Palladium-catalyzed [2+2+1] annulation: access to chromone fused cyclopentanones with cyclopropenone as the CO source

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Electronic Supplementary Information

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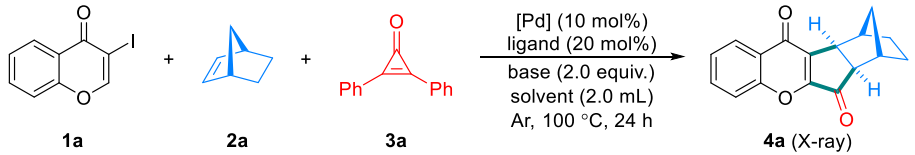
1. General experimental information

Unless otherwise noted, all commercially available reagents were used without further purification. All of the solvents were treated according to known methods. Column chromatography was performed on silica gel (200-400 mesh). ^{1}H NMR (400 MHz) chemical shifts were reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. ^{13}C NMR (100 MHz) chemical shifts were reported in ppm (δ) from tetramethylsilane (TMS) with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets, tt = triplet of triplets, dq = doublet of quartets, qd = quartet of doublets, m = multiplet), coupling constants (Hz) and integration. HRMS measurements were obtained on a TOF analyzer. Melting points were uncorrected.

3-Iodochromones (**1**) were prepared according to the reported procedures.[1a] Bridged olefins **2a**–**2e** were purchased from commercial suppliers. Bridged olefins **2f**–**2h** were prepared according to the reported procedures.[2,3] Cyclopropenone **3a** was purchased from commercial suppliers. Cyclopropenone **3b** was prepared according to the reported procedures.[4a]

2. Optimization of the reaction conditions for the construction of 4a [a)]



1a **2a** **3a** **4a** (X-ray)

Entry	Ligand	[Pd]	Solvent	Base	Yield (%)[b]
1	PPh_3	$Pd(OAc)_2$	PhMe	Cs_2CO_3	48
2	TFP	$Pd(OAc)_2$	PhMe	Cs_2CO_3	29
3	PCy_3	$Pd(OAc)_2$	PhMe	Cs_2CO_3	33
4	$P(^nBu)_3$	$Pd(OAc)_2$	PhMe	Cs_2CO_3	18
5	$P(2\text{-}MeC_6H_4)_3$	$Pd(OAc)_2$	PhMe	Cs_2CO_3	68
6	$P(3\text{-}MeC_6H_4)_3$	$Pd(OAc)_2$	PhMe	Cs_2CO_3	66
7	$P(4\text{-}MeC_6H_4)_3$	$Pd(OAc)_2$	PhMe	Cs_2CO_3	62
8	$P(2\text{-}OMeC_6H_4)_3$	$Pd(OAc)_2$	PhMe	Cs_2CO_3	44
9	$P(3\text{-}OMeC_6H_4)_3$	$Pd(OAc)_2$	PhMe	Cs_2CO_3	52
10	$P(3\text{-}FC_6H_4)_3$	$Pd(OAc)_2$	PhMe	Cs_2CO_3	69
11	$P(4\text{-}OMeC_6H_4)_3$	$Pd(OAc)_2$	PhMe	Cs_2CO_3	39
12	$P(4\text{-}CF_3C_6H_4)_3$	$Pd(OAc)_2$	PhMe	Cs_2CO_3	79
13	tris(2,6-dimethoxyphenyl)phosphine	$Pd(OAc)_2$	PhMe	Cs_2CO_3	35
14	trimesitylphosphine	$Pd(OAc)_2$	PhMe	Cs_2CO_3	39
15	$PhPCy_2$	$Pd(OAc)_2$	PhMe	Cs_2CO_3	24
16	$^nBuPAd_2$	$Pd(OAc)_2$	PhMe	Cs_2CO_3	37

17	diphenyl(pentafluorophenyl)phosphine	$Pd(OAc)_2$	PhMe	Cs_2CO_3	41
18	methyldiphenylphosphine	$Pd(OAc)_2$	PhMe	Cs_2CO_3	36
19	dppm	$Pd(OAc)_2$	PhMe	Cs_2CO_3	19
20	dppe	$Pd(OAc)_2$	PhMe	Cs_2CO_3	11
21	dppp	$Pd(OAc)_2$	PhMe	Cs_2CO_3	11
22	dppb	$Pd(OAc)_2$	PhMe	Cs_2CO_3	trace
23	dpppe	$Pd(OAc)_2$	PhMe	Cs_2CO_3	4
24	dpph	$Pd(OAc)_2$	PhMe	Cs_2CO_3	8
25	*cis*-1,2-bis(diphenylphosphino)ethylene	$Pd(OAc)_2$	PhMe	Cs_2CO_3	12
26	Xantphos	$Pd(OAc)_2$	PhMe	Cs_2CO_3	8
27	*rac*-BINAP	$Pd(OAc)_2$	PhMe	Cs_2CO_3	7
28	JohnPhos	$Pd(OAc)_2$	PhMe	Cs_2CO_3	43
29	CyJohnPhos	$Pd(OAc)_2$	PhMe	Cs_2CO_3	34
30	2-(diphenylphosphino)-biphenyl	$Pd(OAc)_2$	PhMe	Cs_2CO_3	59
31	BrettPhos	$Pd(OAc)_2$	PhMe	Cs_2CO_3	25
32	^{t}BuXPhos	$Pd(OAc)_2$	PhMe	Cs_2CO_3	22
33	Sphos	$Pd(OAc)_2$	PhMe	Cs_2CO_3	22
34	RuPhos	$Pd(OAc)_2$	PhMe	Cs_2CO_3	25
35	DavePhos	$Pd(OAc)_2$	PhMe	Cs_2CO_3	47
36	$P(4\text{-}CF_3C_6H_4)_3$	$Pd(TFA)_2$	PhMe	Cs_2CO_3	84
37	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	PhMe	Cs_2CO_3	86
38	$P(4\text{-}CF_3C_6H_4)_3$	$PdBr_2$	PhMe	Cs_2CO_3	70

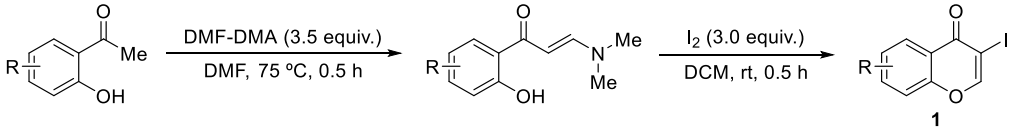
39	$P(4\text{-}CF_3C_6H_4)_3$	$Pd(dppf)_2Cl_2$	PhMe	Cs_2CO_3	39
40	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2(dppe)$	PhMe	Cs_2CO_3	83
41	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2(dppb)$	PhMe	Cs_2CO_3	62
42	$P(4\text{-}CF_3C_6H_4)_3$	$[Pd(C_4H_9)_3PBr]_2$	PhMe	Cs_2CO_3	66
43	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2(dippp)$	PhMe	Cs_2CO_3	62
44	$P(4\text{-}CF_3C_6H_4)_3$	$[(cinnamyl)PdCl]_2$	PhMe	Cs_2CO_3	74
45	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2[P(C_2H_5)_3]_2$	PhMe	Cs_2CO_3	50
46	$P(4\text{-}CF_3C_6H_4)_3$	$Pd(OTf)_2(dippp)$	PhMe	Cs_2CO_3	39
47	$P(4\text{-}CF_3C_6H_4)_3$	$Pd(dppf)Cl_2$	PhMe	Cs_2CO_3	51
48	$P(4\text{-}CF_3C_6H_4)_3$	$Pd(Phos)Cl_2$	PhMe	Cs_2CO_3	81
49	$P(4\text{-}CF_3C_6H_4)_3$	$Pd(PPh_3)_4$	PhMe	Cs_2CO_3	41
50	$P(4\text{-}CF_3C_6H_4)_3$	$Pd_2(dba)_3$	PhMe	Cs_2CO_3	75
51	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	*o*-xylene	Cs_2CO_3	78
52	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	*m*-xylene	Cs_2CO_3	72
53	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	*p*-xylene	Cs_2CO_3	70
54	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	mesitylene	Cs_2CO_3	57
55	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	$PhCF_3$	Cs_2CO_3	70
56	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	anisole	Cs_2CO_3	54
57	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	PhF	Cs_2CO_3	91
58	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	$PhNO_2$	Cs_2CO_3	65
59	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	PhCl	Cs_2CO_3	77
60	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	1,2-dichlorobenzne	Cs_2CO_3	87

61	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	DMSO	Cs_2CO_3	10
62	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	DMF	Cs_2CO_3	23
63	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	DMA	Cs_2CO_3	36
64	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	HMPA	Cs_2CO_3	23
65	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	NMM	Cs_2CO_3	47
66	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	NMP	Cs_2CO_3	31
67	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	DCE	Cs_2CO_3	82
68	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	1,4-dioxane	Cs_2CO_3	54
69	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	glyme	Cs_2CO_3	42
70	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	THF	Cs_2CO_3	56
71	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	CH_3CN	Cs_2CO_3	30
72	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	*t*-amylol	Cs_2CO_3	58
73	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	HFIP	Cs_2CO_3	NR
74	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	MTBE	Cs_2CO_3	50
75	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	CH_3NO_2	Cs_2CO_3	10
76	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	PhF	K_2CO_3	29
77	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	PhF	Na_2CO_3	17
78	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	PhF	KO^tBu	19
79	$P(4\text{-}CF_3C_6H_4)_3$	$PdCl_2$	PhF	K_3PO_4	55

[a]All reactions were performed with **1a** (0.2 mmol), **2a** (0.8 mmol), **3a** (0.2 mmol), Pd-catalyst (0.02 mmol), ligand (0.04 mmol), base (0.4 mmol) in 2.0 mL of solvent under Ar atmosphere at 100 °C for 24 h. [b]Isolated yields based on **1a**.

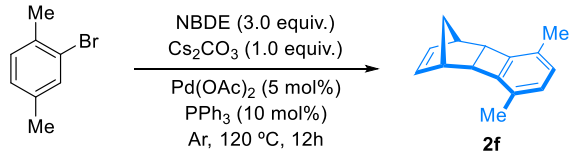
3. Synthetic methods of substrates

3.1 Synthesis of 3-Iodochromones (**1**)



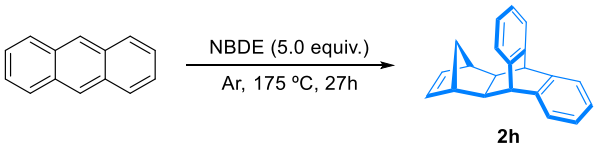
A mixture of substituted 2-hydroxyacetophenones (0.5 mmol) and *N*,*N*-dimethylformamide dimethylacetal (DMF-DMA, 1.75 mmol, 2.5 equiv.) was dissolved in *N*,*N*-dimethylformamide (DMF, 25 mL) and heated at 75 °C for 0.5 h. After completion of the reaction, saturated brine was added to the mixture. The solid was separated to afford the substituted 3-(dimethylamino)-1-(2-hydroxyphenyl)propanones. To a solution of the solid in CH_2Cl_2 (15 mL) was added iodine (1.5 mmol, 3.0 equiv.), and the mixture was stirred at room temperature for 0.5 h. After completion of the reaction, the solution was diluted with saturated $NaHSO_3$ (15 mL), and the aqueous layer was extracted with CH_2Cl_2 (60 mL). The combined organic fractions were condensed and purified by flash column chromatography to afford 3-Iodochromones (**1**) in 50 ~ 80% yields.[1a]

3.2 Synthesis of Bridged olefins (**2**)



To a 40 mL glass vial were added 2-bromo-*p*-xylene (2.0 g, 10.8 mmol), Cs_2CO_3 (3.6 g, 10.8 mmol) and norbornadiene (3.3 mL, 32.4 mmol) followed by dry 1,4-dioxane (20 mL) under argon atmosphere. The reaction vial was evacuated and filled with argon three times. $Pd(OAc)_2$ (121mg, 0.54 mmol) and PPh_3 (283 mg, 1.08 mmol) were added to this solution. Then the reaction mixture was stirred at 25 °C for 5 min, and then heated to 130 °C for 12 h. After completion of the reaction, the mixture was cooled to 25 °C and passed through a thin layer of Celite bed and washed with EtOAc (50 mL) to remove inorganic salts. The filtrate was evaporated under reduced pressure and purified by silica gel chromatography (eluted with hexanes) to afford compound **2f** as a colorless oil (954.0 mg, 45% yield). Under the same conditions, replacing 2-bromo-*p*-xylene with

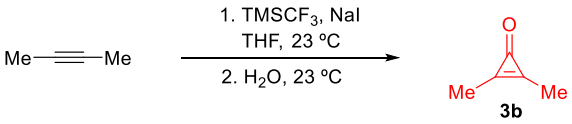
9-bromophenanthrene can obtain compound **2g** as a white solid. Spectra matched those previously reported.[2]



2h

A sealed glass tube containing anthracene (891.2 mg, 5 mmol) and norbornadiene (NBDE, 2.3 g, 25 mmol) under argon atmosphere was heated at 175 °C for 27 h in an oil bath. After the completion of the reaction and Cooled to room temperature, the norbornadiene was stripped from the reaction mixture at reduced pressure. The yellow residue was purified by flash column chromatography on silica gel (petroleum ether) to afford the desired product **2h** as a white solid (1.08 g, 79% yield). Spectra matched those previously reported.[3]

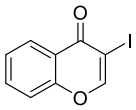
3.3 Synthesis of Cyclopropenones (**3b**)



3b

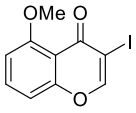
To an oven-dried sealed tube containing a stir bar was added NaI (330 mg, 2.2 mmol). The NaI was gently flame-dried under vacuum and then allowed to cool to room temperature. A solution of 2-butyne (0.08 mL, 1.0 mmol) in anhydrous THF (3.0 mL) was added under an atmosphere of Ar. Trifluoromethyltrimethylsilane (0.30 mL, 2.0 mmol) was added, and the tube was sealed. The solution was stirred rapidly at room temperature for 2 d, then diluted with H_2O (15 mL) and extracted into CH_2Cl_2 (60 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (eluting with 30% acetone/CH_2Cl_2) to afford compound **3b** as a yellow oil (57.5 mg, 70% yield). Spectra matched those previously reported.[4]

4. Characterization data of 1a-1w, 2a-2h and 3a-3b



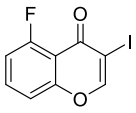
1a

3-iodo-4*H*-chromen-4-one (**1a**). White solid, mp 101.1 – 102.9 °C (lit.[1a] mp 102 – 103 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.24 (dd, J = 8.0, 1.2 Hz, 1H), 7.71 (ddd, J = 8.6, 7.2, 1.6 Hz, 1H), 7.49 – 7.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 157.9, 156.2, 134.2, 126.7, 126.1, 121.9, 118.1, 87.0.



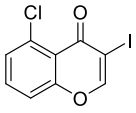
1b

3-iodo-5-methoxy-4*H*-chromen-4-one (**1b**). White solid, mp 141.7 – 143.0 °C (lit.[1a] mp 143 – 145 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.54 (t, J = 8.4 Hz, 1H), 6.97 (d, J = 8.4 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 159.7, 158.1, 156.0, 134.2, 112.6, 109.8, 106.9, 89.4, 56.6.



1c

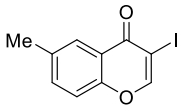
3-iodo-5-fluoro-4*H*-chromen-4-one (**1c**). White solid, mp 99.6 – 101.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 1.6 Hz, 1H), 7.68 – 7.60 (m, 1H), 7.27 (d, J = 8.6 Hz, 1H), 7.11 (t, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1 (d, J = 2.3 Hz), 160.4 (d, J = 266.8 Hz), 157.1 (d, J = 3.1 Hz), 157.0, 134.3 (d, J = 10.7 Hz), 114.0 (d, J = 4.7 Hz), 112.7 (d, J = 20.7 Hz), 112.4 (d, J = 10.1 Hz), 88.26.



1d

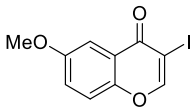
3-iodo-5-chloro-4*H*-chromen-4-one (**1d**). Yellow solid, mp 123.7 – 125.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 3.0 Hz, 1H), 7.56 (ddd, J = 8.4, 3.6, 2.0 Hz, 1H), 7.45 (ddd, J = 5.0,

3.4, 1.1 Hz, 1H), 7.41 – 7.36 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 157.7, 156.6, 134.1, 133.4, 128.8, 119.1, 117.3, 88.8.



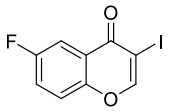
1e

3-iodo-6-methyl-4*H*-chromen-4-one (**1e**). White solid, mp 142.6 – 143.9 ℃ (lit.[1b] mp 138 – 140 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 2.0 Hz, 1H), 8.00 (s, 1H), 7.50 (d, J = 8.6 Hz, 1H), 7.35 (d, J = 8.6 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 157.7, 154.5, 136.2, 135.5, 125.9, 121.5, 117.8, 86.8, 21.1.



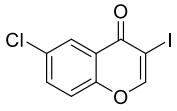
1f

3-iodo-6-methoxy-4*H*-chromen-4-one (**1f**). White solid, mp 109.2 – 111.0 ℃ (lit.[1a] mp 112 – 113 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.56 (d, J = 3.0 Hz, 1H), 7.39 (d, J = 9.2 Hz, 1H), 7.28 (dd, J = 9.2, 3.0 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 157.6, 157.5, 151.1, 124.4, 122.5, 119.6, 105.5, 86.08, 56.1.



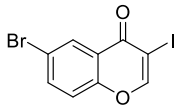
1g

3-iodo-6-fluoro-4*H*-chromen-4-one (**1g**). White solid, mp 116.9 – 118.2 ℃ (lit.[1a] mp 120 – 122 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 2.2 Hz, 1H), 7.86 (dt, J = 8.2, 2.4 Hz, 1H), 7.49 (ddd, J = 9.0, 4.2, 2.2 Hz, 1H), 7.46 – 7.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9 (d, J = 2.4 Hz), 159.8 (d, J = 248.3 Hz), 158.0, 152.5 (d, J = 1.8 Hz), 122.9 (d, J = 7.6 Hz), 122.7 (d, J = 25.5 Hz), 120.4 (d, J = 8.2 Hz), 111.5 (d, J = 23.9 Hz), 86.1 (d, J = 1.2 Hz).



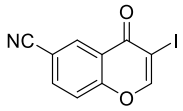
1h

3-iodo-6-chloro-4*H*-chromen-4-one (**1h**). White solid, mp 139.5 – 140.8 °C (lit.[1b] mp 138 – 140 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.17 (d, J = 2.6 Hz, 1H), 7.63 (dd, J = 9.0, 2.6 Hz, 1H), 7.43 (d, J = 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 157.9, 154.5, 134.5, 131.9, 126.0, 122.6, 119.9, 86.7.



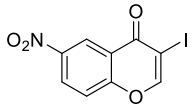
1i

3-iodo-6-bromo-4*H*-chromen-4-one (**1i**). White solid, mp 113.0 – 114.2 °C (lit.[1b] mp 115 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 2.4 Hz, 1H), 8.30 (s, 1H), 7.79 (dd, J = 9.0, 2.4 Hz, 1H), 7.38 (d, J = 8.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 158.0, 155.0, 137.3, 129.2, 123.0, 120.1, 119.4, 86.8.



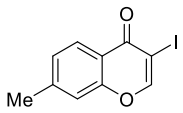
1j

3-iodo-4-oxo-4*H*-chromene-6-carbonitrile (**1j**). White solid, mp 199.7 – 201.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 1.6 Hz, 1H), 8.33 (s, 1H), 7.93 (dd, J = 8.8, 1.5 Hz, 1H), 7.60 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 158.1, 157.9, 136.5, 132.3, 122.0, 119.9, 117.3, 110.4, 87.5.



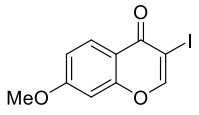
1k

3-iodo-6-nitro-4*H*-chromen-4-one (**1k**). White solid, mp 107.7 – 109.2 °C (lit.[1c] mp 110 – 111 °C); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.89 (s, 1H), 8.65 (s, 1H), 8.55 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.3, 159.7, 158.7, 144.6, 128.6, 121.7, 120.9, 120.8, 87.2.



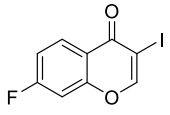
1l

3-iodo-7-methyl-4*H*-chromen-4-one (**1l**). Yellow solid, mp 87.8 – 89.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.10 (d, J = 8.6 Hz, 1H), 7.24 (d, J = 6.8 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 157.6, 156.4, 145.7, 127.6, 126.4, 119.6, 117.7, 87.0, 22.0.



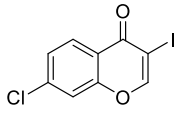
1m

3-iodo-7-methoxy-4*H*-chromen-4-one (**1m**). Yellow solid, mp 108.4 – 109.8 °C (lit.[1a] mp 103 – 105 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.13 (d, J = 9.0 Hz, 1H), 6.99 (dd, J = 9.0, 2.4 Hz, 1H), 6.83 (d, J = 2.3 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 164.4, 158.0, 157.3, 128.2, 115.8, 115.5, 100.1, 87.3, 56.1.



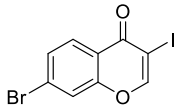
1n

3-iodo-7-fluoro-4*H*-chromen-4-one (**1n**). White solid, mp 106.1 – 107.6 °C (lit.[1a] mp 107 – 109 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.24 (t, J = 8.6 Hz, 1H), 7.19 – 7.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 165.8 (d, J = 256.5 Hz), 157.9 (d, J = 1.3 Hz), 157.2 (d, J = 13.4 Hz), 129.4 (d, J = 10.7 Hz), 118.6 (d, J = 2.5 Hz), 115.0 (d, J = 22.9 Hz), 104.8 (d, J = 25.5 Hz), 87.2.



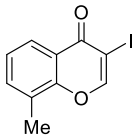
1o

3-iodo-7-chloro-4*H*-chromen-4-one (**1o**). Yellow solid, mp 115.9 – 117.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.16 (d, J = 8.6 Hz, 1H), 7.48 (d, J = 1.6 Hz, 1H), 7.40 (dd, J = 8.6, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 157.8, 156.3, 140.4, 128.1, 127.0, 120.3, 118.2, 87.2.



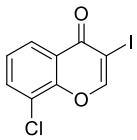
1p

3-iodo-7-bromo-4*H*-chromen-4-one (**1p**). White solid, mp 162.7 – 164.1 ℃ (lit.[1c] mp 163 – 164 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.10 (d, J = 8.5 Hz, 1H), 7.67 (d, J = 1.7 Hz, 1H), 7.57 (dd, J = 8.5, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 157.7, 156.2, 129.8, 128.6, 128.2, 121.2, 120.7, 87.3.



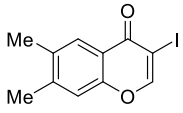
1q

3-iodo-8-methyl-4*H*-chromen-4-one (**1g**). White solid, mp 106.6 – 107.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 7.2 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 157.6, 154.7, 135.1, 127.6, 125.6, 124.2, 121.8, 87.0, 15.70.



1r

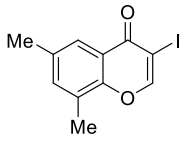
3-iodo-8-chloro-4*H*-chromen-4-one (**1r**). White solid, mp 116.7 – 118.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.12 (dd, J = 8.0, 1.4 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 157.6, 151.9, 134.5, 126.1, 125.3, 123.7, 123.0, 87.3.



1s

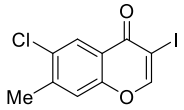
3-iodo-6,7-dimethyl-4*H*-chromen-4-one (**1s**). White solid, mp 154.5 – 156.3 ℃ (lit.[1c] mp 156 – 157 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.93 (s, 1H), 7.21 (s, 1H), 2.37 (s, 3H), 2.34

(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 157.5, 154.8, 144.9, 135.5, 126.1, 119.8, 118.1, 86.9, 20.6, 19.5.



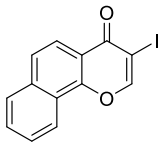
1t

3-iodo-6,8-dimethyl-4*H*-chromen-4-one (**1t**). White solid, mp 139.5 – 141.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.83 (s, 1H), 7.34 (s, 1H), 2.41 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 157.5, 153.1, 136.5, 135.6, 127.3, 123.5, 121.6, 86.8, 21.1, 15.6.



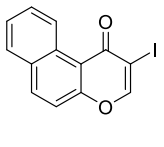
1u

3-iodo-6-chloro-7-methyl-4*H*-chromen-4-one (**1u**). White solid, mp 166.2 – 167.9 ℃ (lit.[1c] mp 167 – 168 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.15 (s, 1H), 7.34 (s, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 157.7, 154.5, 143.8, 132.7, 126.2, 120.7, 119.9, 86.6, 21.05.



1v

3-iodo-4*H*-benzo[*h*]chromen-4-one (**1v**). Yellow solid, mp 153.7 – 155.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.40 (d, J = 8.2 Hz, 1H), 8.13 (d, J = 8.8 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.79 – 7.64 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 157.0, 153.8, 135.9, 129.8, 128.3, 127.6, 126.3, 123.6, 122.3, 121.4, 118.1, 89.0.



1w

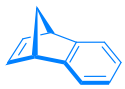
2-iodo-1*H*-benzo[*f*]chromen-1-one (**1w**). White solid, mp 136.2 – 137.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (d, J = 8.8 Hz, 1H), 8.33 (s, 1H), 8.08 (d, J = 9.2 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.76 (t, J = 7.8 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.46 (d, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 157.6, 155.6, 136.2, 130.8, 130.2, 129.7, 128.4, 127.4, 127.2, 117.2, 115.3, 91.5.

2a

bicyclo[2.2.1]hept-2-ene (**2a**). **2a** was purchased from commercial supplier. Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (s, 2H), 2.85 (s, 2H), 1.71 – 1.53 (m, 2H), 1.32 (d, J = 8.0 Hz, 1H), 1.08 (d, J = 8.0 Hz, 1H), 1.03 – 0.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 48.7, 41.9, 24.7.

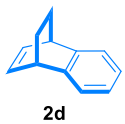
2b

bicyclo[2.2.1]hepta-2,5-diene (**2b**). **2b** was purchased from commercial supplier. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 – 6.86 (m, 4H), 3.71 (s, 2H), 2.23 – 2.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 75.2, 50.2.



2c

1,4-dihydro-1,4-methanonaphthalene (**2c**). **2c** was purchased from commercial supplier. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (td, J = 5.4, 3.2 Hz, 2H), 7.0 (td, J = 5.2, 3.0 Hz, 2H), 6.87 (t, J = 1.6 Hz, 2H), 3.96 (t, J = 1.8 Hz, 2H), 2.39 (dt, J = 7.1, 1.5 Hz, 1H), 2.32 (d, J = 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 143.1, 124.3, 121.6, 70.3, 50.4.



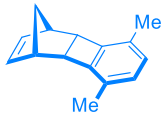
2d

1,4-dihydro-1,4-ethanonaphthalene (**2d**). **2d** was purchased from commercial supplier. Colorless

oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (dt, J = 12.0, 3.6 Hz, 2H), 7.13 (dt, J = 8.6, 3.2 Hz, 2H), 4.02 (qd, J = 2.8, 1.4 Hz, 2H), 1.65 – 1.59 (m, 2H), 1.54 – 1.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 135.2, 125.0, 122.7, 40.3, 25.9.

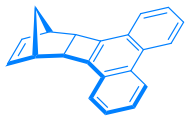
2e

1,2,3,4,4a,5,8,8a-octahydro-1,4:5,8-dimethanonaphthalene (**2e**). **2e** was purchased from commercial supplier. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 (t, J = 1.6 Hz, 2H), 2.83 (t, J = 1.6 Hz, 2H), 2.04 (ddd, J = 9.8, 4.2, 2.1 Hz, 1H), 2.00 (s, 2H), 1.94 (s, 2H), 1.42 – 1.35 (m, 2H), 1.27 (dt, J = 7.7, 1.6 Hz, 1H), 1.15 (d, J = 7.7 Hz, 1H), 1.02 – 0.95 (qd, J = 7.2, 2.4 Hz, 2H), 0.53 (d, J = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3, 53.0, 48.7, 46.8, 37.9, 33.9, 32.0.



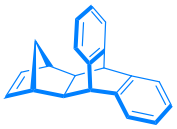
2f

5,8-dimethyl-1,4,4a,8b-tetrahydro-1,4-methanobiphenylene (**2f**).[2] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (s, 2H), 6.36 (s, 2H), 3.22 (s, 2H), 2.93 (s, 2H), 2.33 (s, 6H), 1.43 (d, J = 8.8 Hz, 1H), 1.02 (d, J = 8.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 136.6, 129.0, 128.4, 46.0, 41.7, 40.8, 16.5.



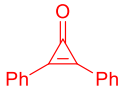
2g

8c,9,12,12a-tetrahydro-9,12-methanobenzo[3,4]cyclobuta[1,2-*l*]phenanthrene (**2g**). White solid, mp 117.3 – 118.5 °C (lit.[2] mp 220 – 222 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (dt, J = 9.4, 3.6 Hz, 2H), 7.86 (dt, J = 7.2, 3.4 Hz, 2H), 7.63 (dt, J = 9.4, 3.4 Hz, 4H), 6.36 (s, 2H), 3.46 (s, 2H), 2.95 (s, 2H), 1.36 (d, J = 9.2 Hz, 1H), 0.91 (d, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 136.6, 130.9, 128.3, 126.7, 125.8, 124.0, 123.0, 46.1, 41.7, 40.0.



2h

9,10-dihydro-9,10-[2]bicycloanthracene (**2h**). White solid, mp 143.0 – 144.3 °C (lit.[3] mp 144 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dq, J = 13.0, 6.0 Hz, 4H), 7.13 (dt, J = 9.2, 4.0 Hz, 2H), 7.06 (dt, J = 9.2, 4.0 Hz, 2H), 6.16 (s, 2H), 4.17 (s, 2H), 2.50 (s, 2H), 2.07 (s, 2H), 0.75 (d, J = 9.4 Hz, 1H), -0.13 (d, J = 94 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 142.8, 140.2, 126.1, 125.5, 124.7, 123.4, 48.4, 47.7, 44.6, 40.6.



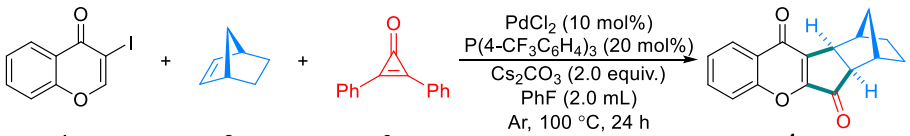
3a

2,3-diphenylcycloprop-2-en-1-one (**3a**). **3a** was purchased from commercial supplier. Yellow solid, mp 119.2 – 121.3 °C (lit.[4a] mp 120 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.60 – 7.52 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 148.3, 132.8, 131.6, 129.4, 124.0.

3b

2,3-dimethylcycloprop-2-en-1-one (**3b**).[4b] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.9, 11.40.

5. Representative procedure for the synthesis of compound 4a (Scheme 2)



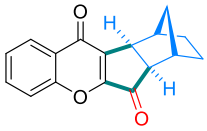
1a 2a 3a 4a

To a 4 mL flame-dried vial with a stir bar, 3-iodochromone (**1a**, 54.5 mg, 0.2 mmol), NBE (**2a**, 75.3 mg, 0.8 mmol), diphenylcyclopropenone (**3a**, 41.2 mg, 0.2 mmol), $PdCl_2$ (3.5 mg, 0.02 mmol), $P(4\text{-}CF_3C_6H_4)_3$ (18.7 mg, 0.04 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol) and fluorobenzene (2.0 mL) were added under argon atmosphere at 100 °C for 24 h. After the completion of the

reaction detected by thin layer chromatography (TLC), the mixture was cooled to room temperature and purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 40:1 ~ 5:1) to afford the desired product **4a** as a yellow solid (48.5 mg, 91% yield).

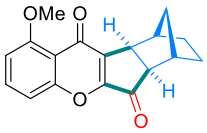
6. Characterization data of compounds 4a-4ad

Scheme 2, 4a



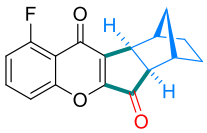
Compound **4a**: yellow solid, 48.5 mg, 91% yield, mp 116.7 – 118.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, J = 8.0, 1.6 Hz, 1H), 7.62 (ddd, J = 8.8, 7.2, 1.6 Hz, 1H), 7.44 (d, J = 8.2 Hz, 1H), 7.32 (td, J = 7.4, 0.4 Hz, 1H), 2.99 (d, J = 5.4 Hz, 1H), 2.53 (d, J = 4.0 Hz, 1H), 2.43 (d, J = 4.0 Hz, 1H), 2.36 (d, J = 5.2 Hz, 1H), 1.64 (tt, J = 11.6, 4.2 Hz, 1H), 1.53 (tt, J = 12.0, 4.0 Hz, 1H), 1.42 – 1.34 (m, 1H), 1.29 – 1.22 (m, 1H), 0.95 (d, J = 11.0 Hz, 1H), 0.87 (d, J = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 177.6, 159.3, 155.8, 141.1, 134.8, 125.8, 125.6, 124.8, 119.0, 53.0, 42.0, 39.7, 37.2, 31.9, 28.8, 28.4; HRMS (ESI-TOF): calcd. for $C_{17}H_{15}O_3$ $[M + H]^+$ 267.1016; found 267.1012.

Scheme 2, 4b



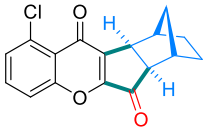
Compound **4b**: yellow solid, 30.3 mg, 51% yield, mp 163.8 – 165.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (t, J = 8.4 Hz, 1H), 7.13 (d, J = 8.4 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 3.98 (s, 3H), 3.06 (d, J = 5.2 Hz, 1H), 2.67 (d, J = 3.8 Hz, 1H), 2.53 (d, J = 3.4 Hz, 1H), 2.43 (d, J = 5.2 Hz, 1H), 1.73 (tt, J = 12.0, 4.2 Hz, 1H), 1.63 (tt, J = 11.8, 4.2 Hz, 1H), 1.52 – 1.43 (m, 1H), 1.39 – 1.30 (m, 1H), 1.05 (d, J = 11.0 Hz, 1H), 0.98 (d, J = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 177.7, 160.4, 158.3, 157.9, 142.9, 135.2, 115.9, 111.0, 107.0, 56.6, 53.4, 42.3, 39.8, 37.3, 32.1, 29.0, 28.7; HRMS (ESI-TOF): calcd. for $C_{18}H_{17}O_4$ $[M + H]^+$ 297.1121; found 297.1122.

Scheme 2, 4c



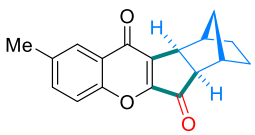
Compound **4c**: yellow solid, 35.3 mg, 62% yield, mp 168.7 – 170.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (td, J = 8.4, 5.6 Hz, 1H), 7.39 (d, J = 8.6 Hz, 1H), 7.09 (dd, J = 10.2, 8.6 Hz, 1H), 3.09 (d, J = 5.2 Hz, 1H), 2.66 (d, J = 4.0 Hz, 1H), 2.56 (d, J = 3.6 Hz, 1H), 2.46 (d, J = 5.2 Hz, 1H), 1.76 (tt, J = 11.8, 4.2 Hz, 1H), 1.65 (tt, J = 12.0, 4.2 Hz, 1H), 1.53 – 1.44 (m, 1H), 1.41 – 1.32 (m, 1H), 1.08 (d, J = 11.0 Hz, 1H), 0.98 (d, J = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 176.3, 161.1 (d, J = 266.2 Hz), 158.7, 157.2, 142.2, 135.1 (d, J = 10.9 Hz), 115.7 (d, J = 10.5 Hz), 115.1 (d, J = 4.6 Hz), 112.8 (d, J = 20.7 Hz), 53.4, 42.2, 39.9, 37.4, 32.2, 29.1, 28.7; HRMS (ESI-TOF): calcd. for $C_{17}H_{14}FO_3$ $[M + H]^+$ 285.0921; found 285.0921.

Scheme 2, 4d



Compound **4d**: yellow solid, 37.3 mg, 62% yield, mp 175.8 – 177.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (t, J = 8.2 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 7.6 Hz, 1H), 3.09 (d, J = 5.2 Hz, 1H), 2.68 (d, J = 3.6 Hz, 1H), 2.56 (d, J = 3.2 Hz, 1H), 2.46 (d, J = 5.2 Hz, 1H), 1.75 (tt, J = 12.0, 4.2 Hz, 1H), 1.65 (tt, J = 11.8, 4.2 Hz, 1H), 1.51 – 1.44 (m, 1H), 1.42 – 1.33 (m, 1H), 1.08 (d, J = 11.0 Hz, 1H), 0.99 (d, J = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3, 176.9, 158.2, 157.9, 142.3, 134.2, 134.1, 128.9, 122.2, 118.4, 53.5, 42.4, 39.9, 37.4, 32.2, 29.0, 28.7; HRMS (ESI-TOF): calcd. for $C_{17}H_{14}ClO_3$ $[M + H]^+$ 301.0626; found 301.0623.

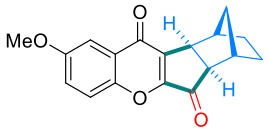
Scheme 2, 4e



Compound **4e**: yellow solid, 44.9 mg, 80% yield, mp 164.8 – 165.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.53 (dd, J = 8.6, 1.8 Hz, 1H), 7.47 (d, J = 8.6 Hz, 1H), 3.10 (d, J = 5.2 Hz, 1H), 2.65 (d, J = 3.8 Hz, 1H), 2.55 (d, J = 3.4 Hz, 1H), 2.45 (s, 4H), 1.75 (tt, J = 12.0, 4.2 Hz, 1H),

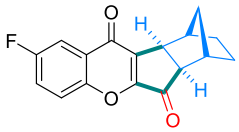
1.63 (tt, *J* = 11.8, 4.2 Hz, 1H), 1.53 – 1.45 (m, 1H), 1.42 – 1.32 (m, 1H), 1.06 (d, *J* = 11.0 Hz, 1H), 0.97 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 178.1, 159.4, 154.4, 141.3, 136.4, 136.0, 125.4, 124.8, 119.0, 53.3, 42.2, 39.9, 37.4, 32.1, 29.1, 28.7, 21.0; HRMS (ESI-TOF): calcd. for $C_{18}H_{17}O_3$ $[M + H]^+$ 281.1172; found 281.1173.

Scheme 2, 4f



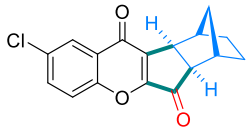
Compound **4f**: yellow solid, 42.1 mg, 71% yield, mp 181.5 – 182.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 3.0 Hz, 1H), 7.51 (d, *J* = 9.2 Hz, 1H), 7.30 (dd, *J* = 9.2, 3.0 Hz, 1H), 3.89 (s, 3H), 3.11 (d, *J* = 5.2 Hz, 1H), 2.65 (d, *J* = 3.6 Hz, 1H), 2.56 (d, *J* = 3.2 Hz, 1H), 2.46 (d, *J* = 5.2 Hz, 1H), 1.75 (tt, *J* = 12.0, 4.2 Hz, 1H), 1.64 (tt, *J* = 12.0, 4.2 Hz, 1H), 1.54 – 1.45 (m, 1H), 1.41 – 1.32 (m, 1H), 1.06 (d, *J* = 11.0 Hz, 1H), 0.97 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 177.8, 159.3, 157.5, 150.9, 140.4, 125.8, 125.2, 120.6, 105.1, 56.1, 53.3, 42.2, 40.0, 37.4, 32.1, 29.1, 28.7; HRMS (ESI-TOF): calcd. for $C_{18}H_{17}O_4$ $[M + H]^+$ 297.1121; found 297.1122.

Scheme 2, 4g



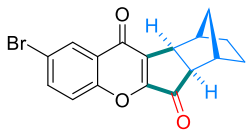
Compound **4g**: yellow solid, 39.8 mg, 70% yield, mp 160.6 – 162.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.0, 3.2 Hz, 1H), 7.61 (dd, *J* = 9.2, 4.0 Hz, 1H), 7.46 (ddd, *J* = 9.2, 7.6, 3.2 Hz, 1H), 3.12 (d, *J* = 5.4 Hz, 1H), 2.66 (d, *J* = 3.8 Hz, 1H), 2.57 (d, *J* = 3.4 Hz, 1H), 2.48 (d, *J* = 5.2 Hz, 1H), 1.75 (tt, *J* = 11.6, 3.8 Hz, 1H), 1.66 (tt, *J* = 12.0, 4.0 Hz, 1H), 1.54 – 1.46 (m, 1H), 1.42 – 1.33 (m, 1H), 1.08 (d, *J* = 11.0 Hz, 1H), 0.98 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 177.3, 159.9 (d, *J* = 248.4 Hz), 159.8, 152.3, 140.5, 126.3 (d, *J* = 7.3 Hz), 123.3 (d, *J* = 25.5 Hz), 121.4 (d, *J* = 8.1 Hz), 111.1 (d, *J* = 23.8 Hz), 53.4, 42.2, 40.0, 37.5, 32.2, 29.1, 28.7; HRMS (ESI-TOF): calcd. for $C_{17}H_{14}FO_3$ $[M + H]^+$ 285.0921; found 285.0922.

Scheme 2, 4h



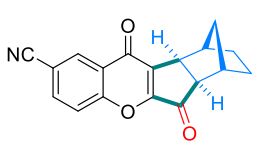
Compound **4h**: yellow solid, 45.2 mg, 75% yield, mp 196.8 – 198.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 2.4 Hz, 1H), 7.66 (dd, J = 9.0, 2.4 Hz, 1H), 7.55 (d, J = 9.0 Hz, 1H), 3.11 (d, J = 5.2 Hz, 1H), 2.65 (d, J = 3.4 Hz, 1H), 2.57 (d, J = 3.2 Hz, 1H), 2.48 (d, J = 5.2 Hz, 1H), 1.76 (tt, J = 11.6, 4.2 Hz, 1H), 1.65 (tt, J = 11.8, 4.2 Hz, 1H), 1.53 – 1.43 (m, 1H), 1.41 – 1.33 (m, 1H), 1.08 (d, J = 11.0 Hz, 1H), 0.97 (d, J = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 176.8, 159.7, 154.5, 141.2, 135.3, 132.0, 126.0, 125.6, 121.0, 53.3, 42.2, 40.0, 37.5, 32.2, 29.1, 28.7; HRMS (ESI-TOF): calcd. for $C_{17}H_{14}ClO_3$ $[M + H]^+$ 301.0626; found 301.0627.

Scheme 2, 4i



Compound **4i**: yellow solid, 39.4 mg, 57% yield, mp 185.3 – 187.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 2.4 Hz, 1H), 7.81 (dd, J = 9.0, 2.4 Hz, 1H), 7.50 (d, J = 9.0 Hz, 1H), 3.12 (d, J = 5.2 Hz, 1H), 2.66 (d, J = 3.6 Hz, 1H), 2.58 (d, J = 3.4 Hz, 1H), 2.49 (d, J = 5.2 Hz, 1H), 1.77 (tt, J = 12.0, 4.2 Hz, 1H), 1.66 (tt, J = 11.8, 4.2 Hz, 1H), 1.55 – 1.46 (m, 1H), 1.43 – 1.34 (m, 1H), 1.09 (d, J = 11.0 Hz, 1H), 0.98 (d, J = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3, 176.7, 159.7, 155.0, 141.4, 138.1, 128.8, 126.4, 121.2, 119.5, 53.4, 42.3, 40.0, 37.5, 32.2, 29.1, 28.7; HRMS (ESI-TOF): calcd. for $C_{17}H_{14}BrO_3$ $[M + H]^+$ 345.0121; found 345.0121.

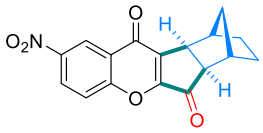
Scheme 2, 4j



Compound **4j**: yellow solid, 41.4 mg, 71% yield, mp 199.7 – 200.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 2.0 Hz, 1H), 7.97 (dd, J = 8.8, 2.0 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 3.15 (d, J = 5.4 Hz, 1H), 2.67 (d, J = 4.0 Hz, 1H), 2.61 (d, J = 3.6 Hz, 1H), 2.52 (d, J = 5.4 Hz, 1H), 1.79 (tt, J = 11.8, 4.2 Hz, 1H), 1.68 (tt, J = 12.0, 4.2 Hz, 1H), 1.56 – 1.48 (m, 1H), 1.44 – 1.36 (m, 1H),

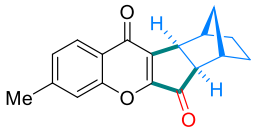
1.13 (d, *J* = 11.0 Hz, 1H), 1.00 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 176.3, 160.0, 158.0, 142.0, 137.2, 131.9, 125.5, 121.0, 117.3, 110.3, 53.4, 42.3, 40.1, 37.5, 32.3, 29.1, 28.7; HRMS (ESI-TOF): calcd. for $C_{18}H_{14}NO_3$ $[M + H]^+$ 292.0968; found 292.0967.

Scheme 2, 4k



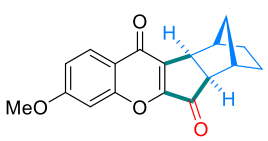
Compound **4k**: yellow solid, 54.2 mg, 87% yield, mp 214.9 – 216.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (d, *J* = 2.8 Hz, 1H), 8.57 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.77 (d, *J* = 9.2 Hz, 1H), 3.16 (d, *J* = 5.2 Hz, 1H), 2.68 (d, *J* = 3.6 Hz, 1H), 2.61 (d, *J* = 3.0 Hz, 1H), 2.53 (d, *J* = 5.2 Hz, 1H), 1.80 (tt, *J* = 12.0, 4.2 Hz, 1H), 1.68 (tt, *J* = 12.0, 4.2 Hz, 1H), 1.56 – 1.48 (m, 1H), 1.44 – 1.35 (m, 1H), 1.13 (dd, *J* = 11.0, 1.2 Hz, 1H), 1.00 (dd, *J* = 11.0, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 176.5, 160.0, 159.0, 145.2, 141.7, 129.3, 125.2, 123.0, 121.1, 53.4, 42.2, 40.1, 37.5, 32.3, 29.1, 28.6; HRMS (ESI-TOF): calcd. for $C_{17}H_{14}NO_5$ $[M + H]^+$ 312.0866; found 312.0866.

Scheme 2, 4l



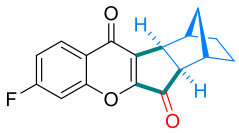
Compound **4l**: yellow solid, 39.3 mg, 70% yield, mp 141.0 – 142.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.2 Hz, 1H), 7.34 (s, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 3.08 (d, *J* = 5.2 Hz, 1H), 2.63 (d, *J* = 3.4 Hz, 1H), 2.53 (d, *J* = 3.4 Hz, 1H), 2.47 (s, 3H), 2.43 (d, *J* = 5.2 Hz, 1H), 1.73 (tt, *J* = 12.0, 4.2 Hz, 1H), 1.62 (tt, *J* = 11.8, 4.2 Hz, 1H), 1.50 – 1.43 (m, 1H), 1.38 – 1.30 (m, 1H), 1.04 (d, *J* = 11.0 Hz, 1H), 0.96 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 177.8, 159.4, 156.3, 146.8, 141.6, 127.4, 125.9, 122.9, 118.9, 53.3, 42.2, 39.9, 37.4, 32.1, 29.1, 28.7, 22.1; HRMS (ESI-TOF): calcd. for $C_{18}H_{17}O_3$ $[M + H]^+$ 281.1172; found 281.1171.

Scheme 2, 4m



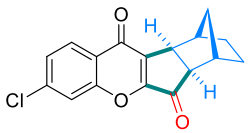
Compound **4m**: yellow solid, 42.7 mg, 72% yield, mp 179.6 – 180.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 9.0 Hz, 1H), 7.02 – 6.92 (m, 2H), 3.89 (s, 3H), 3.09 (d, J = 5.2 Hz, 1H), 2.65 (d, J = 3.8 Hz, 1H), 2.55 (d, J = 3.4 Hz, 1H), 2.45 (d, J = 5.2 Hz, 1H), 1.75 (tt, tt, J = 11.8, 4.2 Hz 1H), 1.64(tt, J = 11.8, 4.2 Hz, 1H), 1.53 – 1.45 (m, 1H), 1.40 – 1.32 (m, 1H), 1.06 (d, J = 11.0 Hz, 1H), 0.98 (d, J = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 177.1, 165.2, 159.4, 158.2, 142.0, 127.5, 119.1, 115.5, 101.0, 56.1, 53.4, 42.3, 39.9, 37.4, 32.1, 29.1, 28.7; HRMS (ESI-TOF): calcd. for $C_{18}H_{17}O_4$ $[M + H]^+$ 297.1121; found 297.1122.

Scheme 2, 4n



Compound **4n**: yellow solid, 46.1 mg, 81% yield, mp 192.6 – 194.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, J = 8.8, 6.4 Hz, 1H), 7.26 (dd, J = 8.8, 2.0 Hz, 1H), 7.18 (td, J = 8.6, 2.2 Hz, 1H), 3.11 (d, J = 5.2 Hz, 1H), 2.65 (d, J = 3.4 Hz, 1H), 2.57 (d, J = 2.8 Hz, 1H), 2.48 (d, J = 5.2 Hz, 1H), 1.76 (tt, J = 12.0, 4.4 Hz, 1H), 1.65 (tt, J = 11.8, 4.2 Hz, 1H), 1.53 – 1.46 (m, 1H), 1.41 – 1.33 (m, 1H), 1.08 (d, J = 11.0 Hz, 1H), 0.99 (d, J = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 177.0, 166.4 (d, J = 257.3 Hz), 159.9, 157.4 (d, J = 13.4 Hz), 141.8, 128.8 (d, J = 10.8 Hz), 122.0 (d, J = 2.3 Hz), 114.8 (d, J = 22.9 Hz), 105.9 (d, J = 25.6 Hz); 53.4, 42.2, 40.0, 37.5, 32.1, 29.1, 28.7; HRMS (ESI-TOF): calcd. for $C_{17}H_{14}FO_3$ $[M + H]^+$ 285.0921; found 285.0924.

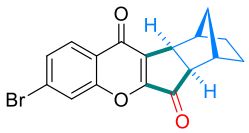
Scheme 2, 4o



Compound **4o**: yellow solid, 44.0 mg, 73% yield, mp 193.8 – 195.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.6 Hz, 1H), 7.55 (d, J = 1.6 Hz, 1H), 7.38 (dd, J = 8.6, 1.6 Hz, 1H), 3.08 (d, J = 5.2 Hz, 1H), 2.62 (d, J = 3.6 Hz, 1H), 2.54 (d, J = 3.2 Hz, 1H), 2.45 (d, J = 5.2 Hz, 1H), 1.74 (tt, J = 11.6, 4.0 Hz, 1H), 1.63 (tt, J = 11.8, 4.2 Hz, 1H), 1.51 – 1.43 (m, 1H), 1.38 – 1.31 (m, 1H), 1.06 (d, J = 11.0 Hz, 1H), 0.96 (d, J = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 177.1, 159.6, 156.2, 141.7, 141.1, 127.5, 126.7, 123.6, 119.1, 53.3, 42.2, 40.0, 37.4, 32.1, 29.0, 28.6;

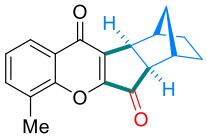
HRMS (ESI-TOF): calcd. for $C_{17}H_{14}ClO_3$ $[M + H]^+$ 301.0626; found 301.0626.

Scheme 2, 4p



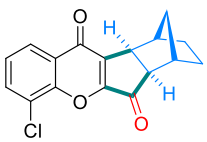
Compound **4p**: yellow solid, 37.3 mg, 54% yield, mp 196.5 – 197.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.6 Hz, 1H), 7.79 (d, J = 1.4 Hz, 1H), 7.57 (dd, J = 8.6, 1.4 Hz, 1H), 3.12 (d, J = 5.4 Hz, 1H), 2.66 (d, J = 3.6 Hz, 1H), 2.58 (d, J = 3.4 Hz, 1H), 2.48 (d, J = 5.4 Hz, 1H), 1.77 (tt, J = 12.0, 4.2 Hz, 1H), 1.66 (tt, J = 12.0, 4.0 Hz, 1H), 1.54 – 1.47 (m, 1H), 1.42 – 1.35 (m, 1H), 1.09 (d, J = 11.0 Hz, 1H), 0.99 (d, J = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 177.3, 159.6, 156.2, 141.8, 129.7, 129.5, 127.6, 124.0, 122.3, 53.4, 42.3, 40.0, 37.5, 32.2, 29.2, 28.7; HRMS (ESI-TOF): calcd. for $C_{17}H_{14}BrO_3$ $[M + H]^+$ 345.0121; found 345.0121.

Scheme 2, 4q



Compound **4q**: yellow solid, 39.9 mg, 71% yield, mp 141.8 – 143.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, J = 8.0, 1.0 Hz, 1H), 7.57 (d, J = 6.8 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 3.12 (d, J = 5.2 Hz, 1H), 2.67 (d, J = 4.0 Hz, 1H), 2.57 (d, J = 3.8 Hz, 1H), 2.54 (s, 3H), 2.47 (d, J = 5.2 Hz, 1H), 1.76 (tt, J = 12.0, 4.2 Hz, 1H), 1.66 (tt, J = 12.0, 4.0 Hz, 1H), 1.57 – 1.46 (m, 1H), 1.43 – 1.33 (m, 1H), 1.07 (d, J = 11.0 Hz, 1H), 1.00 (d, J = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 178.4, 159.5, 154.6, 141.2, 136.1, 129.0, 125.4, 125.1, 123.8, 53.3, 42.2, 40.0, 37.5, 32.1, 29.1, 28.7, 15.9; HRMS (ESI-TOF): calcd. for $C_{18}H_{17}O_3$ $[M + H]^+$ 281.1172; found 281.1171.

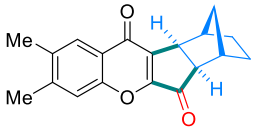
Scheme 2, 4r



Compound **4r**: yellow solid, 49.4 mg, 82% yield, mp 148.5 – 150.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, J = 8.0, 1.2 Hz, 1H), 7.75 (dd, J = 7.8, 1.2 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H),

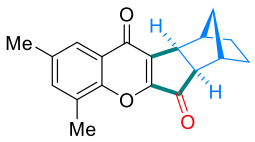
3.09 (d, *J* = 5.2 Hz, 1H), 2.62 (d, *J* = 3.6 Hz, 1H), 2.55 (d, *J* = 3.2 Hz, 1H), 2.47 (d, *J* = 5.2 Hz, 1H), 1.74 (tt, *J* = 12.0, 4.2 Hz, 1H), 1.63 (tt, *J* = 11.8, 4.2 Hz, 1H), 1.51– 1.43 (m, 1H), 1.39 – 1.32 (m, 1H), 1.06 (d, *J* = 11.0 Hz, 1H), 0.97 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR (100 MHz,$CDCl_3$) δ 201.5, 177.3, 159.5, 151.8, 141.2, 135.3, 126.3, 125.8, 124.7, 124.4, 53.2, 42.1, 40.0, 37.4, 32.1, 29.0, 28.6; HRMS (ESI-TOF): calcd. for $C_{17}H_{14}ClO_3$ $[M + H]^+$ 301.0626; found 301.0626.

Scheme 2, 4S



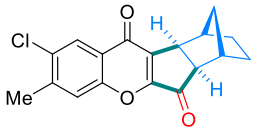
Compound **4s**: yellow solid, 38.9 mg, 66% yield, mp 178.6 – 179.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.33 (s, 1H), 3.10 (d, *J* = 5.2 Hz, 1H), 2.65 (d, *J* = 3.6 Hz, 1H), 2.55 (d, *J* = 3.2 Hz, 1H), 2.44 (d, *J* = 5.2 Hz, 1H), 2.38 (s, 3H), 2.35 (s, 3H), 1.75 (tt, *J* = 12.0, 4.2 Hz, 1H), 1.64 (tt, *J* = 11.8, 4.2 Hz, 1H), 1.53 – 1.44 (m, 1H), 1.40 – 1.32 (m, 1H), 1.05 (d, *J* = 11.0 Hz, 1H), 0.97 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.8, 177.9, 159.3, 154.7, 145.9, 141.4, 135.4, 125.7, 123.0, 119.2, 53.3, 42.3, 39.9, 37.4, 32.1, 29.1, 28.7, 20.7, 19.5; HRMS (ESI-TOF): calcd. for $C_{19}H_{19}O_3$ $[M + H]^+$ 295.1329; found 295.1328.

Scheme 2, 4t



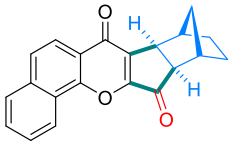
Compound **4t**: yellow solid, 41.2 mg, 70% yield, mp 166.3 – 167.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.39 (s, 1H), 3.11 (d, *J* = 5.2 Hz, 1H), 2.66 (d, *J* = 3.8 Hz, 1H), 2.56 (d, *J* = 3.2 Hz, 1H), 2.49 (s, 3H), 2.46 (d, *J* = 5.2 Hz, 1H), 2.41 (s, 3H), 1.75 (tt, *J* = 12.0, 4.2 Hz, 1H), 1.65 (tt, *J* = 11.8, 4.2 Hz, 1H), 1.53 – 1.46 (m, 1H), 1.40 – 1.33 (dd, *J* = m, 1H), 1.06 (d, *J* = 11.0 Hz, 1H), 0.98 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 178.4, 159.3, 152.9, 141.0, 137.4, 135.4, 128.6, 124.8, 123.0, 53.3, 42.2, 40.0, 37.5, 32.1, 29.1, 28.7, 21.0, 15.8; HRMS (ESI-TOF): calcd. for $C_{19}H_{19}O_3$ $[M + H]^+$ 295.1329; found 295.1328.

Scheme 2, 4u



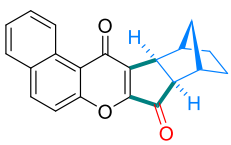
Compound **4u**: yellow solid, 41.0 mg, 65% yield, mp 180.2 – 181.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.46 (s, 1H), 3.10 (d, J = 5.2 Hz, 1H), 2.65 (d, J = 3.4 Hz, 1H), 2.55 (d, J = 2.8 Hz, 1H), 2.53 – 2.44 (m, 4H), 1.83 – 1.60 (m, 2H), 1.54 – 1.45 (m, 1H), 1.42 – 1.33 (m, 1H), 1.08 (d, J = 10.8 Hz, 1H), 0.97 (d, J = 10.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3, 176.8, 159.6, 154.4, 144.7, 141.3, 132.8, 125.8, 124.2, 120.9, 53.3, 42.2, 40.0, 37.5, 32.2, 29.1, 28.7, 21.1; HRMS (ESI-TOF): calcd. for $C_{18}H_{16}ClO_3$ $[M + H]^+$ 315.0782; found 315.0780.

Scheme 2, 4v



Compound **4v**: yellow solid, 35.5 mg, 56% yield, mp 165.9 – 167.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 8.2 Hz, 1H), 8.15 (d, J = 8.8 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.75 – 7.65 (m, 2H), 3.18 (d, J = 5.2 Hz, 1H), 2.73 (d, J = 3.2 Hz, 1H), 2.62 (d, J = 2.8 Hz, 1H), 2.53 (d, J = 5.2 Hz, 1H), 1.79 (tt, J = 12.0, 4.2 Hz, 1H), 1.68 (tt, J = 12.0, 4.2 Hz, 1H), 1.58 – 1.50 (m, 1H), 1.47 – 1.36 (m, 1H), 1.10 (d, J = 11.0 Hz, 1H), 1.04 (d, J = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 177.7, 159.1, 153.8, 142.9, 136.5, 130.1, 128.2, 127.6, 126.2, 124.4, 123.1, 121.7, 120.7, 53.5, 42.4, 40.0, 37.5, 32.2, 29.2, 28.8; HRMS (ESI-TOF): calcd. for $C_{21}H_{17}O_3$ $[M + H]^+$ 317.1172; found 317.1171.

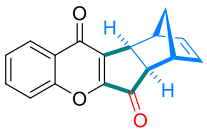
Scheme 2, 4w



Compound **4w**: yellow solid, 31.7 mg, 50% yield, mp 202.4 – 203.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (d, J = 8.6 Hz, 1H), 8.14 (d, J = 9.2 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.81 (td, J = 7.8, 1.2 Hz, 1H), 7.68 – 7.60 (m, 2H), 3.19 (d, J = 5.2 Hz, 1H), 2.76 (d, J = 3.8 Hz, 1H), 2.60 (d, J = 3.6 Hz, 1H), 2.51 (d, J = 5.2 Hz, 1H), 1.80 (tt, J = 11.8, 4.2 Hz, 1H), 1.68 (tt, J = 11.8, 4.2 Hz,

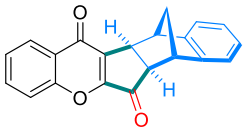
1H), 1.61 – 1.50 (m, 1H), 1.47 – 1.36 (m, 1H), 1.10 (d, *J* = 11.0 Hz, 1H), 1.03 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3, 179.7, 157.8, 157.6, 144.2, 137.1, 130.9, 130.6, 129.9, 128.6, 127.3, 126.9, 118.8, 118.2, 53.7, 42.6, 39.9, 37.5, 32.3, 29.2, 28.8; HRMS (ESI-TOF): calcd. for $C_{21}H_{17}O_3$ $[M + H]^+$ 317.1172; found 317.1168.

Figure 1, 4x



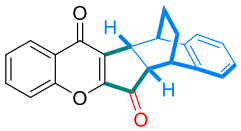
Compound **4x**: yellow solid, 35.4 mg, 67% yield, mp 118.9 – 120.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.75 (td, *J* = 7.8, 1.6 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 6.46 (dd, *J* = 5.4, 3.0 Hz, 1H), 6.27 (dd, *J* = 5.4, 3.0 Hz, 1H), 3.21 (d, *J* = 5.2 Hz, 1H), 3.18 (s, 1H), 3.11 (s, 1H), 1.48 (d, *J* = 9.8 Hz, 1H), 1.17 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.6, 177.8, 159.6, 156.2, 142.0, 139.6, 136.6, 135.2, 126.2, 126.0, 125.2, 119.3, 51.7, 44.5, 42.3, 42.0, 41.0; HRMS (ESI-TOF): calcd. for $C_{17}H_{13}O_3$ $[M + H]^+$ 265.0859; found 265.0854.

Figure 1, 4y



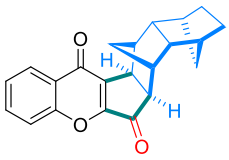
Compound **4y**: yellow solid, 28.3 mg, 45% yield, mp 191.4 – 193.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.78 (td, *J* = 7.8, 1.6 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.50 (td, *J* = 7.6, 0.8 Hz, 1H), 7.41 (dd, *J* = 5.6, 2.4 Hz, 1H), 7.28 (dd, *J* = 5.6, 2.6 Hz, 1H), 7.19 – 7.11 (m, 2H), 3.72 (s, 1H), 3.62 (s, 1H), 3.31 (d, *J* = 5.2 Hz, 1H), 2.67 (d, *J* = 5.2 Hz, 1H), 1.80 (d, *J* = 10.2 Hz, 1H), 1.52 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 177.8, 159.9, 156.2, 147.9, 146.1, 141.4, 135.3, 126.7, 126.6, 126.3, 126.2, 125.2, 122.2, 121.5, 119.4, 52.8, 46.0, 44.1, 42.6, 42.3; HRMS (ESI-TOF): calcd. for $C_{21}H_{15}O_3$ $[M + H]^+$ 315.1016; found 215.1013.

Figure 1, 4z



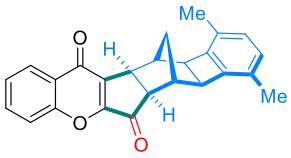
Compound **4z**: yellow solid, 39.4 mg, 60% yield, mp 189.3 – 190.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, J = 8.0, 1.6 Hz, 1H), 7.65 (ddd, J = 8.6, 7.2, 1.6 Hz, 1H), 7.48 – 7.34 (m, 2H), 7.09 – 7.03 (m, 2H), 7.02 – 6.94 (m, 1H), 6.91 (d, J = 7.2 Hz, 1H), 3.90 (q, 1H), 3.66 (dd, J = 6.4, 2.8 Hz, 1H), 3.60 (q, 1H), 2.94 (dd, J = 6.4, 3.2 Hz, 1H), 2.13 – 2.03 (m, 1H), 2.02 – 1.92 (m, 1H), 1.67 (tt, J = 12.0, 3.4 Hz, 1H), 1.56 (m, J = 12.0, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9, 177.8, 158.4, 155.8, 141.9, 139.2, 138.1, 135.0, 127.3, 127.1, 126.1, 125.8, 125.1, 124.8, 124.7, 119.2, 49.2, 38.9, 38.5, 36.7, 25.7, 25.2; HRMS (ESI-TOF): calcd. for $C_{22}H_{17}O_3$ $[M + H]^+$ 329.1172; found 329.1169.

Figure 1, 4aa



Compound **4aa**: yellow solid, 40.6 mg, 61% yield, mp 233.7 – 235.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, J = 8.0, 1.6 Hz, 1H), 7.73 (td, J = 7.8, 1.6 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.44 (td, J = 7.2, 0.8 Hz, 1H), 3.48 (d, J = 5.0 Hz, 1H), 2.78 (d, J = 5.0 Hz, 1H), 2.71 (d, J = 4.6 Hz, 1H), 2.58 (d, J = 4.4 Hz, 1H), 2.43 (s, 1H), 2.26 (s, 1H), 1.87 (ddd, J = 47.8, 9.6, 4.8 Hz, 2H), 1.61 – 1.50 (m, 3H), 1.11 – 0.98 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.8, 177.8, 159.3, 156.1, 141.5, 135.1, 126.2, 125.9, 125.1, 119.3, 50.0, 49.7, 49.4, 44.4, 41.8, 37.8, 36.3, 36.2, 35.5, 35.2, 31.1, 31.1; HRMS (ESI-TOF): calcd. for $C_{17}H_{13}O_3$ $[M + H]^+$ 265.0859; found 265.0854.

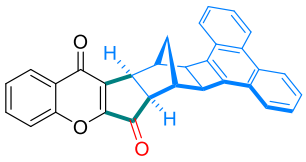
Figure 1, 4ab



Compound **4ab**: yellow solid, 60.5 mg, 82% yield, mp 184.9 – 186.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, J = 8.0, 1.6 Hz, 1H), 7.76 (td, J = 11.8, 1.6 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 6.90 (s, 2H), 3.51 (d, J = 3.6 Hz, 1H), 3.35 (d, J = 3.6 Hz, 1H), 3.21 (d, J

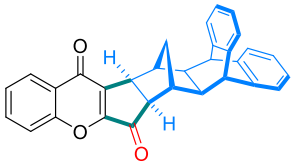
= 5.2 Hz, 1H), 2.76 (s, 1H), 2.68 (s, 1H), 2.55 (d, *J* = 5.2 Hz, 1H), 2.16 (s, 3H), 2.14 (s, 3H), 0.82 (q, *J* = 11.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 178.0, 159.1, 156.1, 143.1, 142.3, 141.2, 135.2, 129.7, 129.6, 129.2, 129.0, 126.2, 126.0, 125.1, 119.3, 52.1, 49.1, 48.0, 41.1, 39.0, 37.1, 26.5, 16.4, 16.2; HRMS (ESI-TOF): calcd. for $C_{25}H_{21}O_3$ $[M + H]^+$ 369.1485; found 369.1480.

Figure 1, 4ac



Compound **4ac**: yellow solid, 80.2 mg, 91% yield, mp 161.3 – 163.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.66 (m 2H), 8.29 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.90 – 7.82 (m, 1H), 7.81 – 7.72 (m, 2H), 7.66 – 7.55 (m, 5H), 7.48 (td, *J* = 7.6, 1.0 Hz, 1H), 3.87 (d, *J* = 3.2 Hz, 1H), 3.71 (d, *J* = 3.2 Hz, 1H), 3.33 (d, *J* = 5.2 Hz, 1H), 2.94 (s, 1H), 2.86 (s, 1H), 2.67 (d, *J* = 5.2 Hz, 1H), 0.84 (q, *J* = 12.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 178.0, 159.1, 156.2, 141.2, 139.6, 138.7, 135.2, 132.7, 132.6, 131.2, 131.1, 128.0, 127.0, 126.3, 126.23, 126.21, 126.0, 125.1, 124.0, 123.9, 123.2, 122.8, 119.3, 52.4, 49.3, 48.2, 41.5, 38.5, 36.6, 26.4; HRMS (ESI-TOF): calcd. for $C_{31}H_{21}O_3$ $[M + H]^+$ 441.1485; found 441.1480.

Figure 1, 4ad

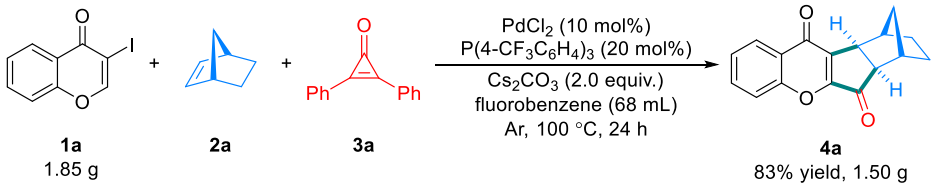


Compound **4ad**: yellow solid, 79.7 mg, 90% yield, mp 245.7 – 247.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.0 Hz, 1H), 7.71 (td, *J* = 10.2, 1.2 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.21 – 7.00 (m, 6H), 4.41 (d, *J* = 2.4 Hz, 1H), 4.32 (d, *J* = 2.4 Hz, 1H), 3.02 (d, *J* = 5.0 Hz, 1H), 2.49 (s, 1H), 2.40 (s, 1H), 2.33 (d, *J* = 4.8 Hz, 1H), 2.26 (dd, *J* = 8.4, 2.2 Hz, 1H), 2.07 (dd, *J* = 8.4, 2.2 Hz, 1H), 0.15 (d, *J* = 12.2 Hz, 1H), -0.50 (d, *J* = 12.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 177.9, 159.8, 156.0, 144.4, 144.2, 142.0, 141.6, 140.3, 135.2, 126.4, 126.1, 126.0, 125.9, 125.0, 124.5, 123.6, 123.5, 119.2, 54.4, 49.9, 48.6, 48.2, 48.1, 43.4, 42.8, 40.6, 27.1; HRMS (ESI-TOF): calcd. for $C_{31}H_{21}O_3$ $[M + H]^+$ 443.1642; found

443.1637.

7. Preparative-scale experiments

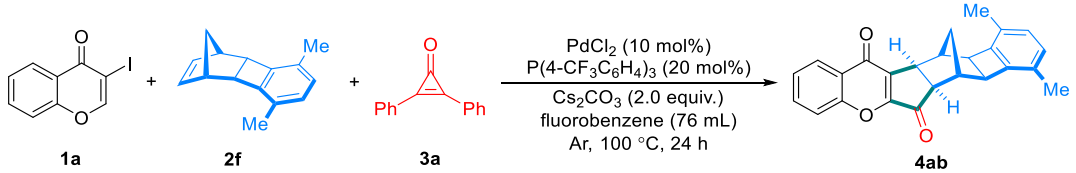
7.1 Synthesis of **4a** on a gram-scale (**Scheme 3a**)



1a 1.85 g | **2a** | **3a** | **4a** 83% yield, 1.50 g

To a 350 mL flame-dried pressure tube with a stir bar, **1a** (1.85 g, 6.8 mmol), **2a** (2.56 g, 27.2 mmol), **3a** (1.40 g, 6.8 mmol), $PdCl_2$ (120.6 mg, 0.7 mmol), $P(4\text{-}CF_3C_6H_4)_3$ (629.5 mg, 1.4 mmol), Cs_2CO_3 (4.43 g, 13.6 mmol), and fluorobenzene (68 mL) were added. Then, the reaction tube was evacuated and backfilled with argon three times, and the mixture was stirred at 100 ℃ for 24 h. After completed of the reaction, it was concentrated to remove solvent and purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 40:1 ~ 5:1) to afford the desired product **4a** (1.50 g, 83% yield).

7.2 Synthesis of **4ab** on a gram-scale (**Scheme 3b**)

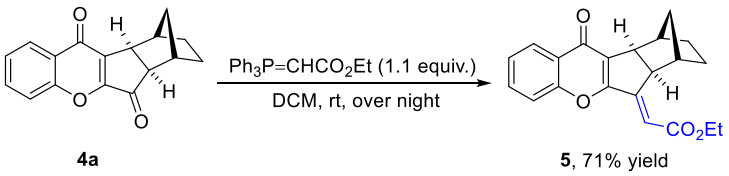


1a 2.07 g | **2f** | **3a** | **4ab** 81% yield, 2.28 g

To a 350 mL flame-dried pressure tube with a stir bar, **1a** (2.07 g, 7.6 mmol), **2f** (2.98 g, 15.2 mmol), **3a** (1.57 g, 7.6 mmol), $PdCl_2$ (134.8 mg, 0.8 mmol), $P(4\text{-}CF_3C_6H_4)_3$ (708.7 mg, 1.5 mmol), Cs_2CO_3 (4.95 g, 15.2 mmol), fluorobenzene (76 mL) were added. Then, the reaction tube was evacuated and backfilled with argon three times, and the mixture was stirred at 100 ℃ for 24 h. After completed of the reaction, it was concentrated to remove solvent and purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 40:1 ~ 5:1) to afford the desired product **4ab** (2.28 g, 81% yield).

8. Transformation of 4a into 5, 6, 7

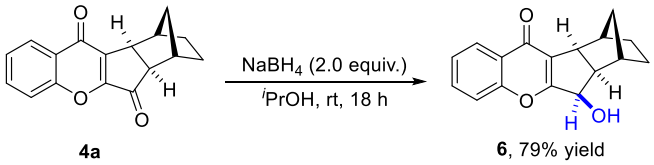
8.1 Synthesis of **5** from **4a** (**Scheme 4**)



4a **5**, 71% yield

To a 4 mL dried vial with a stir bar, **4a** (53.3 mg, 0.2 mmol), $Ph_3P{=}CHCO_2Et$ (76.6 mg, 0.22 mmol) and dichloromethane (2.0 mL) were added at room temperature overnight. After the completion of the reaction, it was concentrated by vacuum and purified by flash column chromatography to afford the desired product **5** (47.8 mg, 71% yield).[5] Yellow solid, mp 135.2 – 137.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, J = 8.0, 1.6 Hz, 1H), 7.67 (td, J = 7.0, 1.6 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 6.43 (d, J = 2.4 Hz, 1H), 4.36 – 4.19 (m, 2H), 3.35 – 3.30 (m, 1H), 3.14 (d, J = 5.4 Hz, 1H), 2.61 (d, J = 3.6 Hz, 1H), 2.49 (d, J = 3.6 Hz, 1H), 1.74 – 1.65 (m, 1H), 1.65 – 1.55 (m, 1H), 1.53 – 1.43 (m, 2H), 1.35 (t, J = 7.2 Hz, 3H), 1.06 (d, J = 10.6 Hz, 1H), 1.00 (d, J = 10.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 165.9, 163.2, 157.4, 156.4, 134.0, 130.8, 126.1, 125.4, 124.9, 118.4, 114.1, 60.6, 48.5, 47.9, 42.1, 38.5, 32.1, 29.3, 28.8, 14.4; HRMS (ESI-TOF): calcd. for $C_{21}H_{21}O_4$ $[M + H]^+$ 337.1434; found 337.1431.

8.2 Synthesis of **6** from **4a** (**Scheme 4**)

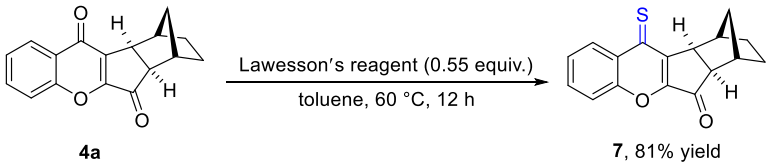


4a **6**, 79% yield

To a 4 mL dried vial with a stir bar, **4a** (53.3 mg, 0.2 mmol), sodium borohydride (15.1 mg, 0.4 mmol), and ^{i}PrOH (2.0 mL) were added at room temperature for 18 h. Detected by thin layer chromatography (TLC) until the reaction was completed. Then, it was concentrated to remove solvent and purified by flash column chromatography to afford the desired product **6** (42.4 mg, 79% yield).[6] Yellow solid, mp 104.1 – 105.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 7.8 Hz, 1H), 7.64 (t, J = 7.8 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.39 (t, J = 7.4 Hz, 1H), 5.27 (dd, J = 9.2, 5.6 Hz, 1H), 3.08 (d, J = 7.0 Hz, 1H), 2.59 (s, 1H), 2.50 (s, 2H), 2.41 (t, J = 8.2 Hz, 1H), 1.68 – 1.55 (m, 2H), 1.39 (t, J = 8.6 Hz, 1H), 1.29 (d, J = 10.6 Hz, 1H), 1.23 (d, J = 9.0 Hz, 1H), 1.12 (d, J = 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 167.3, 157.2, 133.5, 126.0, 125.2,

124.6, 122.3, 118.4, 74.6, 48.5, 45.6, 37.8, 35.4, 34.0, 28.7, 28.5; HRMS (ESI-TOF): calcd. for $C_{17}H_{17}O_3$ $[M + H]^+$ 269.1172; found 269.1180.

