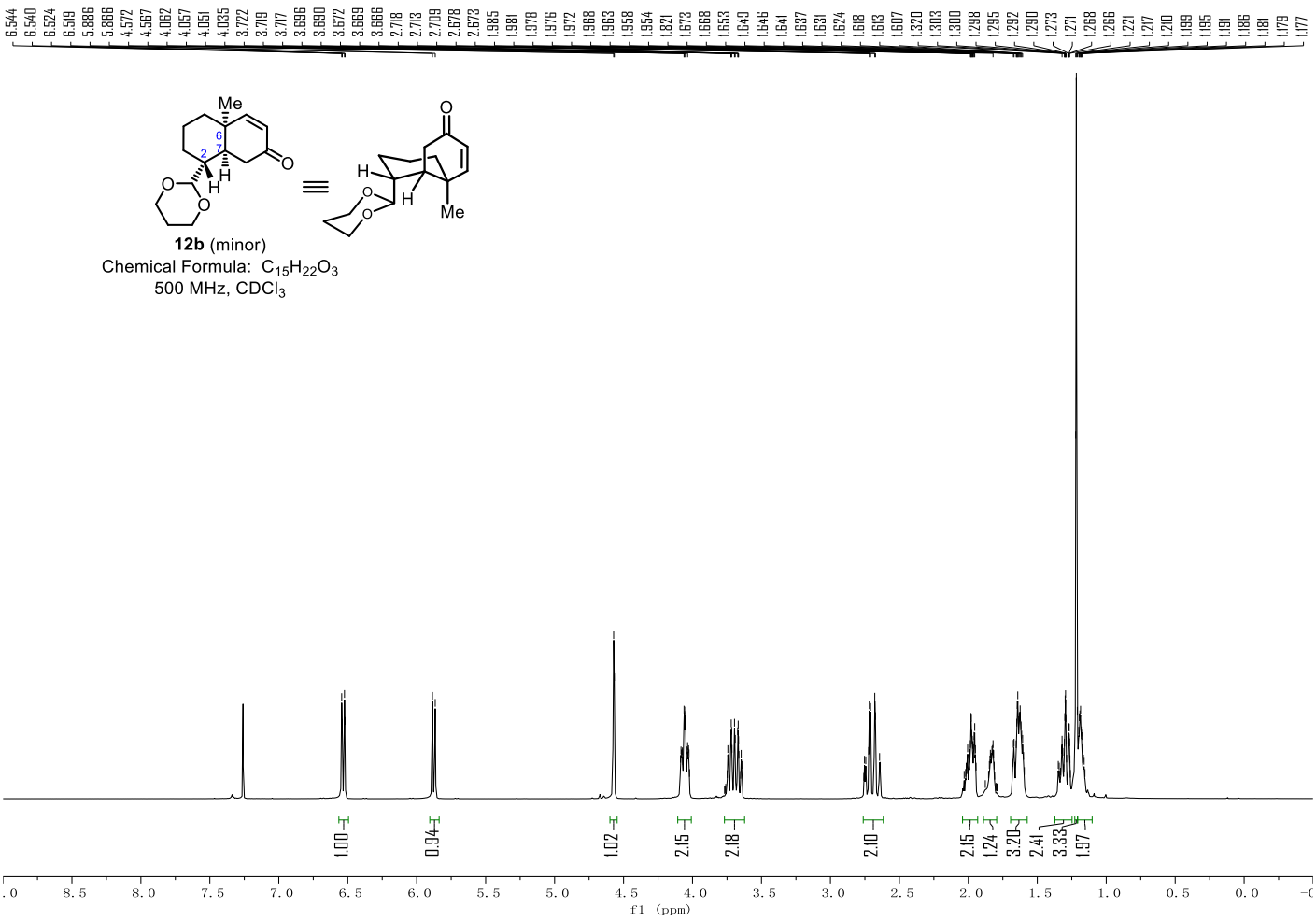
13

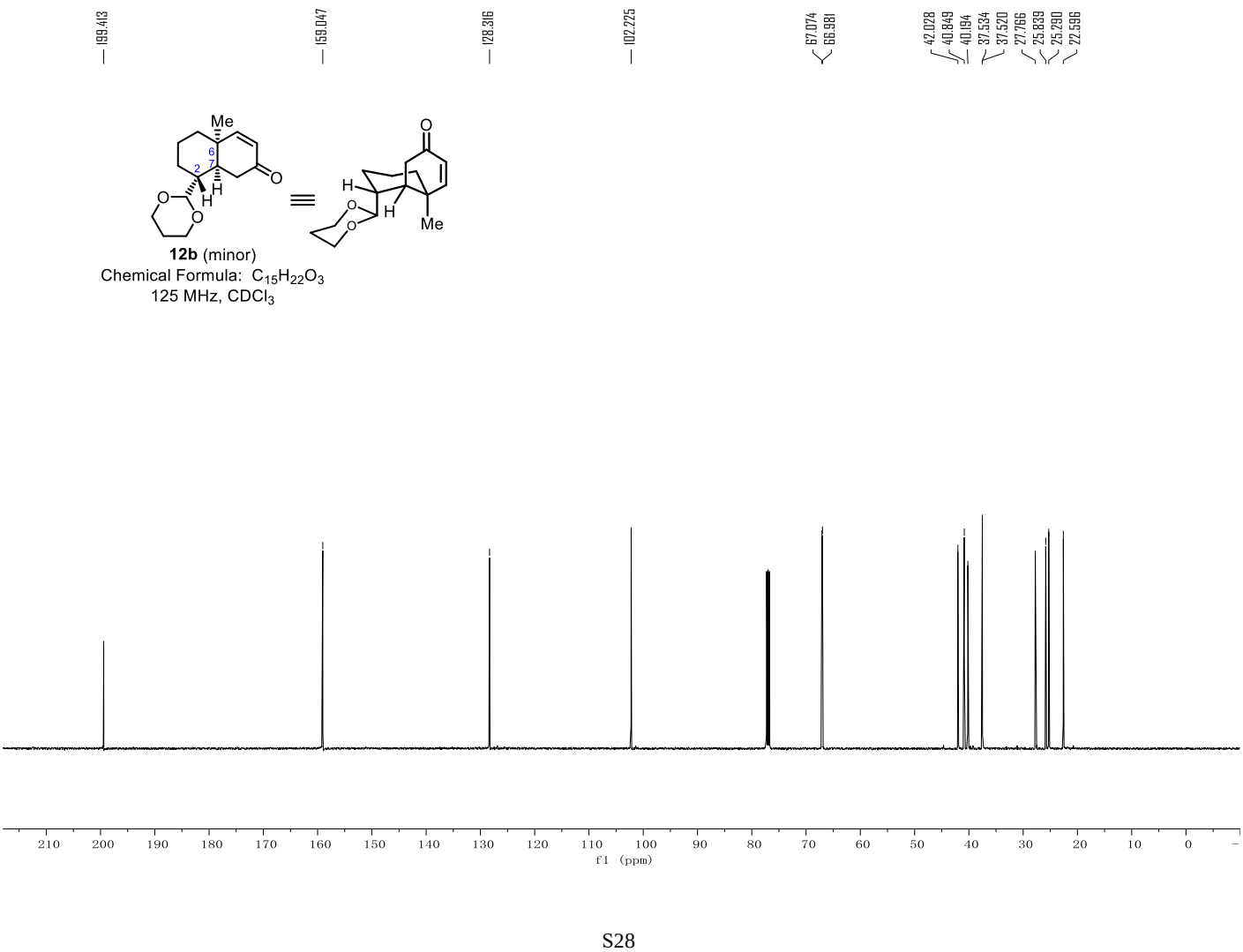
Chemical Formula: $C_{12}H_{16}O_2$

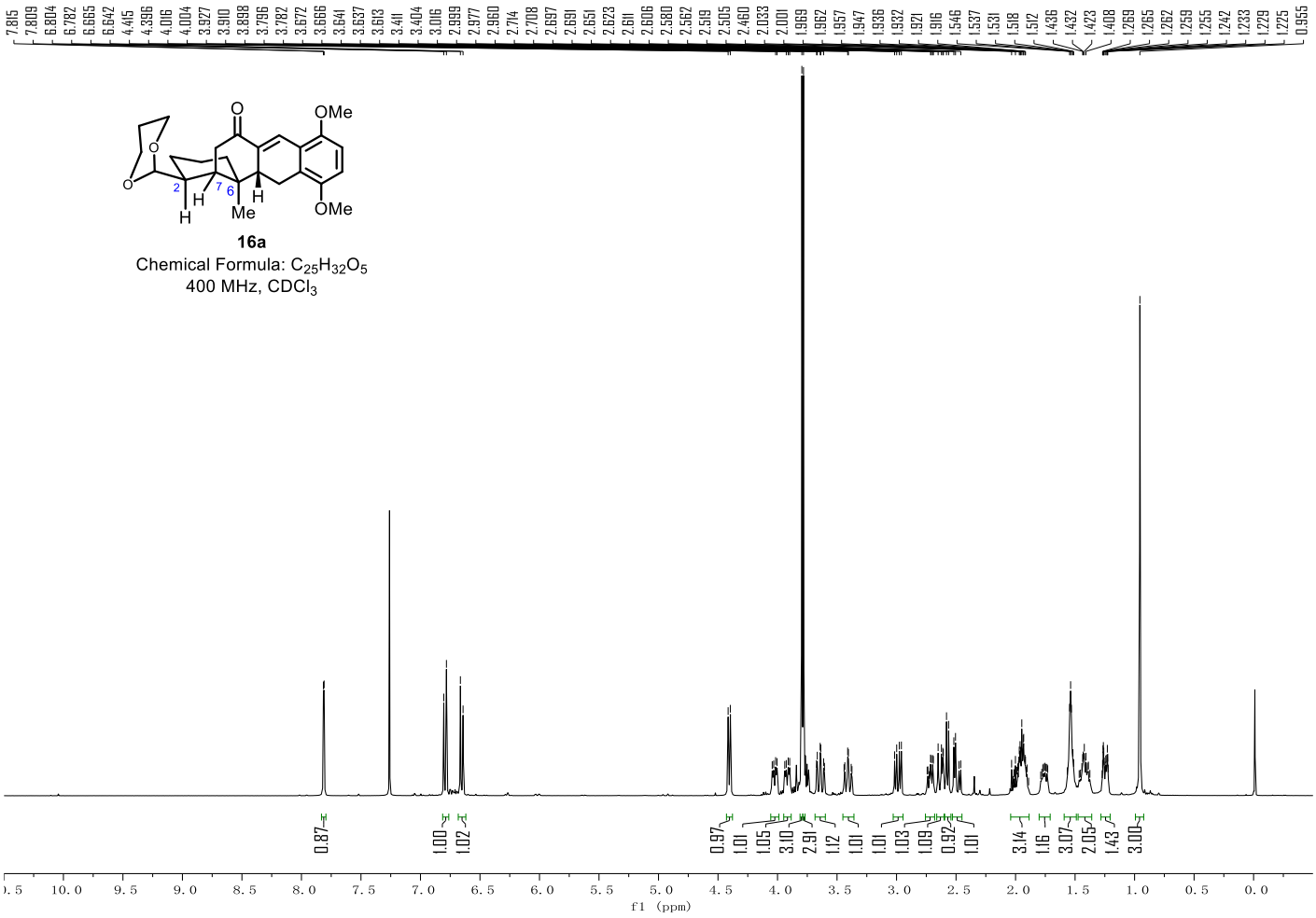
125 MHz, $CDCl_3$

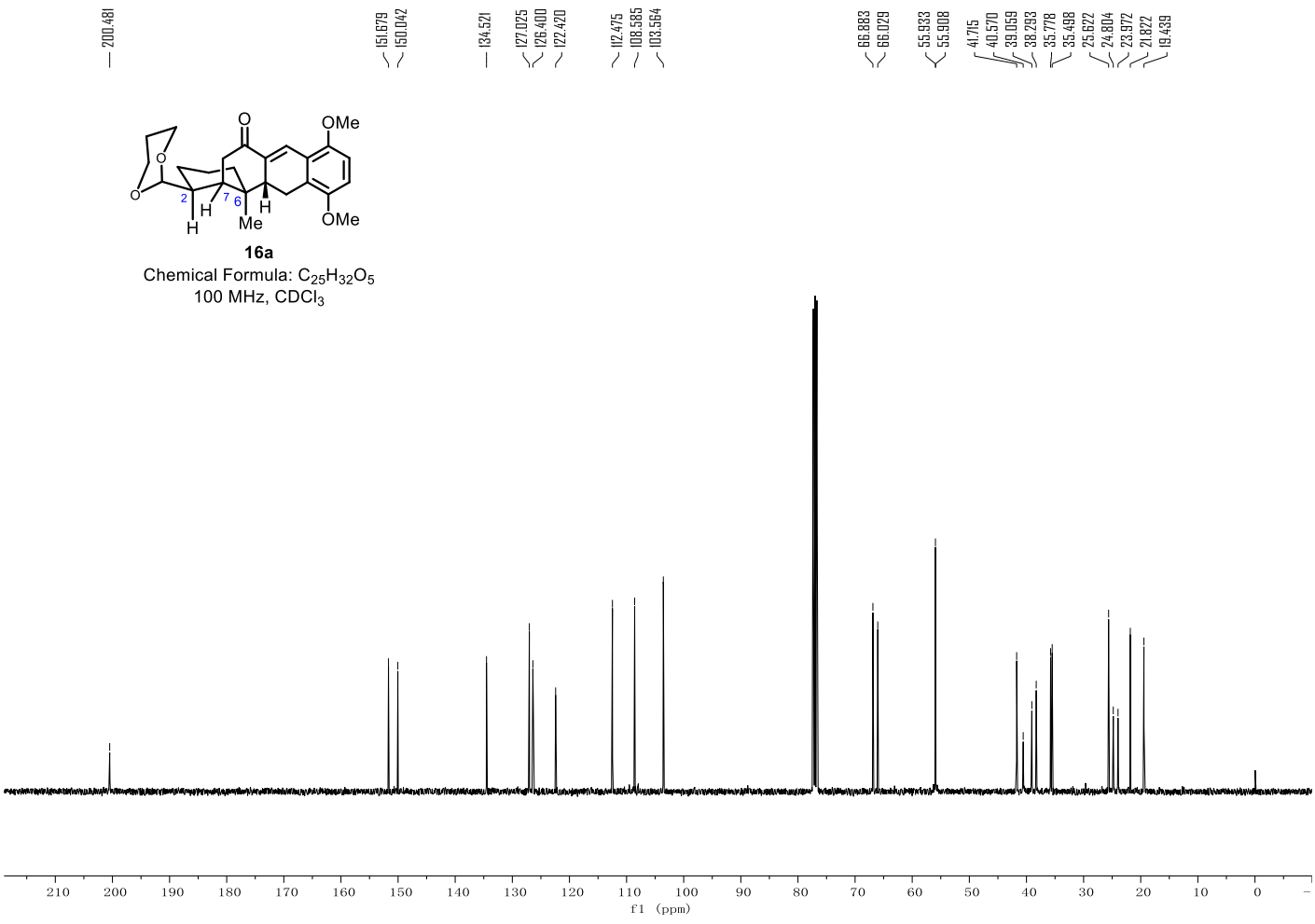

6.633
6.613
5.850
5.830
4.250
4.235
4.096
4.093
4.086
4.083
4.076
4.073
4.066
4.063
4.057
4.054
4.044
3.732
3.713
3.708
3.706
3.700
3.689
3.683
3.681
3.675
3.657
2.409
2.404
2.378
2.373
2.285
2.276
2.249
2.246
2.053
2.051
2.026
1.988
1.981
1.969
1.962
1.733
1.728
1.708
1.701
1.637
1.631
1.501
1.476
1.470
1.462
1.453
1.449
1.443
1.425
1.418
1.405
1.402
1.399
1.396
1.394
1.340
1.313
1.156
1.151
1.140
1.131
Me
6
7
2
H
O
O
O
H
O
O
H
Me
12a (major)
Chemical Formula: C15H22O3
500 MHz, CDCl3
1.00
0.95
1.03
2.12
2.13
1.12
2.15
1.00
1.26
1.46
1.18
3.36
1.17
3.32
0.89
f1 (ppm)

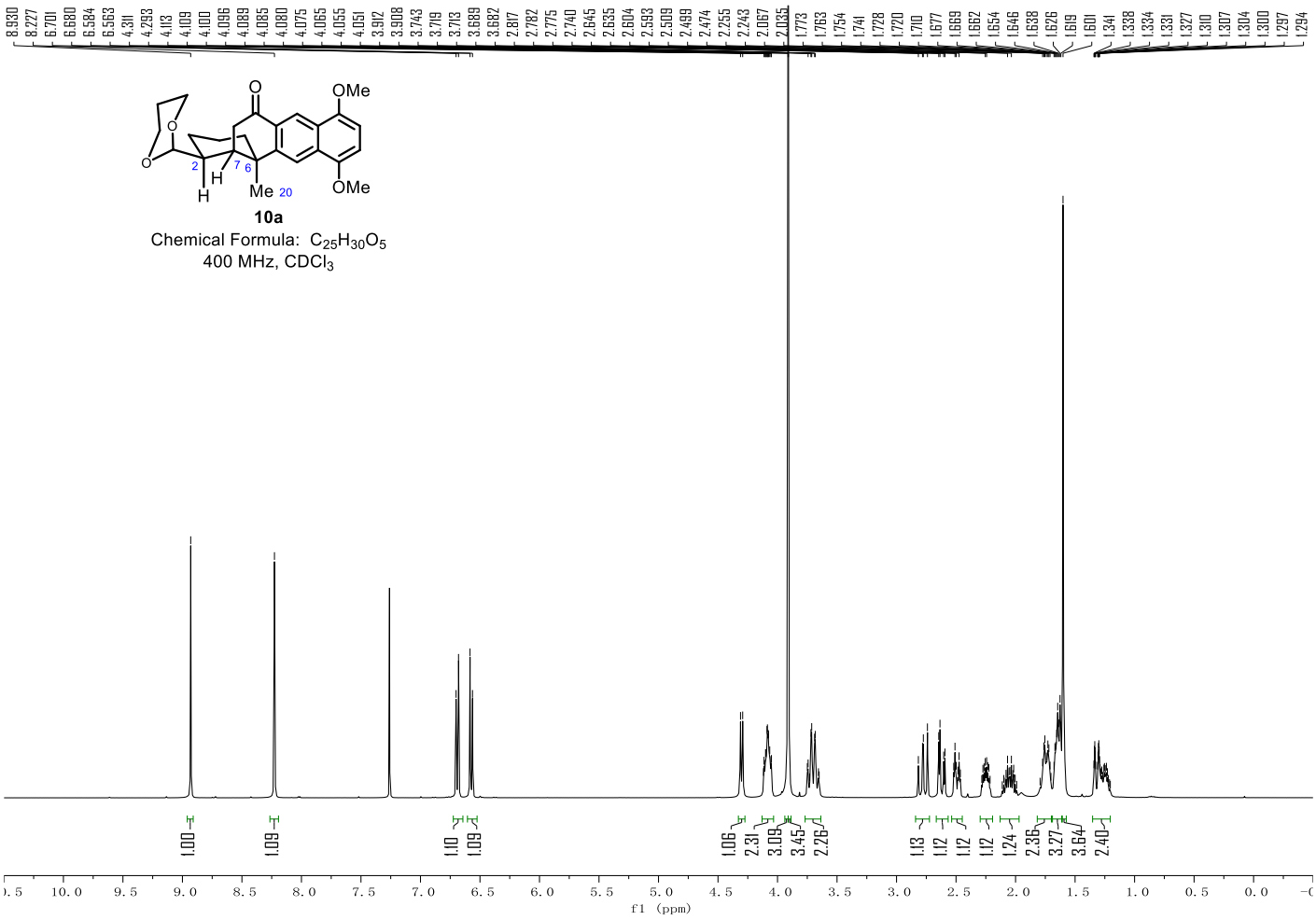

200.587
161.466
126.007
103.092
67.005
66.968
40.058
38.324
36.098
34.697
31.323
25.869
24.338
21.336
20.272
Me
6
7
2
H
O
O
O
H
O
O
