Supporting Information

Synthesis of Functionalized 3-Isochromanones via Metal-Free Intramolecular Alkoxylation-Initiated Cascade Cyclization

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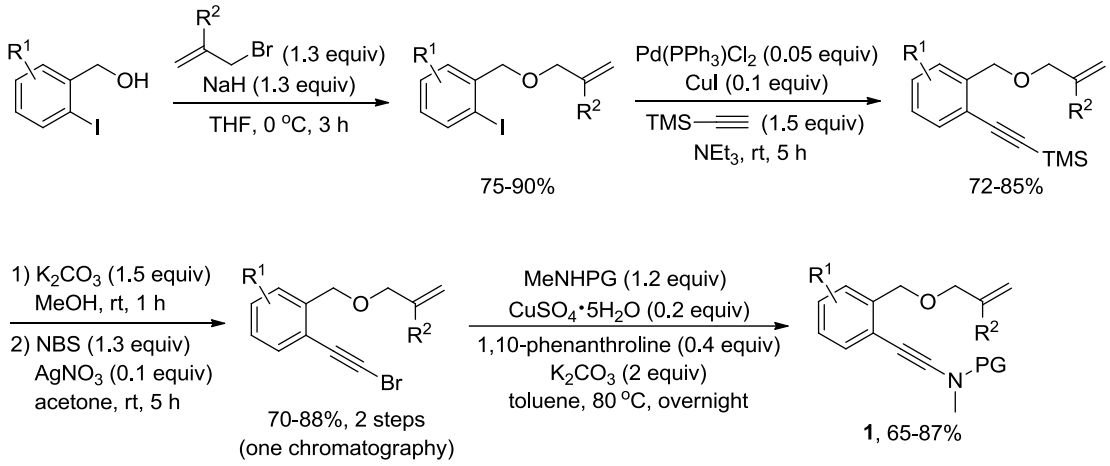
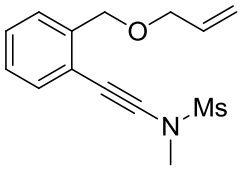
General Information. Ethyl acetate (ACS grade), hexanes (ACS grade) and anhydrous 1, 2-dichloroethane (ACS grade) were obtained commercially and used without further purification. Methylene chloride, tetrahydrofuran and diethyl ether were purified according to standard methods unless otherwise noted. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using pre-coated silica gel plates. Flash column chromatography was performed over silica gel (300-400 mesh). Mass spectra were recorded with Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer using electron spray ionization.

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer and a Bruker AV-500 spectrometer in chloroform-d_3. For ^{1}H NMR spectra, chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. For ^{13}C NMR spectra, chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard.

Representative synthetic procedures for the preparation of ynamides 1:[1]



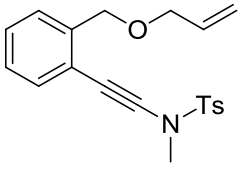
***N*-((2-((allyloxy)methyl)phenyl)ethynyl)-*N*-methylmethanesulfonamide (1a)**



1a

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, 1H, *J* = 7.6 Hz), 7.41 – 7.36 (m, 1H), 7.32 – 7.26 (m, 1H), 7.25 – 7.19 (m, 1H), 6.02 – 5.91 (m, 1H), 5.35 – 5.27 (m, 1H), 5.24 – 5.17 (m, 1H), 4.63 (s, 2H), 4.09 – 4.06 (m, 2H), 3.29 (s, 3H), 3.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 134.7, 131.3, 127.9, 127.8, 127.2, 121.1, 116.9, 87.3, 71.3, 70.2, 67.4, 39.0, 36.7; HRESIMS Calcd for $[C_{14}H_{17}NNaO_3S]^+$ (M + Na^+) 302.0821, found 302.0825.

***N*-((2-((allyloxy)methyl)phenyl)ethynyl)-*N*,4-dimethylbenzenesulfonamide (1b)**

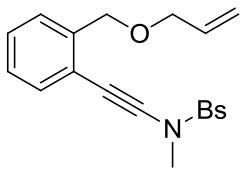


1b

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, 2H, *J* = 8.4 Hz), 7.48 – 7.44 (m, 1H), 7.38 – 7.25 (m, 4H), 7.23 – 7.18 (m, 1H), 6.02 – 5.91 (m, 1H), 5.35 – 5.28

(m, 1H), 5.22 – 5.16 (m, 1H), 4.62 (s, 2H), 4.09 – 4.06 (m, 2H), 3.17 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 139.4, 134.6, 133.1, 131.2, 129.7, 127.6, 127.5, 127.4, 127.0, 121.1, 116.6, 88.1, 71.3, 70.0, 66.7, 39.1, 21.3; HRESIMS Calcd for $[C_{20}H_{21}NNaO_3S]^+$ (M + Na^+) 378.1134, found 378.1136.

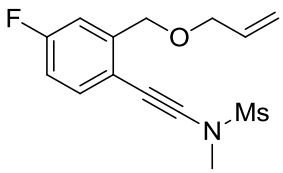
***N*-((2-((allyloxy)methyl)phenyl)ethynyl)-4-bromo-*N*-methylbenzenesulfonamide (1c)**



1c

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.71 – 7.65 (m, 2H), 7.45 (d, *J*= 7.2 Hz, 1H), 7.35 – 7.17 (m, 3H), 6.02 – 5.90 (m, 1H), 5.36 –5.26 (m, 1H), 5.24–5.15 (m, 1H), 4.60 (s, 2H), 4.07 (d, *J* = 4.0 Hz, 2H), 3.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 134.7, 134.4, 132.2, 131.1, 128.8, 128.6, 127.7, 127.4, 126.9, 120.7, 116.5, 87.3, 71.1, 69.9, 66.9, 39.0; HRESIMS Calcd for $[C_{19}H_{18}BrNNaO_3S]^+$ (M + Na^+) 442.0083, found 442.0085.

***N*-((2-((allyloxy)methyl)-4-fluorophenyl)ethynyl)-*N*-methylmethanesulfonamide (1d)**

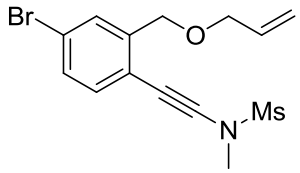


1d

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 1H), 7.23 – 7.18 (m, 1H), 6.95 – 6.88 (m, 1H), 6.02 – 5.91 (m, 1H), 5.33 (d, *J* = 17.2 Hz, 1H), 5.21 (d, *J* = 10.4 Hz, 1H), 4.61 (s, 2H), 4.09 (d, *J* = 4.8 Hz, 2H), 3.28 (s, 3H), 3.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 247.4 Hz), 142.8 (d, *J* = 8.0 Hz), 134.3, 133.1 (d, *J* = 8.0 Hz), 117.0, 116.4 (d, *J* = 3.0 Hz), 114.3 (d, *J* = 21.0 Hz), 114.0 (d, *J*

= 20.0 Hz), 87.0, 71.4, 69.4, 66.0, 38.9, 36.5; HRESIMS Calcd for $[C_{14}H_{16}FNNaO_3S]^+$ (M + Na^+) 320.0727, found 320.0726.

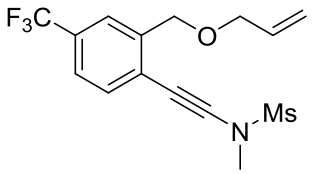
_N_-((2-((allyloxy)methyl)-4-bromophenyl)ethynyl)-_N_-methylmethanesulfonamide (1e)



1e

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 1H), 7.38 – 7.33 (m, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 6.02 – 5.91 (m, 1H), 5.37 – 5.28 (m, 1H), 5.26 – 5.20 (m, 1H), 4.59 (s, 2H), 4.09 (d, *J* = 5.2 Hz, 2H), 3.30 (s, 3H), 3.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 134.4, 132.5, 130.6, 130.3, 122.2, 120.0, 117.3, 88.5, 71.7, 69.6, 66.8, 39.0, 37.0; HRESIMS Calcd for $[C_{14}H_{16}BrNNaO_3S]^+$ (M + Na^+) 379.9926, found 379.9925.

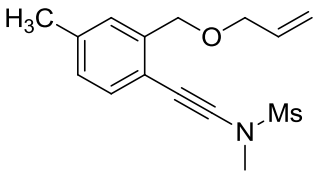
_N_-((2-((allyloxy)methyl)-4-(trifluoromethyl)phenyl)ethynyl)-_N_-methylmethanesulfonamide (1f)



1f

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.51 – 7.44 (m, 2H), 6.05 – 5.94 (m, 1H), 5.39 – 5.32 (m, 1H), 5.27 – 5.22 (m, 1H), 4.66 (s, 2H), 4.15 – 4.10 (m, 2H), 3.34 (s, 3H), 3.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 134.3, 130.9, 129.4 (q, *J* = 32.3 Hz), 124.8, 124.3 (q, *J* = 3.9 Hz), 123.9(3) (q, *J* = 3.6 Hz), 123.9(2) (q, *J* = 270.3 Hz), 117.4, 89.9, 71.8, 69.7, 67.0, 39.0, 37.2; HRESIMS Calcd for $[C_{15}H_{16}F_3NNaO_3S]^+$ (M + Na^+) 370.0695, found 370.0705.

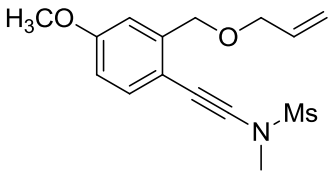
***N*-((2-((allyloxy)methyl)-4-methylphenyl)ethynyl)-*N*-methylmethanesulfonamide (1g)**



1g

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.03 – 5.91 (m, 1H), 5.37 –5.15 (m, 2H), 4.60 (s, 2H), 4.08 (d, *J* = 5.2 Hz, 2H), 3.27 (s, 3H), 3.10 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 138.1, 134.7, 131.4, 128.5, 128.0, 118.0, 116.9, 86.5, 71.4, 70.2, 67.3, 39.0, 36.5, 21.3; HRESIMS Calcd for $[C_{15}H_{19}NNaO_3S]^+$ (M + Na^+) 316.0978, found 316.0975.

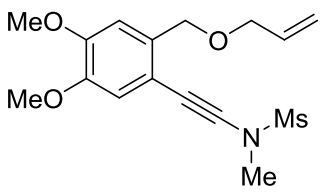
***N*-((2-((allyloxy)methyl)-4-methoxyphenyl)ethynyl)-*N*-methylmethanesulfonamid -e (1h)**



1h

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 1H), 7.02 (s, 1H), 6.78 – 6.73 (m, 1H), 6.02 – 5.90 (m, 1H), 5.33 (d, *J* = 17.2 Hz, 1H), 5.20 (d, *J* = 10.4 Hz, 1H), 4.62 (s, 2H), 4.08 (d, *J* = 4.8 Hz, 2H), 3.80 (s, 3H), 3.27 (s, 3H), 3.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 142.0, 134.6, 133.2, 116.9, 113.0, 112.8, 112.7, 85.8, 71.4, 70.1, 66.8, 55.2, 39.1, 36.4; HRESIMS Calcd for $[C_{15}H_{19}NNaO_4S]^+$ (M + Na^+) 332.0927, found 332.0929. `

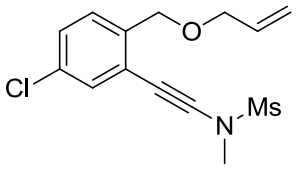
***N*-((2-((allyloxy)methyl)-4,5-dimethoxyphenyl)ethynyl)-*N*-methylmethanesulfona mide (1i)**



1i

Pale yellow oil.[1]H NMR (400 MHz, $CDCl_3$) δ 6.97 (s, 1H), 6.88 (s, 1H), 6.02 – 5.91 (m, 1H), 5.34 – 5.29 (m, 1H), 5.22 – 5.18 (m, 1H), 4.59 (s, 2H), 4.08 – 4.04 (m, 2H), 3.90 (s, 3H), 3.86 (s, 3H), 3.29 (s, 3H), 3.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 147.9, 134.8, 133.5, 117.0, 114.3, 113.0, 111.0, 85.6, 71.3, 70.1, 67.3, 56.0, 55.9, 39.1, 36.7; HRESIMS Calcd for $[C_{16}H_{21}NNaO_5S]^+$ (M + Na^+) 362.1033, found 362.1034.

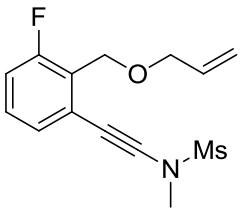
***N*-((2-((allyloxy)methyl)-5-chlorophenyl)ethynyl)-*N*-methylmethanesulfonamide (1j)**



1j

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.23 – 7.19 (m, 1H), 5.98 – 5.86 (m, 1H), 5.33 – 5.25 (m, 1H), 5.20 – 5.15 (m, 1H), 4.54 (s, 2H), 4.03 (d, *J* = 5.6 Hz, 2H), 3.26 (s, 3H), 3.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 134.4, 132.6, 130.4, 128.9, 127.7, 122.7, 116.9, 88.4, 71.3, 69.5, 66.4, 38.8, 36.8; HRESIMS Calcd for $[C_{14}H_{16}ClNNaO_3S]^+$ (M + Na^+) 336.0432, found 336.0436.

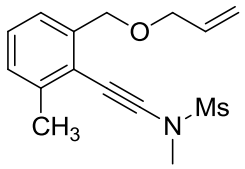
***N*-((2-((allyloxy)methyl)-3-fluorophenyl)ethynyl)-*N*-methylmethanesulfonamide (1k)**



1k

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.15 (m, 2H), 7.02 – 6.95 (m, 1H), 5.99 – 5.88 (m, 1H), 5.33 – 5.27 (m, 1H), 5.19 – 5.15 (m, 1H), 4.66 (d, *J* = 1.6 Hz, 2H), 4.06 (d, *J* = 5.6 Hz, 2H), 3.31 (s, 3H), 3.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5 (d, *J* = 246.0 Hz), 134.7, 129.5 (d, *J* = 9.0 Hz), 127.1 (d, *J* = 3.0 Hz), 125.7 (d, *J* = 16.0 Hz), 125.6 (d, *J* = 5.0 Hz), 116.9, 115.1 (d, *J* = 23.0 Hz), 87.5, 71.3, 67.4, 63.6, 38.9, 37.0; HRESIMS Calcd for $[C_{14}H_{16}FNNaO_3S]^+$ (M + Na^+) 320.0727, found 320.0726.

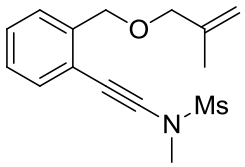
***N*-((2-((allyloxy)methyl)-6-methylphenyl)ethynyl)-*N*-methylmethanesulfonamide (1l)**



1l

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 1H), 7.21 – 7.09 (m, 2H), 6.02 – 5.91 (m, 1H), 5.39 –5.29 (m, 1H), 5.19 (d, *J* = 10.4 Hz, 1H), 4.62 (s, 2H), 4.07 (d, *J* = 5.5 Hz, 2H), 3.30 (s, 3H), 3.11 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 139.3, 139.1, 134.7, 128.4, 127.3, 125.1, 121.0, 116.8, 91.6, 71.3, 70.6, 66.4, 39.1, 36.6, 20.7; HRESIMS Calcd for $[C_{15}H_{19}NNaO_3S]^+$ (M + Na^+) 3316.0978, found 316.0977.

***N*-methyl-*N*-((2-(((2-methylallyl)oxy)methyl)phenyl)ethynyl)methanesulfonamide (1m)**

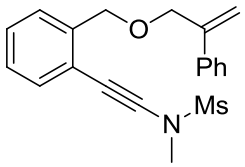


1m

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.6 Hz, 1H), 7.38 (d, *J* =

7.6 Hz, 1H), 7.32 – 7.19 (m, 2H), 5.02 (s, 1H), 4.91 (s, 1H), 4.61 (s, 2H), 3.98 (s, 2H), 3.29 (s, 3H), 3.11 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 139.6, 131.2, 127.9, 127.6, 127.1, 121.0, 111.9, 87.3, 74.2, 70.0, 67.3, 39.0, 36.6, 19.4; HRESIMS Calcd for $[C_{15}H_{19}NNaO_3S]^+$ (M + Na^+) 316.0978, found 316.0981.

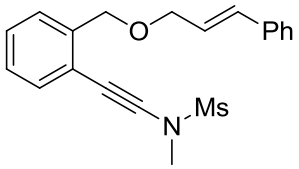
***N*-methyl-*N*-((2-(((2-phenylallyl)oxy)methyl)phenyl)ethynyl)methanesulfonamide (1n)**



1n

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.20 (m, 5H), 5.54 (s, 1H), 5.39 (s, 1H), 4.70 (s, 2H), 4.45 (s, 2H), 3.25 (s, 3H), 3.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 139.4, 138.8, 131.3, 128.3, 128.1, 128.0, 127.7, 127.4, 126.1, 121.4, 114.4, 87.4, 72.3, 70.4, 67.7, 39.1, 36.8; HRESIMS Calcd for $[C_{20}H_{21}NNaO_3S]^+$ (M + Na^+) 378.1134, found 378.1136.

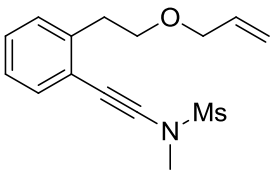
***N*-((2-((cinnamyloxy)methyl)phenyl)ethynyl)-*N*-methylmethanesulfonamide (1o)**



1o

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.34 (m, 4H), 7.33 – 7.17 (m, 5H), 6.68 – 6.58 (m, 1H), 6.38 – 6.27 (m, 1H), 4.68 (s, 2H), 4.26 – 4.22 (m, 2H), 3.22 (s, 3H), 3.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 136.6, 132.4, 131.3, 128.5, 128.0, 127.9, 126.4, 126.0, 121.2, 87.4, 71.0, 70.2, 67.5, 39.0, 36.6; HRESIMS Calcd for $[C_{20}H_{21}NNaO_3S]^+$ (M + Na^+) 378.1134, found 378.1138.

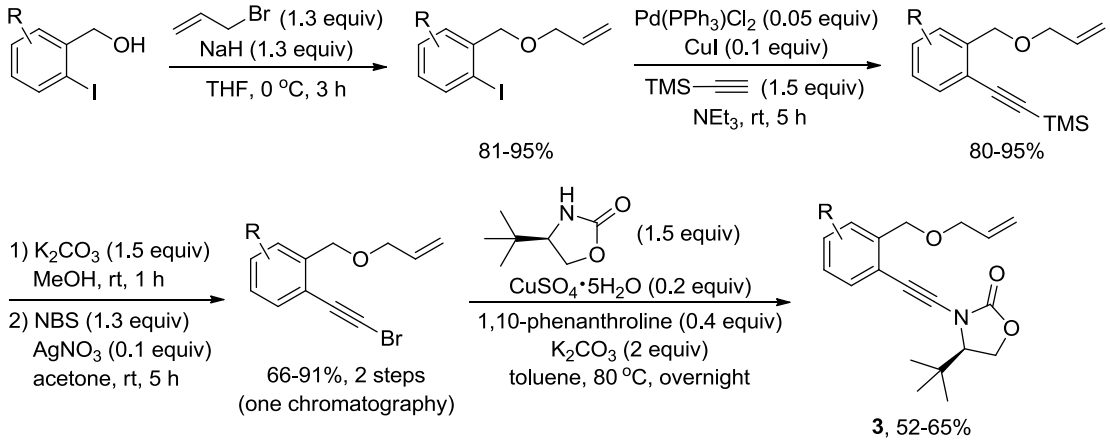
***N*-((2-(2-(allyloxy)ethyl)phenyl)ethynyl)-*N*-methylmethanesulfonamide (1p)**



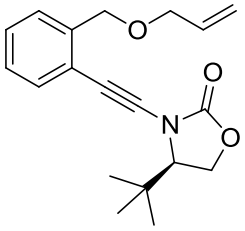
1p

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 1H), 7.25 – 7.20 (m, 2H), 7.19 – 7.14 (m, 1H), 5.96 – 5.84 (m, 1H), 5.28 – 5.21 (m, 1H), 5.18 – 5.13 (m, 1H), 4.01 – 3.98 (m, 2H), 3.68 (t, *J* = 7.3 Hz, 2H), 3.31 (s, 3H), 3.13 (s, 3H), 3.06 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 134.9, 131.8, 129.5, 128.1, 126.2, 122.2, 116.7, 86.5, 71.8, 70.2, 68.2, 39.2, 36.8, 35.2; HRESIMS Calcd for $[C_{15}H_{19}NNaO_3S]^+$ (M + Na^+) 316.0978, found 316.0980.

Representative synthetic procedures for the preparation of ynamides 3:[1]



(*R*)-3-((2-((allyloxy)methyl)phenyl)ethynyl)-4-(*tert*-butyl)oxazolidin-2-one (3a)

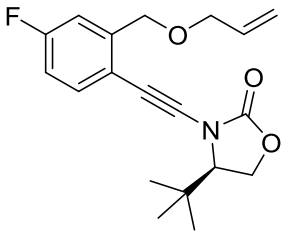


3a

Pale yellow oil. $[\alpha]_D^{20}$ = -89.8 °(c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.4 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.35 – 7.29 (m, 1H), 7.27 – 7.20 (m, 1H), 6.06 – 5.94 (m, 1H), 5.39 – 5.31 (m, 1H), 5.25 – 5.18 (m, 1H), 4.71 (s, 2H), 4.44 (t, *J*

= 9.0 Hz, 1H), 4.31 – 4.25 (m, 1H), 4.14 – 4.10 (m, 2H), 3.90 – 3.84 (m, 1H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 139.7, 134.7, 131.5, 128.1, 127.4, 127.1, 121.0, 117.0, 84.7, 71.6, 70.2, 69.9, 66.1, 65.5, 34.8, 25.2; HRESIMS Calcd for $[C_{19}H_{23}NNaO_3]^+$ (M + Na^+) 336.1570, found 336.1579.

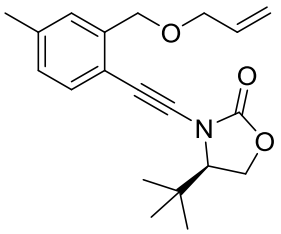
(*R*)-3-((2-((allyloxy)methyl)-4-fluorophenyl)ethynyl)-4-(*tert*-butyl)oxazolidin-2-one (3d)



3d

Pale yellow oil. $[\alpha]_D^{20}$ = -122.2 º(c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 1H), 7.26 – 7.21 (m, 1H), 6.95 – 6.88 (m, 1H), 6.04 – 5.92 (m, 1H), 5.38 – 5.31 (m, 1H), 5.25 – 5.20 (m, 1H), 4.67 (s, 2H), 4.43 (t, *J* = 9.0 Hz, 1H), 4.30 – 4.25 (m, 1H), 4.13 – 4.10 (m, 2H), 3.88 – 3.83 (m, 1H), 1.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, *J* = 248.0 Hz), 156.3, 143.0 (d, *J* = 7.8 Hz), 134.4, 133.3 (d, *J* = 8.4 Hz), 117.2, 116.3 (d, *J* = 3.3 Hz), 114.1 (d, *J* = 23.0 Hz), 84.5, 71.7, 69.6, 68.7, 66.1, 65.5, 34.7, 25.2; HRESIMS Calcd for $[C_{19}H_{22}FNNaO_3]^+$ (M + Na^+) 354.1476, found 354.1473.

(*R*)-3-((2-((allyloxy)methyl)-4-methylphenyl)ethynyl)-4-(*tert*-butyl)oxazolidin-2-one (3g)

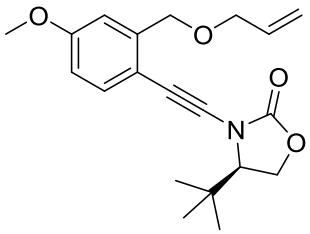


3g

Pale yellow oil. $[\alpha]_D^{20}$ = -99.4 º(c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.06 – 7.01 (m, 1H), 6.09 – 6.94 (m, 1H), 5.38 – 5.31 (m, 1H), 5.24 –

5.19 (m, 1H), 4.67 (s, 2H), 4.41 (t, *J* = 9.0 Hz, 1H), 4.28 – 4.22 (m, 1H), 4.13 – 4.09 (m, 2H), 3.87 – 3.81 (m, 1H), 2.35 (s, 3H), 1.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 139.5, 138.2, 134.7, 131.5, 128.1, 127.8, 117.9, 116.9, 83.9, 71.5, 70.1, 69.7, 66.0, 65.4, 34.6, 25.2, 21.3; HRESIMS Calcd for $[C_{20}H_{25}NNaO_3]^+$ (M + Na^+) 350.1727, found 350.1736.

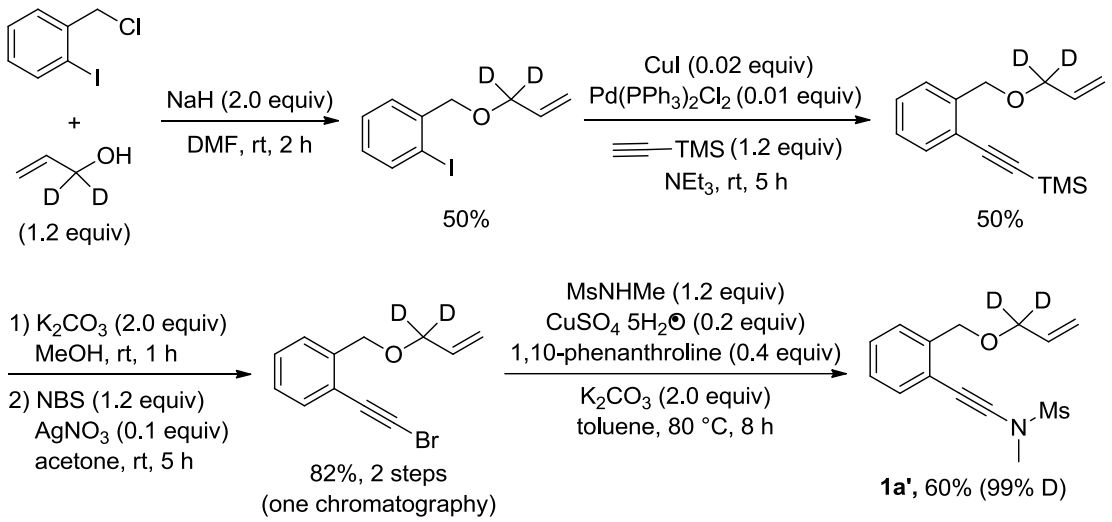
(*R*)-3-((2-((allyloxy)methyl)-4-methoxyphenyl)ethynyl)-4-(*tert*-butyl)oxazolidin-2-one (3h)



3h

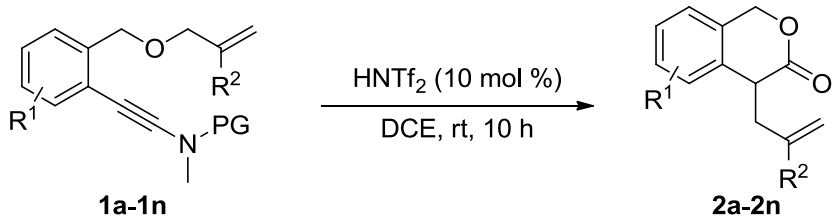
Pale yellow oil. $[\alpha]_D^{20}$ = -126.4 º(c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.5 Hz, 1H), 7.06 (d, *J* = 2.6 Hz, 1H), 6.79 – 6.74 (m, 1H), 6.04 – 5.93 (m, 1H), 5.38 – 5.31 (m, 1H), 5.24 – 5.18 (m, 1H), 4.68 (s, 2H), 4.41 (t, *J* = 9.0 Hz, 1H), 4.28 – 4.22 (m, 1H), 4.13 – 4.09 (m, 2H), 3.86 – 3.80 (m, 4H), 1.09 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 156.4, 142.0, 134.6, 133.3, 116.9, 113.0, 112.6, 112.3, 83.3, 71.5, 70.0, 69.3, 66.1, 65.4, 55.2, 34.7, 25.2; HRESIMS Calcd for $[C_{20}H_{25}NNaO_4]^+$ (M + Na^+) 366.1676, found 366.1686.

***N*-((2-(((allyl-1,1-*d*$_2$)oxy)methyl)phenyl)ethynyl)-*N*-methylmethanesulfonamide (1a′)**



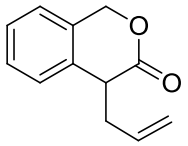
1a′ was prepared according to the above known procedures.[1] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 1H), 7.42 – 7.38 (m, 1H), 7.35 – 7.29 (m, 1H), 7.27 – 7.21 (m, 1H), 6.04 – 5.94 (m, 1H), 5.38 – 5.31 (m, 1H), 5.25 – 5.20 (m, 1H), 4.66 (s, 2H), 3.32 (s, 3H), 3.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 134.6, 131.3, 128.0, 127.8, 127.2, 121.1, 117.1, 87.3, 70.2, 67.5, 39.1, 36.7.

General procedure for the synthesis of 3-isochromanones 2a–2n:



$HNTf_2$ (8.5 mg, 0.03 mmol) was added to the ynamide **1a**–**1n** (0.30 mmol) in DCE (6.0 mL) at room temperature. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. The reaction typically took 10 h. Upon completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the desired product **2a**–**2n**.

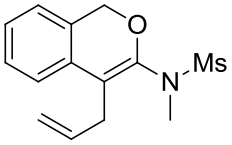
4-allylisochroman-3-one (2a)



2a

Compound **2a** was prepared according to the general procedure. 99% yield (PG = Ms, 55.8 mg), 98% yield (PG = Ts, 55.3 mg, 16 h), 93% yield (PG = Bs, 52.5 mg, 16 h). This compound is known and the spectroscopic data match those reported.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.20 (m, 4H), 5.93 – 5.81 (m, 1H), 5.41 (d, *J* = 14.0 Hz，1H), 5.28 (d, 1H, *J* = 14.0 Hz), 5.17 – 5.09 (m, 2H), 3.70 (t, 1H, *J* = 6.8 Hz), 2.87 – 2.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 134.2, 134.0, 131.4, 128.6, 127.2, 126.6, 124.6, 118.1, 69.5, 45.3, 34.2.

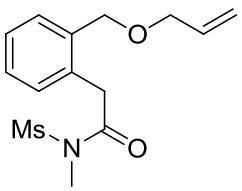
***N*-(4-allyl-1*H*-isochromen-3-yl)-*N*-methylmethanesulfonamide (2aa)**



2aa

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 7.20 – 7.15 (m, 1H), 7.02 (d, *J* = 7.3 Hz, 1H), 5.94 – 5.84 (m, 1H), 5.14 – 5.08 (m, 1H), 5.06 (s, 2H), 5.04 – 5.00 (m, 1H), 3.35 (d, *J* = 5.8 Hz, 2H), 3.12 (s, 3H), 2.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 136.1, 132.1, 128.8, 128.1, 127.1, 123.7, 122.9, 116.0, 111.3, 69.8, 38.4, 37.1, 30.4; HRESIMS Calcd for $[C_{14}H_{17}NNaO_3S]^+$ (M + Na^+) 302.0821, found 302.0828.

2-(2-((allyloxy)methyl)phenyl)-*N*-methyl-*N*-(methylsulfonyl)acetamide (2ab)

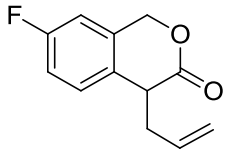


2ab

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 3H), 7.20 (d, *J* = 7.2

Hz, 1H), 5.93 – 5.82 (m, 1H), 5.28 – 5.21 (m, 1H), 5.21 – 5.16 (m, 1H), 4.51 (s, 2H), 4.09 (s, 2H), 3.91 – 3.87 (m, 2H), 3.29 (s, 3H), 3.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 136.0, 134.4, 133.0, 130.9, 130.0, 128.5, 127.4, 117.5, 71.2, 70.7, 41.3, 40.4, 32.6; HRESIMS Calcd for $[C_{14}H_{19}NNaO_4S]^+$ (M + Na^+) 320.0927, found 320.0927.

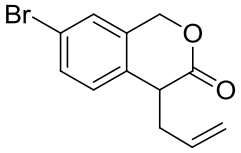
4-allyl-7-fluoroisochroman-3-one (2d)



2d

Compound **2d** was prepared in 99% yield (61.2 mg) according to the general procedure. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 1H), 7.08 – 7.01 (m, 1H), 6.97 – 6.93 (m, 1H), 5.90 – 5.78 (m, 1H), 5.38 (d, *J* = 13.6 Hz, 1H), 5.28 (d, *J* = 13.6 Hz, 1H), 5.15 – 5.06 (m, 2H), 3.68 (t, 1H, *J* = 6.4 Hz), 2.87 –2.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 161.6 (d, *J* = 245.0 Hz), 133.8, 133.2 (d, *J* = 7.0 Hz), 129.6 (d, *J* = 3.0 Hz), 128.4 (d, *J* = 8.0 Hz), 118.3, 115.4 (d, *J* = 22.0 Hz), 111.8 (d, *J* = 23.0 Hz), 68.9, 44.6, 34.3; HRESIMS Calcd for $[C_{12}H_{11}FNaO_2]^+$ (M + Na^+) 229.0635, found 229.0638.

4-allyl-7-bromoisochroman-3-one (2e)

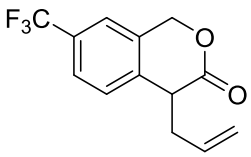


2e

Compound **2e** was prepared in 98% yield (78.5 mg) according to the general procedure. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.30 (m, 2H), 7.19 – 7.05 (m, 1H), 5.90 – 5.75 (m, 1H), 5.36 (d, *J* = 14.0 Hz, 1H), 5.23 (d, *J* = 14.0 Hz, 1H), 5.21– 5.08 (m, 2H), 3.65 (t, *J* = 5.2 Hz, 1H), 2.85 – 2.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 133.7, 133.3, 132.9, 131.5, 128.3, 127.7, 121.0, 118.4, 68.6,

44.7, 34.0; HRESIMS Calcd for $[C_{12}H_{11}BrNaO_2]^+$ (M + Na^+) 288.9835, found 288.9836.

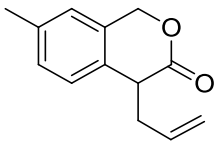
4-allyl-7-(trifluoromethyl)isochroman-3-one (2f)



2f

Compound **2f** was prepared in 98% yield (75.3 mg) according to the general procedure except for 2 equiv of H_2O as an additive. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 1H), 7.52 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 5.93 – 5.80 (m, 1H), 5.48 (d, *J* = 14.4 Hz, 1H), 5.36 (d, *J* = 14.4 Hz, 1H), 5.20 – 5.11 (m, 2H), 3.78 (t, *J* = 6.7 Hz, 1H), 2.93 – 2.84 (m, 1H), 2.79 – 2.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 138.1, 133.5, 132.2, 129.9 (q, *J* = 32.3 Hz), 127.4, 125.6 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 270.7 Hz), 121.8 (q, *J* = 3.7 Hz), 118.7, 68.9, 45.2, 34.1. HRESIMS Calcd for $[C_{13}H_{11}F_3NaO_2]^+$ (M + Na^+) 279.0603, found 279.0609.

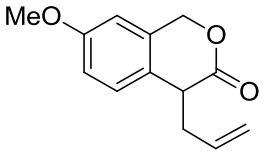
4-allyl-7-methylisochroman-3-one (2g)



2g

Compound **2g** was prepared in 99% (56.0 mg) yield according to the general procedure. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.10 (m, 2H), 7.02 (s, 1H), 5.92 – 5.80 (m, 1H), 5.36 (d, *J* = 14.0 Hz, 1H), 5.23 (d, *J* = 14.0 Hz, 1H), 5.15 – 5.08 (m, 2H), 3.65 (t, *J* = 6.8 Hz, 1H), 2.84 – 2.61 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 137.0, 134.3, 131.2, 130.8, 129.2, 126.4, 125.2, 117.9, 69.5, 44.9, 34.2, 20.9; HRESIMS Calcd for $[C_{13}H_{14}NaO_2]^+$ (M + Na^+) 225.0886, found 225.0885.

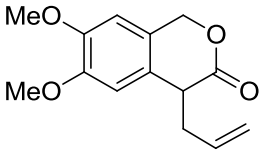
4-allyl-7-methoxyisochroman-3-one (2h)



2h

Compound **2h** was prepared in 99% yield (64.7 mg) according to the general procedure. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.4 Hz, 1H), 6.89 – 6.85 (m, 1H), 6.78 – 6.73 (m, 1H), 5.91 – 5.79 (m, 1H), 5.35 (d, *J* = 14.0 Hz, 1H), 5.22 (d, *J* = 14.0 Hz, 1H), 5.15 – 5.07 (m, 2H), 3.80 (s, 3H), 3.64 (t, *J* = 6.4 Hz, 1H), 2.83 – 2.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 158.7, 134.2, 132.4, 127.7, 125.6, 117.9, 113.9, 110.1, 69.4, 55.3, 44.5, 34.3; HRESIMS Calcd for $[C_{13}H_{14}NaO_3]^+$ (M + Na^+) 241.0835, found 241.0833.

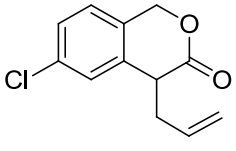
4-allyl-6,7-dimethoxyisochroman-3-one (2i)



2i

Compound **2i** was prepared in 68% yield (50.6 mg) according to the general procedure except for changing the solvent to Et_2O and reacting for 16 h. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (s, 1H), 6.69 (s, 1H), 5.91 – 5.75 (m, 1H), 5.36 (d, *J* = 14.0 Hz, 1H), 5.19 (d, *J* = 14.0 Hz, 1H), 5.16 – 5.04 (m, 2H), 3.87 (s, 6H), 3.62 (t, *J* = 6.8 Hz, 1H), 2.84 – 2.72 (m, 1H), 2.71 – 2.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 149.1, 148.2, 134.2, 126.0, 123.2, 118.1, 109.9, 107.7, 69.4, 56.0, 44.8, 34.9; HRESIMS Calcd for $[C_{14}H_{16}NaO_4]^+$ (M + Na^+) 271.0941, found 271.0945.

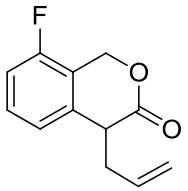
4-allyl-6-chloroisochroman-3-one (2j)



2j

Compound **2j** was prepared in 98% yield (65.6 mg) according to the general procedure. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 5.91 – 5.79 (m, 1H), 5.36 (d, *J* = 14.0 Hz, 1H), 5.25 (d, *J* = 14.0 Hz, 1H), 5.18 – 5.08 (m, 2H), 3.66 (t, *J* = 6.8 Hz, 1H), 2.86 – 2.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 135.9, 134.4, 133.6, 129.8, 127.4, 126.7, 126.0, 118.4, 68.8, 44.9, 33.9; HRESIMS Calcd for $[C_{12}H_{11}ClNaO_2]^+$ (M + Na^+) 245.0340, found 245.0341.

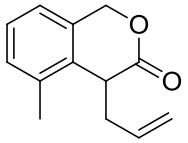
4-allyl-8-fluoroisochroman-3-one (2k)



2k

Compound **2k** was prepared in 99% yield (61.2 mg) according to the general procedure. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 1H), 7.06 – 6.97 (m, 2H), 5.89 – 5.76 (m, 1H), 5.48 – 5.36 (m, 2H), 5.15 – 5.08 (m, 2H), 3.73 (t, *J* = 6.8 Hz, 1H), 2.85 – 2.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 157.9 (d, *J* = 247.0 Hz), 136.6 (d, *J* = 3.0 Hz), 133.6, 130.0 (d, *J* = 8.0 Hz), 122.3 (d, *J* = 4.0 Hz), 118.5 (d, *J* = 18.0 Hz), 118.4, 113.9 (d, *J* = 20.0 Hz), 63.4, 44.9, 34.7; HRESIMS Calcd for $[C_{12}H_{11}FNaO_2]^+$ (M + Na^+) 229.0635, found 229.0636.

4-allyl-5-methylisochroman-3-one (2l)

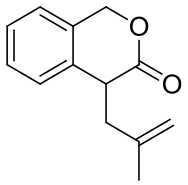


2l

Compound **2l** was prepared in 99% yield (60.0 mg) according to the general procedure. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.16 (m, 2H), 7.06 –

7.00 (m, 1H), 5.88 – 5.76 (m, 1H), 5.56 (d, *J* = 14.4 Hz, 1H), 5.17 (d, *J* = 14.0 Hz, 1H), 5.12 – 5.06 (m, 2H), 3.97 (t, *J* = 7.5 Hz, 1H), 2.64 – 2.47 (m, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 135.2, 133.5, 132.5, 130.5, 130.4, 127.1, 122.4, 118.4, 69.8, 43.8, 35.5, 18.2; HRESIMS Calcd for $[C_{13}H_{14}NaO_2]^+$ (M + Na^+) 225.0886, found 225.0888.

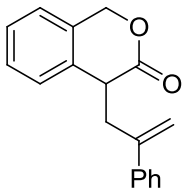
4-(2-methylallyl)isochroman-3-one (2m)



2m

Compound **2m** was prepared in 72% yield (43.6 mg) according to the general procedure except for the reaction time of 16 h. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.23 – 7.18 (m, 2H), 5.43 (d, *J* = 14.0 Hz, 1H), 5.29 (d, *J* = 14.0 Hz, 1H), 4.85 (s, 1H), 4.64 (s, 1H), 3.84 – 3.79 (m, 1H), 2.82 – 2.76 (m, 1H), 2.58 – 2.51 (m, 1H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 141.3, 134.3, 131.2, 128.5, 127.2, 126.7, 124.5, 113.3, 69.4, 44.1, 38.0, 22.4; HRESIMS Calcd for $[C_{13}H_{14}NaO_2]^+$ (M + Na^+) 225.0886, found 225.0888.

4-(2-phenylallyl)isochroman-3-one (2n)

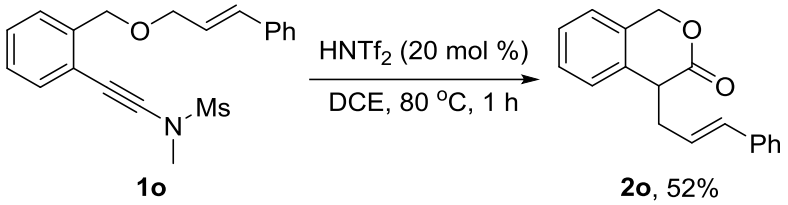


2n

Compound **2n** was prepared in 81% yield (64.2 mg) according to the general procedure. Pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.24 (m, 3H), 7.21 – 7.19 (m, 1H), 7.10 – 7.05 (m, 1H), 5.42 (d, *J* = 14.0 Hz, 1H), 5.36 (s, 1H), 5.25 (d, *J* = 14.0 Hz, 1H), 4.98 (s, 1H), 3.79 – 3.73 (m, 1H), 3.44 – 3.37 (m, 1H), 3.00 – 2.92 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.4,

144.3, 139.7, 134.1, 131.2, 128.6, 128.4, 127.9, 127.2, 127.0, 126.3, 124.6, 115.7, 69.5, 44.2, 35.9; HRESIMS Calcd for $[C_{18}H_{16}NaO_2]^+$ (M + Na^+) 287.1043, found 287.1047.

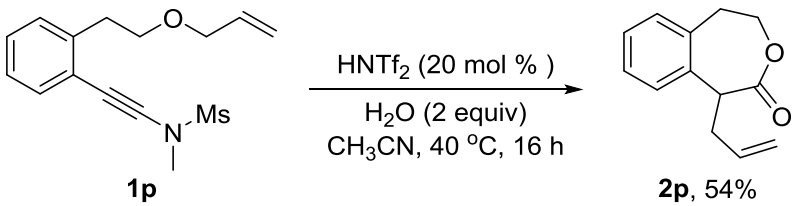
4-cinnamylisochroman-3-one (2o)



1o **2o**, 52%

$HNTf_2$ (16.9 mg, 0.06 mmol) was added to the ynamide **1o** (0.30 mmol) in DCE (6.0 mL) at room temperature. The reaction mixture was stirred at 80 °C and the progress of the reaction was monitored by TLC. The reaction took 1 h. Upon completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the desired product **2o** (41.2 mg, 52% yield, pale yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.17 (m, 9H), 6.46 (d, *J* = 15.6 Hz, 1H), 6.28 – 6.18 (m, 1H), 5.41 (d, *J* = 14.0 Hz, 1H), 5.29 (d, *J* = 14.0 Hz, 1H), 3.78 (t, *J* = 6.6 Hz, 1H), 3.08 – 2.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 137.0, 133.9, 133.2, 131.4, 128.7, 128.5, 127.4, 127.3, 126.7, 126.2, 125.5, 124.7, 69.6, 45.7, 33.7; HRESIMS Calcd for $[C_{18}H_{16}NaO_2]^+$ (M + Na^+) 287.1043, found 287.1042.

1-allyl-4,5-dihydrobenzo[*d*]oxepin-2(1*H*)-one (2p)

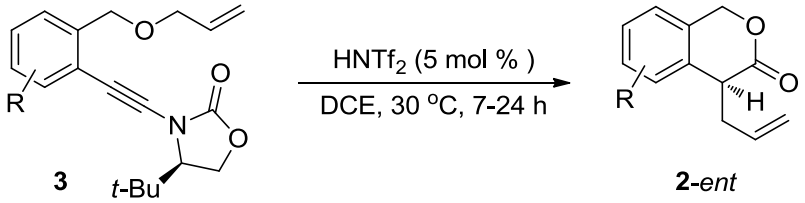


1p **2p**, 54%

$HNTf_2$ (16.9 mg, 0.06 mmol) and H_2O (10.8 mg, 0.6 mmol) were added to the ynamide **1p** (0.30 mmol) in CH_3CN (6.0 mL) at room temperature. The reaction mixture was stirred at 40 °C and the progress of the reaction was monitored by TLC. The reaction took 16 h. Upon completion, the mixture was then concentrated and the

residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the desired product **2p** (32.7 mg, 54% yield, pale yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.19 (m, 3H), 7.15 – 7.11 (m, 1H), 5.99 – 5.87 (m, 1H), 5.23 – 5.16 (m, 1H), 5.15 – 5.10 (m, 1H), 4.86 – 4.78 (m, 1H), 4.57 – 4.49 (m, 1H), 4.43 – 4.37 (m, 1H), 3.42 – 3.30 (m, 2H), 3.01 – 2.91 (m, 1H), 2.80 – 2.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 135.3, 135.0, 132.9, 130.5, 127.5, 127.0, 126.9, 117.6, 65.1, 46.0, 34.0, 33.9; HRESIMS Calcd for $[C_{13}H_{14}NaO_2]^+$ (M + Na^+) 225.0886, found 225.0888.

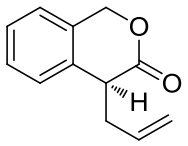
General procedure for the synthesis of 3-isochromanones 2-*ent*:



3 **2-*ent***

$HNTf_2$ (4.2 mg, 0.015 mmol) was added to the ynamide **3** (0.30 mmol) in DCE (6.0 mL) at 30 °C. The reaction mixture was stirred at 30 °C and the progress of the reaction was monitored by TLC. The reaction took 7 - 24 h. Upon completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the desired product **2-*ent***.

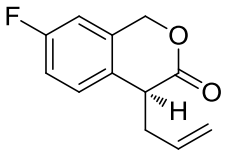
(*S*)-4-allylisochroman-3-one (2a-*ent*)



2a-*ent*

Compound **2a-*ent*** was prepared in 72% yield (40.6 mg) according to the general procedure (eq 3, entry 1). $[\alpha]_D^{20}$ = -170.8 °(c = 1.0, $CHCl_3$). 94% ee (determined by HPLC: Chiralcel AD-H Column, 5/95 *i*-PrOH/hexane, 1.0 mL/min, 256 nm; TR = 13.48 min (minor), 16.32 min (major)).

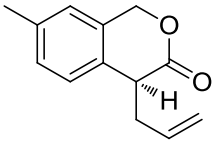
(*S*)-4-allyl-7-fluoroisochroman-3-one (2d-*ent*)



2d-*ent*

Compound **2d**-*ent* was prepared in 62% yield (38.3 mg) according to the general procedure except for adding 2 equiv of H_2O as an additive (eq 3, entry 2). $[\alpha]_D^{20}$ = -197.7 °(c = 1.0, $CHCl_3$). 90% ee (determined by HPLC: Chiralcel AD-H Column, 5/95 *i*-PrOH/hexane, 1.0 mL/min, 256 nm; TR = 13.35 min (minor), 14.99 min (major)).

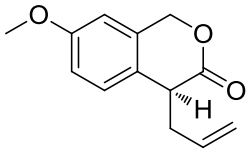
(*S*)-4-allyl-7-methylisochroman-3-one (2g-*ent*)



2g-*ent*

Compound **2g**-*ent* was prepared in 85% yield (51.5 mg) according to the general procedure (eq 3, entry 3). $[\alpha]_D^{20}$ = -18.1 °(c = 1.0, $CHCl_3$). 95% ee (determined by HPLC: Chiralcel AD-H Column, 5/95 *i*-PrOH/hexane, 1.0 mL/min, 256 nm; TR = 12.27 min (minor), 16.07 min (major)).

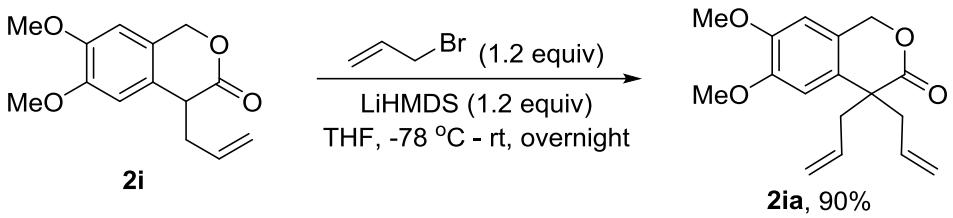
(*S*)-4-allyl-7-methoxyisochroman-3-one (2h-*ent*)



2h-*ent*

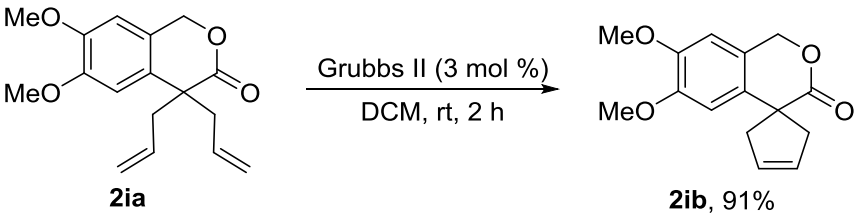
Compound **2h**-*ent* was prepared in 66% yield (43.2 mg) according to the general procedure (eq 3, entry 4). $[\alpha]_D^{20}$ = -175.6 °(c = 1.0, $CHCl_3$). 93% ee (determined by HPLC: Chiralcel AD-H Column, 5/95 *i*-PrOH/hexane, 1.0 mL/min, 256 nm; TR = 20.02 min (minor), 25.91 min (major)).

4,4-diallyl-6,7-dimethoxyisochroman-3-one (2ia)



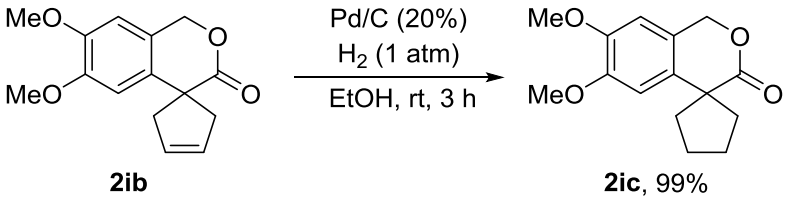
Compound **2ia** was prepared in 90% yield according to the above procedure. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (s, 1H), 6.55 (s, 1H), 5.55 – 5.43 (m, 2H), 5.28 (s, 2H), 5.07 – 4.96 (m, 4H), 3.87 (s, 3H), 3.85 (s, 3H), 2.90 – 2.82 (m, 2H), 2.61 – 2.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 149.0, 148.1, 132.6, 126.6, 123.0, 119.2, 109.3, 106.5, 69.1, 56.1, 55.9, 49.8, 43.4; HRESIMS Calcd for $[C_{17}H_{20}NaO_4]^+$ (M + Na^+) 311.1254, found 311.1258.

6',7'-dimethoxyspiro[cyclopent[3]ene-1,4'-isochroman]-3'-one (2ib)



Compound **2ib** was prepared in 91% yield according to the above procedure. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (s, 1H), 6.67 (s, 1H), 5.72 (s, 2H), 5.28 (s, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 3.35 (d, *J* = 15.3 Hz, 2H), 2.69 (d, *J* = 15.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 149.2, 148.0, 132.1, 127.6, 122.5, 108.1, 107.8, 68.9, 56.0, 50.7, 43.7; HRESIMS Calcd for $[C_{15}H_{16}NaO_4]^+$ (M + Na^+) 283.0941, found 283.0945.

