Palladium-catalyzed decarboxylation [2 + 2 + 2] annulation approach to chromone-containing polycyclic compounds

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Supporting Information

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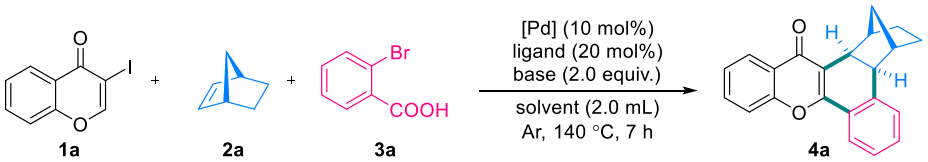
1. General experimental information

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. X-ray crystallographic data were collected by a diffractometer Rigaku Oxford Diffraction Supernova Dual Source. For reactions that require heating, an oil bath was used.

3-Iodochromones **1** were prepared according to the reported procedures.[1] Bridged olefins **2a**−**2d** were purchased from commercial suppliers. Bridged olefins **2e**−**2g** were prepared according to the reported procedures.[2,3] *o*-Chlorobenzoic acid, *o*-bromobenzoic acids **3** and *o*-iodobenzoic acid was purchased from commercial suppliers. *o*-Bromocyclopentane carboxylic acids **5** was prepared according to the reported procedures.[4]

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



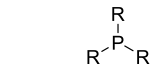
Entry	Temperature (°C)	Ligand	[Pd]	Base	Solvent	Yield (%)[b]
1	90	**L1**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	N.R.
2	110	**L1**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	trace
3	130	**L1**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	45
4	140	**L1**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	52
5	150	**L1**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	49
6	140	**L2**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	trace
7	140	**L3**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	50
8	140	**L4**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	46
9	140	**L5**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	52
10	140	**L6**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	55
11	140	**L7**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	38
12	140	**L8**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	48
13	140	**L9**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	25
14	140	**L10**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	36
15	140	**L11**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	Trace
16	140	**L12**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	10
17	140	**L13**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	trace
18	140	**L14**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	trace
19	140	**L15**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	22
20	140	**L16**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	13
21	140	**L17**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	31
22	140	**L18**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	trace
23	140	**L19**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	trace
24	140	**L20**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	61
25	140	**L21**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	34
26	140	**L22**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	39
27	140	**L23**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	28
28	140	**L24**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	24
29	140	**L25**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	49
30	140	**L26**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	10
31	140	**L27**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	13
32	140	**L28**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	trace
33	140	**L29**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	trace
34	140	**L30**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	14

35	140	**L31**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	22
36	140	**L32**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	25
37	140	**L33**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	38
38	140	**L34**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	33
39	140	**L35**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	30
40	140	**L36**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	66
41	140	**L37**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	55
42	140	**L38**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	25
43	140	**L39**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	trace
44	140	**L40**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	18
45	140	**L41**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	37
46	140	**L42**	$Pd(OAc)_2$	Cs_2CO_3	PhMe	trace
47	140	**L36**	$Pd(OPiv)_2$	Cs_2CO_3	PhMe	57
48	140	**L36**	$Pd(TFA)_2$	Cs_2CO_3	PhMe	67
49	140	**L36**	$PdCl_2$	Cs_2CO_3	PhMe	47
50	140	**L36**	$PdBr_2$	Cs_2CO_3	PhMe	58
51	140	**L36**	PdI_2	Cs_2CO_3	PhMe	66
52	140	**L36**	$PdCl_2(nbd)$	Cs_2CO_3	PhMe	68
53	140	**L36**	$PdCl_2(PPh_3)_2$	Cs_2CO_3	PhMe	58
54	140	**L36**	$PdCl_2(dppb)$	Cs_2CO_3	PhMe	31
55	140	**L36**	$PdCl_2(dppe)$	Cs_2CO_3	PhMe	42
56	140	**L36**	$Pd(dppf)Cl_2$	Cs_2CO_3	PhMe	29
57	140	**L36**	$Pd(dppf)Cl_2 \cdot DCM$	Cs_2CO_3	PhMe	37
58	140	**L36**	$[(cinnamyl)PdCl]_2$	Cs_2CO_3	PhMe	36
59	140	**L36**	$Pd(Phos)Cl_2$	Cs_2CO_3	PhMe	68
60	140	**L36**	$[(SIPr)PdCl_2]_2$	Cs_2CO_3	PhMe	48
61	140	**L36**	$Pd(CH_3CN)_2Cl_2$	Cs_2CO_3	PhMe	75
62	140	**L36**	$PdCl_2(CH_3CN)_4(BF_4)_2$	Cs_2CO_3	PhMe	59
63	140	**L36**	$Pd(PCy_3)_2$	Cs_2CO_3	PhMe	44
64	140	**L36**	[(NHC)Pd(allyl)Cl]	Cs_2CO_3	PhMe	25
65	140	**L36**	$[Pd(1\text{-methylallyl})Cl]_2$	Cs_2CO_3	PhMe	50
66	140	**L36**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	PhMe	66
67	140	**L36**	$Pd(P^tBu_3)_2$	Cs_2CO_3	PhMe	60
68	140	**L36**	$[Pd(2\text{-methylallyl})Cl]_2$	Cs_2CO_3	PhMe	66
69	140	**L36**	$Pd(dba)_2$	Cs_2CO_3	PhMe	43
70	140	**L36**	$Pd_2(dba)_3$	Cs_2CO_3	PhMe	56
71	140	**L36**	$Pd_2(dba)_3 \cdot CHCl_3$	Cs_2CO_3	PhMe	52
72	140	**L36**	$Pd(PPh_3)_4$	Cs_2CO_3	PhMe	37
73	140	**L36**	CX22	Cs_2CO_3	PhMe	42
74	140	**L36**	Pd-117	Cs_2CO_3	PhMe	62
75	140	**L36**	$Pd(diphos)_2$	Cs_2CO_3	PhMe	20
76	140	**L36**	Pd-PEPPSI-IPent	Cs_2CO_3	PhMe	43
77	140	**L36**	Xphos Pd G1	Cs_2CO_3	PhMe	34
78	140	**L36**	Xphos Pd G2	Cs_2CO_3	PhMe	45

79	140	**L36**	Xphos Pd G3	Cs_2CO_3	PhMe	57
80	140	**L36**	Umicore CX31	Cs_2CO_3	PhMe	29
81	140	**L36**	NHC-Pd(II)-Im	Cs_2CO_3	PhMe	27
82	140	**L36**	Pd-PEPPSI-IPr	Cs_2CO_3	PhMe	26
83	140	**L36**	$Pd(CH_3CN)_2Cl_2$	K_2CO_3	PhMe	21
84	140	**L36**	$Pd(CH_3CN)_2Cl_2$	K_3PO_4	PhMe	11
85	140	**L36**	$Pd(CH_3CN)_2Cl_2$	CH_3COONa	PhMe	trace
86	140	**L36**	$Pd(CH_3CN)_2Cl_2$	CH_3COOk	PhMe	trace
87	140	**L36**	$Pd(CH_3CN)_2Cl_2$	CF_3COONa	PhMe	N.R.
88	140	**L36**	$Pd(CH_3CN)_2Cl_2$	CF_3COOCs	PhMe	N.R.
89	140	**L36**	$Pd(CH_3CN)_2Cl_2$	CsF	PhMe	trace
90	140	**L36**	$Pd(CH_3CN)_2Cl_2$	NaF	PhMe	trace
91	140	**L36**	$Pd(CH_3CN)_2Cl_2$	KF	PhMe	trace
92	140	**L36**	$Pd(CH_3CN)_2Cl_2$	NaOPiv	PhMe	N.R.
93	140	**L36**	$Pd(CH_3CN)_2Cl_2$	CsOPiv	PhMe	30
94	140	**L36**	$Pd(CH_3CN)_2Cl_2$	LiO^{t}Bu	PhMe	N.R.
95	140	**L36**	$Pd(CH_3CN)_2Cl_2$	NaO^{t}Bu	PhMe	N.R.
96	140	**L36**	$Pd(CH_3CN)_2Cl_2$	KO^{t}Bu	PhMe	N.R.
97	140	**L36**	$Pd(CH_3CN)_2Cl_2$	NaOMe	PhMe	N.R.
98	140	**L36**	$Pd(CH_3CN)_2Cl_2$	NaOEt	PhMe	N.R.
99	140	**L36**	$Pd(CH_3CN)_2Cl_2$	Cs_2CO_3	1,4-dioxane	55
100	140	**L36**	$Pd(CH_3CN)_2Cl_2$	Cs_2CO_3	*o*-xylene	86; 33[c]; trace[d]
101	140	**L36**	$Pd(CH_3CN)_2Cl_2$	Cs_2CO_3	*m*-xylene	69
102	140	**L36**	$Pd(CH_3CN)_2Cl_2$	Cs_2CO_3	*p*-xylene	76
103	140	**L36**	$Pd(CH_3CN)_2Cl_2$	Cs_2CO_3	mesitylene	16
104	140	**L36**	$Pd(CH_3CN)_2Cl_2$	Cs_2CO_3	PhCl	72
105	140	**L36**	$Pd(CH_3CN)_2Cl_2$	Cs_2CO_3	*o*-DCB	82
106	140	**L36**	$Pd(CH_3CN)_2Cl_2$	Cs_2CO_3	DMSO	33
107	140	**L36**	$Pd(CH_3CN)_2Cl_2$	Cs_2CO_3	DMA	35
108	140	**L36**	$Pd(CH_3CN)_2Cl_2$	Cs_2CO_3	CPME	43
109	140	**L36**	$Pd(CH_3CN)_2Cl_2$	Cs_2CO_3	BnOH	trace
110	140	**L36**	$Pd(CH_3CN)_2Cl_2$	Cs_2CO_3	DMF	40

[a] Unless otherwise noted, all reactions were performed with **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), **3a** (0.6 mmol, 3.0 equiv.), Pd-catalyst (10 mol%), ligand (20 mol%), base (0.4 mmol, 2.0 equiv.) in 2.0 mL of solvent under an Ar atmosphere at 140 ˚C for 7 h. [b] Isolated yields based on **1a**. [c] Useing *o*-chlorobenzoic acid instead of *o*-bromobenzoic acid. [d] Using *o*-iodobenzoic acid instead of *o*-bromobenzoic acid.

Ligands examined in this work:

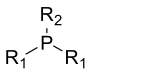


L1: R = Ph;
L2: R = 2-MeC_6H_4;
L3: R = 2-$OMeC_6H_4$;
L4: R = 2-FC_6H_4;

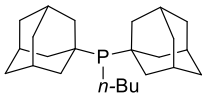
L5: R = 3-MeC_6H_4;
L6: R = 3-$OMeC_6H_4$;
L7: R = 3-FC_6H_4;
L8: R = 4-MeC_6H_4;

L9: R = 4-FC_6H_4;
L10: R = 4-$CF_3C_6H_4$;
L11: R = 3,5-$(CF_3)_2C_6H_3$;
L12: R = 2,6-$(OMe)_2C_6H_3$;

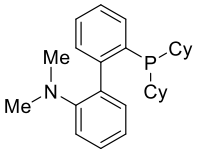
L13: R = 2,4,6-$(Me)_3C_6H_2$;
L14: R = 2,4,6-$(OMe)_3C_6H_2$;
L15: R = 2-furyl;
L16: R = Cy, PCy_3;



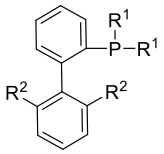
L17: R^1 = Ph, R^2 = Me;
L18: R^1 = Ph, R^2 = C_6F_5;
L19: R^1 = Ph, R^2 = 2-$CO_2HC_6H_4$;
L20: R^1 = Cy, R^2 = Ph, $PhPCy_2$;



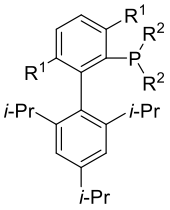
L21: ^{n}BuPAd$_2$;



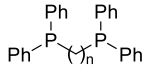
L22: DavePhos;



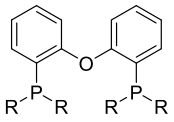
L23: R^1 = Ph, R^2 = H;
L24: R^1 = ^{t}Bu, R^2 = H, JohnPhos;
L25: R^1 = Cy, R^2 = H, CyJohnPhos;
L26: R^1 = Cy, R^2 = OMe, Sphos;
L27: R^1 = Cy, R^2 = isopropoxy, RuPhos;



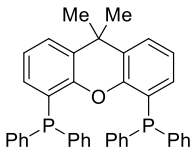
L28: R^1 = H, R^2 = Cy, Xphos;
L29: R^1 = H, R^2 = ^{t}Bu, ^{t}BuXphos;



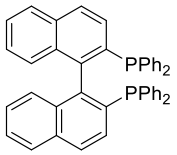
L30: n = 1, DPPM;
L31: n = 2, DPPE;
L32: n = 3, DPPP;
L33: n = 4, DPPB;
L34: n = 5, DPPPE;
L35: n = 6, DPPH;



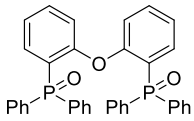
L36: R = Ph, DPEphos;
L37: R = Cy, Cy-DPEphos;



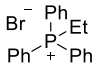
L38: Xantphos;



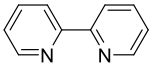
L39: *rac*-BINAP;



L40: DPEPO;



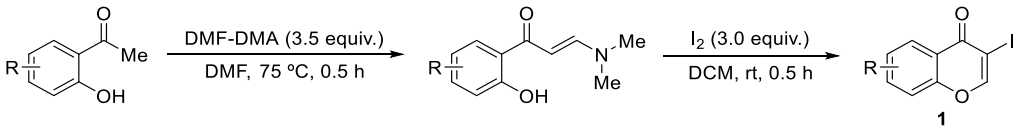
L41: ETPPBr;



L42

3. Synthetic methods of substrates

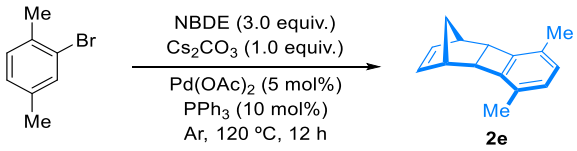
3.1 Synthesis of 3-iodochromones (**1**)



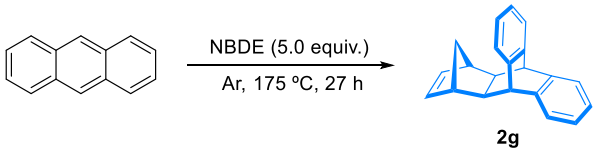
A mixture of substituted 2-hydroxyacetophenones (0.5 mmol) and *N,N*-dimethylformamide dimethylacetal (DMF-DMA, 1.75 mmol, 2.5 equiv.) was dissolved in *N,N*-dimethylformamide (DMF, 25 mL) and heated at 75 °C for 0.5 h. After completion of the reaction, saturated brine was added to the mixture. The solid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

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

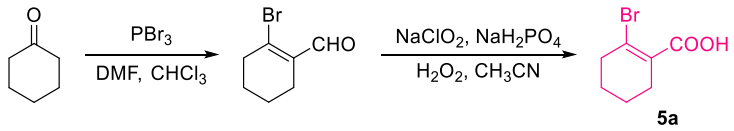


To a 40 mL glass vial were added 2-bromo-*p*-xylene (2.0 g, 10.8 mmol), Cs_2CO_3 (3.6 g, 10.8 mmol) and norbornadiene (3.3 mL, 32.4 mmol) followed by dry 1,4-dioxane (20 mL) under argon atmosphere. The reaction vial was evacuated and filled with argon three times. $Pd(OAc)_2$ (121mg, 0.54 mmol) and PPh_3 (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 **2e** as a colorless oil (954.0 mg, 45% yield). Under the same conditions, replacing 2-bromo-*p*-xylene with 9-bromophenanthrene can obtain compound **2f** as a white solid. Spectra matched those previously reported.[2]



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 **2g** as a white solid (1.08 g, 79% yield). Spectra matched those previously reported.[3]

3.3 Synthesis of *o*-bromocyclopentane carboxylic acids (**5**)

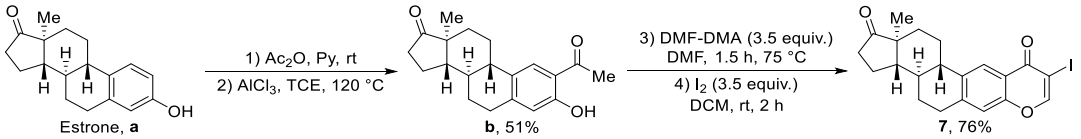


5a

To a mixture of DMF (10.0 mL) and $CHCl_3$ (20.0 mL) was slowly added PBr_3 (12.0 mmol, 1.2 mL 1.2 equiv,) at 0 °C under Ar. The pale yellow slurry was stirred at room temperature for 2.5 h. Then, cyclopentanone (10.0 mmol, 1.0 equiv., 0.9 mL) was added dropwise at reflux temperature. The mixture was stirred at this temperature for 3 h, then poured into KOH aqueous solution (20.0 mL), and extracted with ethyl acetate (3 × 10.0 mL). The extract was dried over anhydrous Na_2SO_4. The organic phase was removed under reduced pressure, and the crude product was purified by flash column chromatography (eluent: petroleum ether/EtOAc = 100:1) to afford 2-Bromo-1-cyclohexenecarbaldehyde (1.6 g, 60% yield).

A solution of $NaClO_2$ (8.4 mmol, 1.4 equiv., 0.9 g) in water (10.0 mL) was added dropwise in 3 h to a stirred mixture of 2-Bromo-1-cyclohexenecarbaldehyde (6.0 mmol, 1.0 equiv., 1.6 g) in CH_3CN (10.0 mL), NaH_2PO_4 (1.6 mmol, 0.27 equiv., 0.2 g) in water (5.0 mL) and 30% aqueous H_2O_2 (0.7 mL), keeping the temperature at 10 °C with water cooling for 6 h. After completion of the reaction (monitored by TLC), the mixture was poured into saturated Na_2CO_3 aqueous solution, and washed with ethyl acetate. The aqueous phase was poured into HCl solution, and extracted with ethyl acetate. The extract was dried over Na_2SO_4. The organic phase was removed under reduced pressure to afford *o*-Bromocyclopentane Carboxylic Acid **5a** as a white solid (1.0 g, 83% yield).[4] Analogues of **5** can be obtained with the same approach.

3.4 Synthesis of substrate **7**



Estrone, **a** **b**, 51% **7**, 76%

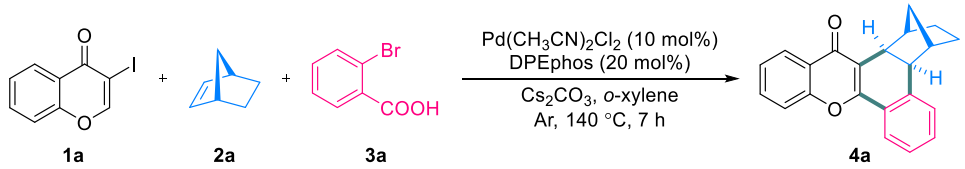
To a solution of estrone (**a**, 1.35 g, 5.0 mmol, 1.0 equiv.) in pyridine (7.0 mL) was added acetic anhydride (3.31 g, 32.5 mmol, 6.5 equiv.) at ice-bath condition and the reaction was stirred at room temperature for 16 h. The reaction mixture was then poured into ice water (70.0 mL) and the

resulting solid was filtrated, washed with water to afford estrone acetate in quantitative yield. To the tetrachloroethane (TCE) (50 mL, 0.1 M) was added $AlCl_3$ (1.67 g, 12.5 mmol, 2.5 equiv.) and the mixture was stirred at 90 ˚C (oil bath) for 10 min, followed by the addition of a solution of estrone acetate (1562 mg, 5 mmol, 1.0 equiv.) in DCM (5 mL, 1 M). The reaction was stirred at 120 ˚C (oil bath) for 8 h before poured into cold 2 M HCl (30 mL) and extracted with DCM (3 × 50 mL). The organic phase was washed with saturated $NaHCO_3$ solution (30 mL), brine (30 mL) and dried over Na_2SO_4. After the evaporation of solvent, the crude product was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to give the product **b** as a yellow solid (796.7 mg, 51% yield). [5b]

A solution of **b** (137.5 mg, 0.44 mmol, 1.0 equiv.) and DMF-DMA (183.6 mg, 1.54 mmol, 3.5 equiv.) in DMF (10 mL) was stirred at 75 ˚C (oil bath) for 1.5 h. After completion of the reaction, saturated brine (30 mL) was added to the mixture, and the resulting solid was filtrated. To a solution of the solid in DCM (10 mL) was added iodine (390.9 mg, 1.54 mmol, 3.5 equiv.), and the mixture was stirred at room temperature for 2 h. After completion of the reaction, the solution was quenched with 5% $NaHSO_3$ (20 mL), and was extracted with DCM three times (3 × 20 mL). The combined organic fractions were condensed and purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1) to give the product **7** as a white solid (150.0 mg, 76% yield).[5c]

Characterization data of **1**, **2**, **5** and **7** can be found in previously reported.[4-5]

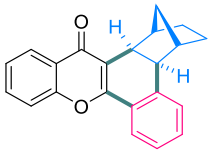
4. Representative procedure for the synthesis of compound 4a (Scheme 2)



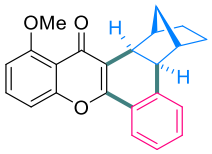
To a 15 mL oven-dried sealed tube containing a stir bar, 3-iodochromone (**1a**, 54.5 mg, 0.2 mmol), NBE (**2a**, 37.6 mg, 0.4 mmol), *o*-bromobenzoic acid (**3a**, 120.6 mg, 0.6 mmol), $Pd(CH_3CN)_2Cl_2$ (5.2 mg, 0.02 mmol), DPEphos (21.5 mg, 0.04 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol) and *o*-xylene (2.0 mL) were added under an argon atmosphere at 140 °C for 7 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 = 20:1 ~ 5:1) to afford the desired product **4a** as a white solid (51.4 mg, 86% yield).

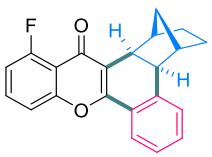
5. Characterization data of compounds 4a-ap, 6a(6a')-c(c'), 8



Compound **4a**: white solid, 54.1 mg, 86% yield, mp 191.7 – 192.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, J = 8.0, 1.6 Hz, 1H), 7.91 – 7.87 (m, 1H), 7.58 (ddd, J = 8.6, 7.2, 1.6 Hz, 1H), 7.44 (d, J = 8.4 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.24 – 7.18 (m, 2H), 3.20 (dd, J = 25.4, 10.2 Hz, 2H), 2.47 (s, 1H), 2.31 (s, 1H), 1.75 – 1.53 (m, 4H), 1.32 (d, J = 10.2 Hz, 1H), 1.08 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 156.4, 155.3, 141.5, 133.1, 131.3, 129.4, 126.6, 126.3, 125.5, 124.6, 123.7, 123.1, 117.7, 117.0, 49.1, 45.5, 44.6, 40.0, 33.8, 30.4, 29.9; HRMS (ESI-TOF): calcd. for $C_{22}H_{19}O_2$ $[M + H]^+$ 315.1380; found 315.1384.

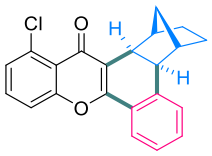


Compound **4b**: yellow solid, 34.3 mg, 50% yield, mp 182.6 – 183.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 1H), 7.51 (t, J = 8.4 Hz, 1H), 7.38 – 7.32 (m, 1H), 7.25 (t, J = 6.8 Hz, 2H), 7.07 (d, J = 8.4 Hz, 1H), 6.76 (d, J = 8.4 Hz, 1H), 3.97 (s, 3H), 3.29 – 3.19 (m, 2H), 2.50 (s, 1H), 2.35 (s, 1H), 1.75 – 1.56 (m, 4H), 1.33 (d, J = 10.2 Hz, 1H), 1.09 (d, J = 10.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 159.8, 157.5, 154.6, 141.5, 133.3, 131.1, 129.4, 126.7, 126.4, 123.0, 118.2, 114.4, 110.0, 105.8, 56.4, 49.2, 45.7, 44.8, 40.0, 33.9, 30.6, 29.9; HRMS (ESI-TOF): calcd. for $C_{23}H_{21}O_3$ $[M + H]^+$ 345.1485; found 345.1483.

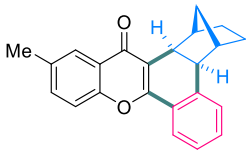


Compound **4c**: yellow solid, 51.1 mg, 77% yield, mp 162.7 – 163.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.6 Hz, 1H), 7.54 (td, J = 8.4, 5.6 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.32 – 7.23 (m, 3H),

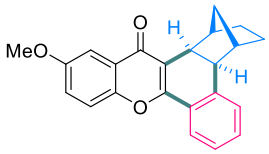
7.02 – 6.96 (m, 1H), 3.28 – 3.19 (m, 2H), 2.49 (s, 1H), 2.35 (s, 1H), 1.74 – 1.58 (m, 4H), 1.33 (d, J = 10.2 Hz, 1H), 1.11 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 160.7 (d, J = 264.2 Hz), 156.5 (d, J = 3.9 Hz), 155.8, 141.6, 133.1 (d, J = 10.8 Hz), 131.6, 129.5, 126.5, 126.3, 123.2, 118.0, 114.2 (d, J = 9.9 Hz), 113.8 (d, J = 4.6 Hz), 111.6 (d, J = 20.8 Hz), 49.2, 45.6, 44.7, 39.9, 34.0, 30.5, 29.9; HRMS (ESI-TOF): calcd. for $C_{22}H_{18}FO_2$ $[M + H]^+$ 333.1285; found 333.1283.



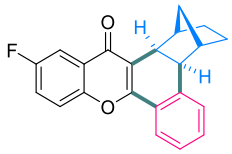
Compound **4d**: white solid, 35.7 mg, 51% yield, mp 194.9 – 196.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.37 (ddd, J = 8.8, 8.2, 1.2 Hz, 2H), 7.30 (dd, J = 7.6, 1.2 Hz, 1H), 7.24 (t, J = 7.8 Hz, 2H), 3.23 – 3.15 (m, 2H), 2.47 (s, 1H), 2.34 (s, 1H), 1.72 – 1.55 (m, 4H), 1.31 (d, J = 10.2 Hz, 1H), 1.10 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 156.9, 155.3, 141.5, 133.3, 132.3, 131.5, 129.5, 127.7, 126.4, 126.2, 123.0, 120.5, 118.0, 117.2, 49.2, 45.6, 44.6, 40.1, 33.9, 30.6, 29.9; HRMS (ESI-TOF): calcd. for $C_{22}H_{18}ClO_2$ $[M + H]^+$ 349.0990; found 349.0991.



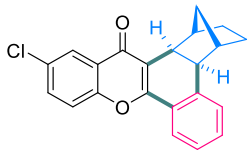
Compound **4e**: white solid, 53.6 mg, 82% yield, mp 213.4 – 213.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 0.8 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.43 – 7.31 (m, 3H), 7.23 (dd, J = 9.4, 8.0 Hz, 2H), 3.22 (dd, J = 25.2, 10.2 Hz, 2H), 2.48 (s, 1H), 2.42 (s, 3H), 2.33 (s, 1H), 1.76 – 1.57 (m, 4H), 1.33 (d, J = 10.2 Hz, 1H), 1.09 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 156.3, 153.6, 141.5, 134.4, 134.4, 131.3, 129.4, 126.8, 126.3, 124.9, 123.4, 123.2, 117.5, 116.9, 49.2, 45.5, 44.6, 40.1, 33.8, 30.5, 29.9, 21.0; HRMS (ESI-TOF): calcd. for $C_{23}H_{21}O_2$ $[M + H]^+$ 329.1536; found 329.1536.



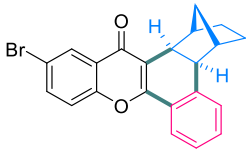
Compound **4f**: white solid, 63.3 mg, 92% yield, mp 201.9 – 202.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.8 Hz, 1H), 7.57 (d, J = 3.2 Hz, 1H), 7.44 (d, J = 9.0 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.30 – 7.21 (m, 3H), 3.89 (s, 3H), 3.27 (dd, J = 22.8, 10.2 Hz, 2H), 2.50 (s, 1H), 2.36 (s, 1H), 1.78 – 1.58 (m, 4H), 1.36 (d, J = 10.2 Hz, 1H), 1.11 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 156.6, 156.4, 150.3, 141.6, 131.3, 129.5, 126.9, 126.5, 124.3, 123.3, 123.2, 119.3, 116.5, 104.8, 55.9, 49.3, 45.6, 44.7, 40.2, 33.9, 30.5, 30.0; HRMS (ESI-TOF): calcd. for $C_{23}H_{21}O_3$ $[M + H]^+$ 345.1485; found 345.1487.



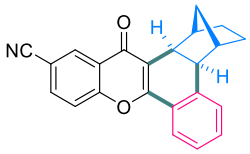
Compound **4g**: white solid, 43.8 mg, 66% yield, mp 180.7 – 181.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.8 Hz, 1H), 7.78 (dd, J = 8.4, 3.2 Hz, 1H), 7.46 (dd, J = 9.2, 4.2 Hz, 1H), 7.40 – 7.29 (m, 2H), 7.28 – 7.19 (m, 2H), 3.24 – 3.15 (m, 2H), 2.45 (s, 1H), 2.33 (s, 1H), 1.74 – 1.55 (m, 4H), 1.32 (d, J = 10.2 Hz, 1H), 1.09 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8 (d, J = 2.3 Hz), 159.3 (d, J = 245.7 Hz), 156.8, 151.5 (d, J = 1.5 Hz), 141.6, 131.6, 129.5, 126.5, 126.4, 124.7 (d, J = 7.2 Hz), 123.2, 121.3 (d, J = 25.5 Hz), 119.9 (d, J = 8.0 Hz), 116.5, 110.4 (d, J = 23.5 Hz), 49.2, 45.5, 44.6, 40.0, 33.9, 30.5, 29.9; HRMS (ESI-TOF): calcd. for $C_{22}H_{18}FO_2$ $[M + H]^+$ 333.1285; found 333.1286.



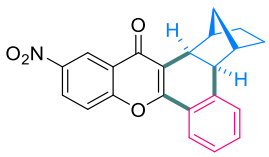
Compound **4h**: white solid, 38.4 mg, 55% yield, mp 221.4 – 222.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 2.4 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.53 (dd, J = 9.0, 2.6 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.28 – 7.20 (m, 2H), 3.25 – 3.14 (m, 2H), 2.45 (s, 1H), 2.33 (s, 1H), 1.76 – 1.54 (m, 4H), 1.31 (d, J = 10.2 Hz, 1H), 1.10 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 156.8, 153.6, 141.6, 133.3, 131.7, 130.5, 129.5, 126.5, 126.3, 125.0, 124.6, 123.2, 119.6, 117.1, 49.2, 45.5, 44.6, 40.1, 33.9, 30.5, 29.9; HRMS (ESI-TOF): calcd. for $C_{22}H_{18}ClO_2$ $[M + H]^+$ 349.0990; found 349.0991.



Compound **4i**: yellow solid, 41.3 mg, 53% yield, mp 233.5 – 234.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 2.4 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.70 (dd, J = 8.8, 2.4 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.31 – 7.24 (m, 2H), 3.29 – 3.20 (m, 2H), 2.47 (s, 1H), 2.36 (s, 1H), 1.78 – 1.59 (m, 4H), 1.34 (d, J = 10.2 Hz, 1H), 1.12 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 156.9, 154.2, 141.7, 136.1, 131.7, 129.6, 128.3, 126.6, 126.4, 125.1, 123.3, 119.9, 118.1, 117.3, 49.3, 45.6, 44.7, 40.1, 34.0, 30.5, 30.0; HRMS (ESI-TOF): calcd. for $C_{22}H_{18}BrO_2$ $[M + H]^+$ 393.0485; found 393.0480.

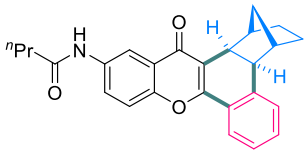


Compound **4j**: white solid, 31.7 mg, 47% yield, mp 272.9 – 273.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 2.0 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.85 (dd, J = 8.8, 2.0 Hz, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.42 (t, J = 7.2 Hz, 1H), 7.29 (t, J = 8.0 Hz, 2H), 3.25 (s, 2H), 2.46 (s, 1H), 2.37 (s, 1H), 1.78 – 1.60 (m, 4H), 1.34 (d, J = 10.3 Hz, 1H), 1.14 (d, J = 10.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 157.3, 157.2, 141.8, 135.5, 132.2, 131.5, 129.7, 126.7, 125.9, 124.1, 123.3, 119.6, 118.0, 117.9, 108.8, 49.3, 45.5, 44.7, 40.1, 34.0, 30.5, 29.9; HRMS (ESI-TOF): calcd. for $C_{23}H_{18}NO_2$ $[M + H]^+$ 340.1332; found 340.1336.

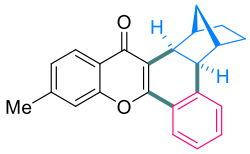


Compound **4k**: white solid, 33.0 mg, 46% yield, mp 266.1 – 267.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (d, J = 2.4 Hz, 1H), 8.47 (dd, J = 9.2, 2.6 Hz, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 9.2 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.31 (t, J = 8.0 Hz, 2H), 3.28 (s, 2H), 2.49 (s, 1H), 2.39 (s, 1H), 1.78 – 1.62 (m, 4H), 1.36 (d, J = 10.2 Hz, 1H), 1.16 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 158.3, 157.4, 144.5, 141.9, 132.3, 129.8, 127.6, 126.7, 125.9, 123.7, 123.4, 122.6,

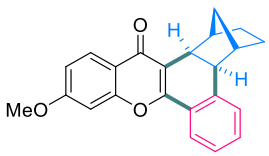
119.6, 117.8, 49.4, 45.6, 44.7, 40.1, 34.0, 30.5, 29.9; HRMS (ESI-TOF): calcd. for $C_{22}H_{18}NO_4$ [M + H]$^+$ 360.1230; found 360.1235.



Compound **4l**: white solid, 38.3 mg, 48% yield, mp 240.2 – 241.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.39 (d, J = 8.2 Hz, 1H), 7.94 (d, J = 9.0 Hz, 2H), 7.44 (d, J = 9.0 Hz, 1H), 7.38 (t, J = 7.2 Hz, 1H), 7.29 – 7.23 (m, 2H), 3.23 (q, J = 10.4 Hz, 2H), 2.44 (t, J = 7.2 Hz, 3H), 2.34 (s, 1H), 1.84 – 1.73 (m, 2H), 1.73 – 1.55 (m, 4H), 1.35 (d, J = 10.2 Hz, 1H), 1.10 (d, J = 10.2 Hz, 1H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 172.3, 156.9, 151.8, 141.6, 135.8, 131.6, 129.6, 126.9, 126.7, 126.5, 123.7, 123.4, 118.5, 116.5, 115.0, 49.3, 45.6, 44.7, 40.2, 39.5, 33.9, 30.5, 30.0, 19.2, 14.0; HRMS (ESI-TOF): calcd. for $C_{26}H_{26}NO_3$ [M + H]$^+$ 400.1907; found 400.1907.

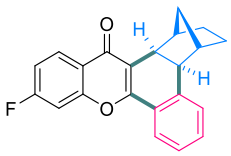


Compound **4m**: white solid, 40.7 mg, 62% yield, mp 177.0 – 178.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.36 (td, J = 7.6, 1.4 Hz, 1H), 7.32 – 7.23 (m, 3H), 7.16 (dd, J = 8.0, 1.0 Hz, 1H), 3.26 (q, J = 10.4 Hz, 2H), 2.50 (s, 1H), 2.48 (s, 3H), 2.35 (s, 1H), 1.76 – 1.58 (m, 4H), 1.36 (d, J = 10.2 Hz, 1H), 1.11 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 156.2, 155.5, 144.4, 141.6, 131.3, 129.5, 127.0, 126.4, 126.2, 125.5, 123.2, 121.6, 117.6, 117.0, 49.3, 45.6, 44.7, 40.1, 33.9, 30.5, 30.0, 21.9; HRMS (ESI-TOF): calcd. for $C_{23}H_{21}O_2$ [M + H]$^+$ 329.1536; found 329.1536.

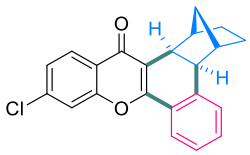


Compound **4n**: white solid, 55.8 mg, 81% yield, mp 227.1 – 228.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.8 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.26 (t, J = 7.6 Hz, 2H), 6.93 (dd, J = 8.8, 2.4 Hz, 1H), 6.89 (d, J = 2.4 Hz, 1H), 3.91 (s, 3H), 3.25 (q, J = 10.4 Hz, 2H), 2.49

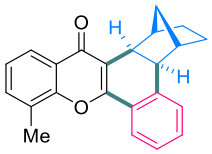
(s, 1H), 2.35 (s, 1H), 1.76 – 1.58 (m, 4H), 1.36 (d, J = 10.2 Hz, 1H), 1.11 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 163.8, 157.1, 156.2, 141.4, 131.2, 129.5, 127.1, 126.9, 126.4, 123.0, 117.8, 116.9, 114.1, 100.0, 55.9, 49.3, 45.6, 44.8, 40.1, 33.9, 30.5, 30.0; HRMS (ESI-TOF): calcd. for $C_{23}H_{21}O_3$ $[M + H]^+$ 345.1485; found 345.1487.



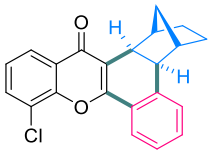
Compound **4o**: white solid, 42.8 mg, 64% yield, mp 180.5 – 181.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, J = 9.0, 6.4 Hz, 1H), 7.90 (d, J =8.0 Hz, 1H), 7.44 – 7.34 (m, 1H), 7.30 – 7.24 (m, 2H), 7.18 (dd, J = 9.0, 2.4 Hz, 1H), 7.08 (td, J = 8.6, 2.4 Hz, 1H), 3.29 – 3.21 (m, 2H), 2.48 (s, 1H), 2.36 (s, 1H), 1.76 – 1.59 (m, 4H), 1.36 (d, J = 10.2 Hz, 1H), 1.12 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 165.5 (d, J = 253.9 Hz), 156.9 (d, J = 1.4 Hz), 156.4 (d, J = 13.4 Hz), 141.6, 131.6, 129.6, 128.3, 128.2, 126.5, 123.2, 120.7 (d, J = 2.4 Hz), 117.1, 113.5 (d, J = 22.8 Hz), 104.5 (d, J = 25.1 Hz), 49.3, 45.6, 44.7, 40.0, 34.0, 30.5, 30.0; HRMS (ESI-TOF): calcd. for $C_{22}H_{18}FO_2$ $[M + H]^+$ 333.1285; found 333.1284.



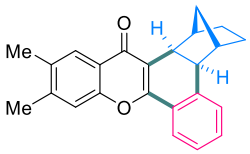
Compound **4p**: white solid, 36.4 mg, 52% yield, mp 98.7 – 99.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, J = 8.0, 1.6 Hz, 1H), 8.06 (dd, J = 7.8, 1.0 Hz, 1H), 7.68 (dd, J = 7.8, 1.6 Hz, 1H), 7.39 (td, J = 7.6, 1.2 Hz, 1H), 7.32 – 7.24 (m, 3H), 3.35 – 3.22 (m, 2H), 2.49 (s, 1H), 2.38 (s, 1H), 1.78 – 1.59 (m, 4H), 1.37 (d, J = 10.2 Hz, 1H), 1.13 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 156.8, 151.1, 141.7, 133.4, 131.8, 129.5, 126.7, 126.6, 125.1, 124.8, 124.4, 123.8, 123.1, 117.2, 49.3, 45.6, 44.7, 40.1, 34.0, 30.5, 30.0; HRMS (ESI-TOF): calcd. for $C_{22}H_{18}ClO_2$ $[M + H]^+$ 349.0990; found 349.0991.



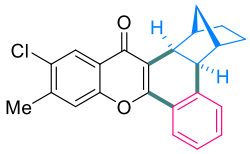
Compound **4q**: white solid, 47.3 mg, 72% yield, mp 172.9 – 174.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 7.8 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.42 – 7.37 (m, 1H), 7.32 – 7.24 (m, 3H), 3.29 (q, J = 10.4 Hz, 2H), 2.61 (s, 3H), 2.51 (s, 1H), 2.37 (s, 1H), 1.78 – 1.60 (m, 4H), 1.38 (d, J = 10.2 Hz, 1H), 1.13 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 156.2, 153.9, 141.7, 134.2, 131.4, 129.6, 127.3, 127.2, 126.5, 124.4, 123.7, 123.4, 123.1, 117.0, 49.3, 45.6, 44.7, 40.1, 34.0, 30.5, 30.0, 15.9; HRMS (ESI-TOF): calcd. for $C_{23}H_{21}O_2$ $[M + H]^+$ 329.1536; found 329.1536.



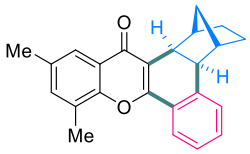
Compound **4r**: white solid, 39.7 mg, 57% yield, mp 159.8 – 161.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, J = 15.6, 8.0 Hz, 2H), 7.68 (d, J = 7.8 Hz, 1H), 7.39 (t, J = 7.4 Hz, 1H), 7.32 – 7.23 (m, 3H), 3.29 – 3.23 (m, 2H), 2.48 (s, 1H), 2.37 (s, 1H), 1.78 – 1.60 (m, 4H), 1.36 (d, J = 10.2 Hz, 1H), 1.13 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 156.8, 151.1, 141.6, 133.4, 131.8, 129.5, 126.7, 126.6, 125.1, 124.8, 124.3, 123.8, 123.1, 117.2, 49.3, 45.6, 44.6, 40.1, 34.0, 30.5, 30.0; HRMS (ESI-TOF): calcd. for $C_{22}H_{18}ClO_2$ $[M + H]^+$ 349.0990; found 349.0991.



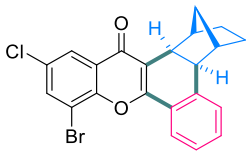
Compound **4s**: white solid, 47.6 mg, 70% yield, mp 234.6 – 235.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.86 (m, 2H), 7.35 (td, J = 7.6, 1.4 Hz, 1H), 7.28 – 7.21 (m, 3H), 3.24 (dd, J = 23.6, 10.2 Hz, 2H), 2.49 (s, 1H), 2.36 (s, 3H), 2.35 – 2.31 (m, 4H), 1.76 – 1.58 (m, 4H), 1.35 (d, J = 10.2 Hz, 1H), 1.10 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 156.1, 154.0, 143.5, 141.5, 133.8, 131.1, 129.5, 127.1, 126.4, 125.3, 123.1, 121.7, 118.0, 116.9, 49.3, 45.6, 44.7, 40.1, 33.9, 30.5, 30.0, 20.5, 19.4; HRMS (ESI-TOF): calcd. for $C_{24}H_{23}O_2$ $[M + H]^+$ 343.1692; found 343.1698.



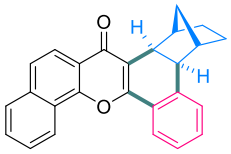
Compound **4t**: white solid, 59.3 mg, 82% yield, mp 209.7 – 211.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.42 – 7.31 (m, 2H), 7.25 (td, J = 7.8, 4.0 Hz, 2H), 3.29 – 3.12 (m, 2H), 2.50 – 2.45 (m, 4H), 2.34 (s, 1H), 1.65 (ddd, J = 19.6, 17.4, 11.4 Hz, 4H), 1.33 (d, J = 10.1 Hz, 1H), 1.11 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 156.5, 153.6, 142.3, 141.6, 131.5, 131.3, 129.6, 126.6, 126.5, 125.3, 123.2, 122.8, 119.7, 116.9, 49.3, 45.5, 44.6, 40.1, 33.9, 30.5, 30.0, 20.9; HRMS (ESI-TOF): calcd. for $C_{23}H_{20}ClO_2$ $[M + H]^+$ 363.1146; found 363.1148.



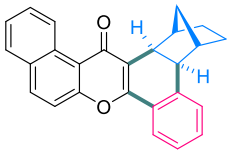
Compound **4u**: white solid, 42.3 mg, 62% yield, mp 209.6 – 210.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.8 Hz, 1H), 7.80 (s, 1H), 7.37 (dd, J = 10.8, 4.0 Hz, 1H), 7.29 – 7.22 (m, 3H), 3.24 (q, J = 10.4 Hz, 2H), 2.54 (s, 3H), 2.49 (s, 1H), 2.39 (s, 3H), 2.35 (s, 1H), 1.77 – 1.58 (m, 4H), 1.35 (d, J = 10.2 Hz, 1H), 1.10 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 156.0, 152.1, 141.6, 135.4, 134.0, 131.2, 129.5, 127.2, 126.9, 126.4, 123.3, 123.0, 122.6, 116.7, 49.3, 45.6, 44.6, 40.1, 33.9, 30.5, 30.0, 21.1, 15.8; HRMS (ESI-TOF): calcd. for $C_{24}H_{23}O_2$ $[M + H]^+$ 343.1692; found 343.1693.



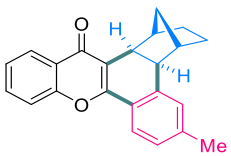
Compound **4v**: white solid, 29.0 mg, 34% yield, mp 227.8 – 229.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 2.4 Hz, 1H), 8.03 (d, J = 7.6 Hz, 1H), 7.81 (d, J = 2.4 Hz, 1H), 7.40 (t, J = 7.0 Hz, 1H), 7.27 (dd, J = 18.2, 7.0 Hz, 2H), 3.27 – 3.20 (m, 2H), 2.45 (s, 1H), 2.36 (s, 1H), 1.76 – 1.60 (m, 4H), 1.34 (d, J = 10.2 Hz, 1H), 1.13 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 157.3, 150.6, 141.7, 136.1, 132.0, 130.7, 129.6, 126.8, 126.2, 125.3, 124.6, 123.9, 117.2, 112.7, 49.3, 45.6, 44.6, 40.1, 34.0, 30.5, 30.0; HRMS (ESI-TOF): calcd. for $C_{22}H_{16}ClBrO_2Na$ $[M + Na]^+$ 448.9914; found 448.9917.



Compound **4w**: white solid, 34.4 mg, 47% yield, mp 232.9 – 233.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (d, J = 8.6 Hz, 1H), 8.02 (d, J = 9.0 Hz, 1H), 7.95 (d, J = 7.4 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.76 – 7.67 (m, 1H), 7.61 – 7.50 (m, 2H), 7.38 (td, J = 7.4, 1.2 Hz, 1H), 7.31 – 7.26 (m, 2H), 3.31 (dd, J = 35.0, 10.2 Hz, 2H), 2.57 (s, 1H), 2.39 (s, 1H), 1.83 – 1.62 (m, 4H), 1.39 (d, J = 10.2 Hz, 1H), 1.14 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.4, 156.4, 154.5, 141.3, 135.0, 131.2, 130.7, 130.5, 129.5, 129.1, 128.2, 127.2, 126.7, 126.5, 126.4, 122.9, 119.5, 117.7, 116.8, 49.2, 45.8, 44.8, 40.4, 34.1, 30.7, 30.0; HRMS (ESI-TOF): calcd. for $C_{26}H_{21}O_2$ $[M + H]^+$ 365.1536; found 365.1535.

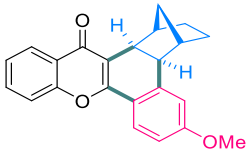


Compound **4x**: white solid, 38.4 mg, 53% yield, mp 243.8 – 244.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 4.8 Hz, 1H), 8.10 (dd, J = 18.0, 8.2 Hz, 2H), 7.87 (d, J = 4.6 Hz, 1H), 7.75 – 7.57 (m, 3H), 7.45 – 7.22 (m, 3H), 3.36 – 3.20 (m, 2H), 2.56 (s, 1H), 2.38 (s, 1H), 1.87 – 1.58 (m, 4H), 1.40 (d, J = 9.8 Hz, 1H), 1.14 (d, J = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 155.9, 152.5, 141.5, 135.8, 131.4, 129.7, 129.0, 128.2, 127.1, 127.0, 126.6, 124.8, 124.3, 123.0, 122.3, 121.1, 120.0, 118.4, 49.3, 45.7, 44.7, 40.2, 34.0, 30.6, 30.0; HRMS (ESI-TOF): calcd. for $C_{26}H_{21}O_2$ $[M + H]^+$ 365.1536; found 365.1536.

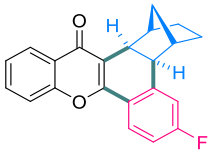


Compound **4y**: yellow solid, 37.1 mg, 56% yield, mp 165.8 – 167.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, J = 8.0, 1.2 Hz, 1H), 7.78 (s, 1H), 7.67 – 7.61 (m, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.18 (dd, J = 18.8, 8.2 Hz, 2H), 3.29 (d, J = 10.4 Hz, 1H), 3.22 (d, J = 10.4 Hz, 1H), 2.49 (s, 1H), 2.40 (s, 3H), 2.34 (s, 1H), 1.77 – 1.65 (m, 3H), 1.64 – 1.57 (m, 1H), 1.36 (d, J = 10.2 Hz, 1H), 1.11 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 156.8, 155.4, 138.8, 136.1,

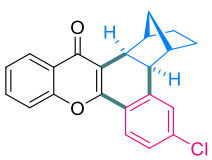
133.2, 132.4, 129.5, 126.6, 125.7, 124.7, 123.8, 123.6, 117.9, 117.3, 49.2, 45.2, 44.7, 40.2, 33.9, 30.5, 29.9, 21.3; HRMS (ESI-TOF): calcd. for $C_{23}H_{21}O_2$ $[M + H]^+$ 329.1536; found 329.1538.



Compound **4z**: yellow solid, 27.8 mg, 40% yield, mp 175.4 – 176.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, J = 8.0, 1.2 Hz, 1H), 7.68 – 7.61 (m, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.48 (d, J = 2.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 8.4 Hz, 1H), 6.96 (dd, J = 8.4, 2.8 Hz, 1H), 3.88 (s, 3H), 3.29 (d, J = 10.4 Hz, 1H), 3.21 (d, J = 10.4 Hz, 1H), 2.48 (s, 1H), 2.32 (s, 1H), 1.74 – 1.65 (m, 3H), 1.64 – 1.58 (m, 1H), 1.35 (d, J = 10.2 Hz, 1H), 1.11 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 158.2, 156.4, 155.4, 133.9, 133.3, 130.6, 127.8, 125.8, 124.8, 123.8, 117.9, 117.7, 117.5, 108.1, 55.6, 49.1, 44.9, 44.7, 40.3, 33.9, 30.6, 29.8; HRMS (ESI-TOF): calcd. for $C_{23}H_{21}O_3$ $[M + H]^+$ 345.1485; found 345.1485.

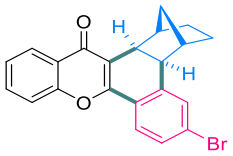


Compound **4aa**: white solid, 31.2 mg, 47% yield, mp 206.8 – 207.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 7.8 Hz, 1H), 7.69 – 7.60 (m, 2H), 7.50 (d, J = 8.4 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.22 (dd, J = 8.4, 5.6 Hz, 1H), 7.07 (td, J = 8.4, 2.4 Hz, 1H), 3.25 (q, J = 10.2 Hz, 2H), 2.49 (s, 1H), 2.32 (s, 1H), 1.77 – 1.65 (m, 3H), 1.65 – 1.57 (m, 1H), 1.34 (d, J = 10.2 Hz, 1H), 1.13 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 161.5 (d, J = 244.4 Hz), 155.3, 137.1 (d, J = 3.2 Hz), 133.5, 131.1 (d, J = 7.8 Hz), 128.6 (d, J = 8.0 Hz), 125.8, 124.9, 123.7, 118.4, 118.2, 117.9, 117.8, 109.9 (d, J = 23.8 Hz), 49.3, 45.0, 44.7, 40.3, 33.9, 30.5, 29.8; HRMS (ESI-TOF): calcd. for $C_{22}H_{18}FO_2$ $[M + H]^+$ 333.1285; found 333.1281.

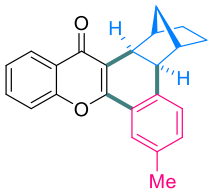


Compound **4ab**: white solid, 50.7 mg, 73% yield, mp 236.8 – 237.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, J = 8.0, 1.6 Hz, 1H), 7.90 (d, J = 2.2 Hz, 1H), 7.66 (ddd, J = 8.6, 7.2, 1.6 Hz, 1H), 7.52

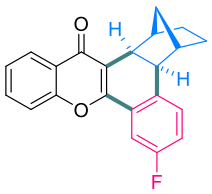
(d, *J* = 8.4 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.32 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 3.27 (d, *J* = 10.2 Hz, 1H), 3.20 (d, *J* = 10.2 Hz, 1H), 2.48 (s, 1H), 2.31 (s, 1H), 1.76 – 1.66 (m, 3H), 1.65 – 1.58 (m, 1H), 1.32 (d, *J* = 10.2 Hz, 1H), 1.13 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 155.3, 155.1, 139.9, 133.5, 132.4, 131.2, 130.9, 128.5, 125.8, 125.0, 123.7, 123.1, 117.9, 117.7, 49.3, 45.1, 44.6, 40.2, 33.9, 30.5, 29.9; HRMS (ESI-TOF): calcd. for $C_{22}H_{18}ClO_2$ [M + H]$^+$ 349.0990; found 349.0990.



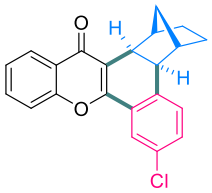
Compound **4ac**: white solid, 48.7 mg, 62% yield, mp 215.8 – 217.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 2.0 Hz, 1H), 7.70 – 7.62 (m, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.47 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 1H), 3.27 (d, *J* = 10.2 Hz, 1H), 3.17 (d, *J* = 10.2 Hz, 1H), 2.48 (s, 1H), 2.31 (s, 1H), 1.77 – 1.65 (m, 3H), 1.65 – 1.58 (m, 1H), 1.32 (d, *J* = 10.2 Hz, 1H), 1.13 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 155.3, 155.0, 140.4, 134.1, 133.6, 131.2, 128.8, 126.0, 125.7, 125.0, 123.7, 120.3, 117.9, 117.7, 49.3, 45.2, 44.6, 40.1, 33.9, 30.5, 29.9; HRMS (ESI-TOF): calcd. for $C_{22}H_{18}BrO_2$ [M + H]$^+$ 393.0485; found 393.0485.



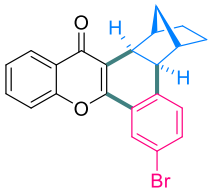
Compound **4ad**: white solid, 47.3 mg, 72% yield, mp 201.9 – 203.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.87 – 7.80 (m, 1H), 7.66 – 7.58 (m, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.39 – 7.32 (m, 1H), 7.07 (d, *J* = 3.6 Hz, 2H), 3.27 (d, *J* = 10.2 Hz, 1H), 3.19 (d, *J* = 10.4 Hz, 1H), 2.50 (s, 1H), 2.36 (s, 4H), 1.76 – 1.65 (m, 3H), 1.65 – 1.57 (m, 1H), 1.35 (d, *J* = 10.2 Hz, 1H), 1.11 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 156.9, 155.4, 141.9, 141.7, 133.1, 130.2, 127.4, 125.7, 124.6, 124.2, 123.8, 123.3, 117.8, 116.5, 49.2, 45.5, 44.7, 40.2, 34.0, 30.5, 30.0, 21.7; HRMS (ESI-TOF): calcd. for $C_{23}H_{21}O_2$ [M + H]$^+$ 329.1536; found 329.1538.



Compound **4ae**: yellow solid, 41.5 mg, 62% yield, mp 177.5 – 178.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, J = 8.0, 1.2 Hz, 1H), 7.95 (dd, J = 9.6, 5.8 Hz, 1H), 7.67 – 7.60 (m, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.36 (dd, J = 11.2, 4.0 Hz, 1H), 7.00 – 6.93 (m, 2H), 3.25 (q, J = 10.4 Hz, 2H), 2.50 (s, 1H), 2.36 (s, 1H), 1.78 – 1.65 (m, 3H), 1.65 – 1.57 (m, 1H), 1.34 (d, J = 10.2 Hz, 1H), 1.14 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 164.7 (d, J = 251.9 Hz), 155.9, 155.3, 144.8 (d, J = 8.0 Hz), 133.3, 125.7, 125.6 (d, J = 9.0 Hz), 124.8, 123.7, 123.2 (d, J = 2.7 Hz), 117.8, 116.6, 116.2 (d, J = 21.6 Hz), 113.9 (d, J = 22.0 Hz), 49.2, 45.8 (d, J = 1.5 Hz), 44.7, 40.2, 34.0, 30.4, 29.9; HRMS (ESI-TOF): calcd. for $C_{22}H_{18}FO_2$ $[M + H]^+$ 333.1285; found 333.1282.

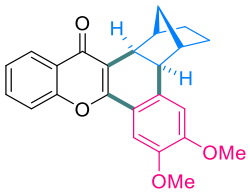


Compound **4af**: white solid, 46.9 mg, 67% yield, mp 141.2 – 142.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, J = 8.0, 1.2 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.68 – 7.60 (m, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.26 – 7.21 (m, 2H), 3.27 (d, J = 10.2 Hz, 1H), 3.19 (d, J = 10.2 Hz, 1H), 2.49 (s, 1H), 2.36 (s, 1H), 1.77 – 1.65 (m, 3H), 1.65 – 1.57 (m, 1H), 1.33 (d, J = 10.2 Hz, 1H), 1.14 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 155.7, 155.3, 143.5, 137.3, 133.4, 129.5, 126.8, 125.8, 125.5, 124.9, 124.7, 123.7, 117.8, 117.1, 49.3, 45.5, 44.7, 40.2, 34.0, 30.5, 29.9; HRMS (ESI-TOF): calcd. for $C_{22}H_{18}ClO_2$ $[M + H]^+$ 349.0990; found 349.0993.

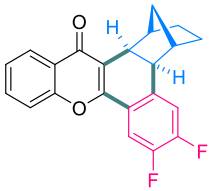


Compound **ag**: white solid, 33.9 mg, 43% yield, mp 144.1 – 145.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, J = 8.0, 1.2 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.42 – 7.33 (m, 3H), 3.25 (d, J = 10.2 Hz, 1H), 3.17 (d, J = 10.2 Hz, 1H), 2.48 (s, 1H), 2.35 (s,

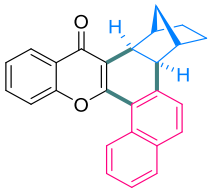
1H), 1.76 – 1.65 (m, 3H), 1.64 – 1.56 (m, 1H), 1.32 (d, *J* = 10.2 Hz, 1H), 1.13 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 155.7, 155.3, 143.6, 133.4, 132.5, 129.7, 125.9, 125.8, 125.7, 124.9, 124.8, 123.7, 117.8, 117.2, 49.3, 45.4, 44.6, 40.2, 34.0, 30.4, 29.9; HRMS (ESI-TOF): calcd. for $C_{22}H_{18}BrO_2$ $[M + H]^+$ 393.0485; found 393.0488.