H
Me
12a (major)
Chemical Formula: C15H22O3
125 MHz, CDCl3
f1 (ppm)


6.544 6.540 6.524 6.519 5.886 5.866 4.572 4.567 4.062 4.057 4.051 4.035 3.722 3.719 3.717 3.696 3.690 3.672 3.669 3.666 2.718 2.713 2.709 2.678 2.673 1.985 1.981 1.978 1.976 1.972 1.968 1.963 1.958 1.954 1.821 1.673 1.668 1.653 1.649 1.646 1.641 1.637 1.631 1.624 1.618 1.613 1.607 1.320 1.303 1.300 1.298 1.295 1.292 1.290 1.273 1.271 1.268 1.266 1.221 1.217 1.210 1.199 1.195 1.191 1.186 1.181 1.179 1.177
Me
O
H
O
O
H
O
H
Me
12b (minor)
Chemical Formula: C15H22O3
500 MHz, CDCl3
1.00 0.94 1.02 2.15 2.18 2.10 2.15 1.24 3.20 2.41 3.33 1.97
f1 (ppm)


199.413 159.047 128.316 102.225 67.074 66.981 42.028 40.849 40.194 37.534 37.520 27.766 25.839 25.290 22.596
Me
O
H
O
O
H
O
H
Me
12b (minor)
Chemical Formula: C15H22O3
125 MHz, CDCl3
f1 (ppm)


16a
Chemical Formula: C25H32O5
400 MHz, CDCl3
f1 (ppm)

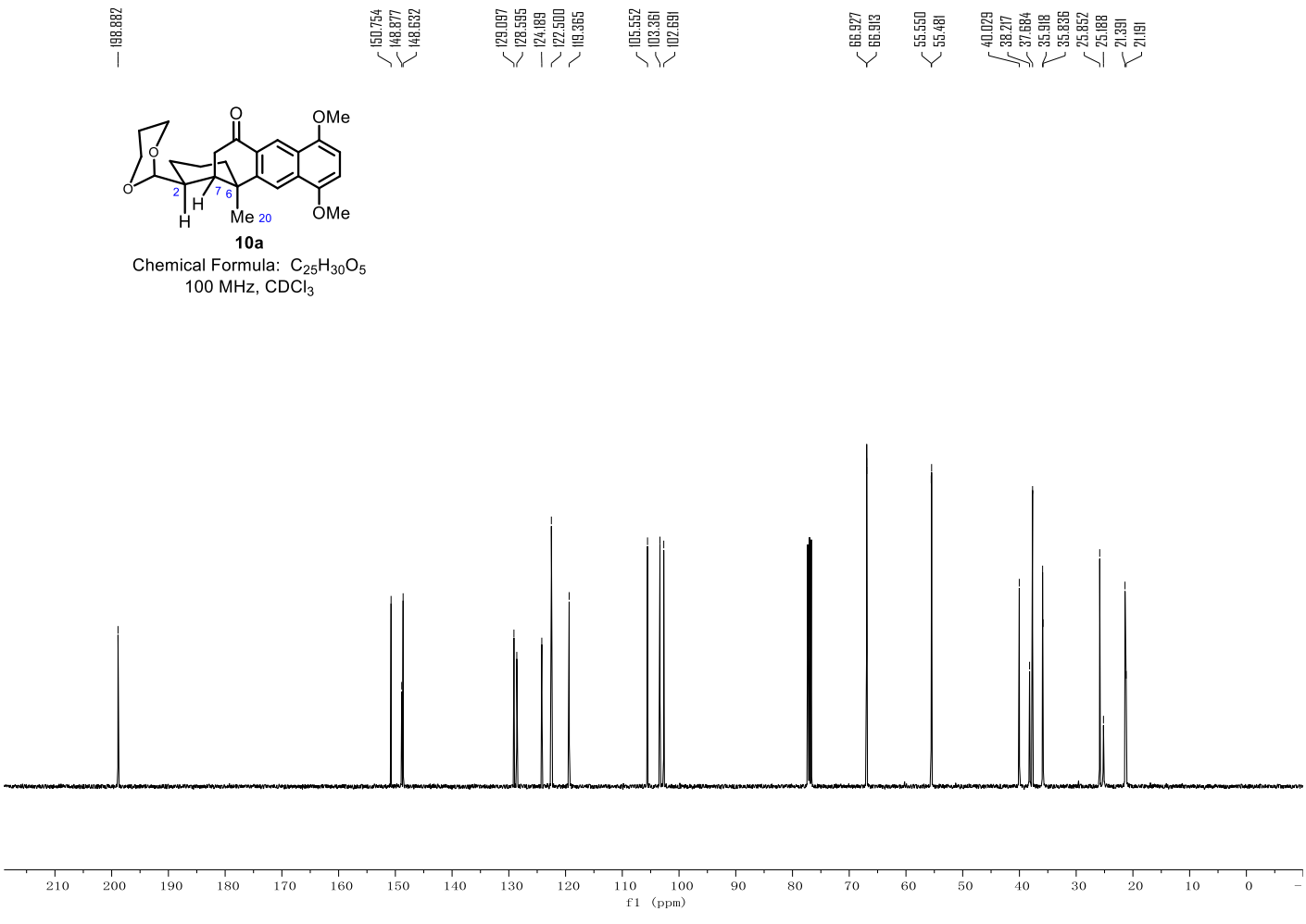

16a
Chemical Formula: C25H32O5
100 MHz, CDCl3
f1 (ppm)



