

A Ligand-Enabled Copper(II)-Catalyzed Highly Selective and Efficient for Synthesis of 2*E*-Alkenylfurans from Ynenones

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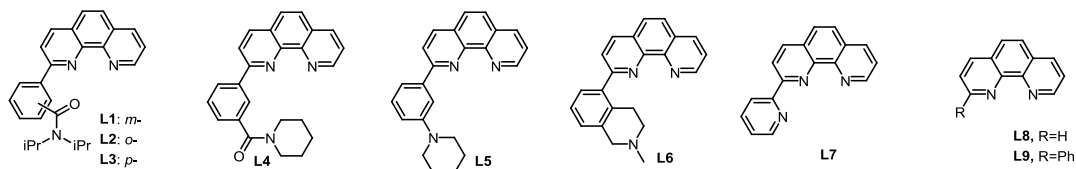
1. General information

All reactions were carried out in a round flask with magnetic stirring. Unless otherwise noted, all reagents were purchased from Aladdin, Energy Chemical for direct use, or prepared as described in the literature. Anhydrous tetrahydrofuran (THF) and toluene were heated over sodium under N₂ for at least four hours before distilled to use. Anhydrous DCM was heated over calcium hydride for two hours before distilled to use. The reactions that sensitive to air or moisture were conducted under nitrogen atmosphere in dry solvents. For chromatographic purification, 200-300 mesh silica gel (Qingdao, China) was employed. For thin layer chromatography (TLC) analysis, Merck 25 TLC aluminium sheets (silica gel 60 GF254, 0.25 mm) were used. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Advance spectrometer at 500 MHz and 126 MHz or 400 MHz and 101 MHz, respectively. The chemical shift were reported in parts per million (δ) relative to internal standard TMS (0 ppm) and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), doublet (d), triplet (t), doublet of doublets(dd), triplet double(td), multiplet(m). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). High resolution mass spectrometry (HRMS) was performed with a Thermo Scientific LTQ Orbitrap XL and AB SCIEX Triple TOF5600+, among them, **1q** and **2q** were analyzed by Life Instrument Sharing Platform of NWAUFU and others were analyzed by KeeCloud Biotech. The ene-yne-ketones **1** were prepared according to the literature procedures¹. The ene-yne-ketones (**1d**, **1e**, **1h-1j**, **1l**, **1n-1p**) were new compounds.

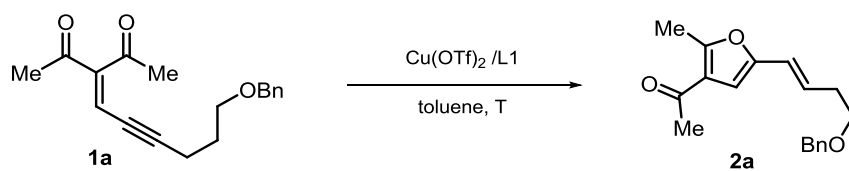
2. Catalyst Screening and Optimization of the Reaction Conditions^a



Entry	Conditions	2a (%) ^b	3a (%) ^b
1	none	99	-
2	without L1	<2	97
3	without $\text{Cu}(\text{OTf})_2$	-	-
4	L2 instead of L1	73	17
5	L3 instead of L1	70	23
6	L4 instead of L1	77	19
7	L5 instead of L1	8	-
8	L6 instead of L1	-	-
9	L7 instead of L1	-	-
10	L8 instead of L1	<2	-
11	L9 instead of L1	<2	-
12	CuBr instead of $\text{Cu}(\text{OTf})_2$	<2	15
13	CuOTf instead of $\text{Cu}(\text{OTf})_2$	<2	-
14	$\text{Cu}(\text{OAc})_2$ instead of $\text{Cu}(\text{OTf})_2$	-	-
15	DCM as the solvent	92	5
16	DCE as the solvent	94	<2
17	MeCN as the solvent	16	8
18	THF as the solvent	18	<2
19	DMSO as the solvent	-	-
20	DMF as the solvent	-	-
21	Acetone as the solvent	89	8



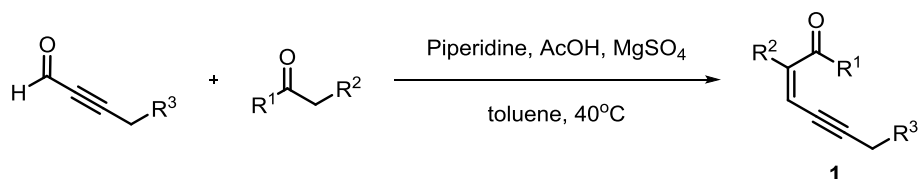
^a The reactions were conducted with everything in a vial under an air atmosphere. Initially, $[1a] = 0.1 \text{ M}$. ^b Isolated yield.



Entry	[Cu]/ L	temperature, concentration	2a (%)	TONs
1	Cu(OTf) ₂ /L1(10%/12%)	rt., 0.1M	99	9.9
2	Cu(OTf) ₂ /L1(5%/6%)	rt., 0.1M	99	19.8
3	Cu(OTf) ₂ /L1 (1%/1.2%)	rt., 0.1M	99	99
4	Cu(OTf) ₂ /L1 (0.5%/0.6%)	rt., 0.3M	91	182
5	Cu(OTf) ₂ /L1 (0.5%/0.6%)	rt., 0.5M	98	196
6	Cu(OTf) ₂ /L1 (0.5%/0.6%)	rt., 0.8M	49	98
7	Cu(OTf) ₂ /L1 (0.1%/0.12%)	rt., 0.5M	<2	
8	Cu(OTf) ₂ /L1 (0.1%/0.12%)	rt., 1M	<2	
9	Cu(OTf) ₂ /L1 (0.1%/0.12%)	60°C, 0.5M	97	970
10	Cu(OTf) ₂ /L1 (500ppm/600ppm.)	60°C, 0.75M	82	1640
11	Cu(OTf) ₂ /L1 (100ppm/120ppm.)	60°C, 0.5M	<2	
12	Cu(OTf)₂/L1 (100ppm/120ppm.)	Reflux, 1M	86	8600
13	Cu(OTf) ₂ /L1 (100ppm/120ppm.)	Reflux, 1.5M	81	8100
14	Cu(OTf) ₂ /L1 (50ppm/60ppm.)	Reflux, 0.75M	40	8000
15	Cu(OTf) ₂ /L1 (50ppm/60ppm.)	Reflux, 1M	40	8000

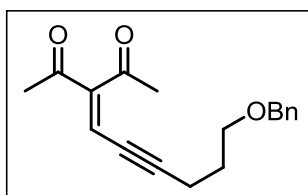
Experiment Producers:

3. General Procedure A for the Synthesis of Ene-yne-ketone 1:



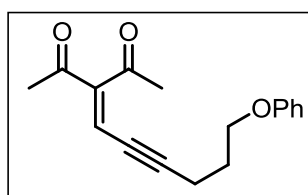
Piperidine (85.1 mg, 1.0 mmol, 0.1 eq), acetic acid (360.3 mg, 6.0 mmol, 0.6 eq), and magnesium sulfate (204.7 mg, 2.0 mmol, 0.2 eq) were added to a stirred solution of aldehyde (10.0 mmol, 1.0 eq) and ketone (10.1 mmol, 1.01 eq) in toluene (30 mL) at ambient temperature. The reaction mixture was stirred at 40 °C with an oil bath and the progress of the reaction was monitored by TLC. Upon completion, the reaction was quenched by the addition of water (30 cm³). The aqueous layer was extracted with EtOAc, dried over Na₂SO₄, filtered, and concentrated to get the residue which was purified by chromatography to get the desired substrate **1**.

3-(6-(benzyloxy)hex-2-yn-1-ylidene)pentane-2,4-dione(1a)



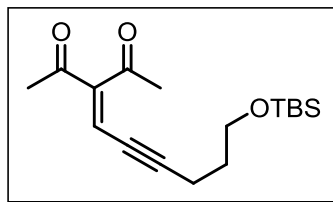
Reported compound,² was synthesized according to the general procedure A. Isolated by column chromatography (hexanes/ethyl acetate = 15: 1), yellow liquid. ¹H NMR (500 MHz, CDCl₃) δ 7.37-7.31 (m, 4H), 7.30-7.26 (m, 1H), 6.66 (t, *J* = 2.5 Hz, 1H), 4.51 (s, 2H), 3.55 (t, *J* = 6.0 Hz, 2H), 2.57 (td, *J* = 7.1, 2.5 Hz, 2H), 2.44 (s, 3H), 2.31 (s, 3H), 1.91-1.80 (m, 2H).

3-(6-phenoxyhex-2-yn-1-ylidene)pentane-2,4-dione(1b)



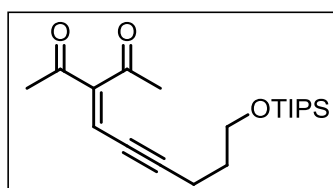
Reported compound,² was synthesized according to the general procedure A. Isolated by column chromatography (hexanes/ethyl acetate = 20: 1), yellow liquid. ¹H NMR (500 MHz, CDCl₃) δ 7.28 (dd, *J* = 8.8, 7.5 Hz, 2H), 6.94 (tt, *J* = 7.5, 1.1 Hz, 1H), 6.89 (dd, *J* = 8.8, 1.1 Hz, 2H), 6.65 (t, *J* = 2.5 Hz, 1H), 4.03 (t, *J* = 5.9 Hz, 2H), 2.67 (td, *J* = 7.0, 2.4 Hz, 2H), 2.41 (s, 3H), 2.29 (s, 3H), 2.08- 1.99 (m, 2H).

3-(6-(((tert-butyl)dimethylsilyl)oxy)hex-2-yn-1-ylidene)pentane-2,4-dione(1c)



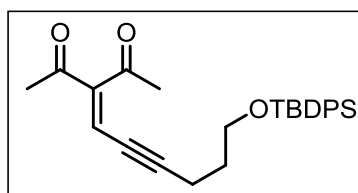
Reported compound,² was synthesized according to the general procedure A. Isolated by column chromatography (hexanes/ethyl acetate = 20: 1), yellow liquid. ¹H NMR (500 MHz, CDCl₃) δ 6.68 (t, *J* = 2.5 Hz, 1H), 3.66 (t, *J* = 5.9 Hz, 2H), 2.52 (td, *J* = 7.1, 2.5 Hz, 2H), 2.46 (s, 3H), 2.30 (s, 3H), 1.79-1.70 (m, 2H), 0.88 (s, 9H), 0.04 (s, 6H).

3-(6-(((triisopropyl)silyl)oxy)hex-2-yn-1-ylidene)pentane-2,4-dione(1d)



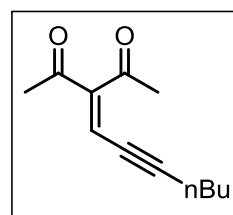
New compound, was synthesized according to the general procedure A. Isolated by column chromatography (hexanes/ethyl acetate = 30: 1), yellow liquid. ¹H NMR (500 MHz, CDCl₃) δ 6.67 (t, *J* = 2.5 Hz, 1H), 3.74 (t, *J* = 5.9 Hz, 2H), 2.55 (td, *J* = 7.1, 2.5 Hz, 2H), 2.44 (s, 3H), 2.29 (s, 3H), 1.80-1.72 (m, 2H), 1.05 (d, *J* = 5.0 Hz, 3H), 1.03 (d, *J* = 5.0 Hz, 18H). ¹³C NMR (126 MHz, CDCl₃) δ 201.3, 195.9, 149.6, 123.3, 110.3, 76.9, 61.7, 31.5, 31.0, 27.3, 18.1, 16.8, 12.0. HRMS (ESI): calcd for C₂₀H₃₅O₃Si⁺ [M+H]⁺ 351.2350, found 351.2350.

3-(6-(((tert-butyl)diphenyl)silyl)oxy)hex-2-yn-1-ylidene)pentane-2,4-dione(1e)



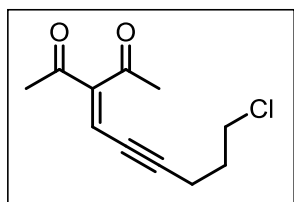
New compound, was synthesized according to the general procedure A. Isolated by column chromatography (hexanes/ethyl acetate = 20: 1), yellow liquid. ¹H NMR (500 MHz, CDCl₃) δ 7.70-7.62 (m, 4H), 7.47-7.35 (m, 6H), 6.67 (t, *J* = 2.5 Hz, 1H), 3.74 (t, *J* = 5.9 Hz, 2H), 2.61 (td, *J* = 7.1, 2.5 Hz, 2H), 2.43 (s, 3H), 2.32 (s, 3H), 1.87-1.75 (m, 2H), 1.06 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 201.3, 195.9, 149.5, 135.6, 133.7, 129.8, 127.8, 123.3, 110.1, 77.1, 62.2, 31.1, 31.0, 27.4, 26.9, 19.3, 16.9. HRMS (ESI): calcd for C₂₇H₃₃O₃Si⁺ [M+H]⁺ 433.2193, found 433.2195.

3-(hept-2-yn-1-ylidene)pentane-2,4-dione (1f)



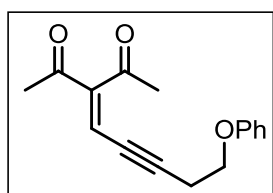
Reported compound,² was synthesized according to the general procedure A. Isolated by column chromatography (hexanes/ethyl acetate = 30: 1), yellow liquid. ¹H NMR (500 MHz, CDCl₃) δ 6.69-6.66 (m, 1H), 2.45 (d, *J* = 1.0 Hz, 3H), 2.42 (td, *J* = 7.5, 2.3 Hz, 2H), 2.29 (d, *J* = 1.0 Hz, 3H), 1.56-1.50 (m, 2H), 1.46-1.34 (m, 2H), 0.91 (td, *J* = 7.5, 1.0 Hz, 3H).

3-(6-chlorohex-2-yn-1-ylidene)pentane-2,4-dione(1g)



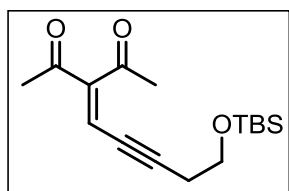
Reported compound,² was synthesized according to the general procedure A. Isolated by column chromatography (hexanes/ethyl acetate = 30: 1), yellow liquid. ¹H NMR (500 MHz, CDCl₃) δ 6.64 (t, *J* = 2.5 Hz, 1H), 3.62 (t, *J* = 6.2 Hz, 2H), 2.63 (td, *J* = 6.9, 2.5 Hz, 2H), 2.44 (s, 3H), 2.30 (s, 3H), 2.04-1.95 (m, 2H).

3-(5-phenoxy-pent-2-yn-1-ylidene)pentane-2,4-dione(1h)



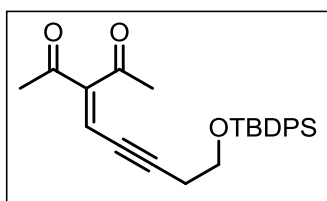
New compound, was synthesized according to the general procedure A. Isolated by column chromatography (hexanes/ethyl acetate = 15: 1), yellow liquid. ¹H NMR (500 MHz, CDCl₃) δ 7.27 (t, *J* = 8.0 Hz, 2H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.66 (t, *J* = 2.5 Hz, 1H), 4.08 (t, *J* = 6.5 Hz, 2H), 2.89 (td, *J* = 6.5, 2.5 Hz, 2H), 2.44 (s, 3H), 2.28 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 201.2, 195.7, 158.2, 150.1, 129.5, 122.3, 121.2, 114.6, 105.5, 77.9, 65.2, 30.9, 27.2, 21.3. HRMS (ESI): calcd for C₁₆H₁₇O₃⁺ [M+H]⁺ 257.1172, found 257.1179.

3-(5-((tert-butyldimethylsilyl)oxy)pent-2-yn-1-ylidene)pentane-2,4-dione(1i)



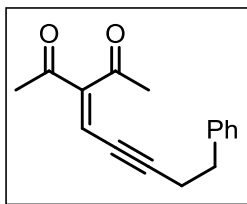
New compound, was synthesized according to the general procedure A. Isolated by column chromatography (hexanes/ethyl acetate = 15: 1), yellow liquid. ¹H NMR (500 MHz, CDCl₃) δ 6.68 (s, 1H), 3.75 (t, *J* = 5.7 Hz, 2H), 2.68-2.61 (m, 2H), 2.47 (s, 3H), 2.30 (s, 3H), 0.88 (s, 9H), 0.06 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 201.3, 195.8, 149.8, 123.0, 107.3, 77.8, 61.2, 31.1, 27.5, 26.0, 24.8, 18.4, -5.2. HRMS (ESI): calcd for C₁₆H₂₇O₃Si⁺ [M+H]⁺ 295.1724, found 295.1725.

3-(5-((tert-butyldiphenylsilyl)oxy)pent-2-yn-1-ylidene)pentane-2,4-dione(1j)



New compound, was synthesized according to the general procedure A. Isolated by column chromatography (hexanes/ethyl acetate = 20: 1), yellow liquid. ¹H NMR (500 MHz, CDCl₃) δ 7.70-7.62 (m, 4H), 7.47-7.36 (m, 6H), 6.68 (t, *J* = 2.5 Hz, 1H), 3.83 (t, *J* = 6.6 Hz, 2H), 2.69 (td, *J* = 6.6, 2.5 Hz, 2H), 2.45 (s, 3H), 2.31 (s, 3H), 1.08 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 201.2, 195.8, 149.7, 135.6, 133.3, 129.9, 127.8, 122.9, 107.3, 77.8, 61.8, 31.0, 27.4, 26.8, 24.5, 19.2. HRMS (ESI): calcd for C₂₆H₃₁O₃Si⁺ [M+H]⁺ 419.2037, found 419.2036.

3-(5-phenylpent-2-yn-1-ylidene)pentane-2,4-dione(1k)

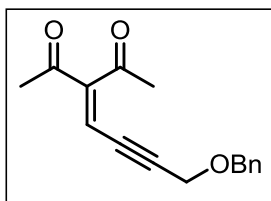


Reported compound,² was synthesized according to the general procedure A.

Isolated by column chromatography (hexanes/ethyl acetate = 20: 1), yellow liquid. ¹H NMR (500 MHz, CDCl₃) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.25-7.17 (m, 3H), 6.65 (t, *J* = 2.5 Hz, 1H), 2.87 (t, *J* = 7.5 Hz, 2H), 2.75 (td, *J* = 7.5, 2.5 Hz, 2H),

2.34 (s, 3H), 2.29 (s, 3H).

3-(4-(benzyloxy)but-2-yn-1-ylidene)pentane-2,4-dione (1l)

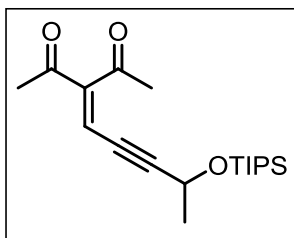


New compound, was synthesized according to the general procedure A.

Isolated by column chromatography (hexanes/ethyl acetate = 10: 1), yellow liquid. ¹H NMR (500 MHz, CDCl₃) δ 7.38-7.31 (m, 5H), 6.70 (t, *J* = 2.0 Hz, 1H), 4.59 (s, 2H), 4.37 (d, *J* = 2.0 Hz, 2H), 2.47 (s, 3H), 2.33 (s, 3H). ¹³C

NMR (126 MHz, CDCl₃) δ 200.9, 195.6, 150.7, 137.0, 128.6, 128.2, 128.2, 121.2, 103.4, 82.0, 72.1, 57.8, 31.0, 27.3. HRMS (ESI): calcd for C₁₆H₁₇O₃⁺ [M+H]⁺ 257.1172, found 257.1171.

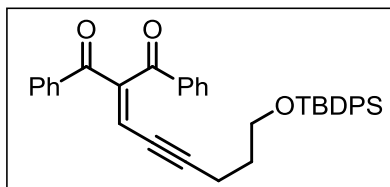
3-(4-(((triisopropylsilyl)oxy)pent-2-yn-1-ylidene)pentane-2,4-dione (1m)



Reported compound,² was synthesized according to the general procedure

A. Isolated by column chromatography (hexanes/ethyl acetate = 20: 1), yellow liquid. ¹H NMR (500 MHz, CDCl₃) δ 6.71 (s, 1H), 4.79 (q, *J* = 6.5 Hz, 1H), 2.47 (s, 3H), 2.31 (s, 3H), 1.48 (d, *J* = 6.5 Hz, 3H), 1.07 (d, *J* = 3.9 Hz, 21H).

2-(6-(((tert-butyl)diphenylsilyl)oxy)hex-2-yn-1-ylidene)-1,3-diphenylpropane-1,3-dione(1n)

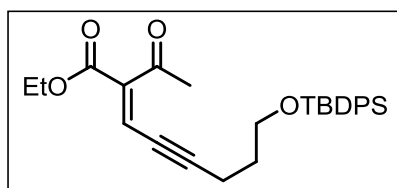


New compound, was synthesized according to the general procedure

A. Isolated by column chromatography (hexanes/ethyl acetate = 20: 1), yellow liquid. ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 7.5 Hz, 4H), 7.53 (dt,

J = 24.0, 7.5 Hz, 2H), 7.47-7.37 (m, 10H), 6.73 (t, *J* = 2.5 Hz, 1H), 3.53 (t, *J* = 5.8 Hz, 2H), 2.39 (td, *J* = 7.5, 2.5 Hz, 2H), 1.56-1.48 (m, 2H), 1.06 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 194.3, 193.2, 147.9, 137.0, 136.5, 135.6, 133.8, 133.6, 132.9, 129.7, 129.6, 129.4, 128.7, 128.6, 127.7, 125.5, 109.3, 77.0, 62.1, 31.0, 26.9, 19.3, 16.7. HRMS (ESI): calcd for C₃₇H₃₇O₃Si⁺ [M+H]⁺ 557.2506, found 557.2509.

ethyl (*E*)-2-acetyl-8-((tert-butyldiphenylsilyl)oxy)oct-2-en-4-ynoate(1o)

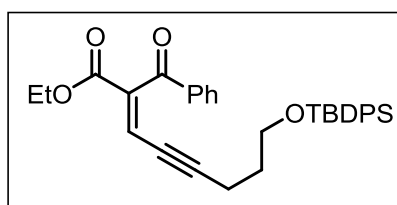


New compound, was synthesized according to the general procedure

A. Isolated by column chromatography (hexanes/ethyl acetate = 50: 1), yellow liquid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.67 (d, $J = 7.1$ Hz, 4H), 7.49-7.32 (m, 6H), 6.78 (s, 1H), 4.27 (q, $J = 7.5$ Hz, 2H),

3.75 (t, $J = 6.0$ Hz, 2H), 2.59 (t, $J = 6.8$ Hz, 2H), 2.41 (s, 3H), 1.91-1.70 (m, 2H), 1.31 (t, $J = 7.5$ Hz, 3H), 1.07 (s, 9H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 199.0, 164.1, 142.3, 135.7, 133.8, 129.8, 127.8, 124.0, 107.9, 76.8, 62.3, 61.6, 31.2, 30.5, 27.0, 19.4, 16.9, 14.2. HRMS (ESI): calcd for $\text{C}_{28}\text{H}_{35}\text{O}_4\text{Si}^+$ $[\text{M}+\text{H}]^+$ 463.2299, found 463.2295.

ethyl (*E*)-2-benzoyl-8-((tert-butyldiphenylsilyl)oxy)oct-2-en-4-ynoate(1p)

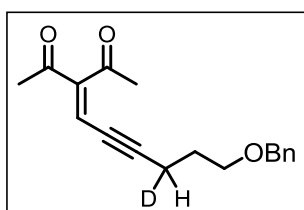


New compound, was synthesized according to the general procedure

A. Isolated by column chromatography (hexanes/ethyl acetate = 20: 1), yellow liquid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.88 (d, $J = 8.0$ Hz, 2H), 7.64 (d, $J = 7.5$ Hz, 4H), 7.50 (t, $J = 7.5$ Hz, 1H), 7.44

(d, $J = 7.0$ Hz, 2H), 7.40 (t, $J = 7.5$ Hz, 6H), 7.03 (t, $J = 2.5$ Hz, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 3.50 (t, $J = 5.5$ Hz, 2H), 2.36 (td, $J = 7.0, 2.5$ Hz, 2H), 1.53-1.46 (m, 2H), 1.20 (t, $J = 7.2$ Hz, 3H), 1.04 (s, 9H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 193.0, 164.2, 141.0, 136.2, 135.6, 133.8, 133.6, 129.7, 129.4, 128.6, 127.7, 124.6, 107.4, 76.6, 62.0, 61.6, 31.0, 26.9, 19.3, 16.5, 14.1. HRMS (ESI): calcd for $\text{C}_{33}\text{H}_{37}\text{O}_4\text{Si}^+$ $[\text{M}+\text{H}]^+$ 525.2456, found 525.2459.

3-(6-(benzyloxy)hex-2-yn-1-ylidene-4-d)pentane-2,4-dione(1q)

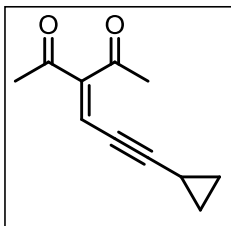


New compound, was synthesized according to the general procedure A.

Isolated by column chromatography (hexanes/ethyl acetate = 15: 1), yellow liquid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37-7.25 (m, 5H), 6.66 (d, $J = 2.4$ Hz, 1H), 4.51 (s, 2H), 3.54 (t, $J = 6.0$ Hz, 2H), 2.55 (td, $J = 6.8, 2.4$ Hz, 1H),

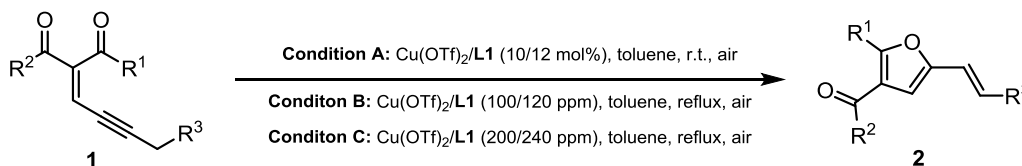
2.43 (s, 3H), 2.30 (s, 3H), 1.85 (q, $J = 6.4$ Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 201.4, 195.9, 149.7, 138.4, 128.5, 128.5, 127.7, 109.6, 77.4, 73.1, 68.5, 31.0, 28.3, 27.3, 17.0 (t). HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{19}\text{DO}_3^+$ $[\text{M}+\text{H}]^+$ 286.1548, found 286.1548.

3-(3-cyclopropylprop-2-yn-1-ylidene)pentane-2,4-dione(1r)



Reported compound,² was synthesized according to the general procedure A. Isolated by column chromatography (hexanes/ethyl acetate = 15: 1), yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 6.65 (s, 1H), 2.41 (s, 3H), 2.26 (s, 3H), 1.59-1.28 (m, 1H), 0.99-0.90 (m, 2H), 0.86-0.76 (m, 2H).

4. General Procedure B for the Synthesis of 2-Alkenylfuran 2:

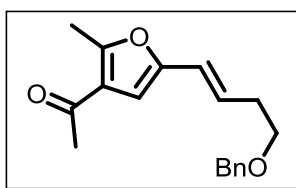


Condition A: Ynenones (0.2 mmol), Cu(OTf)₂ (10 mol%, 7.2 mg), **L1** (12 mol%, 9.2 mg) and anhydrous toluene (2 mL) was stirred under air at room temperature for 1-18 h and the progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was concentrated under vacuum. The residue was purified by chromatography on silica gel to afford the desired product **2**.

Condition B: An oven-dried flask (200 mL) was charged with Cu(OTf)₂ (1.8 mg) and **L1** (2.3 mg) in acetone (100 mL) and stirred at room temperature for 1 h. The solution (2 mL) was added to the reaction flask with a syringe and was concentrated under vacuum. The solution of **1** (1 mmol, 1.0 eq) in toluene (1 mL) was added to the flask. The resulting mixture was refluxed for about 3-11 hours and the progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was concentrated under vacuum. The residue was purified by chromatography on silica gel to afford the desired product **2**.

Condition C: An oven-dried flask (200 mL) was charged with Cu(OTf)₂ (1.8 mg) and **L1** (2.3 mg) in acetone (100 mL) and stirred at room temperature for 1 h. The solution (4 mL) was added to the reaction flask with a syringe and was concentrated under vacuum. The solution of **1g** (1 mmol, 1.0 eq) in toluene (1 mL) was added to the flask. The resulting mixture was refluxed for about 3 hours and the progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was concentrated under vacuum. The residue was purified by chromatography on silica gel to afford the desired product **2g**.

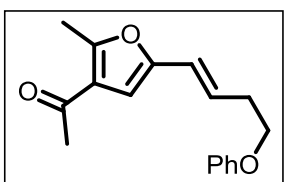
(E)-1-(5-(4-(benzyloxy)but-1-en-1-yl)-2-methylfuran-3-yl)ethan-1-one(2a)



New compound, was synthesized according to the general procedure B. The product was obtained by condition A in 56.1 mg, yield 99%; condition B in 244.5 mg, yield 86% with 8600 TONs. Isolated by column chromatography (hexanes/ethyl acetate = 12: 1), yellow liquid. ^1H NMR (500 MHz, CDCl_3)

δ 7.35 (d, $J = 4.5$ Hz, 4H), 7.31-7.27 (m, 1H), 6.33 (s, 1H), 6.23-6.16 (m, 2H), 4.54 (s, 2H), 3.58 (t, $J = 6.5$ Hz, 2H), 2.58 (s, 3H), 2.53-2.47 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 194.2, 157.7, 150.8, 138.5, 128.5, 127.8, 127.7, 127.1, 122.8, 119.5, 106.6, 73.1, 69.6, 33.4, 29.2, 14.5. HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{21}\text{O}_3^+$ $[\text{M}+\text{H}]^+$ 285.1485, found 285.1487.

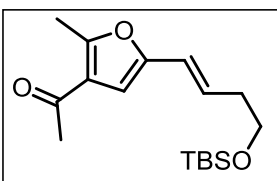
(E)-1-(2-methyl-5-(4-phenoxybut-1-en-1-yl)furan-3-yl)ethan-1-one(2b)



New compound, was synthesized according to the general procedure B. The product was obtained by condition A in 53.1 mg, yield 99%; condition B in 243.3 mg, yield 90% with 9000 TONs. Isolated by column chromatography (hexanes/ethyl acetate = 15: 1), yellow liquid. ^1H NMR (500 MHz, CDCl_3)

δ 7.29 (t, $J = 8.0$ Hz, 2H), 6.98-6.90 (m, 3H), 6.37 (s, 1H), 6.28-6.20 (m, 2H), 4.07 (t, $J = 6.5$ Hz, 2H), 2.71-2.65 (m, 2H), 2.59 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 194.2, 158.9, 157.8, 150.6, 129.6, 126.2, 122.8, 120.9, 120.0, 114.7, 107.0, 67.1, 32.8, 29.2, 14.6. HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{19}\text{O}_3^+$ $[\text{M}+\text{H}]^+$ 271.1329, found 271.1331.