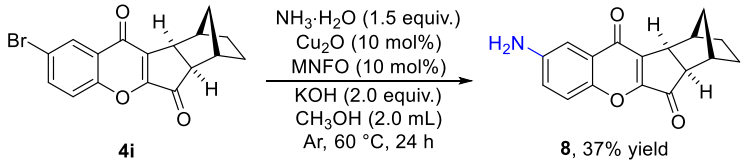
8.3 Synthesis of **7** from **4a** (**Scheme 4**)



To a 4 mL dried vial with a stir bar, **4a** (53.3 mg, 0.2 mmol), Lawesson's reagent (45.2 mg, 0.1 mmol), and toluene (2.0 mL) were added at 60 ℃ for 12 h. After the completion of the reaction, it was concentrated to remove solvent and purified by flash column chromatography to afford the desired product **7** (45.8 mg, 81% yield).[7] Green solid, mp 145.7 – 147.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 8.2 Hz, 1H), 7.75 (td, J = 7.8, 1.0 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 3.22 (d, J = 5.6 Hz, 1H), 2.80 (d, J = 3.6 Hz, 1H), 2.61 (d, J = 3.2 Hz, 1H), 2.47 (d, J = 5.6 Hz, 1H), 1.80 – 1.60 (m, 2H), 1.55 – 1.44 (m, 1H), 1.45 – 1.36 (m, 1H), 1.07 (d, J = 11.0 Hz, 1H), 0.96 (d, J = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6, 203.3, 150.8, 149.5, 148.6, 135.1, 132.3, 128.1, 126.9, 119.7, 53.8, 44.9, 40.0, 37.2, 32.7, 29.1, 28.8; HRMS (ESI-TOF): calcd. for $C_{17}H_{15}SO_2$ $[M + H]^+$ 283.0787; found 283.0794.

9. Transformation of 4i into 8, 9, 10

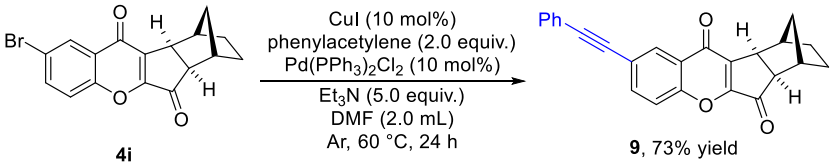
9.1 Synthesis of **8** from **4i** (**Scheme 4**)



To a 4 mL flame-dried vial with a stir bar, **4i** (69.0 mg, 0.2 mmol), MNFO (6.0 mg, 0.02 mmol), Cu_2O (3.0 mg, 0.02mmol), potassium hydroxide (22.4 mg, 0.4 mmol), ammonia (100 μL, 0.3 mmol) and methanol (2.0 mL) were added under argon atmosphere at 60 ℃ for 24 h. After the completion of the reaction, it was concentrated and purified by flash column chromatography to afford the desired product **8** (20.9 mg, 37% yield).[8] Yellow solid, mp 159.3 – 160.6 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.45 (d, J = 8.6 Hz, 1H), 7.19 – 7.02 (m, 2H), 5.70 (s, 2H), 2.93 (d, J =

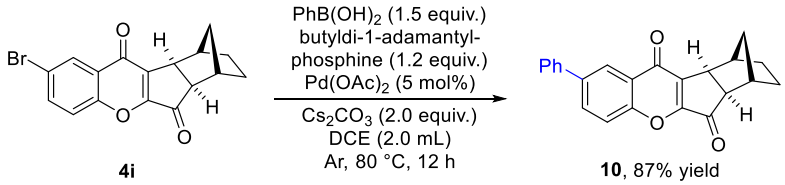
5.2 Hz, 1H), 2.44 (t, *J* = 5.8 Hz, 2H), 2.33 (d, *J* = 3.0 Hz, 1H), 1.69 – 1.60 (m, 1H), 1.58 – 1.49 (m, 1H), 1.42 – 1.28 (m, 2H), 1.00 – 0.86 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 202.1, 177.1, 158.5, 147.6, 147.3, 138.9, 125.4, 123.0, 119.8, 104.7, 79.3, 52.4, 31.7, 28.5, 28.0; HRMS (ESI-TOF): calcd. for $C_{17}H_{16}NO_3$ $[M + H]^+$ 282.1125; found 282.1134.

9.2 Synthesis of **9** from **4i** (**Scheme 4**)



To a 4 mL flame-dried vial with a stir bar, **4i** (69.0 mg, 0.2 mmol), phenylacetylene (40.8 mg, 0.4 mmol), $Pd(PPh_3)_2Cl_2$ (14.0 mg, 0.02 mmol), CuI (4.0 mg, 0.02 mmol), triethylamine (101.2 mg, 1 mmol), and DMF (2.0 mL) were added under argon atmosphere at 60 ℃ for 24 h. After the completion of the reaction, it was diluted with water, extracted with dichloromethane (15 mL × 3). The combined organic phase was concentrated and purified by flash column chromatography to afford the desired product **9** (53.5 mg, 73% yield).[9] Yellow solid, mp 204.3 – 205.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 2.0 Hz, 1H), 7.84 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.41 – 7.33 (m, 3H), 3.14 (d, *J* = 5.2 Hz, 1H), 2.69 (d, *J* = 4.0 Hz, 1H), 2.59 (d, *J* = 3.6 Hz, 1H), 2.49 (d, *J* = 5.2 Hz, 1H), 1.78 (tt, *J* = 11.6, 4.0 Hz, 1H), 1.67 (tt, *J* = 12.0, 4.2 Hz, 1H), 1.56 – 1.46 (m, 1H), 1.43 – 1.34 (m, 1H), 1.10 (d, *J* = 11.0 Hz, 1H), 1.01 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 177.2, 159.6, 155.5, 141.5, 137.7, 131.8, 129.3, 128.9, 128.6, 125.1, 122.6, 121.6, 119.6, 91.2, 87.5, 53.3, 42.3, 40.0, 37.5, 32.2, 29.1, 28.7; HRMS (ESI-TOF): calcd. for $C_{25}H_{19}O_3$ $[M + H]^+$ 367.1329; found 367.1325.

9.3 Synthesis of **10** from **4i** (**Scheme 4**)

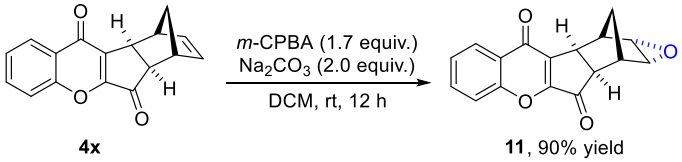


To a 4 mL flame-dried vial with a stir bar, **4i** (69.0 mg, 0.2 mmol), phenylboronic acid (36.6 mg, 0.3 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), Cs_2CO_3 (65.2 mg, 0.4 mmol),

butyldi-1-adamantylphosphine (4.4 mg, 0.24 mmol), and DCE (2.0 mL) were added under argon atmosphere at 80 ℃ for 12 h. After the completion of the reaction, it was concentrated and purified by flash column chromatography to afford the desired product **10** (59.6 mg, 87% yield).[10] Yellow solid, mp 163.7 – 165.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 2.4 Hz, 1H), 7.98 (dd, J = 8.8, 2.4 Hz, 1H), 7.70 – 7.63 (m, 3H), 7.48 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.2 Hz, 1H), 3.16 (d, J = 5.2 Hz, 1H), 2.70 (d, J = 3.8 Hz, 1H), 2.60 (d, J = 3.6 Hz, 1H), 2.50 (d, J = 5.2 Hz, 1H), 1.79 (tt, J = 11.6, 4.2 Hz, 1H), 1.68 (tt, J = 11.8, 4.4 Hz, 1H), 1.57 – 1.49 (m, 1H), 1.45 – 1.34 (m, 1H), 1.10 (d, J = 11.0 Hz, 1H), 1.02 (d, J = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 178.1, 159.6, 155.5, 141.5, 139.1, 139.0, 134.0, 129.2, 128.2, 127.3, 125.3, 124.0, 119.8, 53.4, 42.3, 40.0, 37.5, 32.2, 29.1, 28.7; HRMS (ESI-TOF): calcd. for $C_{23}H_{19}O_3$ $[M + H]^+$ 343.1329; found 343.1336.

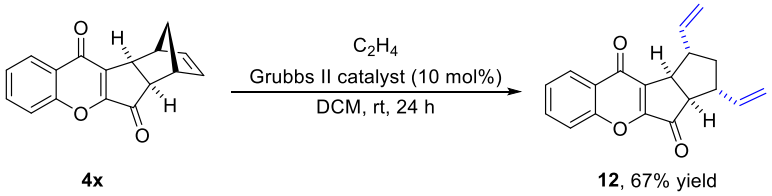
10. Transformation of 4x into 11, 12 (Scheme 4)

10.1 Synthesis of **11** from **4x** (**Scheme 4**)



To a 4 mL flame-dried vial with a stir bar, **4x** (53.3 mg, 0.2 mmol), *m*-chloroperoxybenzoic acid (58.6 mg, 0.34 mmol), sodium carbonate (42.4 mg, 0.40 mmol) and dichloromethane (2.0 mL) were added at room temperature for 12 h. After the completion of the reaction, it was quenched with saturated sodium thiosulfate. the mixture was extracted with dichloromethane (15 mL × 3). The combined organic phase was dried with anhydrous sodium sulfate, concentrated by vacuum and purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 ~ 5:1) to afford the desired product **11** (50.5 mg, 90% yield).[11] Yellow solid, mp 146.5 – 148.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.0 Hz, 1H), 7.75 (t, J = 7.6 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 3.46 (s, 1H), 3.32 (s, 1H), 3.28 (d, J = 5.0 Hz, 1H), 2.93 (s, 1H), 2.84 (s, 1H), 2.63 (d, J = 4.8 Hz, 1H), 1.30 (d, J = 11.4 Hz, 1H), 0.60 (d, J = 11.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 177.5, 159.3, 156.0, 140.1, 135.4, 126.2, 124.9, 119.3, 52.7, 51.0, 50.0, 40.0, 39.2, 38.4, 20.3; HRMS (ESI-TOF): calcd. for $C_{17}H_{13}O_4$ $[M + H]^+$ 281.0808; found 281.0807.

10.2 Synthesis of **12** from **4x** (**Scheme 4**)



To a 100 mL dry round bottom flask with a stir bar, **4x** (53.3 mg, 0.2 mmol) and dichloromethane (40 mL) were added. Bubbling ethylene into the solution, and adding Grubbs II catalyst (17 mg, 0.02 mmol) after 10 minutes. Then, the mixture was stirred under ethylene atmosphere at room temperature for 24 h. After the completion of the reaction detected by thin layer chromatography (TLC), concentrated under vacuum to remove solvent, and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1 ~ 10:1) to afford the desired product **12** (39.2 mg, 67% yield).[12] Yellow solid, mp 91.1 – 93.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, J = 8.0, 1.6 Hz, 1H), 7.73 (td, J = 7.8, 1.4 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 6.36 (ddd, J = 17.2, 10.2, 6.2 Hz, 1H), 5.98 (ddd, J = 17.2, 10.2, 7.0 Hz, 1H), 5.26 – 5.10 (m, 4H), 3.54 (t, J = 7.6 Hz, 1H), 3.02 – 2.94 (m, 1H), 2.65 (dq, J = 15.6, 7.0 Hz, 1H), 2.52 (dq, J = 13.6, 6.6 Hz, 1H), 2.19 (dt, J = 11.8, 5.8 Hz, 1H), 1.85 (q, J = 11.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 177.8, 156.2, 155.3, 142.0, 140.2, 139.1, 135.1, 126.2, 126.0, 125.2, 119.2, 115.9, 114.4, 55.4, 48.0, 45.6, 45.5, 42.7; HRMS (ESI-TOF): calcd. for $C_{19}H_{17}O_3$ $[M + H]^+$ 293.1172; found 293.1171.

11. References

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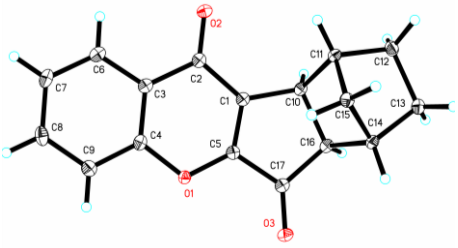
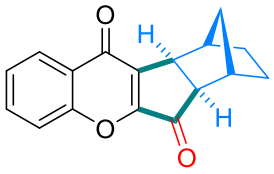
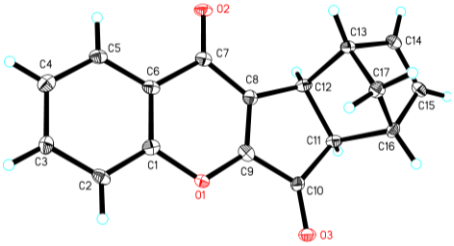
12. X-ray crystal data for 4a, 4x, 4y, 4z, 4aa, 4ab, 4ad, 5, 6 and 7

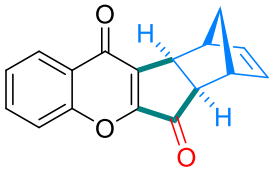




4a (CCDC: 2056365)

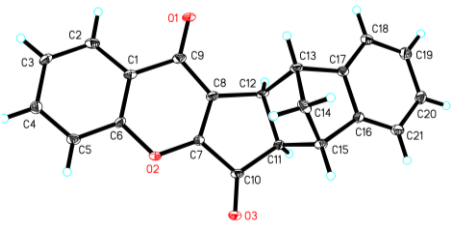
Identification code	**4a**
Empirical formula	$C_{17}H_{14}O_3$
Formula weight	266.28
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	24.0388(11)
b/Å	11.3009(4)
c/Å	36.9112(15)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	10027.3(7)
Z	32
ρ_{calc}g/cm^3	1.411
μ/mm^{-1}	0.096
F(000)	4480.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	4.044 to 49.996
Index ranges	-23 ≤ h ≤ 28, -11 ≤ k ≤ 13, -43 ≤ l ≤ 41
Reflections collected	32274
Independent reflections	8832 [R_{int} = 0.0515, R_{sigma} = 0.0469]
Data/restraints/parameters	8832/0/721
Goodness-of-fit on F^2	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0550, wR_2 = 0.1361
Final R indexes [all data]	R_1 = 0.0704, wR_2 = 0.1474
Largest diff. peak/hole / e Å^{-3}	0.58/-0.33

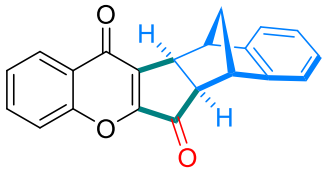




4x (CCDC: 2056366)

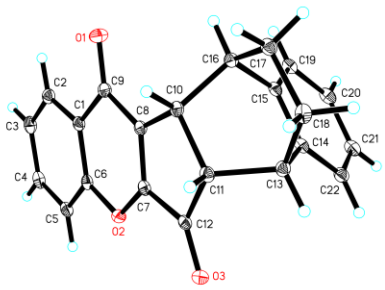
Identification code	**4x**
Empirical formula	$C_{17}H_{12}O_3$
Formula weight	264.27
Temperature/K	100.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	5.5036(10)
b/Å	8.1424(13)
c/Å	13.547(2)
α/°	84.568(13)
β/°	85.441(14)
γ/°	89.725(14)
Volume/Å^3	602.42(18)
Z	2
ρ_{calc}g/cm^3	1.457
μ/mm^{-1}	0.100
F(000)	276.0
Crystal size/mm^3	0.14 × 0.13 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	5.026 to 50.01
Index ranges	$-6 \le h \le 6$, $-9 \le k \le 9$, $-3 \le l \le 16$
Reflections collected	2104
Independent reflections	2104 [R_{int} = 0705, R_{sigma} = 0.1121]
Data/restraints/parameters	2104/0/182
Goodness-of-fit on F^2	1.101
Final R indexes [I>=2σ (I)]	R_1 = 0.1031, wR_2 = 0.2622
Final R indexes [all data]	R_1 = 0.1452, wR_2 = 0.2866
Largest diff. peak/hole / e Å^{-3}	0.47/-0.54

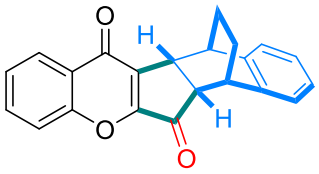




4y (CCDC: 2056367)

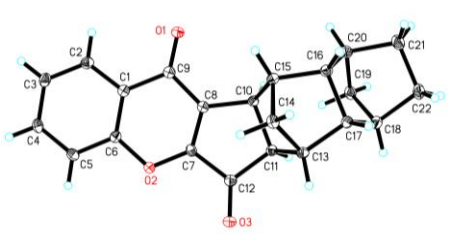
Identification code	**4y**
Empirical formula	$C_{21}H_{14}O_3$
Formula weight	314.32
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	5.8572(6)
b/Å	8.3393(9)
c/Å	14.637(2)
α/°	93.034(10)
β/°	96.799(10)
γ/°	90.121(9)
Volume/Å^3	708.92(15)
Z	2
ρ_{calc}g/cm^3	1.473
μ/mm^{-1}	0.792
F(000)	328.0
Crystal size/mm^3	0.13 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.09 to 148.886
Index ranges	$-7 \le h \le 6$, $-10 \le k \le 10$, $-17 \le l \le 17$
Reflections collected	2748
Independent reflections	2748 [R_{int} =0.0517, R_{sigma} = 0.0859]
Data/restraints/parameters	2748/0/218
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.1202, wR_2 = 0.2766
Final R indexes [all data]	R_1 = 0.1374, wR_2 = 0.2844
Largest diff. peak/hole / e Å^{-3}	0.46/-0.65

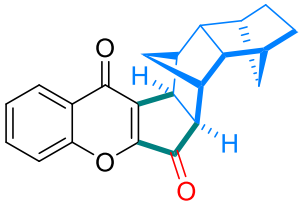




4z (CCDC: 2056368)

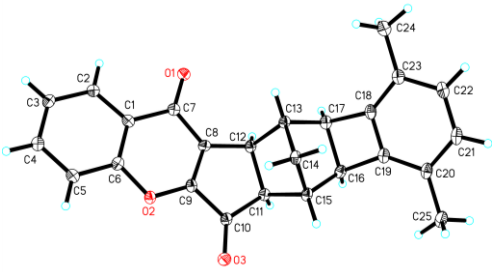
Identification code	**4z**
Empirical formula	$C_{22}H_{16}O_3$
Formula weight	328.35
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.1695(4)
b/Å	11.3093(6)
c/Å	16.4310(9)
α/°	90
β/°	92.784(5)
γ/°	90
Volume/Å^3	1516.28(14)
Z	4
ρ_{calc}g/cm^3	1.438
μ/mm^{-1}	0.765
F(000)	688.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	9.498 to 147.558
Index ranges	$-10 \le h \le 9$, $-11 \le k \le 13$, $-20 \le l \le 12$
Reflections collected	5466
Independent reflections	2957 [R_{int} = 0.0295, R_{sigma} = 0.0352]
Data/restraints/parameters	2957/0/226
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0549, wR_2 = 0.1477
Final R indexes [all data]	R_1 = 0.0595, wR_2 = 0.1532
Largest diff. peak/hole / e Å^{-3}	0.40/-0.26

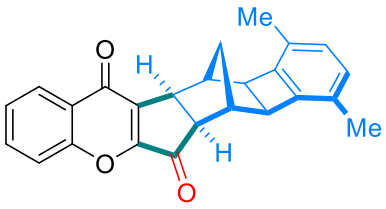




4aa (CCDC: 2056370)

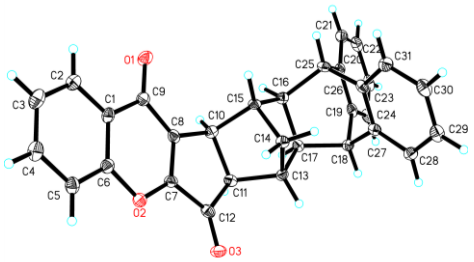
Identification code	**4aa**
Empirical formula	$C_{22}H_{20}O_3$
Formula weight	332.38
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	P2/c
a/Å	11.4543(7)
b/Å	6.0539(5)
c/Å	23.3796(14)
α/°	90
β/°	102.119(6)
γ/°	90
Volume/Å^3	1585.10(19)
Z	4
ρ_{calc}g/cm^3	1.393
μ/mm^{-1}	0.092
F(000)	704.0
Crystal size/mm^3	0.14 × 0.13 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	4.526 to 49.992
Index ranges	-12 ≤ h ≤ 13, -7 ≤ k ≤ 5, -27 ≤ l ≤ 26
Reflections collected	6346
Independent reflections	2775 [R_{int} = 0.0227, R_{sigma} = 0.0336]
Data/restraints/parameters	2775/0/226
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0412, wR_2 = 0.0899
Final R indexes [all data]	R_1 = 0.0491, wR_2 = 0.0951
Largest diff. peak/hole / e Å^{-3}	0.23/-0.23

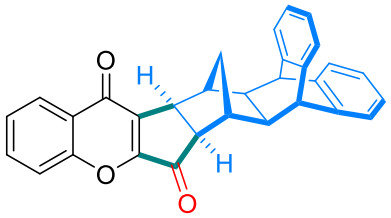




4ab (CCDC: 2056371)

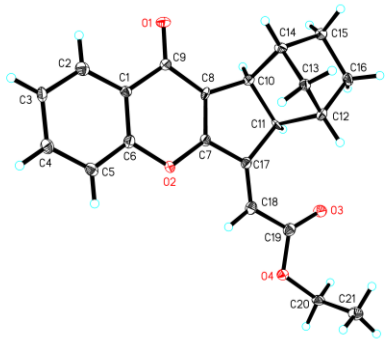
Identification code	**4ab**
Empirical formula	$C_{25}H_{20}O_3$
Formula weight	368.41
Temperature/K	99.98(11)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.2707(6)
b/Å	43.553(5)
c/Å	5.7823(5)
α/°	90
β/°	96.002(8)
γ/°	90
Volume/Å^3	1821.0(3)
Z	4
ρ_{calc}g/cm^3	1.344
μ/mm^{-1}	0.697
F(000)	776.0
Crystal size/mm^3	0.13 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	8.12 to 147.298
Index ranges	$-7 \le h \le 8$, $-53 \le k \le 52$, $-7 \le l \le 4$
Reflections collected	7718
Independent reflections	3542 [R_{int} = 0.0662, R_{sigma} = 0.0812]
Data/restraints/parameters	3542/0/255
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0846, wR_2 = 0.2269
Final R indexes [all data]	R_1 = 0.1082, wR_2 = 0.2450
Largest diff. peak/hole / e Å^{-3}	0.39/-0.39

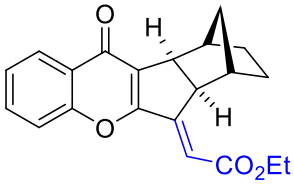




4ad (CCDC: 2056382)

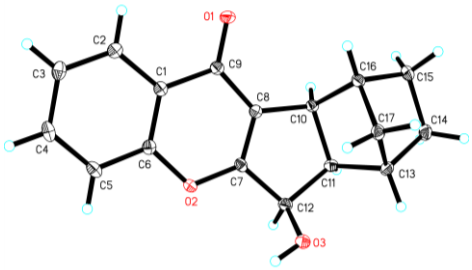
Identification code	**4ad**
Empirical formula	$C_{31}H_{22}O_3$
Formula weight	442.48
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.2504(6)
b/Å	6.3375(3)
c/Å	23.4812(10)
α/°	90
β/°	99.254(4)
γ/°	90
Volume/Å^3	2093.04(16)
Z	4
ρ_{calc}g/cm^3	1.404
μ/mm^{-1}	0.710
F(000)	928.0
Crystal size/mm^3	0.13 × 0.11 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.806 to 147.818
Index ranges	$-17 \le h \le 17$, $-7 \le k \le 7$, $-5 \le l \le 29$
Reflections collected	4126
Independent reflections	4126 [R_{int} = 0.0478, R_{sigma} = 0.0572]
Data/restraints/parameters	4126/0/308
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.1271, wR_2 = 0.3248
Final R indexes [all data]	R_1 = 0.1377, wR_2 = 0.3292
Largest diff. peak/hole / e Å^{-3}	0.55/-0.50

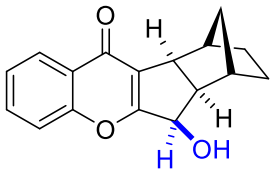




5 (CCDC: 2056383)

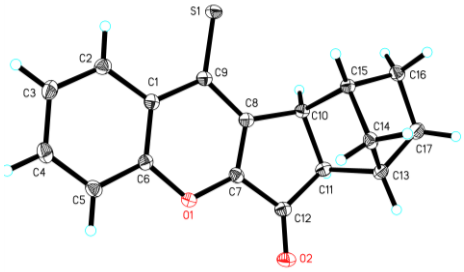
Identification code	**5**
Empirical formula	$C_{21}H_{20}O_4$
Formula weight	336.37
Temperature/K	100.01(11)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	5.6748(14)
b/Å	13.565(3)
c/Å	10.788(3)
α/°	90
β/°	101.16(3)
γ/°	90
Volume/Å^3	814.8(4)
Z	2
ρ_{calc}g/cm^3	1.371
μ/mm^{-1}	0.094
F(000)	356.0
Crystal size/mm^3	0.12 × 0.11 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	3.848 to 50.12
Index ranges	$-6 \le h \le 6$, $-16 \le k \le 16$, $-2 \le l \le 12$
Reflections collected	2283
Independent reflections	2283 [R_{int} = 0.0572, R_{sigma} = 0.1055]
Data/restraints/parameters	2283/7/228
Goodness-of-fit on F^2	1.186
Final R indexes [I>=2σ (I)]	R_1 = 0.0767, wR_2 = 0.2175
Final R indexes [all data]	R_1 = 0.0926, wR_2 = 0.2294
Largest diff. peak/hole / e Å^{-3}	0.39/-0.41
Flack parameter	1.0(10)

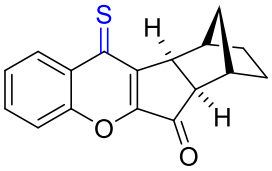




6 (CCDC: 2056385)

Identification code	**6**
Empirical formula	$C_{17}H_{16}O_3$
Formula weight	268.30
Temperature/K	149.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	6.8459(5)
b/Å	8.6461(6)
c/Å	11.8123(8)
α/°	107.918(6)
β/°	101.256(6)
γ/°	98.709(6)
Volume/Å^3	635.49(8)
Z	2
ρ_{calc}g/cm^3	1.402
μ/mm^{-1}	0.095
F(000)	284.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	5.084 to 49.99
Index ranges	$-7 \le h \le 8$, $-10 \le k \le 9$, $-10 \le l \le 14$
Reflections collected	4187
Independent reflections	2228 [R_{int} = 0.0209, R_{sigma} = 0.0359]
Data/restraints/parameters	2228/0/183
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0387, wR_2 = 0.0942
Final R indexes [all data]	R_1 = 0.0452, wR_2 = 0.1000
Largest diff. peak/hole / e Å^{-3}	0.23/-0.18

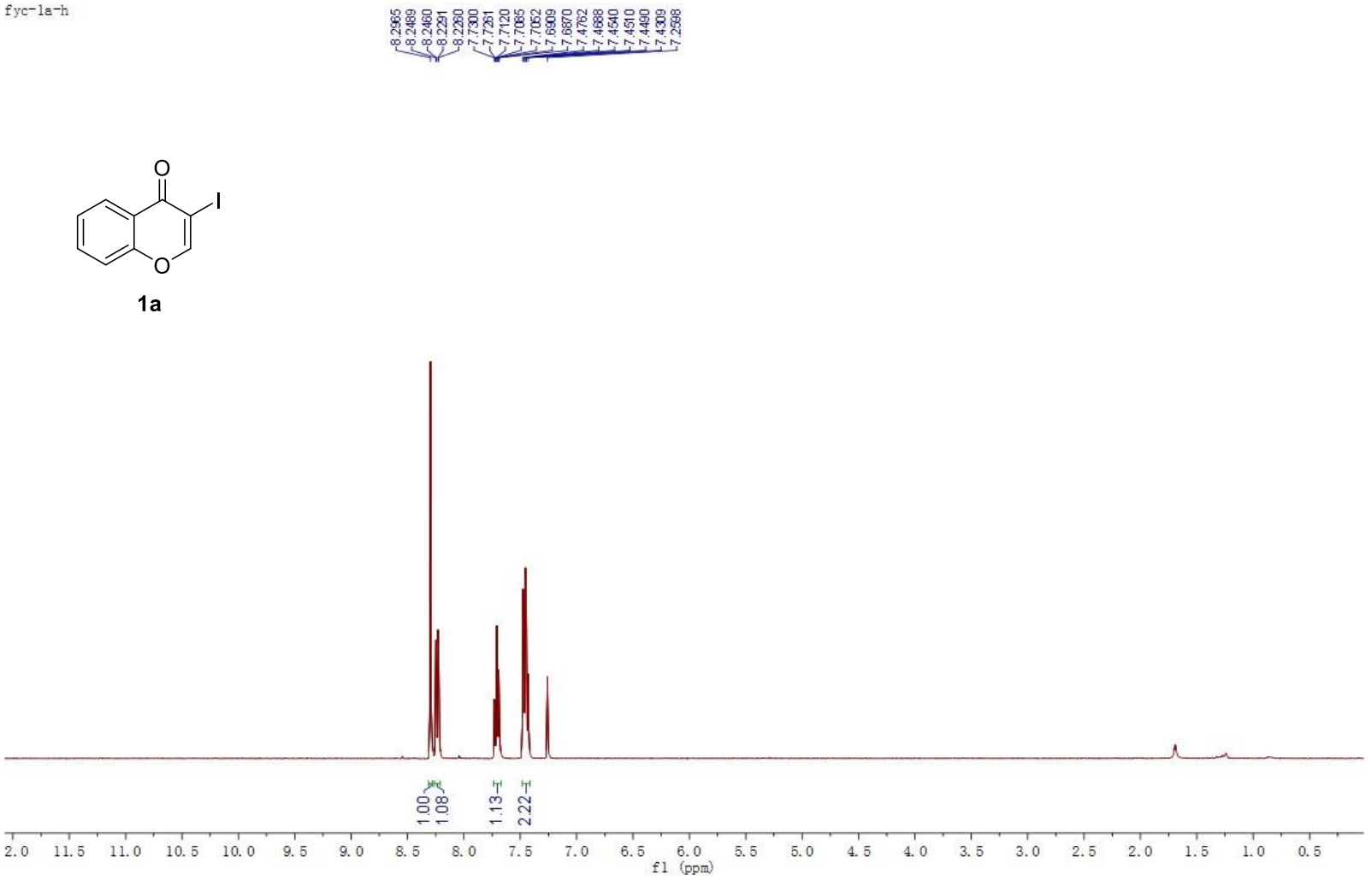


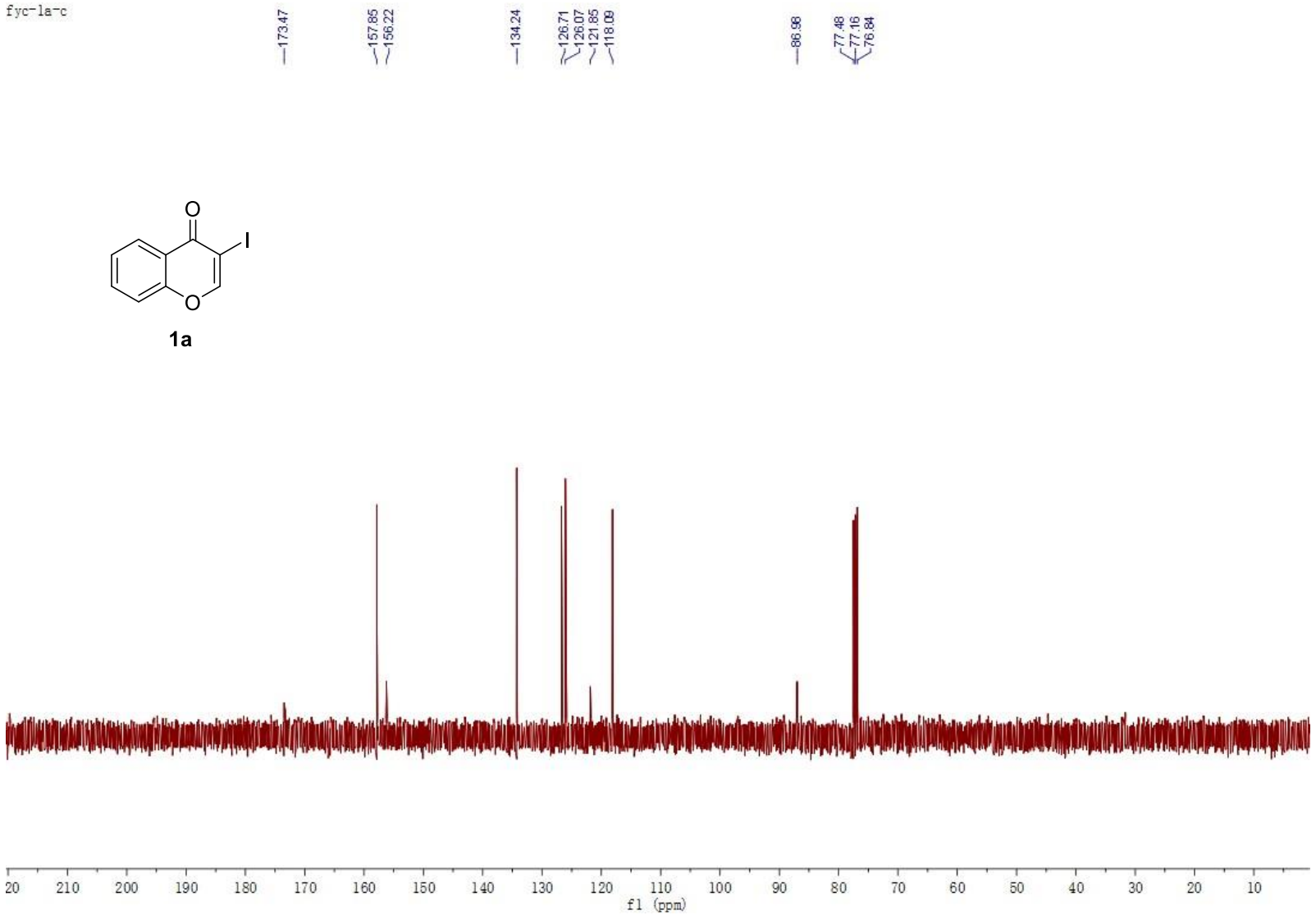


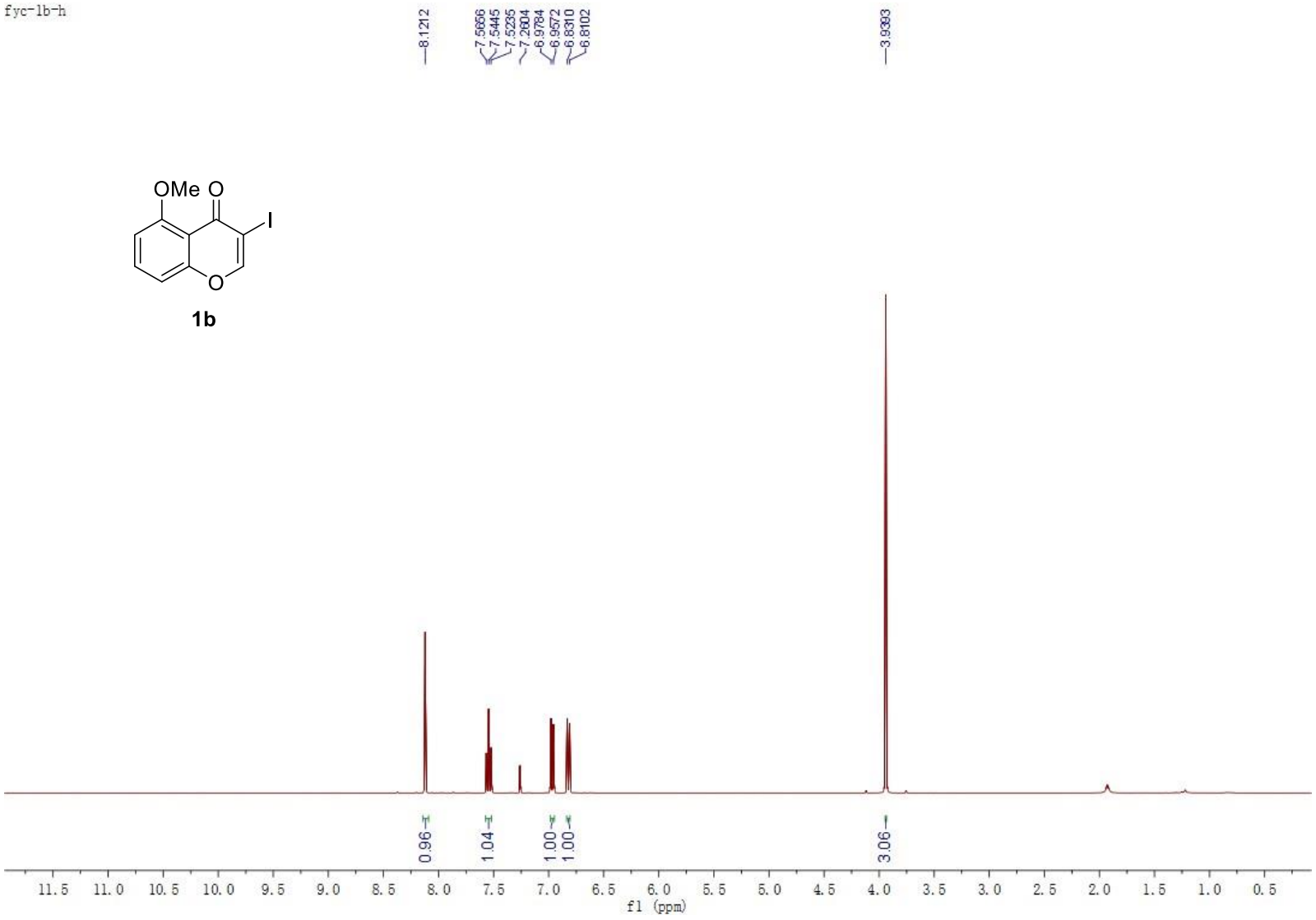
7 (CCDC: 2058395)

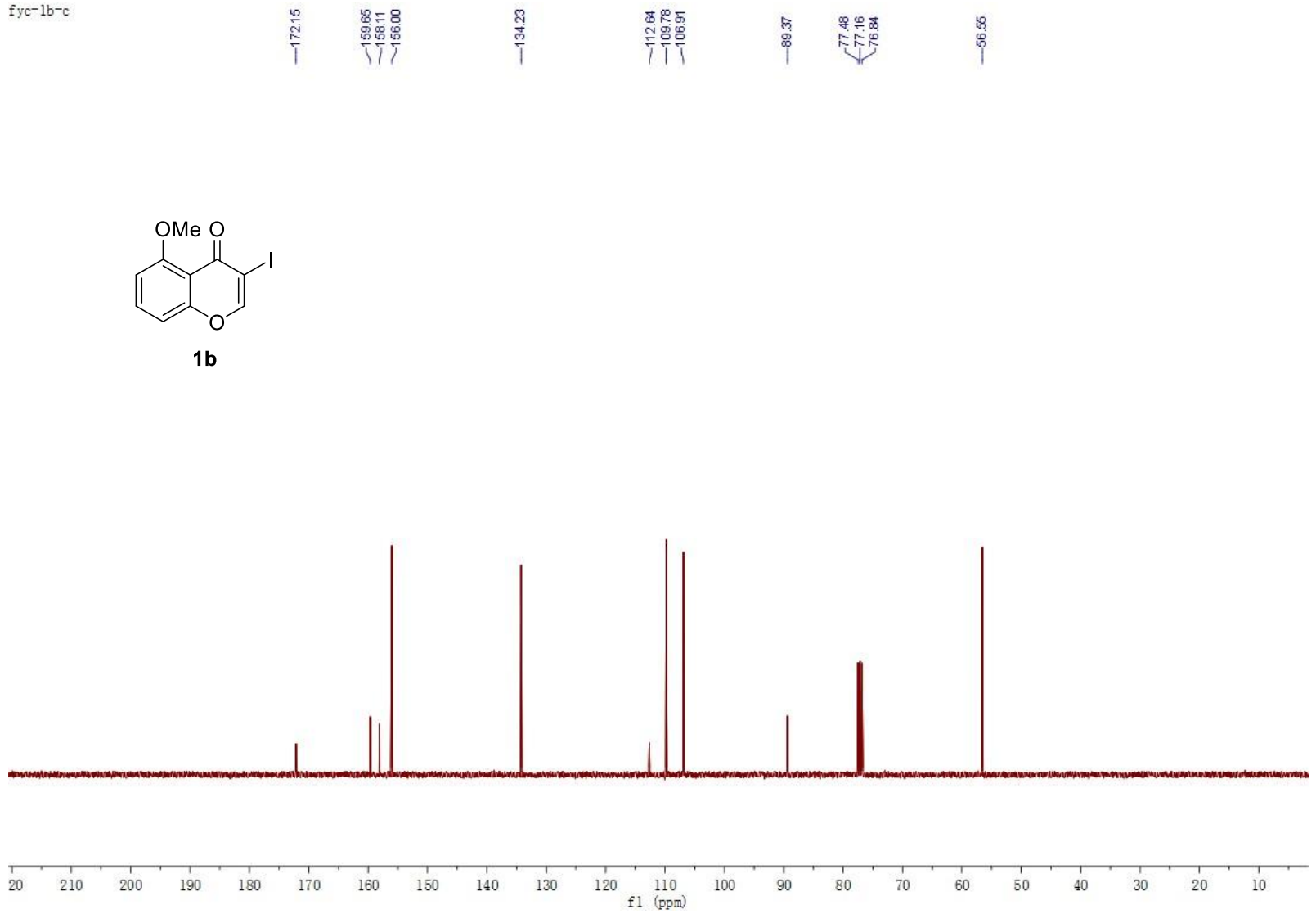
Identification code	**7**
Empirical formula	$C_{17}H_{14}O_2S$
Formula weight	282.34
Temperature/K	150.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	13.3198(8)
b/Å	9.2495(7)
c/Å	21.0527(14)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2593.7(3)
Z	8
ρ_{calc}g/cm^3	1.446
μ/mm^{-1}	0.247
F(000)	1184.0
Crystal size/mm^3	0.13 × 0.12 × 0.08
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	4.932 to 49.984
Index ranges	-15 ≤ h ≤ 15, -9 ≤ k ≤ 10, -25 ≤ l ≤ 20
Reflections collected	7667
Independent reflections	2282 [R_{int} = 0.0292, R_{sigma} = 0.0292]
Data/restraints/parameters	2282/0/181
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0344, wR_2 = 0.0782
Final R indexes [all data]	R_1 = 0.0437, wR_2 = 0.0840
Largest diff. peak/hole / e Å^{-3}	0.22/-0.20

13. ^{1}H and ^{13}C NMR spectra of 1a-1w, 2a-2h and 3a-3b



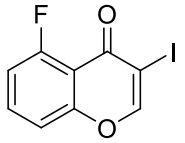

fyc-1a-c
173.47
157.85
156.22
134.24
126.71
126.07
121.85
118.09
86.98
77.48
77.16
76.84
O
I
O
1a
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


fyc-1b-h
8.1212
7.5666
7.5445
7.5235
7.2604
6.9784
6.9572
6.8310
6.8102
3.9383
OMe
O
I
O
1b
0.96
1.04
1.00
1.00
3.06
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

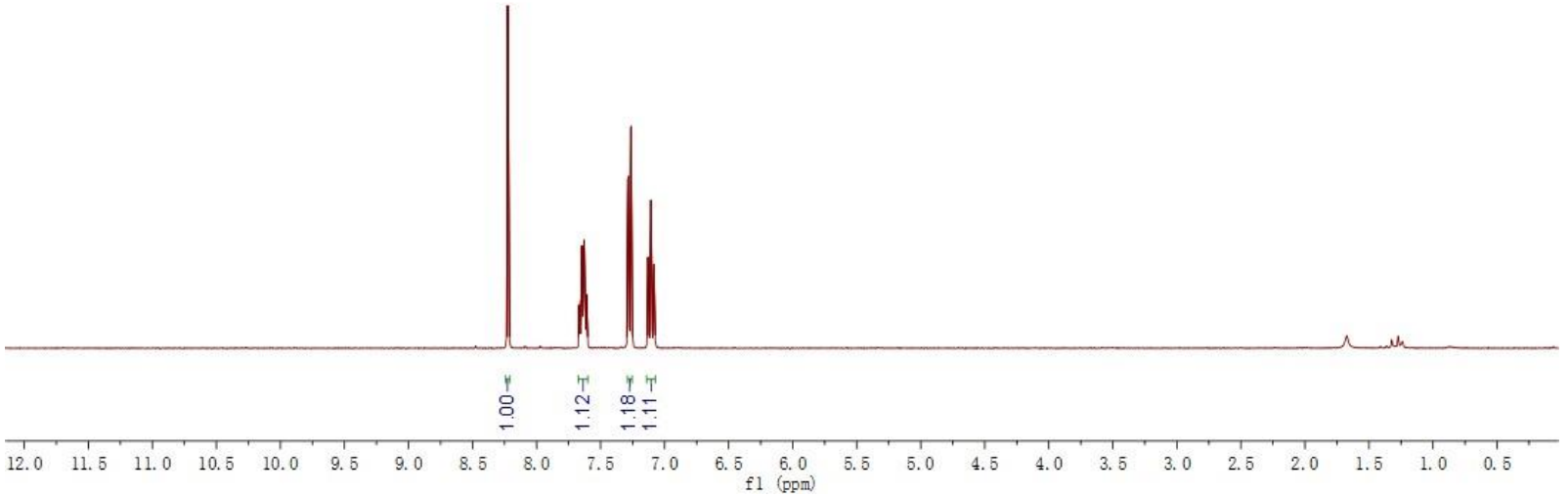

fyc-1b-c
172.15
159.65
158.11
156.00
134.23
112.64
109.78
106.91
89.37
77.48
77.16
76.84
56.55
OMe
O
I
O
1b
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

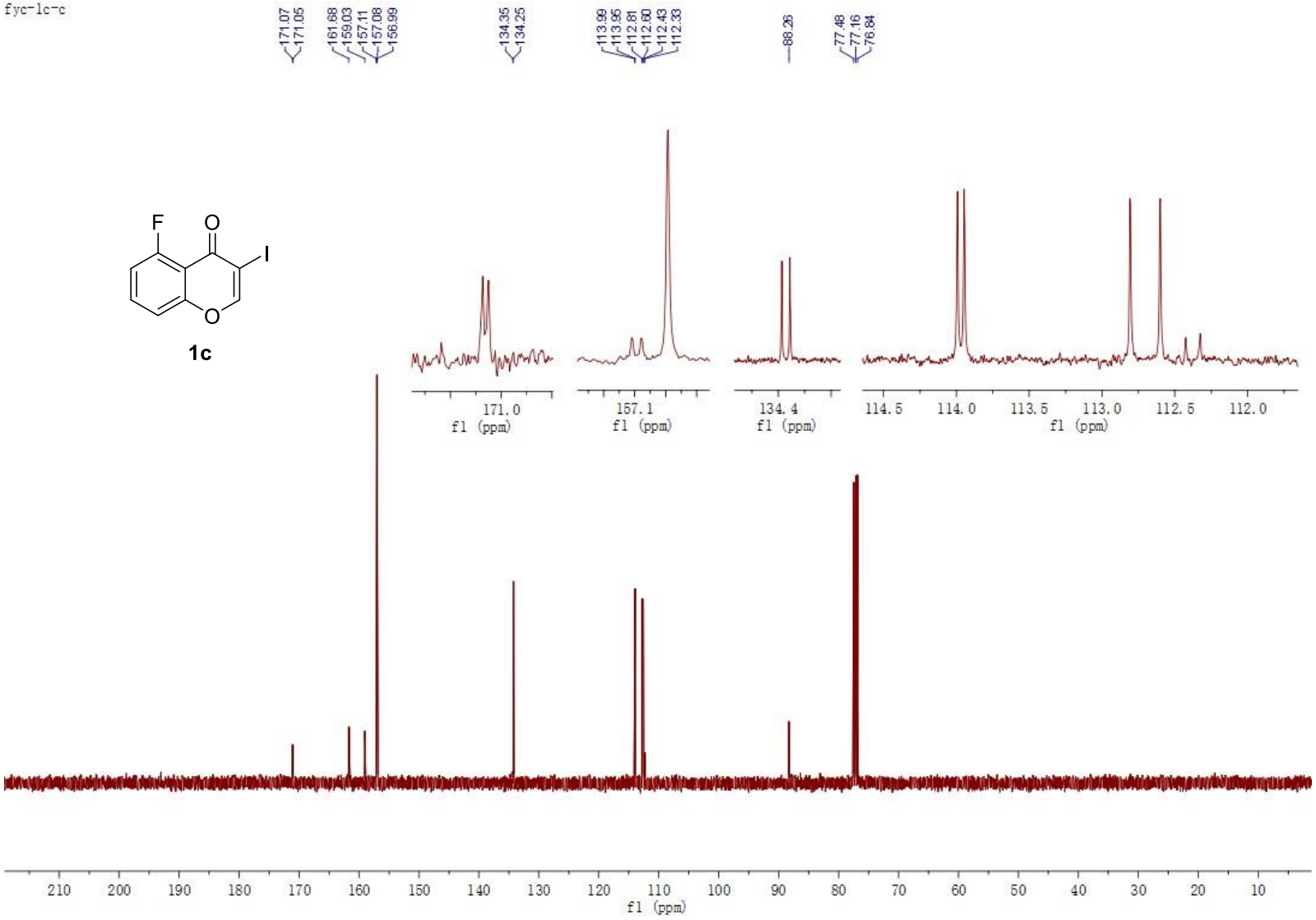
fyc-1c-h


8.2259
8.2220
7.6462
7.6324
7.6280
7.2620
7.1298
7.1068
7.0833


F
O
I
O

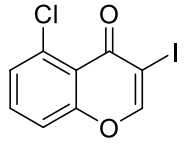
1c


1.00
1.12
1.18
1.11
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

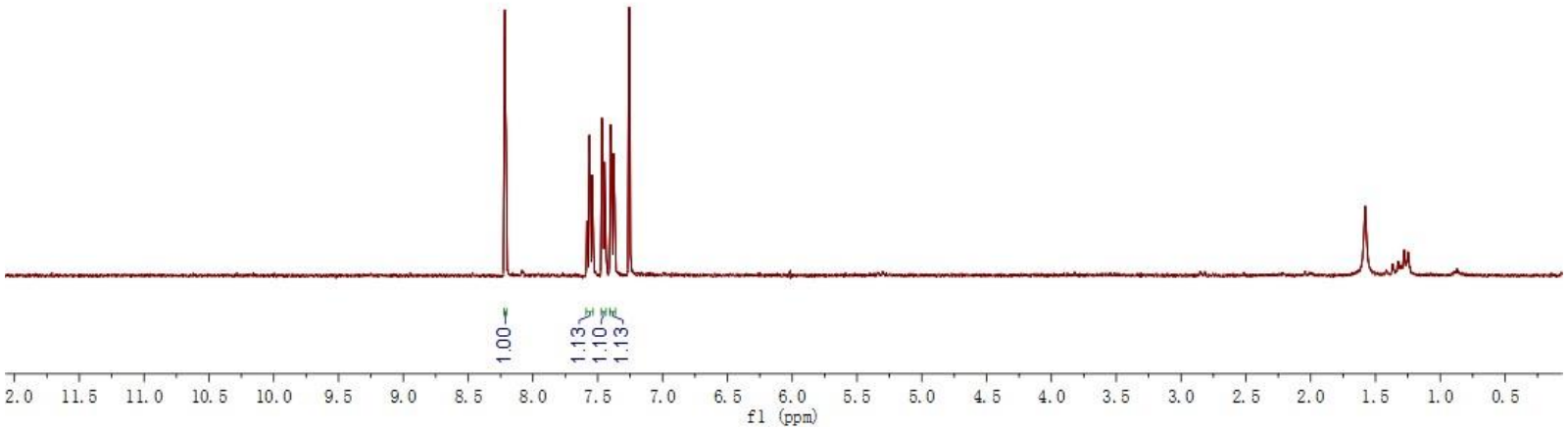

fyc-1c-c
171.07
171.05
161.68
159.03
157.11
157.08
156.99
134.35
134.25
113.99
113.95
112.81
112.80
112.43
112.33
88.26
77.48
77.16
76.84
F
O
O
I
1c
171.0
f1 (ppm)
157.1
f1 (ppm)
134.4
f1 (ppm)
114.5
114.0
113.5
113.0
112.5
112.0
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

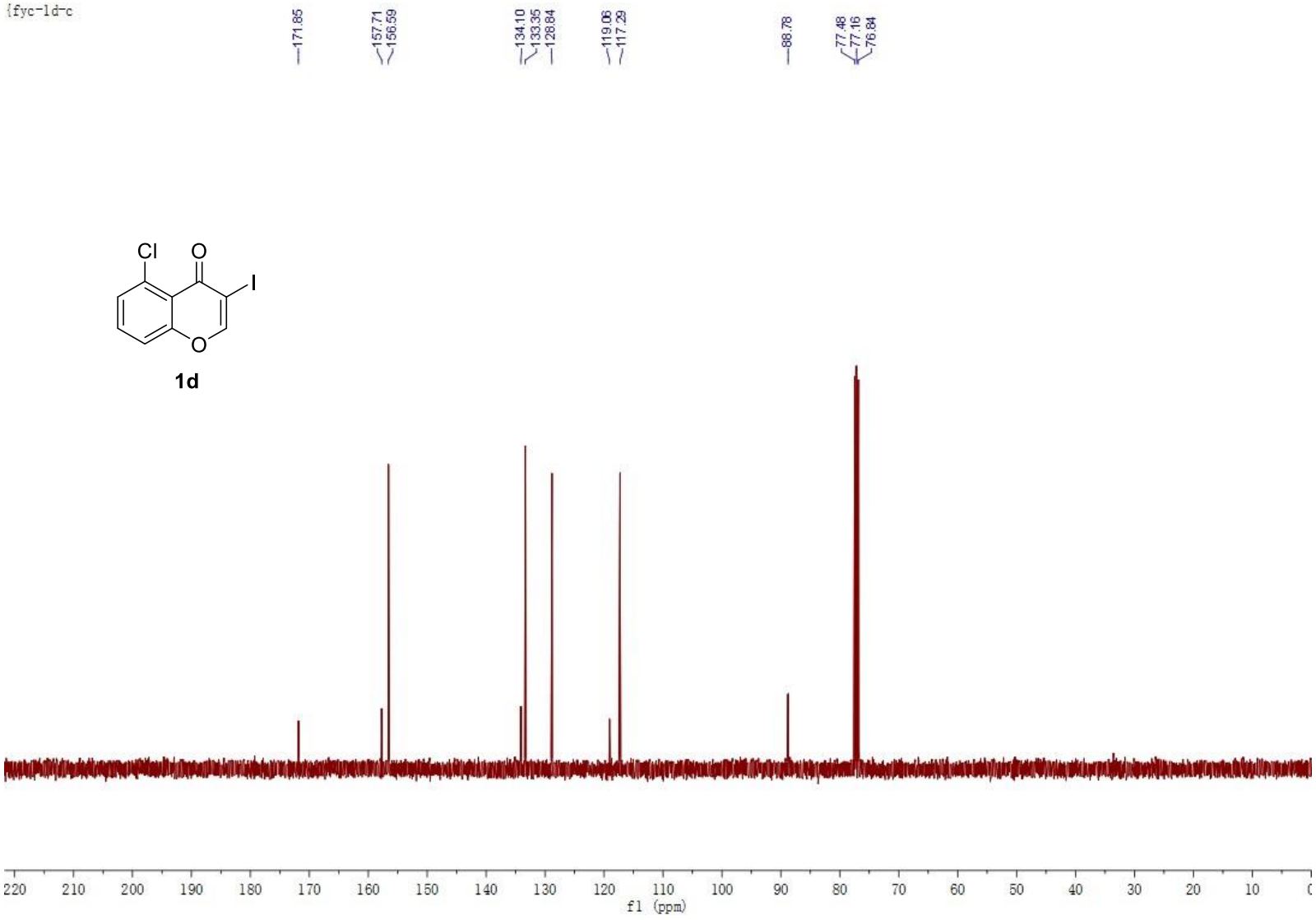
fyc-1d-h


8.2162
8.2090
7.5880
7.5840
7.5773
7.5641
7.5572
7.5459
7.5439
7.5364
7.4672
7.4646
7.4604
7.4576
7.4504
7.4476
7.4408
7.4380
7.3997
7.3990
7.3904
7.3786
7.3720
7.3692
7.2626
7.2600
7.2529

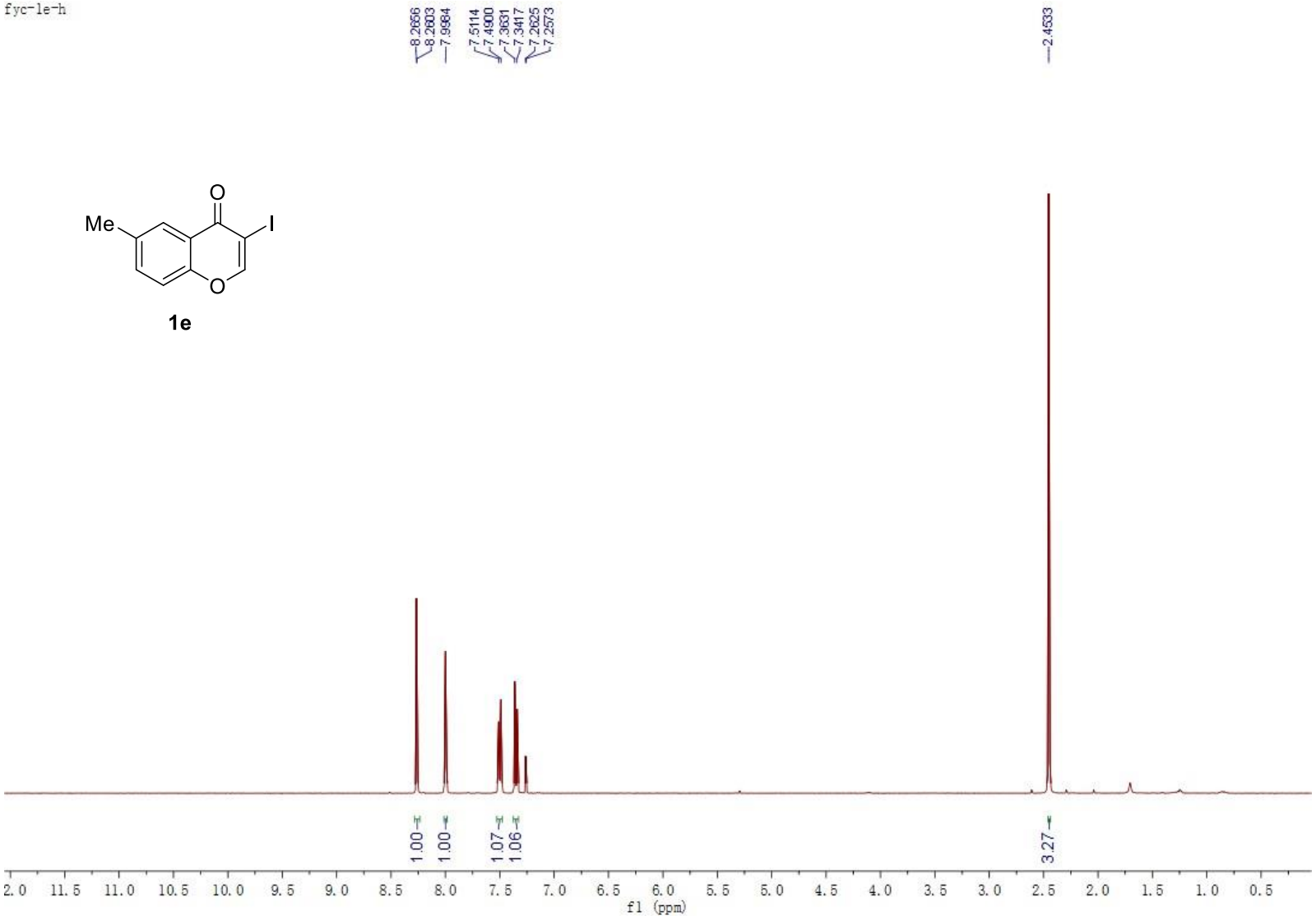

Cl
O
I
O

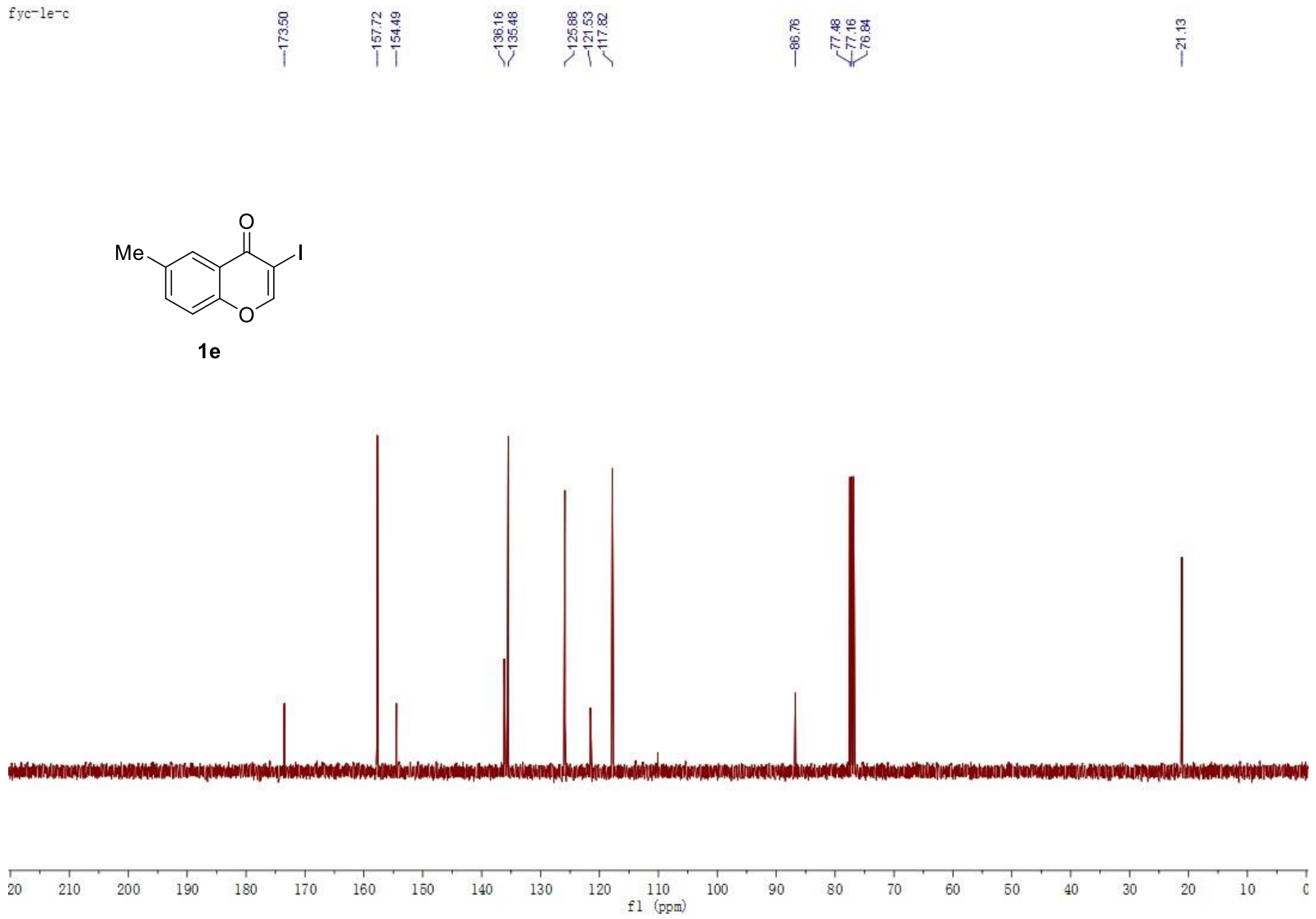
1d

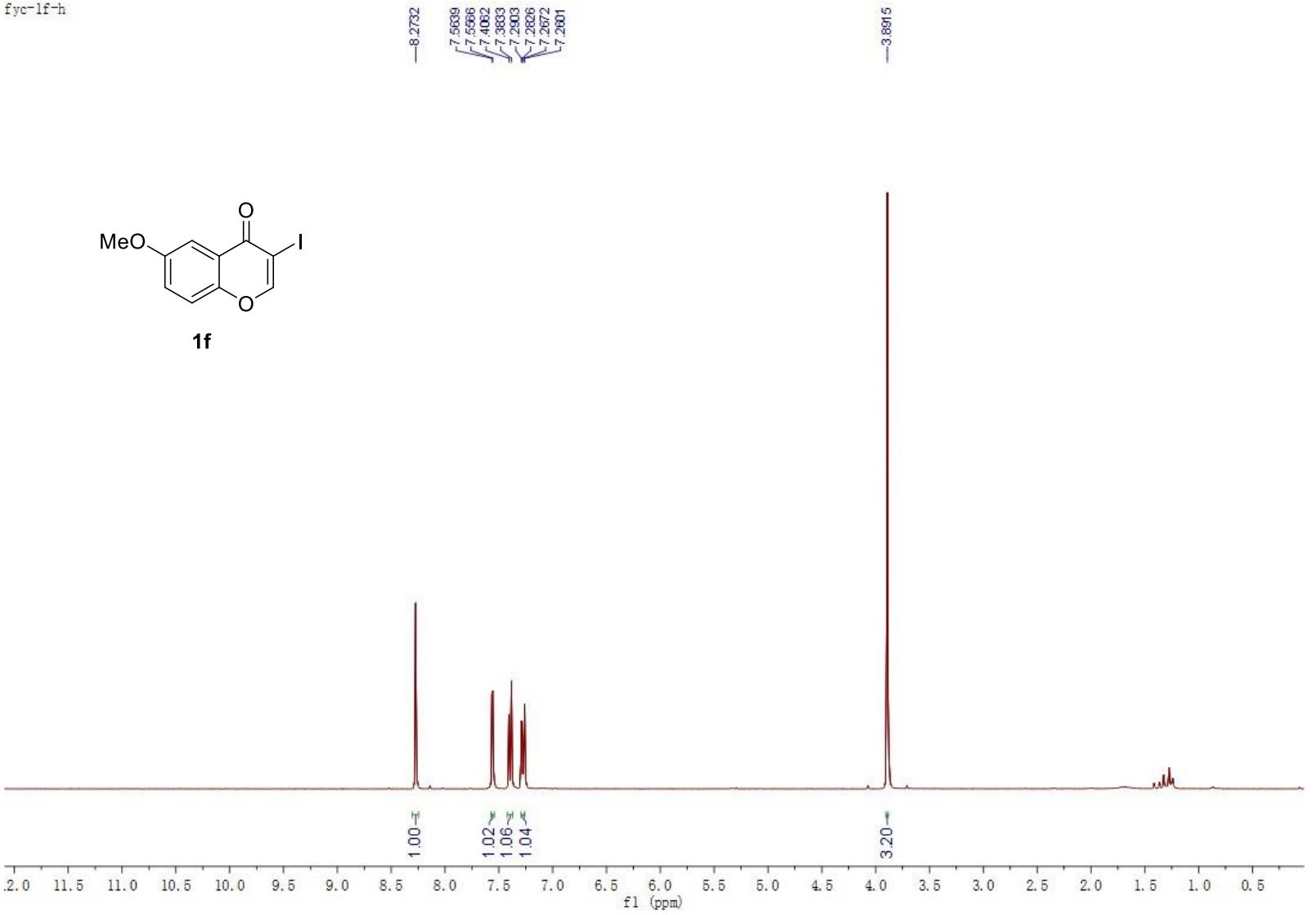

1.00
1.13
1.10
1.13
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

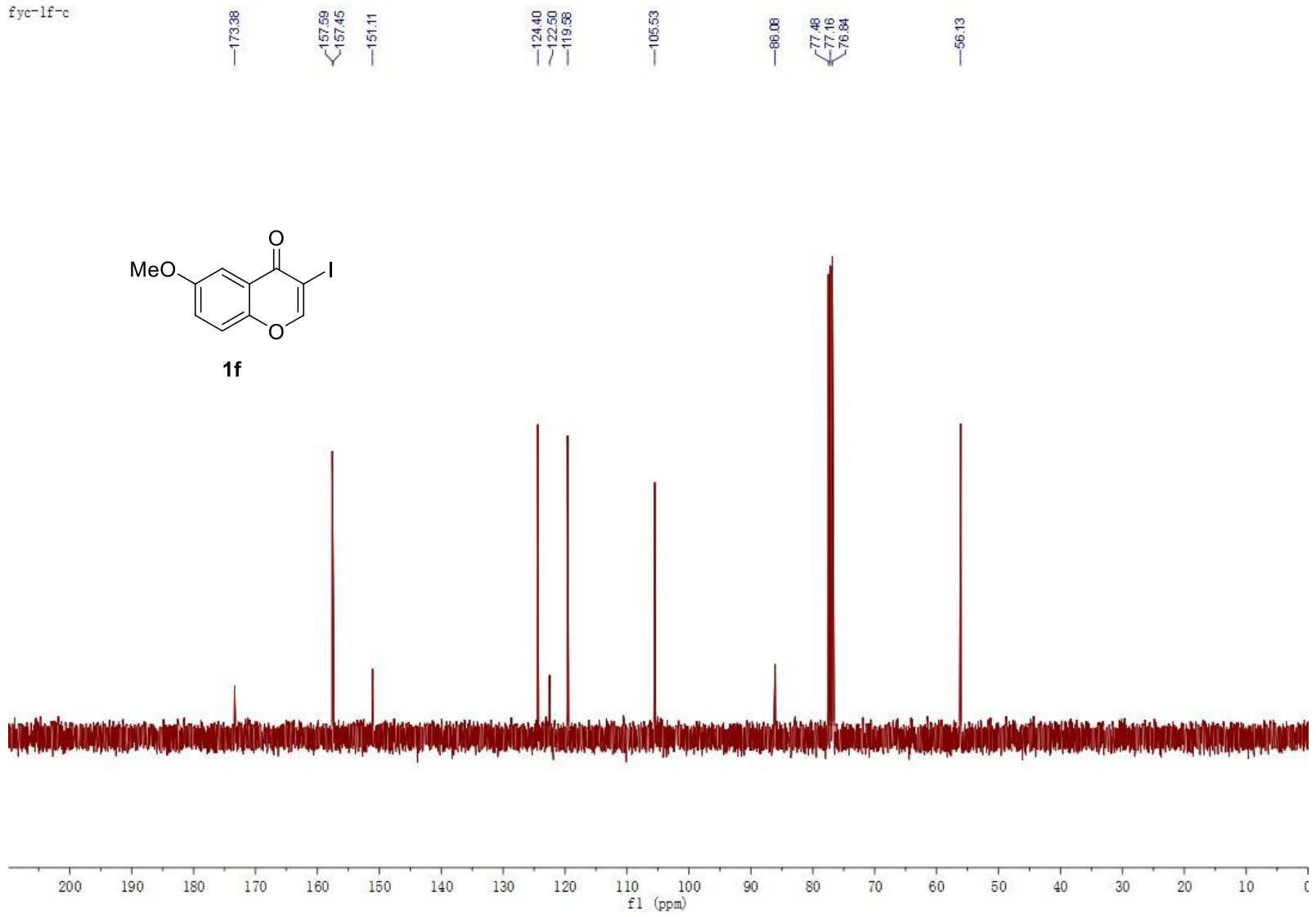

{fyc-1d-c
171.85
157.71
156.59
134.10
133.35
128.84
119.06
117.29
88.78
77.48
77.16
76.84
Cl
O
I
O
1d
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

fyc-1e-h

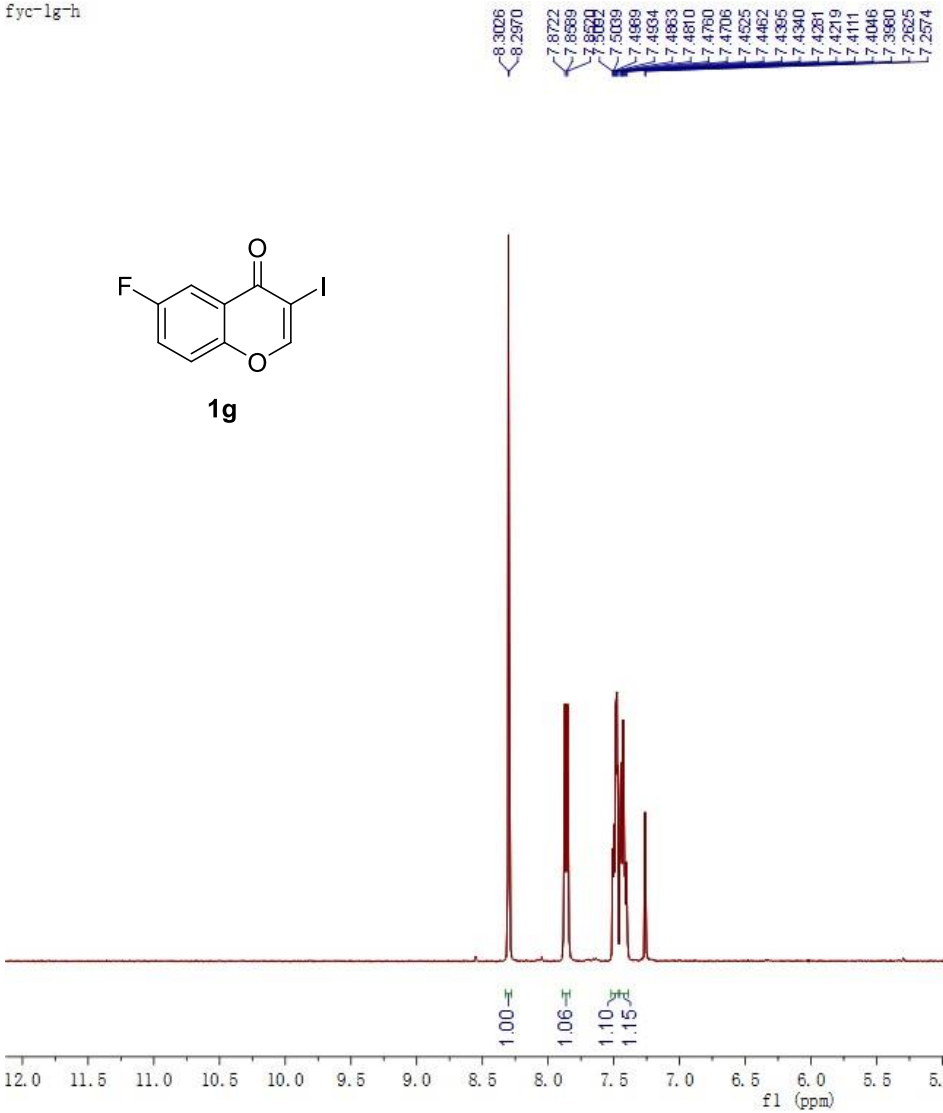

8.2656
8.2603
7.9984
7.5114
7.4900
7.3631
7.3417
7.2625
7.2573
2.4533
Me
I
O
O
1e
1.00
1.00
1.07
1.06
3.27
f1 (ppm)

