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Electrochemical-induced solvent-tuned selective C(sp3)-H bond activation towards the synthesis of C3-functionalized chromone derivatives

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Supporting Information

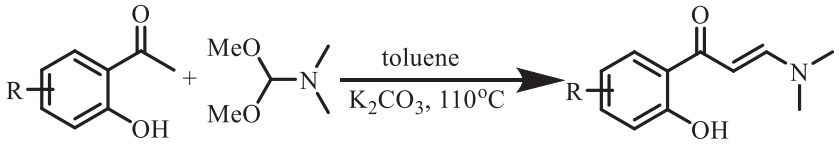
Contents

(A) Materials and equipment

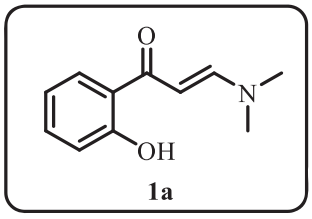
All solvents and reagents were obtained from commercial sources and were purified following the standard procedure before use. All glassware was oven-dried at 110 ℃ for hours and cooled down under a vacuum. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis was a dual-display potentiostat (DJS-292B) (made in China). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200- 300 mesh silica gel in petroleum (bp. 60-90℃). ^{1}H, ^{13}C, and ^{19}F NMR data for all compounds were recorded with Bruker Advance III (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are reported relative to tetramethylsilane and D-solvent peaks (77.00 ppm, chloroform), respectively. High resolution mass spectral analysis (HRMS) data were measured on a Waters Acquity UPLC I-Class plus Xevo G2-XS (Q-TOF) mass spectrum using the ESI technique. Crystallographic data were obtained from a Bruker D8 Ouest diffractometer.

(B) Typical experimental procedure

1. General procedure for the synthesis of enaminones **1**:



To a stirred solution of *o*-hydroxy aryl methyl ketone (5.0 mmol, 1.0 eq.) in toluene (5.0 mL), 1,1-dimethoxy-*N,N*-dimethylmethanamine (7.0 mmol, 1.4 eq.) was added and stirred at 110 ℃. After completion of the reaction (monitored by TLC), rotate and evaporate under vacuum and pressure at 60 ℃ to obtain the product, which turns into yellow solid after cooling. Wash the solid with petroleum ether with the aid of ultrasound and discard the supernatant. In this way, pure yellow solid can be obtained after three times of washing to give the enaminones **1**. [1]

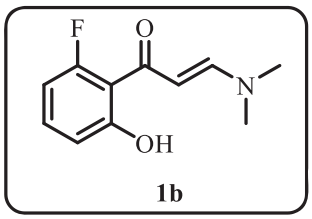


1a

(*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one (1a)

According to the general procedure, **1a** was obtained using 1-(2-hydroxyphenyl)ethan-1-one (680.3 mg, 5.0 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (834.1 mg, 929.9 μL, 7.0 mmol) in 95% yield (907.3 mg) as a yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.953 (s, 1H), 7.863 (d, *J* = 12.0 Hz, 1H), 7.697 - 7.673 (m, 1H), 7.360 - 7.318 (m, 1H), 6.932 - 6.908 (m, 1H), 6.827 - 6.786 (m, 1H), 5.763 (d, *J* = 12.0 Hz, 1H), 3.162 (s, 3H), 2.944 (s, 3H);



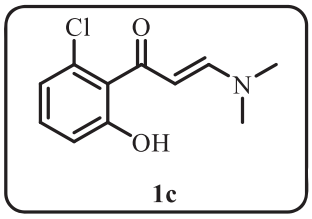
1b

(*E*)-3-(dimethylamino)-1-(2-fluoro-6-hydroxyphenyl)prop-2-en-1-one (1b)

According to the general procedure, **1b** was obtained using 1-(2-fluoro-6-hydroxyphenyl)ethan-1-one (770.2 mg, 5.0 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (834.1 mg, 929.9 μL, 7.0 mmol) in 84% yield (877.8 mg) as a yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ: 14.452 (s, 1H), 7.999 - 7.961 (m, 1H), 7.248 - 7.191 (m, 1H), 6.719 - 6.693 (m, 1H), 6.531 - 6.477 (m, 1H), 5.913 (d, *J* = 12.0 Hz, 1H), 3.190 (s, 3H), 2.951 (s, 3H);

^{19}F NMR (376 MHz, $CDCl_3$) δ: -107.20.

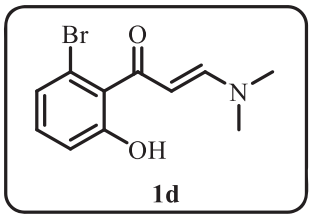


1c

(*E*)-1-(2-chloro-6-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one (1c)

According to the general procedure, **1c** was obtained using 1-(2-chloro-6-hydroxyphenyl)ethan-1-one (850.1 mg, 5.0 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (834.1 mg, 929.9 μL, 7.0 mmol) in 86% yield (967.5 mg) as a yellow solid

^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.134 (s, 1H), 7.885 (d, *J* = 12.0 Hz, 1H), 7.163 - 7.120 (m, 1H), 6.888 - 6.824 (m, 2H), 5.977 (d, *J* = 12.0 Hz, 1H), 3.193 (s, 3H), 2.954 (s, 3H);

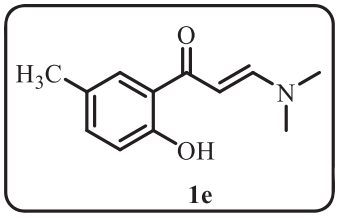


1d

(*E*)-1-(2-bromo-6-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one (1d)

According to the general procedure, **1d** was obtained using 1-(2-bromo-6-hydroxyphenyl)ethan-1-one (1069.6 mg, 5.0 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (834.1 mg, 929.9 μL, 7.0 mmol) in 88% yield (1183.6 mg) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.546 (s, 1H), 7.861 - 7.829 (m, 1H), 7.118 - 7.046 (m, 2H), 6.907 - 6.884 (m, 1H), 5.933 (d, *J* = 12.4 Hz, 1H), 3.200 (s, 3H), 2.972 (s, 3H);

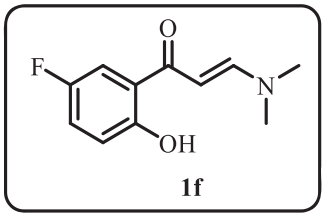


1e

(*E*)-3-(dimethylamino)-1-(2-hydroxy-5-methylphenyl)prop-2-en-1-one (1e)

According to the general procedure, **1e** was obtained using 1-(2-hydroxy-5-methylphenyl)ethan-1-one (750.3 mg, 5.0 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (834.1 mg, 929.9 μL, 7.0 mmol) in 92% yield (943.1 mg) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.705 (s, 1H), 7.890 - 7.847 (m, 1H), 7.470 - 7.465 (m, 1H), 7.179 - 7.152 (m, 1H), 6.850 - 6.823 (m, 1H), 5.790 - 5.750 (m, 1H), 3.180 (s, 3H), 2.983 (s, 3H), 2.296 (s, 3H);



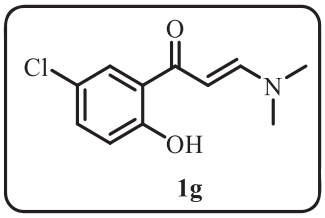
1f

(*E*)-3-(dimethylamino)-1-(5-fluoro-2-hydroxyphenyl)prop-2-en-1-one (1f)

According to the general procedure, **1f** was obtained using 1-(5-fluoro-2-hydroxyphenyl)ethan-1-one (770.2 mg, 5.0 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (834.1 mg, 929.9 μL, 7.0 mmol) in 93% yield (971.9 mg) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.627 (s, 1H), 7.899 (d, *J* = 12.0 Hz, 1H), 7.364 - 7.332 (m, 1H), 7.103 - 7.053 (m, 1H), 6.897 - 6.862 (m, 1H), 5.659 (d, *J* = 12.0 Hz, 1H), 3.211 (s, 3H), 2.987 (s, 3H);

^{19}F NMR (376 MHz, $CDCl_3$) δ: -125.90.

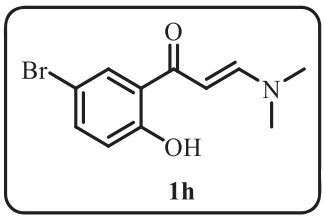


1g

(*E*)-1-(5-chloro-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one (1g)

According to the general procedure, **1g** was obtained using 1-(5-chloro-2-hydroxyphenyl)ethan-1-one (850.1 mg, 5.0 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (834.1 mg, 929.9 μL, 7.0 mmol) in 86% yield (967.5 mg) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.157 (s, 1H), 7.899 (d, *J* = 10.0 Hz, 1H), 7.628 - 7.621 (m, 1H), 7.295 - 7.267 (m, 1H), 6.874 (d, *J* = 8.8 Hz, 1H), 5.676 (d, *J* = 12.0 Hz, 1H), 3.208 (s, 3H), 2.995 (s, 3H);

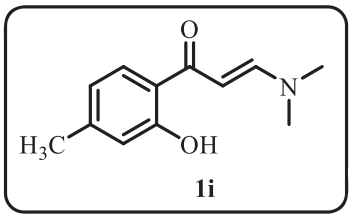


1h

(*E*)-1-(5-bromo-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one (1h)

According to the general procedure, **1h** was obtained using 1-(5-bromo-2-hydroxyphenyl)ethan-1-one (1069.8 mg, 5.0 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (834.1 mg, 929.9 μL, 7.0 mmol) in 83% yield (1120.5 mg) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.946 (s, 1H), 7.883 (d, *J* = 12.0 Hz, 1H), 7.760 - 7.754 (m, 1H), 7.418 - 7.389 (m, 1H), 6.822 (d, *J* = 8.8 Hz, 1H), 5.662 (d, *J* = 12.0 Hz, 1H), 3.200 (s, 3H), 2.987 (s, 3H);

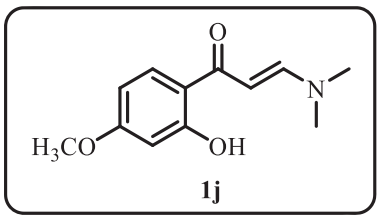


1i

(*E*)-3-(dimethylamino)-1-(2-hydroxy-4-methylphenyl)prop-2-en-1-one (1i)

According to the general procedure, **1i** was obtained using 1-(2-hydroxy-4-methylphenyl)ethan-1-one (750.3 mg, 5.0 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (834.1 mg, 929.9 μL, 7.0 mmol) in 82% yield (840.5 mg) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.815 (s, 1H), 7.853 (d, *J* = 12.0 Hz, 1H), 7.571 (d, *J* = 8.4 Hz, 1H), 6.741 (s, 1H), 6.637 - 6.612 (m, 1H), 5.741 (d, *J* = 12.0 Hz, 1H), 3.167 (s, 3H), 2.953 (s, 3H), 2.314 (s, 3H);

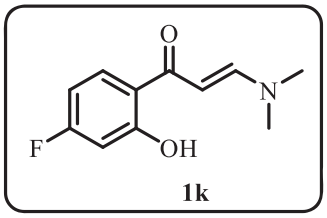


1j

(*E*)-3-(dimethylamino)-1-(2-hydroxy-4-methoxyphenyl)prop-2-en-1-one (1j)

According to the general procedure, **1j** was obtained using 1-(2-hydroxy-4-methoxyphenyl)ethan-1-one (830.3 mg, 5.0 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (834.1 mg, 929.9 μL, 7.0 mmol) in 80% yield (884.4 mg) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.393 (s, 1H), 7.866 (d, *J* = 12.0 Hz, 1H), 7.180 (s, 1H), 6.999 -6.972 (m, 1H), 6.879 - 6.857 (m, 1H), 5.705 (d, *J* = 12.0 Hz, 1H), 3.786 (s, 3H), 3.173 (s, 3H), 2.951 (s, 3H);



1k

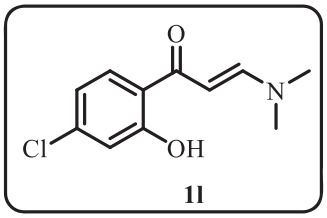
(*E*)-3-(dimethylamino)-1-(4-fluoro-2-hydroxyphenyl)prop-2-en-1-one (1k)

According to the general procedure, **1k** was obtained using 1-(4-fluoro-2-hydroxyphenyl)ethan-1-one (770.2 mg, 5.0 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (834.1 mg, 929.9 μL, 7.0

mmol) in 87% yield (909.1 mg) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 14.422 (s, 1H), 7.884 - 7.850 (m, 1H), 7.686 - 7.647 (m, 1H), 6.614 - 6.581 (m, 1H), 6.534 - 6.485 (m, 1H), 5.661 (d, *J* = 12.0 Hz, 1H), 3.186 (s, 3H), 2.960 (s, 3H);

^{19}F NMR (376 MHz, $CDCl_3$) δ: -104.34.

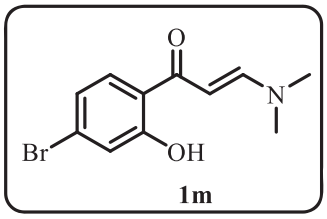


1l

(*E*)-1-(4-chloro-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one (1l)

According to the general procedure, **1l** was obtained using 1-(4-chloro-2-hydroxyphenyl)ethan-1-one (840.1 mg, 5.0 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (834.1 mg, 929.9 μL, 7.0 mmol) in 86% yield (967.5 mg) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.930 (s, 1H), 7.890 (d, *J* = 12.0 Hz, 1H), 7.595 (d, *J* = 8.8 Hz, 1H), 6.938 - 6.933 (m, 1H), 6.792 - 6.765 (m, 1H), 5.690 (d, *J* = 12.0 Hz, 1H), 3.206 (s, 3H), 2.980 (s, 3H);

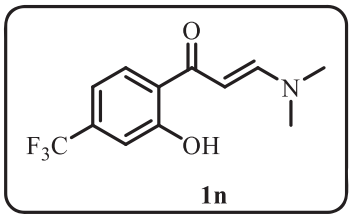


1m

(*E*)-1-(4-bromo-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one (1m)

According to the general procedure, **1m** was obtained using 1-(4-bromo-2-hydroxyphenyl)ethan-1-one (1069.8 mg, 5.0 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (834.1 mg, 929.9 μL, 7.0 mmol) in 88% yield (1183.6 mg) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.156 (s, 1H), 7.892 (d, *J* = 8.0 Hz, 1H), 7.506 (d, *J* = 8.4 Hz, 1H), 7.112 - 7.107 (m, 1H), 6.945 - 6.919 (m, 1H), 5.690 (d, *J* = 12.0 Hz, 1H), 3.203 (s, 3H), 2.978 (s, 3H);



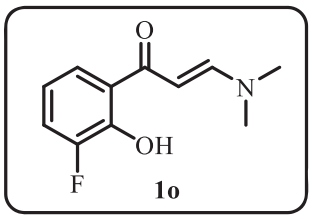
1n

(*E*)-3-(dimethylamino)-1-(2-hydroxy-4-(trifluoromethyl)phenyl)prop-2-en-1-one (1n)

According to the general procedure, **1n** was obtained using 1-(2-hydroxy-4-(trifluoromethyl)phenyl)ethan-1-one (1020.5 mg, 5.0 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (834.1 mg, 929.9 μL, 7.0 mmol) in 81% yield (1048.9 mg) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 14.064 (s, 1H), 7.928 (d, *J* = 12.0 Hz, 1H), 7.746 (d, *J* = 8.4 Hz, 1H), 7.178 - 7.173 (m, 1H), 7.039 - 7.013 (m, 1H), 5.751 (d, *J* = 12.0 Hz, 1H), 3.225 (s, 3H), 3.002 (s, 3H);

^{19}F NMR (376 MHz, $CDCl_3$) δ: -63.48.



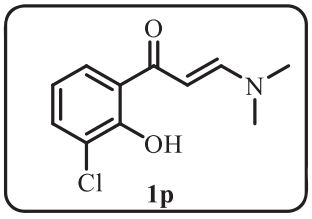
1o

(*E*)-3-(dimethylamino)-1-(3-fluoro-2-hydroxyphenyl)prop-2-en-1-one (1o)

According to the general procedure, **1o** was obtained using 1-(3-fluoro-2-hydroxyphenyl)ethan-1-one (770.2 mg, 5.0 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (834.1 mg, 929.9 μL, 7.0 mmol) in 95% yield (992.7 mg) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.630 (s, 1H), 7.893 (d, *J* = 12.0 Hz, 1H), 7.361 - 7.329 (m, 1H), 7.100 - 7.050 (m, 1H), 6.893 - 6.858 (m, 1H), 5.654 (d, *J* = 12.0 Hz, 1H), 3.204 (s, 3H), 2.979 (s, 3H);

^{19}F NMR (376 MHz, $CDCl_3$) δ: -125.88.

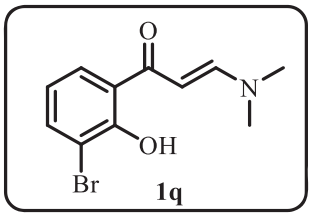


1p

(*E*)-1-(3-chloro-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one (1p)

According to the general procedure, **1p** was obtained using 1-(3-chloro-2-hydroxyphenyl)ethan-1-one (850.1 mg, 5.0 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (834.1 mg, 929.9 μL, 7.0 mmol) in 90% yield (1012.5 mg) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.940 (s, 1H), 7.888 - 7.852 (m, 1H), 7.617 - 7.610 (m, 1H), 7.282 - 7.254 (m, 1H), 6.872 - 6.849 (m, 1H), 5.674 - 5.639 (m, 1H), 3.178 (s, 3H), 2.961 (s, 3H);

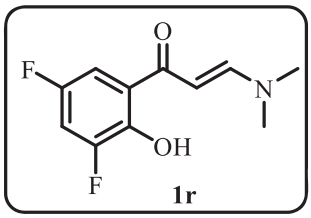


1q

(*E*)-1-(3-bromo-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one (1q)

According to the general procedure, **1q** was obtained using 1-(3-bromo-2-hydroxyphenyl)ethan-1-one (1069.8 mg, 5.0 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (834.1 mg, 929.9 μL, 7.0 mmol) in 91% yield (1223.9 mg) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.007 (s, 1H), 7.943 - 7.913 (m, 1H), 7.661 - 7.637 (m, 1H), 7.622 -7.598 (m, 1H), 6.728 - 6.689 (m, 1H), 5.748 (d, *J* = 12.0 Hz, 1H), 3.214 (s, 3H), 2.989 (s, 3H);



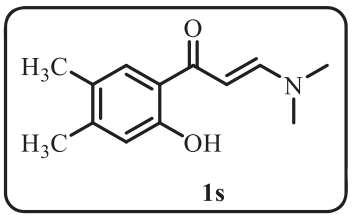
1r

(*E*)-1-(3,5-difluoro-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one (1r)

According to the general procedure, **1r** was obtained using 1-(3,5-difluoro-2-hydroxyphenyl)ethan-1-one (860.1mg, 5.0 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (834.1 mg, 929.9 μL, 7.0 mmol) in 95% yield (1078.3 mg) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.934 (s, 1H), 7.925 (d, *J* = 12.0 Hz, 1H), 7.177 - 7.141 (m, 1H), 6.993 - 6.939 (m, 1H), 5.617 (d, *J* = 12.0 Hz, 1H), 3.232 (s, 3H), 3.002 (s, 3H);

^{19}F NMR (376 MHz, $CDCl_3$) δ: -123.96, -133.32.

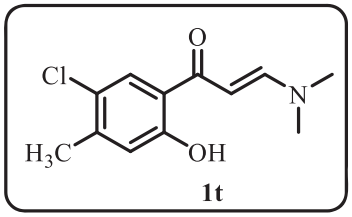


1s

(*E*)-3-(dimethylamino)-1-(2-hydroxy-4,5-dimethylphenyl)prop-2-en-1-one (1s)

According to the general procedure, **1s** was obtained using 1-(2-hydroxy-4,5-dimethylphenyl)ethan-1-one (820.2 mg, 5.0 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (834.1 mg, 929.9 μL, 7.0 mmol) in 95% yield (1040.7 mg) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.737 (s, 1H), 7.823 (d, *J* = 12.0 Hz, 1H), 7.401 (s, 1H), 6.716 (s, 1H), 5.734 (d, *J* = 12.0 Hz, 1H), 3.142 (s, 3H), 2.947 (s, 3H), 2.218 (s, 3H), 2.192 (s, 3H);

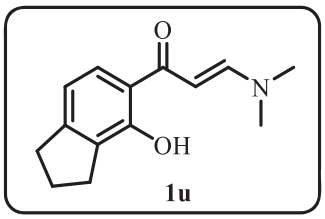


1t

(*E*)-1-(5-chloro-2-hydroxy-4-methylphenyl)-3-(dimethylamino)prop-2-en-1-one (1t)

According to the general procedure, **1t** was obtained using 1-(5-chloro-2-hydroxy-4-methylphenyl)ethan-1-one (920.2 mg, 5.0 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (834.1 mg, 929.9 μL, 7.0 mmol) in 88% yield (1052.1 mg) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.834 (s, 1H), 7.882 - 7.842 (m, 1H), 7.615 - 7.606 (m, 1H), 6.808 - 6.798 (m, 1H), 5.671 - 5.634 (m, 1H), 3.188 (s, 3H), 2.975 (m, 3H), 2.335 (s, 3H);



1u

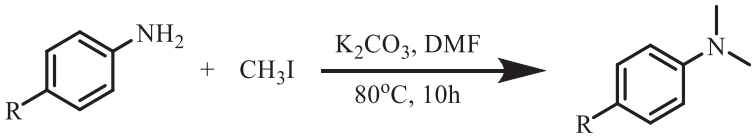
(*E*)-3-(dimethylamino)-1-(4-hydroxy-2,3-dihydro-1H-inden-5-yl)prop-2-en-1-one (1u)

According to the general procedure, **1u** was obtained using 1-(4-hydroxy-2,3-dihydro-1H-inden-5-yl)ethan-1-one (880.4 mg, 5.0 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (834.1 mg, 929.9 μL, 7.0 mmol) in 80% yield (924.4 mg) as a yellow solid.

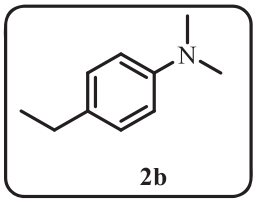
^{1}H NMR (400 MHz, $CDCl_3$) δ: 14.086 (s, 1H), 7.854 (d, *J* = 12.0 Hz, 1H), 7.535 (d, *J* = 8.0 Hz,

1H), 6.716 (d, *J* = 8.0 Hz, 1H), 5.773 (d, *J* = 12.4 Hz, 1H), 3.170 (s, 3H), 2.968 - 2.895 (m, 7H), 2.137 - 2.062 (m, 2H);

2. General procedure for the synthesis of **2**:



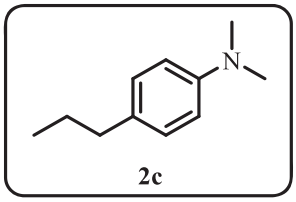
Namely, a mixture of aniline (5.0 mmol), iodomethane (11.0 mmol), and K_2CO_3 (11.0 mmol) in DMF (20 mL) was stirred at 80 °C for 10 h. The reaction was then cooled and diluted with EtOAc (100 mL) and H_2O (100 mL). The layers were separated and the organic layer was washed with brine (20 mL), dried over Na_2SO_4, filtered, concentrated, and purified by flash chromatography to give the products **2**.[2]



4-ethyl-*N*,*N*-dimethylaniline (2b)

According to the general procedure, **2b** was obtained using 4-ethylaniline (605.4 mg, 5.0 mmol) and iodomethane (1561.3 mg, 684.8 μL, 11 mmol) in 60% yield (447.3 mg) as a yellow oily liquid. (silica gel flash chromatography: petroleum ether/EtOAc = 80:1).

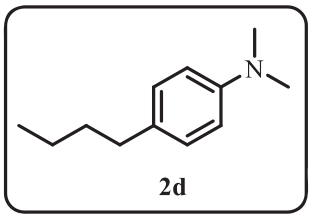
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.136 - 7.108 (m, 2H), 6.765 - 6.738 (m, 2H), 2.938(s, 6H), 2.631 - 2.568 (m, 2H), 1.263 - 1.218 (m, 3H);



***N*,*N*-dimethyl-4-propylaniline (2c)**

According to the general procedure, **2c** was obtained using 4-propylaniline (675.1 mg, 5.0 mmol) and iodomethane (1561.3 mg, 684.8 μL, 11 mmol) in 53% yield (432.2 mg) as a yellow oily liquid. (silica gel flash chromatography: petroleum ether/EtOAc = 80:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.101 - 7.064 (m, 2H), 6.753 - 6.725 (m, 2H), 2.920(s, 6H), 2.529 - 2.491 (m, 2H), 1.640 - 1.583 (m, 2H), 0.944 (t, *J* = 7.2 Hz, 3H);

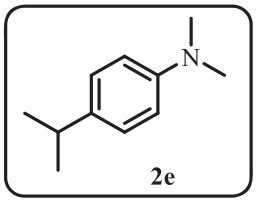


2d

4-butyl-*N,N*-dimethylaniline (2d)

According to the general procedure, **2d** was obtained using 4-butylaniline (745.6 mg, 5.0 mmol) and iodomethane (1561.3 mg, 684.8 μL, 11 mmol) in 55% yield (487.1 mg) as a yellow oily liquid. (silica gel flash chromatography: petroleum ether/EtOAc = 80:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.072 - 7.045 (m, 2H), 6.722 - 6.680 (m, 2H), 2.898(s, 5H), 2.538 - 2.494 (m, 2H), 1.599 - 1.515 (m, 2H), 1.394 - 1.294 (m, 2H), 0.937 - 0.893 (m, 3H);

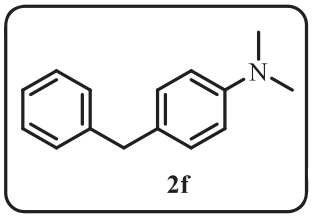


2e

4-isopropyl-*N,N*-dimethylaniline (2e)

According to the general procedure, **2e** was obtained using 4-isopropylaniline (675.1 mg, 5.0 mmol) and iodomethane (1561.3 mg, 684.8 μL, 11 mmol) in 51% yield (415.9 mg) as a yellow oily liquid. (silica gel flash chromatography: petroleum ether/EtOAc = 80:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.186 - 7.158 (m, 2H), 6.785 - 6.758 (m, 2H), 2.957(s, 6H), 2.921 - 2.846 (m, 1H), 1.290 - 1.267 (m, 6H) ;



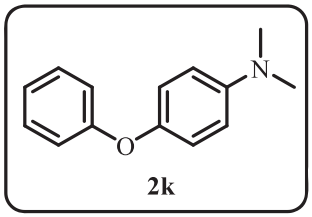
2f

4-benzyl-*N,N*-dimethylaniline (2f)

According to the general procedure, **2f** was obtained using 4-benzylaniline (915.5 mg, 5.0 mmol) and iodomethane (1561.3 mg, 684.8 μL, 11 mmol) in 60% yield (633.3 mg) as a yellow oily liquid. (silica gel flash chromatography: petroleum ether/EtOAc = 80:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.313 - 7.270 (m, 2H), 7.218 - 7.173 (m, 3H), 7.109 - 7.072 (m,

2H), 6.738 - 6.701 (m, 2H), 3.920 (s, 2H), 2.929 (s, 6H);



2k

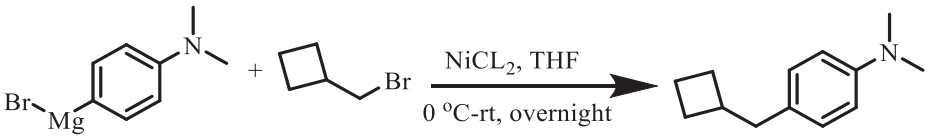
4-benzyl-*N,N*-dimethylaniline (2k)

According to the general procedure, **2k** was obtained using 4-phenoxyaniline (925.4 mg, 5.0 mmol) and iodomethane (1561.3 mg, 684.8 μL, 11 mmol) in 57% yield (607.3 mg) as a yellow oily liquid. (silica gel flash chromatography: petroleum ether/EtOAc = 80:1).

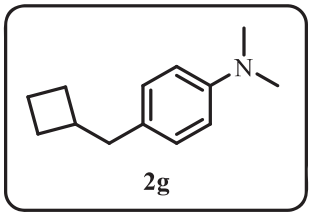
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.333 - 7.281 (m, 2H), 7.058 - 6.951 (m, 5H), 6.791 - 6.750 (m, 2H), 2.959 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.20, 159.18, 147.74, 147.38, 129.60, 122.02, 121.02, 117.23, 114.06, 41.29;

General procedure for preparation of 2h



A 100 mL round bottom flask equipped with a magnetic stir bar and was charged with (bromomethyl)cyclobutane (740.0 mg, 5.0 mmol), $NiCL_2$(dppe) (132.0 mg, 0.25.0 mmol) and 10 mL of freshly distilled THF. The solution was cooled to 0 °C and (4-(dimethylamino)phenyl)magnesium bromide (1 N in THF, 7.5 ml, 7.5.0 mmol) was added dropwise. The solution was maintained at 0 °C during the addition and then warmed to room temperature overnight. The reaction mixture was then quenched with saturated ammonium chloride solutionr and extracted twice with EtOAc. The organic layer was dried by using anhydrous Na_2SO_4, filtered, concentrated, and purified by flash chromatography.[3]



2g

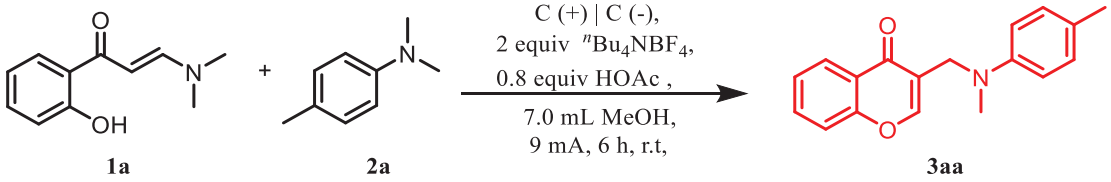
4-(cyclobutylmethyl)-*N,N*-dimethylaniline (2g)

According to the general procedure, **2g** was obtained using (bromomethyl)cyclobutane (739.9 mg, 5.0 mmol) and (4-(dimethylamino)phenyl)magnesium bromide (1 N in THF, 7.5 ml, 7.5 mmol) in 42% yield (397.1 mg) as a yellow oily liquid. (silica gel flash chromatography: petroleum ether/EtOAc = 80:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.092 - 7.066 (m, 2H), 6.753 - 6.727 (m, 2H), 2.955(s, 6H), 2.675 - 2.650 (m, 2H), 2.617 - 2.538 (m, 1H), 2.124 - 2.045 (m, 2H), 1.929 - 1.844 (m, 2H), 1.806 - 1.711 (m, 2H);

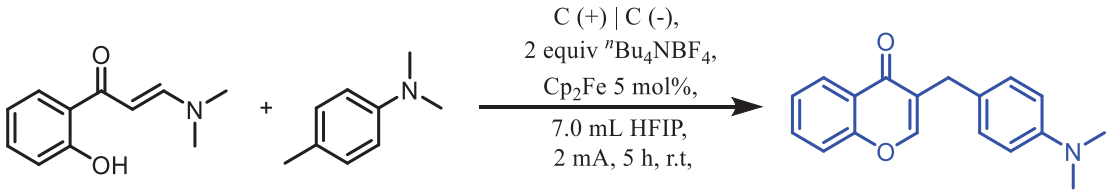
^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.98, 129.90, 129.22, 113.10, 42.11, 41.08, 37.64, 28.32, 18.45;

3. General procedure for the synthesis of products **3** and **4**.



1a **2a** **3aa**

A 10-mL oven-dried three-necked bottle was equipped with carbon rod anode, carbon rod cathode, **1a** (0.2 mmol), **2a** (0.8 mmol), ^{n}Bu$_4$NBF$_4$ (0.2 mmol), HOAc (10 ul), MeOH (7 mL). Then electrolyzed at constant current (9 mA) mode at room temperature for 6 h. The resulting yellow solid was concentrated under a vacuum, the crude product was purified by flash column chromatography using petroleum ether/EtOAc (50:1) to give the title compounds **3aa**.



1a **2a** **4aa**

A 10-mL oven-dried three-necked bottle was equipped with carbon rod anode, carbon rod cathode, **1a** (0.2 mmol), **2a** (0.8 mmol), ^{n}Bu$_4$NBF$_4$ (0.4 mmol), Cp_2Fe (5 mol%), HFIP (6.0 mL), room temperature. Then, it was electrolyzed at constant current (2 mA) mode at room temperature for 5 h. The resulting white solid was concentrated under a vacuum, the crude product was purified by flash column chromatography using petroleum ether/EtOAc (20:1) to give the title compounds **4aa**.

4. Optimization of the reaction conditions **B**

Table S1 Optimization of the reaction conditions **B**.[a]

Entry	Variation from the standard conditions	Yield of **4aa** (%)
1	none	75
2	EtOH instead of HFIP	trace
3	DMSO instead of HFIP	Trace
4	1a:2a=1:2 instead of 1a:2a=1:4	60
5	$^{n}Bu_4NClO_4$ instead of $^{n}Bu_4NBF_4$	61
6	$^{n}Bu_4NPF_6$ instead of $^{n}Bu_4NBF_4$	72
7	Pt (+)/Pt (-)	57
8	Pt (+)/C rod (-)	62
9	I=1.00 mA	50
10	I=3.00 mA	65
11	NO Fc	52
12	NO electric current	n.d

[a] Standard conditions **B**: undivided cell, carbon cod (Φ 5 mm) as anode and cathode, **1a** (0.2 mmol), **2a** (0.8 mmol), $^{n}Bu_4NBF_4$ (0.4 mmol), HFIP (7 mL), Cp_2Fe 5 mol %, CCE = 2 mA, 5h. [b] Isolated yields.

(C) Cyclic voltammetry experiments

Before the experiment, the glassy carbon disk electrode (≈5.0 mm^2) was polished step by step with metallographic sandpaper from 28 μm to 3.5 μm, and then polished to the mirror surface with 1.0, 0.3 μm Al_2O_3 slurry on the suede in turn. After each polishing, the surface dirt was washed first, and then moved into the ultrasonic water bath for cleaning, every 2 ~ 3 min, repeated three times, and finally followed by ultrasonic cleaning with 1 : 1 ethanol, 1 : 1 HNO_3 and distilled water. After thorough washing, the electrode was activated by cyclic voltammetry in 0.5-1.0 mol / L H_2SO_4 solution. The scan range was 1.0 ~ -1.0V, and the scan was repeated until a stable cyclic voltammogram was reached. Finally, the cyclic voltammetry curve of 1×10^{-3} mol / L $K_3Fe(CN)_6$ solution was recorded in 0.20 mol / L KNO_3 to test the electrode performance. The scanning speed

was 50 mV / s and the scanning range was -0.2 ~ 0.6 V. The peak potential difference in the cyclic voltammogram obtained under laboratory conditions is below 80 mV, and as close as possible to 64 mV, the electrode can be used, otherwise the electrode should be reprocessed until it meets the requirements.

Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line under nitrogen at room temperature. The working electrode was a steady glassy carbon disk electrode (≈5.0 mm^2), and the counter electrode was a platinum wire. The reference was an $Ag/AgNO_3$ electrode submerged in 0.1 M $^nBu_4NClO_4$ and 0.01 M $AgNO_3$ in CH_3CN. 3 mL of solvent was poured into the electrochemical cell in all experiments. The redox potential of ferrocene/ferrocenium (Fc/Fc^+) was measured (same experimental conditions) and used to provide an internal reference. The potential values were then adjusted relative to Fc/Fc^+. The scan rate is 0.1 V/s, ranging from -0.2 V to 2.0 V or 3.0 V.

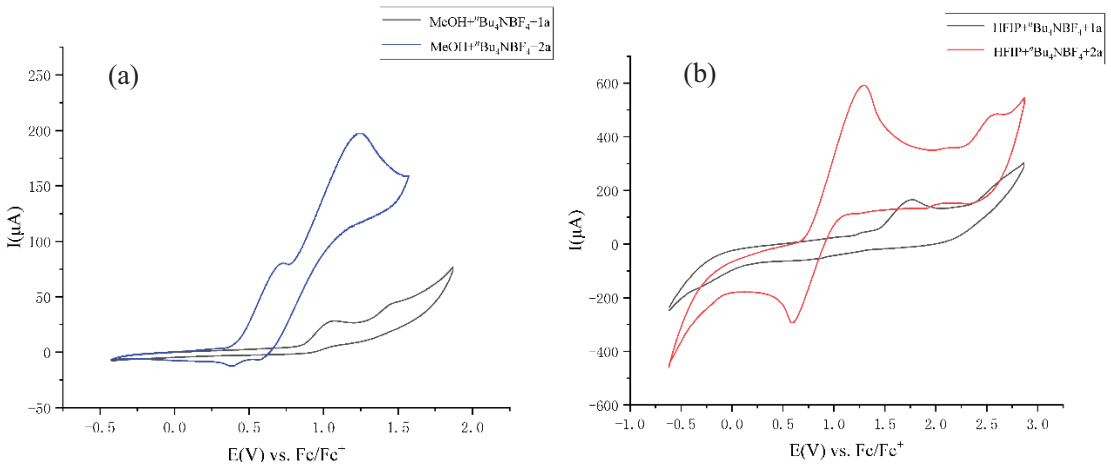
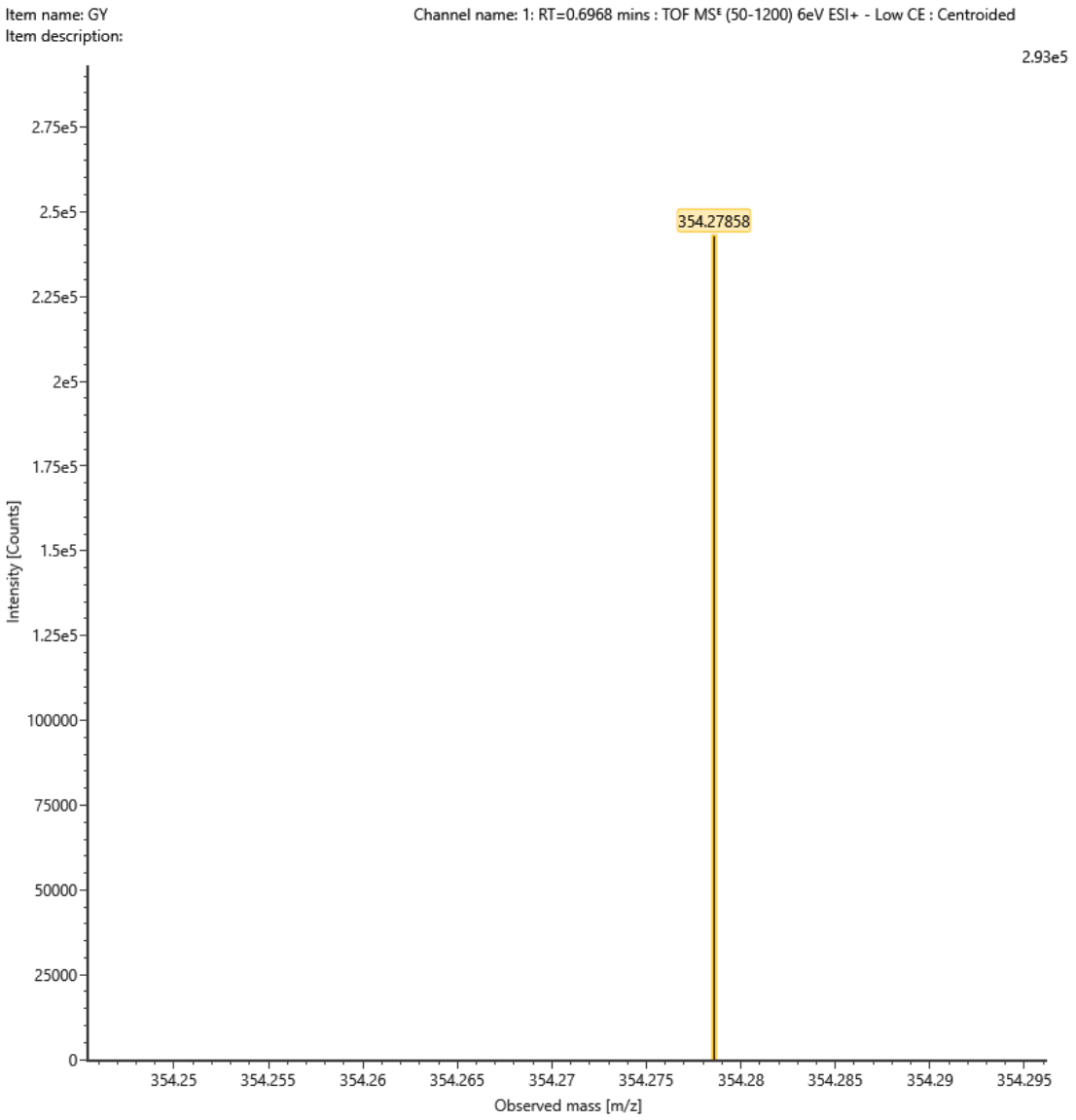
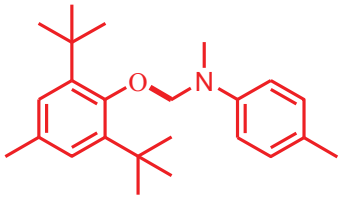


Figure S1. CV plotting convention (IUPAC)

In Figure **S1**, cyclic voltammograms of solutions containing different compounds: (a) black line: 3 mL solution containing $^nBu_4NBF_4$ (0.4 mmol) and **1a** (0.2 mmol), blue line: 3mL MeOH solution containing $^nBu_4NBF_4$ (0.4 mmol) and **2a** (0.2 mmol); (b) 3 mL HFIP solution containing $^nBu_4NBF_4$ (0.4 mmol) and **1a** (0.2 mmol), blue line: 3mL HFIP containing $^nBu_4NBF_4$ (0.4 mmol) and **2a** (0.2 mmol) with a GC disk working electrode (≈5.0 mm^2), Pt counter electrode, and $Ag/AgNO_3$ reference electrode (internal solution, 0.1 M $^nBu_4NClO_4$ and 0.01 M $AgNO_3$ in CH_3CN) at 0.1 V/s scan rate.

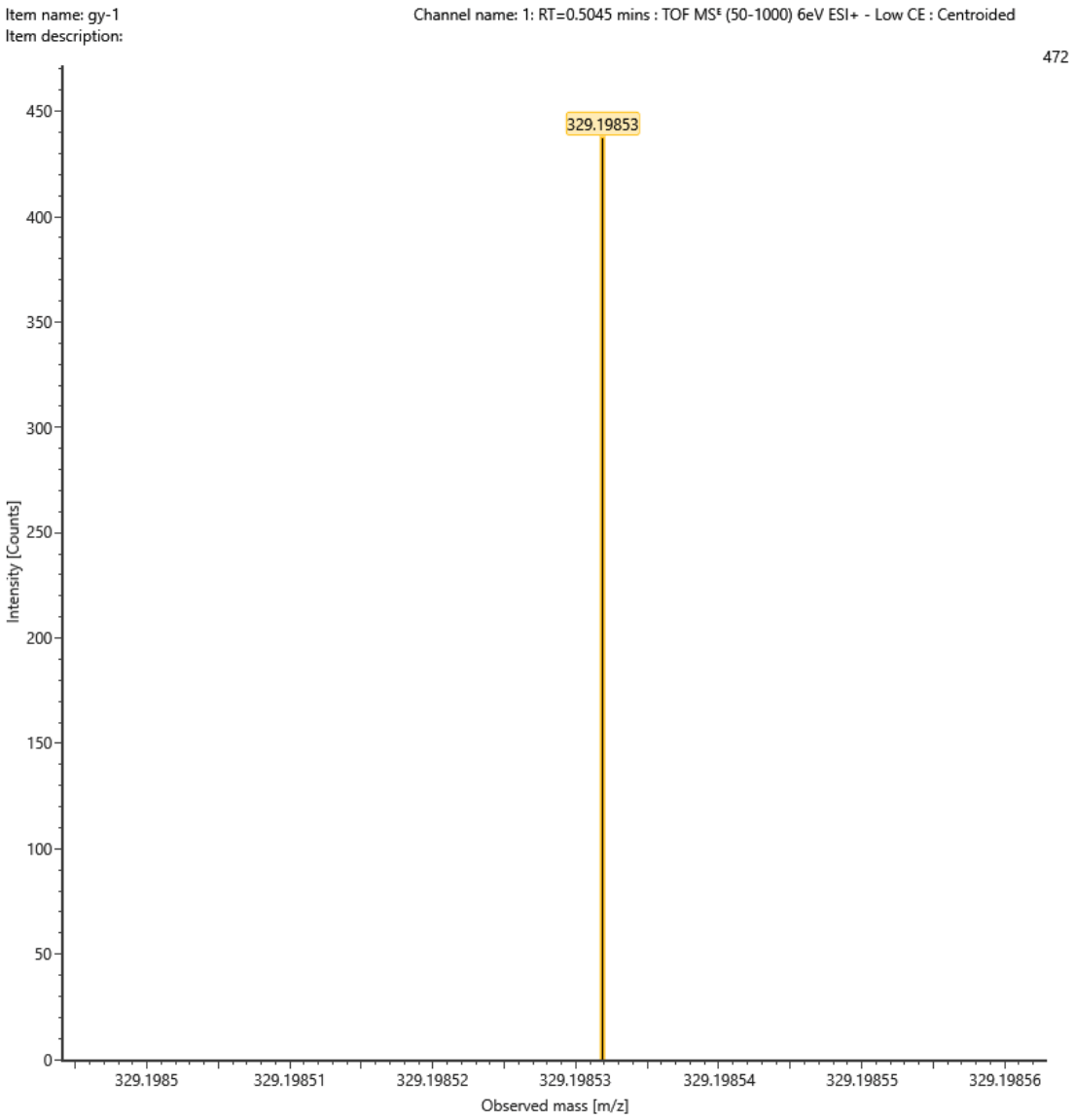
(D) HRMS detection





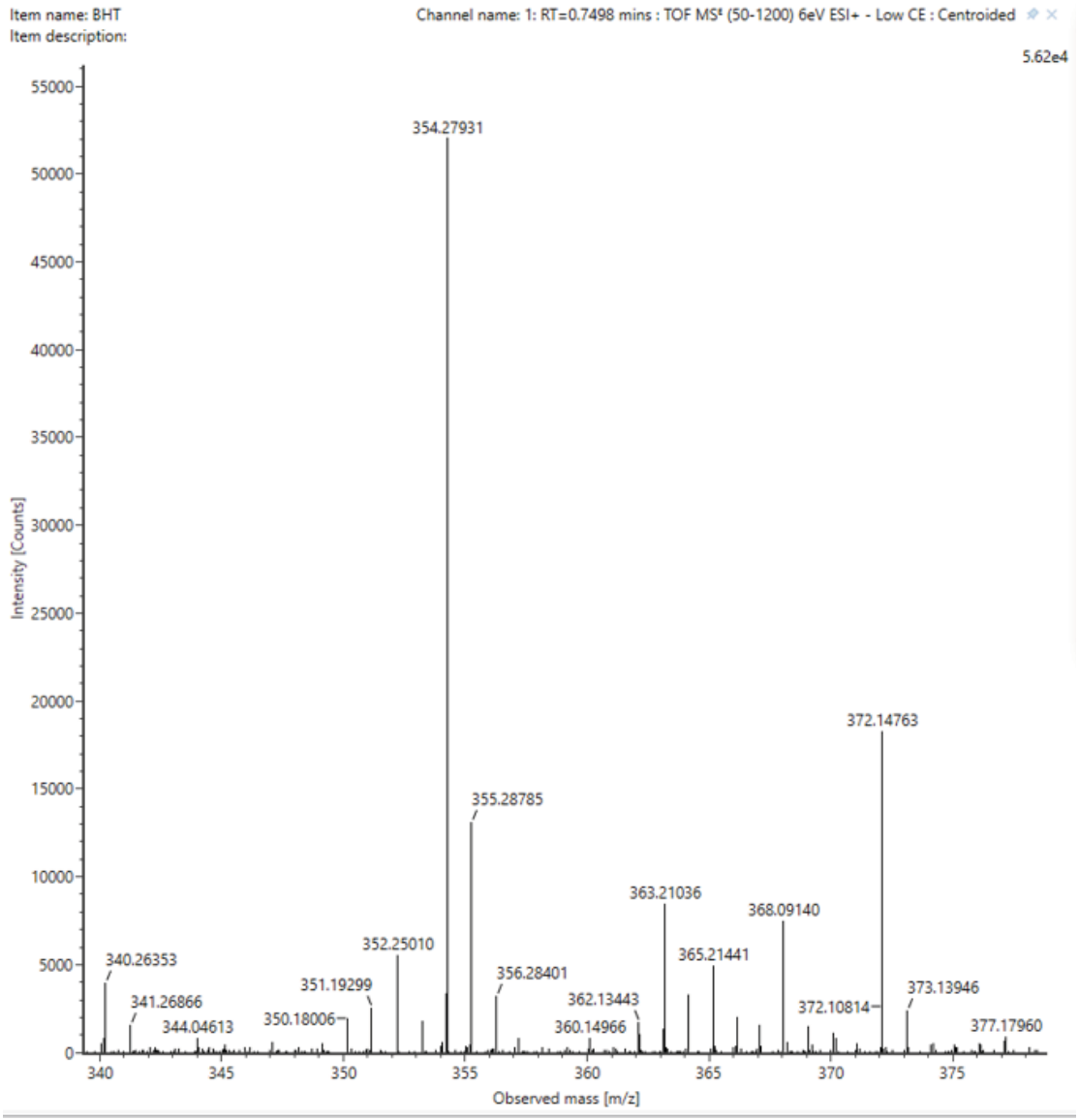
N-((2,6-di-tert-butyl-4-methylphenoxy)methyl)-N,4-dimethylbenzenamine (5a):

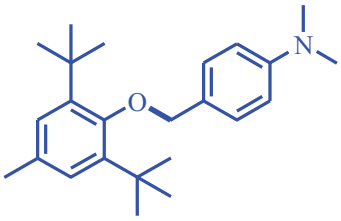
HRMS (ESI) *m/z* calcd. for C24H36NO [(M+H)+]: 354.2791, Found: 354.2786



N,4-dimethyl-N-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)aniline (8a):

HRMS (ESI) *m/z* calcd. for C18H30N2OK [(M+K)+]: 329.1990, Found: 329.1985

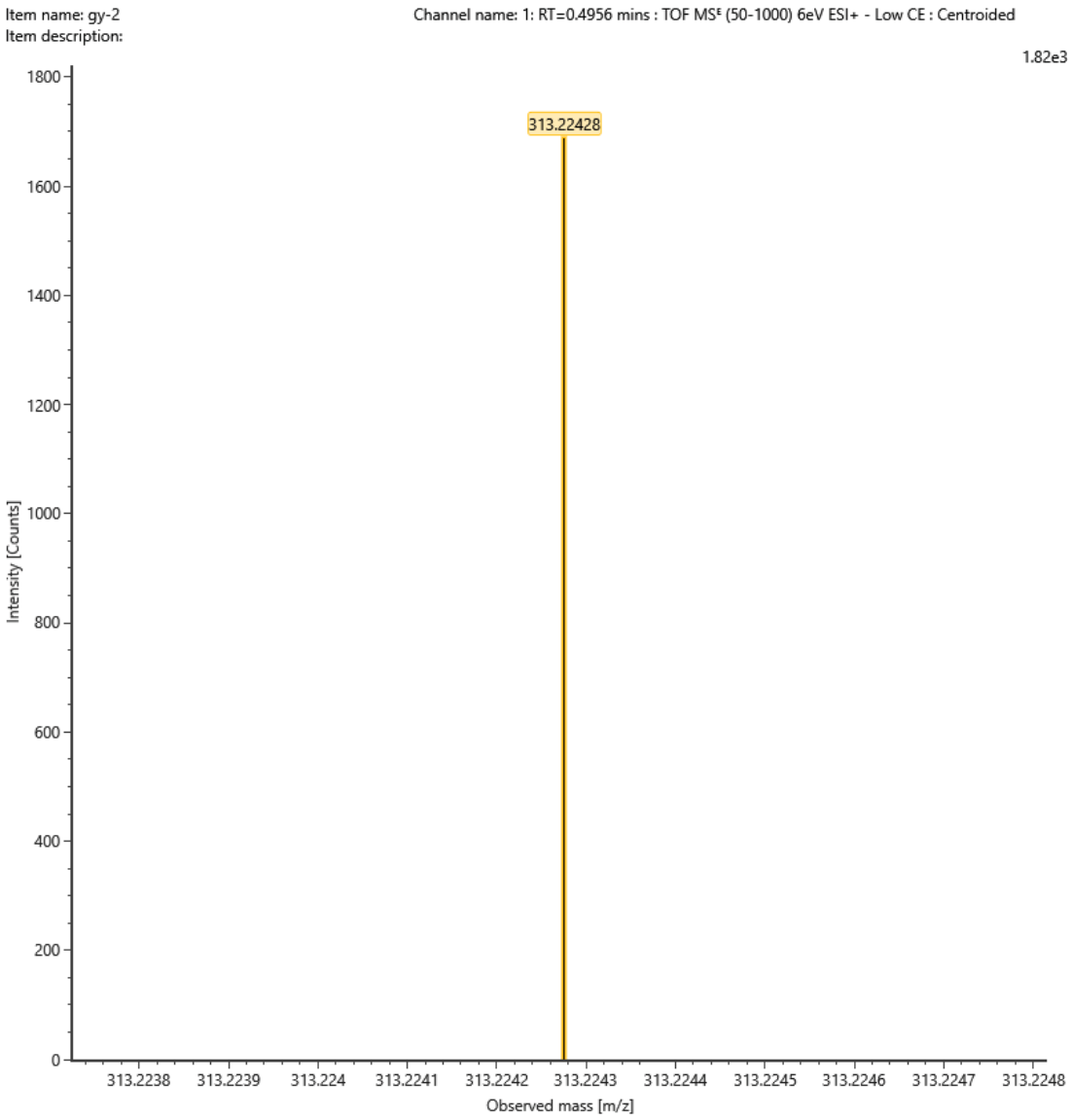


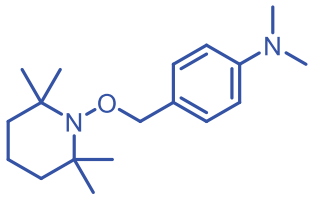


6a

4-((2,6-di-tert-butyl-4-methylphenoxy)methyl)-N,N-dimethylbenzenamine (7a):

HRMS (ESI) *m/z* calcd. for C24H36NO [(M+H)+]: 354.2791, Found: 354.2793

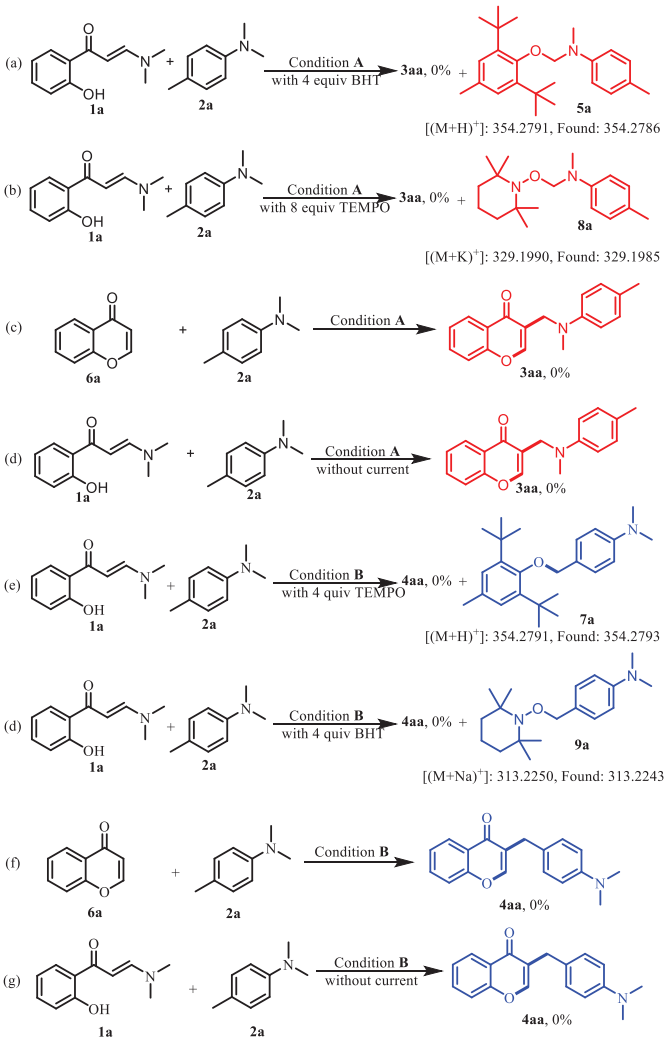




N,N-dimethyl-4-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)aniline (9a):

HRMS (ESI) *m/z* calcd. for C18H30N2ONa [(M+Na)+]: 313.2250, Found: 313.2243

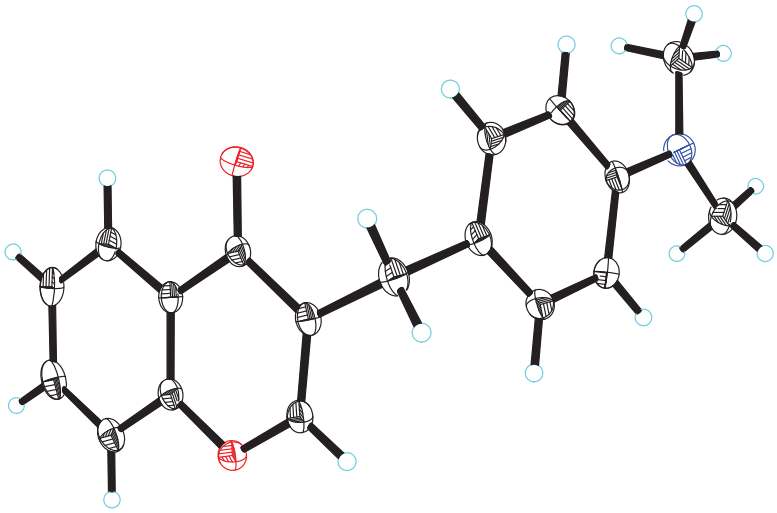
(E) The control experiments



Scheme S1. The control experiments

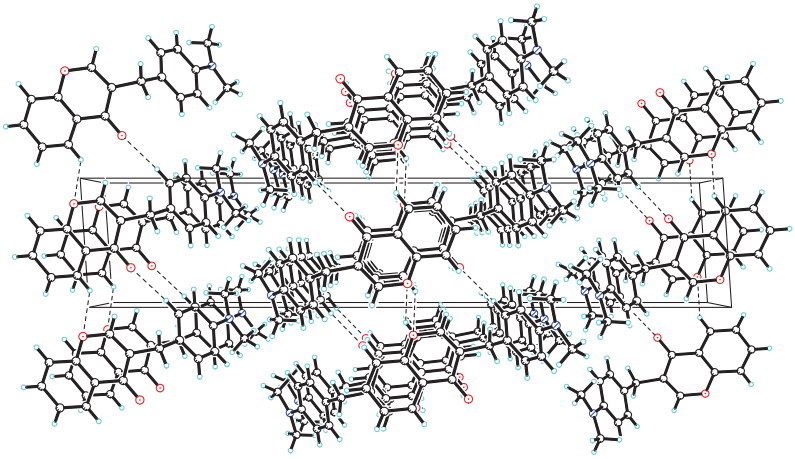
(F) X-Ray crystallographic studies

Crystal data for md_zxj231: $C_{18}H_{17}NO_2$, $M = 279.33$, $a = 6.3783(2)$ Å, $b = 7.1006(3)$ Å, $c = 31.5404(12)$ Å, $\alpha = 90°$, $\beta = 93.880(2)°$, $\gamma = 90°$, $V = 1425.18(9)$ Å^3, $T = 150.(2)$ K, space group $P121/c1$, $Z = 4$, μ(Cu Kα) = 0.676 mm^{-1}, 11026 reflections measured, 2602 independent reflections ($R_{int} = 0.0726$). The final R_1 values were 0.0442 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1100 ($I > 2\sigma(I)$). The final R_1 values were 0.0652 (all data). The final $wR(F^2)$ values were 0.1204 (all data). The goodness of fit on F^2 was 1.072.



View of a molecule of md_zxj231.

Displacement ellipsoids are drawn at the 30% probability level.



View of the pack drawing of md_zxj231.

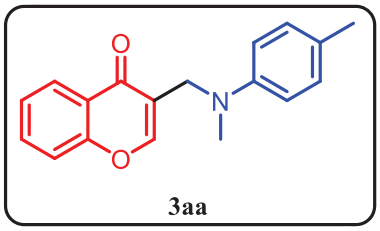
Hydrogen-bonds are shown as dashed lines.

Table 1. Crystal data and structure refinement for md_zxj231_0m.