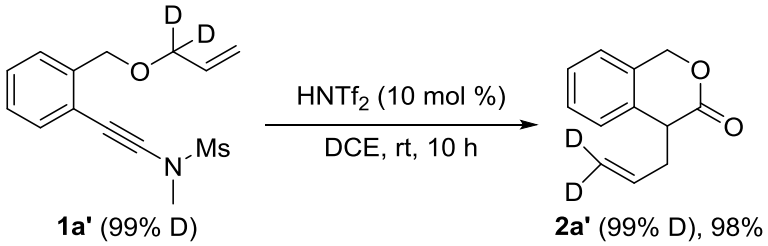
6',7'-dimethoxyspiro[cyclopentane-1,4'-isochroman]-3'-one (2ic)



Compound **2ic** was prepared in 99% yield according to the above procedure. This compound is known and the spectroscopic data match those reported.[3] ^{1}H NMR (400

MHz, $CDCl_3$) δ 6.77 (s, 1H), 6.67 (s, 1H), 5.26 (s, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 2.50 – 2.40 (m, 2H), 1.99 – 1.87 (m, 4H), 1.86 – 1.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 149.0, 147.8, 131.7, 123.5, 108.1, 107.9, 68.9, 56.1, 56.0, 52.4, 35.7, 25.5.

4-(allyl-3,3-d_2)isochroman-3-one (2a′)



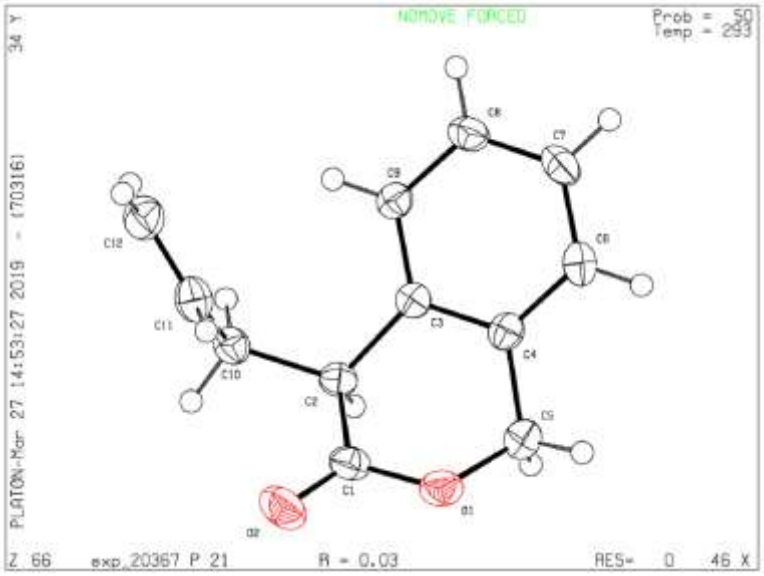
1a' (99% D) **2a'** (99% D), 98%

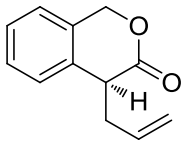
Compound **2a′** was prepared in 98% yield (55.9 mg) according to the above procedure. Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 2H), 7.29 – 7.22 (m, 2H), 5.94 – 5.84 (m, 1H), 5.44 (d, *J* = 14.1 Hz, 1H), 5.30 (d, *J* = 14.1 Hz, 1H), 3.72 (t, *J* = 6.8 Hz, 1H), 2.90 – 2.80 (m, 1H), 2.77 – 2.67 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 133.9(8), 133.9(6), 131.3, 128.6, 127.2, 126.6, 124.6, 69.5, 45.4, 34.1.

Reference:

1. L. Li, X.-Q. Zhu, Y.-Q. Zhang, H.-Z. Bu, P. Yuan, J. Chen, J. Su, X. Deng, L.-W. Ye, *Chem. Sci.* **2019**, *10*, 3213.
2. B. Peng, D. H. O'Donovan, I. D. Jurberg, N. Maulide, *Chem. Eur. J.* **2012**, *18*, 16292.
3. D. S. Goldfarb, U.S. Pat. Appl. Publ. 0163545A1, **2009**.

(*S*)-4-allylisochroman-3-one (2a-*ent*). CCDC Number = 1906229.





Bond precision: C-C = 0.0032 A Wavelength=1.54184

Cell: a=6.7747(3) b=6.9936(2) c=10.2745(4)
alpha=90 beta=99.508(4) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	480.11(3)	480.11(3)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	C12 H12 O2	?
Sum formula	C12 H12 O2	C12 H12 O2
Mr	188.22	188.22
Dx,g cm-3	1.302	1.302
Z	2	2
Mu (mm-1)	0.706	0.706
F000	200.0	200.0
F000'	200.61	
h,k,lmax	8,8,12	7,7,11
Nref	1740[948]	1453
Tmin,Tmax	0.959,0.965	0.720,1.000
Tmin'	0.932	

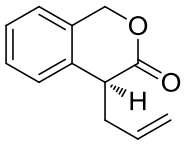
Correction method= # Reported T Limits: Tmin=0.720 Tmax=1.000
AbsCorr = MULTI-SCAN

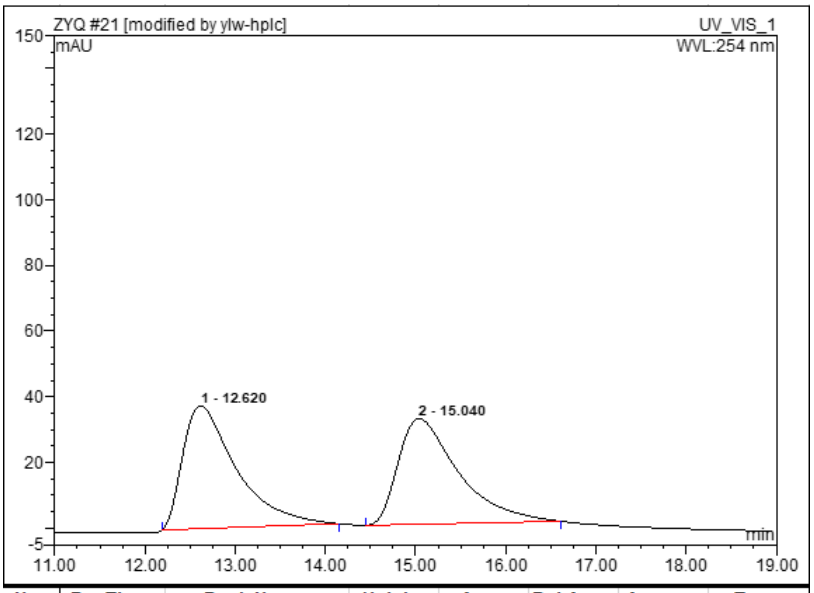
Data completeness= 1.53/0.84 Theta(max)= 67.684

R(reflections)= 0.0308(1429) wR2(reflections)= 0.0782(1453)

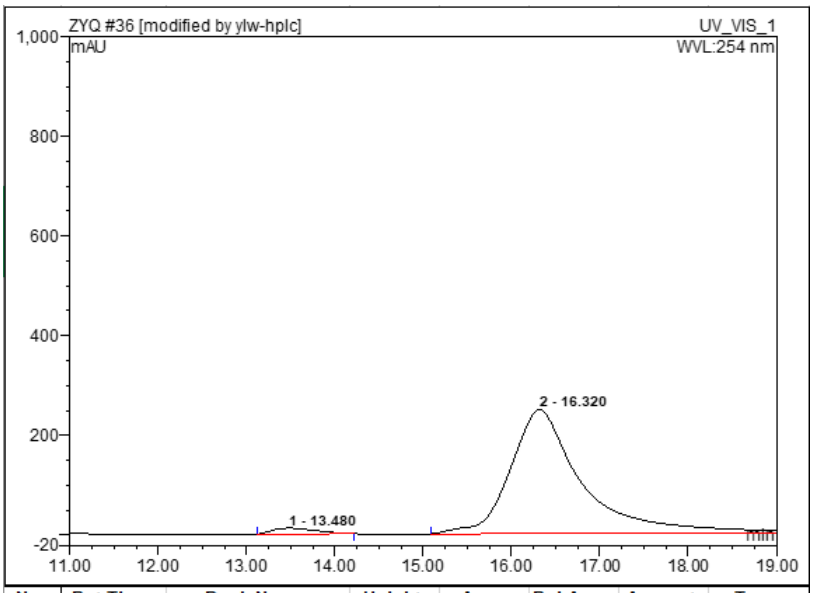
S = 1.079 Npar= 127

Compound **2a**-*ent*



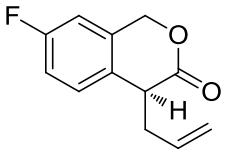


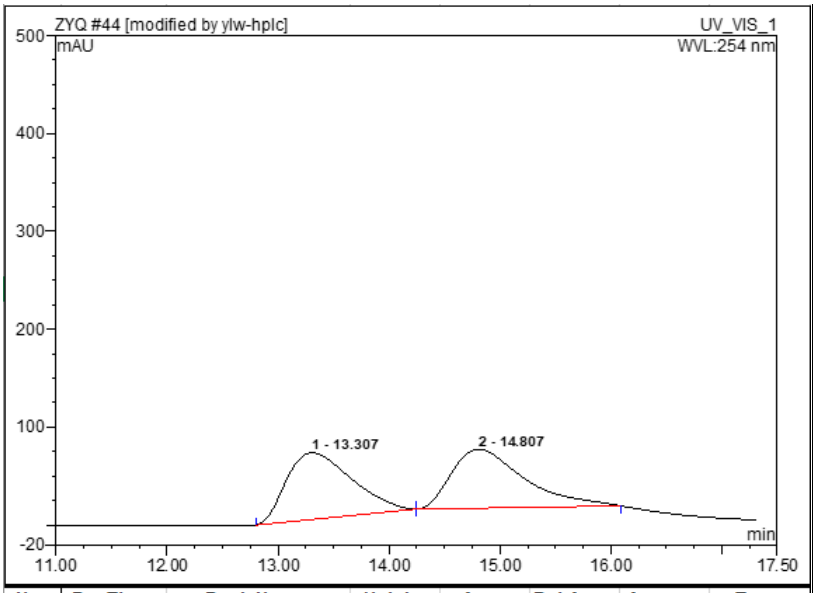
No.	Ret.Time	Peak Name	Height	Area	Rel.Area	Amount	Type
	min		mAU	mAU*min	%	n.a.	
1	12.62	n.a.	37.345	25.704	50.81	n.a.	BMB*
2	15.04	n.a.	32.167	24.886	49.19	n.a.	BMB*
Total:			69.513	50.590	100.00	0.000	



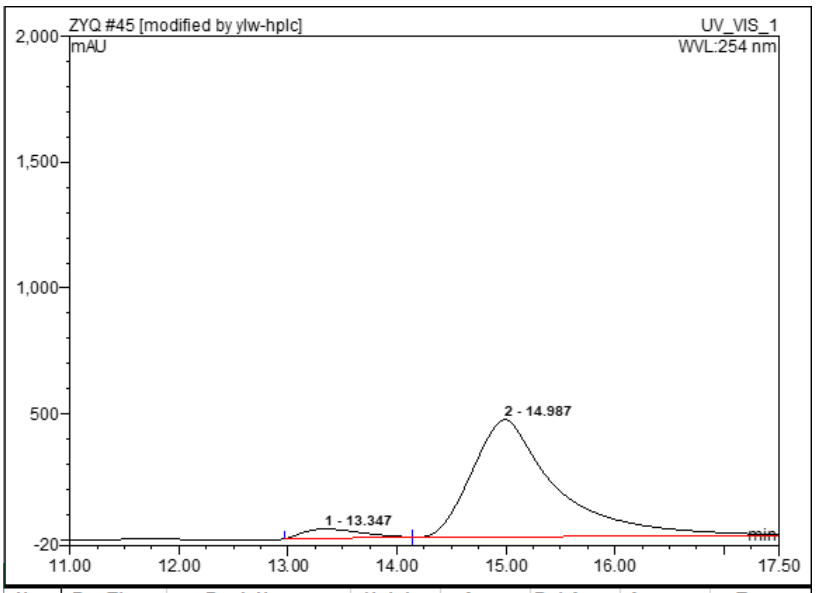
No.	Ret.Time	Peak Name	Height	Area	Rel.Area	Amount	Type
	min		mAU	mAU*min	%	n.a.	
1	13.48	n.a.	11.911	6.786	2.76	n.a.	BMB*
2	16.32	n.a.	249.868	239.347	97.24	n.a.	BMB*
Total:			261.779	246.133	100.00	0.000	

Compound **2d**-*ent*



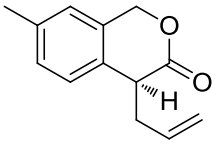


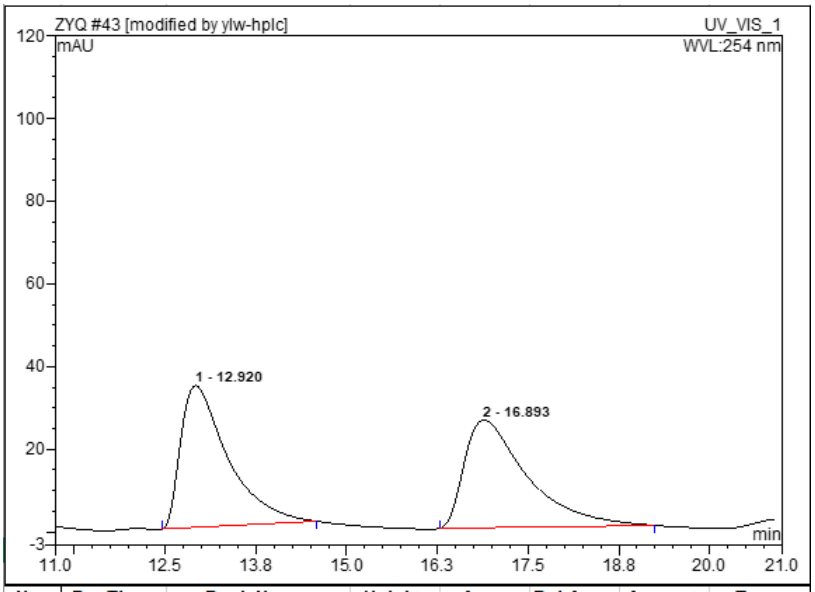
No.	Ret.Time	Peak Name	Height	Area	Rel.Area	Amount	Type
	min		mAU	mAU*min	%	n.a.	
1	13.31	n.a.	68.095	46.165	50.32	n.a.	BMb*
2	14.81	n.a.	60.239	45.584	49.68	n.a.	bMB*
Total:			128.334	91.749	100.00	0.000	



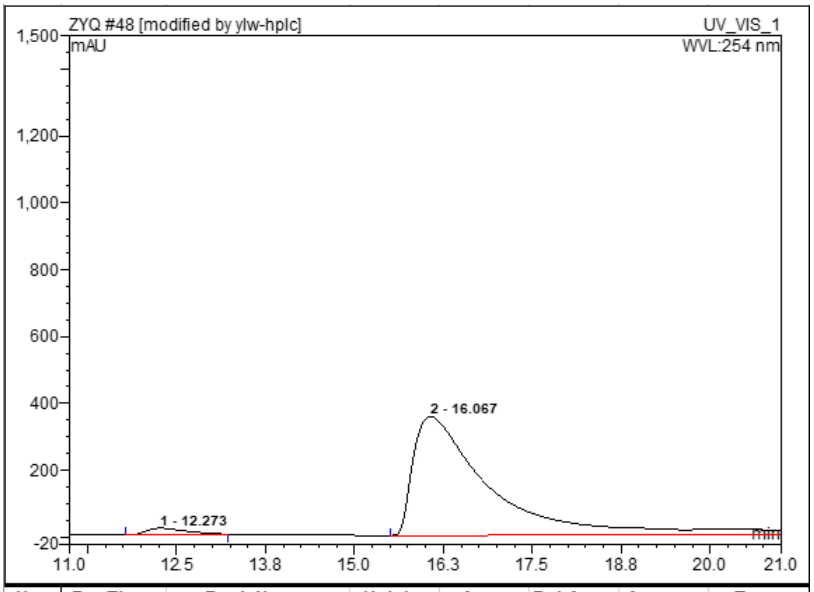
No.	Ret.Time	Peak Name	Height	Area	Rel.Area	Amount	Type
	min		mAU	mAU*min	%	n.a.	
1	13.35	n.a.	36.925	22.450	5.13	n.a.	BMb*
2	14.99	n.a.	464.858	415.156	94.87	n.a.	bMB*
Total:			501.783	437.606	100.00	0.000	

Compound **2g**-*ent*



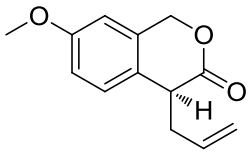


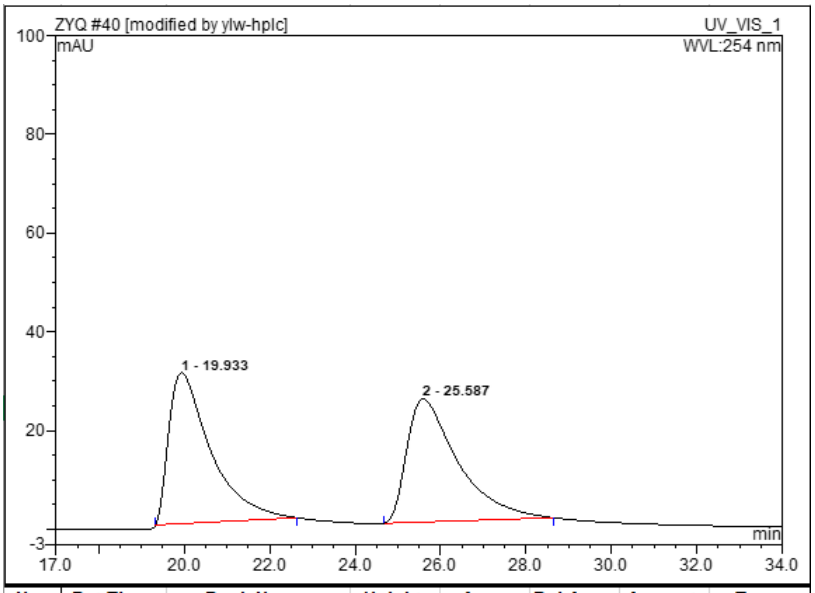
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	12.92	n.a.	34.246	25.843	49.86	n.a.	BMB*
2	16.89	n.a.	26.034	25.993	50.14	n.a.	BMB*
Total:			60.281	51.836	100.00	0.000	



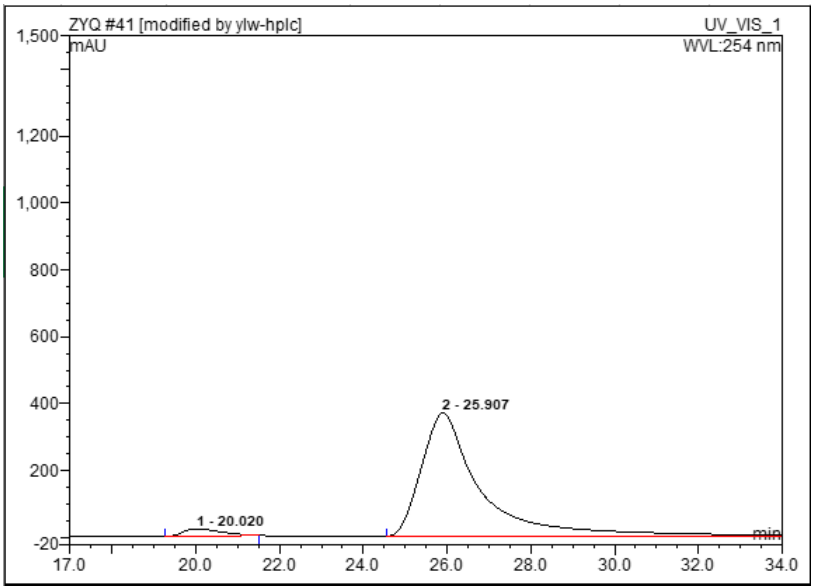
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	12.27	n.a.	20.021	12.952	2.72	n.a.	BMB*
2	16.07	n.a.	355.446	463.904	97.28	n.a.	BMB*
Total:			375.467	476.856	100.00	0.000	

Compound **2h**-*ent*

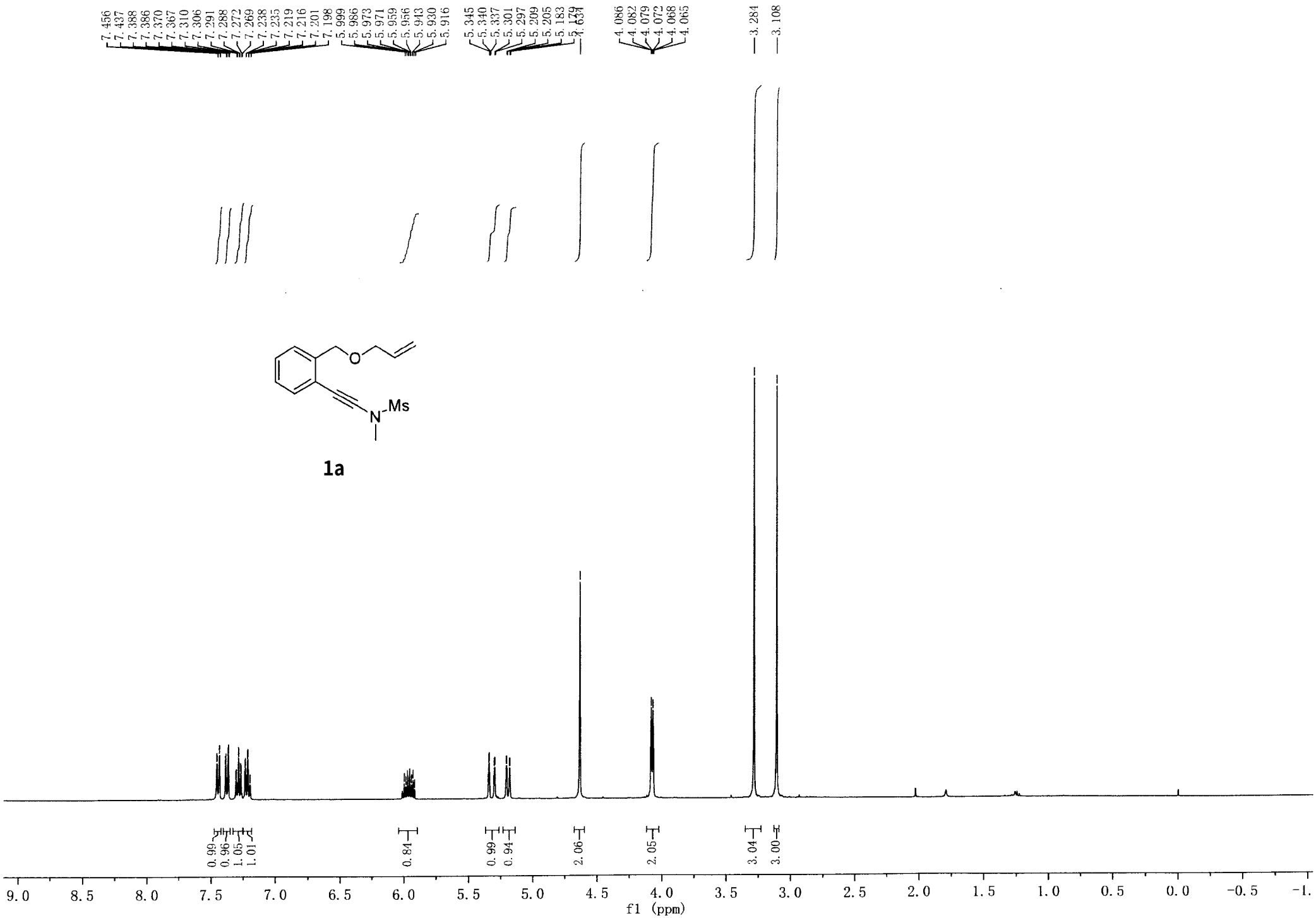




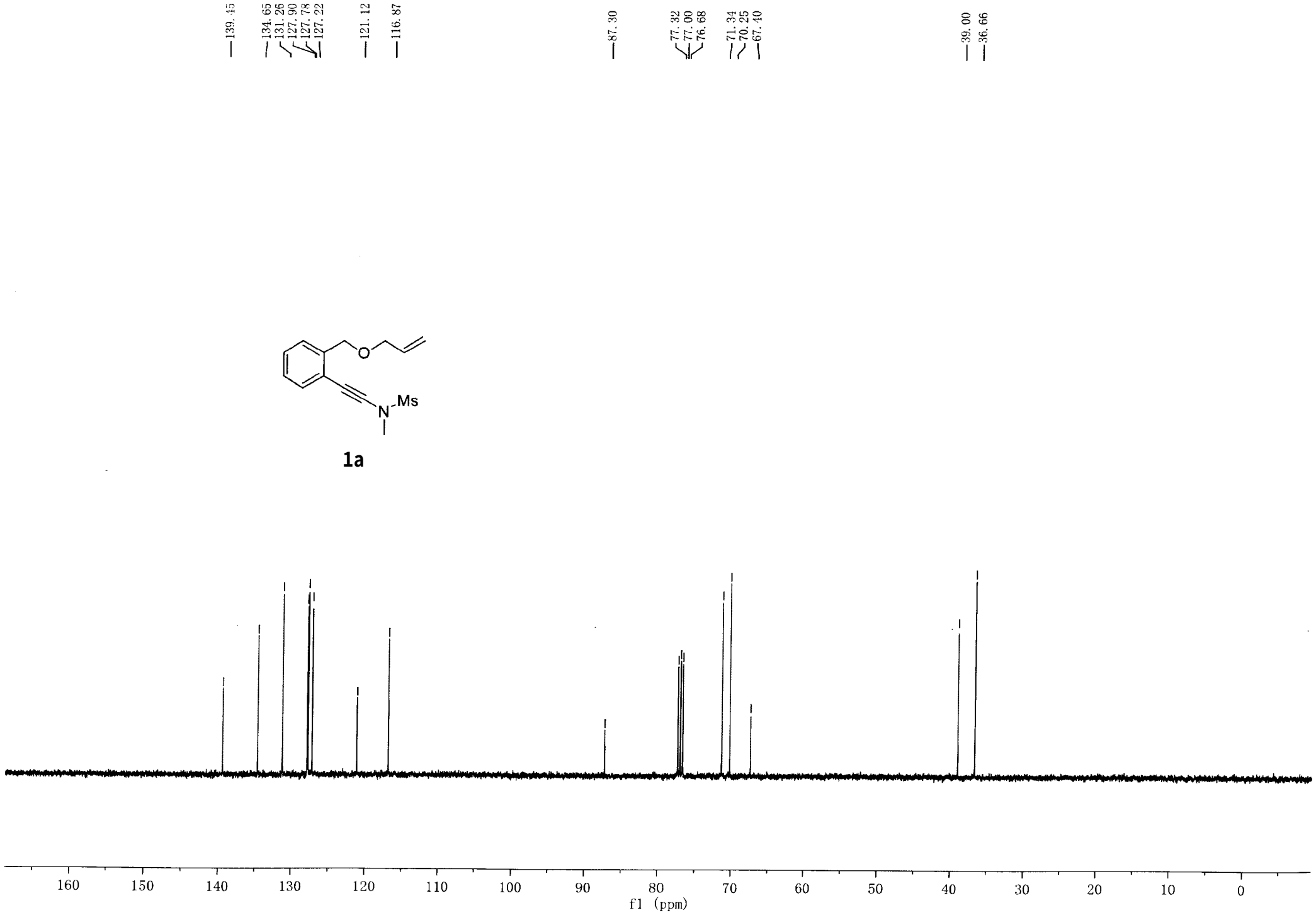
No.	Ret.Time	Peak Name	Height	Area	Rel.Area	Amount	Type
	min		mAU	mAU*min	%	n.a.	
1	19.93	n.a.	30.540	34.740	50.18	n.a.	BMB*
2	25.59	n.a.	24.923	34.485	49.82	n.a.	BMB*
Total:			55.463	69.225	100.00	0.000	



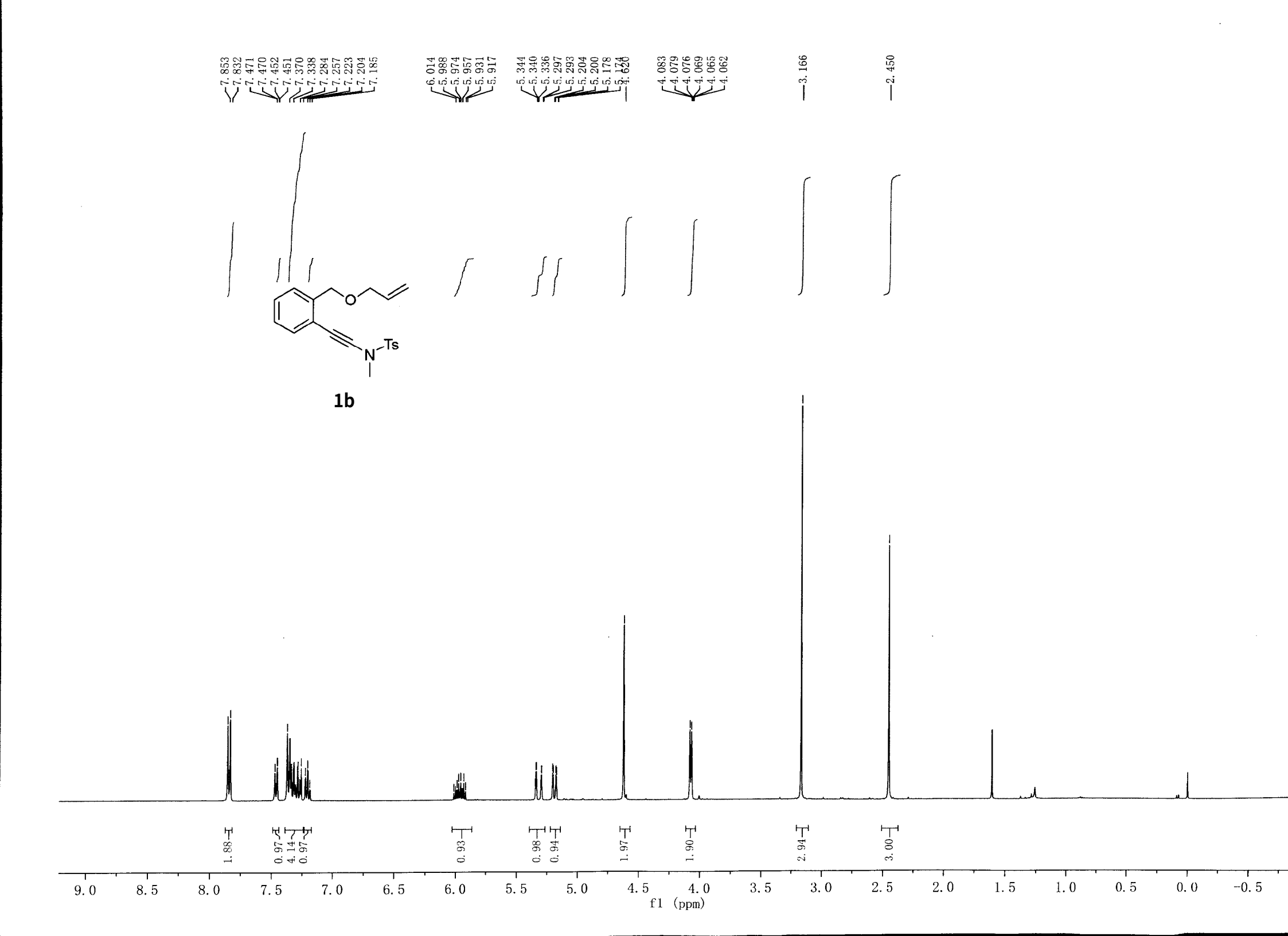
No.	Ret.Time	Peak Name	Height	Area	Rel.Area	Amount	Type
	min		mAU	mAU*min	%	n.a.	
1	20.02	n.a.	21.999	22.352	3.56	n.a.	BMB*
2	25.91	n.a.	368.912	605.345	96.44	n.a.	BMB*
Total:			390.911	627.697	100.00	0.000	


7.456
7.437
7.388
7.386
7.370
7.367
7.310
7.306
7.291
7.288
7.272
7.269
7.238
7.235
7.219
7.216
7.201
7.198
5.999
5.986
5.973
5.971
5.959
5.956
5.943
5.930
5.916
5.345
5.340
5.337
5.301
5.297
5.209
5.205
5.183
5.179
4.637
4.086
4.082
4.079
4.072
4.068
4.065
3.284
3.108
O
N
Ms
0.99
0.96
1.05
1.01
0.84
0.99
0.94
2.06
2.05
3.04
3.00
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)

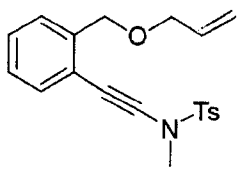
1a


139.45
134.65
131.26
127.90
127.78
127.22
121.12
116.87
87.30
77.32
77.00
76.68
71.34
70.25
67.40
39.00
36.66
O
N
Ms
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

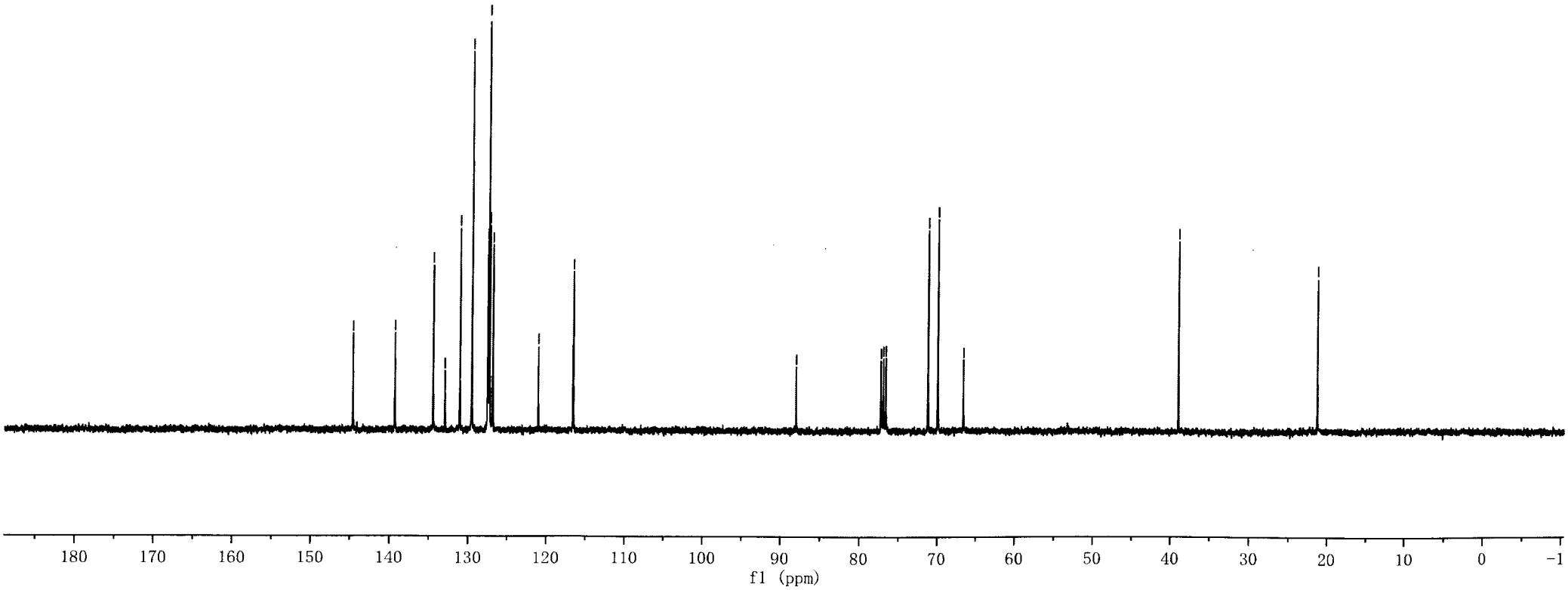
1a

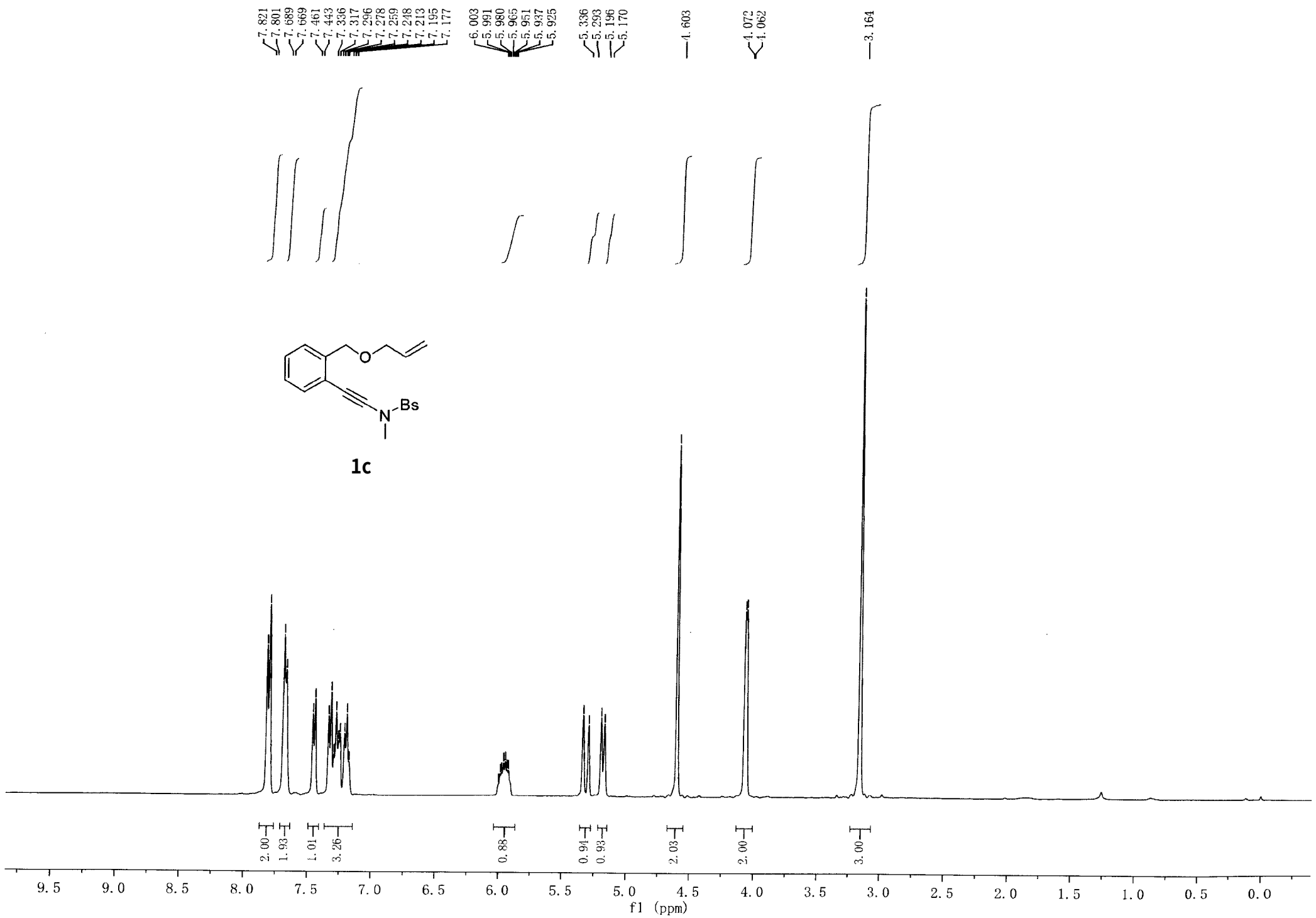

7.853
7.832
7.471
7.470
7.452
7.451
7.370
7.338
7.284
7.257
7.223
7.204
7.185
6.014
5.988
5.974
5.957
5.931
5.917
5.344
5.340
5.336
5.297
5.293
5.204
5.200
5.178
5.174
5.620
4.083
4.079
4.076
4.069
4.065
4.062
3.166
2.450
O
N
Ts
1b
1.88
0.97
4.14
0.97
0.93
0.98
0.94
1.97
1.90
2.94
3.00
9.0
8.5
8.0
7.5
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)

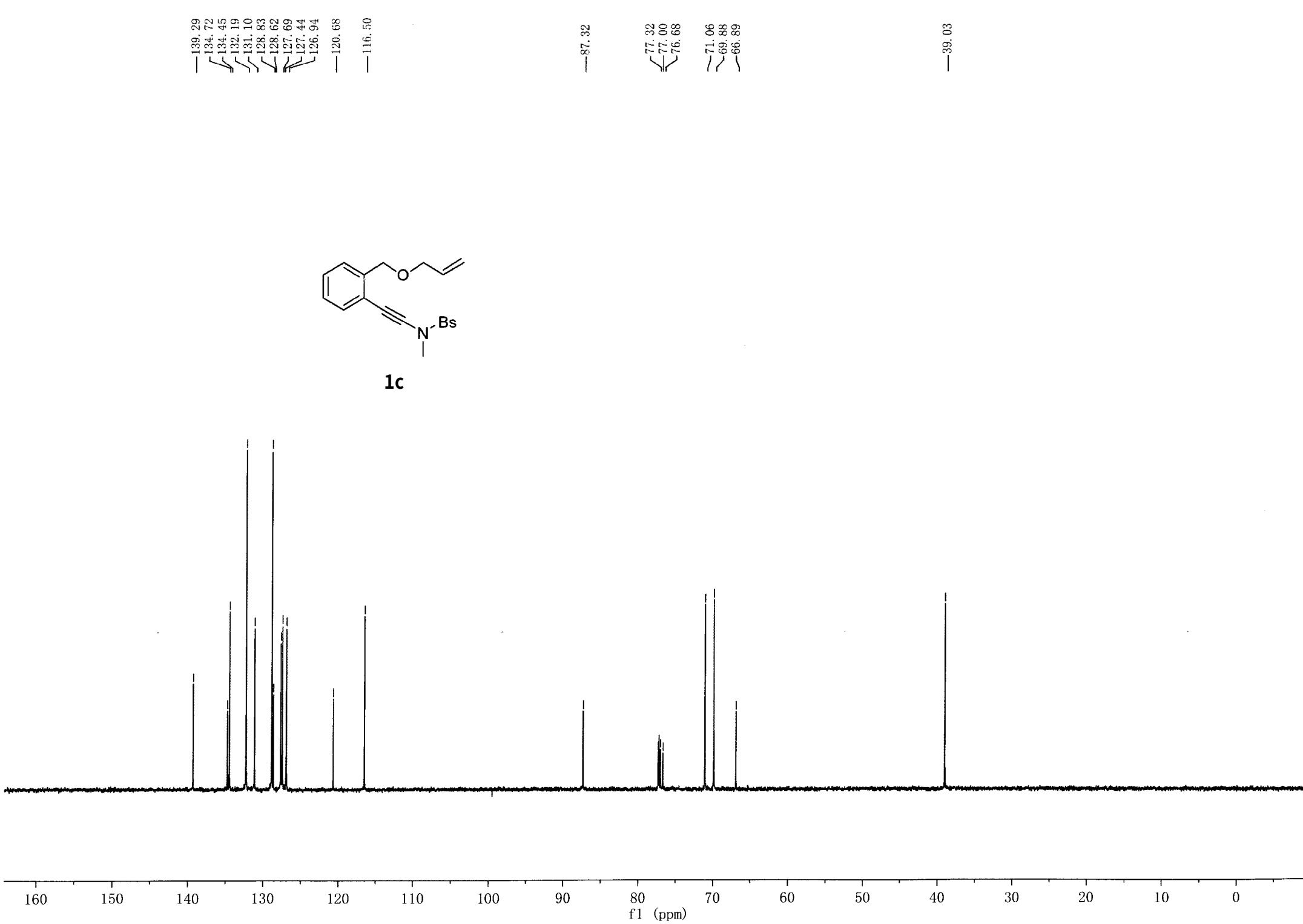
144.67
139.41
134.57
133.06
131.16
129.65
127.64
127.52
127.36
126.97
121.07
116.63
88.05
77.32
77.00
76.68
71.27
70.03
66.70
39.06
21.34



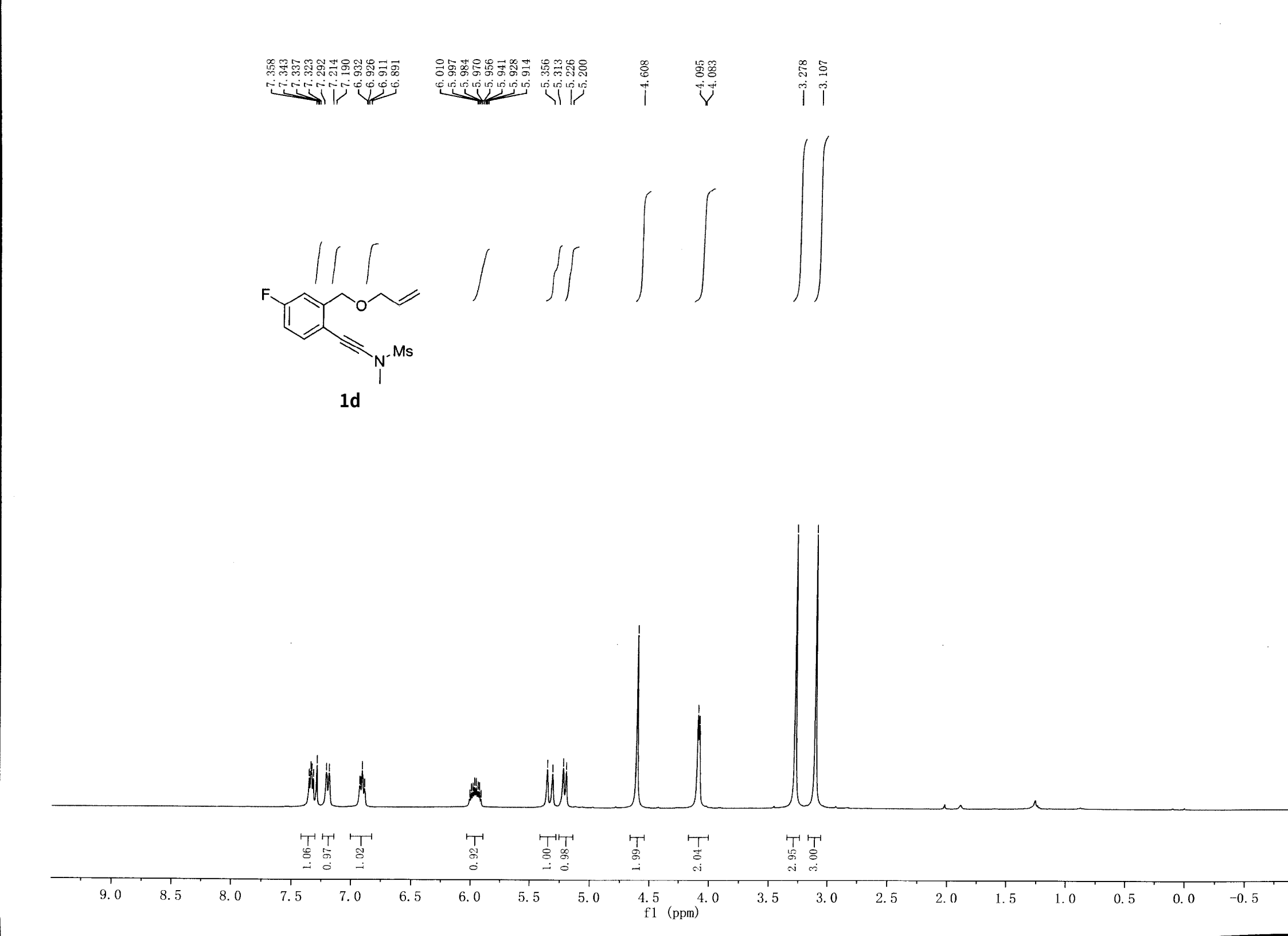
1b

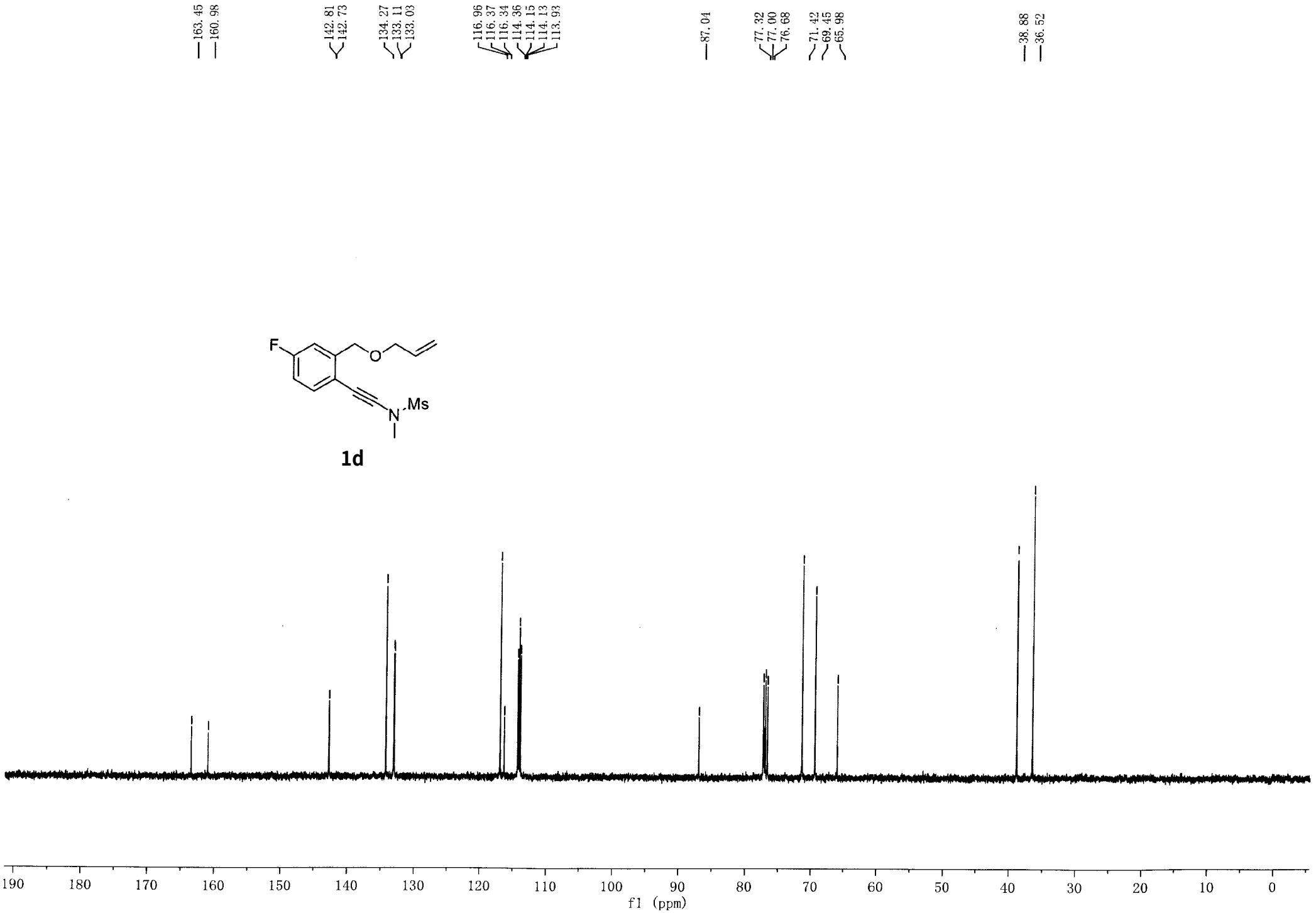


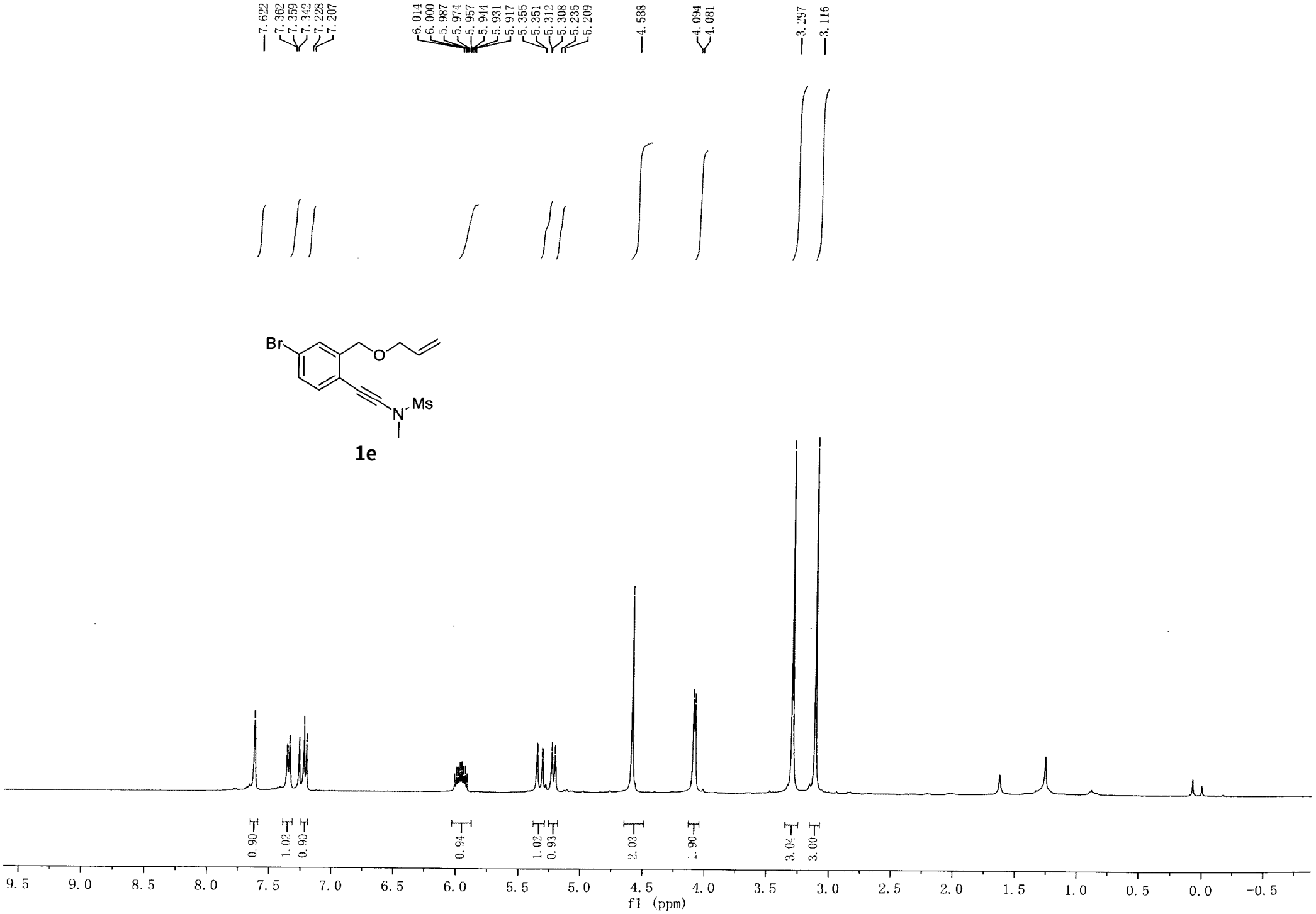

7.821
7.801
7.689
7.669
7.461
7.443
7.336
7.317
7.296
7.278
7.259
7.248
7.213
7.195
7.177
6.003
5.991
5.980
5.965
5.951
5.937
5.925
5.336
5.293
5.196
5.170
1.603
1.072
1.062
3.164
O
N
Bs
1c
2.00
1.93
1.01
3.26
0.88
0.94
0.93
2.03
2.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

