Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Information

Divergent Synthesis of *N*-Heterocyclic 1,6-Enynes through Zinc- catalyzed Decarboxylative A^3 Reaction

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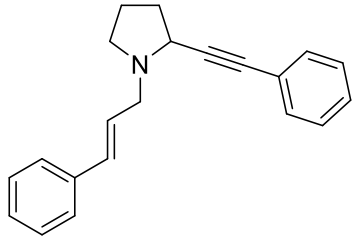
Experimental section

General: Toluene was dried over $CaCl_2$. Reactions were monitored by thin layer chromatography (TLC) on glass plates coated with silica gel with fluorescent indicator. Flash chromatography was performed on silica gel (300–400) with petroleum/EtOAc as eluent. Optical rotations were measured on a polarimeter with a sodium lamp. HRMS were measured on a LTQ-Orbitrap-XL apparatus. IR spectra were recorded using film on a Fourier Transform Infrared Spectrometer. NMR spectra were recorded at 400 MHz or 600 MHz, and chemical shifts are reported in δ (ppm) referenced to an internal TMS standard for ^{1}H NMR and $CDCl_3$ (77.16 ppm) for ^{13}C NMR.

General Procedure for the Synthesis of 4

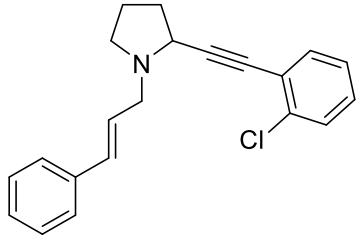
Amino acids **1** (1.5 mmol), terminal alkyne **3** (1.5 mmol) and $ZnBr_2$ (0.2 mmol) were dissolved in dry toluene (5 mL) under Ar atmosphere. The mixture was heated to 120ºC and a solution of *α,β*-unsaturated aldehyde **2** (1.0 mmol) in toluene (2 mL) was slowly added over 12h. Then, the reaction was cooled and concentrated. The residue was purified by flash chromatography on silica gel (PE/EA =5:1 - 10:1) to give the desired product **4**.

1-Cinnamyl-2-(phenylethynyl)pyrrolidine (4aa)



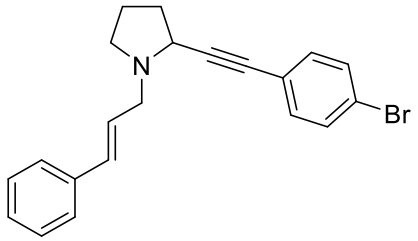
Eluent: PE/EA=5:1, Yellow oil (169 mg, 59%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.42 (m, 2H), 7.40-7.36 (m, 2H), 7.33-7.27 (m, 5H), 7.26-7.20 (m, 1H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.43-6.33 (m, 1H), 3.76-3.67 (m, 2H), 3.28 (dd, *J* = 12.8, 7.6 Hz, 1H), 2.97-2.89 (m, 1H), 2.67-2.58 (m, 1H), 2.27-2.18 (m, 1H), 2.10-1.93 (m, 2H), 1.90-1.80 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 132.7, 131.8, 128.6, 128.3, 128.2, 128.1, 127.5, 127.0, 126.5, 123.3, 88.4, 85.2, 55.5, 54.9, 51.9, 31.9, 22.2 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{21}N^+$: 288.1747, found: 288.1752.

2-((2-Chlorophenyl)ethynyl)-1-cinnamylpyrrolidine (4ab)



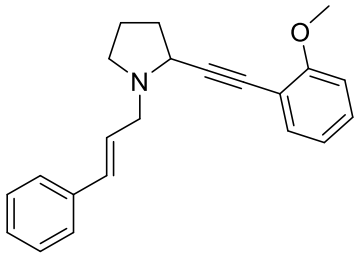
Eluent: PE/EA=5:1, Yellow oil (186 mg, 58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.20 (m, 9H), 6.59 (d, *J* = 15.6 Hz, 1H), 6.40-6.28 (m, 1H), 3.72-3.65 (m, 1H), 3.64-3.56 (m, 1H), 3.27-3.18 (m, 1H), 2.97-2.86 (m, 1H), 2.59-2.47 (m, 1H), 2.25-2.14 (m, 1H), 2.07-1.90 (m, 2H), 1.87-1.78 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 134.1, 133.1, 132.5, 128.7, 127.5, 127.3, 126.5, 121.9, 89.9, 83.8, 55.8, 83.2, 55.8, 54.9, 52.1, 31.9, 22.3 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{21}ClN^+$: 322.1357, found: 322.1359.

2-((4-Bromophenyl)ethynyl)-1-cinnamylpyrrolidine (4ac)



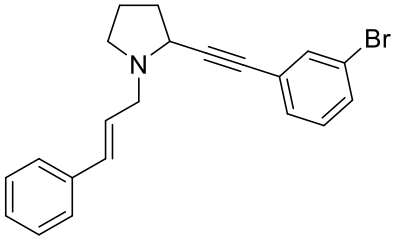
Eluent: PE/EA=5:1, Yellow oil (186 mg, 51%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.35 (m, 4H), 7.34-7.20 (m, 5H), 6.59 (d, *J* = 15.6 Hz, 1H), 6.44-6.34 (m, 1H), 3.73-3.65 (m, 1H), 3.63-3.55 (m, 1H), 3.28-3.17 (m, 1H), 2.98-2.86 (m, 1H), 2.60-2.51 (m, 1H), 2.26-2.13 (m, 1H), 2.07-1.75 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 133.3, 132.5, 131.6, 128.7, 127.6, 127.3, 126.5, 122.4, 122.3, 90.2, 83.9, 55.8, 54.9, 52.2, 31.9, 22.3 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{21}BrN^+$: 366.0852, 368.0831 found: 366.0860, 368.0840.

1-Cinnamyl-2-((2-methoxyphenyl)ethynyl)pyrrolidine (4ad)



Eluent: PE/EA=5:1, Yellow oil (209 mg, 66%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.35 (m, 3H), 7.33-7.18 (m, 4H), 6.93-6.80 (m, 2H), 6.62 (d, *J* = 15.6 Hz, 1H), 6.44-6.34 (m, 1H), 3.86 (s, 3H), 3.76-3.67 (m, 2H), 3.34-3.25 (m, 1H), 2.94-2.85 (m, 1H), 2.65-2.57 (m, 1H), 2.25-2.14 (m, 1H), 2.11-2.04 (m, 1H), 2.00-1.92 (m, 1H), 1.87-1.79 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 133.7, 132.7, 129.5, 128.6, 127.5, 126.5, 120.5, 110.8, 92.5, 81.5, 55.9, 55.3, 55.0, 51.7, 31.9, 22.2 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{24}NO^+$: 318.1852, found: 318.1858.

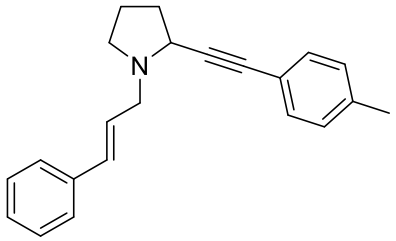
2-((3-Bromophenyl)ethynyl)-1-cinnamylpyrrolidine (4ae)



Eluent: PE/EA=5:1, Yellow oil (245 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.45-7.28 (m, 6H), 7.25-7.20 (m, 1H), 7.18-7.13 (m,

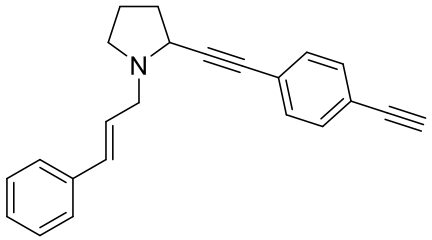
1H), 6.60 (d, *J* = 15.6 Hz, 1H), 6.43-6.31 (m, 1H), 3.72-3.60 (m, 2H), 3.29-3.20 (m, 1H), 2.96-2.85 (m, 1H), 2.63-2.54 (m, 1H), 2.26-2.17 (m, 1H), 2.08-1.93 (m, 2H), 1.90-1.80 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 134.6, 132.8, 131.3, 130.4, 129.8, 128.7, 127.6, 126.9, 126.5, 125.4, 122.2, 90.1, 83.7, 55.6, 54.8, 52.0, 31.9, 22.3 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{21}BrN^+$: 366.0852, 368.0831 found: 366.0861, 368.0843.

1-Cinnamyl-2-(*p*-tolylethynyl)pyrrolidine (4af)



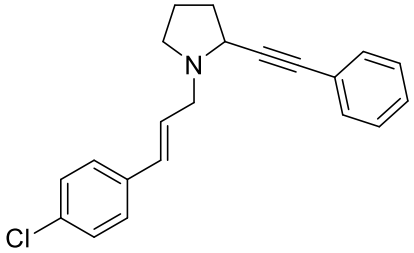
Eluent: PE/EA=5:1, Yellow oil (202 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.28 (m, 6H), 7.23-7.20 (m, 1H), 7.12-7.05 (m, 2H), 6.60 (d, *J* = 15.6 Hz, 1H), 6.43-6.34 (m, 1H), 3.75-3.58 (m, 2H), 3.26 (dd, *J* = 13.2, 7.6 Hz, 1H), 2.96-2.87 (m, 1H), 2.65-2.56 (m, 1H), 2.34 (s, 3H), 2.25-2.16 (m, 1H), 2.10-1.93 (m, 2H), 1.88-1.76 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 137.2, 132.7, 131.7, 129.1, 128.6, 127.5, 127.1, 126.5, 120.3, 87.6, 85.2, 55.5, 54.9, 51.9, 31.9, 22.2, 21.5 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{24}N^+$: 302.1903, found: 302.1909.

1-Cinnamyl-2-((4-ethynylphenyl)ethynyl)pyrrolidine (4ag)



Eluent: PE/EA=5:1, Yellow oil (109 mg, 35%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.36 (m, 6H), 7.32-7.28 (m, 2H), 7.24-7.20 (m, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.41-6.33 (m, 1H), 3.72-3.64 (m, 2H), 3.28 (dd, *J* = 13.2, 7.6 Hz, 1H), 3.15 (s, 1H), 2.92 (ddd, *J* = 12.4, 8.4, 3.6 Hz, 1H), 2.64-2.56 (m, 1H), 2.27-2.18 (m, 1H), 2.07-1.93 (m, 2H), 1.89-1.80 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 132.7, 132.1, 131.7, 128.7, 127.6, 127.2, 126.5, 124.0, 121.8, 90.9, 84.5, 83.4, 78.8, 55.7, 54.9, 52.1, 31.9, 22.3 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{22}N^+$: 312.1747, found: 312.1751.

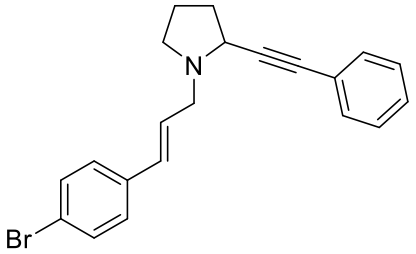
(*E*)-1-(3-(4-Chlorophenyl)allyl)-2-(phenylethynyl)pyrrolidine (4ah)



Eluent: PE/EA=5:1, Yellow oil (157 mg, 49%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.40 (m, 2H), 7.32-7.23 (m, 7H), 6.55 (d, *J* = 16.0 Hz, 1H),

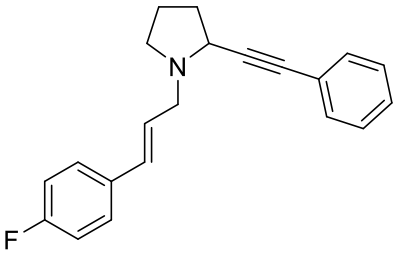
6.40-6.31 (m, 1H), 3.72-3.58 (m, 2H), 3.25 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.96-2.88 (m, 1H), 2.62-2.53 (m, 1H), 2.25-2.17 (m, 1H), 2.10-1.93 (m, 2H), 1.90-1.80 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 133.1, 131.9, 131.2, 128.8, 128.4, 128.2, 128.1, 127.7, 123.4, 88.7, 85.1, 55.6, 55.0, 52.1, 32.0, 22.3 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{21}ClN^+$: 322.1357, found: 322.1363.

(*E*)-1-(3-(4-Bromophenyl)allyl)-2-(phenylethynyl)pyrrolidine (4ai)



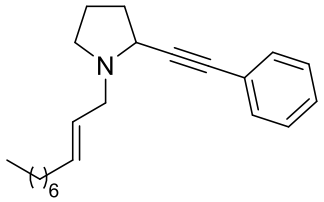
Eluent: PE/EA=5:1, Yellow oil (186 mg, 51%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.38 (m, 4H), 7.31-7.20 (m, 5H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.43-6.32 (m, 1H), 3.72-3.60 (m, 2H), 3.25 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.96-2.87 (m, 1H), 2.61-2.53 (m, 1H), 2.25-2.17 (m, 1H), 2.10-1.92 (m, 2H), 1.90-1.78 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 131.8, 131.7, 131.3, 128.4, 128.2, 128.1, 128.0, 123.4, 121.2, 88.7, 85.1, 55.6, 55.0, 52.1, 32.0, 22.3 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{21}BrN^+$: 366.0852, 368.0831 found: 366.0858, 368.0834.

(*E*)-1-(3-(4-Fluorophenyl)allyl)-2-(phenylethynyl)pyrrolidine (4aj)



Eluent: PE/EA=5:1, Yellow oil (204 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.41 (m, 2H), 7.36-7.27 (m, 5H), 7.02-6.95 (m, 2H), 6.56 (d, *J* = 15.6 Hz, 1H), 6.34-6.26 (m, 1H), 3.72-3.64 (m, 2H), 3.26 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.96-2.89 (m, 1H), 2.64-2.56 (m, 1H), 2.25-2.17 (m, 1H), 2.10-2.03 (m, 1H), 2.02-1.93 (m, 1H), 1.90-1.82 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (*J* = 244.8 Hz), 133.4, 133.4, 131.8, 131.4, 128.4, 128.1, 128.0, 127.9, 127.1, 123.4, 115.6, 115.4, 88.6, 85.1, 55.6, 54.9, 52.0, 31.9, 22.2 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{21}NF^+$: 306.1653, found: 306.1659.

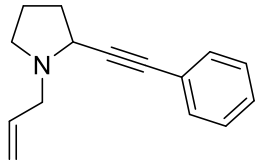
(*E*)-1-(Dec-2-en-1-yl)-2-(phenylethynyl)pyrrolidine (4ak)



Eluent: PE/EA=7:1, Yellow oil (192 mg, 62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.40 (m, 2H), 7.32-7.26 (m, 3H), 5.71-5.49 (m, 2H), 3.63-3.56 (m, 1H), 3.54-3.46 (m, 1H), 3.21-2.98 (m, 1H), 2.93-2.82 (m, 1H), 2.56-2.48 (m, 1H), 2.23-2.13 (m, 1H), 2.10-1.86 (m, 4H), 1.85-1.77

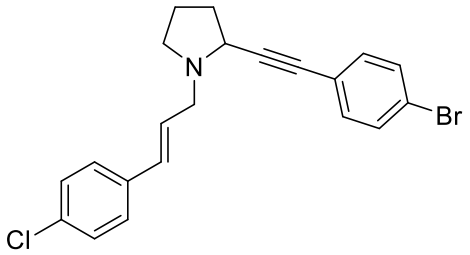
(m, 1H), 1.40-1.32 (m, 2H), 1.30-1.20 (m, 8H), 0.91-0.84 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.3, 132.9, 131.8, 128.3, 128.0, 126.8, 126.3, 123.5, 88.9, 88.8, 84.8, 55.4, 54.8, 54.7, 51.8, 51.7, 49.7, 32.0, 31.9, 29.4, 29.3, 29.3, 29.2, 22.7, 22.1, 14.2 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{32}N^+$: 310.2529, found: 310.2529.

1-Allyl-2-(phenylethynyl)pyrrolidine (4al)



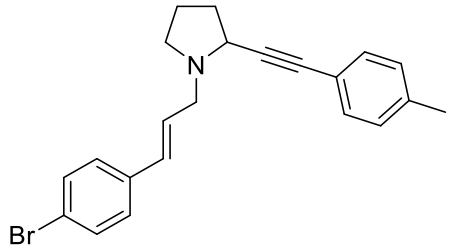
Eluent: PE/EA=5:1, Yellow oil (114 mg, 54%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.16 (m, 2H), 7.11-7.02 (m, 3H), 5.79-5.65 (m, 1H), 5.00 (d, J = 17.2 Hz, 1H), 4.89 (d, J = 10.0 Hz, 1H), 3.37-3.28 (m, 2H), 2.81 (dd, *J* = 13.2, 7.6 Hz, 1H), 2.65-2.58 (m, 1H), 2.30-2.23 (m, 1H), 2.00-1.89 (m, 1H), 1.83-1.52 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 131.8, 128.3, 128.1, 123.5, 117.4, 88.7, 84.8, 56.4, 54.9, 51.8, 31.9, 22.2 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{18}N^+$: 212.1434, found: 212.1432.

(*E*)-2-((4-Bromophenyl)ethynyl)-1-(3-(4-chlorophenyl)allyl)pyrrolidine (4am)



Eluent: PE/EA=5:1, Yellow oil (204 mg, 51%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.40 (m, 2H), 7.31-7.25 (m, 6H), 6.54 (dd, *J* = 16.0 Hz, 1H), 6.39-6.30 (m, 1H), 3.70-3.61 (m, 2H), 3.26 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.92 (ddd, *J* = 13.6, 8.8, 4.8 Hz, 1H), 2.59 (ddd, *J* = 15.5, 8.8, 6.8 Hz, 1H), 2.27-2.17 (m, 1H), 2.08-1.92 (m, 2H), 1.92-1.80 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 133.3, 133.2, 131.6, 131.4, 128.8, 127.9, 127.7, 122.4, 122.3, 89.9, 84.1, 55.6, 55.0, 52.2, 31.9, 22.3 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{20}BrClN^+$: 400.0462, 402.0442, found: 400.0472, 402.0447.

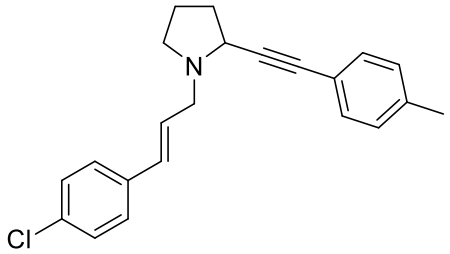
(*E*)-1-(3-(4-Bromophenyl)allyl)-2-(*p*-tolylethynyl)pyrrolidine (4an)



Eluent: PE/EA=5:1, Yellow oil (193 mg, 51%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.38 (m, 2H), 7.34-7.28 (m, 2H), 7.25-7.18 (m, 2H),

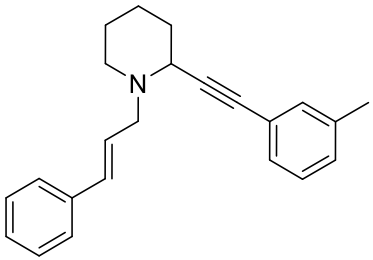
7.12-7.08 (m, 2H), 6.53 (d, *J* = 15.6 Hz, 1H), 6.42-6.33 (m, 1H), 3.71-3.63 (m, 2H), 3.26 (dd, *J* = 12.8, 7.6 Hz, 1H), 2.95-2.83 (m, 1H), 2.63-2.56 (m, 1H), 2.34 (s, 3H), 2.24-2.17 (m, 1H), 2.09-1.93 (m, 2H), 1.89-1.80 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 136.2, 131.7, 131.4, 129.1, 128.1, 128.0, 121.2, 120.2, 87.6, 85.3, 55.5, 55.0, 52.0, 32.0, 22.2, 21.6 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{23}BrN^+$: 380.1008, 382.0988, found: 380.1013, 382.0989.

(*E*)-1-(3-(4-Chlorophenyl)allyl)-2-(*p*-tolylethynyl)pyrrolidine (4ao)



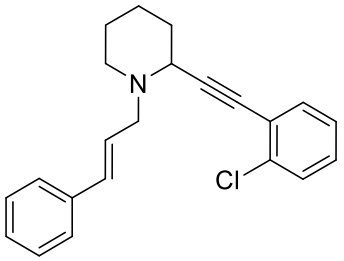
Eluent: PE/EA=5:1, Yellow oil (154 mg, 46%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.24 (m, 6H), 7.13-7.08 (m, 2H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.41-6.33 (m, 1H), 3.72-3.64 (m, 2H), 3.27 (dd, *J* = 13.2, 7.6 Hz, 1H), 2.91 (ddd, *J* = 14.0, 8.8, 5.2 Hz, 1H), 2.64-2.57 (m, 1H), 2.34 (s, 3H), 2.25-2.17 (m, 1H), 2.09-1.93 (m, 2H), 1.90-1.81 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 125.8, 133.1, 131.7, 131.4, 129.1, 128.8, 128.0, 127.7, 120.2, 87.6, 85.3, 55.5, 55.0, 52.0, 32.0, 22.2, 21.6 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{23}ClN^+$: 336.1514, found: 336.1518.

1-Cinnamyl-2-(*m*-tolylethynyl)piperidine (4ba)



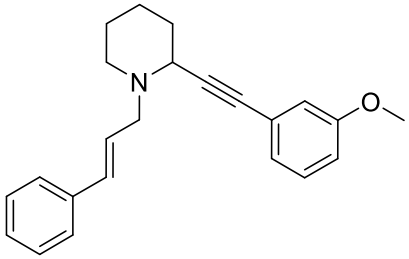
Eluent: PE/EA=6:1, Yellow oil (170 mg, 54%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.36 (m, 2H), 7.33-7.26 (m, 4H), 7.23-7.18 (m, 2H), 7.14-7.08 (m, 1H), 6.58 (d, *J* = 15.6 Hz, 1H), 6.36-6.24 (m, 1H), 3.90-3.81 (m, 1H), 3.45-3.22 (m, 2H), 2.68-2.55 (m, 2H), 2.33 (s, 3H), 1.91-1.82 (m, 2H), 1.73-1.55 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 137.2, 133.1, 132.4, 128.9, 128.6, 128.3, 127.5, 127.0, 126.5, 123.4, 87.0, 86.8, 58.9, 52.3, 49.4, 31.6, 25.9, 21.3, 21.0 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{26}N^+$: 316.2060, found: 316.2062.

2-((2-Chlorophenyl)ethynyl)-1-cinnamylpiperidine (4bb)



Eluent: PE/EA=6:1, Yellow oil (181 mg, 54%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.35 (m, 4H), 7.33-7.27 (m, 4H), 7.24-7.18 (m, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.34-6.25 (m, 1H), 3.90-3.83 (m, 1H), 3.45-3.35 (m, 1H), 3.33-3.25 (m, 1H), 2.65-2.56 (m, 2H), 1.93-1.82 (m, 2H), 1.71-1.54 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 134.0, 133.3, 133.1, 128.7, 128.7, 127.6, 126.8, 126.5, 122.0, 88.3, 85.8, 58.9, 52.3, 49.5, 31.5, 25.8, 21.0 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{23}ClN^+$: 336.1514, found: 336.1518.

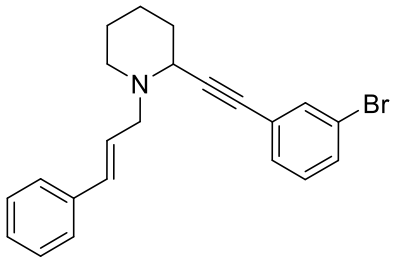
1-Cinnamyl-2-((3-methoxyphenyl)ethynyl)piperidine (4bc)



Eluent: PE/EA=6:1, Yellow oil (228 mg, 69%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.36 (m, 3H), 7.32-7.20 (m, 4H), 6.94-6.86 (m, 2H), 6.63 (d, *J* = 15.6 Hz, 1H), 6.37-6.28 (m ,1H), 3.96-3.93 (m, 1H), 3.89 (s, 3H), 3.43-3.31 (m, 2H), 2.73-2.56 (m, 2H), 1.95-1.86 (m, 2H), 1.85-1.51 (m,

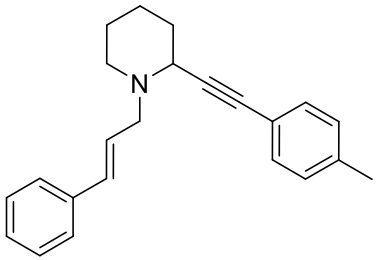
4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 137.4, 133.7, 133.2, 129.4, 128.6, 127.5, 127.1, 126.5, 120.5, 112.9, 110.9, 91.4, 83.0, 58.8, 55.9, 52.5, 49.3, 31.6, 26.0, 20.9 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{26}N^+$: 332.2009, found: 332.2012.

2-((3-Bromophenyl)ethynyl)-1-cinnamylpiperidine (4bd)



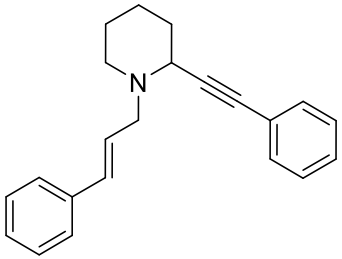
Eluent: PE/EA=6:1, Yellow oil (231 mg, 61%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.46-7.43 (m, 1H), 7.42-7.38 (m, 3H), 7.32-7.27 (m, 2H), 7.25-7.16 (m, 2H), 6.59 (d, *J* = 15.6 Hz, 1H), 6.35-6.26 (m, 1H), 3.91-3.86 (m, 1H), 3.44-3.35 (m, 1H), 3.32-3.24 (m, 1H), 1.91-1.76 (m, 3H), 1.74-1.55 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 134.6, 133.3, 131.2, 130.4, 129.9, 128.7, 127.6, 126.9, 126.5, 125.6, 122.2, 88.9, 85.4, 59.0, 52.3, 49.4, 31.5, 25.8, 21.0 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{23}BrN^+$: 380.1008, 382.0988 found: 380.1018, 382.0996.

1-Cinnamyl-2-(*p*-tolylethynyl)piperidine (4be)



Eluent: PE/EA=10:1, Yellow oil (233 mg, 74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.35 (m, 4H), 7.32-7.26 (m, 2H), 7.23-7.20 (m, 1H), 7.14-7.09 (m, 2H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.35-6.26 (m, 1H), 3.89-3.82 (m, 1H), 3.44-3.35 (m, 1H), 3.35-3.28 (m, 1H), 2.68-2.57 (m, 2H), 2.34 (s, 3H), 1.91-1.84 (m, 2H), 1.75-1.54 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 137.1, 133.1, 131.7, 129.1, 128.6, 127.4, 126.9, 126.4, 120.4, 86.8, 86.3, 58.8, 52.2, 49.3, 31.6, 25.8, 21.5, 20.9 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{26}N^+$: 316.2060, found: 316.2062.

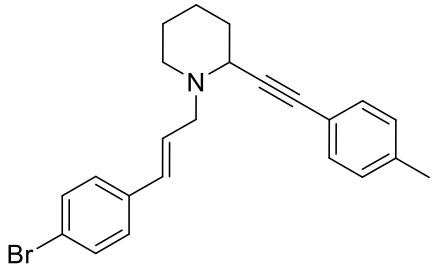
1-Cinnamyl-2-(phenylethynyl)piperidine (4bf)



Eluent: PE/EA=6:1, Yellow oil (211 mg, 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.44 (m, 2H), 7.41-7.37 (m, 2H), 7.35-7.27 (m, 5H),

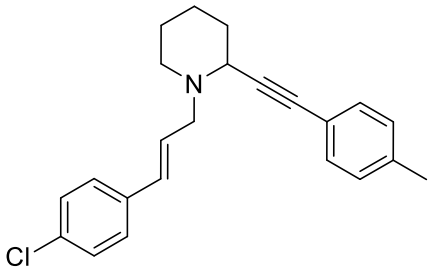
7.24-7.22 (m, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.35-6.26 (m, 1H), 3.93-3.85 (m, 1H), 3.49-3.36 (m, 1H), 3.34-3.26 (m, 1H), 2.68-2.57 (m, 2H), 1.91-1.84 (m, 2H), 1.78-1.53 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 133.3, 131.8, 128.6, 128.4, 128.3, 128.0, 127.5, 126.8, 126.5, 123.5, 87.1, 86.9, 58.9, 52.2, 49.4, 31.5, 25.8, 20.9 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{24}N^+$: 302.1903, found: 302.1906.

(*E*)-1-(3-(4-Bromophenyl)allyl)-2-(*p*-tolylethynyl)piperidine (4bg)



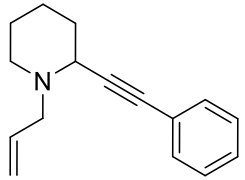
Eluent: PE/EA=6:1, Yellow oil (150 mg, 38%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.40 (m, 2H), 7.39-7.33 (m, 2H), 7.27-7.21 (m, 2H), 7.15-7.08 (m, 2H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.35-6.25 (m, 1H), 3.90-3.82 (m, 1H), 3.42-3.24 (m, 2H), 2.67-2.55 (m, 2H), 2.36 (s, 3H), 1.92-1.85 (m, 2H), 1.77-1.70 (m, 1H), 1.66-1.56 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 136.2, 132.0, 131.7, 129.2, 128.0, 127.8, 121.3, 120.4, 87.0, 86.2, 58.8, 52.4, 49.4, 31.6, 25.8, 21.6, 20.9 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{25}BrN^+$: 394.1165, 396.1144, found: 394.1165, 396.1174.

(*E*)-1-(3-(4-Chlorophenyl)allyl)-2-(*p*-tolylethynyl)piperidine (4bh)



Eluent: PE/EA=6:1, Yellow oil (140 mg, 40%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.21 (m, 6H), 7.15-7.07 (m, 2H), 6.54 (d, *J* = 15.6 Hz, 1H), 6.34-6.23 (m, 1H), 3.90-3.81 (m, 1H), 3.43-3.35 (m, 1H), 3.34-3.25 (m, 1H), 2.67-2.55 (m, 2H), 2.36 (s, 3H), 1.93-1.83 (m, 2H), 1.71-1.51 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 135.8, 133.1, 131.9, 131.7, 129.2, 128.8, 127.8, 127.7, 120.4, 87.0, 86.3, 58.8, 52.4, 49.4, 31.6, 25.9, 21.6, 20.9 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{25}ClN^+$: 350.1670, found: 350.1677.

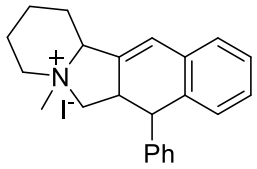
1-Allyl-2-(phenylethynyl)piperidine (4bi)



Eluent: PE/EA=5:1, Yellow oil (83 mg, 37%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.43 (m, 2H), 7.34-7.27 (m, 3H), 5.95-5.83 (m, 1H), 5.26 (d, *J* = 16.8 Hz, 1H), 5.16 (d, *J* = 10.0 Hz, 1H), 3.85-3.75 (m, 1H), 3.27-3.19 (m, 1H), 3.18-3.09 (m, 1H), 2.62-2.49 (m, 2H), 1.90-1.81 (m, 2H), 1.75-1.53 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 131.8, 128.4, 128.0, 123.6, 118.1, 87.3, 86.7, 59.7, 52.2, 49.3, 31.6, 25.9, 21.0

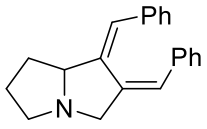
ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{20}N^+$: 226.1590, found: 226.1587.

5-Methyl-7-phenyl-2,3,4,5,6,6a,7,12b-octahydro-1*H*-benzo[*f*]pyrido[2,1-*α*]isoindol-5-ium iodide (10)



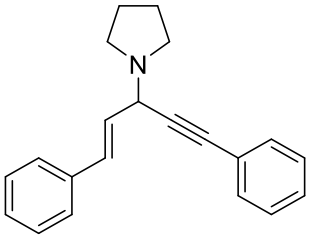
To a solution of **4bf** (300 mg, 1 mmol) in MeCN (10 mL) was added MeI (426 mg, 3 mmol), after being stirred for 12 h at room temperature, the reaction mixture was concentrated to give the **9** which was used without further purification. The iodide salt **9** was dissolved in a mixture of EtOH (1 mL) and 3 *N* KOH (1 mL) solution, then warmed to 90ºC and stirred for 6 h. After cooled, concentrated the **10** was recrystallized from absolute EtOH as white solid (310 mg, 70%); mp 257-259°C; ^{1}H NMR (400 MHz, DMSO-d_6/CCl_4) δ 7.53-7.40 (m, 4H), 7.34-7.28 (m, 3H), 7.24-7.19 (m, 1H), 7.17-7.13 (m, 1H), 6.80-6.75 (m, 1H), 4.56-4.48 (m, 1H), 4.25 (d, *J* = 16.4, 1H), 3.88-3.81 (m, 1H), 3.57-3.48 (m, 1H), 3.43-3.40 (m, 1H), 3.24 (s, 3H), 3.02 (dd, *J* = 14.4, 5.2 Hz, 1H), 2.80-2.70 (m, 1H), 2.23-2.14 (m, 1H), 2.01-1.93 (m, 2H), 1.73-1.60 (m, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6/CCl_4) δ 136.7, 135.4, 134.2, 133.6, 131.0, 128.9, 128.7, 127.9, 127.8, 127.5, 126.8, 125.1, 73.6, 68.0, 57.2, 46.7, 37.3, 30.9, 19.7, 19.6, 15.4 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M]^+$ Calcd for $C_{23}H_{26}N^+$: 316.2060, found: 316.2064.

1,2-Di((*E*)-benzylidene)hexahydro-1H-pyrrolizine (11)

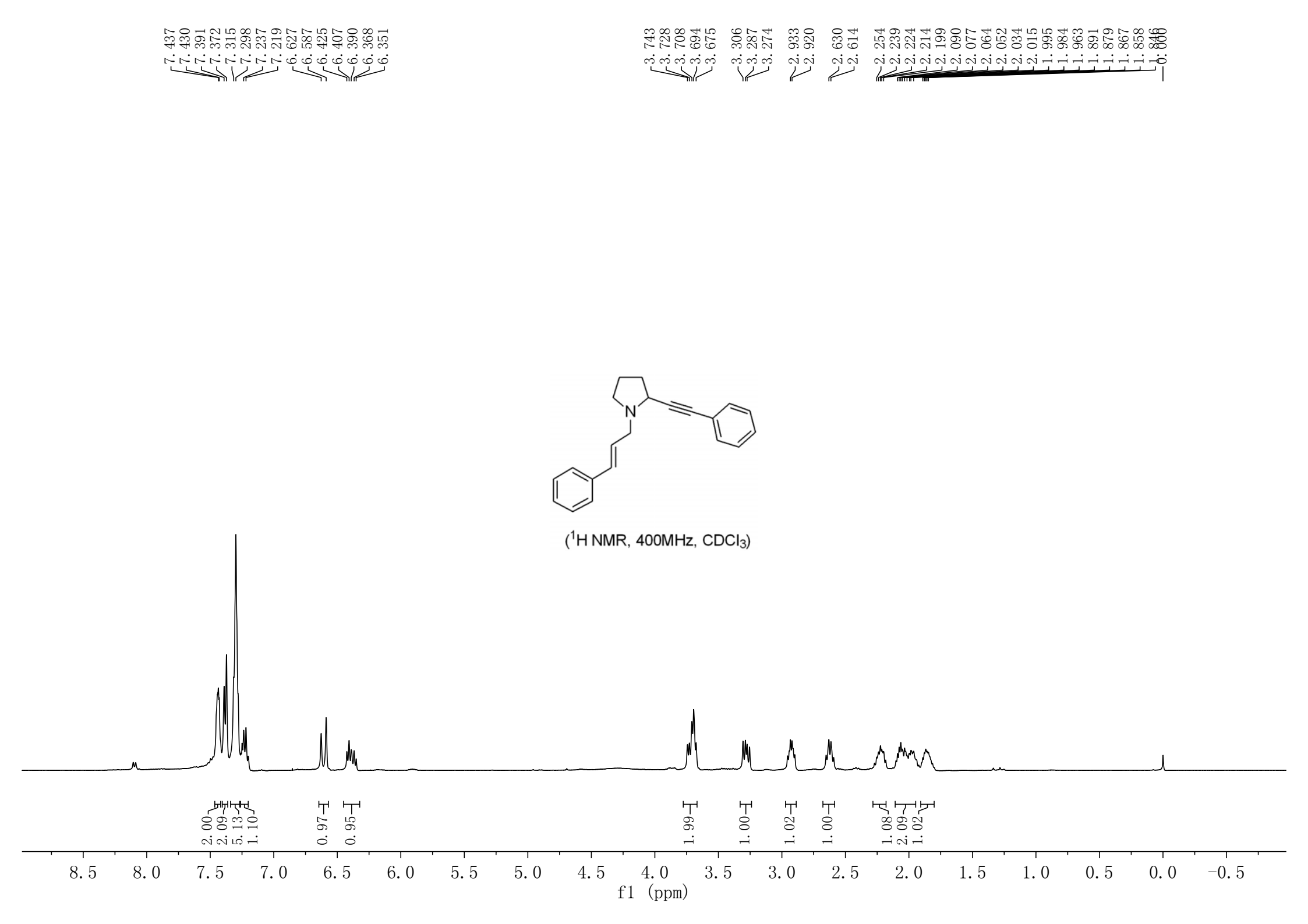


To a solution of **4aa** (287 mg, 1 mmol) in toluene (3 mL) was added $Pd(OAc)_2$ (45 mg, 0.2 mmol) and (p-MePh)$_3$P (92 mg, 0.3 mmol) under N_2 protection, then the reaction mixture was warmed to 60°C and stirred for 6 h. After cooled, concentrated the residue was purified by flash chromatography on silica gel (DCM/MeOH/TEA=50:1:0.1) to give the **11** as yellow oil (242 mg, 84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.34 (m, 5H), 7.32-7.28 (m, 2H), 7.25-7.22 (m, 3H), 6.98-6.94 (m, 2H), 4.63-4.57 (m, 1H), 4.16-4.09 (m, 1H), 3.74-3.68 (m, 1H), 3.08-3.02 (m, 1H), 2.73-2.65 (m, 1H), 2.34-2.27 (m, 1H), 1.84-1.77 (m, 2H), 1.65-1.57 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 140.8, 137.6, 137.0, 129.1, 129.0, 128.6, 128.5, 127.0, 120.2, 120.1, 66.7, 56.9, 54.8, 31.8, 25.3 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M]^+$ Calcd for $C_{21}H_{22}N^+$: 288.1747, found: 288.1747.

