

Supporting Information
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SUPPLEMENTARY INFORMATION

Iron-Mediated Bromocyclization of Olefinic Amides for the Synthesis of Bromobenzoxazines

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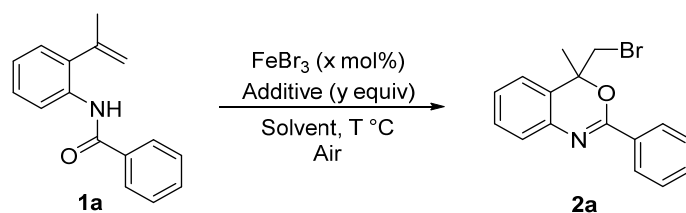
† These authors contributed equally to this work.

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1. Optimization details

Table S1. Optimization of reaction conditions^[a]



Entry	FeBr ₃ (x mol%)	Solvent	Additive (y equiv)	T (°C)	Time (h)	Yield (%)
1	FeBr ₃ (50)	DMAc	---	100	10	42
2	FeBr ₃ (50)	DMAc	K ₂ CO ₃ (1.0)	100	10	trace
3	FeBr ₃ (50)	DMAc	Na ₂ CO ₃ (1.0)	100	10	trace
4	FeBr ₃ (50)	DMAc	K ₃ PO ₄ (1.0)	100	10	trace
5	FeBr ₃ (50)	DMAc	DABCO (1.0)	100	10	trace
6	FeBr ₃ (50)	DMAc	AcOH (1.0)	100	10	39
7	FeBr ₃ (50)	DMAc	NaBr (1.0)	100	10	<5
8	FeBr ₃ (50)	DMSO	---	100	10	<5
9	FeBr ₃ (50)	DMF	---	100	10	36
10	FeBr ₃ (50)	PhCl	---	100	10	22
11	FeBr ₃ (50)	H ₂ O	---	100	10	trace
12	FeBr₃ (100)	DMAc	---	100	5	91
13	FeBr ₃ (200)	DMAc	---	100	1.5	91
14	FeBr ₃ (100)	DMAc	---	80	10	35
15	FeBr ₃ (100)	DMAc	---	120	5	91
16 ^[b]	FeBr ₃ (100)	DMAc	---	100	10	trace
17	FeCl ₃ (100)	DMAc	---	100	5	---
18 ^[c]	FeBr ₃ (100)	DMAc	---	100	5	90
19 ^[d]	FeBr ₃ (100)	DMAc	---	100	5	79

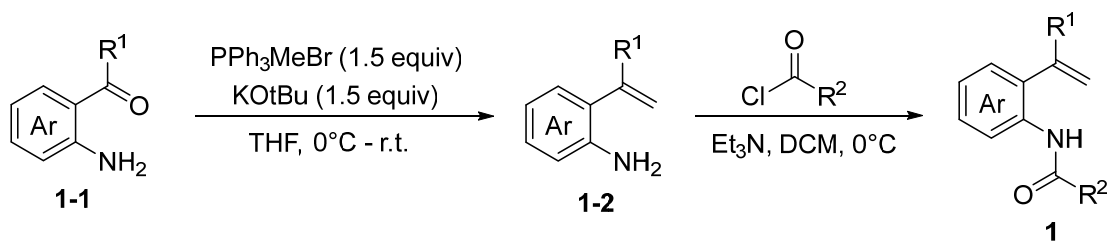
[a] Reaction conditions: **1a** (0.8 mmol, 1.0 equiv.) in solvent (0.25M) under open air. Isolated yields for each product.

[b] In an Ar atmosphere.

[c] In dark.

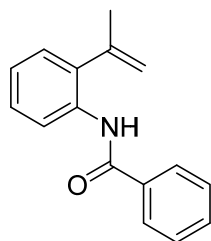
[d] In an O₂ atmosphere.

2. General procedure for the synthesis of substrate **1**^[1]



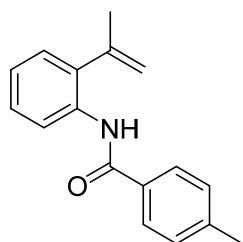
To a suspension of PPh_3MeBr (15 mmol, 1.5 equiv.) in dry THF (30 mL) at 0°C was added KOtBu (15 mmol, 1.5 equiv) in two portions over 10 min. The resulting yellow mixture was allowed to stir for 30 minutes at room temperature before it was cooled to 0°C again and the corresponding 2'-aminoacetophenone or 2-aminobenzophenone (10 mmol, 1 equiv) was added. After five minutes the cooling bath was removed and the mixture was allowed to warm to ambient temperature. After completion of the reaction the mixture was diluted with EtOAc (20 mL) and sat. NaHCO_3 (20 mL). The phases were separated and the aqueous phase was extracted with EtOAc (2×30 mL). The combined organic phases were washed with brine, dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The resulting residue was loaded on silica and purified via column chromatography to give **1-2**.

To a solution of **1-2** (3.0 mmol) and Et_3N (0.46 g, 4.5 mmol) in CH_2Cl_2 (6.0 mL) was added the solution of benzoylchloride (2.5 mL, 3.6 mmol) in dichloromethane (2.0 mL) dropwise at 0°C . After completion, the reaction mixture was purified via column chromatography to give the pure product **1**.



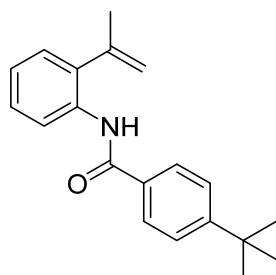
N-(2-(prop-1-en-2-yl)phenyl)benzamide (1a)^[2]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 80% yield (569 mg). Mp $82\text{--}83^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 8.55–8.39 (m, 2H, NH and ArH), 7.89–7.75 (m, 2H, ArH), 7.61–7.43 (m, 3H, ArH), 7.39–7.28 (m, 1H, ArH), 7.19 (dd, $J_1 = 2.0$ Hz, $J_2 = 8.0$ Hz, 1H, ArH), 7.12 (m, 1H, ArH), 5.48 (t, $J = 1.6$ Hz, 1H, CH_2), 5.12 (d, $J = 0.8$ Hz, 1H, CH_2), 2.12 (s, 3H, CH_3). ^{13}C NMR (101 MHz, CDCl_3): δ 165.2, 143.4, 135.2, 134.1, 133.6, 131.9, 129.0, 128.2, 127.8, 127.0, 124.0, 120.8, 117.0, 24.8.



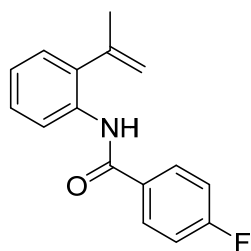
4-Methyl-N-(2-(prop-1-en-2-yl)phenyl)benzamide (1b)^[2]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 96% yield (724 mg). Mp 73–74°C. ¹H NMR (400 MHz, CDCl₃): δ 8.44 (s, 2H, NH and ArH), 7.72 (d, *J* = 8.4 Hz, 2H, ArH), 7.36–7.26 (m, 3H, ArH), 7.18 (dd, *J*₁ = 1.6 Hz, *J*₂ = 7.6 Hz, 1H, ArH), 7.10 (m, 1H, ArH), 5.57–5.39 (m, 1H, CH₂), 5.11 (s, 1H, CH₂), 2.42 (s, 3H, CH₃), 2.11 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 165.1, 143.4, 142.4, 134.2, 133.5, 132.4, 129.6, 128.1, 127.7, 127.0, 123.9, 120.8, 116.9, 24.8, 21.6.



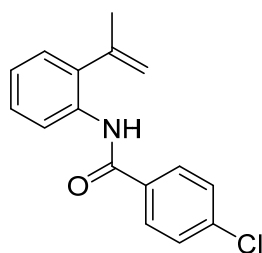
4-(Tert-butyl)-N-(2-(prop-1-en-2-yl)phenyl)benzamide (1c)^[3]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 49% yield (431 mg). Mp 124–126°C. ¹H NMR (400 MHz, CDCl₃): δ 8.49 (d, *J* = 7.6 Hz, 2H, ArH), 7.78 (d, *J* = 8.4 Hz, 2H, ArH), 7.49 (d, *J* = 8.4 Hz, 2H, ArH), 7.34–7.25 (m, 1H, ArH), 7.17 (dd, *J*₁ = 1.2 Hz, *J*₂ = 7.6 Hz 1H, ArH), 7.13–7.04 (m, 1H, ArH), 5.46 (s, 1H, CH₂), 5.10 (s, 1H, CH₂), 2.10 (s, 3H, CH₃), 1.34 (s, 9H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 165.0, 155.3, 143.3, 134.2, 133.5, 132.2, 128.0, 127.7, 126.8, 126.8, 125.8, 123.8, 120.8, 116.8, 35.0, 31.2, 24.7.



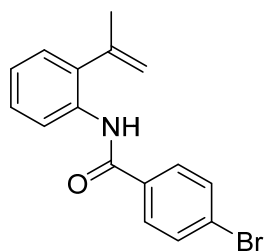
N-(1-(4-fluorophenyl)vinyl)-2-(prop-1-en-2-yl)aniline (1d)^[3]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 71% yield (544 mg). Mp 113–114°C. ¹H NMR (400 MHz, CDCl₃): δ 8.53–8.20 (m, 2H, NH and ArH), 7.83 (dd, *J*₁ = 5.2 Hz, *J*₂ = 8.4 Hz, 2H, ArH), 7.32 (t, *J* = 7.2 Hz, 1H, ArH), 7.15 (m, 4H, ArH), 5.48 (s, 1H, CH₂), 5.11 (s, 1H, CH₂), 2.12 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 165.2 (d, *J*_{CF} = 250.8 Hz, Ar-F), 163.7, 143.5, 134.0, 133.7, 131.4, 131.3, 129.4, 129.3, 128.2, 127.8, 124.2, 120.9, 116.9, 116.1, 115.9, 24.8. ¹⁹F NMR (376 MHz, CDCl₃): δ -107.5, -107.5, -107.5, -107.5, -107.5, -107.6, -107.6.



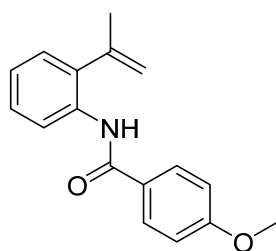
4-Chloro-N-(2-(prop-1-en-2-yl)phenyl)benzamide (1e)^[3]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 71% yield (570 mg). Mp 115–117°C. ¹H NMR (400 MHz, CDCl₃): δ 8.59–8.26 (m, 2H, NH and ArH), 7.76 (d, *J* = 8.8 Hz, 2H, ArH), 7.46 (d, *J* = 8.4 Hz, 2H, ArH), 7.36–7.28 (m, 1H, ArH), 7.20 (dd, *J*₁ = 1.6 Hz, *J*₂ = 7.6 Hz, 1H, ArH), 7.13 (m, 1H, ArH), 5.48 (t, *J* = 1.6 Hz, 1H, CH₂), 5.11 (d, *J* = 1.2 Hz, 1H, CH₂), 2.11 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 164.1, 143.4, 138.2, 133.9, 133.6, 133.6, 129.2, 128.5, 128.2, 127.8, 124.3, 120.8, 117.0, 24.8.



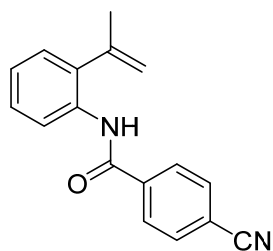
4-Bromo-N-(2-(prop-1-en-2-yl)phenyl)benzamide (1f)^[3]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 79% yield (746 mg). Mp 126-128°C. ¹H NMR (400 MHz, CDCl₃): δ 8.53–8.34 (m, 2H, NH and ArH), 7.69 (d, *J* = 8.4 Hz, 2H, ArH), 7.62 (d, *J* = 8.8 Hz, 2H, ArH), 7.37–7.28 (m, 1H, ArH), 7.19 (dd, *J*₁ = 1.6 Hz, *J*₂ = 7.6 Hz, 1H, ArH), 7.17–7.09 (m, 1H, ArH), 5.56–5.42 (m, 1H, CH₂), 5.10 (s, 1H, CH₂), 2.11 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 164.2, 143.4, 134.0, 133.8, 133.6, 132.2, 128.6, 128.2, 127.8, 126.7, 124.3, 120.8, 117.0, 24.8.



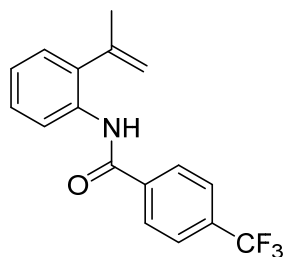
4-Methoxy-N-(2-(prop-1-en-2-yl)phenyl)benzamide (1g)^[3]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 73% yield (585 mg). Mp 115-117°C. ¹H NMR (400 MHz, CDCl₃): δ 8.48 (d, *J* = 8.0 Hz, 1H, NH), 8.39 (s, 1H, ArH), 7.79 (d, *J* = 8.8 Hz, 2H, ArH), 7.36–7.28 (m, 1H, ArH), 7.18 (dd, *J*₁ = 1.2 Hz, *J*₂ = 7.6 Hz, 1H, ArH), 7.10 (t, *J* = 7.2 Hz, 1H, ArH), 6.98 (d, *J* = 8.8 Hz, 2H, ArH), 5.48 (s, 1H, CH₂), 5.11 (s, 1H, CH₂), 3.87 (s, 3H, CH₃), 2.11 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 164.7, 162.5, 143.5, 134.3, 133.4, 128.9, 128.1, 127.7, 127.4, 123.8, 120.7, 116.9, 114.2, 55.6, 24.8.



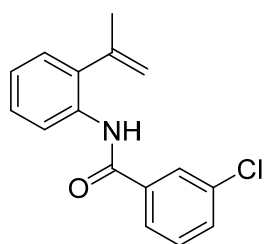
4-Cyano-N-(2-(prop-1-en-2-yl)phenyl)benzamide (1h)^[4]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 69% yield (544 mg). Mp 128-130°C. ¹H NMR (400 MHz, CDCl₃): δ 8.51 (s, 1H, NH), 8.40 (d, *J* = 8.0 Hz, 1H, ArH), 7.91 (d, *J* = 8.0 Hz, 2H, ArH), 7.77 (d, *J* = 8.4 Hz, 2H, ArH), 7.33 (t, *J* = 8.0 Hz, 1H, ArH), 7.27–7.11 (m, 2H, ArH), 5.49 (s, 1H, CH₂), 5.11 (s, 1H, CH₂), 2.12 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 163.3, 143.2, 138.9, 133.9, 133.4, 132.7, 128.2, 127.9, 127.7, 124.7, 121.0, 118.0, 117.0, 115.4, 24.7.



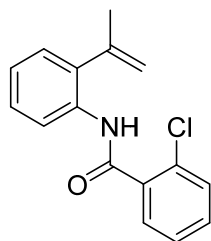
N-(2-(prop-1-en-2-yl)phenyl)-4-(trifluoromethyl)benzamide (1i)^[4]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 66% yield (604 mg). Mp 139-141°C. ¹H NMR (400 MHz, CDCl₃): δ 8.61–8.34 (m, 2H, NH and ArH), 7.93 (d, *J* = 8.0 Hz, 2H, ArH), 7.76 (d, *J* = 8.0 Hz, 2H, ArH), 7.38–7.30 (m, 1H, ArH), 7.25–7.11 (m, 2H, ArH), 5.55–5.45 (m, 1H, CH₂), 5.20–5.05 (m, 1H, CH₂), 2.12 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 163.9, 143.4, 138.5, 133.8, 133.7, 128.3, 127.9, 127.5, 126.1, 126.0 (q, *J*_{CF} = 3.6 Hz, CF₃), 124.5, 120.9, 117.0, 24.8. ¹⁹F NMR (376 MHz, CDCl₃): δ -62.98.



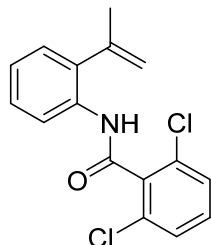
3-Chloro-N-(2-(prop-1-en-2-yl)phenyl)benzamide (1j)^[3]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 85% yield (690 mg). Mp 67-68°C. ¹H NMR (400 MHz, CDCl₃): δ 8.33 (d, *J* = 6.0 Hz, 2H, NH and ArH), 7.75 (s, 1H, ArH), 7.56 (d, *J* = 7.6 Hz, 1H, ArH), 7.42 (d, *J* = 7.6 Hz, 1H, ArH), 7.33 (dt, *J*₁ = 2.4 Hz, *J*₂ = 7.6 Hz, 1H, ArH), 7.23 (t, *J* = 7.2 Hz, 1H, ArH), 7.11 (d, *J* = 7.6 Hz, 1H, ArH), 7.04 (t, *J* = 7.2 Hz, 1H, ArH), 5.39 (s, 1H, CH₂), 5.02 (s, 1H, CH₂), 2.03 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 163.8, 143.3, 137.0, 135.2, 133.8, 133.7, 131.9, 130.2, 128.2, 127.8, 127.7, 127.6, 124.8, 124.4, 121.0, 121.0, 117.0, 116.9, 24.7, 24.7.



2-Chloro-N-(2-(prop-1-en-2-yl)phenyl)benzamide (1k)^[3]

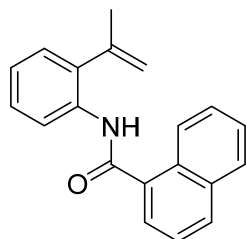
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 89% yield (724 mg). Mp 82-83°C. ¹H NMR (400 MHz, CDCl₃): δ 8.39 (d, *J* = 8.0 Hz, 1H, NH), 8.23 (s, 1H, ArH), 7.64 (dd, *J*₁ = 1.6 Hz, *J*₂ = 7.2 Hz, 1H, ArH), 7.42–7.18 (m, 4H, ArH), 7.14–6.95 (m, 2H, ArH), 5.39–5.18 (m, 1H, CH₂), 5.09–4.85 (m, 1H, CH₂), 1.98 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 164.4, 142.7, 135.5, 134.1, 133.9, 131.7, 130.6, 130.5, 130.3, 128.0, 127.9, 127.4, 124.4, 121.1, 117.3, 24.8.



2,6-Dichloro-N-(2-(prop-1-en-2-yl)phenyl)benzamide (1l)^[4]

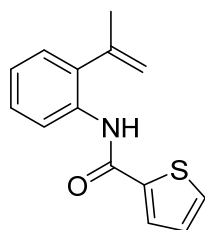
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 55% yield (503 mg). Mp 150-152°C. ¹H

NMR (400 MHz, CDCl₃): δ 8.45 (d, J = 8.0 Hz, 1H, NH), 7.73 (s, 1H, ArH), 7.40–7.24 (m, 4H, ArH), 7.23–7.11 (m, 2H, ArH), 5.38–5.25 (m, 1H, CH₂), 5.06 (s, 1H, CH₂), 2.08 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 162.5, 142.5, 136.2, 134.1, 133.4, 132.4, 131.0, 128.4, 128.1, 128.0, 124.8, 121.5, 117.5, 24.8.



N-(2-(prop-1-en-2-yl)phenyl)-1-naphthamide (1m)^[3]

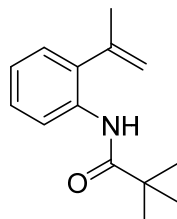
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 91% yield (784 mg). Mp 126–128°C. ¹H NMR (400 MHz, CDCl₃): δ 8.57 (d, J = 7.2 Hz, 1H, NH), 8.41 (d, J = 7.6 Hz, 1H, ArH), 8.18 (s, 1H, ArH), 7.90 (dd, J_1 = 8.4 Hz, J_2 = 24.4 Hz, 2H, ArH), 7.66 (d, J = 6.8 Hz, 1H, ArH), 7.50 (m, 3H, ArH), 7.35 (t, J = 7.2 Hz, 1H, ArH), 7.16 (m, 2H, ArH), 5.27 (s, 1H, CH₂), 5.02 (s, 1H, CH₂), 2.04 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 167.4, 142.8, 134.7, 134.2, 134.0, 133.9, 131.2, 131.1, 130.2, 128.5, 128.4, 128.1, 127.9, 127.4, 126.7, 125.5, 125.4, 124.9, 124.3, 121.1, 117.1, 117.1, 24.6, 24.6.



N-(2-(prop-1-en-2-yl)phenyl)thiophene-2-carboxamide (1n)^[3]

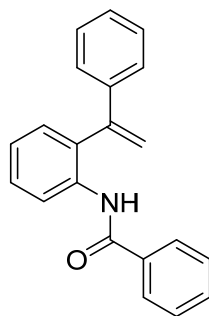
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 49% yield (356 mg). Mp 83–84°C. ¹H NMR (400 MHz, CDCl₃): δ 8.41 (d, J = 9.2 Hz, 1H, NH), 8.35 (s, 1H, ArH), 7.51 (d, J = 4.4 Hz, 2H, ArH), 7.33–7.24 (m, 1H, ArH), 7.18 (dd, J_1 = 1.6 Hz, J_2 = 7.6 Hz, 1H, ArH), 7.14–7.06 (m, 2H, ArH), 5.49 (t, J = 3.2 Hz, 1H, CH₂), 5.10 (d, J = 0.8 Hz, 1H, CH₂), 2.11 (s, 3H, CH₃). ¹³C NMR (101 MHz,

CDCl₃): δ 159.6, 143.2, 139.8, 133.8, 133.3, 130.7, 128.2, 128.1, 127.9, 127.7, 124.0, 120.7, 116.9, 24.7.



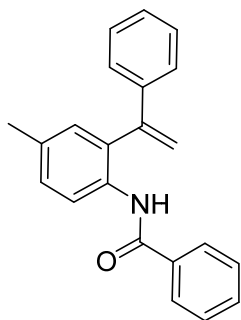
N-(2-(prop-1-en-2-yl)phenyl)pivalamide (1o)^[3]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 83% yield (540 mg). Mp 59–60°C. ¹H NMR (400 MHz, CDCl₃): δ 8.34 (d, J = 8.4 Hz, 1H, NH), 7.96 (s, 1H, ArH), 7.29–7.21 (m, 1H, ArH), 7.12 (dd, J_1 = 1.6 Hz, J_2 = 7.6 Hz, 1H, ArH), 7.05 (t, J = 7.6 Hz, 1H, ArH), 5.42 (s, 1H, CH₂), 5.03 (s, 1H, CH₂), 2.07 (s, 3H, CH₃), 1.28 (s, 9H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 176.4, 143.4, 134.3, 133.3, 128.1, 127.9, 127.7, 127.6, 127.6, 123.6, 123.5, 120.6, 120.5, 116.9, 116.8, 116.6, 116.6, 40.1, 27.9, 27.7, 27.6, 27.4, 24.6, 24.5.



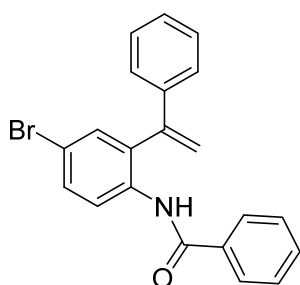
N-(2-(1-phenylvinyl)phenyl)benzamide (1p)^[4]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 67% yield (601 mg). Mp 88–89°C. ¹H NMR (400 MHz, CDCl₃): δ 8.49 (d, J = 8.4 Hz, 1H, NH), 7.80 (s, 1H, ArH), 7.46–7.24 (m, 12H ArH), 7.19 (t, J = 7.6 Hz, 1H, ArH), 5.90 (s, 1H, CH₂), 5.42 (s, 1H, CH₂). ¹³C NMR (101 MHz, CDCl₃): δ 165.1, 146.4, 139.0, 135.5, 134.9, 131.7, 131.6, 130.7, 129.2, 129.1, 128.9, 128.6, 126.9, 126.8, 124.4, 121.1, 117.9.



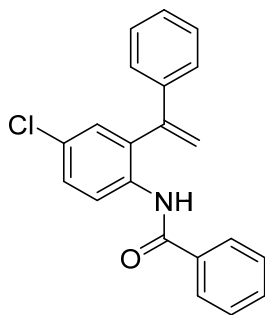
N-(4-methyl-2-(1-phenylvinyl)phenyl)benzamide (1q)^[5]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 41% yield (386 mg). Mp 96–97°C. ¹H NMR (400 MHz, CDCl₃): δ 8.34 (d, *J* = 8.4 Hz, 1H, NH), 7.71 (s, 1H, ArH), 7.50–7.32 (m, 6H, ArH), 7.32–7.19 (m, 5H, ArH), 7.14 (d, *J* = 1.6 Hz, 1H, ArH), 5.88 (d, *J* = 0.8 Hz, 1H, CH₂), 5.41 (d, *J* = 0.8 Hz, 1H, CH₂), 2.37 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 165.0, 146.6, 139.2, 135.0, 134.7, 134.0, 133.0, 131.8, 131.6, 131.2, 130.7, 129.6, 129.1, 129.0, 128.8, 128.6, 126.9, 126.8, 121.2, 117.6, 21.0.



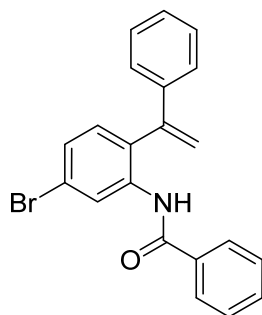
N-(4-bromo-2-(1-phenylvinyl)phenyl)benzamide (1r)^[5]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 86% yield (971 mg). Mp 117–119°C. ¹H NMR (400 MHz, CDCl₃): δ 8.41 (d, *J* = 8.8 Hz, 1H, NH), 7.74 (s, 1H, ArH), 7.52 (dd, *J*₁ = 2.4 Hz, *J*₂ = 8.8 Hz, 1H, ArH), 7.47 (d, *J* = 2.4 Hz, 1H, ArH), 7.36 (s, 6H, ArH), 7.26 (t, *J* = 7.6 Hz, 2H, ArH), 7.20 (s, 1H, ArH), 5.89 (s, 1H, CH₂), 5.41 (s, 1H, CH₂). ¹³C NMR (101 MHz, CDCl₃): δ 164.9, 145.1, 138.2, 134.6, 134.4, 133.5, 133.1, 133.0, 131.9, 131.7, 129.2, 129.1, 128.6, 126.7, 126.7, 122.6, 122.5, 118.7, 118.6, 116.9.



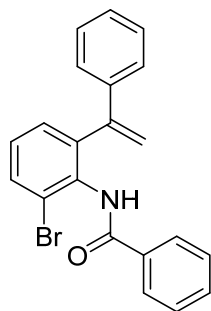
N-(4-chloro-2-(1-phenylvinyl)phenyl)benzamide (1s)^[5]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 96% yield (960 mg). Mp 93–94°C. ¹H NMR (400 MHz, CDCl₃): δ 8.46 (d, *J* = 8.8 Hz, 1H, NH), 7.73 (s, 1H, ArH), 7.62–7.34 (m, 7H, ArH), 7.33 (d, *J* = 2.4 Hz, 1H, ArH), 7.31–7.10 (m, 4H, ArH), 5.91 (s, 1H, CH₂), 5.43 (s, 1H, CH₂). ¹³C NMR (101 MHz, CDCl₃): δ 165.1, 145.4, 138.4, 134.6, 134.2, 133.7, 133.3, 131.9, 130.3, 129.4, 129.3, 129.2, 129.0, 128.7, 128.5, 126.8, 126.8, 122.4, 118.6.



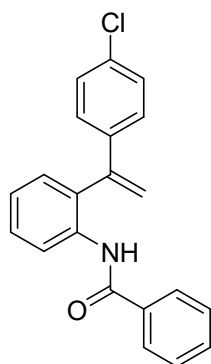
N-(5-bromo-2-(1-phenylvinyl)phenyl)benzamide (1t)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 86% yield (960 mg). Mp 137–138°C. ¹H NMR (400 MHz, CDCl₃): δ 8.60 (dd, *J*₁ = 2.8 Hz, *J*₂ = 8.4 Hz, 1H, NH), 8.20 (s, 1H, ArH), 7.74–7.07 (m, 12H, ArH), 6.24 (d, *J* = 2.8 Hz, 1H, CH₂), 5.43 (d, *J* = 2.8 Hz, 1H, CH₂). ¹³C NMR (101 MHz, CDCl₃): δ 165.3, 144.6, 137.3, 137.2, 134.8, 132.0, 131.8, 129.8, 129.1, 129.0, 128.9, 128.3, 126.9, 126.2, 123.8, 119.3, 119.3, 118.6, 118.5. HRMS (ESI) *m/z*: calcd for C₂₁H₁₇BrNO⁺ ([M+H]⁺), 378.0488; found, 378.0482.



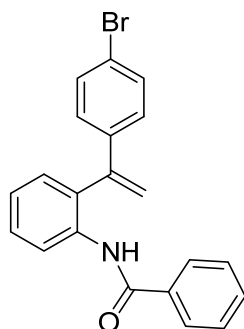
N-(2-bromo-6-(1-phenylvinyl)phenyl)benzamide (1u)^[6]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 43% yield (488 mg). Mp 185–187°C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.90 (s, 1H, NH), 7.75 (dd, *J*₁ = 8.0 Hz, *J*₂ = 24.4 Hz, 3H, ArH), 7.54 (t, *J* = 7.2 Hz, 1H, ArH), 7.45 (t, *J* = 7.2 Hz, 2H, ArH), 7.40–7.15 (m, 7H, ArH), 5.73 (s, 1H, CH₂), 5.37 (s, 1H, CH₂). ¹³C NMR (101 MHz, DMSO-*d*₆): δ 165.8, 146.4, 143.5, 140.5, 135.4, 134.6, 132.4, 131.8, 130.2, 129.2, 128.6, 128.6, 128.1, 127.9, 127.3, 125.1, 117.1.



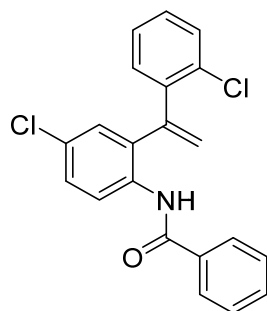
N-(2-(1-(4-chlorophenyl)vinyl)phenyl)benzamide (1v)^[6]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 97% yield (968 mg). Mp 148–150°C. ¹H NMR (400 MHz, CDCl₃): δ 8.36 (d, *J* = 8.4 Hz, 1H, NH), 7.67 (s, 1H, ArH), 7.41–7.32 (m, 2H, ArH), 7.27 (d, *J* = 3.2 Hz, 3H, ArH), 7.22 (s, 4H, ArH), 7.21–7.15 (m, 1H, ArH), 7.14–7.07 (m, 1H, ArH), 5.82 (s, 1H, CH₂), 5.36 (s, 1H, CH₂). ¹³C NMR (101 MHz, CDCl₃): δ 165.2, 145.4, 137.6, 135.4, 134.9, 134.8, 131.8, 131.4, 130.6, 129.3, 129.2, 128.7, 128.2, 126.8, 124.6, 121.5, 118.2.



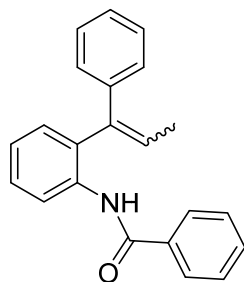
N-(2-(1-(4-bromophenyl)vinyl)phenyl)benzamide (1w)^[1]

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 91% yield (1028 mg). Mp 162–164°C. ¹H NMR (400 MHz, CDCl₃): δ 8.44 (d, *J* = 8.0 Hz, 1H, NH), 7.74 (s, 1H, ArH), 7.56–7.40 (m, 4H, ArH), 7.34 (d, *J* = 4.4 Hz, 3H, ArH), 7.33–7.09 (m, 4H, ArH), 5.91 (d, *J* = 0.8 Hz, 1H, CH₂), 5.45 (d, *J* = 0.8 Hz, 1H, CH₂). ¹³C NMR (101 MHz, CDCl₃): δ 165.3, 145.5, 138.1, 135.4, 134.9, 132.3, 132.2, 131.9, 131.4, 130.6, 129.4, 128.8, 128.5, 126.8, 124.6, 123.0, 121.6, 121.5, 118.3, 118.2.



N-(4-chloro-2-(1-(2-chlorophenyl)vinyl)phenyl)benzamide (1x)

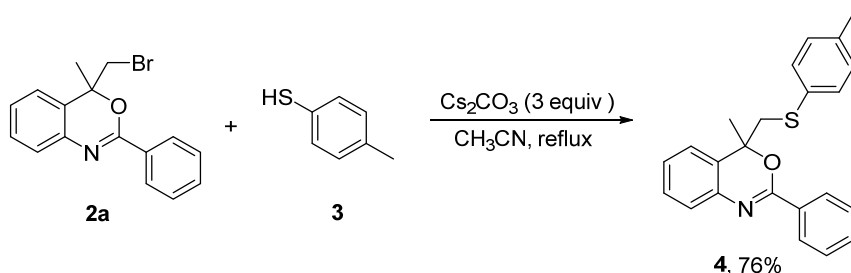
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1–20:1, v/v) as a white solid in 72% yield (791 mg). Mp 100–101°C. ¹H NMR (400 MHz, CDCl₃): δ 8.29 (d, *J* = 8.8 Hz, 1H, NH), 8.16 (s, 1H, ArH), 7.59 (d, *J* = 7.2 Hz, 2H, ArH), 7.43 (t, *J* = 7.6 Hz, 1H, ArH), 7.33 (t, *J* = 7.6 Hz, 2H, ArH), 7.29–7.09 (m, 5H, ArH), 7.01 (s, 1H, ArH), 5.69 (s, 1H, CH₂), 5.58 (s, 1H, CH₂). ¹³C NMR (101 MHz, CDCl₃): δ 165.1, 143.9, 139.4, 134.5, 133.8, 133.29, 132.5, 131.9, 131.1, 130.3, 129.7, 129.3, 129.0, 128.7, 128.6, 127.4, 127.0, 123.2, 123.1.



N-(2-(1-phenylprop-1-en-1-yl)phenyl)benzamide (1y)

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 100:1–80:1, v/v) as a colorless oily liquid in 65% yield (611 mg). ¹H NMR (400 MHz, CDCl₃): δ 8.61 (d, *J* = 8.0 Hz, 1H, NH), 7.92 (s, 1H, ArH), 7.54–7.40 (m, 4H, ArH), 7.38–7.22 (m, 7H, ArH), 7.22–7.12 (m, 2H, ArH), 6.51 (m, 1H, CH), 1.71 (d, *J* = 7.2 Hz, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 165.2, 140.2, 138.2, 136.0, 135.1, 131.7, 130.7, 128.9, 128.9, 128.7, 128.7, 127.9, 127.5, 126.8, 126.4, 124.2, 120.5, 15.9. HRMS (ESI) *m/z*: calcd for C₂₂H₁₈BrNO⁺ ([M+e]⁺), 312.1388; found, 312.1390.

3. Product transformations processes for compound 4



In a 25-mL reaction flask, equipped with a magnetic stirring bar, 2a (1 equiv, 0.4 mmol), 4-methylbenzenethiol (2 equiv, 0.8 mmol) and CsCO₃ (3 equiv, 1.2 mmol) were added to CH₃CN (10 mL/mmol, 4.0 mL). Then the resulting mixture was refluxed at 80 °C. The formation of the products was monitored by TLC. After completion of the reaction, the mixture was diluted with ethyl acetate (5.0 mL), then quenched with cold water (30 mL) and extracted with ethyl acetate (2×40 mL). After drying with anhydrous Na₂SO₄, the organic layer was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (200/1-180/1) as eluent to afford the pure product. The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = 200:1–180:1, v/v) as a colorless oily liquid in 73% yield (105 mg). ¹H NMR (400 MHz, CDCl₃): δ 8.16–7.97 (m, 2H, ArH), 7.49–7.26 (m, 5H, ArH), 7.22–7.06 (m, 4H, ArH), 6.93 (d, *J* = 7.9 Hz, 2H, ArH), 3.52 (d, *J* = 13.7 Hz, 1H, CH₂), 3.31 (d, *J* = 13.7 Hz,

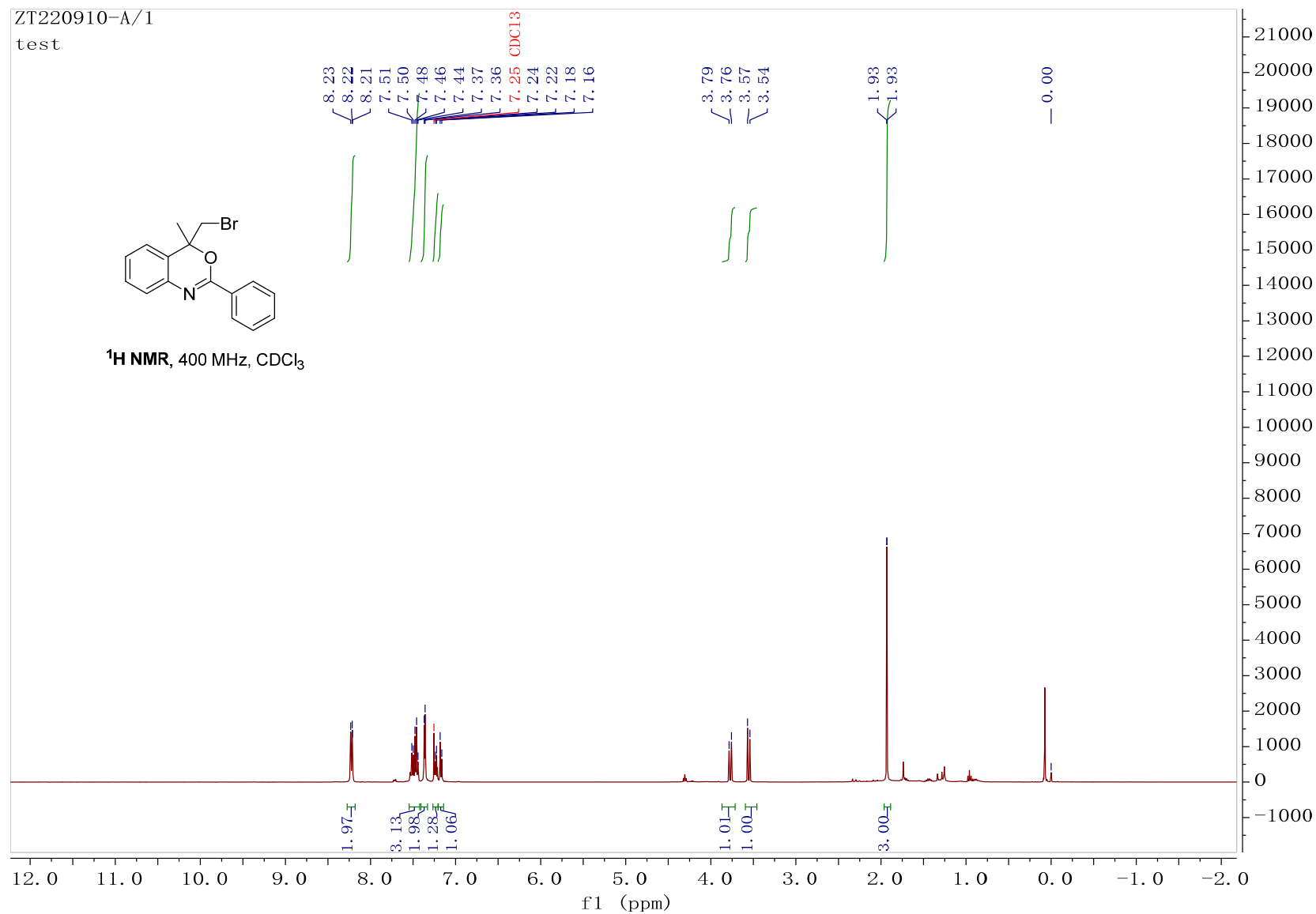
1H, CH₂), 2.21 (s, 3H, CH₃), 1.85 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 156.3, 139.0, 136.5, 132.7, 132.5, 131.3, 130.6, 129.6, 129.0, 128.6, 128.1, 128.1, 126.6, 125.3, 123.3, 80.2, 77.4, 77.1, 76.7, 46.4, 25.9, 21.0. HRMS (ESI) m/z: calcd for C₂₃H₂₂NOS⁺ ([M+H]⁺), 360.1417; found, 360.1418.

4. References

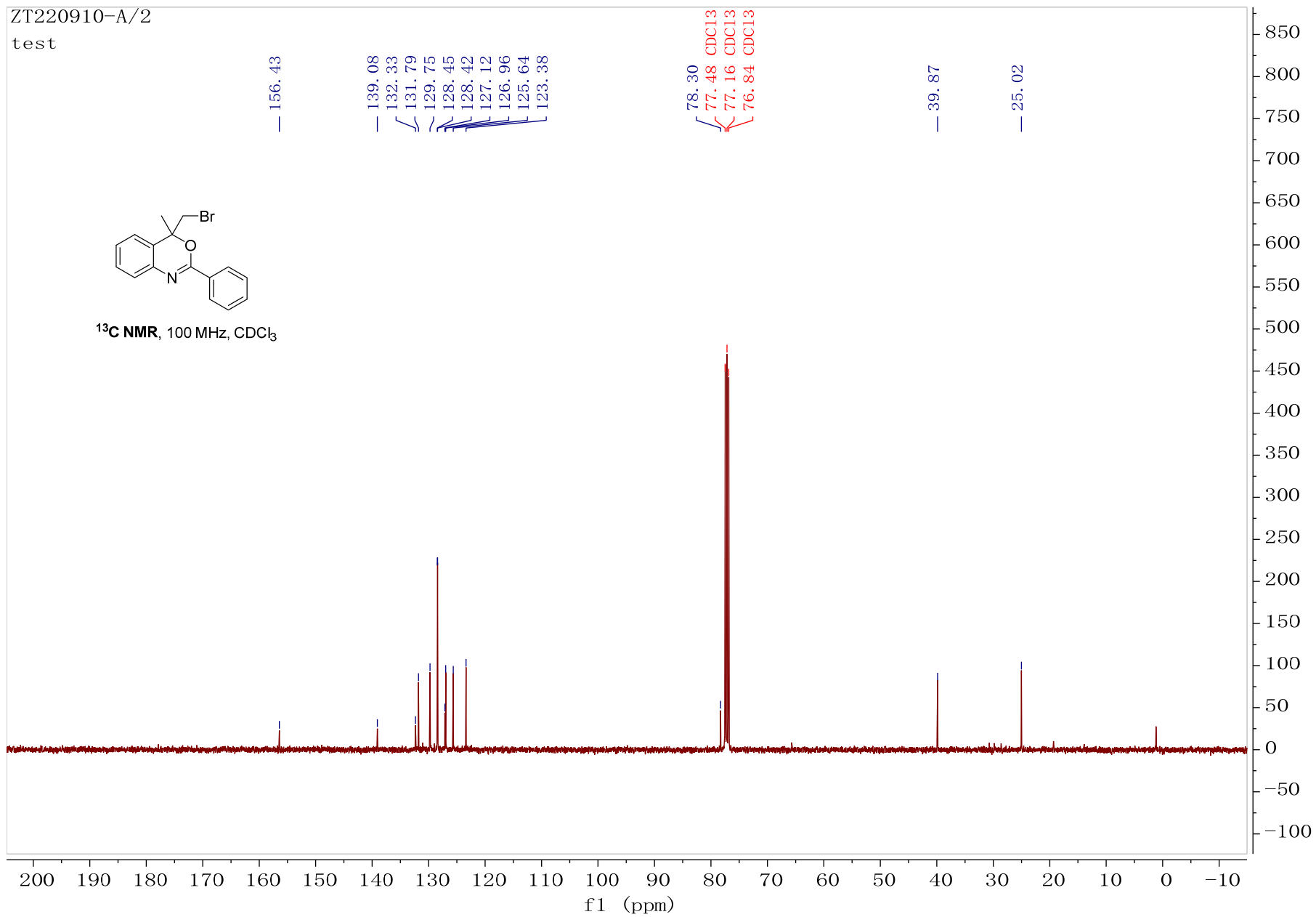
- [1] F.-L. Lu, J. Xu, H. Li, K. Wang, D.-D. Ouyang, L.-H. Sun, M.-N. Huang, J.-W. Jiang, J.-G. Hu, H. Alhumade, L.-J. Lu, A.-W. Lei, *Green Chem.* **2021**, *23*, 7982.
- [2] S. Qian, P. Xu, Y. Zheng, S. Huang, *Tetrahedron Lett.* **2023**, *116*, 154341.
- [3] S. Jana, A. Ashokan, S. Kumar, A. Verma, S. Kumar, *Org. Biomol. Chem.* **2015**, *13*, 8411.
- [4] W. Fu, X. Han, M. Zhu, C. Xu, Z. Wang, B. Ji, X.-Q. Hao, M.-P. Song, *Chem. Commun.* **2016**, *52*, 13413.
- [5] M. Chaitanya, P. Anbarasan, *Org. Lett.* **2018**, *20*, 1183.
- [6] J.-L. Wu, Y.-Y. Zong, C.-X. Zhao, Q.-Q. Yan, L.-X. Sun, Y.-M. Li, J.-C. Zhao, Y.-X. Ge and Z.-J. Li, *Org. Biomol. Chem.* **2019**, *17*, 794.

5. Spectroscopic data for bromobenzoxazines 2

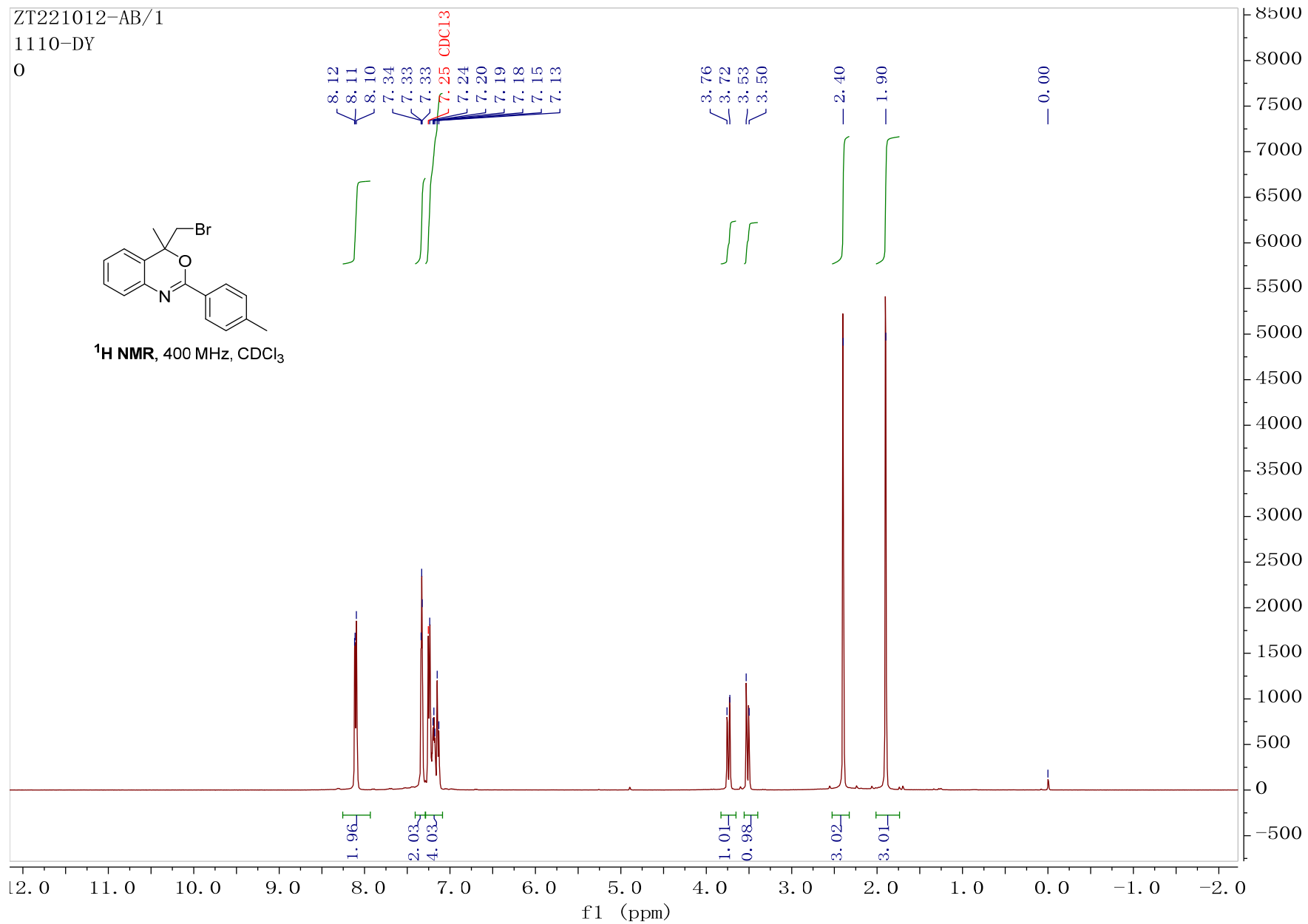
^1H NMR spectrum of Compound 2a (CDCl_3 , 400 MHz)



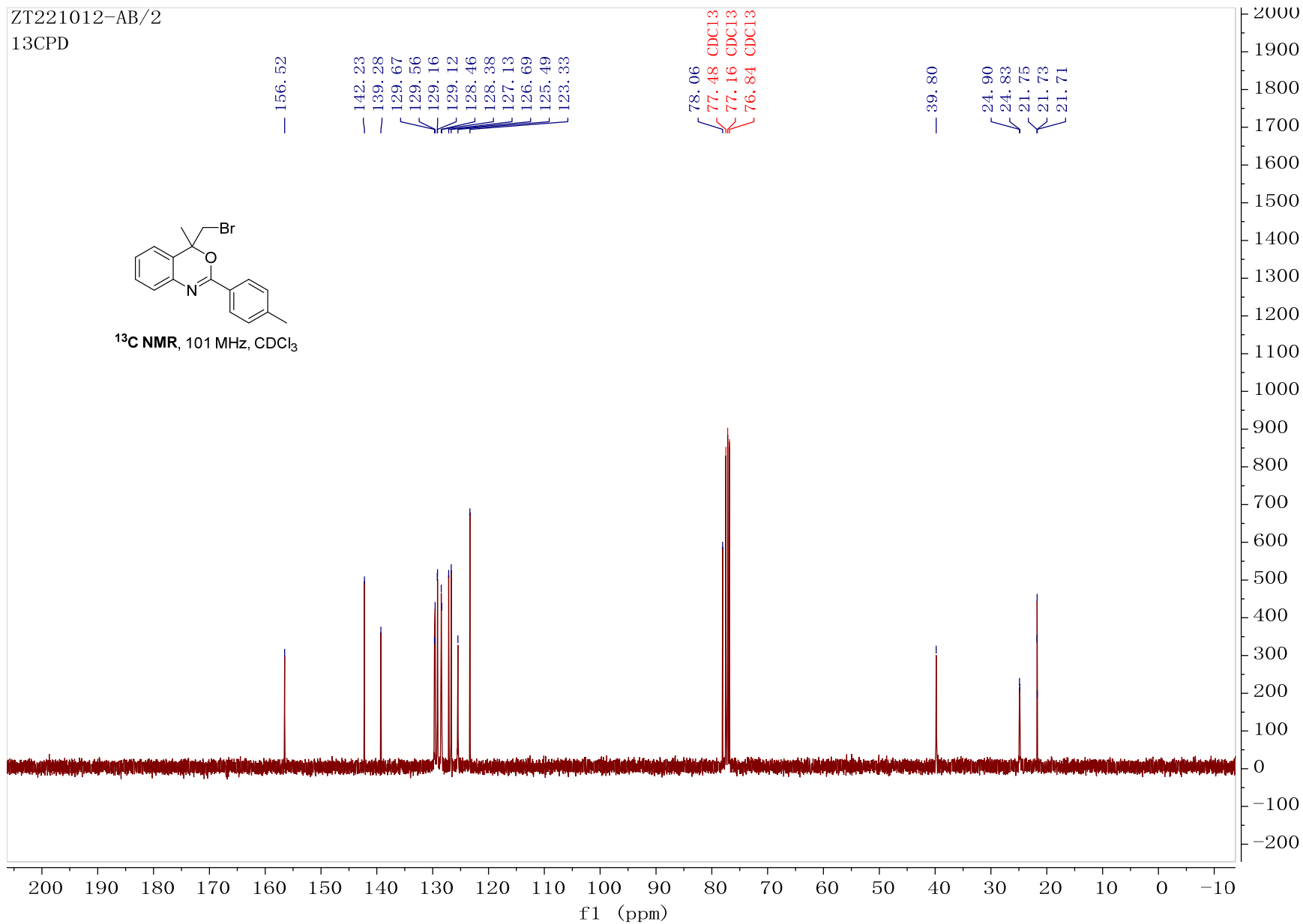
¹³C NMR spectrum of Compound 2a (CDCl₃, 101 MHz)



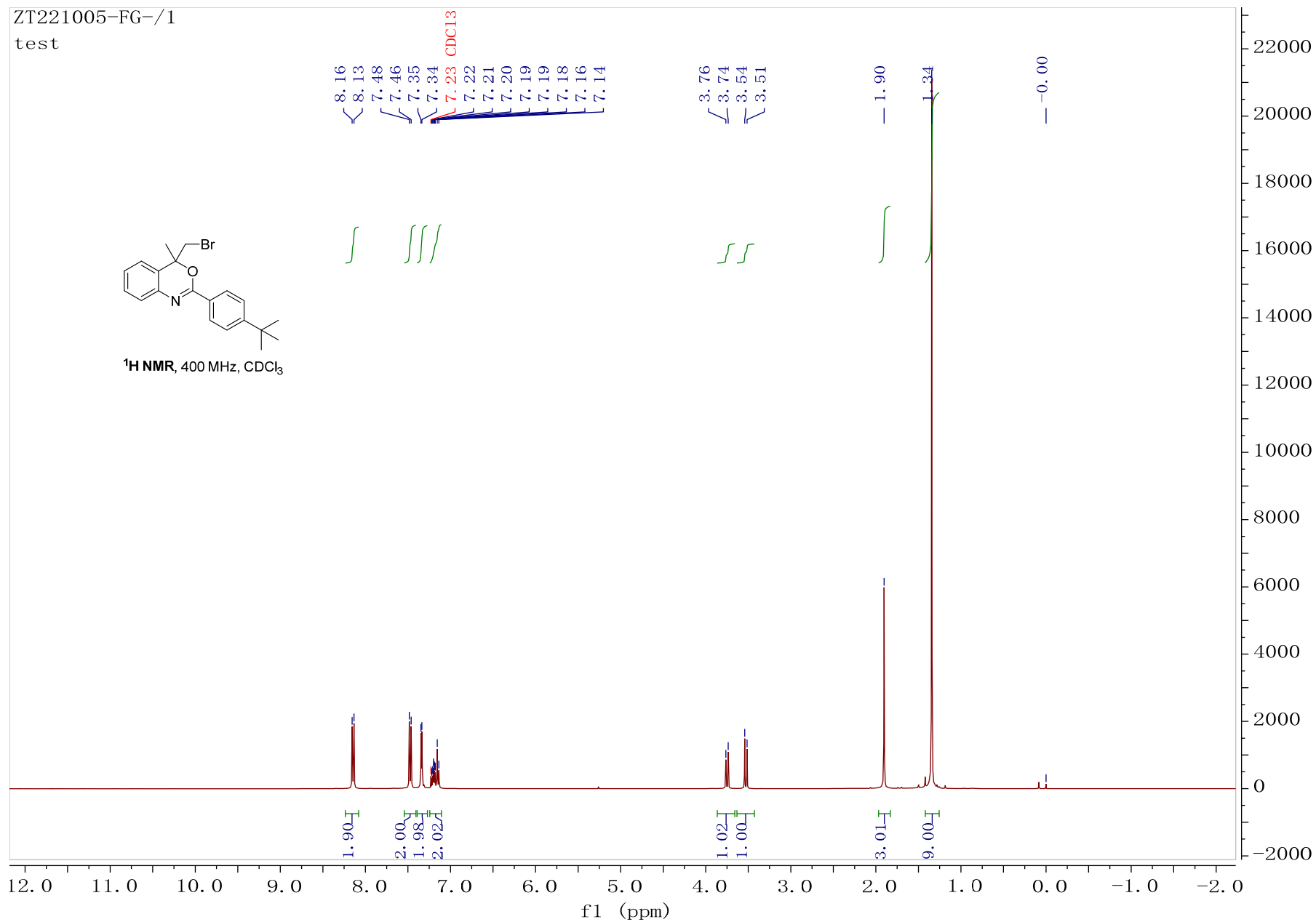
¹H NMR spectrum of Compound 2b (CDCl₃, 400 MHz)



