Supporting Information (experimental procedures and spectra data) for

Total Syntheses of (+)-Adunctins C and D: Assignment of Their Absolute Configurations

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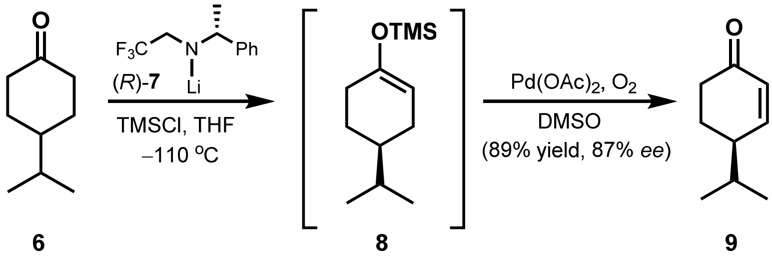
General procedure

For product purification by flash column chromatography, SiliaFlash P60 (particle size: 40~63 μm, pore size 60A) and petroleum ether (bp. 60~90 °C) were used. All solvents were purified and dried by standard techniques and distilled prior to use. All of experiments were conducted under an argon or nitrogen atmosphere in oven-dried or flame-dried glassware with magnetic stirring, unless otherwise specified. Organic extracts were dried over Na_2SO_4, unless otherwise noted. IR spectra were recorded on a *Nicolet* FT-170SX spectrometer. ^1H and ^{13}C NMR spectra were taken on a *Bruker* AM-400 spectrometer with TMS as an internal standard and $CDCl_3$ as solvent unless otherwise noted. HRMS were determined on a *Bruker Daltonics* APEXII 47e FT-ICR spectrometer with ESI positive ion mode. The X-ray diffraction studies were carried out on a Bruker SMART Apex CCD area detector diffractometer equipped with graphite-monochromated Cu-Kα radiation source. Melting points were measured on *Kofler* hot stage and are uncorrected.

Preparation of cryptone (9)



Cryptone (**9**) was prepared according to the protocol described by Clark and co-workers,[1a] with modifications. In a 100 mL round-bottom flask, [(*R*)-1-phenylethyl]-2,2,2- trifluoroethylamine[1b] (2.50 g, 12.3 mmol) was dissolved in anhydrous THF (15 mL), and the resulting solution was cooled to −78 °C followed by the addition of *n*-BuLi (2.5 M, 5.9 mL, 14.8 mmol, 1.2 equiv) dropwise. After 20 minutes at −78 °C, freshly distilled TMSCl (5.5 mL, 43 mmol, 3.5 equiv) was added and the resulting mixture was cooled to −110 °C. A cold (−78 °C) solution of 4-isopropylcyclohexanone **6** (1.68 g, 12.3 mmol) in THF (10 mL) was added dropwise over a period of 10 minutes, and the mixture was stirred at −110 °C for 50 minutes. The reaction mixture was then quenched by the addition of Et_3N (8 mL) and saturated aqueous $NaHCO_3$ (8 mL), and the mixture was allowed to warm to room temperature. The resultant mixture was extracted with hexane (3 × 70 mL), the combined organic layers were washed with saturated aqueous citric acid (2 × 20 mL), water (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude silyl enol ether **8** could be used directly for the next reaction without further purification.

In a 100 mL round-bottom flask, the above silyl enol ether **8** was dissolved in anhydrous DMSO (50 mL). The reaction mixture was purged with oxygen, followed by the addition of $Pd(OAc)_2$ (99%, 279 mg, 1.23 mmol, 0.1 equiv) in one portion. The resulting black solution was stirred at ambient temperature under an atmosphere of oxygen for 15 h. The reaction mixture was then treated with saturated aqueous NH_4Cl (10 mL) at 0 °C and extracted with Et_2O (2 × 80 mL). The combined organic layers

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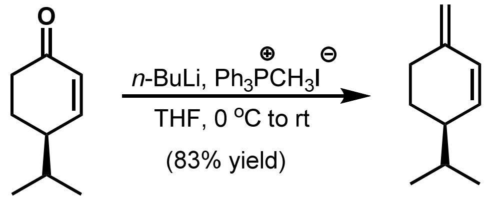
[1] (a) Clark, J. S.; Vignard, D.; Parkin, A. *Org. Lett.* **2011**, *13*, 3980. (b) Pache, S.; Botuha, C.; Franz, R.; Kündig, E. P. *Helv. Chim. Acta* **2000**, *83*, 2436.

were washed with water (2 × 20 mL) and brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether/EtOAc = 20 : 1 → petroleum ether/EtOAc = 10 : 1) on silica gel to afford ketone **9** (1.51 g, 89% yield) as a colorless oil. $[\alpha]_{D}^{19}$ = –64.00 (c = 1.00, $CHCl_3$) [ref[1a]: $[\alpha]_{D}^{30}$ = –97.9 (c = 1.00, $CHCl_3$)]; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.89 (dt, J = 10.4, 2.0 Hz, 1H), 6.01 (dd, J = 10.4, 2.8 Hz, 1H), 2.50 (dt, J = 16.4, 4.4 Hz, 1H), 2.35 (dd, J = 13.6, 5.2 Hz, 1H), 2.30–2.26 (m, 1H), 2.03–1.96 (m, 1H), 1.86–1.72 (m, 2H), 0.97 (t, J = 6.0 Hz, 3H), 0.95 (t, J = 6.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.2, 154.4, 129.7, 42.5, 37.4, 31.5, 25.2, 19.6, 19.4 ppm; HPLC (Chiralpak AD-H column n-hexane/i-PrOH = 99/1, flow rate = 1.0 mL/min, retention time: t_{major} = 8.429 min, t_{minor} = 7.324 min, 87% *ee*).

Preparation of (–) and (±)-β-phellandrene 5



9 (–)-**5**

To a 100 mL round-bottom flask containing methyltriphenylphosphonium iodide (98%, 2.28 g, 5.5 mmol, 1.1 equiv) was added THF (30 mL), and the mixture was cooled to 0 °C. n-BuLi (2.5 M, 2.0 ml, 5 mmol, 1.0 equiv) was then added, followed by the addition of the solution of the above ketone **9** (690 mg, 5 mmol) in dry THF (10 mL) after 30 minutes. The reaction mixture was stirred for 1 h at room temperature, and treated with MeOH (3 mL) and H_2O (3 mL). The resultant mixture was extracted with CH_2Cl_2 (2 × 60 mL), and the combined organic layers were washed with water (15 mL) and brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether/EtOAc = 50 : 1 → petroleum ether/EtOAc = 20 : 1) on silica gel to afford (–)-β-phellandrene **5**[2] (564 mg, 83% yield) as a colorless oil. R_f

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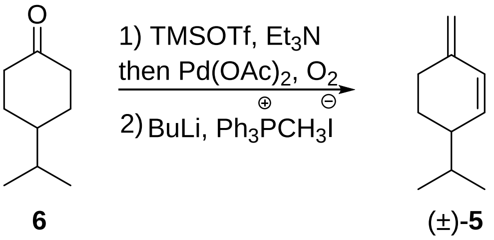
[2] Kang, J. S.; Kim, E.; Lee, S. H.; Park, I. K. *Pestic. Biochem. Phys.* **2013**, *105*, 50.

= 0.85 (petroleum ether/EtOAc = 10 : 1); $[\alpha]_D^{22}$ = −50.54 (*c* = 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 6.16 (dd, *J* = 10.0, 2.8 Hz, 1H), 5.76 (d, *J* = 8.8 Hz, 1H), 4.76 (d, *J* = 7.6 Hz, 2H), 2.45 (dt, *J* = 14.8, 4.4 Hz, 1H), 2.34–2.25 (m, 1H), 2.09–2.05 (m, 1H), 1.81−1.74 (m, 1H), 1.71−1.63 (m, 1H), 1.47−1.37 (m, 1H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.7, 134.2, 129.5, 109.9, 42.1, 31.9, 30.2, 25.7, 19.7, 19.5 ppm.



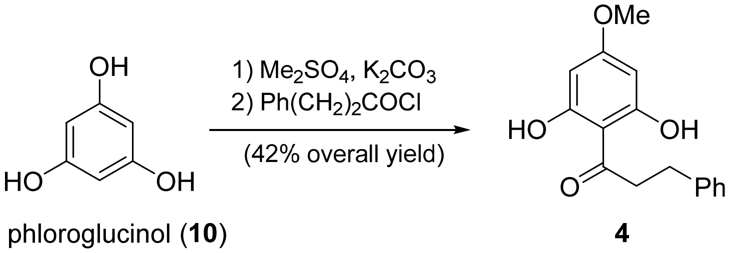
In a 200 mL round-bottom flask, commercially available 4-isopropylcyclohexanone **6** (98%, 2.80 g, 20 mmol) was dissolved in anhydrous CH_2Cl_2 (50 mL). The resulting solution was cooled to −78 °C, followed by the addition of Et_3N (13.9 mL, 100 mmol, 5.0 equiv) and TMSOTf (99%, 10.9 mL, 60 mmol, 3.0 equiv) dropwise. The resultant mixture was then quenched by the addition saturated aqueous $NaHCO_3$ (10 mL), and extracted with CH_2Cl_2 (2 × 60 mL). The combined organic layers were washed with water (2 × 15 mL) and brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting enoxysilane could be used directly for the next reaction without further purification.