(*E*)-1-(1,5-Diphenylpent-1-en-4-yn-3-yl)pyrrolidine (5)



Eluent: PE/EA=5:1, Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.47 (m, 2H), 7.45-7.41 (m, 2H), 7.35-7.30 (m, 5H), 7.27-7.23 (m, 1H), 6.86 (d, *J* = 16.0 Hz, 1H), 6.37 (dd, *J* = 15.6, 5.6 Hz, 1H), 4.52 (d, *J* = 6.0 Hz, 1H), 2.85-2.74 (m, 4H), 1.86-1.81 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 132.1, 132.0, 128.7, 128.4, 128.3, 128.2, 127.8, 126.8, 123.3, 87.3, 85.8, 56.9, 50.2, 23.7 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{21}N^+$: 288.1747, found: 288.1756.


7.437
7.430
7.391
7.372
7.315
7.298
7.237
7.219
6.627
6.587
6.425
6.407
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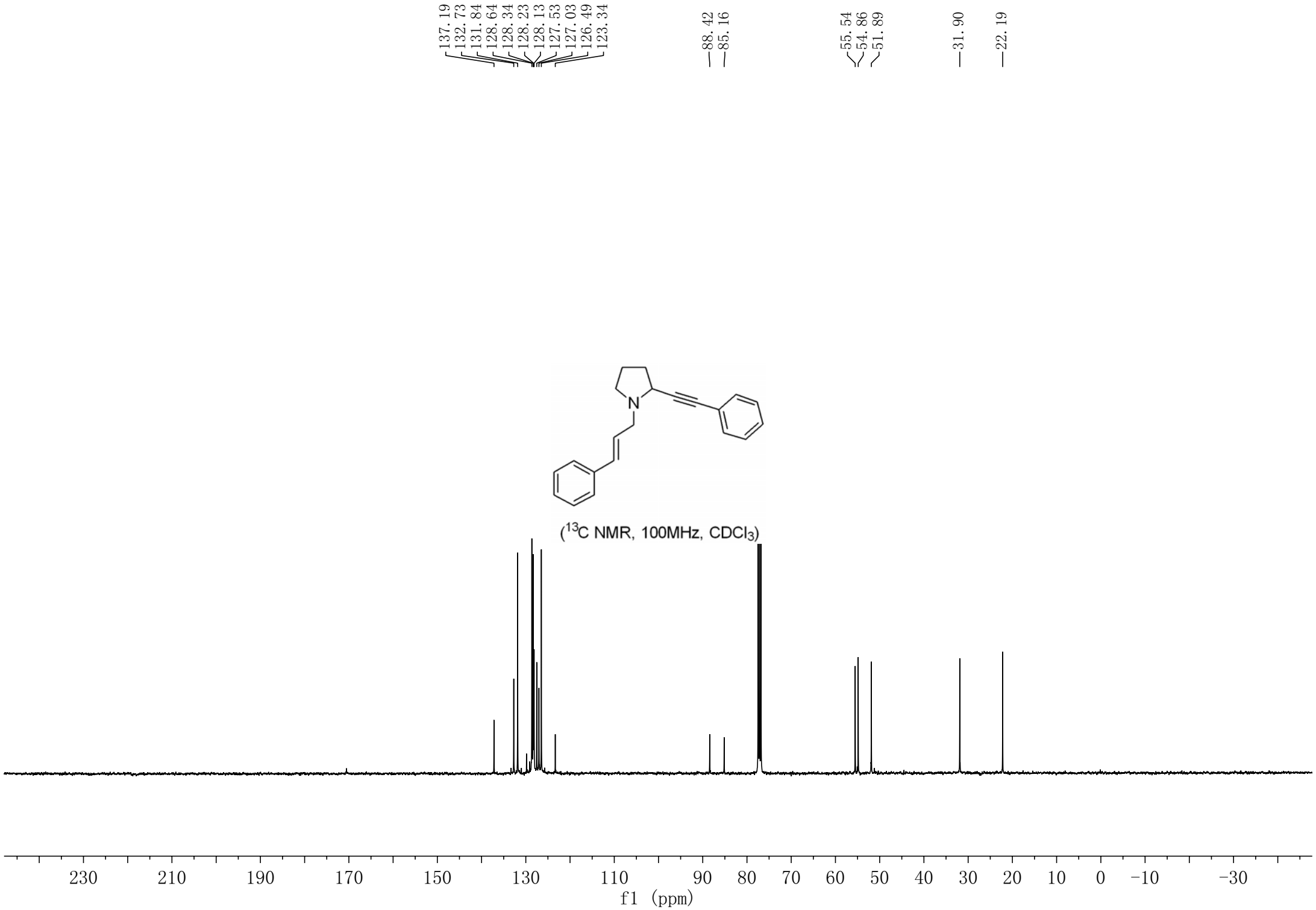
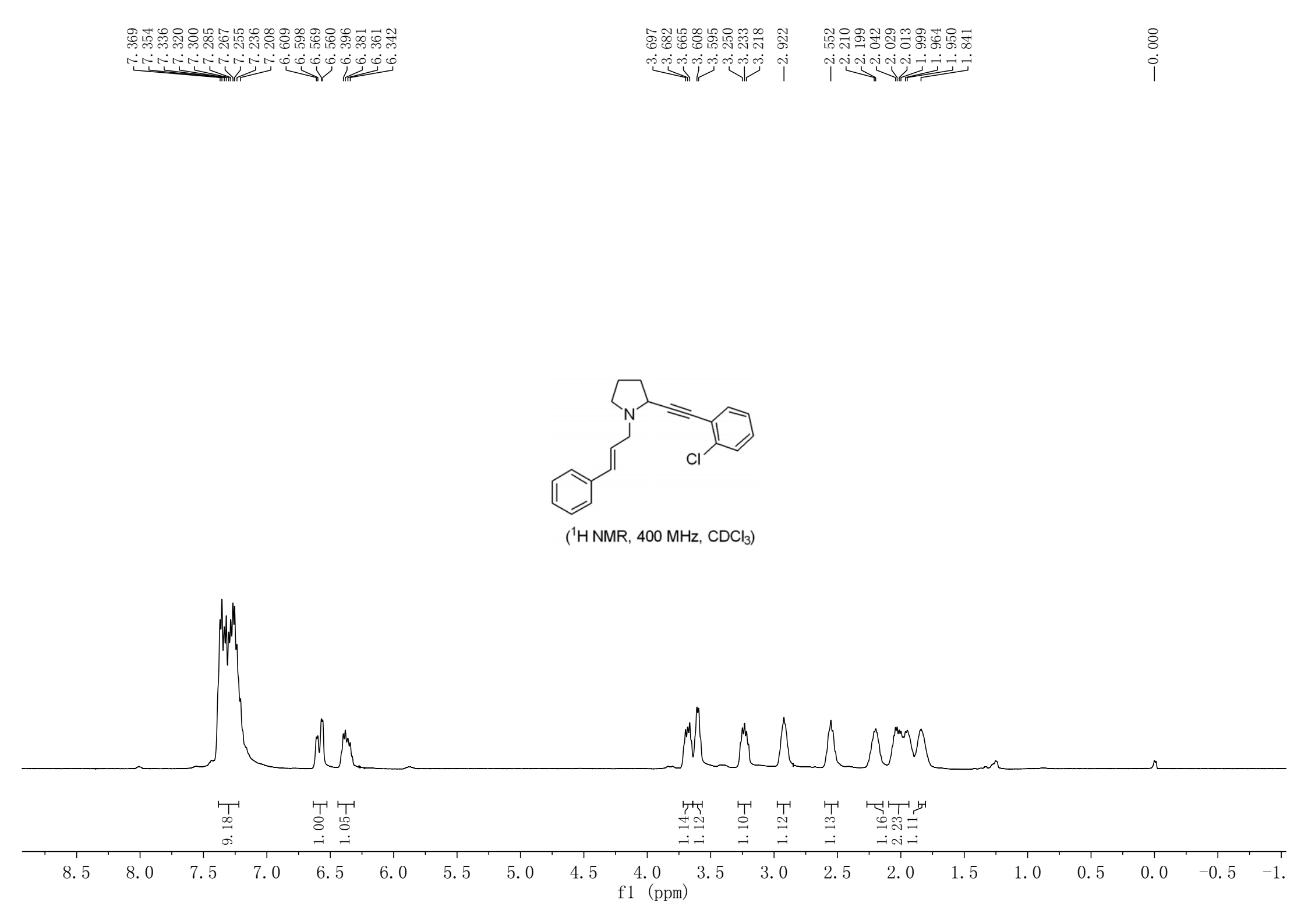
6.368
6.351
3.743
3.728
3.708
3.694
3.675
3.306
3.287
3.274
2.933
2.920
2.630
2.614
2.254
2.239
2.224
2.214
2.199
2.090
2.077
2.064
2.052
2.034
2.015
1.995
1.984
1.963
1.891
1.879
1.867
1.858
1.846
0.000
N
(1H NMR, 400MHz, CDCl3)
2.00
2.09
5.13
1.10
0.97
0.95
1.99
1.00
1.02
1.00
1.08
2.09
1.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


137.19
132.73
131.84
128.64
128.34
128.23
128.13
127.53
127.03
126.49
123.34
88.42
85.16
55.54
54.86
51.89
31.90
22.19
N
(^{13}C NMR, 100MHz, $CDCl_3$)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)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7.354
7.336
7.320
7.300
7.285
7.267
7.255
7.236
7.208
6.609
6.598
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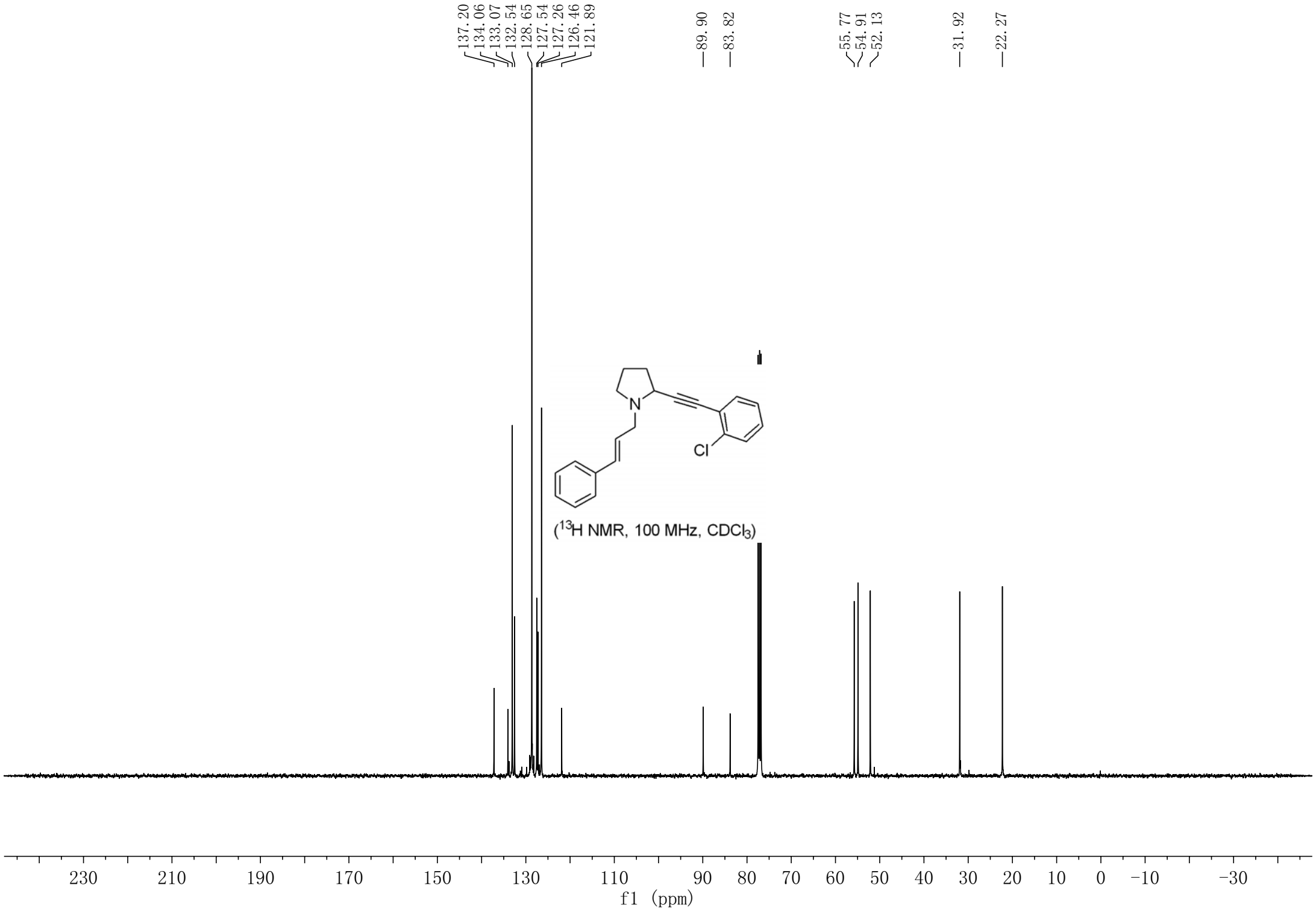
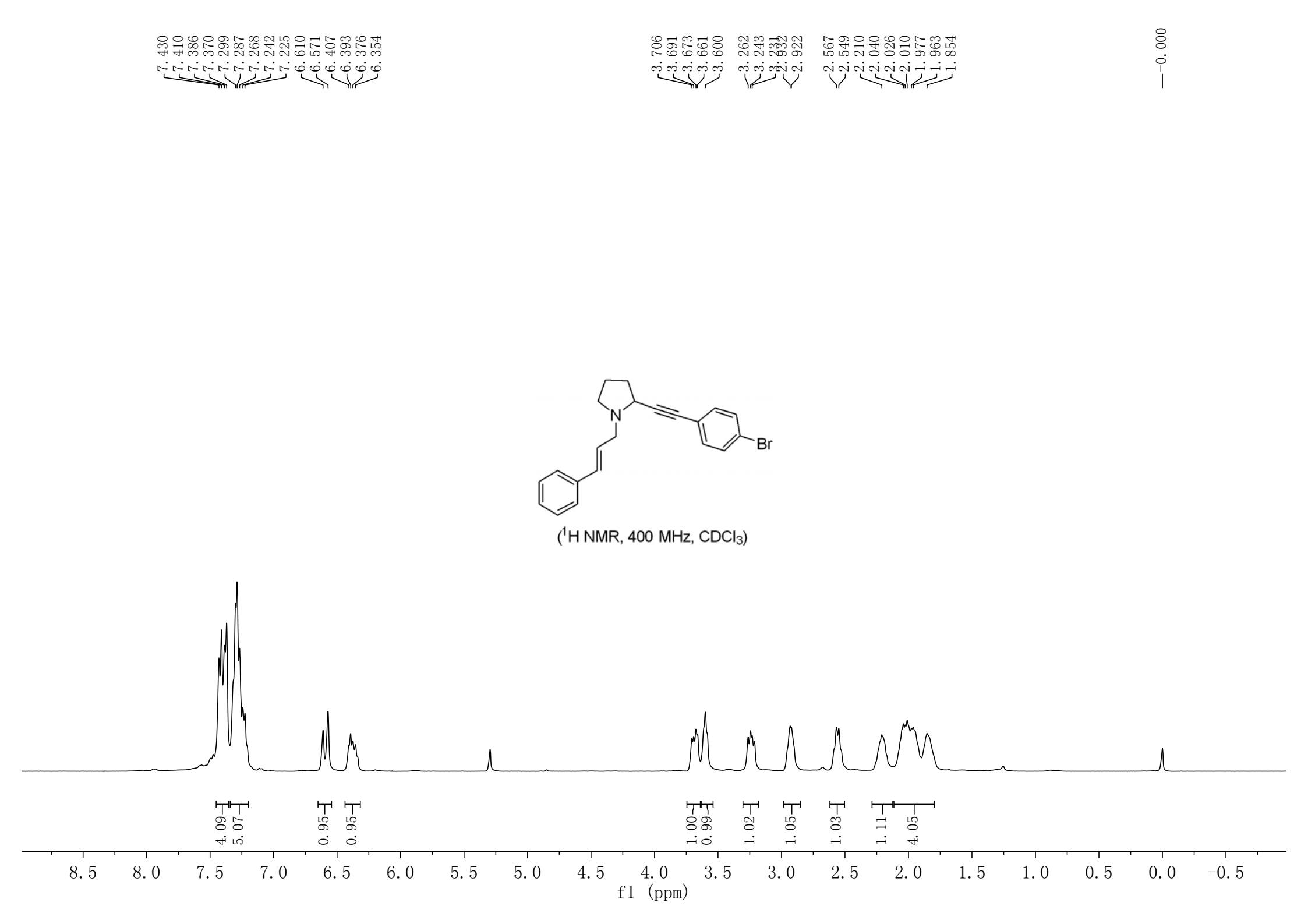
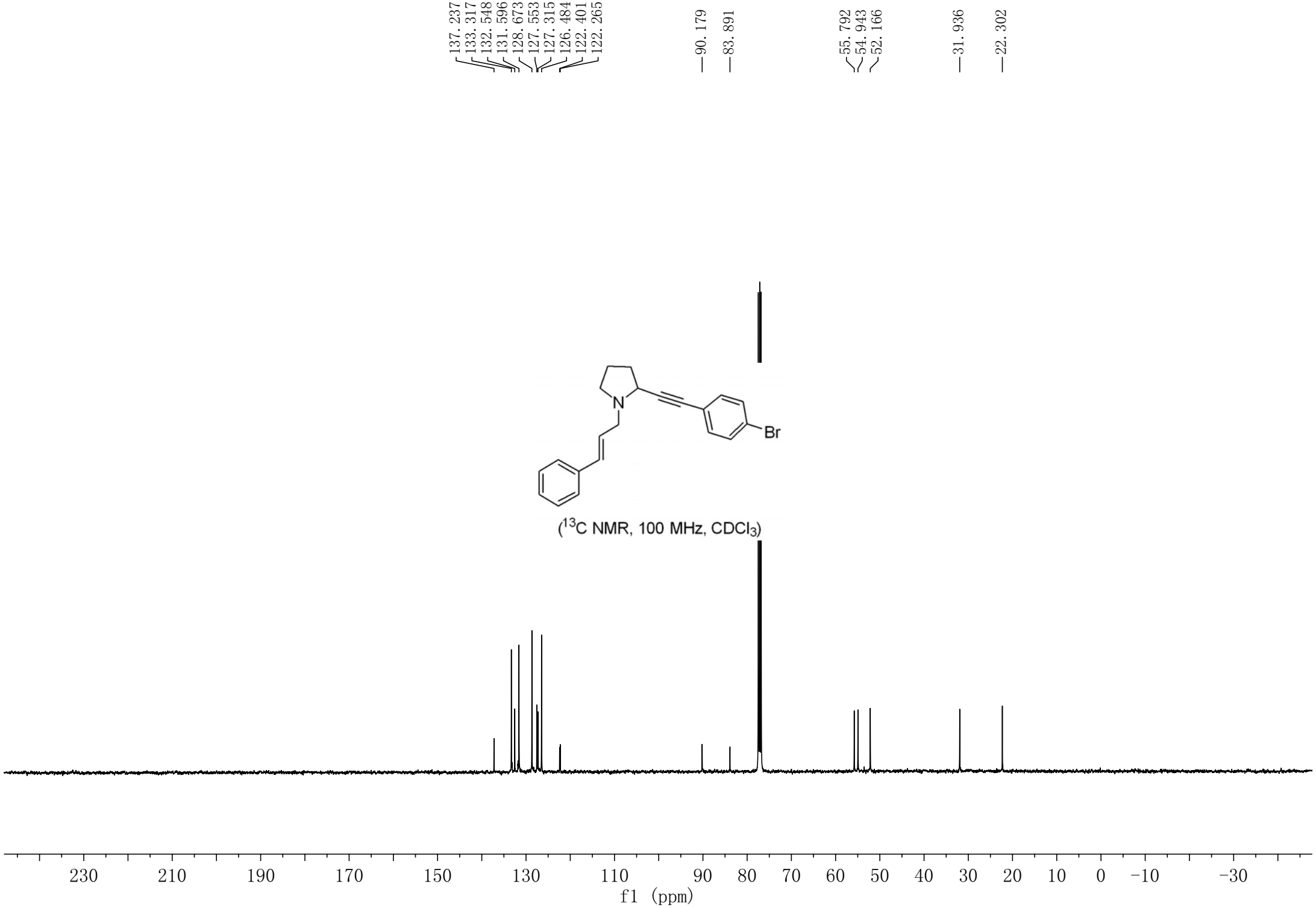
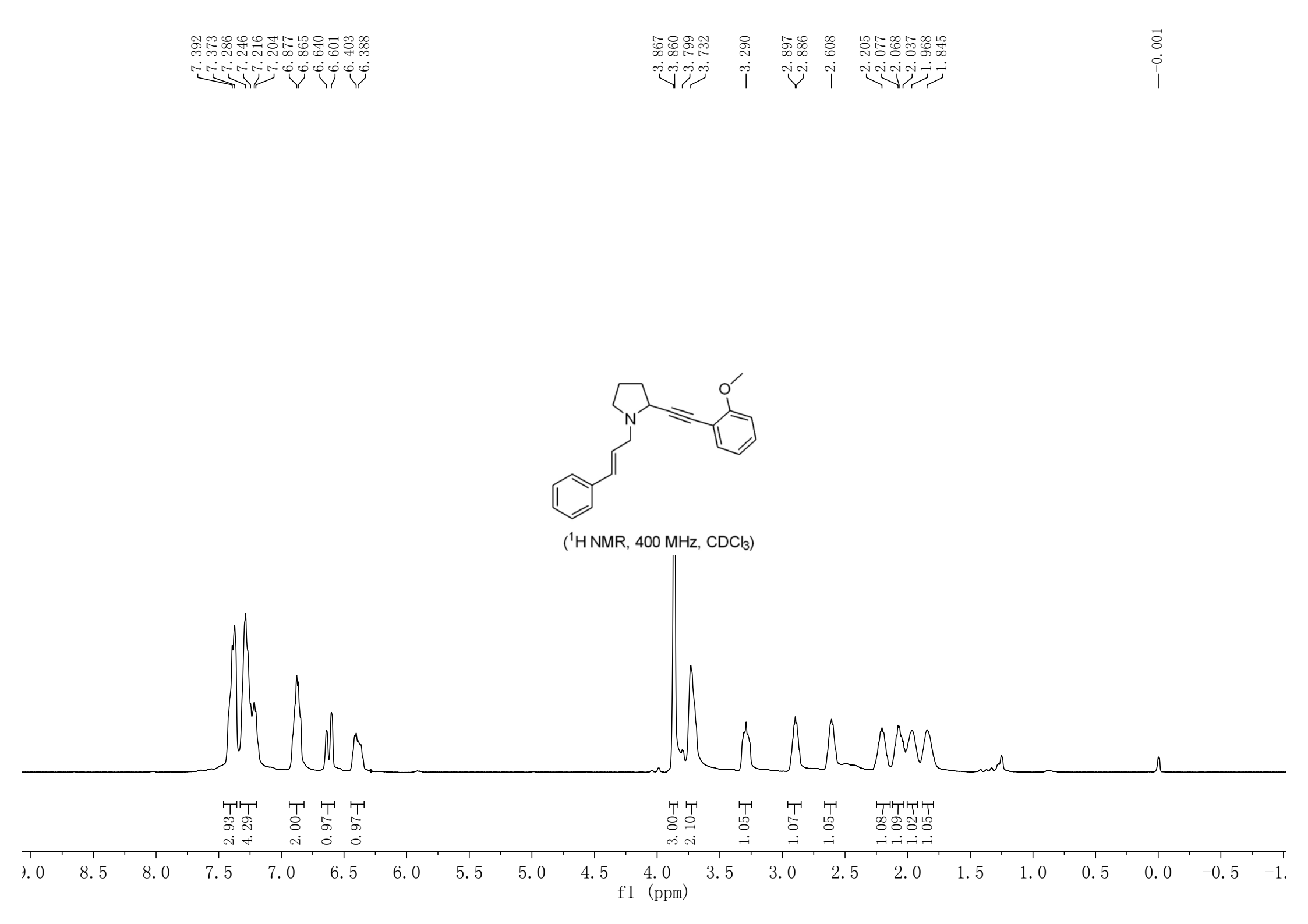
6.560
6.396
6.381
6.361
6.342
3.697
3.682
3.665
3.608
3.595
3.250
3.233
3.218
2.922
2.552
2.210
2.199
2.042
2.029
2.013
1.999
1.964
1.950
1.841
0.000
N
Cl
(1H NMR, 400 MHz, CDCl3)
9.18
1.00
1.05
1.14
1.12
1.10
1.12
1.13
1.16
2.23
1.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)

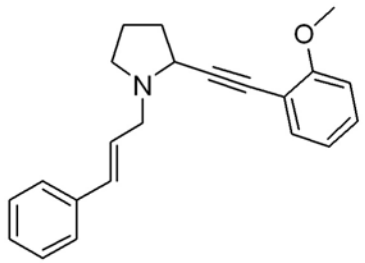

137.20
134.06
133.07
132.54
128.65
127.54
127.26
126.46
121.89
89.90
83.82
55.77
54.91
52.13
31.92
22.27
N
Cl
(^{13}H NMR, 100 MHz, $CDCl_3$)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)


7.430
7.410
7.386
7.370
7.299
7.287
7.268
7.242
7.225
6.610
6.571
6.407
6.393
6.376
6.354
3.706
3.691
3.673
3.661
3.600
3.262
3.243
3.231
2.922
2.567
2.549
2.210
2.040
2.026
2.010
1.977
1.963
1.854
0.000
N
Br
(1H NMR, 400 MHz, CDCl3)
4.09
5.07
0.95
0.95
1.00
0.99
1.02
1.05
1.03
1.11
4.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

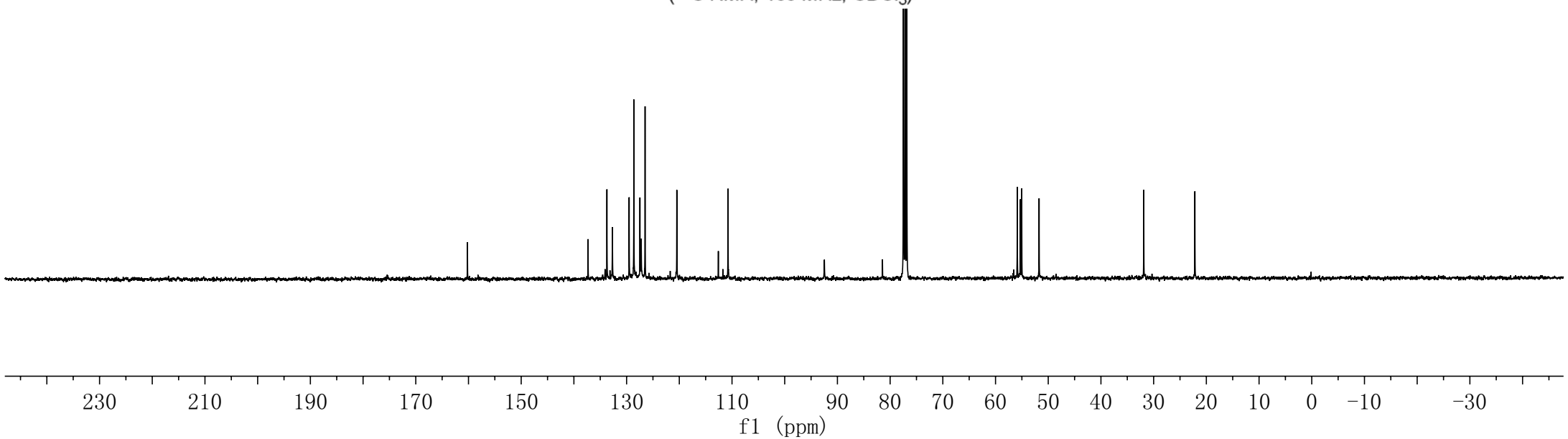

137.237
133.317
132.548
131.596
128.673
127.553
127.315
126.484
122.401
122.265
90.179
83.891
55.792
54.943
52.166
31.936
22.302
N
Br
(^{13}C NMR, 100 MHz, $CDCl_3$)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)

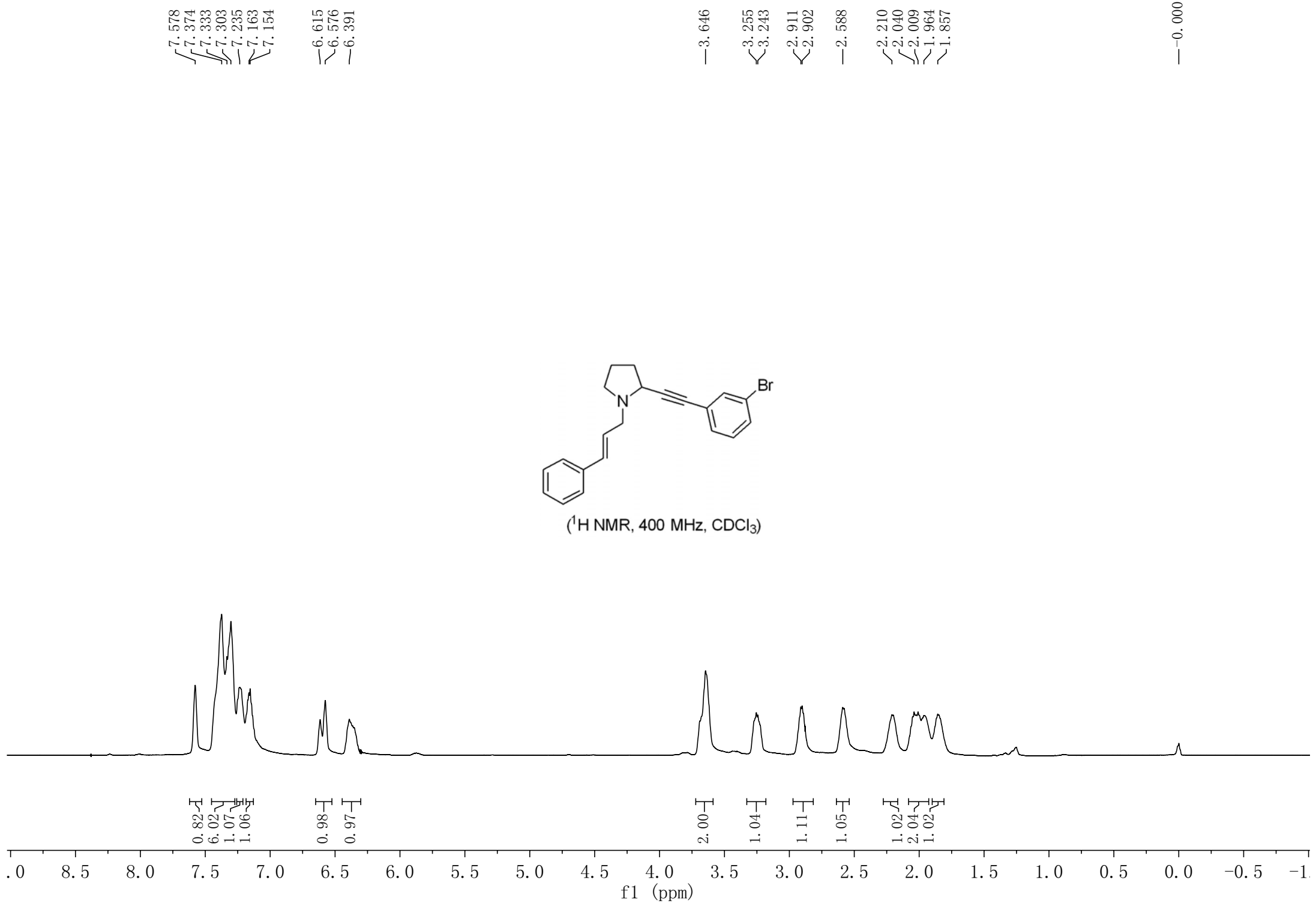

7.392
7.373
7.286
7.246
7.216
7.204
6.877
6.865
6.640
6.601
6.403
6.388
3.867
3.860
3.799
3.732
3.290
2.897
2.886
2.608
2.205
2.077
2.068
2.037
1.968
1.845
-0.001
N
O
(1H NMR, 400 MHz, CDCl3)
2.93
4.29
2.00
0.97
0.97
3.00
2.10
1.05
1.07
1.05
1.08
1.09
1.02
1.05
f1 (ppm)