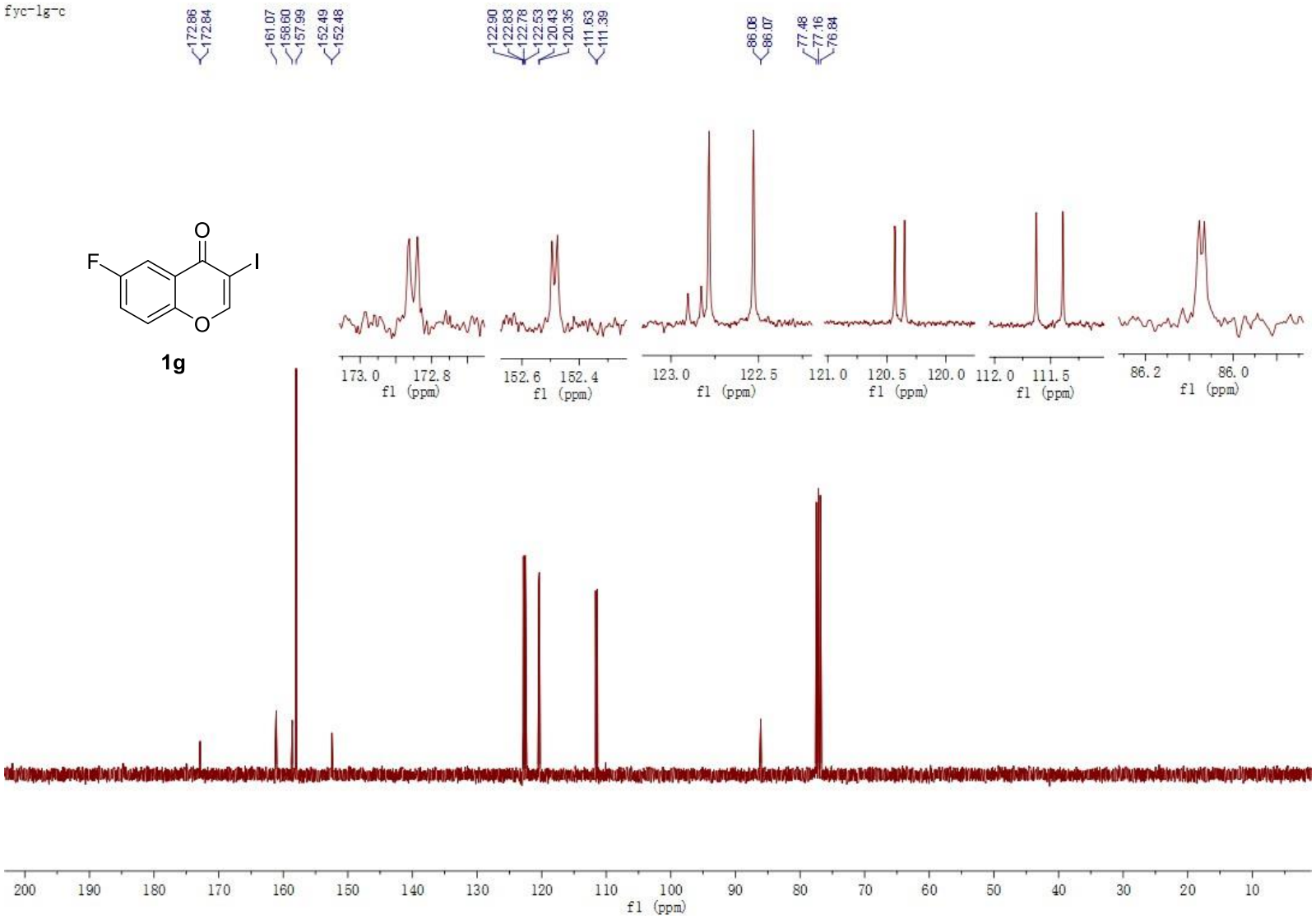

fyc-1e-c
173.50
157.72
154.49
136.16
135.48
125.88
121.53
117.82
86.76
77.48
77.16
76.84
21.13
Me
O
I
O
1e
f1 (ppm)


fyc-1f-h
8.2732
7.5639
7.5966
7.4052
7.3833
7.2903
7.2826
7.2672
7.2601
3.8915
MeO
O
I
O
1f
1.00
1.02
1.06
1.04
3.20
f1 (ppm)

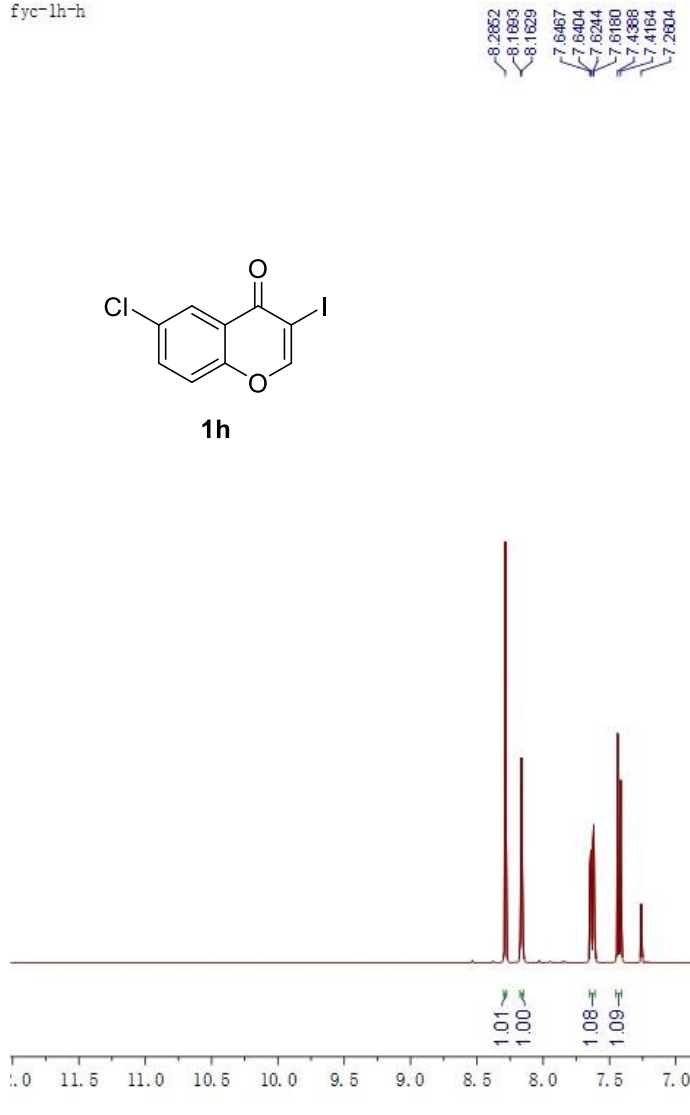

fyc-1f-c
173.38
157.59
157.45
151.11
124.40
122.50
119.58
105.53
86.08
77.48
77.16
76.84
56.13
MeO
O
I
O
1f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

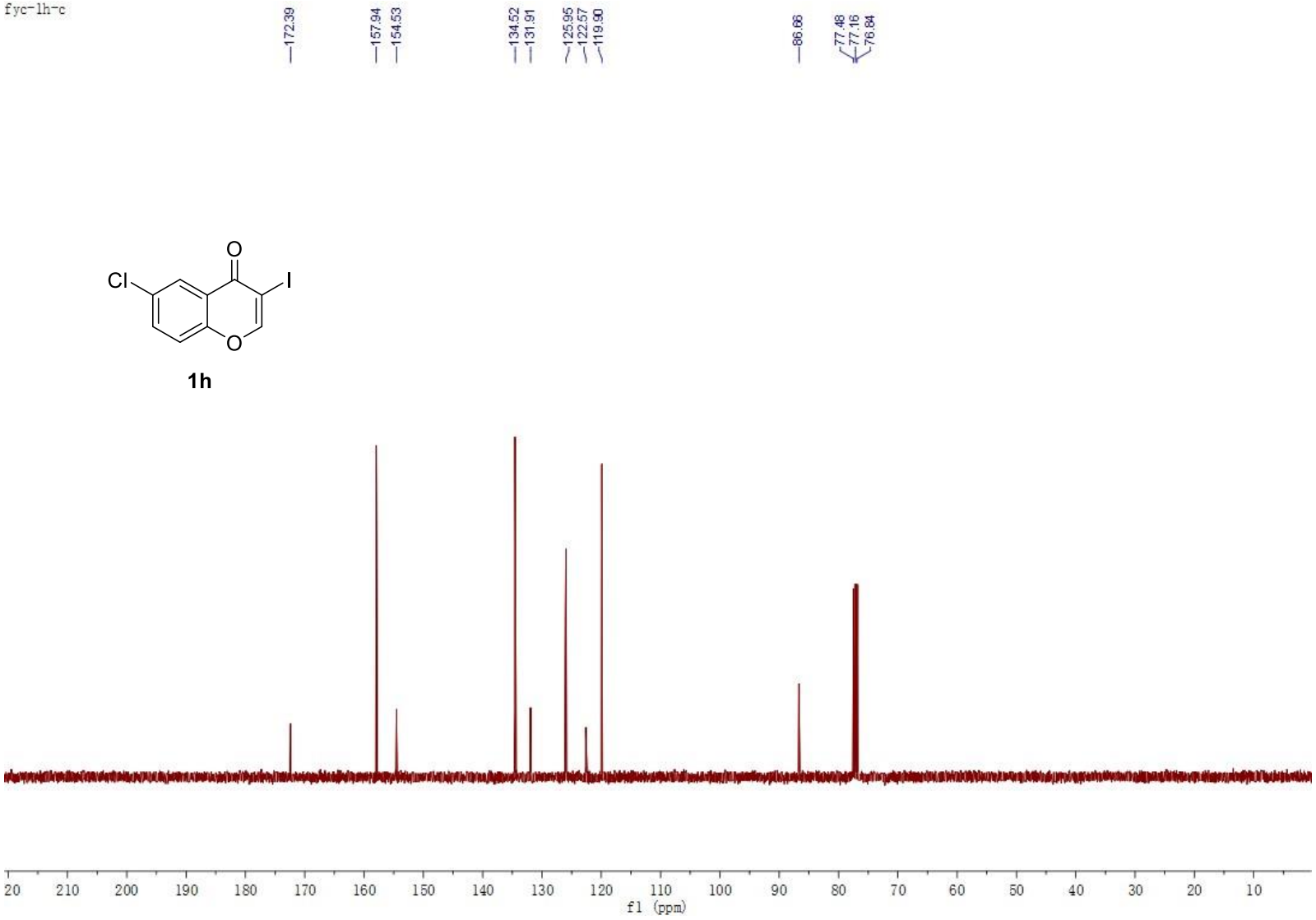
fyc-1g-h


8.3026
8.2970
7.8722
7.8689
7.5039
7.4969
7.4934
7.4863
7.4810
7.4760
7.4706
7.4525
7.4462
7.4395
7.4340
7.4281
7.4219
7.4111
7.4046
7.3980
7.2625
7.2574
F
O
I
O
1g
1.00
1.06
1.10
1.15
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

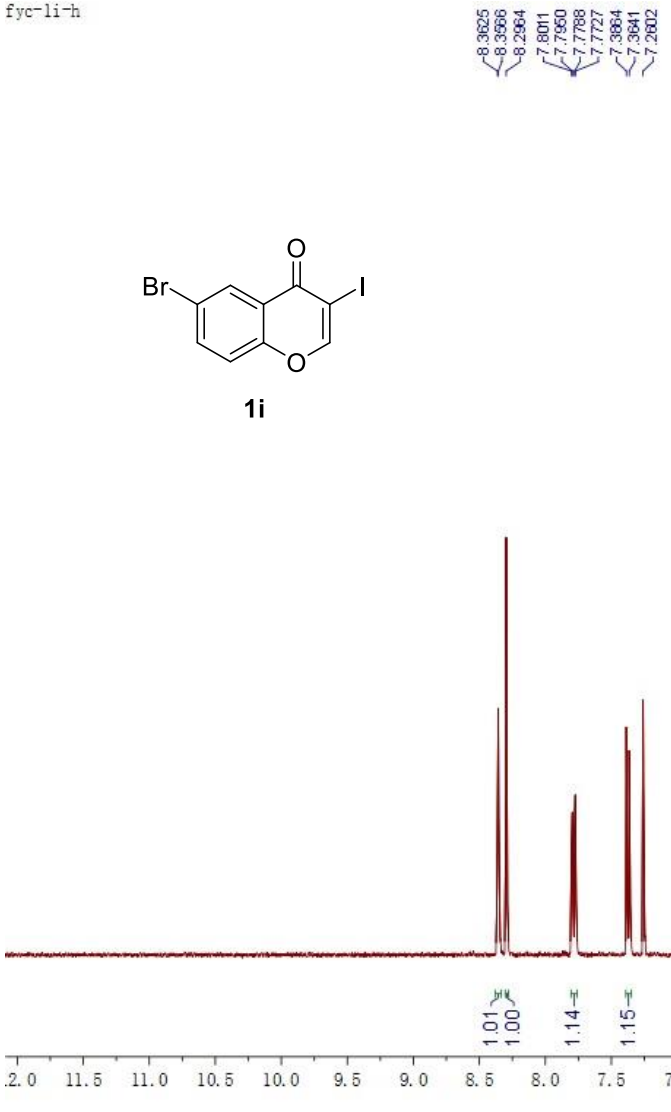

fyc-1g-c
172.86
172.84
161.07
158.60
157.99
152.49
152.48
122.90
122.83
122.78
122.53
120.43
120.35
111.63
111.39
86.08
86.07
77.48
77.16
76.84
F
O
I
O
1g
173.0
172.8
f1 (ppm)
152.6
152.4
f1 (ppm)
123.0
122.5
f1 (ppm)
121.0
120.5
120.0
f1 (ppm)
112.0
111.5
f1 (ppm)
86.2
86.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

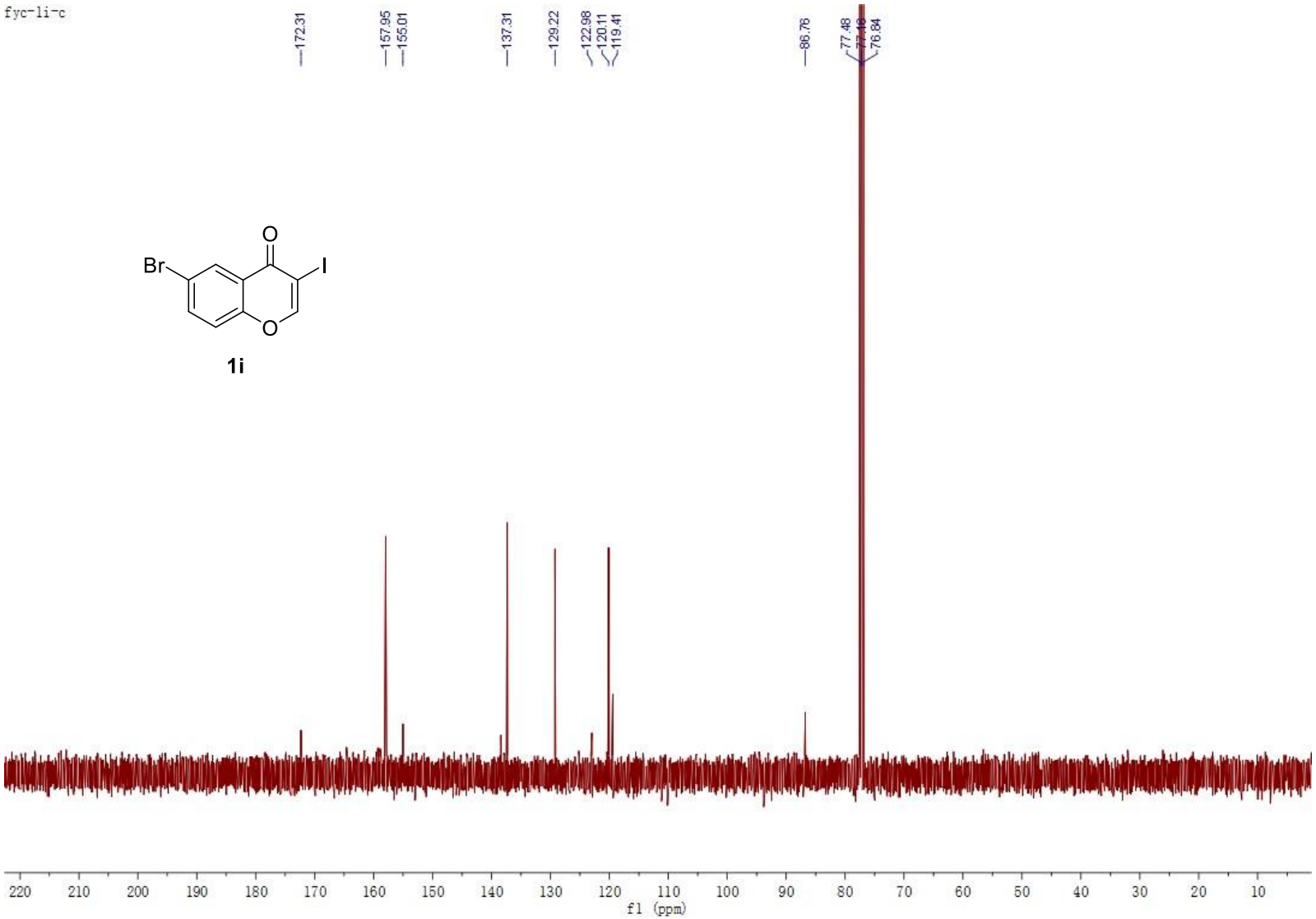
fyc-1h-h


8.2652
8.1693
8.1629
7.6467
7.6404
7.6244
7.6180
7.4388
7.4164
7.2604
O
Cl
I
O
1h
1.01
1.00
1.08
1.09
f1 (ppm)

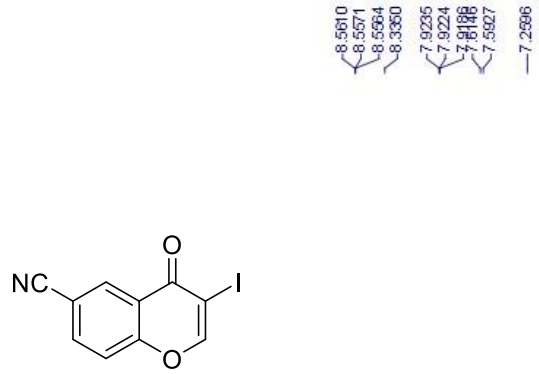

fyc-1h-c
172.39
157.94
154.53
134.52
131.91
125.95
122.57
119.90
86.66
77.48
77.16
76.84
O
Cl
I
O
1h
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

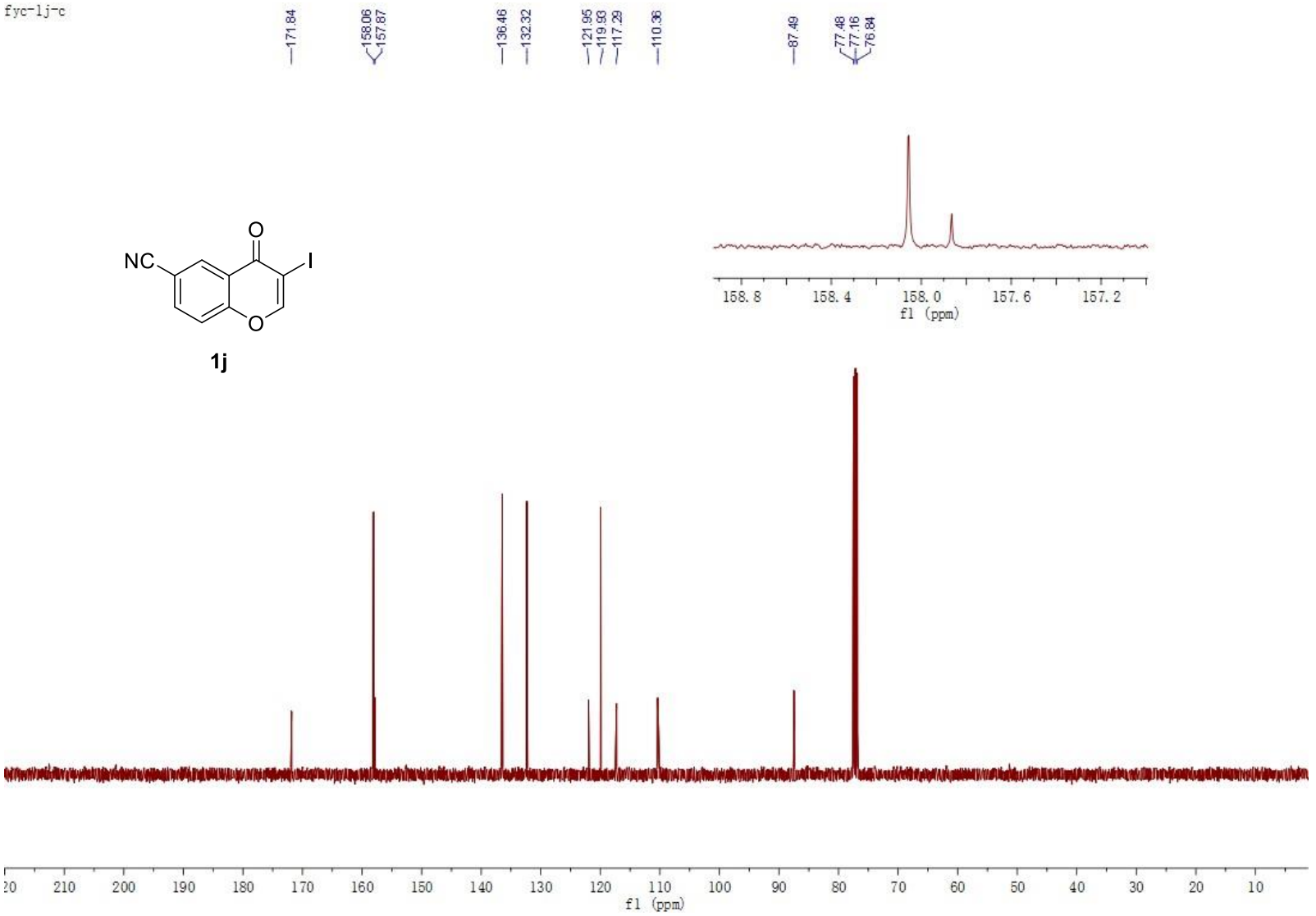
fyc-1i-h

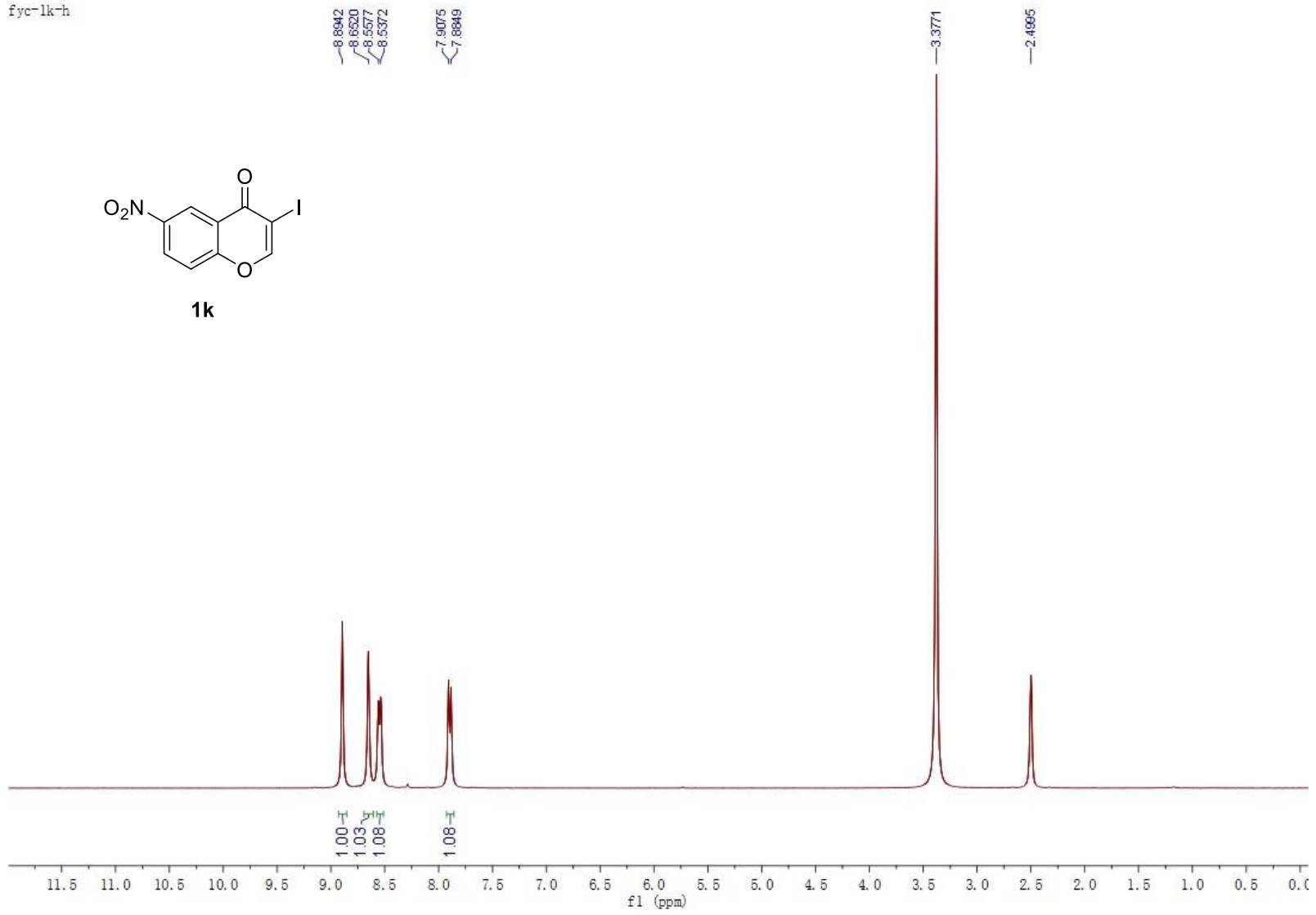

8.3625
8.3566
8.2964
7.8011
7.7950
7.7788
7.7727
7.3664
7.3641
7.2602
O
Br
I
O
1i
1.01
1.00
1.14
1.15
f1 (ppm)

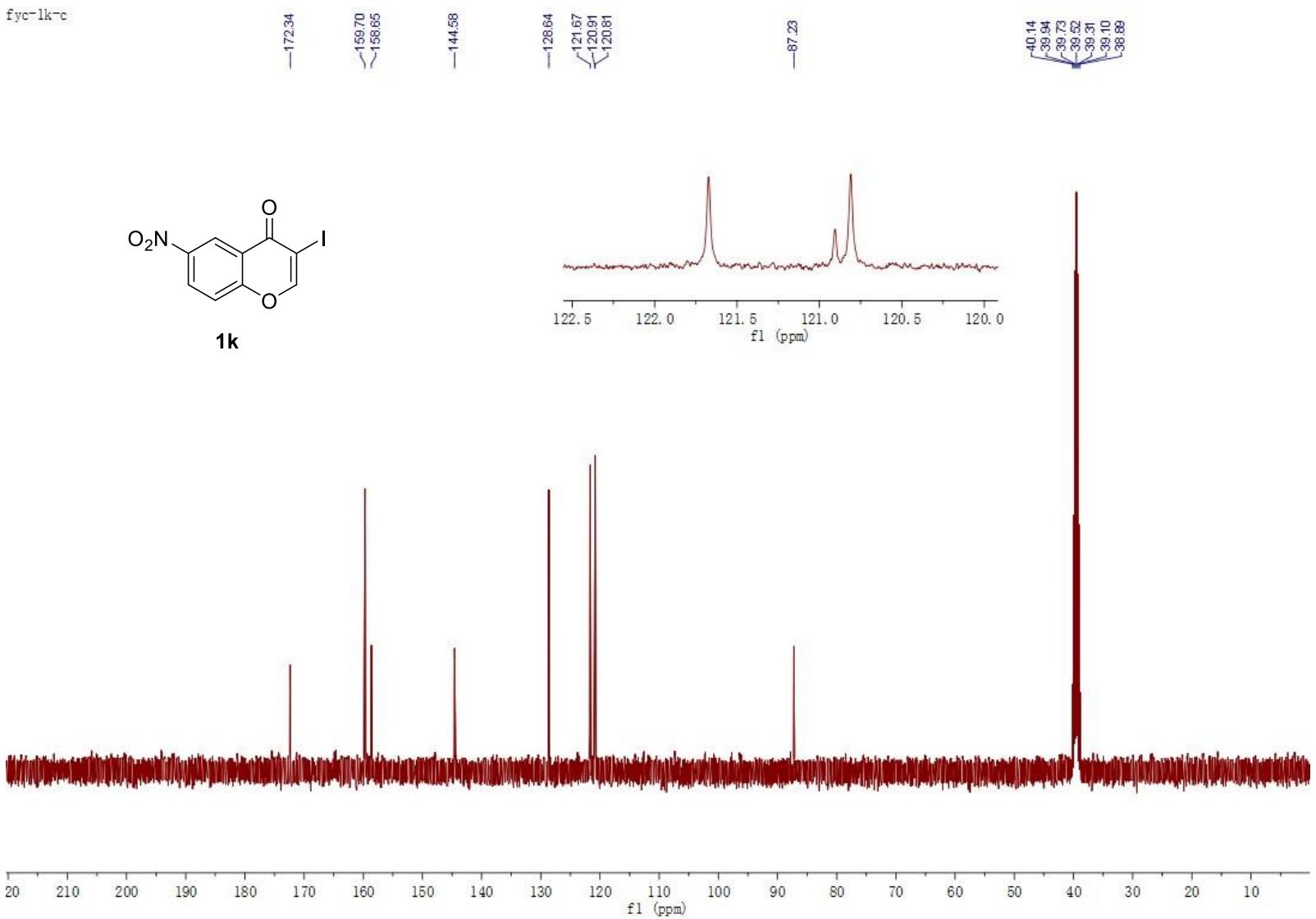

fyc-1i-c
172.31
157.95
155.01
137.31
129.22
122.98
120.11
119.41
86.76
77.48
76.84
Br
I
O
O
1i
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

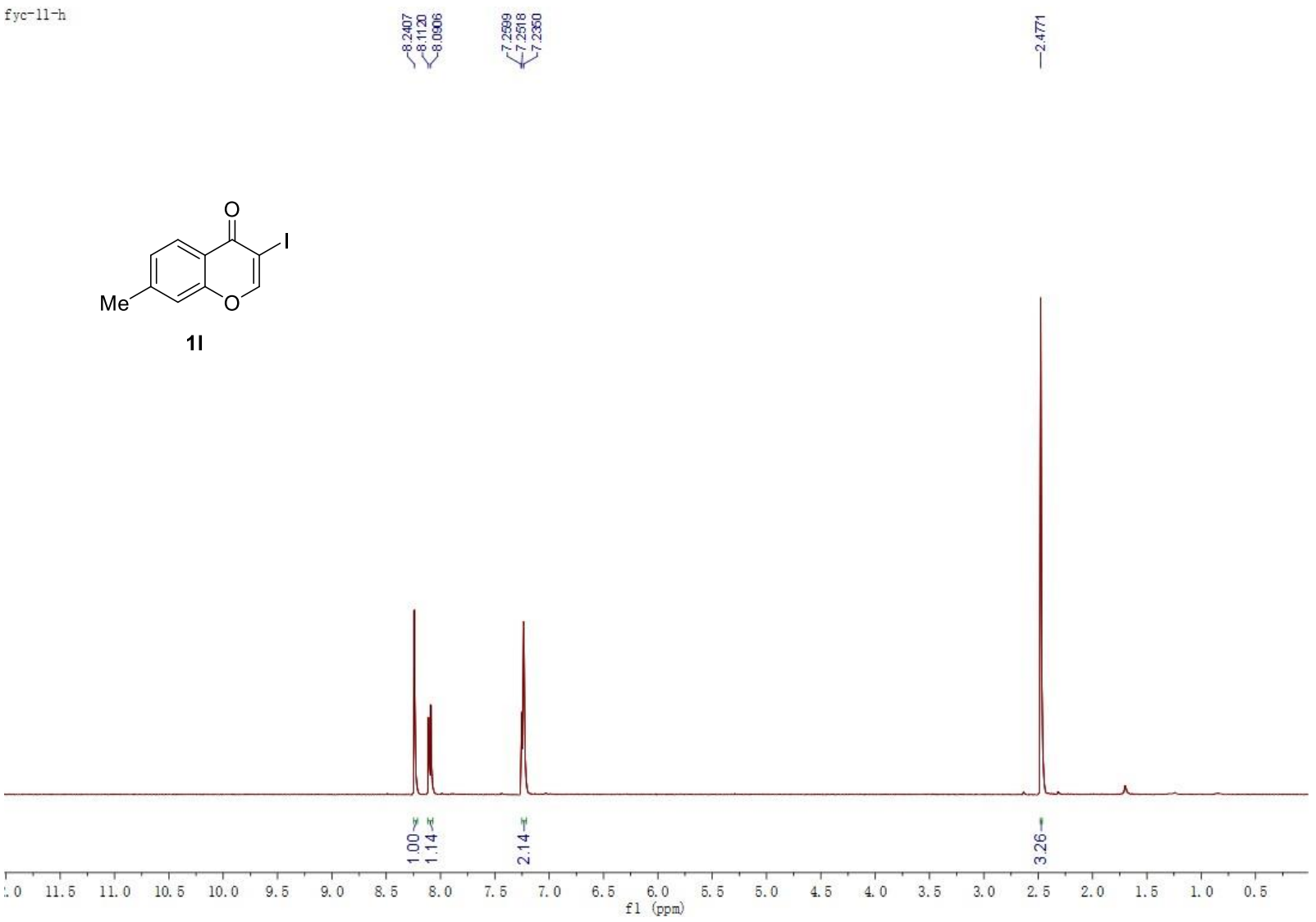
fyc-1j-h

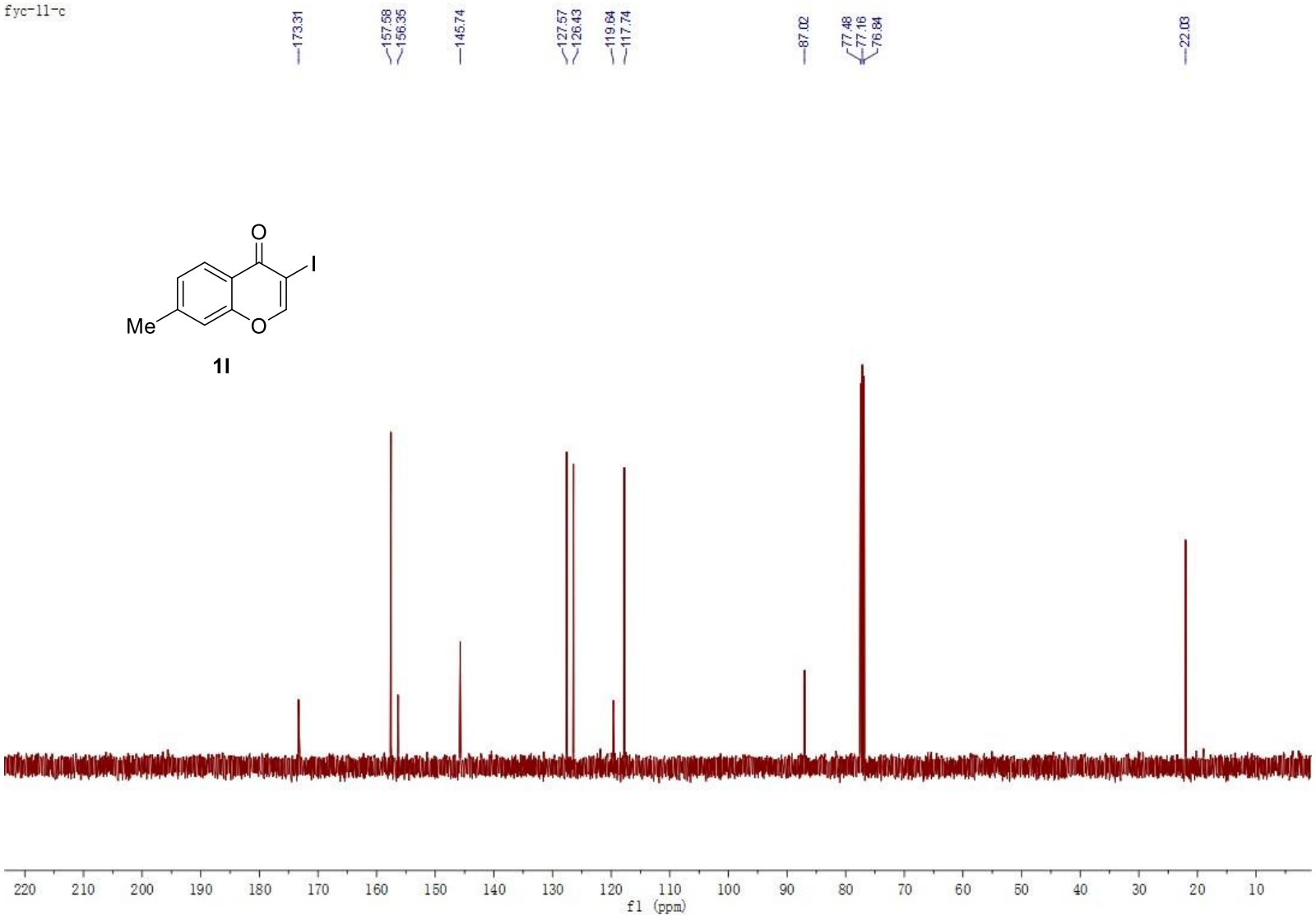

8.5610
8.5571
8.5564
8.3360
7.9235
7.9224
7.5927
7.2596
NC
O
I
O
1j
0.96
1.00
1.06
1.04
f1 (ppm)

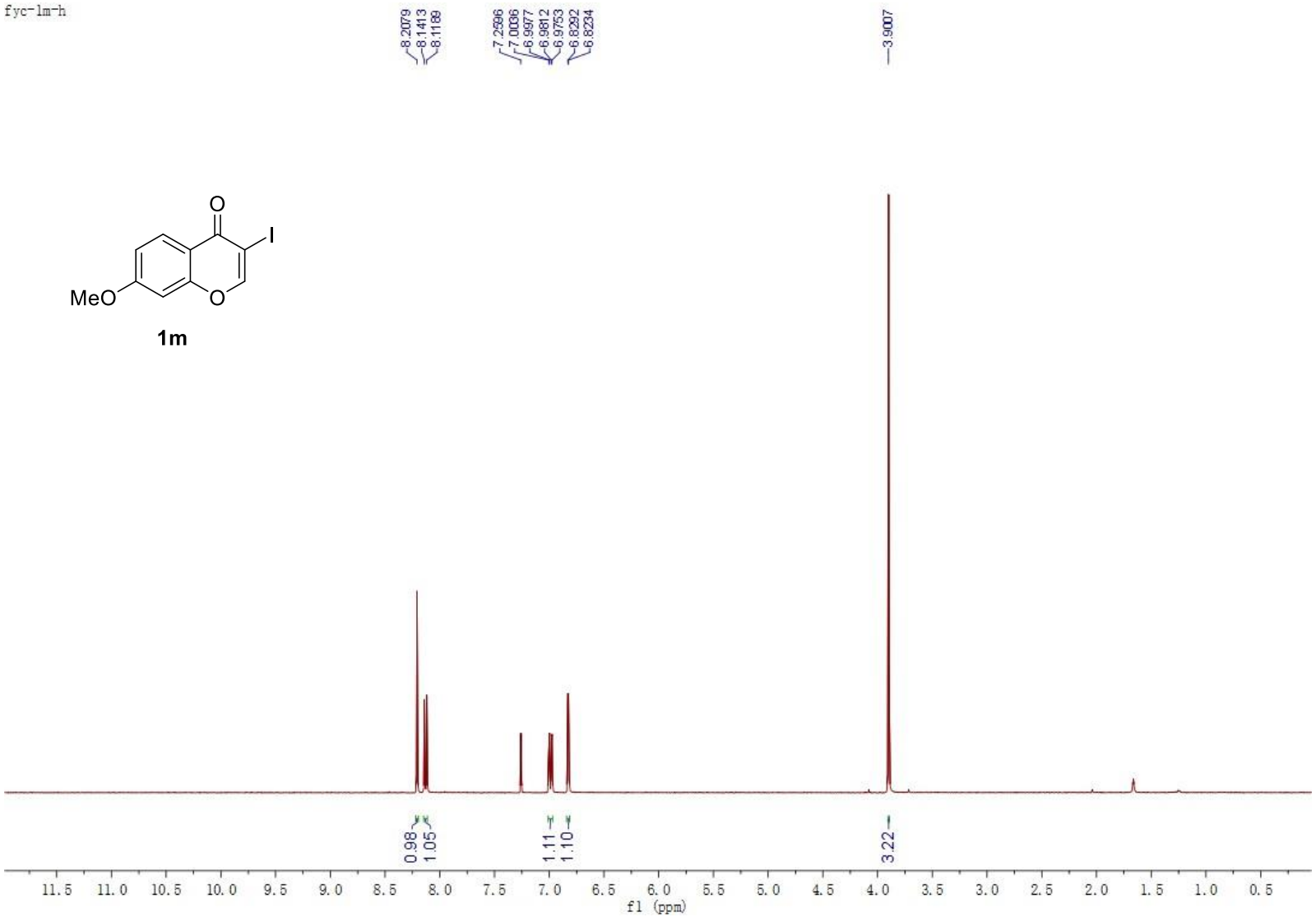

fyc-1j-c
171.84
158.06
157.87
136.46
132.32
121.95
119.93
117.29
110.36
87.49
77.48
77.16
76.84
NC
O
I
O
1j
158.8
158.4
158.0
157.6
157.2
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

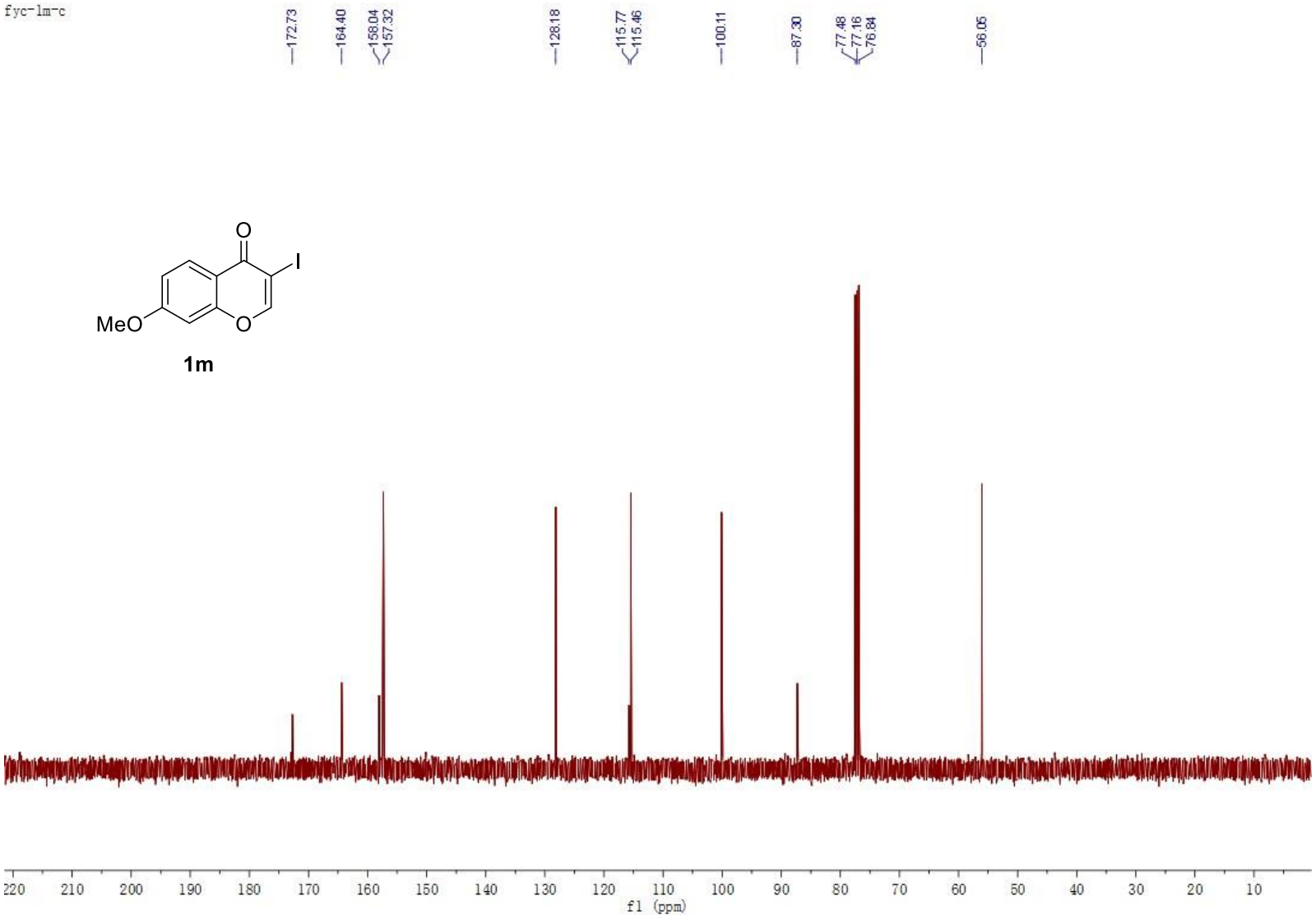

fyc-1k-h
8.8942
8.6520
8.5577
8.5372
7.9075
7.8849
3.3771
2.4995
O
O2N
I
O
1k
1.00
1.03
1.08
1.08
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


fyc-1k-c
172.34
159.70
158.65
144.58
128.64
121.67
120.91
120.81
87.23
40.14
39.94
39.73
39.52
39.31
39.10
38.89
O2N
O
I
O
1k
122.5
122.0
121.5
121.0
120.5
120.0
f1 (ppm)
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

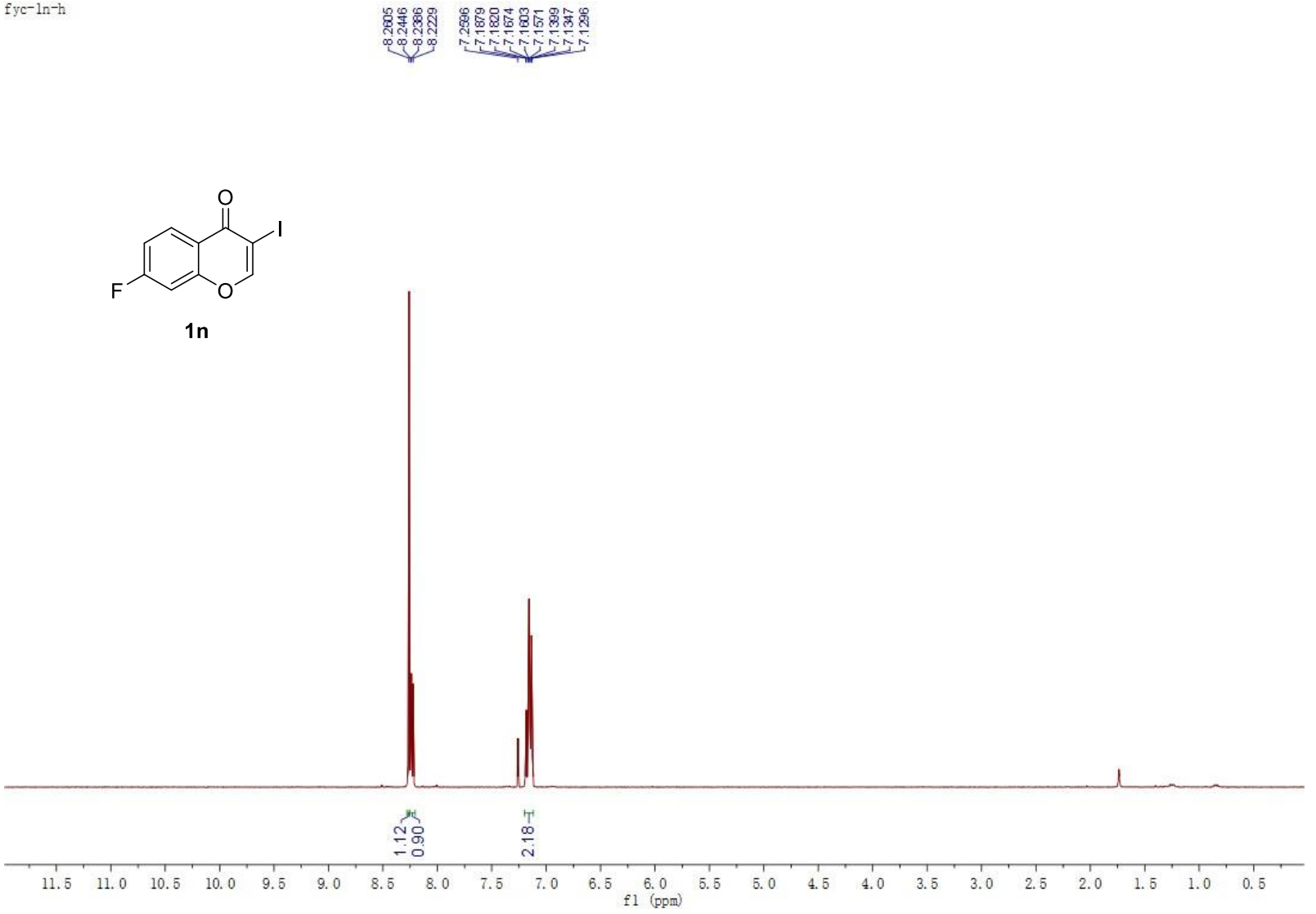

fyc-11-h
8.2407
8.1120
8.0906
7.2599
7.2518
7.2360
2.4771
O
I
Me
O
1I
1.00
1.14
2.14
3.26
f1 (ppm)

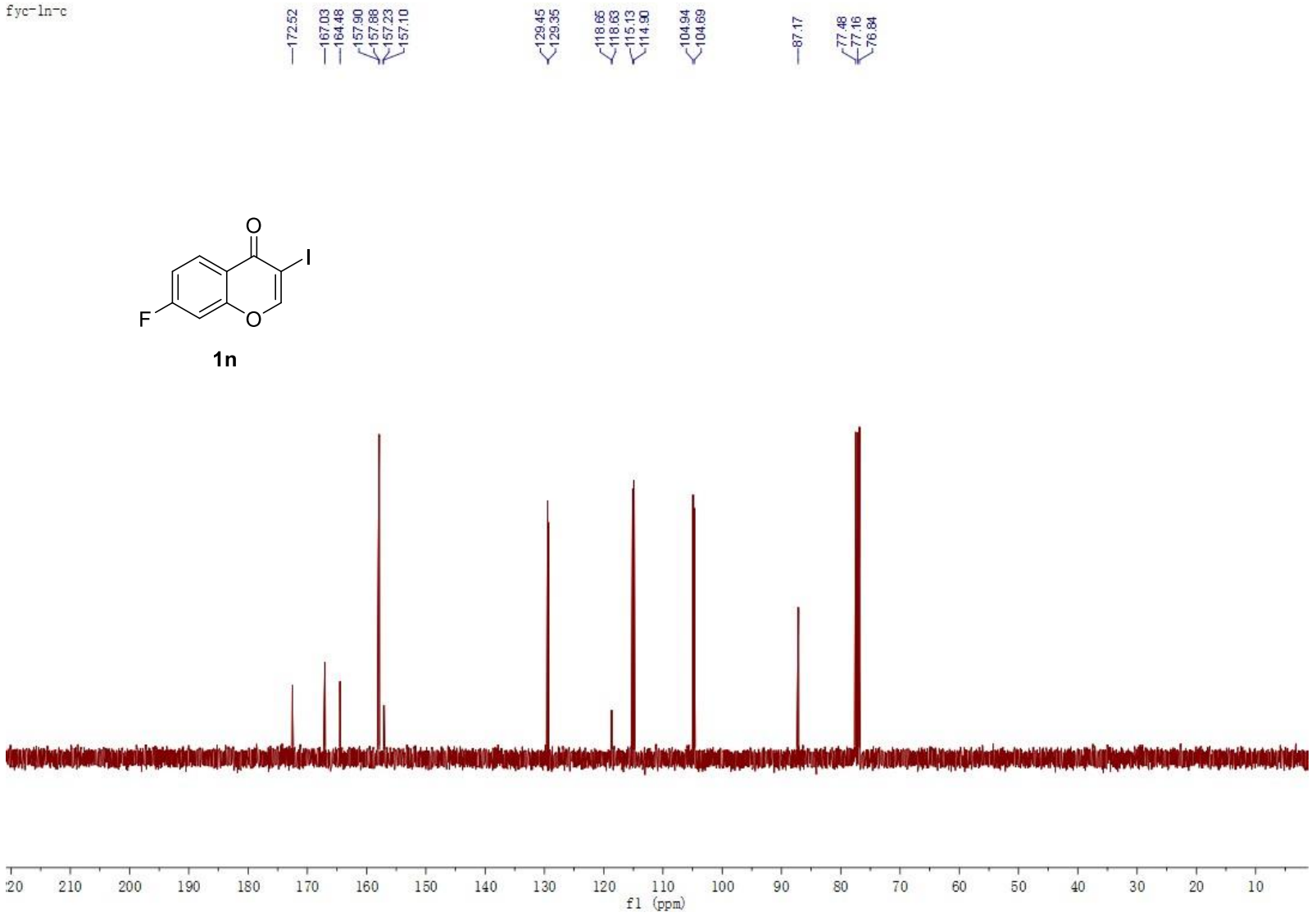

fyc-11-c
173.31
157.58
156.35
145.74
127.57
126.43
119.64
117.74
87.02
77.48
77.16
76.84
22.03
O
I
Me
O
1l
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


fyc-1m-h
8.2079
8.1413
8.1189
7.2596
7.0096
6.9977
6.9812
6.9753
6.8292
6.8234
3.9007
O
I
MeO
O
1m
0.98
1.05
1.11
1.10
3.22
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


fyc-1m-c
172.73
164.40
158.04
157.32
128.18
115.77
115.46
100.11
87.30
77.48
77.16
76.84
56.05
O
I
MeO
O
1m
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

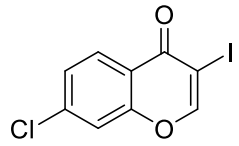
fyc-1n-h


8.2605
8.2446
8.2386
8.2229
7.2596
7.1879
7.1820
7.1674
7.1603
7.1571
7.1399
7.1347
7.1296
O
I
F
O
1n
1.12
0.90
2.18
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

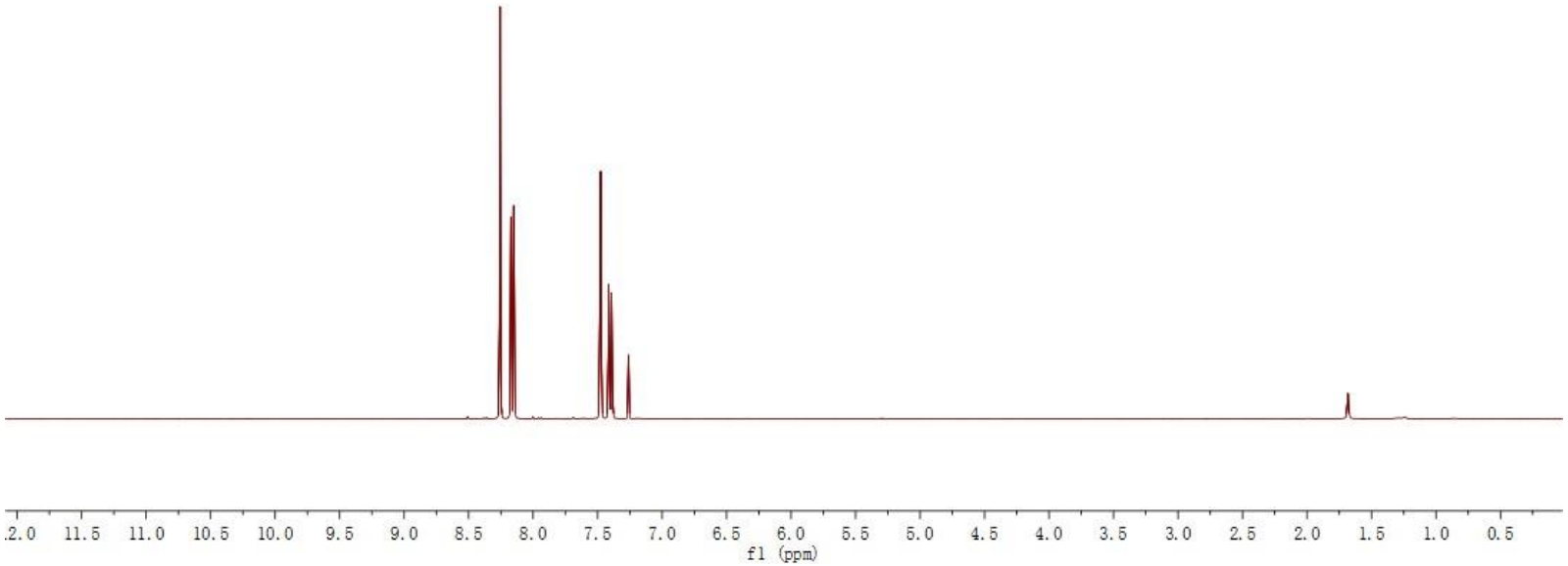

fyc-ln-c
172.52
167.03
164.48
157.90
157.88
157.23
157.10
129.45
129.35
118.65
118.63
115.13
114.90
104.94
104.69
87.17
77.48
77.16
76.84
O
I
F
O
1n
f1 (ppm)

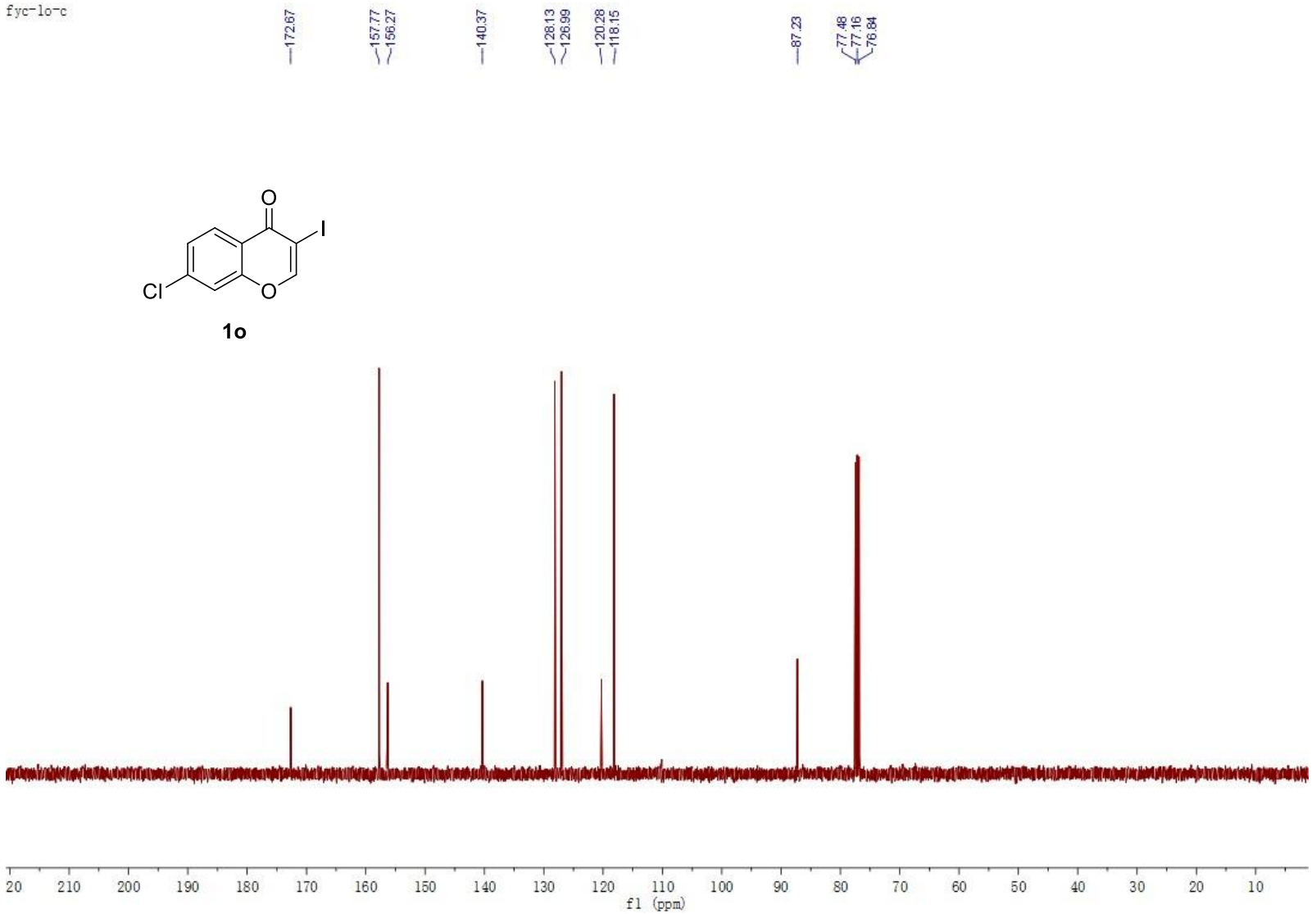
fyc-1o-h


8.2568
8.1714
8.1499
7.4801
7.4762
7.4139
7.4097
7.3924
7.3882
7.2601

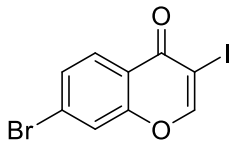

O
I
Cl
O

1o


.2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

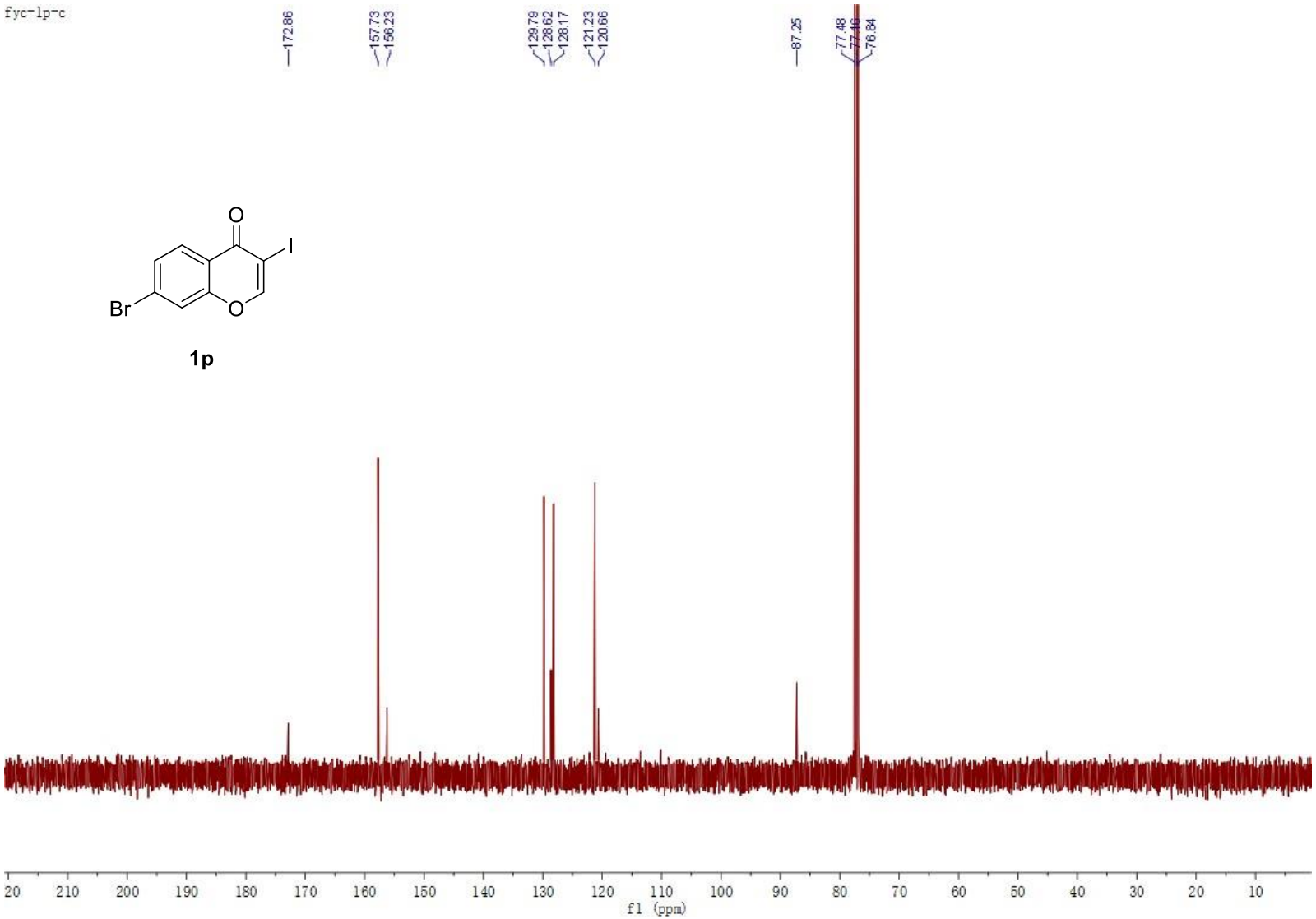

fyc-1o-c
172.67
157.77
156.27
140.37
128.13
126.99
120.28
118.15
87.23
77.48
77.16
76.84
O
I
Cl
O
1o
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

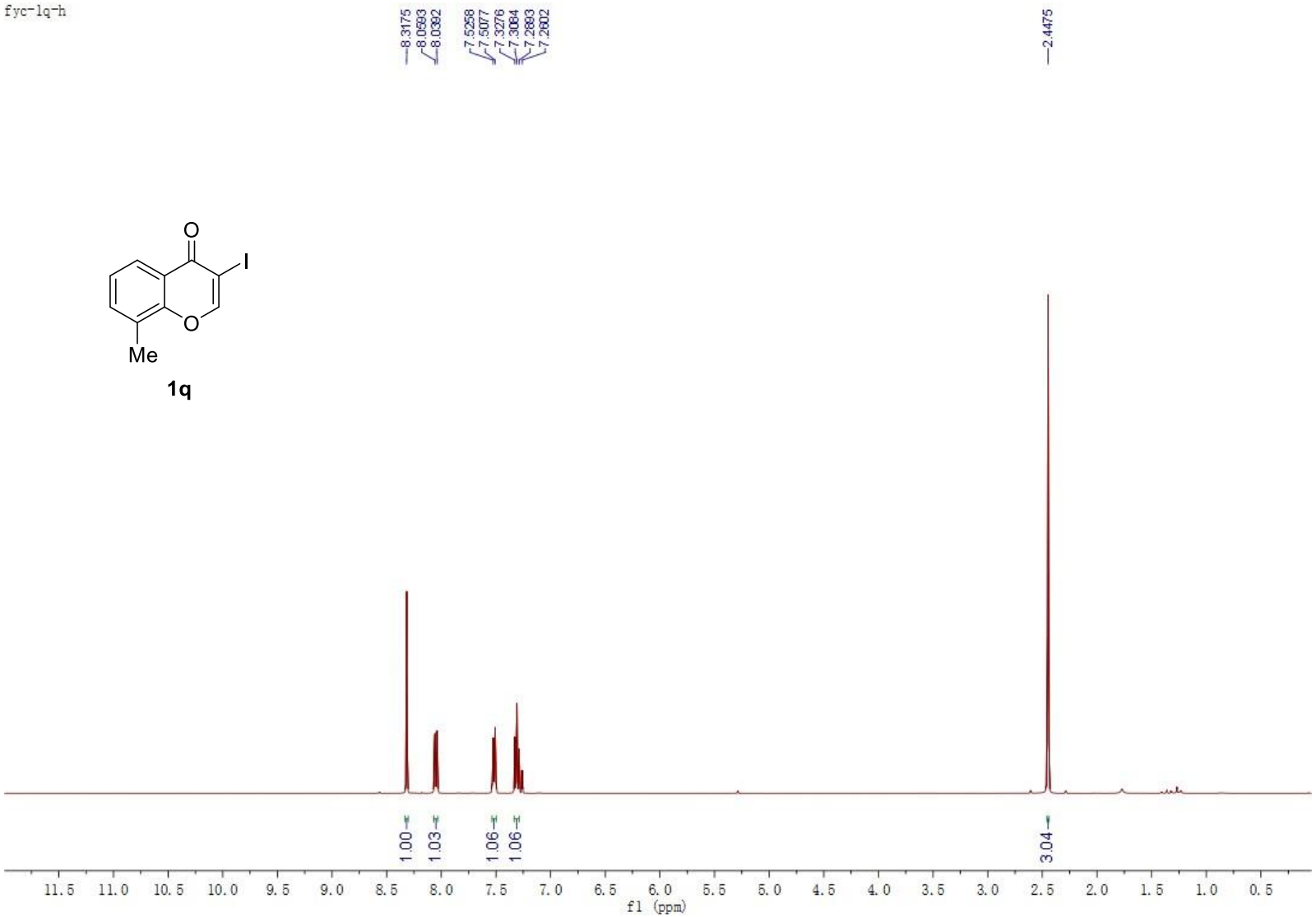
fyc-1p-h

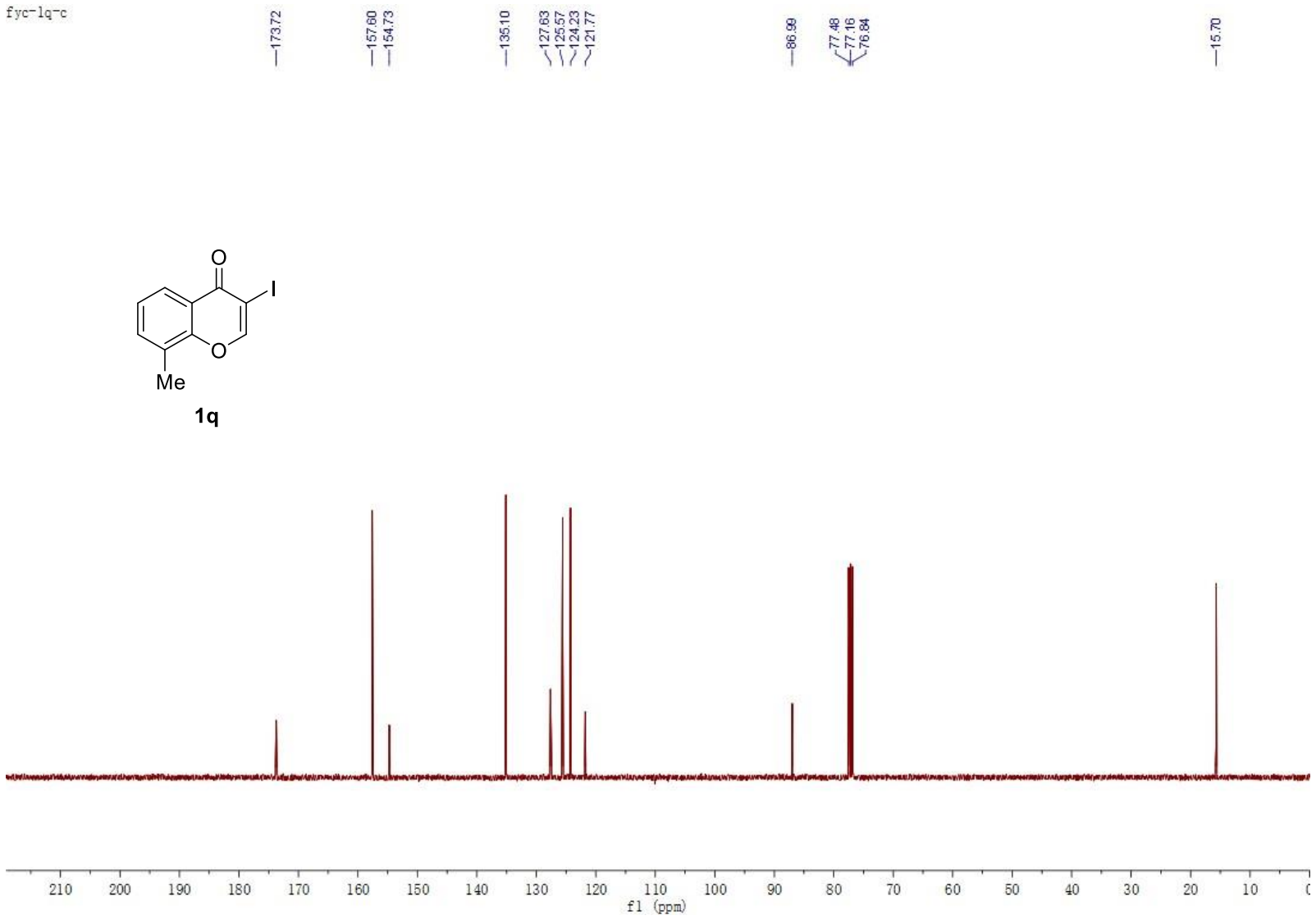

O
I
Br
O

1p

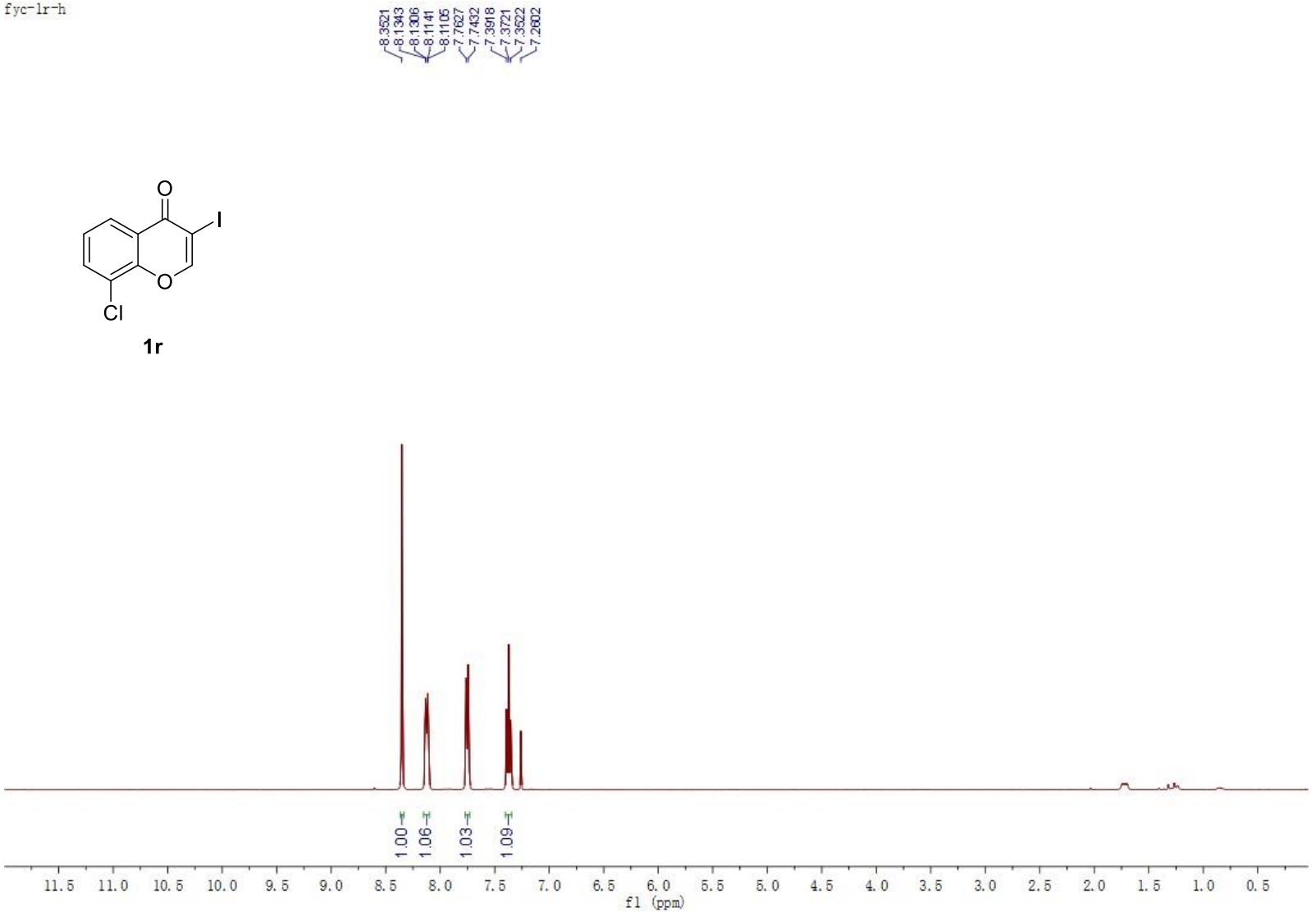
8.2569
8.1096
8.0883
7.6708
7.6665
7.5755
1.00
1.18
1.05
1.09
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