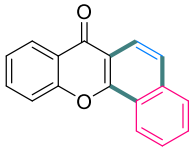
Compound **4ah**: white solid, 47.1 mg, 63% yield, mp 166.8 – 168.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 5.8 Hz, 1H), 7.61 (dd, *J* = 10.6, 4.8 Hz, 1H), 7.50 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.39 (d, *J* = 3.4 Hz, 1H), 7.34 (dd, *J* = 8.4, 6.4 Hz, 1H), 6.70 (d, *J* = 2.8 Hz, 1H), 3.97 (d, *J* = 3.6 Hz, 3H), 3.93 (d, *J* = 3.6 Hz, 3H), 3.26 (d, *J* = 10.0 Hz, 1H), 3.18 (d, *J* = 9.6 Hz, 1H), 2.49 (s, 1H), 2.34 (s, 1H), 1.76 – 1.55 (m, 4H), 1.37 (d, *J* = 9.6 Hz, 1H), 1.11 (d, *J* = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 157.0, 155.2, 151.8, 147.7, 135.6, 132.9, 125.7, 124.7, 123.8, 119.2, 117.7, 115.8, 111.7, 105.7, 56.2, 56.1, 48.9, 45.6, 44.9, 40.3, 34.0, 30.3, 29.9; HRMS (ESI-TOF): calcd. for $C_{24}H_{23}O_4$ $[M + H]^+$ 375.1591; found 375.1592.



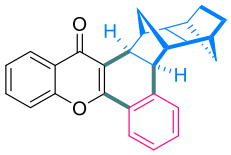
Compound **4ai**: white solid, 31.0 mg, 44% yield, mp 197.4 – 198.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.75 (dd, *J* = 11.2, 8.0 Hz, 1H), 7.69 – 7.63 (m, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.06 (dd, *J* = 10.8, 7.6 Hz, 1H), 3.29 (d, *J* = 10.4 Hz, 1H), 3.20 (d, *J* = 10.4 Hz, 1H), 2.50 (s, 1H), 2.32 (s, 1H), 1.76 – 1.66 (m, 4H), 1.65 – 1.57 (m, 1H), 1.34 (d, *J* = 10.4 Hz, 1H), 1.16 (d, *J* = 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 155.3, 154.7, 152.1 (dd, *J* = 254.1, 13.1 Hz), 149.2 (dd, *J* = 247.1, 13.2 Hz), 139.0 (dd, *J* = 6.1, 3.8 Hz), 133.6, 125.8, 125.1, 123.8 (dd, *J* = 6.1, 3.2 Hz), 123.7, 118.2 (d, *J* = 17.5 Hz), 117.8, 117.2 (d, *J* = 1.1 Hz), 112.4 (dd, *J* = 19.0, 0.5 Hz), 49.2, 45.2, 44.7, 40.2, 34.0, 30.4, 29.8; HRMS (ESI-TOF): calcd. for $C_{22}H_{17}F_2O_2$ $[M + H]^+$ 351.1191; found 351.1191.



Compound **4aj**: yellow solid, 66.1 mg, 91% yield, mp 237.2 – 238.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, J = 8.0, 1.4 Hz, 1H), 8.02 (d, J = 8.6 Hz, 1H), 7.94 (d, J = 7.8 Hz, 1H), 7.79 (dd, J = 7.2, 2.0 Hz, 1H), 7.72 (d, J = 8.6 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.56 – 7.47 (m, 3H), 7.38 – 7.33 (m, 1H), 3.66 (d, J = 10.4 Hz, 1H), 3.40 (d, J = 10.4 Hz, 1H), 2.62 (s, 1H), 2.41 (s, 1H), 1.82 – 1.69 (m, 4H), 1.45 (d, J = 10.4 Hz, 1H), 1.08 (d, J = 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 157.2, 155.4, 138.2, 135.2, 133.1, 131.3, 128.8, 127.3, 127.2, 126.7, 125.6, 125.0, 124.7, 123.9, 123.8, 120.0, 117.9, 116.5, 48.3, 44.8, 43.0, 40.9, 34.2, 30.7, 29.8; HRMS (ESI-TOF): calcd. for $C_{26}H_{21}O_2$ $[M + H]^+$ 365.1536; found 365.1538.

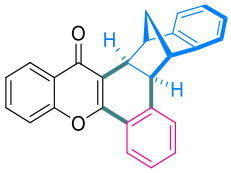


Compound **4ak**: white solid, 37.9 mg, 77% yield, mp 151.7 – 153.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ8.62 (dd, J = 8.4, 1.2 Hz, 1H), 8.39 (dd, J = 8.0, 1.4 Hz, 1H), 8.24 (d, J = 8.8 Hz, 1H), 7.89 (dd, J = 7.4, 1.8 Hz, 1H), 7.76 (ddd, J = 8.6, 7.2, 1.8 Hz, 1H), 7.72 – 7.63 (m, 4H), 7.46 – 7.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 155.8, 153.7, 136.6, 134.5, 129.7, 128.2, 127.0, 126.6, 124.5, 124.1, 123.0, 122.5, 121.6, 118.2, 117.7; HRMS (ESI-TOF): calcd. for $C_{17}H_{11}O_2$ $[M + H]^+$ 247.0754; found 247.0755.

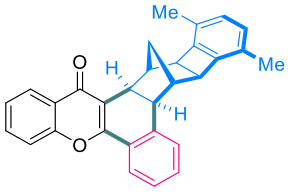


Compound **4al**: white solid, 43.3 mg, 57% yield, mp 218.9 – 219.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, J = 8.0, 1.4 Hz, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.66 – 7.59 (m, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.36 (qd, J = 7.2, 1.0 Hz, 2H), 7.26 (t, J = 7.6 Hz, 1H), 7.20 (d, J = 7.6 Hz, 1H), 3.70 (d, J = 10.0 Hz, 1H), 3.53 (d, J = 10.0 Hz, 1H), 2.60 (s, 1H), 2.51 (s, 1H), 2.34 (d, J = 9.4 Hz, 2H), 1.92 – 1.84 (m, 2H), 1.78 (d, J = 11.2 Hz, 1H), 1.58 (d, J = 7.6 Hz, 2H), 1.37 (d, J = 10.0 Hz, 1H), 1.12

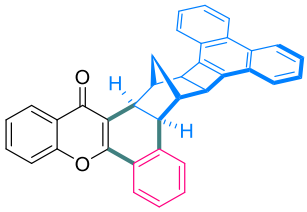
(dd, *J* = 10.4, 5.6 Hz, 2H), 1.06 (dd, *J* = 7.6, 0.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 177.6, 156.7, 155.4, 142.2, 133.2, 131.4, 129.5, 127.1, 126.3, 125.6, 124.7, 123.8, 123.2, 117.7, 117.4, 54.5, 51.6, 51.4, 49.2, 39.7, 37.1, 36.7, 36.6, 34.7, 34.2, 31.6, 31.5; HRMS (ESI-TOF): calcd. for $C_{27}H_{25}O_2$ $[M + H]^+$ 381.1849; found 381.1846.



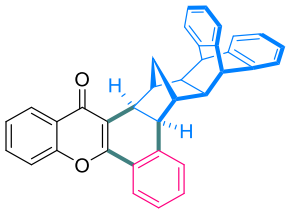
Compound **4am**: white solid, 52.2 mg, 72% yield, mp 189.7 – 191.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.27 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.57 – 7.45 (m, 4H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.24 – 7.16 (m, 2H), 3.73 (s, 1H), 3.48 (s, 1H), 3.35 – 3.26 (m, 2H), 1.72 (d, *J* = 9.6 Hz, 1H), 1.65 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 177.7, 157.0, 155.4, 148.7, 147.5, 140.8, 133.4, 131.6, 129.8, 127.1, 126.8, 126.5, 126.1, 125.7, 124.9, 123.8, 123.7, 121.7, 120.9, 117.9, 117.1, 56.6, 51.5, 44.2, 43.2, 38.4; HRMS (ESI-TOF): calcd. for $C_{26}H_{19}O_2$ $[M + H]^+$ 363.1380; found 363.1384.



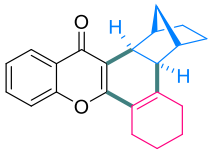
Compound **4an**: white solid, 43.3mg, 52% yield, mp 275.4 – 276.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.25 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.47 – 7.37 (m, 3H), 7.33 (t, *J* = 7.4 Hz, 1H), 6.91 (s, 2H), 3.69 (d, *J* = 3.2 Hz, 1H), 3.54 (d, *J* = 3.2 Hz, 1H), 3.32 – 3.24 (m, 2H), 2.65 (s, 1H), 2.44 (s, 1H), 2.19 (s, 6H), 1.12 (d, *J* = 10.8 Hz, 1H), 0.75 (d, *J* = 10.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 177.8, 156.5, 155.5, 144.0, 143.5, 141.5, 133.4, 131.5, 129.8, 129.7, 129.1, 128.8, 128.6, 126.9, 126.7, 125.7, 124.9, 123.8, 123.5, 117.9, 117.0, 49.5, 48.9, 48.9, 43.9, 38.9, 27.8, 16.6, 16.4; HRMS (ESI-TOF): calcd. for $C_{30}H_{25}O_2$ $[M + H]^+$ 417.1849; found 417.1841.



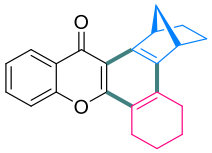
Compound **4ao**: white solid, 52.7 mg, 54% yield, mp 293.1 – 294.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (dd, J = 9.2, 5.6 Hz, 2H), 8.29 (d, J = 7.6 Hz, 1H), 8.01 (d, J = 7.8 Hz, 1H), 7.99 – 7.92 (m, 1H), 7.90 – 7.83 (m, 1H), 7.66 (t, J = 7.4 Hz, 1H), 7.64 – 7.55 (m, 4H), 7.52 (d, J = 8.4 Hz, 1H), 7.49 – 7.36 (m, 3H), 7.36 – 7.29 (m, 1H), 4.05 (s, 1H), 3.90 (d, J = 2.2 Hz, 1H), 3.39 (q, J = 10.2 Hz, 2H), 2.83 (s, 1H), 2.62 (s, 1H), 1.10 (d, J = 11.2 Hz, 1H), 0.71 (d, J = 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 156.5, 155.5, 141.4, 140.1, 139.2, 133.4, 131.5, 131.0, 130.9, 129.7, 128.2, 128.2, 126.8, 126.7, 126.7, 126.0, 125.8, 125.7, 124.9, 124.0, 123.8, 123.6, 123.5, 122.9, 117.9, 117.0, 49.7, 49.1, 48.5, 44.2, 43.5, 39.2, 27.7; HRMS (ESI-TOF): calcd. for $C_{36}H_{25}O_2$ $[M + H]^+$ 489.1849; found 489.1848.



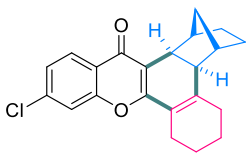
Compound **4ap**: white solid, 52.2 mg, 53% yield, mp > 310.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.36 (t, J = 7.8 Hz, 2H), 7.32 – 7.21 (m, 4H), 7.17 – 7.06 (m, 4H), 7.04 – 6.96 (m, 2H), 4.45 (d, J = 2.4 Hz, 1H), 4.36 (d, J = 2.4 Hz, 1H), 3.19 – 3.10 (m, 2H), 2.48 (dd, J = 8.6, 2.0 Hz, 1H), 2.39 – 2.30 (m, 2H), 2.14 (s, 1H), 0.62 (d, J = 11.4 Hz, 1H), -0.52 (d, J = 11.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 156.8, 155.3, 144.6, 144.3, 142.3, 141.9, 141.0, 133.4, 131.4, 129.6, 127.0, 126.6, 126.2, 126.0, 125.9, 125.7, 125.6, 124.9, 124.5, 124.3,124.0, 123.6, 123.3, 117.9, 116.6, 52.8, 50.0, 49.6, 48.5, 48.2, 47.6, 46.6, 41.7, 28.8; HRMS (ESI-TOF): calcd. for $C_{36}H_{27}O_2$ $[M + H]^+$ 491.2006; found 491.2006.



Compound **6a**: yellow solid, 6.5 mg, 10% yield, mp 107.2 – 108.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.0 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 3.14 (d, J = 11.0 Hz, 1H), 2.54 – 2.43 (m, 3H), 2.40 – 2.29 (m, 3H), 1.93 (d, J = 18.0 Hz, 1H), 1.87 – 1.72 (m, 2H), 1.70 – 1.50 (m, 5H), 1.49 – 1.39 (m, 2H), 1.12 (d, J = 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 159.9, 155.1, 146.1, 132.5, 125.5, 124.5, 124.1, 122.7, 117.8, 114.4, 49.5, 45.0, 43.5, 39.9, 34.3, 30.5, 30.3, 29.9, 22.7, 22.5, 22.2; HRMS (ESI-TOF): calcd. for $C_{22}H_{23}O_2$ $[M + H]^+$ 319.1693; found 319.1691.

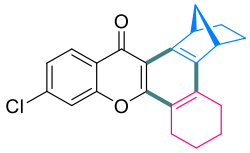


Compound **6a'**: white solid, 12.5 mg, 20% yield, mp 159.0 – 160.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (dd, J = 8.0, 1.6 Hz, 1H), 7.65 (ddd, J = 8.6, 7.2, 1.8 Hz, 1H), 7.45 (d, J = 8.2 Hz, 1H), 7.32 (td, J = 8.0, 1.0 Hz, 1H), 4.75 (d, J = 2.4 Hz, 1H), 3.47 (d, J = 2.0 Hz, 1H), 2.97 (p, J = 8.4 Hz, 3H), 2.74 (dt, J = 16.4, 4.8 Hz, 1H), 2.04 (tt, J = 10.4, 4.0 Hz, 1H), 1.96 – 1.81 (m, 5H), 1.73 (dt, J = 8.8, 1.6 Hz, 1H), 1.54 (d, J = 8.8 Hz, 1H), 1.22 – 1.14 (m, 1H), 1.07 – 1.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 155.9, 152.7, 144.9, 142.5, 137.7, 134.1, 126.5, 123.3, 122.8, 122.4, 117.9, 114.3, 49.3, 43.4, 40.2, 27.4, 26.3, 25.7, 23.4, 22.44, 22.42; HRMS (ESI-TOF): calcd. for $C_{22}H_{21}O_2$ $[M + H]^+$ 317.1536; found 317.1538.

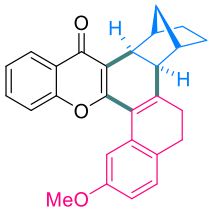


Compound **6b**: white solid, 6.4 mg, 9% yield, mp 188.7 – 190.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.6 Hz, 1H), 7.42 (s, 1H), 7.29 (d, J = 8.4 Hz, 1H), 3.14 (d, J = 10.8 Hz, 1H), 2.54 – 2.43 (m, 3H), 2.40 – 2.30 (m, 3H), 1.96 (dt, J = 19.0, 4.6 Hz, 1H), 1.86 – 1.75 (m, 2H), 1.71 – 1.64 (m, 2H), 1.61 – 1.52 (m, 3H), 1.48 – 1.41 (m, 2H), 1.15 (d, J = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 160.2, 155.3, 146.8, 138.4, 127.0, 125.4, 122.7, 122.5, 117.9, 114.8, 49.6, 45.1,

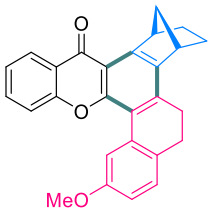
43.6, 39.9, 34.4, 30.6, 30.3, 30.0, 22.8, 22.5, 22.2; HRMS (ESI-TOF): calcd. for $C_{22}H_{22}ClO_2$ [M + H]$^+$ 353.1303; found 353.1308.



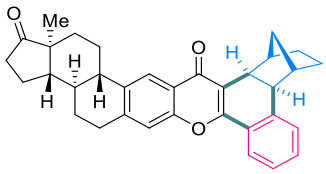
Compound **6b'**: white solid, 8.5 mg, 12% yield, mp 156.4 – 157.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.6 Hz, 1H), 7.49 (d, J = 1.6 Hz, 1H), 7.28 (dd, J = 8.6, 1.8 Hz, 1H), 4.71 (d, J = 2.4 Hz, 1H), 3.47 (s, 1H), 3.02 – 2.91 (m, 3H), 2.74 (dt, J = 10.0, 5.4 Hz, 1H), 2.03 (tt, J = 11.2, 4.0 Hz, 1H), 1.96 – 1.81 (m, 5H), 1.71 (d, J = 8.8 Hz, 1H), 1.54 (d, J = 8.8 Hz, 1H), 1.20 – 1.13 (m, 1H), 1.07 – 0.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 156.1, 152.6, 145.0, 143.0, 140.1, 138.1, 128.0, 124.2, 122.9, 121.0, 117.9, 114.2, 49.3, 43.4, 40.3, 27.5, 26.3, 25.7, 23.3, 22.39, 22.38; HRMS (ESI-TOF): calcd. for $C_{22}H_{20}ClO_2$ [M + H]$^+$ 351.1146; found 351.1144.



Compound **6c**: Yellow solid, 18.3 mg, 23% yield, mp 140.6 – 142.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.0 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.13 (d, J = 8.2 Hz, 1H), 6.98 (d, J = 2.0 Hz, 1H), 6.80 (dd, J = 8.2, 2.0 Hz, 1H), 3.83 (s, 3H), 3.33 (dd, J = 27.4, 12.0 Hz, 2H), 3.09 (ddd, J = 16.4, 6.0, 2.8 Hz, 1H), 2.87 – 2.68 (m, 2H), 2.59 (s, 1H), 2.40 – 2.27 (m, 2H), 1.78 – 1.58 (m, 5H), 1.16 (d, J = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 158.9, 158.4, 155.3, 141.1, 135.2, 132.8, 130.1, 128.3, 125.6, 125.5, 124.7, 124.1, 117.8, 115.6, 113.0, 110.6, 55.5, 45.8, 45.3, 43.3, 40.4, 34.6, 30.3, 30.2, 27.1, 20.9; HRMS (ESI-TOF): calcd. for $C_{27}H_{25}O_3$ [M + H]$^+$ 397.1798; found 357.1797.



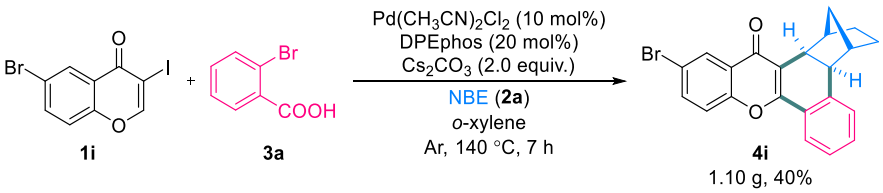
Compound **6c'**: Yellow solid, 10.0 mg, 13% yield, mp 105.8 – 107.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 7.8 Hz, 1H), 8.02 (d, J = 2.4 Hz, 1H), 7.70 (t, J = 7.8 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.24 (d, J = 8.2 Hz, 1H), 6.86 (dd, J = 8.2, 2.4 Hz, 1H), 4.86 (d, J = 3.0 Hz, 1H), 3.92 (s, 3H), 3.59 (s, 1H), 3.00 – 2.70 (m, 4H), 2.15 – 2.06 (m, 1H), 2.02 – 1.93 (m, 1H), 1.80 (d, J = 9.0 Hz, 1H), 1.61 (d, J = 9.0 Hz, 1H), 1.30 – 1.26 (m, 1H), 1.17 – 1.10 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 158.2, 155.7, 151.9, 148.6, 141.9, 139.3, 134.6, 132.8, 130.8, 128.4, 126.7, 123.7, 122.3, 120.8, 117.8, 115.8, 114.5, 112.9, 55.6, 48.8, 44.0, 40.8, 28.4, 27.4, 26.3, 26.2; HRMS (ESI-TOF): calcd. for $C_{27}H_{23}O_3$ $[M + H]^+$ 395.1642; found 395.1641.



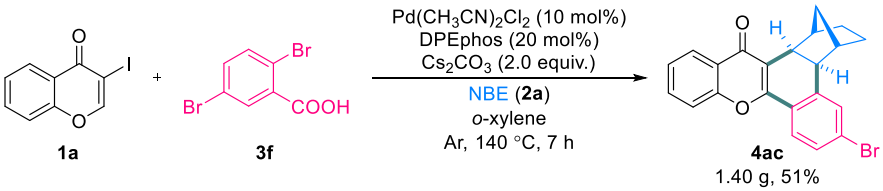
Compound **8**: white solid, 51.7 mg, 53% yield, mp 314.5 – 315.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 7.4 Hz, 1H), 7.30 – 7.24 (m, 3H), 3.28 (q, J = 10.6 Hz, 2H), 3.12 – 2.97 (m, 2H), 2.63 – 2.46 (m, 3H), 2.39 – 2.31 (m, 2H), 2.21 – 1.98 (m, 4H), 1.77 – 1.58 (m, 7H), 1.53 (ddd, J = 21.6, 14.0, 7.0 Hz, 3H), 1.39 – 1.33 (m, 1H), 1.11 (d, J = 10.0 Hz, 1H), 0.92 (d, J = 2.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.8, 177.8, 156.2 (d, J = 2.7 Hz), 153.7 (d, J = 1.2 Hz), 143.6, 141.7, 137.4 (d, J = 4.4 Hz), 131.3, 129.6, 127.1 (d, J = 2.1 Hz), 126.4, 123.2, 121.9 (d, J = 4.8 Hz), 121.7 (d, J = 1.4 Hz), 117.1 (d, J = 1.5 Hz), 116.8 (d, J = 1.1 Hz), 50.6 (d, J = 3.2 Hz), 49.3, 48.0 (d, J = 1.2 Hz), 45.6, 44.8, 44.2 (d, J = 3.1 Hz), 40.1, 38.0 (d, J = 5.5 Hz), 36.0, 33.9 (d, J = 2.9 Hz), 31.5, 30.5 (d, J = 5.3 Hz), 30.0, 29.8, 26.3 (d, J = 5.3 Hz), 25.8 (d, J = 10.7 Hz), 21.7, 13.9; HRMS (ESI-TOF): calcd. for $C_{34}H_{35}O_3$ $[M + H]^+$ 491.2581; found 419.2584.

6. Preparative-scale experiments

Synthesis of **4i** and **4ac** on a gram-scale (**Scheme 4**)



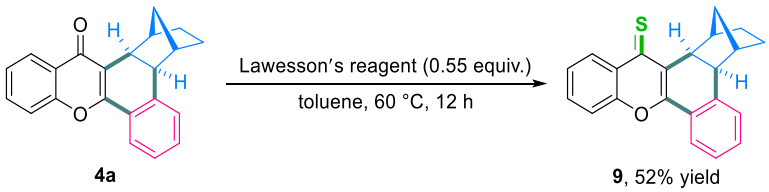
To a 250 mL flame-dried round bottom flask with a stir bar, **1i** (2.53 g, 7.2 mmol), **2a** (1.36 g, 14.4 mmol), **3a** (4.34 g, 21.6 mmol), $Pd(CH_3CN)_2Cl_2$ (186.8 mg, 0.7 mmol), DPEphos (775.5 mg, 1.4 mmol), Cs_2CO_3 (4.69 g, 14.4 mmol), and *o*-xylene (72 mL) were added. Then, the reaction tube was evacuated and backfilled with argon for three times, and the mixture was stirred at 140 ℃ for 7 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 = 20:1 ~ 5:1) to afford the desired product **4i** (1.10 g, 39% yield).



To a 250 mL flame-dried round bottom flask with a stir bar, **1a** (1.96 g, 7.2 mmol), **2a** (1.36 g, 14.4 mmol), **3f** (6.05 g, 21.6 mmol), $Pd(CH_3CN)_2Cl_2$ (186.8 mg, 0.7 mmol), DPEphos (775.5 mg, 1.4 mmol), Cs_2CO_3 (4.69 g, 14.4 mmol), and *o*-xylene (72 mL) were added. Then, the reaction tube was evacuated and backfilled with argon for three times, and the mixture was stirred at 140 ℃ for 7 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 = 20:1 ~ 5:1) to afford the desired product **4ac** (1.40 g, 50% yield).

7. Transformation of 4a into 9

Synthesis of **9** from **4a** (**Scheme 5**)

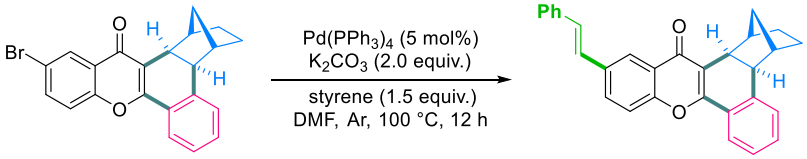


4a **9**, 52% yield

To a 4 mL dried vial with a stir bar, **4a** (62.9 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 **9** (34.6 mg, 52% yield).[6] Green solid, mp 221.5 – 223.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (dd, J = 8.2, 1.4 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.66 (ddd, J = 8.6, 7.2, 1.6 Hz, 1H), 7.54 (dd, J = 8.2, 0.8 Hz, 1H), 7.44 (td, J = 7.6, 1.2 Hz, 1H), 7.39 (ddd, J = 8.2, 7.2, 1.2 Hz, 1H), 7.31 (t, J = 7.8 Hz, 2H), 3.78 (d, J = 10.2 Hz, 1H), 3.33 (d, J = 10.2 Hz, 1H), 2.59 (s, 1H), 2.42 (d, J = 3.4 Hz, 1H), 1.84 – 1.72 (m, 2H), 1.71 – 1.62 (m, 2H), 1.31 (d, J = 10.2 Hz, 1H), 1.11 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 150.7, 150.1, 142.4, 133.1, 132.1, 130.7, 129.5, 129.3, 128.0, 126.9, 126.8, 125.9, 124.30, 118.2, 49.3, 46.3, 44.9, 43.9, 34.2, 30.9, 29.7; HRMS (ESI-TOF): calcd. for $C_{22}H_{19}OS$ $[M + H]^+$ 331.1151; found 331.1151.

8. Transformation of 4i into 10, 11, 12 and 13

8.1 Synthesis of **10** from **4i** (**Scheme 5**)

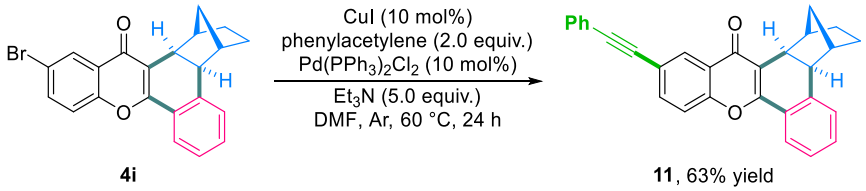


4i **10**, 75% yield

To a 4.0 mL flame-dried vial with a stir bar, **4i** (78.6 mg, 0.2 mmol), styrene (34.3 μL, 0.3 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol), K_2CO_3 (55.3 mg, 0.4 mmol), and DMF (2.0 mL) were added. The reaction vial was evacuated and backfilled with argon for three times, and the mixture was stirred at 100 ˚C for 12 h. After completed of the reaction, the reaction solution was extracted with ethyl acetate. The organic phase was separated, washed with water (3 × 10 mL), and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed by concentration. The residue was subjected to flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 – 3:1) to afford the

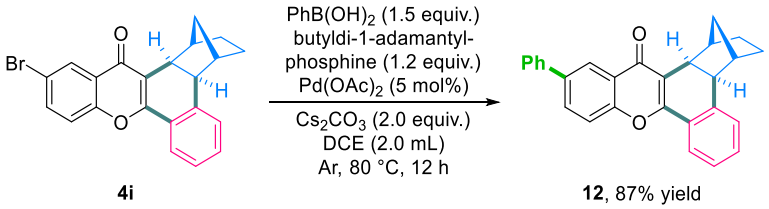
product **10** (62.2 mg, 75% yield).[7] Yellow solid, mp 211.4 – 212.6 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.94 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.52 (d, J = 7.6 Hz, 2H), 7.46 (d, J = 8.8 Hz, 1H), 7.37 (t, J = 7.4 Hz, 3H), 7.27 (q, J = 7.4 Hz, 3H), 7.19 – 7.10 (m, 2H), 3.30 (d, J = 10.2 Hz, 1H), 3.23 (d, J = 10.2 Hz, 1H), 2.52 (s, 1H), 2.36 (s, 1H), 1.81 – 1.60 (m, 4H), 1.37 (d, J = 10.2 Hz, 1H), 1.13 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 156.5, 154.8, 141.6, 137.0, 134.1, 131.4, 131.0, 129.8, 129.6, 128.8, 128.0, 127.1, 126.8, 126.7, 126.5, 123.8, 123.3, 123.2, 118.3, 117.1, 49.3, 45.6, 44.7, 40.2, 34.0, 30.5, 30.0; HRMS (ESI-TOF): calcd. for $C_{30}H_{25}O_2$ $[M + H]^+$ 417.1849; found 417.1847.

8.2 Synthesis of **11** from **4i** (**Scheme 5**)



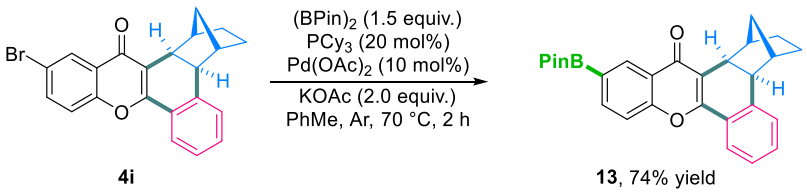
To a 4 mL flame-dried vial with a stir bar, **4i** (78.6 mg, 0.2 mmol), phenylacetylene (40.8 mg, 0.4 mmol), CuI (4.0 mg, 0.02 mmol), $Pd(PPh_3)_2Cl_2$ (14.0 mg, 0.02 mmol), triethylamine (101.2 mg, 1 mmol), and DMF (2.0 mL) were added under argon atmosphere at 60 ℃ for 24 h. After the completion of 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 (petroleum ether/ethyl acetate = 20:1 – 5:1) to afford the desired product **11** (52.5 mg, 63% yield).[8] White solid, mp 199.7 – 201.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 2.0 Hz, 1H), 7.92 (dd, J = 7.4, 0.4 Hz, 1H), 7.74 (dd, J = 8.6, 2.2 Hz, 1H), 7.55 (dd, J = 6.6, 3.2 Hz, 2H), 7.46 (d, J = 8.6 Hz, 1H), 7.42 – 7.32 (m, 4H), 7.26 (q, J = 7.8 Hz, 2H), 3.25 (q, J = 10.4 Hz, 2H), 2.51 (s, 1H), 2.36 (s, 1H), 1.78 – 1.67 (m, 3H), 1.66 – 1.59 (m, 1H), 1.37 (d, J = 11.6 Hz, 1H), 1.13 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 156.6, 154.8, 141.6, 136.0, 131.8, 131.6, 129.6, 129.0, 128.6, 128.5, 126.5, 126.5, 123.7, 123.2, 123.0, 120.1, 118.2, 117.3, 90.1, 88.3, 49.3, 45.6, 44.7, 40.1, 34.0, 30.5, 30.0; HRMS (ESI-TOF): calcd. for $C_{30}H_{23}O_2$ $[M + H]^+$ 415.1693; found 415.1699.

8.3 Synthesis of **12** from **4i** (**Scheme 5**)



To a 4 mL flame-dried vial with a stir bar, **4i** (78.6 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 (petroleum ether/ethyl acetate = 20:1 – 5:1)to afford the desired product **12** (68.2 mg, 87% yield).[10] White solid, mp 158.9 – 160.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 2.4 Hz, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.85 (dd, J = 8.8, 2.4 Hz, 1H), 7.65 (dd, J = 8.0, 0.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.37 (td, J = 7.4, 1.0 Hz, 2H), 7.26 (q, J = 7.8 Hz, 2H), 3.30 (d, J = 10.2 Hz, 1H), 3.23 (d, J = 10.2 Hz, 1H), 2.53 (s, 1H), 2.36 (s, 1H), 1.79 – 1.67 (m, 3H), 1.67 – 1.60 (m, 1H), 1.38 (d, J = 10.2 Hz, 1H), 1.13 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 156.5, 154.8, 141.6, 139.6, 137.7, 132.0, 131.4, 129.5, 129.0, 127.7, 127.1, 126.7, 126.4, 123.8, 123.4, 123.2, 118.3, 117.1, 49.2, 45.6, 44.7, 40.1, 33.9, 30.5, 23.0; HRMS (ESI-TOF): calcd. for $C_{28}H_{23}O_2$ $[M + H]^+$ 391.1693; found 391.1697.

8.4 Synthesis of **13** from **4i** (**Scheme 5**)

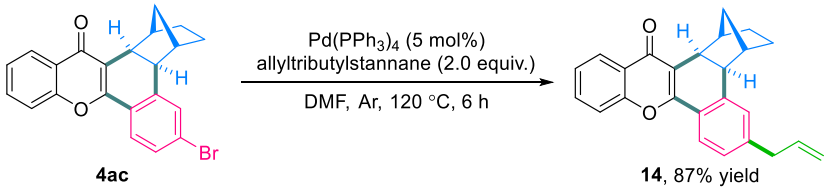


To a 4 mL flame-dried vial with a magnetic stir bar, **4i** (78.6 mg, 0.2 mmol), $(BPin)_2$ (76.2 mg, 0.3 mmol), KOAc (40.0 mg, 0.4 mmol), PCy_3 (11.3 mg, 20 mol%), $Pd(OAc)_2$ (4.5 mg, 10 mol%), and PhMe (2.0 mL) were added under argon atmosphere, and the mixture was stirred at 70 ˚C for 2 h. After the completion of the reaction, it was purified by flash column chromatography on silica

gel (petroleum ether/ethyl acetate = 20:1 – 2:1) to afford the desired product **13** (65.1 mg, 74% yield).[10] White solid, mp 186.7 – 187.3 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 1.4 Hz, 1H), 8.04 (dd, J = 8.4, 1.6 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.38 (td, J = 7.6, 1.4 Hz, 1H), 7.27 (t, J = 7.6 Hz, 2H), 3.32 (d, J = 10.2 Hz, 1H), 3.26 (d, J = 10.2 Hz, 1H), 2.49 (s, 1H), 2.36 (s, 1H), 1.78 – 1.59 (m, 4H), 1.43 – 1.29 (m, 13H), 1.12 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 157.4, 156.4, 141.7, 139.0, 133.5, 131.4, 129.6, 126.8, 126.5, 123.3, 123.2, 117.5, 117.2, 84.3, 49.4, 45.6, 44.7, 40.1, 34.0, 30.5, 30.0, 25.1, 25.0; HRMS (ESI-TOF): calcd. for $C_{28}H_{30}BO_4$ $[M + H]^+$ 441.2232; found 441.2231.

9. Transformation of 4ac into 14

Synthesis of **14** from **4ac** (**Scheme 5**)



To a 4 mL flame-dried vial with a magnetic stir bar, **4ae** (78.6 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.6 mg, 5 mol%), allyltributylstannane (124.0 µL, 0.4 mmol), and DMF (2.0 mL) were added under argon atmosphere, and the mixture was stirred at 120 ˚C for 6 h. After the completion of the reaction, it was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1 – 4:1) to afford the desired product **14** (61.7 mg, 87% yield).[11] White solid, mp 128.4 – 129.0 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 7.4 Hz, 1H), 7.76 (s, 1H), 7.65 – 7.57 (m, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.18 (q, J = 8.4 Hz, 2H), 6.00 (ddt, J = 16.8, 10.2, 6.8 Hz, 1H), 5.18 – 5.08 (m, 2H), 3.43 (d, J = 6.8 Hz, 2H), 3.26 (d, J = 10.2 Hz, 1H), 3.19 (d, J = 10.2 Hz, 1H), 2.49 (s, 1H), 2.33 (s, 1H), 1.74 – 1.57 (m, 4H), 1.34 (d, J = 10.2 Hz, 1H), 1.10 (d, J = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 156.6, 155.3, 139.4, 138.2, 137.1, 133.1, 131.8, 129.6, 126.8, 125.6, 124.6, 123.7, 123.2, 117.9, 117.2, 116.3, 49.1, 45.2, 44.6, 40.1, 39.9, 33.9, 30.5, 29.9; HRMS (ESI-TOF): calcd. for $C_{25}H_{23}O_2$ $[M + H]^+$ 355.1693; found 355.1691.

10. References

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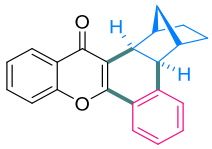
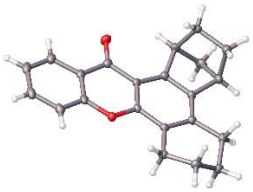
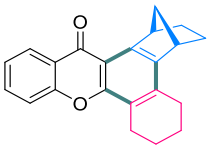
11. X-ray crystal data for 4a, 6a', 6b, 6b', 6c'



4a (CCDC: 2262984)

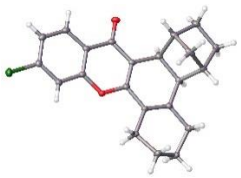
Identification code	**4a**
Empirical formula	$C_{22}H_{18}O_2$
Formula weight	314.36
Temperature/K	200.00(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.1431(2)
b/Å	13.4252(4)
c/Å	18.6599(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1538.93(8)
Z	4
ρ_{calc}g/cm^3	1.357
μ/mm^{-1}	0.675
F(000)	664.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	8.114 to 143.124
Index ranges	$-7 \le h \le 5$, $-15 \le k \le 16$, $-22 \le l \le 20$
Reflections collected	7093
Independent reflections	2940 [R_{int} = 0.0286, R_{sigma} = 0.0326]
Data/restraints/parameters	2940/0/218
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0312, wR_2 = 0.0801
Final R indexes [all data]	R_1 = 0.0326, wR_2 = 0.0820
Largest diff. peak/hole / e Å^{-3}	0.17/-0.14
Flack parameter	-0.09(12)

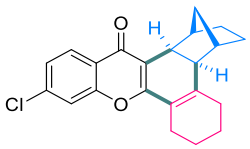




6a' (CCDC: 2262985)

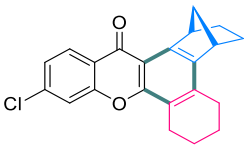
Identification code	**6a'**
Empirical formula	$C_{22}H_{20}O_2$
Formula weight	316.38
Temperature/K	149.99(10)
Crystal system	tetragonal
Space group	$P4_2/n$
a/Å	18.4553(2)
b/Å	18.4553(2)
c/Å	8.9917(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3062.55(10)
Z	8
ρ_{calc}g/cm^3	1.372
μ/mm^{-1}	0.679
F(000)	1344.0
Crystal size/mm^3	0.13 × 0.11 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.774 to 143.274
Index ranges	-22 ≤ h ≤ 22, -20 ≤ k ≤ 21, -10 ≤ l ≤ 8
Reflections collected	8576
Independent reflections	2933 [R_{int} = 0.0192, R_{sigma} = 0.0209]
Data/restraints/parameters	2933/0/217
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0466, wR_2 = 0.1183
Final R indexes [all data]	R_1 = 0.0494, wR_2 = 0.1204
Largest diff. peak/hole / e Å^{-3}	0.48/-0.23





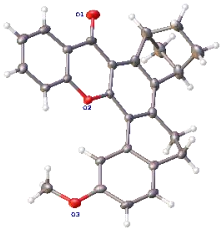
6b (CCDC: 2262994)

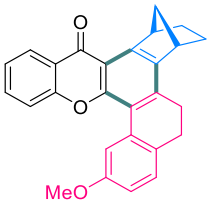
Identification code	**6b**
Empirical formula	$C_{22}H_{21}ClO_2$
Formula weight	352.84
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.6148(3)
b/Å	9.7230(2)
c/Å	13.8502(4)
α/°	90
β/°	113.786(3)
γ/°	90
Volume/Å^3	1677.71(8)
Z	4
ρ_{calc}g/cm^3	1.397
μ/mm^{-1}	2.108
F(000)	744.0
Crystal size/mm^3	0.15 × 0.12 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.686 to 147.554
Index ranges	$-16 \le h \le 12$, $-11 \le k \le 10$, $-16 \le l \le 17$
Reflections collected	6070
Independent reflections	3289 [R_{int} = 0.0199, R_{sigma} = 0.0269]
Data/restraints/parameters	3289/0/227
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0341, wR_2 = 0.0927
Final R indexes [all data]	R_1 = 0.0371, wR_2 = 0.0959
Largest diff. peak/hole / e Å^{-3}	0.22/-0.28



6b' (CCDC: 2262996)

Identification code	**6b'**
Empirical formula	$C_{22}H_{19}ClO_2$
Formula weight	350.82
Temperature/K	200.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.8200(9)
b/Å	8.9290(8)
c/Å	17.3043(14)
α/°	90
β/°	99.806(7)
γ/°	90
Volume/Å^3	1647.4(2)
Z	4
ρ_{calc}g/cm^3	1.414
μ/mm^{-1}	0.245
F(000)	736.0
Crystal size/mm^3	0.15 × 0.12 × 0.09
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	4.146 to 49.998
Index ranges	$-12 \le h \le 9$, $-8 \le k \le 10$, $-20 \le l \le 20$
Reflections collected	6835
Independent reflections	2895 [R_{int} = 0.0219, R_{sigma} = 0.0327]
Data/restraints/parameters	2895/0/226
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0484, wR_2 = 0.1081
Final R indexes [all data]	R_1 = 0.0577, wR_2 = 0.1146
Largest diff. peak/hole / e Å^{-3}	0.69/-0.28

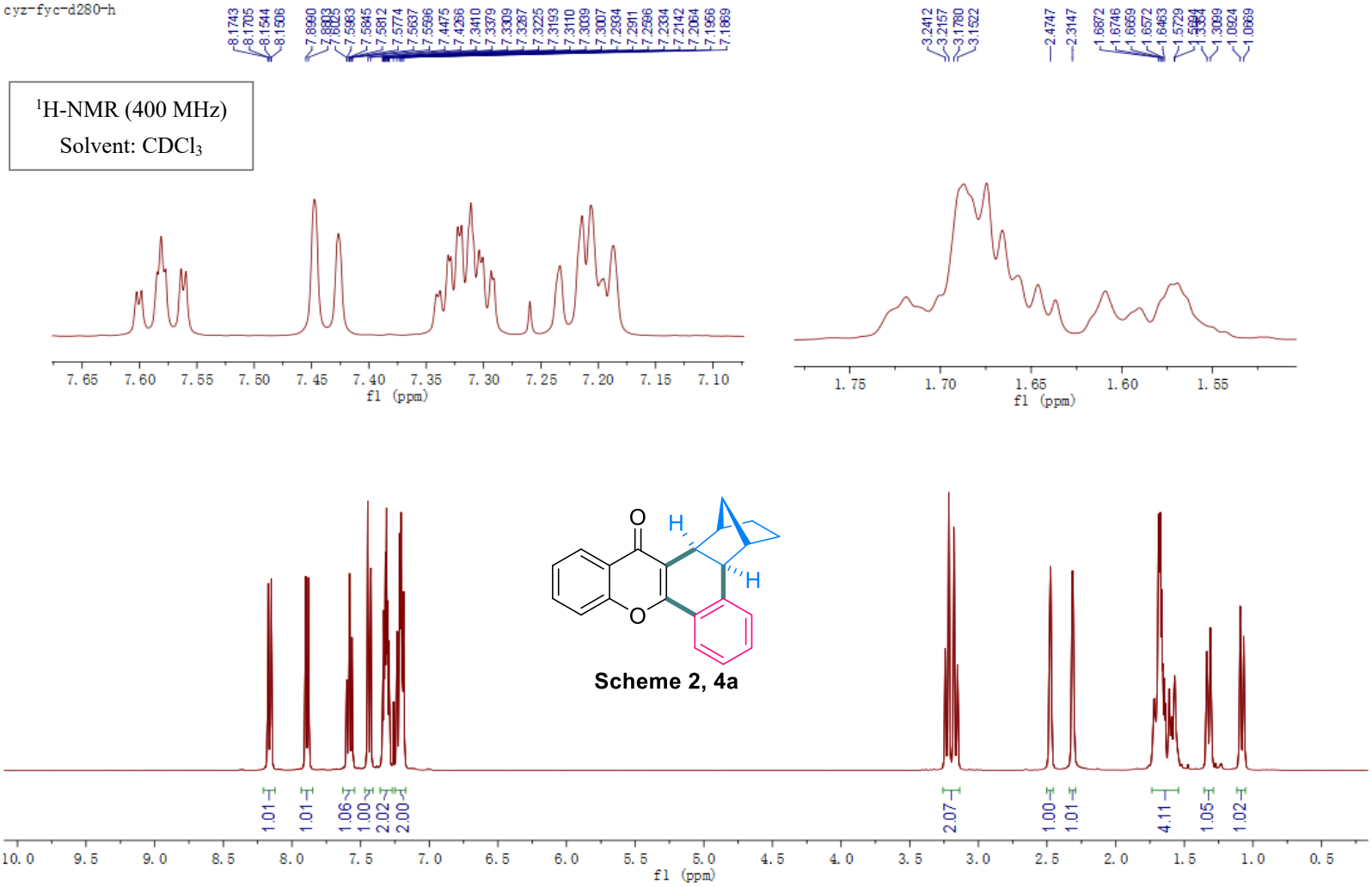


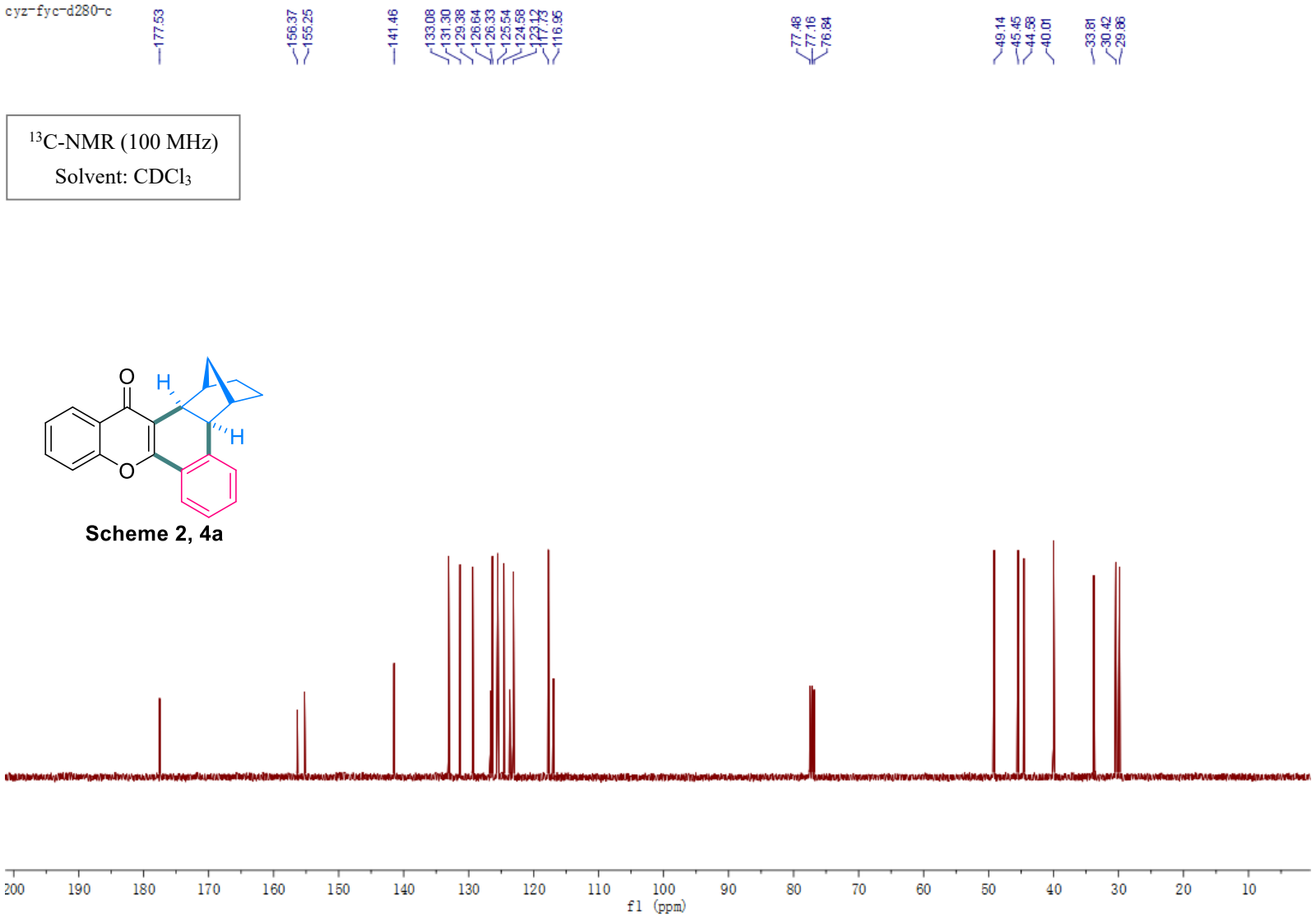


6c' (CCDC: 2262997)

Identification code	**6c'**
Empirical formula	$C_{27}H_{22}O_3$
Formula weight	394.44
Temperature/K	170.00(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	42.685(2)
b/Å	16.6789(10)
c/Å	22.1208(12)
α/°	90
β/°	94.575(5)
γ/°	90
Volume/Å^3	15698.6(15)
Z	32
ρ_{calc}g/cm^3	1.335
μ/mm^{-1}	0.086
F(000)	6656.0
Crystal size/mm^3	0.15 × 0.11 × 0.09
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	3.828 to 49.998
Index ranges	-49 ≤ h ≤ 50, -19 ≤ k ≤ 19, -26 ≤ l ≤ 24
Reflections collected	40112
Independent reflections	13809 [R_{int} = 0.0565, R_{sigma} = 0.0791]
Data/restraints/parameters	13809/7/1085
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0740, wR_2 = 0.1882
Final R indexes [all data]	R_1 = 0.1319, wR_2 = 0.2336
Largest diff. peak/hole / e Å^{-3}	0.44/-0.32

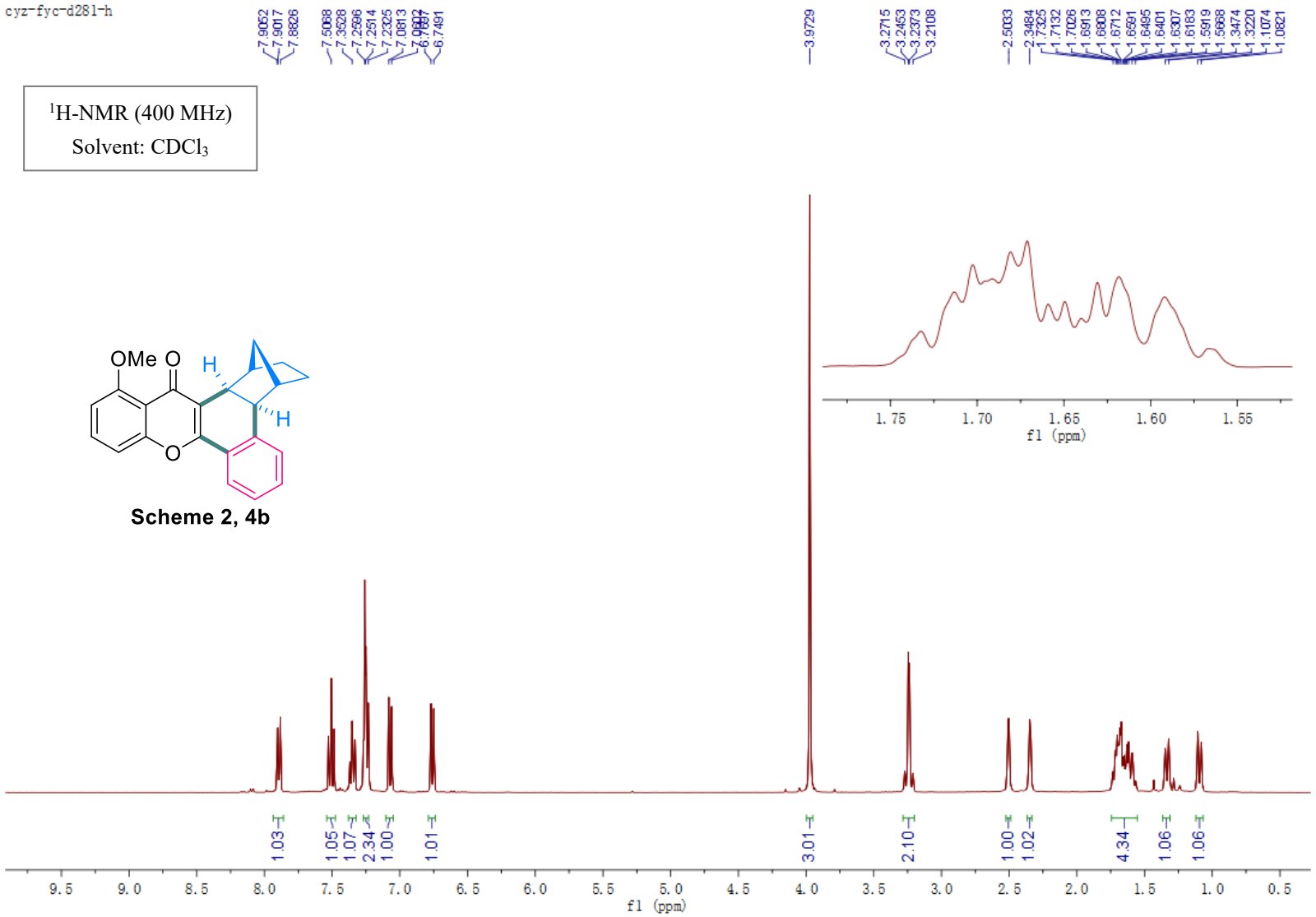
12. ^{1}H and ^{13}C NMR spectra of 4a-ap, 6a(a')-c(c') and 8-14





^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

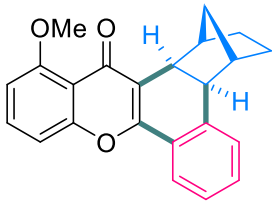
Scheme 2, 4a


cyz-fyc-d281-h
7.9052
7.9017
7.8826
7.5068
7.3528
7.2696
7.2514
7.2325
7.0813
6.7491
3.9729
3.2715
3.2453
3.2373
3.2108
2.5033
2.3484
1.7325
1.7132
1.7026
1.6913
1.6808
1.6712
1.6591
1.6495
1.6401
1.6307
1.6183
1.5919
1.5668
1.3474
1.3220
1.1074
1.0821
[1]H-NMR (400 MHz)
Solvent: CDCl3
OMe
O
H
H
O
Scheme 2, 4b
1.03
1.05
1.07
2.34
1.00
1.01
3.01
2.10
1.00
1.02
4.34
1.06
1.06
f1 (ppm)

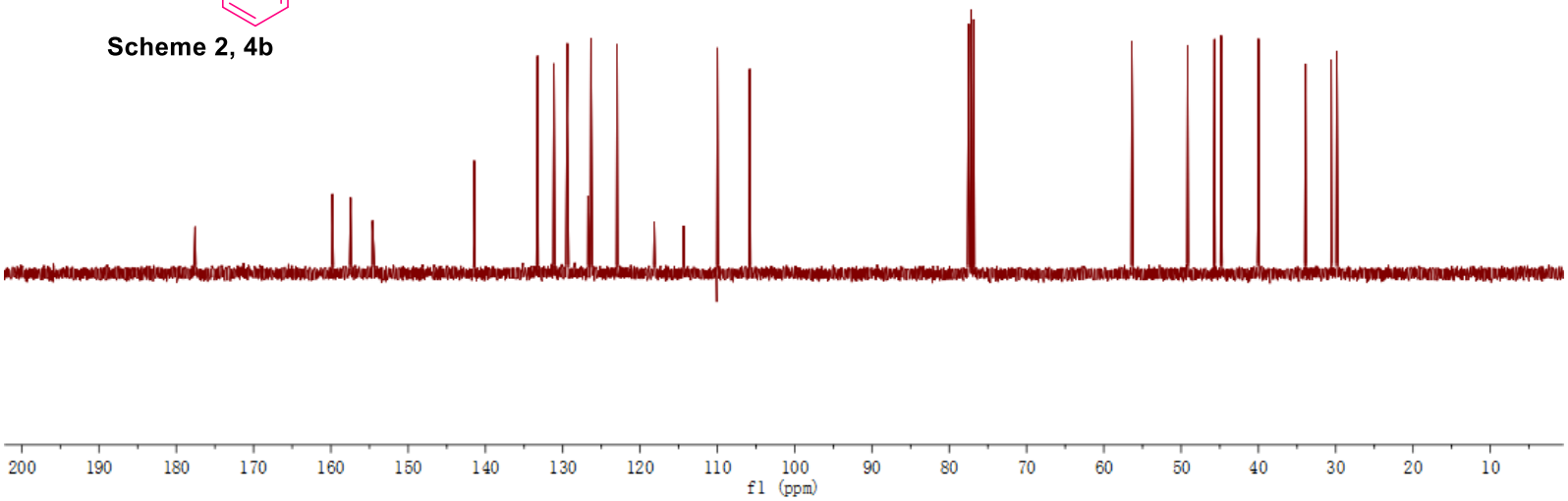
cyz-fyc-d281-c

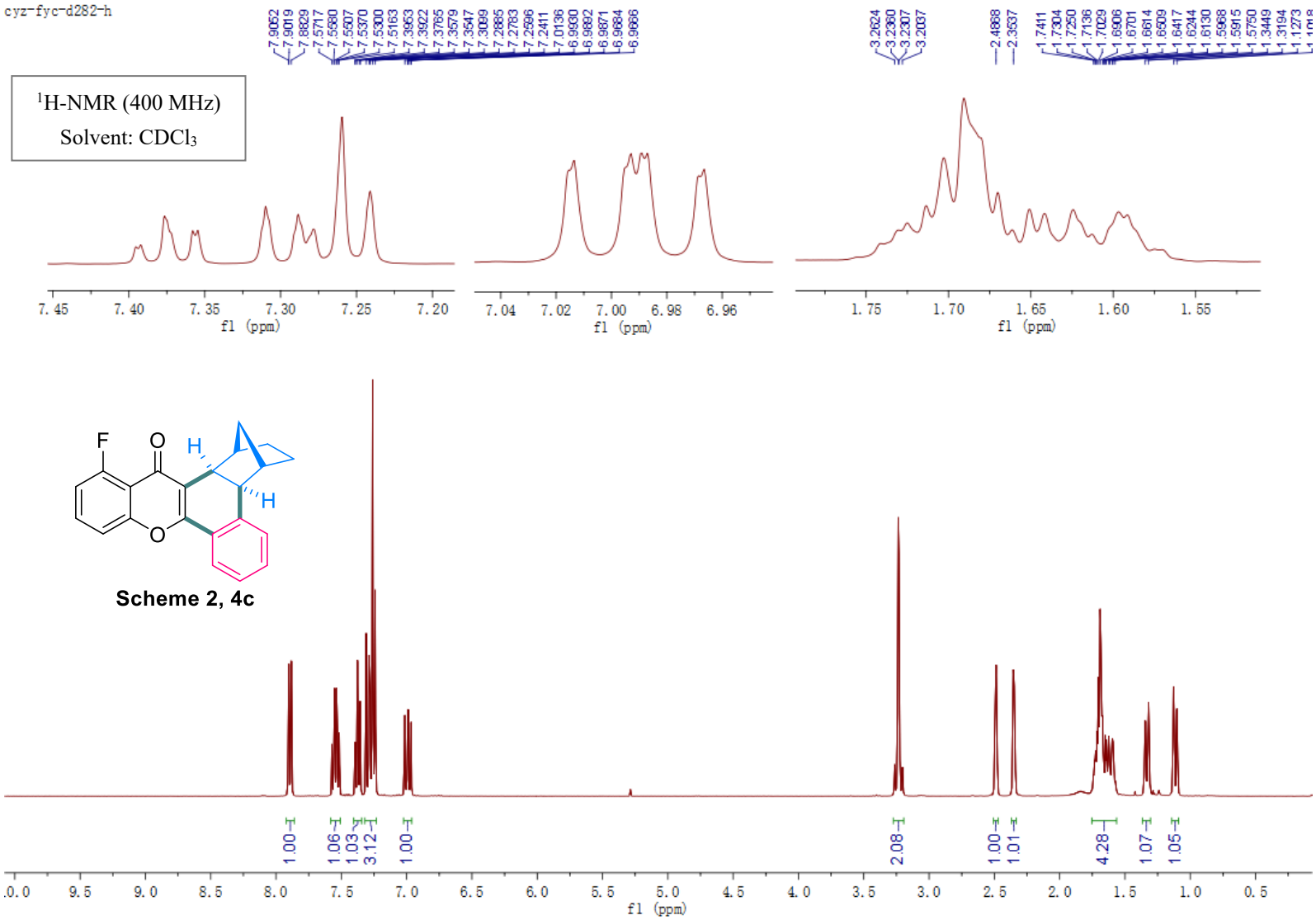
177.56
159.80
157.45
154.60
141.46
133.25
131.14
129.41
126.73
126.35
122.98
118.16
114.37
109.99
105.81
77.48
77.16
76.84
56.38
49.16
45.88
44.62
39.99
33.92
30.58
29.86