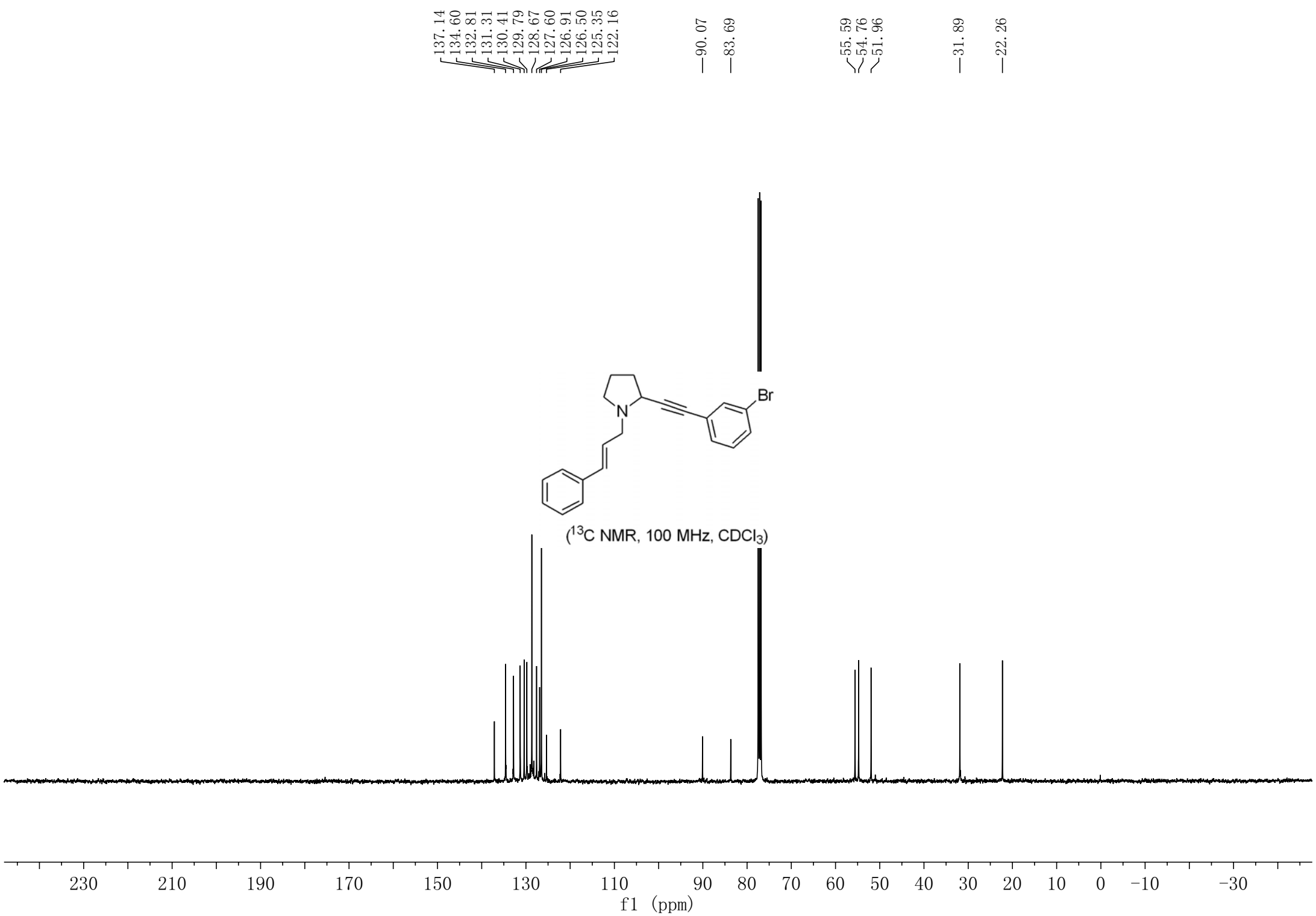
160.196
133.732
132.691
129.518
128.618
127.469
126.492
120.471
110.754
92.474
81.454
55.871
55.288
55.027
51.732
31.874
22.175

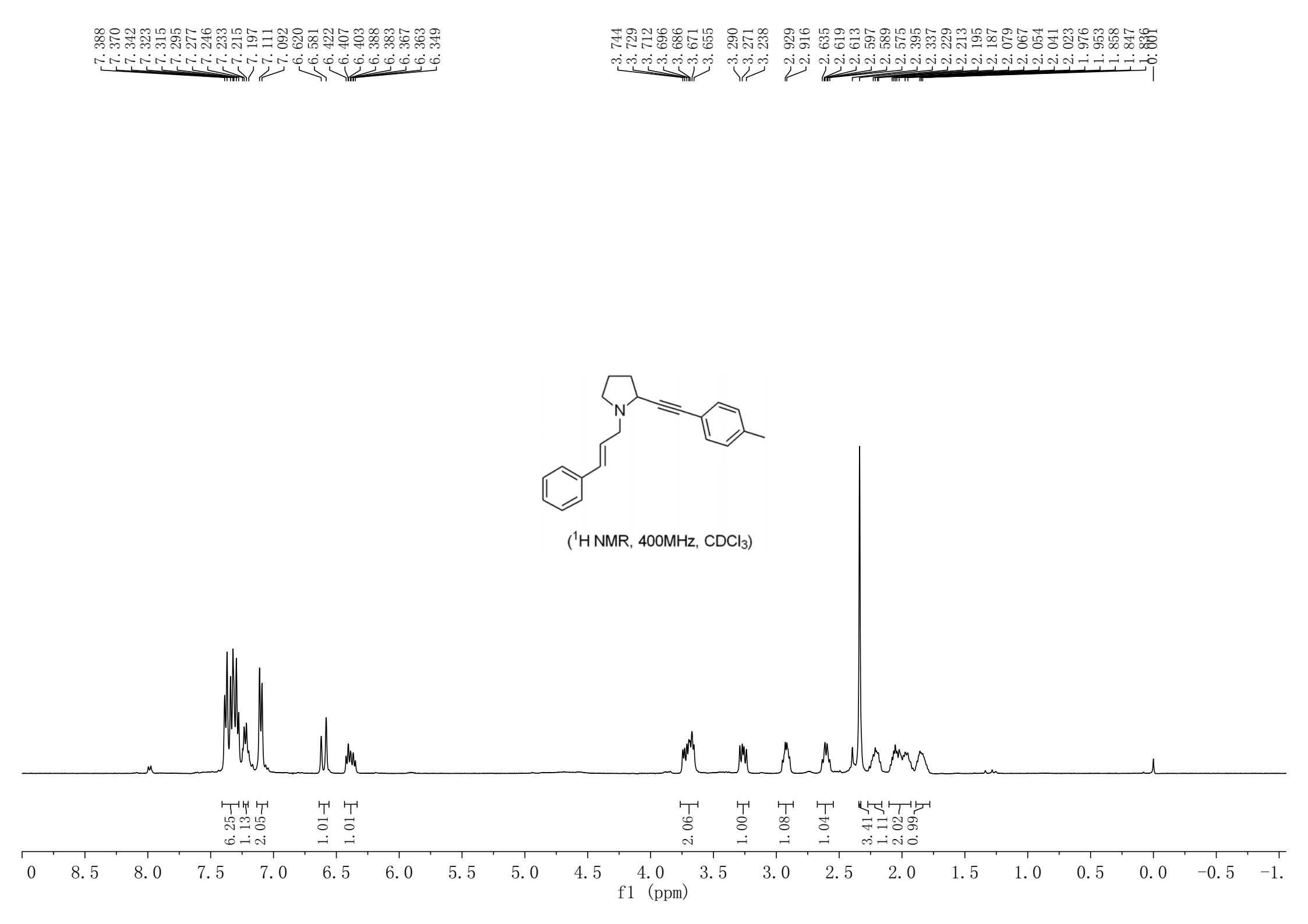


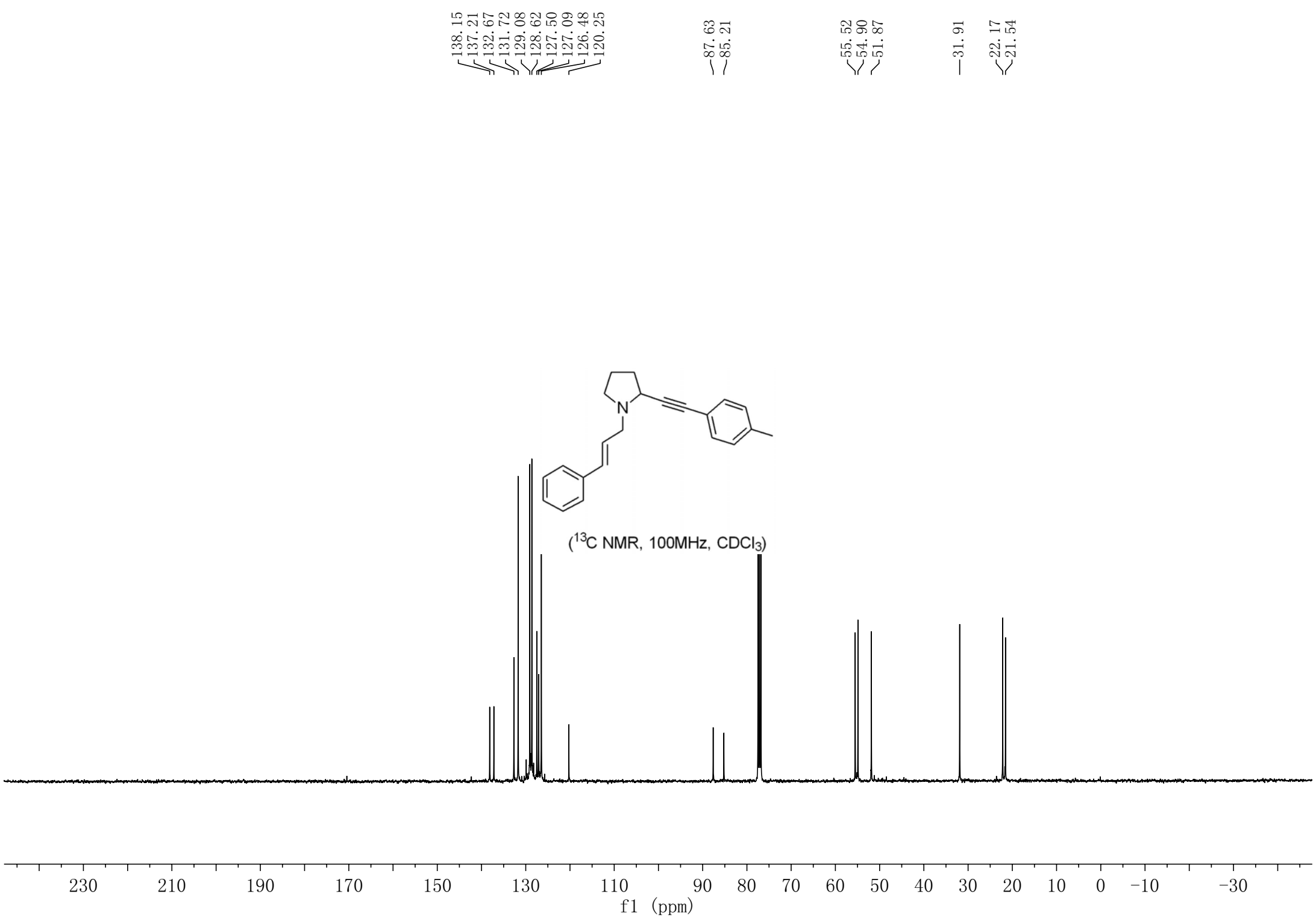
(^{13}C NMR, 100 MHz, $CDCl_3$)

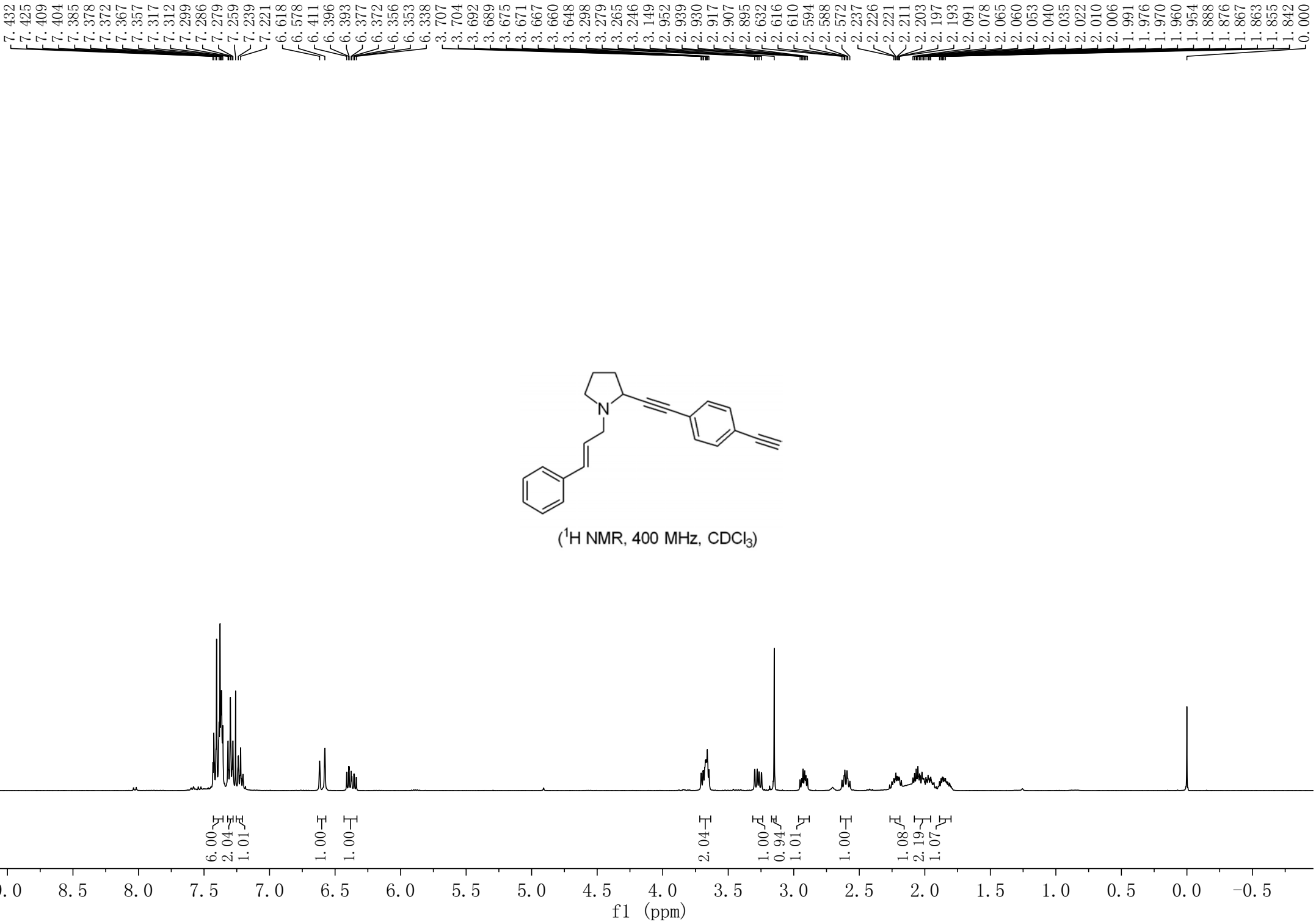


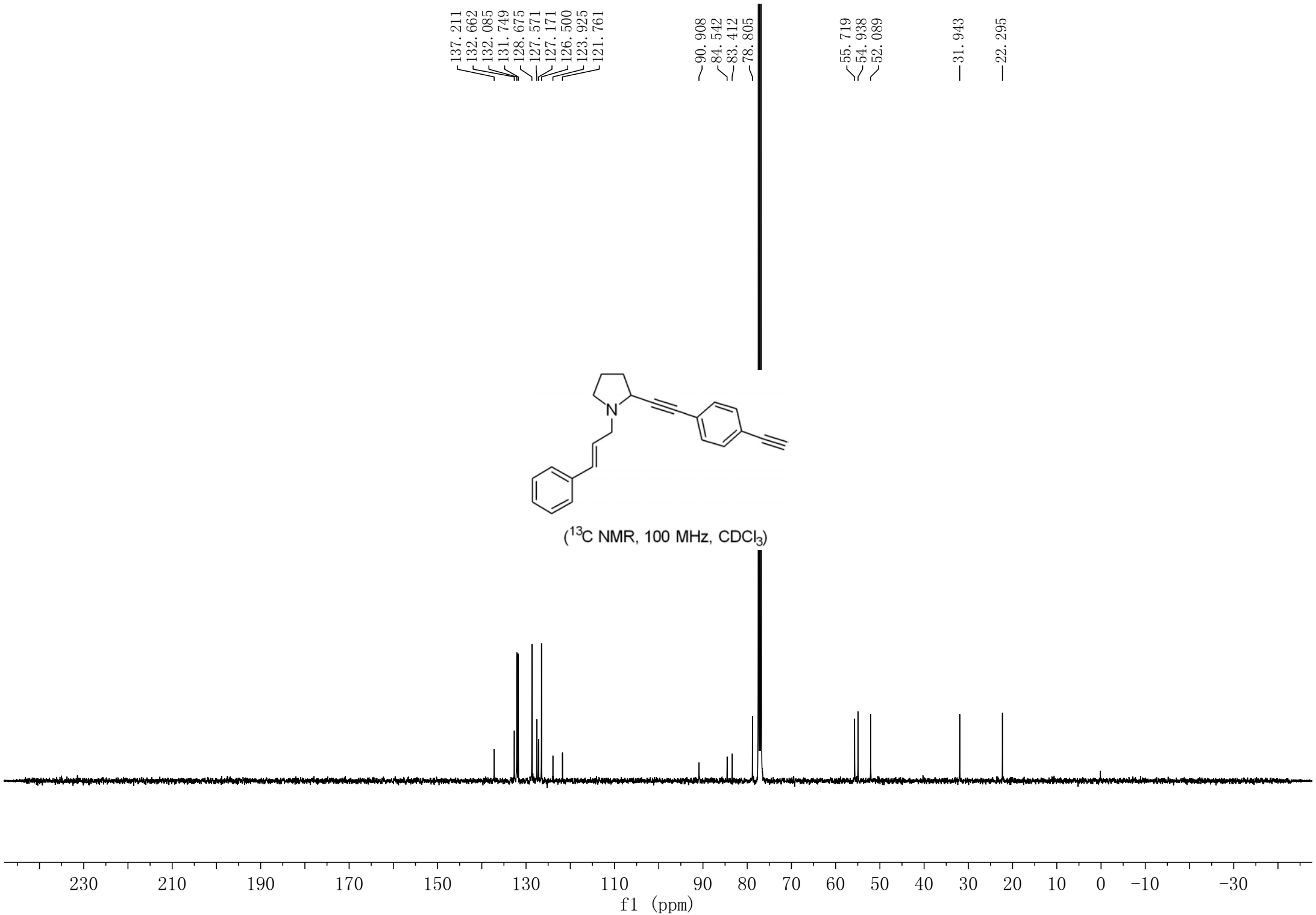

7.578
7.374
7.333
7.303
7.235
7.163
7.154
6.615
6.576
6.391
3.646
3.255
3.243
2.911
2.902
2.588
2.210
2.040
2.009
1.964
1.857
0.000
Br
N
(1H NMR, 400 MHz, CDCl3)
0.82
6.02
1.07
1.06
0.98
0.97
2.00
1.04
1.11
1.05
1.02
2.04
1.02
f1 (ppm)

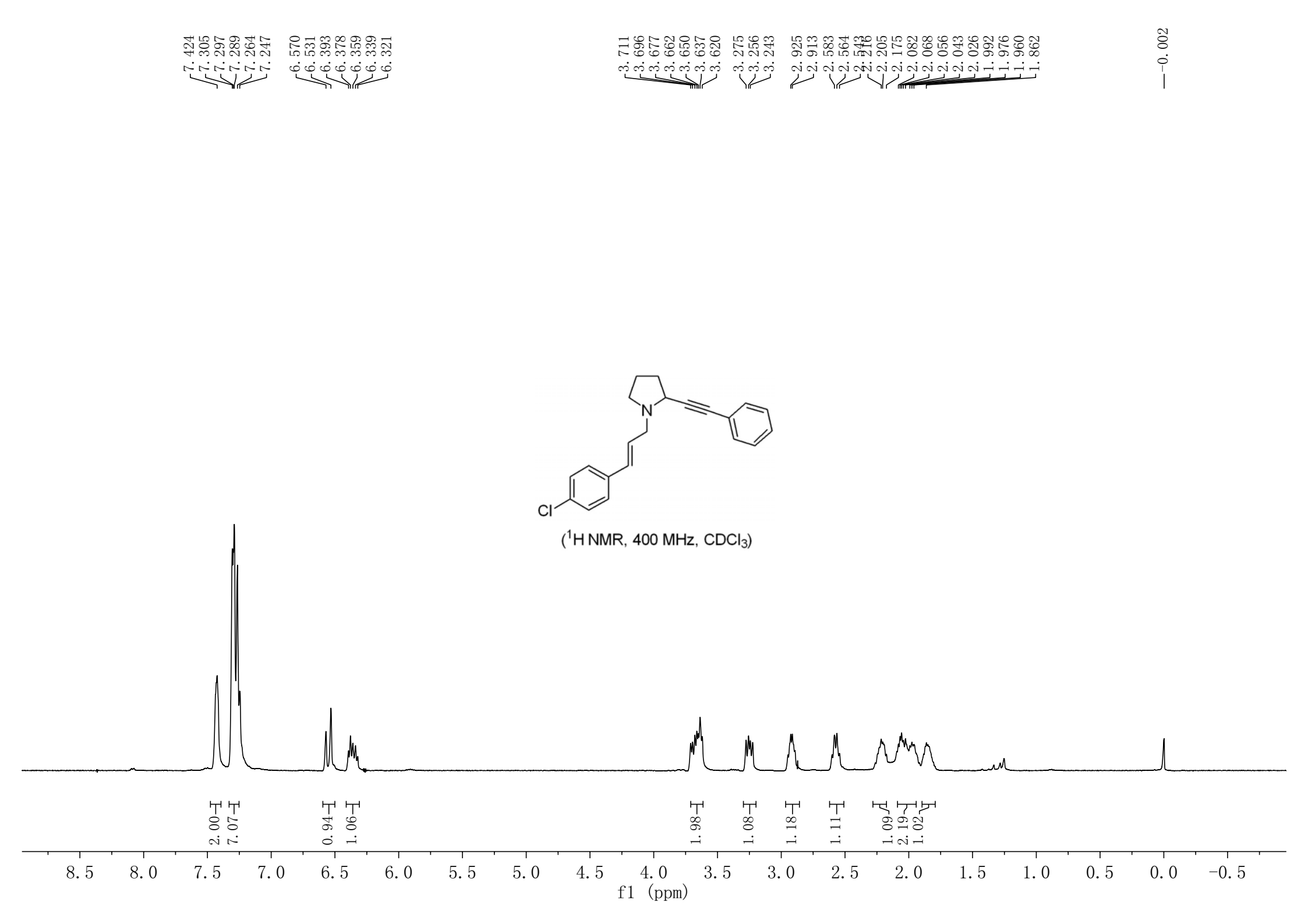

137.14
134.60
132.81
131.31
130.41
129.79
128.67
127.60
126.91
126.50
125.35
122.16
90.07
83.69
55.59
54.76
51.96
31.89
22.26
Br
N
(^{13}C NMR, 100 MHz, $CDCl_3$)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)

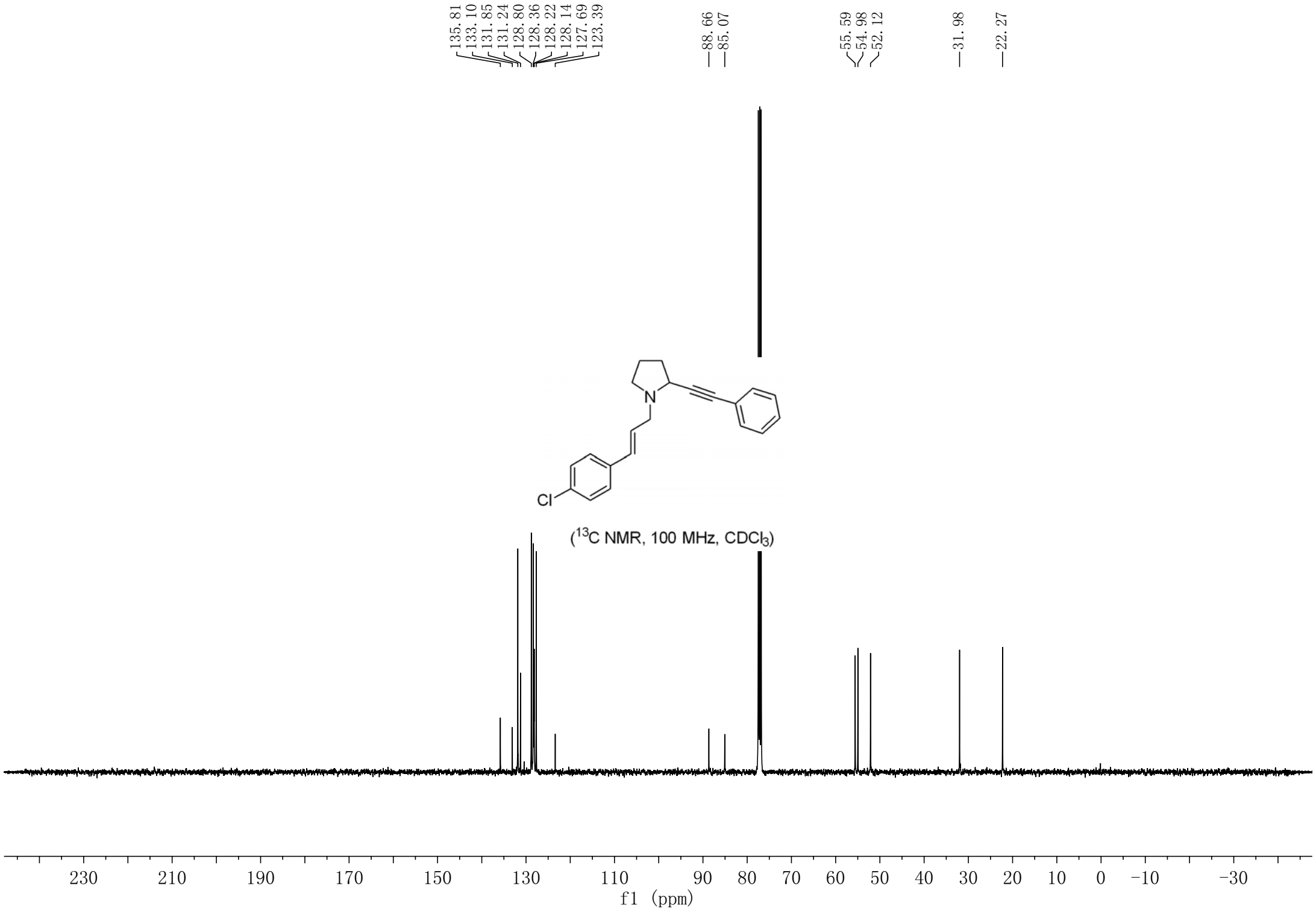

7.388
7.370
7.342
7.323
7.315
7.295
7.277
7.246
7.233
7.215
7.197
7.111
7.092
6.620
6.581
6.422
6.407
6.403
6.388
6.383
6.367
6.363
6.349
3.744
3.729
3.712
3.696
3.686
3.671
3.655
3.290
3.271
3.238
2.929
2.916
2.635
2.619
2.613
2.597
2.589
2.575
2.395
2.337
2.229
2.213
2.195
2.187
2.079
2.067
2.054
2.041
2.023
1.976
1.953
1.858
1.847
0.001
N
(^{1}H NMR, 400MHz, $CDCl_3$)
6.25
1.13
2.05
1.01
1.01
2.06
1.00
1.08
1.04
3.41
1.11
2.02
0.99
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)

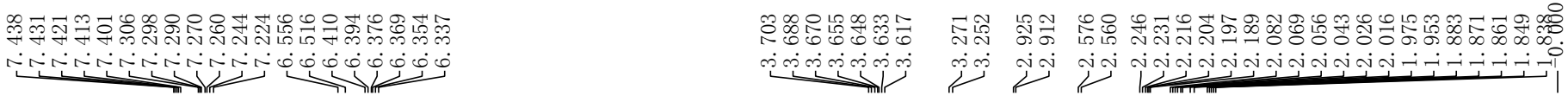

138.15
137.21
132.67
131.72
129.08
128.62
127.50
127.09
126.48
120.25
87.63
85.21
55.52
54.90
51.87
31.91
22.17
21.54
N
(^{13}C NMR, 100MHz, $CDCl_3$)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)

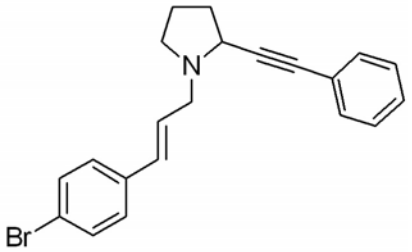

7.432
7.425
7.409
7.404
7.385
7.378
7.372
7.367
7.357
7.317
7.312
7.299
7.286
7.279
7.259
7.239
7.221
6.618
6.578
6.411
6.396
6.393
6.377
6.372
6.356
6.353
6.338
3.707
3.704
3.692
3.689
3.675
3.671
3.667
3.660
3.648
3.298
3.279
3.265
3.246
3.149
2.952
2.939
2.930
2.917
2.907
2.895
2.632
2.616
2.610
2.594
2.588
2.572
2.237
2.226
2.221
2.211
2.203
2.197
2.193
2.091
2.078
2.065
2.060
2.053
2.040
2.035
2.022
2.010
2.006
1.991
1.976
1.970
1.960
1.954
1.888
1.876
1.867
1.863
1.855
1.842
0.000
N
(1H NMR, 400 MHz, CDCl3)
6.00
2.04
1.01
1.00
1.00
2.04
1.00
0.94
1.01
1.00
1.08
2.19
1.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


137.211
132.662
132.085
131.749
128.675
127.571
127.171
126.500
123.925
121.761
90.908
84.542
83.412
78.805
55.719
54.938
52.089
31.943
22.295
N
(13C NMR, 100 MHz, CDCl3)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)

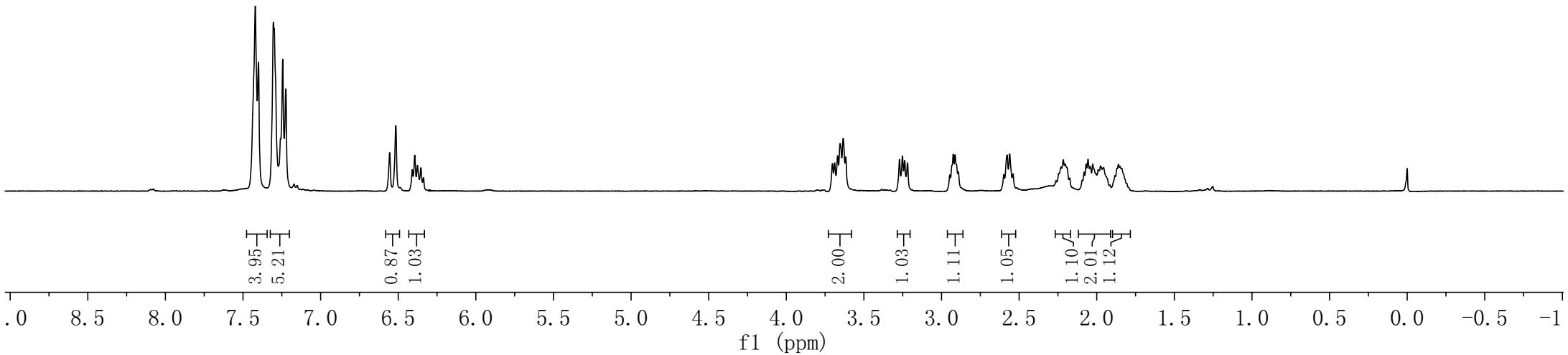

7.424
7.305
7.297
7.289
7.264
7.247
6.570
6.531
6.393
6.378
6.359
6.339
6.321
3.711
3.696
3.677
3.662
3.650
3.637
3.620
3.275
3.256
3.243
2.925
2.913
2.583
2.564
2.205
2.175
2.082
2.068
2.056
2.043
2.026
1.992
1.976
1.960
1.862
-0.002
N
Cl
(1H NMR, 400 MHz, CDCl3)
2.00
7.07
0.94
1.06
1.98
1.08
1.18
1.11
1.09
2.19
1.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

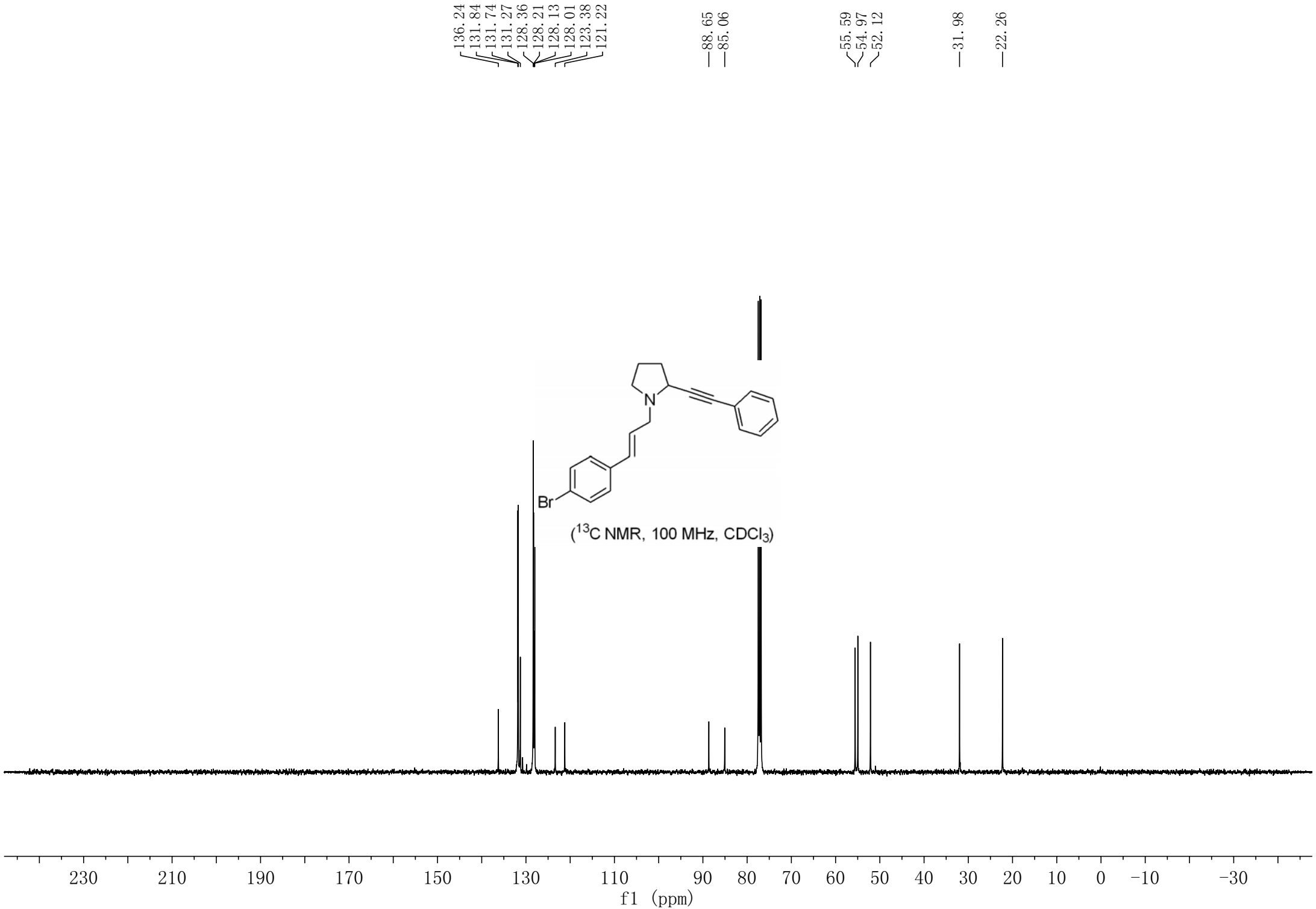

135.81
133.10
131.85
131.24
128.80
128.36
128.22
128.14
127.69
123.39
88.66
85.07
55.59
54.98
52.12
31.98
22.27
N
Cl
(^{13}C NMR, 100 MHz, $CDCl_3$)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)

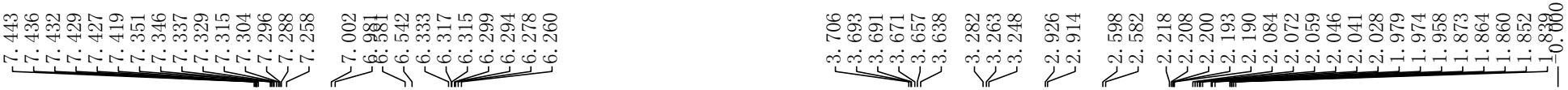


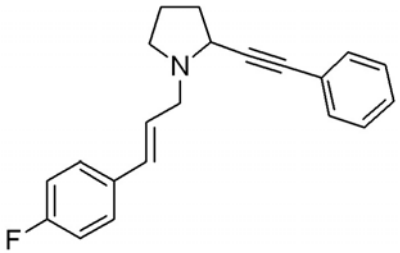


(^{1}H NMR, 400 MHz, $CDCl_3$)