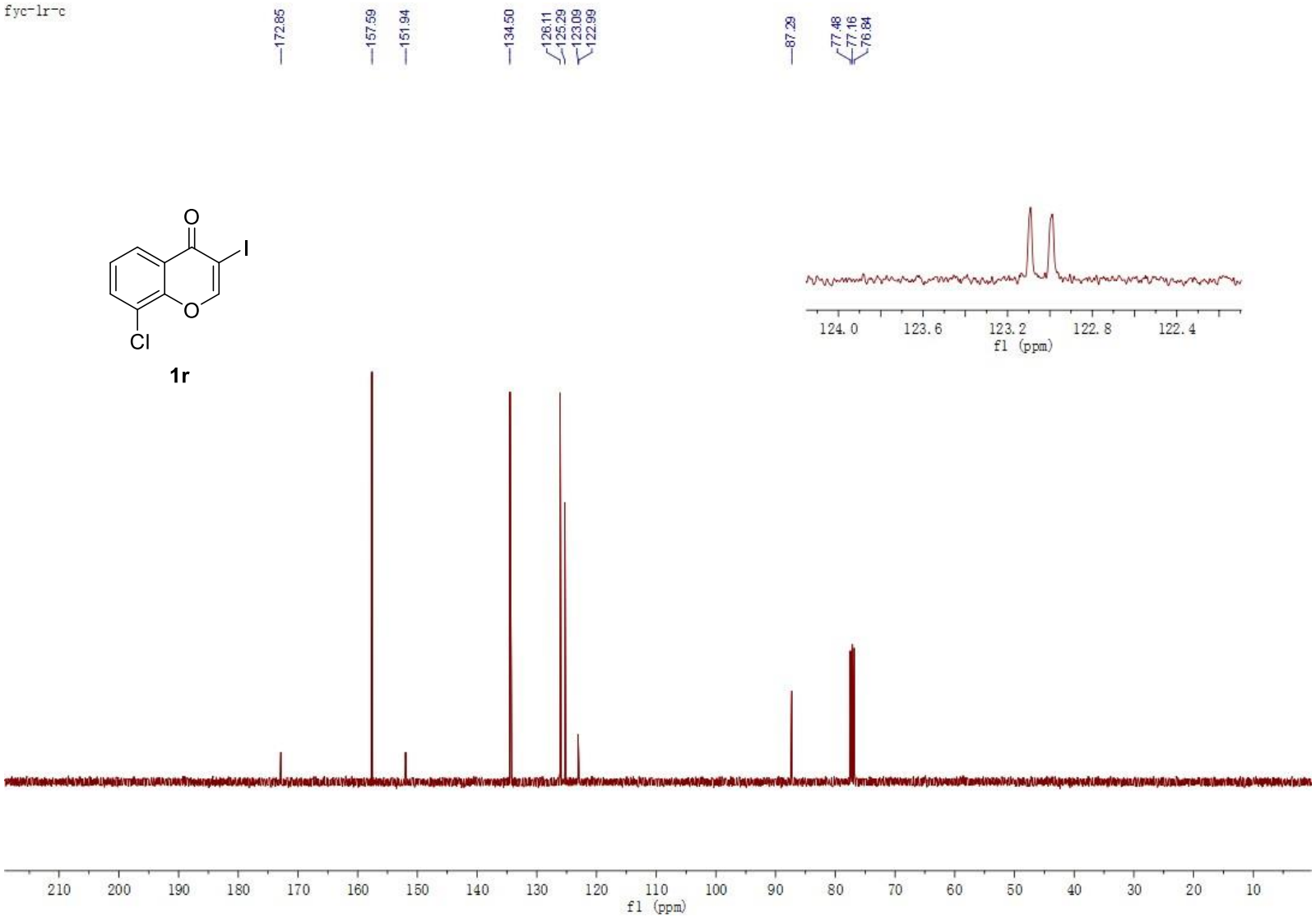

fyc-1p-c
172.86
157.73
156.23
129.79
128.62
128.17
121.23
120.66
87.25
77.48
77.16
76.84
O
I
Br
O
1p
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


fyc-1q-h
8.3175
8.0593
8.0392
7.5258
7.5077
7.3276
7.3064
7.2893
7.2602
2.4475
O
I
O
Me
1q
1.00
1.03
1.06
1.06
3.04
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

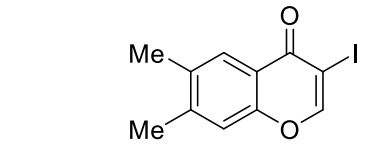

fyc-1q-c
173.72
157.60
154.73
135.10
127.63
125.57
124.23
121.77
86.99
77.48
77.16
76.84
15.70
O
I
O
Me
1q
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

fyc-1r-h

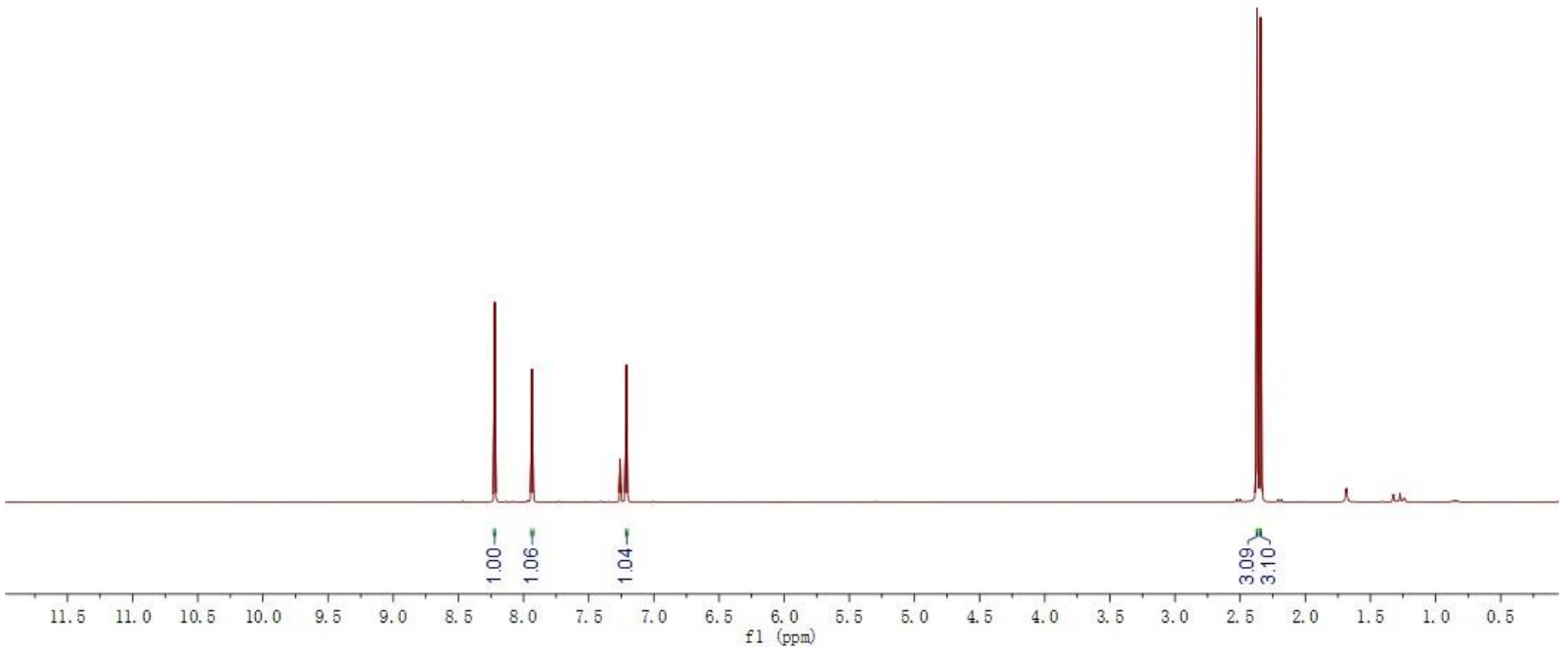

8.3521
8.1343
8.1306
8.1141
8.1105
7.7627
7.7432
7.3918
7.3721
7.3522
7.2602
O
I
O
Cl
1r
1.00
1.06
1.03
1.09
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

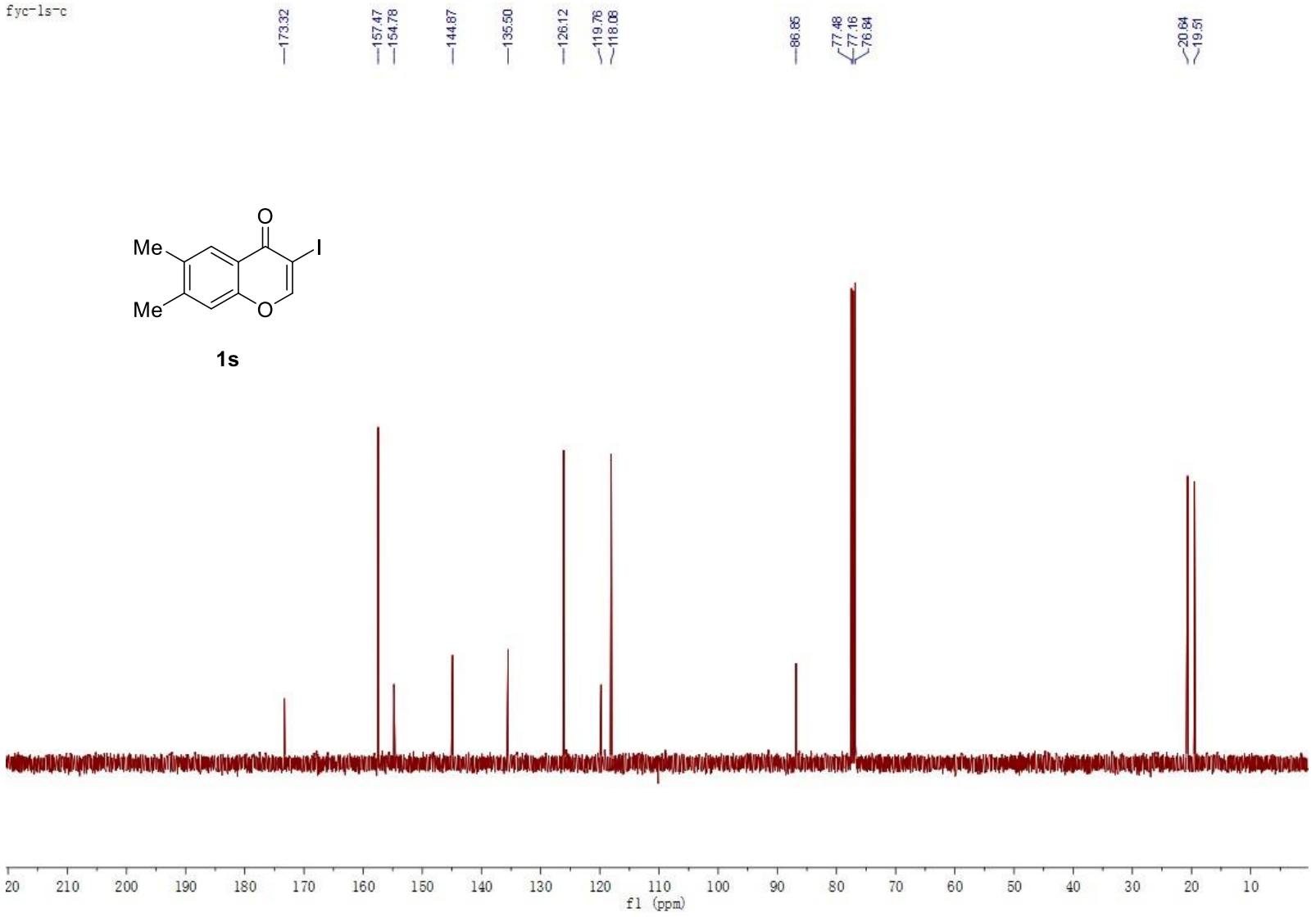

fyc-1r-c
172.85
157.59
151.94
134.50
126.11
125.29
123.09
122.99
87.29
77.48
77.16
76.84
O
I
O
Cl
1r
124.0
123.6
123.2
122.8
122.4
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

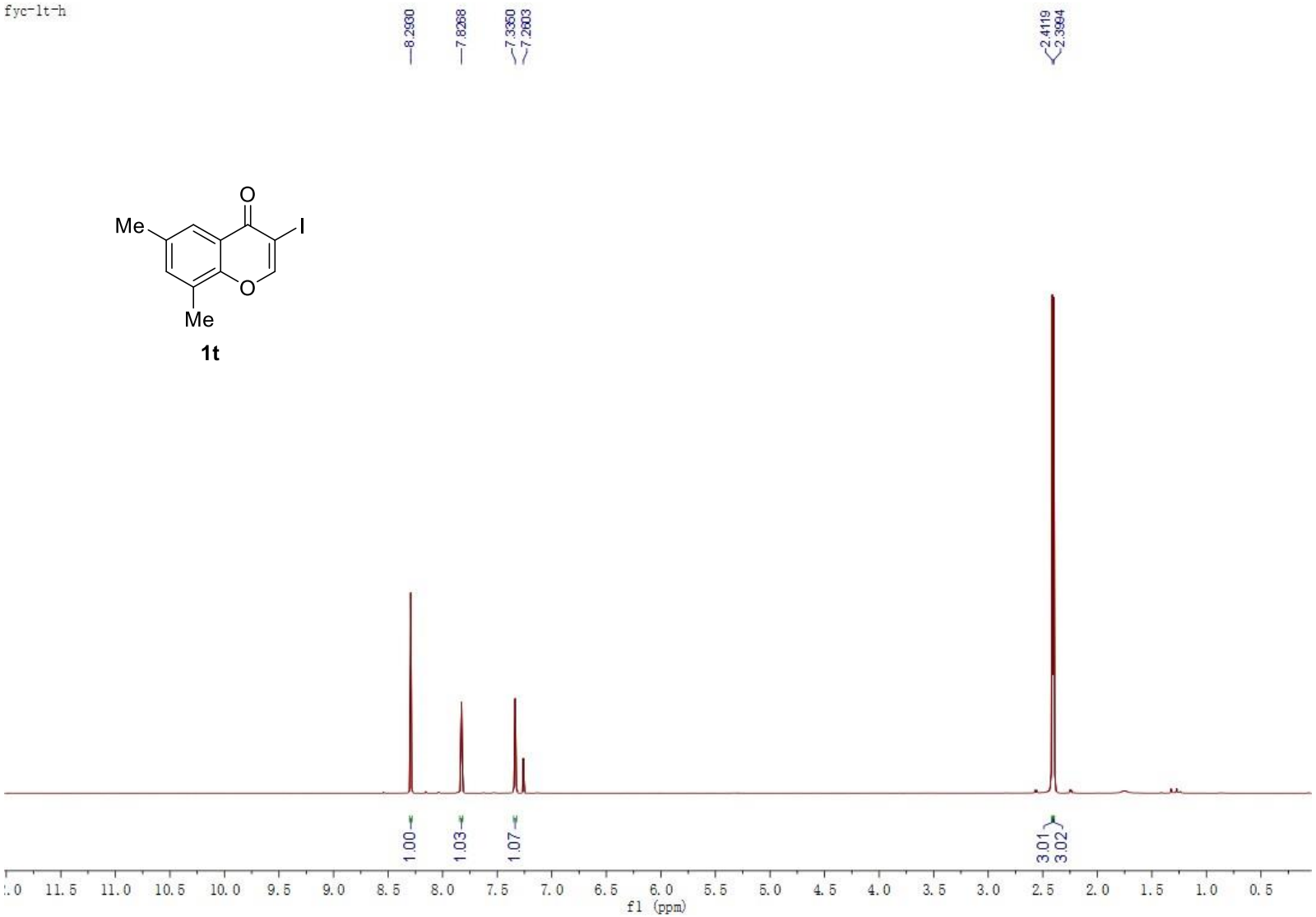
fyc-1s-h

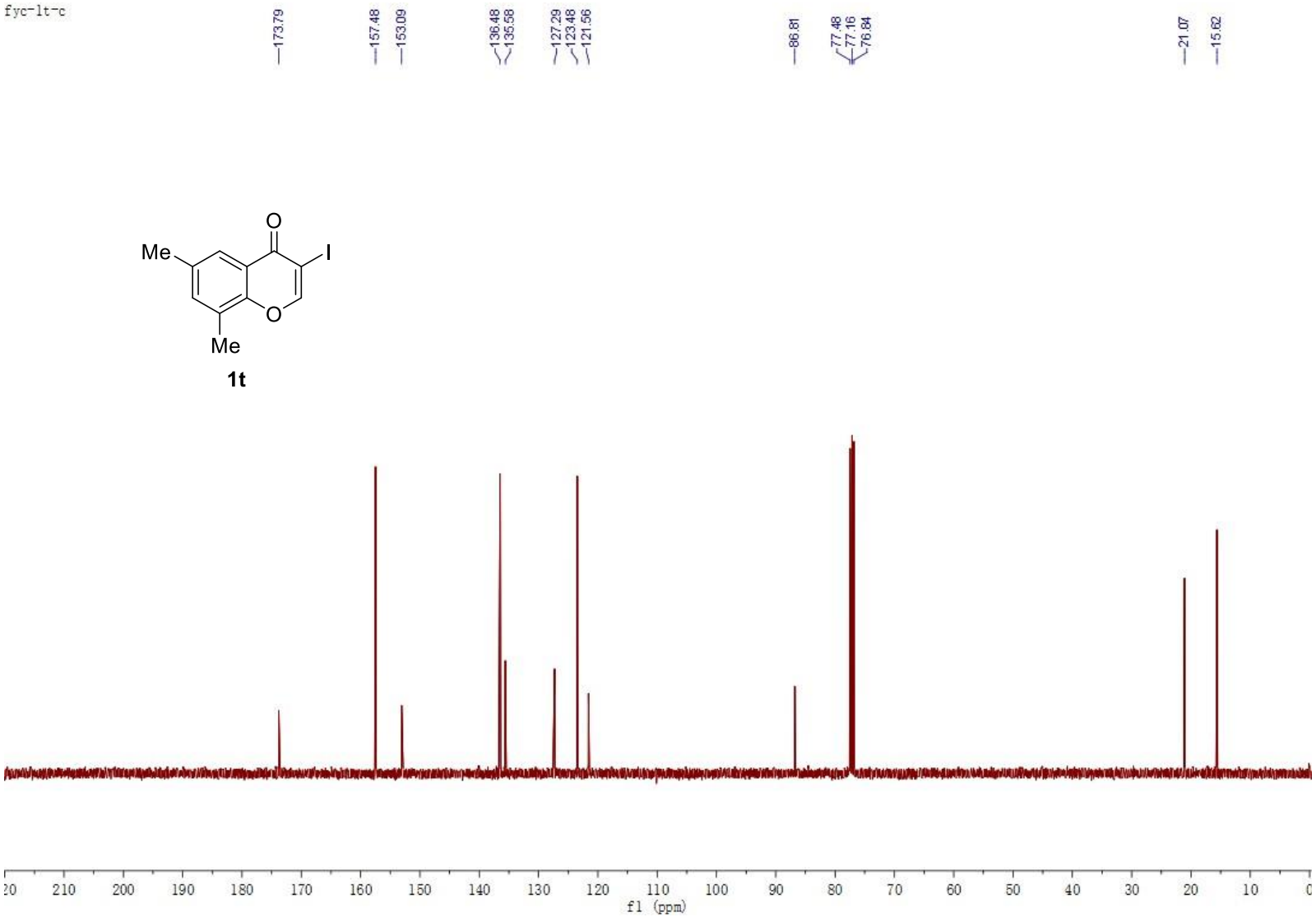

O
Me
I
Me
O

1s


8.2209
7.9396
7.2596
7.2102
2.3696
2.3436
1.00
1.06
1.04
3.09
3.10
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

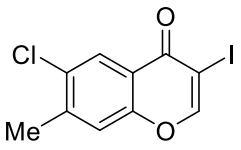

fyc-1s-c
173.32
157.47
154.78
144.87
135.50
126.12
119.76
118.08
86.85
77.48
77.16
76.84
20.64
19.51
O
Me
I
Me
O
1s
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


fyc-1t-h
8.2930
7.8268
7.3350
7.2603
2.4119
2.3994
O
Me
I
O
Me
1t
1.00
1.03
1.07
3.01
3.02
f1 (ppm)


fyc-1t-c
173.79
157.48
153.09
136.48
135.58
127.29
123.48
121.56
86.81
77.48
77.16
76.84
21.07
15.62
O
Me
I
O
Me
f1 (ppm)

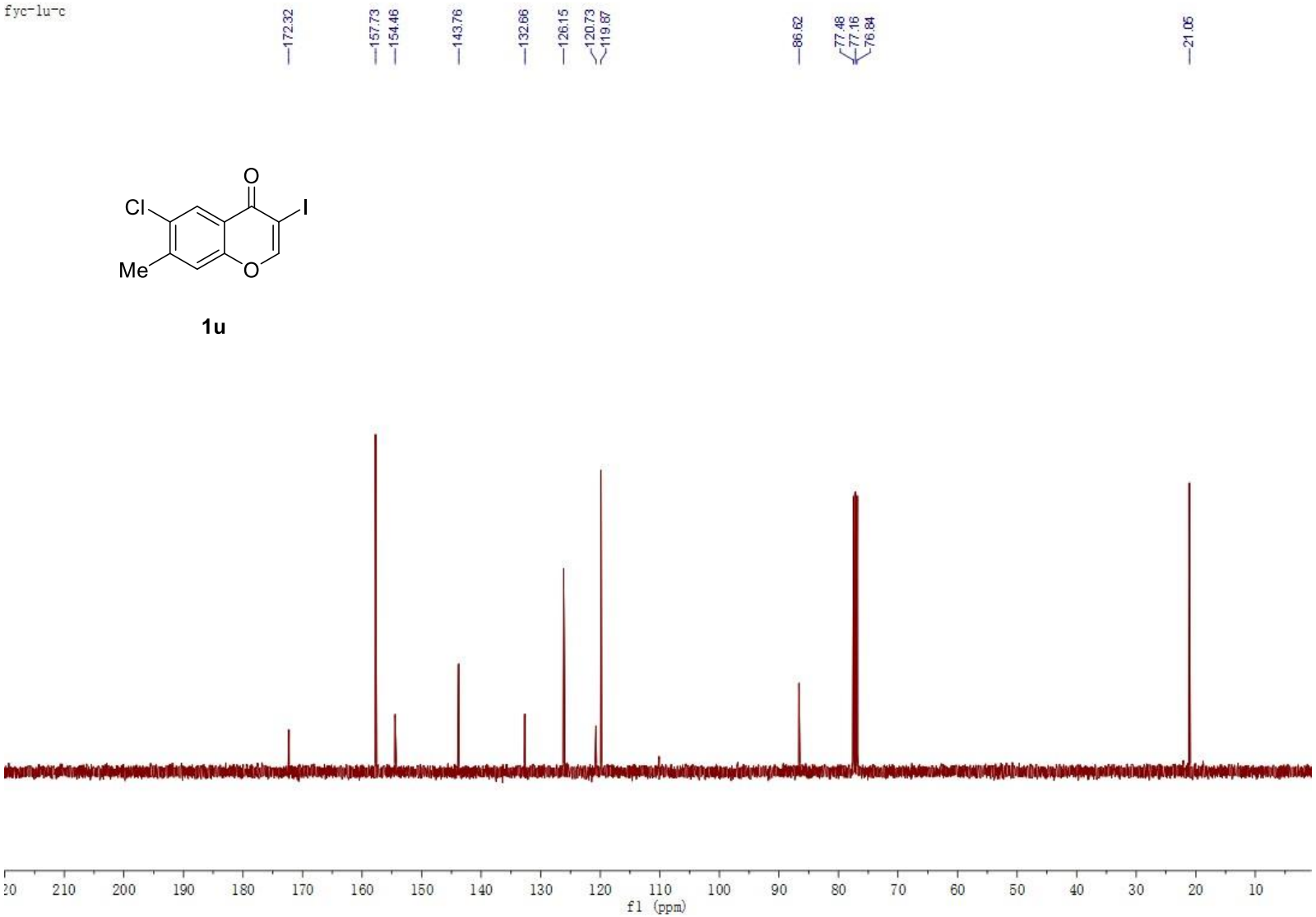
1t

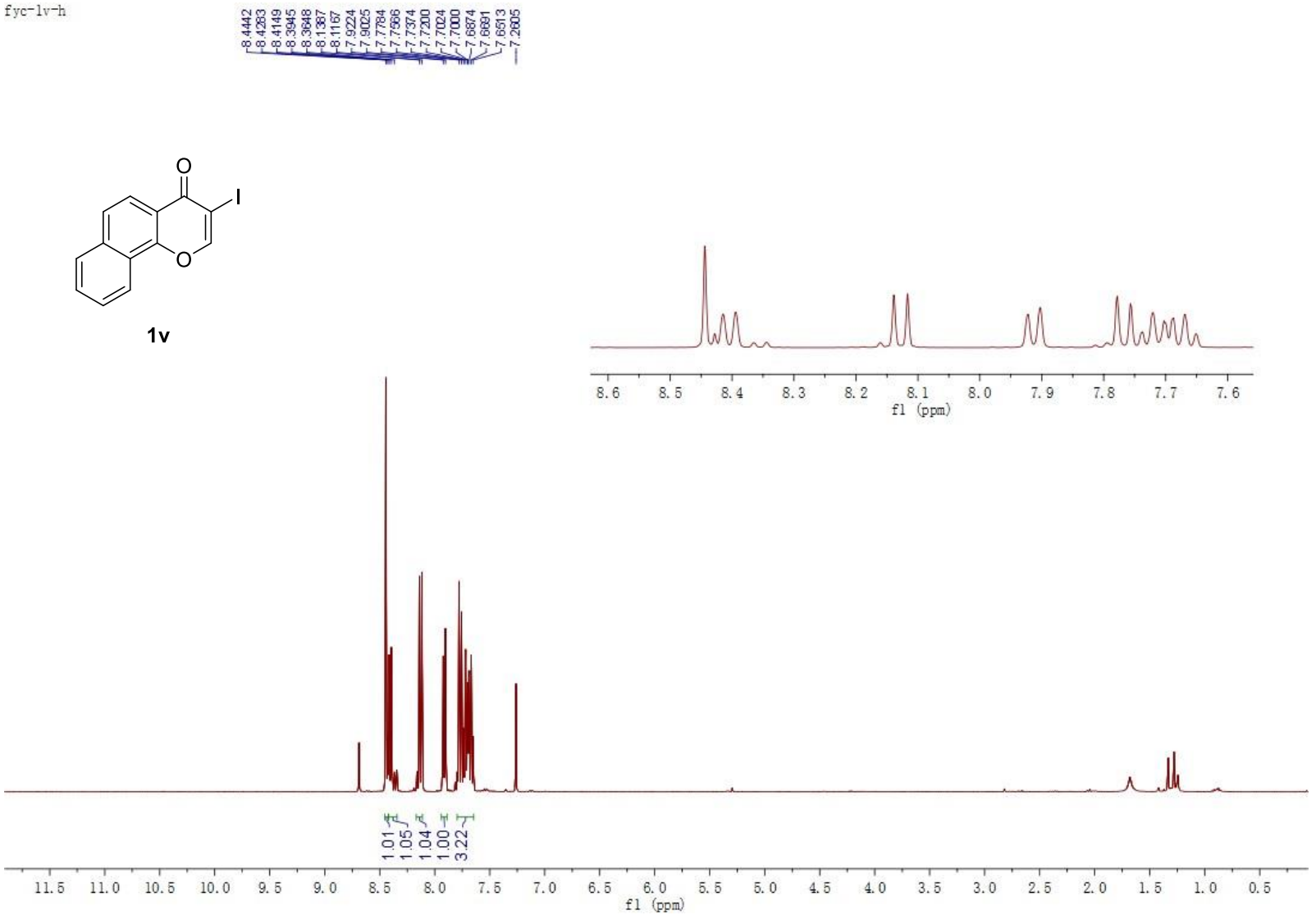
fyc-1u-h

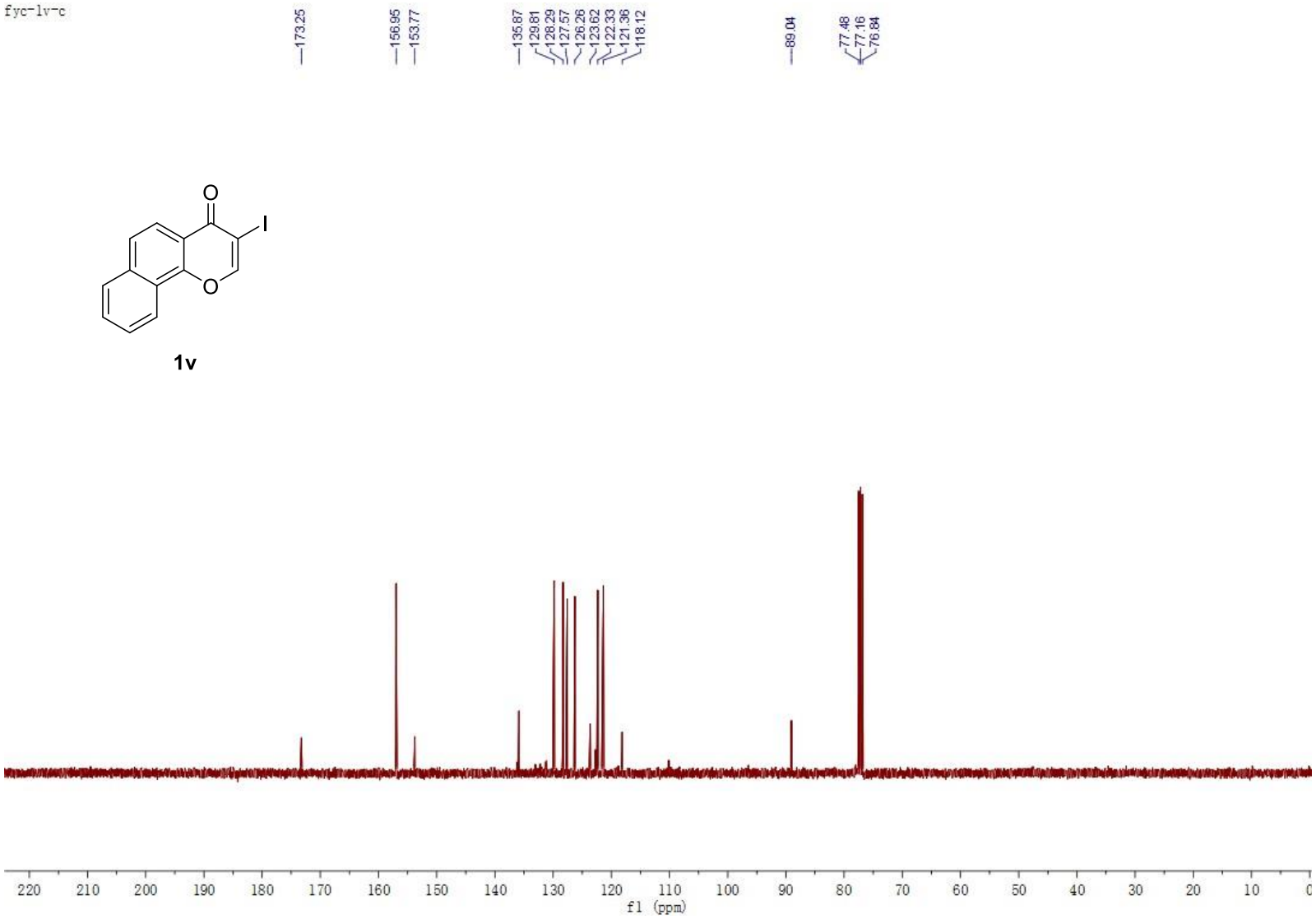

O
Cl
I
Me
O

1u

8.2410
8.1464
7.3365
7.2603
2.4842
1.00
1.02
1.08
3.18
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


fyc-1u-c
172.32
157.73
154.46
143.76
132.66
126.15
120.73
119.87
86.62
77.48
77.16
76.84
21.05
O
Cl
I
Me
O
1u
f1 (ppm)

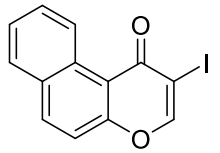

fyc-1v-h
8.4442
8.4283
8.4149
8.3945
8.3648
8.1387
8.1167
7.9224
7.9025
7.7784
7.7566
7.7374
7.7200
7.7024
7.7000
7.6874
7.6691
7.6513
7.2605
O
I
O
1v
8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6
f1 (ppm)
1.01
1.05
1.04
1.00
3.22
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


fyc-1v-c
173.25
156.95
153.77
135.87
129.81
128.29
127.57
126.26
123.62
122.33
121.36
118.12
89.04
77.48
77.16
76.84
O
I
O
1v
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

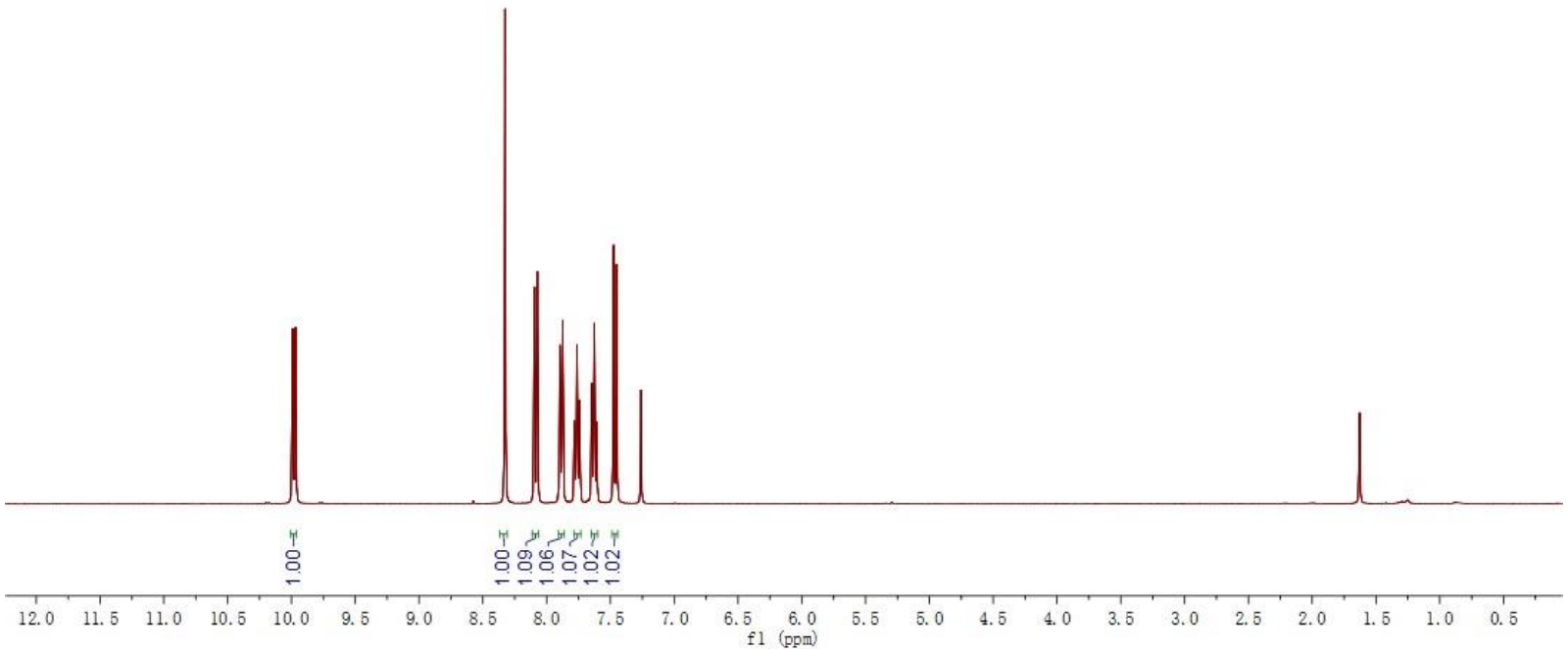
fyc-1w-h

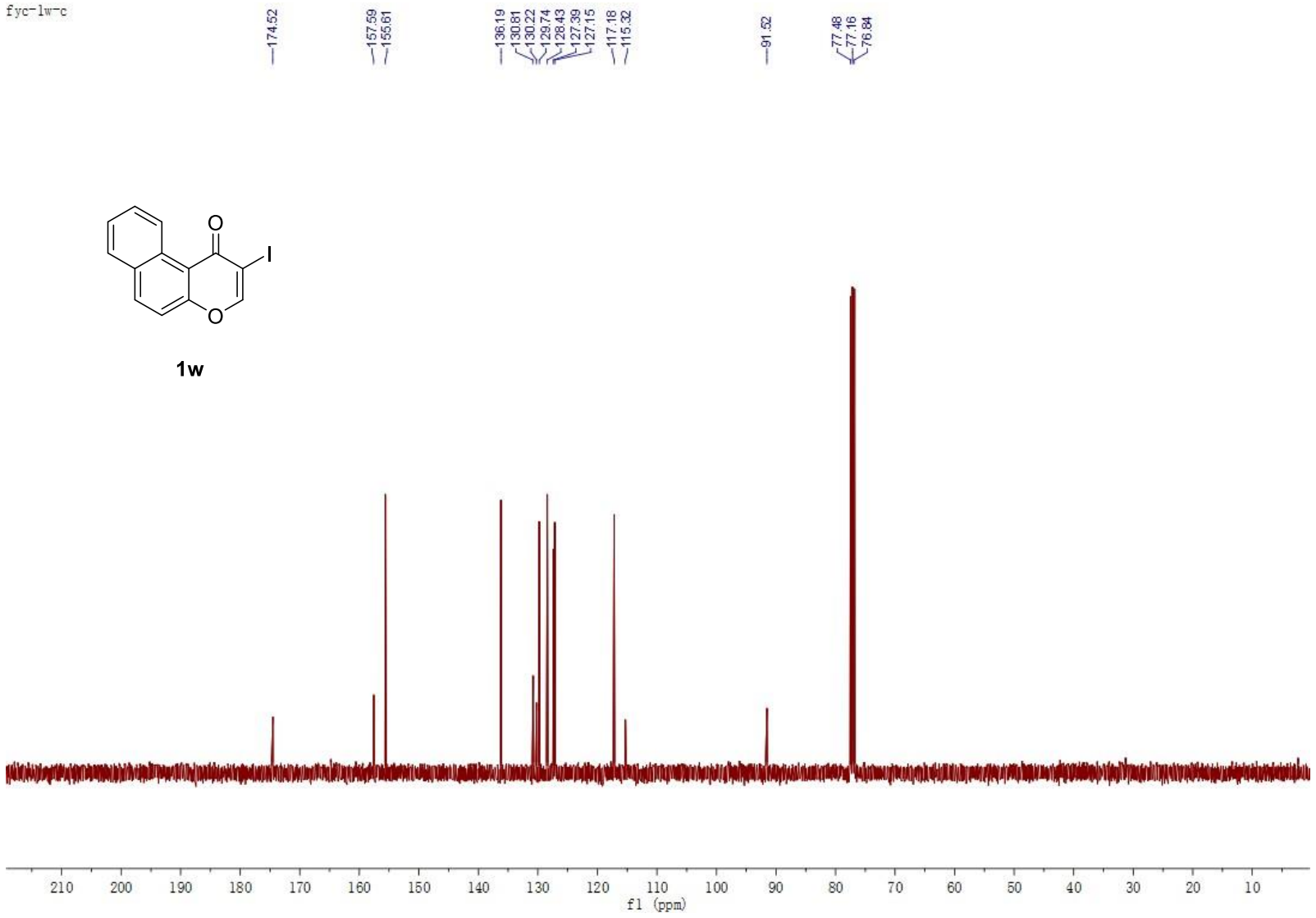
9.9899
9.9883

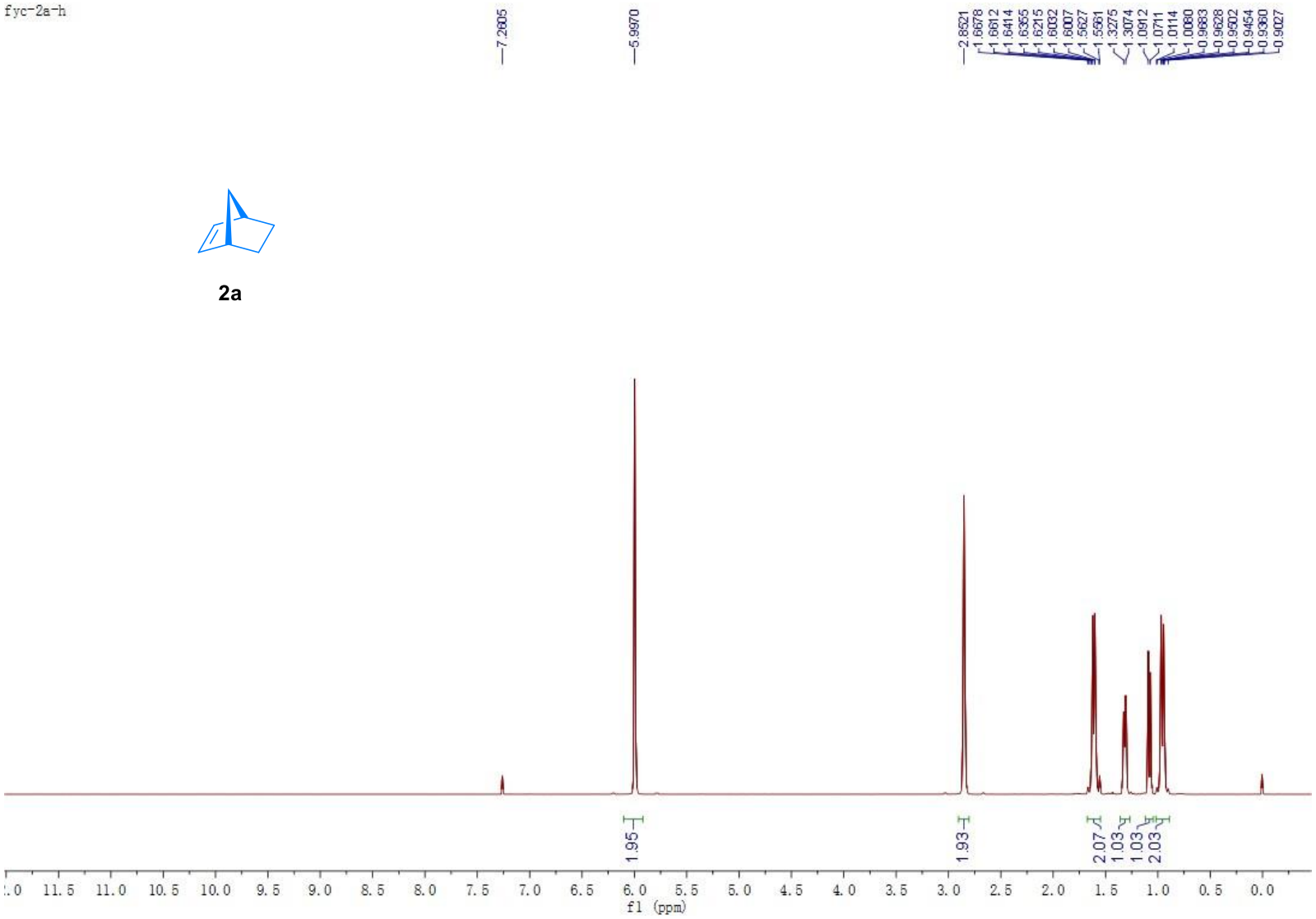
8.3252
8.0951
8.0724
7.8947
7.8747
7.7818
7.7613
7.7428
7.6457
7.6264
7.6064
7.4741
7.4514
7.2599



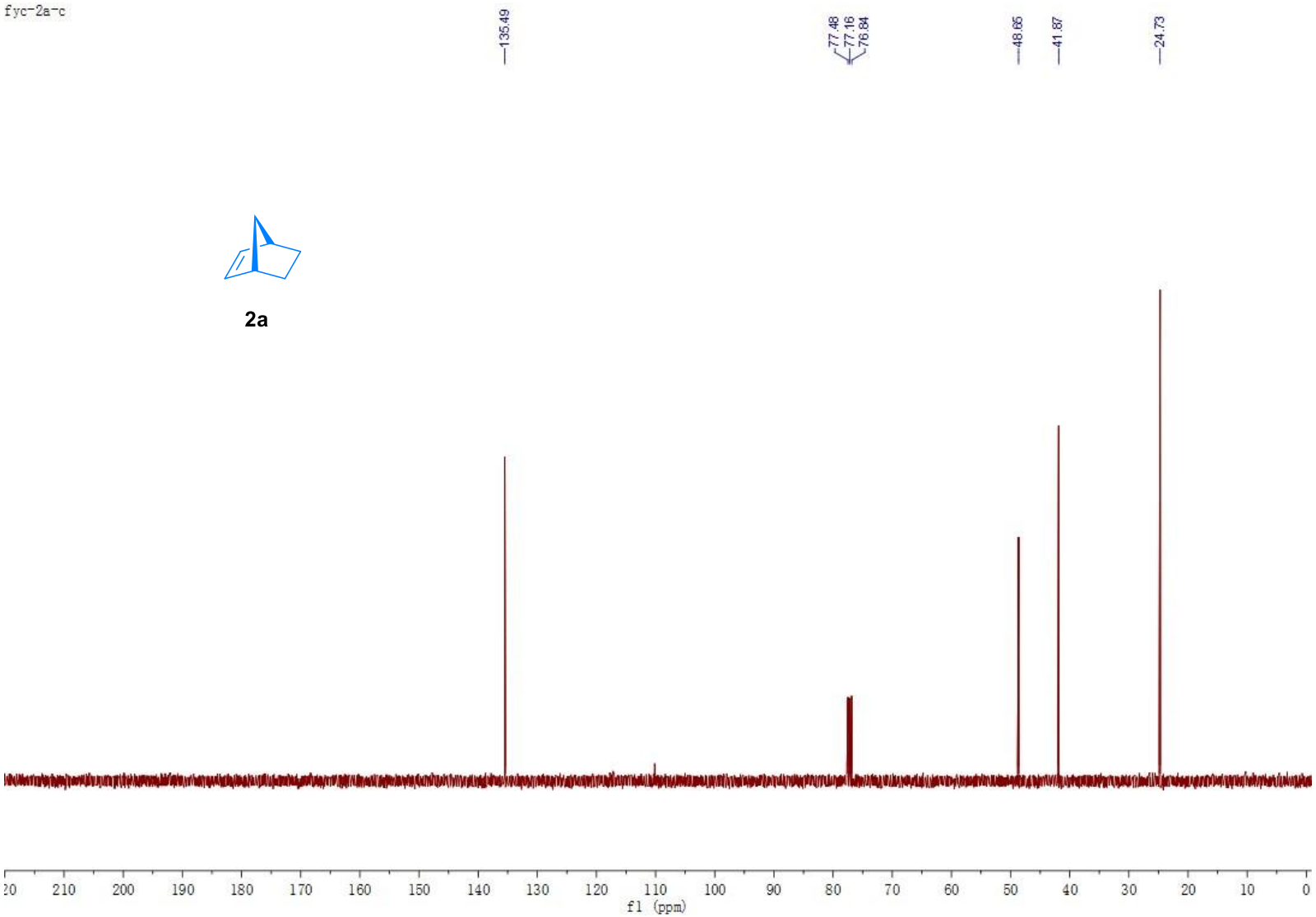
1w




fyc-1w-c
174.52
157.59
155.61
136.19
130.81
130.22
129.74
128.43
127.39
127.15
117.18
115.32
91.52
77.48
77.16
76.84
O
I
O
1w
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

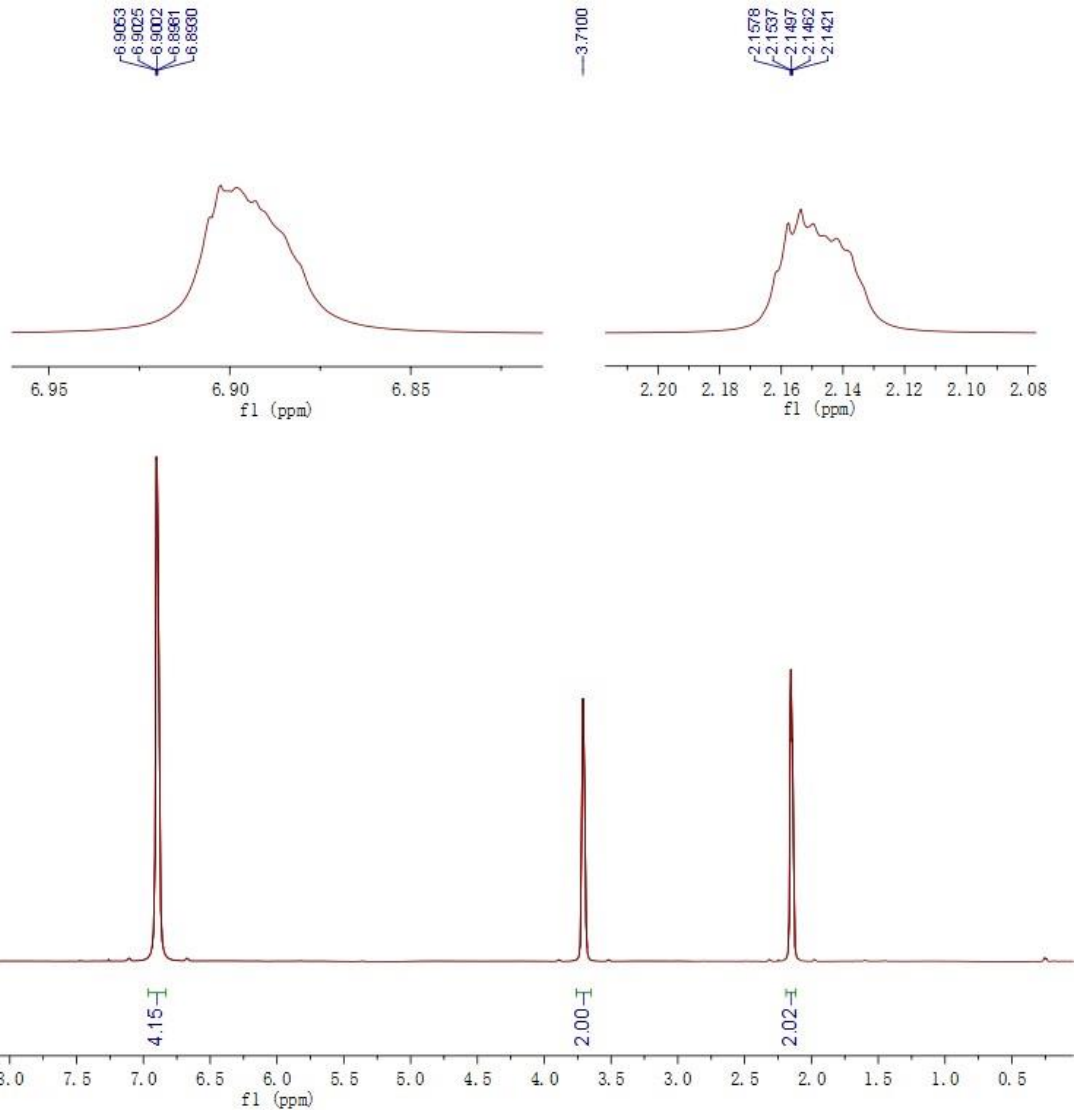

fyc-2a-h
7.2605
5.9970
2.8521
1.6678
1.6612
1.6414
1.6365
1.6215
1.6032
1.6007
1.5627
1.5561
1.3275
1.3074
1.0912
1.0711
1.0114
1.0060
0.9683
0.9628
0.9502
0.9454
0.9360
0.9027
1.95
1.93
2.07
1.03
1.03
2.03
f1 (ppm)

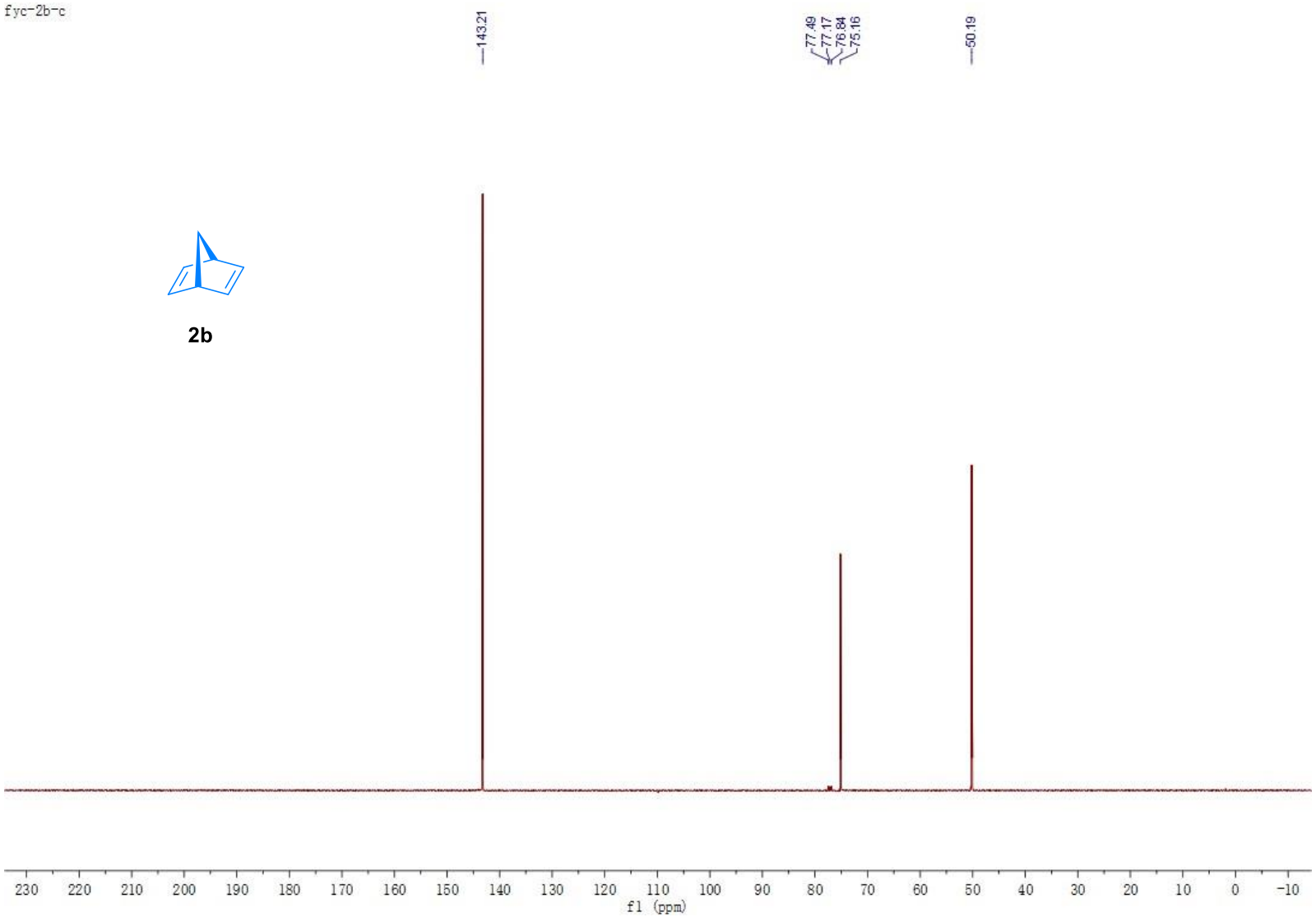
2a

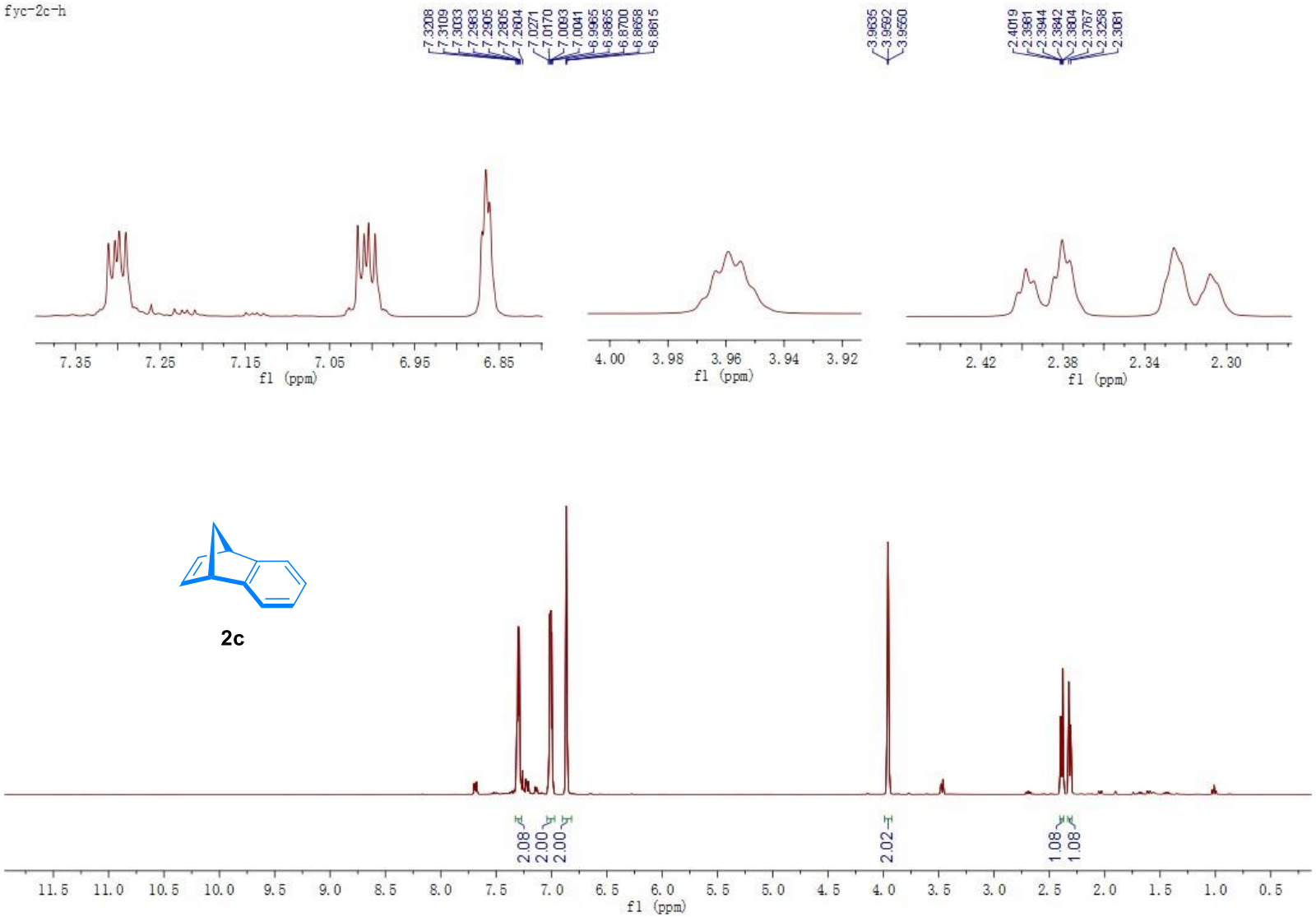

fyc-2a-c
135.49
77.48
77.16
76.84
48.65
41.87
24.73
2a
f1 (ppm)

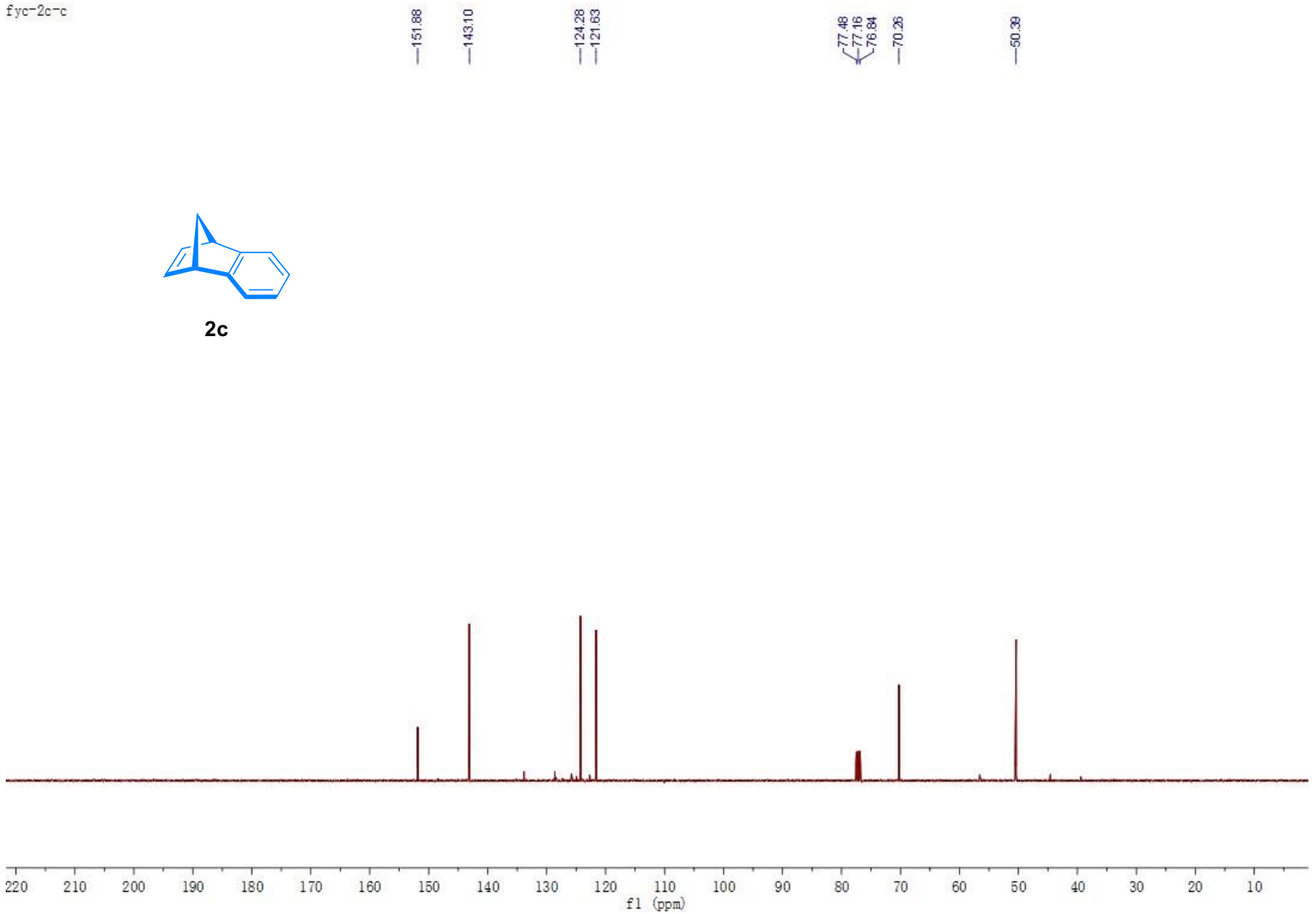
fyc-2b-h

2b

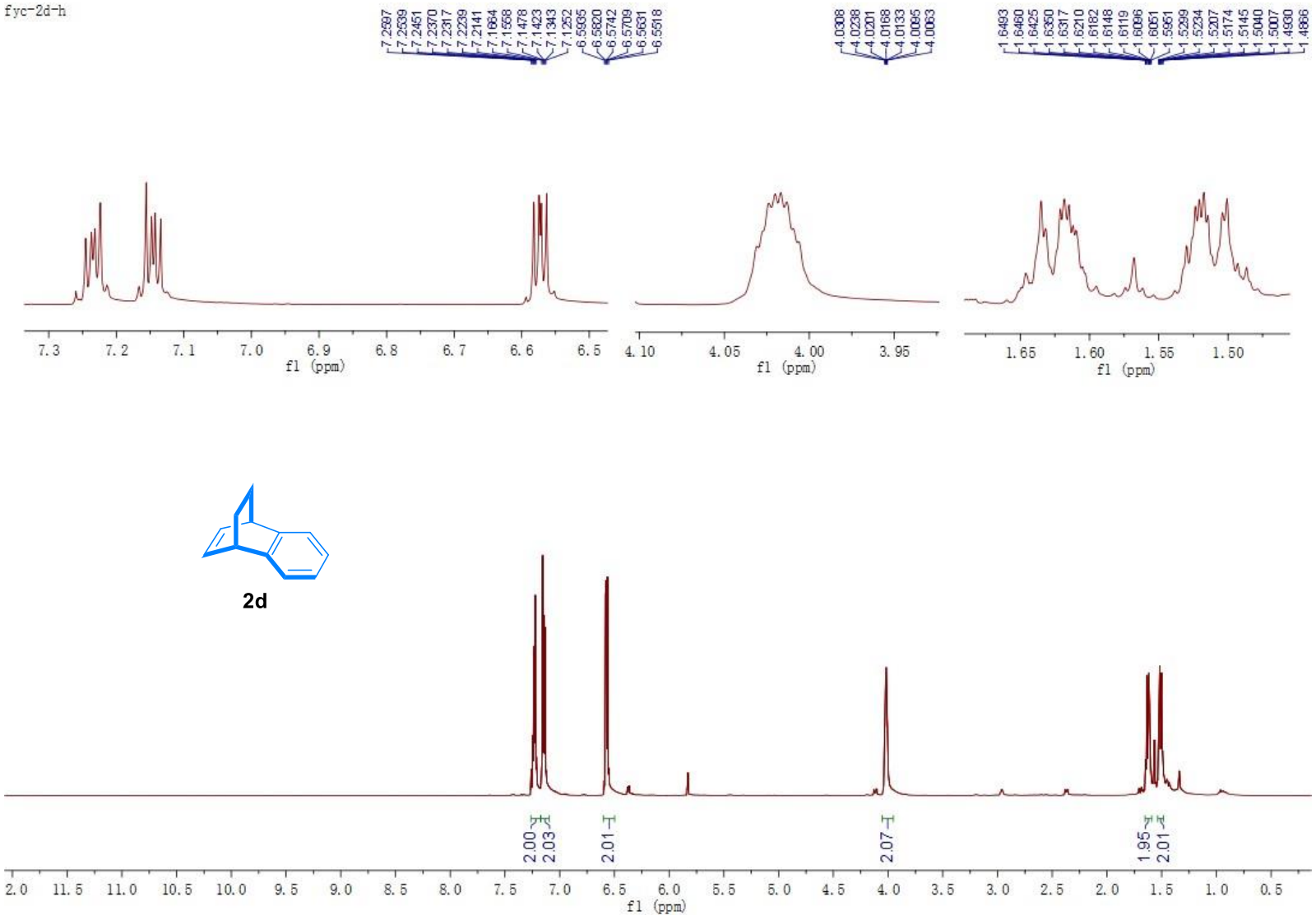

6.9053
6.9025
6.9002
6.8961
6.8930
3.7100
2.1578
2.1537
2.1497
2.1462
2.1421
6.95
6.90
6.85
f1 (ppm)
2.20
2.18
2.16
2.14
2.12
2.10
2.08
f1 (ppm)
4.15
2.00
2.02
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

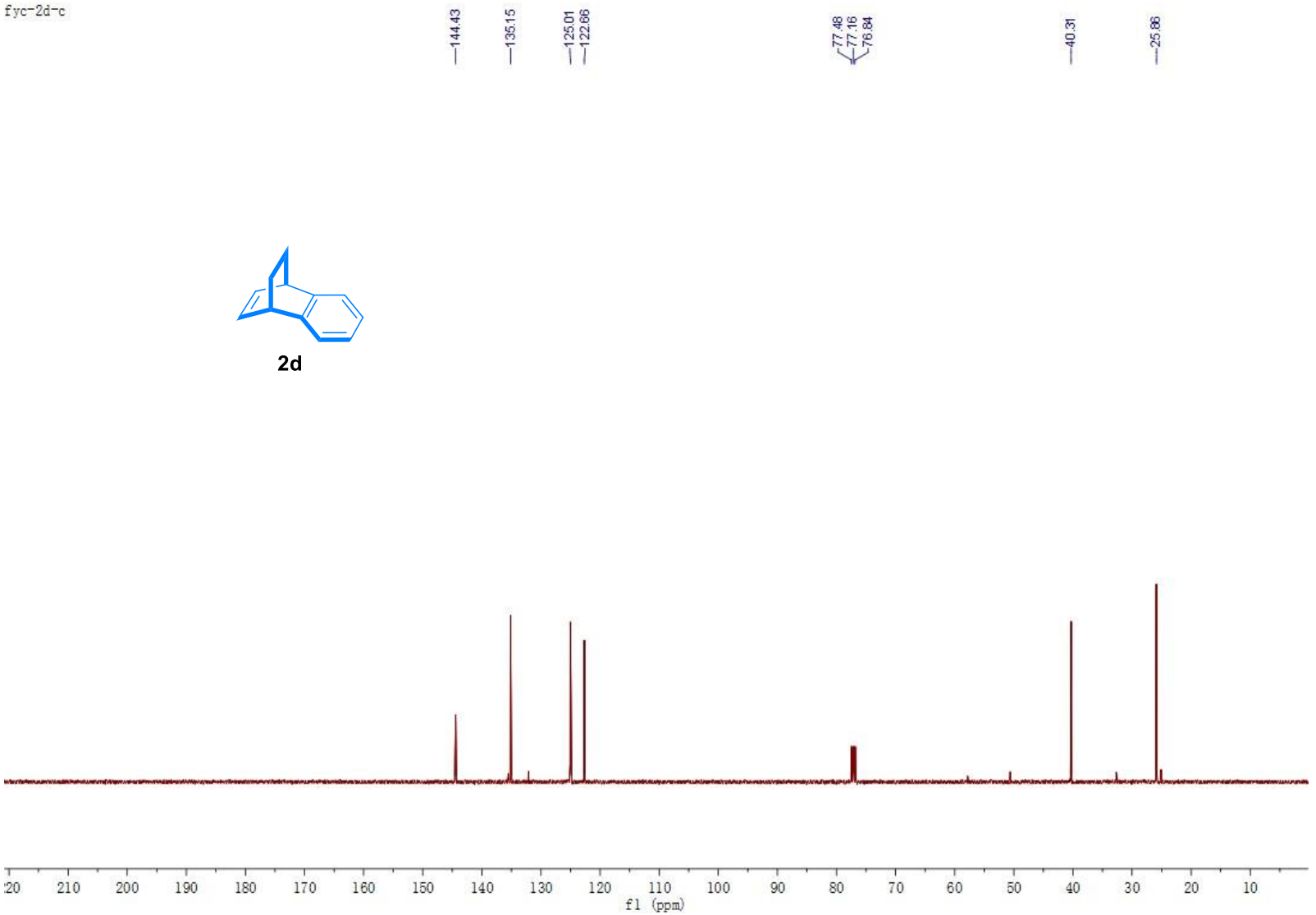

fyc-2b-c
143.21
77.49
77.17
76.84
75.16
50.19
2b
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

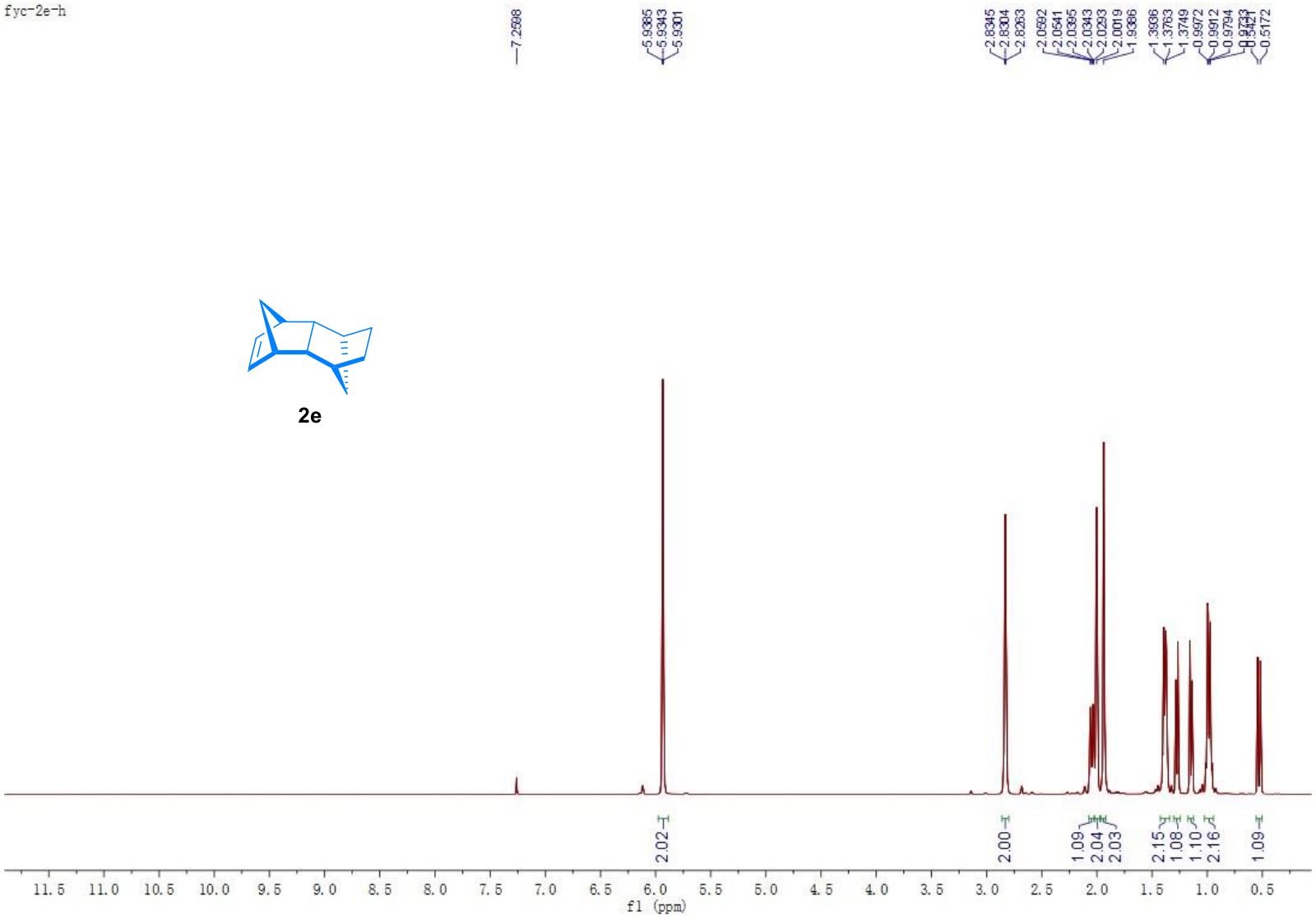

fyc-2c-h
7.3208
7.3109
7.3033
7.2963
7.2905
7.2805
7.2604
7.0271
7.0170
7.0083
7.0041
6.9965
6.9865
6.8700
6.8658
6.8615
3.9635
3.9592
3.9550
2.4019
2.3961
2.3944
2.3842
2.3804
2.3767
2.3258
2.3061
7.35
7.25
7.15
7.05
6.95
6.85
f1 (ppm)
4.00
3.98
3.96
3.94
3.92
f1 (ppm)
2.42
2.38
2.34
2.30
f1 (ppm)
2c
2.08
2.00
2.00
2.02
1.08
1.08
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

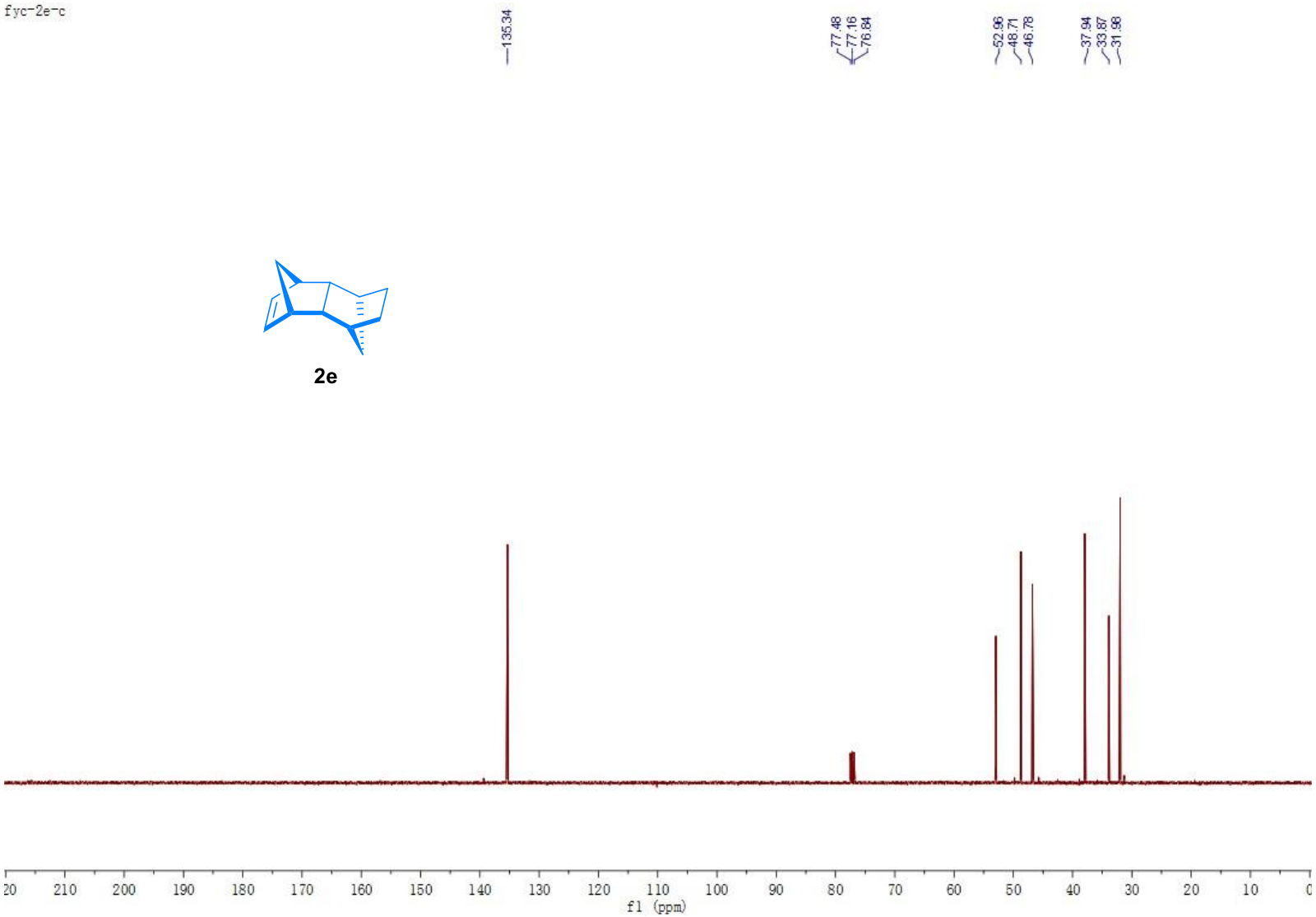

fyc-2c-c
151.88
143.10
124.28
121.63
77.48
77.16
76.84
70.26
50.39
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

