Supporting Information

Selective Radical Cascade (4+2) Annulation with Olefins towards the Synthesis of Chroman Derivatives via Organo-Photoredox Catalysis

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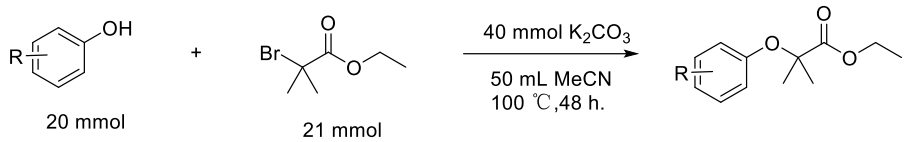
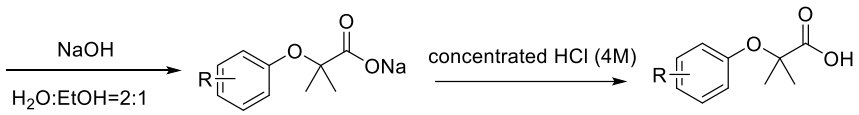
General information

All manipulations were carried out by standard schlenk techniques. Unless otherwise stated, analytical grade solvents and commercially available reagents were used to conduct the reactions. LED irradiation was accomplished using the blue photochemical reactors. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel. Gradient flash chromatography was conducted and eluted with a continuous gradient from petroleum ether to ethyl acetate. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR and HRMS. The known compounds were characterized by ^{1}H NMR and ^{13}C NMR. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. The chemical shifts (δ) were given in part per million relative to internal tetramethyl silane (TMS, 0 ppm for ^{1}H NMR), $CDCl_3$ (77.16 ppm for ^{13}C NMR) and DMSO-d^6 (2.50 ppm for ^{1}H NMR, 39.52 ppm for ^{13}C NMR), respectively. High resolution mass spectra (HRMS) were measured with a Bruker UltiMate3000 & Compact instrument and accurate masses were reported for the molecular ion Hydrogen $(M+H)^+$. EPR spectra were recorded on a Bruker X-band A200 spectrometer. GC-MS spectra were recorded on Varian GC MS 3900-2100T or SHIMADZU GC MS-2010.

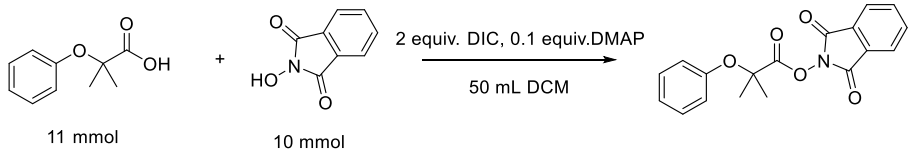
Experimental Procedures

1. General Procedure for Synthesis of 1,3-dioxoisoindolin-2-yl 2-methyl-2-phenoxypropanoate



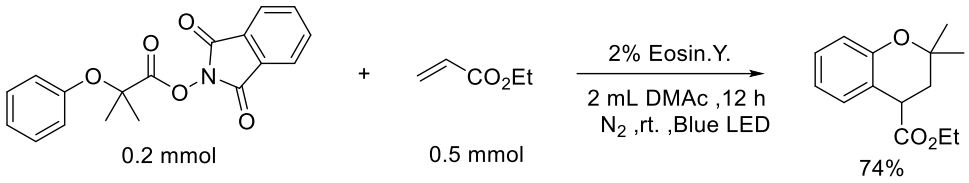


In a round-bottom flask with phenol (20 mmol) and K_2CO_3 (40 mmol), acetonitrile (40 mL) was added to the mixture and the mixture was stirred vigorously. After Ethyl 2-bromo-2-methylpropionate (21 mmol) was added, the reaction mixture was stirred at 100 ℃ for 48 hours . After completion of the reaction, the reaction system was quenched by aqueous solution. The aqueous solution was extracted with ethyl acetate (3 × 30 mL) and the combined extracts were dried with anhydrous Na_2SO_4. The solvents were removed under reduced pressure by rotary evaporation. Then, the pure product was obtained by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1). Adding 14 mmol NaOH, H_2O (40 mL) and MeOH (20 mL) to the product until the product disappeared. The aqueous mixture was adjusted to pH=1 with concentrated HCl (4 M × 6 mL) and extracted with ethyl acetate (20 mL × 4). The combined extracts were washed with brine, dried with sodium sulfate and concentrated to give the target compound.



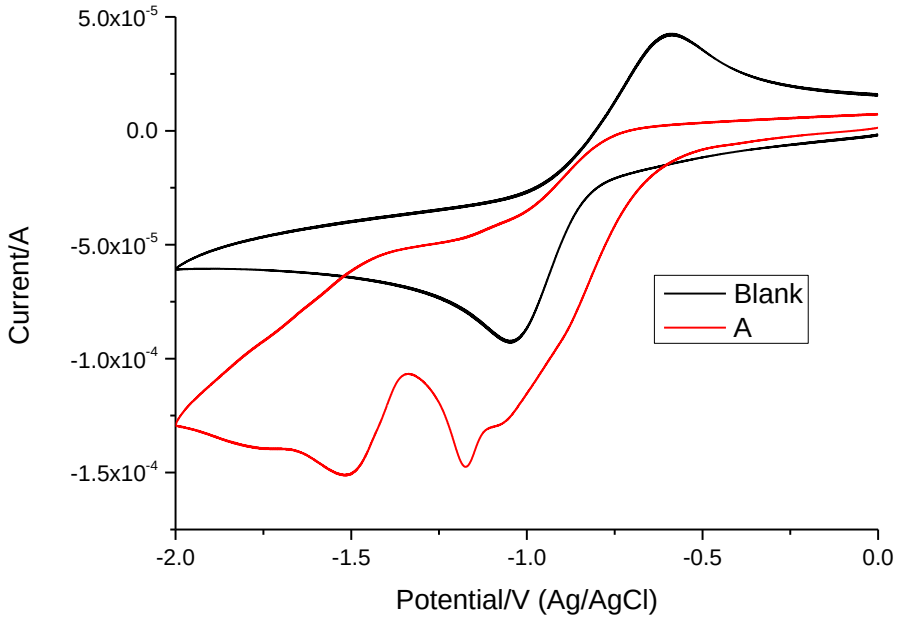
2-methyl-2-phenoxypropanoic acid (5.0 mmol), N-hydroxy-phthalimide (1.0 equiv), 4-Dimethylaminopyridine (DMAP, 0.1 equiv) and dichloromethane (50 mL) were placed in a round-bottom flask. Adding to the mixture. After stirring the mixture vigorously, N, N'-diisopropylcarbodiimide (DIC, 1.0 equiv) was added dropwise to the mixture and the mixture was stirred for 12 hours. After completion of the reaction, the product was identified by TLC. Rinse the mixture with additional CH_2Cl_2/Et_2O. Remove the solvent under reduced pressure. The solvent was removed under reduced pressure by an aspirator, then the pure product was obtained by flash column chromatography on silica gel (silica gel, 10:1 petroleum ether : EtOAc).

2. General Procedure for Organo-Photoredox (4+2) Annulation with Alkenes



A solution of ethyl acrylate (0.5 mmol, 2.5 equiv), 1,3-dioxoisoindolin-2-yl 2-methyl-2-phenoxypropanoate (0.2 mmol), and Eosin.Y (2%, 2.6 mg) in DMAc (2.0 mL) were stirred under nitrogen atmosphere and irradiated by 24 W blue LEDs at 25 ˚C for 12 h. After completion of the reaction, the reaction system was extracted by saturated NaCl aqueous solution. The aqueous solution was extracted with ethyl acetate (3 × 2 mL) and the combined extracts were dried with anhydrous Na_2SO_4. The solvents were removed under reduced pressure by rotary evaporation. Then, the pure product was obtained by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1).

3. General Procedure for Cyclic Voltammetry (CV)

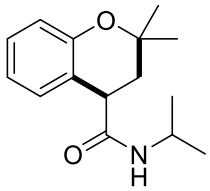


Cyclic voltammetry experiment was performed in a three-electrode cell connected to a Schlenk line under air at room temperature. The working electrode was a glass carbon electrode, the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in 10 ml DMAc, Corresponding undertested matter: 1,3-dioxoisoindolin-2-yl 2-methyl-2-phenoxypropanoate (0.1 mmol), $^{n}Bu_4NH_4F_4$ (0.5 mmol), in a three-electrode cell, solvent DMAc 10 mL containing $nBu_4NH_4F_4$ (0.5 mmol) were poured into the electrochemical cell in all experiments. The scan rate is 0.1 V/s.

Crystallography Data

Single crystal of the compounds were selected, mounted onto a cryoloop, and transferred in a cold nitrogen gasstream. Intensity data were collected with a BRUKER Kappa-APEXII diffractometer with graphite-monochromated Cu-Kα radiation (λ = 0.71073 Å). Data collection were performed with APEX2 suite (BRUKER). Unitcell parameters refinement, integration and data reduction were carried out with SAINT program (BRUKER). SADABS (BRUKER) was used for scaling and multi-scan absorption corrections. In the WinGX suite of programs, the structure were solved with Sir2014 program and refined by fullmatrix least-squares methods using SHELXL-14.

CCDC 2089433 contain the supplementary crystallographic data for this paper



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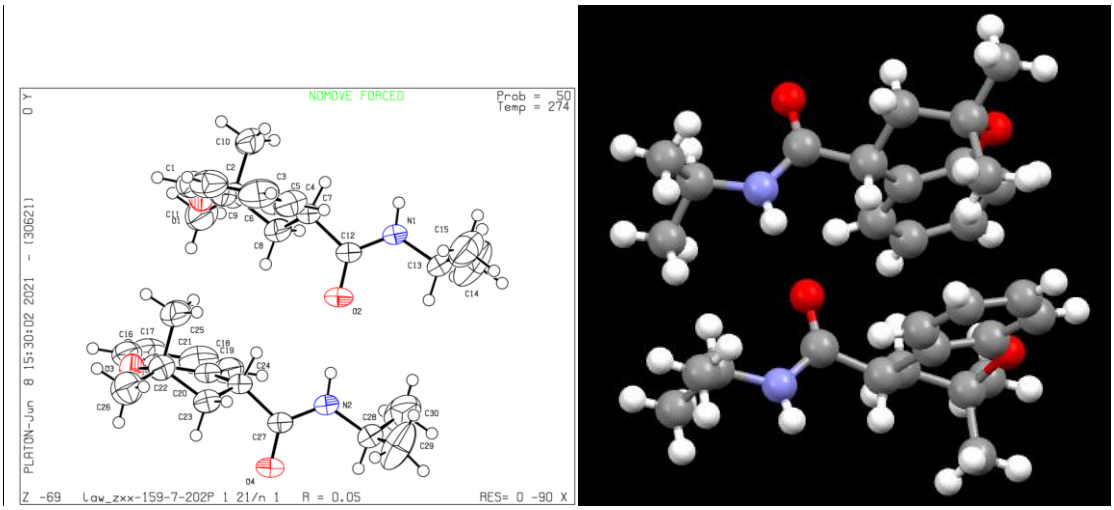


Table 1. Crystal data and structure refinement for final-LAW_ZXX-159-7-20210524-rt.

Identification code	law_zxx-159-7-20210524-rt	
Empirical formula	C15 H21 N O2	
Formula weight	247.33	
Temperature	274(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 9.77660(10) Å	α= 90°.
	b = 13.9140(2) Å	β= 97.7580(10)°.
	c = 21.1903(3) Å	γ = 90°.
Volume	2856.17(6) Å^3	

Z	8
Density (calculated)	1.150 Mg/m^3
Absorption coefficient	0.600 mm^{-1}
F(000)	1072
Crystal size	0.05 x 0.04 x 0.03 mm^3
Theta range for data collection	3.811 to 71.709°.
Index ranges	-11<=h<=11, -16<=k<=17, -25<=l<=25
Reflections collected	50596
Independent reflections	5527 [R(int) = 0.0457]
Completeness to theta = 67.684°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.39191
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5527 / 0 / 333
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0490, wR2 = 0.1344
R indices (all data)	R1 = 0.0627, wR2 = 0.1451
Extinction coefficient	n/a
Largest diff. peak and hole	0.173 and -0.158 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for final-LAW_ZXX-159-7-20210524-rt. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	5246(1)	2311(1)	1140(1)	62(1)
O(3)	182(1)	2989(1)	1101(1)	62(1)
O(4)	-374(1)	2637(1)	3193(1)	71(1)
O(2)	4645(1)	2860(1)	3230(1)	70(1)
N(1)	6901(1)	2838(1)	3610(1)	58(1)
N(2)	1885(1)	2603(1)	3575(1)	58(1)
C(20)	1079(1)	2036(1)	2027(1)	49(1)
C(12)	5854(1)	2766(1)	3145(1)	50(1)
C(27)	844(1)	2705(1)	3110(1)	50(1)
C(21)	591(1)	2133(1)	1381(1)	53(1)
C(6)	5577(1)	3203(1)	1387(1)	52(1)
C(5)	6022(1)	3371(1)	2032(1)	50(1)
C(7)	6251(1)	2540(1)	2491(1)	49(1)
C(24)	1246(1)	2911(1)	2453(1)	48(1)
C(9)	5699(2)	1483(1)	1526(1)	53(1)
C(22)	599(2)	3865(1)	1446(1)	56(1)
C(13)	6756(2)	3003(1)	4280(1)	57(1)
C(8)	5447(2)	1667(1)	2209(1)	55(1)
C(23)	393(2)	3737(1)	2140(1)	55(1)
C(28)	1712(2)	2418(1)	4239(1)	62(1)
C(19)	1403(2)	1118(1)	2256(1)	65(1)
C(4)	6270(2)	4319(1)	2222(1)	68(1)
C(10)	7214(2)	1322(1)	1474(1)	66(1)
C(1)	5412(2)	3960(1)	957(1)	68(1)
C(16)	453(2)	1332(1)	984(1)	68(1)
C(25)	2096(2)	4063(1)	1367(1)	68(1)
C(17)	782(2)	434(2)	1231(1)	79(1)
C(2)	5665(2)	4889(2)	1165(1)	80(1)
C(18)	1258(2)	322(1)	1867(1)	80(1)
C(3)	6095(2)	5072(2)	1798(1)	83(1)
C(11)	4816(2)	666(2)	1233(1)	82(1)
C(26)	-349(2)	4633(2)	1127(1)	84(1)

C(15)	7500(3)	3895(2)	4514(1)	103(1)
C(30)	2692(3)	1668(2)	4519(1)	109(1)
C(14)	7233(3)	2144(2)	4666(1)	123(1)
C(29)	1853(3)	3335(2)	4609(1)	125(1)

Table 3. Bond lengths [Å] and angles [°] for final-LAW_ZXX-159-7-20210524-rt.

O(1)-C(6)	1.3679(19)
O(1)-C(9)	1.4471(18)
O(3)-C(21)	1.3659(19)
O(3)-C(22)	1.4505(19)
O(4)-C(27)	1.2299(16)
O(2)-C(12)	1.2261(16)
N(1)-H(1)	0.8600
N(1)-C(12)	1.3261(18)
N(1)-C(13)	1.4631(17)
N(2)-H(2A)	0.8600
N(2)-C(27)	1.3256(18)
N(2)-C(28)	1.4624(18)
C(20)-C(21)	1.393(2)
C(20)-C(24)	1.512(2)
C(20)-C(19)	1.388(2)
C(12)-C(7)	1.5212(18)
C(27)-C(24)	1.5240(18)
C(21)-C(16)	1.392(2)
C(6)-C(5)	1.397(2)
C(6)-C(1)	1.388(2)
C(5)-C(7)	1.510(2)
C(5)-C(4)	1.390(2)
C(7)-H(7)	0.9800
C(7)-C(8)	1.524(2)
C(24)-H(24)	0.9800
C(24)-C(23)	1.519(2)
C(9)-C(8)	1.5229(19)
C(9)-C(10)	1.517(2)
C(9)-C(11)	1.508(2)
C(22)-C(23)	1.522(2)
C(22)-C(25)	1.521(2)
C(22)-C(26)	1.512(2)
C(13)-H(13)	0.9800
C(13)-C(15)	1.489(3)
C(13)-C(14)	1.487(3)
C(8)-H(8A)	0.9700

C(8)-H(8B)	0.9700
C(23)-H(23A)	0.9700
C(23)-H(23B)	0.9700
C(28)-H(28)	0.9800
C(28)-C(30)	1.485(3)
C(28)-C(29)	1.493(3)
C(19)-H(19)	0.9300
C(19)-C(18)	1.376(3)
C(4)-H(4)	0.9300
C(4)-C(3)	1.376(3)
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(1)-H(1A)	0.9300
C(1)-C(2)	1.377(3)
C(16)-H(16)	0.9300
C(16)-C(17)	1.377(3)
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600
C(17)-H(17)	0.9300
C(17)-C(18)	1.373(3)
C(2)-H(2)	0.9300
C(2)-C(3)	1.374(3)
C(18)-H(18)	0.9300
C(3)-H(3)	0.9300
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(26)-H(26A)	0.9600
C(26)-H(26B)	0.9600
C(26)-H(26C)	0.9600
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(30)-H(30A)	0.9600
C(30)-H(30B)	0.9600
C(30)-H(30C)	0.9600

C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(29)-H(29A)	0.9600
C(29)-H(29B)	0.9600
C(29)-H(29C)	0.9600

C(6)-O(1)-C(9)	117.92(11)
C(21)-O(3)-C(22)	117.88(11)
C(12)-N(1)-H(1)	117.7
C(12)-N(1)-C(13)	124.52(11)
C(13)-N(1)-H(1)	117.7
C(27)-N(2)-H(2A)	118.1
C(27)-N(2)-C(28)	123.88(12)
C(28)-N(2)-H(2A)	118.1
C(21)-C(20)-C(24)	120.22(13)
C(19)-C(20)-C(21)	117.71(14)
C(19)-C(20)-C(24)	122.08(14)
O(2)-C(12)-N(1)	123.09(13)
O(2)-C(12)-C(7)	121.67(12)
N(1)-C(12)-C(7)	115.23(11)
O(4)-C(27)-N(2)	123.12(13)
O(4)-C(27)-C(24)	121.22(12)
N(2)-C(27)-C(24)	115.66(11)
O(3)-C(21)-C(20)	123.57(13)
O(3)-C(21)-C(16)	115.88(14)
C(16)-C(21)-C(20)	120.52(16)
O(1)-C(6)-C(5)	123.51(14)
O(1)-C(6)-C(1)	115.98(14)
C(1)-C(6)-C(5)	120.48(16)
C(6)-C(5)-C(7)	120.13(14)
C(4)-C(5)-C(6)	117.50(15)
C(4)-C(5)-C(7)	122.35(14)
C(12)-C(7)-H(7)	108.0
C(12)-C(7)-C(8)	109.91(11)
C(5)-C(7)-C(12)	113.28(12)
C(5)-C(7)-H(7)	108.0
C(5)-C(7)-C(8)	109.50(11)

C(8)-C(7)-H(7)	108.0
C(20)-C(24)-C(27)	112.02(12)
C(20)-C(24)-H(24)	108.2
C(20)-C(24)-C(23)	109.89(11)
C(27)-C(24)-H(24)	108.2
C(23)-C(24)-C(27)	110.30(11)
C(23)-C(24)-H(24)	108.2
O(1)-C(9)-C(8)	109.03(12)
O(1)-C(9)-C(10)	107.69(12)
O(1)-C(9)-C(11)	104.67(13)
C(10)-C(9)-C(8)	112.24(13)
C(11)-C(9)-C(8)	111.15(13)
C(11)-C(9)-C(10)	111.68(15)
O(3)-C(22)-C(23)	108.88(12)
O(3)-C(22)-C(25)	107.83(12)
O(3)-C(22)-C(26)	104.81(13)
C(25)-C(22)-C(23)	112.48(13)
C(26)-C(22)-C(23)	111.13(13)
C(26)-C(22)-C(25)	111.33(15)
N(1)-C(13)-H(13)	107.9
N(1)-C(13)-C(15)	110.26(14)
N(1)-C(13)-C(14)	110.10(15)
C(15)-C(13)-H(13)	107.9
C(14)-C(13)-H(13)	107.9
C(14)-C(13)-C(15)	112.57(18)
C(7)-C(8)-H(8A)	109.3
C(7)-C(8)-H(8B)	109.3
C(9)-C(8)-C(7)	111.48(11)
C(9)-C(8)-H(8A)	109.3
C(9)-C(8)-H(8B)	109.3
H(8A)-C(8)-H(8B)	108.0
C(24)-C(23)-C(22)	111.95(12)
C(24)-C(23)-H(23A)	109.2
C(24)-C(23)-H(23B)	109.2
C(22)-C(23)-H(23A)	109.2
C(22)-C(23)-H(23B)	109.2
H(23A)-C(23)-H(23B)	107.9
N(2)-C(28)-H(28)	107.8

N(2)-C(28)-C(30)	110.81(14)
N(2)-C(28)-C(29)	109.87(16)
C(30)-C(28)-H(28)	107.8
C(30)-C(28)-C(29)	112.46(18)
C(29)-C(28)-H(28)	107.8
C(20)-C(19)-H(19)	119.0
C(18)-C(19)-C(20)	122.07(17)
C(18)-C(19)-H(19)	119.0
C(5)-C(4)-H(4)	118.9
C(3)-C(4)-C(5)	122.11(18)
C(3)-C(4)-H(4)	118.9
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(6)-C(1)-H(1A)	119.9
C(2)-C(1)-C(6)	120.26(17)
C(2)-C(1)-H(1A)	119.9
C(21)-C(16)-H(16)	120.0
C(17)-C(16)-C(21)	119.91(17)
C(17)-C(16)-H(16)	120.0
C(22)-C(25)-H(25A)	109.5
C(22)-C(25)-H(25B)	109.5
C(22)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(16)-C(17)-H(17)	119.8
C(18)-C(17)-C(16)	120.45(18)
C(18)-C(17)-H(17)	119.8
C(1)-C(2)-H(2)	119.9
C(3)-C(2)-C(1)	120.22(18)
C(3)-C(2)-H(2)	119.9
C(19)-C(18)-H(18)	120.3
C(17)-C(18)-C(19)	119.34(19)
C(17)-C(18)-H(18)	120.3

C(4)-C(3)-H(3)	120.3
C(2)-C(3)-C(4)	119.42(19)
C(2)-C(3)-H(3)	120.3
C(9)-C(11)-H(11A)	109.5
C(9)-C(11)-H(11B)	109.5
C(9)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(22)-C(26)-H(26A)	109.5
C(22)-C(26)-H(26B)	109.5
C(22)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(28)-C(30)-H(30A)	109.5
C(28)-C(30)-H(30B)	109.5
C(28)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(28)-C(29)-H(29A)	109.5
C(28)-C(29)-H(29B)	109.5
C(28)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29C)	109.5

H(29B)-C(29)-H(29C) 109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for final-LAW_ZXX-159-7-20210524-rt. The anisotropic

displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	63(1)	73(1)	47(1)	1(1)	-1(1)	3(1)
O(3)	62(1)	77(1)	46(1)	-2(1)	1(1)	-5(1)
O(4)	34(1)	124(1)	56(1)	2(1)	17(1)	-2(1)
O(2)	35(1)	122(1)	58(1)	-6(1)	18(1)	2(1)
N(1)	36(1)	99(1)	41(1)	-4(1)	13(1)	0(1)
N(2)	36(1)	98(1)	42(1)	0(1)	12(1)	-3(1)
C(20)	36(1)	65(1)	50(1)	-2(1)	17(1)	-1(1)
C(12)	34(1)	71(1)	45(1)	0(1)	14(1)	-1(1)
C(27)	35(1)	72(1)	45(1)	-4(1)	13(1)	-2(1)
C(21)	40(1)	68(1)	53(1)	-6(1)	14(1)	-5(1)
C(6)	40(1)	66(1)	53(1)	5(1)	12(1)	5(1)
C(5)	37(1)	66(1)	51(1)	1(1)	16(1)	-1(1)
C(7)	34(1)	72(1)	42(1)	-1(1)	12(1)	1(1)
C(24)	33(1)	71(1)	43(1)	-2(1)	12(1)	-2(1)
C(9)	52(1)	62(1)	46(1)	0(1)	10(1)	-2(1)
C(22)	52(1)	66(1)	50(1)	1(1)	11(1)	3(1)
C(13)	47(1)	87(1)	40(1)	0(1)	15(1)	-1(1)
C(8)	48(1)	70(1)	49(1)	1(1)	15(1)	-7(1)
C(23)	48(1)	69(1)	51(1)	-4(1)	15(1)	6(1)
C(28)	48(1)	96(1)	42(1)	1(1)	13(1)	-2(1)
C(19)	61(1)	72(1)	67(1)	6(1)	24(1)	8(1)
C(4)	68(1)	69(1)	71(1)	-10(1)	28(1)	-9(1)
C(10)	60(1)	84(1)	58(1)	-1(1)	17(1)	14(1)
C(1)	59(1)	85(1)	63(1)	19(1)	15(1)	13(1)
C(16)	56(1)	91(1)	61(1)	-22(1)	18(1)	-12(1)
C(25)	62(1)	82(1)	64(1)	2(1)	21(1)	-12(1)
C(17)	68(1)	73(1)	102(2)	-28(1)	34(1)	-11(1)
C(2)	72(1)	75(1)	99(2)	28(1)	34(1)	14(1)
C(18)	78(1)	65(1)	104(2)	-2(1)	38(1)	4(1)
C(3)	85(1)	63(1)	110(2)	2(1)	44(1)	-2(1)
C(11)	87(1)	88(1)	72(1)	-17(1)	17(1)	-26(1)
C(26)	85(1)	94(2)	75(1)	17(1)	13(1)	22(1)

C(15)	125(2)	122(2)	68(1)	-22(1)	33(1)	-39(2)
C(30)	120(2)	129(2)	82(1)	36(1)	32(1)	41(2)
C(14)	207(3)	105(2)	65(1)	23(1)	48(2)	35(2)
C(29)	208(3)	112(2)	60(1)	-13(1)	32(2)	13(2)

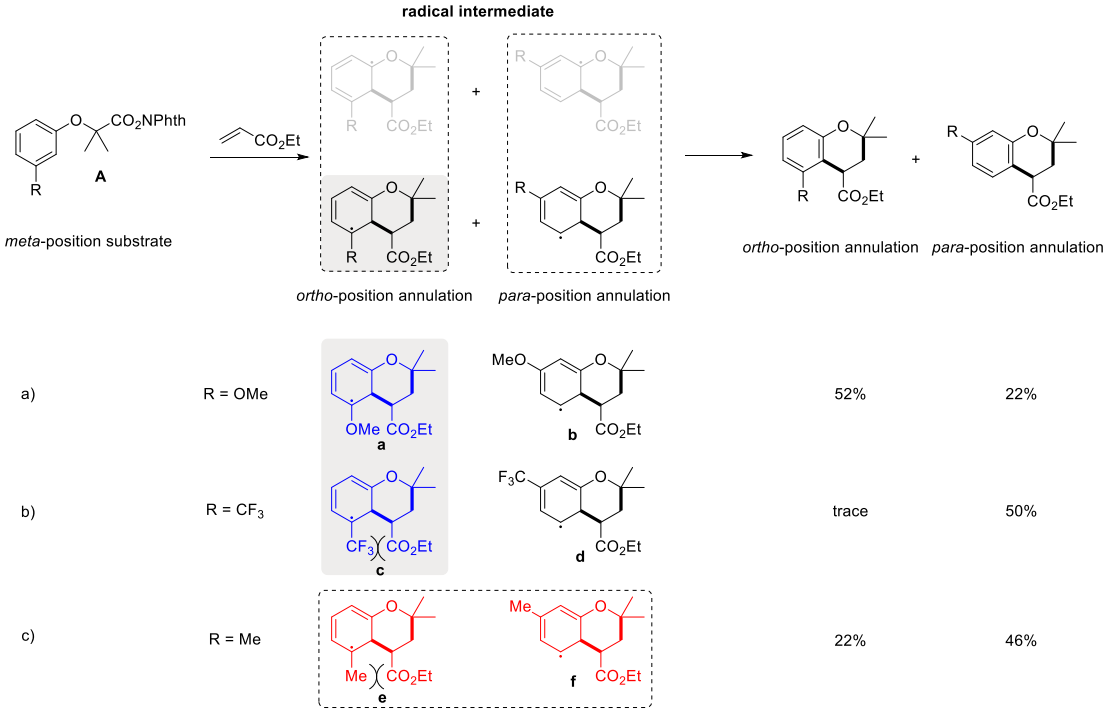
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for final-LAW_ZXX-159-7-20210524-rt.

	x	y	z	U(eq)
H(1)	7723	2785	3511	69
H(2A)	2711	2647	3481	69
H(7)	7235	2378	2545	58
H(24)	2219	3102	2506	58
H(13)	5773	3095	4310	68
H(8A)	5723	1106	2467	66
H(8B)	4469	1771	2218	66
H(23A)	651	4326	2371	66
H(23B)	-576	3618	2164	66
H(28)	773	2175	4247	74
H(19)	1728	1038	2685	78
H(4)	6563	4448	2649	81
H(10A)	7316	1150	1044	100
H(10B)	7564	813	1756	100
H(10C)	7720	1901	1589	100
H(1A)	5129	3840	528	82
H(16)	138	1404	552	82
H(25A)	2654	3520	1517	102
H(25B)	2412	4622	1609	102
H(25C)	2168	4170	925	102
H(17)	682	-101	966	95
H(2)	5545	5395	875	96
H(18)	1479	-286	2033	96
H(3)	6265	5699	1938	100
H(11A)	3864	799	1264	123
H(11B)	5086	81	1455	123
H(11C)	4937	600	793	123
H(26A)	-273	4650	680	127
H(26B)	-91	5246	1314	127
H(26C)	-1284	4490	1185	127
H(15A)	8470	3817	4497	155
H(15B)	7349	4017	4945	155

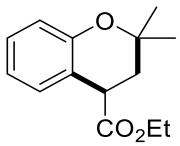
H(15C)	7159	4427	4250	155
H(30A)	2501	1075	4294	163
H(30B)	2590	1578	4960	163
H(30C)	3620	1867	4486	163
H(14A)	6677	1599	4518	184
H(14B)	7150	2263	5105	184
H(14C)	8181	2015	4623	184
H(29A)	2795	3546	4654	188
H(29B)	1583	3231	5022	188
H(29C)	1270	3816	4387	188

Table 6. Torsion angles [°] for final-LAW_ZXX-159-7-20210524-rt.

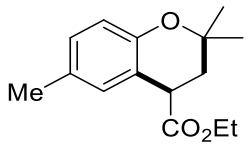
both electronic and steric effects played key roles in controlling the regioselectivity of the annulation reaction. As shown in following Figure 2a, when R group is -OMe (electron-rich), the key radical intermediate **a** resulting from *ortho*-annulation is more stable than intermediate **b** resulting from *para*-annulation, meanwhile, radical **a** is easier to be oxidized. Therefore, *ortho*-position annulation product was formed primarily in this case. However, when R group is -Me, the steric hindrance might be the main factor to control the regioselectivity, as *para*-position where is less hindrance, was attacked easily leading to the primary *para*-selectivity. When R group is -CF_3, both electronic and steric effects contributed to the excellent *para*-position, since the key radical **d** is more electron-rich as well as less hindrance.



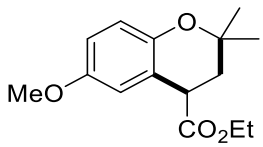
Characterization of Products



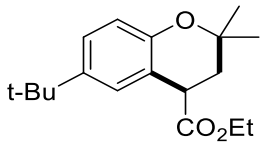
Ethyl-2,2-dimethylchromane-4-carboxylate (1). Colorless liquid was obtained in 70% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (t, J = 7.7 Hz, 2H), 6.86 (m, 1H), 6.80 (dd, J = 7.8, 1.5 Hz, 1H), 4.23 (m, 2H), 3.85 (dd, J = 10.6, 6.4 Hz, 1H), 2.23 (dd, J = 13.6, 10.6 Hz, 1H), 2.03 (dd, J = 13.6, 6.4 Hz, 1H), 1.41 (s, 3H), 1.35–1.19 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.86, 153.54, 128.85, 128.69, 120.16, 117.99, 117.91, 73.73, 61.24, 39.85, 36.31, 28.89, 25.05, 14.36. **HRMS (ESI)** calcd for $C_{14}H_{19}O_3^+$, $[M+H]^+$, 235.1329, found 235.1326.



Ethyl-2,2,6-trimethylchromane-4-carboxylate (2). Faint yellow liquid was obtained in 65% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.02–6.97 (m, 2H), 6.74 (d, J = 8.9 Hz, 1H), 4.28 (m, 2H), 3.85 (dd, J = 10.7, 6.4 Hz, 1H), 2.36 – 2.15 (m, 4H), 2.05 (dd, J = 13.5, 6.4 Hz, 1H), 1.44 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H), 1.29 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.01, 151.28, 129.46, 129.29, 129.00, 117.64, 117.59, 73.53, 61.19, 39.90, 36.44, 28.91, 24.90, 20.71, 14.36. **HRMS (ESI)** calcd for $C_{15}H_{21}O_3^+$, $[M+H]^+$, 249.1485, found 249.1484.

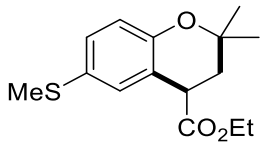


Ethyl-6-methoxy-2,2-dimethylchromane-4-carboxylate (3). Faint yellow liquid was obtained in 73% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.78–6.69 (m, 3H), 4.24 (m, 2H), 3.82 (m, 1H), 3.74 (s, 3H), 2.21 (dd, J = 13.6, 10.6 Hz, 1H), 2.01 (dd, J = 13.6, 6.5 Hz, 1H), 1.40 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H), 1.25 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.59, 153.04, 147.44, 118.39, 118.24, 114.96, 113.09, 73.35, 61.17, 55.71, 40.01, 36.16, 28.80, 24.66, 14.29. **HRMS (ESI)** calcd for $C_{15}H_{21}O_4^+$, $[M+H]^+$, 265.1434, found 265.1433.

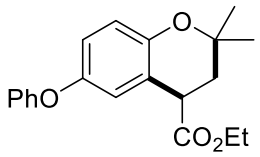


Ethyl-6-(tert-butyl)-2,2-dimethylchromane-4-carboxylate (4). Yellow liquid was obtained in 68% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20–7.14 (m, 2H), 6.77–6.70 (m, 1H), 4.24 (m, 2H), 3.84 (dd, J = 10.6, 6.3 Hz, 1H), 2.23 (dd, J = 13.5, 10.5 Hz, 1H), 2.01 (dd, J = 13.5, 6.4 Hz, 1H), 1.39 (s, 3H), 1.35–1.12 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.93, 151.16, 142.63, 125.77, 125.44, 117.21,

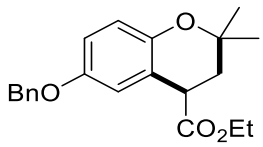
116.99, 73.54, 61.12, 40.07, 36.37, 34.18, 31.64, 28.93, 25.12, 14.45. **HRMS (ESI)** calcd for $C_{18}H_{27}O_3^+$, $[M+H]^+$, 291.1955, found 291.1952.



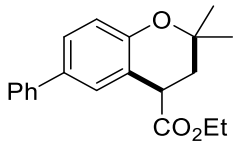
Ethyl-2,2-dimethyl-6-(methylthio)chromane-4-carboxylate (5). Faint yellow liquid was obtained in 45% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23–7.11 (m, 2H), 6.75 (d, *J* = 8.5 Hz, 1H), 4.25 (m, 2H), 3.81 (dd, *J* = 10.5, 6.4 Hz, 1H), 2.42 (s, 3H), 2.22 (dd, *J* = 13.6, 10.5 Hz, 1H), 2.02 (dd, *J* = 13.6, 6.4 Hz, 1H), 1.40 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.26 (s,3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.48, 152.25, 129.70, 129.58, 128.07, 118.65, 118.63, 73.98, 61.36, 39.72, 36.14, 28.76, 25.05, 18.27, 14.38. **HRMS (ESI)** calcd for $C_{15}H_{21}O_3S^+$, $[M+H]^+$, 281.1206, found 281.1200.



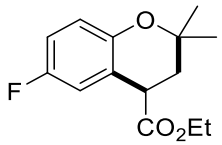
Ethyl (R)-2,2-dimethyl-6-phenoxychromane-4-carboxylate (6). Faint yellow liquid was obtained in 52% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.23 (m, 2H), 7.04 (d, *J* = 7.4 Hz, 1H), 6.98–6.91 (m, 2H), 6.91–6.83 (m, 2H), 6.78 (d, *J* = 8.7 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.81 (dd, *J* = 10.5, 6.5 Hz, 1H), 2.23 (m, 1H), 2.04 (m, 1H), 1.41 (s, 3H), 1.28 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.43, 158.50, 149.77, 149.49, 129.68, 122.51, 120.51, 119.84, 118.82, 117.77, 73.82, 61.35, 39.91, 36.06, 28.78, 25.01, 14.27. **HRMS (ESI)** calcd for $C_{20}H_{23}O_4^+$, $[M+H]^+$, 327.1596, found 327.1585.



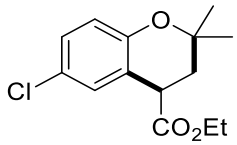
Ethyl-6-(benzyloxy)-2,2-dimethylchromane-4-carboxylate (7). Faint yellow liquid was obtained in 44% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46–7.34 (m, 4H), 7.33–7.27 (m, 1H), 6.85–6.77 (m, 2H), 6.73 (d, *J* = 8.6 Hz, 1H), 4.97 (s, 2H), 4.20 (m, 2H), 3.81 (dd, *J* = 10.7, 6.4 Hz, 1H), 2.21 (dd, *J* = 13.6, 10.6 Hz, 1H), 2.00 (dd, *J* = 13.6, 6.5 Hz, 1H), 1.39 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 2H), 1.25 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.67, 152.40, 147.77, 137.42, 128.64, 127.97, 127.60, 118.49, 118.38, 116.09, 114.44, 73.49, 70.77, 61.28, 40.13, 36.26, 28.90, 24.80, 14.37. **HRMS (ESI)** calcd for $C_{21}H_{25}O_4^+$, $[M+H]^+$,341.1747, found 341.1748.



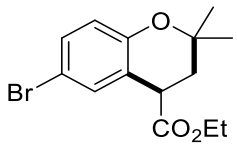
Ethyl-2,2-dimethyl-6-phenylchromane-4-carboxylate (8). Colorless liquid was obtained in 56% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56–7.48 (m, 2H), 7.39 (m, 4H), 7.29 (d, *J* = 7.2 Hz, 1H), 6.91–6.84 (m, 1H), 4.34–4.18 (m, 2H), 3.91 (dd, *J* = 10.5, 6.4 Hz, 1H), 2.27 (dd, *J* = 13.6, 10.5 Hz, 1H), 2.07 (dd, *J* = 13.8, 6.6 Hz, 1H), 1.43 (s, 3H), 1.36–1.28 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.74, 153.21, 141.04, 133.30, 128.79, 127.59, 127.56, 126.83, 126.69, 118.28, 118.14, 61.33, 39.95, 36.33, 28.86, 25.15, 14.42. **HRMS (ESI)** calcd for $C_{20}H_{23}O_3^+$, $[M+H]^+$, 311.1642, found 311.1637.



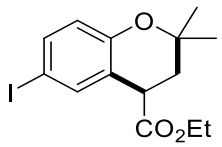
Ethyl-6-fluoro-2,2-dimethylchromane-4-carboxylate (9). Faint yellow liquid was obtained in 55% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.94–6.82 (m, 2H), 6.74 (m, 1H), 4.25 (m, 2H), 3.87–3.72 (m, 1H), 2.21 (dd, *J* = 13.6, 10.5 Hz, 1H), 2.10–1.96 (m, 1H), 1.39 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.26 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.25, δ 156.58 (d, *J* = 237.6 Hz), 149.63 (d, *J* = 2.1 Hz), 118.85, 118.78 (d, *J* = 8.0 Hz), 115.67 (d, *J* = 23.0 Hz), 114.85 (d, *J* = 23.6 Hz).73.88, 61.47, 39.87, 35.94, 28.72, 24.91, 14.34. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -124.18. **HRMS (ESI)** calcd for $C_{14}H_{18}FO_3^+$, $[M+H]^+$, 253.1234, found 253.1233.



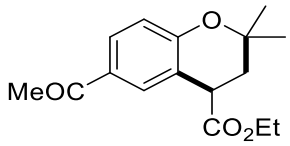
Ehyl-6-chloro-2,2-dimethylchromane-4-carboxylate (10). Faint yellow liquid was obtained in 64% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 2.7, 1.1 Hz, 1H), 7.10 (m, 1H), 6.74 (d, *J* = 8.7 Hz, 1H), 4.25 (m, 2H), 3.80 (m, 1H), 2.21 (dd, *J* = 13.7, 10.4 Hz, 1H), 2.02 (dd, *J* = 13.7, 6.5 Hz, 1H), 1.39 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.26 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.18, 152.25, 128.75, 128.62, 124.82, 119.40, 119.26, 74.17, 61.51, 39.61, 35.90, 28.64, 25.01, 14.33. **HRMS (ESI)** calcd for $C_{14}H_{18}ClO_3^+$, $[M+H]^+$, 269.0939, found 269.0938.



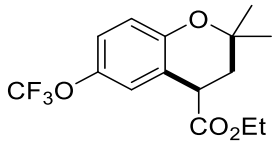
Ethyl-6-bromo-2,2-dimethylchromane-4-carboxylate (11). Yellow liquid was obtained in 56% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 2.4, 1.1 Hz, 1H), 7.28–7.19 (m, 1H), 6.69 (d, *J* = 8.7 Hz, 1H), 4.25 (m, 2H), 3.80 (dd, *J* = 10.4, 6.5 Hz, 1H), 2.21 (dd, *J* = 13.7, 10.4 Hz, 1H), 2.02 (dd, *J* = 13.7, 6.5 Hz, 1H), 1.39 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.26 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.15, 152.79, 131.62, 131.59, 120.01, 119.75, 112.11, 74.20, 61.52, 39.56, 35.91, 28.63, 25.06, 14.34. **HRMS (ESI)** calcd for $C_{14}H_{18}BrO_3^+$, $[M+H]^+$, 313.0434, found 313.0428.



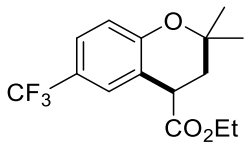
Ethyl-6-iodo-2,2-dimethylchromane-4-carboxylate (12). Dark yellow liquid was obtained in 58% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 2.2, 1.0 Hz, 1H), 7.41 (m, 1H), 6.57 (d, *J* = 8.6 Hz, 1H), 4.25 (m, 2H), 3.79 (dd, *J* = 10.3, 6.5 Hz, 1H), 2.20 (dd, *J* = 13.7, 10.3 Hz, 1H), 2.01 (dd, *J* = 13.7, 6.4 Hz, 1H), 1.39 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.26 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.16, 153.58, 137.59, 137.46, 120.66, 120.28, 81.96, 74.19, 61.49, 39.38, 35.89, 28.61, 25.09, 14.35. **HRMS (ESI)** calcd for $C_{14}H_{18}IO_3^+$, $[M+H]^+$, 361.0295, found 361.0290.



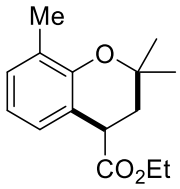
Ethyl-6-acetyl-2,2-dimethylchromane-4-carboxylate (13). Faint yellow liquid was obtained in 54% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92–7.84 (m, 1H), 7.79 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.84 (d, *J* = 8.6 Hz, 1H), 4.27 (m, 2H), 3.87 (dd, *J* = 10.2, 6.4 Hz, 1H), 2.53 (s, 2H), 2.26 (dd, *J* = 13.8, 10.2 Hz, 1H), 2.09 (dd, *J* = 13.7, 6.4 Hz, 1H), 1.42 (s, 3H), 1.36–1.26 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.84, 173.23, 158.02, 130.51, 129.84, 129.40, 117.99, 117.83, 75.08, 61.52, 39.48, 35.97, 28.54, 26.40, 25.39, 14.36. **HRMS (ESI)** calcd for $C_{16}H_{21}O_4^+$, $[M+H]^+$,277.1434, found 277.1437.



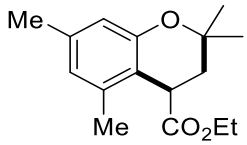
Ethyl-2,2-dimethyl-6-(trifluoromethoxy)chromane-4-carboxylate (14). Faint yellow liquid was obtained in 60% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 2.9 Hz, 1H), 7.02 (dd, *J* = 9.0, 2.9 Hz, 1H), 6.79 (d, *J* = 8.9 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.82 (dd, *J* = 10.2, 6.5 Hz, 1H), 2.23 (dd, *J* = 13.7, 10.2 Hz, 1H), 2.04 (dd, *J* = 13.7, 6.5 Hz, 1H), 1.40 (s, 3H), 1.29 (q, *J* = 9.1, 8.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.98, 152.23, 142.06, 142.04, 121.93, 120.72(q, *J* = 256.54 Hz) 118.78, 77.48, 77.16, 76.84, 74.29, 61.55, 39.67, 35.76, 28.55, 25.16, 14.23. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -58.38. **HRMS (ESI)** calcd for $C_{15}H_{18}F_3O_4^+$, $[M+H]^+$,319.1152, found 319.1155.



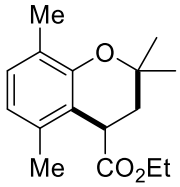
Ethyl-2,2-dimethyl-6-(trifluoromethyl)chromane-4-carboxylate (15). White solid was obtained in 53% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 2.2 Hz, 1H), 7.39 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 1H), 4.26 (m, 2H), 3.85 (dd, *J* = 10.2, 6.4 Hz, 1H), 2.26 (dd, *J* = 13.8, 10.2 Hz, 1H), 2.07 (dd, *J* = 13.8, 6.5 Hz, 1H), 1.42 (s, 3H), 1.36–1.23 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.99, 156.37, 126.73, 126.69, 126.66, 125.82, 125.78,δ 122.17 (q, *J* = 32.7 Hz). 118.35, 118.17, 77.48, 74.81, 61.60, 39.47, 35.84, 28.55, 25.32, 14.29. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -61.50. **HRMS (ESI)** calcd for $C_{15}H_{18}F_3O_3Na^+$, $[M+Na]^+$,325.1022, found 325.1020.



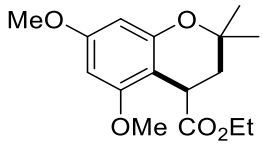
Ethyl-2,2,8-trimethylchromane-4-carboxylate (16). Faint yellow liquid was obtained in 45% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.00 (dd, *J* = 11.6, 7.5 Hz,2H), 6.76 (t, *J* = 7.5 Hz, 1H), 4.23 (m, 2H), 3.85 (dd, *J* = 10.8, 6.4 Hz, 1H), 2.32–2.09 (m, 4H), 2.02 (dd, *J* = 13.4, 6.4 Hz, 1H), 1.42 (s, 3H), 1.35–1.20 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.18, 151.70, 129.68, 126.91, 126.19, 119.37, 117.35, 77.48, 73.49, 61.17, 40.14, 36.38, 29.12, 25.20, 16.31, 14.36. **HRMS (ESI)** calcd for $C_{15}H_{21}O_3^+$, $[M+H]^+$,249.1485, found 249.1481.



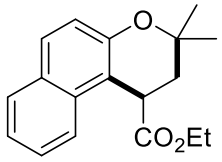
Ethyl-2,2,5,7-tetramethylchromane-4-carboxylate (17). Faint yellow liquid was obtained in 51% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.58 (d, *J* = 1.7 Hz, 1H), 6.52 (d, *J* = 1.7 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.73 (t, *J* = 7.2 Hz, 1H), 2.28–2.18 (m, 4H), 2.17–2.05 (m, 4H), 1.32 (s, 3H), 1.28 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.58, 153.76, 138.22, 138.02, 123.42, 116.07, 114.25, 73.12, 61.13, 38.73, 37.66, 27.22, 26.47, 21.15, 19.50, 14.26. **HRMS (ESI)** calcd for $C_{16}H_{23}O_3^+$, $[M+H]^+$,263.1642, found 263.1640.



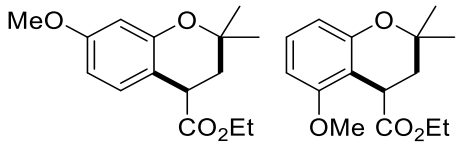
Ethyl-2,2,5,8-tetramethylchromane-4-carboxylate (18). Faint yellow liquid was obtained in 76% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.94 (d, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.77 (t, *J* = 7.4 Hz, 1H), 2.34–2.00 (m, 8H), 1.34 (s, 3H), 1.30–1.21 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.67, 152.02, 135.45, 129.31, 124.34, 121.31, 116.68, 72.93, 61.10, 39.20, 37.59, 27.51, 26.51, 19.39, 16.22, 14.24. **HRMS (ESI)** calcd for $C_{16}H_{23}O_3^+$, $[M+H]^+$,263.1642, found 263.1639.



Ethyl-5,7-dimethoxy-2,2-dimethylchromane-4-carboxylate (19). Faint yellow liquid was obtained in 66% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.08–5.99 (m, 2H), 4.16 (m, 2H), 3.74 (d, *J* = 8.0 Hz, 6H), 3.65 (dd, *J* = 10.1, 7.0 Hz, 1H), 2.07 (dd, *J* = 13.4, 7.0 Hz, 1H), 1.99 (dd, *J* = 13.4, 10.2 Hz, 1H), 1.39 (s, 3H), 1.31–1.18 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.30, 160.53, 158.77, 155.02, 100.86, 94.04, 91.63, 74.11, 60.64, 55.50, 55.36, 37.01, 36.58, 28.64, 24.54, 14.39. **HRMS (ESI)** calcd for $C_{16}H_{23}O_5^+$, $[M+H]^+$,295.1540, found 295.1545.

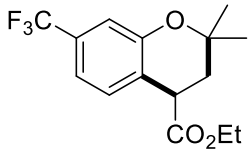


Ethyl-3,3-dimethyl-2,3-dihydro-1H-benzo[f]chromene-1-carboxylate (20). Colorless liquid was obtained in 68% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80–7.72 (m, 1H), 7.68 (d, *J* = 9.0 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.43 (m, 1H), 7.37–7.27 (m, 1H), 7.04 (d, *J* = 8.9 Hz, 1H), 4.24–4.12 (m, 3H), 2.43–2.18 (m, 2H), 1.42 (s, 3H), 1.34 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.91, 151.86, 133.16, 129.55, 129.15, 128.72, 126.57, 126.54, 123.18, 122.35, 119.93, 110.14, 73.84, 61.24, 38.28, 37.48, 27.46, 25.85, 14.19. **HRMS (ESI)** calcd for $C_{15}H_{21}O_3^+$, $[M+H]^+$, 285.1485, found 285.1484.

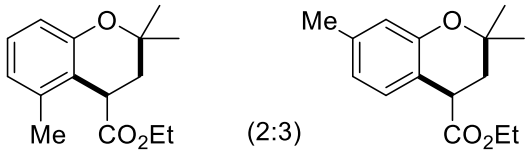


Ethyl-7-methoxy-2,2-dimethylchromane-4-carboxylate and Ehyl-5-methoxy-2,2 -dimethylchromane-4-carboxylate (21). Colorless liquid was obtained in 74% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.6 Hz, 1H), 6.47 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.36 (d, *J* = 2.7 Hz, 1H), 4.23 (m, 2H), 3.75 (s, 4H), 2.20 (dd, *J* = 13.6, 10.4 Hz, 1H), 2.01 (dd, *J* = 13.5, 6.4 Hz, 1H), 1.40 (s, 3H), 1.34–1.22 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.09, 160.05, 154.48, 129.55, 110.20, 107.65, 102.08, 74.01, 61.20, 55.35, 39.26, 36.38, 28.82, 25.03, 14.38.

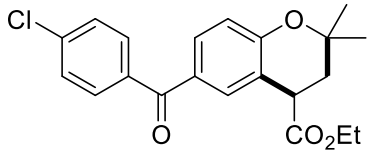
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, *J* = 8.2 Hz, 1H), 6.47 (d, *J* = 8.3 Hz, 1H), 6.41 (d, *J* = 8.1 Hz, 1H), 4.17 (m, 2H), 3.80–3.66 (m, 4H), 2.19–1.92 (m, 2H), 1.40 (s, 3H), 1.32–1.13 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.08, 158.07, 154.54, 128.63, 110.63, 108.25, 102.13, 73.72, 60.68, 55.56, 36.98, 36.94, 28.68, 24.54, 14.39. **HRMS (ESI)** calcd for $C_{15}H_{21}O_4^+$, $[M+H]^+$, 265.1434, found 265.1432.



Ethyl -2,2-dimethyl-7-(trifluoromethyl)chromane-4-carboxylate (22). Colorless liquid was obtained in 50% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 1H), 7.16 – 7.09 (m, 2H), 4.33 – 4.23 (m, 2H), 3.89 (m, 1H), 2.28 (m, 1H), 2.11 (m, 1H), 1.44 (s, 3H), 1.38 – 1.29 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.13, 153.79, 130.98 (q, *J* = 32.5 Hz), 129.78, 123.97 (d, *J* = 272.2 Hz), 121.70, 115.17 (q, *J* = 4.0 Hz), 74.56, 61.55, 39.68, 35.92, 28.54, 25.18, 14.30. **^{19}F NMR** (377 MHz, $CDCl_3$) δ-62.85. **HRMS (ESI)** calcd for $C_{15}H_{18}F_3O_3^+$, $[M+H]^+$, 302.1203, found 302.1201.

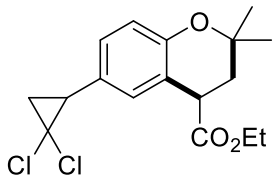


Ethyl -2,2,5-trimethylchromane-4-carboxylate and Ethyl -2,2,7-trimethylchromane-4-carboxylate (23). Colorless liquid was obtained in 68% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 – 6.97 (m, 1H), 6.78 – 6.59 (m, 2H), 4.29 – 4.10 (m, 2H), 3.87 – 3.68 (m, 1H), 2.32 – 1.96 (m, 5H), 1.44 – 1.20 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.38, 174.02, 153.93, 153.29, 138.72, 138.35, 128.58, 128.30, 122.24, 121.22, 118.21, 117.26, 115.70, 114.94, 73.64, 73.17, 61.17, 39.57, 38.93, 37.58, 36.37, 28.90, 27.18, 26.47, 24.99, 21.21, 19.58, 14.35, 14.23. **HRMS (ESI)** calcd for $C_{15}H_{21}O_3^+$, $[M+H]^+$, 249.1485, found 249.1486.

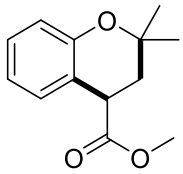


Ethyl-6-(4-chlorobenzoyl)-2,2-dimethylchromane-4-carboxylate (24). White solid was obtained in 56% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75–7.68 (m, 3H), 7.66 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 1H), 4.23 (m, 2H), 3.86 (dd, *J* = 10.2, 6.4 Hz, 1H), 2.28 (dd, *J* = 13.8, 10.2 Hz, 1H), 2.10 (dd, *J* = 13.8, 6.4 Hz, 1H), 1.44 (s, 3H), 1.33 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.26, 173.16, 157.98, 138.30, 136.67, 132.60, 131.29, 131.18, 129.19,

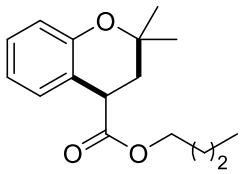
128.57, 118.00, 117.86, 75.19, 61.57, 39.42, 35.94, 28.52, 25.48, 14.28. **HRMS (ESI)** calcd for $C_{21}H_{22}ClO_4^+$, $[M+H]^+$, 373.1201, found 373.1201.



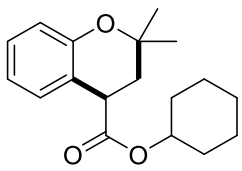
Ethyl-6-(2,2-dichlorocyclopropyl)-2,2-dimethylchromane-4-carboxylate (25). Faint yellow liquid was obtained in 57% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.08–6.98 (m, 2H), 6.78 (d, *J* = 8.7 Hz, 1H), 4.32–4.15 (m, 2H), 3.84 (m, 1H), 2.81 (dd, *J* = 10.7, 8.3 Hz, 1H), 2.23 (m, 1H), 2.04 (dd, *J* = 13.6, 6.4 Hz, 1H), 1.74 (m, 1H), 1.40 (s, 3H), 1.30 (dd, *J* = 13.0, 6.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.64, 173.61, 153.06, 153.05, 129.51, 129.43, 129.34, 128.98, 126.30, 126.08, 117.79, 117.74, 117.70, 117.68, 61.35, 61.33, 61.15, 61.02, 39.79, 36.16, 36.14, 35.04, 34.97, 28.73, 28.71, 26.00, 25.88, 25.20, 14.37. **HRMS (ESI)** calcd for $C_{17}H_{21}Cl_2O_3^+$, $[M+H]^+$, 343.0862, found 343.0861.



Methyl (R)-2,2-dimethylchromane-4-carboxylate (26). Faint yellow liquid was obtained in 64% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12–7.03 (m, 2H), 6.79 (m, 1H), 6.75–6.70 (m, 1H), 3.80 (dd, *J* = 10.5, 6.4 Hz, 1H), 3.69 (s, 3H), 2.16 (dd, *J* = 13.6, 10.5 Hz, 1H), 1.96 (dd, *J* = 13.5, 6.5 Hz, 1H), 1.33 (s, 3H), 1.20 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.34, 153.52, 128.90, 128.76, 120.19, 117.94, 117.80, 73.71, 52.39, 39.77, 36.31, 28.78, 25.05. **HRMS (ESI)** calcd for $C_{13}H_{17}O_3^+$, $[M+H]^+$,221.1172, found 221.1168.