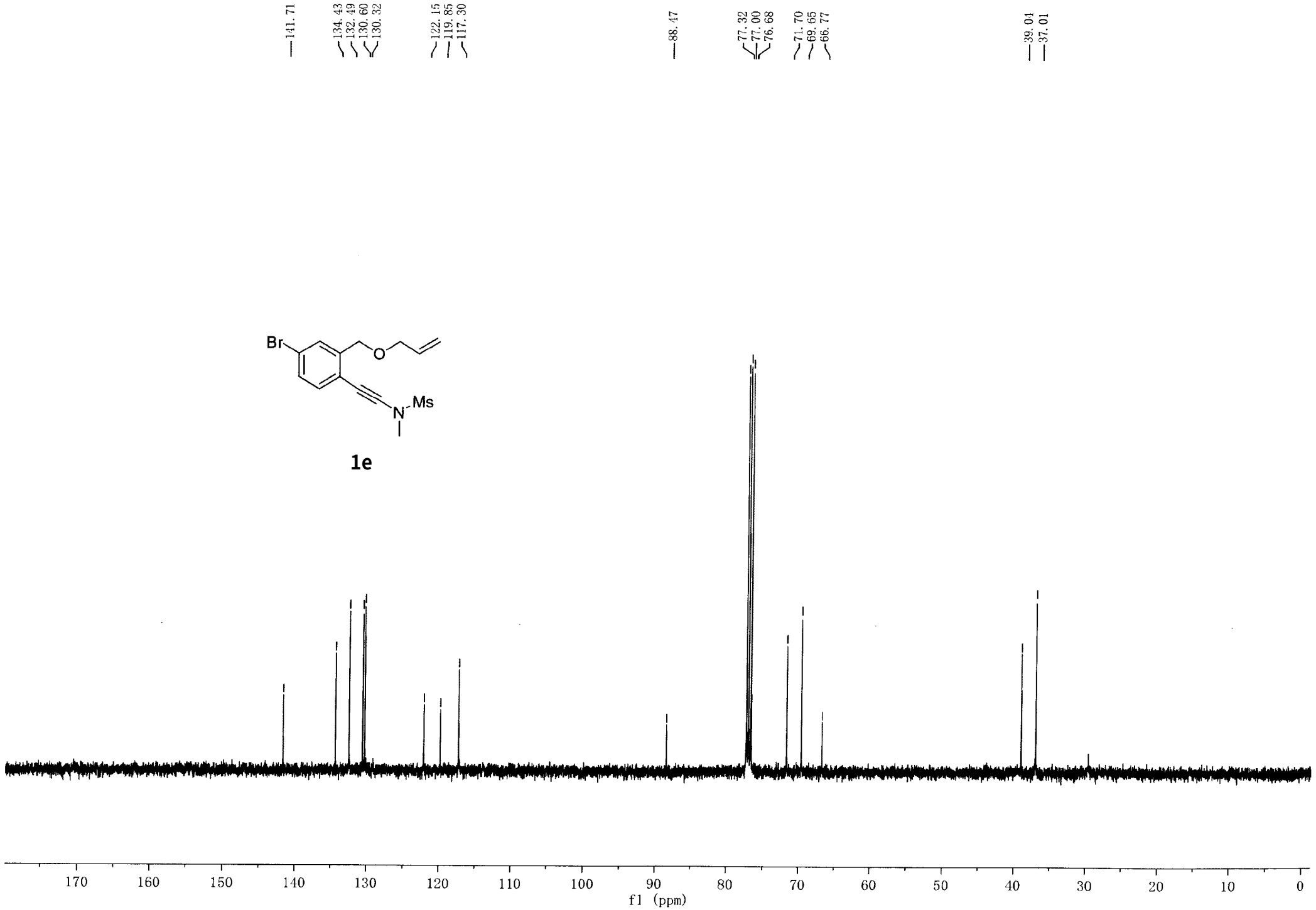

139.29
134.72
134.45
132.19
131.10
128.83
128.62
127.69
127.44
126.94
120.68
116.50
87.32
77.32
77.00
76.68
71.06
69.88
66.89
39.03
O
N
Bs
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

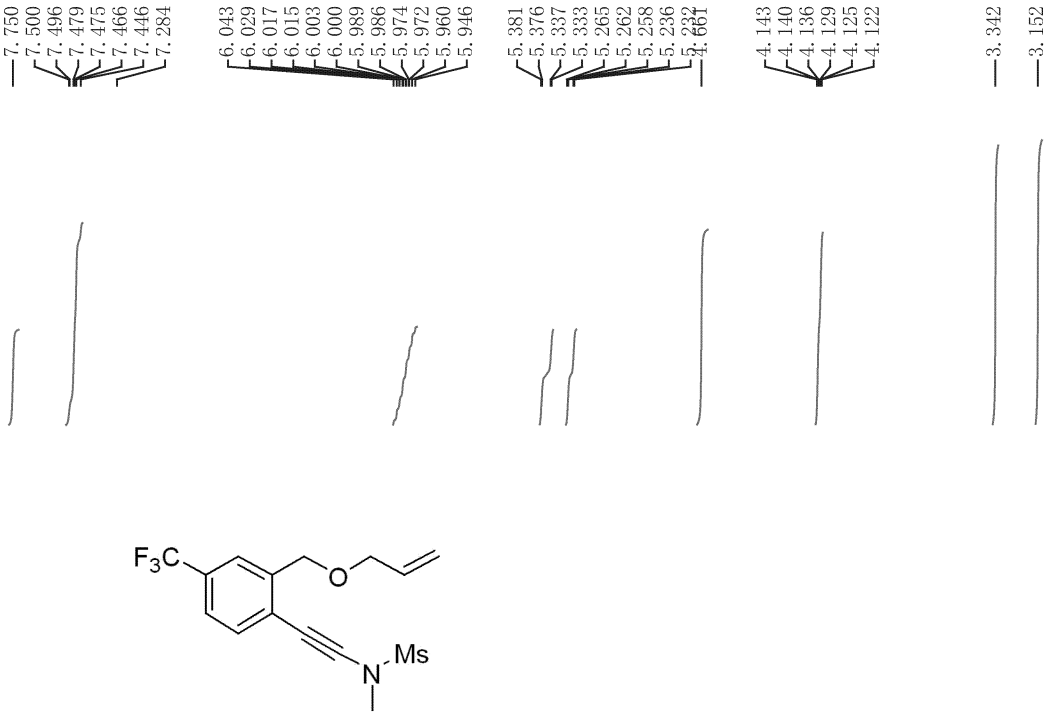
1c


7.358
7.343
7.337
7.323
7.292
7.214
7.190
6.932
6.926
6.911
6.891
6.010
5.997
5.984
5.970
5.956
5.941
5.928
5.914
5.356
5.313
5.226
5.200
4.608
4.095
4.083
3.278
3.107
F
O
N
Ms
1d
1.06
0.97
1.02
0.92
1.00
0.98
1.99
2.04
2.95
3.00
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)

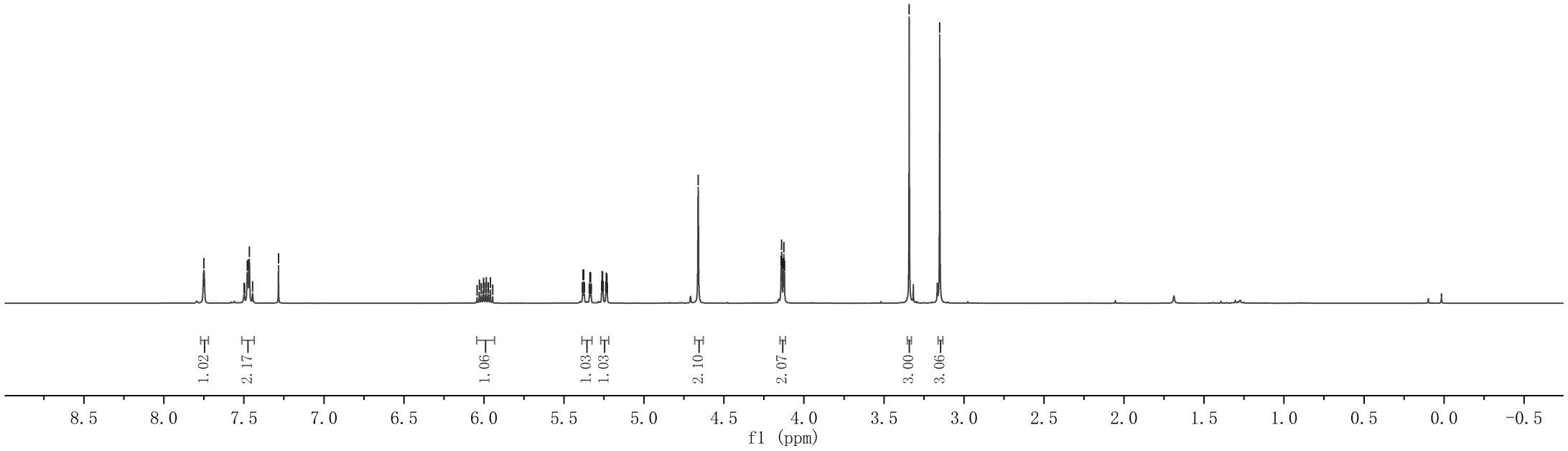

163.45
160.98
142.81
142.73
134.27
133.11
133.03
116.96
116.37
116.34
114.36
114.15
114.13
113.93
87.04
77.32
77.00
76.68
71.42
69.45
65.98
38.88
36.52
F
O
N
Ms
1d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

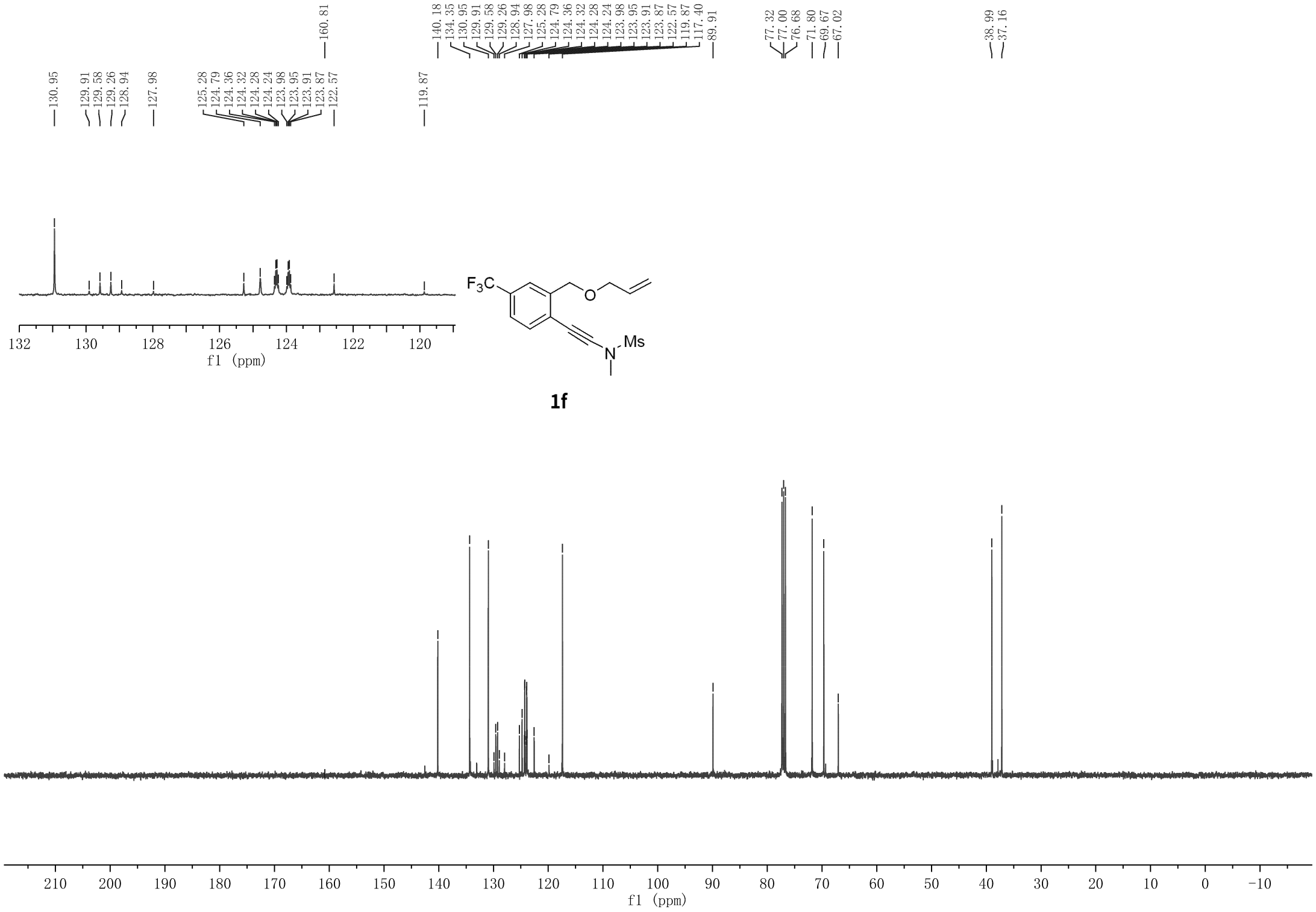

7.622
7.362
7.359
7.342
7.228
7.207
6.014
6.000
5.987
5.971
5.957
5.944
5.931
5.917
5.355
5.351
5.312
5.308
5.235
5.209
4.588
4.094
4.081
3.297
3.116
Br
O
N
Ms
1e
0.90
1.02
0.90
0.94
1.02
0.93
2.03
1.90
3.04
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

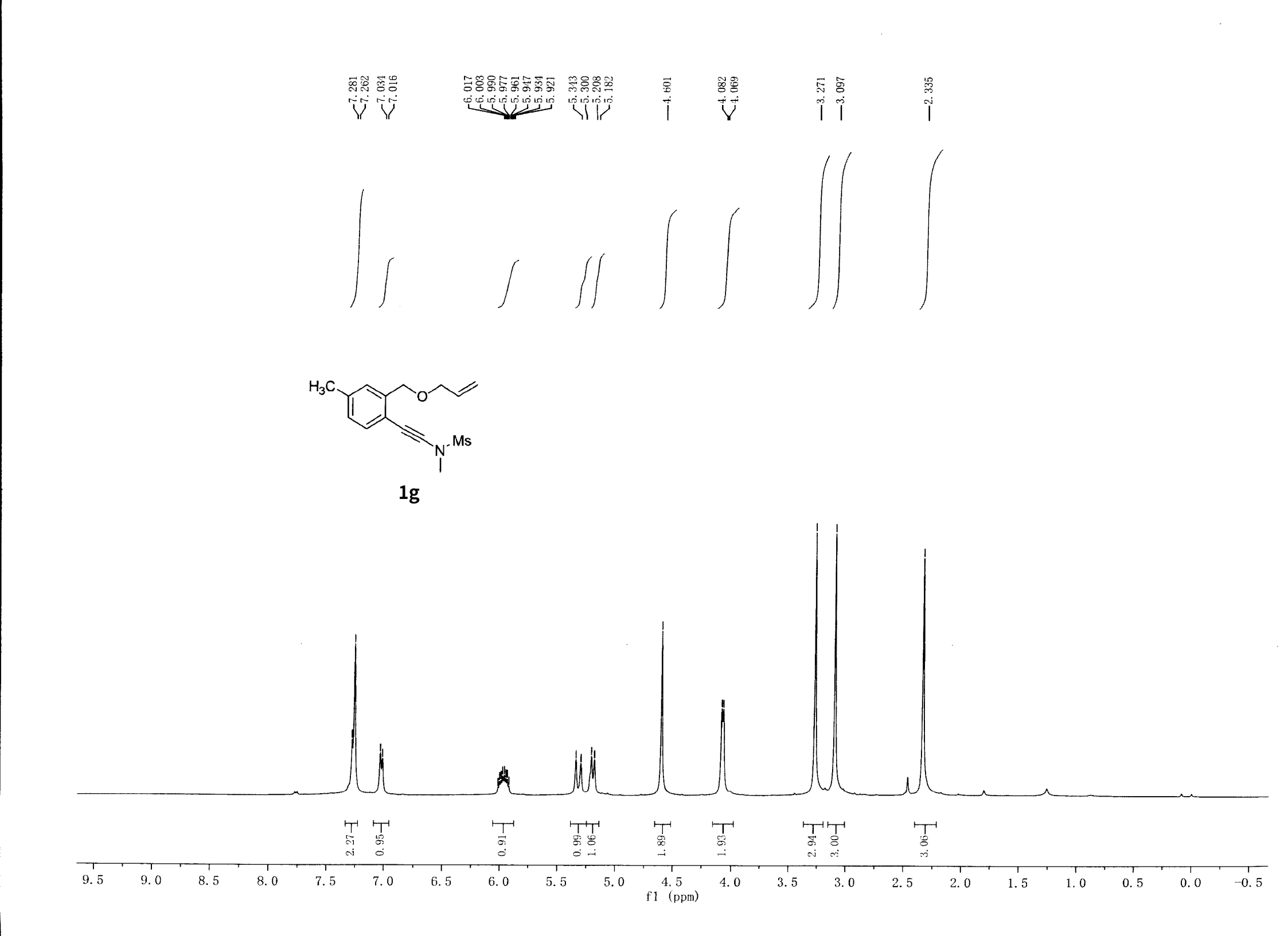

141.71
134.43
132.49
130.60
130.32
122.15
119.85
117.30
88.47
77.32
77.00
76.68
71.70
69.65
66.77
39.04
37.01
Br
O
N
Ms
1e
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

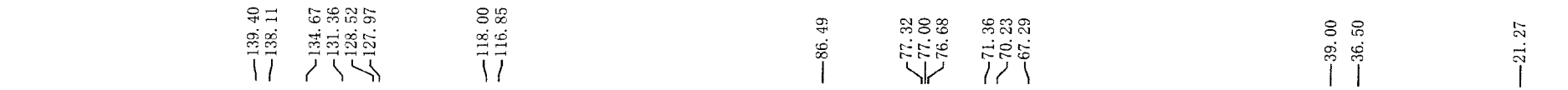

7.750
7.500
7.496
7.479
7.475
7.466
7.446
7.284
6.043
6.029
6.017
6.015
6.003
6.000
5.989
5.986
5.974
5.972
5.960
5.946
5.381
5.376
5.337
5.333
5.265
5.262
5.258
5.236
5.232
4.661
4.143
4.140
4.136
4.129
4.125
4.122
3.342
3.152
F3C
O
N
Ms

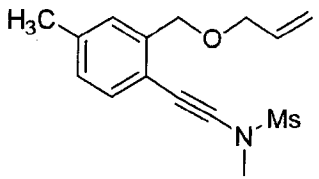
1f


1.02
2.17
1.06
1.03
1.03
2.10
2.07
3.00
3.06
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)

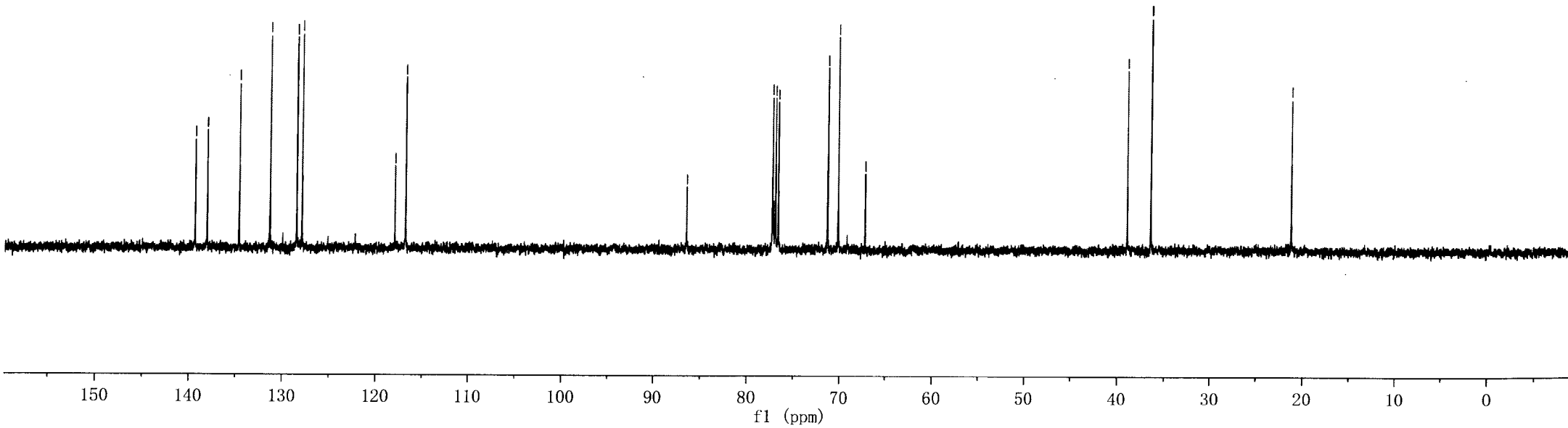

160.81
140.18
134.35
130.95
129.91
129.58
129.26
128.94
127.98
125.28
124.79
124.36
124.32
124.28
124.24
123.98
123.95
123.91
123.87
122.57
119.87
117.40
89.91
77.32
77.00
76.68
71.80
69.67
67.02
38.99
37.16
f1 (ppm)
F3C
O
N
Ms
1f

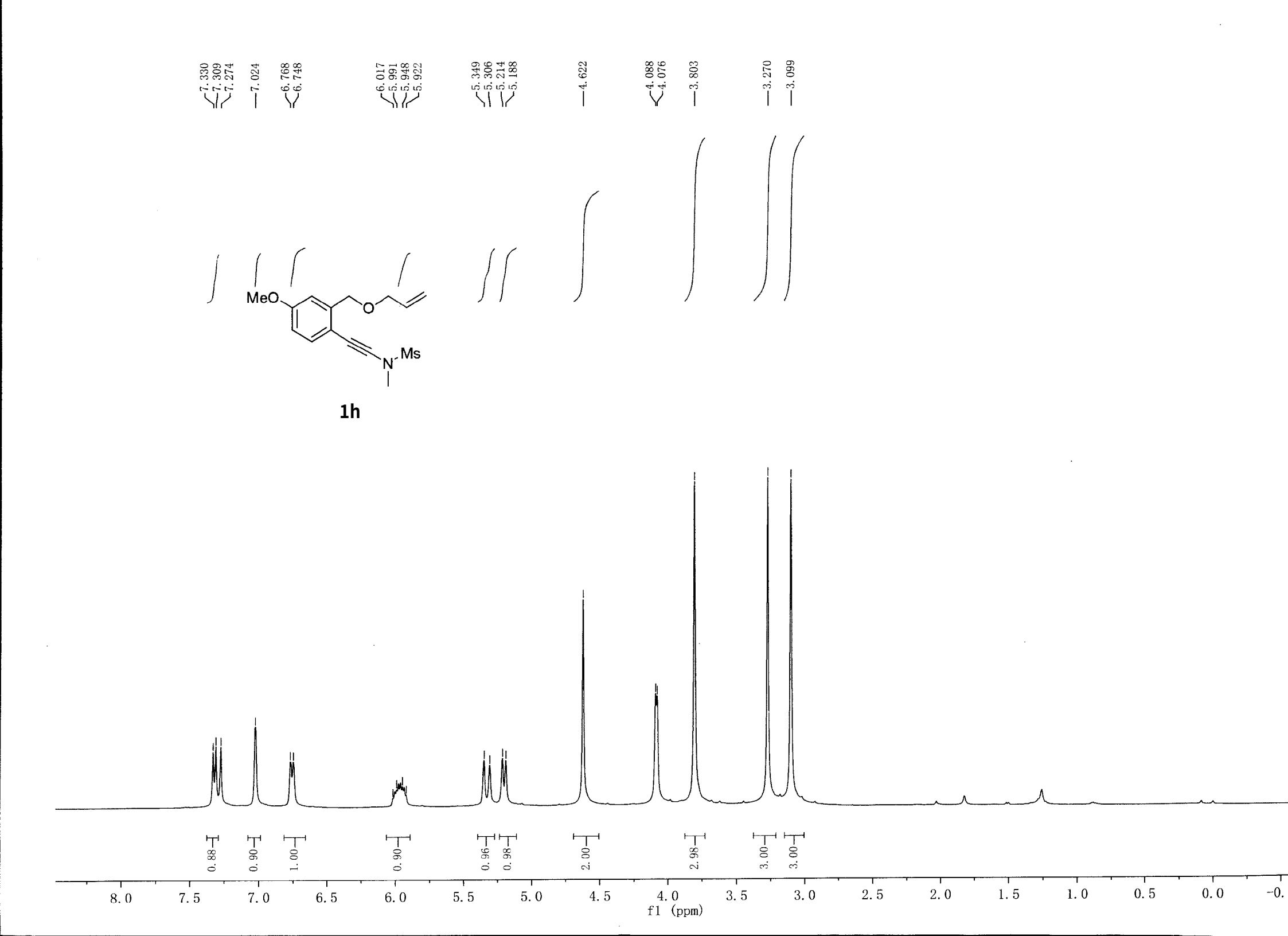

7.281
7.262
7.034
7.016
6.017
6.003
5.990
5.977
5.961
5.947
5.934
5.921
5.343
5.300
5.208
5.182
4.601
4.082
4.069
3.271
3.097
2.335
H3C
O
N
Ms
1g
2.27
0.95
0.91
0.99
1.06
1.89
1.93
2.94
3.00
3.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


139.40
138.11
134.67
131.36
128.52
127.97
118.00
116.85
86.49
77.32
77.00
76.68
71.36
70.23
67.29
39.00
36.50
21.27


H3C
O
N
Ms

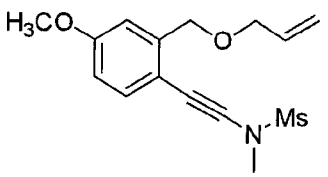
1g


150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

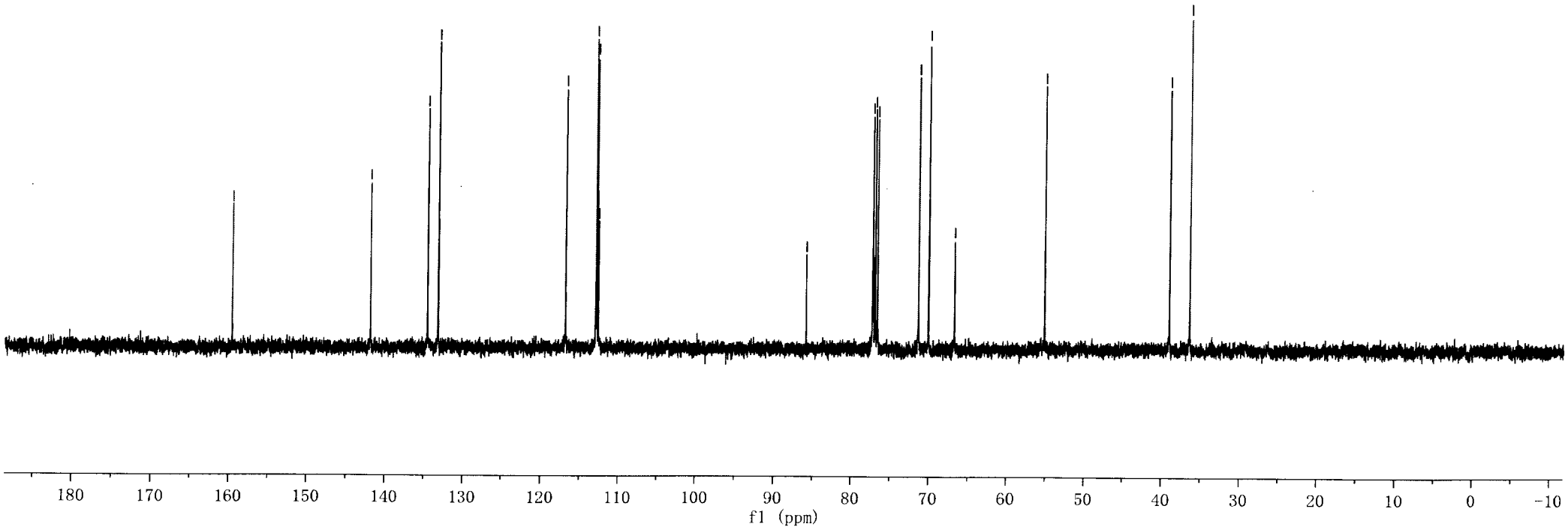

7.330
7.309
7.274
7.024
6.768
6.748
6.017
5.991
5.948
5.922
5.349
5.306
5.214
5.188
4.622
4.088
4.076
3.803
3.270
3.099
MeO
O
N
Ms
0.88
0.90
1.00
0.90
0.96
0.98
2.00
2.98
3.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

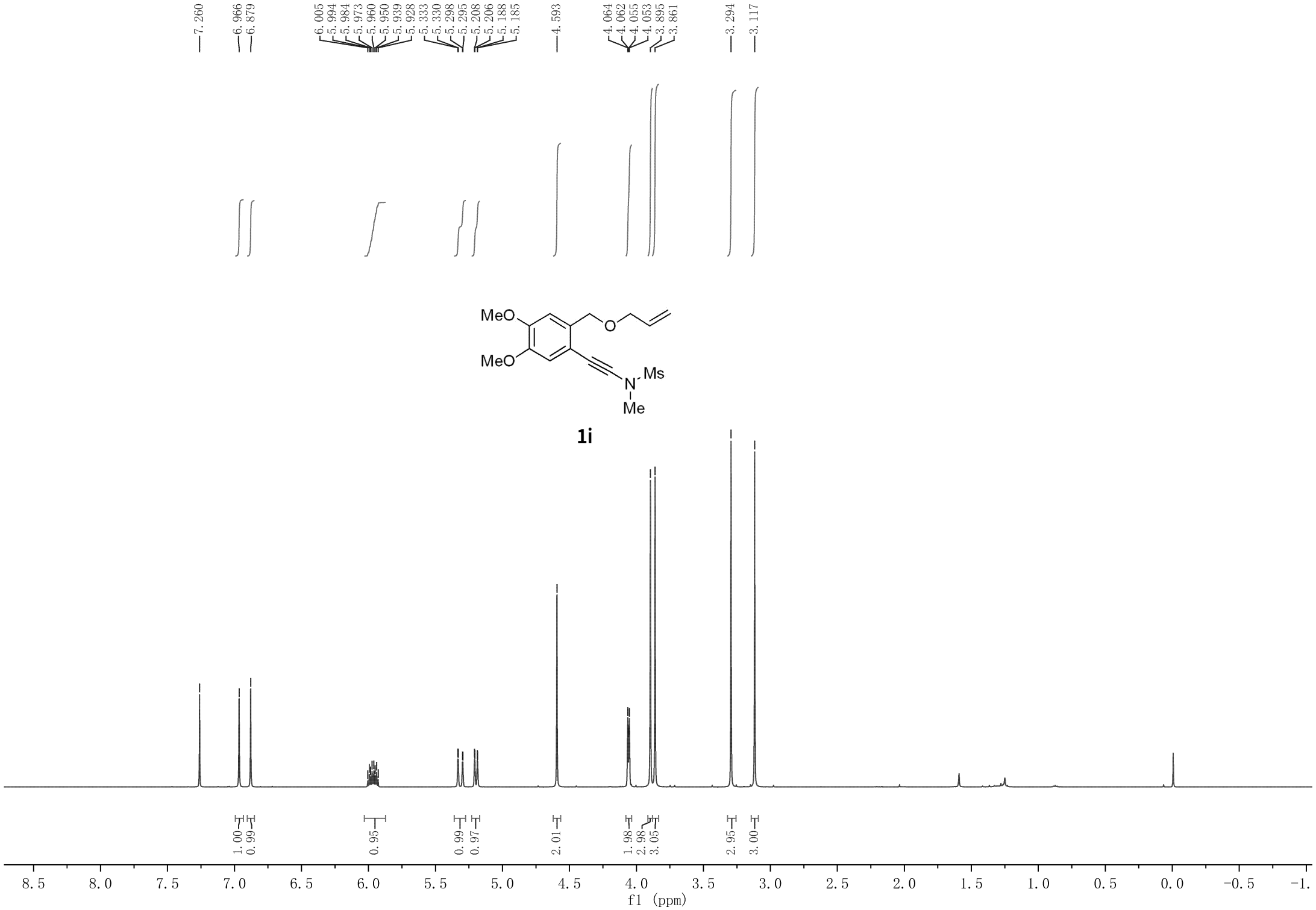
1h

159.64
141.95
134.59
133.25
116.88
112.99
112.83
112.66
85.84
77.32
77.00
76.68
71.37
70.09
66.78
55.16
39.08
36.42

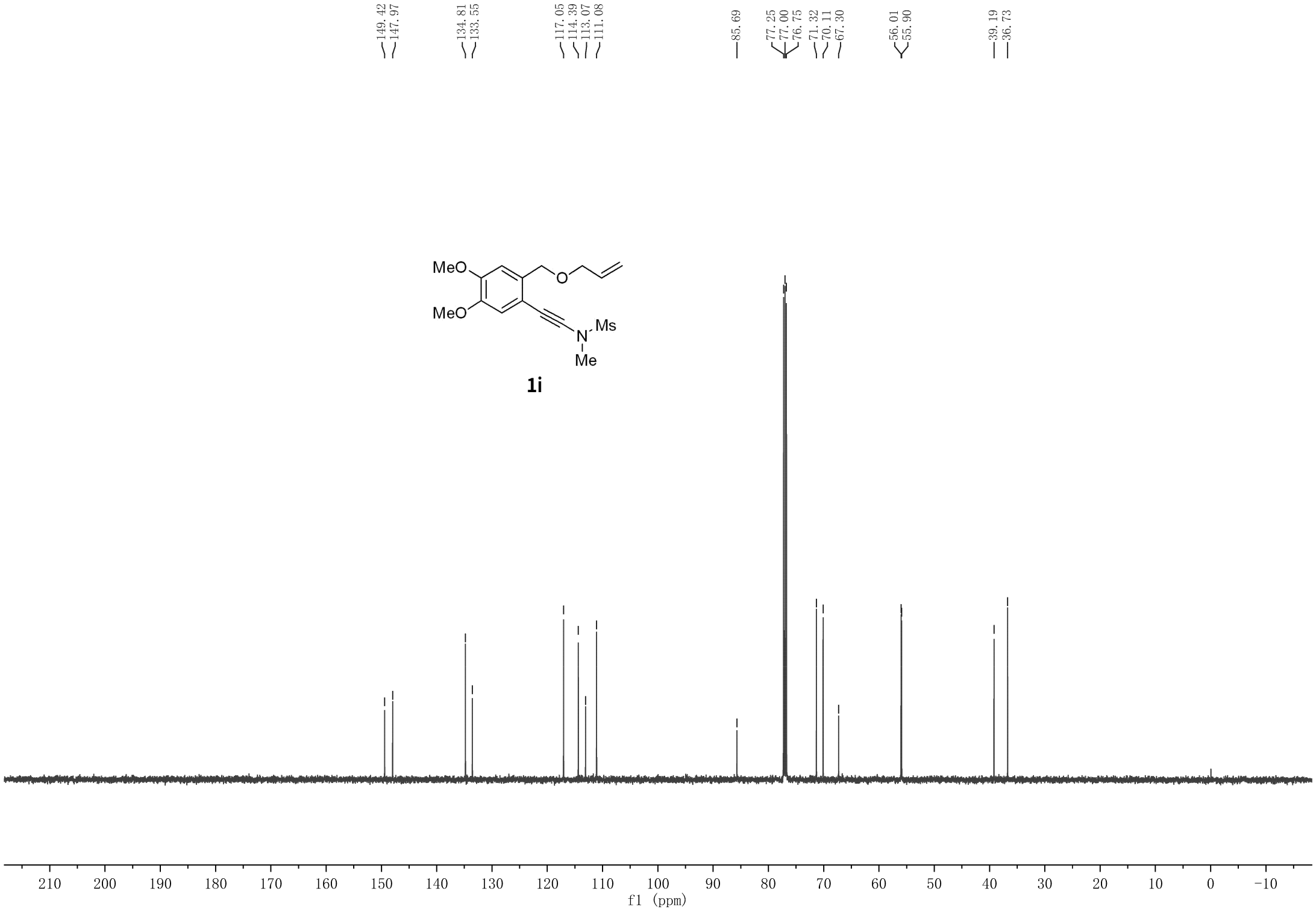


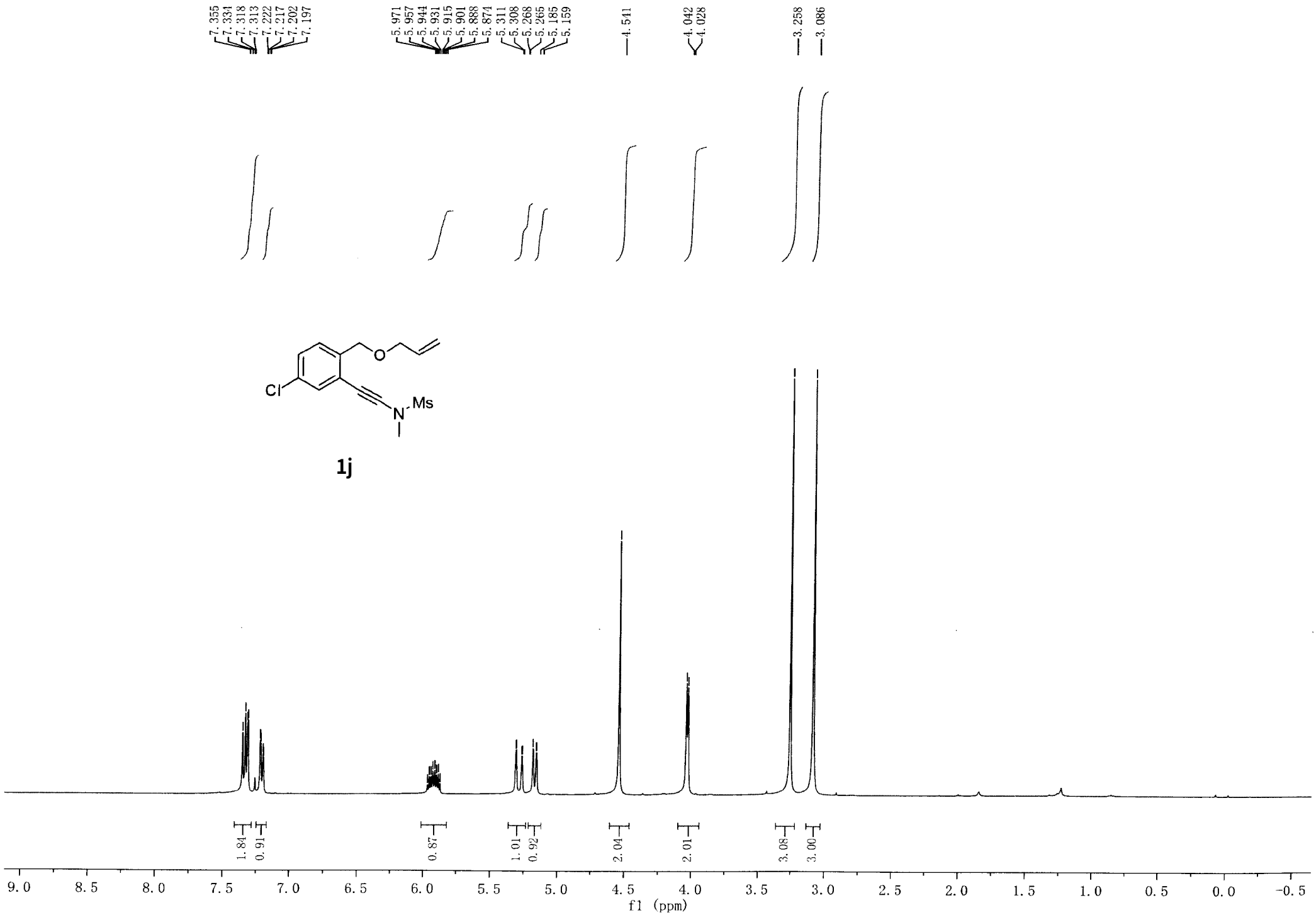
1h




7.260
6.966
6.879
6.005
5.994
5.984
5.973
5.960
5.950
5.939
5.928
5.333
5.330
5.298
5.295
5.208
5.206
5.188
5.185
4.593
4.064
4.062
4.055
4.053
3.895
3.861
3.294
3.117
MeO
MeO
O
N
Ms
Me
1.00
0.99
0.95
0.99
0.97
2.01
1.98
2.98
3.05
2.95
3.00
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)

1i


149.42
147.97
134.81
133.55
117.05
114.39
113.07
111.08
85.69
77.25
77.00
76.75
71.32
70.11
67.30
56.01
55.90
39.19
36.73
MeO
MeO
O
N
Ms
Me
1i
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)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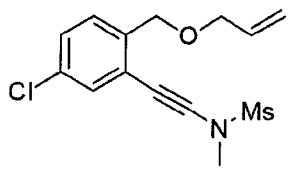
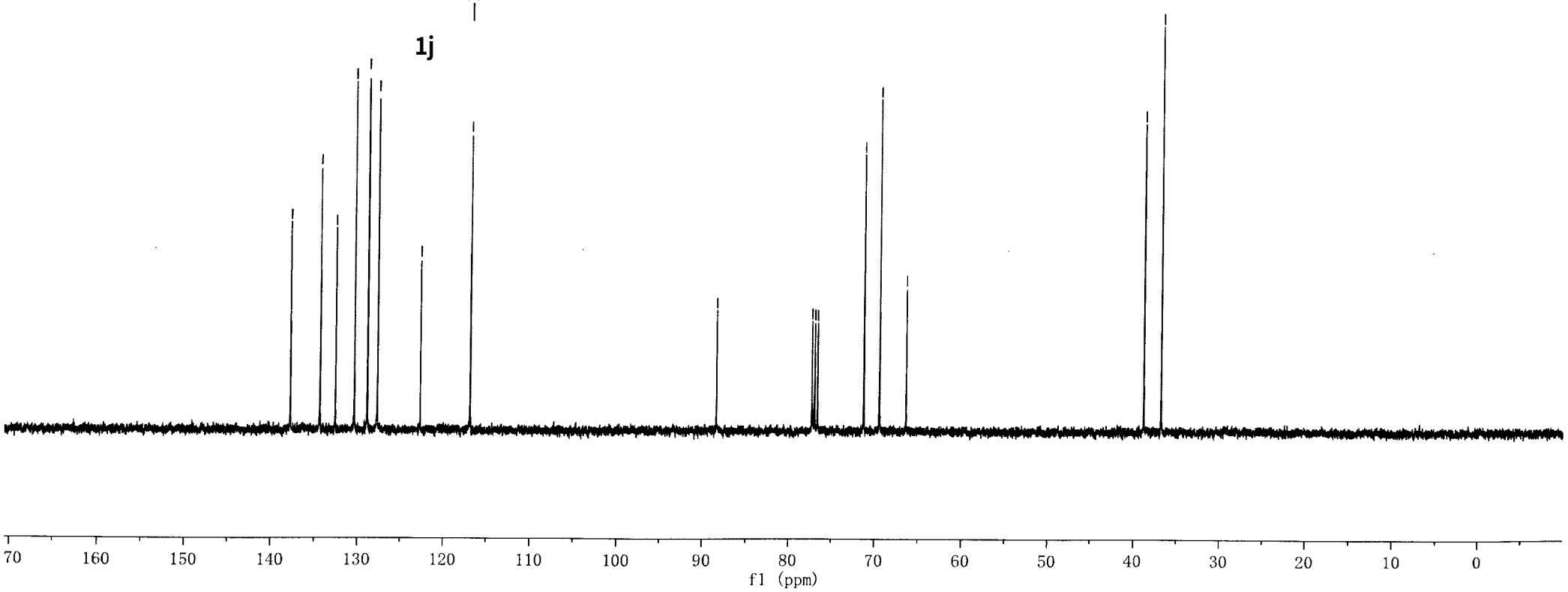
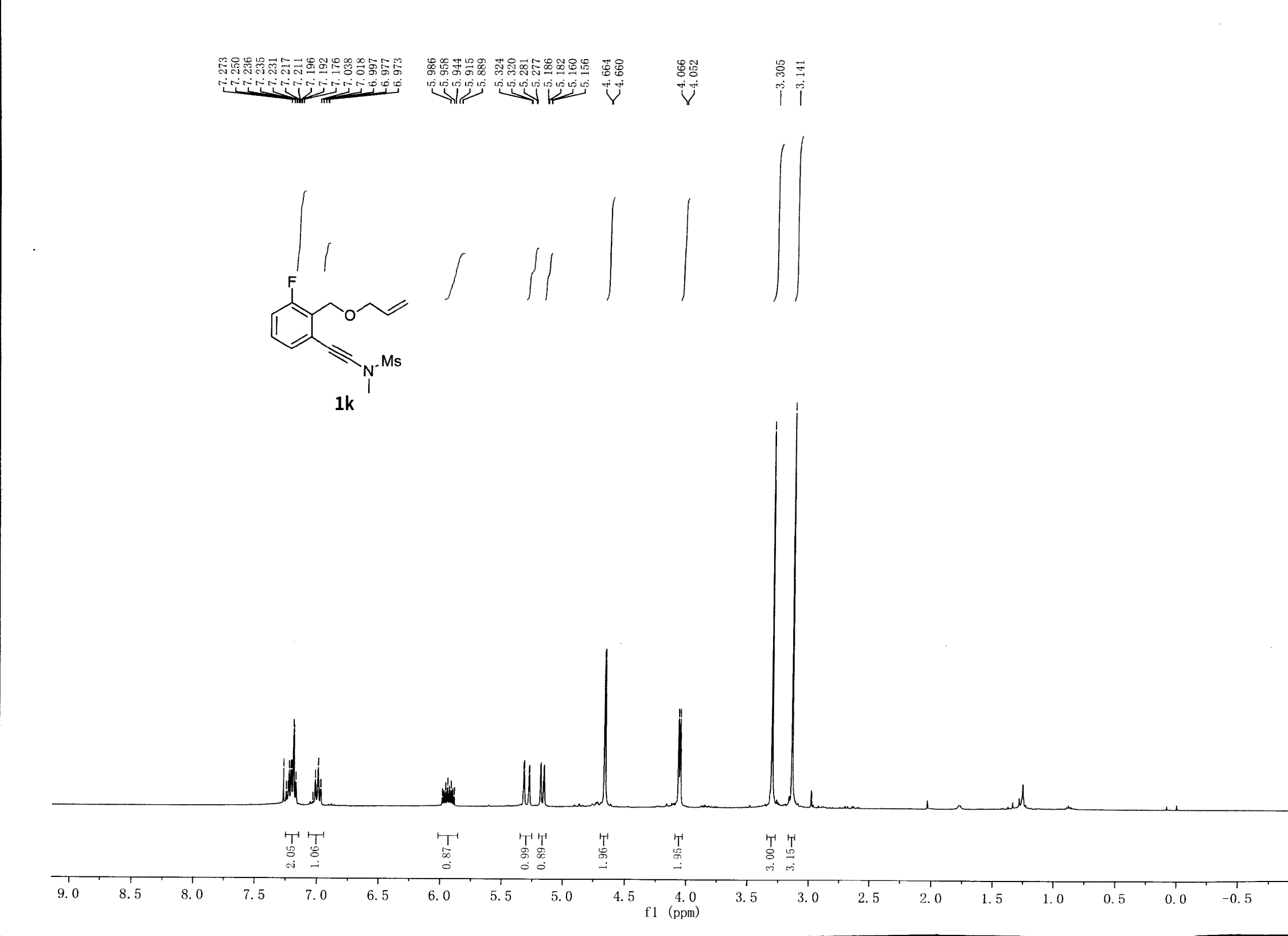
7.334
7.318
7.313
7.222
7.217
7.202
7.197
5.971
5.957
5.944
5.931
5.915
5.901
5.888
5.874
5.311
5.308
5.268
5.265
5.185
5.159
4.541
4.042
4.028
3.258
3.086
Cl
O
N
Ms
1j
1.84
0.91
0.87
1.01
0.92
2.04
2.01
3.08
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

137.79
134.39
132.59
130.41
128.92
127.73
122.72
116.91
88.44
77.32
77.00
76.68
71.30
69.46
66.40
38.83
36.79