In a 200 mL round-bottom flask, the above enoxysilane was dissolved in anhydrous DMSO (50 mL). The reaction mixture was purged with oxygen, followed by the addition of $Pd(OAc)_2$ (99%, 454 mg, 2.0 mmol, 0.1 equiv) in one portion. The resulting black solution was stirred at ambient temperature under an atmosphere of oxygen for 36 h. The reaction mixture was then treated with saturated aqueous NH_4Cl (10 mL) at 0 °C, and extracted with Et_2O (2 × 70 mL). The combined organic layers were washed with water (2 × 15 mL) and brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting ketone (±)-**9** could be used directly for the next reaction without further purification.

To a 100 mL round-bottom flask containing methyltriphenylphosphonium iodide (98%, 9.12 g, 22 mmol, 1.1 equiv) was added THF (60 mL). The mixture was cooled to 0 °C, followed by the addition of *n*-BuLi (1.6 M, 12.5 ml, 20 mmol, 1.0 equiv) dropwise. After 40 minutes, a solution of the above ketone (±)-**9** in dry THF (20 mL) was added dropwise, and the reaction mixture was stirred for 1 h at room temperature. The reaction was treated with MeOH (5 mL) and H_2O (5 mL), and the resultant mixture was extracted with CH_2Cl_2 (2 × 80 mL). The combined organic layers were washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether/EtOAc = 50 : 1 → petroleum ether/EtOAc = 20 : 1) on silica gel to afford (±)-β-phellandrene **5** (2.31 g, 85% overall yield) as a colorless oil.

With the (±)-β-phellandrene **5** in hand, we completed the syntheses of (±)-aduncetin C and (±)-aduncetin D only in 3 steps according to a route similar to asymmetric version described below.

Preparation of dihydrochalcone 4



Dihydrochalcone **4** was prepared according to a general protocol described by Porco, Dethe and co-workers.[3] In a 300 mL round-bottom flask, phloroglucinol (**10**) (99%, 12.7 g, 100 mmol) and oven-dried K_2CO_3 (99%, 13.8 g, 100 mmol, 1.0 equiv) was dissolved in anhydrous acetone (100 mL). Me_2SO_4 (99%, 3.2 mL, 33 mmol, 0.33 equiv) was added dropwise over 10 min, and the reaction mixture was then stirred 10 h at 55 °C. Acetone was removed in vacuo and the resultant mixture was extracted

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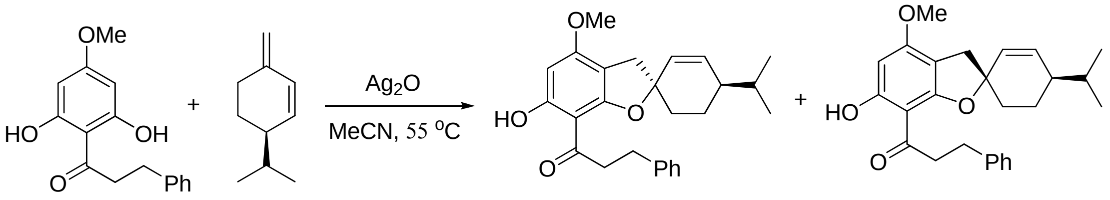
[3] (a) Grenning, A. J.; Boyce, J. H.; Porco, J. A, Jr. *J. Am. Chem. Soc.* **2014**, *136*, 11799. (b) Dethe, D. H.; Dherange, B. D. *J. Org. Chem.* **2018**, *83*, 3392.

with EtOAc (2 × 100 mL). The combined organic layers were washed with 1 M HCl (2 × 20 mL), water (20 mL) and brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether/EtOAc = 5 : 1 → petroleum ether/EtOAc = 2 : 1) on silica gel to afford mono-*O*-methylphloroglucinol in 54% yield (based on dimethylsulfate as limiting reagent).

In a 100 mL round-bottom flask, 3-phenylpropionic acid (98%, 6.1 g, 40 mmol, 2.0 equiv) was dissolved in anhydrous CH_2Cl_2 (40 mL), and the resulting solution was cooled to 0 ^{o}C. Oxalyl chloride (98%, 4.2 ml, 50 mmol, 2.5 equiv) was then added dropwise in 15 minutes, followed by the addition of anhydrous DMF (3 drops). The stirring was continued for 3 h at room temperature. The reaction solvent and excess oxalyl chloride were then distilled off by evacuation, and the generated acyl chloride was ready to use.

Meanwhile, in a 200 mL round-bottom flask, mono-*O*-methylphloroglucinol (2.8 g, 20 mmol) and $AlCl_3$ (99%, 5.4 g, 40 mmol, 2.0 equiv) was added. Anhydrous CH_2Cl_2 (40 mL) was added and cooled to 0 ^{o}C, followed by slow addition of a solution of the above acyl chloride in CH_2Cl_2 (10 mL). The resulting mixture was gradually warmed to room temperature, and stirred further for 10 h. Crushed ice was then added until the reaction was quenched (caution: addition of ice was exothermic). The resultant mixture was extracted with EtOAc (2 × 60 mL), and the combined organic layers were washed with 1 M HCl (2 × 15 mL) water (10 mL) and brine (10 mL) respectively, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether/EtOAc = 8 : 1 → petroleum ether/EtOAc = 5 : 1) on silica gel to afford **4** (4.2 g, 42% overall yield) as a white solid. $R_f = 0.3$ (petroleum ether/EtOAc = 2 : 1); ^{1}H NMR (400 MHz, *d*$_6$-DMSO): $\delta = 12.32$ (s, 2H), 7.30–7.15 (m, 5H), 5.96 (s, 2H), 3.74 (s, 3H), 3.33 (t, $J = 8.0$ Hz, 2H), 2.90 (t, $J = 7.6$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, *d*$_6$-DMSO): $\delta = 205.0$, 166.0, 164.5 (2C), 142.1, 128.83 (2C), 128.80 (2C), 126.3, 105.0, 93.7 (2C), 55.8, 45.7, 30.6 ppm.

Synthesis of (+)-adunctin C (*ent*-1) and (+)-adunctin D (2)



4 (–)-**5** (+)-adunctin C (*ent*-**1**) (47%) (+)-adunctin D (**2**) (22%)

In a 50 mL round-bottom flask, dihydrochalcone **4** (272 mg, 1 mmol) and (−)-β-phellandrene **5** (204 mg, 1.5 mmol, 1.5 equiv) was dissolved in anhydrous MeCN (20 mL). Upon the addition of Ag_2O (99%, 351 mg, 1.5 mmol, 1.5 equiv), the reaction mixture was stirred at 55 °C for 2 h, then filtered and washed with EtOAc (30 mL). The resulting product was purified by short flash column chromatography (petroleum ether/EtOAc = 15 : 1 → petroleum ether/EtOAc = 10 : 1) on silica gel to afford a mixture of (+)-adunctin C and (+)-adunctin D.

This product (320 mg) was dissolved in hexane (15 mL) at 40 °C, and then cooled to room temperature. After 8 days, yellow prisms crystals were obtained by slow evaporation of solvents at room temperature. These crystals were filtered to afford (+)-adunctin C (*ent*-**1**, 191 mg, 47% yield), and the filtrate was then concentrated under reduced pressure to afford (+)-adunctin D (**2**, 89 mg, 22% yield) as a white solid.

Data for (+)-adunctin C (*ent*-**1**): $R_f = 0.64$ (petroleum ether/EtOAc = 2 : 1); $[\alpha]_D^{21} = +122.1$ ($c = 0.47$, MeOH); [ref[4]: $[\alpha]_D^{20} = -71.4$ ($c = 0.73$, MeOH)]; Mp. 75–76 °C; IR (film): ν_{max} = 2953, 1603, 1434, 1375, 1302, 1233, 1146, 1089, 1017, 958, 807, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.36 (s, 1H), 7.27–7.15 (m, 5H), 5.99 (s, 1H), 5.85 (d, J = 10.0 Hz, 1H), 5.78 (d, J = 10.0 Hz, 1H), 3.82 (s, 3H), 3.40–3.25 (m, 2H), 3.04–2.93 (m, 2H), 2.94 (d, J = 15.2 Hz, 1H), 2.86 (d, J = 15.2 Hz, 1H), 2.22–2.15 (m, 1H), 1.99–1.93 (m, 1H), 1.67–1.49 (m, 4H), 0.85 (d, J = 6.8 Hz, 3H), 0.79 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.4, 165.9, 161.8, 161.1, 141.4, 136.1, 129.2, 128.3 (4C), 125.9, 104.5, 101.9, 91.8, 88.1, 55.5, 44.1, 41.7, 38.5, 35.5, 31.6, 30.4, 21.9, 19.5, 19.0 ppm; HRMS (ESI): calcd. for $C_{26}H_{31}O_4^+$ $[M+H]^+$: 407.2217, found: 407.2218.