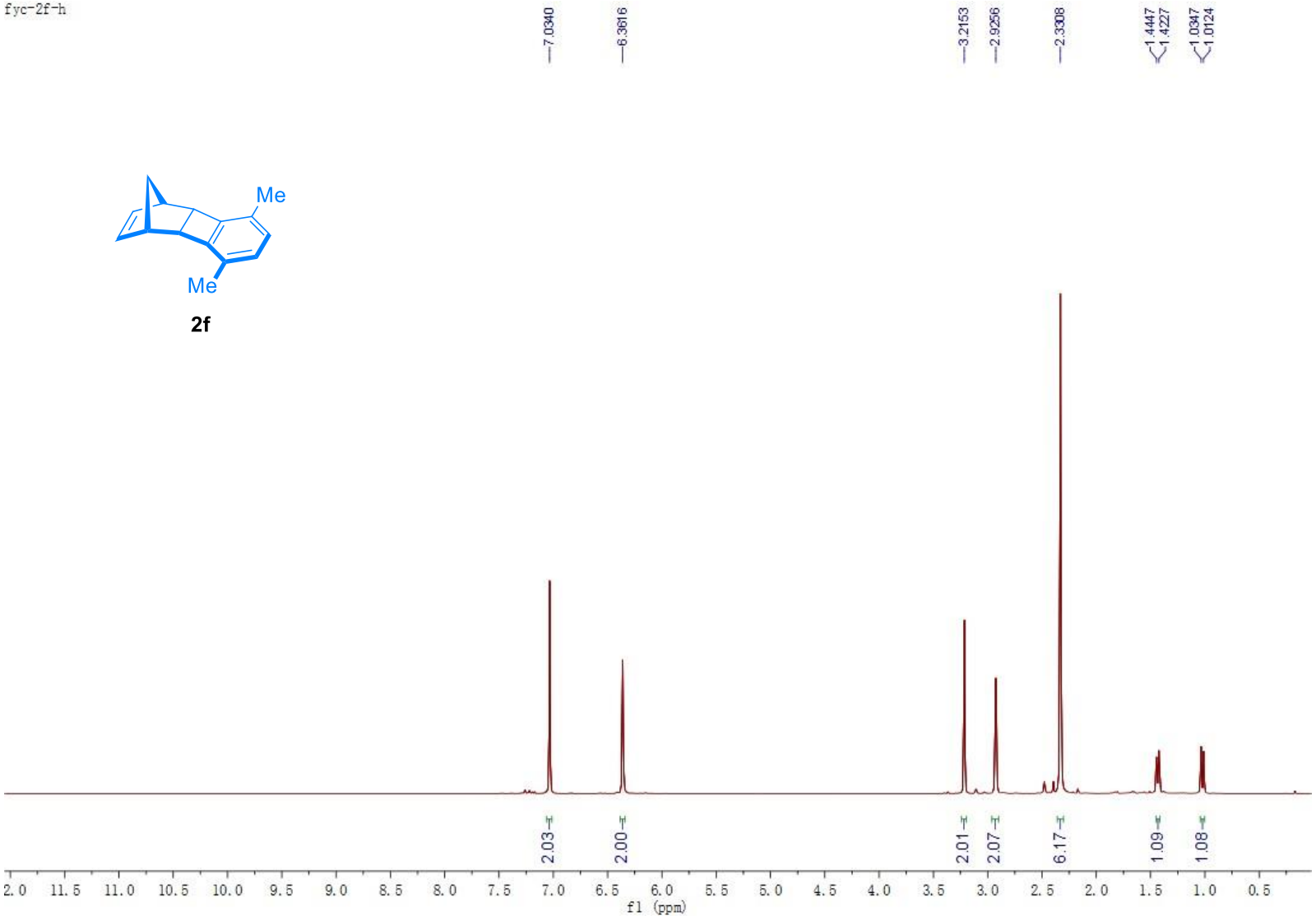
2c

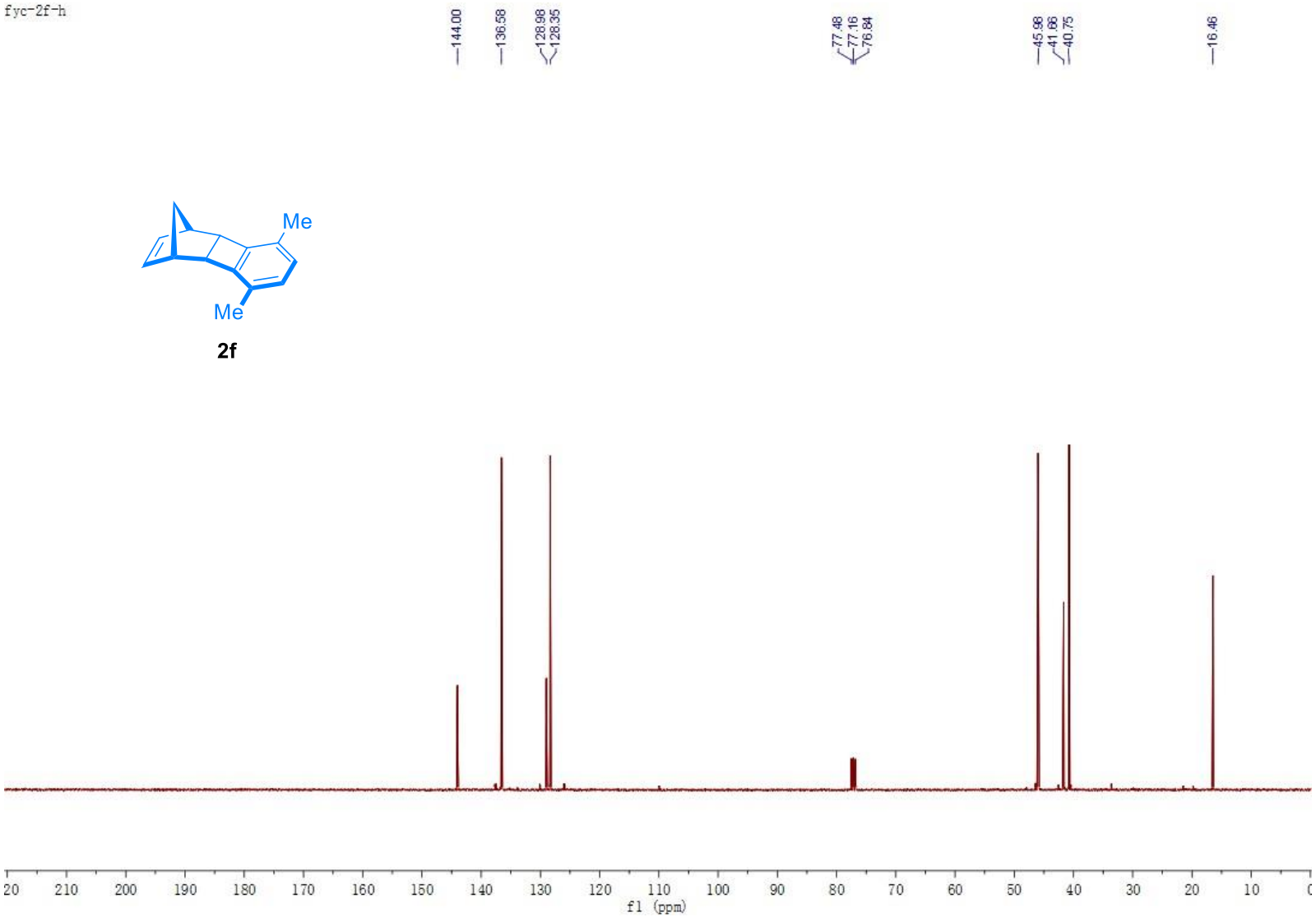

fyc-2d-h
7.2597
7.2539
7.2451
7.2370
7.2317
7.2239
7.2141
7.1664
7.1558
7.1478
7.1423
7.1343
7.1252
6.5935
6.5820
6.5742
6.5709
6.5631
6.5518
4.0308
4.0238
4.0201
4.0168
4.0133
4.0095
4.0063
1.6493
1.6460
1.6425
1.6360
1.6317
1.6210
1.6182
1.6148
1.6119
1.6096
1.6051
1.5961
1.5299
1.5234
1.5207
1.5174
1.5145
1.5040
1.5007
1.4930
1.4886
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
f1 (ppm)
4.10
4.05
4.00
3.95
f1 (ppm)
1.65
1.60
1.55
1.50
f1 (ppm)
2d
2.00
2.03
2.01
2.07
1.95
2.01
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

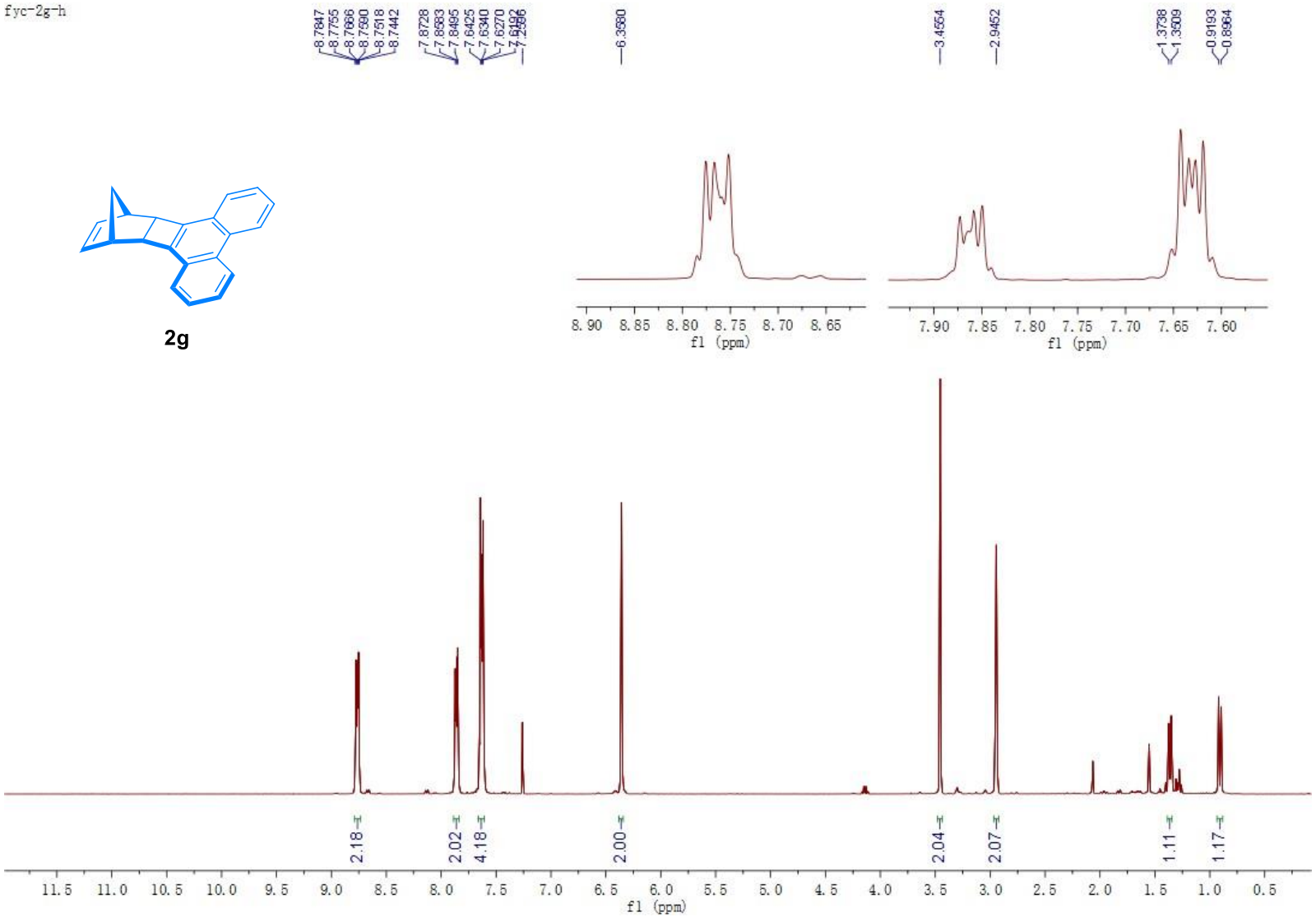

fyc-2d-c
144.43
135.15
125.01
122.66
77.48
77.16
76.84
40.31
25.86
2d
f1 (ppm)

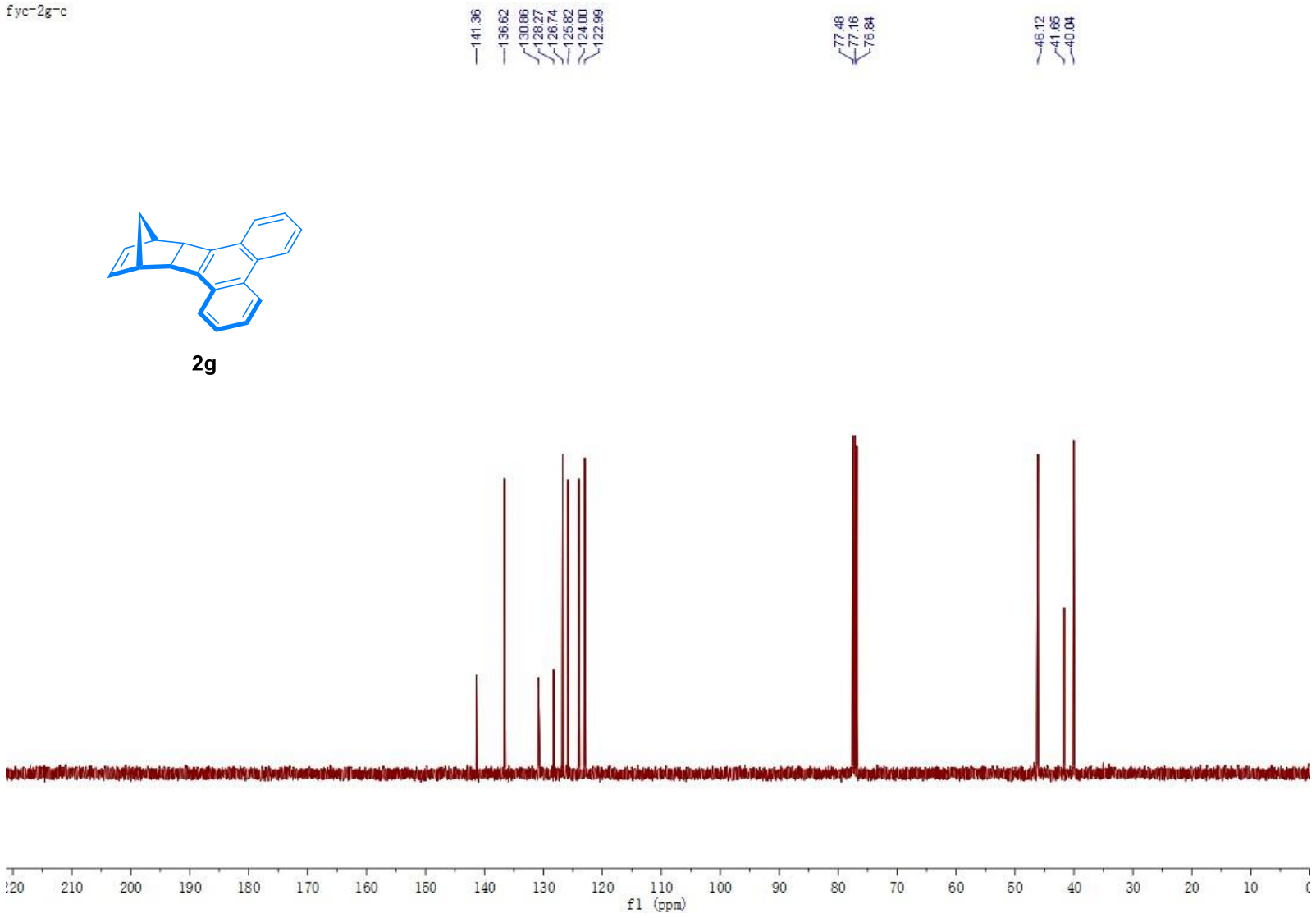

fyc-2e-h
7.2598
5.9385
5.9343
5.9301
2.8345
2.8304
2.8263
2.0692
2.0541
2.0395
2.0343
2.0293
2.0019
1.9986
1.3936
1.3763
1.3749
0.9972
0.9912
0.9794
0.9733
0.5172
2e
2.02
2.00
1.09
2.04
2.03
2.15
1.08
1.10
2.16
1.09
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

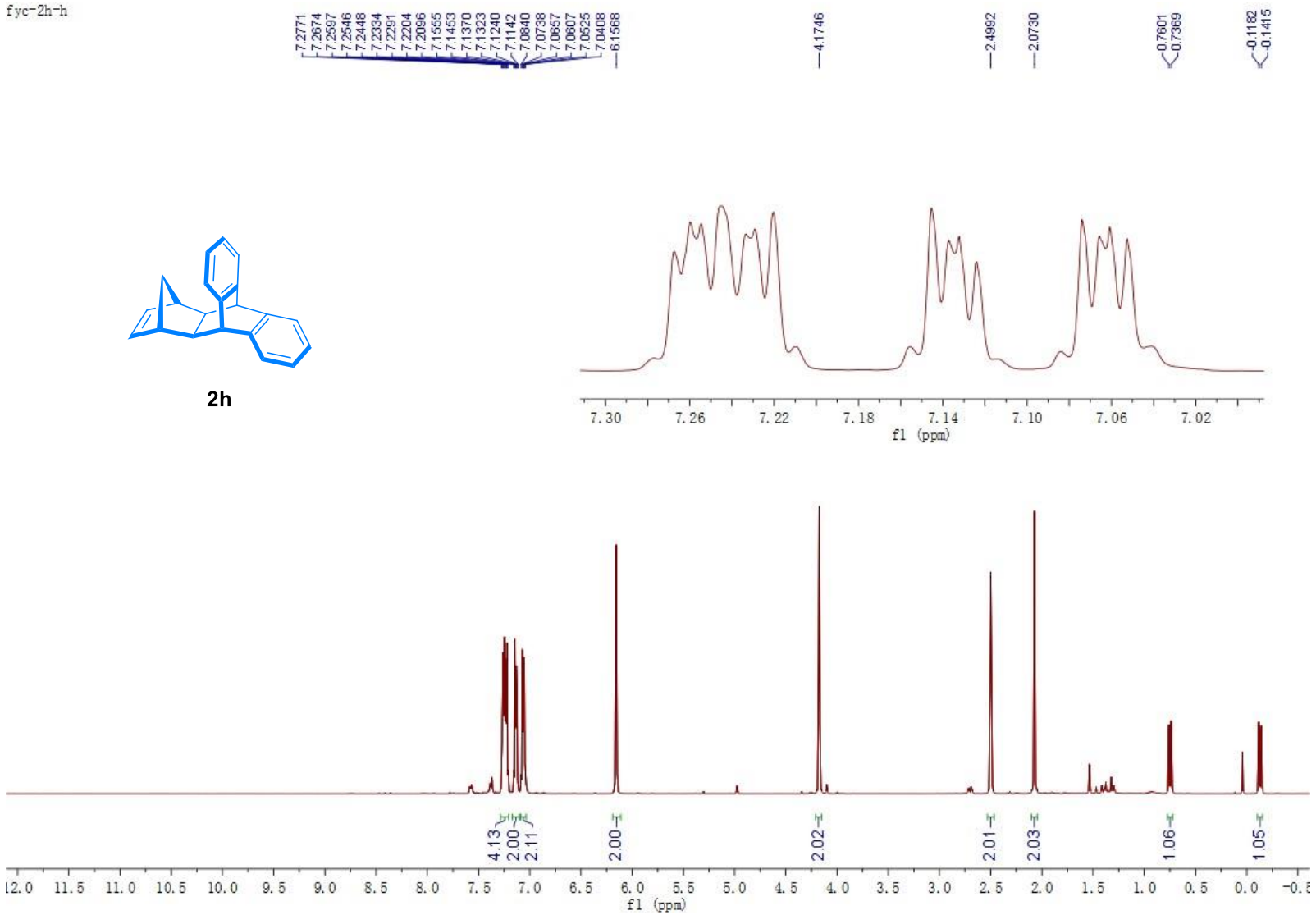

fyc-2e-c
135.34
77.48
77.16
76.84
52.96
48.71
46.78
37.94
33.87
31.98
2e
f1 (ppm)

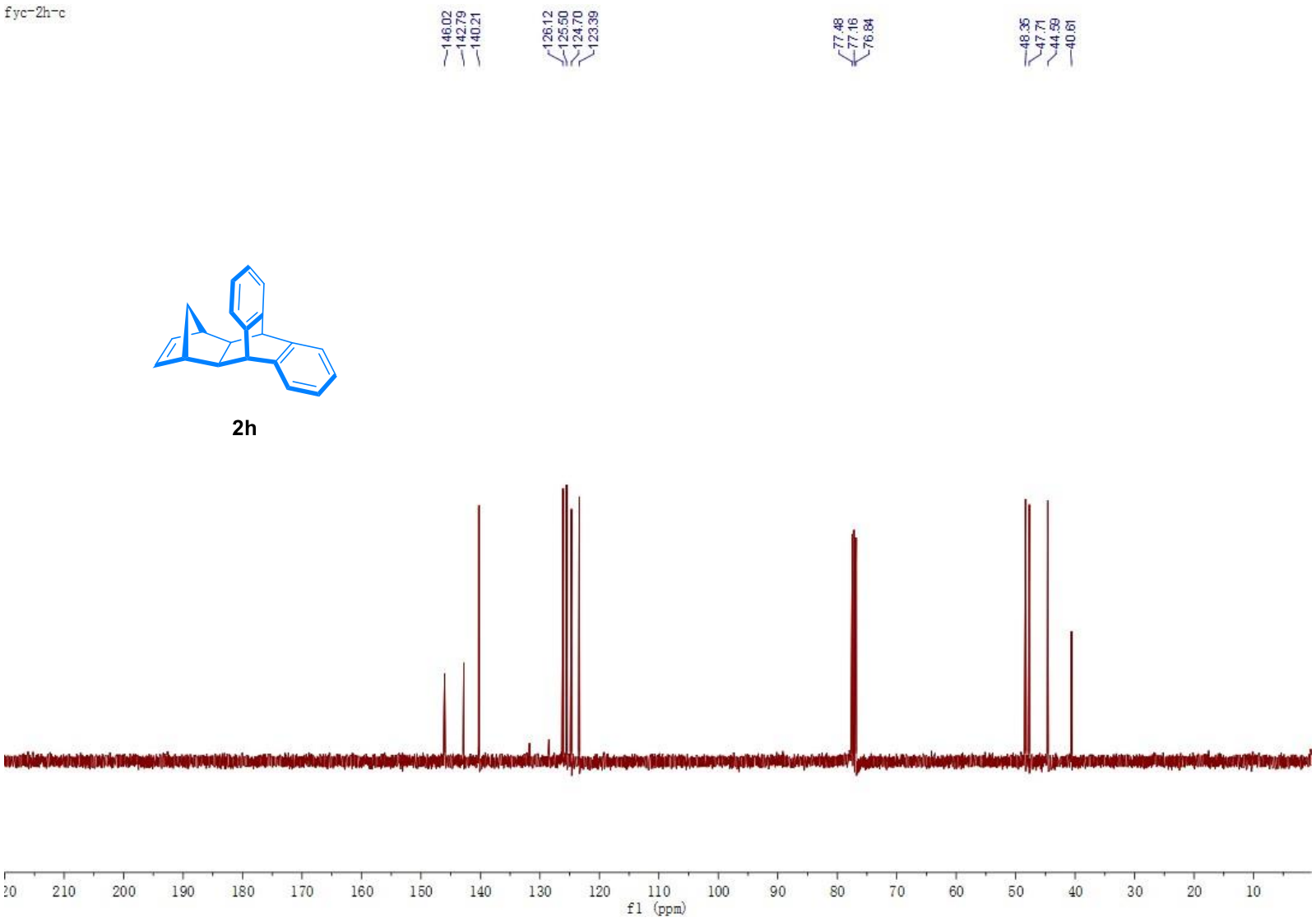

fyc-2f-h
7.0340
6.3616
3.2153
2.9256
2.3308
1.4447
1.4227
1.0347
1.0124
Me
Me
2f
2.03
2.00
2.01
2.07
6.17
1.09
1.08
f1 (ppm)


fyc-2f-h
144.00
136.58
128.98
128.35
77.48
77.16
76.84
45.98
41.66
40.75
16.46
Me
Me
2f
f1 (ppm)


fyc-2g-h
8.7847
8.7755
8.7666
8.7590
8.7518
8.7442
7.8728
7.8593
7.8495
7.6425
7.6340
7.6270
6.3690
3.4554
2.9452
1.3738
1.3609
0.9193
0.8964
2g
8.90 8.85 8.80 8.75 8.70 8.65
f1 (ppm)
7.90 7.85 7.80 7.75 7.70 7.65 7.60
f1 (ppm)
2.18
2.02
4.18
2.00
2.04
2.07
1.11
1.17
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

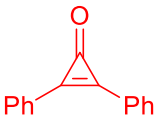

fyc-2g-c
141.36
136.62
130.86
128.27
126.74
125.82
124.00
122.99
77.48
77.16
76.84
46.12
41.65
40.04
2g
f1 (ppm)


fyc-2h-h
7.2771
7.2674
7.2597
7.2546
7.2448
7.2334
7.2291
7.2204
7.2096
7.1555
7.1453
7.1370
7.1323
7.1240
7.1142
7.0840
7.0738
7.0657
7.0607
7.0525
7.0408
6.1568
4.1746
2.4992
2.0730
0.7601
0.7369
0.1182
-0.1415
2h
7.30
7.26
7.22
7.18
7.14
7.10
7.06
7.02
f1 (ppm)
4.13
2.00
2.11
2.00
2.02
2.01
2.03
1.06
1.05
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

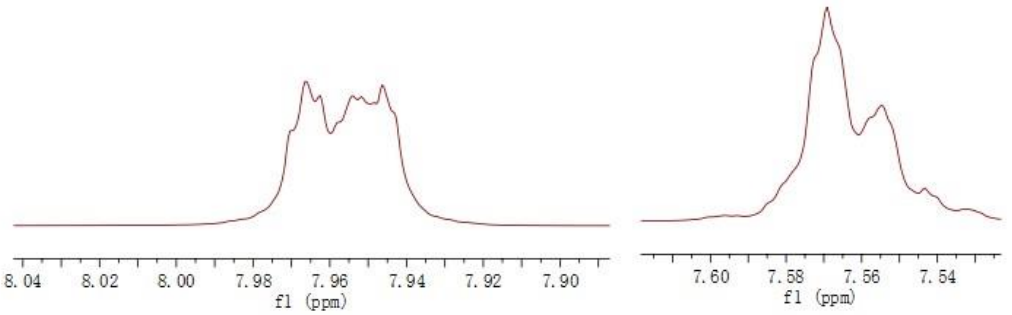

fyc-2h-c
146.02
142.79
140.21
126.12
125.50
124.70
123.39
77.48
77.16
76.84
48.35
47.71
44.59
40.61
2h
f1 (ppm)

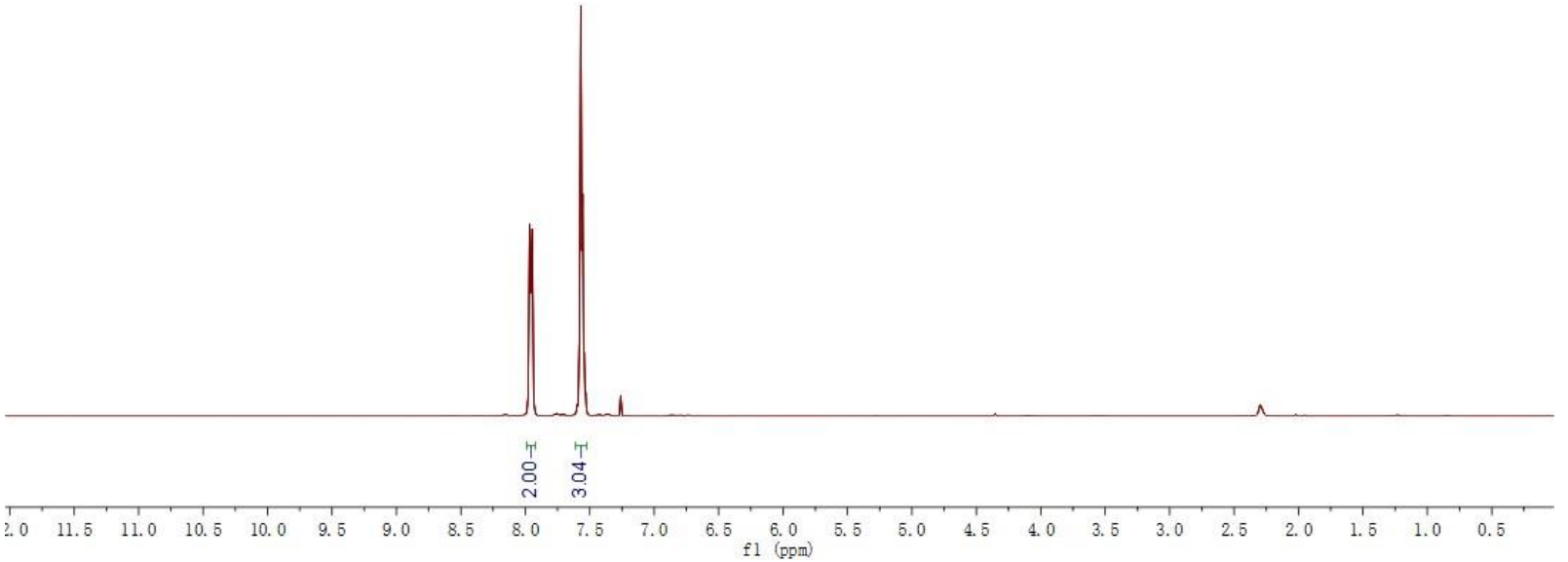
fyc-3a-h

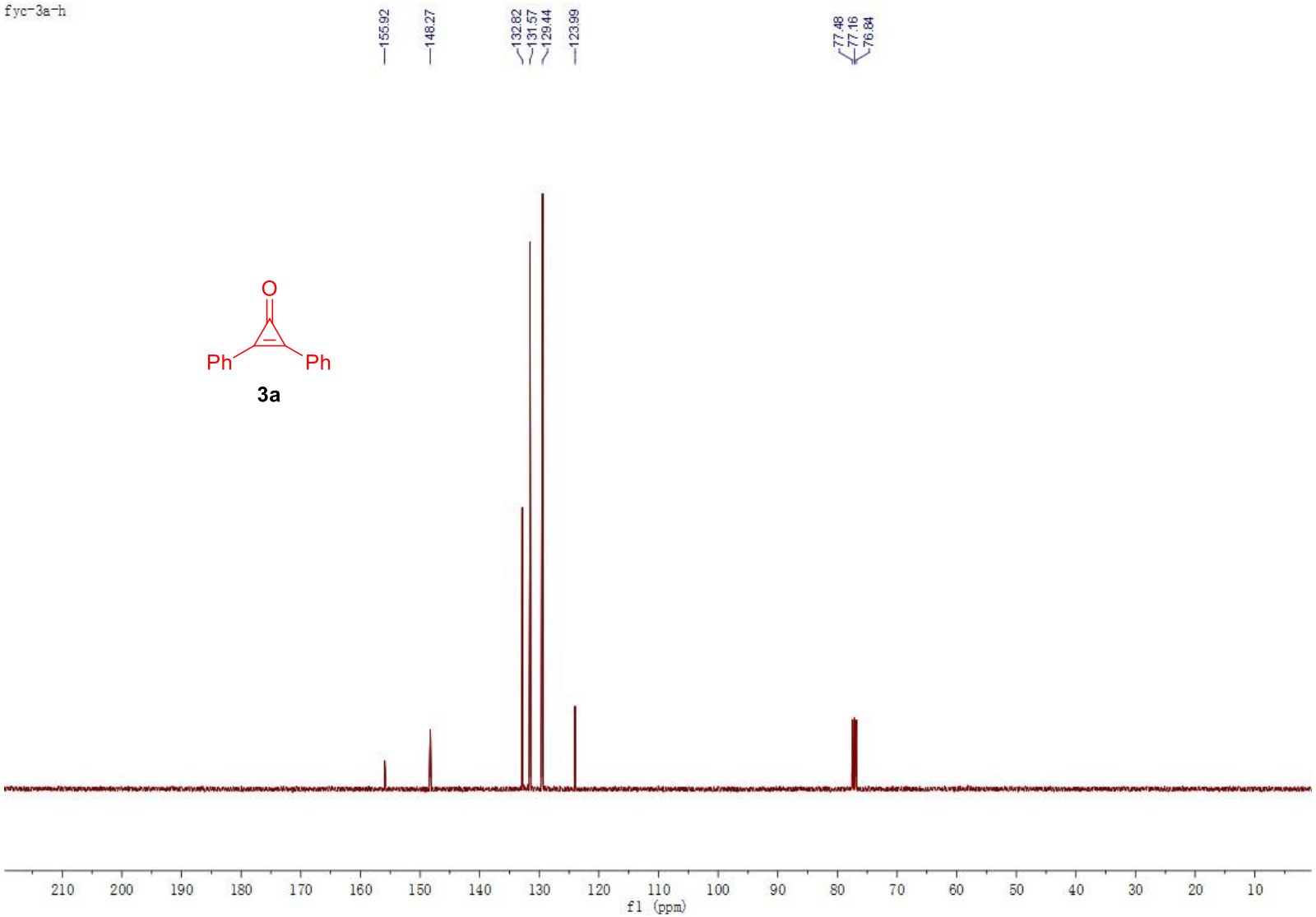

7.9662
7.9627
7.9540
7.9518
7.9484
7.9463
7.5961
7.5929
7.5892
7.5547
7.5433
7.5321
7.2997

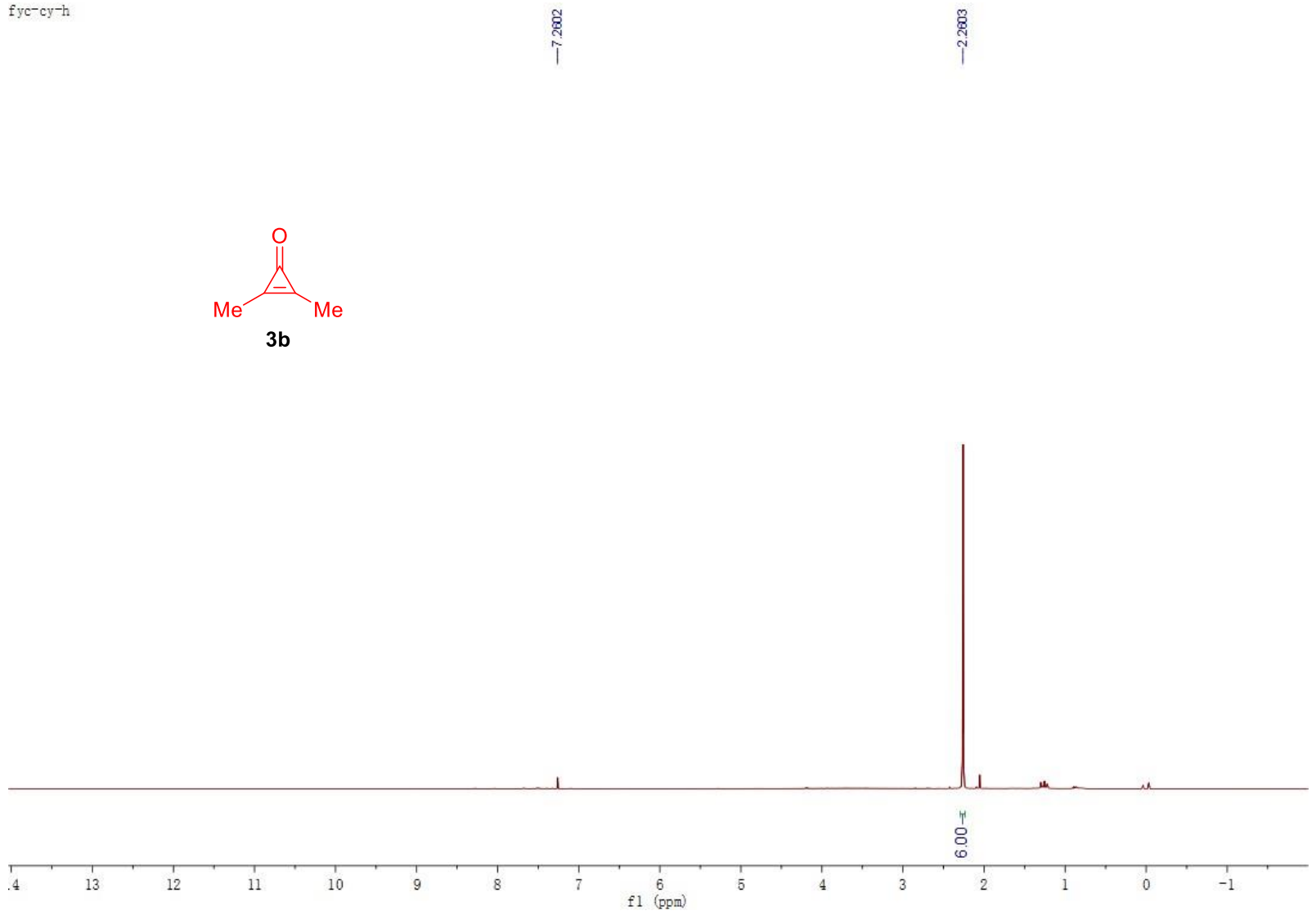

O
Ph
Ph

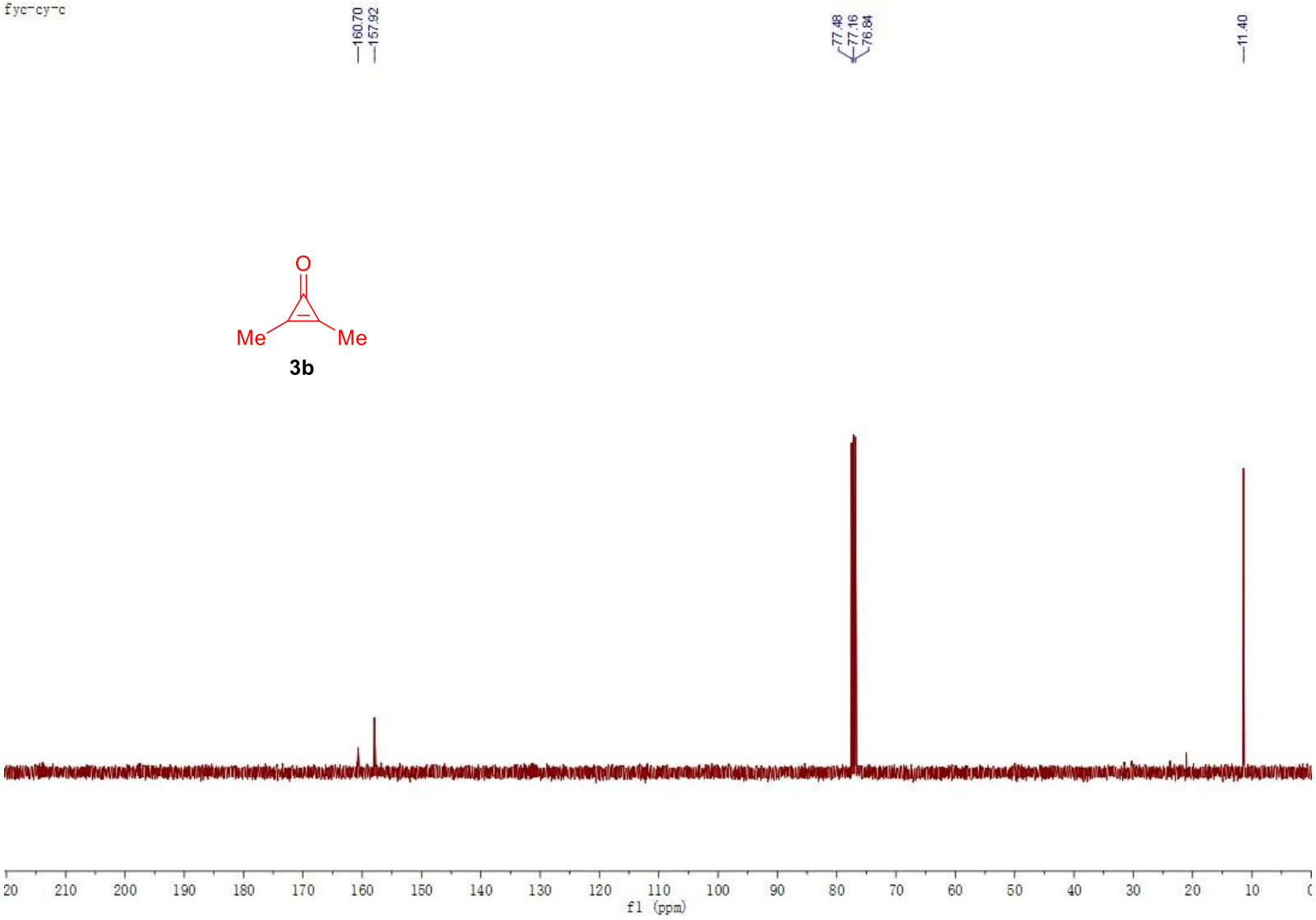
3a


8.04
8.02
8.00
7.98
7.96
7.94
7.92
7.90
f1 (ppm)
7.60
7.58
7.56
7.54
f1 (ppm)


2.00
3.04
f1 (ppm)

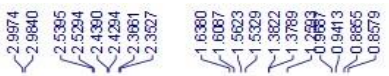

fyc-3a-h
155.92
148.27
132.82
131.57
129.44
123.99
77.48
77.16
76.84
O
Ph
Ph
3a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


fyc-cy-h
7.2602
2.2603
O
Me
Me
3b
6.00
f1 (ppm)

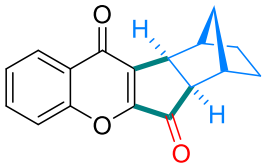

fyc-cy-c
160.70
157.92
77.48
77.16
76.84
11.40
O
Me
Me
3b
f1 (ppm)

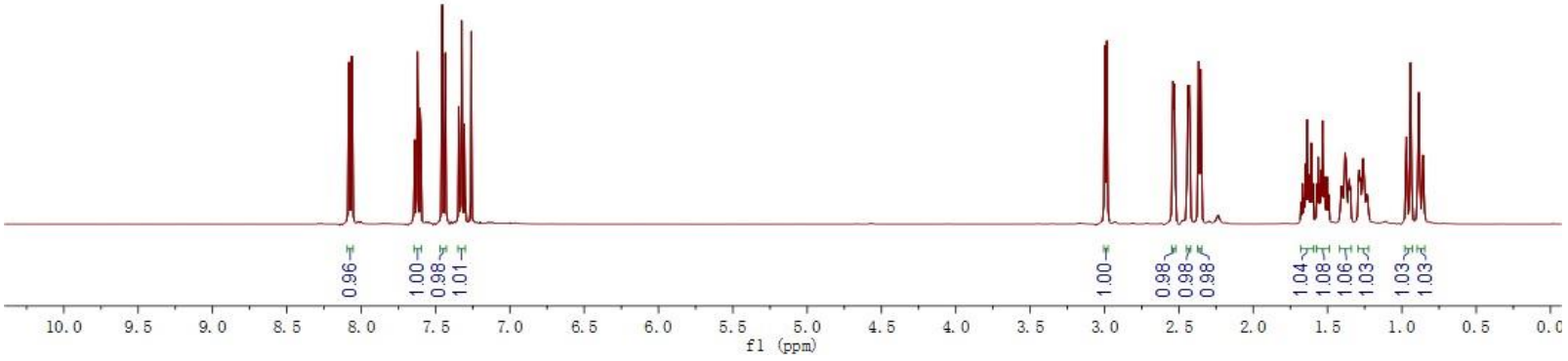
14. ^{1}H and ^{13}C NMR spectra of 4a-4ad and 5-12

fyc-86-0-h



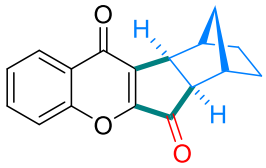
Scheme 2, 4a

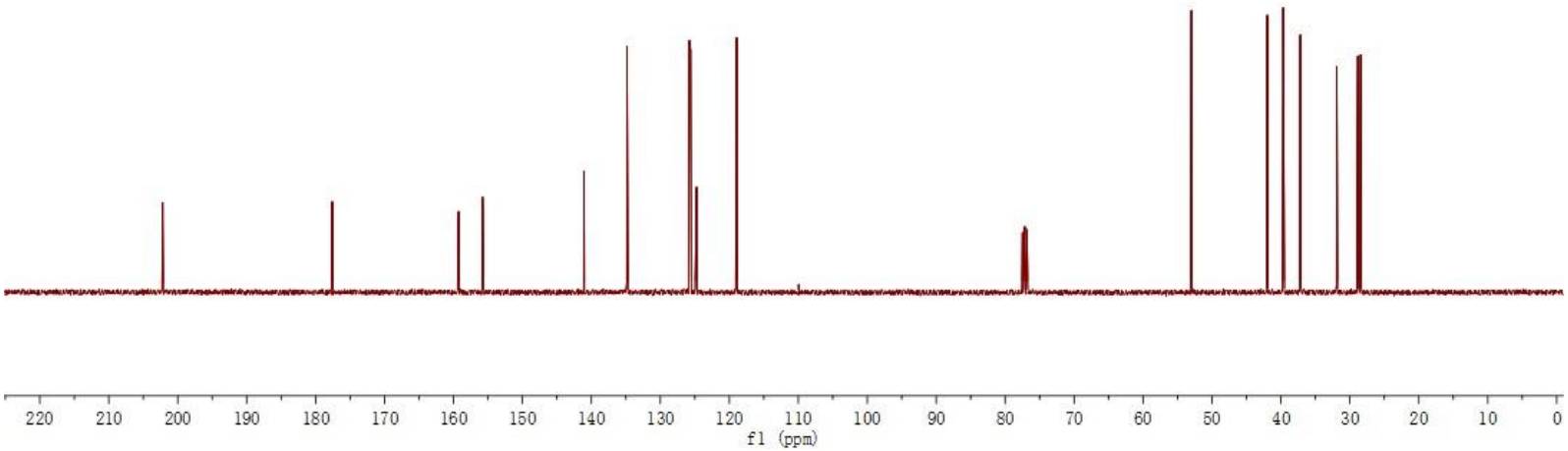


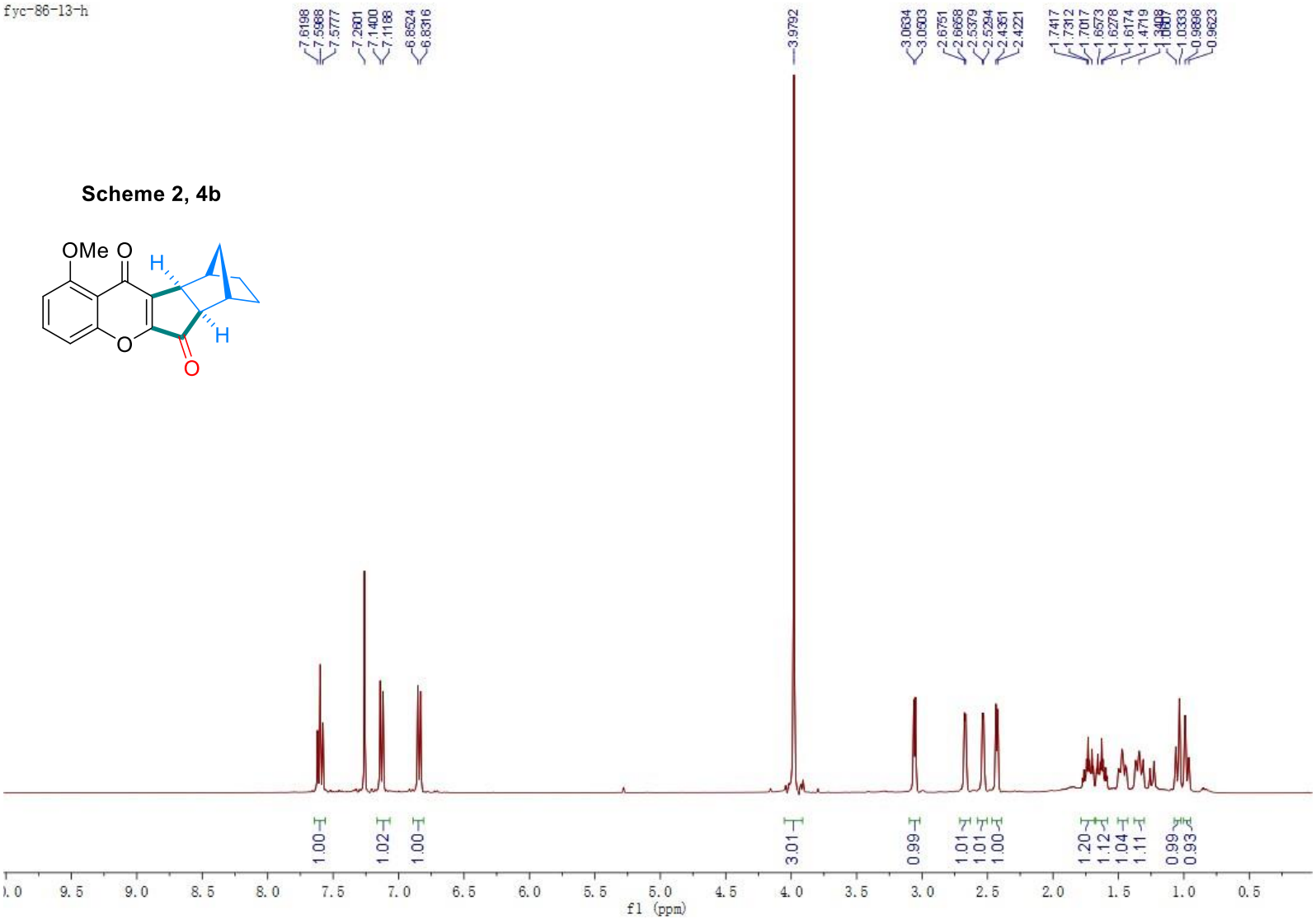



fyc-86-0-c
202.19
177.59
159.26
155.78
141.08
134.84
125.83
125.61
124.75
118.95
77.48
77.16
76.84
52.97
41.97
39.66
37.18
31.89
28.84
28.43

Scheme 2, 4a

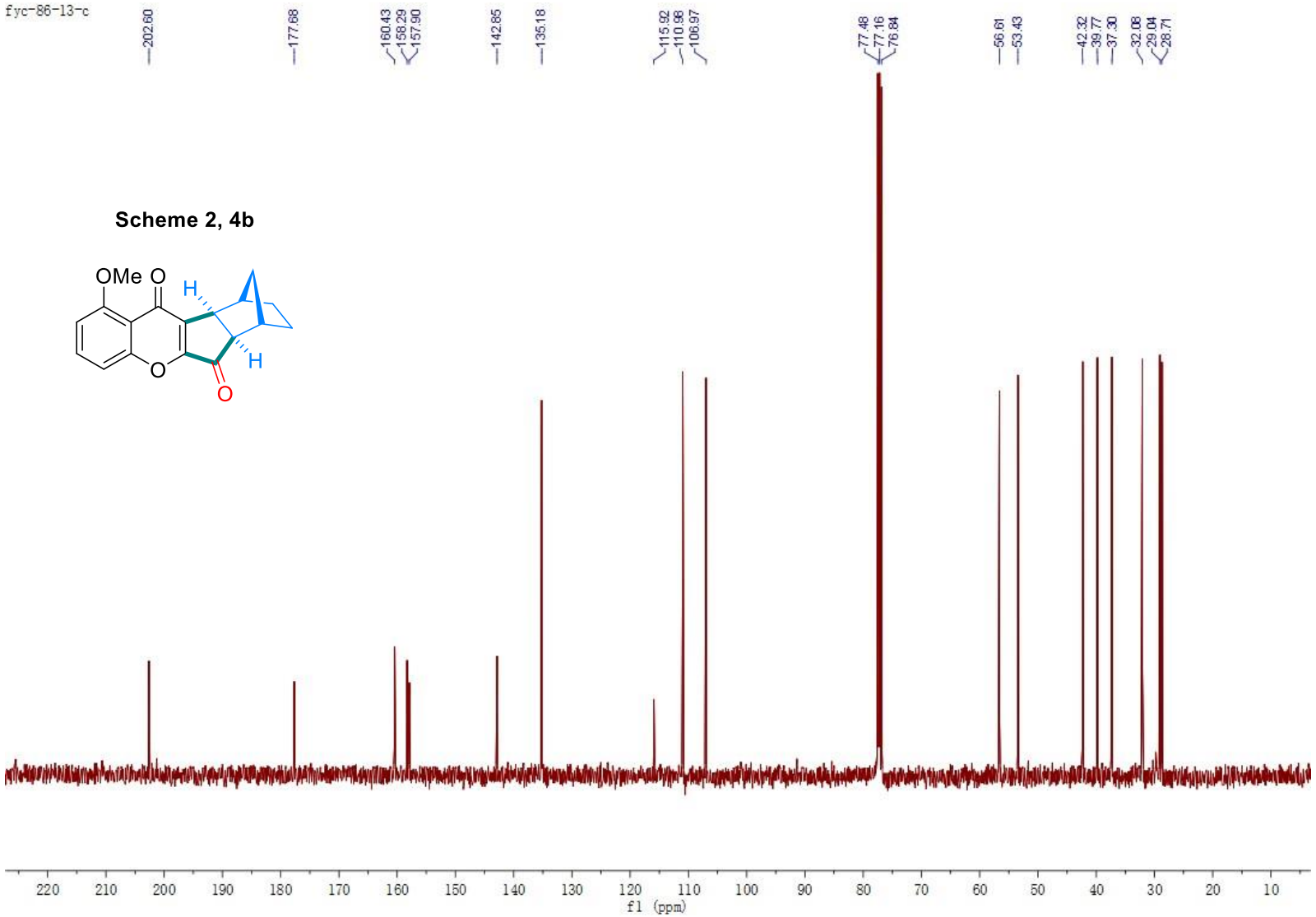

O
H
H
O
O


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


fyc-86-13-h
7.6198
7.5968
7.5777
7.2601
7.1400
7.1188
6.8524
6.8316
3.9792
3.0634
3.0503
2.6751
2.6658
2.5379
2.5294
2.4351
2.4221
1.7417
1.7312
1.7017
1.6573
1.6278
1.6174
1.4719
1.0333
0.9898
0.9623
1.00
1.02
1.00
3.01
0.99
1.01
1.01
1.00
1.20
1.12
1.04
1.11
0.99
0.93
f1 (ppm)

Scheme 2, 4b

OMe
O
H
H
O
O

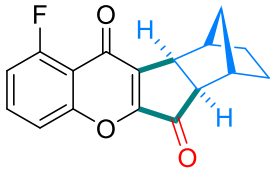

fyc-86-13-c
202.60
177.68
160.43
158.29
157.90
142.85
135.18
115.92
110.98
106.97
77.48
77.16
76.84
56.61
53.43
42.32
39.77
37.30
32.06
29.04
28.71
Scheme 2, 4b
OMe
O
H
H
O
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

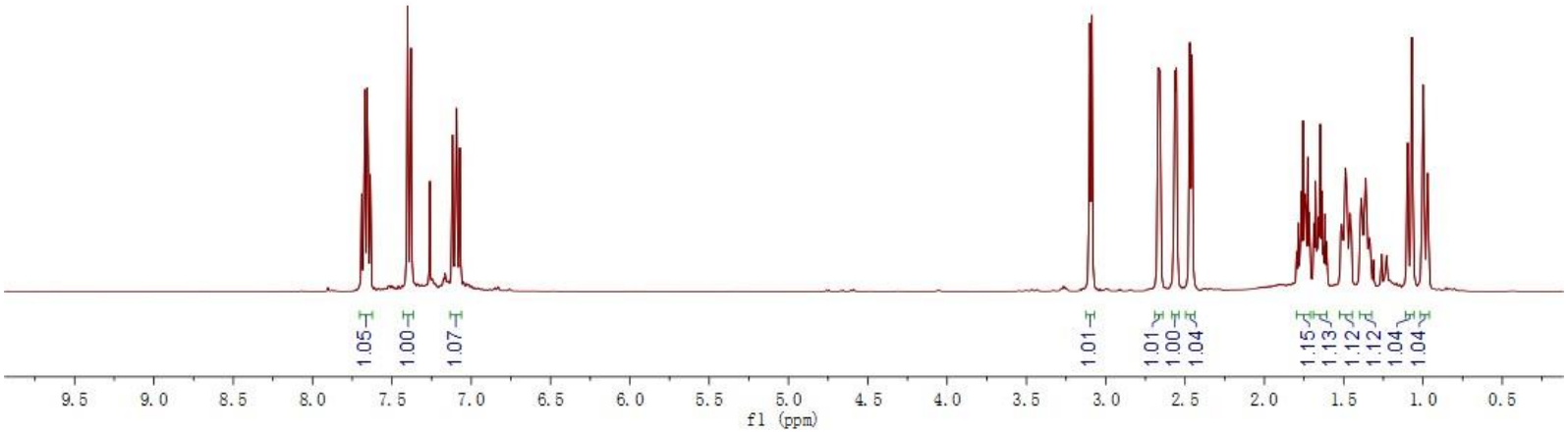
fyc-86-29-h

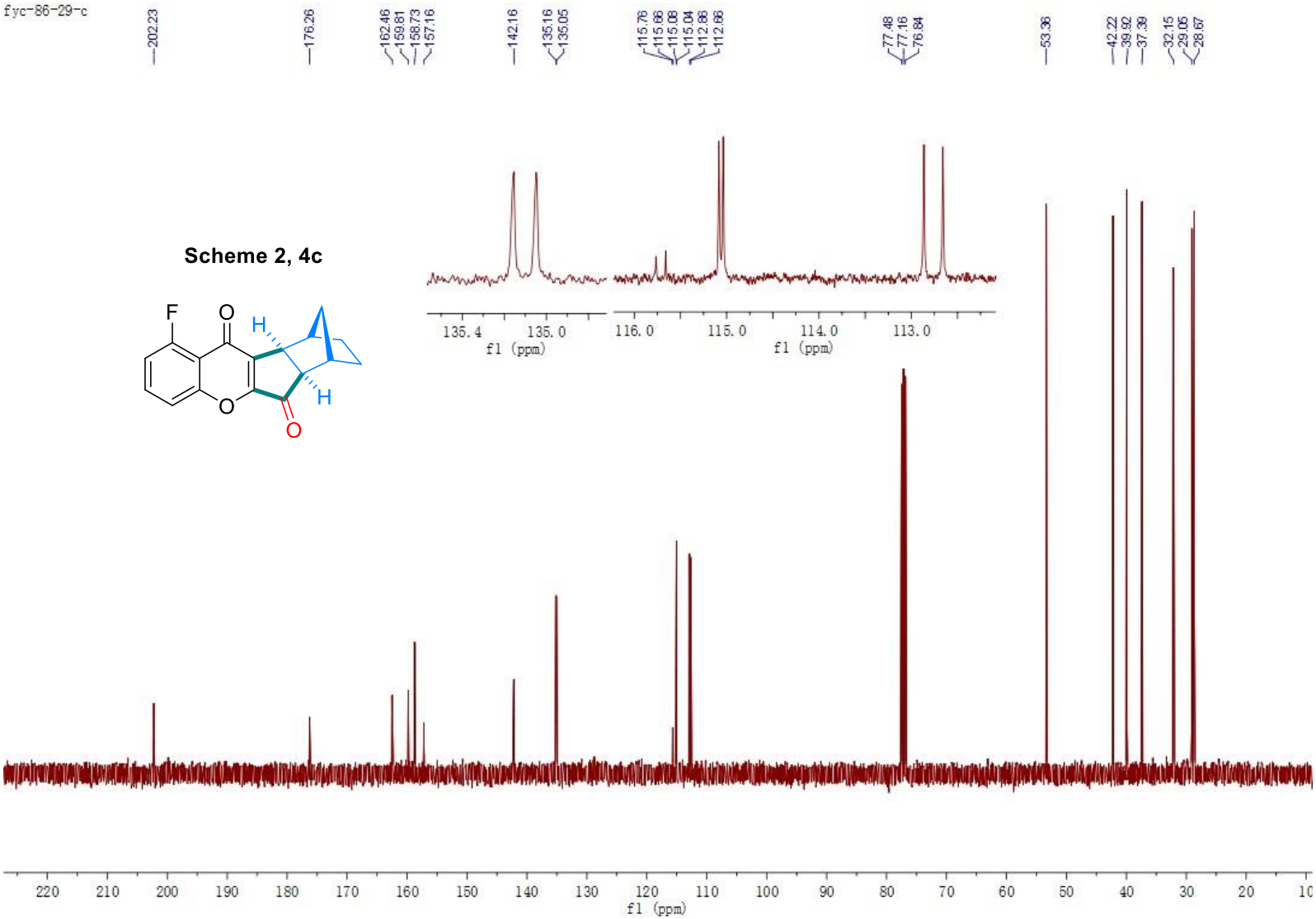
7.6911
7.6773
7.6701
7.6603
7.6491
7.6354
7.4010
7.3795
7.2603
7.1180
7.0957
7.0920
7.0712

3.1007
3.0875
2.6682
2.6585
2.5642
2.5550
2.4695
2.4563
1.7553
1.7258
1.6778
1.6482
1.6377
1.4888
1.3666

Scheme 2, 4c






fyc-86-29-c
202.23
176.26
162.46
159.81
158.73
157.16
142.16
135.16
135.05
115.76
115.66
115.08
115.04
112.86
112.66
77.48
77.16
76.84
53.36
42.22
39.92
37.39
32.15
29.05
28.67
Scheme 2, 4c
F
O
H
H
O
O
135.4
135.0
f1 (ppm)
116.0
115.0
114.0
113.0
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

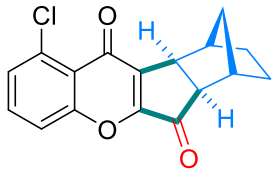
fyc-86-20-h

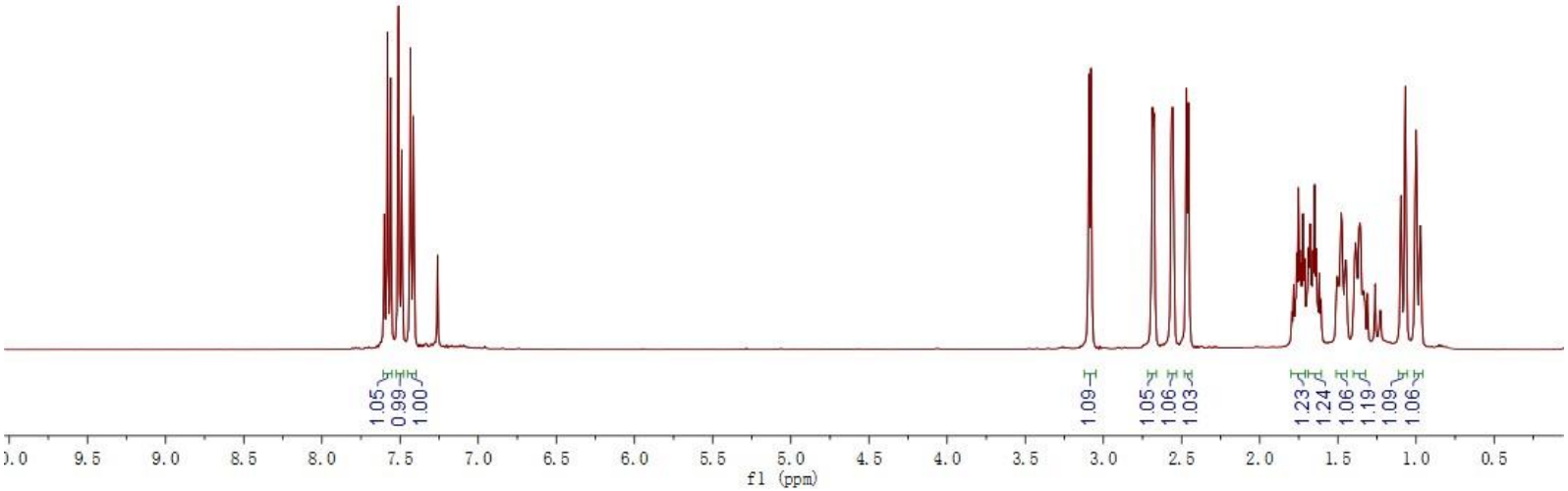
7.6005
7.5800
7.5600
7.5096
7.4896
7.4337
7.4146
7.2598

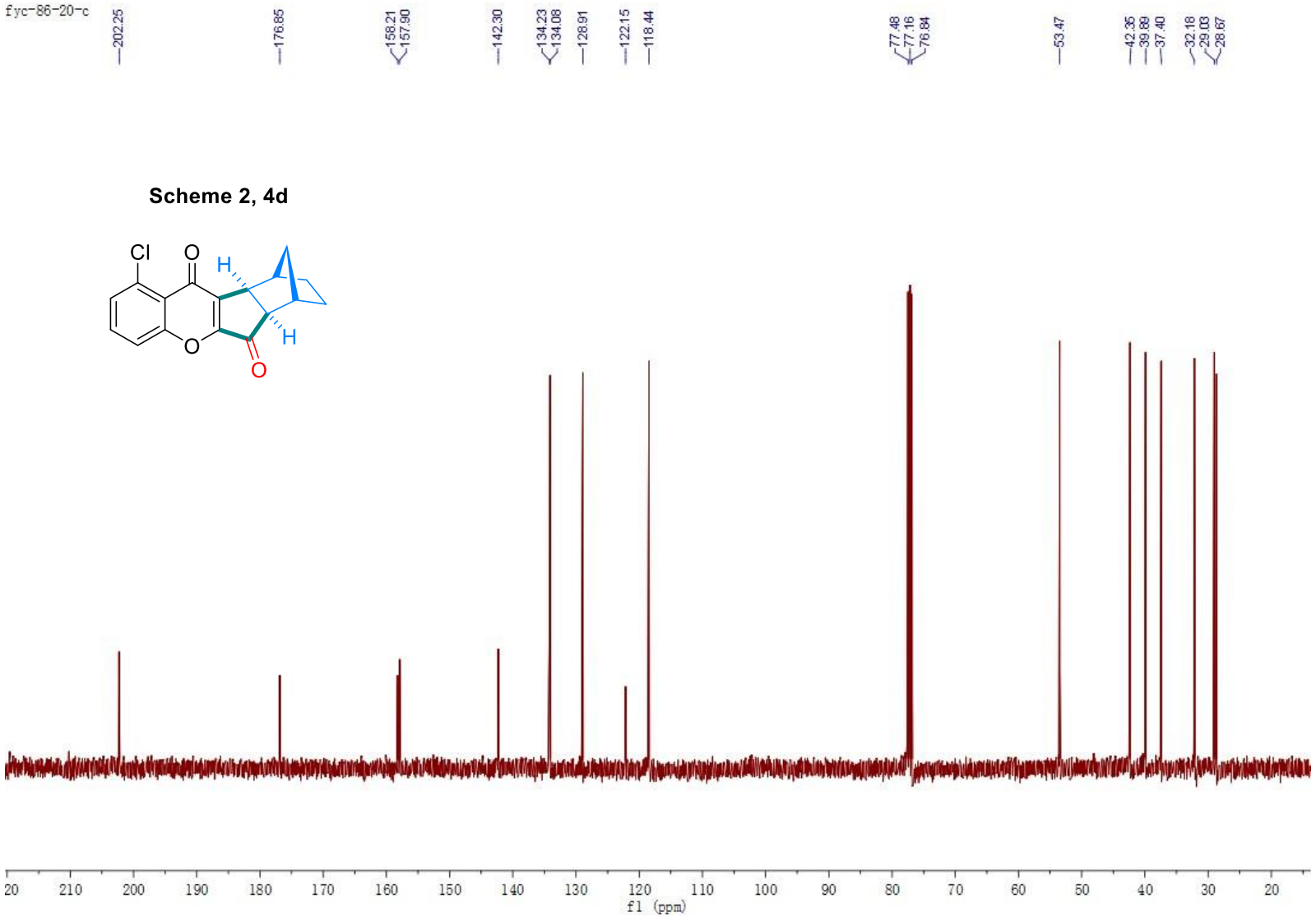
3.0922
3.0791
2.6861
2.6772
2.5632
2.5551
2.4691
2.4561

1.7530
1.7295
1.6875
1.6780
1.6484
1.4787
1.3870
1.3695
1.0958
1.0883
1.0004
0.9729

Scheme 2, 4d

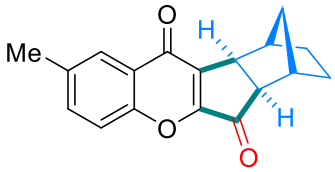


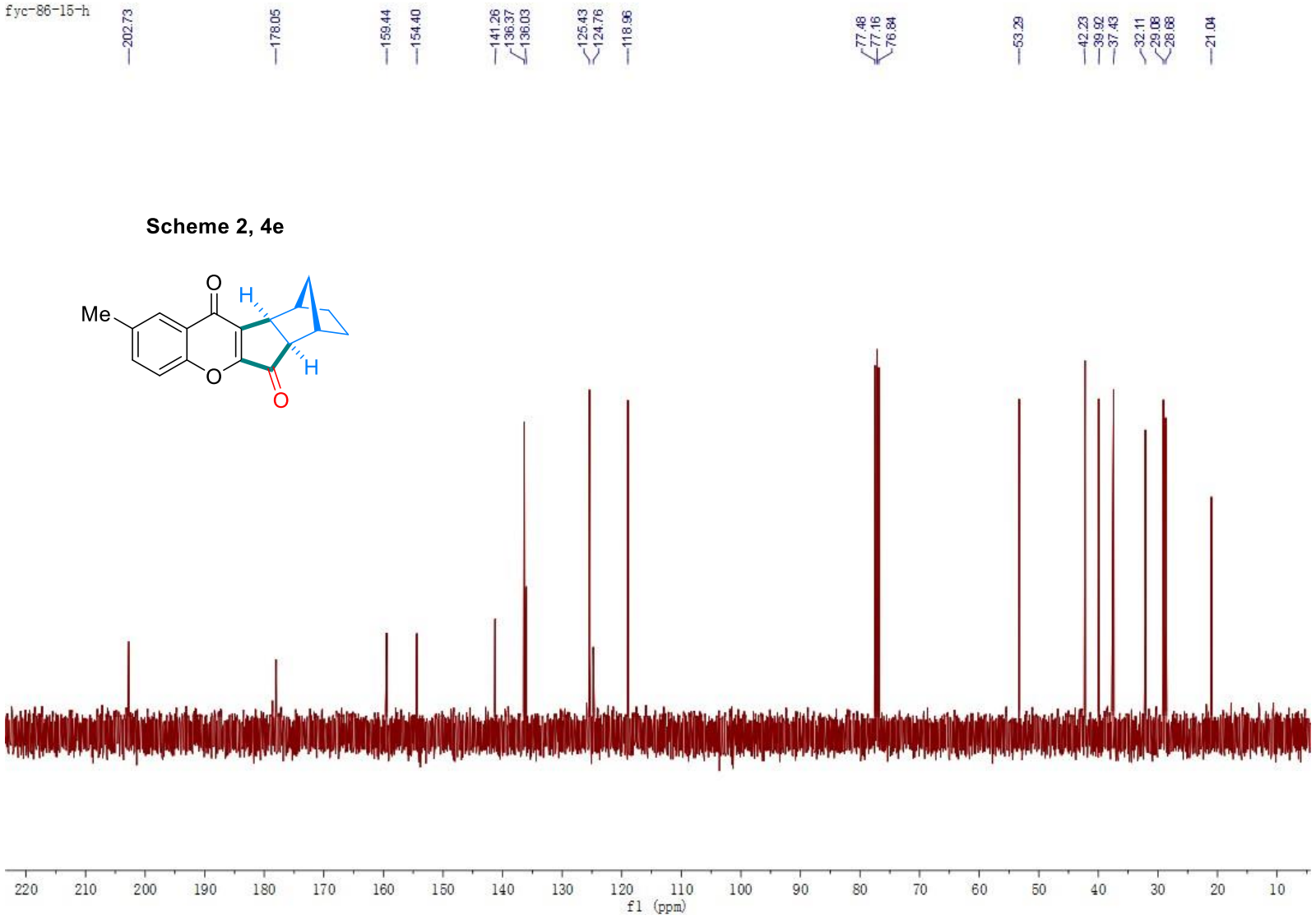


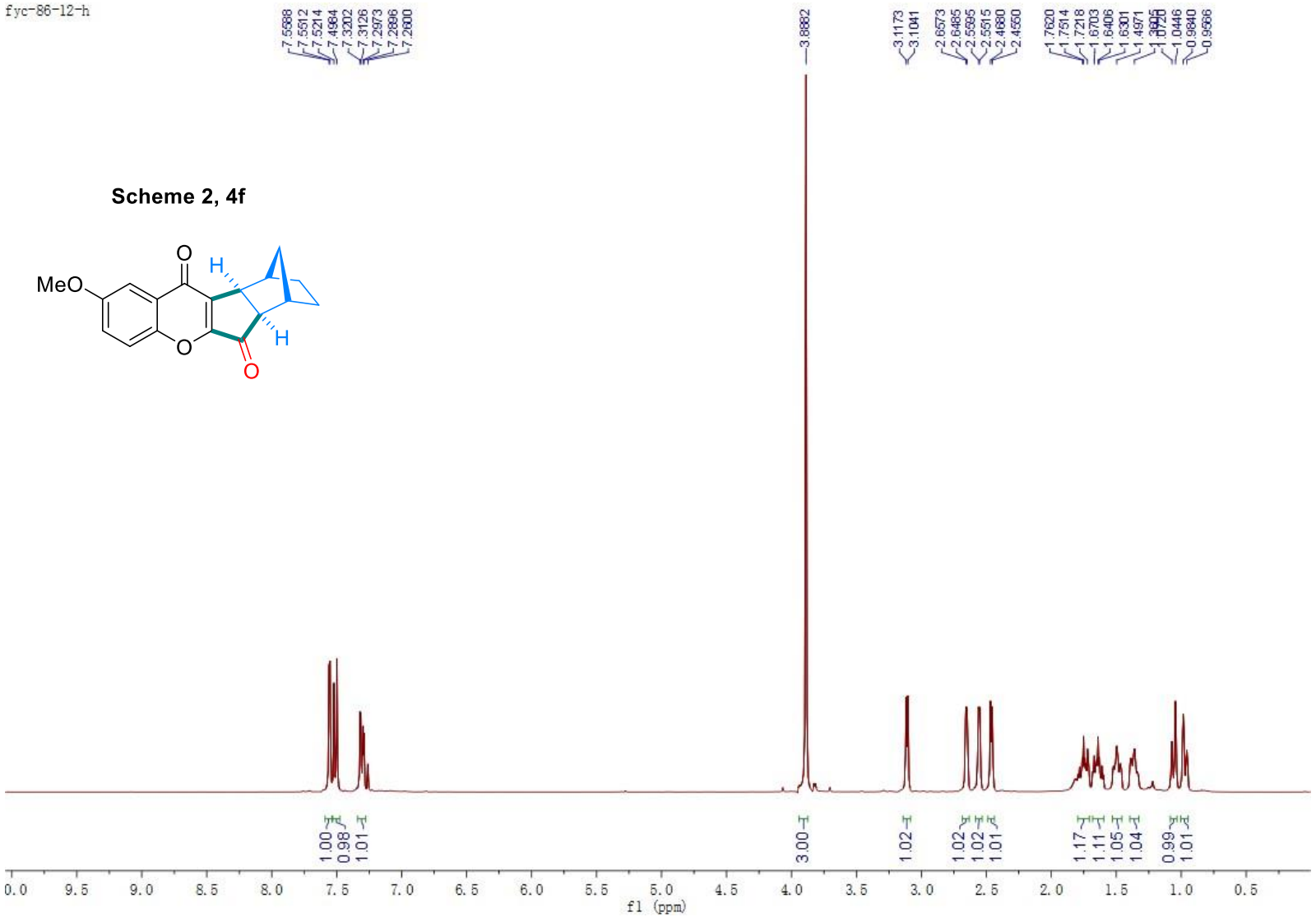

fyc-86-20-c
202.25
176.85
158.21
157.90
142.30
134.23
134.08
128.91
122.15
118.44
77.48
77.16
76.84
53.47
42.35
39.89
37.40
32.18
29.03
28.67
Scheme 2, 4d
Cl
O
H
H
O
O
f1 (ppm)