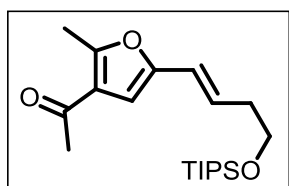
(E)-1-(5-(4-((tert-butyldimethylsilyl)oxy)but-1-en-1-yl)-2-methylfuran-3-yl)ethan-1-one(2c)



New compound, was synthesized according to the general procedure B. The product was obtained by condition A in 60.9 mg, yield 99%; condition B in 246.8 mg, yield 80% with 8000 TONs. Isolated by column chromatography (hexanes/ethyl acetate = 15: 1), yellow liquid. ^1H NMR (500 MHz, CDCl_3)

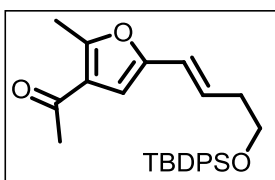
δ 6.32 (s, 1H), 6.21-6.12 (m, 2H), 3.70 (t, $J = 6.7$ Hz, 2H), 2.57 (s, 3H), 2.44-2.38 (m, 2H), 2.37 (s, 3H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 194.2, 157.6, 150.9, 127.3, 122.8, 119.5, 106.4, 62.8, 36.5, 29.2, 26.1, 18.5, 14.5, -5.1. HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{28}\text{O}_3\text{SiNa}^+$ $[\text{M}+\text{Na}]^+$ 331.1700, found 331.1699.

(E)-1-(2-methyl-5-(4-((triisopropylsilyl)oxy)but-1-en-1-yl)furan-3-yl)ethan-1-one(2d)



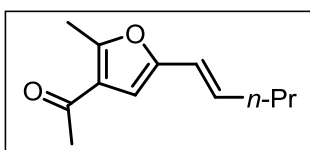
New compound, was synthesized according to the general procedure B. The product was obtained by condition A in 69.1 mg, yield 99%; condition B in 305.0 mg, yield 87% with 8700 TONs. Isolated by column chromatography (hexanes/ethyl acetate = 15: 1), yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 6.29 (s, 1H), 6.19-6.14 (m, 2H), 3.76 (t, $J = 6.5$ Hz, 2H), 2.54 (s, 3H), 2.40 (q, $J = 6.5$ Hz, 2H), 2.34 (s, 3H), 1.08-1.05 (m, 3H), 1.06-1.00 (m, 18H). ^{13}C NMR (126 MHz, CDCl_3) δ 194.1, 157.5, 150.9, 127.3, 122.7, 119.4, 106.3, 63.0, 36.6, 29.1, 18.1, 14.4, 12.1. HRMS (ESI): calcd for $\text{C}_{20}\text{H}_{34}\text{O}_3\text{SiNa}^+$ $[\text{M}+\text{Na}]^+$ 373.2169, found 373.2171.

(E)-1-(5-(4-((tert-butyl)oxy)but-1-en-1-yl)-2-methylfuran-3-yl)ethan-1-one(2e)



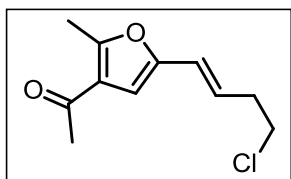
New compound, was synthesized according to the general procedure B. The product was obtained by condition A in 85.3 mg, yield 99%; condition B in 402.4 mg, yield 93% with 9300 TONs. Isolated by column chromatography (hexanes/ethyl acetate = 15: 1), yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 7.72-7.68 (m, 4H), 7.46-7.36 (m, 6H), 6.33 (s, 1H), 6.24-6.13 (m, 2H), 3.79 (t, $J = 6.5$ Hz, 2H), 2.60 (s, 3H), 2.48-2.43 (m, 2H), 2.40 (s, 3H), 1.08 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 194.3, 157.6, 150.9, 135.7, 133.9, 129.7, 127.7, 127.3, 122.8, 119.6, 106.4, 63.5, 36.2, 29.2, 27.0, 19.3, 14.5. HRMS (ESI): calcd for $\text{C}_{28}\text{H}_{34}\text{O}_4\text{SiNa}^+$ $[\text{M}+\text{Na}]^+$ 455.2013, found 455.2015.

(E)-1-(2-methyl-5-(pent-1-en-1-yl)furan-3-yl)ethan-1-one(2f)



Reported compound,² was synthesized according to the general procedure B. The product was obtained by condition A in 37.8 mg, yield 99%; condition B in 128.9 mg, yield 67% with 6700 TONs. Isolated by column chromatography (hexanes/ethyl acetate = 15: 1), yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 6.31 (s, 1H), 6.18 (dt, $J = 16.0, 6.6$ Hz, 1H), 6.11 (d, $J = 16.0$ Hz, 1H), 2.58 (s, 3H), 2.38 (s, 3H), 2.16 (q, $J = 7.0$ Hz, 2H), 1.54-1.42 (m, 2H), 0.94 (t, $J = 7.5$ Hz, 3H).

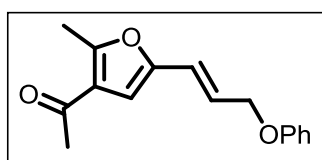
(E)-1-(5-(4-chlorobut-1-en-1-yl)-2-methylfuran-3-yl)ethan-1-one(2g)



New compound, was synthesized according to the general procedure B. The product was obtained by condition A in 42.0 mg, yield 99%; condition C in 165.6 mg, yield 78% with 3900 TONs. Isolated by column chromatography (hexanes/ethyl acetate = 15: 1), yellow liquid. ^1H NMR (500 MHz, CDCl_3)

δ 6.38 (s, 1H), 6.22 (d, $J = 15.5$ Hz, 1H), 6.17-6.09 (m, 1H), 3.60 (t, $J = 7.0$ Hz, 2H), 2.64 (q, $J = 7.0$ Hz, 2H), 2.58 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 194.1, 158.0, 150.2, 125.6, 122.8, 120.5, 107.5, 43.8, 36.0, 29.2, 14.6. HRMS (ESI): calcd for $\text{C}_{11}\text{H}_{14}\text{ClO}_2^+$ $[\text{M}+\text{H}]^+$ 213.0677, found 213.0675.

(E)-1-(2-methyl-5-(3-phenoxyprop-1-en-1-yl)furan-3-yl)ethan-1-one(2h)

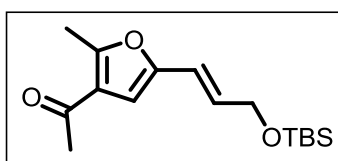


New compound, was synthesized according to the general procedure B.

The product was obtained by condition A in 50.6 mg, yield 99%; condition B in 171.7 mg, yield 67% with 6700 TONs. Isolated by column chromatography (hexanes/ethyl acetate = 15: 1), yellow liquid. ^1H NMR

(500 MHz, CDCl_3) δ 7.30 (t, $J = 8.0$ Hz, 2H), 6.99-6.92 (m, 3H), 6.47 (d, $J = 17.0$ Hz, 2H), 6.36 (dt, $J = 17.0, 5.5$ Hz, 1H), 4.68 (dd, $J = 5.5, 1.5$ Hz, 2H), 2.60 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 194.1, 158.6, 158.4, 150.0, 129.7, 124.1, 123.0, 121.2, 120.0, 114.9, 108.6, 67.9, 29.2, 14.6. HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 279.0992, found 279.0993.

(E)-1-(5-(3-((tert-butyldimethylsilyl)oxy)prop-1-en-1-yl)-2-methylfuran-3-yl)ethan-1-one(2i)

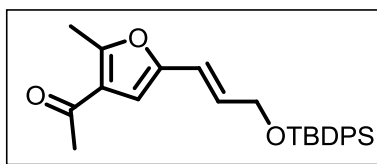


New compound, was synthesized according to the general procedure B.

The product was obtained by condition A in 58.1 mg, yield 99%; condition B in 176.7 mg, yield 60% with 6000 TONs. Isolated by column chromatography (hexanes/ethyl acetate = 15: 1), yellow liquid. ^1H NMR

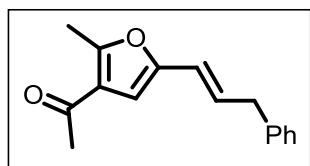
(500 MHz, CDCl_3) δ 6.32 (s, 1H), 6.29 (dt, $J = 15.5, 2.0$ Hz, 1H), 6.16 (dt, $J = 15.5, 4.5$ Hz, 1H), 4.25 (dd, $J = 4.5, 2.0$ Hz, 2H), 2.50 (s, 3H), 2.30 (s, 3H), 0.87 (s, 9H), 0.03 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 193.8, 157.6, 150.5, 128.8, 122.7, 116.6, 107.3, 62.9, 29.0, 25.9, 18.4, 14.3, -5.3. HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{26}\text{O}_3\text{SiNa}^+$ $[\text{M}+\text{Na}]^+$ 317.1543, found 317.1542.

(E)-1-(5-(3-(((tert-butyl)diphenylsilyl)oxy)prop-1-en-1-yl)-2-methylfuran-3-yl)ethan-1-one(2j)



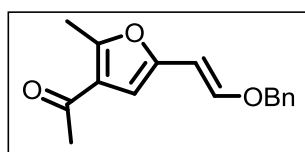
New compound, was synthesized according to the general procedure B. The product was obtained by condition A in 82.5 mg, yield 99%; condition B in 293.0 mg, yield 70% with 7000 TONs. Isolated by column chromatography (hexanes/ethyl acetate = 15: 1), yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 7.76 (dd, $J = 8.0, 2.0$ Hz, 4H), 7.48-7.39 (m, 6H), 6.54 (dt, $J = 15.5, 2.0$ Hz, 1H), 6.45 (s, 1H), 6.30 (dt, $J = 15.5, 4.5$ Hz, 1H), 4.41 (dd, $J = 4.5, 2.0$ Hz, 2H), 2.63 (s, 3H), 2.42 (s, 3H), 1.15 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 194.1, 157.8, 150.6, 135.5, 133.5, 129.8, 128.5, 127.8, 122.8, 116.7, 107.5, 63.7, 29.1, 26.9, 19.3, 14.5. HRMS (ESI): calcd for $\text{C}_{26}\text{H}_{30}\text{O}_3\text{SiNa}^+$ $[\text{M}+\text{Na}]^+$ 441.1856, found 441.1859.

(E)-1-(2-methyl-5-(3-phenylprop-1-en-1-yl)furan-3-yl)ethan-1-one(2k)



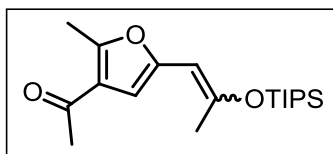
New compound, was synthesized according to the general procedure B. The product was obtained by condition A in 47.3 mg, yield 99%; condition B in 153.8 mg, yield 64% with 6400 TONs. Isolated by column chromatography (hexanes/ethyl acetate = 15: 1), yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 7.32 (t, $J = 8.2$ Hz, 2H), 7.23 (t, $J = 6.8$ Hz, 3H), 6.37-6.29 (m, 2H), 6.15 (d, $J = 15.5$ Hz, 1H), 3.52 (dd, $J = 7.0, 1.5$ Hz, 2H), 2.57 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 194.2, 157.7, 150.8, 139.7, 129.3, 128.8, 128.7, 126.4, 122.8, 118.9, 106.9, 39.2, 29.2, 14.5. HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{17}\text{O}_2^+$ $[\text{M}+\text{H}]^+$ 241.1223, found 241.1224.

(E)-1-(5-(2-(benzyloxy)vinyl)-2-methylfuran-3-yl)ethan-1-one(2l)



New compound, was synthesized according to the general procedure B. The product was obtained by condition A in 50.5 mg, yield 99% (E:Z=5:1); condition B in 184.5 mg, yield 72% (E:Z=3:1) with 7200 TONs. Isolated by column chromatography (hexanes/ethyl acetate = 100:1-20:1), yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 7.43-7.29 (m, 5H), 7.09 (d, $J = 12.5$ Hz, 1H), 6.20 (s, 1H), 5.72 (d, $J = 12.5$ Hz, 1H), 4.86 (s, 2H), 2.55 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 194.0, 156.4, 149.3, 148.1, 136.4, 128.6, 128.2, 127.6, 122.7, 104.4, 96.3, 72.2, 29.1, 14.3. HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 279.0992, found 279.0996.

1-(2-methyl-5-(2-((triisopropylsilyl)oxy)prop-1-en-1-yl)furan-3-yl)ethan-1-one(2m)

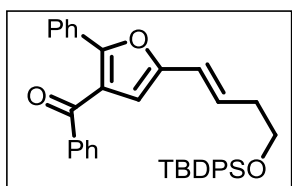


New compound, was synthesized according to the general procedure B.

The product was obtained by condition A in 66.4 mg, yield 99% (E:Z=11:1); condition B in 171.6 mg, yield 51% (E:Z=1:1) with 5100

TONs. Isolated by column chromatography (hexanes/ethyl acetate = 15: 1), yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 6.62 (s, 1H), 6.18 (s, 1H), 5.54 (s, 1H), 5.31 (s, 1H), 2.55 (s, 3H), 2.53 (s, 3H), 2.37 (s, 3H), 2.35 (s, 3H), 2.11 (s, 3H), 2.01 (s, 3H), 1.29-1.24 (m, 3H), 1.22-1.17 (m, 3H), 1.13 (d, $J = 7.1$ Hz, 18H), 1.10 (d, $J = 7.1$ Hz, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.7, 194.3, 156.1, 155.3, 153.5, 150.5, 150.1, 150.0, 122.8, 122.5, 106.2, 105.4, 98.7, 97.7, 29.2, 29.1, 23.6, 20.6, 18.1, 18.0, 14.5, 14.2, 13.7, 12.7. HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{33}\text{O}_3\text{Si}^+$ $[\text{M}+\text{H}]^+$ 337.2193, found 337.2193.

(E)-5-(4-((tert-butyl-diphenylsilyl)oxy)but-1-en-1-yl)-2-phenylfuran-3-yl(phenyl)methanone(2n)

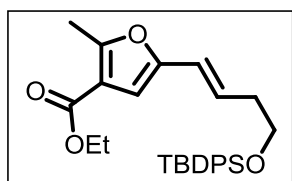


New compound, was synthesized according to the general procedure B. The product was obtained by condition B in 412.0 mg, yield 74% with 7400 TONs.

Isolated by column chromatography (hexanes/ethyl acetate = 15: 1), yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 7.92-7.86 (m, 2H), 7.80-7.74 (m, 2H),

7.77-7.71 (m, 4H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.47-7.38 (m, 9H), 7.35-7.29 (m, 2H), 6.45 (s, 1H), 6.45-6.37 (m, 1H), 6.30 (d, $J = 15.5$ Hz, 1H), 3.86 (t, $J = 6.5$ Hz, 2H), 2.53 (q, $J = 7.0$ Hz, 2H), 1.13 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 191.9, 154.6, 151.7, 138.2, 135.7, 134.0, 132.9, 129.9, 129.8, 129.8, 129.0, 128.8, 128.4, 128.4, 127.8, 127.5, 122.5, 119.5, 110.1, 63.5, 36.3, 27.0, 19.4. HRMS (ESI): calcd for $\text{C}_{37}\text{H}_{36}\text{O}_3\text{SiNa}^+$ $[\text{M}+\text{Na}]^+$ 579.2326, found 579.2329.

ethyl (E)-5-(4-((tert-butyl-diphenylsilyl)oxy)but-1-en-1-yl)-2-methylfuran-3-carboxylate(2o)

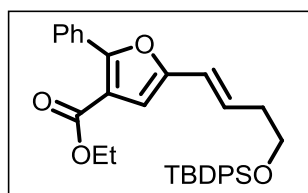


New compound, was synthesized according to the general procedure B. The product was obtained by condition B in 351.6 mg, yield 76% with 7600

TONs. Isolated by column chromatography (hexanes/ethyl acetate = 30: 1), yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 7.77-7.71 (m, 4H), 7.49-7.35

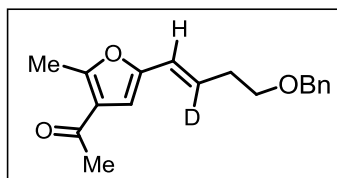
(m, 6H), 6.42 (s, 1H), 6.25-6.16 (m, 2H), 4.33 (q, $J = 7.5$ Hz, 2H), 3.83 (t, $J = 6.5$ Hz, 2H), 2.62 (s, 3H), 2.48 (q, $J = 4.5$ Hz, 2H), 1.38 (t, $J = 7.5$ Hz, 3H), 1.13 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 164.1, 158.2, 151.0, 135.7, 133.9, 129.7, 127.7, 126.9, 119.7, 114.9, 106.8, 63.5, 60.1, 36.2, 26.9, 19.3, 14.4, 13.9. HRMS (ESI): calcd for $\text{C}_{28}\text{H}_{34}\text{O}_4\text{SiNa}^+$ $[\text{M}+\text{Na}]^+$ 485.2119, found 485.2120.

ethyl (*E*)-5-(4-((tert-butyldiphenylsilyl)oxy)but-1-en-1-yl)-2-phenylfuran-3-carboxylate(2p)



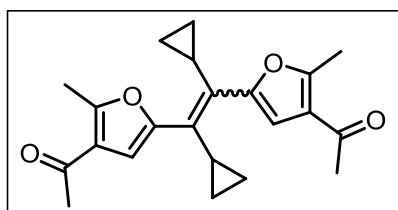
New compound, was synthesized according to the general procedure B. The product was obtained by condition B in 446.0 mg, yield 85% with 8500 TONs. Isolated by column chromatography (hexanes/ethyl acetate = 15: 1), yellow liquid. ¹H NMR (500 MHz, CDCl₃) δ 8.07-8.02 (m, 2H), 7.71 (dd, *J* = 7.8, 1.7 Hz, 4H), 7.50-7.34 (m, 9H), 6.60 (s, 1H), 6.37-6.30 (m, 1H), 6.26 (d, *J* = 16.0 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.83 (t, *J* = 6.5 Hz, 2H), 2.50 (q, *J* = 6.5 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.10 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 163.7, 156.1, 151.7, 135.7, 134.0, 130.0, 129.8, 129.3, 128.6, 128.4, 128.2, 127.8, 119.6, 115.4, 109.2, 63.5, 60.6, 36.3, 27.0, 19.4, 14.4. HRMS (ESI): calcd for C₃₃H₃₆O₄SiNa⁺ [M+Na]⁺ 547.2275, found 547.2278.

(*E*)-1-(5-(5-(benzyloxy)pent-1-en-1-yl-2-d)-2-methylfuran-3-yl)ethan-1-one(2q)



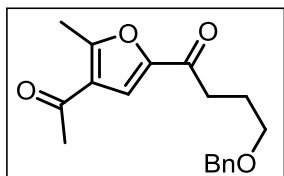
New compound, was synthesized according to the general procedure B. The product was obtained by condition A in 47.3 mg, yield 79%. Isolated by column chromatography (hexanes/ethyl acetate = 15: 1), yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.28 (m, 5H), 6.33 (s, 1H), 6.20-6.16 (m, 1H), 4.54 (s, 2H), 3.58 (t, *J* = 6.6 Hz, 2H), 2.58 (s, 3H), 2.49 (td, *J* = 6.6, 1.7 Hz, 2H), 2.37 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 194.3, 157.7, 150.8, 138.4, 128.5, 127.8, 127.7, 122.8, 119.3, 106.6, 73.1, 69.5, 33.2, 29.2, 14.5. HRMS (ESI): calcd for C₁₈H₁₉DO₃⁺ [M+H]⁺ 286.1548, found 286.1547.

1,1'-((1,2-dicyclopropylethene-1,2-diyl)bis(2-methylfuran-5,3-diyl))bis(ethan-1-one) (2r)



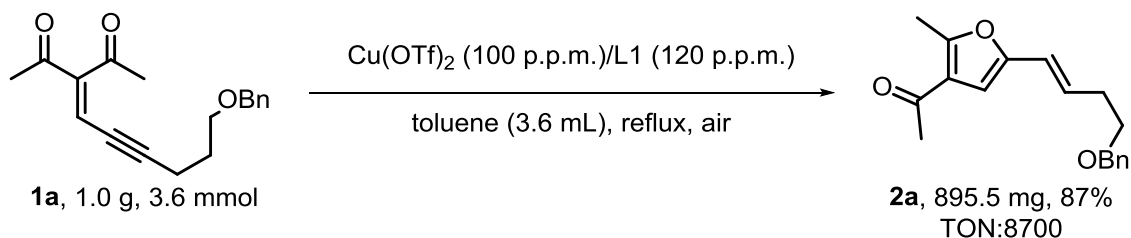
Reported compound,¹ was synthesized according to the general procedure B. The product was obtained by condition A in 34.7 mg, yield 99% (E:Z=1:1); condition B in 172.4 mg, yield 98% (E:Z=1:1) with 9800 TONs. Isolated by column chromatography (hexanes/ethyl acetate = 15: 1), yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 6.61 (s, 1H), 6.24 (s, 1H), 2.59 (s, 3H), 2.41 (s, 6H), 2.31 (s, 3H), 2.04-1.94 (m, 1H), 1.77-1.68 (m, 1H), 0.91-0.85 (m, 2H), 0.70-0.64 (m, 2H), 0.59-0.53 (m, 2H), 0.36-0.29 (m, 2H).

1-(4-acetyl-5-methylfuran-2-yl)-4-(benzyloxy)butan-1-one (3a)



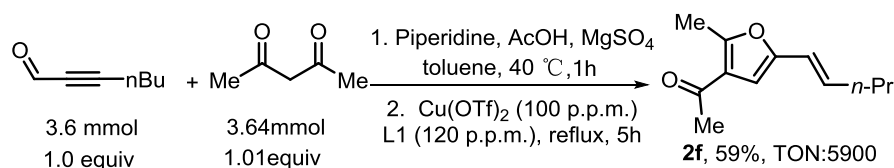
Reported compound,¹ was synthesized according to the general procedure A without **L1**. Isolated by column chromatography (hexanes/ethyl acetate = 8:1) in 58.2 mg, 97%, yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 7.36 (s, 1H), 7.35-7.29 (m, 4H), 7.29-7.26 (m, 1H), 4.48 (s, 2H), 3.55 (t, *J* = 6.0 Hz, 2H), 2.91 (t, *J* = 7.2 Hz, 2H), 2.66 (s, 3H), 2.42 (s, 3H), 2.07-2.00 (m, 2H).

5. A Gram-Scale Synthesis of 2-Alkenylfuran 2a from 1a:



General procedure C: An oven-dried flask (200 mL) was charged with Cu(OTf)₂ (1.8 mg) and **L1** (2.3 mg) in acetone (100 mL) and stirred at room temperature for 1 h. The solution (7.2 mL) was added to the reaction flask with a syringe and was concentrated under vacuum. The solution of **1a** (1.0 g, 3.6 mmol, 1.0 eq) in toluene (3.6 mL) was added to the flask. The resulting mixture was refluxed for 7 h, and the progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was concentrated under vacuum. The residue was purified by chromatography on silica gel (eluant: hexanes/ethyl acetate = 15:1) to afford the desired product **2a** (895.5 mg) in 87% yield as a yellow liquid.

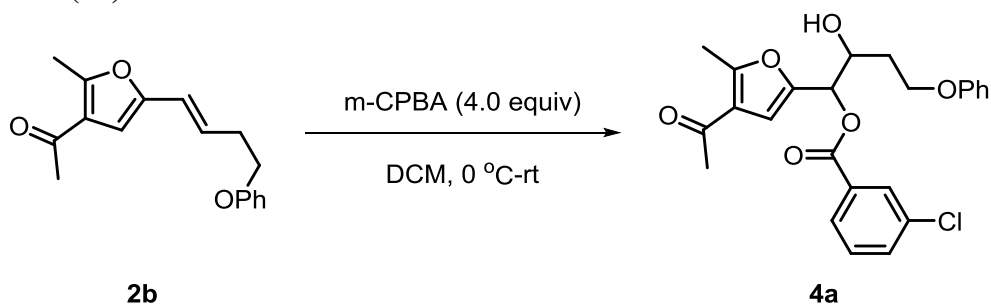
6. A One-Pot Synthesis of 2f from Hept-2-ynal:



General procedure D: Hept-2-ynal (396.6 mg, 3.6 mmol, 1.0 eq) was added to a mixture of HOAc (129.7 mg, 2.2 mmol, 0.6 eq), piperidine (30.7 mg, 0.36 mmol, 0.1 eq) and acetylacetone

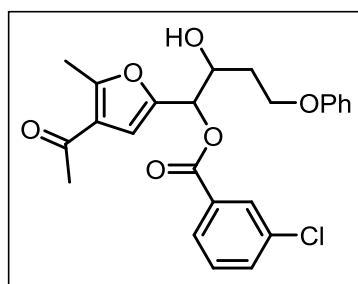
(364.0 mg, 3.64 mmol, 1.01 eq) in toluene (12 mL). MgSO_4 (86.7 mg, 0.72 mmol, 0.2 eq) was introduced and the suspension was stirred at 40°C for 1 h. Then $\text{Cu}(\text{OTf})_2$ (0.13 mg) and **L1** (0.14 mg) were added to the reaction. The resulting mixture was refluxed for about 5 hours, and the progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was concentrated under vacuum. The residue was purified by chromatography on silica gel (eluant: hexanes/ethyl acetate = 15:1) to afford the desired product **2f** (408.4 mg) in 59% yield.

7. Synthesis of 1-(4-acetyl-5-methylfuran-2-yl)-1-hydroxy-4-phenoxybutan-2-yl 3-chlorobenzoate(**4a**)³:



General procedure E: To a DCM (5 mL) solution of (*E*)-1-(2-methyl-5-(4-phenoxybut-1-en-1-yl)furan-3-yl)ethan-1-one **2b** (135.2 mg, 0.5 mmol, 1.0 eq) was added a *m*-CPBA (138.1 mg, 2 mmol, 4.0 eq) at 0°C and the reaction is stirred at room temperature for 2 h. Upon completion, the reaction mixture was concentrated under vacuum. The residue was purified by chromatography on silica gel (eluant: hexanes/ethyl acetate = 4:1) to afford the desired product **4a** (143.9 mg, 0.33 mmol) in 65% yield as a yellow liquid.

1-(4-acetyl-5-methylfuran-2-yl)-1-hydroxy-4-phenoxybutan-2-yl 3-chlorobenzoate(**4a**)



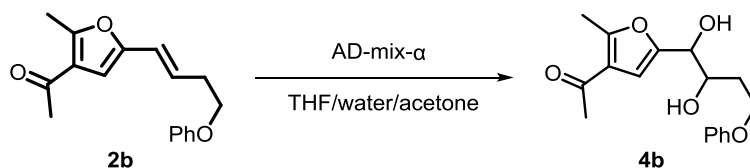
New compound, was synthesized according to the general procedure E.

Isolated by column chromatography (hexanes/ethyl acetate = 3: 1) in 143.9 mg, 65%, yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 8.05 (t, J = 1.5 Hz, 1H), 7.96 (dt, J = 8.0, 1.5 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 7.29 (d, J = 7.8 Hz, 2H), 6.95 (t, J = 7.5 Hz, 1

H), 6.90 (d, J = 8.0 Hz, 2H), 6.73 (s, 1H), 6.01 (d, J = 7.0 Hz, 1H), 4.54 (s, 1H), 4.25-4.19 (m, 1H), 4.18-4.11 (m, 1H), 2.68 (s, 1H), 2.57 (s, 3H), 2.38 (s, 3H), 2.03-1.90 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 193.9, 164.7, 159.1, 158.6, 147.9, 134.8, 133.6, 131.5, 130.0, 129.7, 128.1, 122.2, 121.2, 114.6, 111.2, 72.8, 69.6, 64.6, 32.6, 29.2, 14.6. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{23}\text{ClO}_6\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 465.1075,

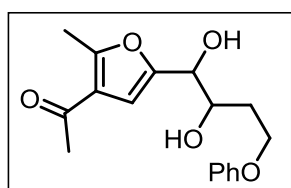
found 465.1076.

8. Synthesis of 1-(5-(1,2-dihydroxy-4-phenoxybutyl)-2-methylfuran-3-yl)ethan-1-one(4b)⁴:



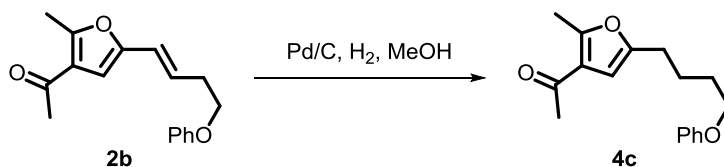
General procedure F: A solution of **2b** (135.2 mg, 0.5 mmol, 1.0 eq), from above, in THF (0.2 mL) was added dropwise to a stirred suspension of commercial AD-mix- α (840 mg, 0.6 mmol, 1.2 eq) in 1:1:1 water:THF:acetone (3.6 mL) and the mixture was then stirred at room temperature overnight. The mixture was quenched with sat. Na₂SO₃ solution (2 mL) and then extracted with EtOAc (3 x 3 mL). The combined organic extracts were washed with sat. Na₂SO₃ solution and brine, and then dried over MgSO₄. The solvents were removed in vacuo and the residue was purified by flash chromatography on silica gel (eluant: petroleum ether:diethyl ether = 2:1 to Et₂O) to give the title compound **4b** as a white solid (129.3 mg, 85%).

1-(5-(1,2-dihydroxy-4-phenoxybutyl)-2-methylfuran-3-yl)ethan-1-one(4b)



New compound, was synthesized according to the general procedure F. Isolated by column chromatography (hexanes/ethyl acetate = 1: 1) in 129.3 mg, 85%, white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.26 (t, J = 8.0 Hz, 2H), 6.94 (t, J = 7.2 Hz, 1H), 6.87 (d, J = 8.0 Hz, 2H), 4.51 (t, J = 5.6 Hz, 1H), 4.23-4.05 (m, 3H), 3.58 (d, J = 5.2 Hz, 1H), 3.39 (d, J = 4.0 Hz, 1H), 2.53 (s, 3H), 2.34 (s, 3H), 2.00-1.89 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 194.5, 158.5, 151.9, 129.6, 122.0, 121.1, 114.5, 108.4, 70.9, 70.8, 64.9, 32.6, 29.2, 14.5. HRMS (ESI): calcd for C₁₇H₂₀O₅Na⁺ [M+Na]⁺ 327.1203, found 327.1202.