Identification code	global
Empirical formula	C18 H17 N O2
Formula weight	279.33
Temperature	150(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic

Space group	P 1 21/c 1	
Unit cell dimensions	a = 6.3783(2) Å	α= 90°.
	b = 7.1006(3) Å	β= 93.880(2)°.
	c = 31.5404(12) Å	γ = 90°.
Volume	1425.18(9) $Å^3$	
Z	4	
Density (calculated)	1.302 Mg/m^3	
Absorption coefficient	0.676 mm^{-1}	
F(000)	592	
Crystal size	0.160 x 0.160 x 0.060 mm^3	
Theta range for data collection	5.62 to 68.33°.	
Index ranges	-7<=h<=7, -8<=k<=6, -37<=l<=37	
Reflections collected	11026	
Independent reflections	2602 [R(int) = 0.0726]	
Completeness to theta = 68.33°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.71	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2602 / 0 / 192	
Goodness-of-fit on F^2	1.072	
Final R indices [I>2sigma(I)]	R1 = 0.0442, wR2 = 0.1100	
R indices (all data)	R1 = 0.0652, wR2 = 0.1204	
Largest diff. peak and hole	0.196 and -0.234 $e.Å^{-3}$	

(G) Analytical data for products 3 and 4



3aa

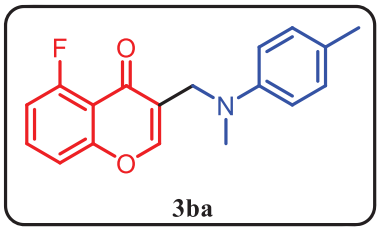
3-((methyl(p-tolyl)amino)methyl)-4H-chromen-4-one (3aa)

According to the general procedure, **3aa** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **1a** (38.2 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 77% yield (43.0 mg) as a yellow solid, m.p. 101.0-102.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.256 (m, 1H), 7.684 - 7.641 (m, 2H), 7.442 - 7.394 (m, 2H), 7.062 - 7.04 (m, 2H), 6.689 - 6.668 (m, 2H), 4.435 - 4.432 (m, 2H), 3.043 (s, 3H), 2.257 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.17, 156.72, 153.01, 147.13, 133.68, 129.95, 126.40, 125.74, 125.17, 123.84, 120.47, 118.27, 112.77, 49.54, 39.20, 20.34;

HRMS (ESI) calcd for $C_{18}H_{18}NO_2$: $[M+H]^+$ 280.1332. Found: m/z 280.1337.



3ba

5-fluoro-3-((methyl(p-tolyl)amino)methyl)-4H-chromen-4-one (3ba)

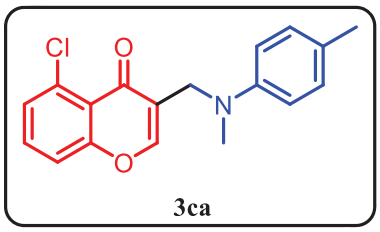
According to the general procedure, **3ba** was obtained using (*E*)-3-(dimethylamino)-1-(2-fluoro-6-hydroxyphenyl)prop-2-en-1-one **1b** (41.8 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 77% yield (39.8 mg) as a yellow solid, m.p. 99.0-100.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.602 - 7.546 (m, 2H), 7.235 - 7.208 (m, 1H), 7.071 - 7.022 (m, 3H), 6.679 - 6.642 (m, 2H), 4.391 - 4.388 (m, 2H), 3.033 (s, 3H), 2.253 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.40, 160.84 (d, J = 259.0 Hz), 159.53, 157.75, 152.03, 146.97, 133.65 (d, J = 14 Hz), 129.97 (d, J = 3.0 Hz), 126.52, 121.50, 114.16, 112.80, 111.91(d, J = 17.0) 49.42, 39.28, 20.33;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -111.54.

HRMS (ESI) calcd for $C_{18}H_{17}FNO_2$: $[M+H]^+$ 298.1238. Found: m/z 298.1247.



3ca

5-chloro-3-((methyl(p-tolyl)amino)methyl)-4H-chromen-4-one (3ca)

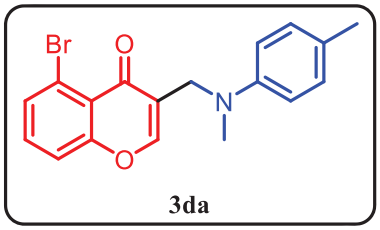
According to the general procedure, **3ca** was obtained using (*E*)-1-(2-chloro-6-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one **1c** (45.0 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 41% yield (27.5 mg) as a yellow solid, m.p. 104.0-105.0 ℃ (silica gel flash

chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.577 - 7.570 (m 1H), 7.523 - 7.482 (m, 1H), 7.399 - 7.376 (m, 1H), 7.347 - 7.323 (m, 1H), 7.064 - 7.027 (m, 2H), 6.671 - 6.633 (m, 2H), 4.396 - 4.392 (m, 2H), 3.035 (s, 3H), 2.253 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.03, 158.31, 151.57, 147.02, 133.56, 132.79, 129.96, 128.11, 126.46, 121.65, 120.76, 117.55, 112.69, 49.63, 39.26, 20.32;

HRMS (ESI) calcd for $C_{18}H_{17}CLNO_2$: $[M+H]^+$ 314.0942. Found: m/z 314.0947.



3da

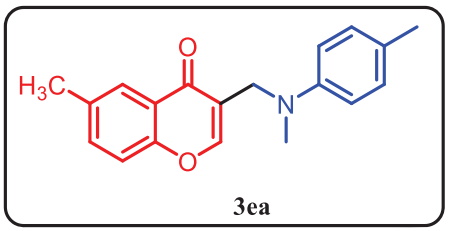
5-bromo-3-((methyl(p-tolyl)amino)methyl)-4H-chromen-4-one (3da)

According to the general procedure, **3da** was obtained using (*E*)-1-(2-bromo-6-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one **1d** (53.8 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 35% yield (25.0 mg) as a yellow solid, m.p. 109.0-110.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.651 - 7.628 (m, 1H), 7.592 -7.585 (m, 1H), 7.440 - 7.376 (m, 2H), 7.065 - 7.027 (m, 2H), 6.668 - 6.639 (m, 2H), 4.402 - 4.398 (m, 2H), 3.036 (s, 3H), 2.253 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.94, 158.12, 151.55, 146.98, 133.15, 131.94, 129.97, 126.47, 121.34, 121.28, 120.32, 118.32, 112.67, 49.70, 39.28, 20.32;

HRMS (ESI) calcd for $C_{18}H_{17}BrNO_2$: $[M+H]^+$ 358.0437. Found: m/z 358.0429.



3ea

6-methyl-3-((methyl(p-tolyl)amino)methyl)-4H-chromen-4-one (3ea)

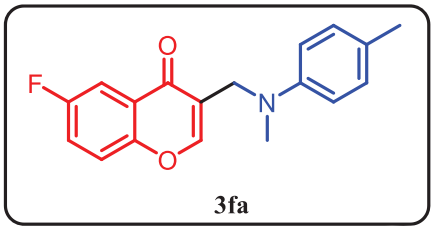
According to the general procedure, **3ea** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxy-5-methylphenyl)prop-2-en-1-one **1e** (41.1 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 43% yield (25.2 mg) as a yellow solid, m.p. 88.0-89.0 ℃ (silica gel flash

chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.028 - 8.025 (m, 1H), 7.658 - 7.651 (m, 1H), 7.480 - 7.453 (m, 1H), 7.324 (d, *J* = 8.8 Hz, 1H), 7.062 - 7.024 (m, 2H), 6.687 - 6.650 (m, 2H), 4.425 - 4.422 (m, 2H), 3.034 (s, 3H), 2.466 (s, 3H), 2.251 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.21, 155.03, 152.96, 147.15, 135.12, 134.95, 129.93, 126.38, 124.99, 123.52, 120.21, 118.01, 112.81, 49.53, 39.21, 21.08, 20.33;

HRMS (ESI) calcd for $C_{19}H_{20}NO_2$: $[M+H]^+$ 294.1489. Found: m/z 294.1495.



3fa

6-fluoro-3-((methyl(p-tolyl)amino)methyl)-4H-chromen-4-one (3fa)

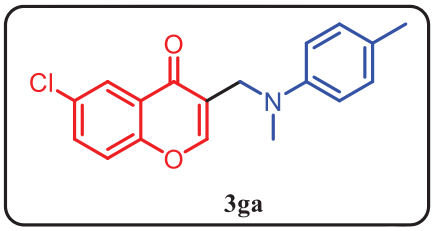
According to the general procedure, **3fa** was obtained using (*E*)-3-(dimethylamino)-1-(5-fluoro-2-hydroxyphenyl)prop-2-en-1-one **1f** (41.8 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 45% yield (26.7 mg) as a yellow solid, m.p. 149.0-150.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.889 - 7.861 (m, 1H), 7.687 (s, 1H), 7.461 - 7.428 (m, 1H), 7.411 - 7.362 (m, 1H), 7.067 - 7.029 (m, 2H), 6.676 - 6.655 (m, 2H), 4.421 - 4.417 (m, 2H), 3.036 (s, 3H), 2.252 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ: 177.45 (d, *J* = 2.0 Hz), 159.64 (d, *J* = 245.0 Hz), 153.29, 152.99 (d, *J* = 2.0 Hz), 147.06, 130.00, 126.60, 124.95 (d, *J* = 7.0 Hz), 122.04 (d, *J* = 26.0 Hz), 120.42(d, *J* = 8.0 Hz), 119.98, 112.83, 110.52(d, *J* = 23.0 Hz), 49.52, 39.28, 20.36;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -115.20.

HRMS (ESI) calcd for $C_{18}H_{17}FNO_2$: $[M+H]^+$ 298.1238. Found: m/z 298.1246.



3ga

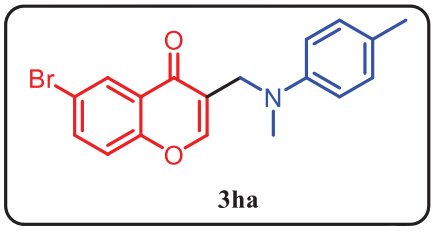
6-chloro-3-((methyl(p-tolyl)amino)methyl)-4H-chromen-4-one (3ga)

According to the general procedure, **3ga** was obtained using (*E*)-1-(5-bromo-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one **1g** (45.1 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 62% yield (38.8 mg) as a yellow solid, m.p. 94.0-96.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.203 - 8.197 (m, 1H), 7.627 (s, 1H), 7.615 - 7.586 (m, 1H), 7.395 (d, *J* = 8.8 Hz, 1H), 7.065 - 7.039 (m, 2H), 6.657 (d, *J* = 8.4 Hz, 2H), 4.418 - 4.414 (m, 2H), 3.036 (s, 3H), 2.252 (s, 3H);

^{13}C NMR (100MHz, $CDCl_3$) δ: 177.01, 155.07, 153.27, 147.00, 133.97, 131.19, 130.01, 126.69, 125.17, 124.74, 120.69, 120.05, 112.86, 49.51, 39.32, 20.35;

HRMS (ESI) calcd for $C_{18}H_{17}CLNO_2$: $[M+H]^+$ 314.0942. Found: m/z 314.0942.



3ha

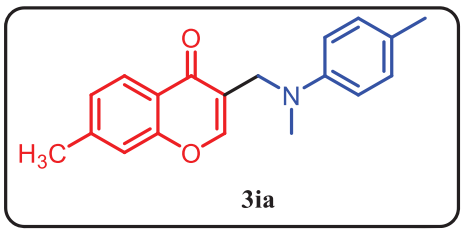
6-bromo-3-((methyl(p-tolyl)amino)methyl)-4H-chromen-4-one (3ha)

According to the general procedure, **3ha** was obtained using (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one **1h** (53.8 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 63% yield (45.1 mg) as a yellow solid, m.p. 113.0-114.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.365 - 8.359 (m, 1H), 7.733 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.678 (s, 1H), 7.327 (d, *J* = 8.8 Hz, 1H), 7.066 - 7.028 (m, 2H), 6.679 - 6.642 (m, 2H), 4.414 - 4.411 (m, 2H), 3.034 (s, 3H), 2.253 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.84, 155.48, 153.23, 146.97, 136.69, 129.99, 128.38, 126.66, 125.11, 120.80, 120.27, 118.62, 112.84, 49.50, 39.31, 20.35;

HRMS (ESI) calcd for $C_{18}H_{17}BrNO_2$: $[M+H]^+$ 358.0437. Found: m/z 358.0433.



3ia

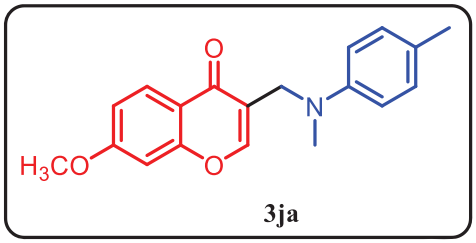
7-methyl-3-((methyl(p-tolyl)amino)methyl)-4H-chromen-4-one (3ia)

According to the general procedure, **3ia** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxy-4-methylphenyl)prop-2-en-1-one **1i** (41.1 mg, 0.2 mmol) and *N*,*N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 50% yield (29.3 mg) as a yellow solid, m.p. 108.0-109.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.135 - 8.113 (m, 1H), 7.637 (s, 1H), 7.234 - 7.213 (m, 2H), 7.063 - 7.026 (m, 2H), 6.675 (d, *J* = 8.4 Hz, 2H), 4.420 - 4.416 (m, 2H), 3.034 (s, 3H), 2.478 (s, 3H), 2.253 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.08, 156.89, 152.84, 147.12, 145.04, 129.95, 126.75, 126.29, 125.49, 121.65, 120.22, 117.95, 112.84, 49.56, 39.23, 21.92, 20.35;

HRMS (ESI) calcd for $C_{19}H_{20}NO_2$: $[M+H]^+$ 294.1489. Found: m/z 294.1495.



3ja

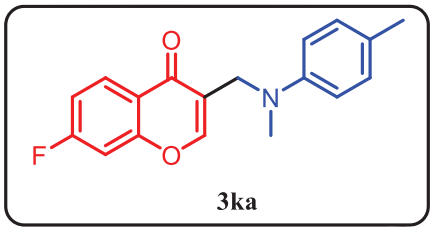
7-methoxy-3-((methyl(p-tolyl)amino)methyl)-4H-chromen-4-one (3ja)

According to the general procedure, **3ja** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxy-5-methoxyphenyl)prop-2-en-1-one **1j** (44.2 mg, 0.2 mmol) and *N*,*N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 54% yield (33.4 mg) as a yellow solid, m.p. 133.0-134.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.145 (d, *J* = 8.8 Hz, 1H), 7.597 - 7.589 (m, 1H), 7.062 - 7.033 (m, 2H), 6.992 - 6.964 (m, 1H), 6.803 - 6.797 (m, 1H), 6.685 - 6.647 (m, 2H), 4.407 - 4.404 (m, 2H), 3.891 (s, 3H), 3.029 (s, 3H), 2.251 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.55, 164.14, 158.53, 152.53, 147.17, 129.93, 127.11, 126.32, 120.25, 117.83, 114.71, 112.73, 100.24, 55.93, 49.50, 39.16, 20.33;

HRMS (ESI) calcd for $C_{19}H_{20}NO_3$: $[M+H]^+$ 310.1438. Found: m/z 310.1439.



3ka

7-fluoro-3-((methyl(p-tolyl)amino)methyl)-4H-chromen-4-one (3ka)

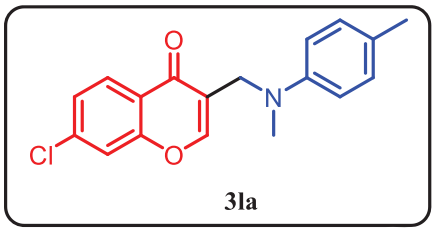
According to the general procedure, **3ka** was obtained using (*E*)-3-(dimethylamino)-1-(4-fluoro-2-hydroxyphenyl)prop-2-en-1-one **1k** (41.8 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 86% yield (51.1 mg) as a yellow solid, m.p. 100.0-101.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.279 - 8.241 (m, 1H), 7.652 - 7.644 (m, 1H), 7.168 - 7.140 (m, 1H), 7.124 - 7.095 (m, 1H), 7.067 - 7.029 (m, 2H), 6.681 - 6.644 (m, 2H), 4.411 - 4.407 (m, 2H), 3.033 (s, 3H), 2.253 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.28, 165.70 (d, J = 253.0 Hz), 157.69 (d, J = 13.0 Hz), 153.16, 146.98, 129.98, 128.30 (d, J = 10.0 Hz), 120.71, 114.13 (d, J = 22.0 Hz), 112.74, 104.84 (d, J = 26.0 Hz), 49.49, 39.25, 20.36;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -102.99.

HRMS (ESI) calcd for $C_{18}H_{17}FNO_2$: $[M+H]^+$ 298.1238. Found: m/z 298.1248.



3la

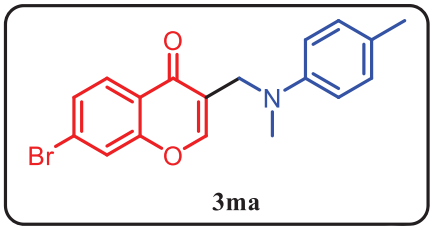
7-chloro-3-((methyl(p-tolyl)amino)methyl)-4H-chromen-4-one (3la)

According to the general procedure, **3la** was obtained using (*E*)-1-(4-chloro-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one **1l** (45.0 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 61% yield (38.2 mg) as a yellow solid, m.p. 111.0-112.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.179 (d, J = 8.4 Hz, 1H), 7.646 - 7.639 (m, 1H), 7.454 - 7.450 (m, 1H), 7.389 - 7.363 (m, 1H), 7.059 - 7.038 (m, 2H), 6.679 - 6.642 (m, 2H), 4.409 - 4.405 (m, 2H), 3.033 (s, 3H), 2.255 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.38, 156.81, 153.03, 147.03, 139.80, 129.98, 127.15, 126.57, 126.10, 122.36, 120.97, 118.30, 112.78, 49.47, 39.24, 20.34;

HRMS (ESI) calcd for $C_{18}H_{17}CLNO_2$: $[M+H]^+$ 314.0942. Found: m/z 314.0948.



3ma

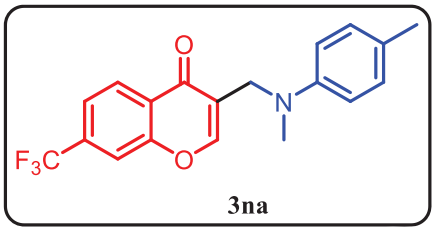
7-bromo-3-((methyl(p-tolyl)amino)methyl)-4H-chromen-4-one (3ma)

According to the general procedure, **3ma** was obtained using (*E*)-1-(4-bromo-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one **1m** (53.8 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 78% yield (55.7 mg) as a yellow solid, m.p. 144.0-145.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.101 (d, *J* = 8.4 Hz, 1H), 7.643 - 7.635 (m, 1H), 7.629 - 7.625 (m, 1H), 7.539 - 7.513 (m, 1H), 7.069 -7.031 (m, 2H), 6.682 - 6.645 (m, 2H), 4.408 - 4.404 (m, 2H), 3.034 (s, 3H), 2.256 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ: 177.45, 156.75, 152.99, 147.00, 129.98, 128.86, 127.99, 127.18, 126.60, 122.70, 121.36, 120.98, 112.80, 49.49, 39.26, 20.34;

HRMS (ESI) calcd for $C_{18}H_{17}BrNO_2$: $[M+H]^+$ 358.0437. Found: m/z 358.0446.



3na

3-((methyl(p-tolyl)amino)methyl)-7-(trifluoromethyl)-4H-chromen-4-one (3na)

According to the general procedure, **3na** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxy-4-(trifluoromethyl)phenyl)prop-2-en-1-one **1n** (51.8 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 45% yield (31.2 mg) as a yellow solid, m.p. 92.0-93.0℃(silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

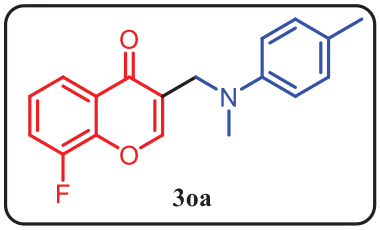
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.375 (d, *J* = 8.4 Hz, 1H), 7.745 - 7.734 (m, 2H), 7.656 - 7.631 (m, 1H), 7.059 (d, *J* = 8.4 Hz, 2H), 6.675 (d, *J* = 8.4 Hz, 2H), 4.438 - 4.435 (m, 2H), 3.052 (s, 3H),

2.262 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.20, 156.09, 153.64, 146.97, 135.34 (q, *J* = 33.0 Hz), 130.01, 127.14, 126.73, 125.85, 124.55, 121.84, 121.50(q, *J* = 3.0 Hz), 116.24 (q, *J* = 4.0 Hz), 112.84, 49.51, 39.30, 20.33;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -63.05;

HRMS (ESI) calcd for $C_{19}H_{17}F_3NO_2$: $[M+H]^+$ 348.1206. Found: m/z 348.1216.



3oa

8-fluoro-3-((methyl(p-tolyl)amino)methyl)-4H-chromen-4-one (3oa)

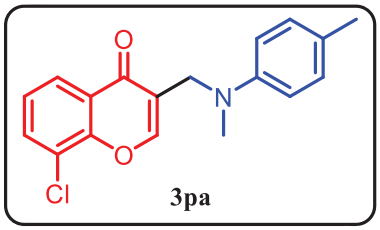
According to the general procedure, **3oa** was obtained using (*E*)-3-(dimethylamino)-1-(3-fluoro-2-hydroxyphenyl)prop-2-en-1-one **1o** (41.8 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 69% yield (41.0 mg) as a yellow solid, m.p. 141.0-142.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.016 - 7.989 (m, 1H), 7.719 - 7.712 (m, 1H), 7.456 - 7.406 (m, 1H), 7.364 - 7.313 (m, 1H), 7.071 - 7.041 (m, 2H), 6.692 - 6.655 (m, 2H), 4.431 - 4.427 (m, 2H), 3.042 (s, 3H), 2.258 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.16, 152.68, 151.33 (d, *J* = 253.0 Hz), 147.02, 145.55 (d, *J* = 12.0 Hz), 129.97, 126.64, 125.71, 124.72(d, *J* = 6.0 Hz), 121.07, 120.75 (d, *J* = 5.0 Hz), 119.33 (d, *J* = 16.0 Hz), 112.87, 49.46, 39.23, 20.32;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -113.60.

HRMS (ESI) calcd for $C_{18}H_{17}FNO_2$: $[M+H]^+$ 298.1238. Found: m/z 298.1242.



3pa

8-chloro-3-((methyl(p-tolyl)amino)methyl)-4H-chromen-4-one (3pa)

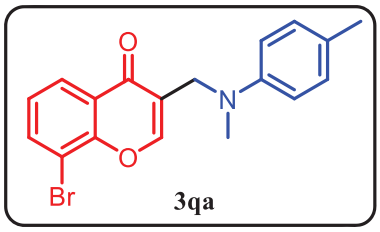
According to the general procedure, **3pa** was obtained using (*E*)-1-(3-chloro-2-hydroxyphenyl)-3-

(dimethylamino)prop-2-en-1-one **1p** (45.1 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 77% yield (48.2 mg) as a yellow solid, m.p. 113.0-114.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.162 - 8.138 (m, 1H), 7.757 - 7.713 (m, 2H), 7.368 -7.329 (m, 1H), 7.060 - 7.039 (m, 2H), 6.667 (d, *J* = 8.4 Hz, 2H), 4.432 - 4.429 (m, 2H), 3.046 (s, 3H), 2.254 (s, 3H);

^{13}C NMR (100 MHz, CDCl3) δ: 177.59, 153.04, 152.45, 146.93, 133.98, 130.02, 126.59, 125.23, 125.17, 124.41, 123.35, 120.90, 112.83, 49.40, 39.29, 20.35;

HRMS (ESI) calcd for $C_{18}H_{17}CLNO_2$: $[M+H]^+$ 314.0942. Found: m/z 314.0936.



3qa

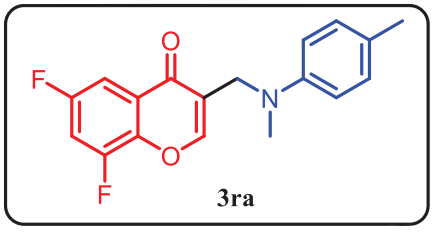
8-bromo-3-((methyl(p-tolyl)amino)methyl)-4H-chromen-4-one (3qa)

According to the general procedure, **3qa** was obtained using (*E*)-1-(3-bromo-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one **1q** (53.8 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 45% yield (32.1mg) as a yellow solid, m.p. 86.0-87.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.211 - 8.187 (m, 1H), 7.906 -7 .882 (m, 1H), 7.761 - 7.754 (m, 1H), 7.311 - 7.272 (m, 1H), 7.067 - 7.029 (m, 2H), 6.680 - 6.643 (m, 2H), 4.430 - 4.427 (m, 2H), 3.046 (s, 3H), 2.255 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.65, 153.32, 153.14, 146.90, 137.21, 130.01, 126.60, 125.82, 125.20, 125.14, 120.80, 112.78, 111.94, 49.37, 39.28, 20.35;

HRMS (ESI) calcd for $C_{18}H_{17}BrNO_2$: $[M+H]^+$ 358.0437. Found: m/z 358.0446.



3ra

6,8-difluoro-3-((methyl(p-tolyl)amino)methyl)-4H-chromen-4-one (3ra)

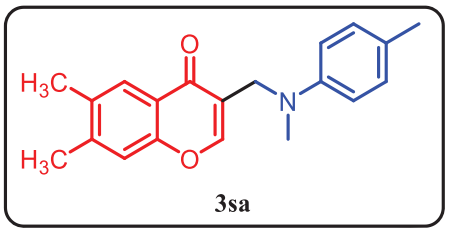
According to the general procedure, **3ra** was obtained using (*E*)-1-(3,5-difluoro-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one **1t** (45.4 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 51% yield (32.1 mg) as a yellow solid, m.p. 75.0-76.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.724 - 7.726 (m, 1H), 7.693 - 7.660 (m, 1H), 7.254 - 7.202 (m, 1H), 7.071 - 7.033 (m, 2H), 6.683 - 6.646 (m, 2H), 4.421 - 4.417 (m, 2H), 3.040 (s, 3H), 2.258 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.26 (t, *J* = 3.0 Hz), 158.40 (dd, *J* = 248.0, 9.0 Hz), 152.93, 151.66 (dd, *J* = 256.0, 11.0 Hz), 146.91, 142.41(dd, *J* = 11.0, 3.0 Hz), 130.00, 126.78, 125.90 (d, *J* = 9.0 Hz), 120.68, 112.88, 109.12 (dd, *J* = 28.0, 20.0 Hz), 105.81 (dd, *J* = 23.0, 5.0 Hz), 49.43, 39.28, 20.32;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -111.87 (d, *J* = 3.8 Hz), -128.02 (d, *J* = 7.5 Hz).

HRMS (ESI) calcd for $C_{18}H_{16}F_2NO_2$: $[M+H]^+$ 316.1144. Found: m/z 316.1142.



3sa

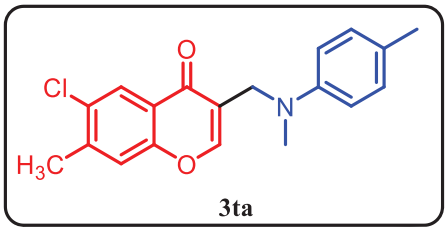
6,7-dimethyl-3-((methyl(p-tolyl)amino)methyl)-4H-chromen-4-one (3sa)

According to the general procedure, **3sa** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxy-4,5-dimethylphenyl)prop-2-en-1-one **1s** (43.8 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 47% yield (28.9 mg) as a yellow solid, m.p. 93.0-94.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ:7.960 (s, 1H), 7.620 (s, 1H), 7.197 (s, 1H), 7.053 - 7.032 (m, 2H), 6.680 - 6.659 (m, 2H), 4.419 - 4.416 (m, 2H), 3.032 (s, 3H), 2.373 (s, 3H), 2.360 (s, 3H), 2.249 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.14, 155.35, 152.68, 147.19, 144.17, 134.48, 129.93, 126.29, 125.26, 121.75, 120.07, 118.32, 112.75, 49.55, 39.18, 20.54, 20.34, 19.48;

HRMS (ESI) calcd for $C_{20}H_{22}NO_2$: $[M+H]^+$ 308.1645. Found: m/z 308.1646.



3ta

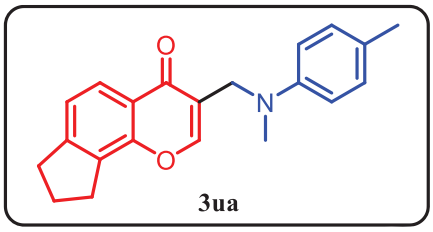
6-chloro-7-methyl-3-((methyl(p-tolyl)amino)methyl)-4H-chromen-4-one (3ta)

According to the general procedure, **3ta** was obtained using (*E*)-1-(5-chloro-2-hydroxy-4-methylphenyl)-3-(dimethylamino)prop-2-en-1-one **1t** (47.8 mg, 0.2 mmol) and *N*,*N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 62% yield (40.5 mg) as a yellow solid, m.p. 136.0-137.0℃(silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.180 (s, 1H), 7.637 (s, 1H), 7.310 (s, 1H), 7.058 - 7.038 (m, 2H), 6.672 - 6.652 (m, 2H), 4.410 - 4.407 (m, 2H), 3.033 (s, 3H), 2.485 (s, 3H), 2.253 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.00, 154.98, 153.00, 146.95, 142.98, 131.91, 129.96, 126.49, 125.32, 122.84, 120.32, 120.04, 112.74, 49.50, 39.27, 20.94, 20.35;

HRMS (ESI) calcd for $C_{19}H_{19}CLNO_2$: $[M+H]^+$ 328.1099. Found: m/z 328.1096.



3ua

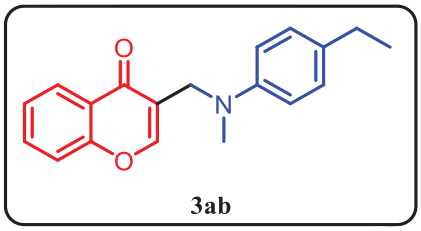
3-((methyl(p-tolyl)amino)methyl)-8,9-dihydrocyclopenta[h]chromen-4(7H)-one (3ua)

According to the general procedure, **3ua** was obtained using (*E*)-3-(dimethylamino)-1-(4-hydroxy-2,3-dihydro-1H-inden-5-yl)prop-2-en-1-one **1u** (46.2 mg, 0.2 mmol) and *N*,*N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 41% yield (26.2 mg) as a yellow solid, m.p. 137.0-138.0℃(silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.058 (d, *J* = 8.0 Hz, 1H), 7.651 (s, 1H), 7.274 (d, *J* = 8.0 Hz, 1H), 7.066 - 7.028 (m, 2H), 6.687 - 6.650 (m, 2H), 4.432 - 4.429 (m, 2H), 3.069 - 3.032 (m, 7H), 2.259 (s, 3H), 2.241 - 2.167 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.48, 152.62, 151.51, 150.83, 146.13, 131.25, 128.93, 125.26, 123.32, 121.35, 120.72, 119.02, 111.76, 48.51, 38.21, 32.82, 28.12, 24.12, 19.34;

HRMS (ESI) calcd for $C_{21}H_{22}NO_2$: $[M+H]^+$ 320.1645. Found: m/z 320.1649.



3ab

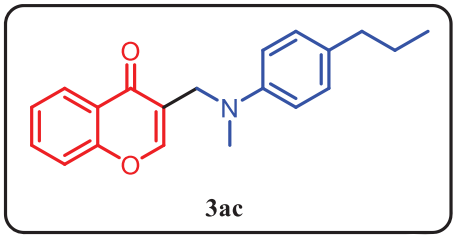
3-(((4-ethylphenyl)(methyl)amino)methyl)-4H-chromen-4-one (3ab)

According to the general procedure, **3ab** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **1a** (38.2 mg, 0.2 mmol) and 4-ethyl-*N,N*-dimethylaniline **2b** (119.2 mg, 0.8 mmol) in 72% yield (42.8 mg) as a yellow solid, m.p. 90.0-91.0℃(silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.271 - 8.247 (m, 1H), 7.701 - 7.642 (m, 2H), 7.445 - 7.396 (m, 2H), 7.093 - 7.072 (m, 2H), 6.713 - 6.692 (m, 2H), 4.443 - 4.440 (m, 2H), 3.051 (s, 3H), 2.565 (q, *J* = 7.6 Hz, 2H), 1.205 (t, *J* = 7.6 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ:178.16, 156.72, 153.01, 147.32, 133.67, 132.99, 128.75, 125.74, 125.16, 123.84, 120.51, 118.27, 112.70, 49.54, 39.17, 27.88, 16.01;

HRMS (ESI) calcd for $C_{19}H_{20}NO_2$: $[M+H]^+$ 294.1489. Found: m/z 294.1495.



3ac

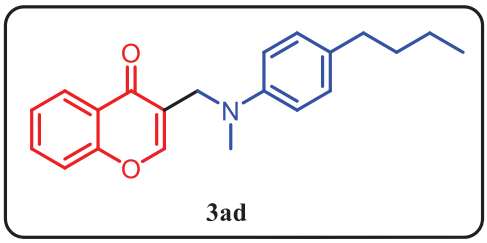
3-((methyl(4-propylphenyl)amino)methyl)-4H-chromen-4-one (3ac)

According to the general procedure, **3ac** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **1a** (38.2 mg, 0.2 mmol) and *N,N*-dimethyl-4-propylaniline **2c** (130.4 mg, 0.8 mmol) in 60% yield (36.8 mg) as a yellow solid, m.p. 89.0-90.0℃(silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.263 - 8.239 (m, 1H), 7.693 - 7.646 (m, 2H), 7.449 - 7.397 (m, 2H), 7.064 - 7.044 (m, 2H), 6.693 - 6.672 (m, 2H), 4.437 - 4.433 (m, 2H), 3.046 (s, 3H), 2.487 (t, *J* = 7.6 Hz, 2H), 1.617 - 1.542 (m, 2H), 0.925 (t, *J* = 7.6 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.24, 156.71, 153.02, 147.29, 133.71, 131.41, 129.37, 125.73, 125.19, 123.80, 120.47, 118.30, 112.51, 49.60, 39.15, 37.13, 25.01, 14.04.;

HRMS (ESI) calcd for $C_{20}H_{22}NO_2$: $[M+H]^+$ 308.1645. Found: m/z 308.1651.



3ad

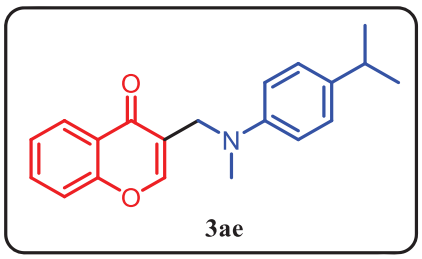
3-(((4-butylphenyl)(methyl)amino)methyl)-4H-chromen-4-one (3ad)

According to the general procedure, **3ad** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **1a** (38.2 mg, 0.2 mmol) and 4-butyl-*N,N*-dimethylaniline **2d** (141.6 mg, 0.8 mmol) in 58% yield (37.2 mg) as a yellow solid, m.p. 88.0-89.0℃(silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.268 - 8.244 (m, 1H), 7.699 (s, 1H), 7.684 - 7.641 (m, 1H), 7.444 - 7.394 (m, 2H), 7.074 - 7.037 (m, 2H), 6.701 - 6.681 (m, 2H), 4.437 - 4.434 (m, 2H), 3.045 (s, 3H), 2.516 (t, *J* = 8.0 Hz, 2H), 1.594 - 1.518 (m, 2H), 1.393 - 1.301 (m, 2H), 0.918 (t, *J* = 7.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ: 178.17, 156.74, 153.04, 147.30, 133.67, 131.66, 129.31, 125.76, 125.17, 123.86, 120.53, 118.28, 112.64, 49.57, 39.17, 34.68, 34.08, 22.50, 14.11;

HRMS (ESI) calcd for $C_{21}H_{24}NO_2$: $[M+H]^+$ 322.1802. Found: m/z 322.1812.



3ae

3-(4-(dimethylamino)benzyl)-4H-chromen-4-one (3ae)

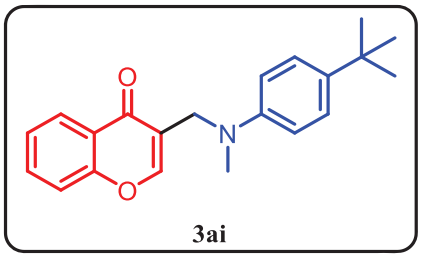
According to the general procedure, **3ae** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **1a** (38.2 mg, 0.2 mmol) and 4-isopropyl-*N,N*-dimethylaniline **2e** (130.4 mg, 0.8 mmol) in 53% yield (32.5 mg) as a yellow solid, m.p. 134.0-135.0℃(silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.273 - 8.248 (m, 1H), 7.713 - 7.706 (m, 1H), 7.687 - 7.643 (m, 1H), 7.448 - 7.397 (m, 2H), 7.133 - 7.095 (m, 2H), 6.727 - 6.690 (m, 2H), 4.442 - 4.439 (m, 2H), 3.052 (s, 3H), 2.890 - 2.779 (m, 1H), 1.223 (d, *J* = 7.2 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.16, 156.73, 153.02, 147.40, 137.61, 133.67, 127.28, 125.74,

125.16, 123.84, 120.55, 118.27, 112.57, 49.55, 39.14, 33.13, 24.32;

HRMS (ESI) calcd for $C_{20}H_{22}NO_2$: $[M+H]^+$ 308.1645. Found: m/z 308.1646.



3ai

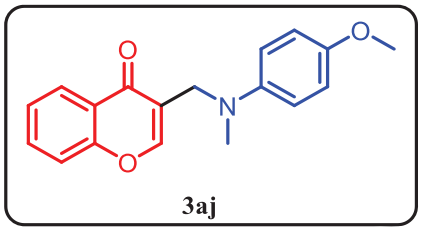
3-(((4-(tert-butyl)phenyl)(methyl)amino)methyl)-4H-chromen-4-one (3ai)

According to the general procedure, **3ai** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **1a** (38.2 mg, 0.2 mmol) and 4-(tert-butyl)-*N,N*-dimethylaniline **2i** (141.6 mg, 0.8 mmol) in 41% yield (26.3 mg) as a yellow solid, m.p. 87.0-88.0℃(silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.273 - 8.249 (m, 1H), 7.720 (s, 1H), 7.691 - 7.648 (m, 1H), 7.452 - 7.400 (m, 2H), 7.290 - 7.252 (m, 2H), 6.715 (d, *J* = 8.4 Hz, 2H), 4.447 - 4.443 (m, 2H), 3.059 (s, 3H), 1.293 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.17, 156.76, 153.08, 146.98, 139.88, 133.69, 126.22, 125.77, 125.19, 123.87, 120.57, 118.29, 112.27, 49.51, 39.12, 33.91, 31.64;

HRMS (ESI) calcd for $C_{21}H_{24}NO_2$: $[M+H]^+$ 322.1802. Found: m/z 322.180.



3aj

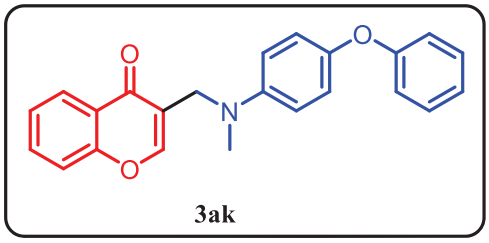
3-(((4-methoxyphenyl)(methyl)amino)methyl)-4H-chromen-4-one (3aj)

According to the general procedure, **3aj** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **1a** (38.2 mg, 0.2 mmol) and 4-methoxy-*N,N*-dimethylaniline **2j** (120.8 mg, 0.8 mmol) in 63% yield (37.2 mg) as a yellow solid, m.p. 93.0-94.0℃(silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.260 - 8.235 (m, 1H), 7.717 - 7.710 (m, 1H), 7.681 - 7.638 (m, 1H), 7.441 - 7.389 (m, 2H), 6.853 - 6.812 (m, 2H), 7.763 - 6.722 (m, 2H), 4.371 - 4.368 (m, 2H), 3.752 (s, 3H), 2.989 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.15, 156.72, 153.24, 152.20, 144.11, 133.69, 125.80, 125.20, 123.90, 120.67, 118.28, 115.01, 114.59, 55.91, 50.17, 39.67;

HRMS (ESI) calcd for $C_{18}H_{18}NO_3$: $[M+H]^+$ 296.1281. Found: m/z 296.1291.



3ak

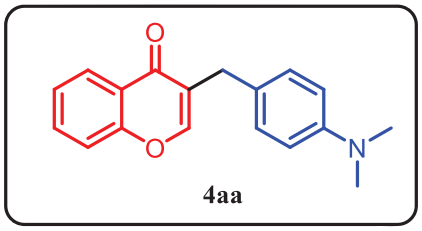
3-((methyl(4-phenoxyphenyl)amino)methyl)-4H-chromen-4-one (3ak)

According to the general procedure, **3ak** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **1a** (38.2 mg, 0.2 mmol) and *N,N*-dimethyl-4-phenoxyaniline **2k** (170.4 mg, 0.8 mmol) in 31% yield (22.1 mg) as a yellow solid, m.p. 125.0-126.0℃(silica gel flash chromatography: petroleum ether/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.266 - 8.242 (m, 1H), 7.736 (s, 1H), 7.695 - 7.652 (m, 1H), 7.442 - 7.400 (m, 2H), 7.305 - 7.271 (m, 2H), 7.032 - 6.989 (m, 1H), 6.970 - 6.925 (m, 4H), 6.757 (d, *J* = 8.4 Hz, 2H), 4.442 - 4.439 (m, 2H), 3.057 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.10, 159.01, 156.73, 153.05, 133.77, 129.64, 125.78, 125.26, 123.86, 122.20, 121.17, 120.35, 118.30, 117.39, 113.88, 49.92, 39.42;

HRMS (ESI) calcd for $C_{23}H_{20}NO_3$: $[M+H]^+$ 358.1438. Found: m/z 358.1441.



4aa

3-(4-(dimethylamino)benzyl)-4H-chromen-4-one (4aa)

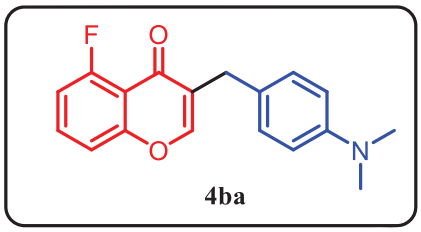
According to the general procedure, **4aa** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **1a** (38.2 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 75% yield (41.8 mg) as a white solid, m.p. 114.0-115.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.249 - 8.225 (m, 1H), 7.647 - 7.604 (m, 1H), 7.574 - 7.567 (m, 1H), 7.408 - 7.352 (m, 2H), 7.192 - 7.163 (m, 2H), 6.735 - 6.698 (m, 2H), 3.733 (s, 2H), 2.921 (s,

6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.79, 156.52, 153.20, 149.49, 133.42, 129.90, 126.39, 126.05, 125.47, 124.92, 123.95, 118.11, 113.16, 40.93, 30.77;

HRMS (ESI) calcd for $C_{18}H_{18}NO_2$: $[M+H]^+$ 280.1332. Found: m/z 280.1325.



4ba

3-(4-(dimethylamino)benzyl)-5-fluoro-4H-chromen-4-one (4ba)

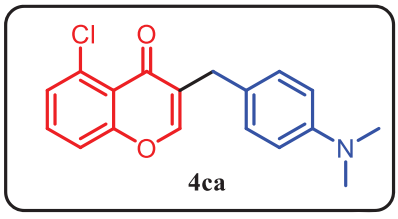
According to the general procedure, **4ba** was obtained using (*E*)-3-(dimethylamino)-1-(2-fluoro-6-hydroxyphenyl)prop-2-en-1-one **1b** (41.8 mg, 0.2 mmol) and *N*,*N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 67% yield (39.8 mg) as a white solid, m.p. 118.0-119.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.556 - 7.500 (m, 1H), 7.480 - 7.473 (m, 1H), 7.188 - 7.144 (m, 3H), 7.022 - 6.972 (m, 1H), 6.726 - 6.688 (m, 2H), 3.683 (s, 2H), 2.917 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.93, 160.95 (d, J = 263.0 Hz), 157.62 (d, J = 4.0 Hz), 152.08, 149.536, 133.35 (d, J = 11.0 Hz), 129.96, 126.60, 126.17, 114.50 (d, J = 10.0 Hz), 114.00 (d, J = 4.0 Hz), 113.17, 111.63 (d, J = 21.0 Hz), 40.89, 30.54;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -111.39.

HRMS (ESI) calcd for $C_{18}H_{17}FNO_2$: $[M+H]^+$ 298.1238. Found: m/z 298.1231.



4ca

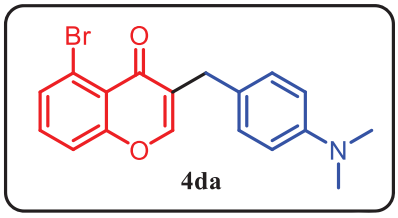
5-chloro-3-(4-(dimethylamino)benzyl)-4H-chromen-4-one (4ca)

According to the general procedure, **4ca** was obtained using (*E*)-1-(2-chloro-6-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one **1c** (45.0 mg, 0.2 mmol) and *N*,*N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 41% yield (27.5 mg) as a white solid 1120.0-121.0℃ (silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.484 - 7.449 (m, 2H), 7.360 - 7.337 (m, 1H), 7.319 - 7.286 (m, 1H), 7.168 - 7.147 (m, 2H), 6.726 - 6.697 (m, 2H), 3.689 (s, 2H), 2.922 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.53, 158.13, 151.73, 149.60, 133.73, 132.54, 130.01, 127.91, 126.76, 126.07, 120.95, 117.42, 113.16, 40.91, 30.74.;

HRMS (ESI) calcd for $C_{18}H_{17}CLNO_2$: $[M+H]^+$ 314.0942. Found: m/z 314.0952.



4da

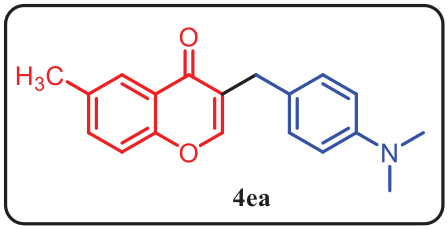
5-bromo-3-(4-(dimethylamino)benzyl)-4H-chromen-4-one (4da)

According to the general procedure, **4da** was obtained using (*E*)-1-(2-bromo-6-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one **1d** (53.8 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 35% yield (25.0 mg) as a white solid, m.p. 124.0-125.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.613 - 7.595 (m, 1H), 7.451 (s, 1H), 7.401 - 7.337 (m, 2H), 7.166 - 7.145 (m, 2H), 6.726 - 6.706 (m, 2H), 3.697 (s, 2H), 2.925 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.44, 157.92, 151.77, 149.56, 132.91, 131.75, 130.03, 126.39, 126.12, 121.53, 120.58, 118.20, 113.22, 40.96, 30.79;

HRMS (ESI) calcd for $C_{18}H_{17}BrNO_2$: $[M+H]^+$ 358.0437. Found: m/z 358.0432.



4ea

3-(4-(dimethylamino)benzyl)-6-methyl-4H-chromen-4-one (4ea)

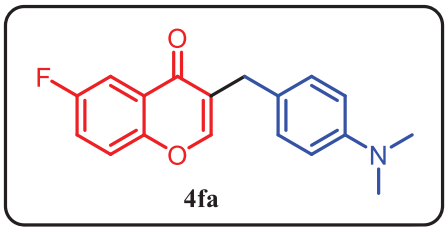
According to the general procedure, **4ea** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxy-5-methylphenyl)prop-2-en-1-one **1e** (41.1 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 69% yield (40.3 mg) as a white solid, m.p. 87.0-88.0℃(silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.021 - 8.013 (m, 1H), 7.542 - 7.536 (m, 1H), 7.439 - 7.412 (m,

1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.185 - 7.148 (m, 2H), 6.730 - 6.693 (m, 2H), 3.728 (s, 2H), 2.916 (s, 6H), 2.438 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.78, 154.81, 153.12, 149.47, 134.77, 134.65, 129.87, 126.61, 125.30, 125.22, 123.63, 117.83, 113.18, 40.91, 30.75, 21.03;

HRMS (ESI) calcd for $C_{19}H_{20}NO_2$: $[M+H]^+$ 294.1489. Found: m/z 294.1482.



4fa

3-(4-(dimethylamino)benzyl)-6-fluoro-4H-chromen-4-one (4fa)

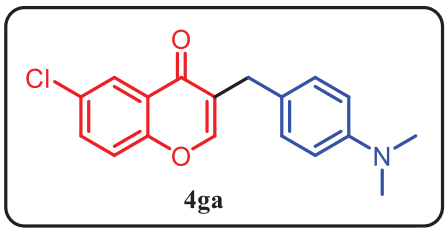
According to the general procedure, **4fa** was obtained using (*E*)-3-(dimethylamino)-1-(5-fluoro-2-hydroxyphenyl)prop-2-en-1-one **1f** (41.8 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 54% yield (32.1 mg) as a white solid, m.p. 149.0-150.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.873 - 7.844 (m, 1H), 7.575 - 7.569 (m, 1H), 7.419 - 7.317 (m, 2H), 7.177 - 7.140 (m, 2H), 6.730 - 6.693 (m, 2H), 3.723 (s, 2H), 2.921 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.99 (d, *J* = 2.0 Hz), 159.45 (d, *J* = 245.0 Hz), 153.39,152.77 (d, *J* = 2.0 Hz), 149.56, 129.87, 126.11, 125.04(d, *J* = 7.0 Hz), 124.91, 121.71 (d, *J* = 25.0 Hz), 120.20 (d, *J* = 8.0 Hz), 113.15, 110.73 (d, *J* = 24.0 Hz), 40.86, 30.70;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -115.68.

HRMS (ESI) calcd for $C_{18}H_{17}FNO_2$: $[M+H]^+$ 298.1238. Found: m/z 298.1232.



4ga

6-chloro-3-(4-(dimethylamino)benzyl)-4H-chromen-4-one (4ga)

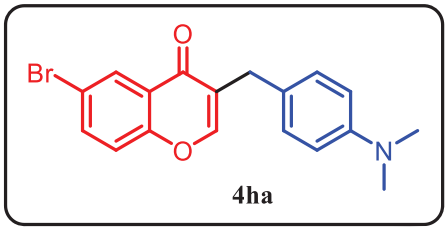
According to the general procedure, **4ga** was obtained using (*E*)-1-(5-bromo-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one **1g** (45.1 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 74% yield (46.3 mg) as a white solid, m.p. 133.0-134.0 ℃ (silica gel flash

chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.188 - 8.181 (m, 1H), 7.568 - 7.539 (m, 2H), 7.350 (d, *J* = 8.8 Hz, 1H), 7.169 - 7.132 (m, 2H), 6.728 - 6.690 (m, 2H), 3.716 (s, 2H), 2.920 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.57, 154.86, 153.35, 149.57, 133.65, 130.83, 129.89, 126.00, 125.67, 125.43, 124.86, 119.88, 113.17, 76.84, 40.88, 30.72;

HRMS (ESI) calcd for $C_{18}H_{17}CLNO_2$: $[M+H]^+$ 314.0942. Found: m/z 314.0949.



4ha

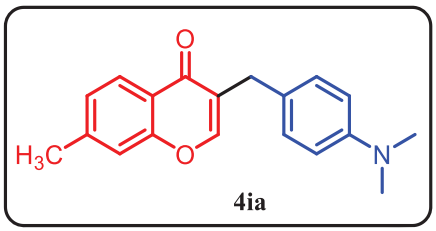
6-bromo-3-(4-(dimethylamino)benzyl)-4H-chromenb -4-one (4ha)

According to the general procedure, **4ha** was obtained using (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one **1h** (53.8 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 63% yield (45.1 mg) as a white solid, m.p. 120.0-121.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.348 - 8.339 (m, 1H), 7.701 - 7.673 (m, 1H), 7.552 - 7.542 (m, 1H), 7.297 - 7.272 (m, 1H), 7.167 - 7.137 (m, 2H), 6.726 - 6.687 (m, 2H), 3.713 (s, 2H), 3.920 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.51, 155.37, 153.43, 149.66, 136.48, 129.98, 128.75, 126.06, 125.88, 125.35, 120.21, 118.39, 113.26, 40.97, 30.83;

HRMS (ESI) calcd for $C_{18}H_{17}BrNO_2$: $[M+H]^+$ 358.0437. Found: m/z 358.0447.



4ia

3-(4-(dimethylamino)benzyl)-7-methyl-4H-chromen-4-one (4ia)

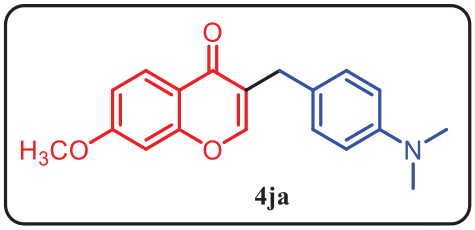
According to the general procedure, **4ia** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxy-4-methylphenyl)prop-2-en-1-one **1i** (41.1 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 54% yield (31.6 mg) as a white solid, m.p. 110.0-111.0 ℃ (silica gel flash

chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.111 (d, *J* = 8.4 Hz, 1H), 7.522 - 7.516 (m, 1H), 7.190 - 7.157 (m, 4H), 6.736 - 6,699 (m, 2H), 3.720 (s, 2H), 2.918 (s, 6H), 2.455 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.64, 156.70, 152.96, 149.45, 144.64, 129.90, 126.48, 125.81, 125.30, 121.77, 117.77, 113.23, 40.94, 30.75, 21.86;

HRMS (ESI) calcd for $C_{19}H_{20}NO_2$: $[M+H]^+$ 294.1489. Found: m/z 294.1489.



4ja

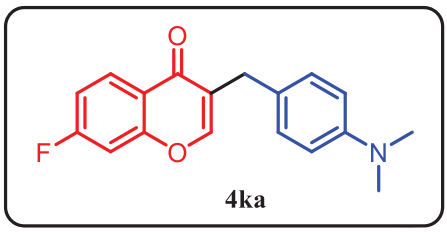
3-(4-(dimethylamino)benzyl)-7-methoxy-4H-chromen-4-one (4ja)

According to the general procedure, **4ja** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxy-4-methoxyphenyl)prop-2-en-1-one **1j** (44.2 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 67% yield (41.4 mg) as a white solid, m.p. 119.0-120.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.128 (d, *J* = 8.8 Hz, 1H), 7.481 - 7.475 (m, 1H), 7.182 - 7.144 (m, 2H), 6.948 - 6.920 (m, 1H), 6.766 - 6.760 (m, 1H), 6.732 - 6.695 (m, 2H), 3.867 (s, 3H), 3.706 (s, 2H), 2.915 (s, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ: 177.10, 163.88, 158.28, 152.72, 149.43, 129.89, 127.41, 126.65, 125.28, 117.95, 114.40, 113.20, 100.07, 55.84, 40.93, 30.67;

HRMS (ESI) calcd for $C_{19}H_{20}NO_3$: $[M+H]^+$ 310.1438. Found: m/z 310.1448.



4ka

3-(4-(dimethylamino)benzyl)-7-fluoro-4H-chromen-4-one (4ka)

According to the general procedure, **4ka** was obtained using (*E*)-3-(dimethylamino)-1-(4-fluoro-2-hydroxyphenyl)prop-2-en-1-one **1k** (41.8 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 52% yield (30.9 mg) as a white solid, m.p. 88.0-89.0 ℃ (silica gel flash chromatography:

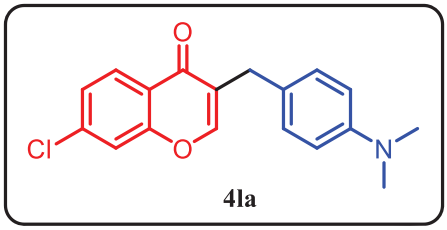
petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.260 - 8.222 (m, 1H), 7.538 - 7.532 (m, 1H), 7.182 - 7.145 (m, 2H), 7.127 - 7.061 (m, 2H), 6.739 - 6.717 (m, 2H), 3.713 (s, 2H), 2.927 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.85, 165.54(d, *J* = 253.0 Hz), 157.52(d, *J* = 13.0 Hz), 153.29, 149.55, 129.90, 128.64(d, *J* = 10.0 Hz), 126.14, 125.73, 120.88, 113.82(d, *J* = 23.0 Hz), 113.19, 104.61(d, *J* = 25.0 Hz), 40.90, 30.66;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -103.57.

HRMS (ESI) calcd for $C_{18}H_{17}FNO_2$: $[M+H]^+$ 298.1238. Found: m/z 298.1235.



4la

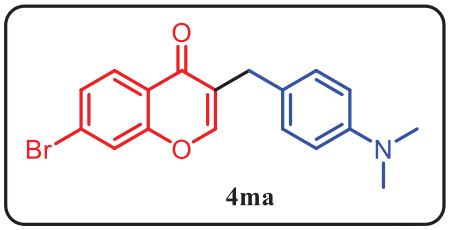
7-chloro-3-(4-(dimethylamino)benzyl)-4H-chromen-4-one (4la)

According to the general procedure, **4la** was obtained using (*E*)-1-(4-chloro-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one **1l** (45.0 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 83% yield (51.9 mg) as a white solid, m.p. 95.0-96.0℃(silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.179 (d, *J* = 8.4 Hz, 1H), 7.526 - 7.520 (m, 1H), 7.418 - 7.414 (m, 1H), 7.345 - 7.319 (m, 1H), 7.172 - 7.135 (m, 2H), 6.736 - 6.699 (m, 2H), 3.708 (s, 2H), 2.923 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.96, 156.64, 153.19, 149.52, 139.48, 129.92, 127.51, 125.95, 125.85, 122.52, 118.13, 113.24, 40.94, 30.71;

HRMS (ESI) calcd for $C_{18}H_{17}CLNO_2$: $[M+H]^+$ 314.0942. Found: m/z 314.0938.



4ma

7-bromo-3-(4-(dimethylamino)benzyl)-4H-chromen-4-one (4ma)

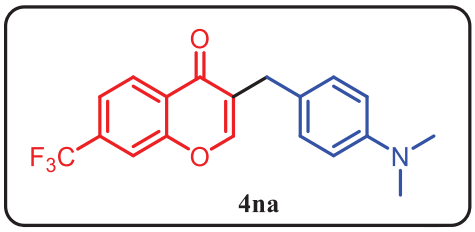
According to the general procedure, **4ma** was obtained using (*E*)-1-(4-bromo-2-hydroxyphenyl)-3-

(dimethylamino)prop-2-en-1-one **1m** (53.8 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 60% yield (42.8 mg) as a white solid, m.p. 105.0-106.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.0835 (d, *J* = 8.4 Hz, 1H), 7.591 -7.586 (m, 1H), 7.517 - 7.511 (m, 1H), 7.492 - 7.467 (m, 1H), 7.171 - 7.134 (m, 2H), 6.731 - 6.694 (m, 2H), 3.709 (s, 2H), 2.922 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.04, 156.58, 153.12, 149.55, 129.90, 128.59, 127.66, 127.54, 125.98, 122.85, 121.18, 113.18, 40.89, 30.71;

HRMS (ESI) calcd for $C_{18}H_{17}BrNO_2$: $[M+H]^+$ 358.0437. Found: m/z 358.0435.



4na

3-(4-(dimethylamino)benzyl)-7-(trifluoromethyl)-4H-chromen-4-one (4na)

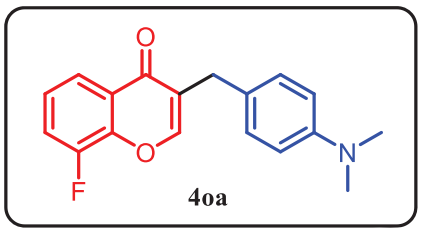
According to the general procedure, **4na** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxy-4-(trifluoromethyl)phenyl)prop-2-en-1-one **1n** (51.8 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 65% yield (45.1 mg) as a white solid, m.p. 118.0-119.0℃(silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.366 - 8.341 (m, 1H), 7.699 - 7.694 (m, 1H), 7.618 - 7.586 (m, 2H), 7.179 - 7.142 (m, 2H), 6.739 - 6.702 (m, 2H), 3.736 (s, 2H), 2.928 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.81, 155.91, 153.74, 149.60, 135.06 (q, *J* = 33.0 Hz), 129.93, 127.47, 126.43, 126.05, 125.76, 124.62, 121.25 (q, *J* = 3.0 Hz), 116.09 (q, *J* = 4.0 Hz), 113.20, 40.88, 30.75;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -63.03.

HRMS (ESI) calcd for $C_{19}H_{17}F_3NO_2$: $[M+H]^+$ 348.1206. Found: m/z 348.1215.



4oa

3-(4-(dimethylamino)benzyl)-8-fluoro-4H-chromen-4-one (4oa)

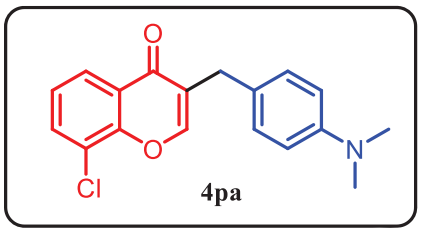
According to the general procedure, **4oa** was obtained using (*E*)-3-(dimethylamino)-1-(3-fluoro-2-hydroxyphenyl)prop-2-en-1-one **1o** (41.8 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 62% yield (36.8 mg) as a white solid, m.p. 185.0-186.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.995 - 7.968 (m, 1H), 7.611 - 7.605 (m, 1H), 7.417 - 7.368 (m, 1H), 7.317 - 7.265 (m, 1H), 7.180 - 7.143 (m, 2H), 6.733 - 6.695 (m, 2H), 3.729 (s, 2H), 2.921 (s, 6H);

^{13}C NMR (100 MHz, CDCl3) δ: 176.75 (d, *J* = 3.0 Hz), 152.77, 151.26 (d, *J* = 252.0 Hz), 149.58, 145.391 (d, *J* = 11.0 Hz), 129.88, 126.02, 125.97, 125.88, 124.45 (d, *J* = 6.0 Hz), 121.09 (d, *J* = 4.0 Hz), 119.04 (d, *J* = 17.0 Hz), 113.20, 40.90, 30.76;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -134.06.