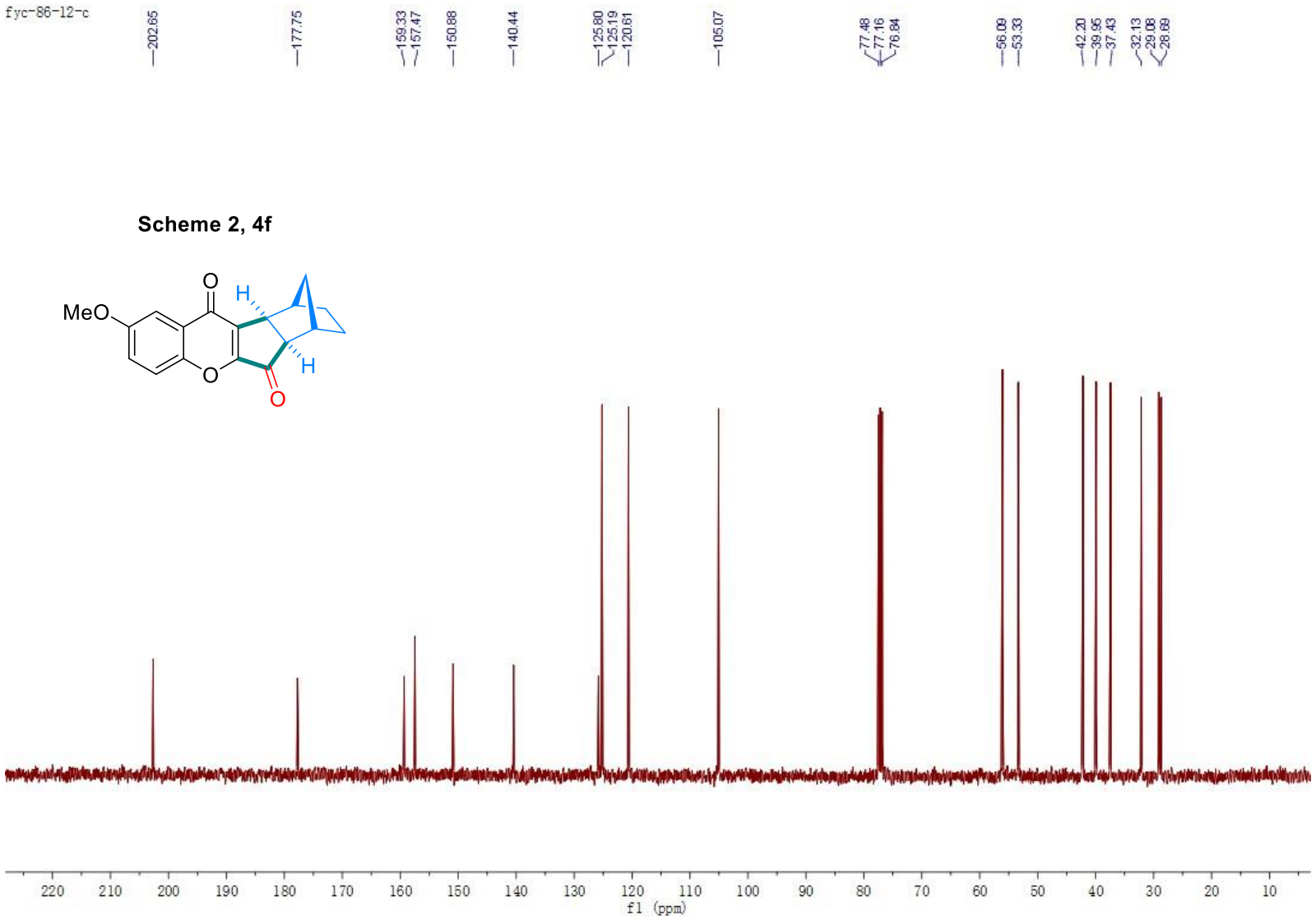
fyc-86-15-h

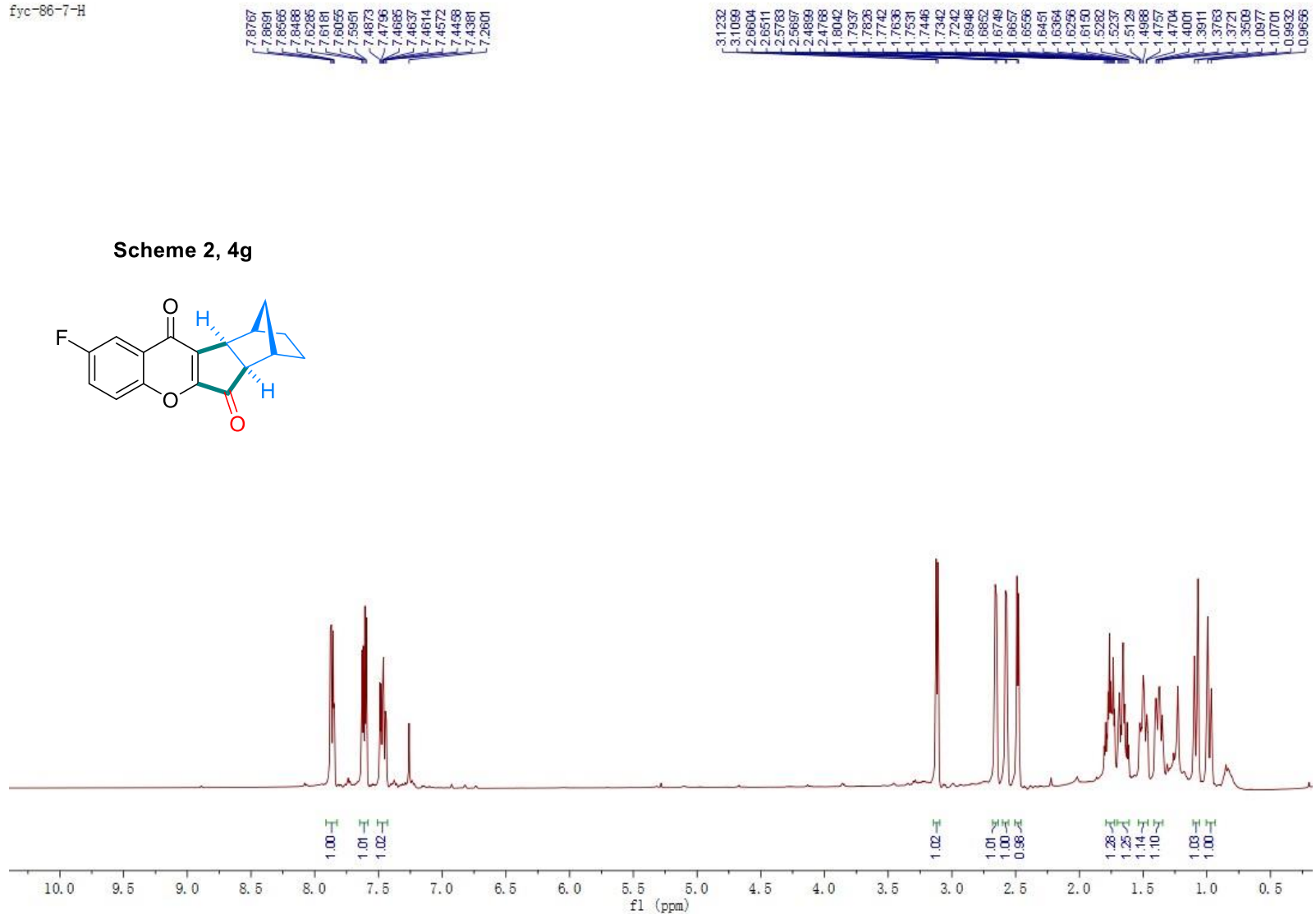
Scheme 2, 4e

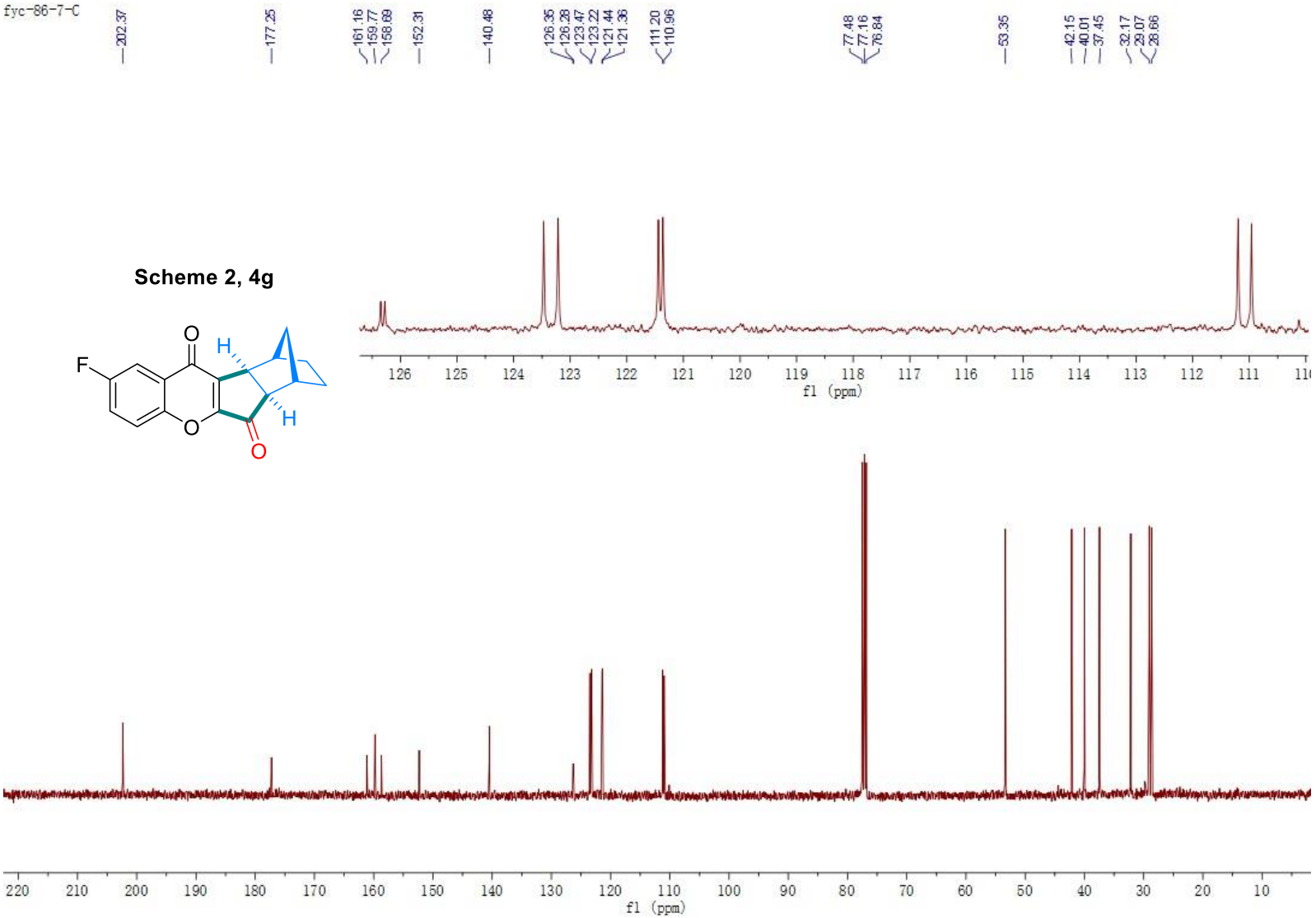



fyc-86-15-h
202.73
178.05
159.44
154.40
141.26
136.37
136.03
125.43
124.76
118.96
77.48
77.16
76.84
53.29
42.23
39.92
37.43
32.11
29.08
28.88
21.04
Scheme 2, 4e
Me
O
H
H
O
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


fyc-86-12-h
7.5698
7.5512
7.5214
7.4964
7.3202
7.3126
7.2973
7.2896
7.2600
3.8882
3.1173
3.1041
2.6573
2.6485
2.5695
2.5515
2.4680
2.4550
1.7620
1.7514
1.7218
1.6703
1.6406
1.6301
1.4971
1.0446
0.9840
0.9566
Scheme 2, 4f
MeO
O
H
H
O
O
1.00
0.98
1.01
3.00
1.02
1.02
1.02
1.01
1.17
1.11
1.05
1.04
0.99
1.01
0.0
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
f1 (ppm)

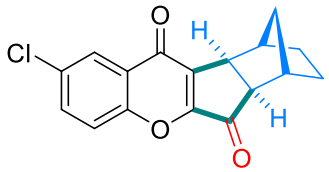

fyc-86-12-c
202.65
177.75
159.33
157.47
150.88
140.44
125.80
125.19
120.61
105.07
77.48
77.16
76.84
56.09
53.33
42.20
39.95
37.43
32.13
29.06
28.69
Scheme 2, 4f
MeO
O
H
H
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

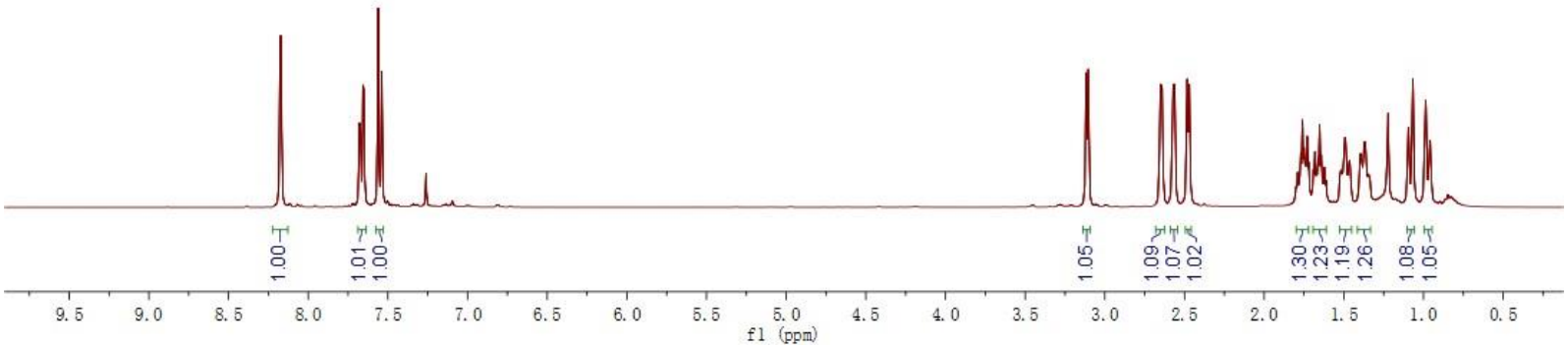

fyc-86-7-H
7.8767
7.8691
7.8565
7.8488
7.6285
7.6181
7.6055
7.5951
7.4873
7.4796
7.4685
7.4637
7.4614
7.4572
7.4438
7.4381
7.2601
3.1232
3.1059
2.6604
2.6511
2.5783
2.5697
2.4899
2.4768
1.8042
1.7937
1.7836
1.7742
1.7636
1.7531
1.7446
1.7342
1.7242
1.6948
1.6852
1.6749
1.6657
1.6556
1.6451
1.6364
1.6256
1.6150
1.5282
1.5237
1.5129
1.4968
1.4757
1.4704
1.4001
1.3911
1.3763
1.3721
1.3509
1.0977
1.0701
0.9932
0.9696
Scheme 2, 4g
O
H
F
H
O
O
1.00
1.01
1.02
1.02
1.01
1.00
0.98
1.28
1.25
1.14
1.10
1.03
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

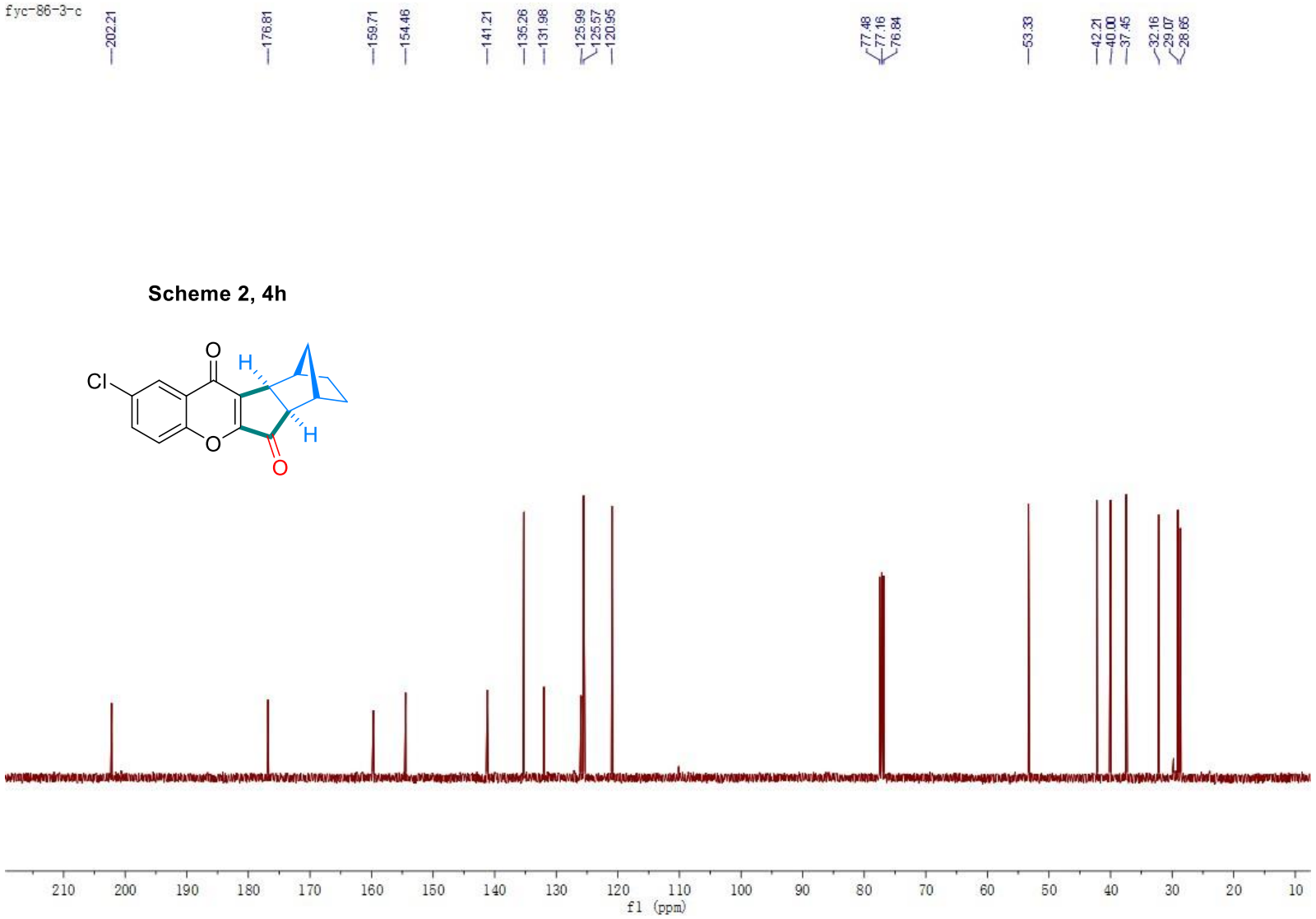

fyc-86-7-C
202.37
177.25
161.16
159.77
158.89
152.31
140.48
126.35
126.28
123.47
123.22
121.44
121.36
111.20
110.96
77.48
77.16
76.84
53.35
42.15
40.01
37.45
32.17
29.07
28.66
Scheme 2, 4g
F
O
H
O
H
O
126 125 124 123 122 121 120 119 118 117 116 115 114 113 112 111
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

fyc-86-3-h

Scheme 2, 4h

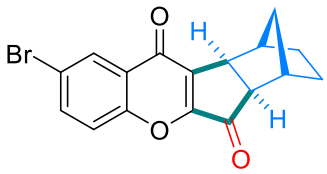


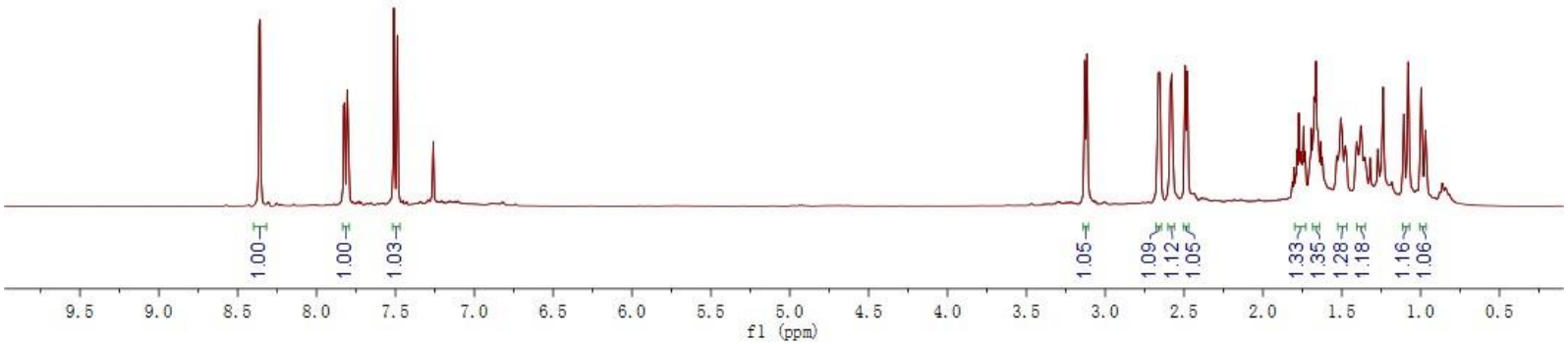



fyc-86-3-c
202.21
176.81
159.71
154.46
141.21
135.26
131.98
125.99
125.57
120.95
77.48
77.16
76.84
53.33
42.21
40.00
37.45
32.16
29.07
28.65
Scheme 2, 4h
Cl
O
H
H
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

fyc-86-4-h

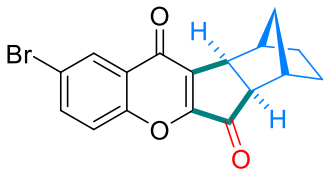
Scheme 2, 4i

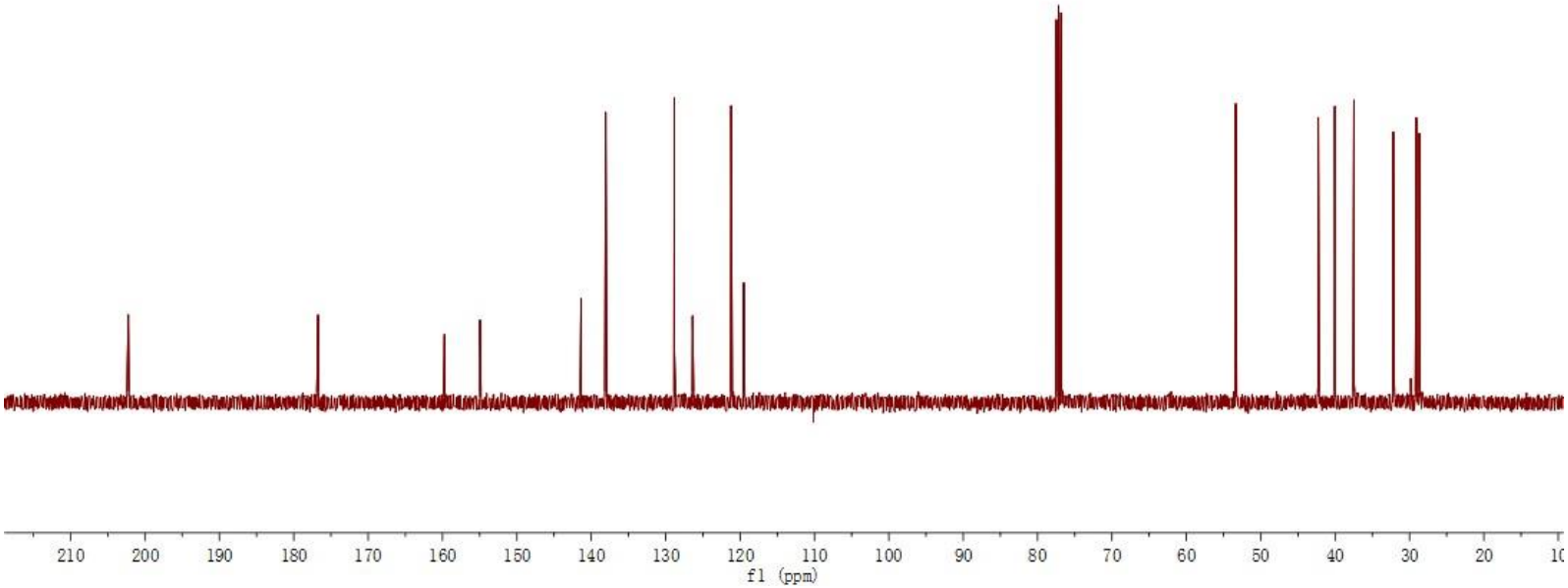


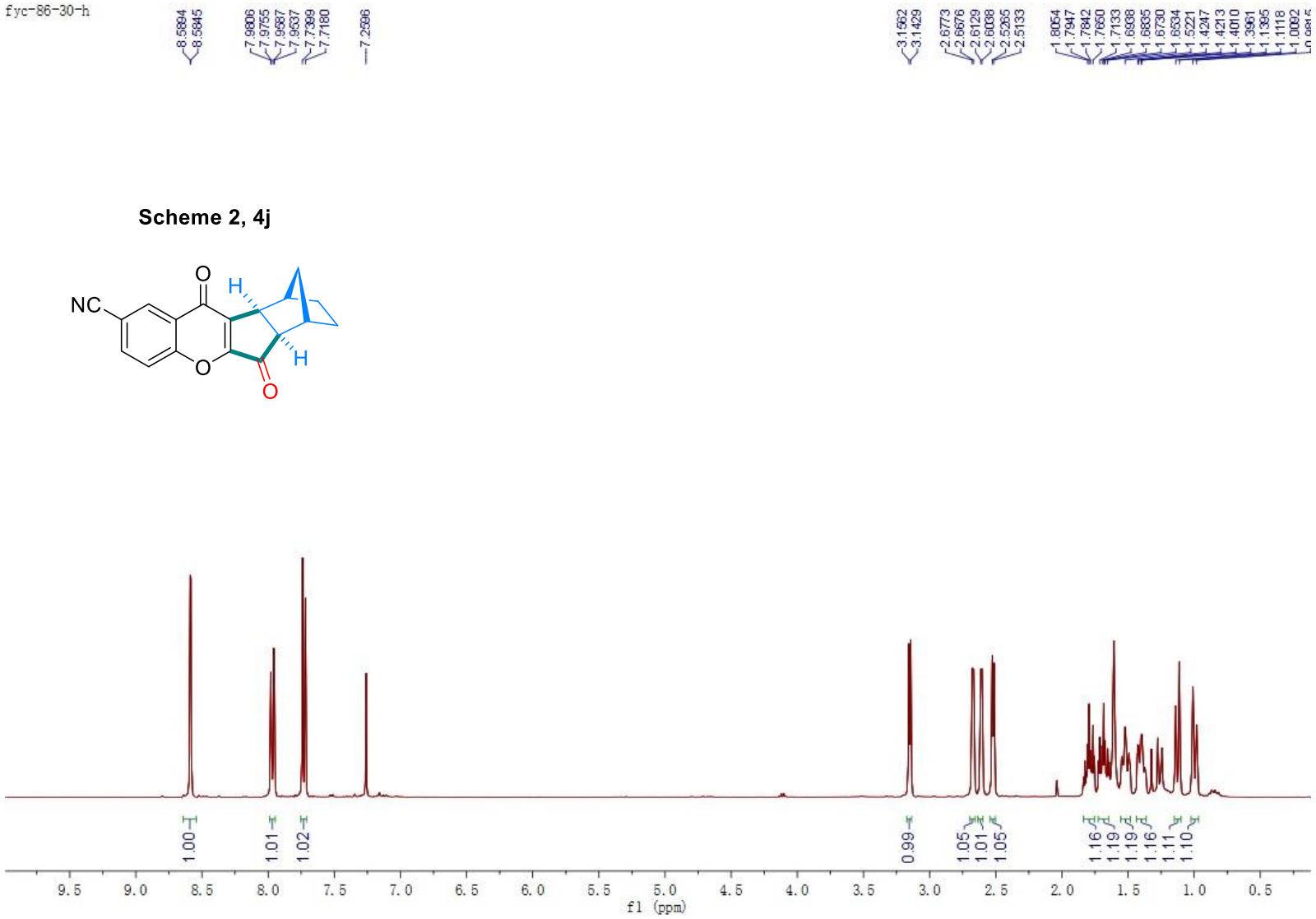



fyc-86-4-c
202.25
176.72
159.73
154.96
141.37
138.06
128.84
126.38
121.19
119.51
77.48
77.16
76.84
53.36
42.26
40.03
37.48
32.19
29.10
28.68

Scheme 2, 4i

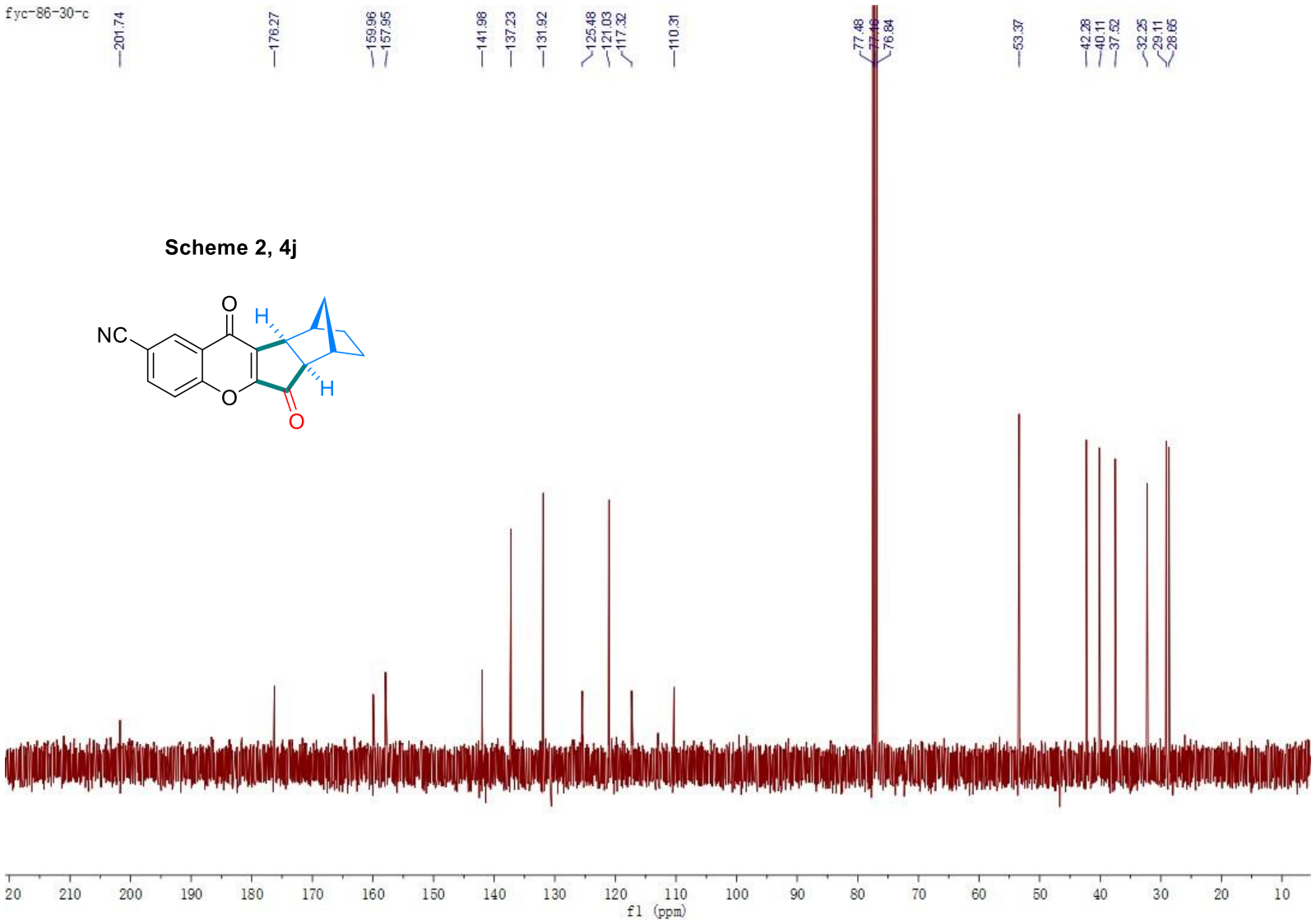

Br
O
H
H
O
O

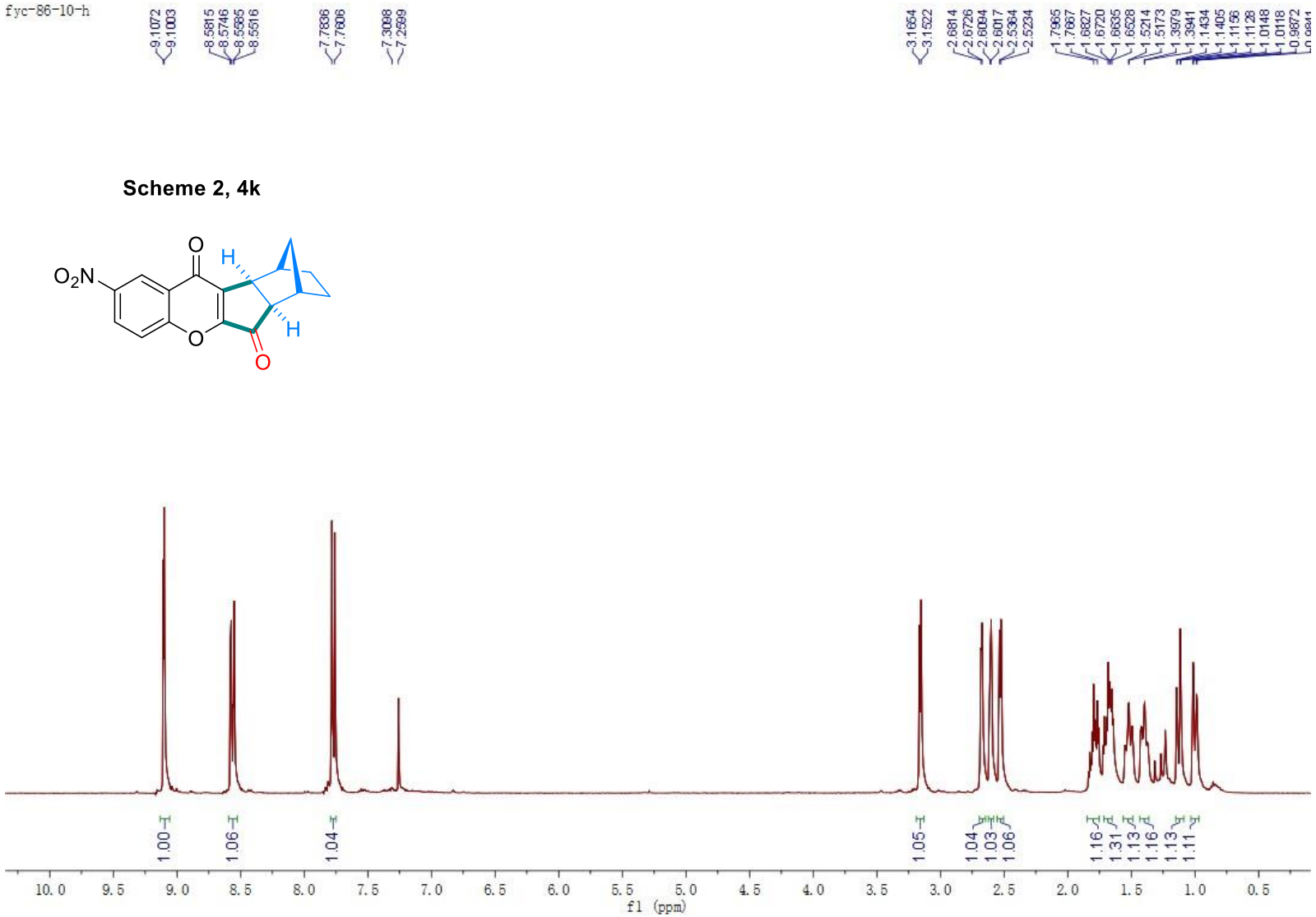

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


fyc-86-30-h
8.5894
8.5845
7.9806
7.9755
7.9687
7.9537
7.7399
7.7160
7.2596
3.1562
3.1429
2.6773
2.6676
2.6129
2.6038
2.5265
2.5133
1.8054
1.7947
1.7842
1.7660
1.7133
1.6938
1.6835
1.6730
1.6534
1.5221
1.4247
1.4213
1.4010
1.3961
1.1395
1.1118
1.0092
1.00
1.01
1.02
0.99
1.05
1.01
1.05
1.16
1.19
1.19
1.16
1.11
1.10
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
f1 (ppm)

Scheme 2, 4j

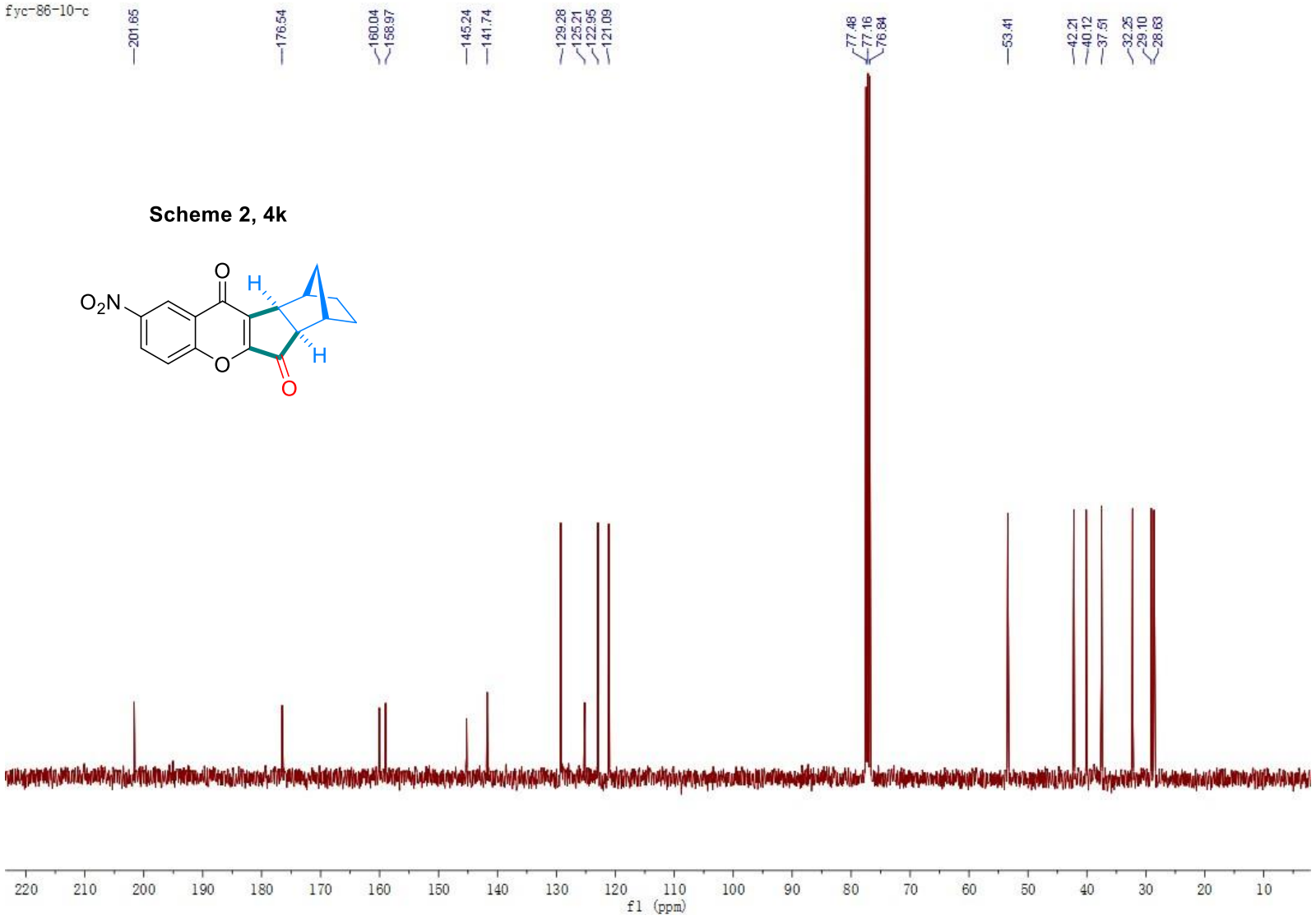
NC
O
H
H
O
O

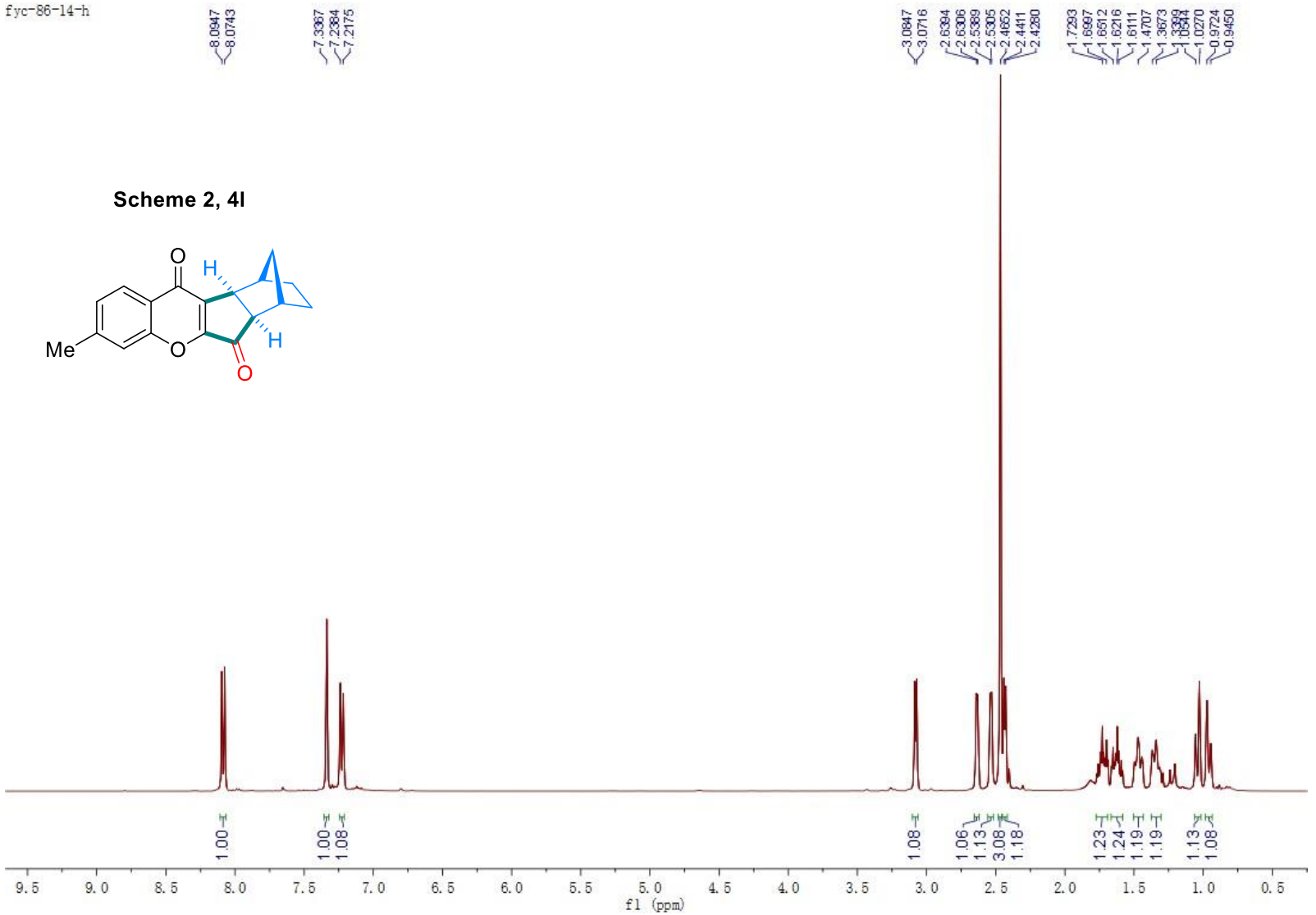

fyc-86-30-c
201.74
176.27
159.96
157.95
141.98
137.23
131.92
125.48
121.03
117.32
110.31
77.48
77.16
76.84
53.37
42.28
40.11
37.52
32.25
29.11
28.65
Scheme 2, 4j
NC
O
H
H
O
O
f1 (ppm)

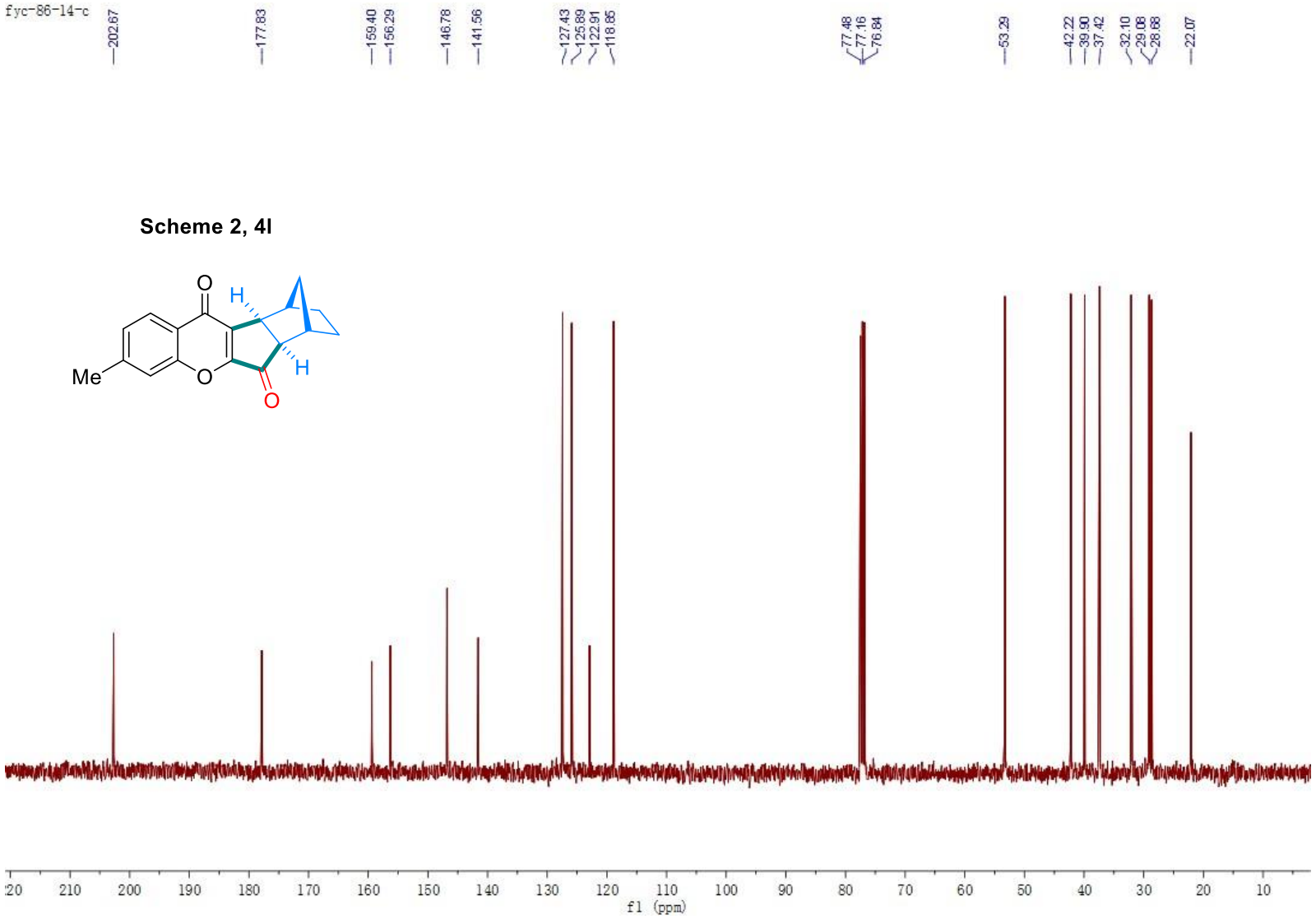

fyc-86-10-h
9.1072
9.1003
8.5815
8.5746
8.5585
8.5516
7.7836
7.7606
7.3098
7.2599
3.1654
3.1522
2.6814
2.6726
2.6094
2.6017
2.5364
2.5234
1.7965
1.7667
1.6827
1.6720
1.6635
1.6528
1.5214
1.5173
1.3979
1.3941
1.1434
1.1405
1.1156
1.1128
1.0148
1.0118
0.9872
1.00
1.06
1.04
1.05
1.04
1.03
1.06
1.16
1.31
1.13
1.16
1.13
1.11
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
f1 (ppm)

Scheme 2, 4k

O
H
O_2N
O
H
O

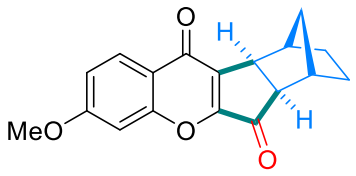

fyc-86-10-c
201.65
176.54
160.04
158.97
145.24
141.74
129.28
125.21
122.95
121.09
77.48
77.16
76.84
53.41
42.21
40.12
37.51
32.25
29.10
28.63
Scheme 2, 4k
O
H
O2N
O
H
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

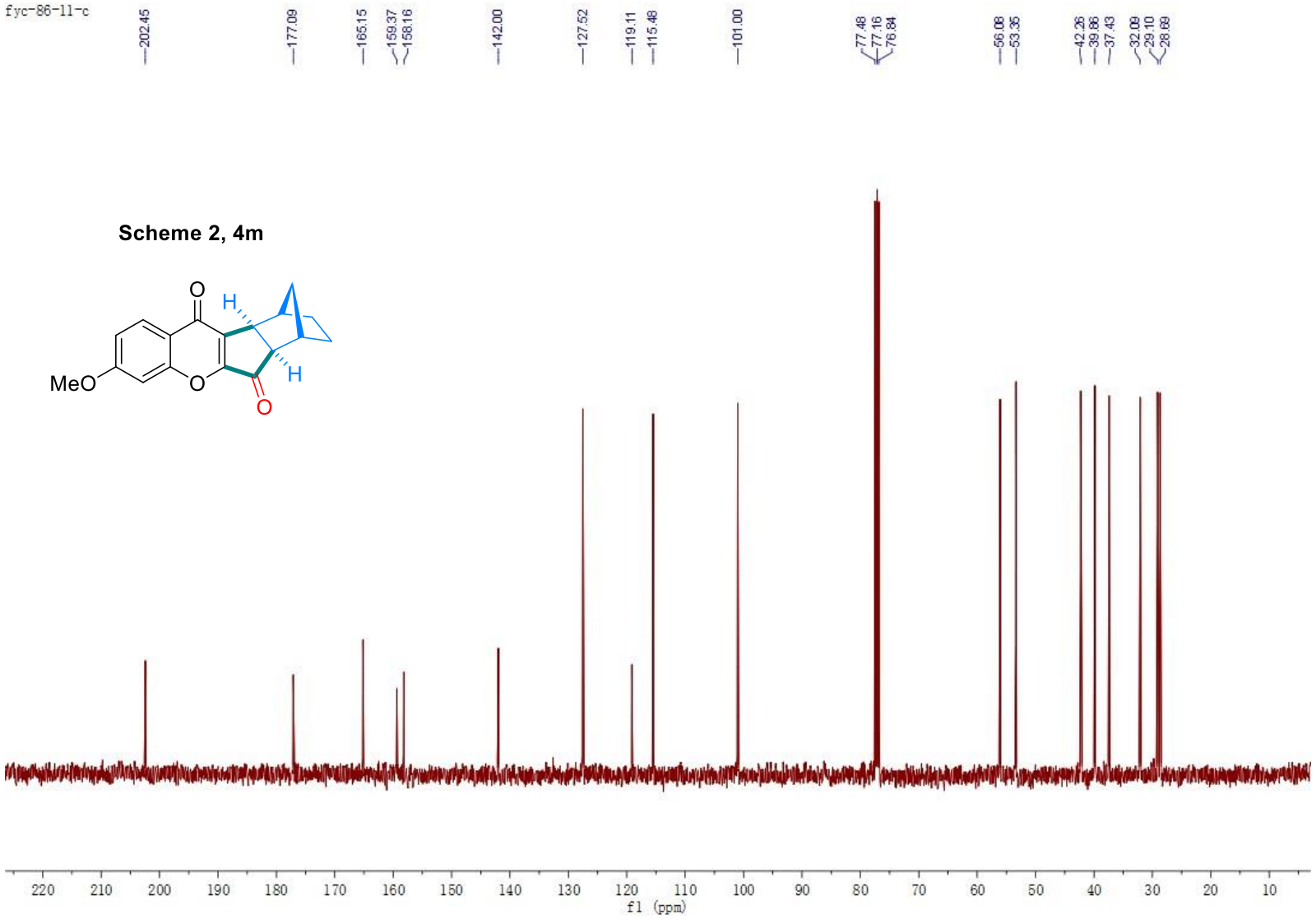

fyc-86-14-h
8.0947
8.0743
7.3367
7.2384
7.2175
3.0847
3.0716
2.6394
2.6306
2.5389
2.5305
2.4652
2.4411
2.4260
1.7293
1.6997
1.6612
1.6216
1.6111
1.4707
1.3673
1.0270
0.9724
0.9450
Scheme 2, 4l
O
H
Me
O
H
O
1.00
1.00
1.08
1.08
1.06
1.13
3.08
1.18
1.23
1.24
1.19
1.19
1.13
1.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


fyc-86-14-c
202.67
177.83
159.40
156.29
146.78
141.56
127.43
125.89
122.91
118.85
77.48
77.16
76.84
53.29
42.22
39.90
37.42
32.10
29.08
28.88
22.07
Scheme 2, 4l
O
H
Me
O
H
O
f1 (ppm)

fyc-86-11-h

Scheme 2, 4m

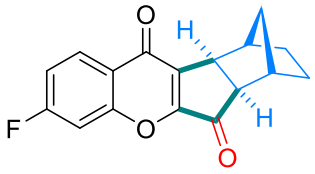


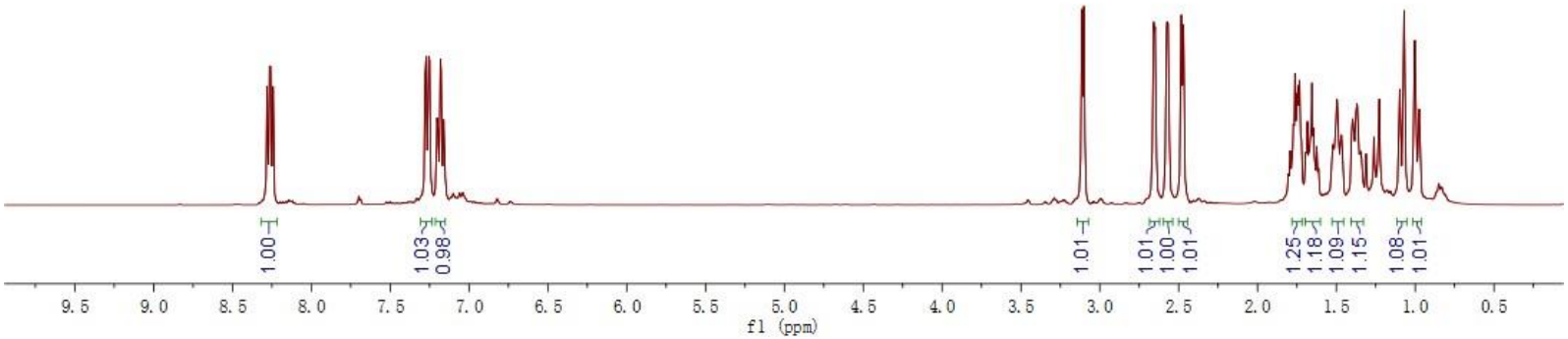

fyc-86-11-c
202.45
177.09
165.15
159.37
158.16
142.00
127.52
119.11
115.48
101.00
77.48
77.16
76.84
56.06
53.35
42.26
39.86
37.43
32.09
29.10
28.69
Scheme 2, 4m
O
H
MeO
O
H
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

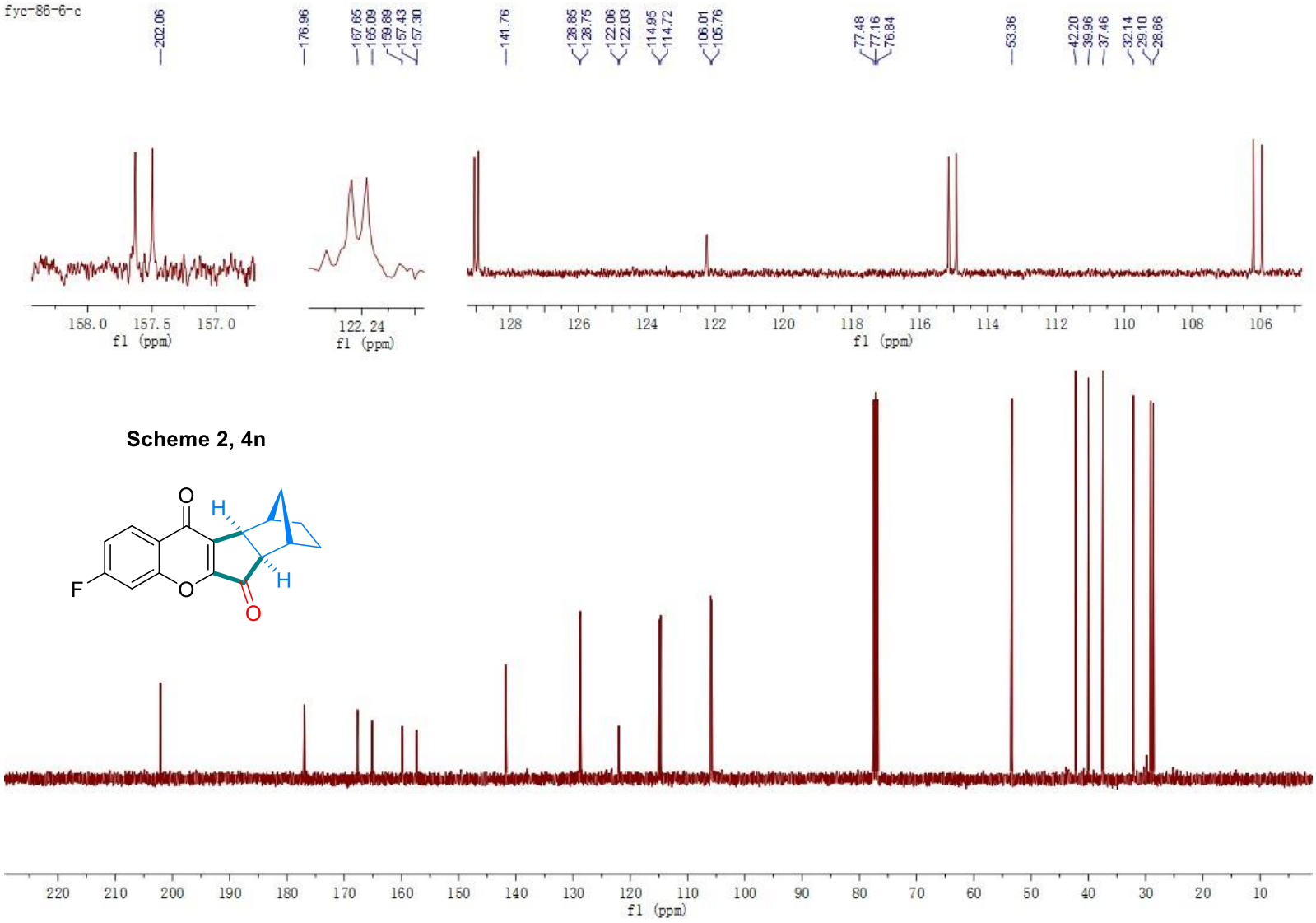
fyc-86-6-h

8.2801
8.2643
8.2561
8.2423
7.2770
7.2718
7.2550
7.2496
7.2026
7.1971
7.1809
7.1606
7.1552
3.1137
3.1006
2.6579
2.6497
2.5742
2.5669
2.4828
2.4701
1.7624
1.7515
1.7434
1.7333
1.6542
1.4965
1.3973
1.0706
1.0021
0.9746

Scheme 2, 4n



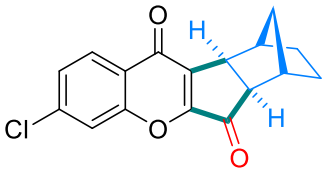


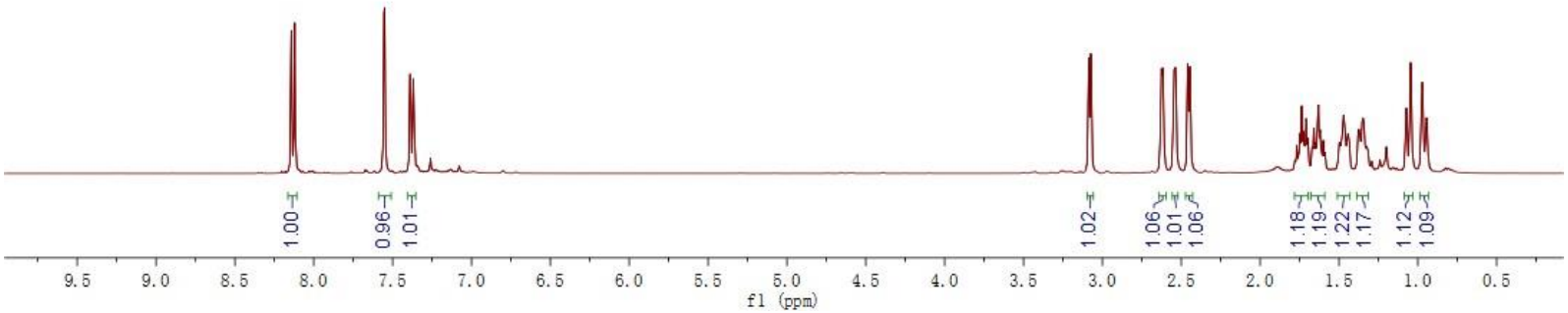

fyc-86-6-c
202.06
176.96
167.65
166.09
159.89
157.43
157.30
141.76
128.85
128.75
122.06
122.03
114.95
114.72
106.01
105.76
77.48
77.16
76.84
53.36
42.20
39.96
37.46
32.14
29.10
28.66
158.0
157.5
157.0
f1 (ppm)
122.24
f1 (ppm)
128
126
124
122
120
118
116
114
112
110
108
106
f1 (ppm)
Scheme 2, 4n
O
H
F
O
H
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

fyc-86-2-h

8.1427
8.1213
7.5547
7.5508
7.3907
7.3866
7.3693
7.3652
7.2601
3.0860
3.0728
2.6255
2.6167
2.5447
2.5367
2.4696
2.4456
1.7370
1.7076
1.6694
1.6298
1.6195
1.4707
1.3748
1.3474
1.0732
1.0457
0.9724
0.9449

Scheme 2, 4o

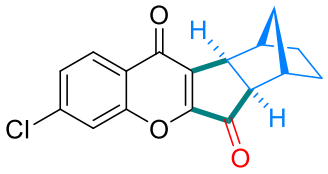


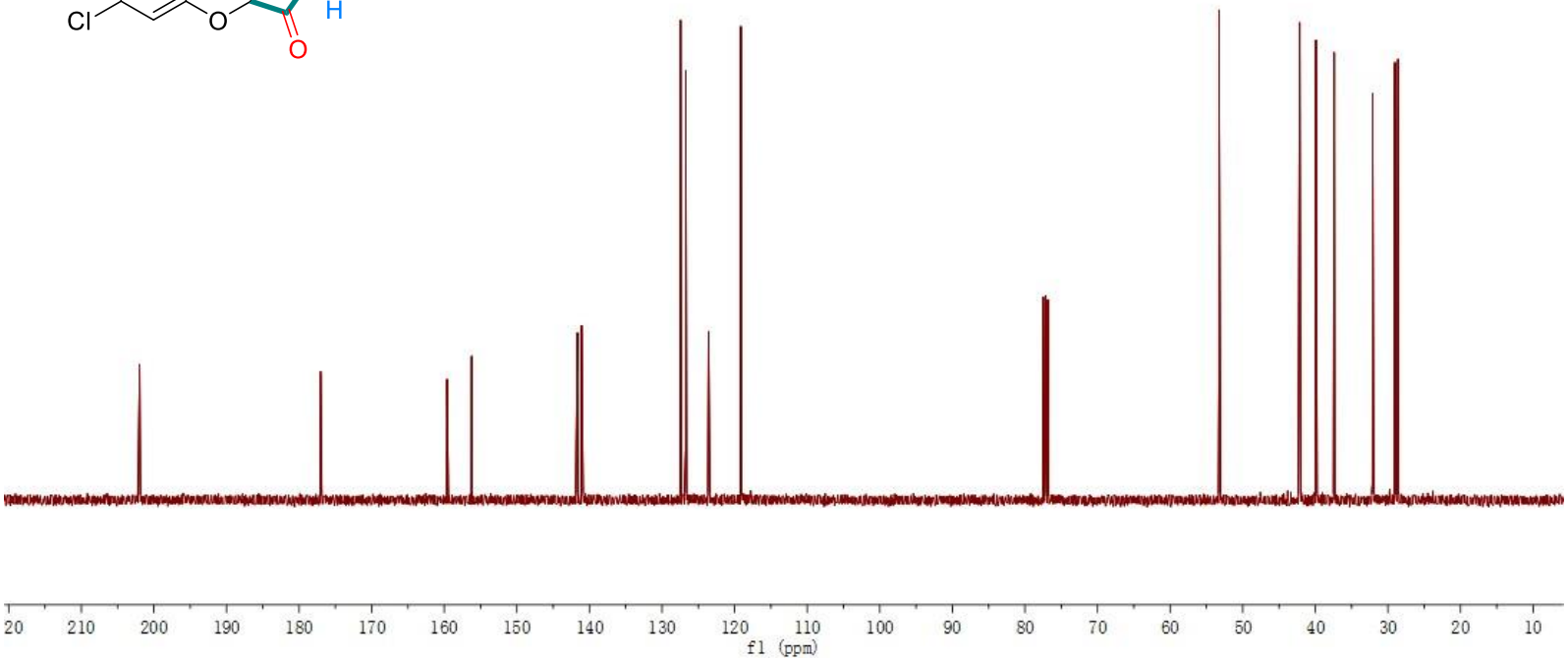


fyc-86-2-c

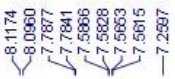
201.98
177.05
159.60
156.22
141.66
141.09
127.46
126.74
123.58
119.14
77.48
77.16
76.84
53.26
42.15
39.92
37.40
32.11
29.04
28.60

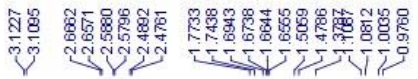
Scheme 2, 4o



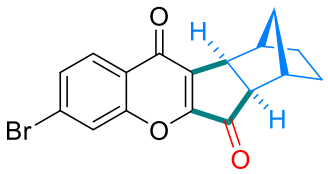


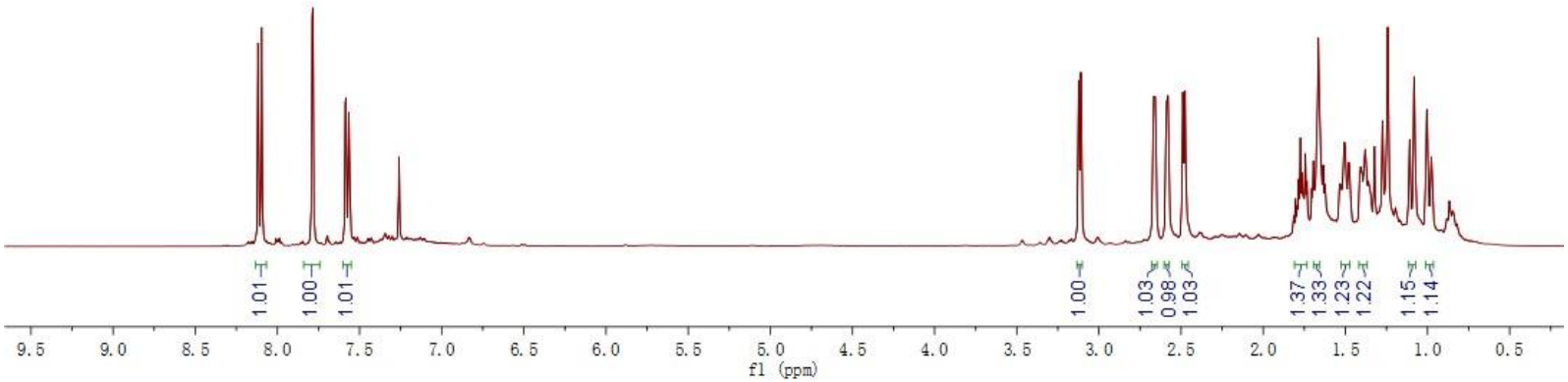
fyc-86-5-h

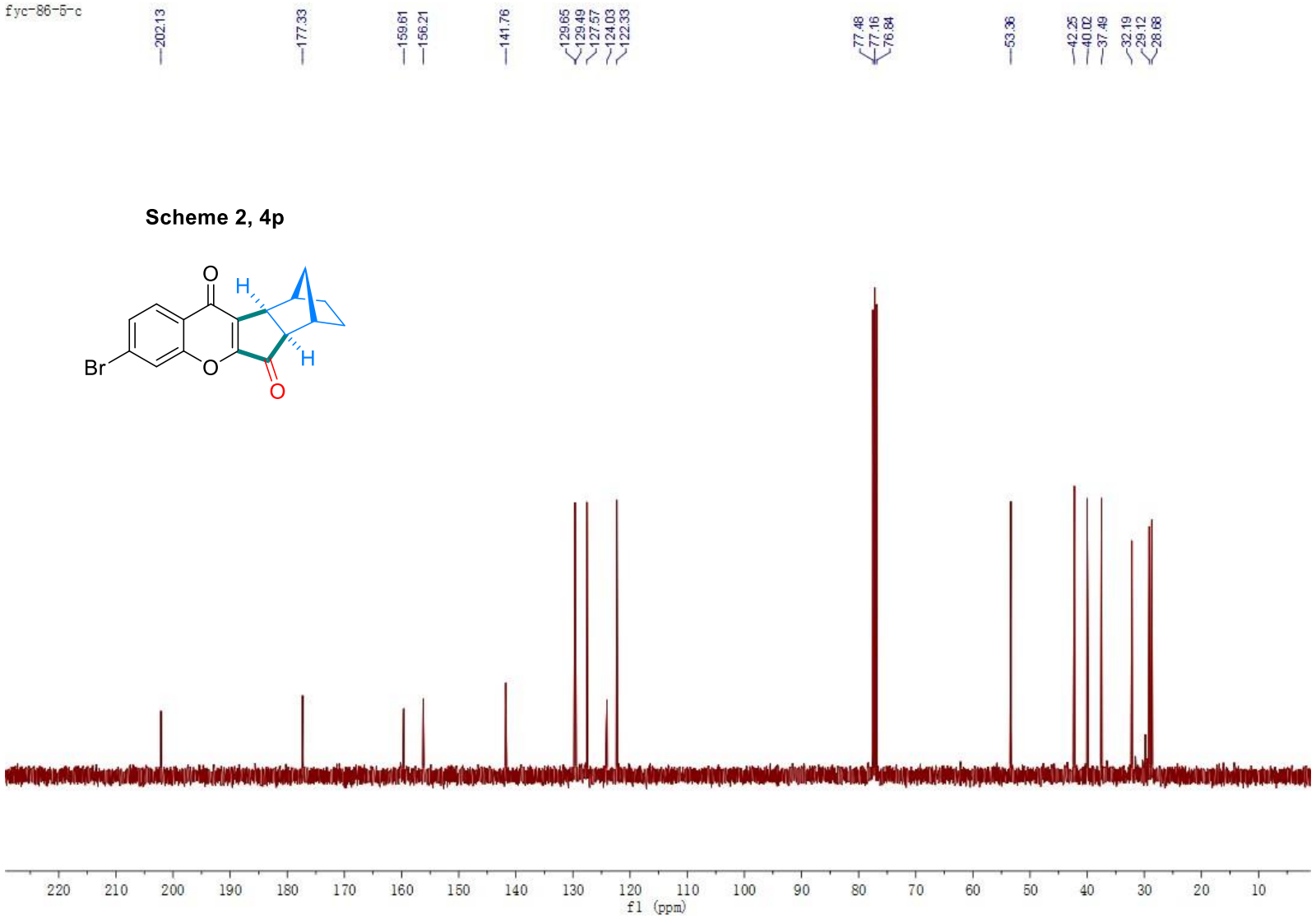


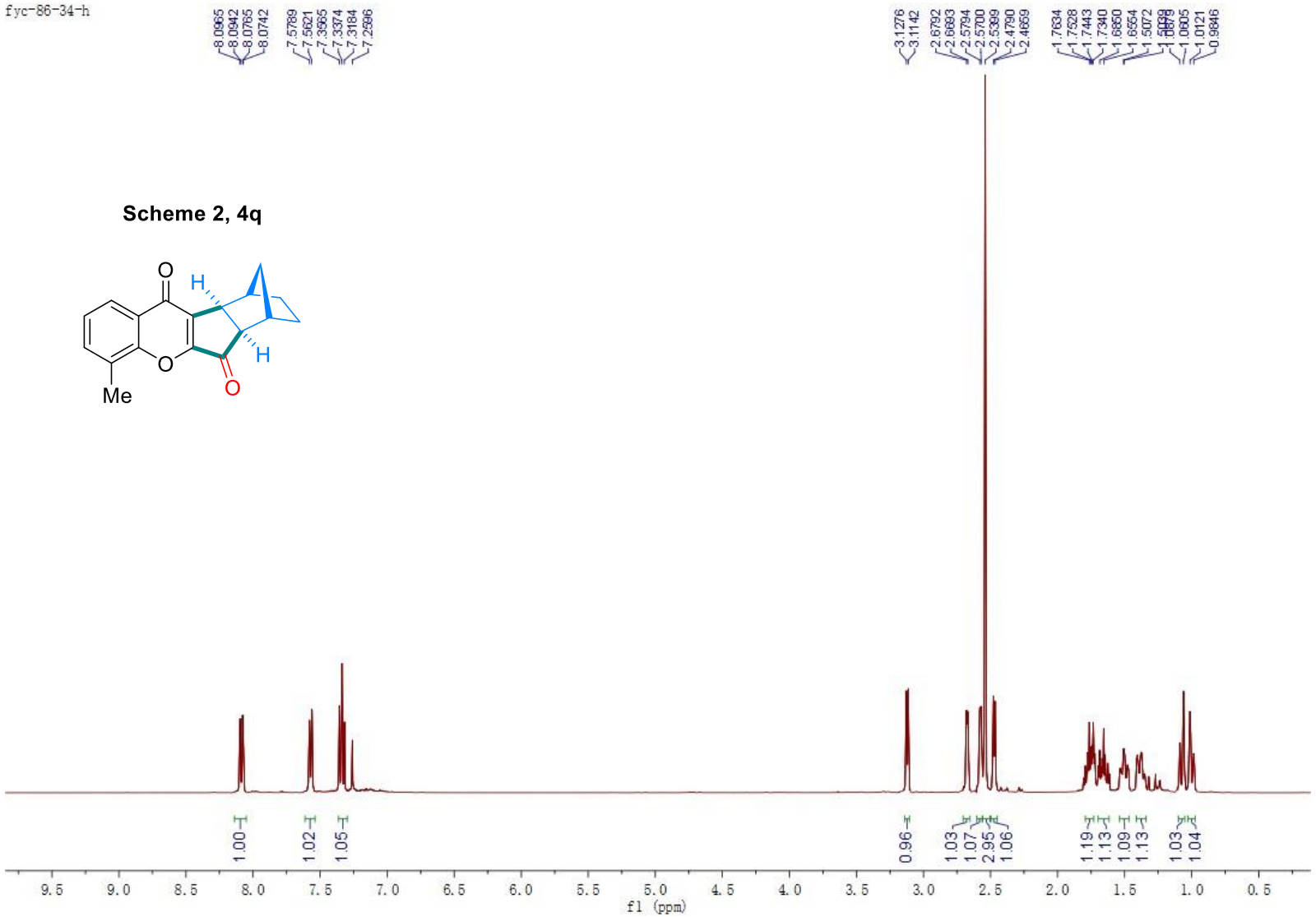


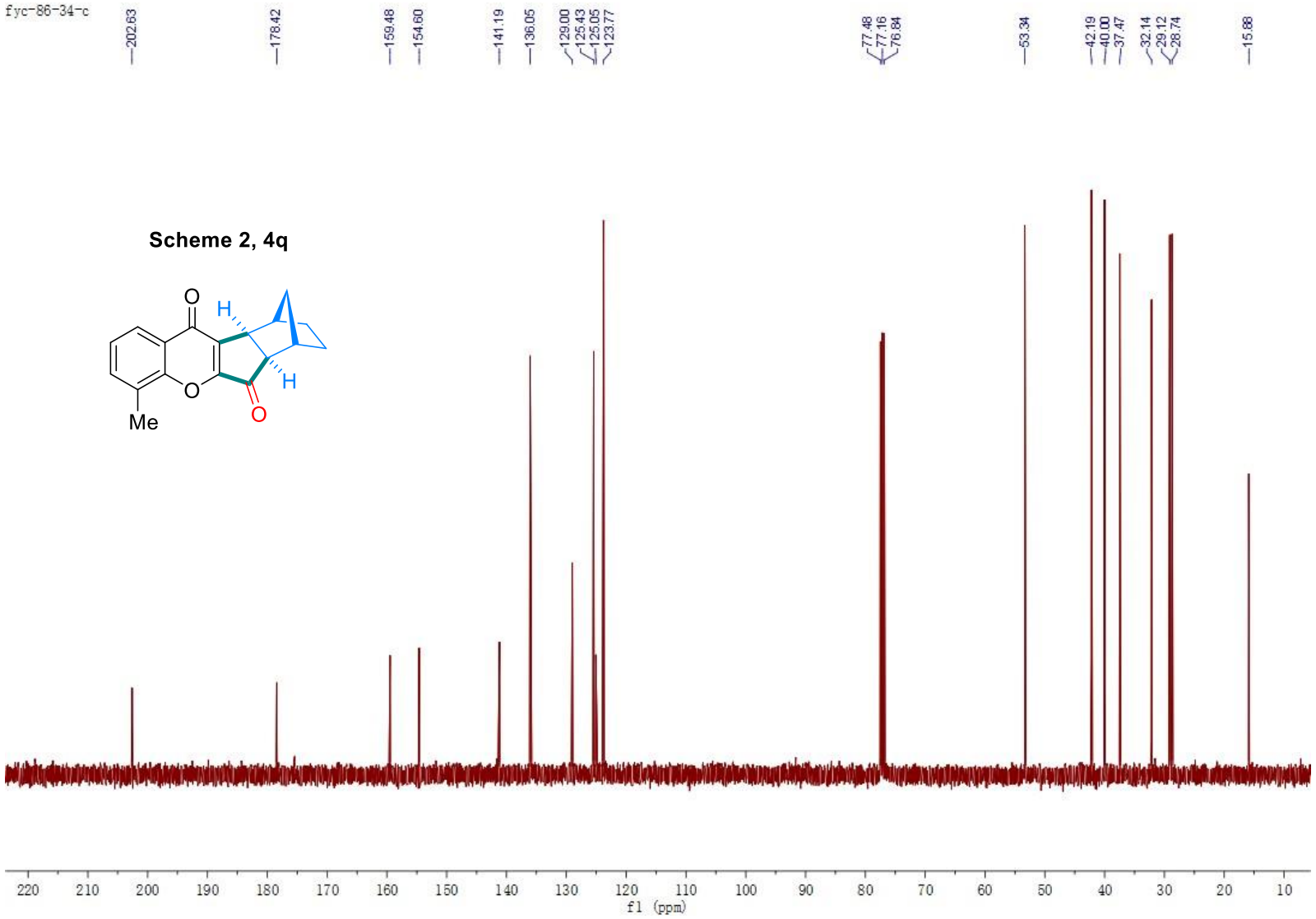
Scheme 2, 4p





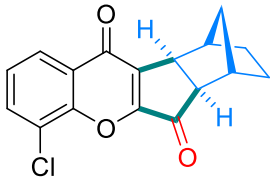

fyc-86-5-c
202.13
177.33
159.61
156.21
141.76
129.65
129.49
127.57
124.03
122.33
77.48
77.16
76.84
53.36
42.25
40.02
37.49
32.19
29.12
28.88
Scheme 2, 4p
O
H
Br
O
H
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