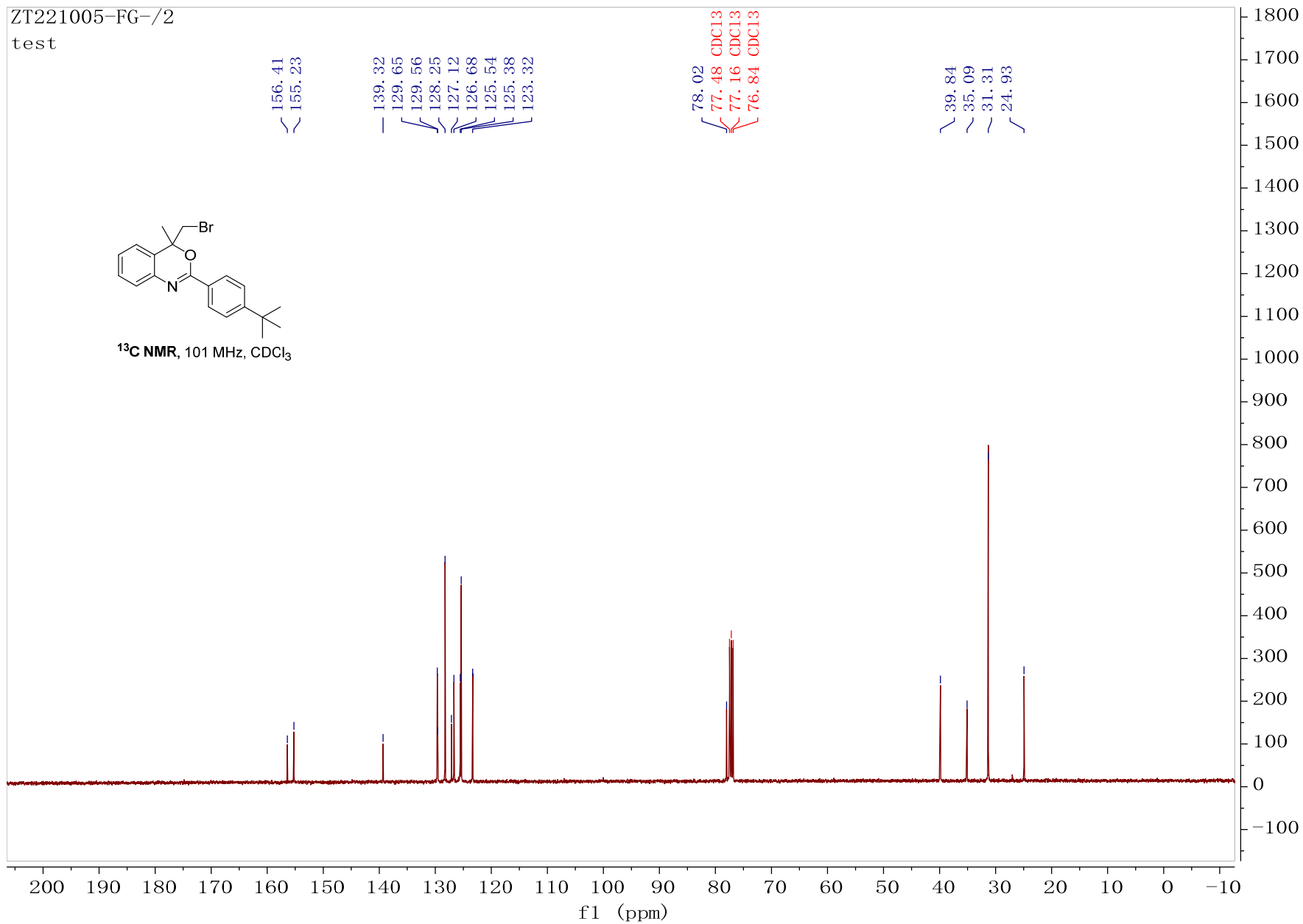
¹³C NMR spectrum of Compound 2b (CDCl₃, 101 MHz)



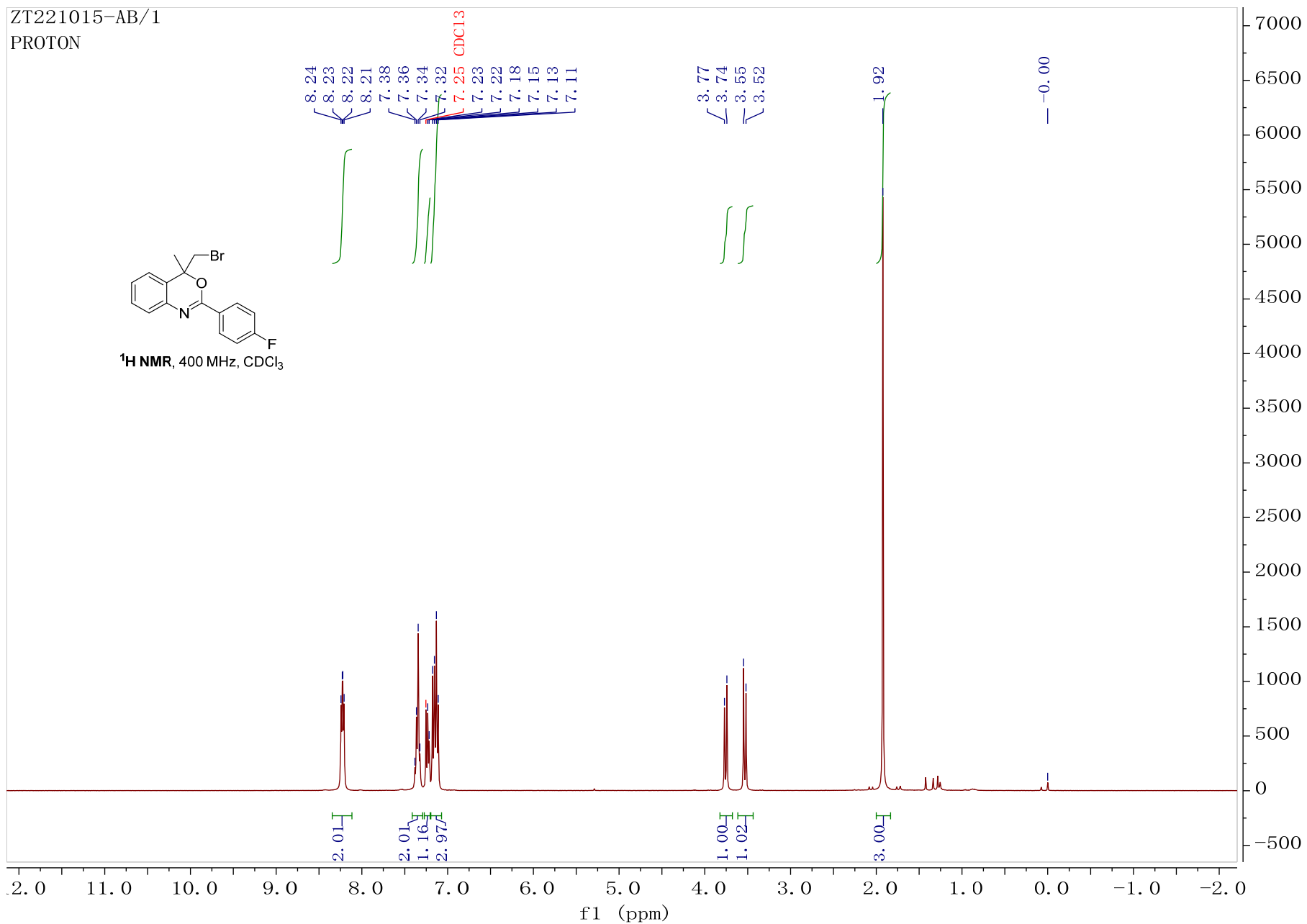
¹H NMR spectrum of Compound 2c (CDCl₃, 400 MHz)



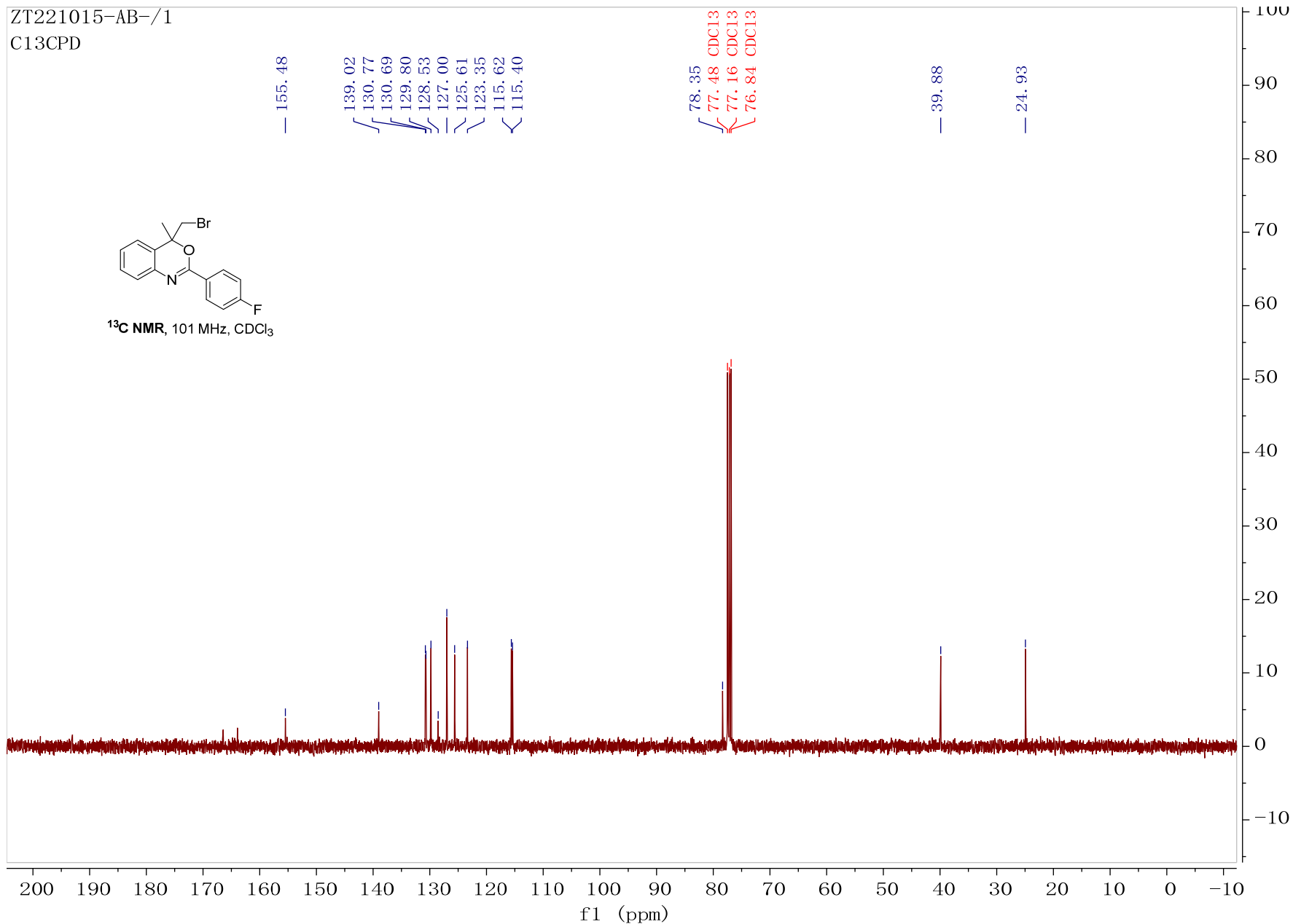
¹³C NMR spectrum of Compound 2c (CDCl₃, 101 MHz)



¹H NMR spectrum of Compound 2d (CDCl₃, 400 MHz)



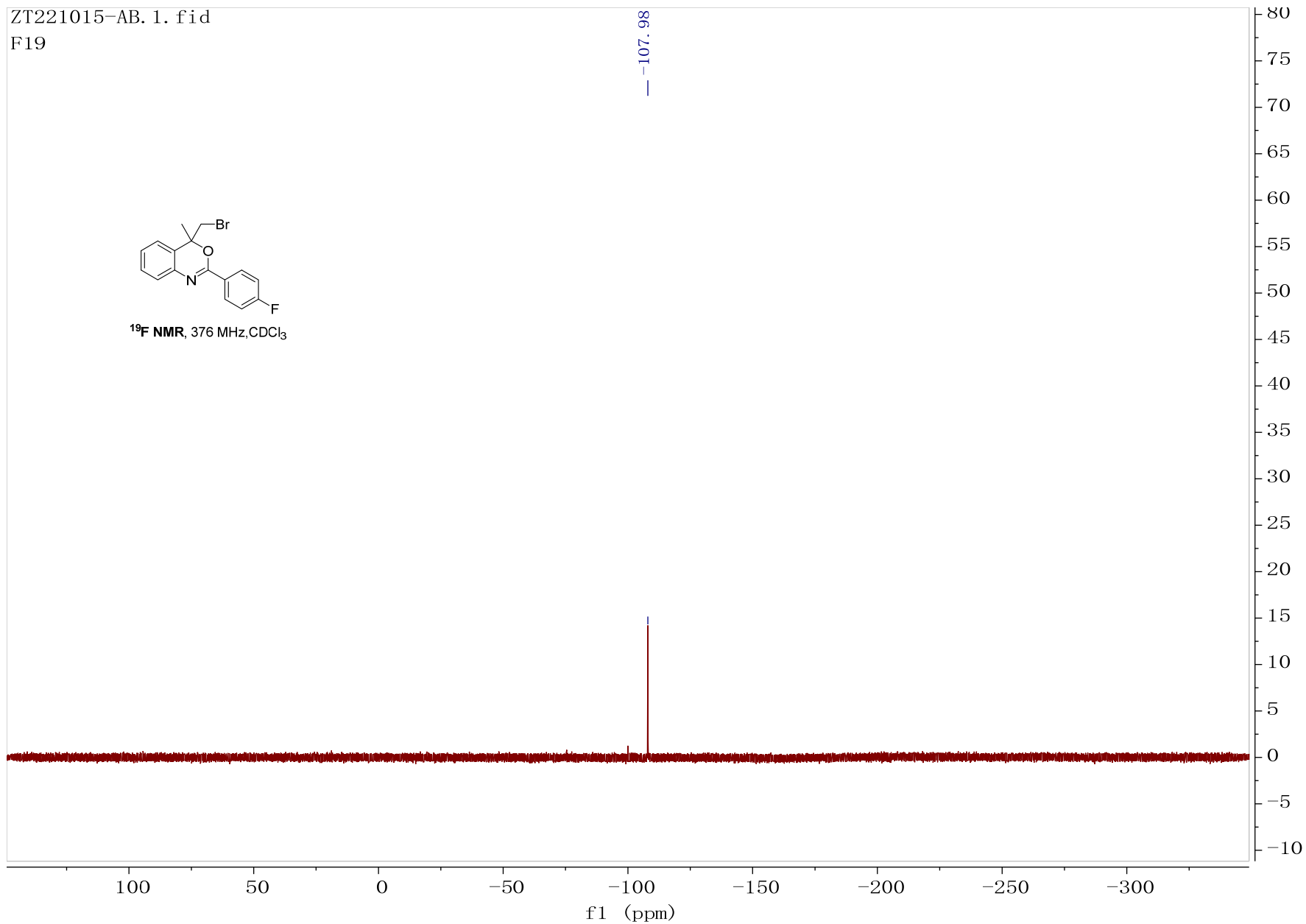
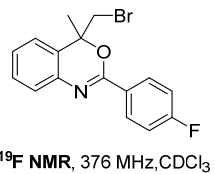
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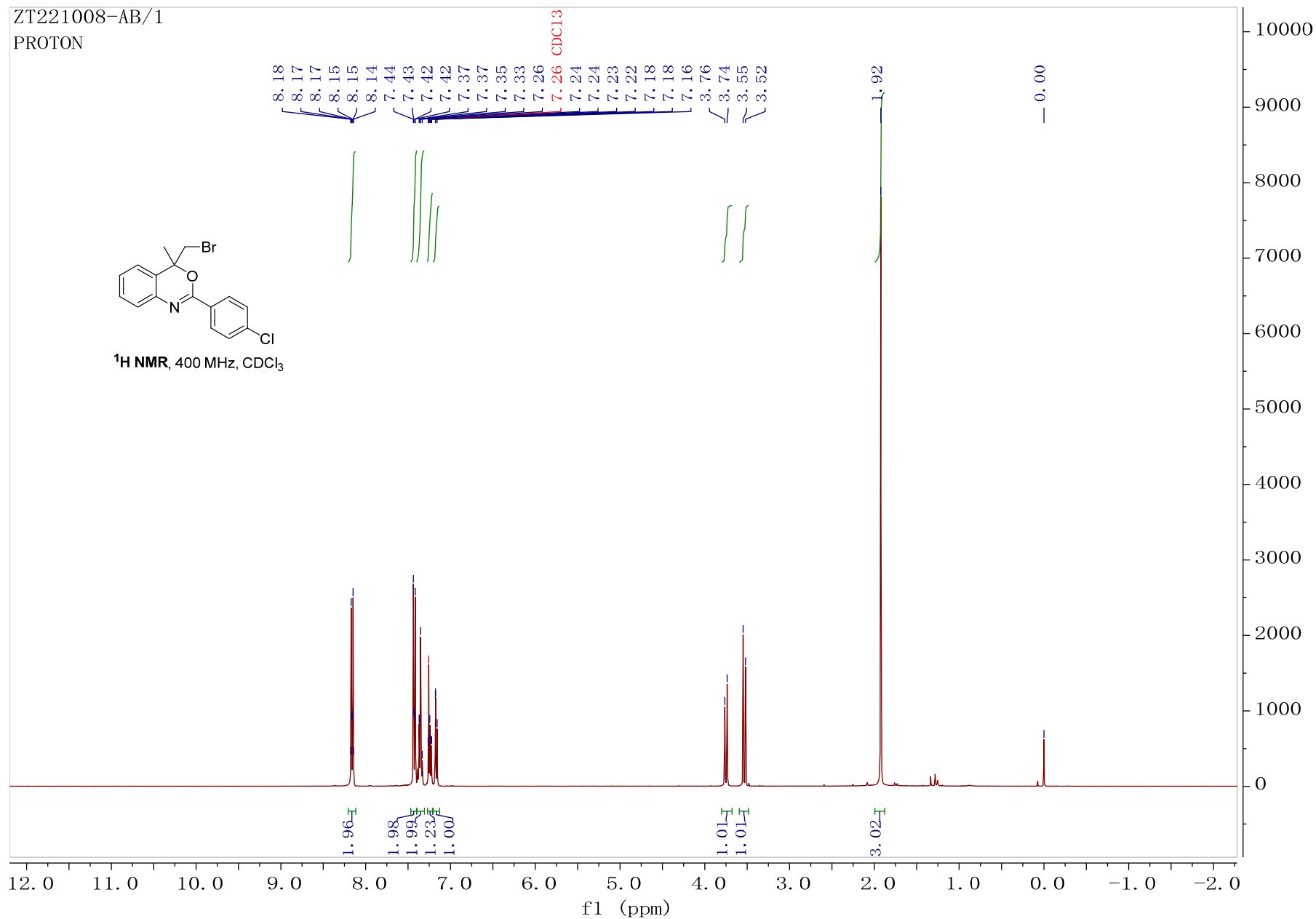
¹⁹F NMR spectrum of Compound 2d (CDCl₃, 376 MHz)

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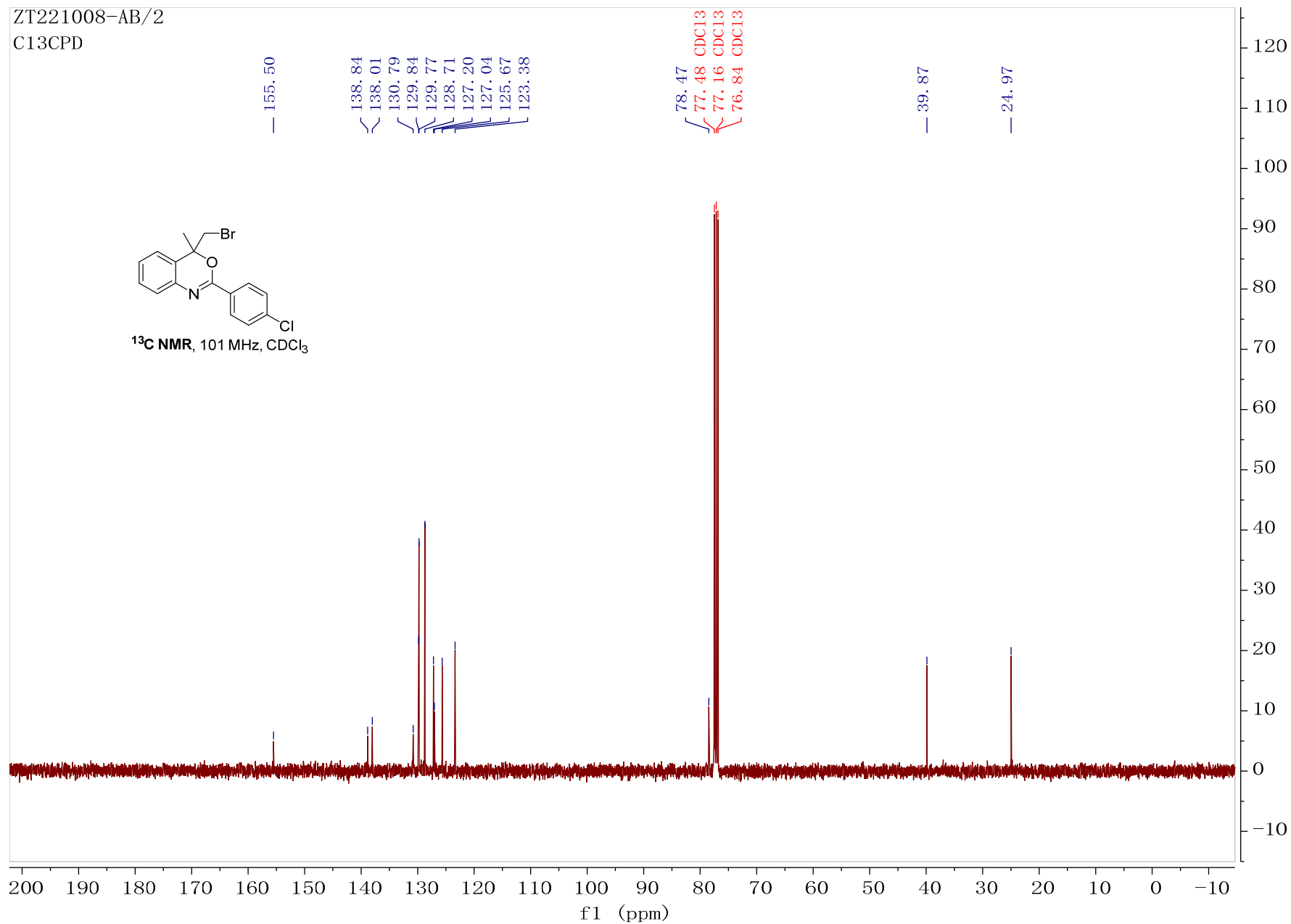
F19



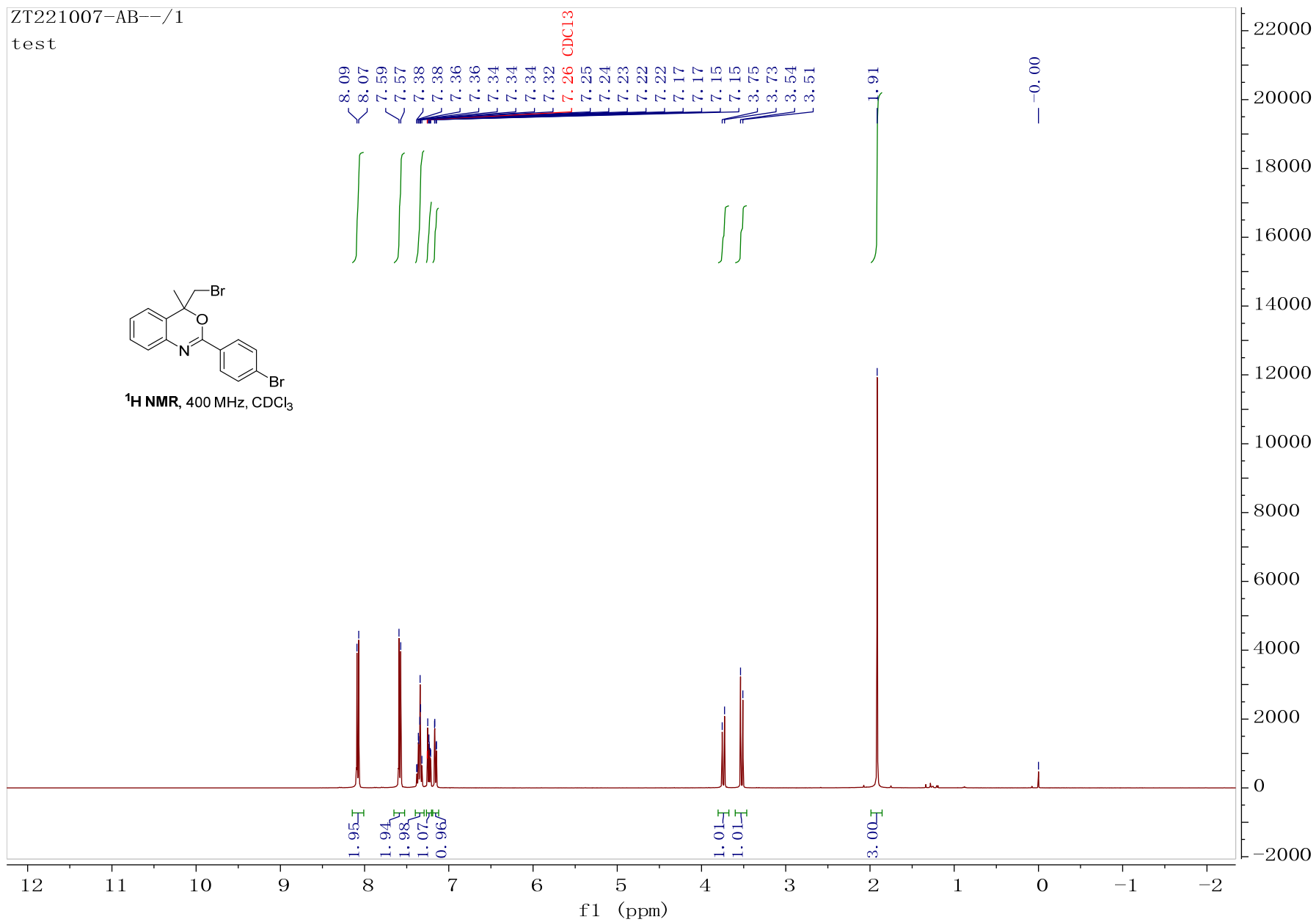
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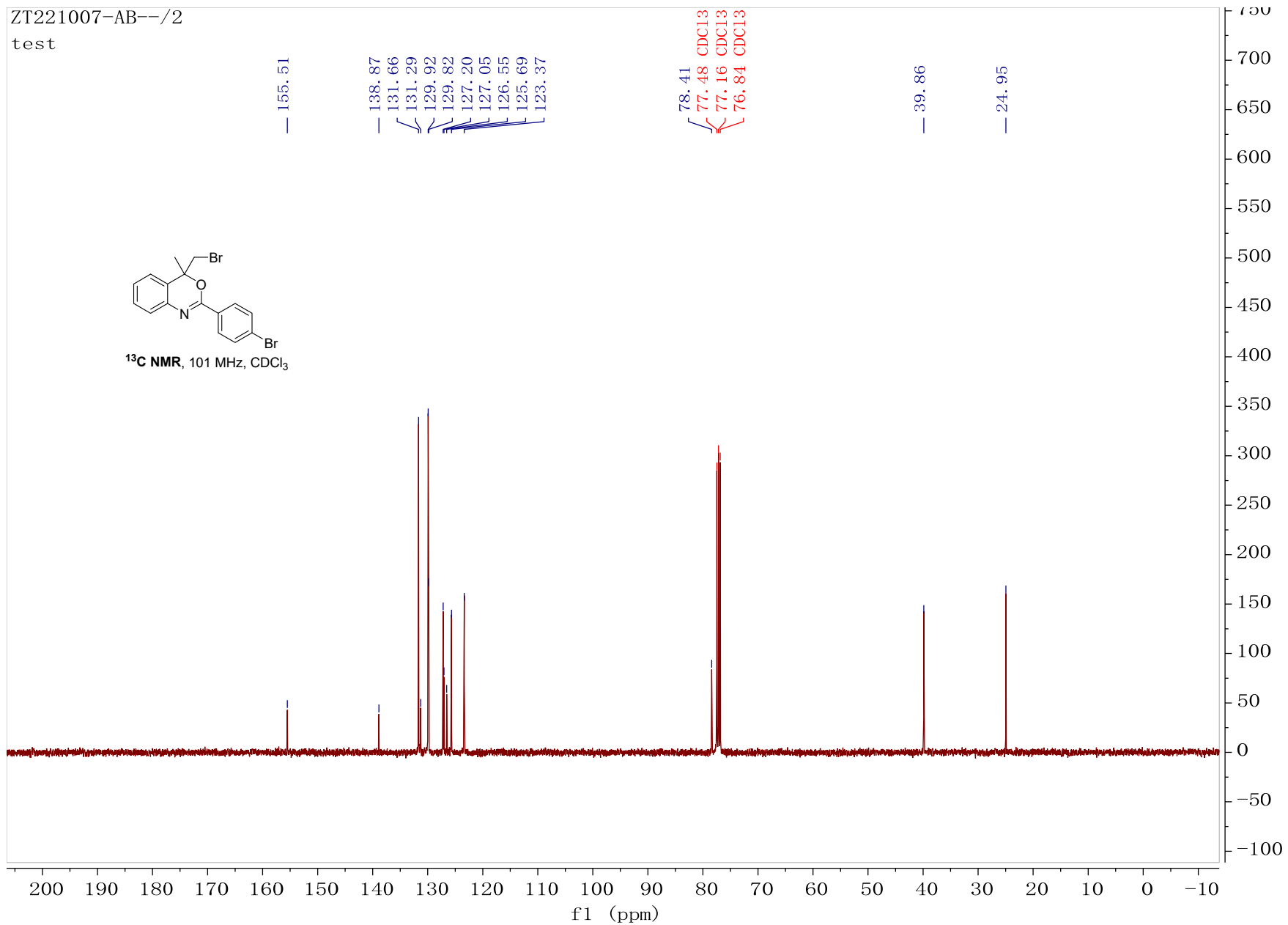
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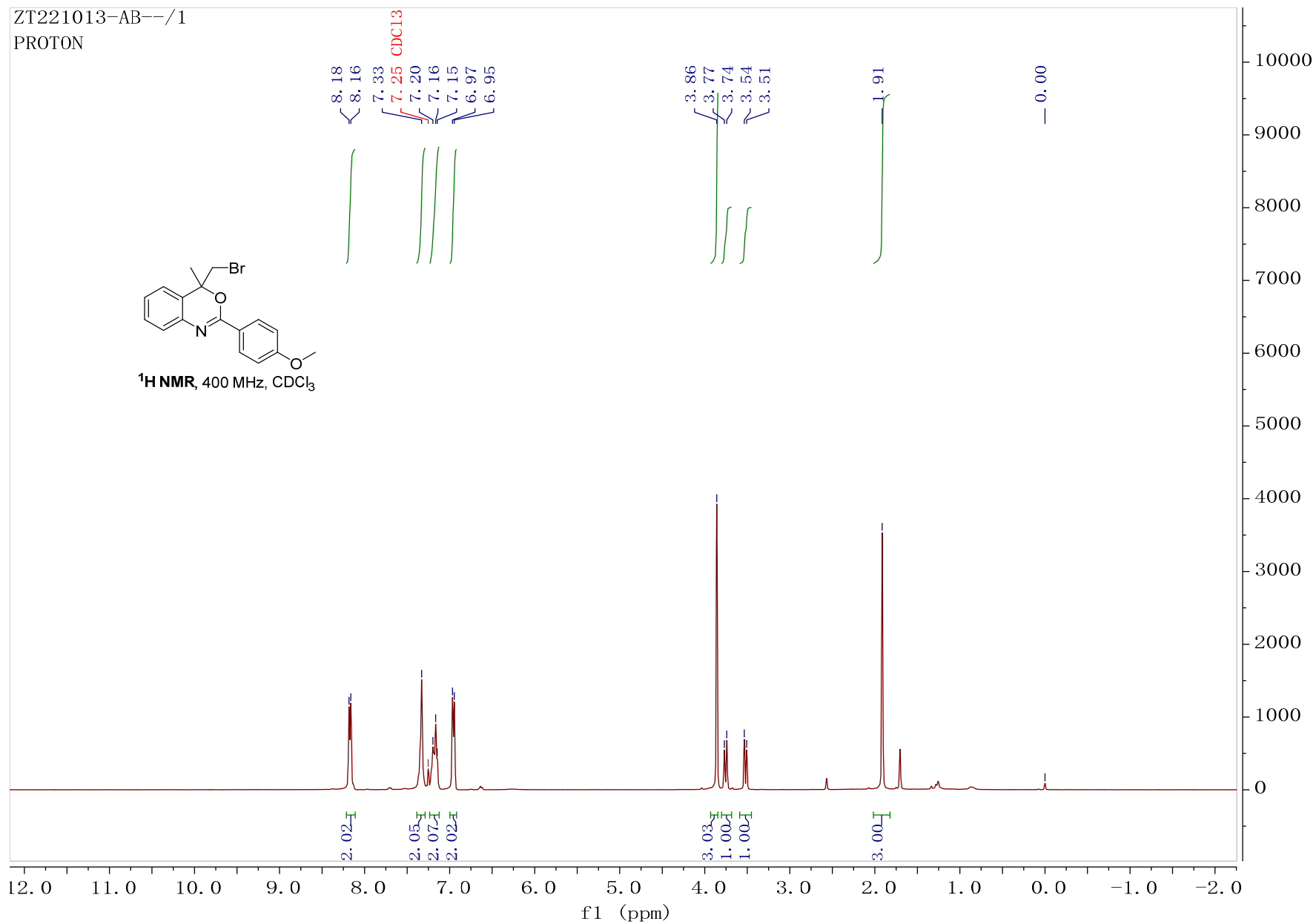
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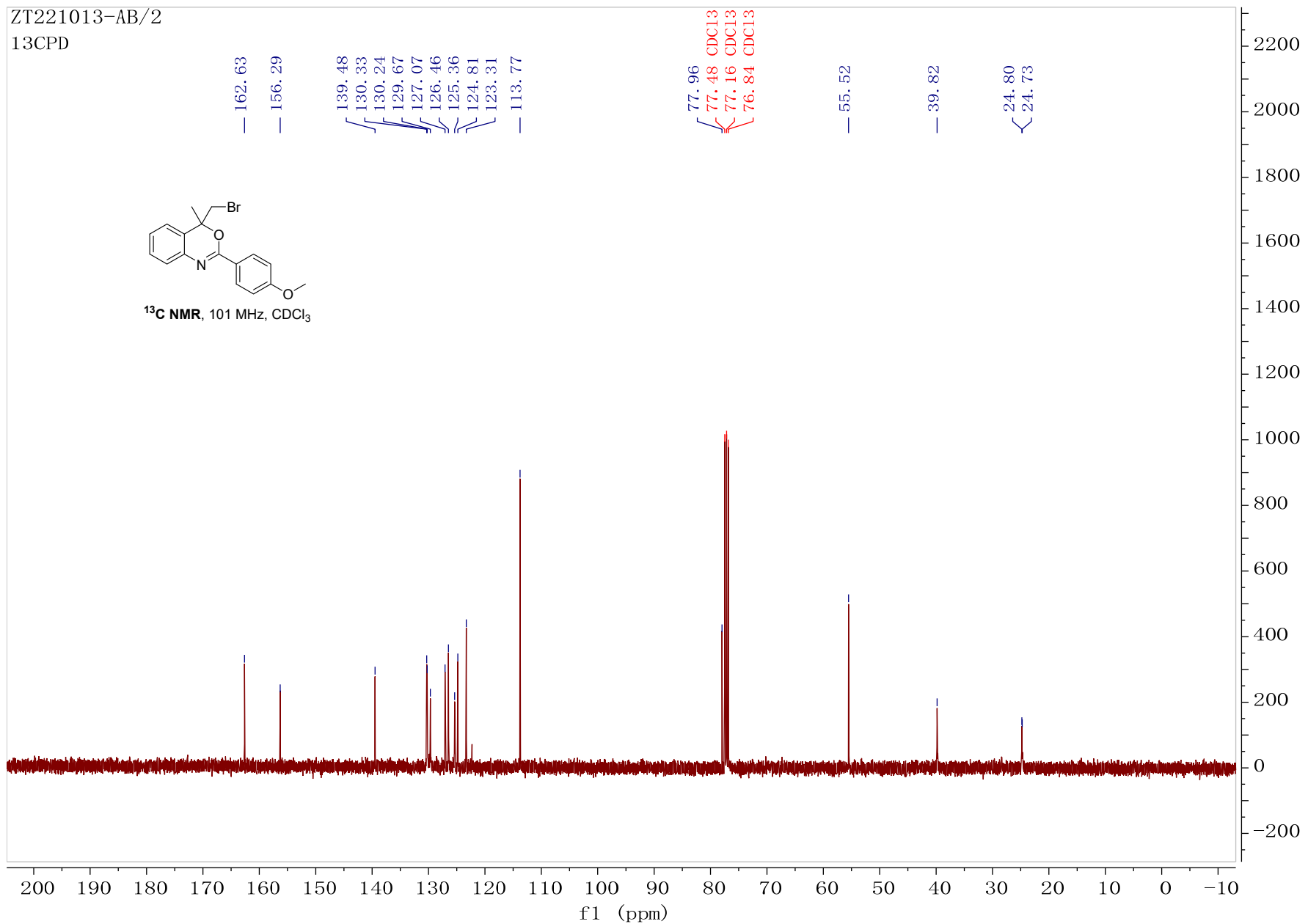
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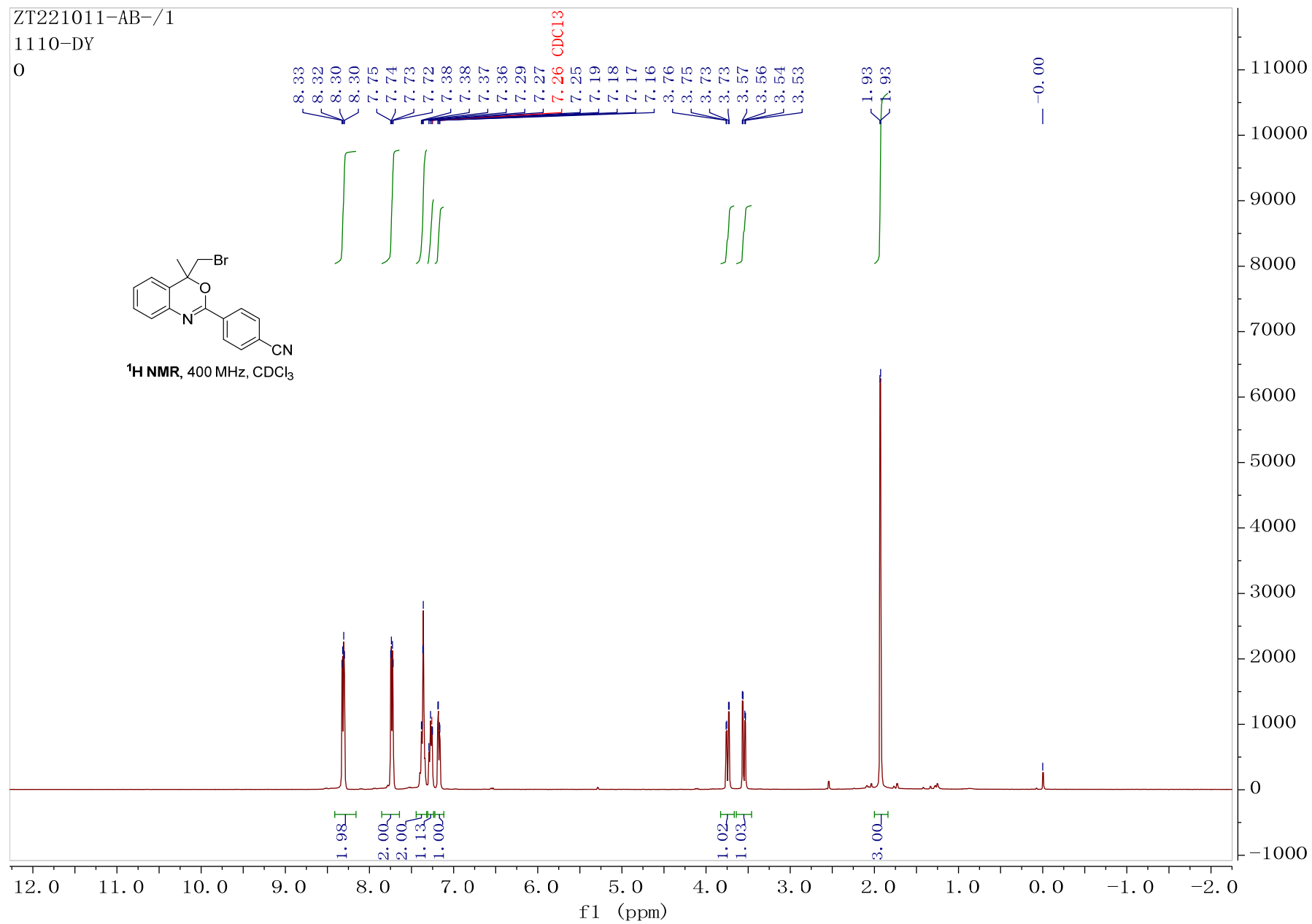
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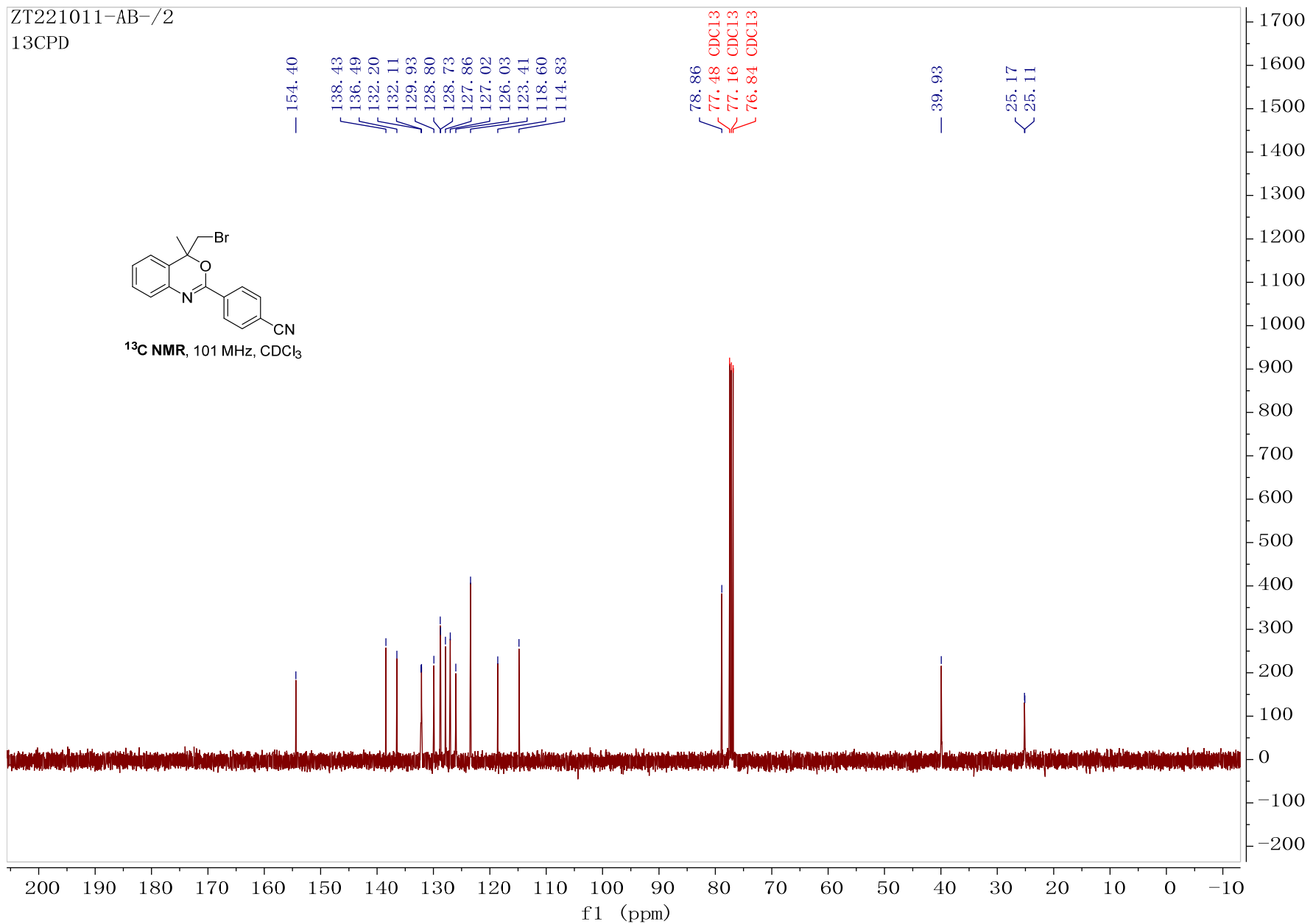
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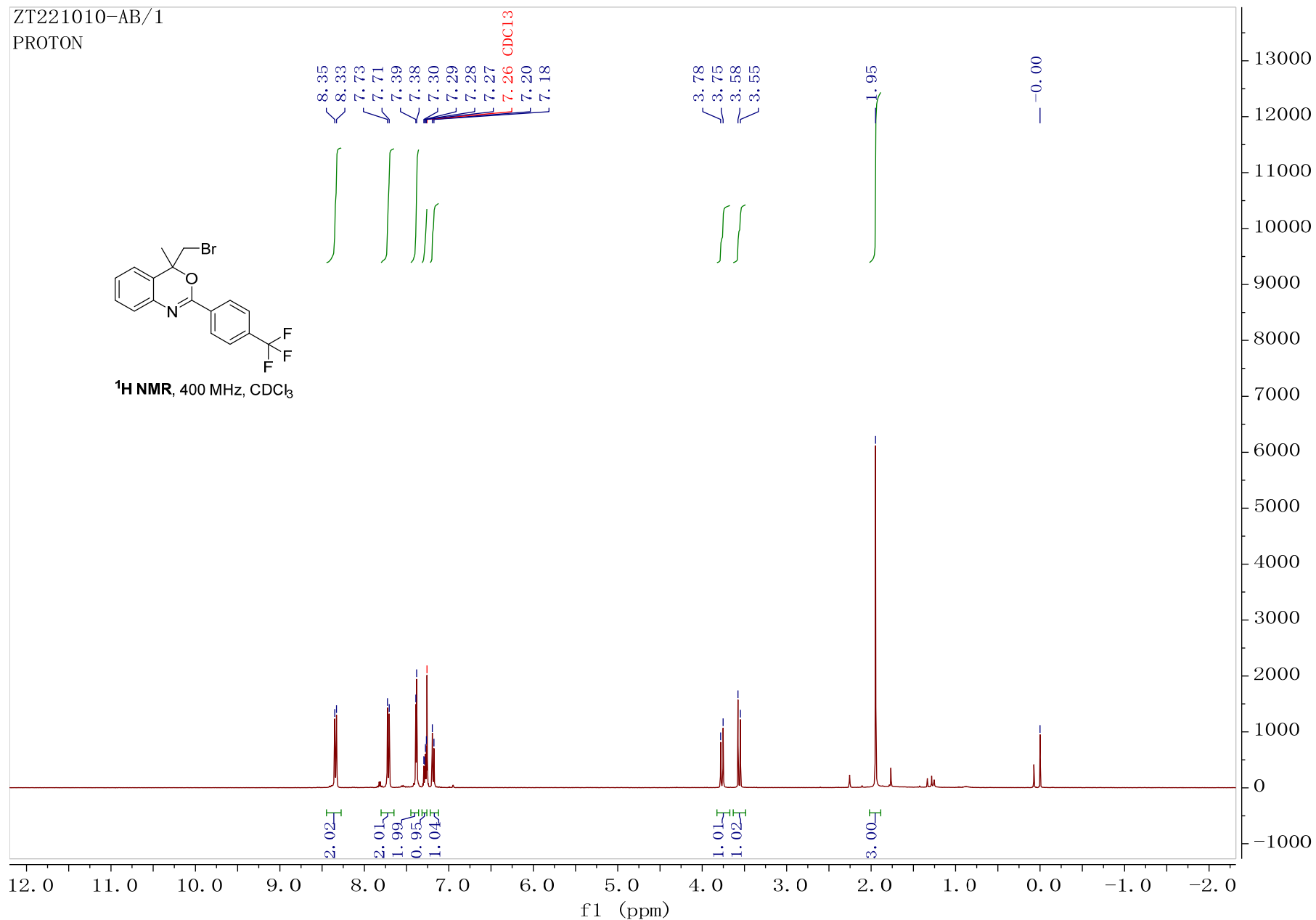
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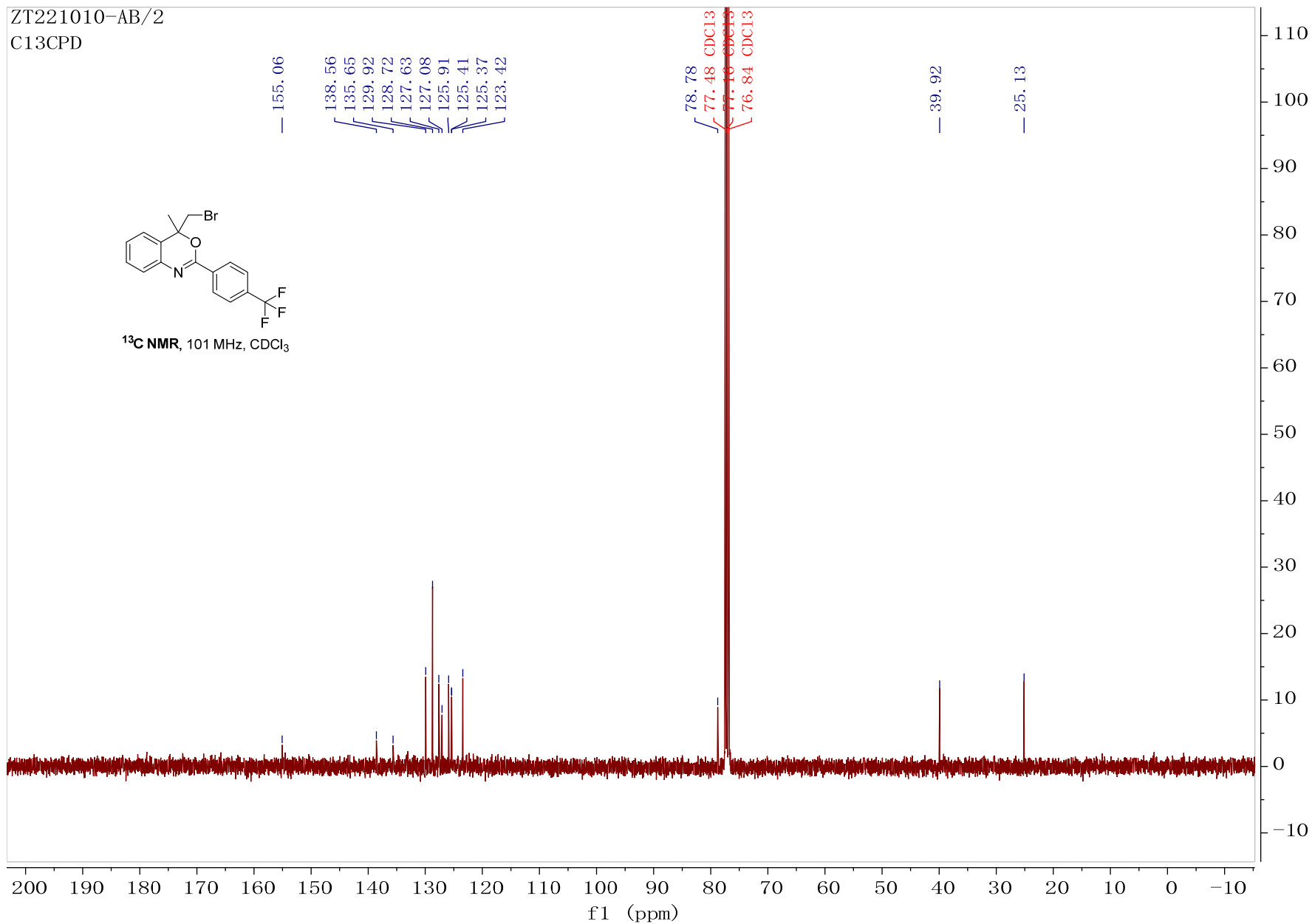
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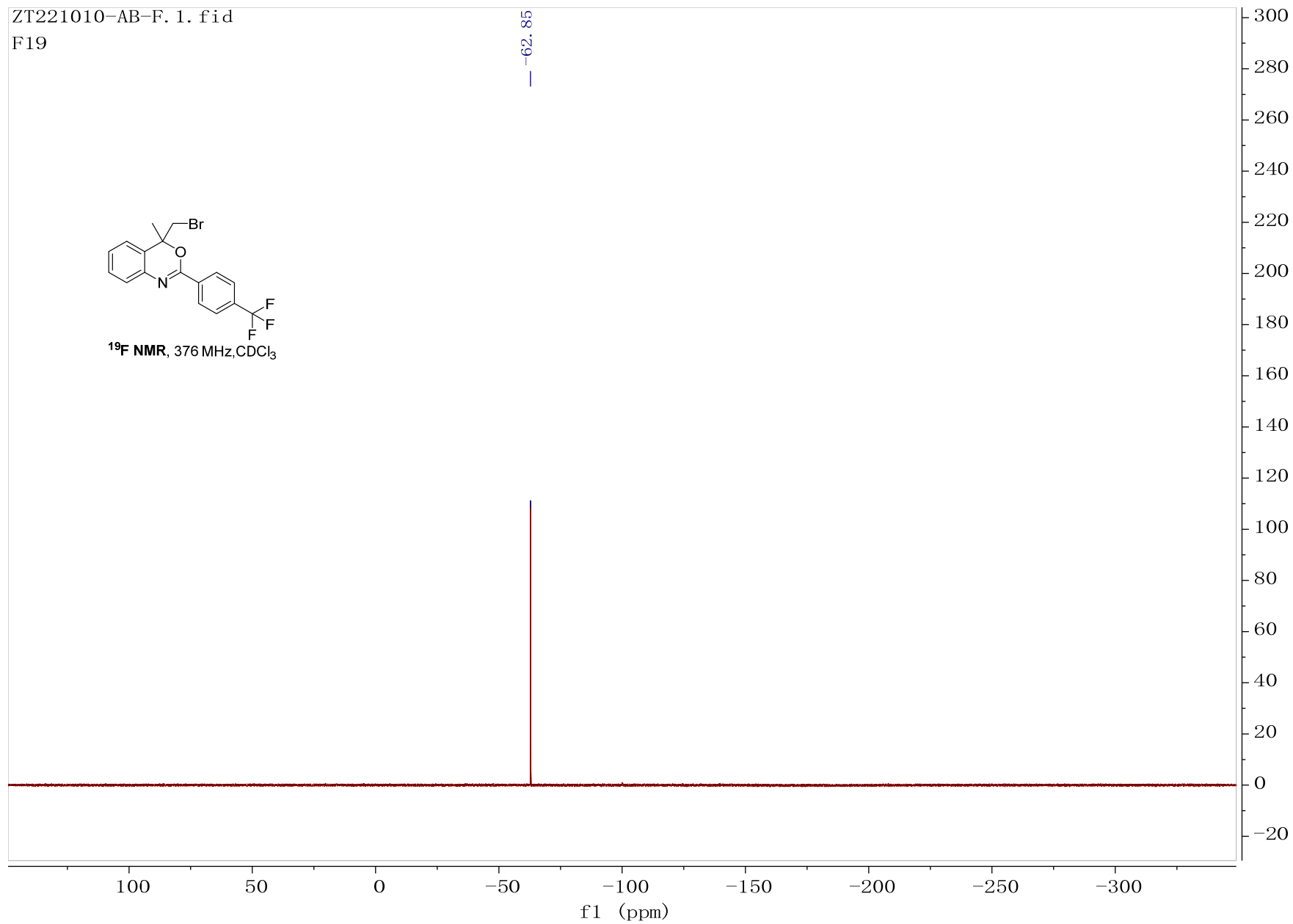
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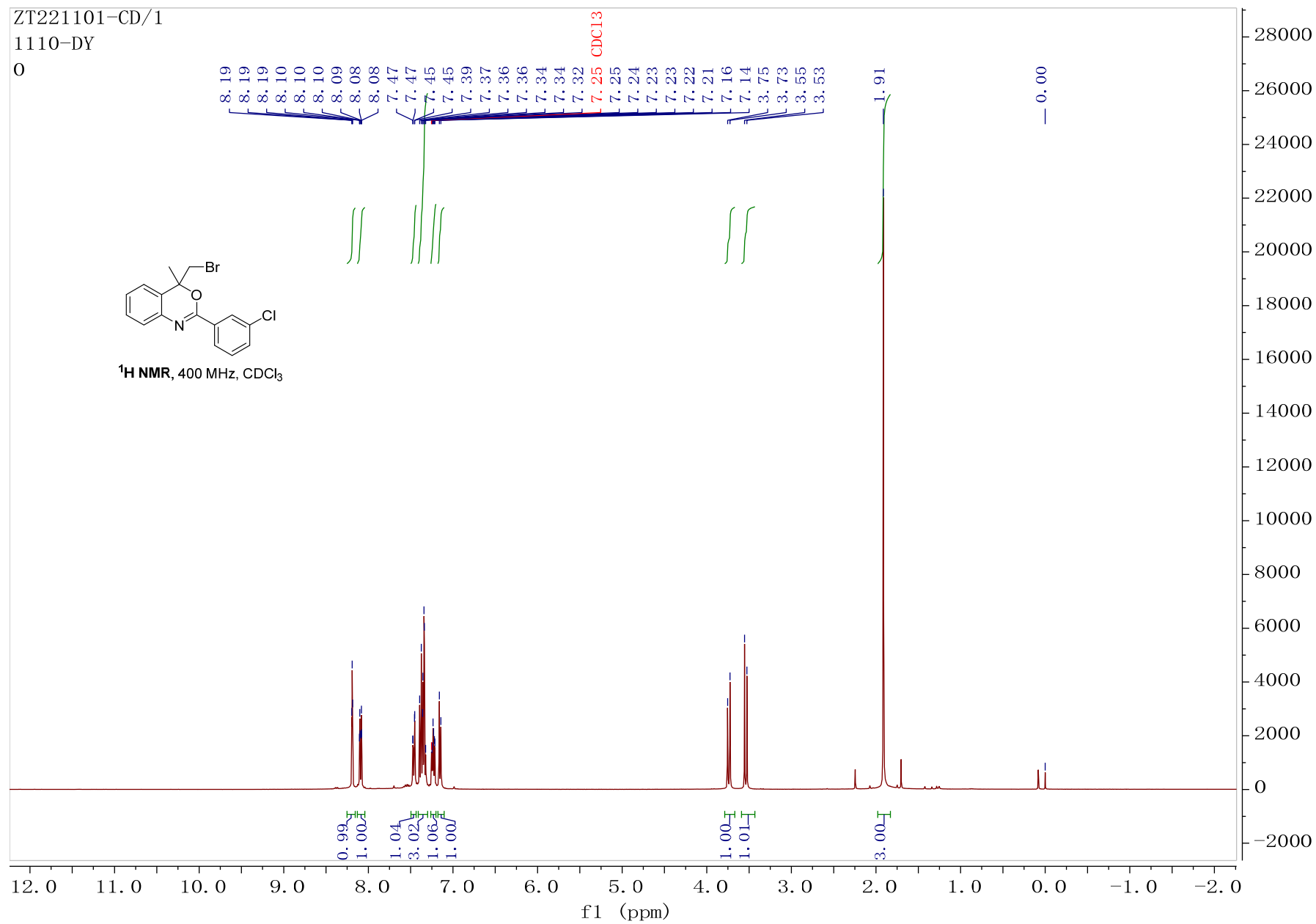
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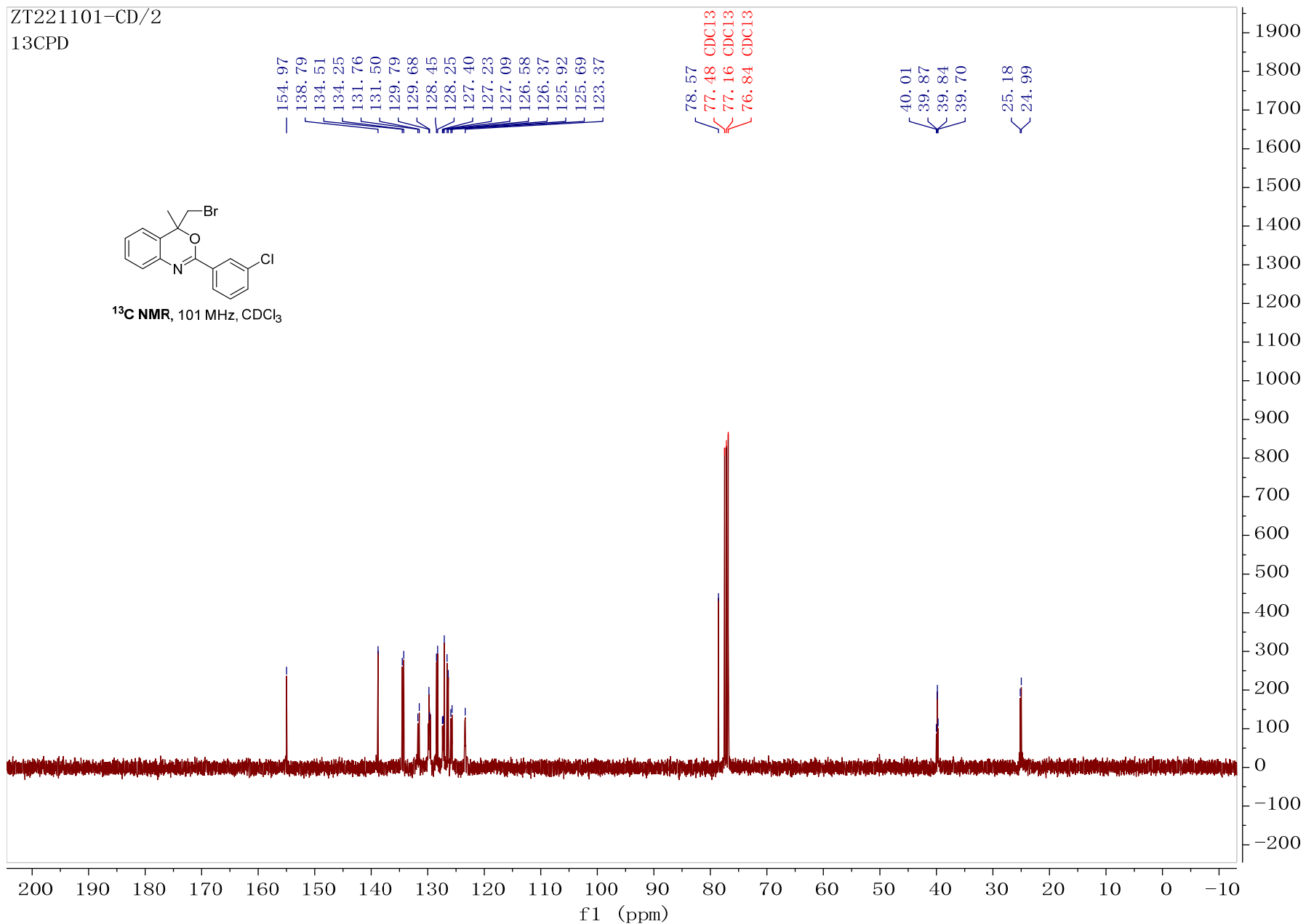
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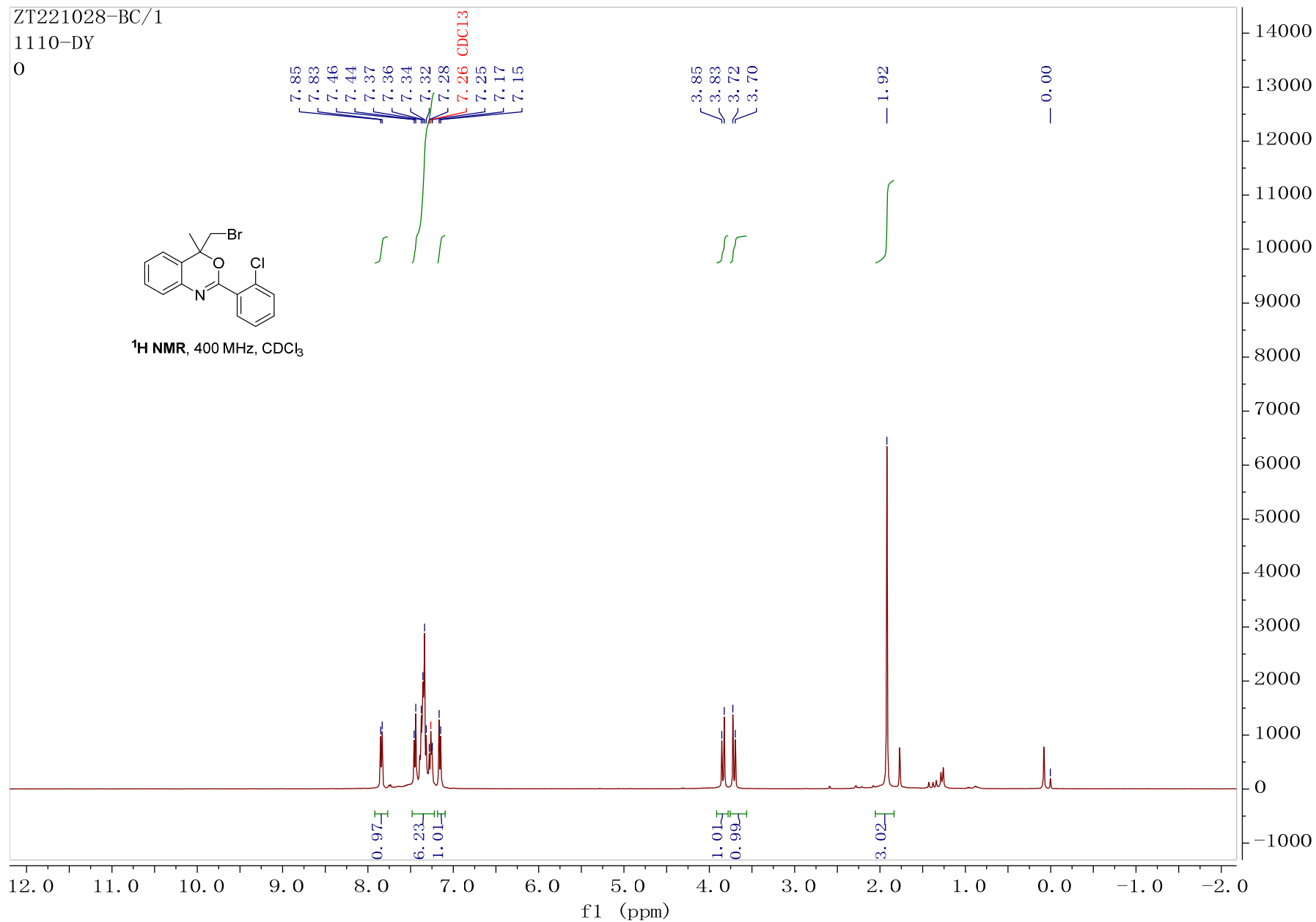
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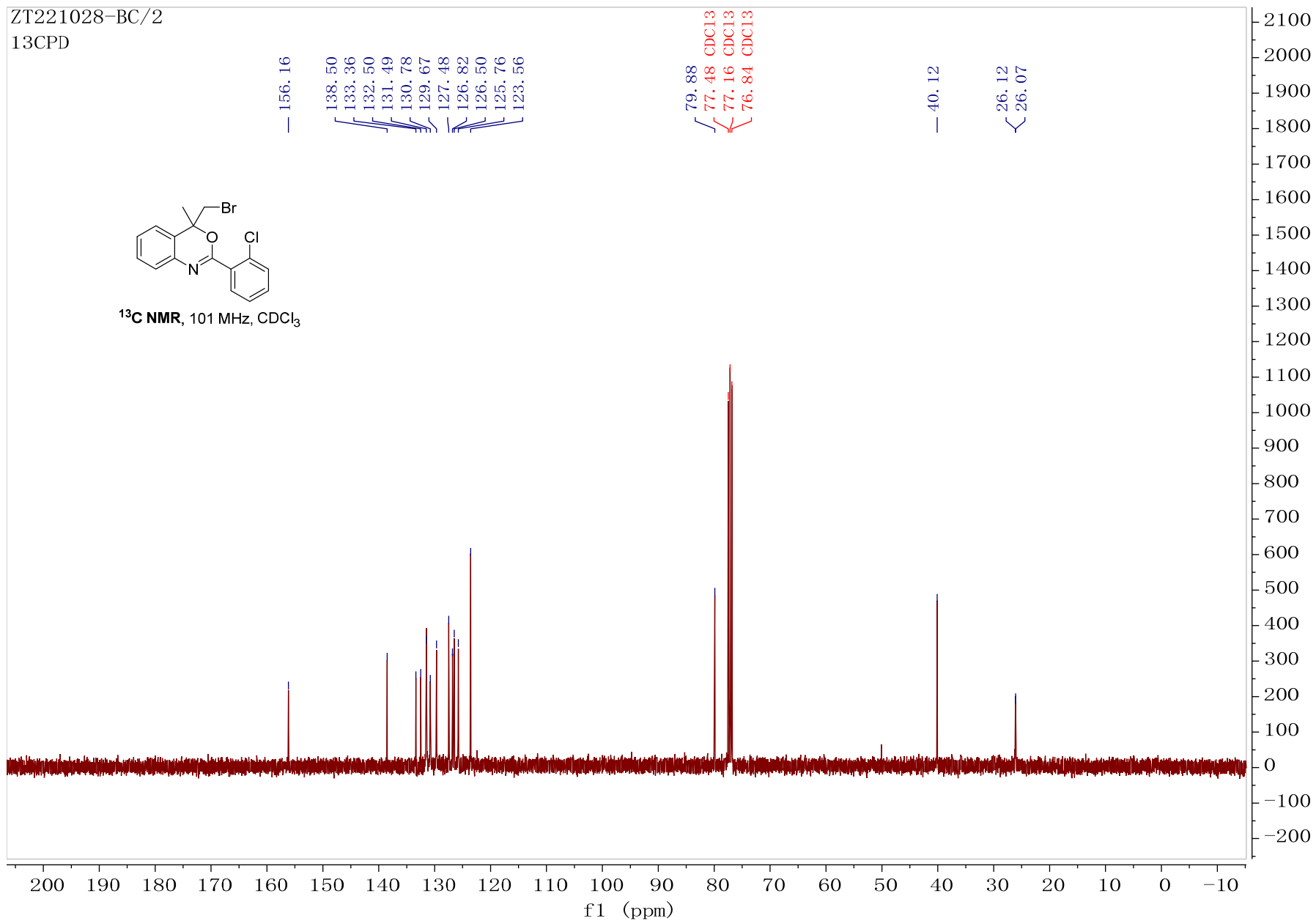
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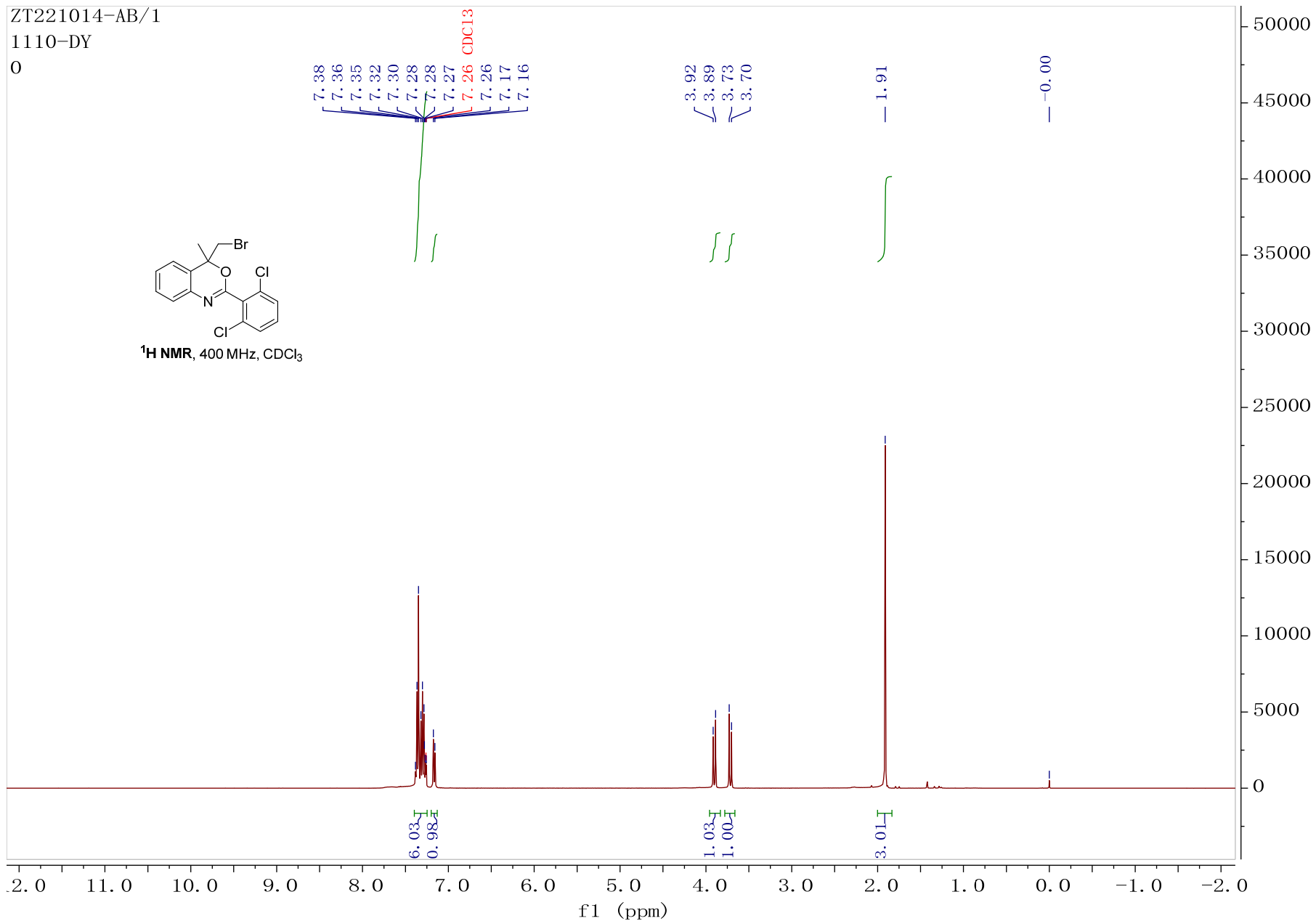
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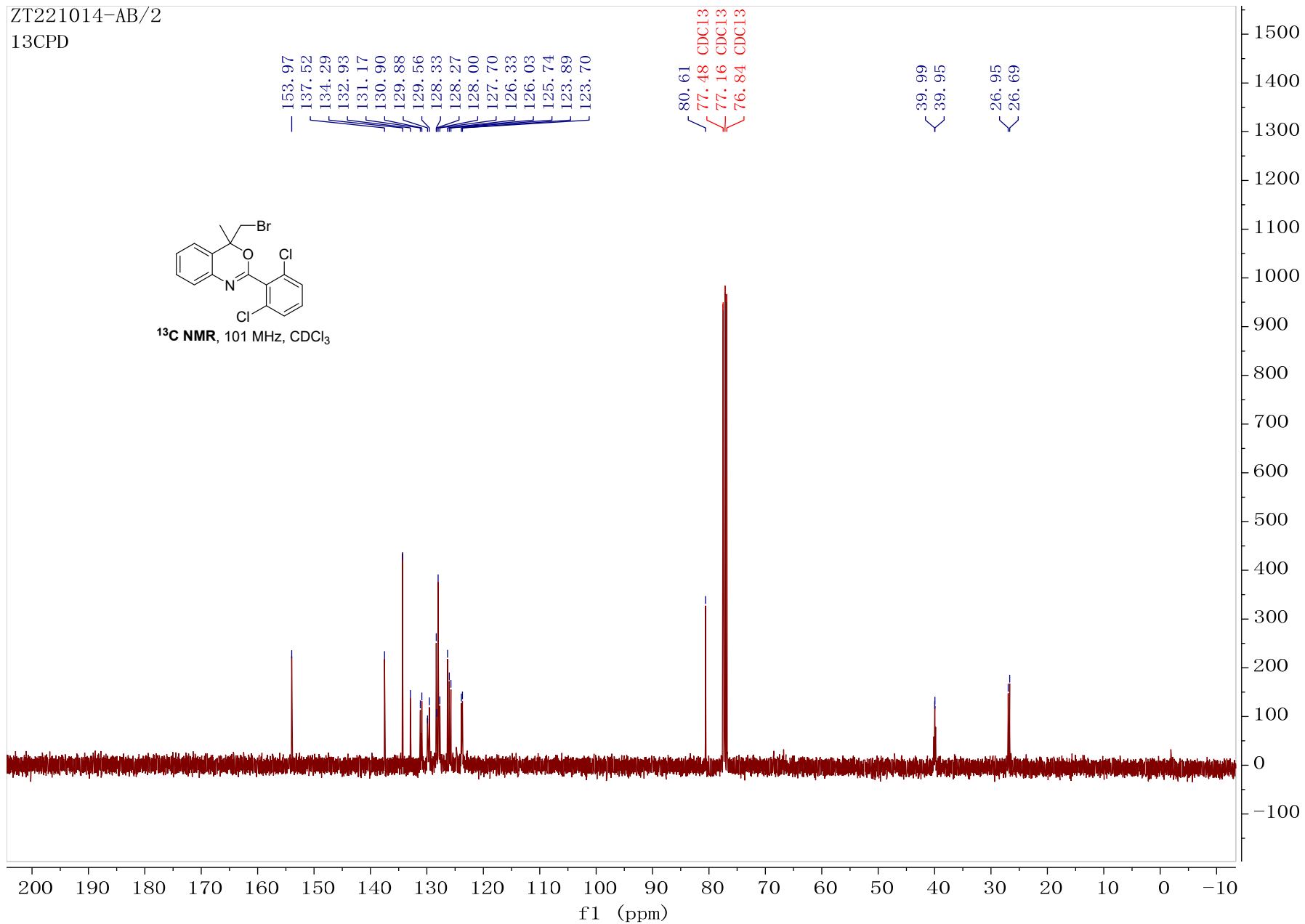
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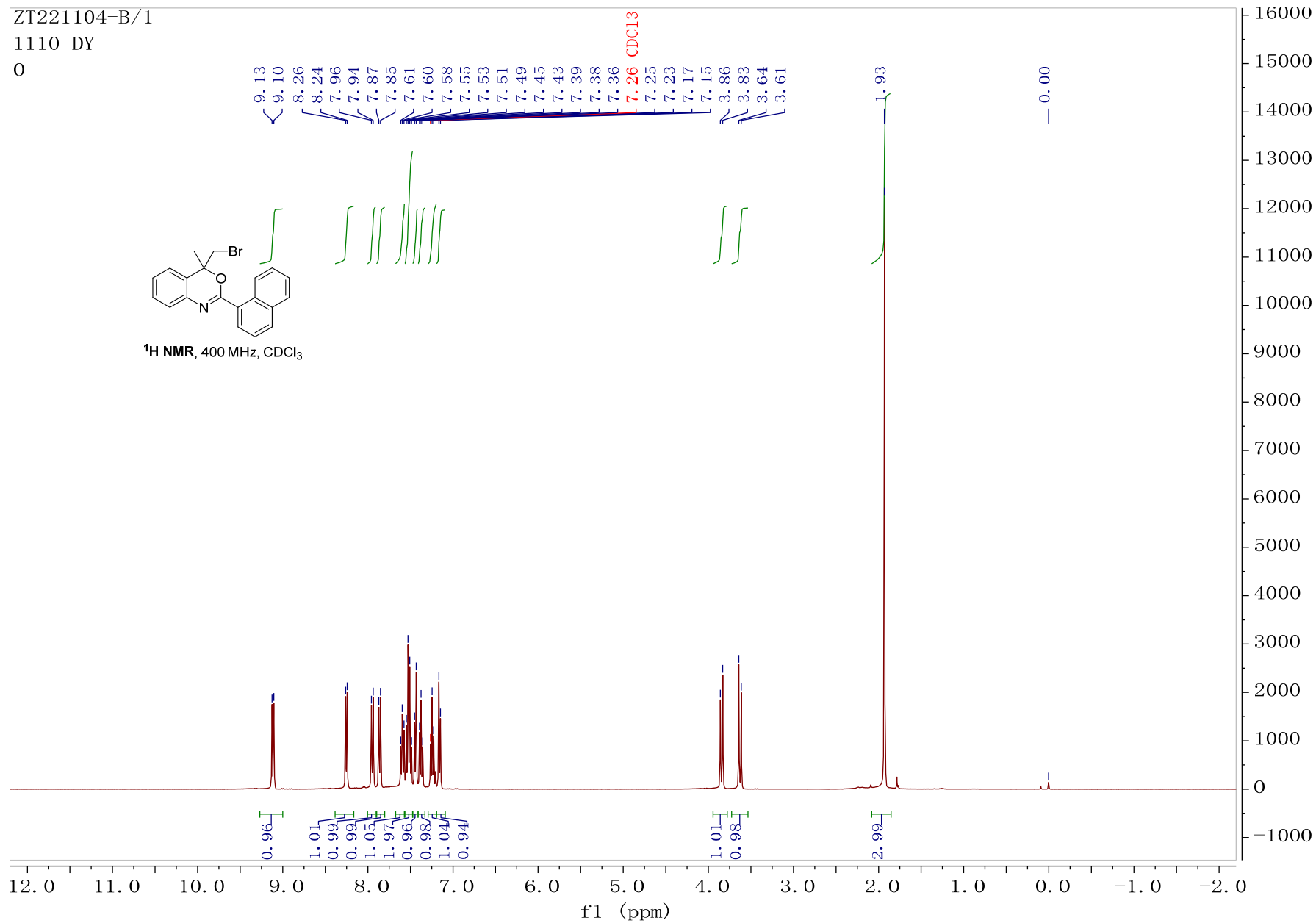
¹H NMR spectrum of Compound 2l (CDCl₃, 400 MHz)