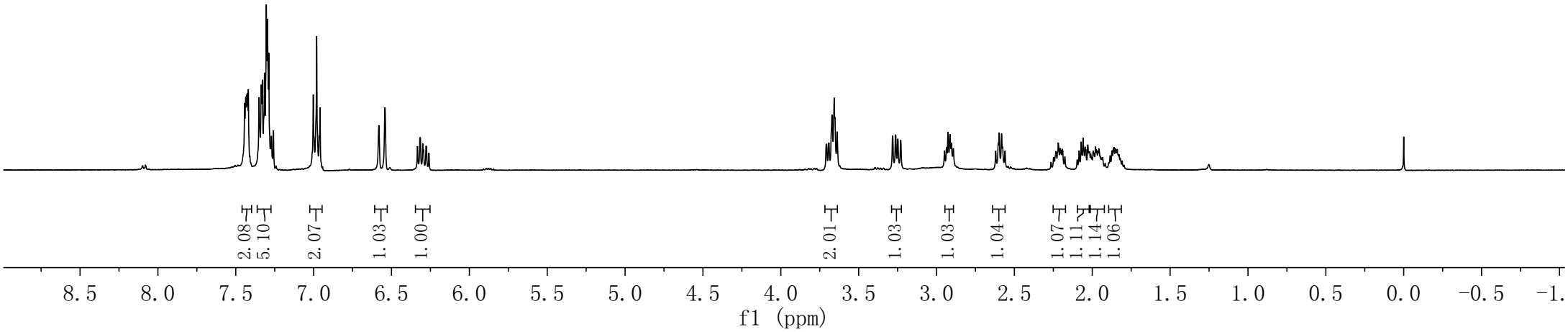


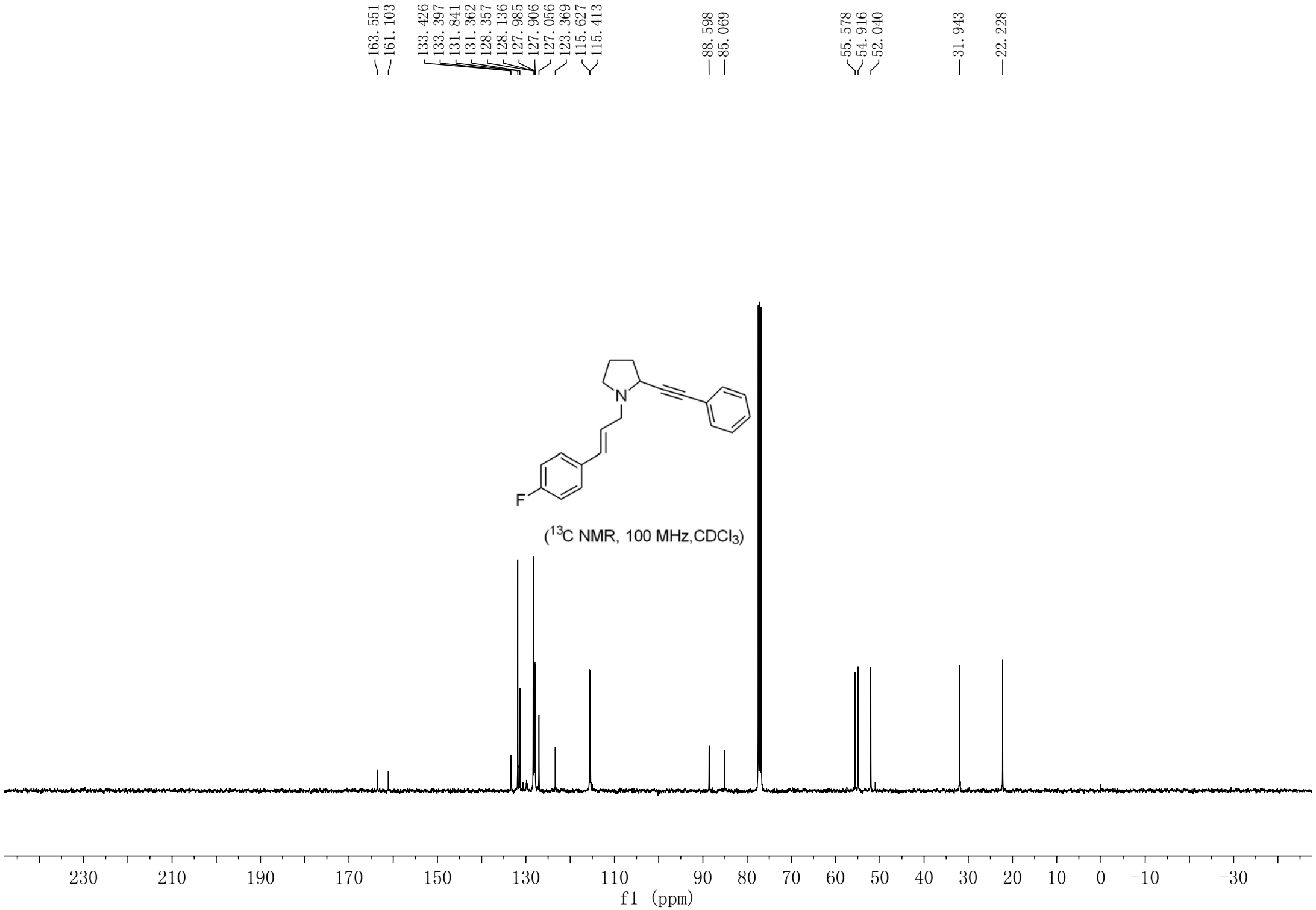

136.24
131.84
131.74
131.27
128.36
128.21
128.13
128.01
123.38
121.22
88.65
85.06
55.59
54.97
52.12
31.98
22.26
N
Br
(^{13}C NMR, 100 MHz, $CDCl_3$)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)

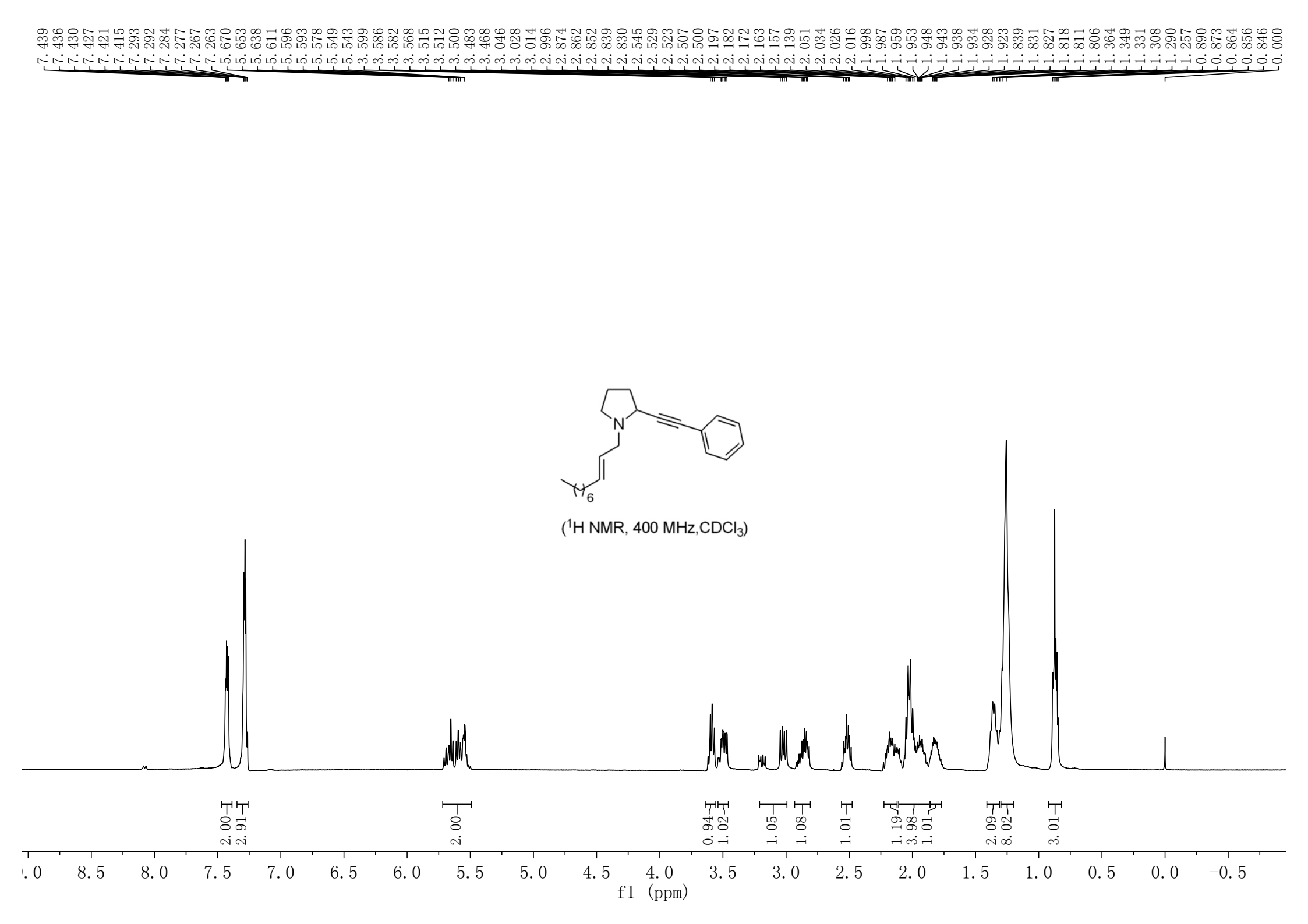


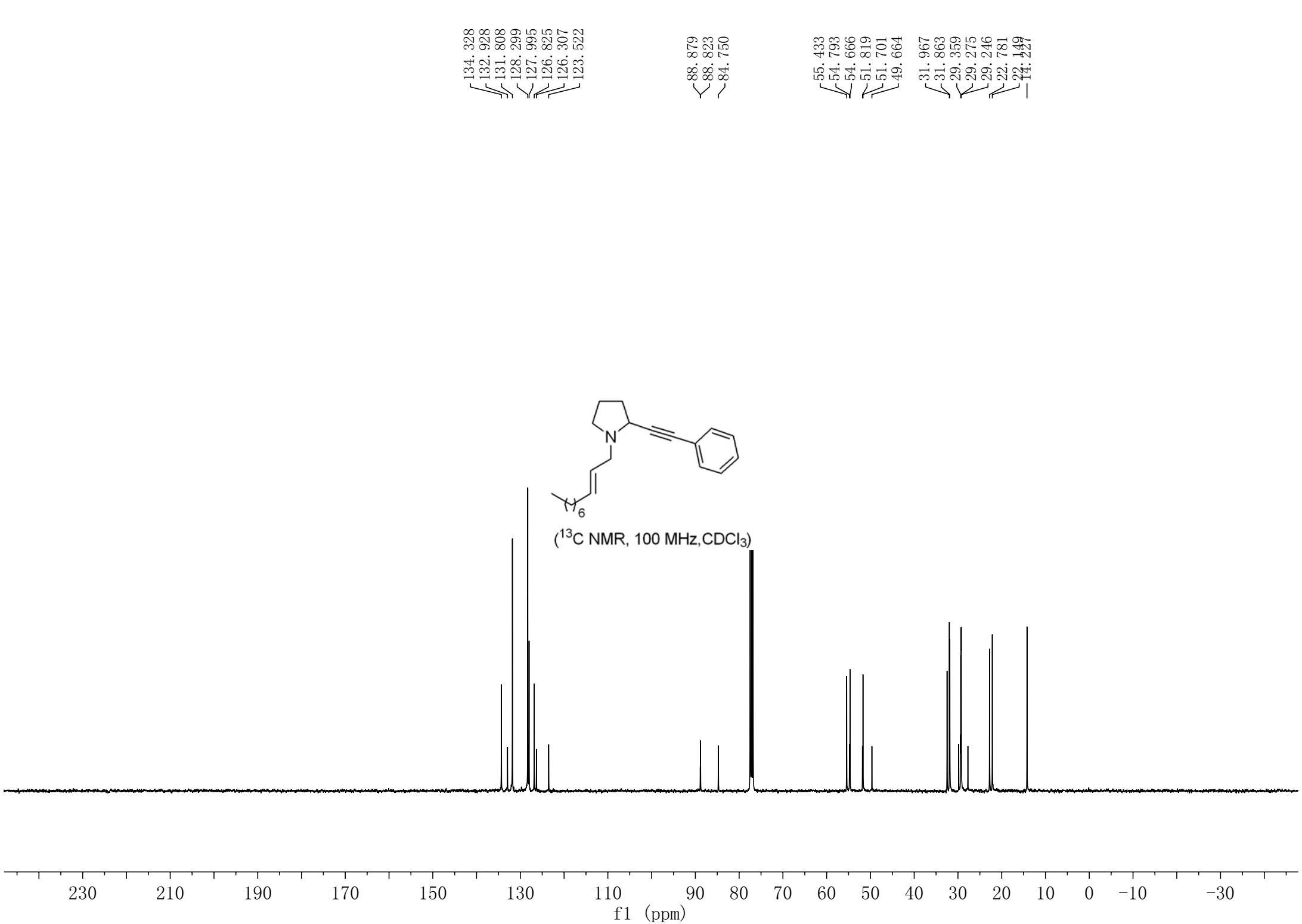


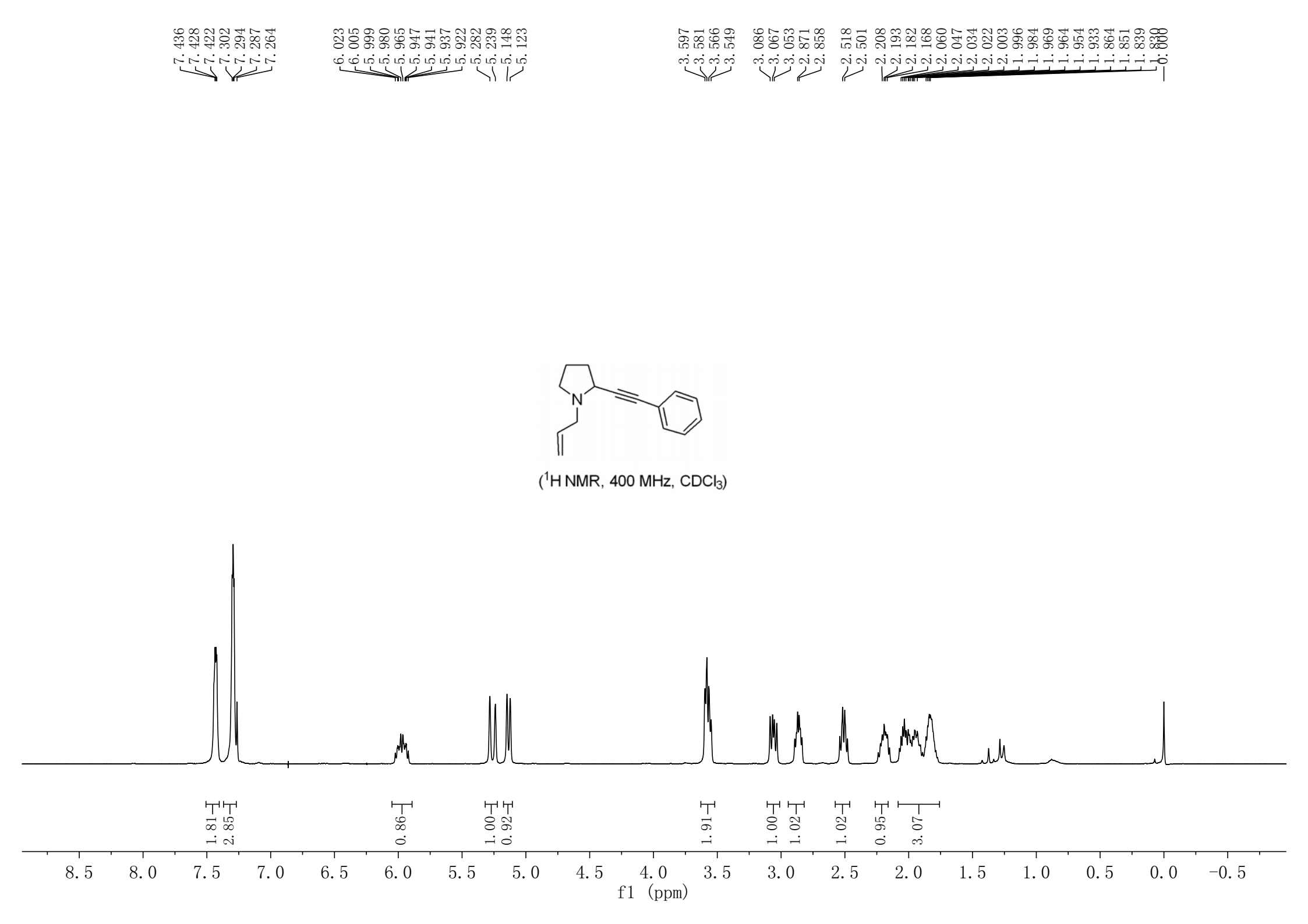
(^{1}H NMR, 400 MHz,$CDCl_3$)

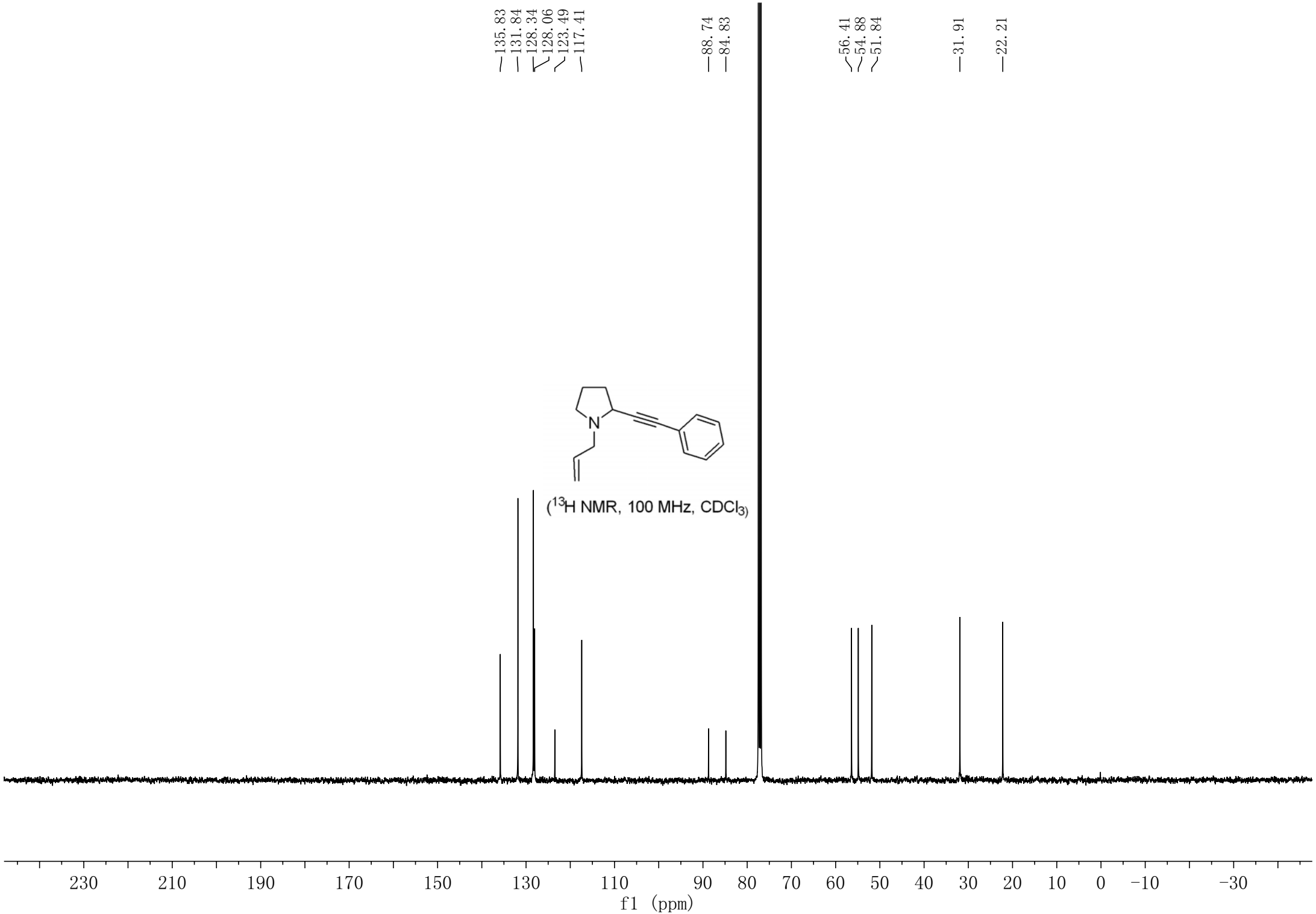


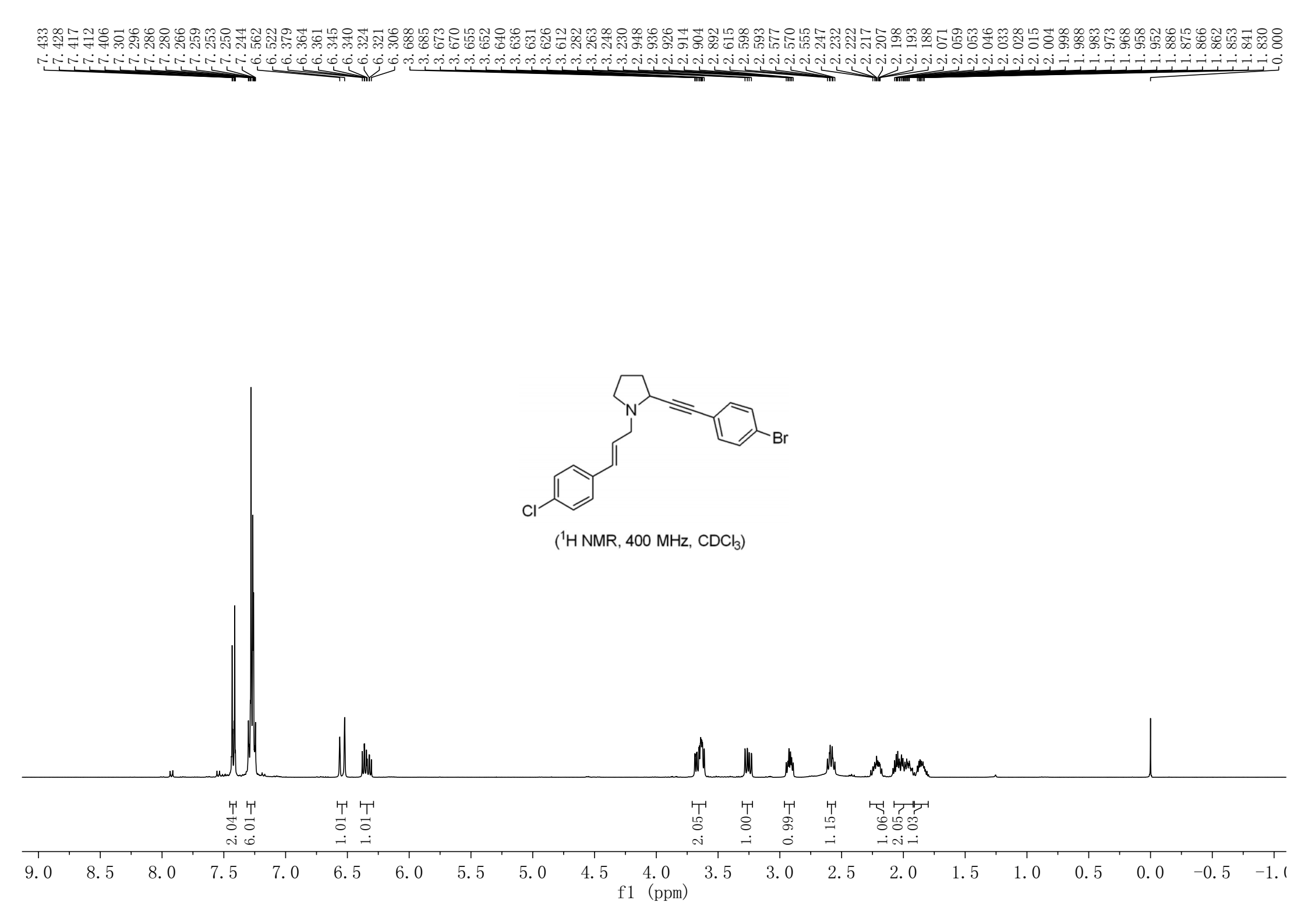

163.551
161.103
133.426
133.397
131.841
131.362
128.357
128.136
127.985
127.906
127.056
123.369
115.627
115.413
88.598
85.069
55.578
54.916
52.040
31.943
22.228
N
F
(^{13}C NMR, 100 MHz,$CDCl_3$)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)


7.439
7.436
7.430
7.427
7.421
7.415
7.293
7.292
7.284
7.277
7.267
7.263
5.670
5.653
5.638
5.611
5.596
5.593
5.578
5.549
5.543
3.599
3.586
3.582
3.568
3.515
3.512
3.500
3.483
3.468
3.046
3.028
3.014
2.996
2.874
2.862
2.852
2.839
2.830
2.545
2.529
2.523
2.507
2.500
2.197
2.182
2.172
2.163
2.157
2.139
2.051
2.034
2.026
2.016
1.998
1.987
1.959
1.953
1.948
1.943
1.938
1.934
1.928
1.923
1.839
1.831
1.827
1.818
1.811
1.806
1.364
1.349
1.331
1.308
1.290
1.257
0.890
0.873
0.864
0.856
0.846
0.000
N
6
(1H NMR, 400 MHz,CDCl3)
2.00
2.91
2.00
0.94
1.02
1.05
1.08
1.01
1.19
3.98
1.01
2.09
8.02
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


134.328
132.928
131.808
128.299
127.995
126.825
126.307
123.522
88.879
88.823
84.750
55.433
54.793
54.666
51.819
51.701
49.664
31.967
31.863
29.359
29.275
29.246
22.781
22.149
14.227
N
6
(^{13}C NMR, 100 MHz,CDCl$_3$)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)


7.436
7.428
7.422
7.302
7.294
7.287
7.264
6.023
6.005
5.999
5.980
5.965
5.947
5.941
5.937
5.922
5.282
5.239
5.148
5.123
3.597
3.581
3.566
3.549
3.086
3.067
3.053
2.871
2.858
2.518
2.501
2.208
2.193
2.182
2.168
2.060
2.047
2.034
2.022
2.003
1.996
1.984
1.969
1.964
1.954
1.933
1.864
1.851
1.839
1.830
0.000
N
(1H NMR, 400 MHz, CDCl3)
1.81
2.85
0.86
1.00
0.92
1.91
1.00
1.02
1.02
0.95
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