1j

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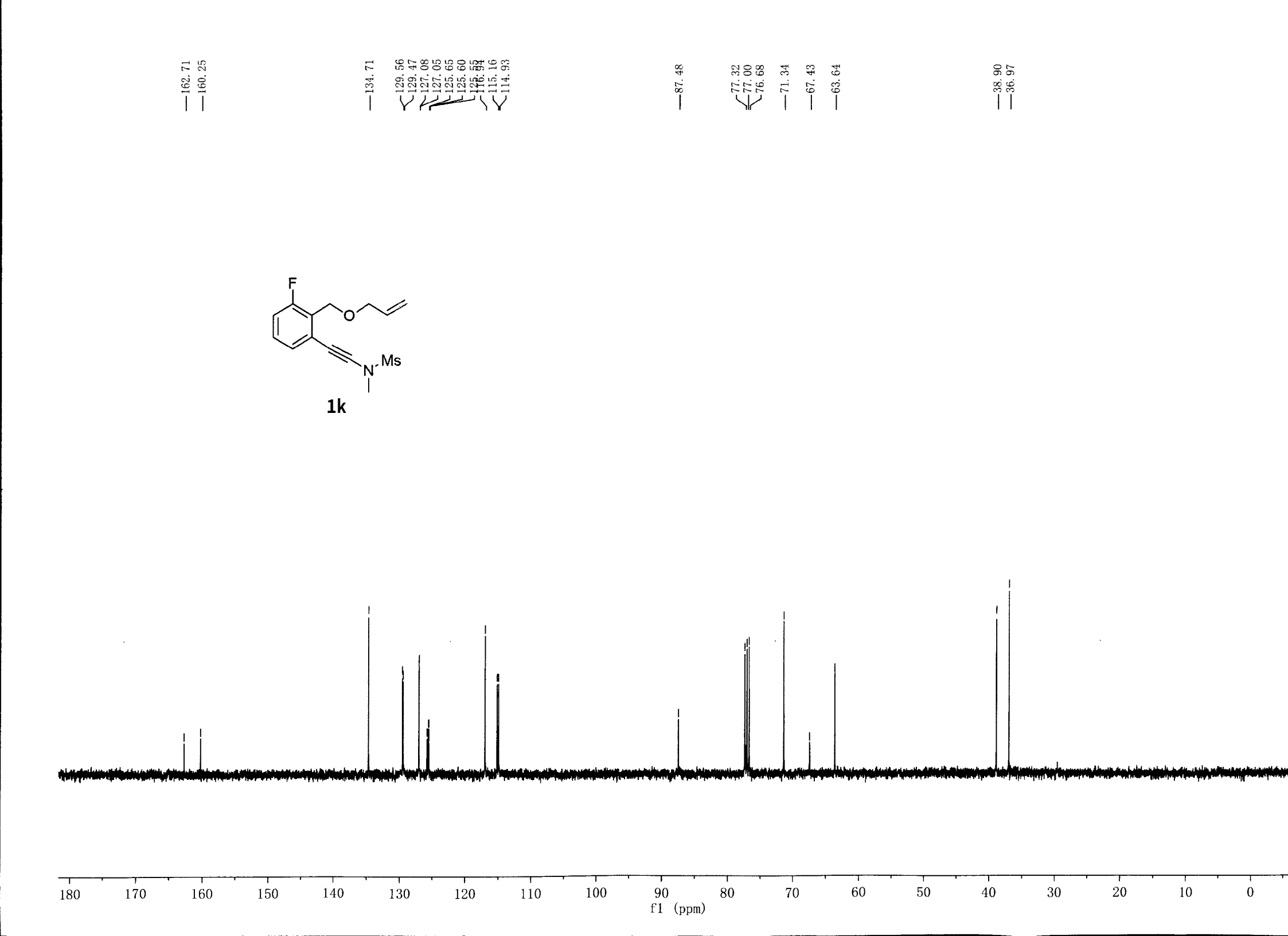
7.250
7.236
7.235
7.231
7.217
7.211
7.196
7.192
7.176
7.038
7.018
6.997
6.977
6.973
5.986
5.958
5.944
5.915
5.889
5.324
5.320
5.281
5.277
5.186
5.182
5.160
5.156
4.664
4.660
4.066
4.052
3.305
3.141
F
O
N
Ms
1k
2.05
1.06
0.87
0.99
0.89
1.96
1.95
3.00
3.15
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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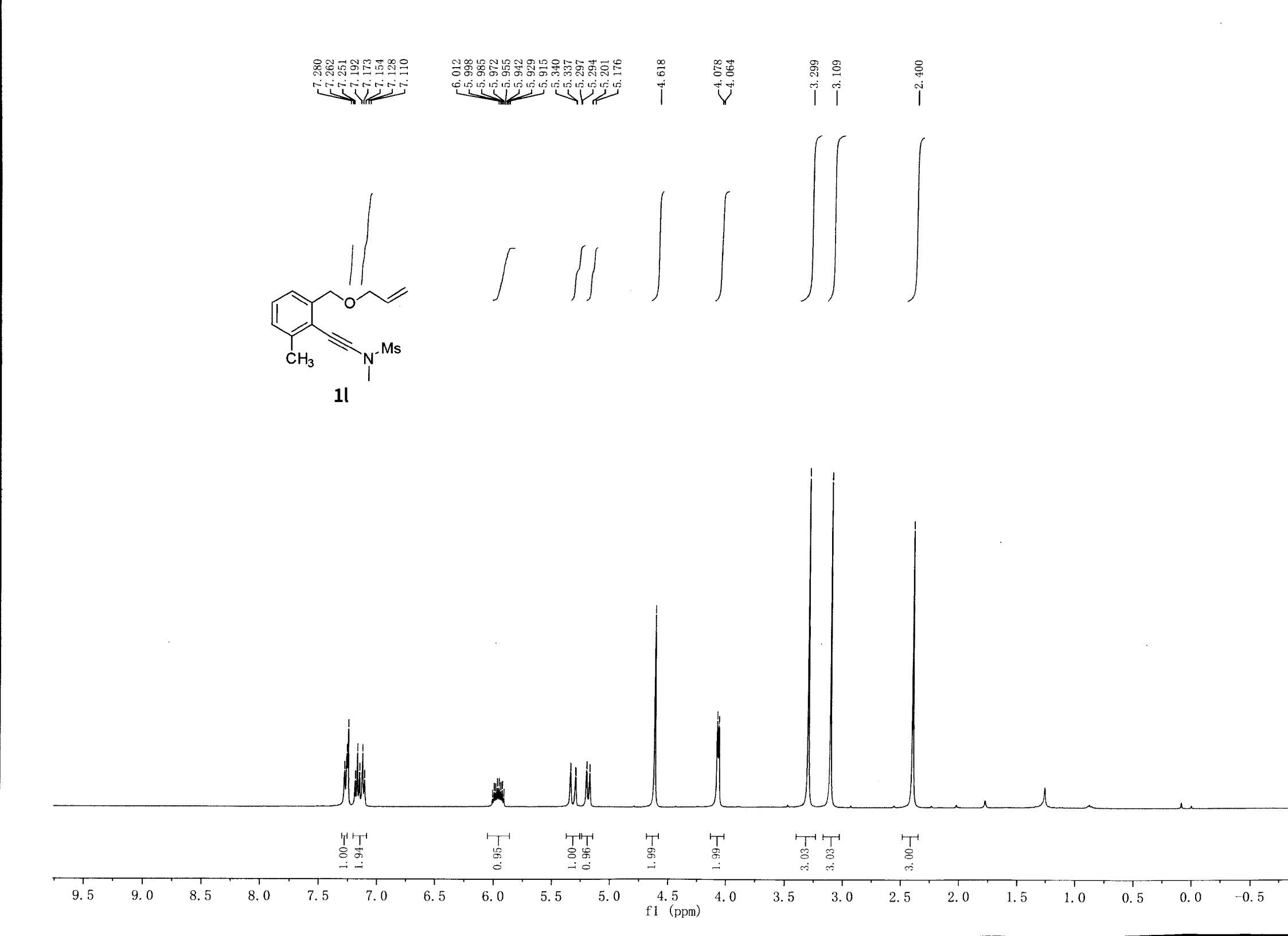
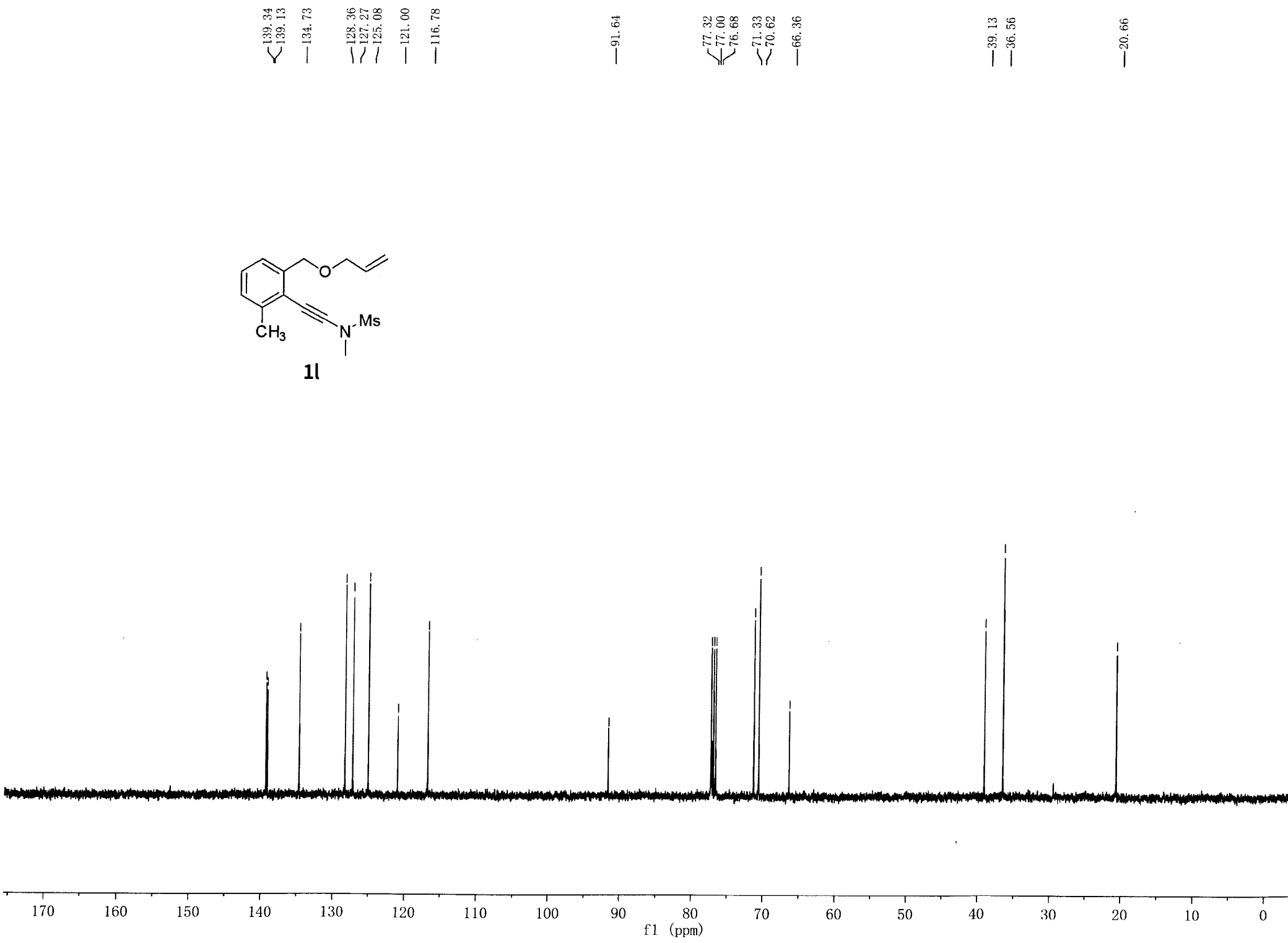
160.25
134.71
129.56
129.47
127.08
127.05
125.65
125.60
115.16
114.93
87.48
77.32
77.00
76.68
71.34
67.43
63.64
38.90
36.97
F
O
N
Ms
1k
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.280
7.262
7.251
7.192
7.173
7.154
7.128
7.110
6.012
5.998
5.985
5.972
5.955
5.942
5.929
5.915
5.340
5.337
5.297
5.294
5.201
5.176
4.618
4.078
4.064
3.299
3.109
2.400
O
CH3
N
Ms
1.00
1.94
0.95
1.00
0.96
1.99
1.99
3.03
3.03
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

1l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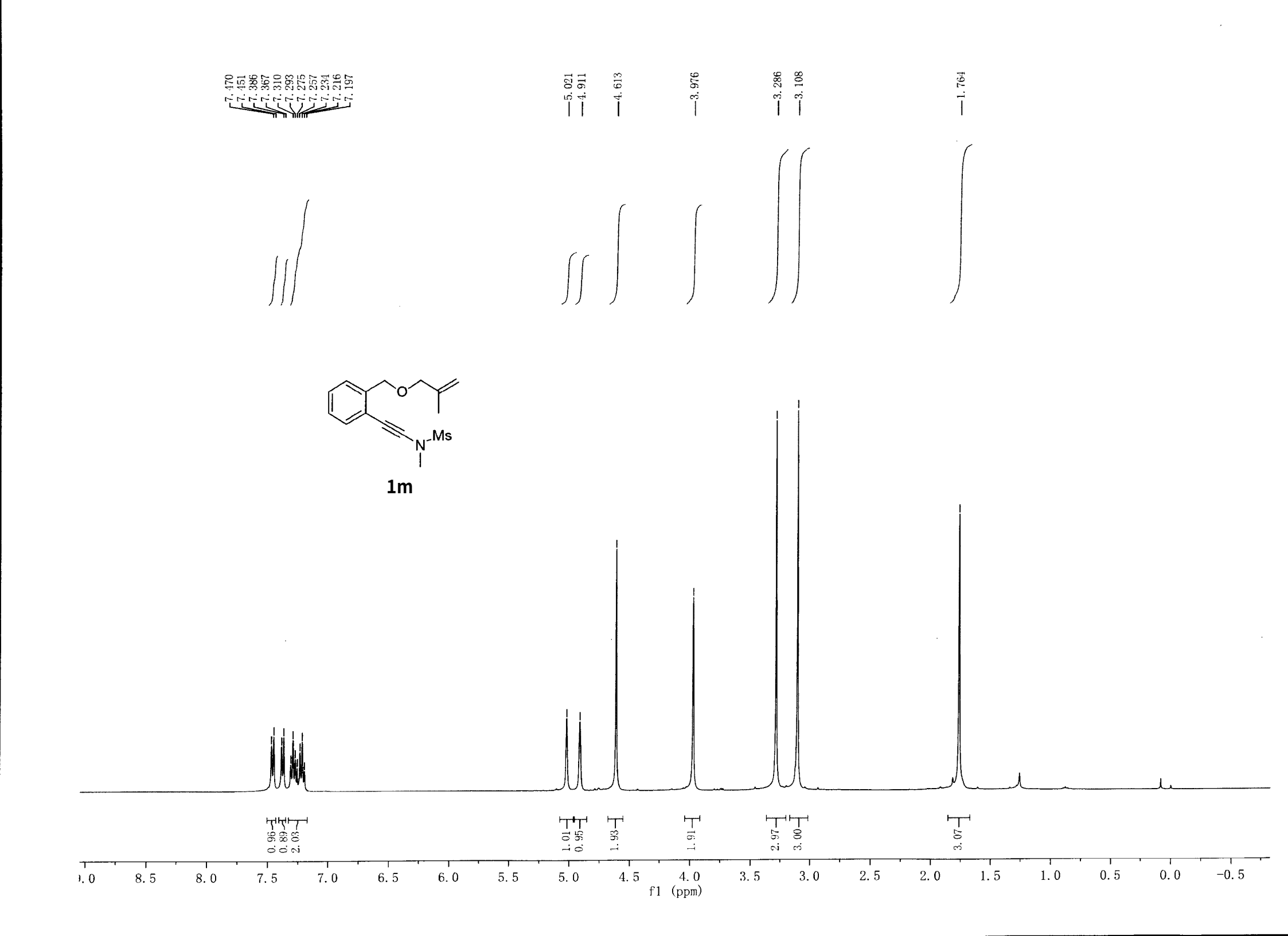
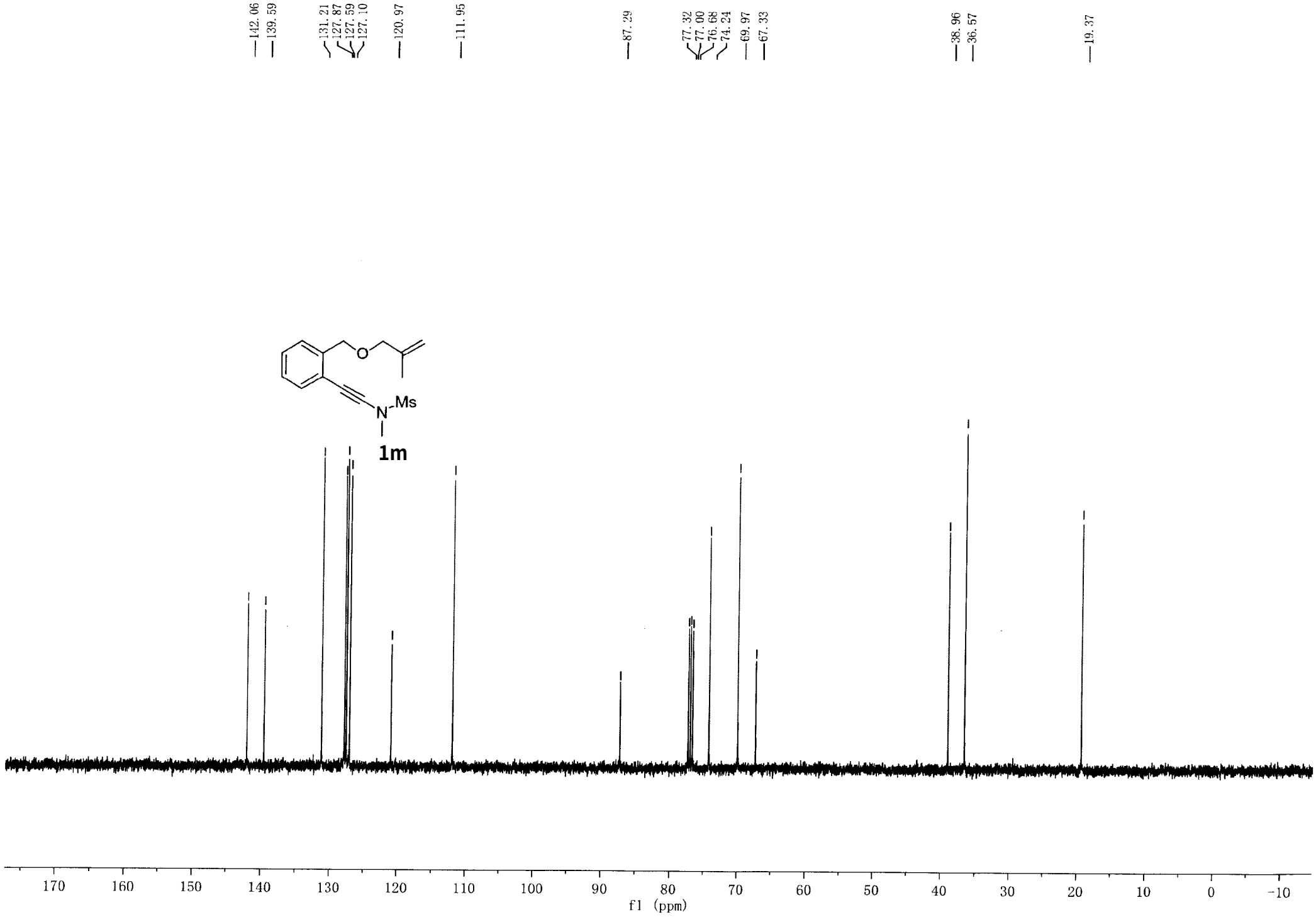
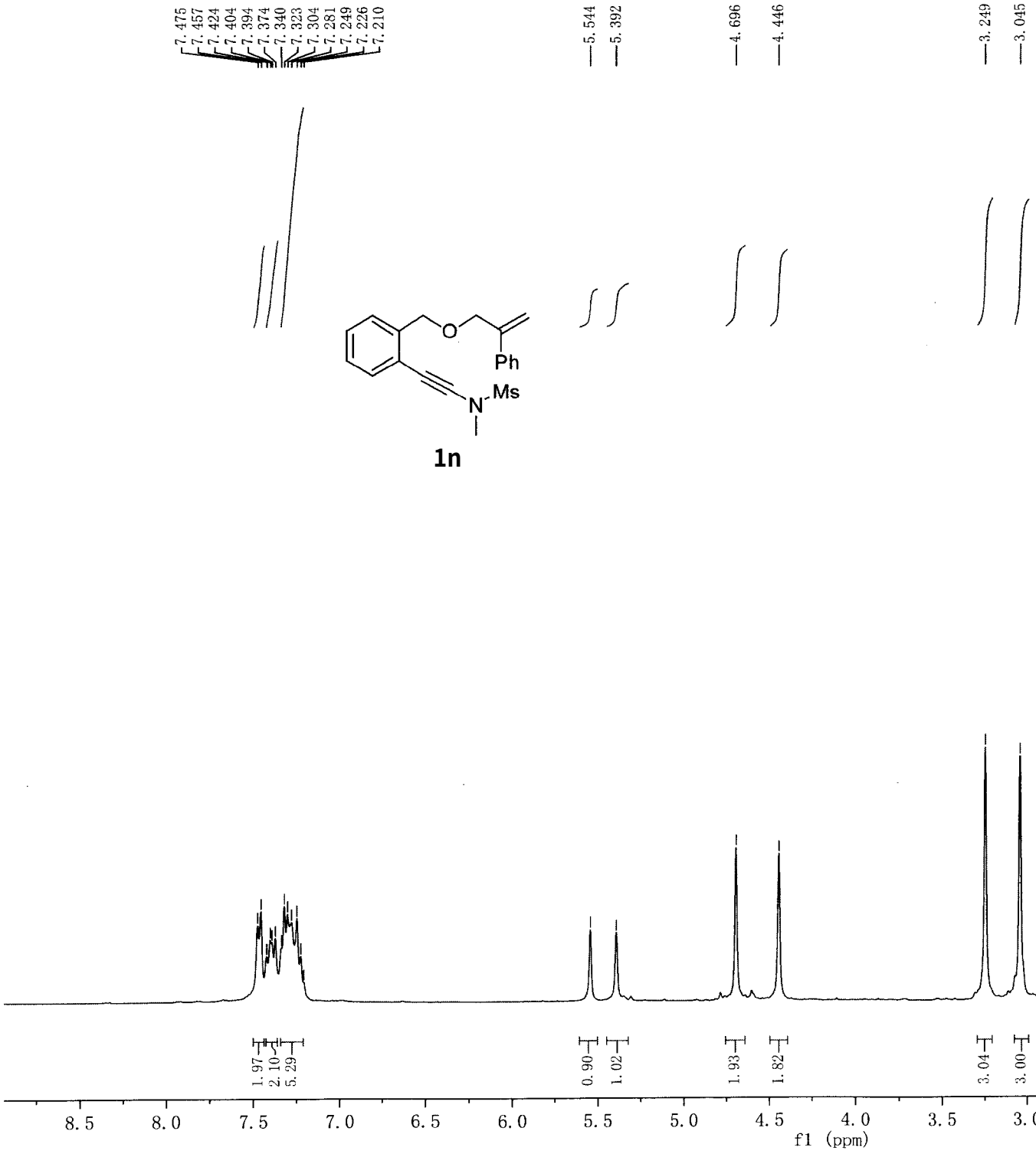
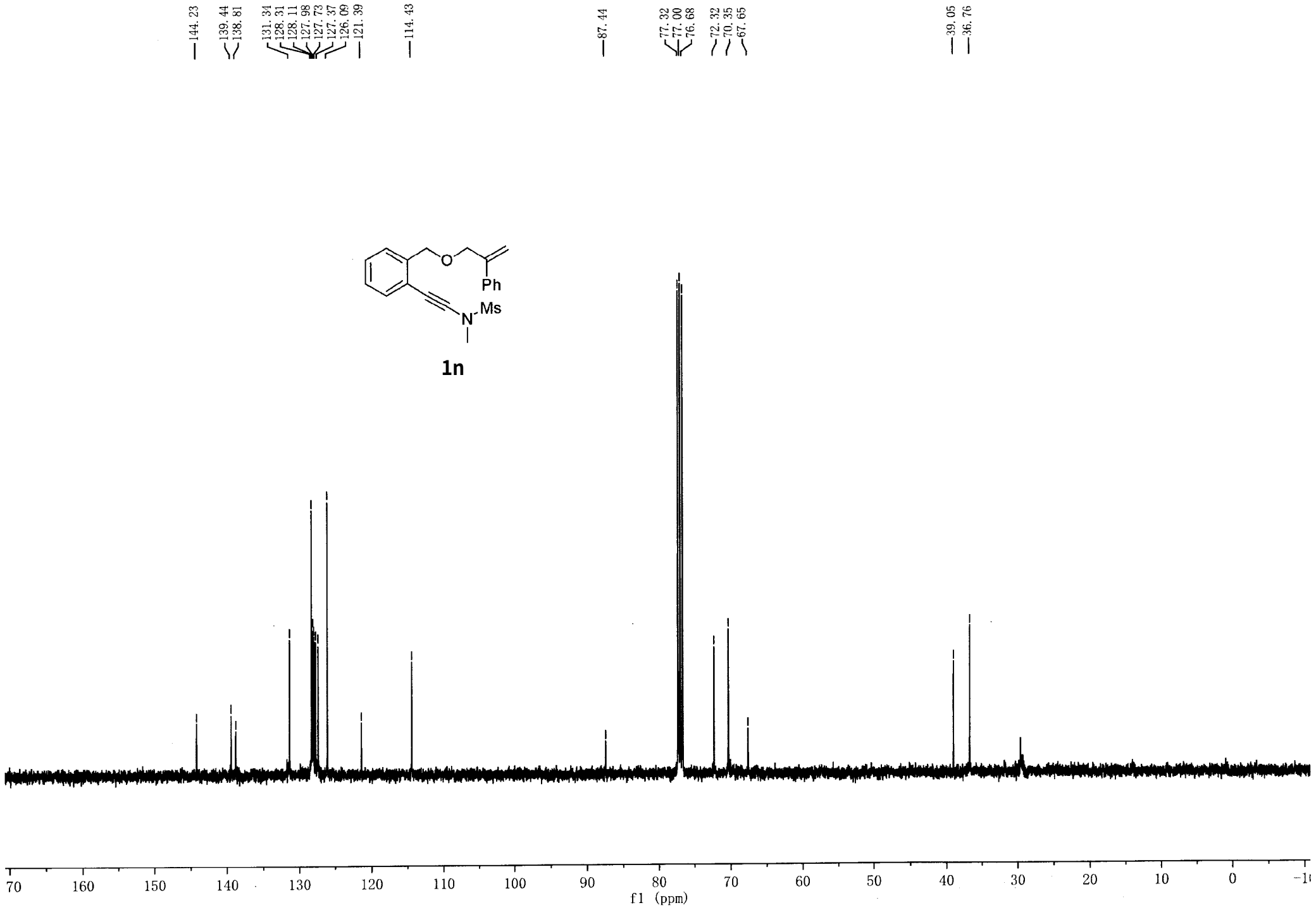
139.13
134.73
128.36
127.27
125.08
121.00
116.78
91.64
77.32
77.00
76.68
71.33
70.62
66.36
39.13
36.56
20.66
O
CH3
N
Ms
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

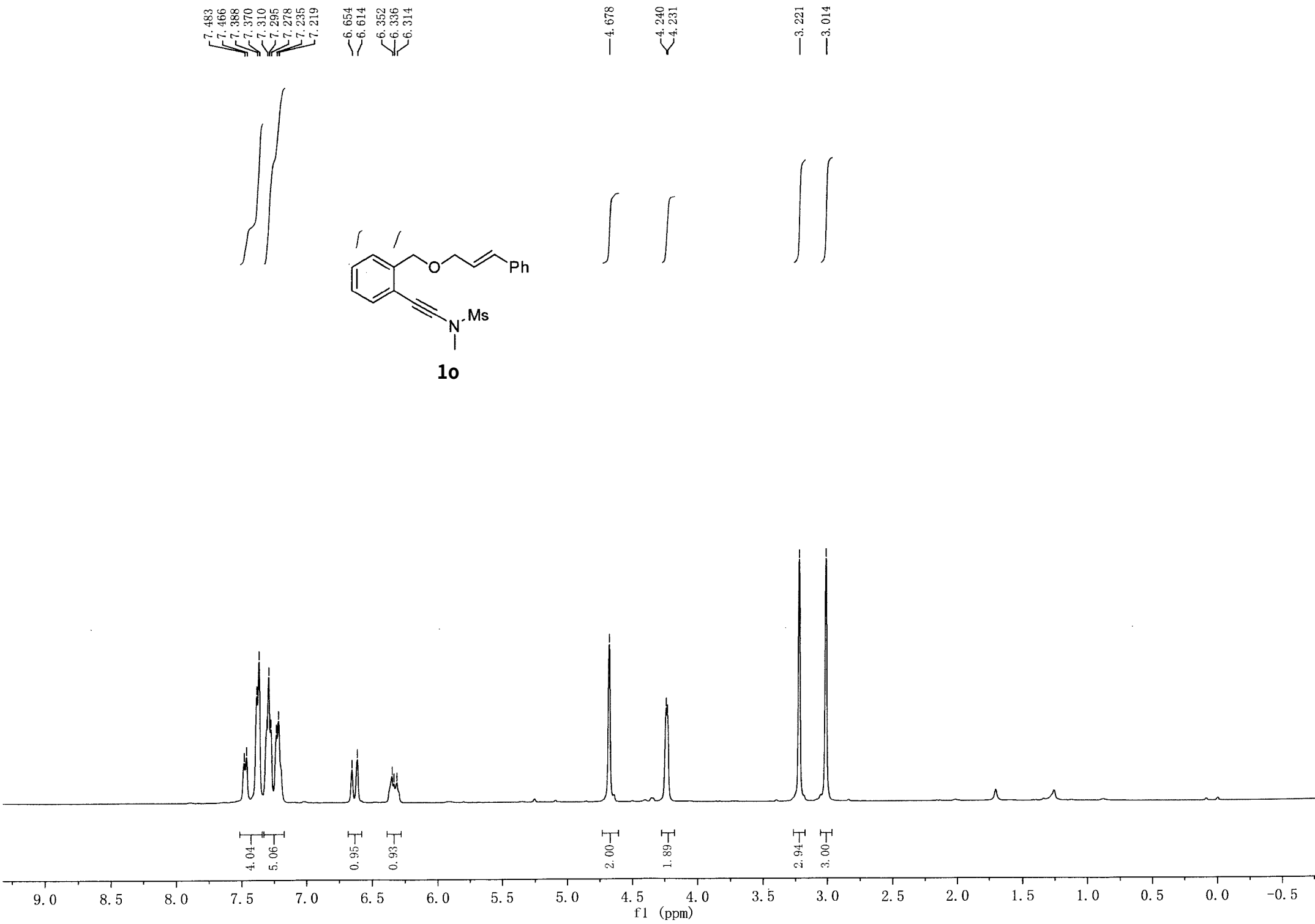
1l


7.470
7.451
7.386
7.367
7.310
7.293
7.275
7.257
7.234
7.216
7.197
5.021
4.911
4.613
3.976
3.286
3.108
1.764
O
N
Ms
1m
0.96
0.89
2.03
1.01
0.95
1.93
1.91
2.97
3.00
3.07
f1 (ppm)


142.06
139.59
131.21
127.87
127.59
127.10
120.97
111.95
87.29
77.32
77.00
76.68
74.24
69.97
67.33
38.96
36.57
19.37
O
N
Ms
1m
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.475
7.457
7.424
7.404
7.394
7.374
7.340
7.323
7.304
7.281
7.249
7.226
7.210
5.544
5.392
4.696
4.446
3.249
3.045
O
Ph
N
Ms
1n
1.97
2.10
5.29
0.90
1.02
1.93
1.82
3.04
3.00
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)


144.23
139.44
138.81
131.34
128.31
128.11
127.98
127.73
127.37
126.09
121.39
114.43
87.44
77.32
77.00
76.68
72.32
70.35
67.65
39.05
36.76
O
Ph
N
Ms
1n
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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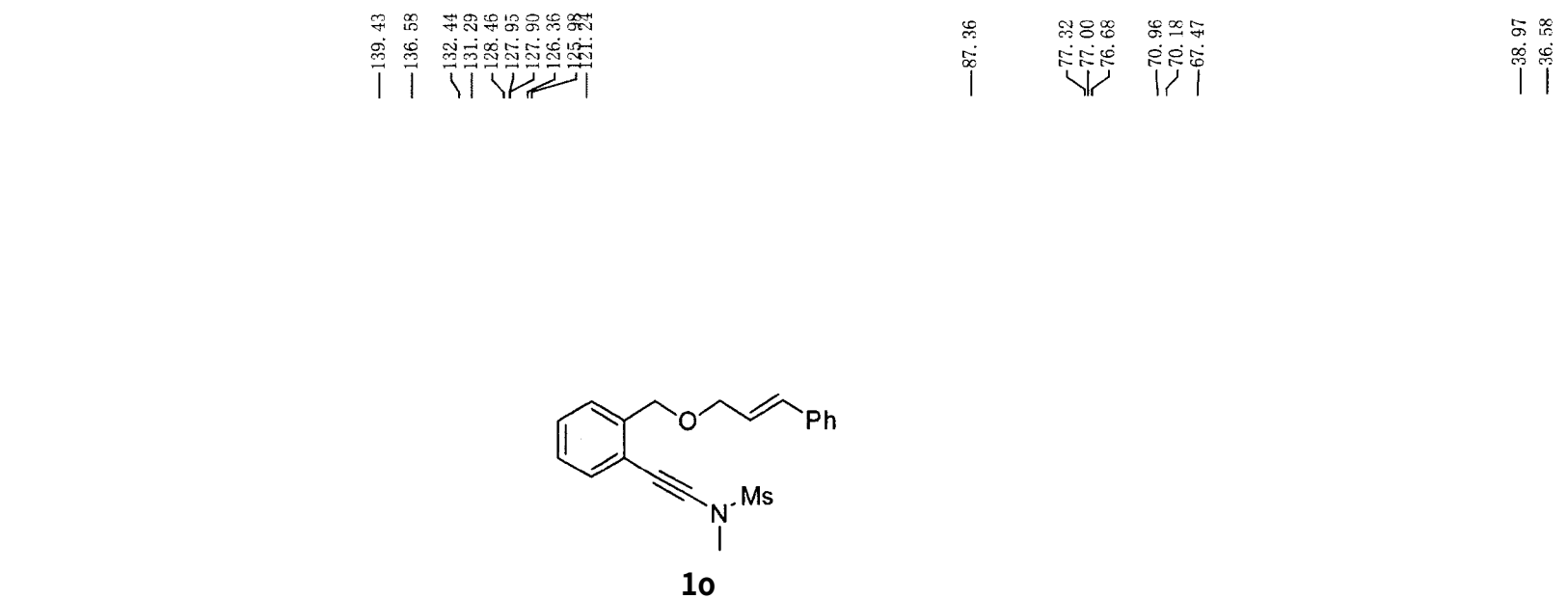
7.388
7.370
7.310
7.295
7.278
7.235
7.219
6.654
6.614
6.352
6.336
6.314
4.678
4.240
4.231
3.221
3.014
O
Ph
N
Ms
4.04
5.06
0.95
0.93
2.00
1.89
2.94
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

1o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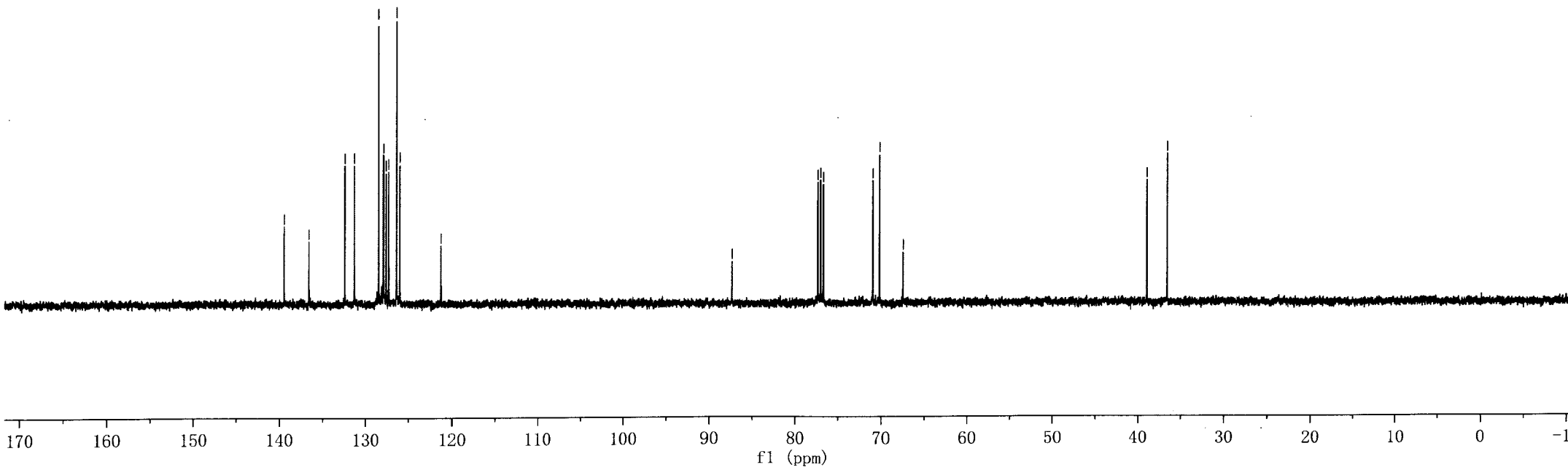
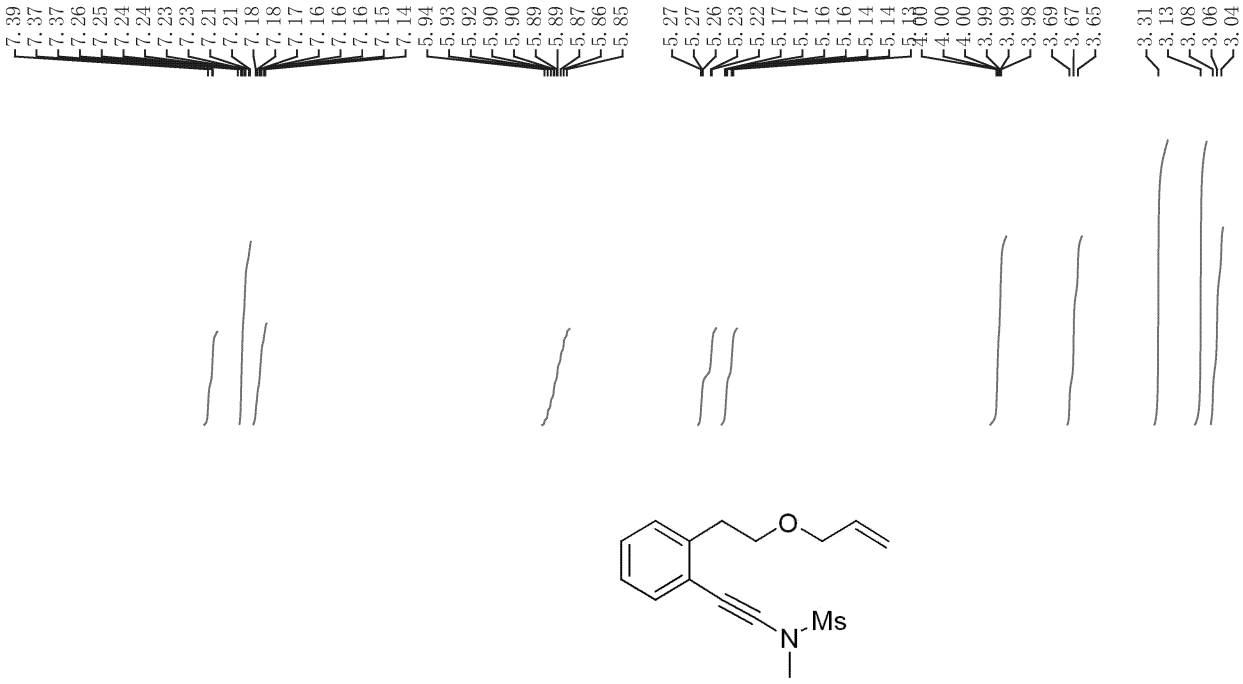
136.58
132.44
131.29
128.46
127.95
127.90
126.36
87.36
77.32
77.00
76.68
70.96
70.18
67.47
38.97
36.58
O
Ph
N
Ms

1o


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.37
7.37
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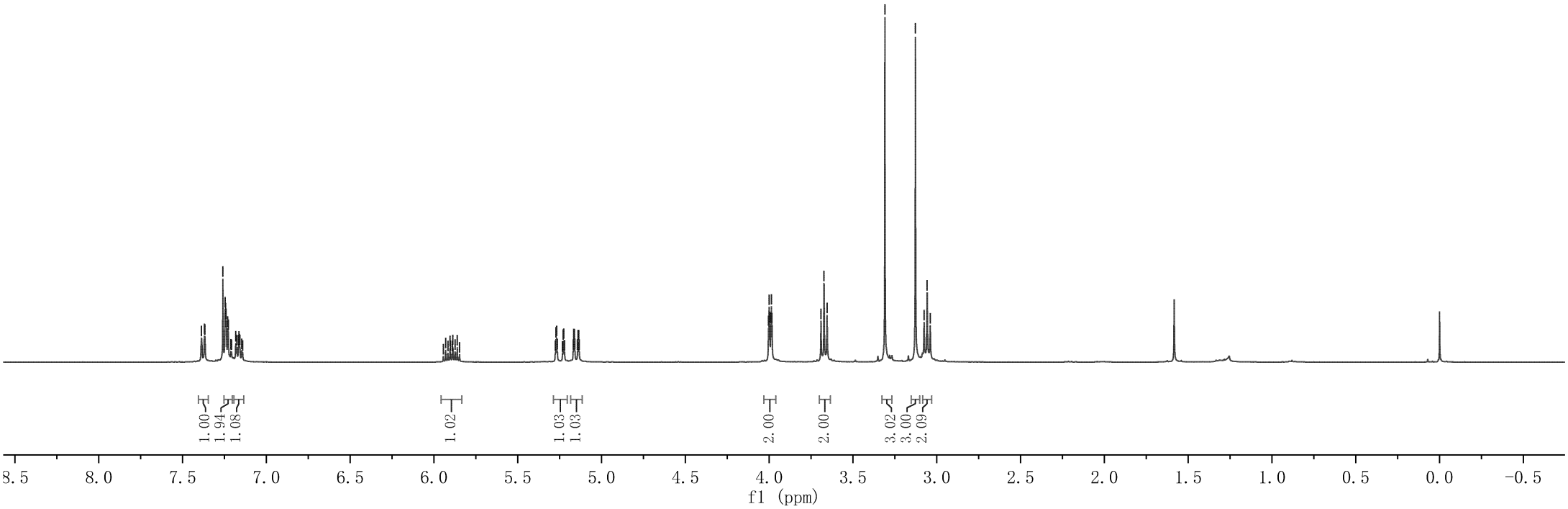
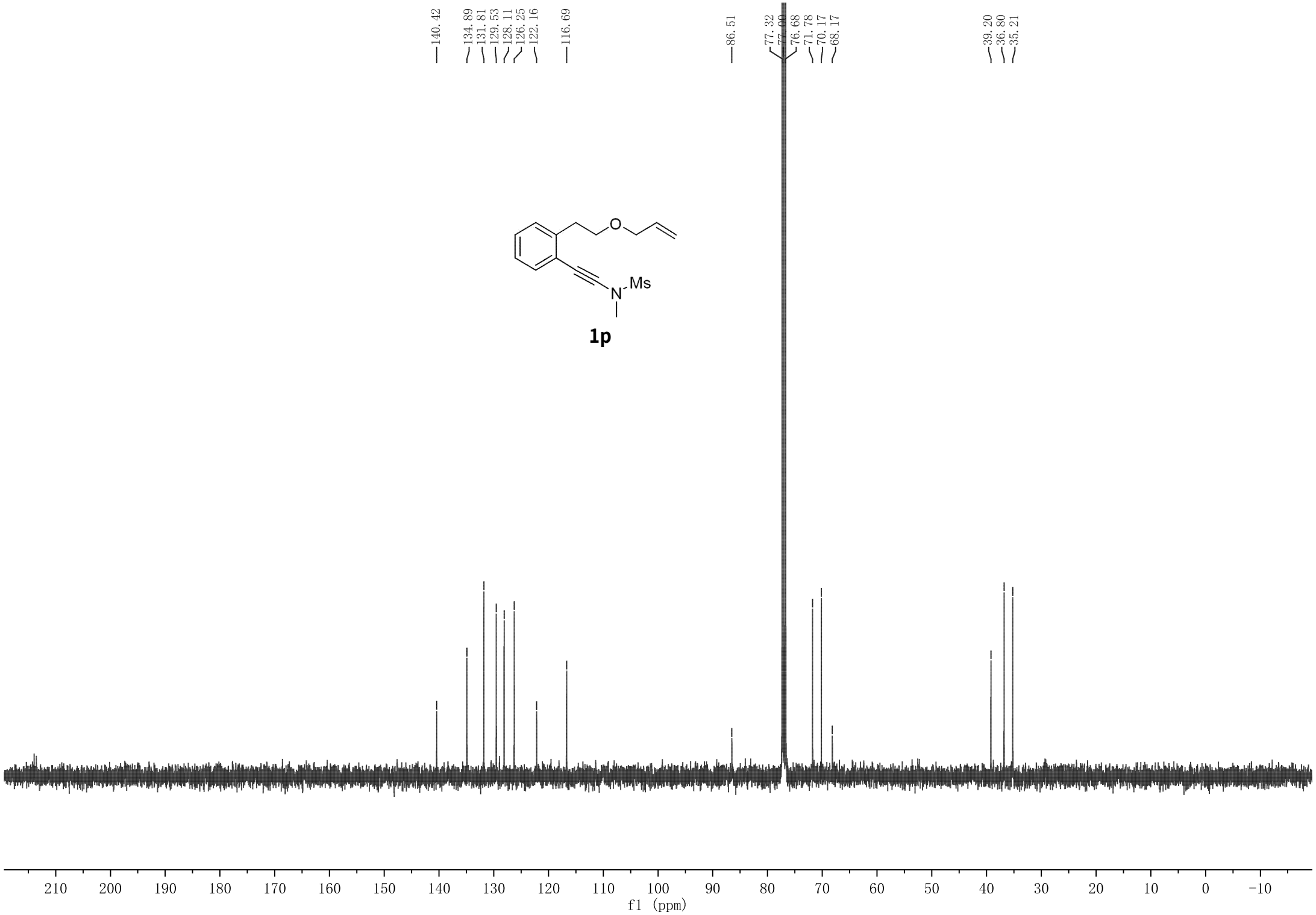
7.25
7.24
7.24
7.23
7.23
7.21
7.21
7.18
7.18
7.17
7.16
7.16
7.16
7.15
7.14
5.94
5.93
5.92
5.90
5.90
5.89
5.89
5.87
5.86
5.85
5.27
5.27
5.26
5.23
5.22
5.17
5.17
5.16
5.16
5.14
5.14
4.00
4.00
4.00
3.99
3.99
3.98
3.69
3.67
3.65
3.31
3.13
3.08
3.06
3.04
O
Ms
N