HRMS (ESI) calcd for $C_{18}H_{17}FNO_2$: $[M+H]^+$ 298.1238. Found: m/z 298.1236.



4pa

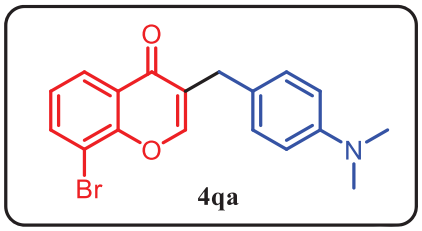
8-chloro-3-(4-(dimethylamino)benzyl)-4H-chromen-4-one (4pa)

According to the general procedure, **4pa** was obtained using (*E*)-1-(3-chloro-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one **1p** (45.1 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 78% yield (48.8 mg) as a white solid, m.p. 196.0-197.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.148 - 8.124 (m, 1H), 7.695 - 7.672 (m, 1H), 7.641 - 7.635 (m, 1H), 7.300 (t, *J* = 8.0 Hz, 1H), 7.177 - 7.140 (m, 2H), 6.737 - 6.700 (m, 2H), 3.730 (s, 2H), 2.922 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.10, 153.11, 152.24, 149.56, 133.68, 129.92, 125.92, 125.29, 124.96, 124.74, 123.08, 113.26, 40.94, 30.76;

HRMS (ESI) calcd for $C_{18}H_{17}CLNO_2$: $[M+H]^+$ 314.0942. Found: m/z 314.0949.



4qa

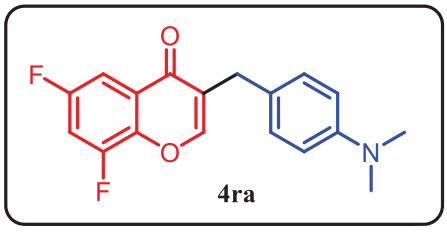
8-bromo-3-(4-(dimethylamino)benzyl)-4H-chromen-4-one (4qa)

According to the general procedure, **4qa** was obtained using (*E*)-1-(3-bromo-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one **1q** (53.8 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 67% yield (47.8 mg) as a white solid, m.p. 176.0-177.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.188 - 8.164 (m, 1H), 7.859 - 7.836 (m, 1H), 7.631 - 7.625 (m, 1H), 7.253 - 7.221 (m, 1H), 7.168 - 7.130 (m, 2H), 6.722 - 6.693 (m, 2H),3.721 (s, 2H), 2.915 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.16, 153.25, 153.09, 149.55, 136.91, 129.93, 125.84, 125.56, 125.54, 125.24, 113.26, 111.70, 77.48, 77.16, 76.84, 40.95, 30.76;

HRMS (ESI) calcd for $C_{18}H_{17}BrNO_2$: $[M+H]^+$ 358.0437. Found: m/z 358.0438.



4ra

3-(4-(dimethylamino)benzyl)-6,8-difluoro-4H-chromen-4-one (4ra)

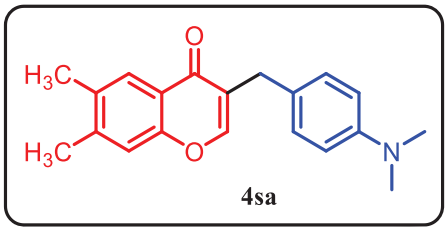
According to the general procedure, **4ra** was obtained using (*E*)-1-(3,5-difluoro-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one **1r** (45.4 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 57% yield (35.9 mg) as a white solid, m.p. 121.0-122.0 ℃ (silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.674 - 7.641 (m, 1H), 7.605 - 7.599 (m, 1H), 7.219 - 7.167 (m, 1H), 7.159 - 7.137 (m, 2H), 6.731 - 6.701 (m, 2H), 3.719 (s, 2H), 2.924 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.89 (t, *J* = 3.0 Hz), 158.24 (dd, *J* = 247.0, 9.0 Hz), 152.98, 151.57 (dd, *J* = 256.0, 2.0 Hz), 149.63, 142.97 (dd, *J* = 11.0, 3.0 Hz),129.89, 126.07 (d, *J* = 8.1 Hz), 125.66, 125.61, 113.20, 108.86 (dd, *J* = 28.0, 20.0 Hz), 106.10 (dd, *J* = 23.0, 5.0 Hz), 40.88, 30.73;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -112.38 (d, *J* = 4.9 Hz), -128.49 (d, *J* = 4.5 Hz).

HRMS (ESI) calcd for $C_{18}H_{16}F_2NO_2$: $[M+H]^+$ 316.1144. Found: m/z 316.1151.



4sa

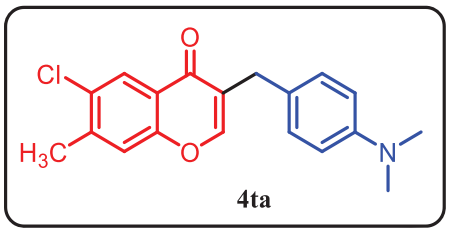
3-(4-(dimethylamino)benzyl)-6,7-dimethyl-4H-chromen-4-one (4sa)

According to the general procedure, **4sa** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxy-4,5-dimethylphenyl)prop-2-en-1-one **1s** (43.8 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 70% yield (43.0 mg) as a white solid, m.p. 143.0-144.0℃ (silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.956 (s, 1H), 7.499 - 7.494 (m, 1H), 7.182 - 7.145 (m, 3H), 6.728 - 6.691 (m, 2H), 3.720 (s, 2H), 2.914 (s, 6H), 2.350 (s, 3H), 2.334 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.67, 155.13, 152.88, 149.45, 143.76, 134.12, 129.89, 126.77, 125.57, 125.11, 121.86, 118.14, 113.19, 40.92, 30.76, 20.45, 19.41;

HRMS (ESI) calcd for $C_{20}H_{22}NO_2$: $[M+H]^+$ 308.1645. Found: m/z 308.1647.



4ta

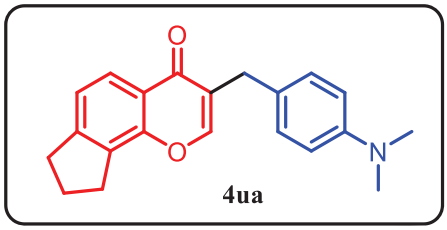
6-chloro-3-(4-(dimethylamino)benzyl)-7-methyl-4H-chromen-4-one (4ta)

According to the general procedure, **4ta** was obtained using (*E*)-1-(5-chloro-2-hydroxy-4-methylphenyl)-3-(dimethylamino)prop-2-en-1-one **1t** (47.8 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 73% yield (47.7 mg) as a white solid, m.p. 180.0-181.0℃ (silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.169 (s, 1H), 7.509 - 7.502 (m, 1H), 7.272 (s, 1H), 7.168 - 7.131 (m, 2H), 6.728 - 6.691 (m, 2H), 3.708 (s, 2H), 2.919 (s, 6H), 2.467 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.61, 154.85, 153.17, 149.54, 142.61, 131.63, 129.91, 126.24, 125.69, 125.44, 123.05, 119.90, 113.21, 40.92, 30.72, 20.87;

HRMS (ESI) calcd for $C_{19}H_{19}CLNO_2$: $[M+H]^+$ 328.1099. Found: m/z 328.1092.



4ua

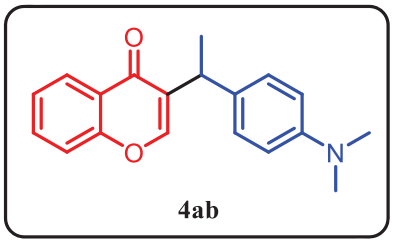
3-(4-(dimethylamino)benzyl)-8,9-dihydrocyclopenta[h]chromen-4(7H)-one (4ua)

According to the general procedure, **4ua** was obtained using (*E*)-3-(dimethylamino)-1-(4-hydroxy-2,3-dihydro-1H-inden-5-yl)prop-2-en-1-one **1u** (46.2 mg, 0.2 mmol) and *N,N*,4-trimethylaniline **2a** (108.1 mg, 0.8 mmol) in 52% yield (33.2 mg) as a white solid, m.p. 106.0-107.0℃(silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.045 (d, *J* = 8.0 Hz, 1H), 7.545 - 7.540 (m, 1H), 7.241 - 7.221 (m, 1H), 7.184 - 7.147 (m, 2H), 6.731 - 6.694 (m, 2H), 3.727 (s, 2H), 3.055 - 3.014 (m, 4H), 2.914 (s, 6H), 2.229 - 2.154 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.97, 153.40, 152.71, 151.41, 149.44, 132.00, 129.87, 126.74, 125.13, 124.60, 122.42, 121.44, 113.23, 77.48, 77.16, 76.84, 40.95, 33.73, 30.79, 29.05, 25.05;

HRMS (ESI) calcd for $C_{21}H_{22}NO_2$: $[M+H]^+$ 320.1645. Found: m/z 320.1640.



4ab

3-(1-(4-(dimethylamino)phenyl)ethyl)-4H-chromen-4-one (4ab)

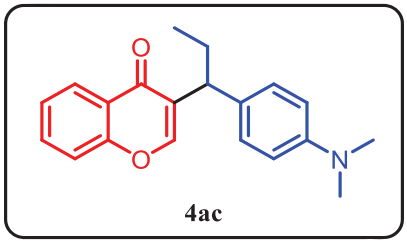
According to the general procedure, **4ab** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **1a** (38.2 mg, 0.2 mmol) and 4-ethyl-*N,N*-dimethylaniline **2b** (119.2 mg, 0.8 mmol) in 43% yield (25.2 mg) as a white solid, m.p. 85.0-86.0℃(silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.234 - 8.209 (m, 1H), 7.637 - 7.594 (m, 1H), 7.582 - 7.579 (m, 1H), 7.399 - 7.338 (m, 2H), 7.228 - 7.190 (m, 2H), 6.744 - 6.706 (m, 2H), 4.380 - 4.326 (m, 1H), 2.921 (s, 6H), 1.561 (d, *J* = 7.6 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.23, 156.33, 153.08, 149.42, 133.36, 131.67, 130.14, 128.40,

126.20, 124.86, 124.16, 118.05, 113.06, 40.93, 34.60, 19.89;

HRMS (ESI) calcd for $C_{19}H_{20}NO_2$: $[M+H]^+$ 294.1489. Found: m/z 294.1494.



4ac

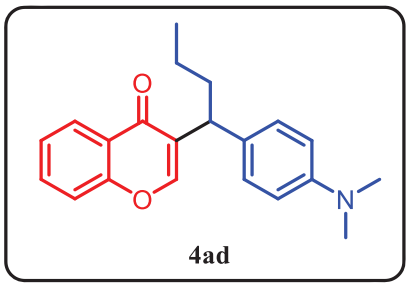
3-(1-(4-(dimethylamino)phenyl)butyl)-4H-chromen-4-one (4ac)

According to the general procedure, **4ac** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **1a** (38.2 mg, 0.2 mmol) and *N,N*-dimethyl-4-propylaniline **2c** (130.4 mg, 0.8 mmol) in 50% yield (30.7 mg) as a white solid, m.p. 124.0-125.0℃(silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.219 - 8.195 (m, 1H), 7.681 (s, 1H), 7.624 - 7.580 (m, 1H), 7.394 - 7.323 (m, 2H), 7.234 - 7.196 (m, 2H), 6.730 - 6.692 (m, 2H), 4.068 - 4.029 (m, 1H), 2.913 (s, 6H), 2.107 - 2.003 (s, 1H), 1.955 - 1.843 (m, 1H), 0.945 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.28, 156.21, 152.87, 149.36, 133.29, 130.32, 128.87, 128.82, 126.16, 124.80, 124.15, 117.98, 112.88, 42.14, 40.82, 26.87, 12.86.;

HRMS (ESI) calcd for $C_{20}H_{22}NO_2$: $[M+H]^+$ 308.1645. Found: m/z 308.1638.



4ad

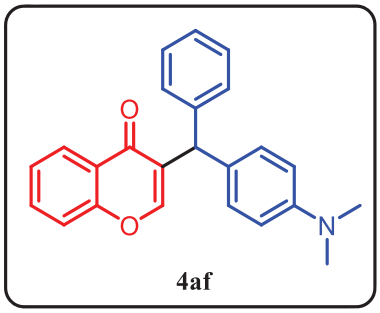
3-(1-(4-(dimethylamino)phenyl)butyl)-4H-chromen-4-one (4ad)

According to the general procedure, **4ad** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **1a** (38.2 mg, 0.2 mmol) and 4-(tert-butyl)-*N,N*-dimethylaniline **2d** (141.6 mg, 0.8 mmol) in 58% yield (37.2 mg) as a white solid, m.p. 85.0-86.0℃(silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.215 - 8.191 (m, 1H), 7.682 (s, 1H), 7.624 - 7.581 (m, 1H), 7.391 - 7.325 (m, 2H), 7.228 - 7.191 (m, 2H), 6.723 - 6.685 (m, 2H), 4.179 - 4.140 (m, 1H), 2.909 (s, 6H), 2.015 -1.833 (m, 2H), 1.378 - 1.312 (m, 2H), 0.928 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.42, 156.23, 152.49, 149.19, 133.29, 130.12, 128.76, 126.80, 126.22, 124.80, 124.23, 117.98, 112.86, 47.04, 40.89, 38.83, 27.88, 27.44, 17.57;

HRMS (ESI) calcd for $C_{22}H_{24}NO_2$: $[M+H]^+$ 334.1802. Found: m/z 334.1807.



4af

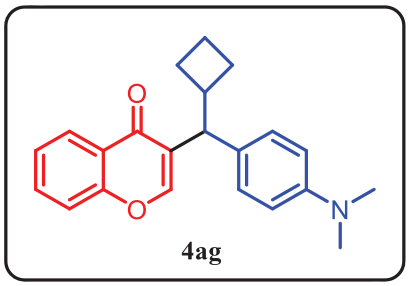
3-((4-(dimethylamino)phenyl)(phenyl)methyl)-4H-chromen-4-one (4af)

According to the general procedure, **4af** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **1a** (38.2 mg, 0.2 mmol) and 4-benzyl-*N,N*-dimethylaniline **2f** (168.8 mg, 0.8 mmol) in 73% yield (51.8 mg) as a white solid, m.p. 133.0-134.0℃(silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.206 - 8.182 (m, 1H), 7.636 - 7.593 ((m, 1H), 7.411 - 7.386 (m, 2H), 7.367 - 7.326 (m, 1H), 7.300 - 7.267 (m, 2H), 7.213 - 7.190 (m, 3H), 7.056 - 7.018 (m, 2H), 6.694 - 6.657 (m, 2H), 5.684 (s, 1H), 2.902 (s, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ: 176.83, 156.36, 155.38, 149.43, 142.23, 133.51, 129.75, 129.25, 128.94, 128.51, 128.46, 126.54, 126.31, 124.99, 123.99, 118.09, 112.84, 46.21, 40.73;

HRMS (ESI) calcd for $C_{24}H_{22}NO_2$: $[M+H]^+$ 356.1645. Found: m/z 356.1637.



4ag

3-(cyclobutyl(4-(dimethylamino)phenyl)methyl)-4H-chromen-4-one (4ag)

According to the general procedure, **4ag** was obtained using (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one **1a** (38.2 mg, 0.2 mmol) and 4-(cyclobutylmethyl)-*N,N*-dimethylaniline **2g** (151.3 mg, 0.8 mmol) in 62% yield (41.3 mg) as a white solid, m.p. 117.0-118.0℃ (silica gel flash chromatography: petroleum ether/EtOAc = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.188 - 8.164 (m, 1H), 7.769 (s, 1H), 7.620 - 7.576 (m, 1H), 7401 - 7.377 (m, 1H), 7.349 - 7.309 (m, 1H), 7.206 - 7.176 (m, 2H), 6.693 - 6.656 (m, 2H), 4.127 (d, *J* = 11.6 Hz, 1H), 3.004 - 2.936 (m, 1H), 2.889 (s, 6H), 2.094 - 1.980 (m, 2H), 1.891 - 1.726 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.42, 156.23, 152.49, 149.19, 133.29, 130.12, 128.76, 126.80, 126.22, 124.80, 124.23, 117.98, 112.86, 47.04, 40.89, 38.83, 27.88, 27.44, 17.57;

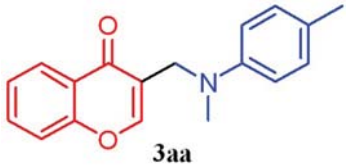
HRMS (ESI) calcd for $C_{22}H_{24}NO_2$: $[M+H]^+$ 334.1802. Found: m/z 334.1807.

[1] Lei, S.-G.; Zhou, Y.; Wang, L.-S.; Yu, Z.-C.; Chen, T.; Wu, Y.-D.; Gao, M.; Wu, A.-X., I2-DMSO mediated dual α,β-C(sp2)–H functionalization/bicyclization of o-hydroxyphenyl enaminones to construct C2,C3-disubstituted chromone derivatives: chromeno[2,3-b]pyrrol-4(1H)-ones. *Organic Chemistry Frontiers* **2023,** *10* (19), 4843-4847.

[2] Zhang, J.; Huang, X.; Zhang, R. K.; Arnold, F. H., Enantiodivergent α-Amino C–H Fluoroalkylation Catalyzed by Engineered Cytochrome P450s. *Journal of the American Chemical Society* **2019,** *141* (25), 9798-9802.

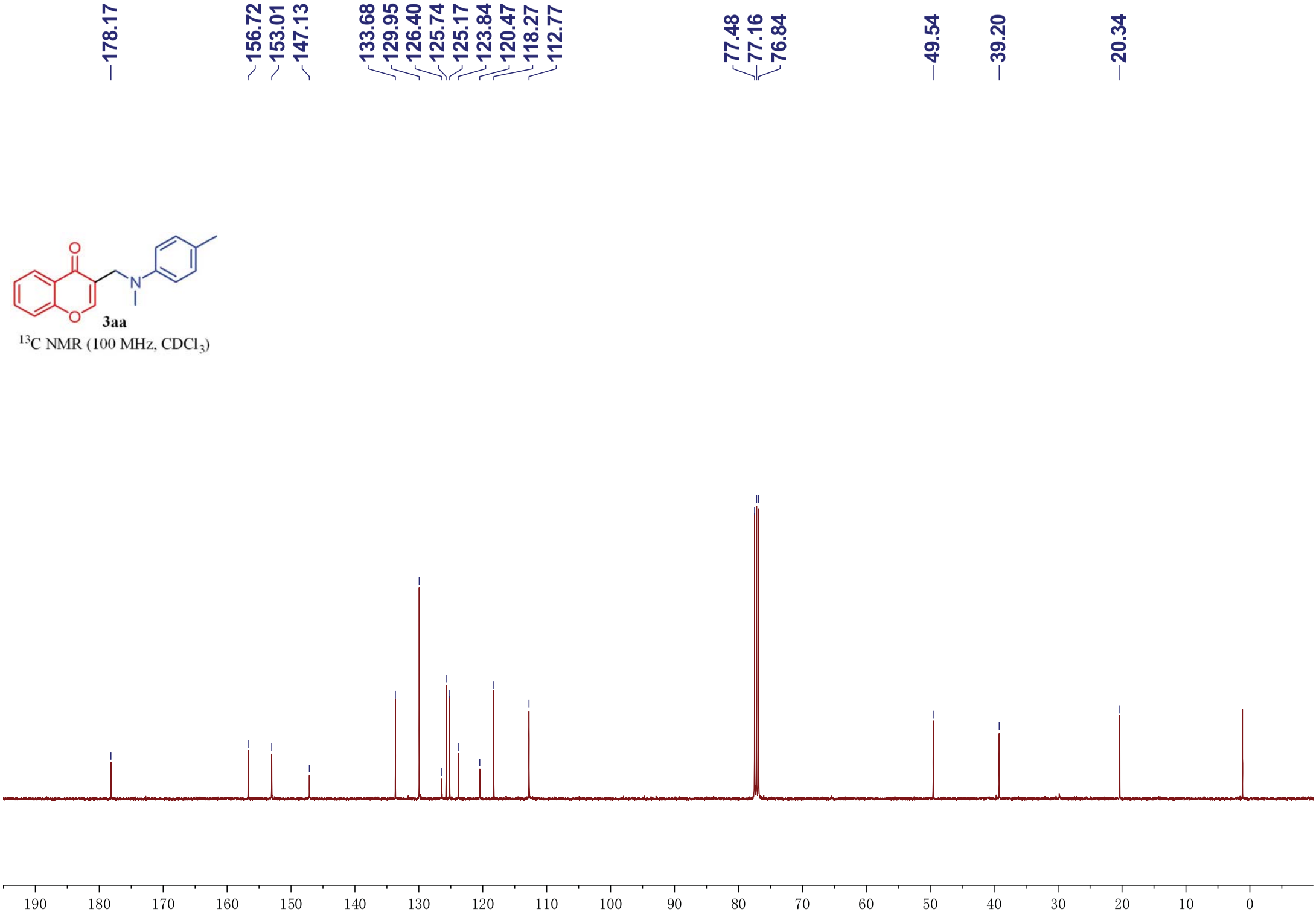
[3] Cicco, S. R.; Martinelli, C.; Pinto, V.; Naso, F.; Farinola, G. M., Oxidative cross-coupling of vinylsilanes in water. *Journal of Organometallic Chemistry* **2013,** *732*, 15-20.

(H) Spectra



3aa

^{1}H NMR (400 MHz, $CDCl_3$)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129.95
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125.74
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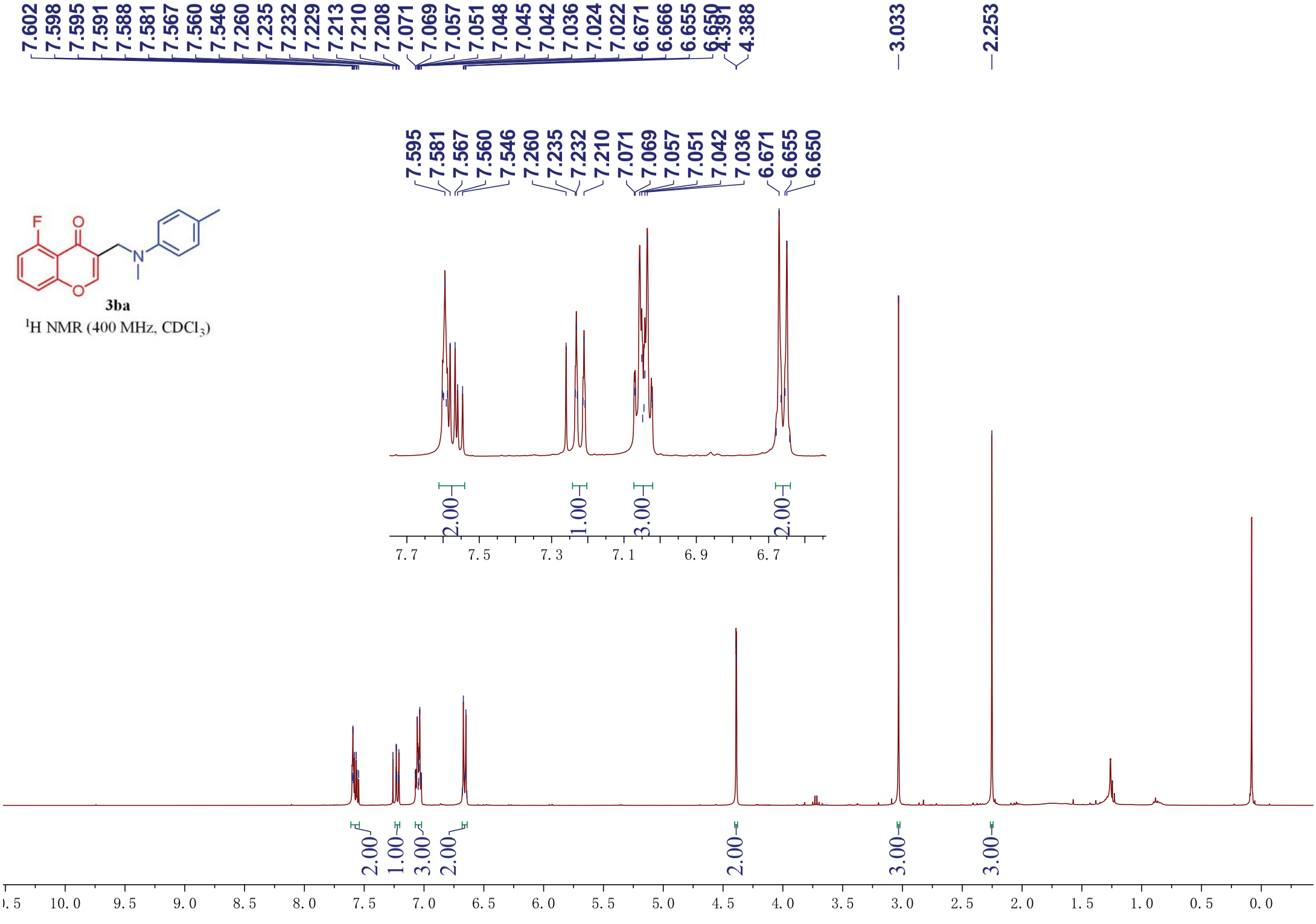
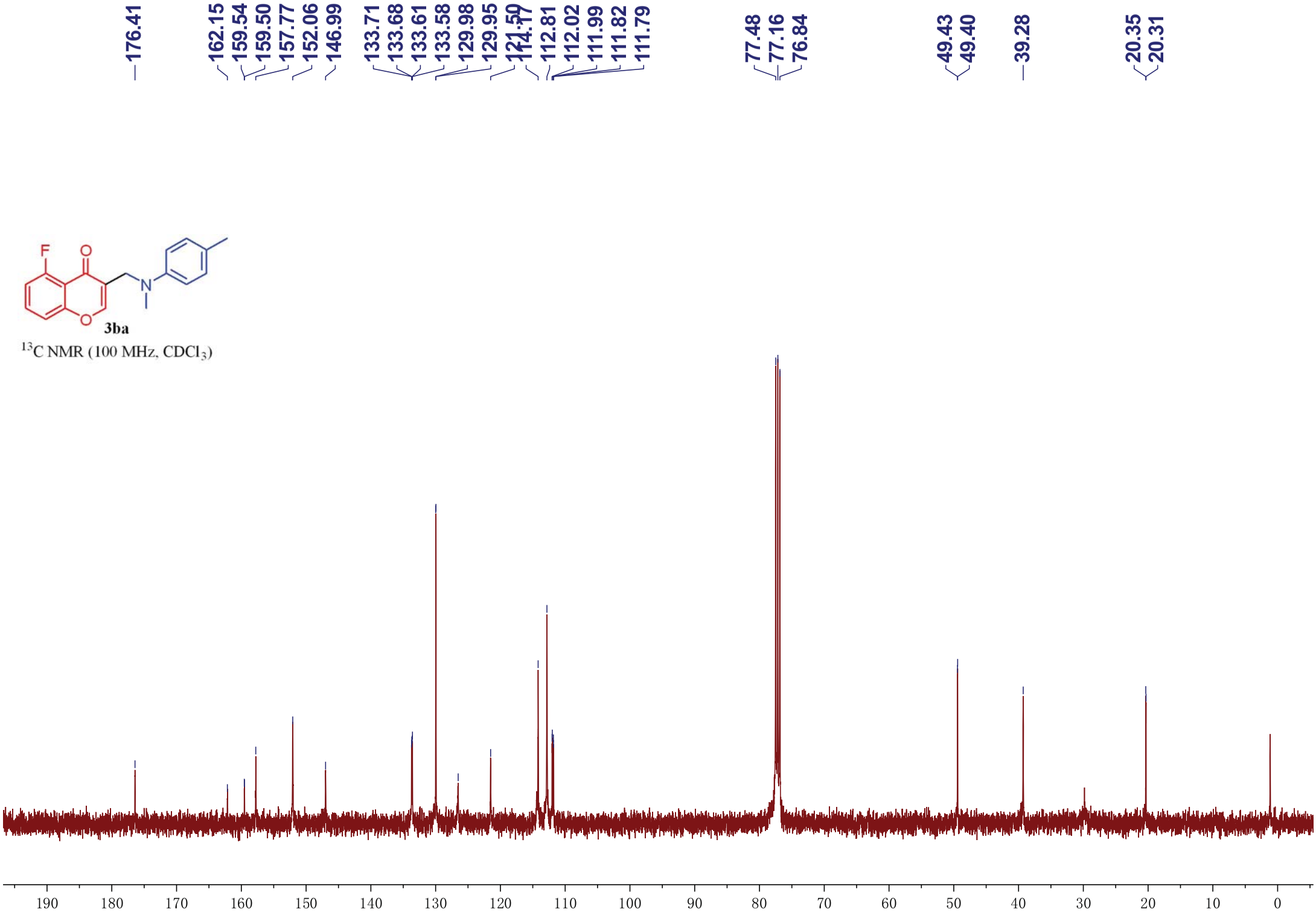
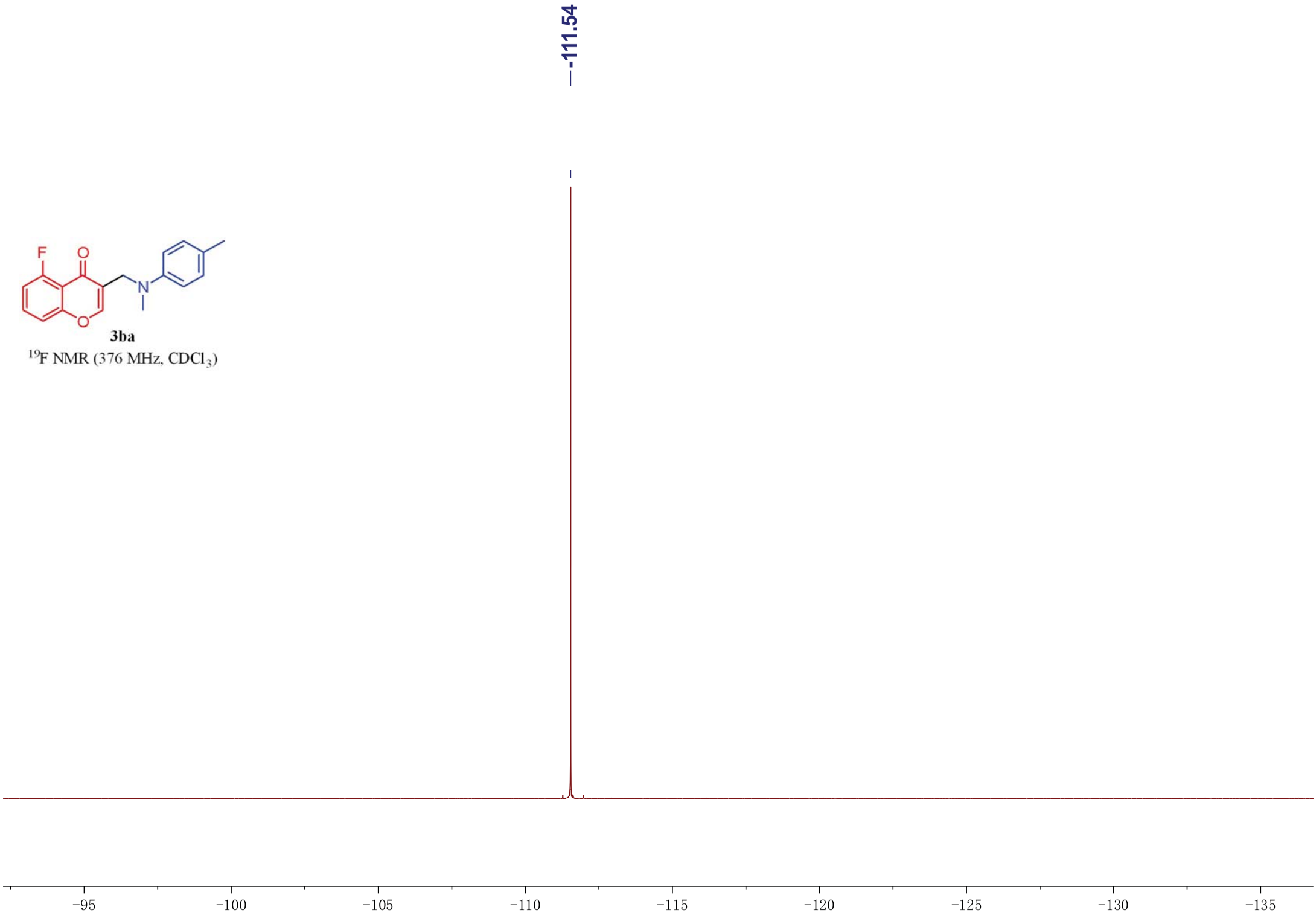
123.84
120.47
118.27
112.77
77.48
77.16
76.84
49.54
39.20
20.34
O
N
O
3aa
^{13}C NMR (100 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

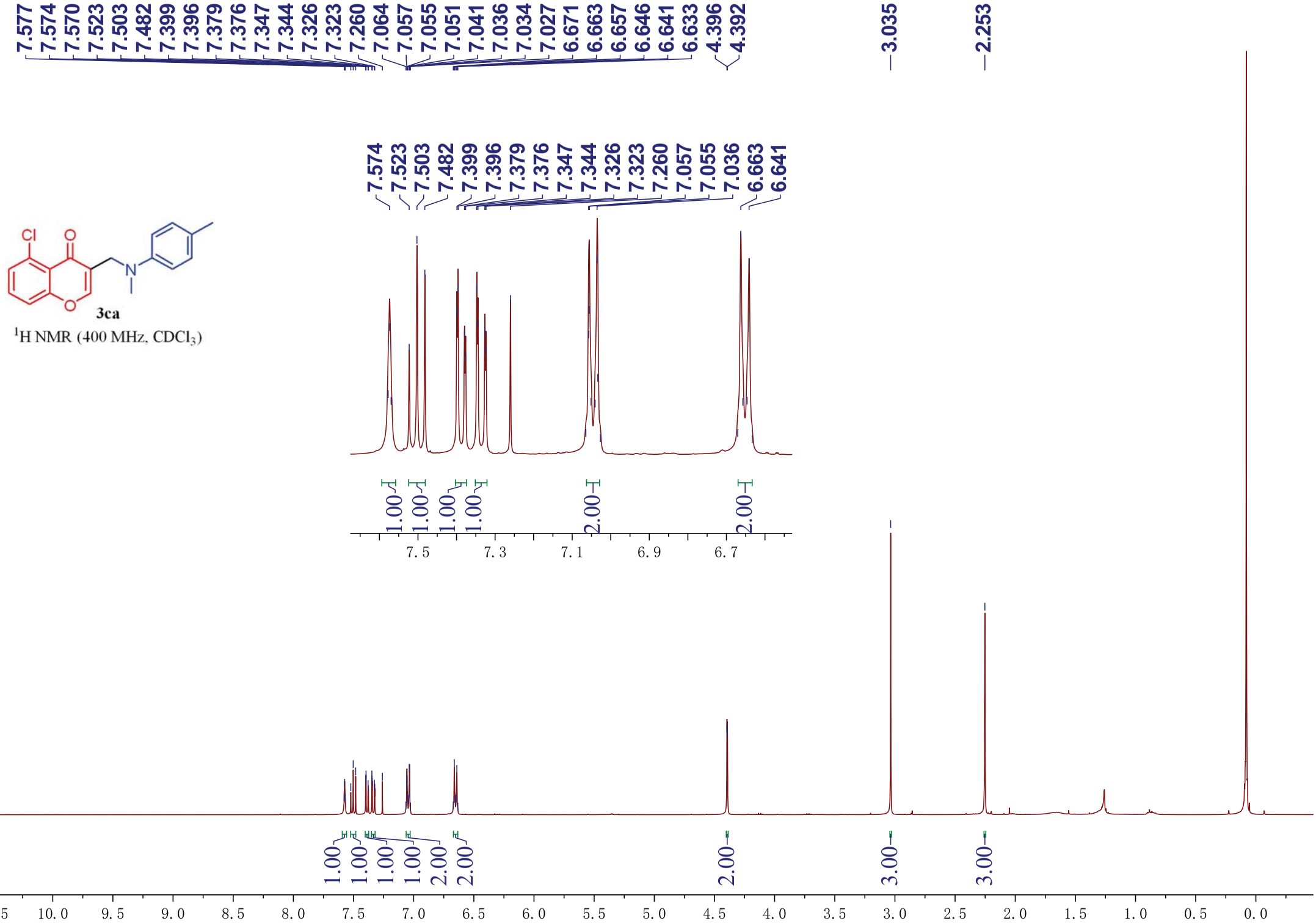

7.602
7.598
7.595
7.591
7.588
7.581
7.567
7.560
7.546
7.260
7.235
7.232
7.229
7.213
7.210
7.208
7.071
7.069
7.057
7.051
7.048
7.045
7.042
7.036
7.024
7.022
6.671
6.666
6.655
6.650
4.391
4.388
3.033
2.253
F
O
N
O
3ba
1H NMR (400 MHz, CDCl3)
2.00
1.00
3.00
2.00
7.7
7.5
7.3
7.1
6.9
6.7
2.00
1.00
3.00
2.00
2.00
3.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

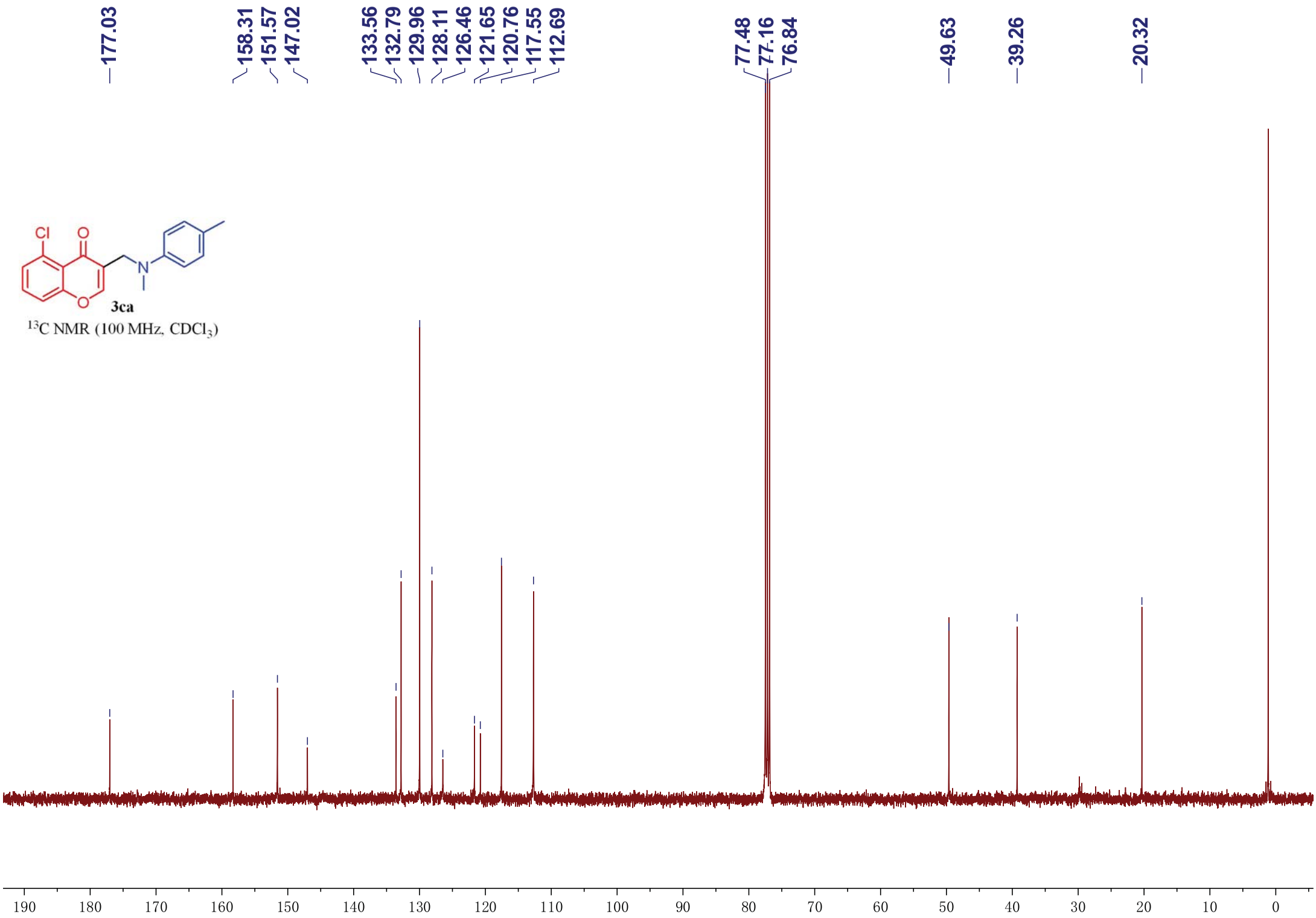

176.41
162.15
159.54
159.50
157.77
152.06
146.99
133.71
133.68
133.61
133.58
129.98
129.95
121.50
114.17
112.81
112.02
111.99
111.82
111.79
77.48
77.16
76.84
49.43
49.40
39.28
20.35
20.31
F
O
N
O
3ba
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

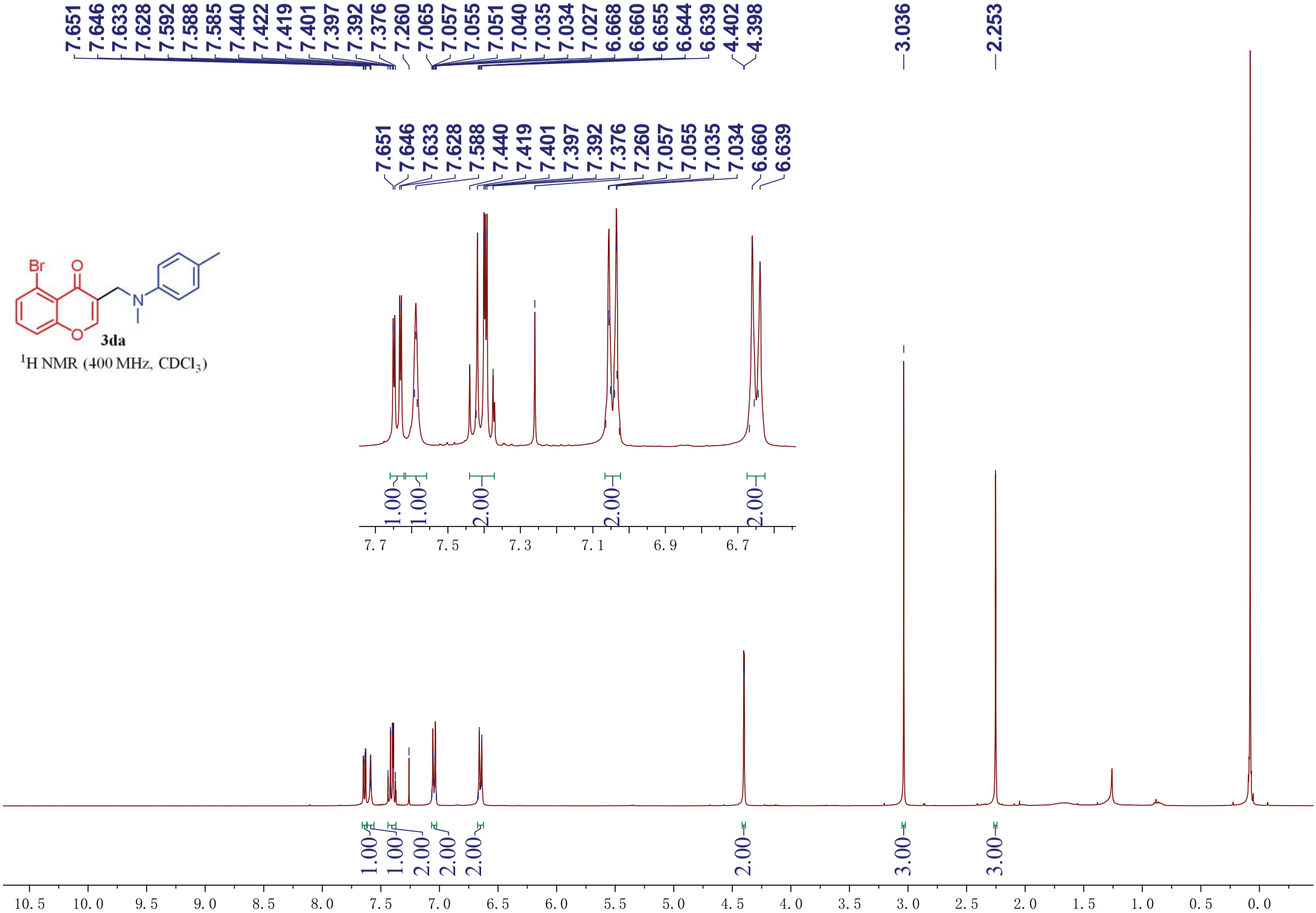
3ba

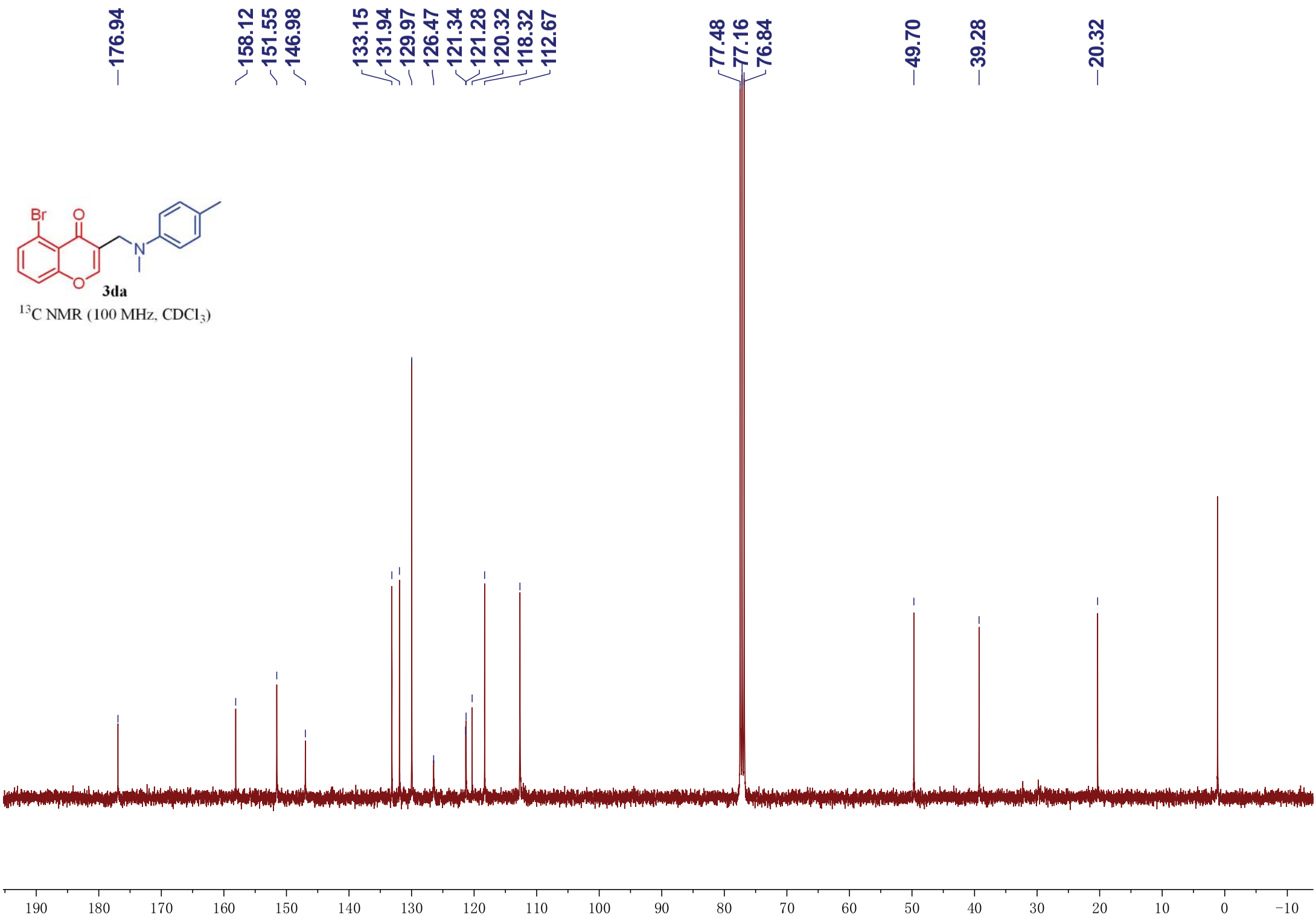
^{19}F NMR (376 MHz, $CDCl_3$)




7.577
7.574
7.570
7.523
7.503
7.482
7.399
7.396
7.379
7.376
7.347
7.344
7.326
7.323
7.260
7.064
7.057
7.055
7.051
7.041
7.036
7.034
7.027
6.671
6.663
6.657
6.646
6.641
6.633
4.396
4.392
3.035
2.253
Cl
O
N
O
3ca
^{1}H NMR (400 MHz, $CDCl_3$)
1.00
1.00
1.00
1.00
2.00
2.00
7.5
7.3
7.1
6.9
6.7
1.00
1.00
1.00
1.00
2.00
2.00
2.00
3.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

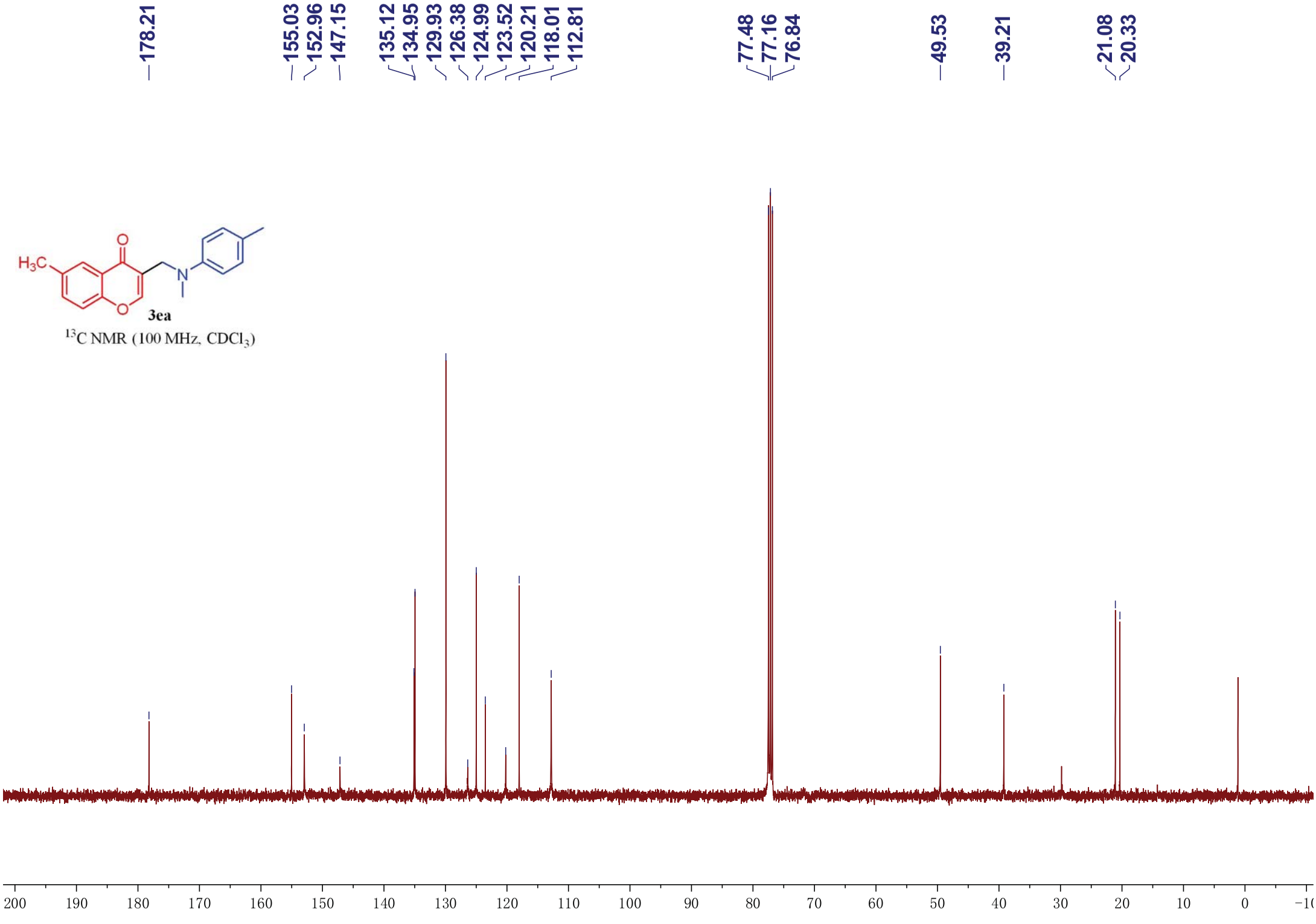

177.03
158.31
151.57
147.02
133.56
132.79
129.96
128.11
126.46
121.65
120.76
117.55
112.69
77.48
77.16
76.84
49.63
39.26
20.32
Cl
O
N
O
3ca
^{13}C NMR (100 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

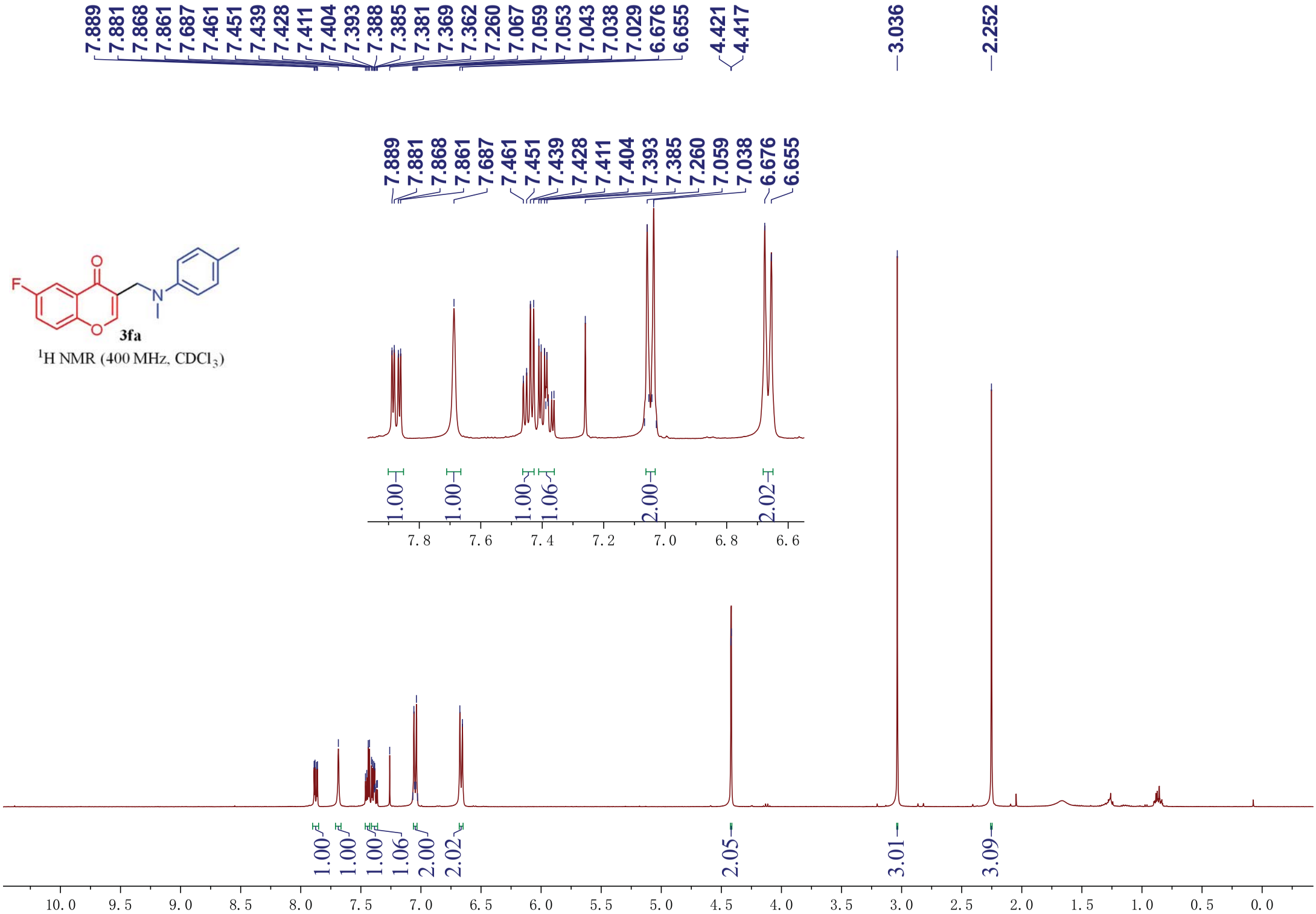

7.651
7.646
7.633
7.628
7.592
7.588
7.585
7.440
7.422
7.419
7.401
7.397
7.392
7.376
7.260
7.065
7.057
7.055
7.051
7.040
7.035
7.034
7.027
6.668
6.660
6.655
6.644
6.639
4.402
4.398
3.036
2.253
Br
O
N
3da
1H NMR (400 MHz, CDCl3)
1.00
1.00
2.00
2.00
2.00
7.7
7.5
7.3
7.1
6.9
6.7
1.00
1.00
2.00
2.00
2.00
3.00
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

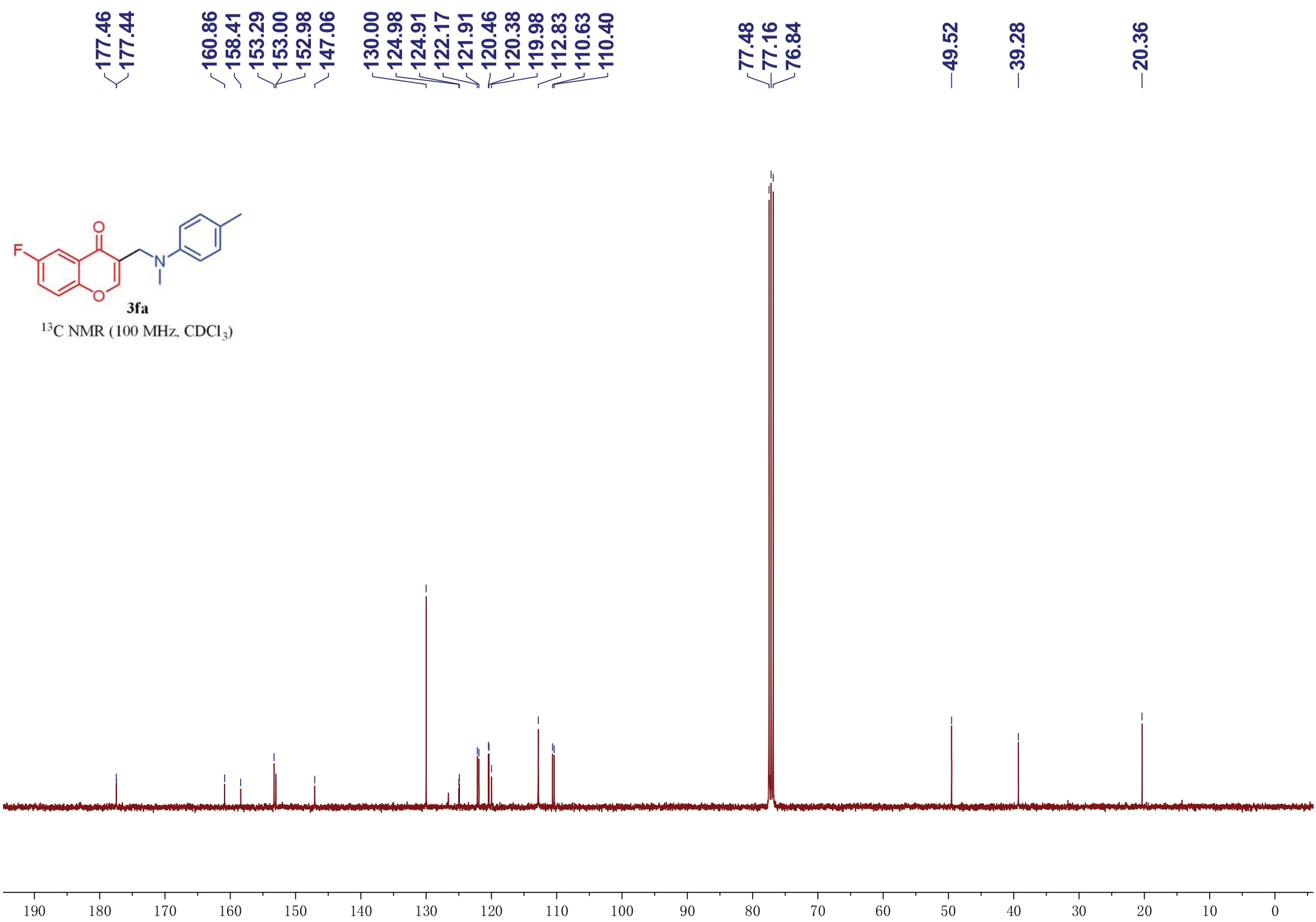

176.94
158.12
151.55
146.98
133.15
131.94
129.97
126.47
121.34
121.28
120.32
118.32
112.67
77.48
77.16
76.84
49.70
39.28
20.32
Br
O
N
O
3da
^{13}C NMR (100 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