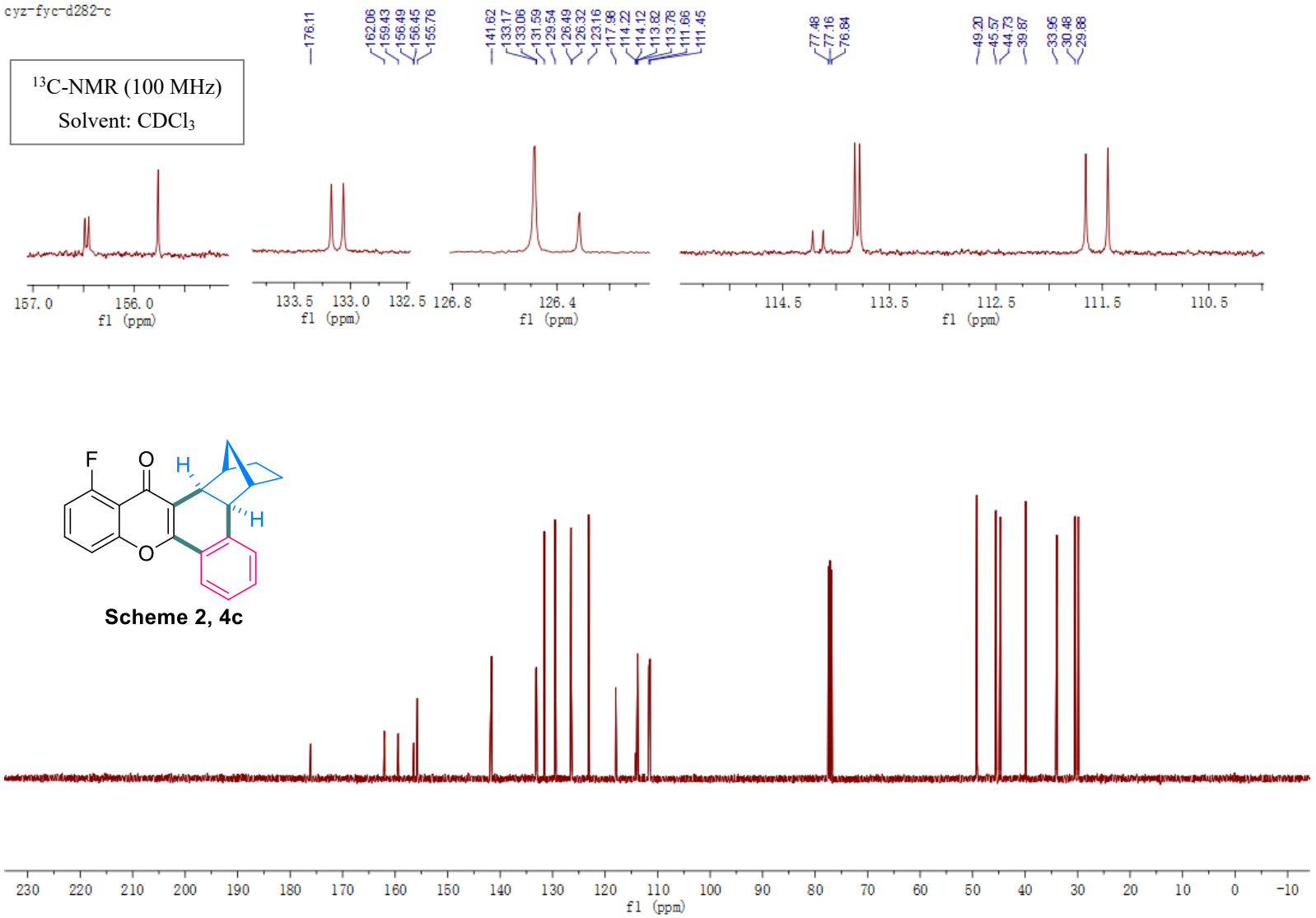
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

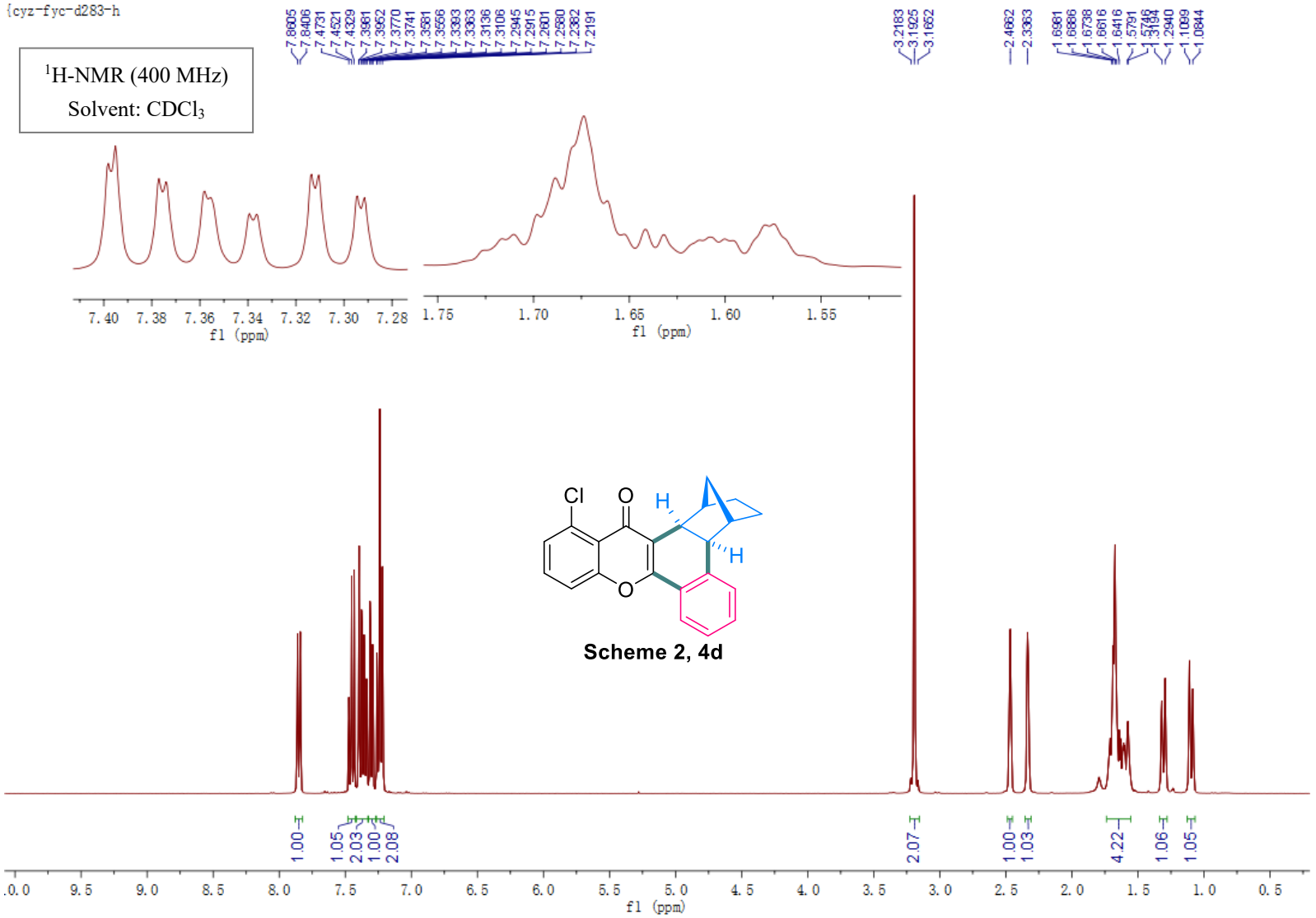


Scheme 2, 4b




cyz-fyc-d282-h
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$
F
O
H
H
O
Scheme 2, 4c
f1 (ppm)

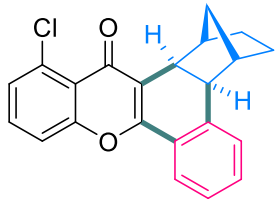

cyz-fyc-d282-c
^{13}C-NMR (100 MHz)
Solvent: CDCl$_3$
176.11
162.06
159.43
156.49
156.45
155.76
141.62
133.17
133.06
131.59
129.54
126.49
126.32
123.16
117.98
114.22
114.12
113.82
113.78
111.66
111.45
77.48
77.16
76.84
49.20
45.57
44.73
39.87
33.95
30.48
29.88
157.0
156.0
f1 (ppm)
133.5
133.0
132.5
126.8
126.4
114.5
113.5
112.5
111.5
110.5
F
O
H
H
O
Scheme 2, 4c
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


{cyz-fyc-d283-h
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$
Cl
O
H
H
O
Scheme 2, 4d
f1 (ppm)

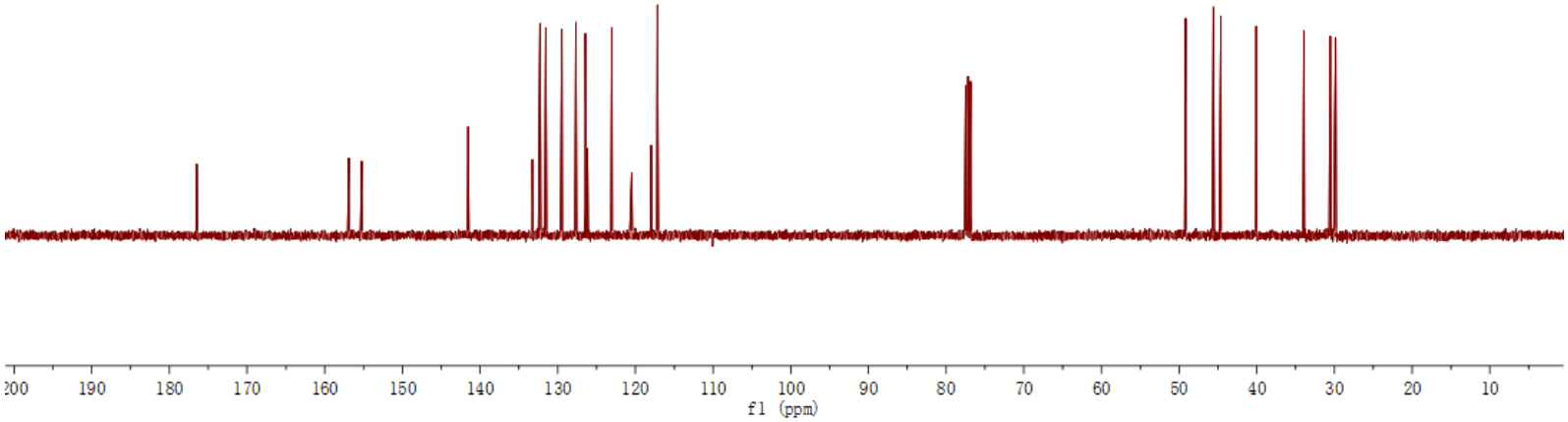
cyz-fyc-d283-c

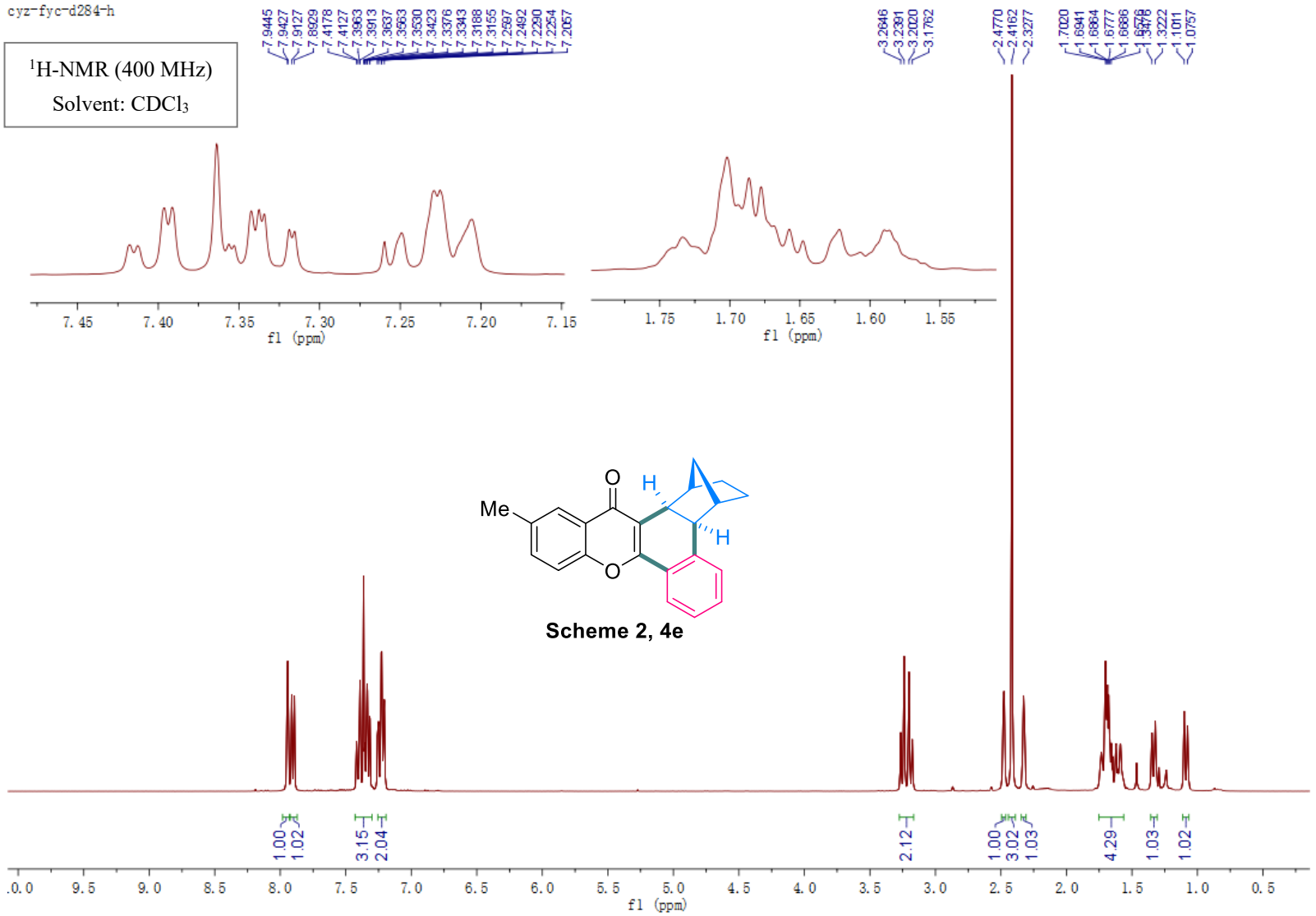
176.49
156.91
155.25
141.54
133.26
132.29
131.54
129.47
127.66
126.43
126.18
123.04
120.46
117.98
117.16
77.48
77.16
76.84
49.17
45.57
44.62
40.06
33.93
30.55
29.85

^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$



Scheme 2, 4d

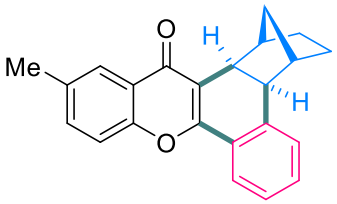



cyz-fyc-d284-h
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$
Me
O
H
H
O
Scheme 2, 4e
f1 (ppm)

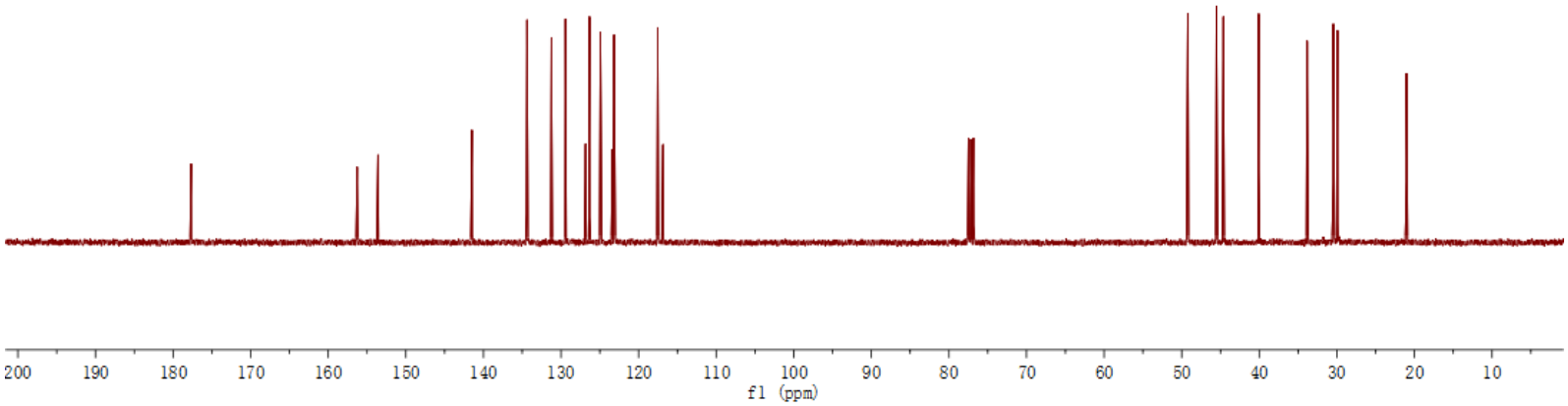
cyz-fyc-d284-c

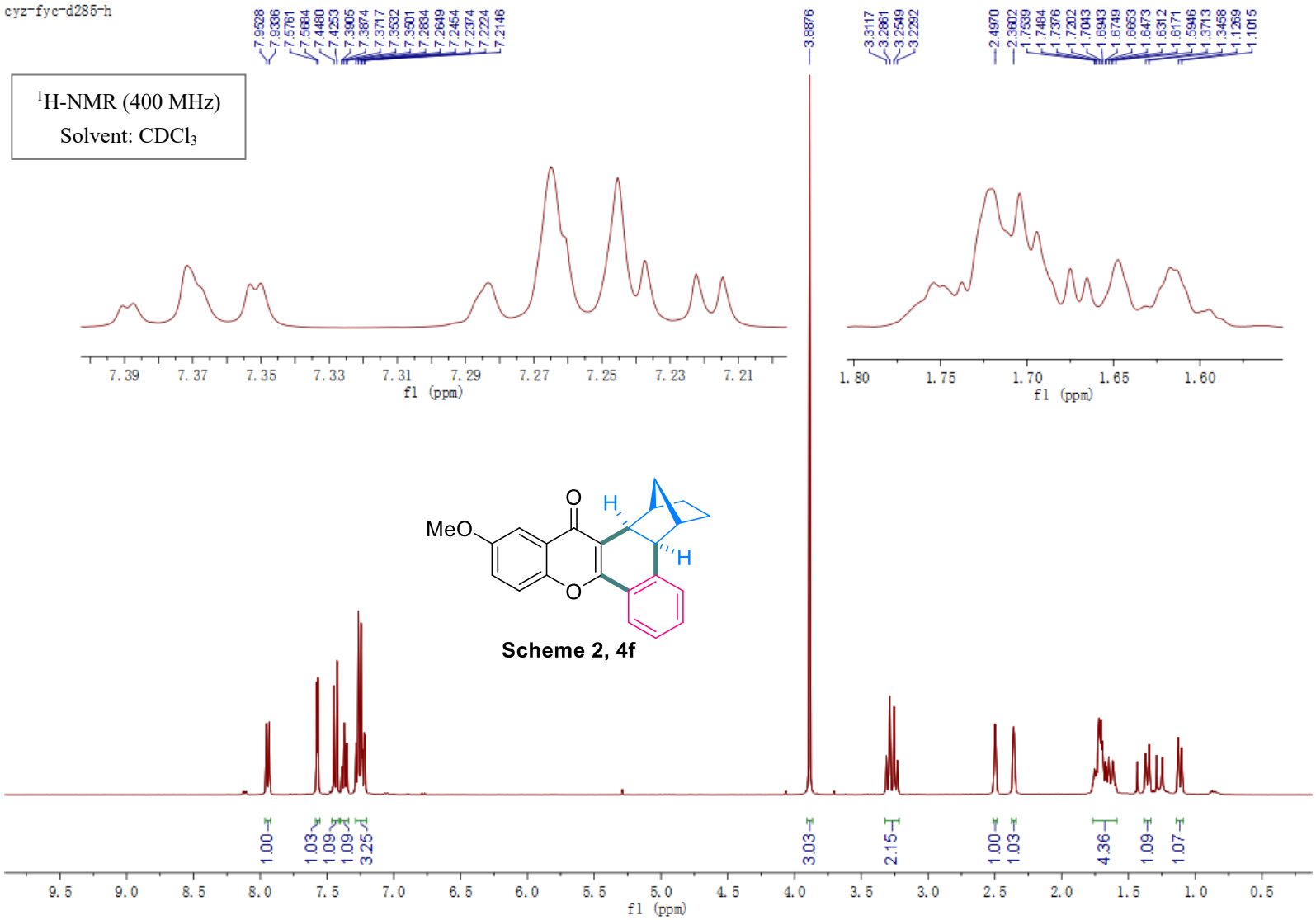
177.68
156.29
153.58
141.49
134.44
134.38
131.24
129.41
126.83
126.34
124.93
123.37
123.15
117.54
116.85
77.48
77.16
76.84
49.21
45.52
44.62
40.07
33.84
30.45
29.93
21.03

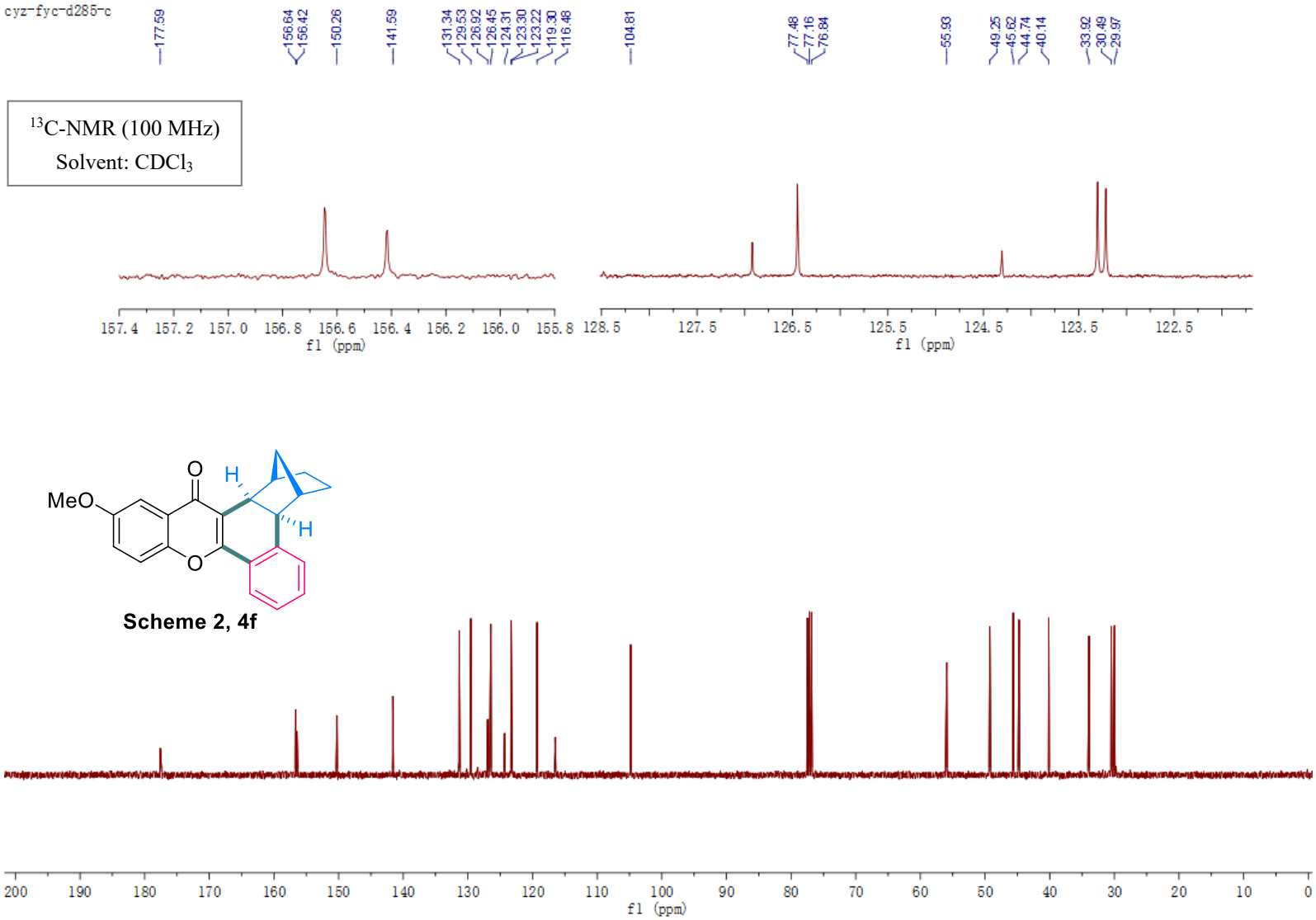
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

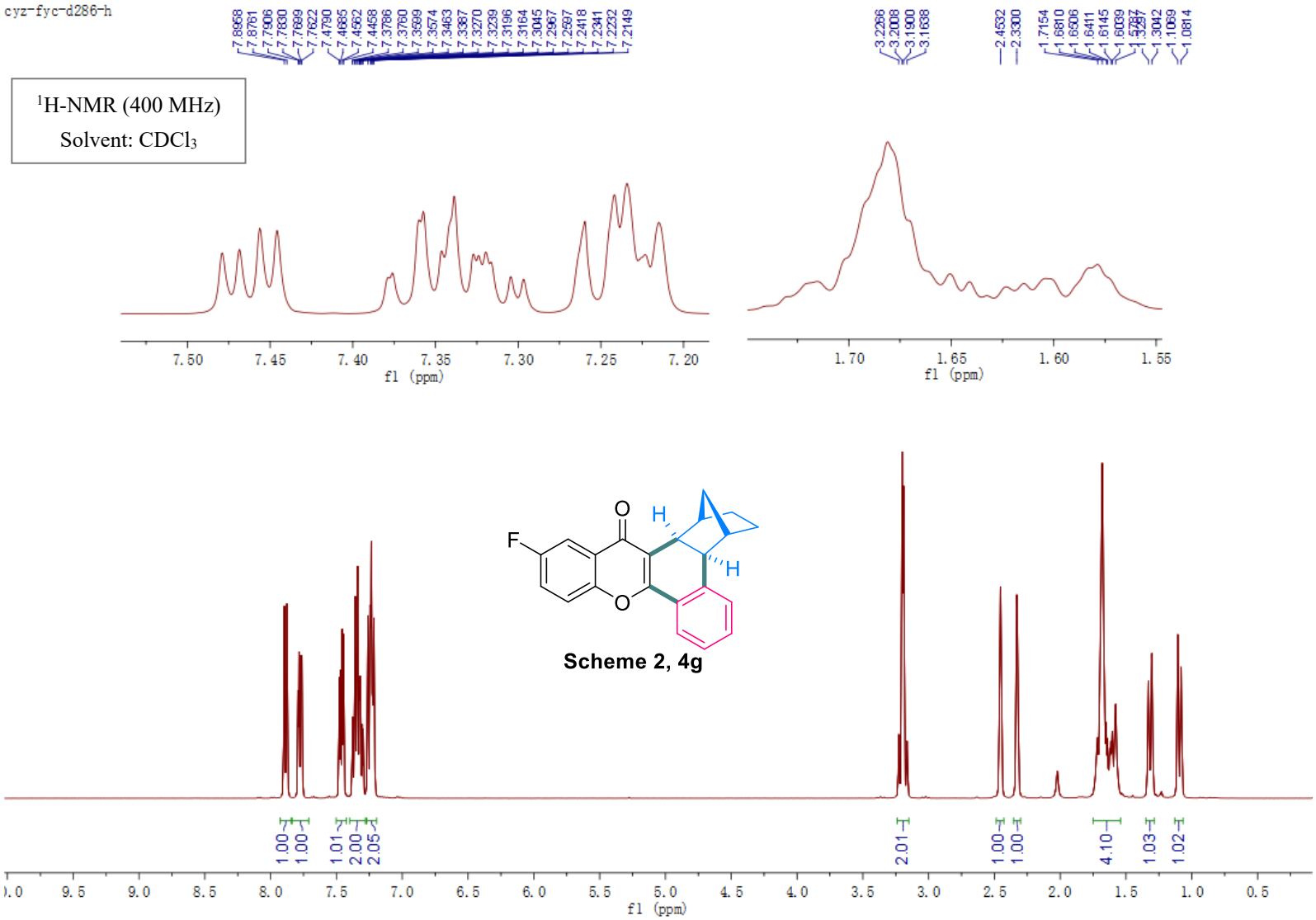


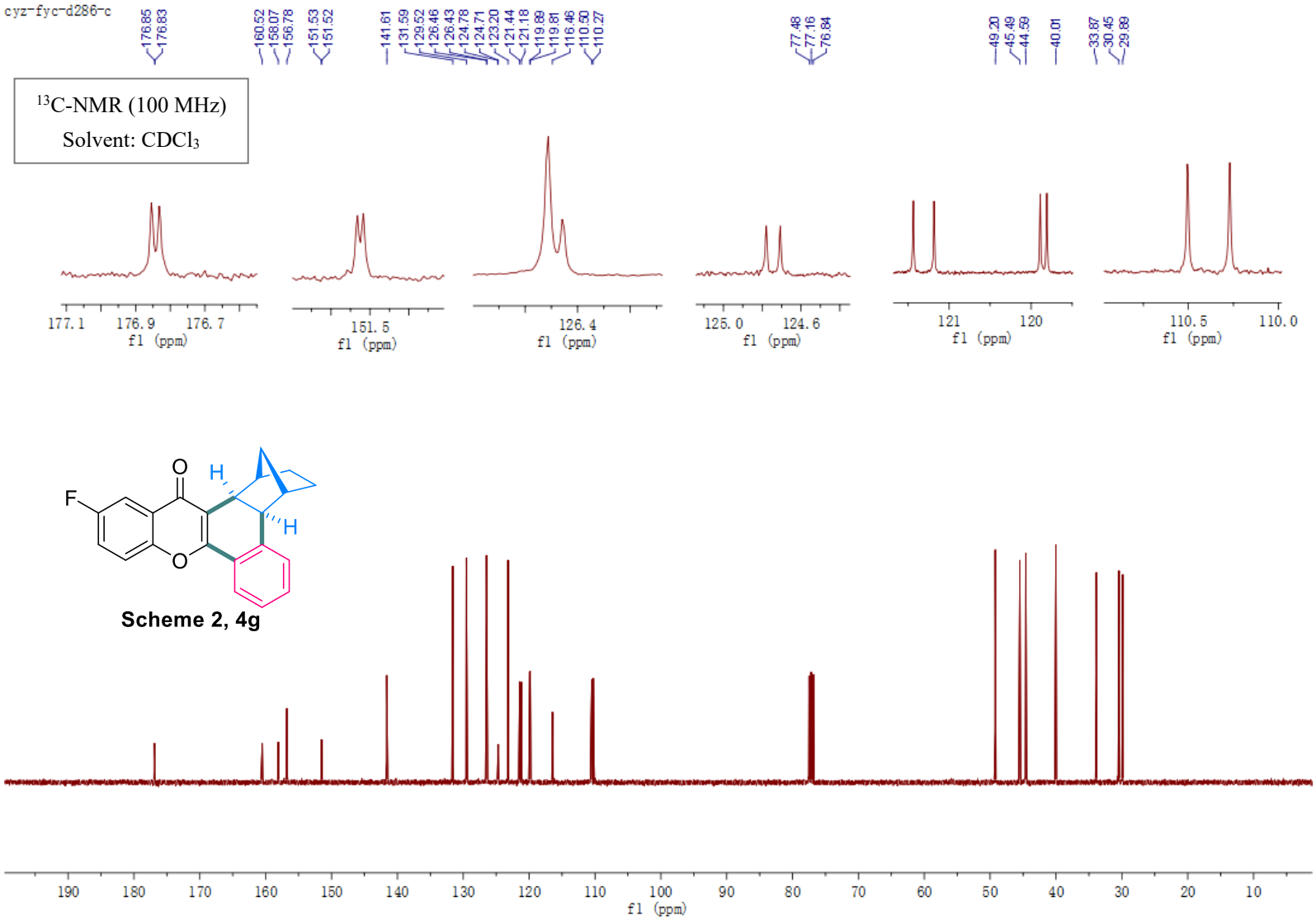
Scheme 2, 4e

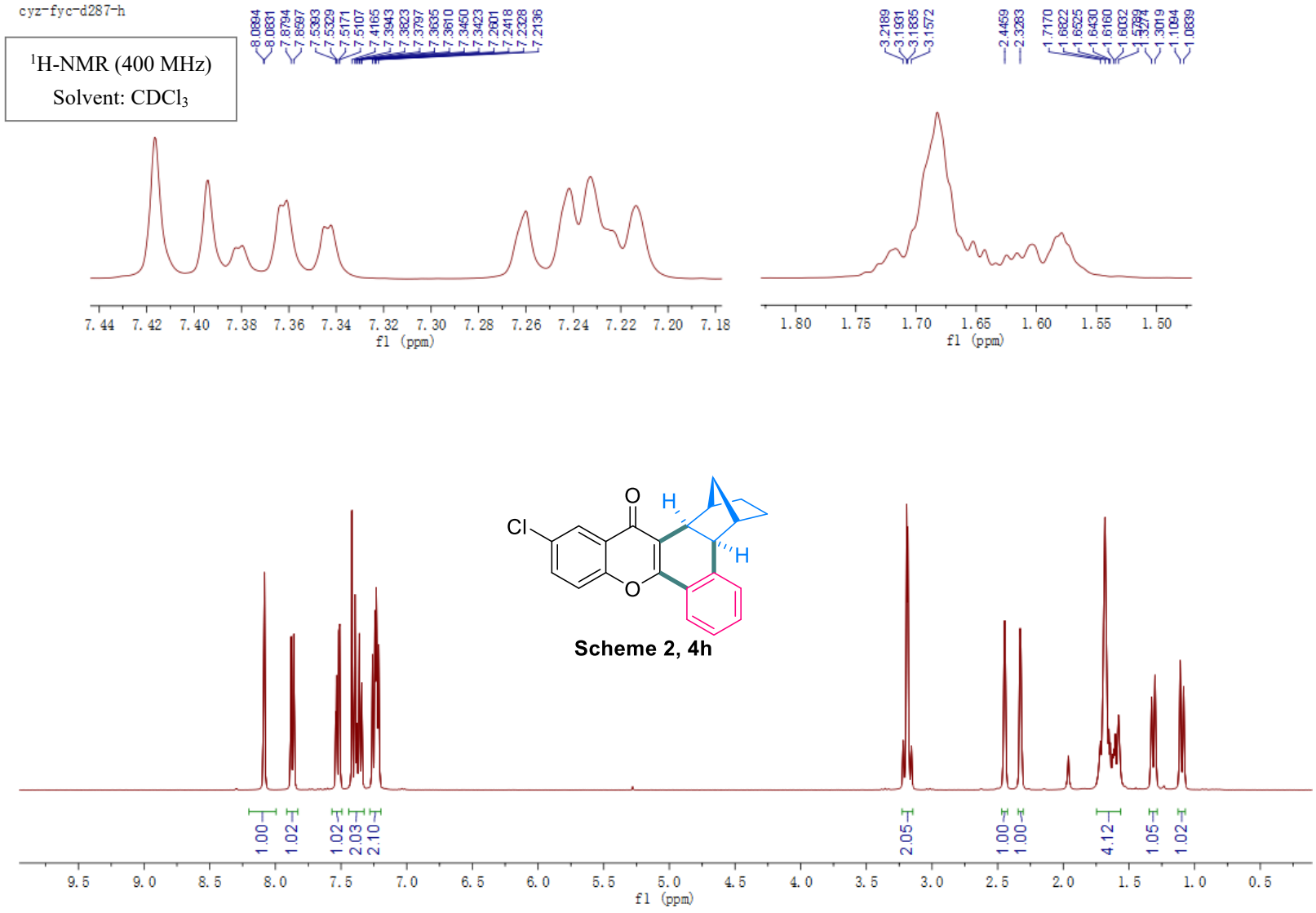


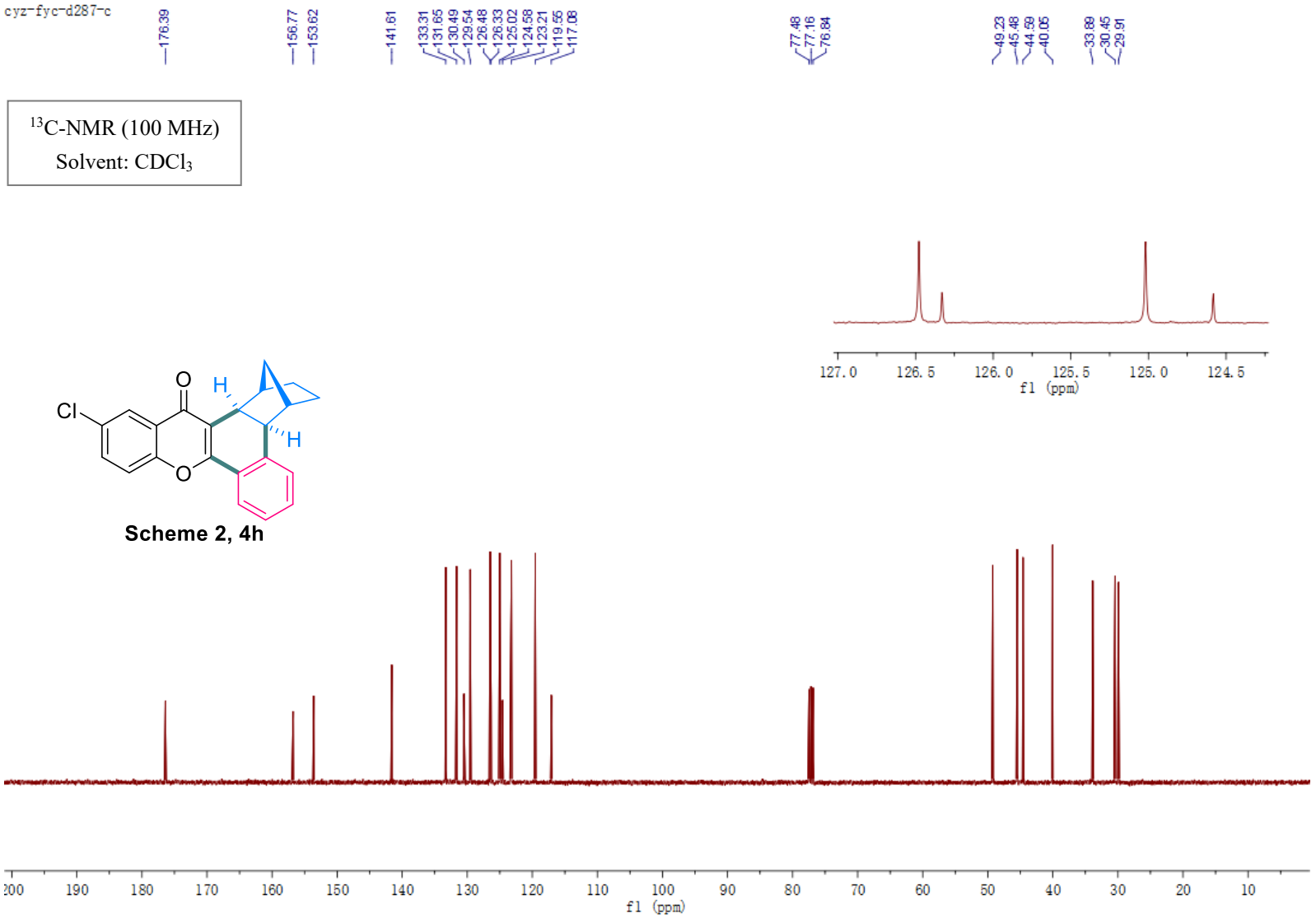

cyz-fyc-d285-h
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$
MeO
O
H
H
O
Scheme 2, 4f
f1 (ppm)

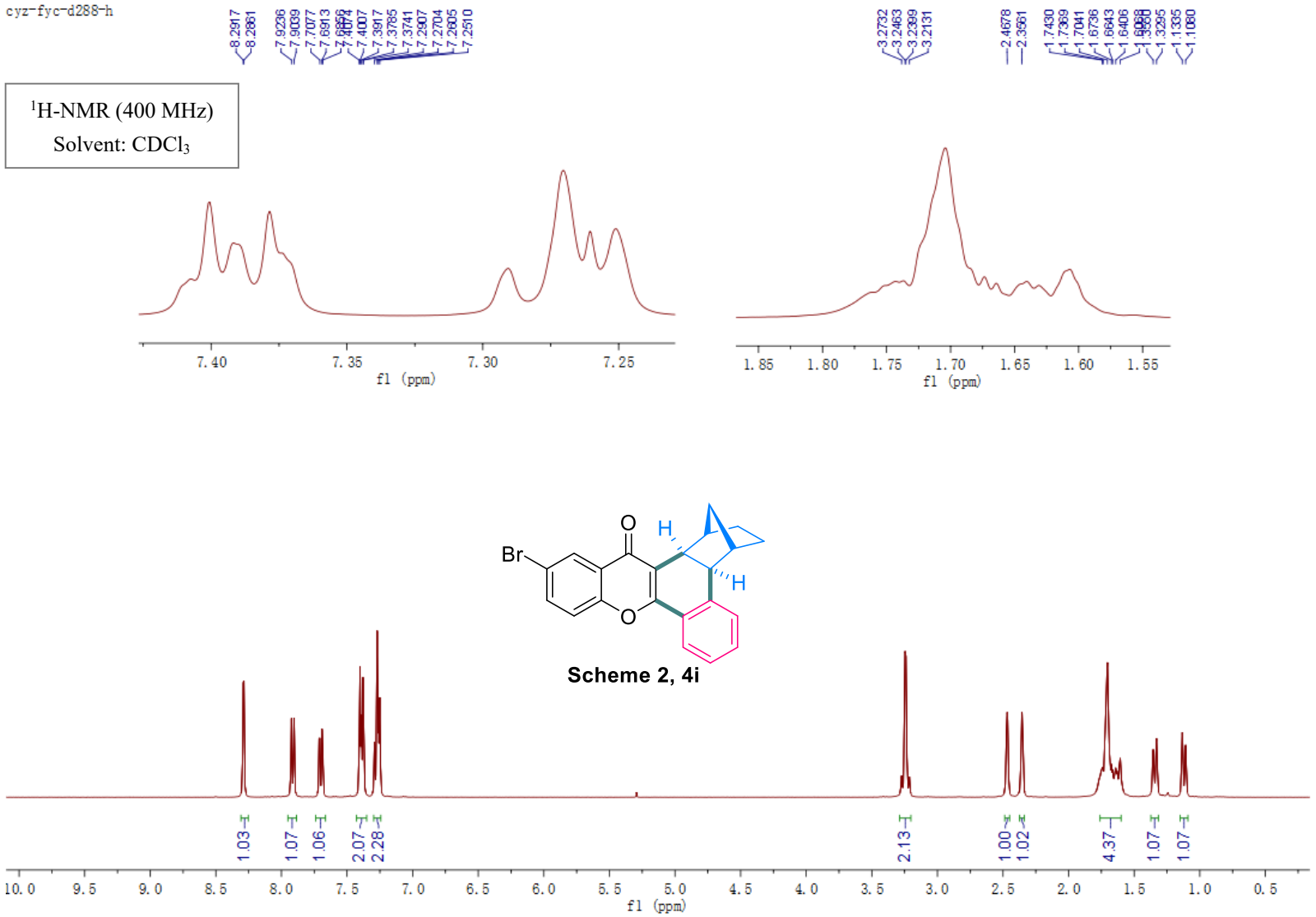

cyz-fyc-d285-c
177.59
156.64
156.42
150.26
141.59
131.34
129.53
126.92
126.45
124.31
123.30
123.22
119.30
116.48
104.81
77.48
77.16
76.84
55.93
49.25
45.62
44.74
40.14
33.92
30.49
29.97
13C-NMR (100 MHz)
Solvent: CDCl3
157.4 157.2 157.0 156.8 156.6 156.4 156.2 156.0 155.8
f1 (ppm)
128.5 127.5 126.5 125.5 124.5 123.5 122.5
f1 (ppm)
MeO
O
H
H
O
Scheme 2, 4f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

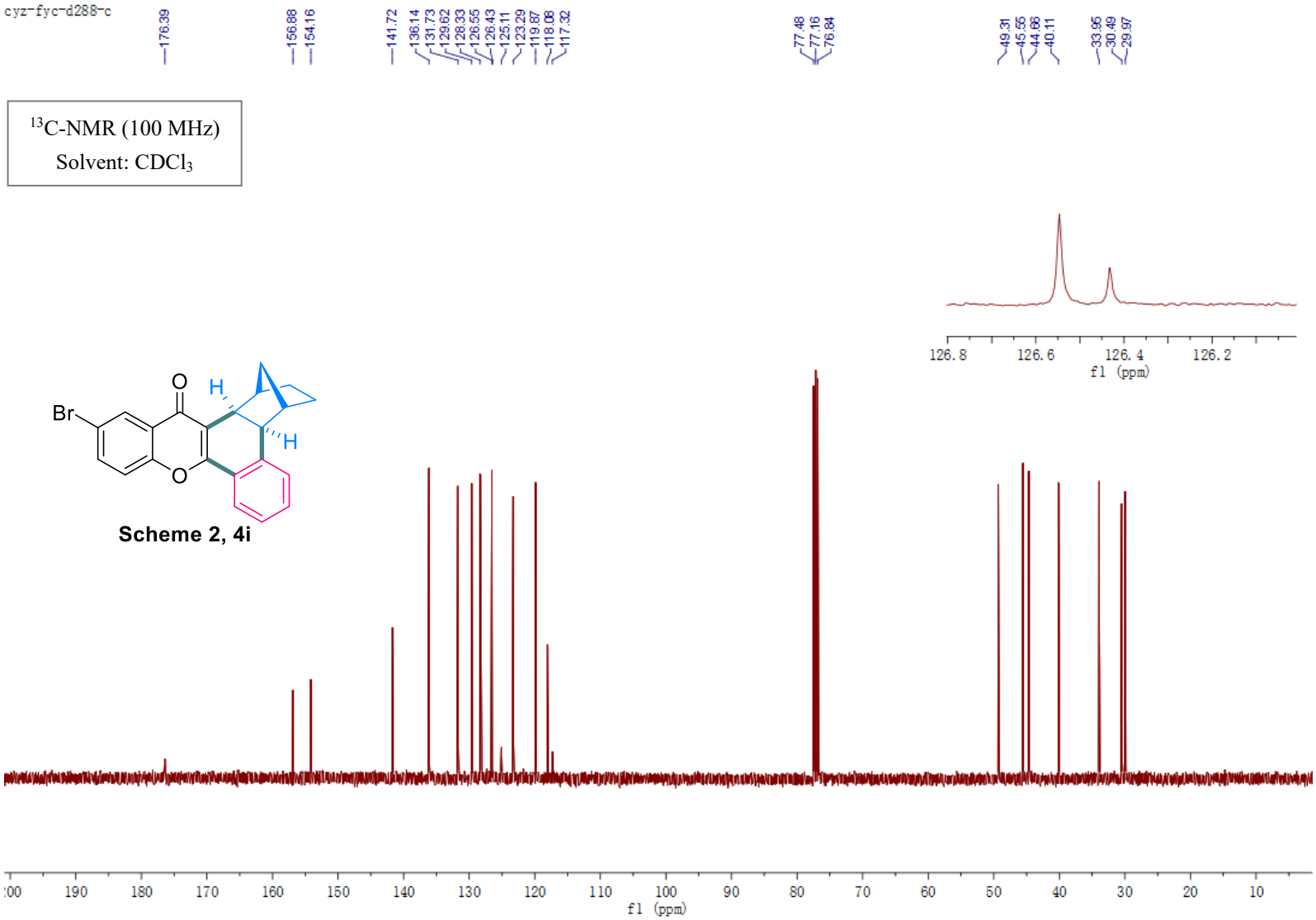

cyz-fyc-d286-h
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$
f1 (ppm)
F
O
H
H
O
Scheme 2, 4g

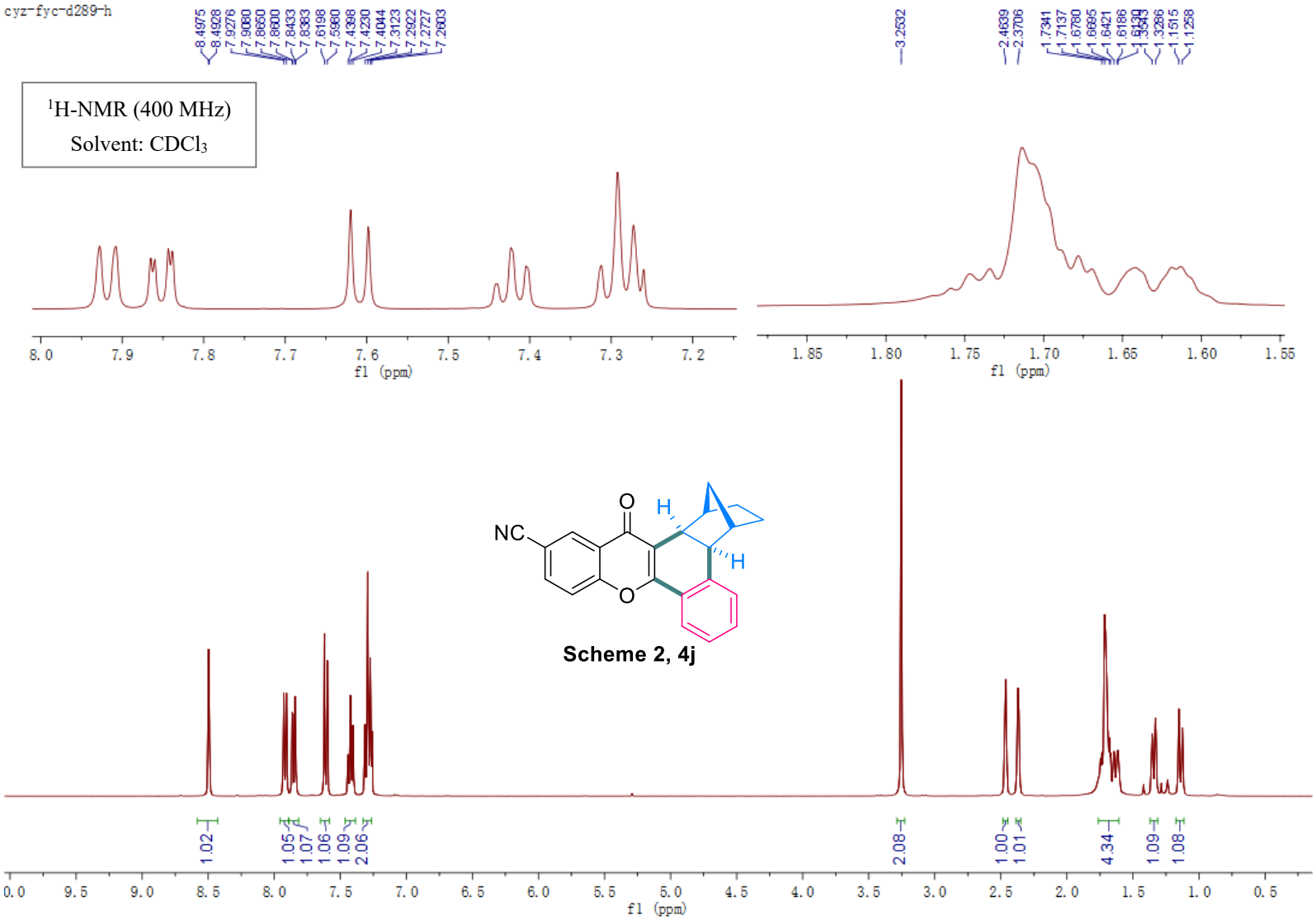

cyz-fyc-d286-c
176.85
176.83
160.52
158.07
156.78
151.53
151.52
141.61
131.59
129.52
126.46
126.43
124.78
124.71
123.20
121.44
121.18
119.89
119.81
116.46
110.50
110.27
77.48
77.16
76.84
49.20
45.49
44.59
40.01
33.87
30.45
29.89
13C-NMR (100 MHz)
Solvent: CDCl3
177.1
176.9
176.7
f1 (ppm)
151.5
f1 (ppm)
126.4
f1 (ppm)
125.0
124.6
f1 (ppm)
121
120
f1 (ppm)
110.5
110.0
f1 (ppm)
O
H
F
H
O
Scheme 2, 4g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

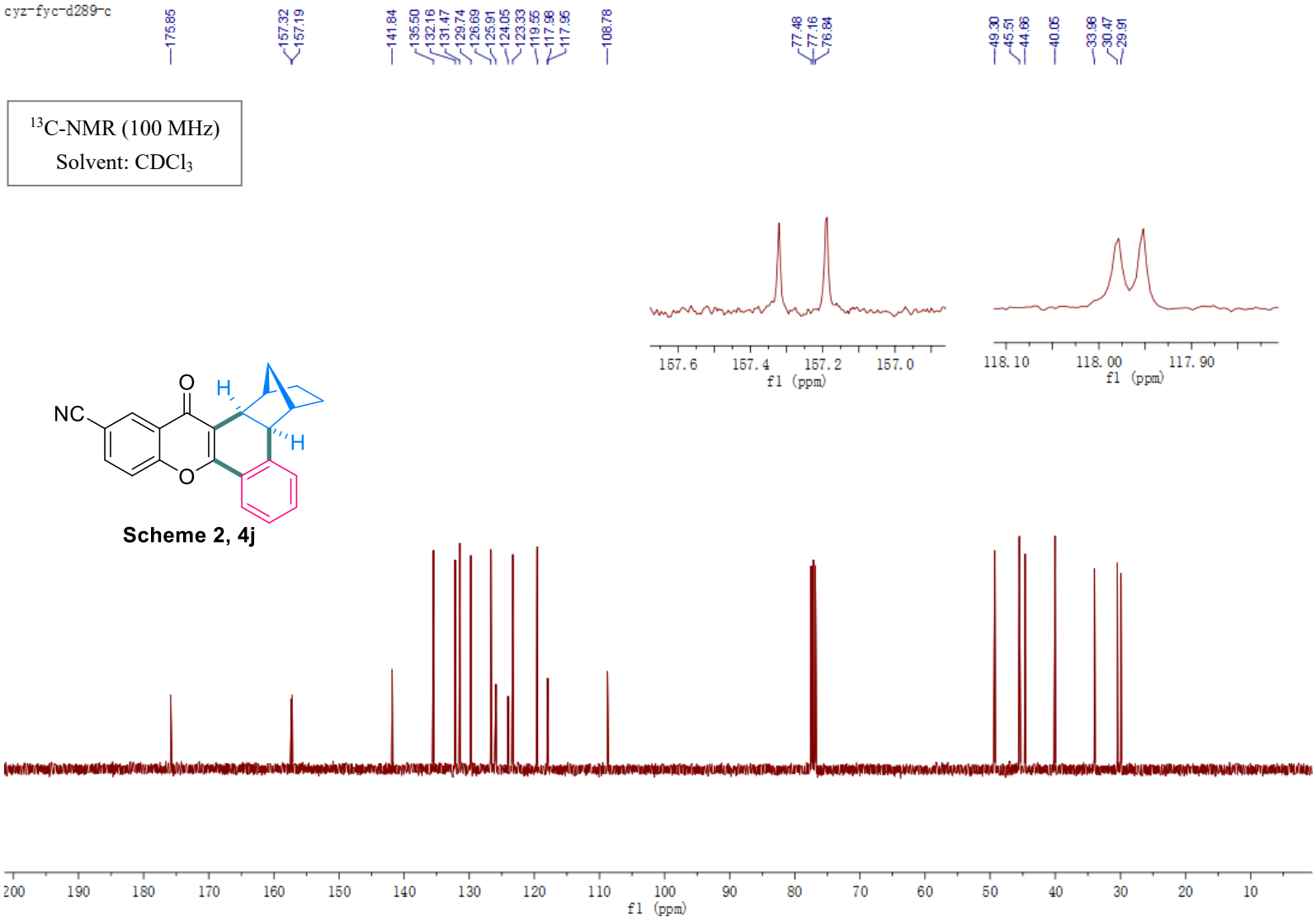

cyz-fyc-d287-h
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$
f1 (ppm)
Cl
O
H
H
O
Scheme 2, 4h