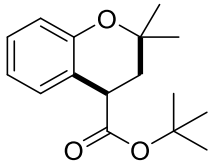


Butyl-2,2-dimethylchromane-4-carboxylate (27). Chartreuse liquid was obtained in 65% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.4 Hz, 2H), 6.86 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 4.17 (t, *J* = 6.7 Hz, 2H), 3.85 (dd, *J* = 10.6, 6.4 Hz, 1H), 2.23 (dd, *J* = 13.5, 10.5 Hz, 1H), 2.03 (dd, *J* = 13.5, 6.4 Hz, 1H), 1.65 (m, 2H), 1.39 (d, *J* = 13.4 Hz, 5H), 1.27 (s, 3H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.95, 153.53, 128.89, 128.67, 120.14, 118.00, 117.89, 73.72, 65.14, 39.91, 36.33, 30.74, 28.87, 25.05, 19.26, 13.82. **HRMS (ESI)** calcd for $C_{16}H_{23}O_3^+$, $[M+H]^+$, 263.1642, found 263.1639.

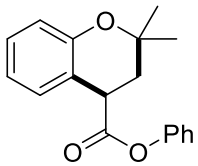


Cyclohexyl-2,2-dimethylchromane-4-carboxylate (28). Faint yellow liquid was obtained in 61% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20–7.10 (m, 2H), 6.85 (m, 1H), 6.80 (dd, *J* = 8.2, 1.2 Hz,

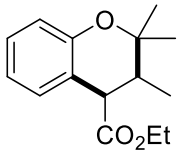
1H), 4.87 (m, 1H), 3.82 (dd, *J* = 10.5, 6.4 Hz, 1H), 2.23 (dd, *J* = 13.5, 10.5 Hz, 1H), 2.02 (dd, *J* = 13.6, 6.4 Hz, 1H), 1.96–1.81 (m, 2H), 1.79–1.65 (m, 2H), 1.59–1.31 (m, 9H), 1.28 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.29, 153.52, 128.89, 128.58, 120.09, 118.21, 117.84, 73.74, 73.51, 40.02, 36.30, 31.73, 31.57, 28.86, 25.46, 25.14, 23.85, 23.81. **HRMS (ESI)** calcd for $C_{18}H_{25}O_3^+$, $[M+H]^+$, 289.1798, found 289.1798.



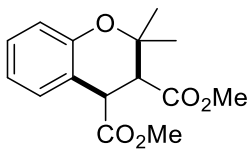
Tert-butyl-2,2-dimethylchromane-4-carboxylate (29). Faint yellow was obtained in 62% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (m, 1H), 7.17–7.09 (m, 1H), 6.86 (m, 1H), 6.79 (dd, *J* = 8.2, 1.3 Hz, 1H), 3.73 (dd, *J* = 10.4, 6.4 Hz, 1H), 2.19 (dd, *J* = 13.6, 10.4 Hz, 1H), 2.00 (dd, *J* = 13.6, 6.5 Hz, 1H), 1.49 (s, 9H), 1.40 (s, 3H), 1.27 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.99, 153.53, 128.88, 128.47, 120.05, 118.49, 117.81, 81.37, 73.75, 40.68, 36.33, 28.86, 28.17, 25.21. **HRMS (ESI)** calcd for $C_{16}H_{23}O_3^+$, $[M+H]^+$, 263.1642, found 263.1633.



Phenyl-2,2-dimethylchromane-4-carboxylate (30). Colorless liquid was obtained in 44% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.9 Hz, 2H), 7.33 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.25–7.16 (m, 2H), 7.14–7.05 (m, 2H), 6.92 (m, 1H), 6.85 (dd, *J* = 8.2, 1.2 Hz, 1H), 4.10 (dd, *J* = 10.4, 6.4 Hz, 1H), 2.40 (dd, *J* = 13.5, 10.4 Hz, 1H), 2.21 (dd, *J* = 13.5, 6.5 Hz, 1H), 1.48 (s, 3H), 1.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.41, 153.62, 150.84, 129.63, 129.02, 128.93, 126.14, 121.48, 120.40, 118.15, 117.39, 73.79, 40.05, 36.27, 28.87, 25.14. **HRMS (ESI)** calcd for $C_{18}H_{19}O_3^+$, $[M+H]^+$, 283.1329, found 283.1319.

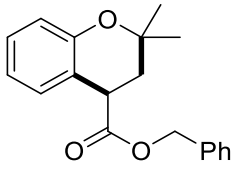


Ethyl-2,2,3-trimethylchromane-4-carboxylate (31). Faint yellow liquid was obtained in 29% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.89–6.75 (m, 2H), 4.25 (m, 2H), 3.47 (d, *J* = 11.3 Hz, 1H), 2.33 (m, 1H), 1.43 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.12 (s, 3H), 1.02 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.94, 153.18, 128.67, 127.70, 120.30, 119.37, 117.84, 61.19, 48.06, 39.00, 27.86, 19.23, 15.40, 14.43. **HRMS (ESI)** calcd for $C_{15}H_{21}O_3^+$, $[M+H]^+$, 249.1485, found 249.1484.

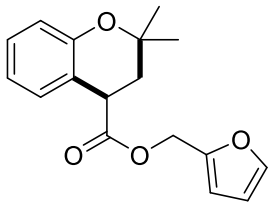


Dimethyl-2,2-dimethylchromane-3,4-dicarboxylate (32). Faint yellow liquid was obtained in 54% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (dt, *J* = 7.8, 1.4

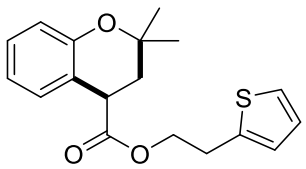
Hz, 1H), 7.17 (m, 1H), 6.89 (td, *J* = 7.5, 1.3 Hz, 1H), 6.83 (dd, *J* = 8.2, 1.3 Hz, 1H), 4.31 – 4.17 (d, *J* = 11.9 Hz, 1H), 3.76 (d, *J* = 12.2 Hz, 8H), 3.30 (d, *J* = 11.9 Hz, 1H), 1.53 (s, 4H), 1.23 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.60, 172.31, 152.40, 128.94, 127.55, 120.87, 117.94, 117.36, 77.48, 77.16, 76.84, 74.92, 52.60, 52.31, 50.71, 42.69, 28.57, 20.89. **HRMS (ESI)** calcd for $C_{15}H_{19}O_5^+$, $[M+H]^+$, 279.1233, found 279.1239.



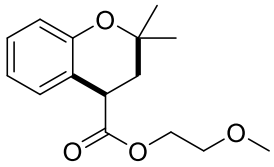
Benzyl-2,2-dimethylchromane-4-carboxylate (33). Yellow liquid was obtained in 64% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45–7.27 (m, 5H), 7.20–7.05 (m, 2H), 6.91–6.72 (m, 2H), 5.21 (s, 2H), 3.96–3.84 (m, 1H), 2.24 (dd, *J* = 13.6, 10.5 Hz, 1H), 2.04 (dd, *J* = 13.6, 6.4 Hz, 1H), 1.38 (s, 3H), 1.26 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.69, 153.54, 135.80, 128.94, 128.76, 128.71, 128.47, 128.45, 120.17, 117.92, 117.75, 73.72, 67.01, 39.83, 36.26, 28.82, 25.03. **HRMS (ESI)** calcd for $C_{19}H_{21}O_3^+$, $[M+H]^+$, 296.1485, found 296.1488.



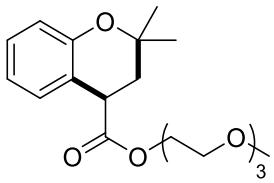
Furan-2-ylmethyl-2,2-dimethylchromane-4-carboxylate (34). Yellow liquid was obtained in 50% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 1.8 Hz, 1H), 7.19–7.04 (m, 2H), 6.90–6.73 (m, 2H), 6.43 (d, *J* = 3.4 Hz, 1H), 6.40–6.30 (m, 1H), 5.21–5.12 (m, 2H), 3.88 (dd, *J* = 10.5, 6.4 Hz, 1H), 2.22 (dd, *J* = 13.6, 10.5 Hz, 1H), 2.03 (dd, *J* = 13.6, 6.4 Hz, 1H), 1.37 (s, 3H), 1.25 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.53, 153.54, 149.34, 143.44, 128.89, 128.77, 120.19, 117.91, 117.64, 111.05, 110.73, 73.71, 58.69, 39.66, 36.19, 28.76, 25.05. **HRMS (ESI)** calcd for $C_{17}H_{19}O_4^+$, $[M+H]^+$, 287.1279, found 287.1274.



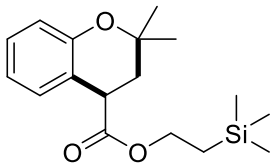
2-(thiophen-2-yl)ethyl-2,2-dimethylchromane-4-carboxylate (35). Yellow liquid was obtained in 67% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18–7.10 (m, 2H), 7.07 (m, 1H), 6.97–6.90 (m, 1H), 6.86–6.75 (m, 3H), 4.48–4.30 (m, 2H), 3.85 (dd, *J* = 10.3, 6.4 Hz, 1H), 3.19 (t, *J* = 6.6 Hz, 2H), 2.22 (dd, *J* = 13.6, 10.3 Hz, 1H), 2.01 (dd, *J* = 13.6, 6.5 Hz, 1H), 1.37 (s, 3H), 1.26 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.72, 153.53, 139.80, 129.02, 128.72, 127.02, 125.82, 124.18, 120.20, 117.90, 117.70, 73.70, 65.41, 39.79, 36.22, 29.35, 28.68, 25.13. **HRMS (ESI)** calcd for $C_{18}H_{21}O_3S^+$, $[M+H]^+$, 317.1206, found 317.1210.



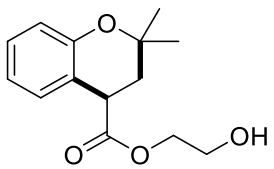
2-**methoxyethyl-2,2-dimethylchromane-4-carboxylate (36).** Faint yellow liquid was obtained in 62% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22–7.09 (m, 2H), 6.86 (m, 1H), 6.80 (dd, *J* = 8.2, 1.2 Hz, 1H), 4.42–4.26 (m, 2H), 3.92 (dd, *J* = 10.7, 6.4 Hz, 1H), 3.63 (t, *J* = 4.7 Hz, 2H), 3.39 (s, 3H), 2.24 (dd, *J* = 13.6, 10.8 Hz, 1H), 2.05 (dd, *J* = 13.6, 6.4 Hz, 1H), 1.41 (s, 3H), 1.27 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.92, 153.57, 128.85, 128.73, 120.19, 117.91, 117.84, 73.72, 70.49, 64.12, 59.08, 39.67, 36.28, 28.93, 24.96. **HRMS (ESI)** calcd for $C_{15}H_{21}O_4^+$, $[M+H]^+$, 265.1434, found 265.1429.



2-methoxyethyl (R)-2,2-dimethylchromane-4-carboxylate (37). Faint yellow liquid was obtained in 67% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (m, 1H), 7.14 (m, 1H), 6.86 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.80 (dd, *J* = 8.2, 1.3 Hz, 1H), 4.35 (m, 2H), 3.90 (dd, *J* = 10.6, 6.4 Hz, 1H), 3.73 (t, *J* = 4.8 Hz, 2H), 3.64 (d, *J* = 8.2 Hz, 6H), 3.55 (dd, *J* = 5.8, 3.5 Hz, 2H), 3.38 (s, 3H), 2.23 (dd, *J* = 13.6, 10.6 Hz, 1H), 2.05 (dd, *J* = 13.6, 6.4 Hz, 1H), 1.41 (s, 3H), 1.27 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.80, 153.50, 128.86, 128.66, 120.12, 117.84, 117.79, 73.66, 71.98, 70.68, 70.64, 70.61, 69.09, 64.17, 59.11, 39.62, 36.19, 28.84, 24.95. **HRMS (ESI)** calcd for $C_{19}H_{29}O_6^+$, $[M+H]^+$, 353.1959, found 353.1962.

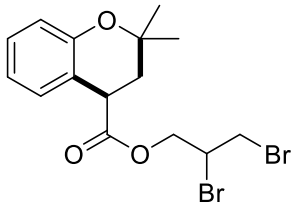


2-(trimethylsilyl)ethyl-2,2-dimethylchromane-4-carboxylate (38). Faint yellow liquid was obtained in 64% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22–7.05 (m, 2H), 6.93–6.83 (m, 1H), 6.83–6.75 (m, 1H), 4.26 (m, 2H), 3.84 (m, 1H), 2.23 (m, 1H), 2.03 (m, 1H), 1.41 (s, 3H), 1.28 (s, 3H), 1.08–0.97 (m, 2H), 0.04 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.02, 153.53, 128.90, 128.65, 120.15, 118.05, 117.89, 73.72, 63.58, 39.99, 36.34, 28.91, 25.03, 17.52, -1.39. **HRMS (ESI)** calcd for $C_{17}H_{26}O_3SiNa^+$, $[M+Na]^+$,329.1543, found 329.1544.

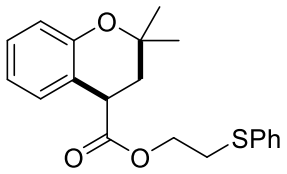


2-hydroxyethyl-2,2-dimethylchromane-4-carboxylate (39). Faint yellow liquid was obtained in 42% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20–7.11 (m, 2H), 6.87 (m, 1H), 6.81 (m, 1H), 4.31 (m,

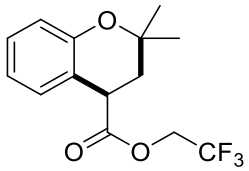
2H), 3.92 (m, 1H), 3.84 (t, *J* = 4.6 Hz, 2H), 2.23 (dd, *J* = 13.5, 10.6 Hz, 1H), 2.07 (dd, *J* = 13.4, 6.3 Hz, 1H), 2.00 (s, 1H), 1.42 (s, 3H), 1.28 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.31, 153.54, 128.87, 128.75, 120.27, 118.03, 117.70, 66.76, 61.23, 39.90, 36.34, 28.90, 24.94. **HRMS (ESI)** calcd for $C_{14}H_{19}O_4^+$, $[M+H]^+$, 251.1278, found 251.1277.



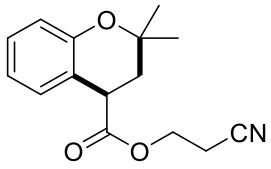
2,3-dibromopropyl-2,2-dimethylchromane-4-carboxylate (40). Faint yellow liquid was obtained in 53% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24–7.11 (m, 2H), 6.88 (m, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 4.71–4.48 (m, 2H), 4.35 (m, 1H), 3.94 (dd, *J* = 10.2, 6.5 Hz, 1H), 3.77 (m, 1H), 3.72–3.62 (m, 1H), 2.26 (m, 1H), 2.15–1.99 (m, 1H), 1.42 (d, *J* = 4.4 Hz, 3H), 1.29 (d, *J* = 1.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.18, 173.16, 153.52, 153.50, 129.27, 129.08, 128.94, 120.26, 120.24, 118.02, 118.00, 117.29, 117.25, 73.71, 65.83, 65.78, 46.69, 46.66, 39.84, 39.74, 36.28, 32.05, 32.00, 28.73, 28.58, 25.26, 25.11. **HRMS (ESI)** calcd for $C_{15}H_{19}Br_2O_3^+$, $[M+H]^+$, 404.9695, found 404.9699.



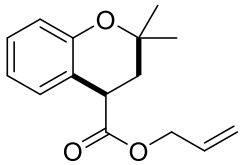
2-(phenylthio)ethyl-2,2-dimethylchromane-4-carboxylate (41). Faint yellow liquid was obtained in 53% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.19 (m, 7.9 Hz, 3H), 6.86 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 4.33 (t, *J* = 6.9 Hz, 2H), 3.83 (dd, *J* = 10.5, 6.5 Hz, 1H), 3.17 (t, *J* = 6.9 Hz, 2H), 2.18 (dd, *J* = 13.6, 10.5 Hz, 1H), 1.99 (dd, *J* = 13.6, 6.5 Hz, 1H), 1.39 (s, 3H), 1.26 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.70, 153.53, 135.06, 130.11, 129.22, 128.95, 128.80, 126.82, 120.22, 117.95, 117.61, 77.48, 77.16, 76.84, 73.70, 63.62, 39.74, 36.22, 32.48, 28.83, 25.00. **HRMS (ESI)** calcd for $C_{20}H_{23}O_3S^+$, $[M+H]^+$, 342.1290, found 342.1280.



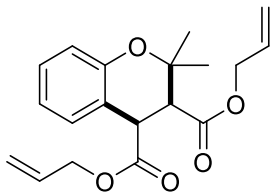
2,2,2-trifluoroethyl (R)-2,2-dimethylchromane-4-carboxylate (42). White solid was obtained in 52% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 4.57 (m, 2H), 3.98 (dd, *J* = 10.4, 6.5 Hz, 1H), 2.24 (dd, *J* = 13.6, 10.3 Hz, 1H), 2.09 (dd, *J* = 13.6, 6.5 Hz, 1H), 1.41 (s, 3H), 1.29 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.46, 153.56, 129.15, 128.86, 123.01 (q, *J* = 277.8 Hz).120.40, 118.14, 116.72, 73.67, 61.34, 60.97, 60.61, 60.24, 39.46, 36.19, 28.68, 25.02, 1.17.**^{19}F NMR** (377 MHz, $CDCl_3$) δ -73.60. **HRMS (ESI)** calcd for $C_{14}H_{15}F_3O_4Na^+$, $[M+Na]^+$, 311.0866, found 311.0865.



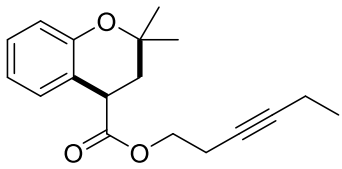
2-cyanoethyl (R)-2,2-dimethylchromane-4-carboxylate (43). Faint yellow liquid was obtained in 59% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 8.0 Hz, 2H), 6.92–6.85 (m, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 4.37 (t, *J* = 6.2 Hz, 2H), 3.93 (dd, *J* = 10.4, 6.5 Hz, 1H), 2.74 (t, *J* = 6.2 Hz, 2H), 2.24 (dd, *J* = 13.6, 10.4 Hz, 1H), 2.09 (dd, *J* = 13.6, 6.5 Hz, 1H), 1.42 (s, 3H), 1.28 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.43, 153.52, 128.99, 128.86, 120.32, 118.06, 117.08, 116.78, 73.68, 59.37, 39.59, 36.22, 28.73, 24.95, 18.09. **HRMS (ESI)** calcd for $C_{15}H_{18}NO_3^+$, $[M+H]^+$,260.1281, found 260.1279.x



Allyl-2,2-dimethylchromane-4-carboxylate (44). Faint yellow liquid was obtained in 51% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.8 Hz, 2H), 6.86 (m, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 5.94 (m, 1H), 5.34 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.26 (dd, *J* = 10.3, 1.4 Hz, 1H), 4.67 (dd, *J* = 5.9, 1.4 Hz, 2H), 3.89 (dd, *J* = 10.5, 6.4 Hz, 1H), 2.25 (dd, *J* = 13.5, 10.5 Hz, 1H), 2.05 (dd, *J* = 13.6, 6.4 Hz, 1H), 1.41 (s, 3H), 1.28 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.53, 153.55, 132.01, 128.93, 128.77, 120.20, 118.86, 117.94, 117.78, 73.73, 65.88, 39.84, 36.32, 28.85, 25.06.**HRMS (ESI)** calcd for $C_{15}H_{19}O_3^+$, $[M+H]^+$, 247.1329, found 247.1327.

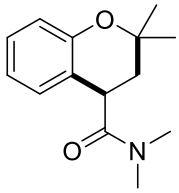


Diallyl-2,2-dimethylchromane-3,4-dicarboxylate (45). Faint yellow liquid was obtained in 31% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (m, 1H), 7.21–7.13 (m, 1H), 6.89 (m, 1H), 6.83 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.04–5.81 (m, 2H), 5.37 (m, 1H), 5.33 (m, 1H), 5.30–5.22 (m, 2H), 4.77–4.54 (m, 4H), 4.25 (d, *J* = 11.9 Hz, 1H), 3.32 (d, *J* = 11.9 Hz, 1H), 1.55 (s, 3H), 1.24 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.76, 171.48, 152.47, 131.75, 131.67, 128.99, 127.63, 120.91, 119.18, 118.99, 117.98, 117.41, 75.04, 66.20, 65.99, 50.85, 42.80, 28.68, 21.01. **HRMS (ESI)** calcd for $C_{19}H_{23}O_5^+$, $[M+H]^+$, 331.1540, found 331.1539.

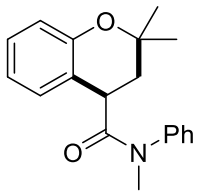


Hex-3-yn-1-yl-2,2-dimethylchromane-4-carboxylate (46). Faint yellow liquid was obtained in 67% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.7 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.89 – 6.83 (m, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 4.24 (m, 2H), 3.88 (dd, *J* = 10.5, 6.4 Hz, 1H), 2.53 (m, 2H), 2.25 (dd, *J* = 13.6, 10.5 Hz, 1H), 2.16 (m, 2H), 2.04 (dd, *J* = 13.6, 6.5 Hz, 1H), 1.41 (s, 3H), 1.28 (s, 3H), 1.12

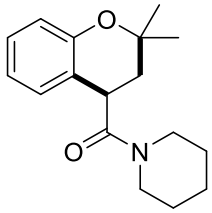
(t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.68, 153.54, 128.98, 128.73, 120.18, 117.91, 117.77, 83.67, 74.93, 73.71, 63.58, 39.75, 36.29, 28.82, 25.07, 19.36, 14.23, 12.48.**HRMS (ESI)** calcd for $C_{18}H_{23}O_3^+$, $[M+H]^+$, 287.1642, found 287.1644.



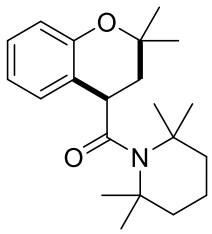
***N*,*N*,2,2-tetramethylchromane-4-carboxamide (47).** Faint yellow liquid was obtained in 47% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17–7.07 (m, 1H), 6.92 (d, *J* = 7.9 Hz, 1H), 6.88 – 6.75 (m, 2H), 4.15 (dd, *J* = 12.3, 5.8 Hz, 1H), 3.07 (d, *J* = 10.0 Hz, 6H), 2.18 (t, *J* = 12.9 Hz, 1H), 1.93 (dd, *J* = 13.5, 5.8 Hz, 1H), 1.46 (s, 3H), 1.29 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.45, 153.66, 128.39, 127.53, 120.39, 119.88, 117.89, 74.09, 37.86, 37.43, 36.55, 36.27, 30.02, 24.82. **HRMS (ESI)** calcd for $C_{14}H_{20}NO_2^+$, $[M+H]^+$, 234.1489, found 234.1487.



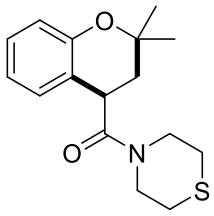
2,2-trimethyl-*N*-phenylchromane-4-carboxamide (48). Colorless solid was obtained in 39% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 3.85 (dd, *J* = 12.3, 5.6 Hz, 1H), 3.40 (s, 3H), 2.17 (t, *J* = 12.8 Hz, 1H), 1.78 (dd, *J* = 13.3, 5.6 Hz, 1H), 1.39 (s, 3H), 0.89 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.19, 153.84, 144.10, 130.17, 128.39, 128.22, 128.11, 127.14, 120.37, 120.21, 117.71, 73.71, 37.88, 37.29, 37.16, 29.92, 24.21. **HRMS (ESI)** calcd for $C_{19}H_{22}NO_2^+$, $[M+H]^+$, 295.1645, found 295.1647.



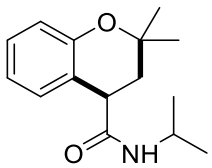
(2,2-dimethylchroman-4-yl)(piperidin-1-yl)methanone (49). Faint yellow liquid was obtained in 45% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 4.15 (dd, *J* = 12.5, 6.1 Hz, 1H), 3.79–3.66 (m, 1H), 3.59 (q, *J* = 9.0, 7.5 Hz, 1H), 3.38 (t, *J* = 5.6 Hz, 2H), 2.14 (t, *J* = 12.9 Hz, 1H), 1.96 (dd, *J* = 13.8, 6.1 Hz, 1H), 1.70–1.34 (m, 9H), 1.28 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.79, 153.36, 128.34, 127.76, 120.41, 120.18, 117.91, 74.20, 47.28, 43.53, 38.32, 36.74, 30.02, 26.49, 25.87, 24.68, 24.60. **HRMS (ESI)** calcd for $C_{17}H_{24}NO_2^+$, $[M+H]^+$, 274.1802, found 274.1801.



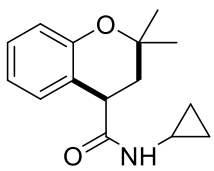
(2,2-dimethylchroman-4-yl)(2,2,6,6-tetramethylpiperidin-1-yl)methanone (50). White solid was obtained in 48% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18–7.06 (m, 2H), 6.87–6.75 (m, 2H), 4.23 (dd, *J* = 12.2, 5.5 Hz, 1H), 2.18 (t, *J* = 12.7 Hz, 1H), 2.03–1.70 (m, 7H), 1.50 (d, *J* = 32.1 Hz, 15H), 1.29 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.81, 154.10, 128.42, 128.03, 121.01, 119.89, 117.78, 74.02, 42.67, 38.60, 30.10, 24.64, 14.51. **HRMS (ESI)** calcd for $C_{21}H_{32}NO_2^+$, $[M+H]^+$, 330.2428, found 330.2430.



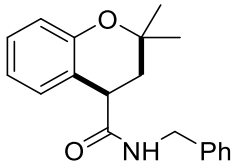
(2,2-dimethylchroman-4-yl)(thiomorpholino)methanone (51). Yellow solid was obtained in 35% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.8 Hz, 1H), 6.98 (t, *J* = 7.7 Hz, 1H), 6.87 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 4.39 (m, 1H), 4.14 (m, 1H), 4.06–3.46 (m, 3H), 3.41–3.22 (m, 1H), 2.04 (m, 2H), 1.87 (d, *J* = 7.0 Hz, 1H), 1.47 (s, 3H), 1.33–1.17 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.05, 153.25, 128.64, 127.57, 120.62, 119.75, 118.16, 74.24, 49.19, 48.54, 44.58, 43.90, 40.97, 40.18, 39.19, 38.83, 36.72, 36.59, 36.10, 35.74, 35.56, 35.28, 24.58, 24.51. **HRMS (ESI)** calcd for $C_{16}H_{22}NO_2S^+$, $[M+H]^+$, 292.1366, found 292.1365.



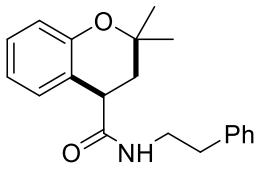
***N*-isopropyl-2,2-dimethylchromane-4-carboxamide (52).** White solid was obtained in 54% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23–7.13 (m, 1H), 7.10 (d, *J* = 7.3 Hz, 1H), 6.89 (m, 1H), 6.86–6.78 (m, 1H), 5.58–5.39 (m, 1H), 4.20–4.04 (m, 1H), 3.66 (dd, *J* = 9.0, 6.7 Hz, 1H), 2.20 (dd, *J* = 13.7, 9.0 Hz, 1H), 2.08 (dd, *J* = 13.7, 6.7 Hz, 1H), 1.37 (s, 3H), 1.29 (s, 3H), 1.11 (dd, *J* = 15.1, 6.6 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.84, 154.25, 129.35, 129.08, 120.47, 118.56, 118.31, 74.46, 41.94, 41.67, 37.24, 28.24, 25.85, 22.60, 22.58. **HRMS (ESI)** calcd for $C_{15}H_{22}NO_2^+$, $[M+H]^+$, 248.1645, found 248.1647.



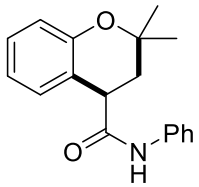
***N*-cyclopropyl-2,2-dimethylchromane-4-carboxamide (53).** White solid was obtained in 57% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22–7.13 (m, 1H), 7.10–7.02 (m, 1H), 6.88 (m, 2H), 6.83 (dd, *J* = 8.2, 1.3 Hz, 1H), 5.79 (s, 1H), 3.67 (dd, *J* = 9.0, 6.7 Hz, 1H), 2.72 (m, 1H), 2.18 (dd, *J* = 13.7, 9.0 Hz, 1H), 2.07 (dd, *J* = 13.7, 6.8 Hz, 1H), 1.31 (d, *J* = 31.2 Hz, 6H), 0.90–0.64 (m, 2H), 0.56–0.29 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.28, 154.21, 129.33, 129.15, 120.53, 118.41, 118.34, 74.45, 41.80, 37.23, 28.23, 25.82, 22.96, 6.73, 6.66. **HRMS (ESI)** calcd for $C_{15}H_{20}NO_3^+$, $[M+H]^+$,246.1489,found 246.1483.



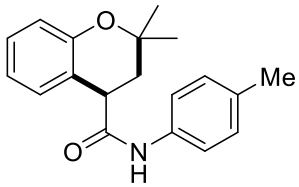
***N*-benzyl-2,2-dimethylchromane-4-carboxamide (54).** White solid was obtained in 59% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35–7.20 (m, 4H), 7.20–7.08 (m, 2H), 6.87 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.05–5.95 (m, 1H), 4.46 (dd, *J* = 5.9, 2.5 Hz, 2H), 3.76 (dd, *J* = 9.2, 6.7 Hz, 1H), 2.17 (dd, *J* = 28.9, 8.0 Hz, 1H), 1.68 (s, 1H), 1.36 (s, 3H), 1.28 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.78, 154.28, 138.12, 129.46, 129.21, 128.83, 127.84, 127.67, 120.56, 118.39, 118.31,74.46, 43.92, 42.00, 37.38, 28.35, 25.69, 1.16.**HRMS (ESI)** calcd for $C_{19}H_{22}NO_2^+$, $[M+H]^+$, 296.1645, found 296.1650.



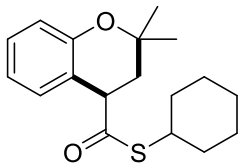
2,2-dimethyl-*N*-phenethylchromane-4-carboxamide (55). White solid was obtained in 55% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 6.5 Hz, 1H), 7.25–7.18 (m, 2H), 7.14 (m, 3H), 6.99–6.88 (m, 1H), 6.86–6.70 (m, 2H), 5.74 (t, *J* = 5.9 Hz, 1H), 3.68–3.59 (m, 1H), 3.59–3.52 (m, 1H), 3.47 (m, 1H), 2.79 (m, 2H), 2.15 (dd, *J* = 13.7, 8.8 Hz, 1H), 2.03 (dd, *J* = 13.6, 6.9 Hz, 1H), 1.28 (d, *J* = 23.5 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.70, 154.16, 138.67, 129.44, 129.02, 128.80, 128.71, 126.61, 120.44, 118.28, 118.22, 74.38, 41.83, 40.87, 37.14, 35.49, 28.09, 25.87. **HRMS (ESI)** calcd for $C_{20}H_{24}NO_2^+$, $[M+H]^+$,310.1802, found 310.1803.



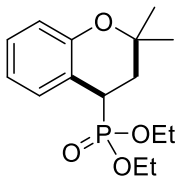
2,2-dimethyl-*N*-phenylchromane-4-carboxamide (56). White solid was obtained in 56% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50–7.40 (m, 3H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.24–7.17 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.93 (m, 1H), 6.90–6.85 (m, 1H), 3.85 (dd, *J* = 9.1, 6.7 Hz, 1H), 2.31 (dd, *J* = 13.7, 9.1 Hz, 1H), 2.16 (dd, *J* = 13.7, 6.7 Hz, 1H), 1.40 (s, 3H), 1.30 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.07, 154.36, 137.66, 129.53, 129.44, 129.11, 124.72, 120.80, 120.07, 118.58, 118.04, 74.52, 43.03, 37.26, 28.33, 25.77. **HRMS (ESI)** calcd for $C_{18}H_{20}NO_2^+$, $[M+H]^+$,282.1489, found 282.1485.



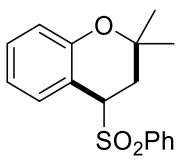
2,2-dimethyl-*N*-(*p*-tolyl)chromane-4-carboxamide (57). White solid was obtained in 57% isolated yield. **^{1}H NMR** (400 MHz,$CDCl_3$) δ 7.43 (s, 1H), 7.32 (dd, *J* = 6.4, 4.3 Hz, 2H), 7.25–7.16 (m, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.92 (m, 1H), 6.90–6.83 (m, 1H), 3.83 (dd, *J* = 9.1, 6.6 Hz, 1H), 2.30 (s, 4H), 2.15 (dd, *J* = 13.7, 6.7 Hz, 1H), 1.39 (s, 3H), 1.30 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.95, 154.35, 135.09, 134.38, 129.57, 129.46, 120.76, 120.17, 118.53, 118.15, 74.51, 42.91, 37.23, 28.29, 25.80, 20.98. **HRMS (ESI)** calcd for $C_{19}H_{22}NO_2^+$, $[M+H]^+$,296.1645, found 296.1648.



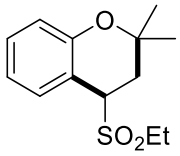
***S*-cyclohexyl-2,2-dimethylchromane-4-carbothioate (58).** Colorless liquid was obtained in 36% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (m, 2H), 6.86 (t, *J* = 7.5 Hz, 1H), 6.83–6.76 (m, 1H), 3.97 (dd, *J* = 10.6, 6.4 Hz, 1H), 3.57 (m, 1H), 2.21 (dd, *J* = 13.5, 10.6 Hz, 1H), 2.04 (dd, *J* = 13.5, 6.5 Hz, 1H), 1.99–1.86 (m, 2H), 1.71 (t, *J* = 7.1 Hz, 2H), 1.42 (d, *J* = 6.1 Hz, 7H), 1.26 (s, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.38, 153.87, 129.32, 129.02, 120.13, 118.09, 117.94, 74.05, 48.38, 42.88, 37.49, 33.14, 33.03, 29.21, 26.10, 25.67, 24.97. **HRMS (ESI)** calcd for $C_{18}H_{25}O_2S^+$, $[M+H]^+$,305.1570, found 305.1571.



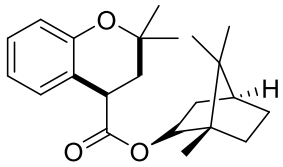
Diethyl-(2,2-dimethylchroman-4-yl)phosphonate (59). White solid was obtained in 67% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 4.24–3.99 (m, 3H), 3.98–3.80 (m, 1H), 3.42 (m, 1H), 2.19–1.95 (m, 2H), 1.47 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.19 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.00, 153.92, 129.46, 129.41, 128.48, 128.46, 120.22, 120.20, 118.09, 115.96, 115.91, 73.28, 73.16, 63.09, 63.03, 61.82, 61.75, 34.95, 34.90, 32.28, 30.84, 29.80, 23.20, 16.55, 16.49, 16.43, 16.38. **HRMS (ESI)** calcd for $C_{15}H_{24}O_4P^+$, $[M+H]^+$,299.1407, found 299.1406.



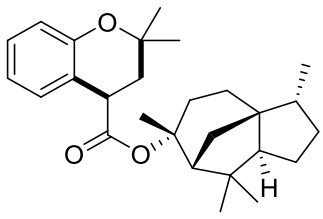
2,2-dimethyl-4-(phenylsulfonyl)chromane (60). Yellow solid was obtained in 50% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.69–7.61 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.25–7.14 (m, 1H), 7.02–6.90 (m, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 4.55 (dd, *J* = 11.4, 7.5 Hz, 1H), 2.19 (dd, *J* = 13.8, 7.6 Hz, 1H), 2.01 (dd, *J* = 13.9, 11.5 Hz, 1H), 1.37 (s, 3H), 1.14 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.71, 136.16, 133.97, 130.30, 129.70, 129.66, 128.95, 120.74, 118.47, 113.38, 74.15, 59.29, 36.08, 29.77, 23.24. **HRMS (ESI)** calcd for $C_{17}H_{19}O_3S^+$, $[M+H]^+$,303.1055 , found 303.1060.



4-(ethylsulfonyl)-2,2-dimethylchromane (61). White solid was obtained in 63% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96–7.87 (m, 1H), 7.27–7.22 (m, 1H), 6.95 (m, 1H), 6.85 (dd, *J* = 8.3, 1.3 Hz, 1H), 4.40 (dd, *J* = 11.9, 7.6 Hz, 1H), 2.88–2.74 (m, 1H), 2.74–2.60 (m, 1H), 2.42 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.16 (dd, *J* = 14.0, 11.9 Hz, 1H), 1.51 (s, 3H), 1.29 (t, *J* = 7.5 Hz, 3H), 1.22 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.45, 130.38, 129.08, 121.18, 118.76, 113.42, 74.47, 58.01, 41.81, 36.19, 29.89, 23.03, 5.13. **HRMS (ESI)** calcd for $C_{13}H_{19}O_3S^+$, $[M+H]^+$,255.1049, found 255.1044.

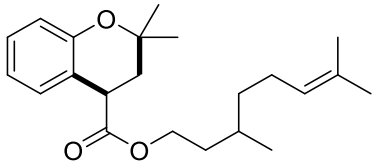


1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl (R)-2,2-dimethylchromane-4-carboxylate (62). Faint yellow liquid was obtained in 63% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (q, *J* = 7.9, 7.1 Hz, 2H), 6.85 (m, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 4.72 (m, 1H), 3.81 (dd, *J* = 10.1, 6.6 Hz, 1H), 2.20 (m, 1H), 2.03 (dd, *J* = 13.6, 6.5 Hz, 1H), 1.84 (m ,1H), 1.71 (m, 3H), 1.55 (m, 1H), 1.39 (d, *J* = 6.5 Hz, 3H), 1.28 (d, *J* = 4.5 Hz, 3H), 1.21–1.03 (m, 2H), 0.86 (d, *J* = 3.9 Hz, 3H), 0.81 (dd, *J* = 8.6, 6.8 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.41, 173.29, 153.46, 129.50, 129.05, 128.58, 120.09, 120.00, 118.03, 117.99, 117.83, 117.76, 82.09, 81.93, 73.71, 48.98, 48.78, 47.04, 45.12, 40.35, 40.16, 38.89, 36.52, 36.34, 33.91, 33.89, 28.86, 28.62, 27.13, 25.32, 25.07, 20.21, 20.19, 20.00, 19.93, 11.79, 11.70. **HRMS (ESI)** calcd for $C_{22}H_{31}O_3^+$, $[M+H]^+$,342.2268, found 342.2269.

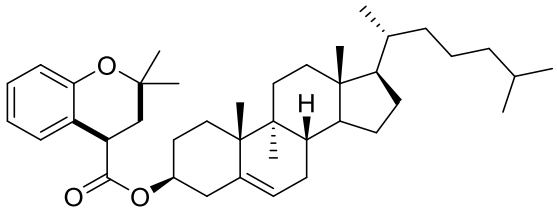


3,6,8,8-tetramethyloctahydro-1*H*-3a,7-methanoazulen-6-yl (R)-2,2-dimethylchromane-4-carboxylate (63). Faint yellow liquid was obtained in 59% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28–7.20 (m, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 6.89 (m, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 3.75 (m, 1H), 2.43 (t, *J* = 4.8 Hz, 1H), 2.33–2.12 (m, 3H), 2.12–1.97 (m, 2H), 1.97–1.78 (m, 3H), 1.70 (m, 3H), 1.61 (d, *J* = 11.2 Hz, 3H), 1.50–1.40 (m, 7H), 1.30 (d, *J* = 5.8 Hz, 3H), 1.17 (d, *J* = 21.3 Hz, 3H), 1.02 (d, *J* = 10.2

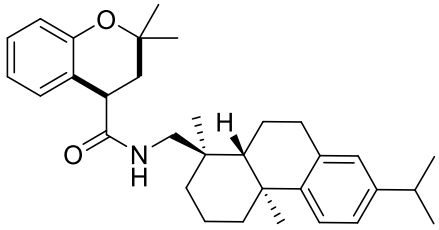
Hz, 3H), 0.88 (dd, *J* = 7.1, 4.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.68, 172.62, 153.61, 153.55, 129.03, 128.83, 128.47, 128.44, 120.08, 119.97, 118.51, 118.34, 117.83, 117.79, 87.88, 87.65, 73.70, 73.67, 57.71, 57.31, 56.78, 56.74, 54.05, 54.02, 43.57, 43.55, 41.41, 41.15, 40.58, 37.06, 36.29, 36.17, 33.28, 32.91, 31.40, 29.23, 28.90, 28.71, 28.64, 27.49, 27.46, 25.80, 25.53, 25.41, 25.17, 24.79, 15.65. **HRMS (ESI)** calcd for $C_{27}H_{38}O_3Na^+$, $[M+H]^+$,433.2713, found 433.2713.



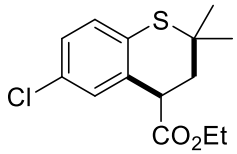
3,7-dimethyloct-6-en-1-yl -2,2-dimethylchromane-4-carboxylate (64). Faint yellow liquid was obtained in 70% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.2 Hz, 2H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 5.08 (t, *J* = 7.2 Hz, 1H), 4.21 (q, *J* = 6.6, 6.1 Hz, 2H), 3.85 (dd, *J* = 10.5, 6.4 Hz, 1H), 3.20 (dd, *J* = 8.7, 4.8 Hz, 1H), 2.23 (dd, *J* = 13.6, 10.5 Hz, 1H), 2.03 (dd, *J* = 13.7, 6.4 Hz, 1H), 1.92 (dd, *J* = 10.7, 5.0 Hz, 2H), 1.73 (dd, *J* = 9.1, 4.7 Hz, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.40 (s, 3H), 1.35–1.29 (m, 3H), 1.27 (s, 3H), 0.91 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.90, 153.50, 131.47, 128.89, 128.87, 128.65, 124.59, 120.12, 117.95, 117.88, 73.69, 63.79, 55.85, 39.90, 37.04, 36.29, 35.54, 35.03, 29.55, 28.82, 25.84, 25.56, 25.49, 25.04, 24.80, 19.47, 17.77. **HRMS (ESI)** calcd for $C_{22}H_{33}O_3^+$, $[M+H]^+$,345.2424, found 345.2426.



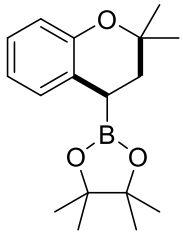
9,10,13-trimethyl-17-(-6-methylheptan-2-yl) 2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl-2,2-dimethylchromane-4-carboxylate (65). White solid was obtained in 59% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20–7.10 (m, 2H), 6.86 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 5.40 (d, *J* = 4.5 Hz, 1H), 4.73 (m, 1H), 3.82 (dd, *J* = 10.6, 6.3 Hz, 1H), 2.35 (dd, *J* = 19.4, 7.6 Hz, 2H), 2.22 (dd, *J* = 13.6, 10.6 Hz, 1H), 2.11–1.73 (m, 6H), 1.71–0.79 (m, 41H), 0.68 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.25, 153.53, 139.58, 128.81, 128.62, 122.97, 122.95, 120.14, 118.14, 117.87, 74.85, 73.73, 56.80, 56.25, 50.12, 42.43, 39.98, 39.84, 39.65, 38.23, 38.08, 37.10, 37.06, 36.73, 36.31, 35.93, 32.04, 31.97, 28.93, 28.37, 28.15, 27.94, 27.77, 25.09, 24.42, 23.96, 22.97, 22.71, 21.16, 19.48, 18.85, 11.99. **HRMS (ESI)** calcd for $C_{39}H_{59}O_3^+$, $[M+H]^+$,574,4459, found 574,4453.



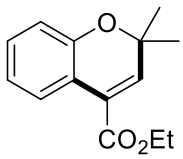
***N*-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-2,2-dimethylchromane-4-carboxamide (66).** Faint yellow liquid was obtained in 56% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.2 Hz, 1H), 7.14–6.98 (m, 3H), 6.93–6.86 (m, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.58 (t, *J* = 7.4 Hz, 1H), 5.71–5.60 (m, 1H), 3.83–3.66 (m, 1H), 3.42 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.95 (dd, *J* = 13.6, 4.9 Hz, 1H), 2.91–2.81 (m, 2H), 2.60 (m, 1H), 2.33 (d, *J* = 12.4 Hz, 1H), 2.21 (dd, *J* = 13.6, 9.0 Hz, 1H), 2.16–2.04 (m, 1H), 1.87–1.60 (m, 4H), 1.37 (s, 5H), 1.31–1.25 (m, 10H), 1.24 (s, 4H), 0.95 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.94, 154.18, 147.16, 145.71, 134.71, 129.73, 129.14, 126.93, 124.24, 123.90, 120.38, 118.35, 74.50, 50.19, 45.50, 42.19, 38.73, 37.84, 37.50, 37.47, 36.38, 33.61, 30.08, 28.35, 25.57, 25.17, 24.25, 24.10, 18.98, 18.68. **HRMS (ESI)** calcd for $C_{32}H_{44}NO_2^+$, $[M+H]^+$,474.3367, found 474.3372.



Ethyl-6-chloro-2,2-dimethylthiochromane-4-carboxylate (67). Faint yellow liquid was obtained in 31% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 2.3 Hz, 1H), 7.10 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 4.26 (m, 2H), 3.90 (dd, *J* = 11.1, 5.6 Hz, 1H), 2.31 (dd, *J* = 13.6, 11.0 Hz, 1H), 2.13 (dd, *J* = 13.6, 5.6 Hz, 1H), 1.43 (s, 3H), 1.39 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.76, 132.50, 131.34, 129.95, 129.04, 128.82, 127.67, 61.53, 44.49, 41.82, 41.30, 30.73, 29.12, 14.32. **HRMS (ESI)** calcd for $C_{14}H_{17}O_2ClS^+$, $[M+H]^+$,284.0638, found 284.0640.

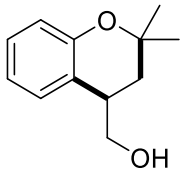


2-(2,2-dimethylchroman-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (68). White liquid was obtained in 48% isolated yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.18 (m, *J* = 7.7, 1.5 Hz, 1H), 7.05 (m, *J* = 7.1, 1.3 Hz, 1H), 6.81 (m, *J* = 7.5, 1.3 Hz, 1H), 6.76 (m, *J* = 8.2, 1.3 Hz, 1H), 2.61 (m, *J* = 10.6, 6.8 Hz, 1H), 2.00– 1.80 (m, 2H), 1.38 (s, 3H), 1.27 (d, *J* = 4.1 Hz, 12H), 1.24 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.68, 129.71, 126.83, 121.73, 119.74, 117.65, 83.77, 73.41, 34.99, 28.91, 24.94, 24.92, 24.86. **HRMS (ESI)** calcd for $C_{17}H_{26}O_3B^+$, $[M+H]^+$,289.1975, found 289.1980.

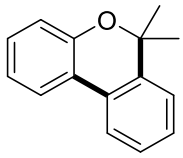


Ethyl 2,2-dimethyl-2*H*-chromene-4-carboxylate (69). Faint yellow liquid was obtained in 55% isolated yield. **H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.94 – 6.84 (m, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 4.10 – 3.85 (m, 2H), 3.06 (d, *J* = 5.7 Hz, 1H), 2.03 – 1.73 (m, 3H), 1.45 (s, 3H), 1.25 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.69, 128.07, 126.80, 121.40, 120.26,

118.02, 74.35, 65.71, 37.05, 34.29, 30.14, 24.28, 1.16. **HRMS (ESI)** calcd for $C_{14}H_{17}O_3^+$, $[M+H]^+$,233.1178, found 233.1180.

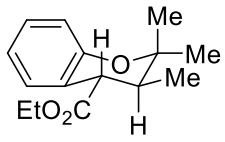


2,2-dimethylchroman-4-yl)methanol (70). Faint yellow liquid was obtained in 94% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.24 (m, 1H), 7.17–7.09 (m, 1H), 6.93–6.84 (m, 1H), 6.84–6.76 (m, 1H), 3.97 (m, *J* = 10.8, 4.9 Hz, 2H), 3.06 (m, *J* = 11.7, 5.7 Hz, 1H), 1.95 (m, *J* = 13.5, 6.4 Hz, 1H), 1.83 (t, *J* = 12.7 Hz, 1H), 1.45 (s, 3H), 1.25 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.69, 128.07, 126.80, 121.40, 120.26, 118.02, 77.48, 77.16, 76.84, 74.35, 65.72, 37.05, 34.30, 30.14, 24.29, 1.17. **HRMS (ESI)** calcd for $C_{12}H_{17}O_2^+$, $[M+H]^+$,193.1223, found 193.1217.



6,6-dimethyl-6*H*-benzo[*c*]chromene (71). Faint yellow liquid was obtained in 91% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31–8.19 (m, 1H), 7.82–7.72 (m, 1H), 7.54–7.43 (m, 2H), 7.38 (d, *J* = 8.5 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 1H), 4.29 (m, 2H), 4.00 (dd, *J* = 10.0, 6.5 Hz, 1H), 2.37 (dd, *J* = 13.5, 10.0 Hz, 1H), 2.18 (dd, *J* = 13.5, 6.5 Hz, 1H), 1.56 (s, 3H), 1.39 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.18, 148.78, 133.91, 127.44, 126.47, 126.32, 125.85, 125.27, 122.14, 119.48, 111.41, 74.29, 61.29, 40.30, 36.42, 28.71, 25.27, 14.38. **HRMS (ESI)** calcd for $C_{15}H_{15}O^+$, $[M+H]^+$,211.1123, found 211.1112.

These ^{1}H NMR and ^{13}C NMR indicate these products have excellent diastereoselectivity (＞20:1 d.r.). We confirm that the product **31** (number after revised manuscript) is shown in the following structure.

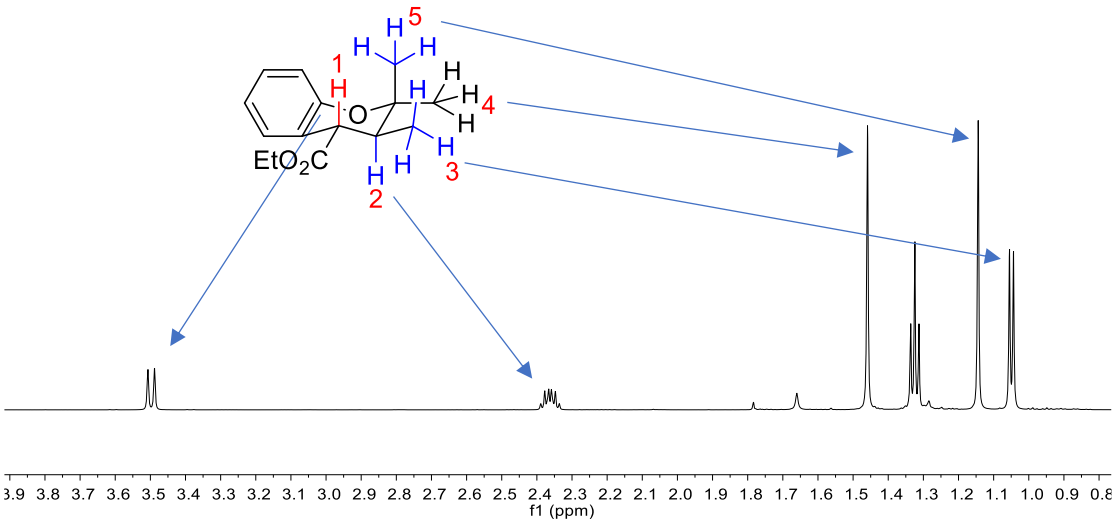


31

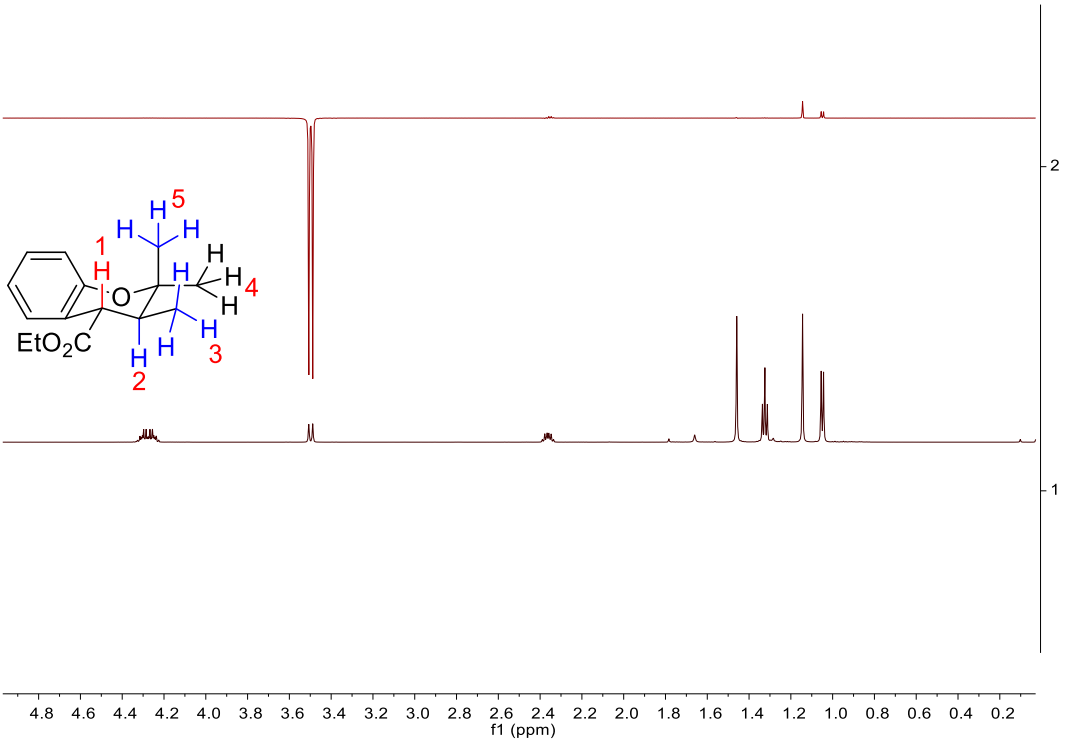
There are two reasons to support above structure.

1) The coupling constant (*J*) of two axial C-H bonds is between 8-13 Hz; The coupling constant (*J*) of two equatorial C-H bonds is between 0-5 Hz; The coupling constant (*J*) of one equatorial C-H bond and one axial C-H bond is between 1-6 Hz (*Williams D H, Fleming I, Spectroscopic Methods in Organic Chemistry, McGraw-Hill, London, 1995, 92-94*). For the product **31**, the coupling constants (*J*) of H are 11.3 Hz (1) and 11.0 Hz (2), which indicate both C-H (1, 2) bonds are axial.

2) When irradiated at the frequency of the proton signal (1), a notable NOE enhancement was observed in the H signal (3, 5), and a weak NOE enhancement was observed in the H signal (2). The result indicate the spatial shift of H (1) and H (3, 5) is close, and the spatial shift of H (1) and H (3, 5) is farther than the spatial shift of H (1) and H (3, 5), which indicate both C-H (1, 2) bonds are axial.

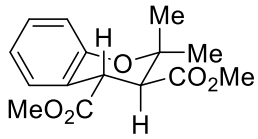


^{1}H NMR spectrum

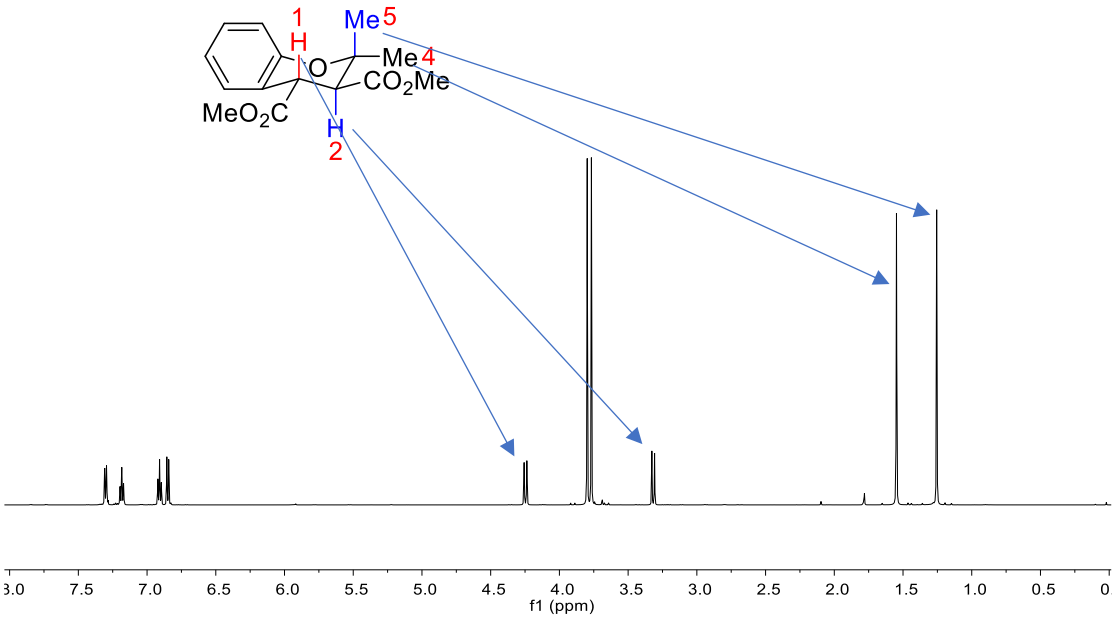


1D NOE spectrum

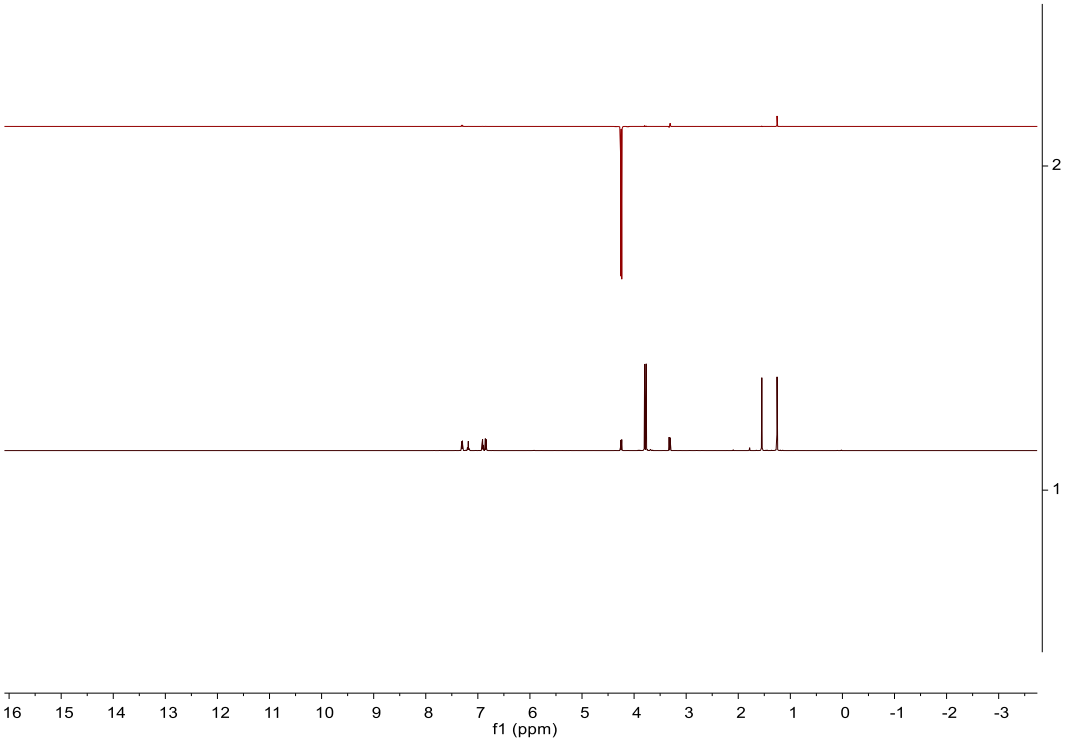
According to these same reasons, we confirm that the product **32** (number after revised manuscript) is shown in the following structure.