10a

Chemical Formula: $C_{25}H_{30}O_5$

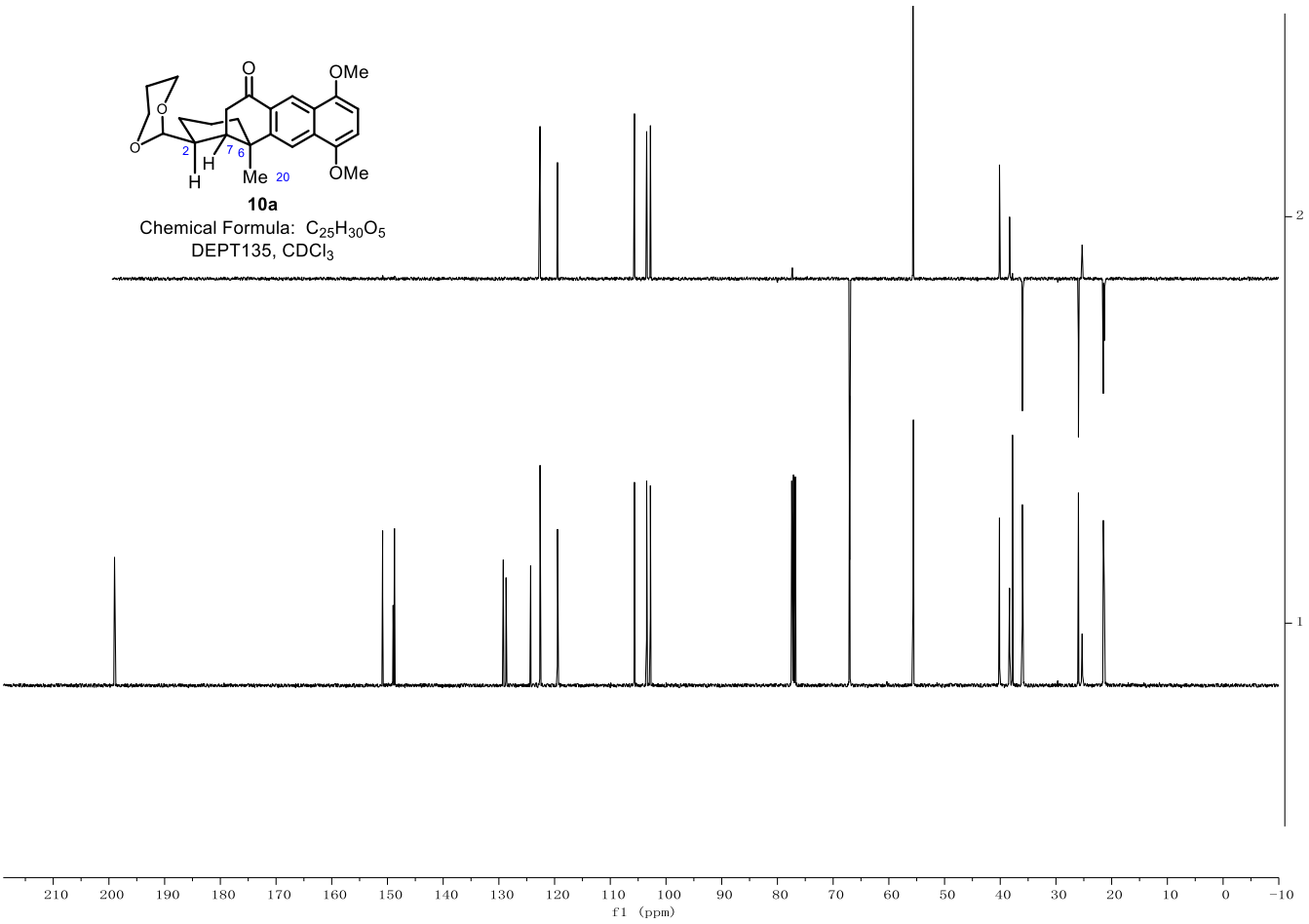
400 MHz, $CDCl_3$

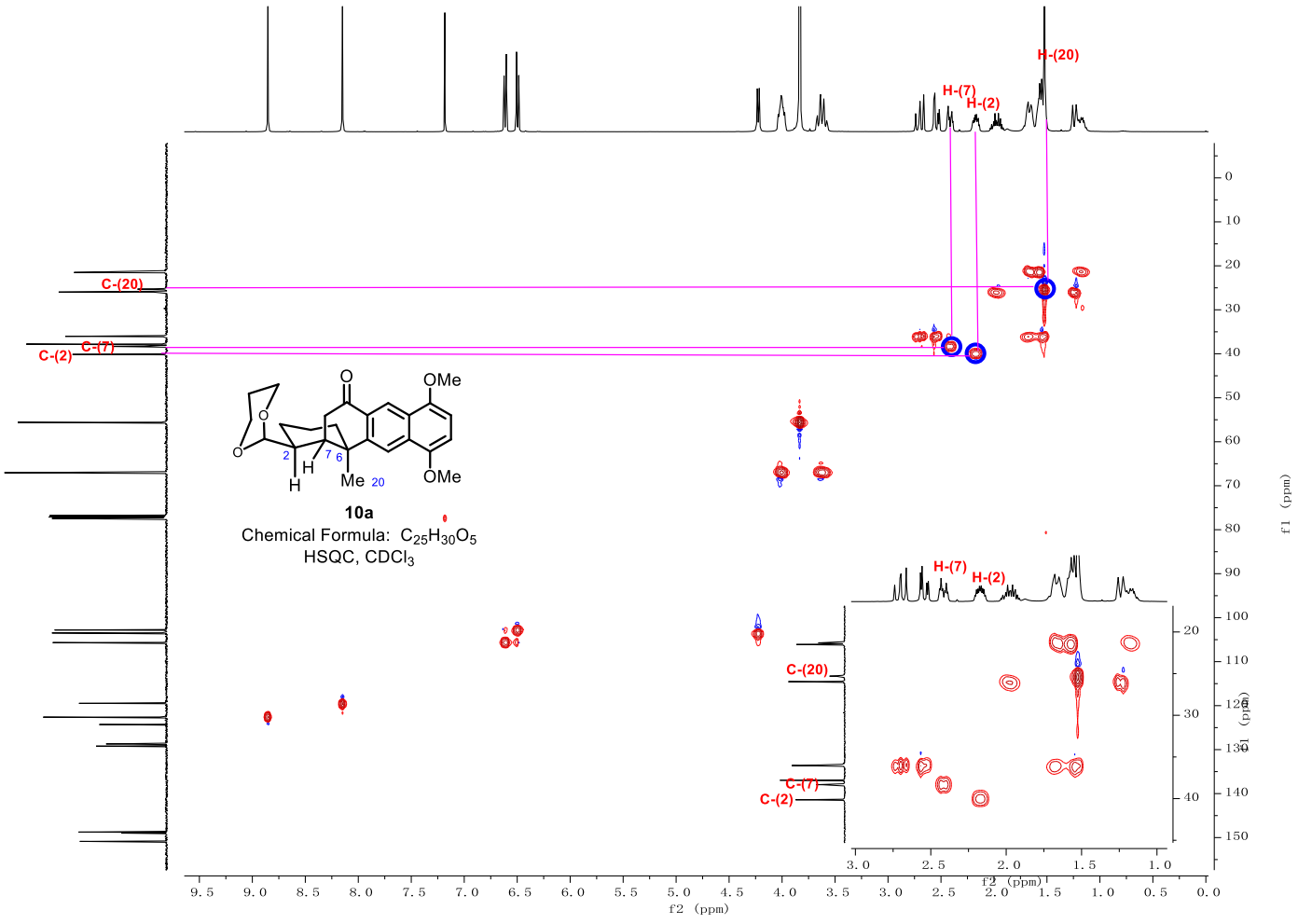


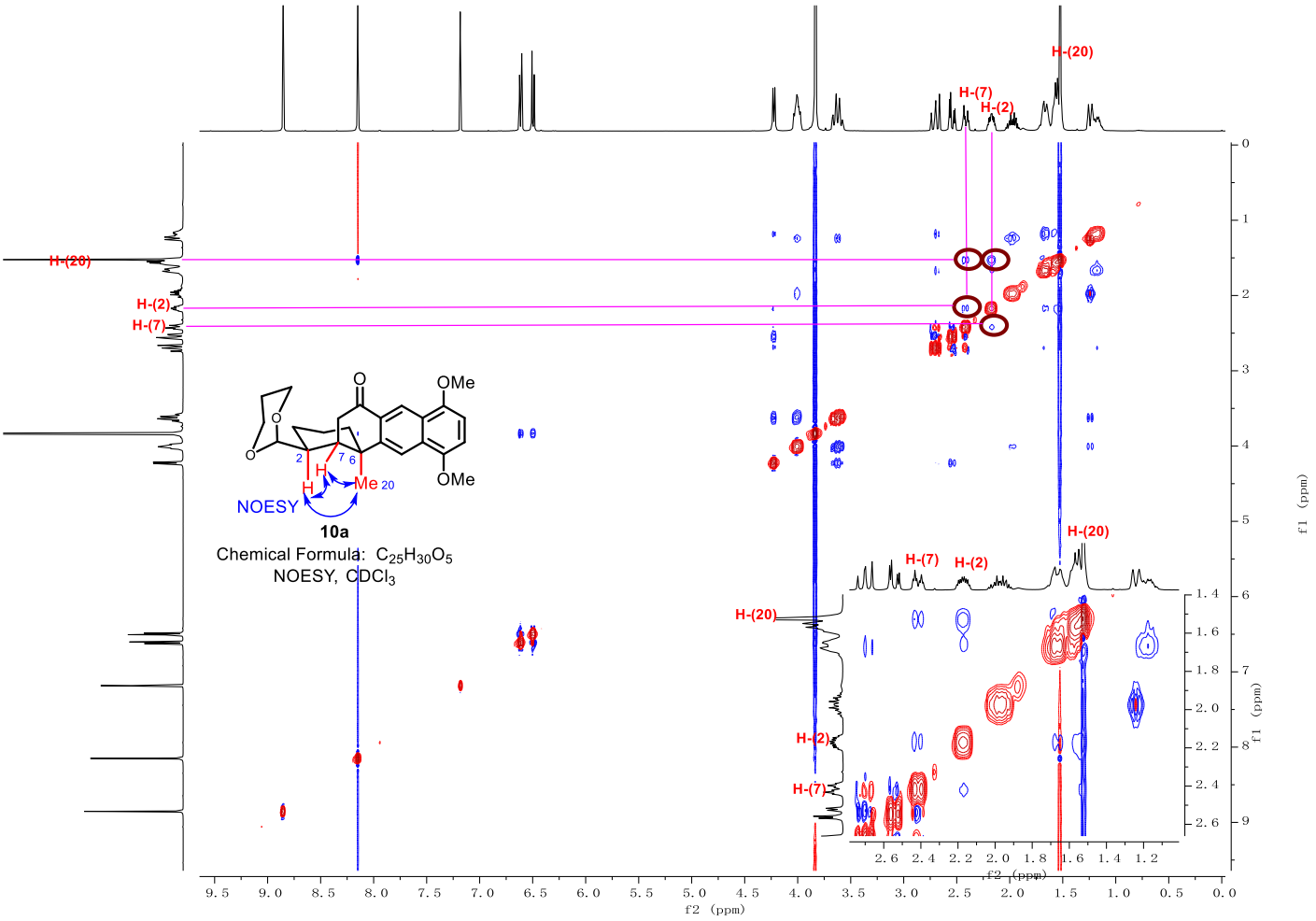
10a

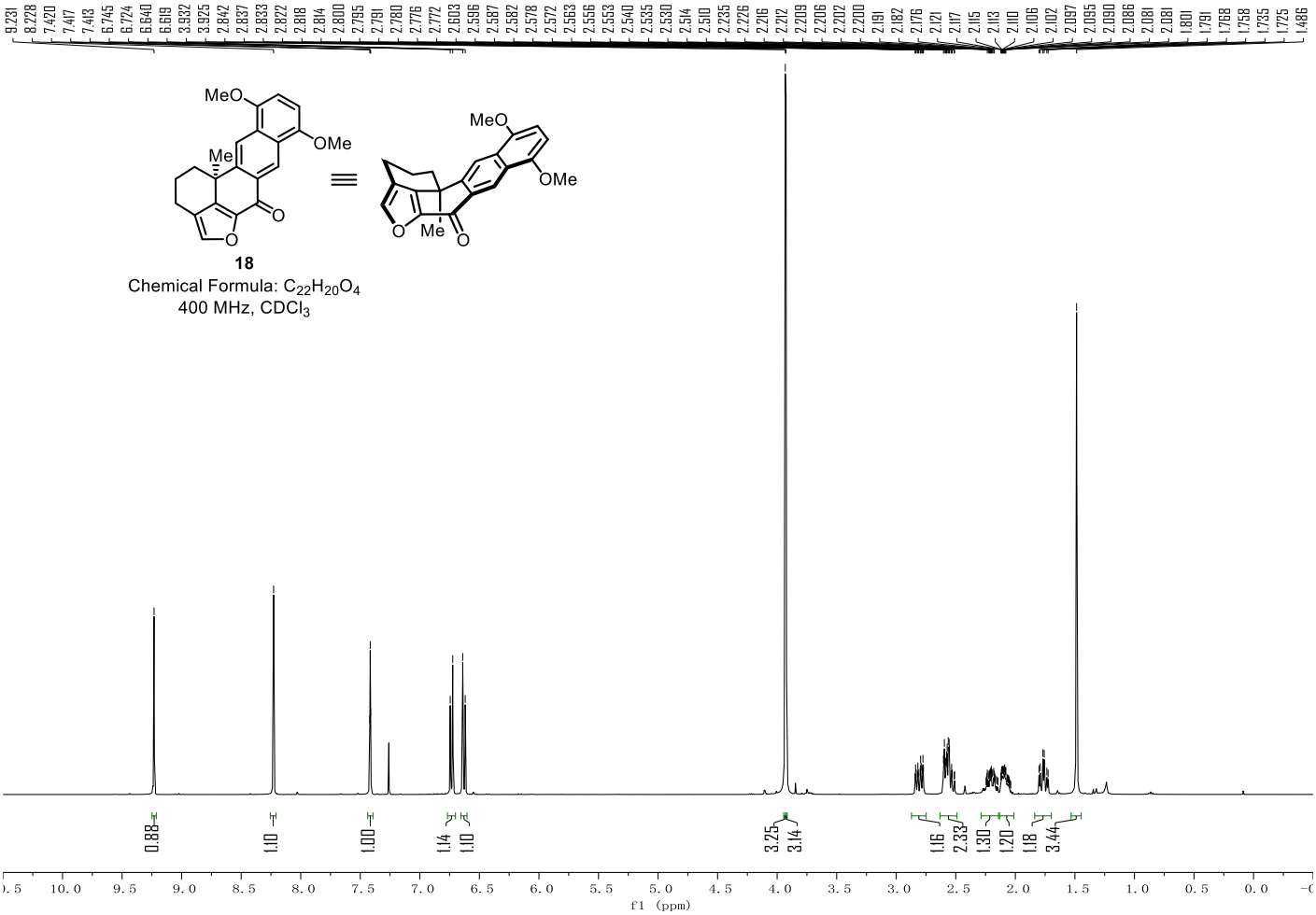
Chemical Formula: $C_{25}H_{30}O_5$

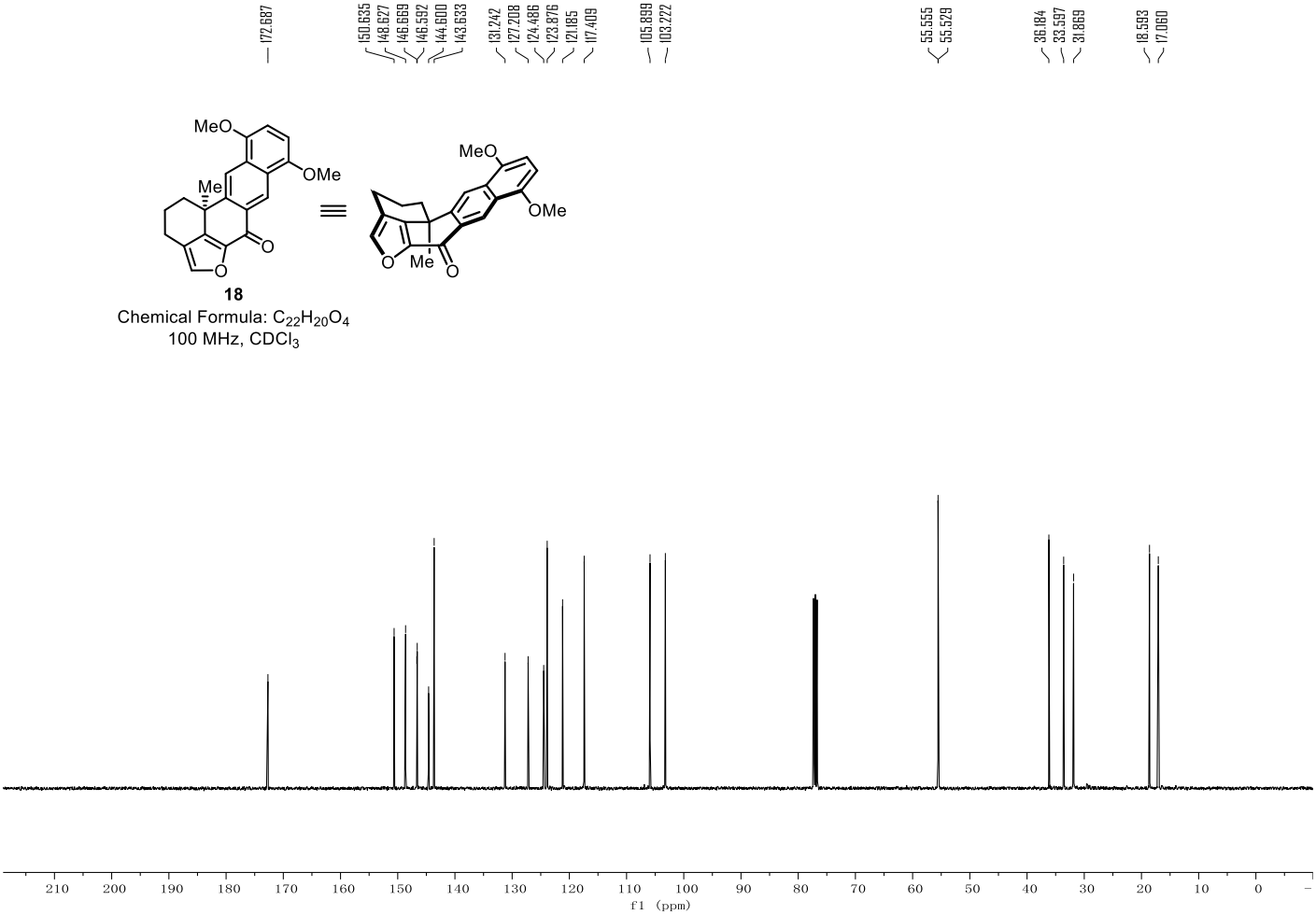
100 MHz, $CDCl_3$


OMe
O
O
2
H
7
6
H
Me 20
OMe
10a
Chemical Formula: C25H30O5
DEPT135, CDCl3
2
1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

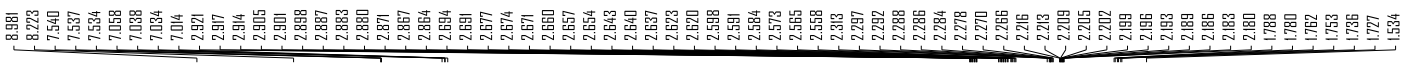

H-(20)
H-(7)
H-(2)
C-(20)