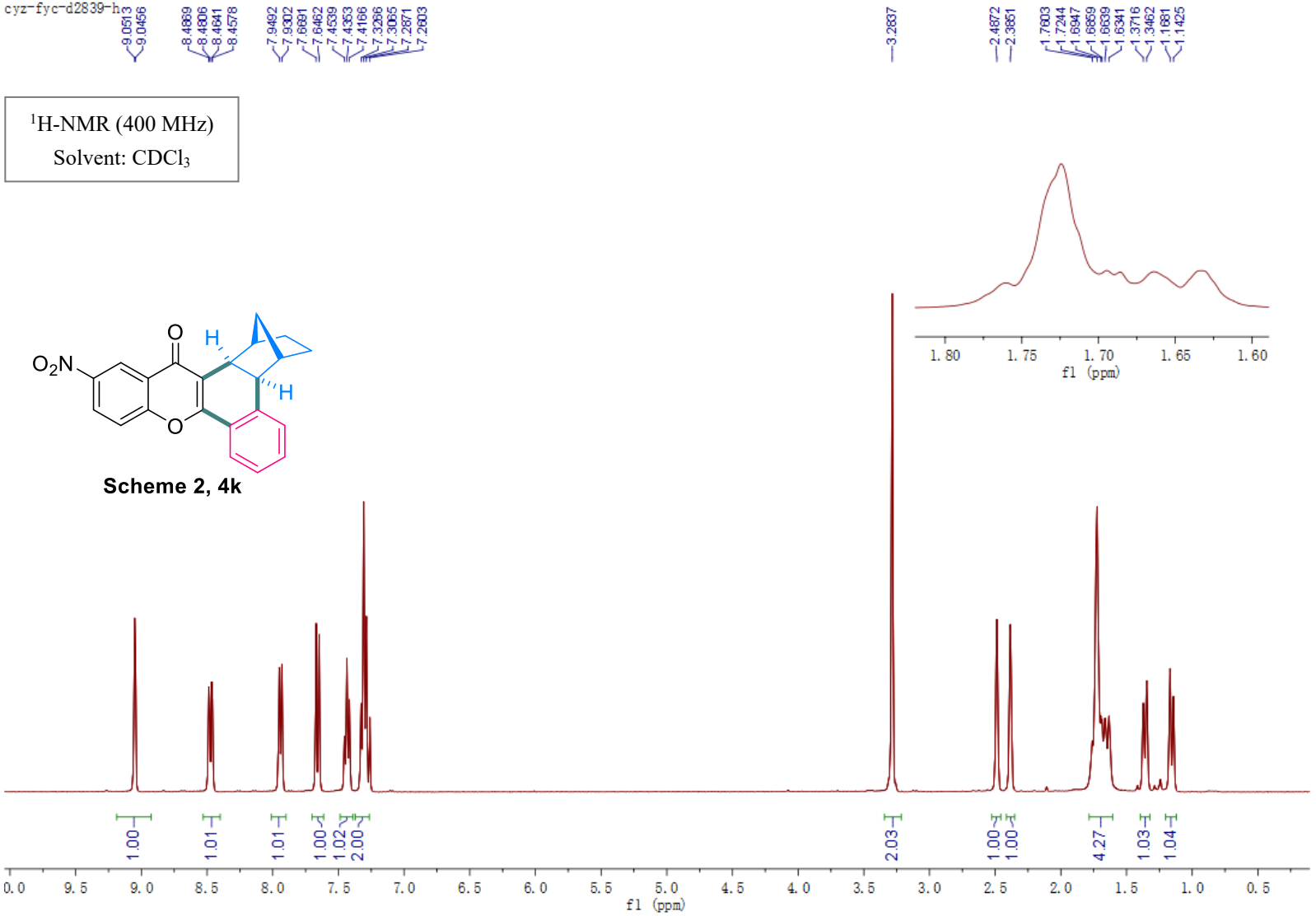

cyz-fyc-d287-c
176.39
156.77
153.62
141.61
133.31
131.65
130.49
129.54
126.48
126.33
125.02
124.58
123.21
119.55
117.08
77.48
77.16
76.84
49.23
45.48
44.59
40.05
33.89
30.45
29.91
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$
Cl
O
H
H
O
Scheme 2, 4h
127.0
126.5
126.0
125.5
125.0
124.5
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


cyz-fyc-d288-h
[1]H-NMR (400 MHz)
Solvent: CDCl3
Br
O
H
H
O
Scheme 2, 4i
f1 (ppm)


cyz-fyc-d288-c
176.39
156.88
154.16
141.72
136.14
131.73
129.62
128.33
126.55
126.43
125.11
123.29
119.87
118.08
117.32
77.48
77.16
76.84
49.31
45.55
44.66
40.11
33.95
30.49
29.97
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$
Br
O
H
H
O
Scheme 2, 4i
126.8
126.6
126.4
126.2
f1 (ppm)
f1 (ppm)


cyz-fyc-d289-h
[1]H-NMR (400 MHz)
Solvent: CDCl3
NC
O
H
H
O
Scheme 2, 4j
f1 (ppm)

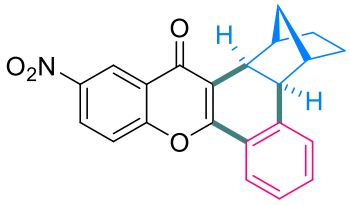

cyz-fyc-d289-c
175.85
157.32
157.19
141.84
135.50
132.16
131.47
129.74
126.69
125.91
124.05
123.33
119.55
117.98
117.95
108.78
77.48
77.16
76.84
49.30
45.51
44.66
40.05
33.96
30.47
29.91
13C-NMR (100 MHz)
Solvent: CDCl3
NC
O
H
H
O
Scheme 2, 4j
157.6
157.4
157.2
157.0
f1 (ppm)
118.10
118.00
117.90
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


cyz-fyc-d2839-h
9.0513
9.0456
8.4669
8.4606
8.4641
8.4578
7.9492
7.9302
7.6691
7.6462
7.4539
7.4353
7.4166
7.3266
7.3065
7.2871
7.2603
3.2637
2.4872
2.3851
1.7603
1.7244
1.6947
1.6869
1.6639
1.6341
1.3716
1.3462
1.1681
1.1425
1H-NMR (400 MHz)
Solvent: CDCl3
O2N
O
H
H
O
Scheme 2, 4k
1.80
1.75
1.70
1.65
1.60
f1 (ppm)
1.00
1.01
1.01
1.00
1.02
2.00
2.03
1.00
1.00
4.27
1.03
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)

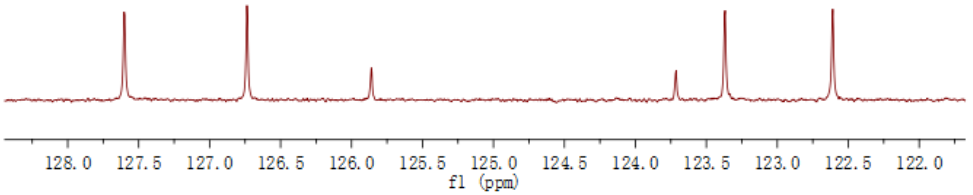
cyz-fyc-d2839-c

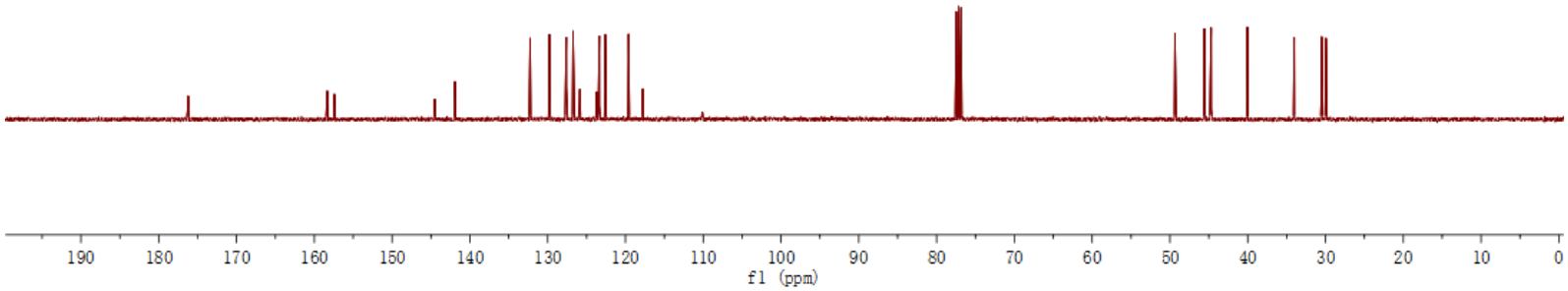
176.23
158.33
157.41
144.50
141.92
132.26
129.79
127.60
126.74
125.86
123.71
123.37
122.61
119.59
117.77
77.48
77.16
76.84
49.36
45.55
44.71
40.06
34.03
30.49
29.94

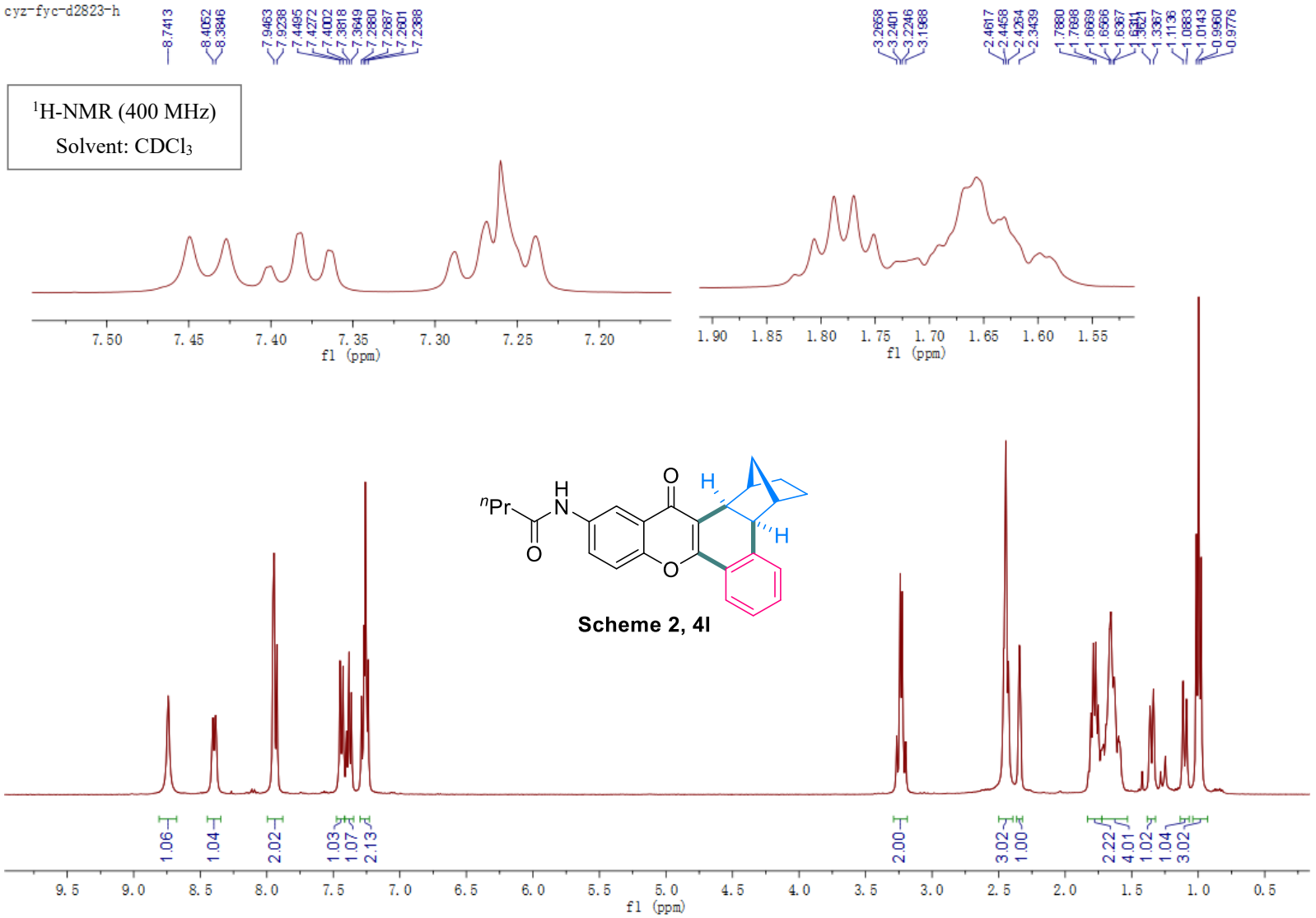
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

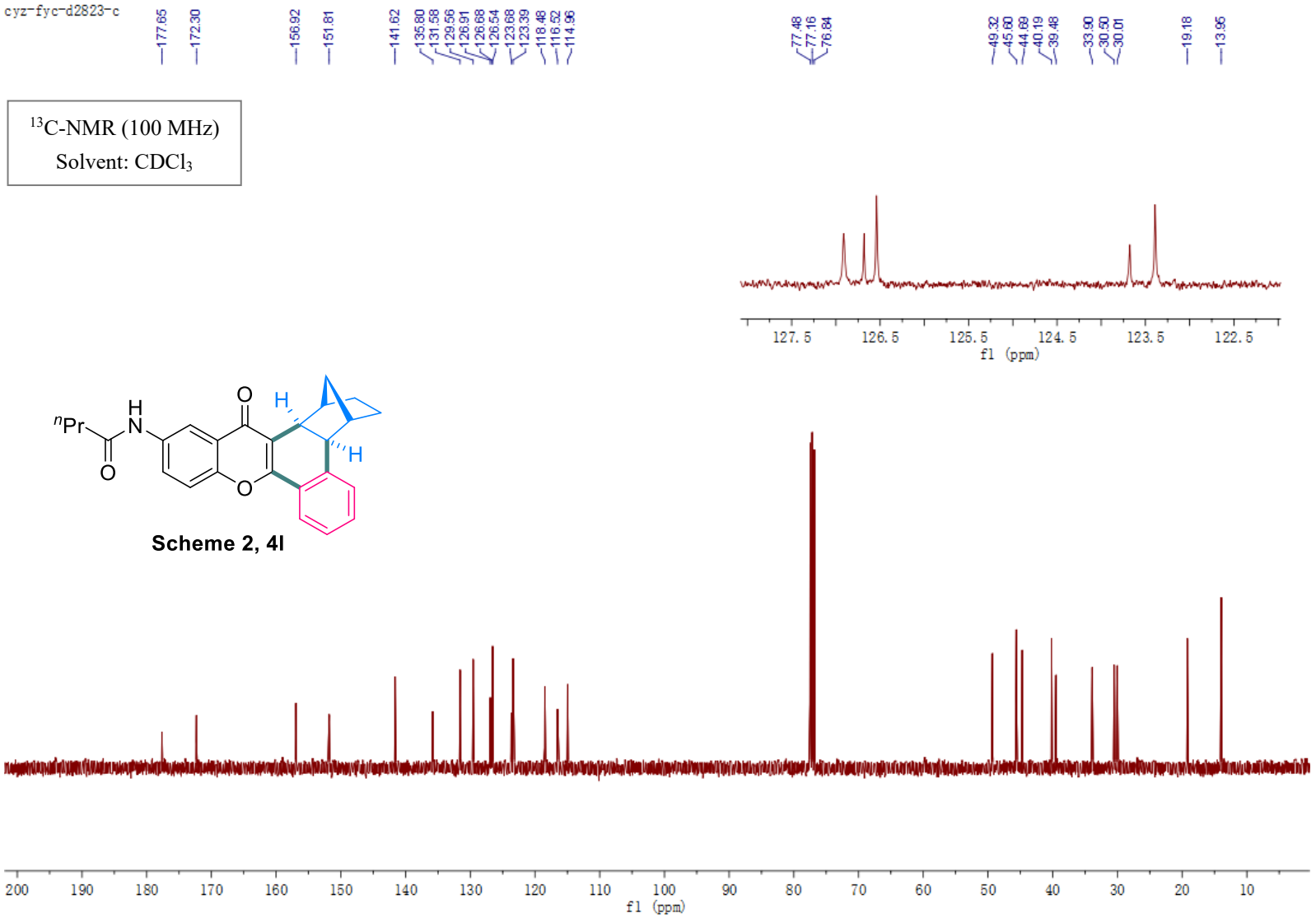


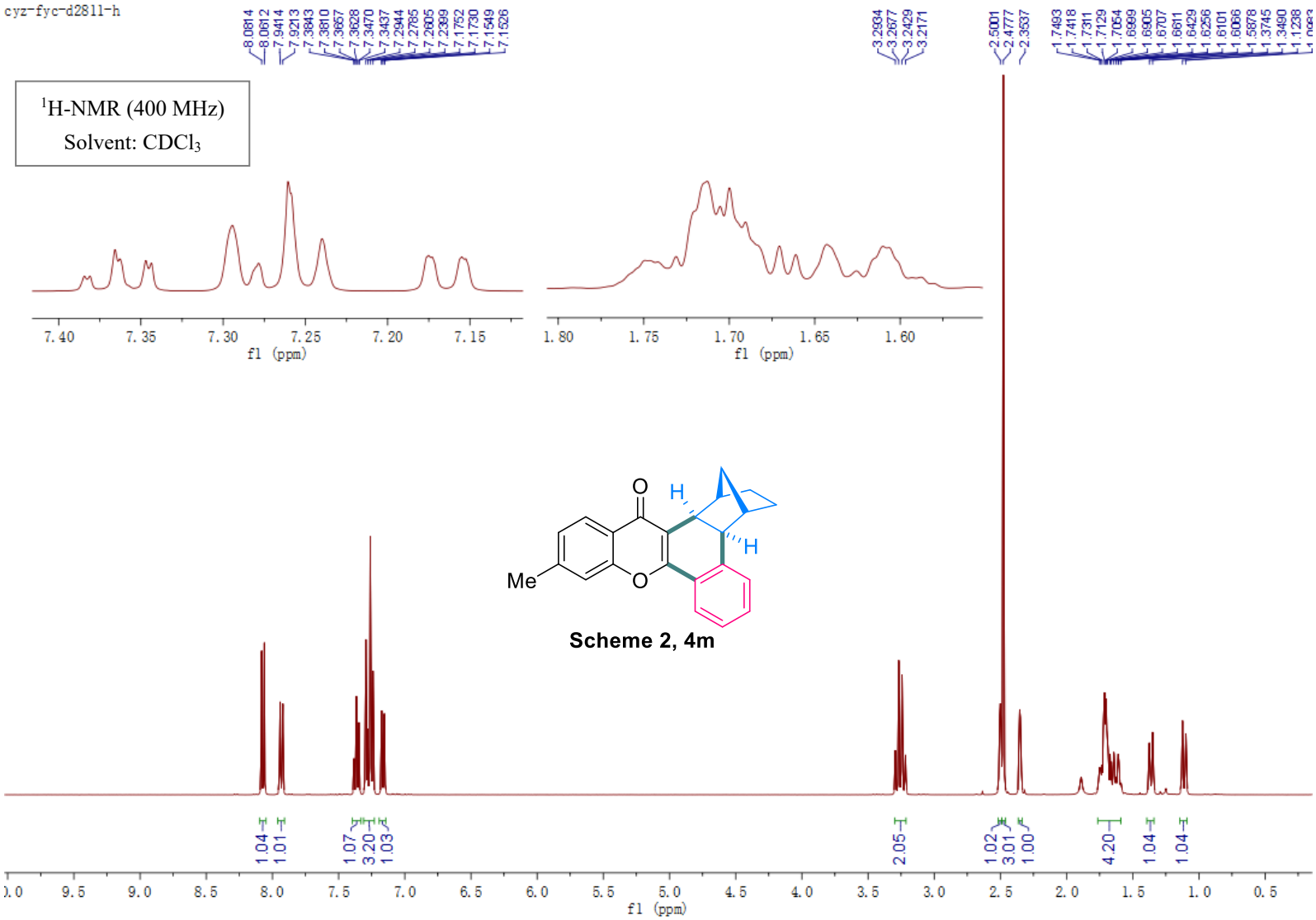
Scheme 2, 4k

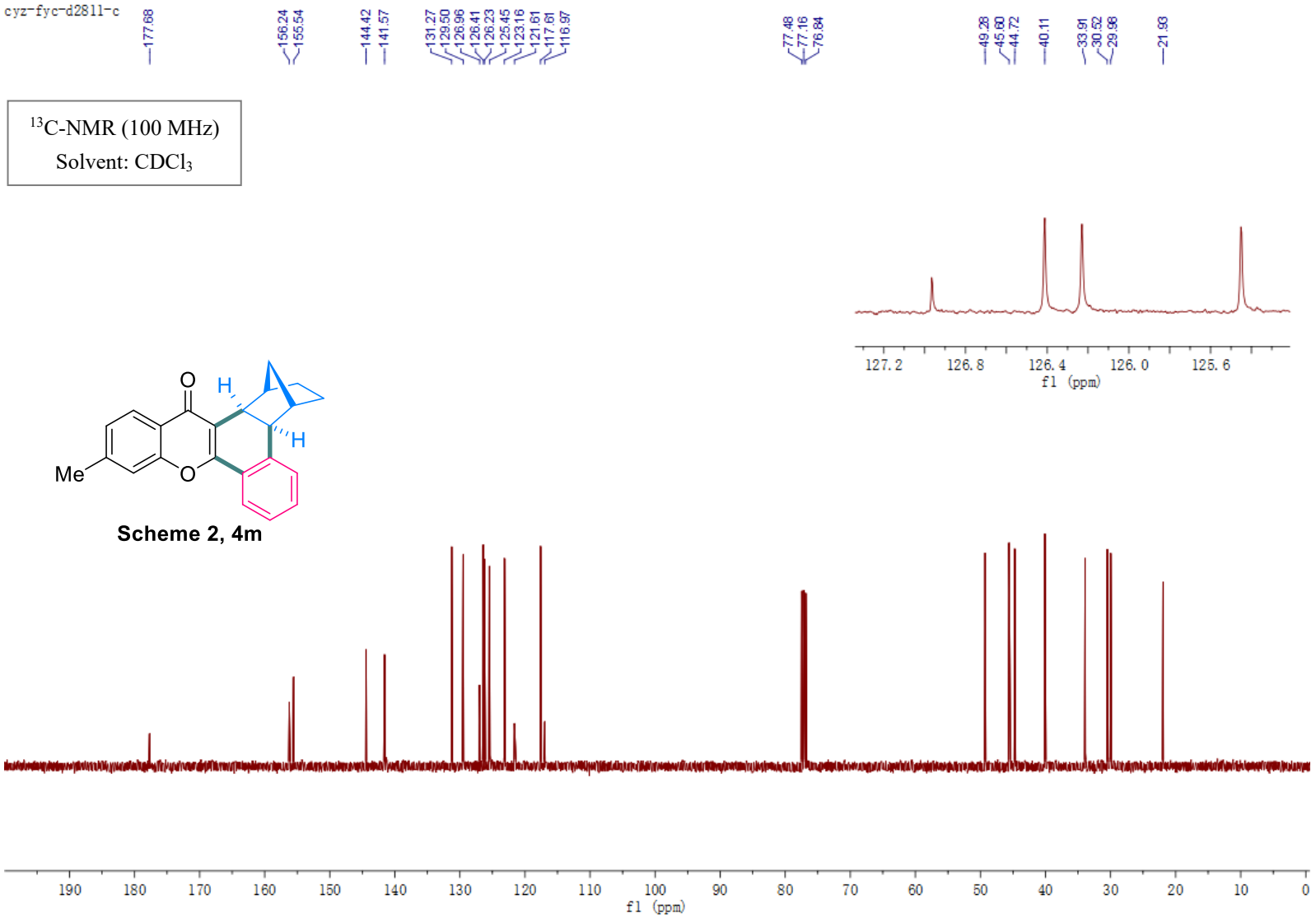





cyz-fyc-d2823-h
1H-NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)
Scheme 2, 4l

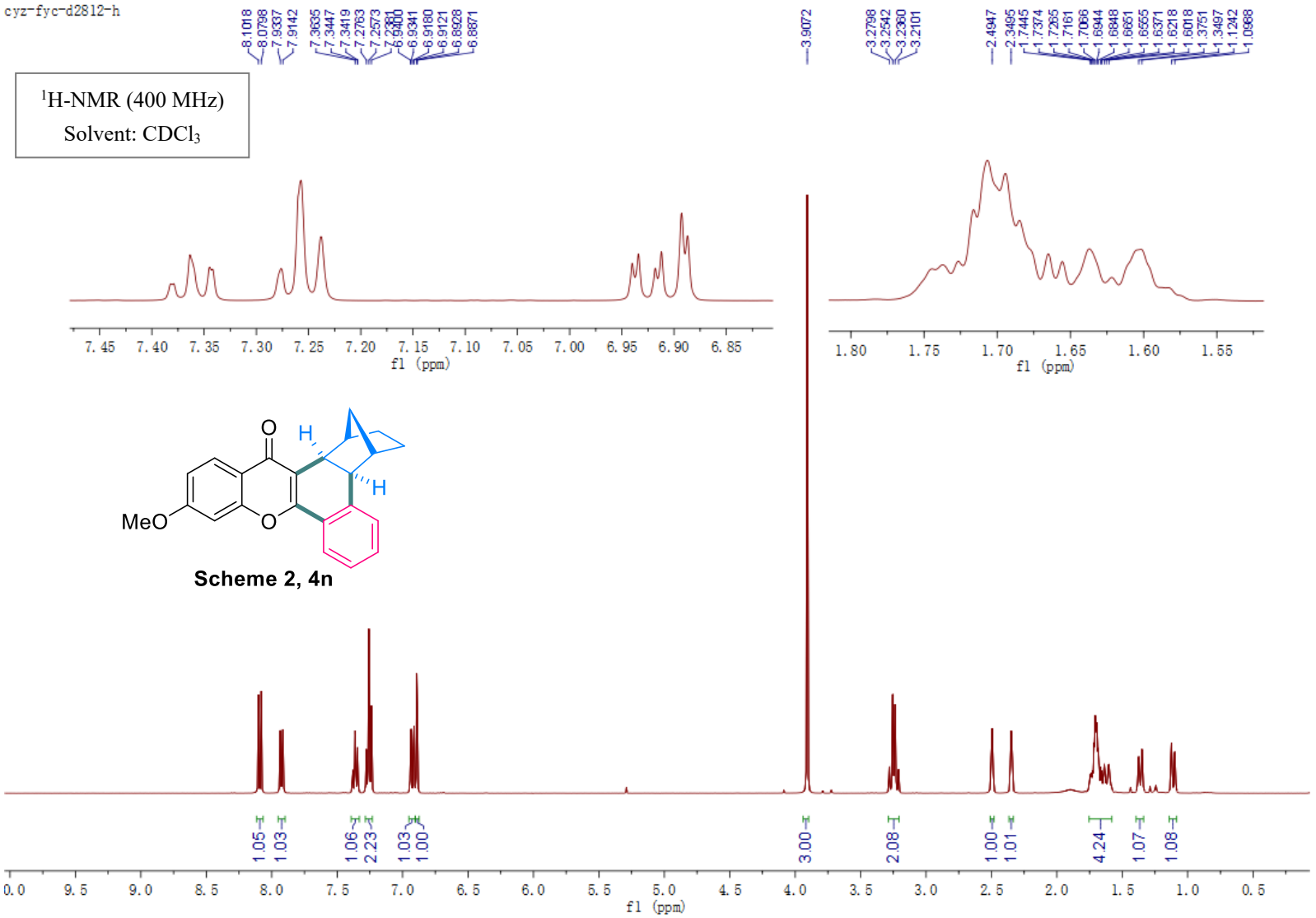

cyz-fyc-d2823-c
177.65
172.30
156.92
151.81
141.62
135.80
131.58
129.56
126.91
126.68
126.54
123.68
123.39
118.48
116.52
114.96
77.48
77.16
76.84
49.32
45.60
44.69
40.19
39.48
33.90
30.60
30.01
19.18
13.95
13C-NMR (100 MHz)
Solvent: CDCl3
nPr
H
N
O
O
O
H
H
Scheme 2, 4l
127.5
126.5
125.5
124.5
123.5
122.5
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

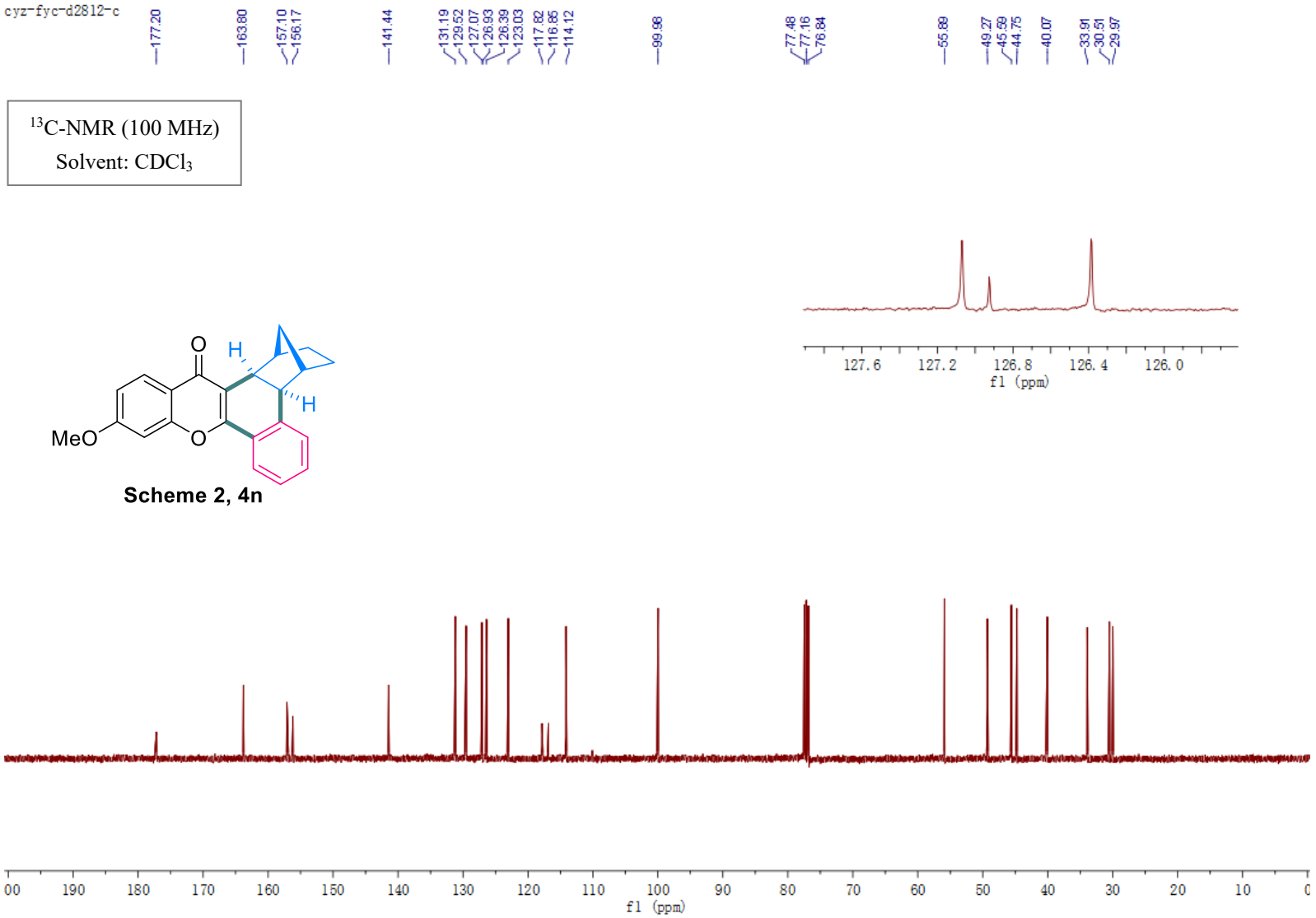

cyz-fyc-d2811-h
1H-NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)
Me
O
H
H
Scheme 2, 4m



^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

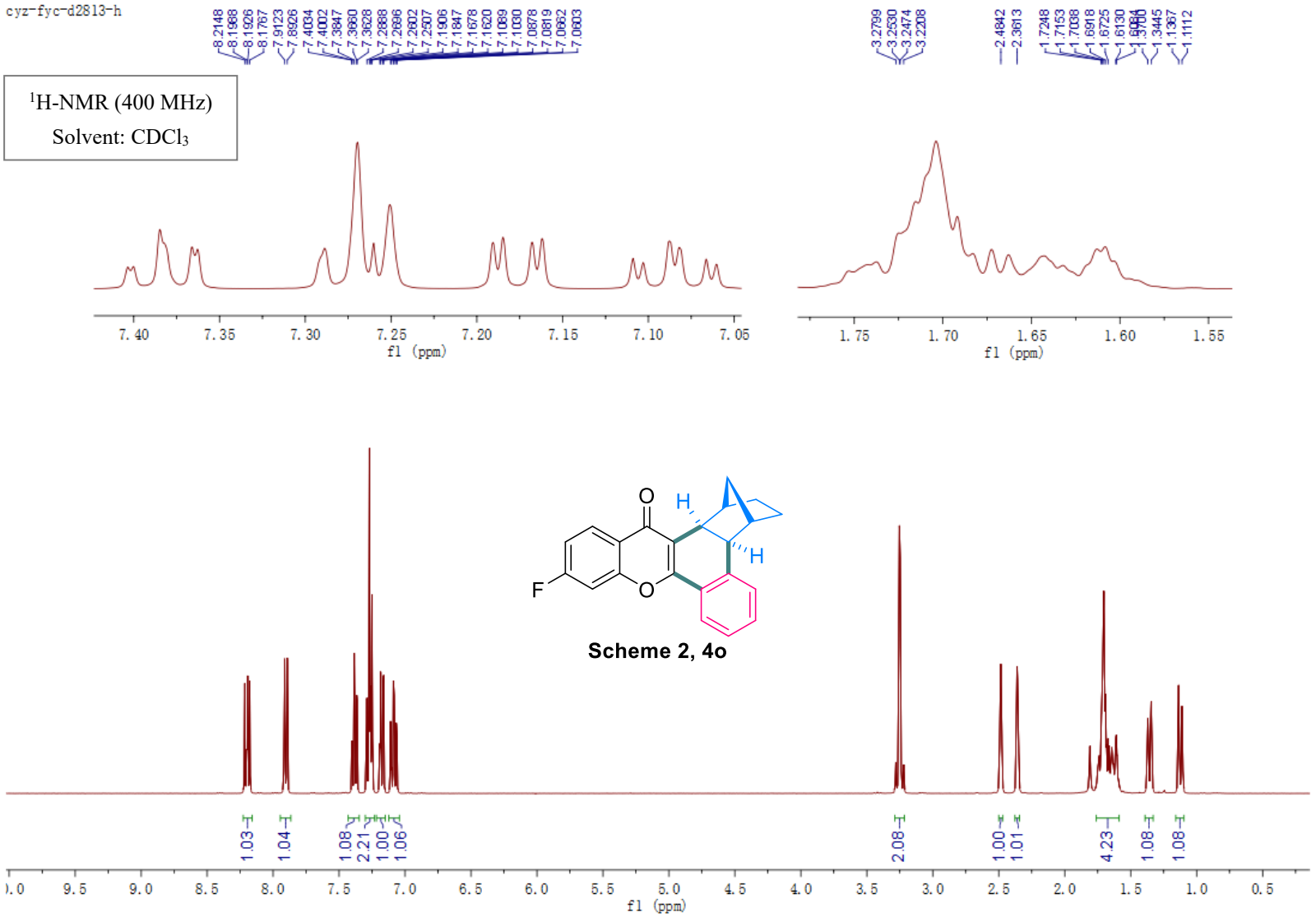
Scheme 2, 4m

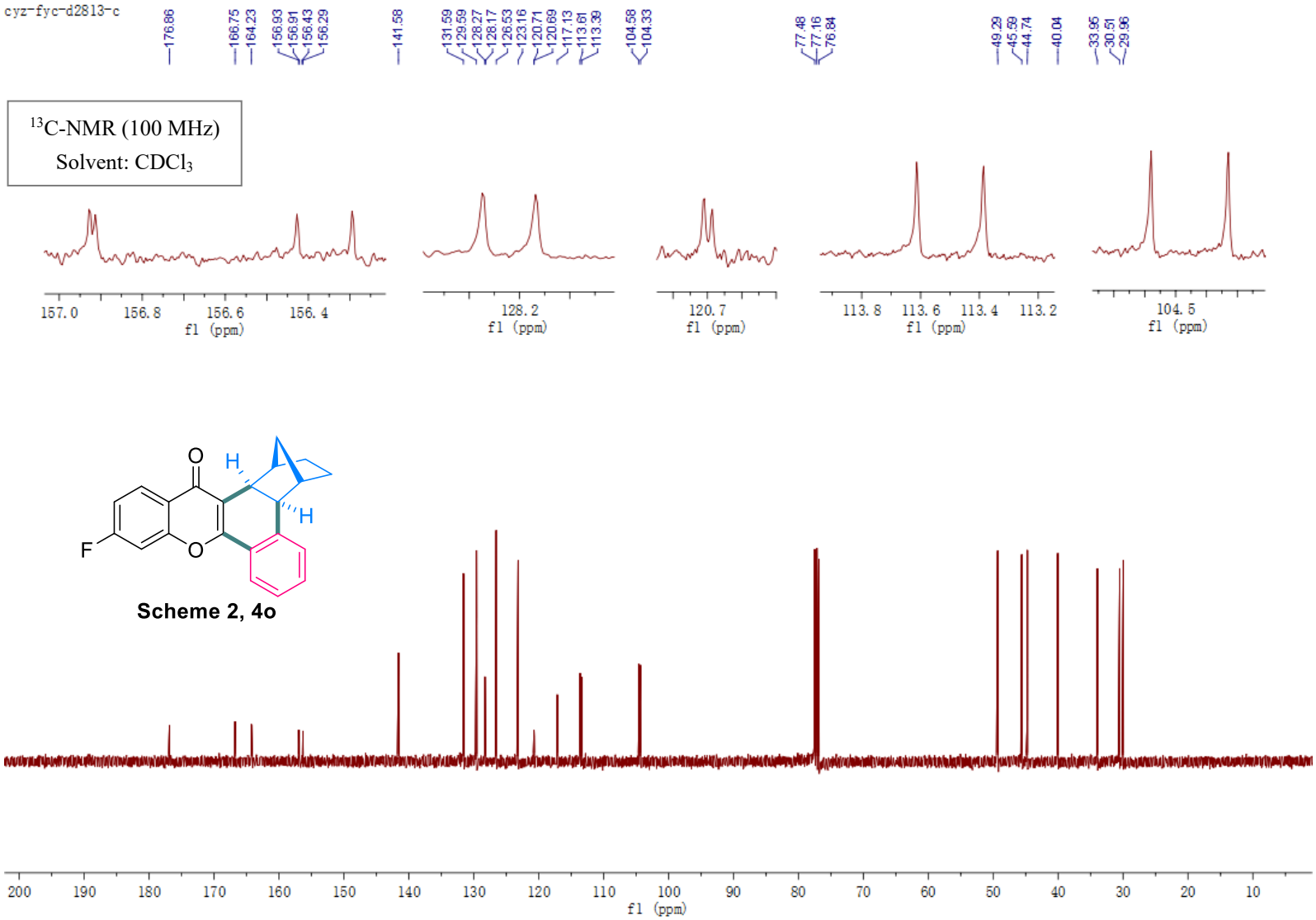

cyz-fyc-d2812-h
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$
MeO
O
H
H
Scheme 2, 4n
f1 (ppm)

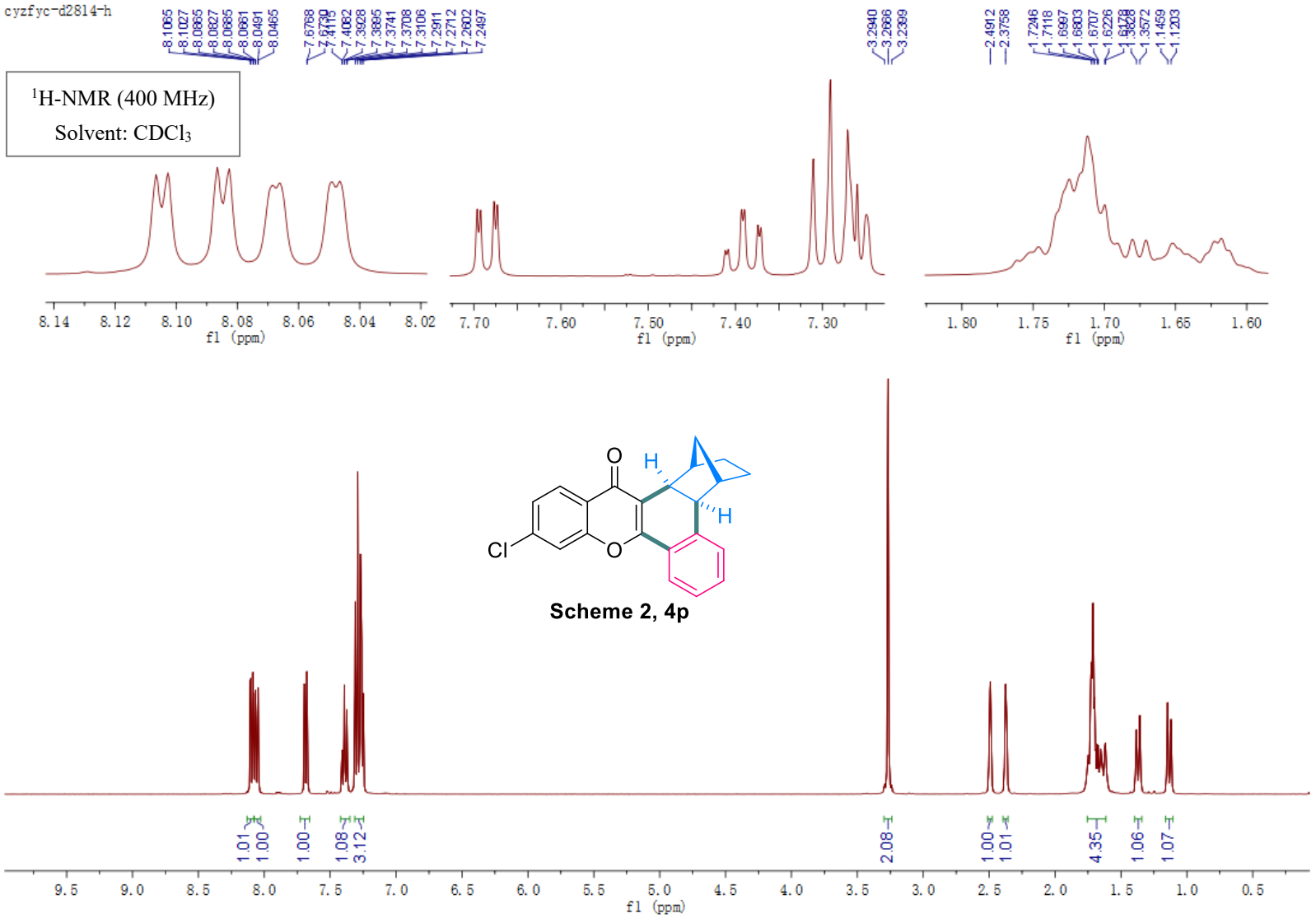


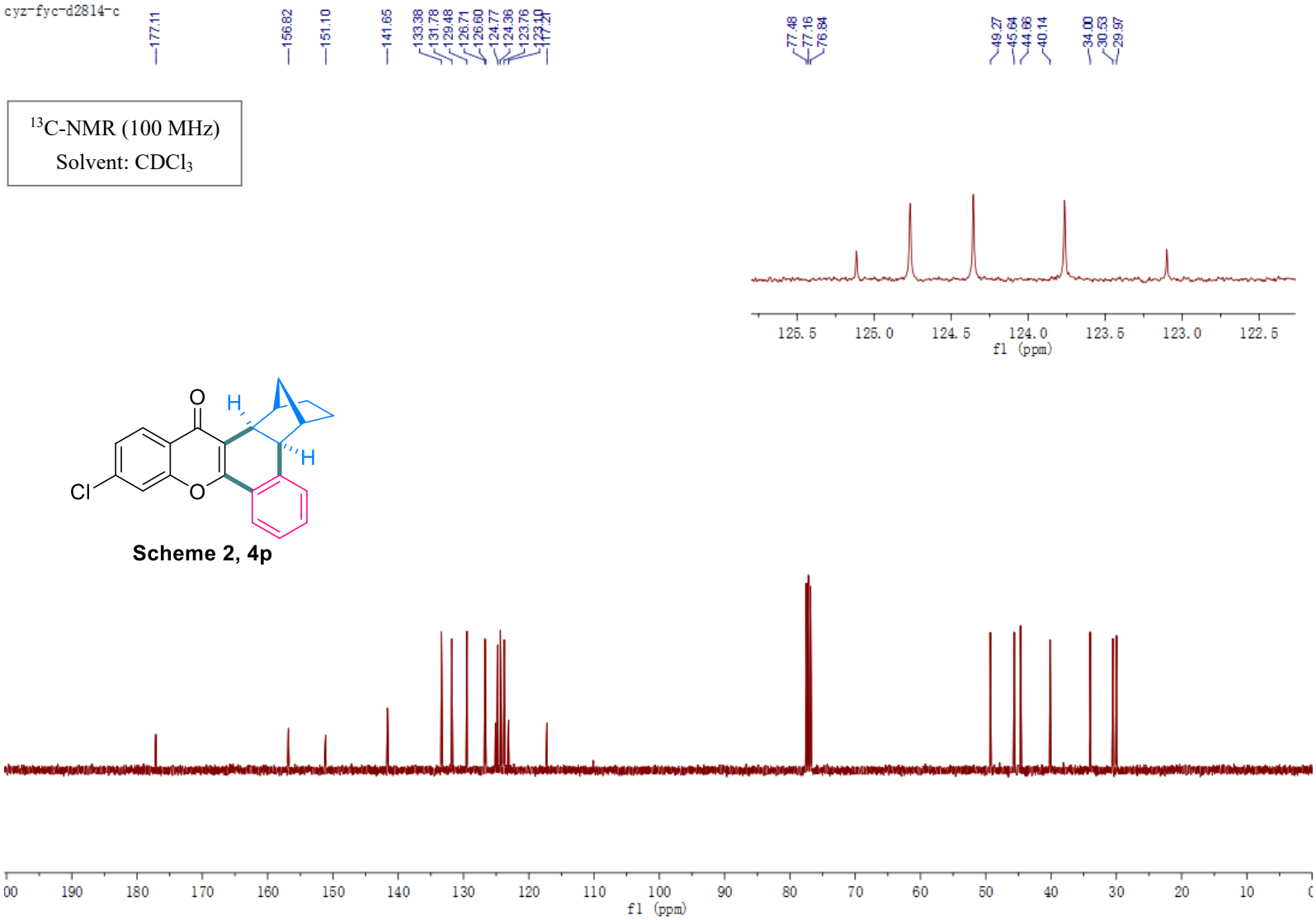
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Scheme 2, 4n


cyz-fyc-d2813-h
1H-NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)
O
H
H
F
O
Scheme 2, 4o

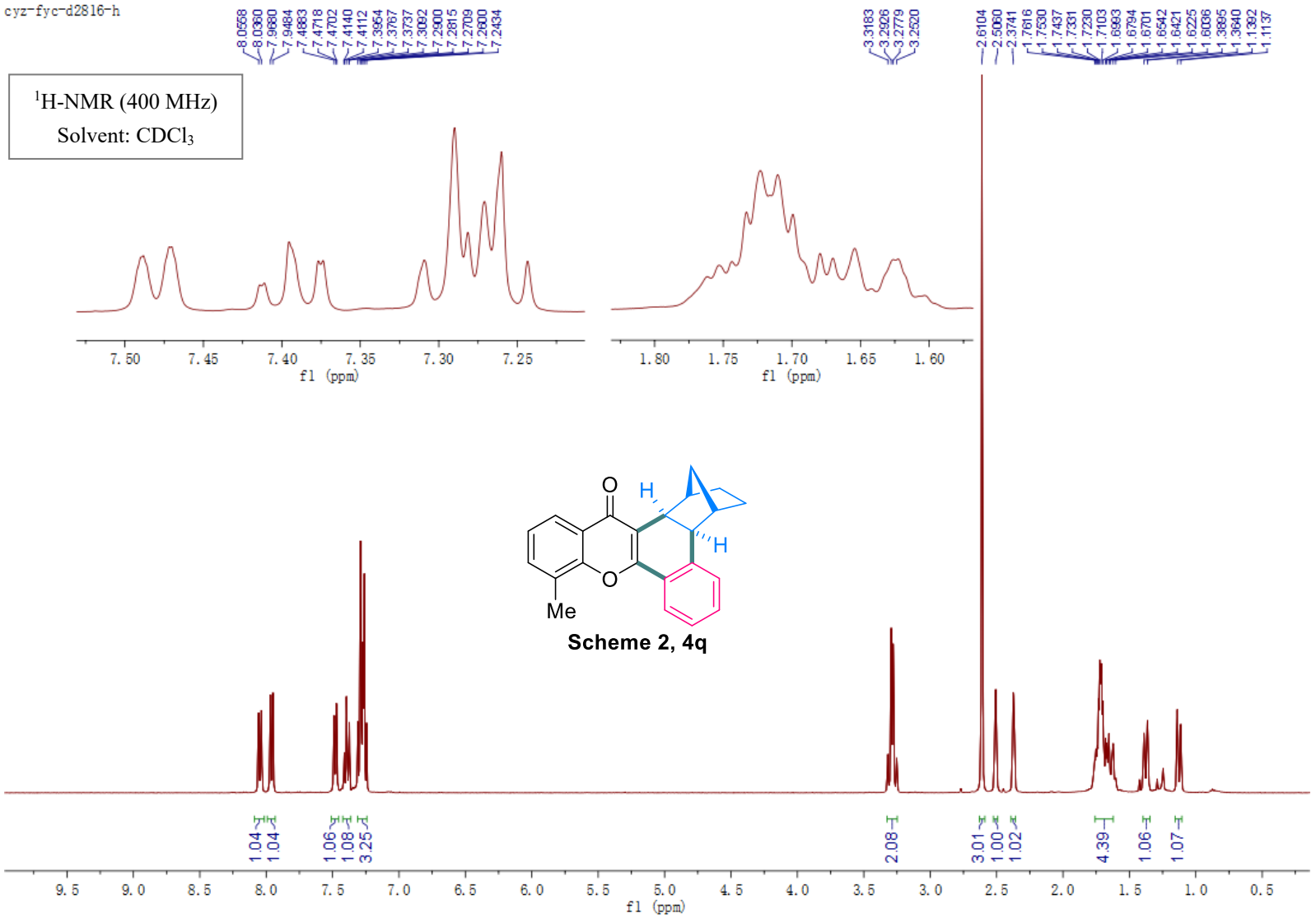

cyz-fyc-d2813-c
176.86
166.75
164.23
156.93
156.91
156.43
156.29
141.58
131.59
129.59
128.27
128.17
126.53
123.16
120.71
120.69
117.13
113.61
113.39
104.58
104.33
77.48
77.16
76.84
49.29
45.59
44.74
40.04
33.95
30.51
29.96
13C-NMR (100 MHz)
Solvent: CDCl3
157.0
156.8
156.6
156.4
f1 (ppm)
128.2
f1 (ppm)
120.7
f1 (ppm)
113.8
113.6
113.4
113.2
f1 (ppm)
104.5
f1 (ppm)
O
H
H
F
O
Scheme 2, 4o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

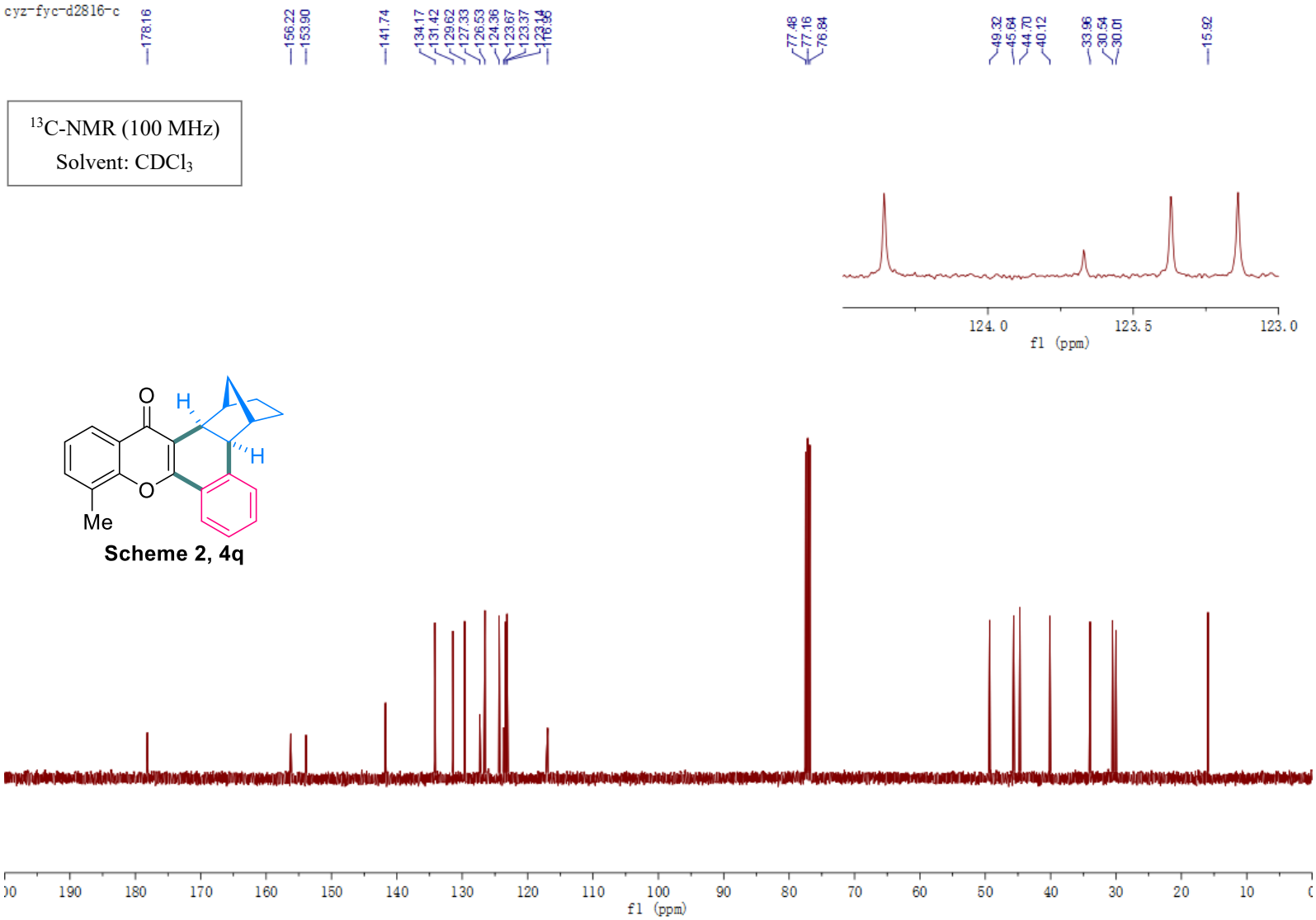

cyzfyc-d2814-h
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$
f1 (ppm)
Cl
O
H
H
Scheme 2, 4p