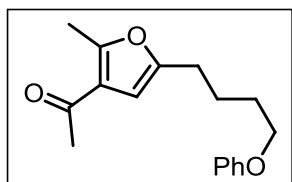
9. Synthesis of 1-(2-methyl-5-(4-phenoxybutyl)furan-3-yl)ethan-1-one(4c)⁵:



General procedure G: A solution of **2b** (135.2 mg, 0.5 mmol 1.0 eq) in methanol (1 mL) was added Pd/C (10 %, 7.0 mg, 0.05 mmol, 0.1 eq) in methanol (4 mL). The flask was evacuated, placed under an hydrogen atmosphere (balloon) and stirred for 3 h at rt. The mixture was then filtered over

celite and the filter cake was washed several times with methanol. The solvents were removed in vacuo and the residue was purified by flash chromatography on silica gel (eluant: hexanes/ethyl acetate = 10:1) to give the title compound **4c** (129.4 mg, 0.48 mmol, 95%) as a yellow liquid .

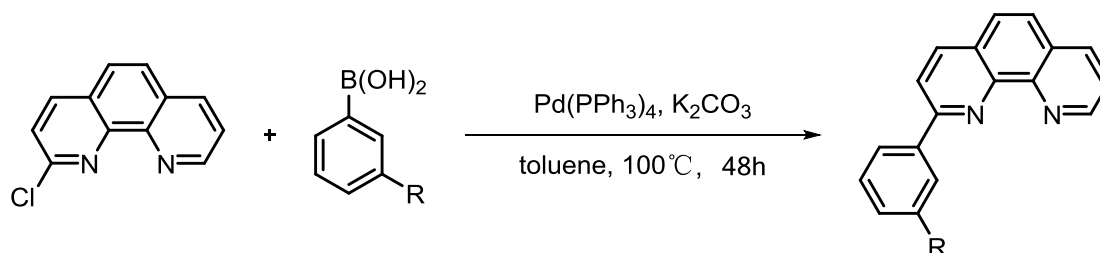
1-(2-methyl-5-(4-phenoxybutyl)furan-3-yl)ethan-1-one(4c)



New compound, was synthesized according to the general procedure G. Isolated by column chromatography (hexanes/ethyl acetate = 10: 1) in 129.4 mg, 95%, yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.28 (t, J = 8.8 Hz, 2H), 6.94 (t, J = 7.3 Hz, 1H), 6.89 (d, J = 8.0 Hz, 2H), 6.23 (s, 1H), 3.98 (t, J = 5.7 Hz, 2H), 2.65 (t, J = 6.6 Hz, 2H), 2.55 (s, 3H), 2.37 (s, 3H), 1.90-1.73 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.5, 159.0, 157.1, 153.8, 129.6, 122.1, 120.7, 114.5, 105.7, 67.4, 29.2, 28.7, 27.5, 24.5, 14.5. HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 295.1305, found 295.1309.

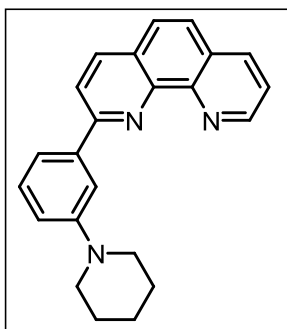
10. Synthesis of Ligands:

Ligands **L1-L4**, **L7**, **L9** are known in the literature⁶.



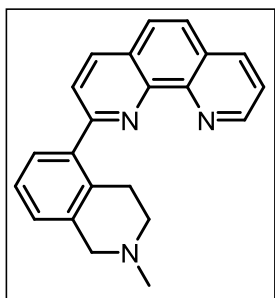
General procedure H: An oven-dried flask (25 mL) was charged with 3-chlorophenanthrene (214.0 mg, 1.0 mmol, 1.1 eq) and phenylboronic acid (0.92 mmol, 1.0 eq). The mixture was dissolved in toluene (8 mL) and purged with N_2 for 10 min. Aq. K_2CO_3 (1M, 4 mL) was added under N_2 purging, followed by $\text{Pd}(\text{PPh}_3)_4$ (53.2 mg, 5 mol%). After purging with N_2 for an additional 10 min, the pressure tube was closed and heated at 100°C for 48 h. Upon cooling to room temperature, the reaction mixture was filtered to remove insoluble impurities. The filtrate was then extracted with CH_2Cl_2 (3×5 mL). The organic layers were collected, dried over Na_2SO_4 purified by chromatography on neutral Al_2O_3 (eluant: hexanes/ethyl acetate = 1:1) to give product.

1-(3-(phenanthren-3-yl)phenyl)piperidine (L4)



New compound, was synthesized according to the general procedure H. Isolated by column chromatography (hexanes/ethyl acetate = 1: 1) in 133.5 mg, 43%, yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 9.20 (dd, $J = 4.4, 1.6$ Hz, 1H), 8.23 (d, $J = 8.4$ Hz, 1H), 8.20 (dd, $J = 8.0, 1.6$ Hz, 1H), 8.03 (d, $J = 8.4$ Hz, 1H), 7.87 (t, $J = 2.0$ Hz, 1H), 7.78-7.68 (m, 3H), 7.59 (dd, $J = 8.0, 4.4$ Hz, 1H), 7.40 (t, $J = 8.4$ Hz, 1H), 7.07-7.02 (m, 1H), 3.29 (t, $J = 5.2$ Hz, 4H), 1.81-1.69 (m, 4H), 1.64-1.54 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.5, 152.9, 150.3, 146.5, 146.1, 140.7, 136.7, 136.1, 129.4, 129.1, 127.5, 126.4, 126.1, 122.9, 121.1, 119.3, 117.7, 116.2, 50.9, 26.0, 24.4. HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{22}\text{N}_3^+$ $[\text{M}+\text{H}]^+$ 340.1808, found 340.1807.

2-(2-methyl-1,2,3,4-tetrahydroisoquinolin-5-yl)-1,10-phenanthroline (L5)



New compound, was synthesized according to the general procedure H. Isolated by column chromatography (hexanes/ethyl acetate = 1: 1) in 163.7 mg, 55%, yellow solid. ^1H NMR (500 MHz, CDCl_3) δ 9.16 (d, $J = 4.5$ Hz, 1H), 8.21 (dd, $J = 15.0, 8.1$ Hz, 2H), 7.76 (q, $J = 8.7$ Hz, 2H), 7.66 (d, $J = 8.5$ Hz, 1H), 7.57 (dd, $J = 8.1, 4.3$ Hz, 1H), 7.37 (d, $J = 7.5$ Hz, 1H), 7.20 (t, $J = 7.5$ Hz, 1H), 7.05 (d, $J = 7.5$ Hz, 1H), 3.64 (s, 2H), 2.96 (t, $J = 6.0$ Hz, 2H), 2.60 (t, $J = 6.0$ Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 160.4, 150.6, 146.5, 146.1, 141.1, 136.1, 136.1, 135.2, 132.1, 129.0, 128.3, 127.3, 126.9, 126.5, 125.8, 124.3, 123.0, 58.6, 53.1, 46.1, 28.0. HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{19}\text{N}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 348.1471, found 348.1474.

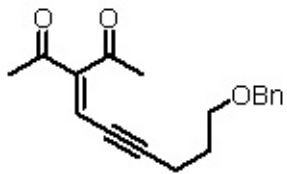
Reference

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- 2 M. Li, F. Yang, T. Yuan, H. Li, J. Li, Z. S. Chen and K. Ji, *J. Org. Chem.*, 2019, **84**, 12617-12625.
- 3 S. D. Tanpure, T.-C. Kuo, M.-J. Cheng and R.-S. Liu, *ACS Catal.*, 2021, **12**, 536-543.
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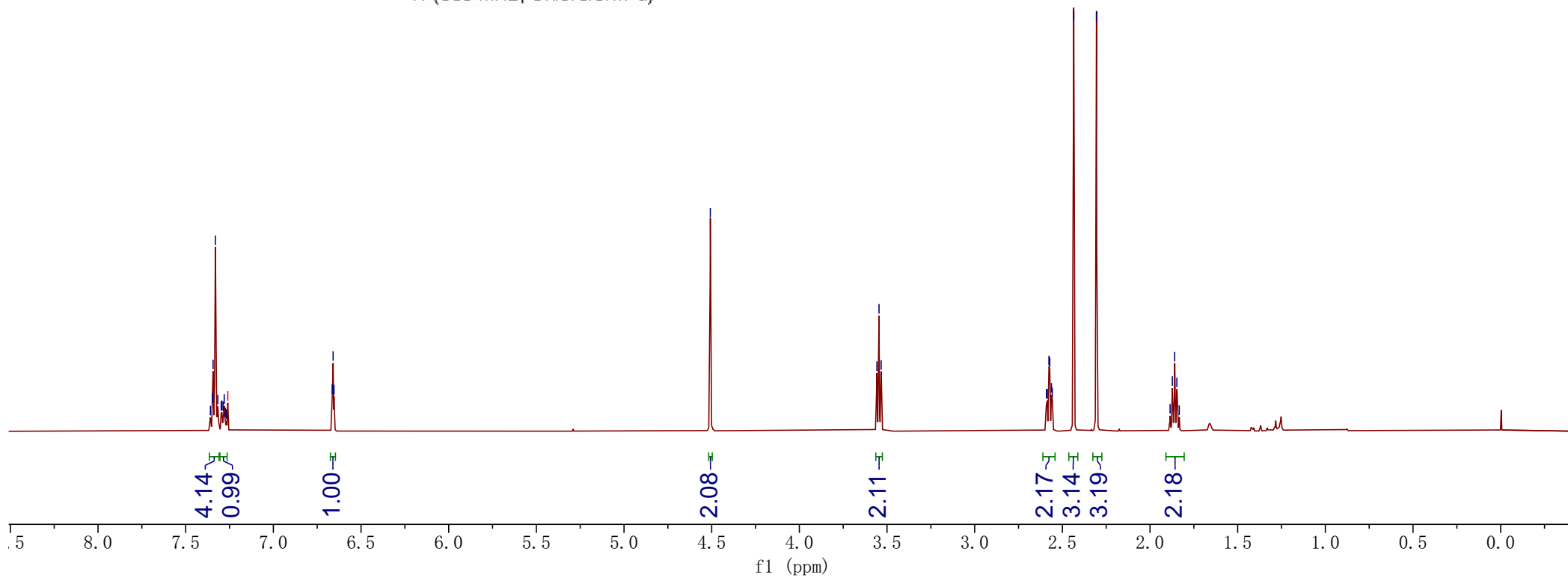
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6.659
6.654

4.508

3.558
3.546
3.534
2.591
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1.873
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1.847
1.833



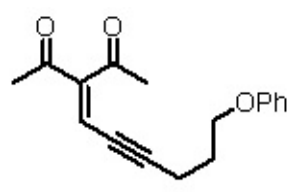
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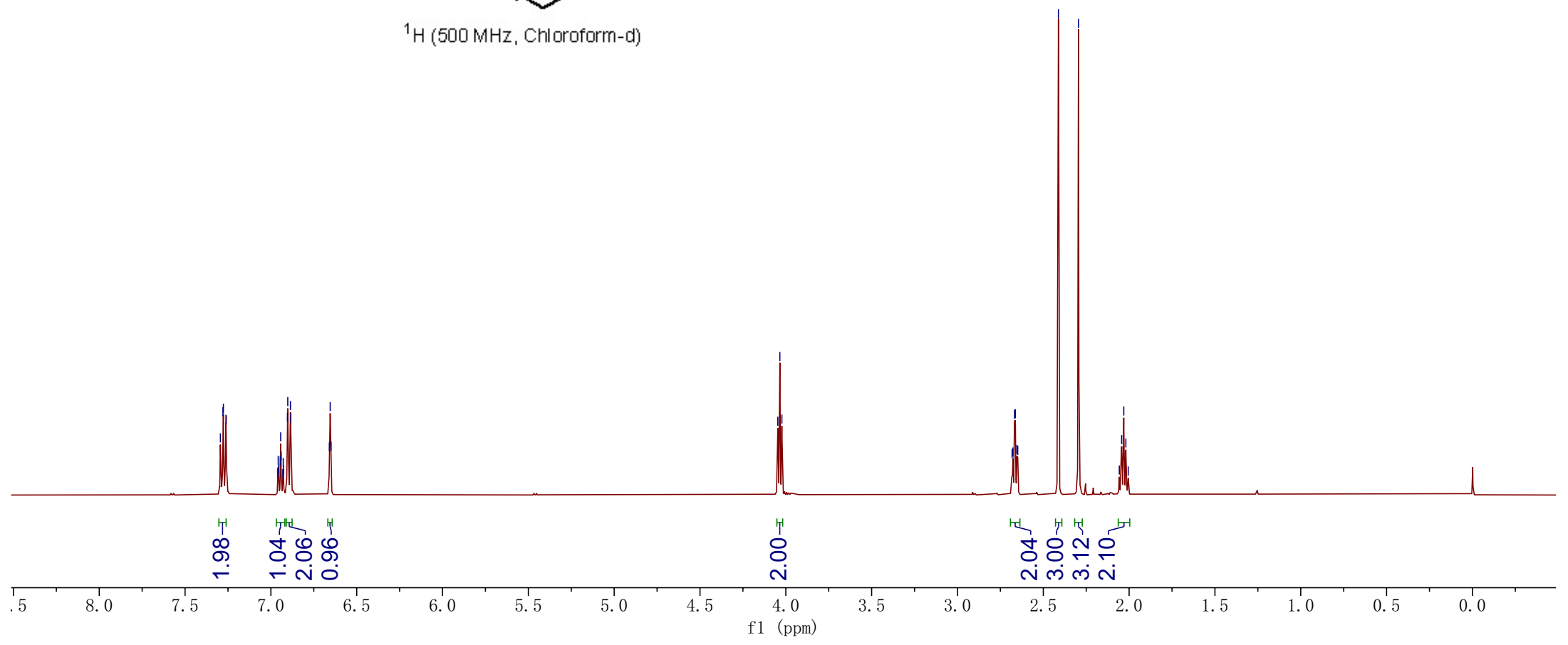
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6.650

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4.035
4.023

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¹H (500 MHz, Chloroform-d)



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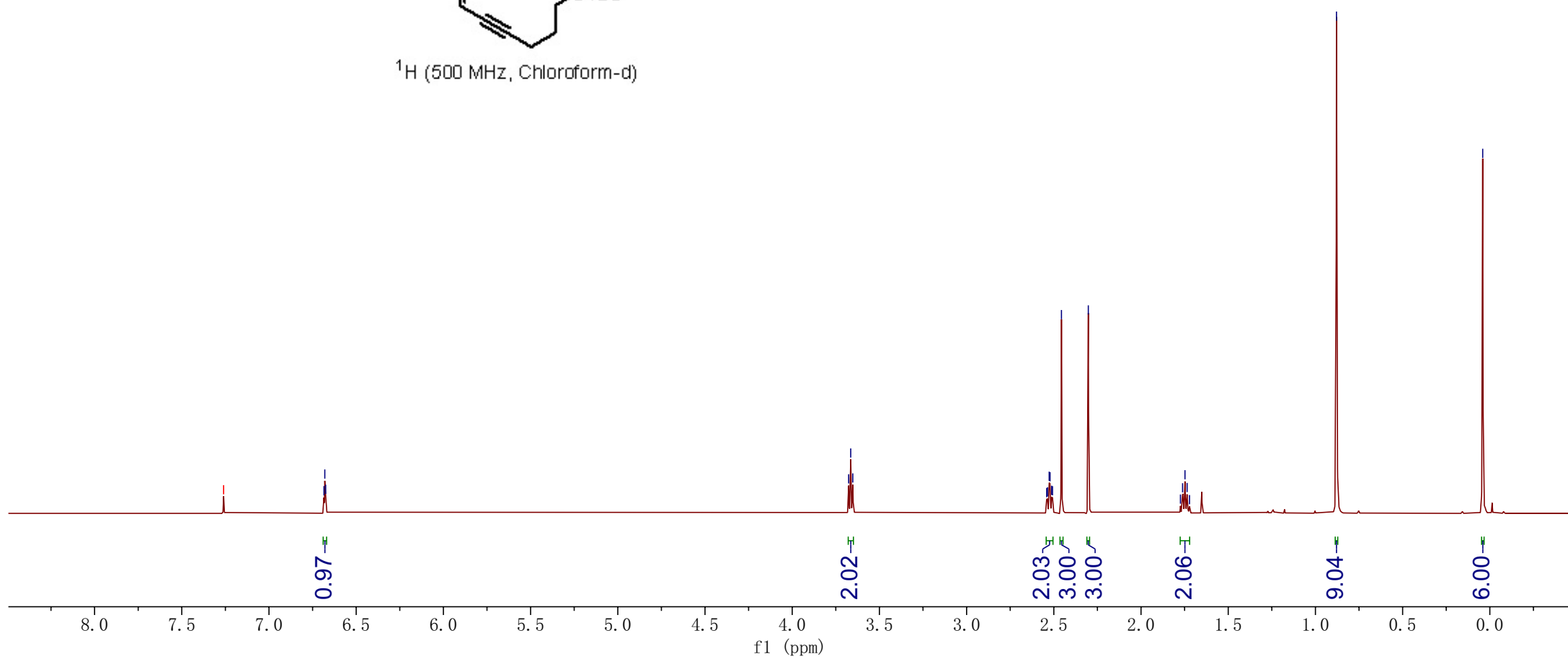
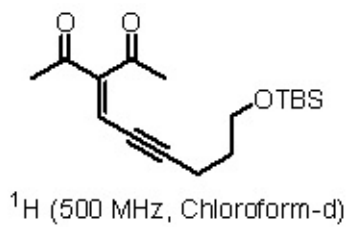
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—0.041



— 7.260 CDCl₃

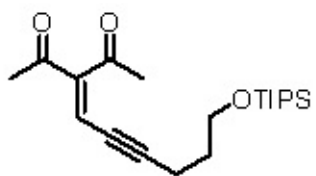
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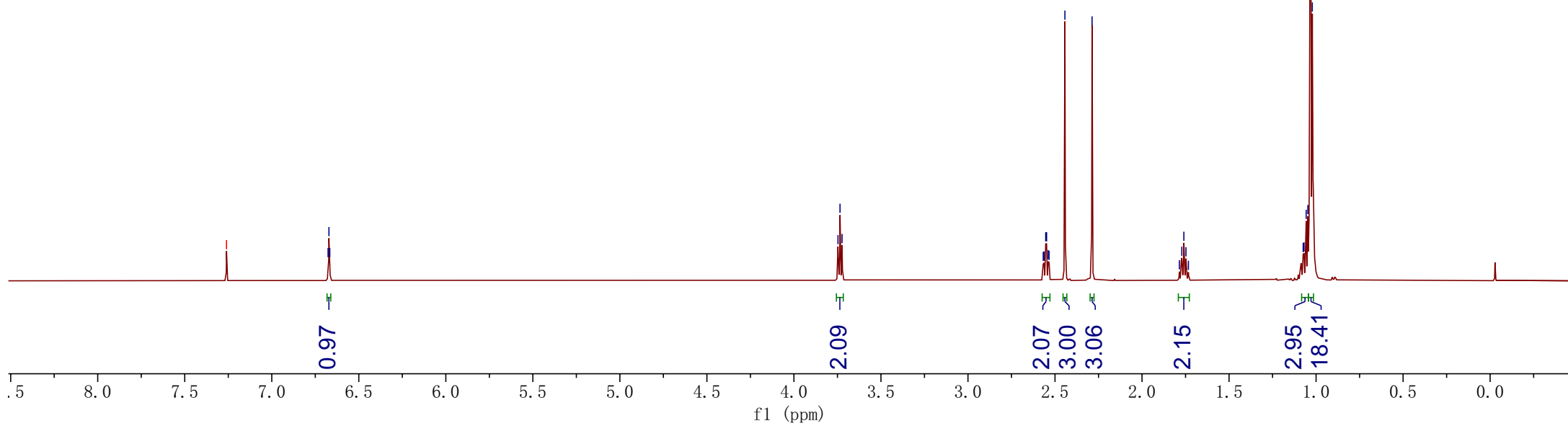
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2.548
2.539
2.534
2.443
2.287

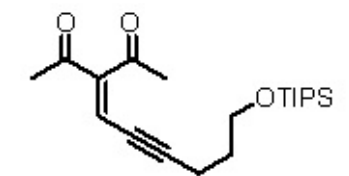
1.786
1.771
1.760
1.748
1.734
1.074

1.069
1.057
1.047
1.032
1.022

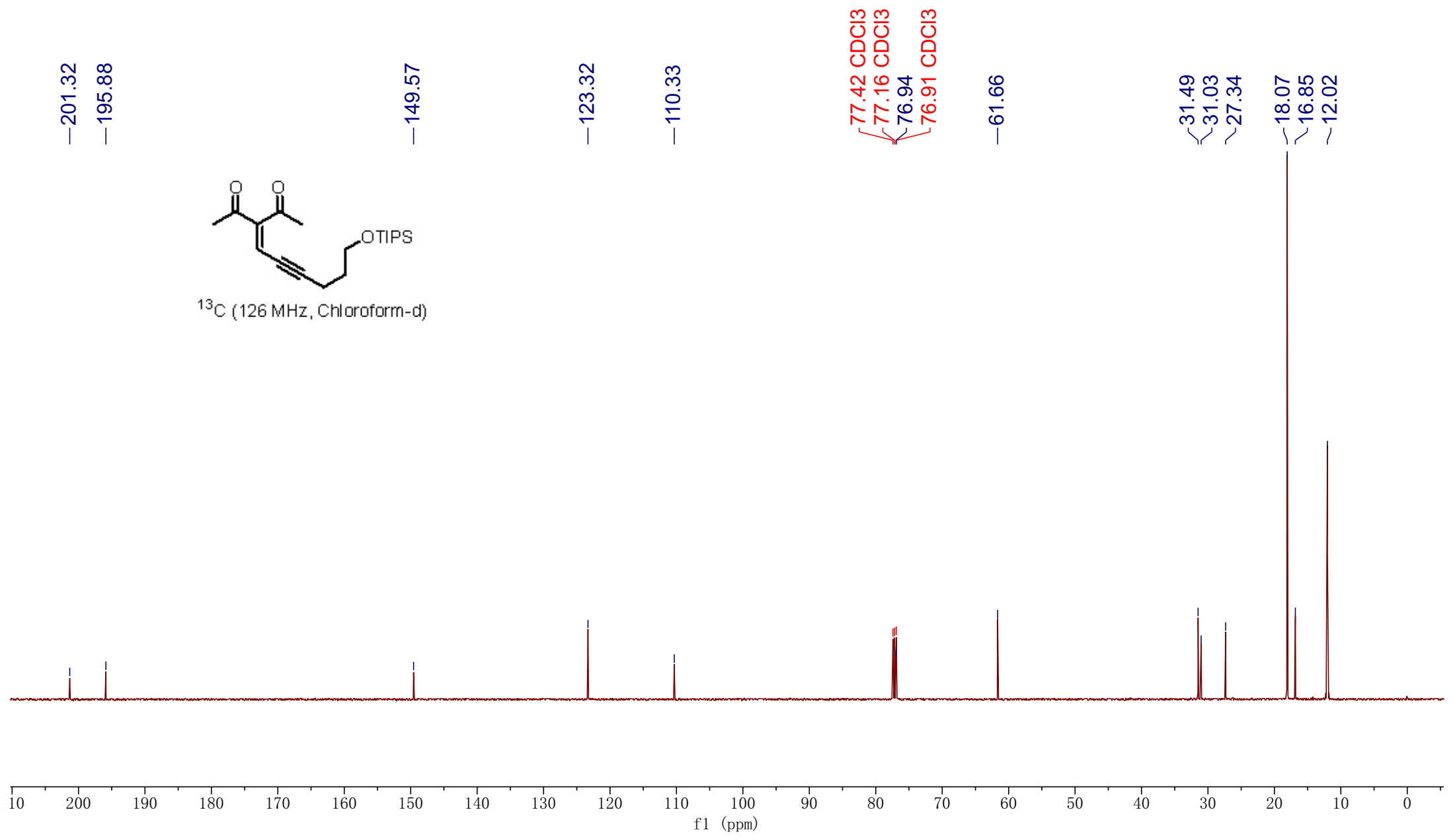


¹H (500 MHz, Chloroform-d)

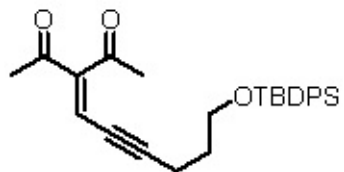




¹³C (126 MHz, Chloroform-d)



7.674
7.671
7.658
7.655
7.435
7.420
7.403
7.389
7.375
7.269 CDCI3
6.673
6.668
6.663



¹H (500 MHz, Chloroform-d)

3.753
3.742
3.730

2.629
2.624
2.614
2.609
2.600
2.595
2.426
2.317
1.836
1.822
1.810
1.797
1.784

1.063

4.15

6.31

0.97

2.13

2.05

3.00

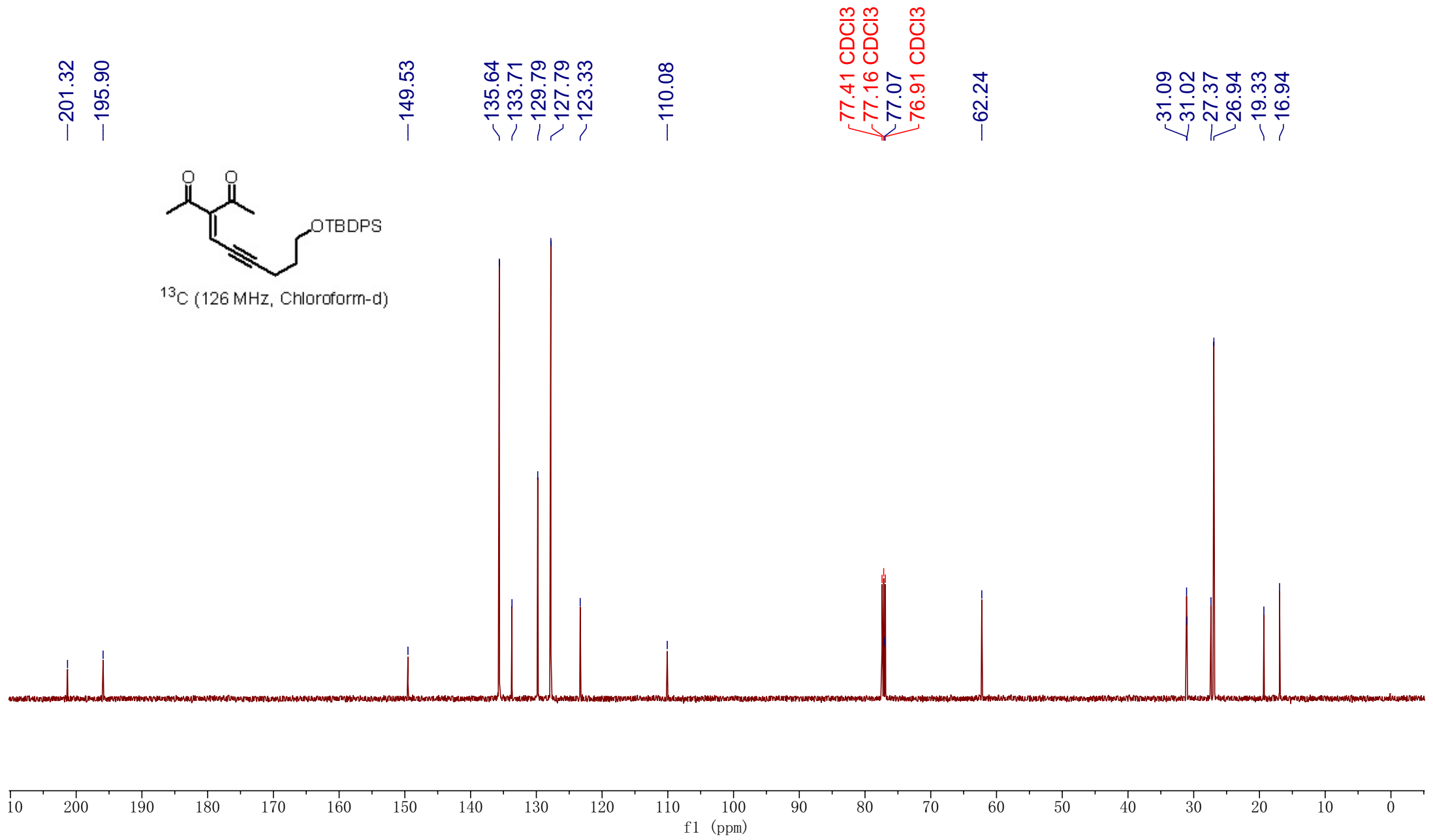
3.07

2.08

9.16

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 -0.0

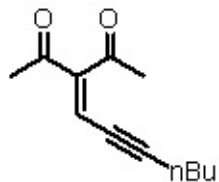
f1 (ppm)



—7.260 CDCI3

6.684
6.682
6.679
6.674
6.672

2.452
2.450
2.441
2.436
2.426
2.422
2.412
2.408
2.293
2.291
1.563
1.549
1.534
1.520
1.505
1.439
1.424
1.408
1.394
1.379
1.365
0.921
0.919
0.906
0.904
0.892
0.890



¹H (500 MHz, Chloroform-d)

1.00

3.00

2.10

3.07

2.13

2.20

3.13

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

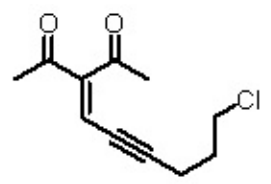
f1 (ppm)