C-(7)
C-(2)
OMe
O
O
2
H
7
6
H
Me 20
OMe
10a
Chemical Formula: C25H30O5
HSQC, CDCl3
H-(7)
H-(2)
C-(20)
C-(7)
C-(2)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)

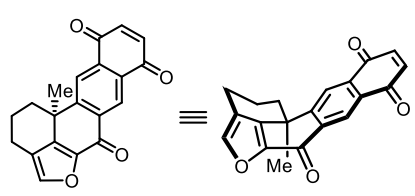

H-(20)
H-(7)
H-(2)
OMe
OMe
NOESY
10a
Chemical Formula: C25H30O5
NOESY, CDCl3
f2 (ppm)
f1 (ppm)


MeO
OMe
Me
O
O
MeO
OMe
Me
O
O
18
Chemical Formula: C22H20O4
400 MHz, CDCl3
f1 (ppm)

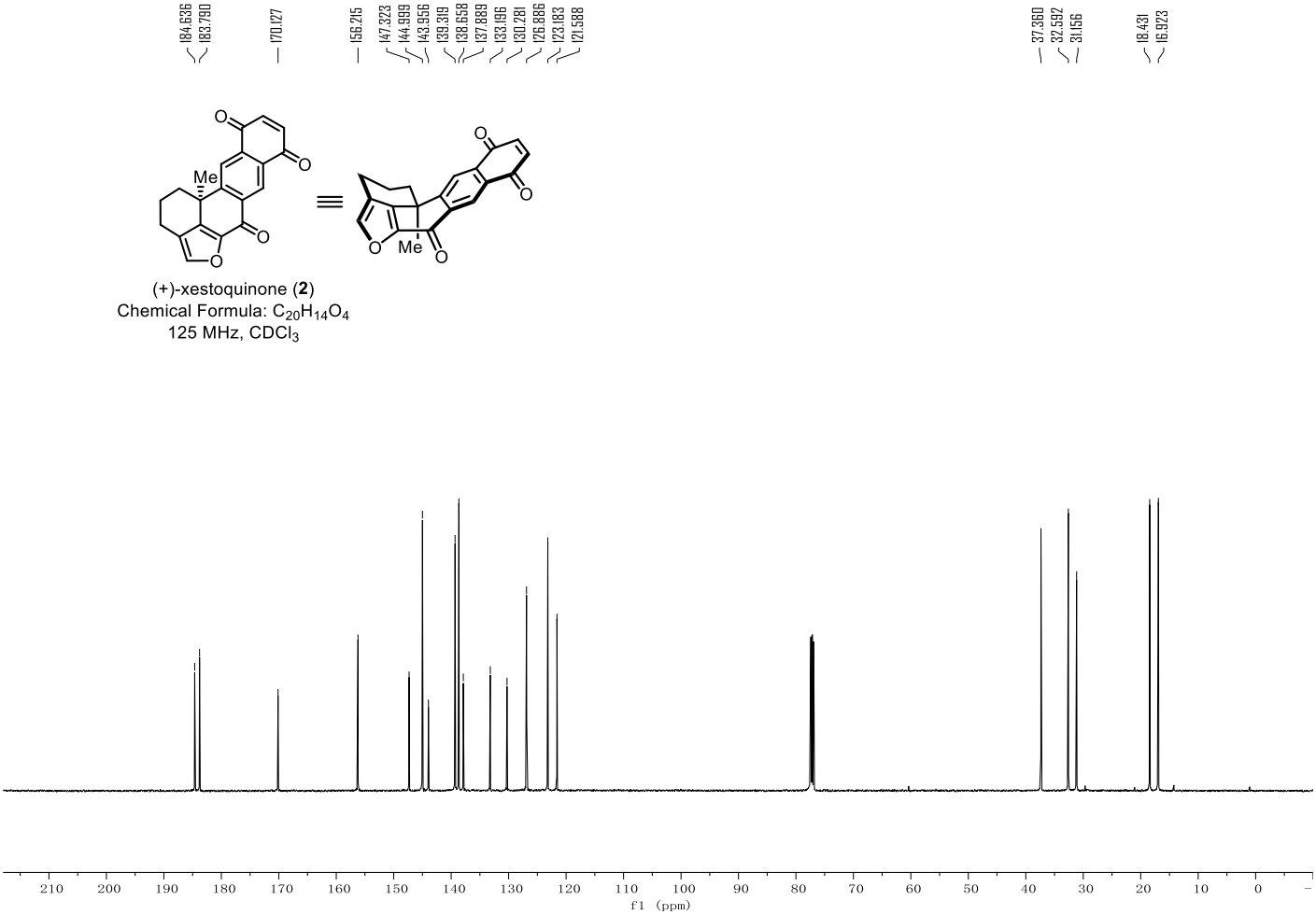


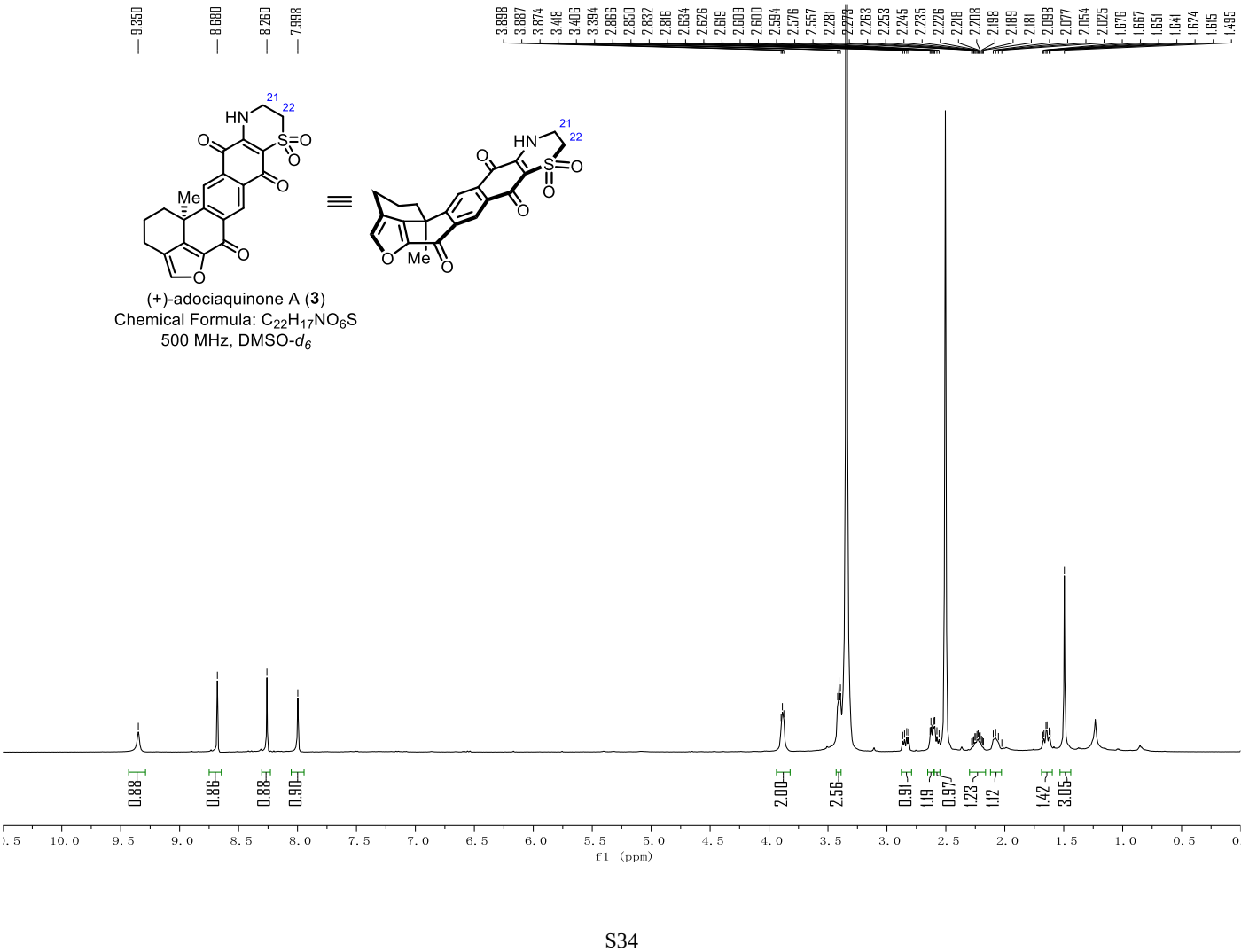
18
Chemical Formula: $C_{22}H_{20}O_4$
100 MHz, $CDCl_3$