3ea

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

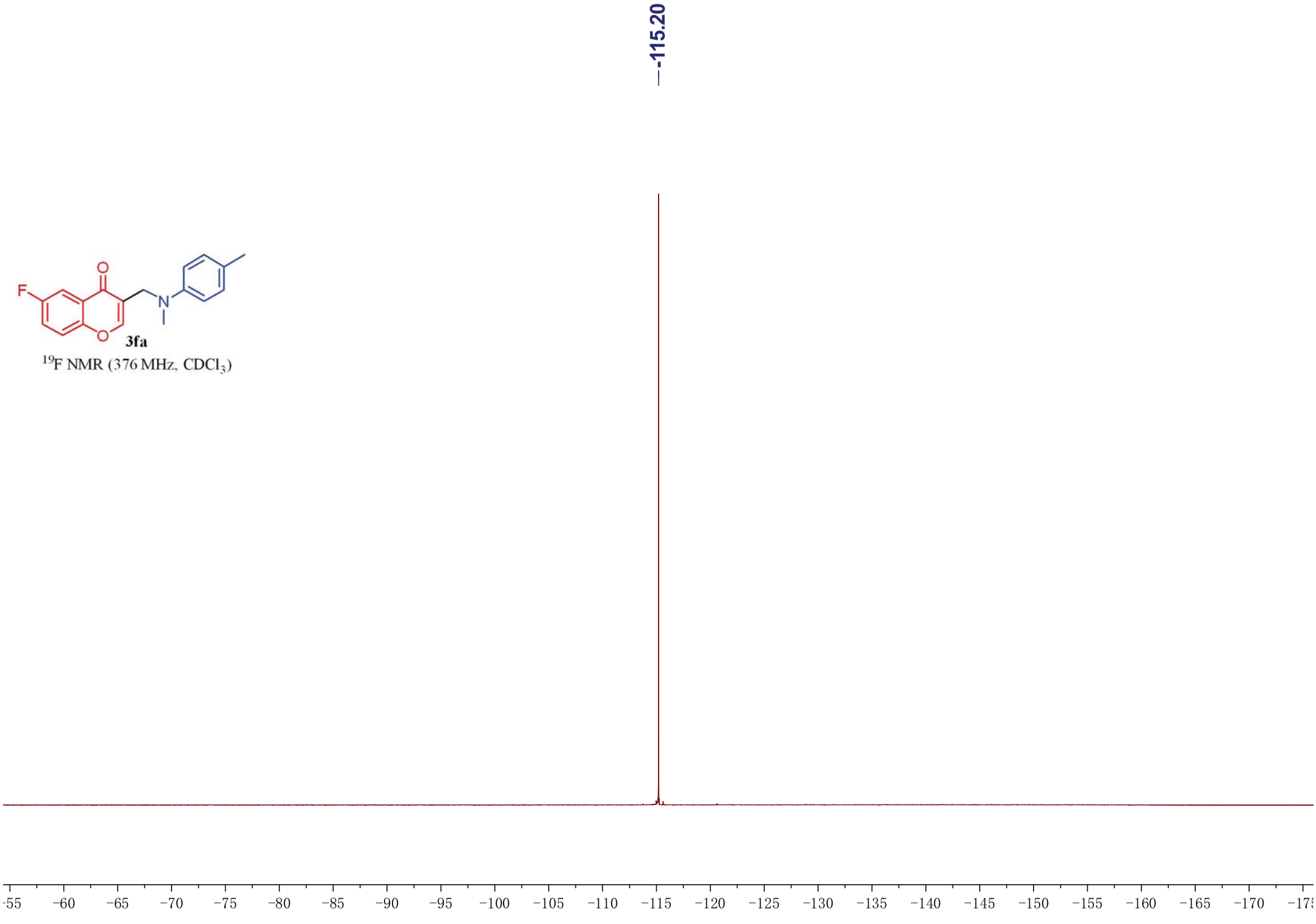

178.21
155.03
152.96
147.15
135.12
134.95
129.93
126.38
124.99
123.52
120.21
118.01
112.81
77.48
77.16
76.84
49.53
39.21
21.08
20.33
H3C
O
N
O
3ea
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

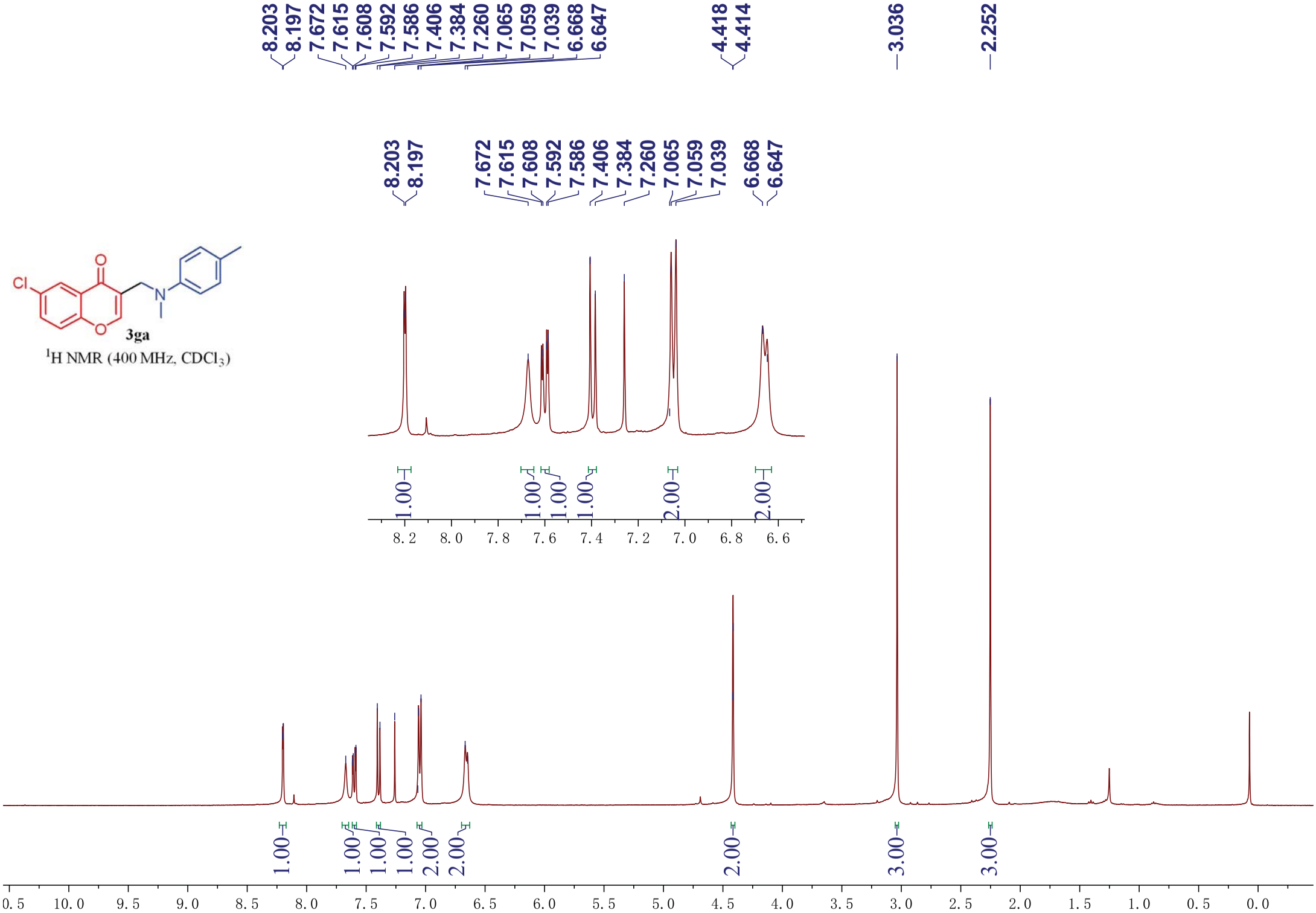

7.889
7.881
7.868
7.861
7.687
7.461
7.451
7.439
7.428
7.411
7.404
7.393
7.388
7.385
7.381
7.369
7.362
7.260
7.067
7.059
7.053
7.043
7.038
7.029
6.676
6.655
4.421
4.417
3.036
2.252
F
O
N
O
3fa
^{1}H NMR (400 MHz, $CDCl_3$)
1.00
1.00
1.00
1.06
2.00
2.02
2.05
3.01
3.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

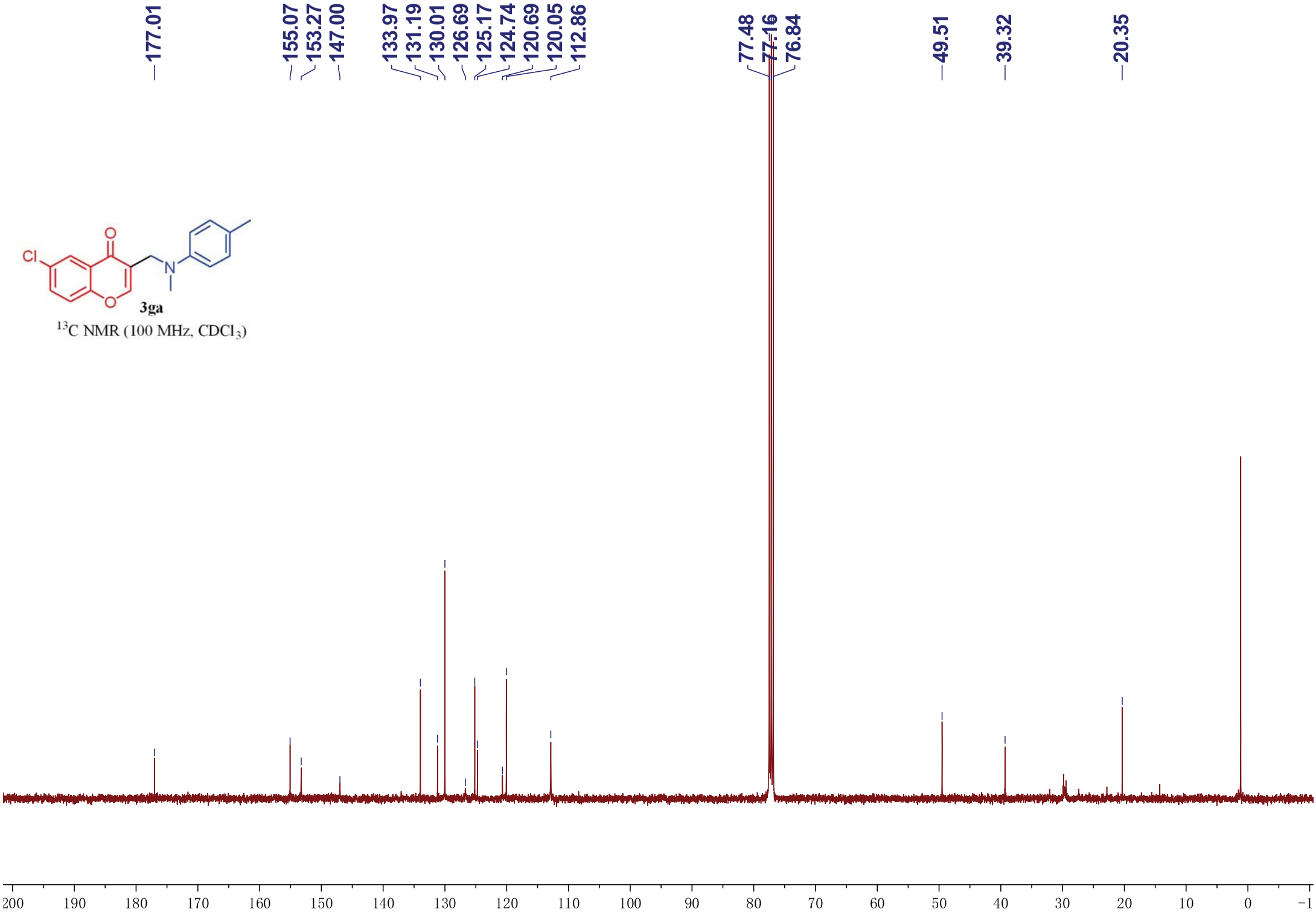

177.46
177.44
160.86
158.41
153.29
153.00
152.98
147.06
130.00
124.98
124.91
122.17
121.91
120.46
120.38
119.98
112.83
110.63
110.40
77.48
77.16
76.84
49.52
39.28
20.36
F
O
N
O
3fa
^{13}C NMR (100 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

3fa

^{19}F NMR (376 MHz, $CDCl_3$)

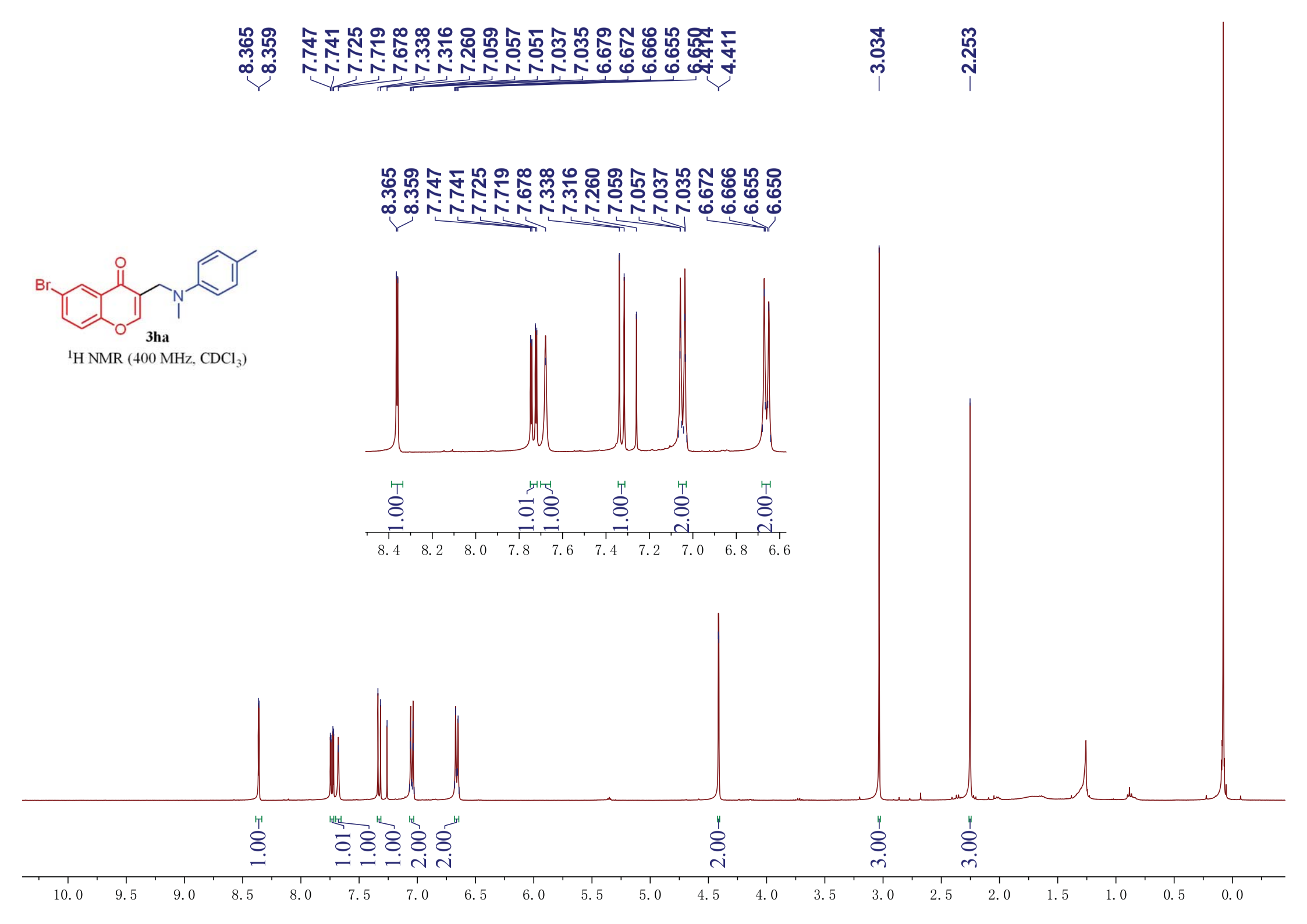


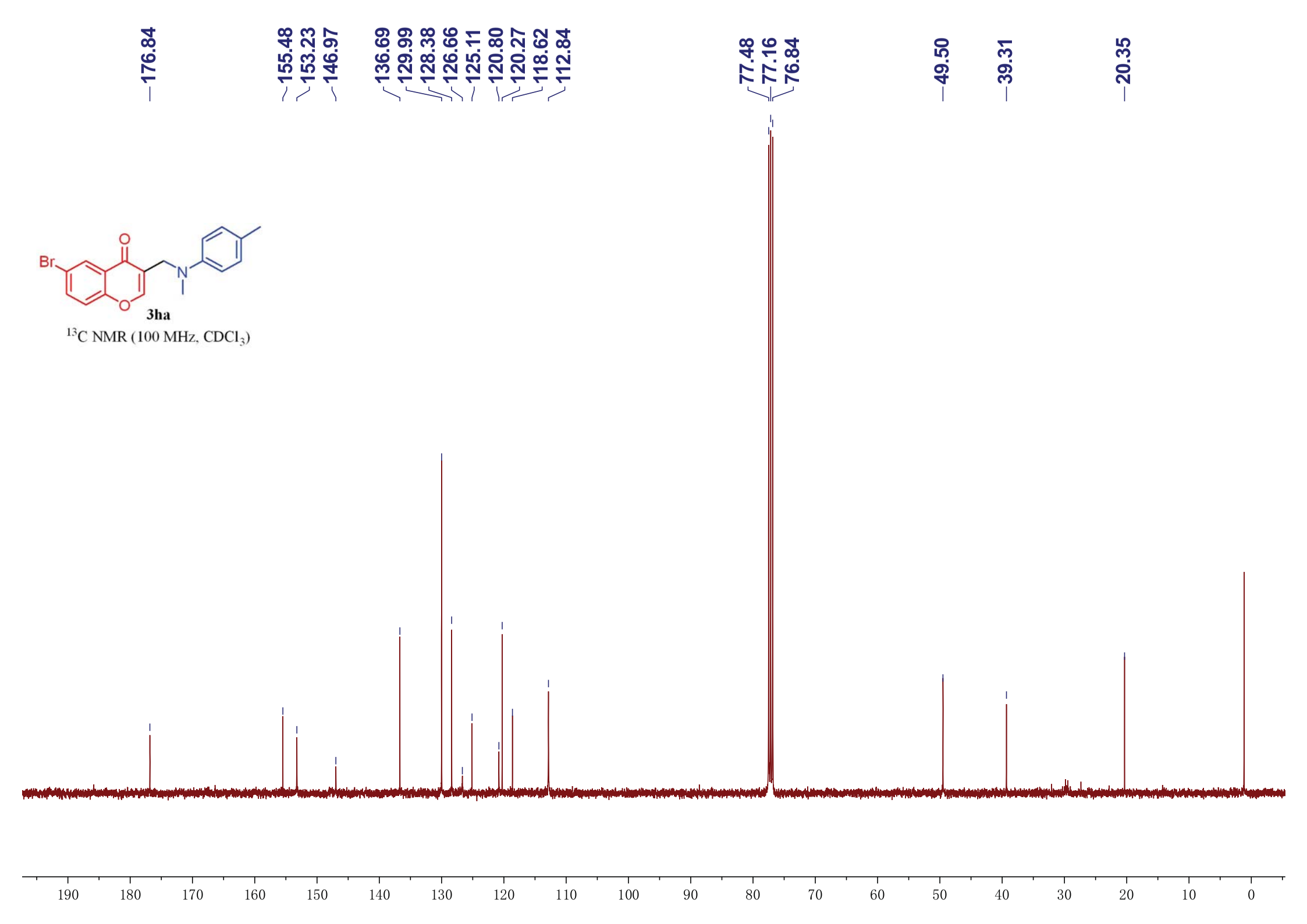

8.203
8.197
7.672
7.615
7.608
7.592
7.586
7.406
7.384
7.260
7.065
7.059
7.039
6.668
6.647
4.418
4.414
3.036
2.252
Cl
O
N
3ga
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.00
1.00
2.00
2.00
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
2.00
3.00
3.00
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



3ga

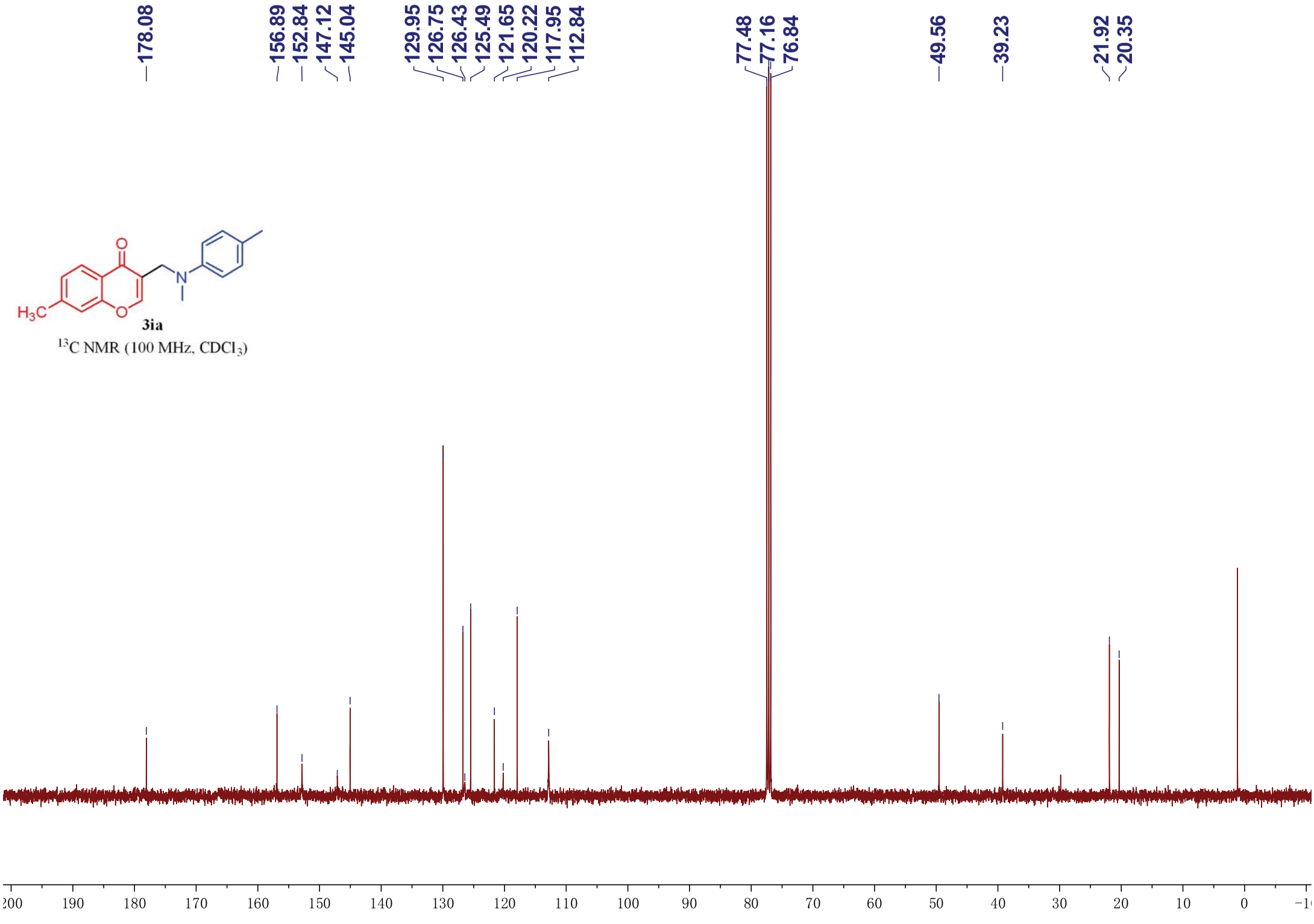
^{13}C NMR (100 MHz, $CDCl_3$)

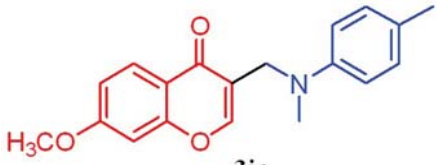

8.365
8.359
7.747
7.741
7.725
7.719
7.678
7.338
7.316
7.260
7.059
7.057
7.051
7.037
7.035
6.679
6.672
6.666
6.655
6.650
4.414
4.411
3.034
2.253
Br
O
N
3ha
1H NMR (400 MHz, CDCl3)
1.00
1.01
1.00
1.00
2.00
2.00
2.00
3.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


176.84
155.48
153.23
146.97
136.69
129.99
128.38
126.66
125.11
120.80
120.27
118.62
112.84
77.48
77.16
76.84
49.50
39.31
20.35
Br
O
O
N
3ha
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

3ia

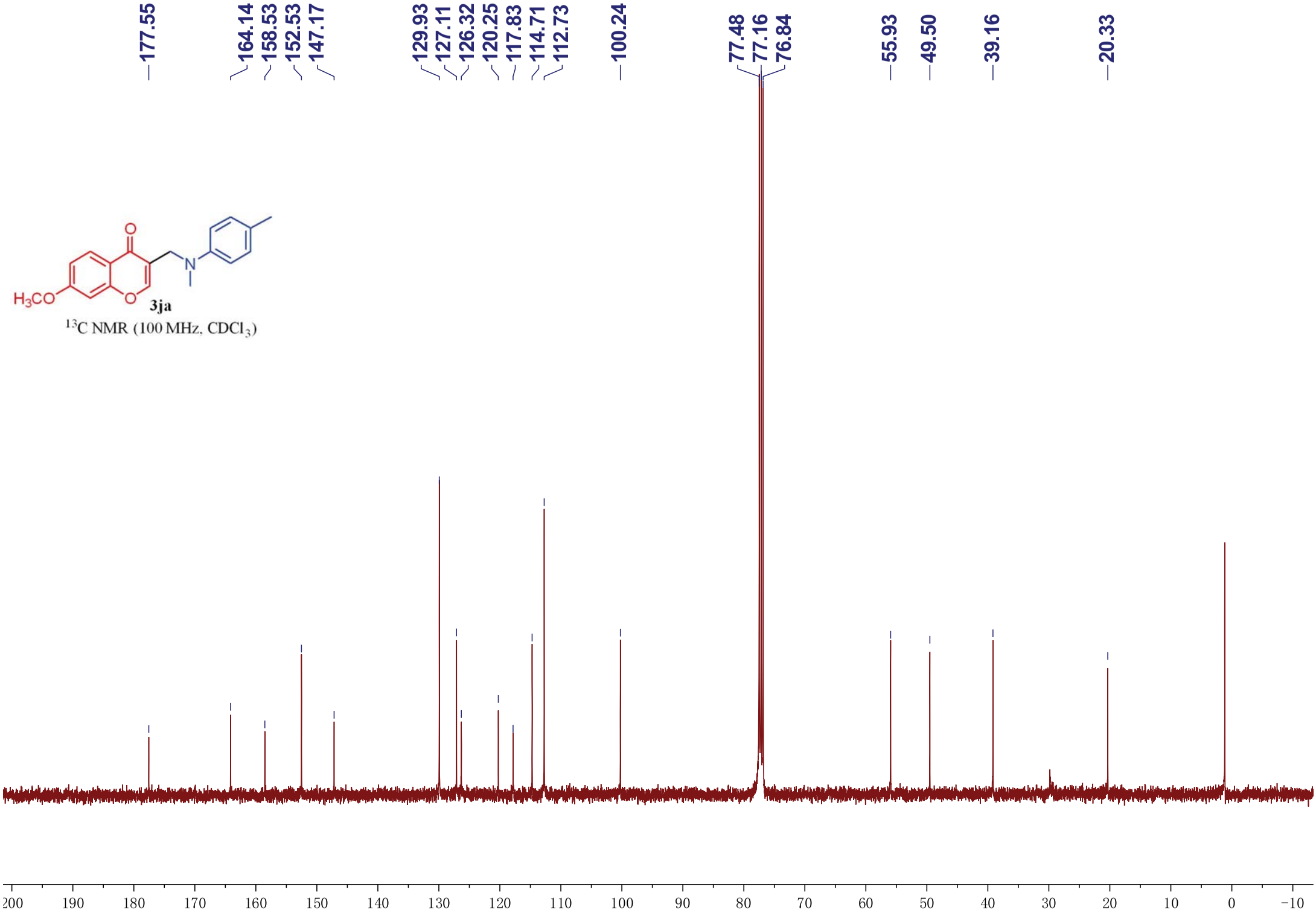
^{1}H NMR (400 MHz, $CDCl_3$)

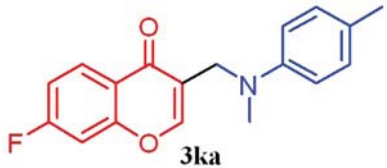

178.08
156.89
152.84
147.12
145.04
129.95
126.75
126.43
125.49
121.65
120.22
117.95
112.84
77.48
77.16
76.84
49.56
39.23
21.92
20.35
O
N
H3C
O
3ia
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



3ja

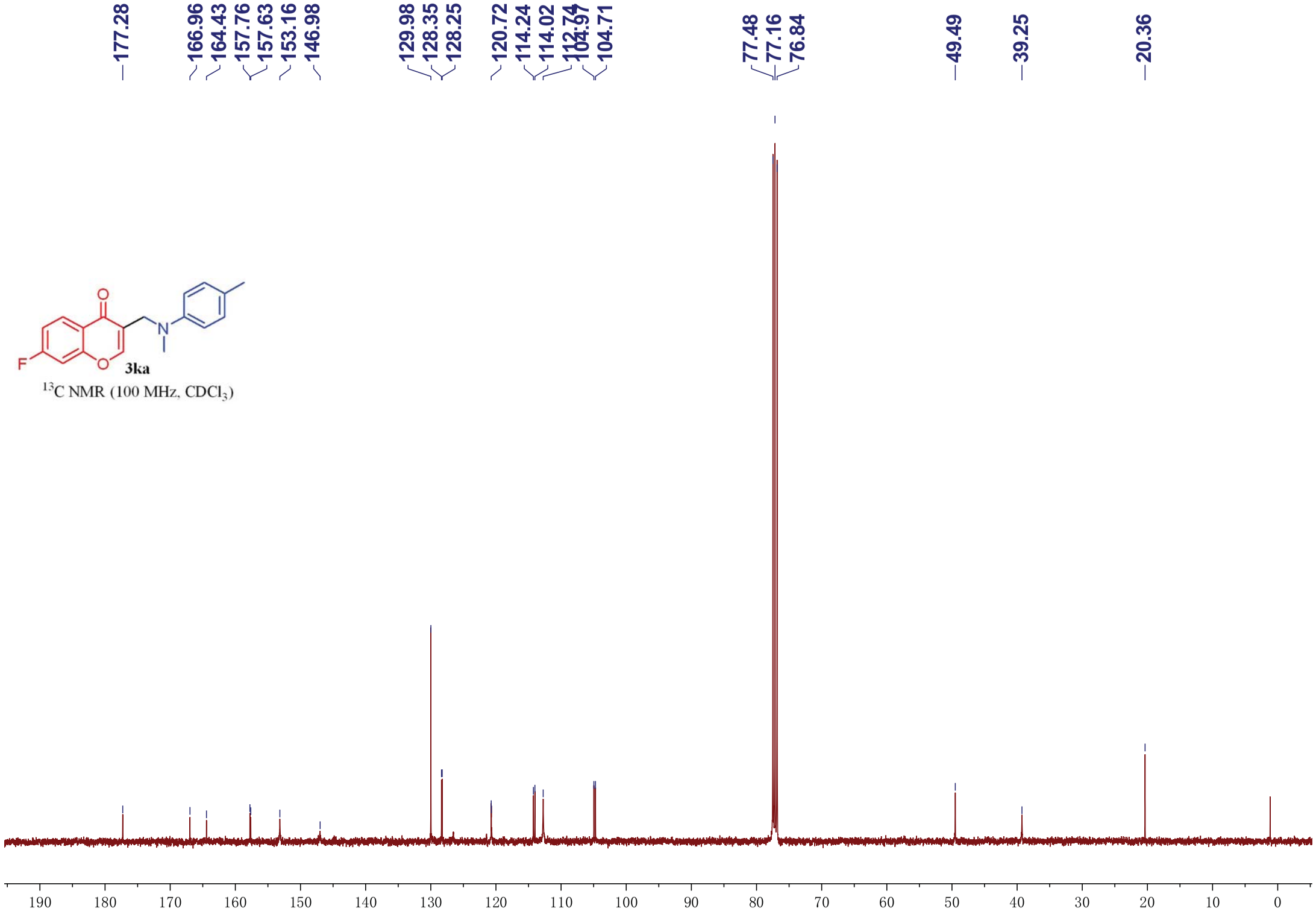
^{1}H NMR (400 MHz, $CDCl_3$)


177.55
164.14
158.53
152.53
147.17
129.93
127.11
126.32
120.25
117.83
114.71
112.73
100.24
77.48
77.16
76.84
55.93
49.50
39.16
20.33
O
N
H3CO
O
3ja
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10



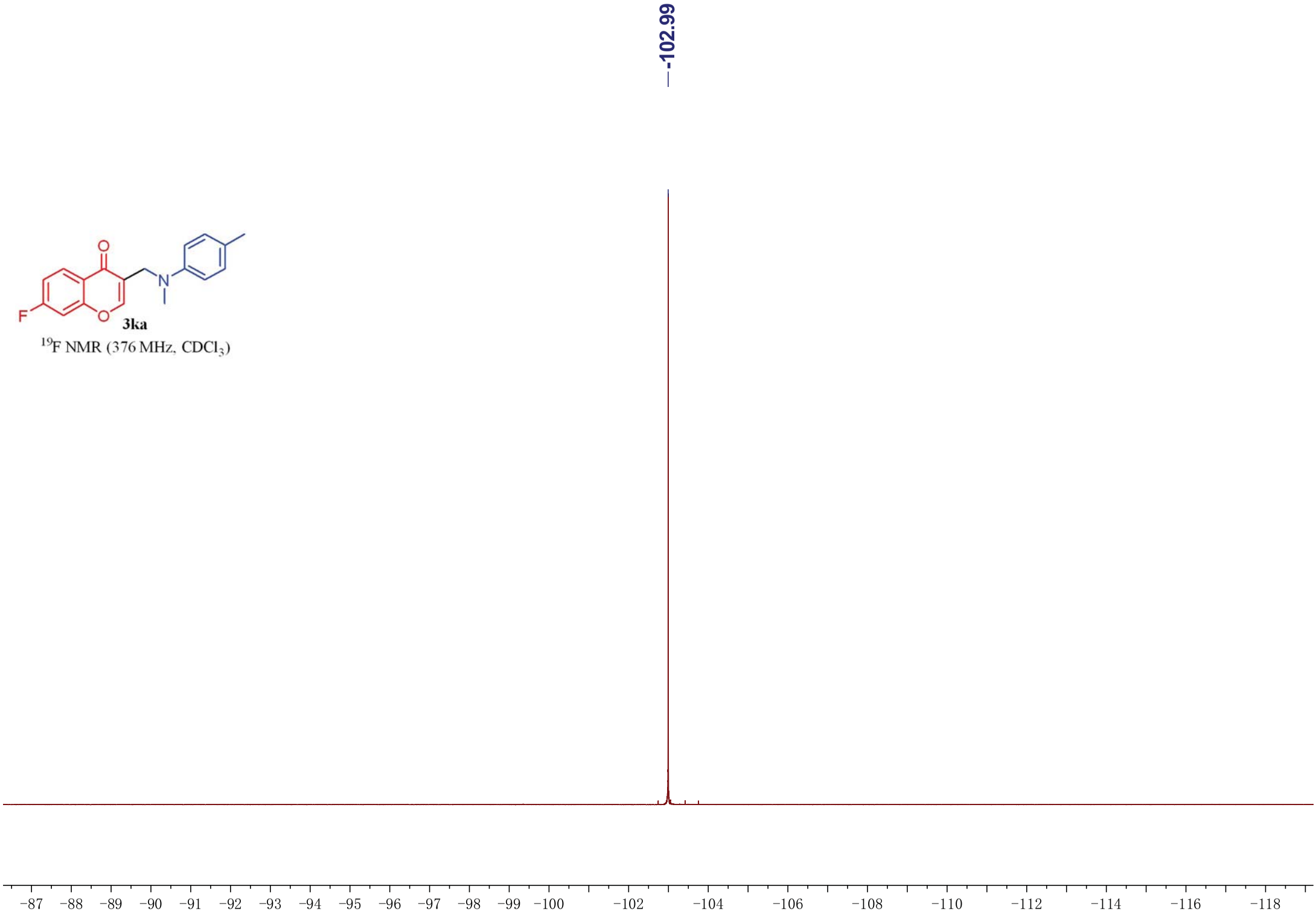
3ka

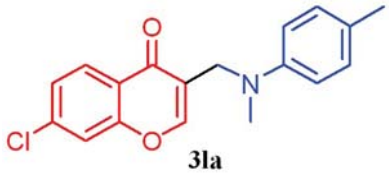
^{1}H NMR (400 MHz, $CDCl_3$)


177.28
166.96
164.43
157.76
157.63
153.16
146.98
129.98
128.35
128.25
120.72
114.24
114.02
112.74
104.97
104.71
77.48
77.16
76.84
49.49
39.25
20.36
O
N
F
O
3ka
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

3ka

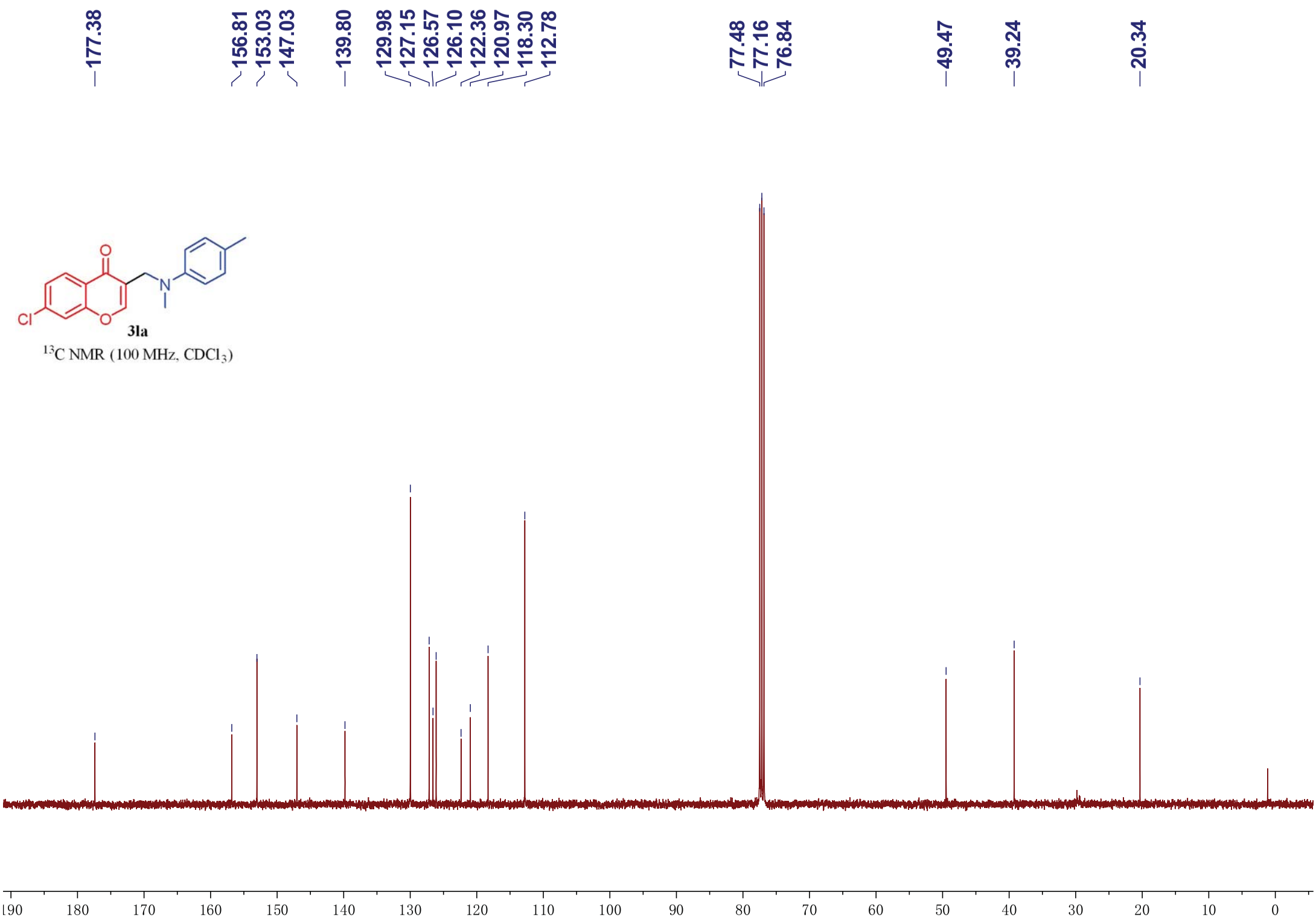
^{19}F NMR (376 MHz, $CDCl_3$)

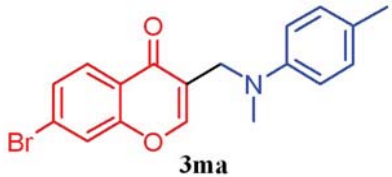




3la

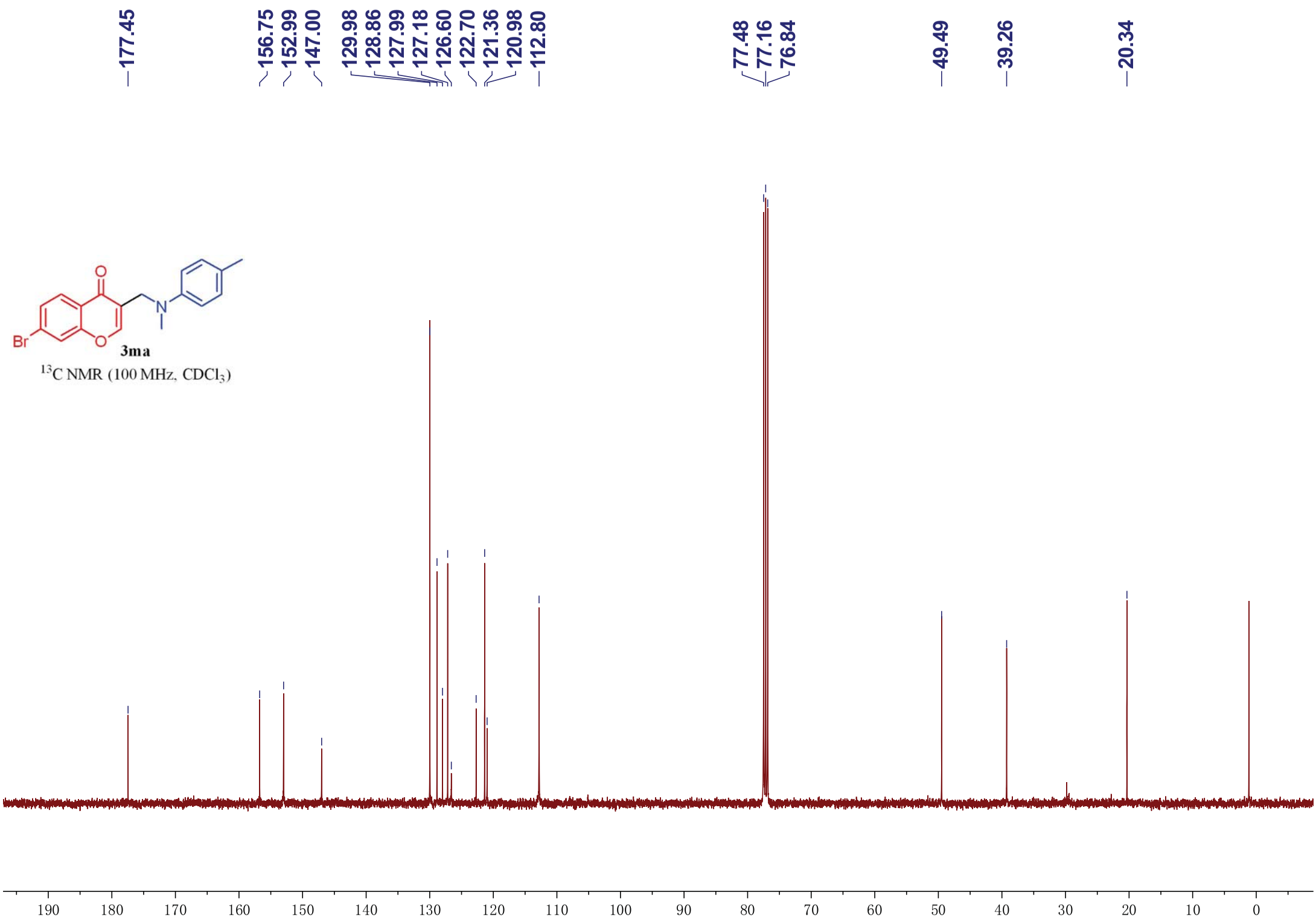
^{1}H NMR (400 MHz, $CDCl_3$)


177.38
156.81
153.03
147.03
139.80
129.98
127.15
126.57
126.10
122.36
120.97
118.30
112.78
77.48
77.16
76.84
49.47
39.24
20.34
O
N
Cl
O
3la
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



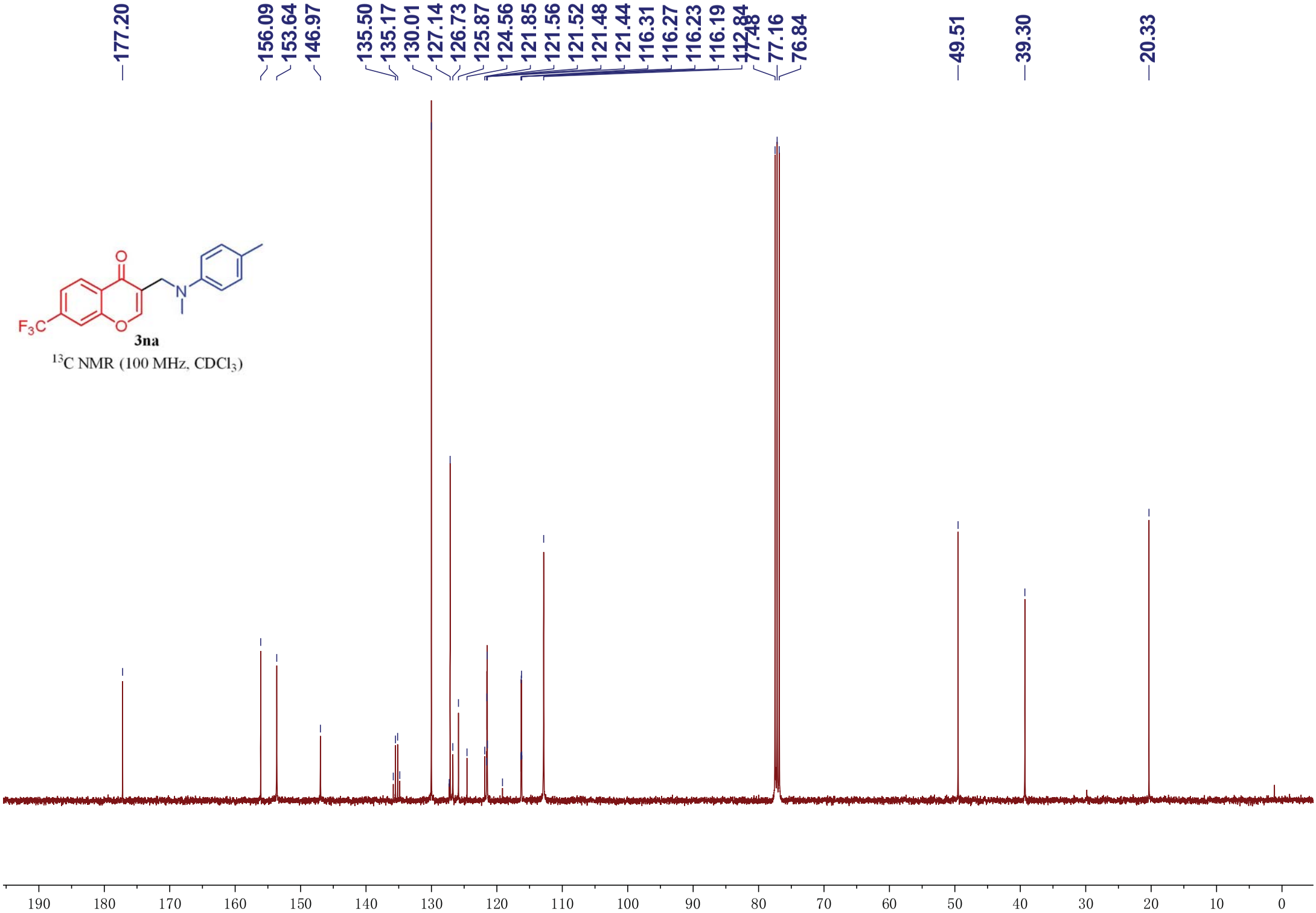
3ma

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


177.45
156.75
152.99
147.00
129.98
128.86
127.99
127.18
126.60
122.70
121.36
120.98
112.80
77.48
77.16
76.84
49.49
39.26
20.34
O
N
Br
O
3ma
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

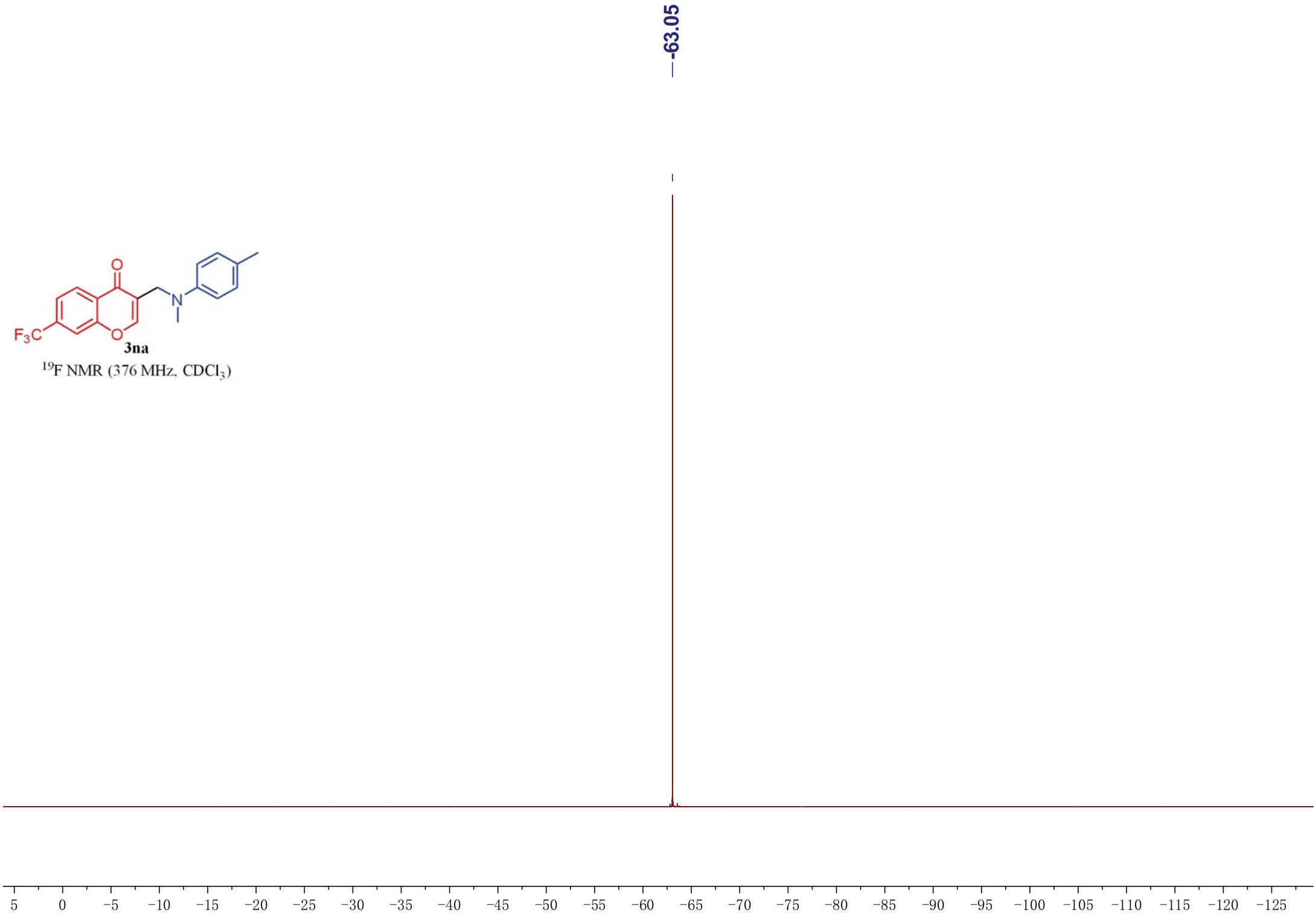
3na

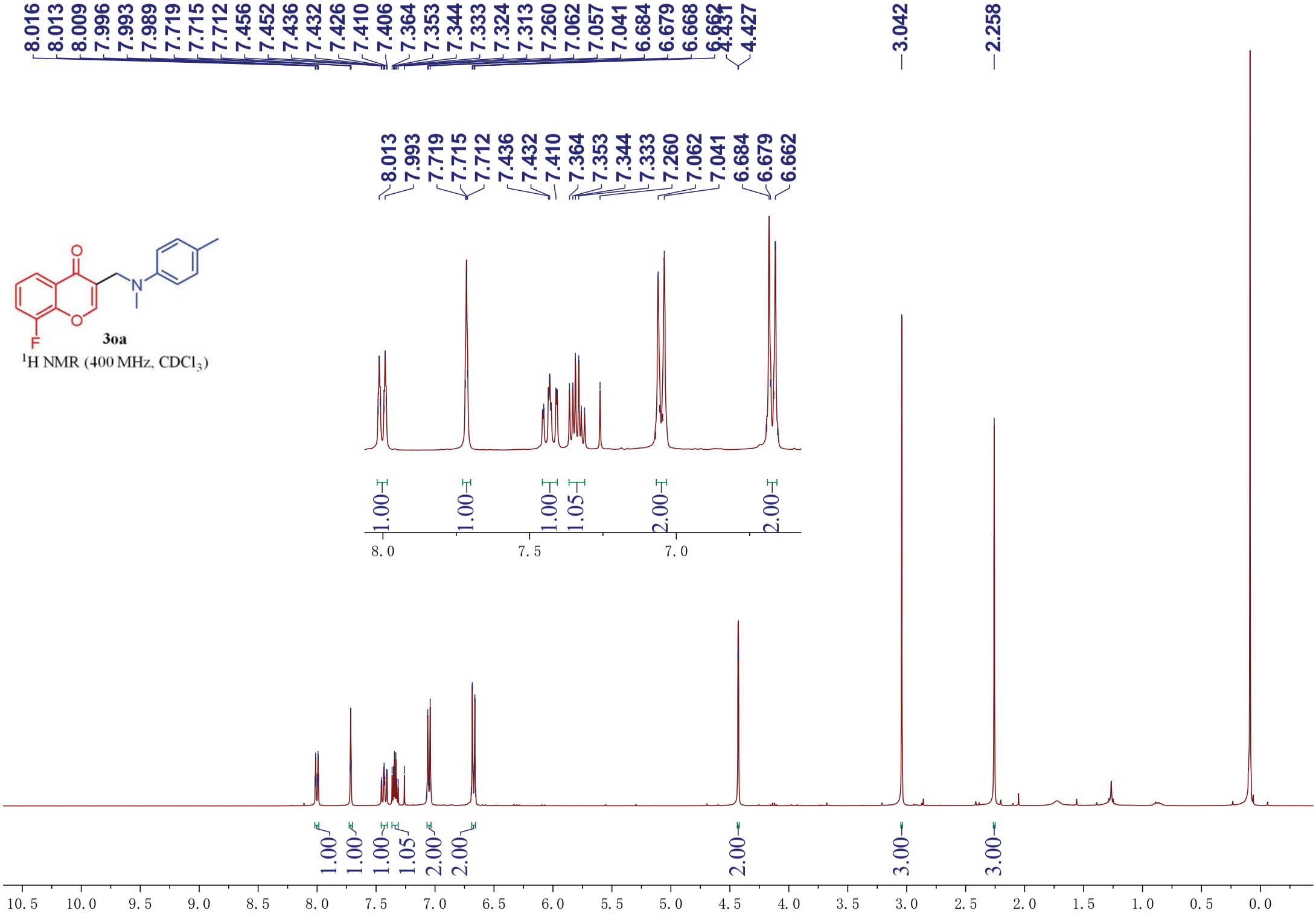
^{1}H NMR (400 MHz, $CDCl_3$)

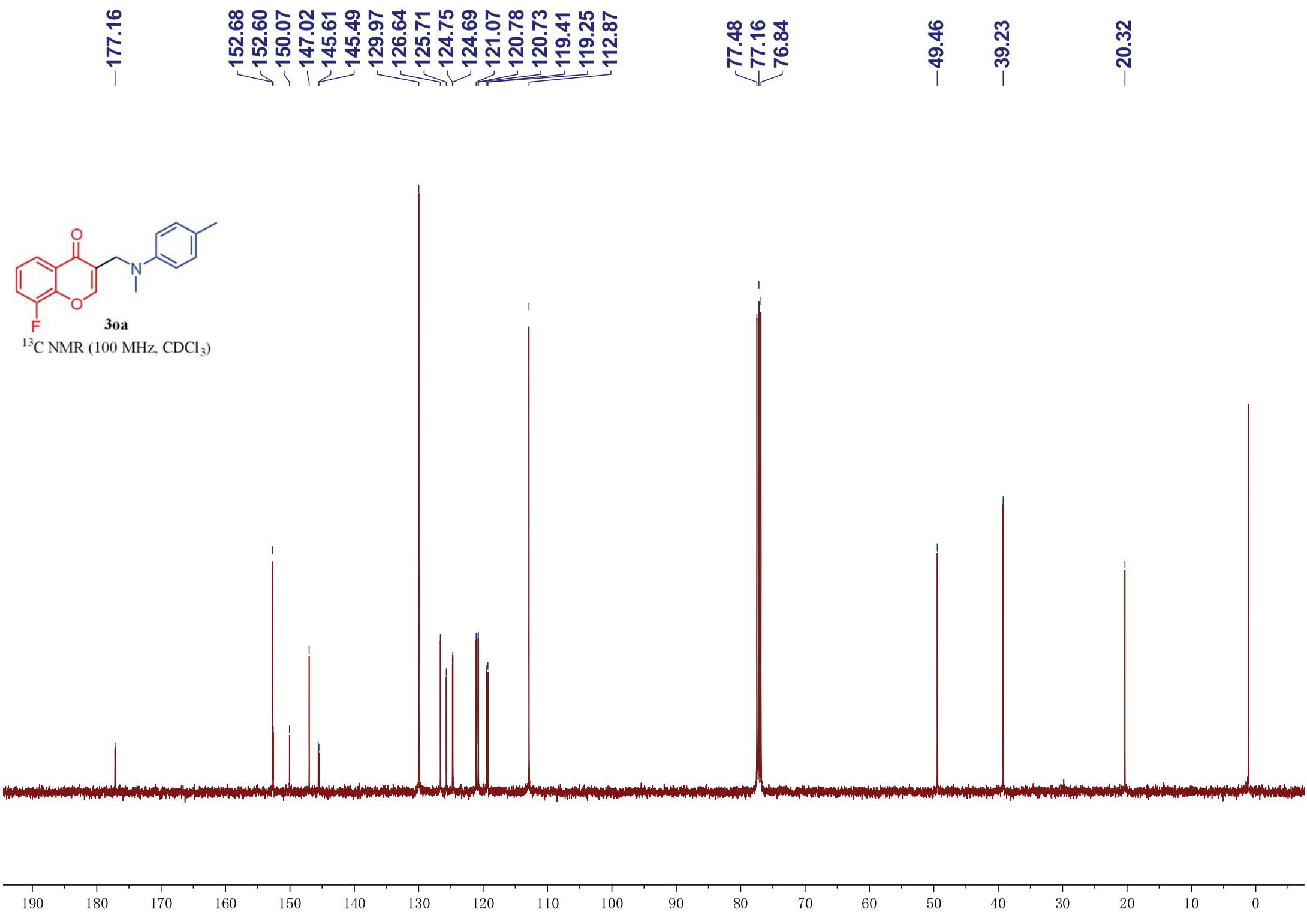

177.20
156.09
153.64
146.97
135.50
135.17
130.01
127.14
126.73
125.87
124.56
121.85
121.56
121.52
121.48
121.44
116.31
116.27
116.23
116.19
112.84
77.48
77.16
76.84
49.51
39.30
20.33
O
N
F3C
O
3na
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

3na

^{19}F NMR (376 MHz, $CDCl_3$)