Data for (+)-adunctin D (**2**): $R_f = 0.64$ (petroleum ether/EtOAc = 2 : 1); $[\alpha]_D^{21}$ = +32.45 (*c* = 0.84, MeOH) [ref[4]: $[\alpha]_D^{20}$ = +31.0 (*c* = 0.52, MeOH)]; Mp. 51–53 °C; IR (film): ν_{max} = 2952, 1606, 1433, 1378, 1215, 1147, 1024, 962, 808 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.40 (s, 1H), 7.30–7.17 (m, 5H), 5.99 (s, 1H), 5.85 (d, *J* = 10.0 Hz, 1H), 5.77 (d, *J* = 10.0 Hz, 1H), 3.82 (s, 3H), 3.34–3.21 (m, 2H), 2.99 (t, *J* = 8.0 Hz, 2H), 2.93 (s, 2H), 2.11–2.01 (m, 2H), 1.96 (td, *J* = 12.4, 3.2 Hz, 1H), 1.86−1.81 (m, 1H), 1.70−1.62 (m, 1H), 1.51−1.40 (m, 1H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.6, 166.1, 161.8, 161.3, 141.5, 133.2, 130.6, 128.5 (2C), 128.3 (2C), 125.9, 104.3, 101.9, 91.8, 90.3, 55.6, 44.4, 41.3, 38.5, 34.7, 31.7, 31.0, 22.8, 19.6, 19.2 ppm; HRMS (ESI): calcd. for $C_{26}H_{30}O_4Na^+$ $[M+Na]^+$: 429.2036, found: 429.2036.

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[4] Orjala, J.; Wright, A. D.; Erdelmeier, C. A. J.; Sticher, O. *Helv. Chim. Acta* **1993**, *76*, 1481.

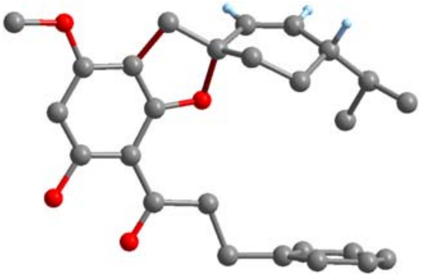


Table S1: X-ray crystal data of racemic adunctin C (selected H atoms have been omitted for clarity)

Empirical formula	$C_{26}H_{30}O_4$
Temperature (K)	293.30(10)
Crystal color	light yellow
Formula weight	406.50
Crystal system	triclinic
Space group	*P*-1
a (Å)	10.5525(9)
b (Å)	10.5881(9)
c (Å)	11.4412(6)
α (°)	102.568(6)
β (°)	105.923(6)
γ (°)	105.637(7)
V ($Å^3$)	1123.59(14)
Z	2
Density (calculated) (g/cm^3)	1.202
F (000)	436
λ (Å)	1.54184
Reflections collected	6710
Independent reflections	3854
2θ Range for data collection (°)	13.24—133.18
Index range	$-12 \le h \le 8$ $-12 \le k \le 12$ $-11 \le l \le 13$
Final *R* indices [I>2σ(*I*)]	$R_1 = 0.0838$, $wR_2 = 0.2422$
Largest difference peak and hole [e $Å^{-3}$]	0.603, –0.252

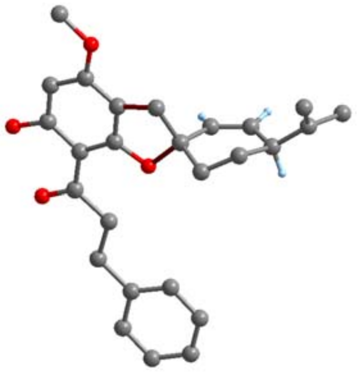


Table S2: X-ray crystal data of racemic aduncting D (selected H atoms have been omitted for clarity)

Empirical formula	$C_{26}H_{30}O_4$
Temperature (K)	293.30(10)
Crystal color	colorless
Formula weight	406.50
Crystal system	monoclinic
Space group	I2/a
a (Å)	20.8005(6)
b (Å)	5.76195(16)
c (Å)	37.1847(13)
α (°)	90
β (°)	98.257(3)
γ (°)	90
V (Å ^{3})	4410.5(2)
Z	8
Density (calculated) (g/cm^3)	1.218
F (000)	1728.0
λ (Å)	1.54184
Reflections collected	6987
Independent reflections	3866
2θ Range for data collection (°)	8.592—133.098
Index range	$-24 \leq h \leq 23$ $-6 \leq k \leq 4$ $-34 \leq l \leq 44$
Final *R* indices [I>2σ(*I*)]	$R_1 = 0.0546$, $wR_2 = 0.1542$
Largest difference peak and hole [e Å $^{-3}$]	0.46, –0.21

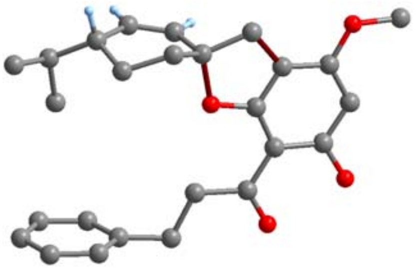


Table S3: X-ray crystal data of (+)-adunctin C (selected H atoms have been omitted for clarity)

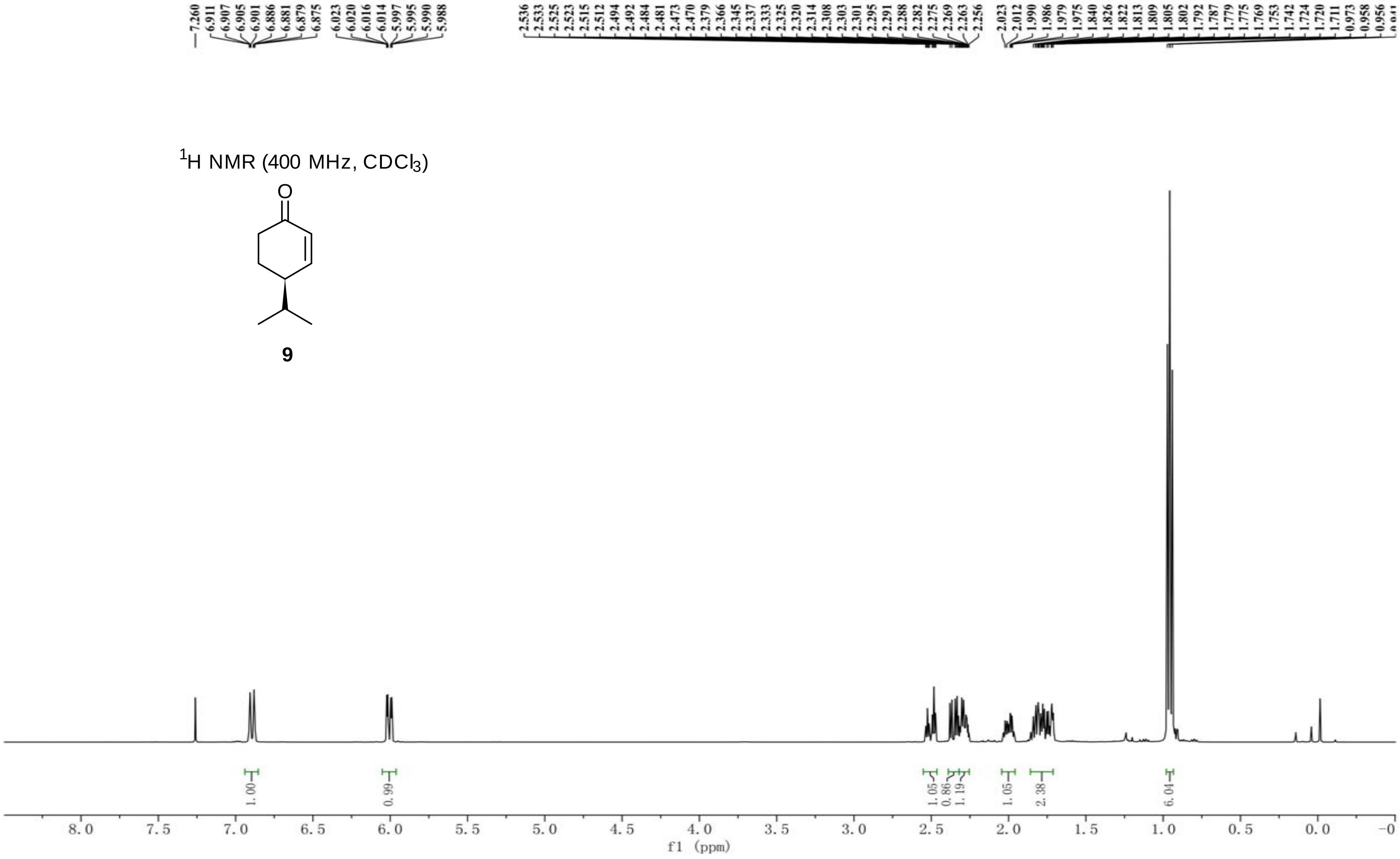
Empirical formula	$C_{26}H_{30}O_4$
Temperature (K)	293.60(10)
Crystal color	colorless
Formula weight	406.50
Crystal system	triclinic
Space group	$P1$
a (Å)	10.6249(4)
b (Å)	10.6722(5)
c (Å)	11.3614(5)
α (°)	105.317(4)
β (°)	102.940(4)
γ (°)	105.980(4)
V (Å^3)	1131.72(9)
Z	2
Density (calculated) (g/cm^3)	1.193
F (000)	436
λ (Å)	1.54184
Reflections collected	16230
Independent reflections	7278
2θ Range for data collection (°)	9.138—133.158
Index range	$-12 \leq h \leq 12$ $-12 \leq k \leq 12$ $-12 \leq l \leq 13$
Final R indices [I>2σ(I)]	$R_1 = 0.0713$, $wR_2 = 0.2089$
Largest difference peak and hole [e Å^{-3}]	0.341, –0.211