The coupling constants (*J*) of H are 11.9 Hz (1) and 11.8 Hz (2), which indicate these double C-H bonds are axial bonds. The NOE spectrum indicate both C-H (1, 2) bonds are axial.

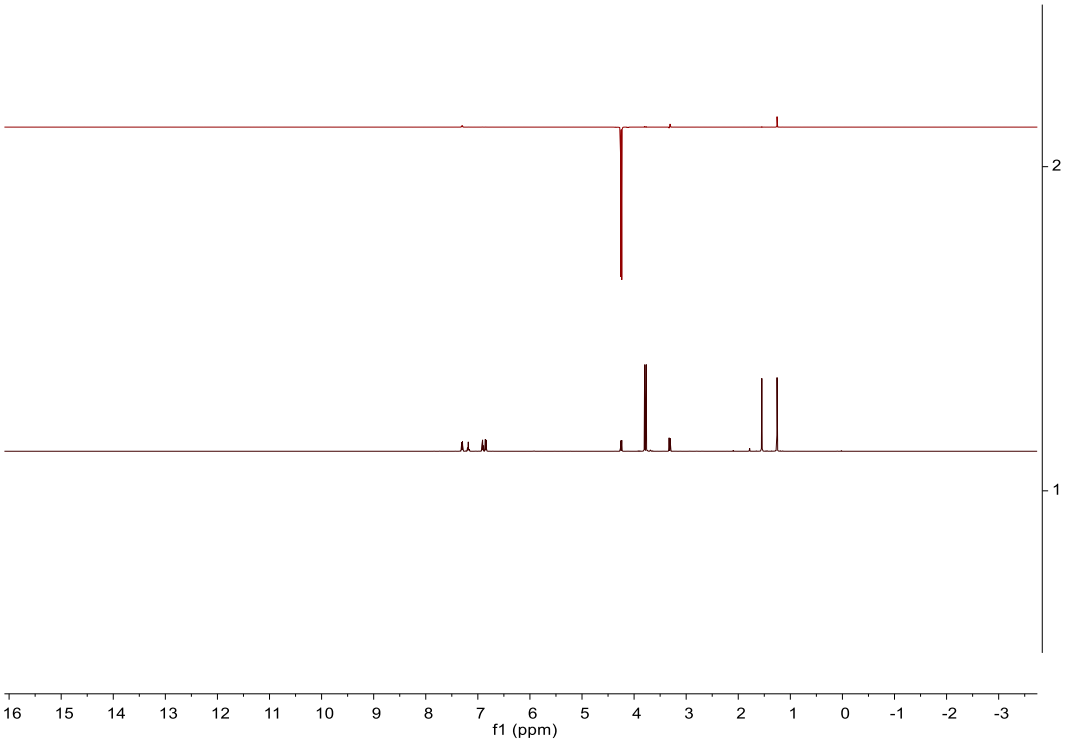


^{1}H NMR spectrum



1D NOE spectrum

According to these coupling constants (*J*), the major diastereomers of other products **62-66** is also same as **31** and **32**.

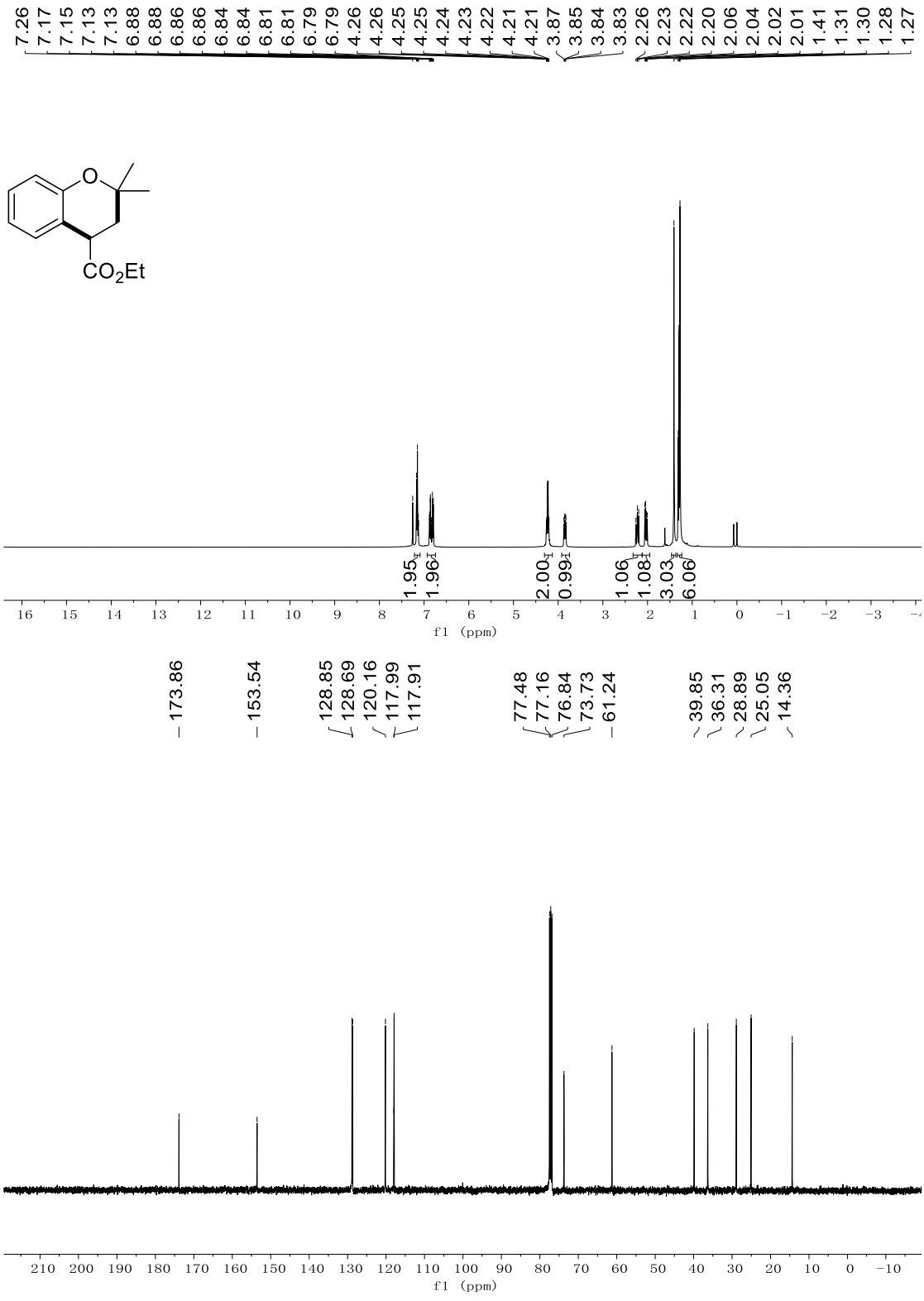


1D NOE spectrum

According to these coupling constants (*J*), the major diastereomers of other products **62**-**66** is also same as **31** and **32**.

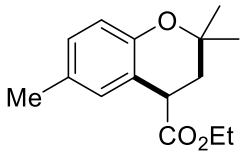
NMR Spectra of Products

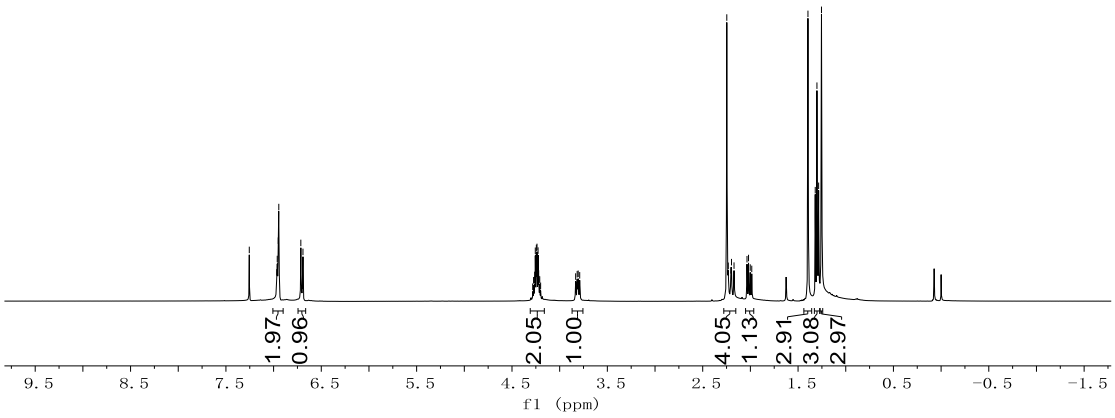
1

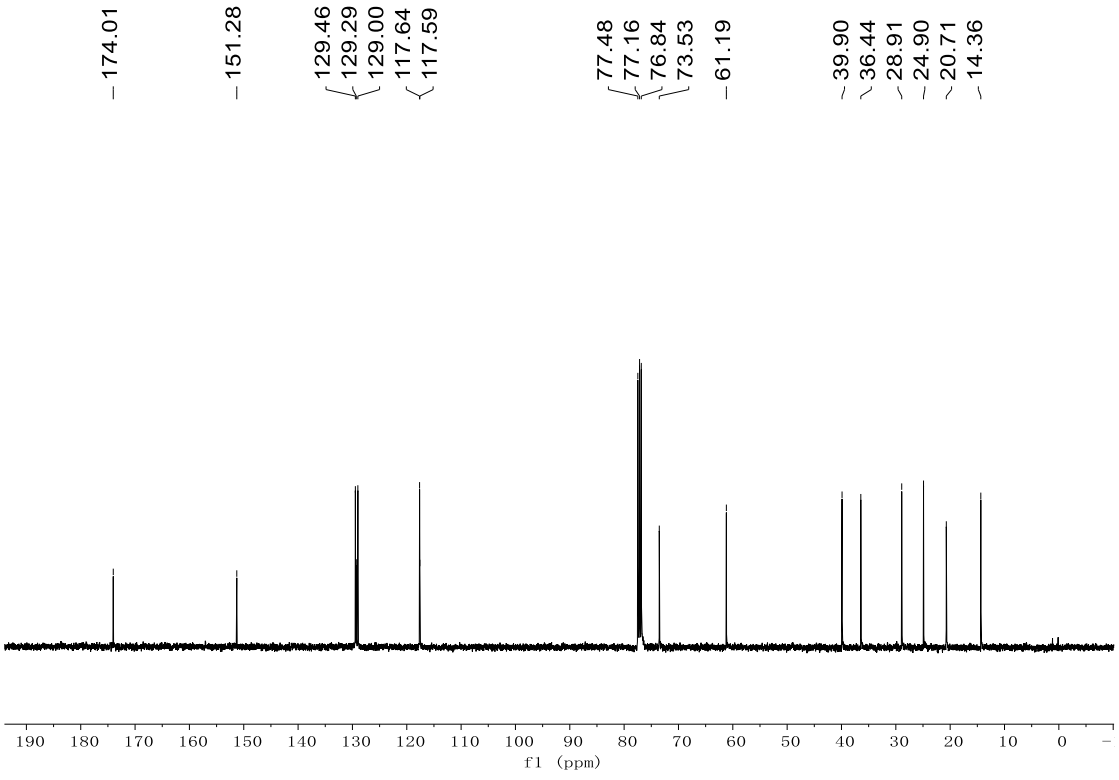


2

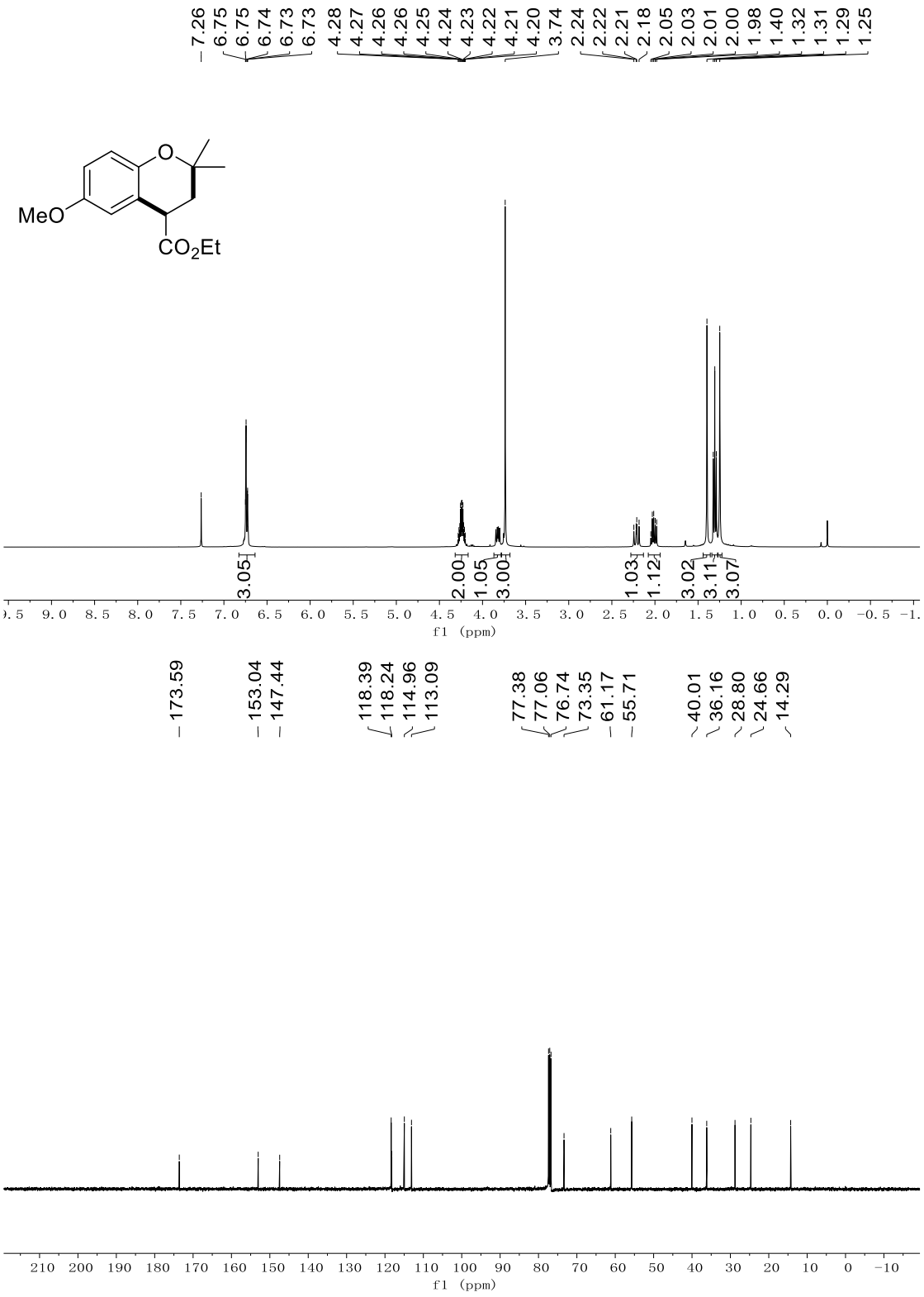

7.26
6.97
6.96
6.95
6.95
6.71
6.69
4.28
4.27
4.26
4.26
4.26
4.24
4.24
4.23
4.22
4.22
4.21
4.20
3.83
3.82
3.81
3.79
2.25
2.23
2.21
2.20
2.17
2.04
2.02
2.00
1.99
1.40
1.32
1.30
1.28
1.25


O
Me
CO2Et

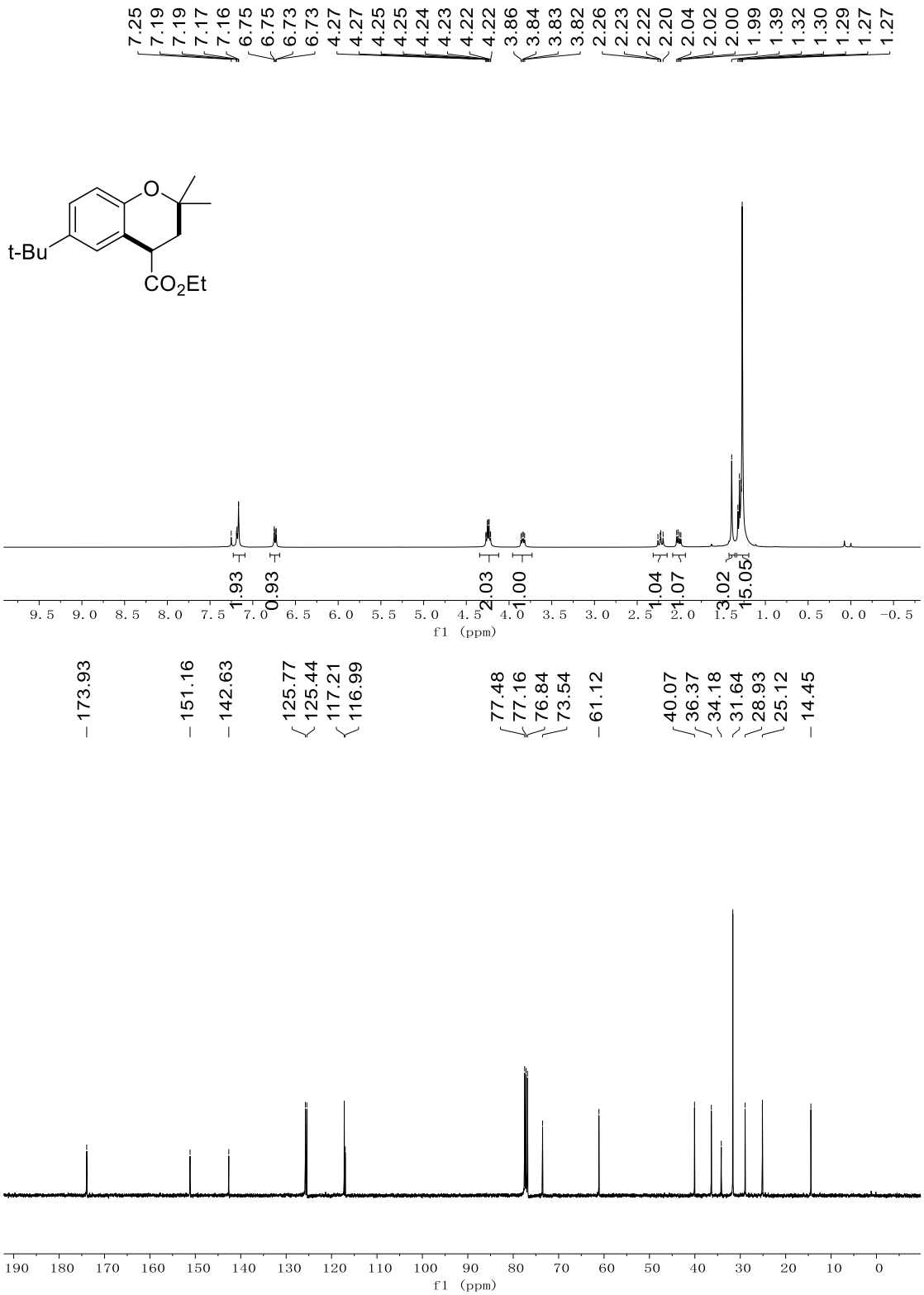

1.97
0.96
2.05
1.00
4.05
1.13
2.91
3.08
2.97
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
−1.5
f1 (ppm)


174.01
151.28
129.46
129.29
129.00
117.64
117.59
77.48
77.16
76.84
73.53
61.19
39.90
36.44
28.91
24.90
20.71
14.36
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

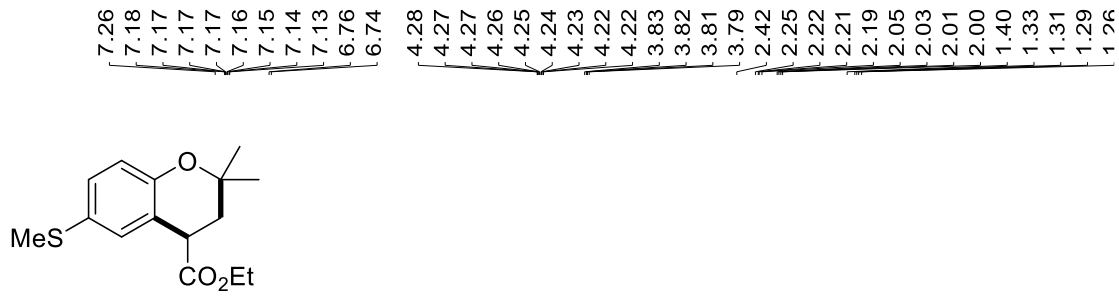
3

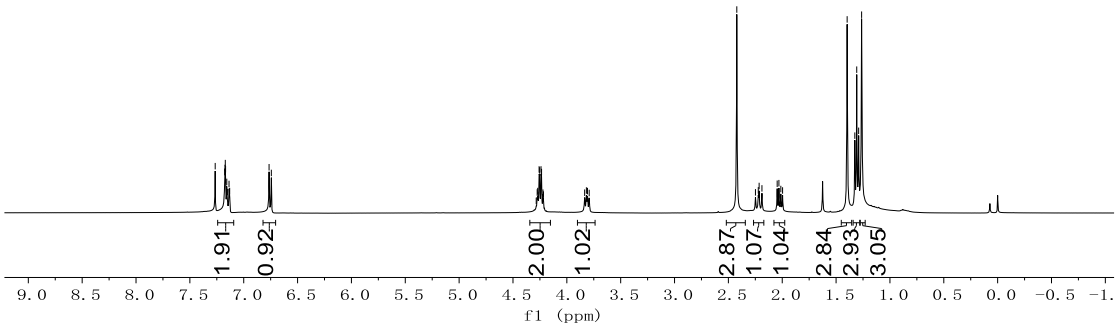

7.26
6.75
6.75
6.74
6.73
6.73
4.28
4.27
4.26
4.26
4.25
4.24
4.23
4.22
4.21
4.20
3.74
2.24
2.22
2.21
2.18
2.05
2.03
2.01
2.00
1.98
1.40
1.32
1.31
1.29
1.25
O
MeO
CO2Et
3.05
2.00
1.05
3.00
1.03
1.12
3.02
3.11
3.07
f1 (ppm)
173.59
153.04
147.44
118.39
118.24
114.96
113.09
77.38
77.06
76.74
73.35
61.17
55.71
40.01
36.16
28.80
24.66
14.29
f1 (ppm)

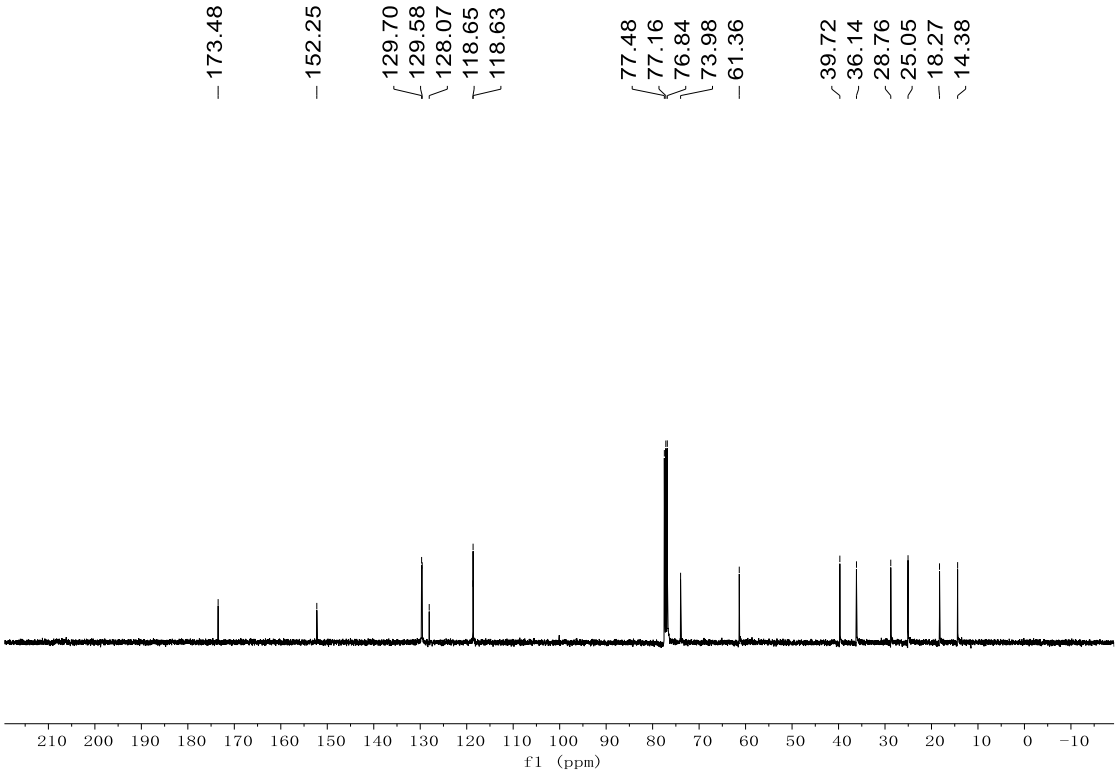
4


7.25
7.19
7.19
7.17
7.16
6.75
6.75
6.73
6.73
4.27
4.27
4.25
4.25
4.24
4.23
4.22
4.22
3.86
3.84
3.83
3.82
2.26
2.23
2.22
2.20
2.04
2.02
2.00
1.99
1.39
1.32
1.30
1.29
1.27
1.27
t-Bu
O
CO2Et
1.93
0.93
2.03
1.00
1.04
1.07
3.02
15.05
f1 (ppm)
173.93
151.16
142.63
125.77
125.44
117.21
116.99
77.48
77.16
76.84
73.54
61.12
40.07
36.37
34.18
31.64
28.93
25.12
14.45
f1 (ppm)

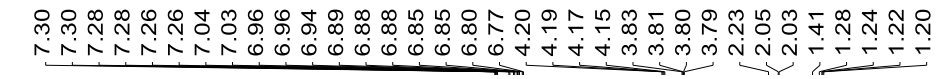
5

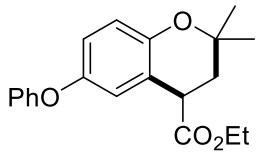

7.26
7.18
7.17
7.17
7.17
7.16
7.15
7.14
7.13
6.76
6.74
4.28
4.27
4.27
4.26
4.25
4.24
4.23
4.22
4.22
3.83
3.82
3.81
3.79
2.42
2.25
2.22
2.21
2.19
2.05
2.03
2.01
2.00
1.40
1.33
1.31
1.29
MeS
O
CO2Et

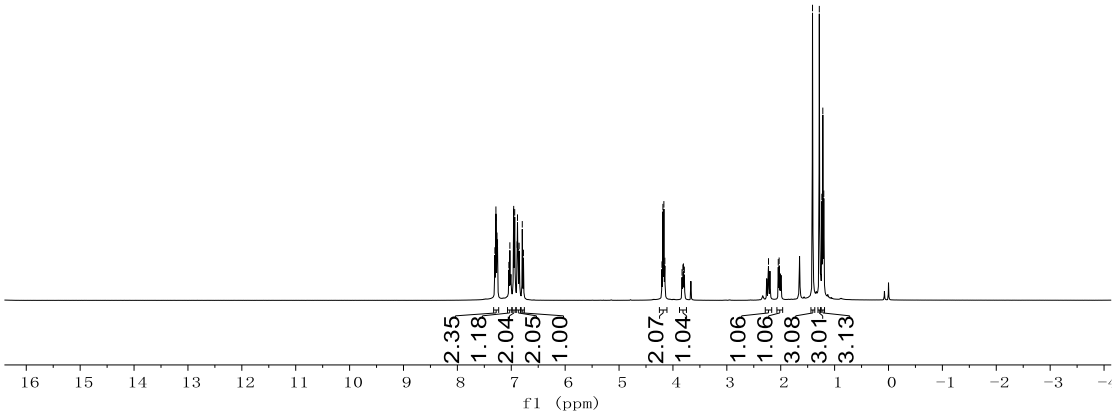

1.91
0.92
2.00
1.02
2.87
1.07
1.04
2.84
2.93
3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.
f1 (ppm)

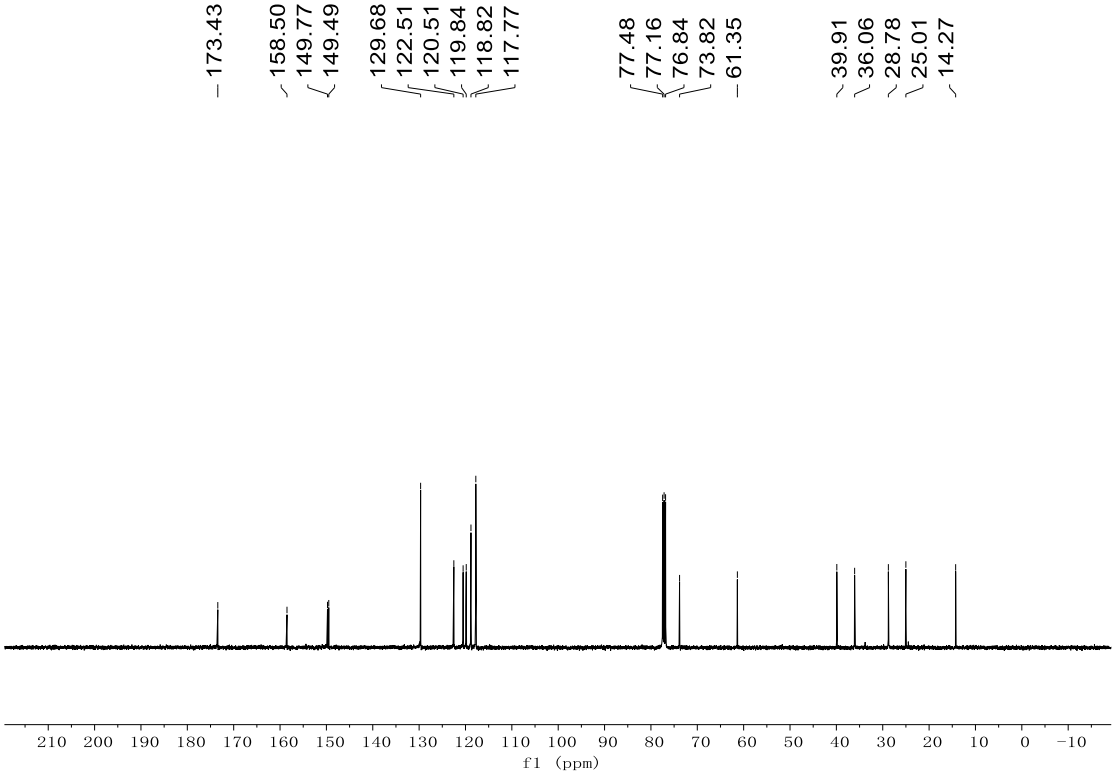

173.48
152.25
129.70
129.58
128.07
118.65
118.63
77.48
77.16
76.84
73.98
61.36
39.72
36.14
28.76
25.05
18.27
14.38
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

6

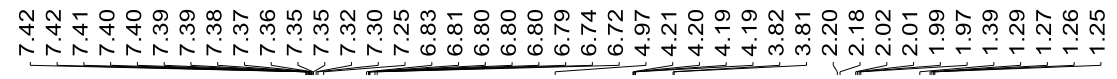

7.30
7.30
7.28
7.28
7.26
7.26
7.04
7.03
6.96
6.96
6.94
6.89
6.88
6.88
6.85
6.85
6.80
6.77
4.20
4.19
4.17
4.15
3.83
3.81
3.80
3.79
2.23
2.05
2.03
1.41
1.28
1.24
1.22
1.20

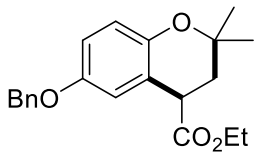

O
PhO
CO2Et

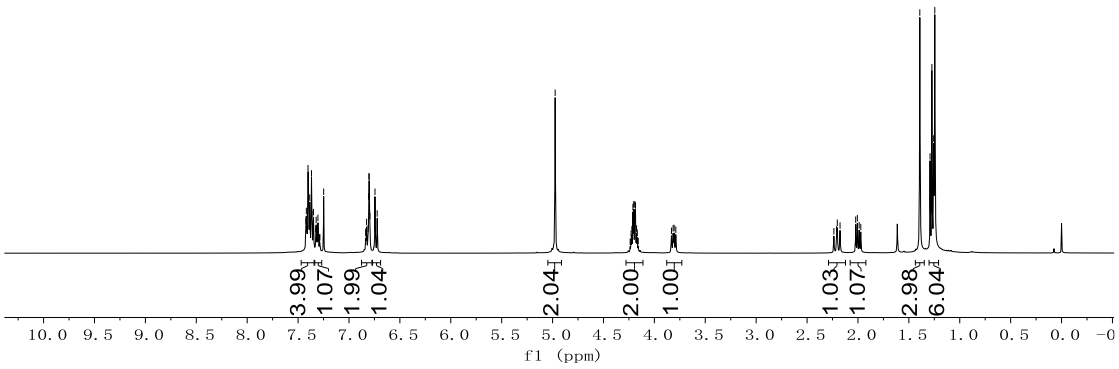

2.35
1.18
2.04
2.05
1.00
2.07
1.04
1.06
1.06
3.08
3.01
3.13
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)

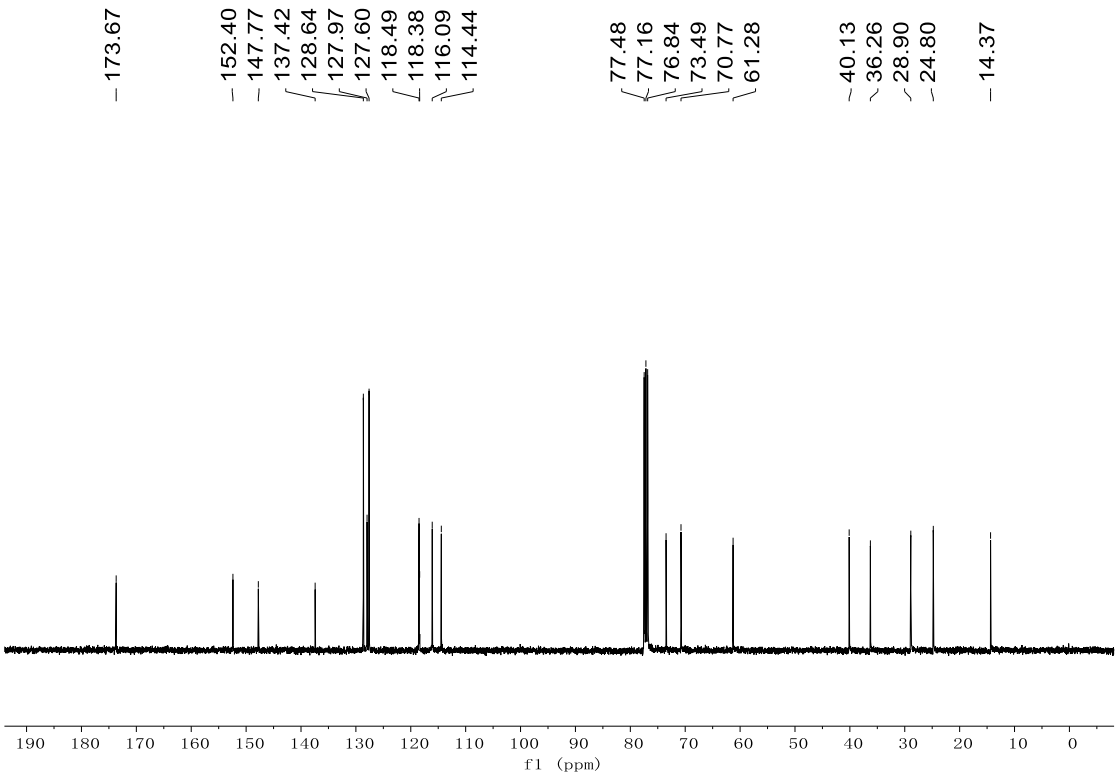

173.43
158.50
149.77
149.49
129.68
122.51
120.51
119.84
118.82
117.77
77.48
77.16
76.84
73.82
61.35
39.91
36.06
28.78
25.01
14.27
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

7

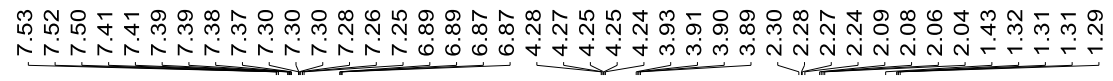

7.42
7.42
7.41
7.40
7.40
7.39
7.39
7.38
7.37
7.36
7.35
7.35
7.32
7.30
7.25
6.83
6.81
6.80
6.80
6.80
6.79
6.74
6.72
4.97
4.21
4.20
4.19
4.19
3.82
3.81
2.20
2.18
2.02
2.01
1.99
1.97
1.39
1.29
1.27
1.26
1.25

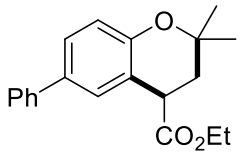

O
BnO
CO2Et

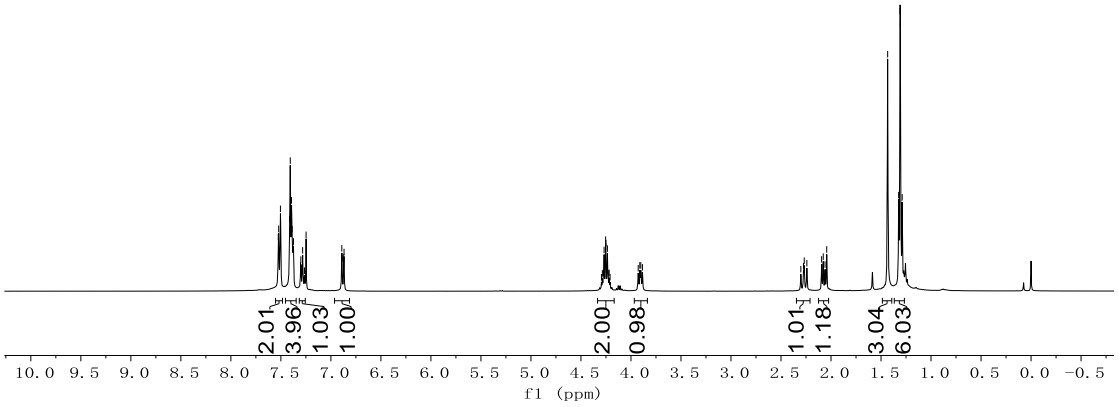

3.99
1.07
1.99
1.04
2.04
2.00
1.00
1.03
1.07
2.98
6.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)

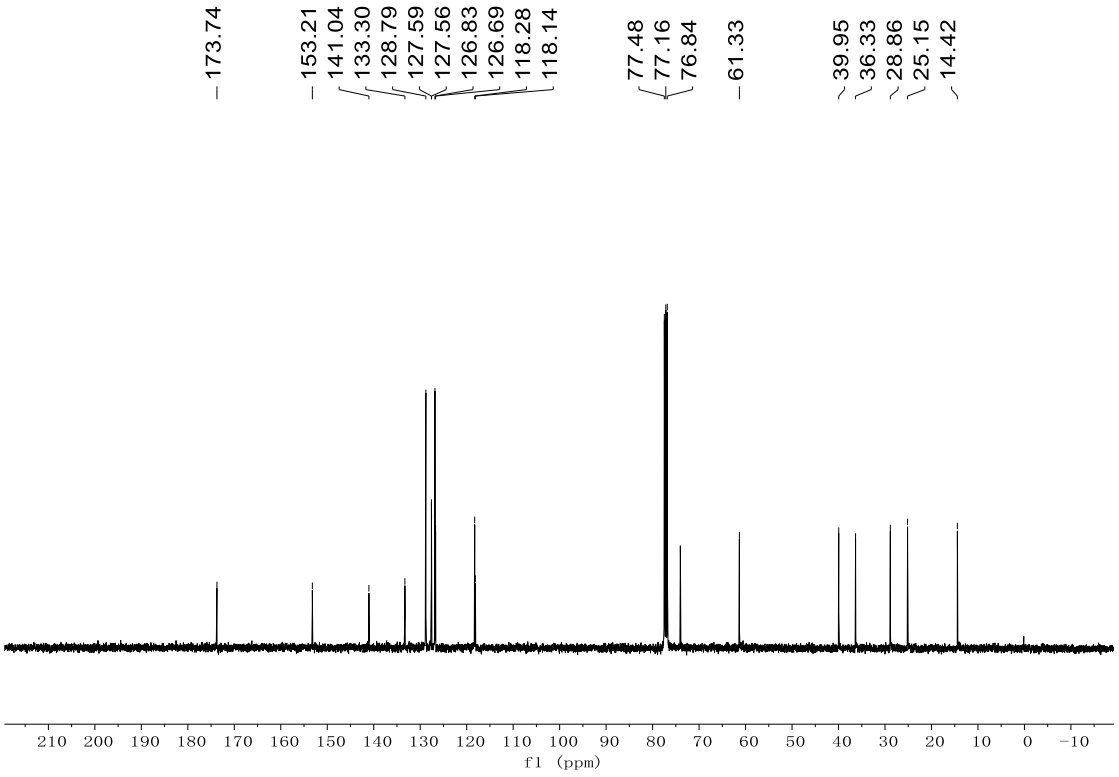

173.67
152.40
147.77
137.42
128.64
127.97
127.60
118.49
118.38
116.09
114.44
77.48
77.16
76.84
73.49
70.77
61.28
40.13
36.26
28.90
24.80
14.37
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

8

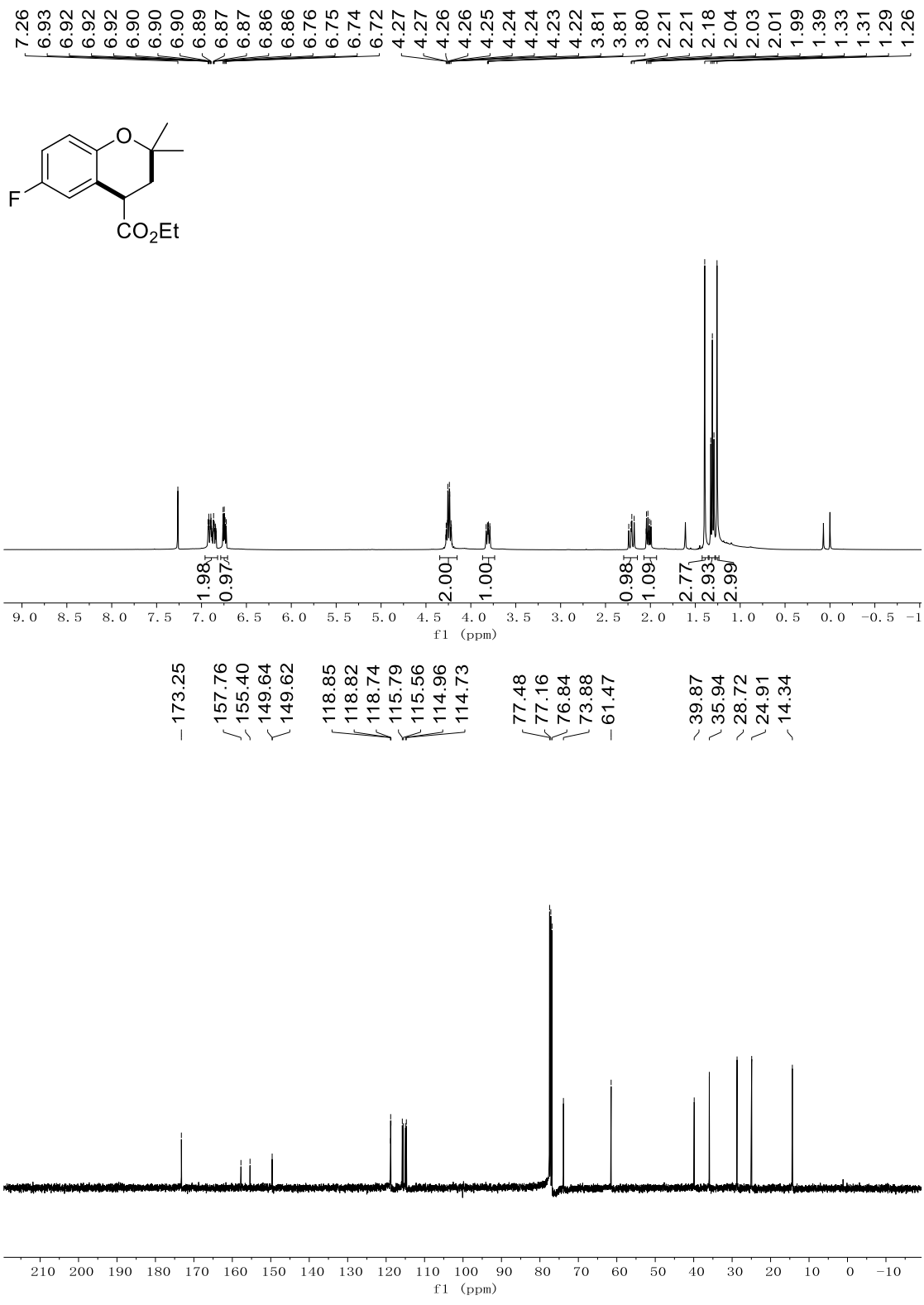

7.53
7.52
7.50
7.41
7.41
7.39
7.39
7.38
7.37
7.30
7.30
7.30
7.28
7.26
7.25
6.89
6.89
6.87
6.87
4.28
4.27
4.25
4.25
4.24
3.93
3.91
3.90
3.89
2.30
2.28
2.27
2.24
2.09
2.08
2.06
2.04
1.43
1.32
1.31
1.31
1.29

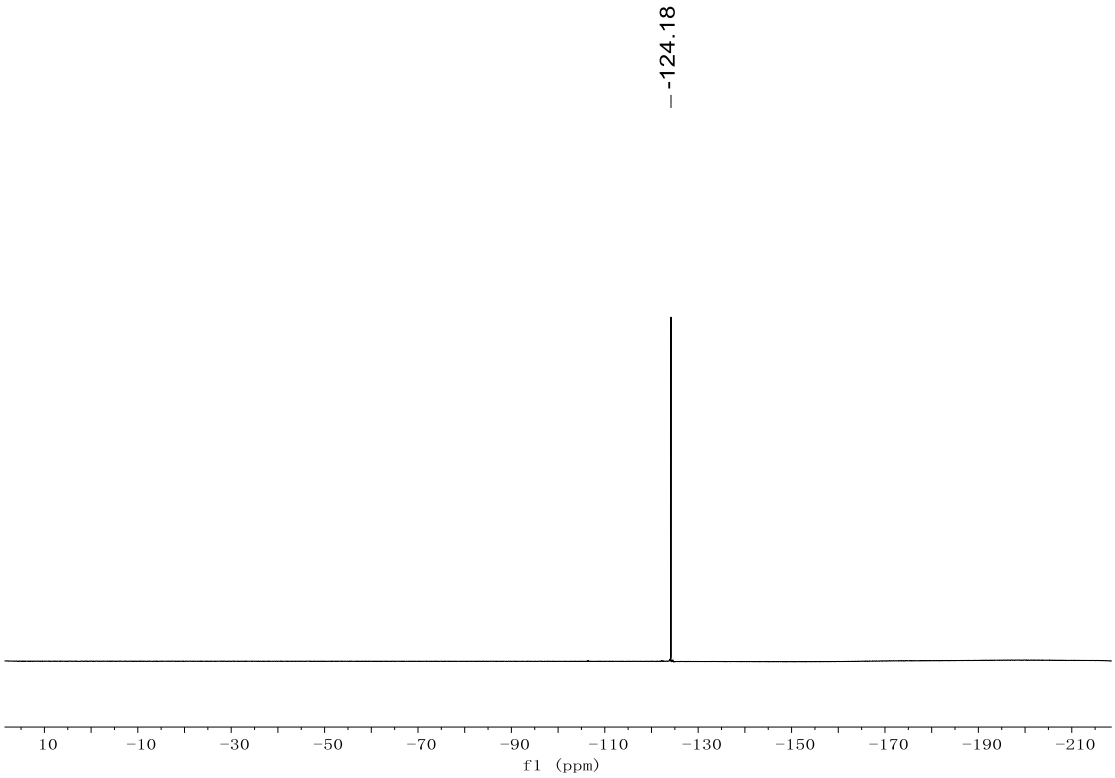

O
Ph
CO2Et


2.01
3.96
1.03
1.00
2.00
0.98
1.01
1.18
3.04
6.03
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
f1 (ppm)

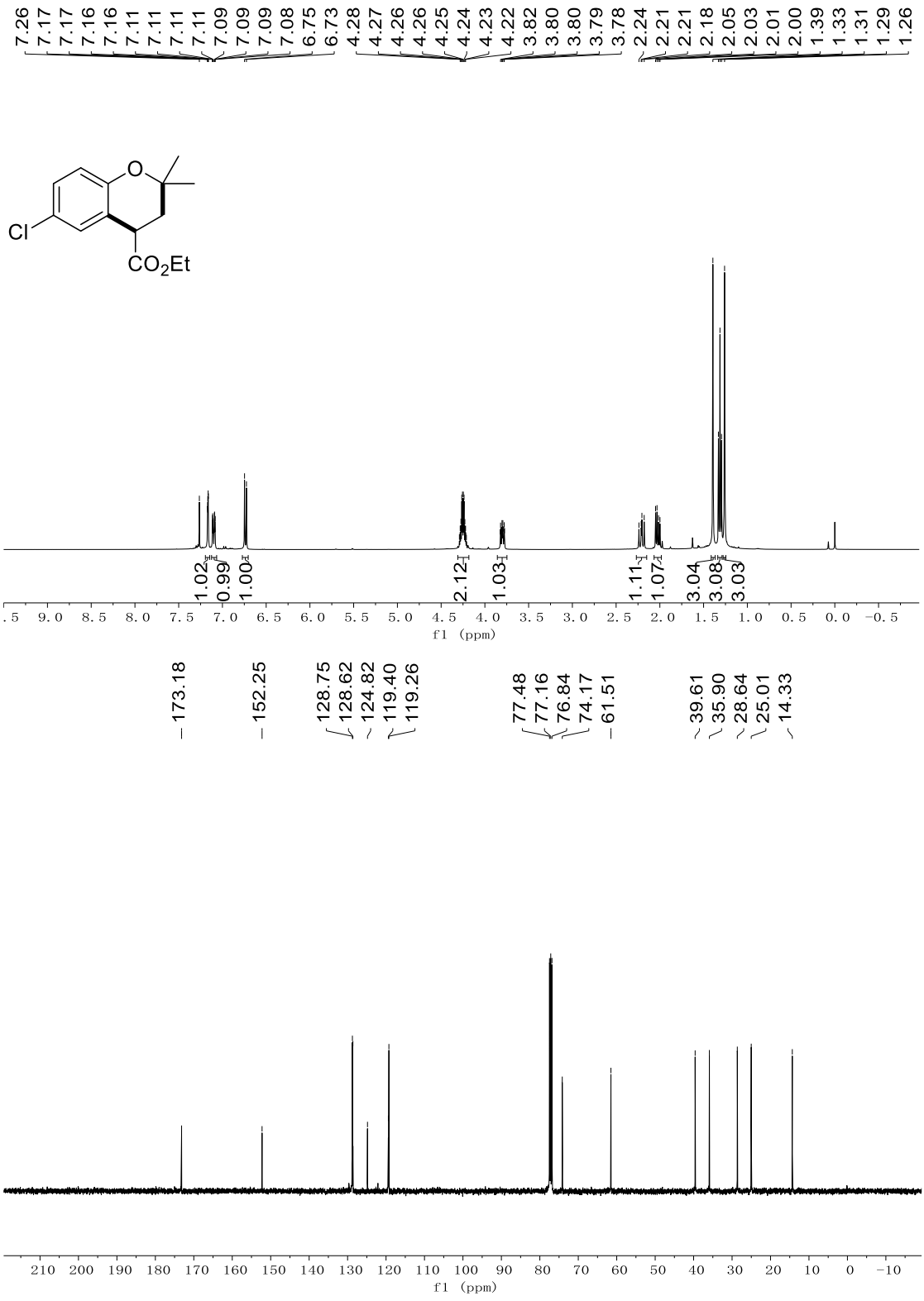

173.74
153.21
141.04
133.30
128.79
127.59
127.56
126.83
126.69
118.28
118.14
77.48
77.16
76.84
61.33
39.95
36.33
28.86
25.15
14.42
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

9

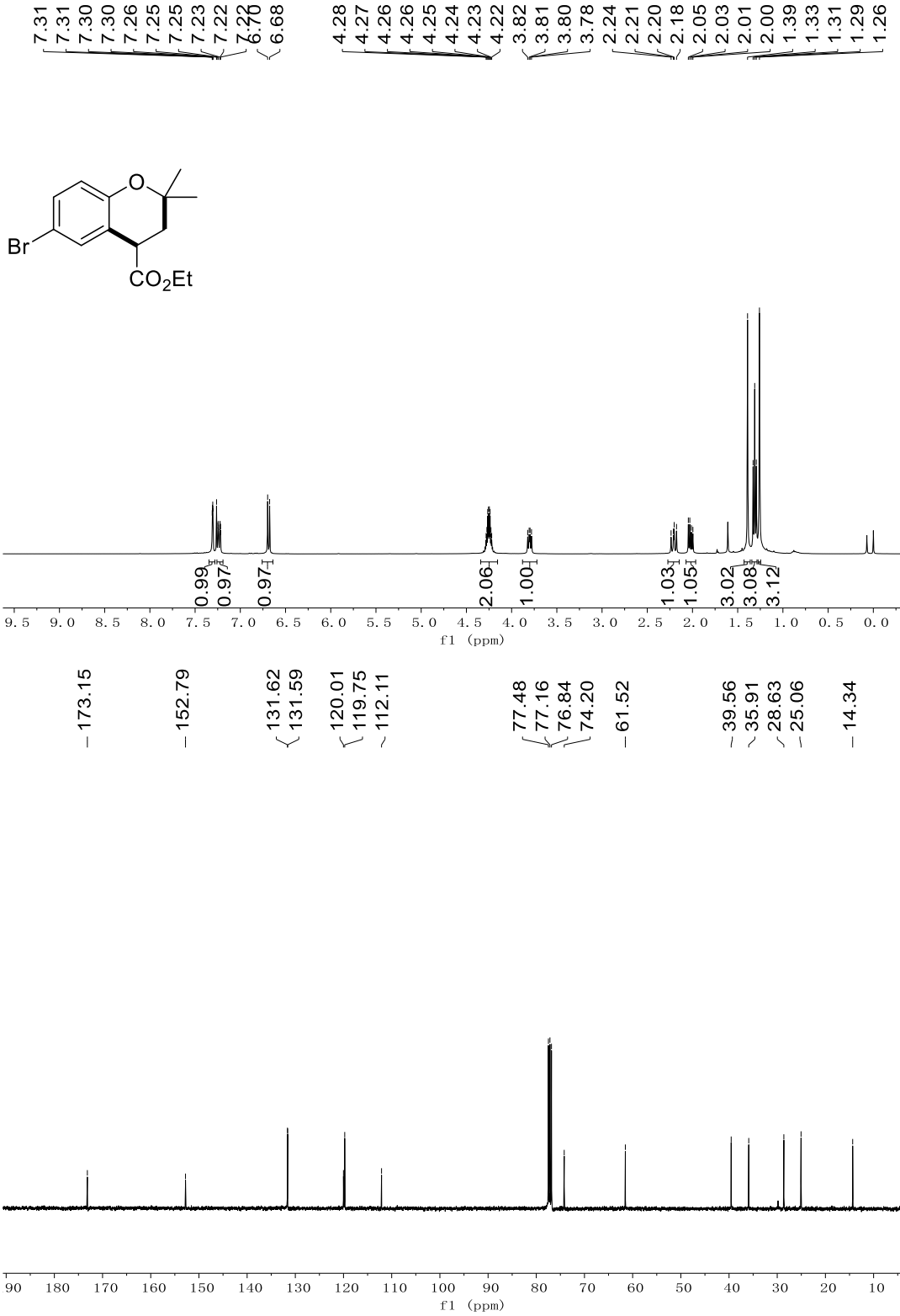

7.26
6.93
6.92
6.92
6.92
6.90
6.90
6.90
6.89
6.87
6.87
6.86
6.86
6.76
6.75
6.74
6.72
4.27
4.27
4.26
4.26
4.25
4.24
4.24
4.23
4.22
3.81
3.81
3.80
2.21
2.21
2.18
2.04
2.03
2.01
1.99
1.39
1.33
1.31
1.29
1.26
O
F
CO2Et
1.98
0.97
2.00
1.00
0.98
1.09
2.77
2.93
2.99
f1 (ppm)
173.25
157.76
155.40
149.64
149.62
118.85
118.82
118.74
115.79
115.56
114.96
114.73
77.48
77.16
76.84
73.88
61.47
39.87
35.94
28.72
24.91
14.34
f1 (ppm)