1p


1.00
1.94
1.08
1.02
1.03
1.03
2.00
2.00
3.02
3.00
2.09
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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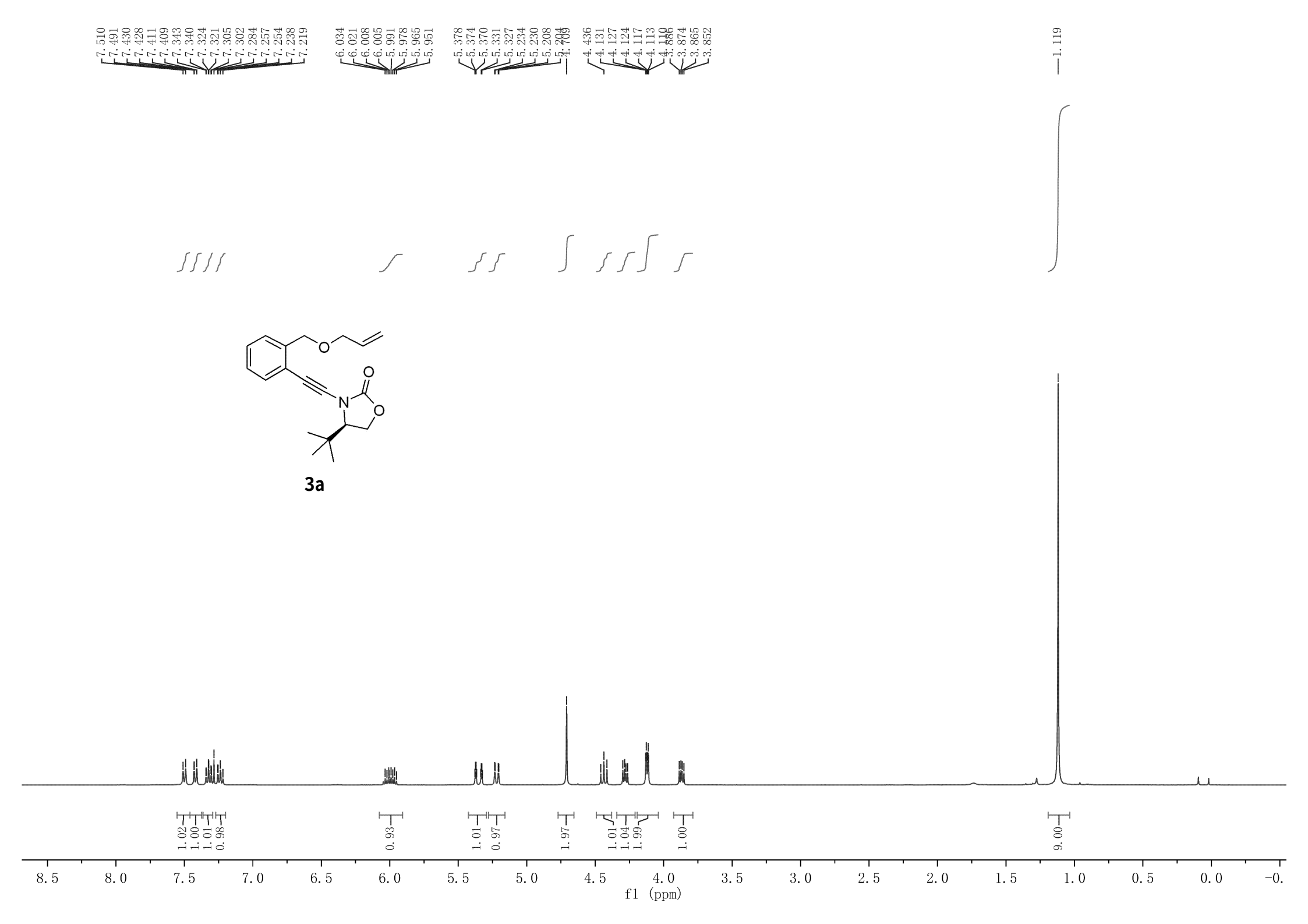
129.53
128.11
126.25
122.16
116.69
86.51
77.32
77.00
76.68
71.78
70.17
68.17
39.20
36.80
35.21
O
N
Ms
1p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.411
7.409
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7.340
7.324
7.321
7.305
7.302
7.284
7.257
7.254
7.238
7.219
6.034
6.021
6.008
6.005
5.991
5.978
5.965
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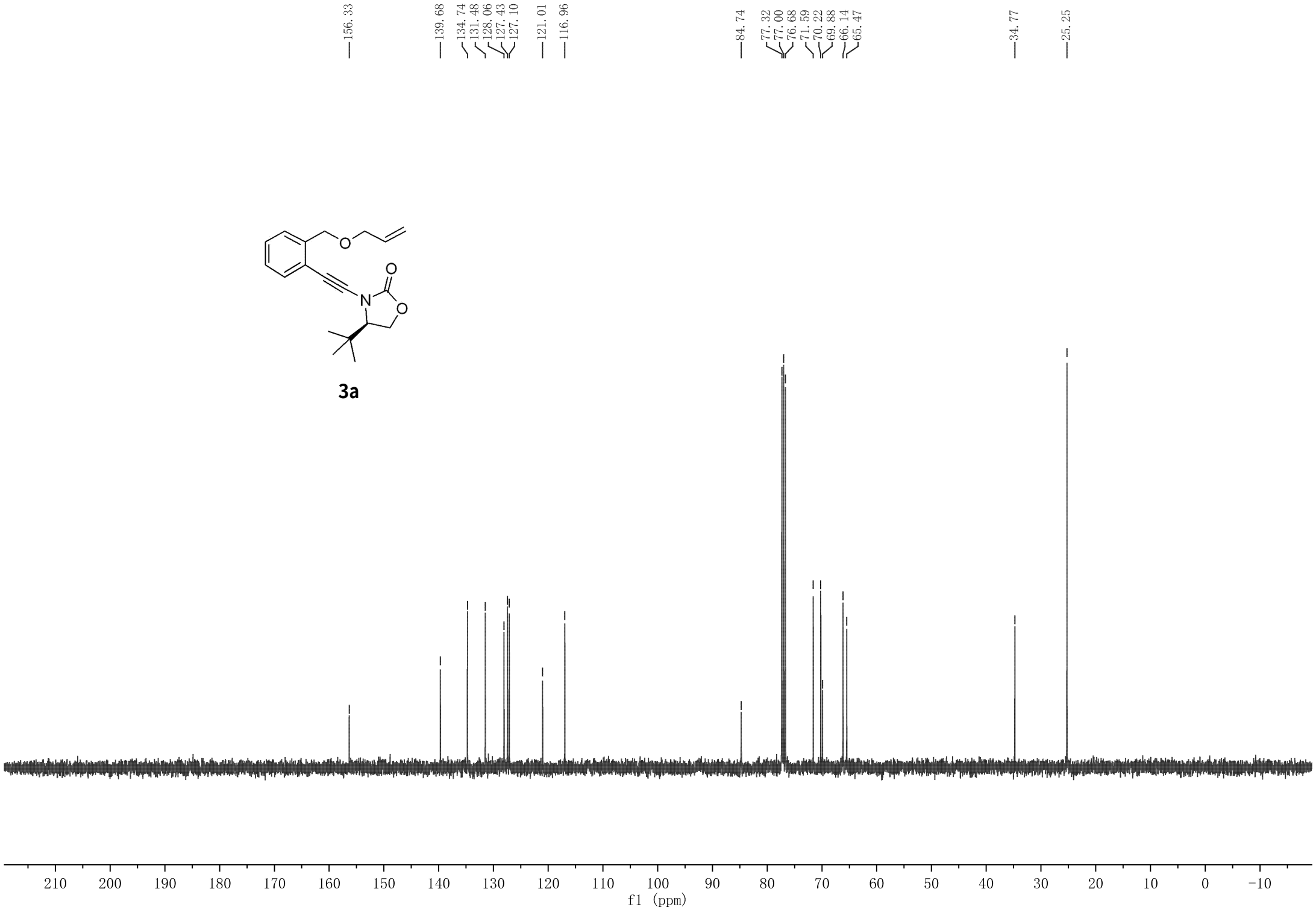
5.374
5.370
5.331
5.327
5.234
5.230
5.208
4.436
4.131
4.127
4.124
4.117
4.113
3.886
3.874
3.865
3.852
1.119
O
O
N
O
3a
1.02
1.00
1.01
0.98
0.93
1.01
0.97
1.97
1.01
1.04
1.99
1.00
9.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)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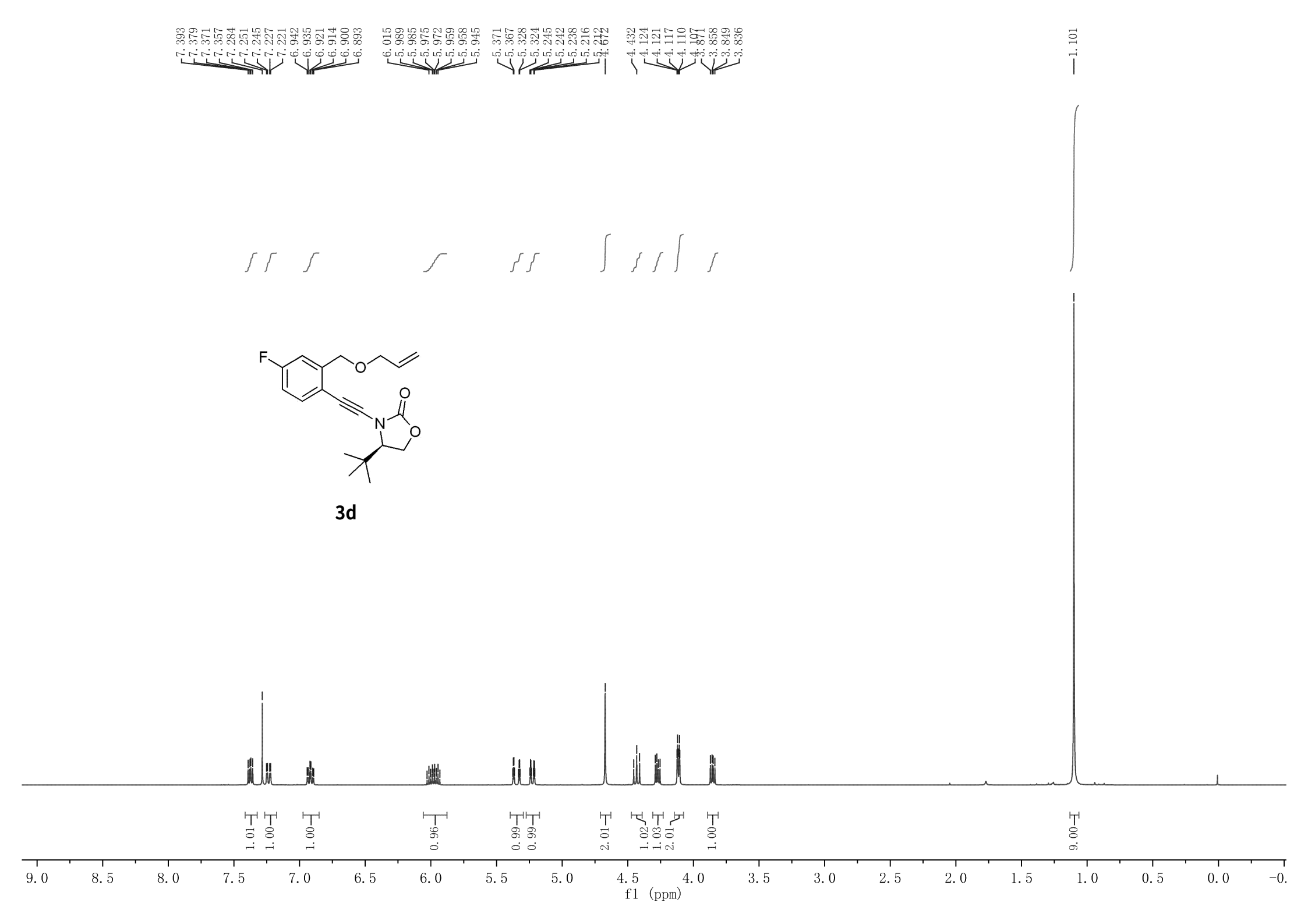
134.74
131.48
128.06
127.43
127.10
121.01
116.96
84.74
77.32
77.00
76.68
71.59
70.22
69.88
66.14
65.47
34.77
25.25
O
O
N
O
3a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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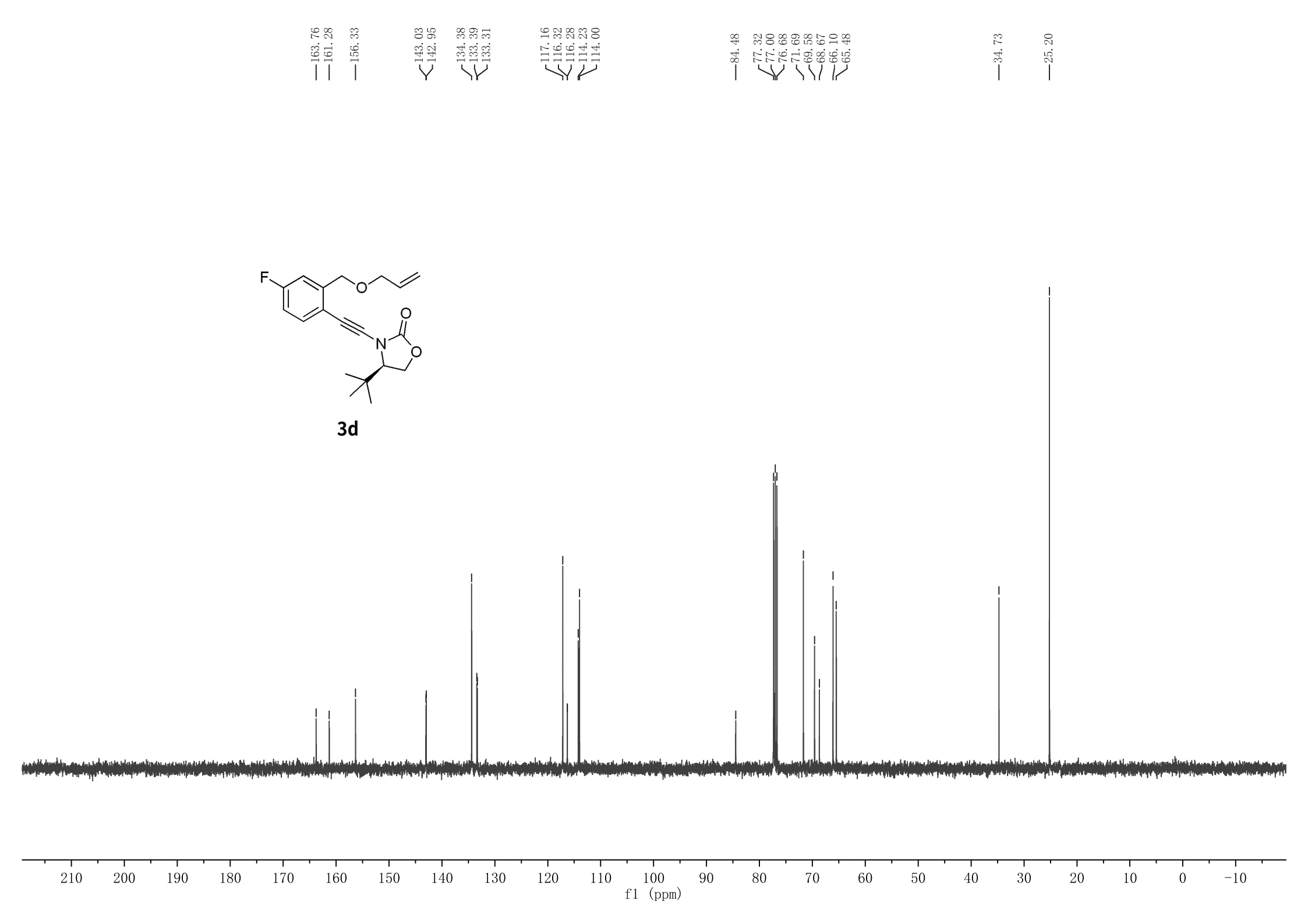
7.251
7.245
7.227
7.221
6.942
6.935
6.921
6.914
6.900
6.893
6.015
5.989
5.985
5.975
5.972
5.959
5.958
5.945
5.371
5.367
5.328
5.324
5.245
5.242
5.238
5.216
4.672
4.432
4.124
4.121
4.117
4.110
4.107
4.101
3.871
3.858
3.849
3.836
1.101
F
O
O
N
O
1.01
1.00
1.00
0.96
0.99
0.99
2.01
1.02
1.03
2.01
1.00
9.00
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
f1 (ppm)

3d


163.76
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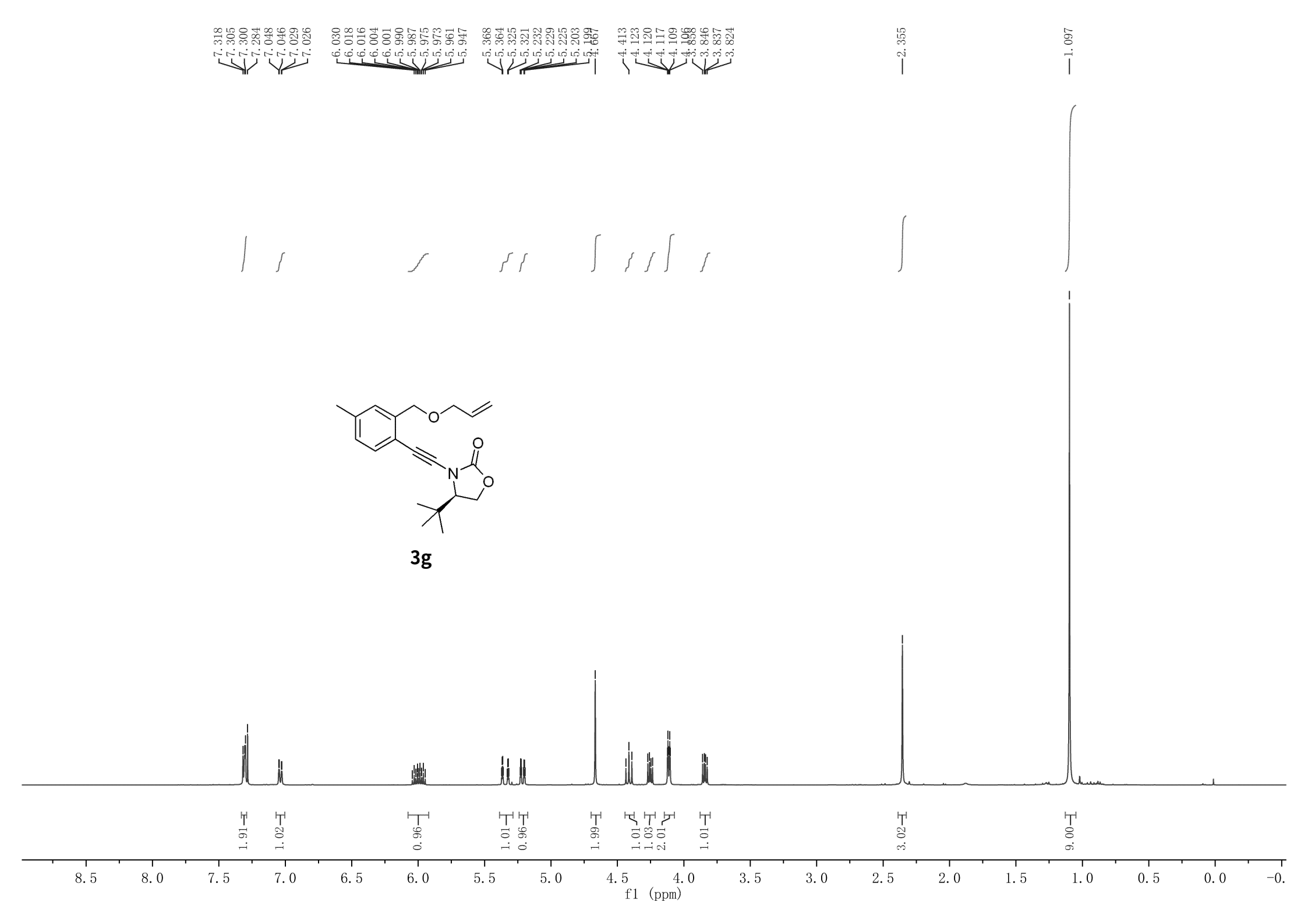
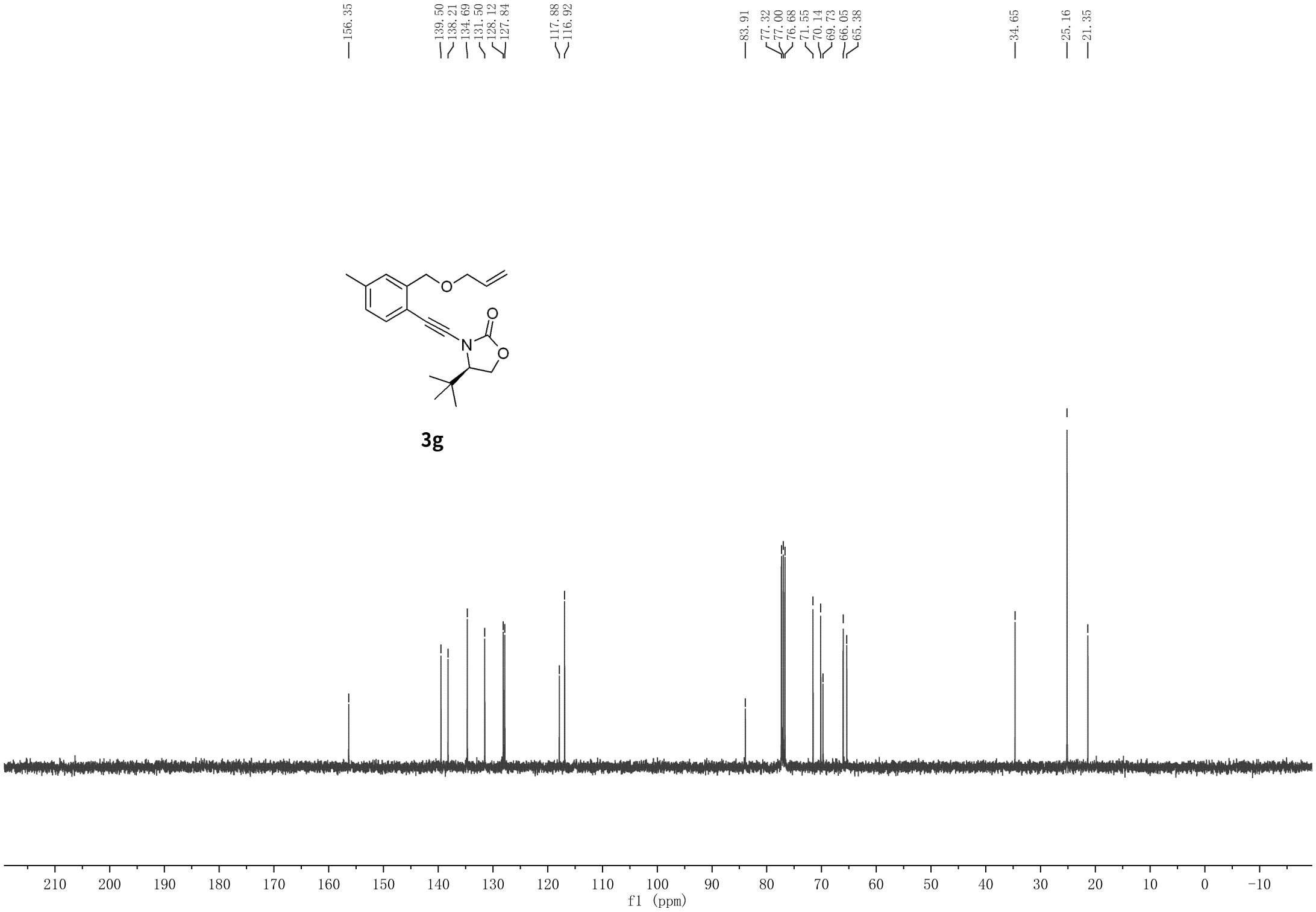
143.03
142.95
134.38
133.39
133.31
117.16
116.32
116.28
114.23
114.00
84.48
77.32
77.00
76.68
71.69
69.58
68.67
66.10
65.48
34.73
25.20
F
O
O
N
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3d


7.318
7.305
7.300
7.284
7.048
7.046
7.029
7.026
6.030
6.018
6.016
6.004
6.001
5.990
5.987
5.975
5.973
5.961
5.947
5.368
5.364
5.325
5.321
5.232
5.229
5.225
5.203
4.413
4.123
4.120
4.117
4.109
3.838
3.837
3.824
2.355
1.097
O
O
N
O
1.91
1.02
0.96
1.01
0.96
1.99
1.01
1.03
2.01
1.01
3.02
9.00
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
f1 (ppm)

3g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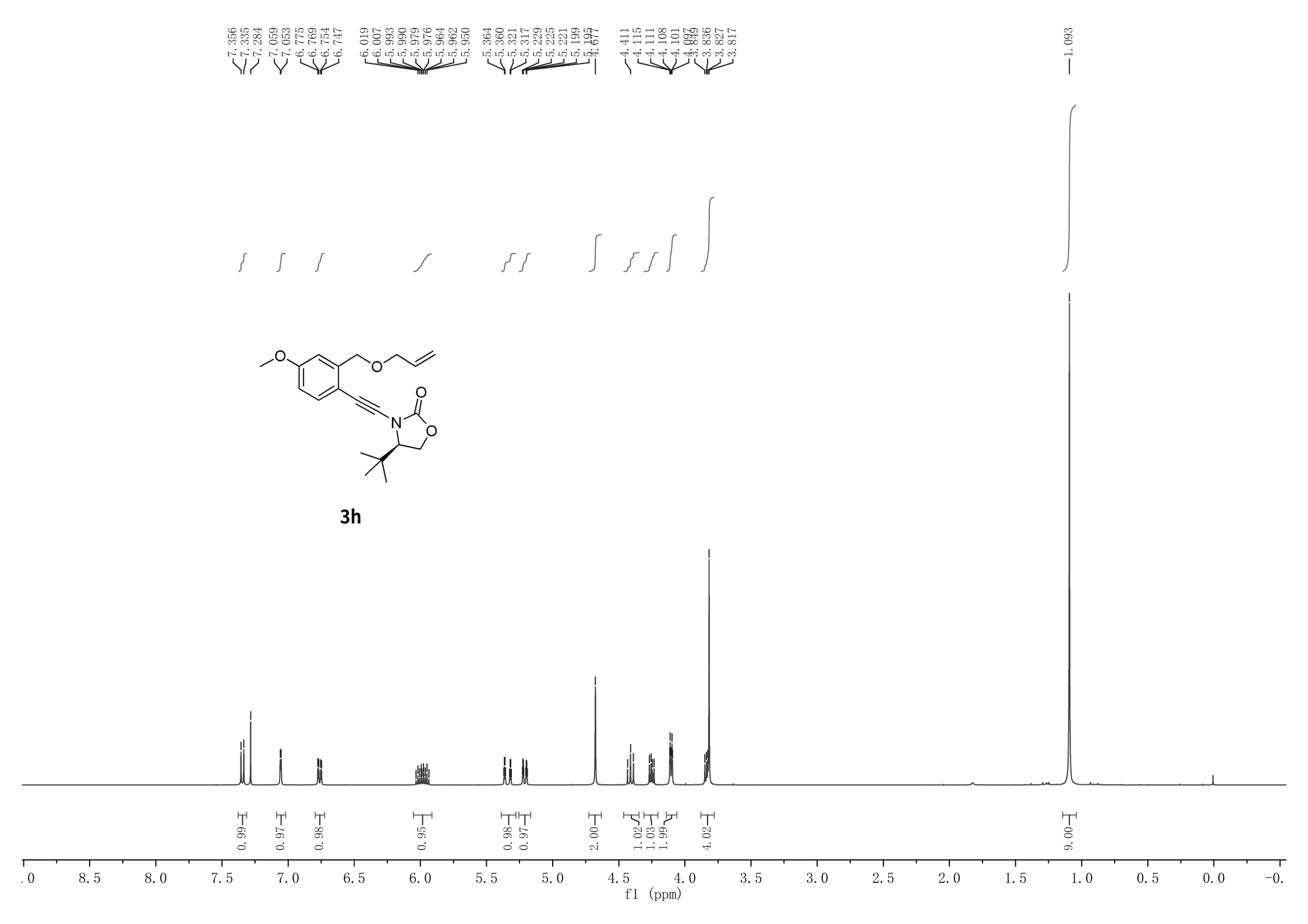
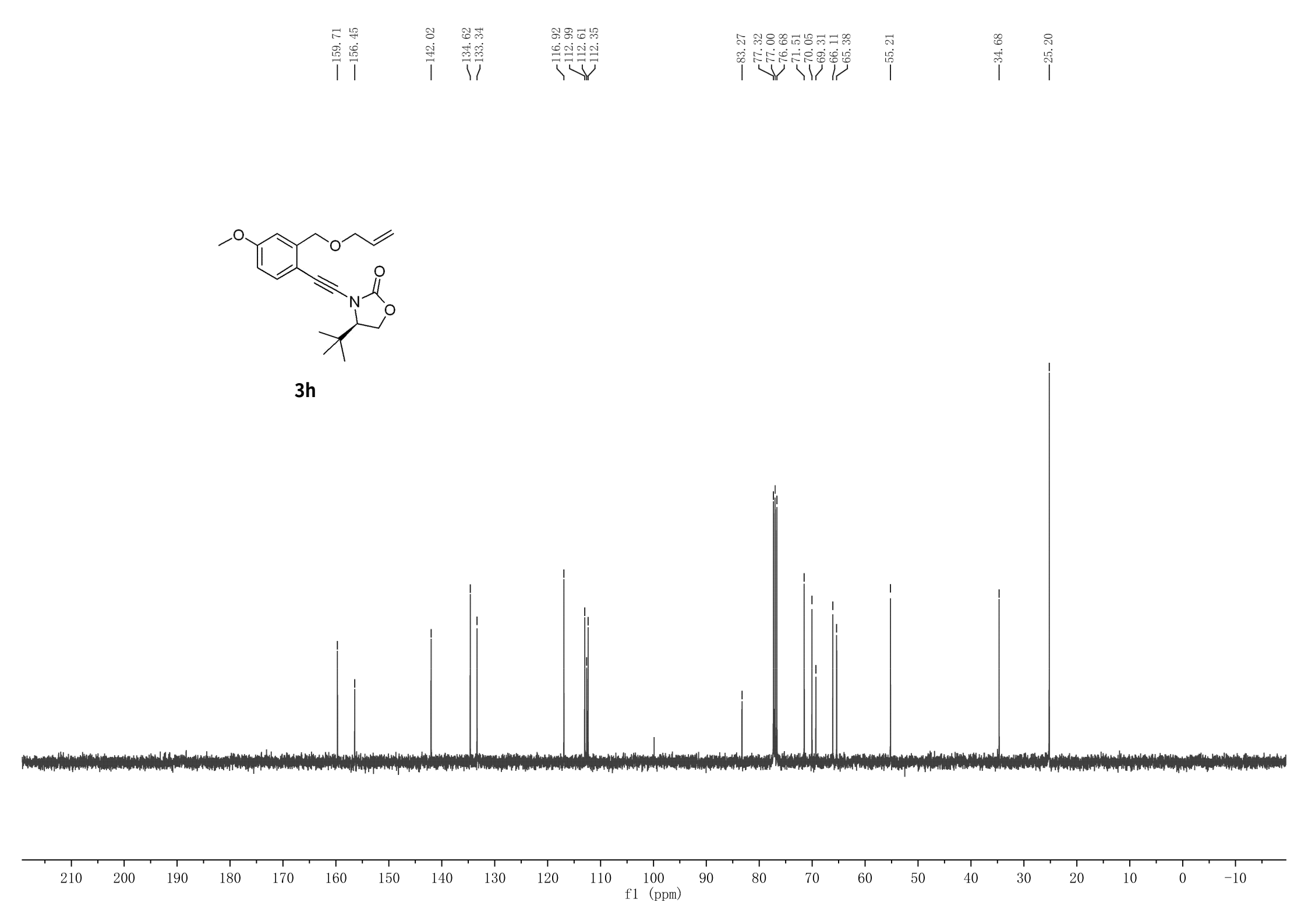
134.69
131.50
128.12
127.84
117.88
116.92
83.91
77.32
77.00
76.68
71.55
70.14
69.73
66.05
65.38
34.65
25.16
21.35
O
O
N
O
3g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.356
7.335
7.284
7.059
7.053
6.775
6.769
6.754
6.747
6.019
6.007
5.993
5.990
5.979
5.976
5.964
5.962
5.950
5.364
5.360
5.321
5.317
5.229
5.225
5.221
5.199
4.411
4.115
4.111
4.108
4.101
3.849
3.836
3.827
3.817
1.093
O
O
N
O
O
0.99
0.97
0.98
0.95
0.98
0.97
2.00
1.02
1.03
1.99
4.02
9.00
f1 (ppm)

3h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156.45
142.02
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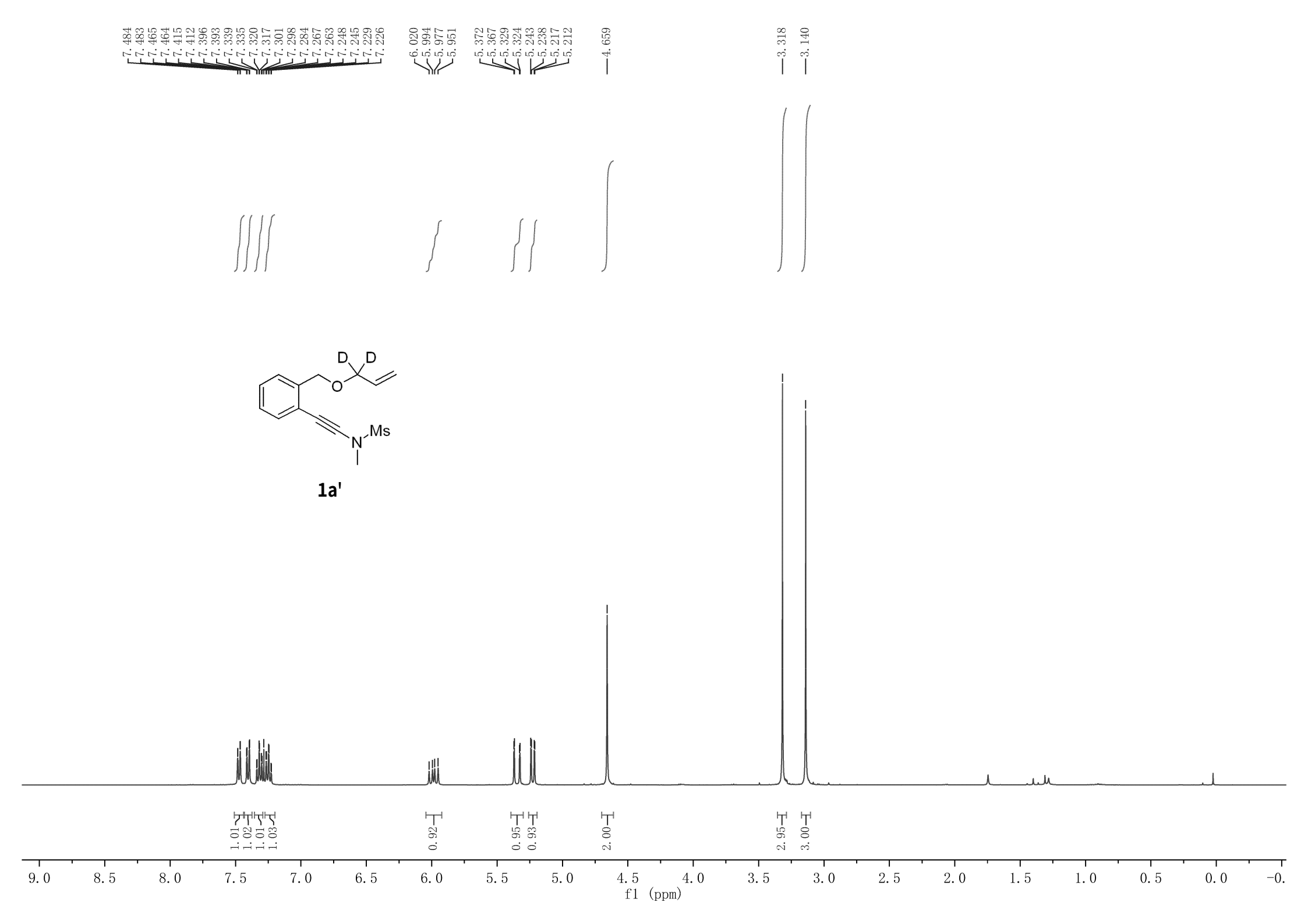
133.34
116.92
112.99
112.61
112.35
83.27
77.32
77.00
76.68
71.51
70.05
69.31
66.11
65.38
55.21
34.68
25.20
O
O
N
O
O
3h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.483
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7.464
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7.412
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7.393
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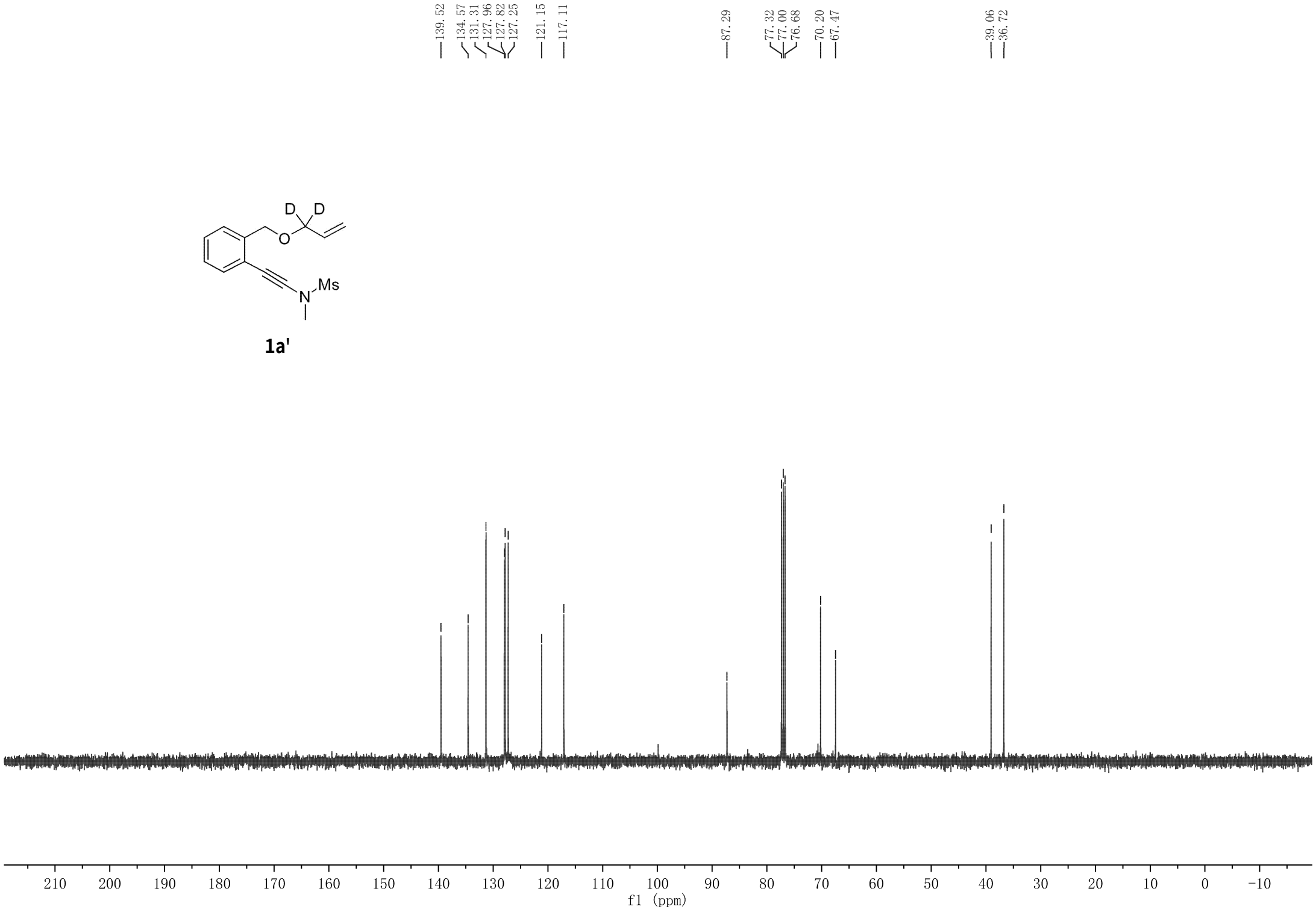
7.335
7.320
7.317
7.301
7.298
7.284
7.267
7.263
7.248
7.245
7.229
7.226
6.020
5.994
5.977
5.951
5.372
5.367
5.329
5.324
5.243
5.238
5.217
5.212
4.659
3.318
3.140
D
D
O
Ms
N
1a'
1.01
1.02
1.01
1.03
0.92
0.95
0.93
2.00
2.95
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

D
D
O
N
Ms

1a'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134.57
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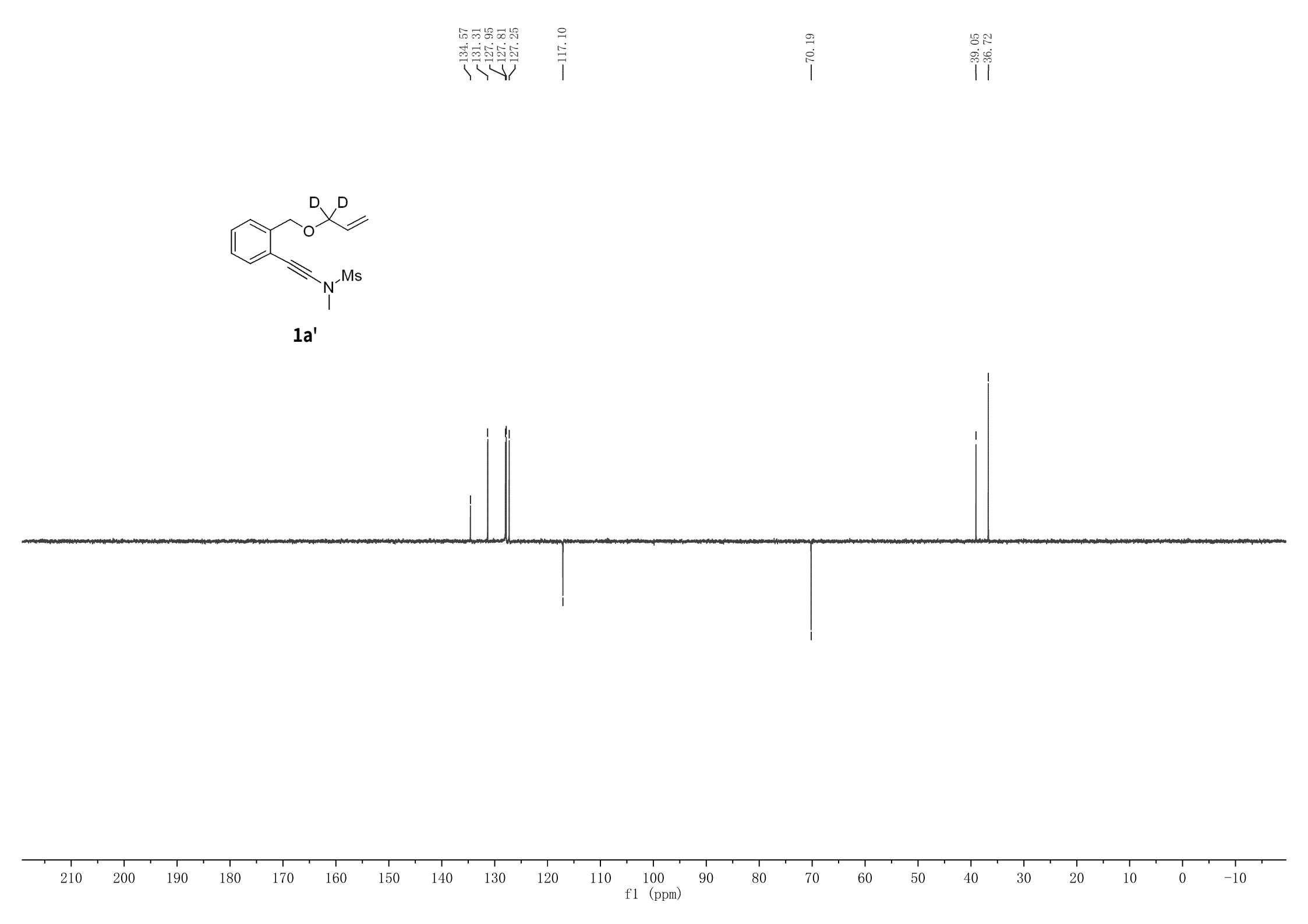
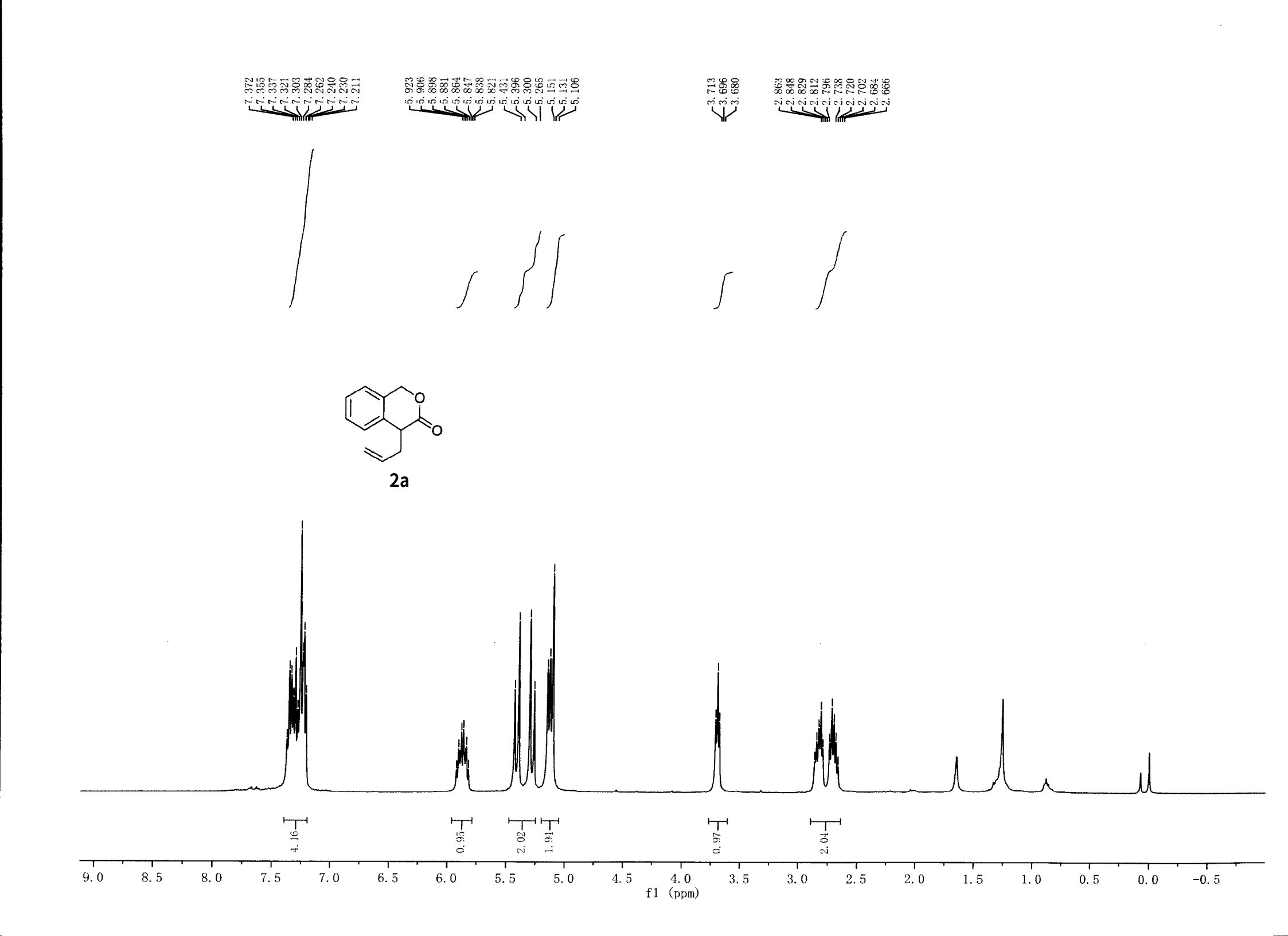
127.25
121.15
117.11
87.29
77.32
77.00
76.68
70.20
67.47
39.06
36.72
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


134.57
131.31
127.95
127.81
127.25
117.10
70.19
39.05
36.72
D
D
O
N
Ms
1a'
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)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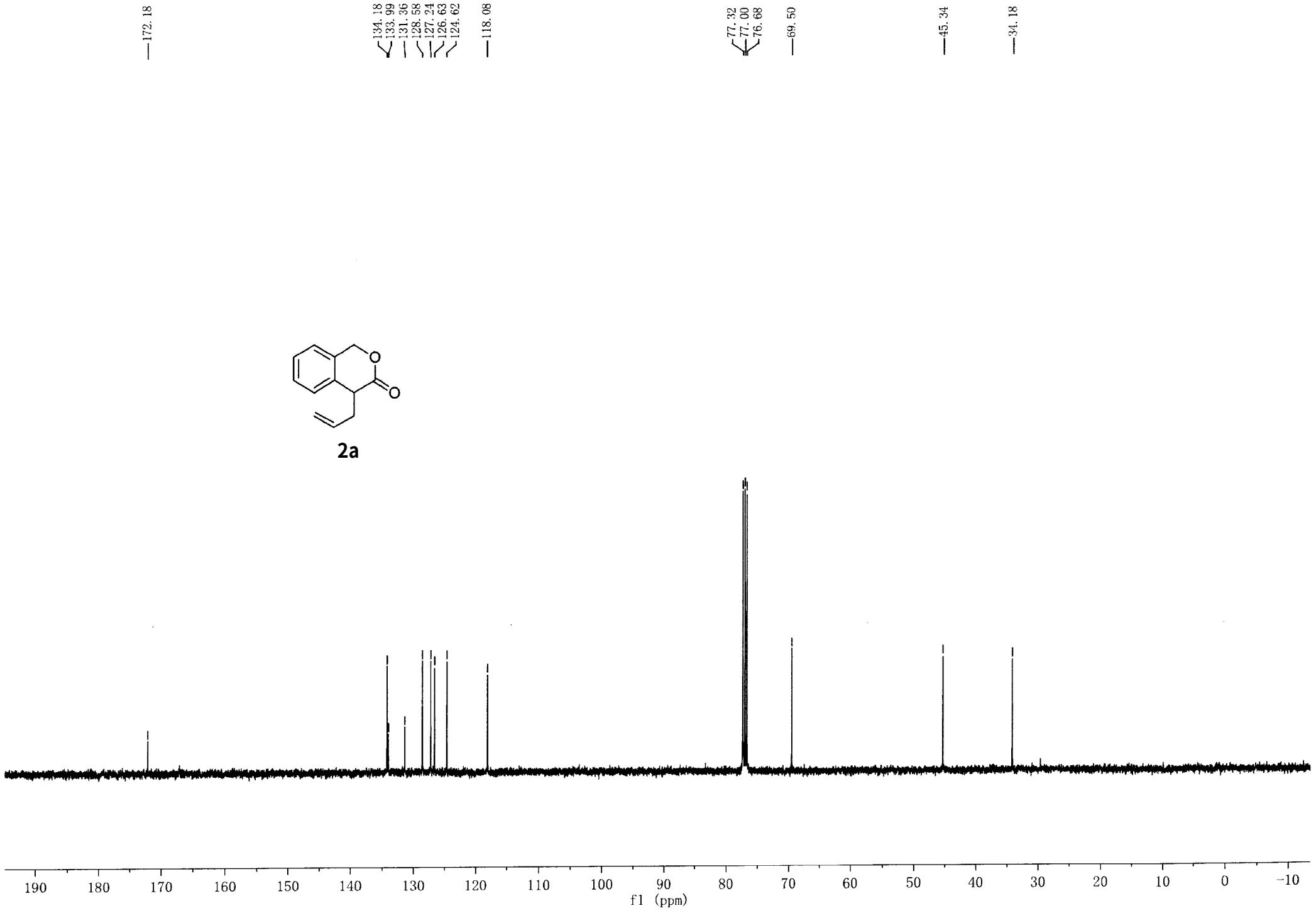
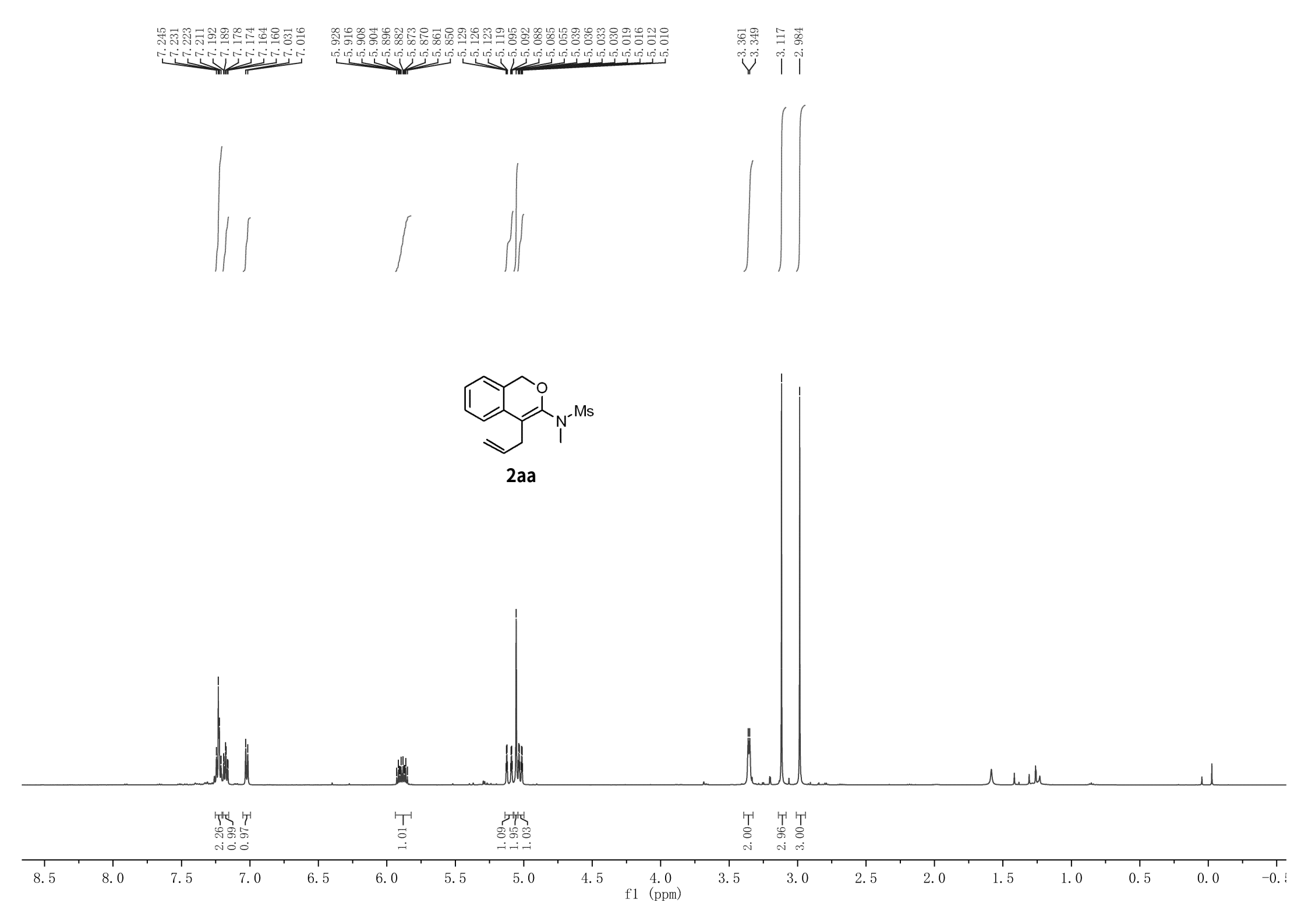
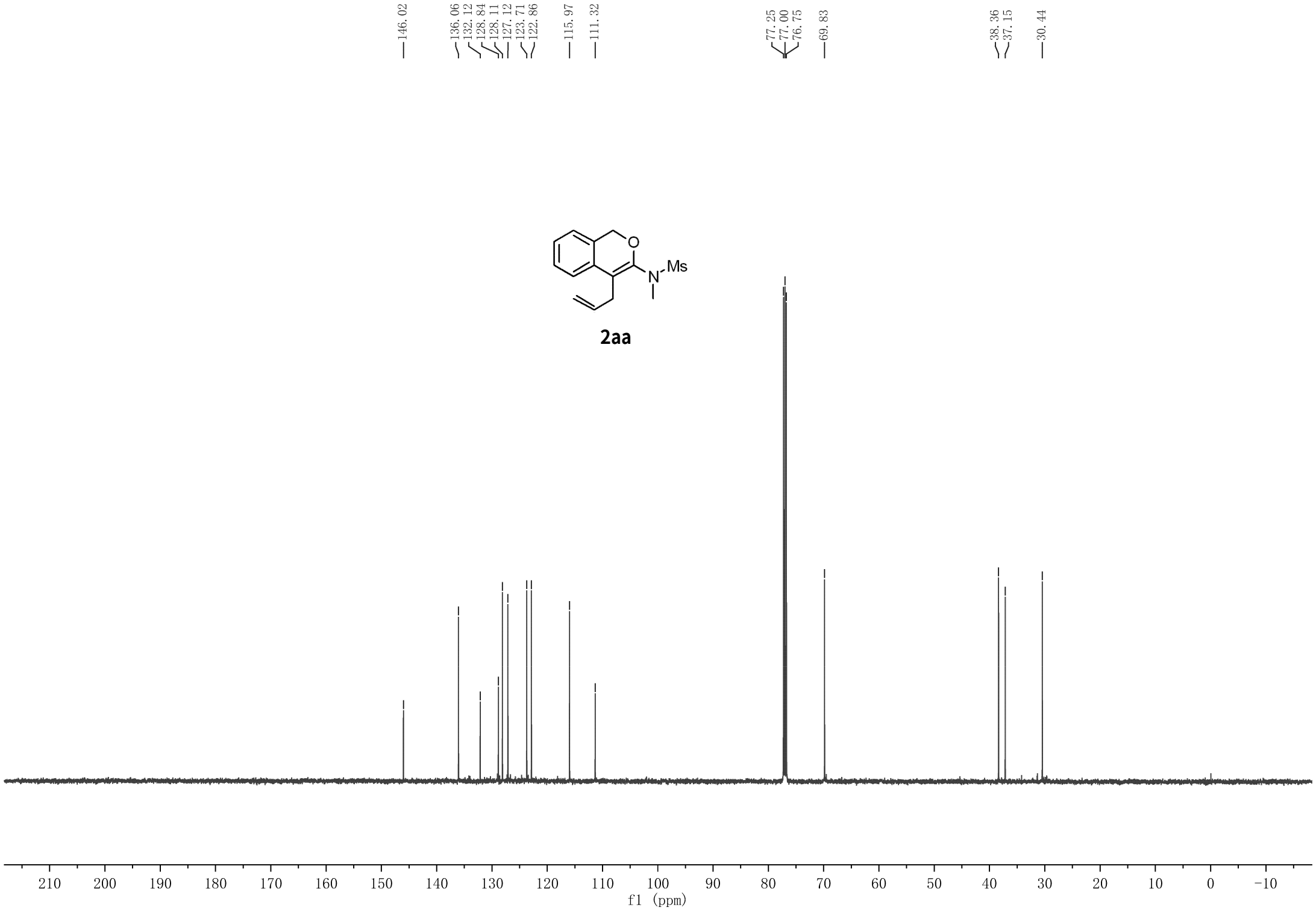
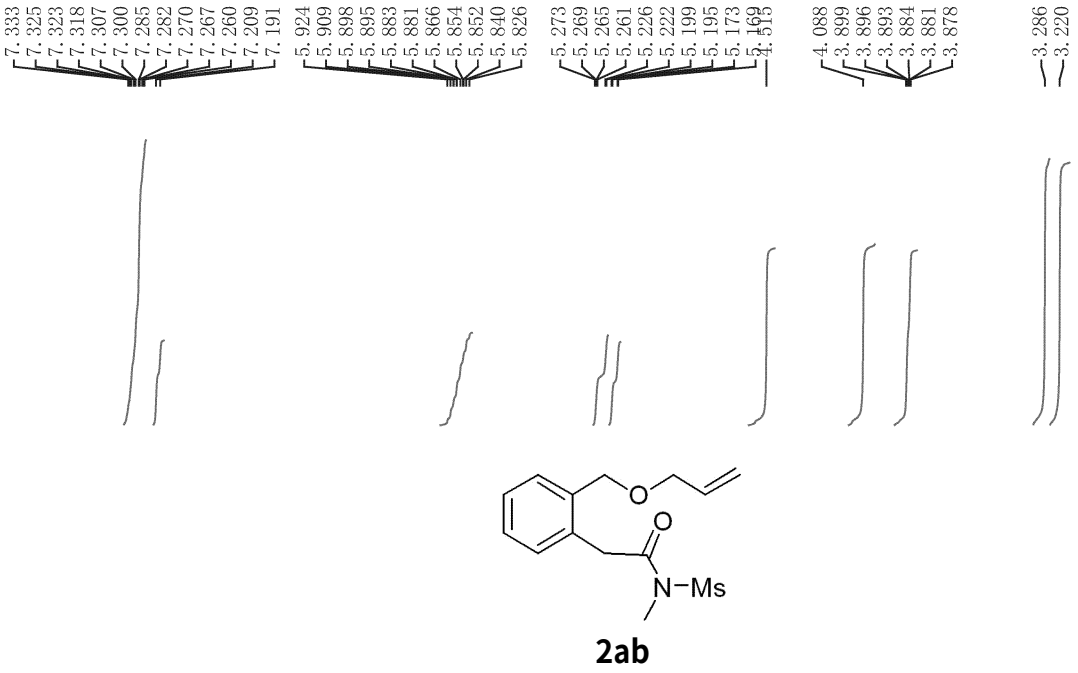
7.355
7.337
7.321
7.303
7.284
7.262
7.240
7.230
7.211
5.923
5.906
5.898
5.881
5.864
5.847
5.838
5.821
5.431
5.396
5.300
5.265
5.151
5.131
5.106
3.713
3.696
3.680
2.863
2.848
2.829
2.812
2.796
2.738
2.720
2.702
2.684
2.666
O
O
4.16
0.95
2.02
1.91
0.97
2.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