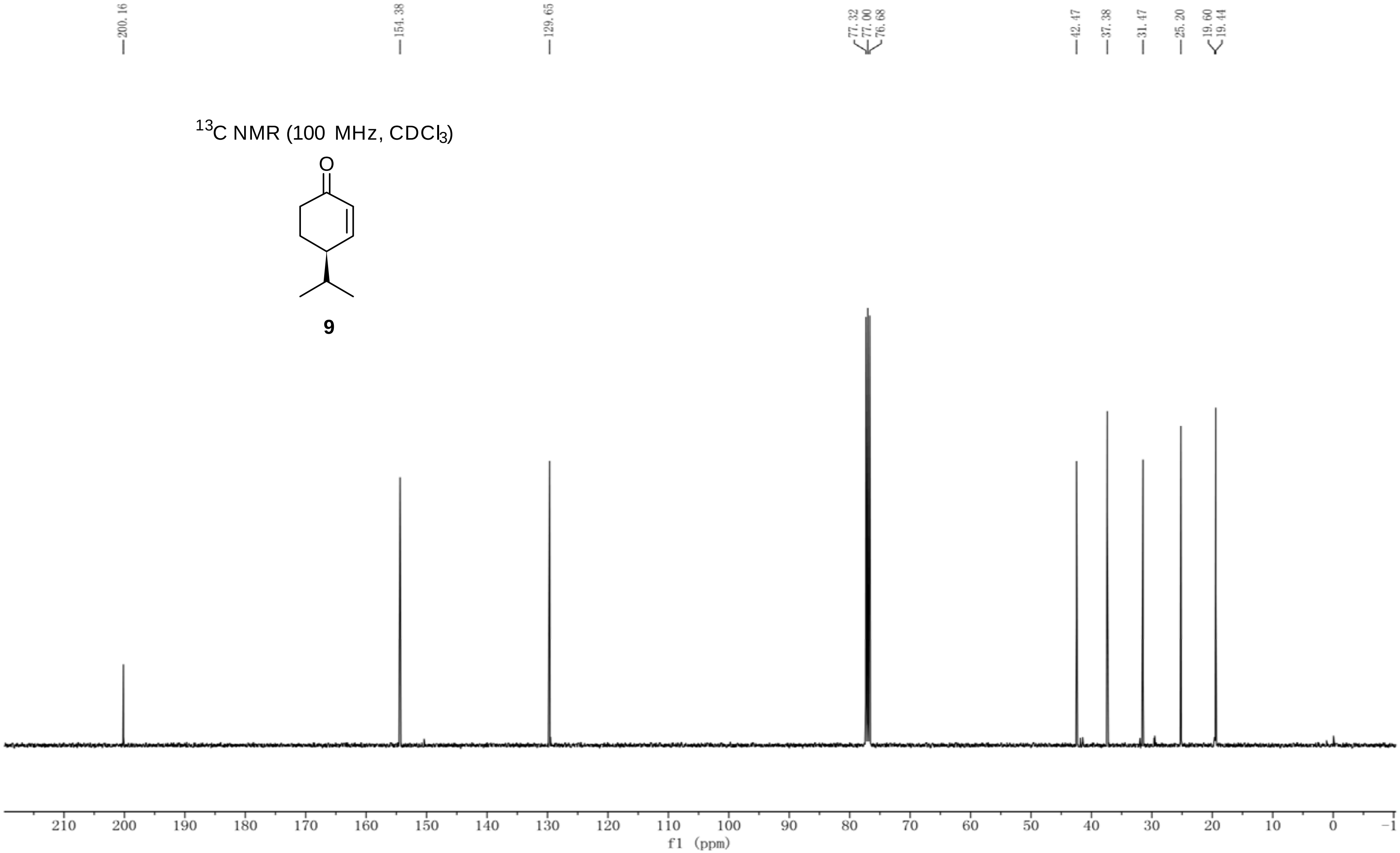
Table S4: NMR Data Comparison of Natural and Synthetic Adunctin C

^{1}H NMR [δ H (ppm), J (Hz)]		**^{13}C NMR [δ C (ppm)]**	
Natural sample[4] ($CDCl_3$, 300 MHz)	Synthetic sample ($CDCl_3$, 400 MHz)	Natural sample[4] ($CDCl_3$, 75.5 MHz)	Synthetic sample ($CDCl_3$, 100 MHz)
13.38 *s*	13.36 *s*	203.4	203.4
7.24 *br.m*	7.27–7.15 *m*	166.0	165.9
6.00 *s*	5.99 *s*	161.8	161.8
5.86 *d* (9.9)	5.85 *d* (10.0)	161.1	161.1
5.79 *d* (9.9)	5.78 *d* (10.0)	141.4	141.4
3.83 *s*	3.82 *s*	136.0	136.1
3.32 *m*	3.40–3.25 *m*	129.2	129.2
3.00 *m*	3.04–2.93 *m*	128.3	128.3
2.95 *d* (15.3)	2.94 *d* (15.2)	125.8	125.9
2.87 *d* (15.3)	2.86 *d* (15.2)	104.4	104.5
2.20 *m*	2.22–2.15 *m*	102.0	101.9
1.96 *m*	1.99–1.93 *m*	91.8	91.8
1.62 *br.m*	1.67–1.49 *m*	88.1	88.1
0.87 *d* (7.0)	0.85 *d* (6.8)	55.5	55.5
0.80 *d* (7.0)	0.79 *d* (6.8)	44.1	44.1
		41.7	41.7
		38.5	38.5
		35.5	35.5
		31.7	31.6
		30.4	30.4
		22.0	21.9
		19.5	19.5
		19.0	19.0

Table S5: NMR Data Comparison of Natural and Synthetic Adunctin D

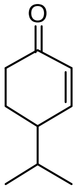
^{1}**H NMR [*δ* H (ppm), *J* (Hz)]**		^{13}**C NMR [*δ* C (ppm)]**	
Natural sample[4] (CDCl$_3$, 300 MHz)	Synthetic sample (CDCl$_3$, 400 MHz)	Natural sample[4] (CDCl$_3$, 75.5 MHz)	Synthetic sample (CDCl$_3$, 100 MHz)
13.40 *s*	13.40 *s*	203.6	203.6
7.24 *br.m*	7.30–7.17 *m*	166.2	166.1
5.99 *s*	5.99 *s*	161.8	161.8
5.85 *br.d* (10.3)	5.85 *d* (10.0)	161.3	161.3
5.76 *br.d* (10.3)	5.77 *d* (10.0)	141.5	141.5
3.82 *s*	3.82 *s*	133.2	133.2
3.28 *t* (6.9)	3.34–3.21 *m*	130.6	130.6
2.99 *t* (7.8)	2.99 *t* (8.0)	128.5	128.5
2.93 *s*	2.93 *s*	128.3	128.3
2.07 *m*	2.11–2.01 *m*	125.9	125.9
1.96 *m*	1.96 *td* (12.4, 3.2)	104.4	104.3
1.85 *m*	1.86–1.81 *m*	102.0	101.9
1.66 *m*	1.70–1.62 *m*	91.9	91.8
1.47 *m*	1.51–1.40 *m*	90.3	90.3
0.93 *d* (7.1)	0.93 *d* (6.8)	55.6	55.6
0.90 *d* (7.1)	0.90 *d* (6.8)	44.3	44.4
		41.3	41.3
		38.5	38.5
		34.8	34.7
		31.7	31.7
		31.0	31.0
		22.8	22.8
		19.6	19.6
		19.2	19.2


7.260
6.911
6.907
6.905
6.901
6.886
6.881
6.879
6.875
6.023
6.020
6.016
6.014
5.997
5.995
5.990
5.988
2.536
2.533
2.525
2.523
2.515
2.512
2.494
2.492
2.484
2.481
2.473
2.470
2.379
2.366
2.345
2.337
2.333
2.325
2.320
2.314
2.308
2.303
2.301
2.295
2.291
2.288
2.282
2.275
2.269
2.263
2.256
2.023
2.012
1.990
1.986
1.979
1.975
1.840
1.826
1.822
1.813
1.809
1.805
1.802
1.792
1.787
1.779
1.775
1.769
1.753
1.742
1.724
1.720
1.711
0.973
0.958
0.956
0.941
^{1}H NMR (400 MHz, CDCl$_3$)
O
9
1.00
0.99
1.05
0.86
1.19
1.05
2.38
6.04
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
−0
f1 (ppm)