-124.18
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

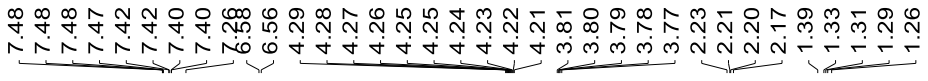
10

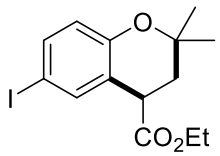

7.26 7.17 7.17 7.16 7.16 7.11 7.11 7.11 7.11 7.09 7.09 7.09 7.08 6.75 6.73
4.28 4.27 4.26 4.26 4.25 4.24 4.23 4.22 3.82 3.80 3.80 3.79 3.78
2.24 2.21 2.21 2.18 2.05 2.03 2.01 2.00 1.39 1.33 1.31 1.29 1.26
O
Cl
CO2Et
1.02 0.99 1.00 2.12 1.03 1.11 1.07 3.04 3.08 3.03
f1 (ppm)
173.18 152.25 128.75 128.62 124.82 119.40 119.26 77.48 77.16 76.84 74.17 61.51 39.61 35.90 28.64 25.01 14.33
f1 (ppm)

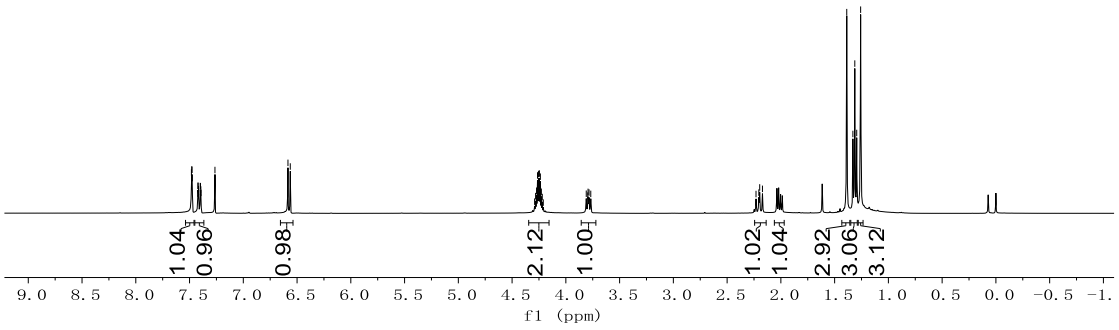
11

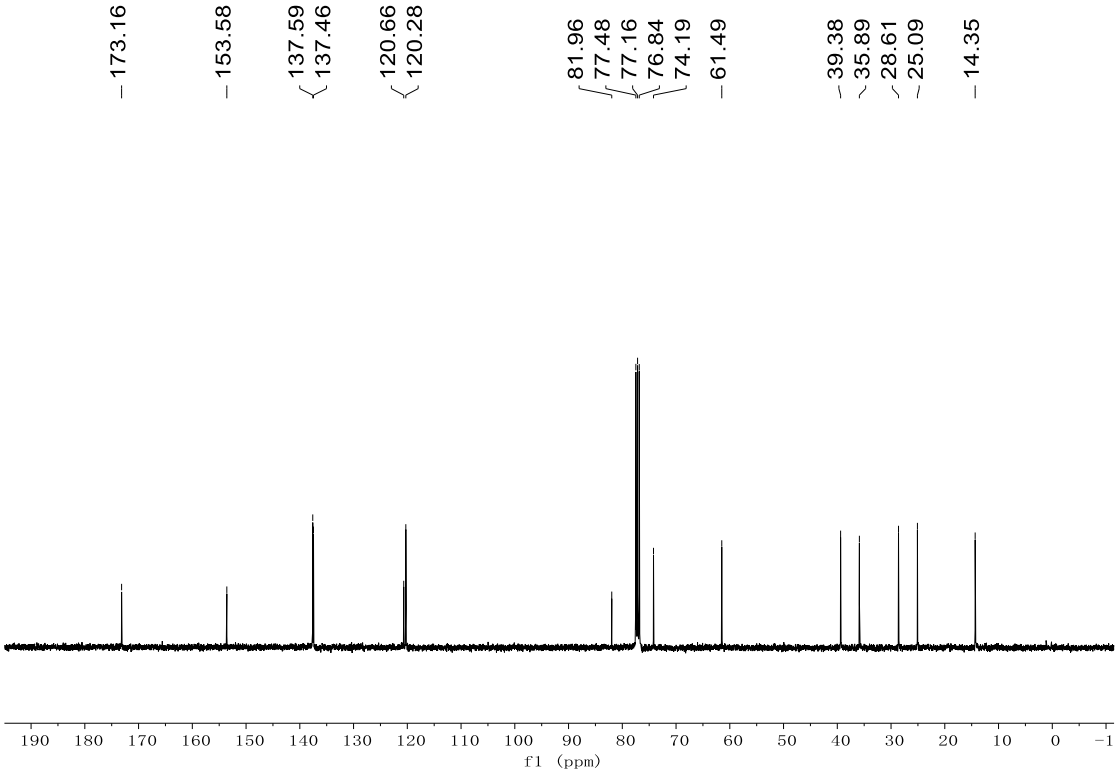

7.31
7.31
7.30
7.30
7.26
7.25
7.25
7.23
7.22
7.22
6.70
6.68
4.28
4.27
4.26
4.26
4.25
4.24
4.23
4.22
3.82
3.81
3.80
3.78
2.24
2.21
2.20
2.18
2.05
2.03
2.01
2.00
1.39
1.33
1.31
1.29
1.26
O
Br
CO2Et
0.99
0.97
0.97
2.06
1.00
1.03
1.05
3.02
3.08
3.12
f1 (ppm)
173.15
152.79
131.62
131.59
120.01
119.75
112.11
77.48
77.16
76.84
74.20
61.52
39.56
35.91
28.63
25.06
14.34
f1 (ppm)

12

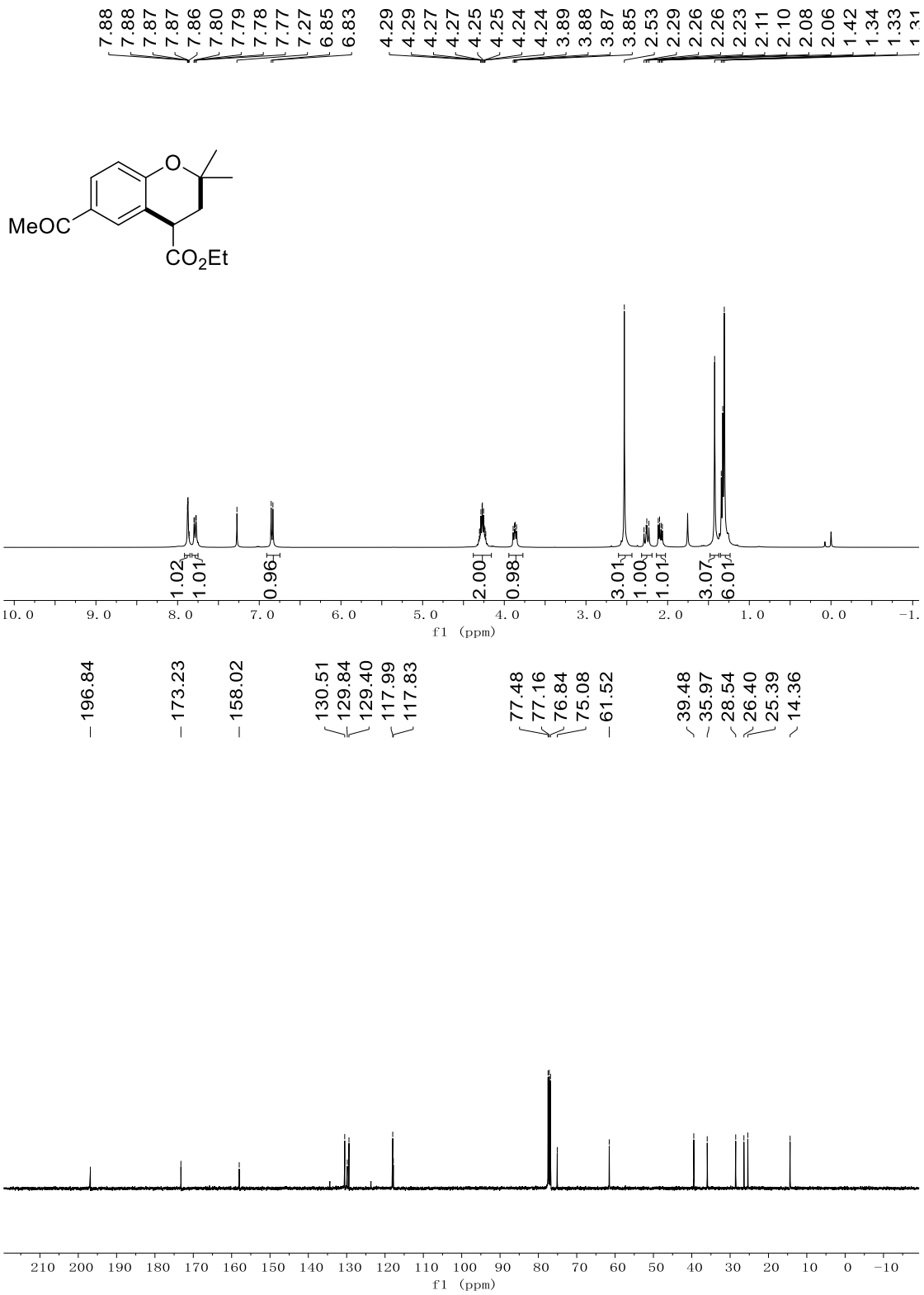

7.48
7.48
7.48
7.47
7.42
7.42
7.40
7.40
7.28
6.58
6.56
4.29
4.28
4.27
4.26
4.25
4.25
4.24
4.23
4.22
4.21
3.81
3.80
3.79
3.78
3.77
2.23
2.21
2.20
2.17
1.39
1.33
1.31
1.29
1.26


O
I
CO2Et

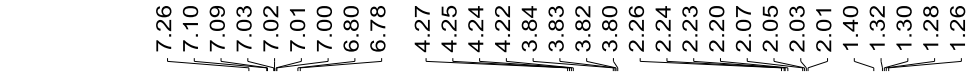

1.04
0.96
0.98
2.12
1.00
1.02
1.04
2.92
3.06
3.12
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.
f1 (ppm)

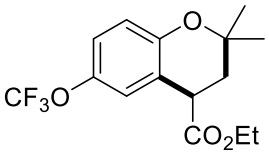

173.16
153.58
137.59
137.46
120.66
120.28
81.96
77.48
77.16
76.84
74.19
61.49
39.38
35.89
28.61
25.09
14.35
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

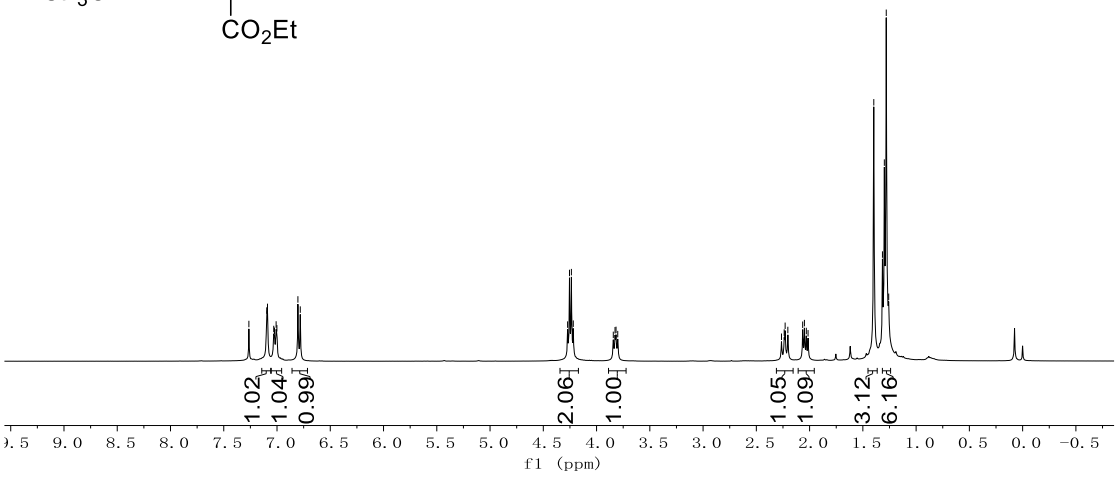
13

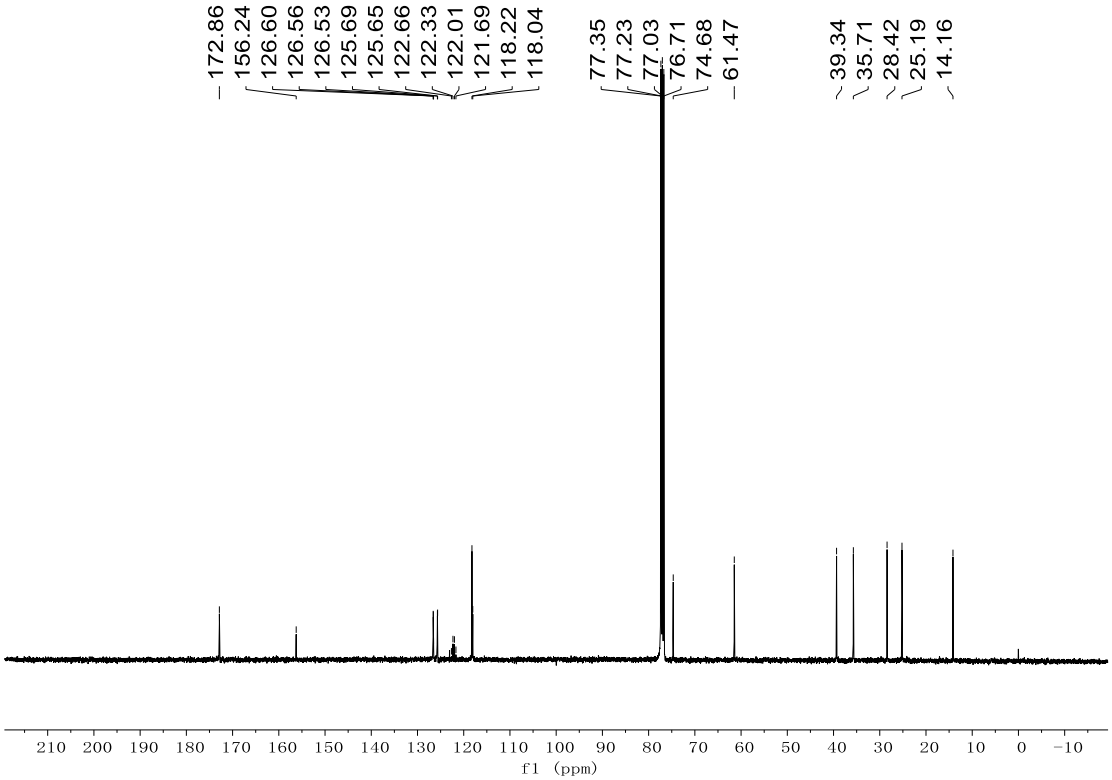

7.88
7.88
7.87
7.87
7.86
7.80
7.79
7.78
7.77
7.27
6.85
6.83
4.29
4.29
4.27
4.27
4.25
4.25
4.24
4.24
3.89
3.88
3.87
3.85
2.53
2.29
2.26
2.26
2.23
2.11
2.10
2.08
2.06
1.42
1.34
1.33
MeOC
O
CO2Et
1.02
1.01
0.96
2.00
0.98
3.01
1.00
1.01
3.07
6.01
f1 (ppm)
196.84
173.23
158.02
130.51
129.84
129.40
117.99
117.83
77.48
77.16
76.84
75.08
61.52
39.48
35.97
28.54
26.40
25.39
14.36
f1 (ppm)

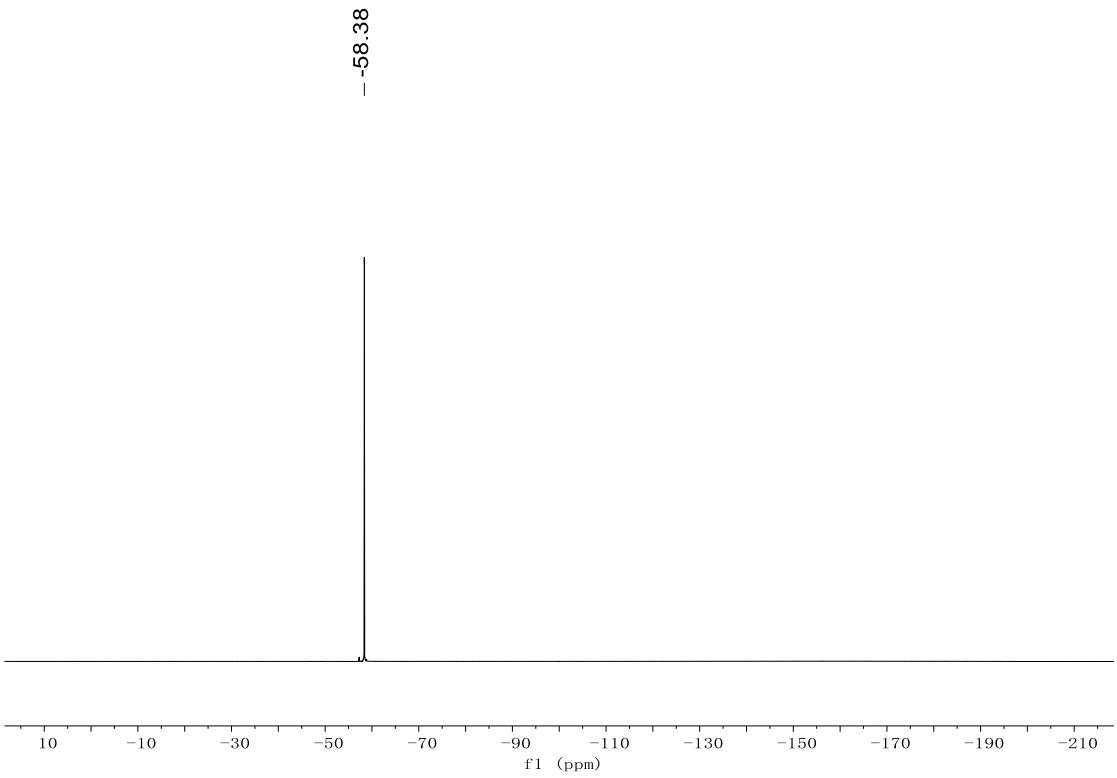
14


7.26
7.10
7.09
7.03
7.02
7.01
7.00
6.80
6.78
4.27
4.25
4.24
4.22
3.84
3.83
3.82
3.80
2.26
2.24
2.23
2.20
2.07
2.05
2.03
2.01
1.40
1.32
1.30
1.28
1.26

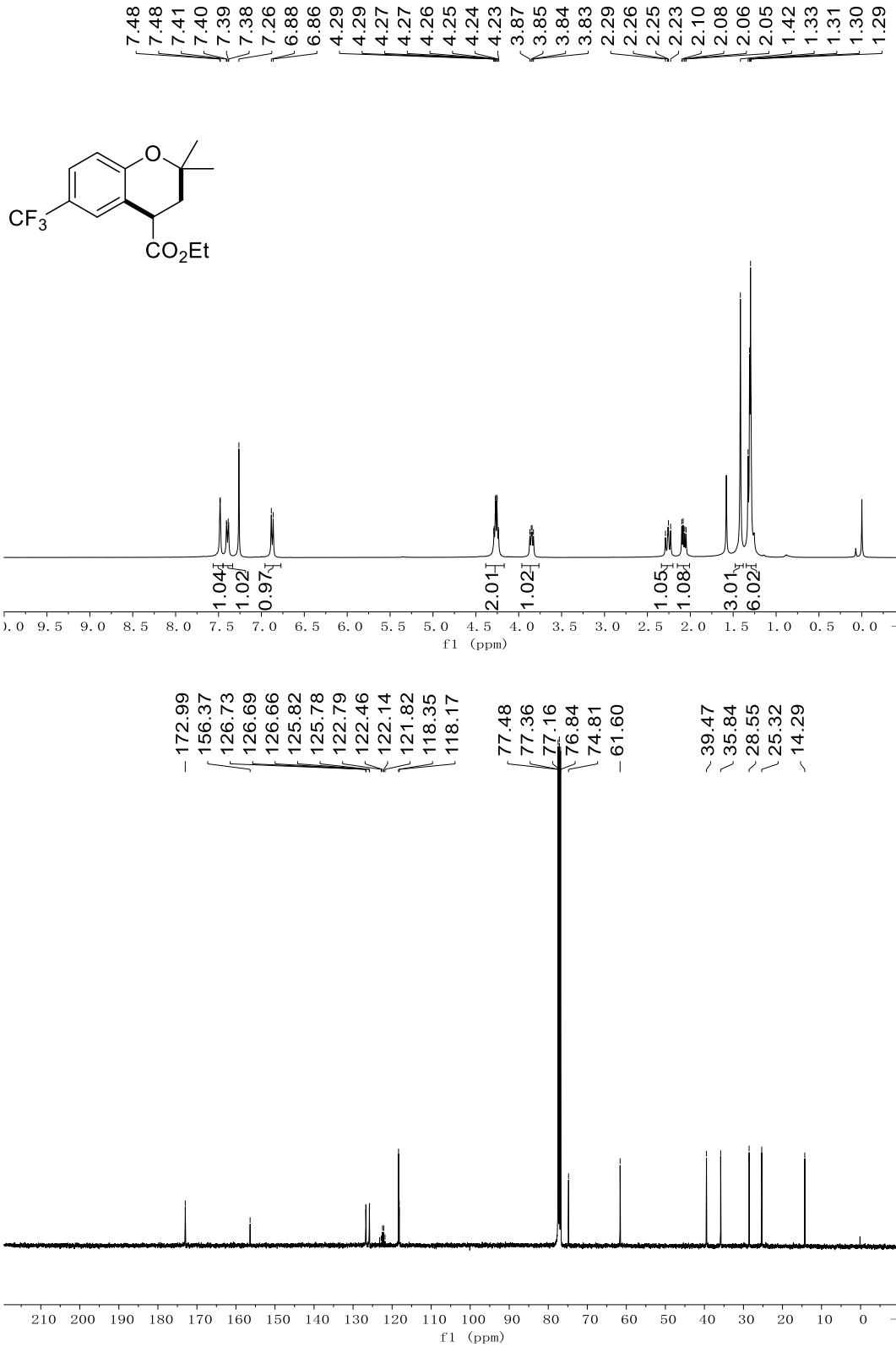

O
CF3O
CO2Et

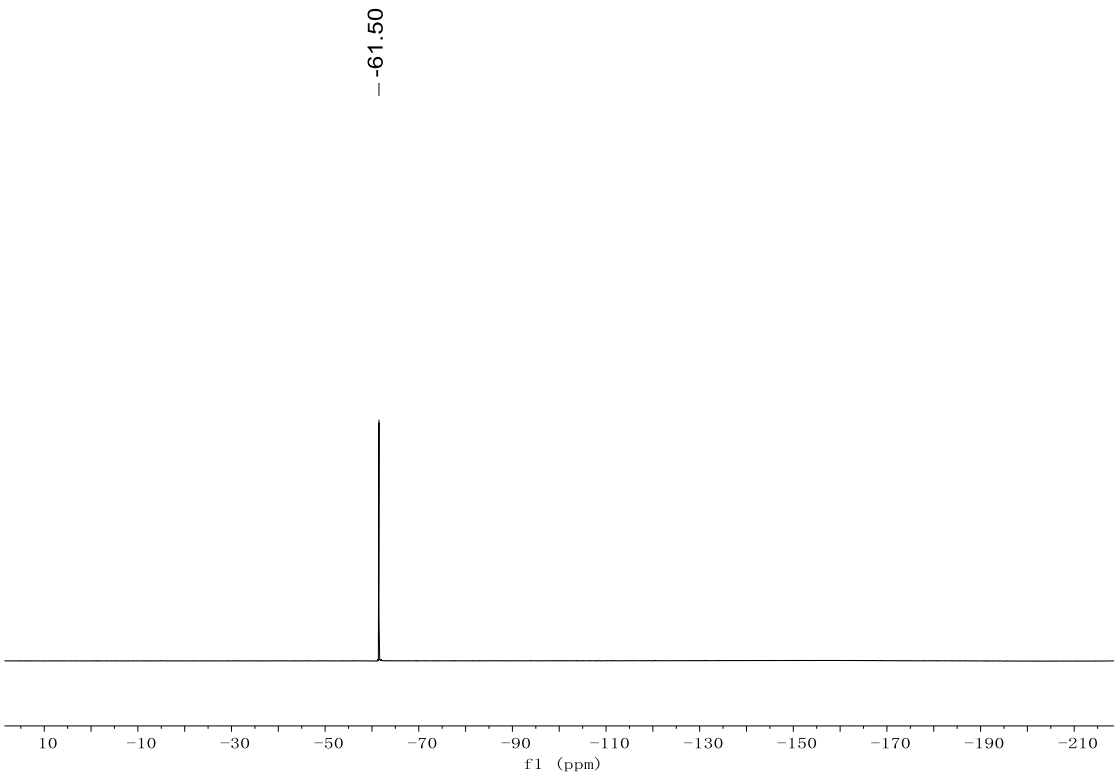

1.02
1.04
0.99
2.06
1.00
1.05
1.09
3.12
6.16
f1 (ppm)


172.86
156.24
126.60
126.56
126.53
125.69
125.65
122.66
122.33
122.01
121.69
118.22
118.04
77.35
77.23
77.03
76.71
74.68
61.47
39.34
35.71
28.42
25.19
14.16
f1 (ppm)

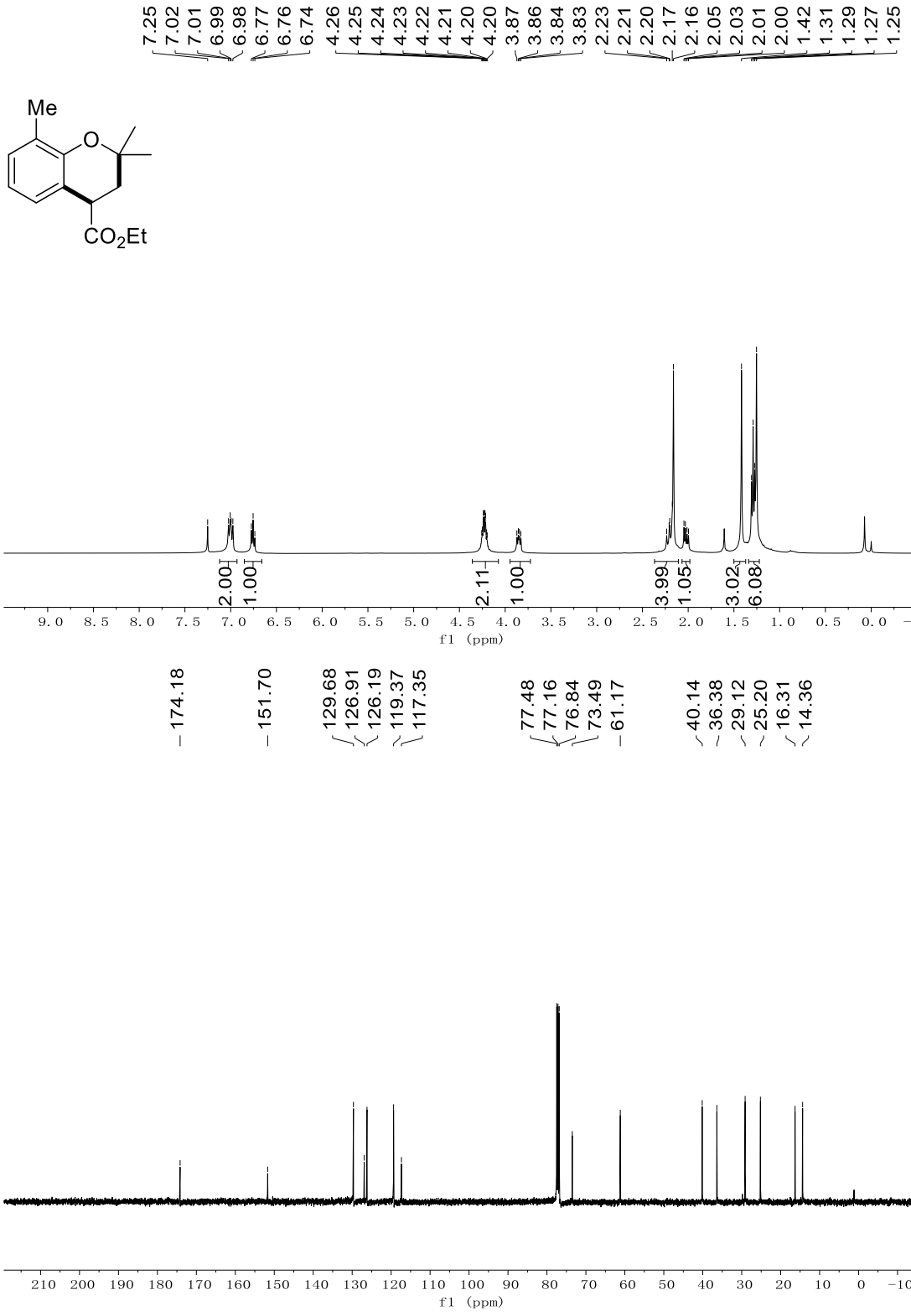

-58.38
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

15

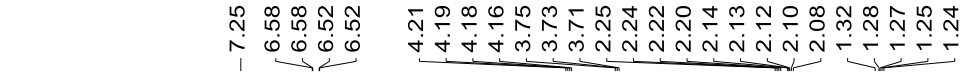

7.48
7.48
7.41
7.40
7.39
7.38
7.26
6.88
6.86
4.29
4.29
4.27
4.27
4.26
4.25
4.24
4.23
3.87
3.85
3.84
3.83
2.29
2.26
2.25
2.23
2.10
2.08
2.06
2.05
1.42
1.33
1.31
1.30
1.29
O
CF3
CO2Et
1.04
1.02
0.97
2.01
1.02
1.05
1.08
3.01
6.02
f1 (ppm)
172.99
156.37
126.73
126.69
126.66
125.82
125.78
122.79
122.46
122.14
121.82
118.35
118.17
77.48
77.36
77.16
76.84
74.81
61.60
39.47
35.84
28.55
25.32
14.29
f1 (ppm)

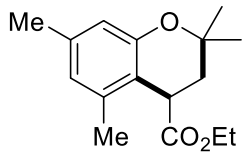

-61.50
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

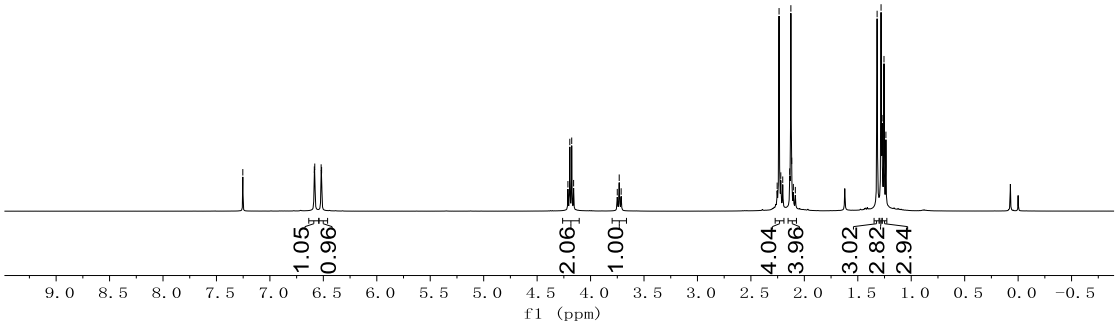
16

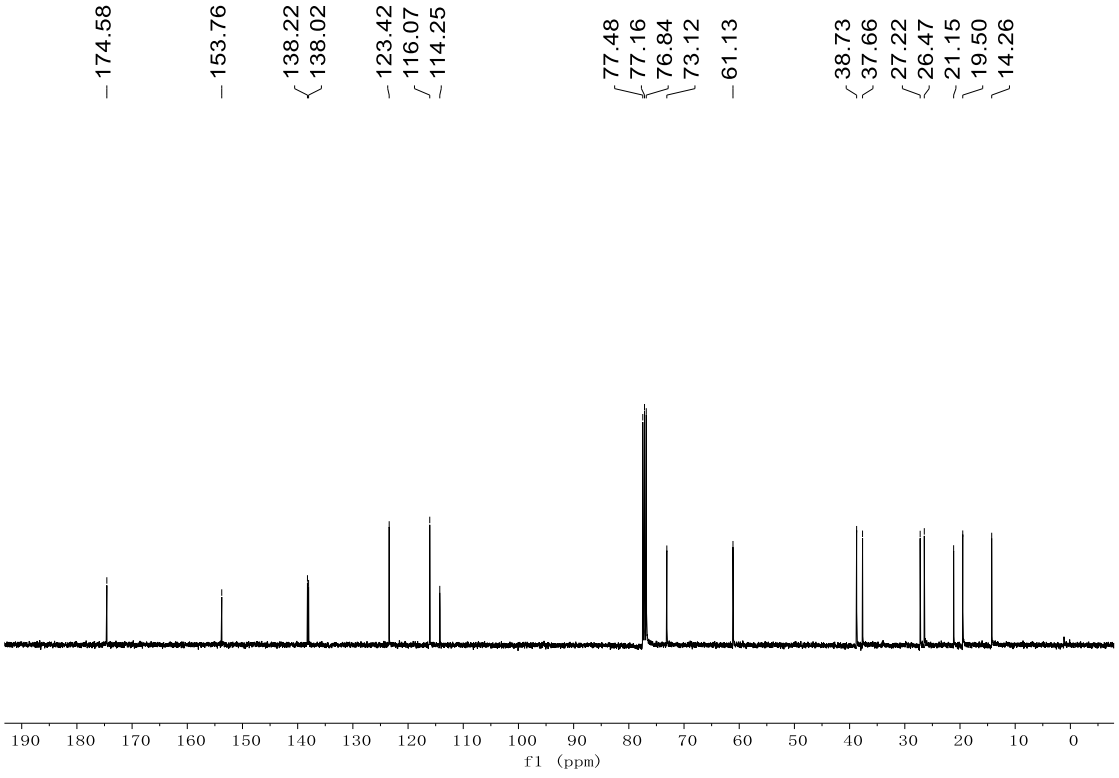

7.25
7.02
7.01
6.99
6.98
6.77
6.76
6.74
4.26
4.25
4.24
4.23
4.22
4.21
4.20
4.20
3.87
3.86
3.84
3.83
2.23
2.21
2.20
2.17
2.16
2.05
2.03
2.01
2.00
1.42
1.31
1.29
1.27
1.25
Me
O
CO2Et
2.00
1.00
2.11
1.00
3.99
1.05
3.02
6.08
f1 (ppm)
174.18
151.70
129.68
126.91
126.19
119.37
117.35
77.48
77.16
76.84
73.49
61.17
40.14
36.38
29.12
25.20
16.31
14.36
f1 (ppm)

17

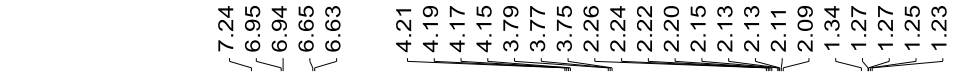

7.25
6.58
6.58
6.52
6.52
4.21
4.19
4.18
4.16
3.75
3.73
3.71
2.25
2.24
2.22
2.20
2.14
2.13
2.12
2.10
2.08
1.32
1.28
1.27
1.25
1.24

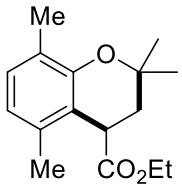

Me
O
Me
CO2Et

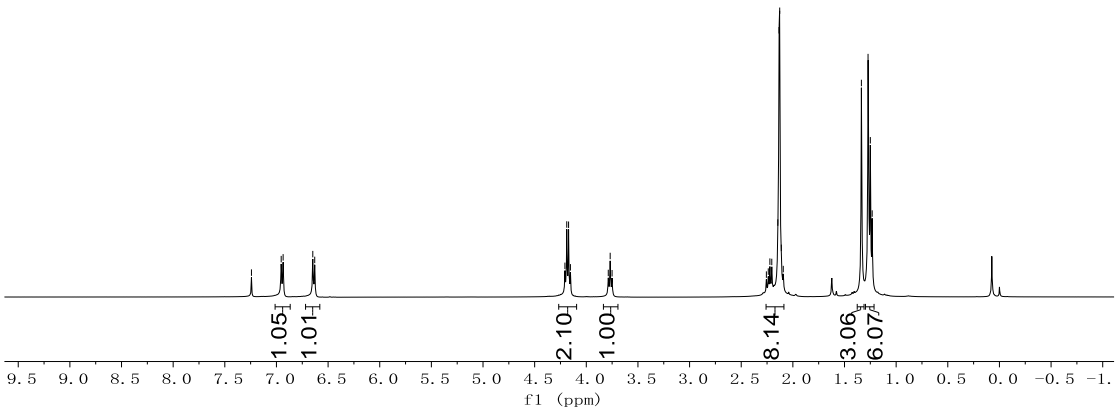

1.05
0.96
2.06
1.00
4.04
3.96
3.02
2.82
2.94
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


174.58
153.76
138.22
138.02
123.42
116.07
114.25
77.48
77.16
76.84
73.12
61.13
38.73
37.66
27.22
26.47
21.15
19.50
14.26
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

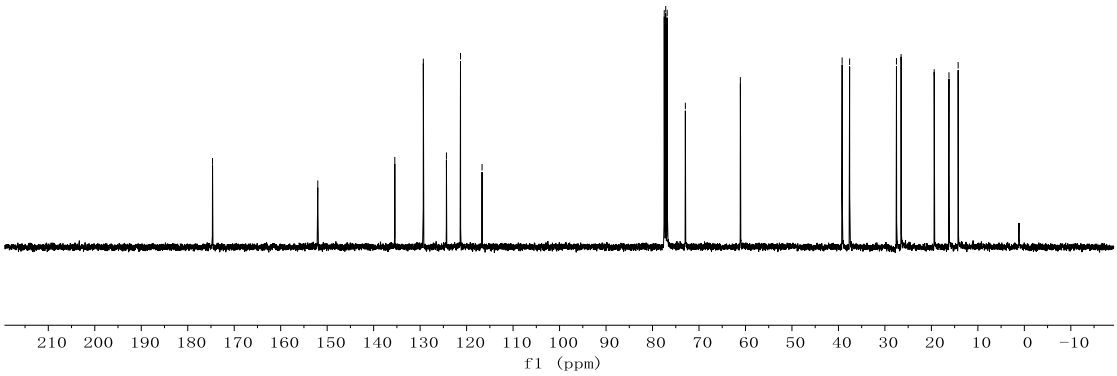
18


7.24
6.95
6.94
6.65
6.63
4.21
4.19
4.17
4.15
3.79
3.77
3.75
2.26
2.24
2.22
2.20
2.15
2.13
2.13
2.11
2.09
1.34
1.27
1.27
1.25
1.23

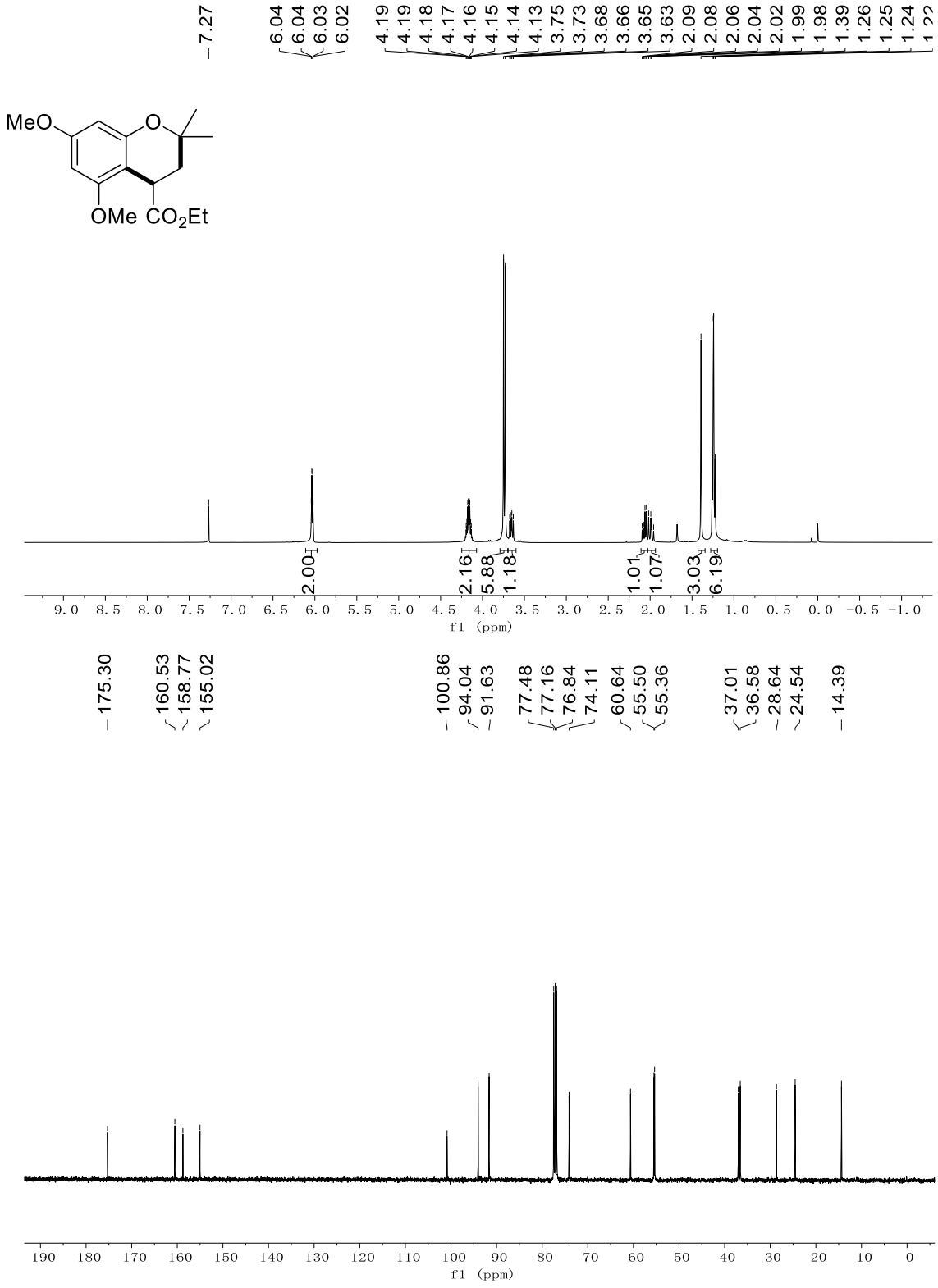

Me
O
Me
CO2Et


1.05
1.01
2.10
1.00
8.14
3.06
6.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.
f1 (ppm)

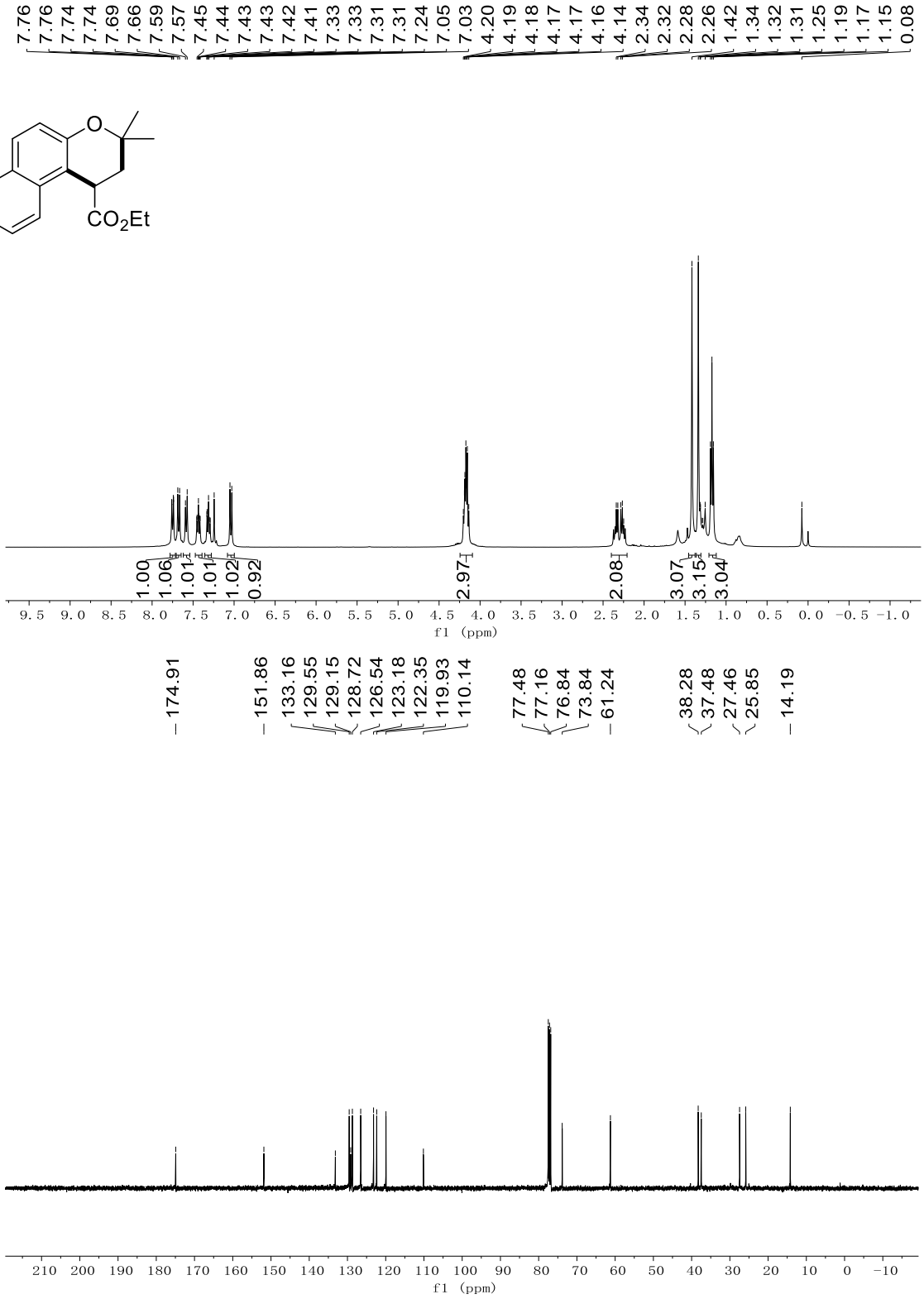

174.67
152.02
135.45
129.31
124.34
121.31
116.68
77.48
77.16
76.84
72.93
61.10
39.20
37.59
27.51
26.51
19.39
16.22
14.24


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

19

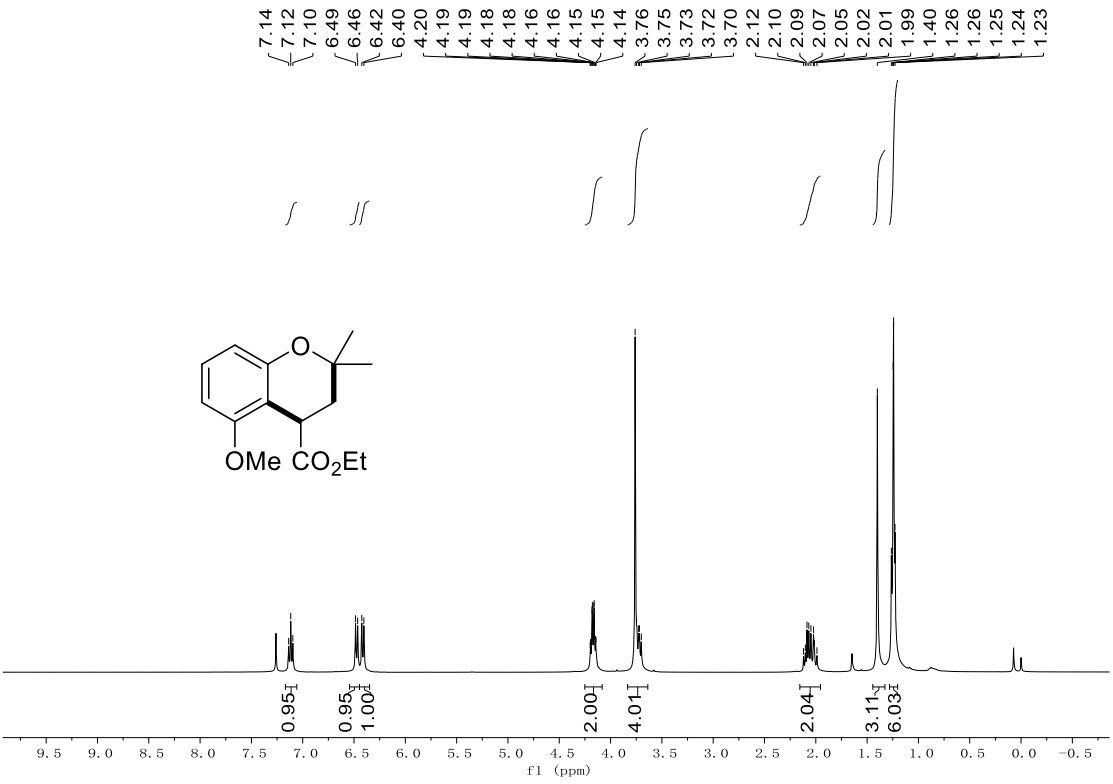

7.27
6.04
6.04
6.03
6.02
4.19
4.19
4.18
4.17
4.16
4.15
4.14
4.13
3.75
3.73
3.68
3.66
3.65
3.63
2.09
2.08
2.06
2.04
2.02
1.99
1.98
1.39
1.26
1.25
1.24
MeO
O
OMe
CO2Et
2.00
2.16
5.88
1.18
1.01
1.07
3.03
6.19
f1 (ppm)
175.30
160.53
158.77
155.02
100.86
94.04
91.63
77.48
77.16
76.84
74.11
60.64
55.50
55.36
37.01
36.58
28.64
24.54
14.39
f1 (ppm)

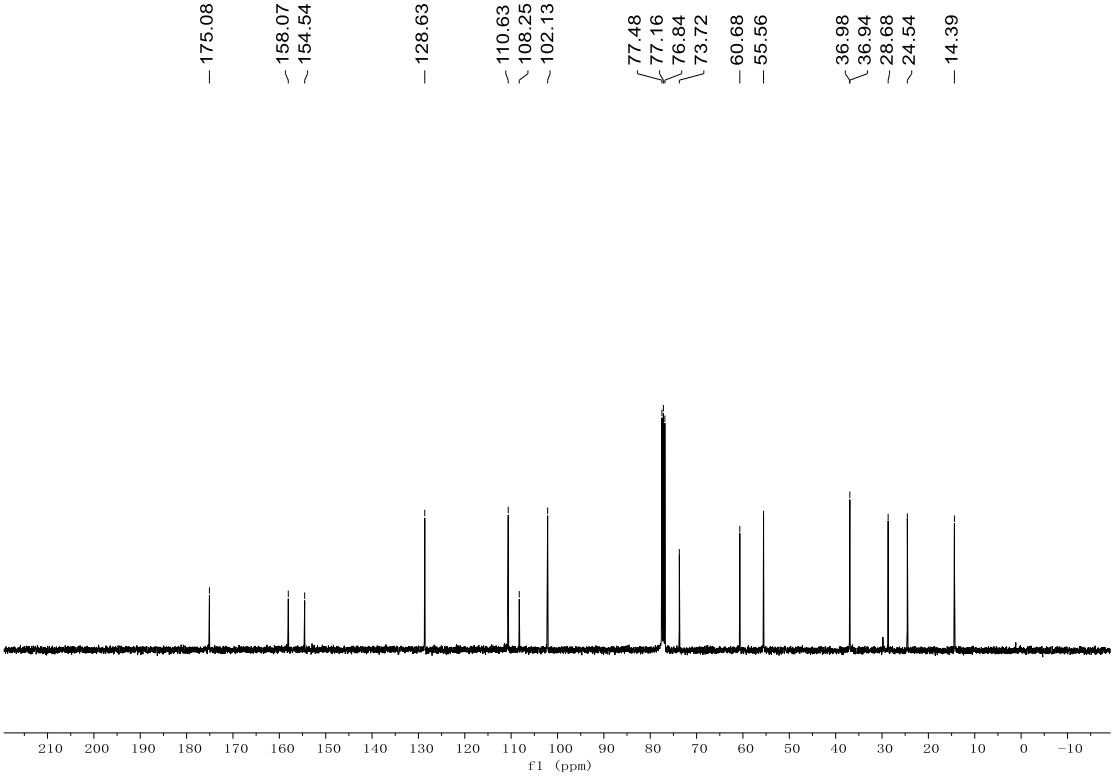
20


7.76 7.76 7.74 7.74 7.69 7.66 7.59 7.57 7.45 7.44 7.43 7.43 7.42 7.41 7.33 7.33 7.31 7.31 7.24 7.05 7.03 4.20 4.19 4.18 4.17 4.17 4.16 4.14 2.34 2.32 2.28 2.26 1.42 1.34 1.32 1.31 1.25 1.19 1.17 1.15 0.08
O
CO2Et
1.00 1.06 1.01 1.01 1.02 0.92 2.97 2.08 3.07 3.15 3.04
f1 (ppm)
174.91 151.86 133.16 129.55 129.15 128.72 126.54 123.18 122.35 119.93 110.14 77.48 77.16 76.84 73.84 61.24 38.28 37.48 27.46 25.85 14.19
f1 (ppm)