2a


172.18
134.18
133.99
131.36
128.58
127.24
126.63
124.62
118.08
77.32
77.00
76.68
69.50
45.34
34.18
O
O
2a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.245
7.231
7.223
7.211
7.192
7.189
7.178
7.174
7.164
7.160
7.031
7.016
5.928
5.916
5.908
5.904
5.896
5.882
5.873
5.870
5.861
5.850
5.129
5.126
5.123
5.119
5.095
5.092
5.088
5.085
5.055
5.039
5.036
5.033
5.030
5.019
5.016
5.012
5.010
3.361
3.349
3.117
2.984
O
N
Ms
2aa
2.26
0.99
0.97
1.01
1.09
1.95
1.03
2.00
2.96
3.00
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
f1 (ppm)


146.02
136.06
132.12
128.84
128.11
127.12
123.71
122.86
115.97
111.32
77.25
77.00
76.75
69.83
38.36
37.15
30.44
O
N
Ms
2aa
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)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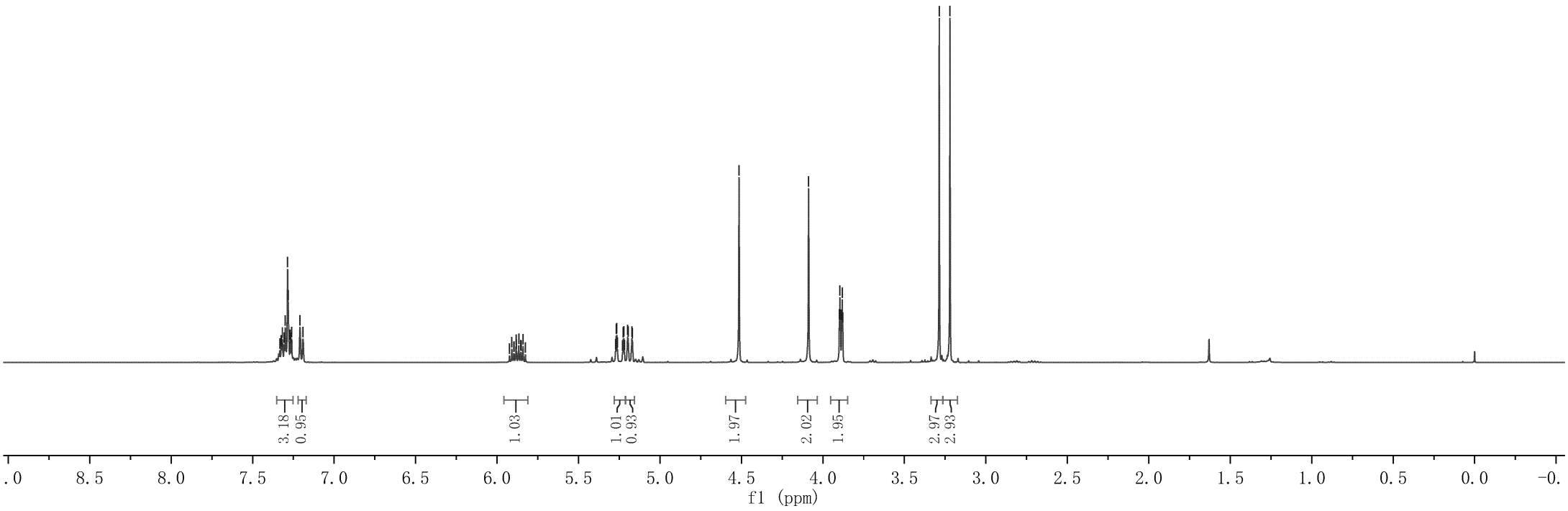
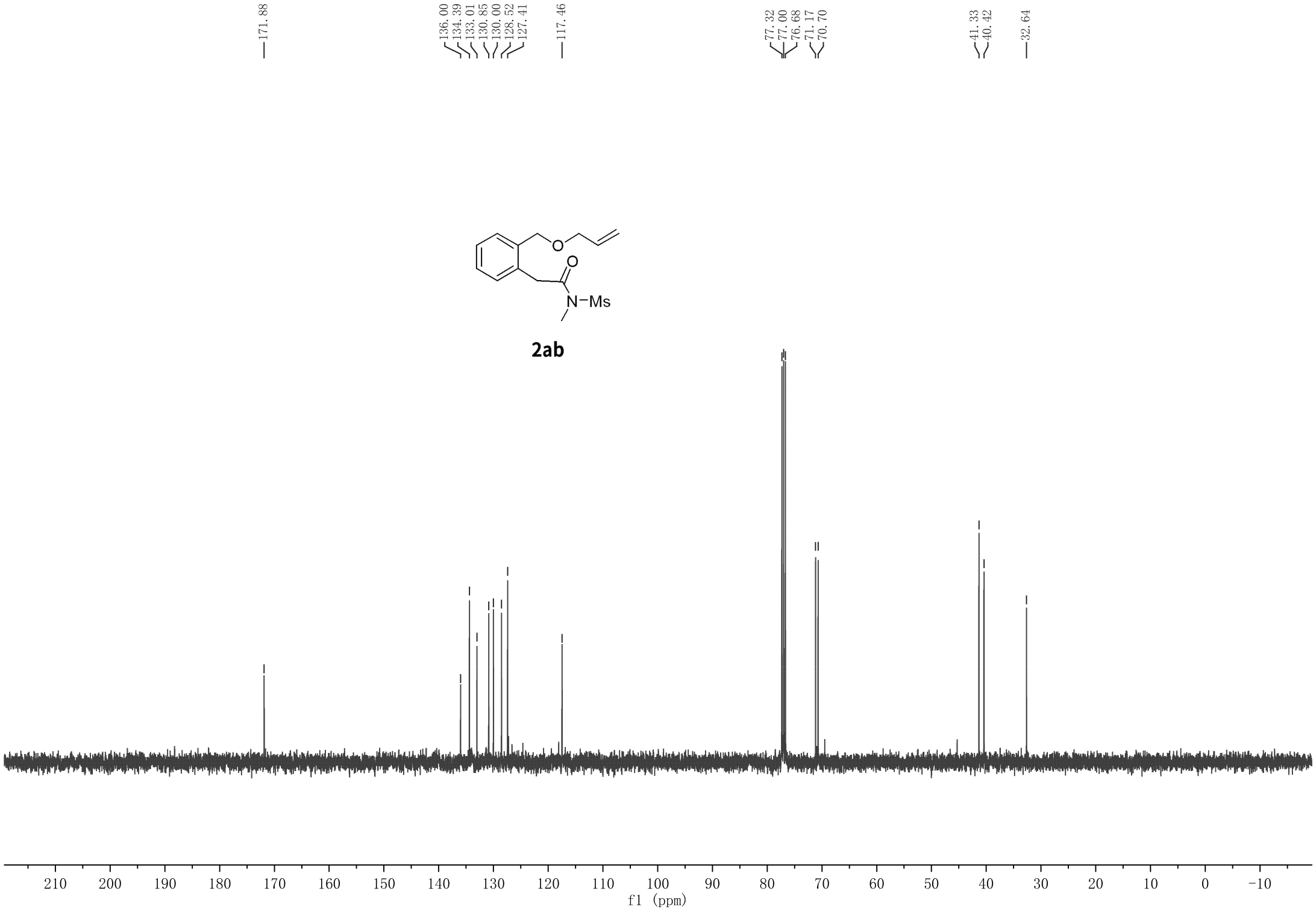
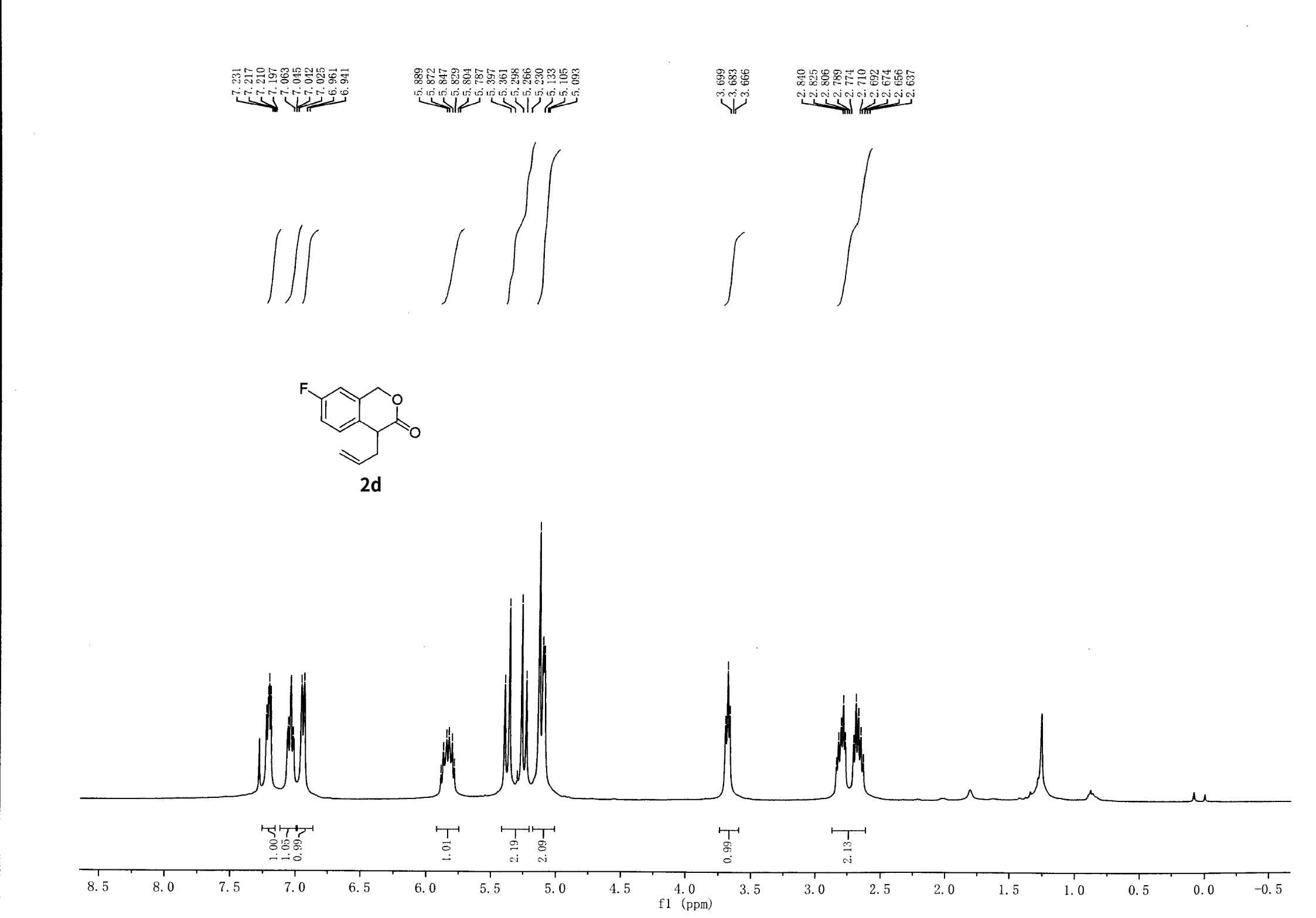
7.325
7.323
7.318
7.307
7.300
7.285
7.282
7.270
7.267
7.260
7.209
7.191
5.924
5.909
5.898
5.895
5.883
5.881
5.866
5.854
5.852
5.840
5.826
5.273
5.269
5.265
5.261
5.226
5.222
5.199
5.195
5.173
5.169
4.513
4.088
3.899
3.896
3.893
3.884
3.881
3.878
3.286
3.220
O
O
N−Ms

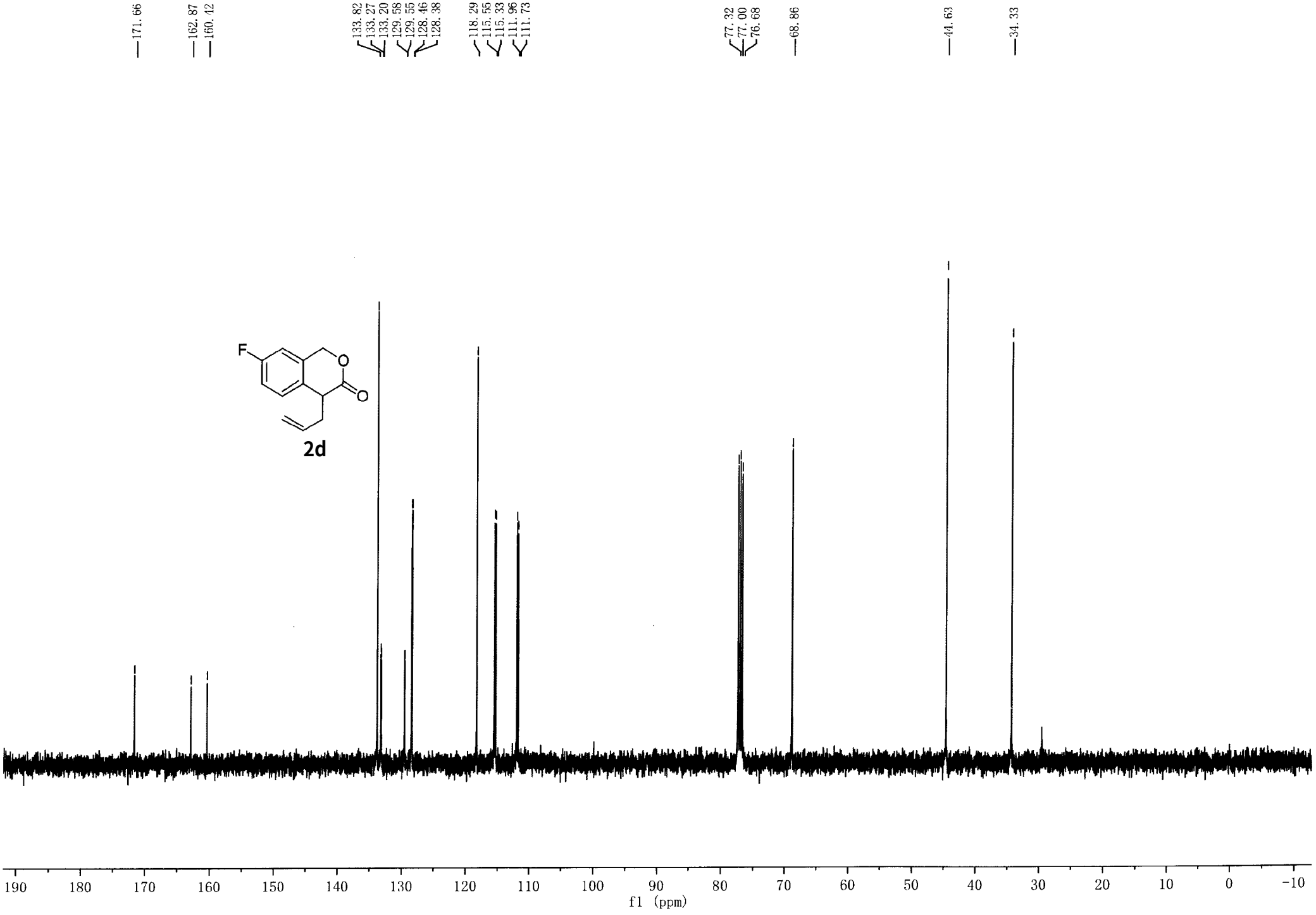
2ab

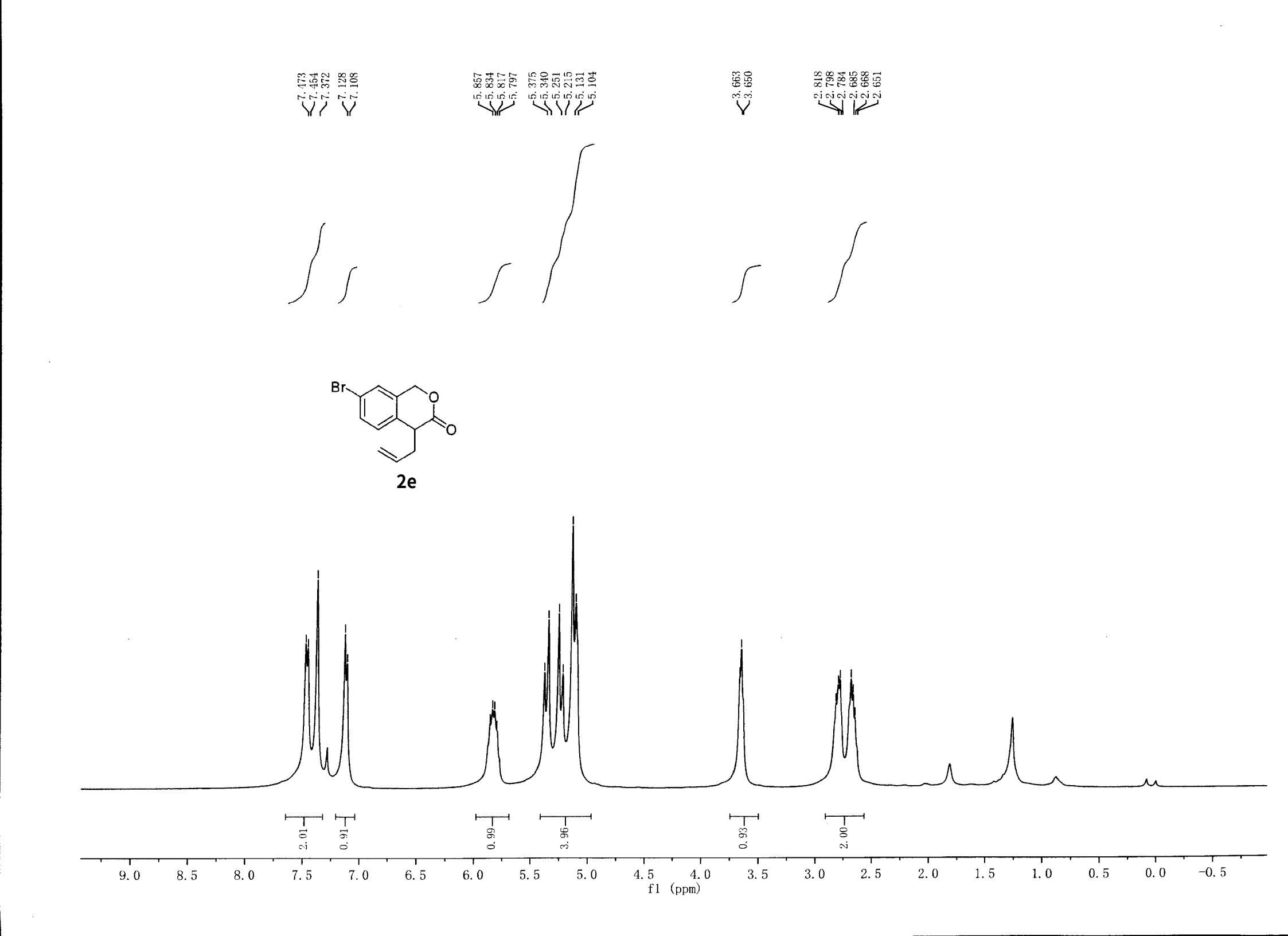

3.18
0.95
1.03
1.01
0.93
1.97
2.02
1.95
2.97
2.93
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


171.88
136.00
134.39
133.01
130.85
130.00
128.52
127.41
117.46
77.32
77.00
76.68
71.17
70.70
41.33
40.42
32.64
O
O
N−Ms
2ab
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)


7.231
7.217
7.210
7.197
7.063
7.045
7.042
7.025
6.961
6.941
5.889
5.872
5.847
5.829
5.804
5.787
5.397
5.361
5.298
5.266
5.230
5.133
5.105
5.093
3.699
3.683
3.666
2.840
2.825
2.806
2.789
2.774
2.710
2.692
2.674
2.656
2.637
F
O
O
1.00
1.05
0.99
1.01
2.19
2.09
0.99
2.13
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)

2d


171.66
162.87
160.42
133.82
133.27
133.20
129.58
129.55
128.46
128.38
118.29
115.55
115.33
111.96
111.73
77.32
77.00
76.68
68.86
44.63
34.33
F
O
O
2d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.473
7.454
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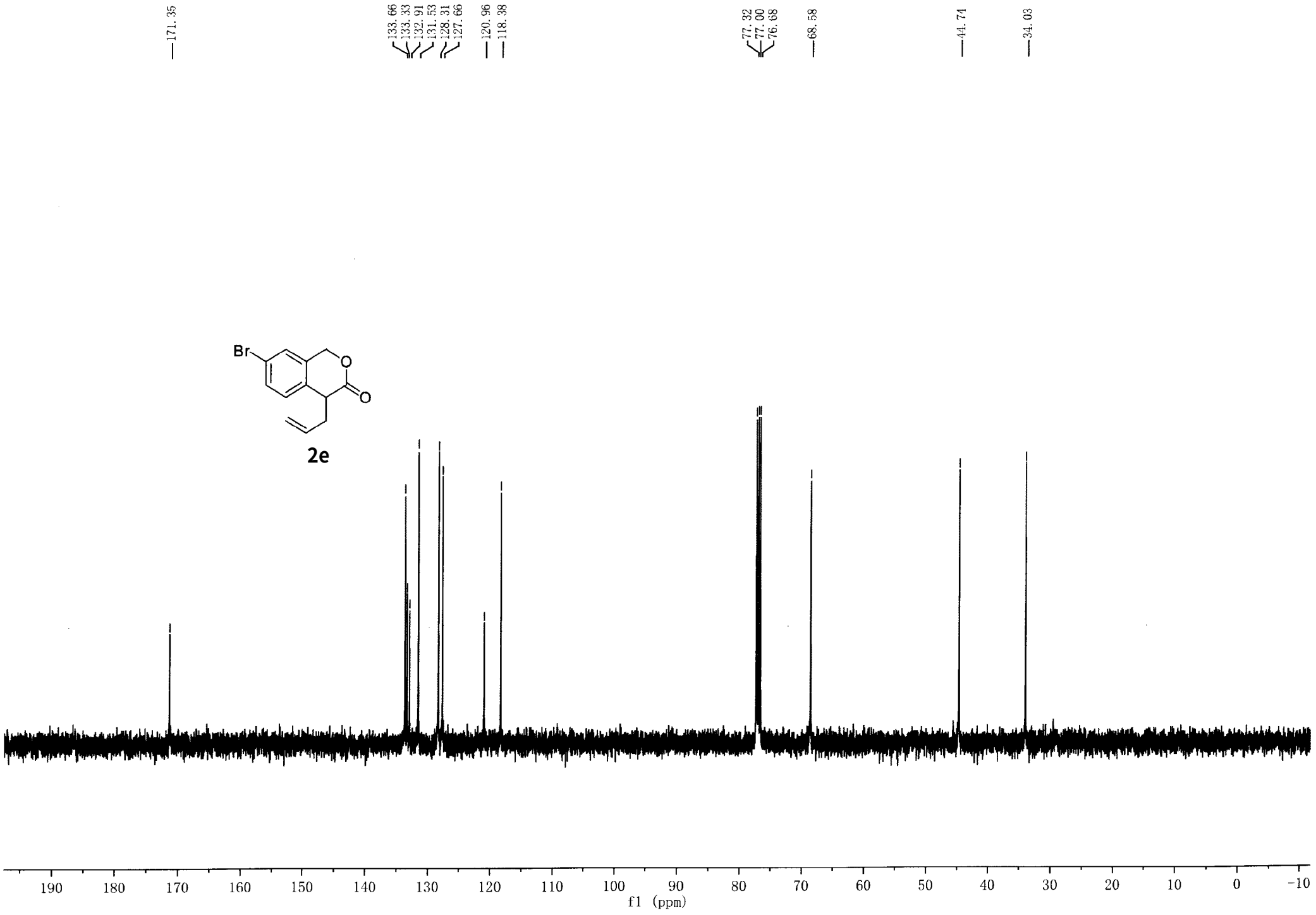
7.128
7.108
5.857
5.834
5.817
5.797
5.375
5.340
5.251
5.215
5.131
5.104
3.663
3.650
2.818
2.798
2.784
2.685
2.668
2.651
Br
O
O
2e
2.01
0.91
0.99
3.96
0.93
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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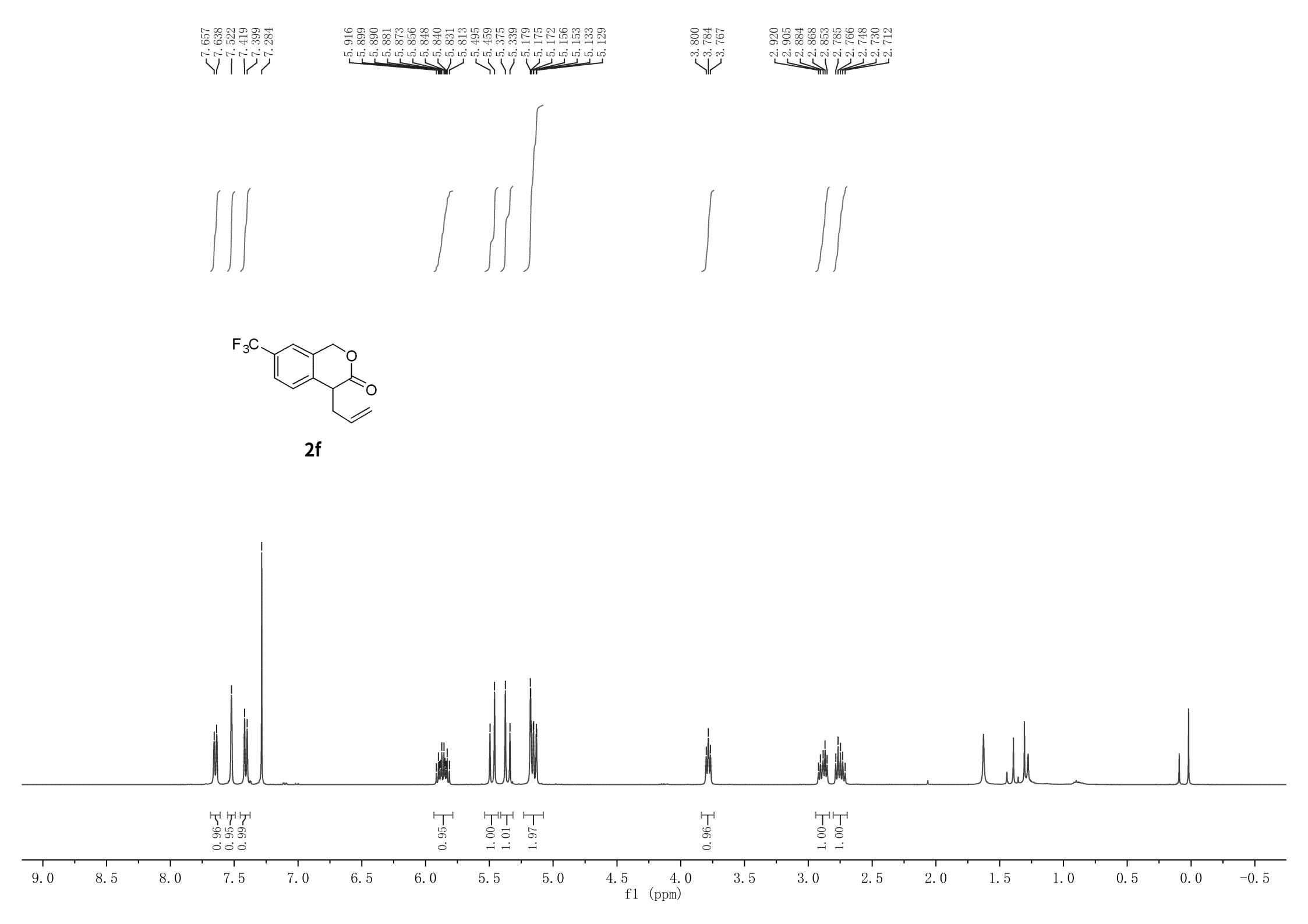
133.66
133.33
132.91
131.53
128.31
127.66
120.96
118.38
77.32
77.00
76.68
68.58
44.74
34.03
Br
O
O
2e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.284
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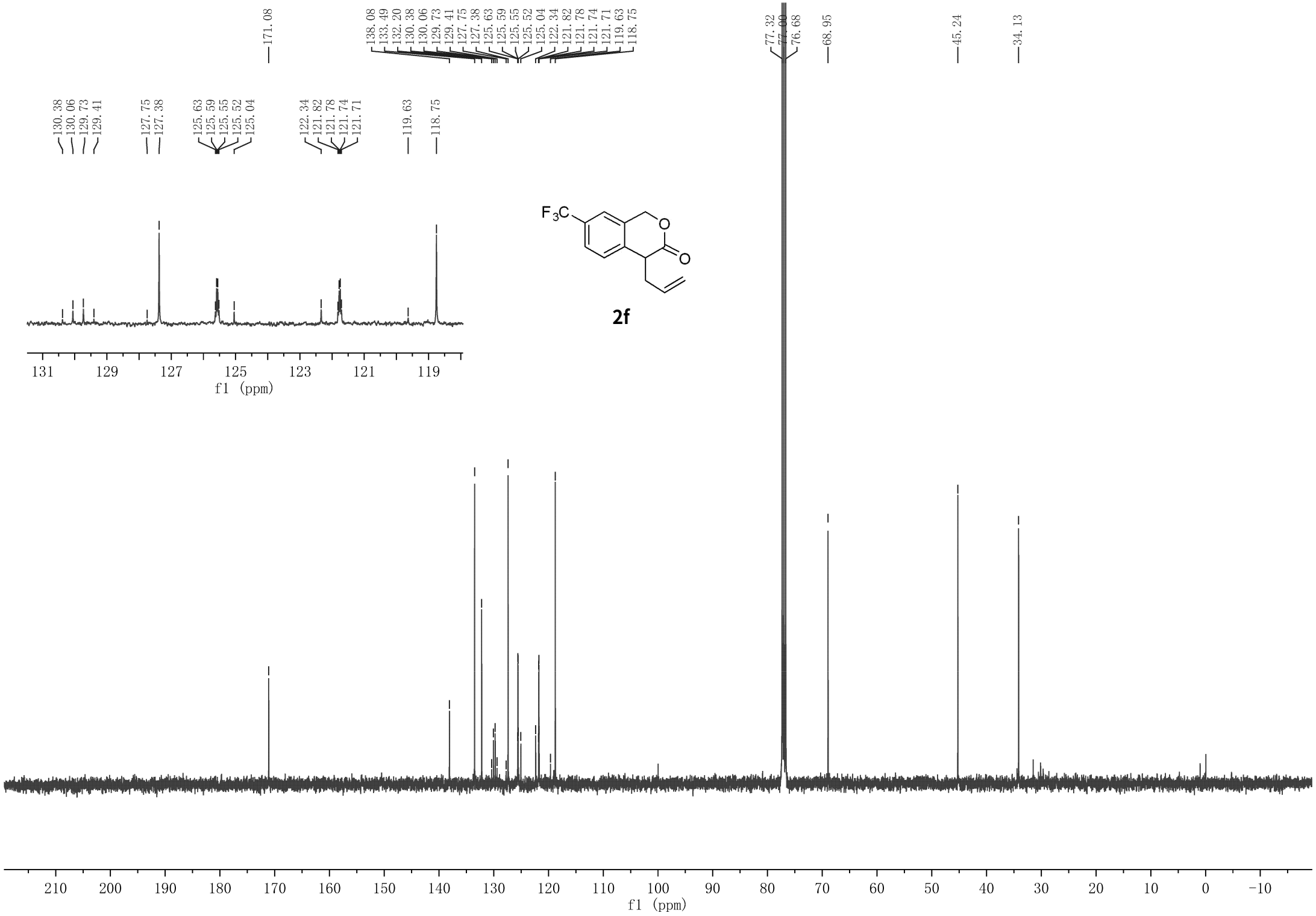
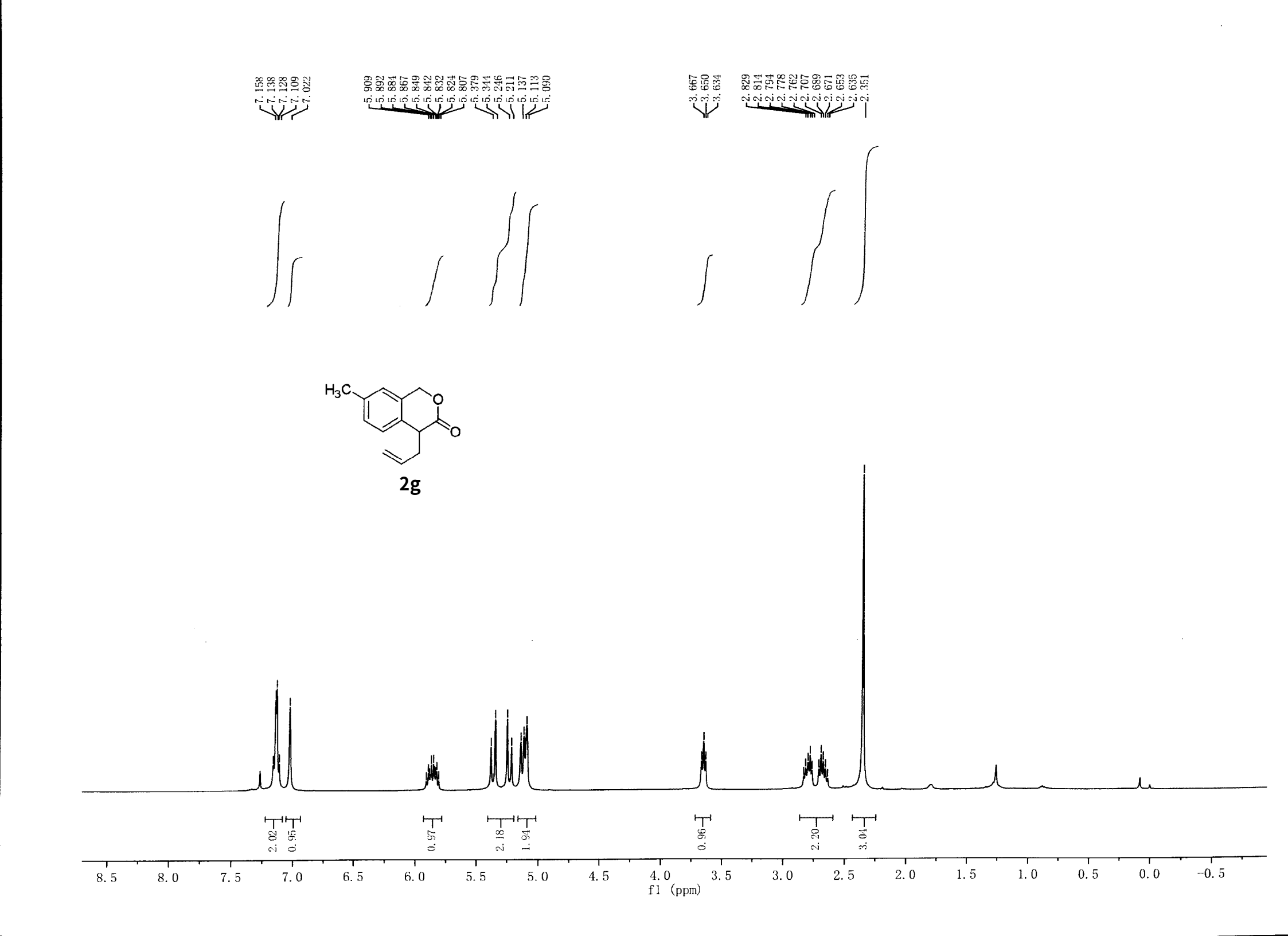
5.899
5.890
5.881
5.873
5.856
5.848
5.840
5.831
5.813
5.495
5.459
5.375
5.339
5.179
5.175
5.172
5.156
5.153
5.133
5.129
3.800
3.784
3.767
2.920
2.905
2.884
2.868
2.853
2.785
2.766
2.748
2.730
2.712
F3C
O
O
2f
0.96
0.95
0.99
0.95
1.00
1.01
1.97
0.96
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


171.08
138.08
133.49
132.20
130.38
130.06
129.73
129.41
127.75
127.38
125.63
125.59
125.55
125.52
125.04
122.34
121.82
121.78
121.74
121.71
119.63
118.75
77.32
77.00
76.68
68.95
45.24
34.13
F3C
O
O
2f
f1 (ppm)
f1 (ppm)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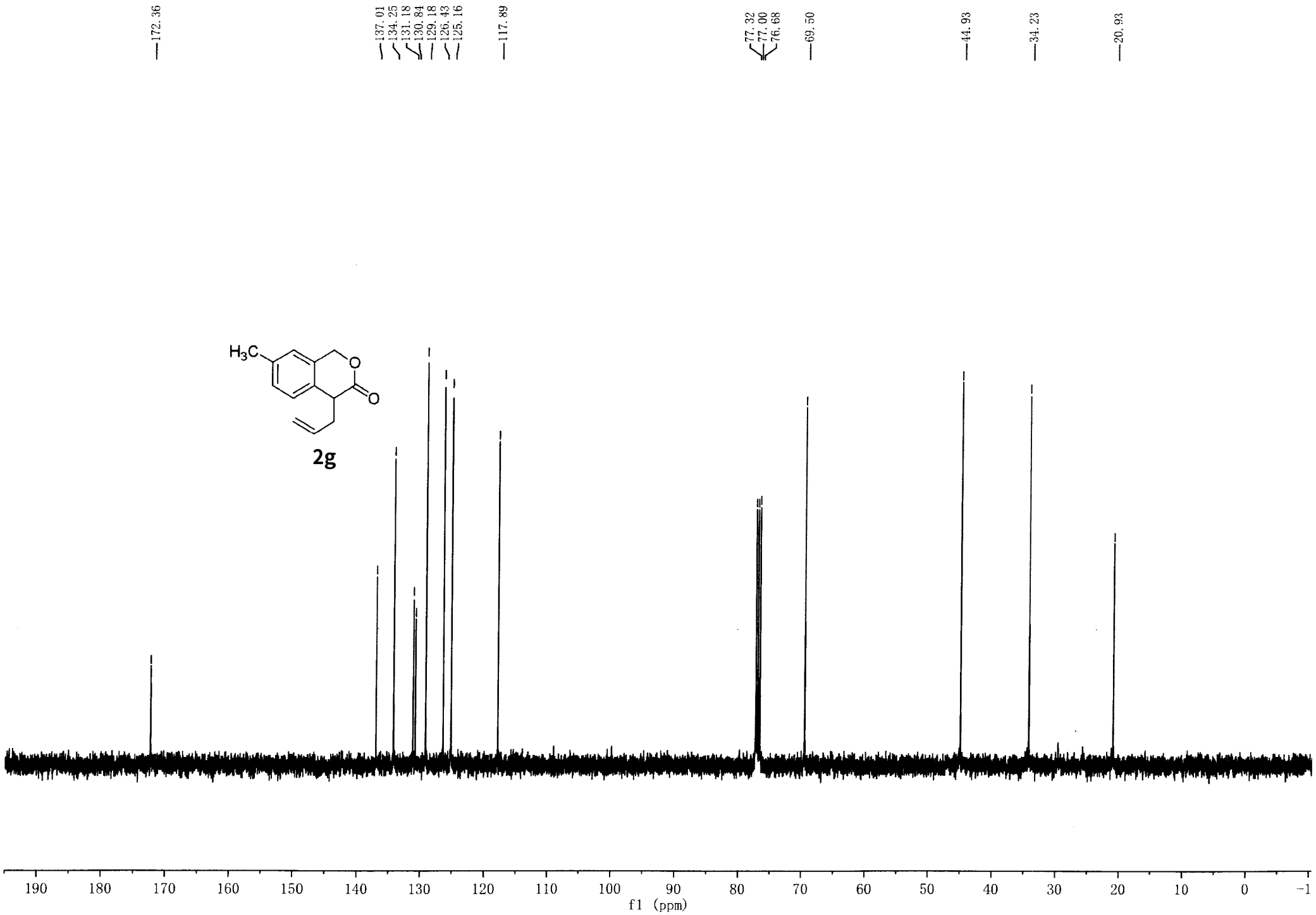
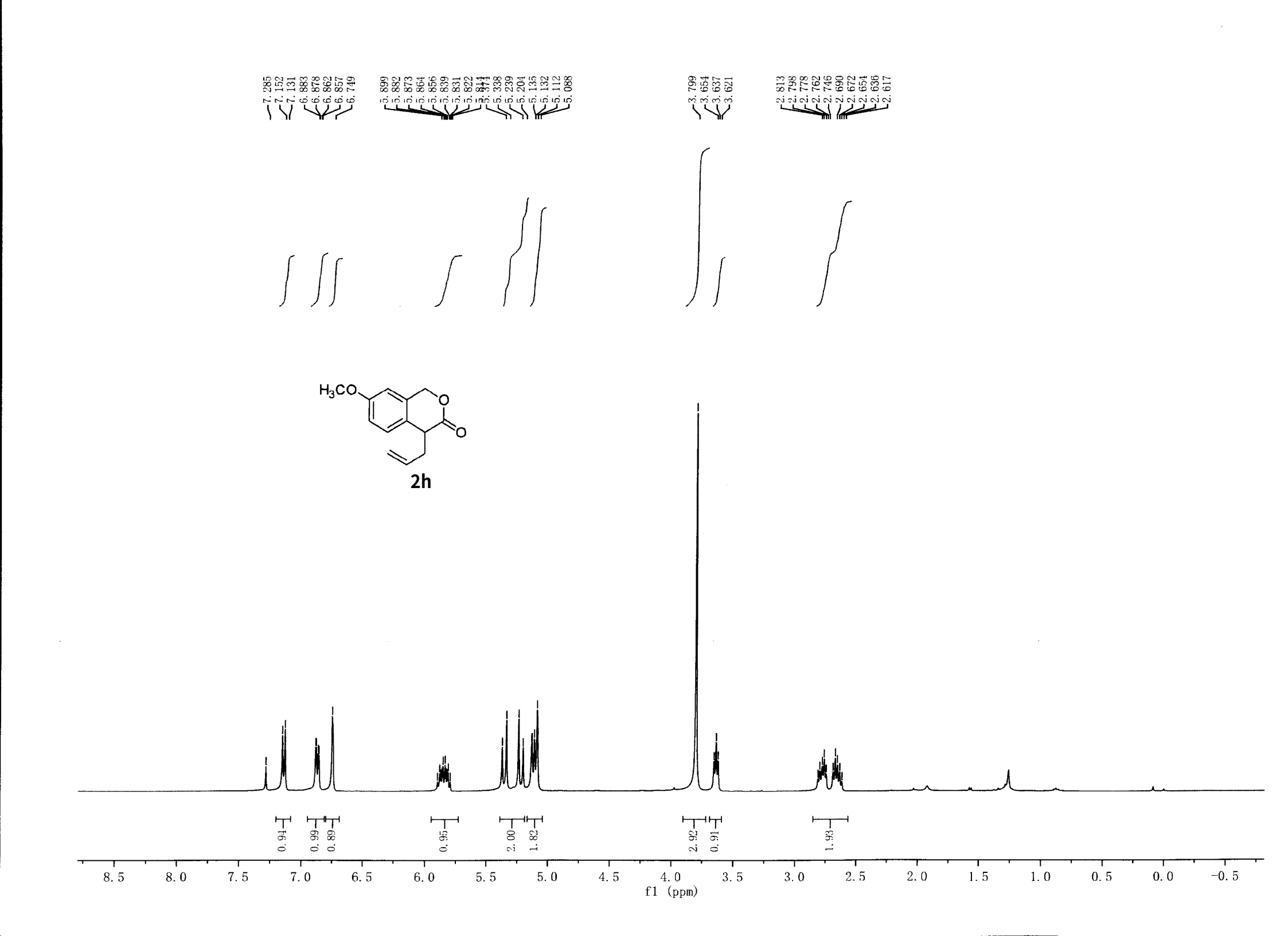
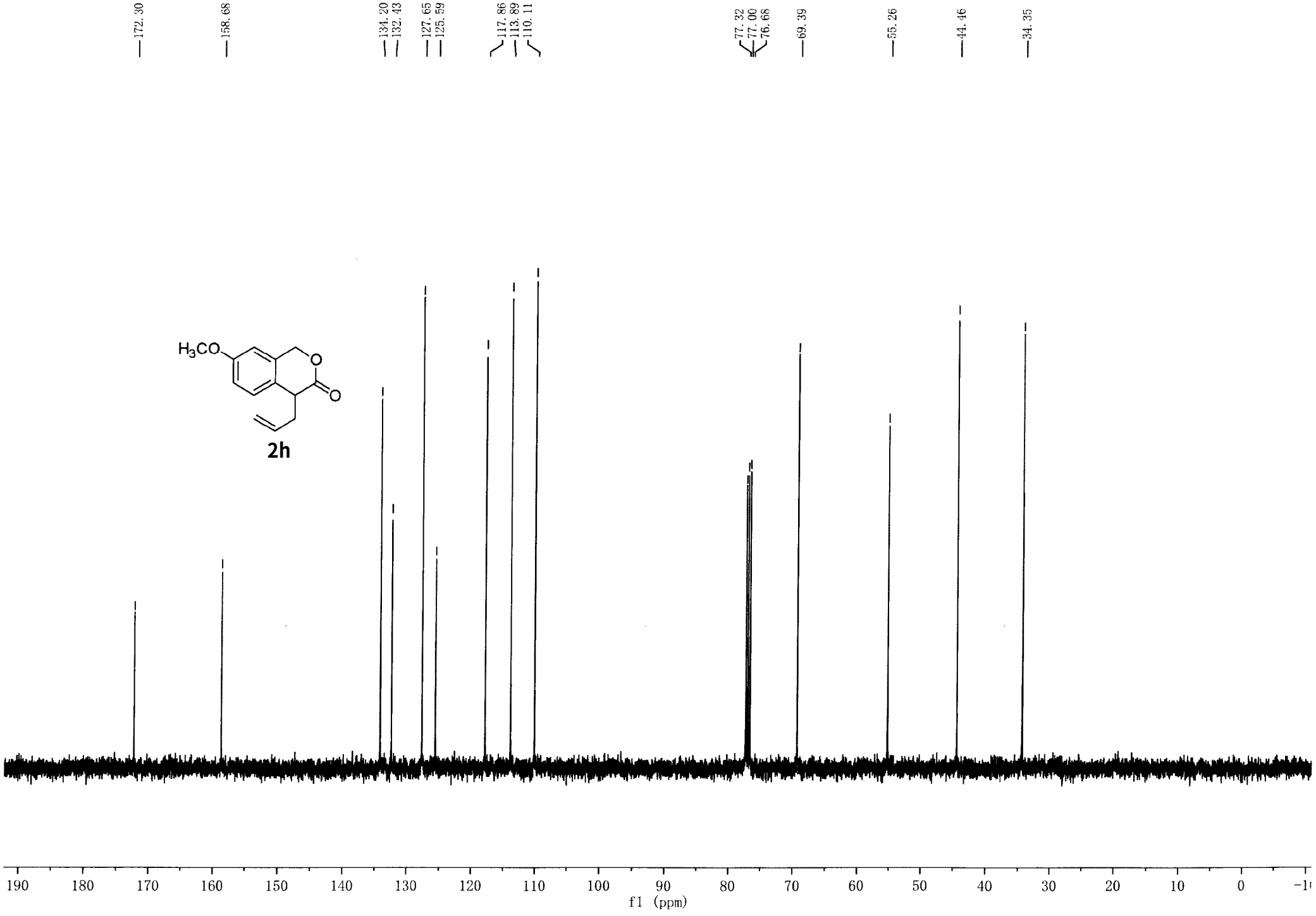
7.138
7.128
7.109
7.022
5.909
5.892
5.884
5.867
5.849
5.842
5.832
5.824
5.807
5.379
5.344
5.246
5.211
5.137
5.113
5.090
3.667
3.650
3.634
2.829
2.814
2.794
2.778
2.762
2.707
2.689
2.671
2.653
2.635
2.351
H3C
O
O
2g
2.02
0.95
0.97
2.18
1.94
0.96
2.20
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


172.36
137.01
134.25
131.18
130.84
129.18
126.43
125.16
117.89
77.32
77.00
76.68
69.50
44.93
34.23
20.93
H3C
O
O
2g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


7.285
7.152
7.131
6.883
6.878
6.862
6.857
6.749
5.899
5.882
5.873
5.864
5.856
5.839
5.831
5.822
5.338
5.239
5.204
5.135
5.132
5.112
5.088
3.799
3.654
3.637
3.621
2.813
2.798
2.778
2.762
2.746
2.690
2.672
2.654
2.636
2.617
H3CO
O
O
0.94
0.99
0.89
0.95
2.00
1.82
2.92
0.91
1.93
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)