135.83
131.84
128.34
128.06
123.49
117.41
88.74
84.83
56.41
54.88
51.84
31.91
22.21
N
(13H NMR, 100 MHz, CDCl3)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)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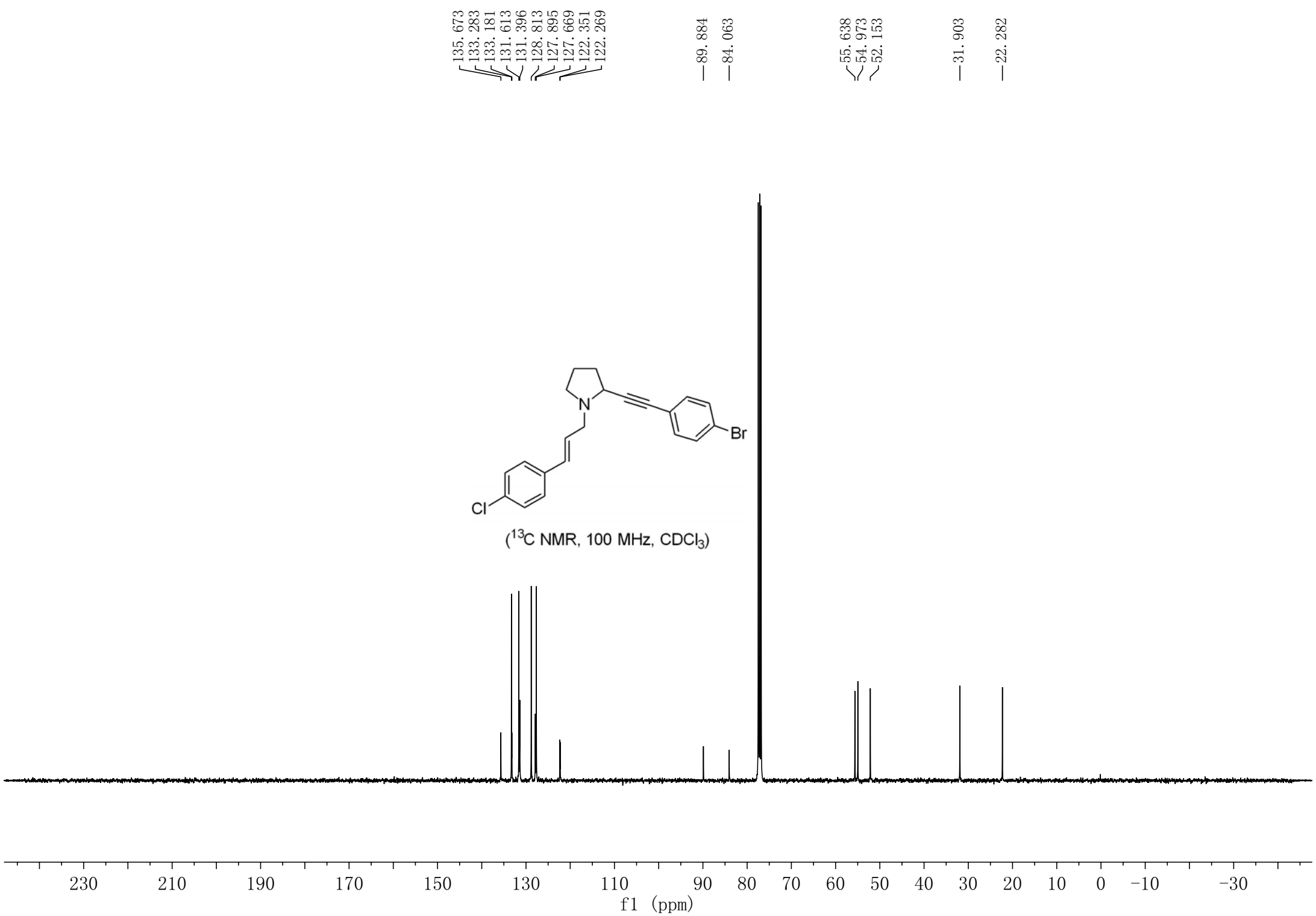
7.428
7.417
7.412
7.406
7.301
7.296
7.286
7.280
7.266
7.259
7.253
7.250
7.244
6.562
6.522
6.379
6.364
6.361
6.345
6.340
6.324
6.321
6.306
3.688
3.685
3.673
3.670
3.655
3.652
3.640
3.636
3.631
3.626
3.612
3.282
3.263
3.248
3.230
2.948
2.936
2.926
2.914
2.904
2.892
2.615
2.598
2.593
2.577
2.570
2.555
2.247
2.232
2.222
2.217
2.207
2.198
2.193
2.188
2.071
2.059
2.053
2.046
2.033
2.028
2.015
2.004
1.998
1.988
1.983
1.973
1.968
1.958
1.952
1.886
1.875
1.866
1.862
1.853
1.841
1.830
0.000
N
Br
Cl
(^{1}H NMR, 400 MHz, $CDCl_3$)
2.04
6.01
1.01
1.01
2.05
1.00
0.99
1.15
1.06
2.05
1.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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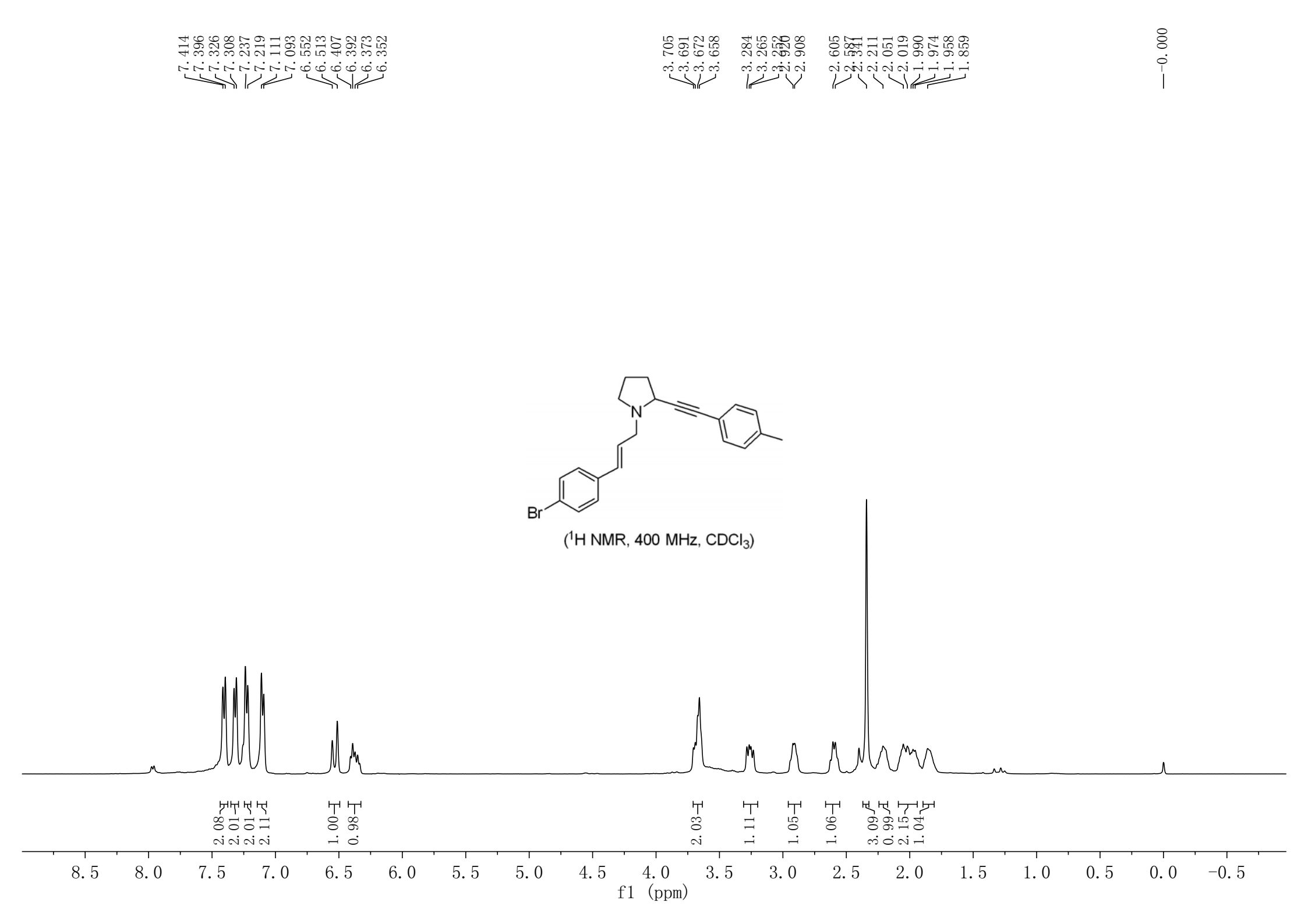
133.283
133.181
131.613
131.396
128.813
127.895
127.669
122.351
122.269
89.884
84.063
55.638
54.973
52.153
31.903
22.282
N
Br
Cl
(^{13}C NMR, 100 MHz, $CDCl_3$)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)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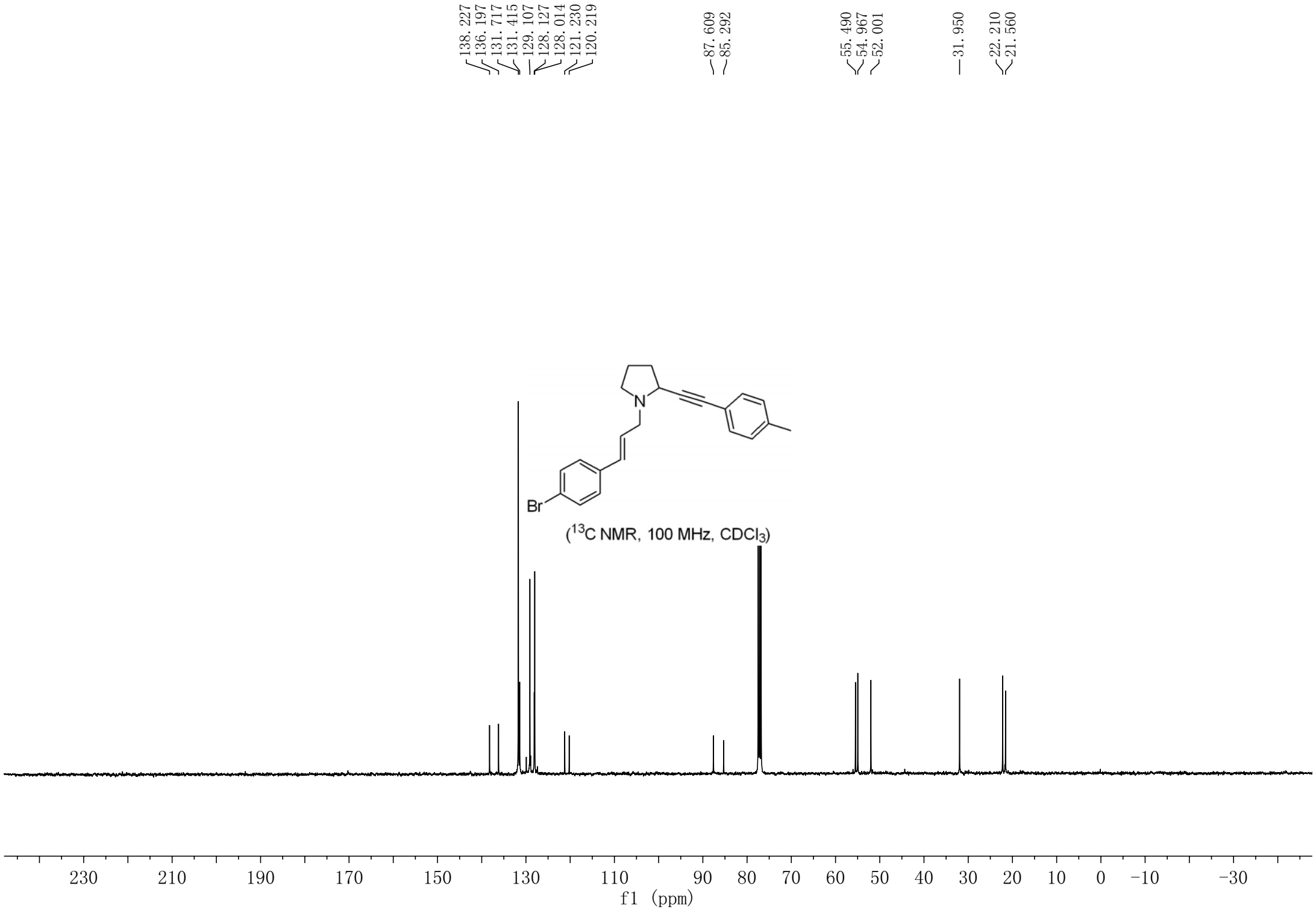
7.396
7.326
7.308
7.237
7.219
7.111
7.093
6.552
6.513
6.407
6.392
6.373
6.352
3.705
3.691
3.672
3.658
3.284
3.265
2.908
2.605
2.587
2.341
2.211
2.051
2.019
1.990
1.974
1.958
1.859
0.000
Br
(1H NMR, 400 MHz, CDCl3)
2.08
2.01
2.01
2.11
1.00
0.98
2.03
1.11
1.05
1.06
3.09
0.99
2.15
1.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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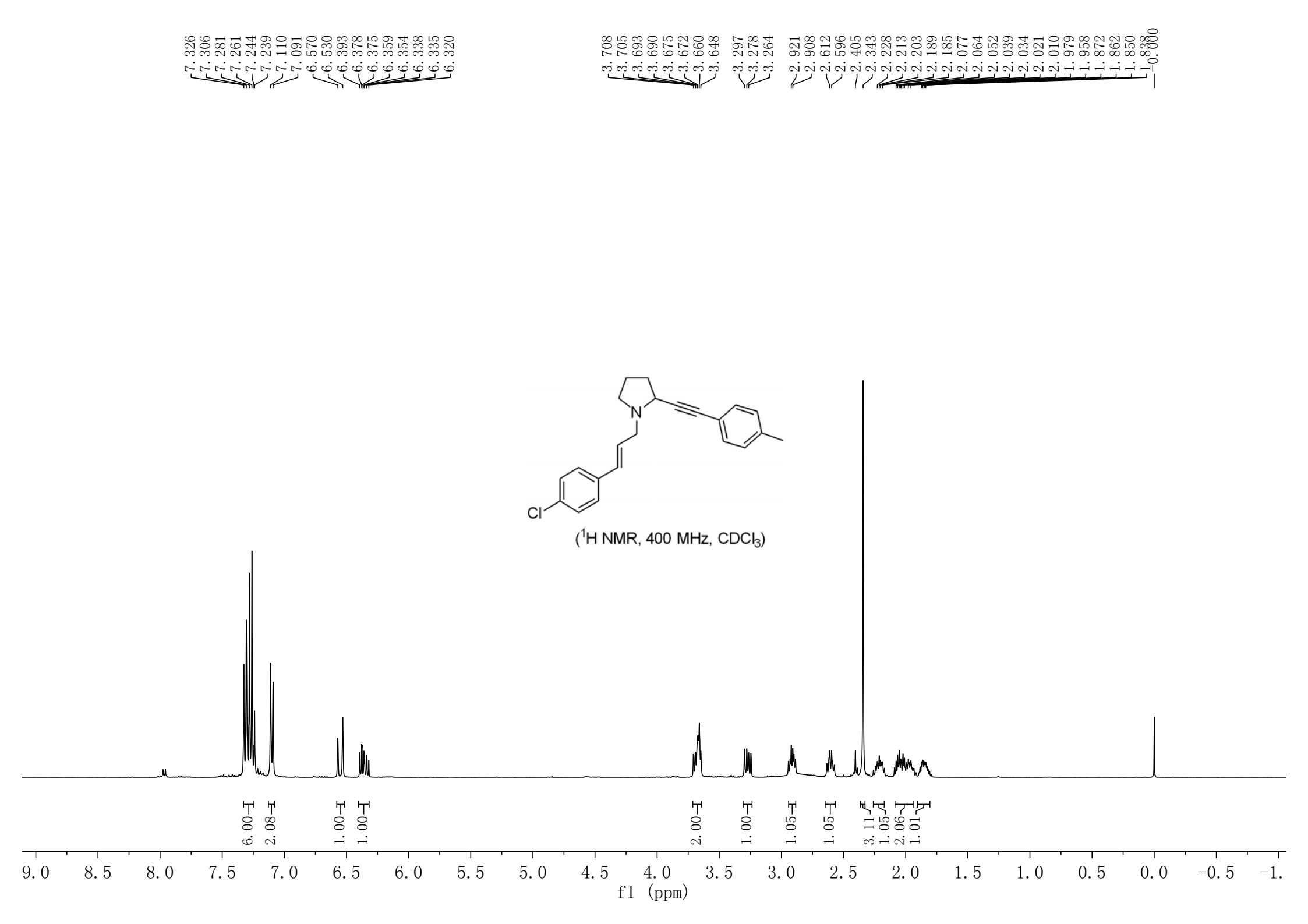
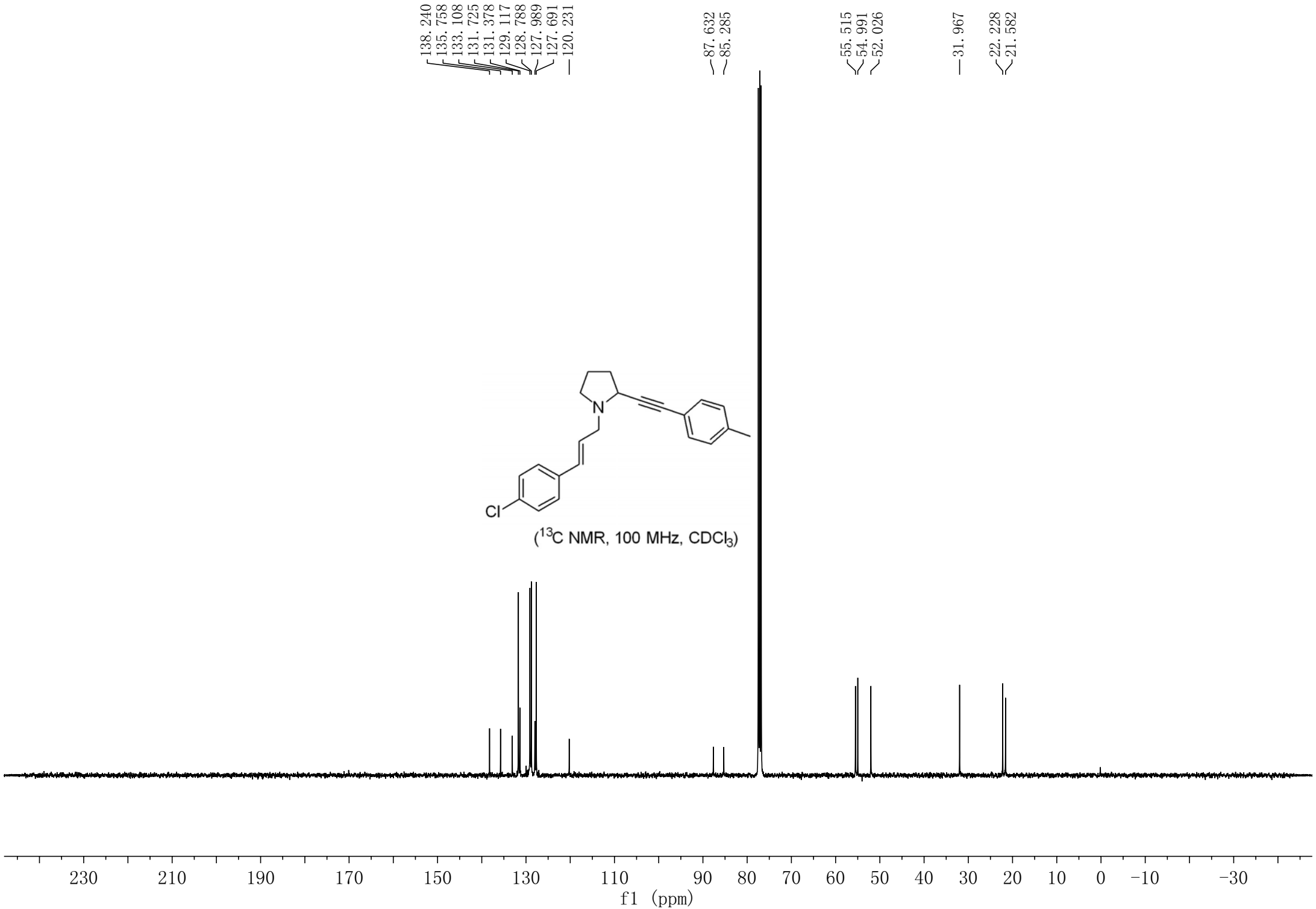
136.197
131.717
131.415
129.107
128.127
128.014
121.230
120.219
87.609
85.292
55.490
54.967
52.001
31.950
22.210
21.560
N
Br
(^{13}C NMR, 100 MHz, $CDCl_3$)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)


7.326
7.306
7.281
7.261
7.244
7.239
7.110
7.091
6.570
6.530
6.393
6.378
6.375
6.359
6.354
6.338
6.335
6.320
3.708
3.705
3.693
3.690
3.675
3.672
3.660
3.648
3.297
3.278
3.264
2.921
2.908
2.612
2.596
2.405
2.343
2.228
2.213
2.203
2.189
2.185
2.077
2.064
2.052
2.039
2.034
2.021
2.010
1.979
1.958
1.872
1.862
1.850
1.838
0.000
N
Cl
(1H NMR, 400 MHz, CDCl3)
6.00
2.08
1.00
1.00
2.00
1.00
1.05
1.05
3.11
1.05
2.06
1.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)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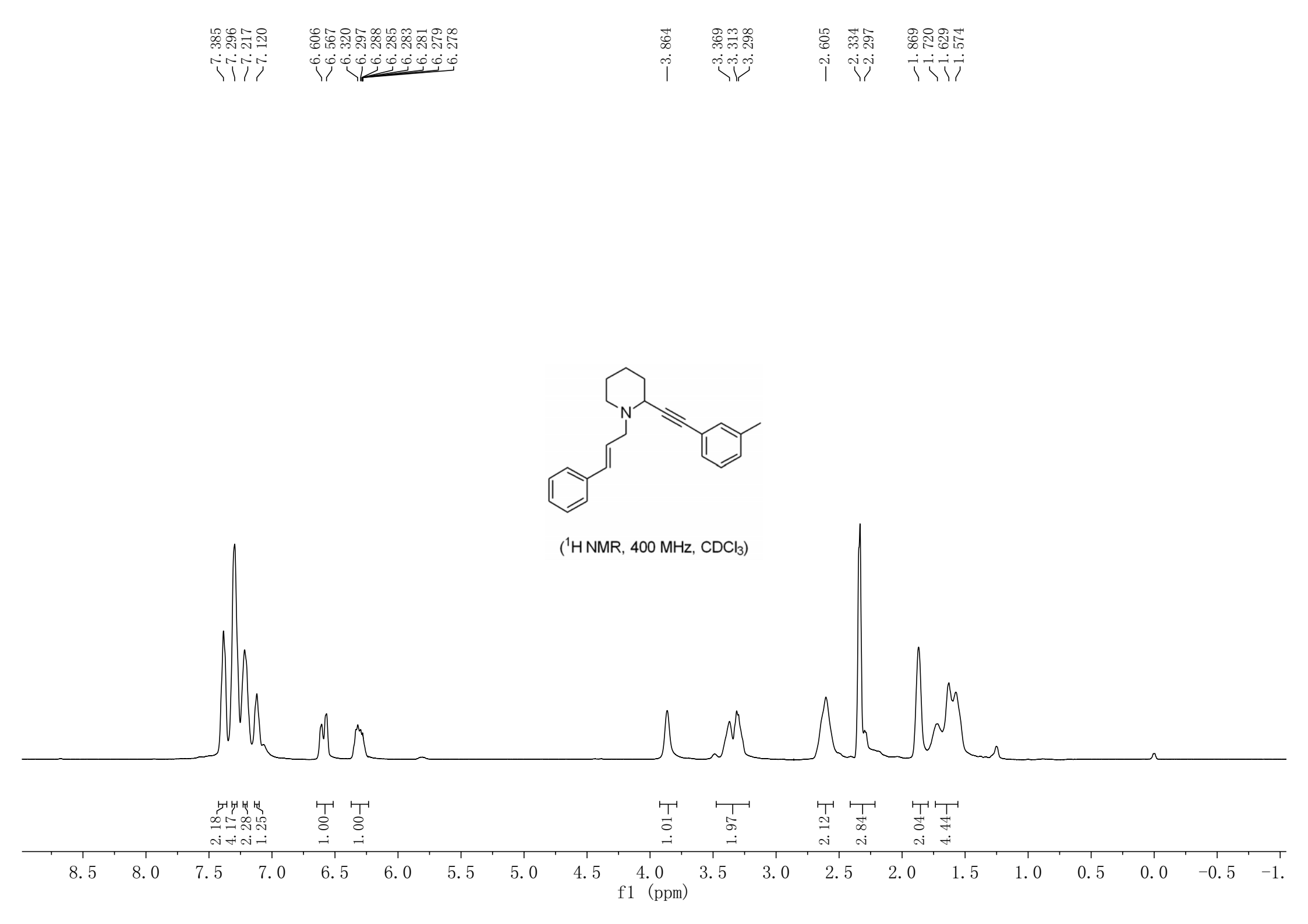
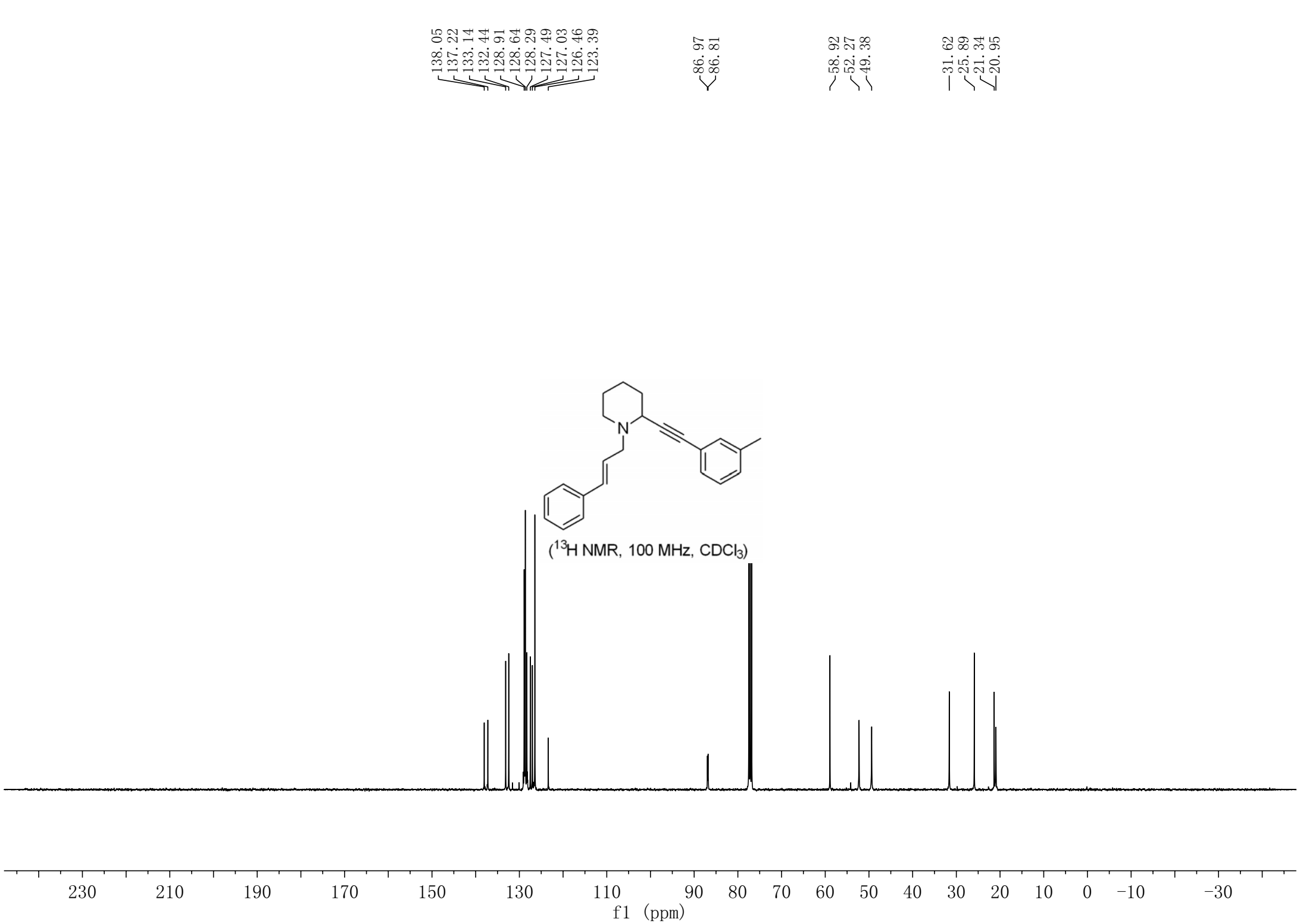
135.758
133.108
131.725
131.378
129.117
128.788
127.989
127.691
120.231
87.632
85.285
55.515
54.991
52.026
31.967
22.228
21.582
N
Cl
(13C NMR, 100 MHz, CDCl3)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)


7.385
7.296
7.217
7.120
6.606
6.567
6.320
6.297
6.288
6.285
6.283
6.281
6.279
6.278
3.864
3.369
3.313
3.298
2.605
2.334
2.297
1.869
1.720
1.629
1.574
N
(1H NMR, 400 MHz, CDCl3)
2.18
4.17
2.28
1.25
1.00
1.00
1.01
1.97
2.12
2.84
2.04
4.44
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)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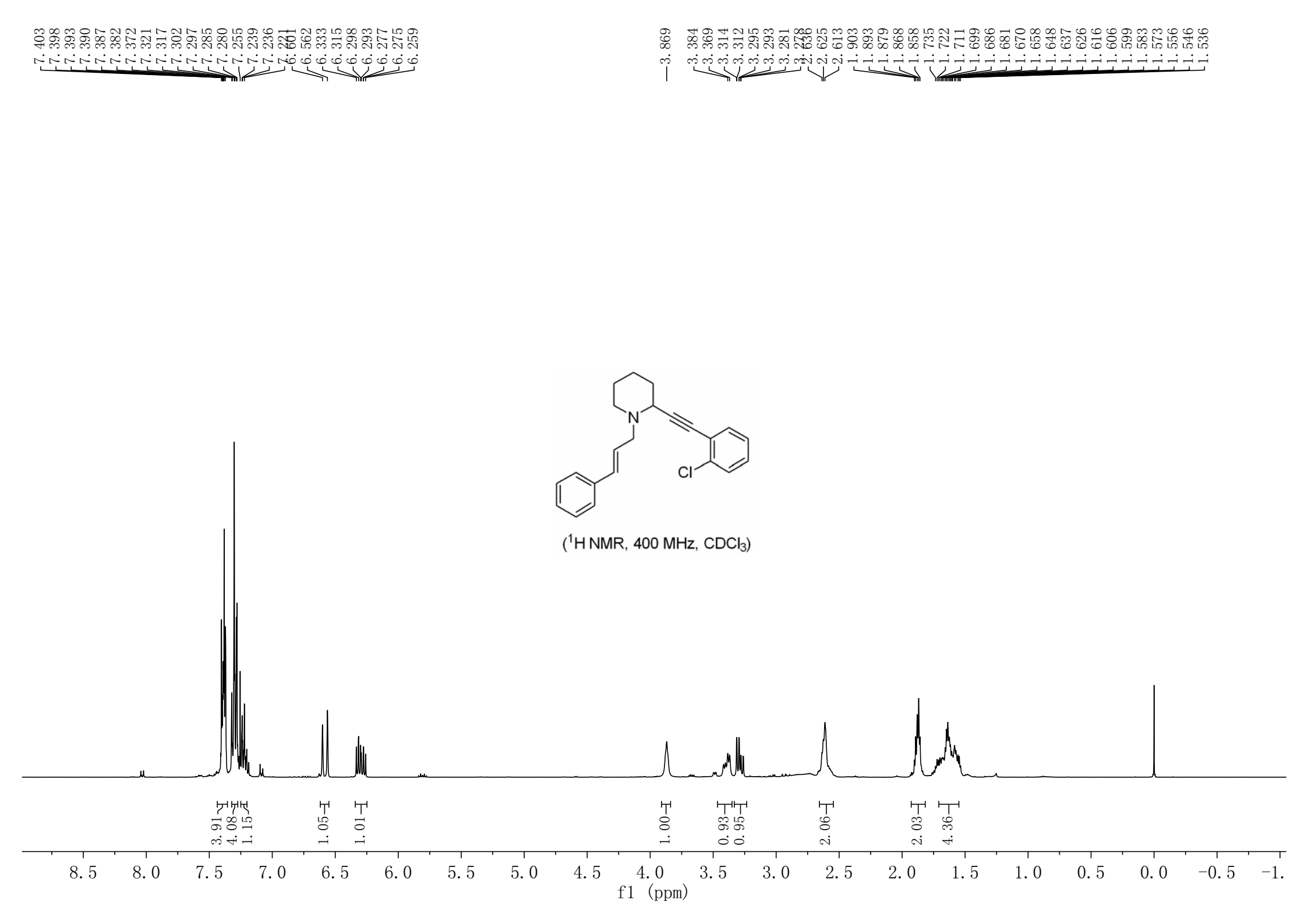
137.22
133.14
132.44
128.91
128.64
128.29
127.49
127.03
126.46
123.39
86.97
86.81
58.92
52.27
49.38
31.62
25.89
21.34
20.95
N
(^{13}H NMR, 100 MHz, $CDCl_3$)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)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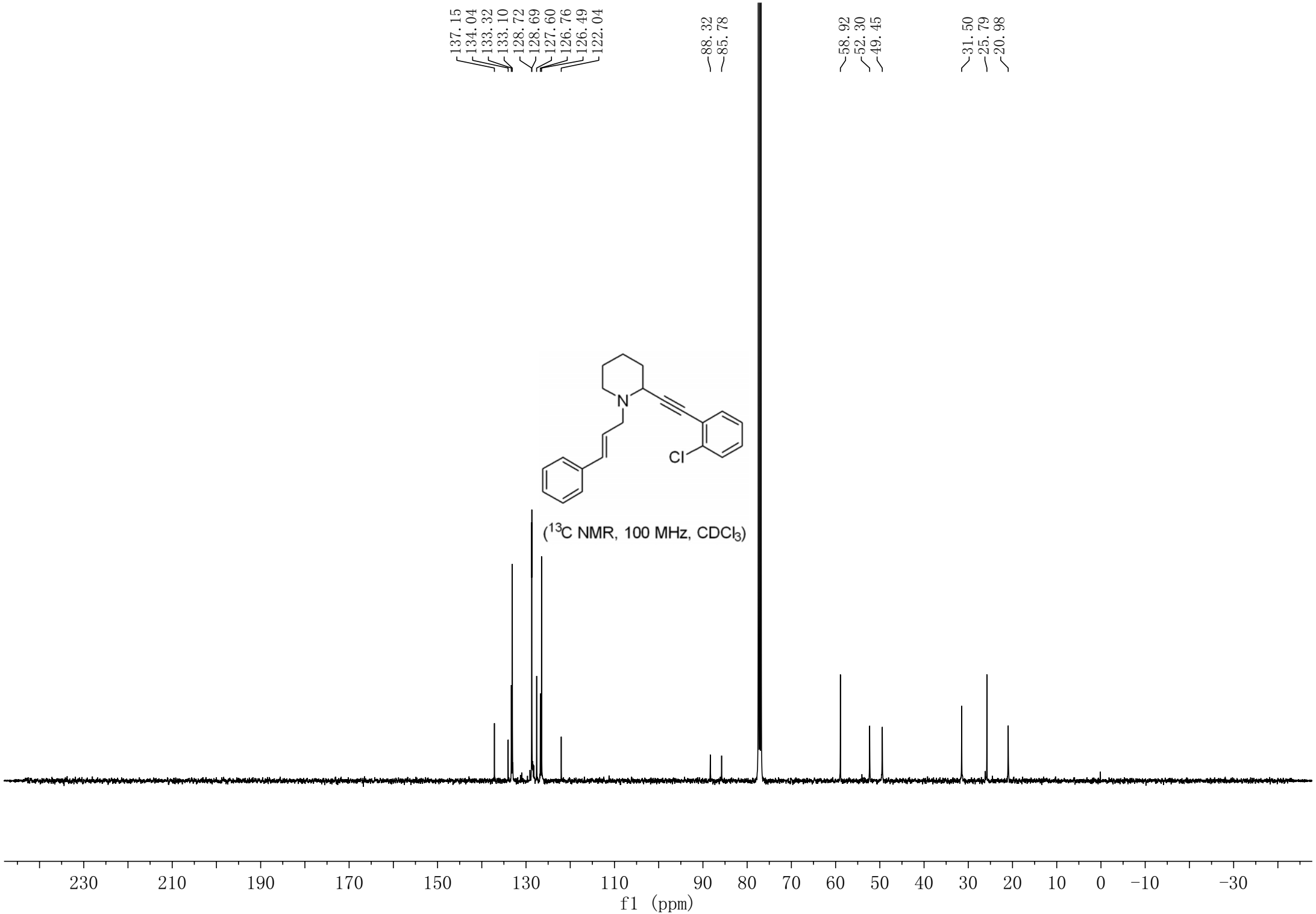
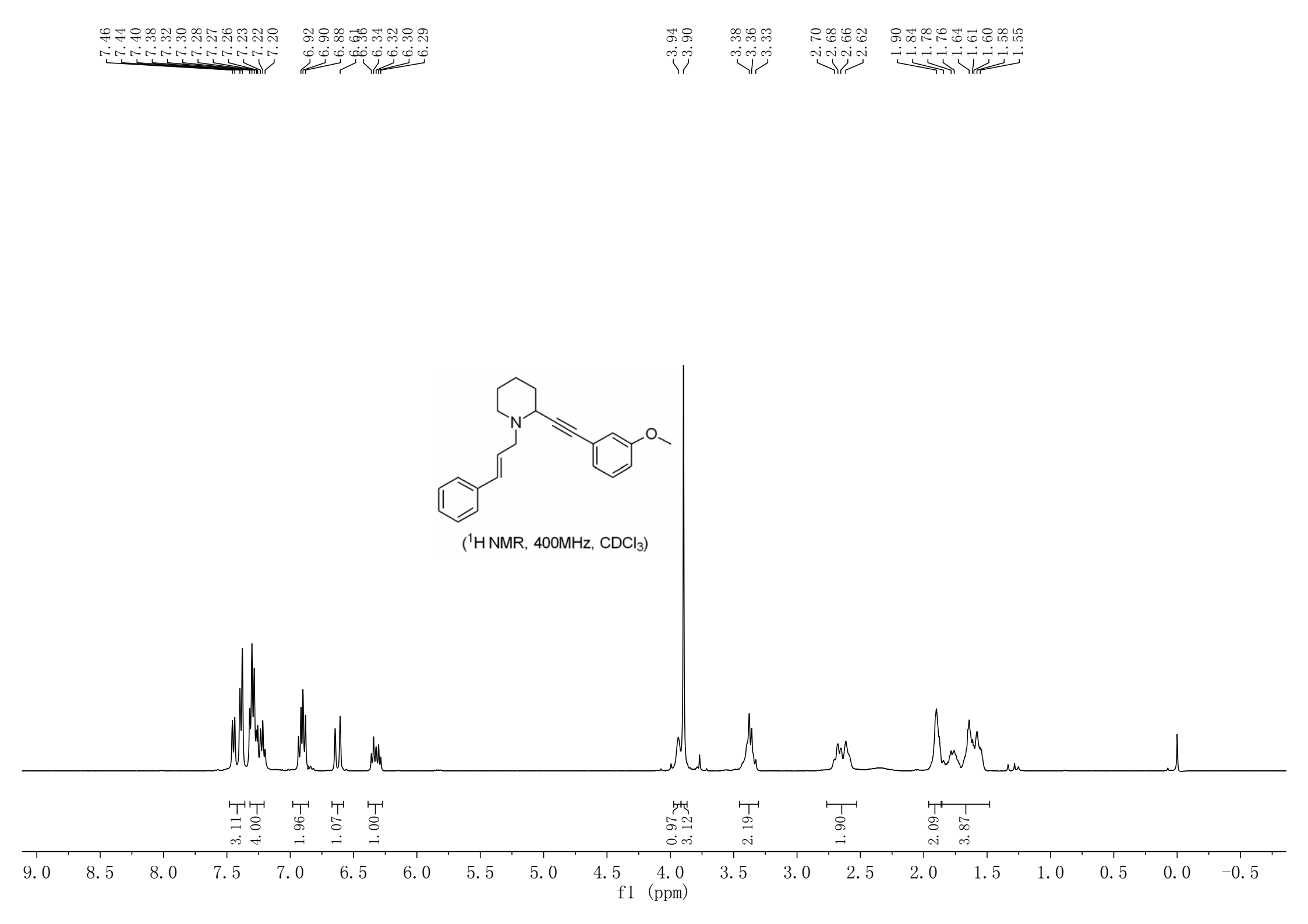
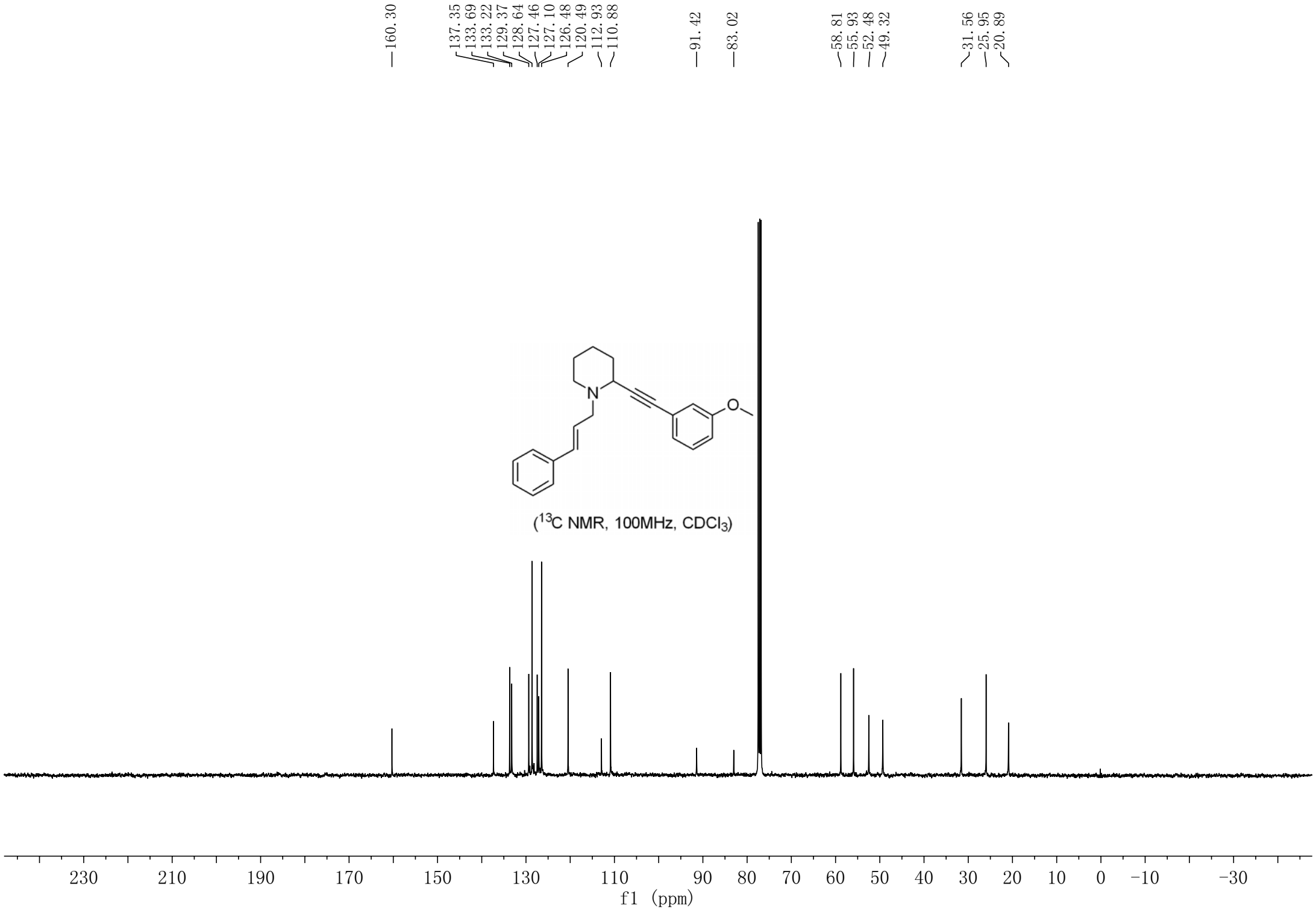
7.398
7.393
7.390
7.387
7.382
7.372
7.321
7.317
7.302
7.297
7.285
7.280
7.255
7.239
7.236
7.221
7.601
6.562
6.333
6.315
6.298
6.293
6.277
6.275
6.259
3.869
3.384
3.369
3.314
3.312
3.295
3.293
3.281
3.278
2.636
2.625
2.613
1.903
1.893
1.879
1.868
1.858
1.735
1.722
1.711
1.699
1.686
1.681
1.670
1.658
1.648
1.637
1.626
1.616
1.606
1.599
1.583
1.573
1.556
1.546
1.536
N
Cl
(1H NMR, 400 MHz, CDCl3)
3.91
4.08
1.15
1.05
1.01
1.00
0.93
0.95
2.06
2.03
4.36
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)


137.15
134.04
133.32
133.10
128.72
128.69
127.60
126.76
126.49
122.04
88.32
85.78
58.92
52.30
49.45
31.50
25.79
20.98
N
Cl
(^{13}C NMR, 100 MHz, $CDCl_3$)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)