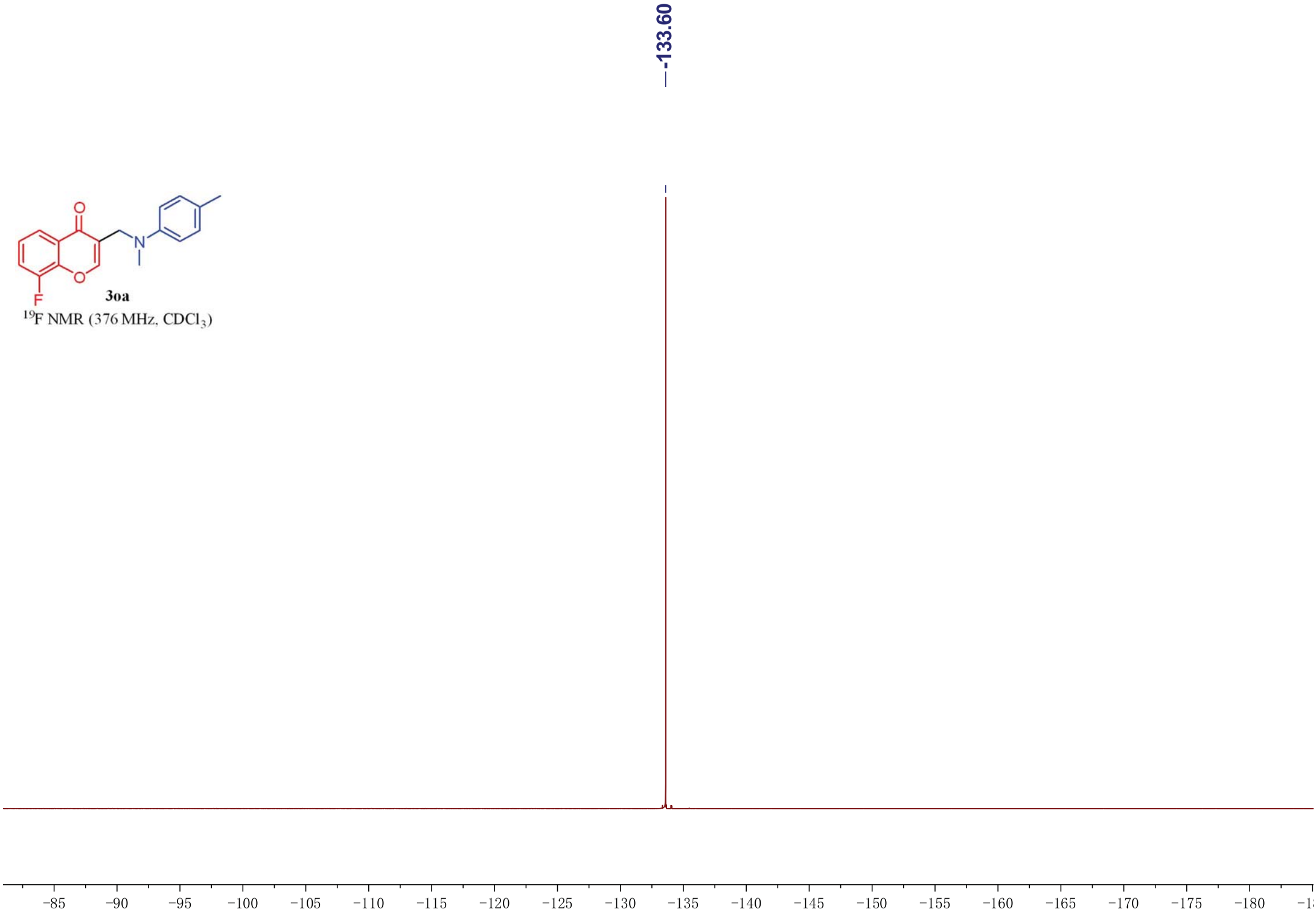


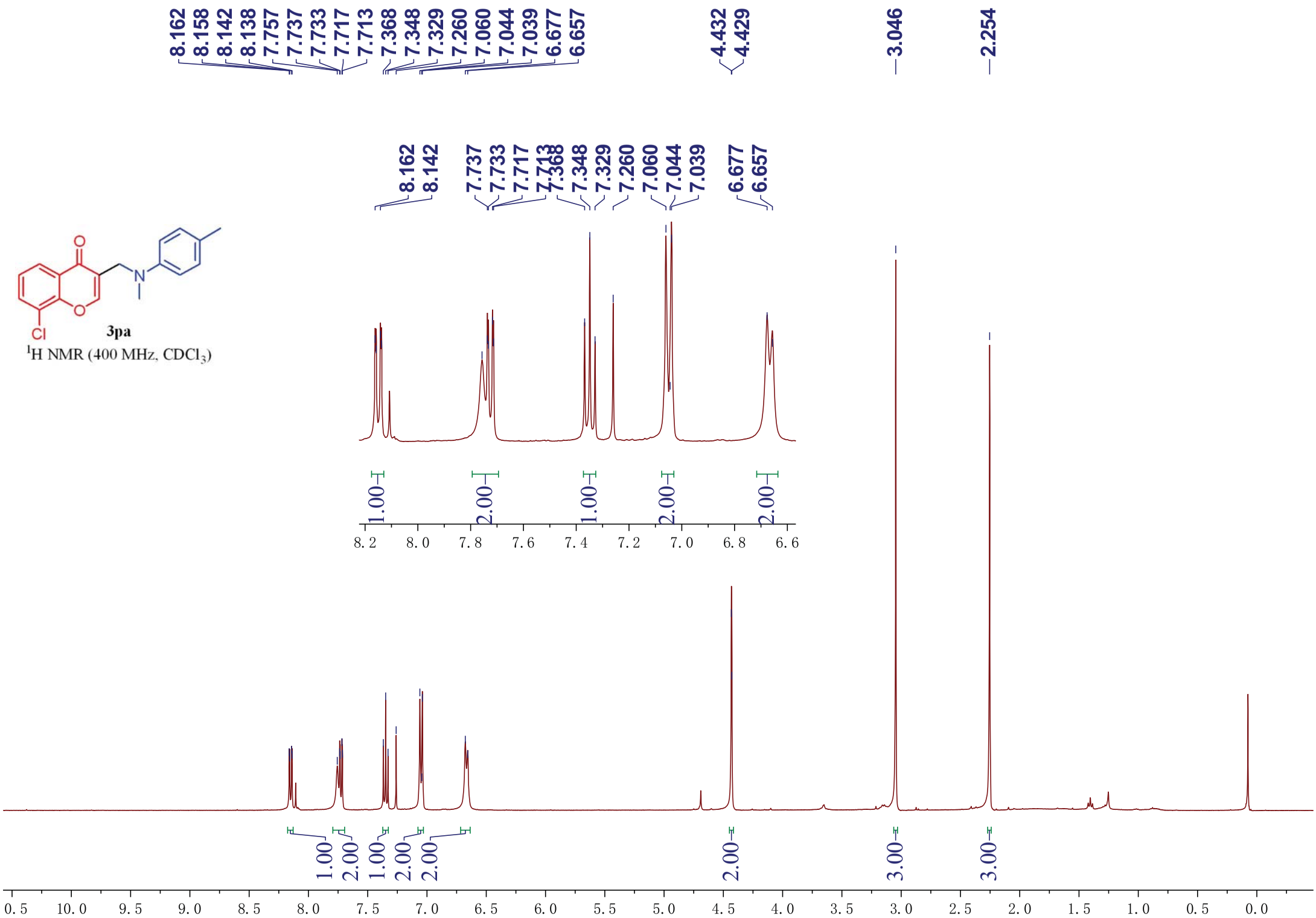

8.016
8.013
8.009
7.996
7.993
7.989
7.719
7.715
7.712
7.456
7.452
7.436
7.432
7.426
7.410
7.406
7.364
7.353
7.344
7.333
7.324
7.313
7.260
7.062
7.057
7.041
6.684
6.679
6.668
6.662
6.651
4.431
4.427
3.042
2.258
3oa
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.00
1.05
2.00
2.00
2.00
3.00
3.00
8.0
7.5
7.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

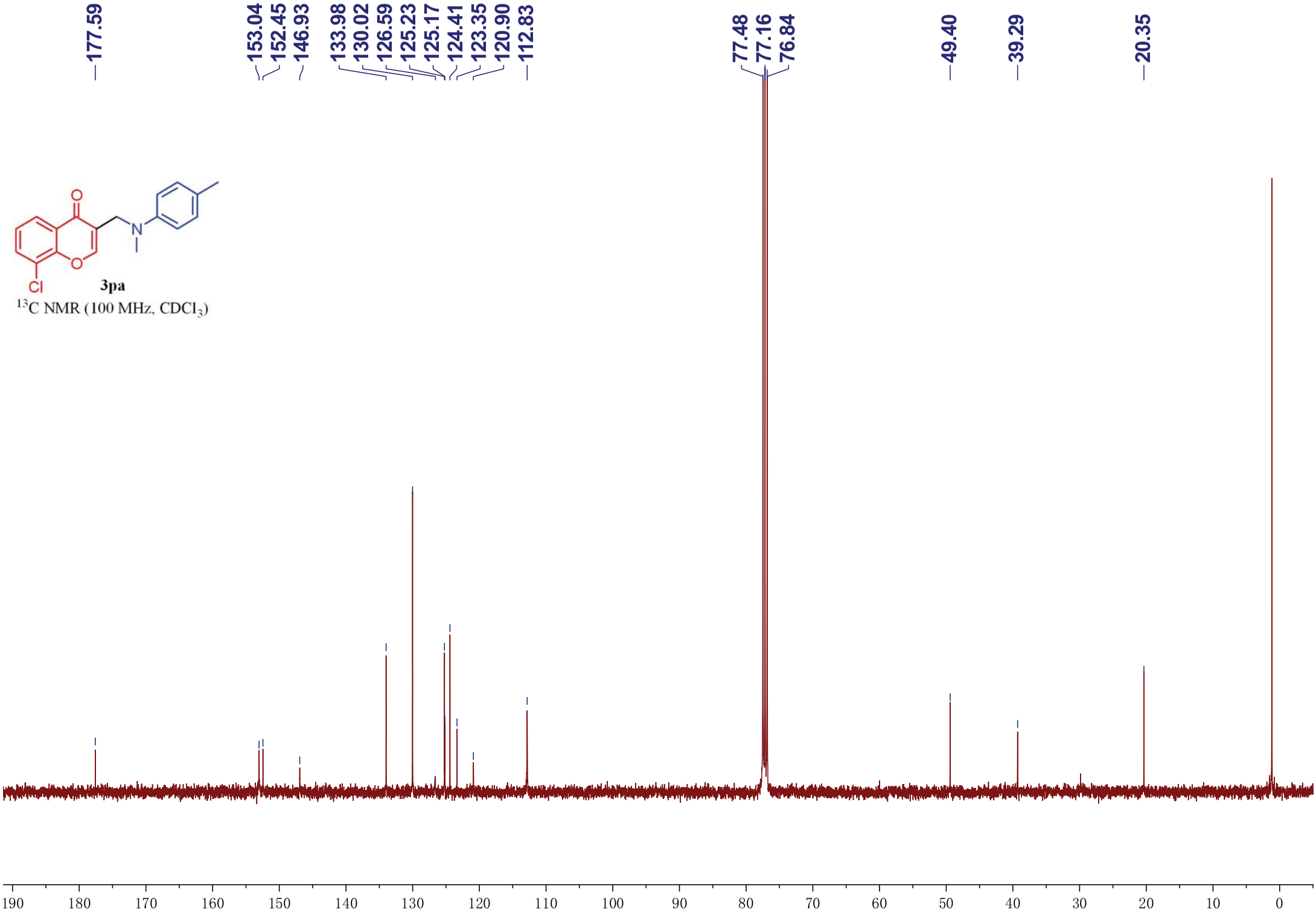

177.16
152.68
152.60
150.07
147.02
145.61
145.49
129.97
126.64
125.71
124.75
124.69
121.07
120.78
120.73
119.41
119.25
112.87
77.48
77.16
76.84
49.46
39.23
20.32
O
N
O
F
3oa
^{13}C NMR (100 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

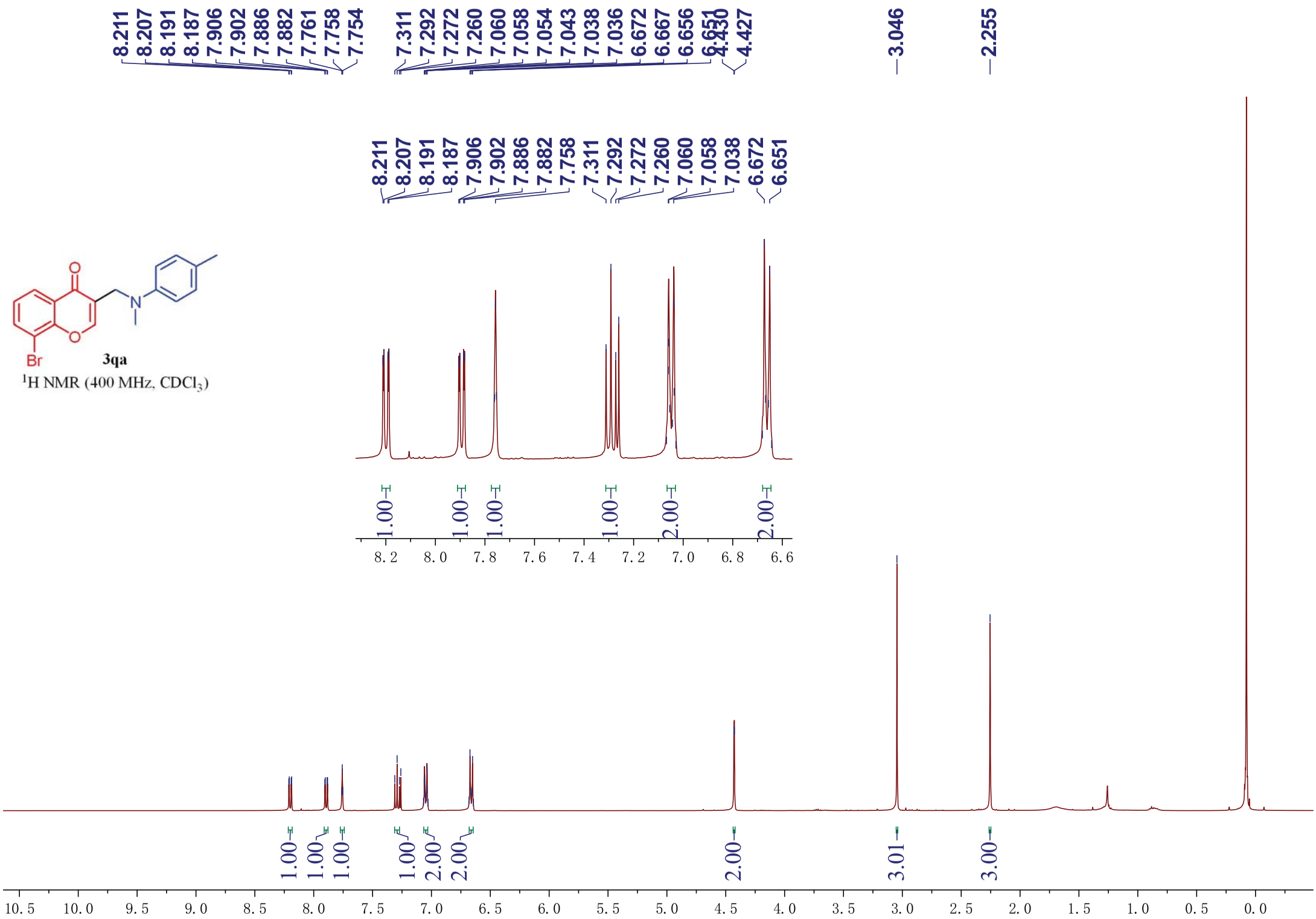
3oa

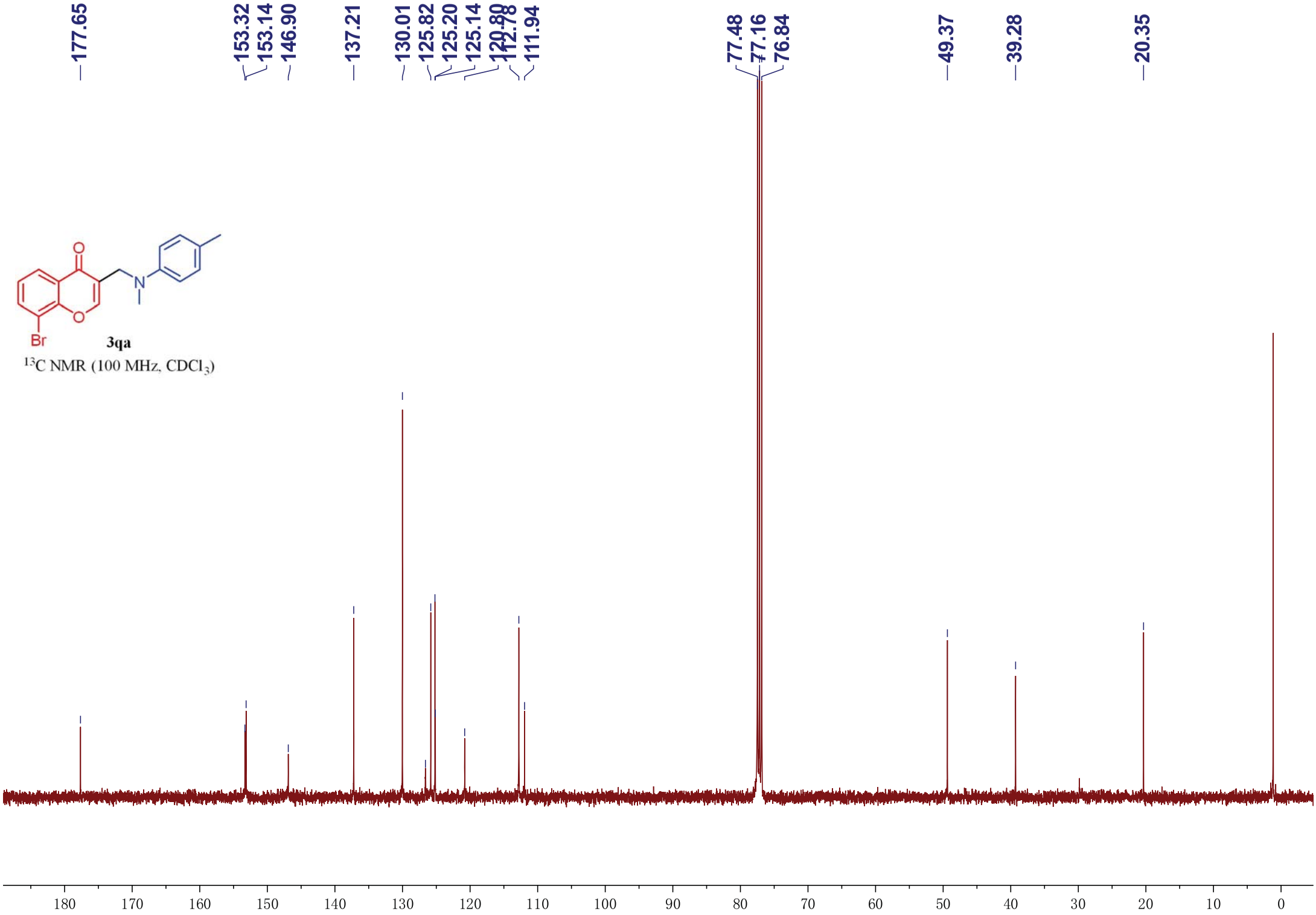
^{19}F NMR (376 MHz, $CDCl_3$)




8.162
8.158
8.142
8.138
7.757
7.737
7.733
7.717
7.713
7.368
7.348
7.329
7.260
7.060
7.044
7.039
6.677
6.657
4.432
4.429
3.046
2.254
O
N
O
Cl
3pa
1H NMR (400 MHz, CDCl3)
1.00
2.00
1.00
2.00
2.00
2.00
1.00
2.00
2.00
2.00
3.00
3.00
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


177.59
153.04
152.45
146.93
133.98
130.02
126.59
125.23
125.17
124.41
123.35
120.90
112.83
77.48
77.16
76.84
49.40
39.29
20.35
O
N
O
Cl
3pa
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.211
8.207
8.191
8.187
7.906
7.902
7.886
7.882
7.761
7.758
7.754
7.311
7.292
7.272
7.260
7.060
7.058
7.054
7.043
7.038
7.036
6.672
6.667
6.656
6.651
4.430
4.427
3.046
2.255
Br
3qa
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.00
1.00
2.00
2.00
2.00
1.00
1.00
1.00
2.00
2.00
3.01
3.00

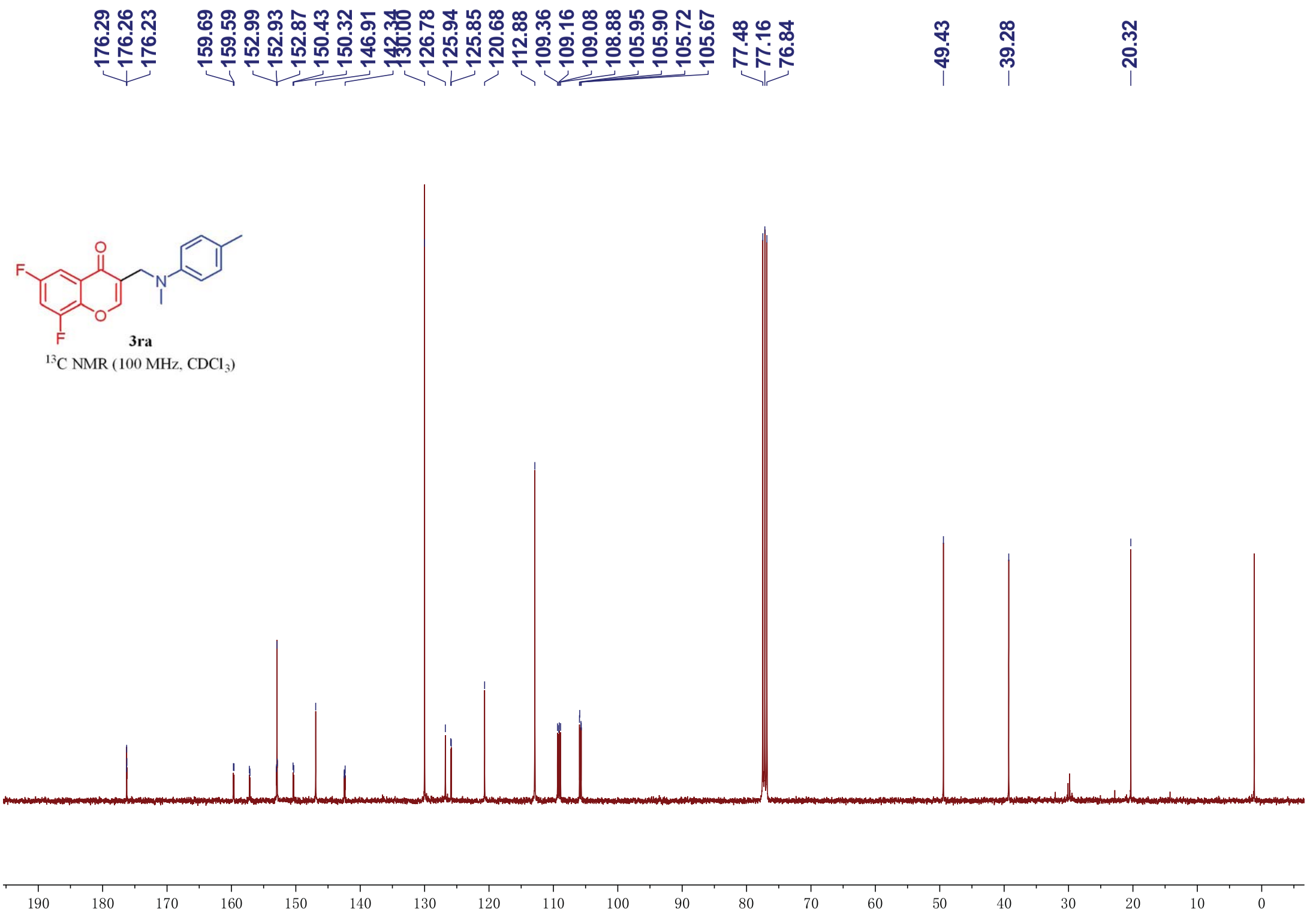


3qa

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

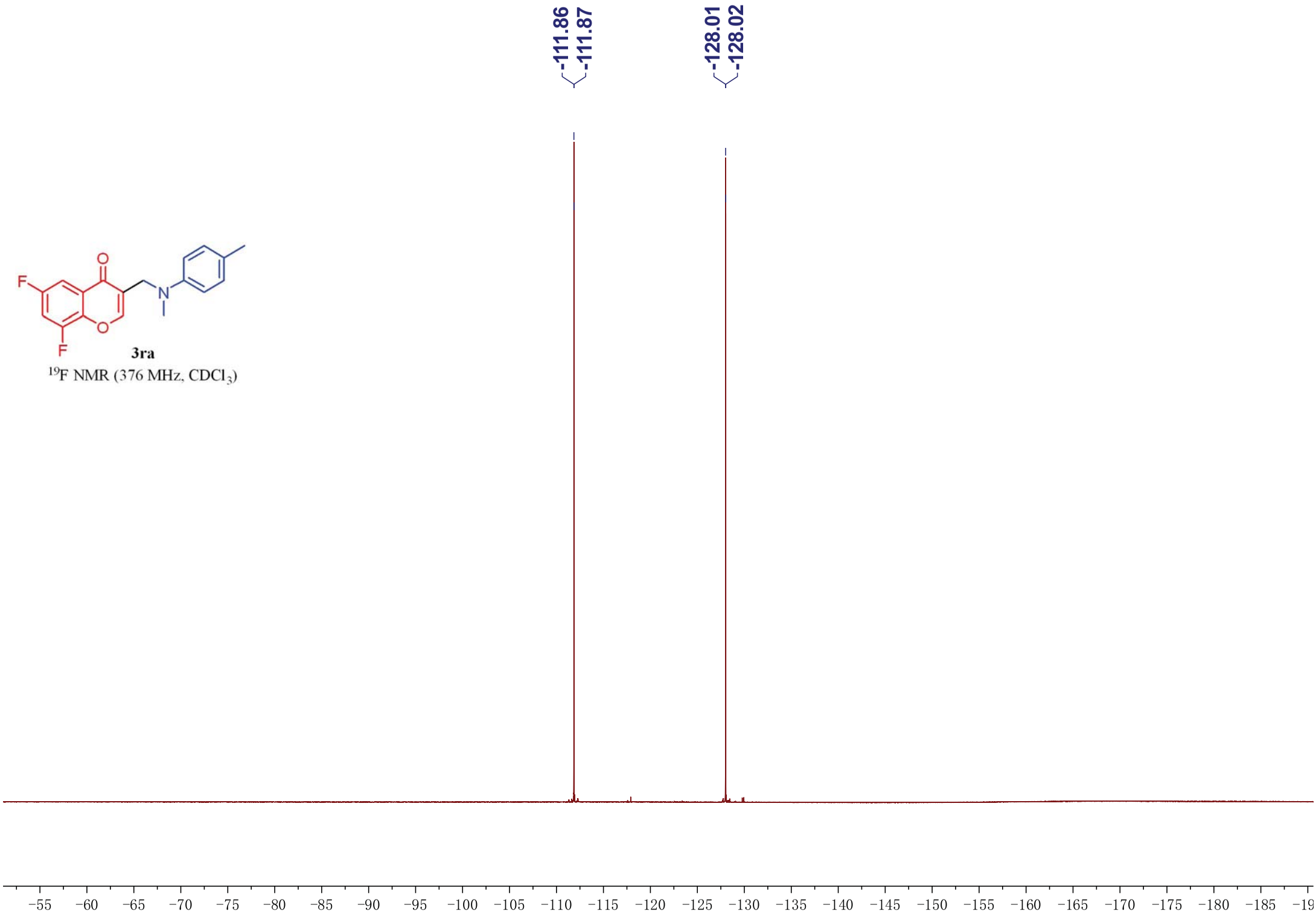
3ra

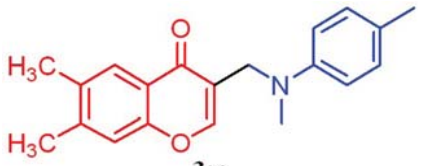
^{1}H NMR (400 MHz, $CDCl_3$)


176.29
176.26
176.23
159.69
159.59
152.99
152.93
152.87
150.43
150.32
146.91
142.34
130.00
126.78
125.94
125.85
120.68
112.88
109.36
109.16
109.08
108.88
105.95
105.90
105.72
105.67
77.48
77.16
76.84
49.43
39.28
20.32
F
O
N
O
F
3ra
^{13}C NMR (100 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

3ra

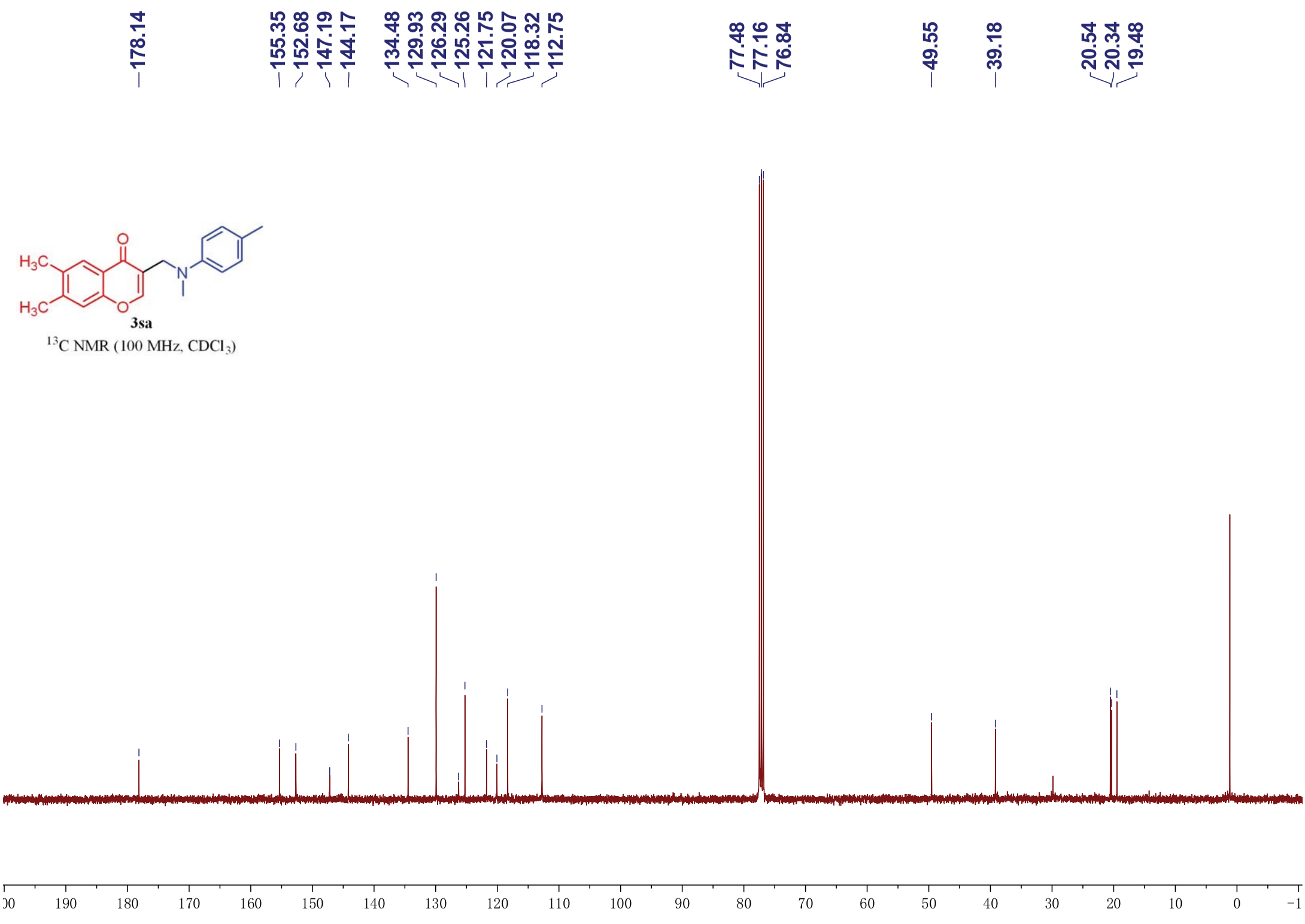
^{19}F NMR (376 MHz, $CDCl_3$)





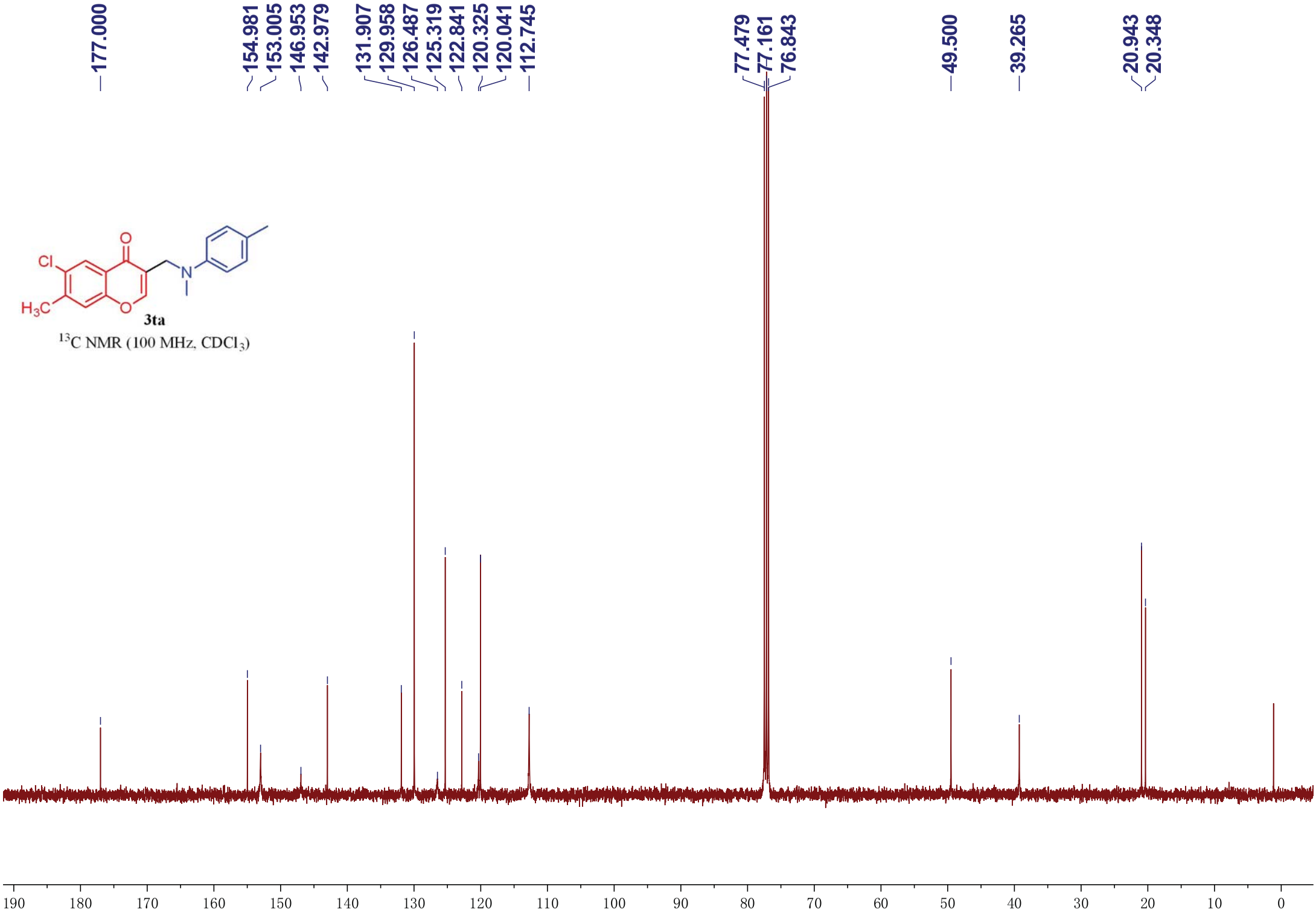
3sa

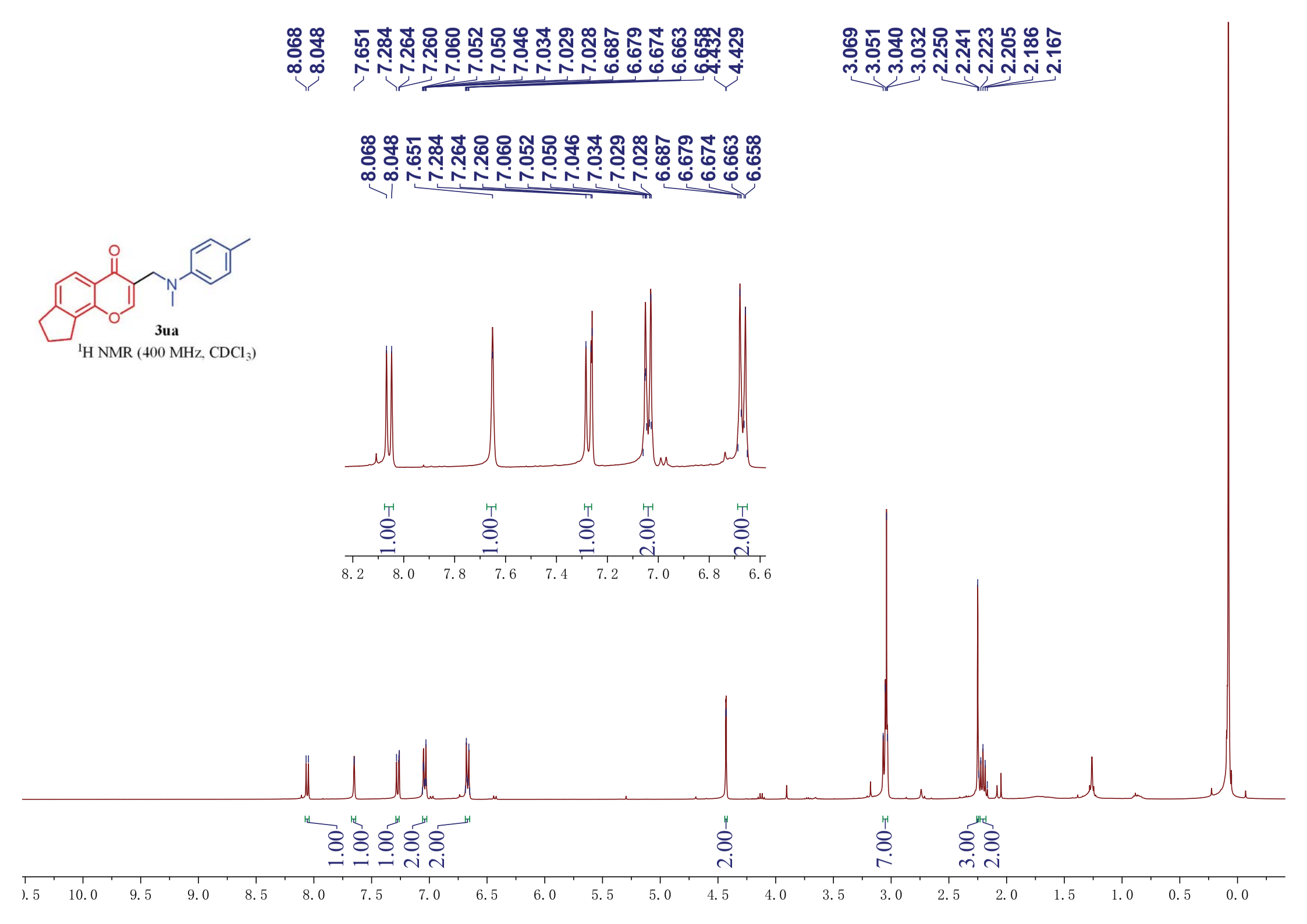
^{1}H NMR (400 MHz, $CDCl_3$)

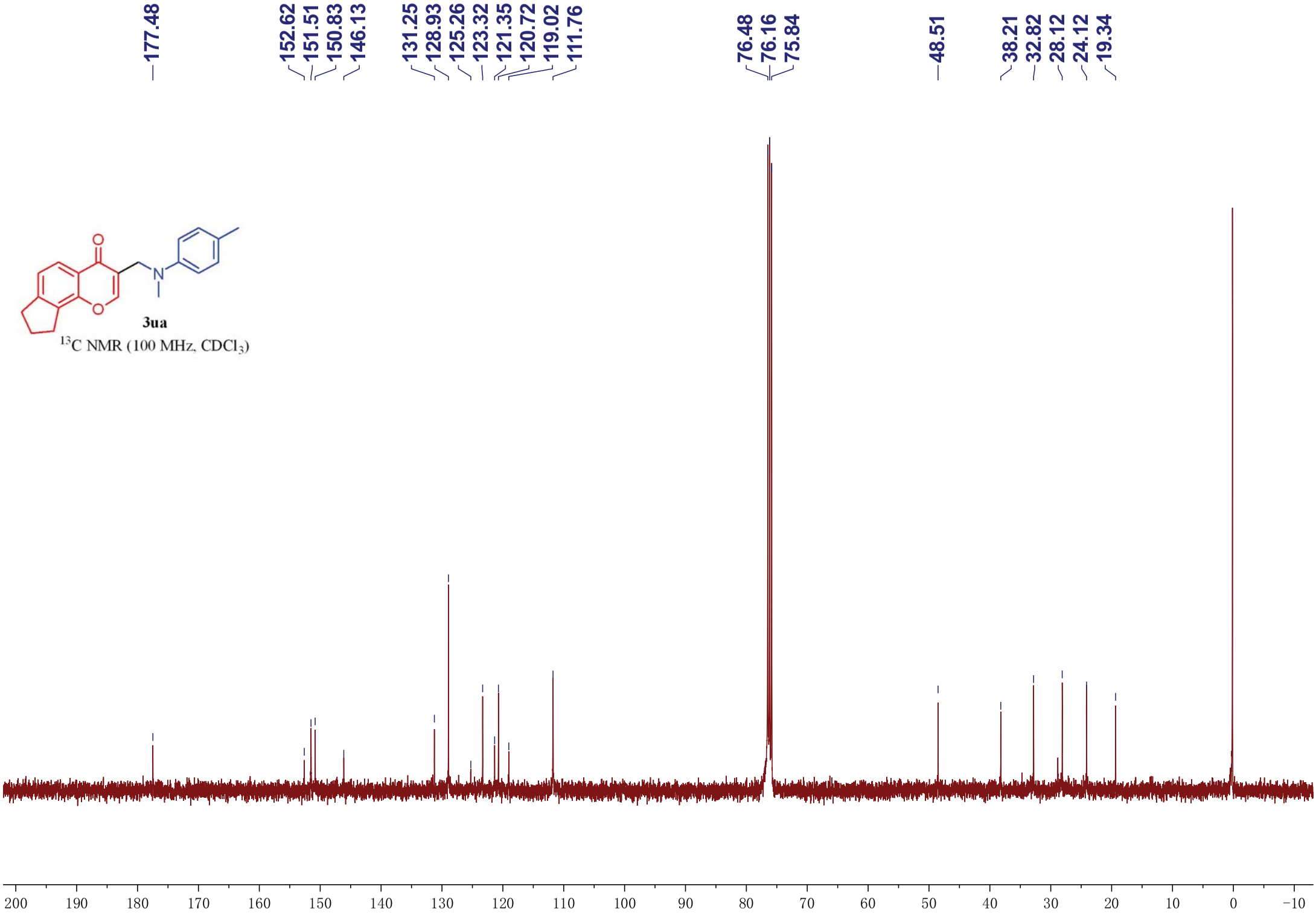

178.14
155.35
152.68
147.19
144.17
134.48
129.93
126.29
125.26
121.75
120.07
118.32
112.75
77.48
77.16
76.84
49.55
39.18
20.54
20.34
19.48
H3C
H3C
O
O
N
3sa
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1

3ta

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

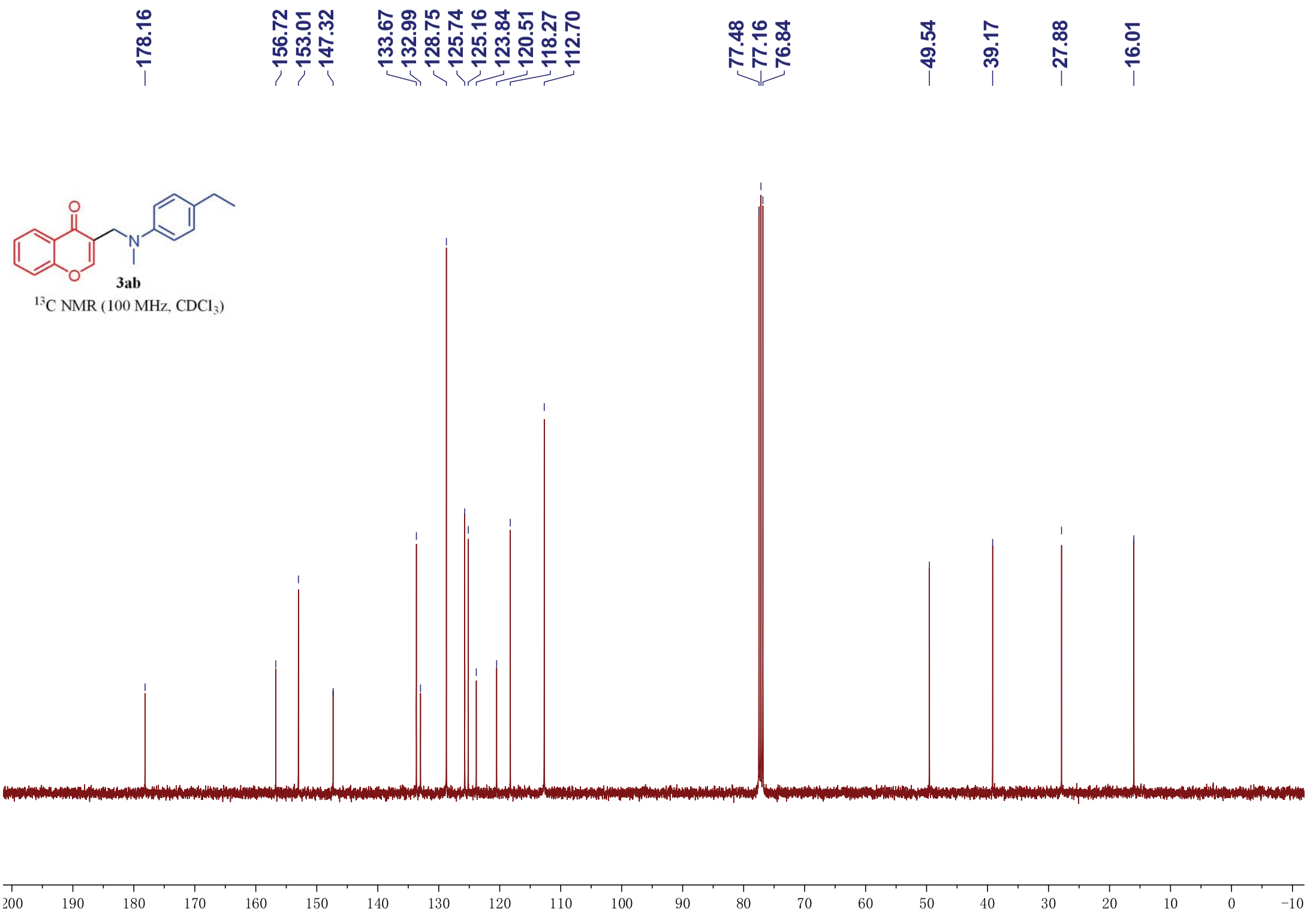

177.000
154.981
153.005
146.953
142.979
131.907
129.958
126.487
125.319
122.841
120.325
120.041
112.745
77.479
77.161
76.843
49.500
39.265
20.943
20.348
Cl
O
N
H3C
O
3ta
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

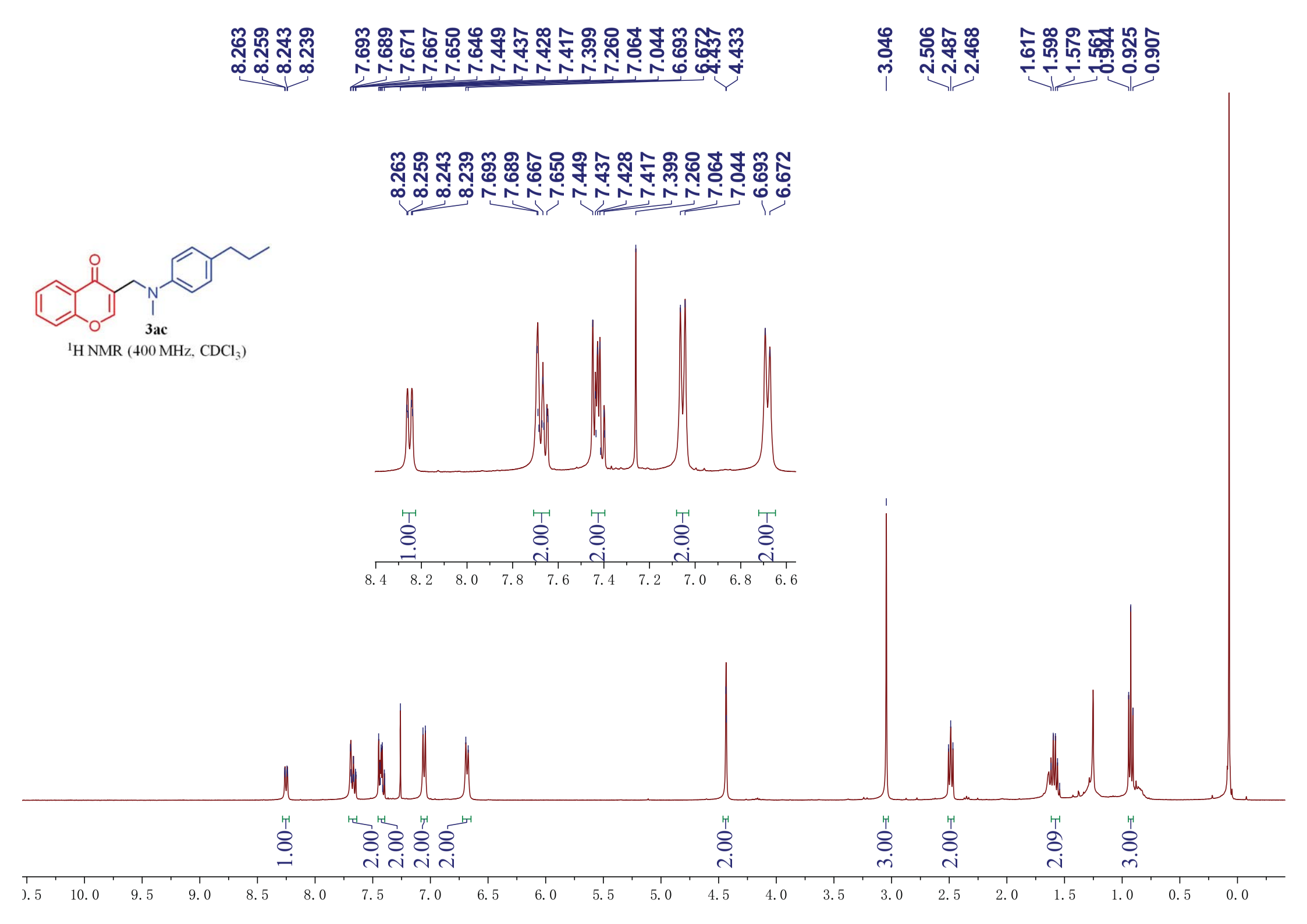

8.068
8.048
7.651
7.284
7.264
7.260
7.060
7.052
7.050
7.046
7.034
7.029
7.028
6.687
6.679
6.674
6.663
6.658
4.432
4.429
3.069
3.051
3.040
3.032
2.250
2.241
2.223
2.205
2.186
2.167
O
N
O
3ua
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.00
2.00
2.00
2.00
7.00
3.00
2.00

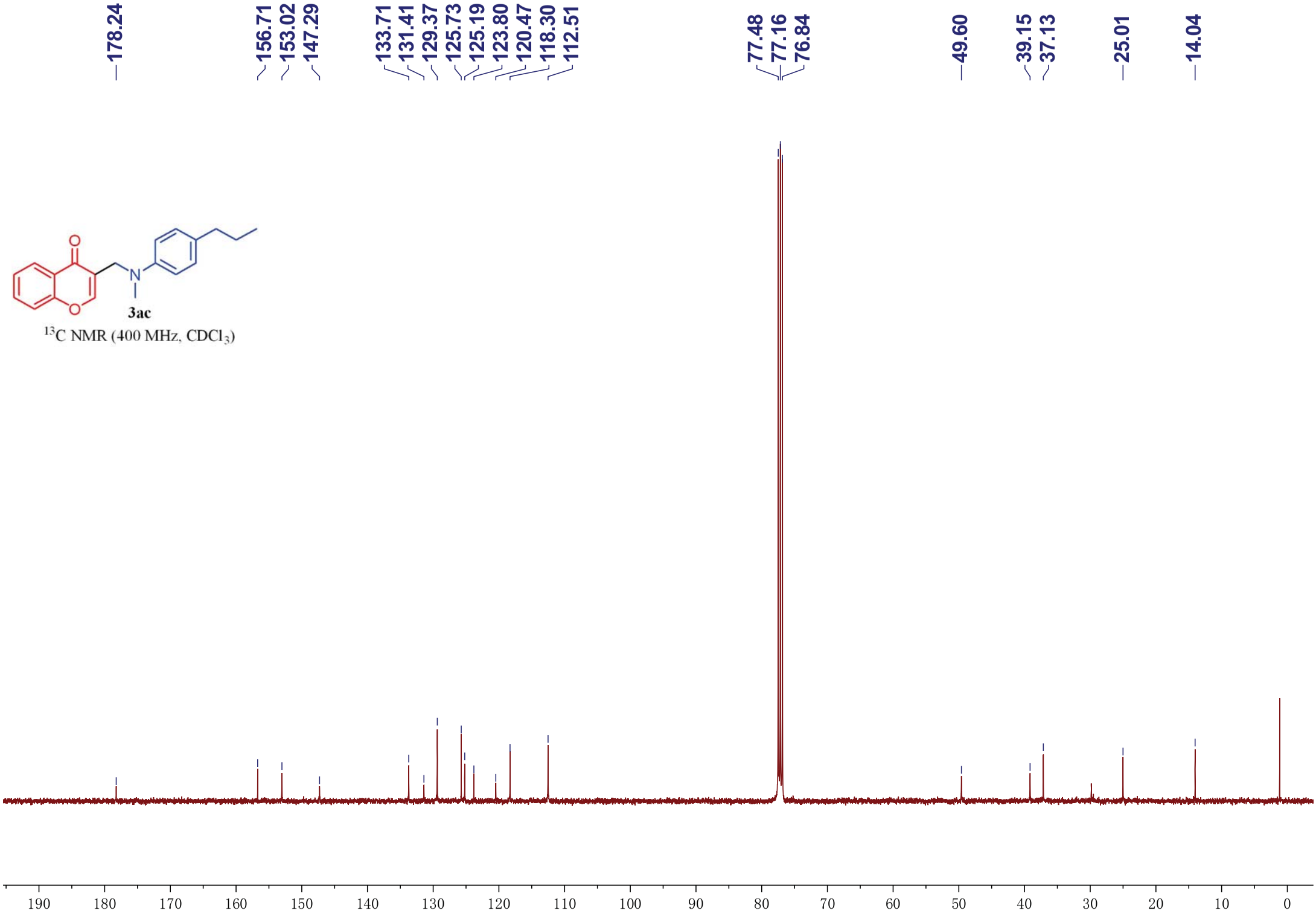

177.48
152.62
151.51
150.83
146.13
131.25
128.93
125.26
123.32
121.35
120.72
119.02
111.76
76.48
76.16
75.84
48.51
38.21
32.82
28.12
24.12
19.34
O
N
O
3ua
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

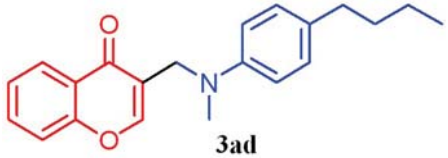
3ab

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


178.16
156.72
153.01
147.32
133.67
132.99
128.75
125.74
125.16
123.84
120.51
118.27
112.70
77.48
77.16
76.84
49.54
39.17
27.88
16.01
O
N
O
3ab
^{13}C NMR (100 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

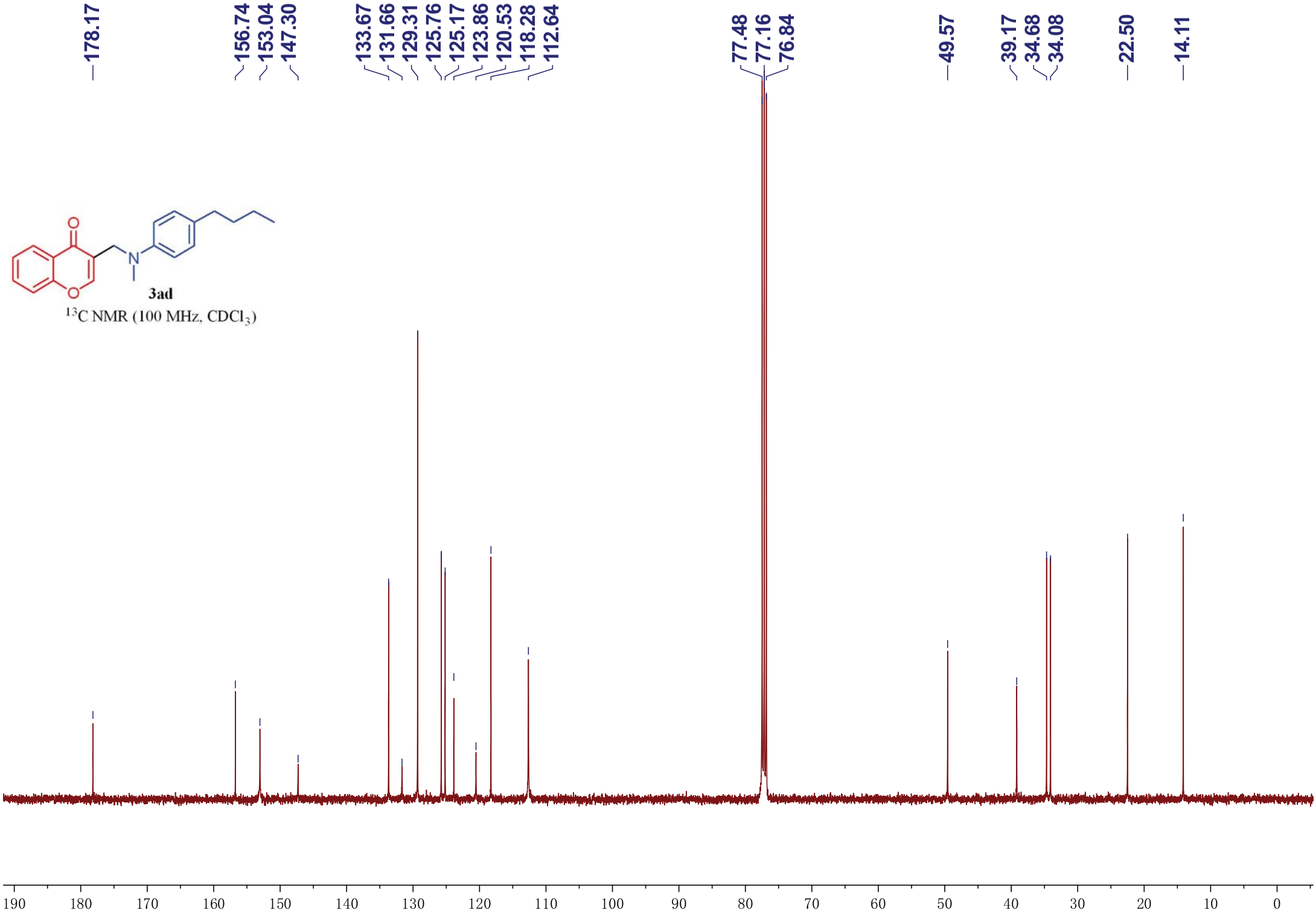

8.263
8.259
8.243
8.239
7.693
7.689
7.671
7.667
7.650
7.646
7.449
7.437
7.428
7.417
7.399
7.260
7.064
7.044
6.693
6.672
4.433
3.046
2.506
2.487
2.468
1.617
1.598
1.579
1.561
0.944
0.925
0.907
3ac
^{1}H NMR (400 MHz, $CDCl_3$)
1.00
2.00
2.00
2.00
2.00
2.00
2.00
2.00
2.09
3.00

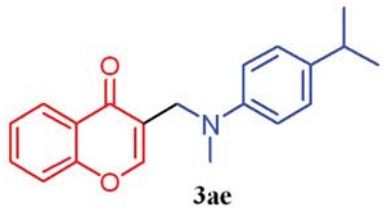

178.24
156.71
153.02
147.29
133.71
131.41
129.37
125.73
125.19
123.80
120.47
118.30
112.51
77.48
77.16
76.84
49.60
39.15
37.13
25.01
14.04
3ac
13C NMR (400 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