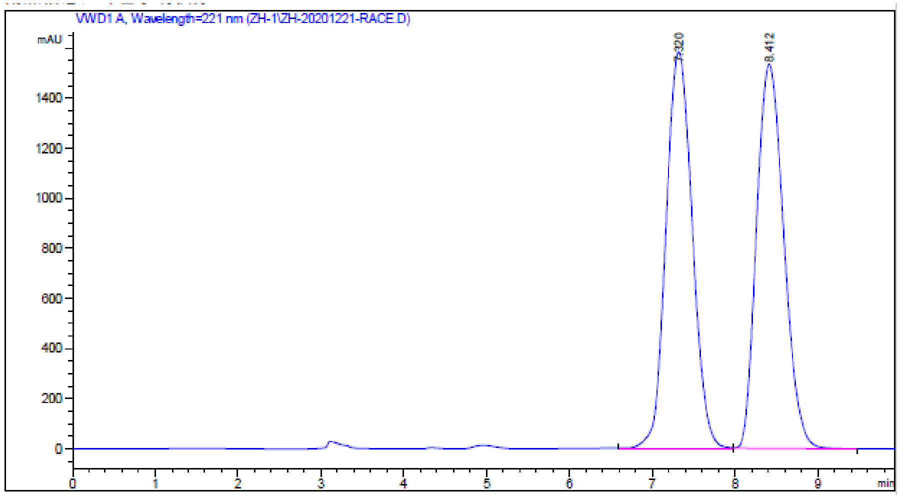


^{13}C NMR (100 MHz, $CDCl_3$)

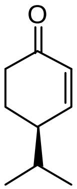
9



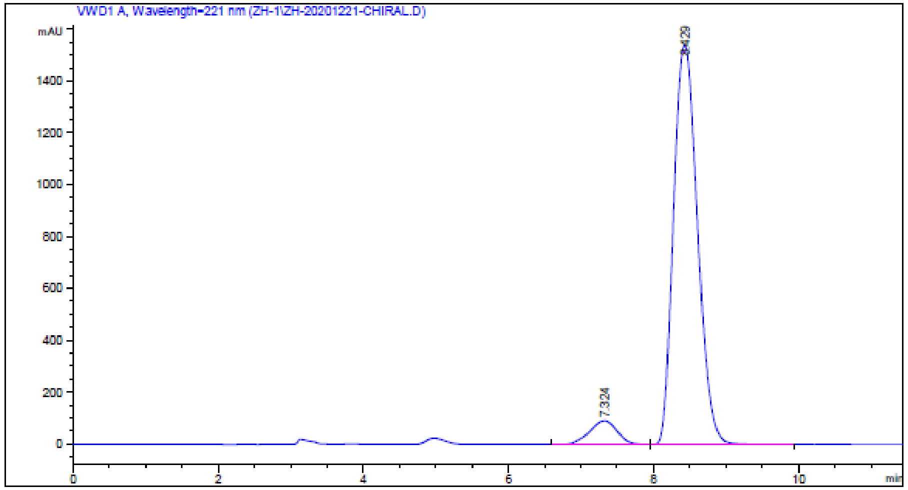
***rac*-9**



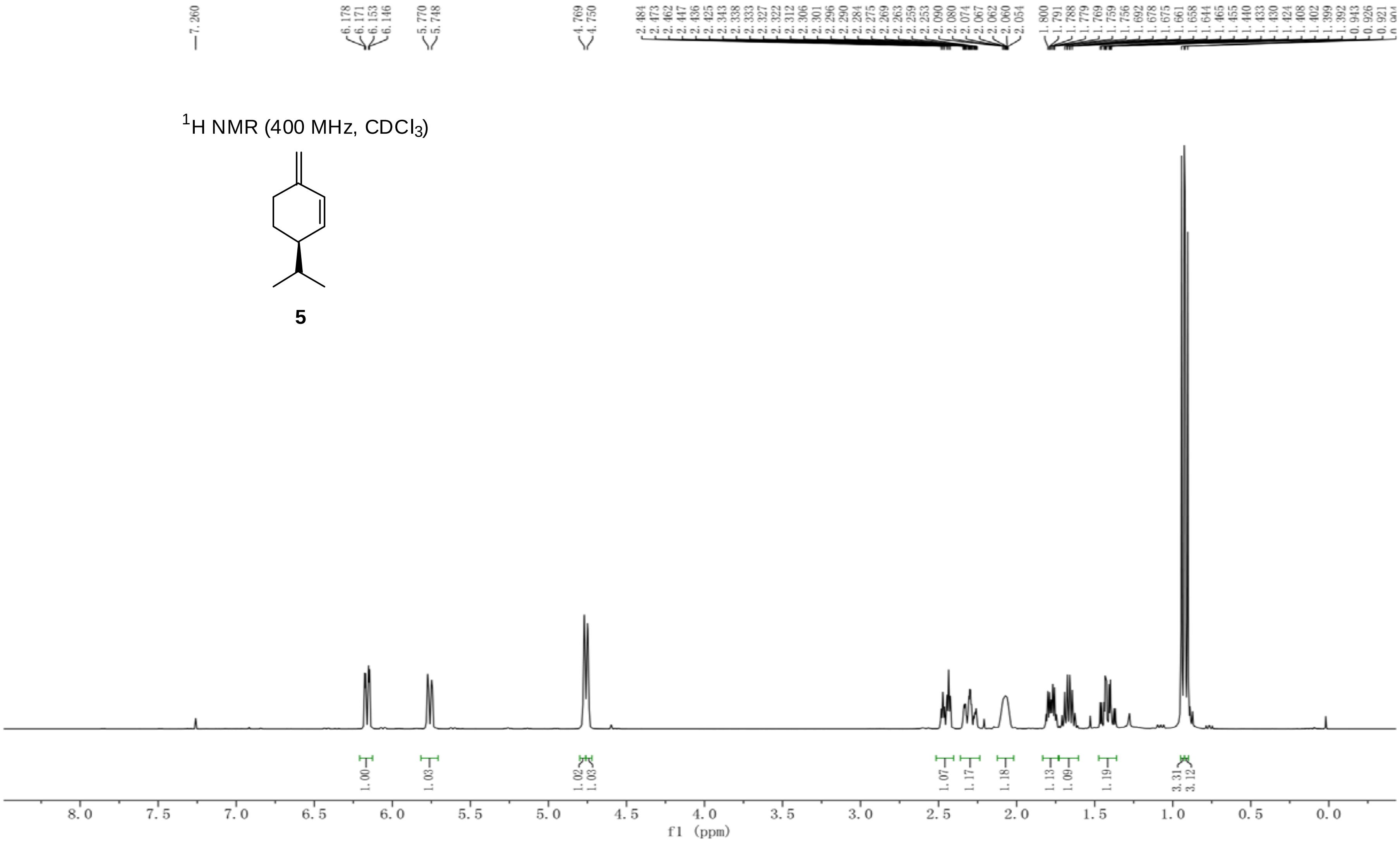
```
信号 1: VWD1 A, Wavelength=221 nm

峰  保留时间 类型  峰宽     峰面积       峰高       峰面积
 #   [min]         [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   7.320 BB    0.3502 3.48364e4 1580.37305  49.9099
   2   8.412 BBA   0.3672 3.49622e4 1532.40576  50.0901
```