-7.260 CDCl3

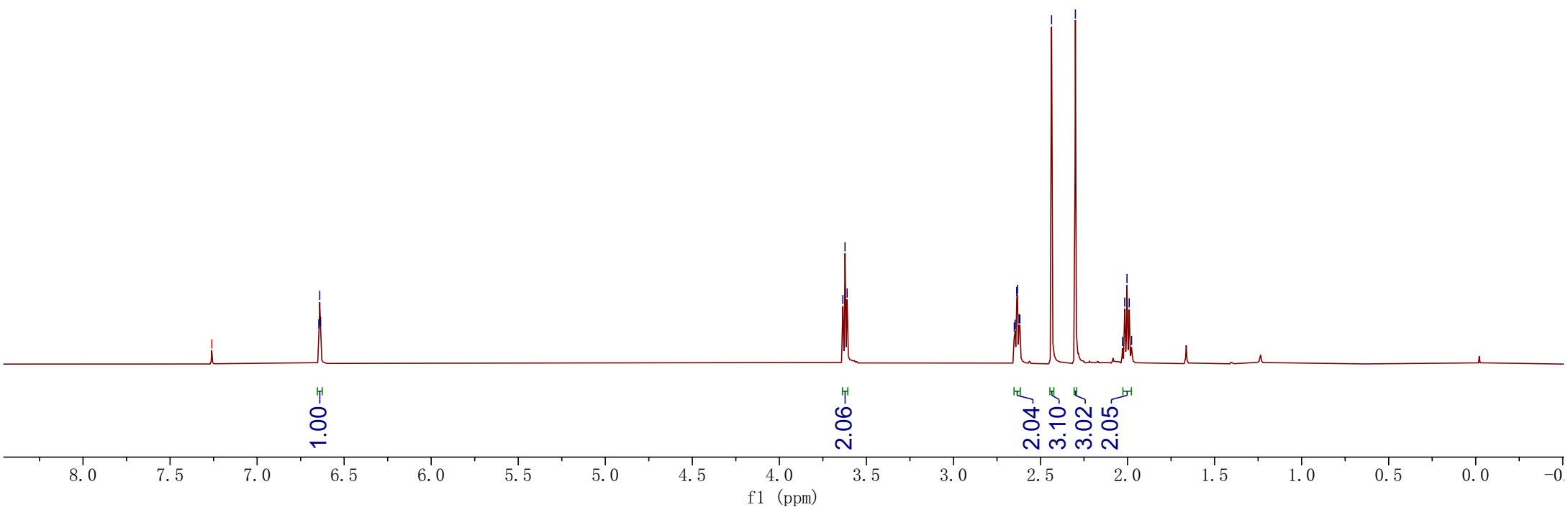
6.645
6.640
6.635

3.635
3.623
3.611

2.650
2.646
2.637
2.632
2.623
2.618
2.436
2.300
2.029
2.016
2.003
1.990
1.977



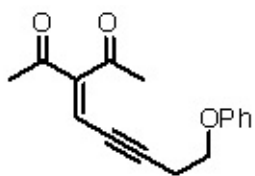
¹H (500 MHz, Chloroform-d)



7.285
7.269
7.260 CDCI3
7.253
6.964
6.949
6.935
6.882
6.866
6.666
6.661
6.656

4.097
4.084
4.071

2.908
2.903
2.895
2.890
2.882
2.877
2.440
2.279



¹H (500 MHz, Chloroform-d)

2.07

0.98

2.00

0.96

2.05

2.04

3.00

3.00

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 -0.0

f1 (ppm)

—201.21
—195.71

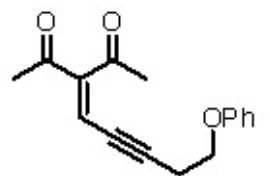
—158.18
—150.13

—129.54
~122.34
~121.25
~114.56
—105.54

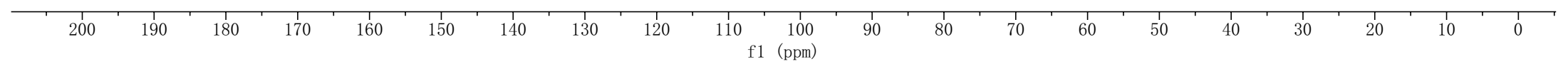
77.85
77.41 CDCI3
77.16 CDCI3
76.90 CDCI3

—65.20

~30.90
~27.18
~21.27



¹³C (126 MHz, Chloroform-d)



—7.260 CDCl3

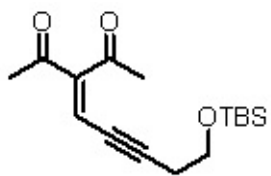
—6.680

3.765
3.754
3.742

2.655
2.647
2.640
2.634
2.626
2.470
2.301

—0.883

—0.059



¹H (500 MHz, Chloroform-d)

0.93

2.05

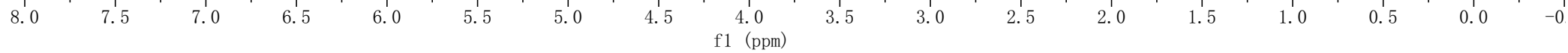
2.03

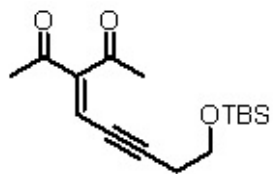
2.89

3.00

9.27

6.00





^{13}C (126 MHz, Chloroform-d)

—201.29

—195.84

—149.85

—122.95

—107.32

77.78
77.41 CDCl₃
77.16 CDCl₃
76.91 CDCl₃

—61.23

~31.11

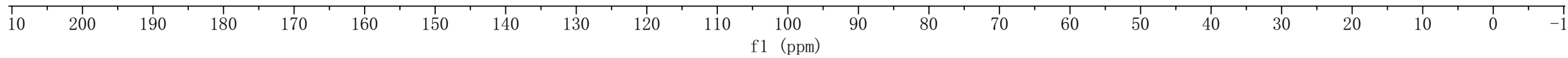
~27.45

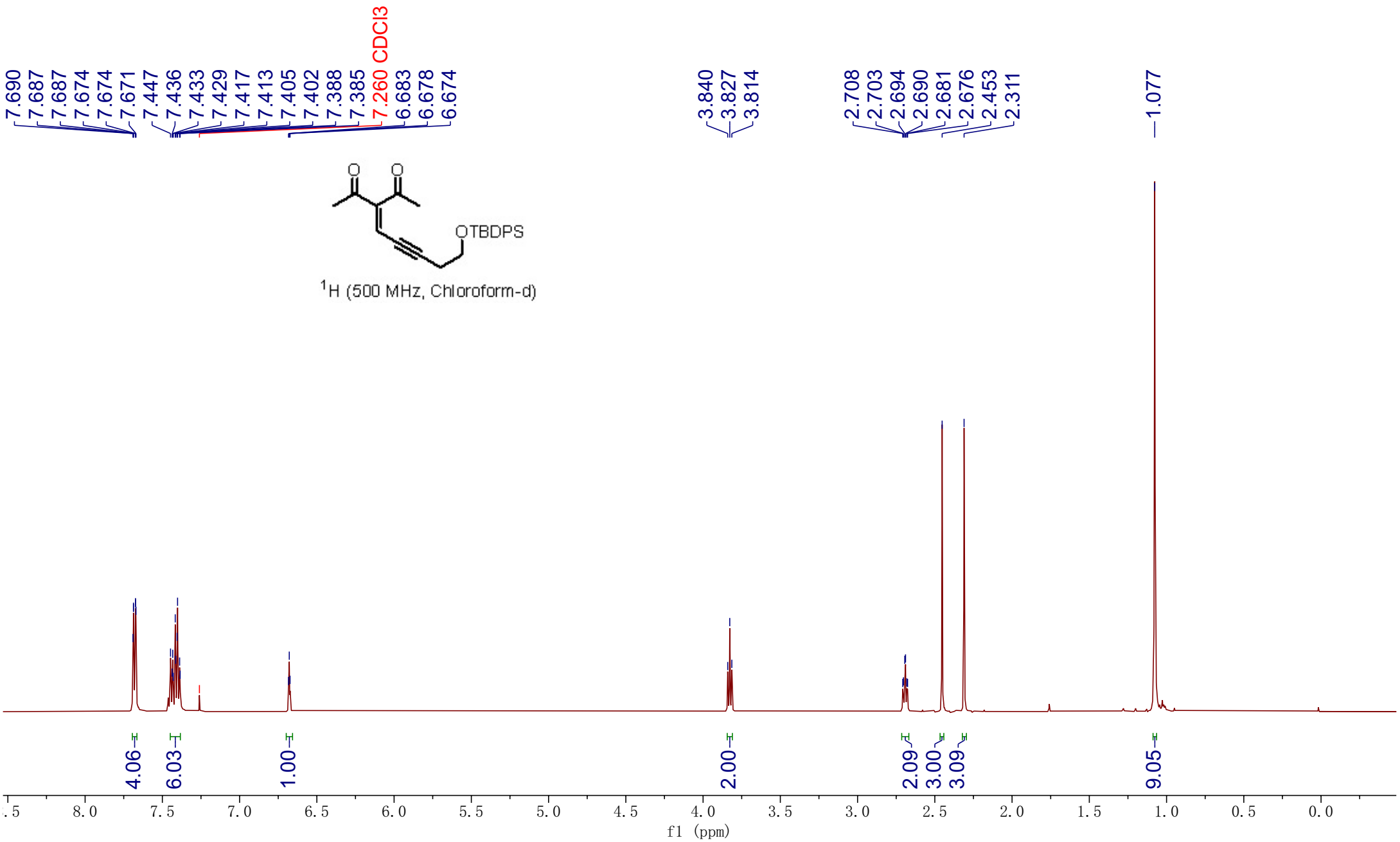
~25.96

~24.79

~18.40

—-5.20





—201.20
—195.79

—149.70

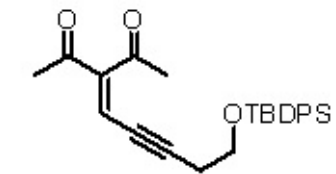
—135.59
—133.34
—129.89
—127.83
—122.89

—107.27

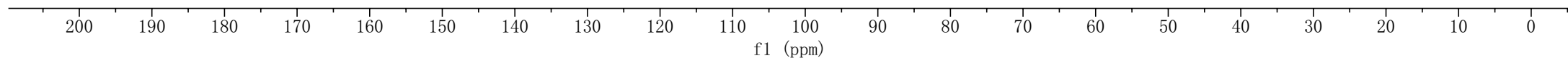
77.78
77.41 CDCI3
77.16 CDCI3
76.90 CDCI3

—61.81

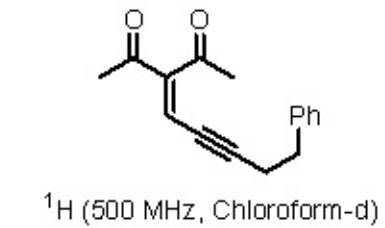
—31.03
—27.39
—26.84
—24.46
—19.24



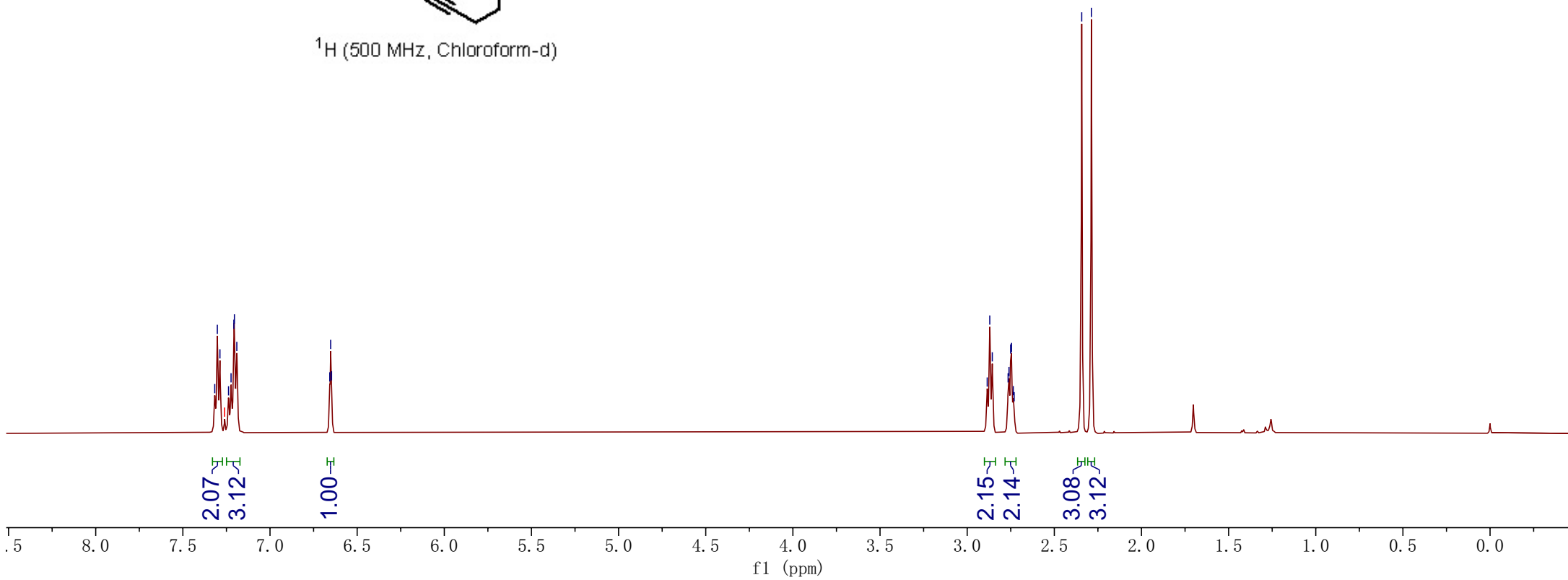
¹³C (126 MHz, Chloroform-d)



7.317
7.302
7.287
7.260 CDCl₃
7.238
7.224
7.207
7.204
7.190



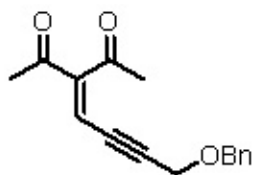
2.885
2.870
2.856
2.765
2.760
2.751
2.746
2.736
2.731
2.343
2.287



7.361
7.348
7.337
7.324
7.308
7.260 CDCl₃
6.703
6.699
6.695

4.592
4.375
4.371

2.470
2.329



¹H (500 MHz, Chloroform-d)

5.30

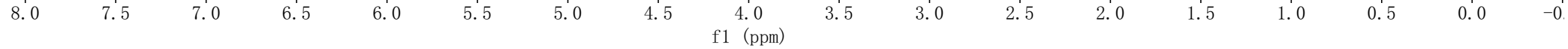
0.97

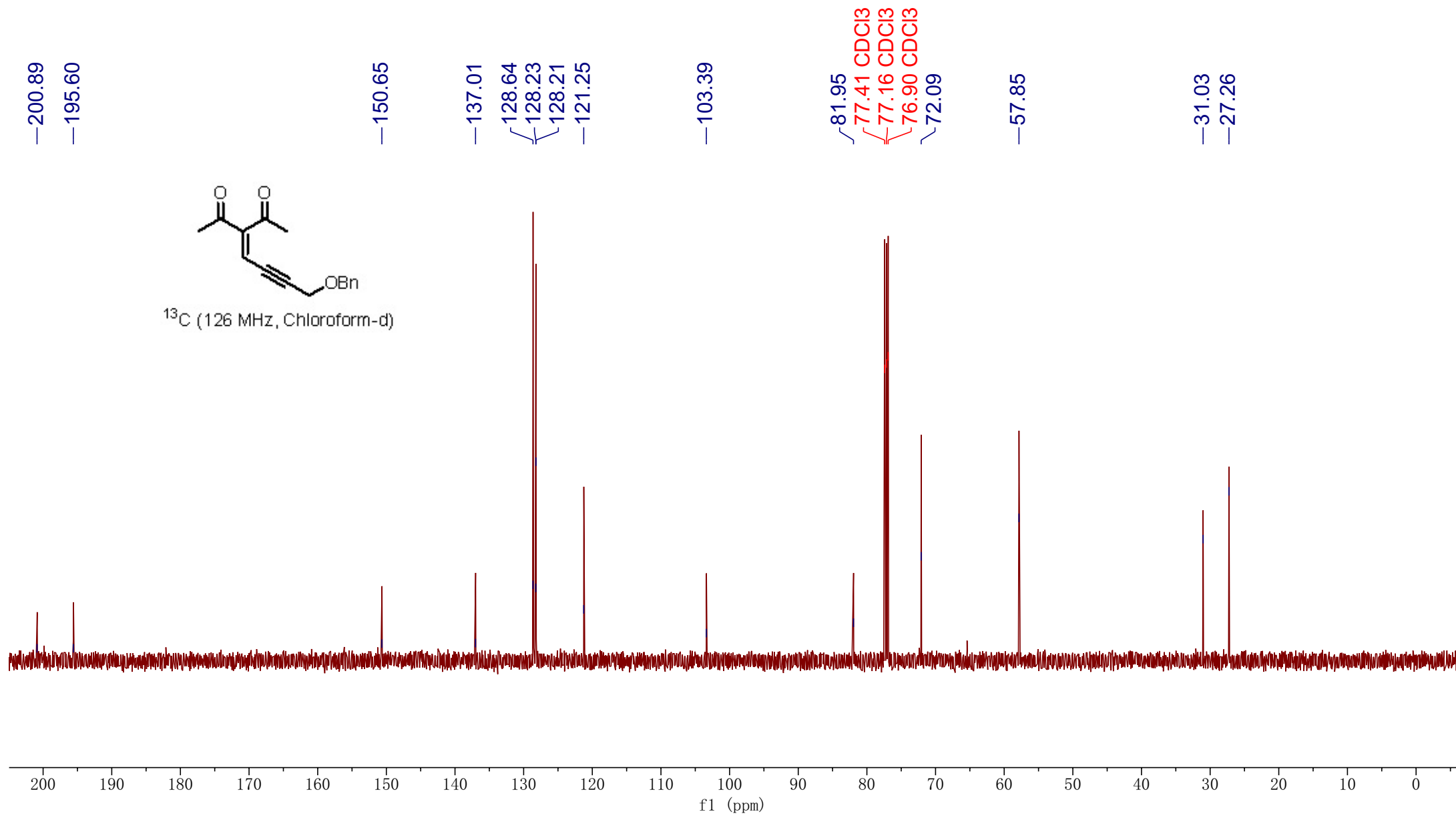
2.08

2.07

3.00

3.06





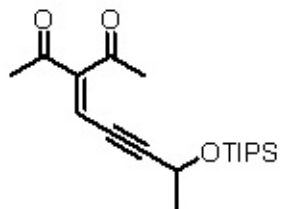
—7.260 CDCl₃

—6.706

4.813
4.800
4.787
4.774

—2.468
—2.311

1.488
1.475
1.074
1.066



¹H (500 MHz, Chloroform-d)

1.00

1.05

3.00

3.08

3.09

21.25

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

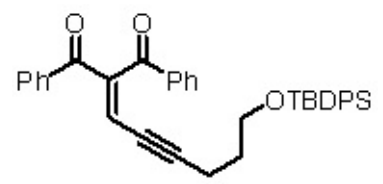
f1 (ppm)

7.943
7.928
7.827
7.811
7.662
7.647
7.569
7.554
7.539
7.521
7.506
7.491
7.464
7.449
7.440
7.428
7.414
7.399
7.384
7.260 CDCl3
6.738
6.733
6.728

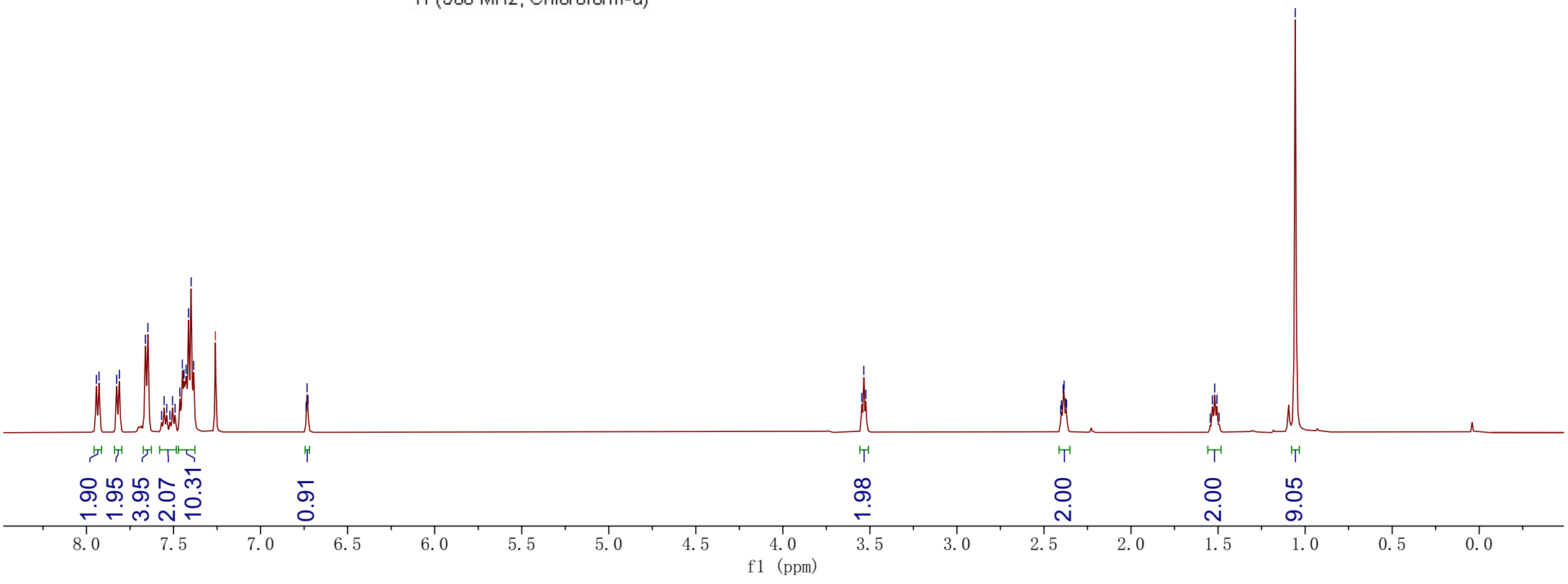
3.546
3.535
3.523

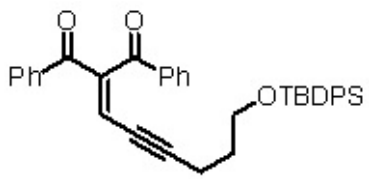
2.404
2.399
2.389
2.385
2.375
2.370

1.544
1.532
1.519
1.506
1.494
1.057



¹H (500 MHz, Chloroform-d)





^{13}C (126 MHz, Chloroform-d)

194.31
193.18

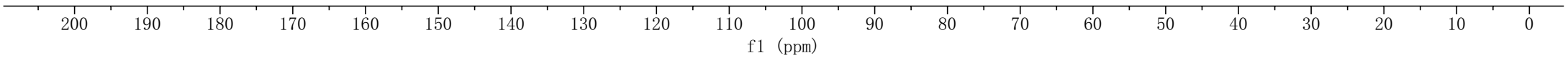
147.95
137.05
136.52
135.62
133.81
133.63
132.91
129.73
129.60
129.36
128.69
128.63
127.74
125.49
109.27

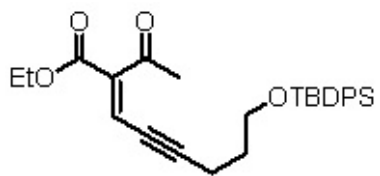
77.41 CDCI3
77.16 CDCI3
77.03
76.91 CDCI3

62.12

30.99
26.94

19.29
16.66





¹³C (126 MHz, Chloroform-d)

— 199.01

— 164.12

— 142.32

— 135.66

— 133.83

— 129.77

— 127.79

— 124.01

— 107.95

77.41 CDCl₃

77.16 CDCl₃

76.91 CDCl₃

76.83

62.33

61.62

31.19

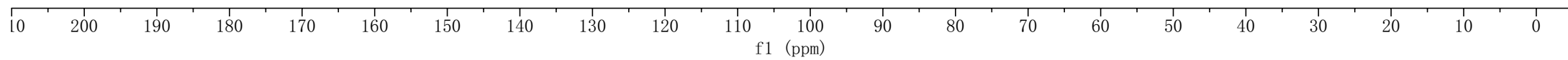
30.50

26.98

19.35

16.87

14.22

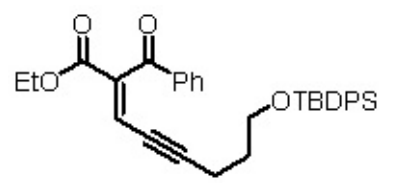


7.891
7.875
7.646
7.631
7.527
7.512
7.497
7.443
7.429
7.410
7.395
7.380
7.260 CDCl3
7.040
7.034
7.029