3ad

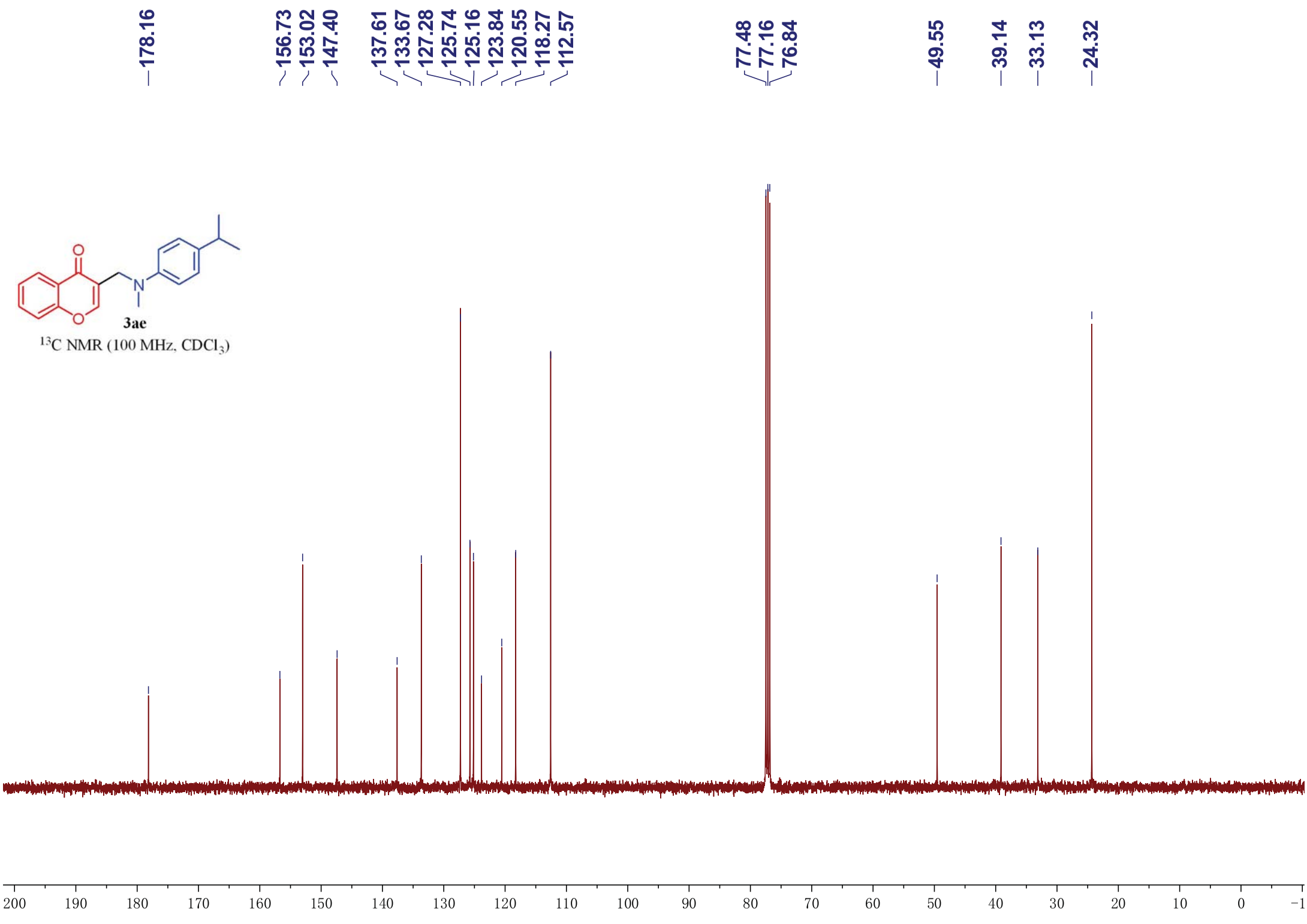
^{1}H NMR (400 MHz, $CDCl_3$)

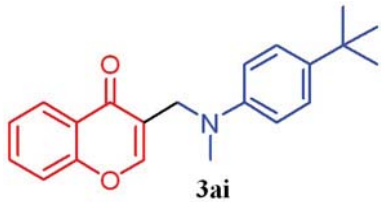

178.17
156.74
153.04
147.30
133.67
131.66
129.31
125.76
125.17
123.86
120.53
118.28
112.64
77.48
77.16
76.84
49.57
39.17
34.68
34.08
22.50
14.11
3ad
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



3ae

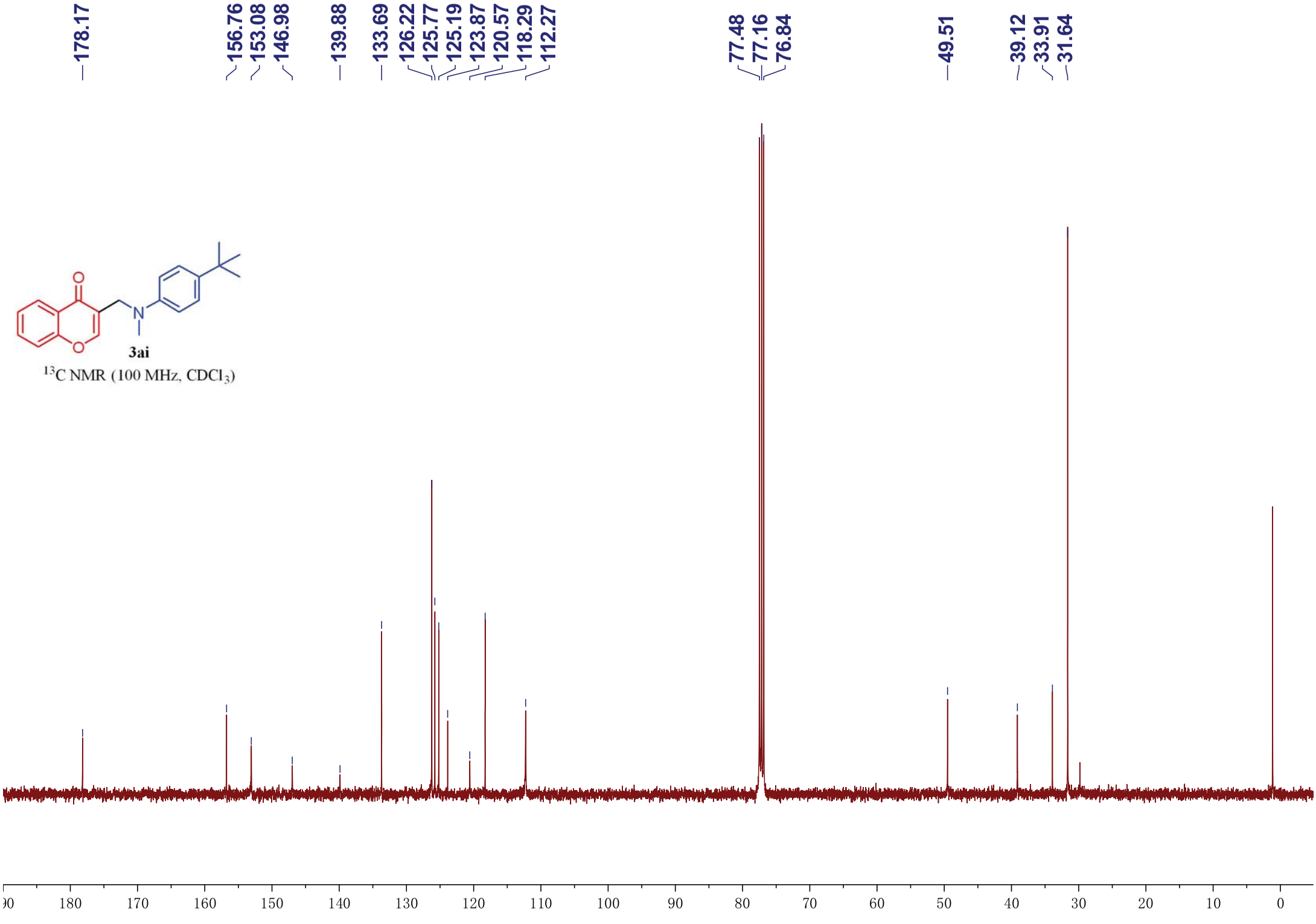
^{1}H NMR (400 MHz, $CDCl_3$)

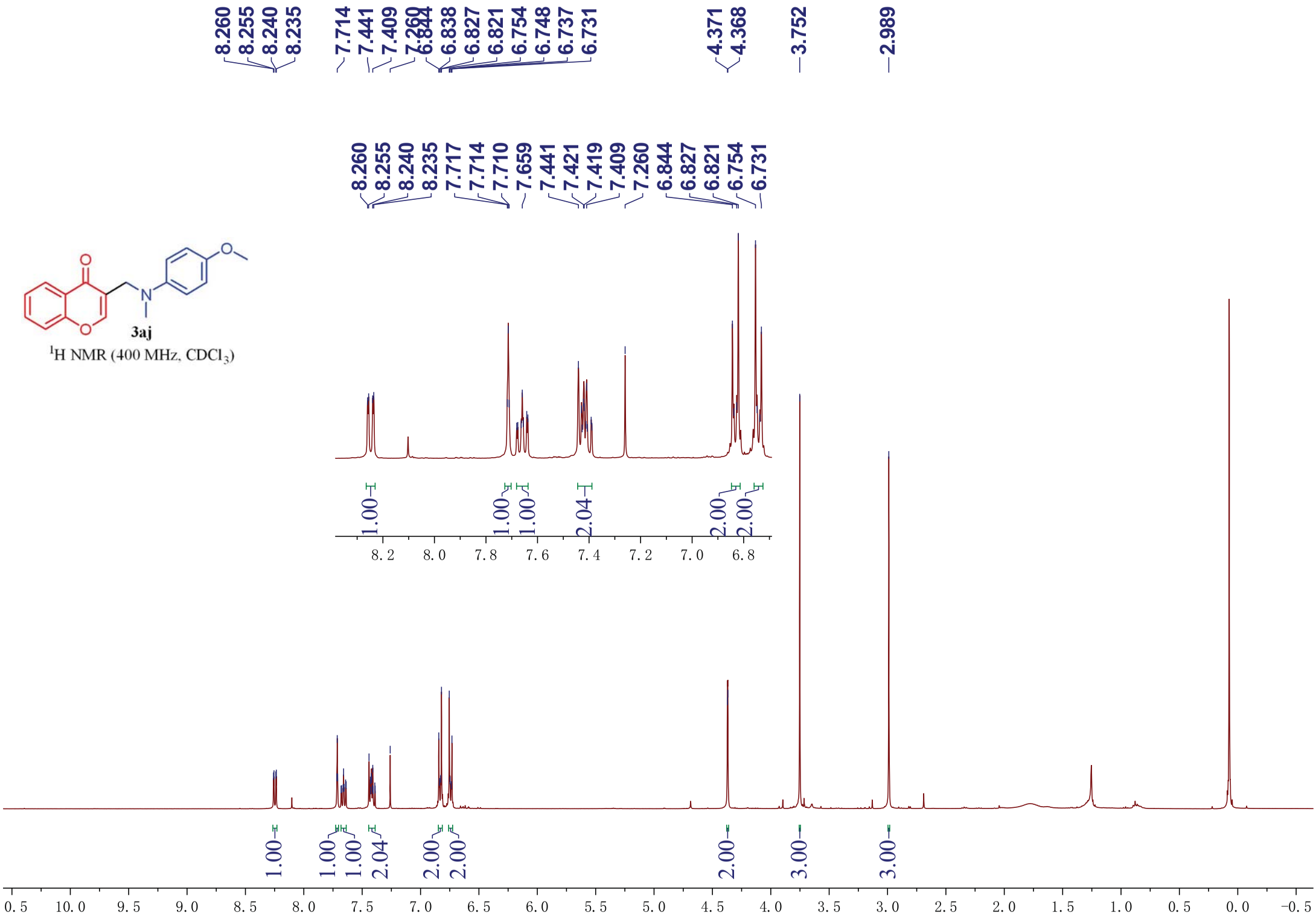

178.16
156.73
153.02
147.40
137.61
133.67
127.28
125.74
125.16
123.84
120.55
118.27
112.57
77.48
77.16
76.84
49.55
39.14
33.13
24.32
O
N
O
3ae
^{13}C NMR (100 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1

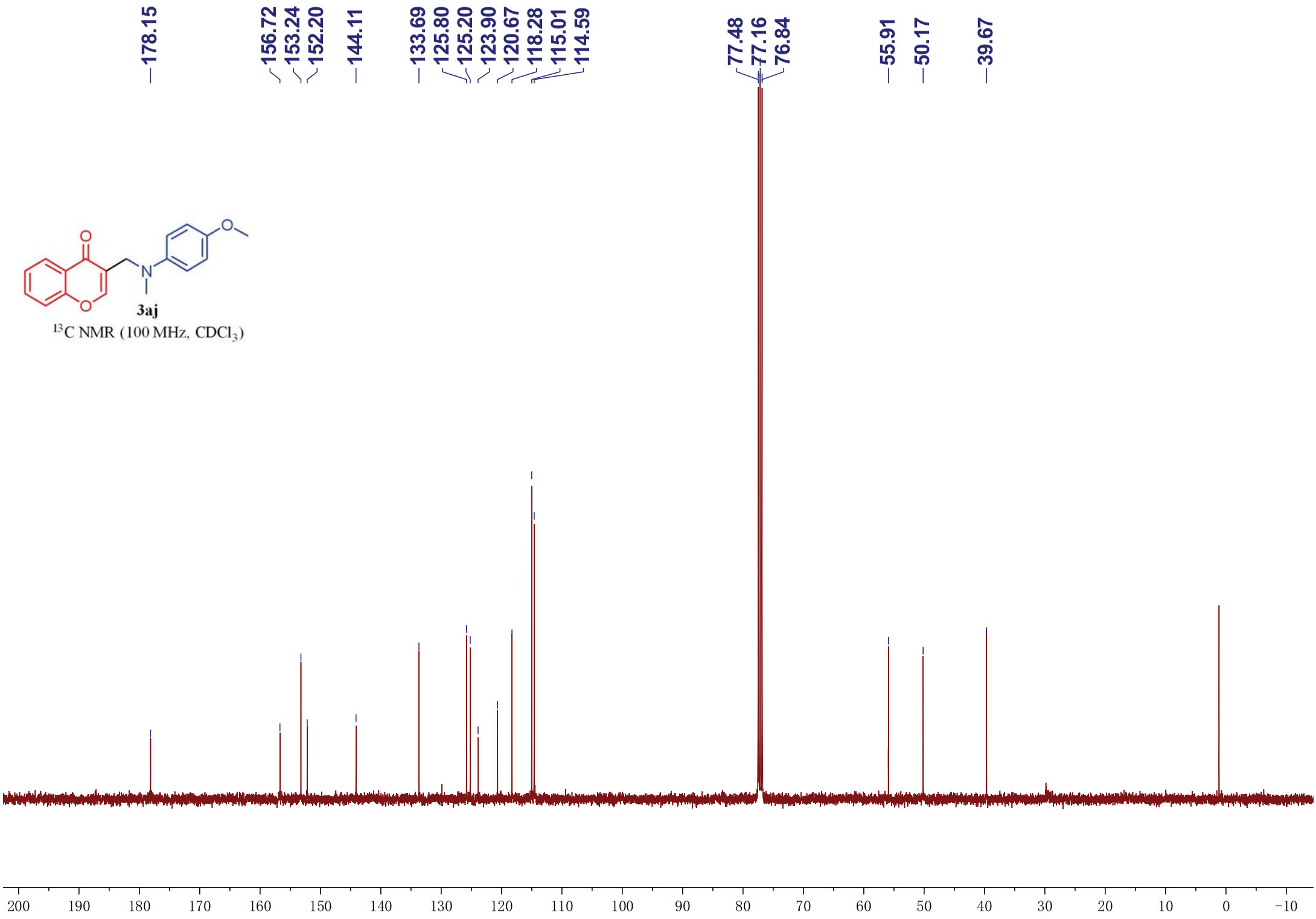


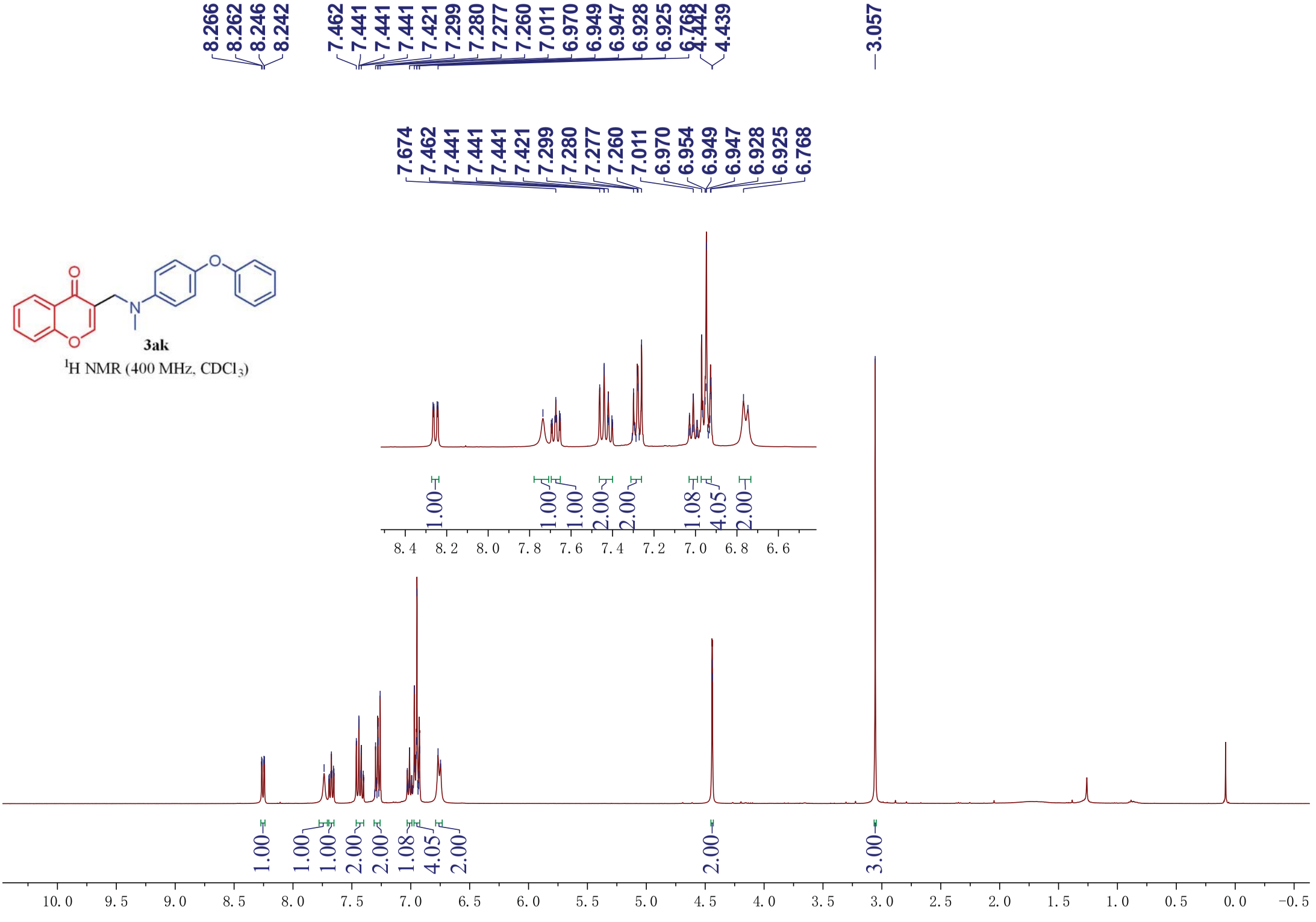
3ai

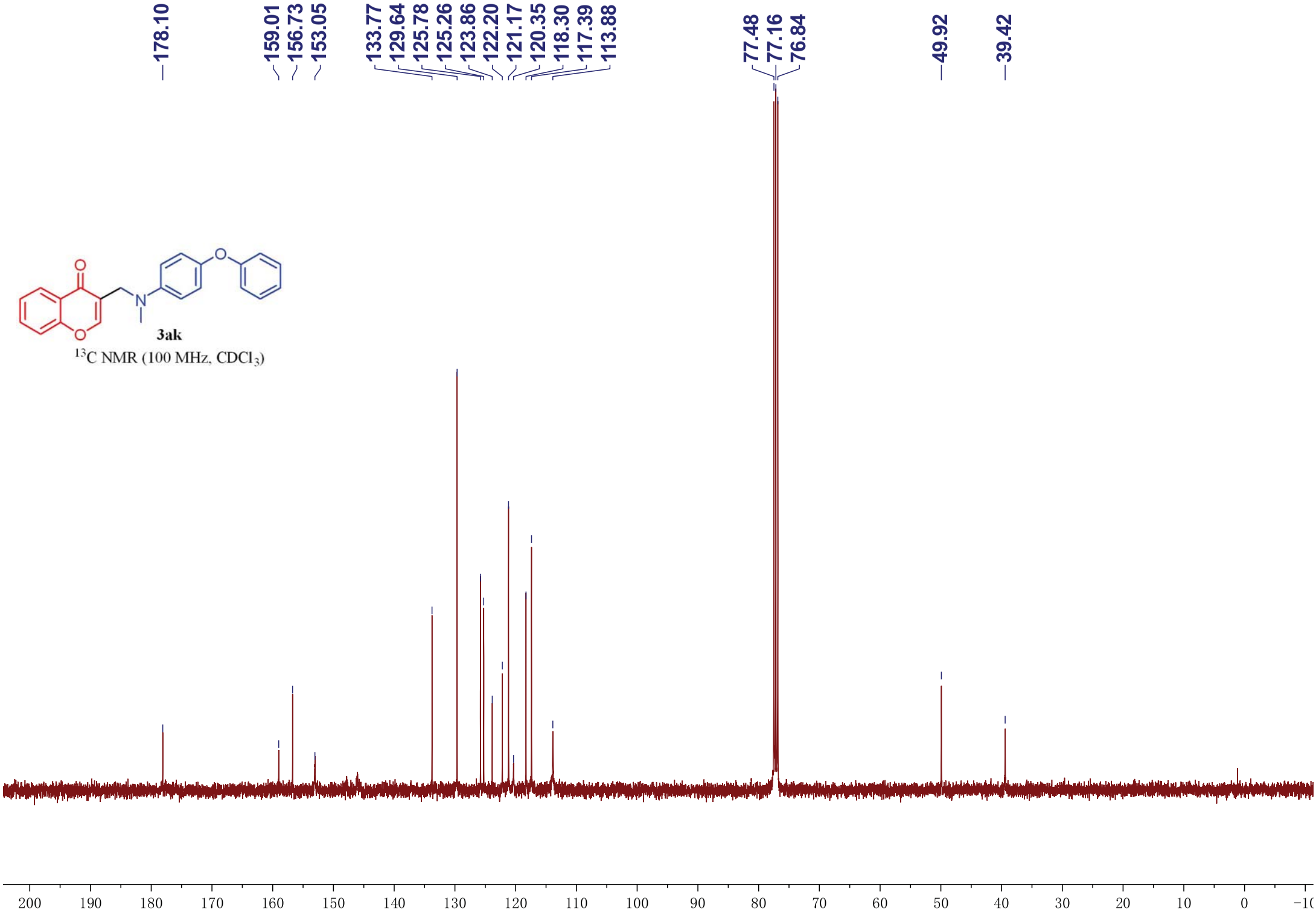
^{1}H NMR (400 MHz, $CDCl_3$)

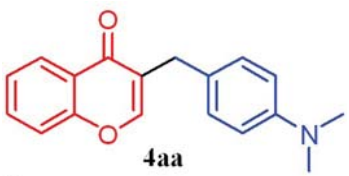

178.17
156.76
153.08
146.98
139.88
133.69
126.22
125.77
125.19
123.87
120.57
118.29
112.27
77.48
77.16
76.84
49.51
39.12
33.91
31.64
O
N
O
3ai
^{13}C NMR (100 MHz, $CDCl_3$)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.260
8.255
8.240
8.235
7.714
7.441
7.409
6.838
6.827
6.821
6.754
6.748
6.737
6.731
4.371
4.368
3.752
2.989
8.260
8.255
8.240
8.235
7.717
7.714
7.710
7.659
7.441
7.421
7.419
7.409
7.260
6.844
6.827
6.821
6.754
6.731
3aj
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.00
2.04
2.00
2.00
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
1.00
1.00
1.00
2.04
2.00
2.00
2.00
3.00
3.00
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


178.15
156.72
153.24
152.20
144.11
133.69
125.80
125.20
123.90
120.67
118.28
115.01
114.59
77.48
77.16
76.84
55.91
50.17
39.67
O
O
N
O
3aj
^{13}C NMR (100 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

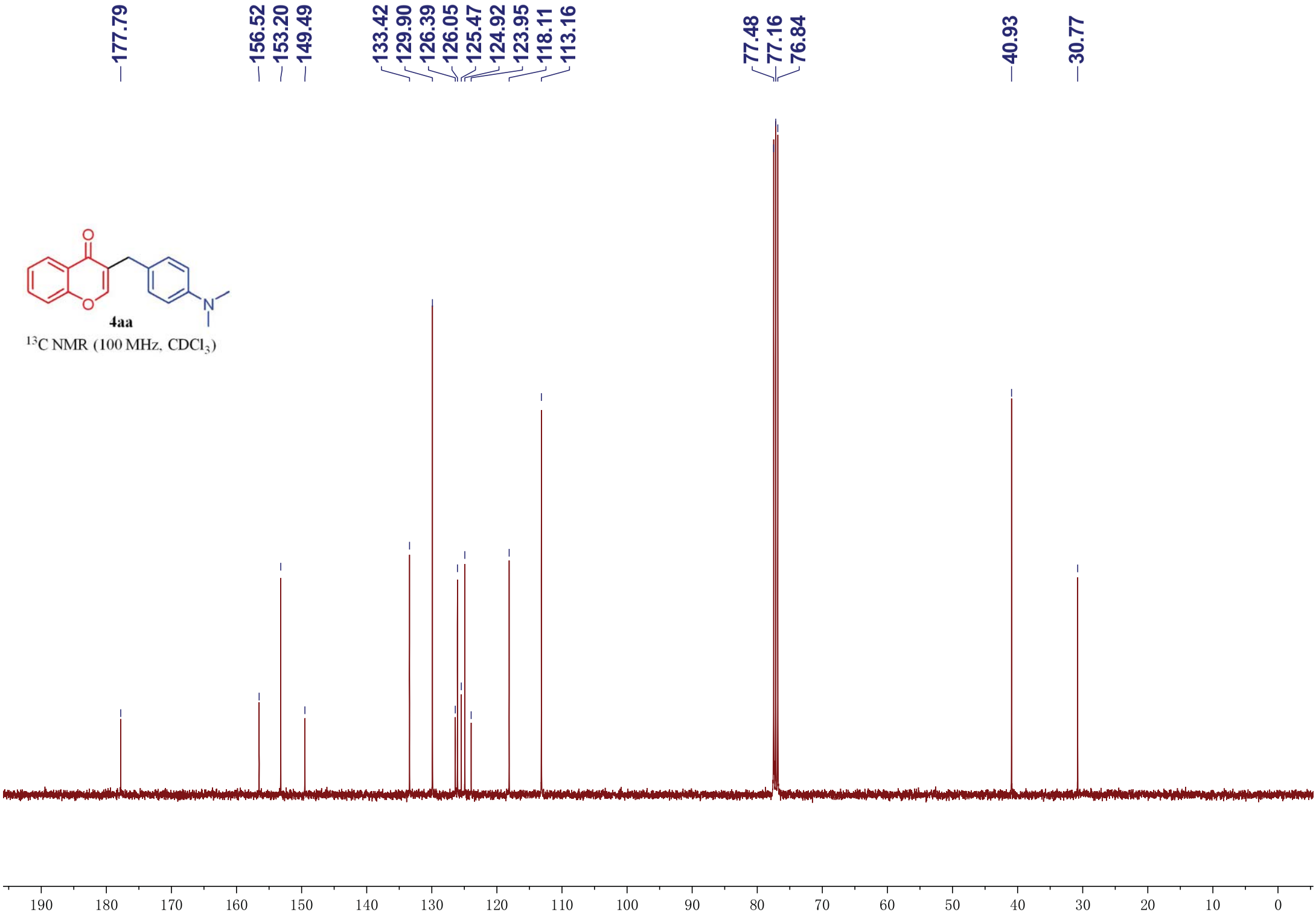

8.266
8.262
8.246
8.242
7.462
7.441
7.441
7.441
7.421
7.299
7.280
7.277
7.260
7.011
6.970
6.949
6.947
6.928
6.925
6.768
4.442
4.439
3.057
7.674
7.462
7.441
7.441
7.441
7.421
7.299
7.280
7.277
7.260
7.011
6.970
6.954
6.949
6.947
6.928
6.925
6.768
O
O
N
O
3ak
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.00
2.00
2.00
1.08
4.05
2.00
2.00
3.00
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

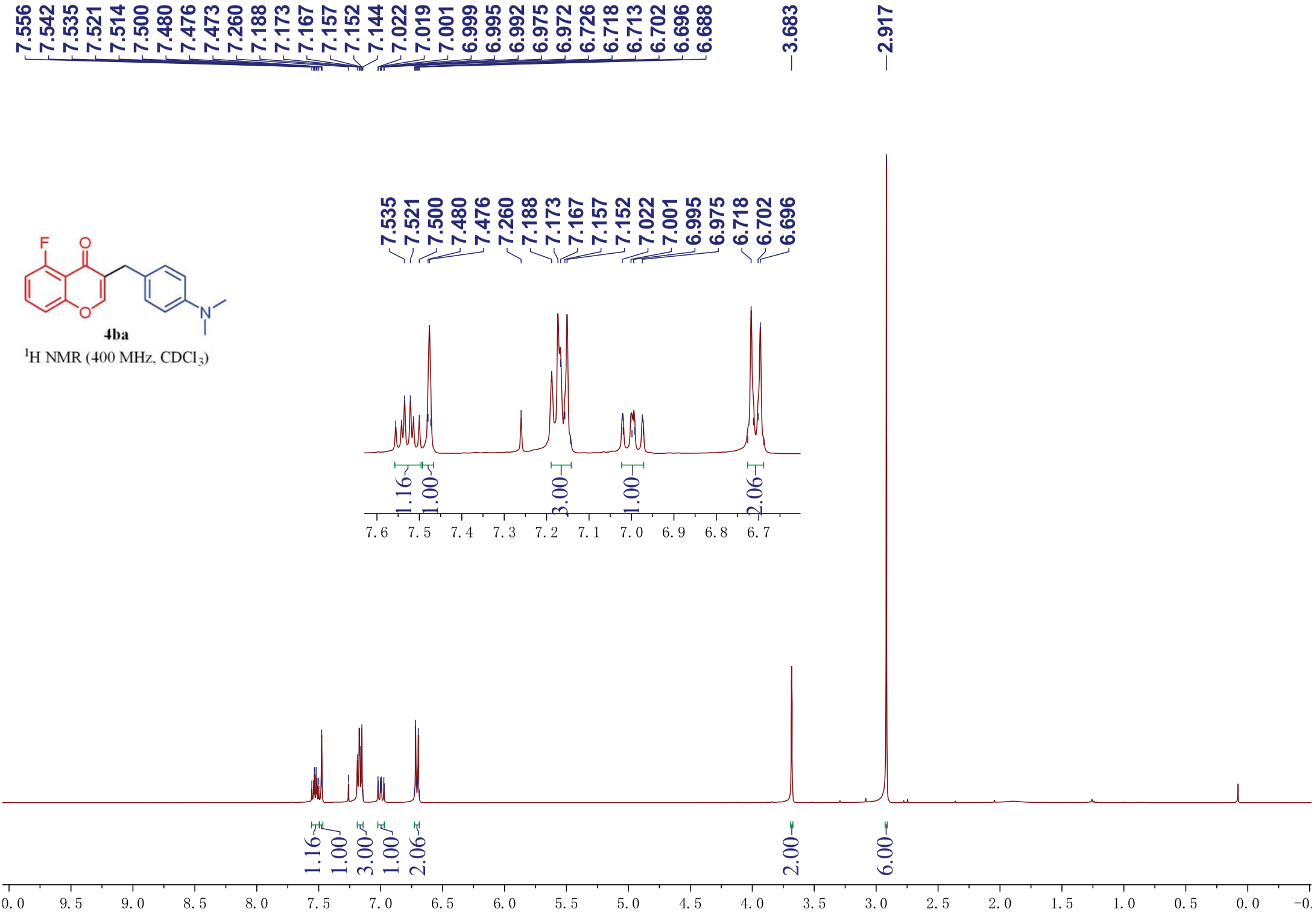

178.10
159.01
156.73
153.05
133.77
129.64
125.78
125.26
123.86
122.20
121.17
120.35
118.30
117.39
113.88
77.48
77.16
76.84
49.92
39.42
O
O
N
O
3ak
^{13}C NMR (100 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

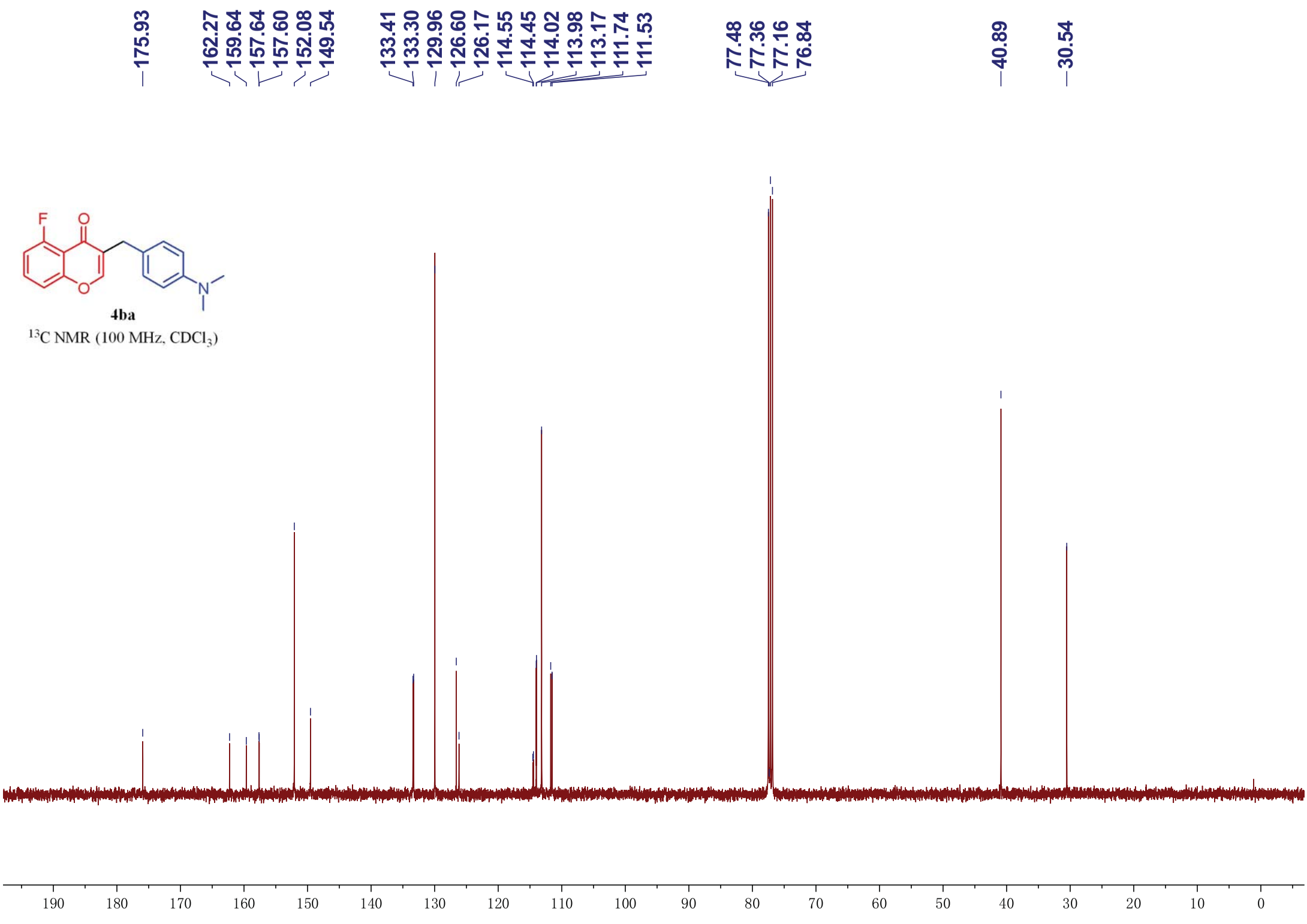


4aa

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

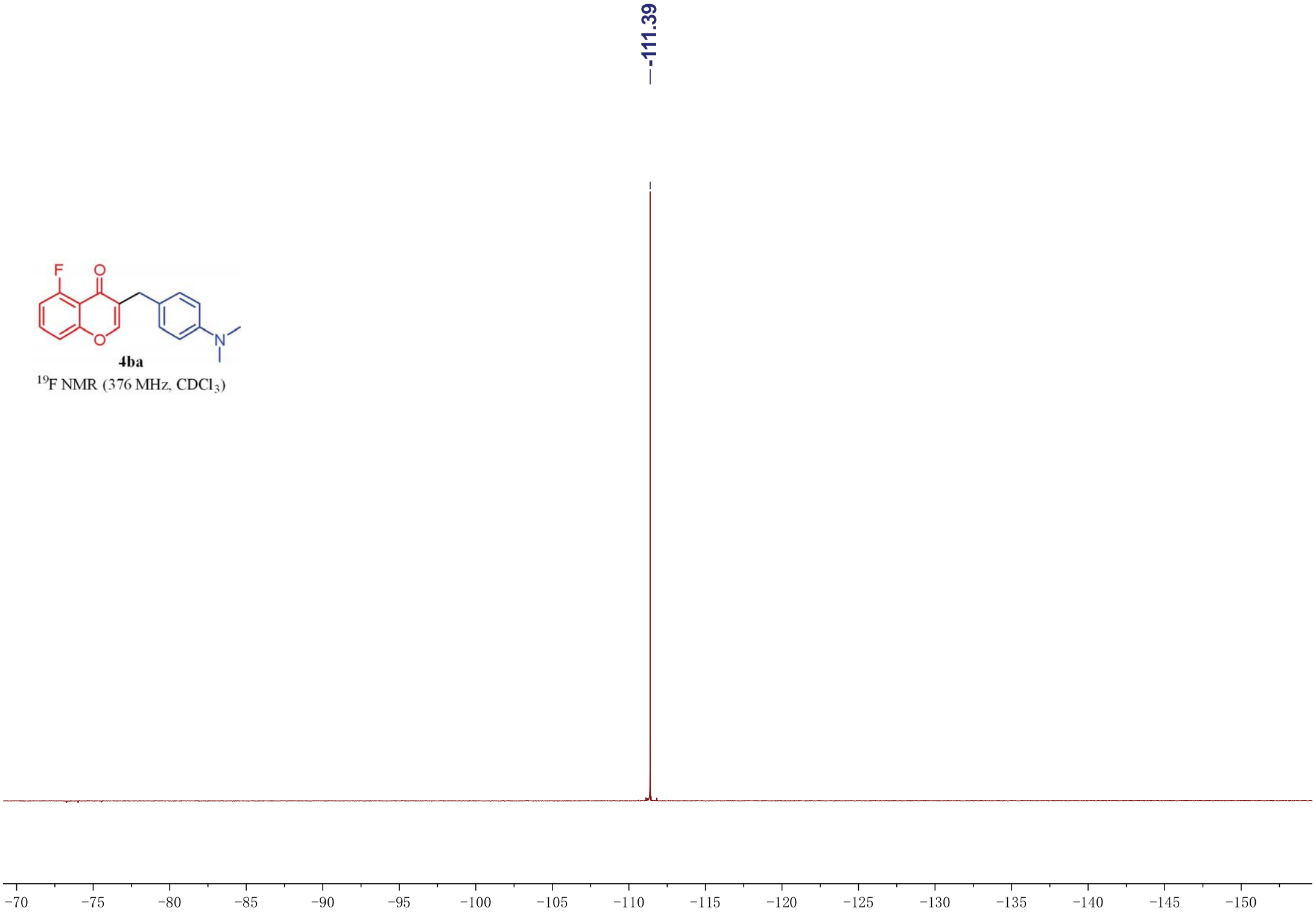

177.79
156.52
153.20
149.49
133.42
129.90
126.39
126.05
125.47
124.92
123.95
118.11
113.16
77.48
77.16
76.84
40.93
30.77
O
O
N
4aa
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

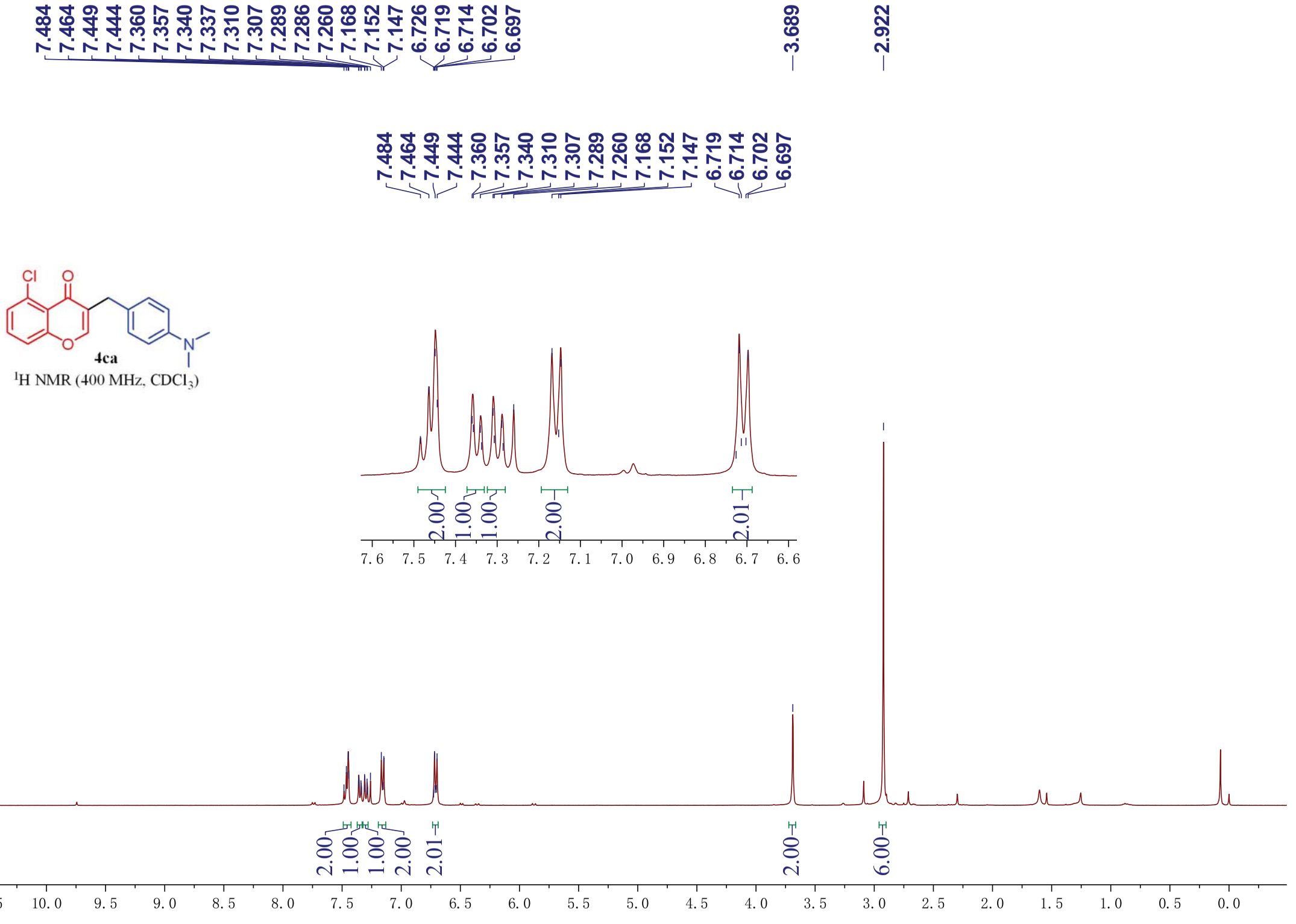

7.556
7.542
7.535
7.521
7.514
7.500
7.480
7.476
7.473
7.260
7.188
7.173
7.167
7.157
7.152
7.144
7.022
7.019
7.001
6.999
6.995
6.992
6.975
6.972
6.726
6.718
6.713
6.702
6.696
6.688
3.683
2.917
F
O
O
N
4ba
^{1}H NMR (400 MHz, $CDCl_3$)
1.16
1.00
3.00
1.00
2.06
2.00
6.00

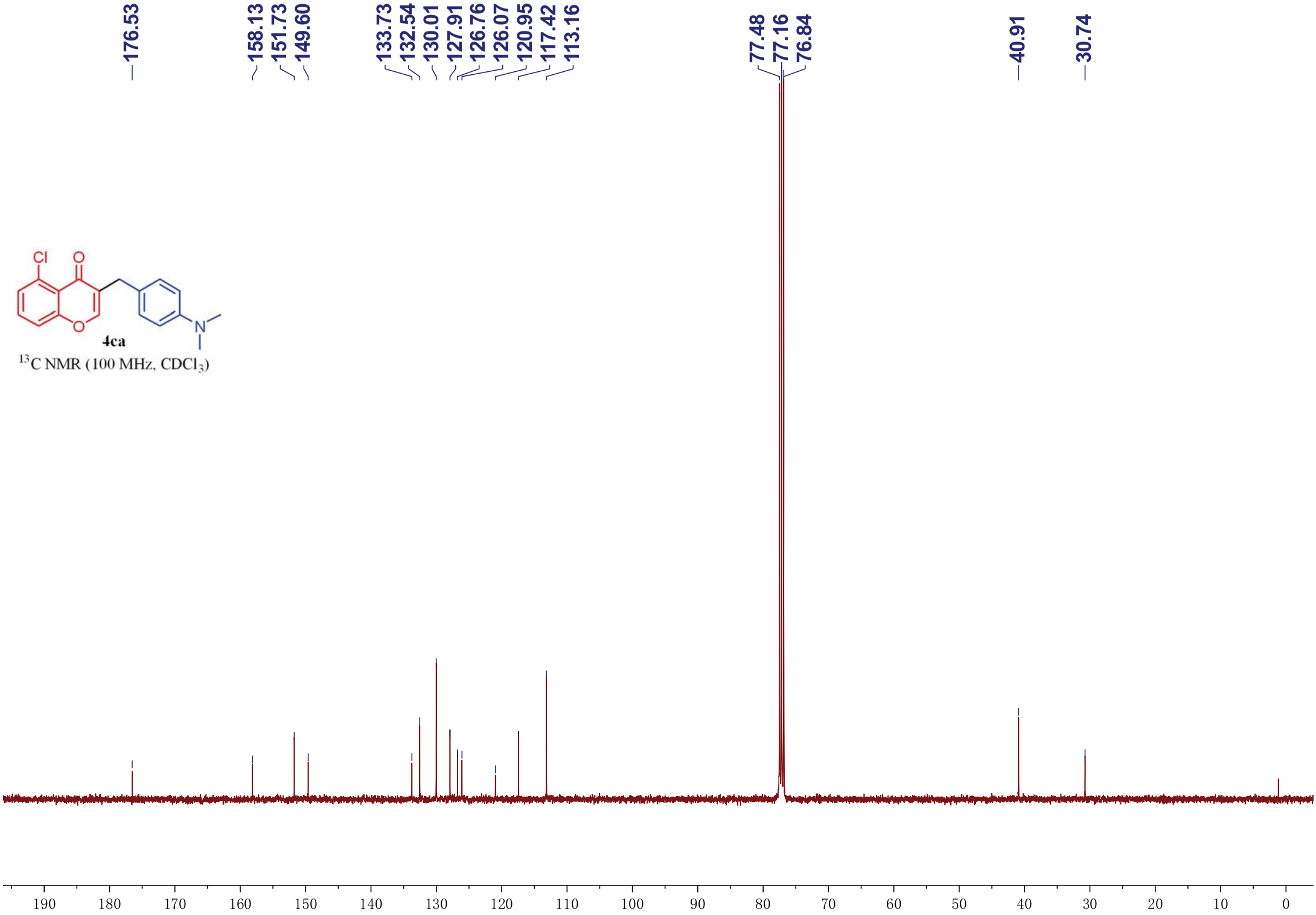

175.93
162.27
159.64
157.64
157.60
152.08
149.54
133.41
133.30
129.96
126.60
126.17
114.55
114.45
114.02
113.98
113.17
111.74
111.53
77.48
77.36
77.16
76.84
40.89
30.54
F
O
O
N
4ba
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

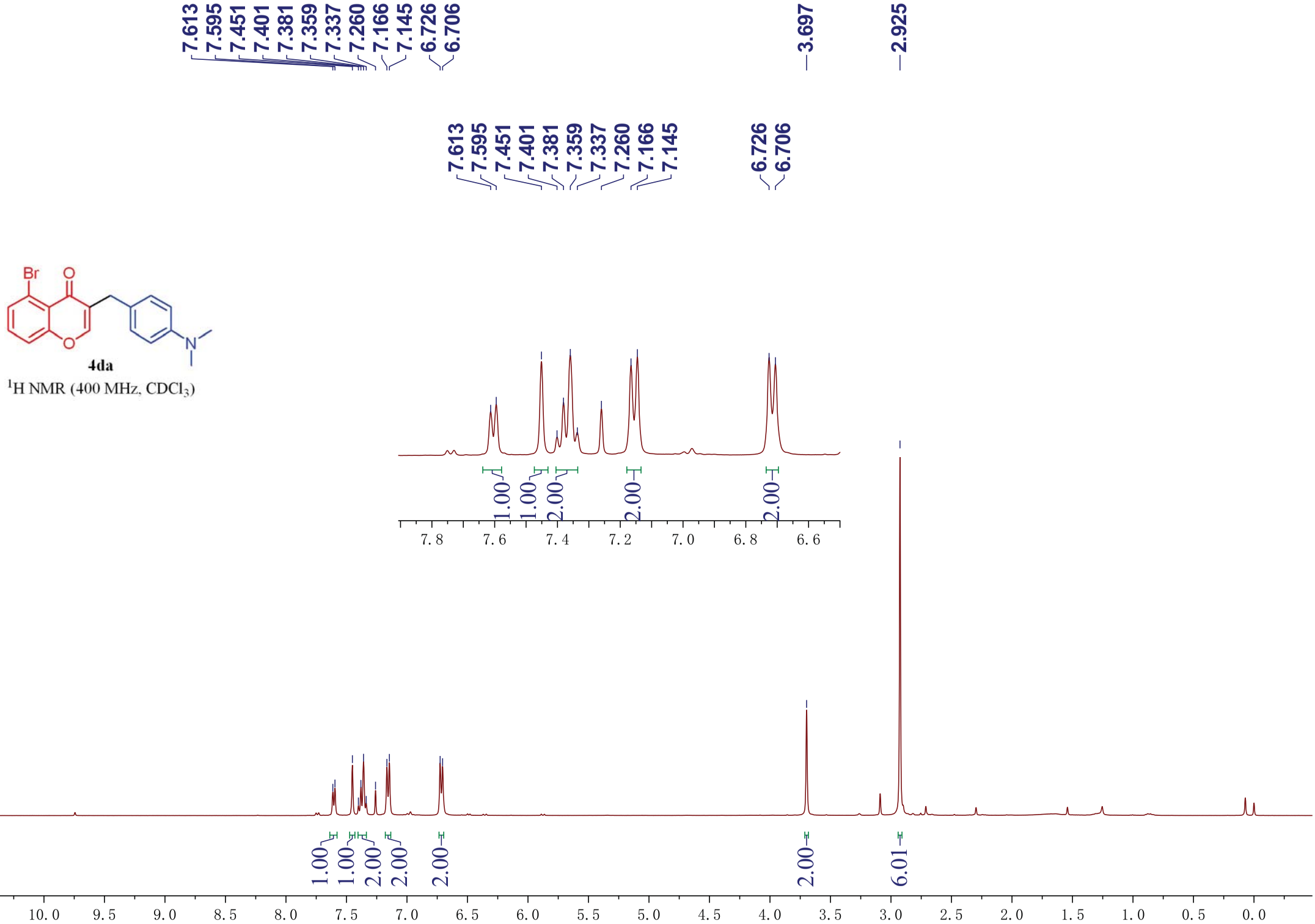
4ba

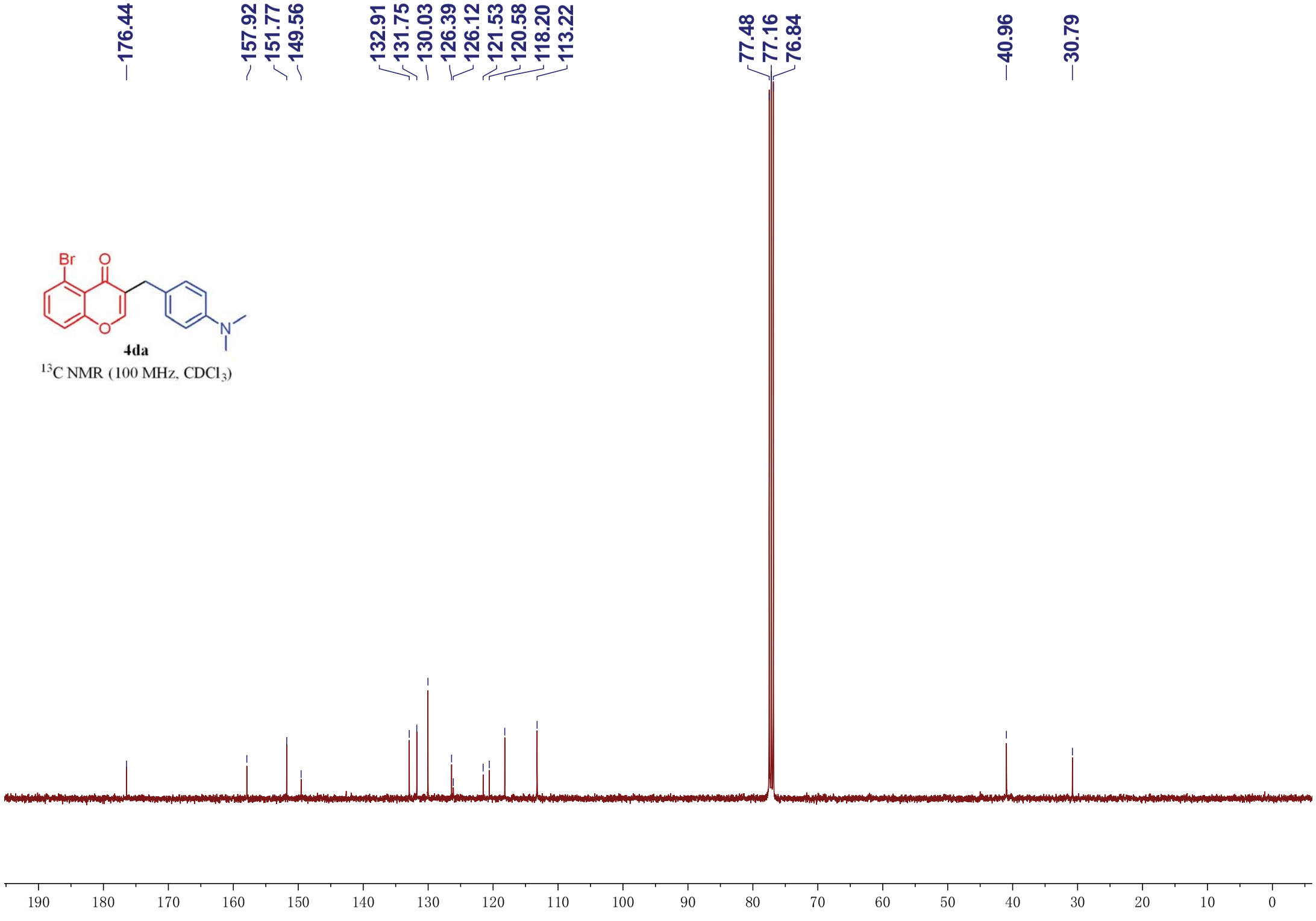
^{19}F NMR (376 MHz, $CDCl_3$)




7.484
7.464
7.449
7.444
7.360
7.357
7.340
7.337
7.310
7.307
7.289
7.286
7.260
7.168
7.152
7.147
6.726
6.719
6.714
6.702
6.697
3.689
2.922
Cl
O
O
N
4ca
1H NMR (400 MHz, CDCl3)
2.00
1.00
1.00
2.00
2.01
2.00
6.00
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

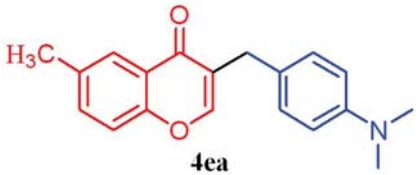

176.53
158.13
151.73
149.60
133.73
132.54
130.01
127.91
126.76
126.07
120.95
117.42
113.16
77.48
77.16
76.84
40.91
30.74
Cl
O
O
N
4ca
^{13}C NMR (100 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.613
7.595
7.451
7.401
7.381
7.359
7.337
7.260
7.166
7.145
6.726
6.706
3.697
2.925
Br
O
O
N
4da
^{1}H NMR (400 MHz, $CDCl_3$)
1.00
1.00
2.00
2.00
2.00
2.00
6.01
7.8
7.6
7.4
7.2
7.0
6.8
6.6
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



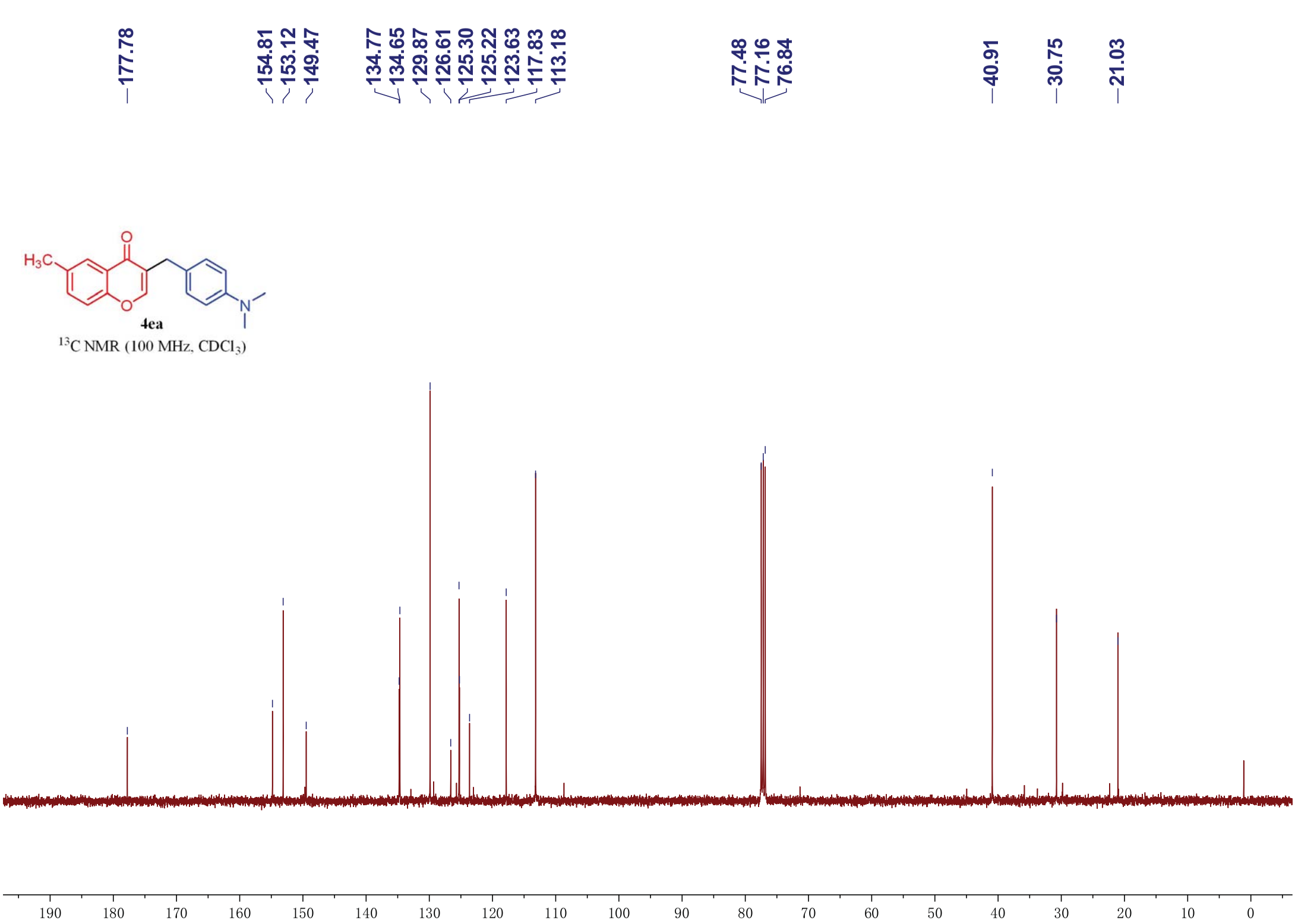
4da

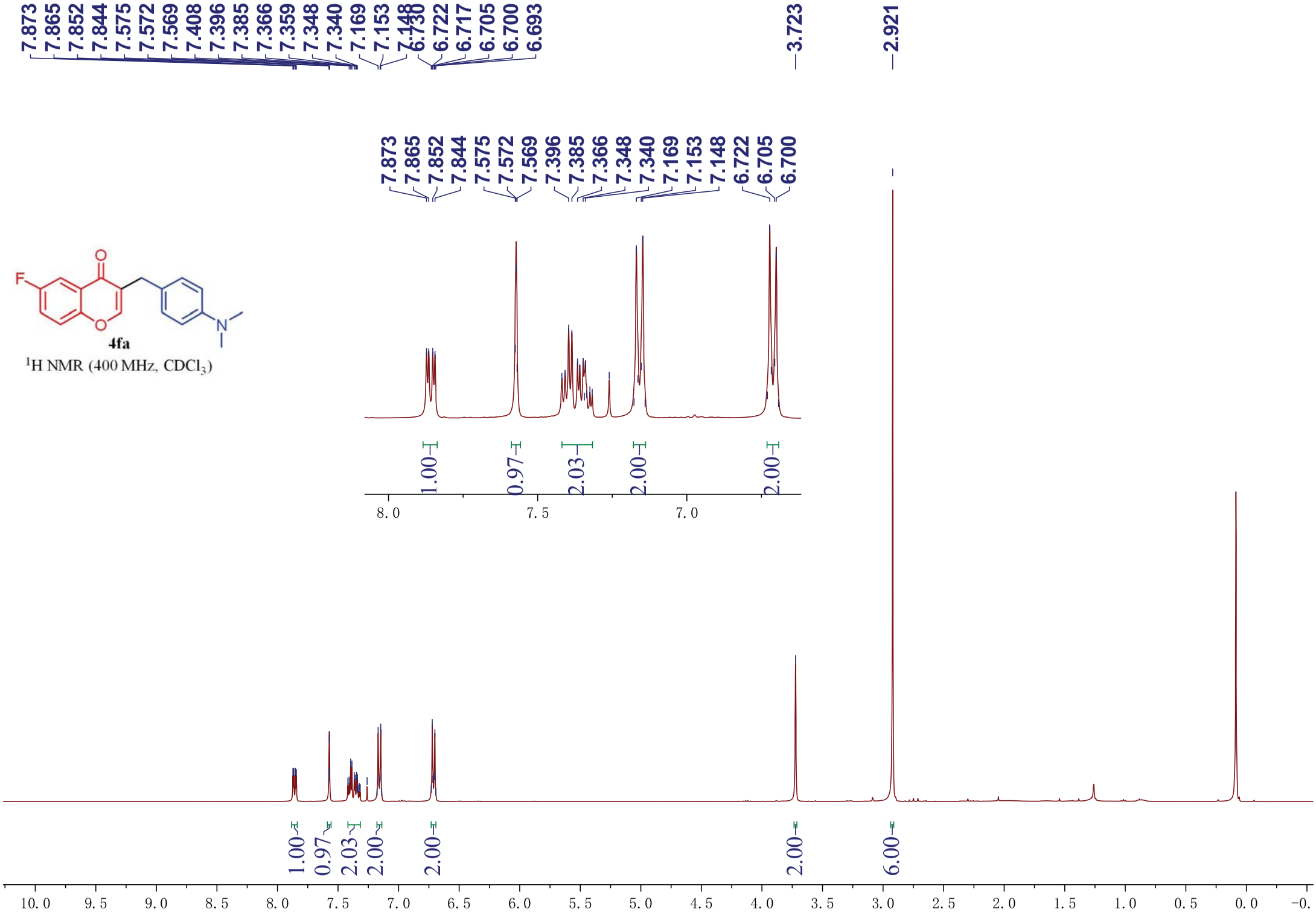
^{13}C NMR (100 MHz, $CDCl_3$)