^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

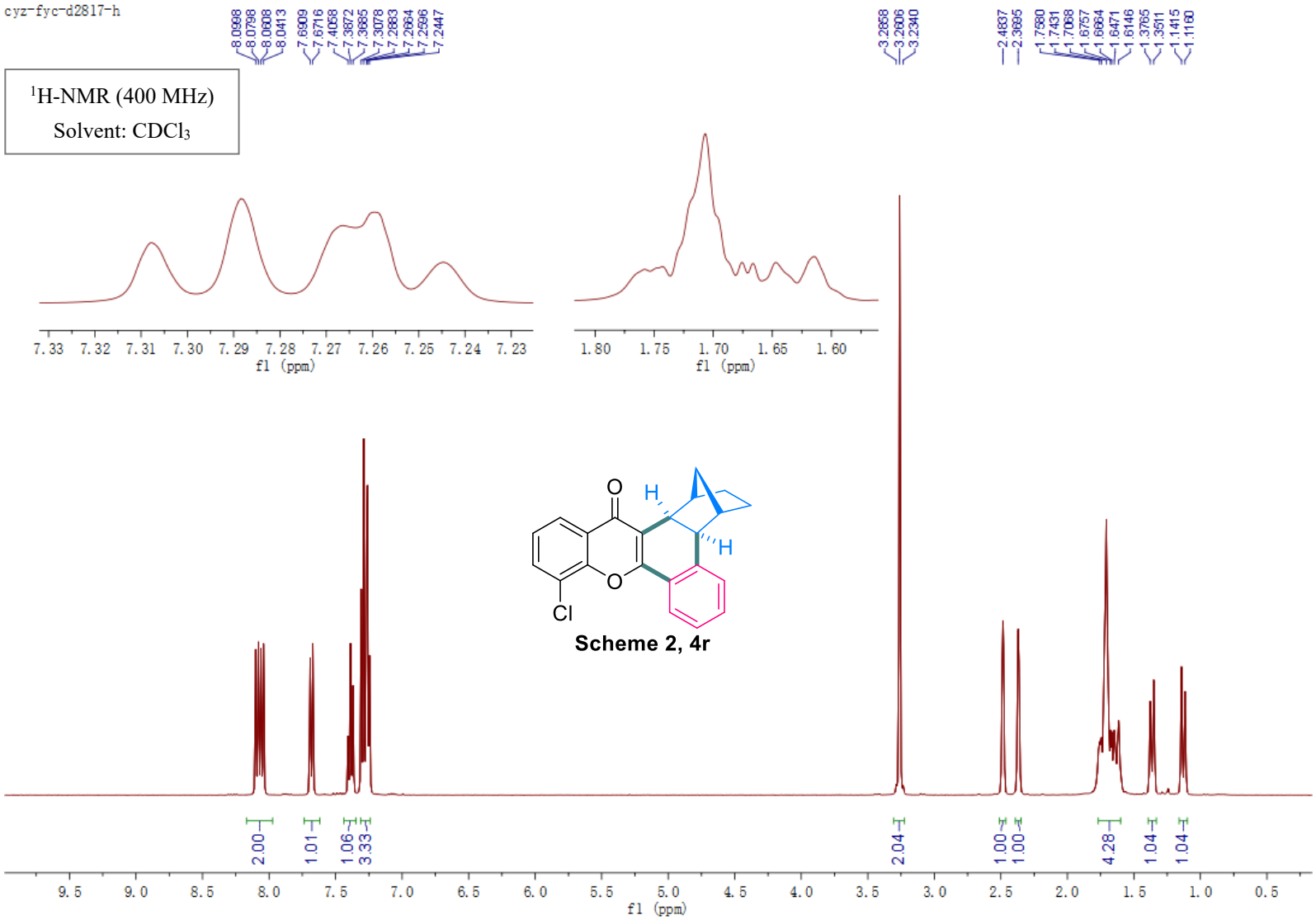
Scheme 2, 4p

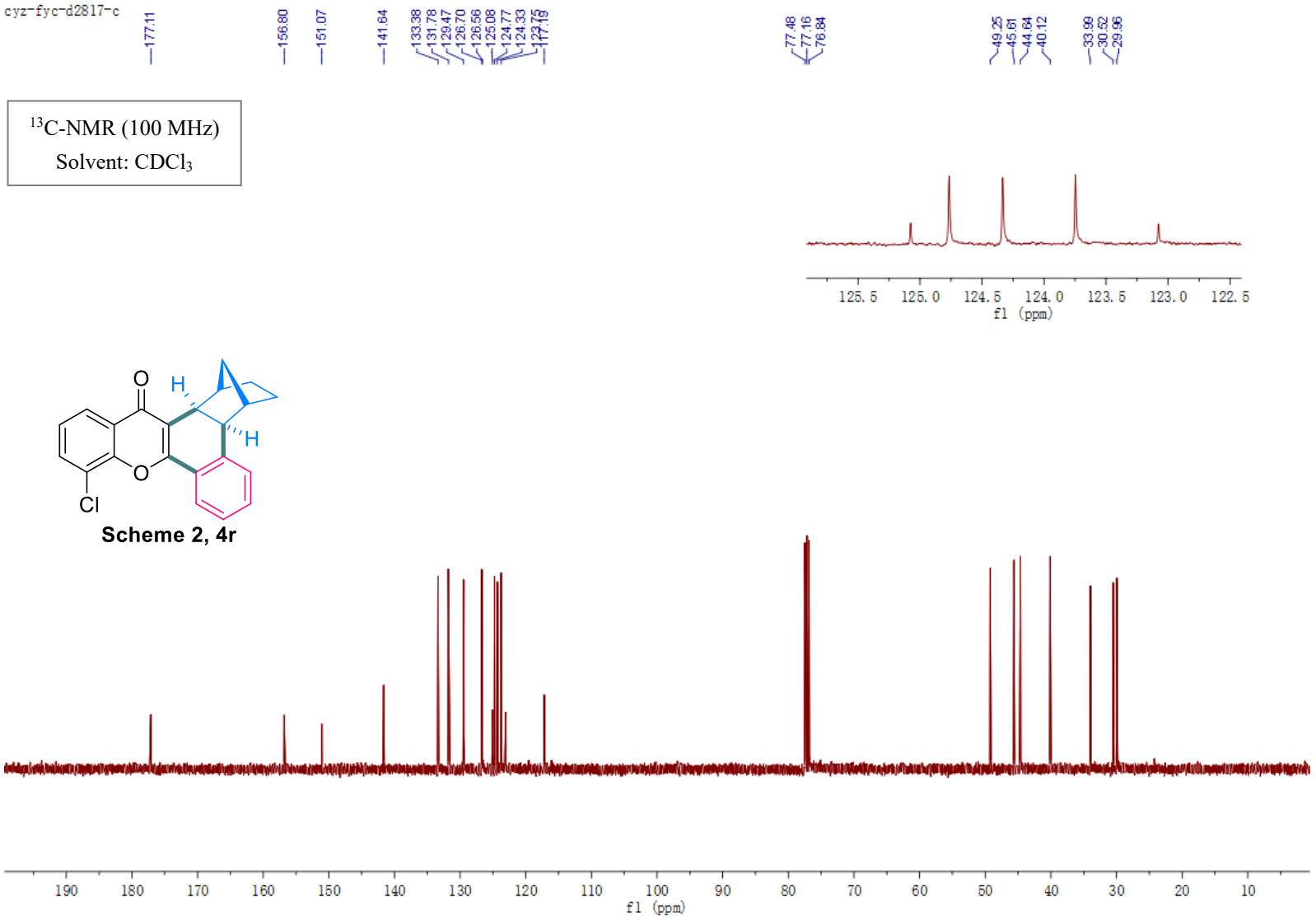

cyz-fyc-d2816-h
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$
f1 (ppm)
O
H
H
O
Me
Scheme 2, 4q



^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

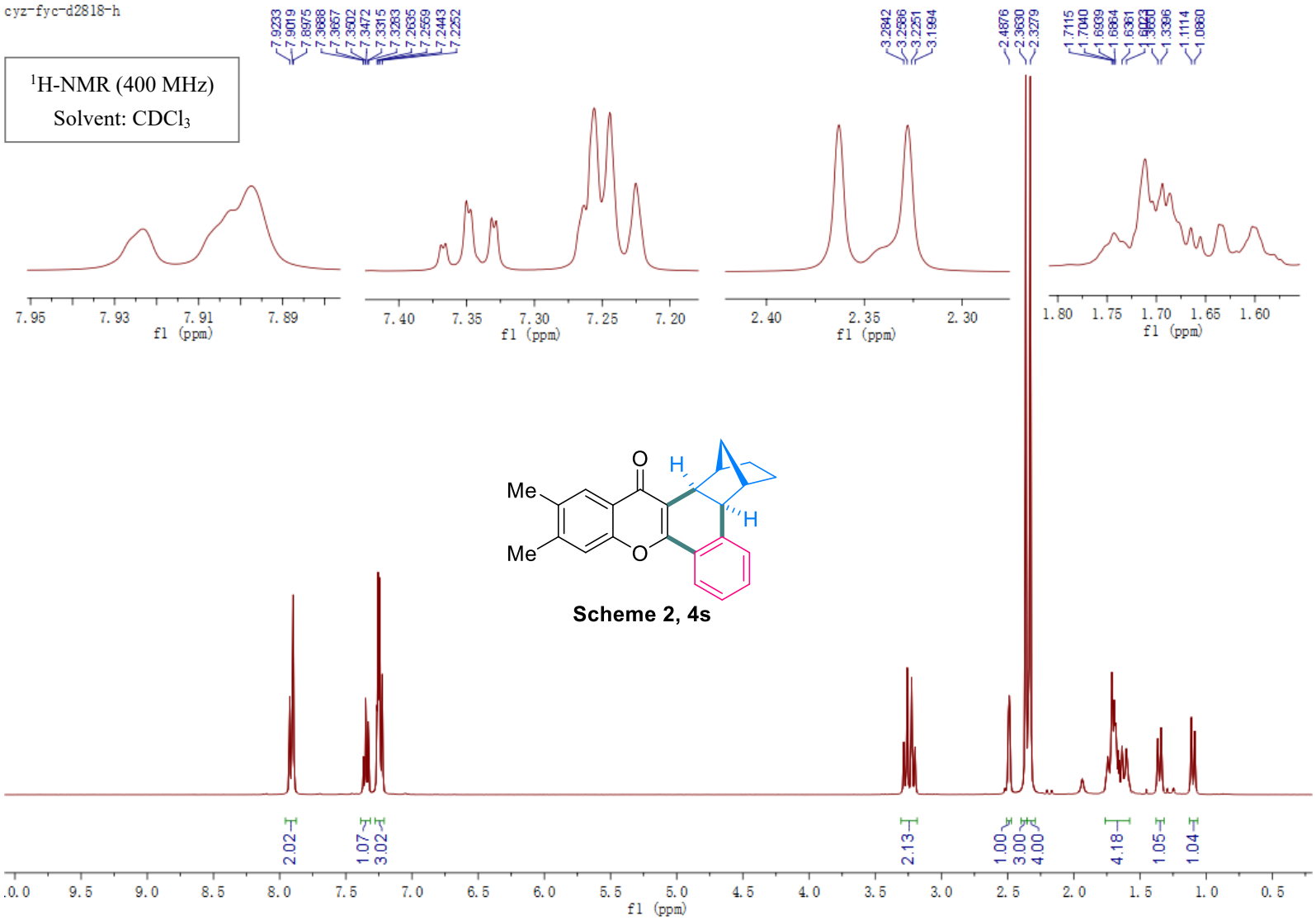
Scheme 2, 4q


cyz-fyc-d2817-h
^{1}H-NMR (400 MHz)
Solvent: CDCl$_3$
Scheme 2, 4r
f1 (ppm)



^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

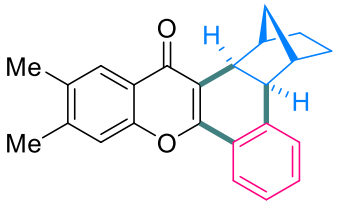
Scheme 2, 4r


cyz-fyc-d2818-h
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$
f1 (ppm)
Me
Me
O
O
H
H
Scheme 2, 4s

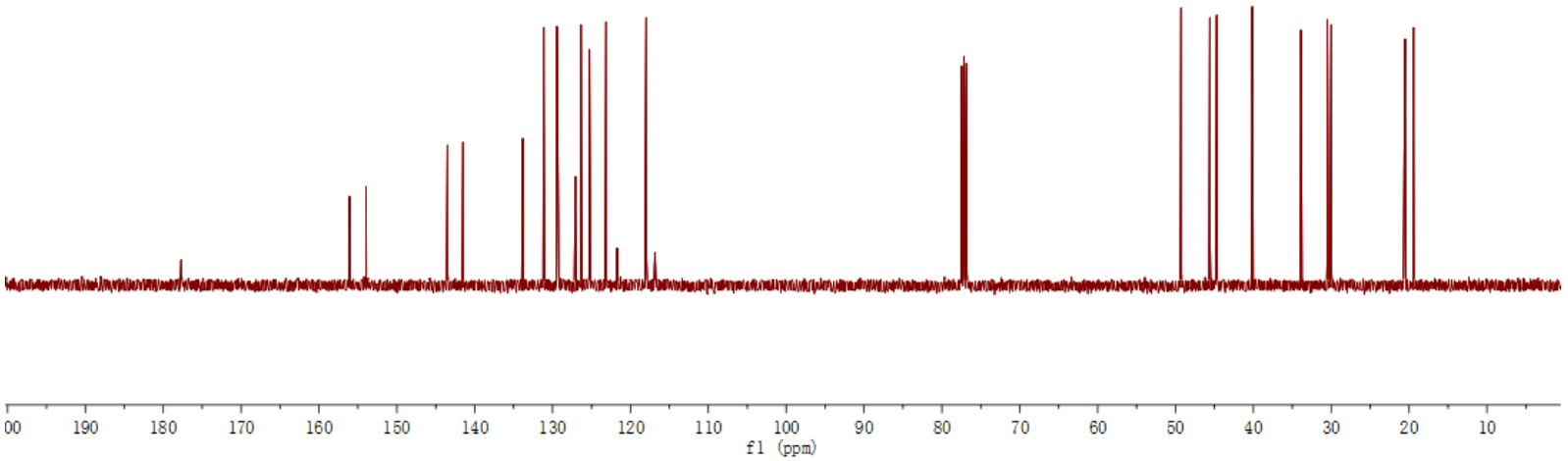
cyz-fyc-D2818-c
training2

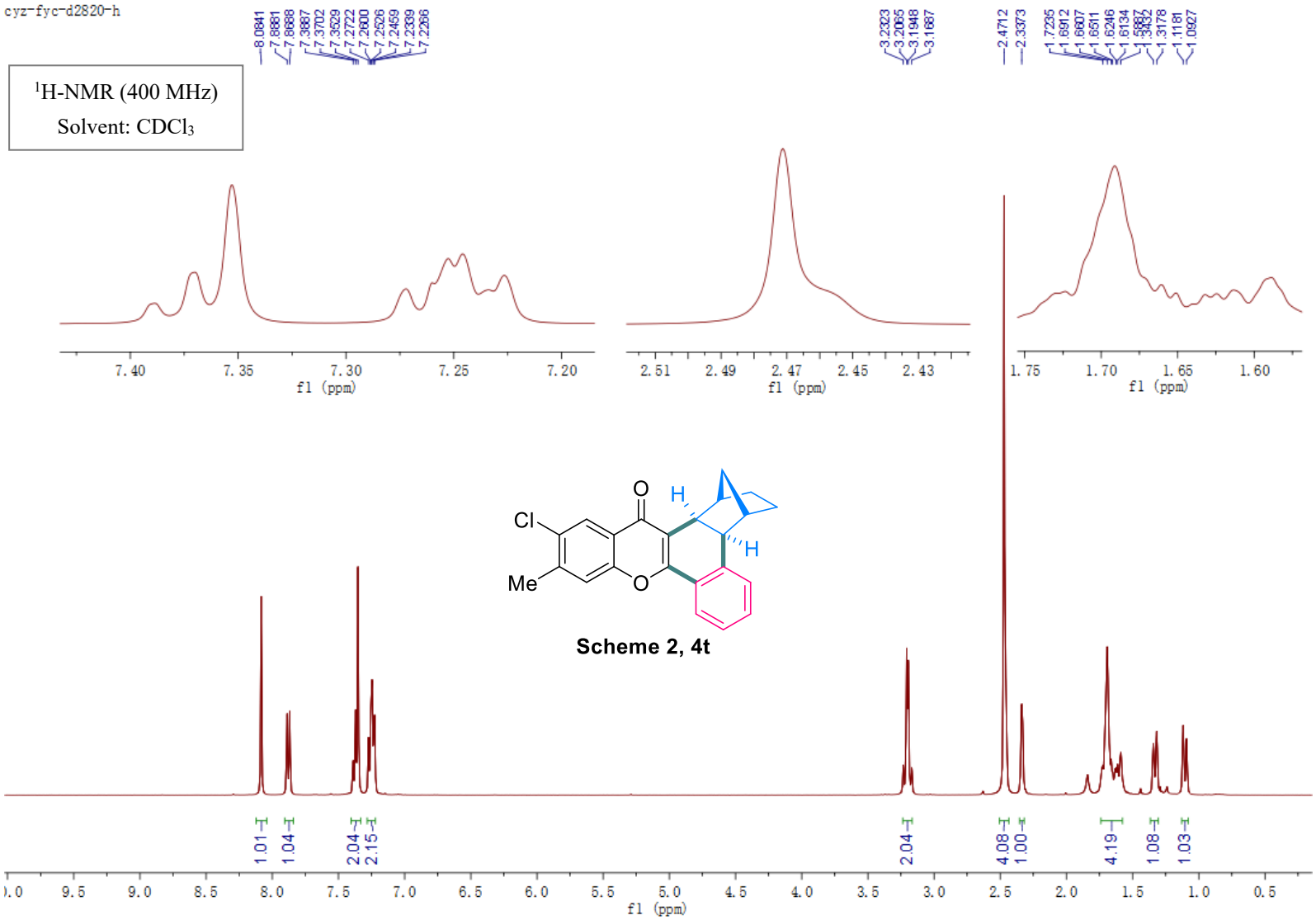
177.69
156.05
153.95
143.50
141.50
133.84
131.14
129.46
127.07
126.36
125.27
123.13
121.71
117.98
116.85
77.48
77.16
76.84
49.28
45.60
44.70
40.13
33.88
30.50
29.99
20.52
19.44

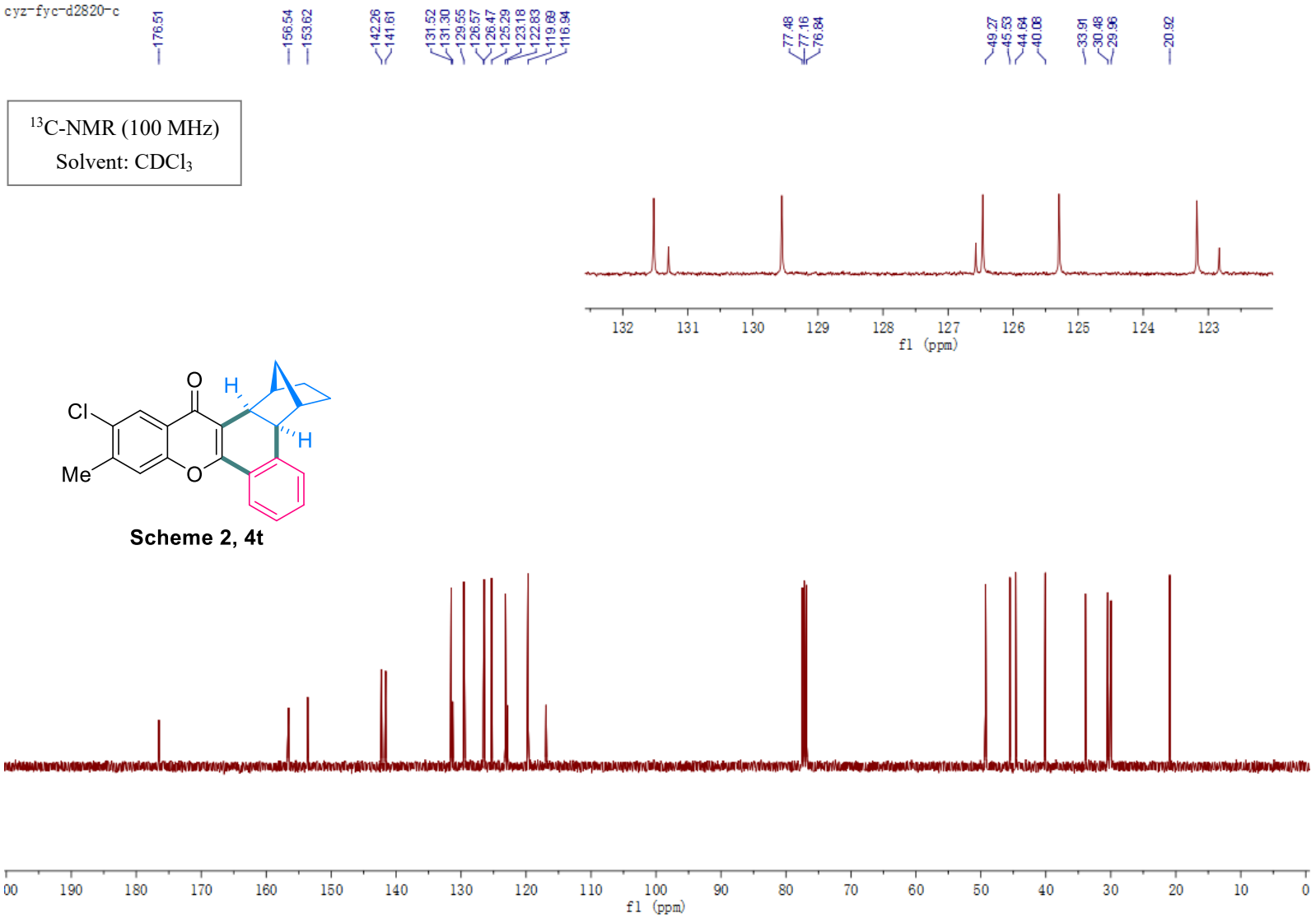
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$



Scheme 2, 4s

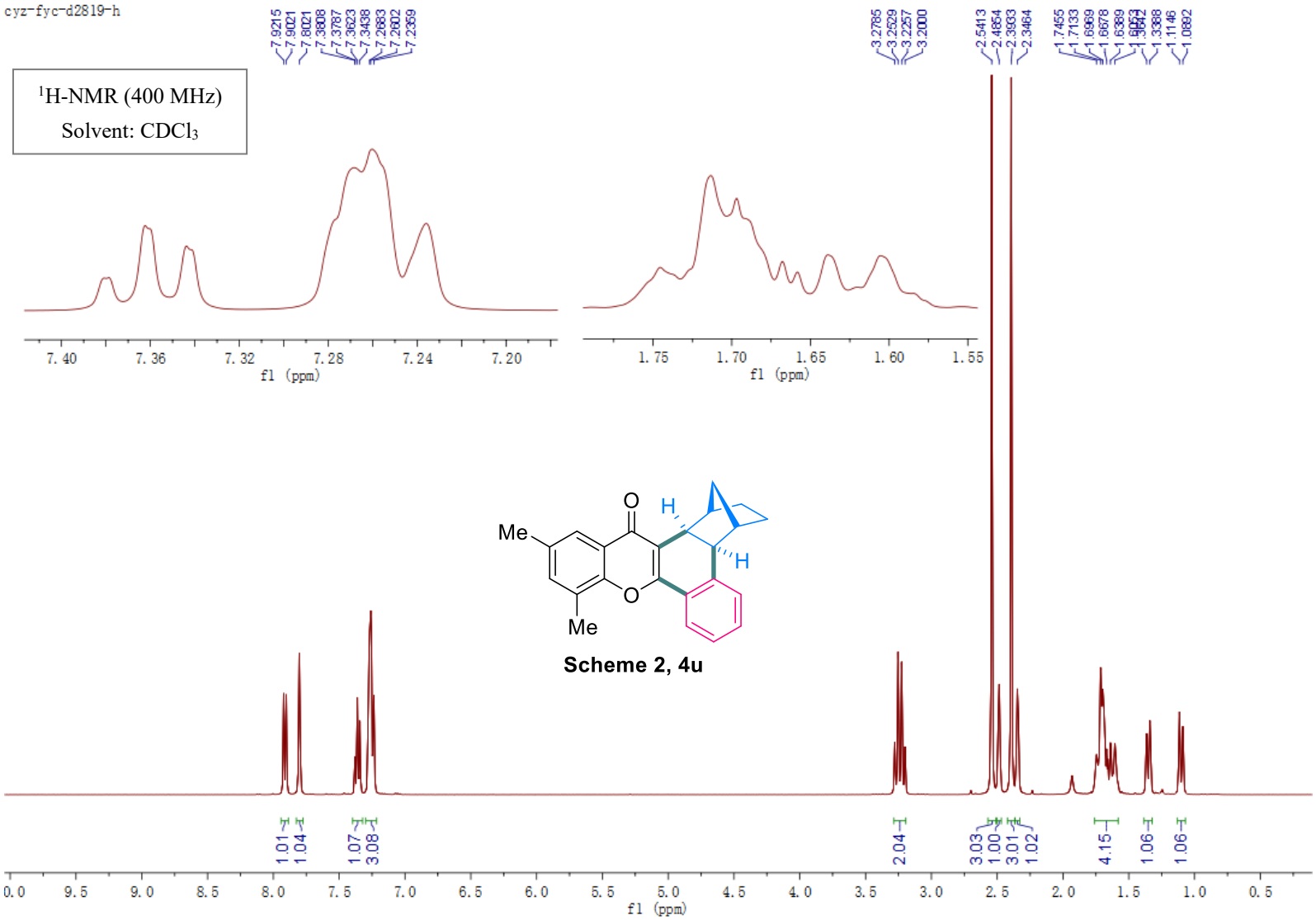


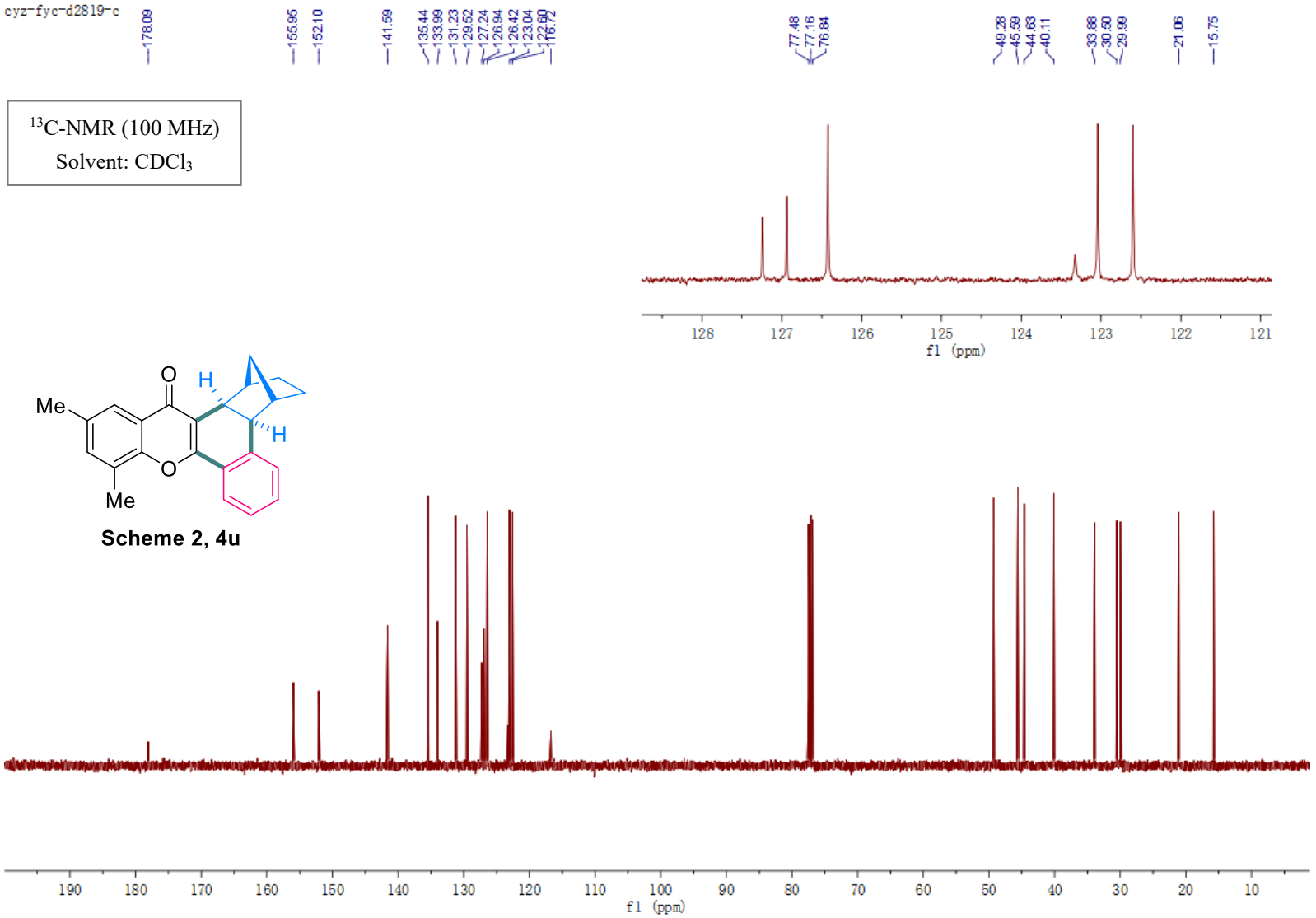

cyz-fyc-d2820-h
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$
f1 (ppm)
Cl
Me
O
H
H
Scheme 2, 4t



^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Scheme 2, 4t


cyz-fyc-d2819-h
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$
f1 (ppm)
Me
Me
O
H
H
Scheme 2, 4u

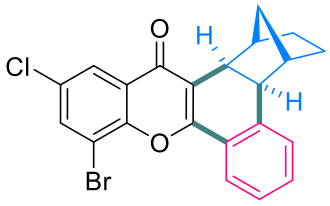


^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Scheme 2, 4u

cyz-fyc-d2840-h

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

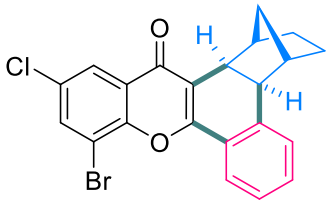


Scheme 2, 4v

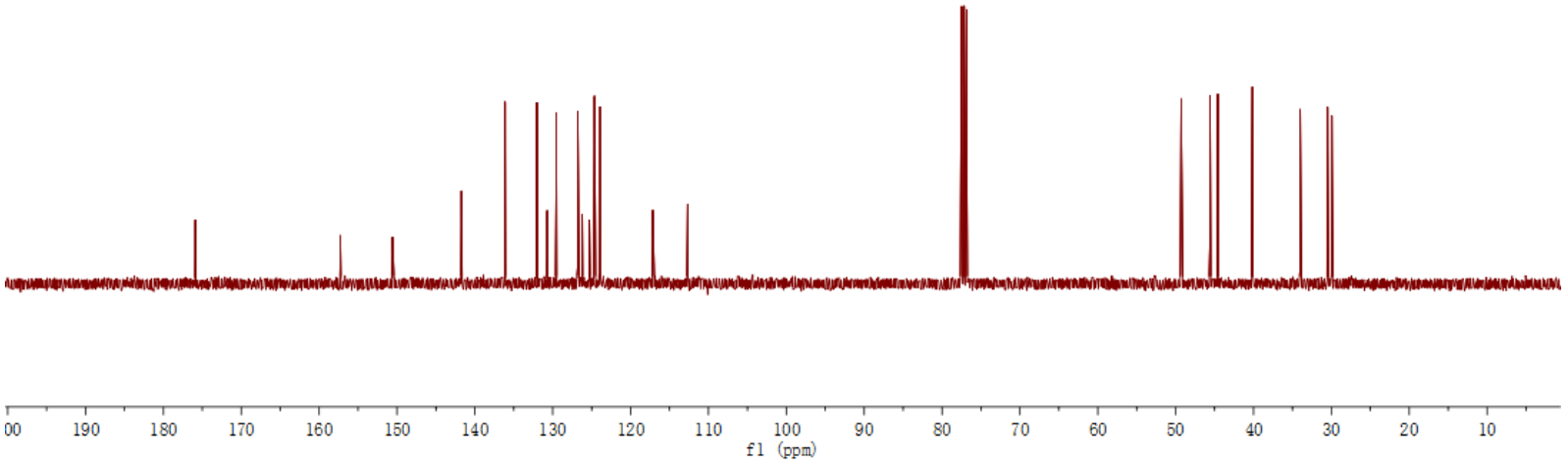
cyz-fyc-d2840-c

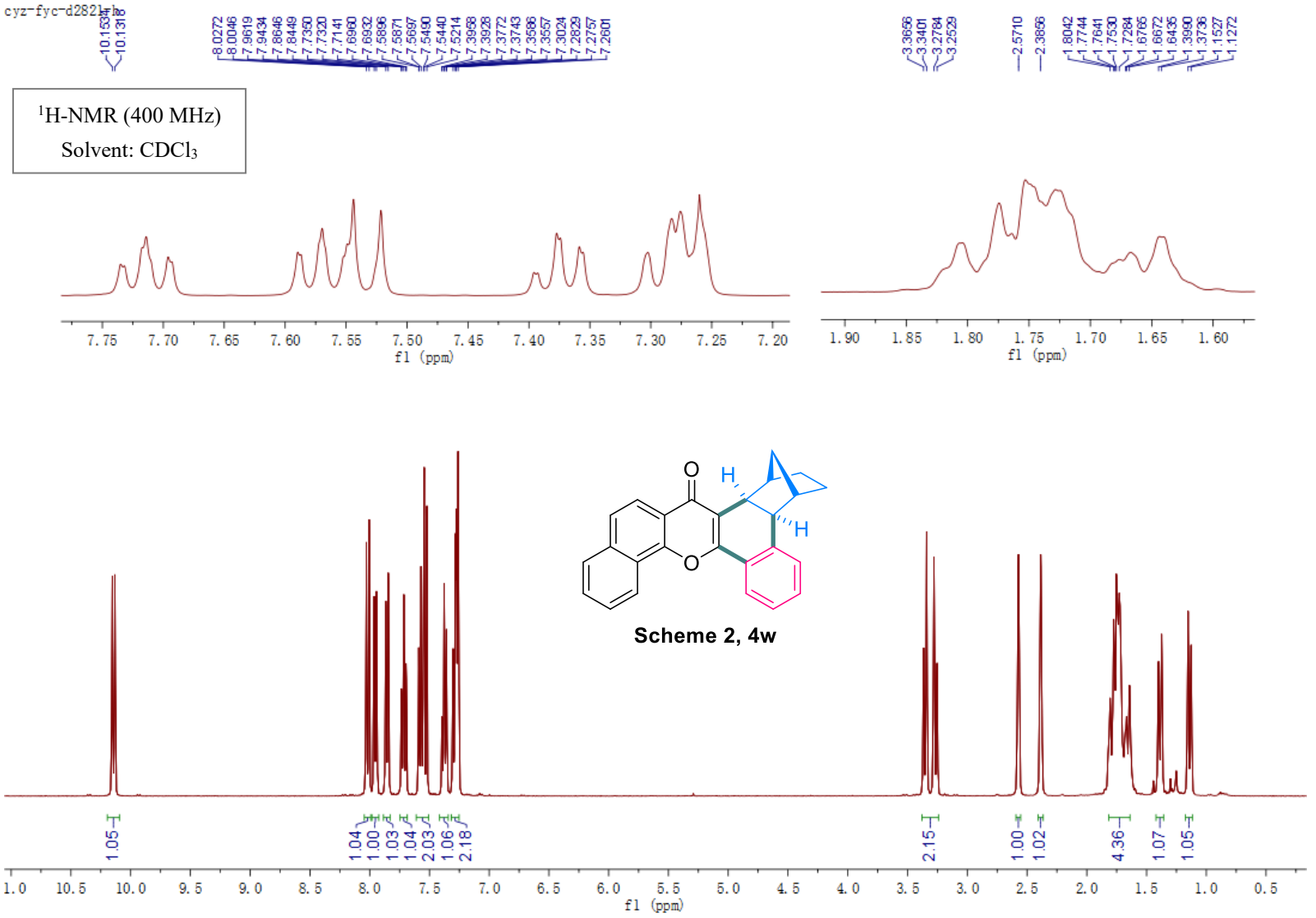
175.89
157.28
150.58
141.71
136.13
132.04
130.71
129.55
126.78
126.21
125.30
124.64
123.90
117.15
112.67
77.48
77.16
76.84
49.28
45.59
44.58
40.13
34.00
30.60
29.95

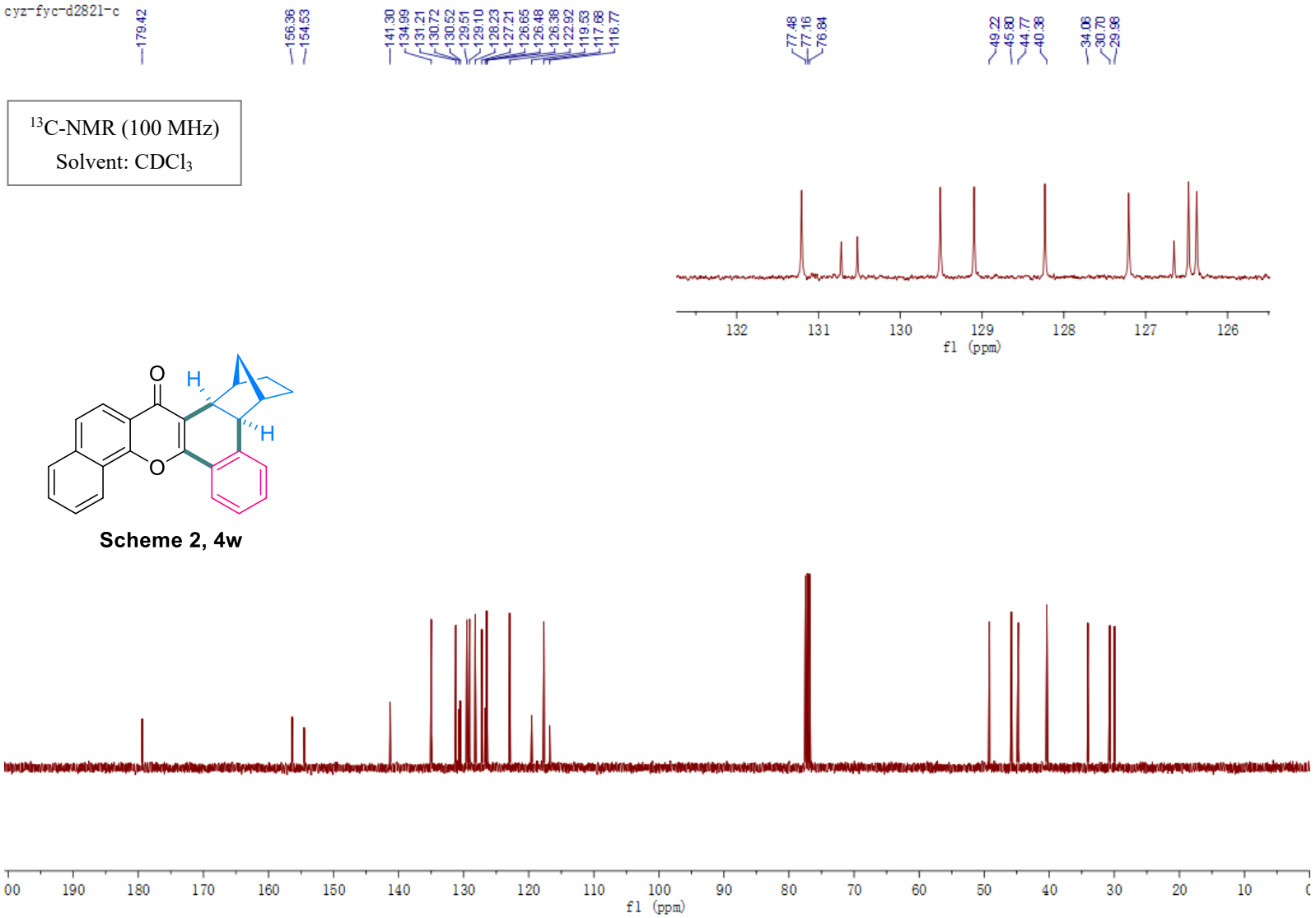
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$



Scheme 2, 4v

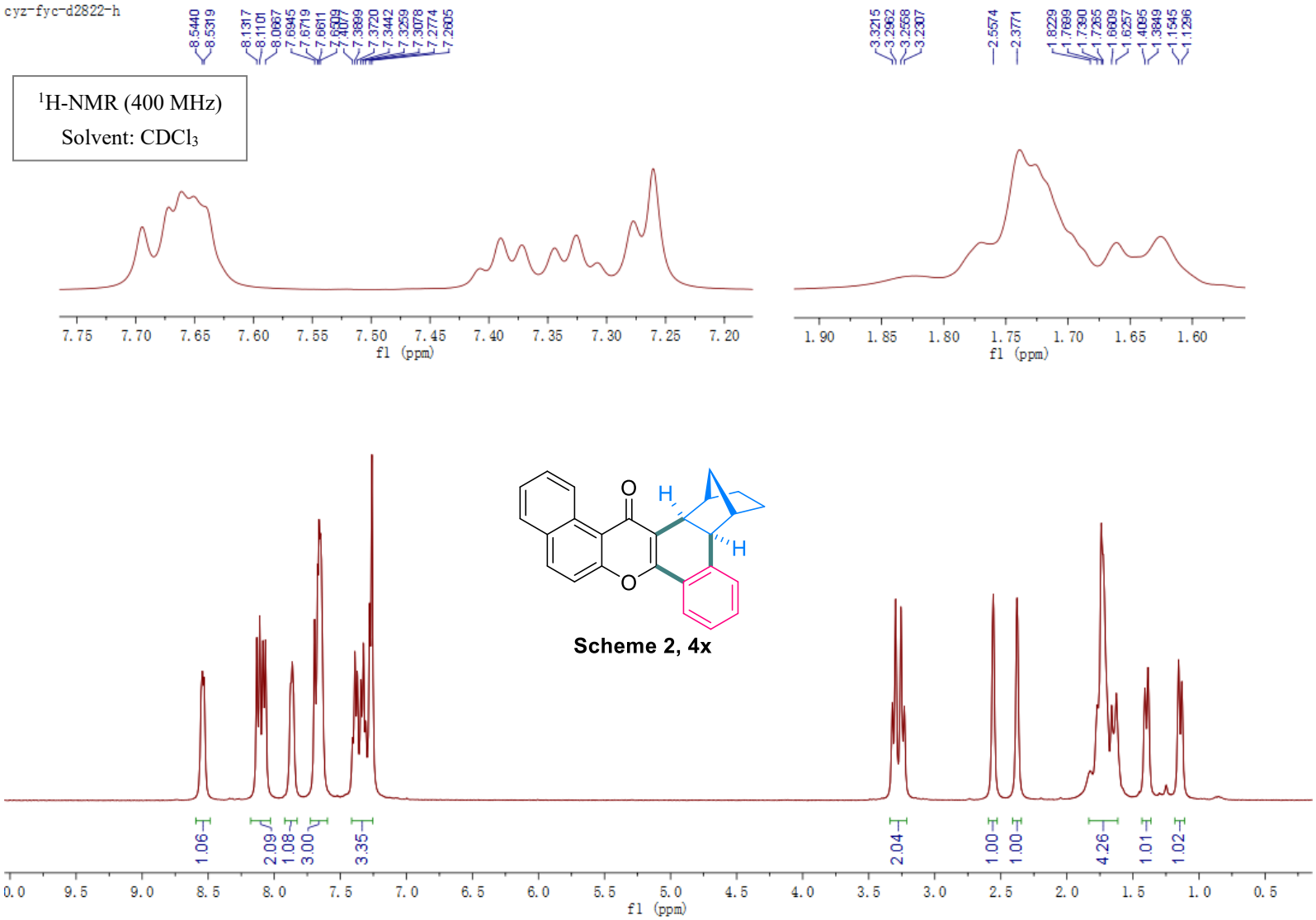


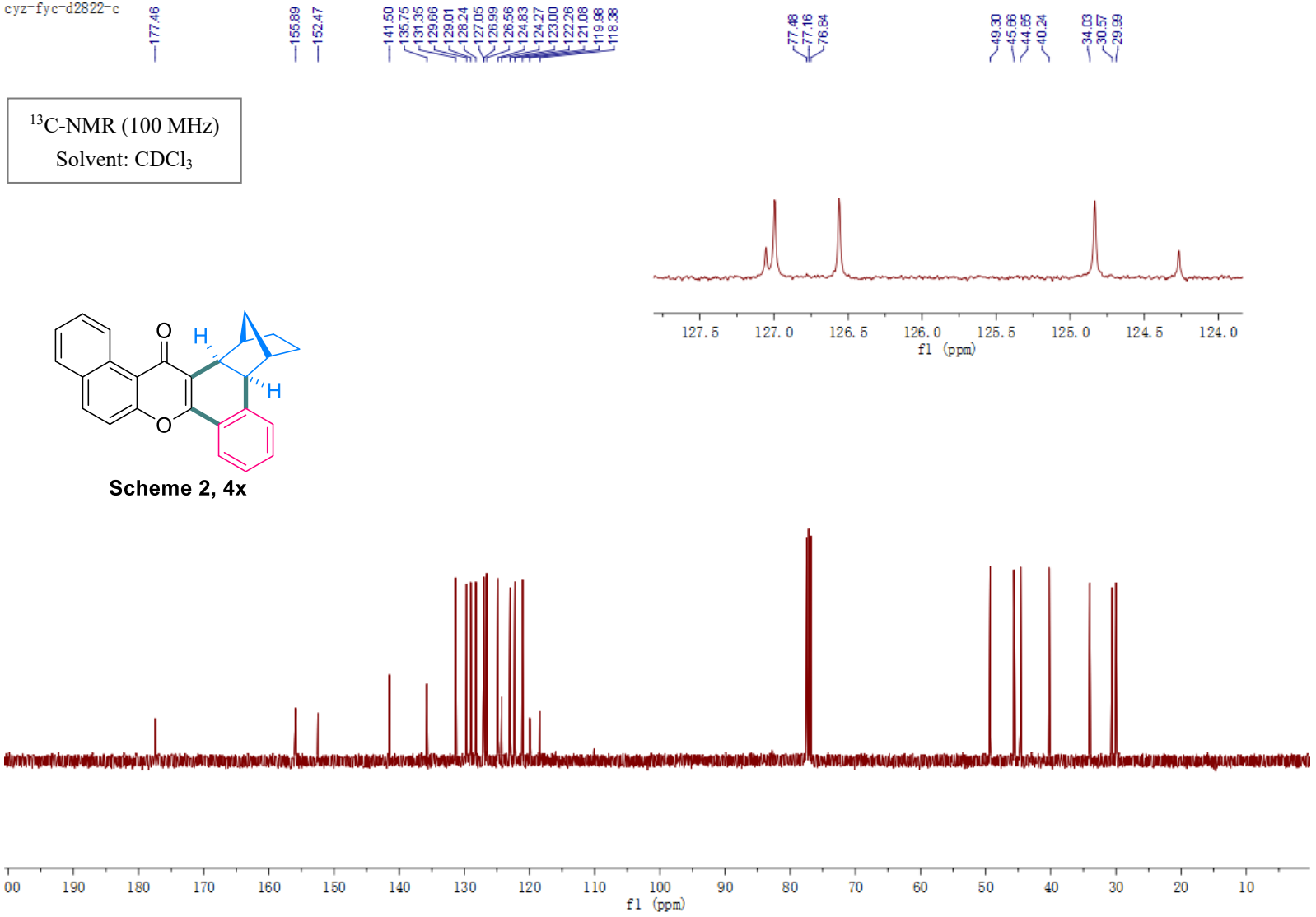

cyz-fyc-d282h
10.1534
10.1318
8.0272
8.0046
7.9619
7.9434
7.8646
7.8449
7.7350
7.7320
7.7141
7.6960
7.6932
7.5896
7.5871
7.5697
7.5490
7.5440
7.5214
7.3958
7.3928
7.3772
7.3743
7.3586
7.3557
7.3024
7.2829
7.2757
7.2601
3.3666
3.3401
3.2784
3.2529
2.5710
2.3866
1.8042
1.7744
1.7641
1.7530
1.7284
1.6766
1.6672
1.6435
1.3990
1.3736
1.1527
1.1272
1H-NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)
f1 (ppm)
O
H
H
O
Scheme 2, 4w
1.05
1.04
1.00
1.03
1.04
2.03
1.06
2.18
2.15
1.00
1.02
4.36
1.07
1.05
f1 (ppm)



^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

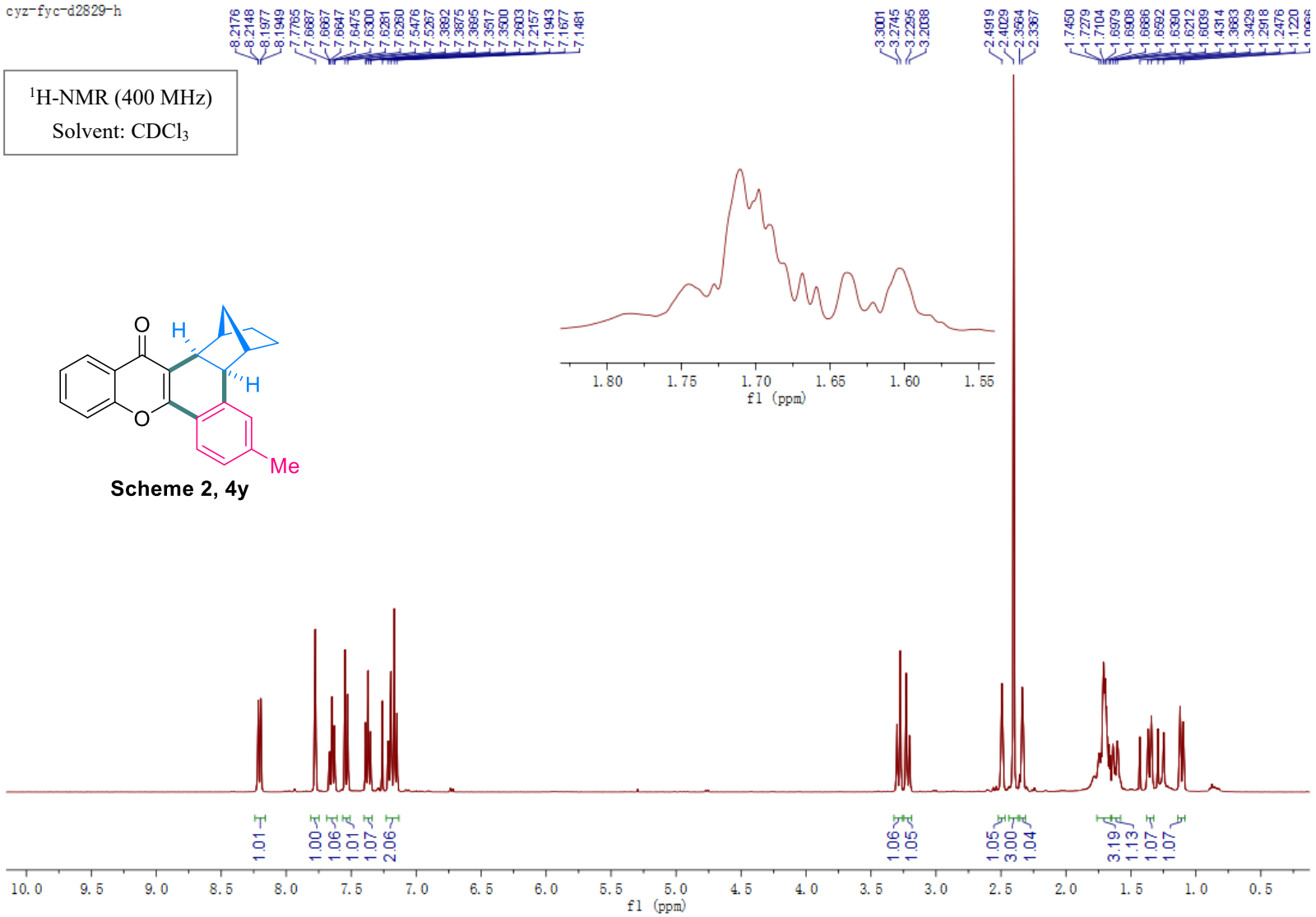
Scheme 2, 4w


cyz-fyc-d2822-h
8.5440
8.5319
8.1317
8.1101
8.0667
7.6945
7.6719
7.6611
7.4077
7.3899
7.3720
7.3442
7.3259
7.3078
7.2774
7.2605
3.3215
3.2962
3.2558
3.2307
2.5574
2.3771
1.8229
1.7899
1.7390
1.7265
1.6609
1.6257
1.4095
1.3849
1.1545
1.1296
1H-NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)
f1 (ppm)
O
H
H
O
Scheme 2, 4x
1.06
2.09
1.08
3.00
3.35
2.04
1.00
1.00
4.26
1.01
1.02
f1 (ppm)

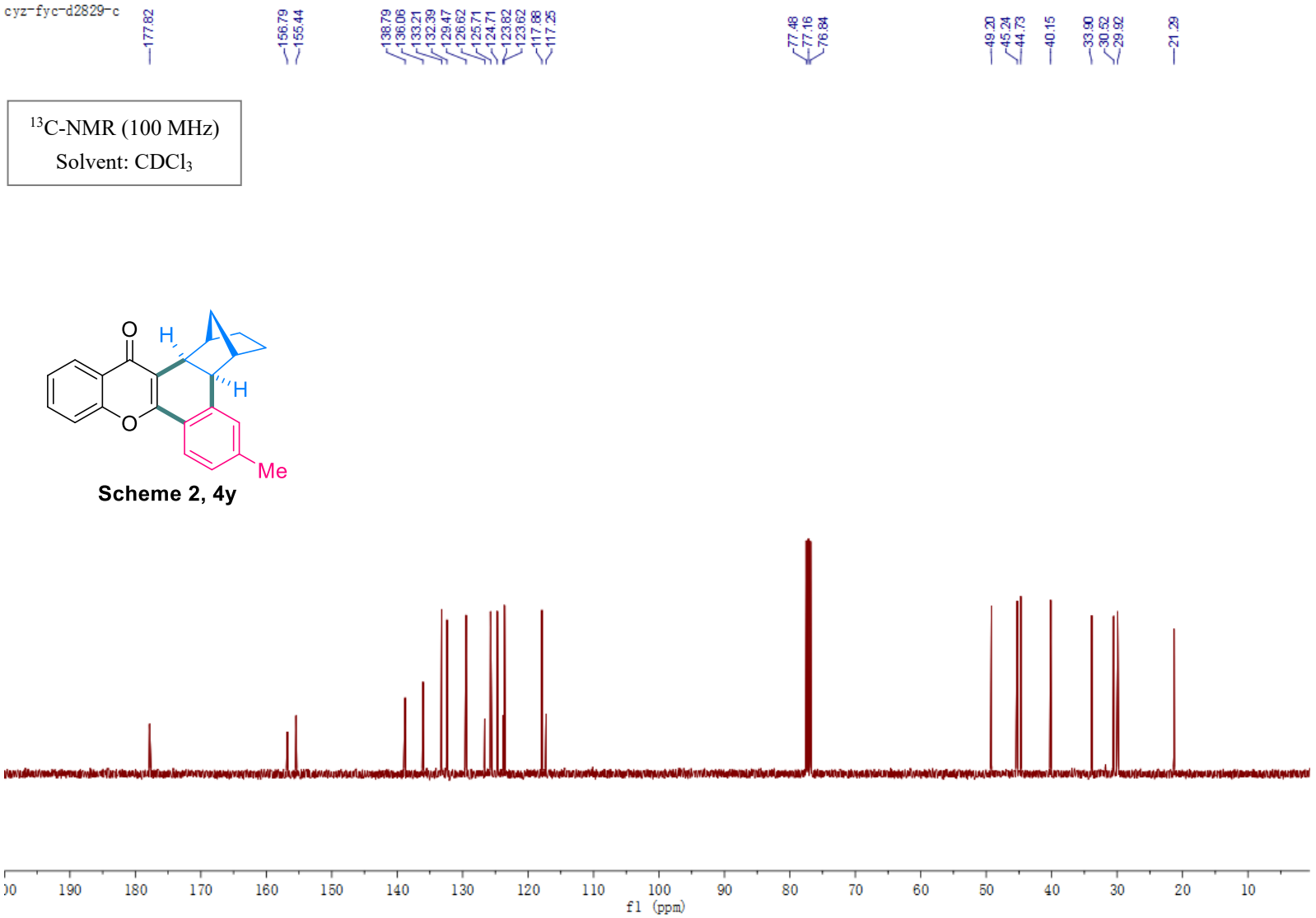


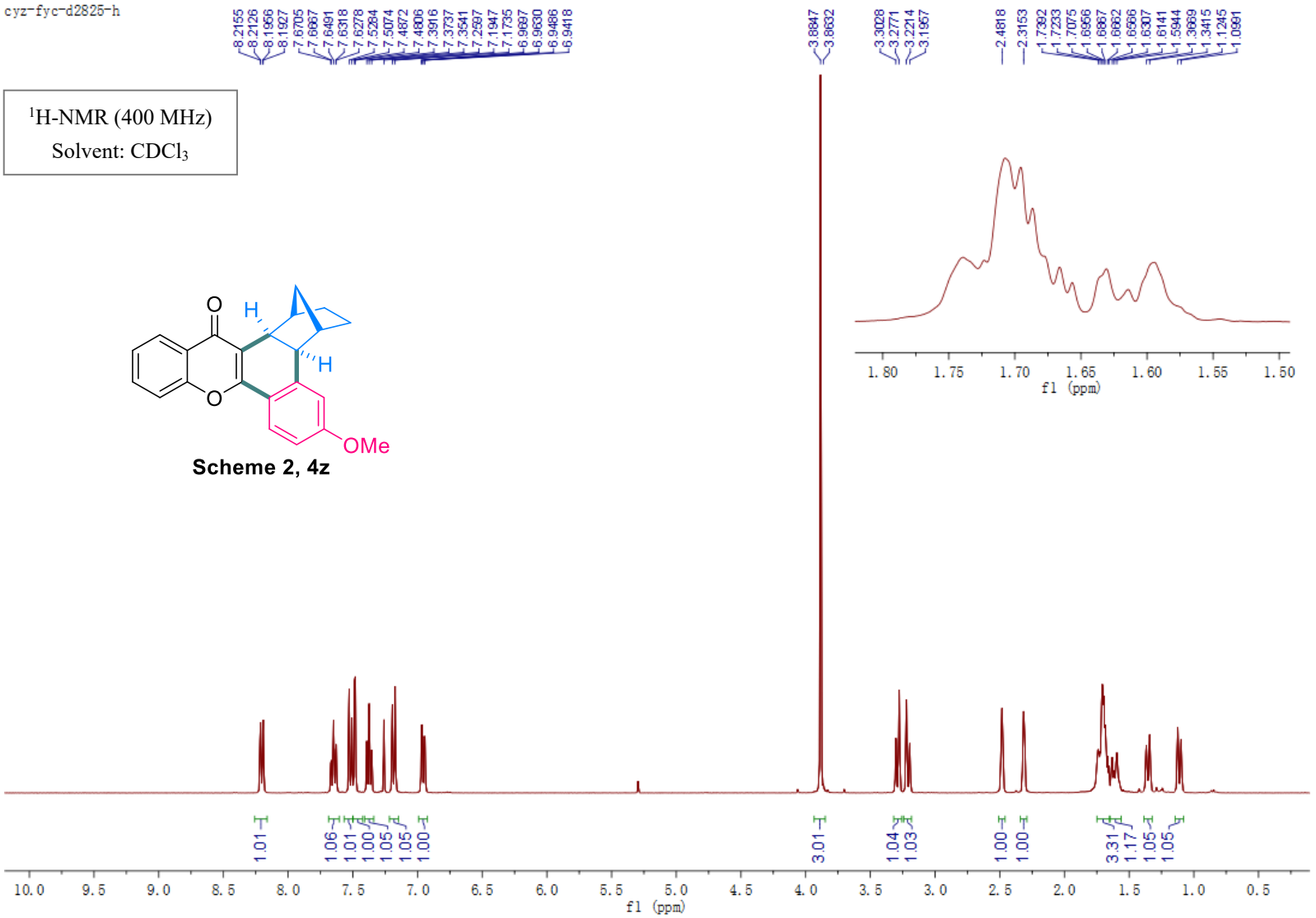
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