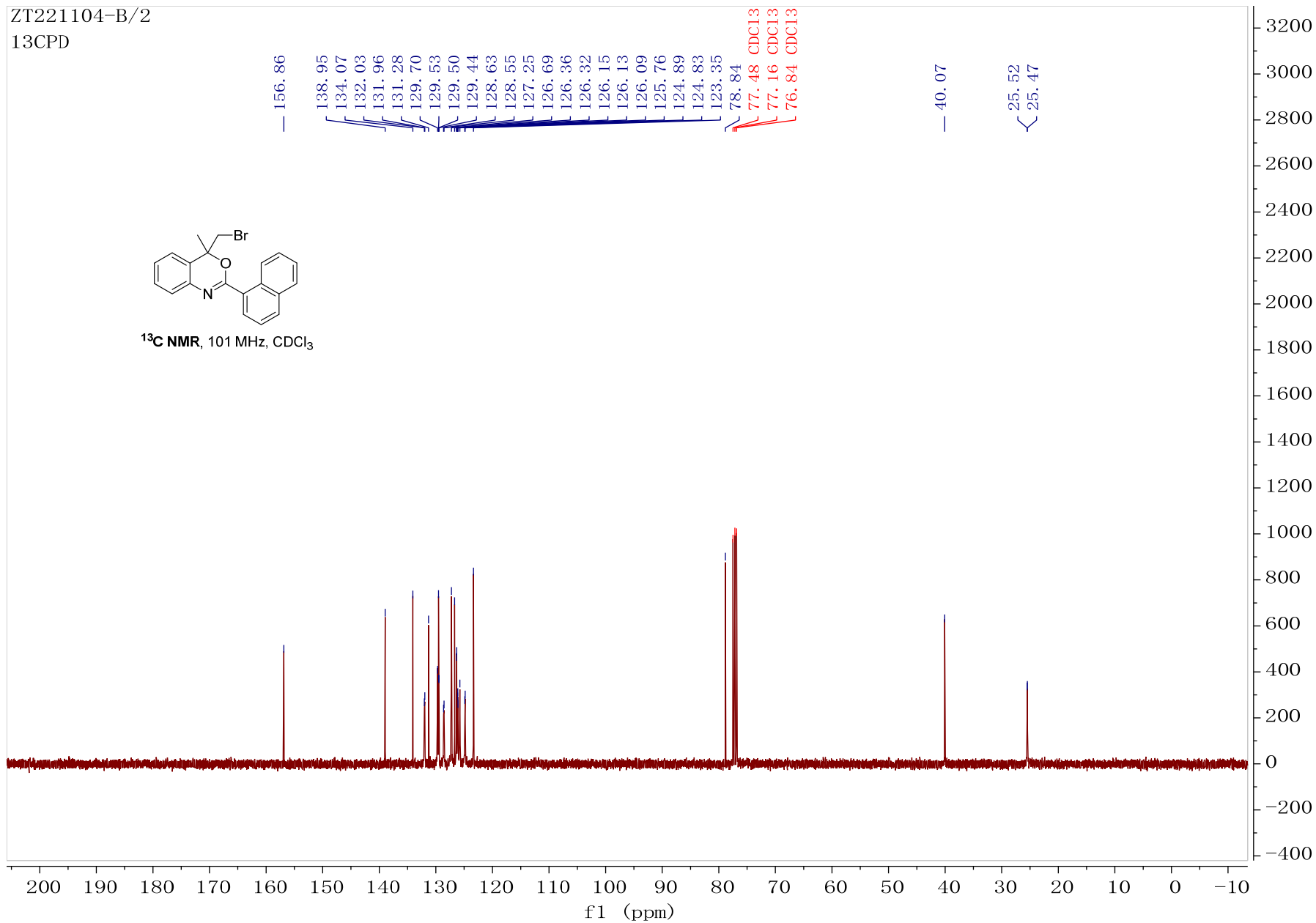
¹³C NMR spectrum of Compound 21 (CDCl₃, 101 MHz)



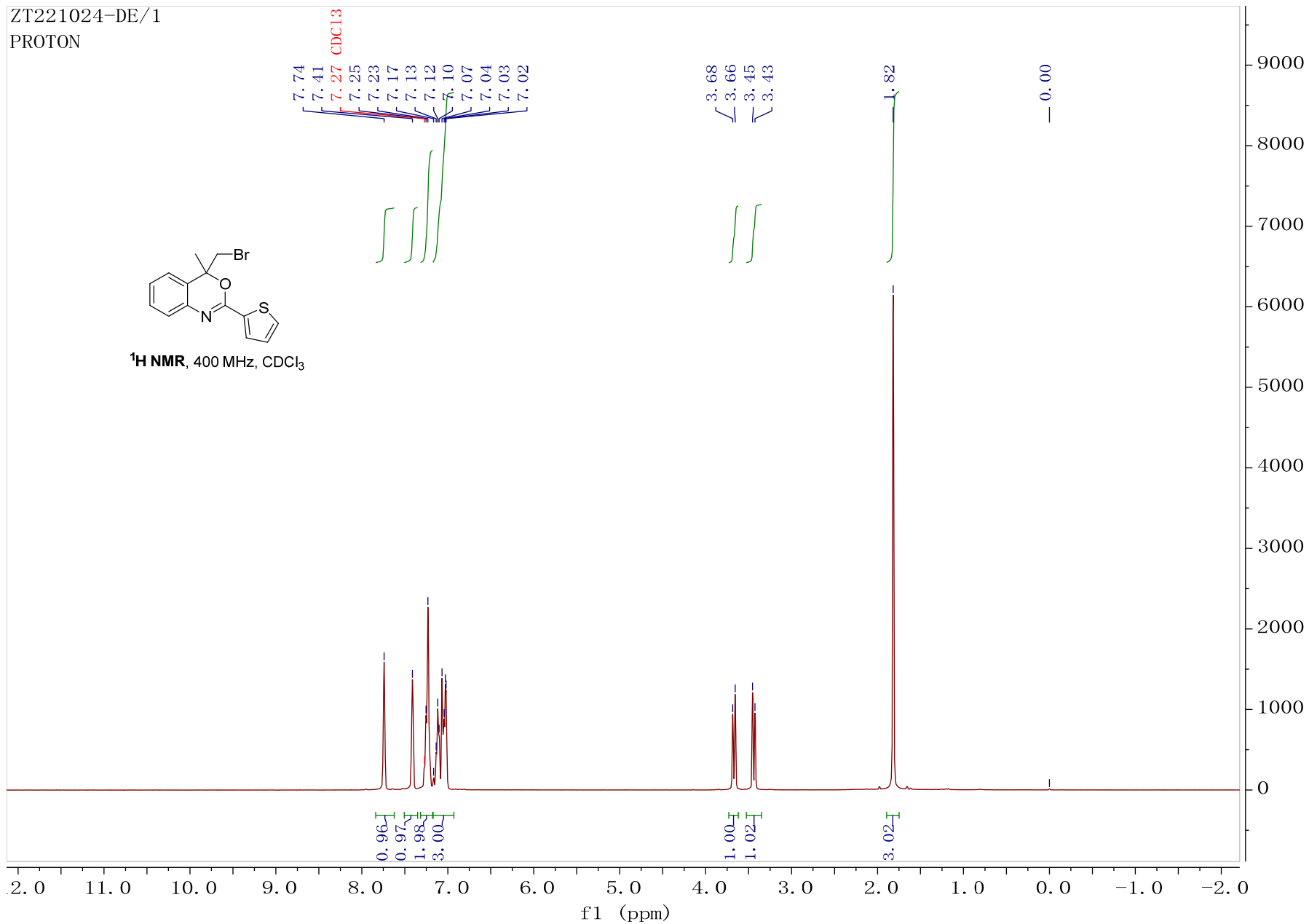
¹H NMR spectrum of Compound 2m (CDCl₃, 400 MHz)



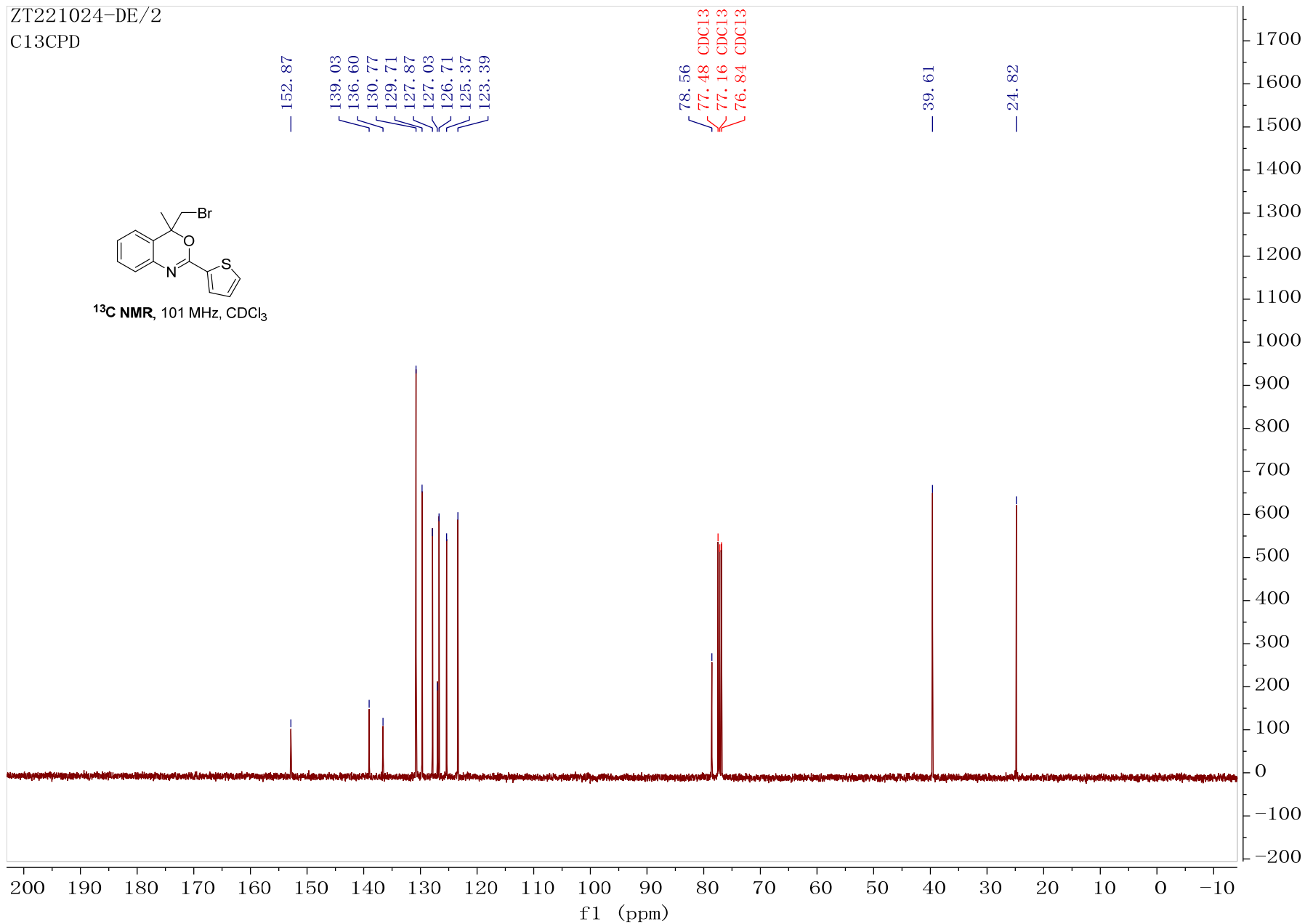
¹³C NMR spectrum of Compound 2m (CDCl₃, 101 MHz)



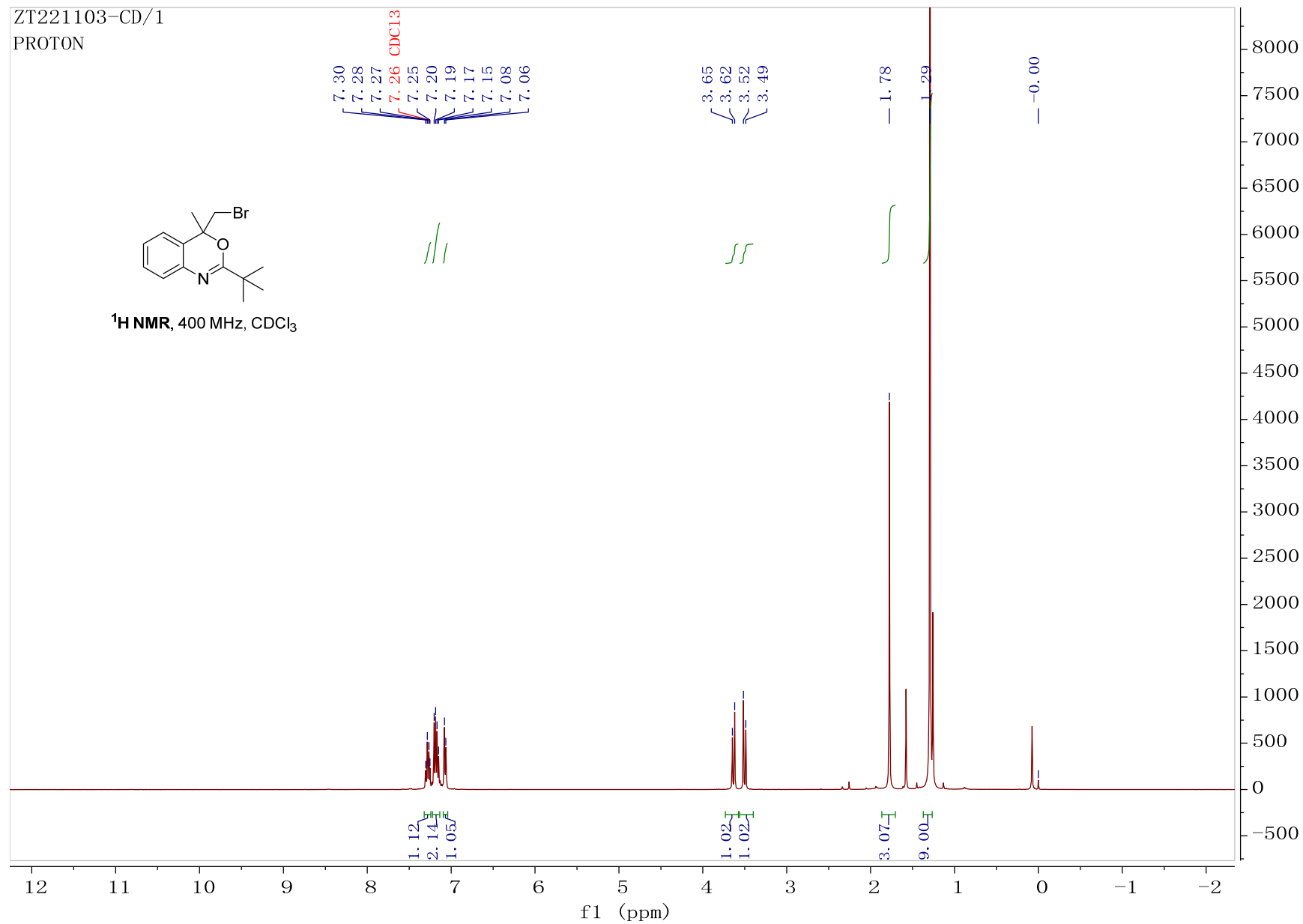
¹H NMR spectrum of Compound 2n (CDCl₃, 400 MHz)



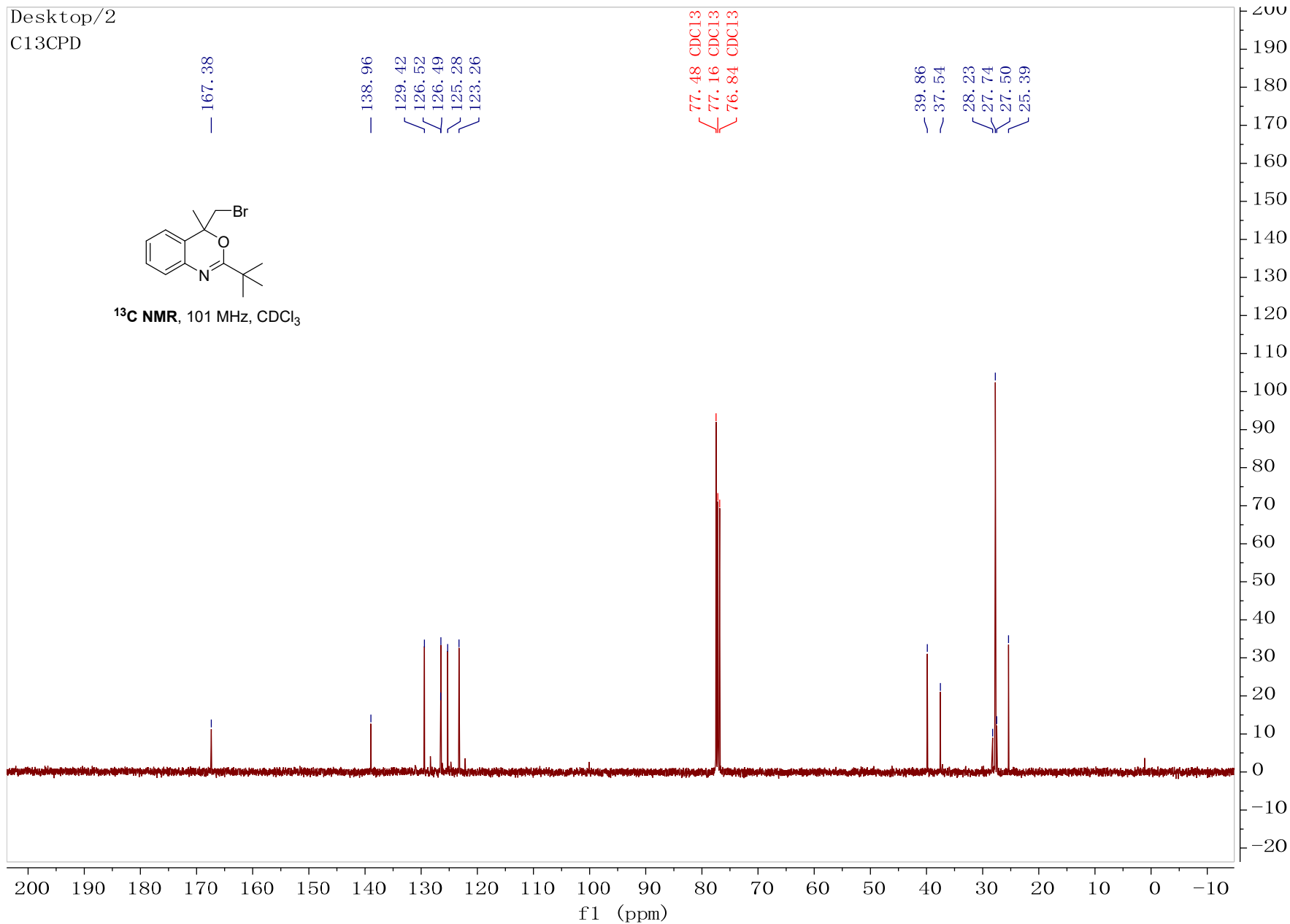
¹³C NMR spectrum of Compound 2n (CDCl₃, 101 MHz)



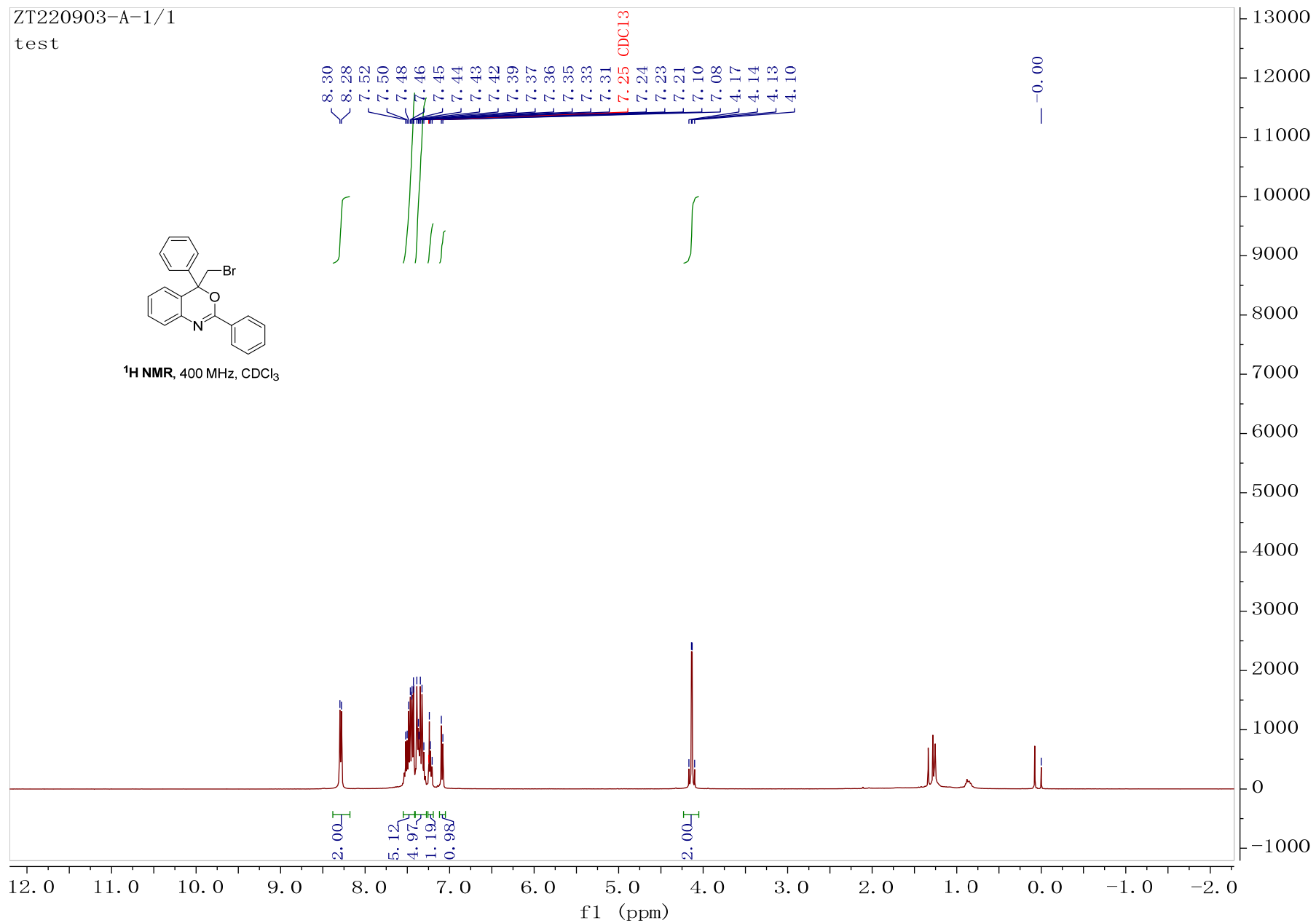
¹H NMR spectrum of Compound 2o (CDCl₃, 400 MHz)



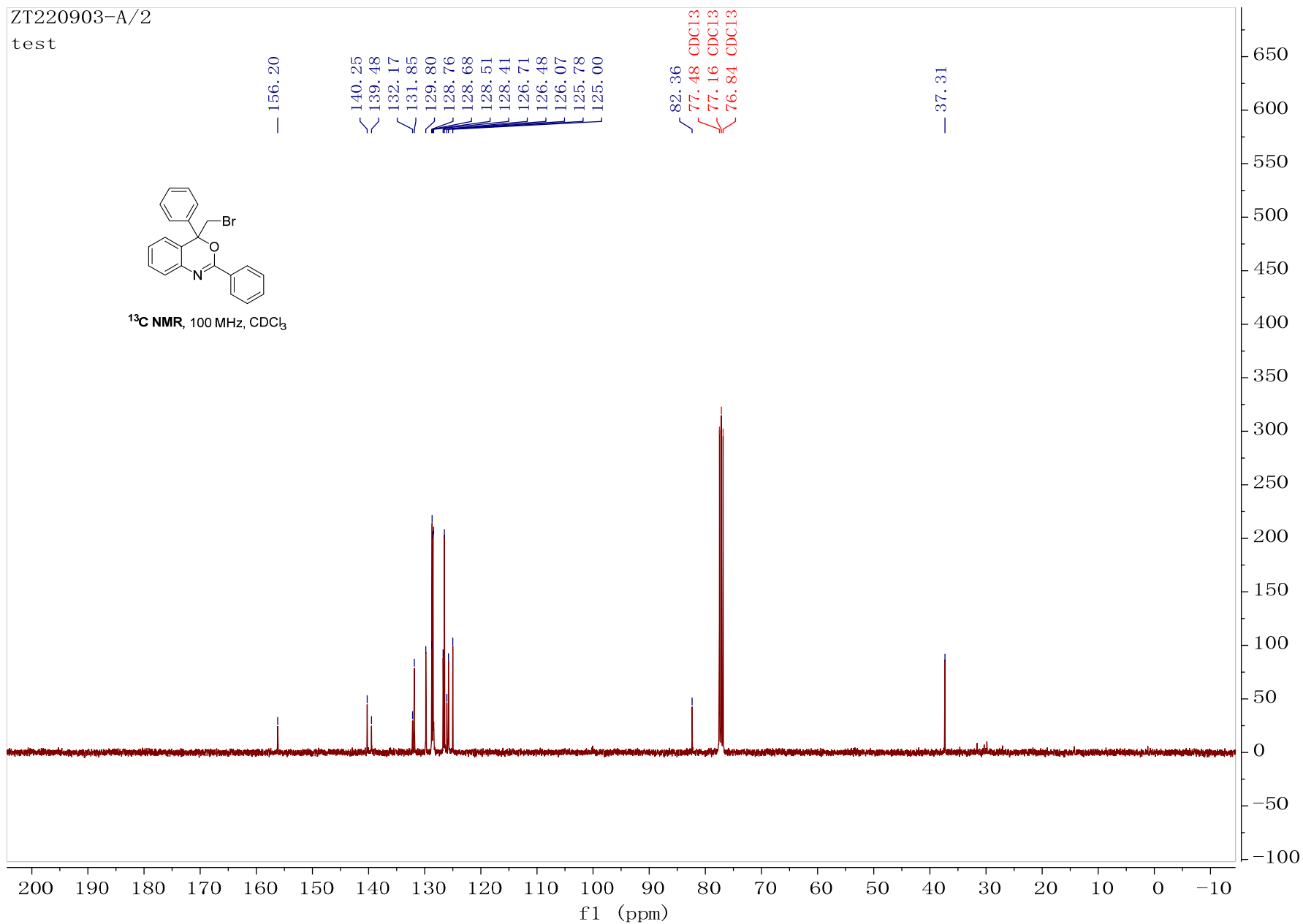
¹³C NMR spectrum of Compound 2o (CDCl₃, 101 MHz)