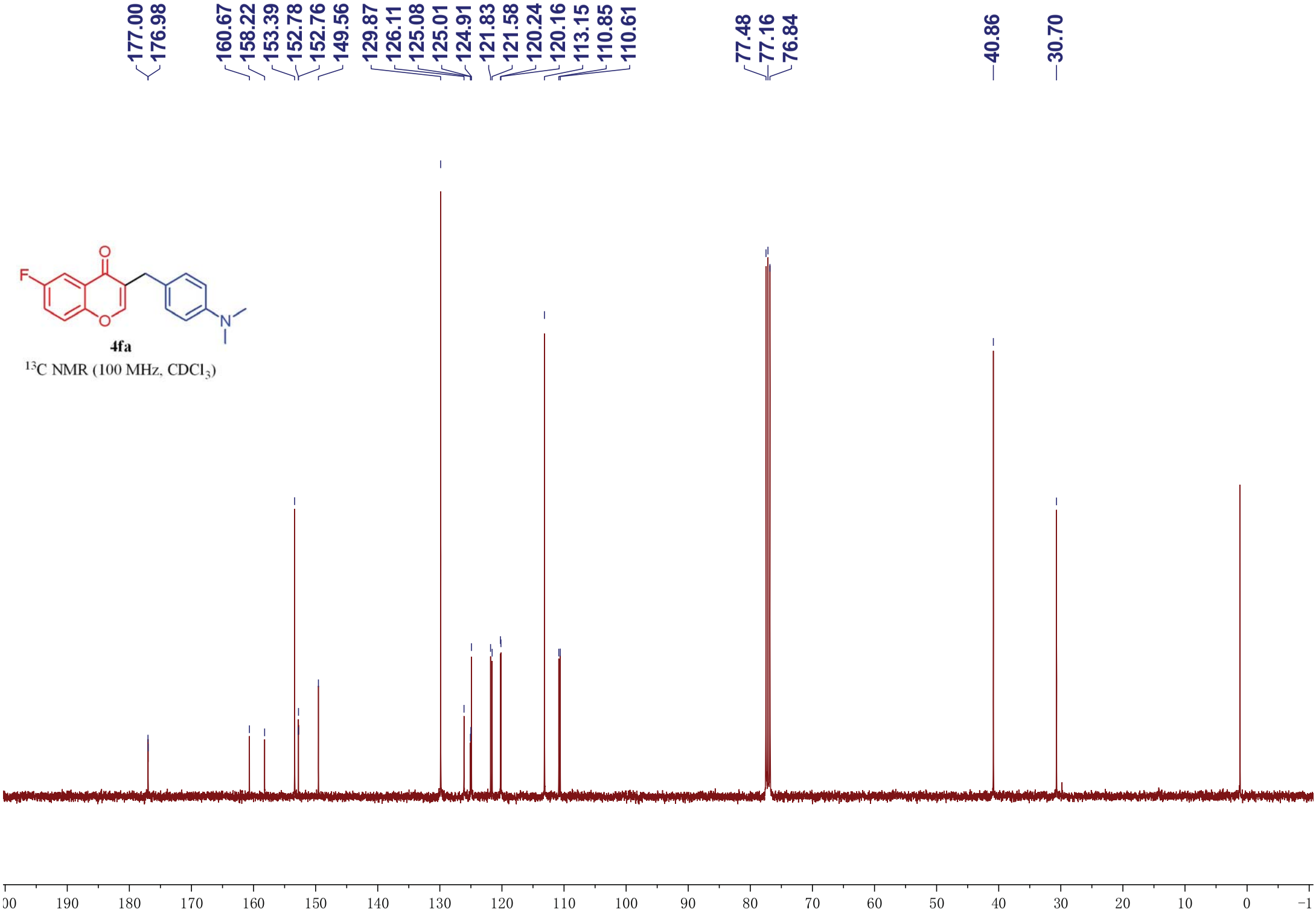


4ea

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

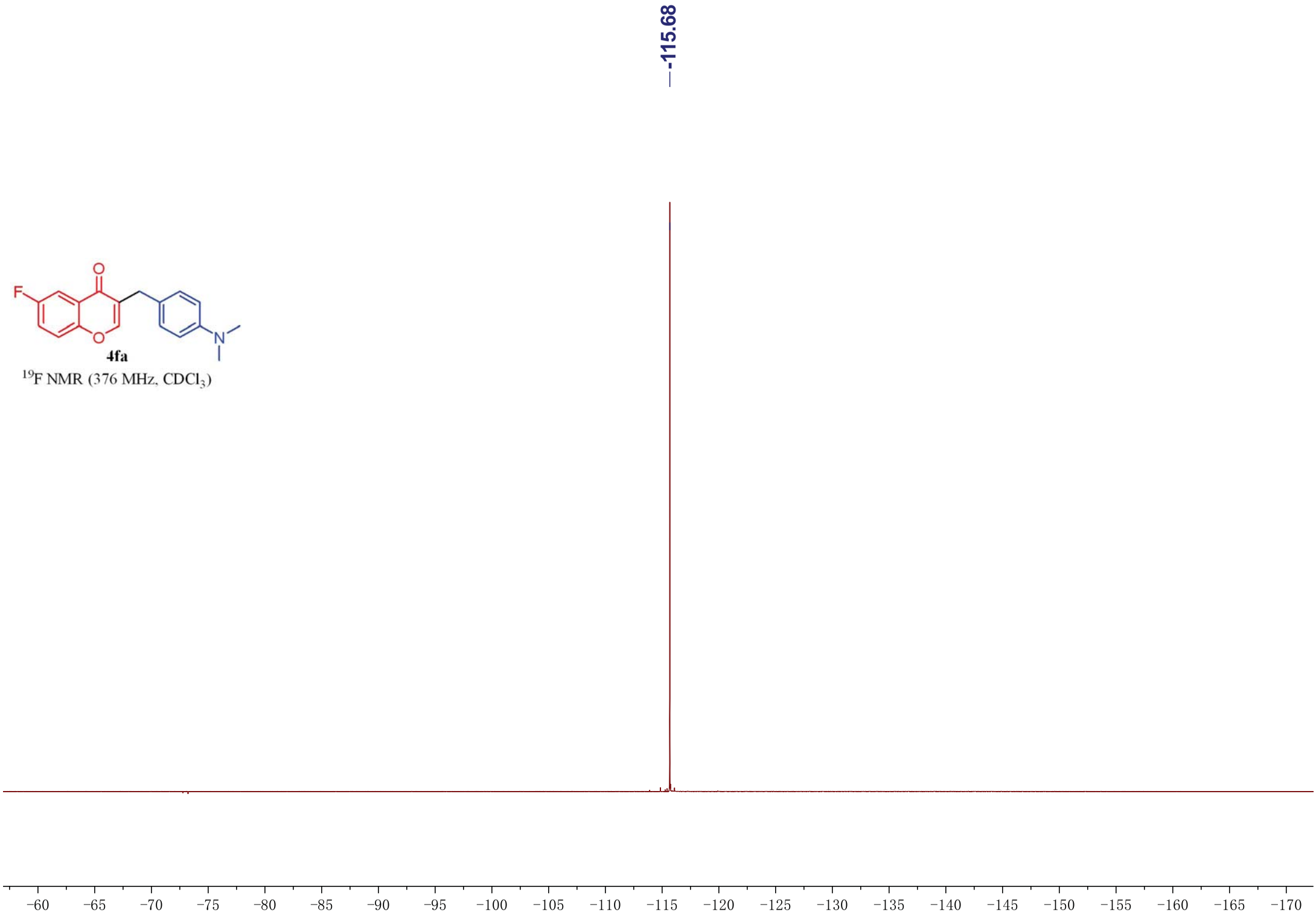

177.78
154.81
153.12
149.47
134.77
134.65
129.87
126.61
125.30
125.22
123.63
117.83
113.18
77.48
77.16
76.84
40.91
30.75
21.03
H3C
O
O
N
4ea
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

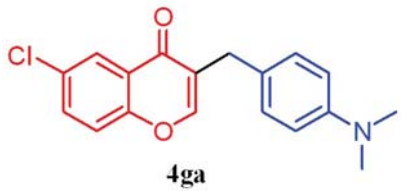

7.873
7.865
7.852
7.844
7.575
7.572
7.569
7.408
7.396
7.385
7.366
7.359
7.348
7.340
7.169
7.153
7.148
6.730
6.722
6.717
6.705
6.700
6.693
3.723
2.921
F
O
O
N
4fa
^{1}H NMR (400 MHz, $CDCl_3$)
1.00
0.97
2.03
2.00
2.00
2.00
6.00
8.0
7.5
7.0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.


177.00
176.98
160.67
158.22
153.39
152.78
152.76
149.56
129.87
126.11
125.08
125.01
124.91
121.83
121.58
120.24
120.16
113.15
110.85
110.61
77.48
77.16
76.84
40.86
30.70
F
O
O
N
4fa
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

4fa

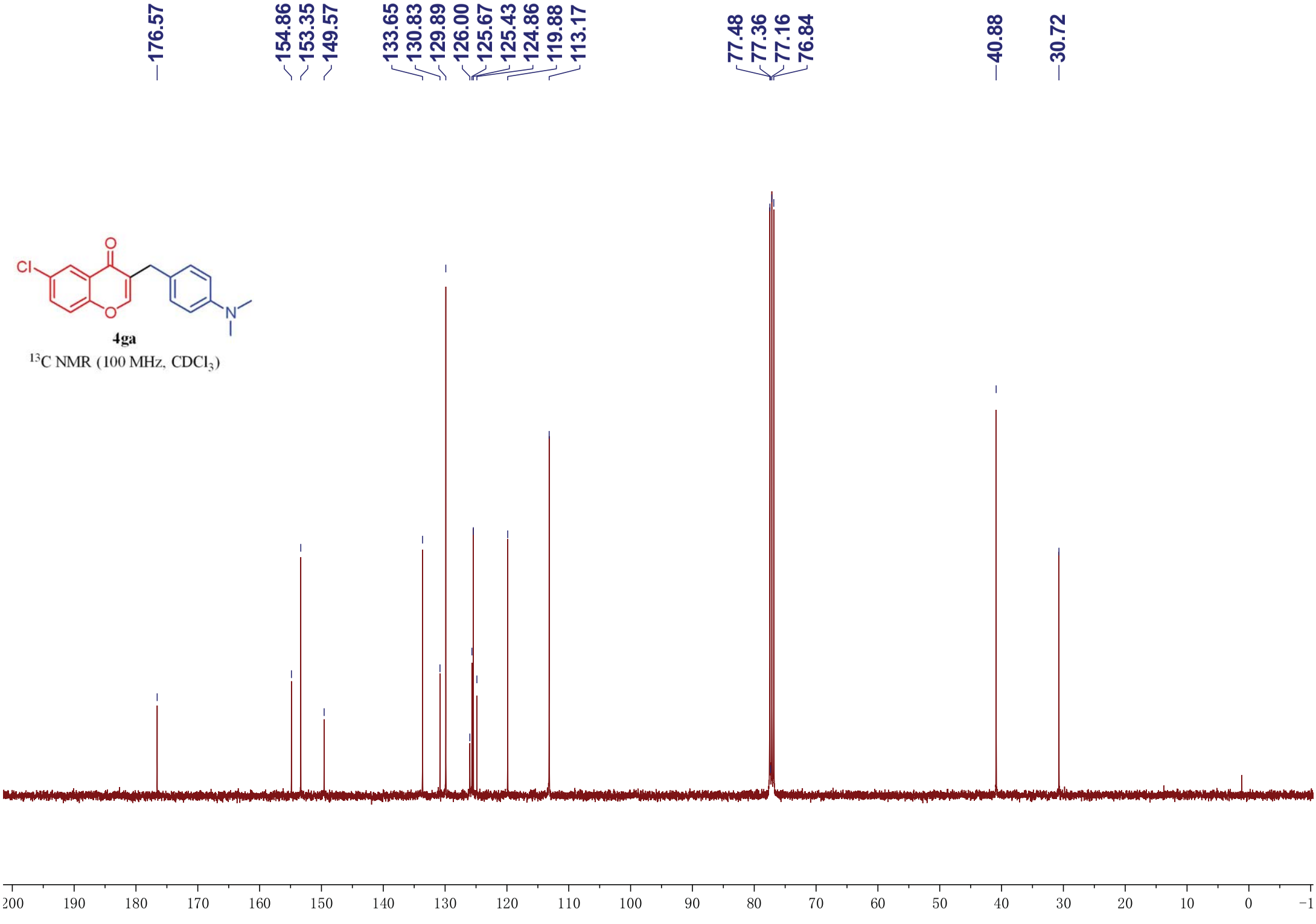
^{19}F NMR (376 MHz, $CDCl_3$)

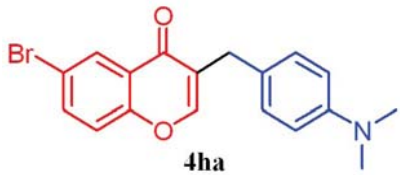




4ga

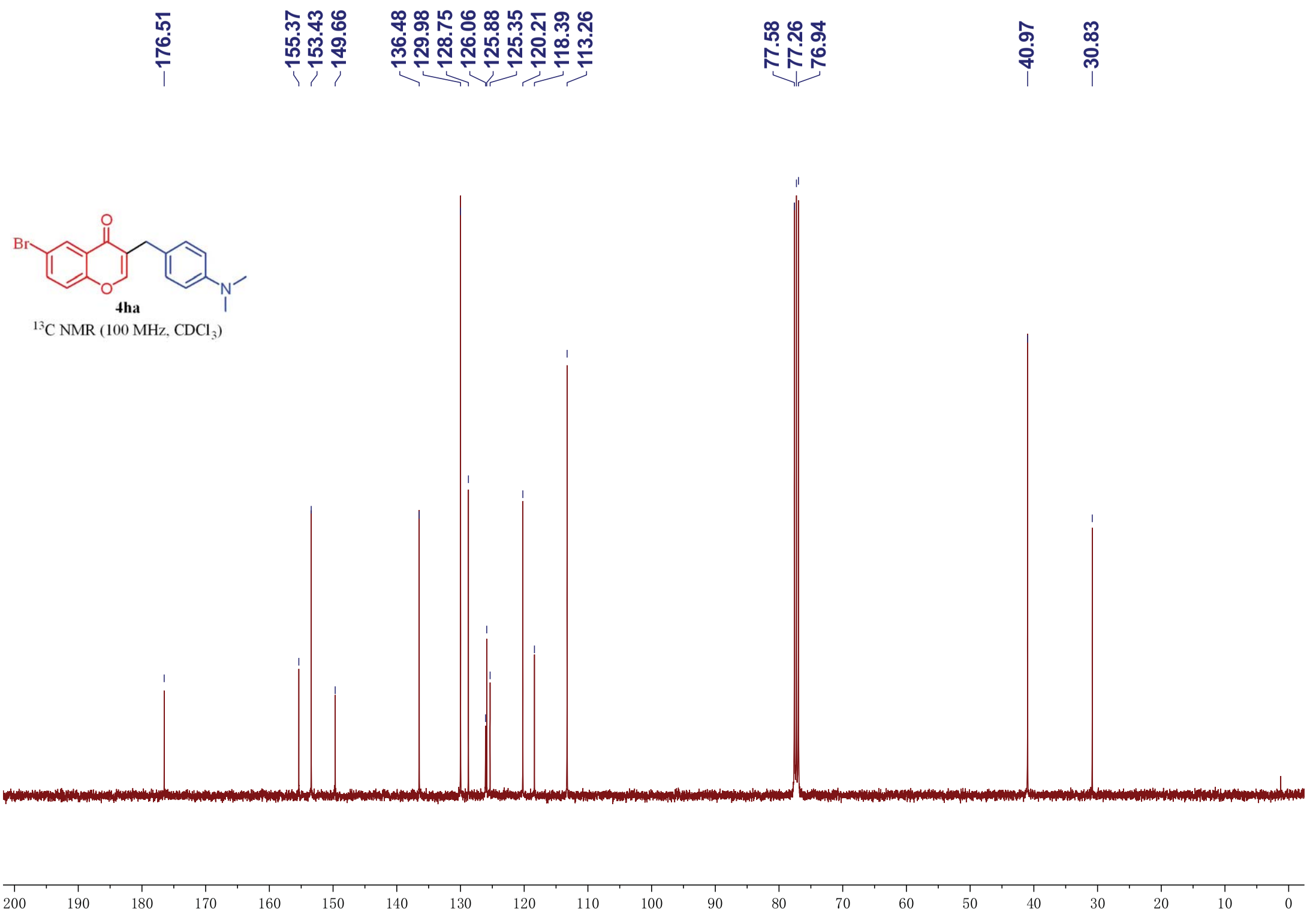
^{1}H NMR (400 MHz, $CDCl_3$)

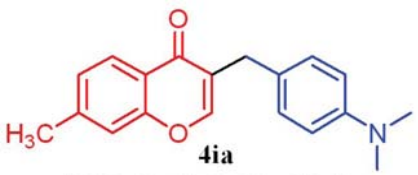

176.57
154.86
153.35
149.57
133.65
130.83
129.89
126.00
125.67
125.43
124.86
119.88
113.17
77.48
77.36
77.16
76.84
40.88
30.72
Cl
O
O
N
4ga
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1



4ha

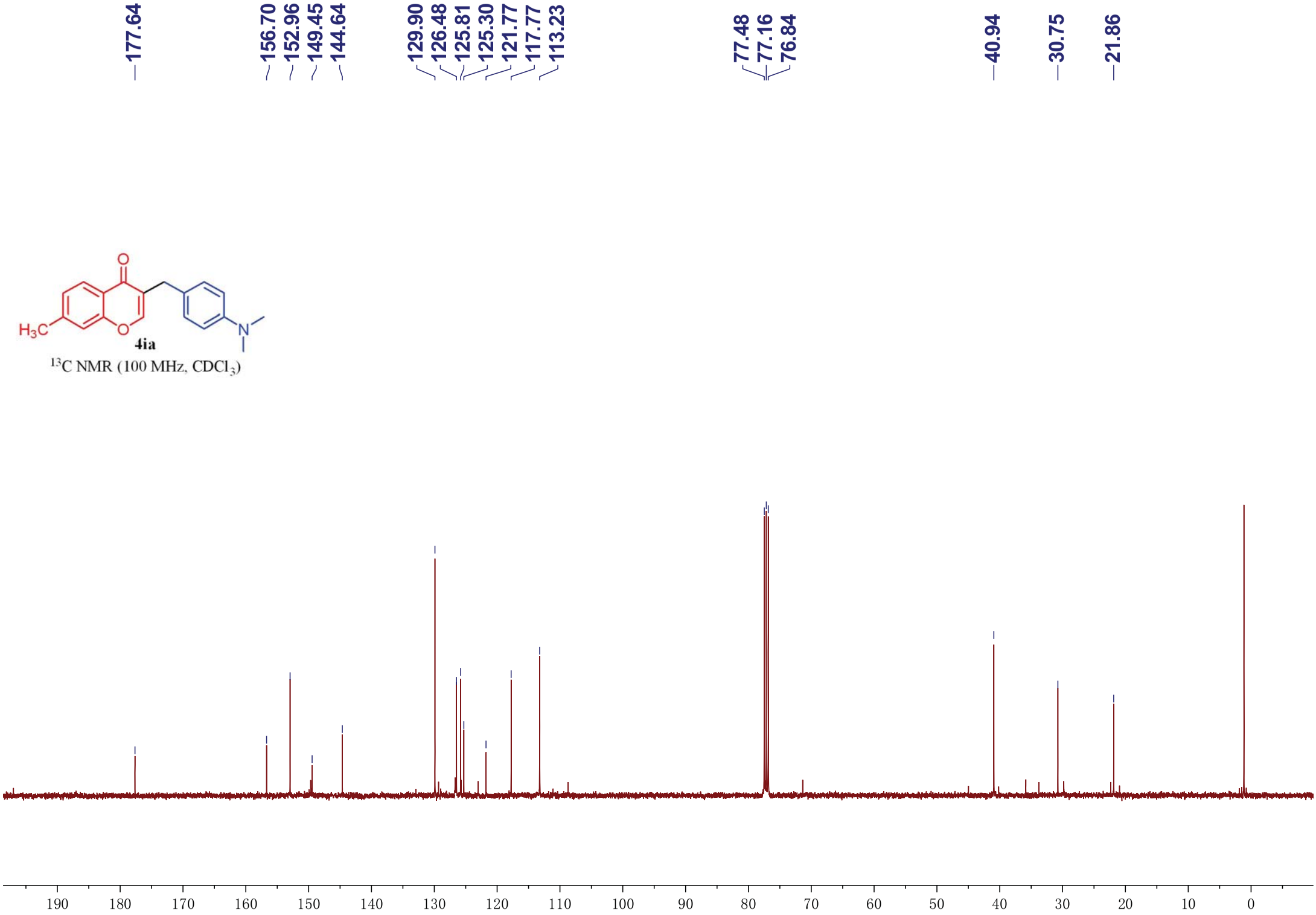
^{1}H NMR (400 MHz, $CDCl_3$)


176.51
155.37
153.43
149.66
136.48
129.98
128.75
126.06
125.88
125.35
120.21
118.39
113.26
77.58
77.26
76.94
40.97
30.83
Br
O
O
N
4ha
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



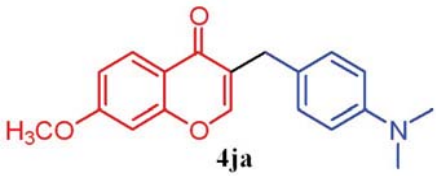
4ia

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



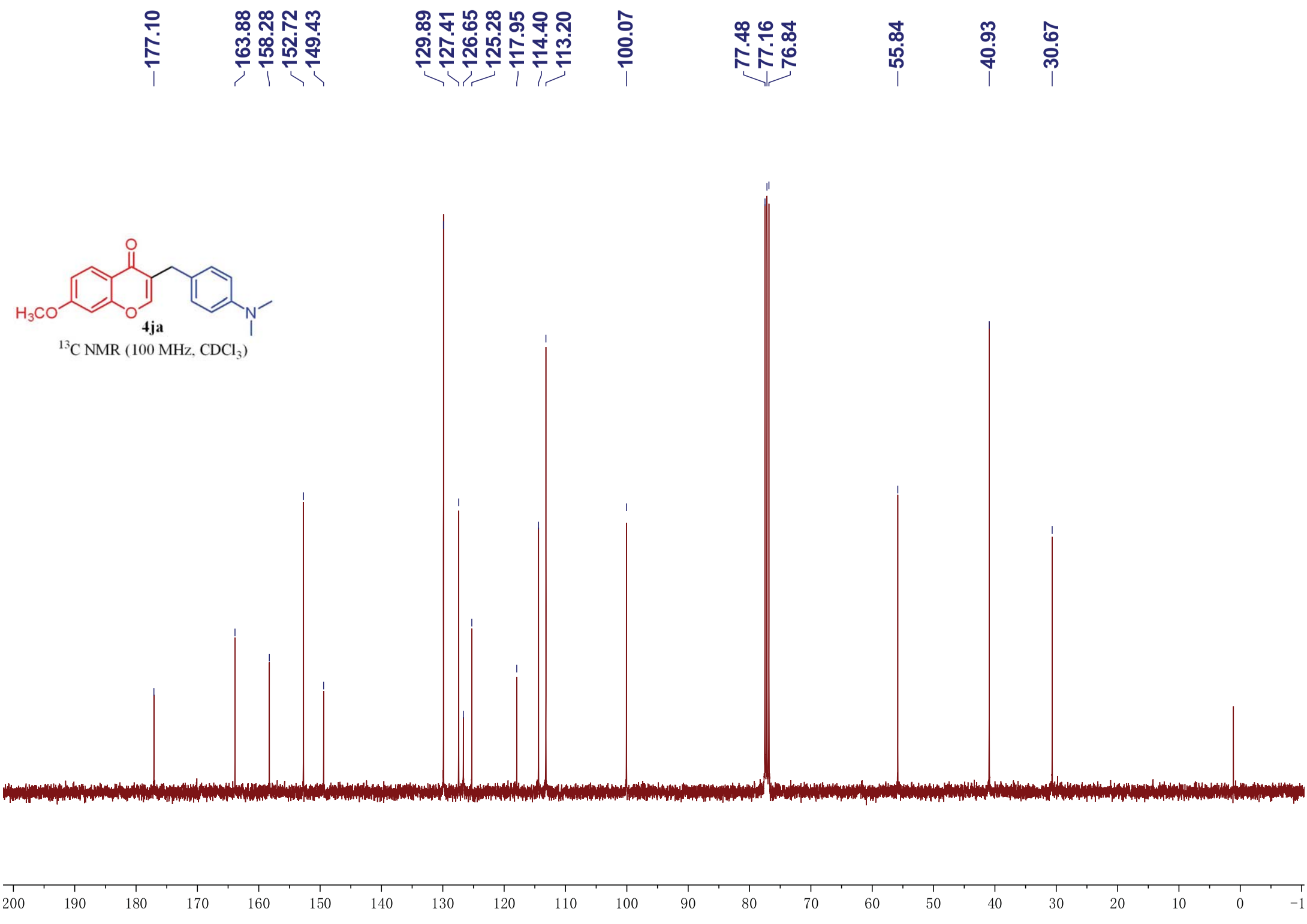
4ia

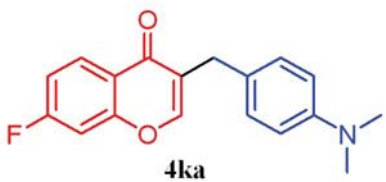
^{13}C NMR (100 MHz, $CDCl_3$)



4ja

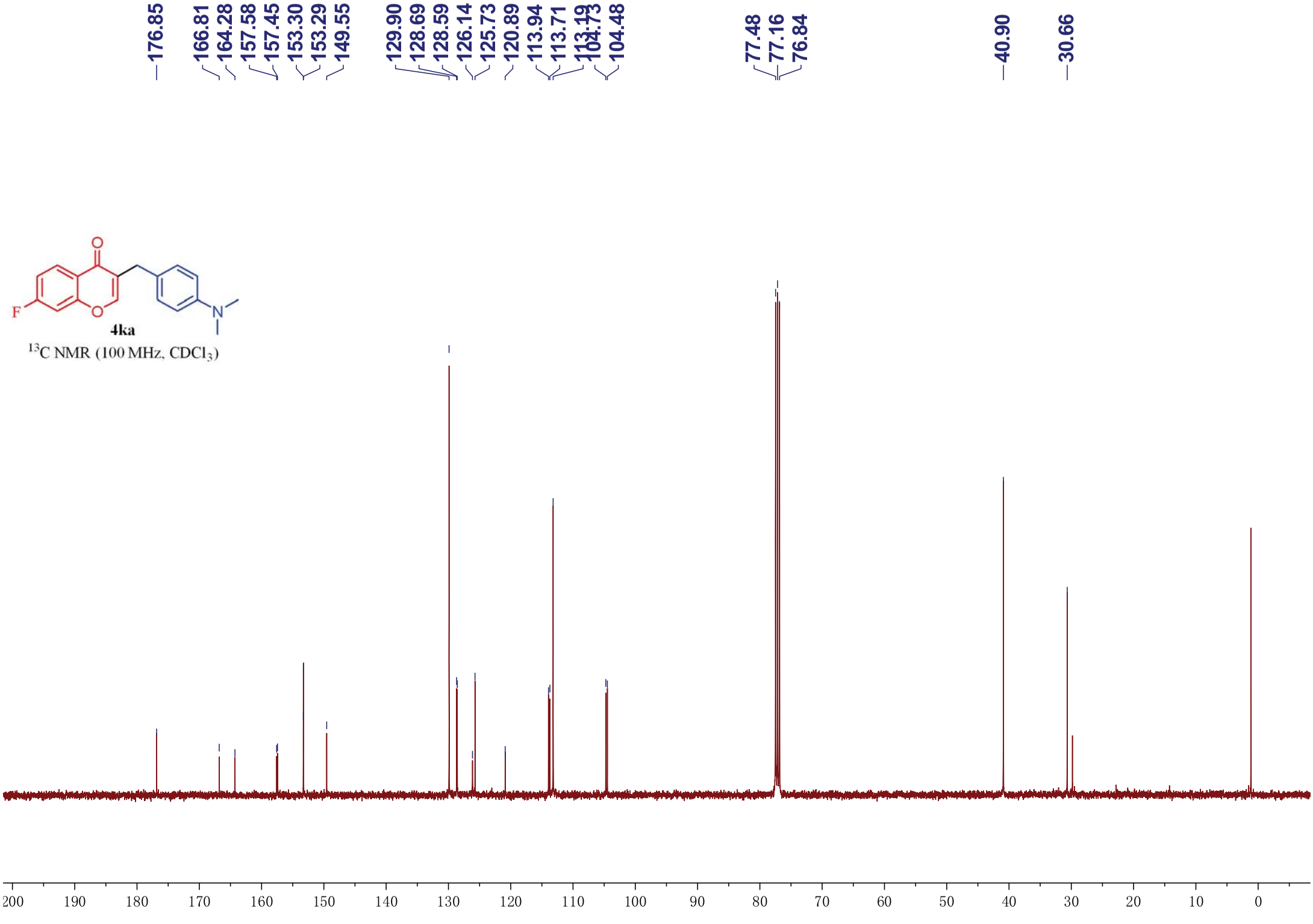
^{1}H NMR (400 MHz, $CDCl_3$)

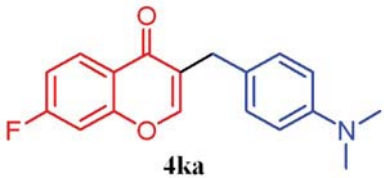

177.10
163.88
158.28
152.72
149.43
129.89
127.41
126.65
125.28
117.95
114.40
113.20
100.07
77.48
77.16
76.84
55.84
40.93
30.67
H3CO
O
O
N
4ja
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1



4ka

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


176.85
166.81
164.28
157.58
157.45
153.30
153.29
149.55
129.90
128.69
128.59
126.14
125.73
120.89
113.94
113.71
113.19
104.73
104.48
77.48
77.16
76.84
40.90
30.66
O
F
O
N
4ka
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

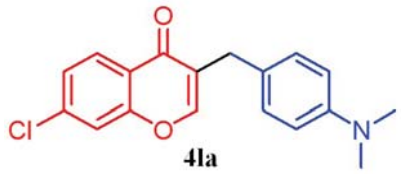


4ka

^{19}F NMR (376 MHz, $CDCl_3$)

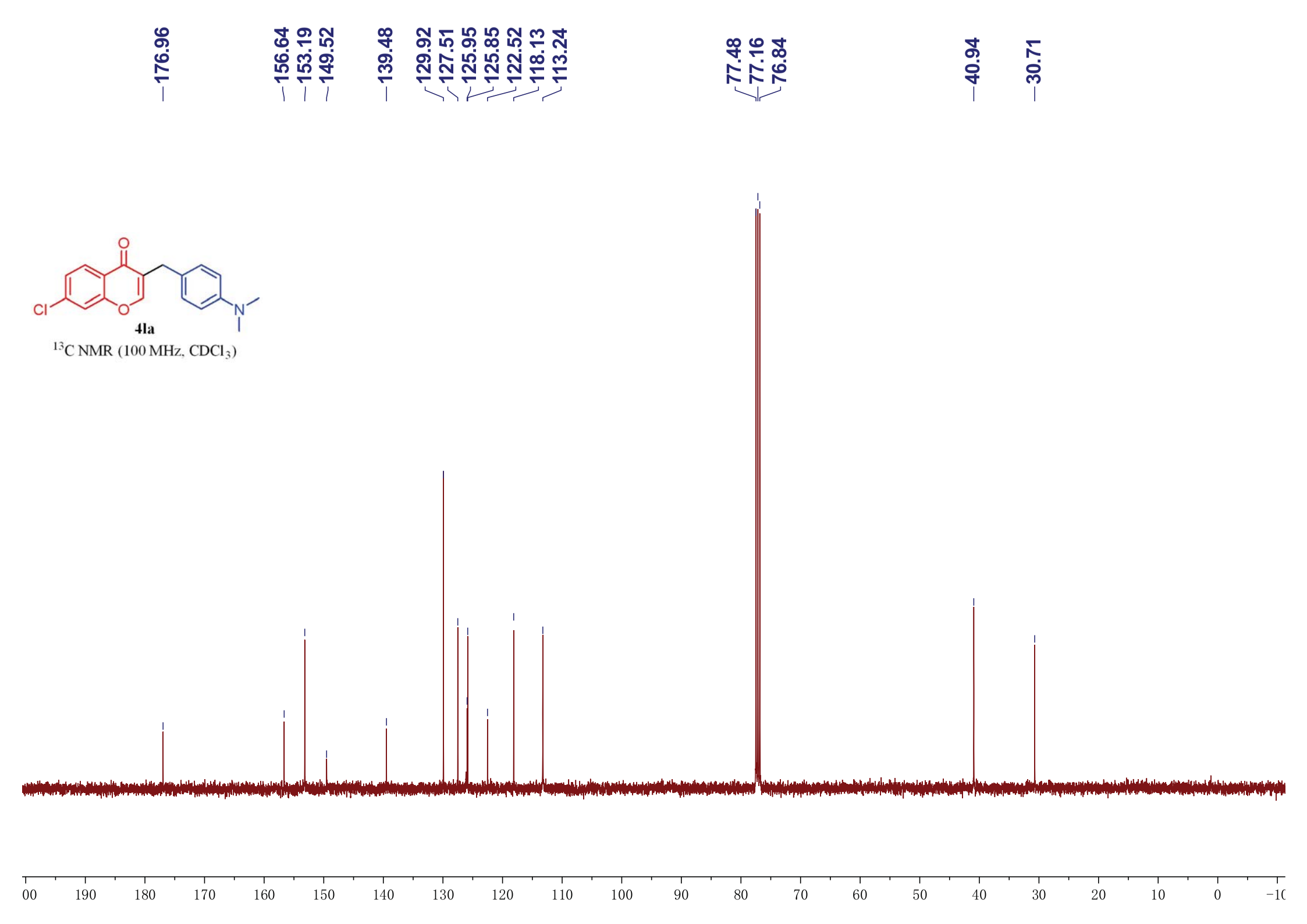
-103.58

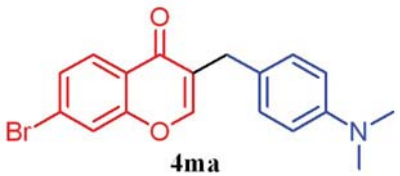
-45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165



4la

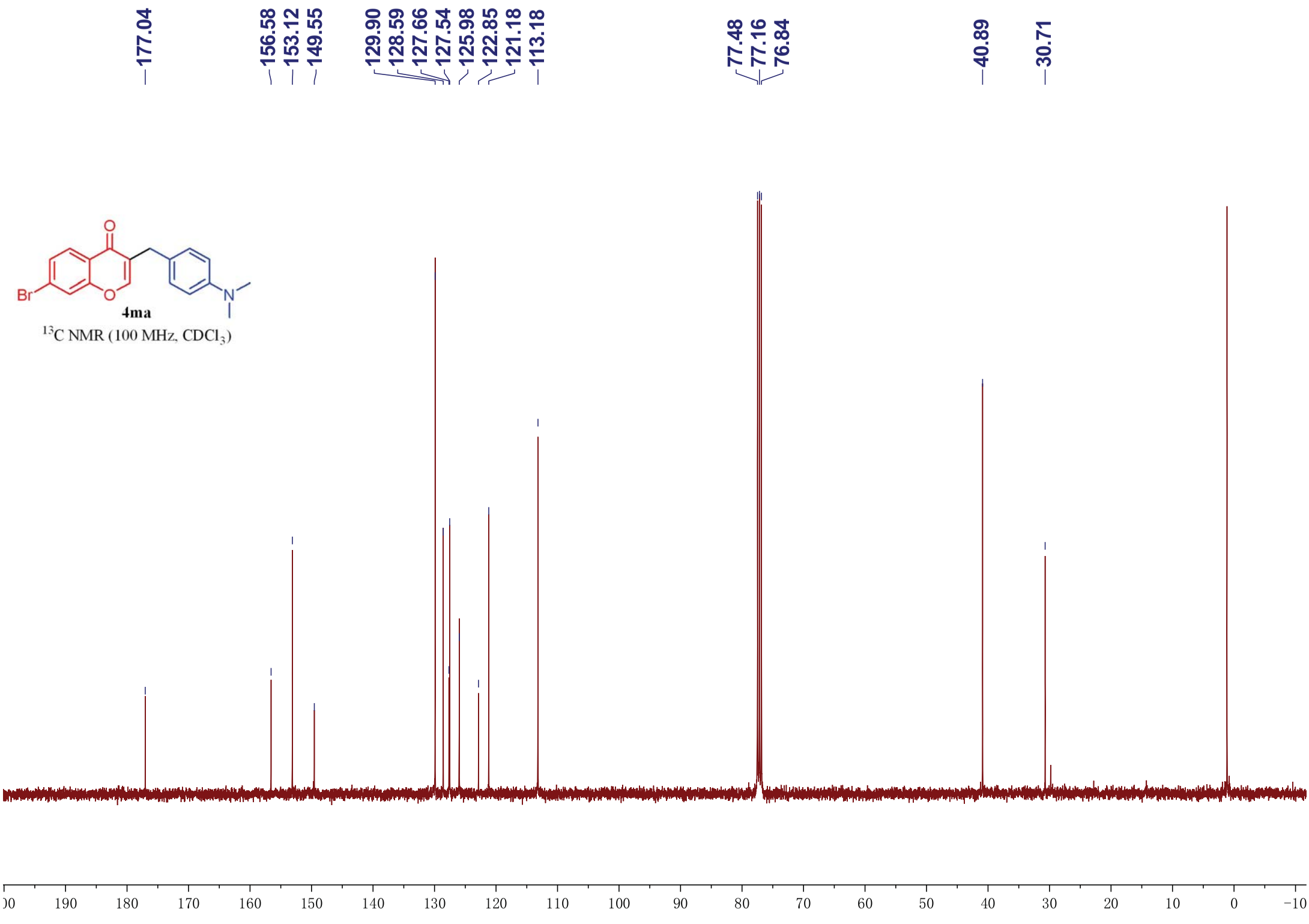
^{1}H NMR (400 MHz, $CDCl_3$)

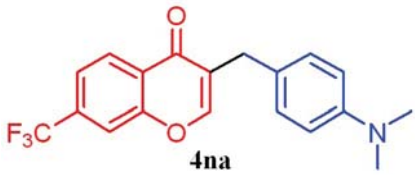

176.96
156.64
153.19
149.52
139.48
129.92
127.51
125.95
125.85
122.52
118.13
113.24
77.48
77.16
76.84
40.94
30.71
O
Cl
O
N
4la
13C NMR (100 MHz, CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10



4ma

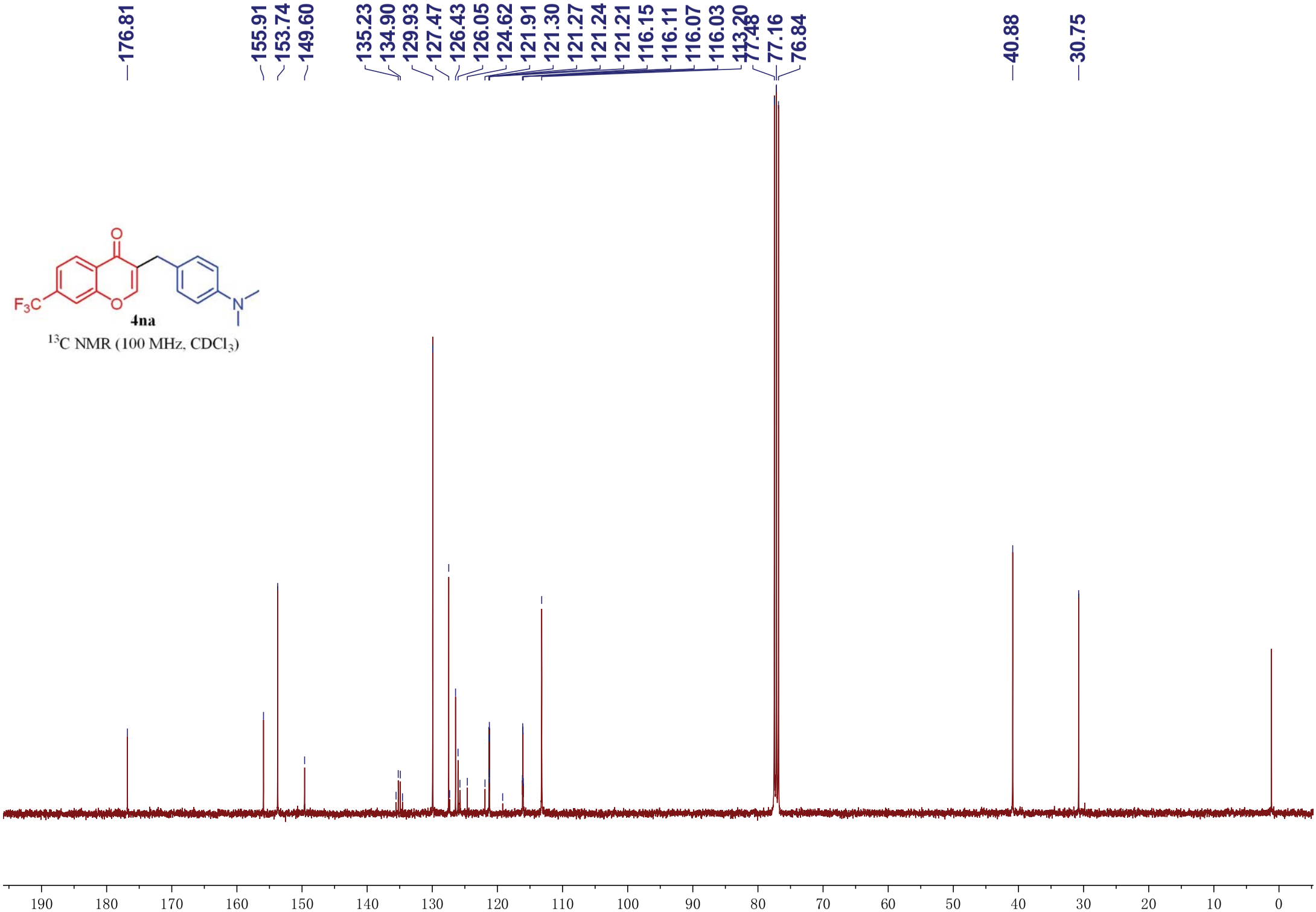
^{1}H NMR (400 MHz, $CDCl_3$)


177.04
156.58
153.12
149.55
129.90
128.59
127.66
127.54
125.98
122.85
121.18
113.18
77.48
77.16
76.84
40.89
30.71
Br
O
O
N
4ma
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10



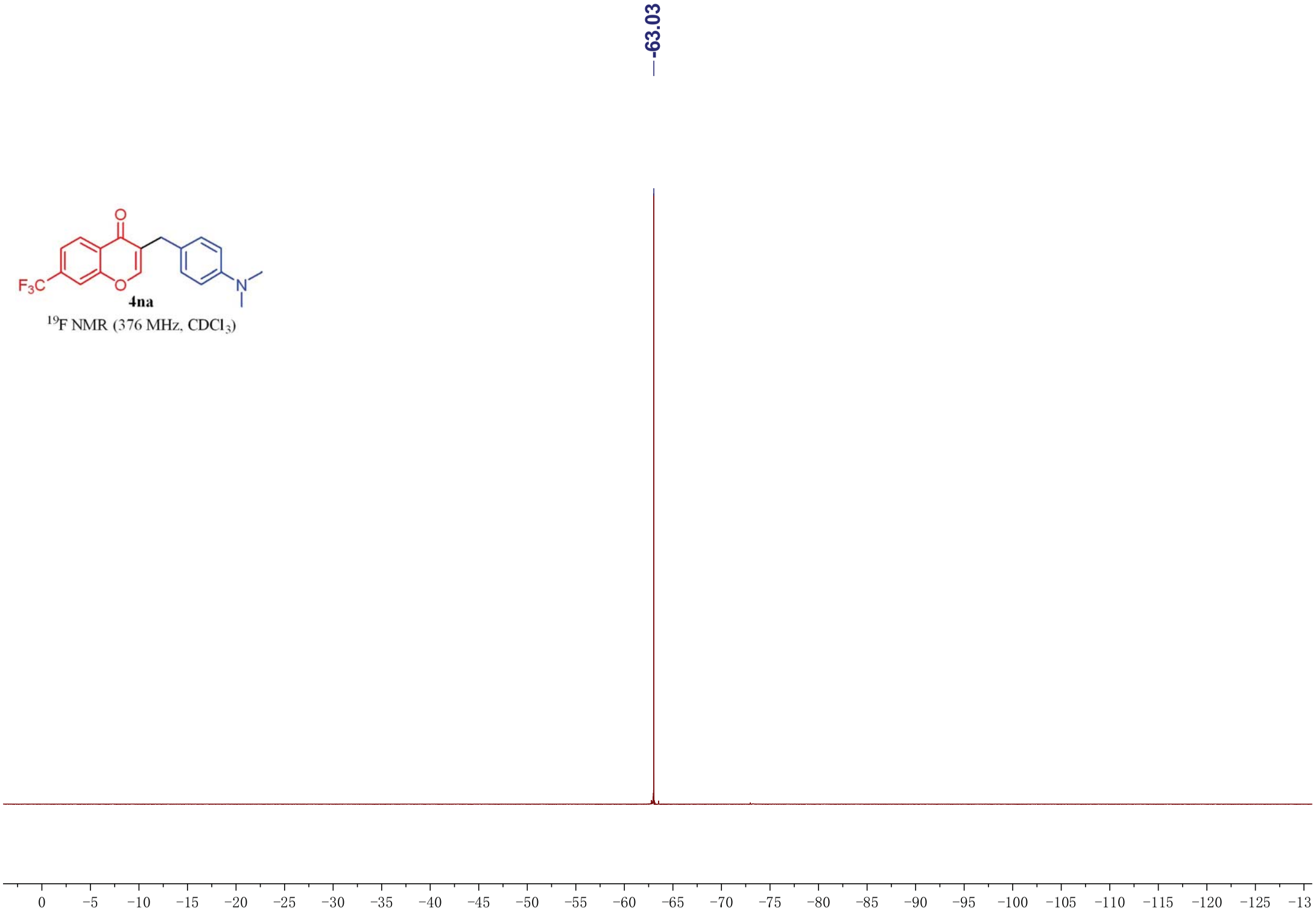
4na

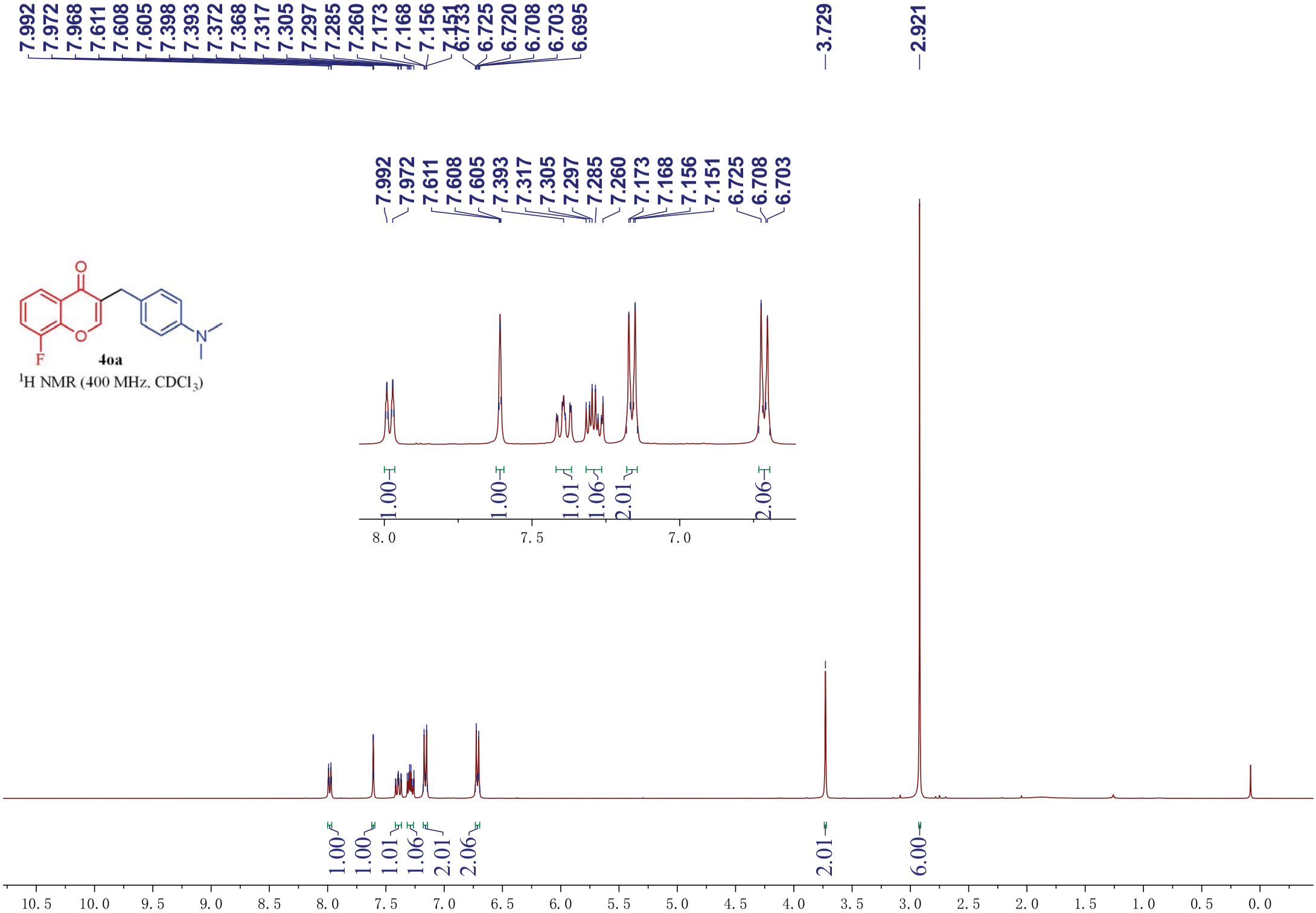
^{1}H NMR (400 MHz, $CDCl_3$)

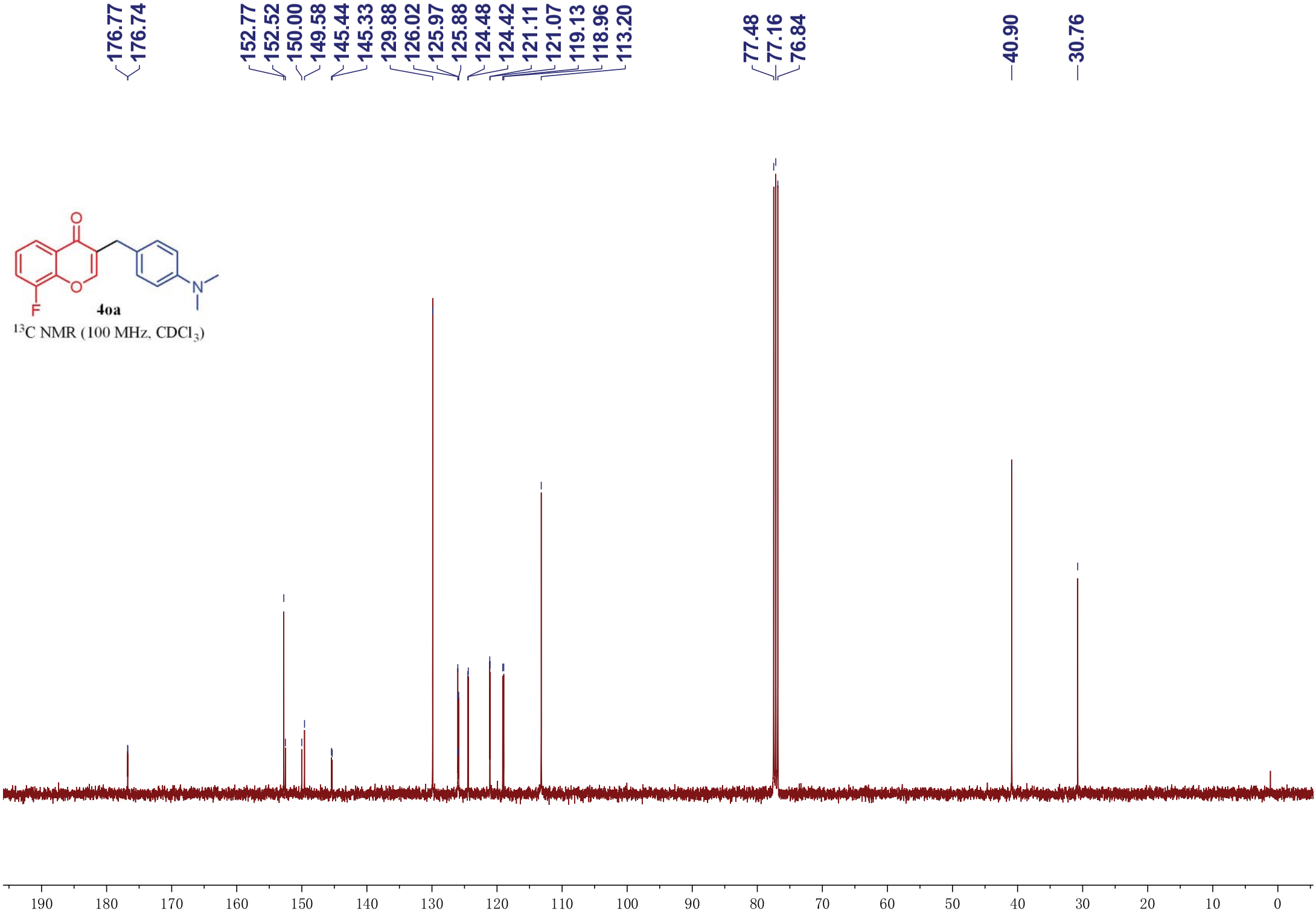

176.81
155.91
153.74
149.60
135.23
134.90
129.93
127.47
126.43
126.05
124.62
121.91
121.30
121.27
121.24
121.21
116.15
116.11
116.07
116.03
113.20
77.48
77.16
76.84
40.88
30.75
F3C
O
O
N
4na
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

4na

^{19}F NMR (376 MHz, $CDCl_3$)

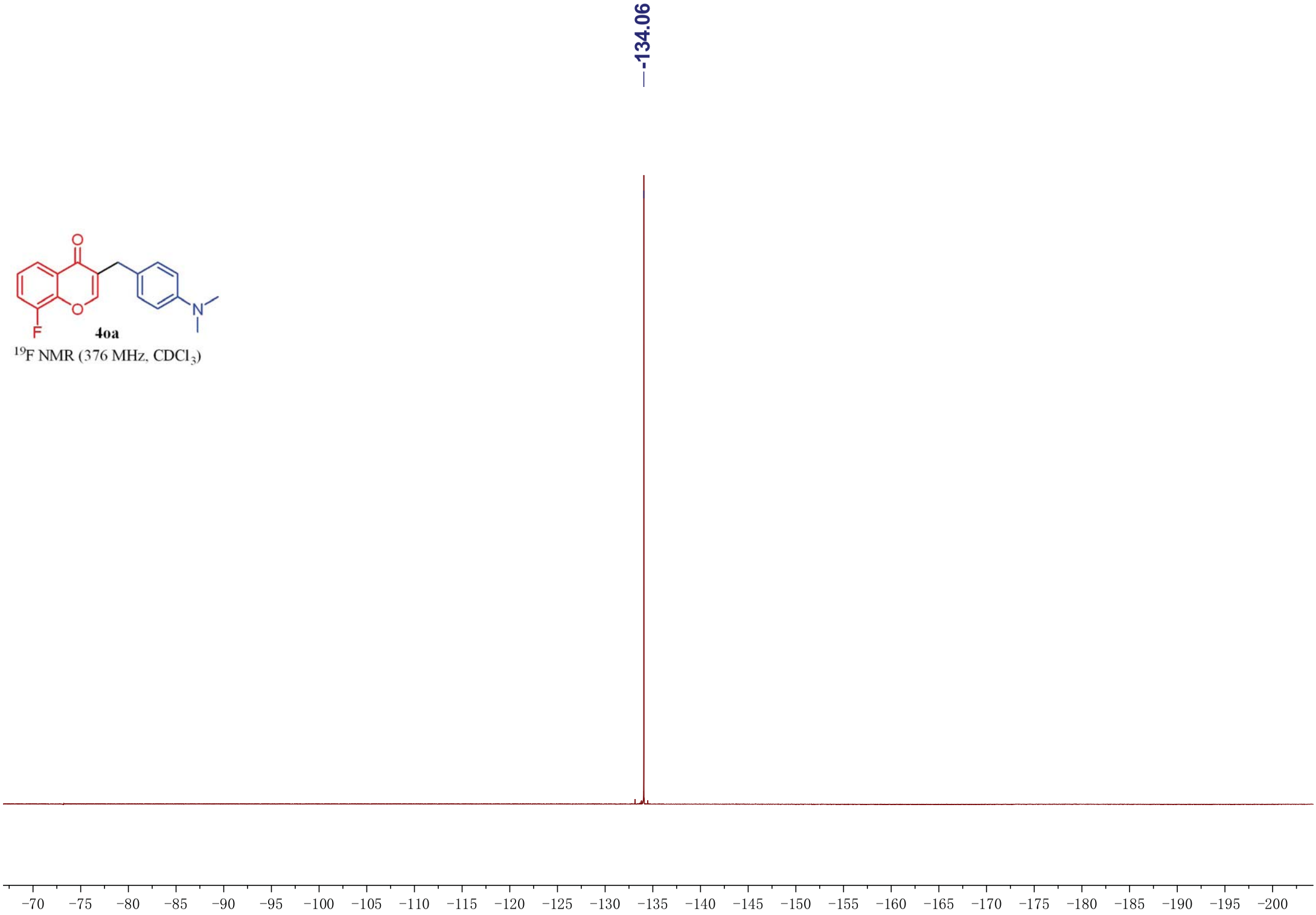


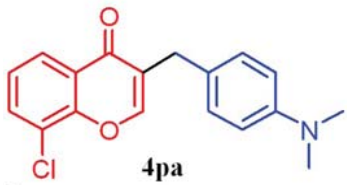

7.992
7.972
7.968
7.611
7.608
7.605
7.398
7.393
7.372
7.368
7.317
7.305
7.297
7.285
7.260
7.173
7.168
7.156
7.151
6.733
6.725
6.720
6.708
6.703
6.695
3.729
2.921
F
4oa
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.01
1.06
2.01
2.06
2.01
6.00
8.0
7.5
7.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


176.77
176.74
152.77
152.52
150.00
149.58
145.44
145.33
129.88
126.02
125.97
125.88
124.48
124.42
121.11
121.07
119.13
118.96
113.20
77.48
77.16
76.84
40.90
30.76
O
O
F
N
4oa
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