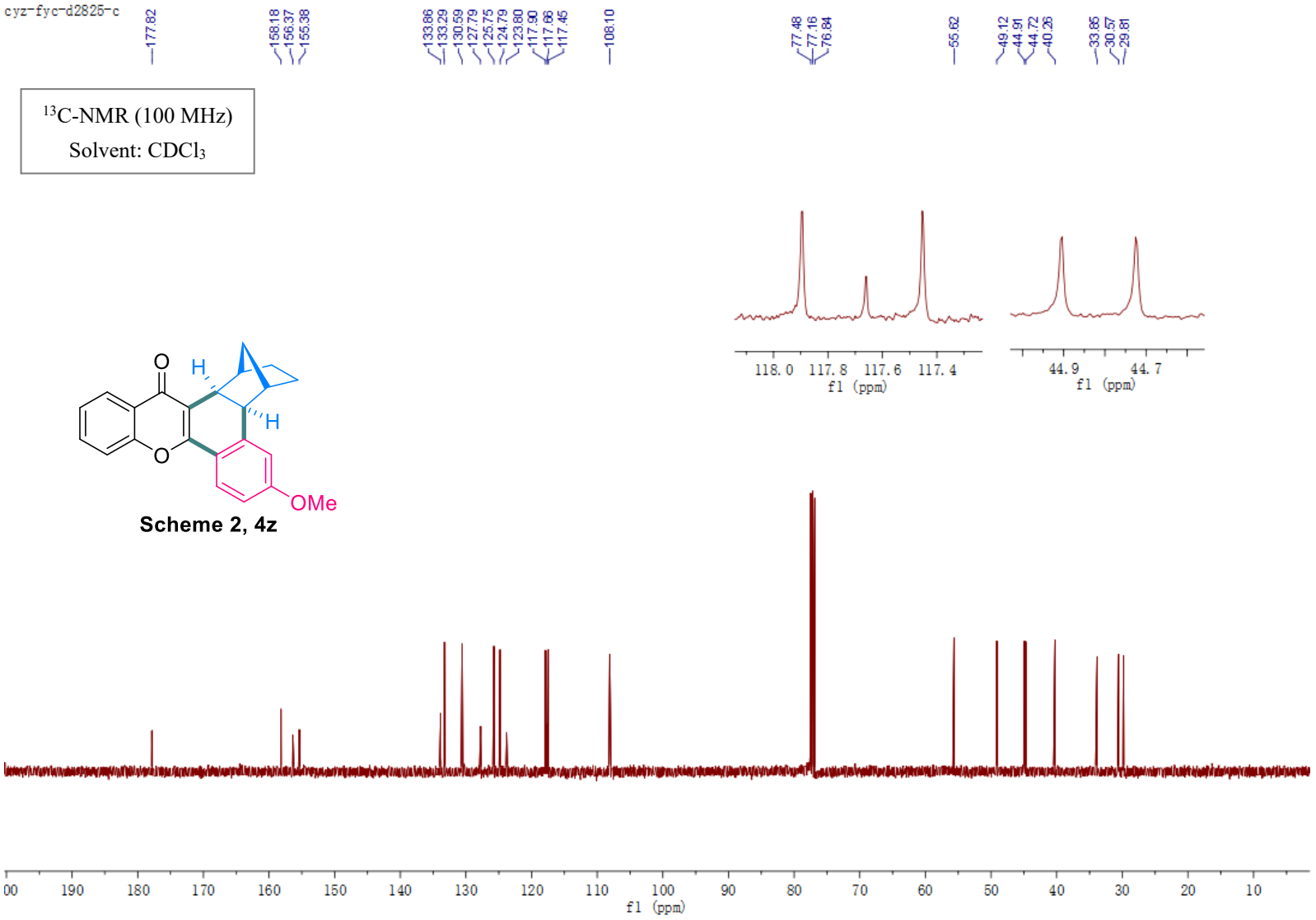
Scheme 2, 4x



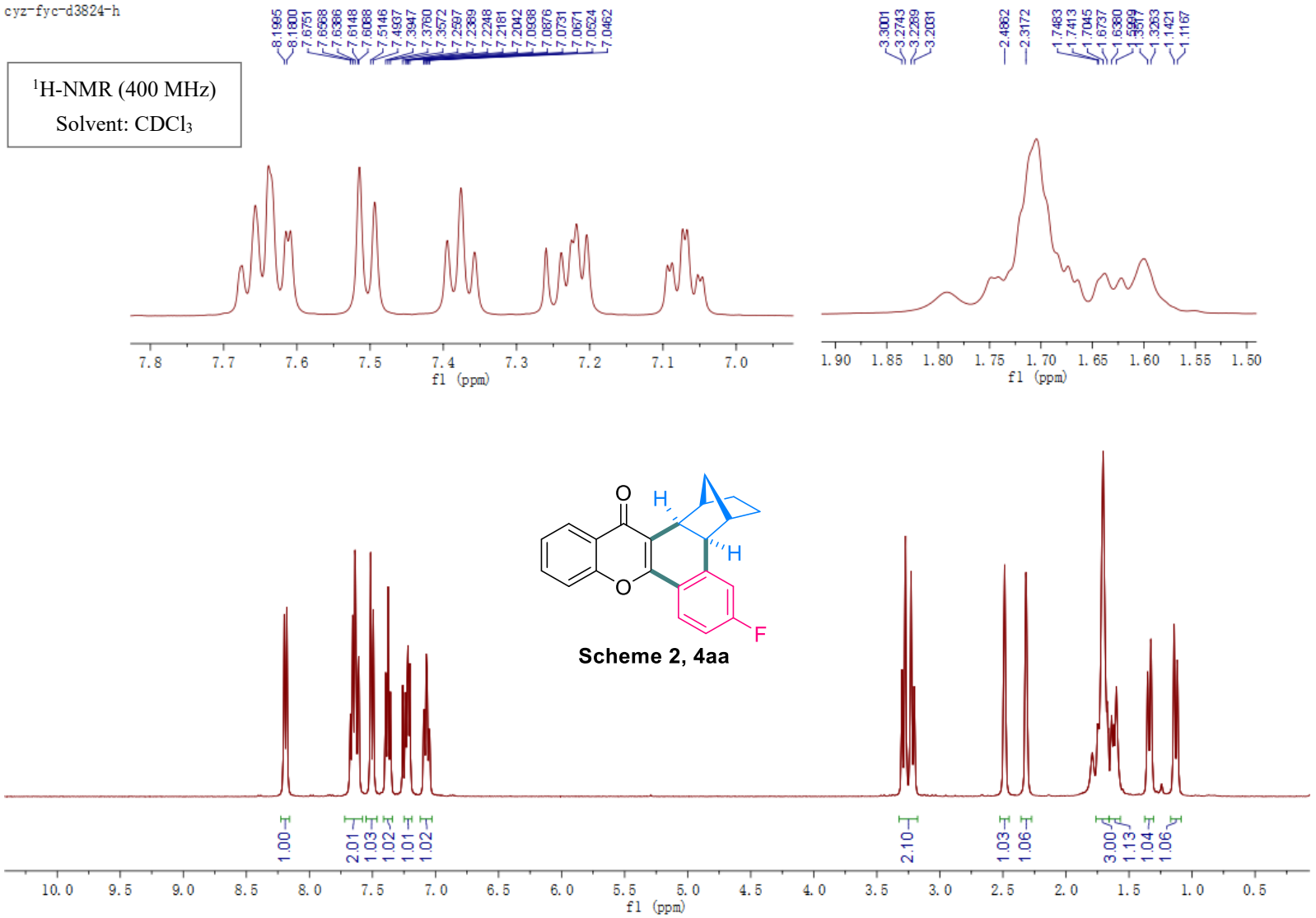
Scheme 2, 4y

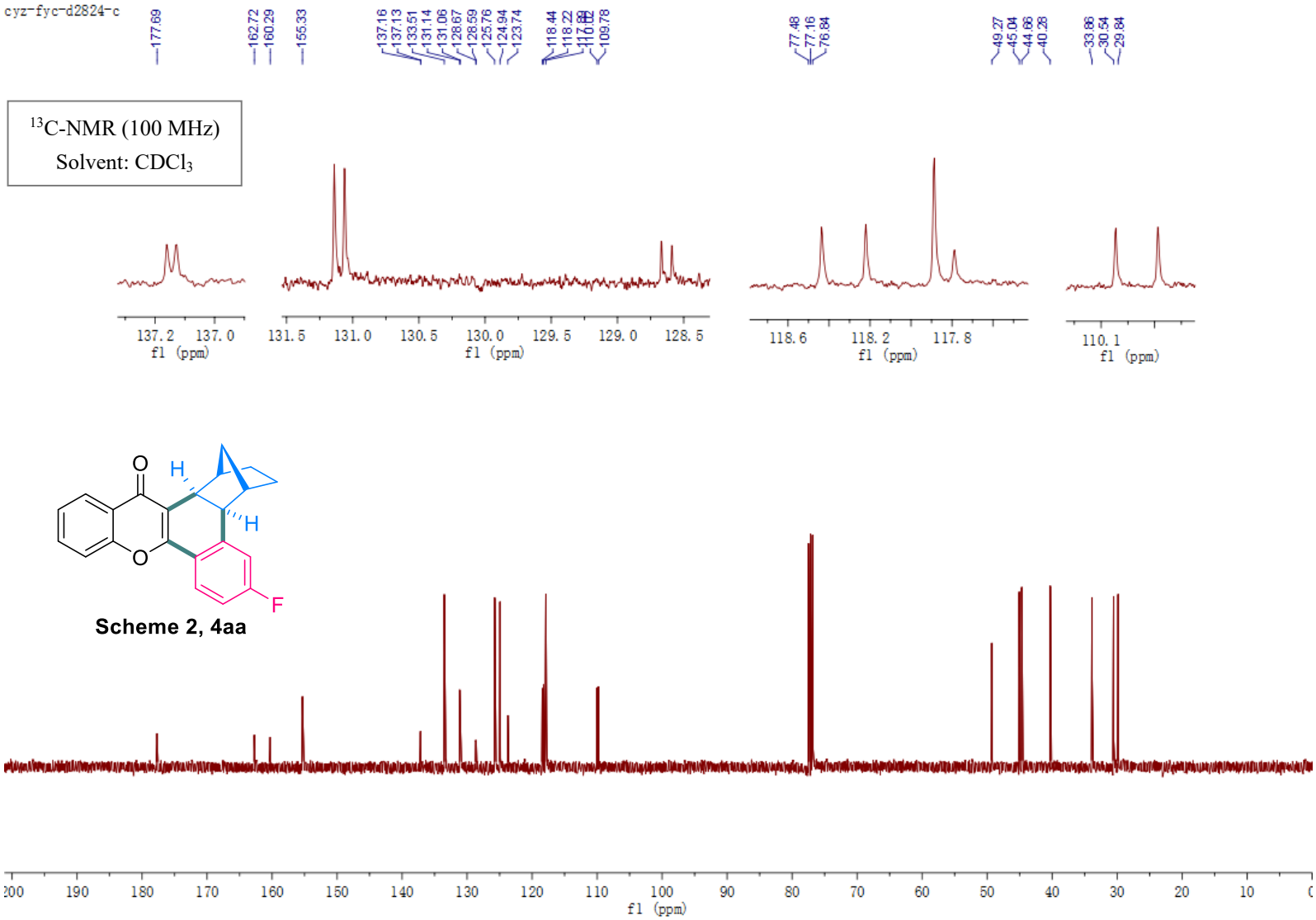

cyz-fyc-d2829-c
177.82
156.79
155.44
138.79
136.06
133.21
132.39
129.47
126.62
125.71
124.71
123.82
123.62
117.88
117.25
77.48
77.16
76.84
49.20
45.24
44.73
40.15
33.90
30.62
29.92
21.29
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$
O
H
H
O
Me
Scheme 2, 4y
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

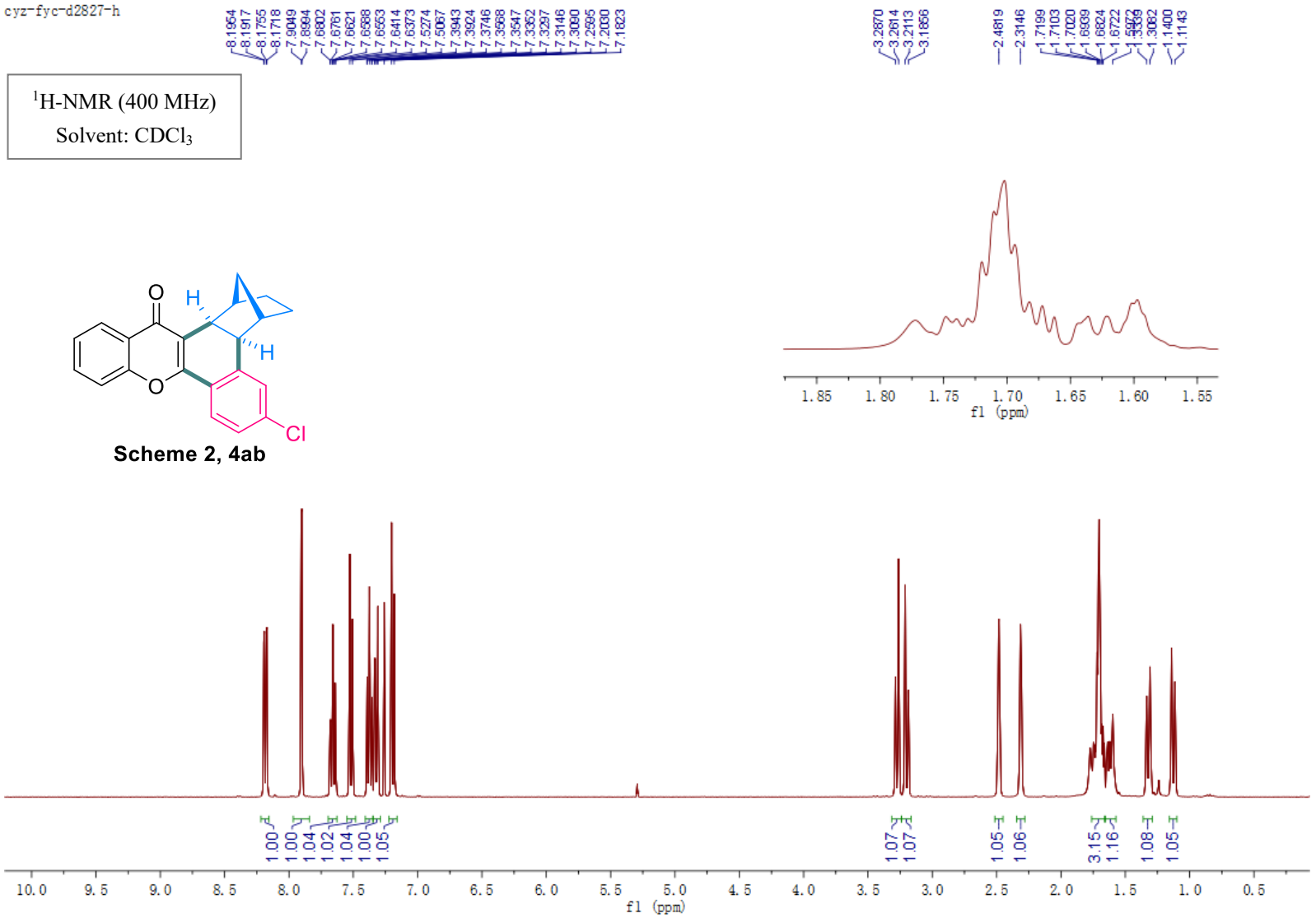

cyz-fyc-d2825-h
8.2155
8.2126
8.1956
8.1927
7.6705
7.6667
7.6491
7.6318
7.6278
7.5284
7.5074
7.4872
7.4806
7.3916
7.3737
7.3541
7.2597
7.1947
7.1735
6.9697
6.9630
6.9486
6.9418
3.8847
3.8632
3.3028
3.2771
3.2214
3.1957
2.4818
2.3153
1.7392
1.7233
1.7075
1.6956
1.6887
1.6862
1.6566
1.6307
1.6141
1.5944
1.3669
1.3415
1.1245
1.0991
1H-NMR (400 MHz)
Solvent: CDCl3
O
H
H
O
OMe
Scheme 2, 4z
1.80
1.75
1.70
1.65
1.60
1.55
1.50
f1 (ppm)
1.01
1.06
1.01
1.00
1.05
1.00
3.01
1.04
1.03
1.00
1.00
3.31
1.17
1.05
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
f1 (ppm)

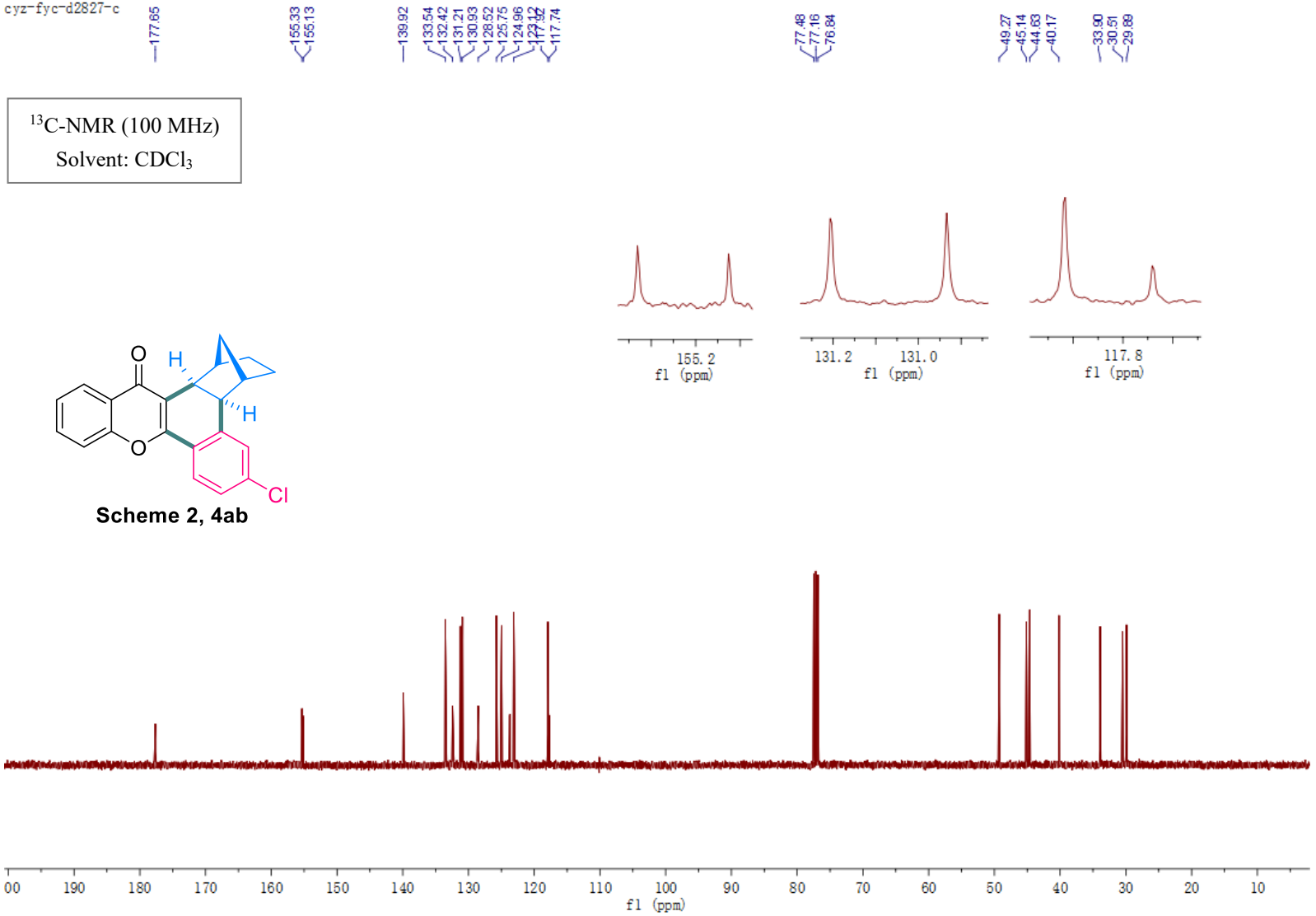

cyz-fyc-d2825-c
177.82
158.18
156.37
155.38
133.86
133.29
130.59
127.79
125.75
124.79
123.80
117.90
117.66
117.45
108.10
77.48
77.16
76.84
55.62
49.12
44.91
44.72
40.26
33.85
30.57
29.81
13C-NMR (100 MHz)
Solvent: CDCl3
O
H
H
O
OMe
118.0
117.8
117.6
117.4
f1 (ppm)
44.9
44.7
f1 (ppm)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Scheme 2, 4z


cyz-fyc-d3824-h
^{1}H-NMR (400 MHz)
Solvent: CDCl$_3$
f1 (ppm)
O
H
H
O
F
Scheme 2, 4aa


cyz-fyc-d2824-c
177.69
162.72
160.29
155.33
137.16
137.13
133.51
131.14
131.06
128.67
128.59
125.76
124.94
123.74
118.44
118.22
117.88
110.02
109.78
77.48
77.16
76.84
49.27
45.04
44.66
40.28
33.86
30.54
29.84
13C-NMR (100 MHz)
Solvent: CDCl3
137.2
137.0
131.5
131.0
130.5
130.0
129.5
129.0
128.5
118.6
118.2
117.8
110.1
f1 (ppm)
O
H
H
O
F
Scheme 2, 4aa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


cyz-fyc-d2827-h
8.1954
8.1917
8.1755
8.1718
7.9049
7.8994
7.6802
7.6761
7.6621
7.6588
7.6553
7.6414
7.6373
7.5274
7.5067
7.3943
7.3924
7.3746
7.3568
7.3547
7.3352
7.3297
7.3146
7.3090
7.2595
7.2030
7.1823
3.2870
3.2614
3.2113
3.1856
2.4819
2.3146
1.7199
1.7103
1.7020
1.6939
1.6824
1.6722
1.3062
1.1400
1.1143
1H-NMR (400 MHz)
Solvent: CDCl3
O
H
H
O
Cl
Scheme 2, 4ab
1.85
1.80
1.75
1.70
1.65
1.60
1.55
f1 (ppm)
1.00
1.00
1.04
1.02
1.04
1.00
1.05
1.07
1.07
1.05
1.06
3.15
1.16
1.08
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
f1 (ppm)

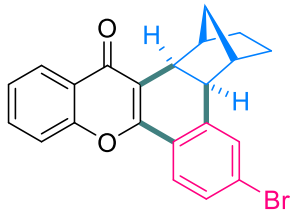


^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

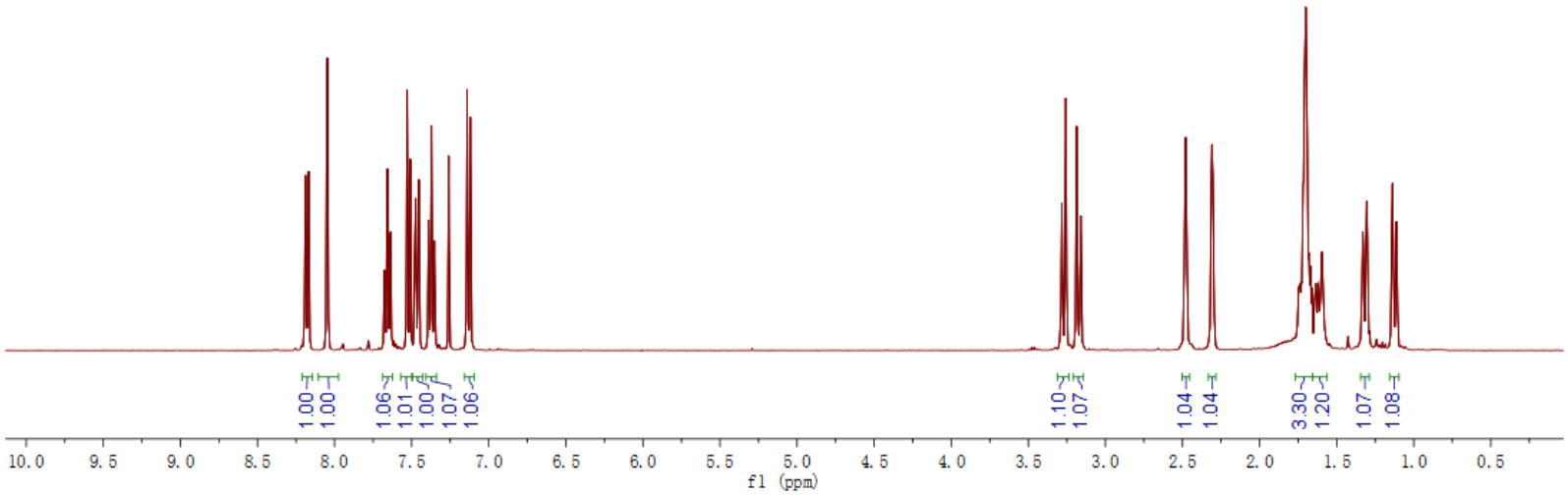
Scheme 2, 4ab

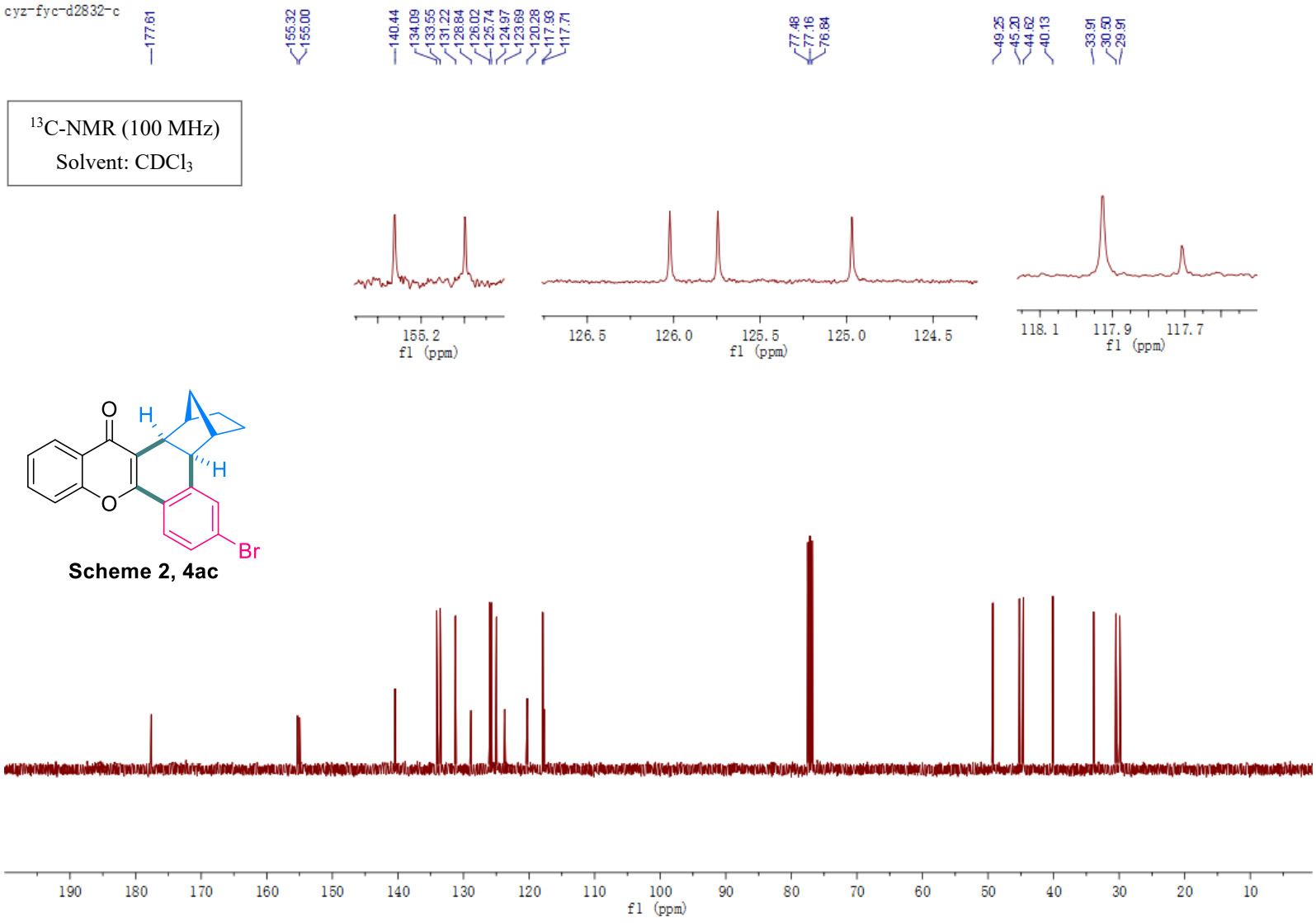
cyz-fyc-d2832-h

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$



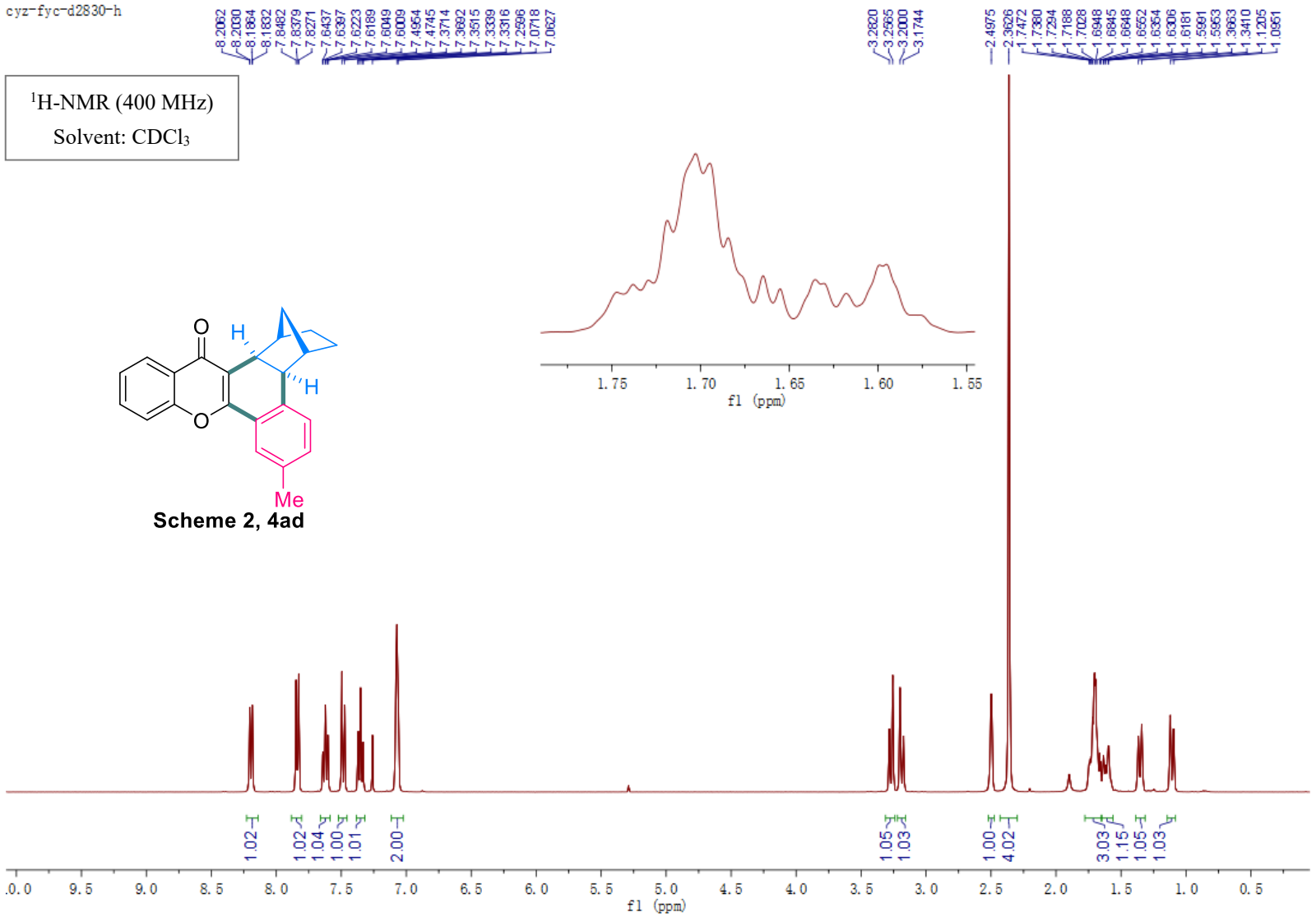
Scheme 2, 4ac



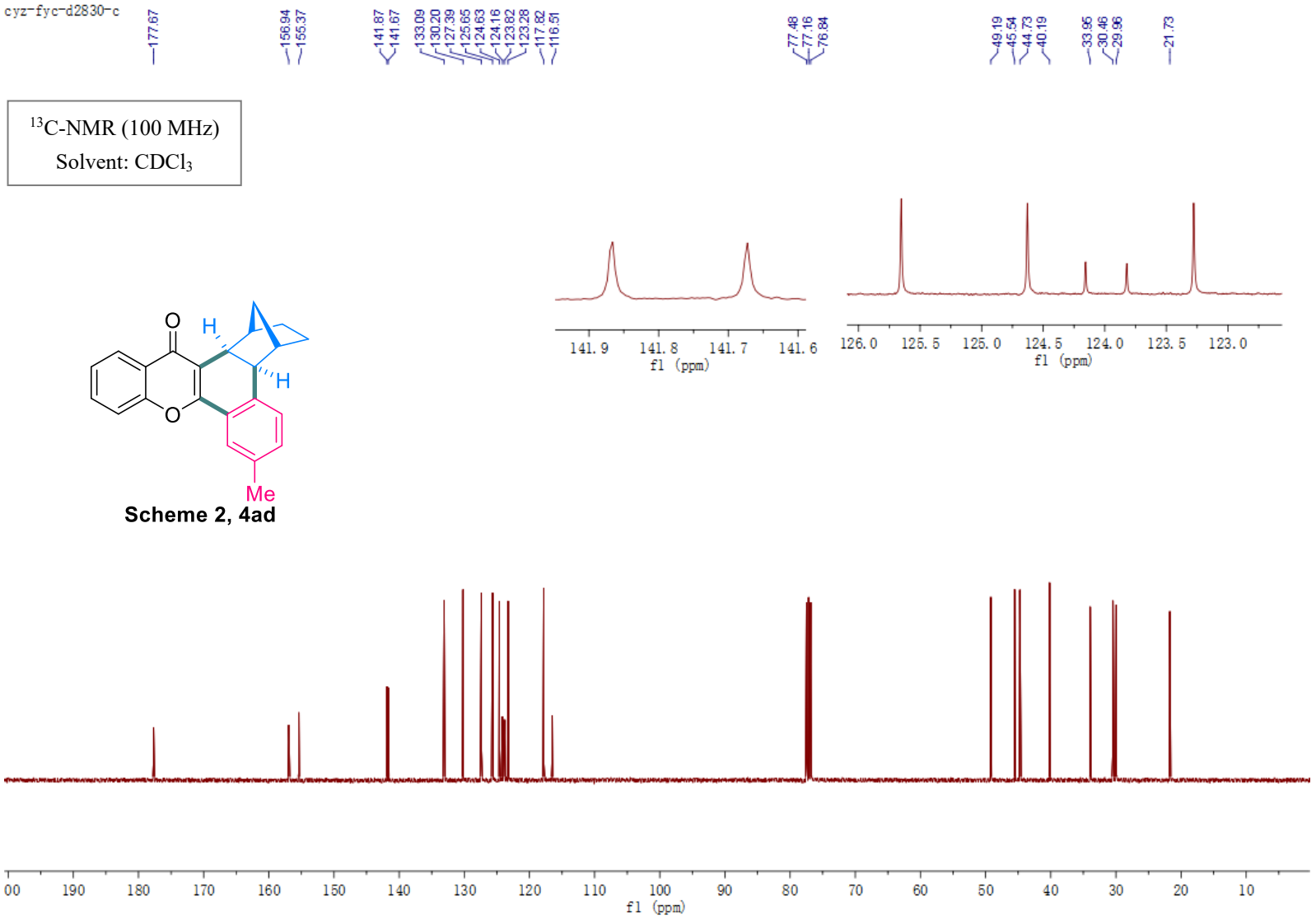


^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Scheme 2, 4ac

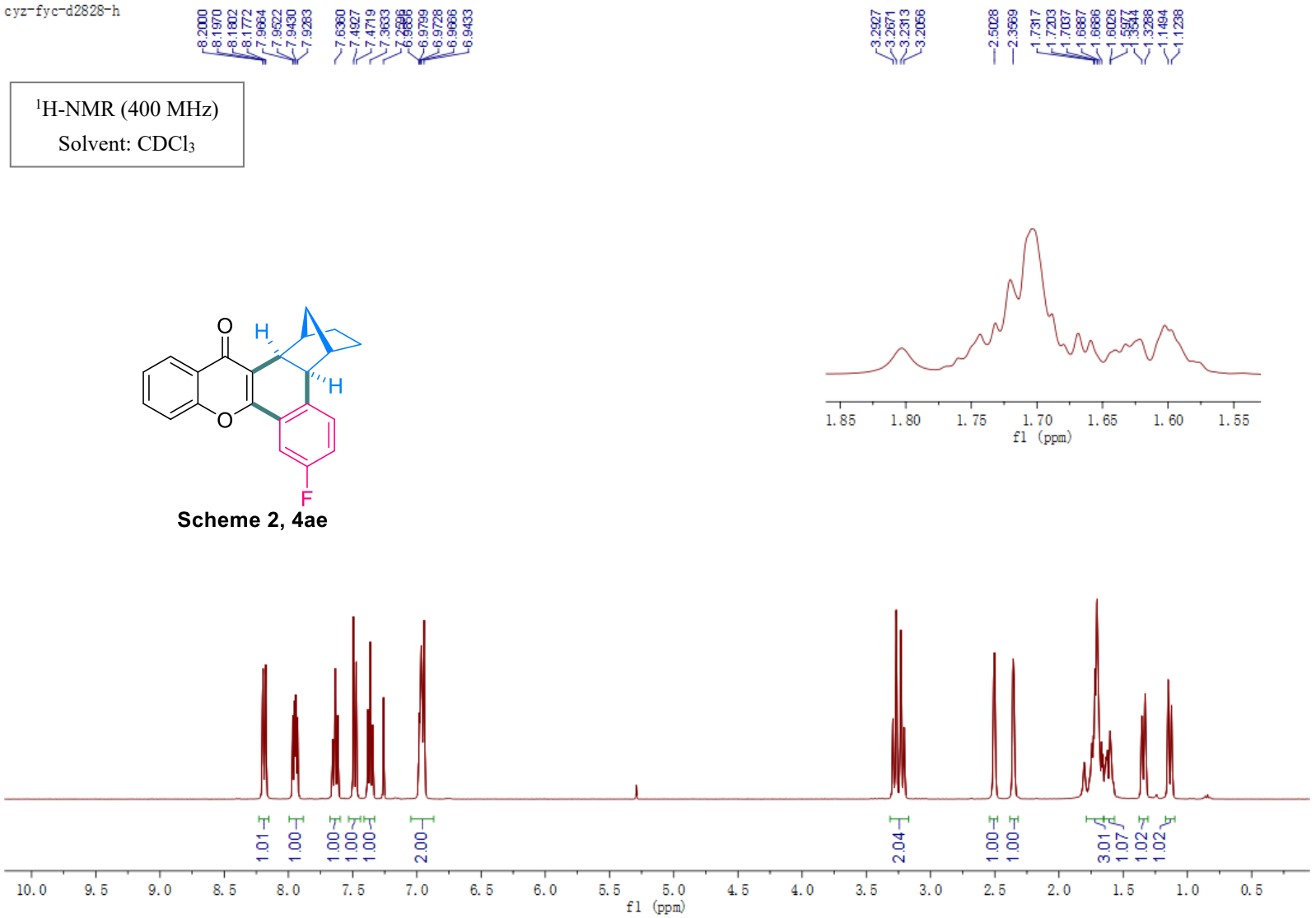


Scheme 2, 4ad

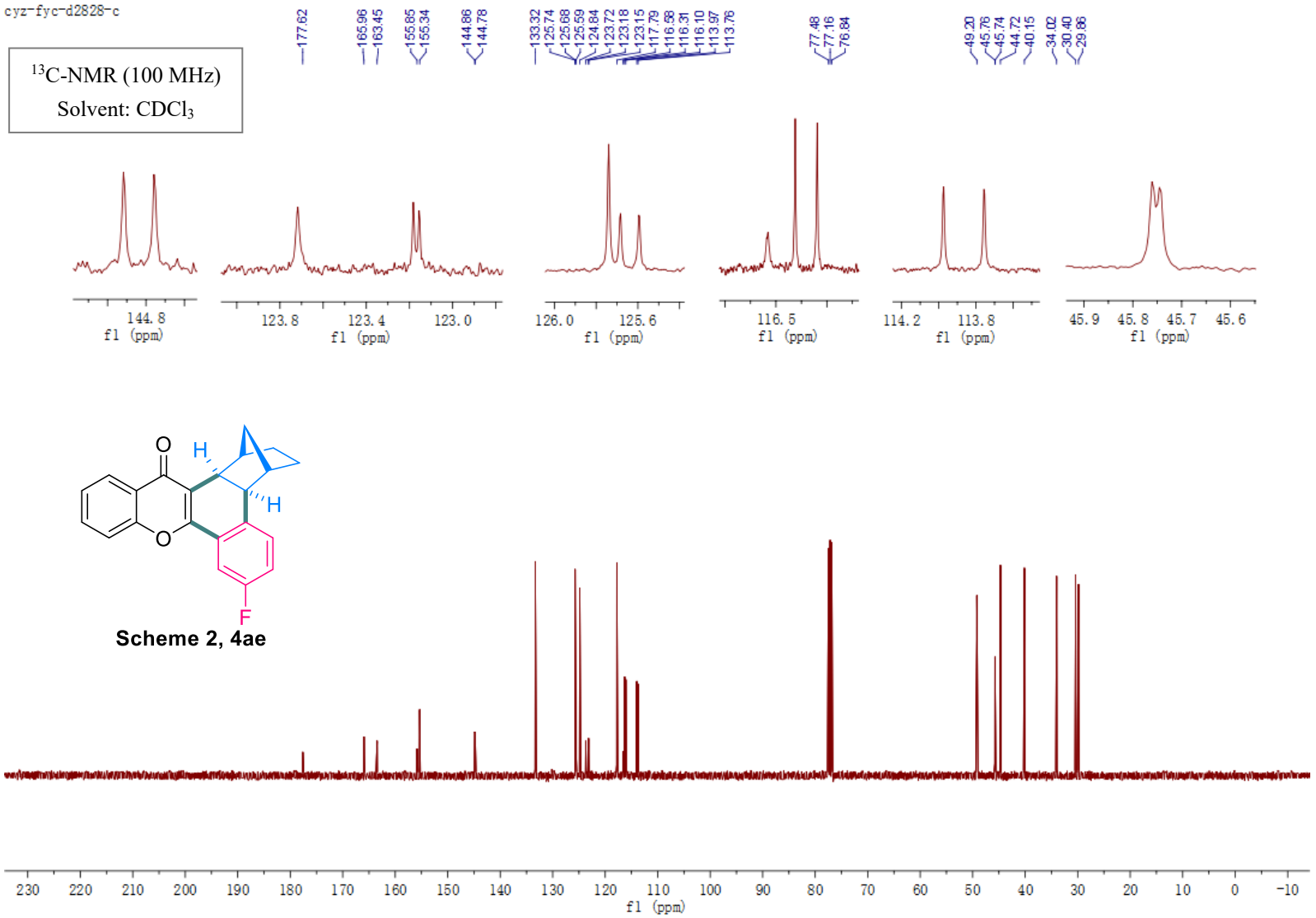


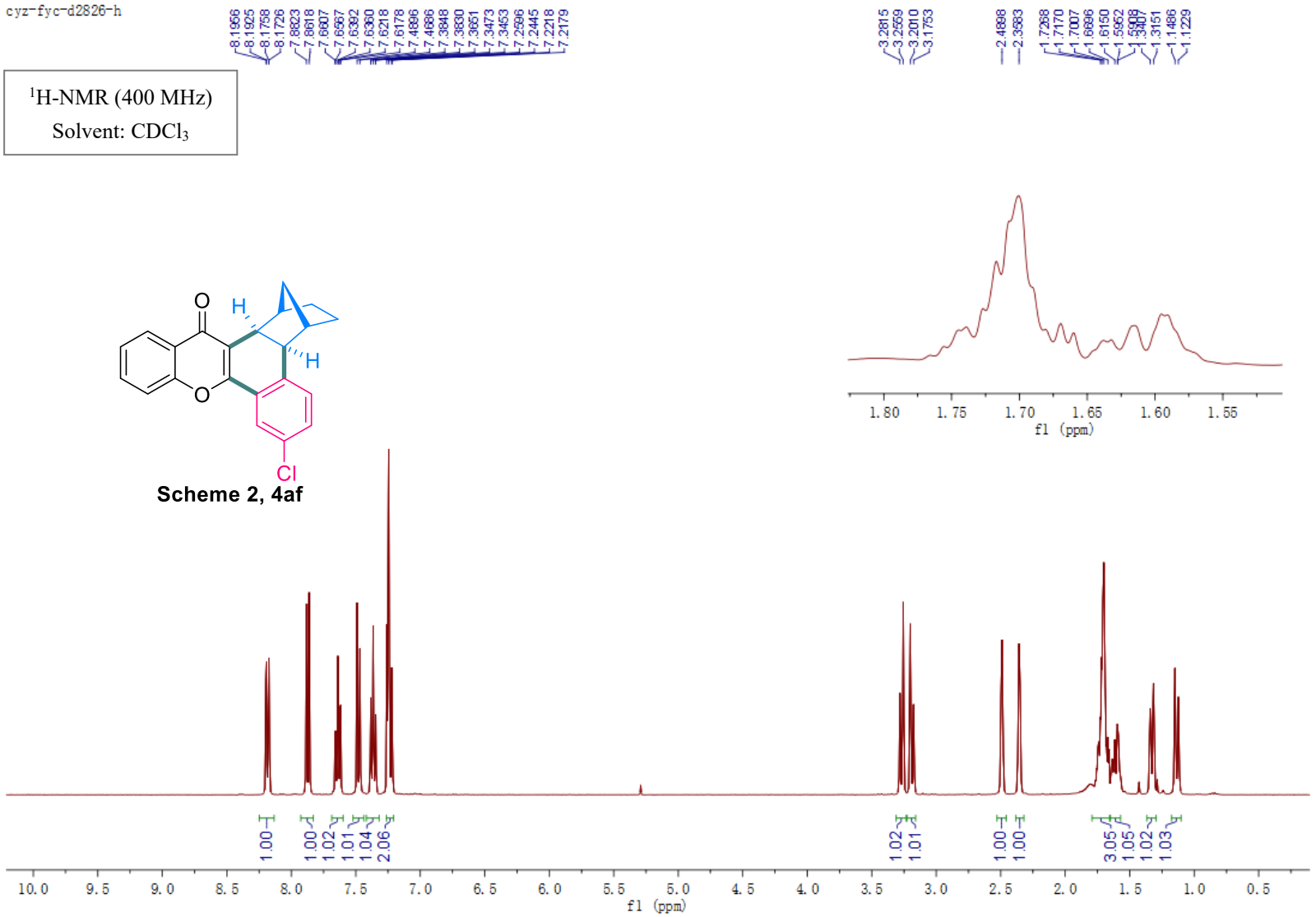
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

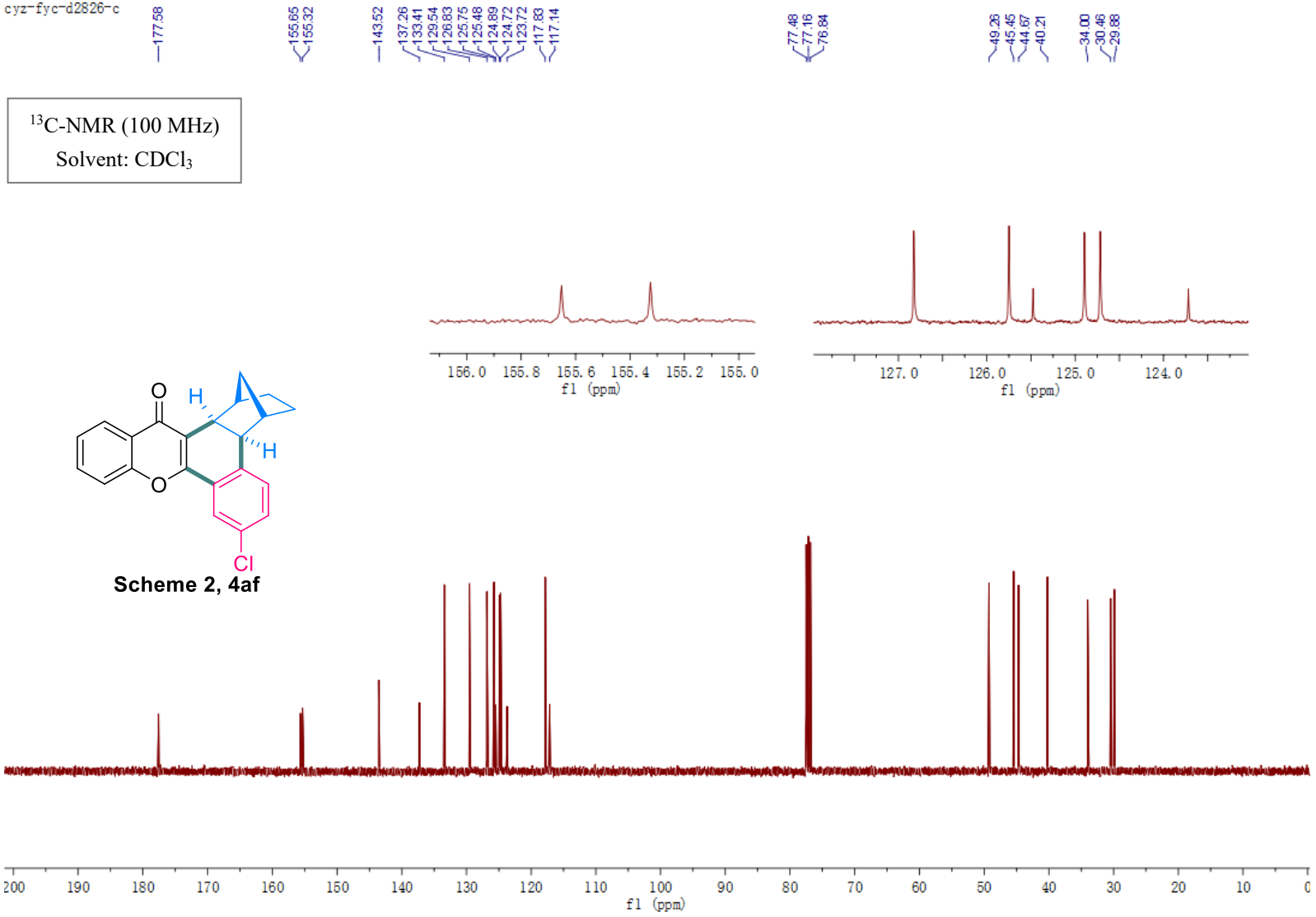
Scheme 2, 4ad


cyz-fyc-d2828-h
8.2000
8.1970
8.1802
8.1772
7.9664
7.9522
7.9430
7.9283
7.6360
7.4927
7.4719
7.3633
6.9799
6.9728
6.9666
6.9433
3.2927
3.2671
3.2313
3.2056
2.5028
2.3569
1.7317
1.7203
1.7037
1.6887
1.6666
1.6026
1.5957
1.3544
1.3268
1.1494
1.1238
1H-NMR (400 MHz)
Solvent: CDCl3
O
H
H
O
F
1.85
1.80
1.75
1.70
1.65
1.60
1.55
f1 (ppm)
1.01
1.00
1.00
1.00
1.00
2.00
2.04
1.00
1.00
3.01
1.07
1.02
1.02
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, 4ae


cyz-fyc-d2828-c
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$
177.62
165.96
163.45
155.85
155.34
144.86
144.78
133.32
125.74
125.68
125.59
124.84
123.72
123.18
123.15
117.79
116.58
116.31
116.10
113.97
113.76
77.48
77.16
76.84
49.20
45.76
45.74
44.72
40.15
34.02
30.40
29.86
144.8
123.8
123.4
123.0
126.0
125.6
116.5
114.2
113.8
45.9
45.8
45.7
45.6
f1 (ppm)
O
H
H
O
F
Scheme 2, 4ae
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)

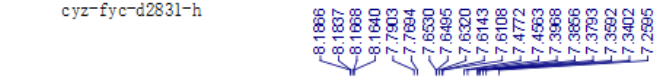

cyz-fyc-d2826-h
8.1956
8.1925
8.1758
8.1726
7.8823
7.8618
7.6607
7.6567
7.6392
7.6360
7.6218
7.6178
7.4896
7.4666
7.3848
7.3830
7.3651
7.3473
7.3453
7.2596
7.2445
7.2218
7.2179
3.2815
3.2559
3.2010
3.1753
2.4898
2.3583
1.7268
1.7170
1.7007
1.6696
1.6150
1.5952
1.5308
1.3407
1.3151
1.1486
1.1229
1H-NMR (400 MHz)
Solvent: CDCl3
O
H
H
O
Cl
Scheme 2, 4af
1.80
1.75
1.70
1.65
1.60
1.55
f1 (ppm)
1.00
1.00
1.02
1.01
1.04
2.06
1.02
1.01
1.00
1.00
3.05
1.05
1.02
1.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

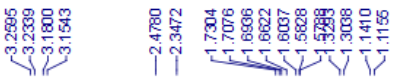


^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

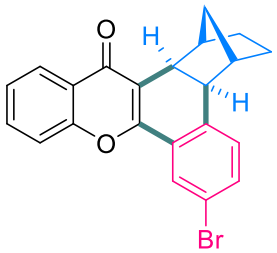
Scheme 2, 4af

cyz-fyc-d2831-h

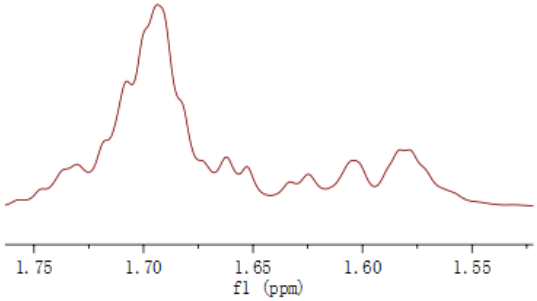


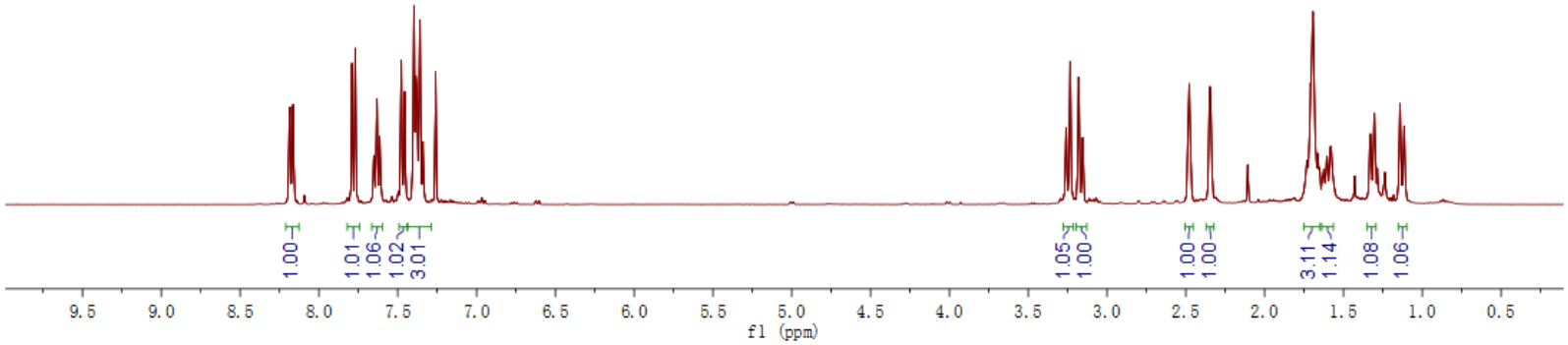


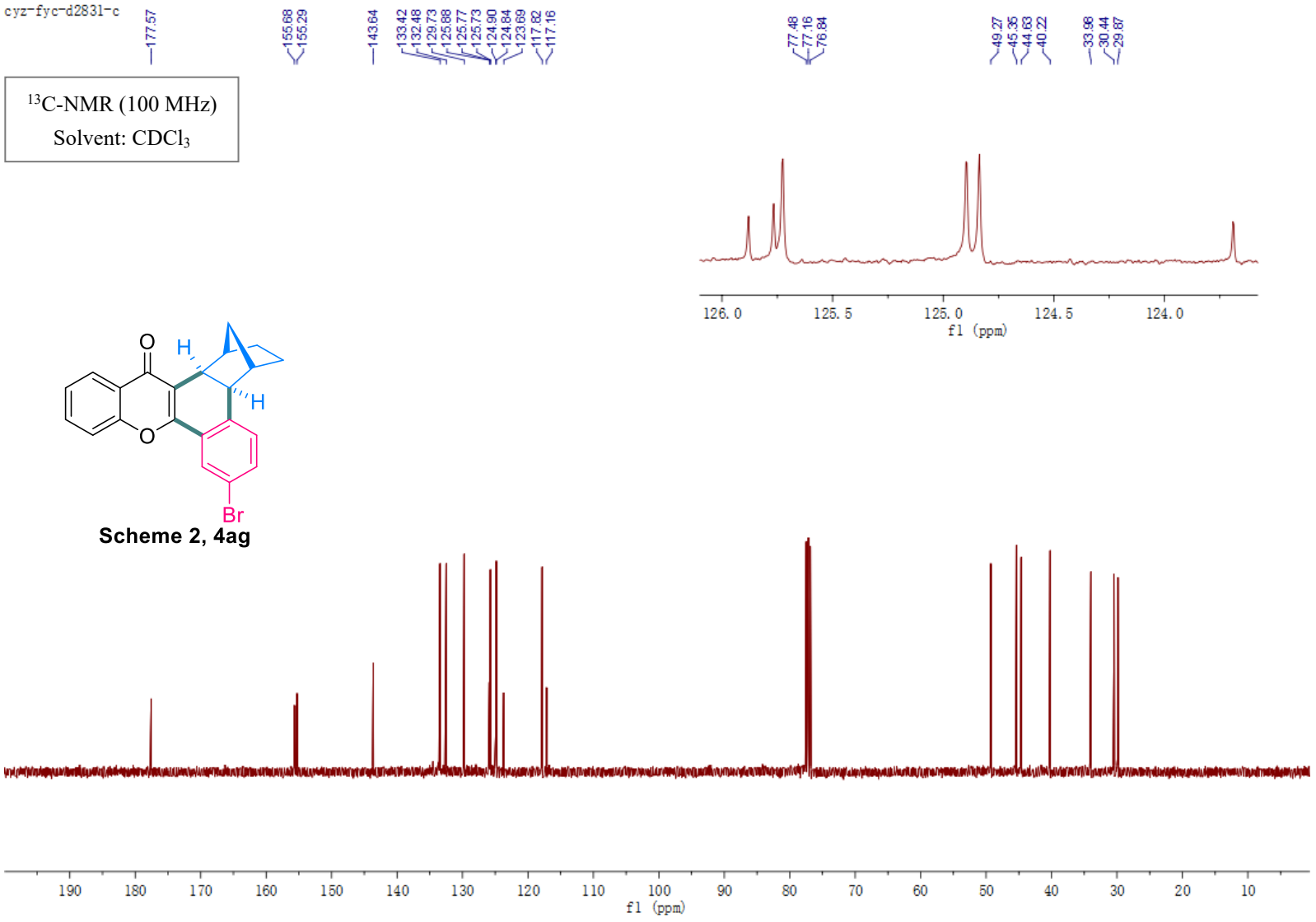
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$