7.46
7.44
7.40
7.38
7.32
7.30
7.28
7.27
7.26
7.23
7.22
7.20
6.92
6.90
6.88
6.34
6.32
6.30
6.29
3.94
3.90
3.38
3.36
3.33
2.70
2.68
2.66
2.62
1.90
1.84
1.78
1.76
1.64
1.61
1.60
1.58
1.55
N
O
(1H NMR, 400MHz, CDCl3)
3.11
4.00
1.96
1.07
1.00
0.97
3.12
2.19
1.90
2.09
3.87
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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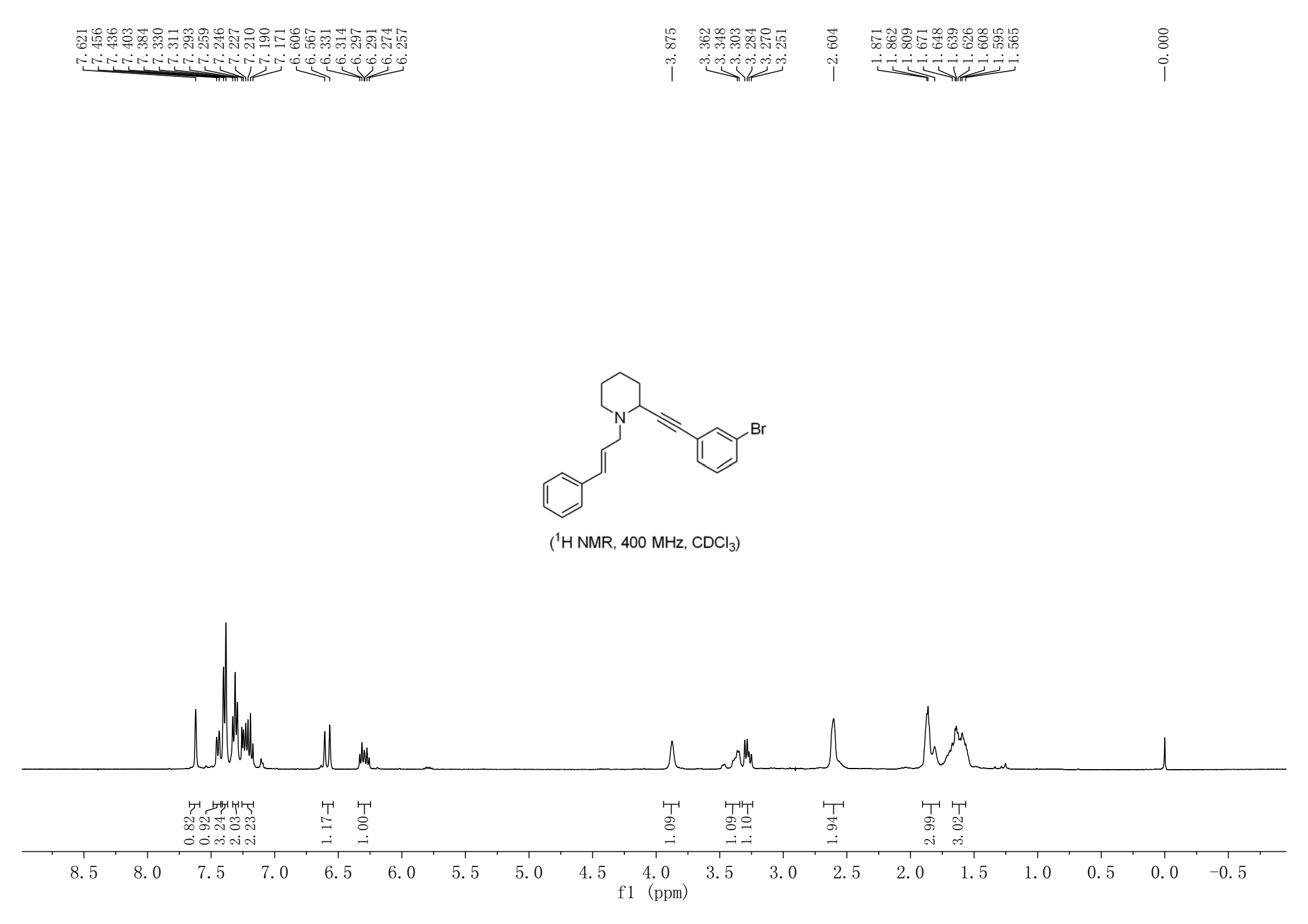
137.35
133.69
133.22
129.37
128.64
127.46
127.10
126.48
120.49
112.93
110.88
91.42
83.02
58.81
55.93
52.48
49.32
31.56
25.95
20.89
N
O
(^{13}C NMR, 100MHz, $CDCl_3$)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)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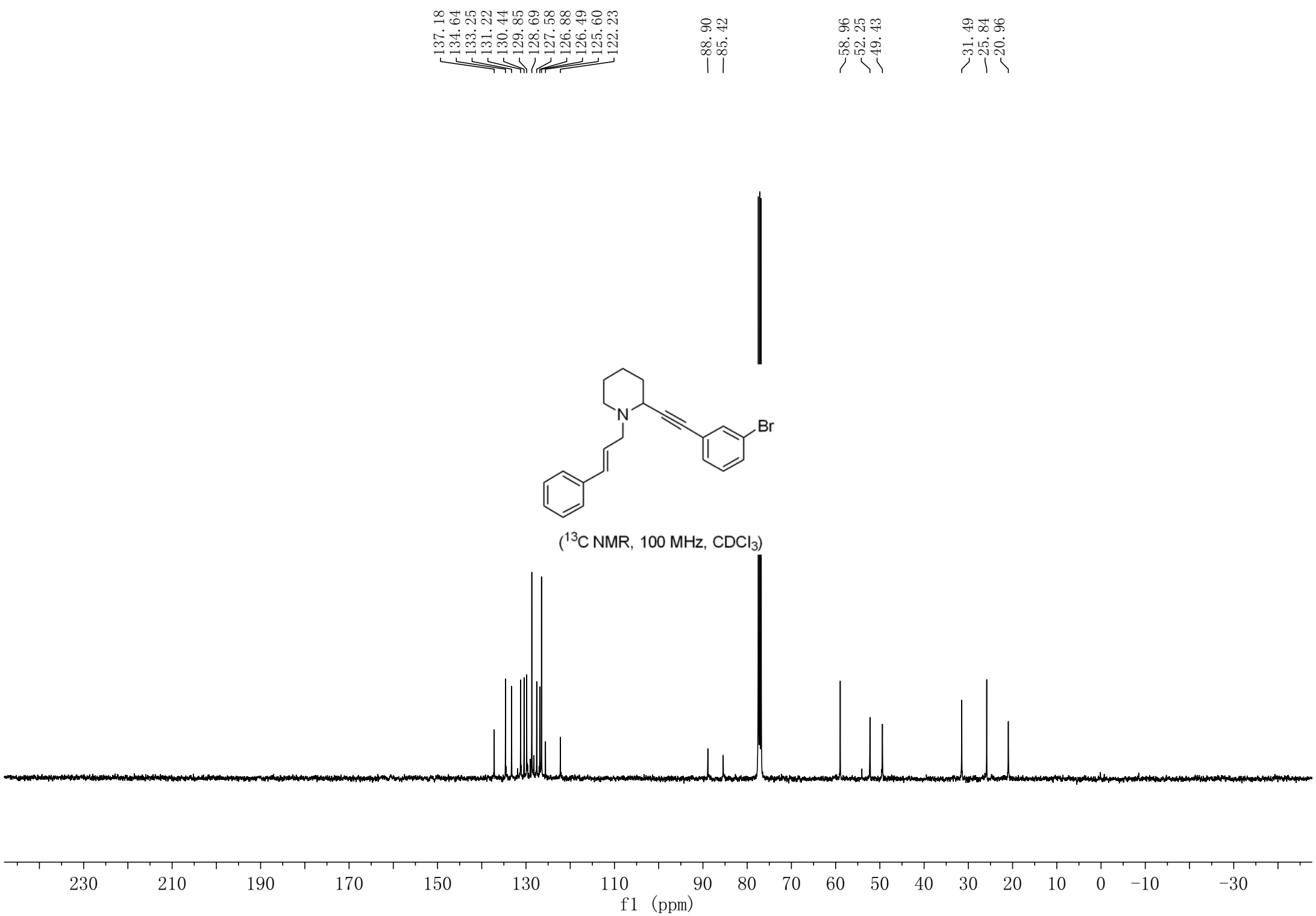
7.456
7.436
7.403
7.384
7.330
7.311
7.293
7.259
7.246
7.227
7.210
7.190
7.171
6.606
6.567
6.331
6.314
6.297
6.291
6.274
6.257
3.875
3.362
3.348
3.303
3.284
3.270
3.251
2.604
1.871
1.862
1.809
1.671
1.648
1.639
1.626
1.608
1.595
1.565
0.000
N
Br
(1H NMR, 400 MHz, CDCl3)
0.82
0.92
3.24
2.03
2.23
1.17
1.00
1.09
1.09
1.10
1.94
2.99
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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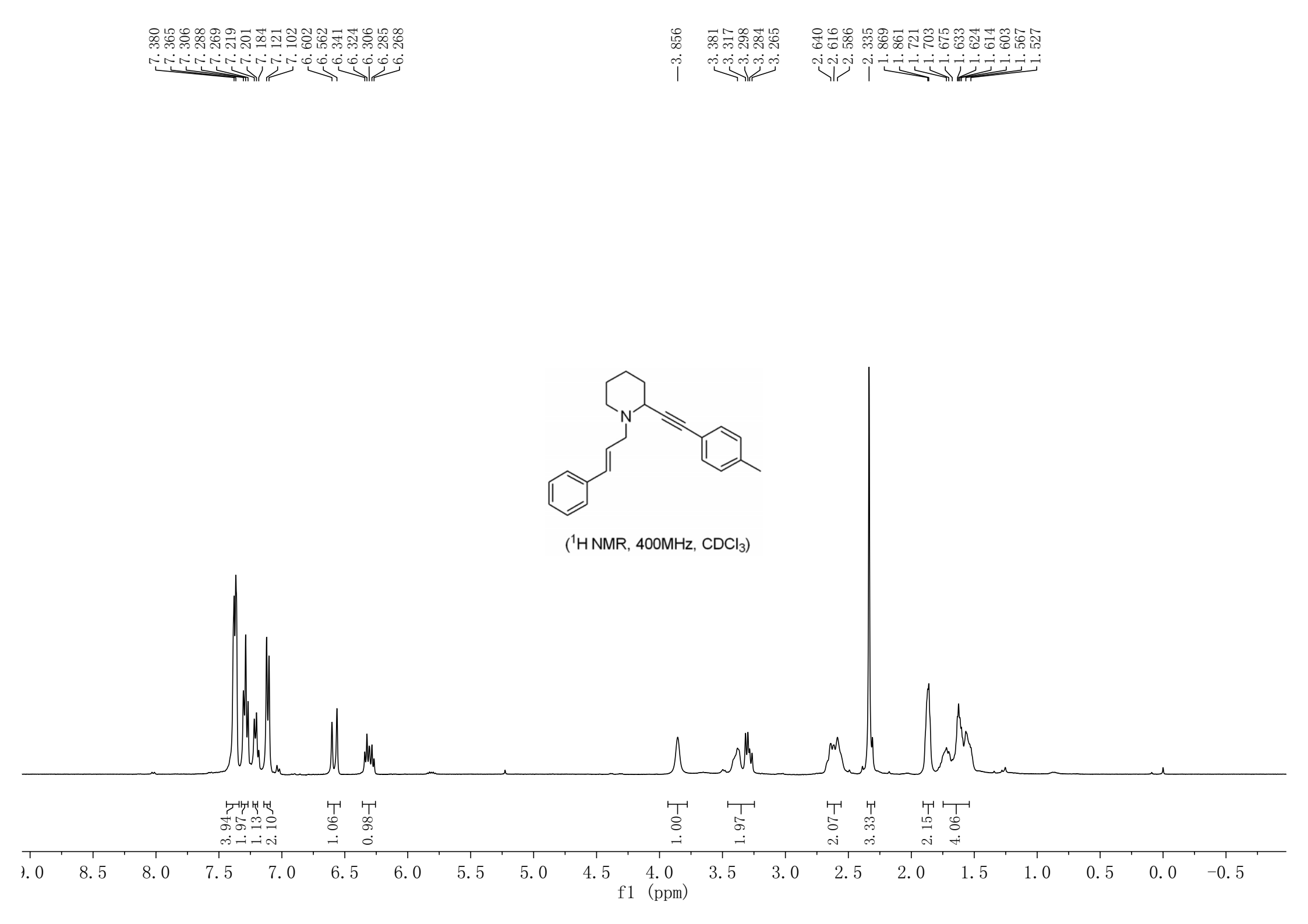
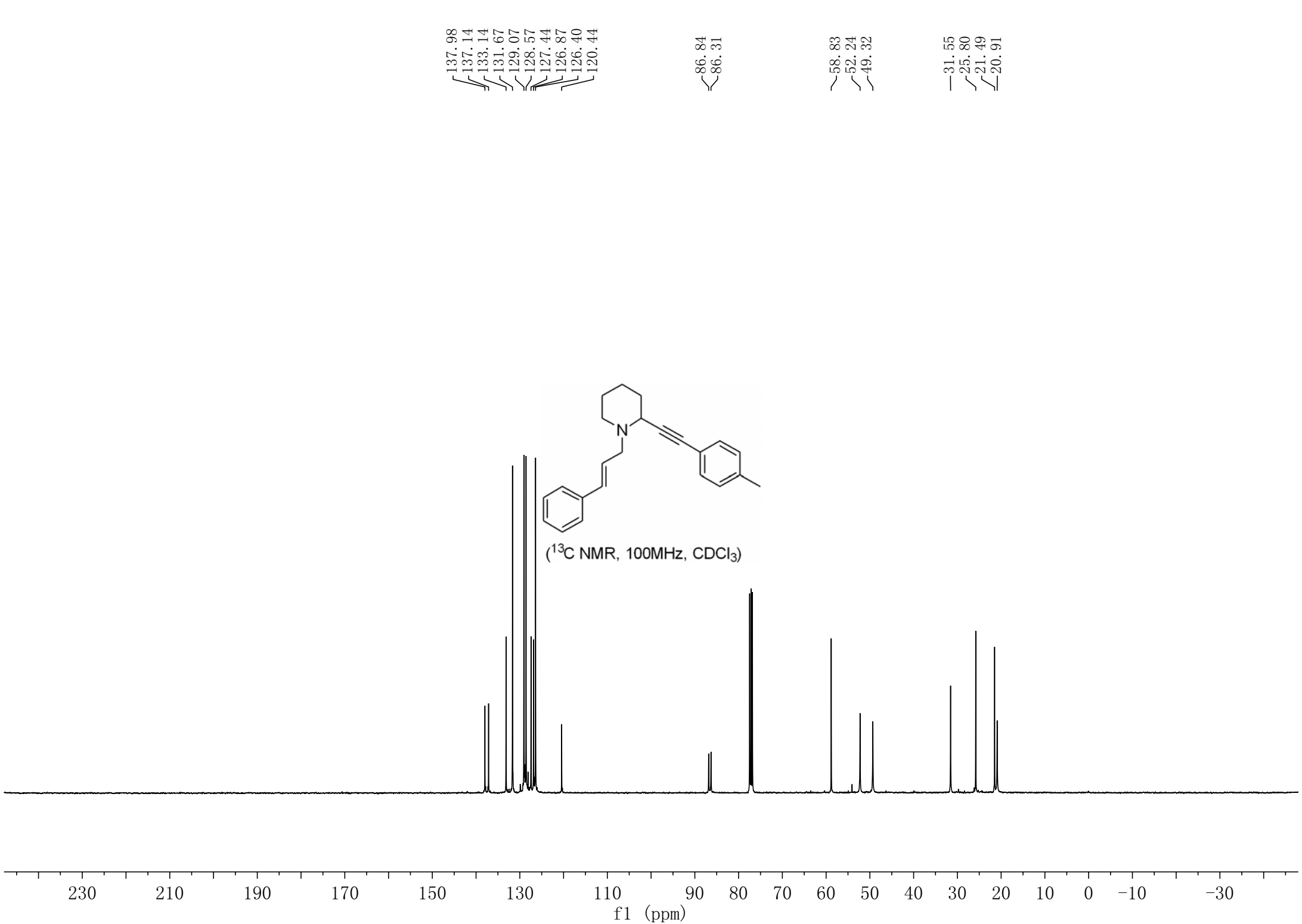
131.22
130.44
129.85
128.69
127.58
126.88
126.49
125.60
122.23
88.90
85.42
58.96
52.25
49.43
31.49
25.84
20.96
N
Br
(13C NMR, 100 MHz, CDCl3)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)


7.380
7.365
7.306
7.288
7.269
7.219
7.201
7.184
7.121
7.102
6.602
6.562
6.341
6.324
6.306
6.285
6.268
3.856
3.381
3.317
3.298
3.284
3.265
2.640
2.616
2.586
2.335
1.869
1.861
1.721
1.703
1.675
1.633
1.624
1.614
1.603
1.567
1.527
N
(1H NMR, 400MHz, CDCl3)
3.94
1.97
1.13
2.10
1.06
0.98
1.00
1.97
2.07
3.33
2.15
4.06
f1 (ppm)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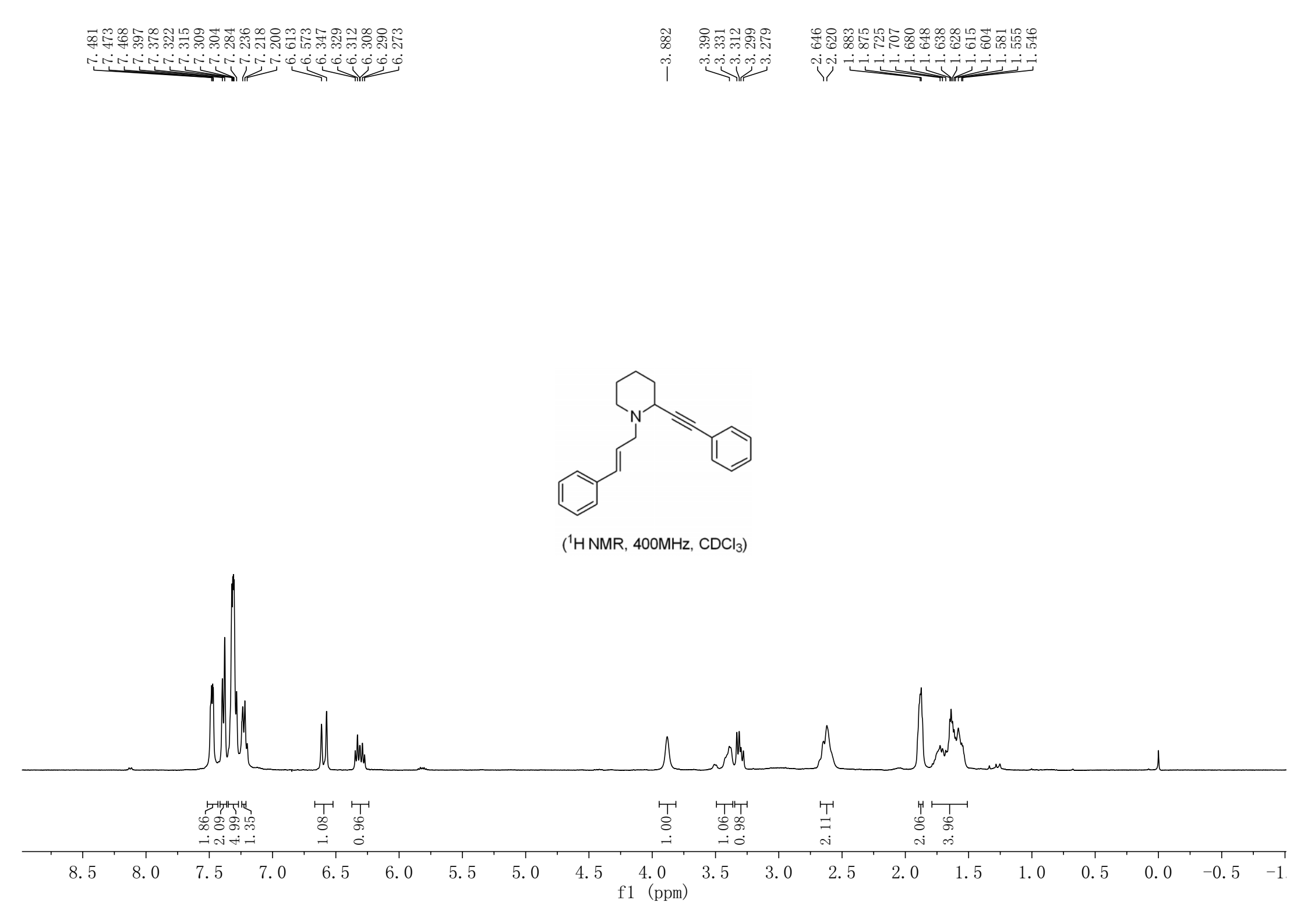
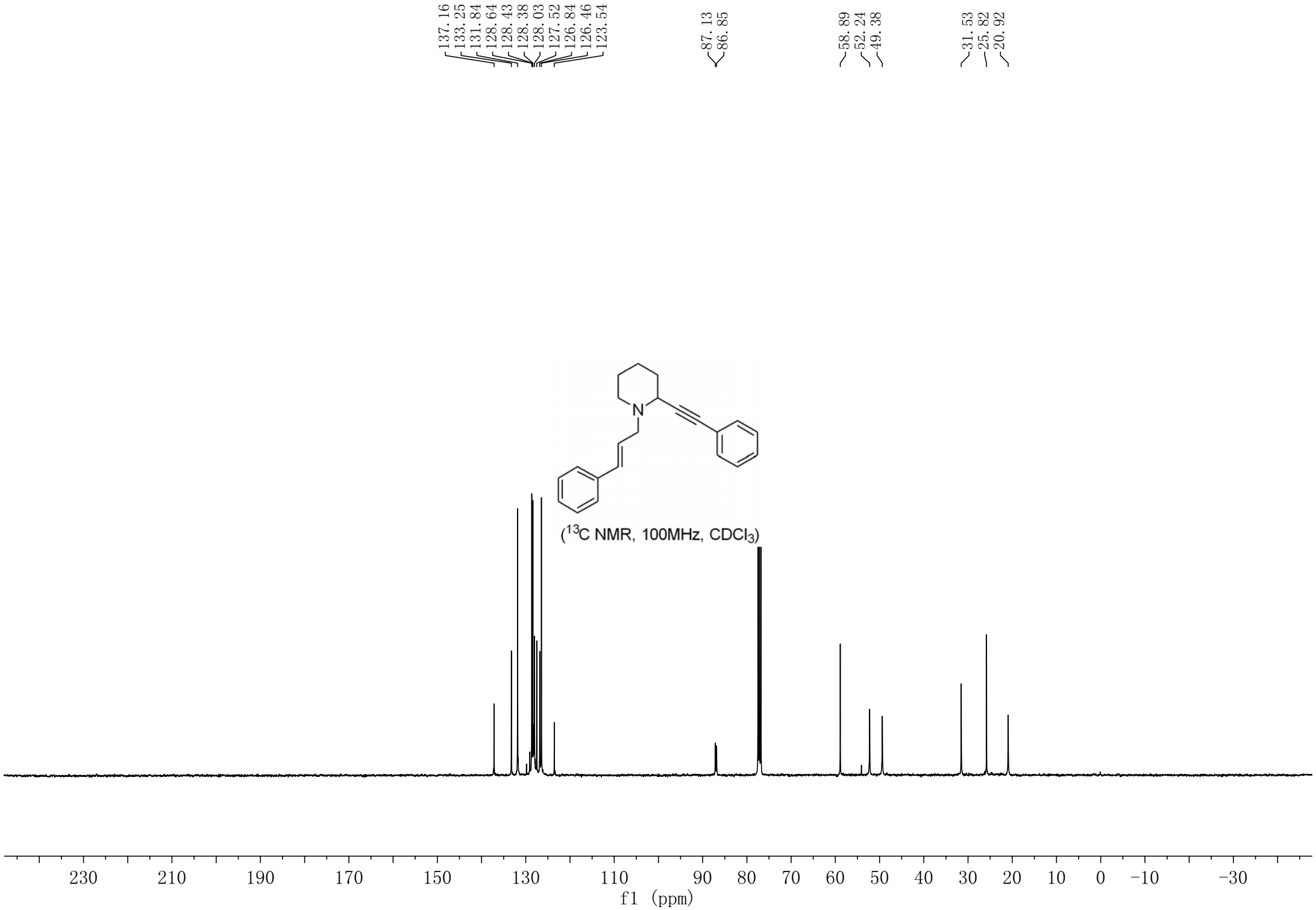
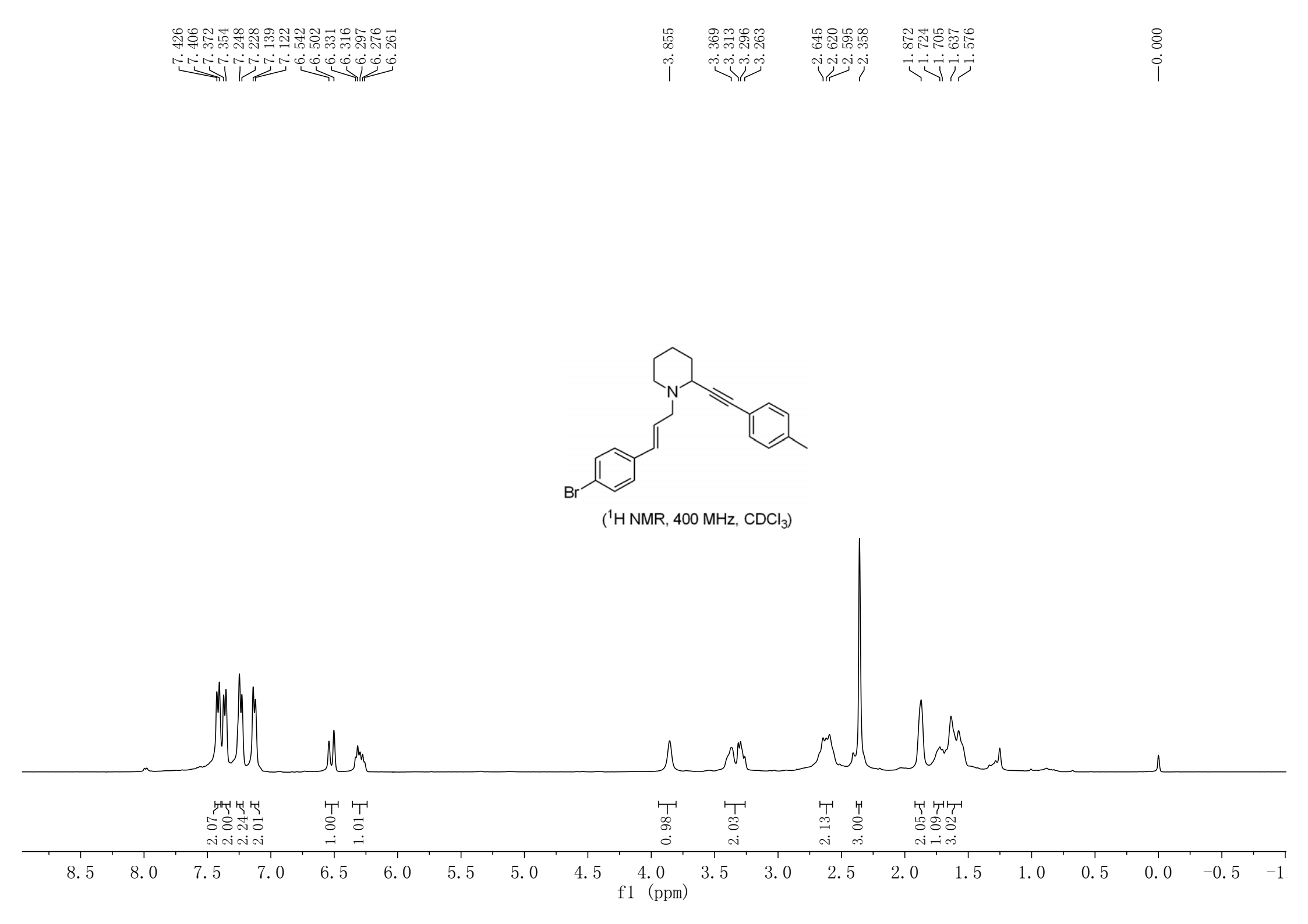
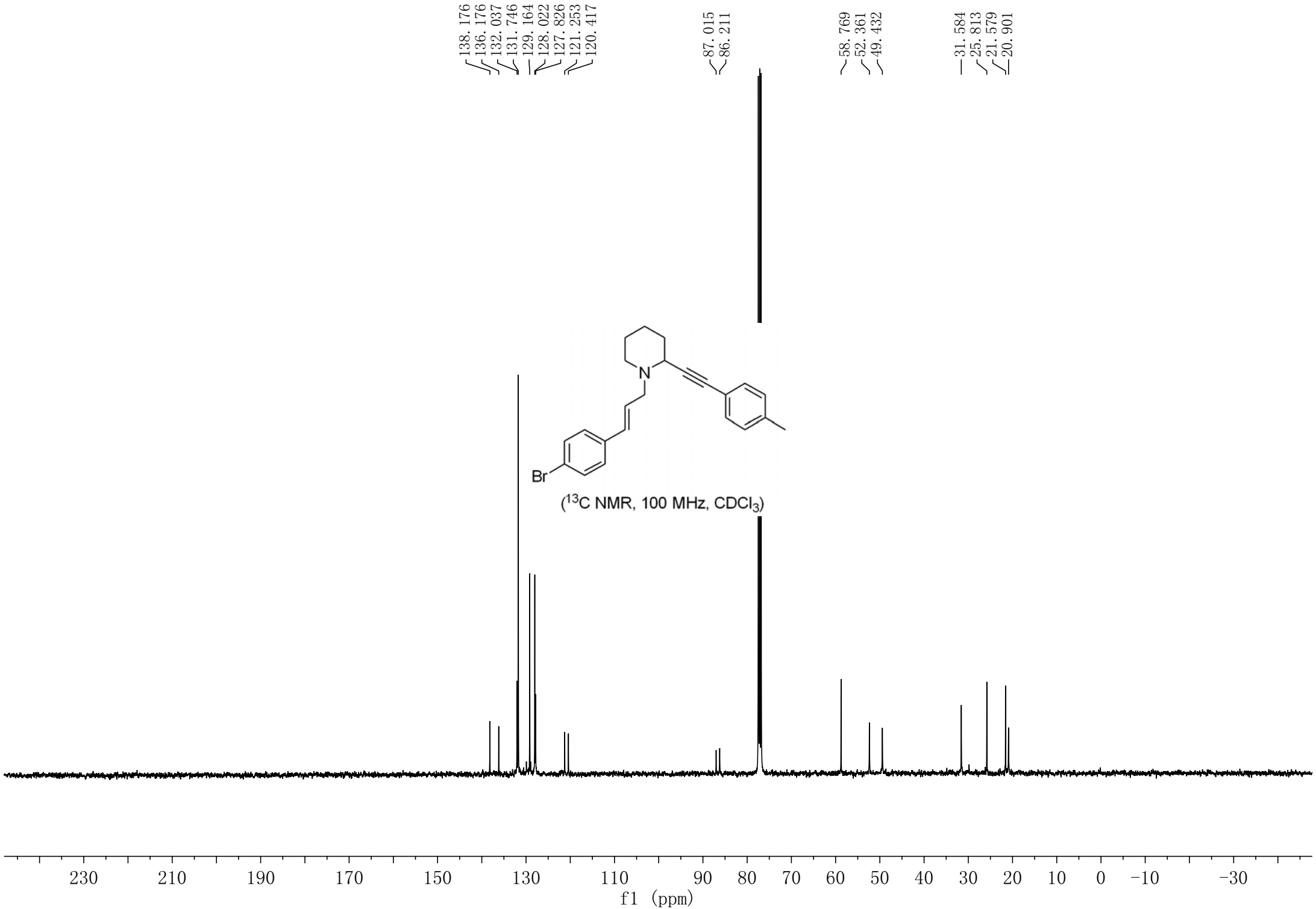
133.14
131.67
129.07
128.57
127.44
126.87
126.40
120.44
86.84
86.31
58.83
52.24
49.32
31.55
25.80
21.49
20.91
N
(^{13}C NMR, 100MHz, $CDCl_3$)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)


7.481
7.473
7.468
7.397
7.378
7.322
7.315
7.309
7.304
7.284
7.236
7.218
7.200
6.613
6.573
6.347
6.329
6.312
6.308
6.290
6.273
3.882
3.390
3.331
3.312
3.299
3.279
2.646
2.620
1.883
1.875
1.725
1.707
1.680
1.648
1.638
1.628
1.615
1.604
1.581
1.555
1.546
N
(1H NMR, 400MHz, CDCl3)
1.86
2.09
4.99
1.35
1.08
0.96
1.00
1.06
0.98
2.11
2.06
3.96
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


137.16
133.25
131.84
128.64
128.43
128.38
128.03
127.52
126.84
126.46
123.54
87.13
86.85
58.89
52.24
49.38
31.53
25.82
20.92
N
(^{13}C NMR, 100MHz, $CDCl_3$)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)