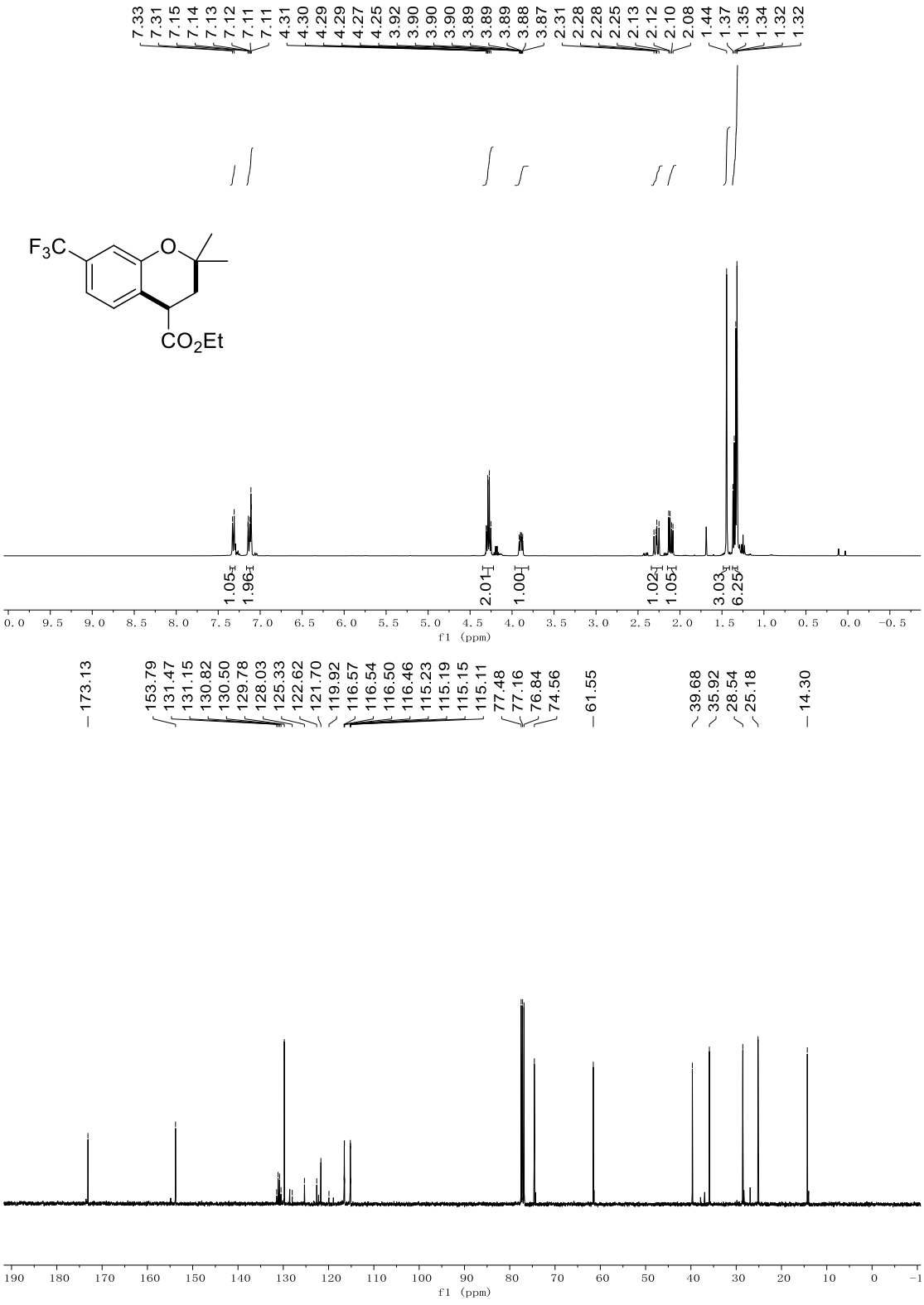
21

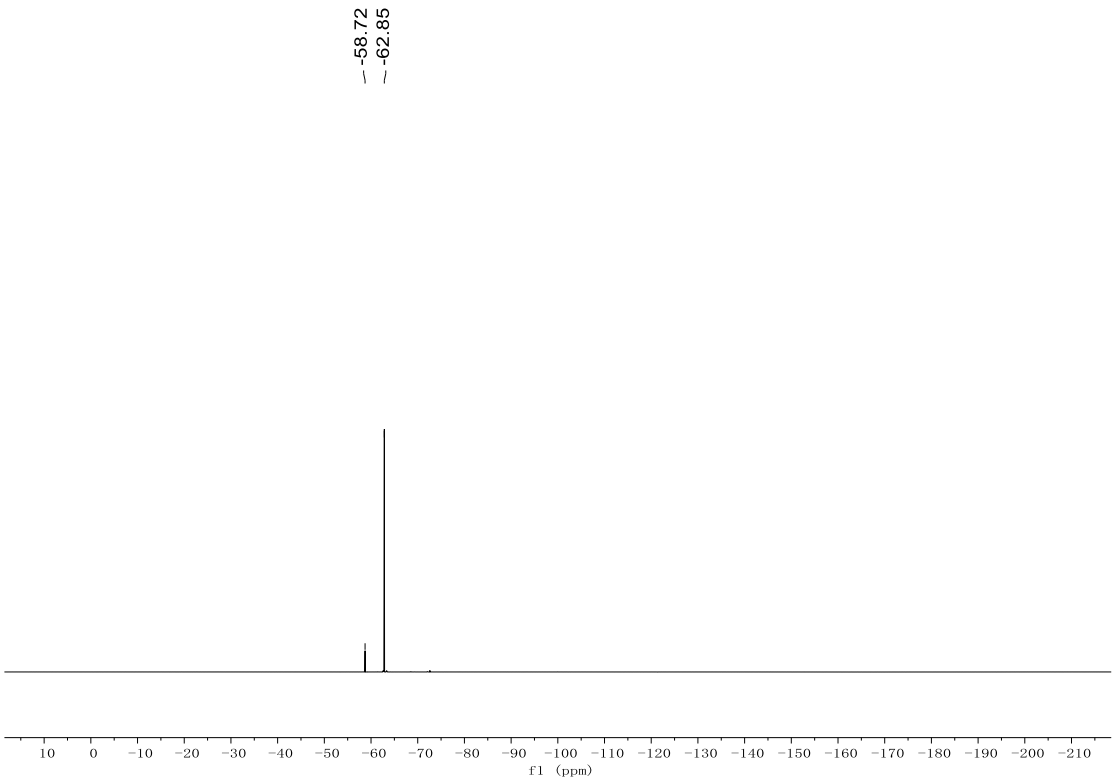

7.26
7.07
7.05
6.48
6.48
6.46
6.46
6.36
6.36
4.25
4.25
4.24
4.23
4.22
4.22
4.20
4.20
3.80
3.78
3.77
3.75
2.23
2.20
2.19
2.17
2.04
2.02
2.01
1.99
1.40
1.31
1.29
1.28
MeO
O
CO2Et
0.99
1.00
0.91
2.09
3.92
1.00
1.09
3.01
6.11
f1 (ppm)
174.09
160.05
154.48
129.55
110.20
107.65
102.08
77.48
77.16
76.84
74.01
61.20
55.35
39.26
36.38
28.82
25.03
14.38
f1 (ppm)


7.14
7.12
7.10
6.49
6.46
6.42
6.40
4.20
4.19
4.19
4.18
4.18
4.16
4.16
4.15
4.15
4.14
3.76
3.75
3.73
3.72
3.70
2.12
2.10
2.09
2.07
2.05
2.02
2.01
1.99
1.40
1.26
1.26
1.25
1.24
1.23
O
OMe CO2Et
0.95
0.95
1.00
2.00
4.01
2.04
3.11
6.03
f1 (ppm)

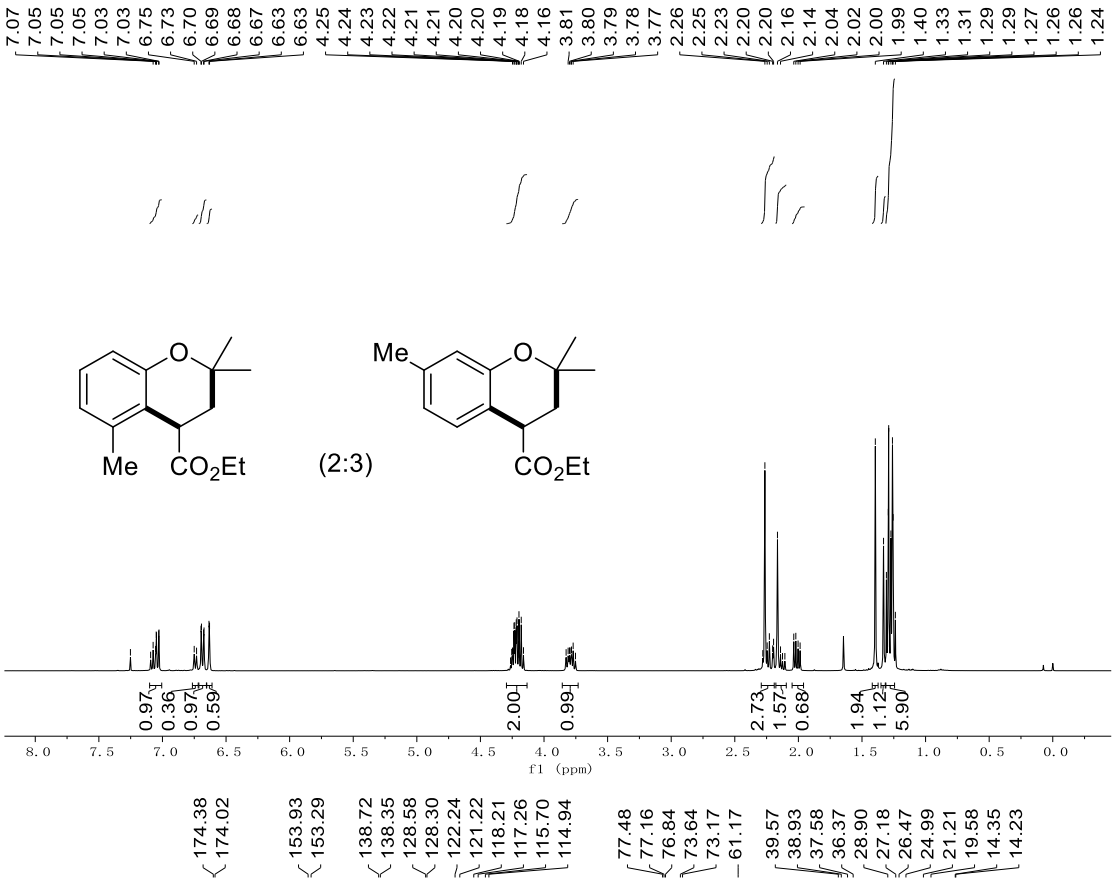

175.08
158.07
154.54
128.63
110.63
108.25
102.13
77.48
77.16
76.84
73.72
60.68
55.56
36.98
36.94
28.68
24.54
14.39
f1 (ppm)

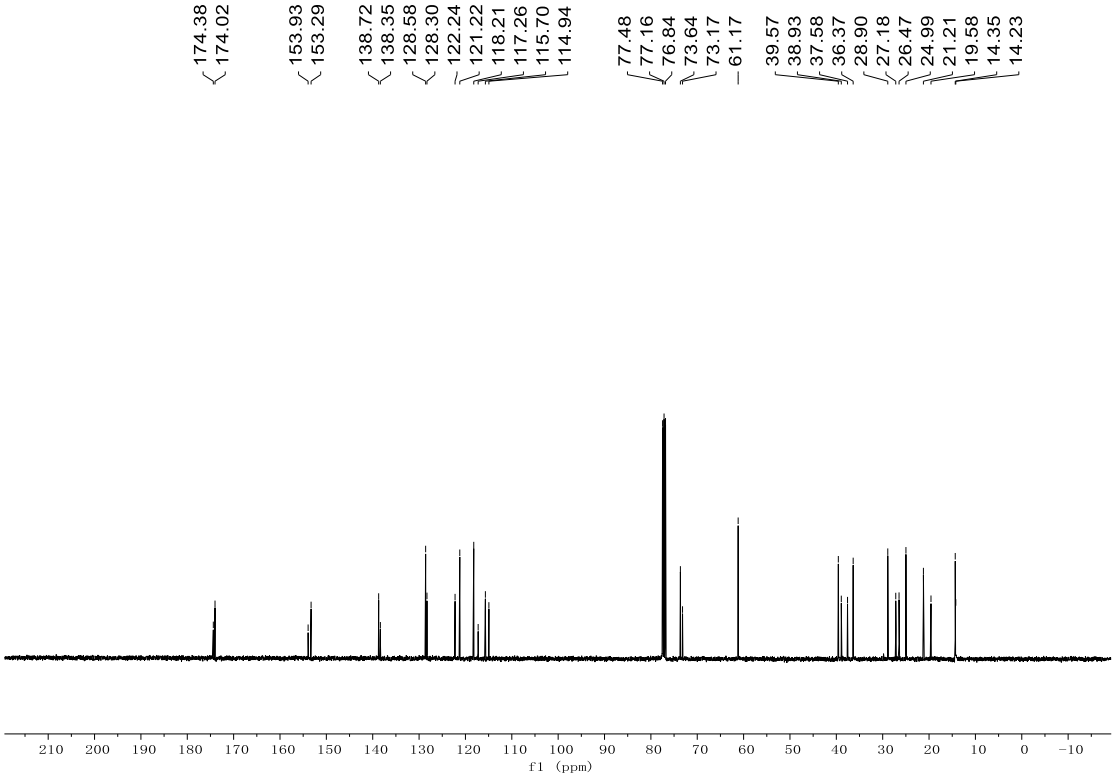
22


7.33
7.31
7.15
7.14
7.13
7.12
7.11
7.11
4.31
4.30
4.29
4.29
4.27
4.25
3.92
3.90
3.90
3.90
3.89
3.89
3.89
3.88
3.87
2.31
2.28
2.25
2.13
2.12
2.10
2.08
1.44
1.37
1.35
1.34
1.32
1.32
F3C
O
CO2Et
1.05
1.96
2.01
1.00
1.02
1.05
3.03
6.25
f1 (ppm)
173.13
153.79
131.47
131.15
130.82
130.50
129.78
128.03
125.33
122.62
121.70
119.92
116.57
116.54
116.50
116.46
115.23
115.19
115.15
115.11
77.48
77.16
76.84
74.56
61.55
39.68
35.92
28.54
25.18
14.30
f1 (ppm)

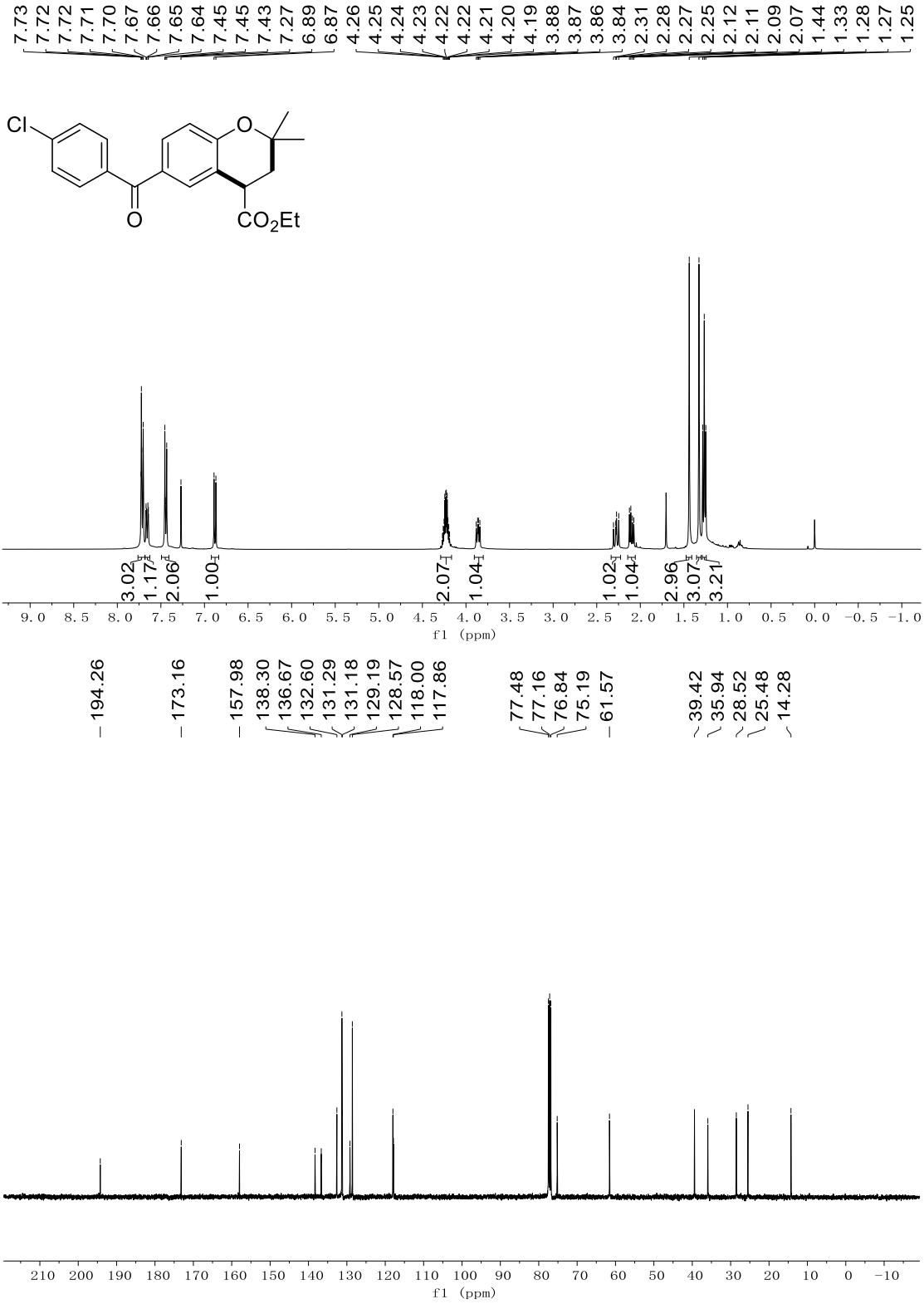

-58.72
-62.85
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

23

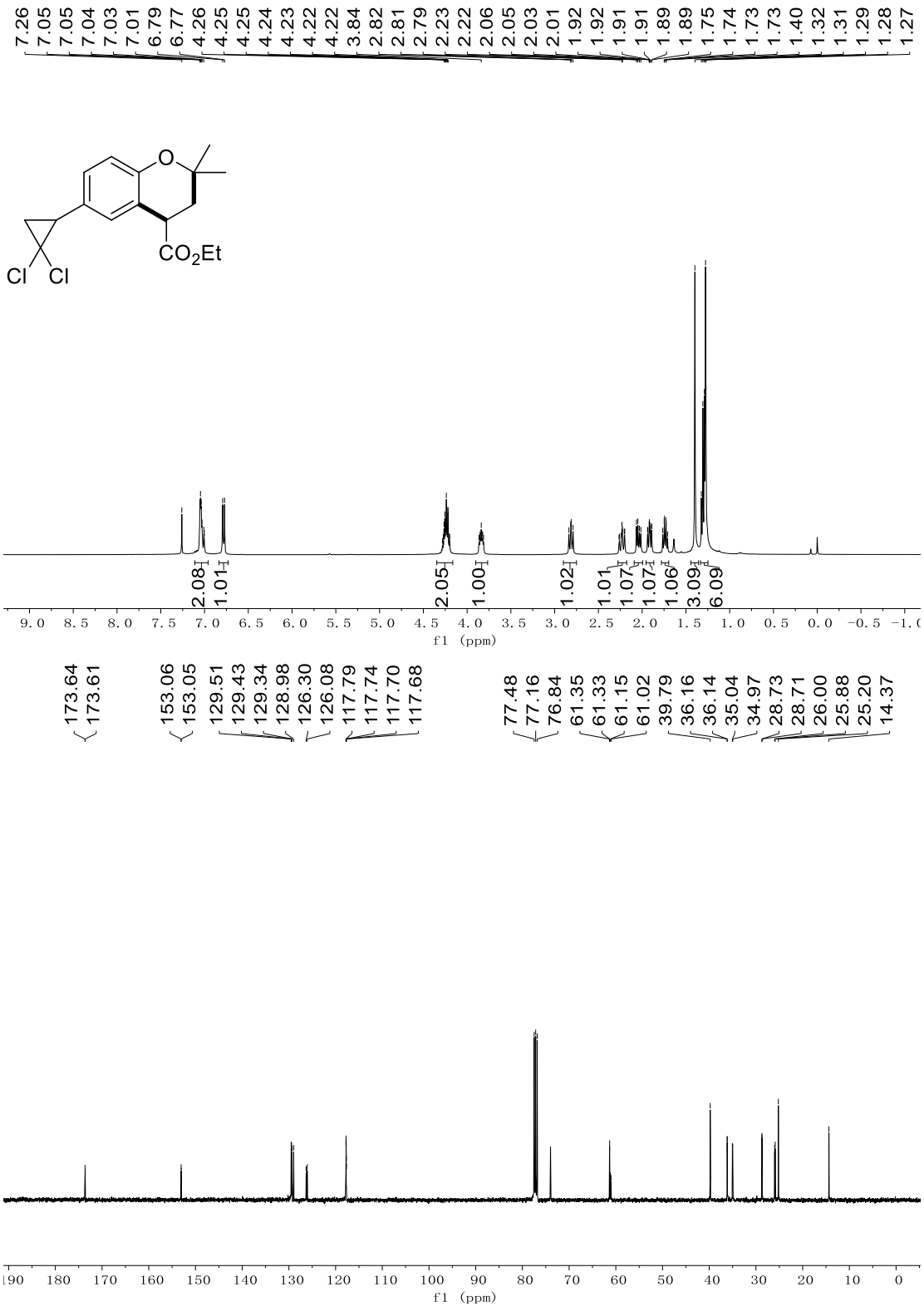

7.07 7.05 7.05 7.05 7.03 7.03 6.75 6.73 6.70 6.69 6.68 6.67 6.63 6.63
4.25 4.24 4.23 4.22 4.21 4.21 4.20 4.20 4.19 4.18 4.16
3.81 3.80 3.79 3.78 3.77
2.26 2.25 2.23 2.20 2.20 2.16 2.14 2.04 2.02 2.00 1.99 1.40 1.33 1.31 1.29 1.29 1.27 1.26 1.26 1.24
O
Me
CO2Et
(2:3)
Me
O
CO2Et
0.97 0.36 0.97 0.59 2.00 0.99 2.73 1.57 0.68 1.94 1.12 5.90
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


174.38 174.02 153.93 153.29 138.72 138.35 128.58 128.30 122.24 121.22 118.21 117.26 115.70 114.94
77.48 77.16 76.84 73.64 73.17 61.17
39.57 38.93 37.58 36.37 28.90 27.18 26.47 24.99 21.21 19.58 14.35 14.23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

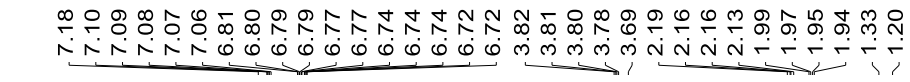
24

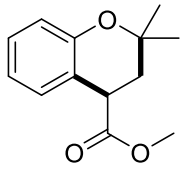

7.73 7.72 7.72 7.71 7.70 7.67 7.66 7.65 7.64 7.45 7.45 7.43 7.27 6.89 6.87
4.26 4.25 4.24 4.23 4.22 4.22 4.21 4.20 4.19 3.88 3.87 3.86 3.84 2.31 2.28 2.27 2.25 2.12 2.11 2.09 2.07 1.44 1.33 1.28 1.27 1.25
Cl
O
O
CO2Et
3.02 1.17 2.06 1.00 2.07 1.04 1.02 1.04 2.96 3.07 3.21
f1 (ppm)
194.26 173.16 157.98 138.30 136.67 132.60 131.29 131.18 129.19 128.57 118.00 117.86 77.48 77.16 76.84 75.19 61.57 39.42 35.94 28.52 25.48 14.28
f1 (ppm)

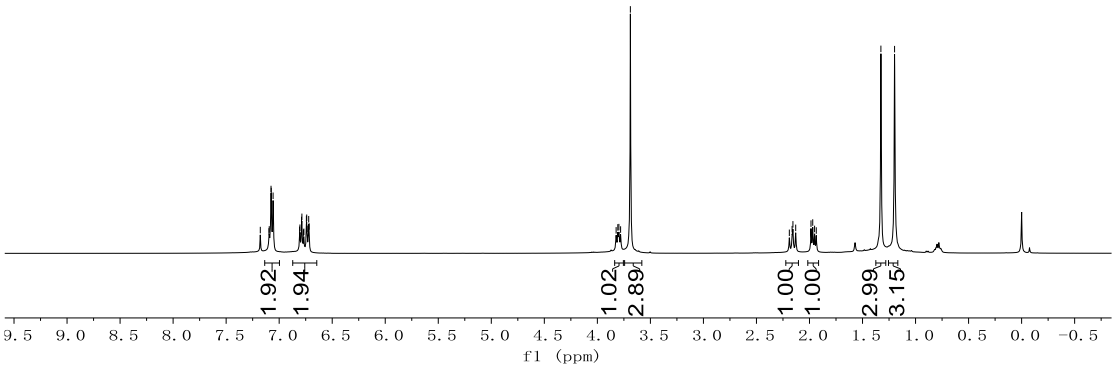
25

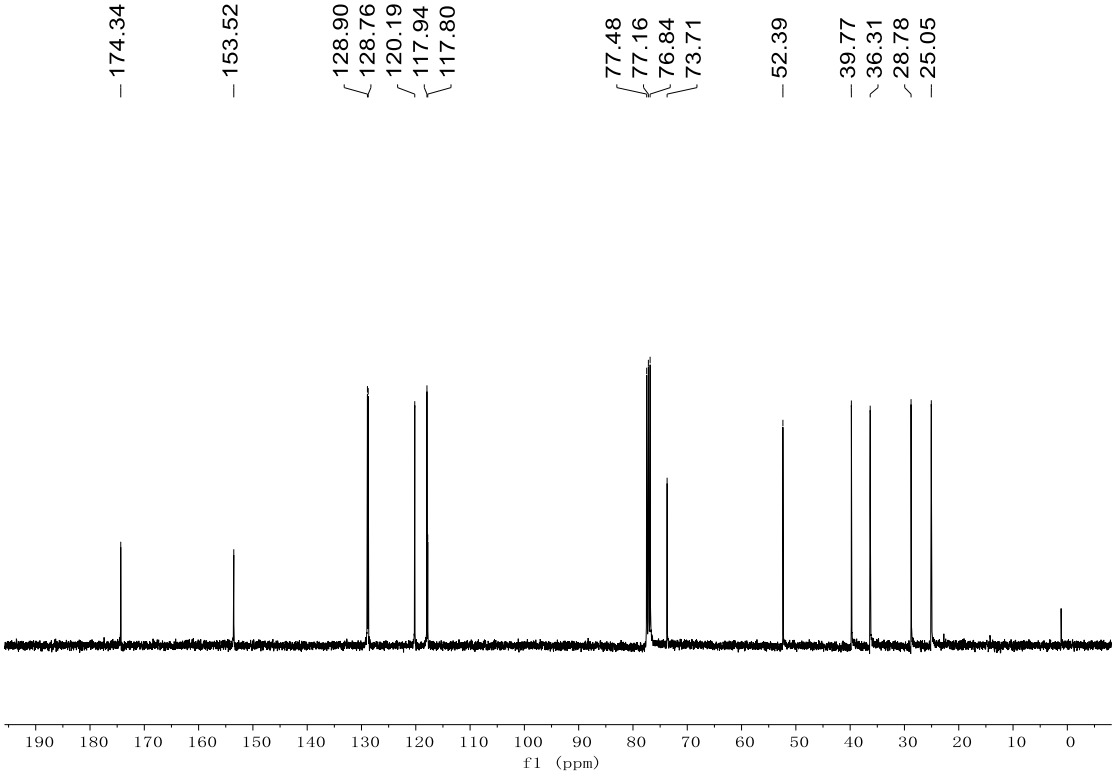

7.26 7.05 7.05 7.04 7.03 7.01 6.79 6.77 4.26 4.25 4.25 4.24 4.23 4.22 4.22 3.84 2.82 2.81 2.79 2.23 2.22 2.06 2.05 2.03 2.01 1.92 1.92 1.91 1.91 1.89 1.89 1.75 1.74 1.73 1.73 1.40 1.32 1.31 1.29 1.28 1.27
O
CO2Et
Cl Cl
2.08 1.01 2.05 1.00 1.02 1.01 1.07 1.07 1.06 3.09 6.09
f1 (ppm)
173.64 173.61 153.06 153.05 129.51 129.43 129.34 128.98 126.30 126.08 117.79 117.74 117.70 117.68 77.48 77.16 76.84 61.35 61.33 61.15 61.02 39.79 36.16 36.14 35.04 34.97 28.73 28.71 26.00 25.88 25.20 14.37
f1 (ppm)

26

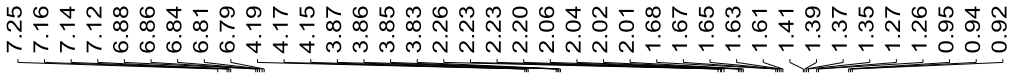

7.18
7.10
7.09
7.08
7.07
7.06
6.81
6.80
6.79
6.79
6.77
6.77
6.74
6.74
6.74
6.72
6.72
3.82
3.81
3.80
3.78
3.69
2.19
2.16
2.16
2.13
1.99
1.97
1.95
1.94
1.33
1.20

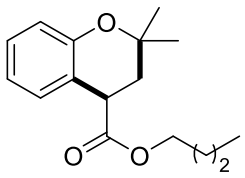

O
O
O

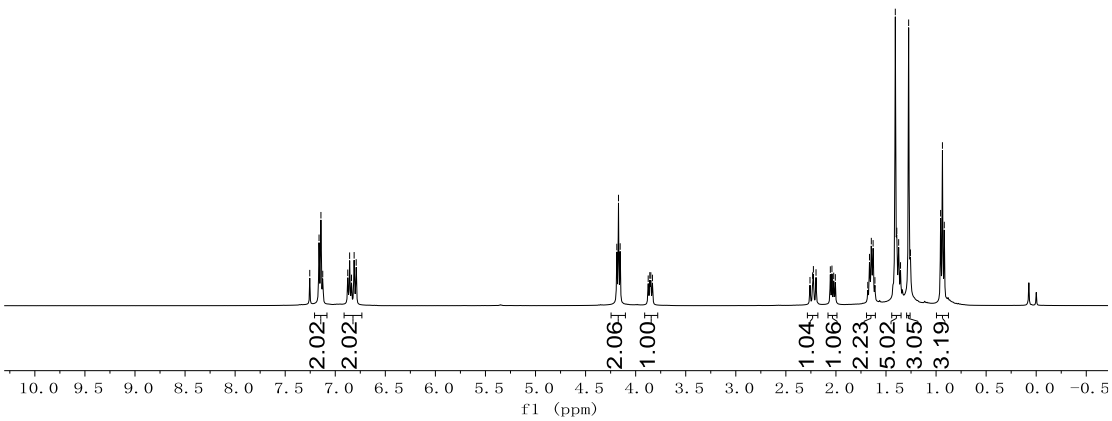

1.92
1.94
1.02
2.89
1.00
1.00
2.99
3.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


174.34
153.52
128.90
128.76
120.19
117.94
117.80
77.48
77.16
76.84
73.71
52.39
39.77
36.31
28.78
25.05
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

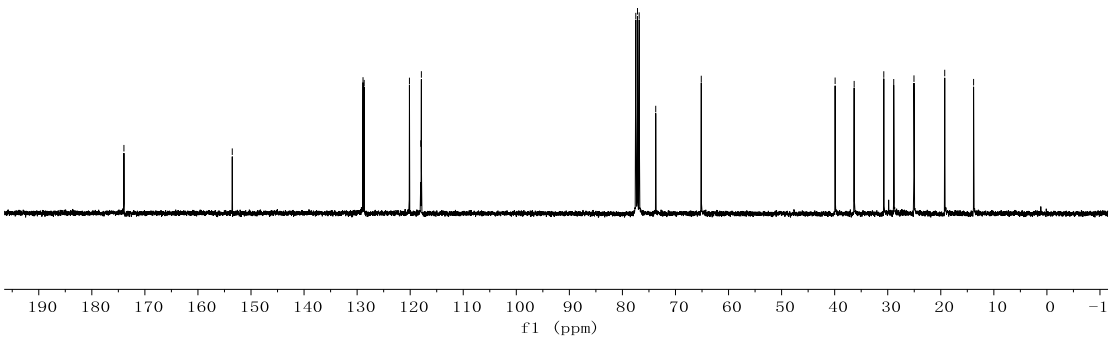
27


7.25
7.16
7.14
7.12
6.88
6.86
6.84
6.81
6.79
4.19
4.17
4.15
3.87
3.86
3.85
3.83
2.26
2.23
2.23
2.20
2.06
2.04
2.02
2.01
1.68
1.67
1.65
1.63
1.61
1.41
1.39
1.37
1.35
1.27
1.26
0.95
0.94
0.92


O
O
O
2


2.02
2.02
2.06
1.00
1.04
1.06
2.23
5.02
3.05
3.19
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
f1 (ppm)

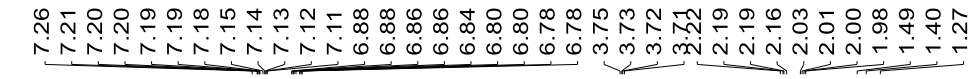

173.95
153.53
128.89
128.67
120.14
118.00
117.89
77.48
77.16
76.84
73.72
65.14
39.91
36.33
30.74
28.87
25.05
19.26
13.82


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

28


7.26 7.18 7.18 7.18 7.16 7.14 7.14 6.87 6.85 6.85 6.81 6.81 6.79 6.79 4.87 3.81 2.22 2.20 2.05 2.03 2.02 2.00 1.88 1.87 1.73 1.72 1.71 1.71 1.70 1.47 1.44 1.43 1.42 1.41 1.39 1.38 1.38 1.37 1.36 1.35 1.28
O
O
O
2.03 0.99 0.97 1.00 1.01 1.10 1.09 2.22 2.20 9.15 3.56
f1 (ppm)
173.29 153.52 128.89 128.58 120.09 118.21 117.84 77.48 77.16 76.84 73.74 73.51 40.02 36.30 31.73 31.57 28.86 25.46 25.14 23.85 23.81
f1 (ppm)

29


7.26
7.21
7.20
7.20
7.19
7.19
7.18
7.15
7.14
7.13
7.12
7.11
6.88
6.88
6.86
6.86
6.84
6.80
6.80
6.78
6.78
3.75
3.73
3.72
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2.19
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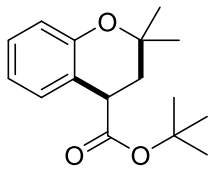
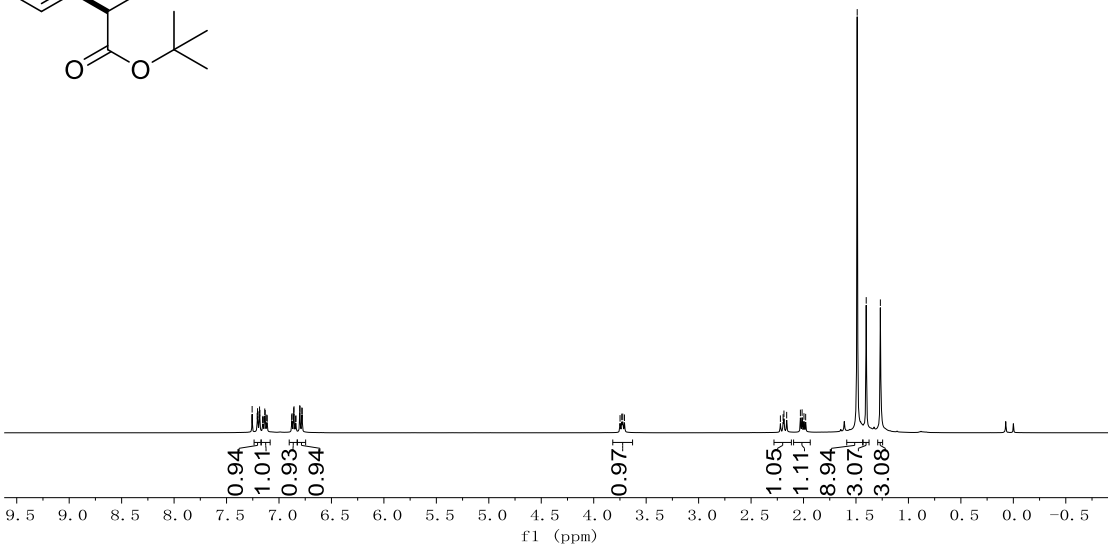
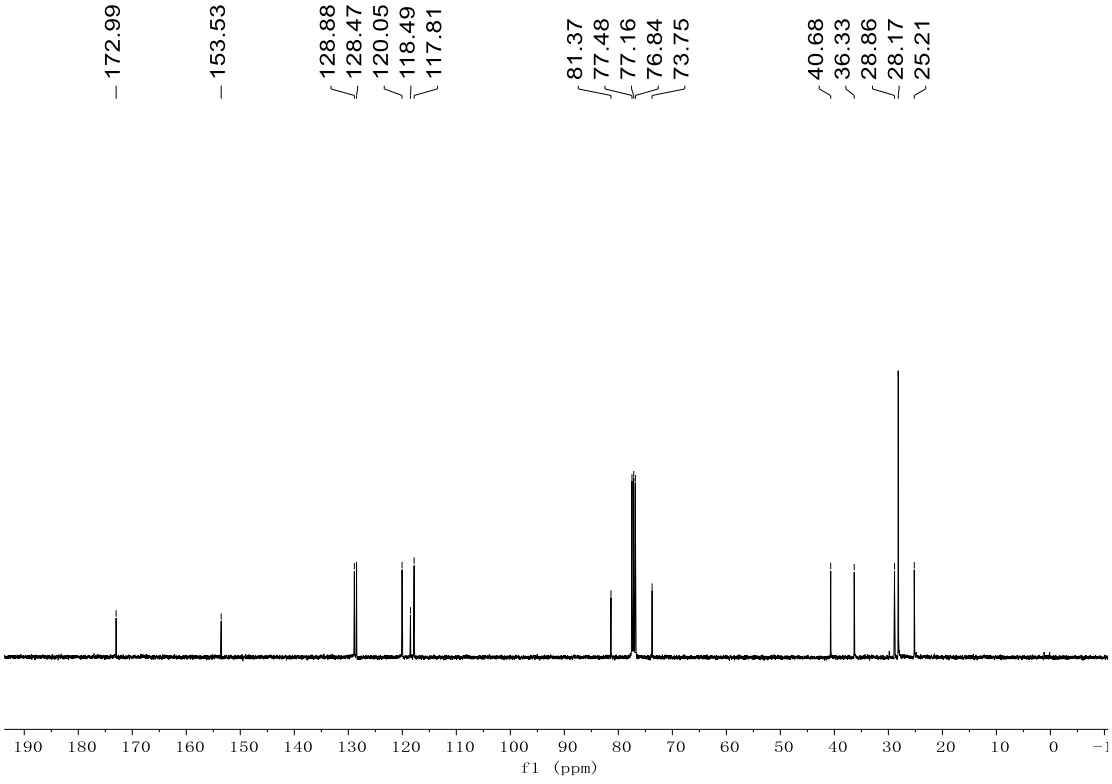
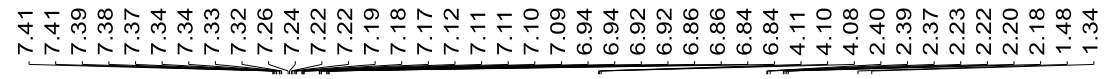
2.01
2.00
1.98
1.49
1.40
1.27


O
O
O


0.94
1.01
0.93
0.94
0.97
1.05
1.11
8.94
3.07
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


172.99
153.53
128.88
128.47
120.05
118.49
117.81
81.37
77.48
77.16
76.84
73.75
40.68
36.33
28.86
28.17
25.21
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

30


7.41
7.41
7.39
7.38
7.37
7.34
7.34
7.33
7.32
7.26
7.24
7.22
7.22
7.19
7.18
7.17
7.12
7.11
7.11
7.10
7.09
6.94
6.94
6.92
6.92
6.86
6.86
6.84
6.84
4.11
4.10
4.08
2.40
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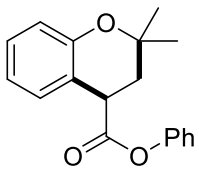
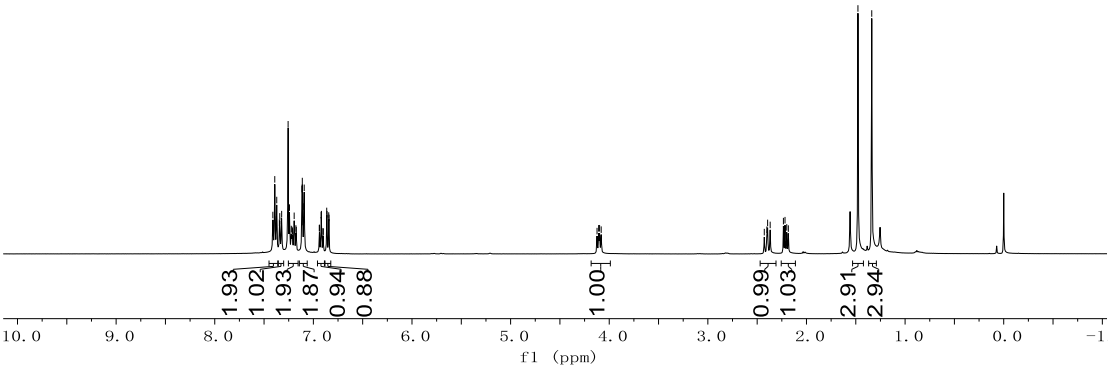
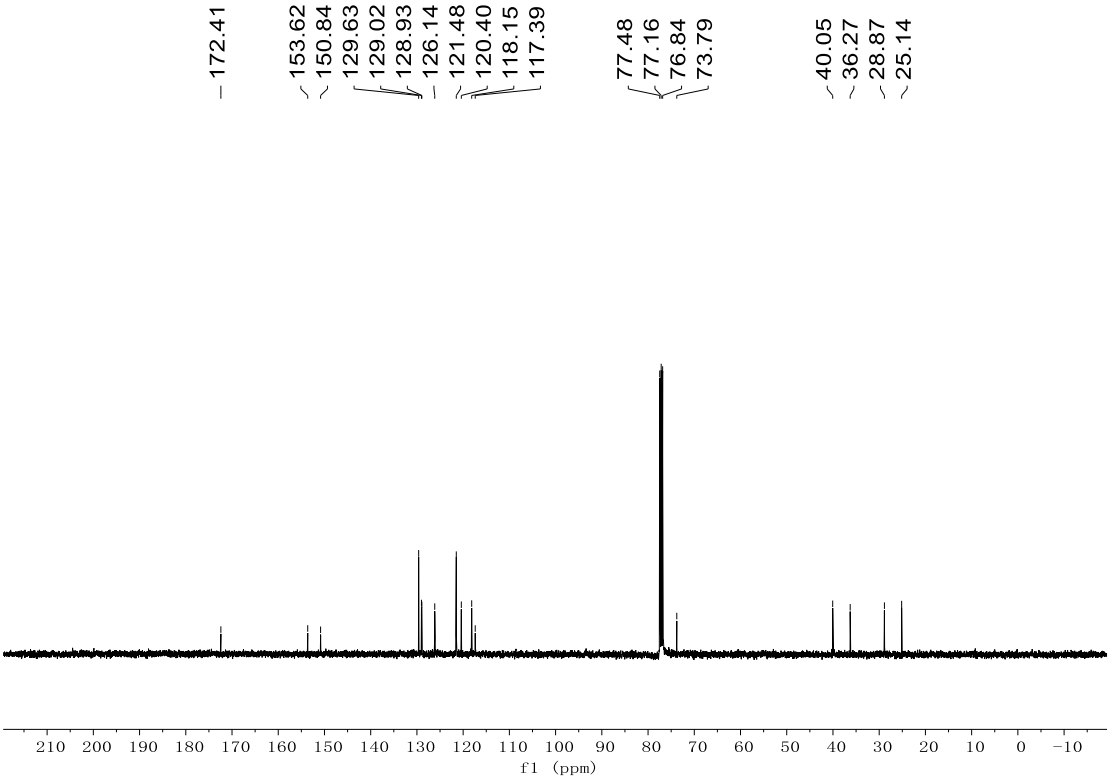
2.37
2.23
2.22
2.20
2.18
1.48
1.34

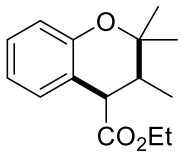

O
O
O
Ph

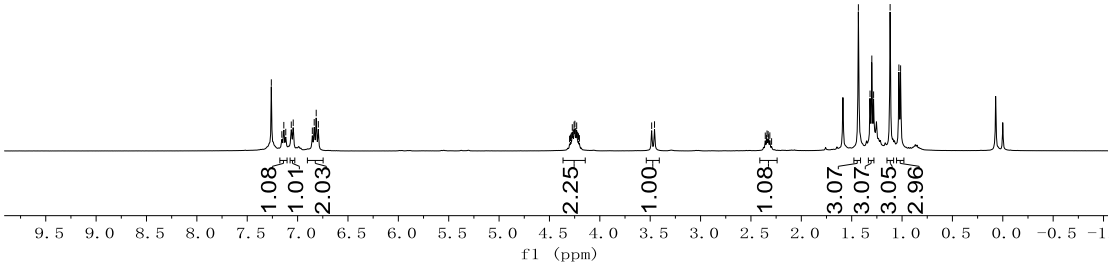

1.93
1.02
1.93
1.87
0.94
0.88
1.00
0.99
1.03
2.91
2.94
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1
f1 (ppm)

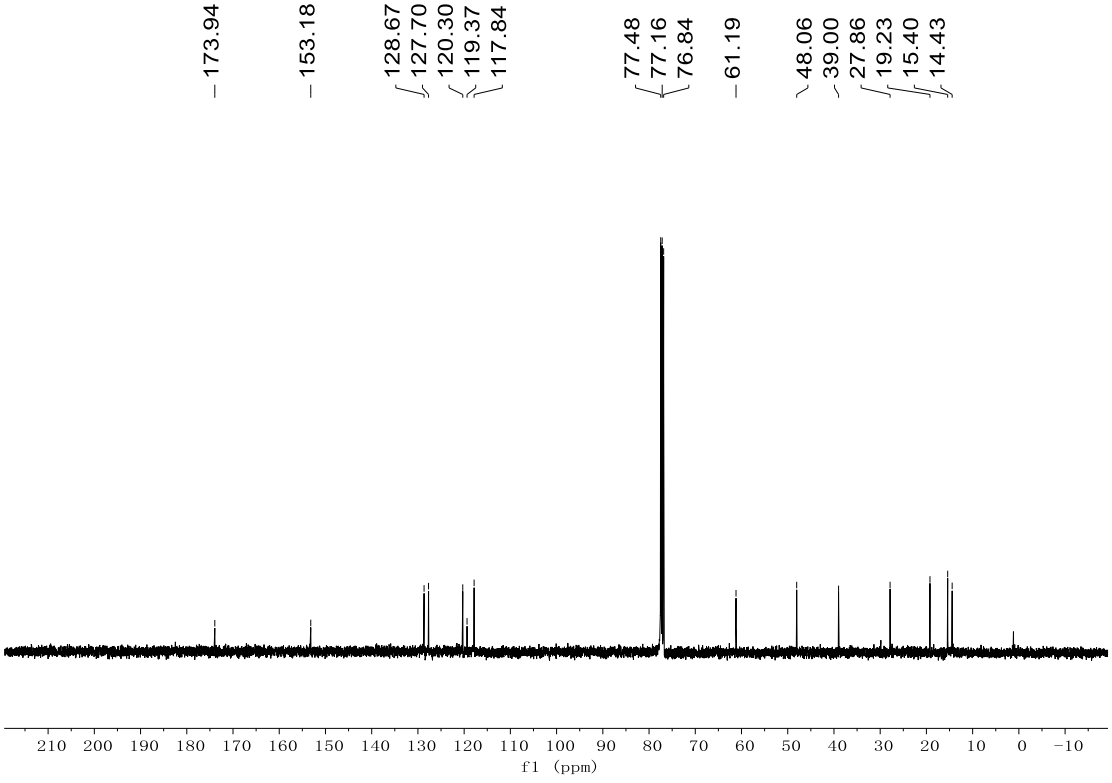

172.41
153.62
150.84
129.63
129.02
128.93
126.14
121.48
120.40
118.15
117.39
77.48
77.16
76.84
73.79
40.05
36.27
28.87
25.14
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

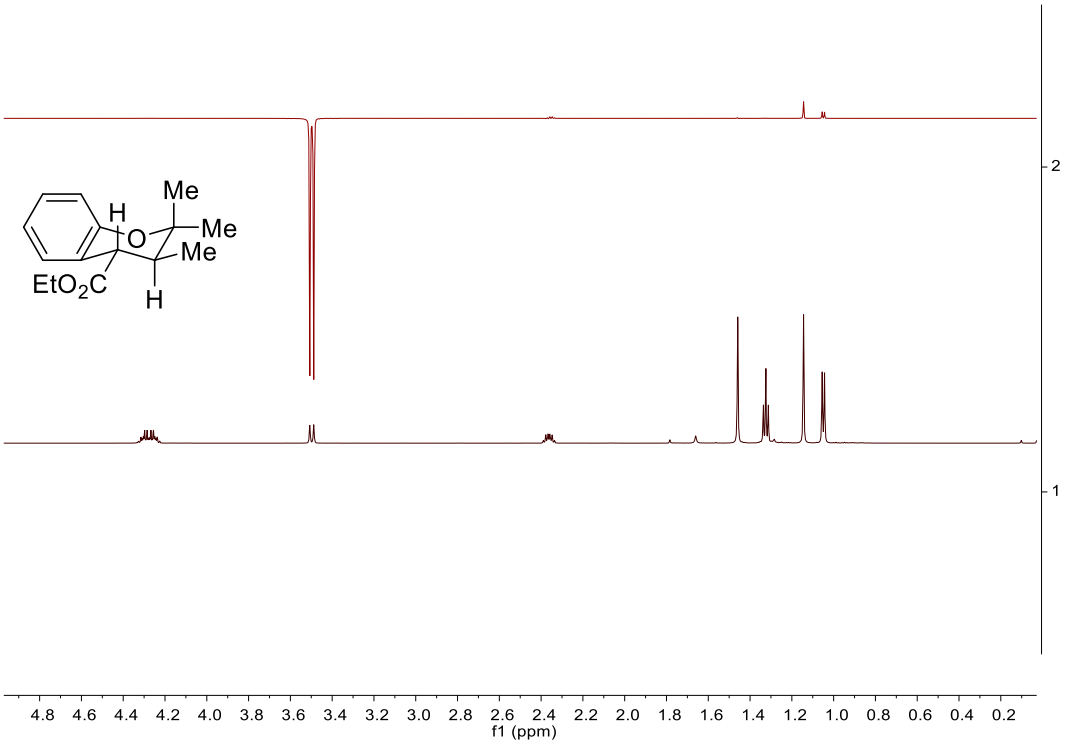
31


7.26
7.16
7.14
7.12
7.06
7.04
6.85
6.84
6.82
6.79
4.30
4.29
4.28
4.27
4.27
4.26
4.25
4.24
4.23
4.22
4.21
4.20
3.49
3.46
2.36
2.35
2.34
2.33
2.32
2.31
2.29
1.43
1.32
1.30
1.28
1.12
1.03
1.01


O
CO2Et

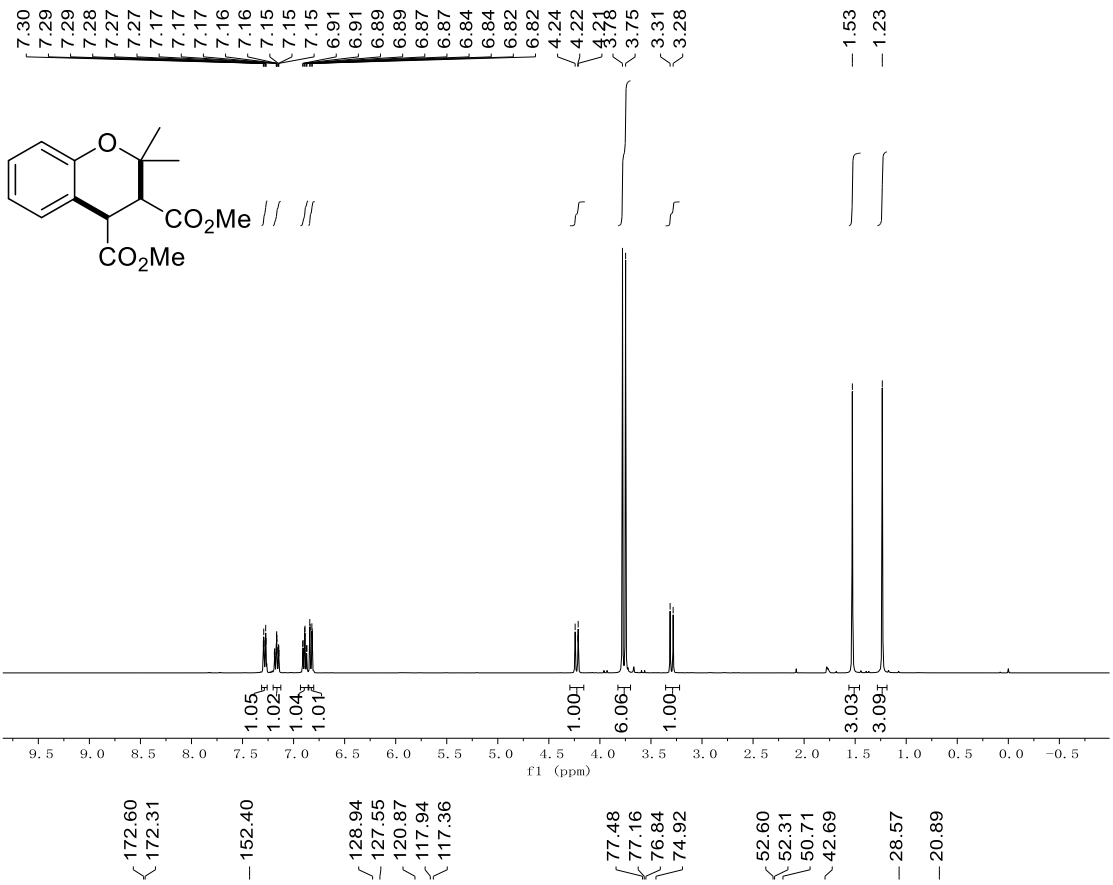

1.08
1.01
2.03
2.25
1.00
1.08
3.07
3.07
3.05
2.96
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

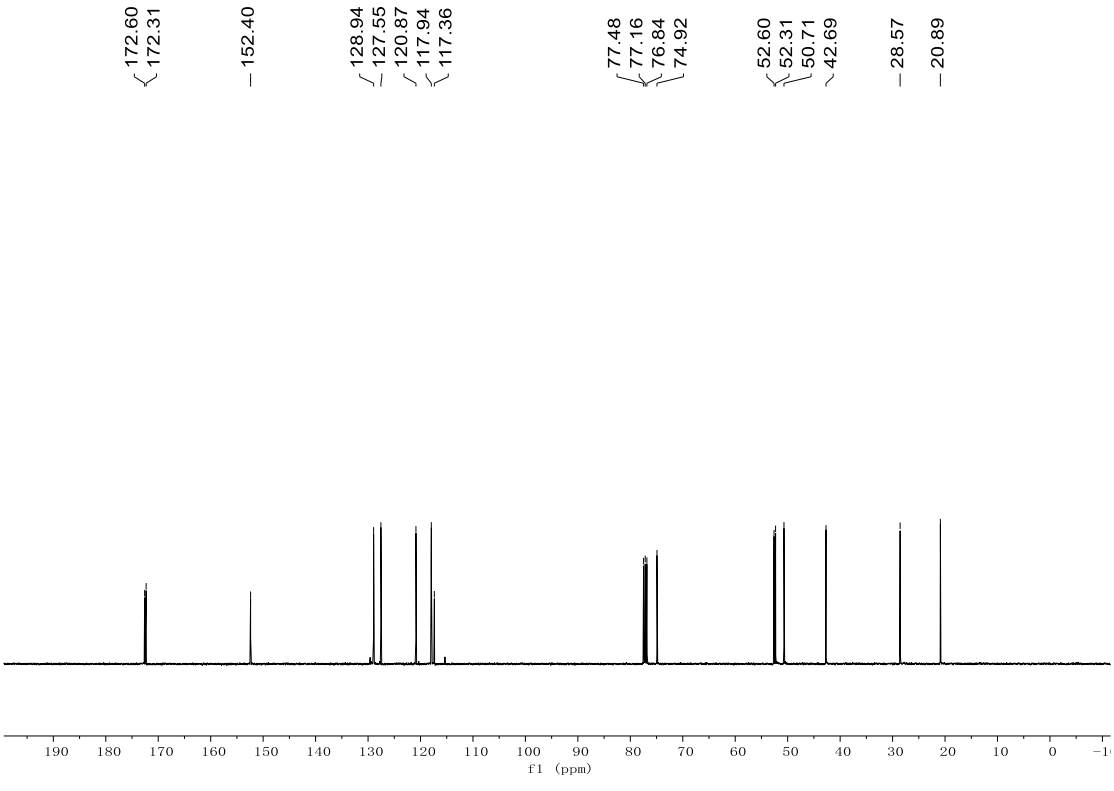

173.94
153.18
128.67
127.70
120.30
119.37
117.84
77.48
77.16
76.84
61.19
48.06
39.00
27.86
19.23
15.40
14.43
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

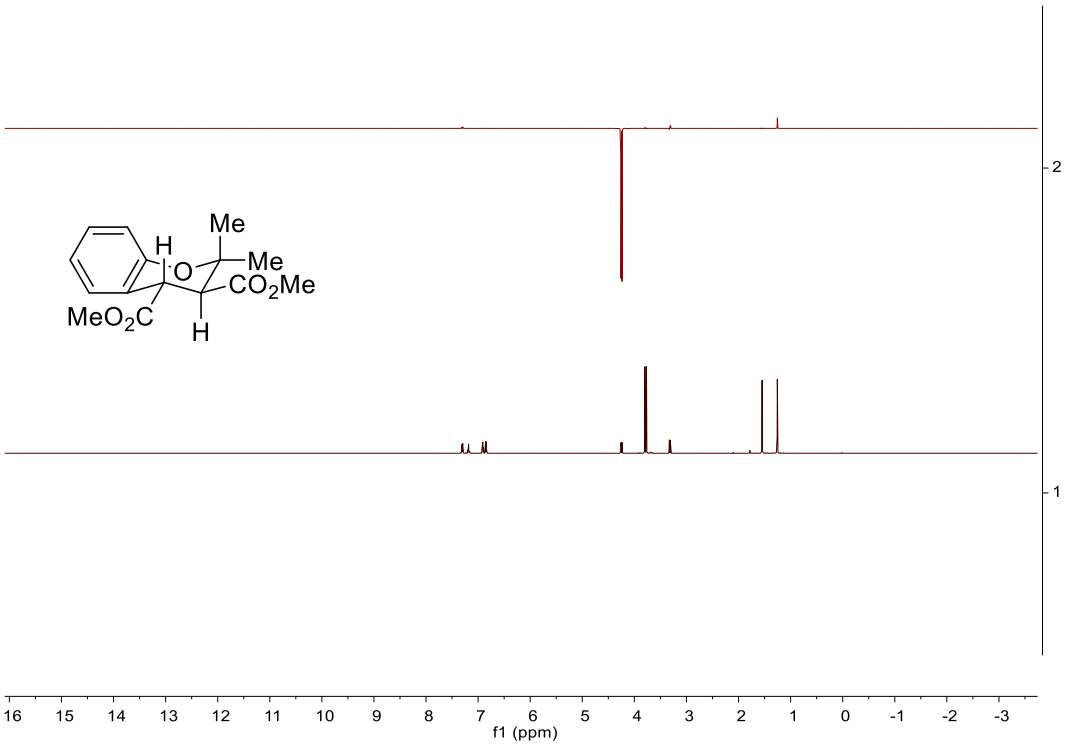

Me
H
O
Me
Me
EtO2C
H
2
1
4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2
f1 (ppm)

1D NOE

32

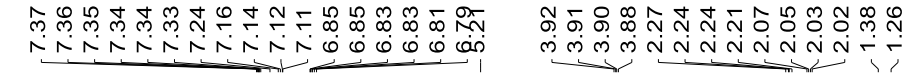

7.30
7.29
7.29
7.28
7.27
7.27
7.17
7.17
7.17
7.16
7.16
7.15
7.15
7.15
6.91
6.91
6.89
6.89
6.87
6.87
6.84
6.84
6.82
6.82
4.24
4.22
4.21
3.78
3.75
3.31
3.28
1.53
1.23
O
CO2Me
CO2Me
1.05
1.02
1.04
1.01
1.00
6.06
1.00
3.03
3.09
f1 (ppm)