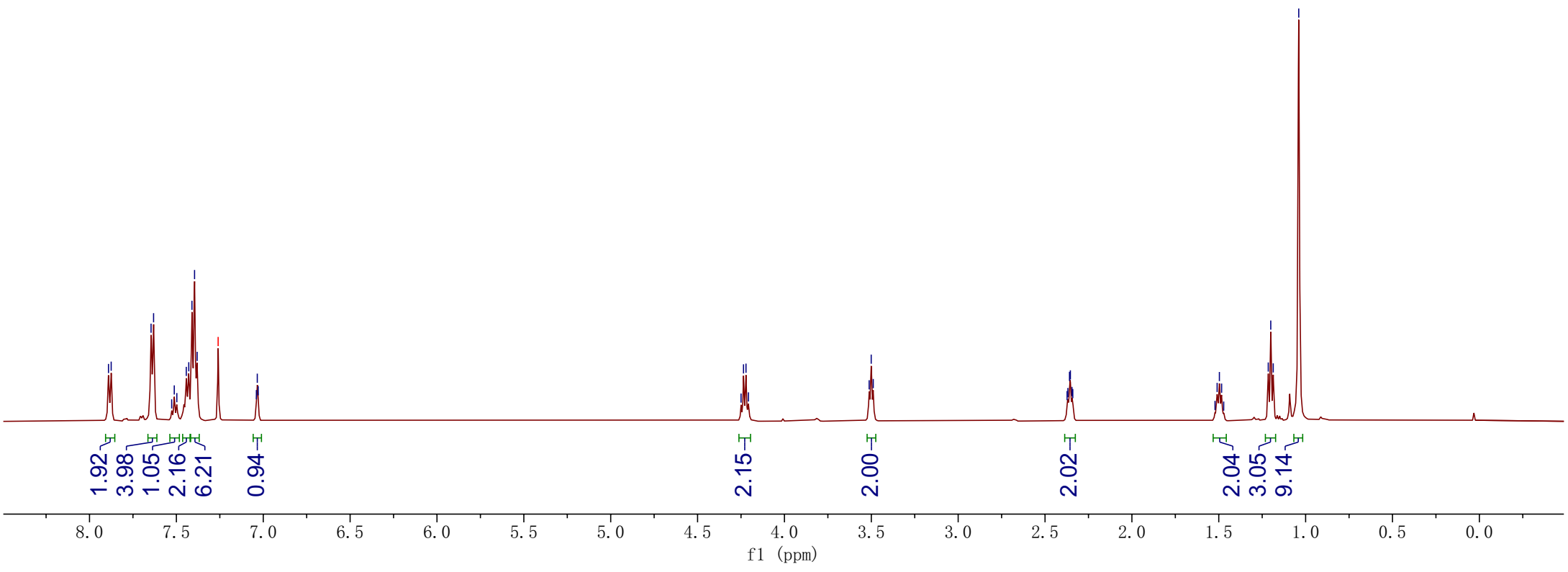
4.250
4.236
4.221
4.207

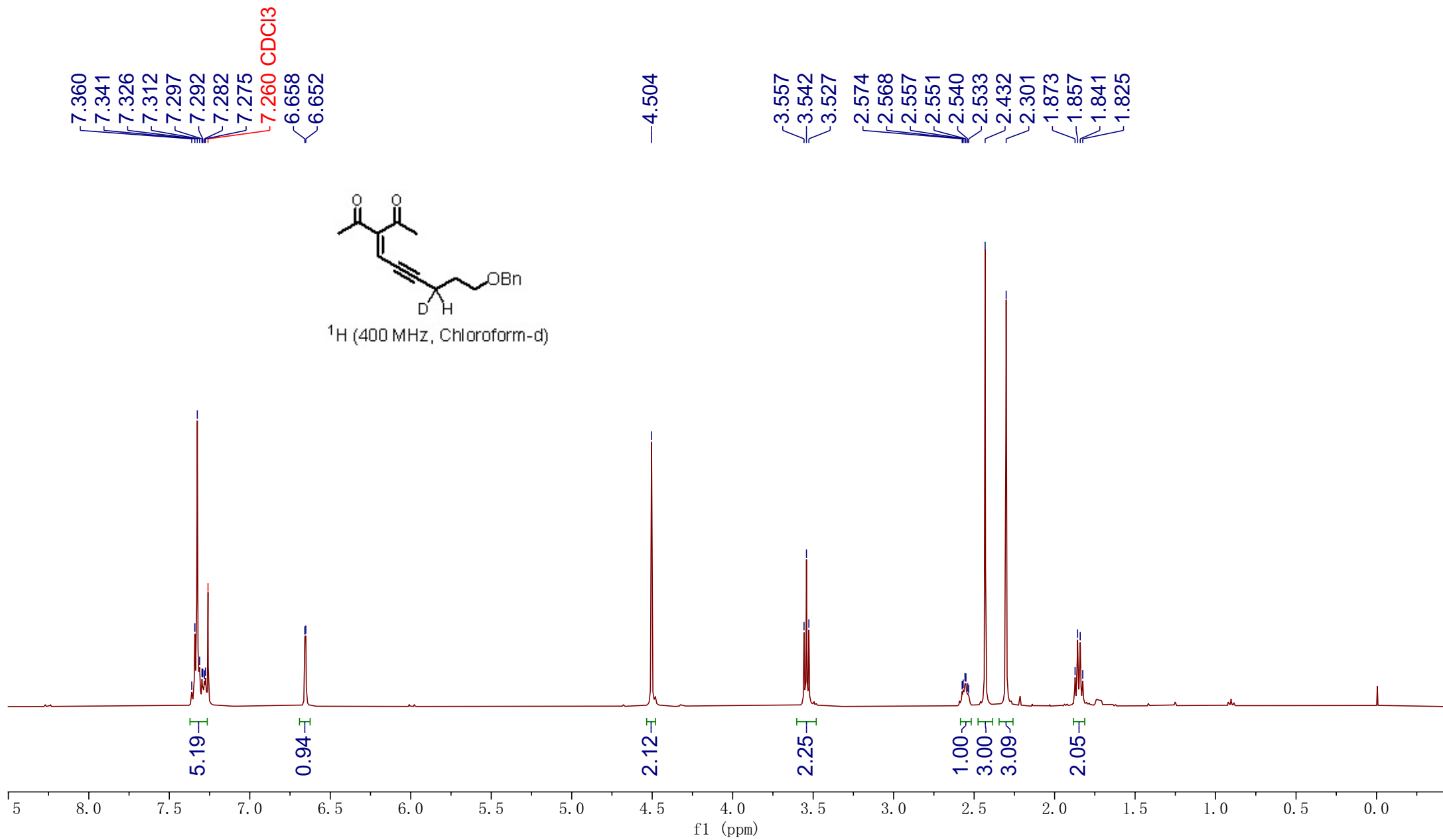
3.512
3.501
3.489

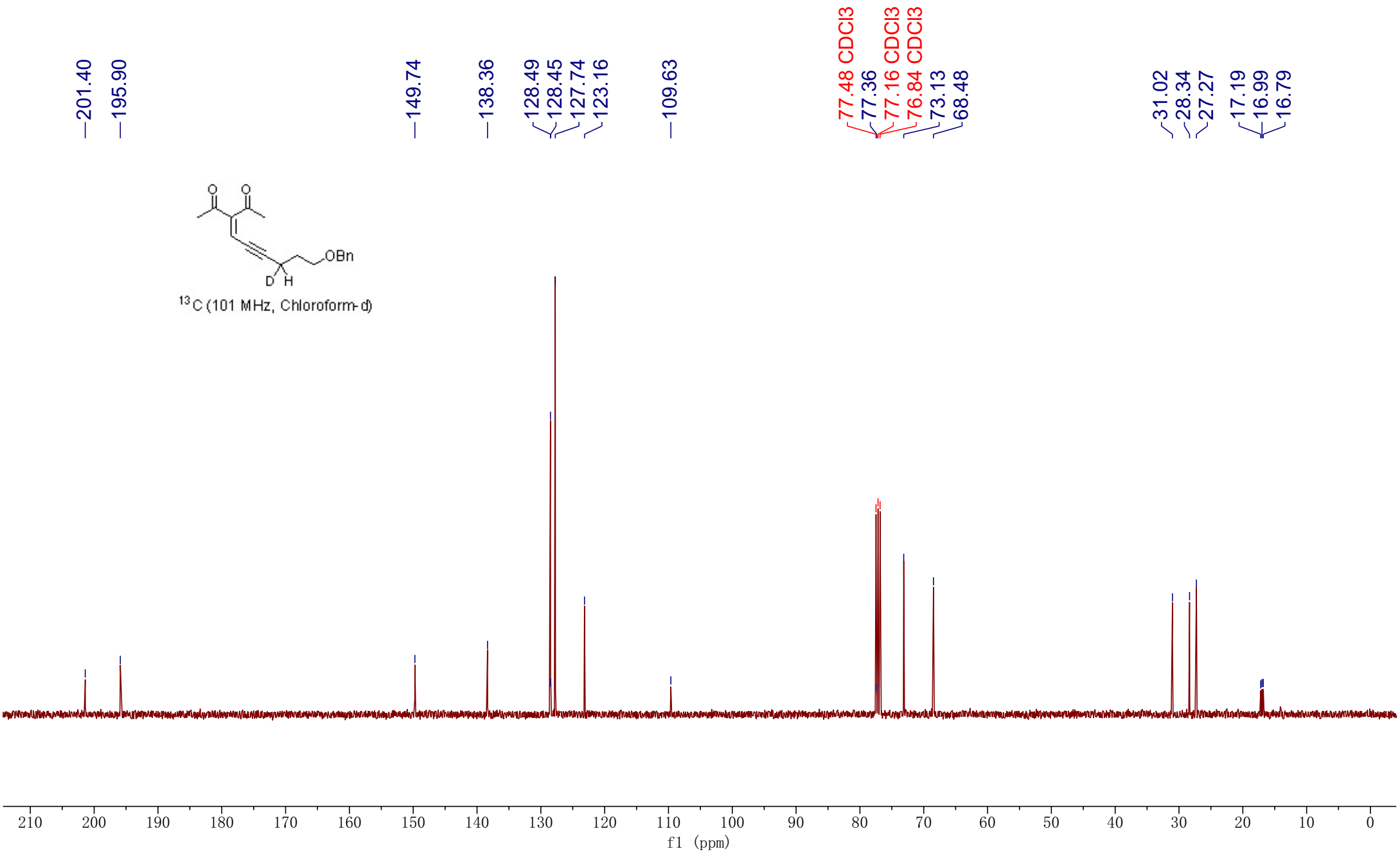
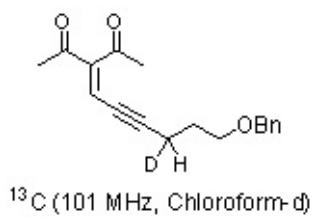
2.373
2.368
2.359
2.354
2.345
2.340
1.522
1.509
1.496
1.484
1.472
1.215
1.201
1.186
1.040



¹H (500 MHz, Chloroform-d)

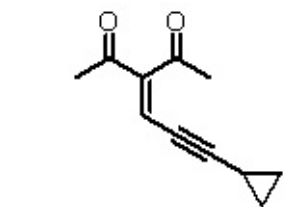






7.260 CDCl3

6.645



¹H (500 MHz, Chloroform-d)

2.407

2.258

1.458

1.453

1.448

1.441

1.434

1.425

0.956

0.950

0.942

0.933

0.926

0.819

0.812

0.807

0.804

0.797

0.790

0.98

3.14

3.22

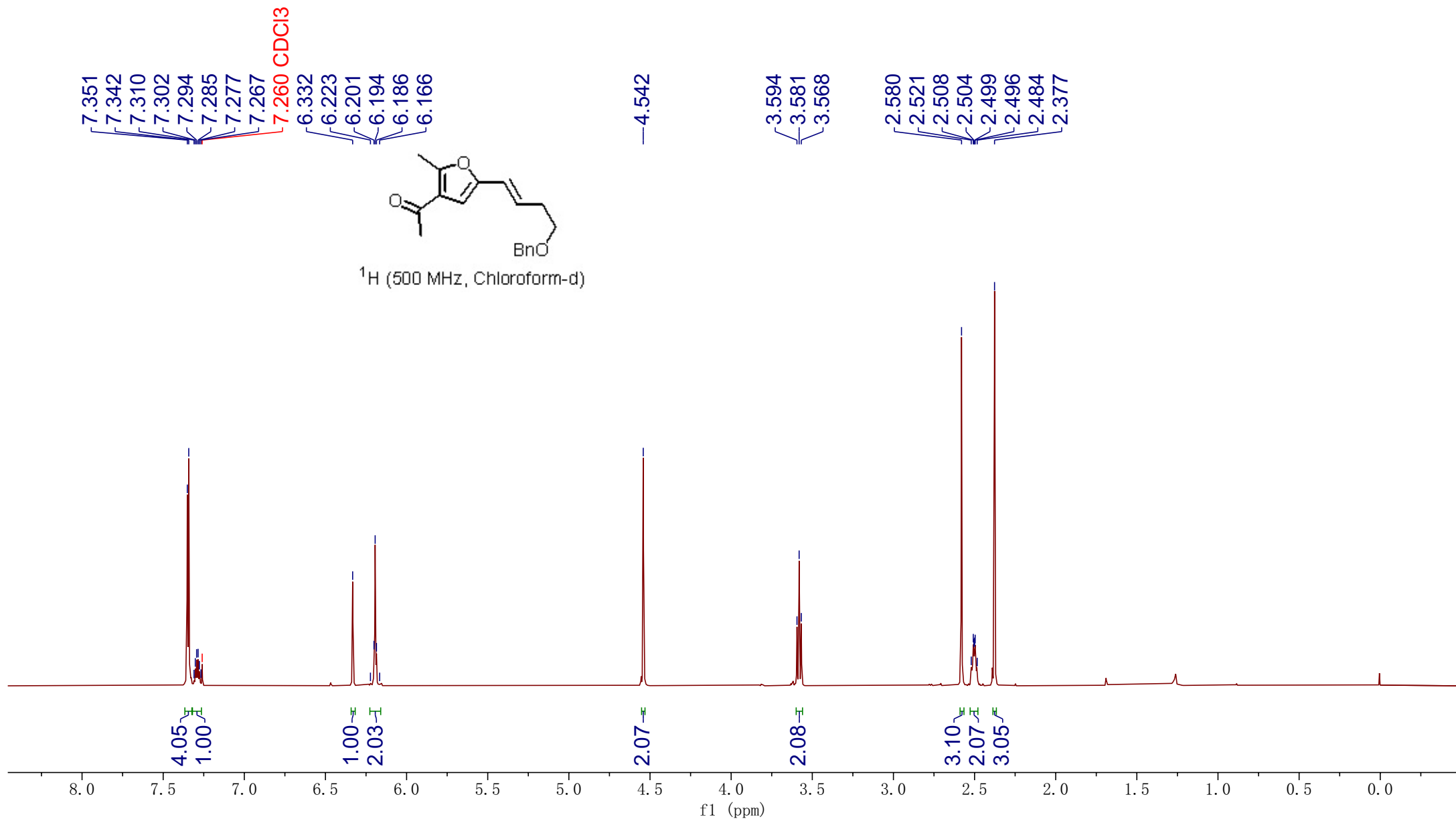
0.98

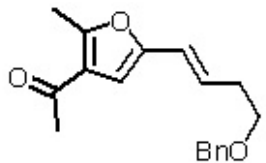
2.16

2.17

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 (126 MHz, Chloroform-d)

—194.20

—157.67

—150.81

—138.47

—128.50

—127.79

—127.72

—127.12

—122.81

—119.49

—106.63

77.41 CDCl₃

77.16 CDCl₃

76.91 CDCl₃

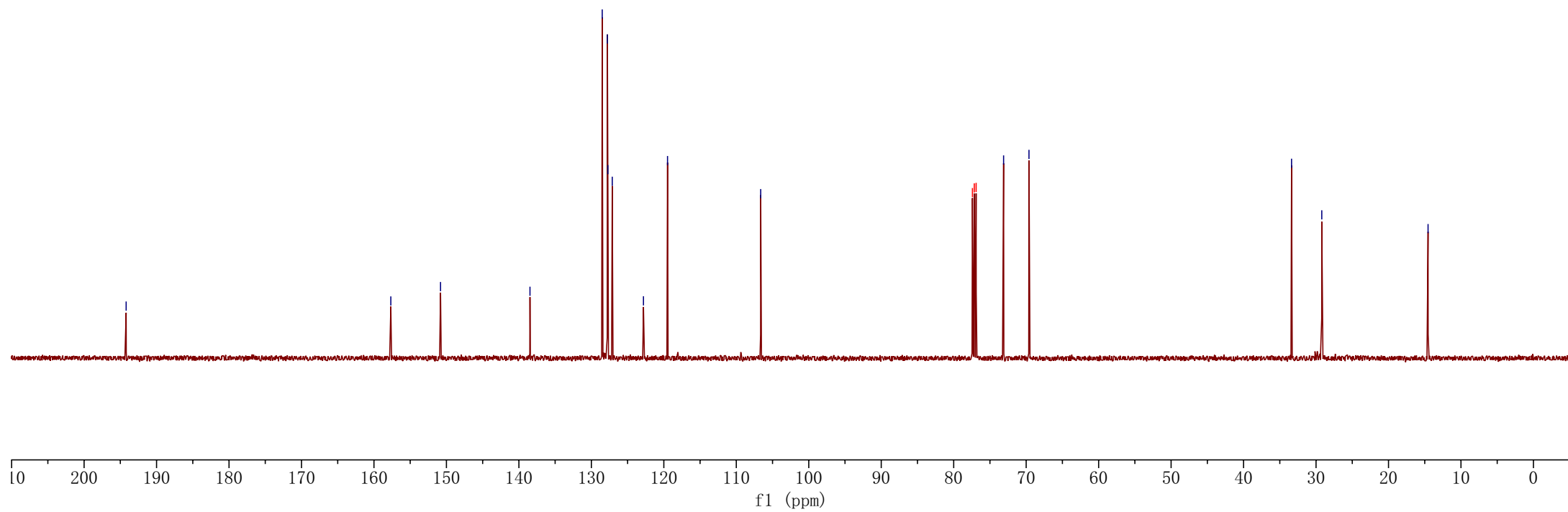
73.11

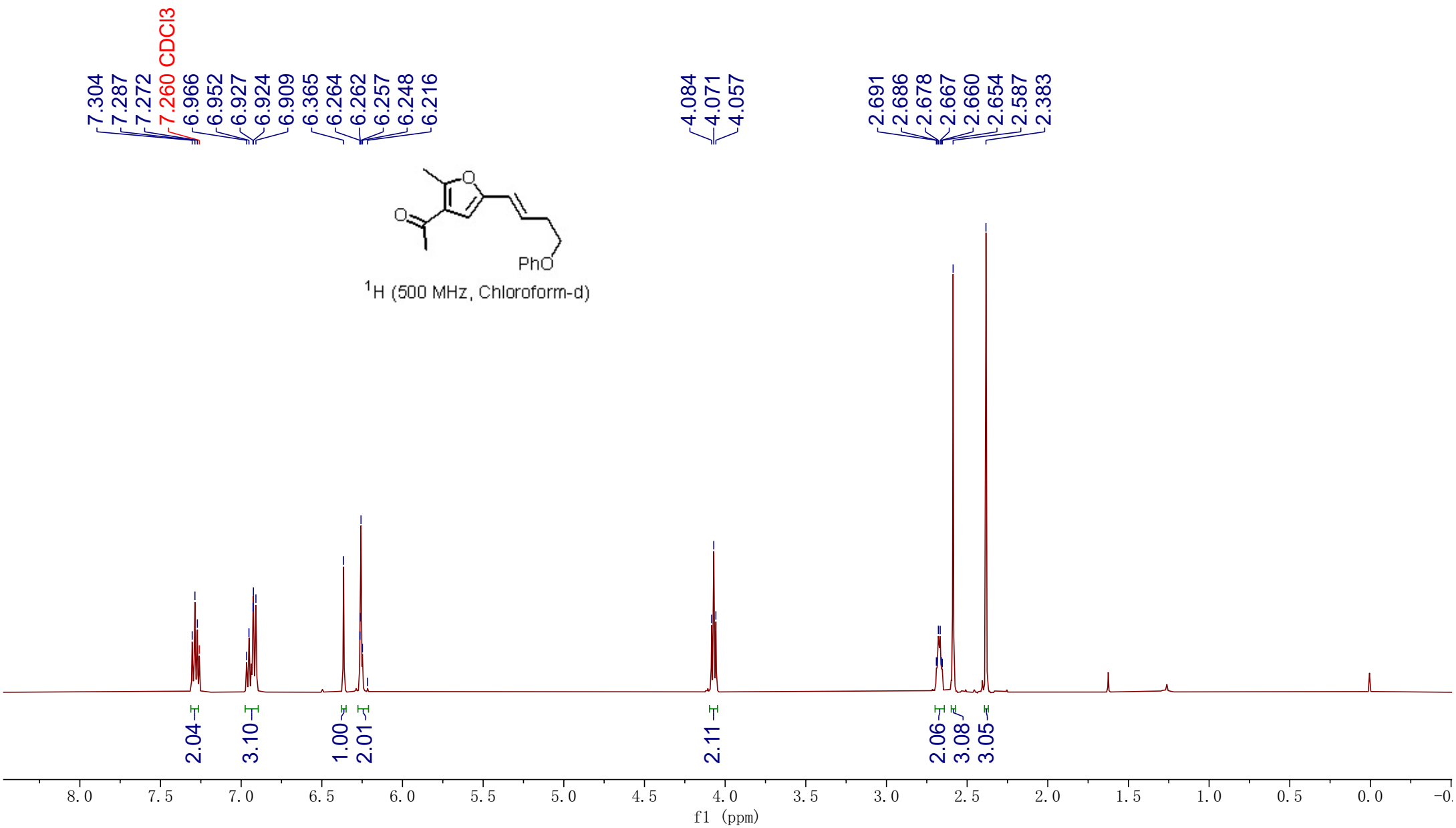
69.61

—33.38

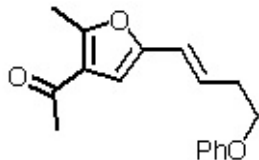
—29.21

—14.54





—194.18



¹³C (126 MHz, Chloroform-d)

~158.92

~157.83

—150.65

~129.59

~126.21

~122.84

~120.93

~119.99

~114.71

—106.97

77.41 CDCl₃

77.16 CDCl₃

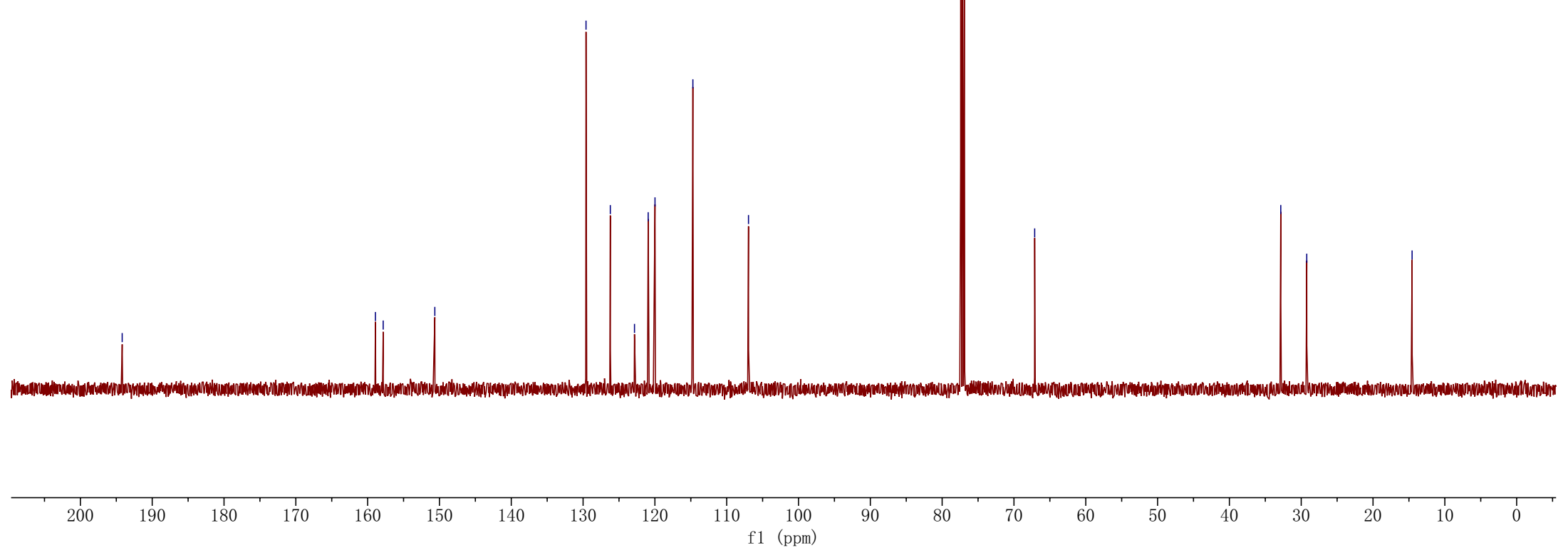
76.91 CDCl₃

—67.11

—32.85

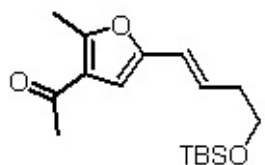
—29.23

—14.56



—7.260 CDCl₃

6.317
6.188
6.166
6.163
6.158
6.149



¹H (500 MHz, Chloroform-d)

3.716
3.703
3.689

2.567
2.435
2.421
2.405
2.392
2.379
2.368

—0.892

—0.054

0.90
1.79

1.96

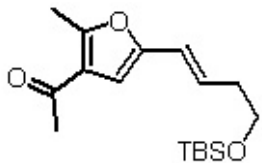
2.85
1.79
3.00

9.00

5.70

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)



¹³C (126 MHz, Chloroform-d)

—194.22

—157.64

—150.95

—127.31

—122.81

—119.52

—106.44

77.41 CDCl₃

77.16 CDCl₃

76.91 CDCl₃

—62.81

—36.53

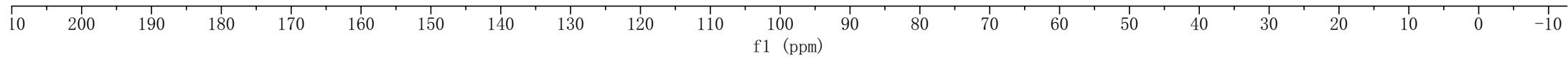
—29.20

—26.07

—18.49

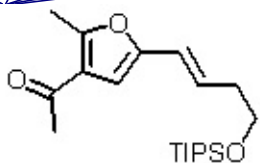
—14.54

—5.12



— 7.260 CDCl₃

6.292
6.207
6.195
6.175
6.164
6.157
6.155
6.125

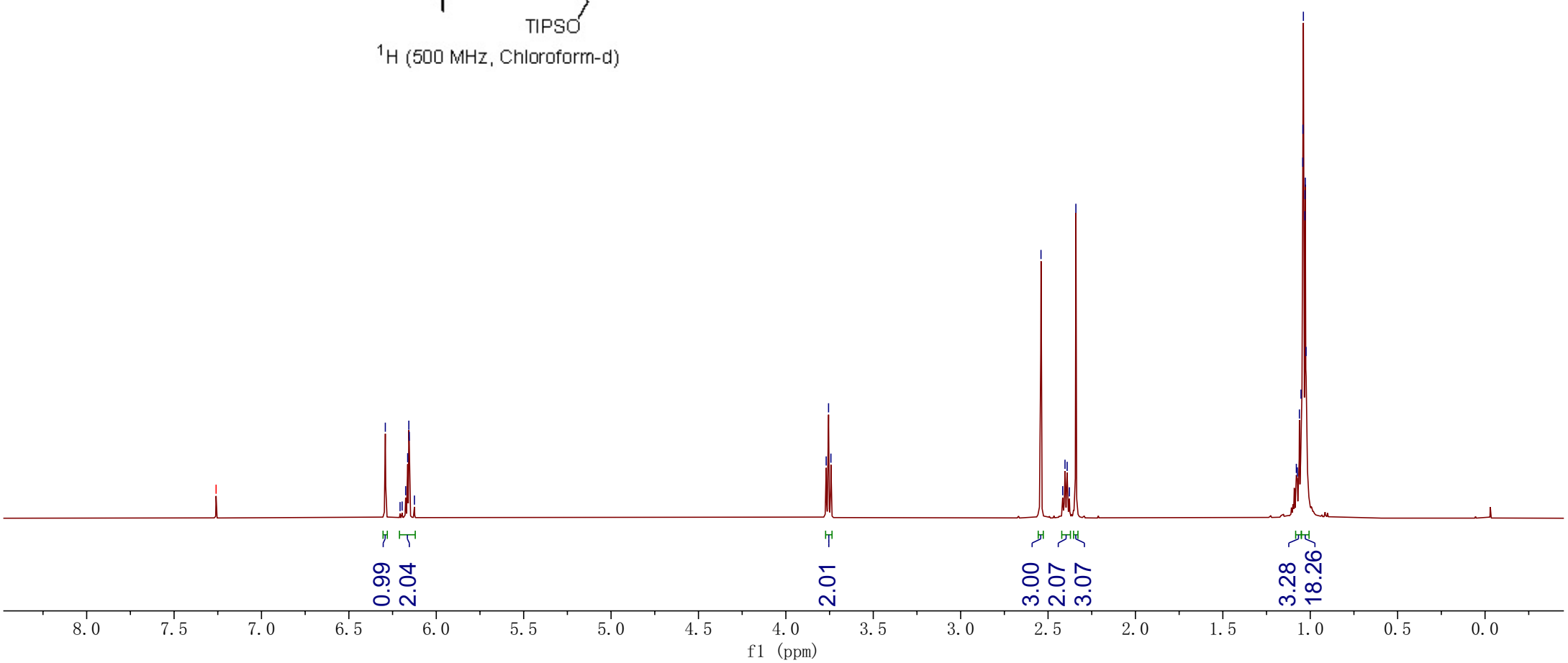


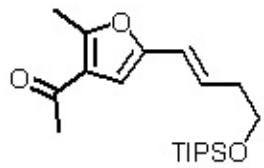
¹H (500 MHz, Chloroform-d)

3.769
3.756
3.742

2.540
2.416
2.403
2.391
2.378
2.341

1.080
1.074
1.062
1.053
1.043
1.042
1.039
1.031
1.030
1.028
1.024





¹³C (126 MHz, Chloroform-d)

—194.10

—157.53

—150.92

~127.34

~122.72

~119.38

—106.34

77.42 CDCl₃

77.16 CDCl₃

76.91 CDCl₃

—63.04

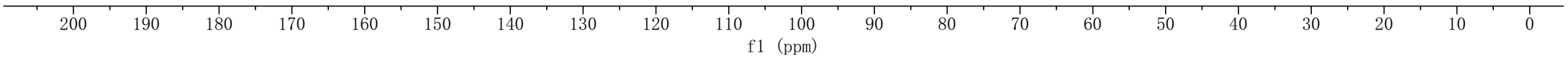
—36.63

—29.11

~18.06

~14.44

~12.07

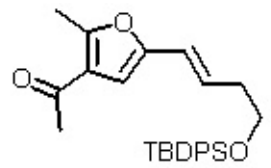


7.710
7.707
7.704
7.693
7.690
7.453
7.444
7.439
7.434
7.427
7.424
7.421
7.402
7.387
7.374
7.260 CDCl3
6.330
6.218
6.208
6.187
6.175
6.169
6.143

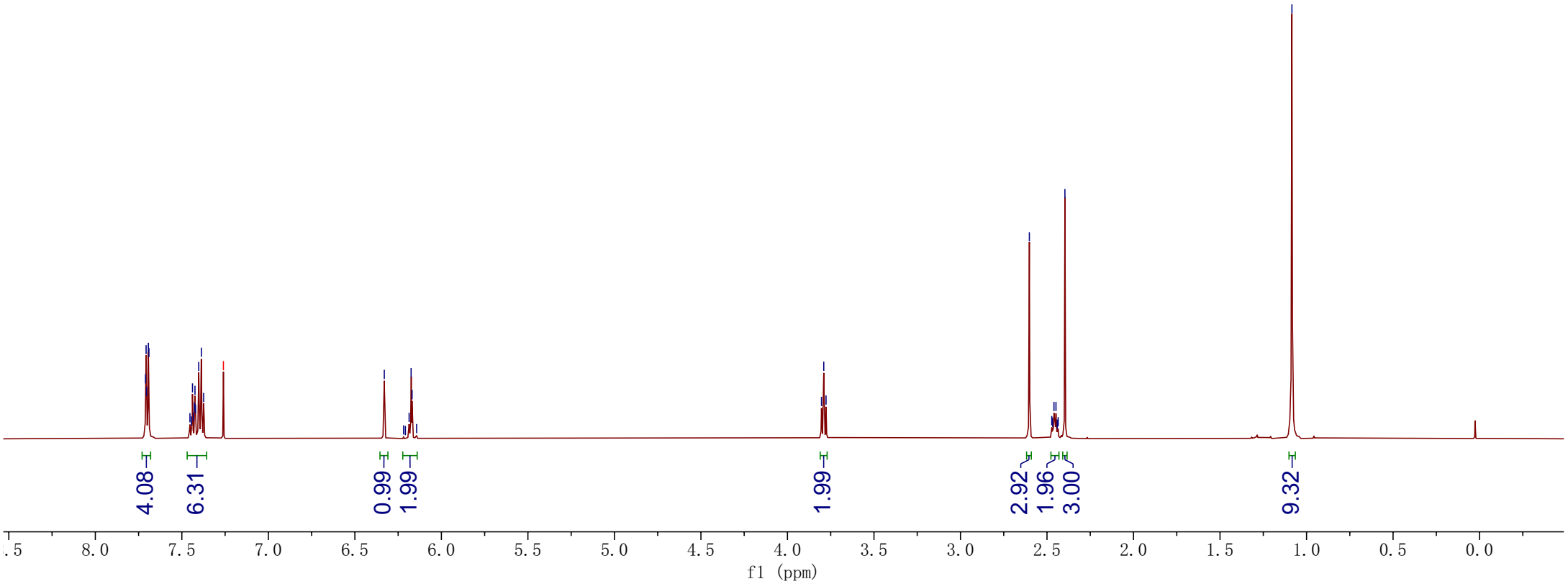
3.803
3.790
3.777

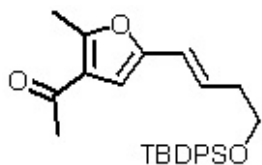
2.602
2.472
2.468
2.460
2.448
2.441
2.435
2.396

1.085



¹H (500 MHz, Chloroform-d)





^{13}C (126 MHz, Chloroform-d)