Scheme 2, 4ag

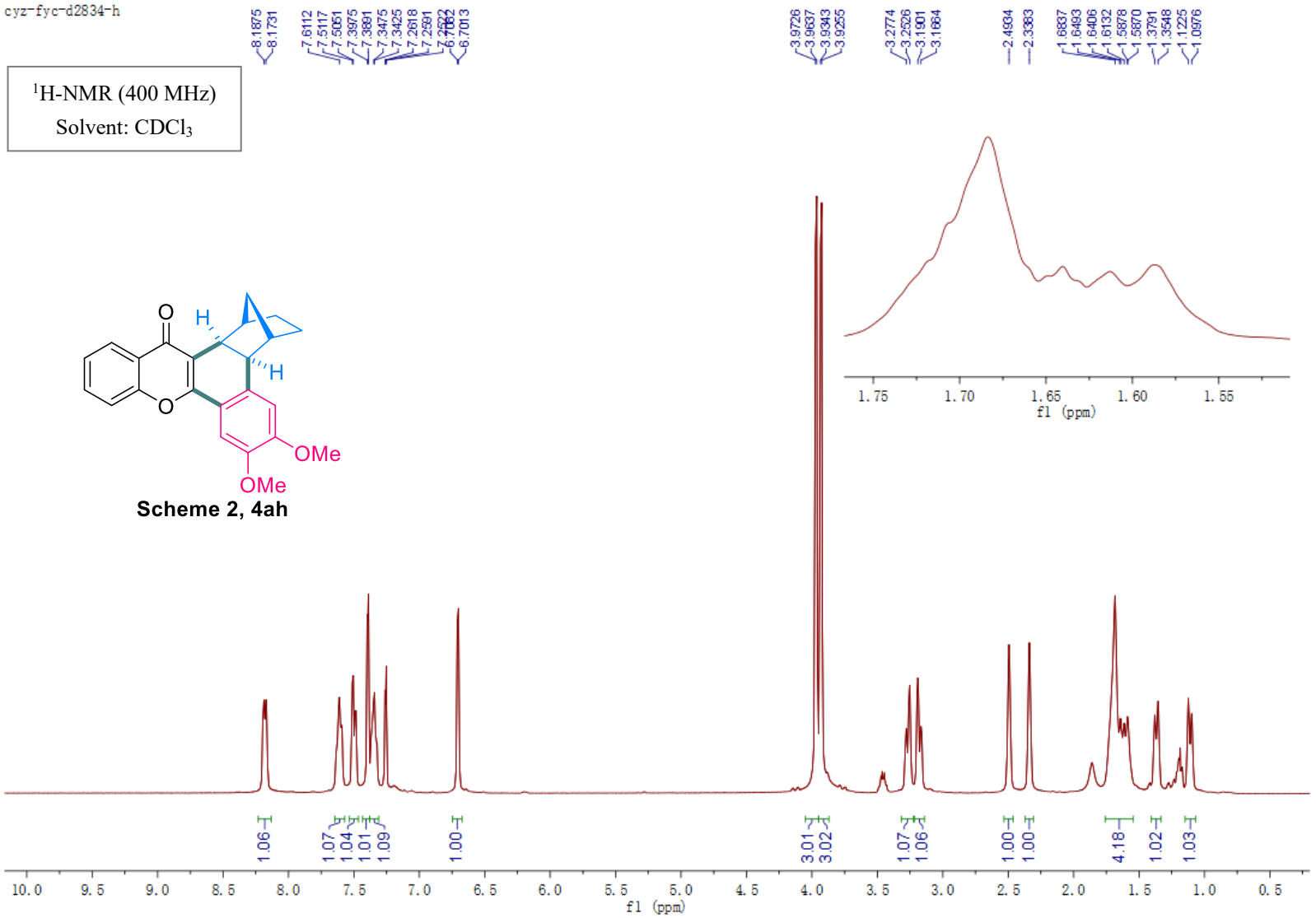






^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

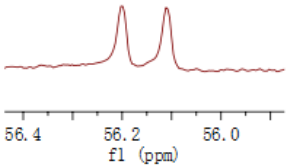
Scheme 2, 4ag

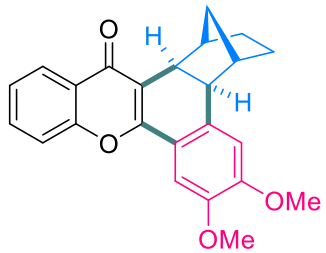

cyz-fyc-d2834-h
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$
O
H
H
O
OMe
OMe
Scheme 2, 4ah
f1 (ppm)

cyz-fyc-d2834-c

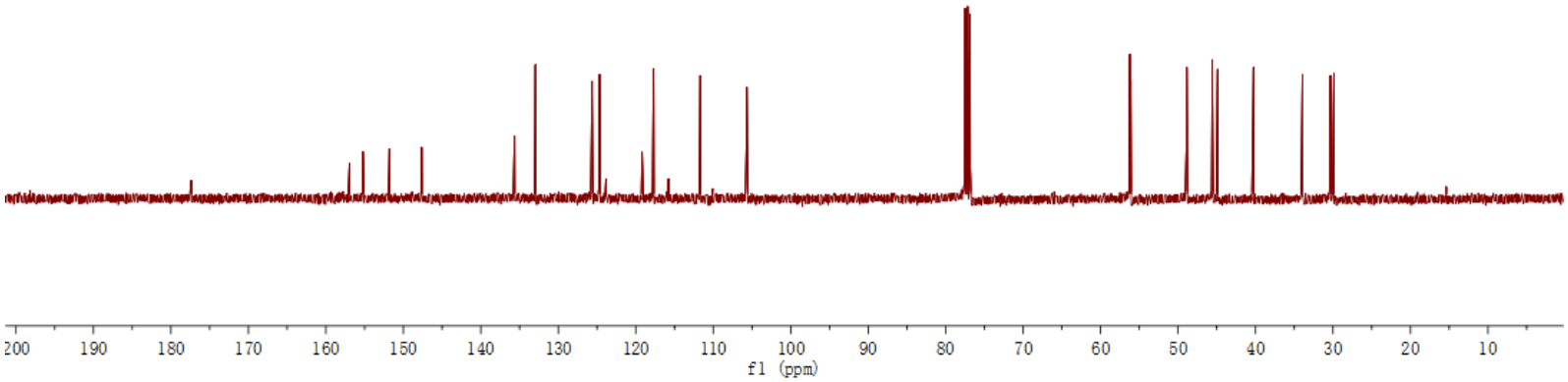
177.37
156.95
155.22
151.79
147.65
135.64
132.94
125.65
124.68
123.84
119.18
117.71
115.77
111.67
105.67
77.48
77.16
76.84
56.20
56.11
48.88
45.57
44.88
40.26
33.95
30.34
29.89

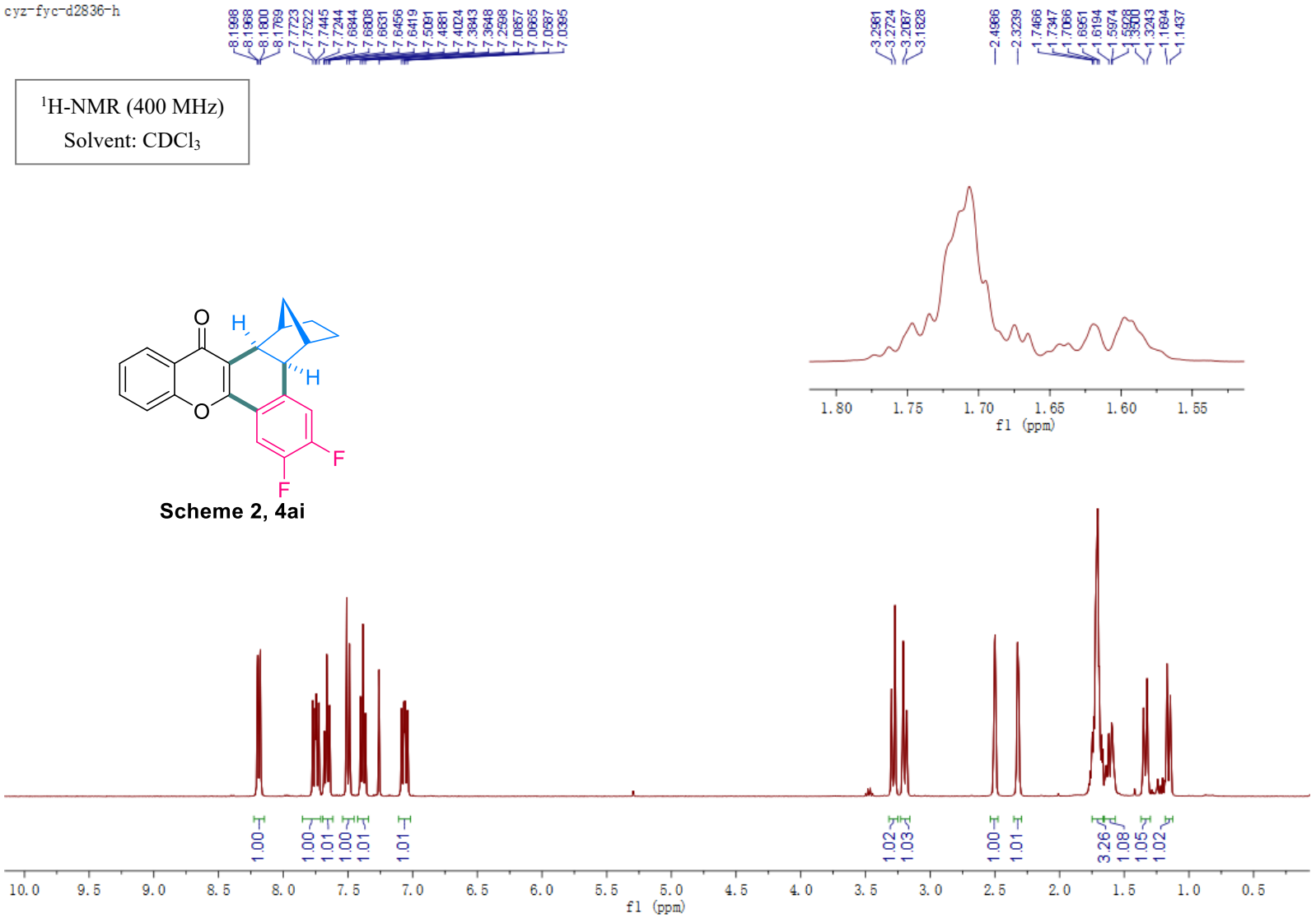
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$



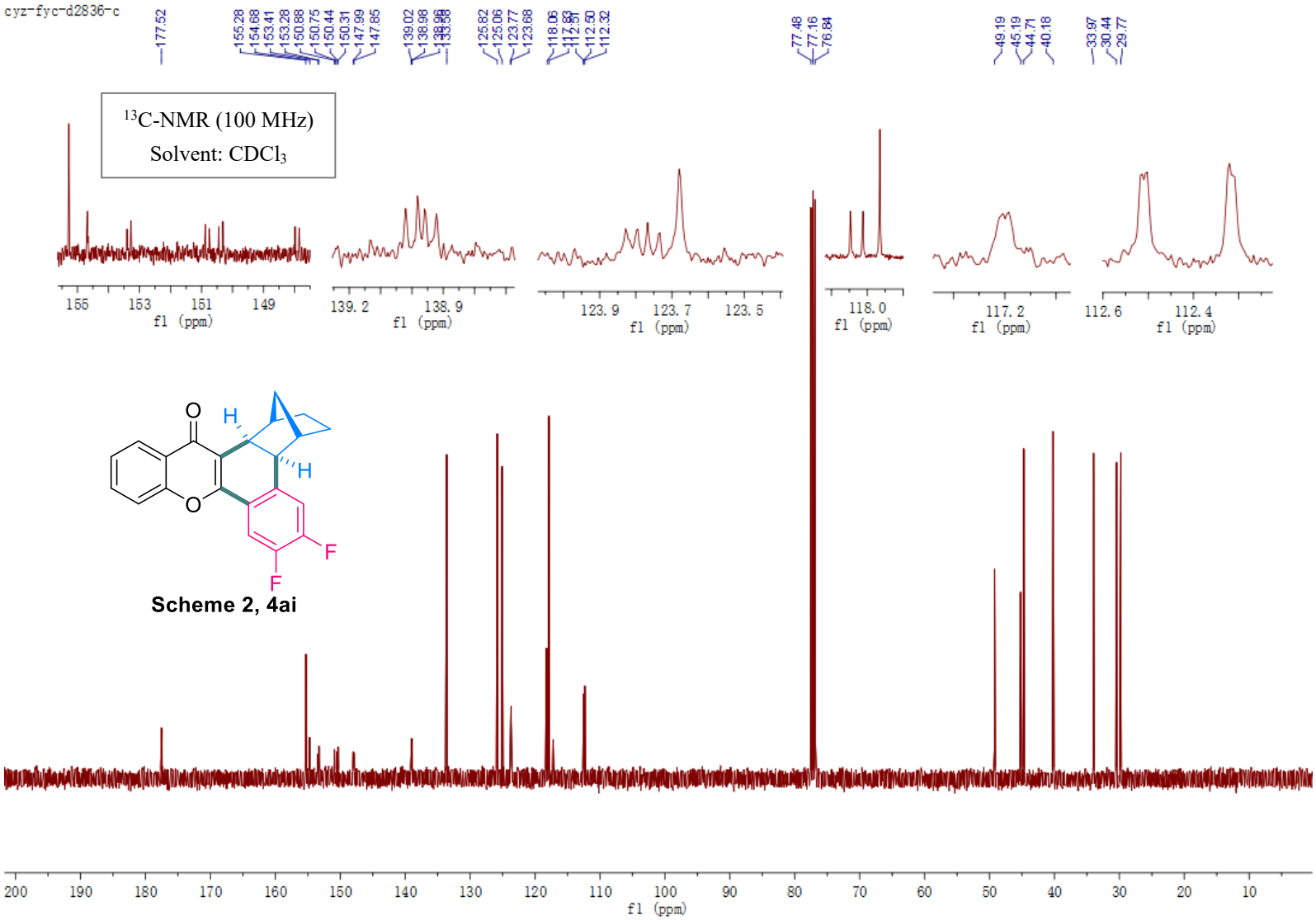


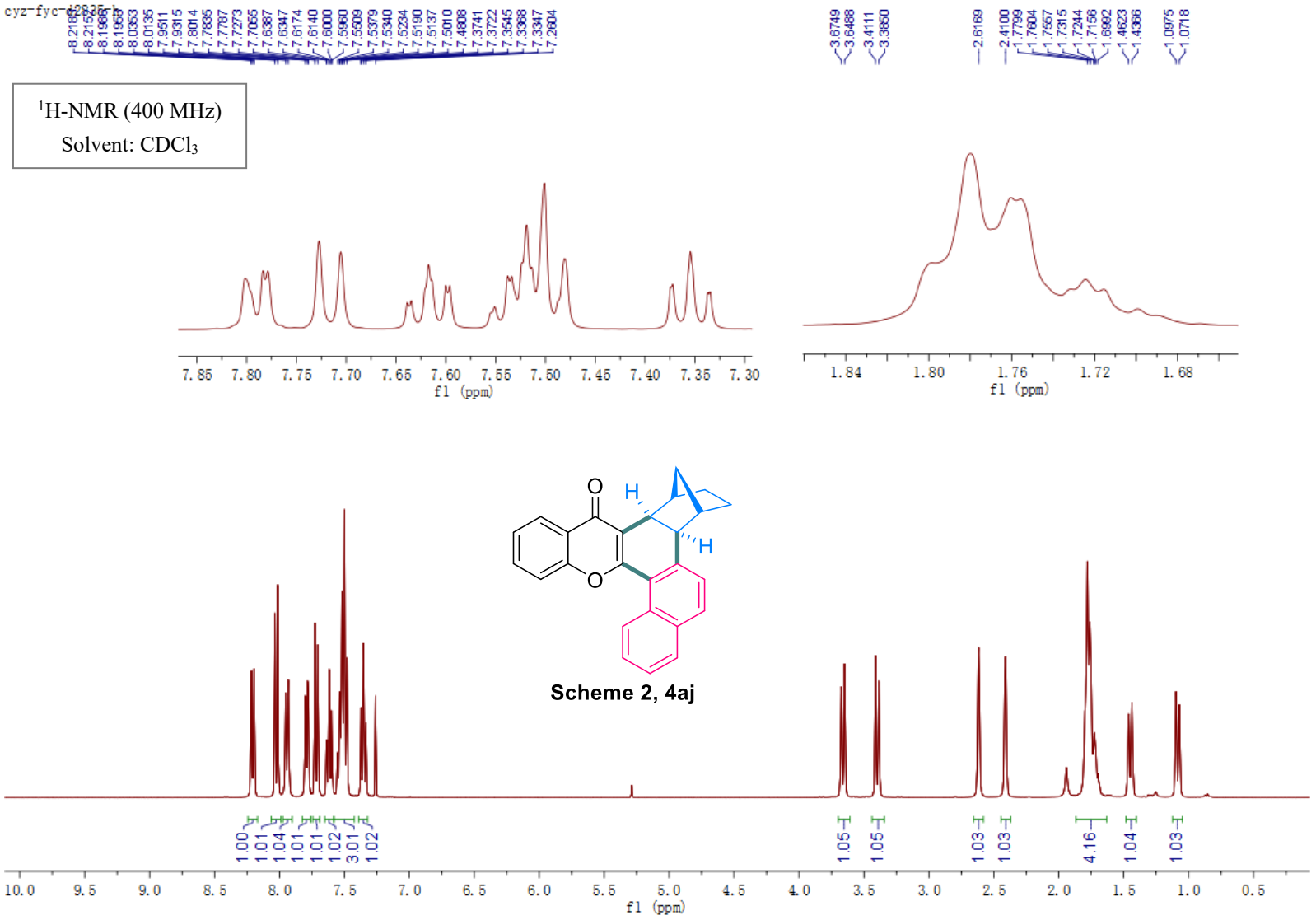
Scheme 2, 4ah




cyz-fyc-d2836-h
8.1998
8.1968
8.1800
8.1769
7.7723
7.7522
7.7445
7.7244
7.6844
7.6808
7.6631
7.6456
7.6419
7.5091
7.4881
7.4024
7.3843
7.3648
7.2598
7.0857
7.0665
7.0387
7.0395
3.2961
3.2724
3.2067
3.1828
2.4966
2.3239
1.7466
1.7347
1.7066
1.6951
1.6194
1.5974
1.5908
1.3500
1.3243
1.1684
1.1437
1H-NMR (400 MHz)
Solvent: CDCl3
O
H
H
O
F
F
1.80
1.75
1.70
1.65
1.60
1.55
f1 (ppm)
1.00
1.00
1.01
1.00
1.01
1.01
1.02
1.03
1.00
1.01
3.26
1.08
1.05
1.02
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, 4ai

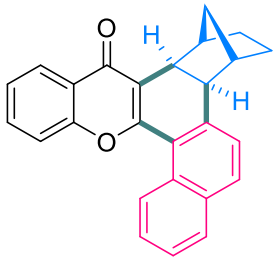

cyz-fyc-d2836-c
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$
Scheme 2, 4ai
f1 (ppm)


cyz-fyc-d2825
8.2186
8.2152
8.1968
8.1955
8.0353
8.0135
7.9511
7.9315
7.8014
7.7835
7.7787
7.7273
7.7055
7.6387
7.6347
7.6174
7.6140
7.6000
7.5960
7.5509
7.5379
7.5340
7.5234
7.5190
7.5137
7.5010
7.4608
7.3741
7.3722
7.3545
7.3368
7.3347
7.2604
3.6749
3.6488
3.4111
3.3850
2.6169
2.4100
1.7799
1.7604
1.7557
1.7315
1.7244
1.7156
1.6992
1.4623
1.4366
1.0975
1.0718
1H-NMR (400 MHz)
Solvent: CDCl3
7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30
f1 (ppm)
1.84 1.80 1.76 1.72 1.68
f1 (ppm)
O
H
H
O
Scheme 2, 4aj
1.00 1.01 1.04 1.01 1.01 1.02 3.01 1.02
1.05 1.05 1.03 1.03 4.16 1.04 1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

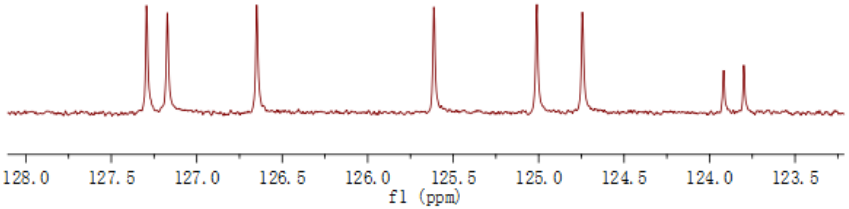
cyz-fyc-d2835-c

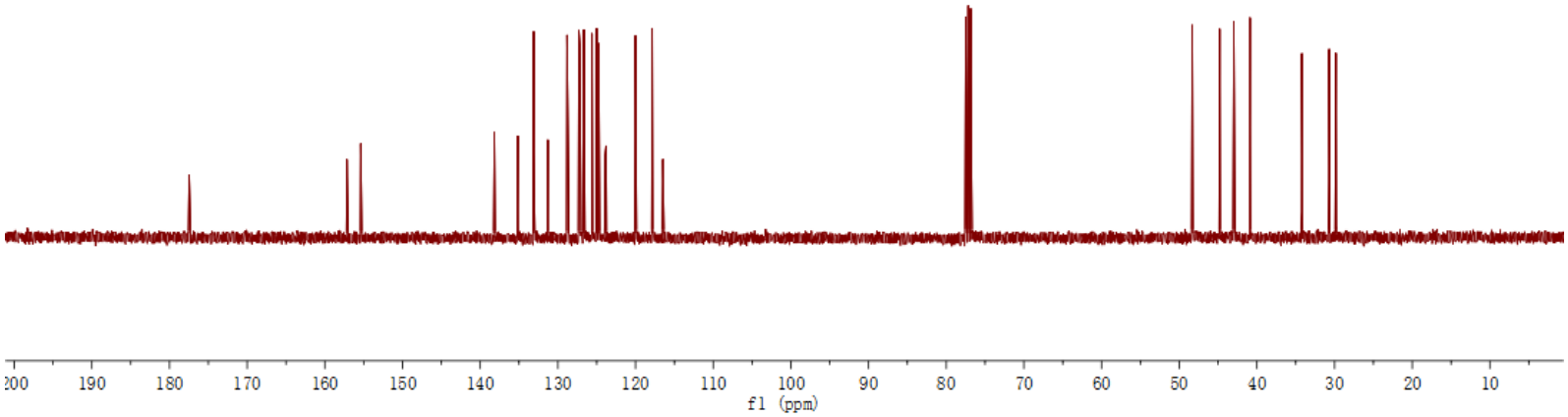
177.48
157.16
155.38
138.18
135.17
133.12
131.29
128.81
127.29
127.17
126.65
125.61
125.01
124.74
123.92
123.80
120.01
117.87
116.47
77.48
77.16
76.84
48.33
44.79
42.97
40.90
34.20
30.70
29.83

^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$



Scheme 2, 4aj





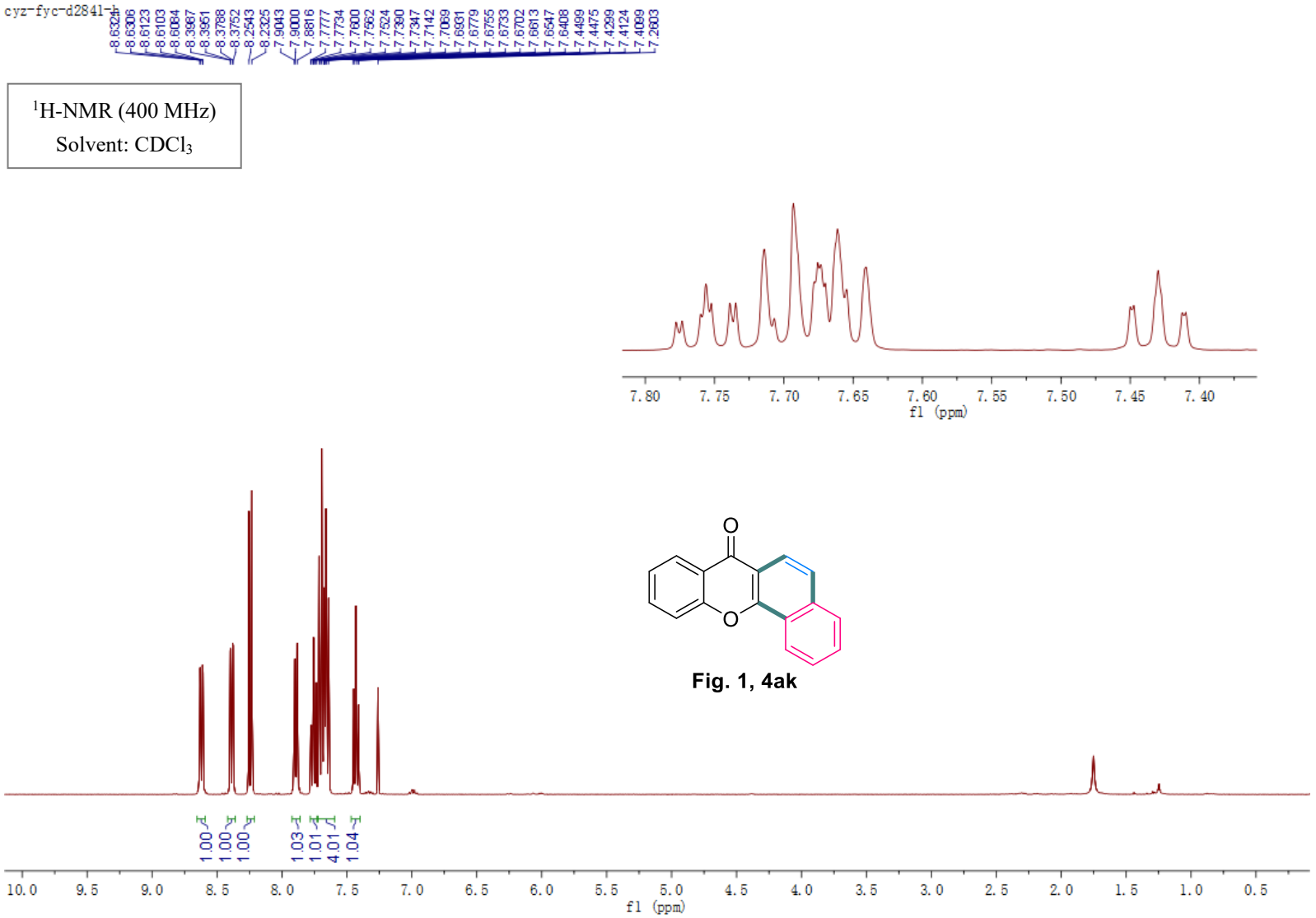
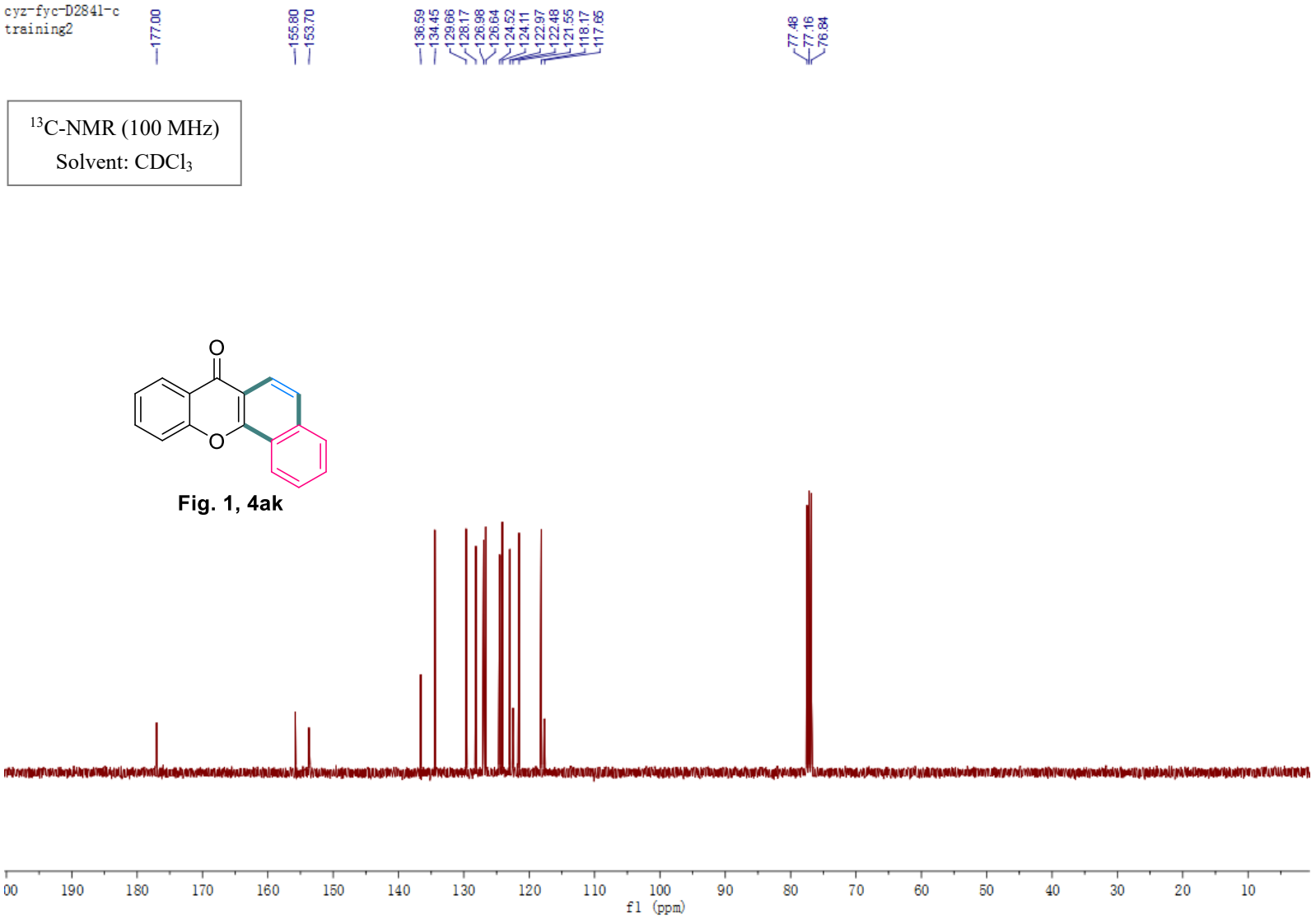

cyz-fyc-d2841-1
8.6324
8.6306
8.6123
8.6103
8.6084
8.3967
8.3951
8.3788
8.3752
8.2543
8.2325
7.9043
7.9000
7.8816
7.7777
7.7734
7.7600
7.7562
7.7524
7.7390
7.7347
7.7142
7.7069
7.6931
7.6779
7.6755
7.6733
7.6702
7.6613
7.6547
7.6408
7.4499
7.4475
7.4299
7.4124
7.4099
7.2803
1H-NMR (400 MHz)
Solvent: CDCl3
7.80
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
f1 (ppm)
O
O
1.00
1.00
1.00
1.03
1.01
4.01
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)

Fig. 1, 4ak



^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Fig. 1, 4ak

cyz-fyc-d2842-h

^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$

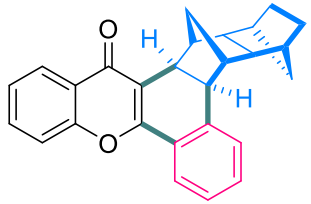
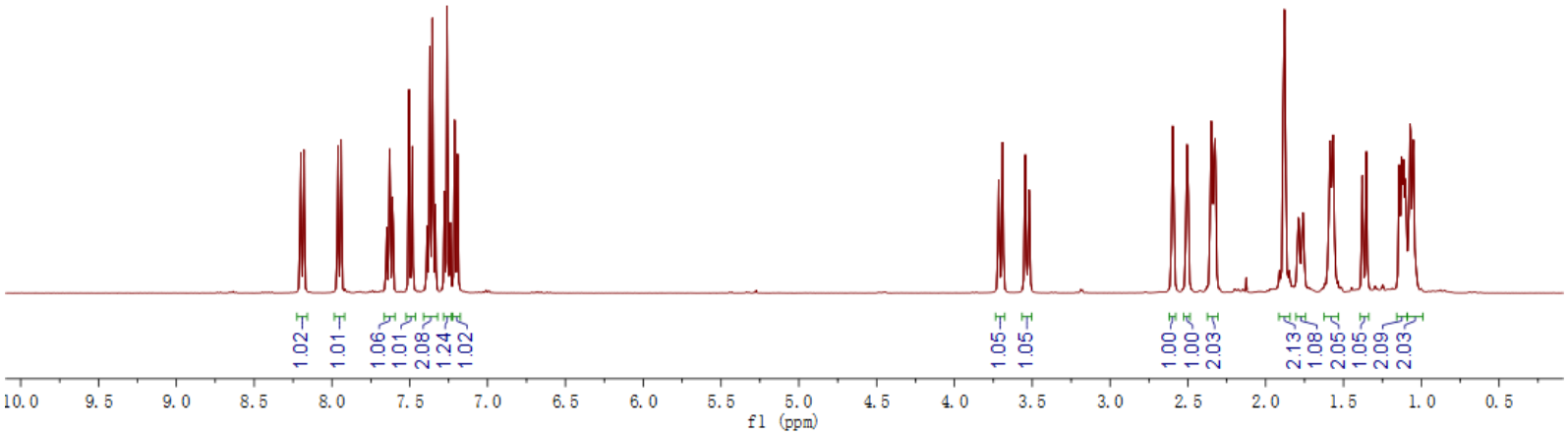
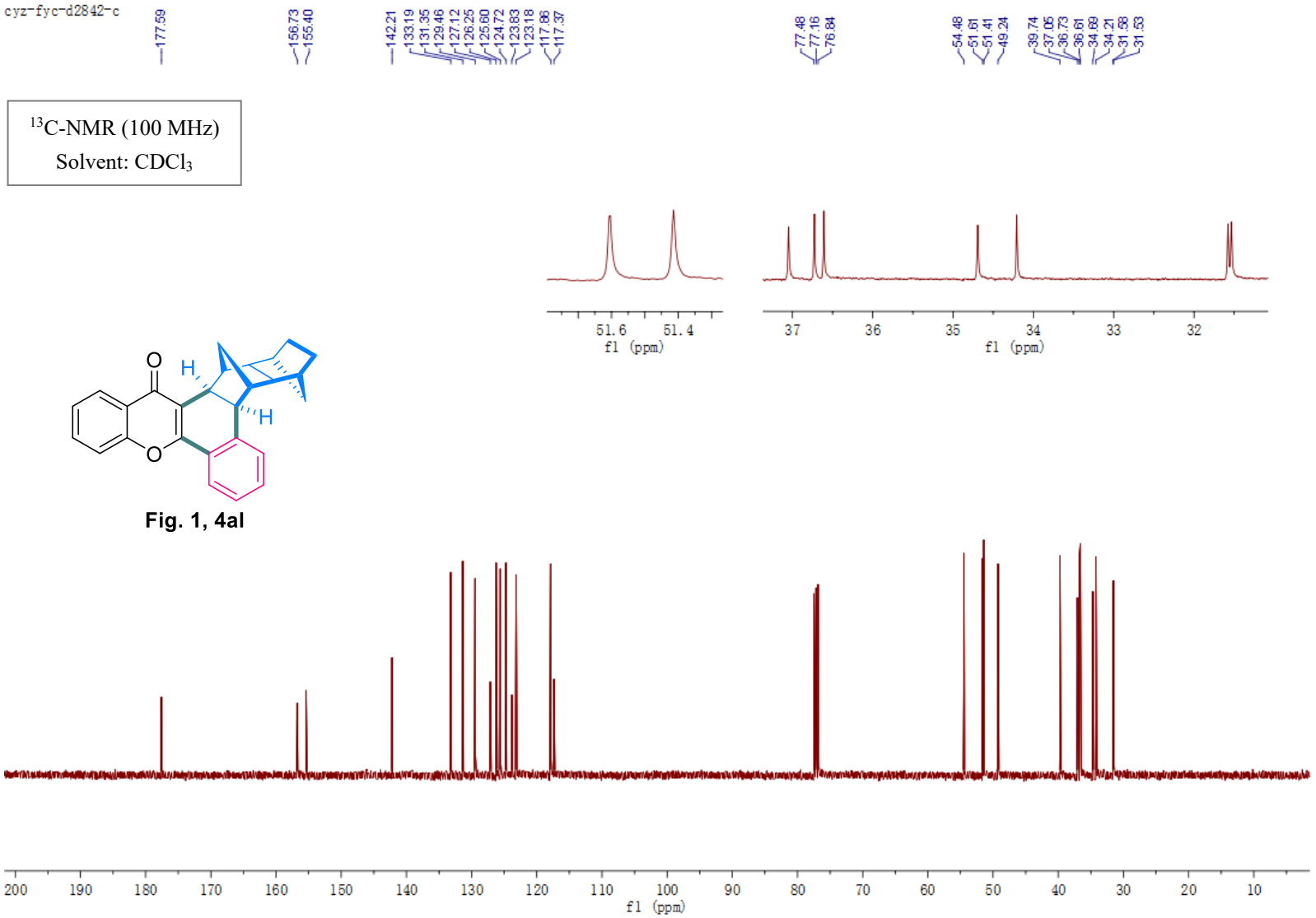


Fig. 1, 4al





^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Fig. 1, 4al

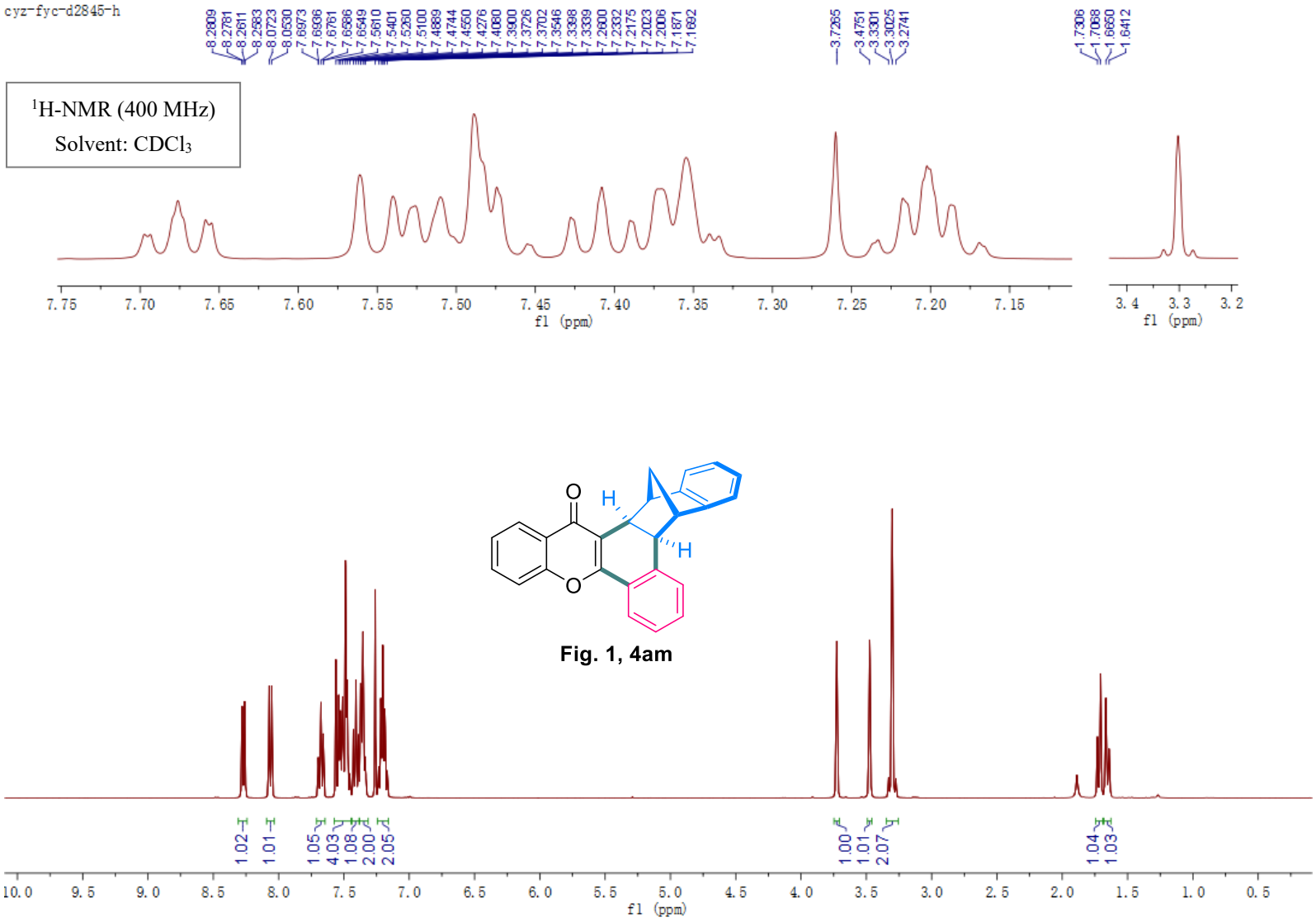

cyz-fyc-d2845-h
8.2809
8.2761
8.2611
8.2583
8.0723
8.0530
7.6973
7.6896
7.6761
7.6696
7.6549
7.5610
7.5401
7.5260
7.5100
7.4889
7.4744
7.4550
7.4276
7.4060
7.3900
7.3726
7.3702
7.3546
7.3398
7.3339
7.2600
7.2332
7.2175
7.2023
7.2006
7.1871
7.1692
3.7265
3.4751
3.3301
3.3025
3.2741
1.7306
1.7068
1.6850
1.6412
[1]H-NMR (400 MHz)
Solvent: CDCl3
7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15
f1 (ppm)
3.4 3.3 3.2
f1 (ppm)
O
H
H
O
1.02
1.01
1.05
4.03
1.08
2.00
2.05
1.00
1.01
2.07
1.04
1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

Fig. 1, 4am

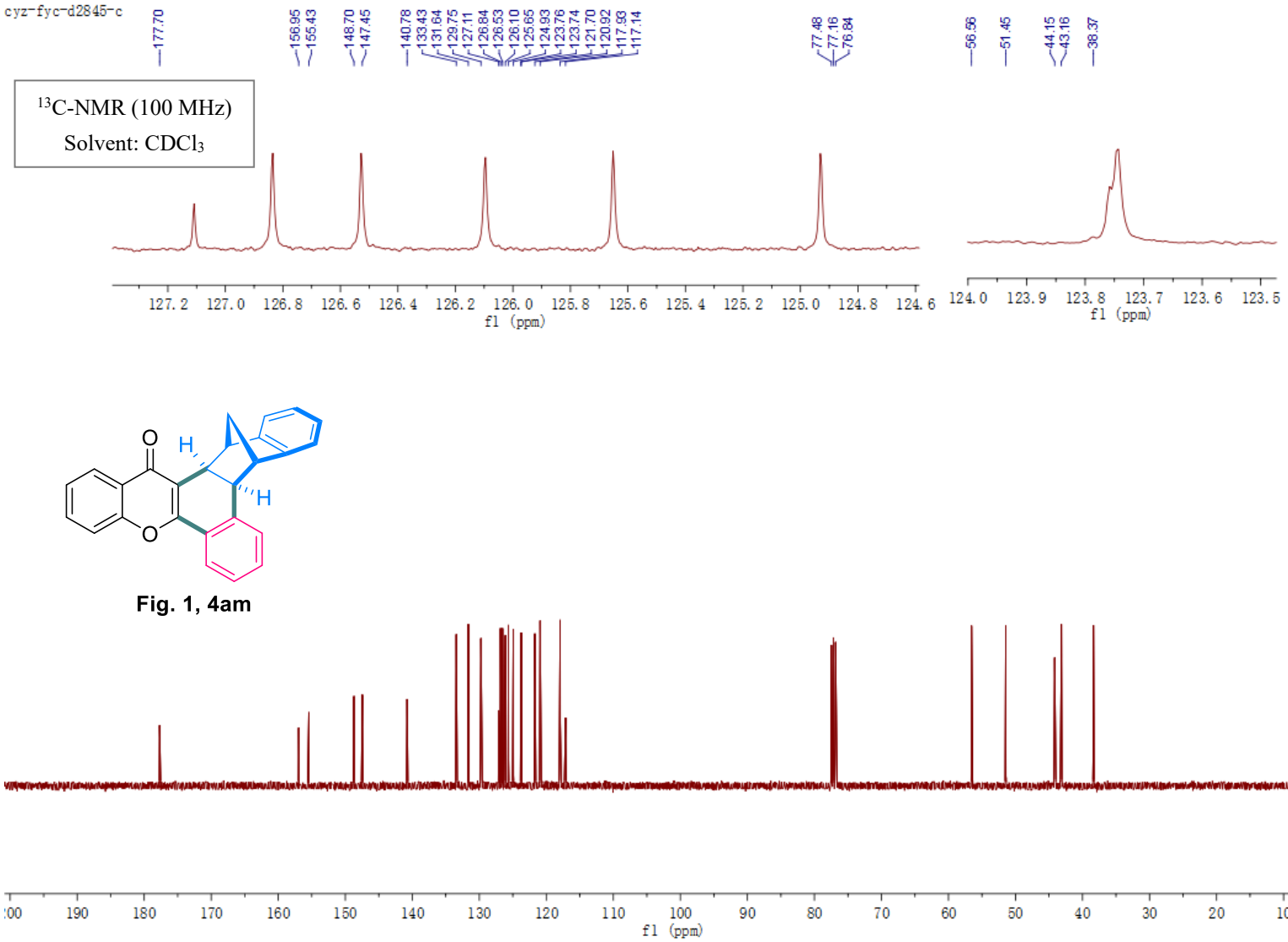

cyz-fyc-d2845-c
177.70
156.95
155.43
148.70
147.45
140.78
133.43
131.64
129.75
127.11
126.84
126.53
126.10
125.65
124.93
123.76
123.74
121.70
120.92
117.93
117.14
77.48
77.16
76.84
56.56
51.45
44.15
43.16
38.37
13C-NMR (100 MHz)
Solvent: CDCl3
127.2 127.0 126.8 126.6 126.4 126.2 126.0 125.8 125.6 125.4 125.2 125.0 124.8 124.6
f1 (ppm)
124.0 123.9 123.8 123.7 123.6 123.5
f1 (ppm)
O
H
H
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Fig. 1, 4am

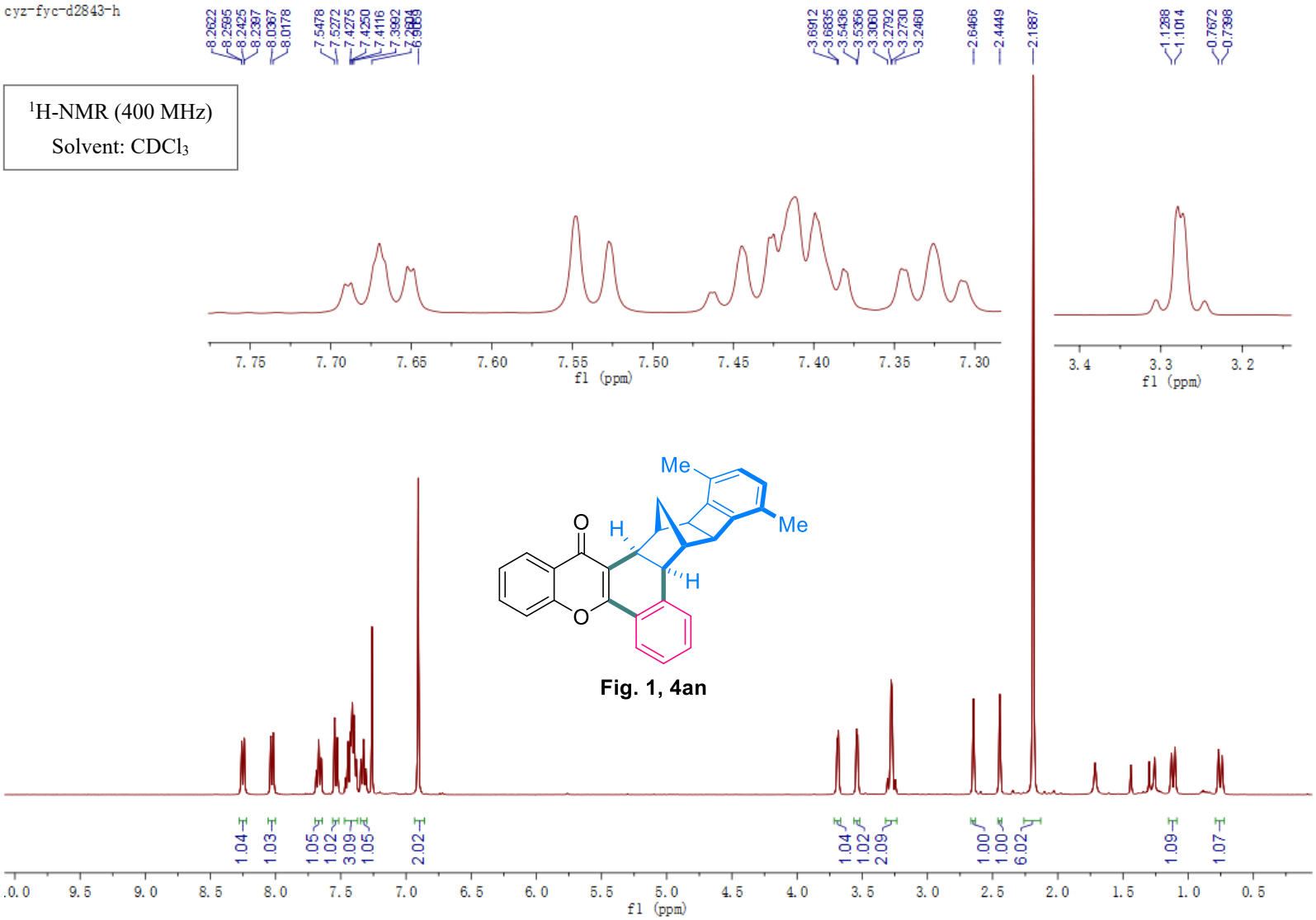


Fig. 1, 4an

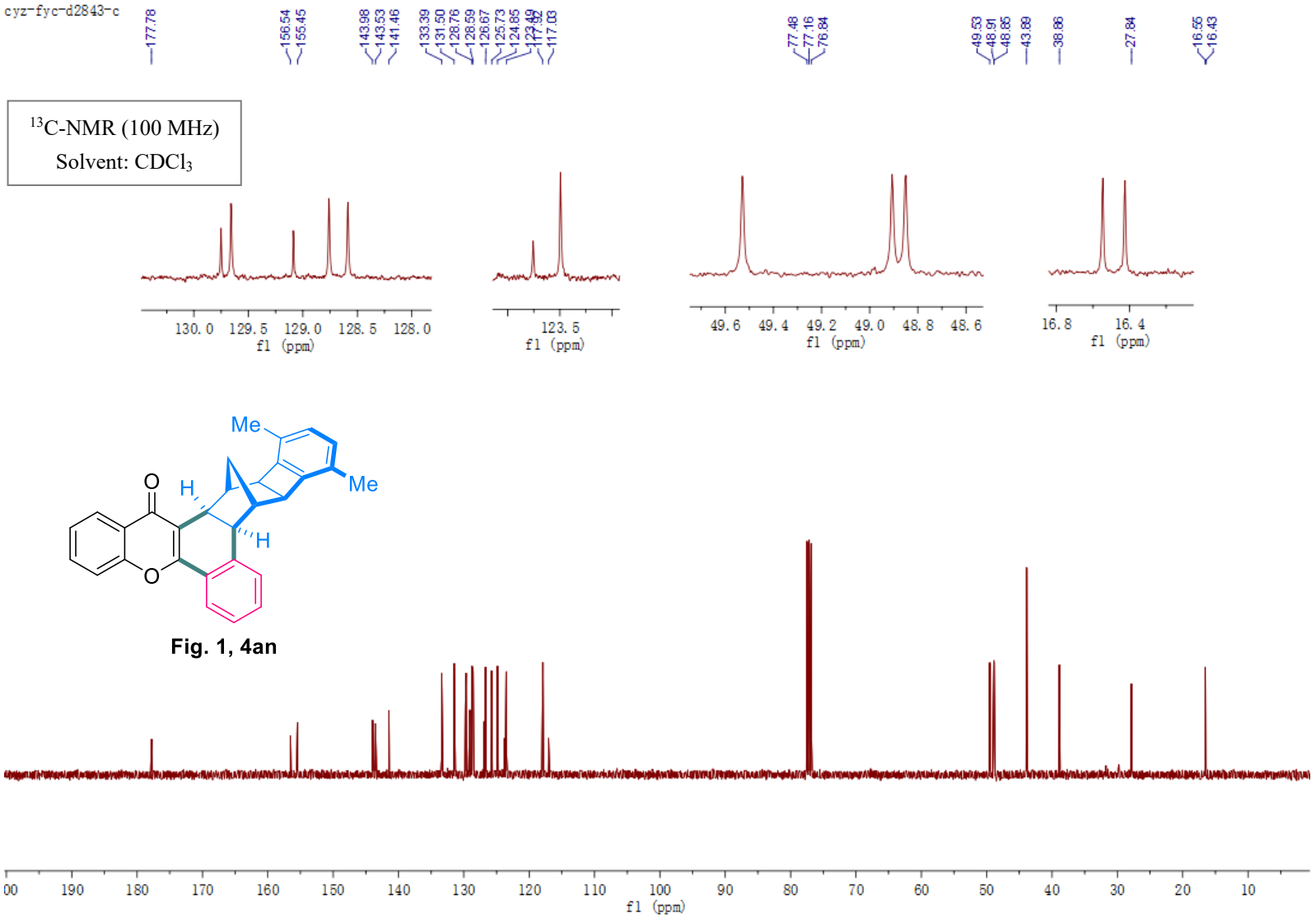

cyz-fyc-d2843-c
177.78
156.54
155.45
143.98
143.53
141.46
133.39
131.50
128.76
128.59
126.67
125.73
124.85
117.03
77.48
77.16
76.84
49.53
48.91
48.85
43.89
38.86
27.84
16.55
16.43
13C-NMR (100 MHz)
Solvent: CDCl3
130.0 129.5 129.0 128.5 128.0
f1 (ppm)
123.5
f1 (ppm)
49.6 49.4 49.2 49.0 48.8 48.6
f1 (ppm)
16.8 16.4
f1 (ppm)
Me
Me
O
H
H
O
f1 (ppm)

Fig. 1, 4an

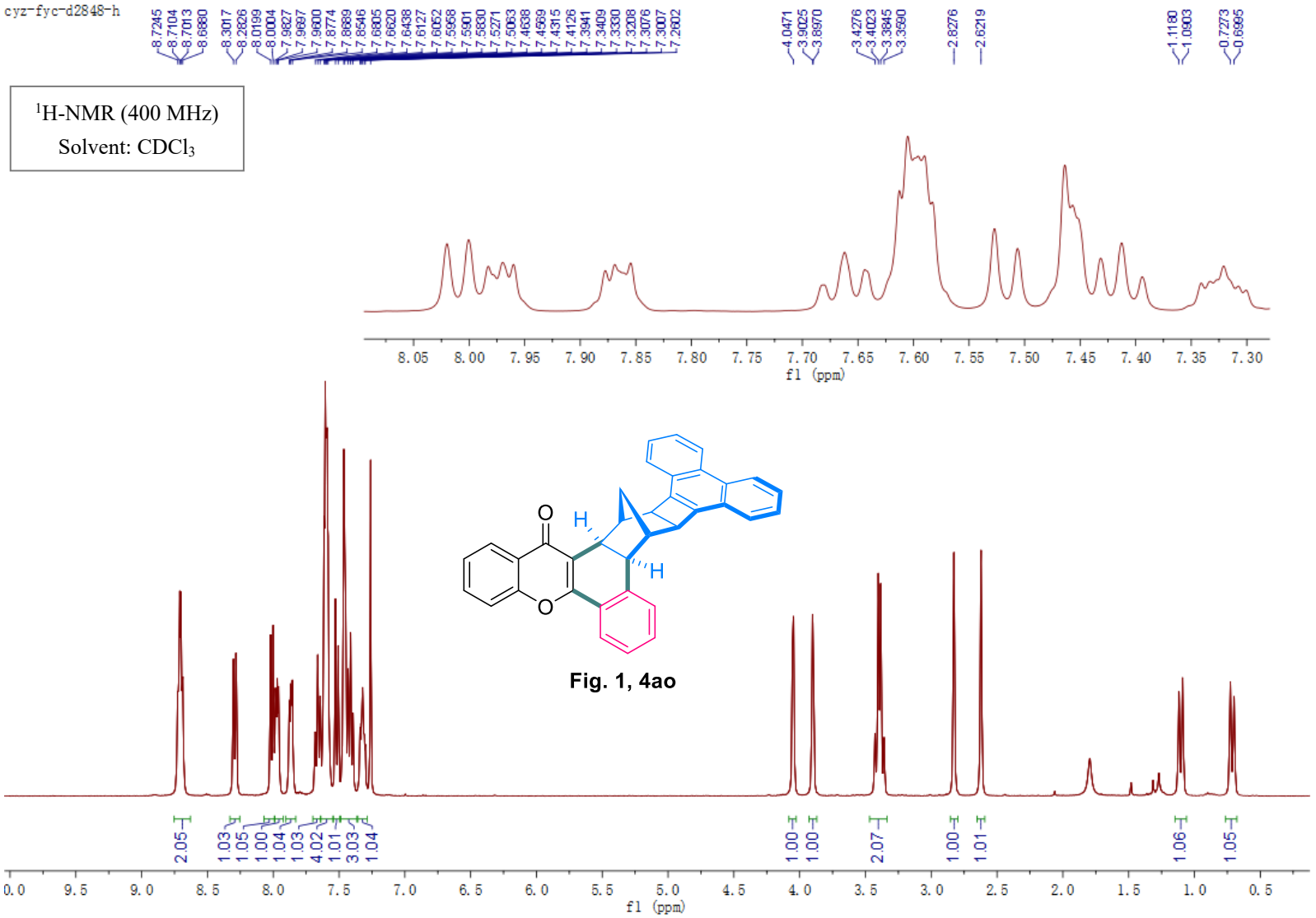

cyz-fyc-d2848-h
8.7245
8.7104
8.7013
8.6880
8.3017
8.2826
8.0199
8.0004
7.9827
7.9697
7.9600
7.8774
7.8669
7.8546
7.6805
7.6620
7.6438
7.6127
7.6052
7.5958
7.5901
7.5830
7.5271
7.5063
7.4638
7.4609
7.4315
7.4126
7.3941
7.3409
7.3330
7.3208
7.3076
7.3007
7.2802
4.0471
3.9025
3.8970
3.4276
3.4023
3.3845
3.3590
2.8276
2.6219
1.1180
1.0903
0.7273
0.6995
[1]H-NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)
O
H
H
O
2.05
1.03
1.05
1.00
1.04
1.03
4.02
1.01
3.03
1.04
1.00
1.00
2.07
1.00
1.01
1.06
1.05
f1 (ppm)