172.60
172.31
152.40
128.94
127.55
120.87
117.94
117.36
77.48
77.16
76.84
74.92
52.60
52.31
50.71
42.69
28.57
20.89
f1 (ppm)


Me
H
O
Me
CO2Me
MeO2C
H
2
1
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

1D NOE

33


7.37
7.36
7.35
7.34
7.34
7.33
7.24
7.16
7.14
7.12
7.11
6.85
6.85
6.83
6.83
6.81
6.79
5.21
3.92
3.91
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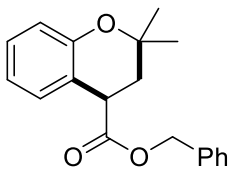
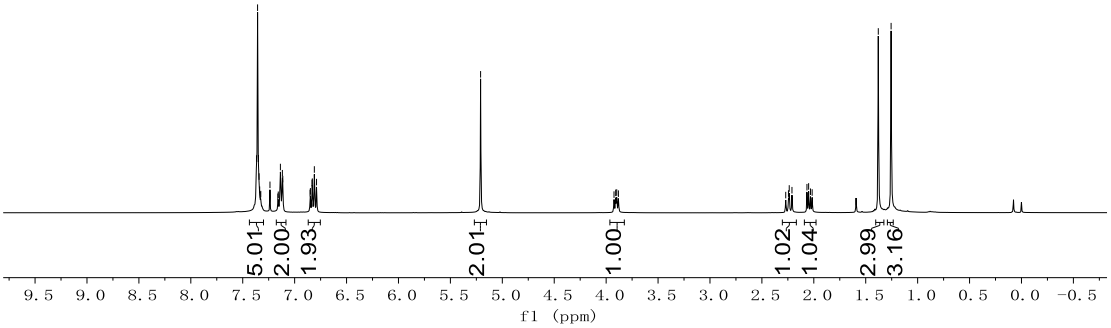
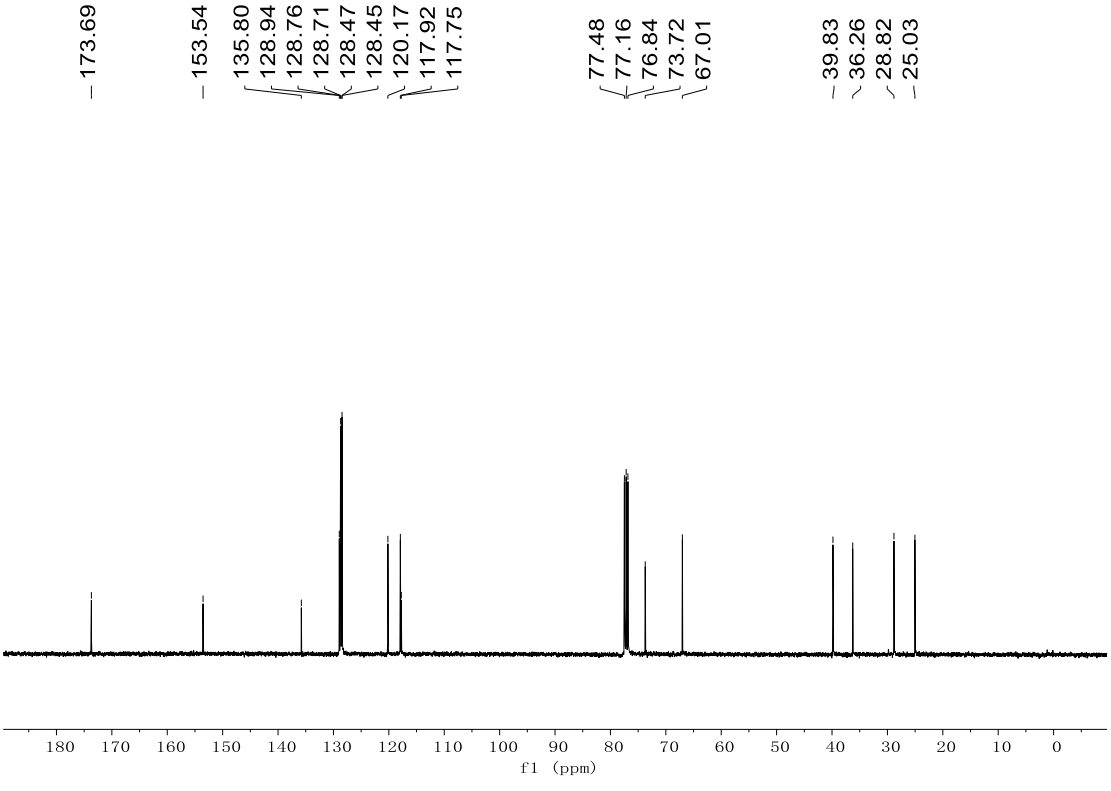
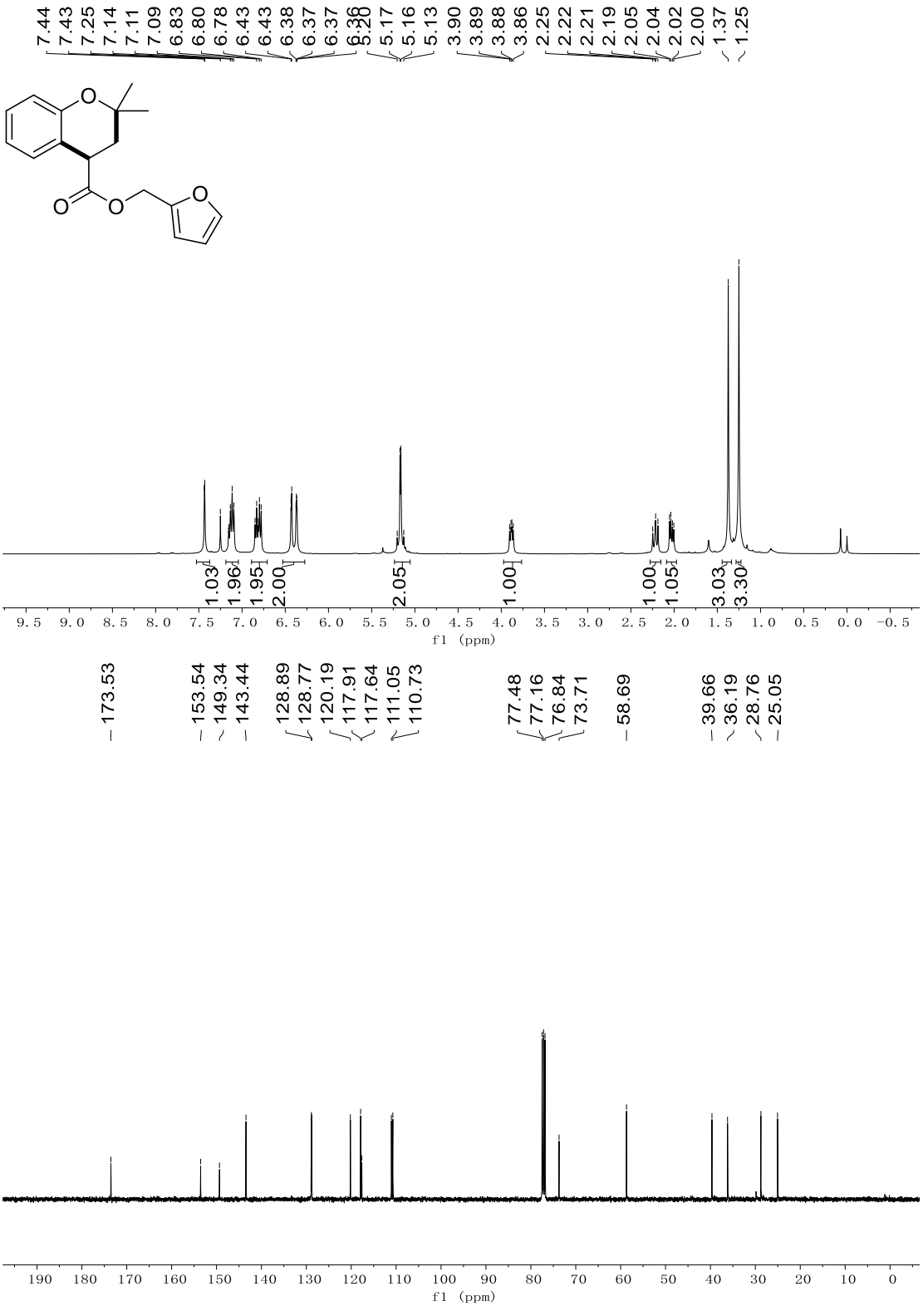
2.07
2.05
2.03
2.02
1.38
1.26


O
O
O
Ph


5.01
2.00
1.93
2.01
1.00
1.02
1.04
2.99
3.16
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


173.69
153.54
135.80
128.94
128.76
128.71
128.47
128.45
120.17
117.92
117.75
77.48
77.16
76.84
73.72
67.01
39.83
36.26
28.82
25.03
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

34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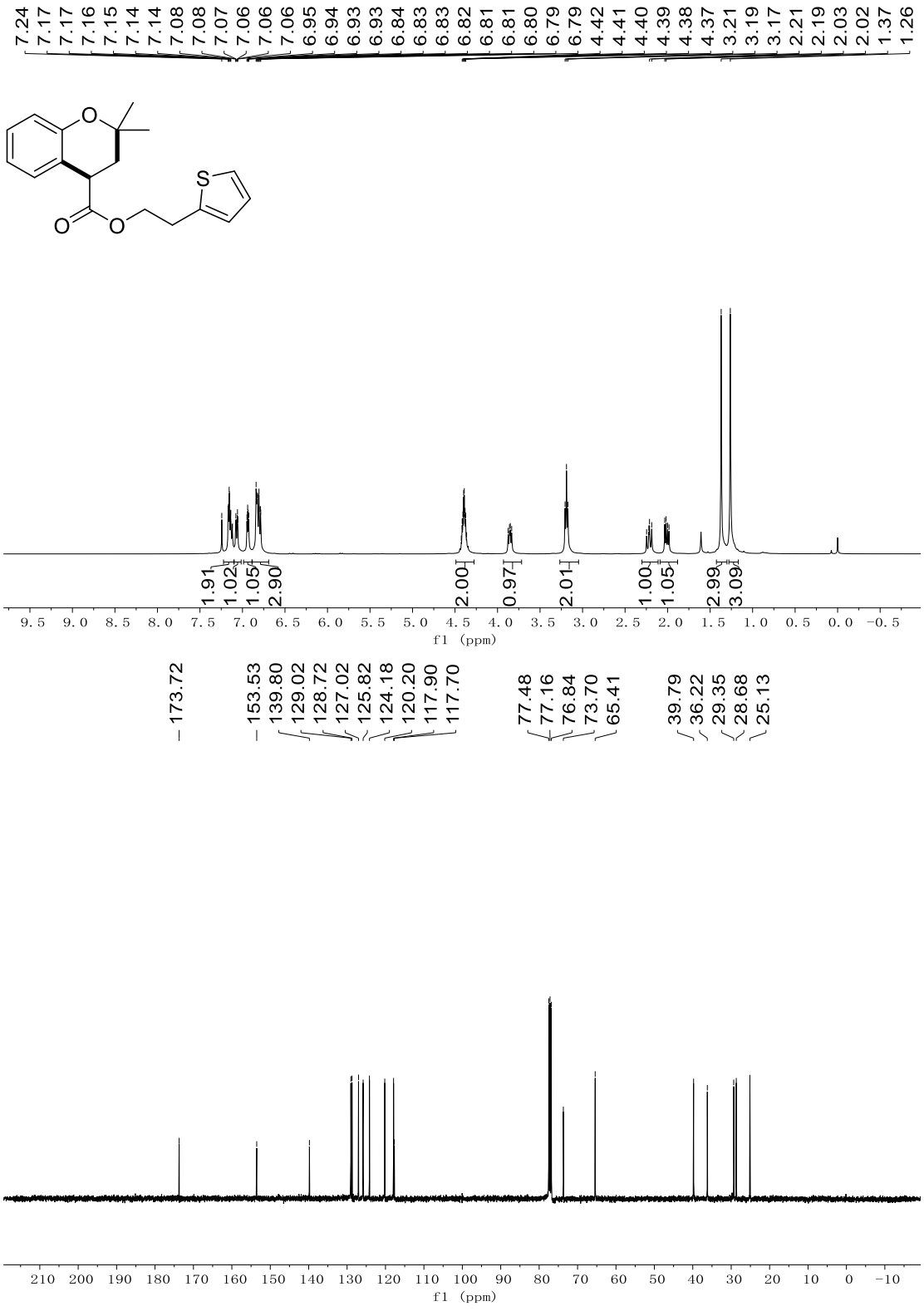
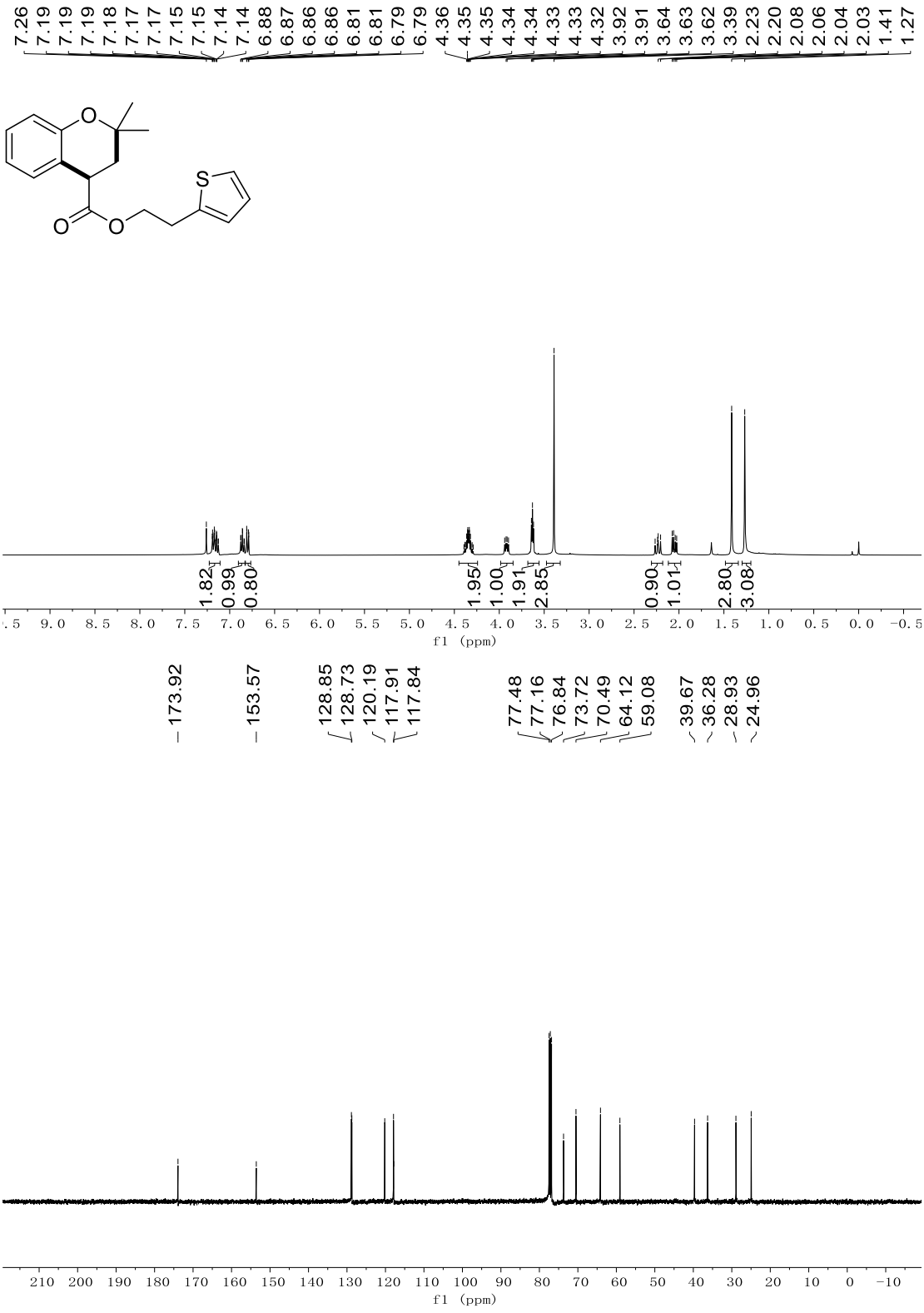
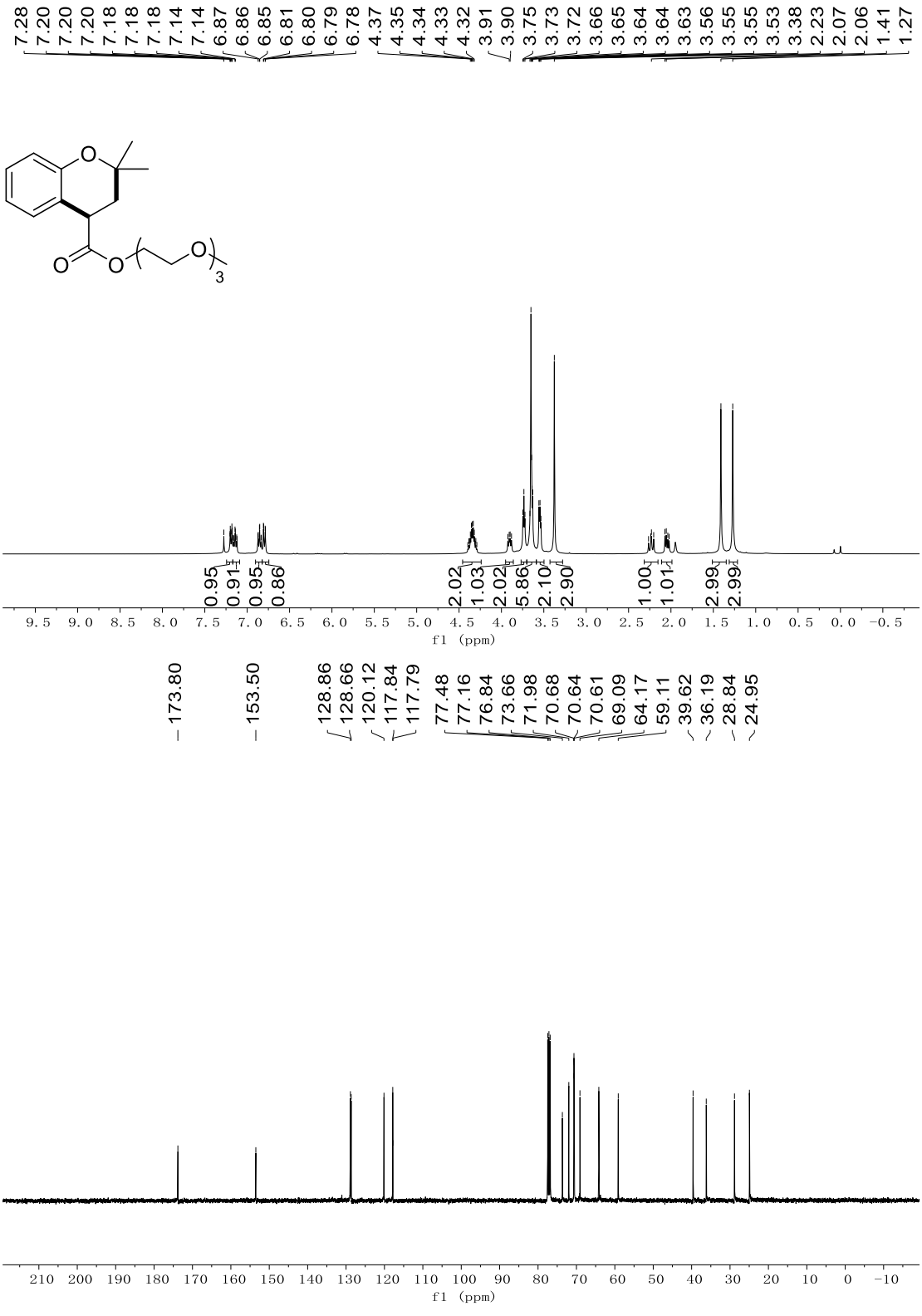
7.11
7.09
6.83
6.80
6.78
6.43
6.43
6.38
6.37
6.37
6.36
5.20
5.17
5.16
5.13
3.90
3.89
3.88
3.86
2.25
2.22
2.21
2.19
2.05
2.04
2.02
2.00
1.37
1.25
O
O
O
O
1.03
1.96
1.95
2.00
2.05
1.00
1.00
1.05
3.03
3.30
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)
173.53
153.54
149.34
143.44
128.89
128.77
120.19
117.91
117.64
111.05
110.73
77.48
77.16
76.84
73.71
58.69
39.66
36.19
28.76
25.05
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

35

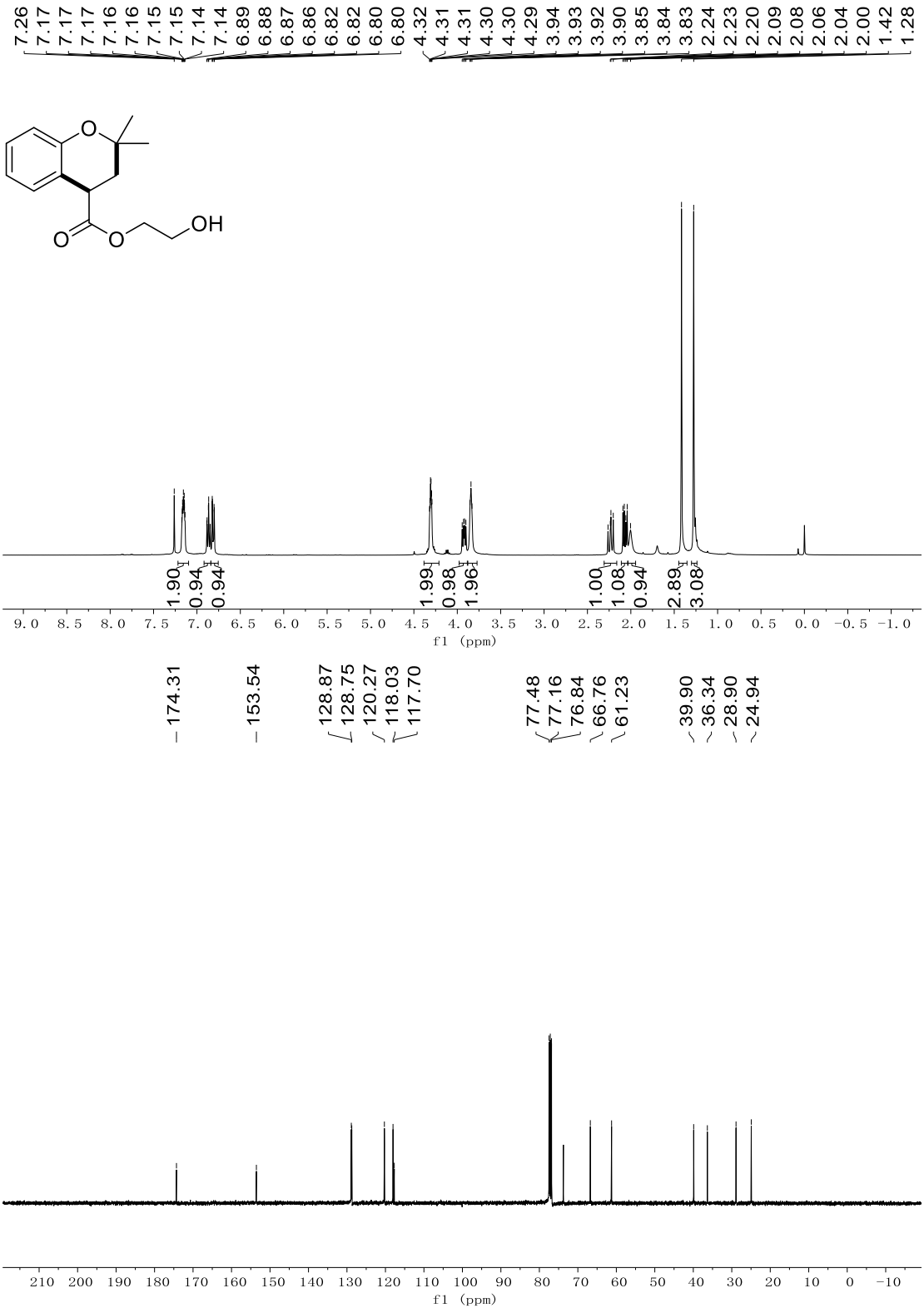

7.24 7.17 7.17 7.16 7.15 7.14 7.14 7.08 7.08 7.07 7.06 7.06 7.06 6.95 6.94 6.93 6.93 6.84 6.83 6.83 6.82 6.81 6.81 6.80 6.79 6.79 4.42 4.41 4.40 4.39 4.38 4.37 3.21 3.19 3.17 2.21 2.19 2.03 2.02 1.37 1.26
O
O
O
S
1.91 1.02 1.05 2.90 2.00 0.97 2.01 1.00 1.05 2.99 3.09
f1 (ppm)
173.72 153.53 139.80 129.02 128.72 127.02 125.82 124.18 120.20 117.90 117.70 77.48 77.16 76.84 73.70 65.41 39.79 36.22 29.35 28.68 25.13
f1 (ppm)

36


7.26 7.19 7.19 7.19 7.18 7.17 7.17 7.15 7.15 7.14 7.14 6.88 6.87 6.86 6.86 6.81 6.81 6.79 6.79 4.36 4.35 4.35 4.34 4.34 4.33 4.33 4.32 3.92 3.91 3.64 3.63 3.62 3.39 2.23 2.20 2.08 2.06 2.04 2.03 1.41 1.27
O
O
S
O
1.82 0.99 0.80 1.95 1.00 1.91 2.85 0.90 1.01 2.80 3.08
f1 (ppm)
173.92 153.57 128.85 128.73 120.19 117.91 117.84 77.48 77.16 76.84 73.72 70.49 64.12 59.08 39.67 36.28 28.93 24.96
f1 (ppm)


7.28 7.20 7.20 7.20 7.18 7.18 7.18 7.14 7.14 6.87 6.86 6.85 6.81 6.80 6.79 6.78
4.37 4.35 4.34 4.33 4.32 3.91 3.90 3.75 3.73 3.72 3.66 3.65 3.64 3.64 3.63 3.56 3.55 3.55 3.53 3.38 2.23 2.07 2.06 1.41 1.27
O
O
O
O
3
0.95 0.91 0.95 0.86 2.02 1.03 2.02 5.86 2.10 2.90 1.00 1.01 2.99 2.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)
173.80 153.50 128.86 128.66 120.12 117.84 117.79 77.48 77.16 76.84 73.66 71.98 70.68 70.64 70.61 69.09 64.17 59.11 39.62 36.19 28.84 24.95
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.26
7.18
7.17
7.16
7.15
7.14
7.13
6.88
6.88
6.87
6.86
6.82
6.81
6.80
6.79
4.29
4.28
4.27
4.26
4.26
4.25
4.24
4.24
3.84
3.83
3.81
2.23
2.22
2.20
2.06
2.04
2.02
2.01
1.41
1.28
1.06
1.04
1.03
1.03
1.01
0.04
O
O
O
Si
1.99
1.99
2.02
1.00
1.01
1.00
3.00
3.00
2.04
9.09
f1 (ppm)
174.02
153.53
128.90
128.65
120.15
118.05
117.89
77.48
77.16
76.84
73.72
63.58
39.99
36.34
28.91
25.03
17.52
-1.39
f1 (ppm)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7.17
7.17
7.17
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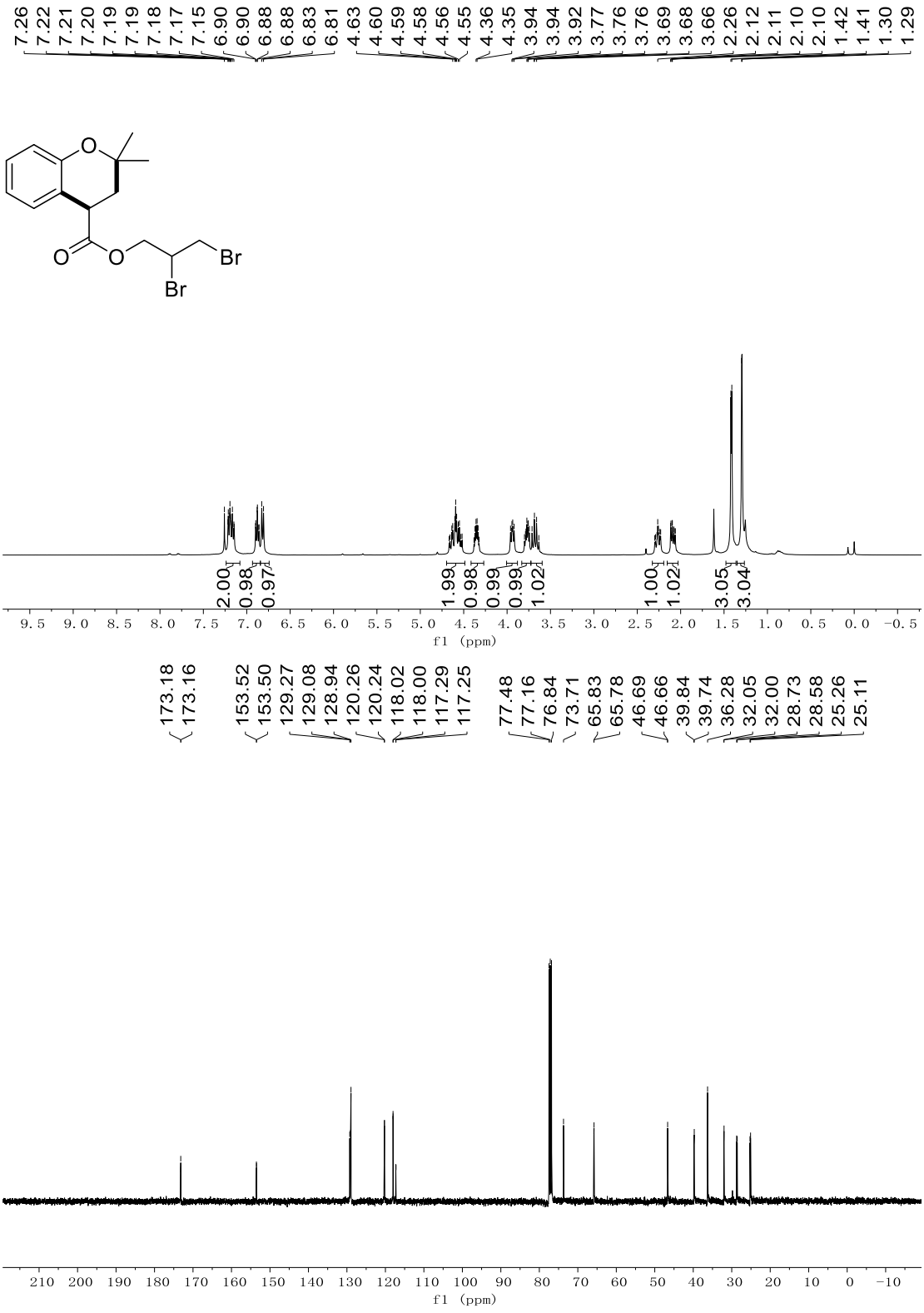
7.16
7.15
7.15
7.14
7.14
6.89
6.88
6.87
6.86
6.82
6.82
6.80
6.80
4.32
4.31
4.31
4.30
4.30
4.29
3.94
3.93
3.92
3.90
3.85
3.84
3.83
2.24
2.23
2.20
2.09
2.08
2.06
2.04
2.00
1.42
1.28
O
O
O
OH
1.90
0.94
0.94
1.99
0.98
1.96
1.00
1.08
0.94
2.89
3.08
f1 (ppm)
174.31
153.54
128.87
128.75
120.27
118.03
117.70
77.48
77.16
76.84
66.76
61.23
39.90
36.34
28.90
24.94
f1 (ppm)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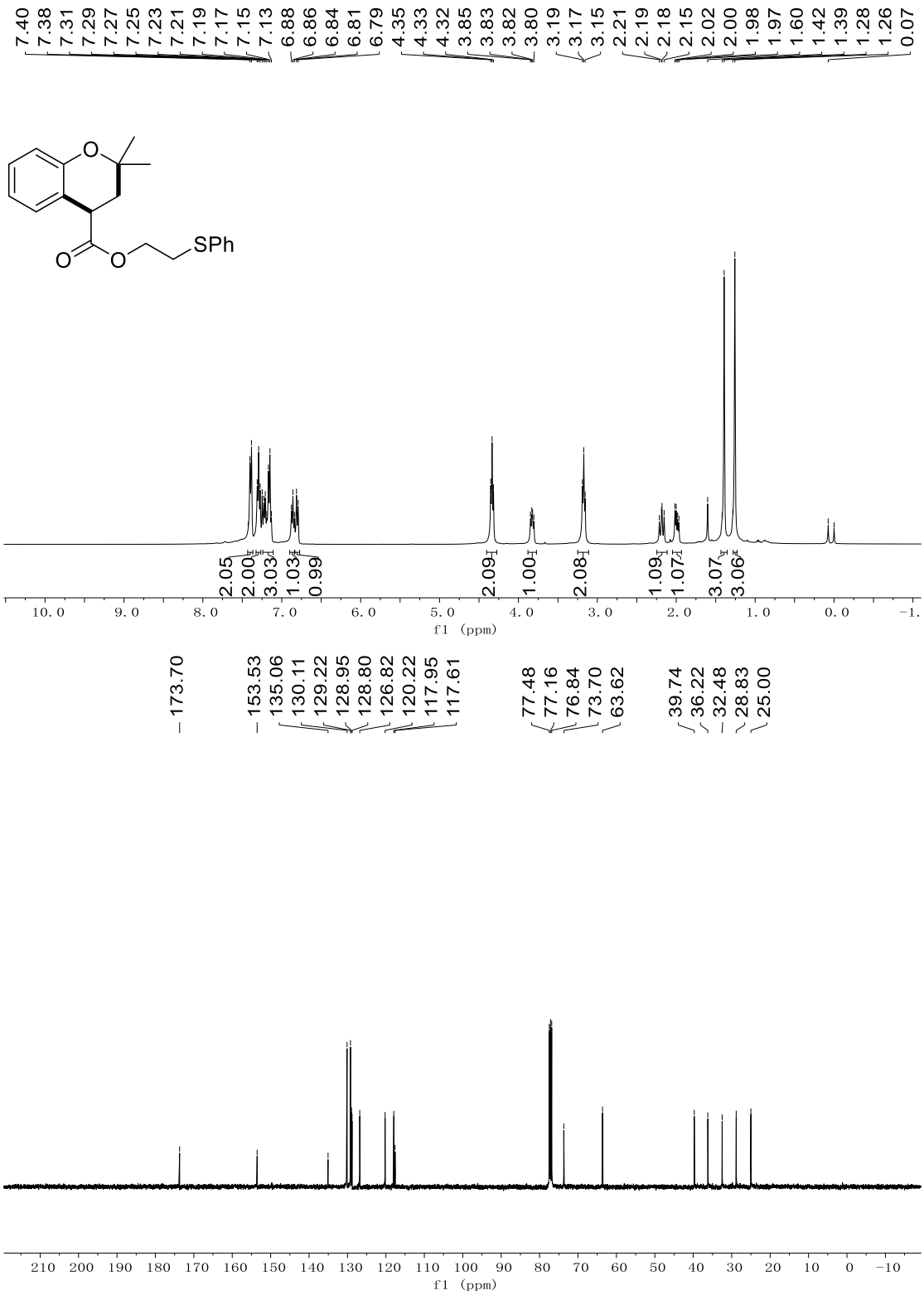
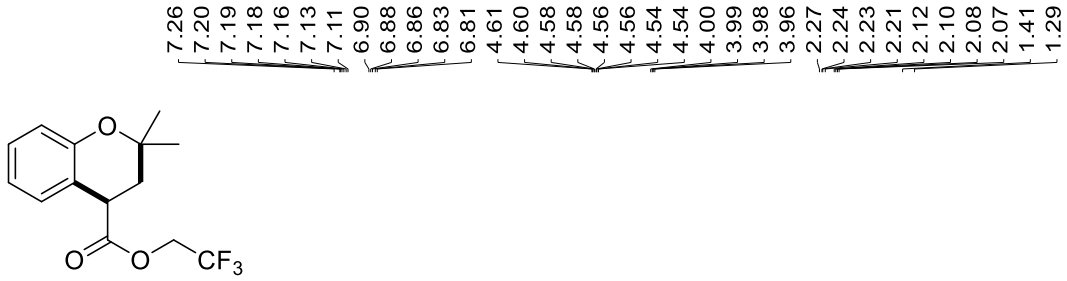
7.22
7.21
7.20
7.19
7.19
7.18
7.17
7.15
6.90
6.90
6.88
6.88
6.83
6.81
4.63
4.60
4.59
4.58
4.56
4.55
4.36
4.35
3.94
3.94
3.92
3.77
3.76
3.76
3.69
3.68
3.66
2.26
2.12
2.11
2.10
2.10
1.42
1.41
1.30
1.29
O
O
O
Br
Br
2.00
0.98
0.97
1.99
0.98
0.99
0.99
1.02
1.00
1.02
3.05
3.04
f1 (ppm)
173.18
173.16
153.52
153.50
129.27
129.08
128.94
120.26
120.24
118.02
118.00
117.29
117.25
77.48
77.16
76.84
73.71
65.83
65.78
46.69
46.66
39.84
39.74
36.28
32.05
32.00
28.73
28.58
25.26
25.11
f1 (ppm)

41


7.40 7.38 7.31 7.29 7.27 7.25 7.23 7.21 7.19 7.17 7.15 7.13 6.88 6.86 6.84 6.81 6.79 4.35 4.33 4.32 3.85 3.83 3.82 3.80 3.19 3.17 3.15 2.21 2.19 2.18 2.15 2.02 2.00 1.98 1.97 1.60 1.42 1.39 1.28 1.26 0.07
O
O
O
SPh
2.05 2.00 3.03 1.03 0.99 2.09 1.00 2.08 1.09 1.07 3.07 3.06
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 −1.
f1 (ppm)
173.70 153.53 135.06 130.11 129.22 128.95 128.80 126.82 120.22 117.95 117.61 77.48 77.16 76.84 73.70 63.62 39.74 36.22 32.48 28.83 25.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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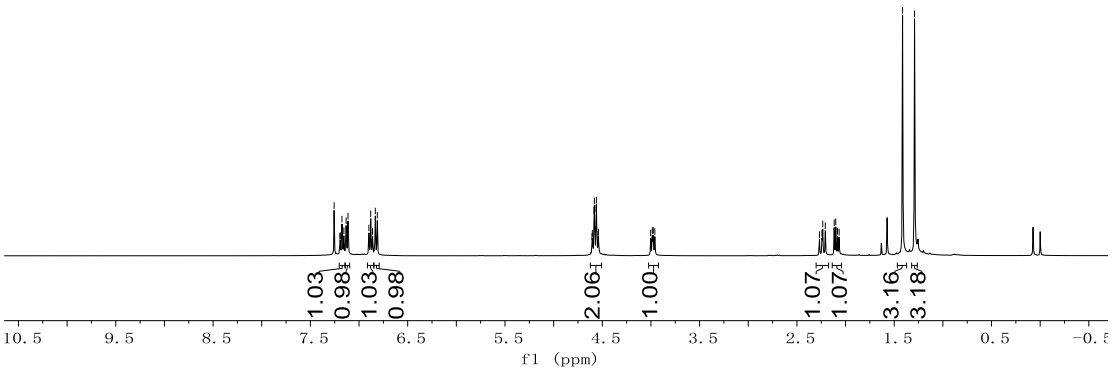
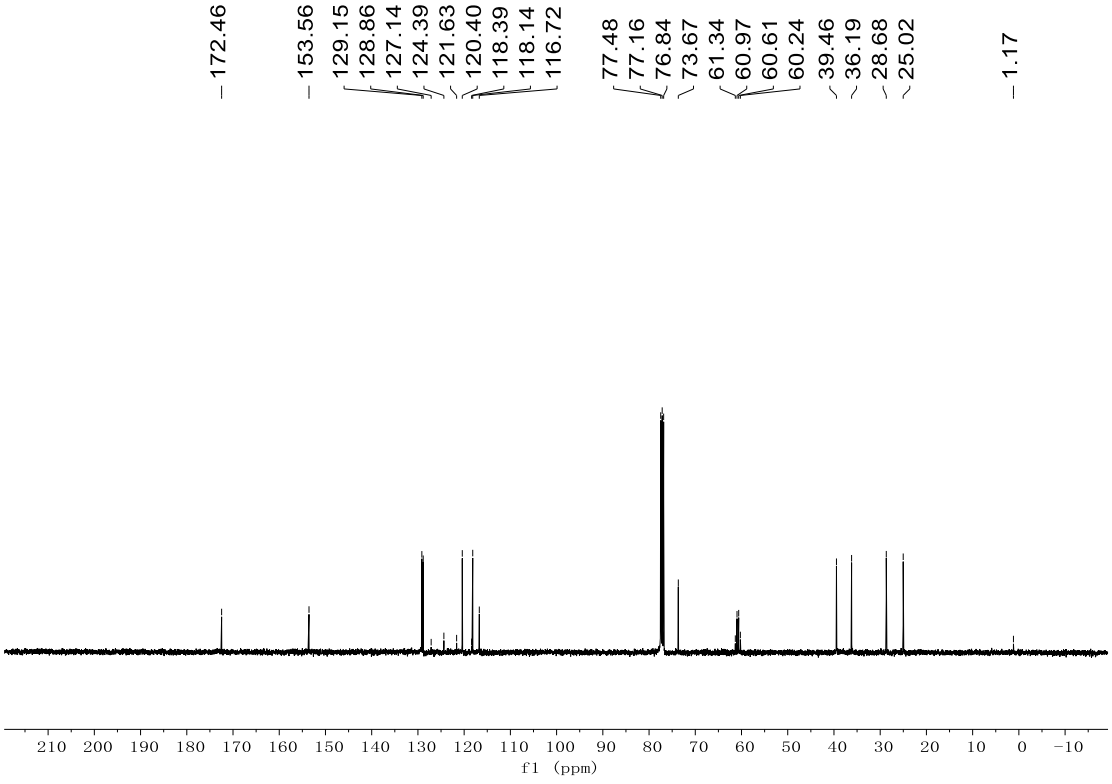
7.19
7.18
7.16
7.13
7.11
6.90
6.88
6.86
6.83
6.81
4.61
4.60
4.58
4.58
4.56
4.56
4.54
4.54
4.00
3.99
3.98
3.96
2.27
2.24
2.23
2.21
2.12
2.10
2.08
2.07
1.41
1.29

O
O
O
CF3


1.03
0.98
1.03
0.98
2.06
1.00
1.07
1.07
3.16
3.18
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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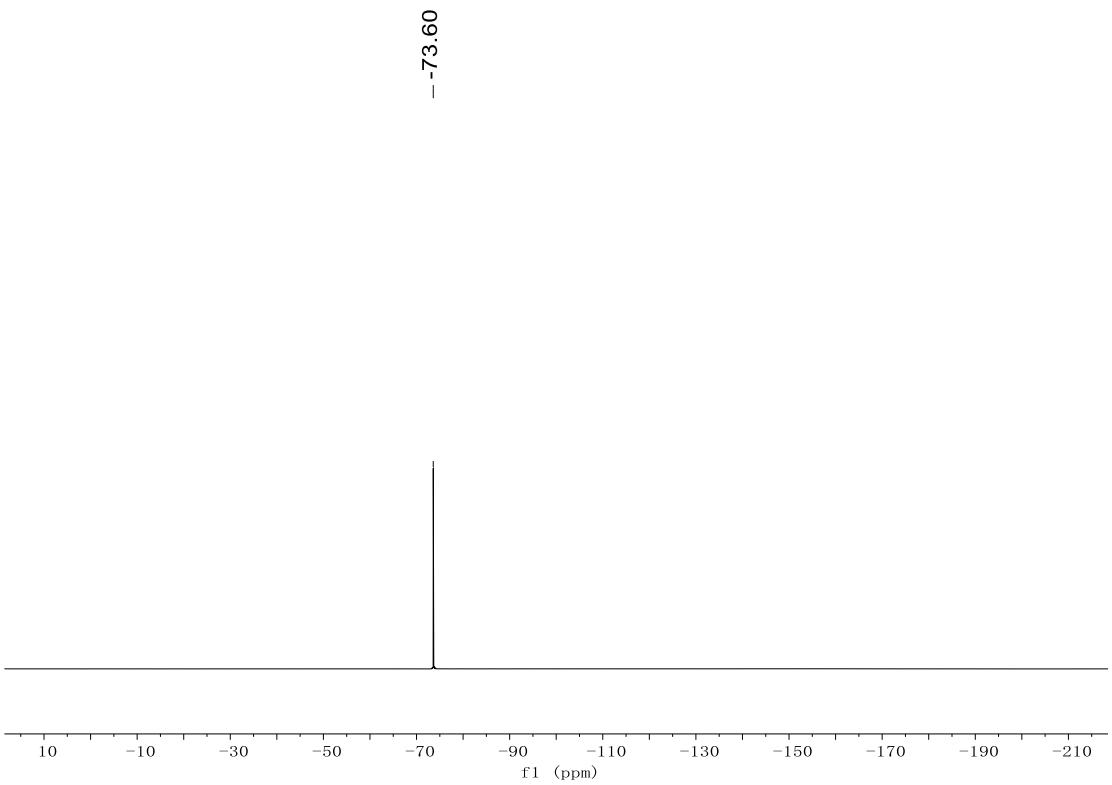
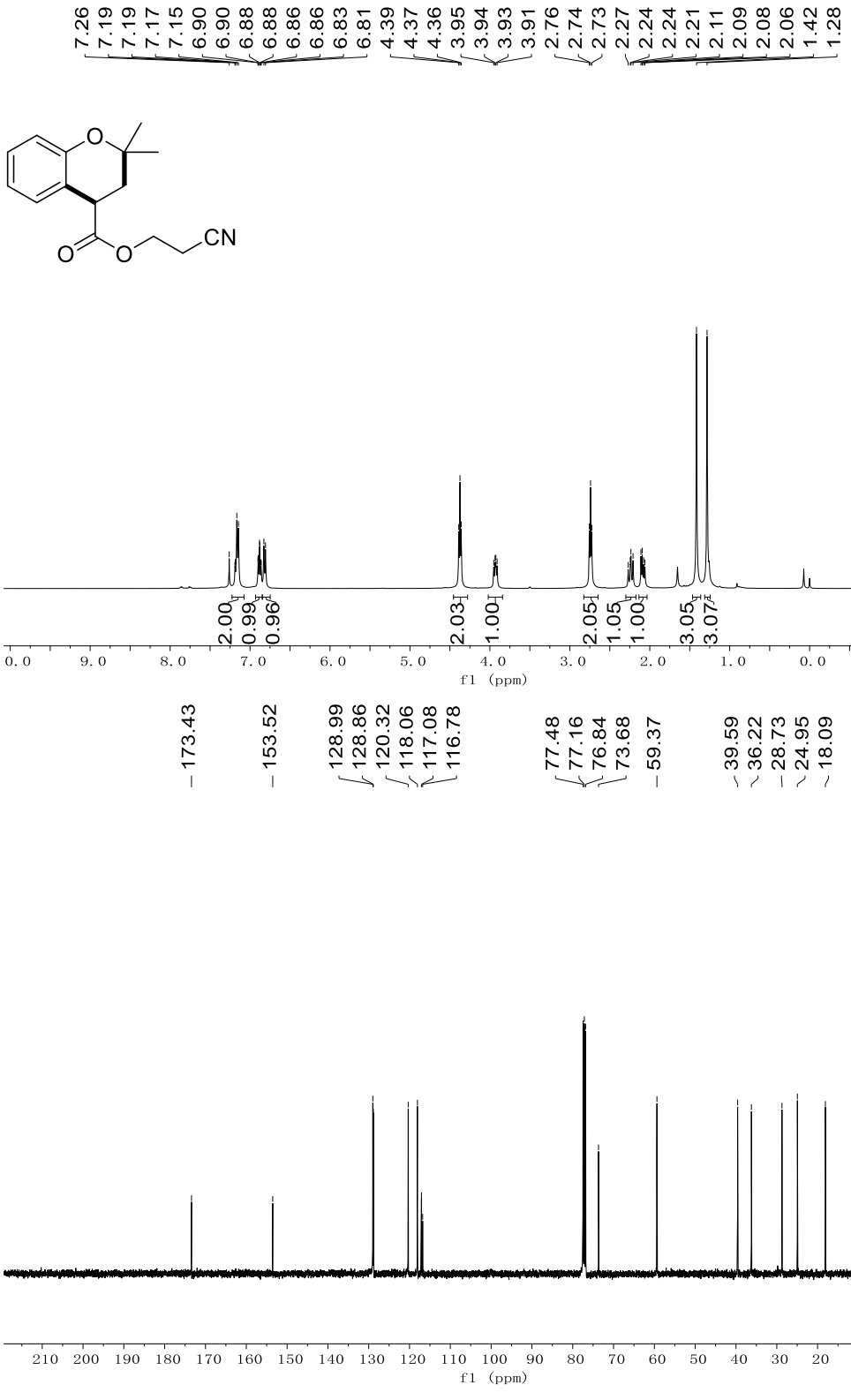
153.56
129.15
128.86
127.14
124.39
121.63
120.40
118.39
118.14
116.72
77.48
77.16
76.84
73.67
61.34
60.97
60.61
60.24
39.46
36.19
28.68
25.02
1.17
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


-73.60
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

43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7.19
7.17
7.15
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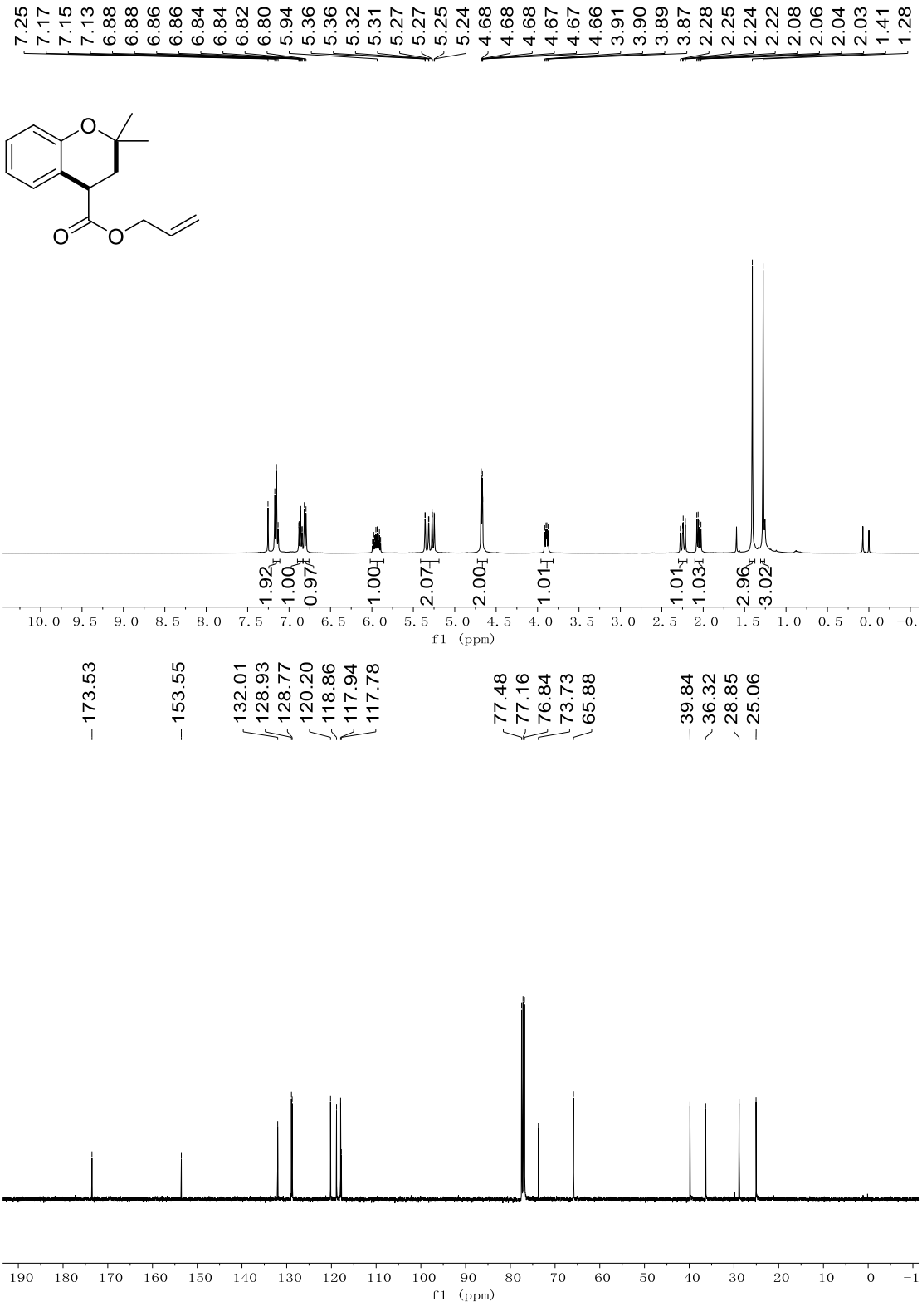
6.90
6.88
6.88
6.86
6.86
6.83
6.81
4.39
4.37
4.36
3.95
3.94
3.93
3.91
2.76
2.74
2.73
2.27
2.24
2.24
2.21
2.11
2.09
2.08
2.06
1.42
1.28
O
O
O
CN
2.00
0.99
0.96
2.03
1.00
2.05
1.05
1.00
3.05
3.07
f1 (ppm)
173.43
153.52
128.99
128.86
120.32
118.06
117.08
116.78
77.48
77.16
76.84
73.68
59.37
39.59
36.22
28.73
24.95
18.09
f1 (ppm)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7.17
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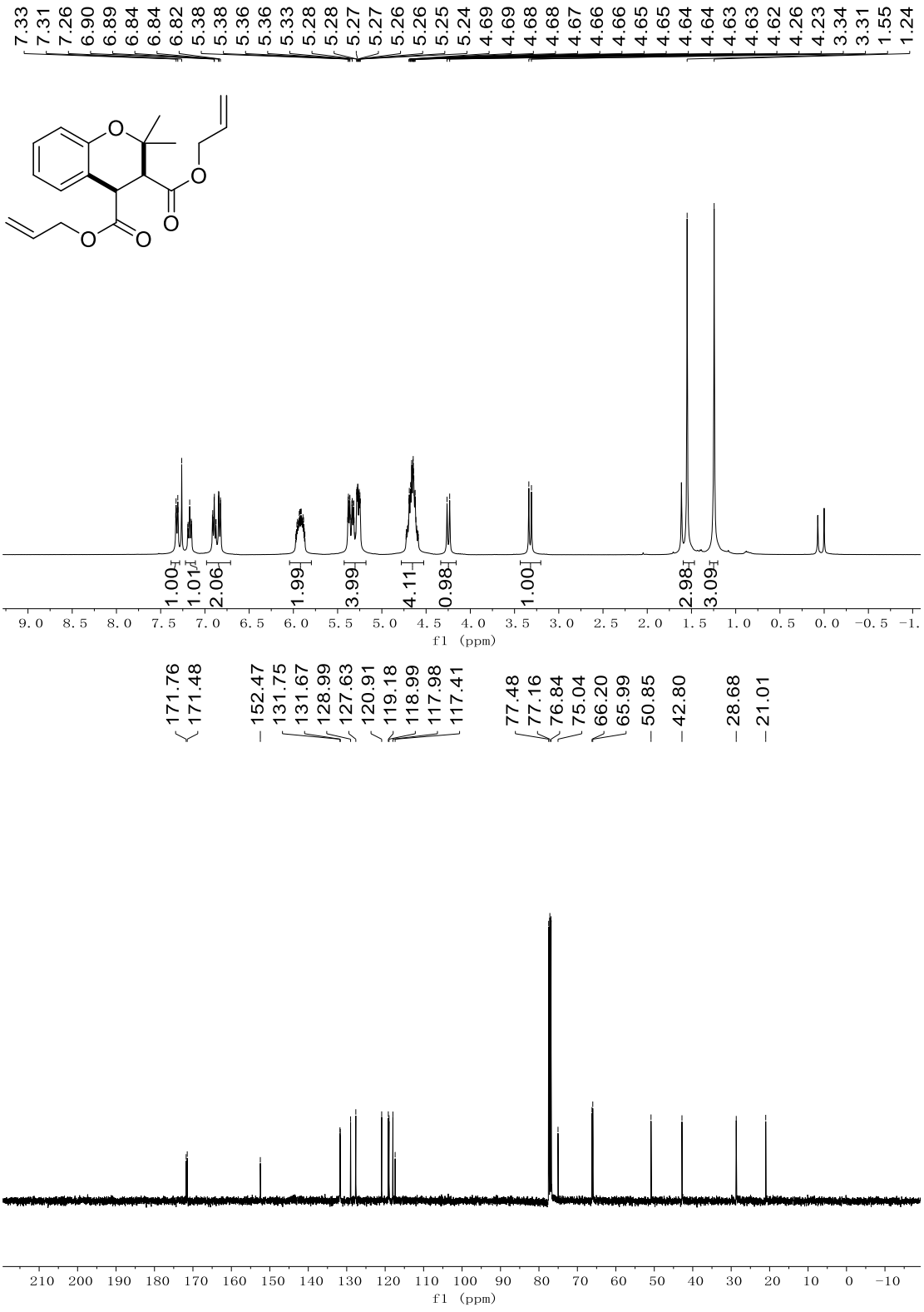
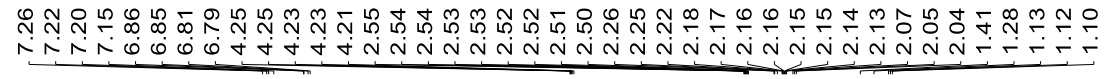
7.13
6.88
6.88
6.86
6.86
6.84
6.84
6.82
6.80
5.94
5.36
5.36
5.32
5.31
5.27
5.27
5.25
5.24
4.68
4.68
4.68
4.67
4.67
4.66
3.91
3.90
3.89
3.87
2.28
2.25
2.24
2.22
2.08
2.06
2.04
2.03
1.41
1.28
O
O
O
1.92
1.00
0.97
1.00
2.07
2.00
1.01
1.01
1.03
2.96
3.02
f1 (ppm)
173.53
153.55
132.01
128.93
128.77
120.20
118.86
117.94
117.78
77.48
77.16
76.84
73.73
65.88
39.84
36.32
28.85
25.06
f1 (ppm)