— 194.25

— 157.62

— 150.93

~ 135.71

~ 133.95

~ 129.73

~ 127.74

~ 127.34

~ 122.78

~ 119.58

— 106.44

~ 77.41 CDCl₃

~ 77.16 CDCl₃

~ 76.91 CDCl₃

— 63.50

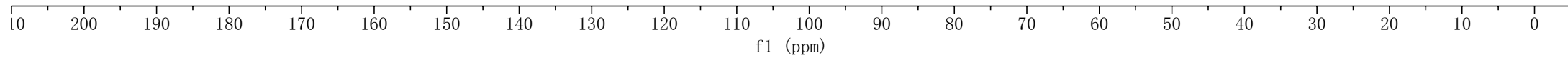
~ 36.23

~ 29.21

~ 26.96

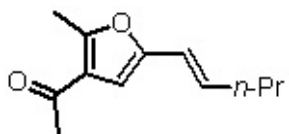
— 19.32

— 14.54



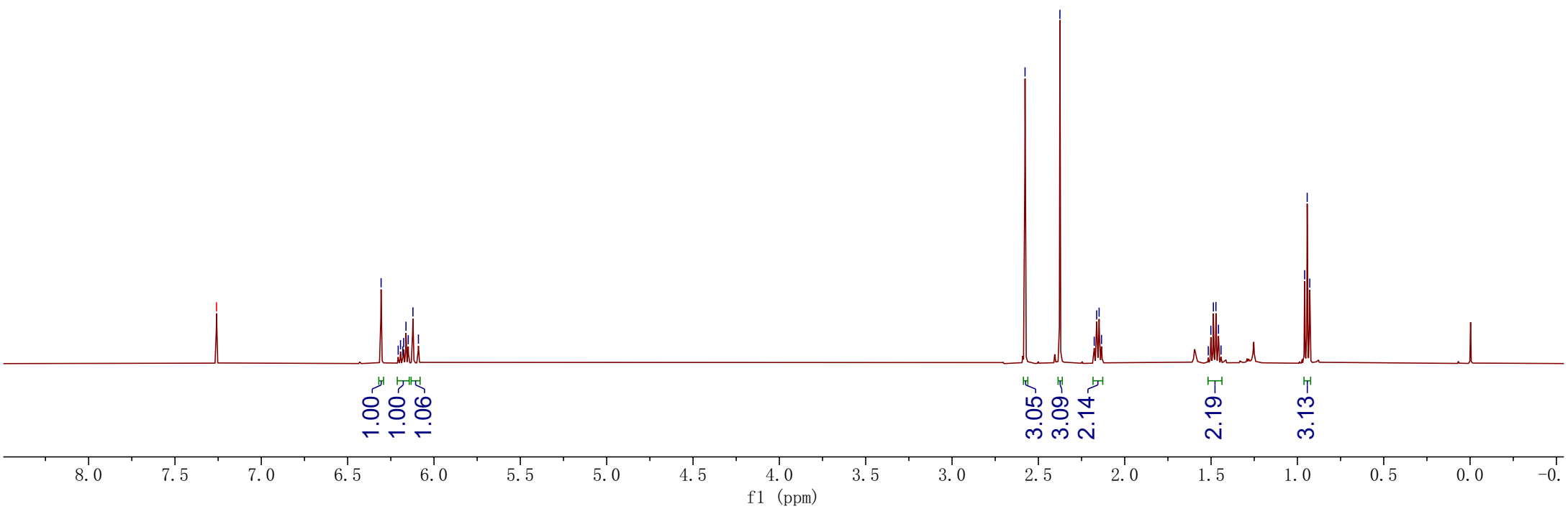
—7.260 CDCI3

6.306
6.207
6.194
6.181
6.176
6.162
6.149
6.122
6.090

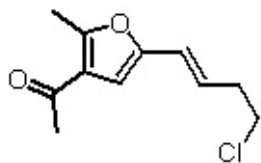


¹H (500 MHz, Chloroform-d)

2.577
2.375
2.177
2.163
2.148
2.135
1.516
1.501
1.486
1.472
1.457
1.442
0.958
0.943
0.929



—7.260 CDCl₃

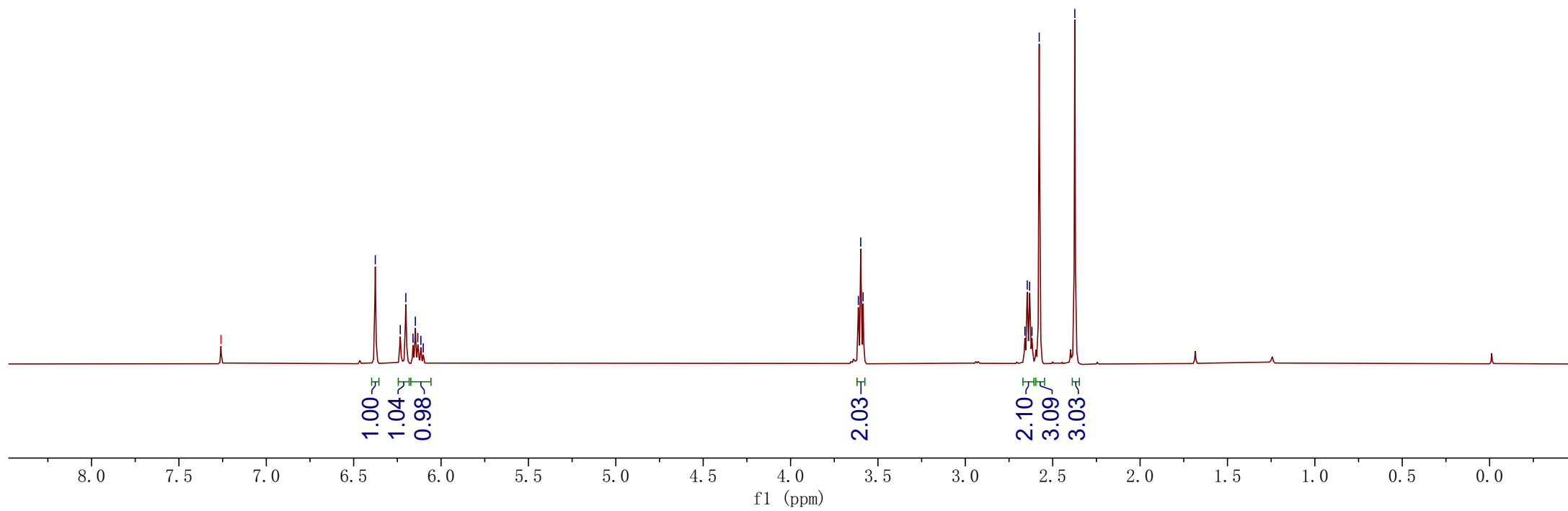


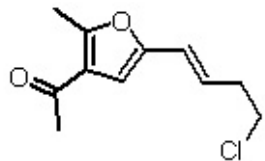
¹H (500 MHz, Chloroform-d)

6.376
6.233
6.202
6.161
6.147
6.133
6.115
6.102

3.612
3.599
3.585

2.659
2.646
2.632
2.619
2.577
2.374





^{13}C (126 MHz, Chloroform-d)

—194.14

—158.02

—150.25

~125.63

—122.84

~120.52

—107.47

77.41 CDCI3

77.16 CDCI3

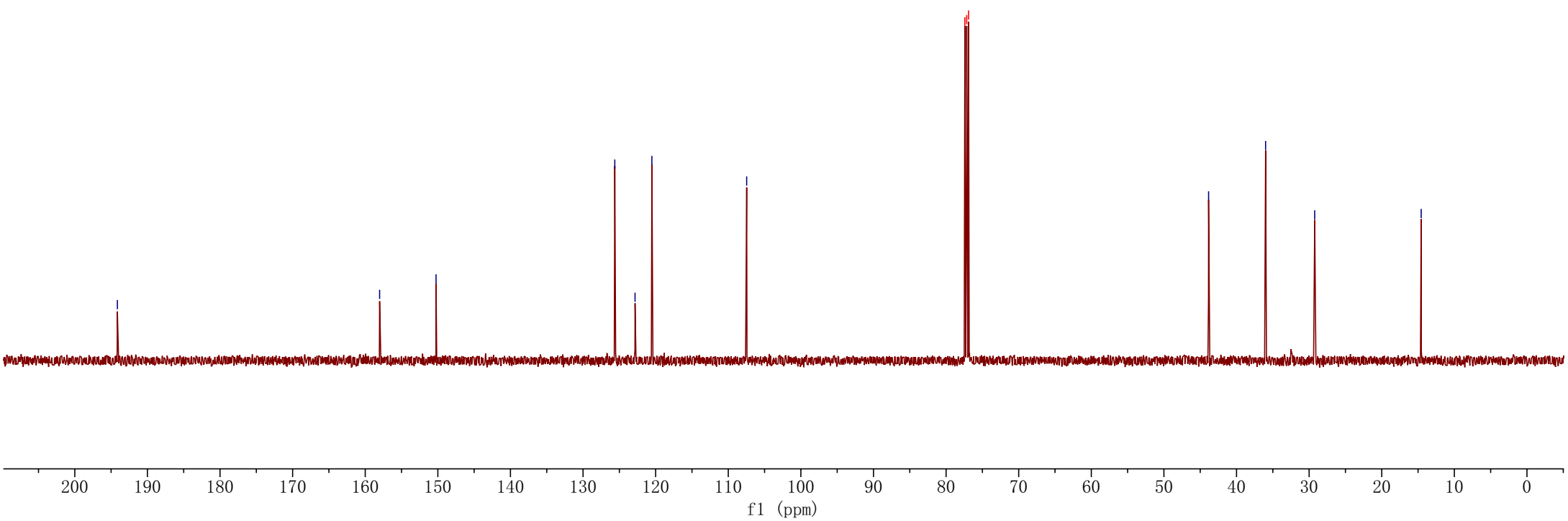
76.91 CDCI3

—43.85

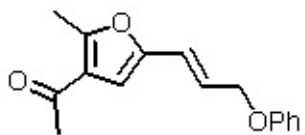
—36.00

—29.23

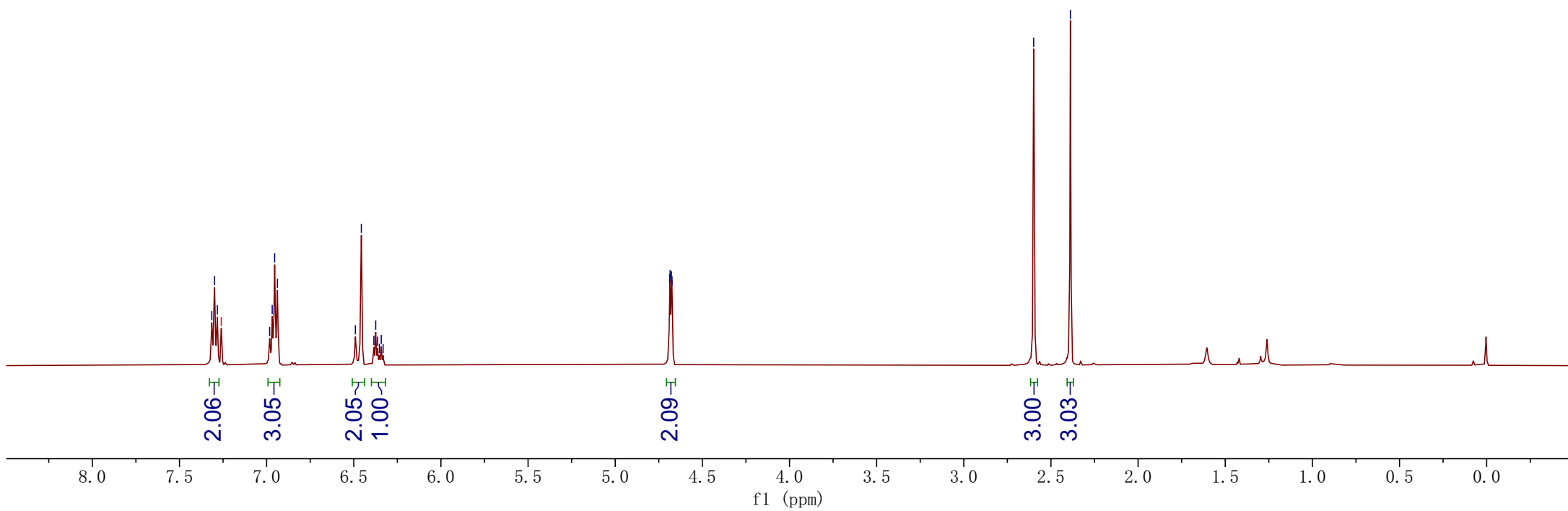
—14.57

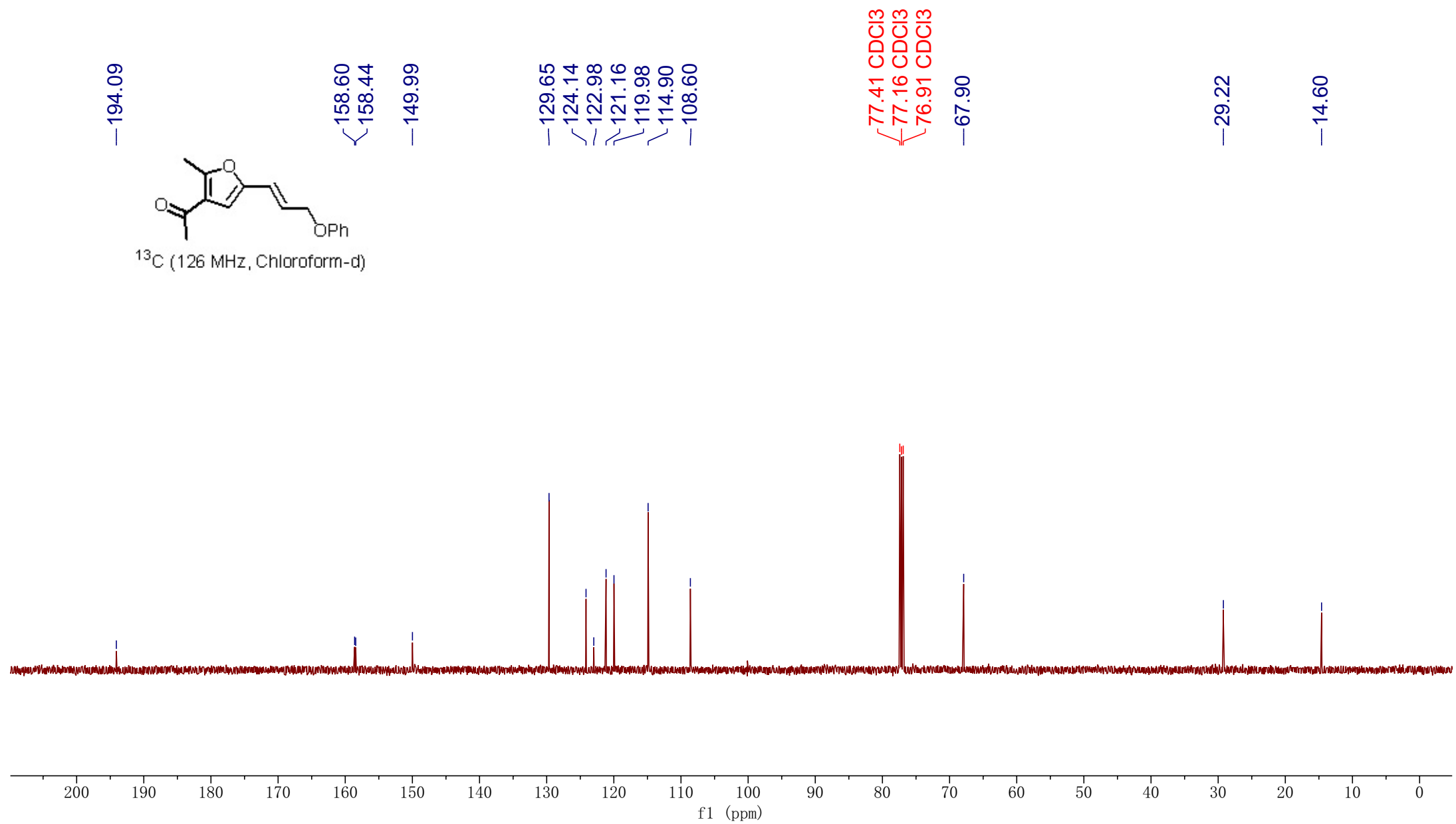


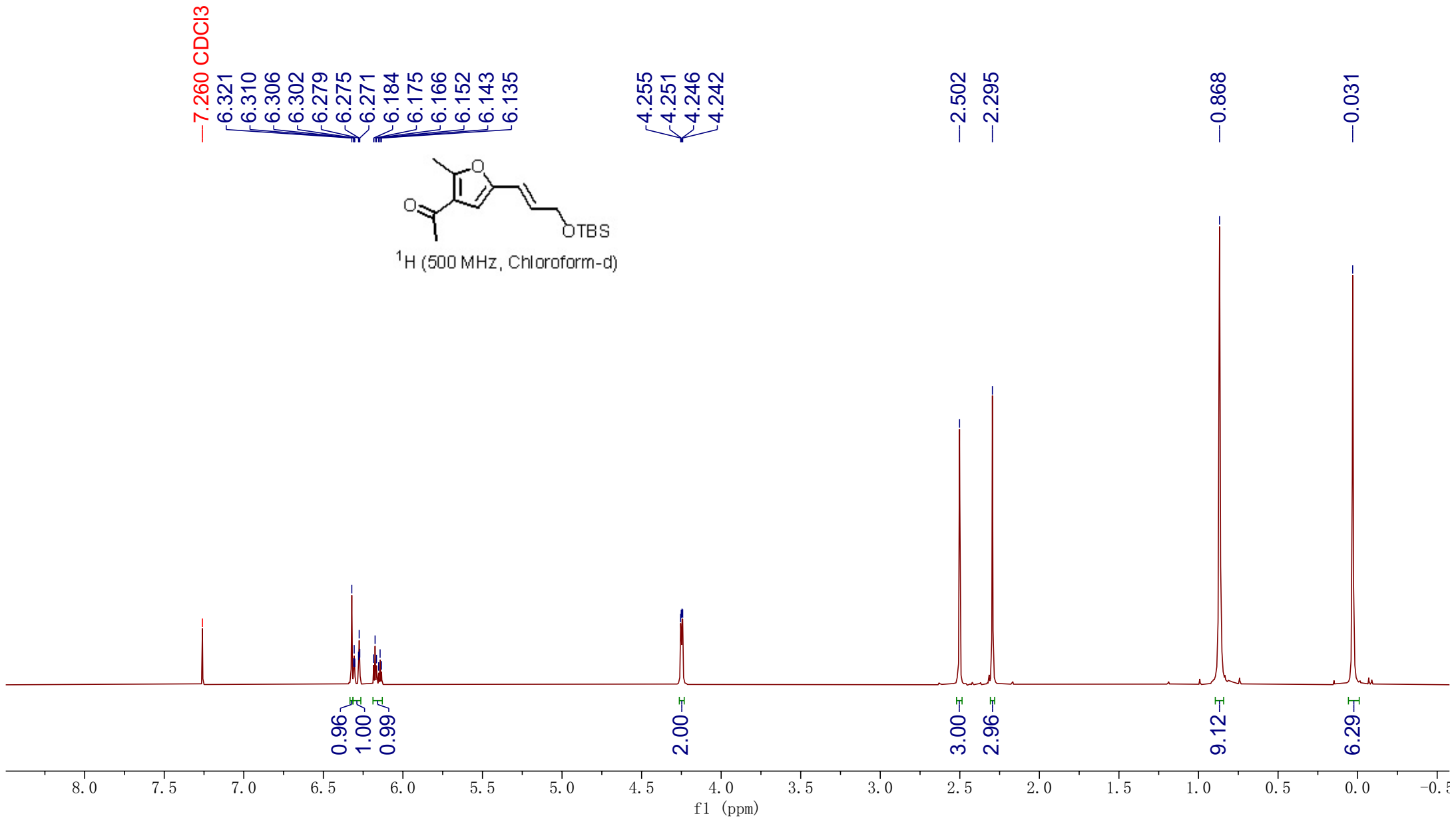
7.315
7.299
7.283
7.260 CDCl₃
6.983
6.968
6.954
6.938
6.491
6.457
6.385
6.374
6.363
6.353
6.342
6.332
4.688
4.685
4.677
4.674
-2.599
-2.388

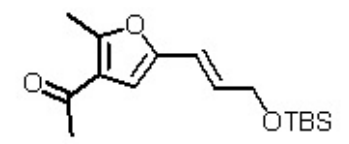


¹H (500 MHz, Chloroform-d)









— 193.81

— 157.64

— 150.54

~ 128.79

— 122.67

~ 116.60

— 107.26

~ 77.42 CDCl₃
~ 77.16 CDCl₃
~ 76.91 CDCl₃

— 62.94

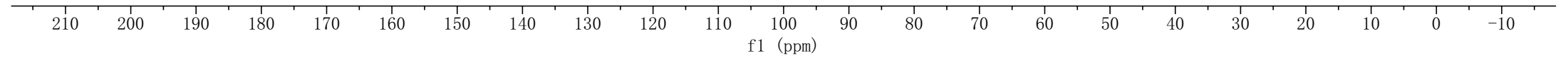
~ 28.98

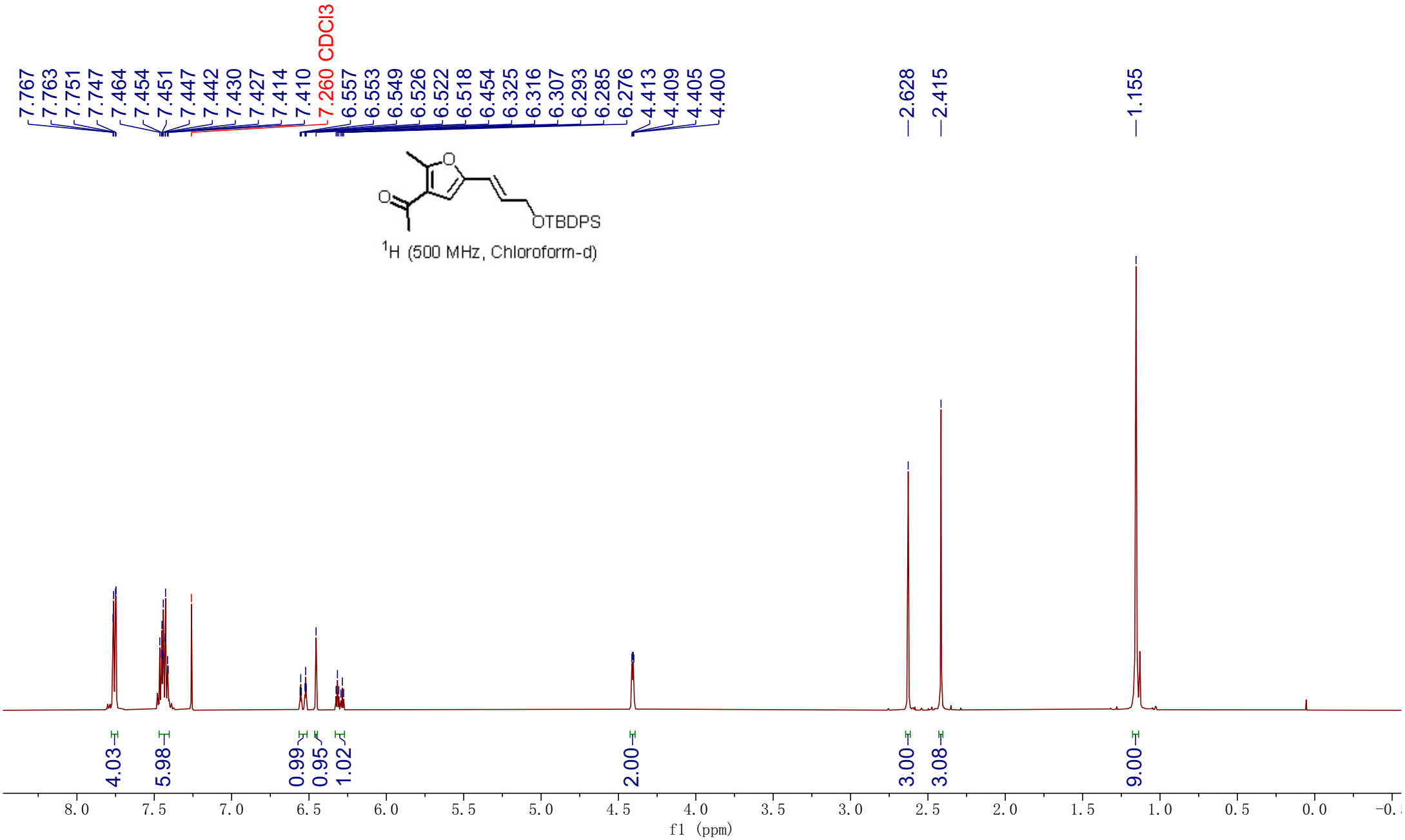
~ 25.90

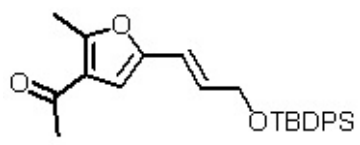
~ 18.37

~ 14.33

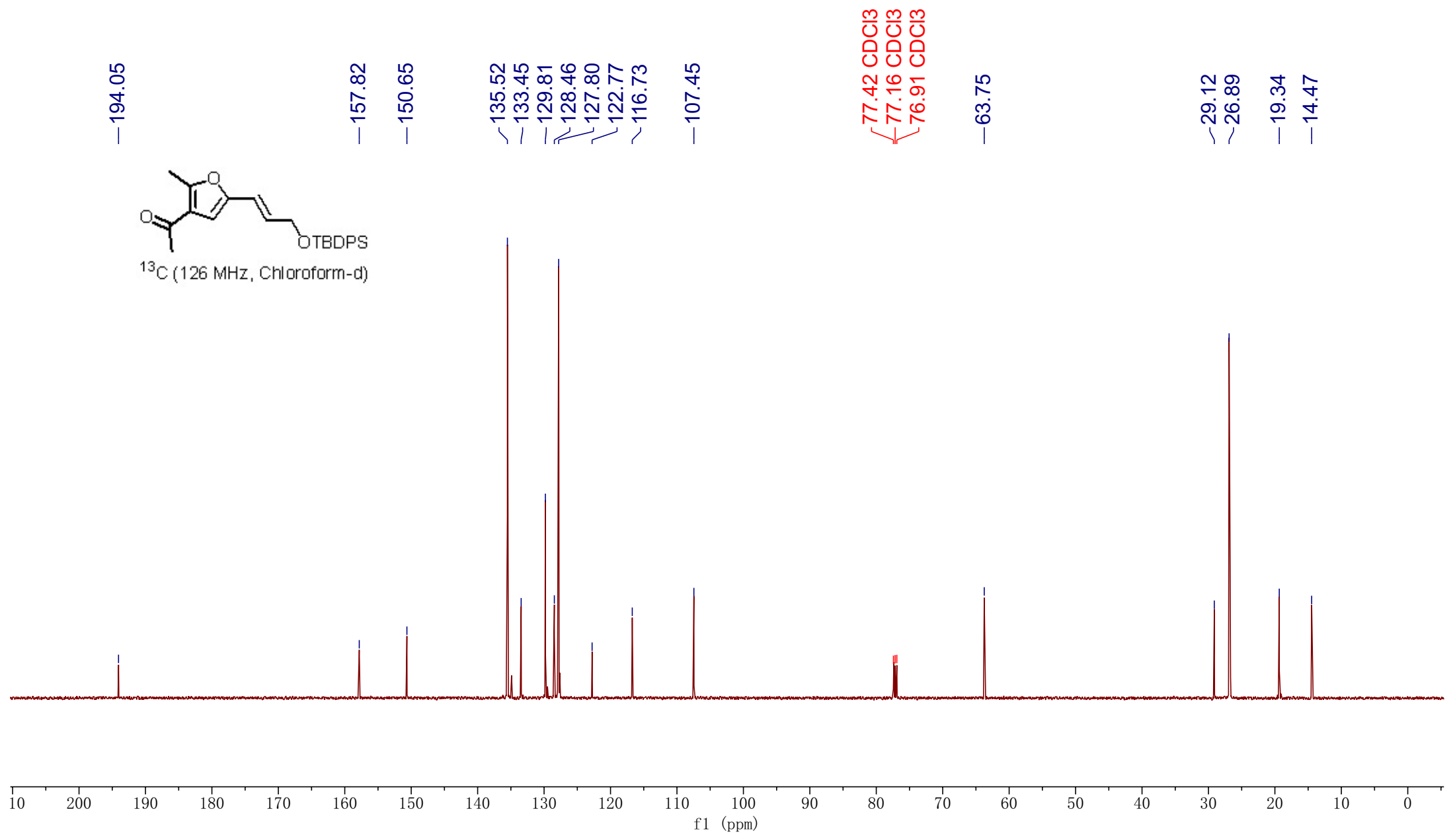
— -5.32

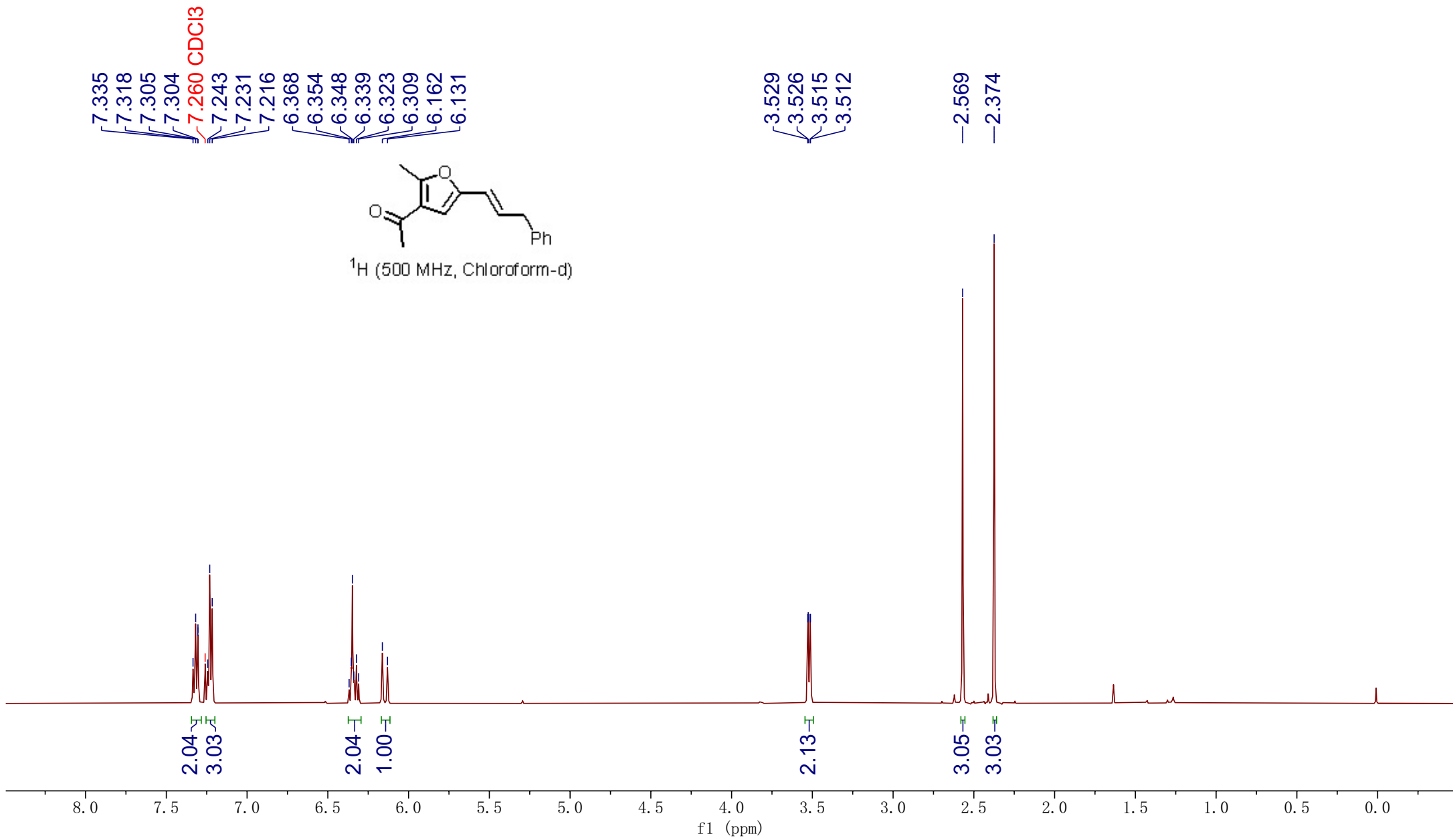


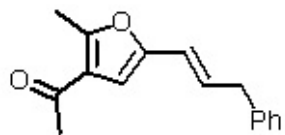




¹³C (126 MHz, Chloroform-d)