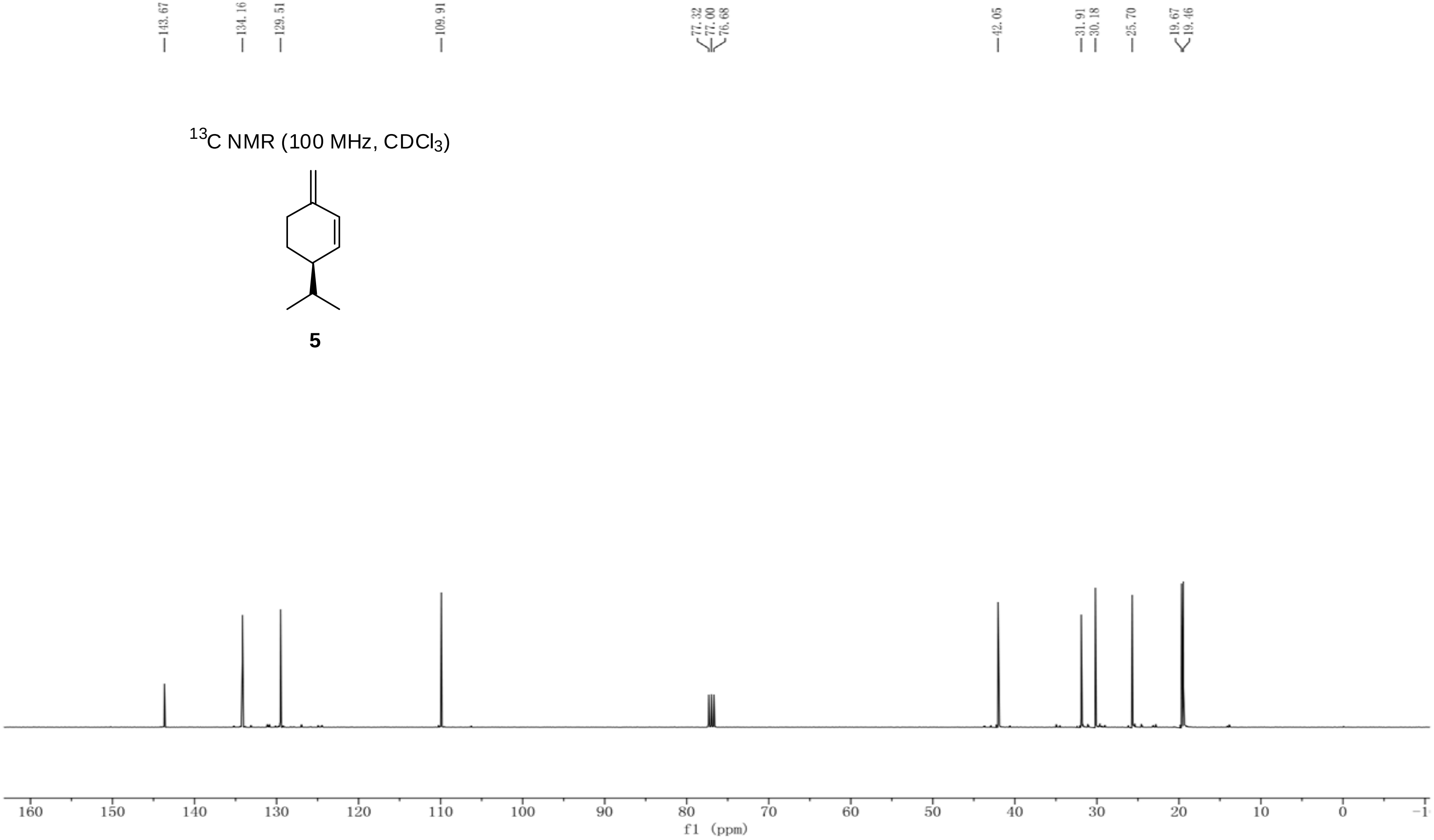


(–)-9



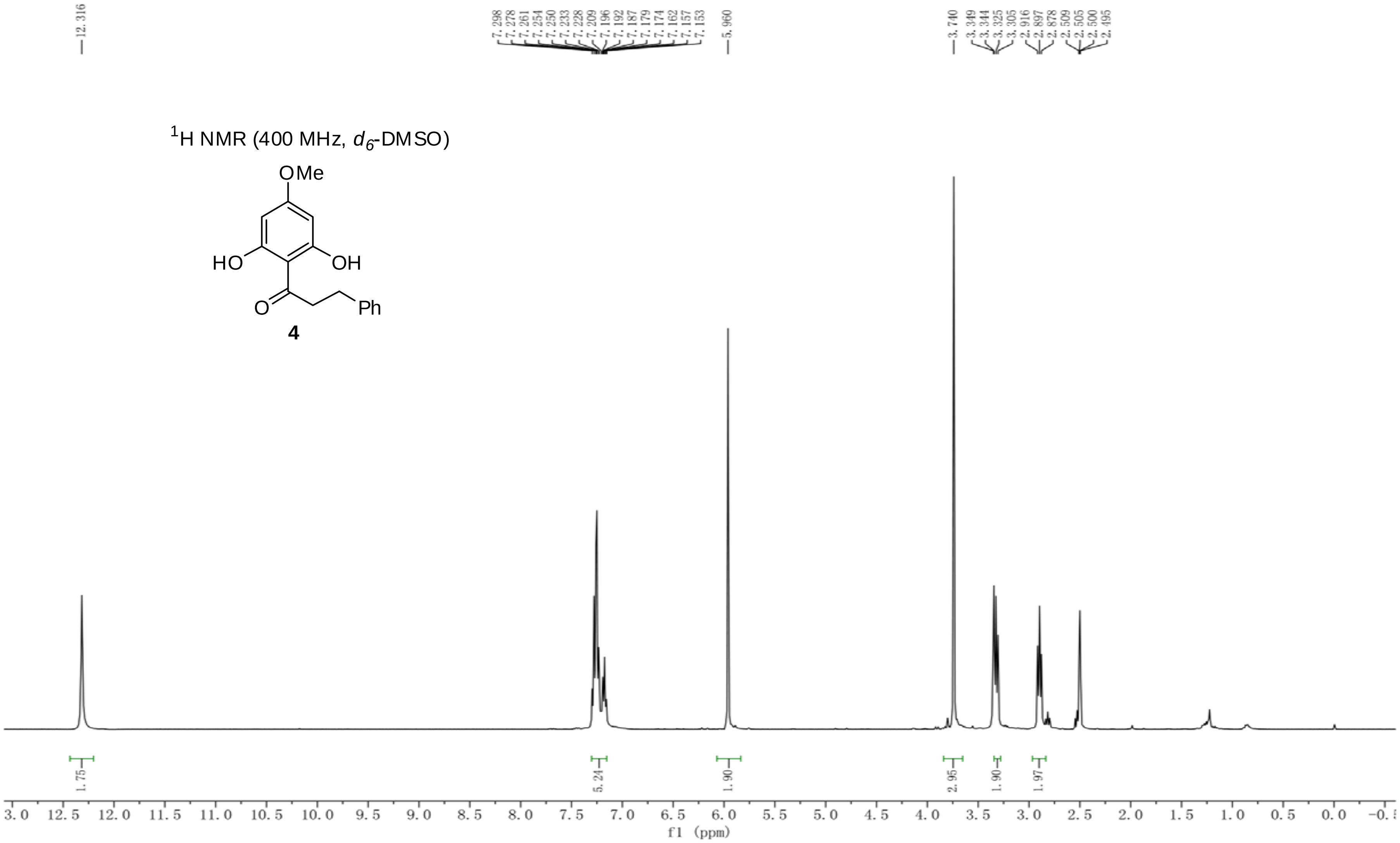
```
信号 1: VWD1 A, Wavelength=221 nm

峰  保留时间 类型  峰宽     峰面积       峰高       峰面积
 #   [min]         [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   7.324 BV    0.4152 2416.65649   90.89587   6.4017
   2   8.429 VB    0.3679 3.53333e4 1538.46838  93.5983
```