45


7.33 7.31 7.26 6.90 6.89 6.84 6.84 6.82 5.38 5.38 5.36 5.36 5.33 5.28 5.28 5.27 5.27 5.26 5.26 5.25 5.24 4.69 4.69 4.68 4.68 4.67 4.66 4.66 4.65 4.65 4.64 4.64 4.63 4.63 4.62 4.26 4.23 3.34 3.31 1.55 1.24
O
O
O
O
O
1.00 1.01 2.06 1.99 3.99 4.11 0.98 1.00 2.98 3.09
f1 (ppm)
171.76 171.48 152.47 131.75 131.67 128.99 127.63 120.91 119.18 118.99 117.98 117.41 77.48 77.16 76.84 75.04 66.20 65.99 50.85 42.80 28.68 21.01
f1 (ppm)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7.22
7.20
7.15
6.86
6.85
6.81
6.79
4.25
4.25
4.23
4.23
4.21
2.55
2.54
2.54
2.53
2.53
2.52
2.52
2.51
2.50
2.26
2.25
2.22
2.18
2.17
2.16
2.16
2.15
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2.13
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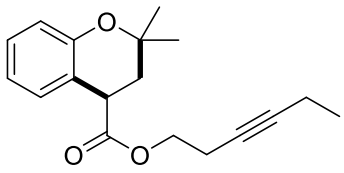
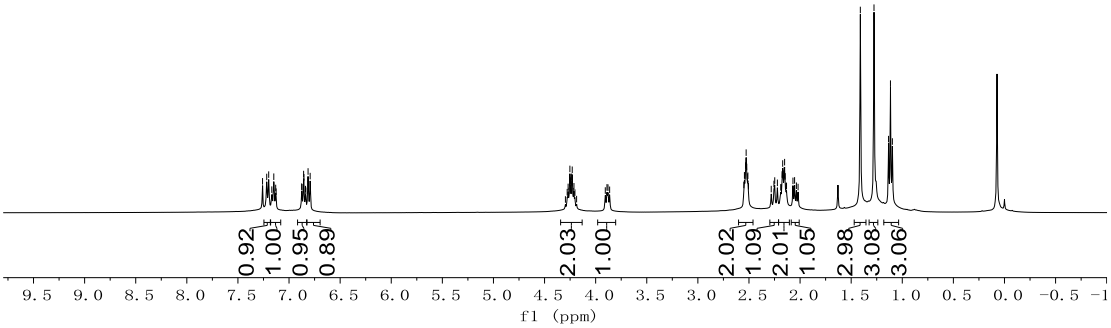
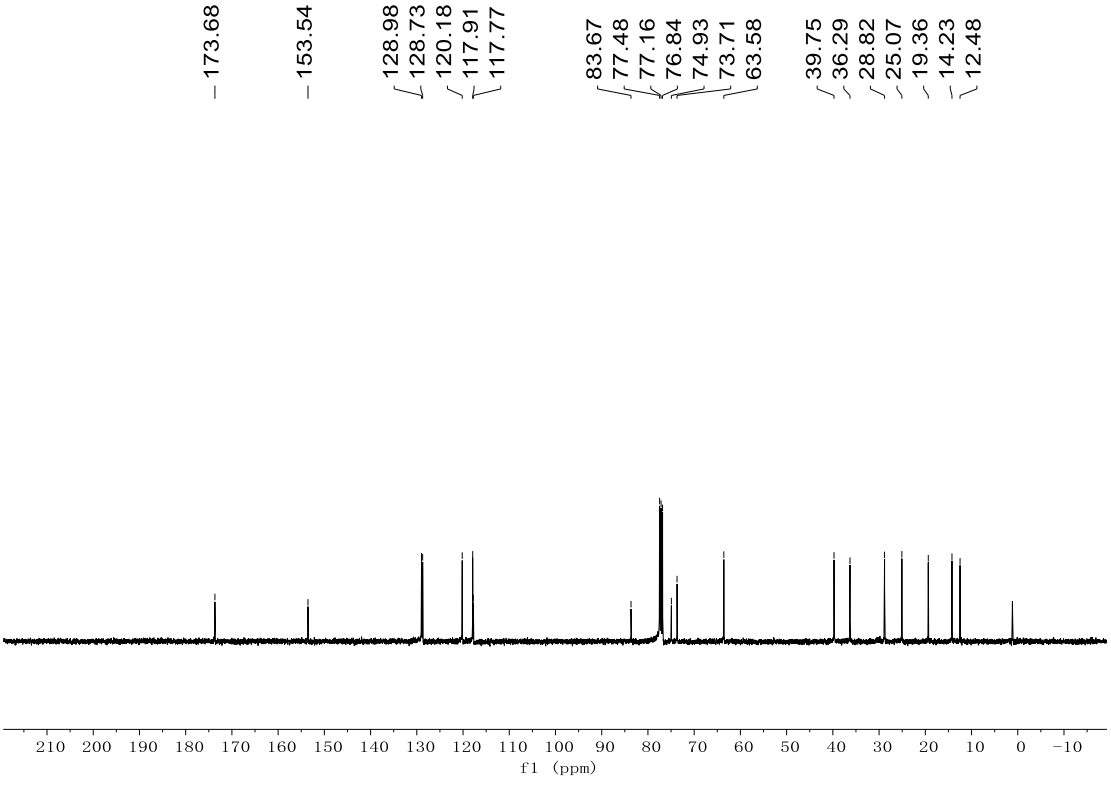
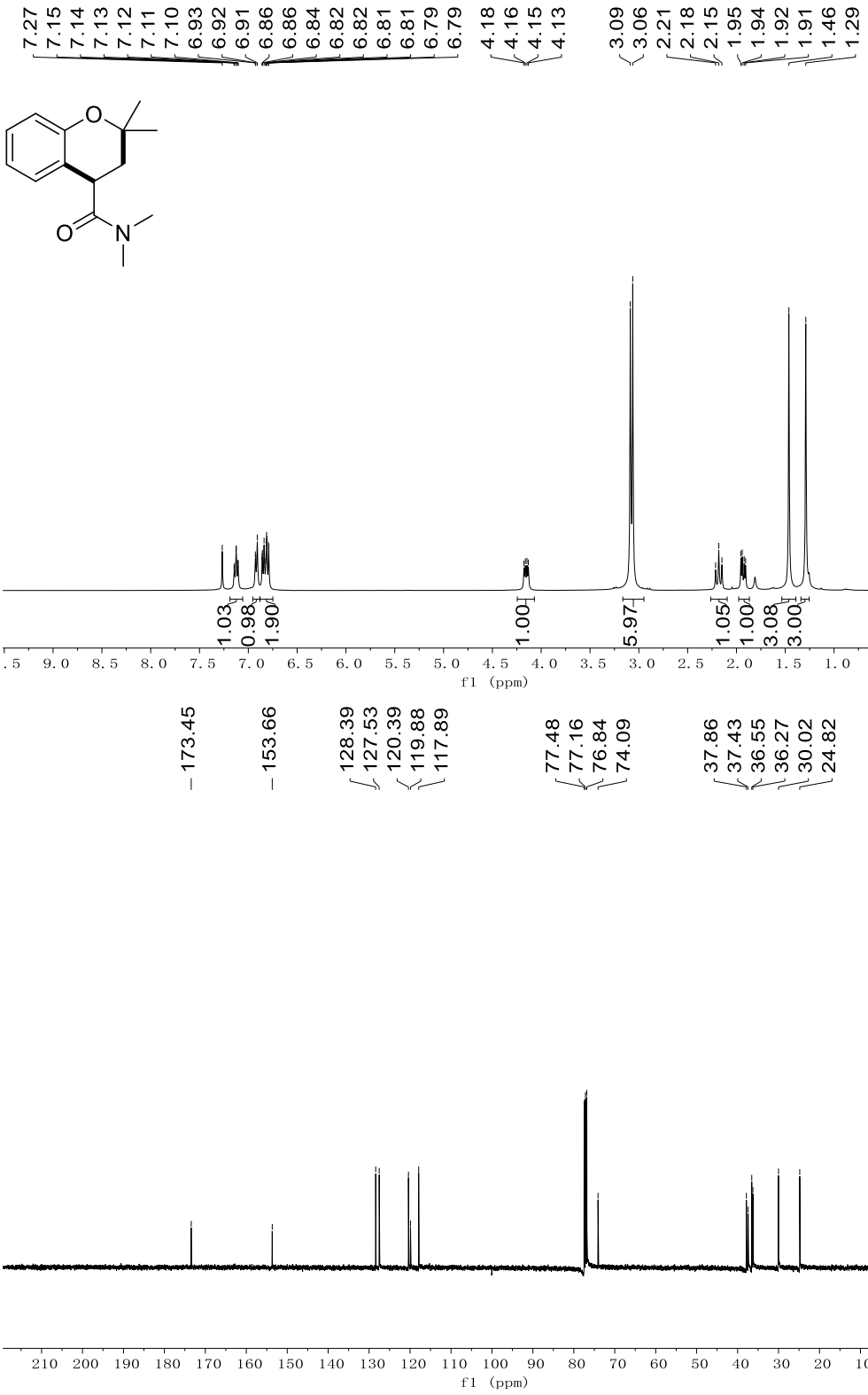
2.04
1.41
1.28
1.13
1.12
1.10


O
O
O


0.92
1.00
0.95
0.89
2.03
1.00
2.02
1.09
2.01
1.05
2.98
3.08
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)


173.68
153.54
128.98
128.73
120.18
117.91
117.77
83.67
77.48
77.16
76.84
74.93
73.71
63.58
39.75
36.29
28.82
25.07
19.36
14.23
12.48
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

47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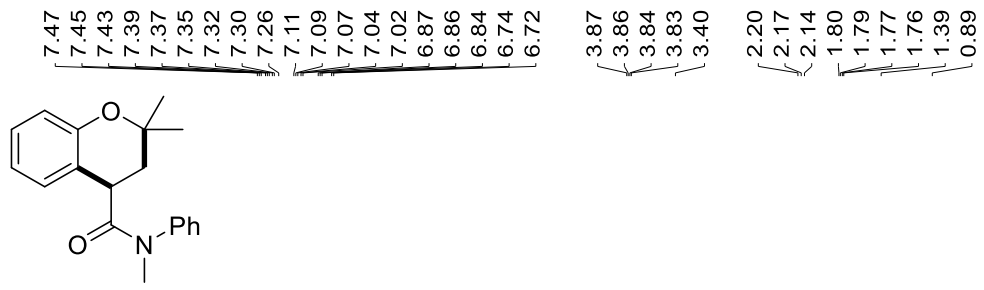
7.12
7.11
7.10
6.93
6.92
6.91
6.86
6.86
6.84
6.82
6.82
6.81
6.81
6.79
6.79
4.18
4.16
4.15
4.13
3.09
3.06
2.21
2.18
2.15
1.95
1.94
1.92
1.91
1.46
1.29
O
O
N
1.03
0.98
1.90
1.00
5.97
1.05
1.00
3.08
3.00
f1 (ppm)
173.45
153.66
128.39
127.53
120.39
119.88
117.89
77.48
77.16
76.84
74.09
37.86
37.43
36.55
36.27
30.02
24.82
f1 (ppm)


7.47
7.45
7.43
7.39
7.37
7.35
7.32
7.30
7.26
7.11
7.09
7.07
7.04
7.02
6.87
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6.74
6.72
3.87
3.86
3.84
3.83
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1.39
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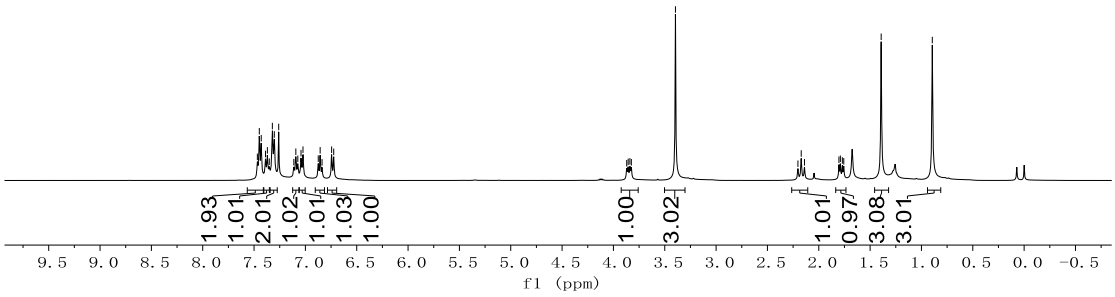
N
Ph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1.00
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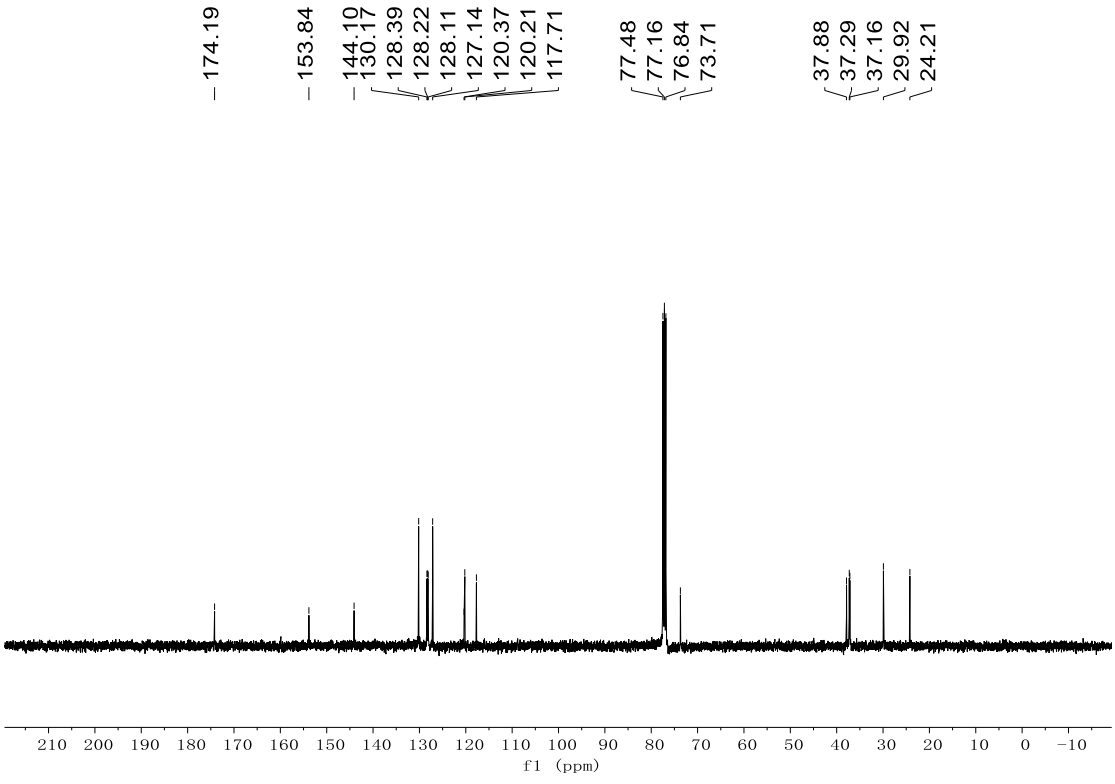
3.01
f1 (ppm)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73.71
37.88
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37.16
29.92
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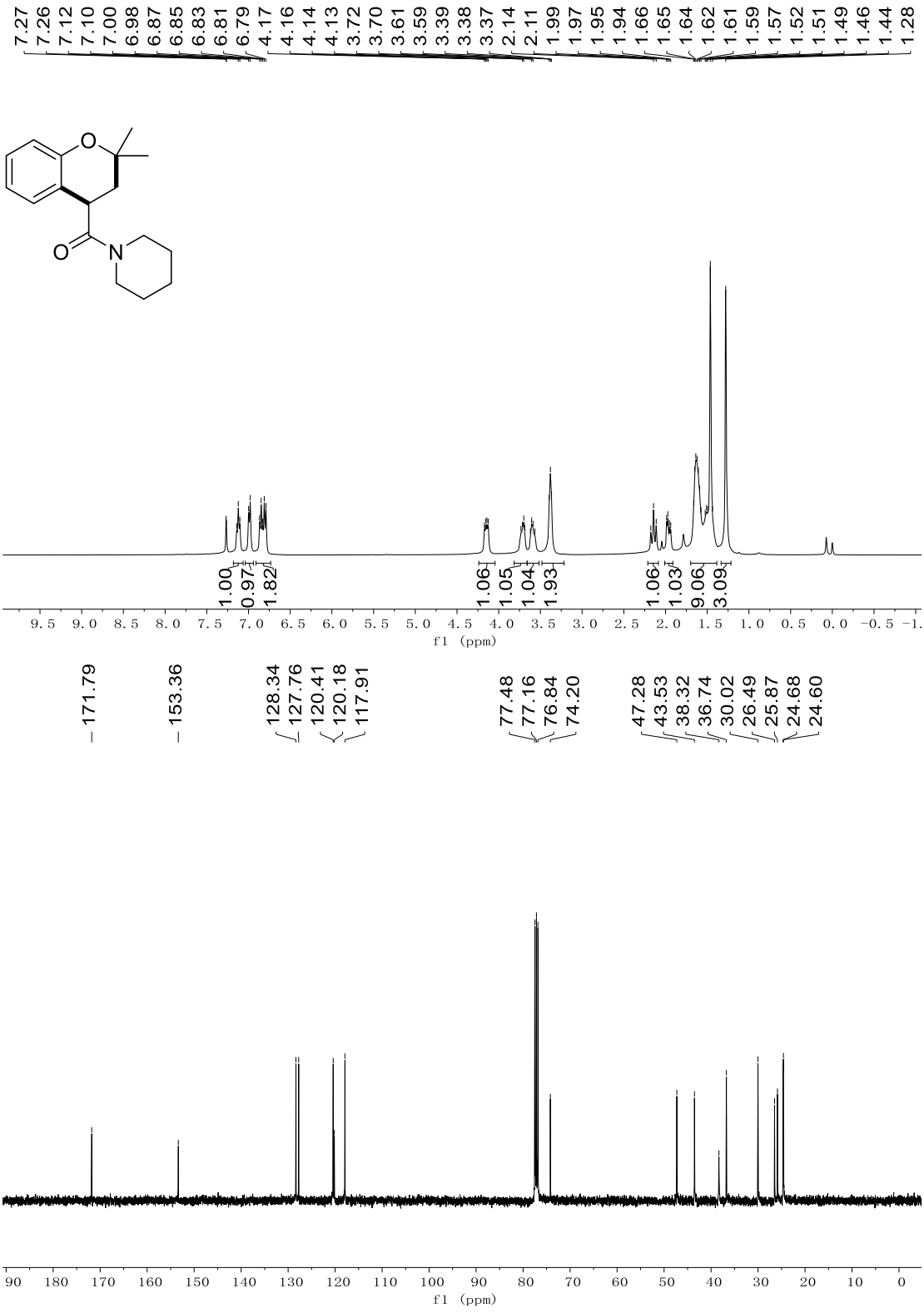
f1 (ppm)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3.37
2.14
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1.95
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1.61
1.59
1.57
1.52
1.51
1.49
1.46
1.44
1.28
O
O
N
1.00
0.97
1.82
1.06
1.05
1.04
1.93
1.06
1.03
9.06
3.09
f1 (ppm)
171.79
153.36
128.34
127.76
120.41
120.18
117.91
77.48
77.16
76.84
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25.87
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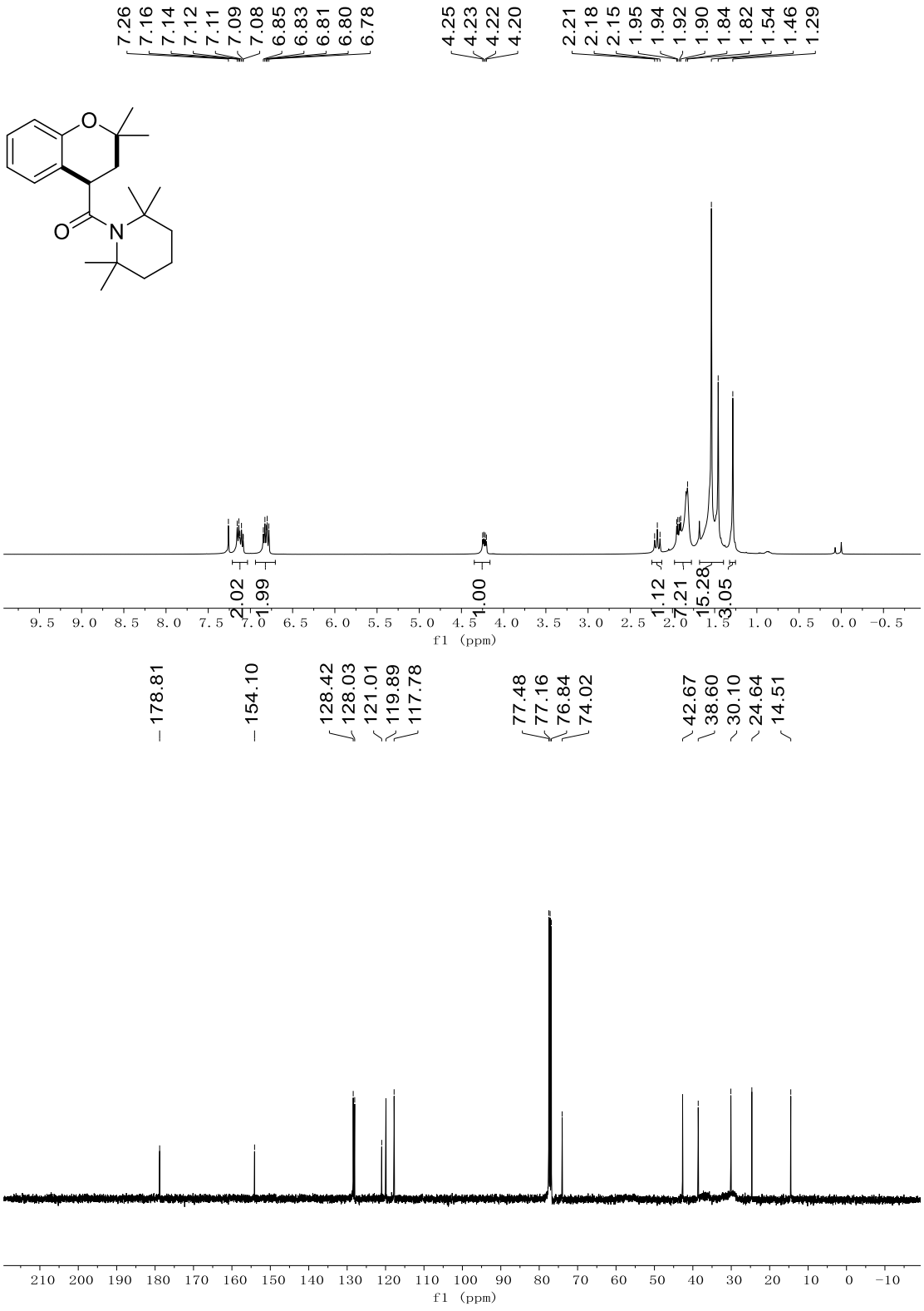
24.60
f1 (ppm)

50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6.81
6.80
6.78
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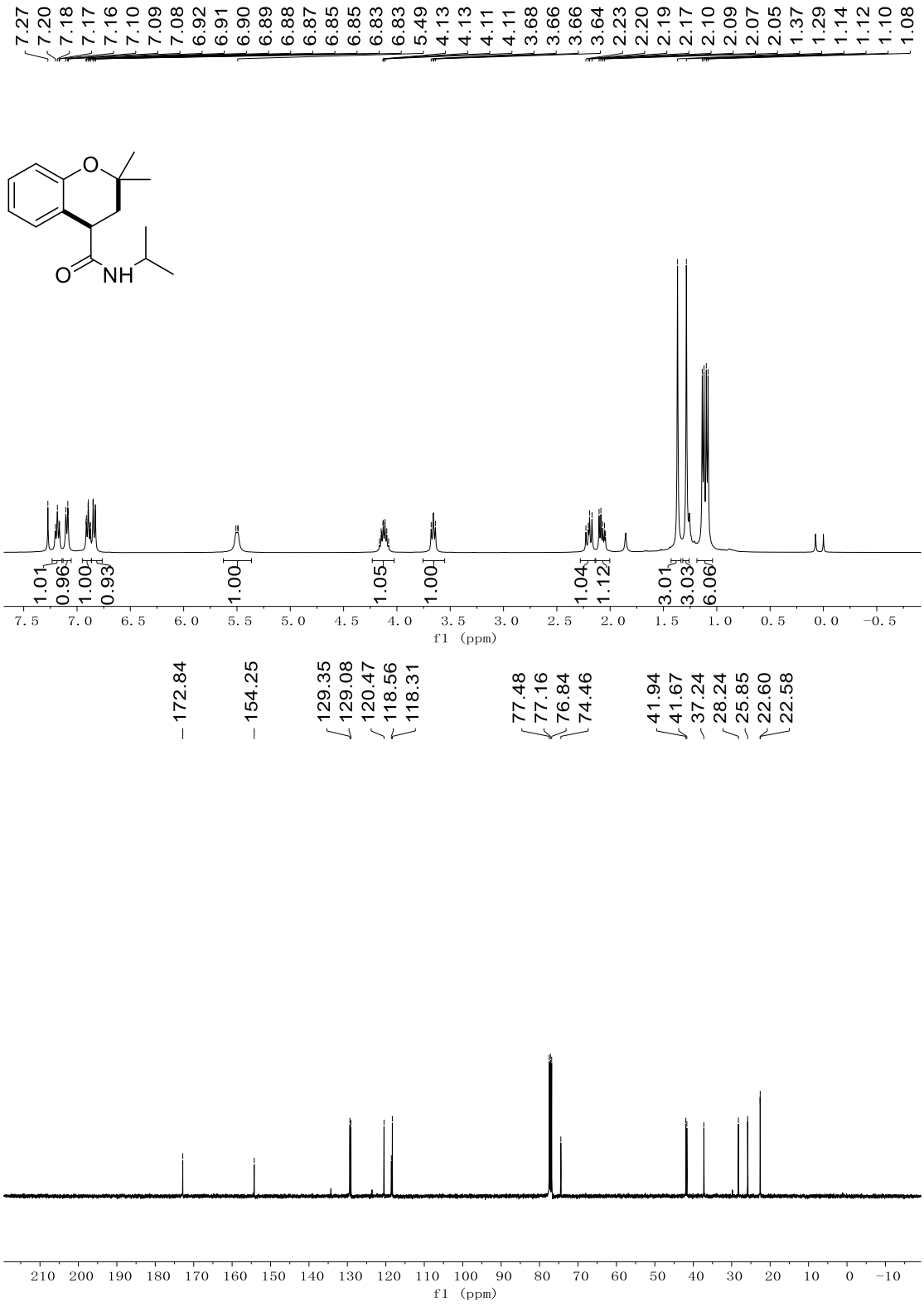
4.23
4.22
4.20
2.21
2.18
2.15
1.95
1.94
1.92
1.90
1.84
1.82
1.54
1.46
1.29
O
O
N
2.02
1.99
1.00
1.12
7.21
15.28
3.05
f1 (ppm)
178.81
154.10
128.42
128.03
121.01
119.89
117.78
77.48
77.16
76.84
74.02
42.67
38.60
30.10
24.64
14.51
f1 (ppm)

51


7.27 7.16 7.14 7.12 7.00 6.98 6.96 6.88 6.87 6.85 6.82 6.80 4.18 4.16 4.15 4.13 3.81 3.62 3.61 3.60 3.59 3.58 3.33 2.14 2.12 2.11 2.09 2.08 2.06 2.05 2.03 2.02 2.00 1.98 1.97 1.88 1.86 1.85 1.47 1.28 1.27
O
O
N
S
1.02 1.02 1.78 1.00 1.19 0.51 0.95 1.46 0.93 4.14 1.36 2.83 3.44
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.
f1 (ppm)
172.05 153.25 128.64 127.57 120.62 119.75 118.16 77.48 77.16 76.84 74.24 49.19 48.54 44.58 43.90 40.97 40.18 39.19 38.83 36.72 36.59 36.10 35.74 35.56 35.28 24.58 24.51
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.08
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6.91
6.90
6.89
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6.87
6.85
6.85
6.83
6.83
5.49
4.13
4.13
4.11
4.11
3.68
3.66
3.66
3.64
2.23
2.20
2.19
2.17
2.10
2.09
2.07
2.05
1.37
1.29
1.14
1.12
1.10
1.08
O
O
NH
1.01
0.96
1.00
0.93
1.00
1.05
1.00
1.04
1.12
3.01
3.03
6.06
f1 (ppm)
172.84
154.25
129.35
129.08
120.47
118.56
118.31
77.48
77.16
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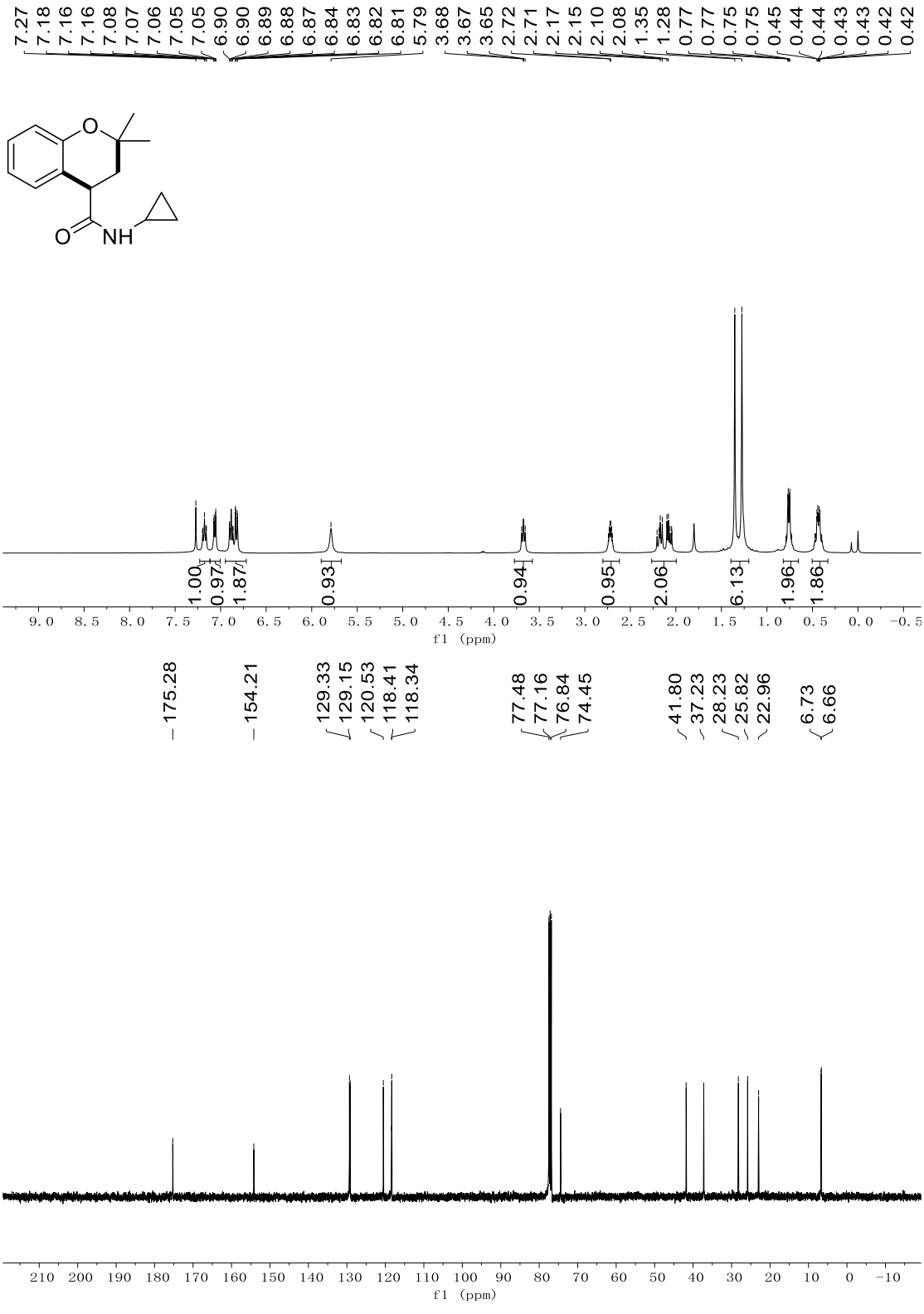
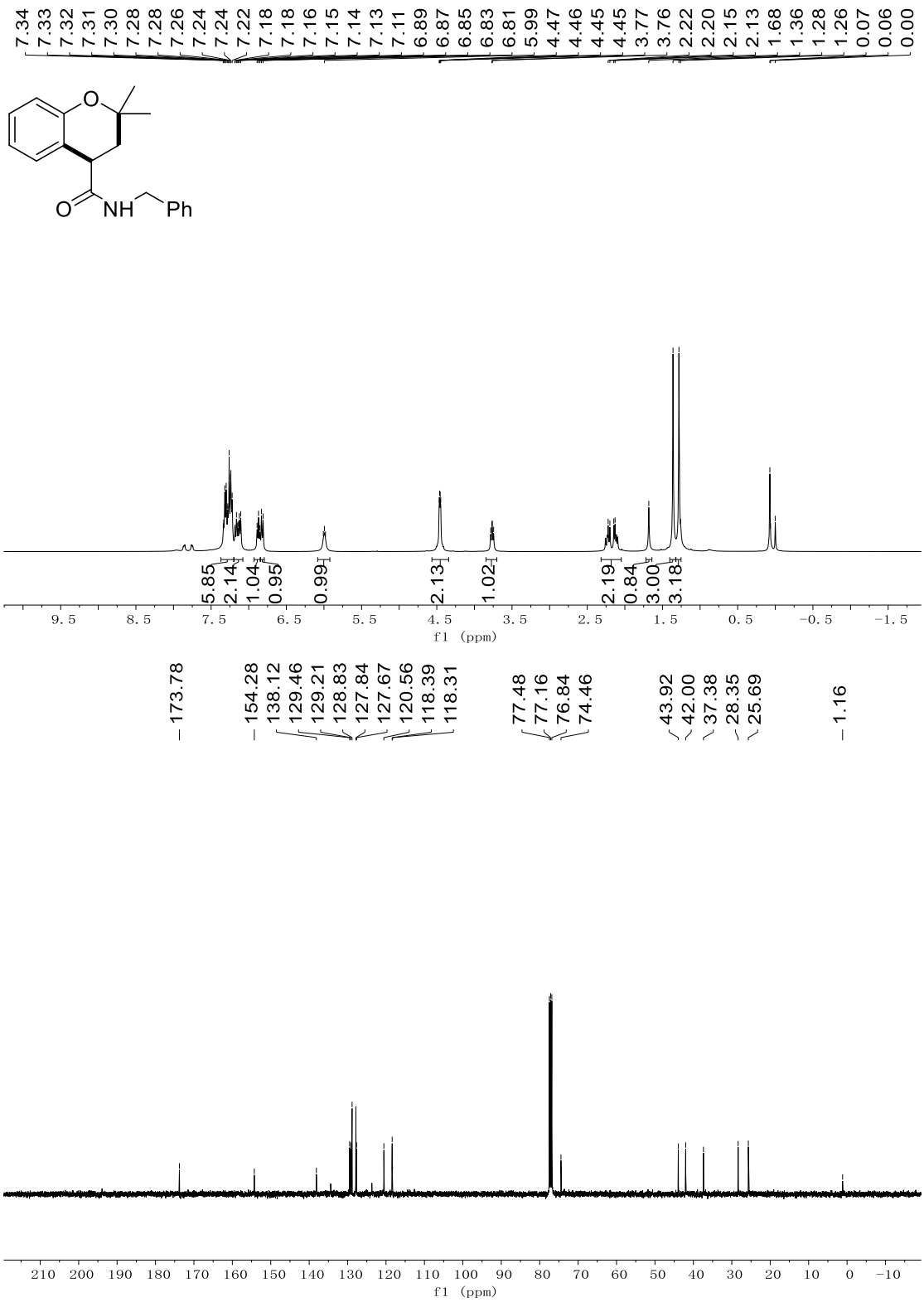
74.46
41.94
41.67
37.24
28.24
25.85
22.60
22.58
f1 (ppm)

53


7.27 7.18 7.16 7.16 7.08 7.07 7.06 7.05 7.05 6.90 6.90 6.89 6.88 6.87 6.84 6.83 6.82 6.81 5.79 3.68 3.67 3.65 2.72 2.71 2.17 2.15 2.10 2.08 1.35 1.28 0.77 0.77 0.75 0.75 0.45 0.44 0.44 0.43 0.43 0.42 0.42
O
O
NH
1.00 0.97 1.87 0.93 0.94 0.95 2.06 6.13 1.96 1.86
f1 (ppm)
175.28 154.21 129.33 129.15 120.53 118.41 118.34 77.48 77.16 76.84 74.45 41.80 37.23 28.23 25.82 22.96 6.73 6.66
f1 (ppm)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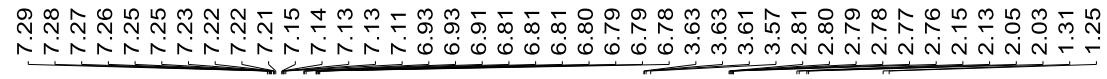
O
O
NH
Ph
5.85 2.14 1.04 0.95 0.99 2.13 1.02 2.19 0.84 3.00 3.18
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 −0.5 −1.5
f1 (ppm)
173.78
154.28 138.12 129.46 129.21 128.83 127.84 127.67 120.56 118.39 118.31
77.48 77.16 76.84 74.46
43.92 42.00 37.38 28.35 25.69
1.16
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

55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7.11
6.93
6.93
6.91
6.81
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6.81
6.80
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6.78
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3.57
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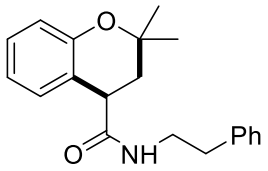
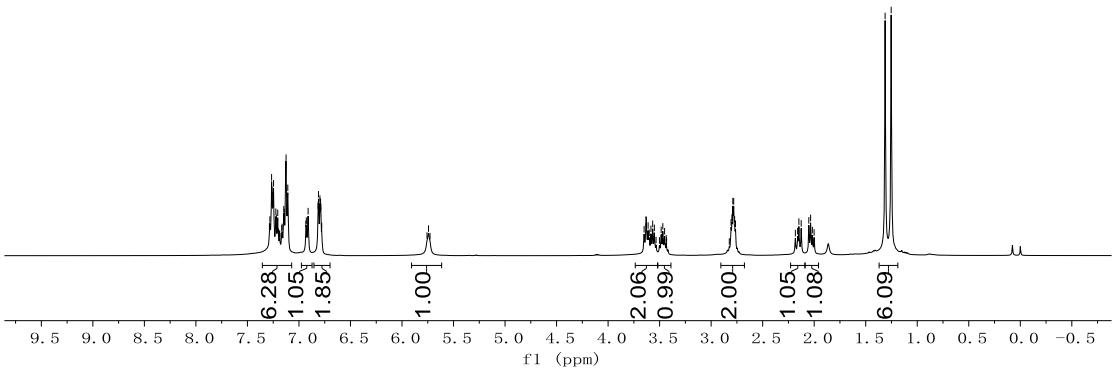
2.13
2.05
2.03
1.31
1.25


O
O
NH
Ph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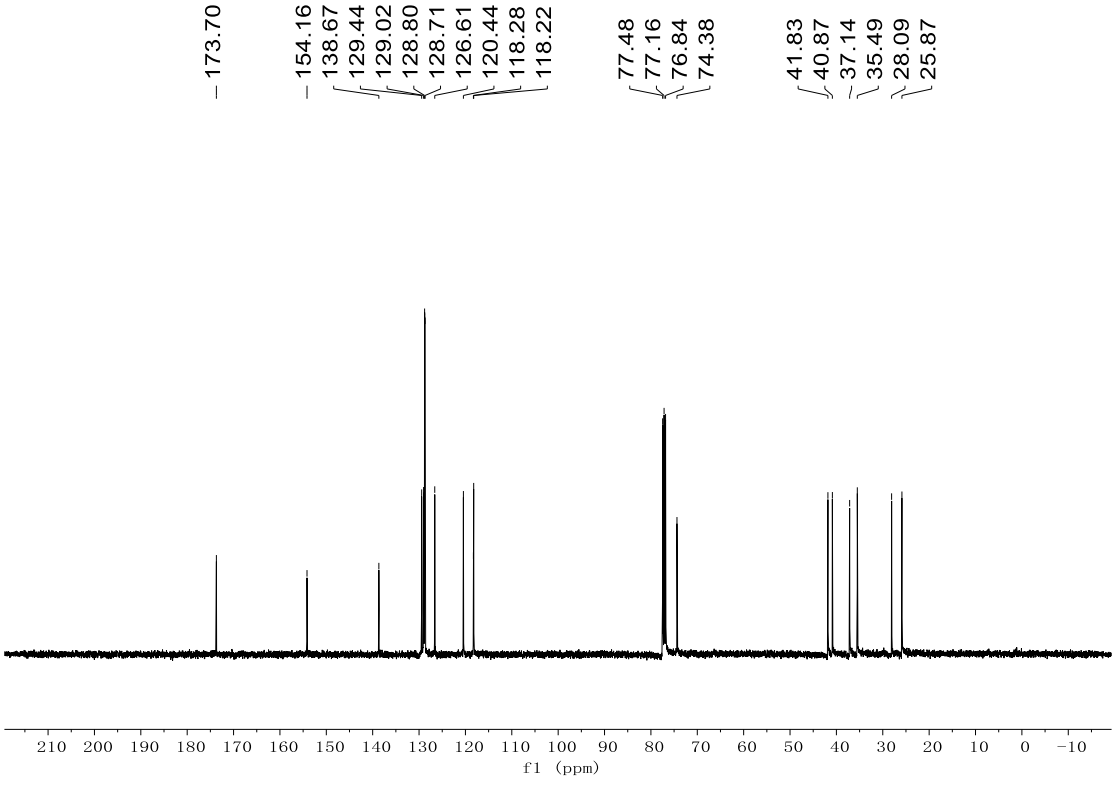
1.85
1.00
2.06
0.99
2.00
1.05
1.08
6.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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118.28
118.22
77.48
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76.84
74.38
41.83
40.87
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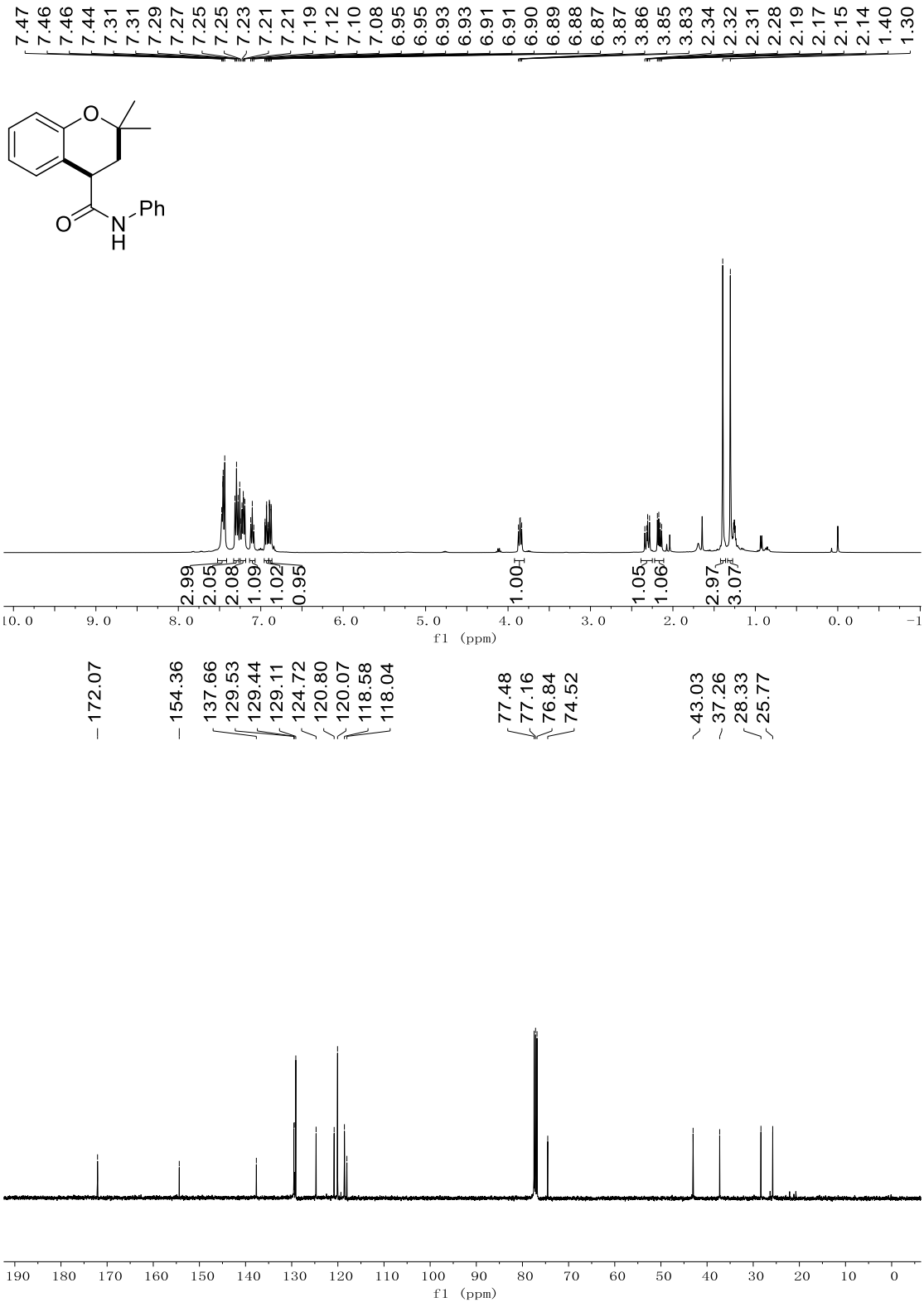
35.49
28.09
25.87
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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7.23
7.21
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3.83
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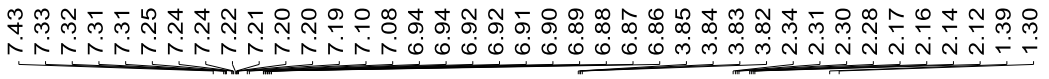
2.31
2.28
2.19
2.17
2.15
2.14
1.40
1.30
O
O
N
H
Ph
2.99
2.05
2.08
1.09
1.02
0.95
1.00
1.05
1.06
2.97
3.07
f1 (ppm)
172.07
154.36
137.66
129.53
129.44
129.11
124.72
120.80
120.07
118.58
118.04
77.48
77.16
76.84
74.52
43.03
37.26
28.33
25.77
f1 (ppm)

57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7.19
7.10
7.08
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6.94
6.92
6.92
6.91
6.90
6.89
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6.87
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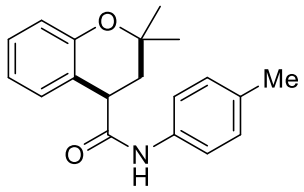
1.39
1.30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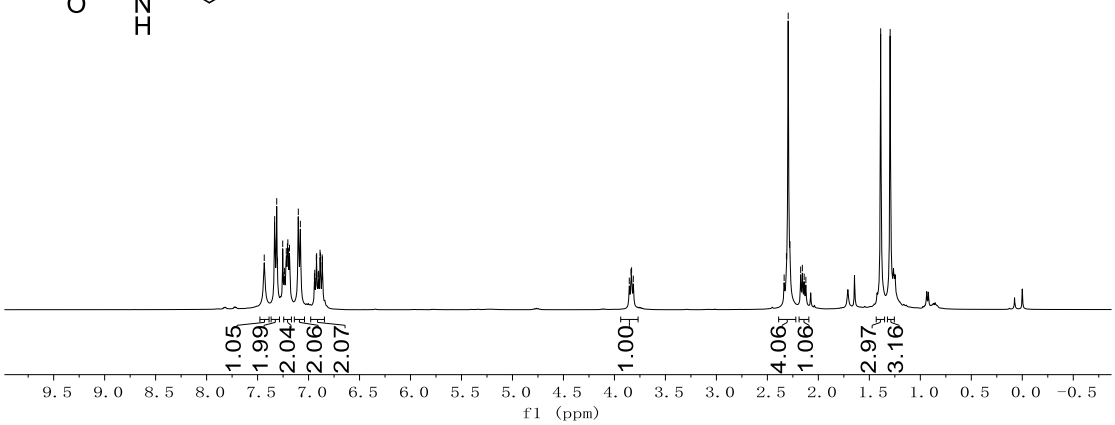
Me
O
N
H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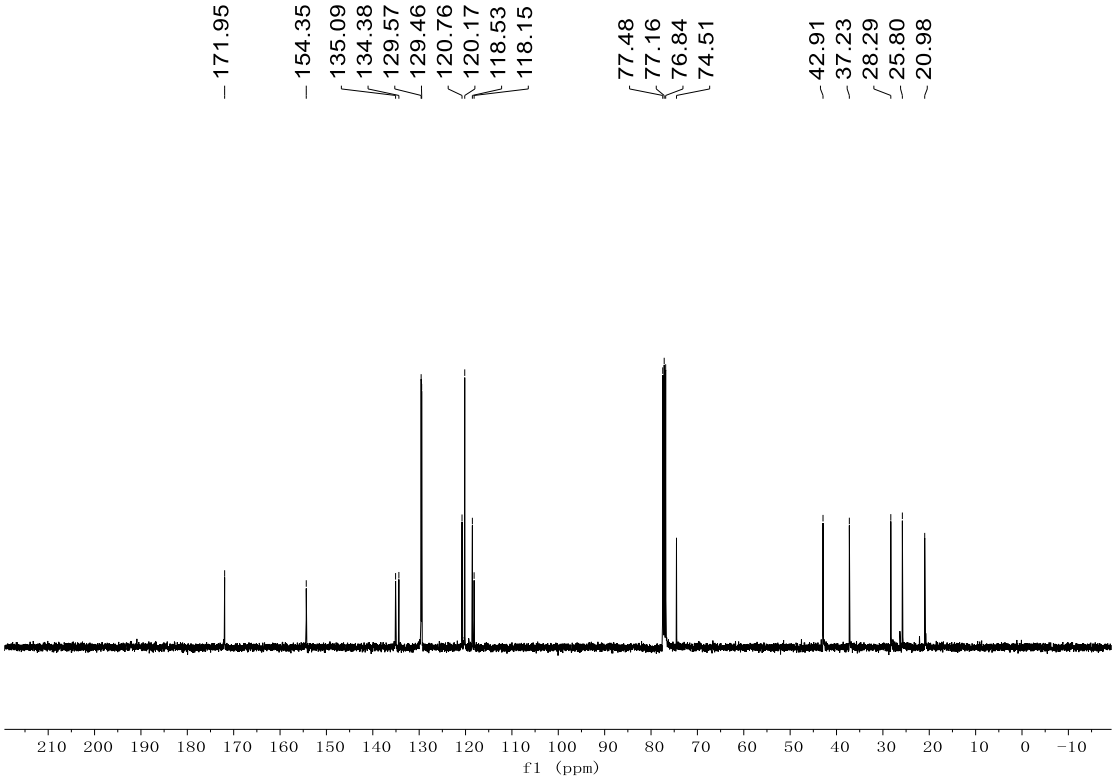
1.00
4.06
1.06
2.97
3.16
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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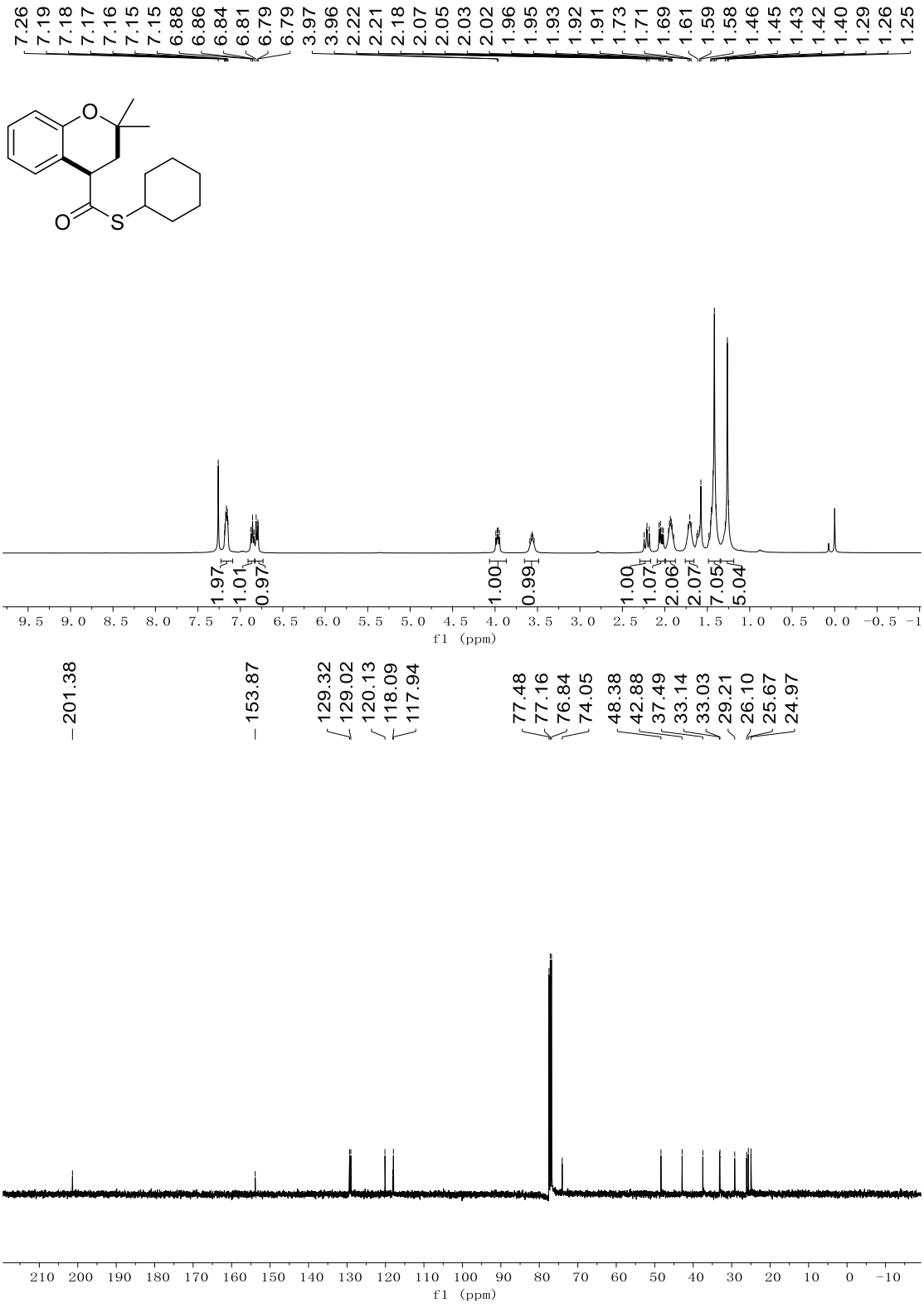
118.15
77.48
77.16
76.84
74.51
42.91
37.23
28.29
25.80
20.98
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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6.79
3.97
3.96
2.22
2.21
2.18
2.07
2.05
2.03
2.02
1.96
1.95
1.93
1.92
1.91
1.73
1.71
1.69
1.61
1.59
1.58
1.46
1.45
1.43
1.42
1.40
1.29
1.26
1.25
O
O
S
1.97
1.01
0.97
1.00
0.99
1.00
1.07
2.06
2.07
7.05
5.04
f1 (ppm)
201.38
153.87
129.32
129.02
120.13
118.09
117.94
77.48
77.16
76.84
74.05
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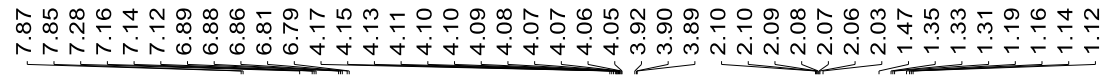
42.88
37.49
33.14
33.03
29.21
26.10
25.67
24.97
f1 (ppm)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6.81
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4.17
4.15
4.13
4.11
4.10
4.10
4.09
4.08
4.07
4.07
4.06
4.05
3.92
3.90
3.89
2.10
2.10
2.09
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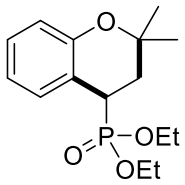
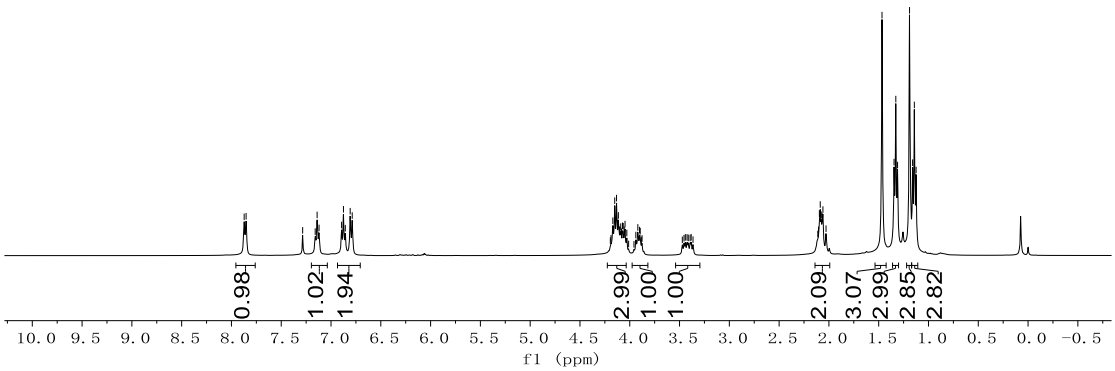
1.31
1.19
1.16
1.14
1.12