4oa

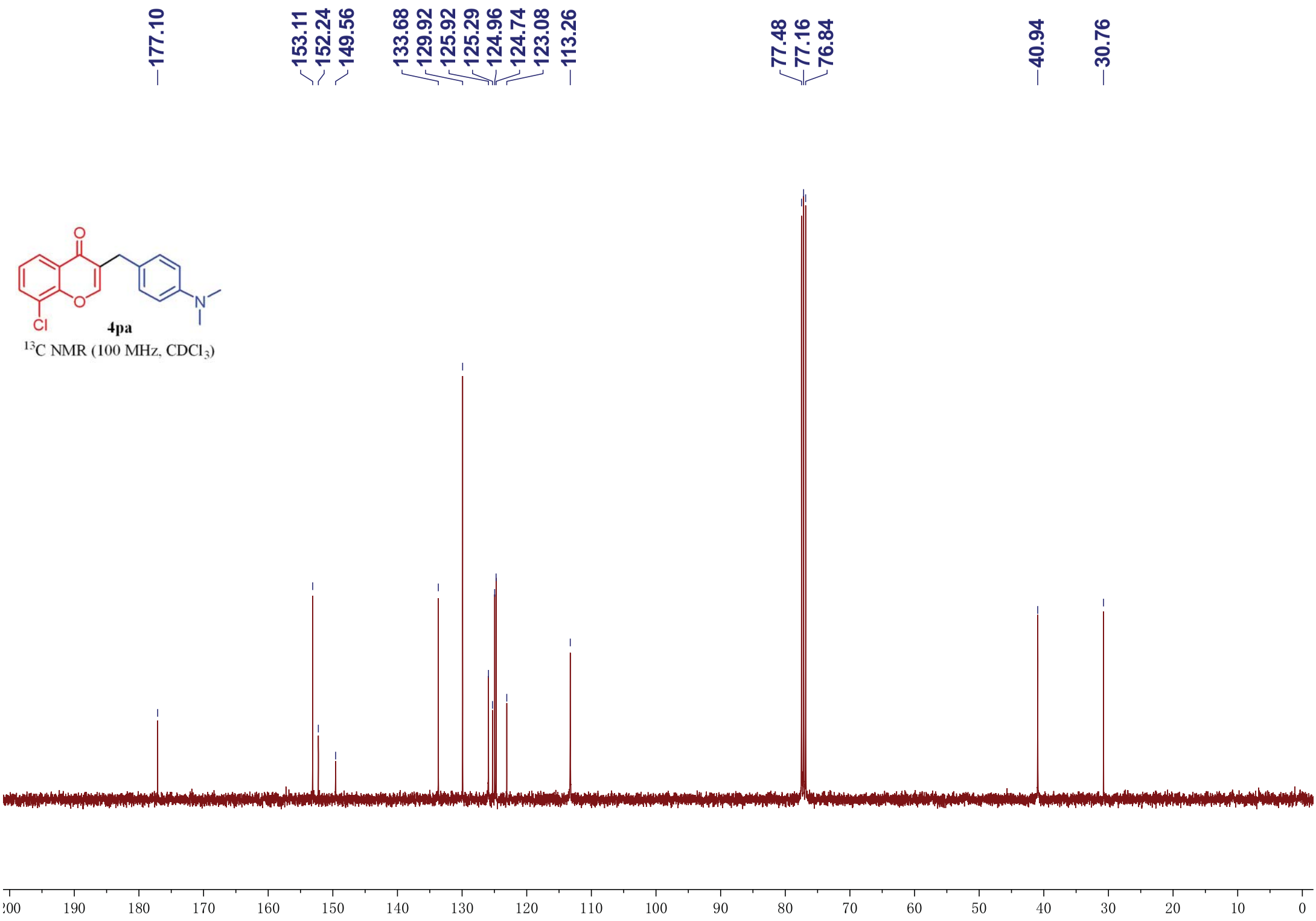
^{19}F NMR (376 MHz, $CDCl_3$)

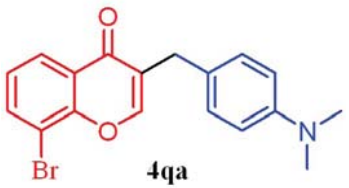




4pa

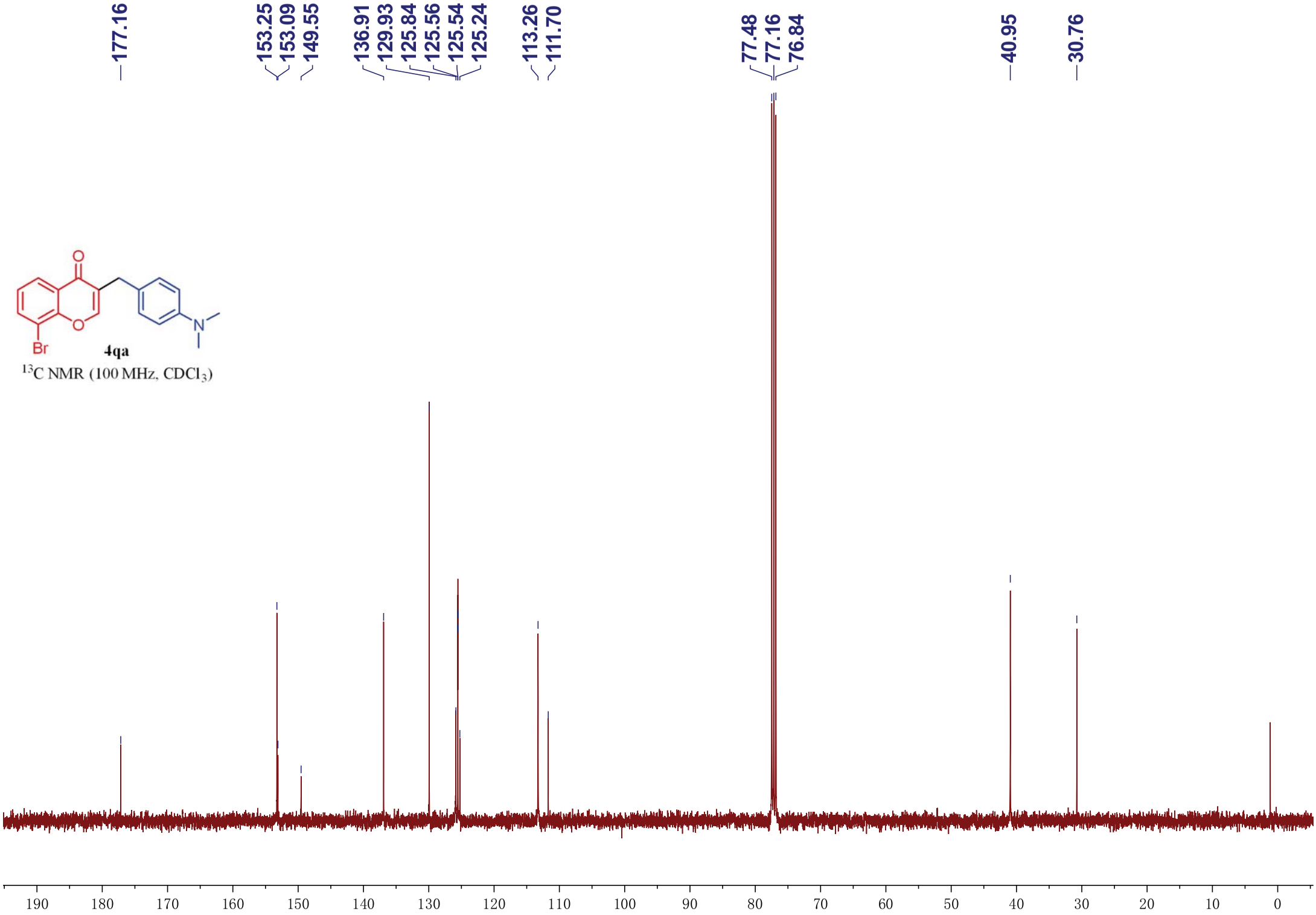
^{1}H NMR (400 MHz, $CDCl_3$)

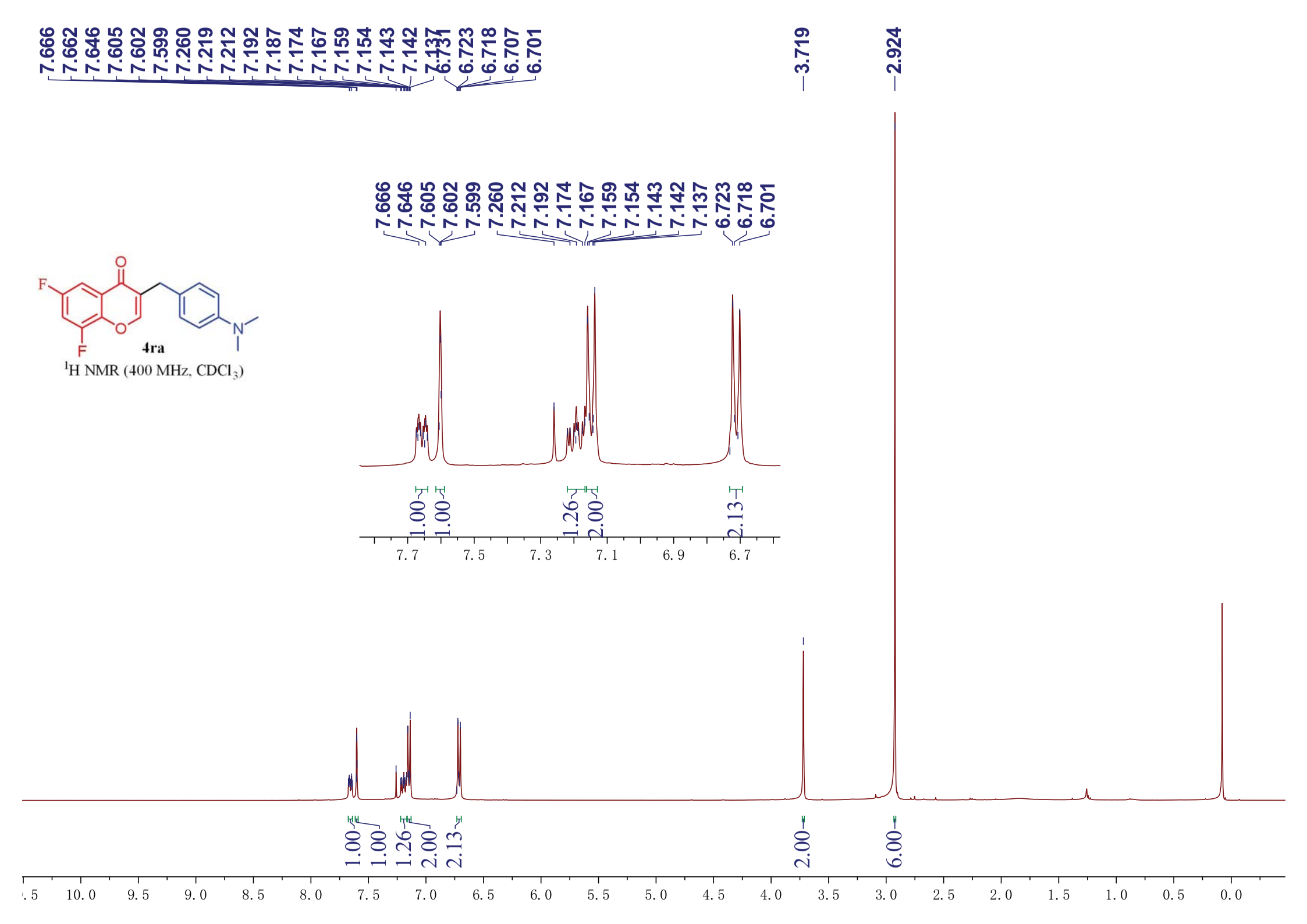

177.10
153.11
152.24
149.56
133.68
129.92
125.92
125.29
124.96
124.74
123.08
113.26
77.48
77.16
76.84
40.94
30.76
O
O
Cl
N
4pa
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

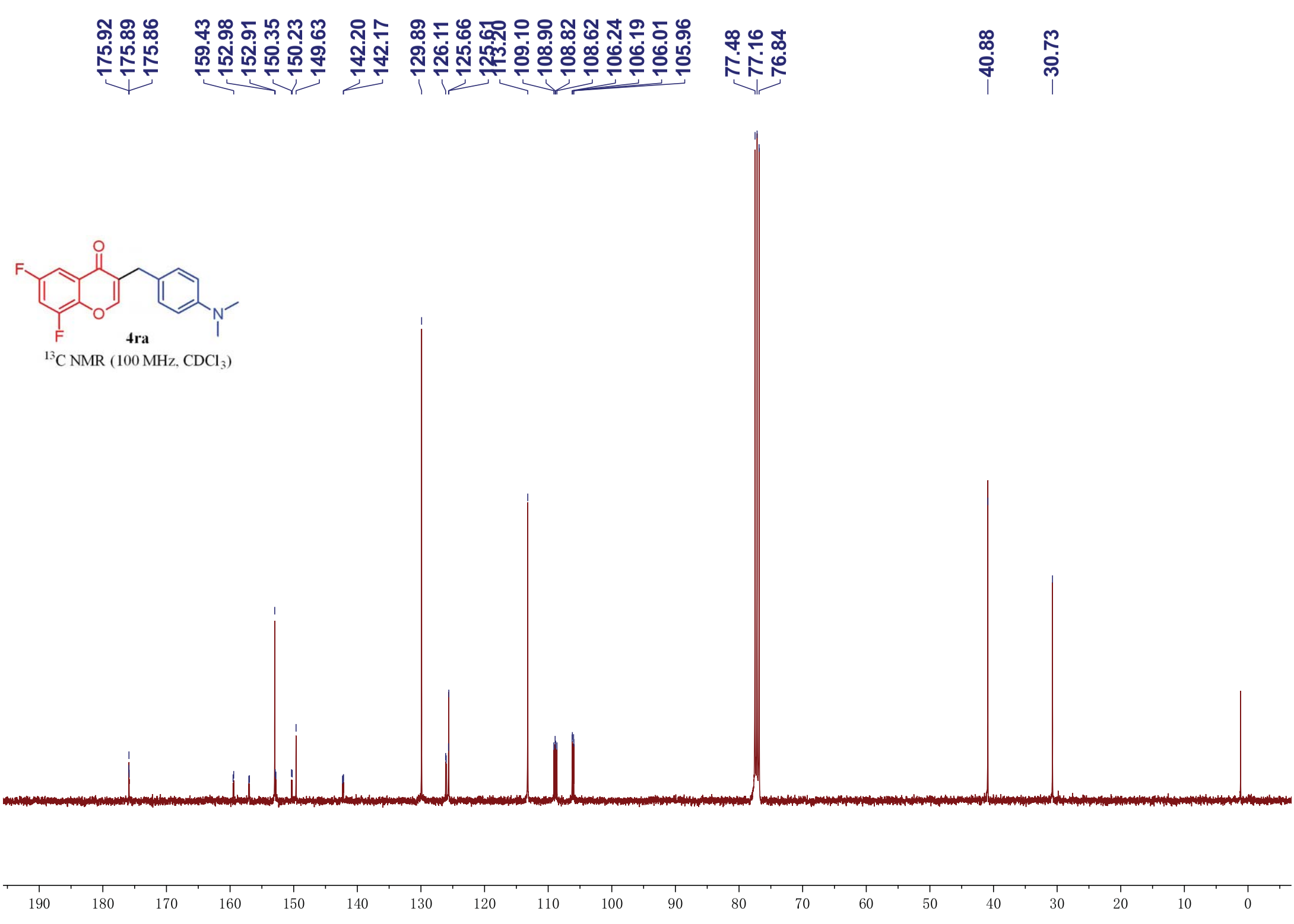


4qa

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

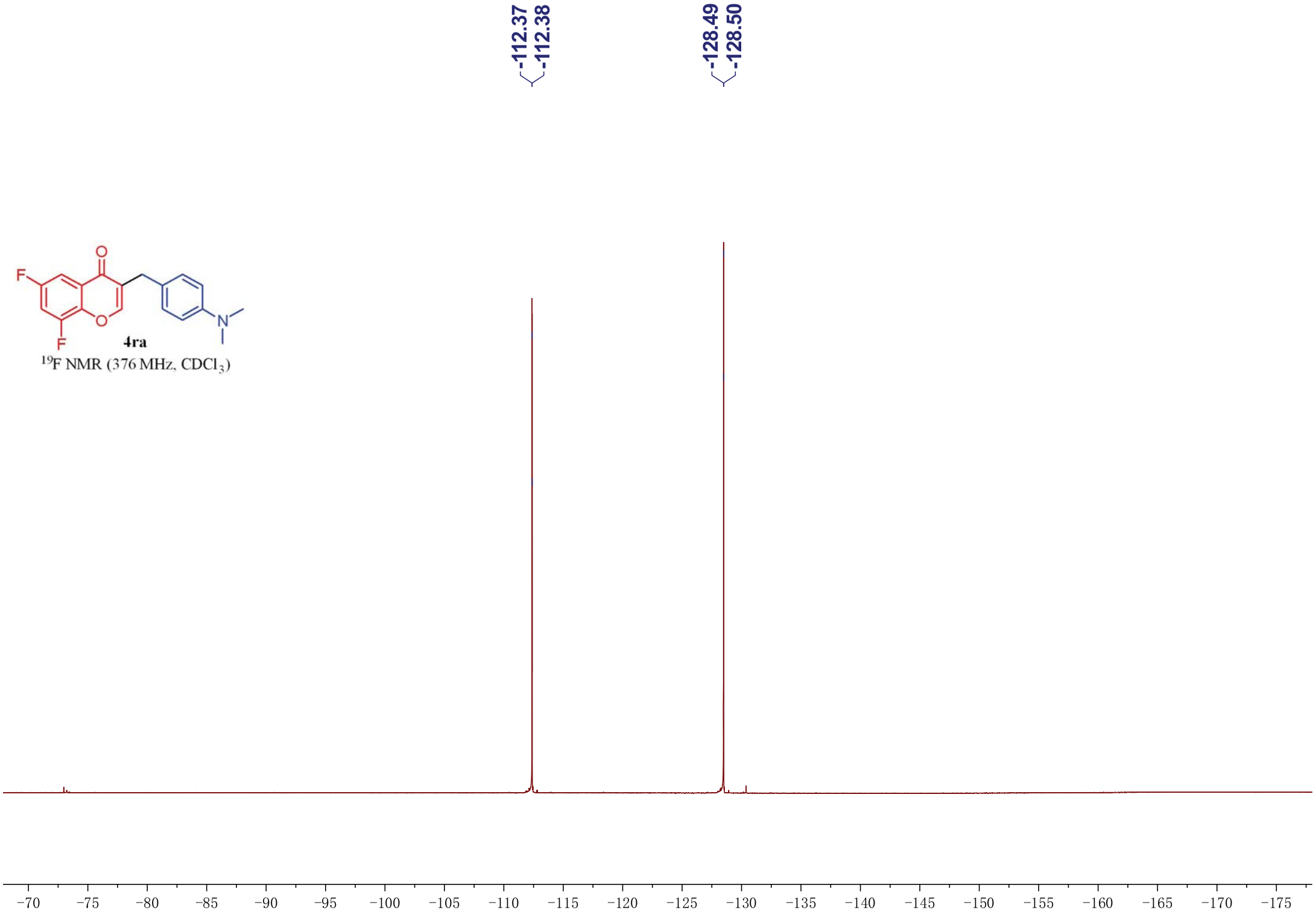

177.16
153.25
153.09
149.55
136.91
129.93
125.84
125.56
125.54
125.24
113.26
111.70
77.48
77.16
76.84
40.95
30.76
O
O
Br
N
4qa
^{13}C NMR (100 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

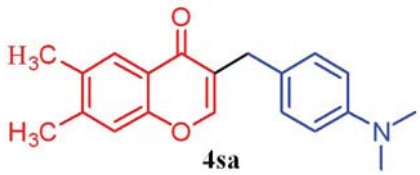

7.666
7.662
7.646
7.605
7.602
7.599
7.260
7.219
7.212
7.192
7.187
7.174
7.167
7.159
7.154
7.143
7.142
7.137
7.131
6.723
6.718
6.707
6.701
3.719
2.924
F
O
N
F
4ra
^{1}H NMR (400 MHz, $CDCl_3$)
1.00
1.00
1.26
2.00
2.13
2.00
6.00
7.7
7.5
7.3
7.1
6.9
6.7


175.92
175.89
175.86
159.43
152.98
152.91
150.35
150.23
149.63
142.20
142.17
129.89
126.11
125.66
125.61
113.20
109.10
108.90
108.82
108.62
106.24
106.19
106.01
105.96
77.48
77.16
76.84
40.88
30.73
F
O
F
O
N
4ra
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

4ra

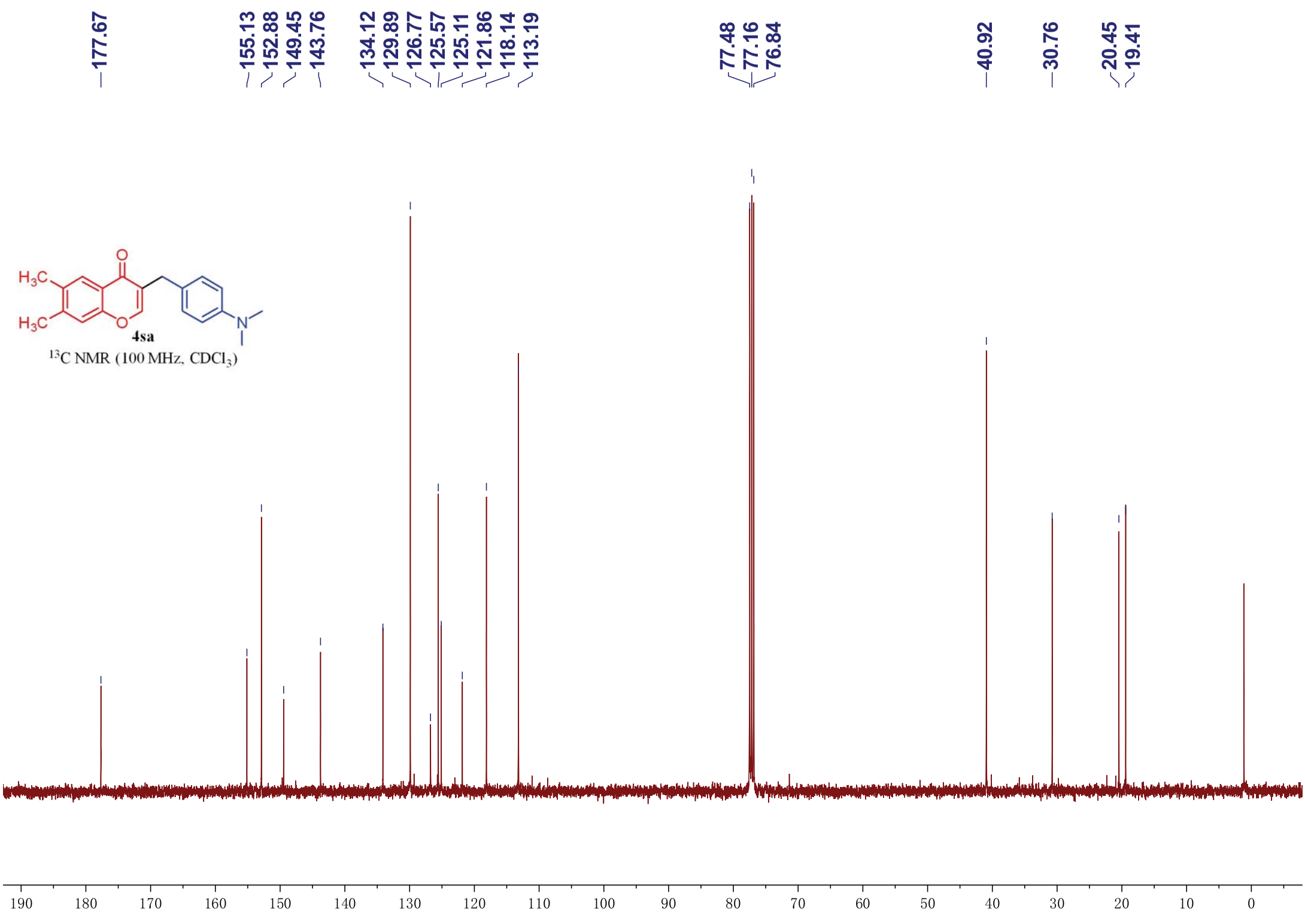
^{19}F NMR (376 MHz, $CDCl_3$)





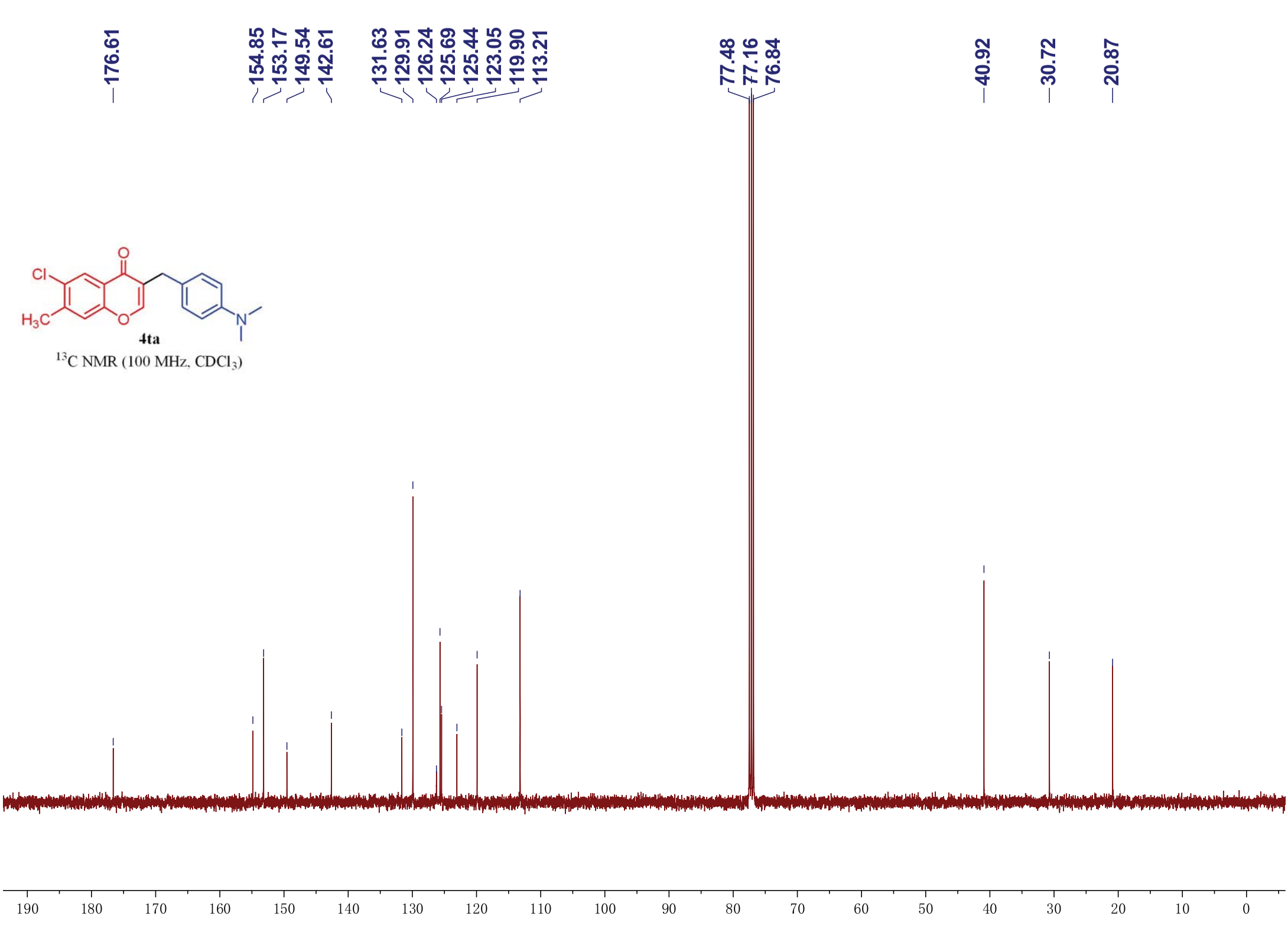
4sa

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


177.67
155.13
152.88
149.45
143.76
134.12
129.89
126.77
125.57
125.11
121.86
118.14
113.19
77.48
77.16
76.84
40.92
30.76
20.45
19.41
H3C
H3C
O
O
N
4sa
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

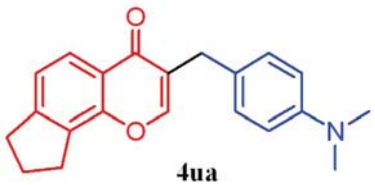
4ta

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



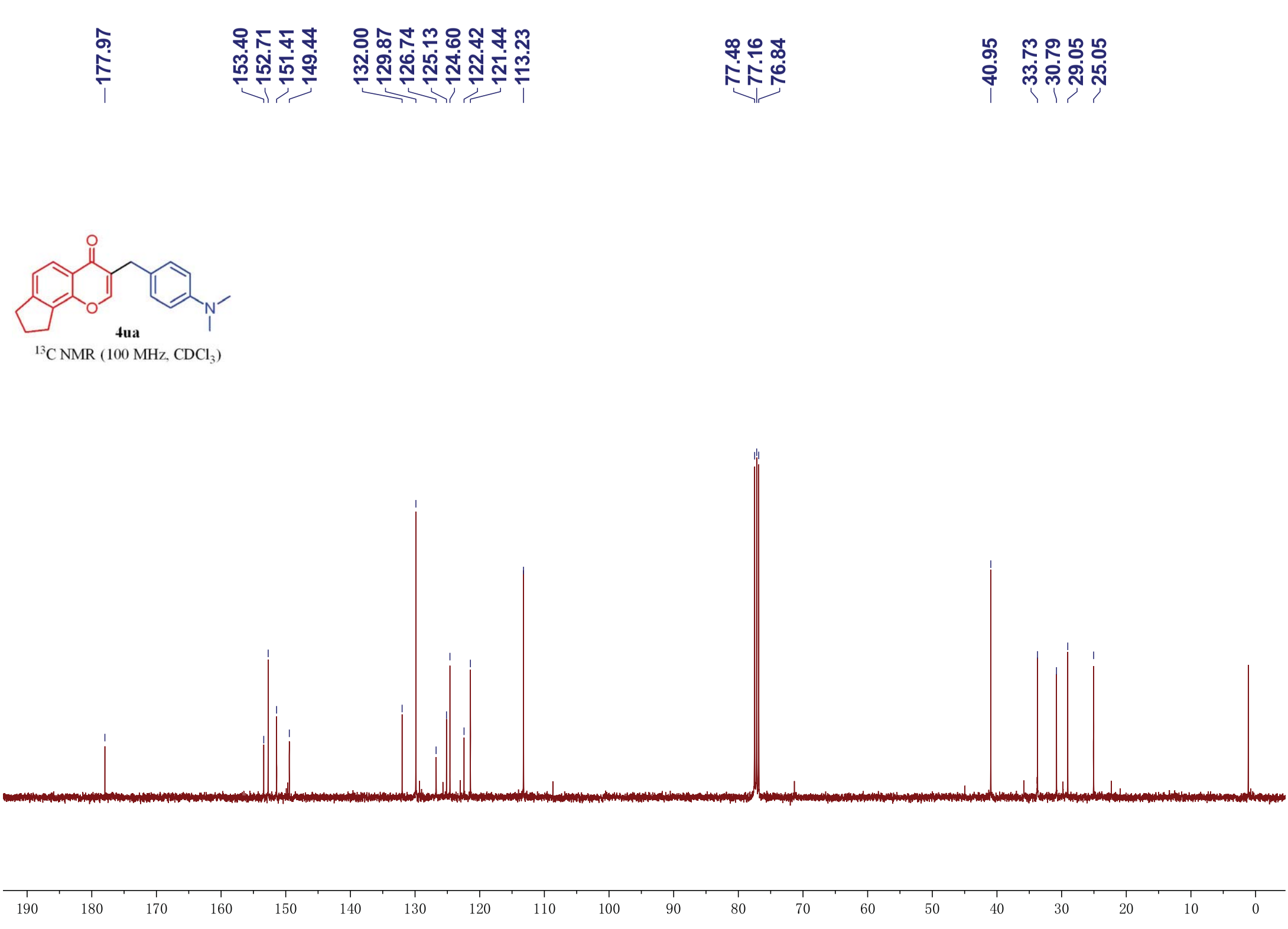
4ta

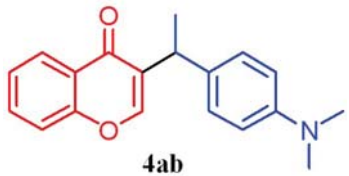
^{13}C NMR (100 MHz, $CDCl_3$)



4ua

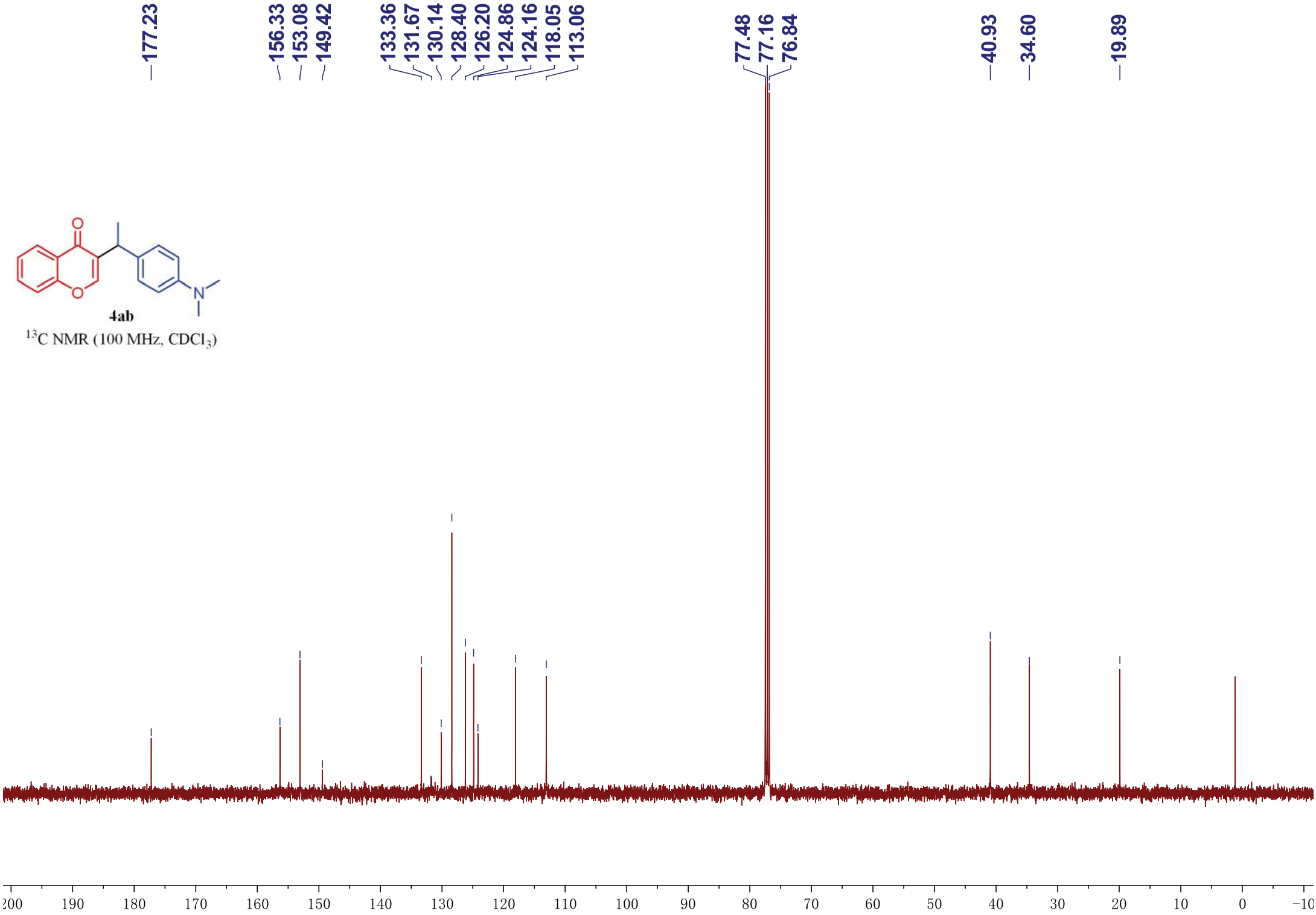
^{1}H NMR (400 MHz, $CDCl_3$)

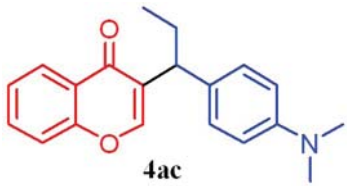

177.97
153.40
152.71
151.41
149.44
132.00
129.87
126.74
125.13
124.60
122.42
121.44
113.23
77.48
77.16
76.84
40.95
33.73
30.79
29.05
25.05
O
O
N
4ua
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



4ab

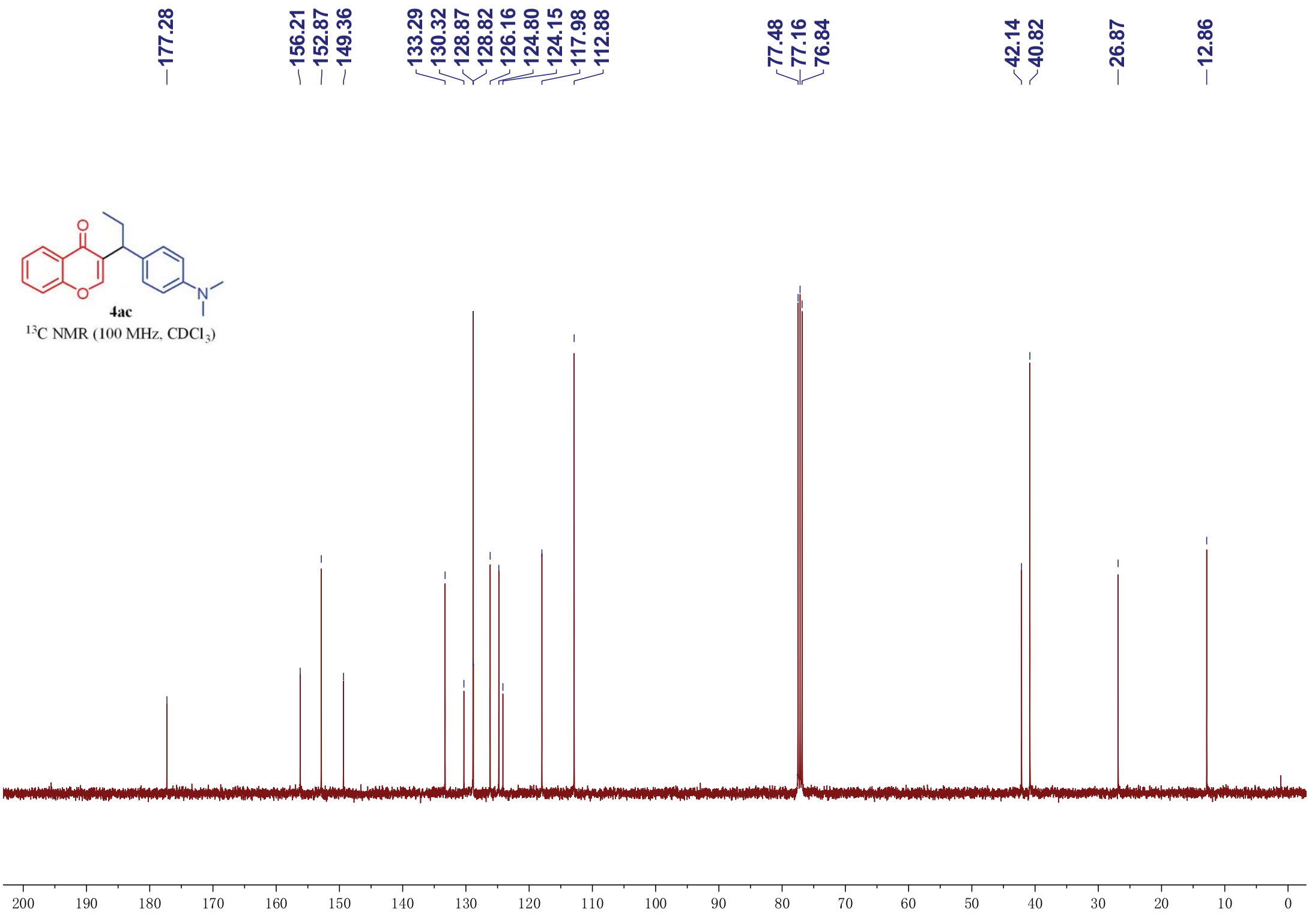
^{1}H NMR (400 MHz, $CDCl_3$)

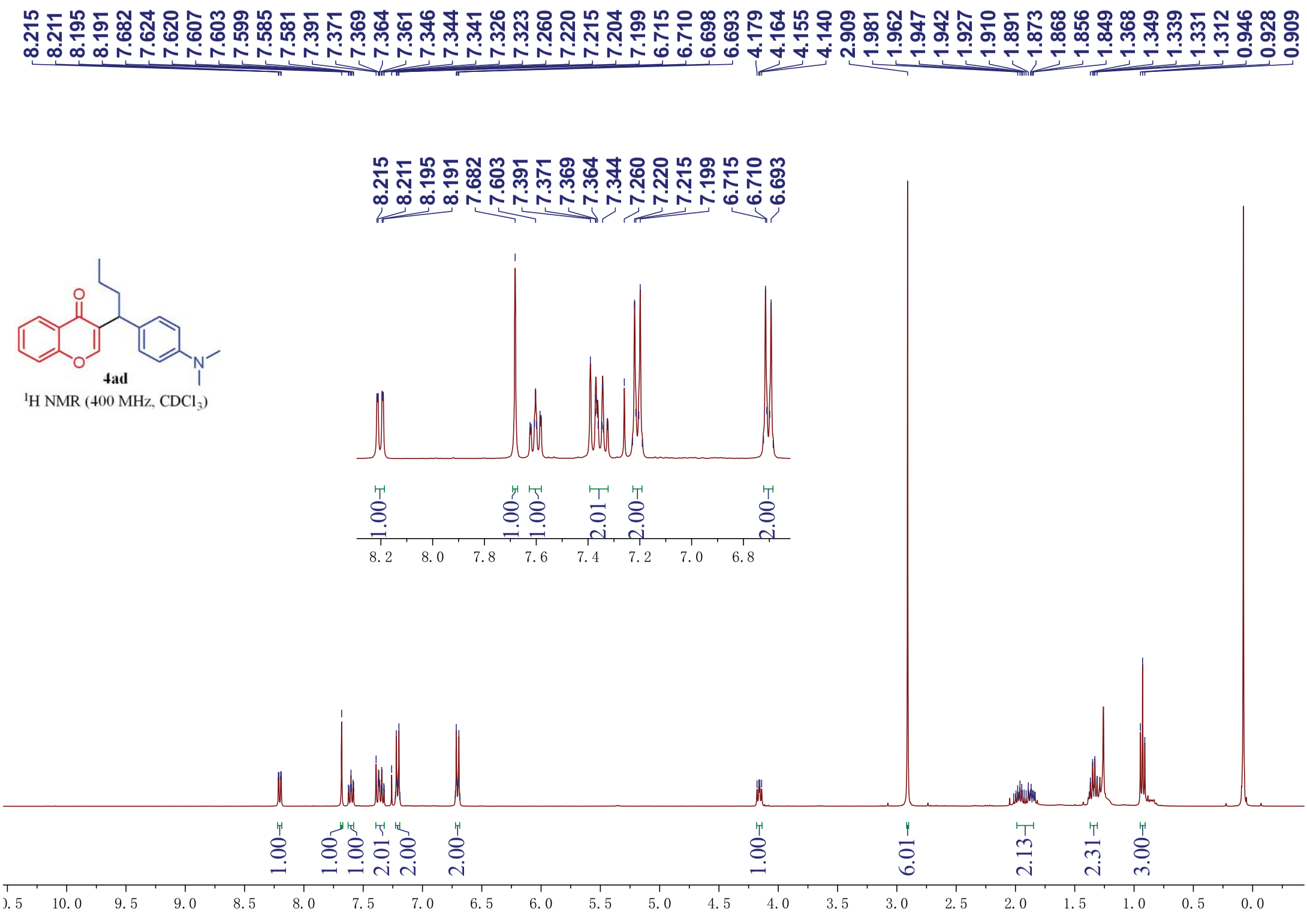

177.23
156.33
153.08
149.42
133.36
131.67
130.14
128.40
126.20
124.86
124.16
118.05
113.06
77.48
77.16
76.84
40.93
34.60
19.89
O
O
N
4ab
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

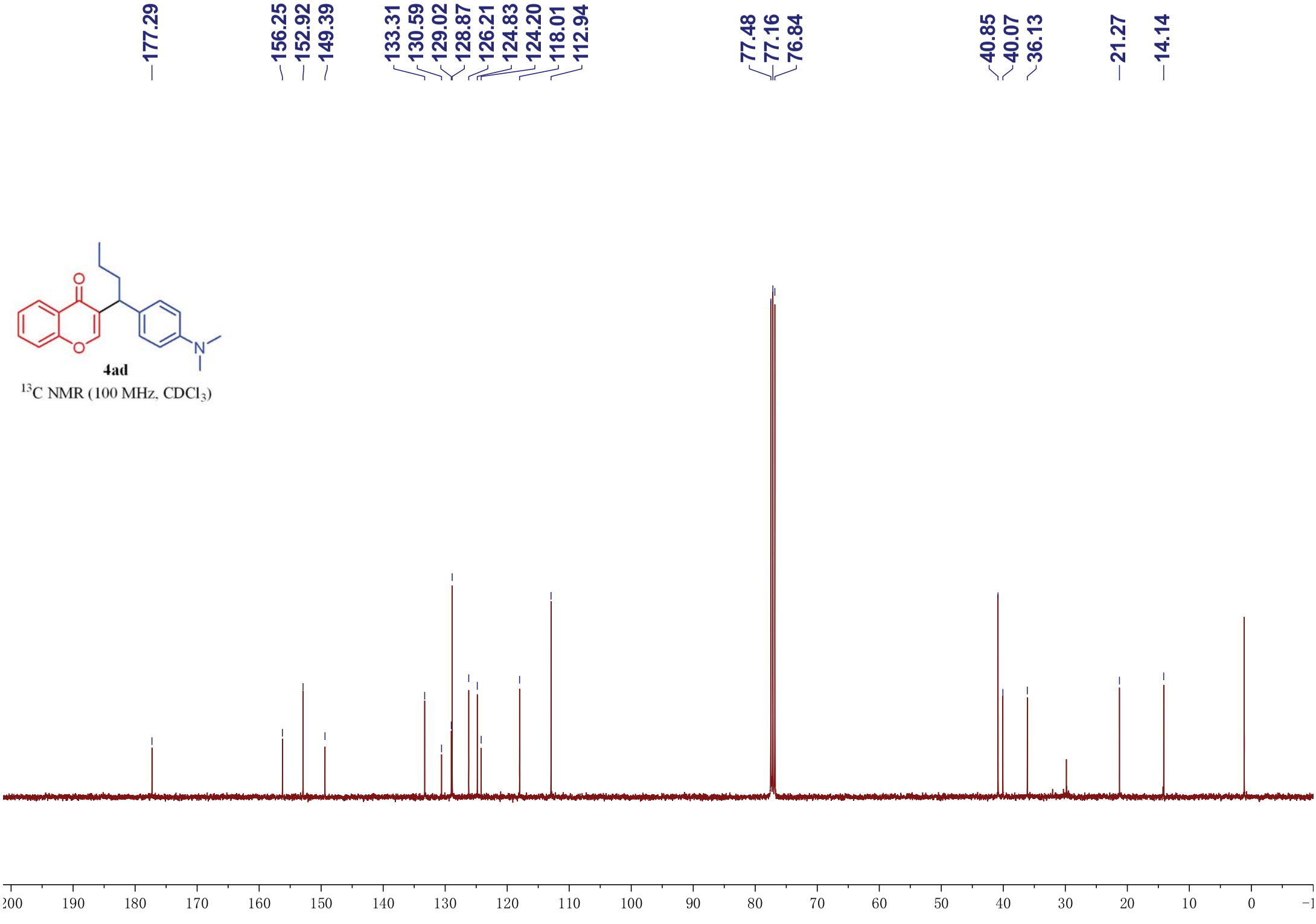


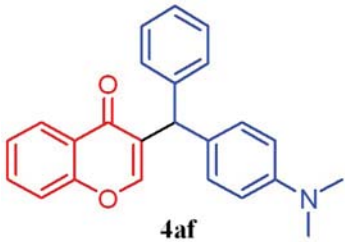
4ac

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


177.28
156.21
152.87
149.36
133.29
130.32
128.87
128.82
126.16
124.80
124.15
117.98
112.88
77.48
77.16
76.84
42.14
40.82
26.87
12.86
O
O
N
4ac
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

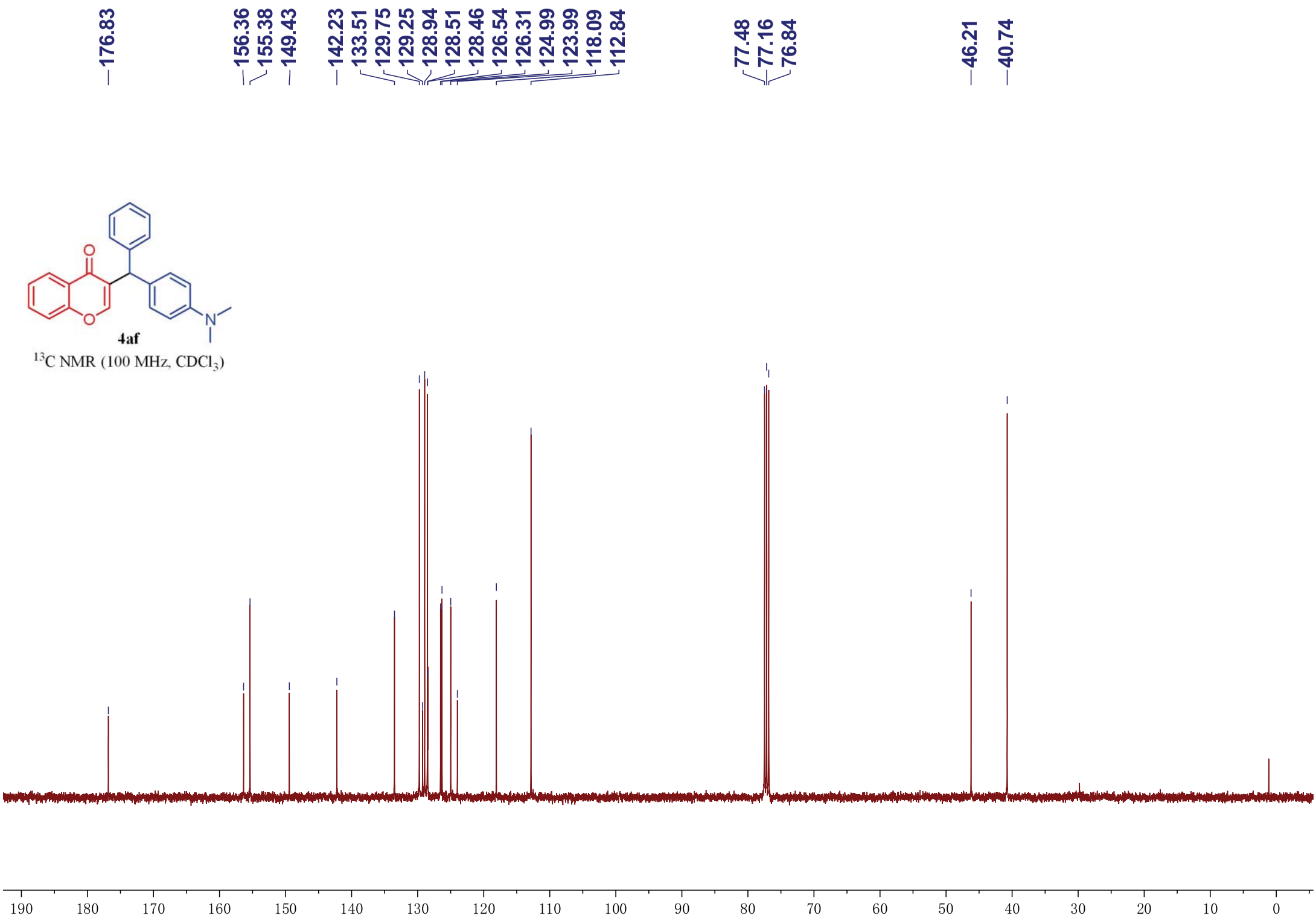

8.215
8.211
8.195
8.191
7.682
7.624
7.620
7.607
7.603
7.599
7.585
7.581
7.391
7.371
7.369
7.364
7.361
7.346
7.344
7.341
7.326
7.323
7.260
7.220
7.215
7.204
7.199
6.715
6.710
6.698
6.693
4.179
4.164
4.155
4.140
2.909
1.981
1.962
1.947
1.942
1.927
1.910
1.891
1.873
1.868
1.856
1.849
1.368
1.349
1.339
1.331
1.312
0.946
0.928
0.909
O
O
N
4ad
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.00
2.01
2.00
2.00
1.00
6.01
2.13
2.31
3.00
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

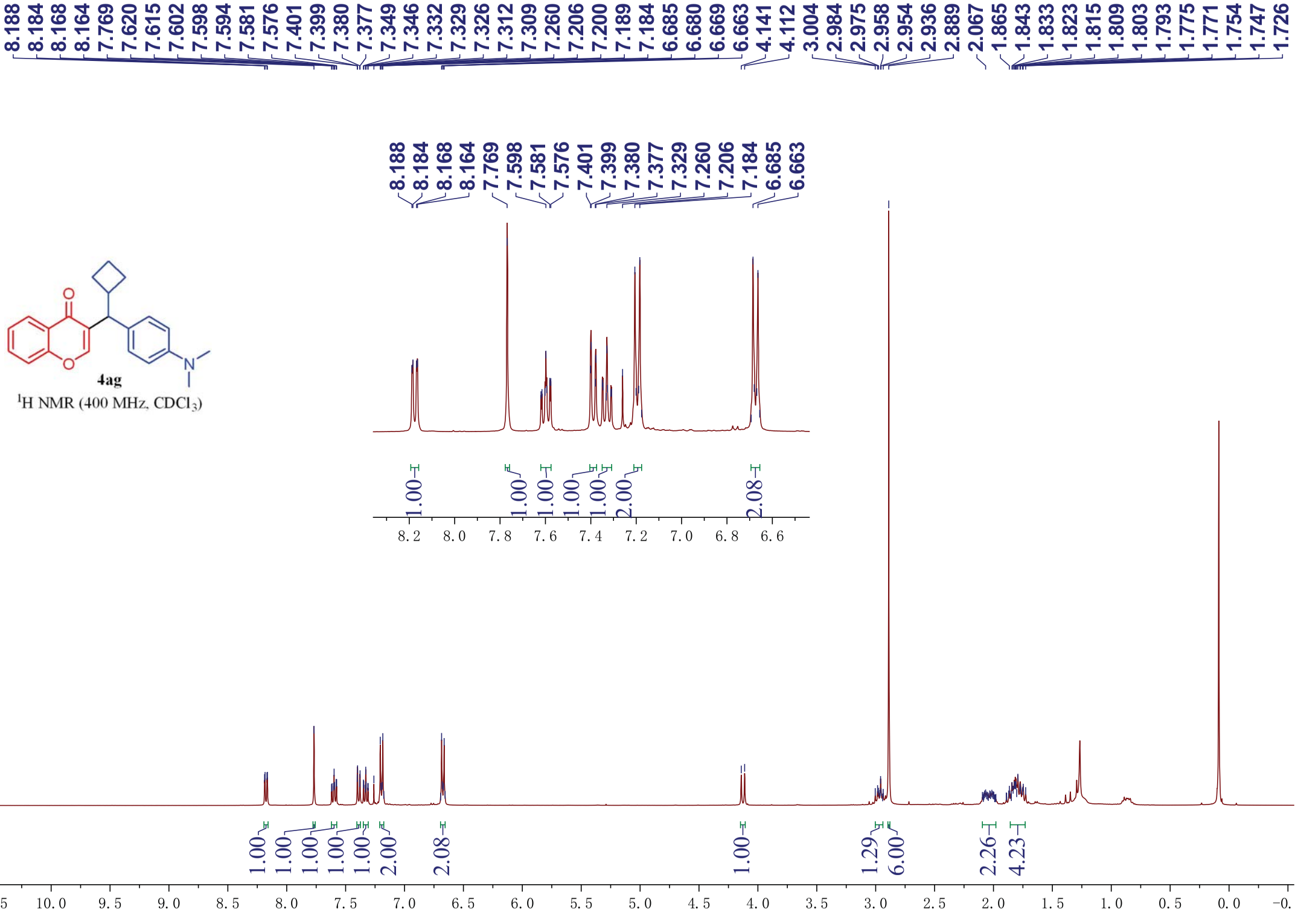

177.29
156.25
152.92
149.39
133.31
130.59
129.02
128.87
126.21
124.83
124.20
118.01
112.94
77.48
77.16
76.84
40.85
40.07
36.13
21.27
14.14
O
O
N
4ad
^{13}C NMR (100 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

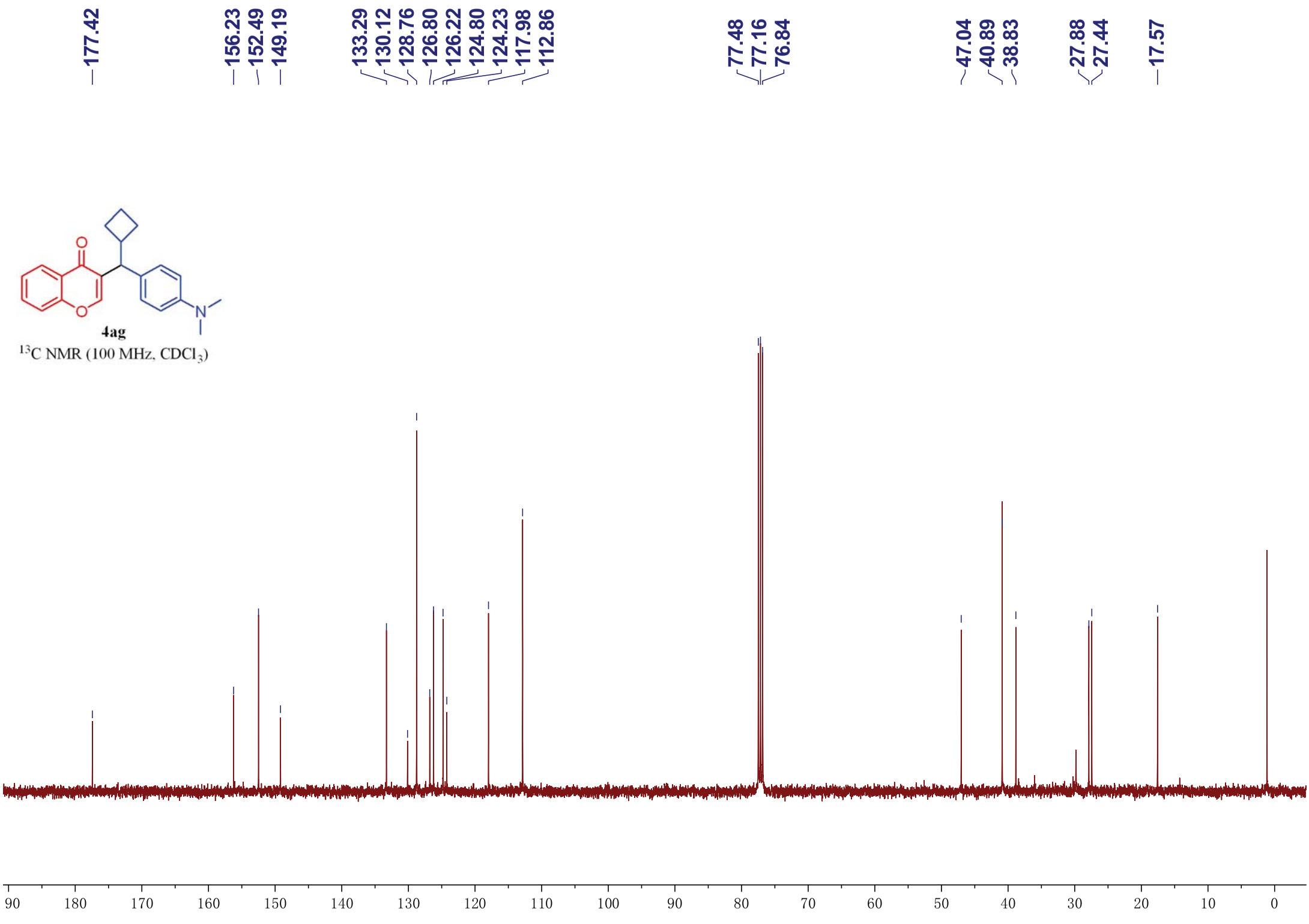


4af

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


176.83
156.36
155.38
149.43
142.23
133.51
129.75
129.25
128.94
128.51
128.46
126.54
126.31
124.99
123.99
118.09
112.84
77.48
77.16
76.84
46.21
40.74
O
O
N
4af
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.188 8.184 8.168 8.164 7.769 7.620 7.615 7.602 7.598 7.594 7.581 7.576 7.401 7.399 7.380 7.377 7.349 7.346 7.332 7.329 7.326 7.312 7.309 7.260 7.206 7.200 7.189 7.184 6.685 6.680 6.669 6.663 4.141 4.112 3.004 2.984 2.975 2.958 2.954 2.936 2.889 2.067 1.865 1.843 1.833 1.823 1.815 1.809 1.803 1.793 1.775 1.771 1.754 1.747 1.726
4ag
^{1}H NMR (400 MHz, $CDCl_3$)
1.00 1.00 1.00 1.00 1.00 2.00 2.08 1.00 1.29 6.00 2.26 4.23
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.


177.42
156.23
152.49
149.19
133.29
130.12
128.76
126.80
126.22
124.80
124.23
117.98
112.86
77.48
77.16
76.84
47.04
40.89
38.83
27.88
27.44
17.57
O
O
N
4ag
13C NMR (100 MHz, CDCl3)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0