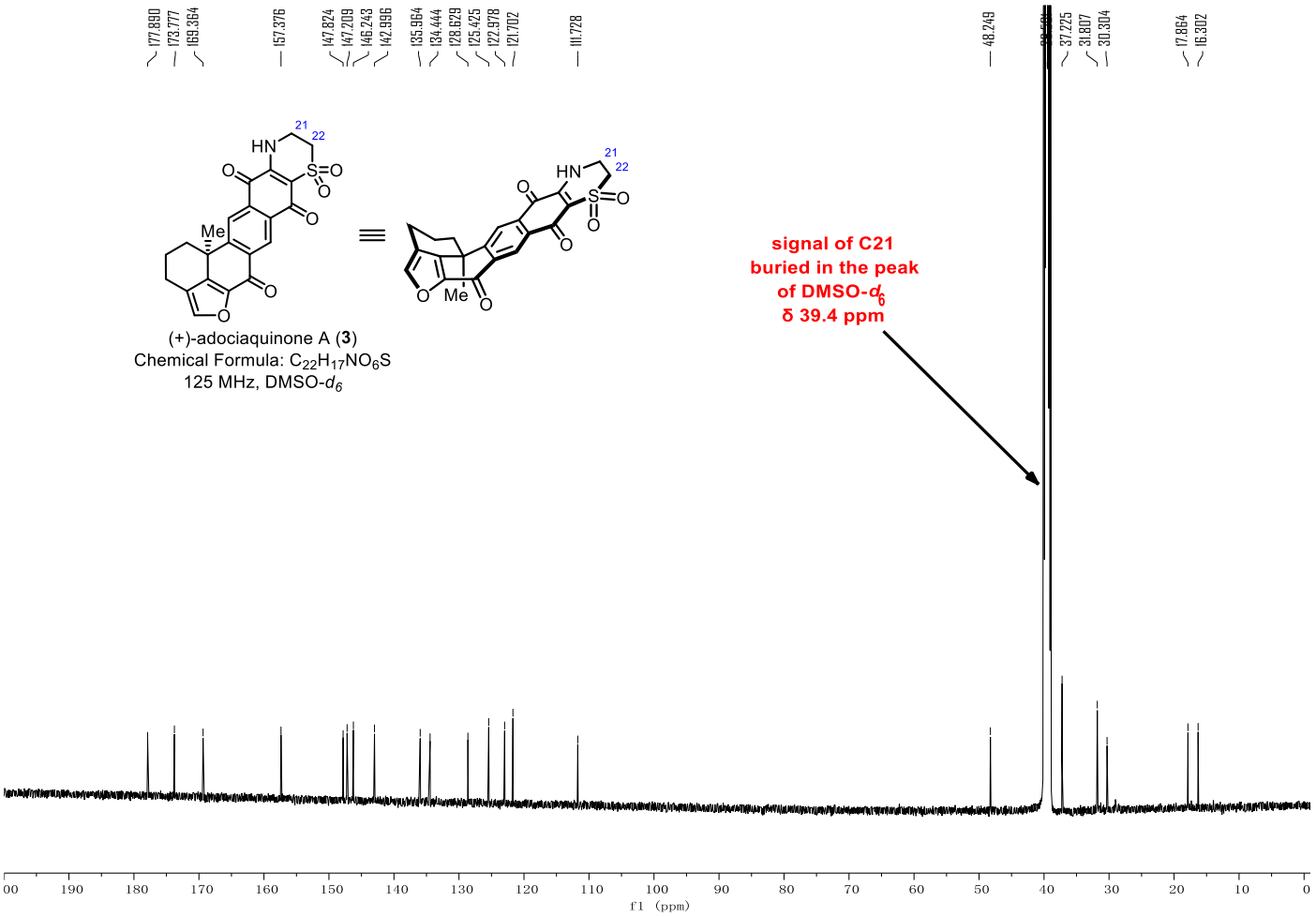


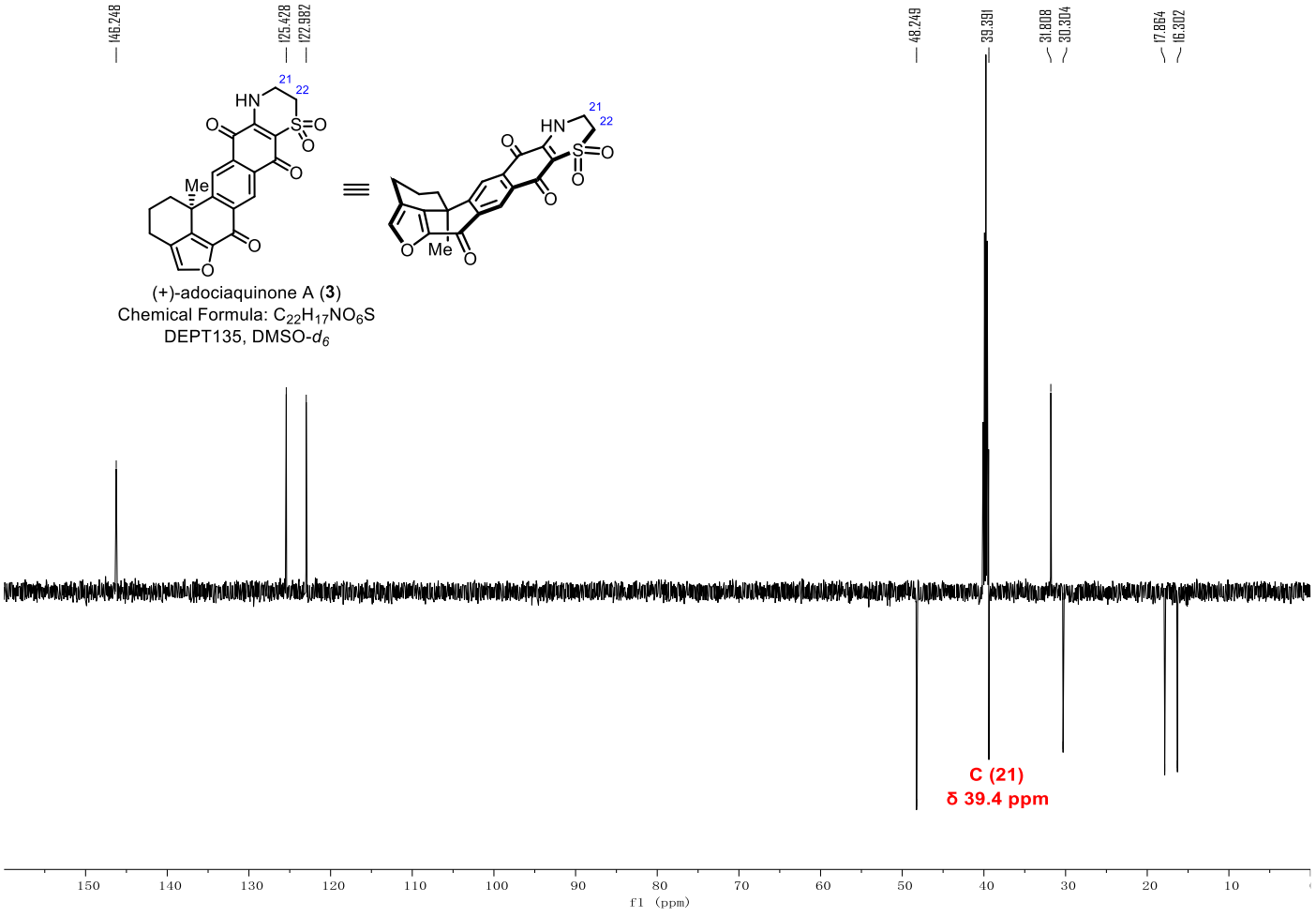


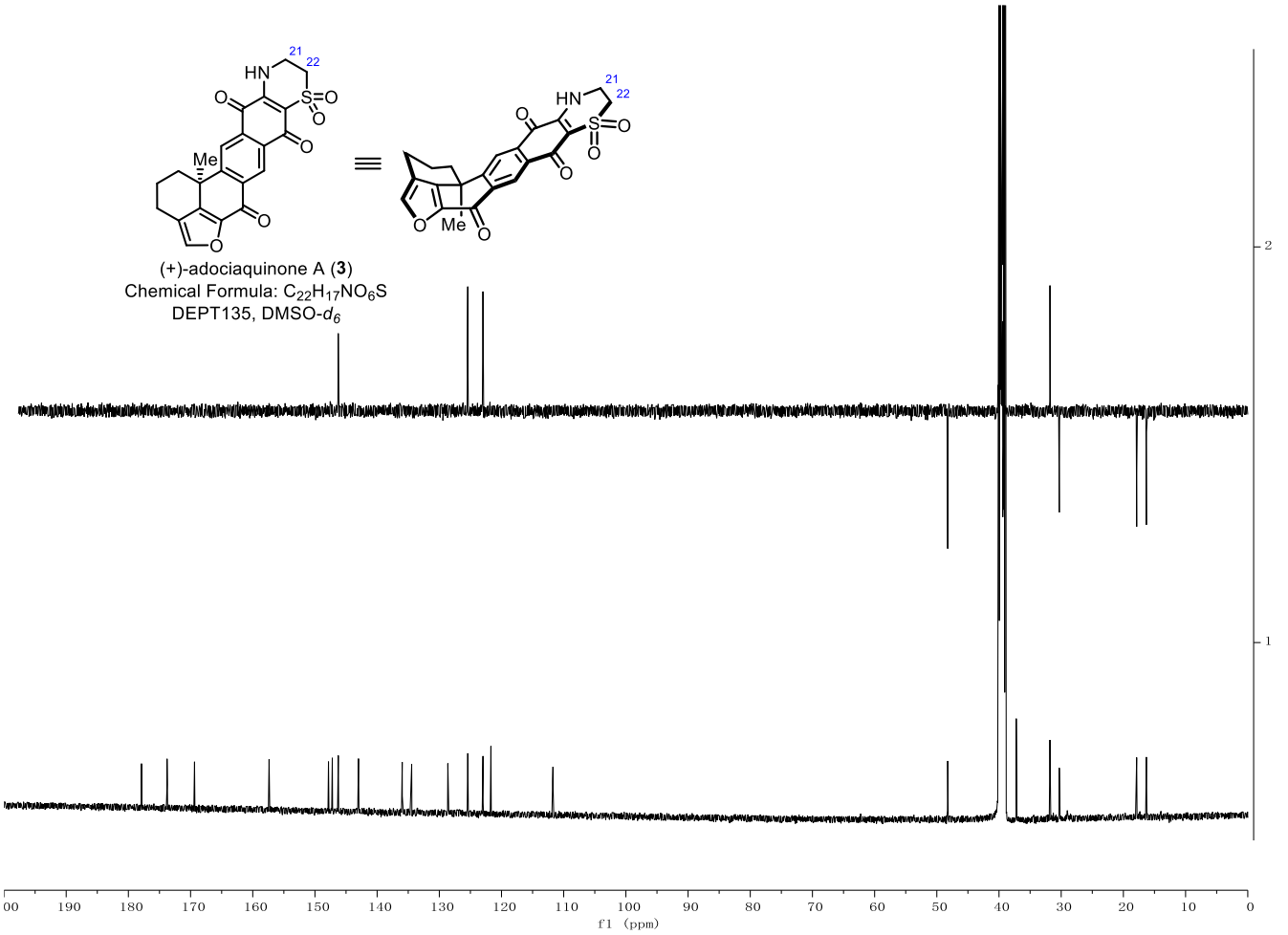
(+)-xestoquinone (**2**)
Chemical Formula: $C_{20}H_{14}O_4$
500 MHz, $CDCl_3$

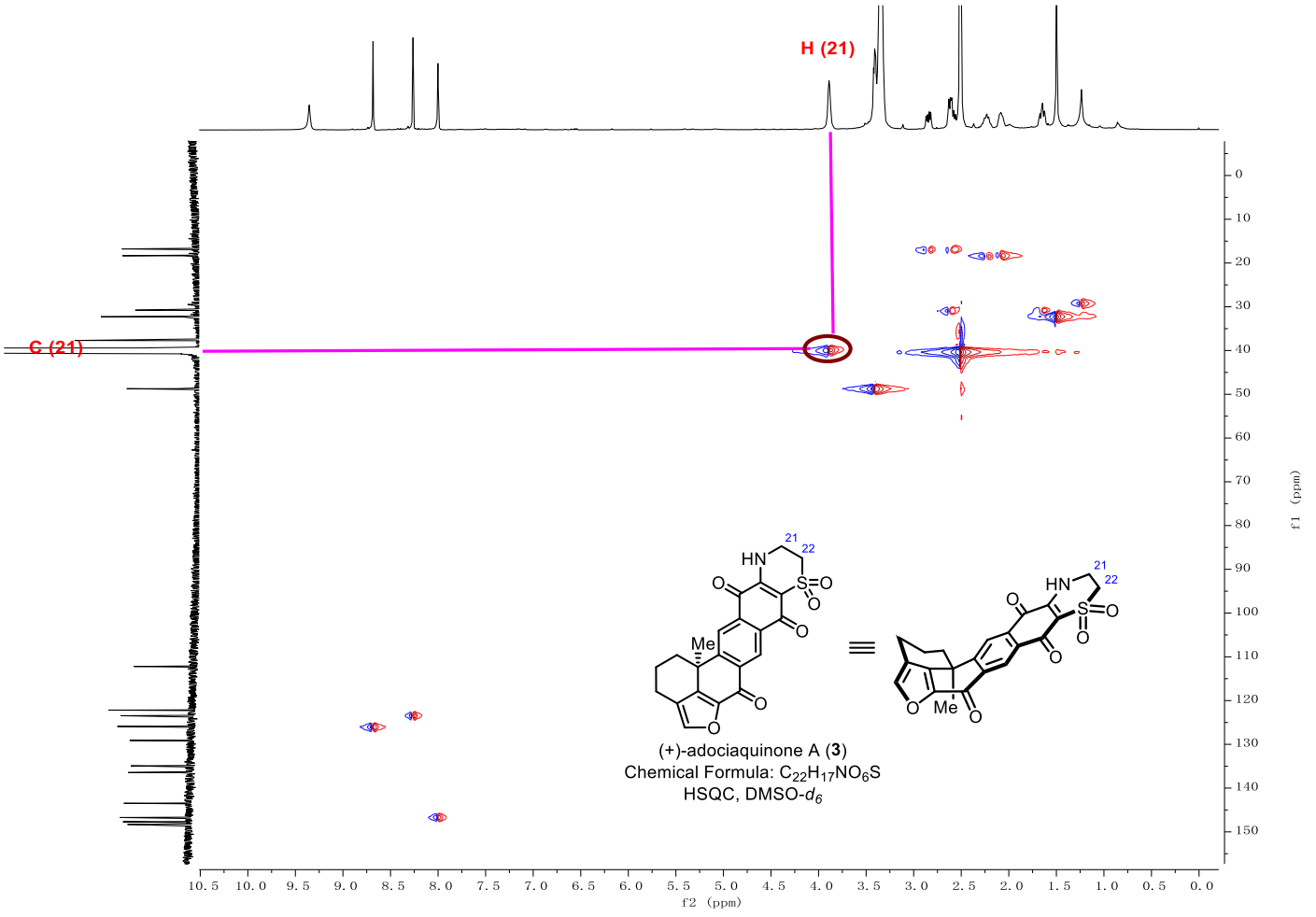

184.636
183.790
170.127
156.215
147.323
144.999
143.956
139.319
138.858
137.889
133.196
130.281
126.886
123.183
121.588
37.360
32.592
31.156
18.431
16.923
Me
Me
(+)-xestoquinone (2)
Chemical Formula: C20H14O4
125 MHz, CDCl3
f1 (ppm)