^{13}C (126 MHz, Chloroform-d)

—194.18

—157.74

—150.75

—139.69

129.35

128.82

128.68

126.45

122.81

118.85

—106.87

77.41 CDC13

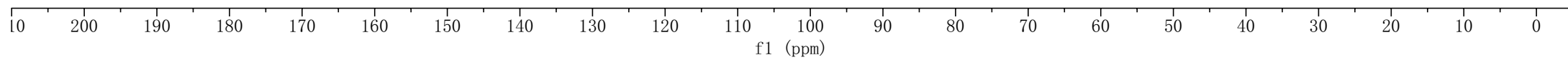
77.16 CDC13

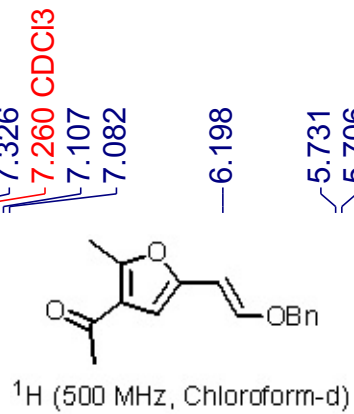
76.91 CDC13

—39.16

—29.22

—14.53





7.380
7.368
7.356
7.342
7.331
7.326
7.260 CDCl₃
7.107
7.082

6.198

5.731
5.706

4.861

2.548

2.350

5.02

0.96

0.93

0.97

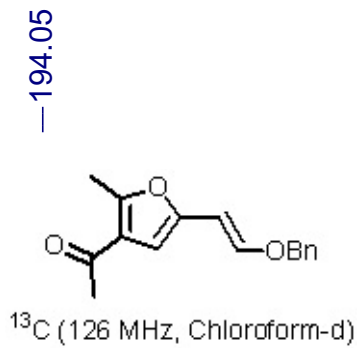
2.01

3.00

3.03

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)



—194.05

—156.38

—149.31

—148.10

—136.41

—128.65

—128.23

—127.57

—122.73

—104.42

—96.34

77.41 CDCI3

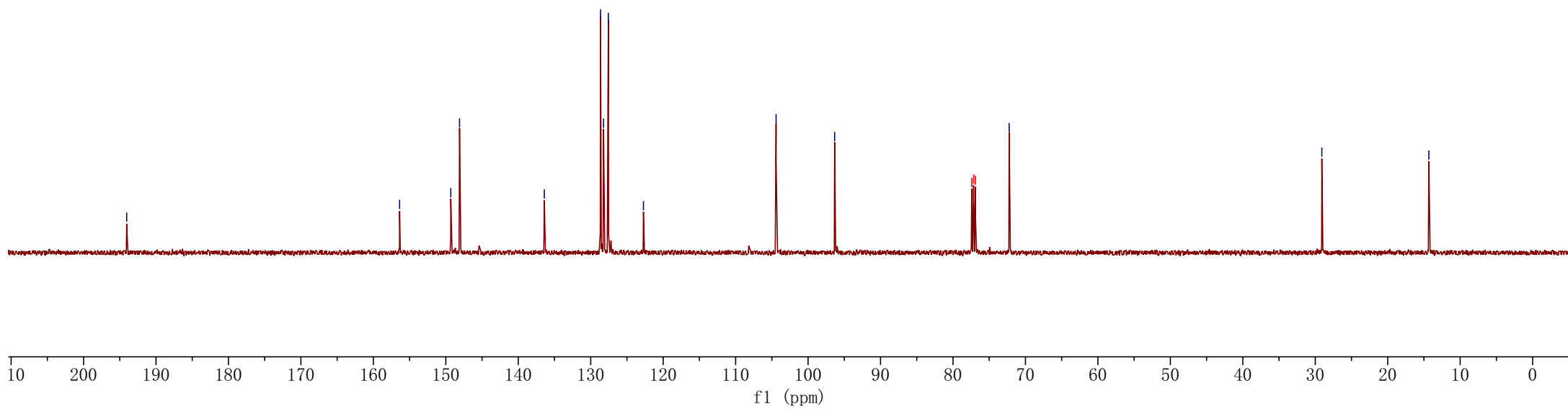
77.16 CDCI3

76.91 CDCI3

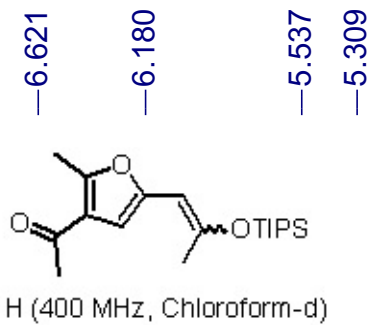
72.25

—29.09

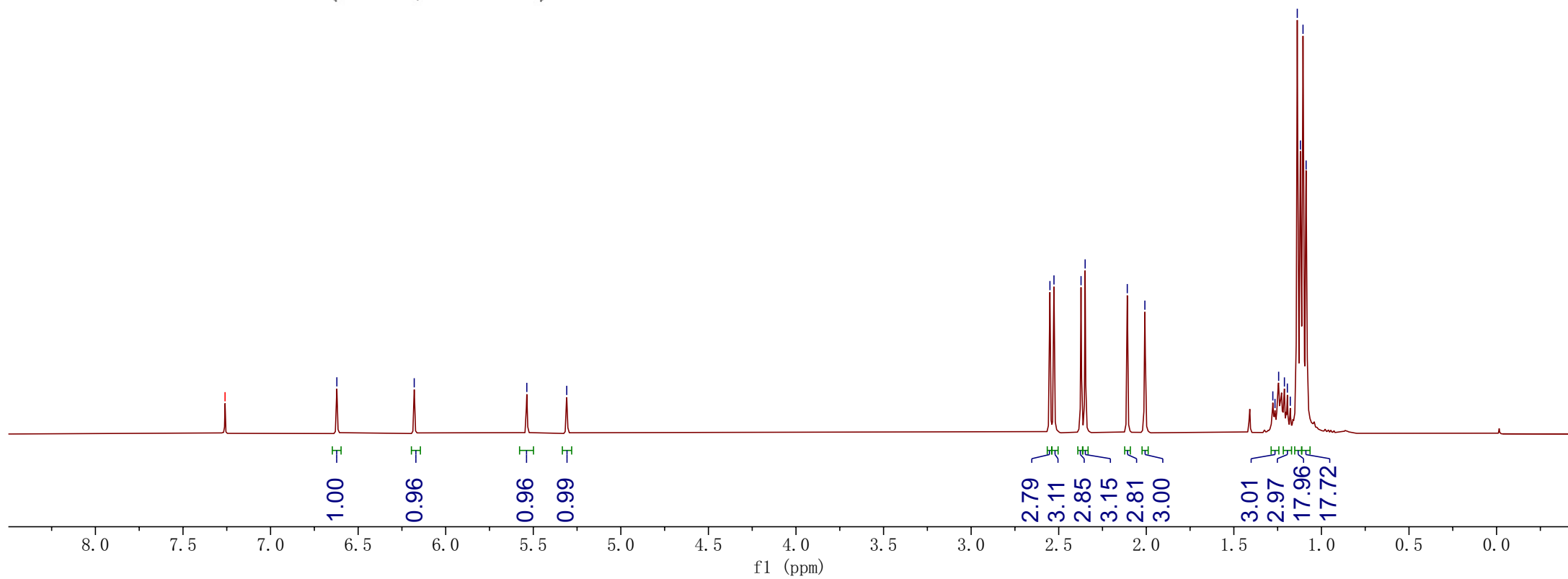
—14.32

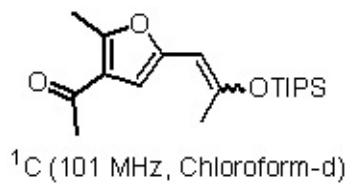


—7.260 CDCl₃



2.550 2.527 2.373 2.349 2.109 2.008 1.277 1.265 1.244 1.211 1.195 1.178 1.138 1.120 1.105 1.087





194.71
194.33

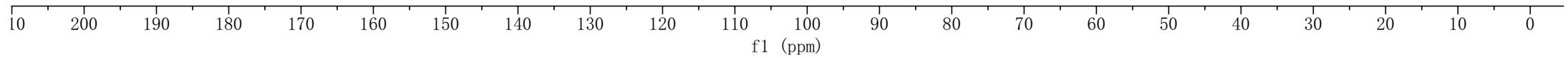
156.14
155.26
153.49
150.46
150.08
150.03

122.81
122.52

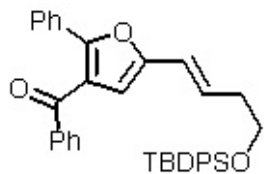
106.24
105.37
98.66
97.74

77.48 CDCI3
77.16 CDCI3
76.84 CDCI3

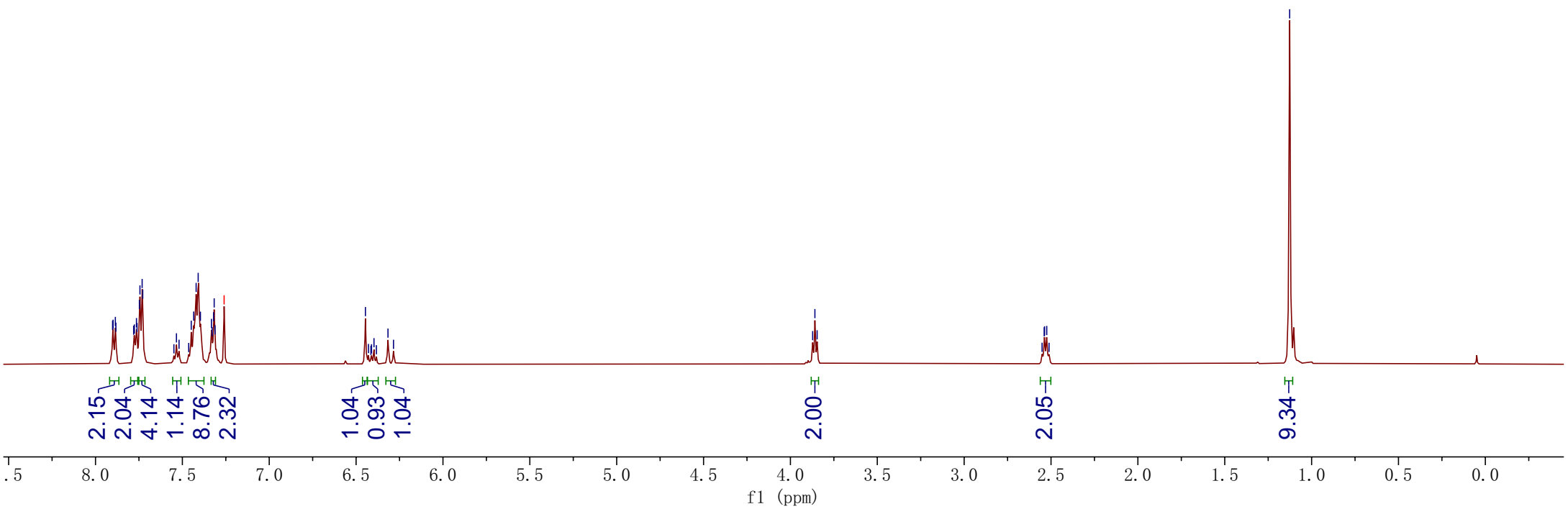
29.21
29.10
23.63
20.58
18.06
18.03
14.48
14.24
13.66
12.73

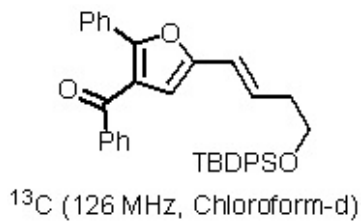


7.902
7.899
7.886
7.883
7.780
7.776
7.764
7.761
7.747
7.744
7.732
7.728
7.549
7.534
7.519
7.463
7.449
7.435
7.421
7.409
7.396
7.332
7.329
7.320
7.317
7.312
-7.260 CDCl3
-6.446
-6.429
-6.415
-6.411
-6.397
-6.383
-6.316
-6.285
-3.872
-3.859
3.846
2.551
2.539
2.537
2.525
2.511
-1.126



¹H (500 MHz, Chloroform-d)





—191.87

154.55
151.71
138.21
135.73
133.95
132.92
129.91
129.83
129.76
128.99
128.83
128.43
128.40
127.78
127.47
122.47
119.54
—110.10

77.41 CDCl₃
77.16 CDCl₃
76.91 CDCl₃

—63.47

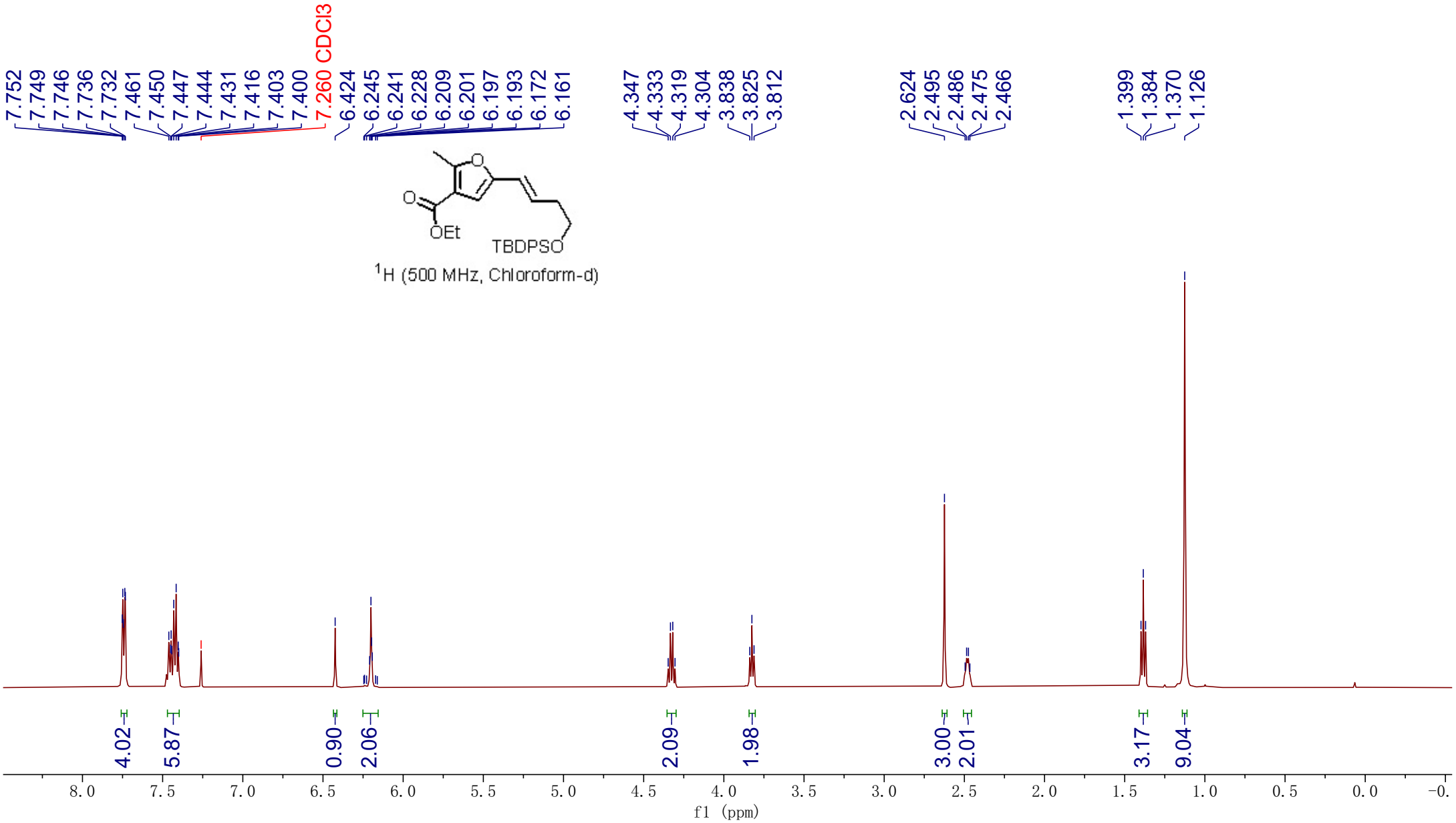
—36.29

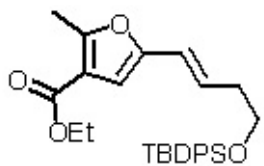
—27.01

—19.39

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)





¹³C (126 MHz, Chloroform-d)

— 164.12

— 158.20

— 150.97

— 135.68

— 133.93

— 129.69

— 127.72

— 126.89

— 119.74

— 114.93

— 106.77

— 77.41 CDCl₃

— 77.16 CDCl₃

— 76.90 CDCl₃

— 63.50

— 60.10

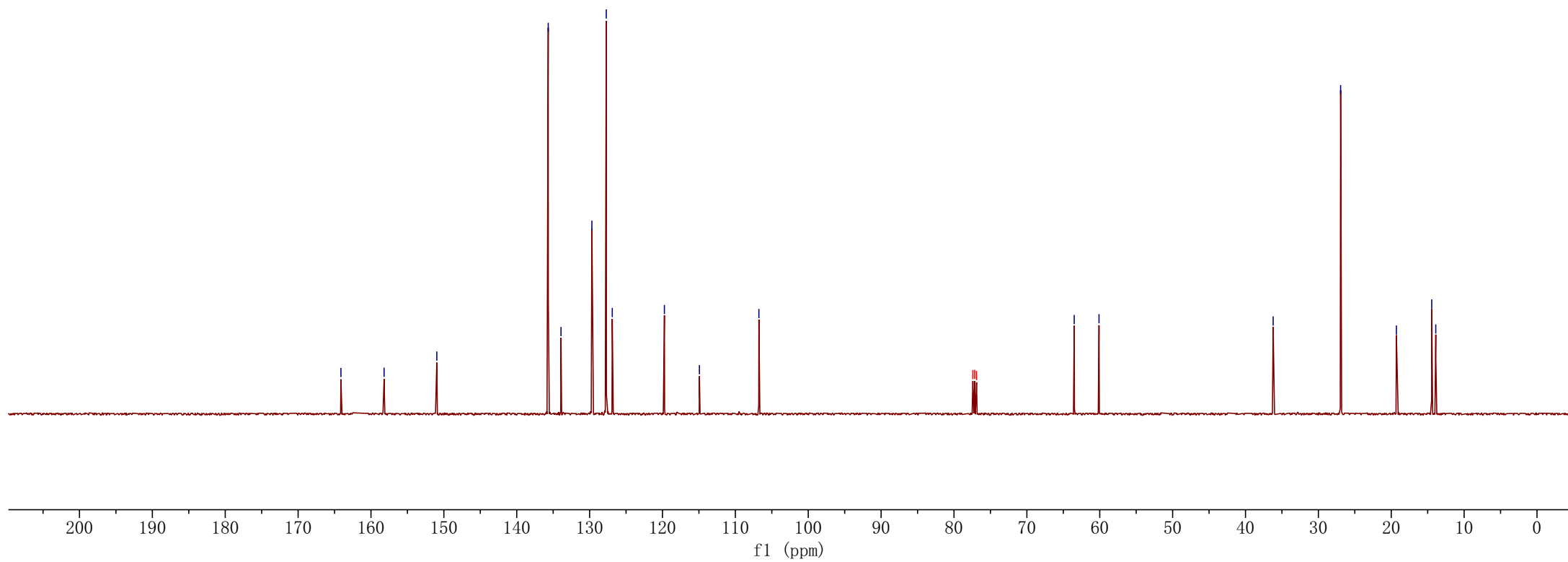
— 36.21

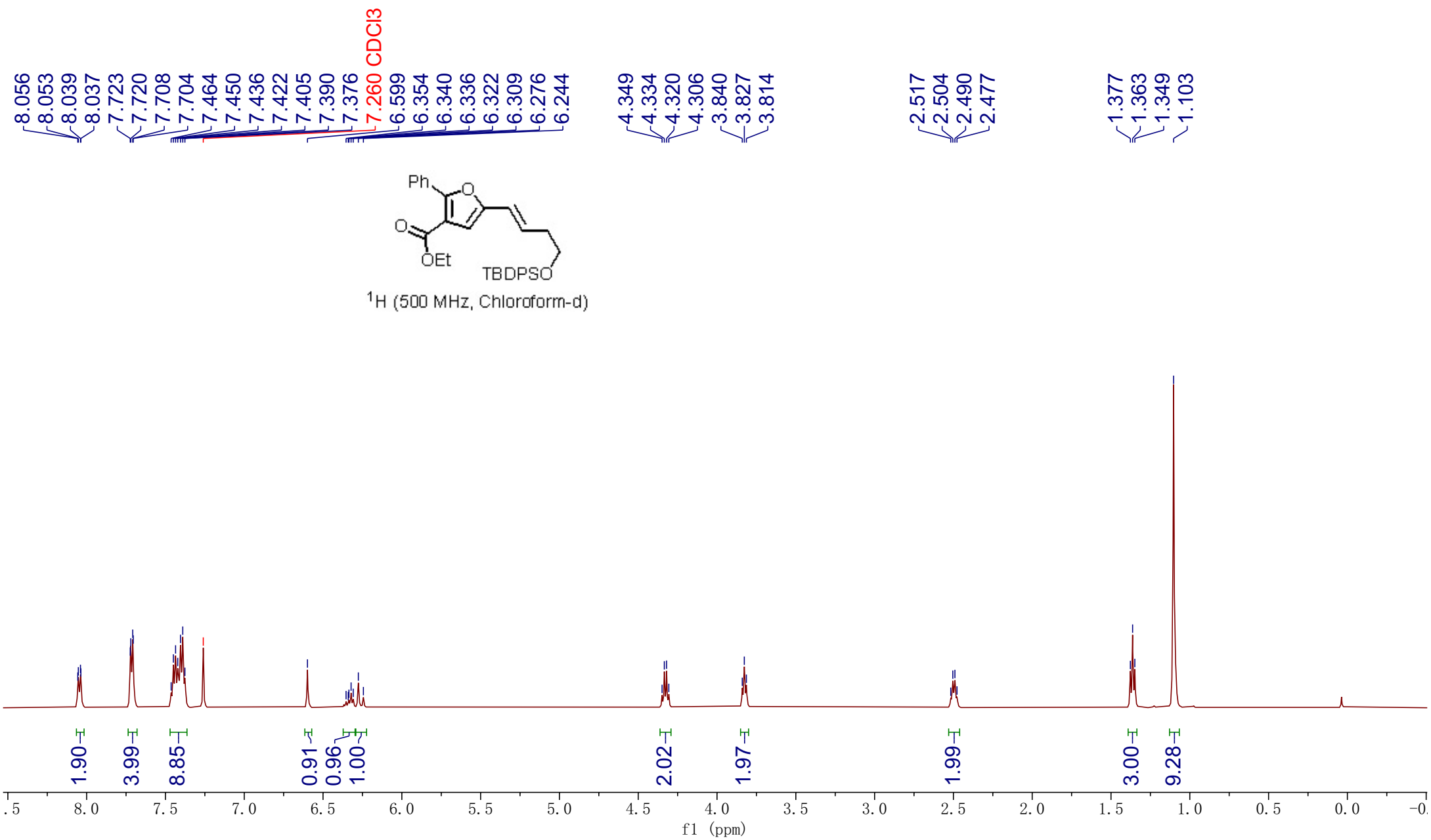
— 26.95

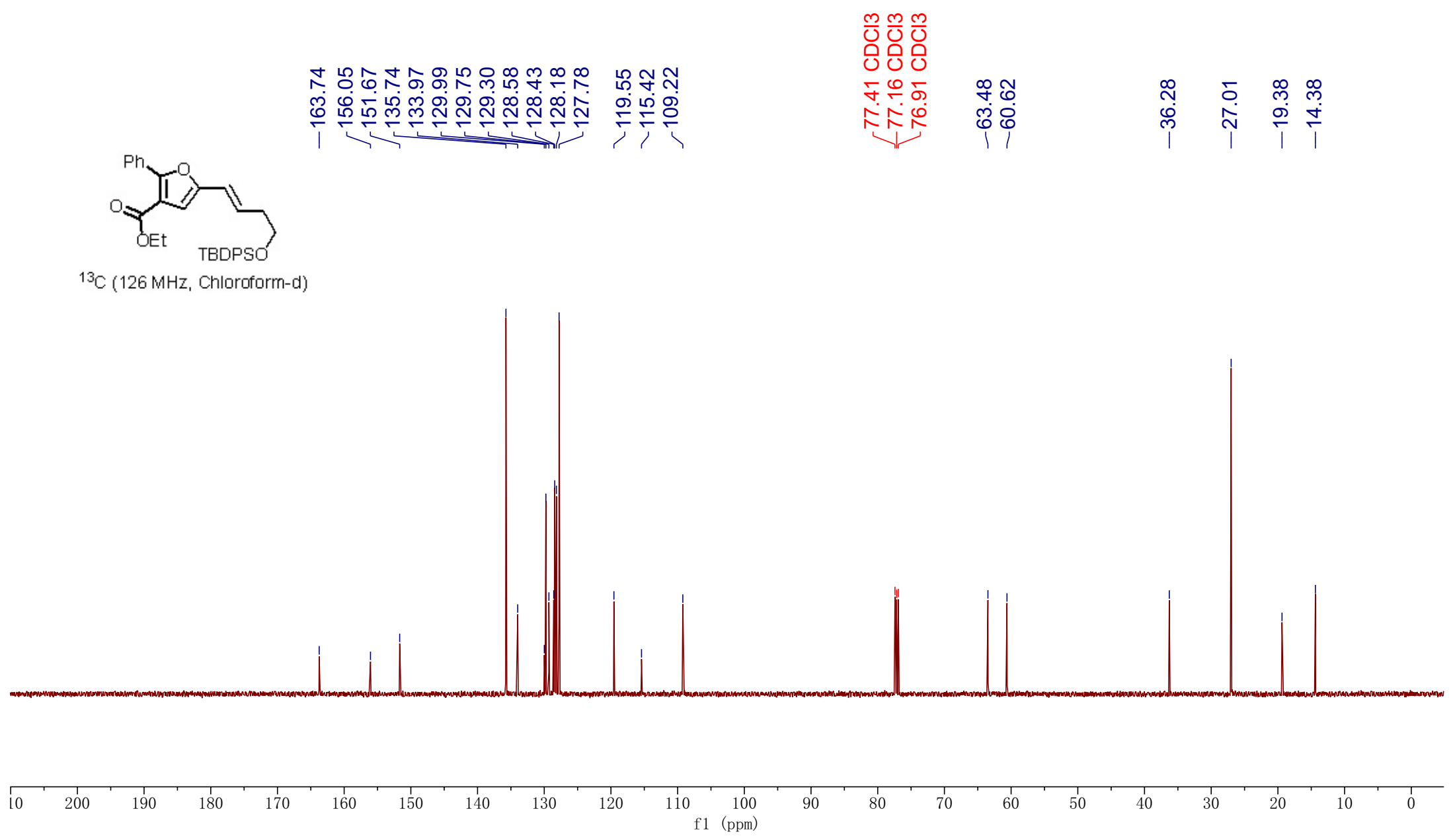
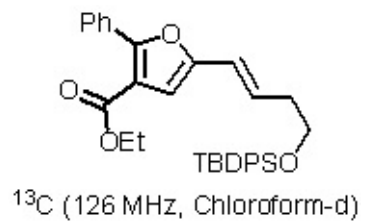
— 19.30