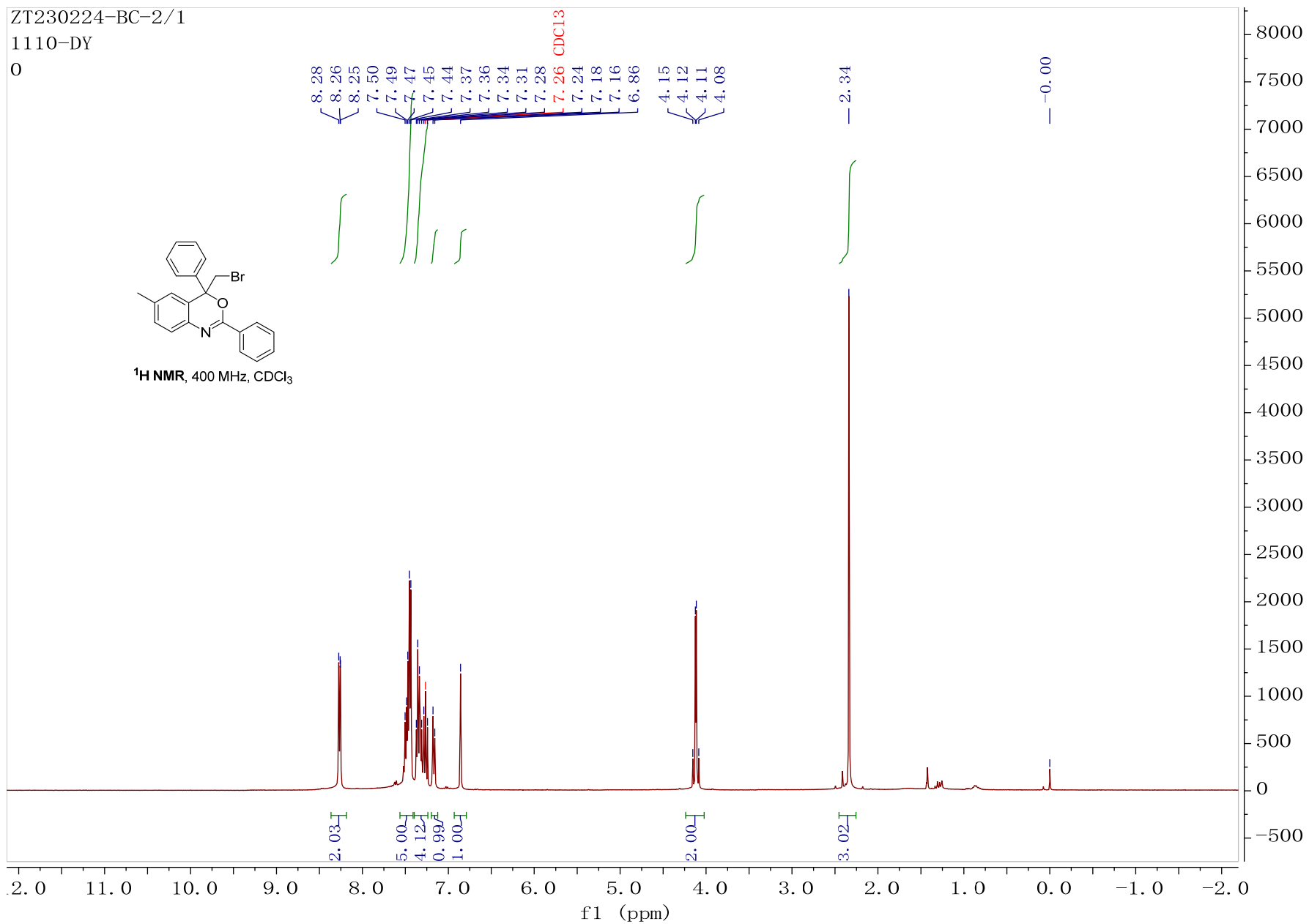
¹H NMR spectrum of Compound 2p (CDCl₃, 400 MHz)



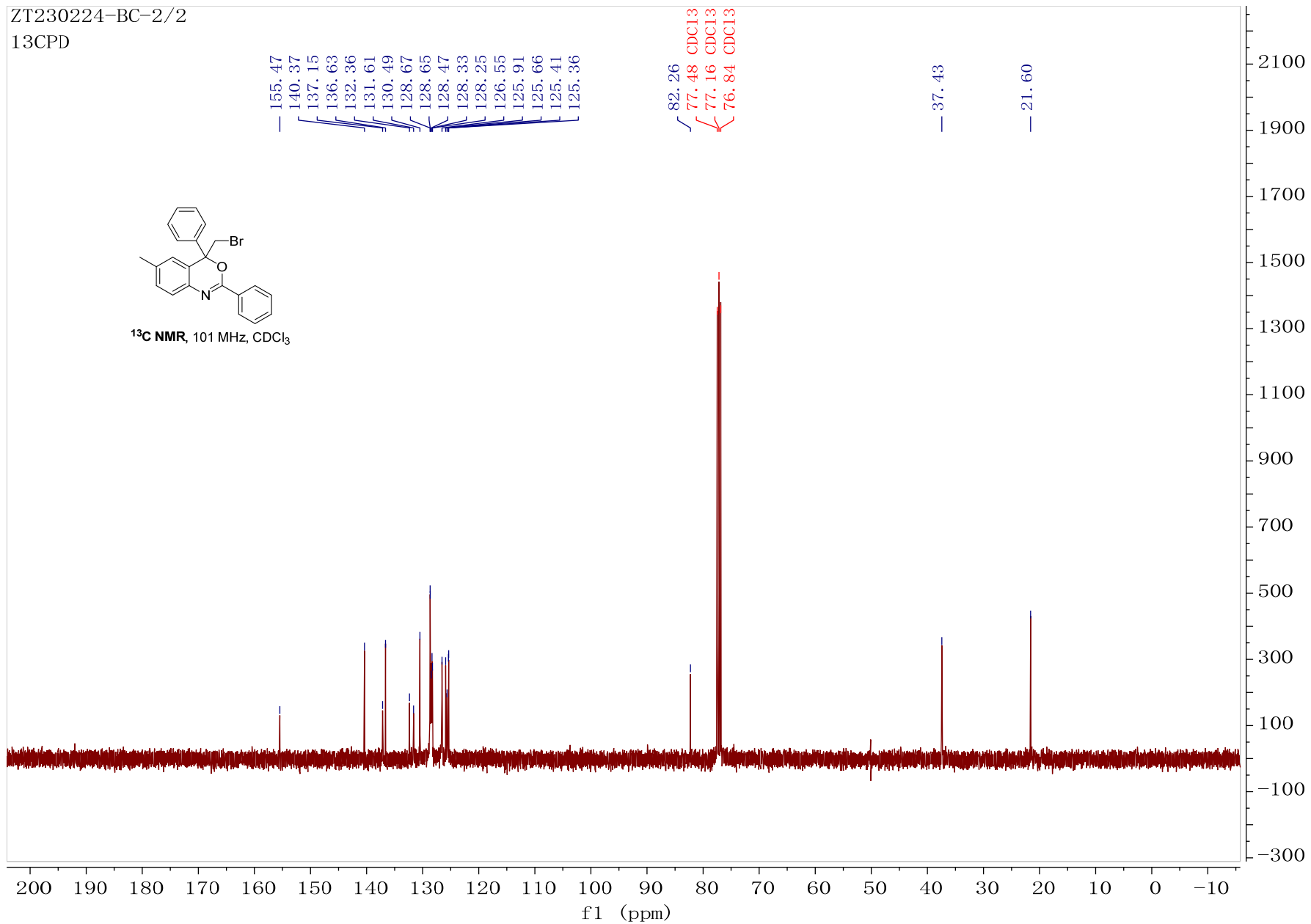
¹³C NMR spectrum of Compound 2p (CDCl₃, 101 MHz)



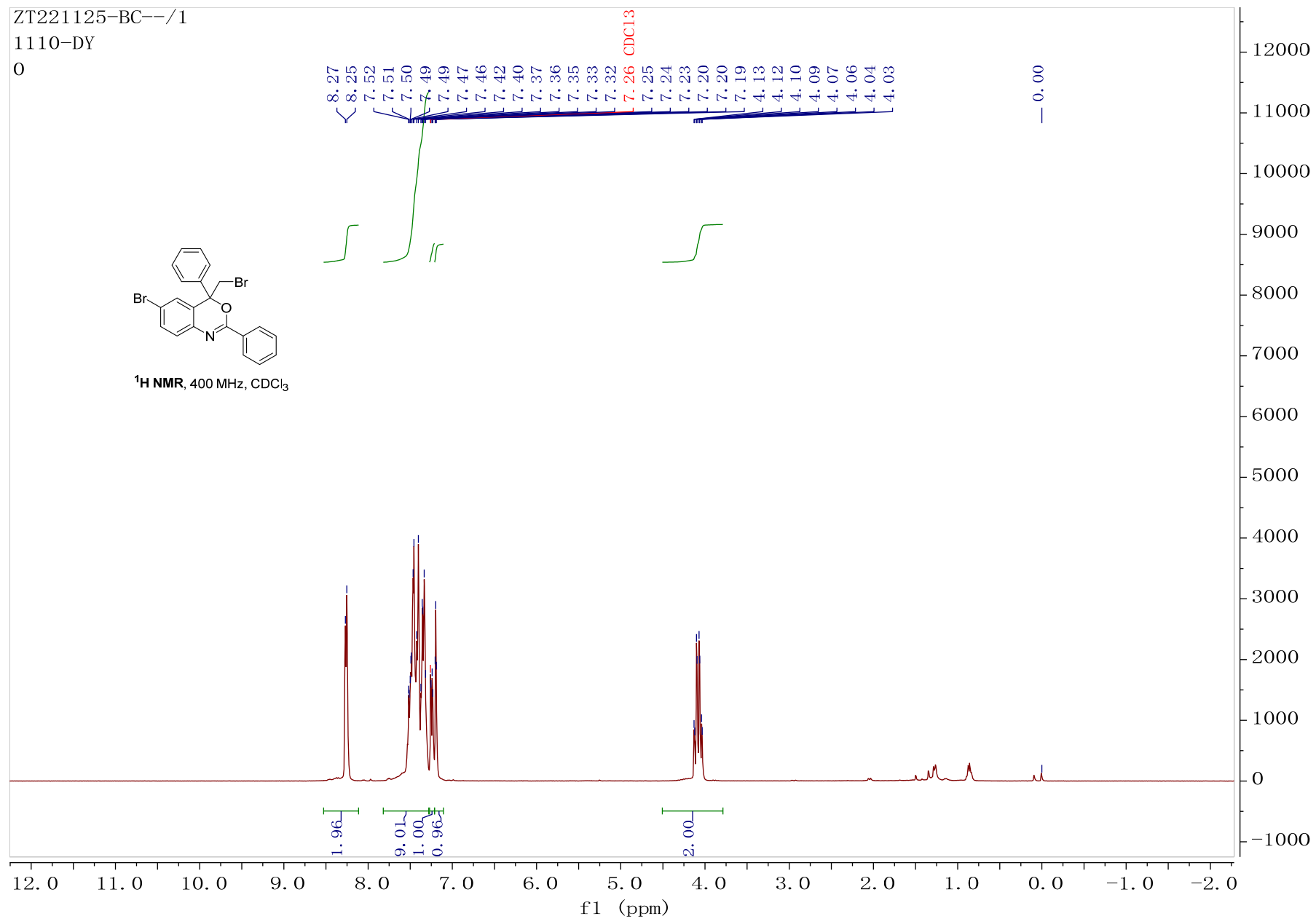
¹H NMR spectrum of Compound 2q (CDCl₃, 400 MHz)



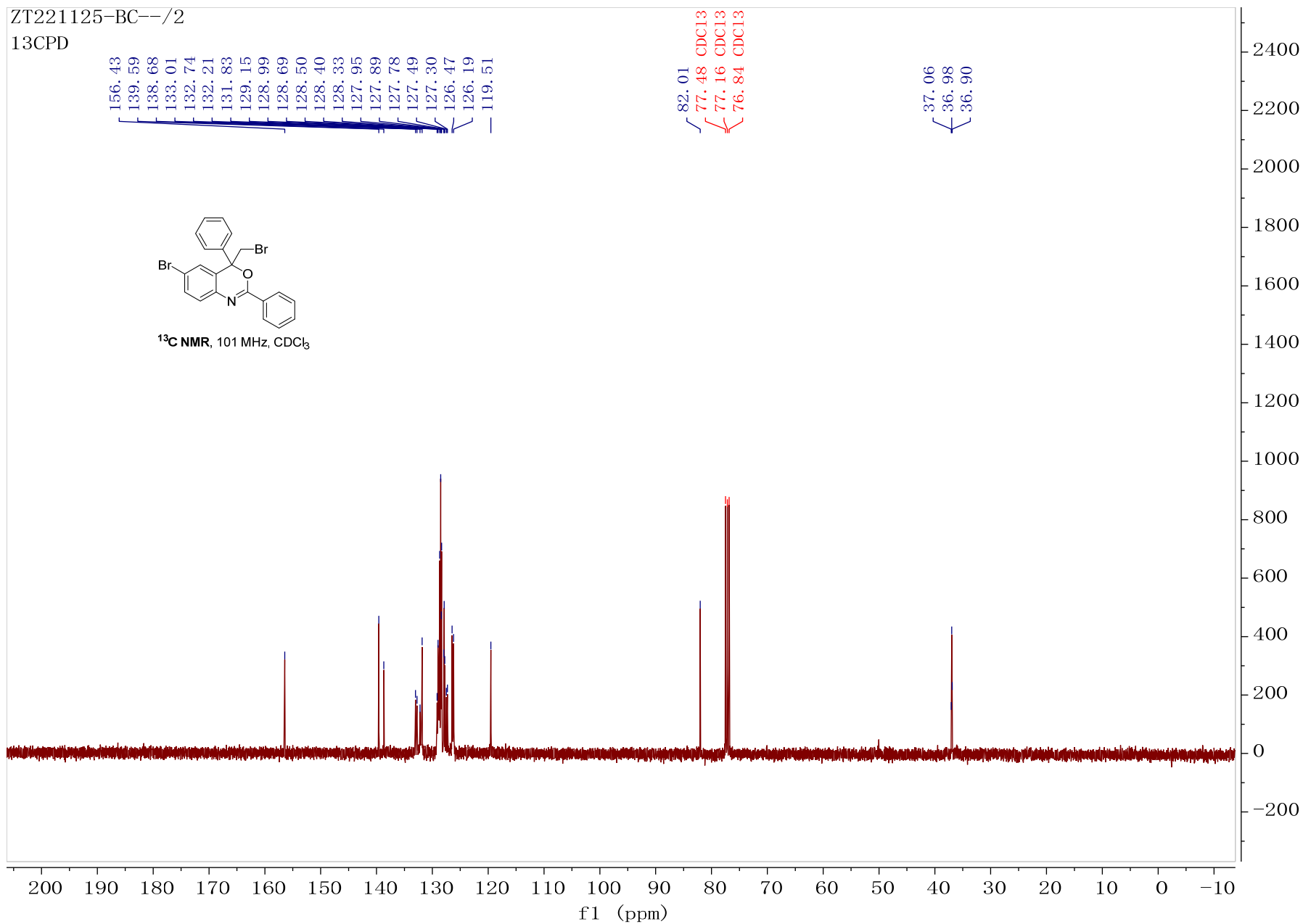
¹³C NMR spectrum of Compound 2q (CDCl₃, 101 MHz)



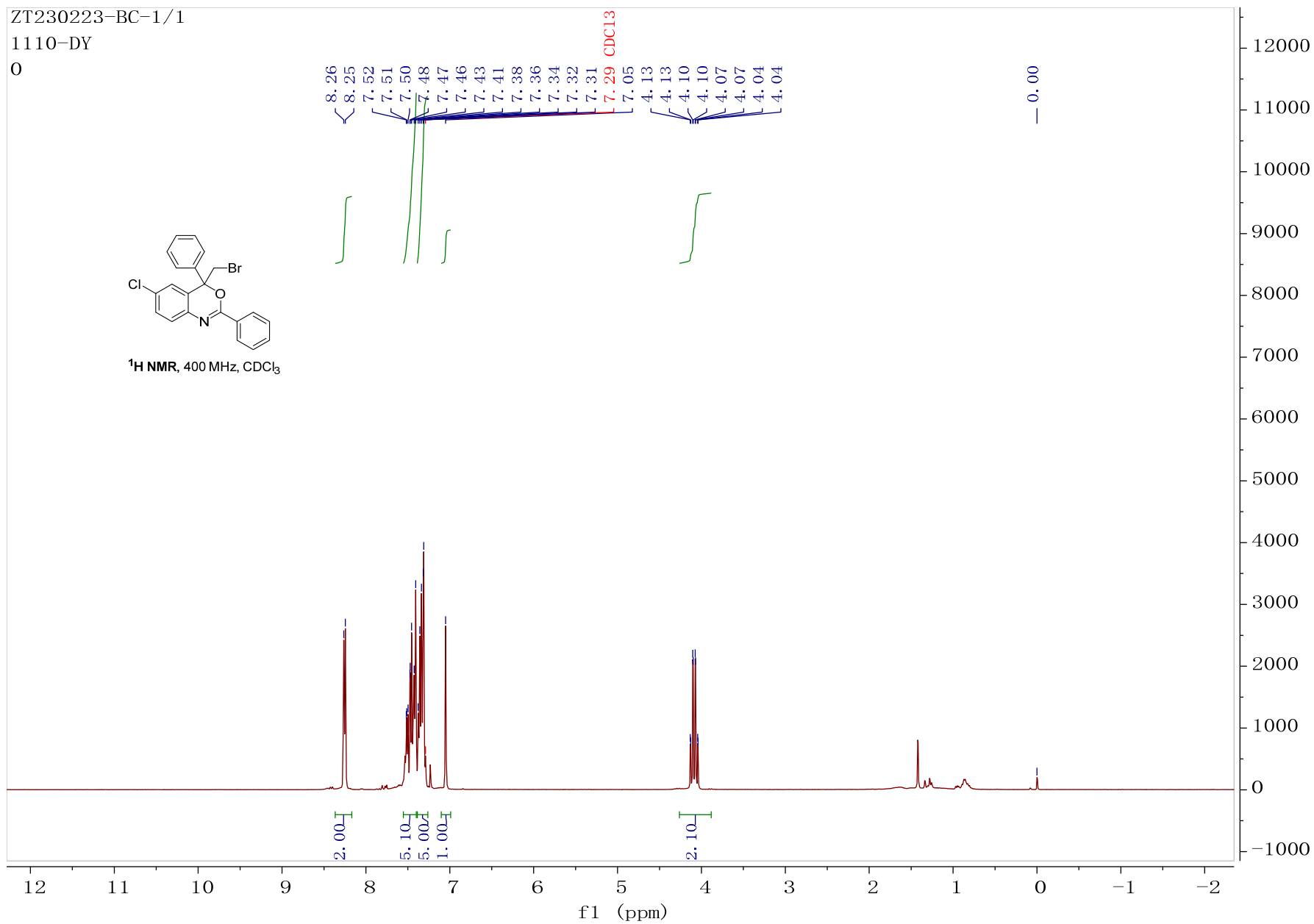
¹H NMR spectrum of Compound 2r (CDCl₃, 400 MHz)



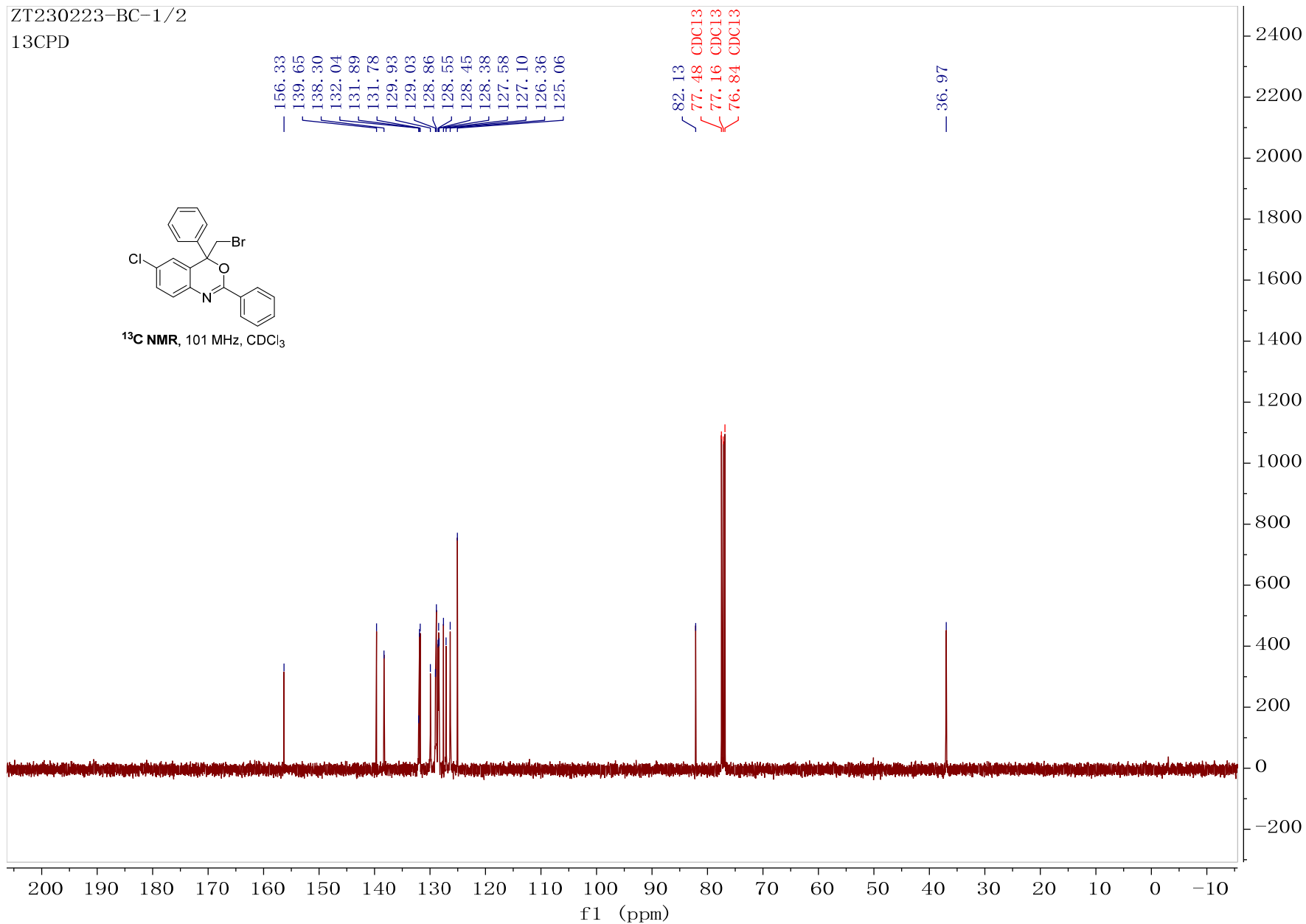
¹³C NMR spectrum of Compound 2r (CDCl₃, 101 MHz)



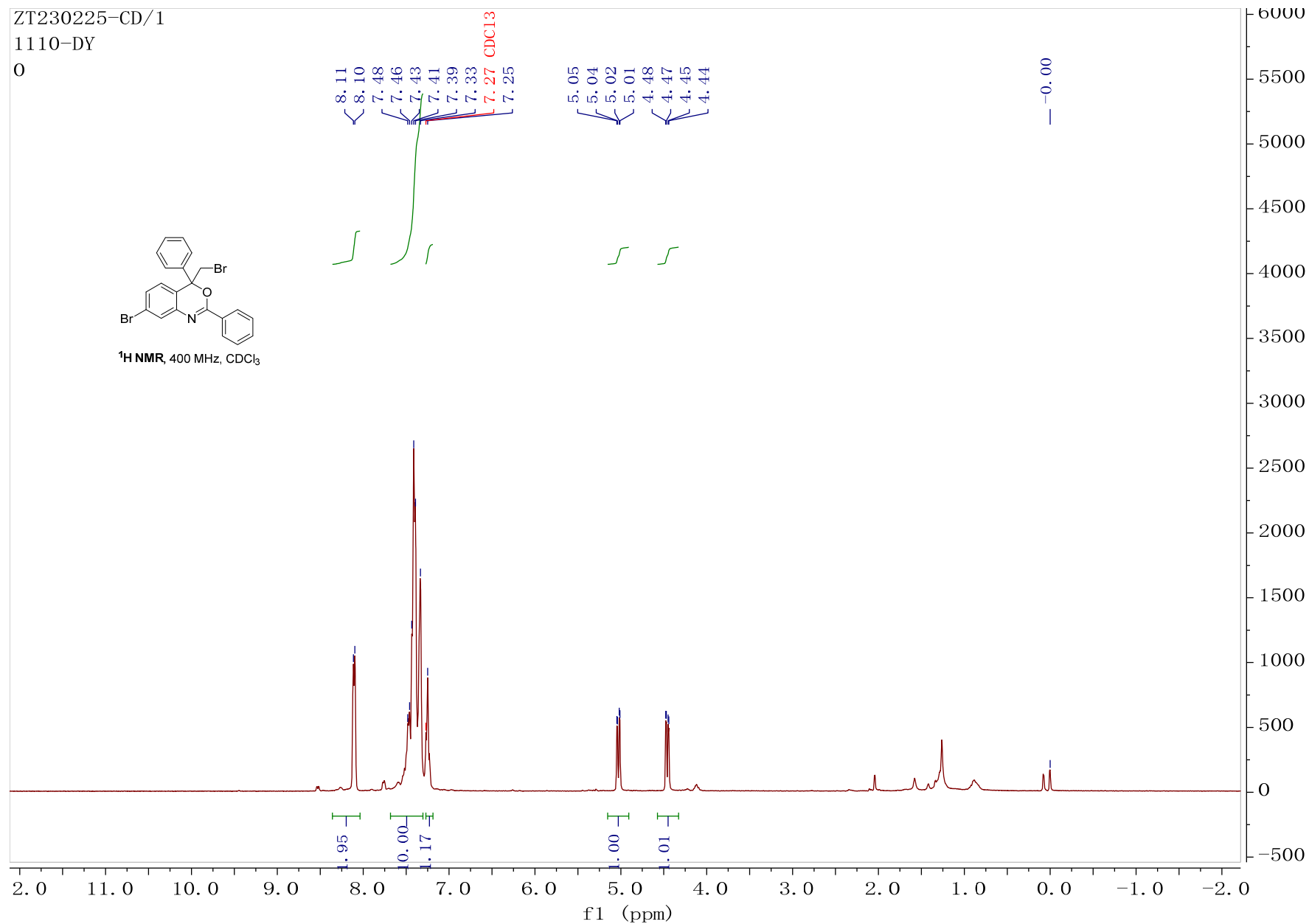
¹H NMR spectrum of Compound 2s (CDCl₃, 400 MHz)



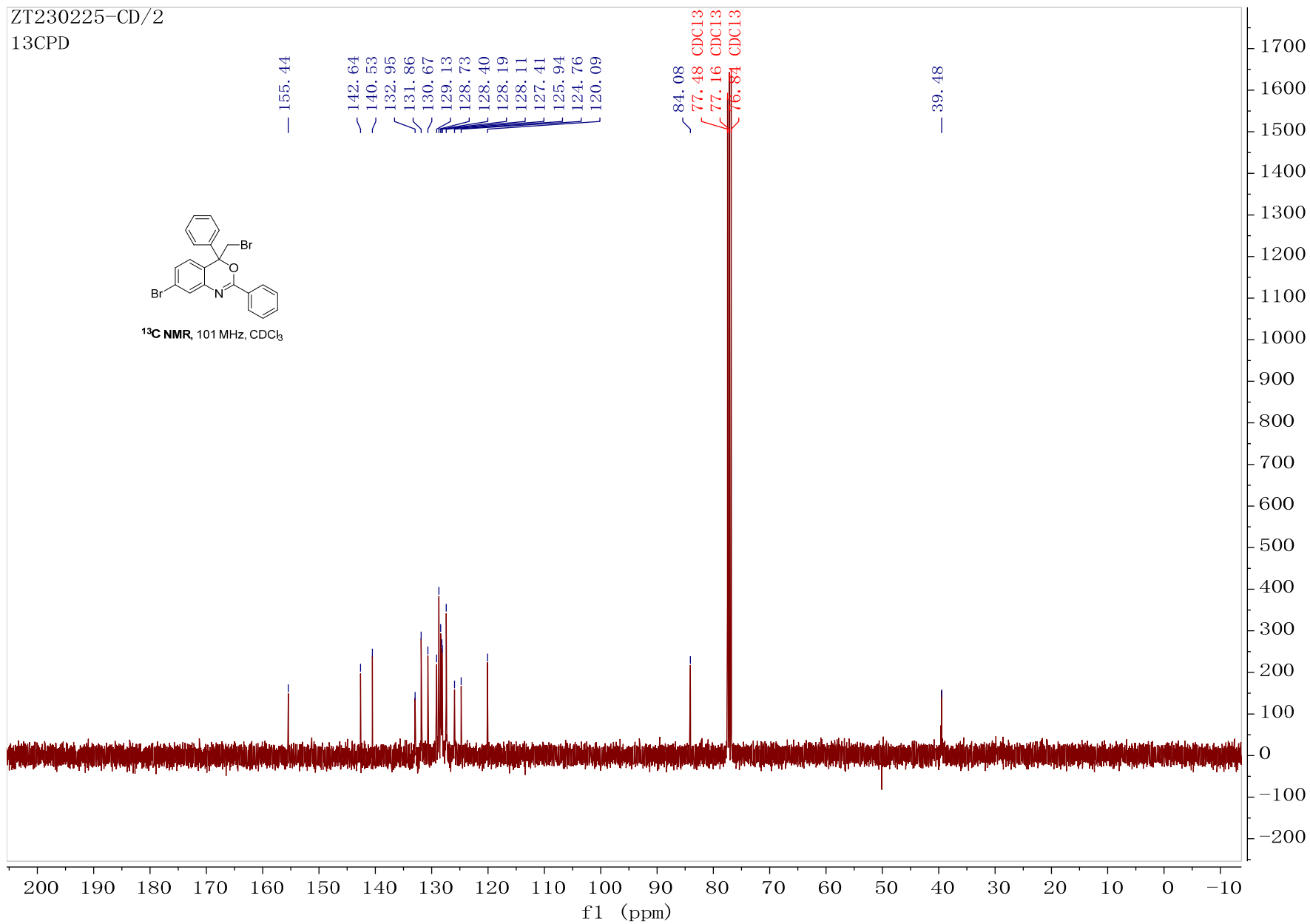
¹³C NMR spectrum of Compound 2s (CDCl₃, 101 MHz)



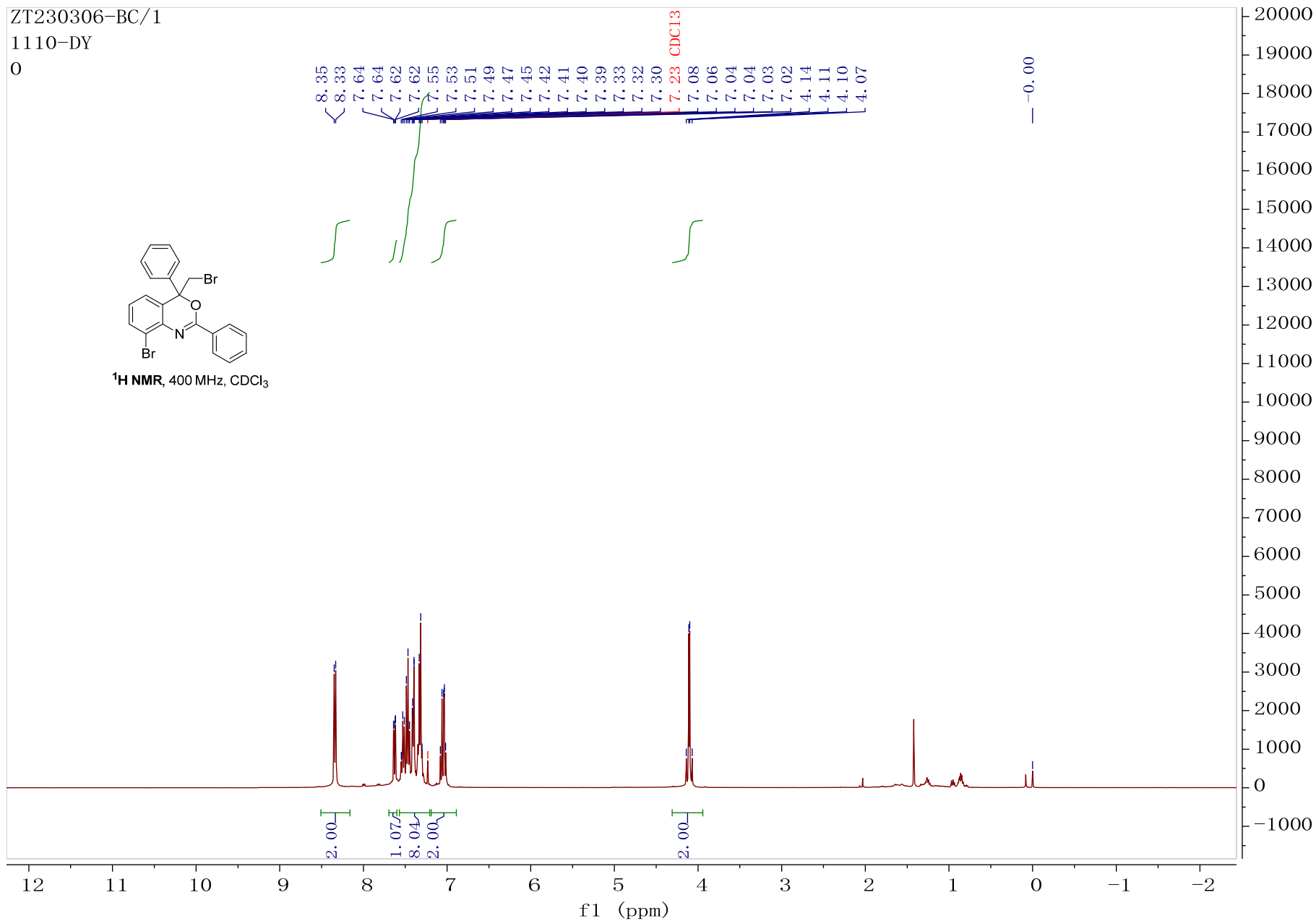
¹H NMR spectrum of Compound 2t (CDCl₃, 400 MHz)



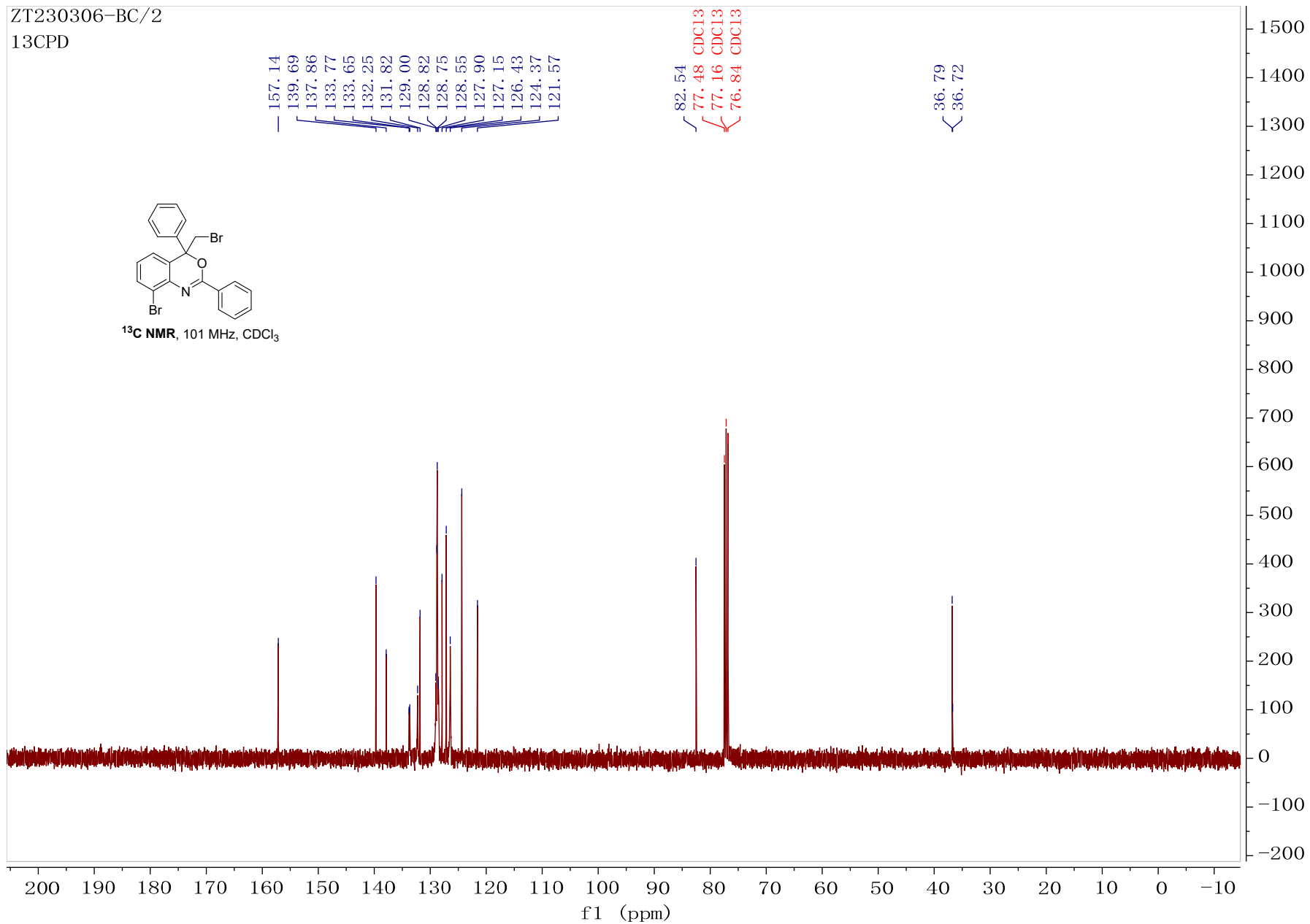
¹³C NMR spectrum of Compound 2t (CDCl₃, 101 MHz)



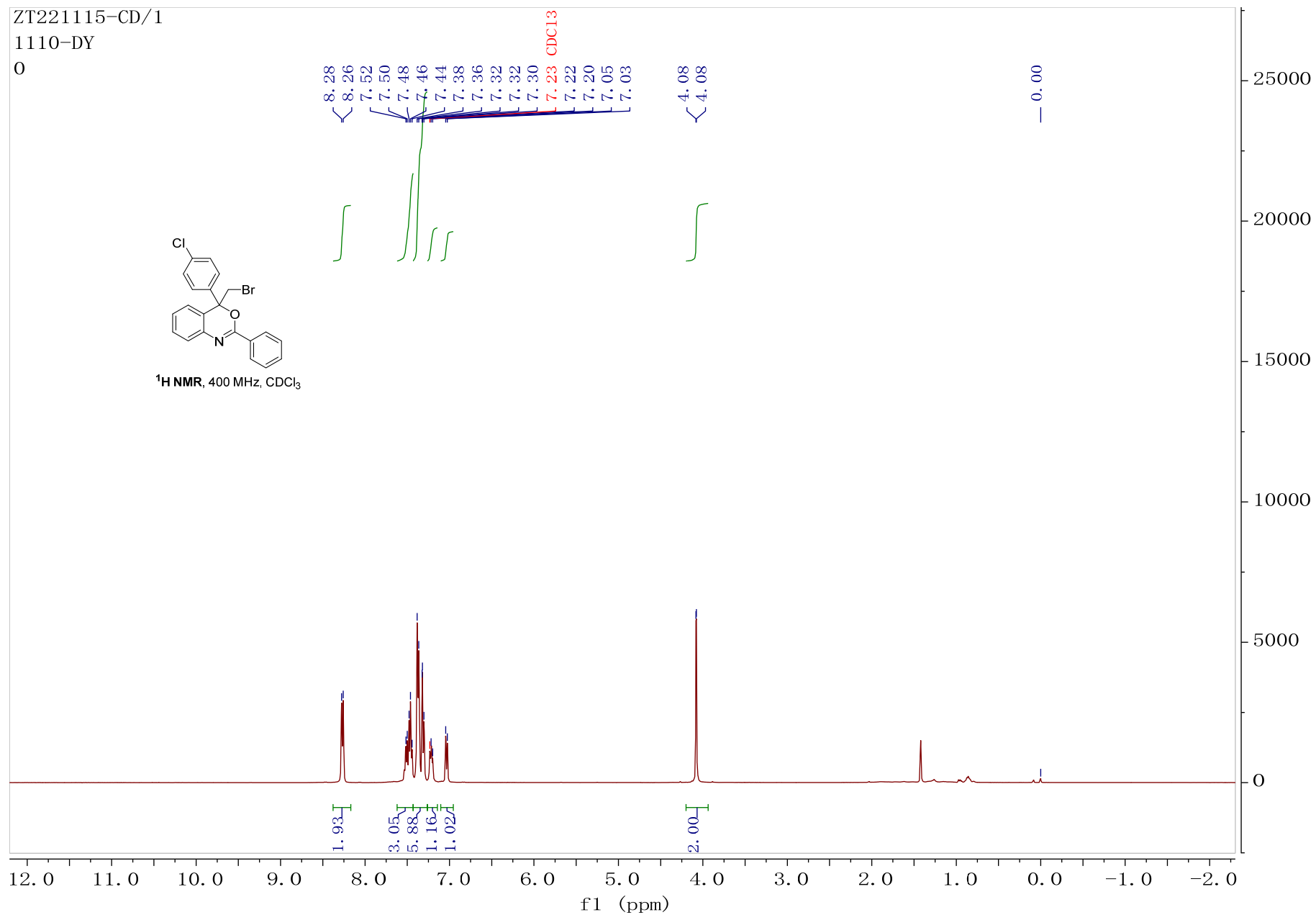
¹H NMR spectrum of Compound 2u (CDCl₃, 400 MHz)



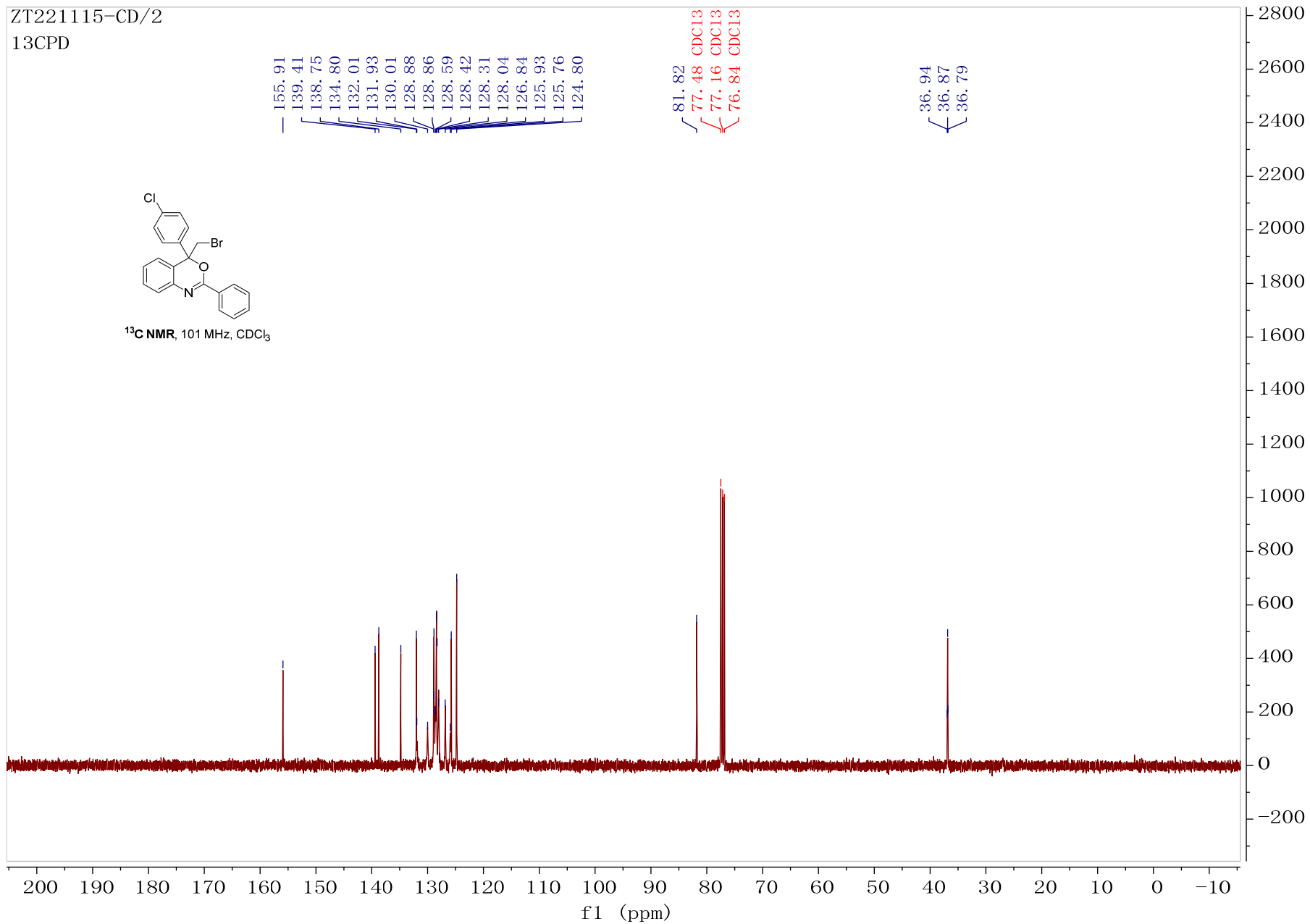
¹³C NMR spectrum of Compound 2u (CDCl₃, 101 MHz)



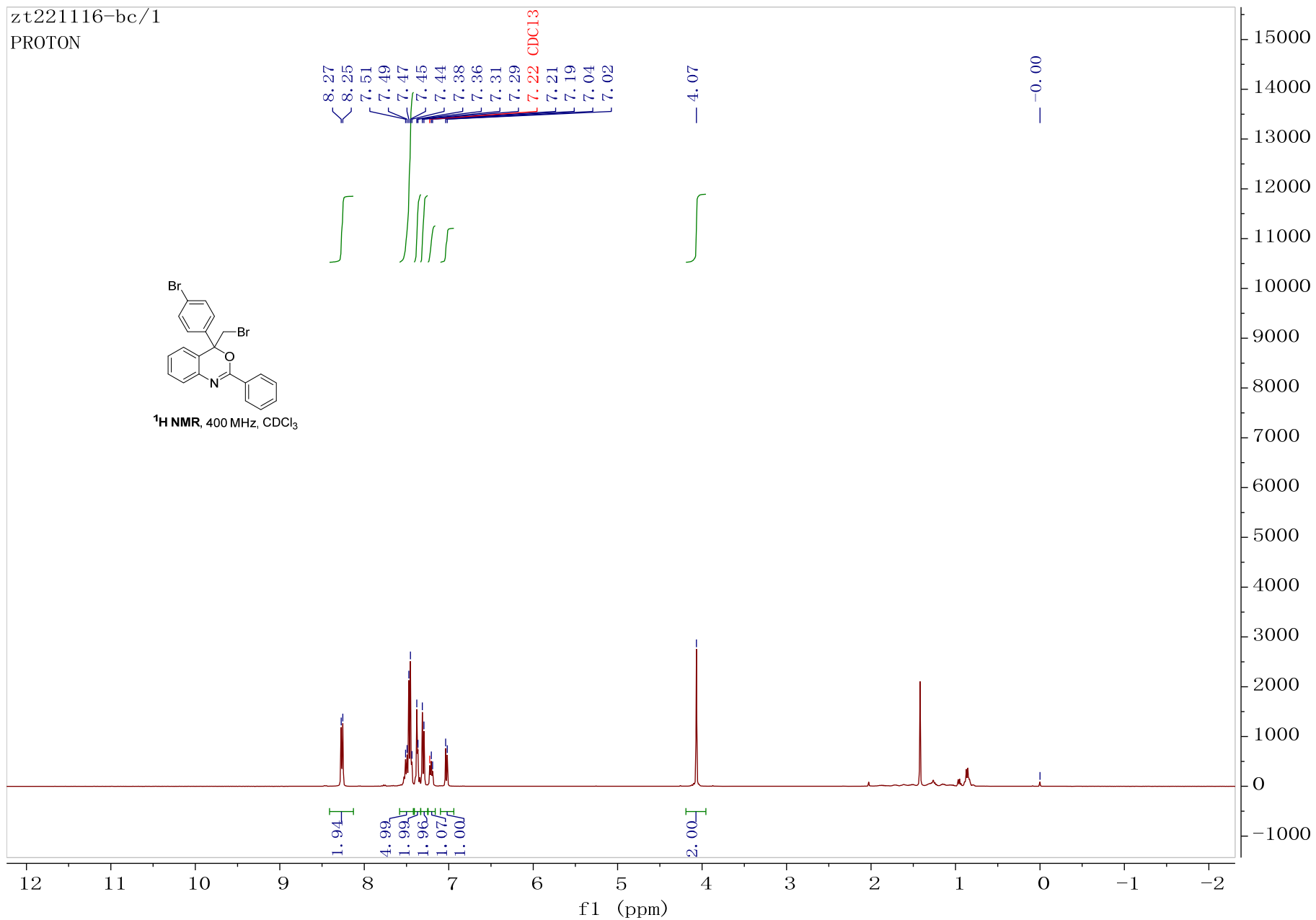
¹H NMR spectrum of Compound 2v (CDCl₃, 400 MHz)



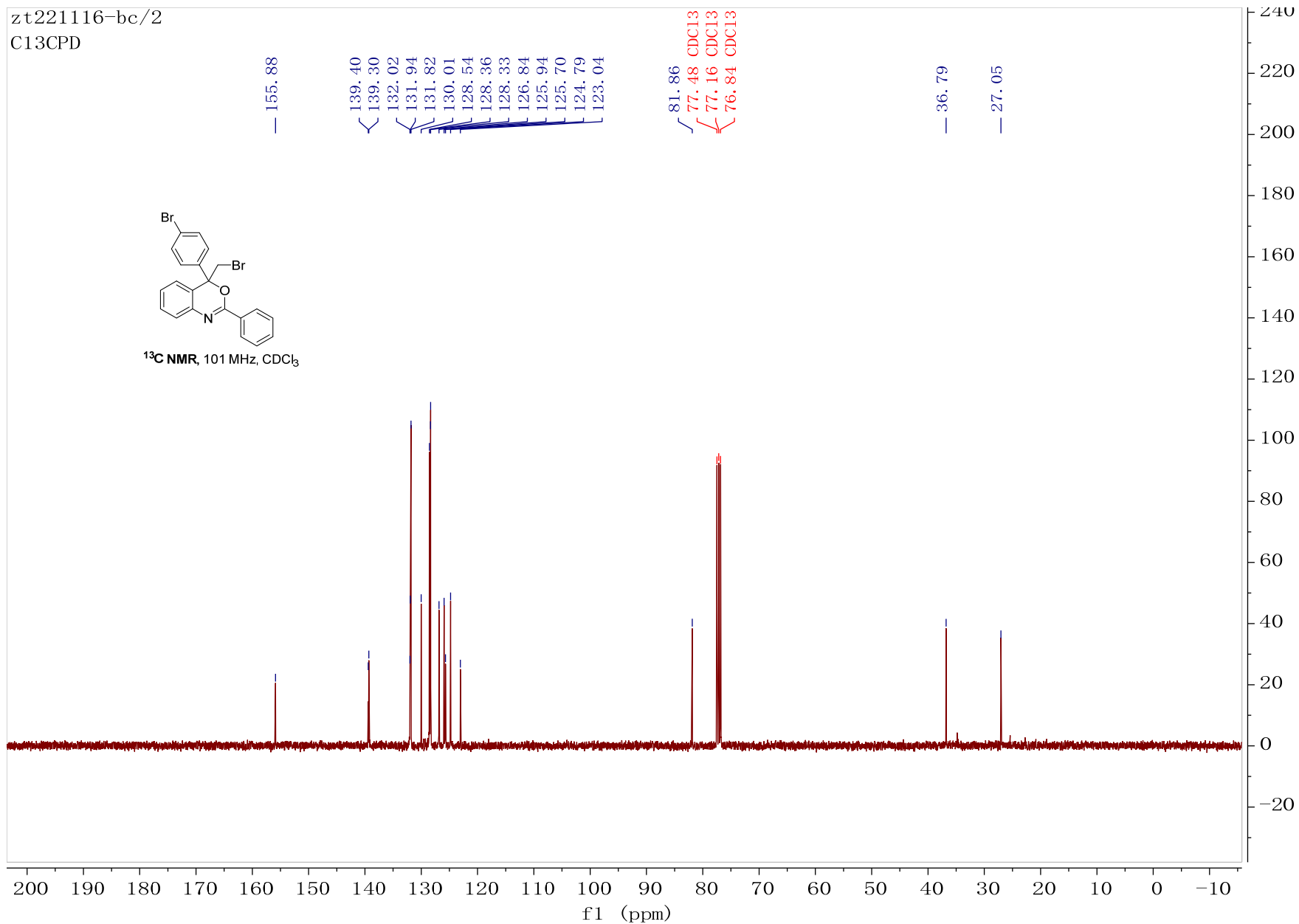
¹³C NMR spectrum of Compound 2v (CDCl₃, 101 MHz)