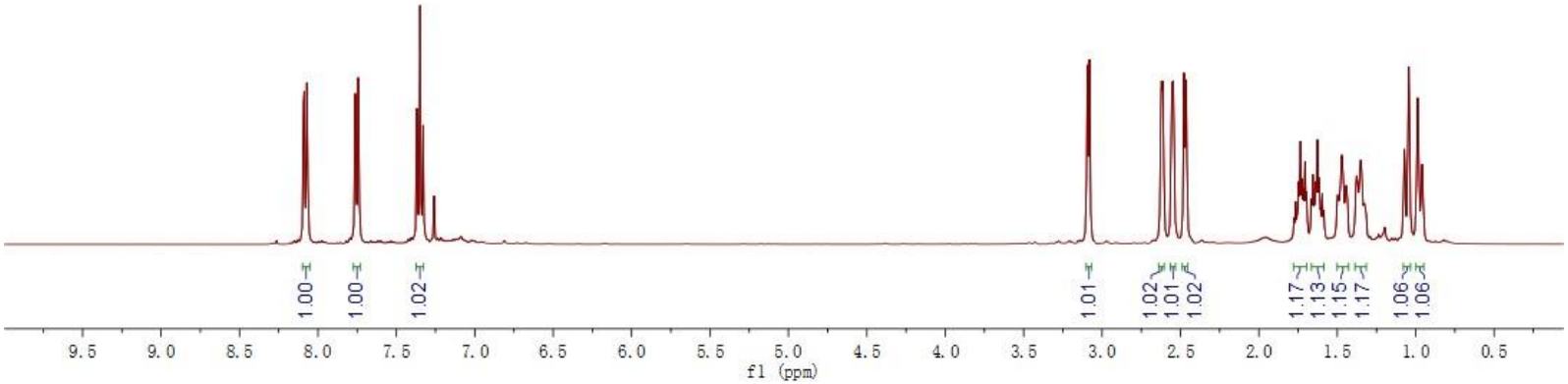

fyc-86-34-h
8.0965
8.0942
8.0765
8.0742
7.5789
7.5621
7.3665
7.3374
7.3184
7.2996
3.1276
3.1142
2.6792
2.6693
2.5794
2.5700
2.5399
2.4790
2.4659
1.7634
1.7528
1.7443
1.7340
1.6850
1.6554
1.5072
1.0805
1.0121
0.9846
Scheme 2, 4q
O
H
H
O
O
Me
1.00
1.02
1.05
0.96
1.03
1.07
2.95
1.06
1.19
1.13
1.09
1.13
1.03
1.04
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
f1 (ppm)

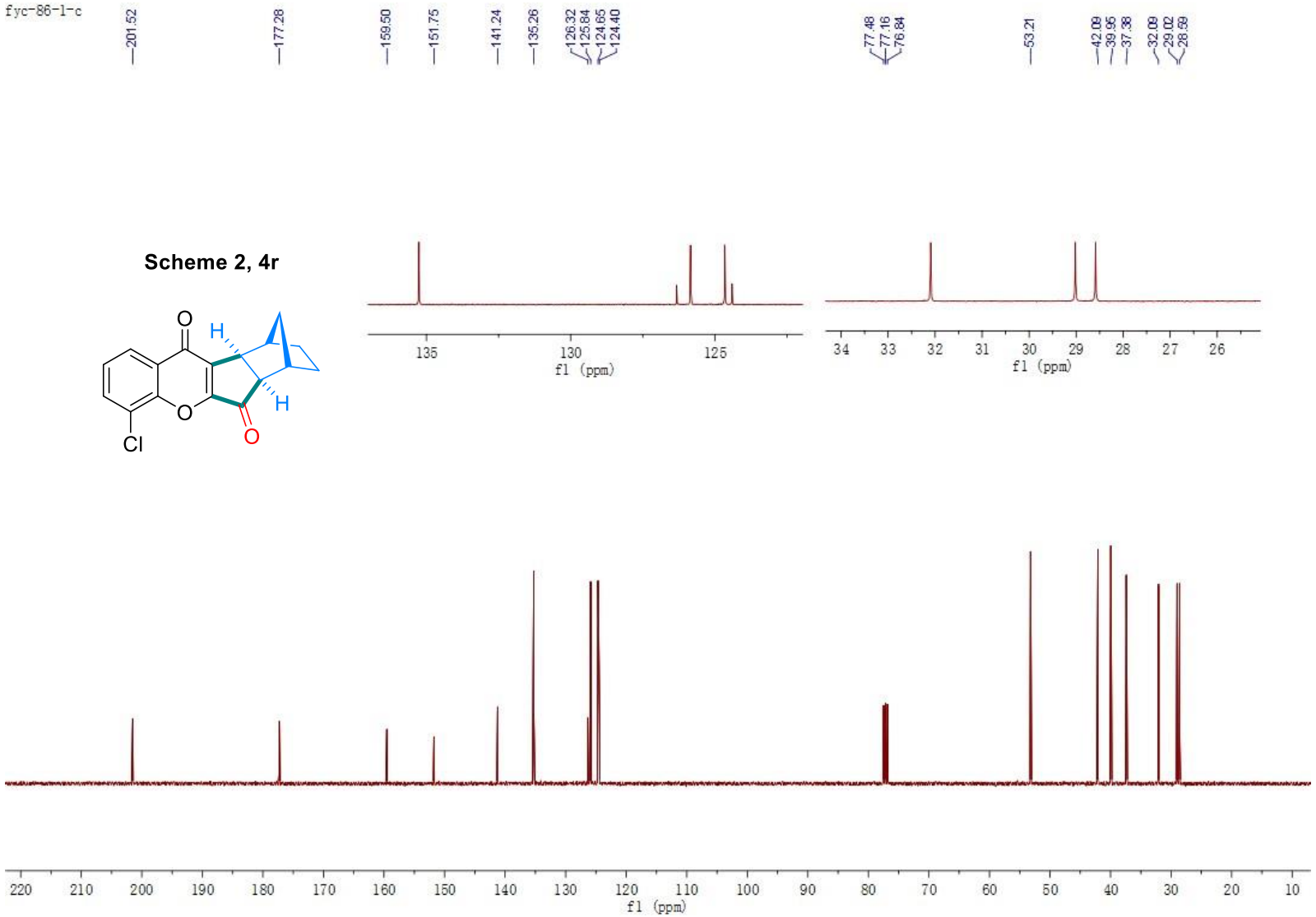

fyc-86-34-c
202.63
178.42
159.48
154.60
141.19
136.05
129.00
125.43
125.05
123.77
77.48
77.16
76.84
53.34
42.19
40.00
37.47
32.14
29.12
28.74
15.88
Scheme 2, 4q
O
H
H
O
O
Me
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

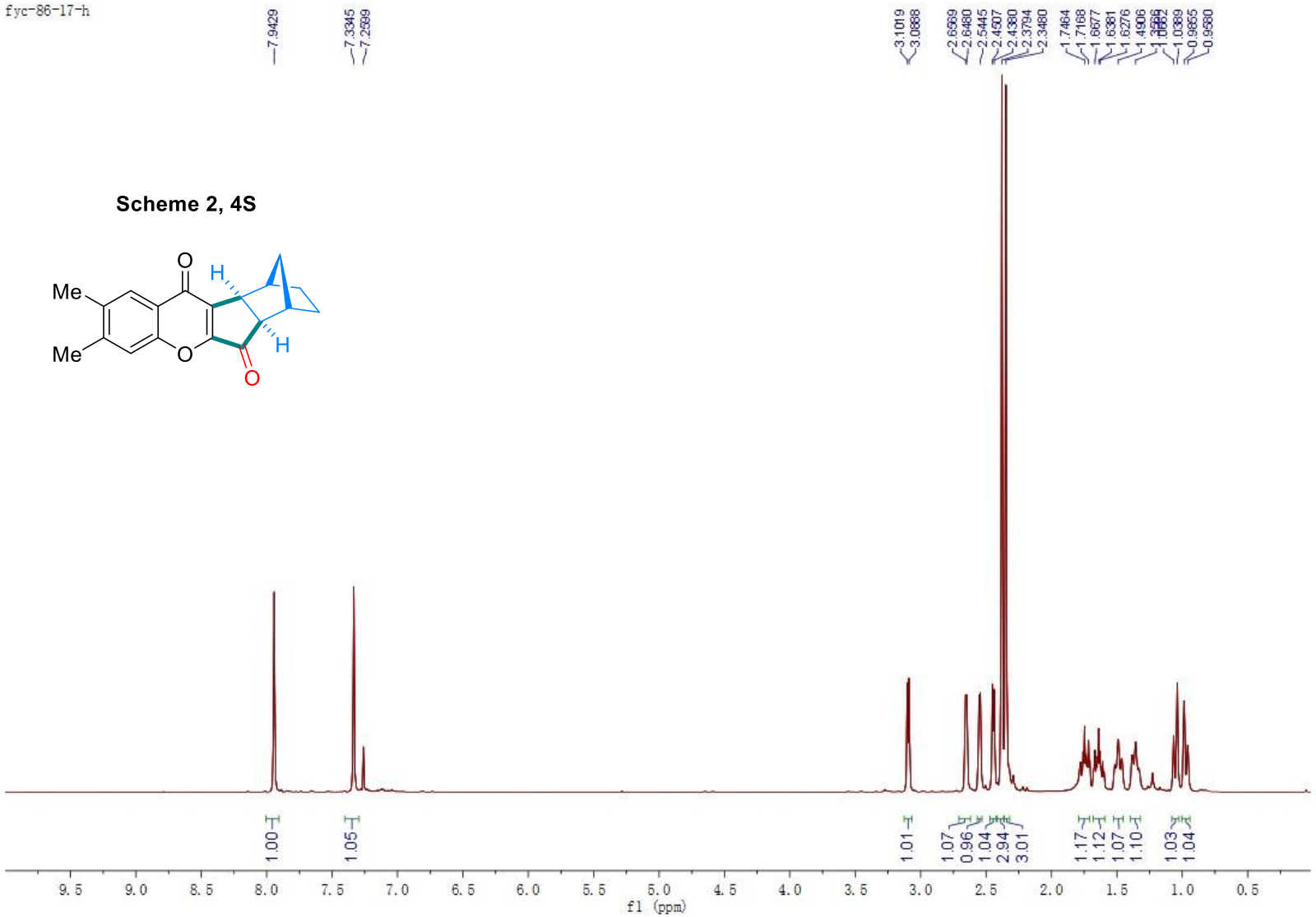
fyc-86-1-h

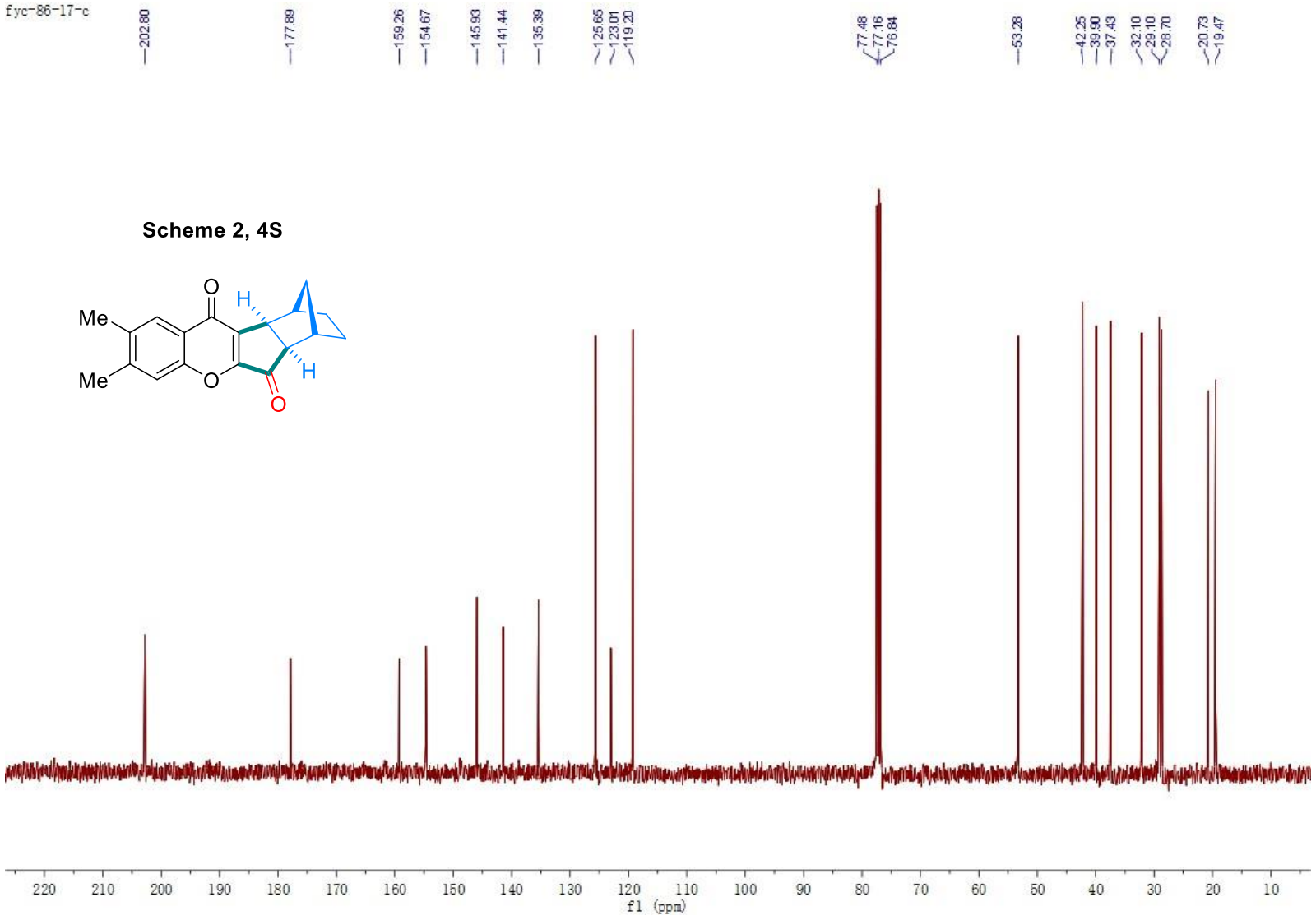
Scheme 2, 4r

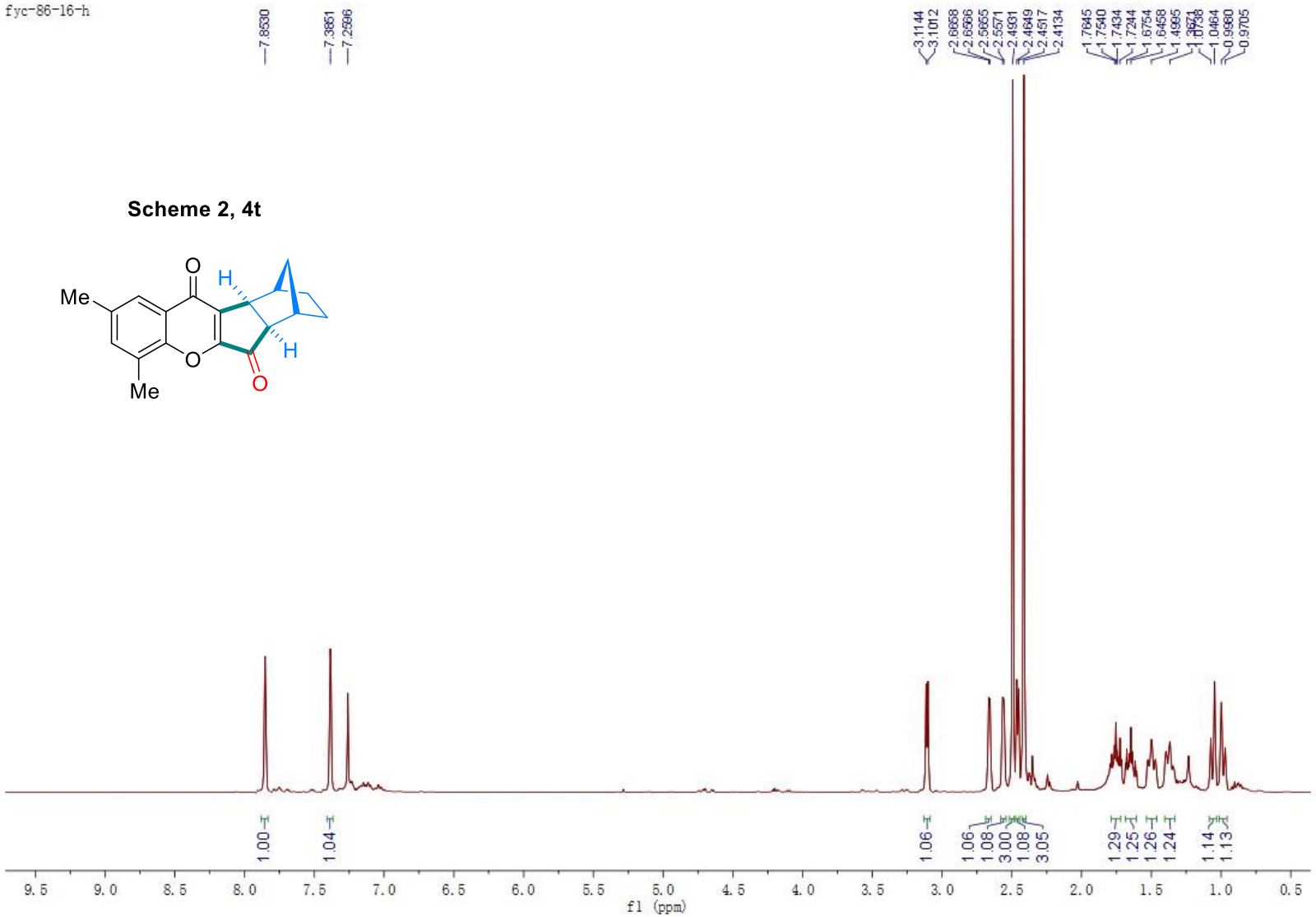





fyc-86-1-c
201.52
177.28
159.50
151.75
141.24
135.26
126.32
125.84
124.65
124.40
77.48
77.16
76.84
53.21
42.09
39.95
37.38
32.09
29.02
28.69
Scheme 2, 4r
O
H
O
H
O
Cl
135
130
125
f1 (ppm)
34
33
32
31
30
29
28
27
26
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


fyc-86-17-h
7.9429
7.3345
7.2599
3.1019
3.0888
2.6569
2.6480
2.5445
2.4507
2.4380
2.3794
2.3480
1.7464
1.7168
1.6677
1.6381
1.6276
1.4906
1.0389
0.9855
0.9680
Scheme 2, 4S
Me
Me
O
O
O
H
H
1.00
1.05
1.01
1.07
0.96
1.04
2.94
3.01
1.17
1.12
1.07
1.10
1.03
1.04
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
f1 (ppm)

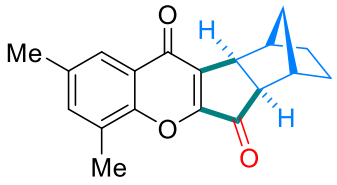

fyc-86-17-c
202.80
177.89
159.26
154.67
145.93
141.44
135.39
125.65
123.01
119.20
77.48
77.16
76.84
53.28
42.25
39.90
37.43
32.10
29.10
28.70
20.73
19.47
Scheme 2, 4S
Me
Me
O
O
O
H
H
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

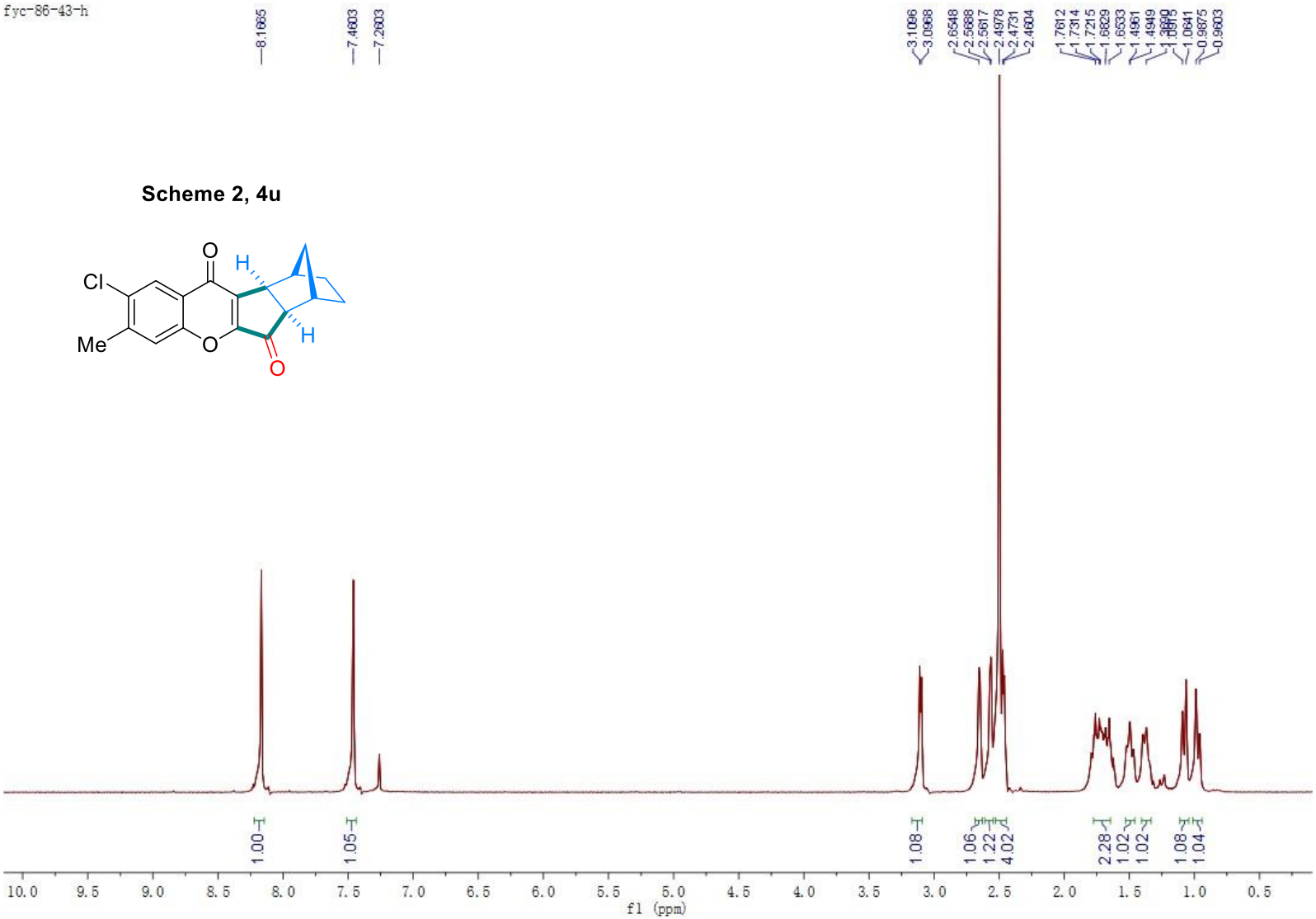

fyc-86-16-h
7.8530
7.3851
7.2596
3.1144
3.1012
2.6868
2.6666
2.5665
2.5571
2.4931
2.4649
2.4517
2.4134
1.7645
1.7540
1.7434
1.7244
1.6754
1.6458
1.4995
1.3671
1.0738
1.0464
0.9960
0.9705
Scheme 2, 4t
Me
O
H
H
O
Me
1.00
1.04
1.06
1.06
1.08
3.00
1.08
3.05
1.29
1.25
1.26
1.24
1.14
1.13
9.5
9.0
8.5
8.0
7.5
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
f1 (ppm)

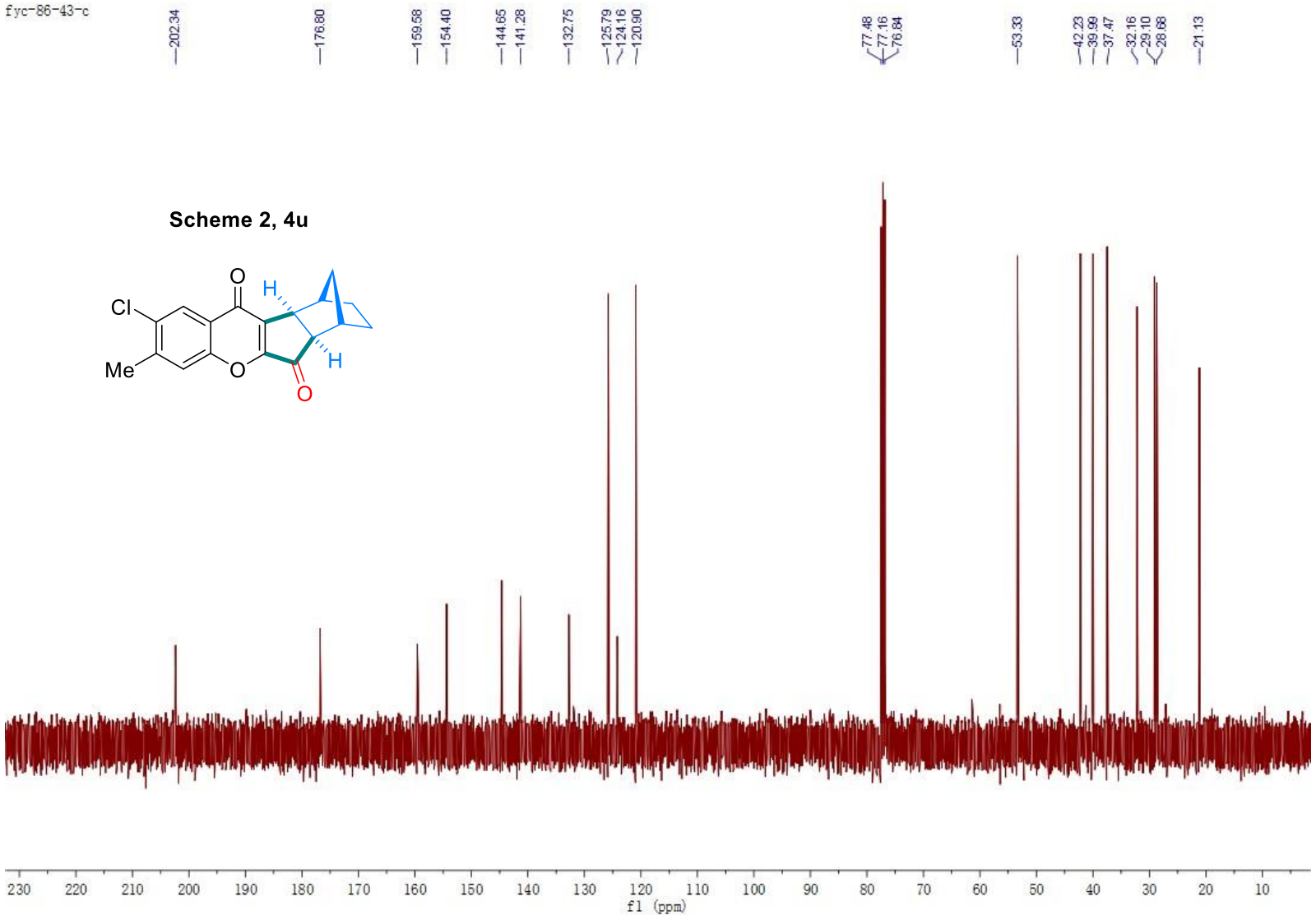
fyc-86-16-c

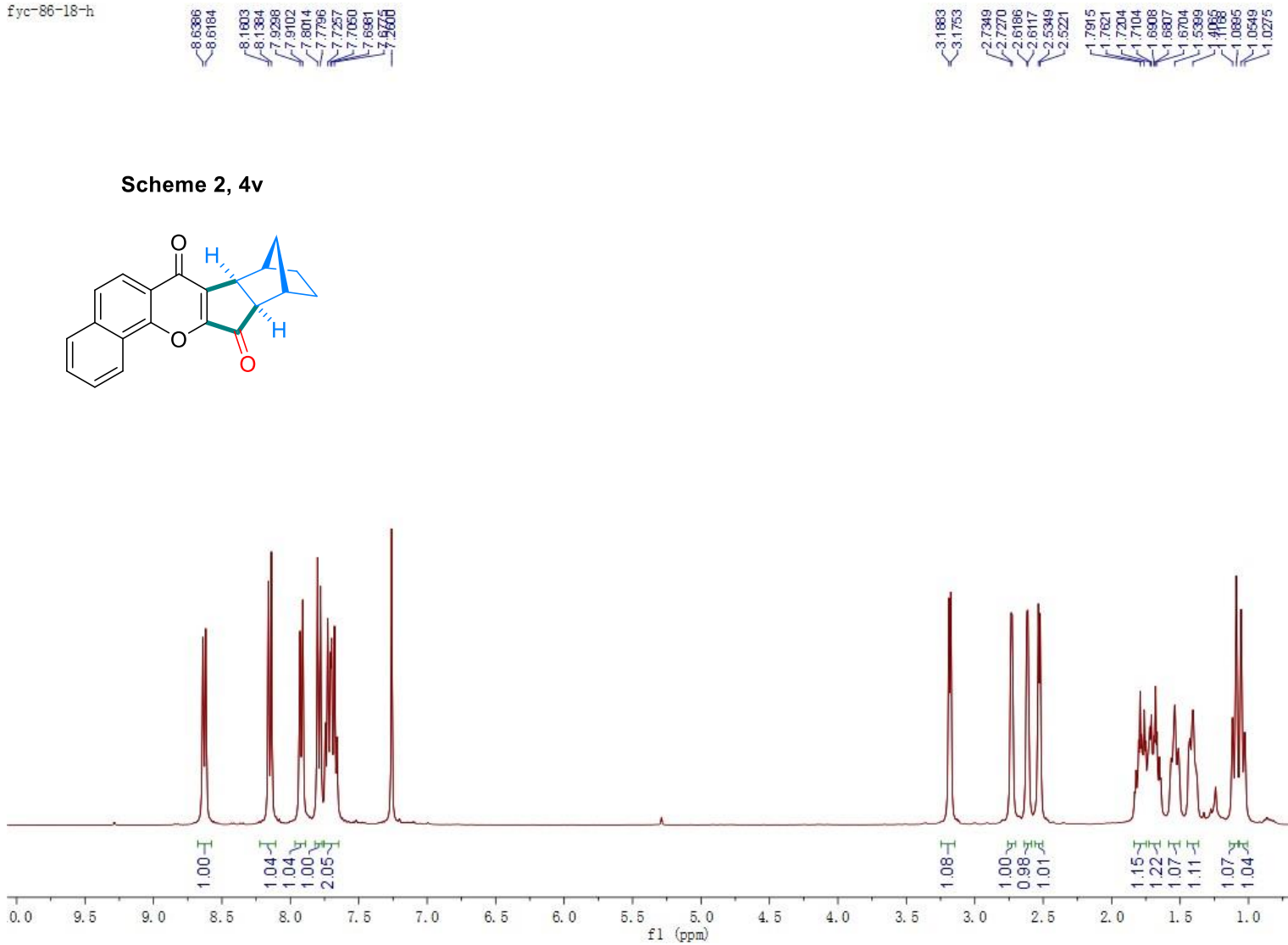
202.74
178.44
159.33
152.89
141.04
137.42
135.44
128.60
124.77
123.03
77.48
77.16
76.84
53.33
42.16
39.97
37.45
32.12
29.10
28.73
20.99
15.78

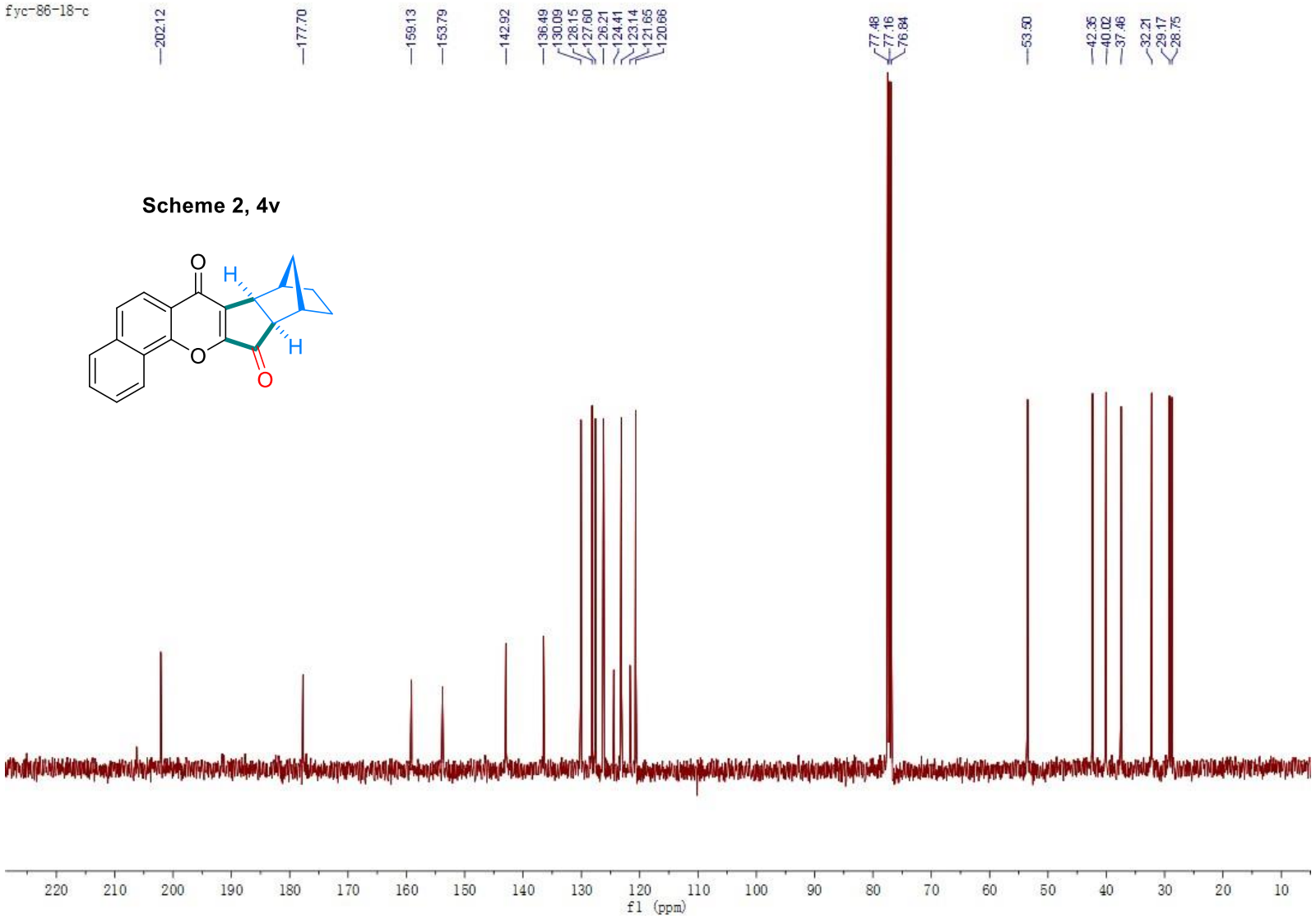
Scheme 2, 4t




fyc-86-43-h
8.1665
7.4603
7.2603
3.1096
3.0968
2.6548
2.5888
2.5617
2.4978
2.4731
2.4604
1.7612
1.7314
1.7215
1.6829
1.6533
1.4961
1.4949
1.0641
0.9875
0.9603
Scheme 2, 4u
Cl
Me
O
O
O
H
H
1.00
1.05
1.08
1.06
1.22
4.02
2.28
1.02
1.02
1.08
1.04
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
f1 (ppm)

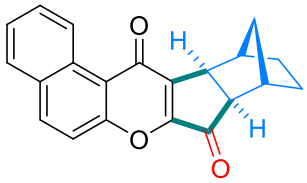

fyc-86-43-c
202.34
176.80
159.58
154.40
144.65
141.28
132.75
125.79
124.16
120.90
77.48
77.16
76.84
53.33
42.23
39.99
37.47
32.16
29.10
28.88
21.13
Scheme 2, 4u
Cl
Me
O
O
O
H
H
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

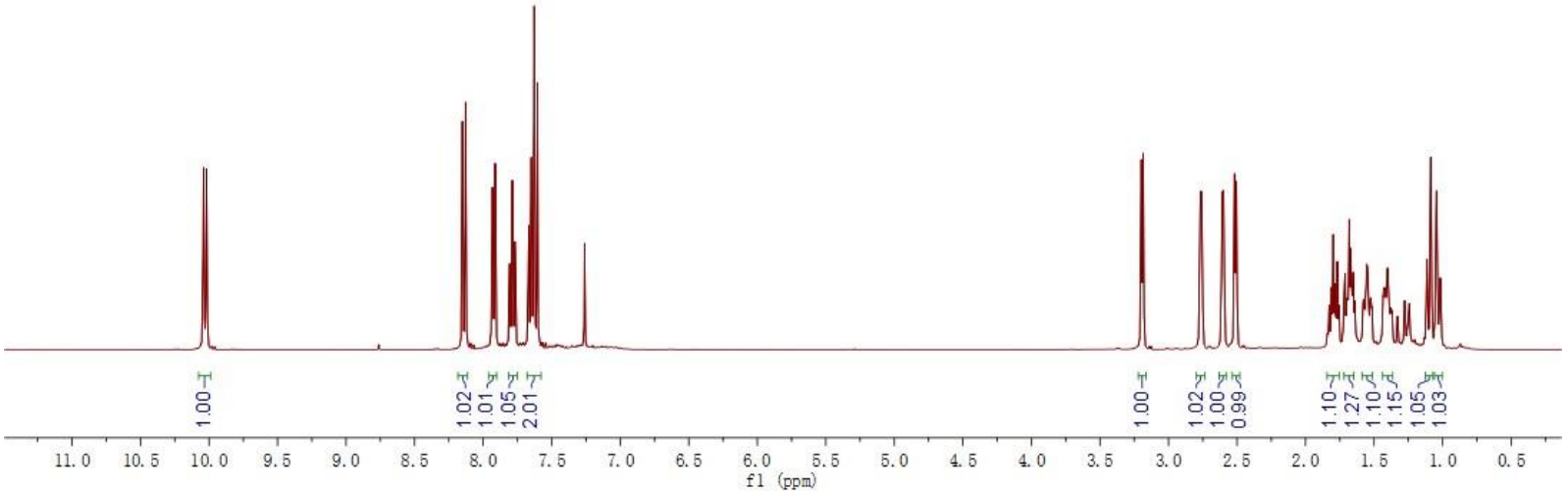

fyc-86-18-h
8.6386
8.6184
8.1603
8.1384
7.9298
7.9102
7.8014
7.7796
7.7257
7.7050
7.6861
3.1883
3.1753
2.7349
2.7270
2.6186
2.6117
2.5349
2.5221
1.7915
1.7621
1.7204
1.7104
1.6908
1.6807
1.6704
1.5399
1.0895
1.0549
1.0275
Scheme 2, 4v
O
H
H
O
O
1.00
1.04
1.04
1.00
2.05
1.08
1.00
0.98
1.01
1.15
1.22
1.07
1.11
1.07
1.04
0.0
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
f1 (ppm)

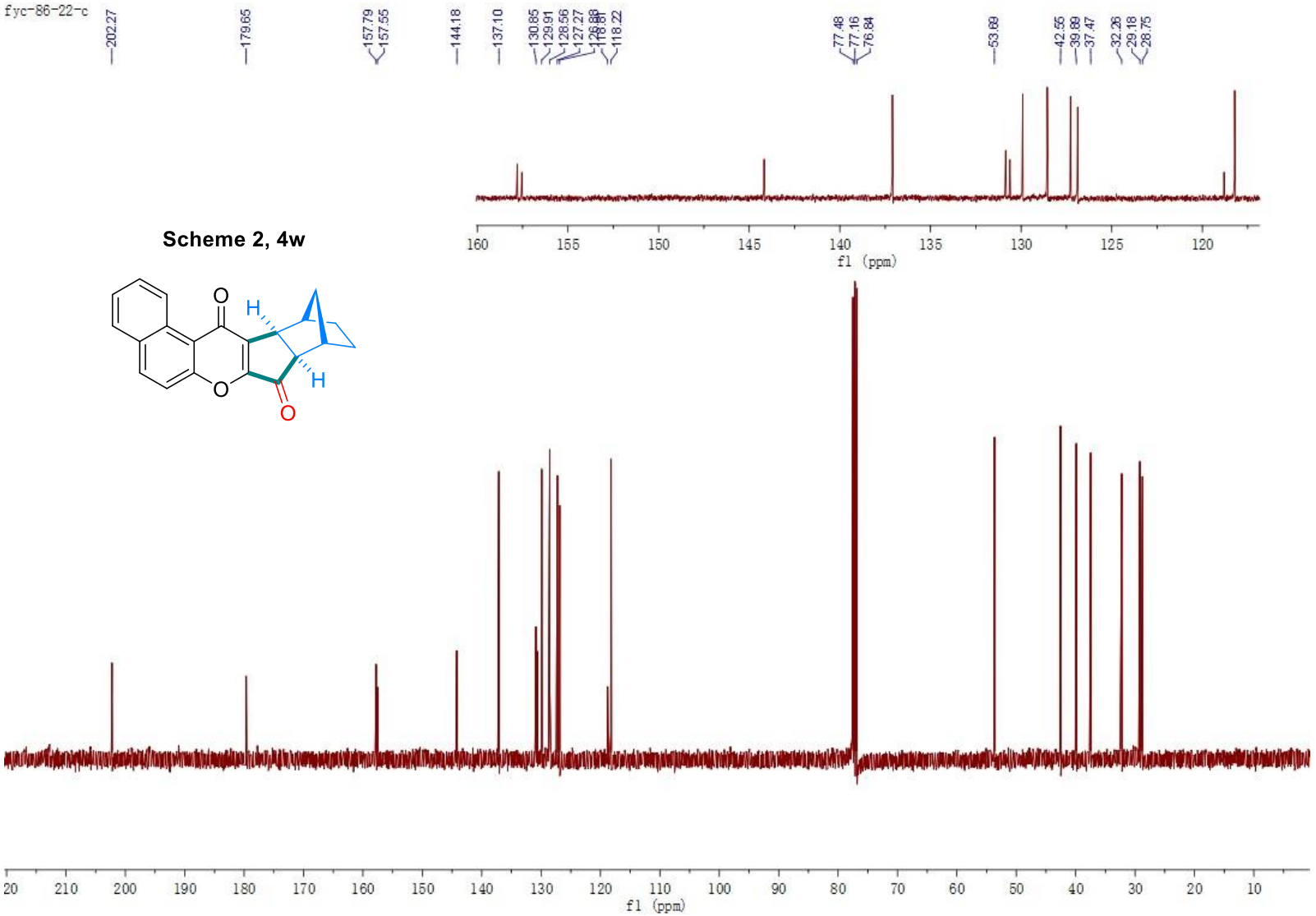

fyc-86-18-c
202.12
177.70
159.13
153.79
142.92
136.49
130.09
128.15
127.60
126.21
124.41
123.14
121.65
120.66
77.48
77.16
76.84
53.50
42.35
40.02
37.46
32.21
29.17
28.75
Scheme 2, 4v
O
H
H
O
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


fyc-86-22-h
10.0390
10.0174
8.1508
8.1281
7.9324
7.9125
7.8075
7.8046
7.7897
7.7866
7.7685
7.7655
7.6666
7.6489
7.6275
7.6046
7.2597
3.1974
3.1843
2.7666
2.7570
2.6073
2.5983
2.5175
2.5044
1.7979
1.7683
1.7111
1.6918
1.6813
1.6706
1.6519
1.5529
1.5493
1.4057
1.4011
1.1138
1.0863
1.0442

Scheme 2, 4w

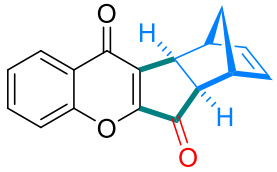

O
H
H
O
O

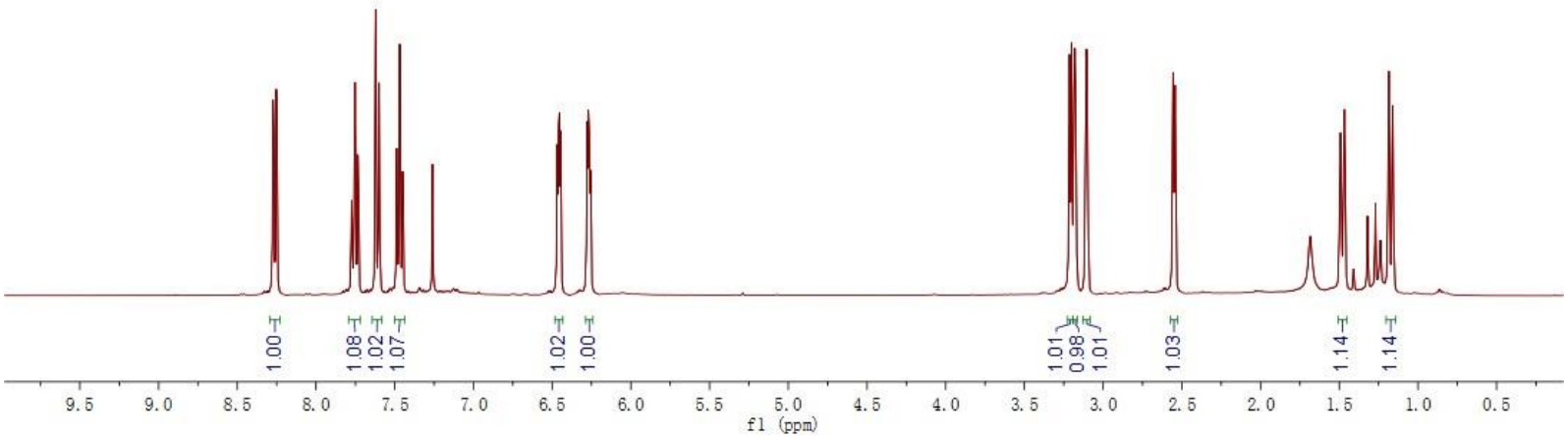

1.00
1.02
1.01
1.05
2.01
1.00
1.02
1.00
0.99
1.10
1.27
1.10
1.15
1.05
1.03
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


fyc-86-22-c
202.27
179.65
157.79
157.55
144.18
137.10
130.85
129.91
128.56
127.27
118.22
77.48
77.16
76.84
53.89
42.55
39.89
37.47
32.26
29.18
28.75
f1 (ppm)
Scheme 2, 4w
O
H
H
O
O
f1 (ppm)

fyc-86-21-h

Figure 1, 4x





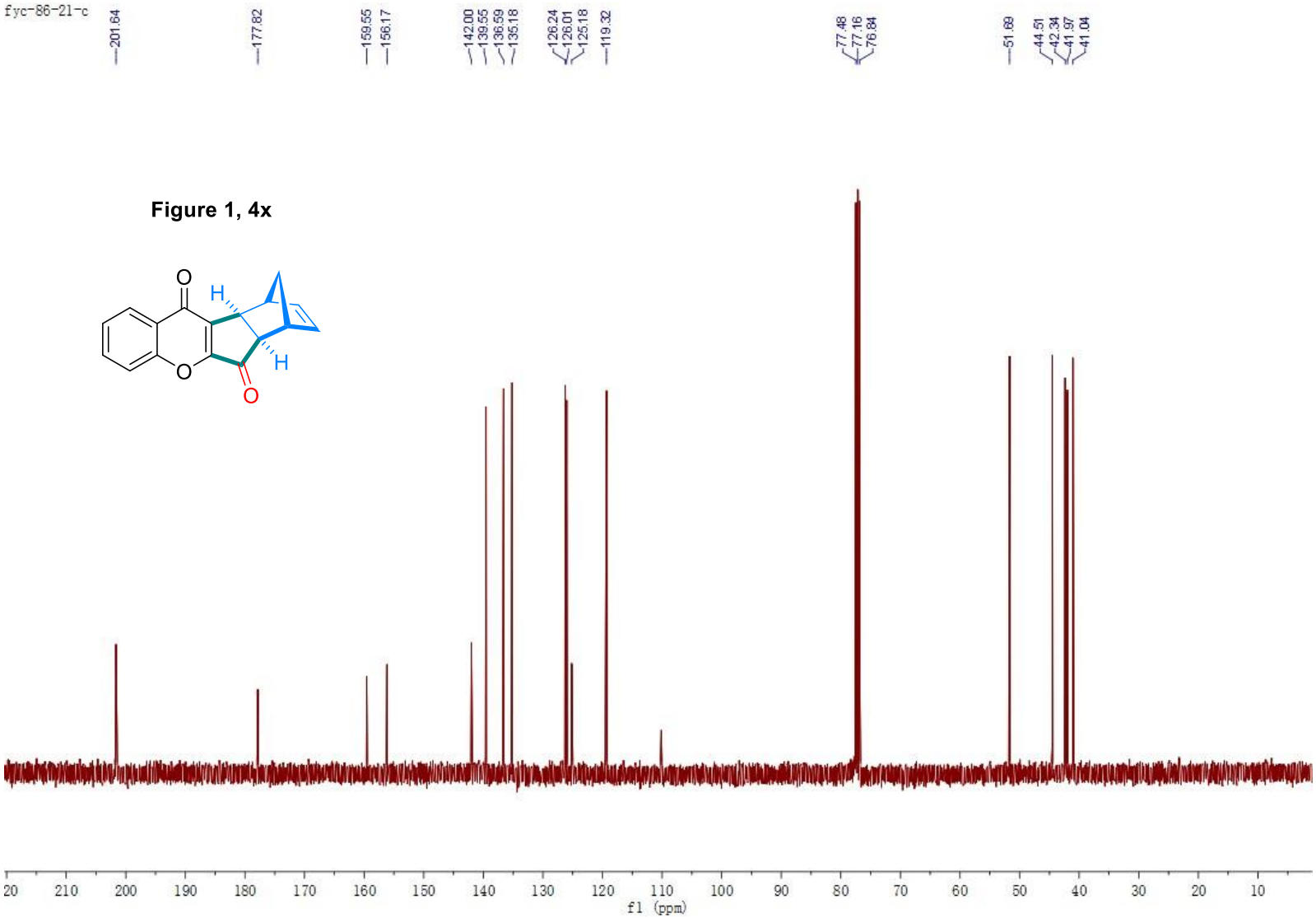
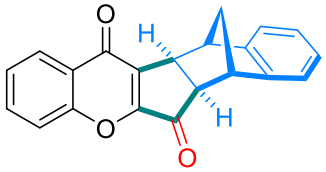

fyc-86-21-c
201.64
177.82
159.55
156.17
142.00
139.55
136.59
135.18
126.24
126.01
125.18
119.32
77.48
77.16
76.84
51.69
44.51
42.34
41.97
41.04
O
H
H
O
O
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Figure 1, 4x

Figure 1, 4y


O
H
H
O
O

fyc-86-32-h
8.3148
8.3110
8.2948
8.2910
7.8050
7.8009
7.7868
7.7835
7.7799
7.7660
7.7619
7.6530
7.6322
7.5218
7.5200
7.5020
7.4841
7.4823
7.4220
7.4168
7.4087
7.4020
7.2934
7.2861
7.2787
7.2732
7.2596
7.1822
7.1779
7.1632
7.1565
7.1493
7.1416
7.1357
7.1206
7.1196
3.7191
3.6222
3.3187
3.3056
2.6728
2.6697
1.8092
1.7834
1.5358
1.5069
f1 (ppm)
1.00
1.02
1.00
1.03
1.03
0.98
2.06
1.07
1.04
1.01
1.01
1.11
1.11
f1 (ppm)

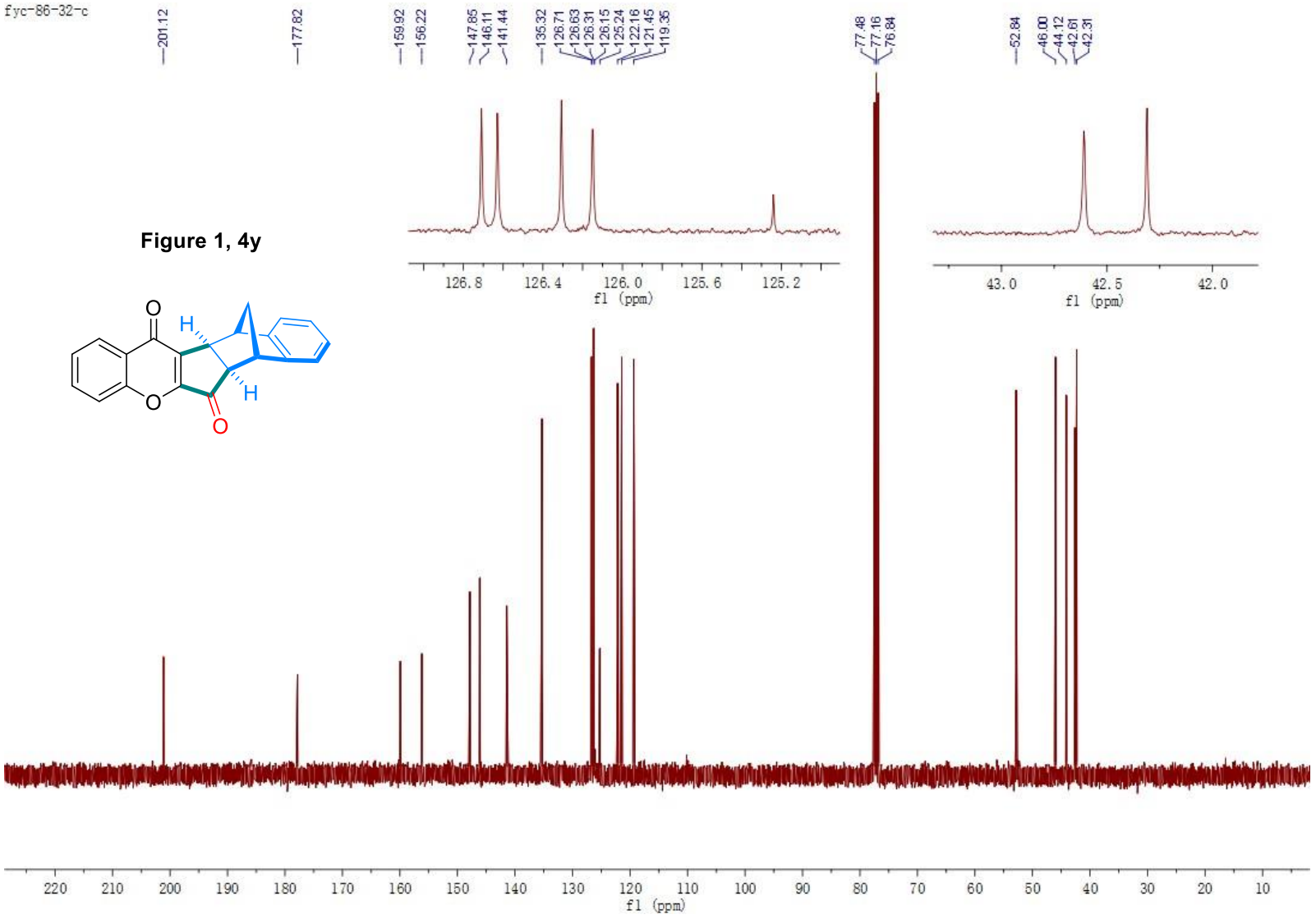
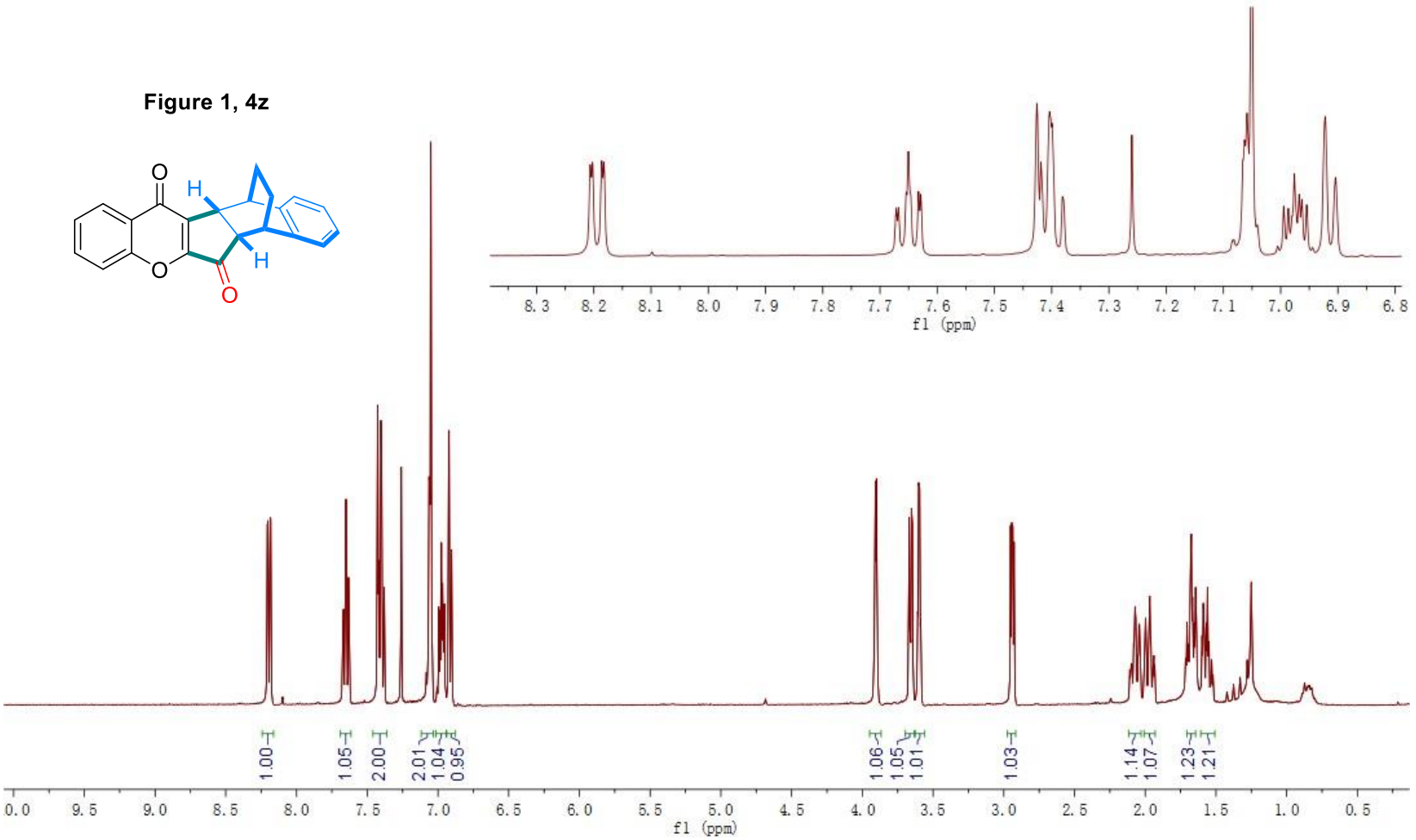

fyc-86-32-c
201.12
177.82
159.92
156.22
147.85
146.11
141.44
135.32
126.71
126.63
126.31
126.15
125.24
122.16
121.45
119.35
77.48
77.16
76.84
52.84
46.00
44.12
42.61
42.31
126.8
126.4
126.0
125.6
125.2
f1 (ppm)
43.0
42.5
42.0
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Figure 1, 4y

Figure 1, 4z



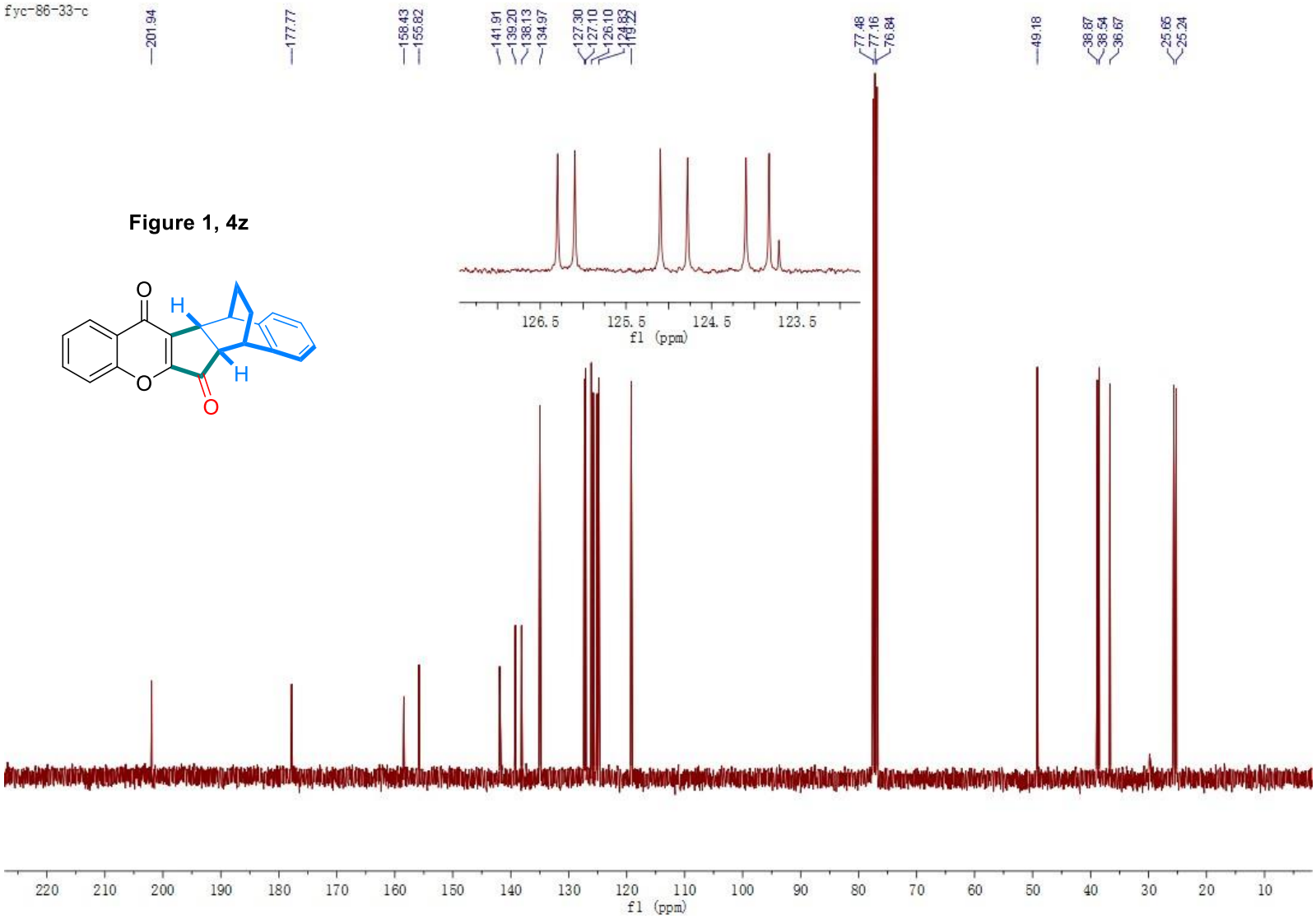

fyc-86-33-c
201.94
177.77
158.43
155.82
141.91
139.20
138.13
134.97
127.30
127.10
126.10
124.83
119.22
77.48
77.16
76.84
49.18
38.87
38.54
36.67
25.65
25.24
126.5
125.5
124.5
123.5
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Figure 1, 4z

O
H
H
O
O

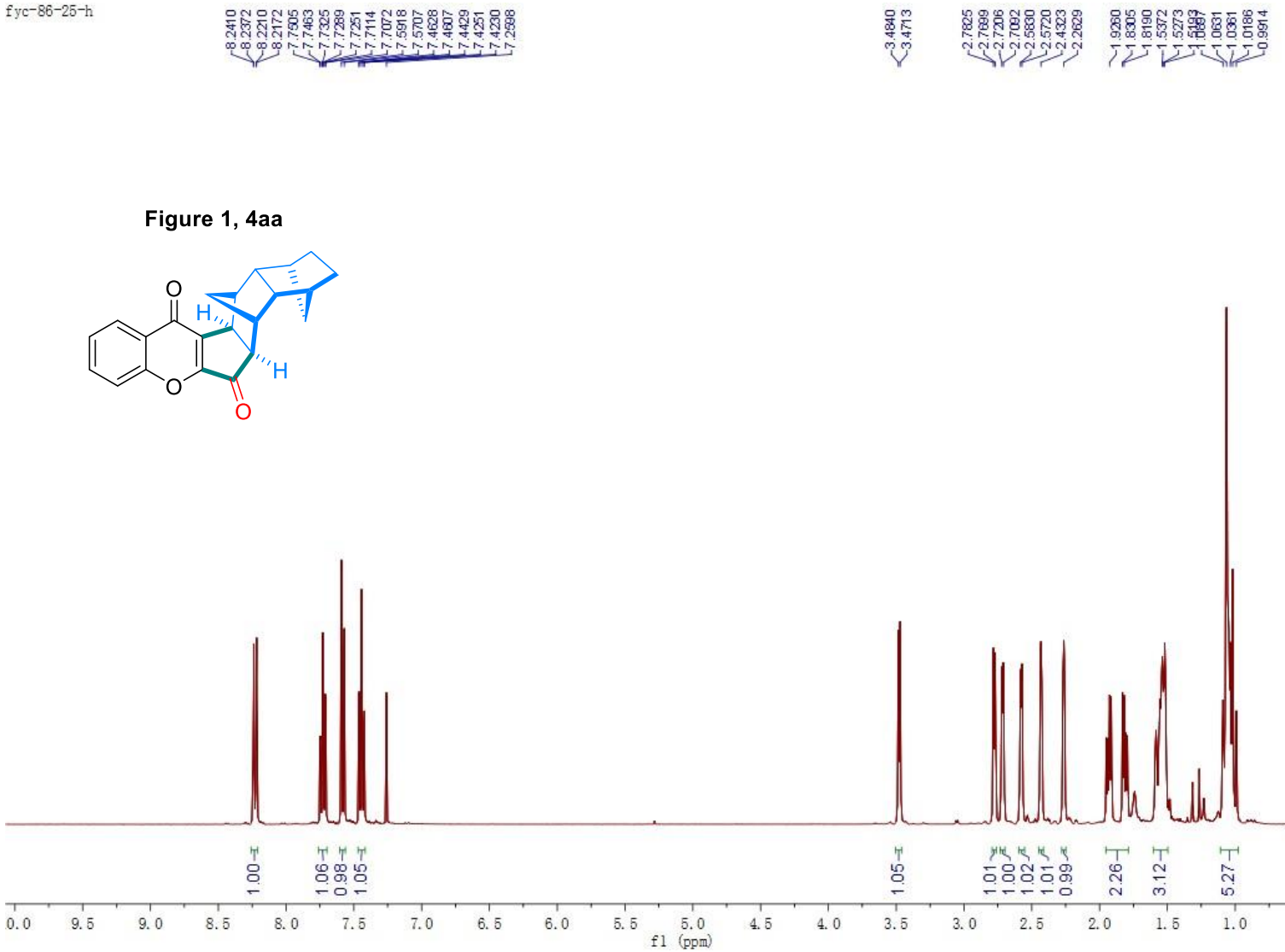

fyc-86-25-h
8.2410
8.2372
8.2210
8.2172
7.7505
7.7463
7.7325
7.7289
7.7251
7.7114
7.7072
7.5918
7.5707
7.4628
7.4607
7.4429
7.4251
7.4230
7.2598
3.4840
3.4713
2.7825
2.7699
2.7206
2.7082
2.5830
2.5720
2.4323
2.2629
1.9250
1.8305
1.8190
1.5372
1.5273
1.0631
1.0361
1.0186
0.9914
O
H
H
O
O
1.00
1.06
0.98
1.05
1.05
1.01
1.00
1.02
1.01
0.99
2.26
3.12
5.27
0.0
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
f1 (ppm)

Figure 1, 4aa

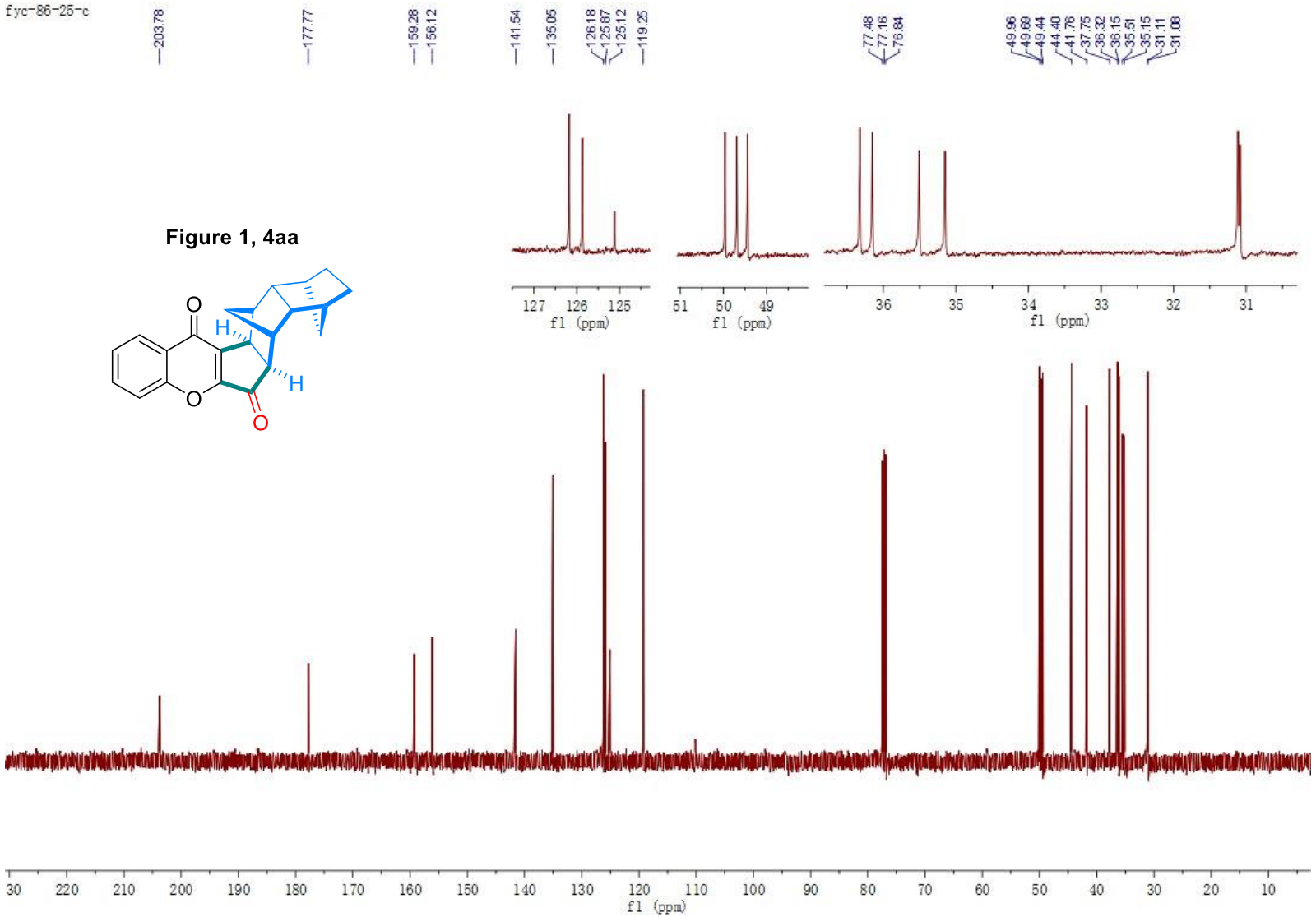

fyc-86-25-c
203.78
177.77
159.28
156.12
141.54
135.05
126.18
125.87
125.12
119.25
77.48
77.16
76.84
49.96
49.69
49.44
44.40
41.76
37.75
36.32
36.15
35.51
35.15
31.11
31.08
O
H
H
O
O
f1 (ppm)

Figure 1, 4aa

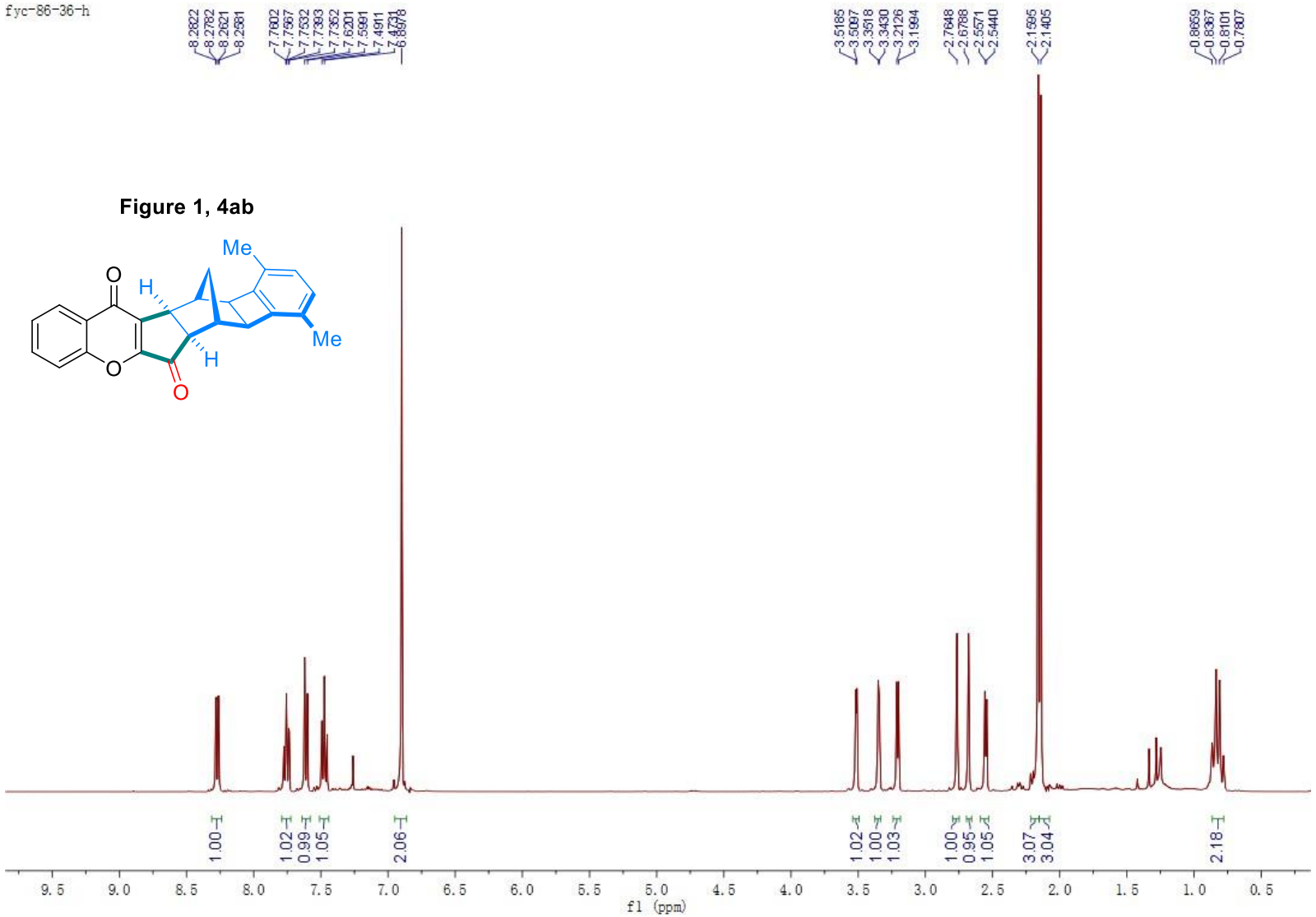

fyc-86-36-h
8.2822
8.2782
8.2621
8.2581
7.7602
7.7567
7.7532
7.7393
7.7352
7.6201
7.5991
7.4911
6.8978
3.5185
3.5097
3.3518
3.3430
3.2126
3.1994
2.7648
2.6788
2.5571
2.5440
2.1595
2.1405
0.8659
0.8367
0.8101
0.7807
1.00
1.02
0.99
1.05
2.06
1.02
1.00
1.03
1.00
0.95
1.05
3.07
3.04
2.18
9.5
9.0
8.5
8.0
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
f1 (ppm)