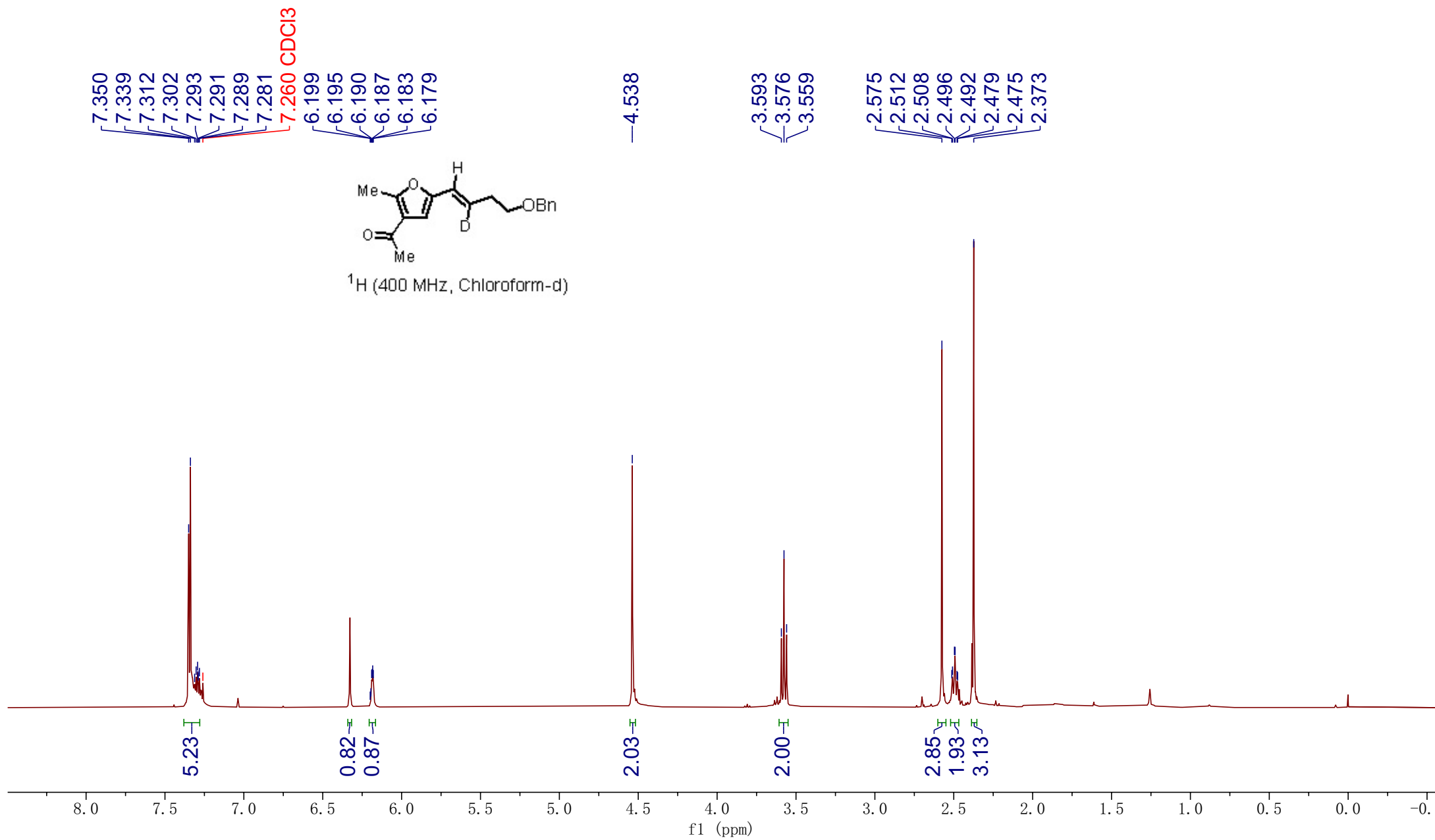
— 14.44

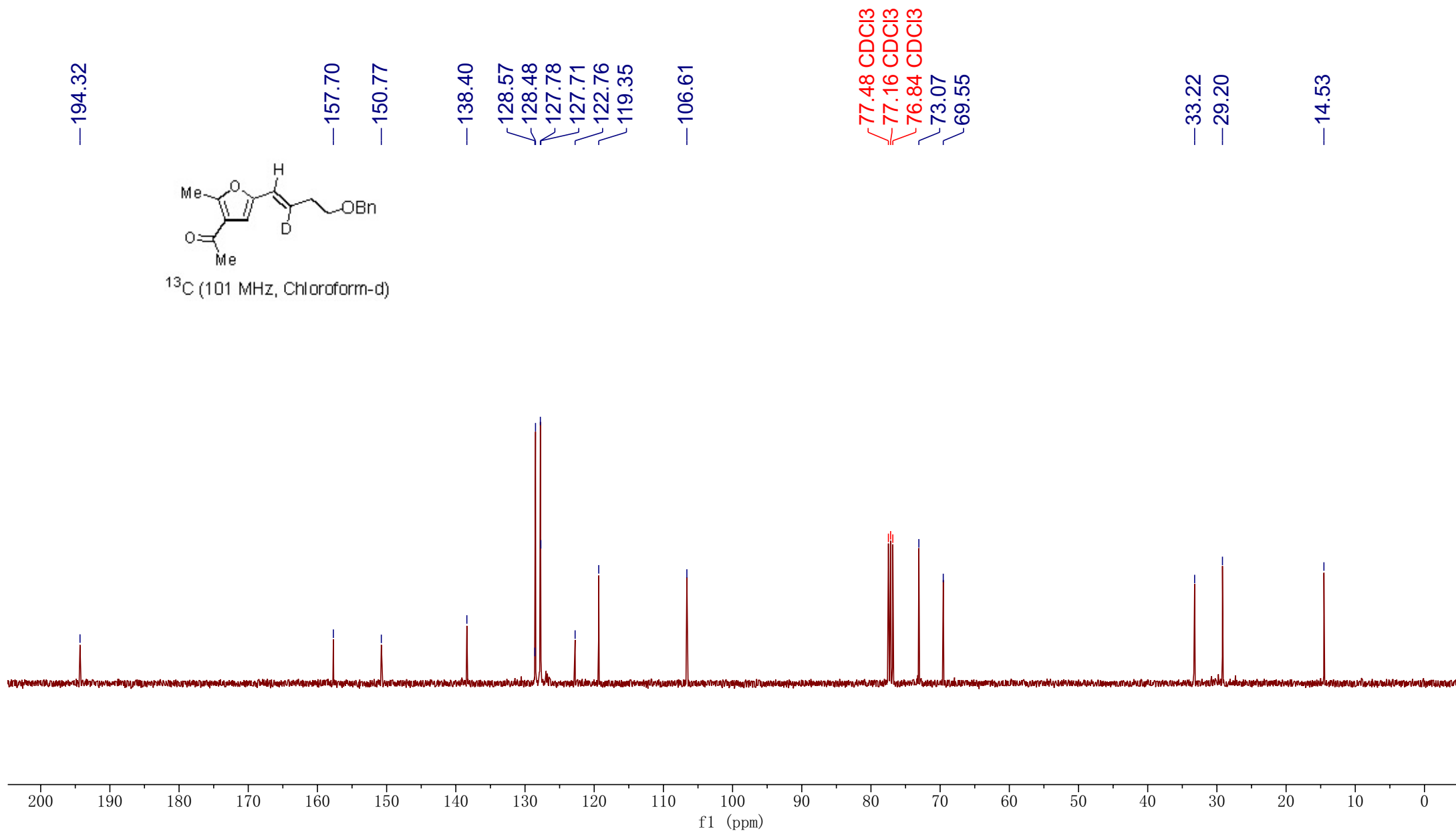
— 13.89

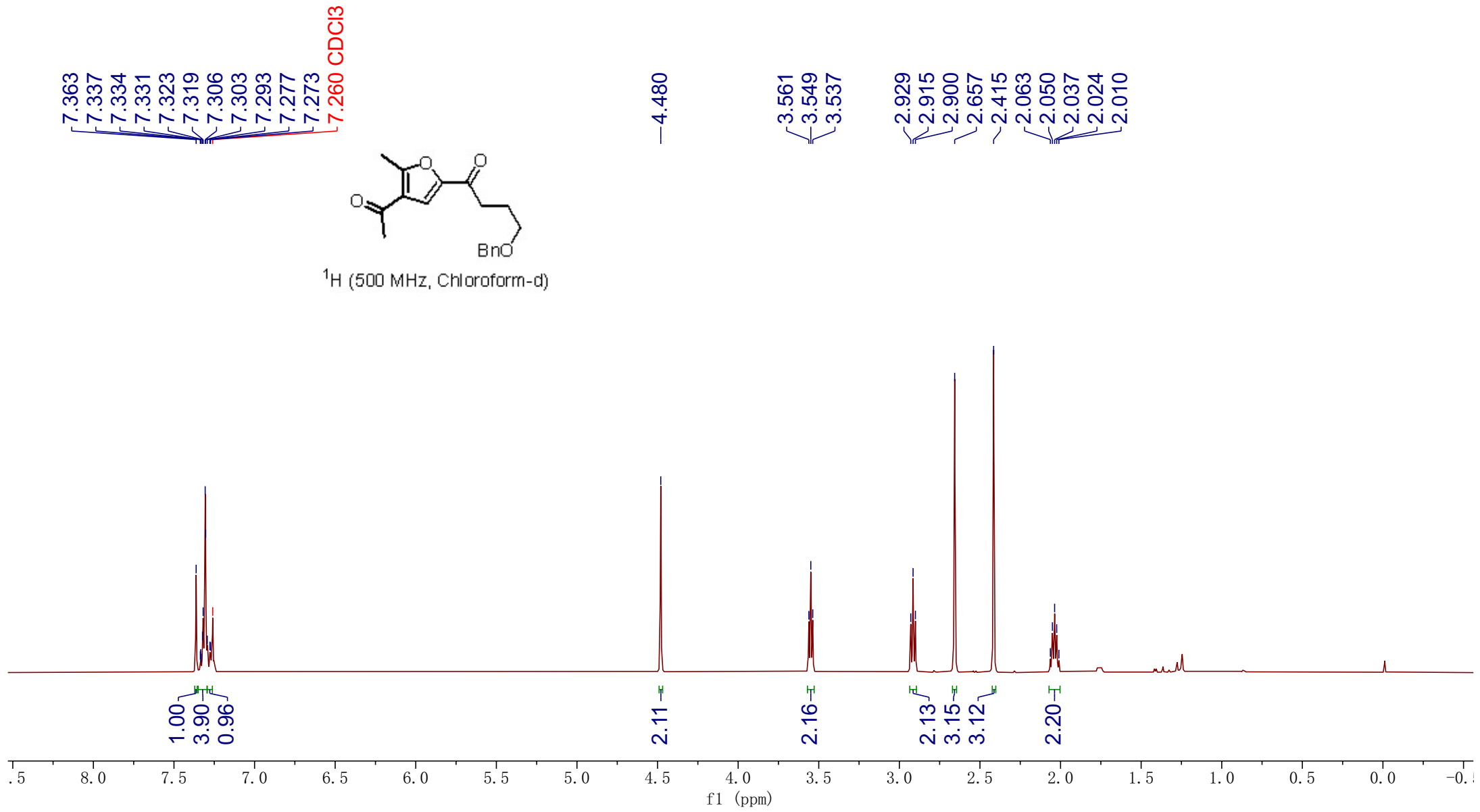


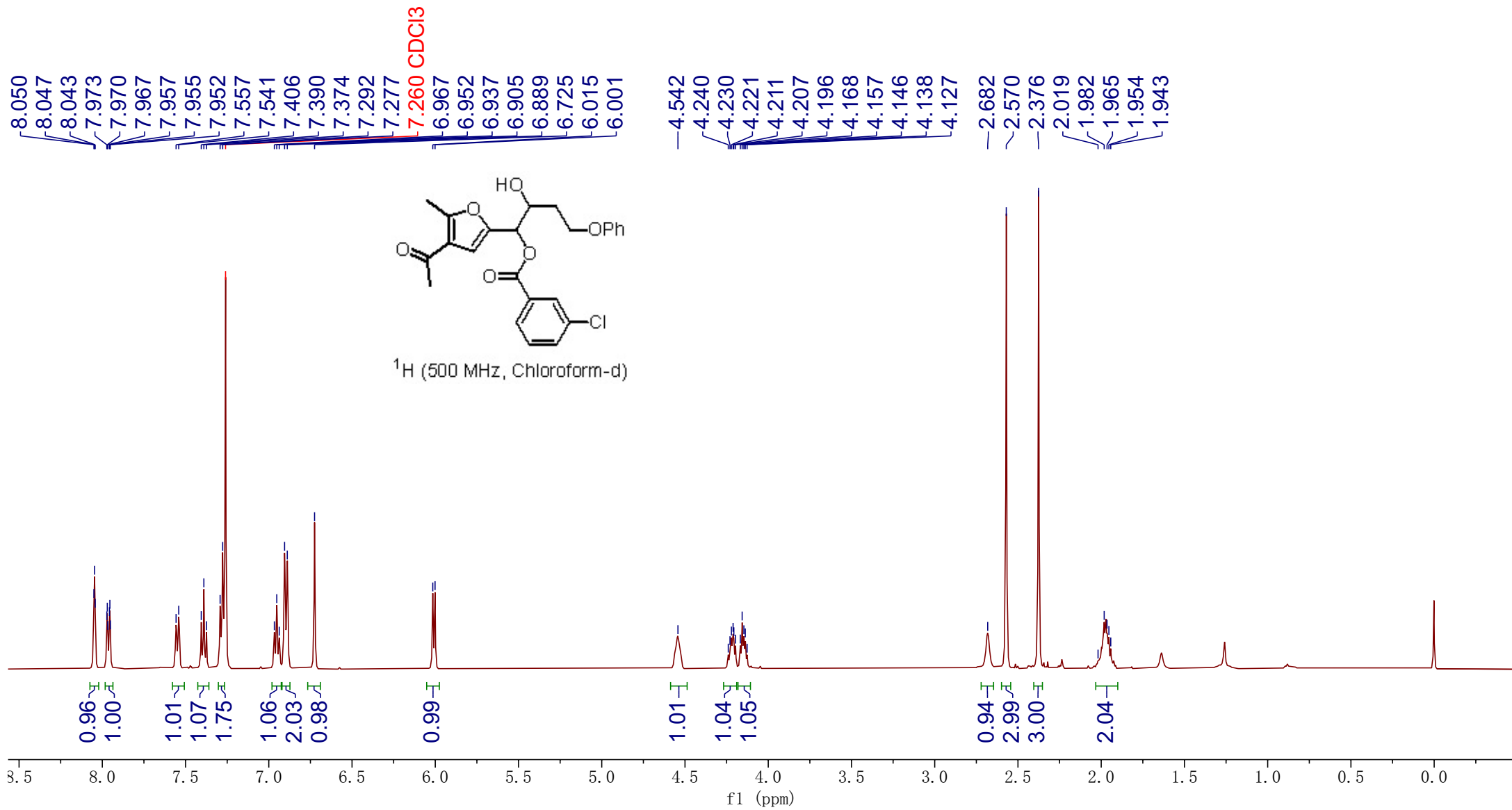


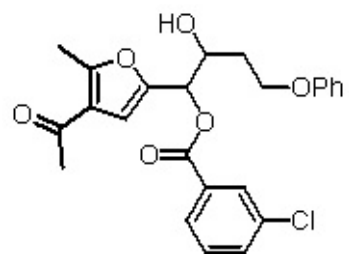












^{13}C (126 MHz, Chloroform-d)

— 193.92

— 164.69

— 159.12

— 158.59

— 147.89

— 134.83

— 133.58

— 131.46

— 129.97

— 129.66

— 128.14

— 122.19

— 121.21

— 114.64

— 111.17

— 77.41 CDCI3

— 77.16 CDCI3

— 76.91 CDCI3

— 72.77

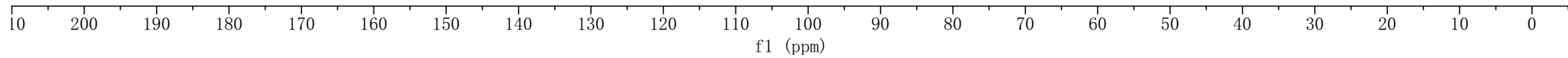
— 69.56

— 64.62

— 32.59

— 29.22

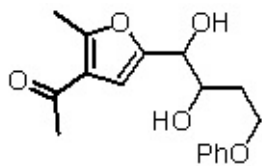
— 14.60



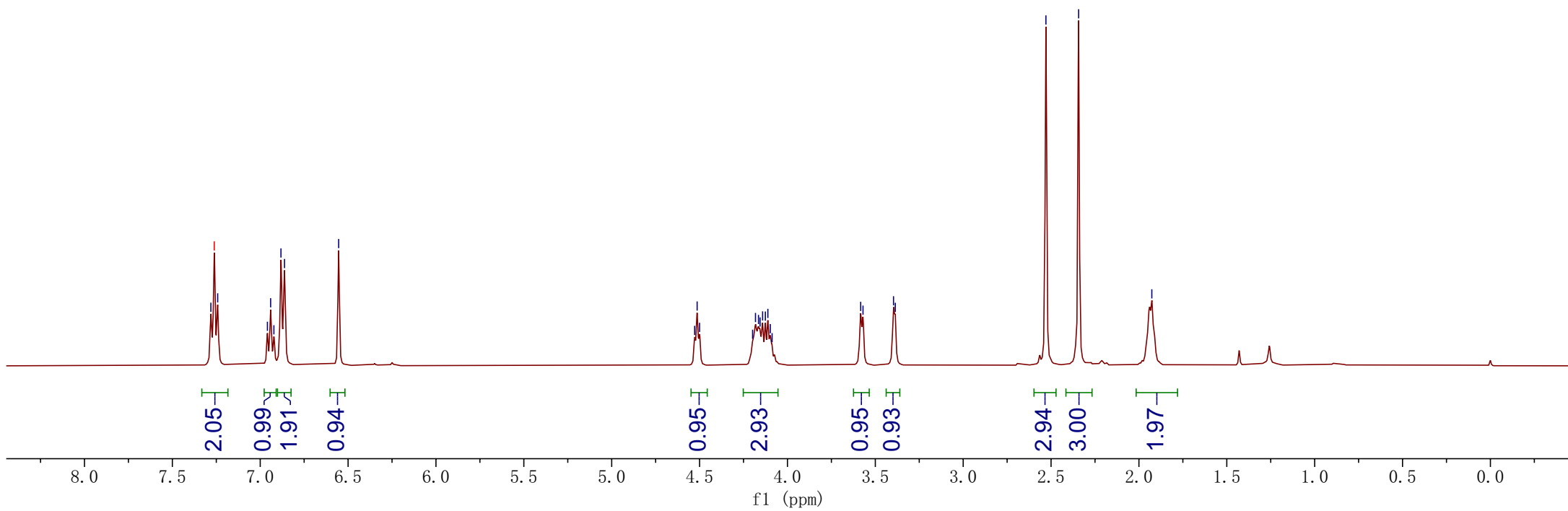
7.281
7.262 CDCl3
7.242
6.959
6.941
6.922
6.882
6.862
6.554

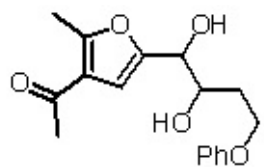
4.528
4.514
4.500
4.198
4.182
4.165
4.156
4.141
4.126
4.111
4.098
4.087
3.583
3.570
3.396
3.386

2.529
2.343
1.927



¹H (400 MHz, Chloroform-d)





^{13}C (101MHz, Chloroform-d)

—194.55

—158.48

—151.92

—129.58

—122.01

—121.09

—114.50

—108.42

77.48 CDCI3

77.16 CDCI3

76.84 CDCI3

70.93

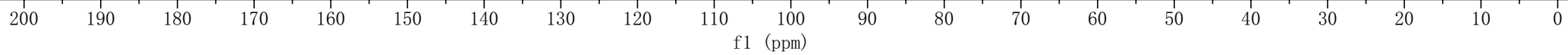
70.83

64.85

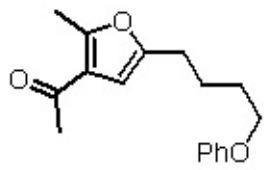
—32.57

—29.15

—14.50



7.300
7.281
7.260 CDCI3
7.256
6.957
6.938
6.920
6.904
6.884
-6.229



¹H (400 MHz, Chloroform-d)

3.996
3.983
3.968

2.668
2.650
2.634
2.545
2.367
1.845
1.836
1.829
1.820
1.811

2.18

1.08

2.34

0.95

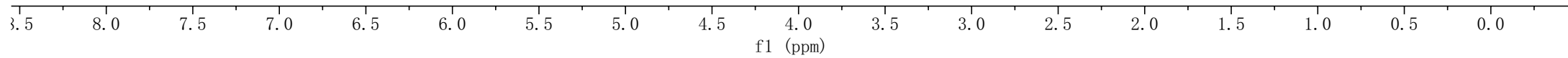
1.95

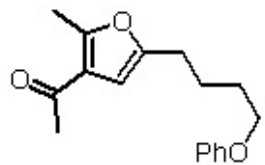
2.16

2.97

3.00

4.03





^{13}C (101MHz, Chloroform-d)

— 194.50

~ 159.02

~ 157.07

~ 153.80

— 129.55

~ 122.05

~ 120.72

~ 114.52

— 105.73

77.48 CDCI3

77.16 CDCI3

76.84 CDCI3

— 67.36

~ 29.24

~ 28.75

~ 27.45

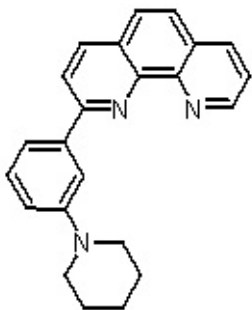
~ 24.53

— 14.47

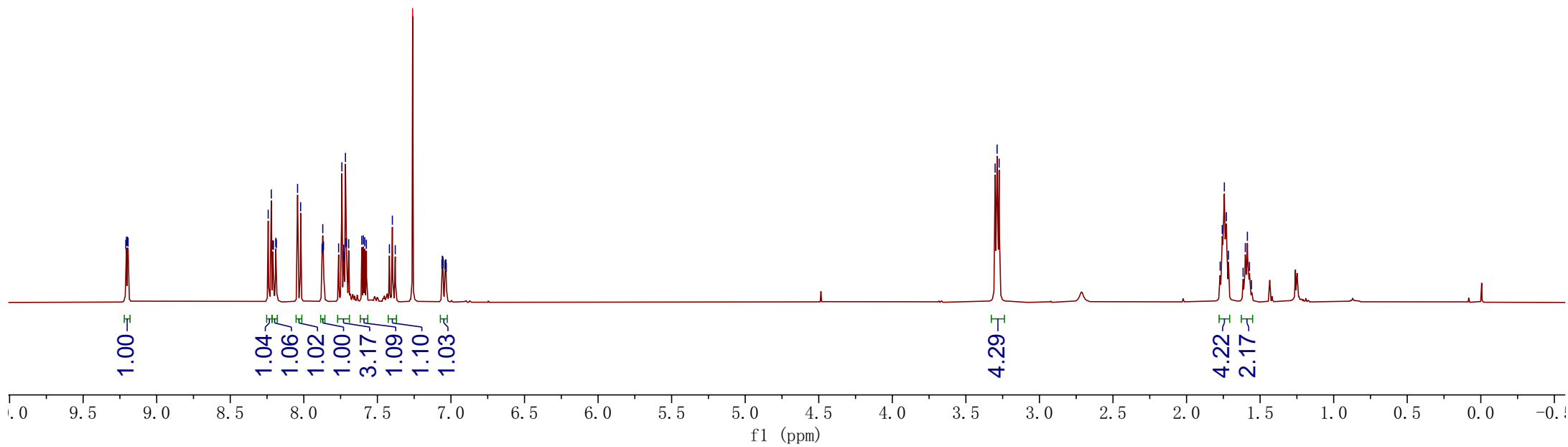
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

9.210
 9.206
 9.199
 9.195
 8.242
 8.221
 8.211
 8.207
 8.191
 8.187
 8.043
 8.022
 7.876
 7.871
 7.866
 7.763
 7.741
 7.731
 7.729
 7.726
 7.717
 7.713
 7.710
 7.695
 7.606
 7.595
 7.586
 7.575
 7.418
 7.398
 7.379
 7.260 CDCl₃
 7.061
 7.059
 7.055
 7.052
 7.041
 7.038
 7.034
 7.032
 3.301
 3.288
 3.274
 1.772
 1.757
 1.743
 1.729
 1.715
 1.616
 1.601
 1.587
 1.572
 1.558



¹H NMR (400 MHz, Chloroform-d)

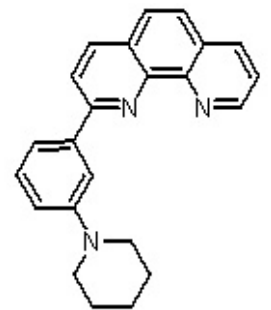


158.49
152.86
150.29
146.46
146.05
140.71
136.70
136.08
129.42
129.07
127.54
126.44
126.12
122.88
121.13
119.33
117.74
116.23

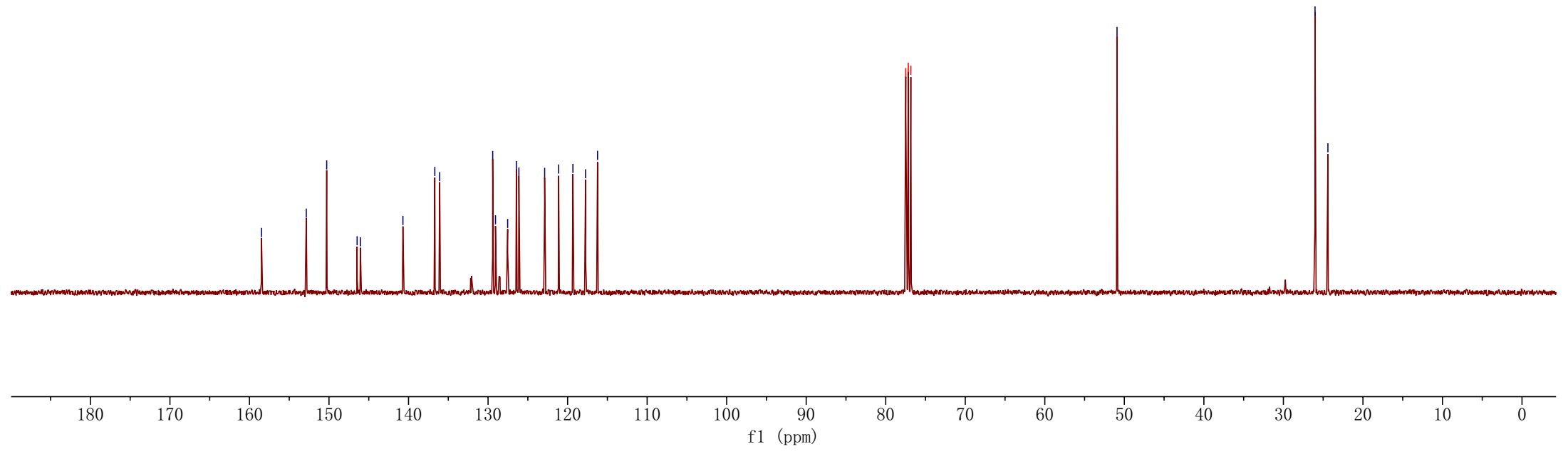
77.48 CDCl₃
77.16 CDCl₃
76.84 CDCl₃

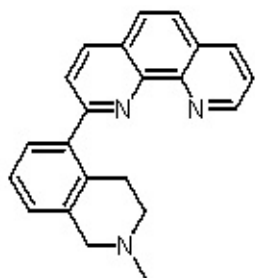
50.92

26.02
24.40

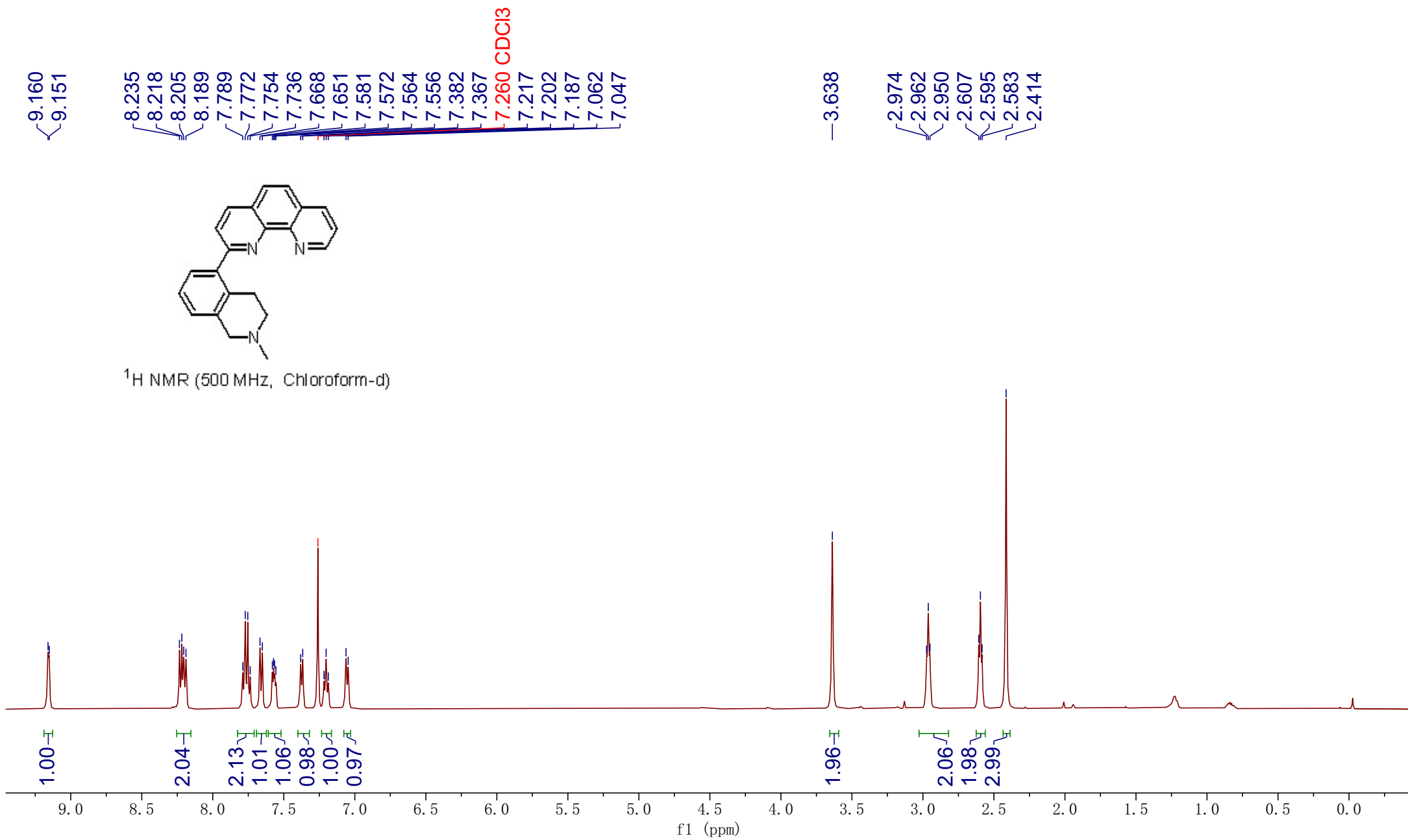


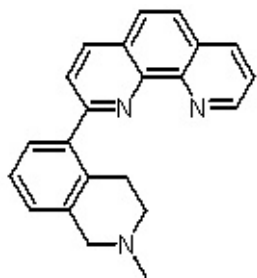
¹³C NMR (101 MHz, Chloroform-d)





¹H NMR (500 MHz, Chloroform-d)





¹³C NMR (101 MHz, Chloroform-d)

160.36
150.56
146.52
146.06
141.13
136.10
136.07
135.15
132.13
129.05
128.26
127.26
126.90
126.50
125.80
124.33
123.02

77.48 CDCl₃
77.16 CDCl₃
76.84 CDCl₃

58.55
53.14
46.12

27.99