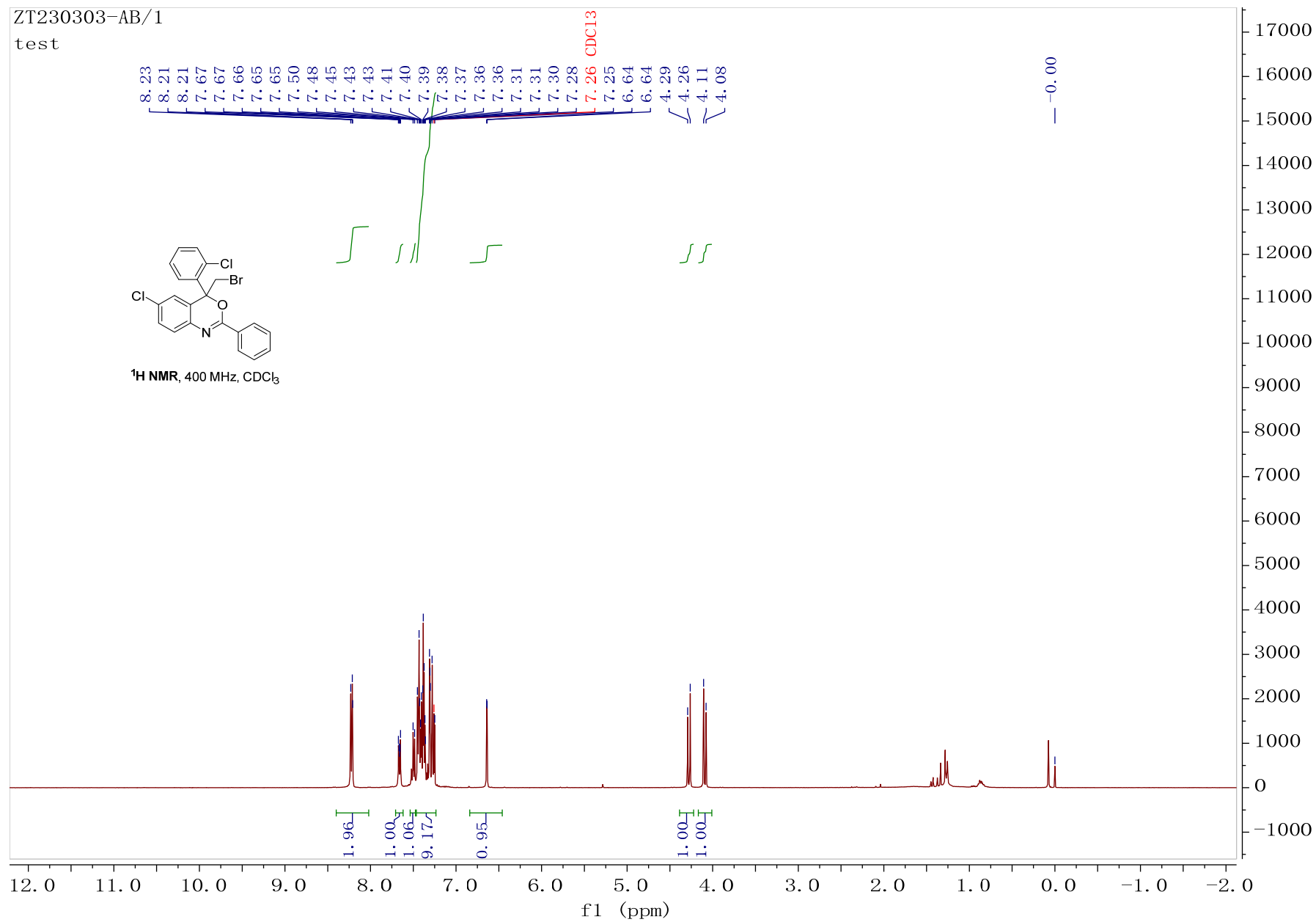
¹H NMR spectrum of Compound 2w (CDCl₃, 400 MHz)



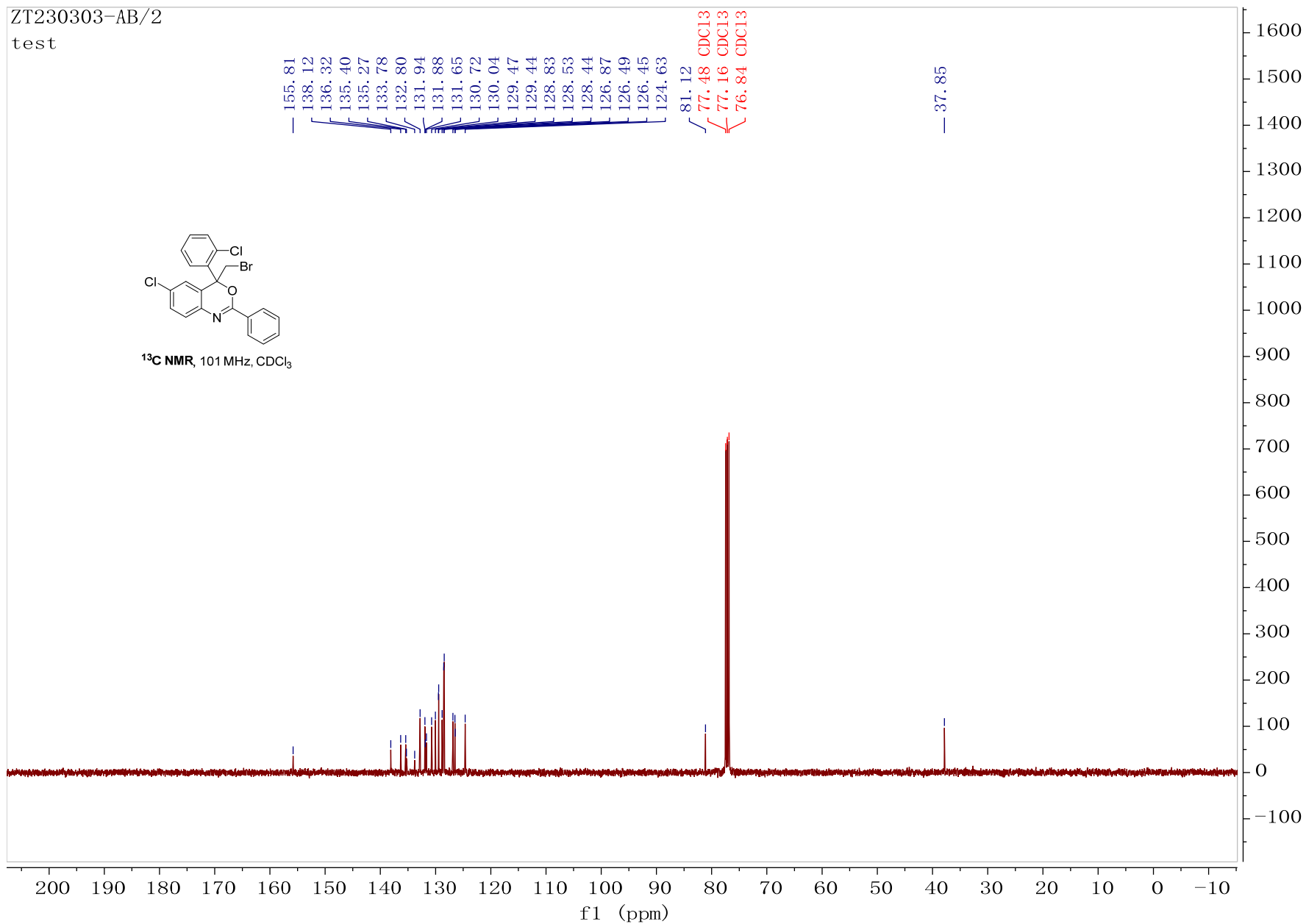
¹³C NMR spectrum of Compound 2w (CDCl₃, 101 MHz)



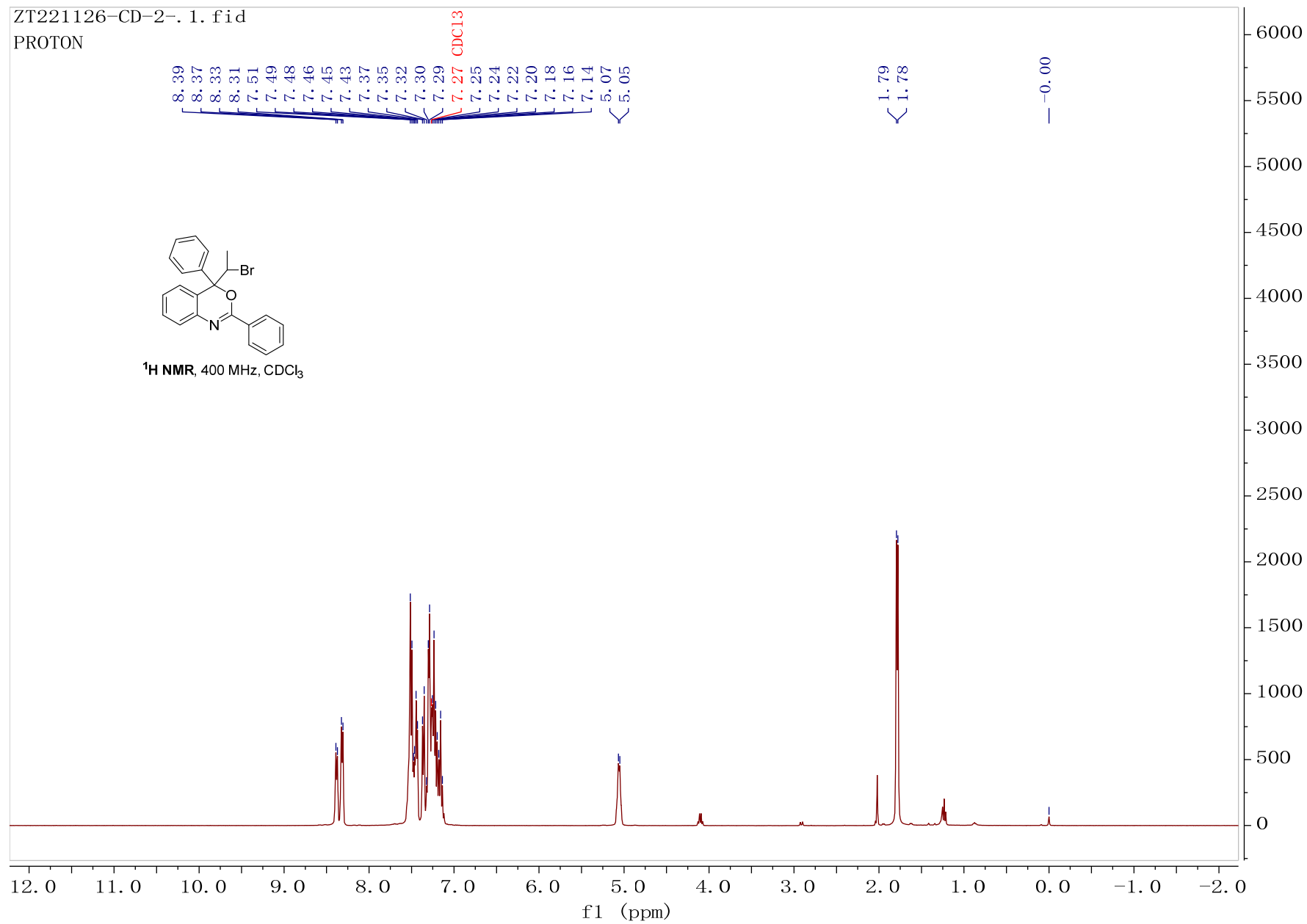
¹H NMR spectrum of Compound 2x (CDCl₃, 400 MHz)



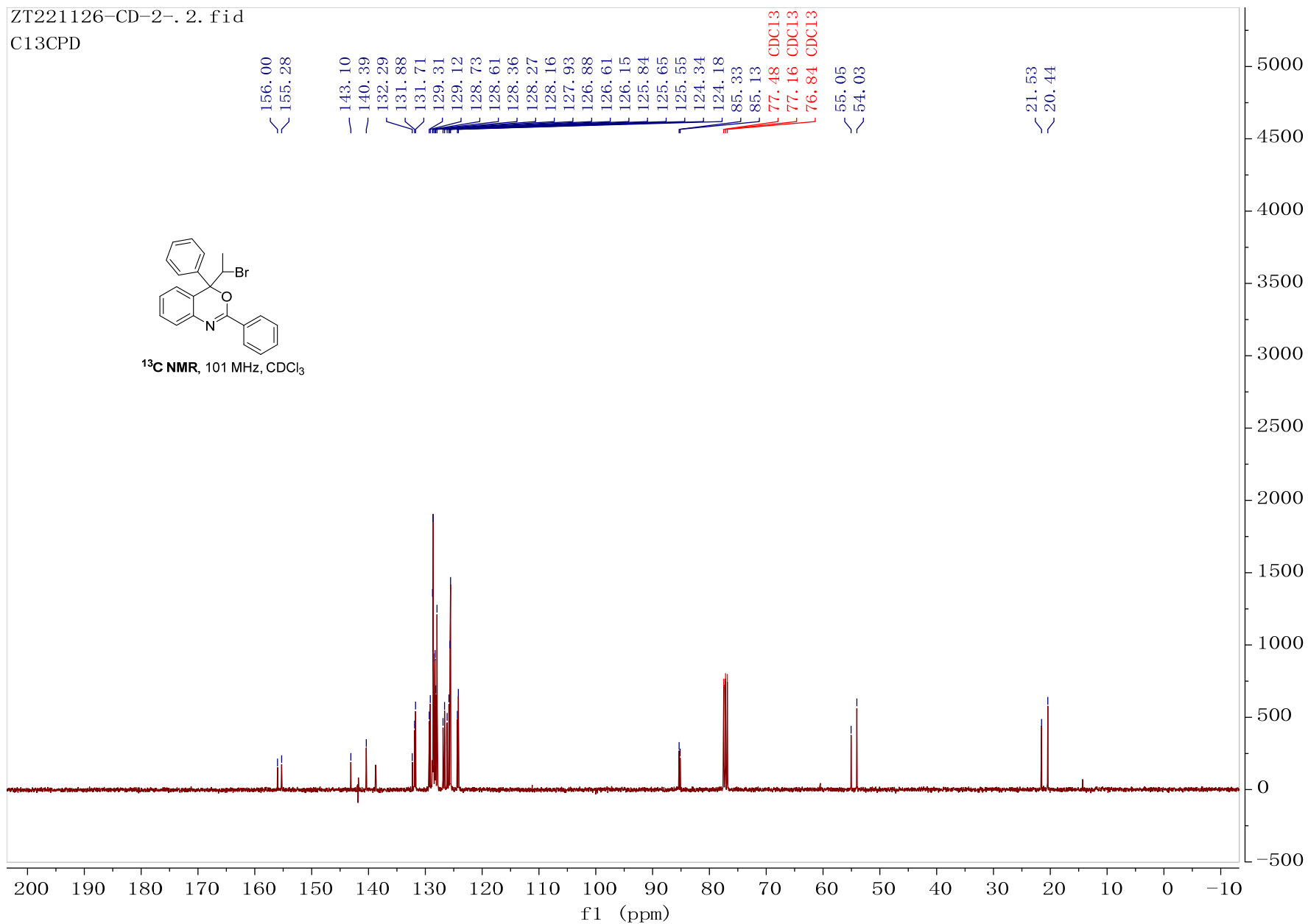
¹³C NMR spectrum of Compound 2x (CDCl₃, 101 MHz)



¹H NMR spectrum of Compound 2y (CDCl₃, 400 MHz)

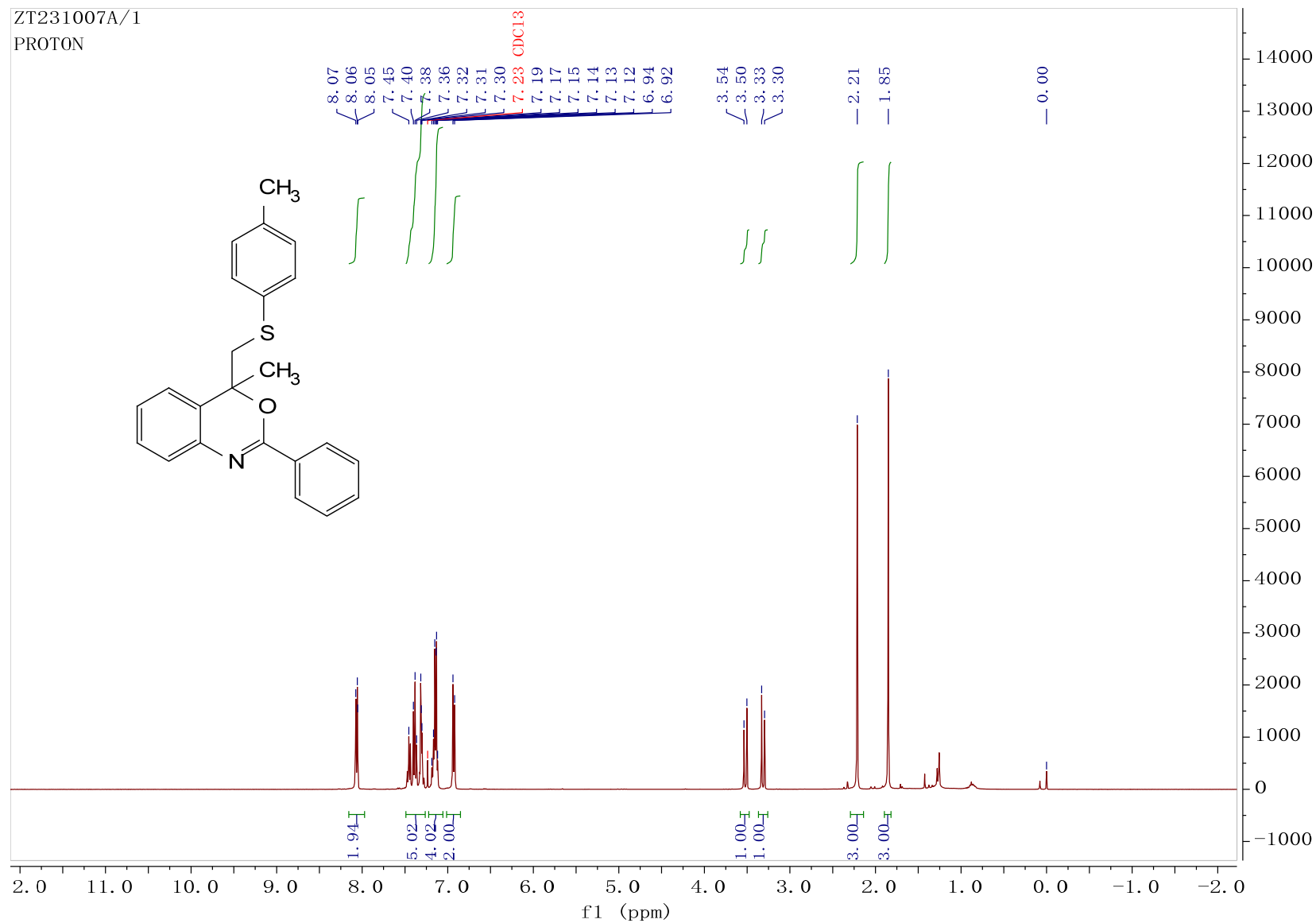


¹³C NMR spectrum of Compound 2y (CDCl₃, 101 MHz)

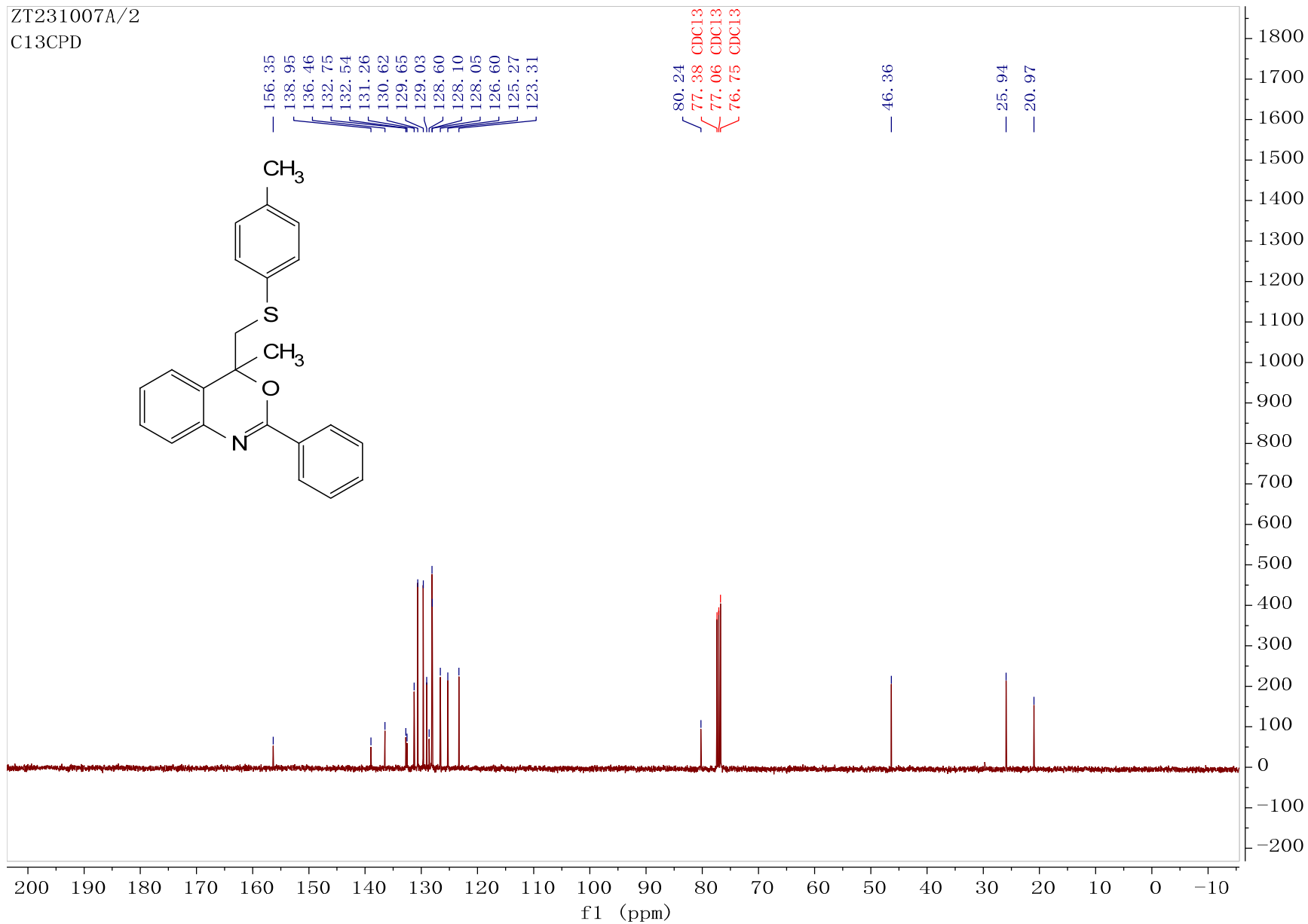


6. Spectroscopic data for compound 4

^1H NMR spectrum of Compound 4 (CDCl_3 , 400 MHz)

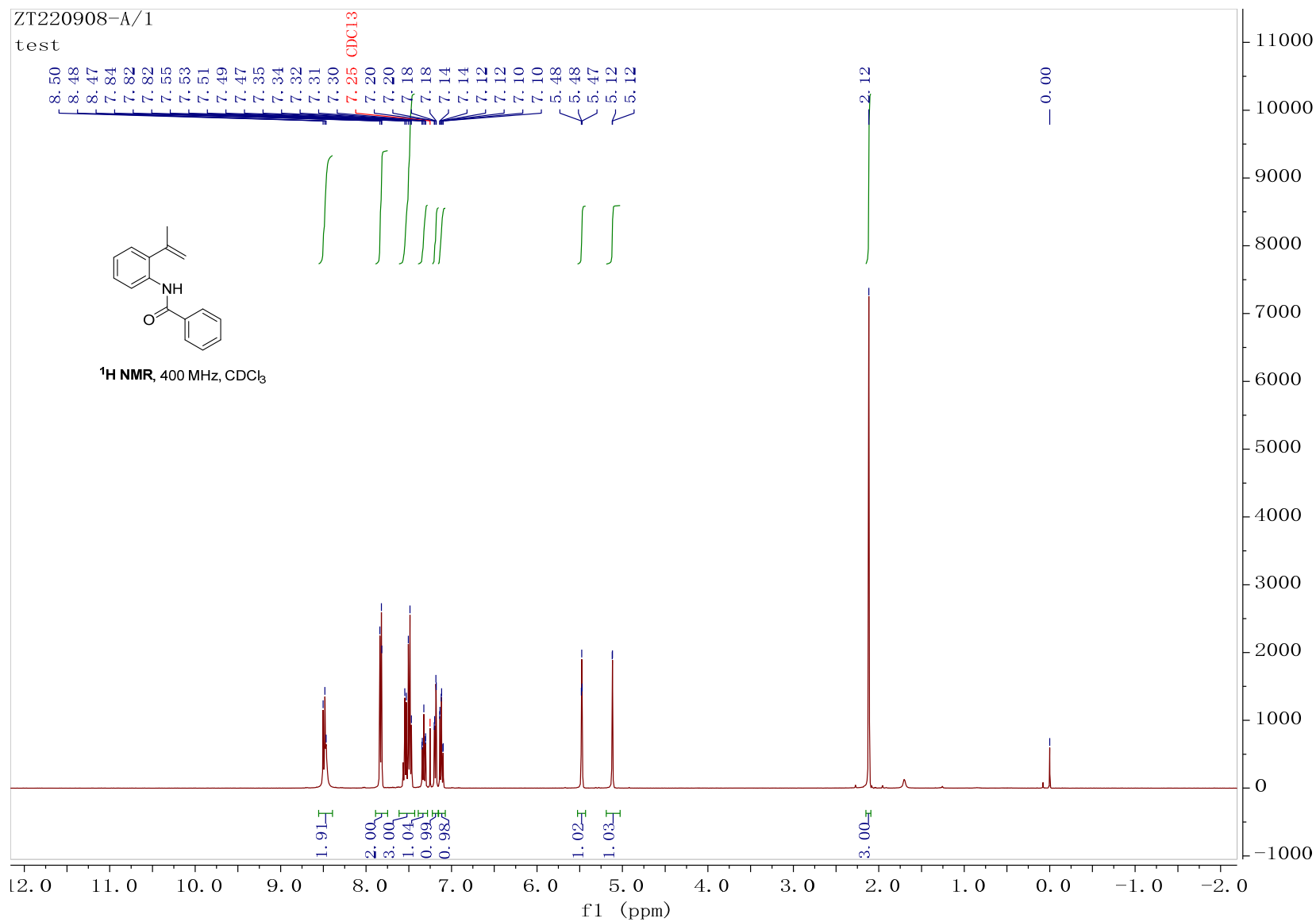


¹³C NMR spectrum of Compound 4 (CDCl₃, 101 MHz)

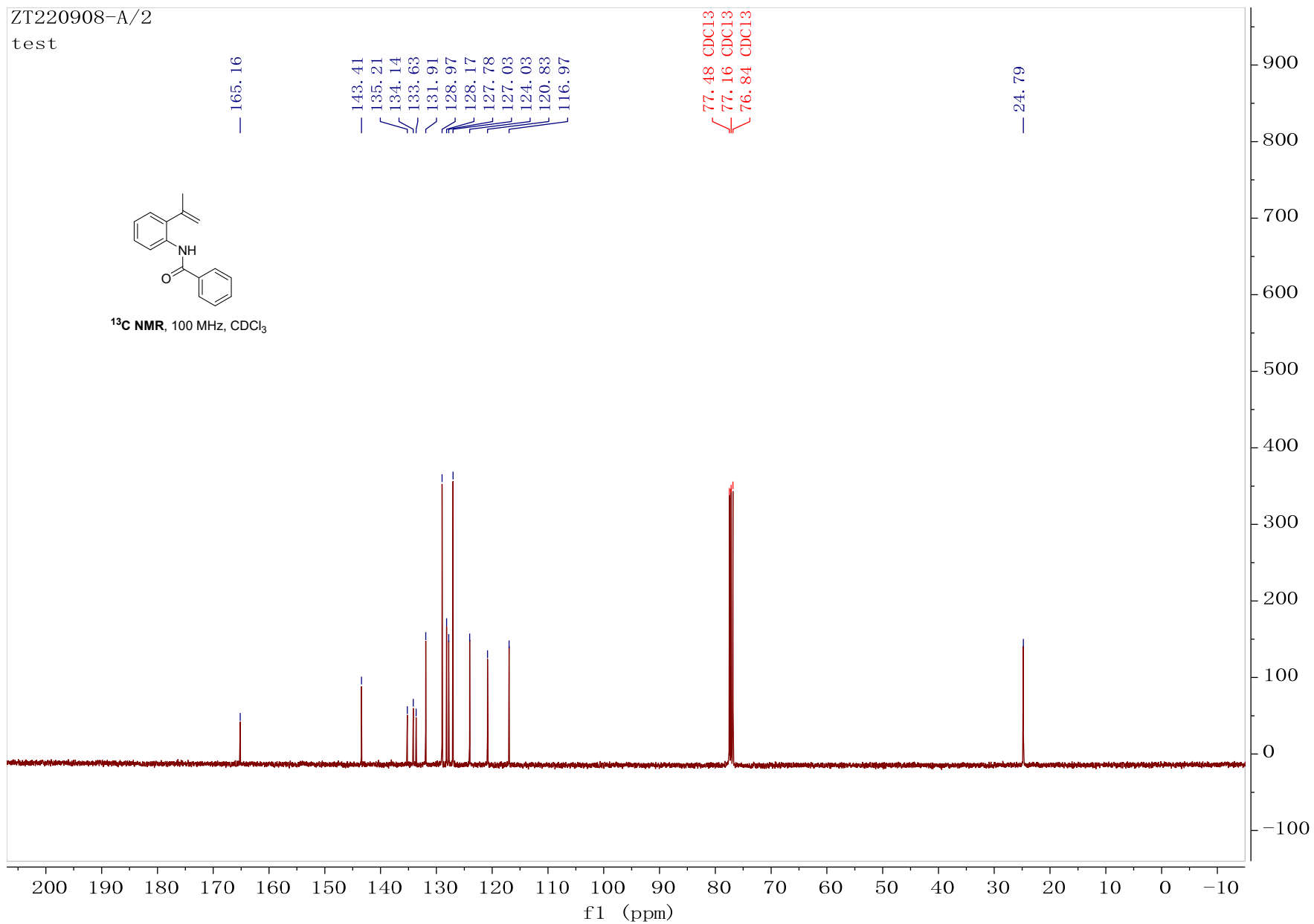


7. Spectroscopic data for substrate 1

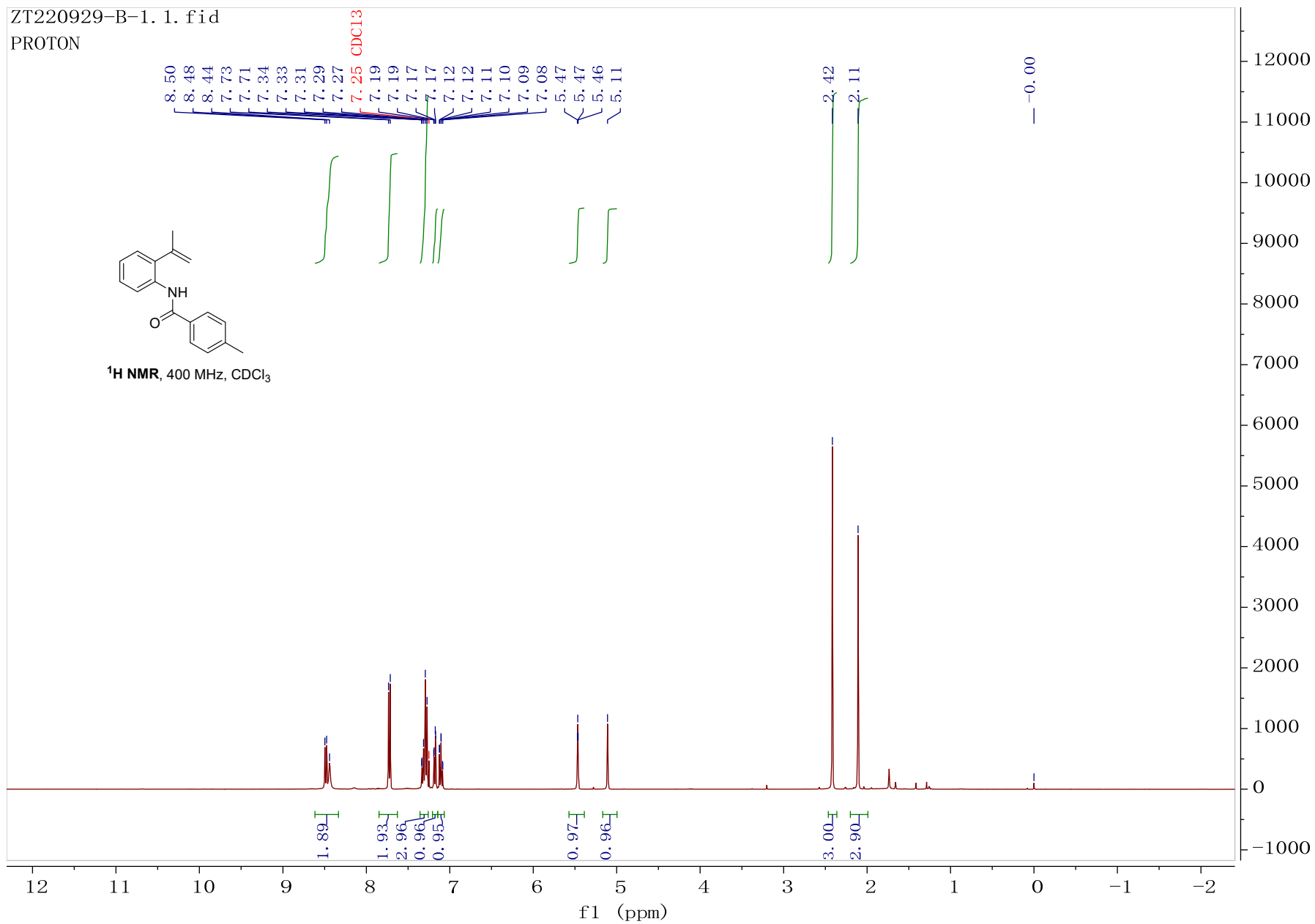
^1H NMR spectrum of Compound 1a (CDCl_3 , 400 MHz)



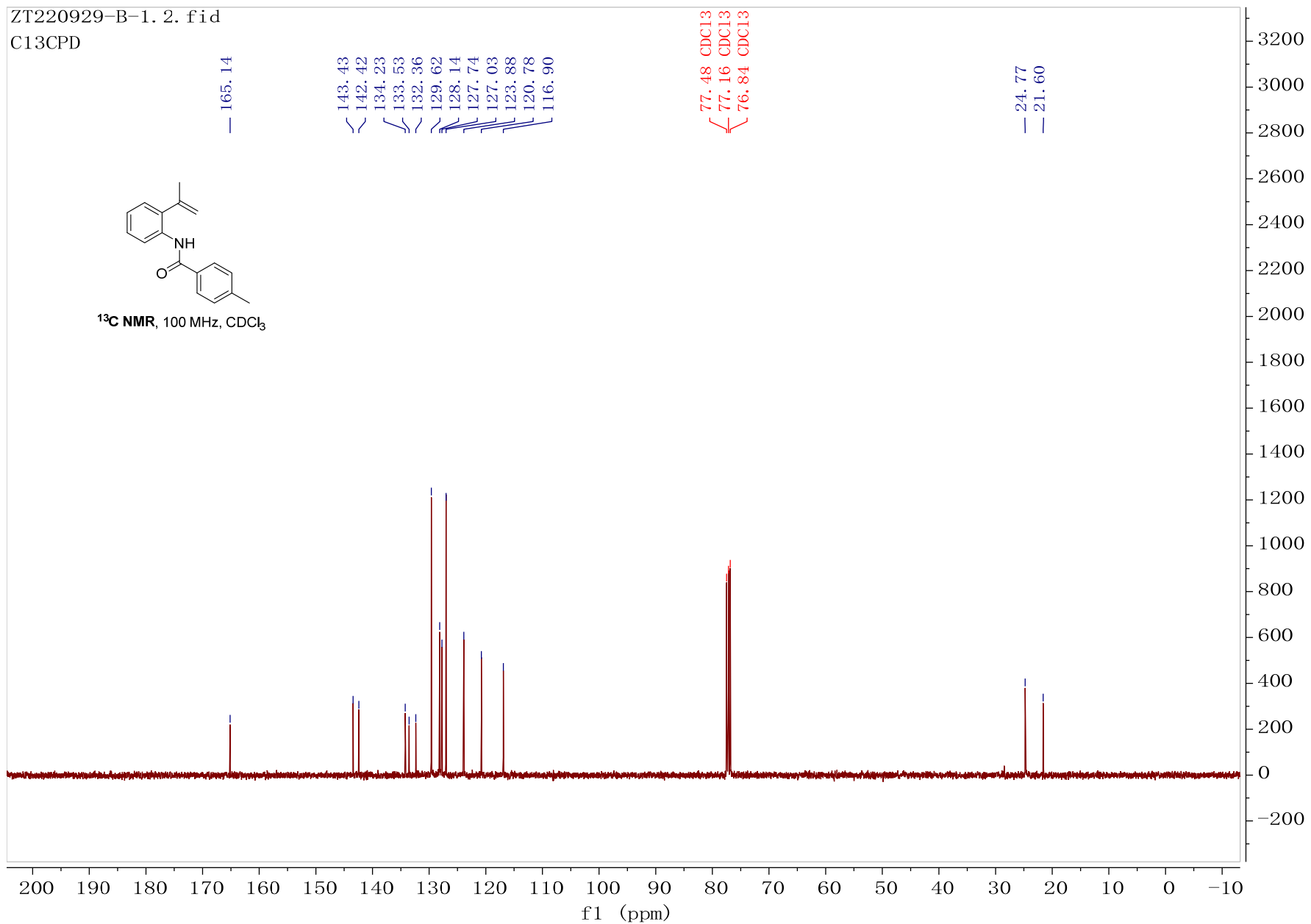
¹³C NMR spectrum of Compound 1a (CDCl₃, 101 MHz)



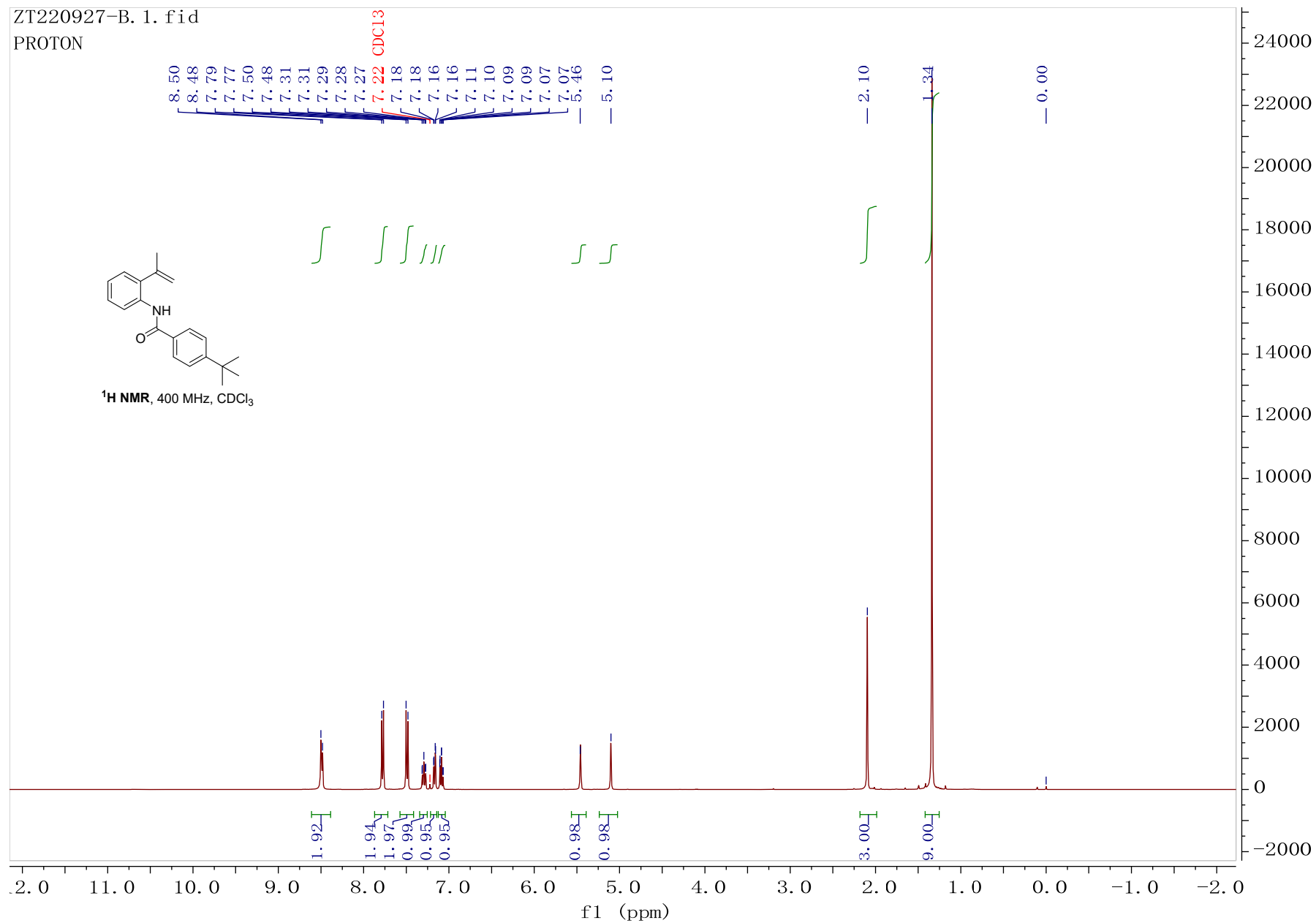
¹H NMR spectrum of Compound 1b (CDCl₃, 400 MHz)



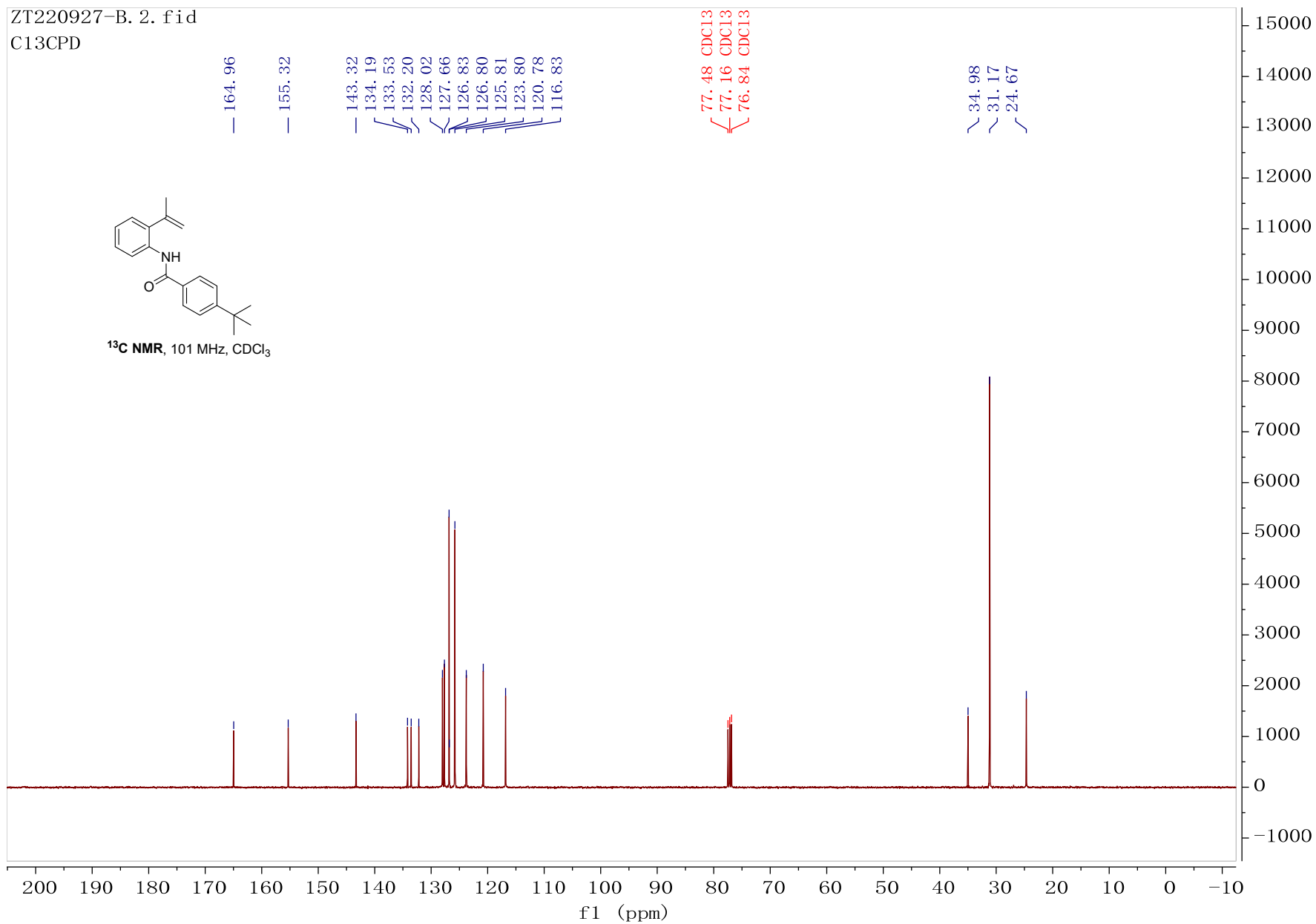
¹³C NMR spectrum of Compound 1b (CDCl₃, 101 MHz)



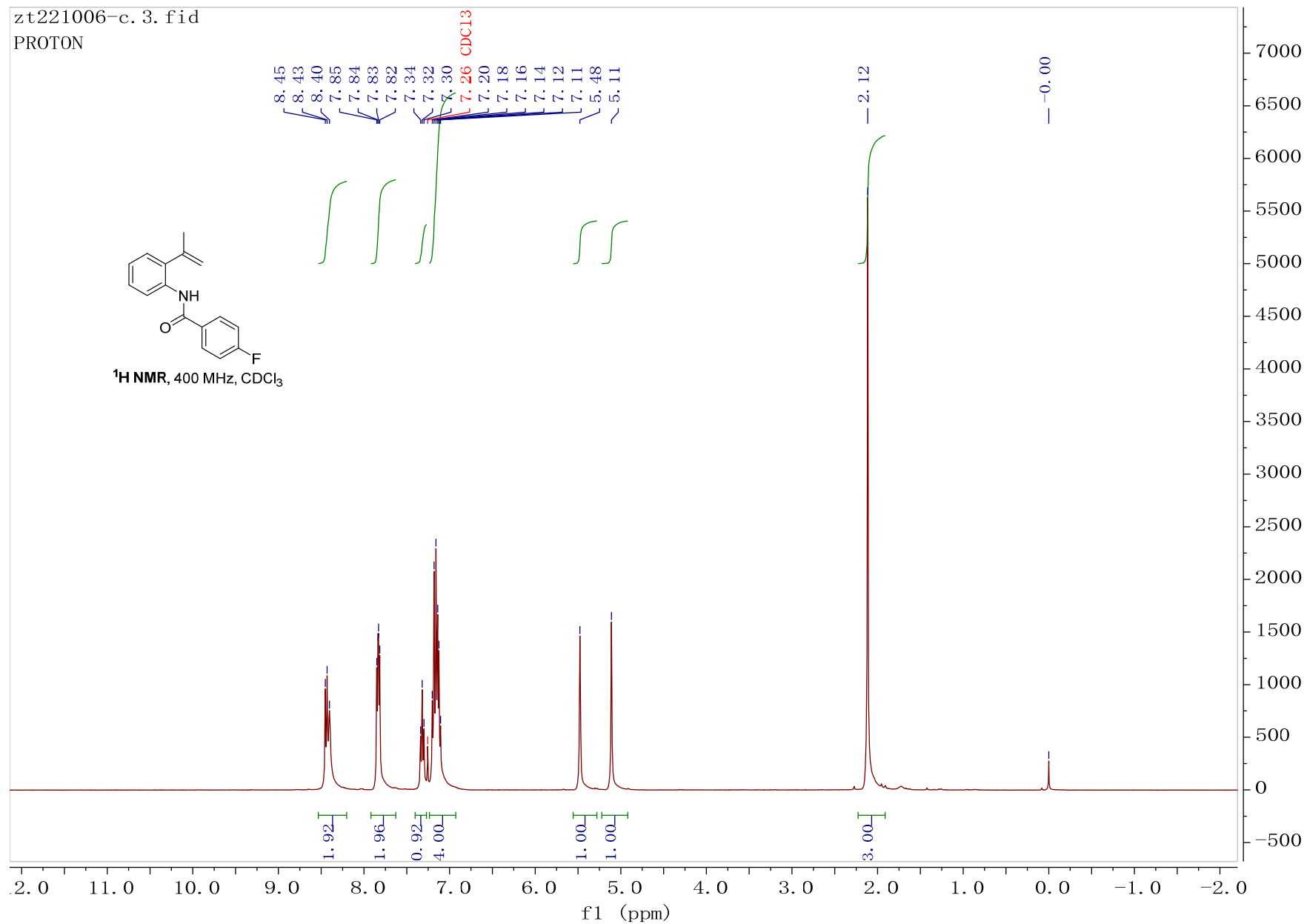
¹H NMR spectrum of Compound 1c (CDCl₃, 400 MHz)



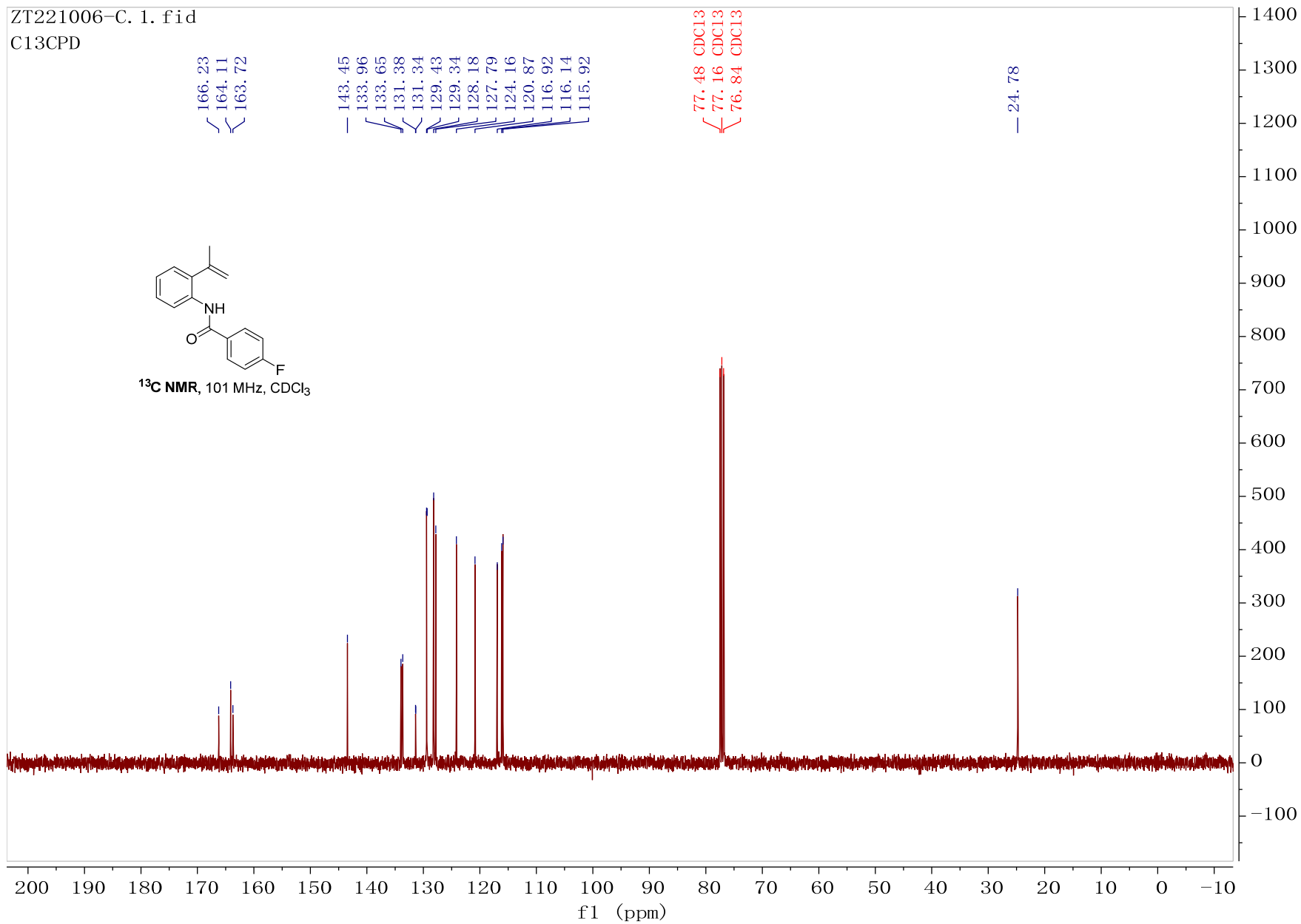
¹³C NMR spectrum of Compound 1c (CDCl₃, 101 MHz)



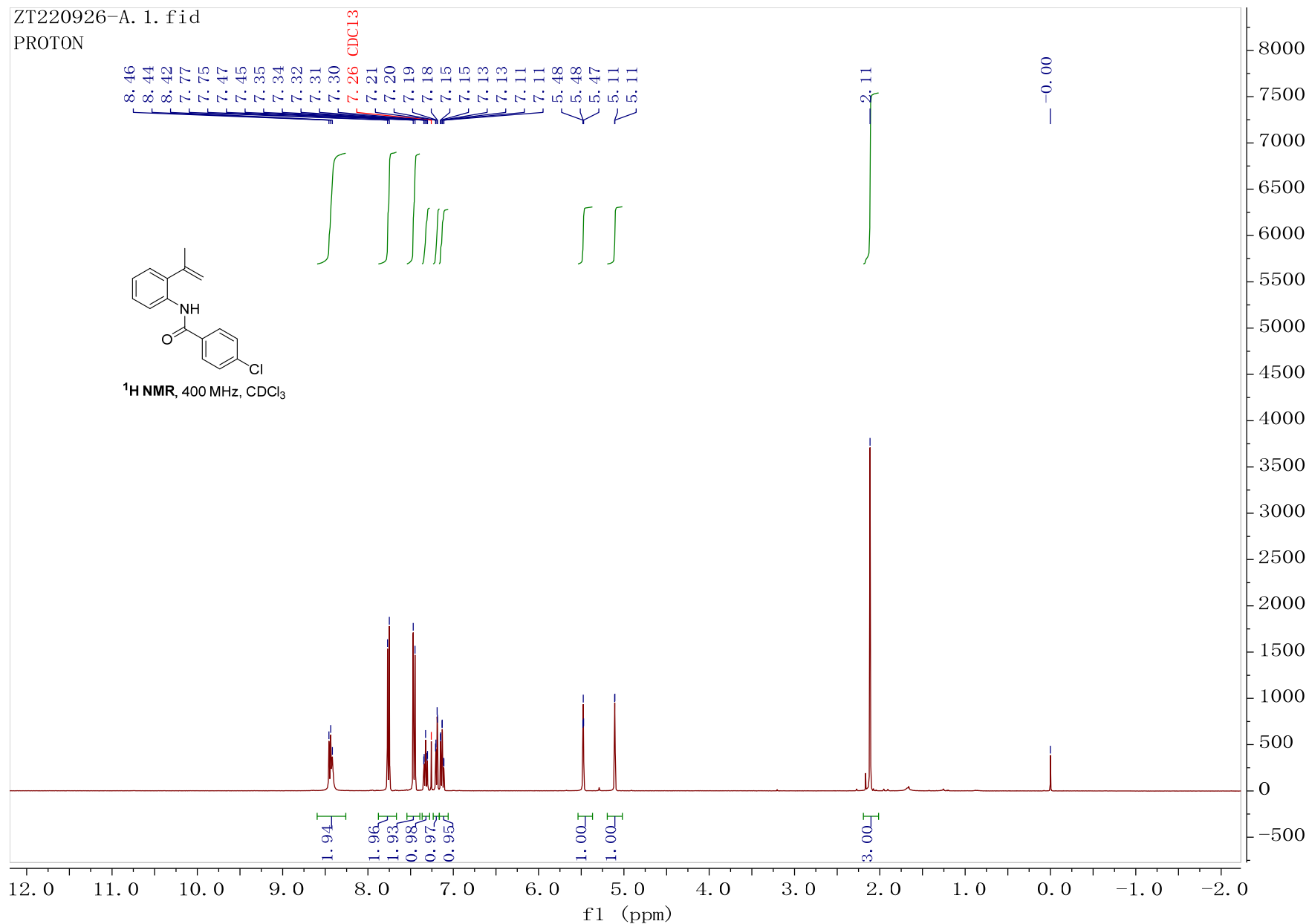
¹H NMR spectrum of Compound 1d (CDCl₃, 400 MHz)