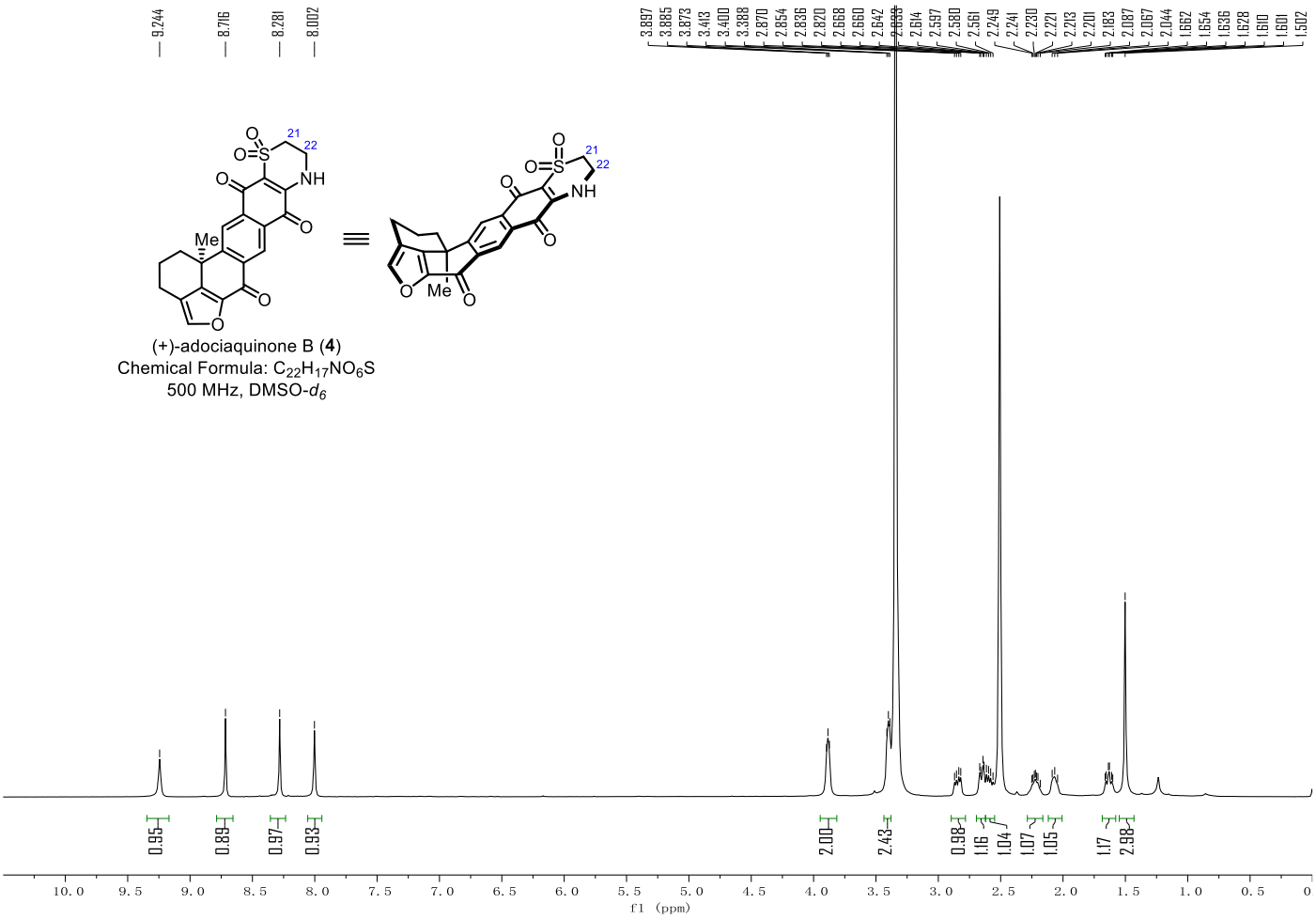

9.350
8.880
8.260
7.998
3.898
3.887
3.874
3.418
3.406
3.394
2.866
2.850
2.832
2.816
2.634
2.626
2.619
2.609
2.600
2.584
2.576
2.557
2.281
2.263
2.253
2.245
2.235
2.226
2.218
2.208
2.198
2.189
2.181
2.098
2.077
2.054
2.025
1.676
1.667
1.651
1.641
1.624
1.615
1.495
HN
21
22
Me
0.88
0.86
0.88
0.90
2.00
2.56
0.91
1.19
0.97
1.23
1.12
1.42
3.05
(+)-adociaquinone A (3)
Chemical Formula: C22H17NO6S
500 MHz, DMSO-d6
f1 (ppm)


177.890
173.777
169.364
157.376
147.824
147.209
146.243
142.996
135.964
134.444
128.629
125.425
122.978
121.702
111.728
48.249
39.581
37.225
31.807
30.304
17.864
16.302
HN
21
22
S
O
Me
(+)-adociaquinone A (3)
Chemical Formula: C22H17NO6S
125 MHz, DMSO-d6
signal of C21
buried in the peak
of DMSO-d6
δ 39.4 ppm
f1 (ppm)

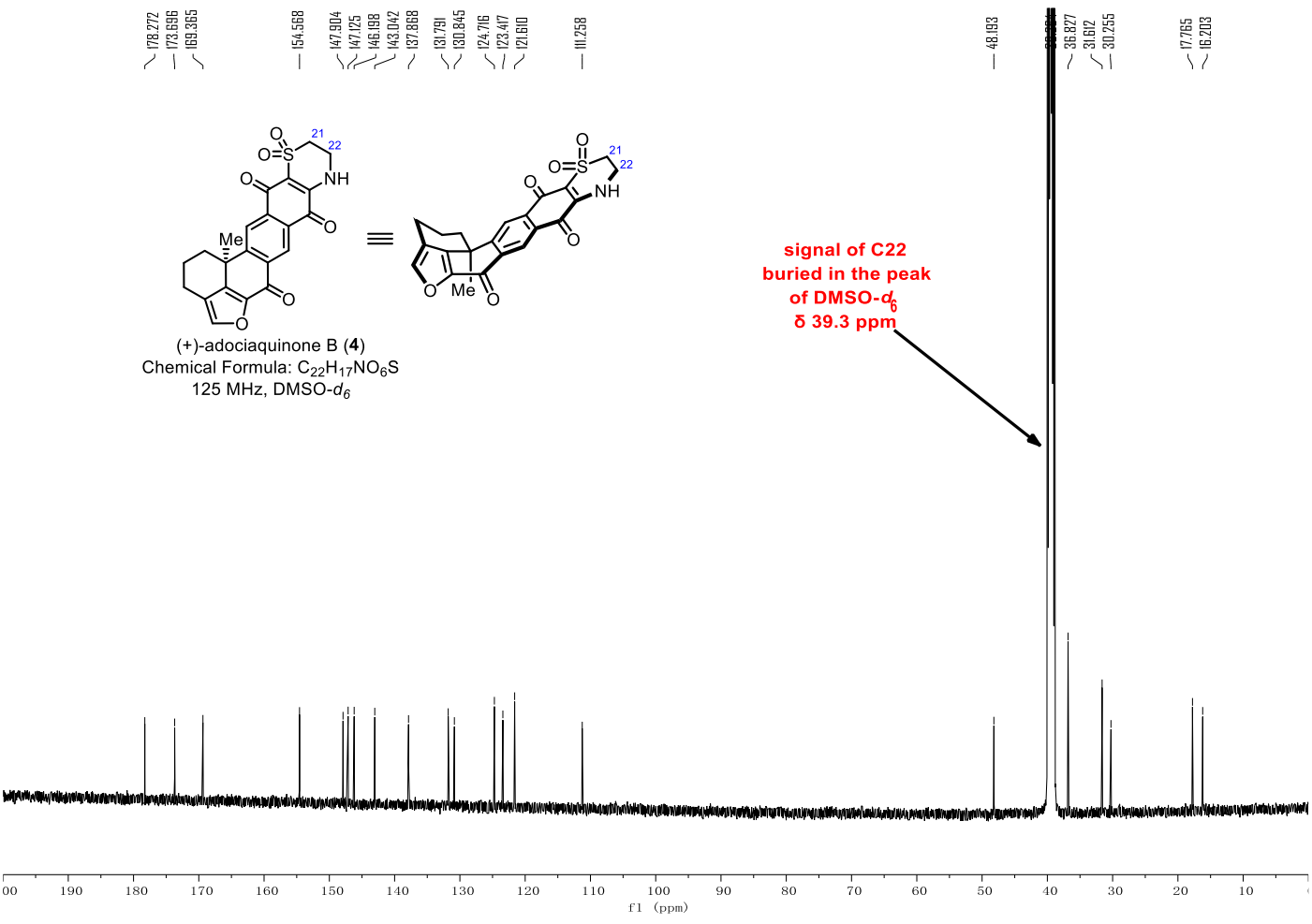

146.248
125.428
122.982
48.249
39.391
31.808
30.304
17.864
16.302
HN
21
22
S
O
Me
(+)-adociaquinone A (3)
Chemical Formula: C22H17NO6S
DEPT135, DMSO-d6
C (21)
δ 39.4 ppm
f1 (ppm)


(+)-adociaquinone A (3)
Chemical Formula: C22H17NO6S
DEPT135, DMSO-d6
f1 (ppm)

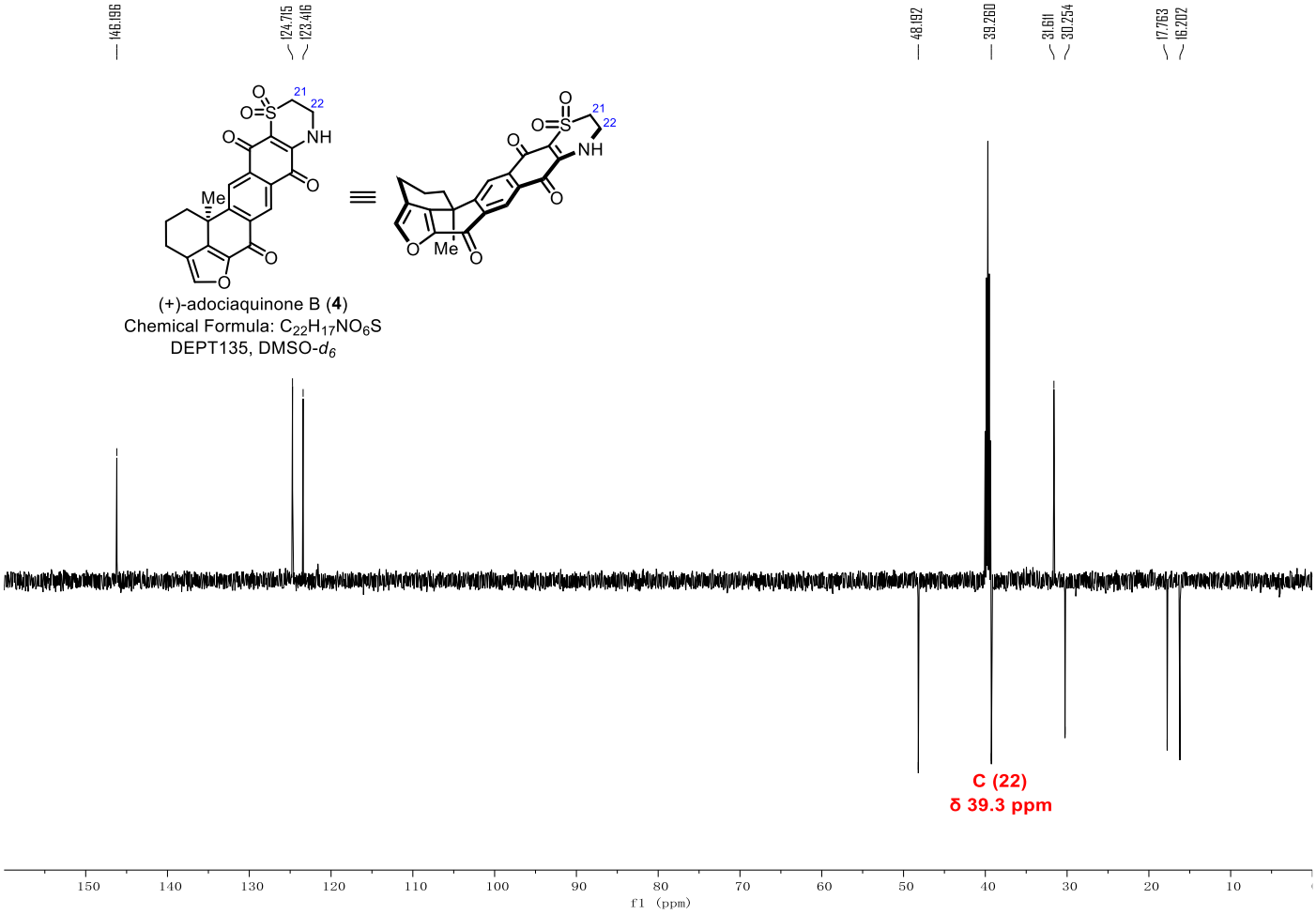

H (21)
C (21)
(+)-adociaquinone A (3)
Chemical Formula: C22H17NO6S
HSQC, DMSO-d6
f2 (ppm)
f1 (ppm)