O
P
OEt
O
OEt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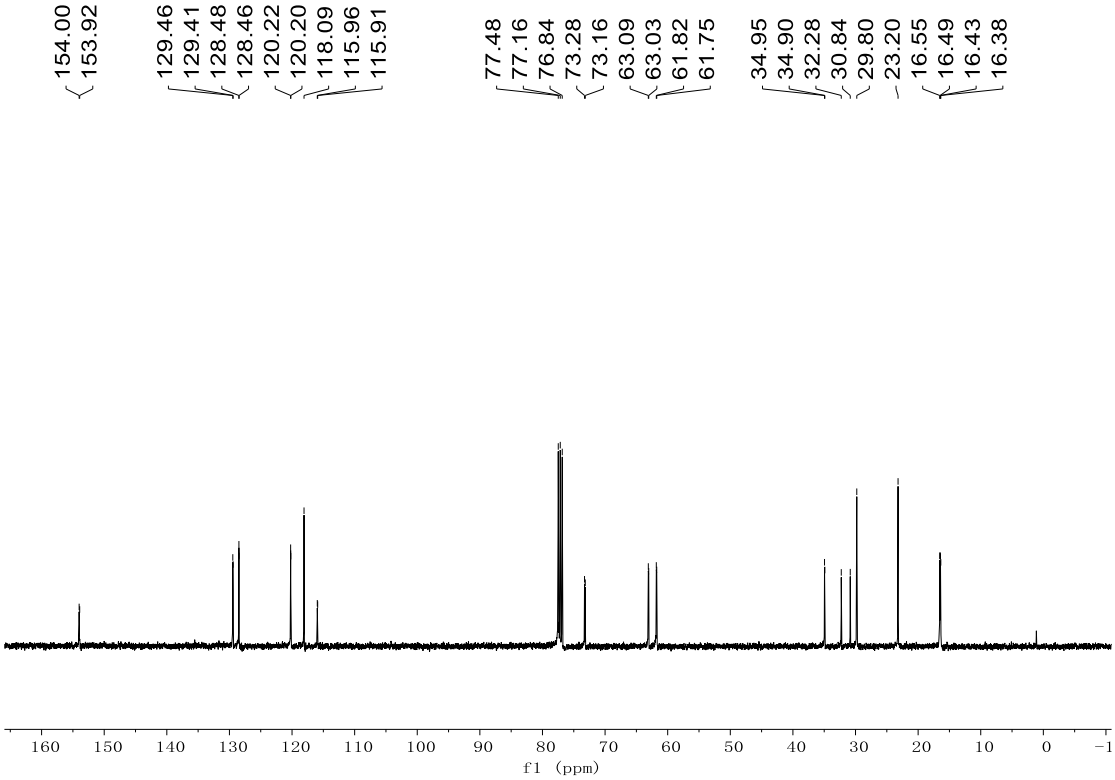
1.94
2.99
1.00
1.00
2.09
3.07
2.99
2.85
2.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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77.48
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76.84
73.28
73.16
63.09
63.03
61.82
61.75
34.95
34.90
32.28
30.84
29.80
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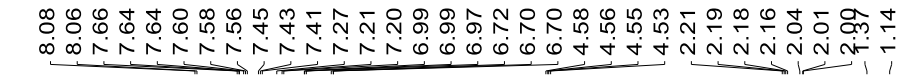
16.49
16.43
16.38
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

60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7.20
6.99
6.99
6.97
6.72
6.70
6.70
4.58
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2.04
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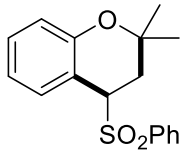
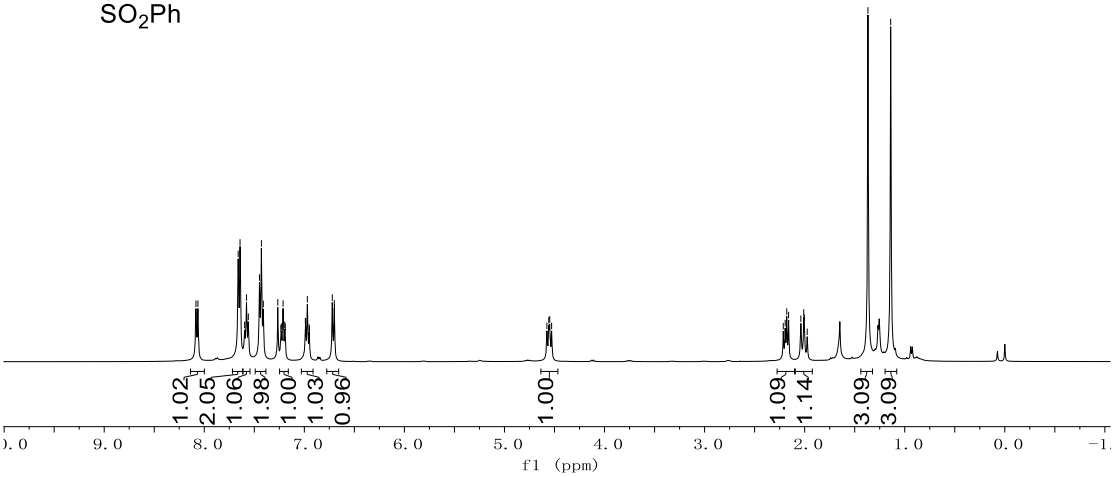
1.14


O
SO2Ph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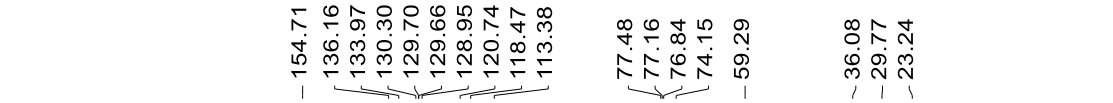
1.00
1.09
1.14
3.09
3.09
f1 (ppm)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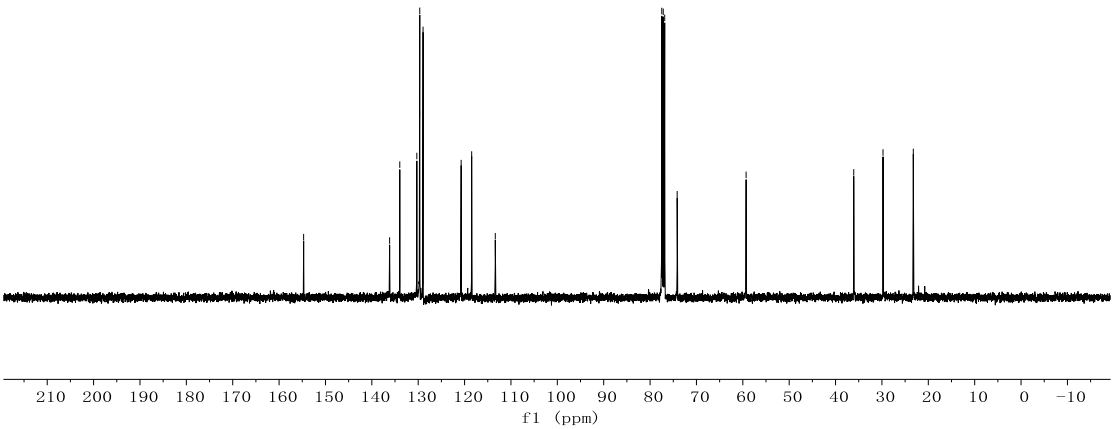
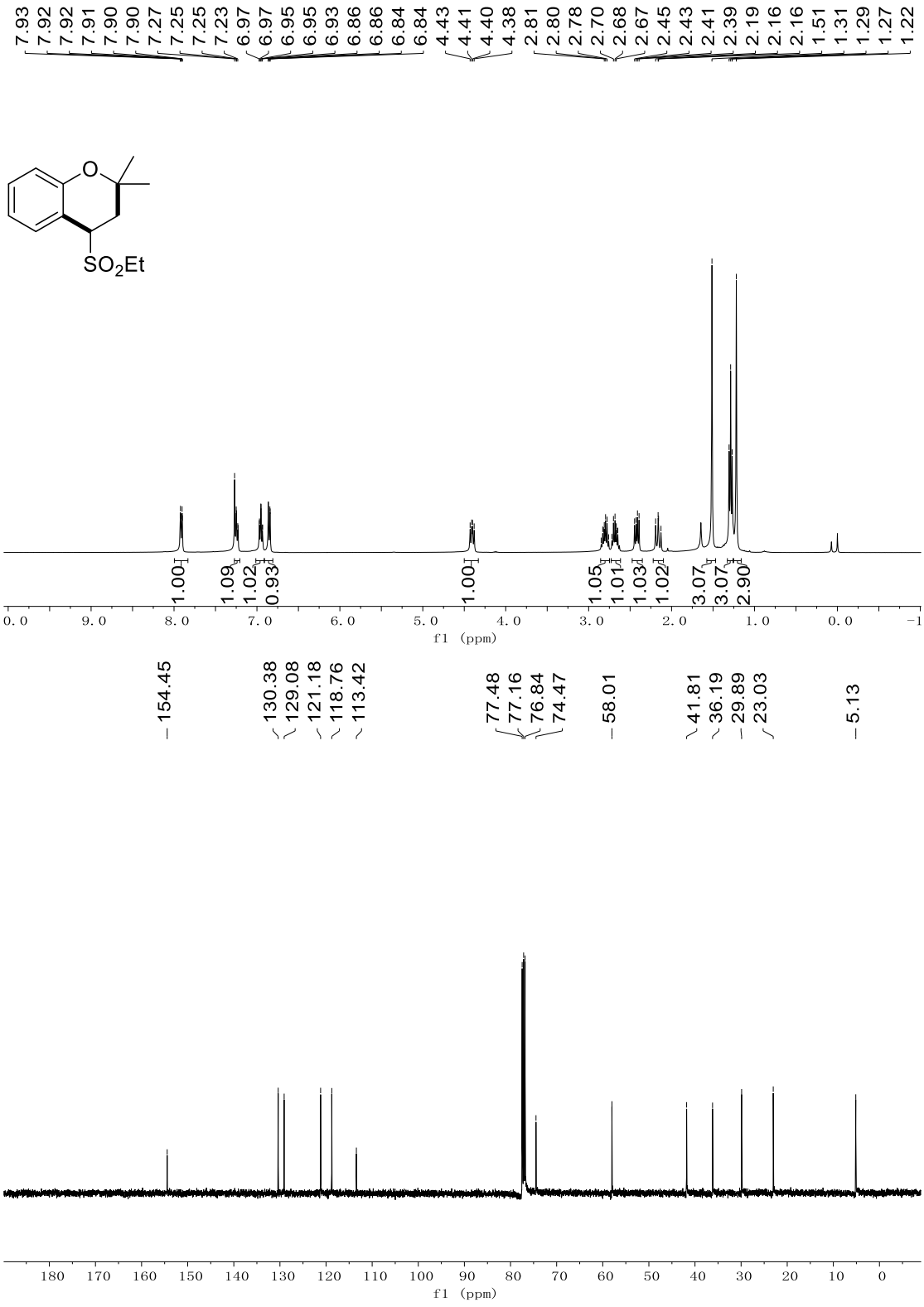
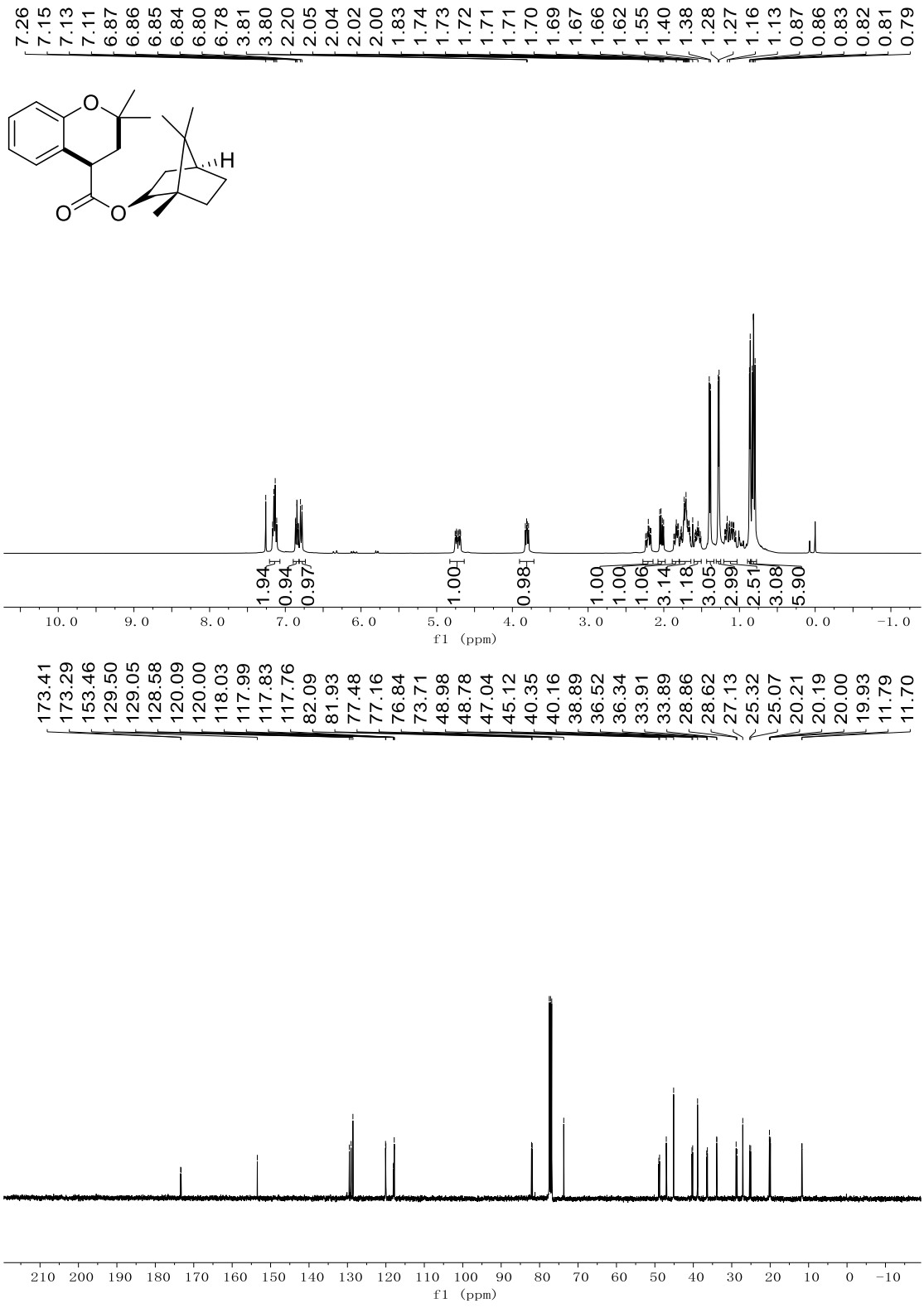
74.15
59.29
36.08
29.77
23.24

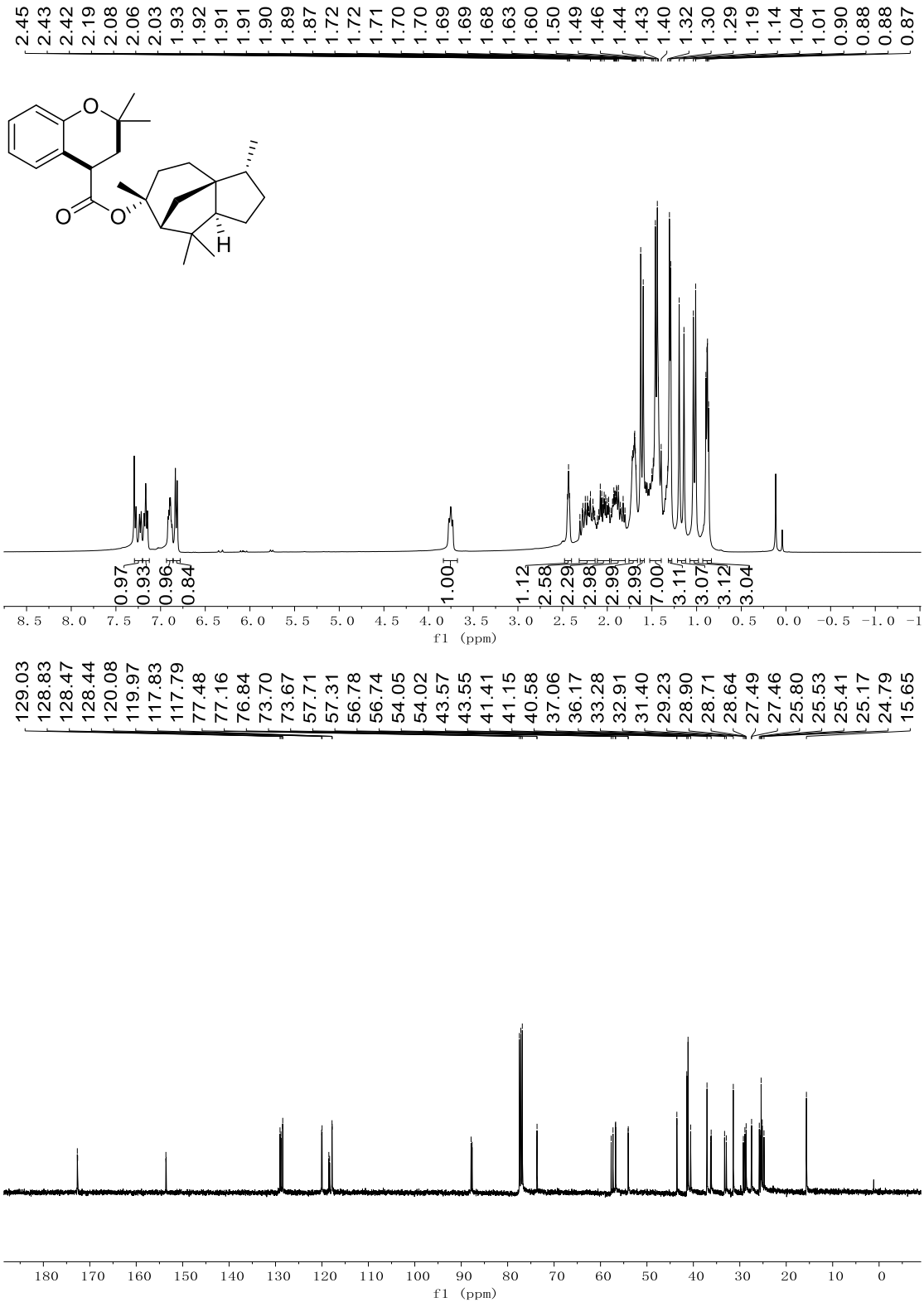

f1 (ppm)

61

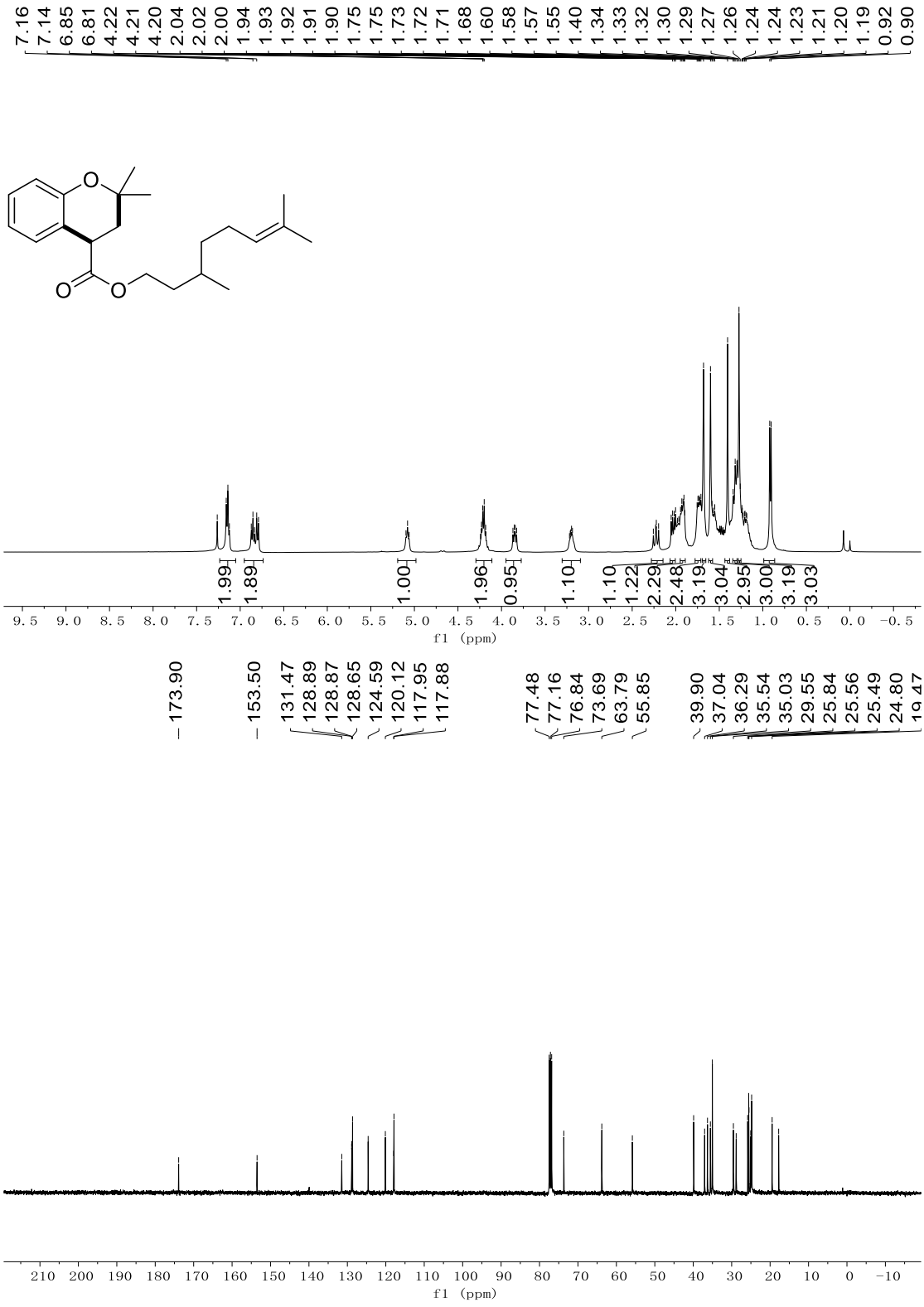

7.93 7.92 7.92 7.91 7.90 7.90 7.27 7.25 7.25 7.23 6.97 6.97 6.95 6.95 6.93 6.86 6.86 6.84 6.84 4.43 4.41 4.40 4.38 2.81 2.80 2.78 2.70 2.68 2.67 2.45 2.43 2.41 2.39 2.19 2.16 2.16 1.51 1.31 1.29 1.27 1.22
O
SO2Et
1.00 1.09 1.02 0.93 1.00 1.05 1.01 1.03 1.02 3.07 3.07 2.90
f1 (ppm)
154.45 130.38 129.08 121.18 118.76 113.42 77.48 77.16 76.84 74.47 58.01 41.81 36.19 29.89 23.03 5.13
f1 (ppm)

62

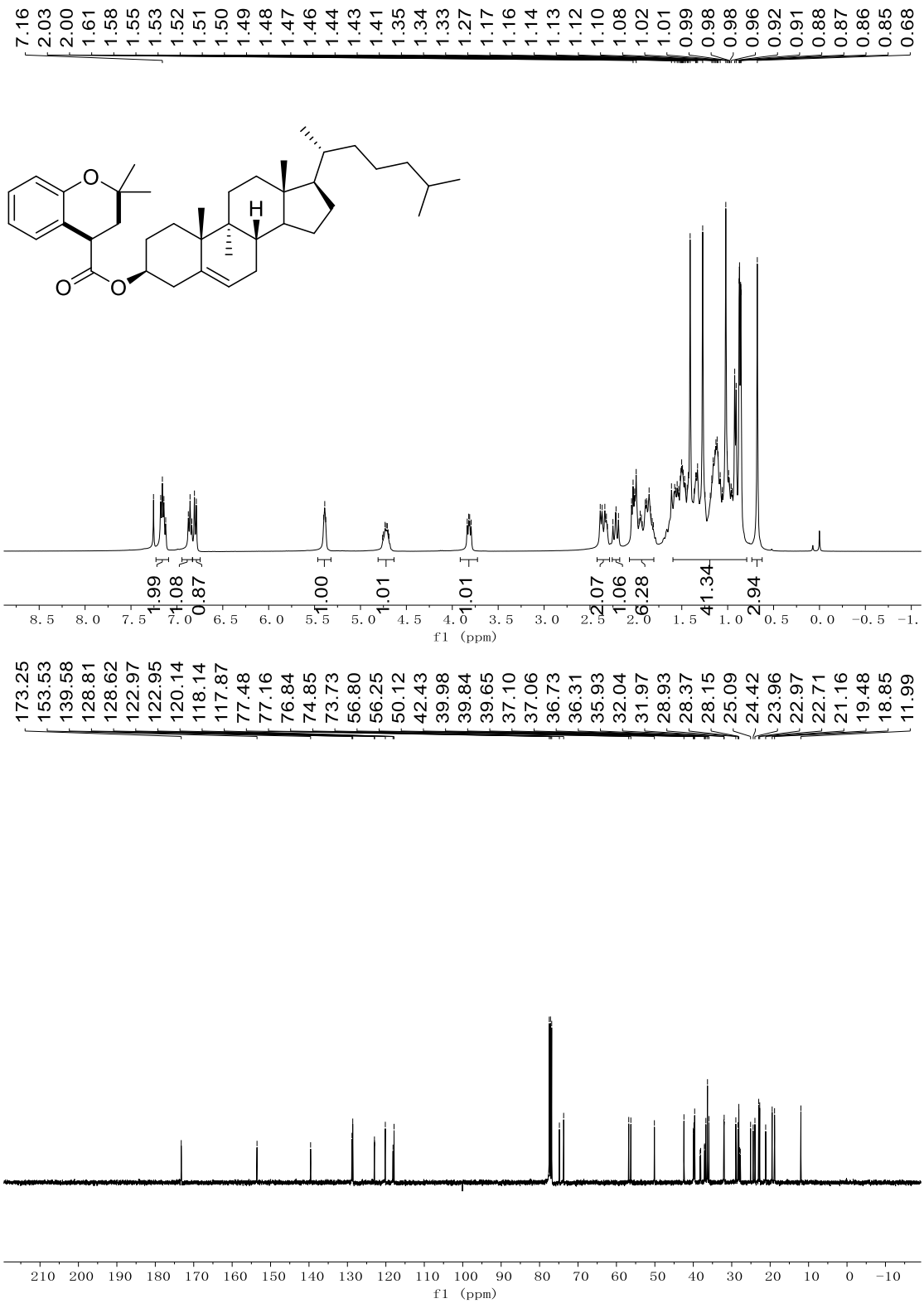

7.26 7.15 7.13 7.11 6.87 6.86 6.85 6.84 6.80 6.78 3.81 3.80 2.20 2.05 2.04 2.02 2.00 1.83 1.74 1.73 1.72 1.71 1.71 1.70 1.69 1.67 1.66 1.62 1.55 1.40 1.38 1.28 1.27 1.16 1.13 0.87 0.86 0.83 0.82 0.81 0.79
O
H
O
O
1.94 0.94 0.97 1.00 0.98 1.00 1.00 1.06 3.14 1.18 3.05 2.99 2.51 3.08 5.90
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 −1.0
f1 (ppm)
173.41 173.29 153.46 129.50 129.05 128.58 120.09 120.00 118.03 117.99 117.83 117.76 82.09 81.93 77.48 77.16 76.84 73.71 48.98 48.78 47.04 45.12 40.35 40.16 38.89 36.52 36.34 33.91 33.89 28.86 28.62 27.13 25.32 25.07 20.21 20.19 20.00 19.93 11.79 11.70
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

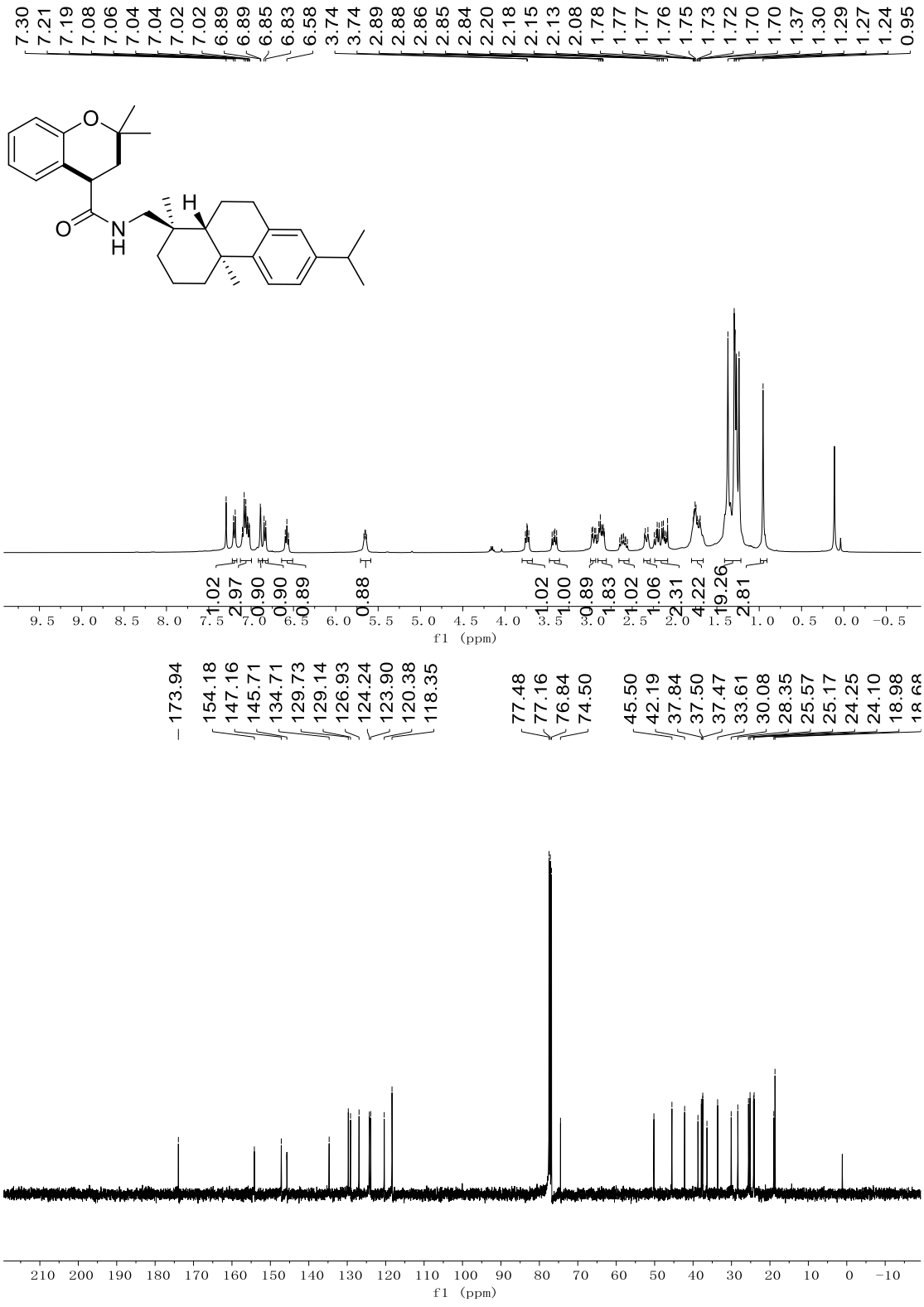

2.45 2.43 2.42 2.19 2.08 2.06 2.03 1.93 1.92 1.91 1.91 1.90 1.89 1.87 1.72 1.72 1.71 1.70 1.70 1.69 1.69 1.68 1.63 1.60 1.50 1.49 1.46 1.44 1.43 1.40 1.32 1.30 1.29 1.19 1.14 1.04 1.01 0.90 0.88 0.88 0.87
O
O
O
H
0.97 0.93 0.96 0.84 1.00 1.12 2.58 2.29 2.98 2.99 2.99 7.00 3.11 3.07 3.12 3.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1
f1 (ppm)
129.03 128.83 128.47 128.44 120.08 119.97 117.83 117.79 77.48 77.16 76.84 73.70 73.67 57.71 57.31 56.78 56.74 54.05 54.02 43.57 43.55 41.41 41.15 40.58 37.06 36.17 33.28 32.91 31.40 29.23 28.90 28.71 28.64 27.49 27.46 25.80 25.53 25.41 25.17 24.79 15.65
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

64

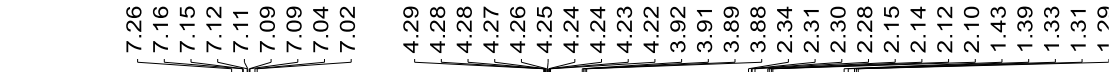

7.16 7.14 6.85 6.81 4.22 4.21 4.20 2.04 2.02 2.00 1.94 1.93 1.92 1.91 1.90 1.75 1.75 1.73 1.72 1.71 1.68 1.60 1.58 1.57 1.55 1.40 1.34 1.33 1.32 1.30 1.29 1.27 1.26 1.24 1.24 1.23 1.21 1.20 1.19 0.92 0.90
O
O
O
1.99 1.89 1.00 1.96 0.95 1.10 1.10 1.22 2.29 2.48 3.19 3.04 2.95 3.00 3.19 3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)
173.90 153.50 131.47 128.89 128.87 128.65 124.59 120.12 117.95 117.88 77.48 77.16 76.84 73.69 63.79 55.85 39.90 37.04 36.29 35.54 35.03 29.55 25.84 25.56 25.49 24.80
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

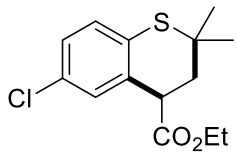
65

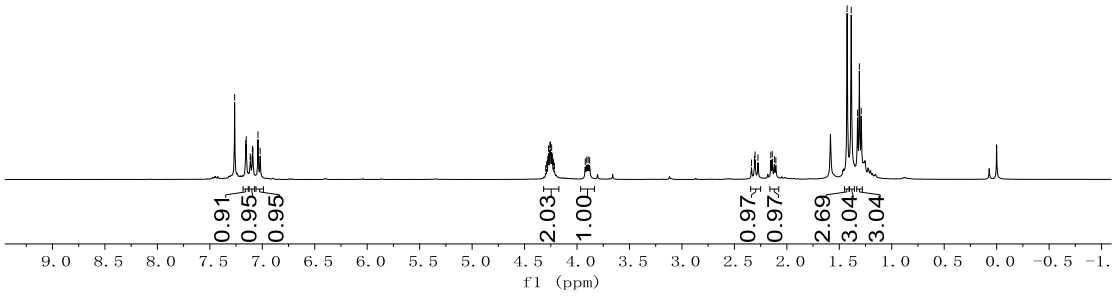

7.16 2.03 2.00 1.61 1.58 1.55 1.53 1.52 1.51 1.50 1.49 1.48 1.47 1.46 1.44 1.43 1.41 1.35 1.34 1.33 1.27 1.17 1.16 1.14 1.13 1.12 1.10 1.08 1.02 1.01 0.99 0.98 0.98 0.96 0.92 0.91 0.88 0.87 0.86 0.85 0.68
O
H
O
O
1.99 1.08 0.87 1.00 1.01 1.01 2.07 1.06 6.28 41.34 2.94
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.
f1 (ppm)
173.25 153.53 139.58 128.81 128.62 122.97 122.95 120.14 118.14 117.87 77.48 77.16 76.84 74.85 73.73 56.80 56.25 50.12 42.43 39.98 39.84 39.65 37.10 37.06 36.73 36.31 35.93 32.04 31.97 28.93 28.37 28.15 25.09 24.42 23.96 22.97 22.71 21.16 19.48 18.85 11.99
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

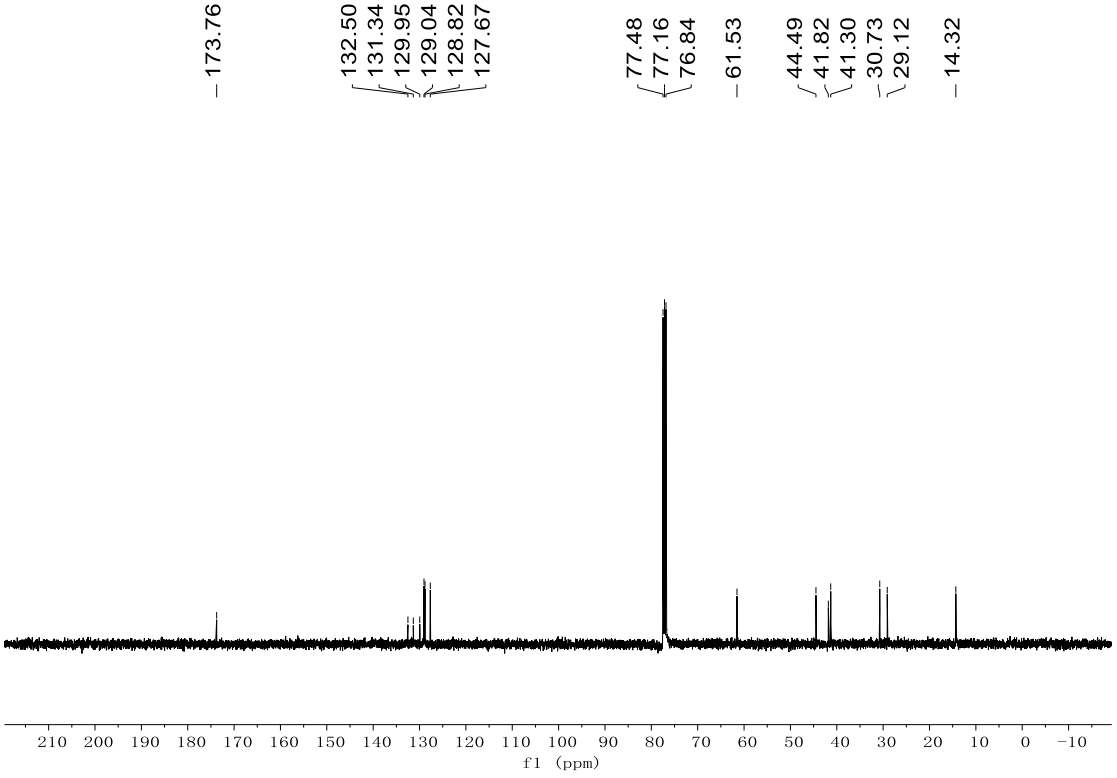

7.30 7.21 7.19 7.08 7.06 7.04 7.04 7.02 7.02 6.89 6.89 6.85 6.83 6.58
3.74 3.74 2.89 2.88 2.86 2.85 2.84 2.20 2.18 2.15 2.13 2.08 1.78 1.77 1.77 1.76 1.75 1.73 1.72 1.70 1.70 1.37 1.30 1.29 1.27 1.24 0.95
O
H
O
N
H
1.02 2.97 0.90 0.90 0.89 0.88 1.02 1.00 0.89 1.83 1.02 1.06 2.31 4.22 19.26 2.81
f1 (ppm)
173.94 154.18 147.16 145.71 134.71 129.73 129.14 126.93 124.24 123.90 120.38 118.35
77.48 77.16 76.84 74.50
45.50 42.19 37.84 37.50 37.47 33.61 30.08 28.35 25.57 25.17 24.25 24.10 18.98
f1 (ppm)

67

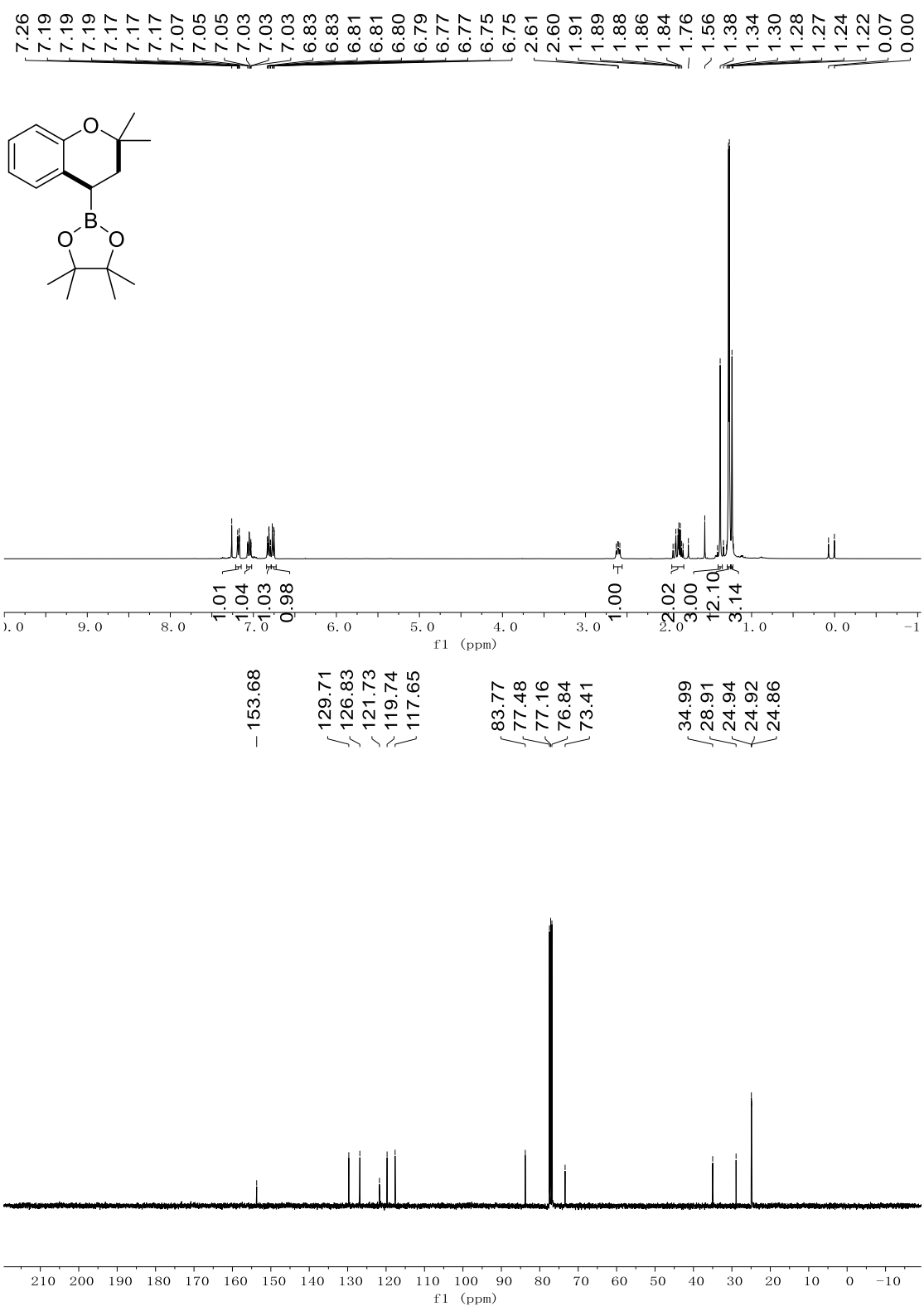

7.26
7.16
7.15
7.12
7.11
7.09
7.09
7.04
7.02
4.29
4.28
4.28
4.27
4.26
4.25
4.24
4.24
4.23
4.22
3.92
3.91
3.89
3.88
2.34
2.31
2.30
2.28
2.15
2.14
2.12
2.10
1.43
1.39
1.33
1.31


S
Cl
CO2Et

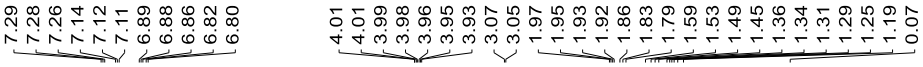

0.91
0.95
0.95
2.03
1.00
0.97
0.97
2.69
3.04
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.
f1 (ppm)


173.76
132.50
131.34
129.95
129.04
128.82
127.67
77.48
77.16
76.84
61.53
44.49
41.82
41.30
30.73
29.12
14.32
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

68


7.26 7.19 7.19 7.19 7.17 7.17 7.17 7.07 7.05 7.05 7.03 7.03 7.03 6.83 6.83 6.81 6.81 6.80 6.79 6.77 6.77 6.75 6.75 2.61 2.60 1.91 1.89 1.88 1.86 1.84 1.76 1.56 1.38 1.34 1.30 1.28 1.27 1.24 1.22 0.07 0.00
O
B
O
O
1.01 1.04 1.03 0.98 1.00 2.02 3.00 12.10 3.14
f1 (ppm)
153.68 129.71 126.83 121.73 119.74 117.65 83.77 77.48 77.16 76.84 73.41 34.99 28.91 24.94 24.92 24.86
f1 (ppm)

69


7.29
7.28
7.26
7.14
7.12
7.11
6.89
6.88
6.86
6.82
6.80
4.01
4.01
3.99
3.98
3.96
3.95
3.93
3.07
3.05
1.97
1.95
1.93
1.92
1.86
1.83
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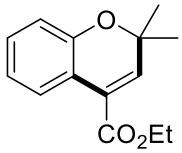
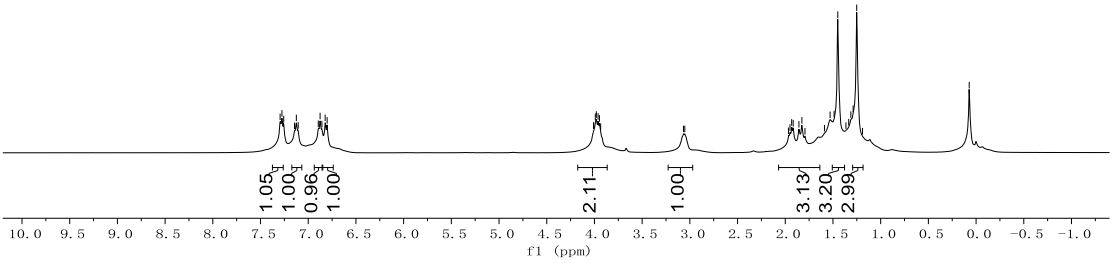
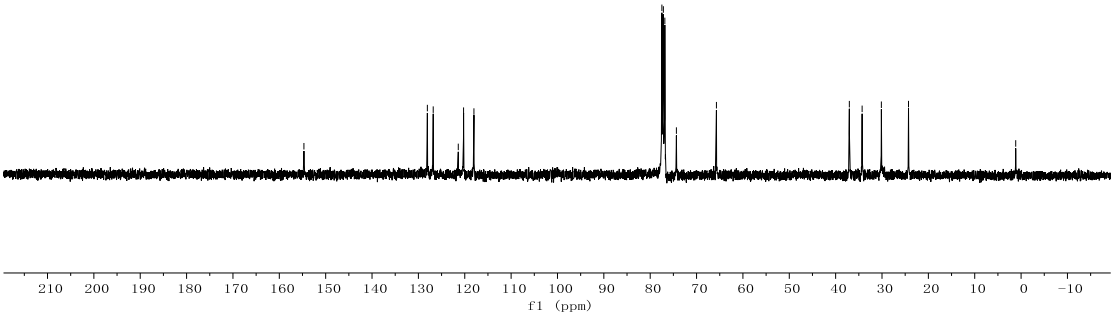
1.34
1.31
1.29
1.25
1.19
0.07

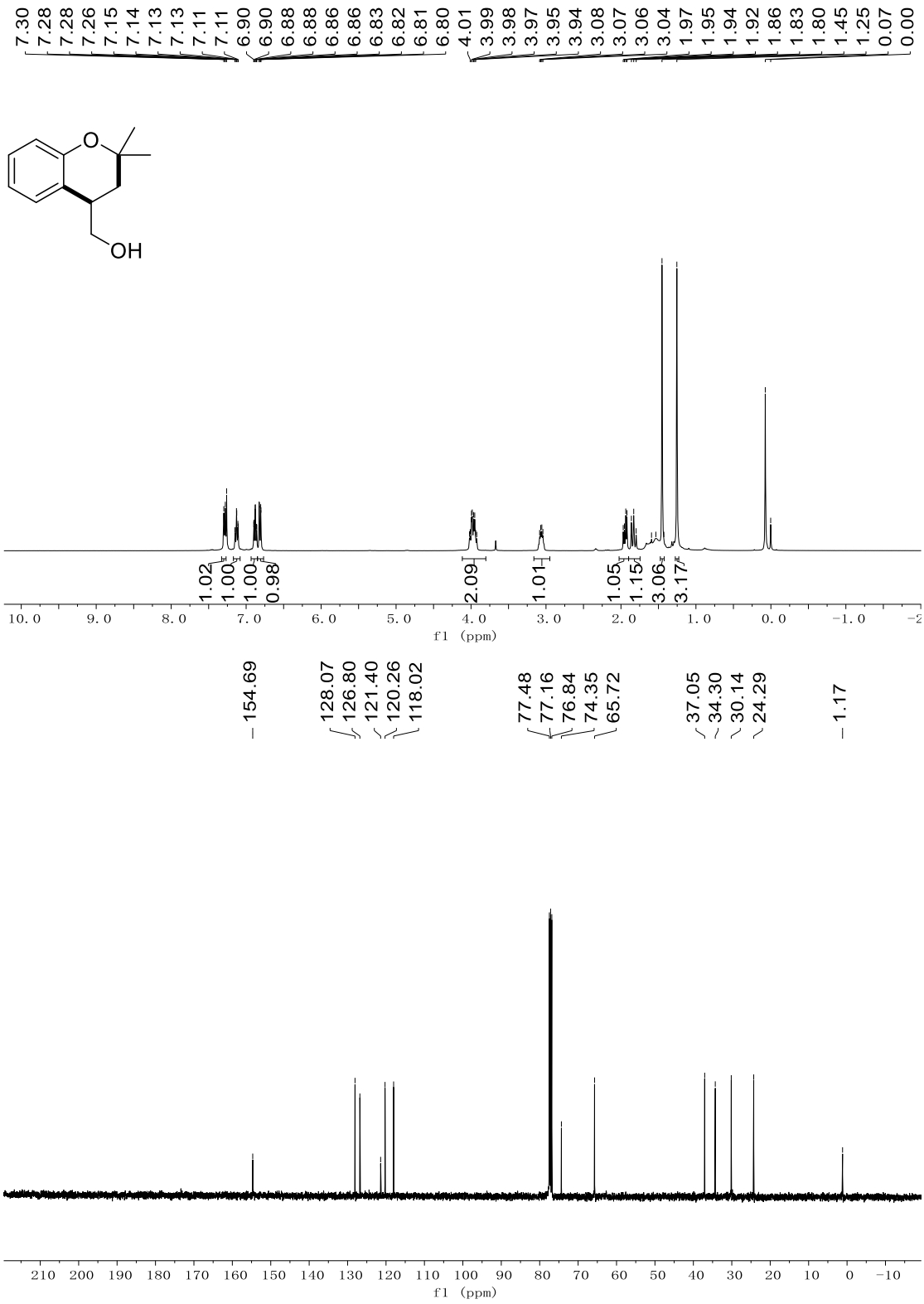

O
CO2Et


1.05
1.00
0.96
1.00
2.11
1.00
3.13
3.20
2.99
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 −1.0
f1 (ppm)

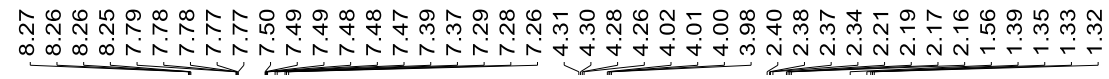

154.69
128.07
126.80
121.40
120.26
118.02
77.48
77.16
76.84
74.35
65.71
37.05
34.29
30.14
24.28
1.16


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

70


7.30 7.28 7.28 7.26 7.15 7.14 7.13 7.13 7.11 7.11 6.90 6.90 6.88 6.88 6.86 6.86 6.83 6.82 6.81 6.80 4.01 3.99 3.98 3.97 3.95 3.94 3.08 3.07 3.06 3.04 1.97 1.95 1.94 1.92 1.86 1.83 1.80 1.45 1.25 0.07 0.00
O
OH
1.02 1.00 1.00 0.98 2.09 1.01 1.05 1.15 3.06 3.17
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 −1.0
f1 (ppm)
154.69 128.07 126.80 121.40 120.26 118.02 77.48 77.16 76.84 74.35 65.72 37.05 34.30 30.14 24.29 1.17
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

71


8.27
8.26
8.26
8.25
7.79
7.78
7.78
7.77
7.77
7.50
7.49
7.49
7.48
7.48
7.47
7.39
7.37
7.29
7.28
7.26
4.31
4.30
4.28
4.26
4.02
4.01
4.00
3.98
2.40
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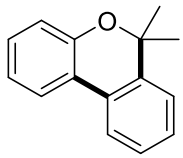
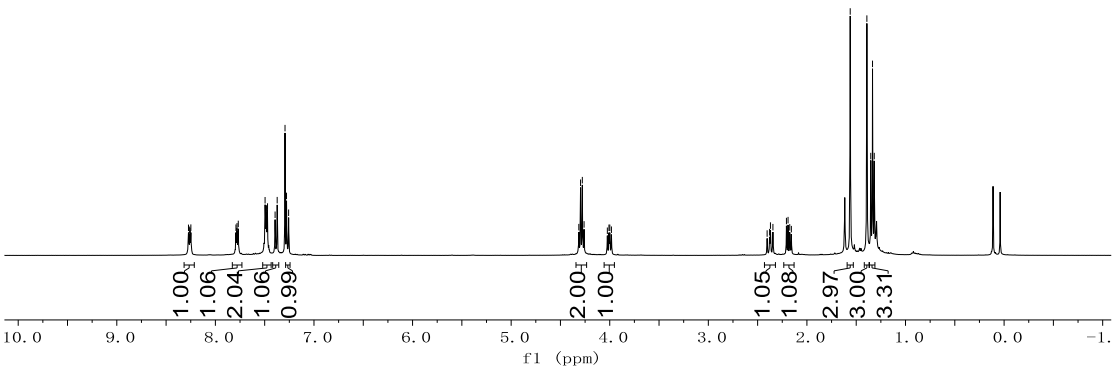
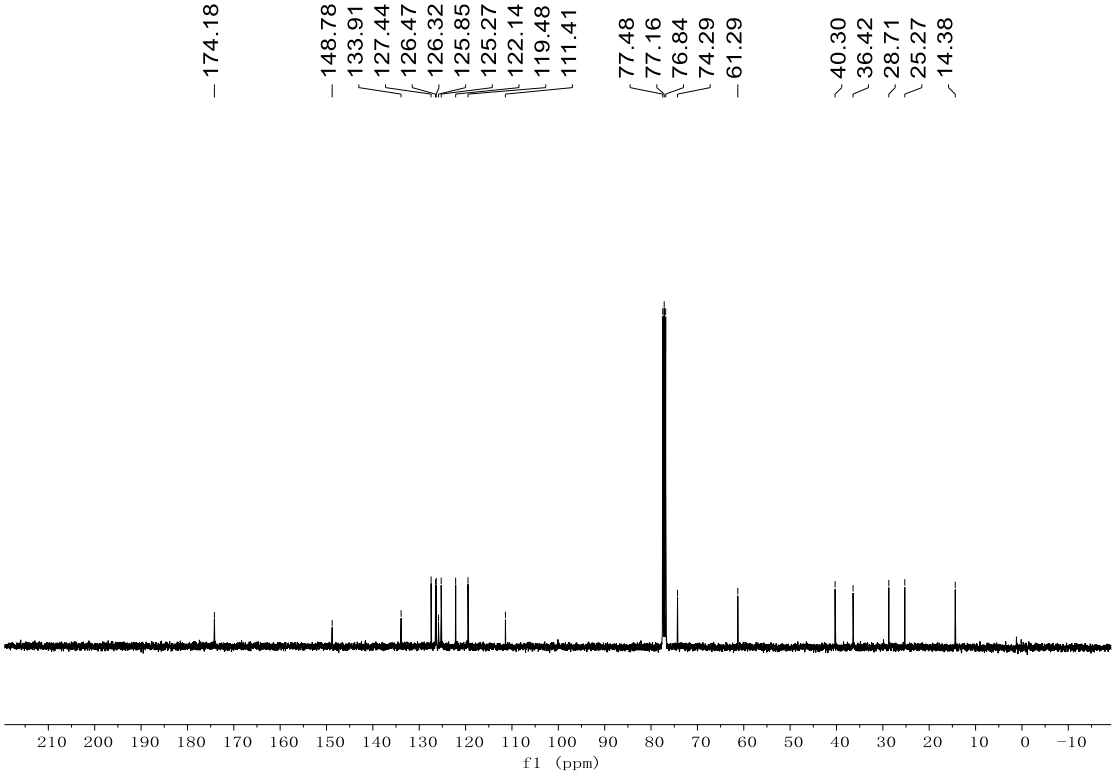
2.16
1.56
1.39
1.35
1.33
1.32


O


1.00
1.06
2.04
1.06
0.99
2.00
1.00
1.05
1.08
2.97
3.00
3.31
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1.
f1 (ppm)


174.18
148.78
133.91
127.44
126.47
126.32
125.85
125.27
122.14
119.48
111.41
77.48
77.16
76.84
74.29
61.29
40.30
36.42
28.71
25.27
14.38
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

^{1}H NMR spectrum of desired product from KIE experiment.