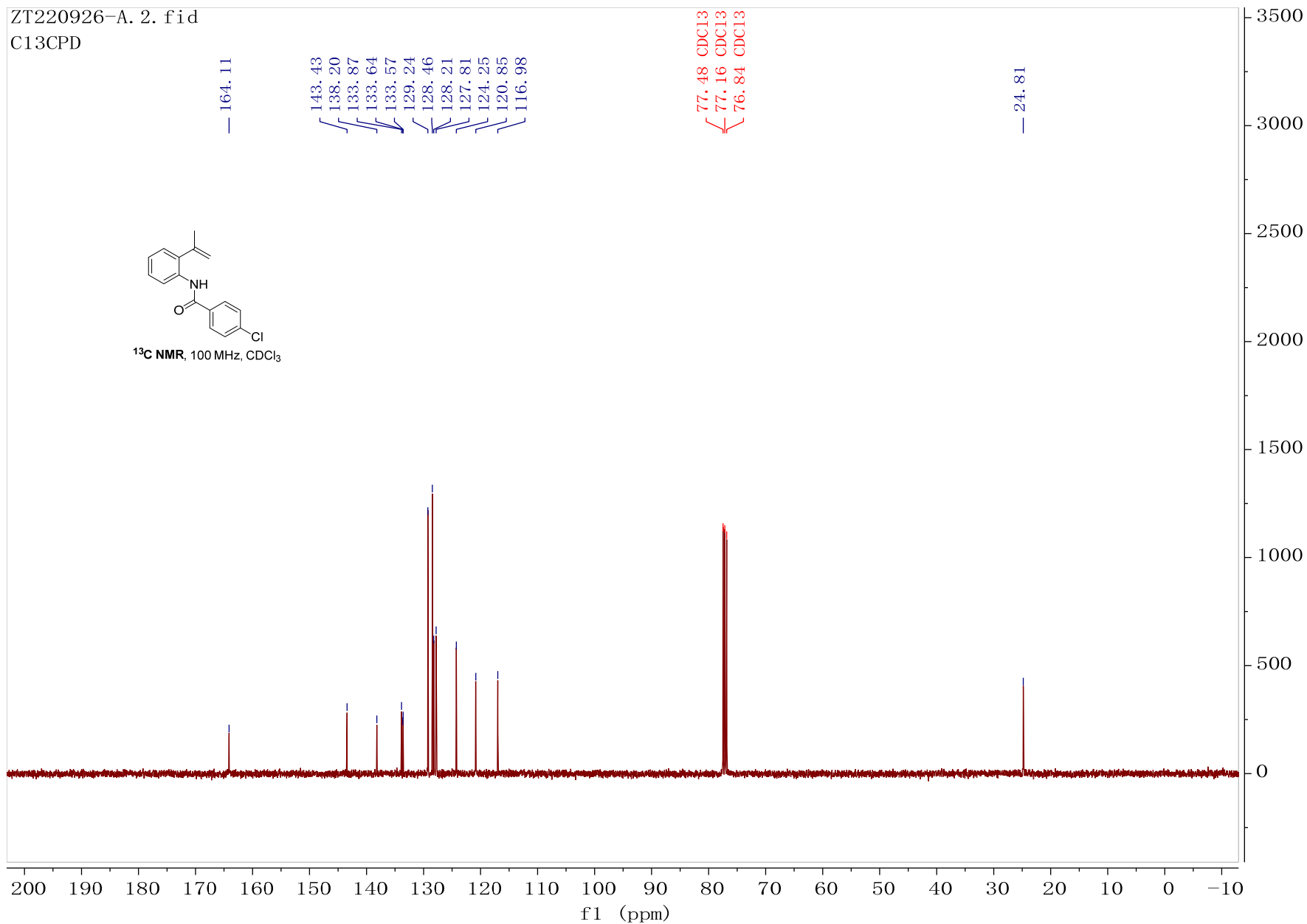
¹³C NMR spectrum of Compound 1d (CDCl₃, 101 MHz)



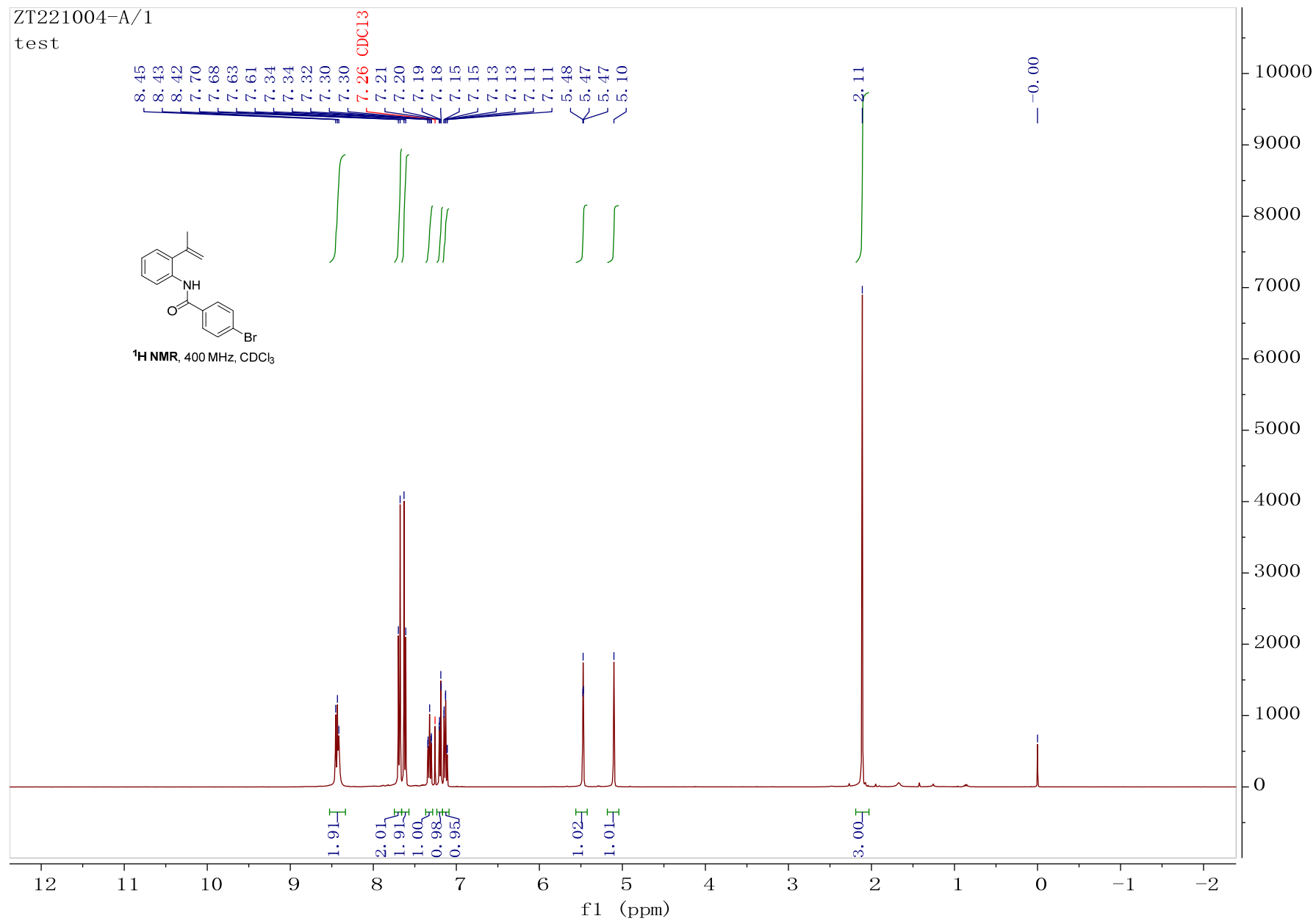
¹H NMR spectrum of Compound 1e (CDCl₃, 400 MHz)



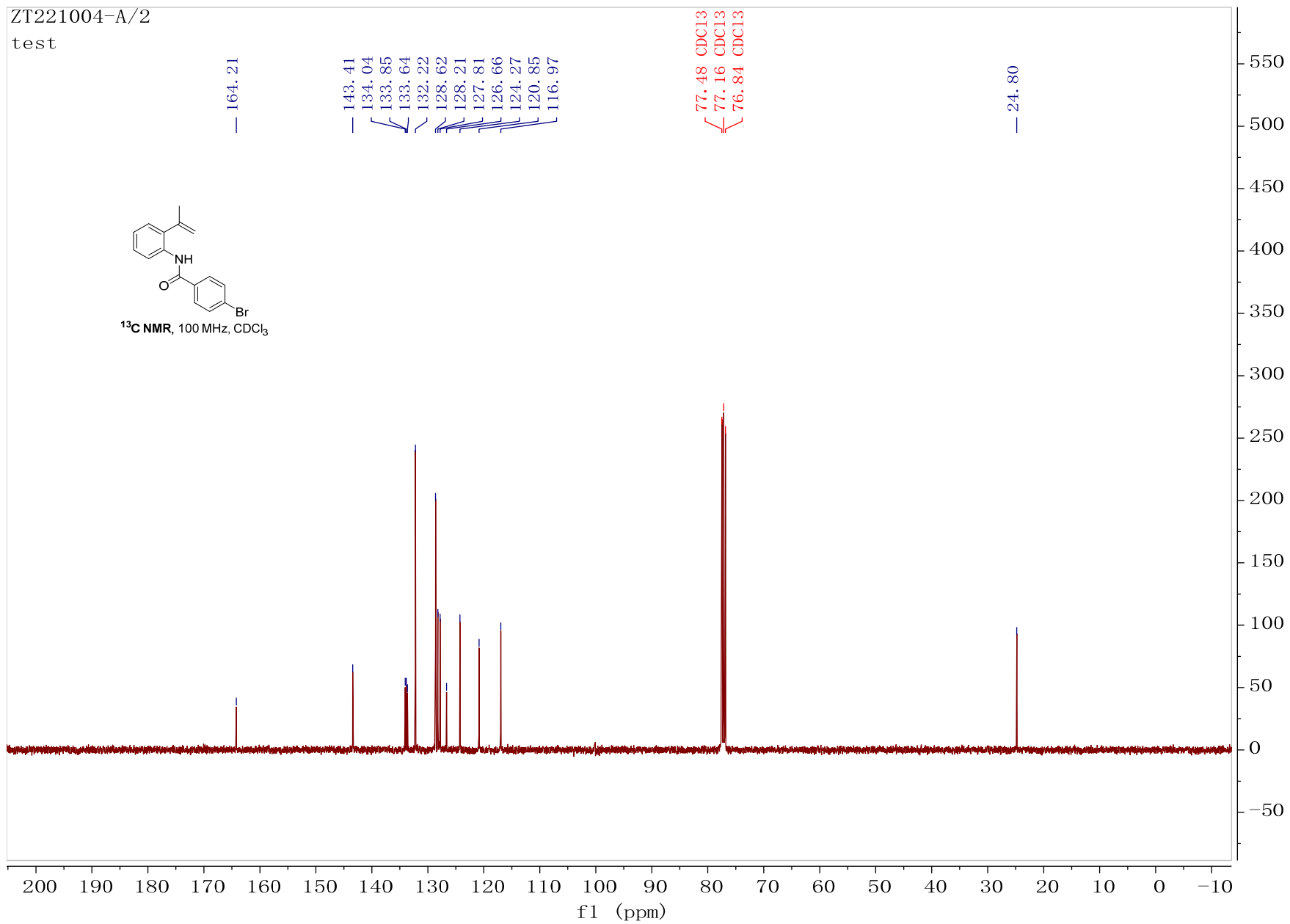
¹³C NMR spectrum of Compound 1e (CDCl₃, 101 MHz)



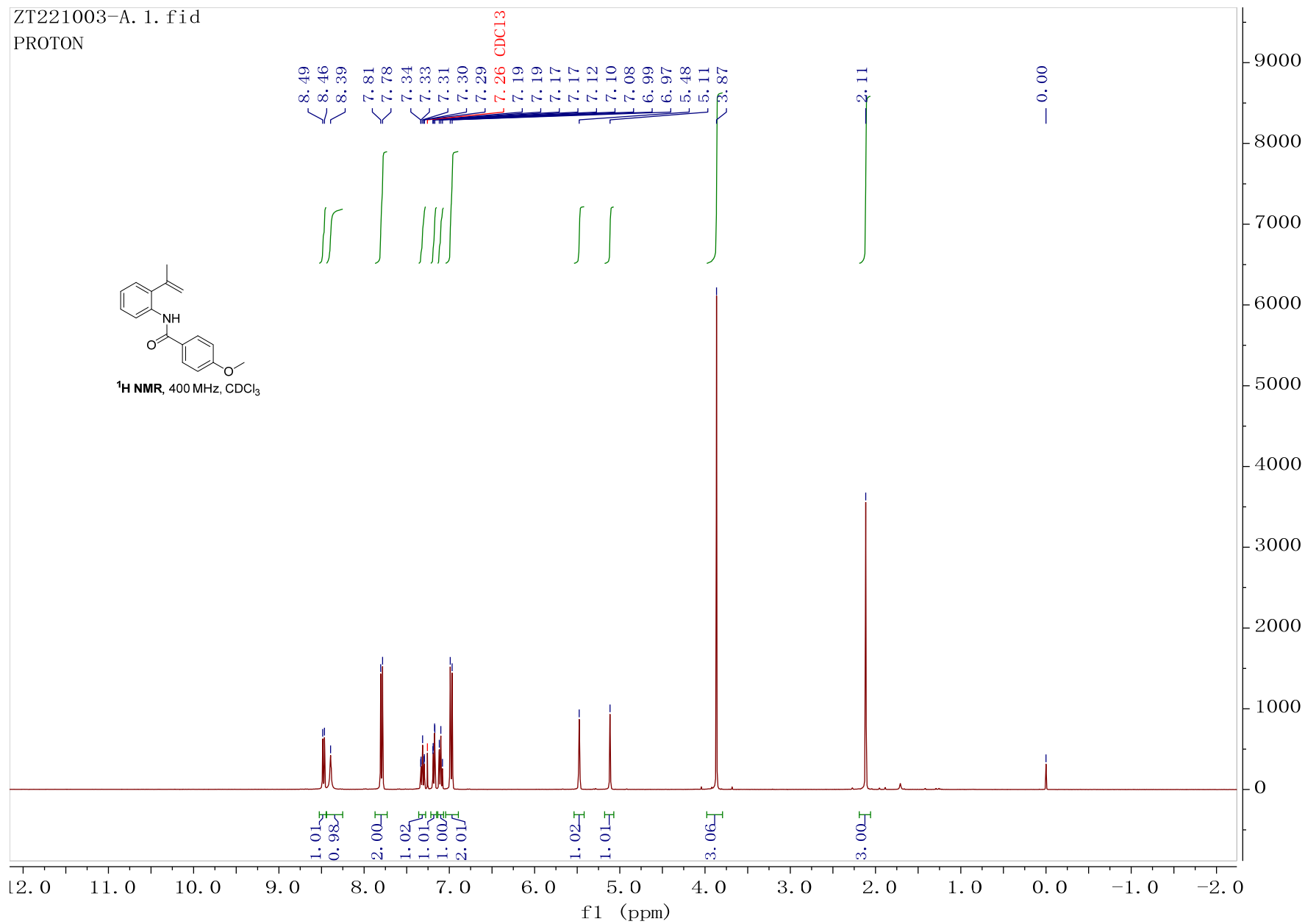
¹H NMR spectrum of Compound 1f (CDCl₃, 400 MHz)



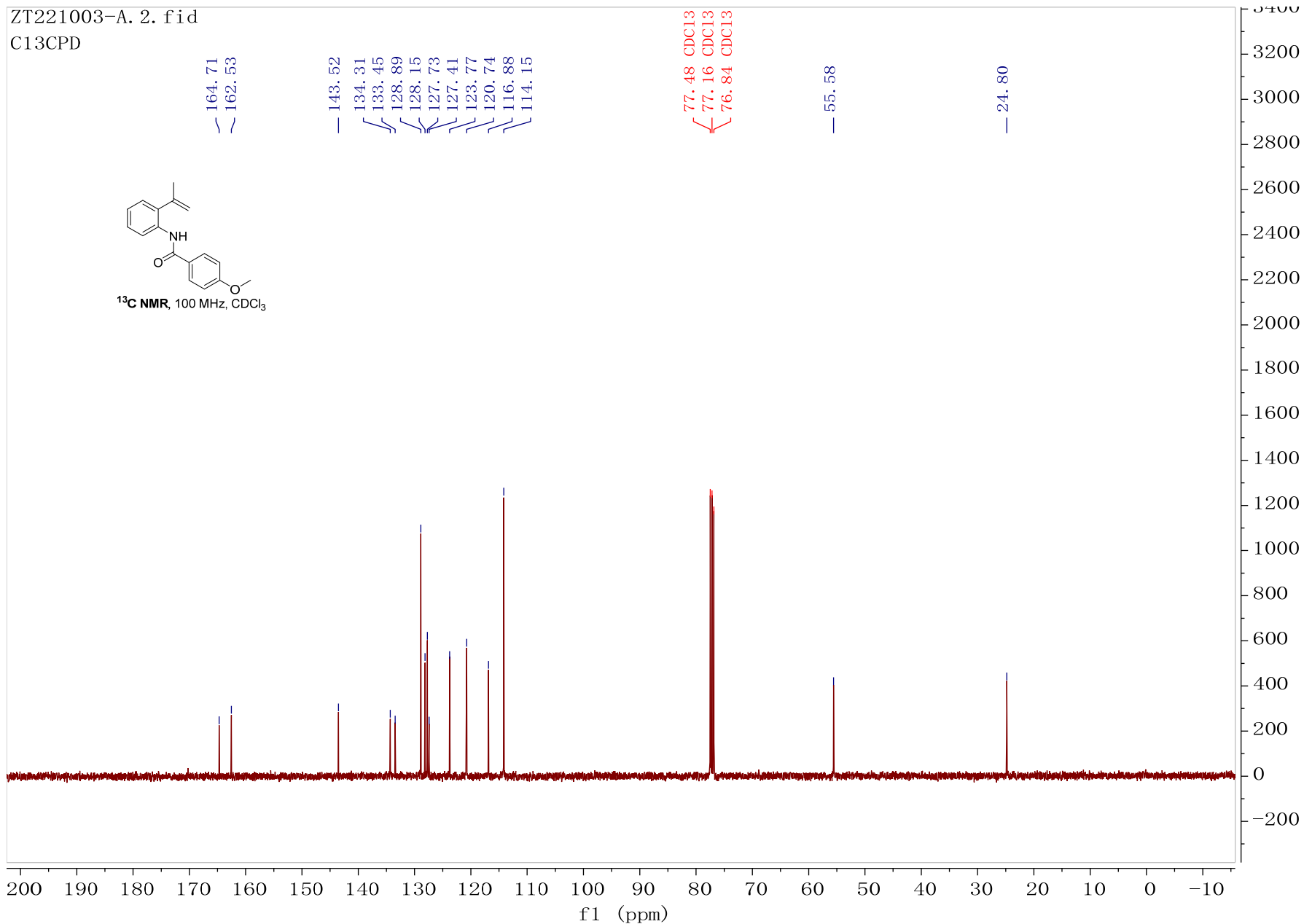
¹³C NMR spectrum of Compound 1f (CDCl₃, 101 MHz)



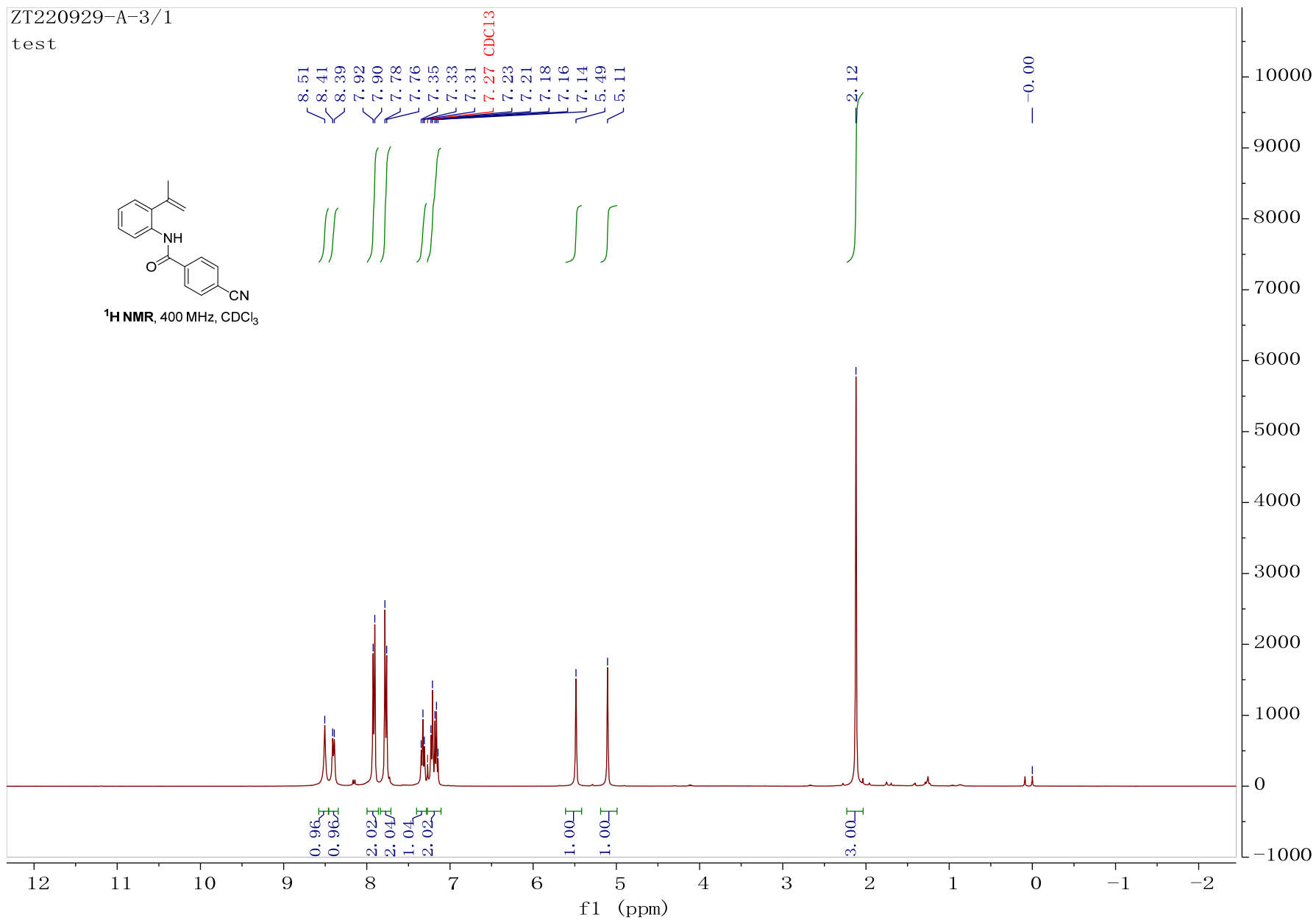
¹H NMR spectrum of Compound 1g (CDCl₃, 400 MHz)



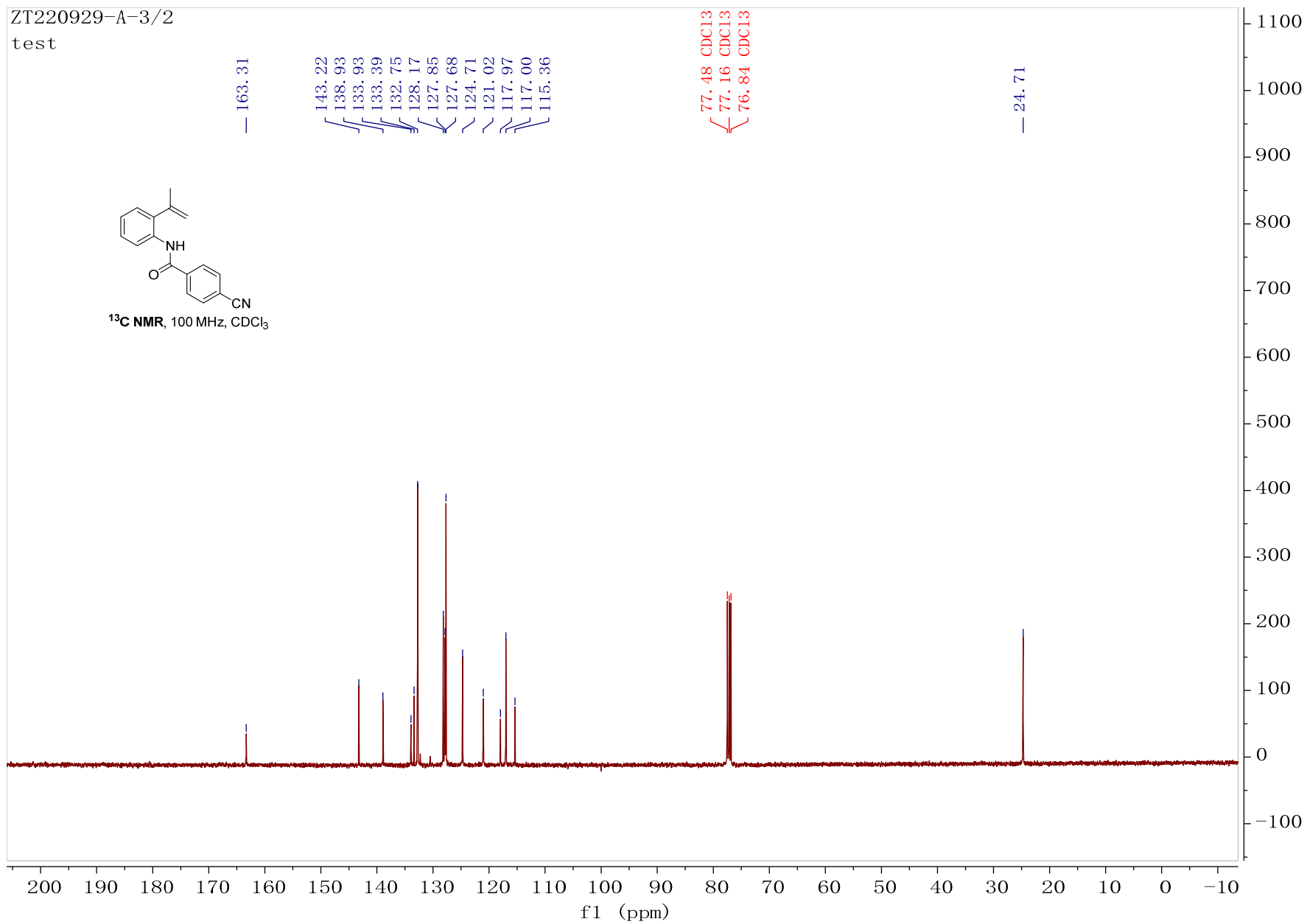
¹³C NMR spectrum of Compound 1g (CDCl₃, 101 MHz)



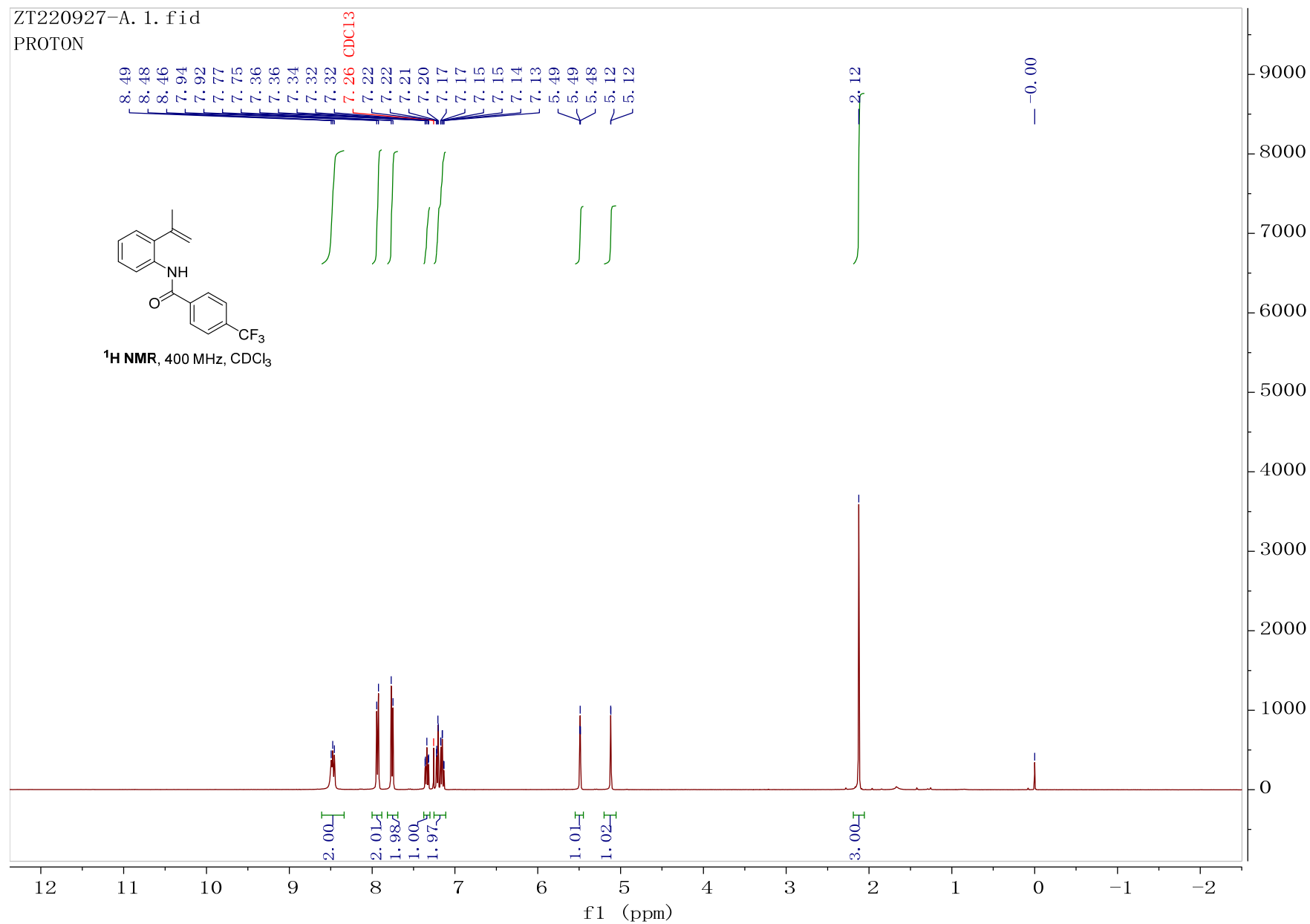
¹H NMR spectrum of Compound 1h (CDCl₃, 400 MHz)



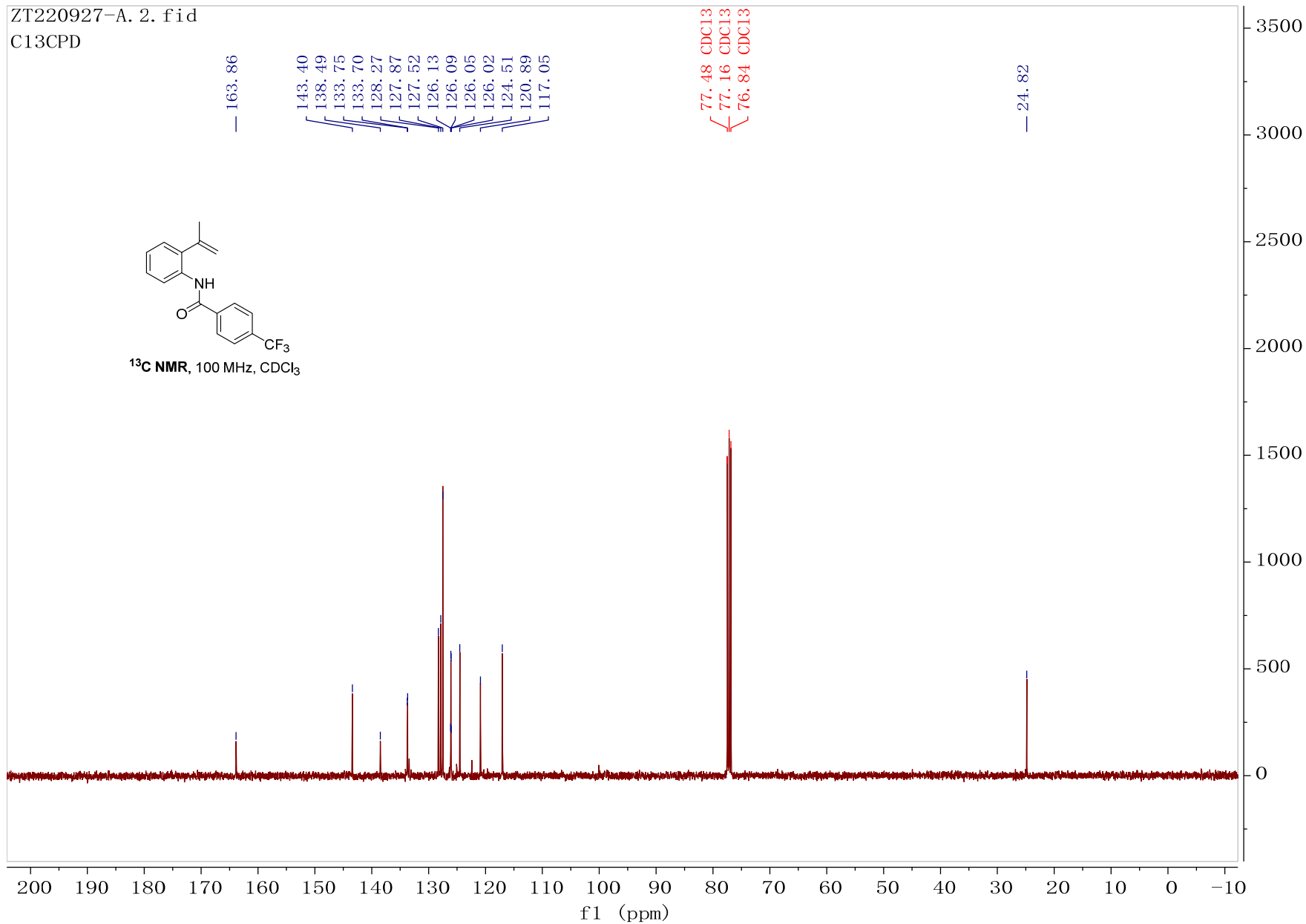
¹³C NMR spectrum of Compound 1h (CDCl₃, 101 MHz)



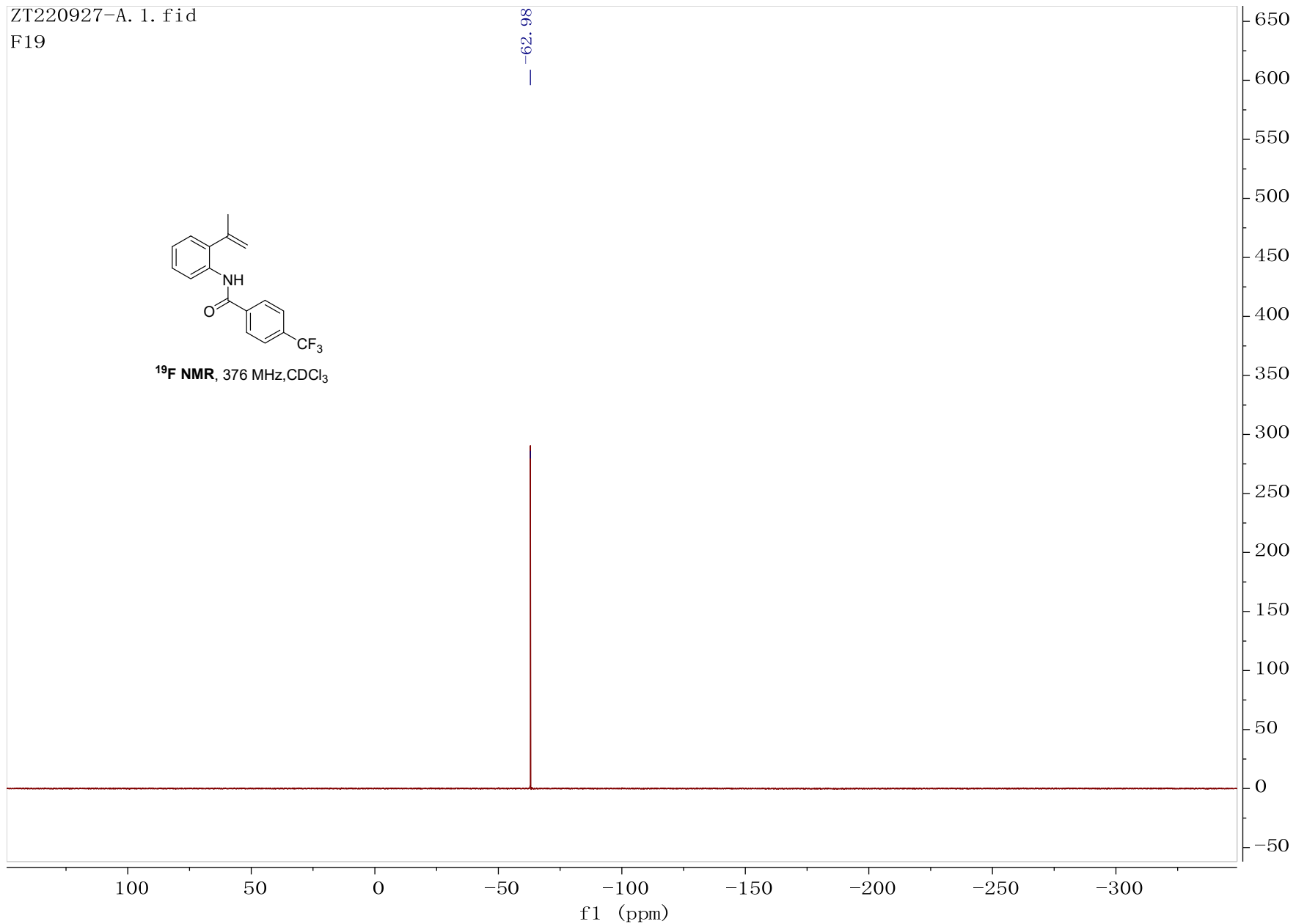
¹H NMR spectrum of Compound 1i (CDCl₃, 400 MHz)



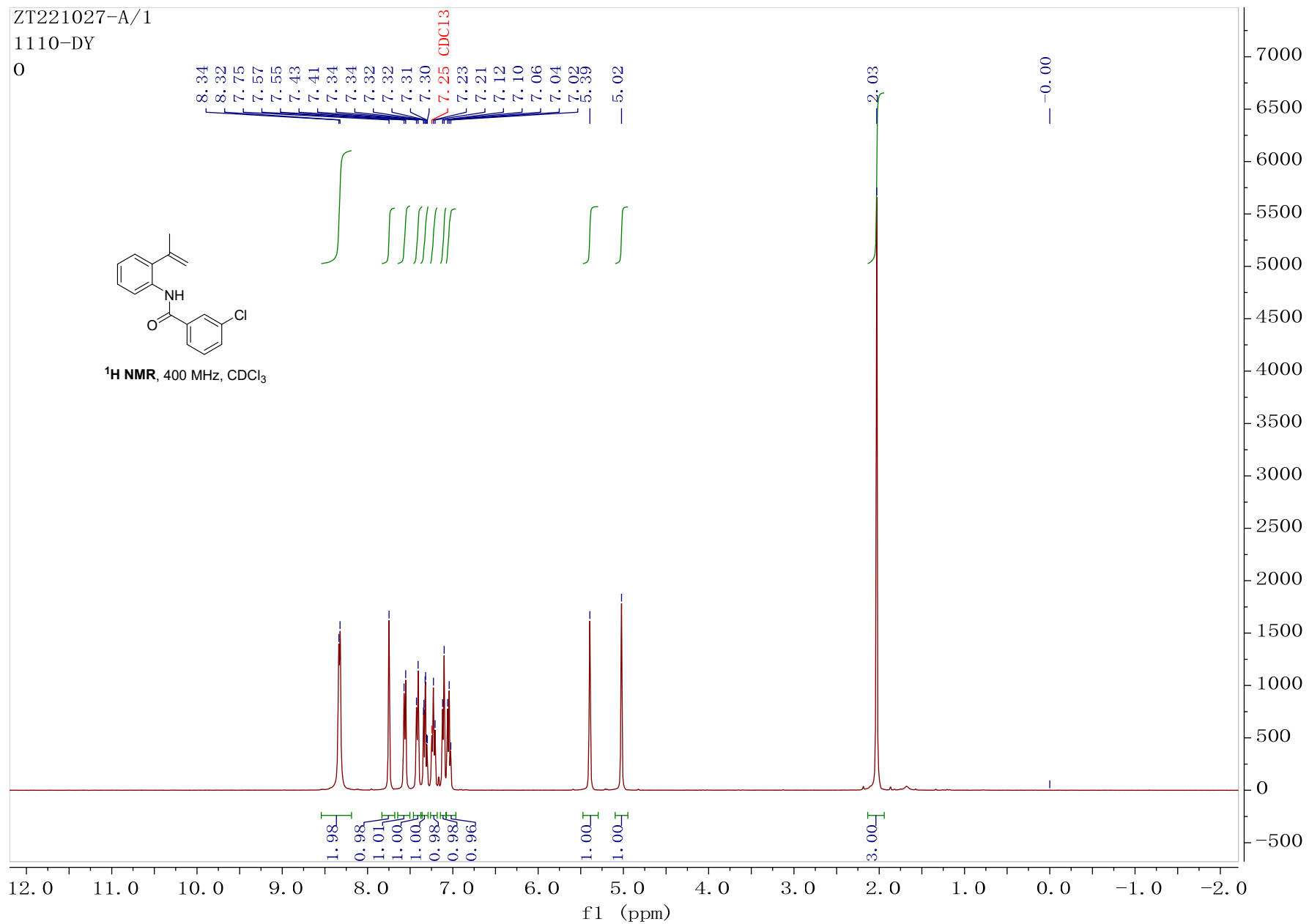
¹³C NMR spectrum of Compound 1i (CDCl₃, 101 MHz)



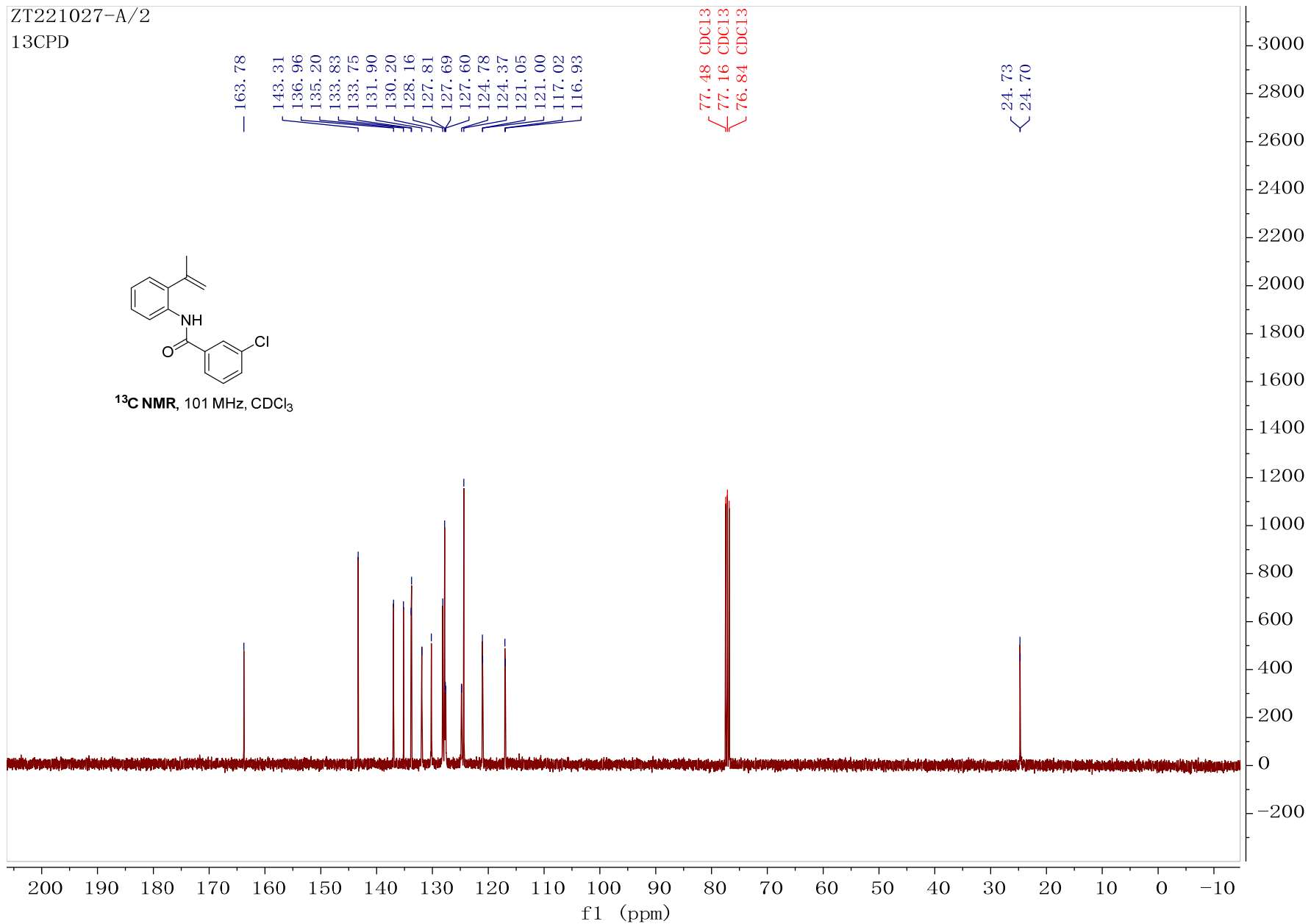
¹⁹F NMR spectrum of Compound 1i (CDCl₃, 376 MHz)



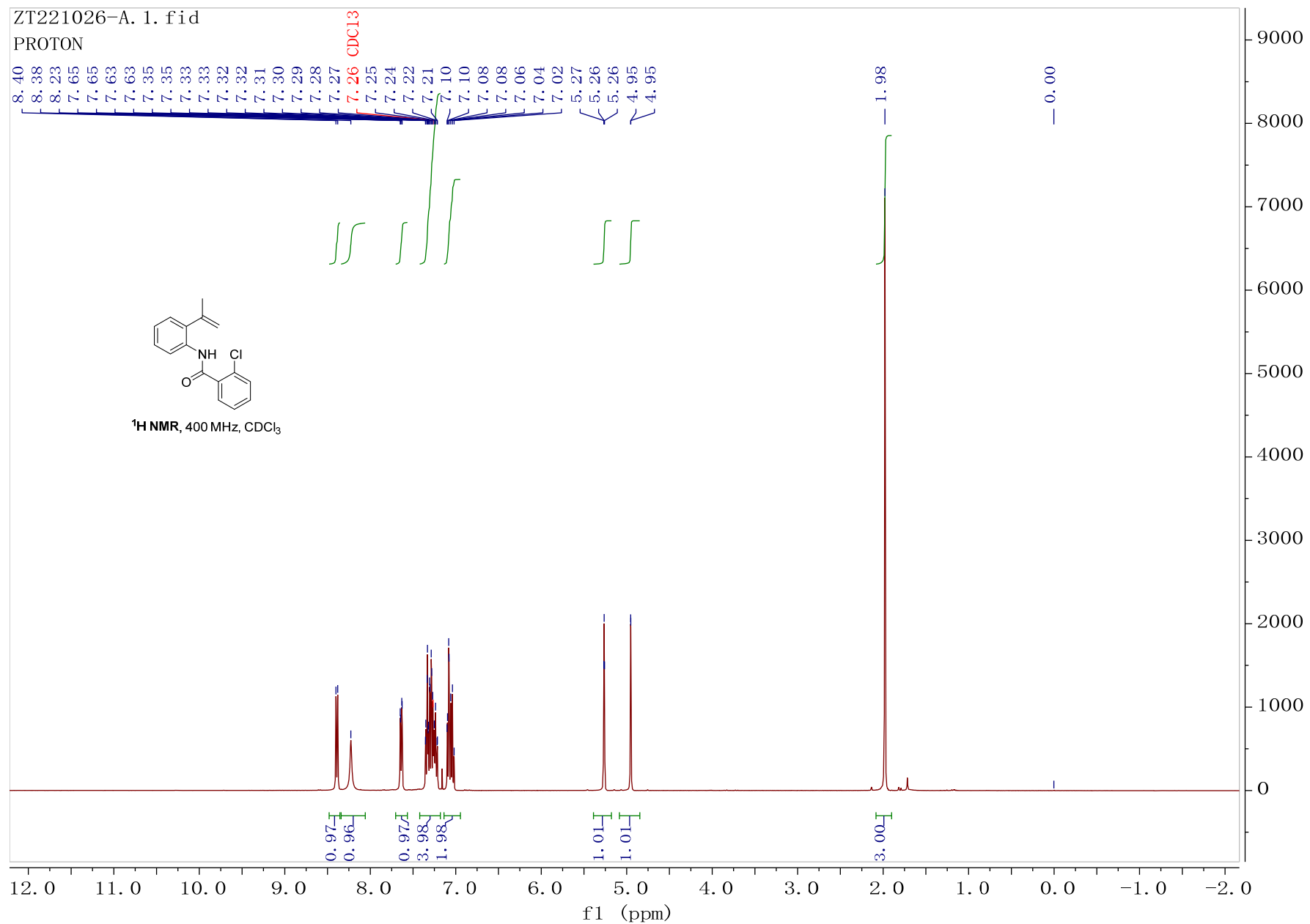
¹H NMR spectrum of Compound 1j (CDCl₃, 400 MHz)



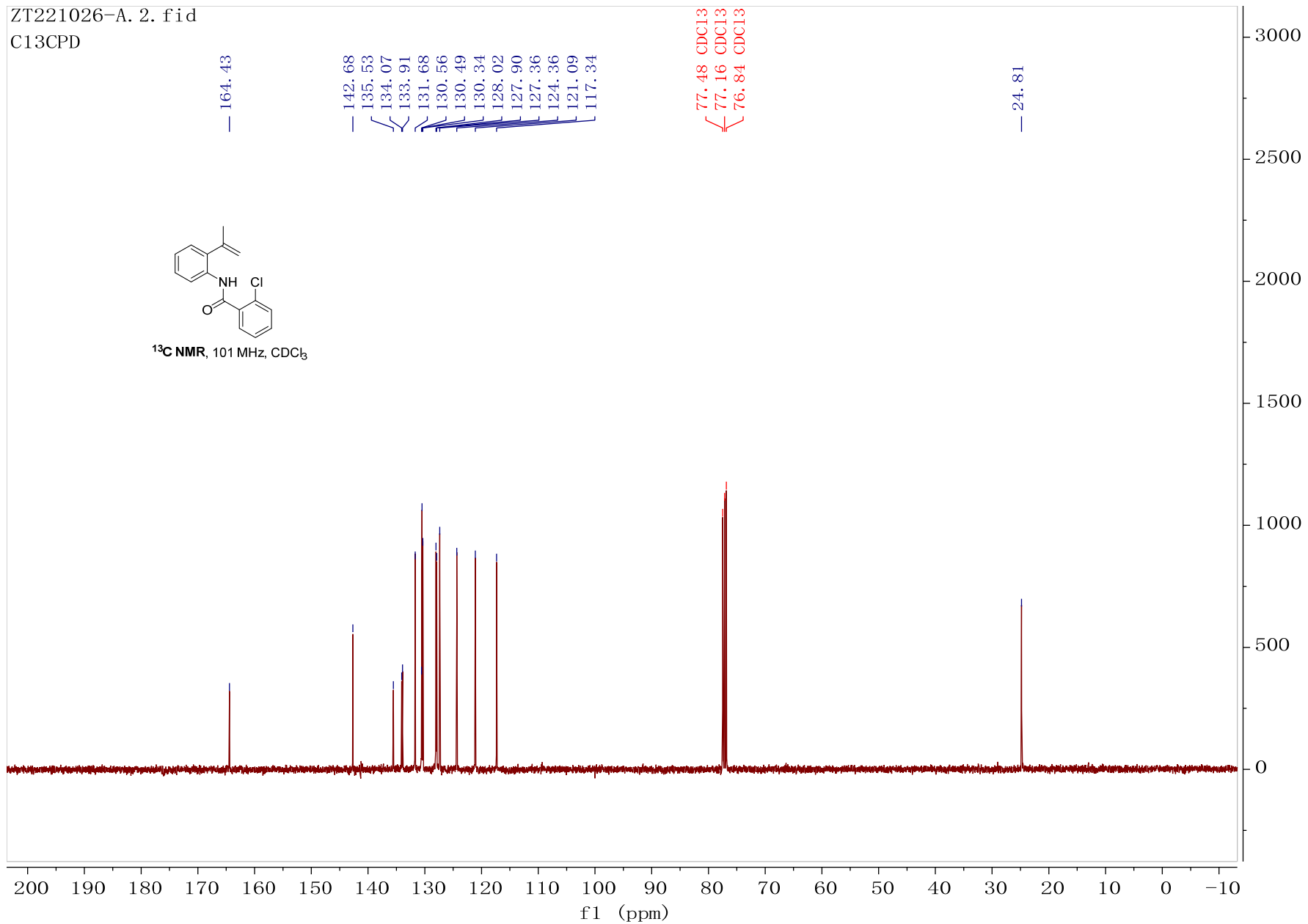
¹³C NMR spectrum of Compound 1j (CDCl₃, 101 MHz)