Figure 1, 4ab

Me
H
Me
H
O
O
O

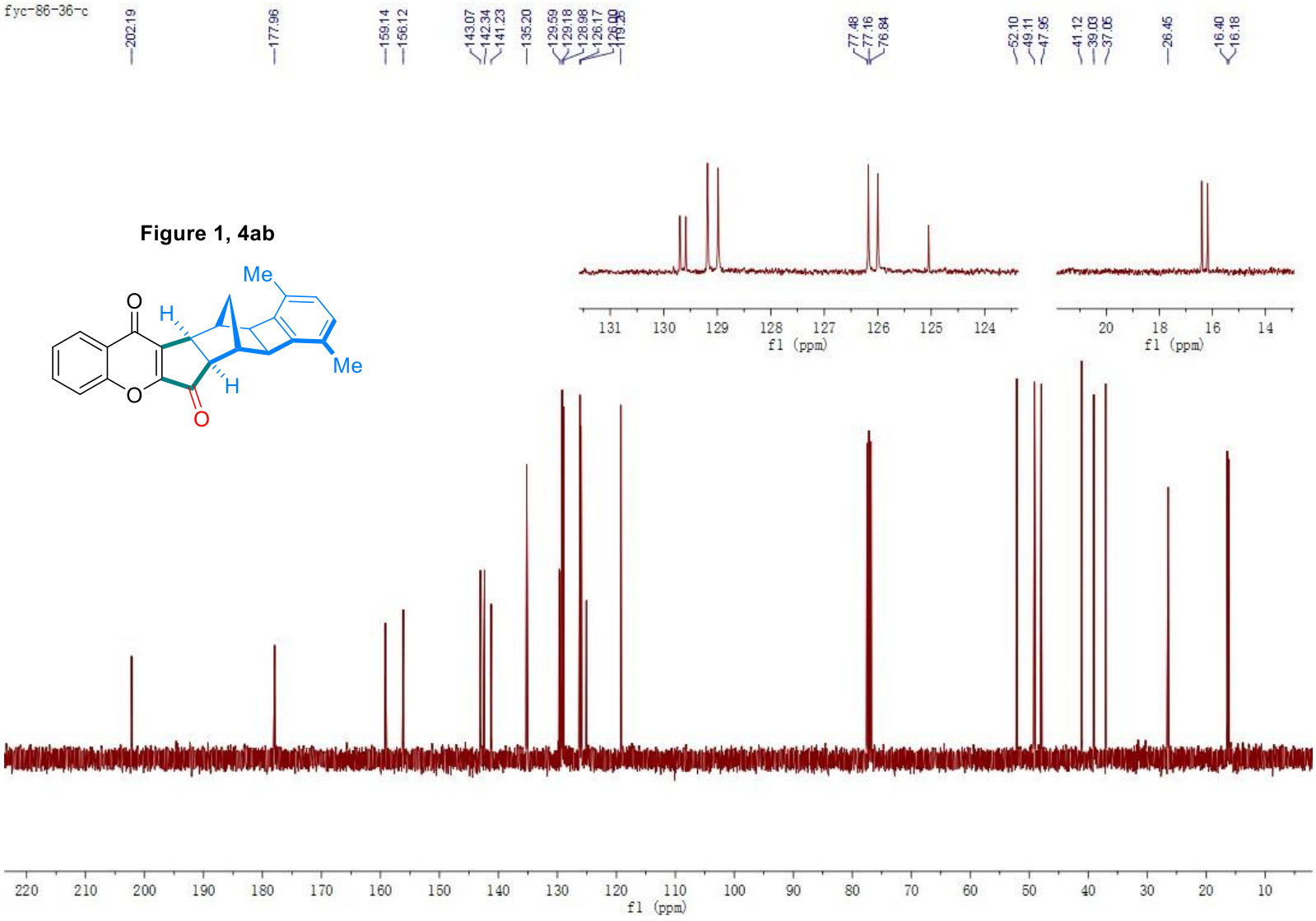
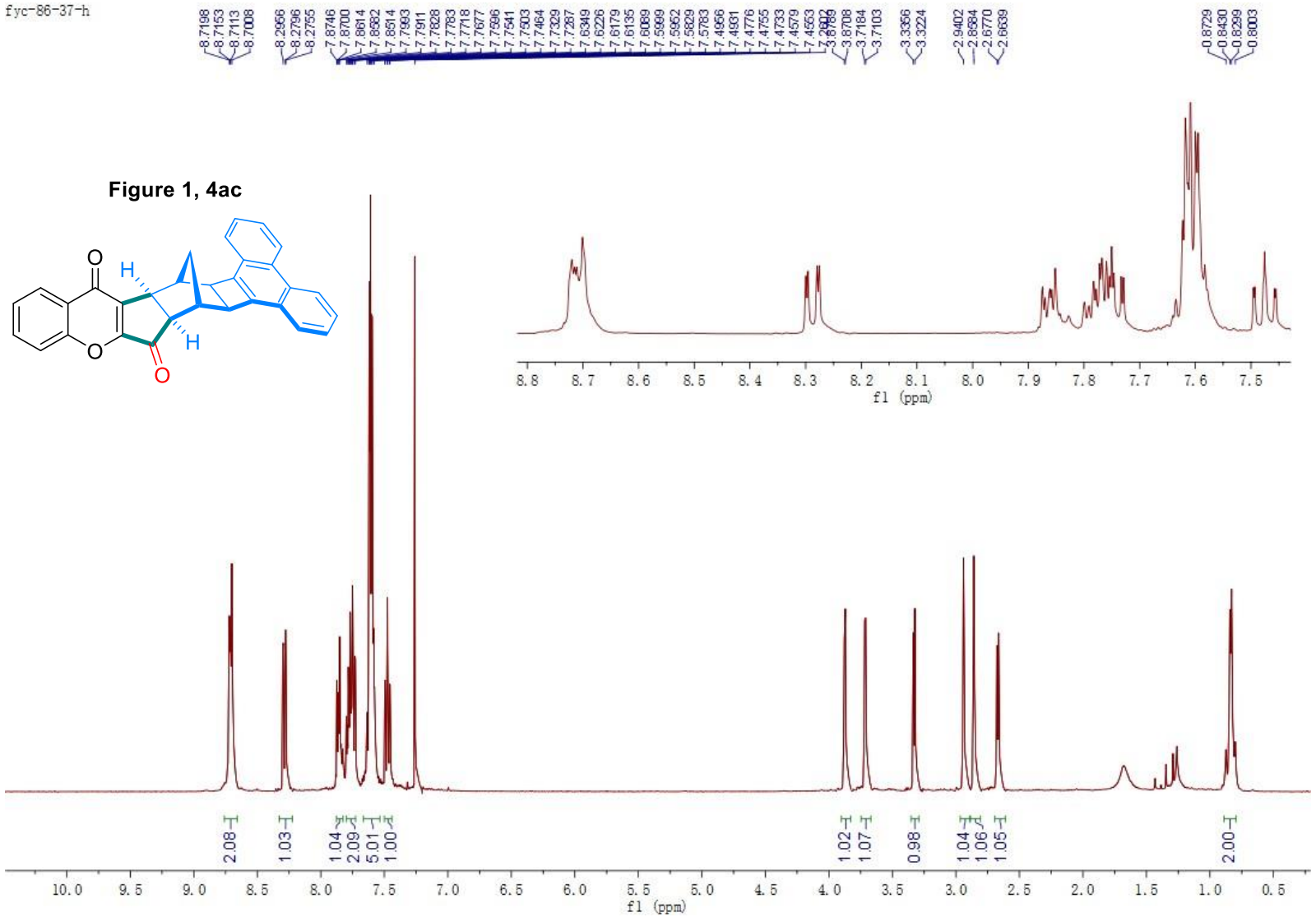

fyc-86-36-c
202.19
177.96
159.14
156.12
143.07
142.34
141.23
135.20
129.59
129.18
128.98
126.17
77.48
77.16
76.84
52.10
49.11
47.95
41.12
39.03
37.05
26.45
16.40
16.18
Me
Me
H
H
O
O
f1 (ppm)

Figure 1, 4ab


fyc-86-37-h
Figure 1, 4ac
O
H
H
O
f1 (ppm)
f1 (ppm)

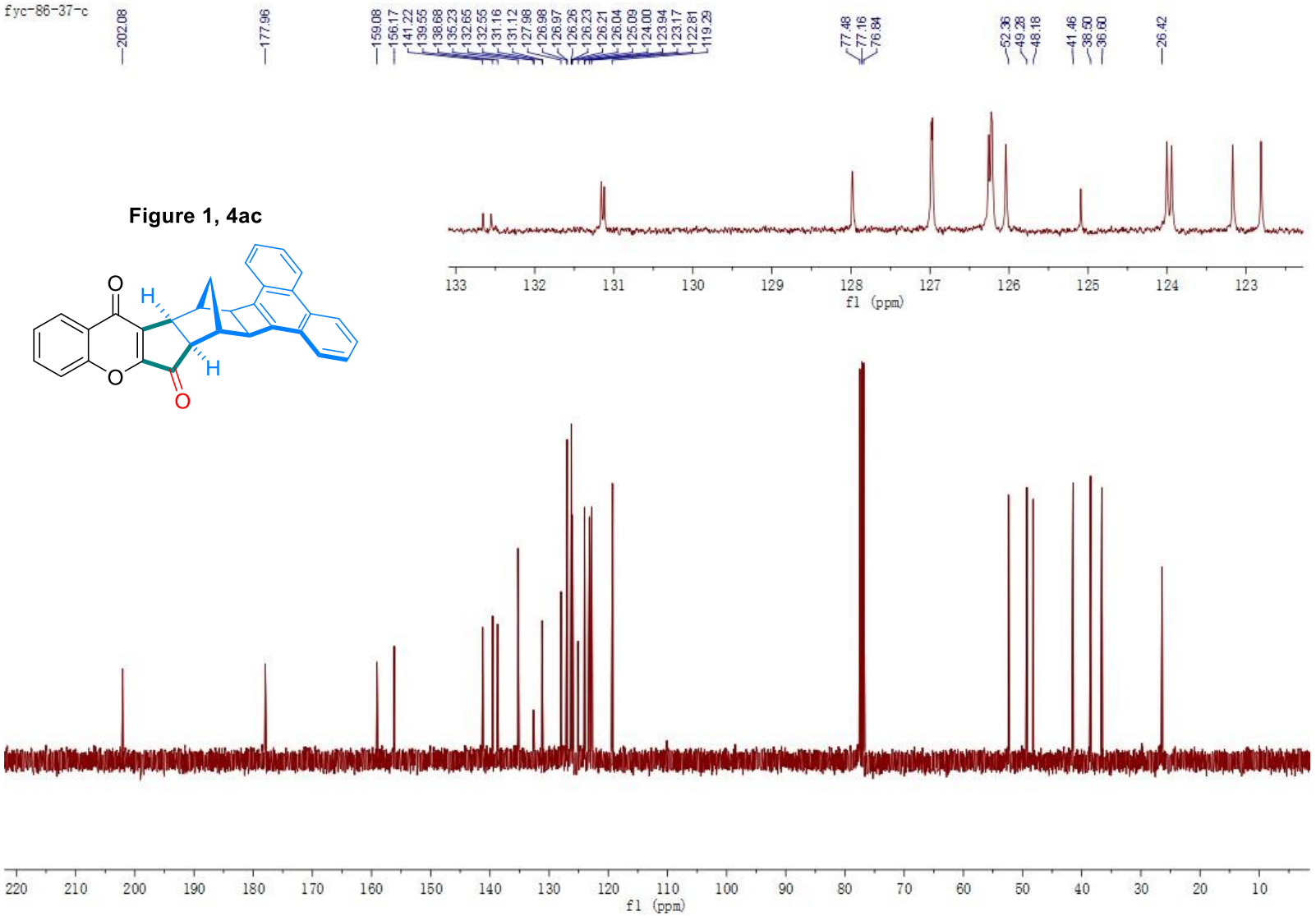

fyc-86-37-c
202.08
177.96
159.08
156.17
141.22
139.55
138.68
135.23
132.65
132.55
131.16
131.12
127.98
126.98
126.97
126.26
126.23
126.21
126.04
125.09
124.00
123.94
123.17
122.81
119.29
77.48
77.16
76.84
52.36
49.28
48.18
41.46
38.50
36.60
26.42
O
H
H
O
O
133
132
131
130
129
128
127
126
125
124
123
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Figure 1, 4ac

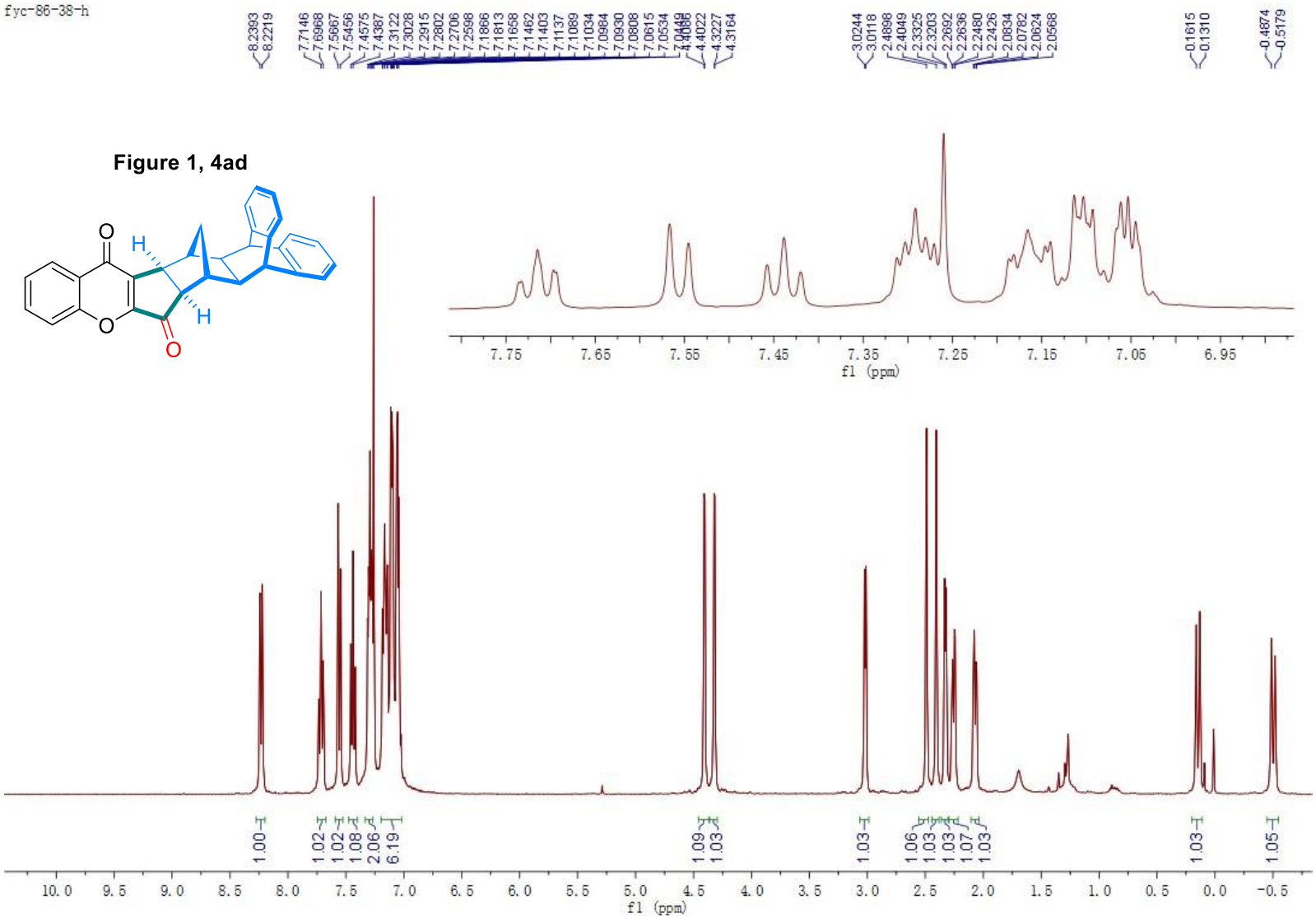

fyc-86-38-h
8.2393
8.2219
7.7146
7.6968
7.5667
7.5456
7.4575
7.4387
7.3122
7.3028
7.2915
7.2802
7.2706
7.2598
7.1866
7.1813
7.1658
7.1462
7.1403
7.1137
7.1089
7.1034
7.0984
7.0930
7.0808
7.0615
7.0534
4.4022
4.3227
4.3164
3.0244
3.0118
2.4898
2.4049
2.3325
2.3203
2.2692
2.2636
2.2480
2.2426
2.0834
2.0782
2.0624
2.0568
0.1615
0.1310
-0.4874
-0.5179
O
H
H
O
O
7.75
7.65
7.55
7.45
7.35
7.25
7.15
7.05
6.95
f1 (ppm)
1.00
1.02
1.02
1.08
2.06
6.19
1.09
1.03
1.03
1.06
1.03
1.03
1.07
1.03
1.03
1.05
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)

Figure 1, 4ad

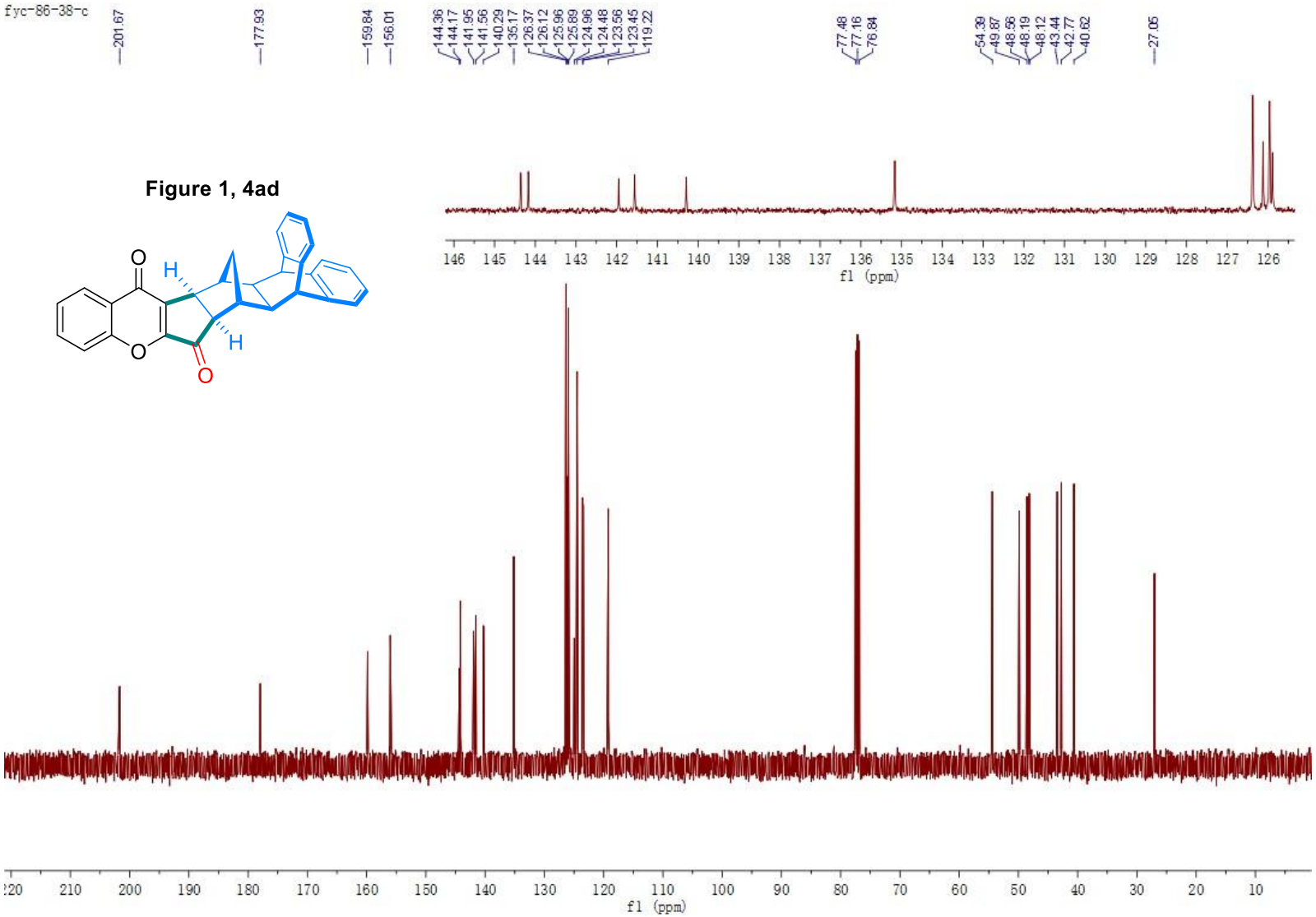
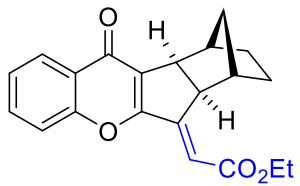
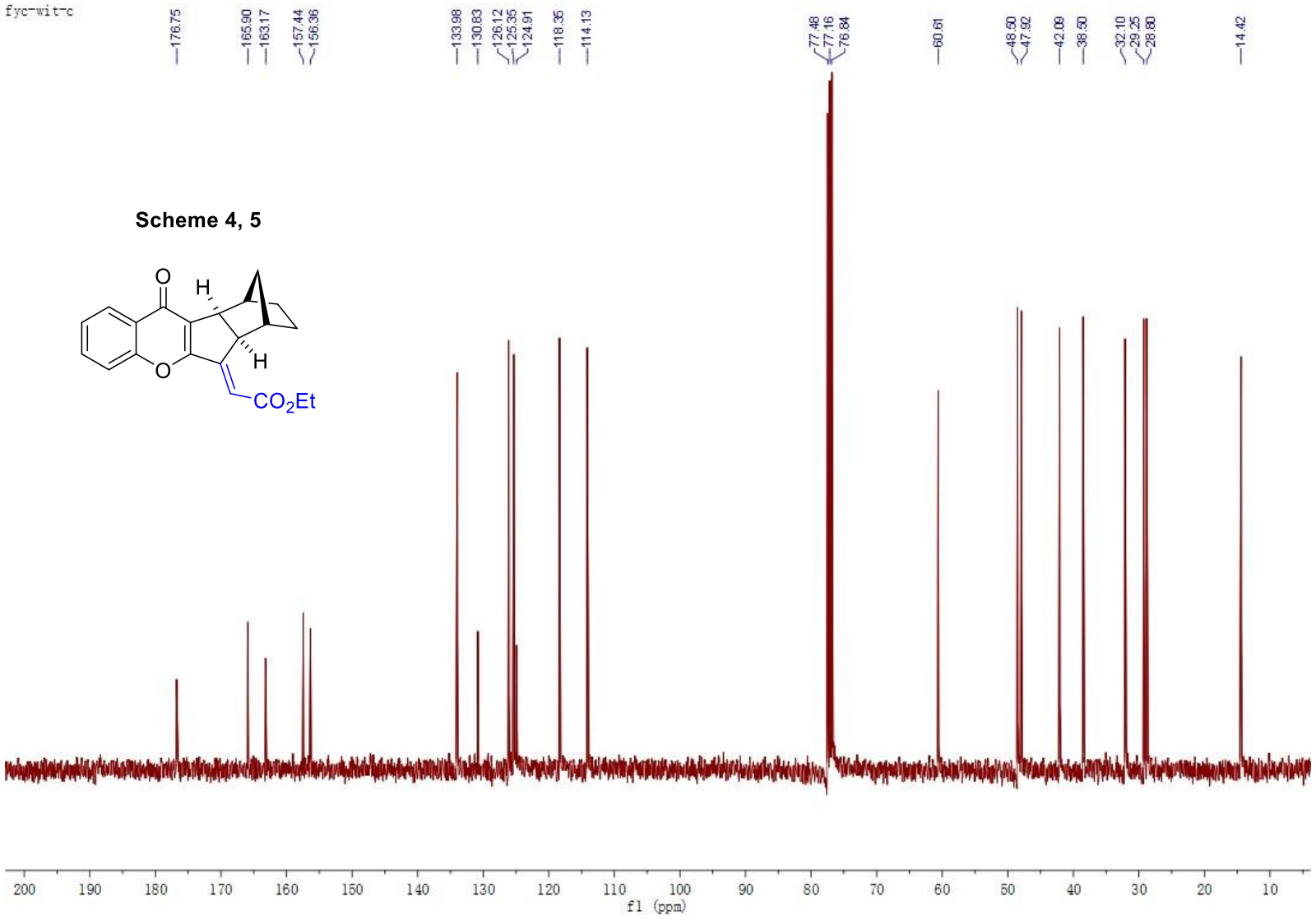
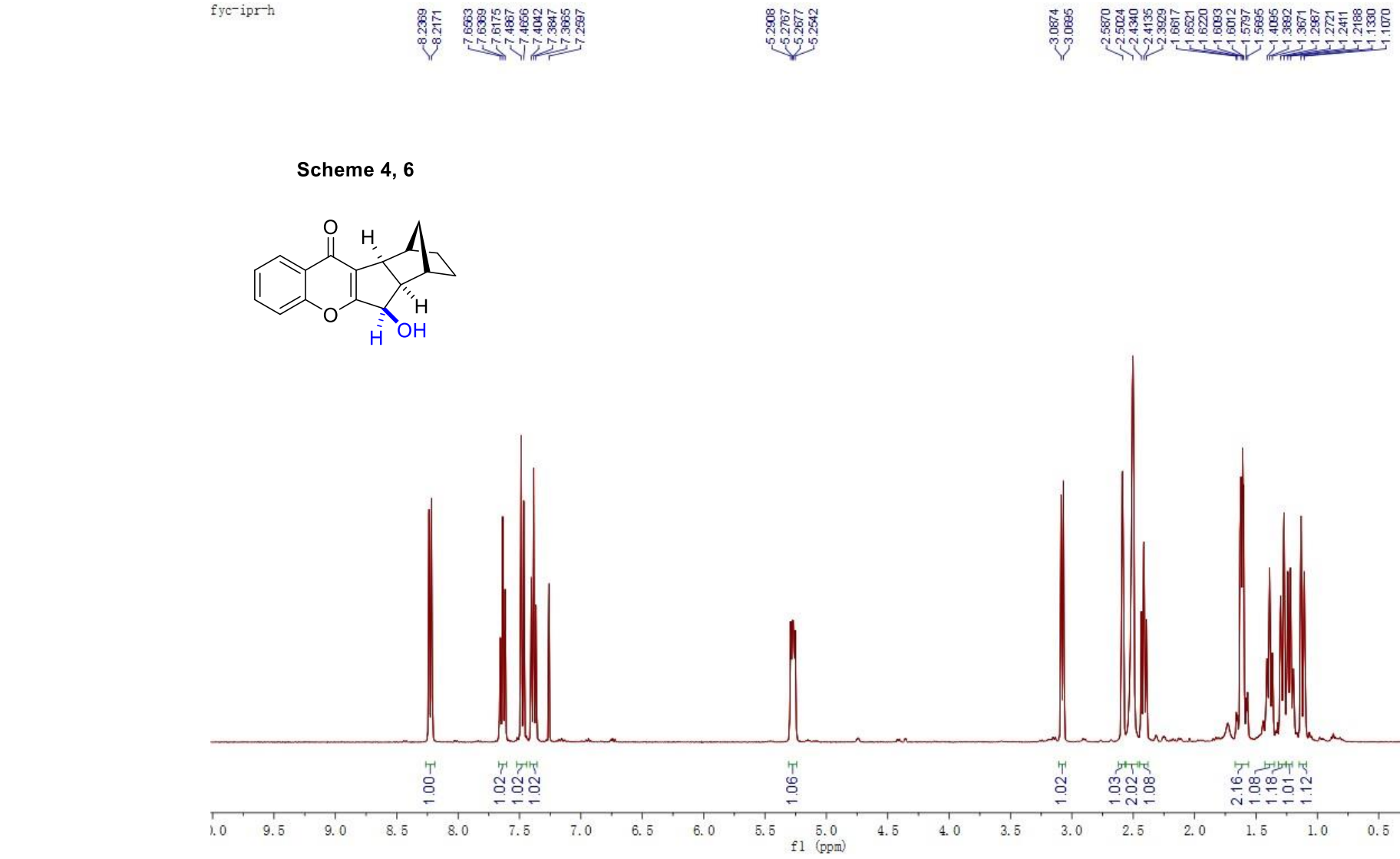

fyc-86-38-c
201.67
177.93
159.84
156.01
144.36
144.17
141.95
141.56
140.29
135.17
126.37
126.12
125.96
125.89
124.96
124.48
123.56
123.45
119.22
77.48
77.16
76.84
54.39
49.87
48.56
48.19
48.12
43.44
42.77
40.62
27.05
f1 (ppm)
f1 (ppm)

Figure 1, 4ad

Scheme 4, 5

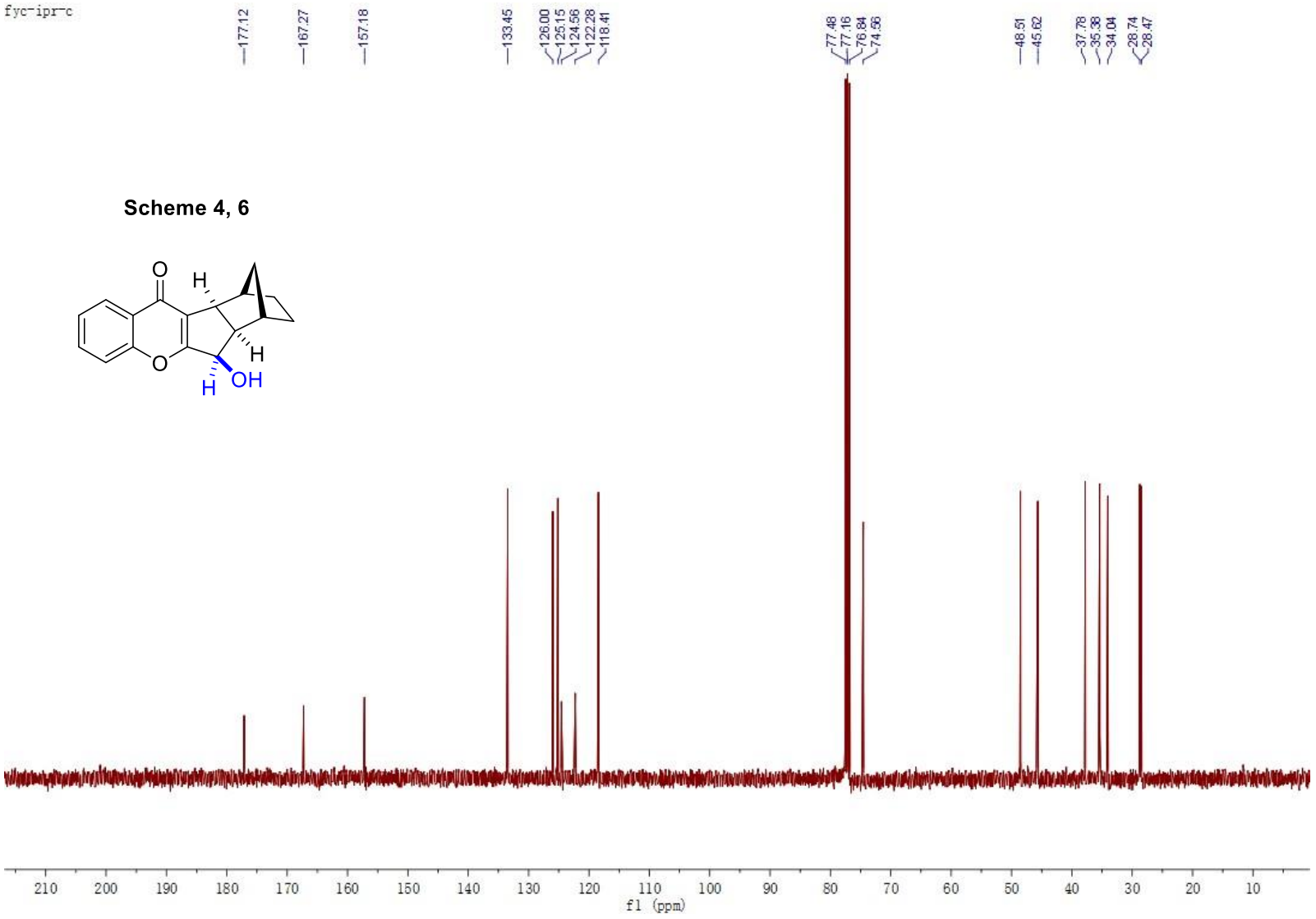


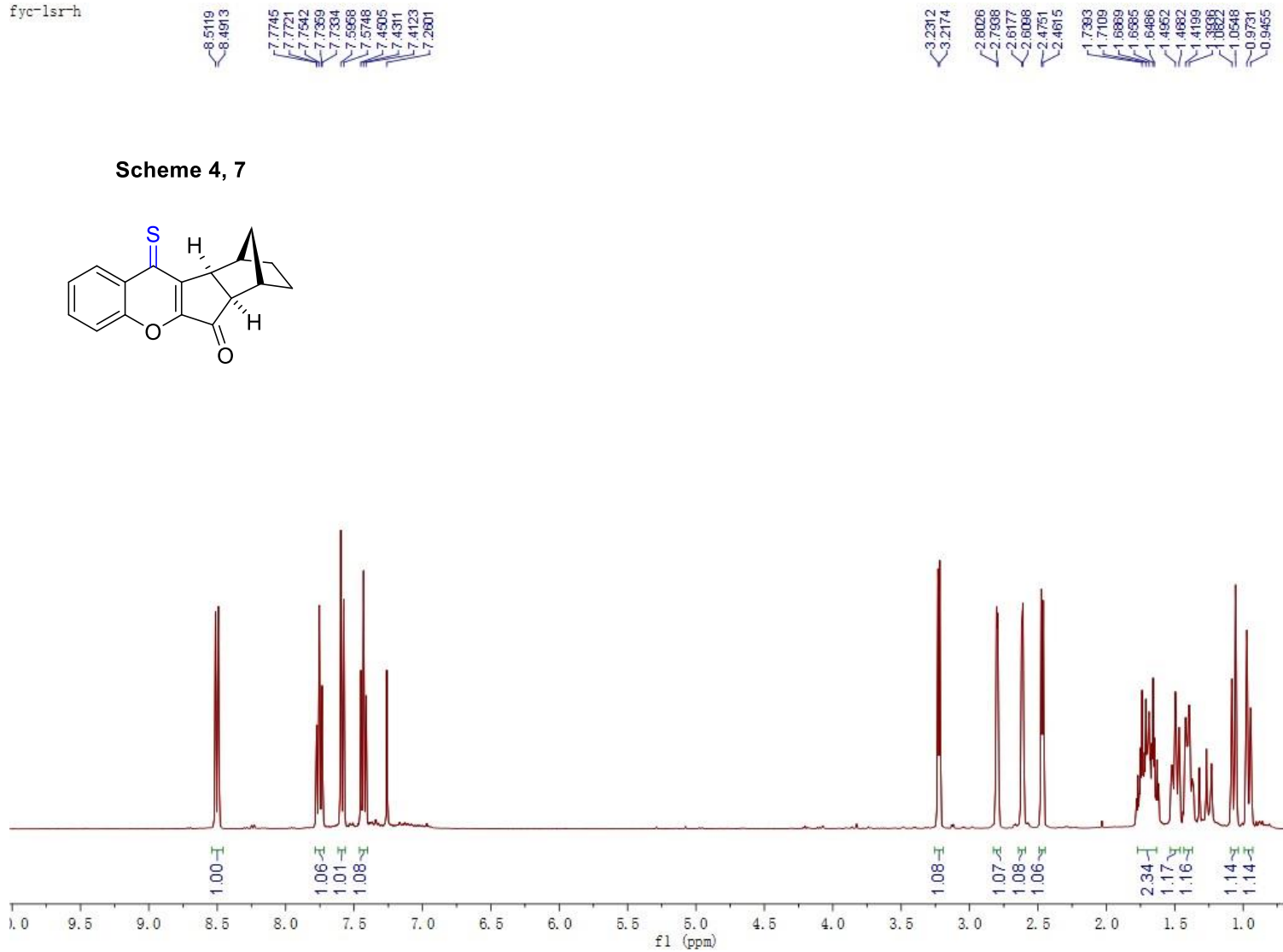

fyc-wit-c
176.75
165.90
163.17
157.44
156.36
133.98
130.83
126.12
125.35
124.91
118.35
114.13
77.48
77.16
76.84
60.61
48.50
47.92
42.09
38.50
32.10
29.25
28.80
14.42
Scheme 4, 5
O
H
H
O
CO2Et
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


fyc-ipr-h
8.2369
8.2171
7.6663
7.6369
7.6175
7.4867
7.4656
7.4042
7.3847
7.3665
7.2597
5.2908
5.2767
5.2677
5.2542
3.0874
3.0695
2.5870
2.5024
2.4340
2.4135
2.3929
1.6617
1.6521
1.6220
1.6093
1.6012
1.5797
1.5695
1.4065
1.3892
1.3671
1.2967
1.2721
1.2411
1.2188
1.1330
1.1070
1.00
1.02
1.02
1.02
1.06
1.02
1.03
2.02
1.08
2.16
1.08
1.18
1.01
1.12
f1 (ppm)

Scheme 4, 6

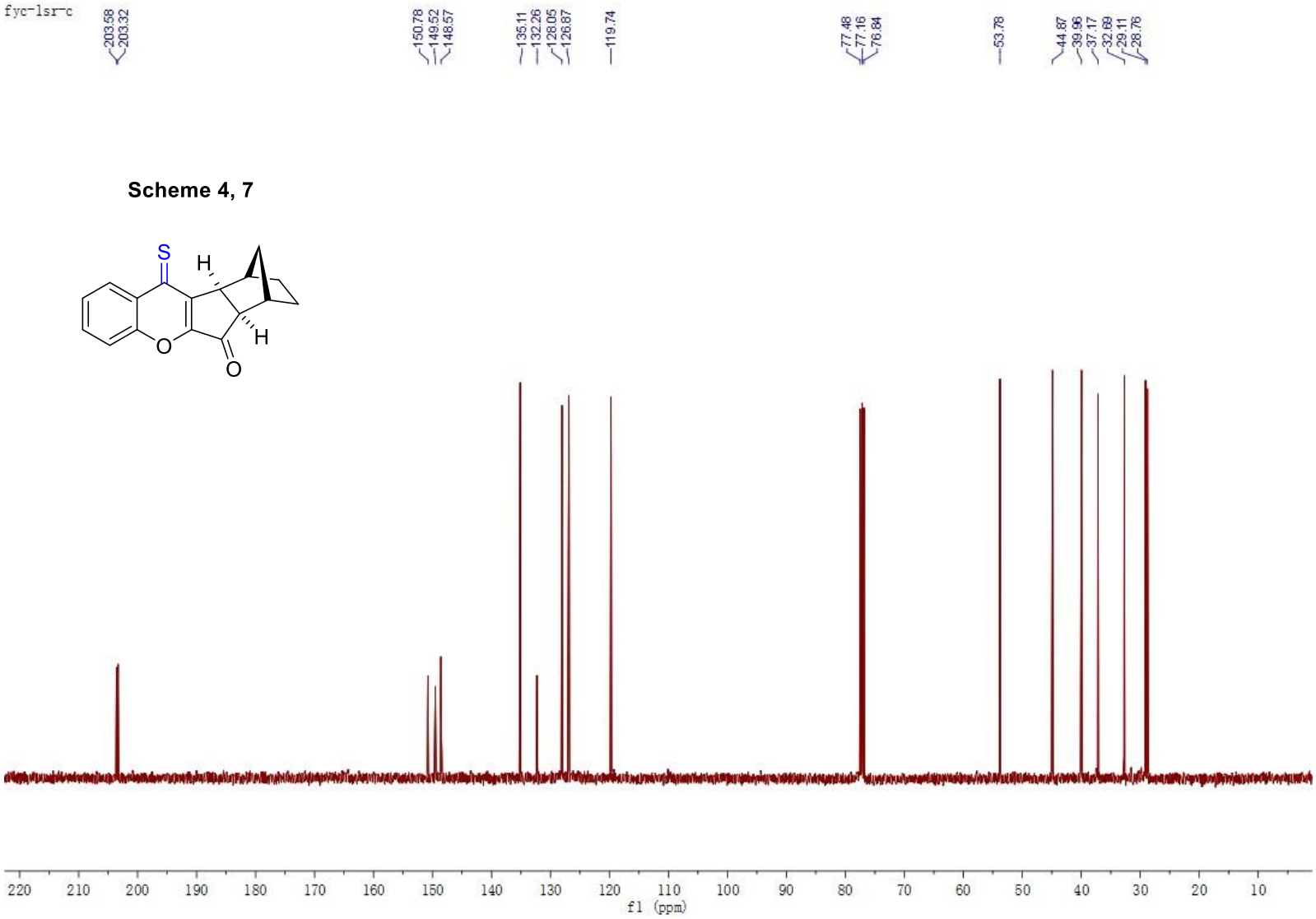
O
H
H
O
H
OH


fyc-ipr-c
177.12
167.27
157.18
133.45
126.00
125.15
124.56
122.28
118.41
77.48
77.16
76.84
74.66
48.51
45.62
37.78
35.38
34.04
28.74
28.47
Scheme 4, 6
O
H
H
O
H
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


fyc-1sr-h
8.5119
8.4913
7.7745
7.7721
7.7542
7.7369
7.7334
7.5968
7.5748
7.4505
7.4311
7.4123
7.2601
3.2312
3.2174
2.8026
2.7938
2.6177
2.6098
2.4751
2.4615
1.7393
1.7109
1.6869
1.6585
1.6486
1.4952
1.4682
1.4199
1.0548
0.9731
0.9455
1.00
1.06
1.01
1.08
1.08
1.07
1.08
1.06
2.34
1.17
1.16
1.14
1.14
f1 (ppm)

Scheme 4, 7

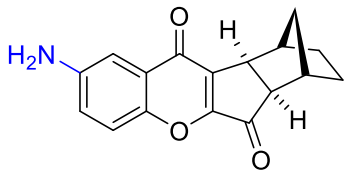
S
H
O
H
O

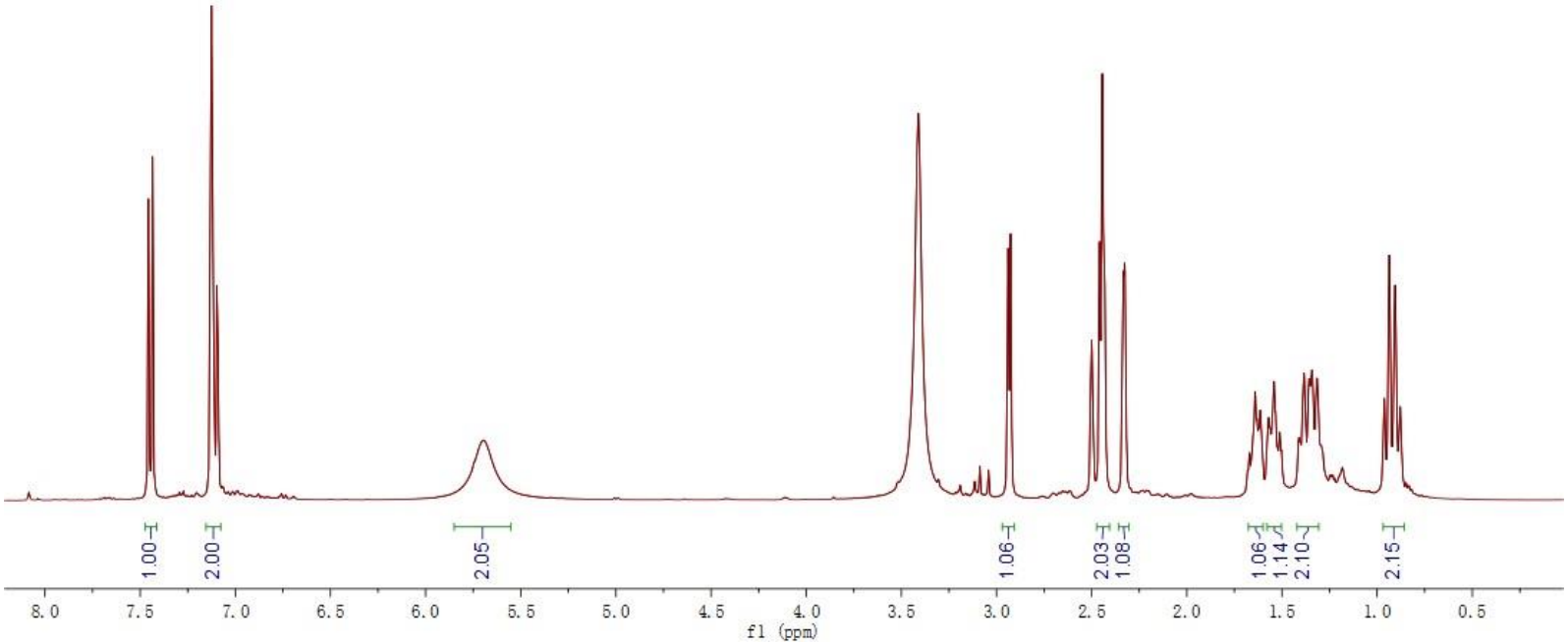

fyc-lsr-c
203.58
203.32
150.78
149.52
148.57
135.11
132.26
128.05
126.87
119.74
77.48
77.16
76.84
53.78
44.67
39.96
37.17
32.69
29.11
28.76
S
H
O
H
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

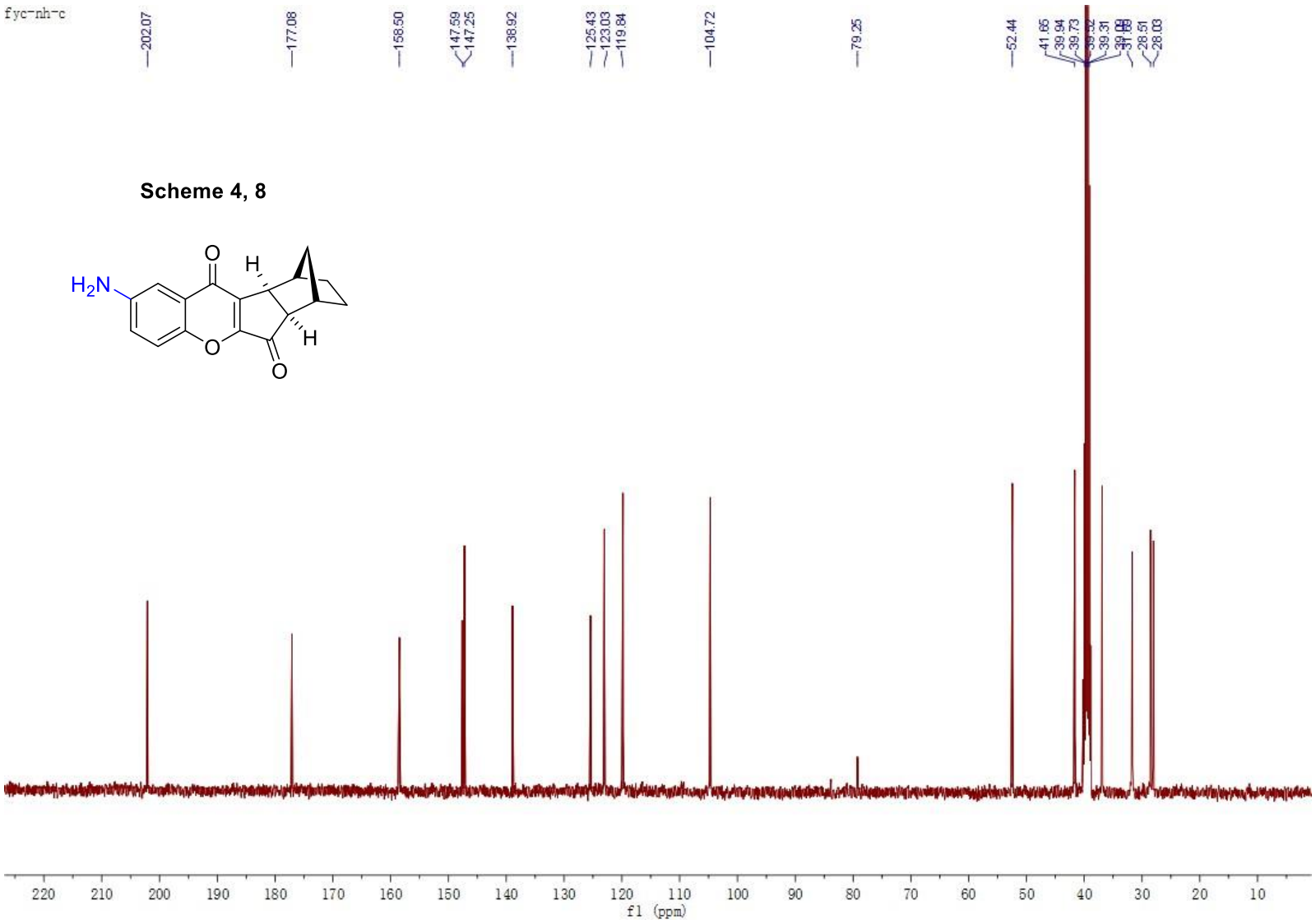
Scheme 4, 7


fyc-nh-h
7.4566
7.4347
7.1315
7.1253
7.1194
7.1126
7.0970
7.0902
5.6976
3.4110
2.9394
2.9261
2.5000
2.4692
2.4439
2.3340
2.3257
1.6413
1.6318
1.6228
1.6142
1.5693
1.5421
1.5340
1.3847
1.3572
1.3419
1.3150
0.9623
0.9357
0.9057
0.8790

Scheme 4, 8


O
H
H2N
O
H
O


1.00
2.00
2.05
1.06
2.03
1.08
1.06
1.14
2.10
2.15
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
f1 (ppm)

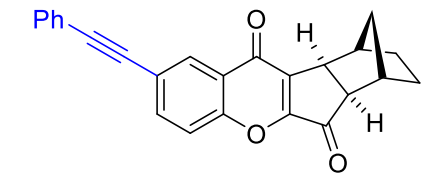

fyc-nh-c
202.07
177.08
158.50
147.59
147.25
138.92
125.43
123.03
119.84
104.72
79.25
52.44
41.65
39.94
39.73
39.52
39.31
28.51
28.03
Scheme 4, 8
O
H
H2N
O
H
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

fyc-phe-h

8.3839
8.3848
7.8571
7.8518
7.8353
7.8300
7.5960
7.5731
7.5698
7.5501
7.5462
7.5412
7.5348
7.3748
7.3662
7.3597

3.1426
3.1294
2.6914
2.6816
2.5961
2.5859
2.4923
2.4792
1.7786
1.7491
1.6965
1.6687
1.6590
1.5145
1.1758
1.0883
1.0257
0.9962

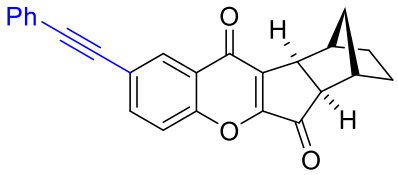
Scheme 4, 9



fyc-phe-c

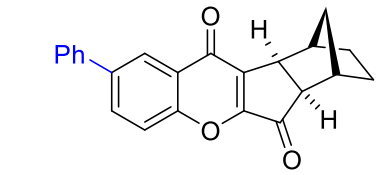
202.36
177.22
159.56
155.49
141.49
137.74
131.81
129.32
128.90
128.56
125.06
122.60
121.56
119.58
91.15
87.52
77.48
77.16
76.84
53.33
42.27
39.99
37.48
32.19
29.10
28.88

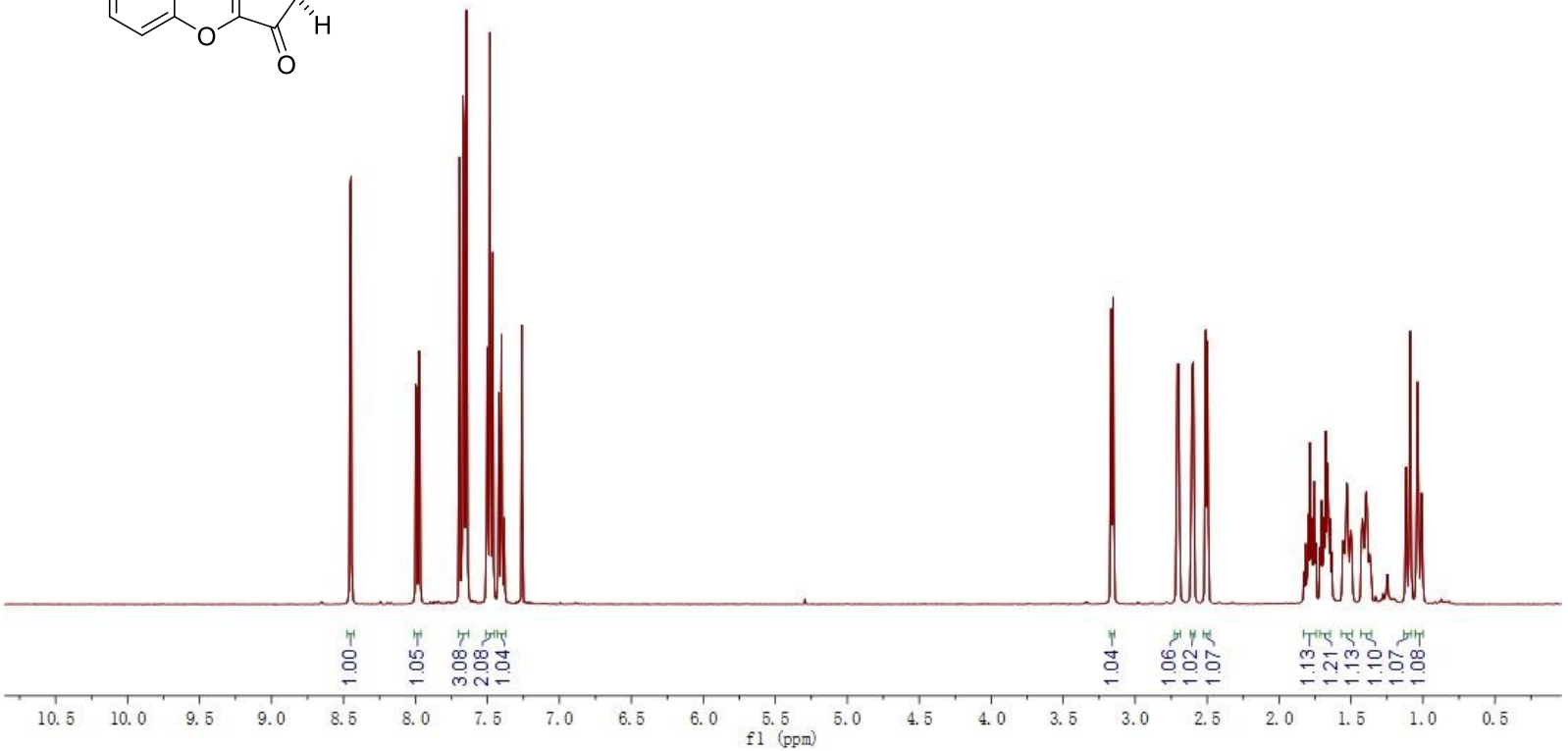
Scheme 4, 9

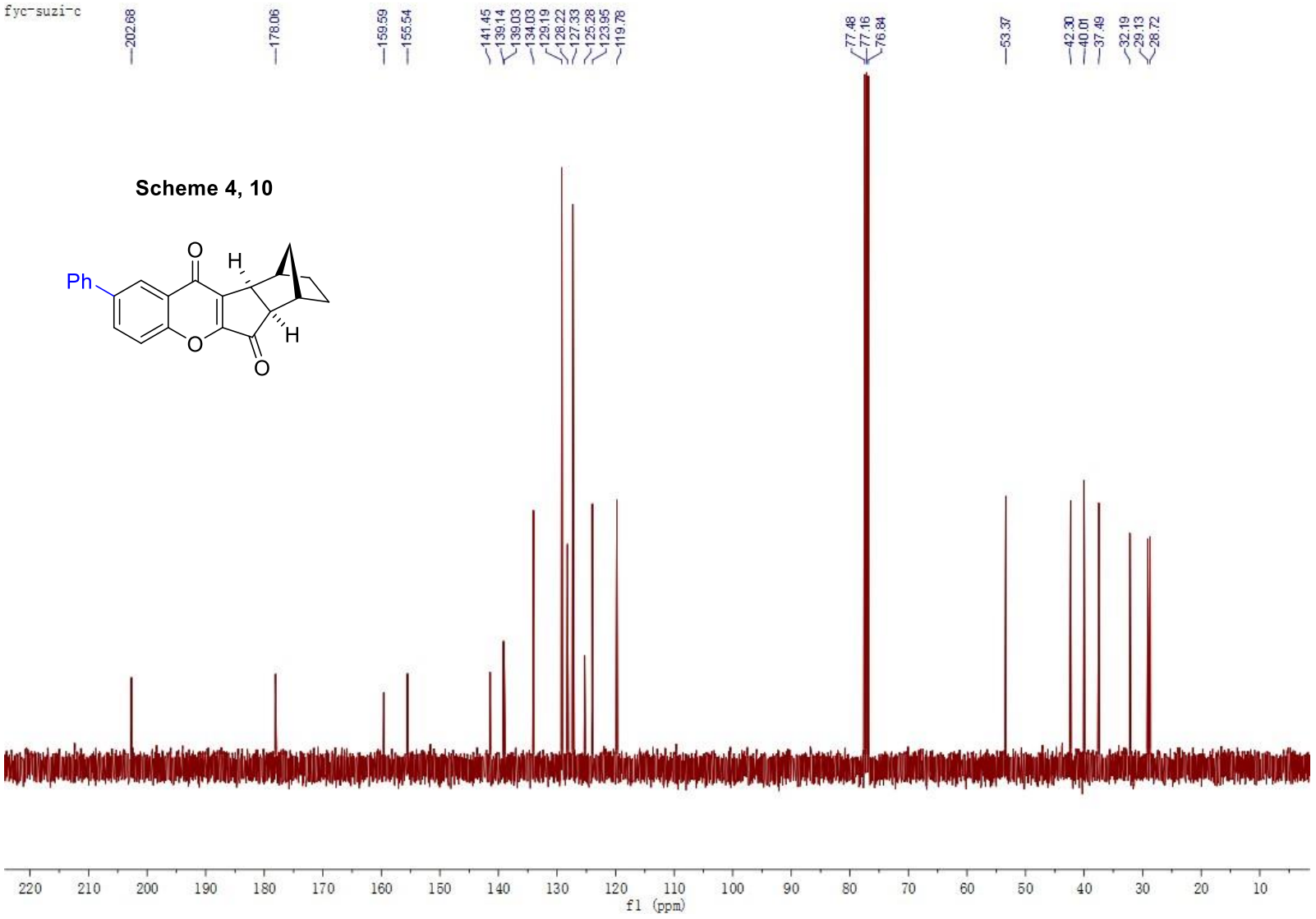


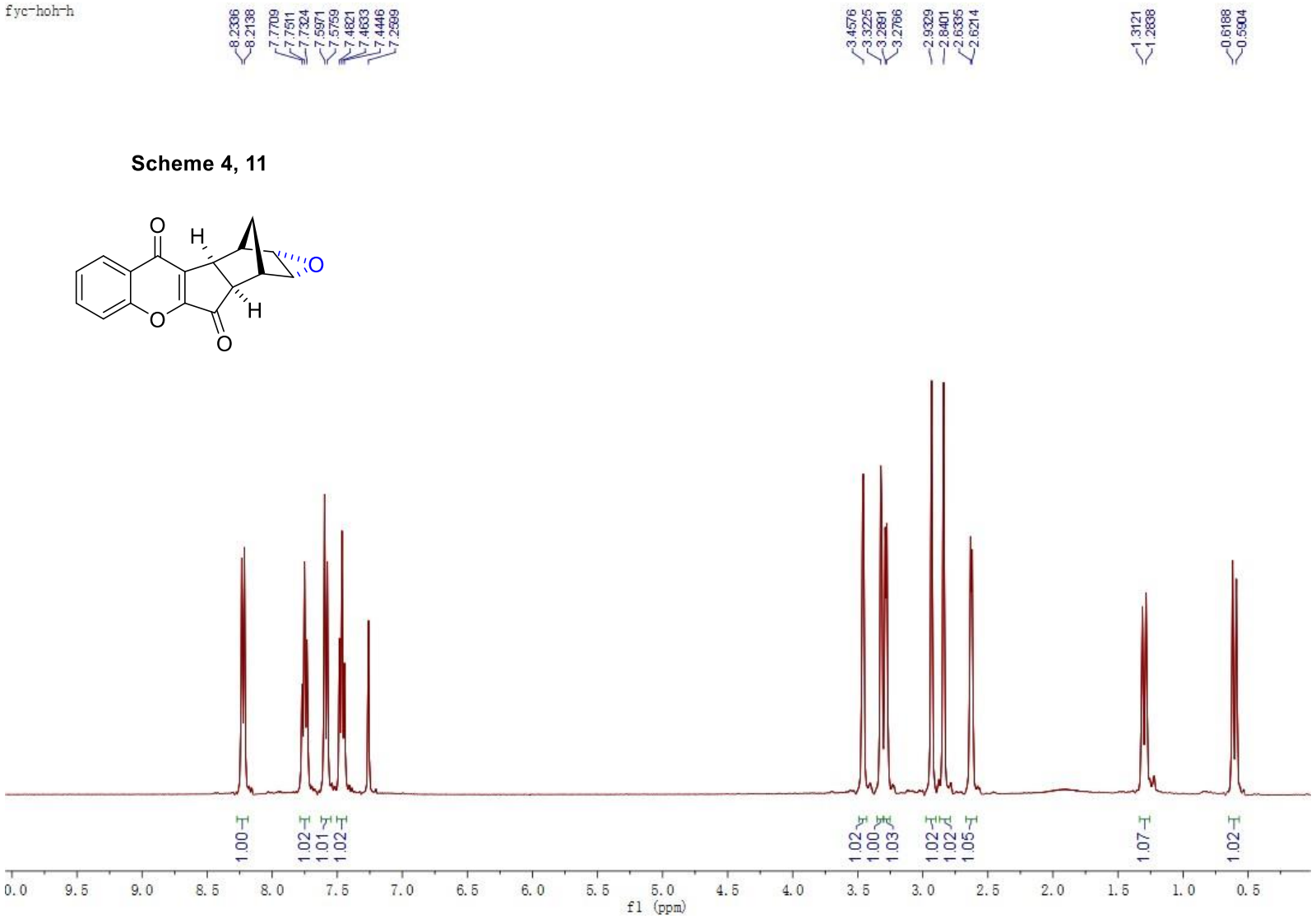
fyc-suzi-h

Scheme 4, 10



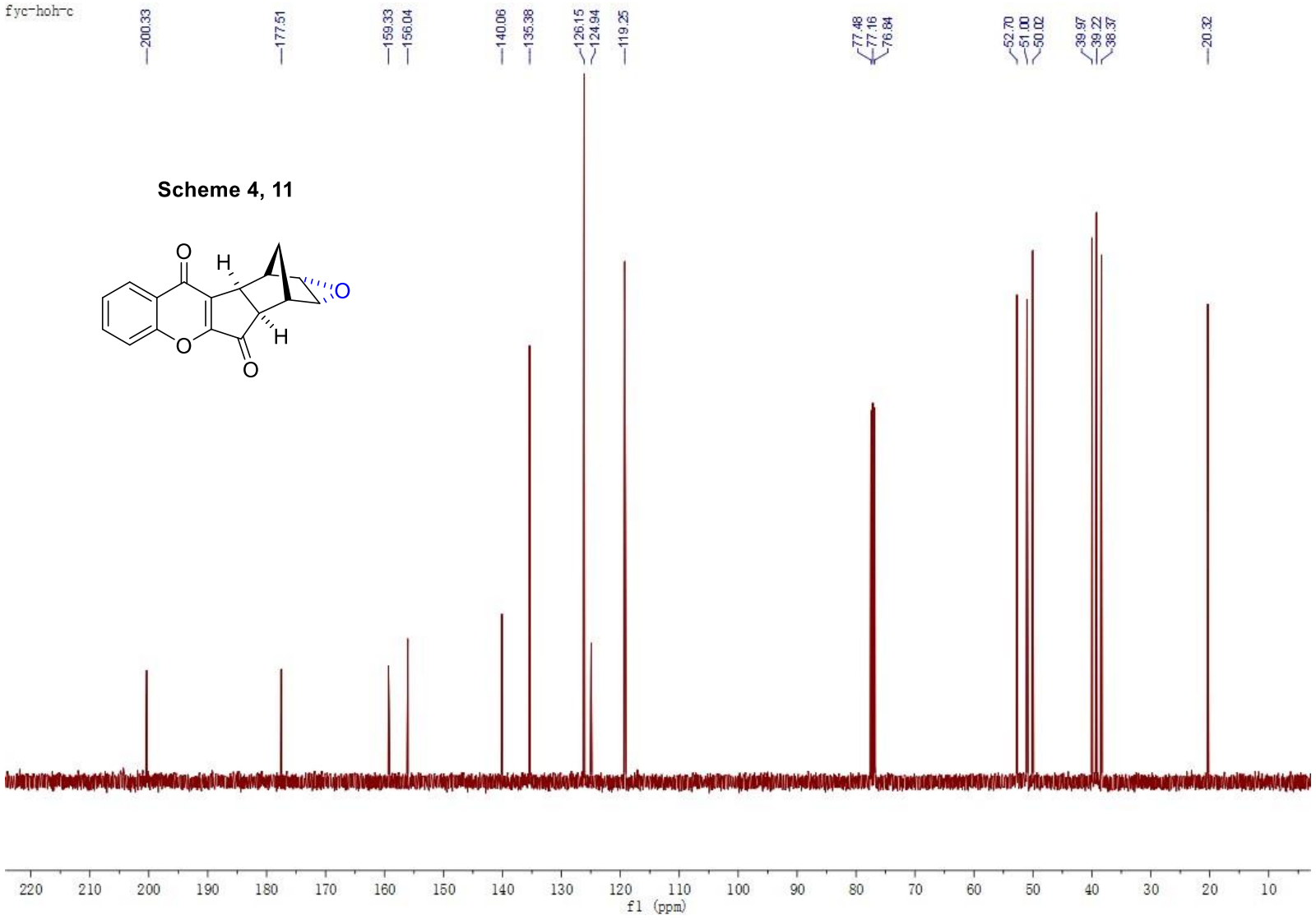



fyc-suzi-c
202.68
178.06
159.59
155.54
141.45
139.14
139.03
134.03
129.19
128.22
127.33
125.28
123.95
119.78
77.48
77.16
76.84
53.37
42.30
40.01
37.49
32.19
29.13
28.72
Scheme 4, 10
Ph
O
H
O
H
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


fyc-hoh-h
8.2336
8.2138
7.7709
7.7511
7.7324
7.5971
7.5759
7.4821
7.4633
7.4446
7.2599
3.4576
3.3225
3.2681
3.2766
2.9329
2.8401
2.6335
2.6214
1.3121
1.2838
0.6188
0.5904
1.00
1.02
1.01
1.02
1.02
1.00
1.03
1.02
1.02
1.05
1.07
1.02
f1 (ppm)

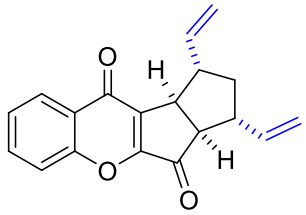
Scheme 4, 11

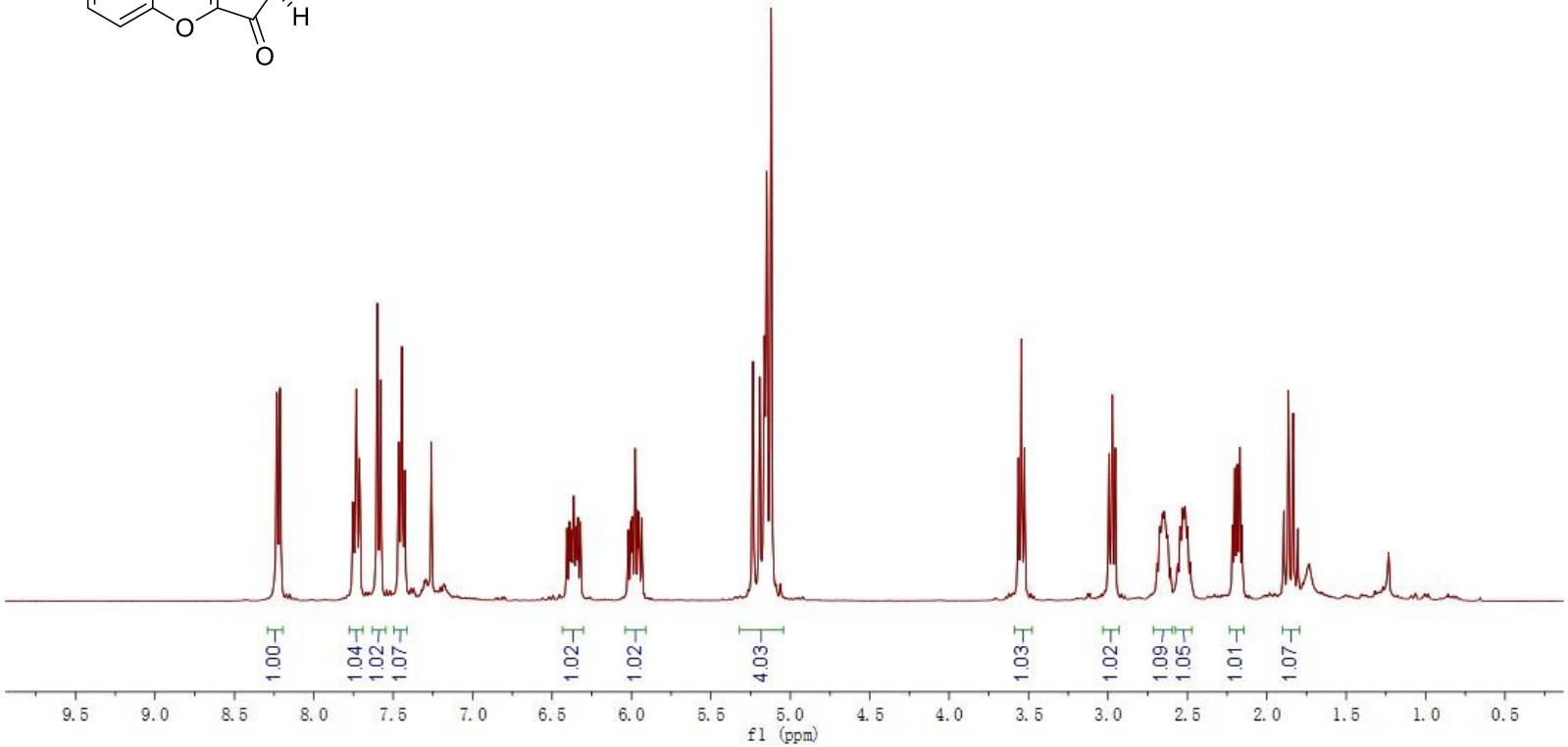
O
H
O
H
O
O

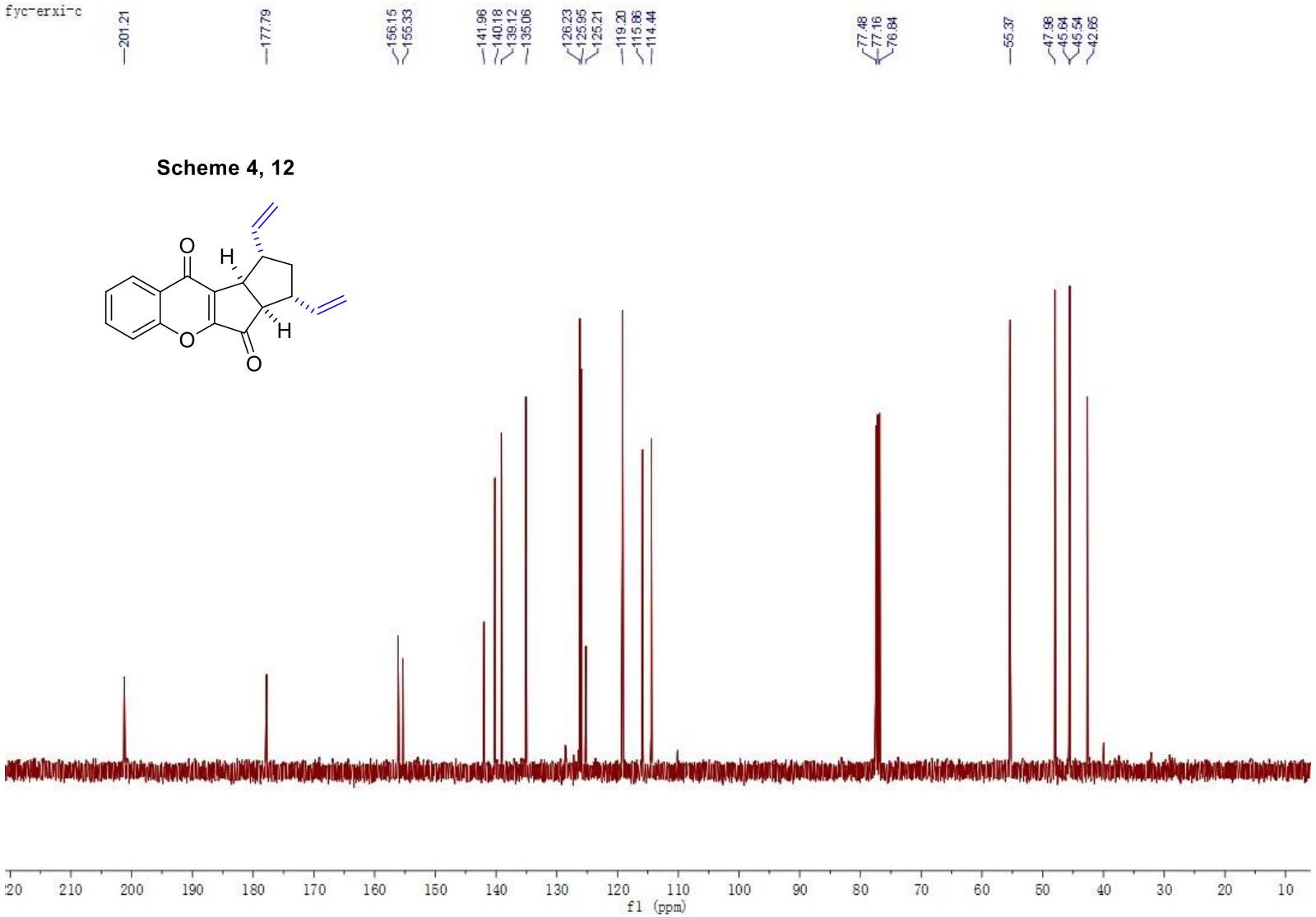

fyc-hoh-c
200.33
177.51
159.33
156.04
140.06
135.38
126.15
124.94
119.25
77.48
77.16
76.84
52.70
51.00
50.02
39.97
39.22
38.37
20.32
Scheme 4, 11
O
H
O
H
O
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

fyc-erxi-h

Scheme 4, 12






fyc-erxi-c
201.21
177.79
156.15
155.33
141.96
140.18
139.12
135.06
126.23
125.95
125.21
119.20
115.86
114.44
77.48
77.16
76.84
55.37
47.98
45.64
45.54
42.65
f1 (ppm)

Scheme 4, 12

O
H
O
H
O