7.426
7.406
7.372
7.354
7.248
7.228
7.139
7.122
6.542
6.502
6.331
6.316
6.297
6.276
6.261
3.855
3.369
3.313
3.296
3.263
2.645
2.620
2.595
2.358
1.872
1.724
1.705
1.637
1.576
0.000
N
Br
(1H NMR, 400 MHz, CDCl3)
2.07
2.00
2.24
2.01
1.00
1.01
0.98
2.03
2.13
3.00
2.05
1.09
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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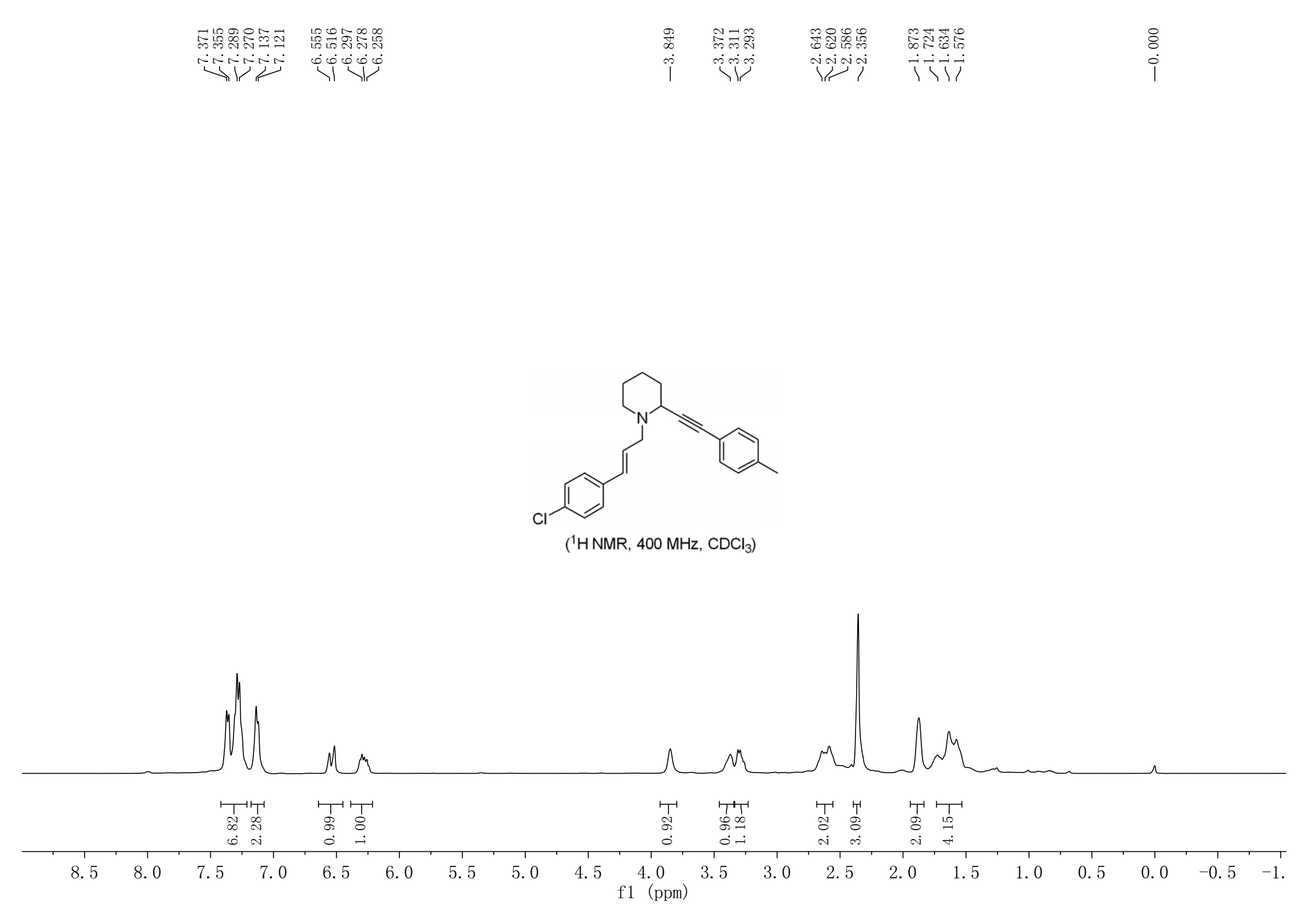
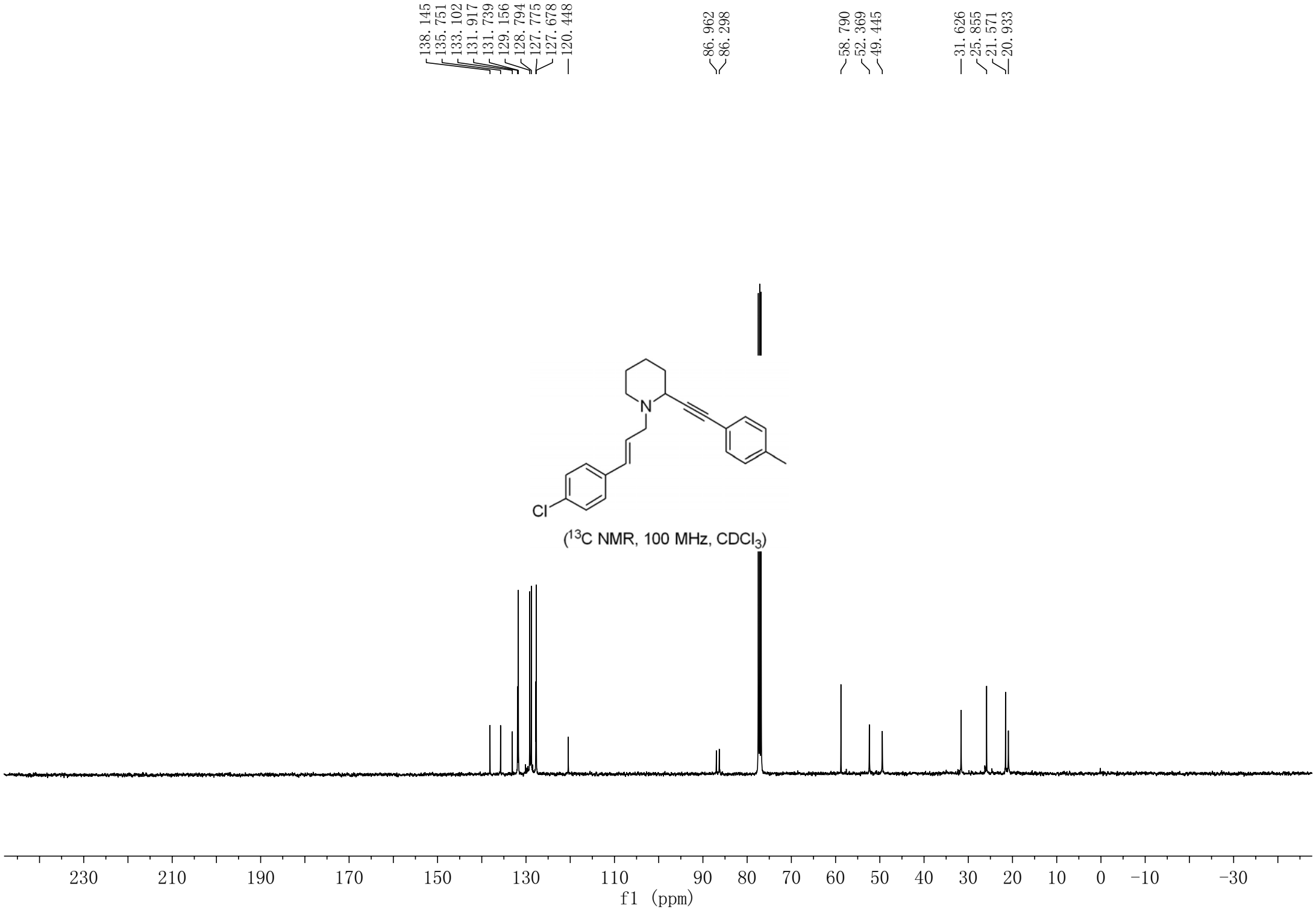
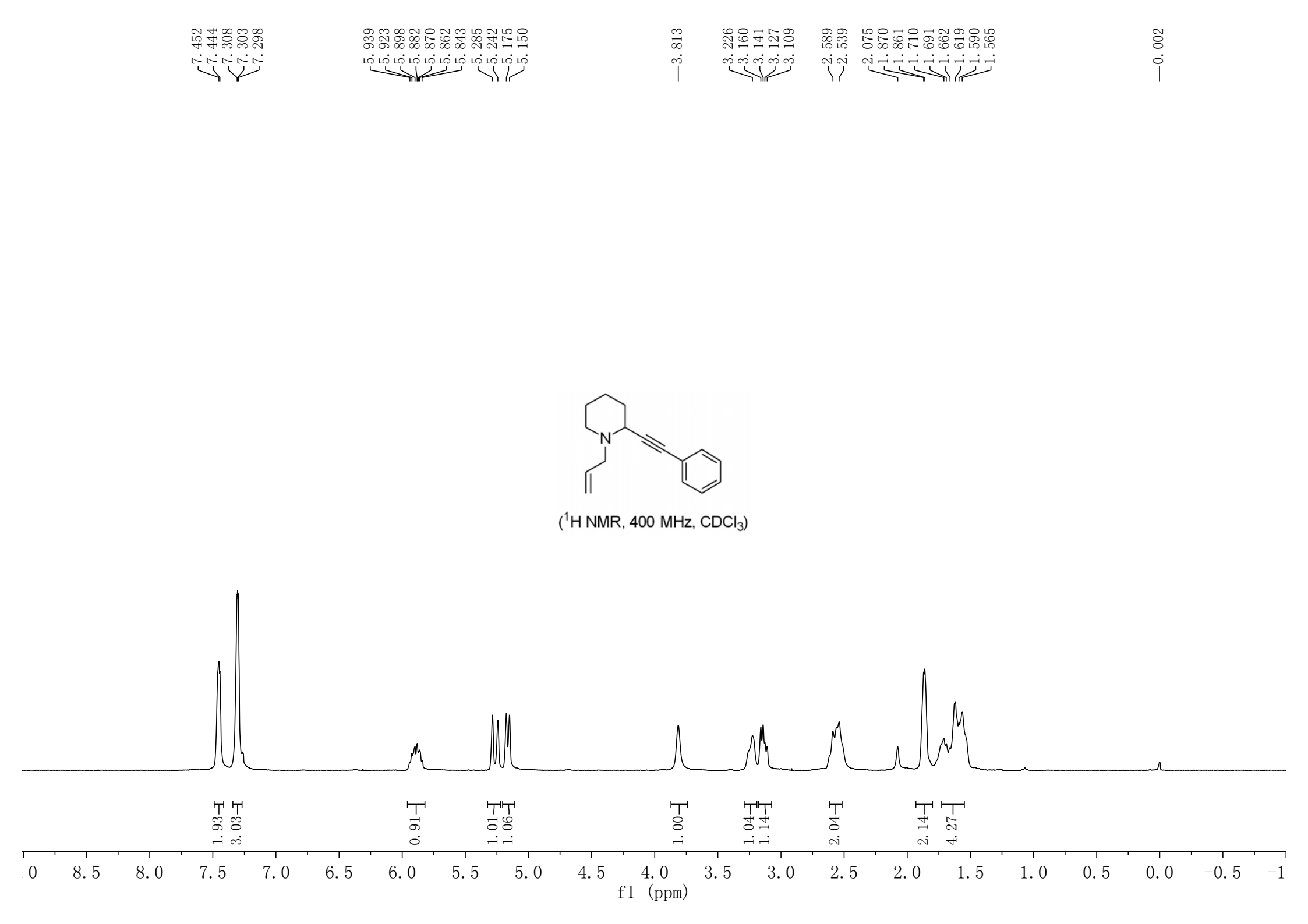
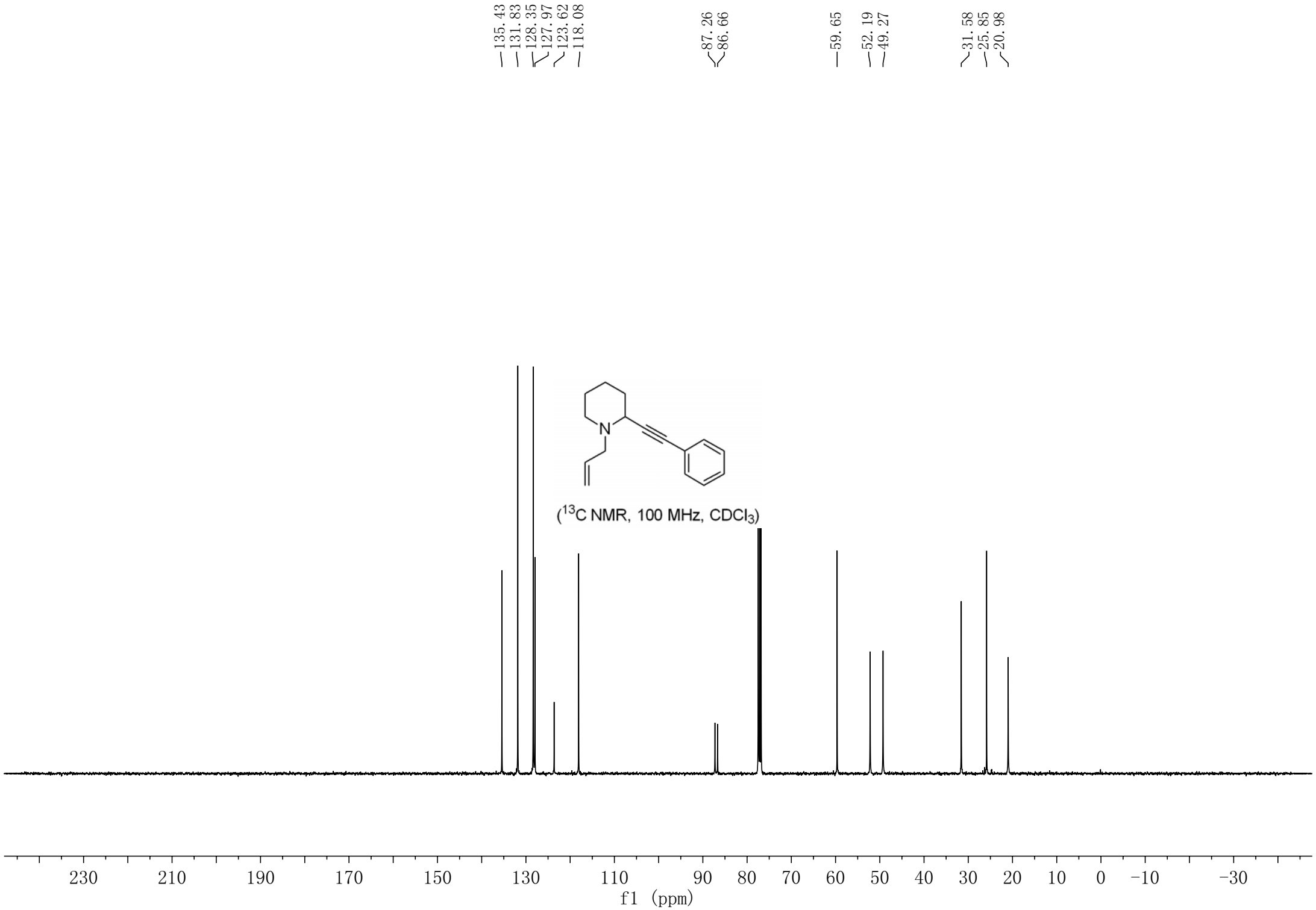
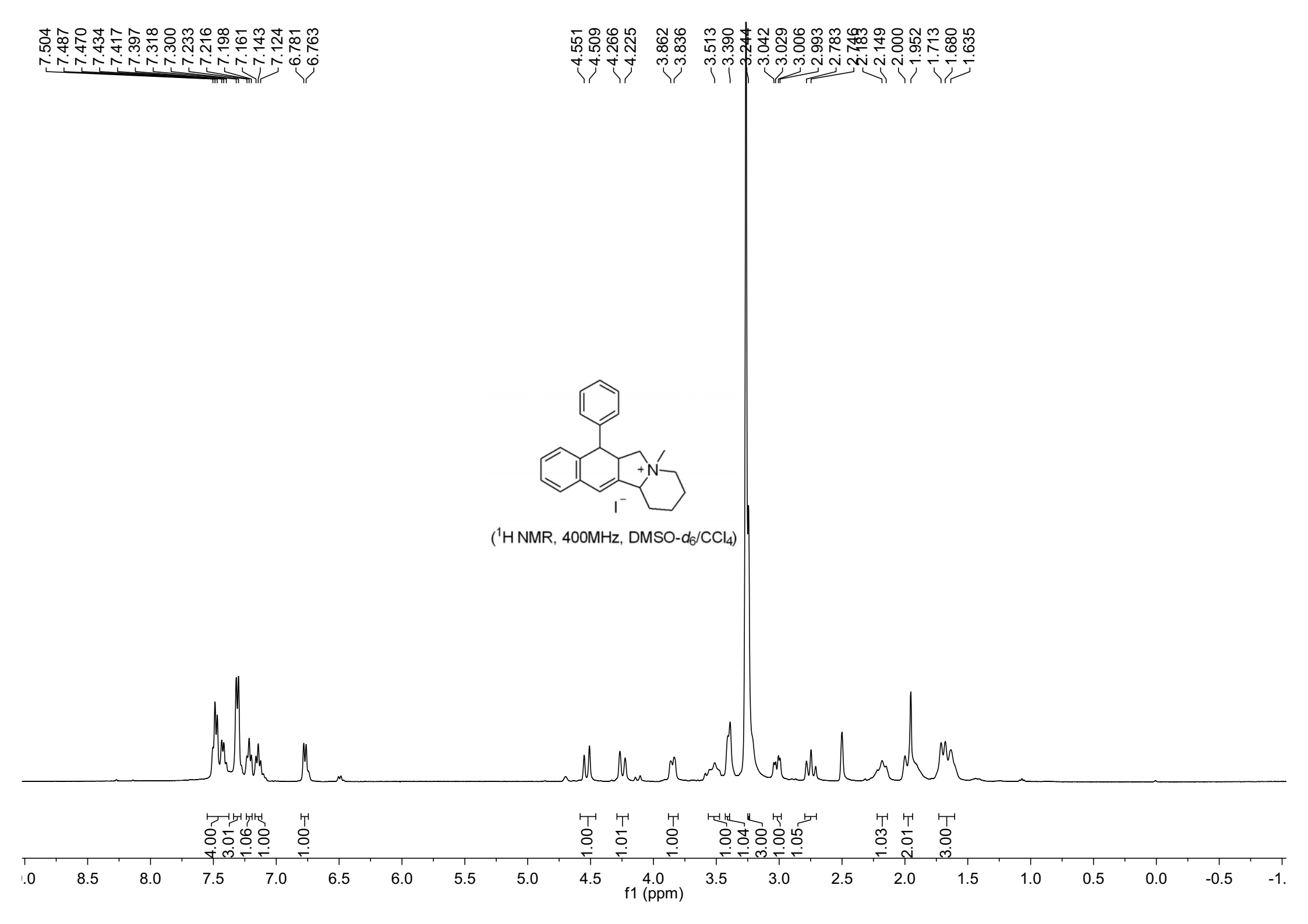
136.176
132.037
131.746
129.164
128.022
127.826
121.253
120.417
87.015
86.211
58.769
52.361
49.432
31.584
25.813
21.579
20.901
N
Br
(13C NMR, 100 MHz, CDCl3)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)

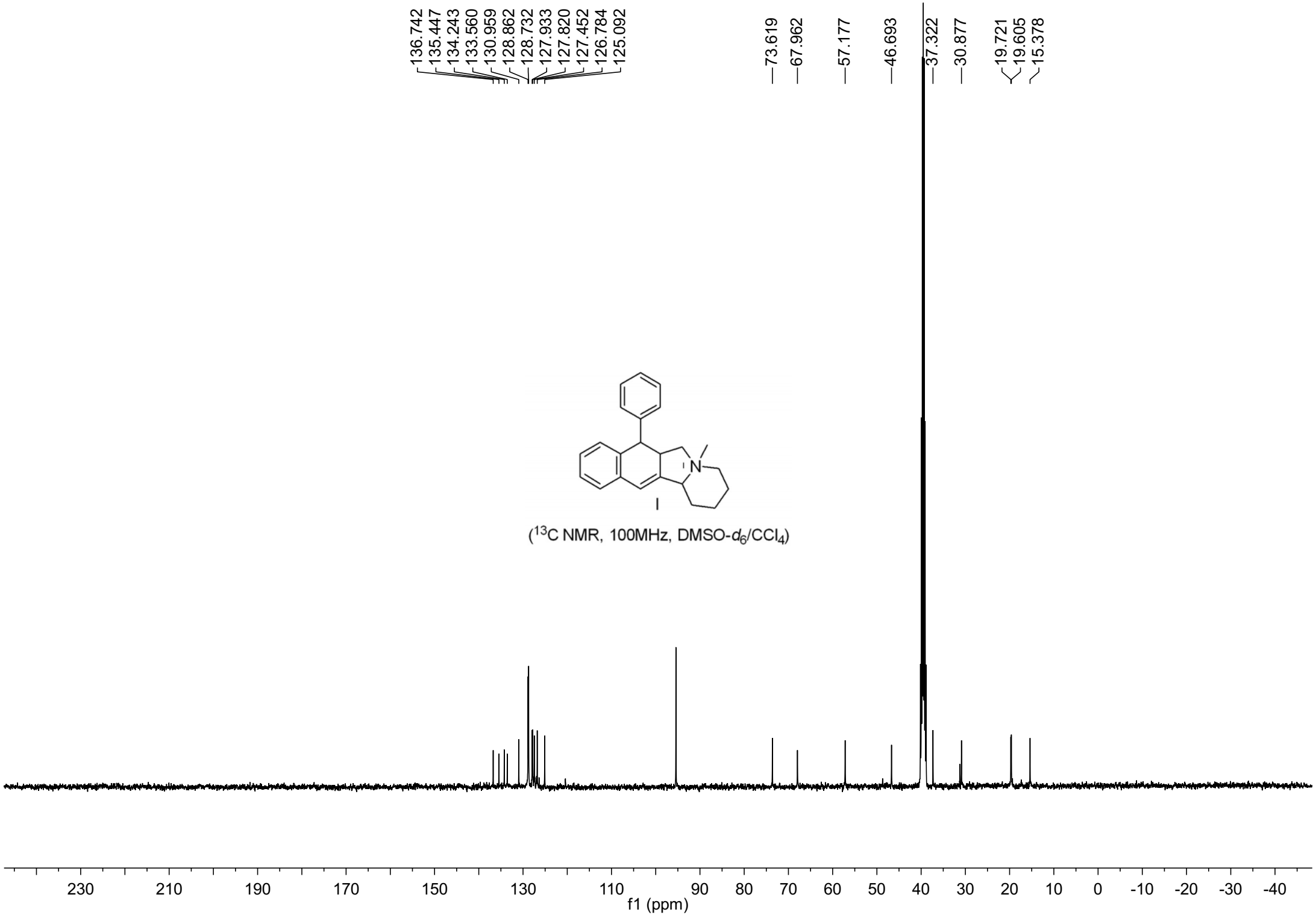

7.371
7.355
7.289
7.270
7.137
7.121
6.555
6.516
6.297
6.278
6.258
3.849
3.372
3.311
3.293
2.643
2.620
2.586
2.356
1.873
1.724
1.634
1.576
0.000
N
Cl
(1H NMR, 400 MHz, CDCl3)
6.82
2.28
0.99
1.00
0.92
0.96
1.18
2.02
3.09
2.09
4.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)

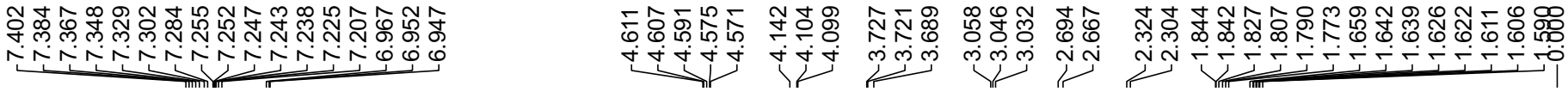

138.145
135.751
133.102
131.917
131.739
129.156
128.794
127.775
127.678
120.448
86.962
86.298
58.790
52.369
49.445
31.626
25.855
21.571
20.933
N
Cl
(13C NMR, 100 MHz, CDCl3)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)

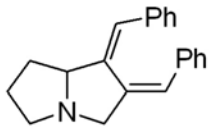

7.452
7.444
7.308
7.303
7.298
5.939
5.923
5.898
5.882
5.870
5.862
5.843
5.285
5.242
5.175
5.150
3.813
3.226
3.160
3.141
3.127
3.109
2.589
2.539
2.075
1.870
1.861
1.710
1.691
1.662
1.619
1.590
1.565
0.002
N
(1H NMR, 400 MHz, CDCl3)
1.93
3.03
0.91
1.01
1.06
1.00
1.04
1.14
2.04
2.14
4.27
f1 (ppm)


135.43
131.83
128.35
127.97
123.62
118.08
87.26
86.66
59.65
52.19
49.27
31.58
25.85
20.98
N
(^{13}C NMR, 100 MHz, $CDCl_3$)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)

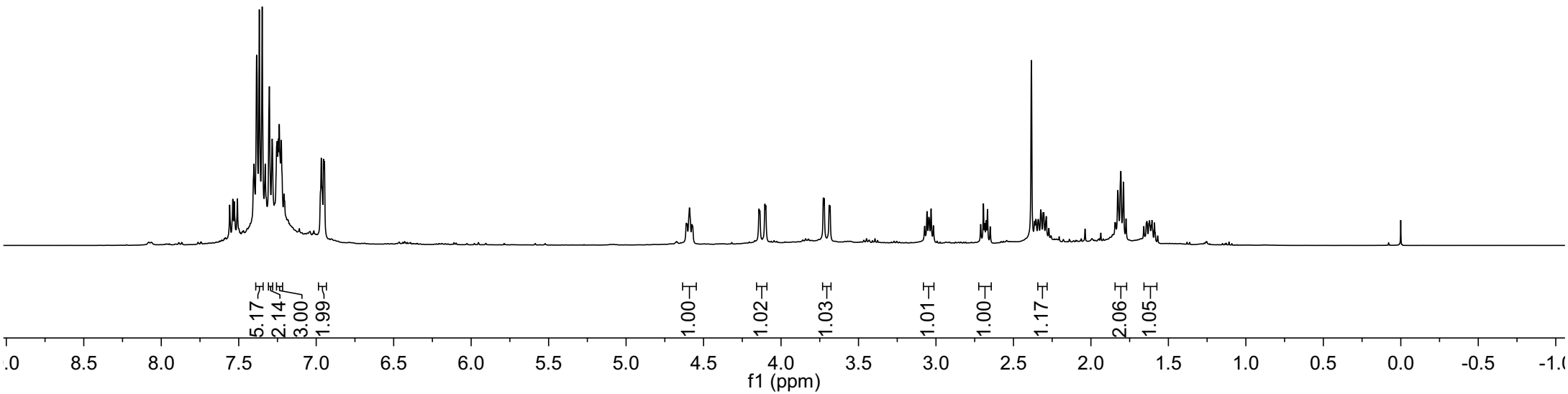

7.504
7.487
7.470
7.434
7.417
7.397
7.318
7.300
7.233
7.216
7.198
7.161
7.143
7.124
6.781
6.763
4.551
4.509
4.266
4.225
3.862
3.836
3.513
3.390
3.244
3.042
3.029
3.006
2.993
2.783
2.746
2.183
2.149
2.000
1.952
1.713
1.680
1.635
I⁻
(¹H NMR, 400MHz, DMSO-d6/CCl4)
4.00
3.01
1.06
1.00
1.00
1.00
1.01
1.00
1.00
1.04
3.00
1.00
1.05
1.03
2.01
3.00
f1 (ppm)

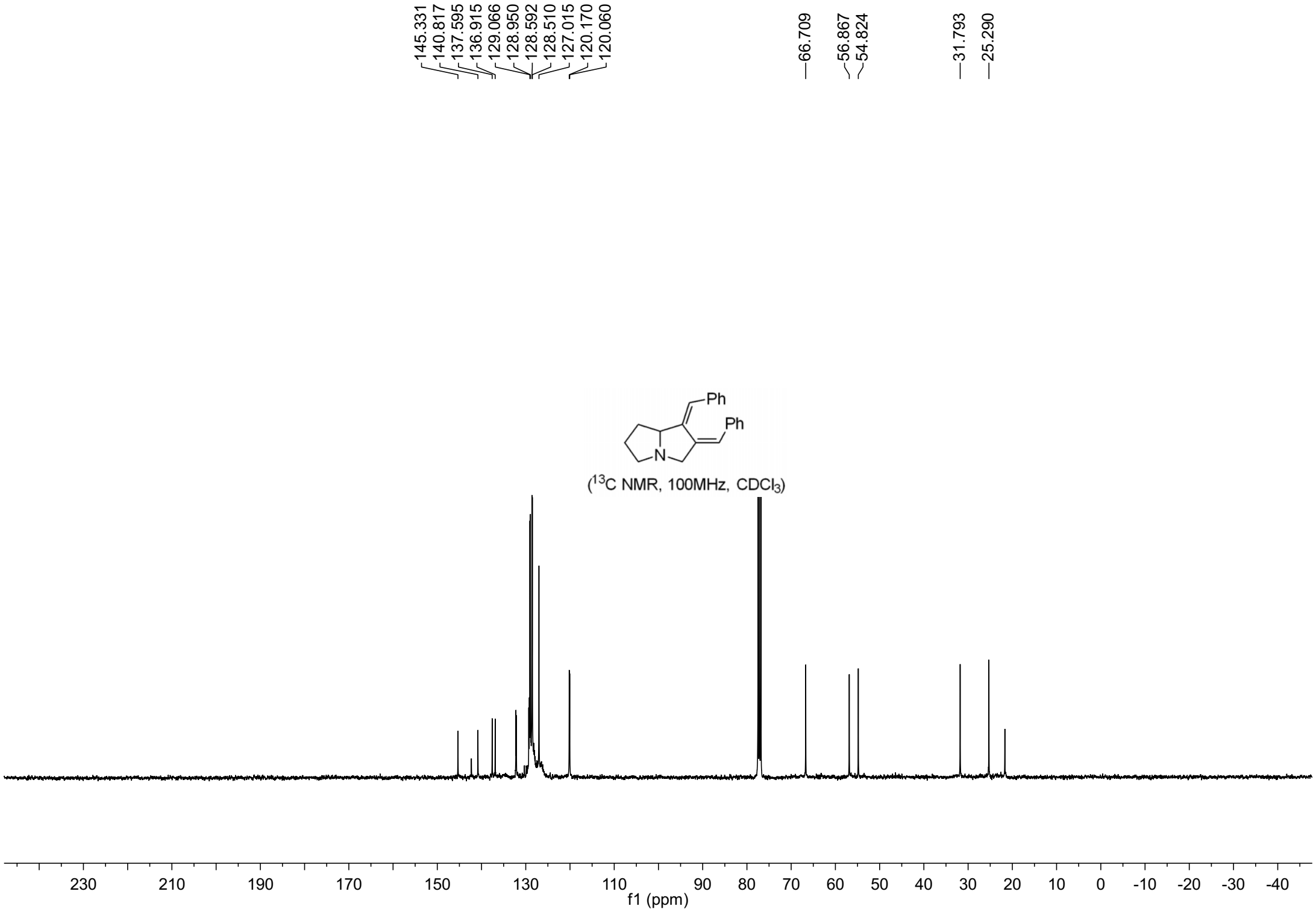

136.742
135.447
134.243
133.560
130.959
128.862
128.732
127.933
127.820
127.452
126.784
125.092
73.619
67.962
57.177
46.693
37.322
30.877
19.721
19.605
15.378
N
I
(13C NMR, 100MHz, DMSO-d6/CCl4)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

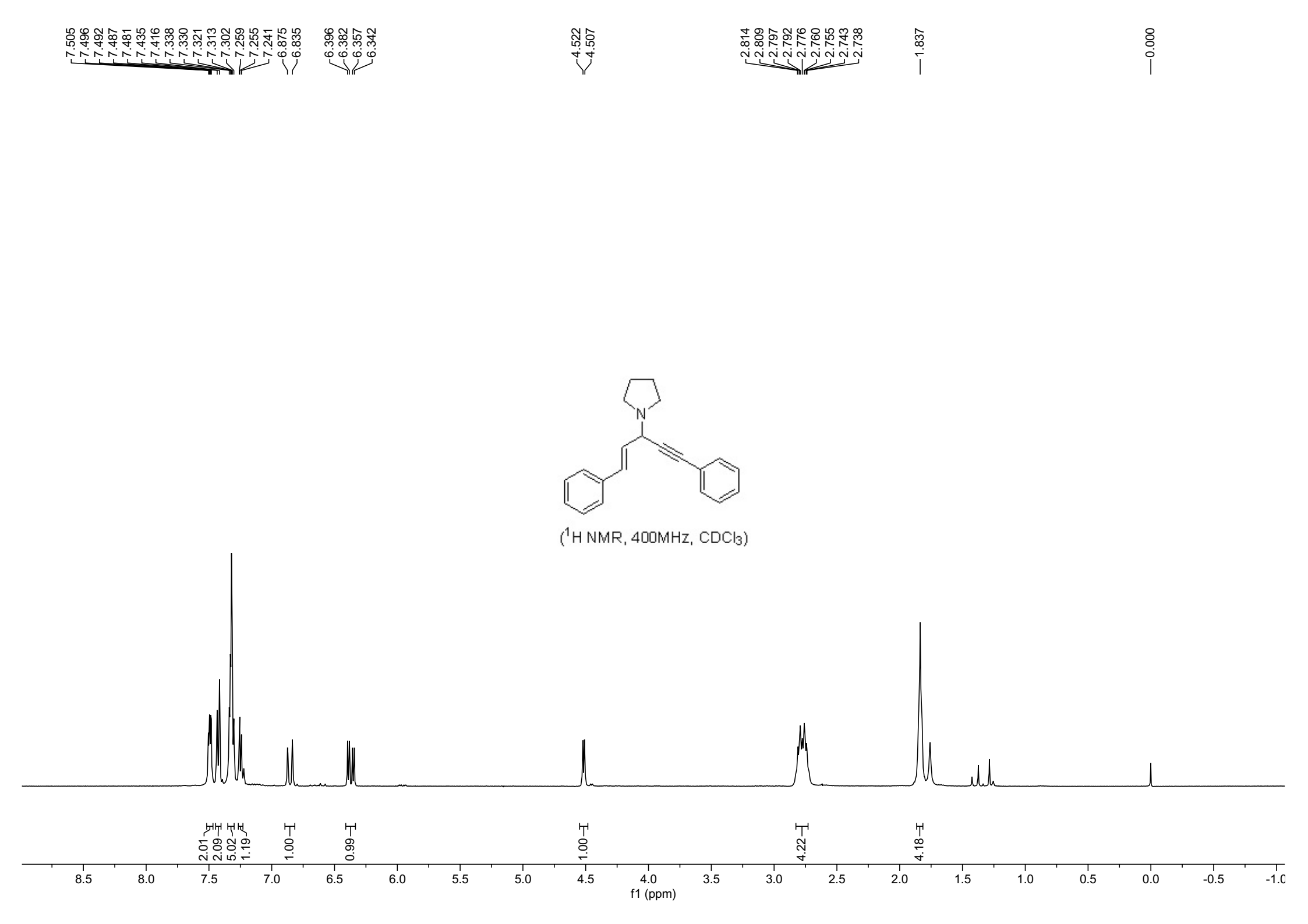


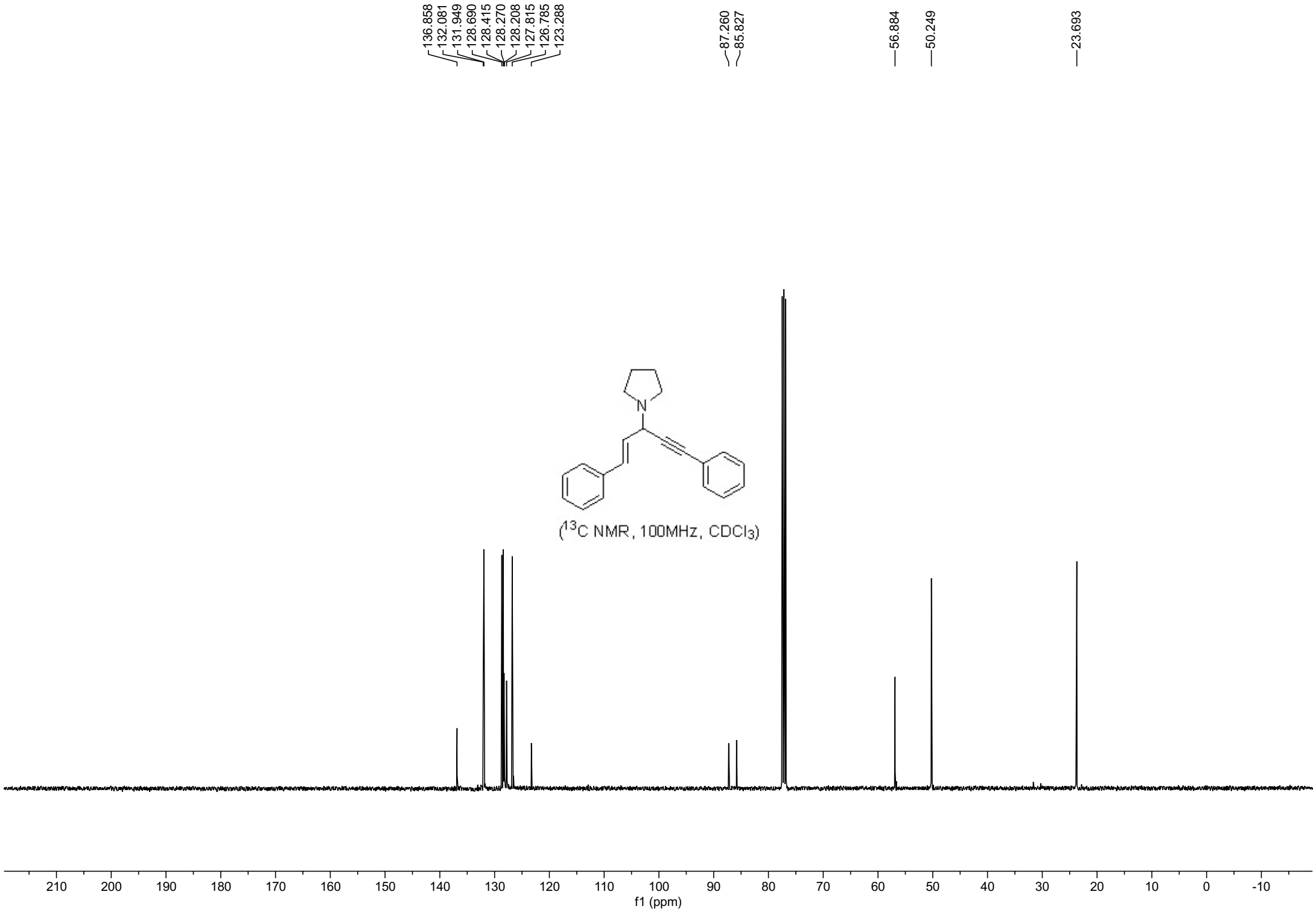


(^{1}H NMR, 400MHz, $CDCl_3$)

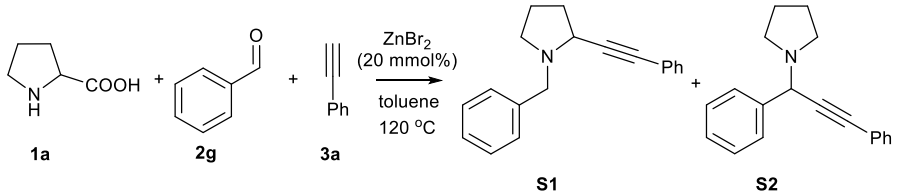



145.331
140.817
137.595
136.915
129.066
128.950
128.592
128.510
127.015
120.170
120.060
66.709
56.867
54.824
31.793
25.290
Ph
Ph
N
(13C NMR, 100MHz, CDCl3)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

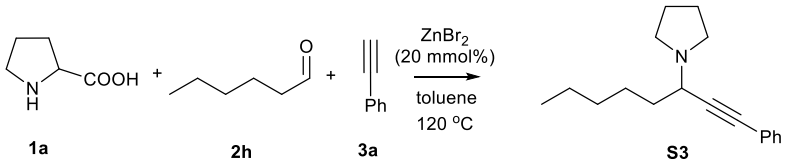

7.505
7.496
7.492
7.487
7.481
7.435
7.416
7.338
7.330
7.321
7.313
7.302
7.259
7.255
7.241
6.875
6.835
6.396
6.382
6.357
6.342
4.522
4.507
2.814
2.809
2.797
2.792
2.776
2.760
2.755
2.743
2.738
1.837
0.000
N
(1H NMR, 400MHz, CDCl3)
2.01
2.09
5.02
1.19
1.00
0.99
1.00
4.22
4.18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


136.858
132.081
131.949
128.690
128.415
128.270
128.208
127.815
126.785
123.288
87.260
85.827
56.884
50.249
23.693
N
(^{13}C NMR, 100MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

The results of decarboxylative A^3 reaction with phenylacetylene and hexanal.