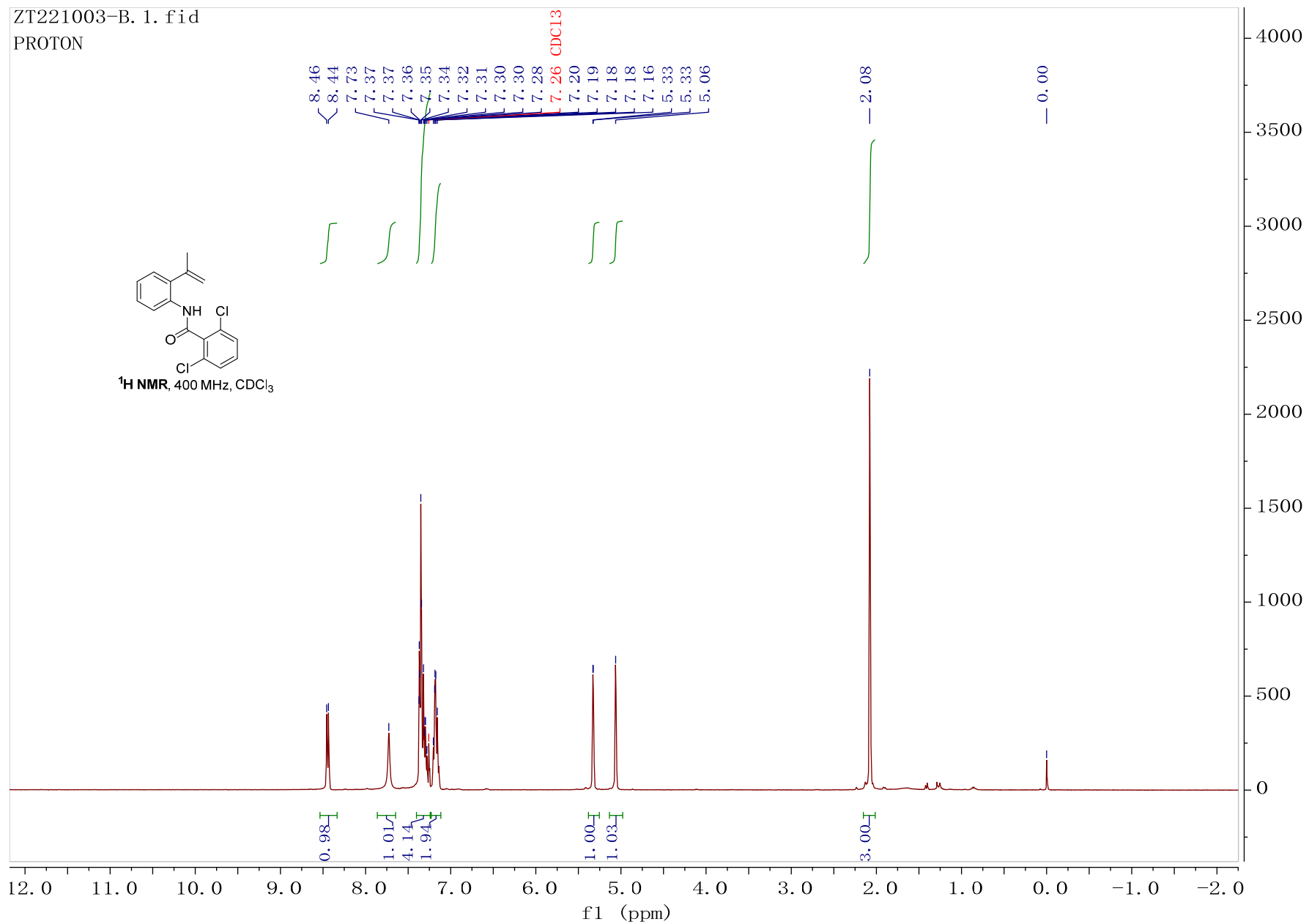
¹H NMR spectrum of Compound 1k (CDCl₃, 400 MHz)



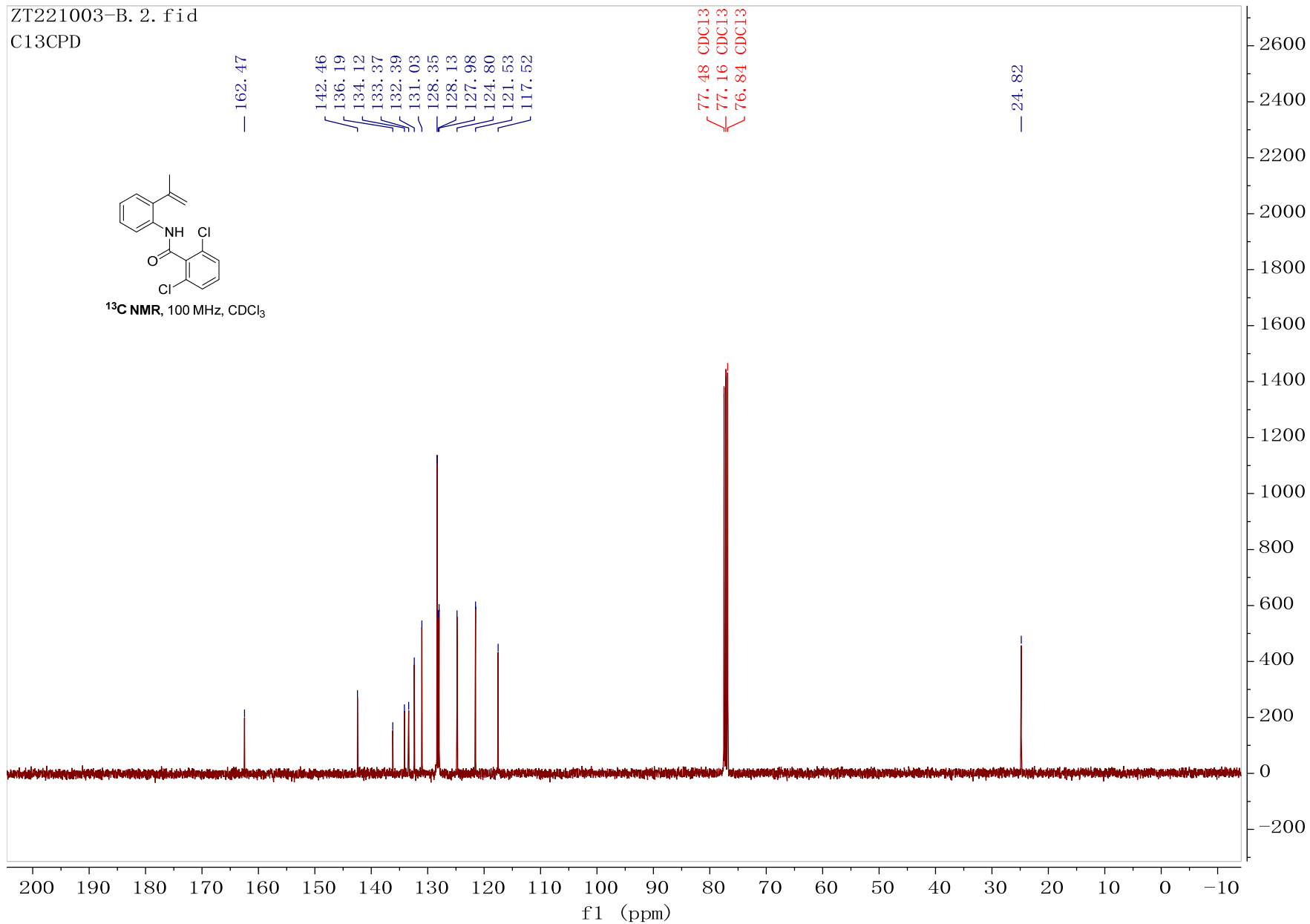
¹³C NMR spectrum of Compound 1k (CDCl₃, 101 MHz)



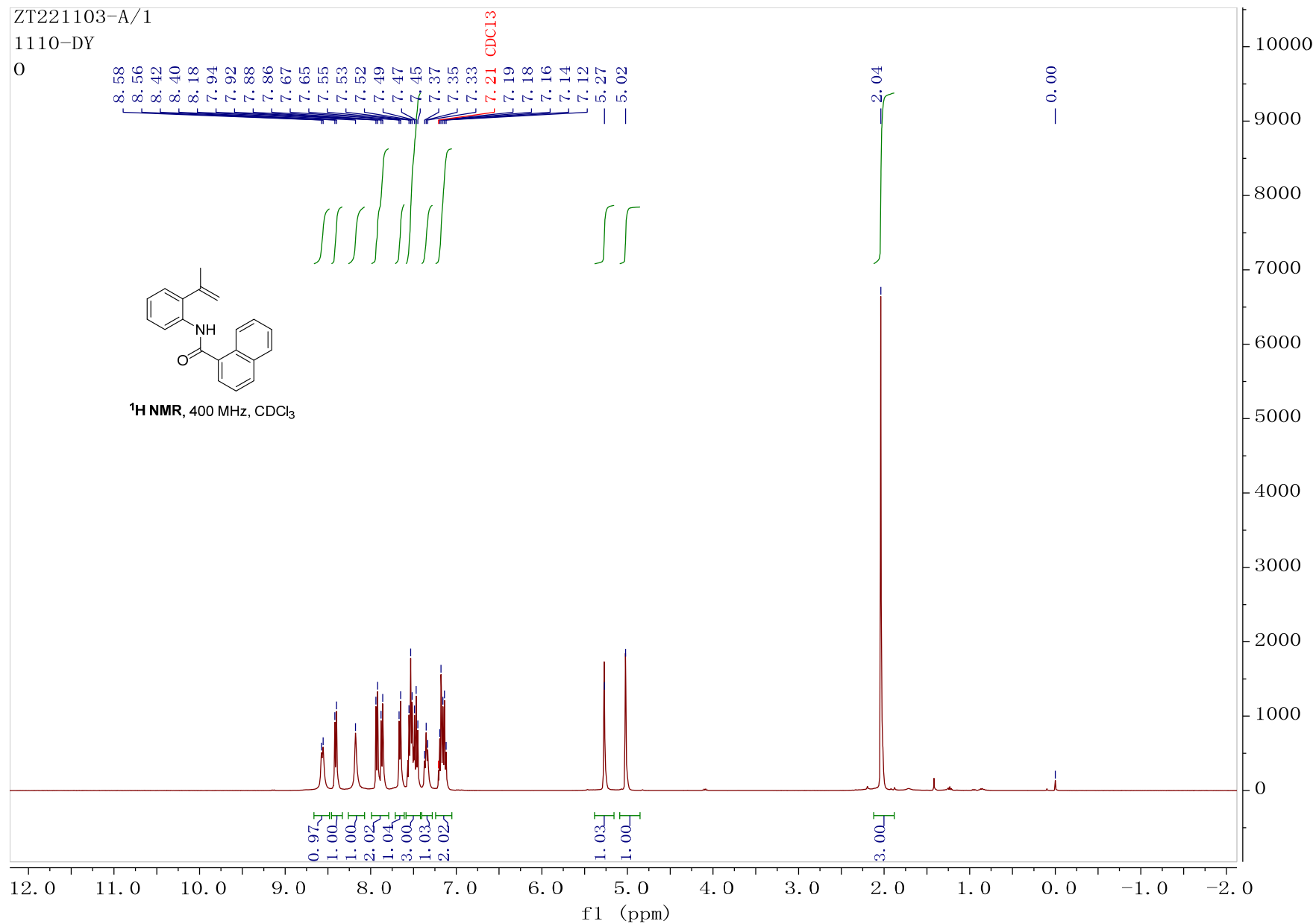
¹H NMR spectrum of Compound 11 (CDCl₃, 400 MHz)



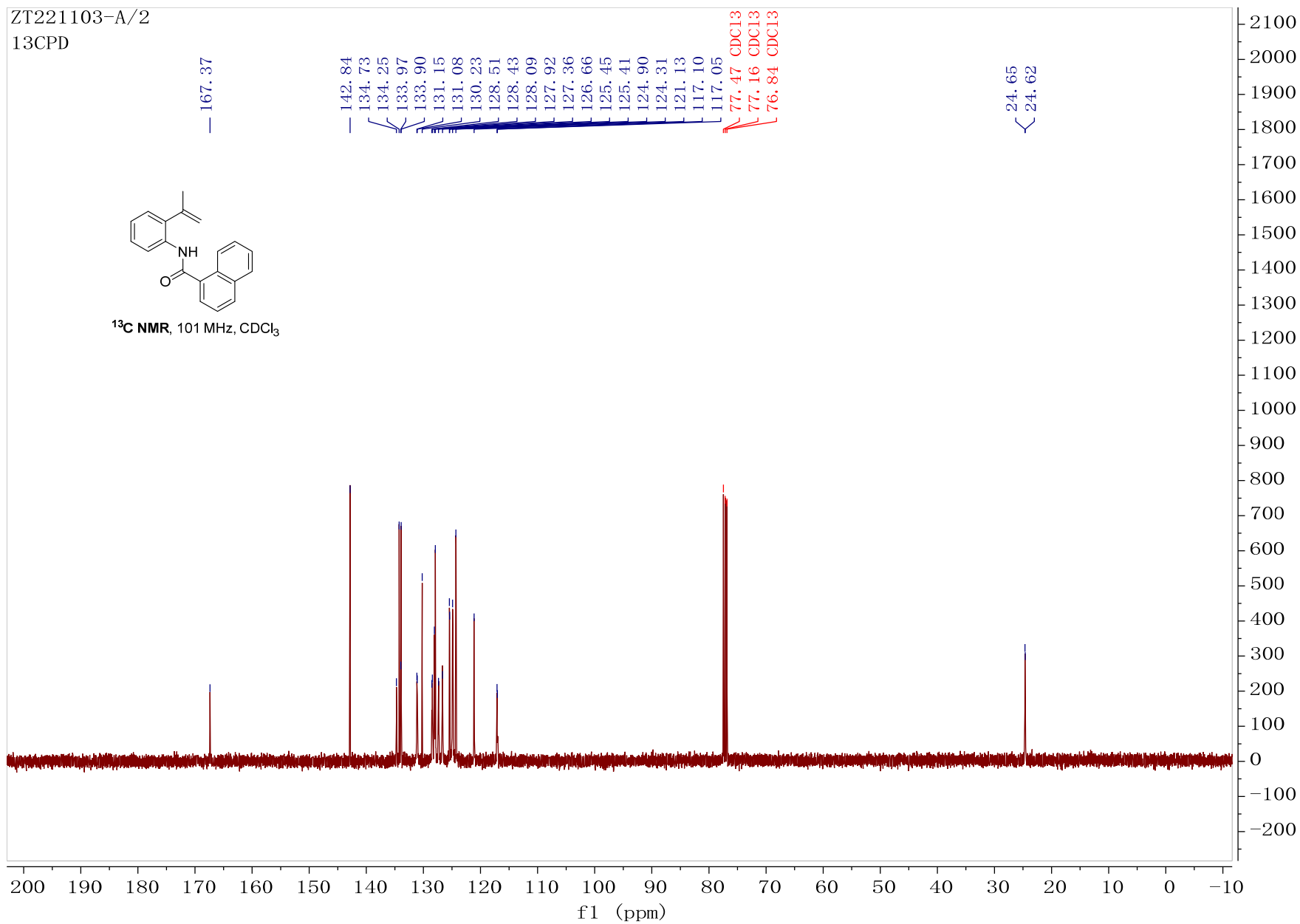
¹³C NMR spectrum of Compound 11 (CDCl₃, 101 MHz)



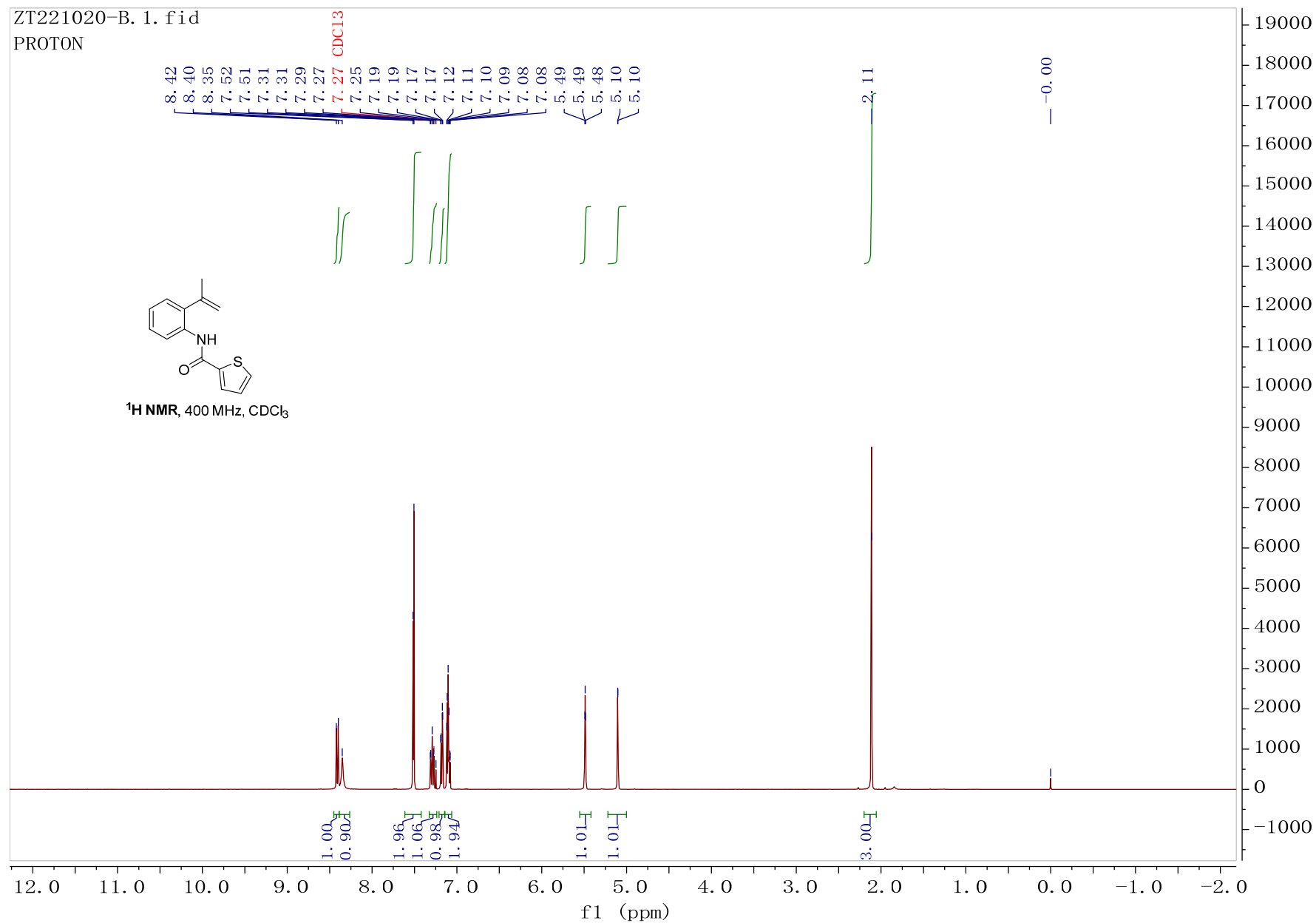
¹H NMR spectrum of Compound 1m (CDCl₃, 400 MHz)



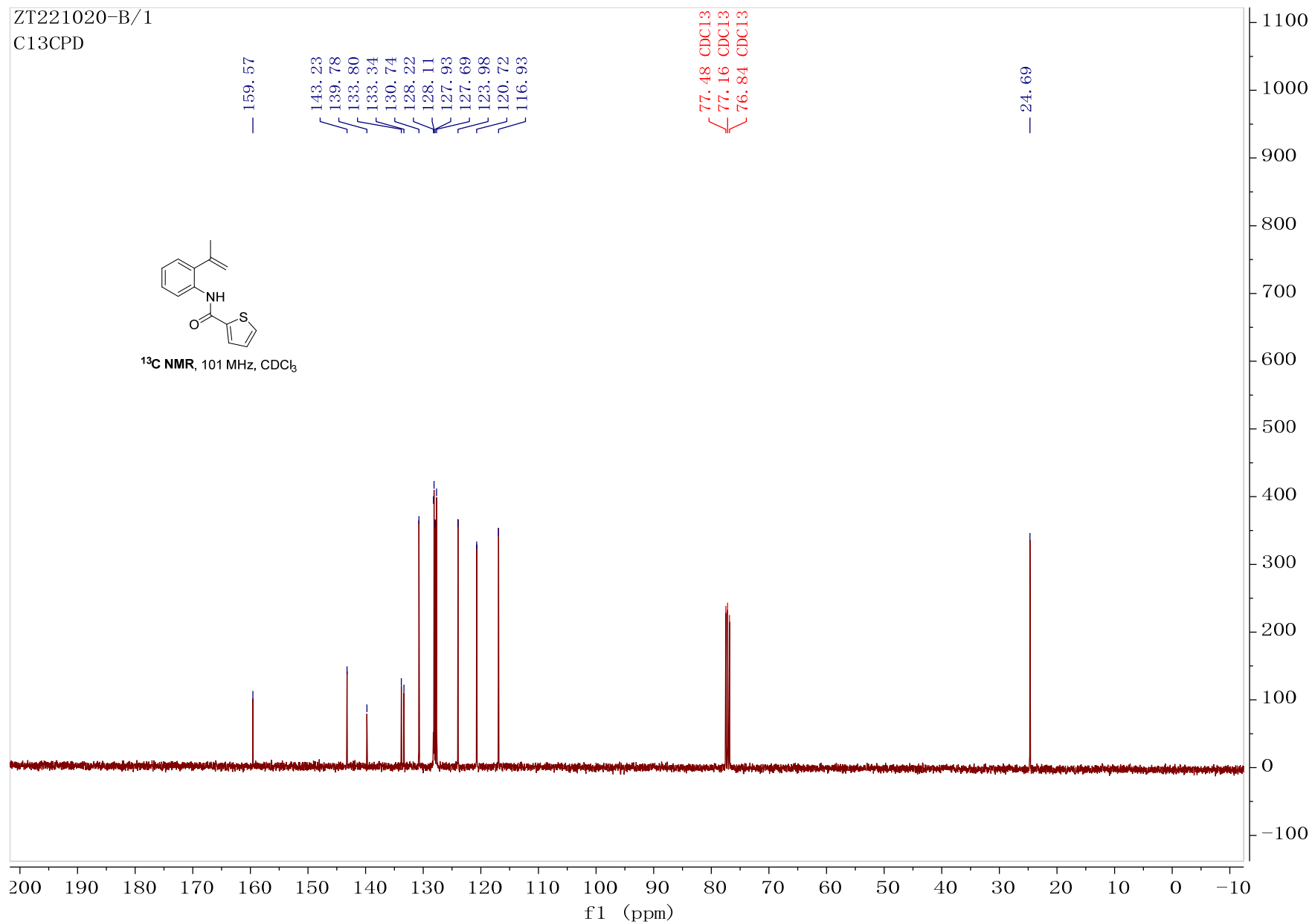
¹³C NMR spectrum of Compound 1m (CDCl₃, 101 MHz)



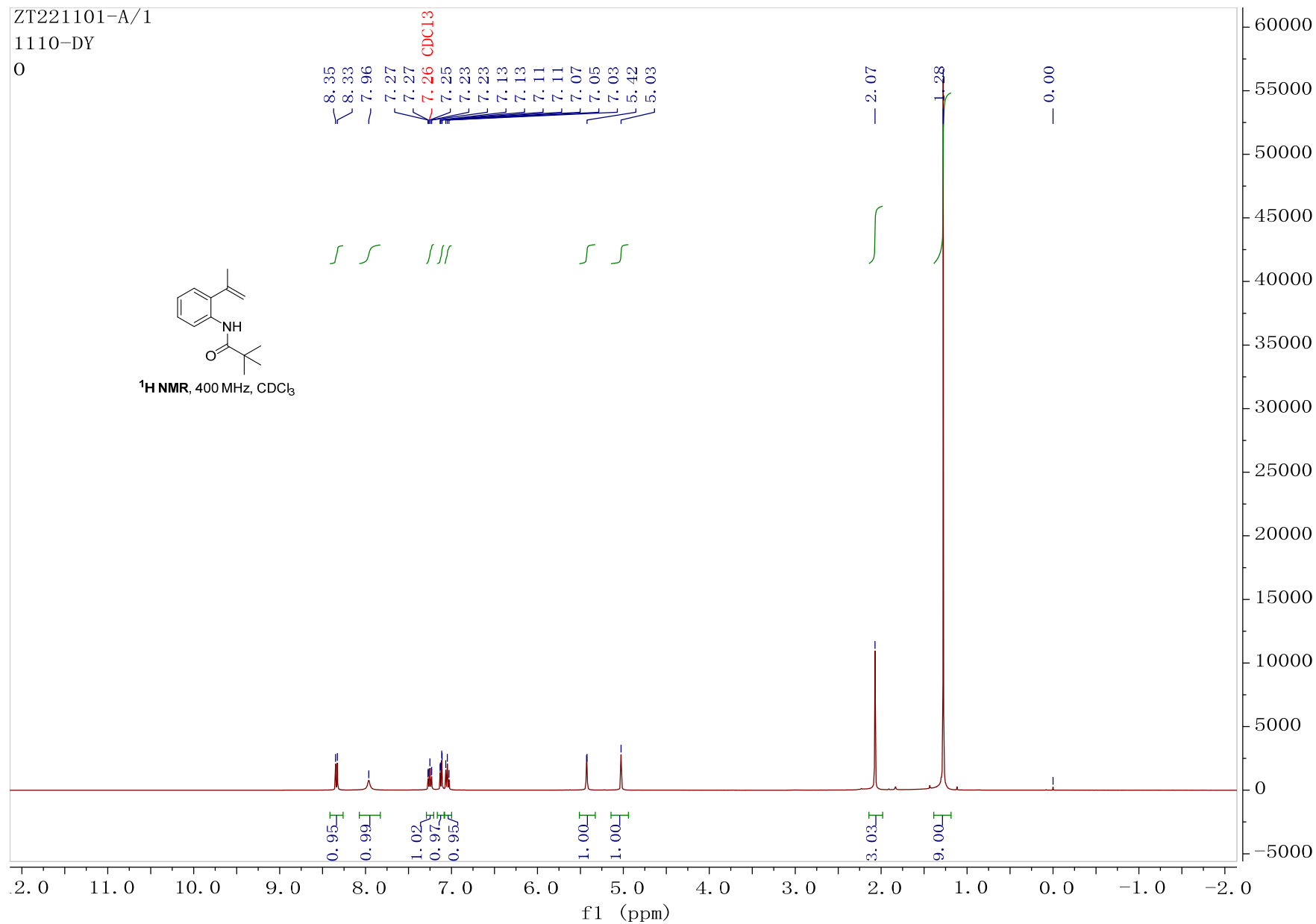
¹H NMR spectrum of Compound 1n (CDCl₃, 400 MHz)



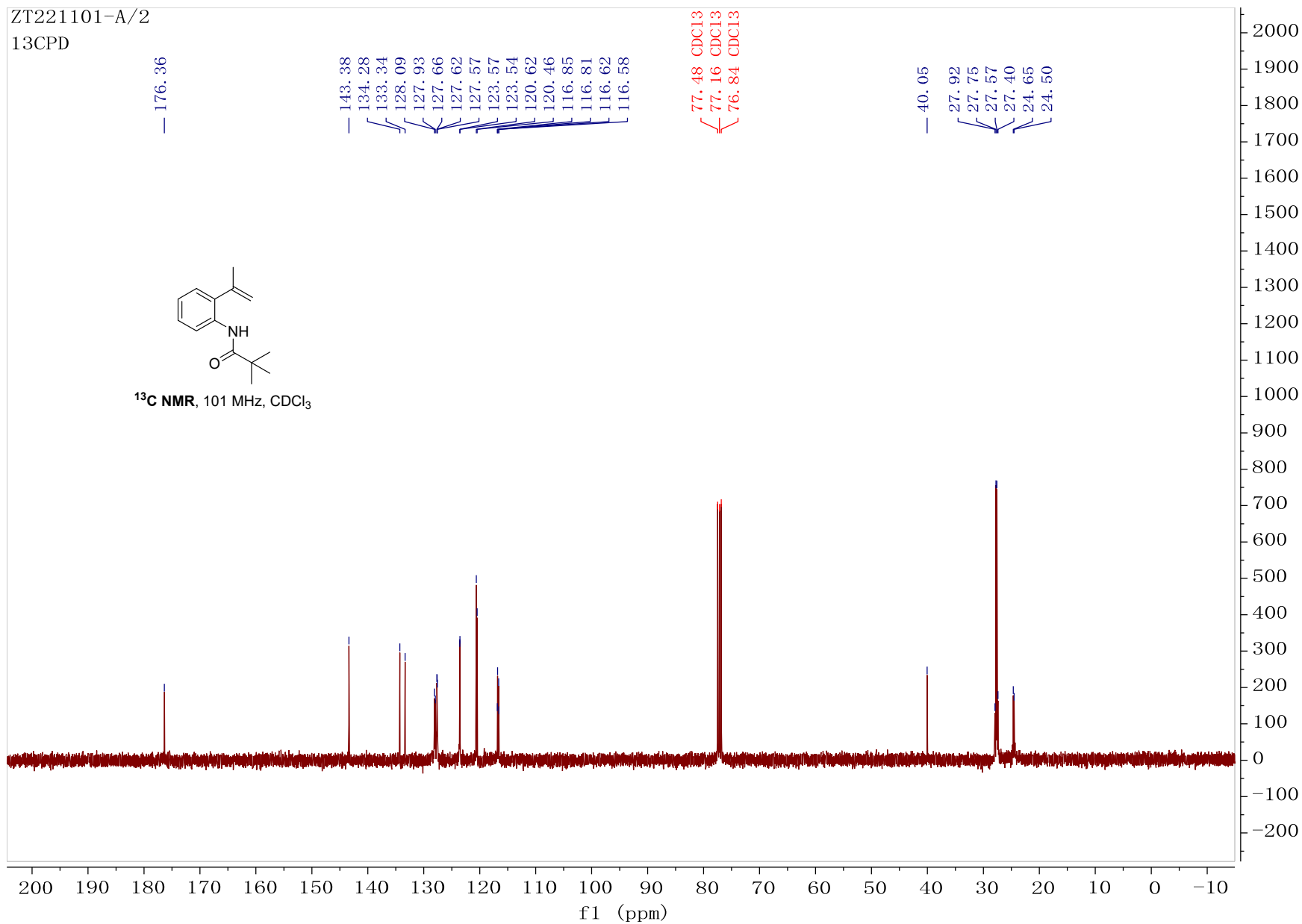
¹³C NMR spectrum of Compound 1n (CDCl₃, 101 MHz)



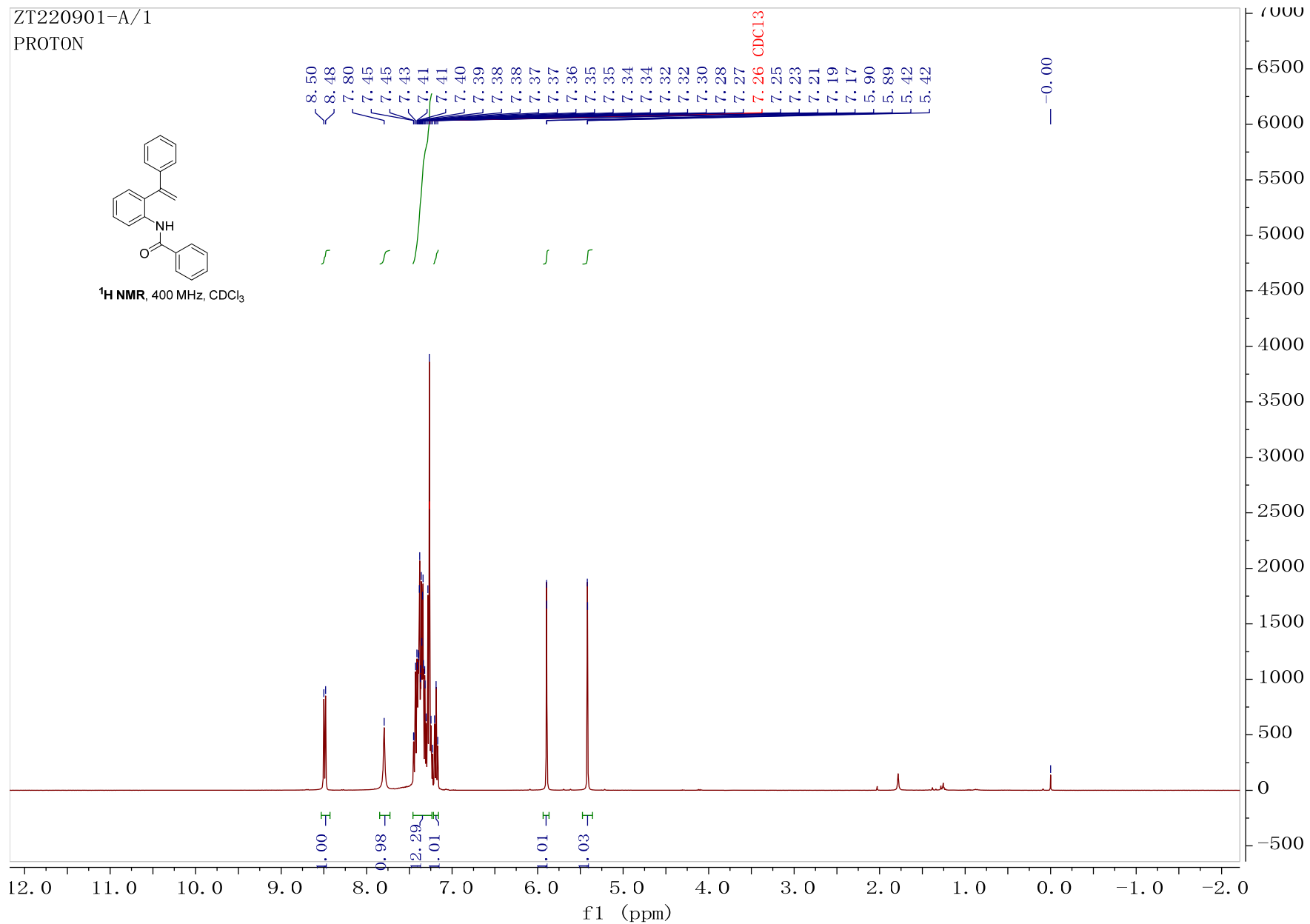
¹H NMR spectrum of Compound 1o (CDCl₃, 400 MHz)



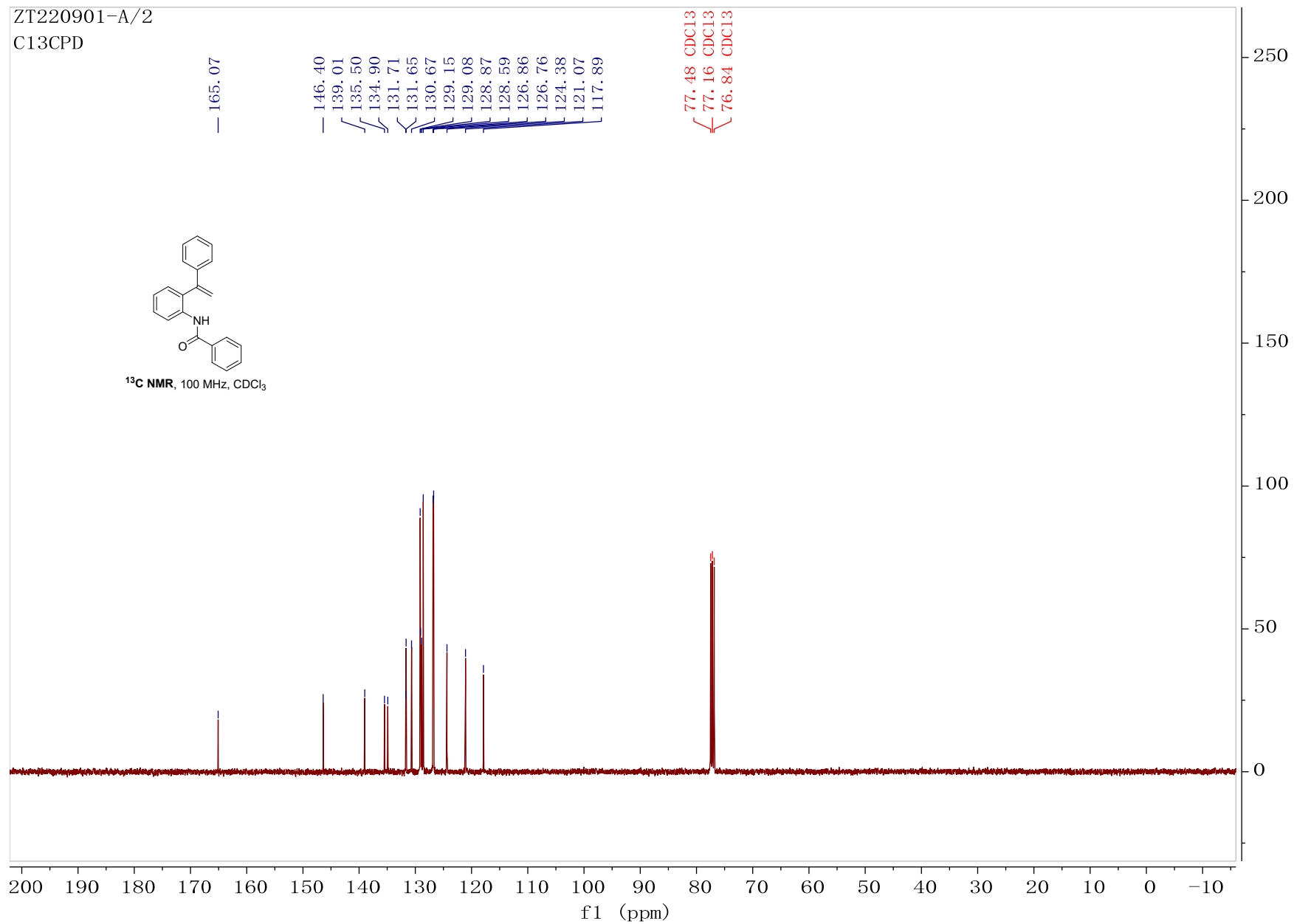
¹³C NMR spectrum of Compound 1o (CDCl₃, 101 MHz)



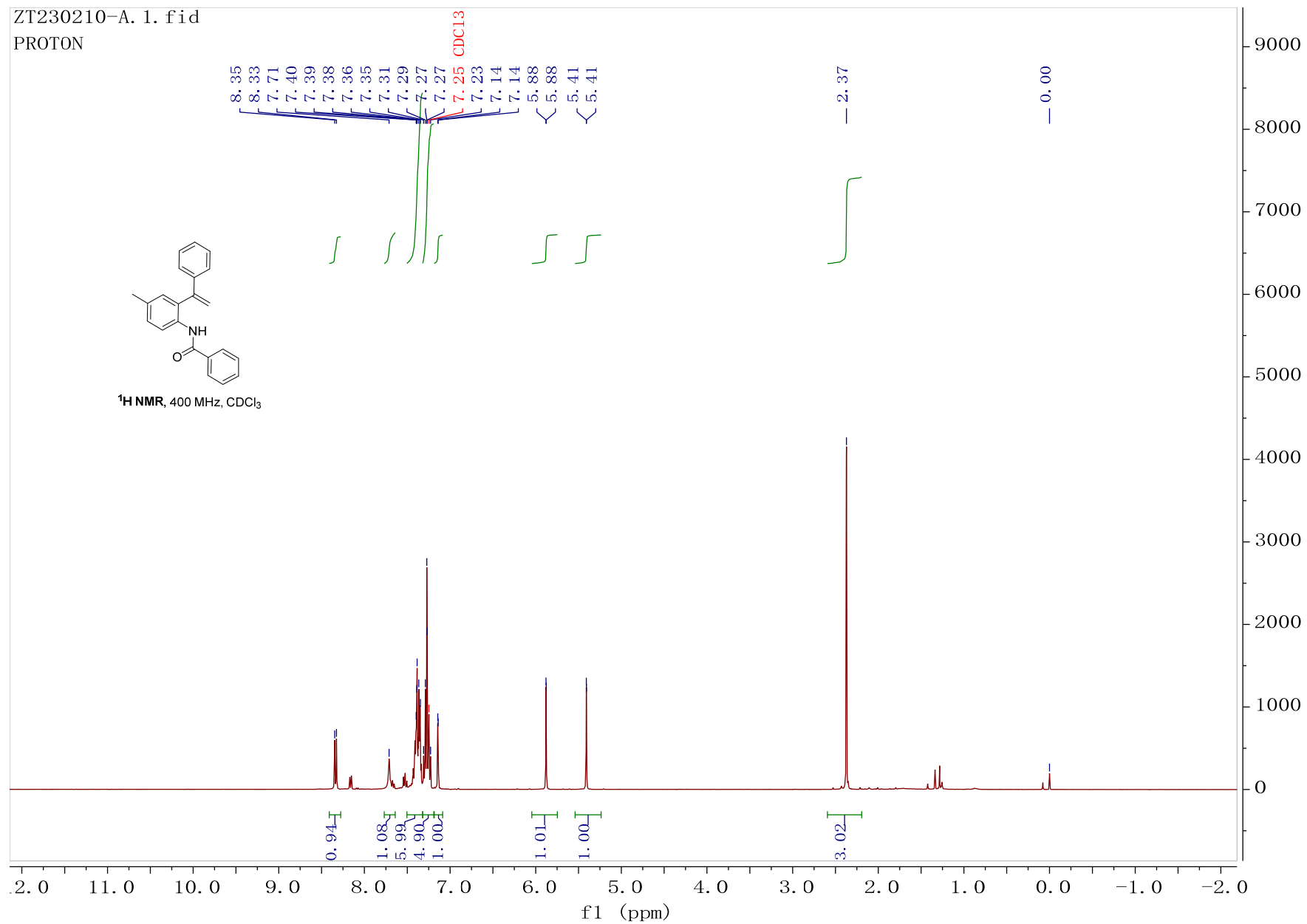
¹H NMR spectrum of Compound 1p (CDCl₃, 400 MHz)



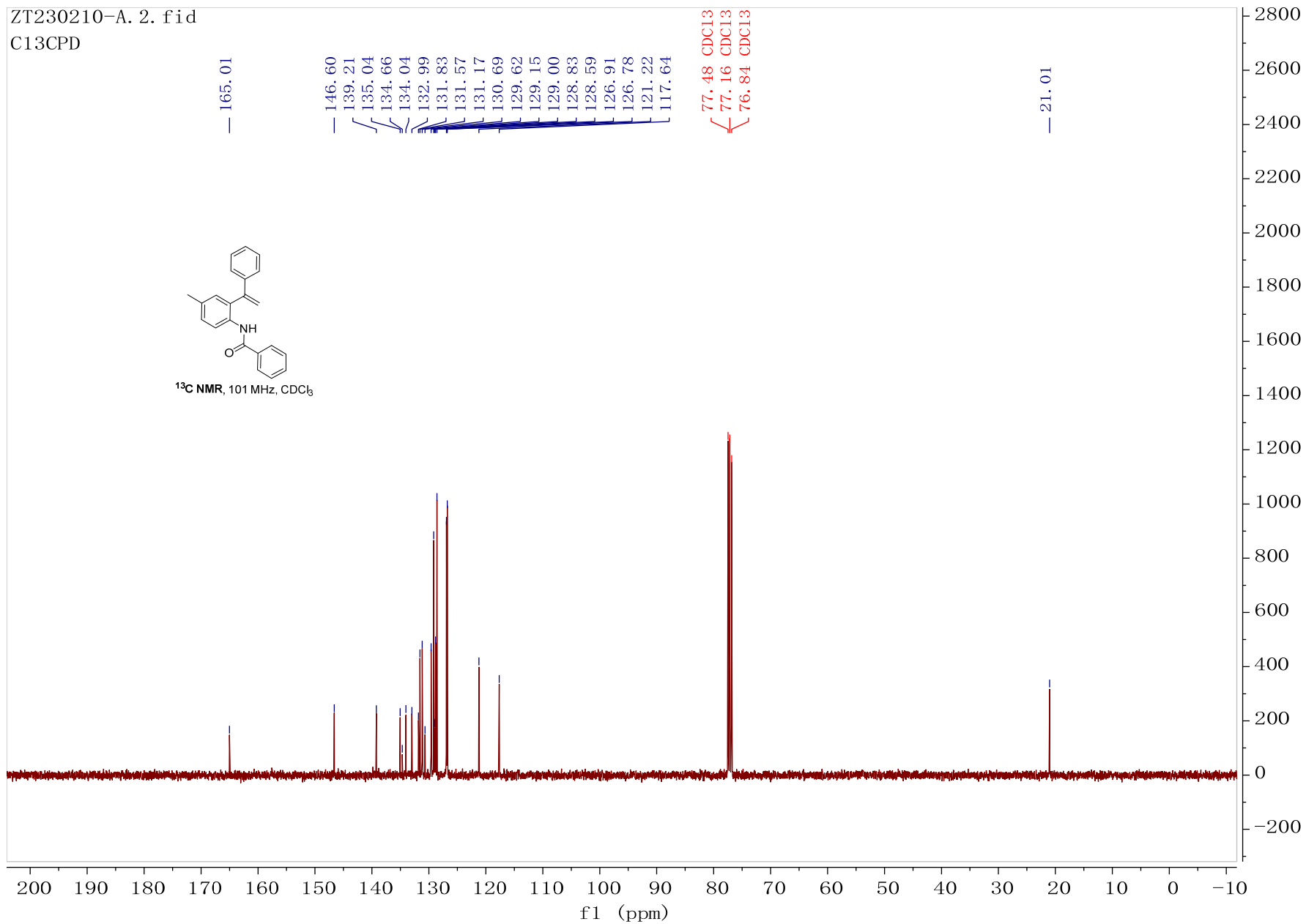
¹³C NMR spectrum of Compound 1p (CDCl₃, 101 MHz)



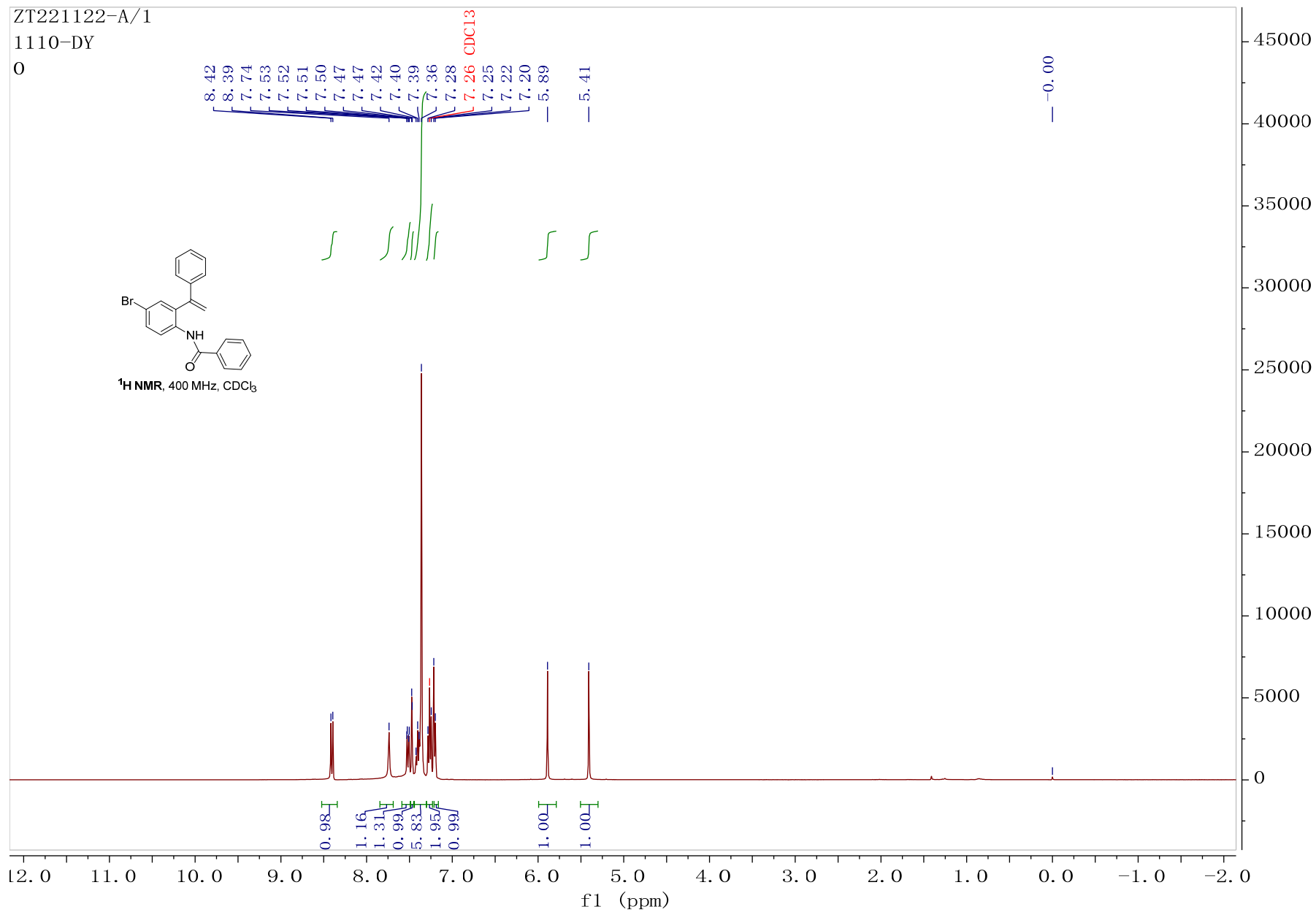
¹H NMR spectrum of Compound 1q (CDCl₃, 400 MHz)



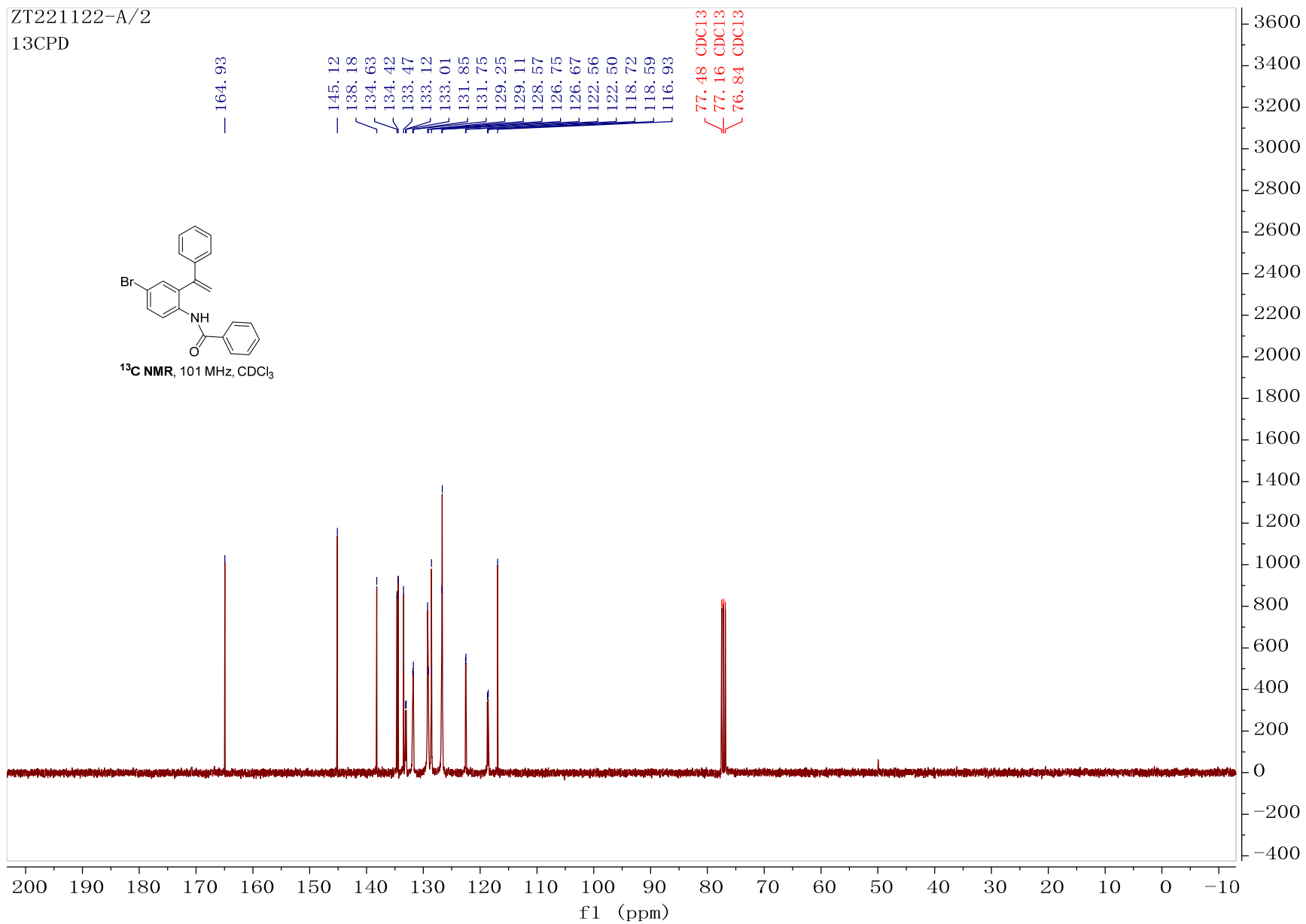
¹³C NMR spectrum of Compound 1q (CDCl₃, 101 MHz)



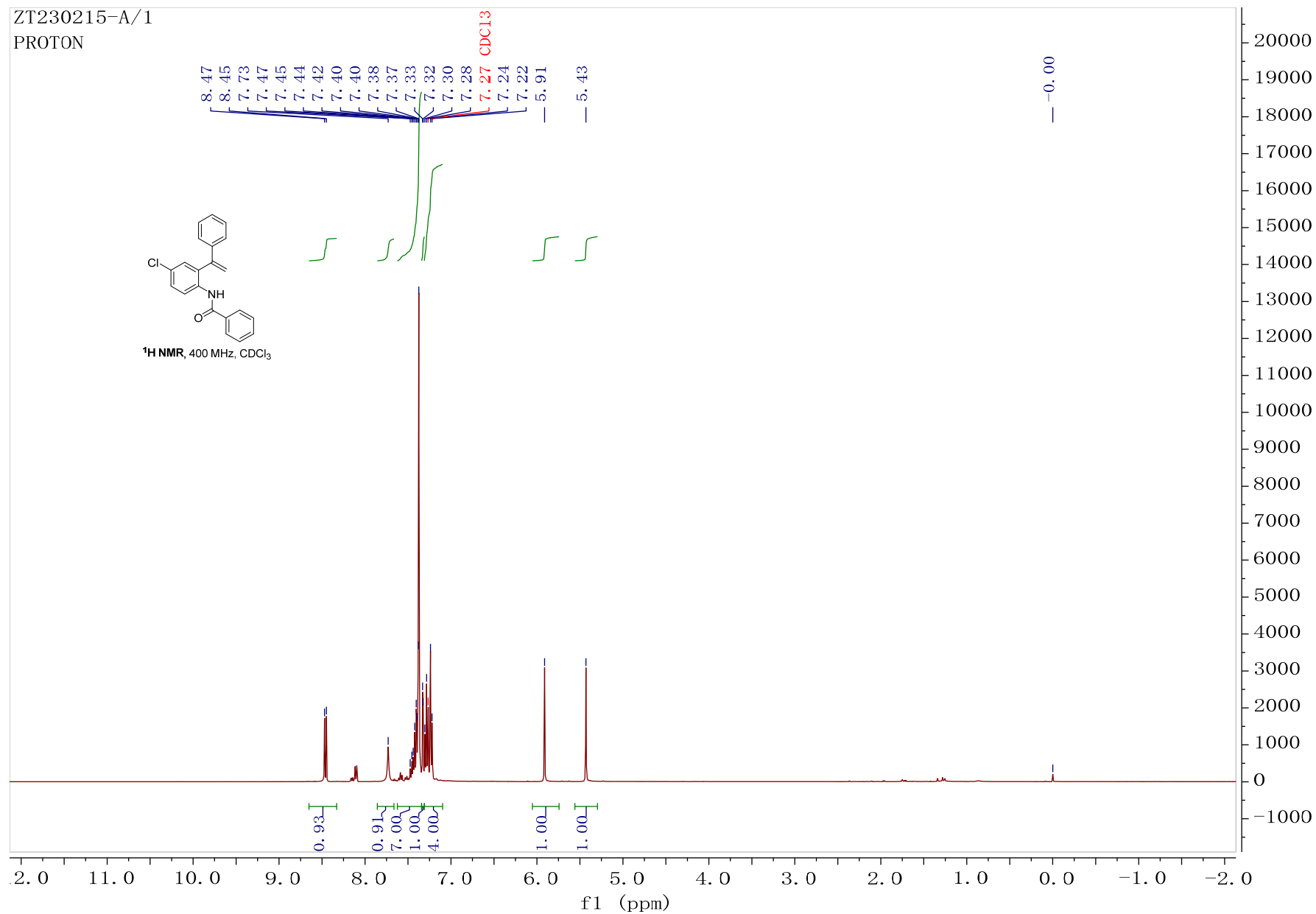
¹H NMR spectrum of Compound 1r (CDCl₃, 400 MHz)