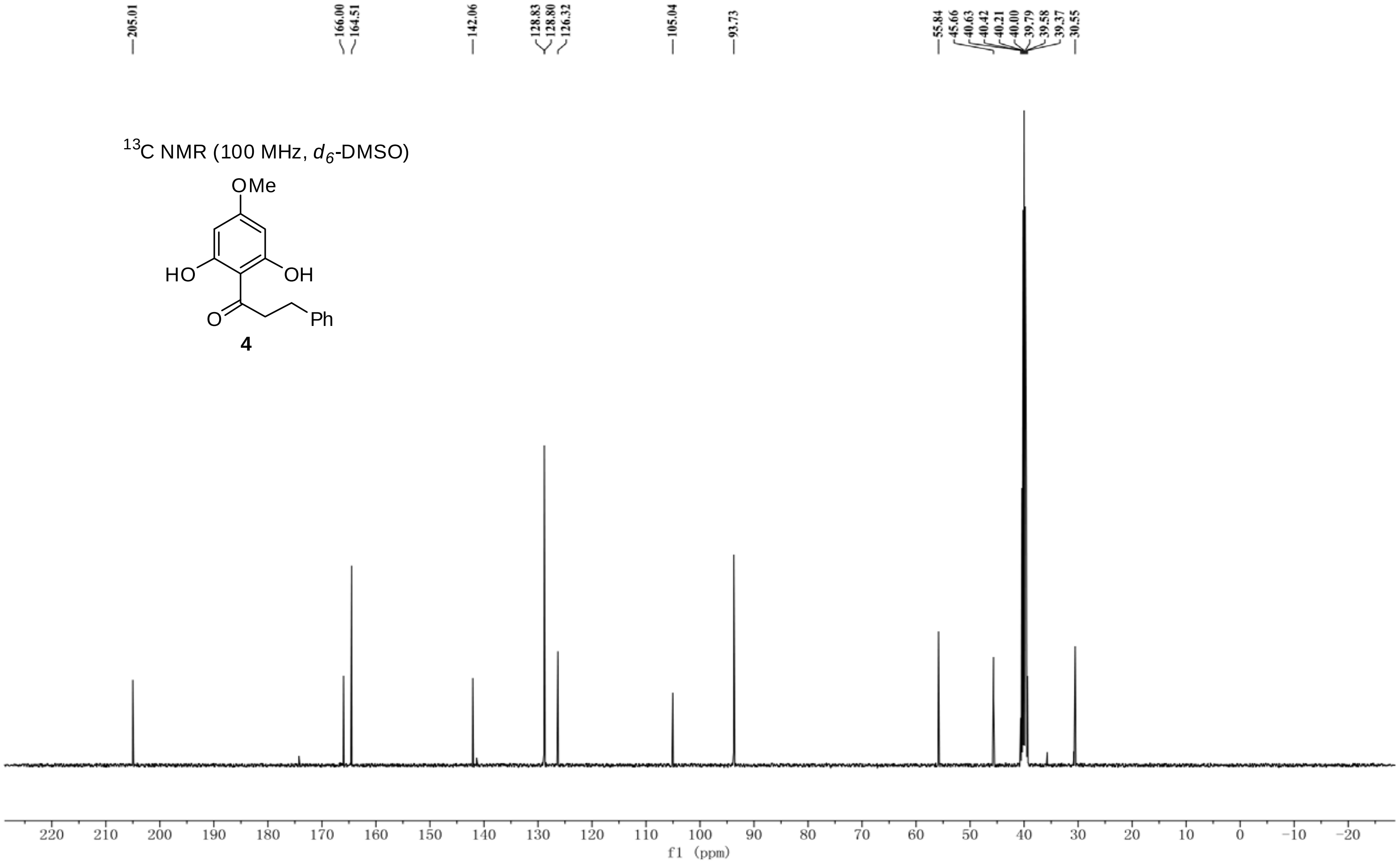

^{1}H NMR (400 MHz, CDCl$_3$)
5
7.260
6.178
6.171
6.153
6.146
5.770
5.748
4.769
4.750
2.484
2.473
2.462
2.447
2.436
2.425
2.343
2.338
2.333
2.327
2.322
2.312
2.306
2.301
2.296
2.290
2.284
2.275
2.269
2.263
2.259
2.253
2.090
2.080
2.074
2.067
2.062
2.060
2.054
1.800
1.791
1.788
1.779
1.769
1.759
1.756
1.692
1.678
1.675
1.661
1.658
1.644
1.465
1.455
1.440
1.433
1.430
1.424
1.408
1.402
1.399
1.392
0.943
0.926
0.921
1.00
1.03
1.02
1.03
1.07
1.17
1.18
1.13
1.09
1.19
3.31
3.12
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
f1 (ppm)

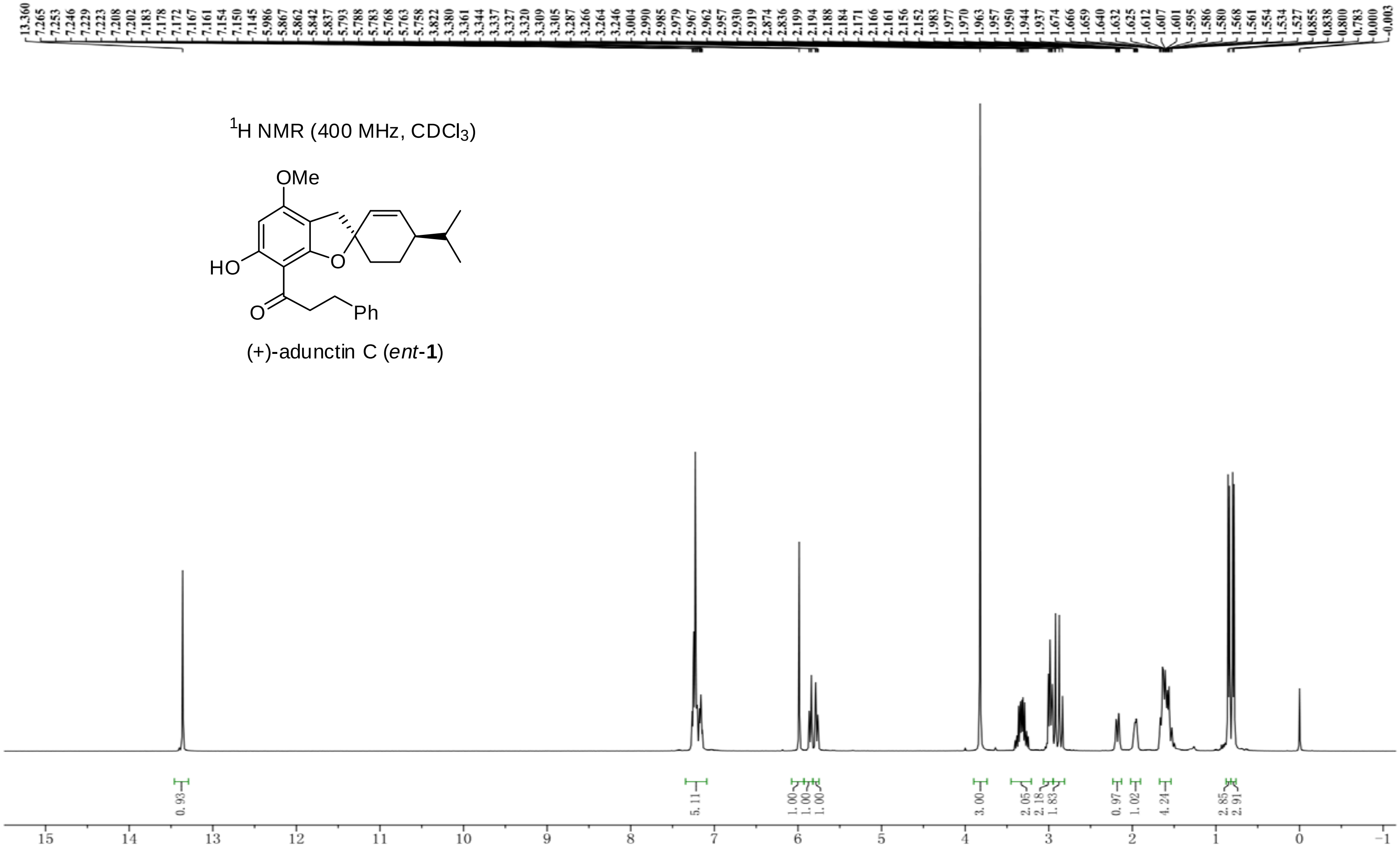


^{13}C NMR (100 MHz, $CDCl_3$)

5

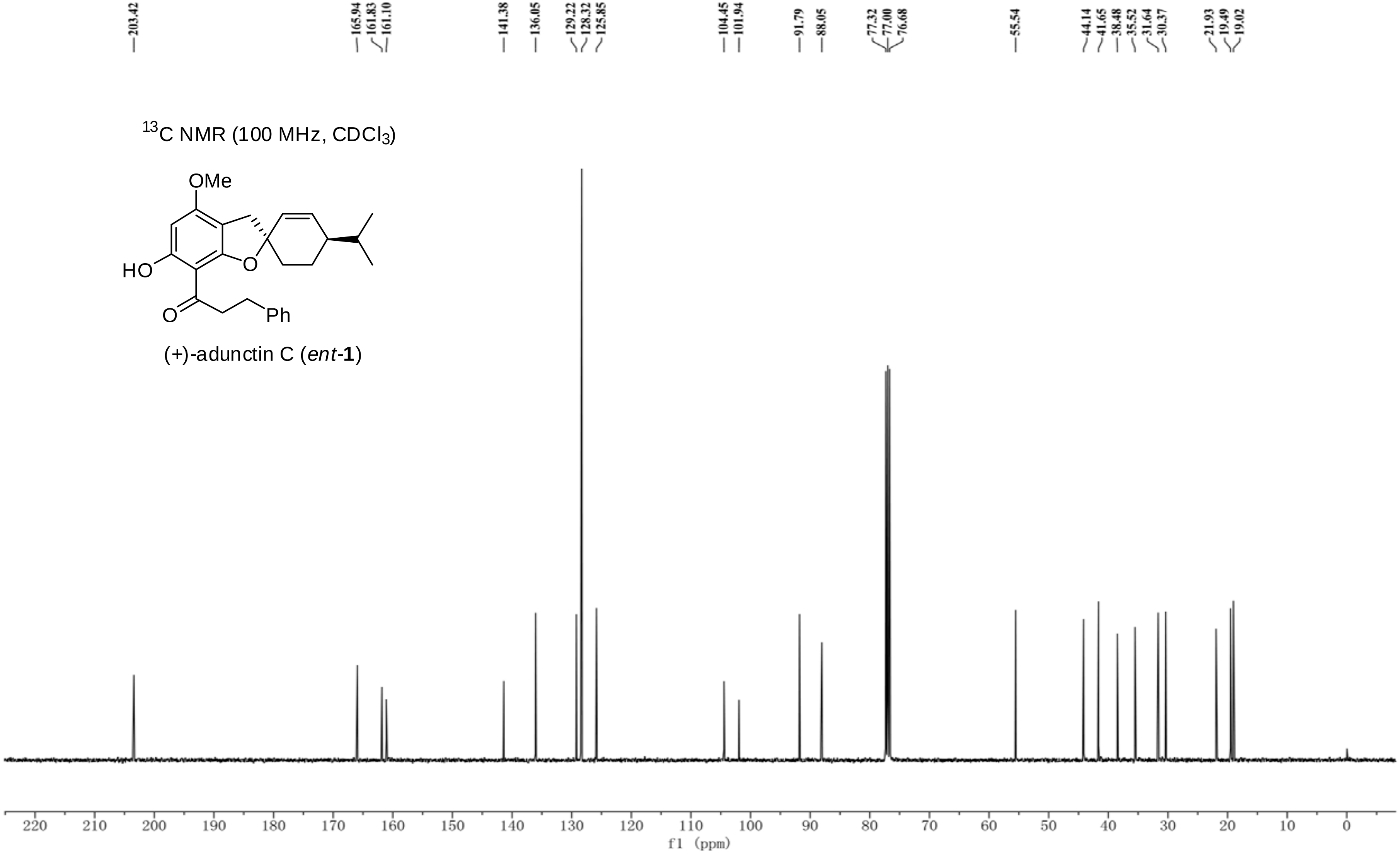

^{1}H NMR (400 MHz, d_6-DMSO)
OMe
HO
OH
O
Ph
4
12.316
7.298
7.278
7.261
7.254
7.250
7.233
7.228
7.209
7.196
7.192
7.187
7.179
7.174
7.162
7.157
7.153
5.960
3.740
3.349
3.344
3.325
3.305
2.916
2.897
2.878
2.509
2.505
2.500
2.495
1.75
5.24
1.90
2.95
1.90
1.97
3.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
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
−0.
f1 (ppm)