Proline **1a** (1.5 mmol), phenylacetylene **3a** (1.5 mmol) and $ZnBr_2$ (0.2 mmol) were dissolved in dry toluene (5 mL) under Ar atmosphere. The mixture was heated to 120°C and a solution of benzaldehyde **2g** (1.0 mmol) in toluene (2 mL) was slowly added over 12h. Then, the reaction was cooled and concentrated. The residue was purified by flash chromatography on silica gel (PE/EA = 10:1) to give the **S1**[1] (133 mg, 51%) and **S2**[2] (42 mg, 16%).

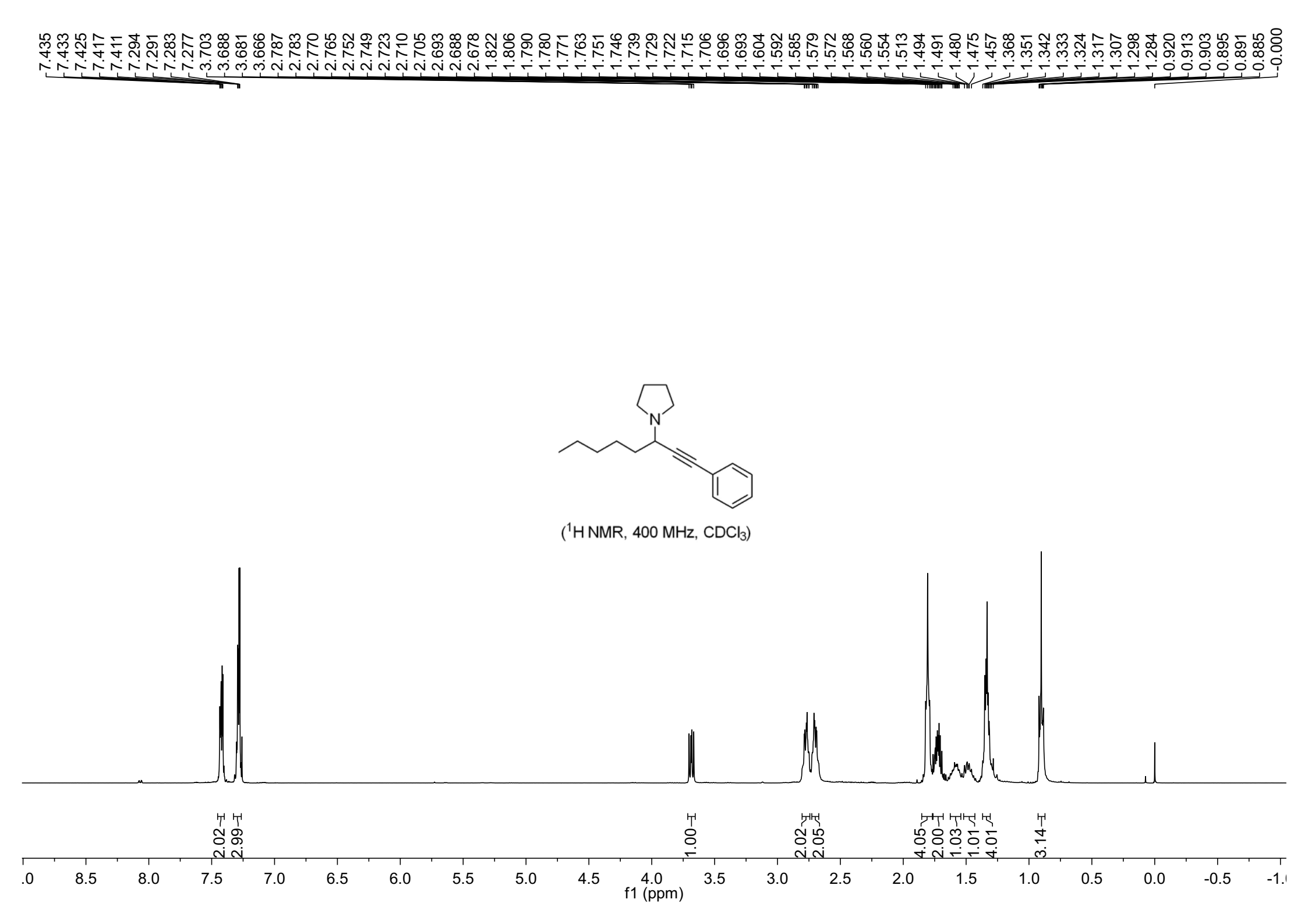


Proline **1a** (1.5 mmol), phenylacetylene **3a** (1.5 mmol) and $ZnBr_2$ (0.2 mmol) were dissolved in dry toluene (5 mL) under Ar atmosphere. The mixture was heated to 120°C and a solution of hexanal **2h** (1.0 mmol) in toluene (2 mL) was slowly added over 12h. Then, the reaction was cooled and concentrated. The residue was purified by flash chromatography on silica gel (PE/EA =5:1) to give the **S3** as colorless oil (170 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.40 (m, 2H), 7.33-7.27 (m, 3H), 3.68 (dd, J = 8.8, 6.0 Hz, 1H), 2.80-2.75 (m, 2H), 2.76-2.68 (m, 2H), 1.84-1.77 (m, 4H), 1.76-1.69 (m, 2H), 1.63-1.54 (m, 1H), 1.52-1.43 (m, 1H), 1.37-1.31 (m, 4H), 0.93-0.88 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.9, 128.3, 127.9, 123.6, 88.4, 85.4, 55.3, 49.9, 35.1, 31.8, 26.5, 23.6, 22.7, 14.2 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{26}N^+$: 256.2060, found: 256.2060.

References

1. H.-P. Bi, Q. Teng, M. Guan, W.-W. Chen, Y.-M. Liang, X. Yao and C.-J. Li, J. Org. Chem., 2010, **75**, 783-788.

2. C. Zhao and D. Seidel, *J. Am. Chem. Soc.*, 2015, **137**, 4650-4653.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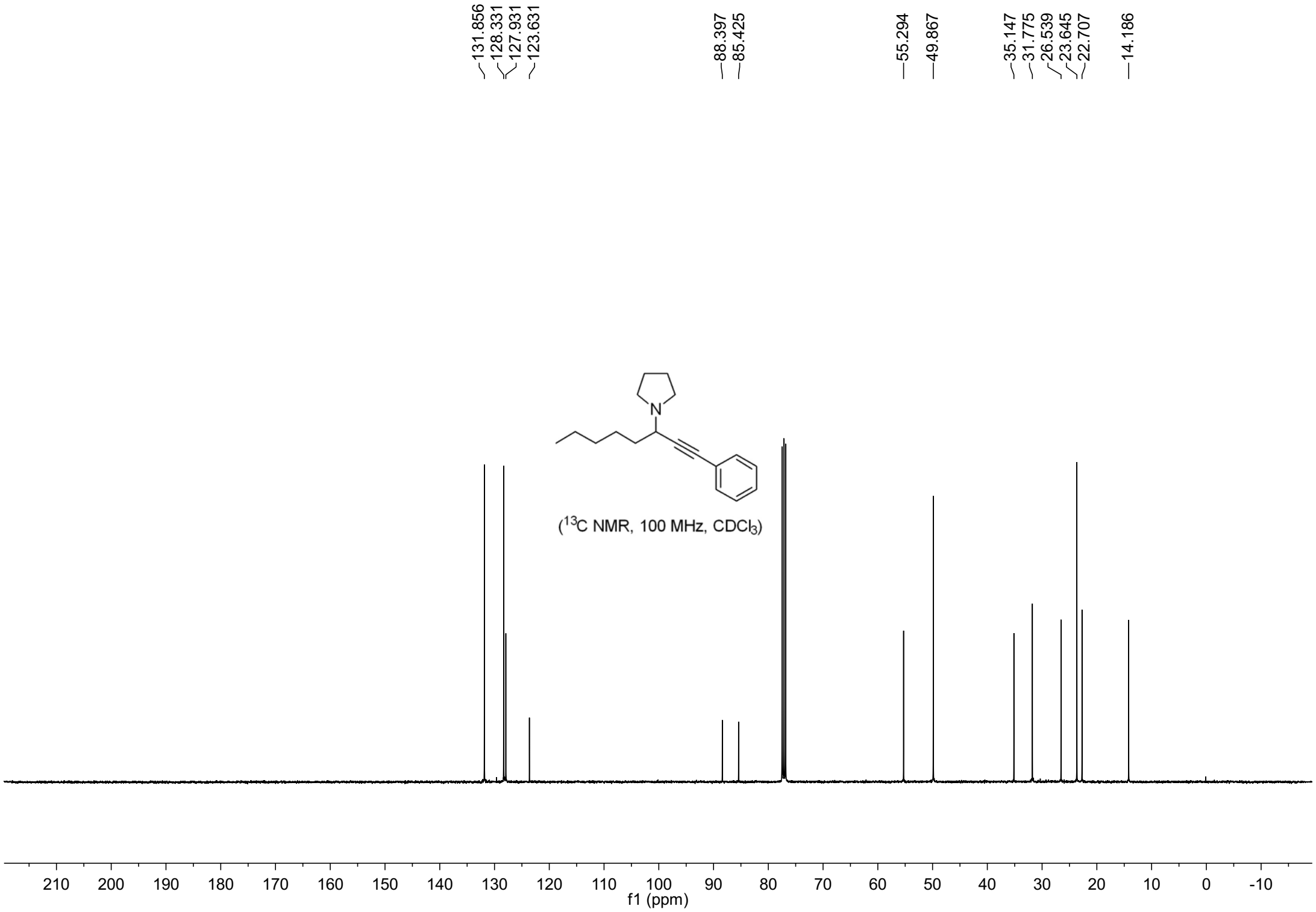
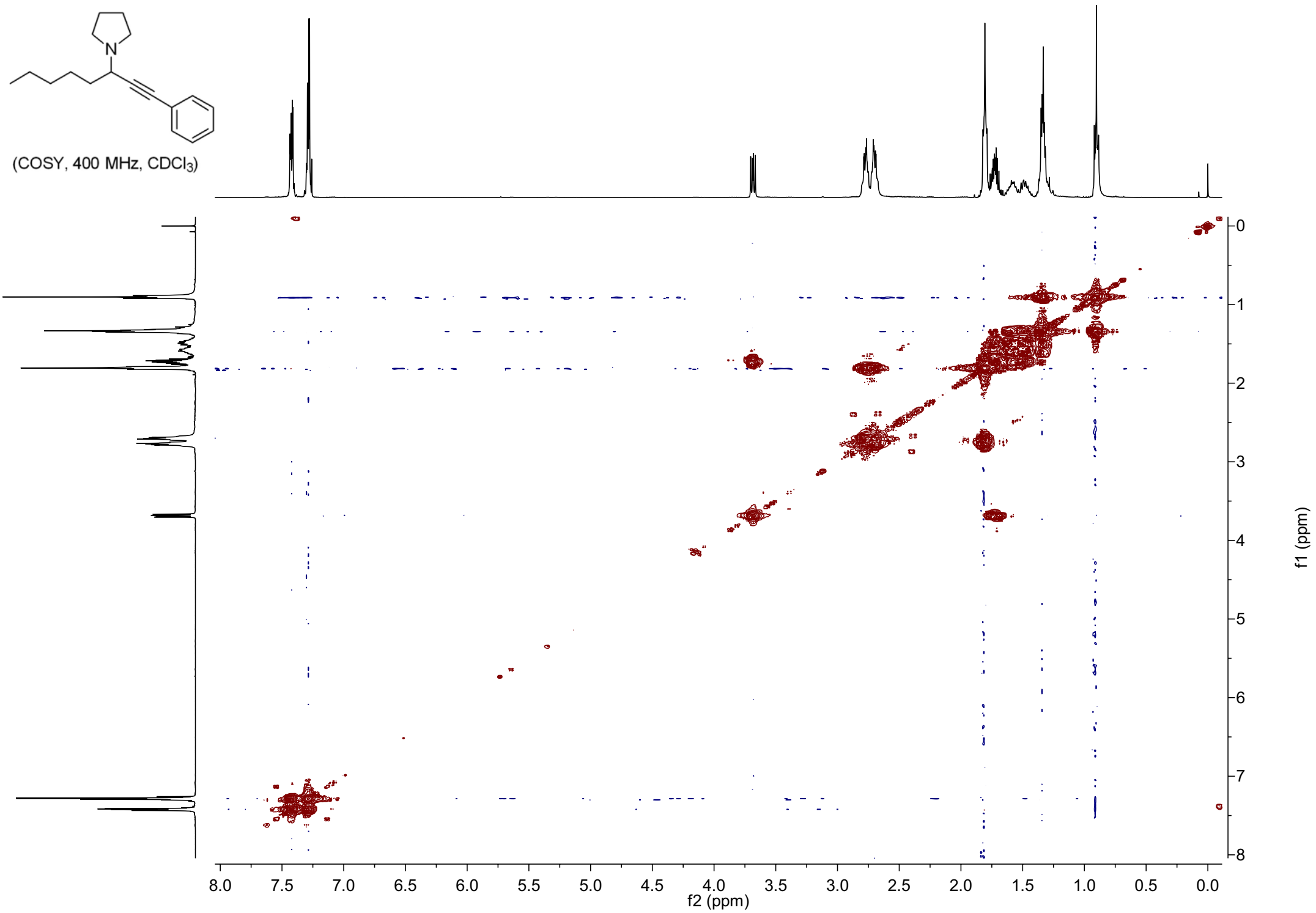
7.433
7.425
7.417
7.411
7.294
7.291
7.283
7.277
3.703
3.688
3.681
3.666
2.787
2.783
2.770
2.765
2.752
2.749
2.723
2.710
2.705
2.693
2.688
2.678
1.822
1.806
1.790
1.780
1.771
1.763
1.751
1.746
1.739
1.729
1.722
1.715
1.706
1.696
1.693
1.604
1.592
1.585
1.579
1.572
1.568
1.560
1.554
1.513
1.494
1.491
1.480
1.475
1.457
1.368
1.351
1.342
1.333
1.324
1.317
1.307
1.298
1.284
0.920
0.913
0.903
0.895
0.891
0.885
-0.000
N
(^{1}H NMR, 400 MHz, $CDCl_3$)
2.02
2.99
1.00
2.02
2.05
4.05
2.00
1.03
1.01
4.01
3.14
f1 (ppm)


131.856
128.331
127.931
123.631
88.397
85.425
55.294
49.867
35.147
31.775
26.539
23.645
22.707
14.186
N
(^{13}C NMR, 100 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


N
(COSY, 400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

The results of DFT calculations.

Computational methods: Calculations were carried out with the Gaussian 09 programs[1]. The geometries of all the species were fully optimized by using DFT of the B3LYP method[2-4] with the 6-31G* basis set.[5,6] All stationary points were verified as either minima (zero imaginary frequencies) or transition states (a single imaginary frequency). Reported relative energies are Gibbs free energies in kcal/mol. Molecular structure graphics were generated using CYLview.[7]

To further explore the regional selectivity of the reaction with different zinc catalysts, the DFT calculations with ZnF_2 and $ZnBr_2$ were performed and the results show that the energy of **7a**-ZnF_2 is ca. 3.06 kJ/mol lower than that of **7b**-ZnF_2. Therefore, **7a**-ZnF_2 is more favorable when ZnF_2 was used, the major product is **5**. When $ZnBr_2$ was used, the energy of **7b**-$ZnBr_2$ is ca. 0.03 kJ/mol lower than that of **7a**-$ZnBr_2$ (Fig. S1). However, the transition state **8b** is ca. 7.08 kJ/mol lower than that of **8a** (Fig. S2). Therefore, **4** was the major product when $ZnBr_2$ was used. Furthermore, the **8b** is the possible transition state for the reaction based on the DFT calculations results.

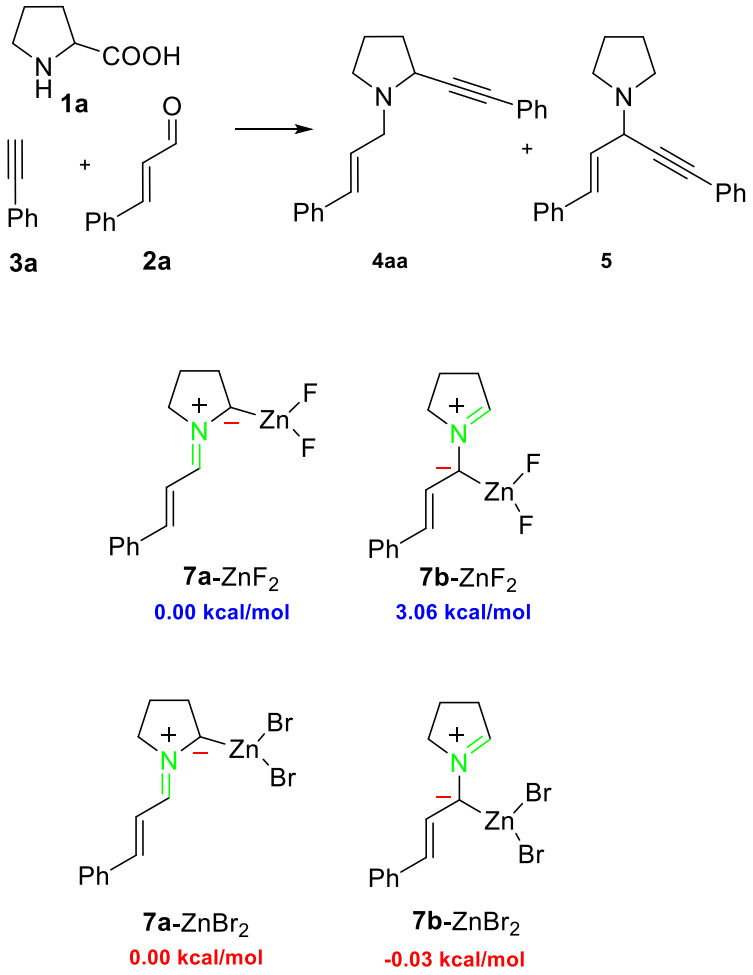


Fig. S1.

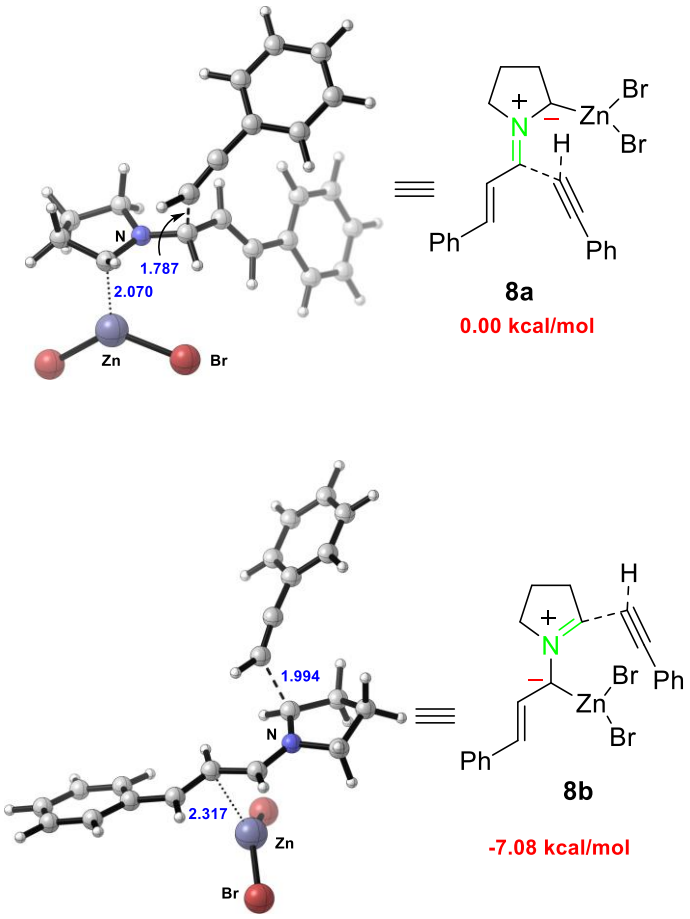
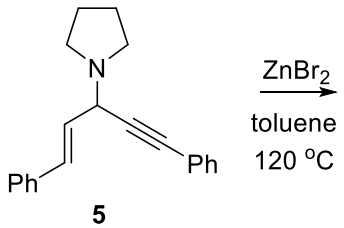


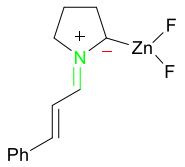
Fig. S2

When **5** was refluxed in toluene in the presence of $ZnBr_2$, the 5 was consumed completely and the reaction mixture was complexed, no major product can be isolated and characterized (Scheme S1). This result explained the high regional selectivity and moderate yields of the reaction.



Scheme S1. 5 (0.5 mmol) in toluene (5 mL) was refluxed in the presence of $ZnBr_2$ (0.1 mmol) for 12h.

Data for the DFT calculations



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N	1.19119600	1.14649600	-0.25774600
C	2.61117300	0.76695200	-0.47681000
C	3.36259300	1.90345800	0.21655200
C	-3.54761200	-0.25810700	-0.05494400
C	-2.10459600	-0.36567800	-0.20709600
C	-1.18156600	0.63274200	-0.16222200
C	0.20070300	0.30054700	-0.32718900
C	2.47509900	3.14314600	-0.01248500
C	-4.31847000	-1.43493900	-0.13384500
C	-5.70318000	-1.39493800	0.00468800
C	-6.34579100	-0.17556300	0.22525800
C	-5.59579900	1.00339400	0.30634700
C	-4.21382100	0.96496100	0.16806600
H	0.49572800	-0.75007600	-0.47974000
H	-1.47727000	1.66444400	0.00517700
H	-1.72660700	-1.37446800	-0.37155000
H	4.37201600	2.02443700	-0.18638400
H	3.46511300	1.71130900	1.29244300
H	0.33024600	3.07117600	-0.55512700
H	0.66948100	2.64556800	1.13597000
H	2.65002800	3.95512100	0.70014200
H	2.63435600	3.54003400	-1.02166100
H	-3.81758000	-2.38452500	-0.30442600
H	-6.27984200	-2.31312100	-0.05887700
H	-7.42610000	-0.14054100	0.33429300
H	-6.09421800	1.95316900	0.47847100
H	-3.64707600	1.88889600	0.23400500
H	2.76860200	0.85017500	-1.56357200
Zn	3.01474700	-1.13831000	0.01496900
F	4.50147300	-1.84921000	0.67639200
F	1.51692500	-2.17838300	-0.25661000

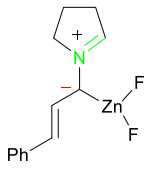
0 of imaginary frequencies

Sum of electronic and zero-point Energies= -2537.752086

Sum of electronic and thermal Energies= -2537.735069

Sum of electronic and thermal Enthalpies= -2537.734125

Sum of electronic and thermal Free Energies= -2537.800071



C	0.86136100	-0.13930300	-0.71440800
C	-0.48441900	-0.36957100	-0.17738200
C	-1.63215500	-0.17763200	-0.86207700
C	3.06891500	-2.79782300	0.67579700
C	1.74826700	-2.16043000	0.38469200
N	1.84427200	-1.12779000	-0.39890800
C	3.26997800	-0.87222000	-0.77444300
C	3.97543300	-2.18711700	-0.41967900
C	-2.99728800	-0.25350200	-0.33579100
C	-4.07288700	-0.30212900	-1.24233900
C	-5.38939300	-0.40150100	-0.79761900
C	-5.66511000	-0.44891300	0.56971400
C	-4.61024100	-0.38811400	1.48528700
C	-3.29556900	-0.28681400	1.04064800
H	0.89705500	0.06381600	-1.78832700
H	-0.53781900	-0.63141900	0.88134400
H	-1.55807500	0.05407700	-1.92495700
H	3.40151300	-2.51572600	1.68590900
H	3.01919500	-3.89139900	0.64809600
H	0.78774700	-2.45899000	0.78509900
H	3.57828600	-0.02406500	-0.15071900
H	3.31228100	-0.60377100	-1.83343600
H	4.01447600	-2.85338400	-1.28750300
H	4.99757400	-2.01707600	-0.07515000
H	-3.86571300	-0.26557600	-2.30947000
H	-6.20075000	-0.43846700	-1.51980900
H	-6.69089400	-0.52090700	0.92052100
H	-4.81548200	-0.40630000	2.55251000
H	-2.49385300	-0.20829900	1.76967700
Zn	1.52761000	1.63484700	0.13096400
F	2.91998200	1.25420300	1.22473600
F	0.94167500	3.22102200	-0.38970900

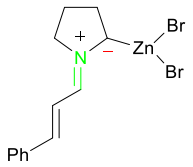
0 of imaginary frequencies

Sum of electronic and zero-point Energies= -2537.746234

Sum of electronic and thermal Energies= -2537.728948

Sum of electronic and thermal Enthalpies= -2537.728004

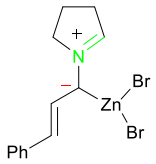
Sum of electronic and thermal Free Energies= -2537.795194



C	-0.17131400	3.03043700	-0.03907900
N	0.03107200	1.62007000	-0.47798700
C	1.43588500	1.36243300	-0.85601700
C	2.15931700	2.65190900	-0.45789400
C	-4.56275800	-0.16332200	0.07542800
C	-3.14036000	-0.14388600	-0.22368200
C	-2.29095900	0.91987200	-0.18767800
C	-0.91454800	0.72098600	-0.51393900
C	1.08277500	3.74822900	-0.54369000
C	-5.24260500	-1.39631900	0.01089300
C	-6.60391200	-1.47892600	0.28908700
C	-7.31451300	-0.32858400	0.63627700
C	-6.65592400	0.90473600	0.70356200
C	-5.29707900	0.98889200	0.42705400
H	-0.58916500	-0.28157100	-0.79186800
H	-2.64079700	1.90602600	0.10109900
H	-2.71139900	-1.10711600	-0.49915900
H	3.01788000	2.84159000	-1.10769700
H	2.54878700	2.58569700	0.56517600
H	-1.10449700	3.41885700	-0.45406600
H	-0.24083600	3.04468500	1.05523000
H	1.30599500	4.63669600	0.05462500
H	0.93477700	4.06600200	-1.58255200
H	-4.68874000	-2.29223500	-0.25793000
H	-7.10956600	-2.43861100	0.23563100
H	-8.37711200	-0.38923700	0.85371200
H	-7.20784000	1.80080900	0.97269600
H	-4.80247200	1.95415400	0.48188400
H	1.43861300	1.23634900	-1.94718300
Zn	2.27111900	-0.34455000	-0.12706200
Br	4.29621300	-0.19965400	0.93596700
Br	1.04582400	-2.28276900	-0.54864600

0 of imaginary frequencies

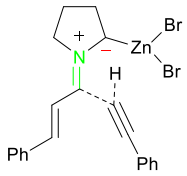
Sum of electronic and zero-point Energies=	-7481.568279
Sum of electronic and thermal Energies=	-7481.550065
Sum of electronic and thermal Enthalpies=	-7481.549121
Sum of electronic and thermal Free Energies=	-7481.621127



C	0.43084300	-0.65548700	-1.19253300
C	-0.88227700	-0.89274600	-0.58192000
C	-2.06075300	-0.50701600	-1.12005300
C	2.78321500	-3.33975700	-0.16744200
C	1.44472500	-2.68098600	-0.23721100
N	1.41414700	-1.67213100	-1.06141800
C	2.75384000	-1.45317700	-1.67867500
C	3.49374400	-2.77162200	-1.41821400
C	-3.36365900	-0.55633600	-0.45230900
C	-4.53720100	-0.54127500	-1.22861100
C	-5.79451400	-0.61710100	-0.63351100
C	-5.90828800	-0.70015500	0.75548000
C	-4.75305700	-0.69425500	1.54259900
C	-3.49657700	-0.61679400	0.94887400
H	0.41413500	-0.27558400	-2.21386700
H	-0.87874100	-1.30760100	0.42619100
H	-2.06544200	-0.12586100	-2.14149300
H	3.28229200	-3.03591600	0.76405100
H	2.71537400	-4.43254500	-0.16028400
H	0.57157900	-2.94688700	0.34196700
H	3.21172200	-0.60386200	-1.15979300
H	2.62673600	-1.19705100	-2.73298900
H	3.36665800	-3.45257800	-2.26551000
H	4.56374500	-2.61472900	-1.26632300
H	-4.45476600	-0.47822200	-2.31132400
H	-6.68642000	-0.60796700	-1.25450700
H	-6.88788000	-0.75295500	1.22256800
H	-4.83295000	-0.73220500	2.62581200
H	-2.61031800	-0.56369500	1.57540500
Zn	0.97189100	0.91298700	0.07750000
Br	1.79283300	-0.08456800	1.99243200
Br	0.71997400	3.04466000	-0.66568400

0 of imaginary frequencies

Sum of electronic and zero-point Energies=	-7481.568786
Sum of electronic and thermal Energies=	-7481.550439
Sum of electronic and thermal Enthalpies=	-7481.549495
Sum of electronic and thermal Free Energies=	-7481.621176



C	-0.44671900	-1.34227700	2.10329200
N	-0.60639200	-1.13450200	0.65478500
C	-1.81264200	-1.71648800	0.16101600
C	-2.33512800	-2.60133600	1.29070600
C	2.40535300	2.55895400	0.42575300
C	1.47772300	1.51506000	-0.02934600
C	1.40137800	0.24684300	0.40671200
C	0.40029900	-0.69525200	-0.16920400
C	-1.82065000	-1.86830500	2.54238800
C	2.15850600	3.88940300	0.04450400
C	2.99626000	4.92307400	0.45967600
C	4.10533500	4.64462600	1.25930200
C	4.37131700	3.32468700	1.63679300
C	3.53325100	2.29320400	1.22427300
H	2.05925400	-0.13120600	1.18586400
H	0.75668800	1.82930300	-0.78477300
H	-1.90811500	-3.61465800	1.23876900
H	-3.42419100	-2.69312800	1.28395900
H	0.34566300	-2.08868600	2.26597700
H	-0.14433500	-0.41122600	2.59150700
H	-2.48632300	-1.03092600	2.77870100
H	-1.75159300	-2.50883800	3.42559000
H	1.29386900	4.10926100	-0.57697400
H	2.78319300	5.94464800	0.15705000
H	4.76268700	5.44734900	1.58205000
H	5.23976500	3.09963700	2.25030700
H	3.76602100	1.27110300	1.50962300
Zn	-3.07439700	-0.16085300	-0.36008400
H	-0.01380200	-0.33752300	-1.11490200
C	1.20307400	-2.16705800	-0.78701700
C	2.45061600	-2.31640800	-0.74593500
C	3.84447000	-2.30169800	-0.62964800
C	4.48653800	-2.86027300	0.50697600
C	4.64643300	-1.74628700	-1.66156500
C	5.87145700	-2.85793100	0.60032000
H	3.87961600	-3.29207900	1.29678100
C	6.02966400	-1.74604600	-1.54850100
H	4.16078900	-1.31964000	-2.53318300
C	6.64851800	-2.30110600	-0.42222100

H	6.35210100	-3.29002100	1.47352300
H	6.63286900	-1.31333800	-2.34149500
H	7.73170100	-2.30055900	-0.34206700
H	0.38838000	-2.78224100	-1.16599900
H	-1.65089900	-2.20659500	-0.81040300
Br	-2.10660200	1.10519300	-2.04084400
Br	-5.09302700	0.01292600	0.69340100

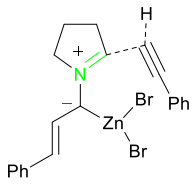
1 of imaginary frequencies

Sum of electronic and zero-point Energies= -7789.821591

Sum of electronic and thermal Energies= -7789.796083

Sum of electronic and thermal Enthalpies= -7789.795139

Sum of electronic and thermal Free Energies= -7789.885784



C	0.39243400	-0.62438800	-1.21509000
C	0.88094200	0.65404300	-0.77289300
C	2.03980600	1.24648300	-1.22024300
C	-2.64713600	-1.76467400	0.48971800
C	-1.71861600	-0.65671600	0.05598700
N	-0.79419200	-1.17641300	-0.79265300
C	-1.16664700	-2.53643200	-1.25132100
C	-2.58959100	-2.72961500	-0.71076000
C	2.62572900	2.47370900	-0.70016300
C	3.60498800	3.14015600	-1.46543700
C	4.18196000	4.32628700	-1.02101800
C	3.80369500	4.87478400	0.20633200
C	2.85034100	4.21554500	0.98898700
C	2.27182100	3.03001200	0.54862700
H	0.80965800	-1.07705800	-2.10899500
H	0.32636000	1.14907100	0.01959200
H	2.56520700	0.78212400	-2.05371400
H	-2.25269500	-2.23389900	1.40042000
H	-3.65488700	-1.39773100	0.70122000
H	-1.36308300	0.06616300	0.78223300
H	-0.44992700	-3.24142000	-0.81291000
H	-1.08792700	-2.59825600	-2.34139900
H	-3.32306700	-2.42866400	-1.46502700

H	-2.78536700	-3.76937900	-0.43789800
H	3.90432900	2.71801500	-2.42184800
H	4.93085600	4.82235600	-1.63272700
H	4.25640100	5.79791800	0.55724300
H	2.56807400	4.62078600	1.95709600
H	1.56813300	2.51154100	1.19410100
Zn	2.02412600	-1.06851800	0.27315900
C	-2.73787800	0.67607000	-1.02230200
C	-3.95583300	0.83356700	-0.81462700
C	-5.31139700	0.87642700	-0.43664900
C	-5.73995000	1.72520500	0.61477200
C	-6.28139300	0.09483000	-1.11303100
C	-7.08075700	1.77633000	0.97479000
H	-5.00549200	2.33305300	1.13393500
C	-7.61903800	0.15959000	-0.74361200
H	-5.96481500	-0.55137600	-1.92614700
C	-8.02663000	0.99664500	0.30067100
H	-7.39322000	2.42933900	1.78508100
H	-8.35096200	-0.44532400	-1.27190500
H	-9.07381200	1.04265700	0.58538500
H	-1.93536500	1.06487300	-1.63368700
Br	3.70449600	-2.15093200	-0.80248300
Br	1.14939200	-0.93568300	2.37926300

1 of imaginary frequencies

Sum of electronic and zero-point Energies=	-7789.832573
Sum of electronic and thermal Energies=	-7789.806719
Sum of electronic and thermal Enthalpies=	-7789.805775
Sum of electronic and thermal Free Energies=	-7789.897058

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