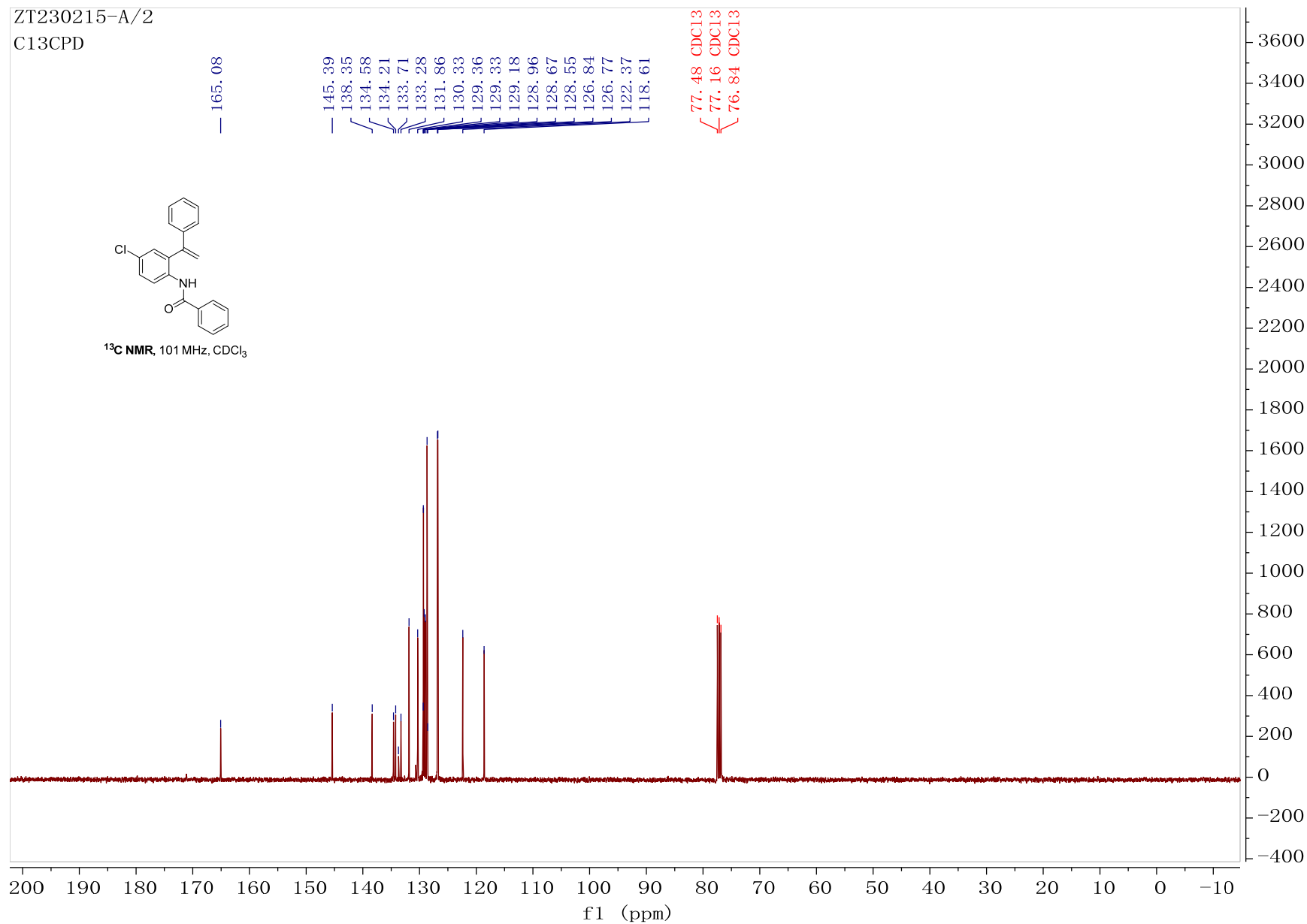
¹³C NMR spectrum of Compound 1r (CDCl₃, 101 MHz)



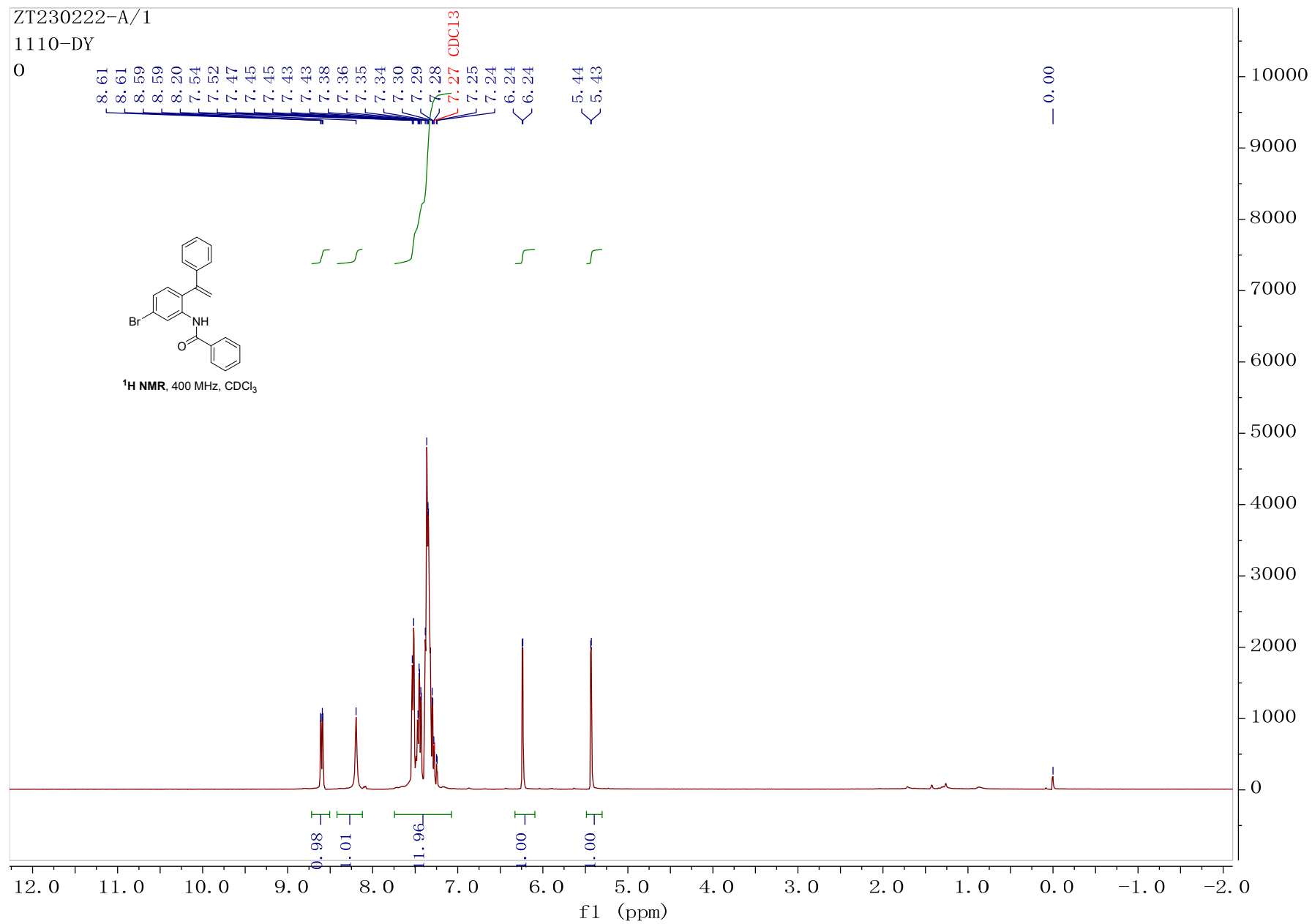
¹H NMR spectrum of Compound 1s (CDCl₃, 400 MHz)



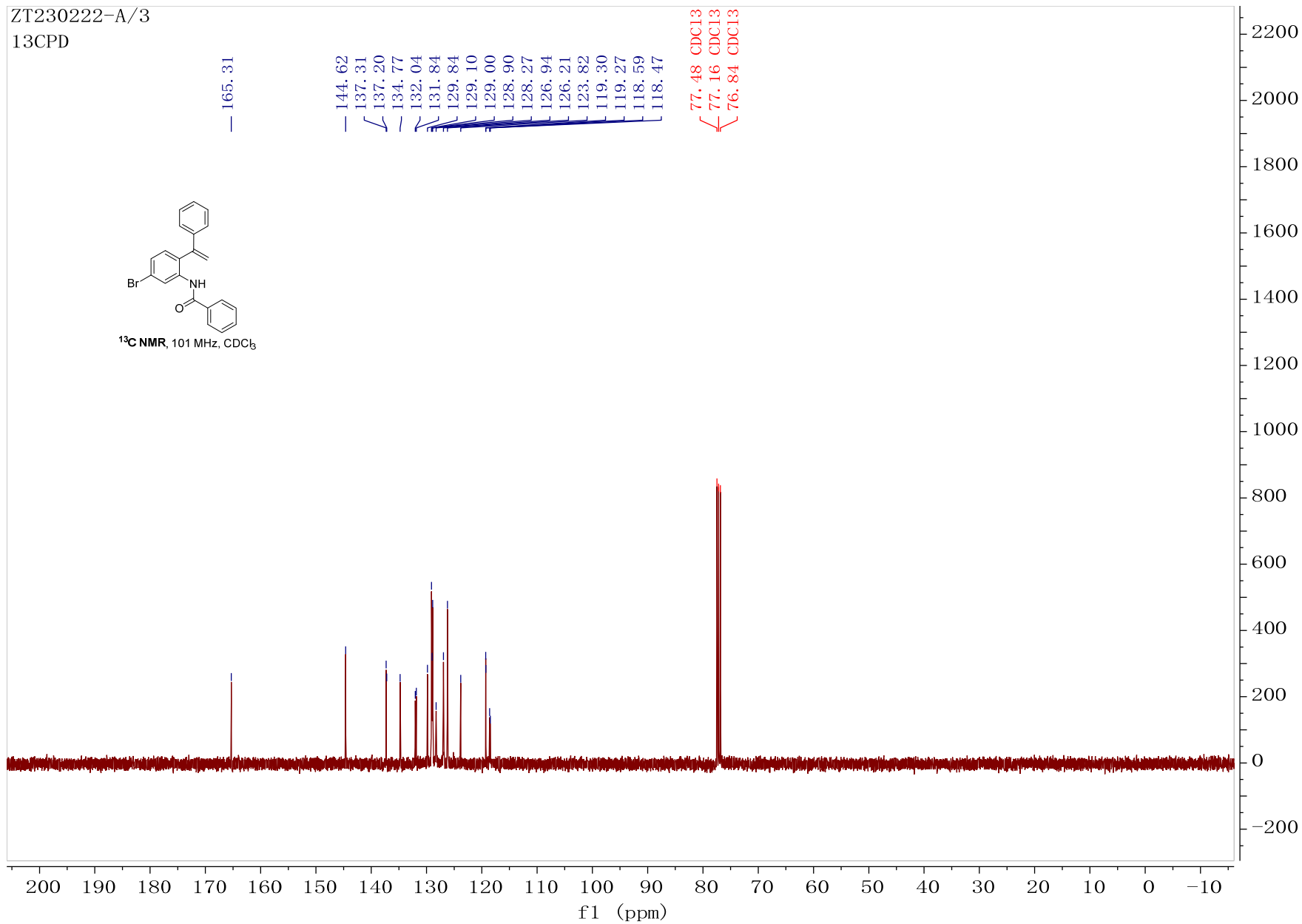
¹³C NMR spectrum of Compound 1s (CDCl₃, 101 MHz)



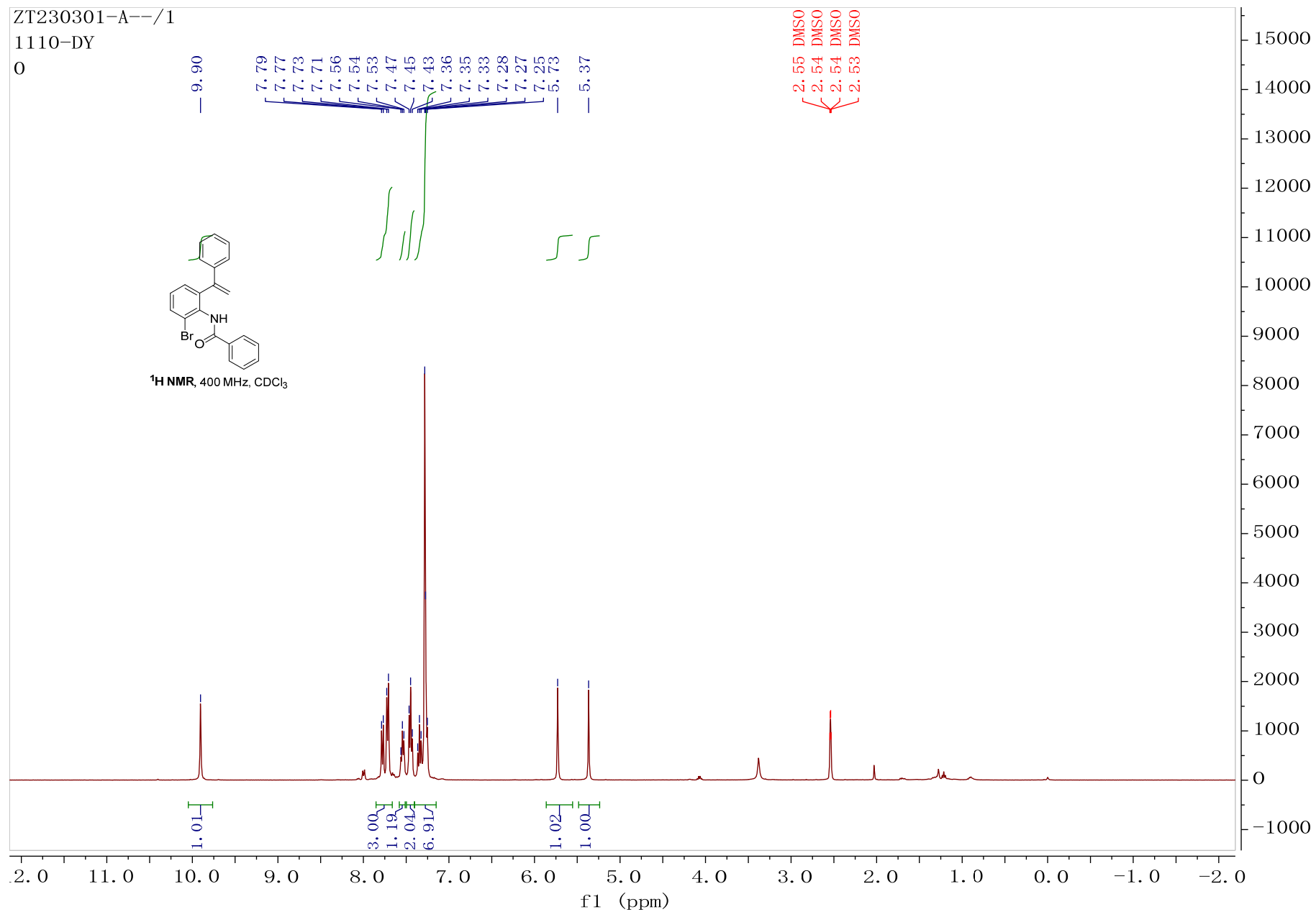
¹H NMR spectrum of Compound 1t (CDCl₃, 400 MHz)



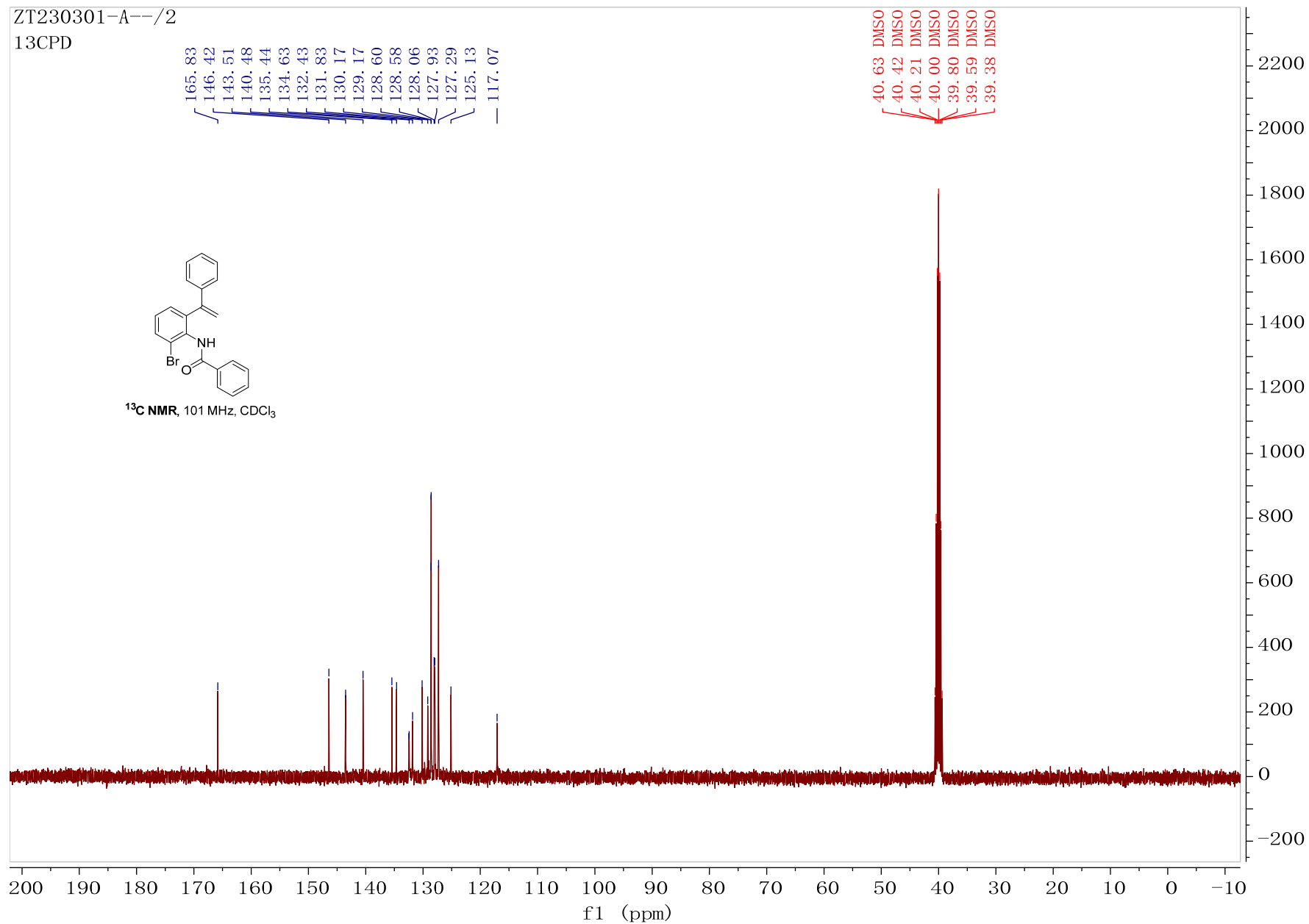
¹³C NMR spectrum of Compound 1t (CDCl₃, 101 MHz)



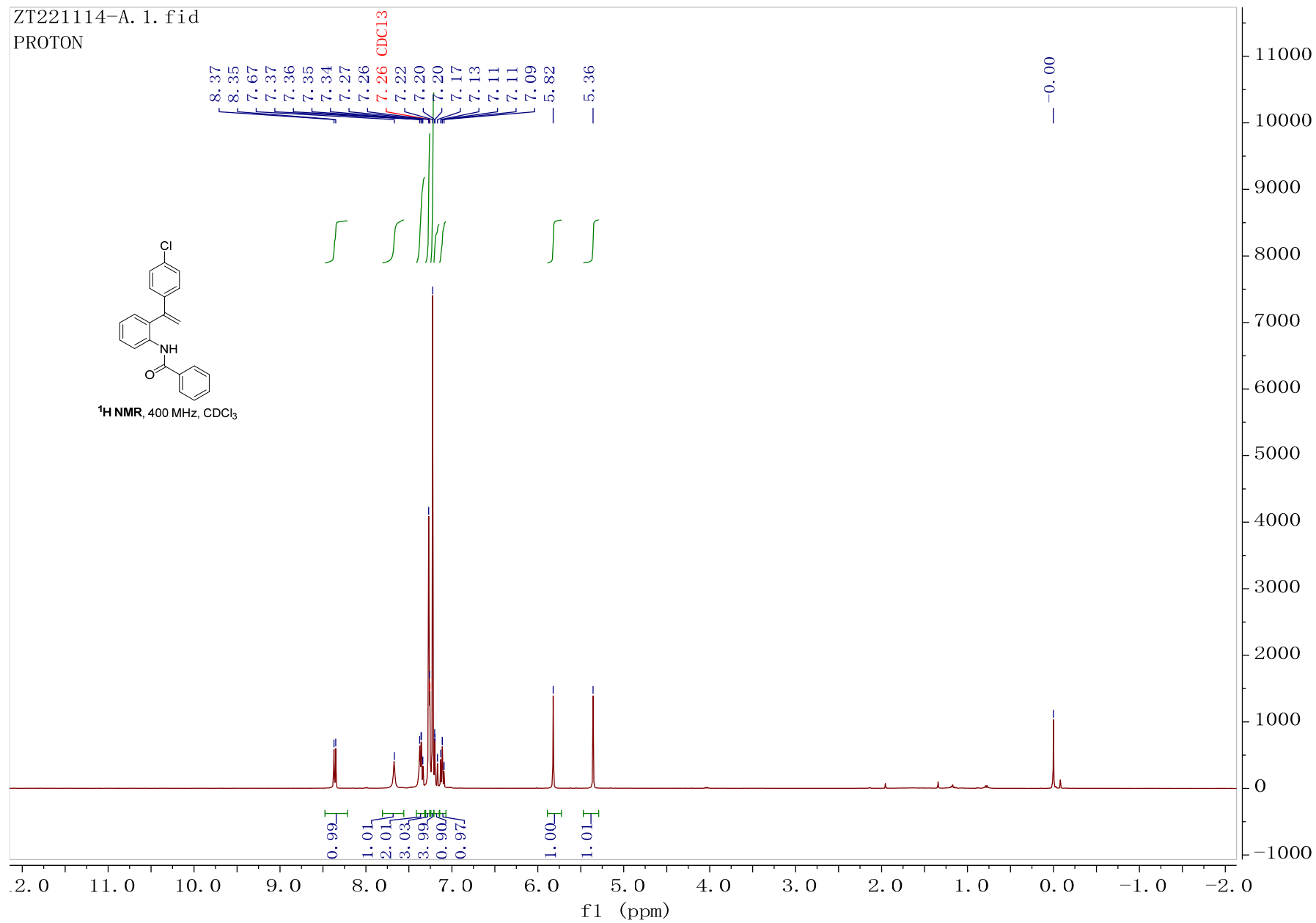
¹H NMR spectrum of Compound 1u (CDCl₃, 400 MHz)



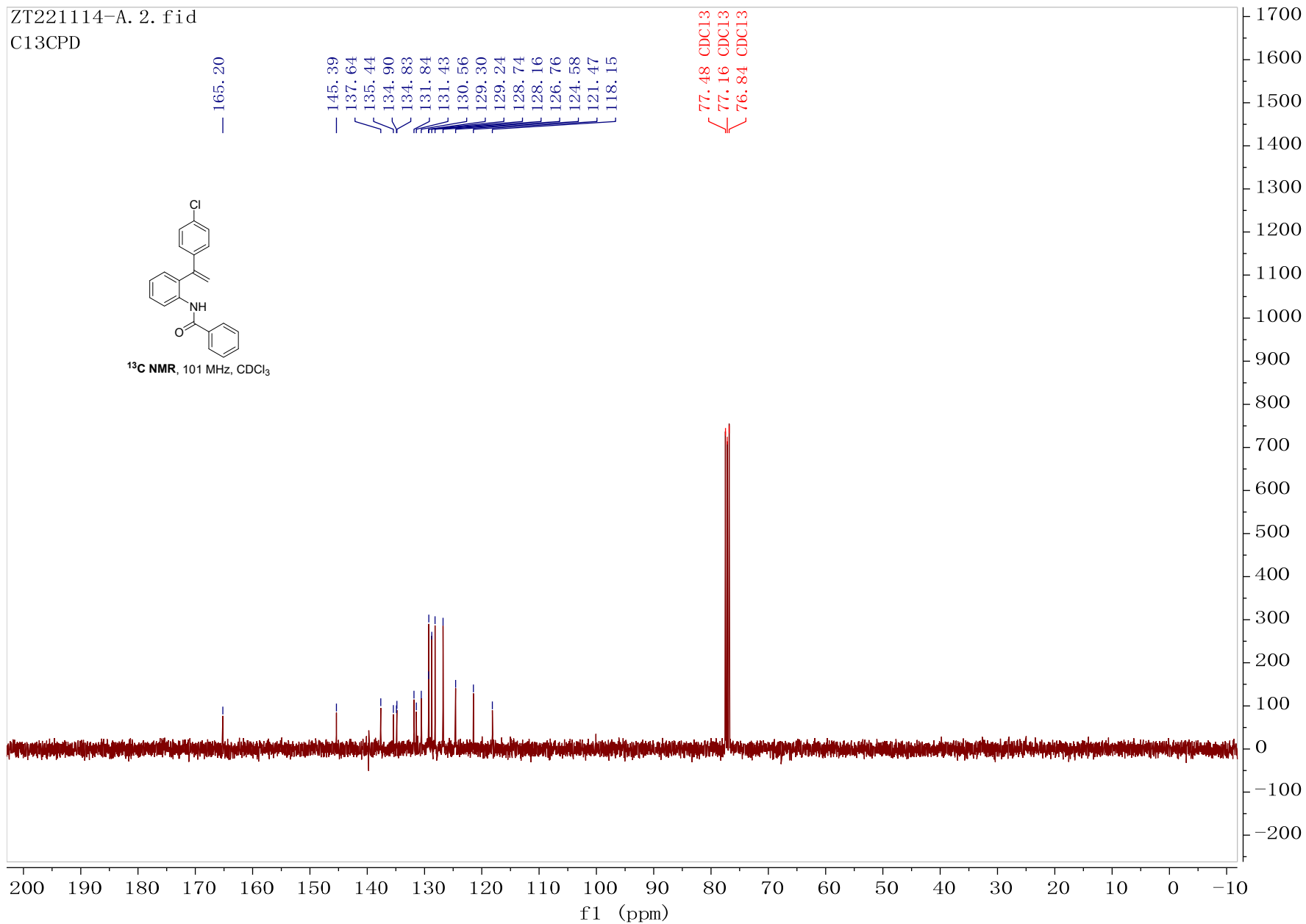
¹³C NMR spectrum of Compound 1u (DMSO, 101 MHz)



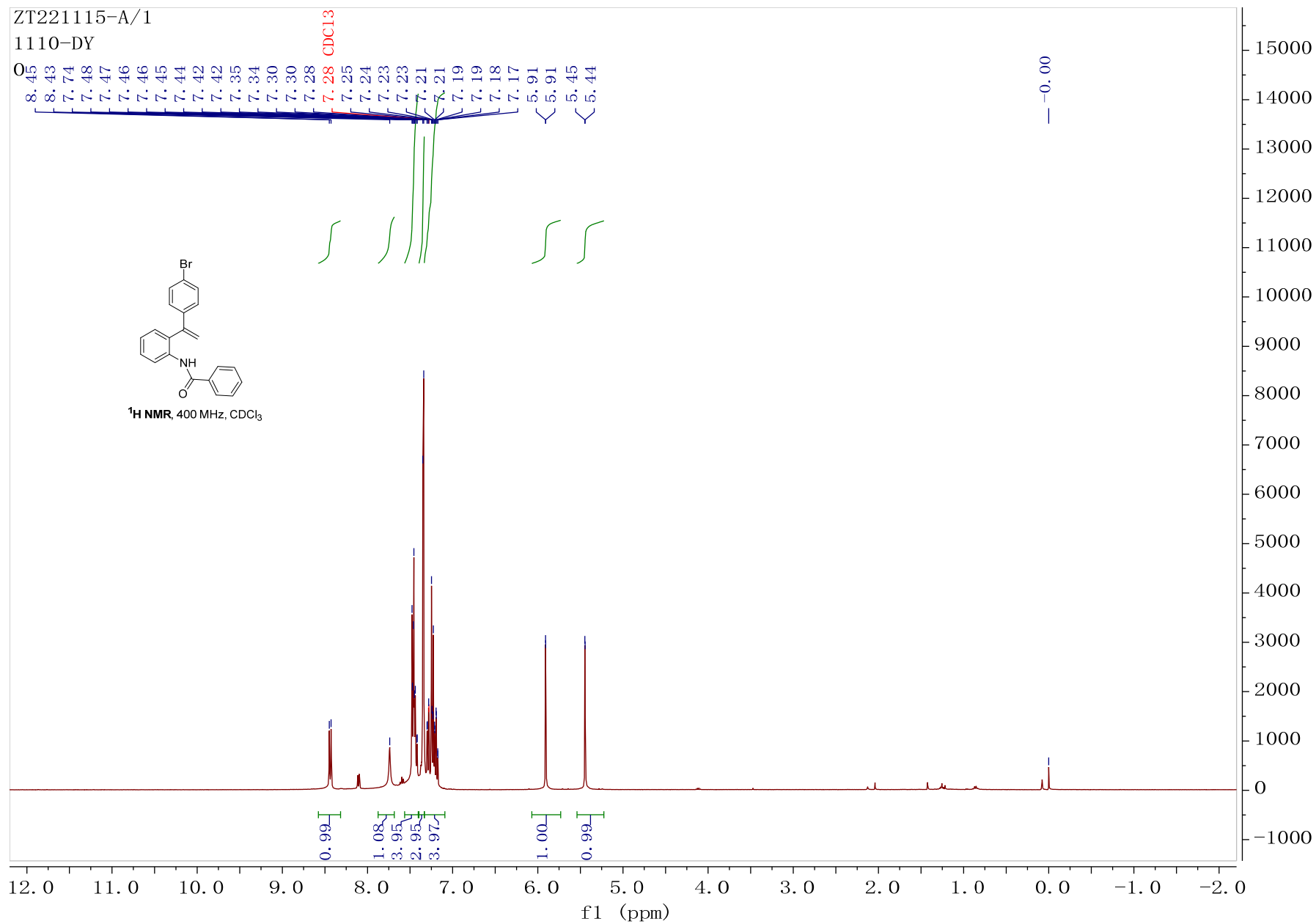
¹H NMR spectrum of Compound 1v (CDCl₃, 400 MHz)



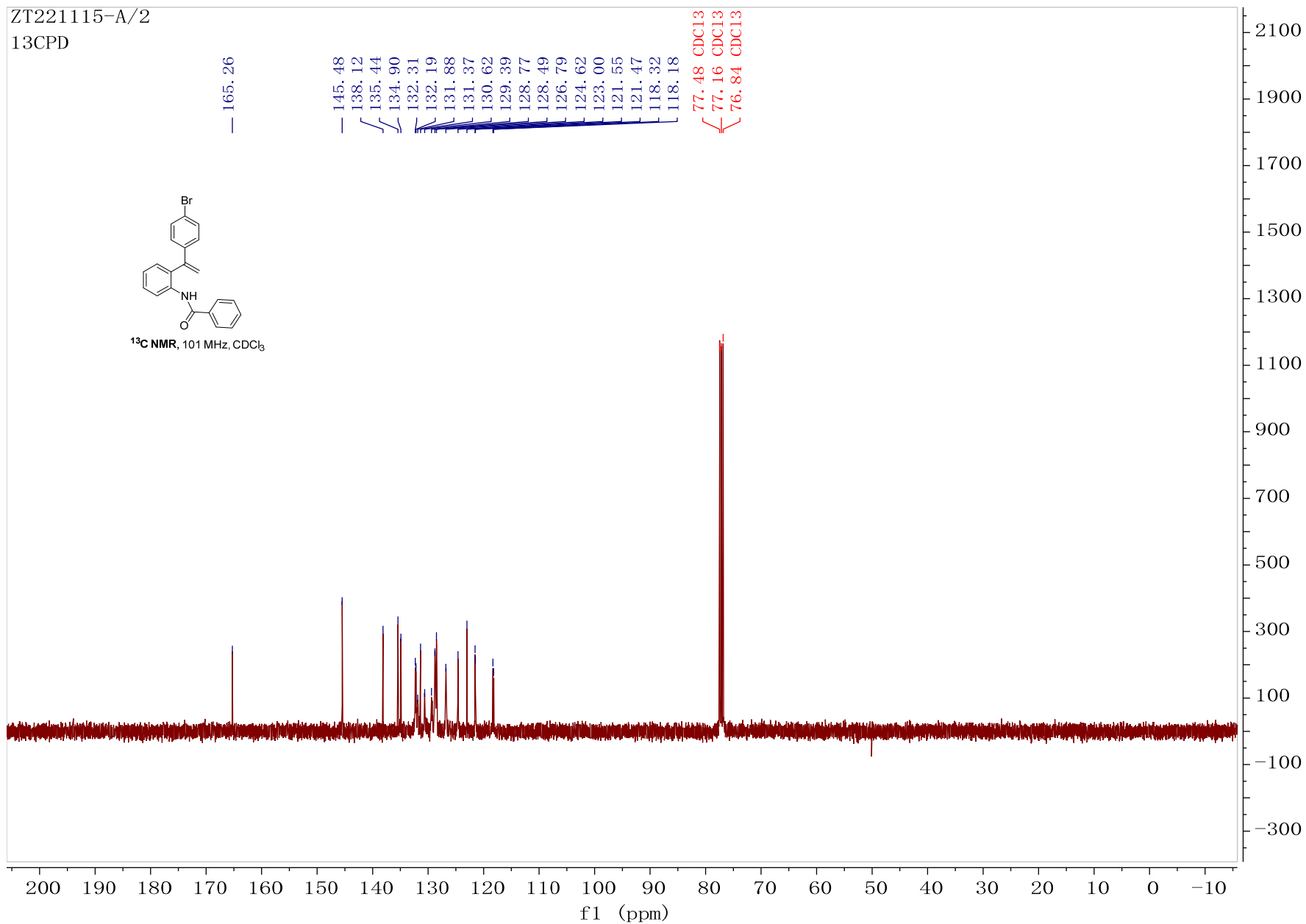
¹³C NMR spectrum of Compound 1v (CDCl₃, 101 MHz)



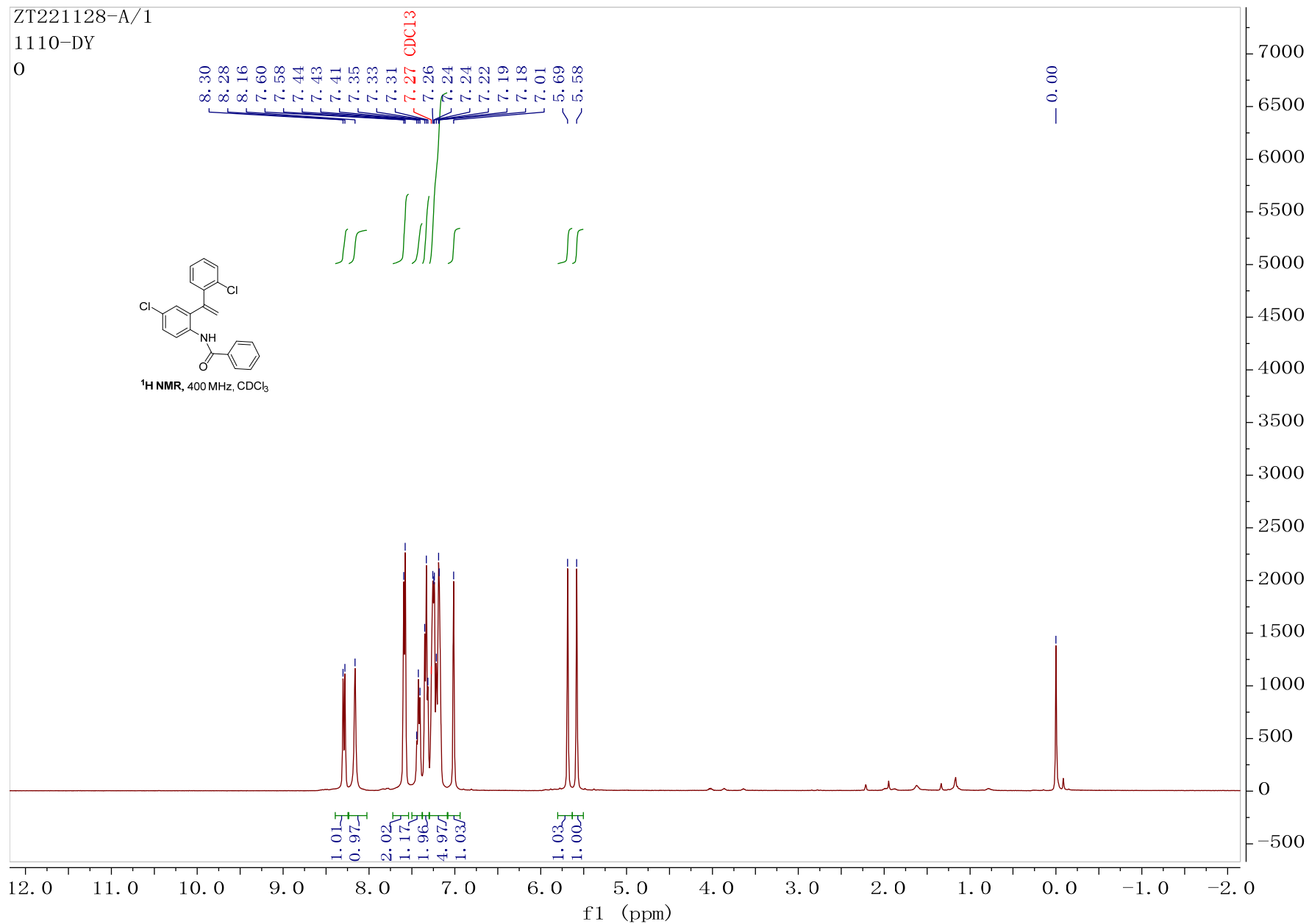
¹H NMR spectrum of Compound 1w (CDCl₃, 400 MHz)



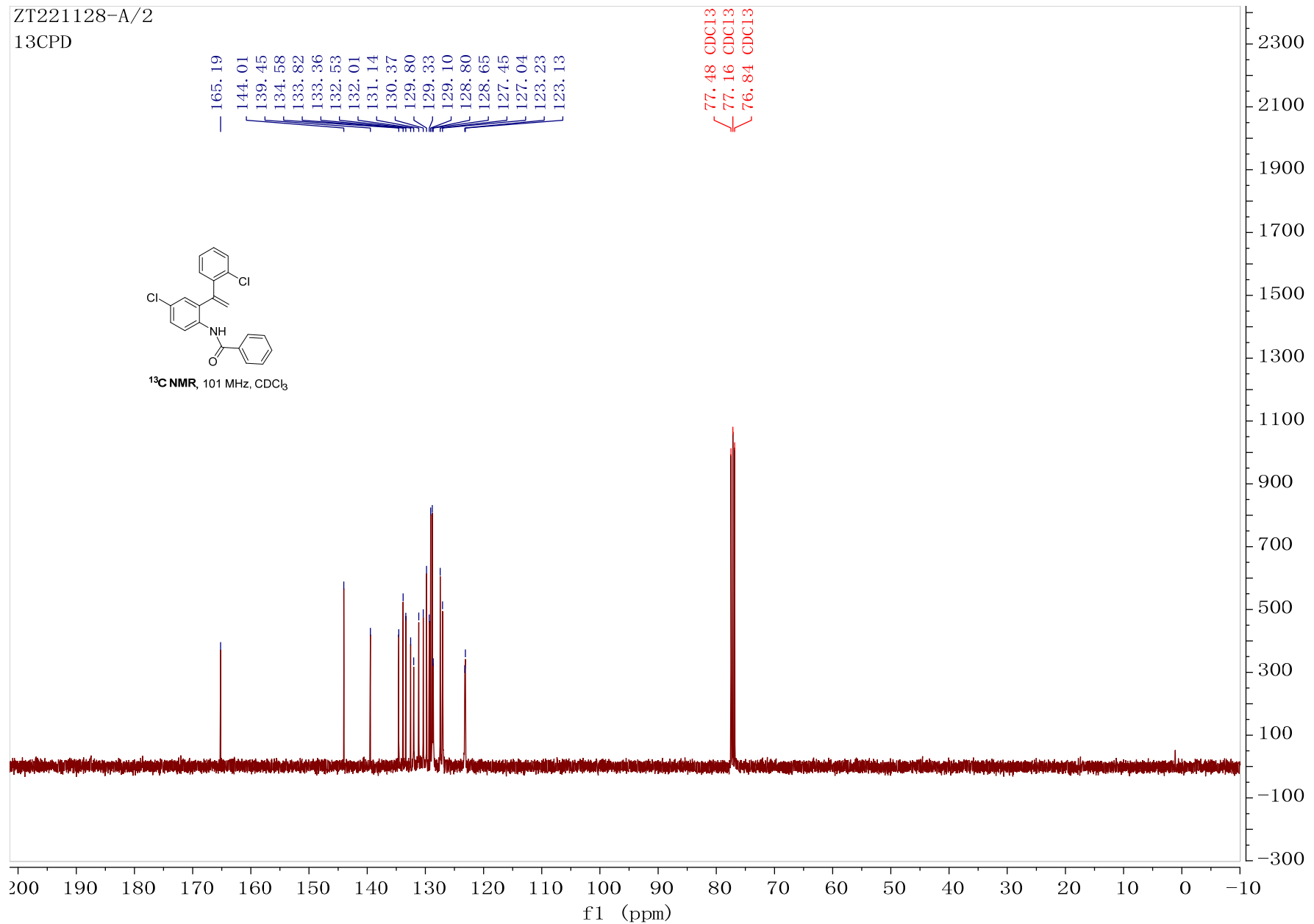
¹³C NMR spectrum of Compound 1w (CDCl₃, 101 MHz)



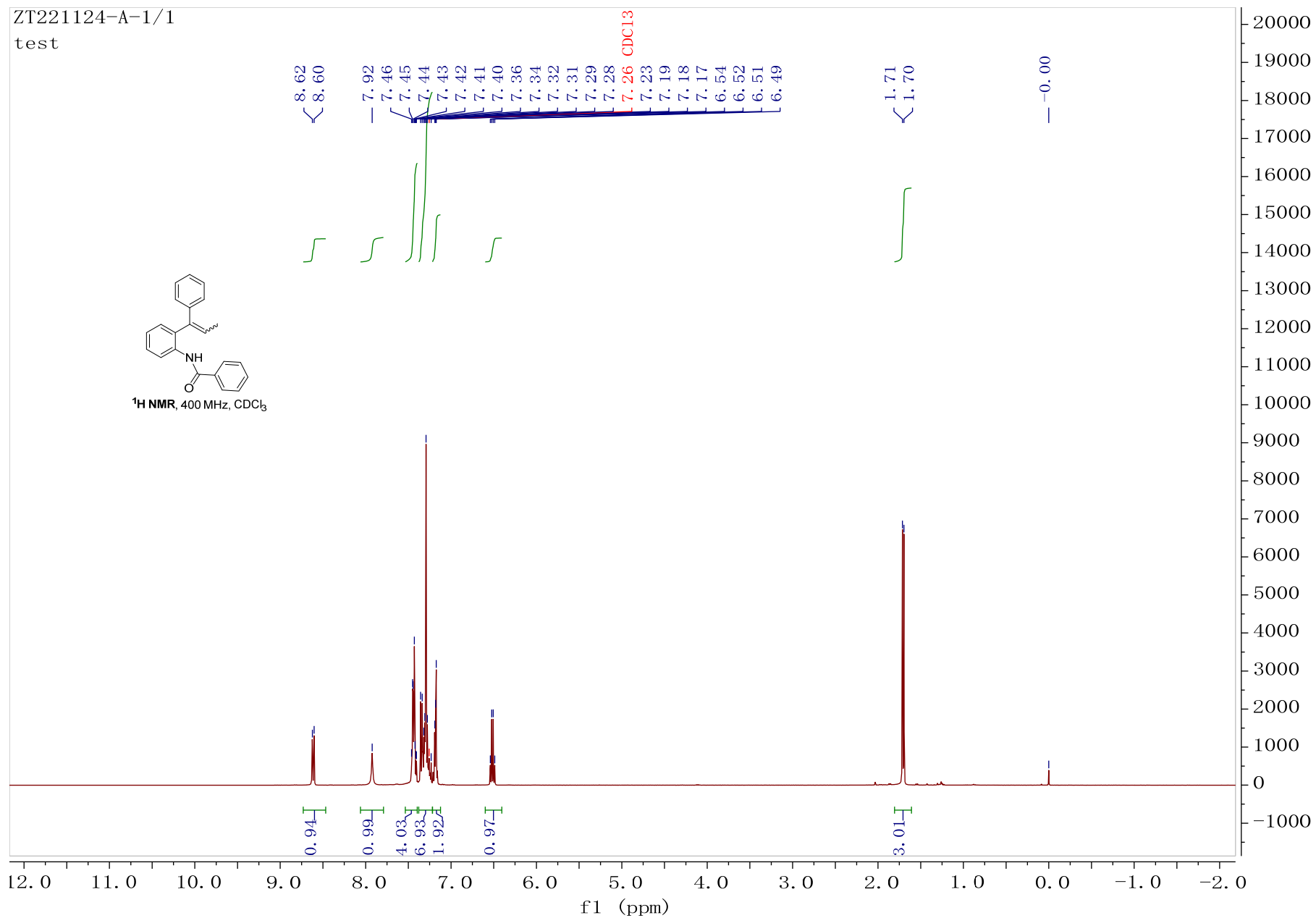
¹H NMR spectrum of Compound 1x (CDCl₃, 400 MHz)



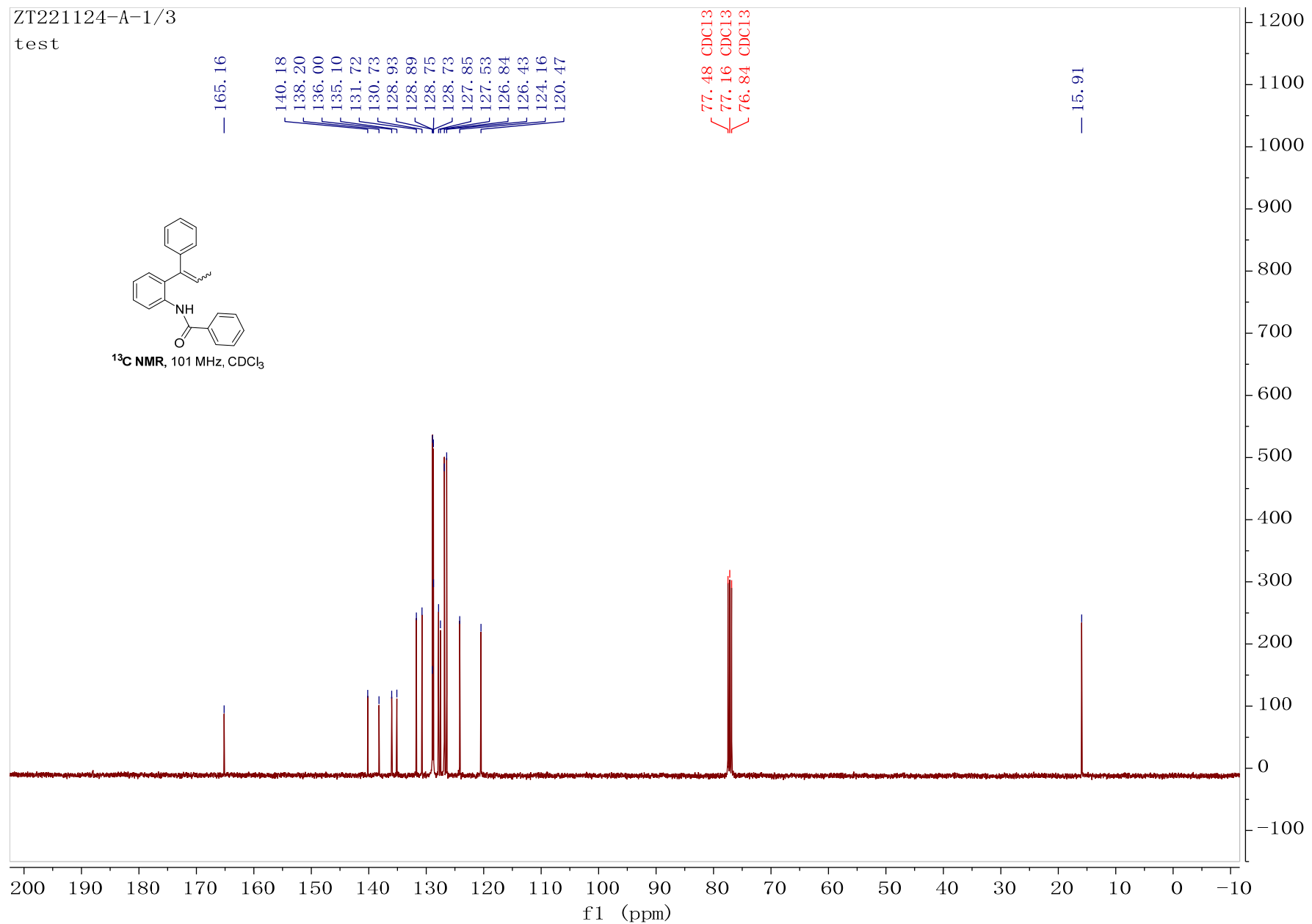
¹³C NMR spectrum of Compound 1x (CDCl₃, 101 MHz)



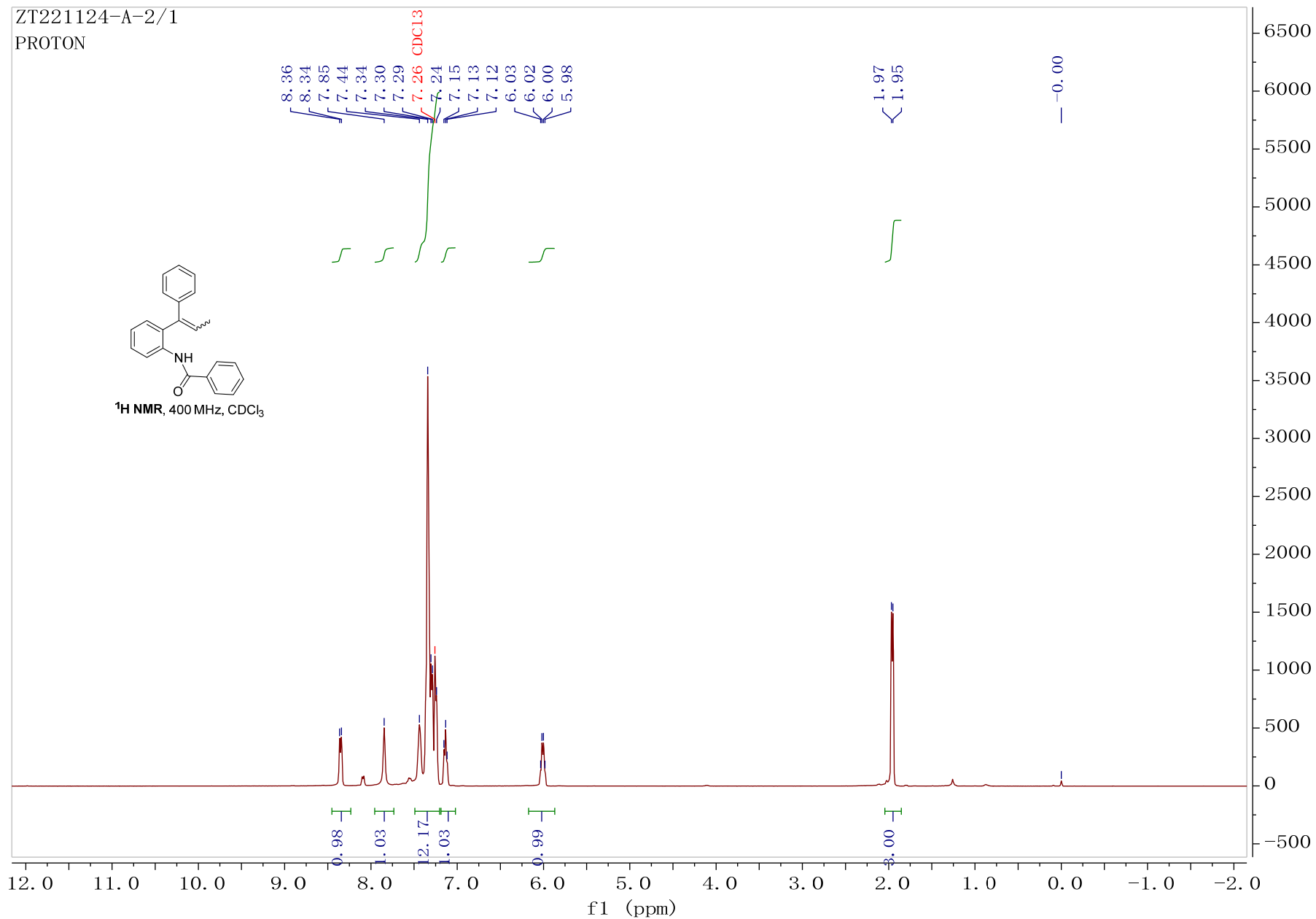
¹H NMR spectrum of Compound 1y (CDCl₃, 400 MHz)



¹³C NMR spectrum of Compound 1y (CDCl₃, 101 MHz)



¹H NMR spectrum of Compound 1y (CDCl₃, 400 MHz)



¹³C NMR spectrum of Compound 1y (CDCl₃, 101 MHz)