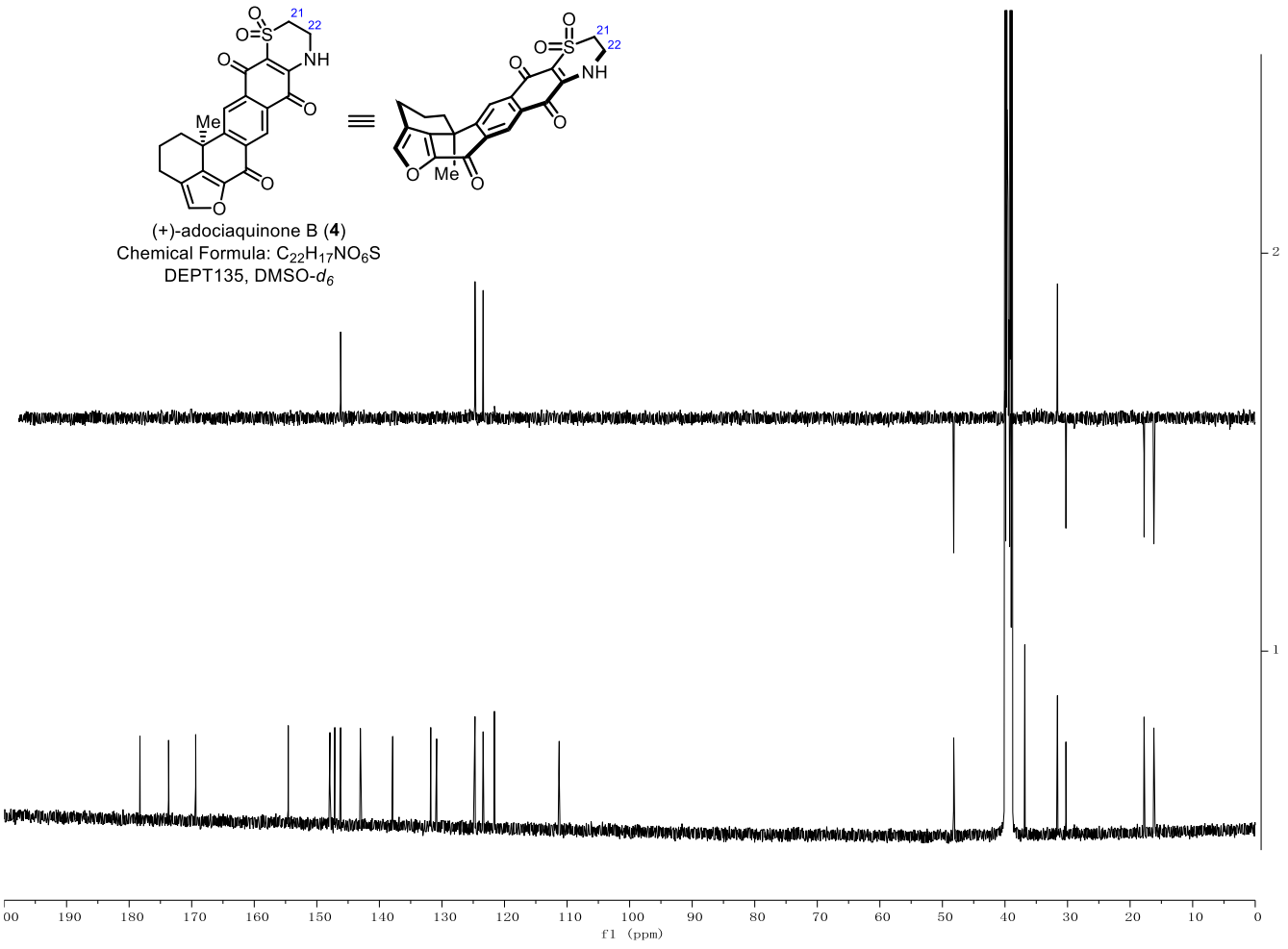


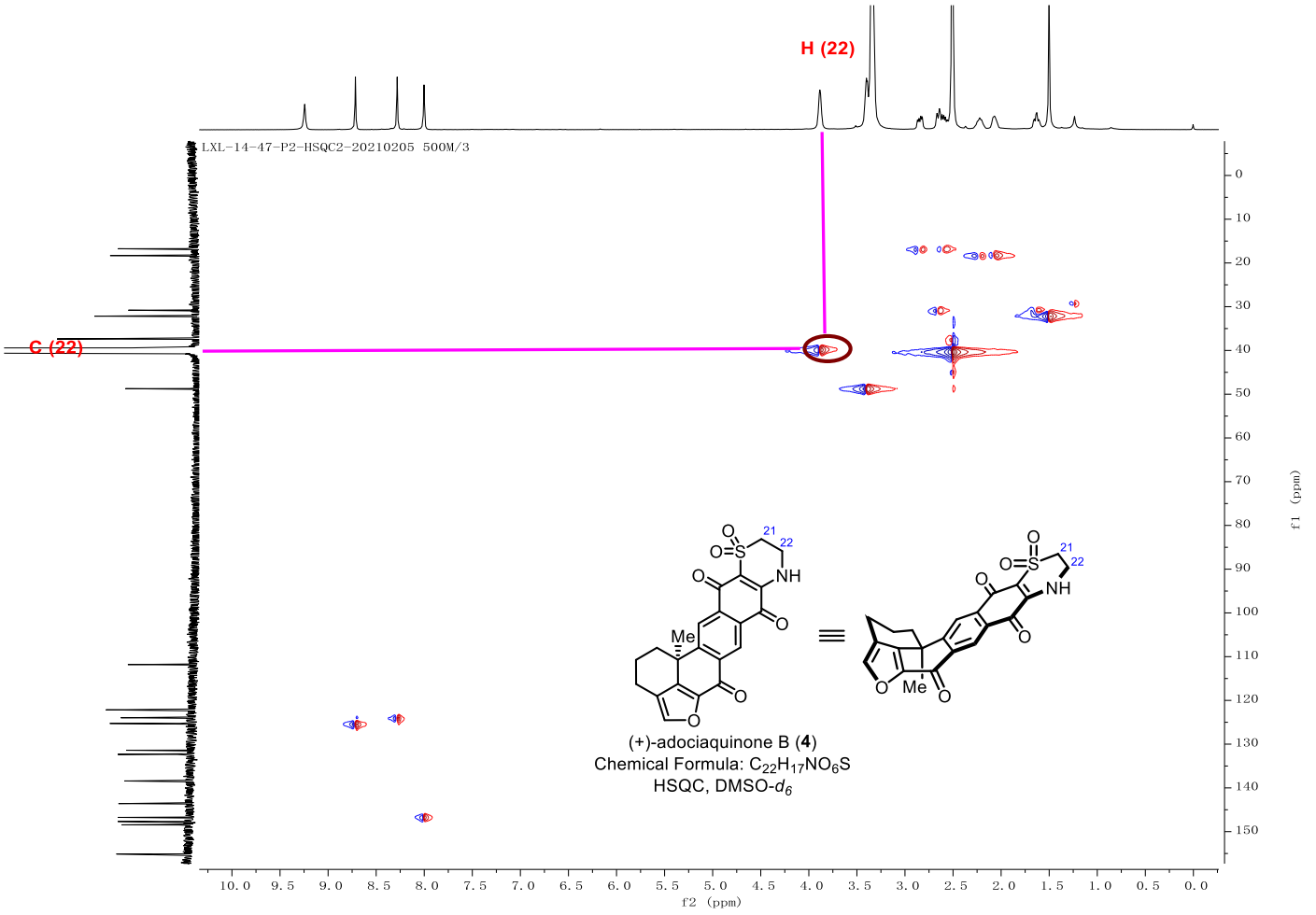
(+)-adociaquinone B (**4**)
Chemical Formula: $C_{22}H_{17}NO_6S$
500 MHz, DMSO-d_6



(+)-adociaquinone B (**4**)
Chemical Formula: $C_{22}H_{17}NO_6S$
125 MHz, DMSO-d_6

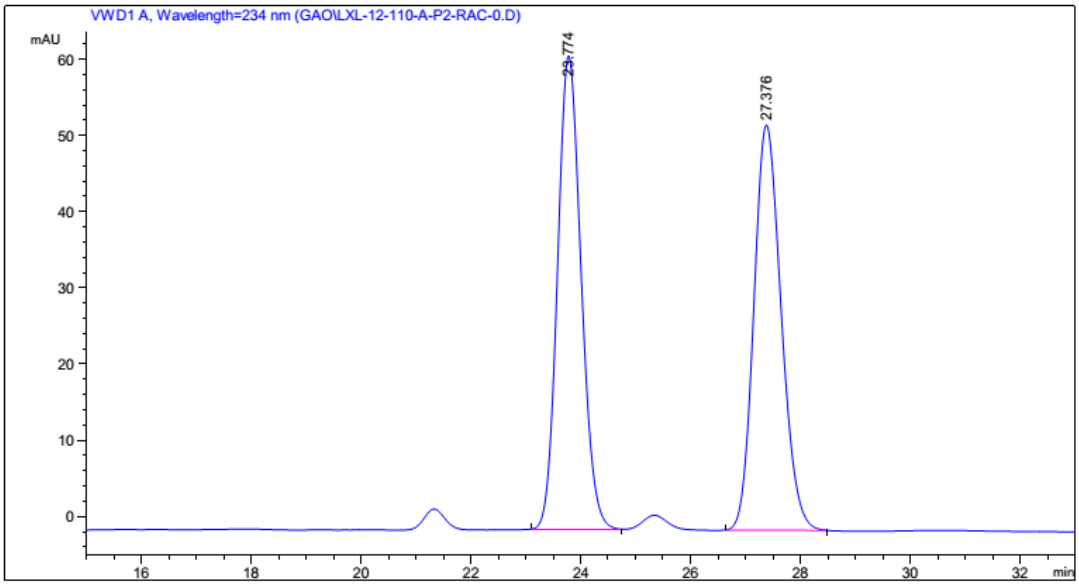

146.196
124.715
123.446
48.192
39.260
31.611
30.254
17.763
16.202
(+)-adociaquinone B (4)
Chemical Formula: C22H17NO6S
DEPT135, DMSO-d6
C (22)
δ 39.3 ppm
f1 (ppm)


(+)-adociaquinone B (4)
Chemical Formula: C22H17NO6S
DEPT135, DMSO-d6
f1 (ppm)



HPLC spectra of product 14.

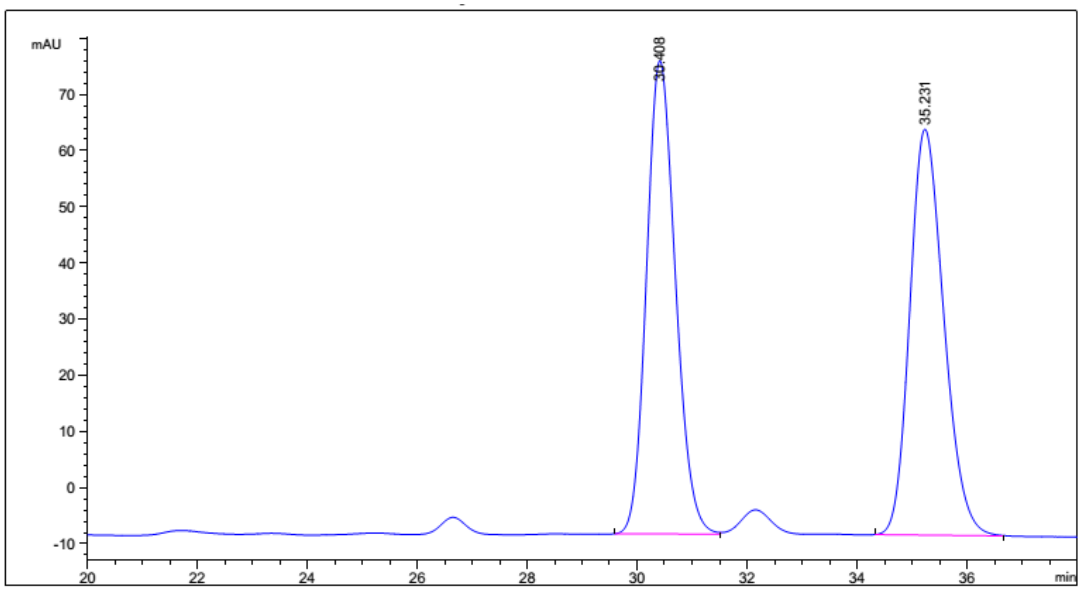
1. Table S1, entry 1, racemate of product **14a/14a'**: HPLC analysis, Chiralpak IG-H, *i*-PrOH/hexane = 20/80, 0.8 mL/min, 234 nm; t_{r1} = 23.774 min, t_{r2} = 27.376 min.



Signal 1: VWD1 A, Wavelength=234 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.774	BB	0.4633	1856.48975	62.19220	50.2387
2	27.376	BB	0.5358	1838.84778	53.19823	49.7613
Totals :				3695.33752	115.39043	

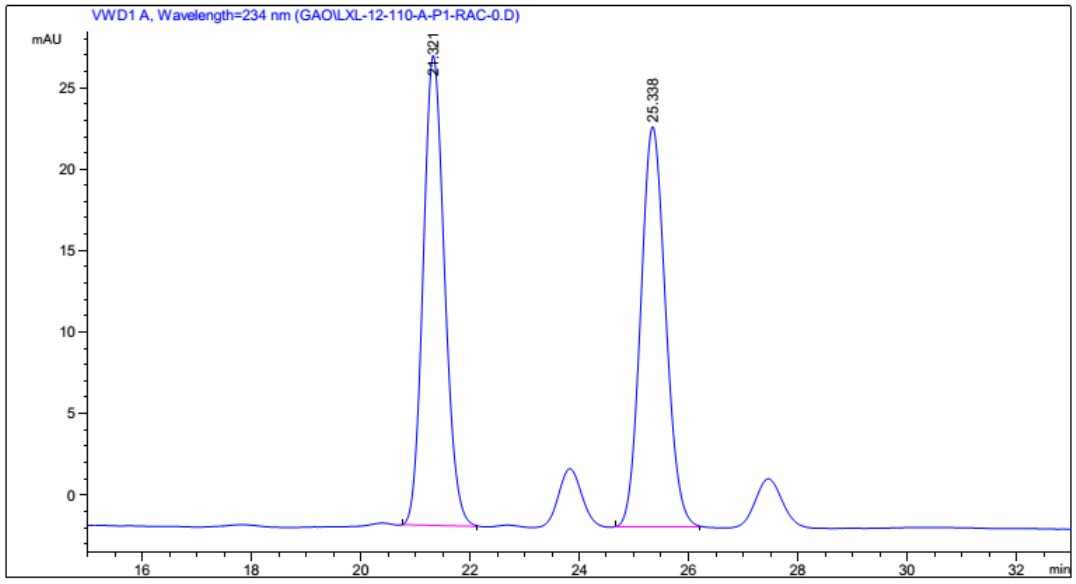
2. Table S1, entry 1, racemate of product **14a/14a'**: HPLC analysis, Chiralpak IG-H, *i*-PrOH/hexane = 15/85, 0.8 mL/min, 234 nm; t_{r1} = 30.408 min, t_{r2} = 35.231 min.