2h


172.30
158.68
134.20
132.43
127.65
125.59
117.86
113.89
110.11
77.32
77.00
76.68
69.39
55.26
44.46
34.35
H3CO
O
O
2h
190
180
170
160
150
140
130
120
110
100
90
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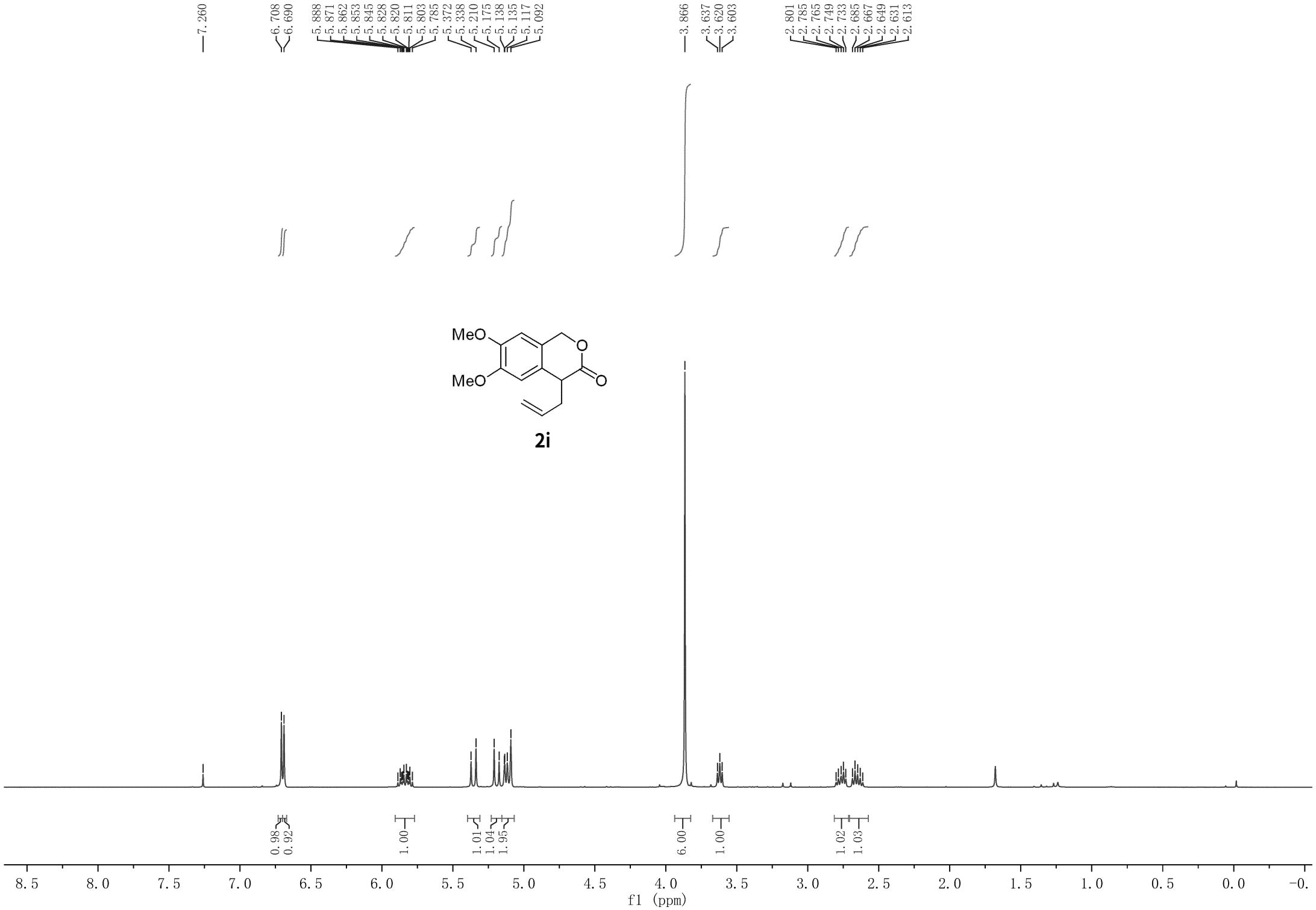
f1 (ppm)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5.862
5.853
5.845
5.828
5.820
5.811
5.803
5.785
5.372
5.338
5.210
5.175
5.138
5.135
5.117
5.092
3.866
3.637
3.620
3.603
2.801
2.785
2.765
2.749
2.733
2.685
2.667
2.649
2.631
2.613
MeO
MeO
O
O
0.98
0.92
1.00
1.01
1.04
1.95
6.00
1.00
1.02
1.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.5
2.0
1.5
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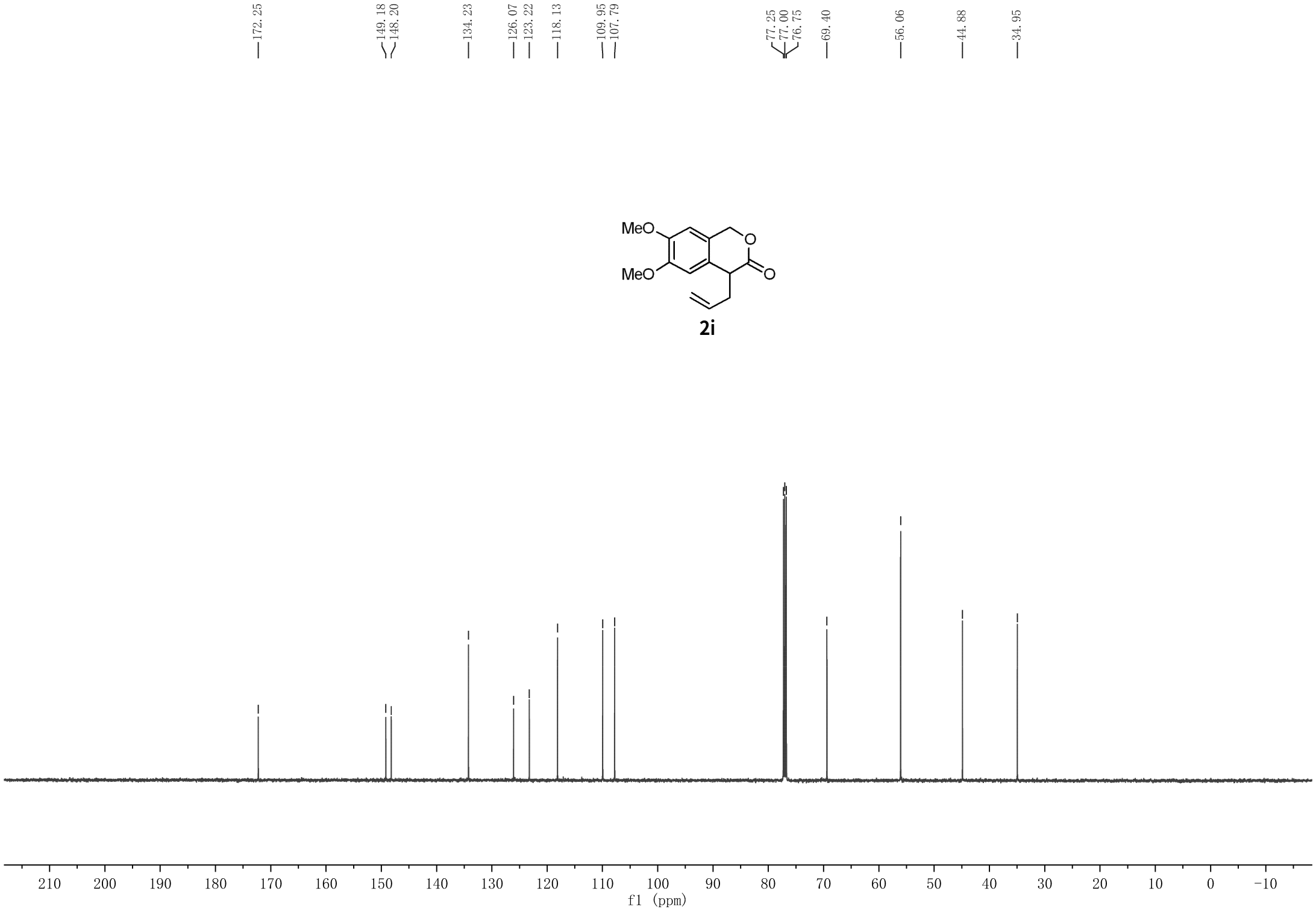
-0.
f1 (ppm)

2i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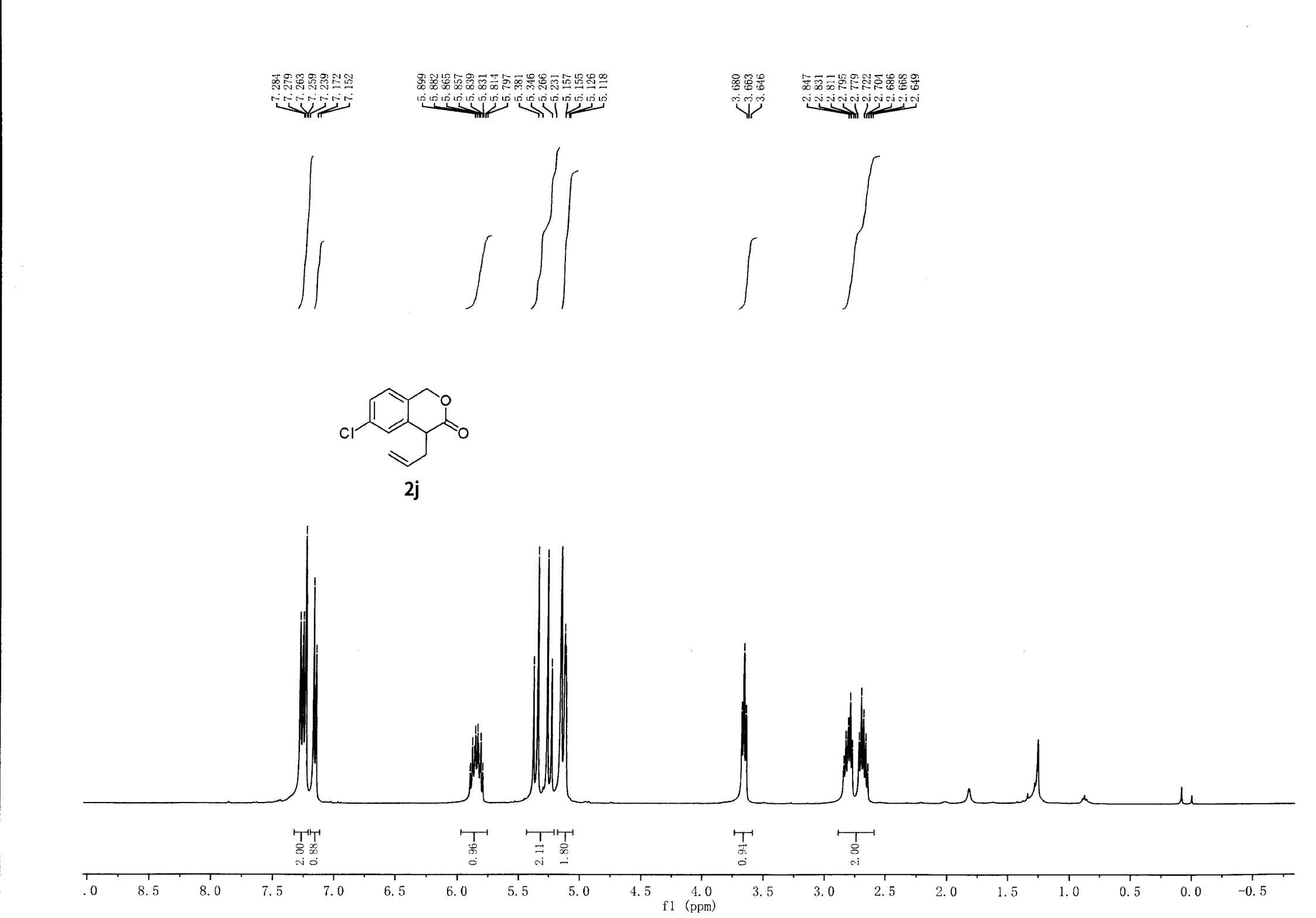
148.20
134.23
126.07
123.22
118.13
109.95
107.79
77.25
77.00
76.75
69.40
56.06
44.88
34.95
MeO
MeO
O
O
2i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.172
7.152
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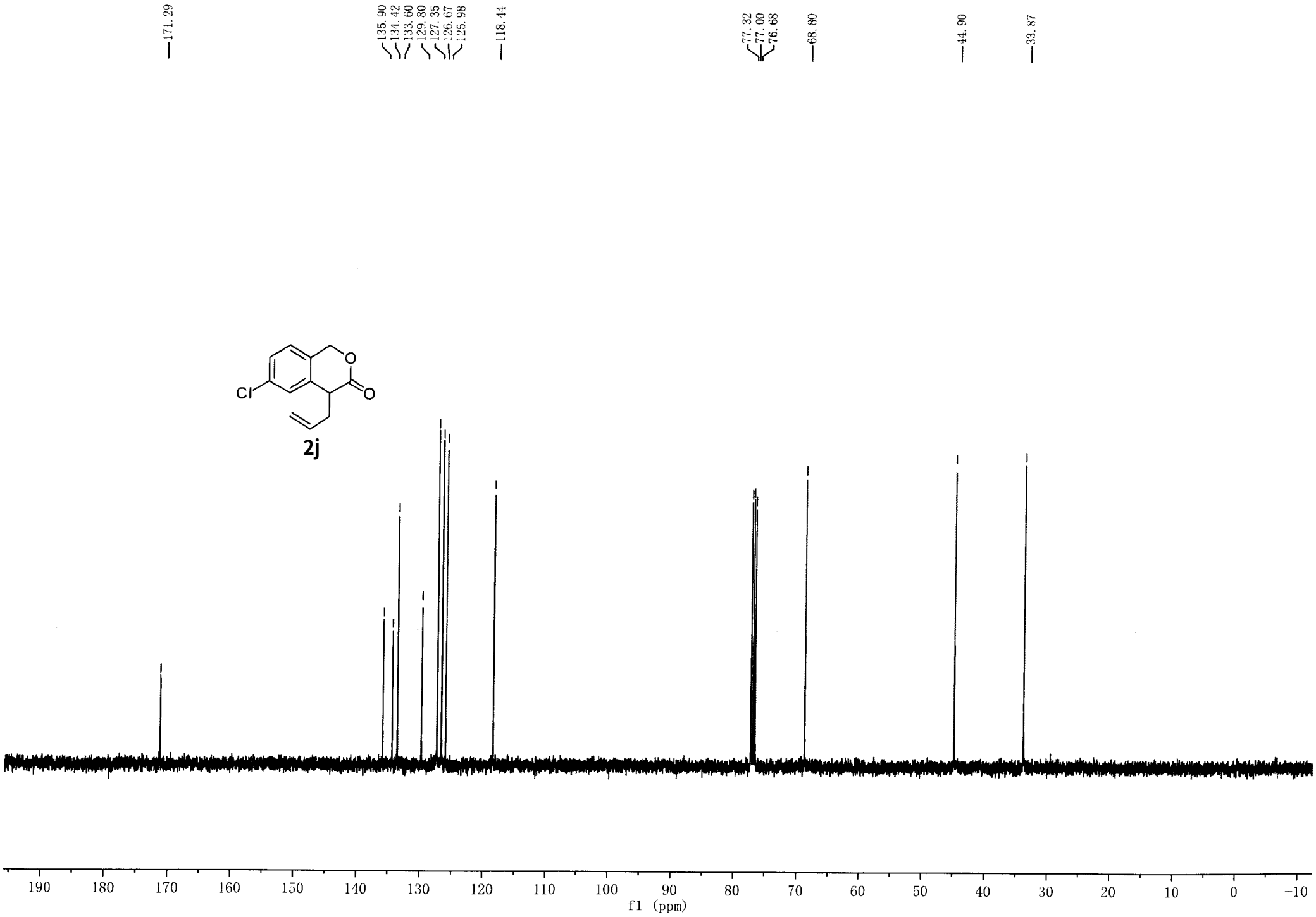
5.882
5.865
5.857
5.839
5.831
5.814
5.797
5.381
5.346
5.266
5.231
5.157
5.155
5.126
5.118
3.680
3.663
3.646
2.847
2.831
2.811
2.795
2.779
2.722
2.704
2.686
2.668
2.649
Cl
O
O
2j
2.00
0.88
0.96
2.11
1.80
0.94
2.00
f1 (ppm)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131.42
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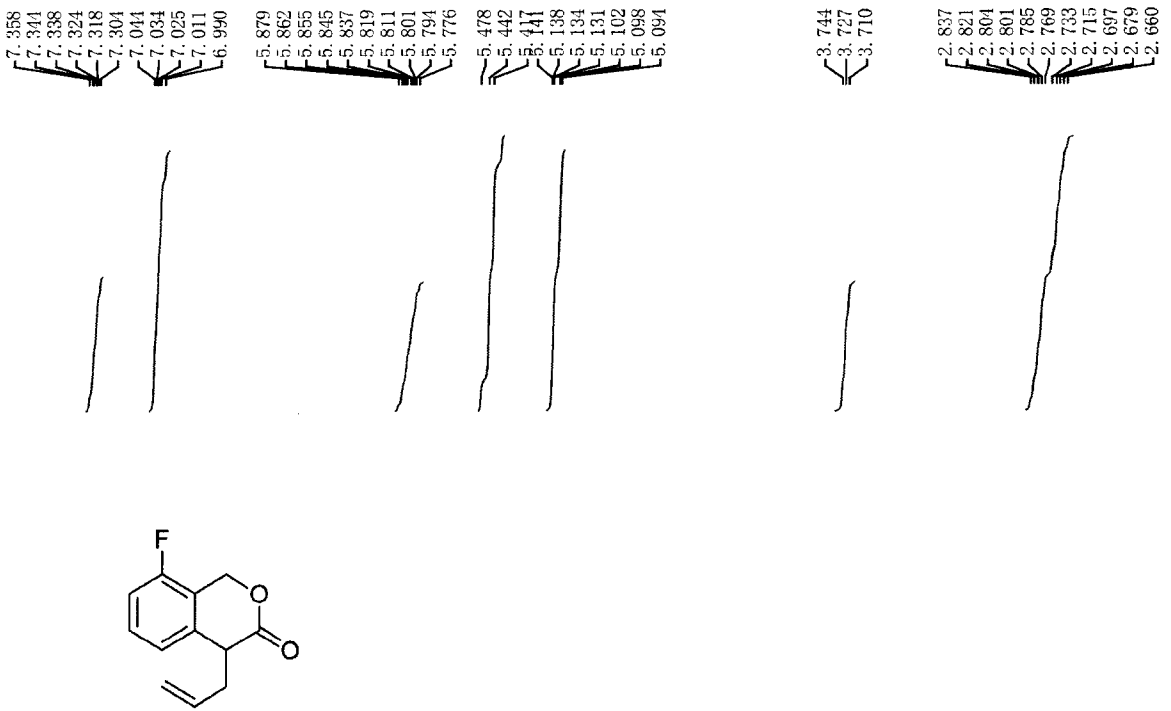
129.80
127.35
126.67
125.98
118.44
77.32
77.00
76.68
68.80
44.90
33.87
Cl
O
O
2j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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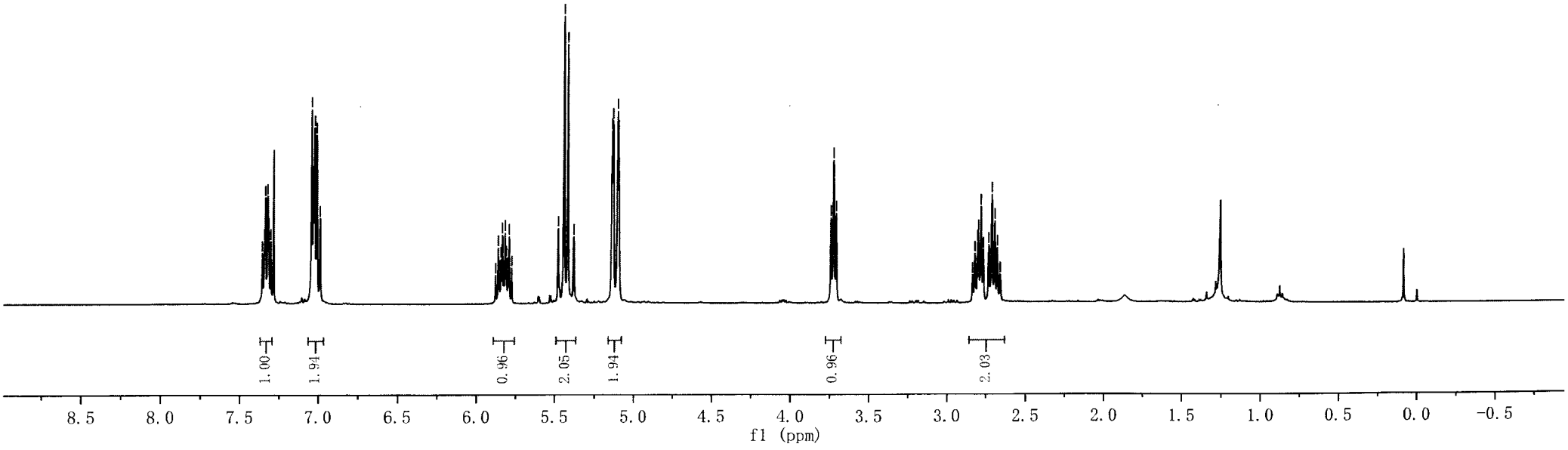
7.034
7.025
7.011
6.990
5.879
5.862
5.855
5.845
5.837
5.819
5.811
5.801
5.794
5.776
5.478
5.442
5.417
5.141
5.138
5.134
5.131
5.102
5.098
5.094
3.744
3.727
3.710
2.837
2.821
2.804
2.801
2.785
2.769
2.733
2.715
2.697
2.679
2.660

F
O
O

2k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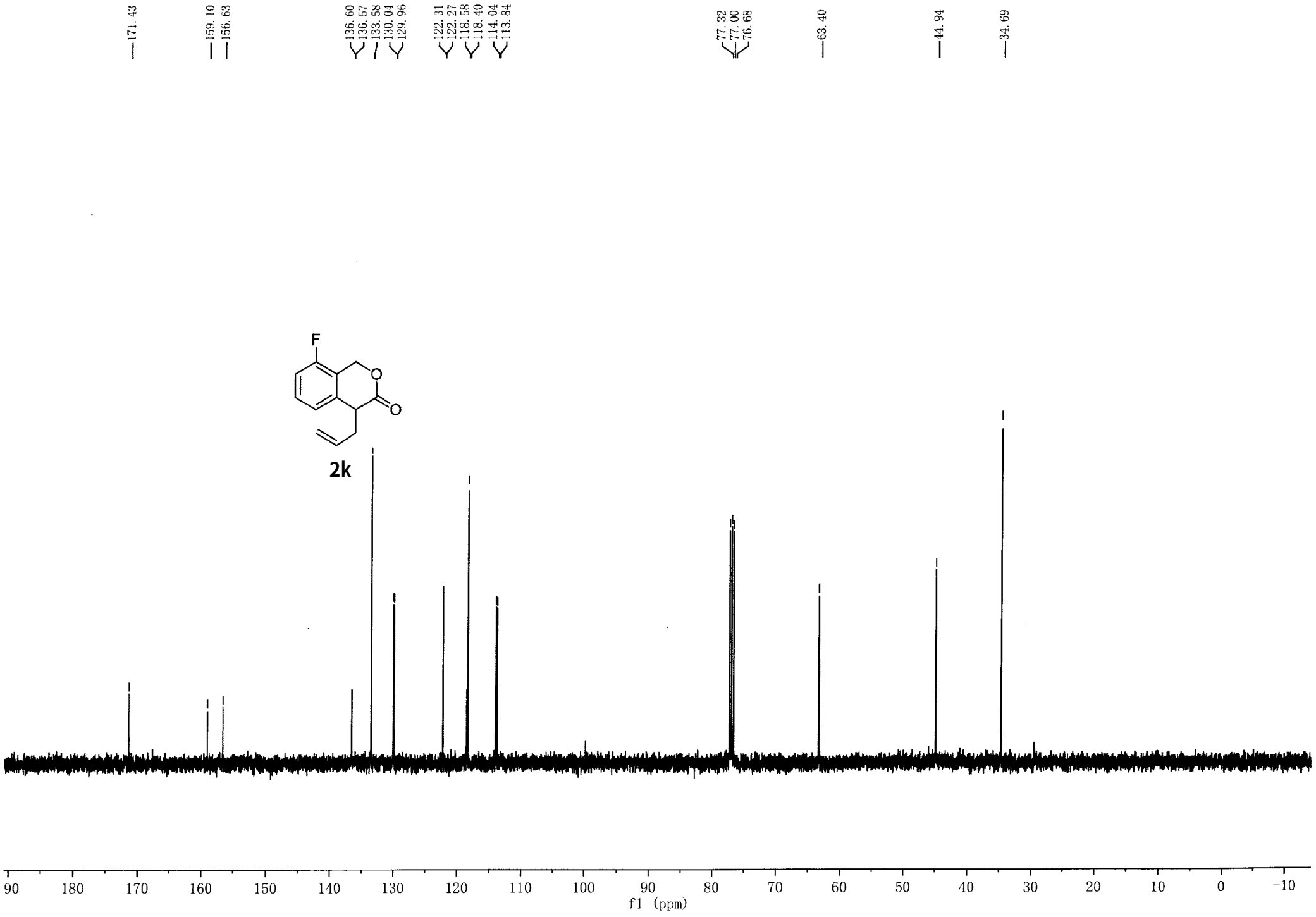
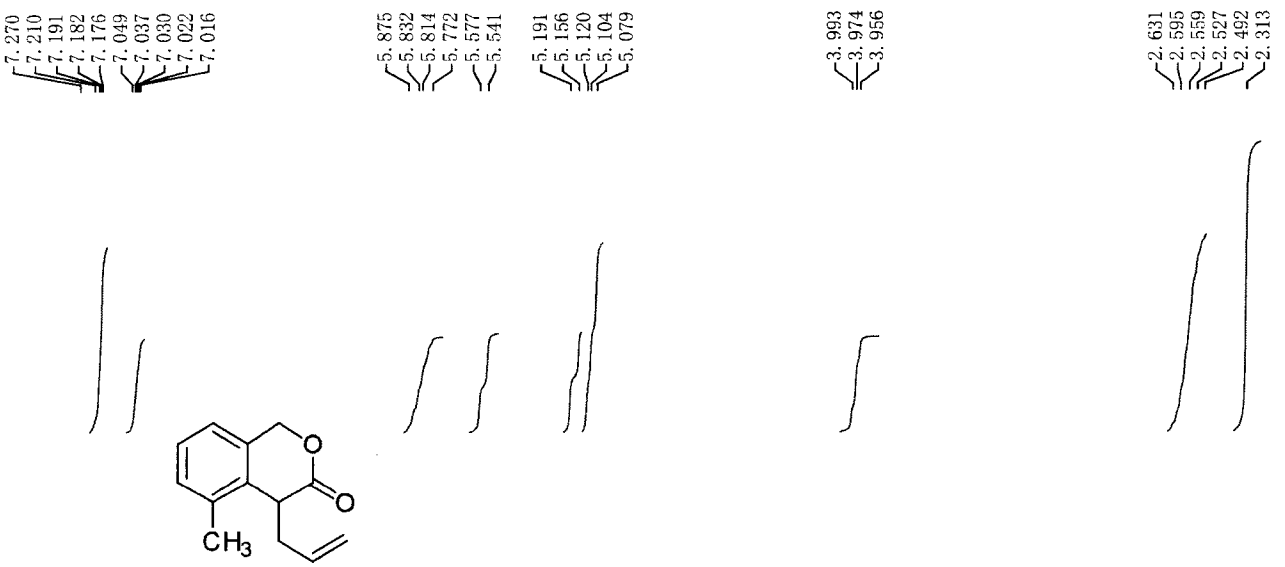
1.94
0.96
2.05
1.94
0.96
2.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


171.43
159.10
156.63
136.60
136.57
133.58
130.01
129.96
122.31
122.27
118.58
118.40
114.04
113.84
77.32
77.00
76.68
63.40
44.94
34.69
F
O
O
2k
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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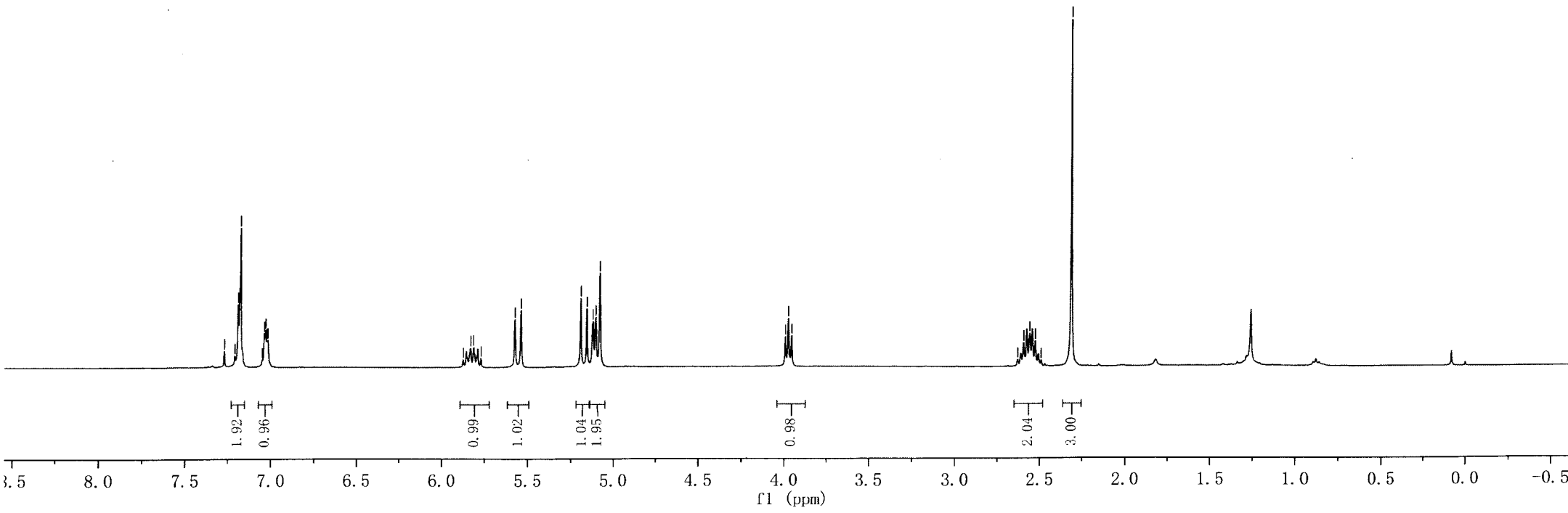
7.210
7.191
7.182
7.176
7.049
7.037
7.030
7.022
7.016
5.875
5.832
5.814
5.772
5.577
5.541
5.191
5.156
5.120
5.104
5.079
3.993
3.974
3.956
2.631
2.595
2.559
2.527
2.492
2.313
O
O
CH3

2l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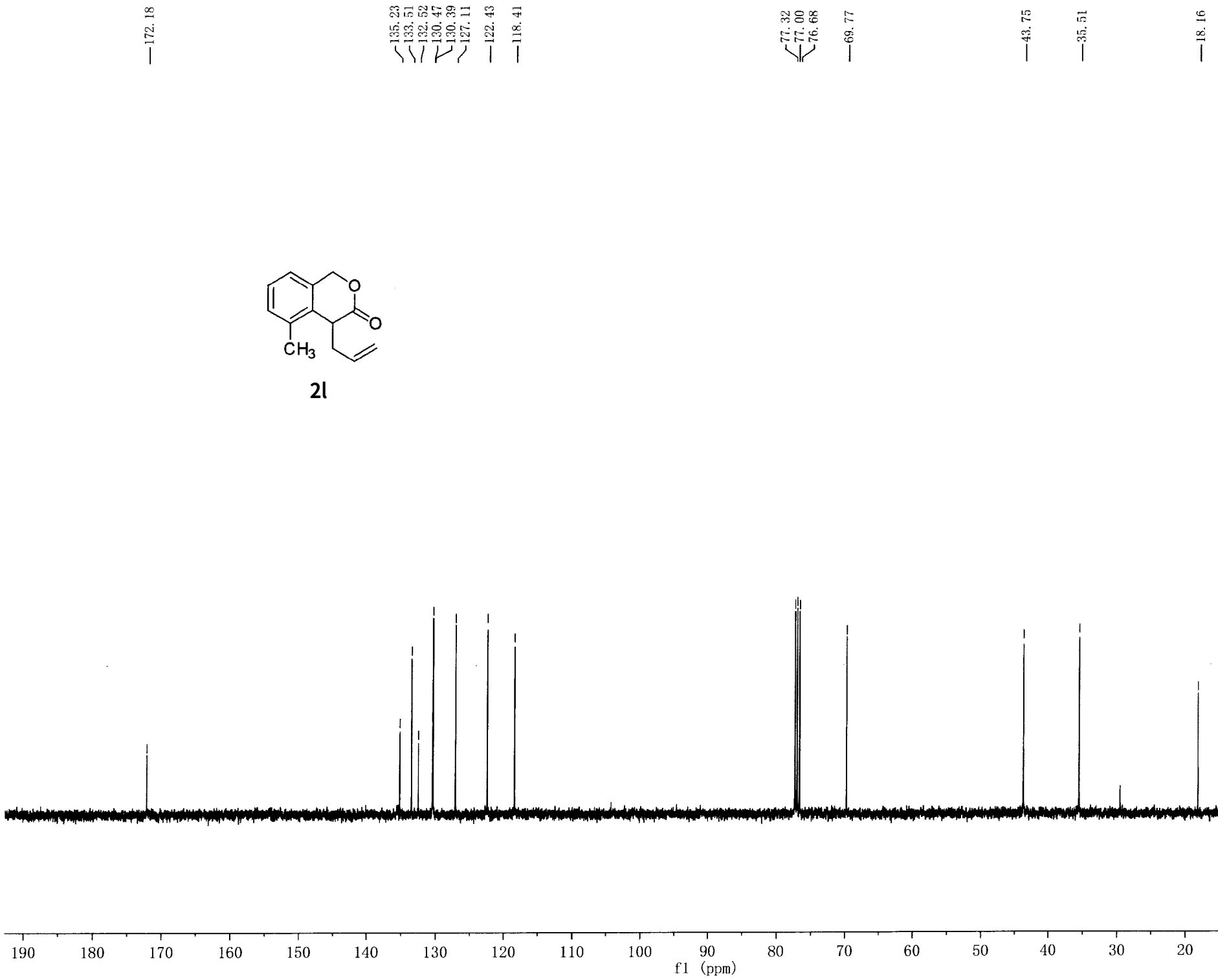
0.96
0.99
1.02
1.04
1.95
0.98
2.04
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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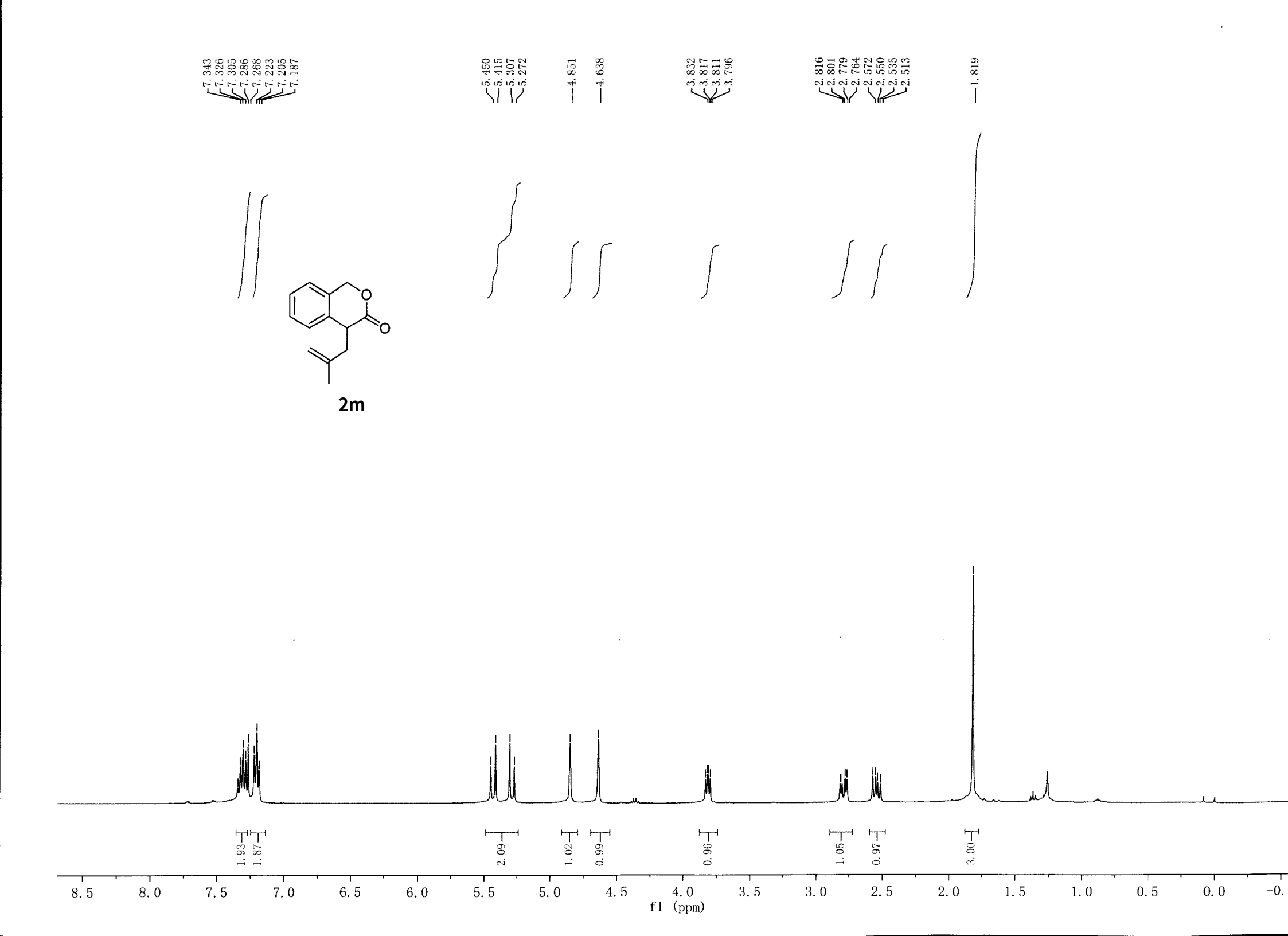
135.23
133.51
132.52
130.47
130.39
127.11
122.43
118.41
77.32
77.00
76.68
69.77
43.75
35.51
18.16
O
O
CH3
2l
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.343
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7.268
7.223
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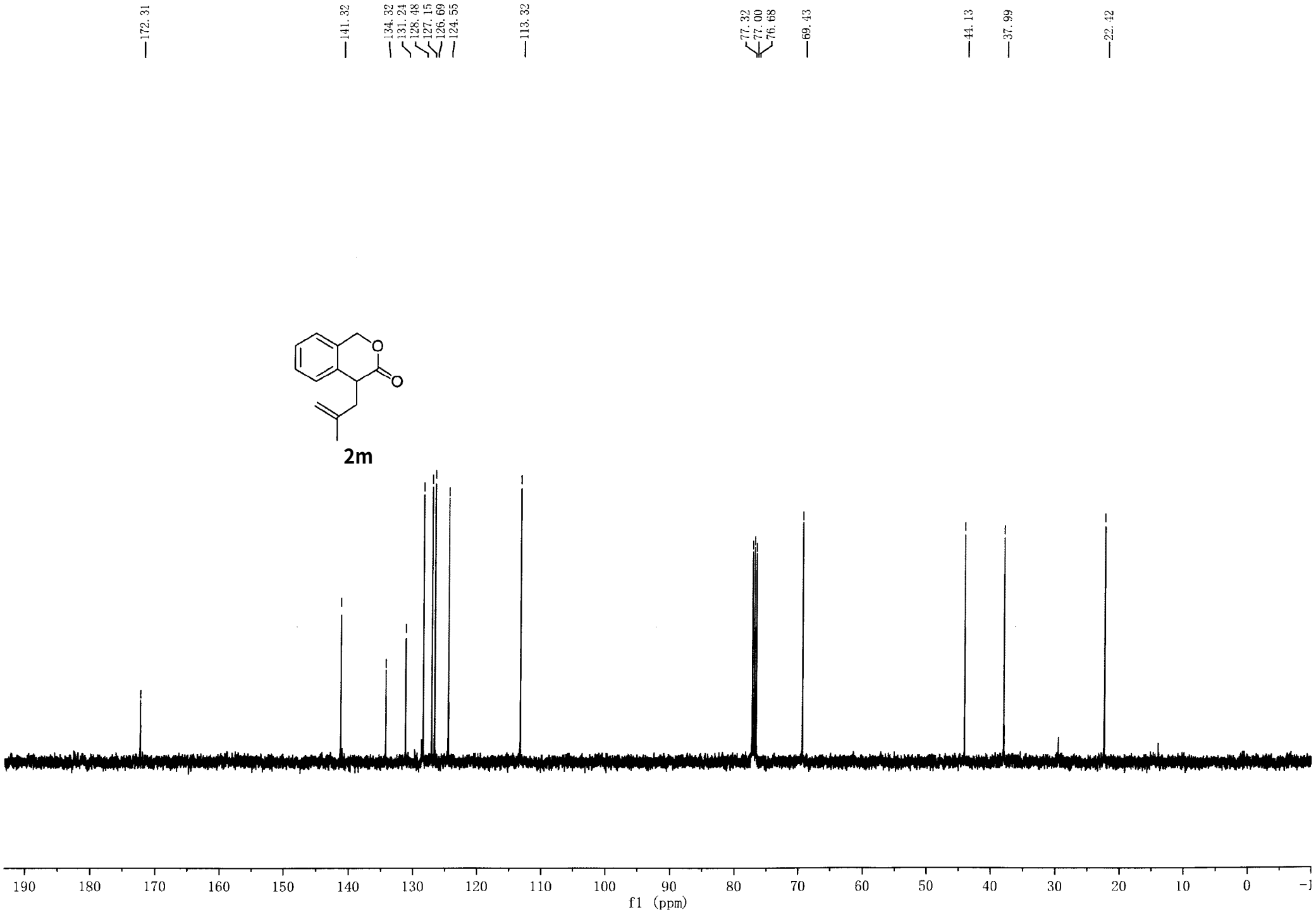
7.187
5.450
5.415
5.307
5.272
4.851
4.638
3.832
3.817
3.811
3.796
2.816
2.801
2.779
2.764
2.572
2.550
2.535
2.513
1.819
O
O
1.93
1.87
2.09
1.02
0.99
0.96
1.05
0.97
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2m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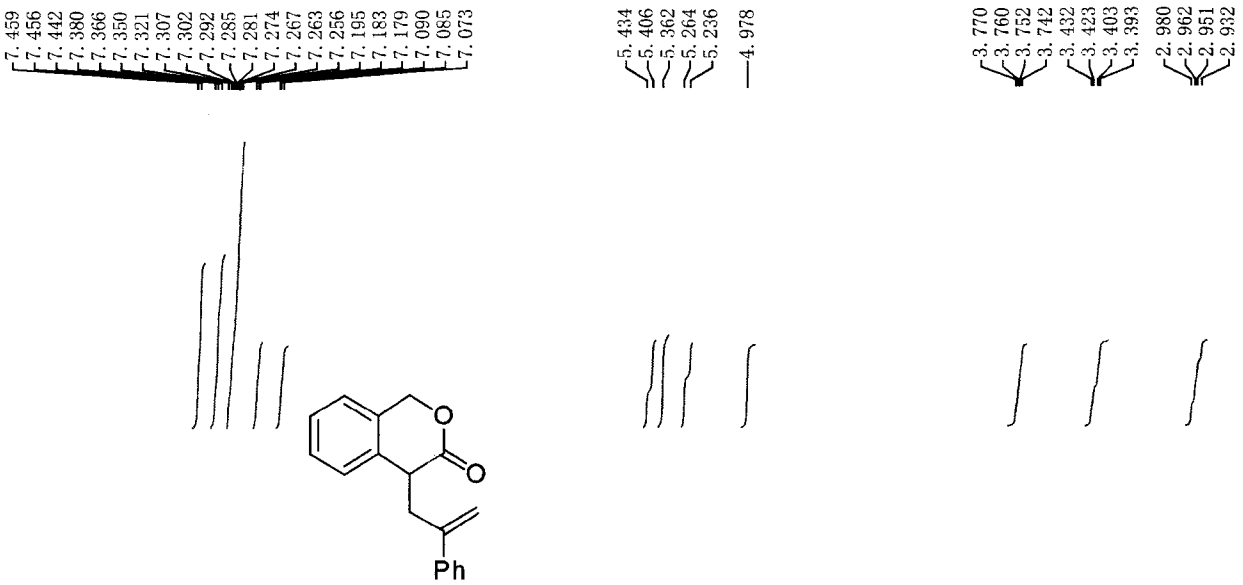
141.32
134.32
131.24
128.48
127.15
126.69
124.55
113.32
77.32
77.00
76.68
69.43
44.13
37.99
22.42
O
O
2m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.456
7.442
7.380
7.366
7.350
7.321
7.307
7.302
7.292
7.285
7.281
7.274
7.267
7.263
7.256
7.195
7.183
7.179
7.090
7.085
7.073
5.434
5.406
5.362
5.264
5.236
4.978
3.770
3.760
3.752
3.742
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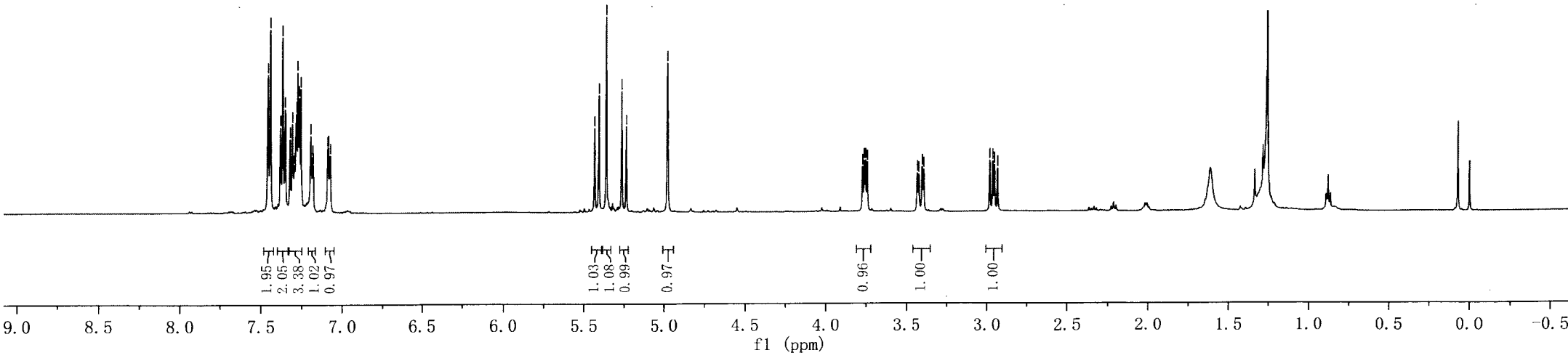
3.423
3.403
3.393
2.980
2.962
2.951
2.932
O
O
Ph