^{13}C NMR (100 MHz, d_6-DMSO)
OMe
HO
OH
O
Ph
4
205.01
166.00
164.51
142.06
128.83
128.80
126.32
105.04
93.73
55.84
45.66
40.63
40.42
40.21
40.00
39.79
39.58
39.37
30.55
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)



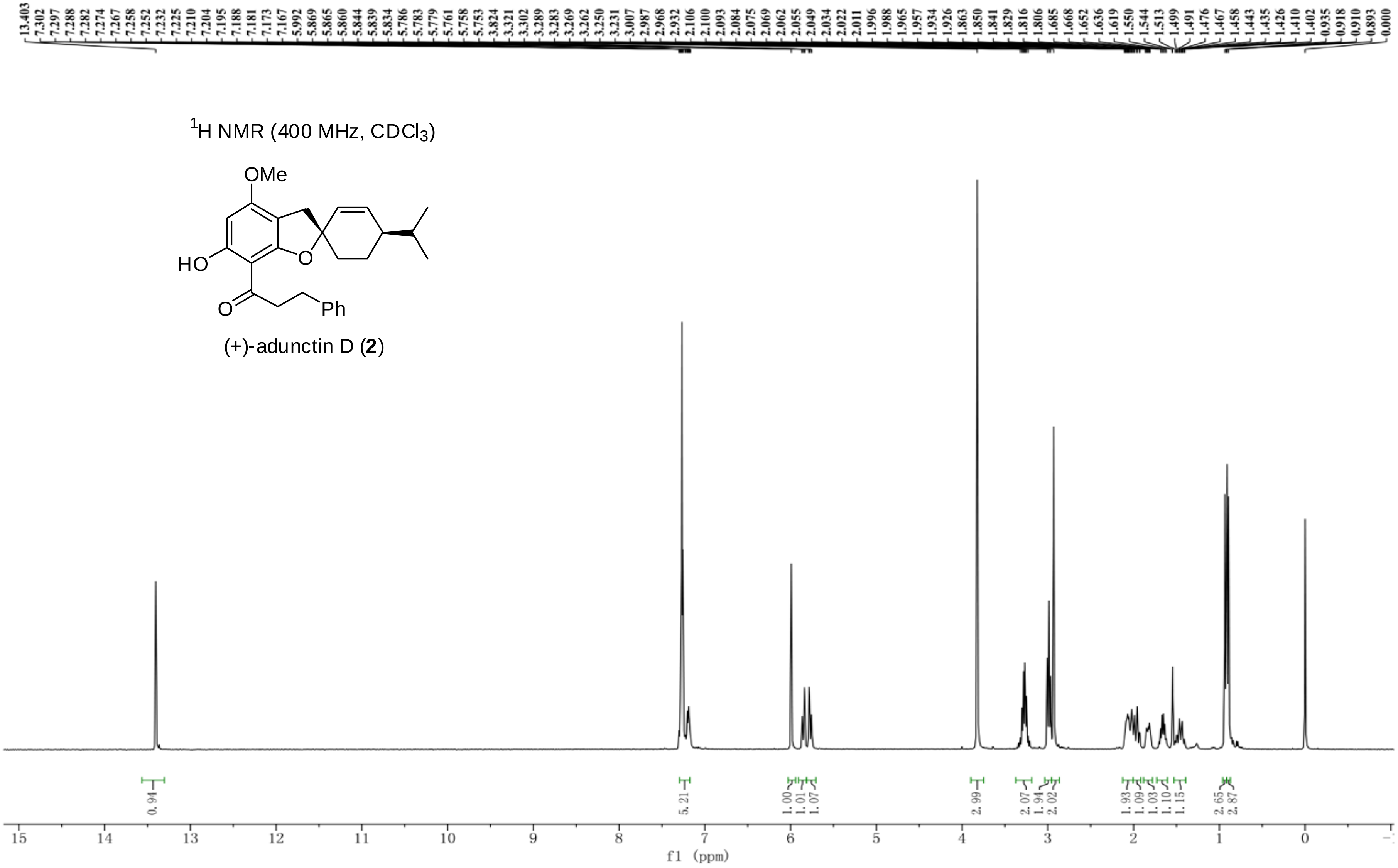
^1H NMR (400 MHz, $CDCl_3$)

(+)-adunctin C (*ent*-**1**)



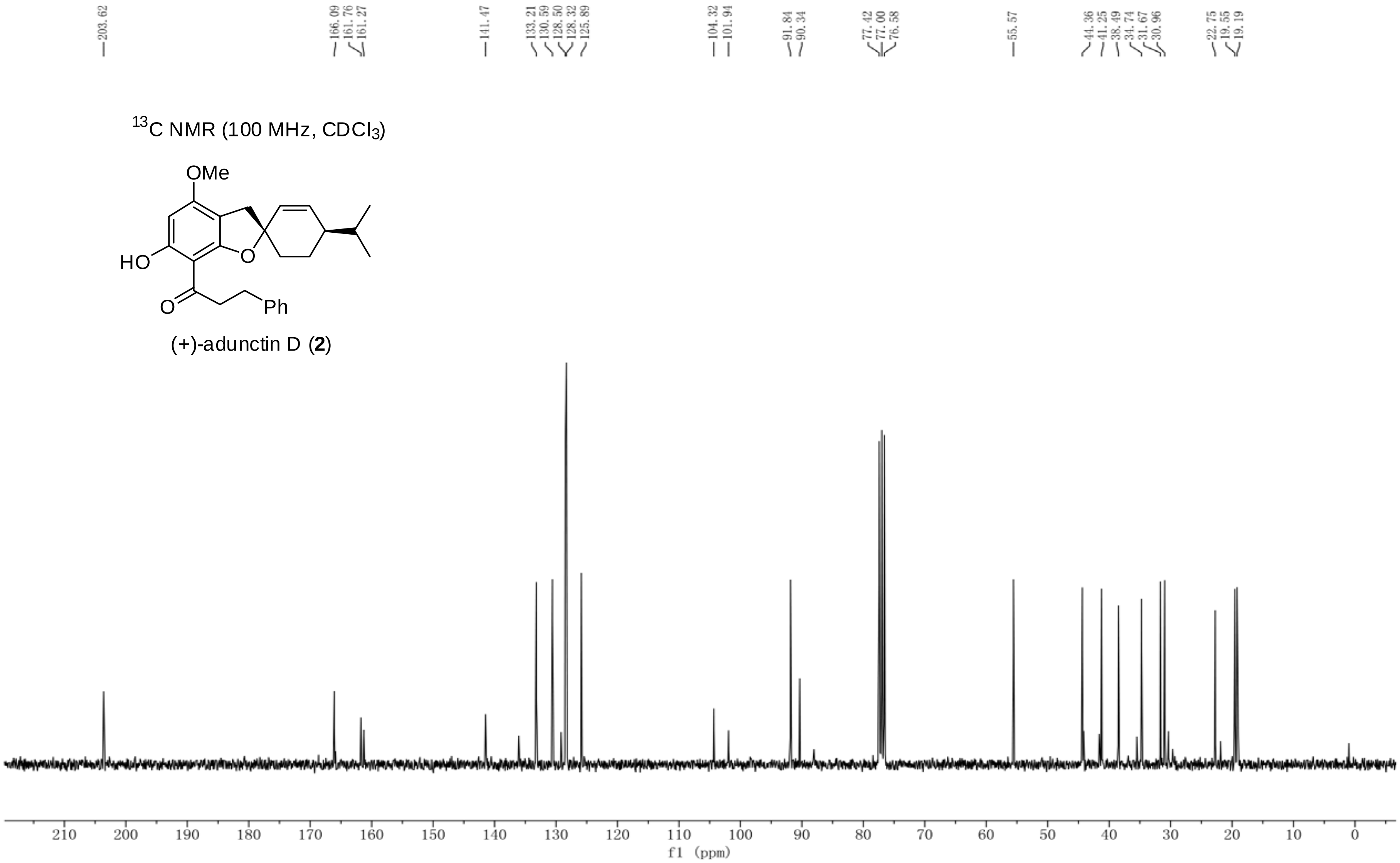
^{13}C NMR (100 MHz, $CDCl_3$)

(+)-adunctin C (*ent*-**1**)



^{1}H NMR (400 MHz, CDCl$_3$)

(+)-adunctin D (**2**)


203.62
166.09
161.76
161.27
141.47
133.21
130.59
128.50
128.32
125.89
104.32
101.94
91.84
90.34
77.42
77.00
76.58
55.57
44.36
41.25
38.49
34.74
31.67
30.96
22.75
19.55
19.19
^{13}C NMR (100 MHz, CDCl$_3$)
OMe
HO
O
O
Ph
(+)-adunctin D (**2**)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)