Signal 1: VWD1 A, Wavelength=234 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	30.408	BB	0.5634	3081.65405	84.29497	49.7363
2	35.231	BB	0.6613	3114.33130	72.29312	50.2637
Totals :				6195.98535	156.58809	

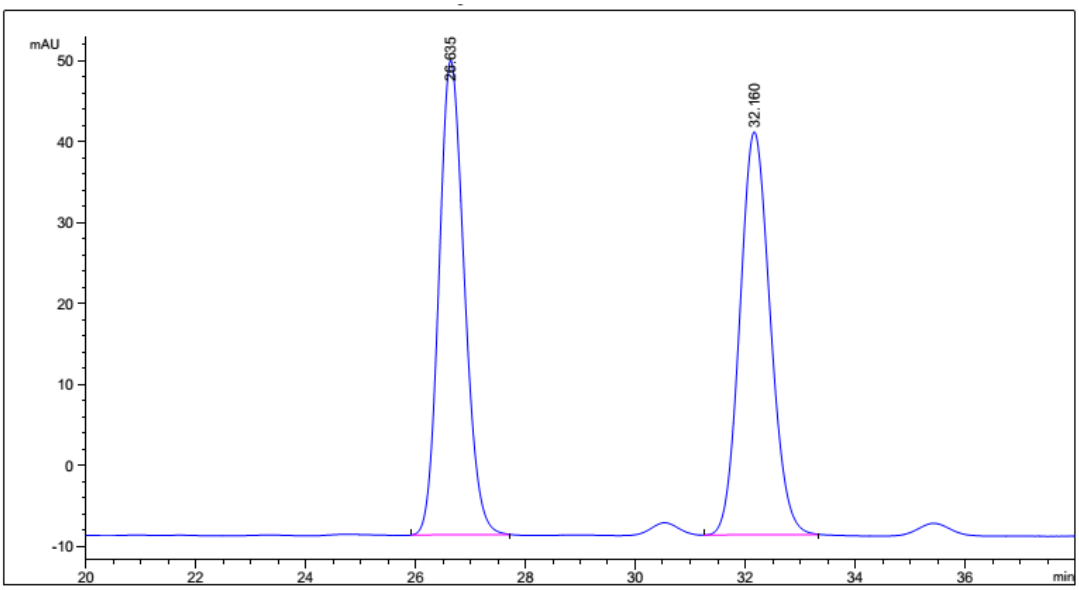
3. Table S1, entry 1, racemate of product **14b/14b'**: HPLC analysis, Chiralpak IG-H, *i*-PrOH/hexane = 20/80, 0.8 mL/min, 234 nm; t_{r1} = 21.321 min, t_{r2} = 25.338 min.



Signal 1: VWD1 A, Wavelength=234 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.321	BB	0.4199	782.72742	28.85401	50.1745
2	25.338	BB	0.4885	777.28302	24.57059	49.8255
Totals :				1560.01044	53.42460	

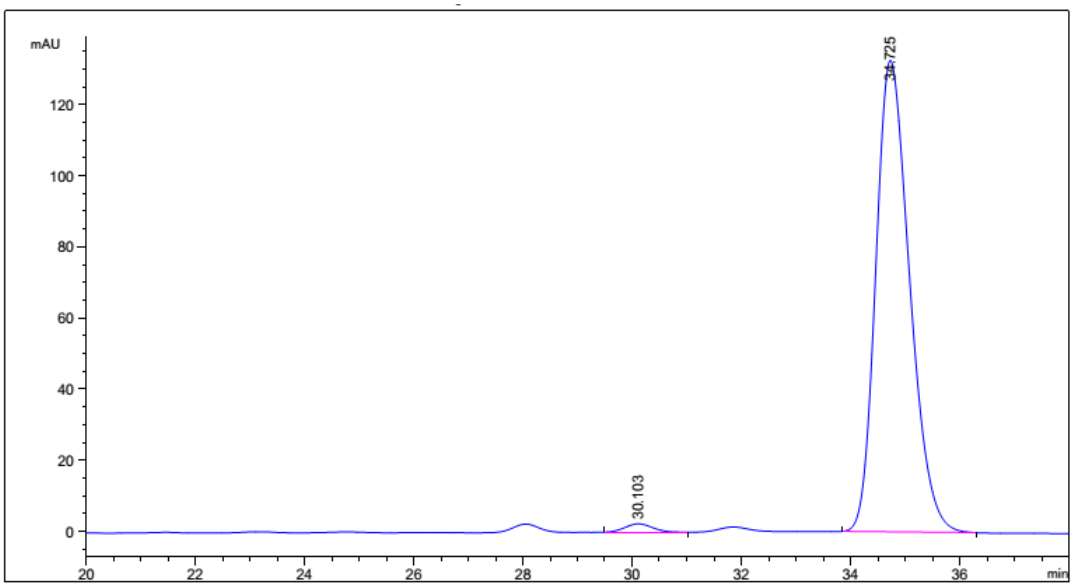
4. Table S1, entry 1, racemate of product **14b/14b'**: HPLC analysis, Chiralpak IG-H, *i*-PrOH/hexane = 15/85, 0.8 mL/min, 234 nm; t_{r1} = 26.635 min, t_{r2} = 32.160 min.



Signal 1: VWD1 A, Wavelength=234 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.635	BB	0.4890	1879.38318	58.63712	49.6089
2	32.160	VB	0.5913	1909.01538	49.80637	50.3911
Totals :				3788.39856	108.44349	

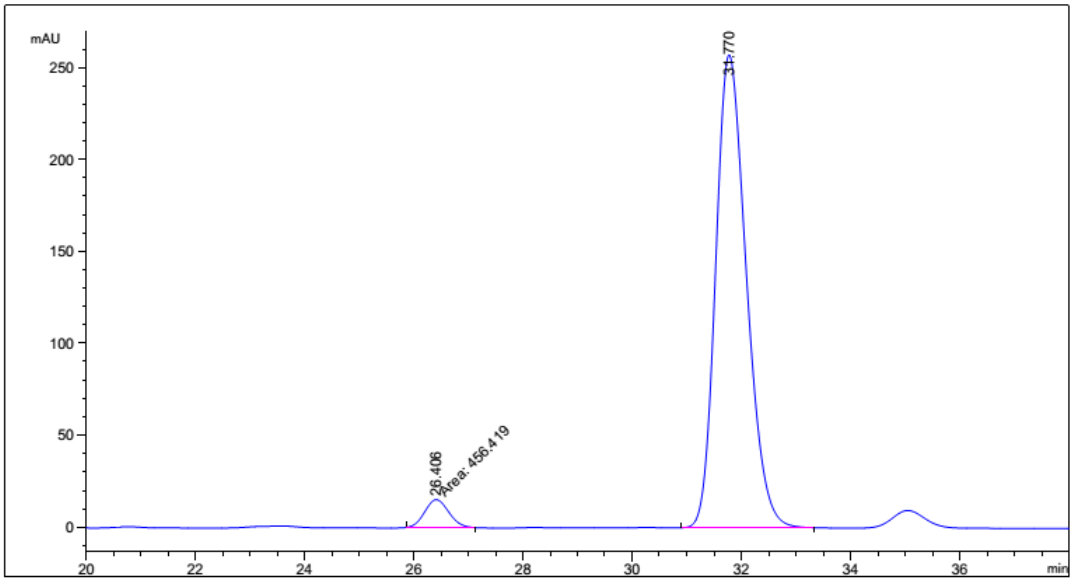
5. Table 1, entry 12, 1.31g scale, 97% e.e. for product **14a**: HPLC analysis, Chiralpak IG-H, *i*-PrOH/hexane = 15/85, 0.8 mL/min, 234 nm; t_{r1} (minor) = 30.103 min, t_{r2} (major)= 34.725 min.



Signal 1: VWD1 A, Wavelength=234 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	30.103	BB	0.4274	83.47428	2.36739	1.4422
2	34.725	BB	0.6506	5704.58008	132.56462	98.5578
Totals :				5788.05436	134.93202	

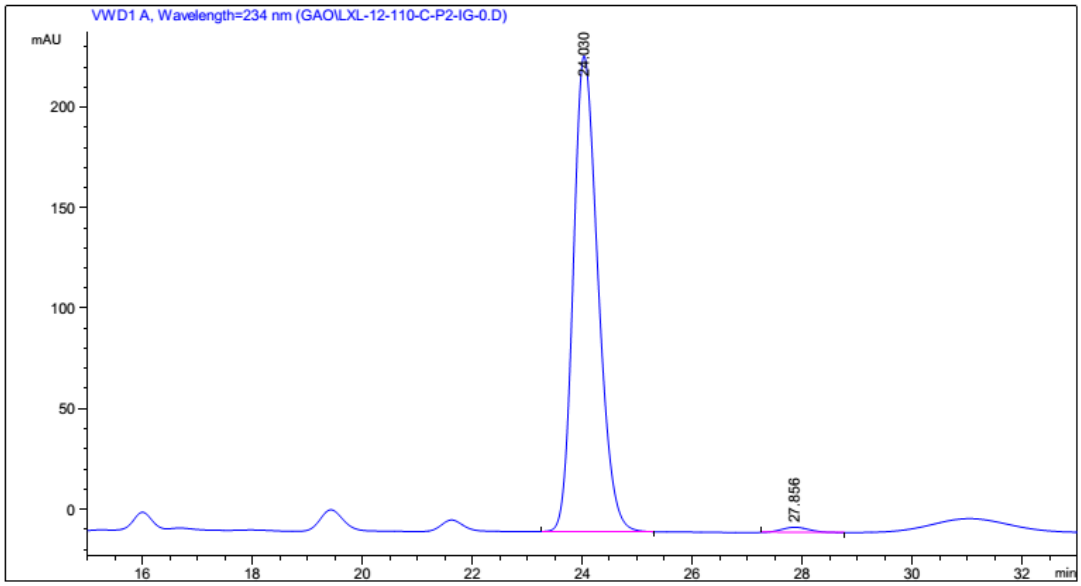
6. Table 1, entry 12, 1.31g scale, 91% e.e. for product **14b**: HPLC analysis, Chiralpak IG-H, *i*-PrOH/hexane = 15/85, 0.8 mL/min, 234 nm; t_{r1} (minor) = 26.406 min, t_{r2} (major)= 31.770 min.



Signal 1: VWD1 A, Wavelength=234 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.406	MM	0.5051	456.41907	15.06138	4.3573
2	31.770	BB	0.5988	1.00185e4	257.10541	95.6427
Totals :				1.04749e4	272.16679	

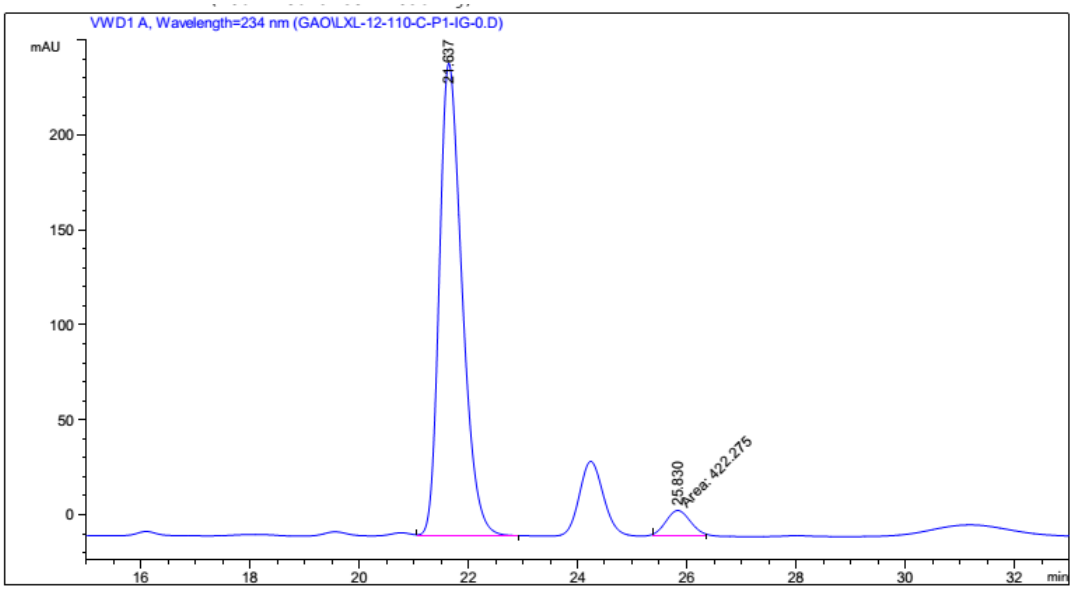
7. Table S1, entry 11, -97% e.e. for product **14a'**: HPLC analysis, Chiralpak IG-H, *i*-PrOH/hexane = 20/80, 0.8 mL/min, 234 nm; t_{r1} (major) = 24.030 min, t_{r2} (minor) = 27.856 min.



Signal 1: VWD1 A, Wavelength=234 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.030	BB	0.4795	7378.74805	236.65709	98.7760
2	27.856	BB	0.4136	91.43444	2.60232	1.2240
Totals :				7470.18249	239.25941	

8. Table S1, entry 11, -89% e.e. for product **14b'**: HPLC analysis, Chiralpak IG-H, *i*-PrOH/hexane = 20/80, 0.8 mL/min, 234 nm; t_{r1} (major) = 21.637 min, t_{r2} (minor) = 25.830 min.



Signal 1: VWD1 A, Wavelength=234 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.637	VB	0.4438	7187.94141	248.97035	94.4512
2	25.830	MM	0.5234	422.27490	13.44546	5.5488
Totals :				7610.21631	262.41581	