2n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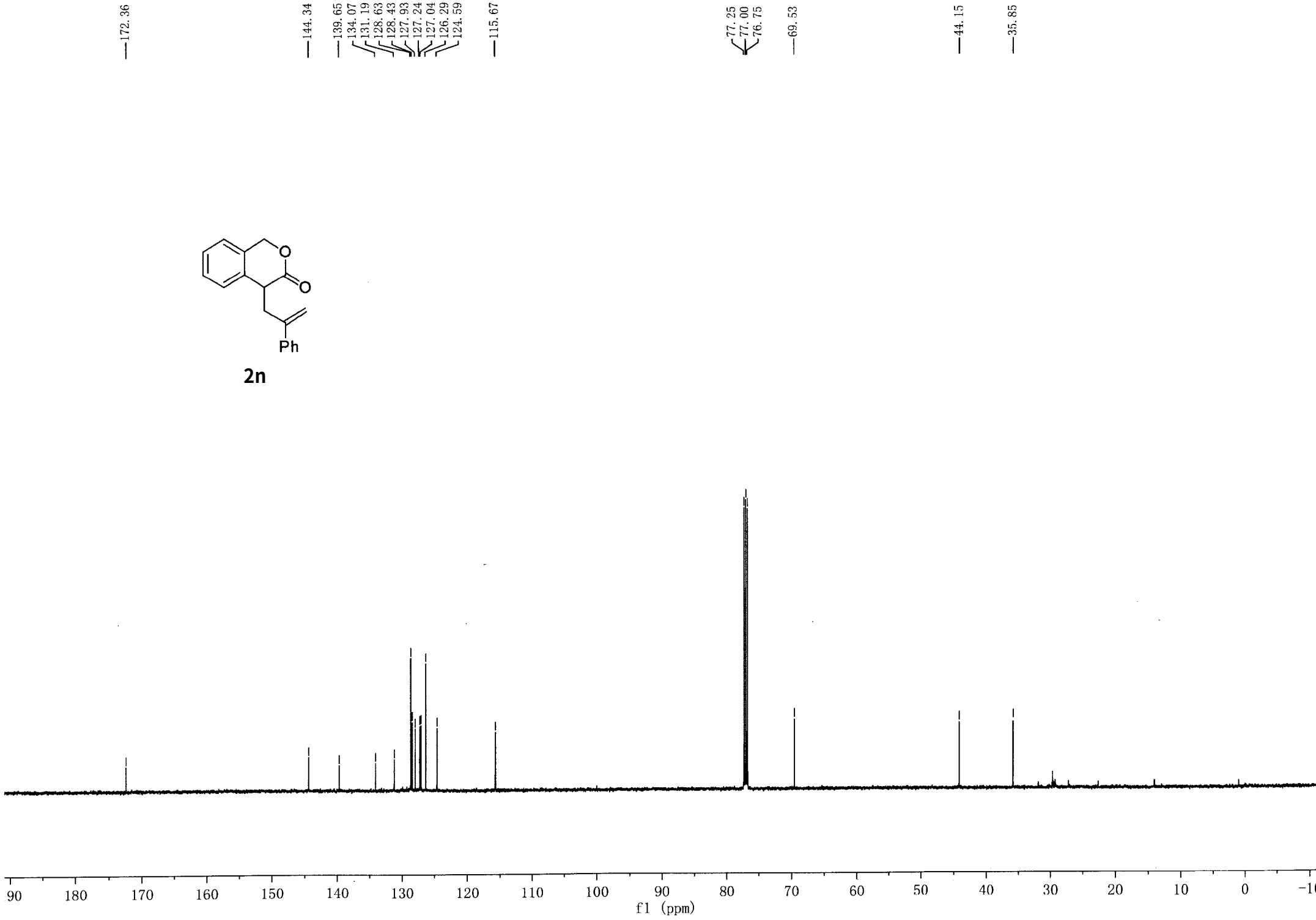
2.05
3.38
1.02
0.97
1.03
1.08
0.99
0.97
0.96
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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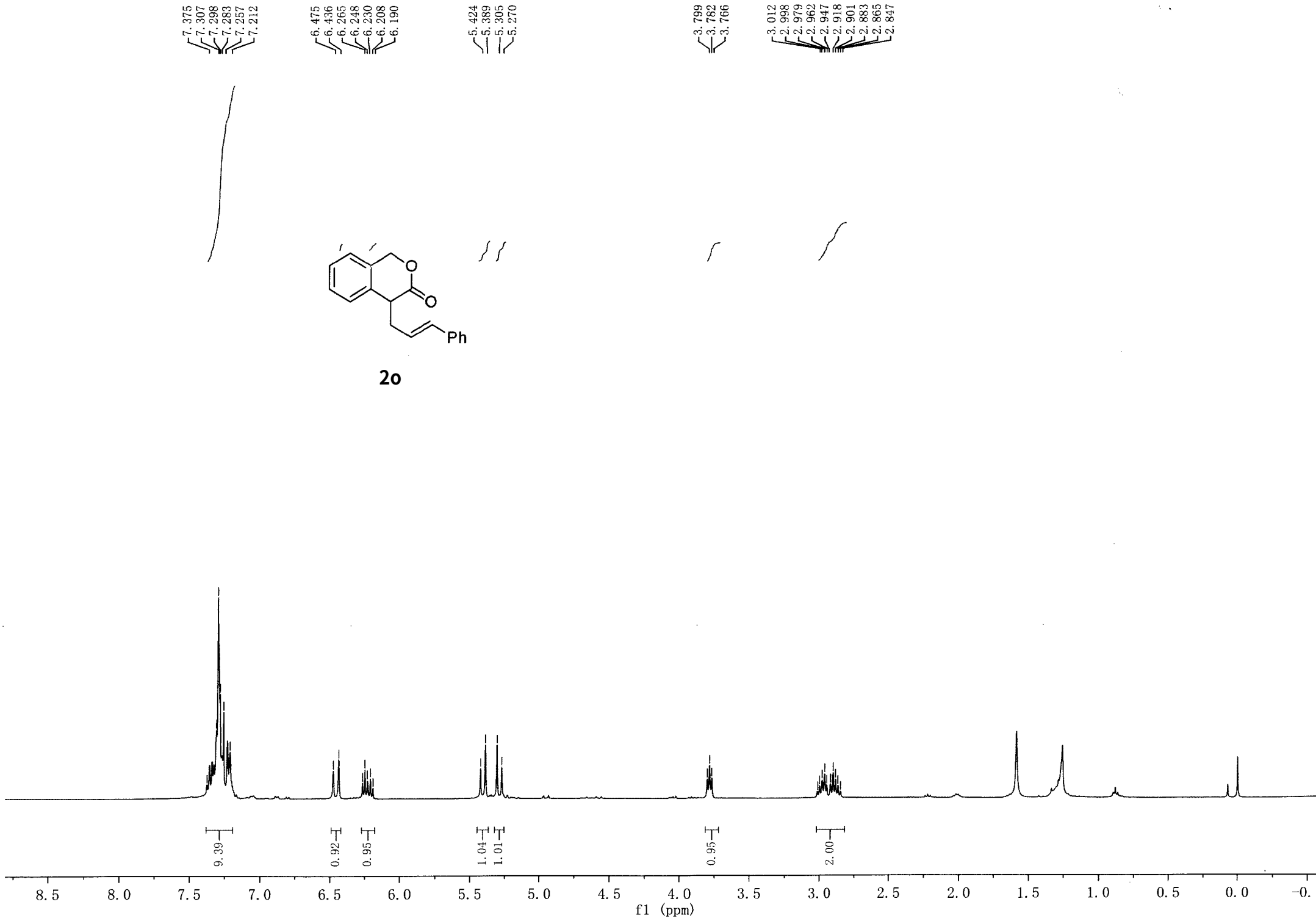
144.34
139.65
134.07
131.19
128.63
128.43
127.93
127.24
127.04
126.29
124.59
115.67
77.25
77.00
76.75
69.53
44.15
35.85
O
O
Ph
2n
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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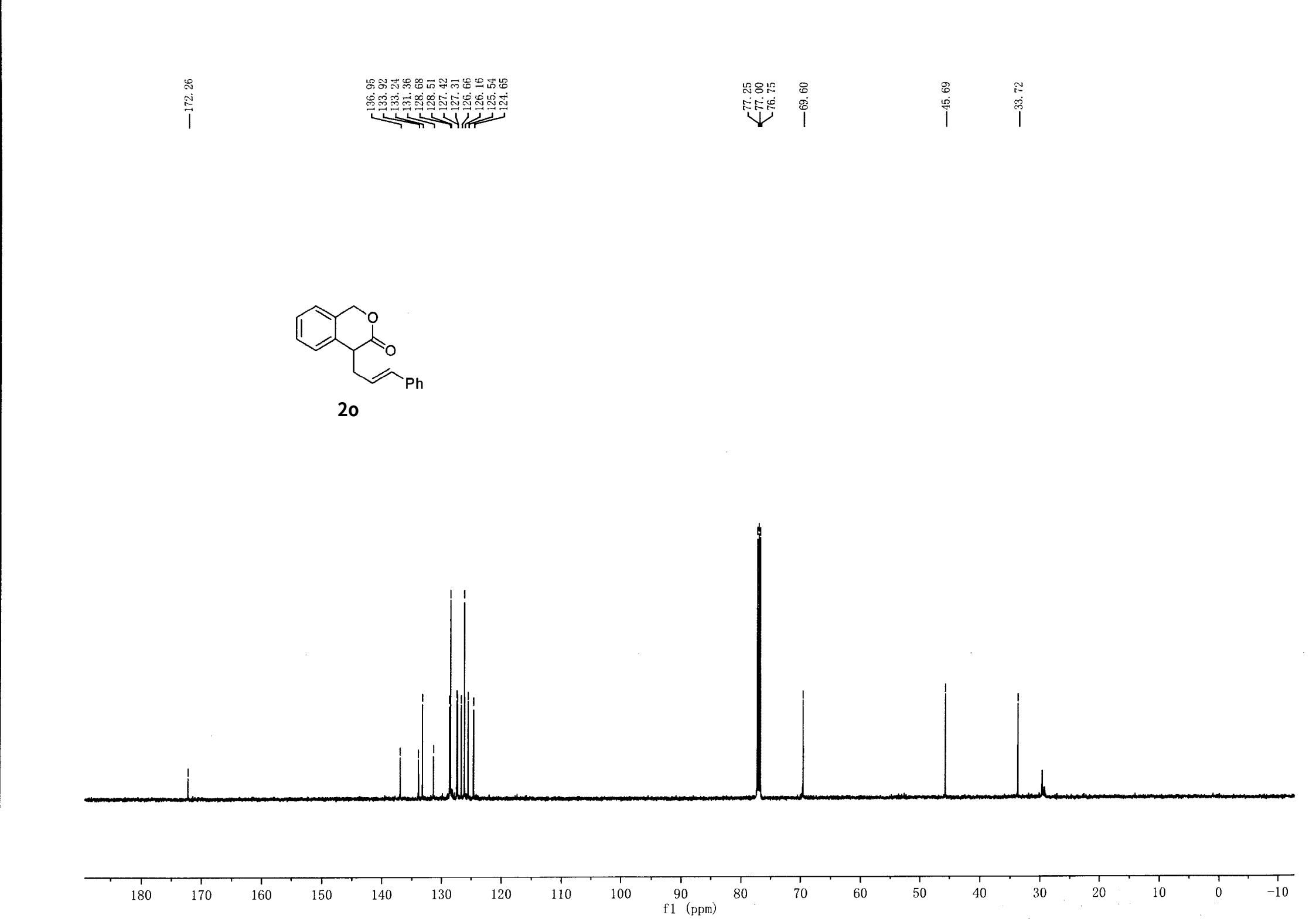
6.436
6.265
6.248
6.230
6.208
6.190
5.424
5.389
5.305
5.270
3.799
3.782
3.766
3.012
2.998
2.979
2.962
2.947
2.918
2.901
2.883
2.865
2.847
O
O
Ph
9.39
0.92
0.95
1.04
1.01
0.95
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2o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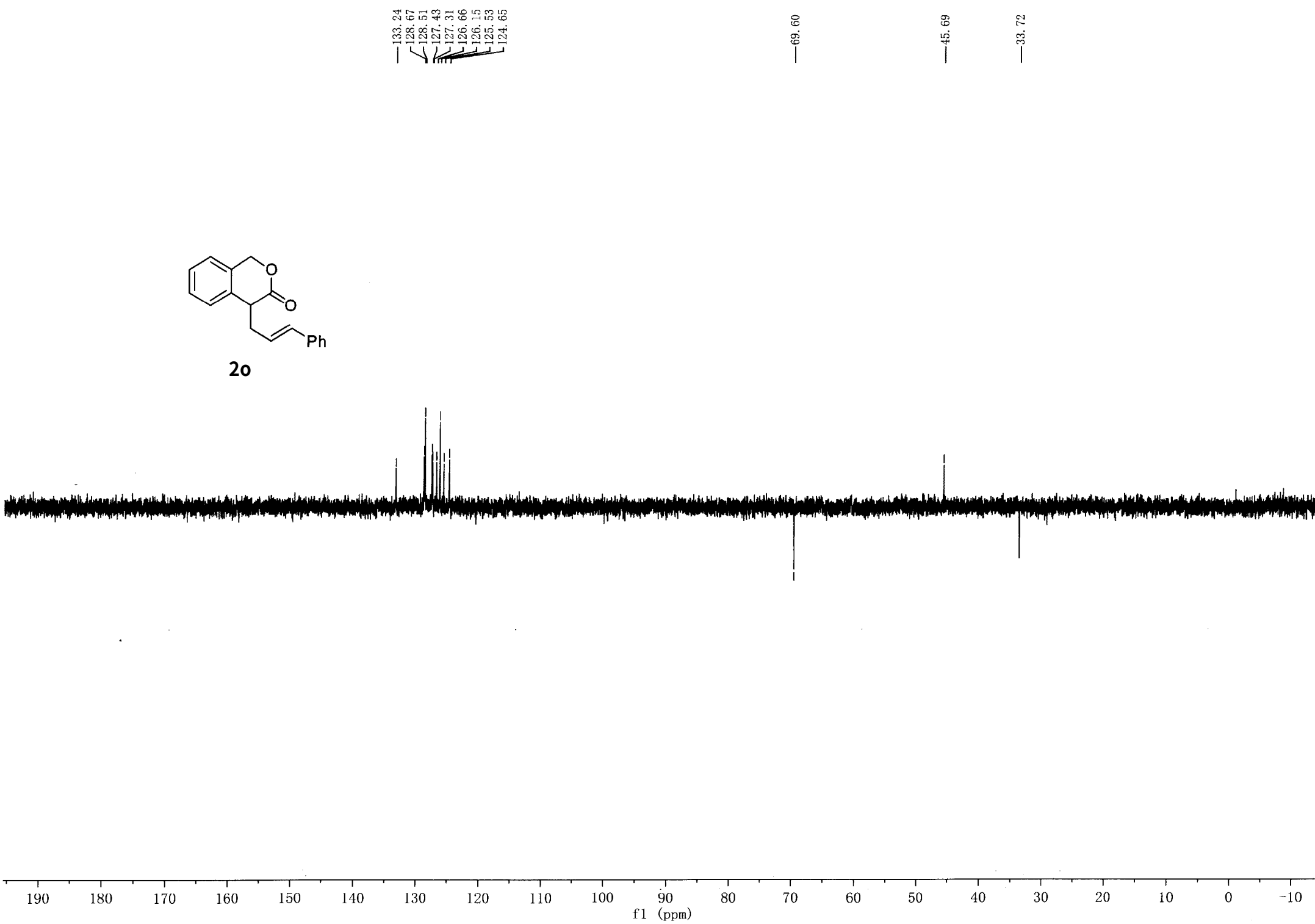
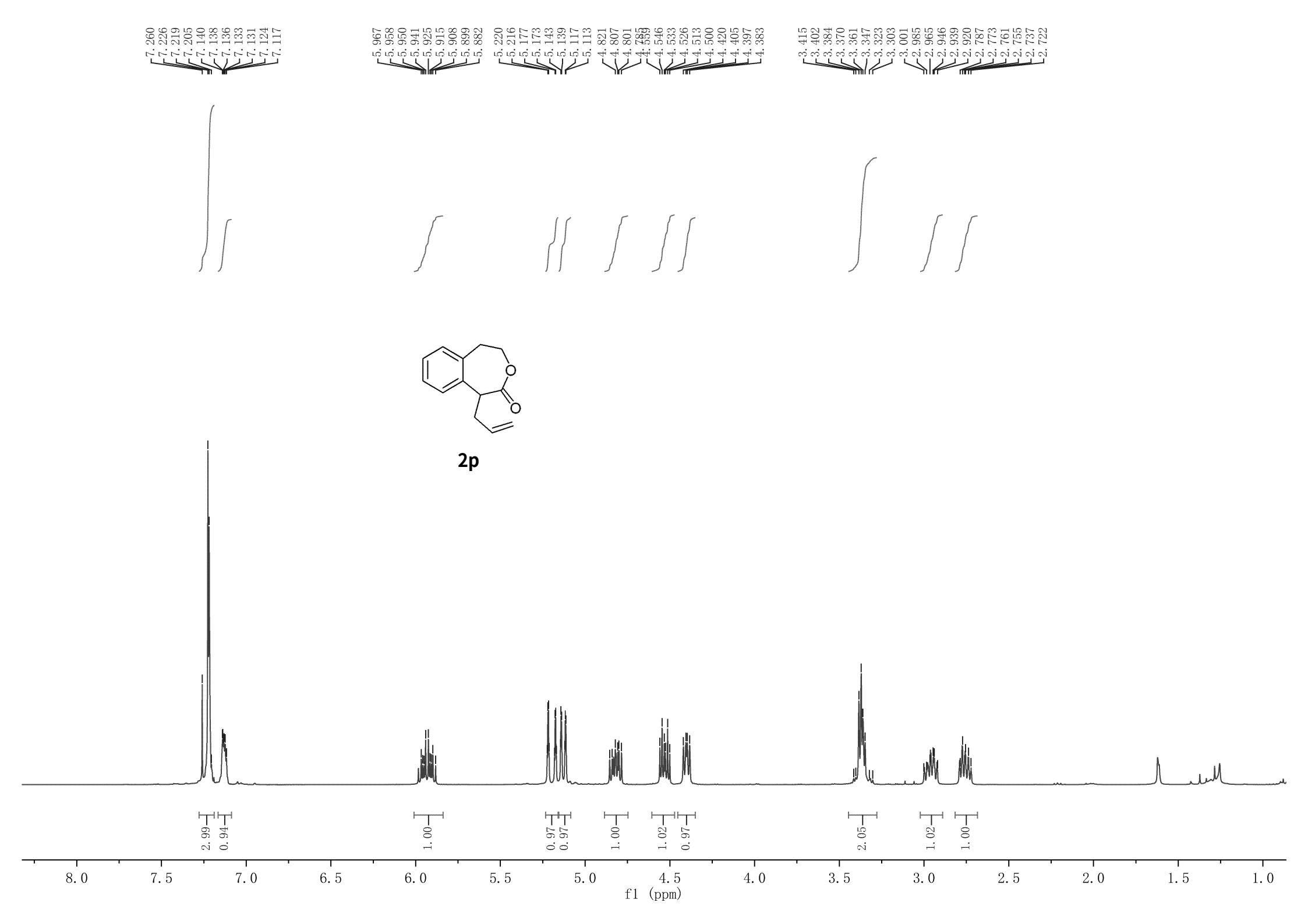
136.95
133.92
133.24
131.36
128.68
128.51
127.42
127.31
126.66
126.16
125.54
124.65
77.25
77.00
76.75
69.60
45.69
33.72
O
O
Ph
2o
f1 (ppm)


133.24
128.67
128.51
127.43
127.31
126.66
126.15
125.53
124.65
69.60
45.69
33.72
O
O
Ph
2o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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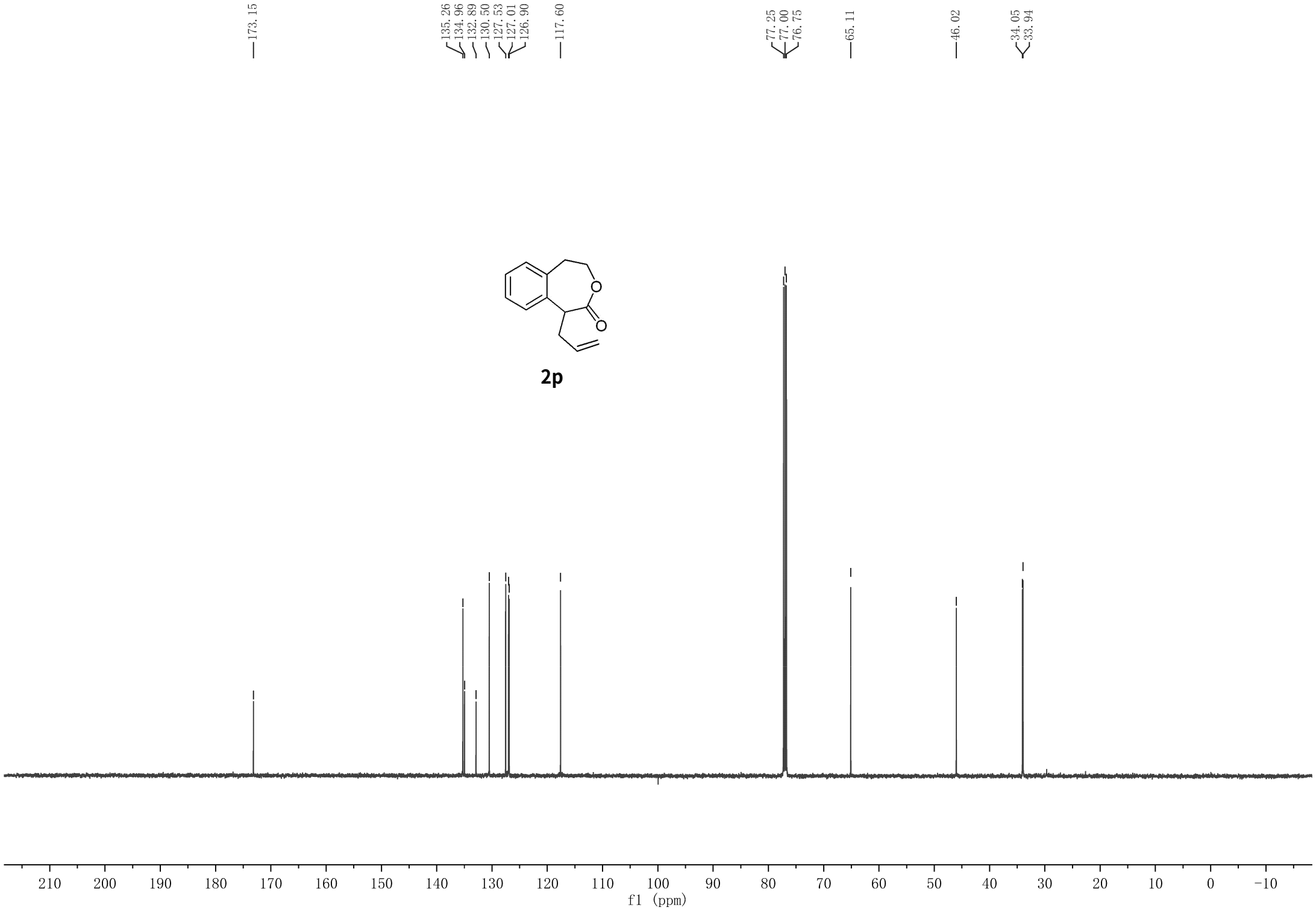
7.226
7.219
7.205
7.140
7.138
7.136
7.133
7.131
7.124
7.117
5.967
5.958
5.950
5.941
5.925
5.915
5.908
5.899
5.882
5.220
5.216
5.177
5.173
5.143
5.139
5.117
5.113
4.821
4.807
4.801
4.546
4.533
4.526
4.513
4.500
4.420
4.405
4.397
4.383
3.415
3.402
3.384
3.370
3.361
3.347
3.323
3.303
3.001
2.985
2.965
2.946
2.939
2.920
2.787
2.773
2.761
2.755
2.737
2.722
O
O
2p
2.99
0.94
1.00
0.97
0.97
1.00
1.02
0.97
2.05
1.02
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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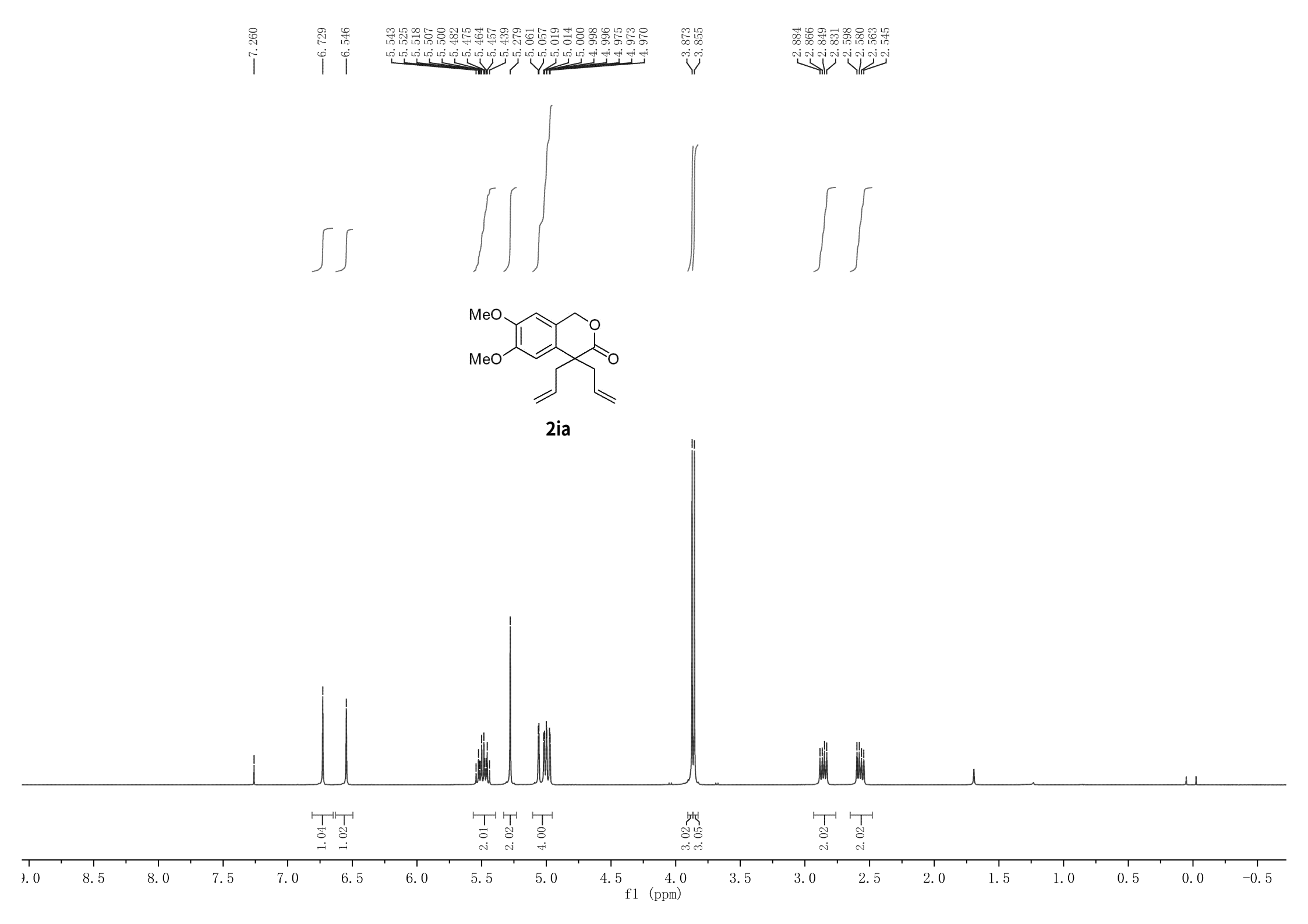
132.89
130.50
127.53
127.01
126.90
117.60
77.25
77.00
76.75
65.11
46.02
34.05
33.94
O
O
2p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.260
6.729
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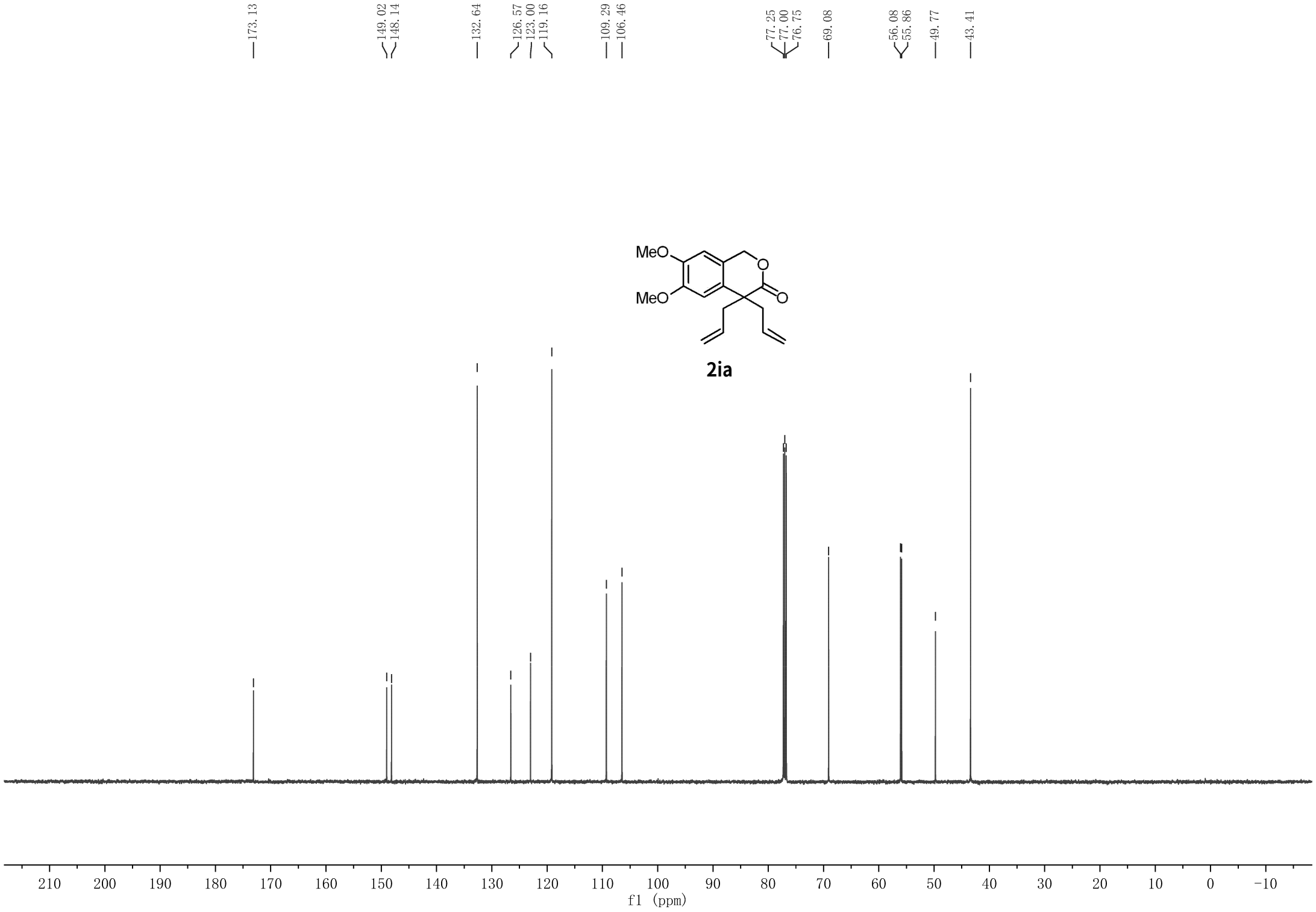
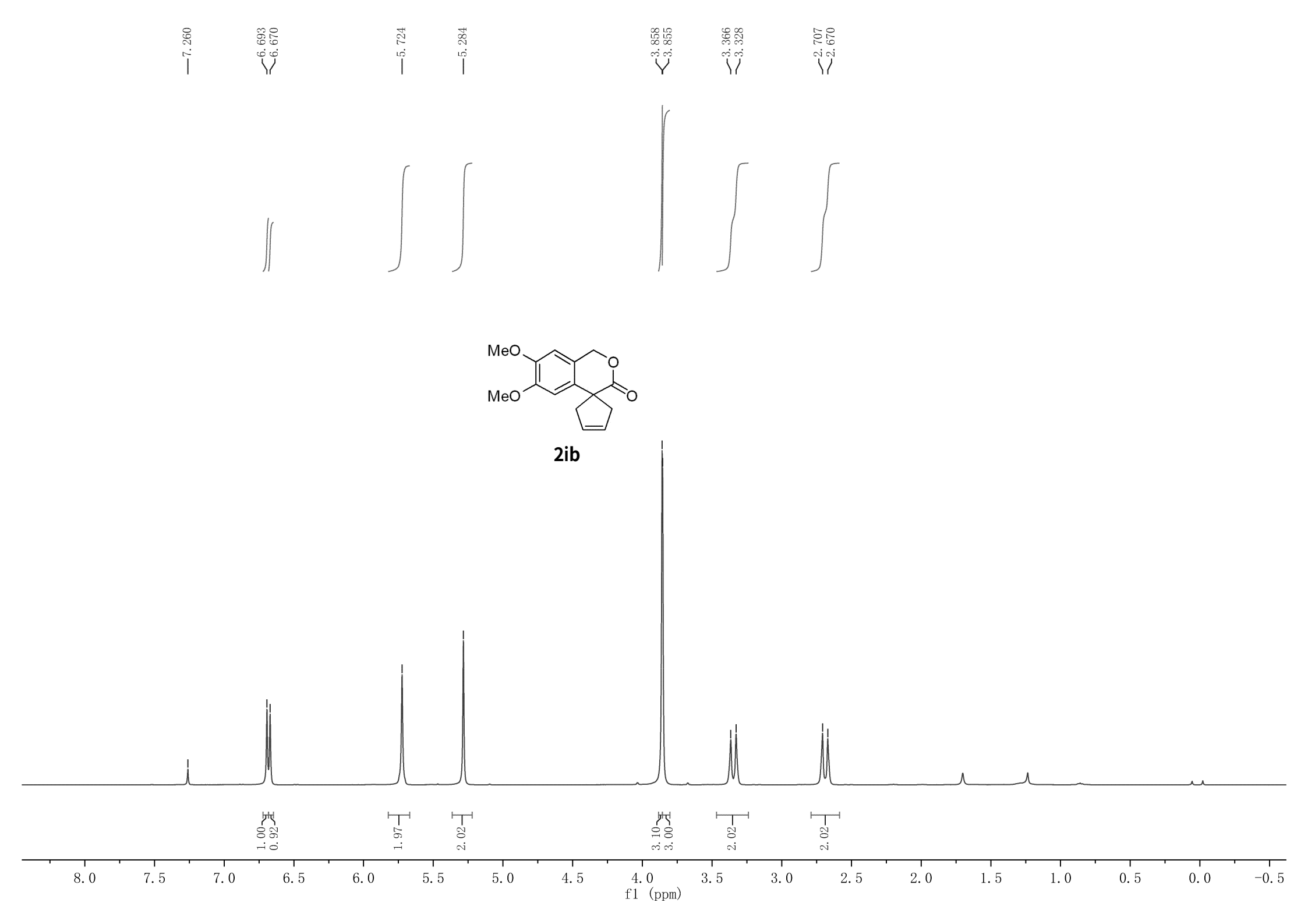
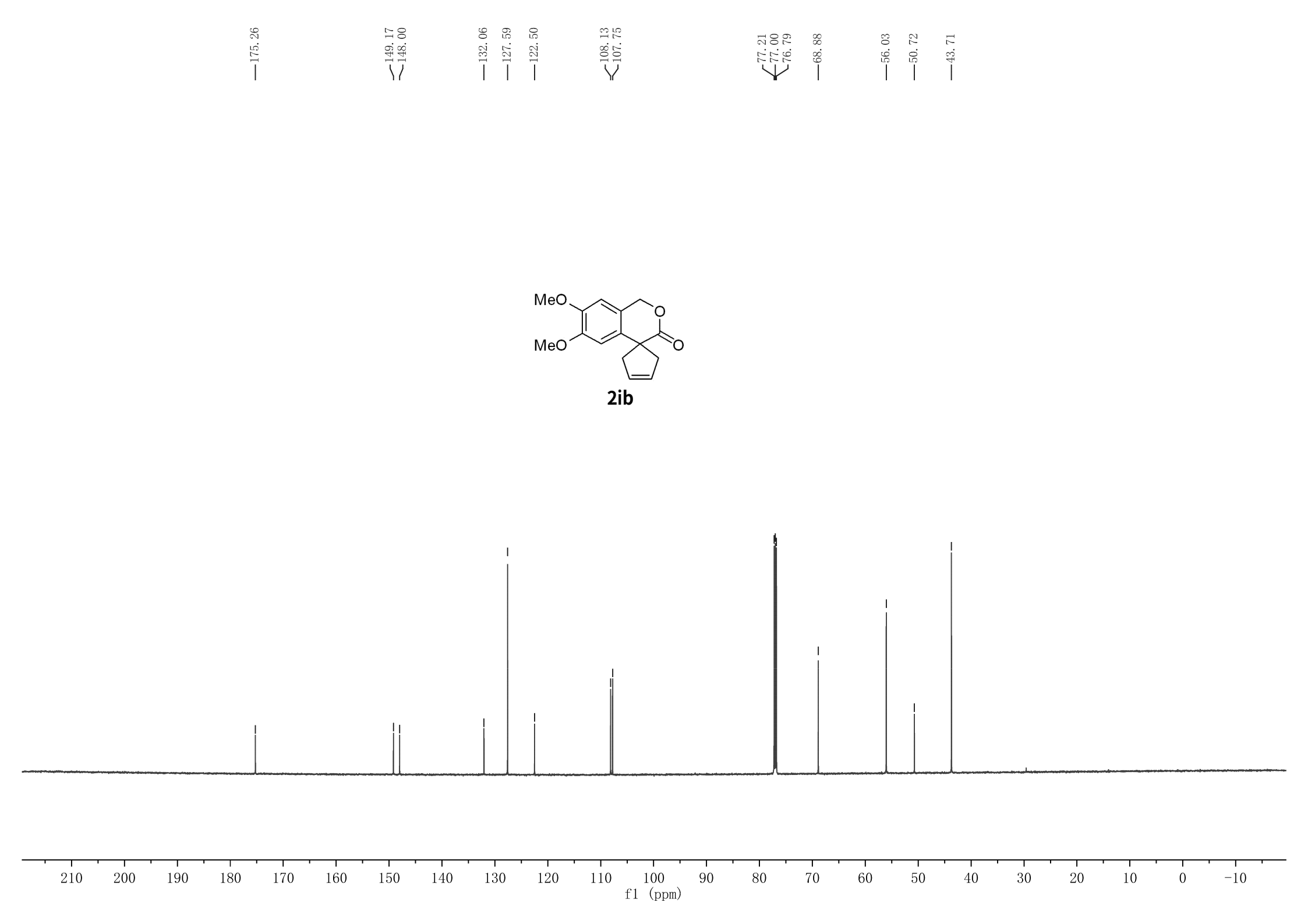
5.543
5.525
5.518
5.507
5.500
5.482
5.475
5.464
5.457
5.439
5.279
5.061
5.057
5.019
5.014
5.000
4.998
4.996
4.975
4.973
4.970
3.873
3.855
2.884
2.866
2.849
2.831
2.598
2.580
2.563
2.545
MeO
MeO
O
O
1.04
1.02
2.01
2.02
4.00
3.02
3.05
2.02
2.02
f1 (ppm)

2ia


173.13
149.02
148.14
132.64
126.57
123.00
119.16
109.29
106.46
77.25
77.00
76.75
69.08
56.08
55.86
49.77
43.41
MeO
MeO
O
O
2ia
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)


7.260
6.693
6.670
5.724
5.284
3.858
3.855
3.366
3.328
2.707
2.670
MeO
MeO
O
O
1.00
0.92
1.97
2.02
3.10
3.00
2.02
2.02
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)

2ib


175.26
149.17
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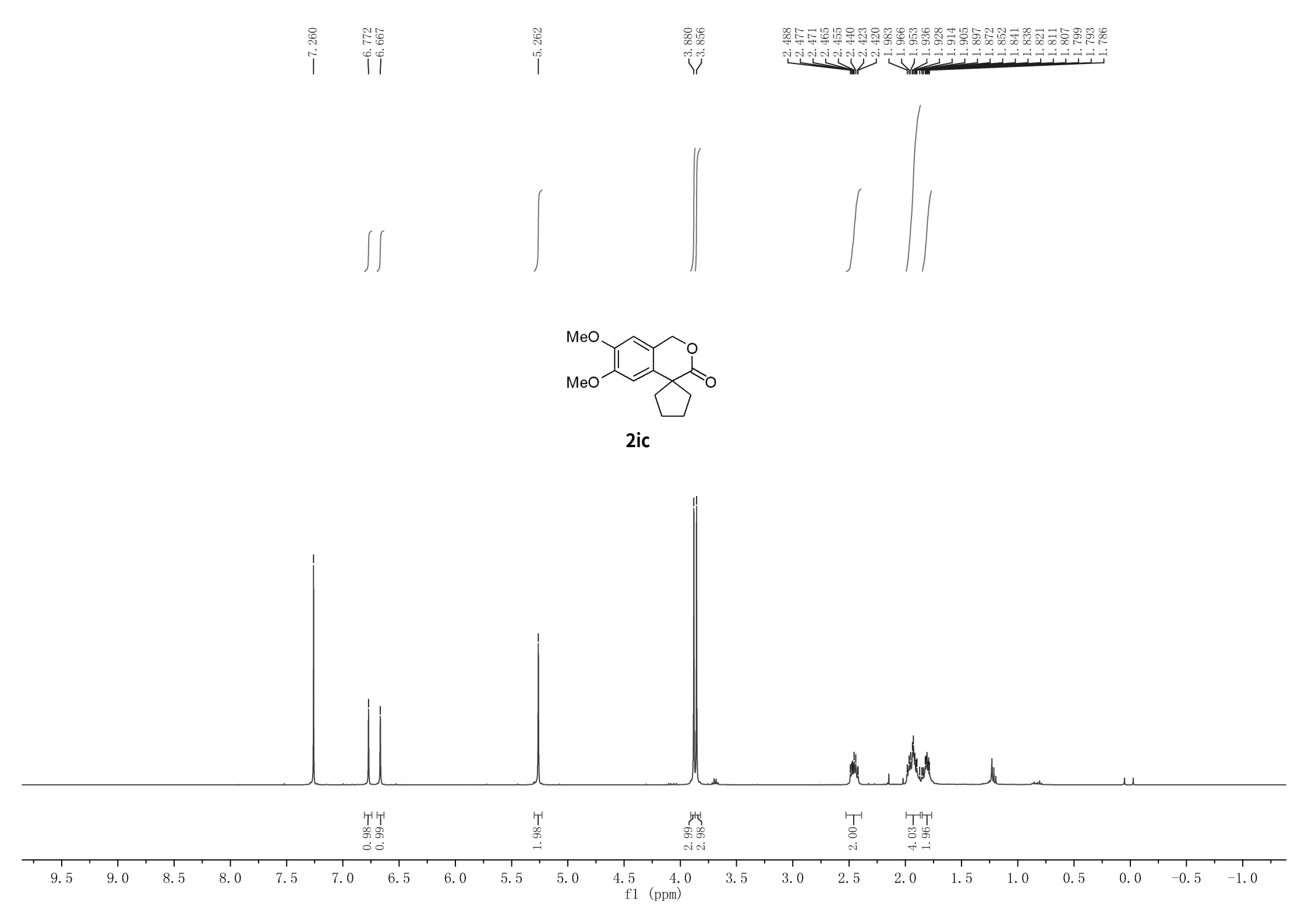
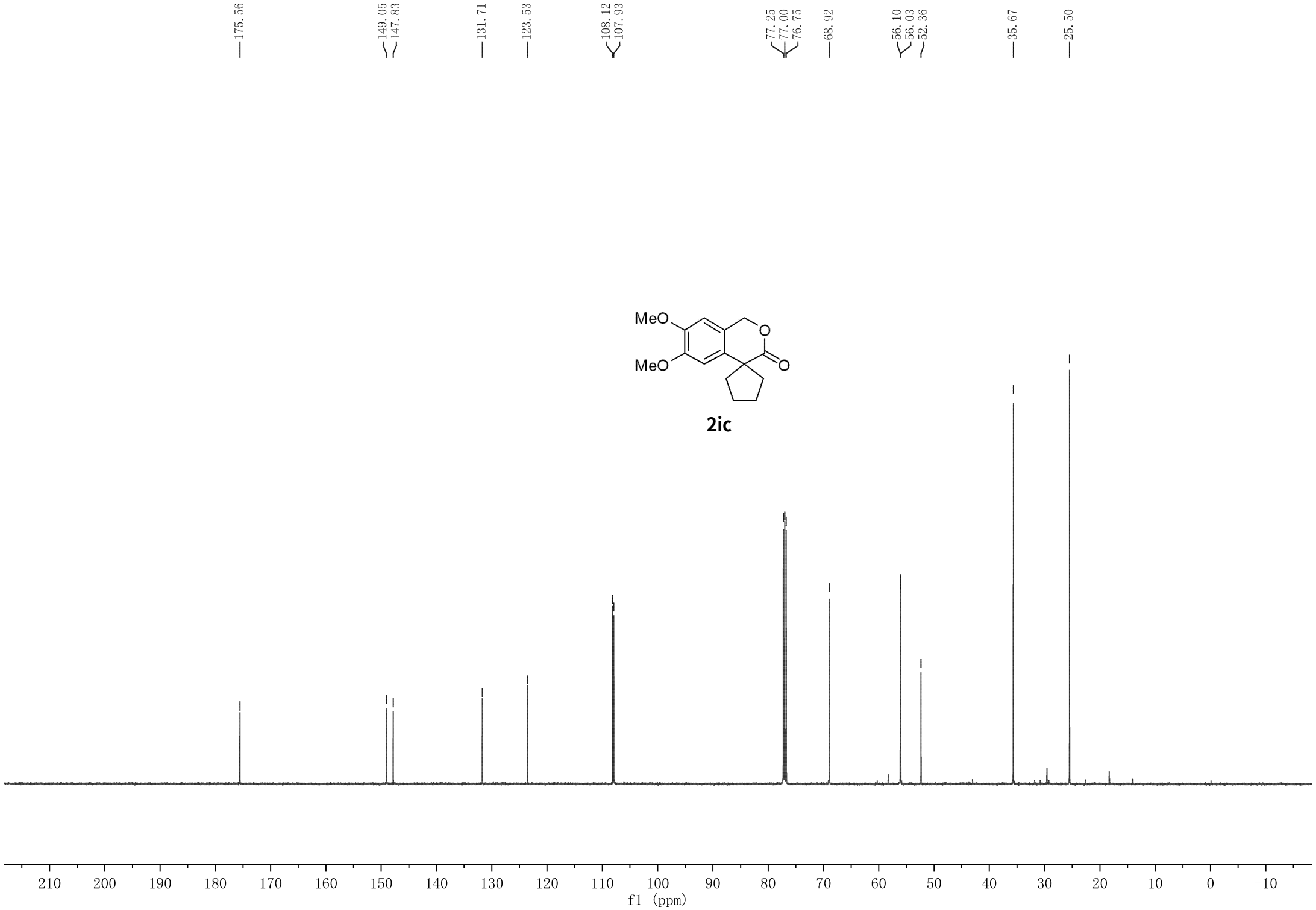
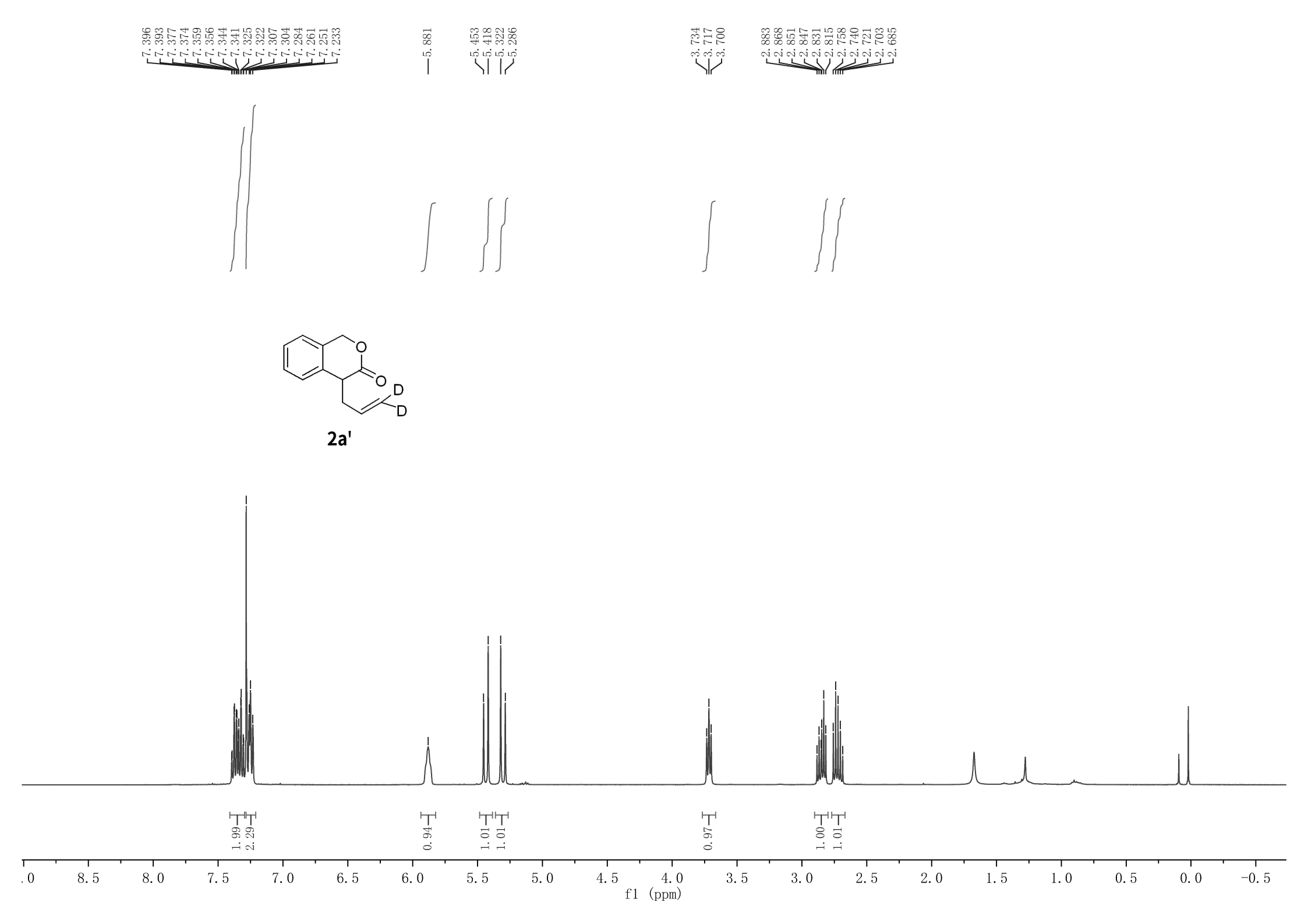
132.06
127.59
122.50
108.13
107.75
77.21
77.00
76.79
68.88
56.03
50.72
43.71
MeO
MeO
O
O
2ib
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

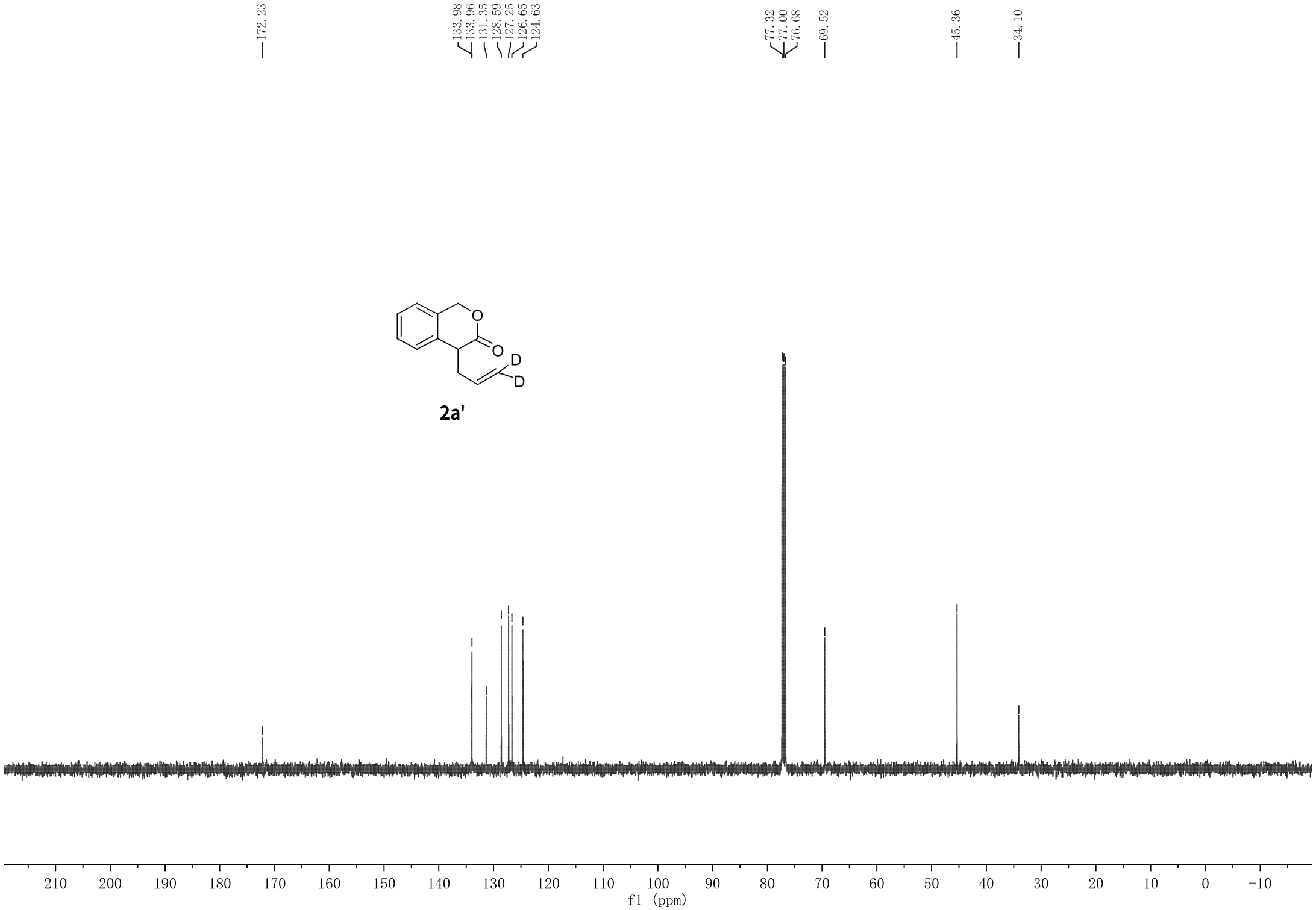

7.260
6.772
6.667
5.262
3.880
3.856
2.488
2.477
2.471
2.465
2.455
2.440
2.423
2.420
1.983
1.966
1.953
1.936
1.928
1.914
1.905
1.897
1.872
1.852
1.841
1.838
1.821
1.811
1.807
1.799
1.793
1.786
MeO
MeO
O
O
0.98
0.99
1.98
2.99
2.98
2.00
4.03
1.96
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

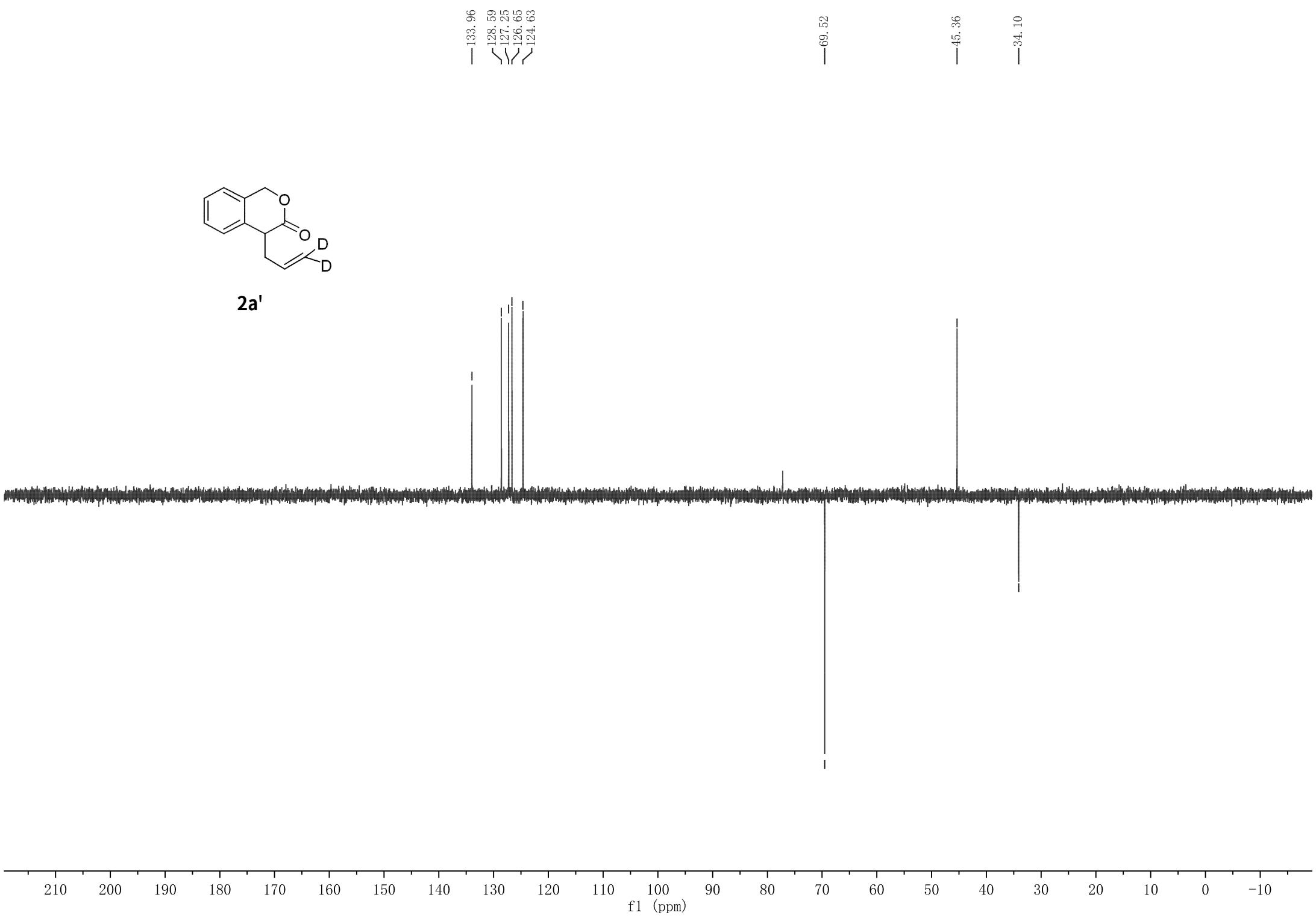
2ic


175.56
149.05
147.83
131.71
123.53
108.12
107.93
77.25
77.00
76.75
68.92
56.10
56.03
52.36
35.67
25.50
MeO
MeO
O
O
2ic
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)


7.396
7.393
7.377
7.374
7.359
7.356
7.344
7.341
7.325
7.322
7.307
7.304
7.284
7.261
7.251
7.233
5.881
5.453
5.418
5.322
5.286
3.734
3.717
3.700
2.883
2.868
2.851
2.847
2.831
2.815
2.758
2.740
2.721
2.703
2.685
O
O
D
D
1.99
2.29
0.94
1.01
1.01
0.97
1.00
1.01
f1 (ppm)

2a'


172.23
133.98
133.96
131.35
128.59
127.25
126.65
124.63
77.32
77.00
76.68
69.52
45.36
34.10
O
O
D
D
2a'
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)


133.96
128.59
127.25
126.65
124.63
69.52
45.36
34.10
O
O
D
D
2a'
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)