Fig. 1, 4ao

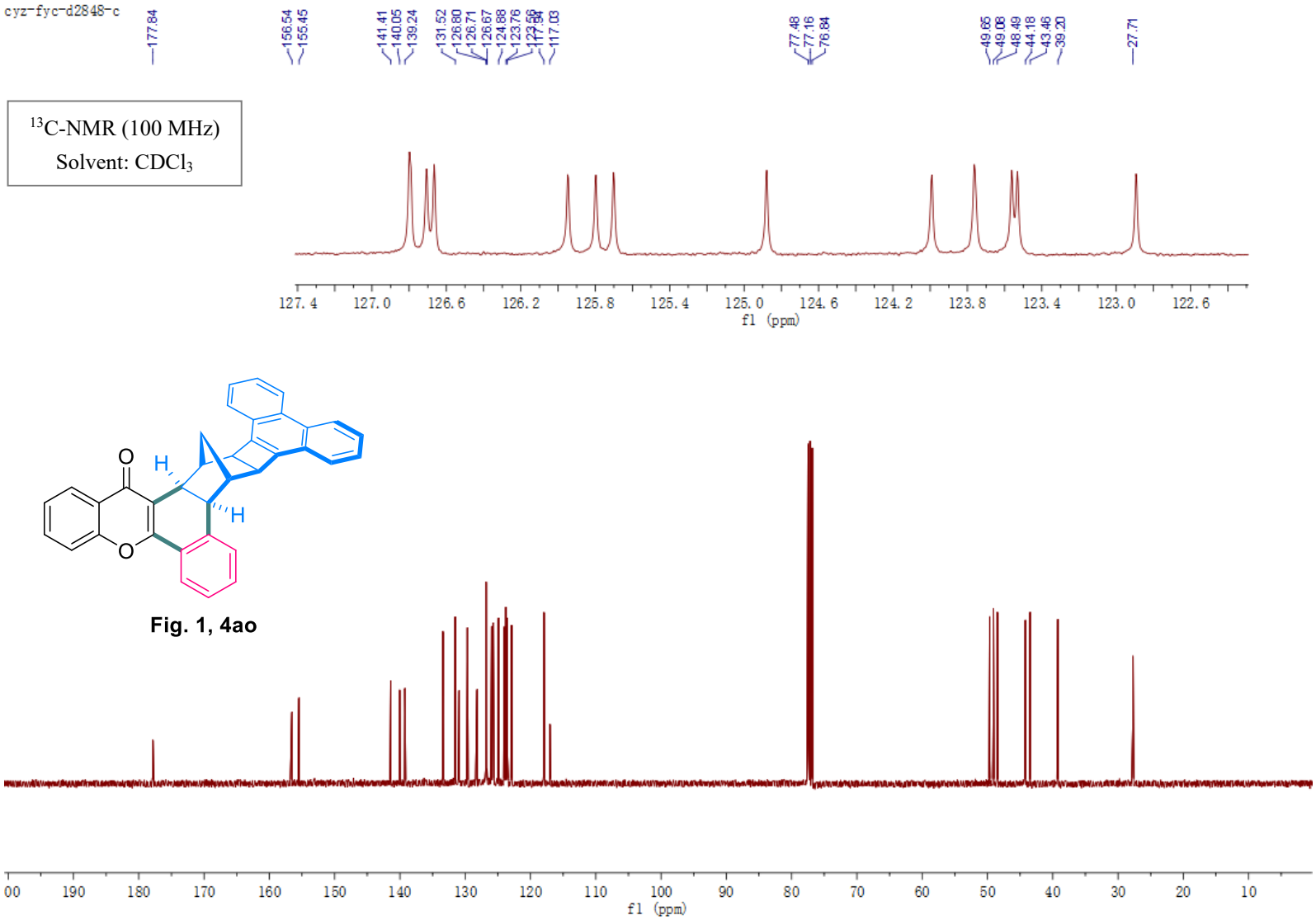

cyz-fyc-d2848-c
177.84
156.54
155.45
141.41
140.05
139.24
131.52
126.80
126.71
126.67
124.88
123.76
117.03
77.48
77.16
76.84
49.65
49.06
48.49
44.18
43.46
39.20
27.71
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$
127.4 127.0 126.6 126.2 125.8 125.4 125.0 124.6 124.2 123.8 123.4 123.0 122.6
f1 (ppm)
O
H
H
O
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Fig. 1, 4ao

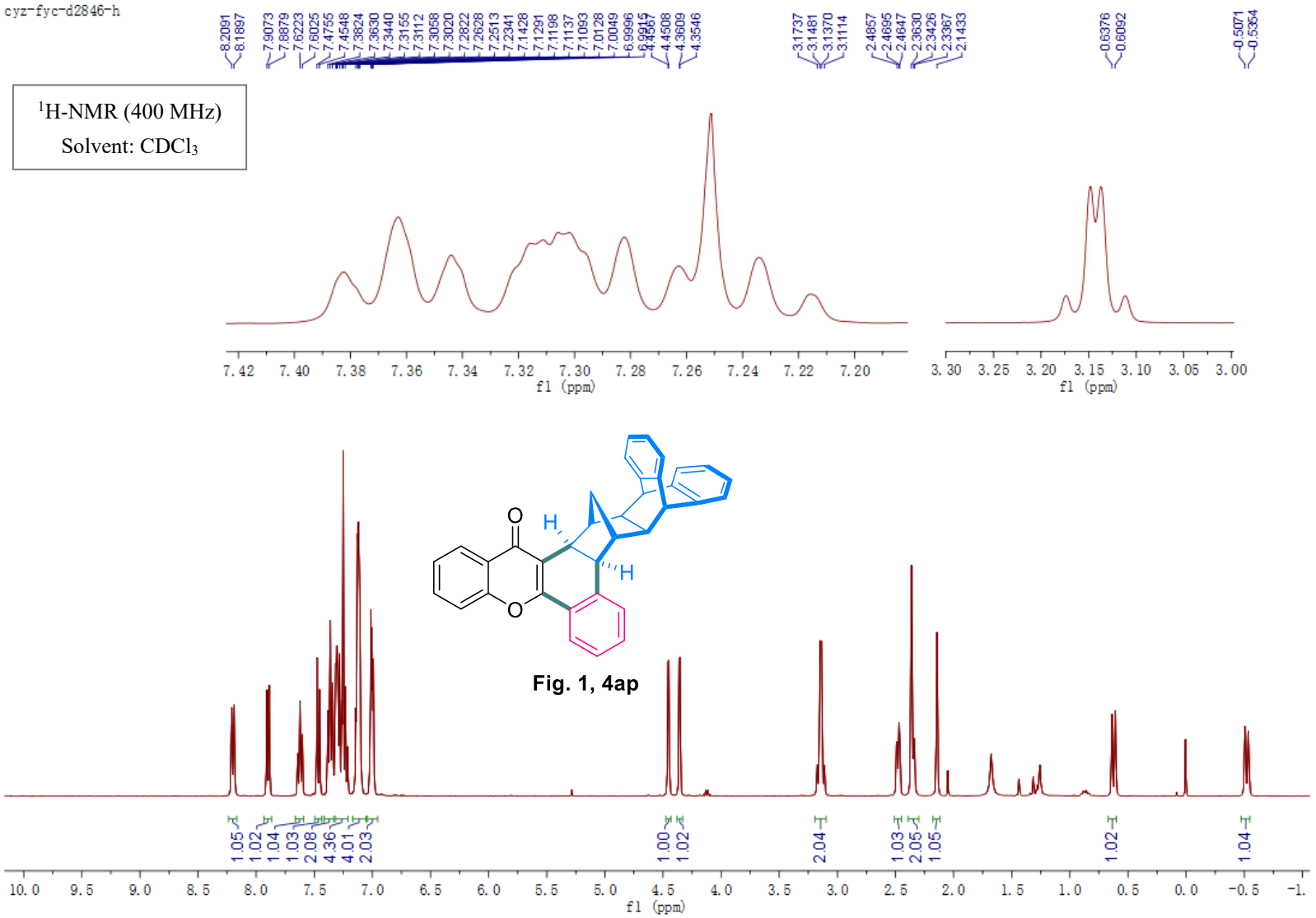


Fig. 1, 4ap

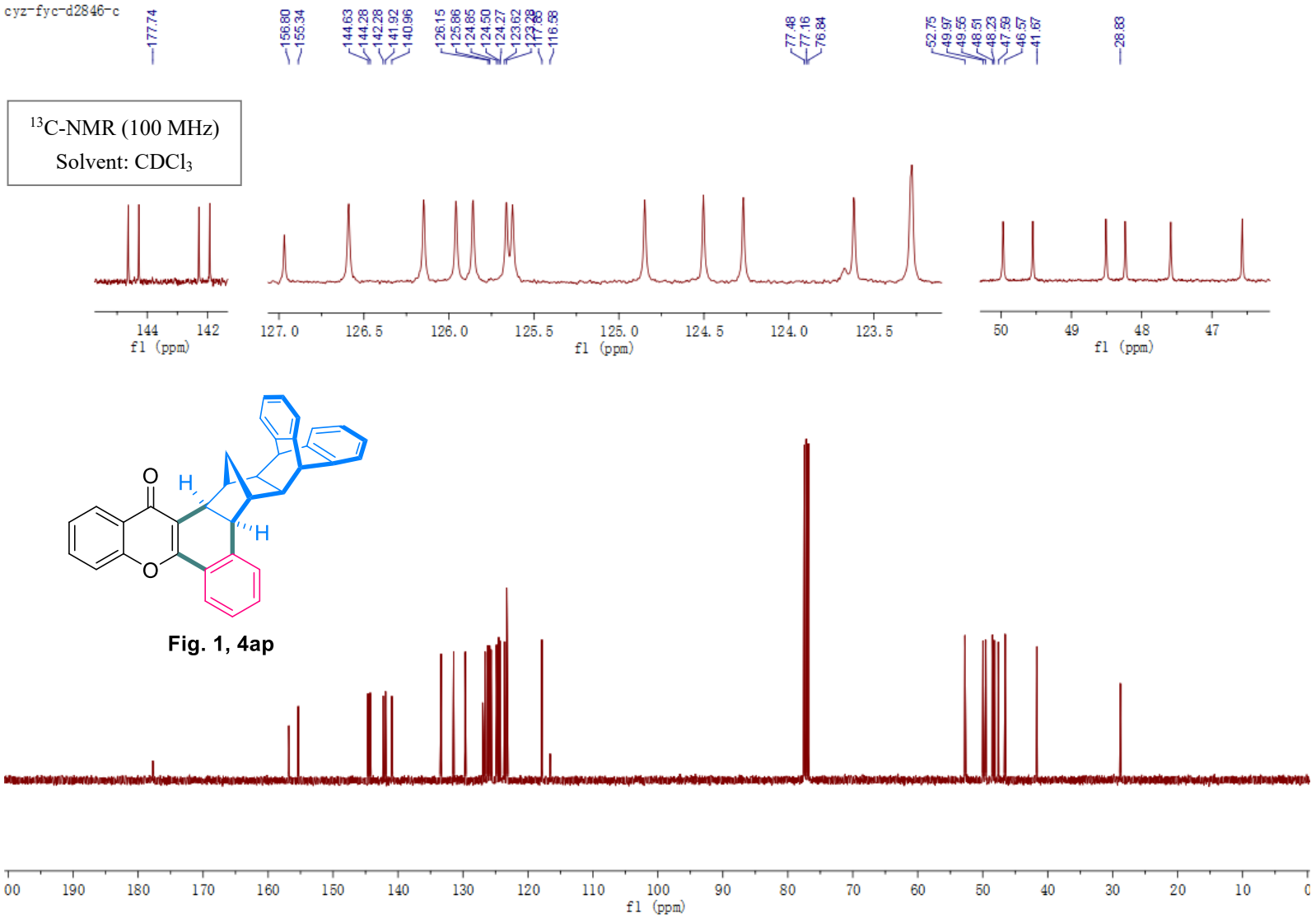
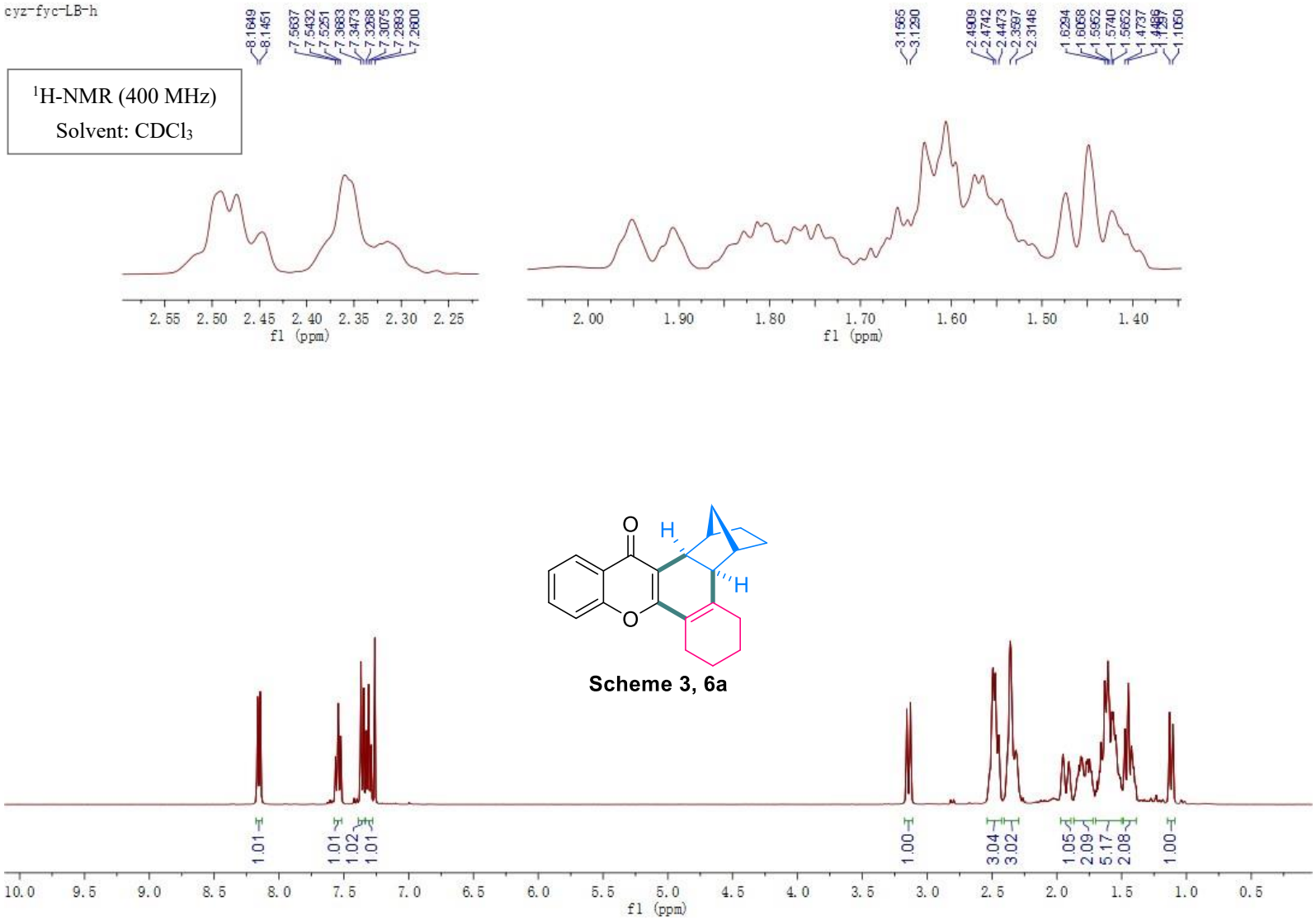
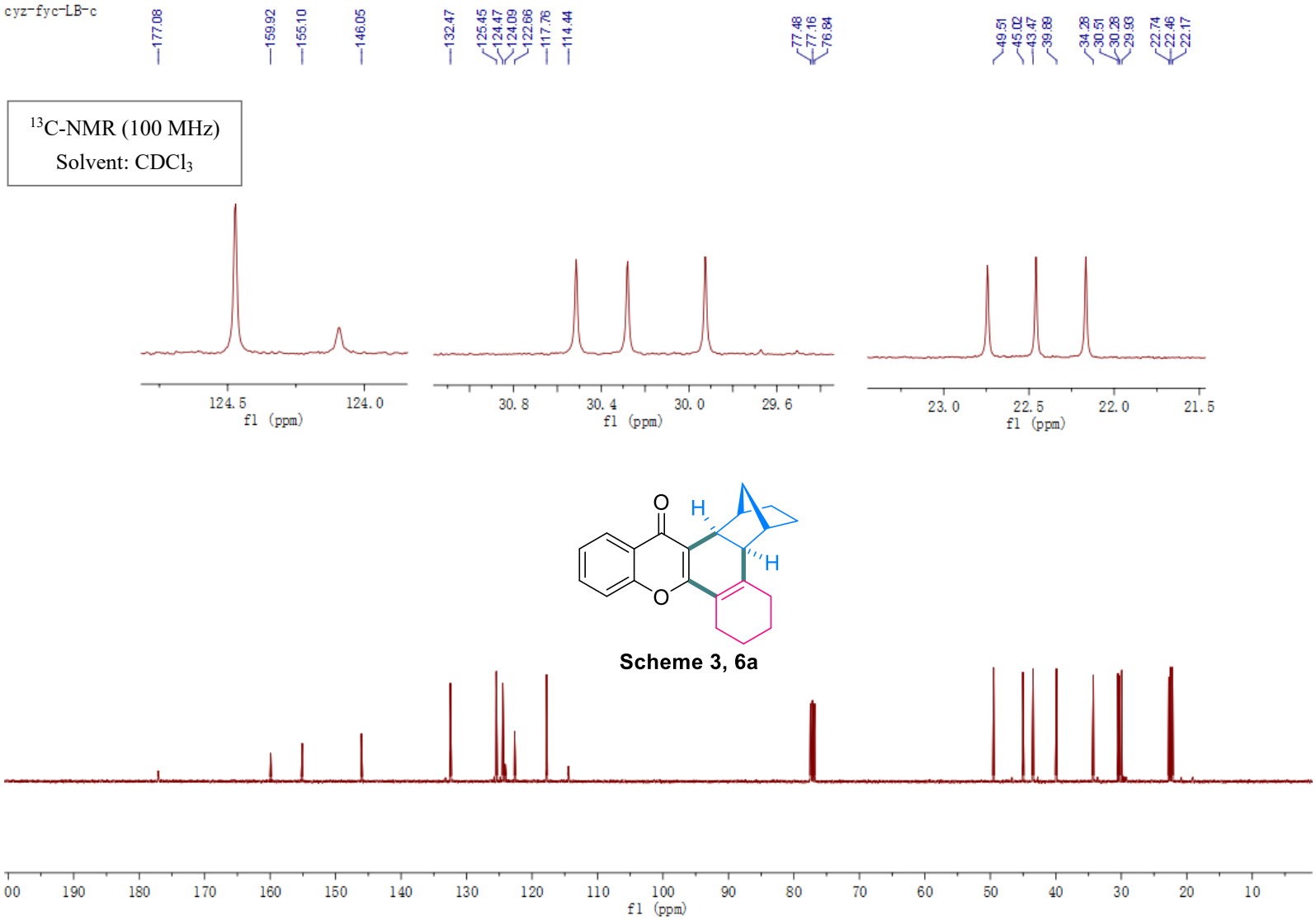
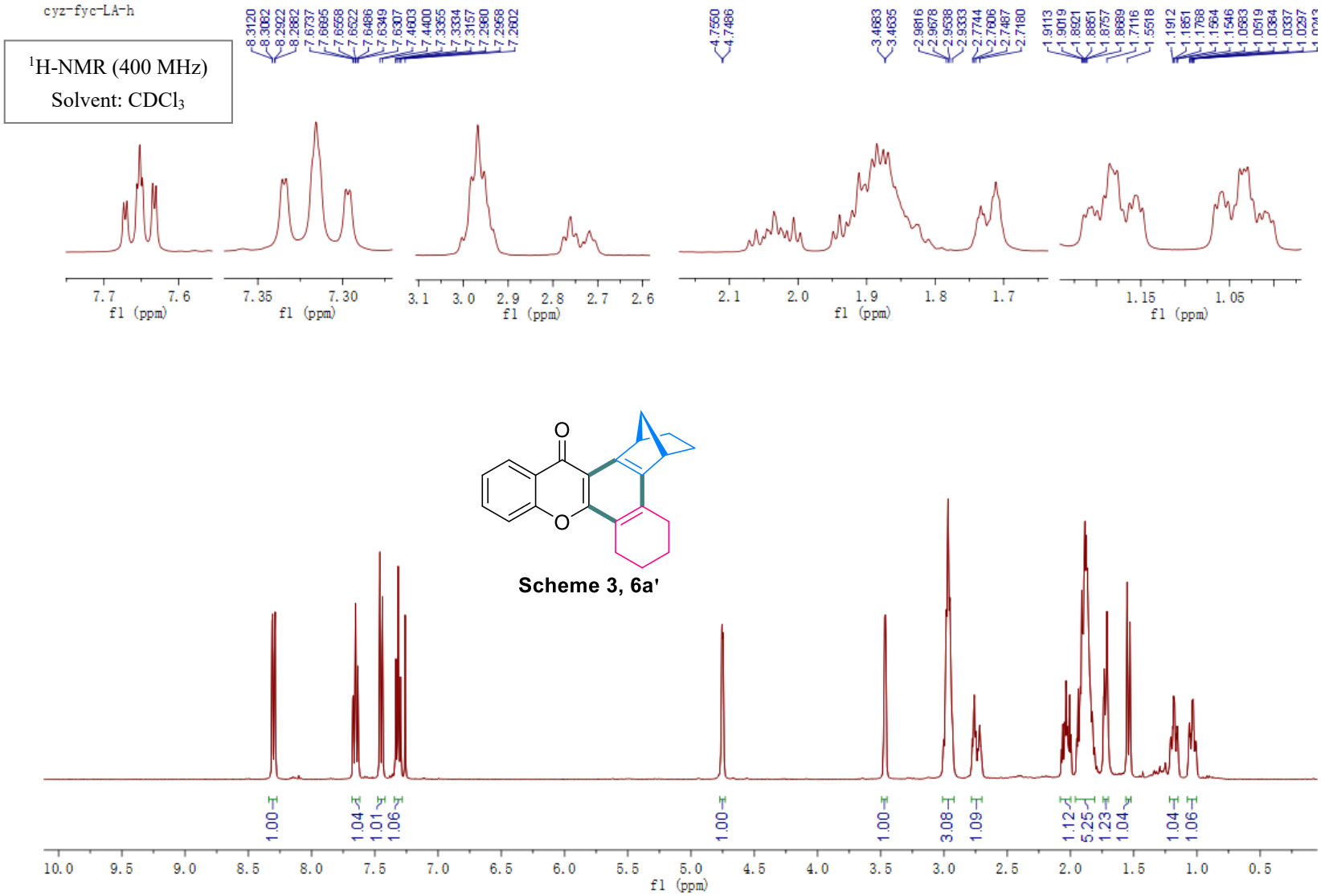

cyz-fyc-d2846-c
177.74
156.80
155.34
144.63
144.28
142.28
141.92
140.96
126.15
125.86
124.85
124.50
124.27
123.62
116.58
77.48
77.16
76.84
52.75
49.97
49.55
48.51
48.23
47.59
46.57
41.67
28.83
13C-NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)
O
H
H
O

Fig. 1, 4ap

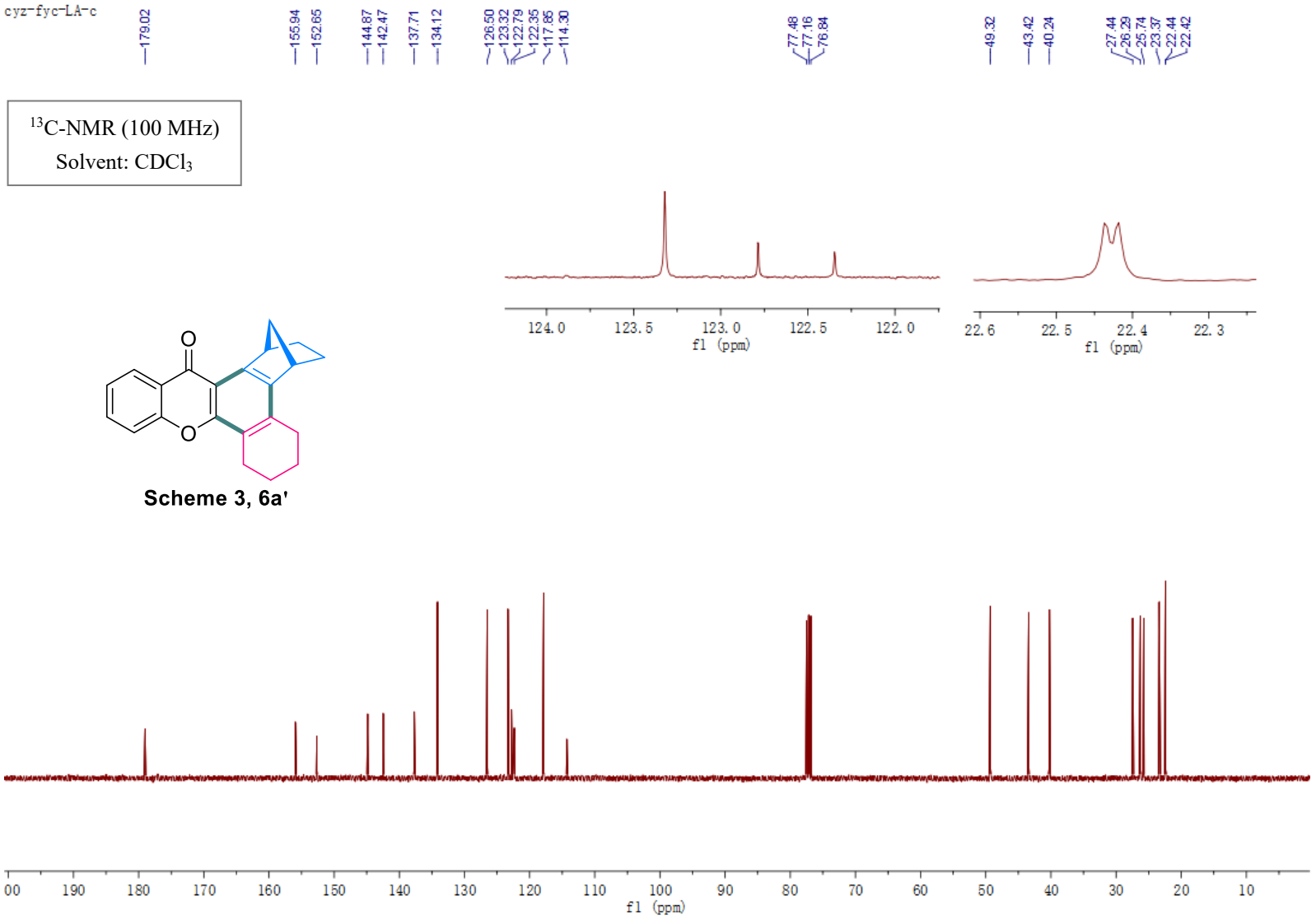


Scheme 3, 6a


cyz-fyc-LB-c
177.08
159.92
155.10
146.05
132.47
125.45
124.47
124.09
122.66
117.76
114.44
77.48
77.16
76.84
49.51
45.02
43.47
39.89
34.28
30.51
30.26
29.93
22.74
22.46
22.17
13C-NMR (100 MHz)
Solvent: CDCl3
124.5
124.0
f1 (ppm)
30.8
30.4
30.0
29.6
f1 (ppm)
23.0
22.5
22.0
21.5
f1 (ppm)
O
H
H
O
Scheme 3, 6a
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

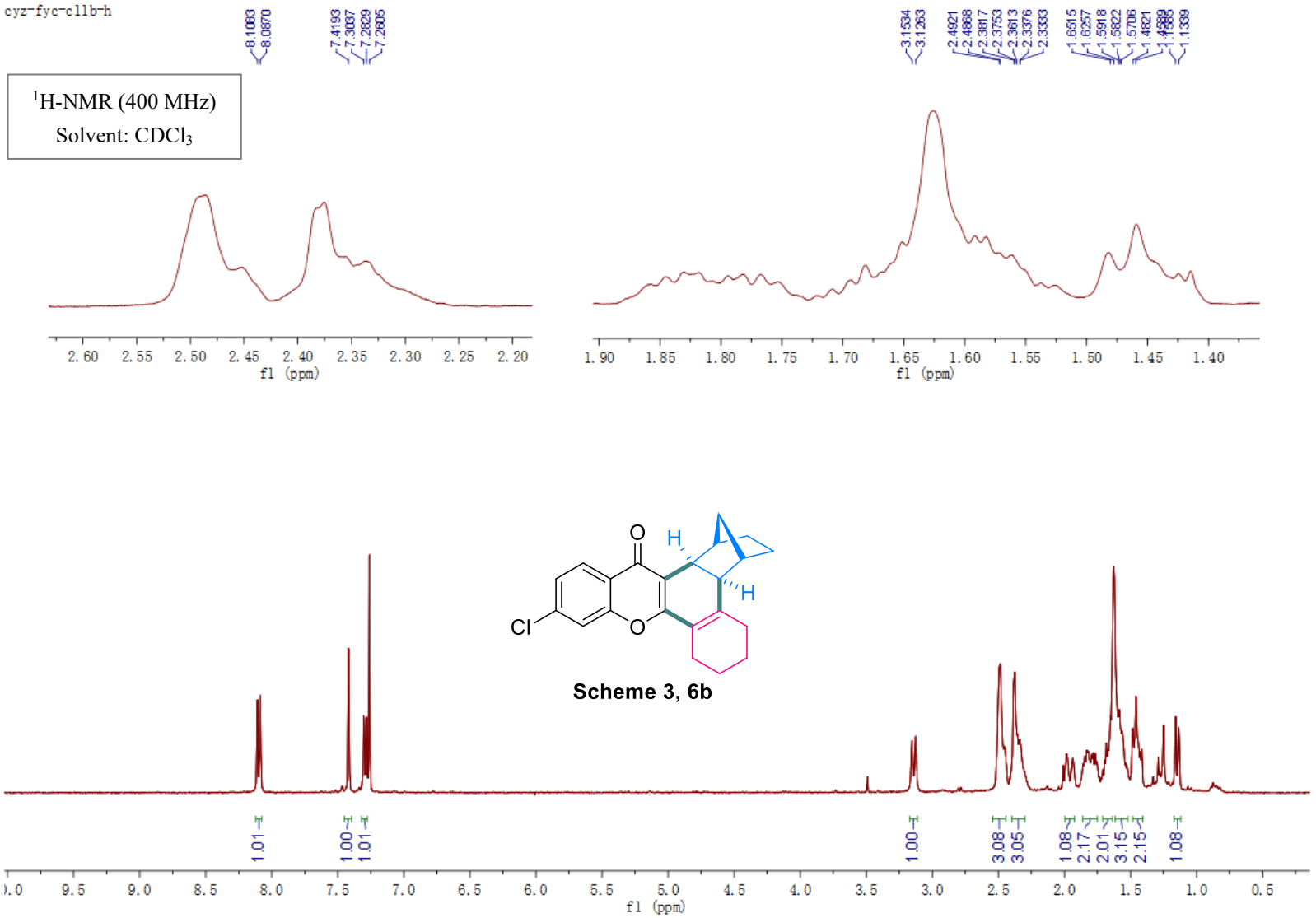


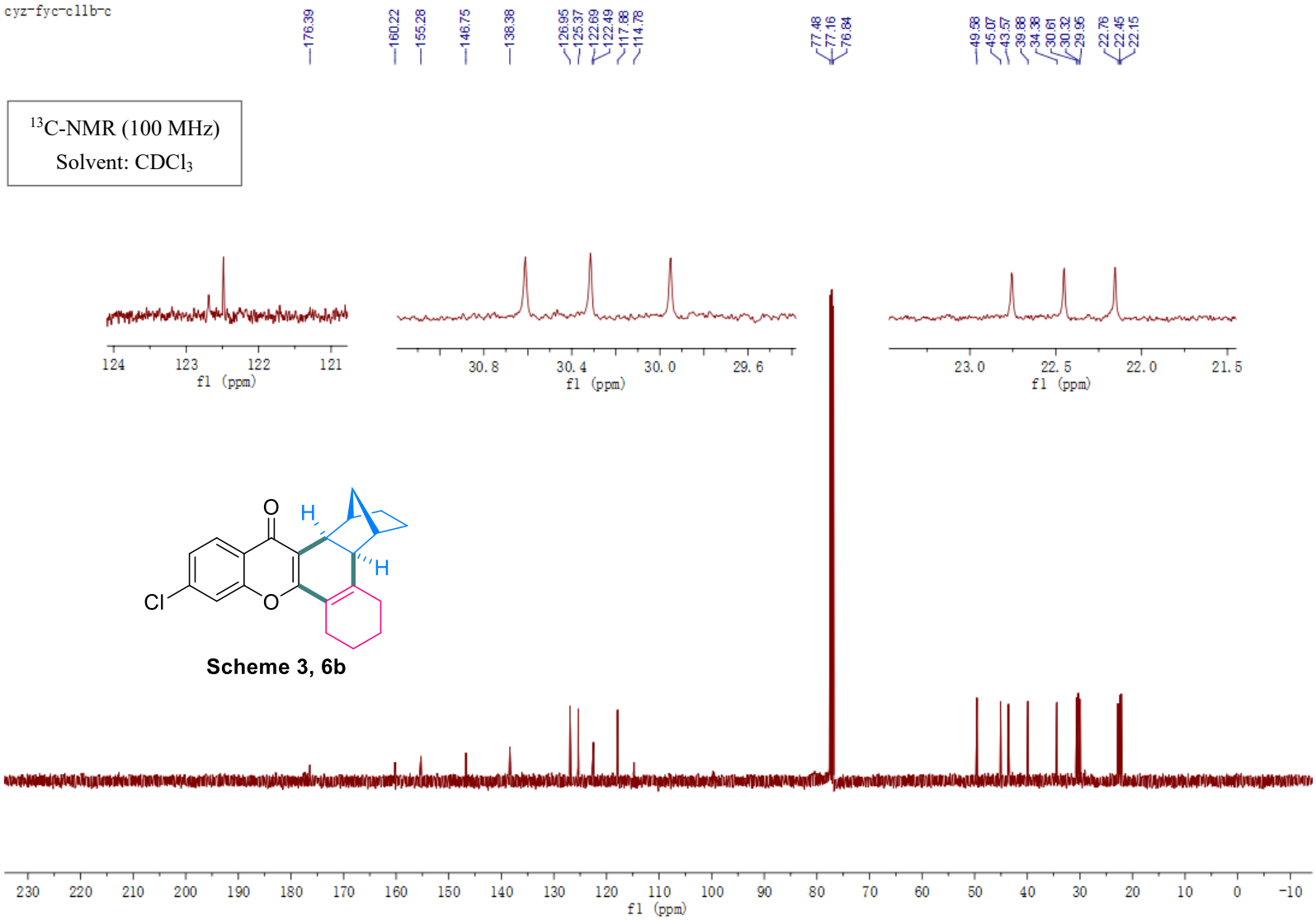
Scheme 3, 6a'

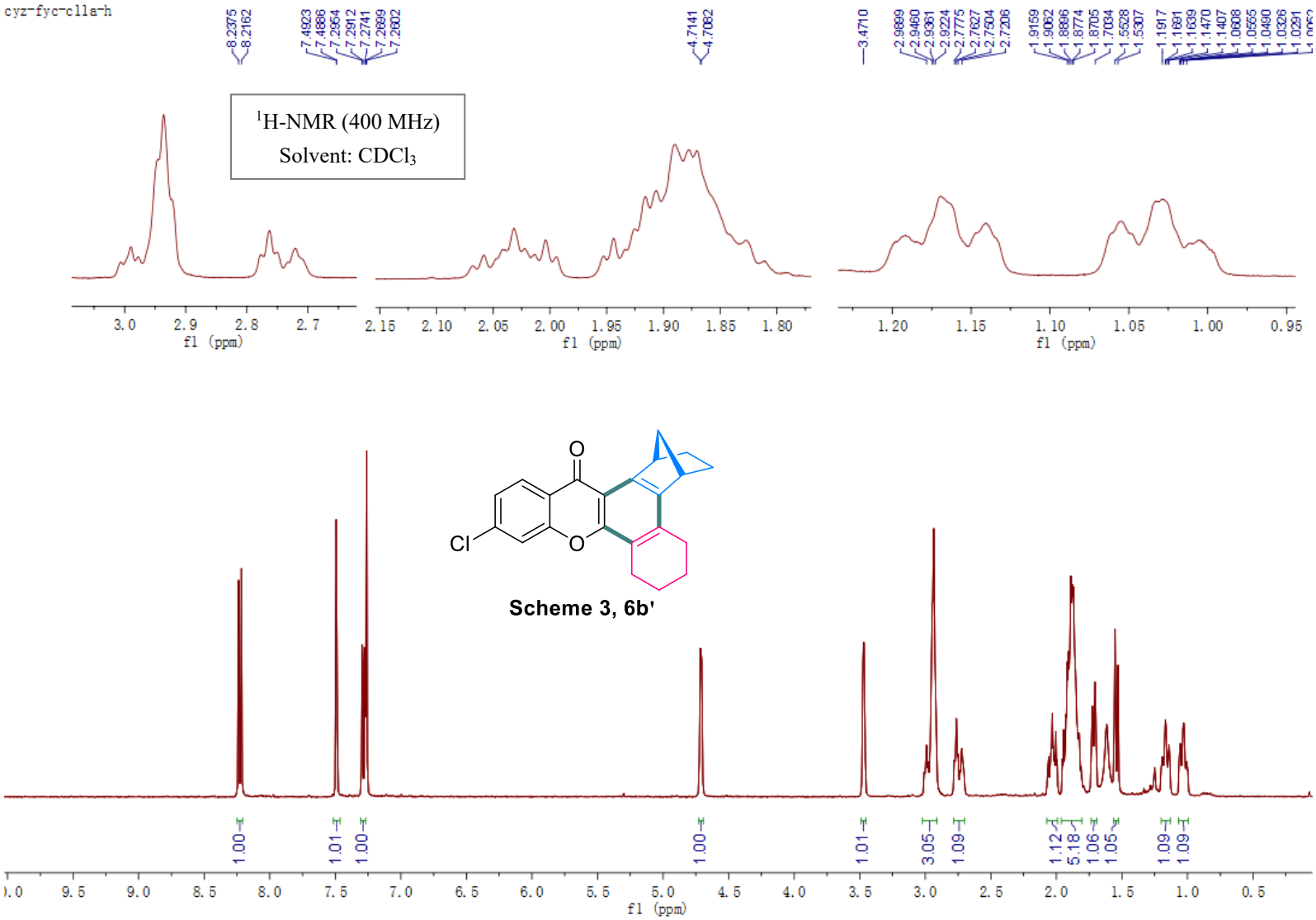


^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

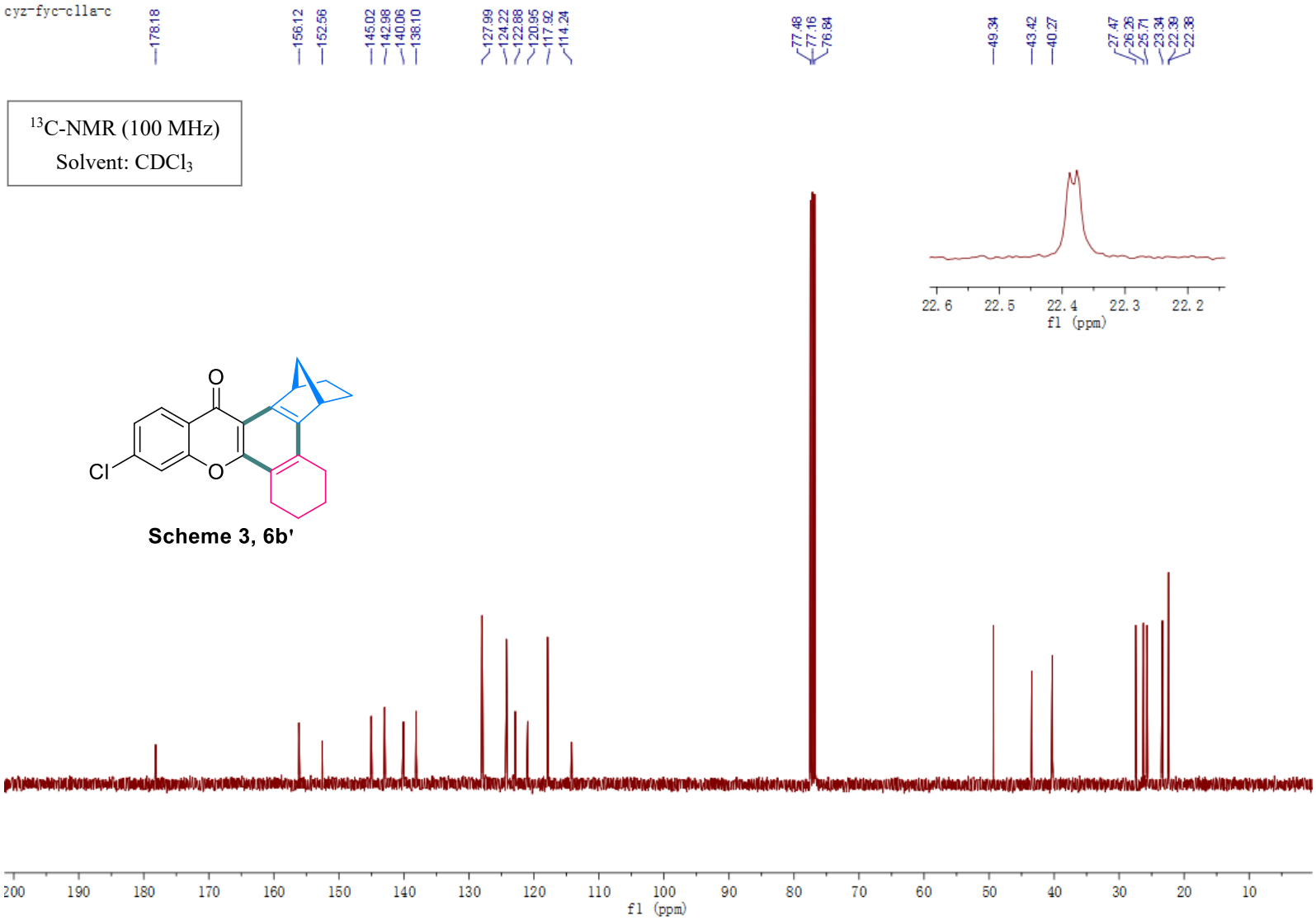
Scheme 3, 6a'

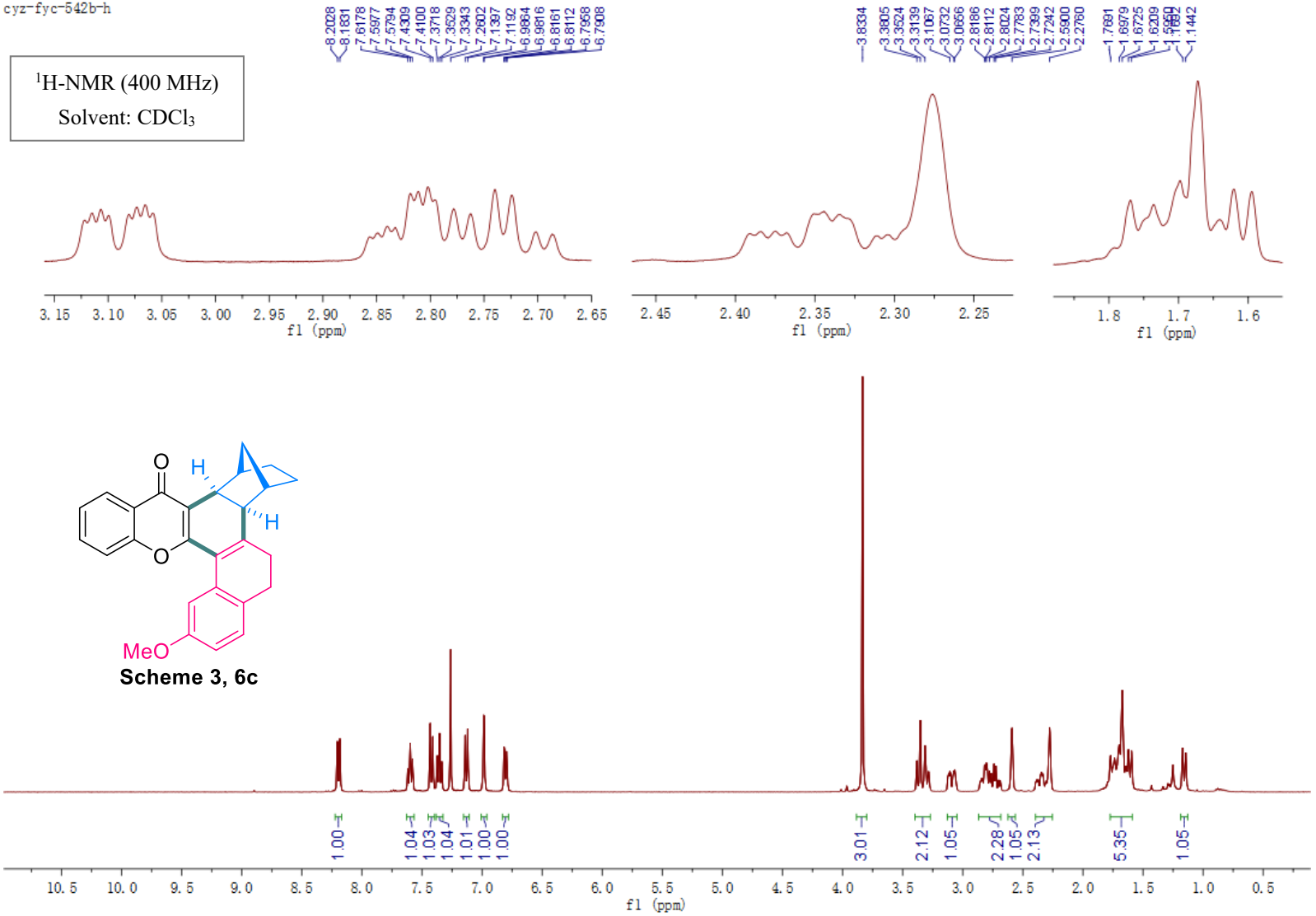

cyz-fyc-c11b-h
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$
f1 (ppm)
Cl
O
H
H
Scheme 3, 6b


cyz-fyc-c11b-c
176.39
160.22
155.28
148.75
138.38
126.95
125.37
122.69
122.49
117.88
114.78
77.48
77.16
76.84
49.88
45.07
43.57
39.88
34.38
30.61
30.32
29.95
22.76
22.45
22.15
13C-NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)
O
H
H
Cl
O
Scheme 3, 6b



Scheme 3, 6b'

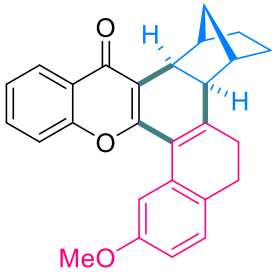

cyz-fyc-clla-c
178.18
156.12
152.56
145.02
142.98
140.06
138.10
127.99
124.22
122.88
120.95
117.92
114.24
77.48
77.16
76.84
49.34
43.42
40.27
27.47
26.26
25.71
23.34
22.39
22.38
13C-NMR (100 MHz)
Solvent: CDCl3
O
Cl
O
Scheme 3, 6b'
22.6
22.5
22.4
22.3
22.2
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


cyz-fyc-542b-h
^{1}H-NMR (400 MHz)
Solvent: CDCl$_3$
f1 (ppm)
MeO
Scheme 3, 6c

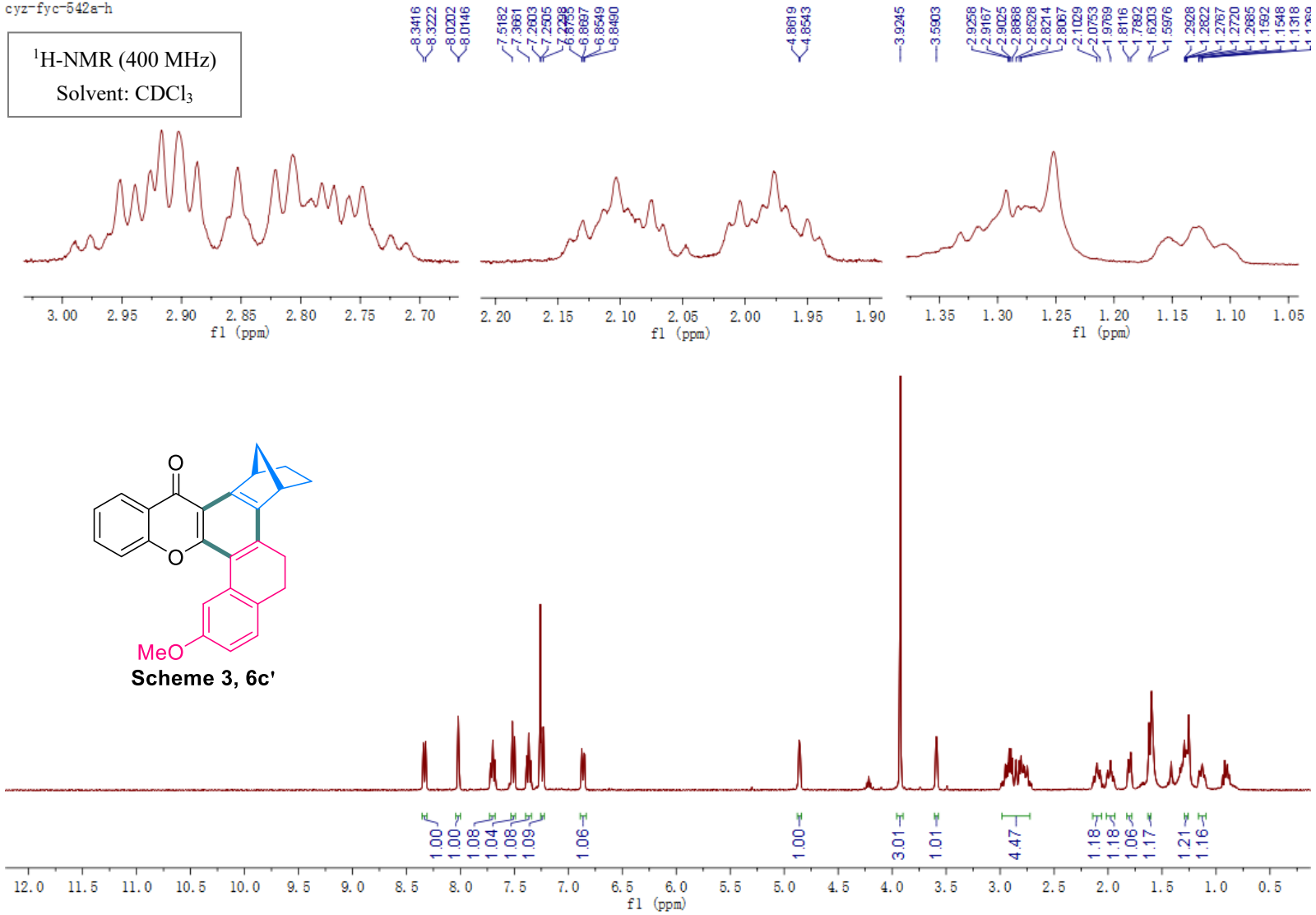
cyz-fyc-542b-c

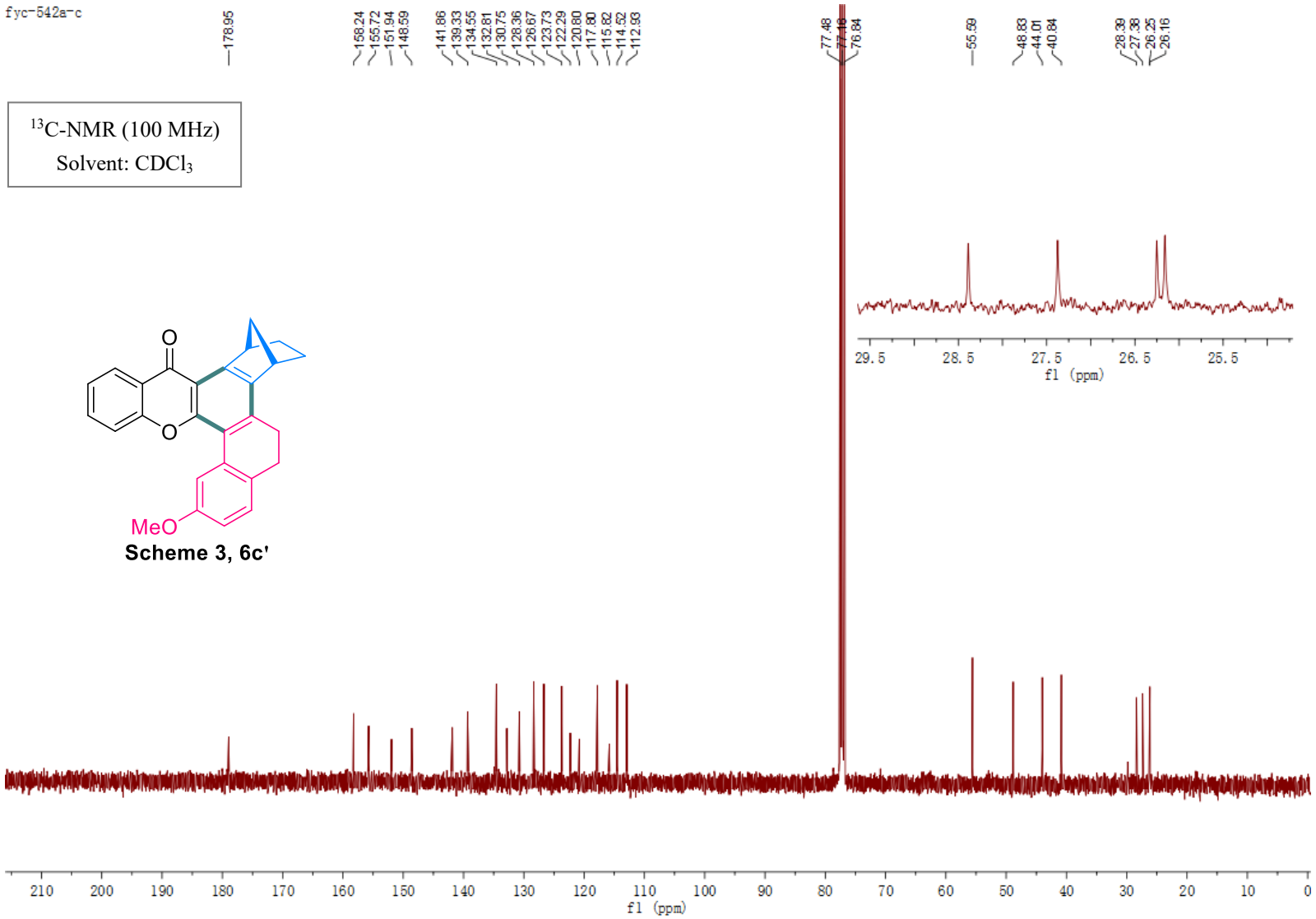
176.99
158.89
158.42
155.26
141.11
135.23
132.81
130.06
128.33
125.58
125.50
124.74
124.14
117.81
115.62
112.97
110.55
77.48
77.16
76.84
55.52
45.78
45.30
43.31
40.42
34.64
30.34
30.25
27.09
20.91

^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

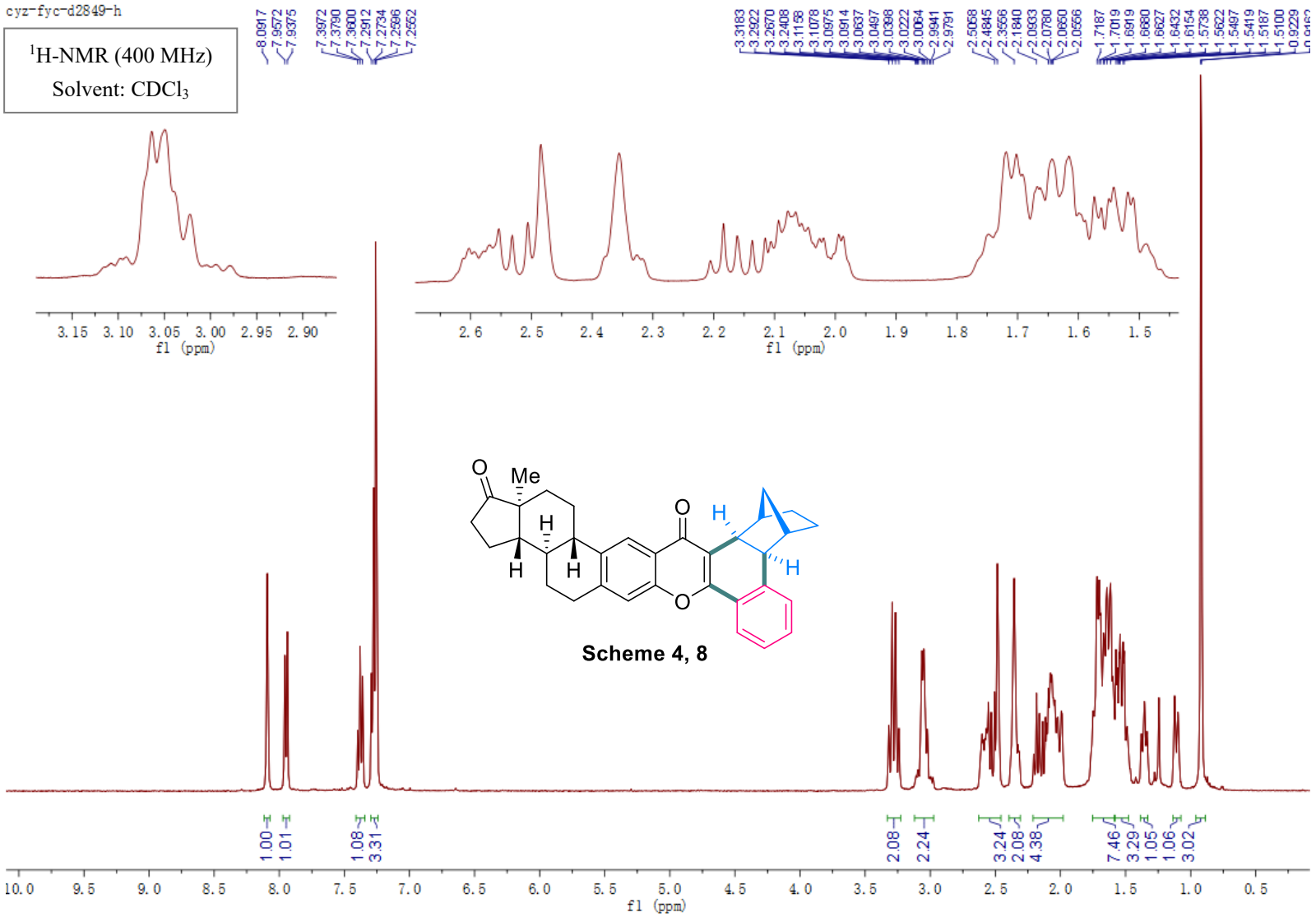


Scheme 3, 6c

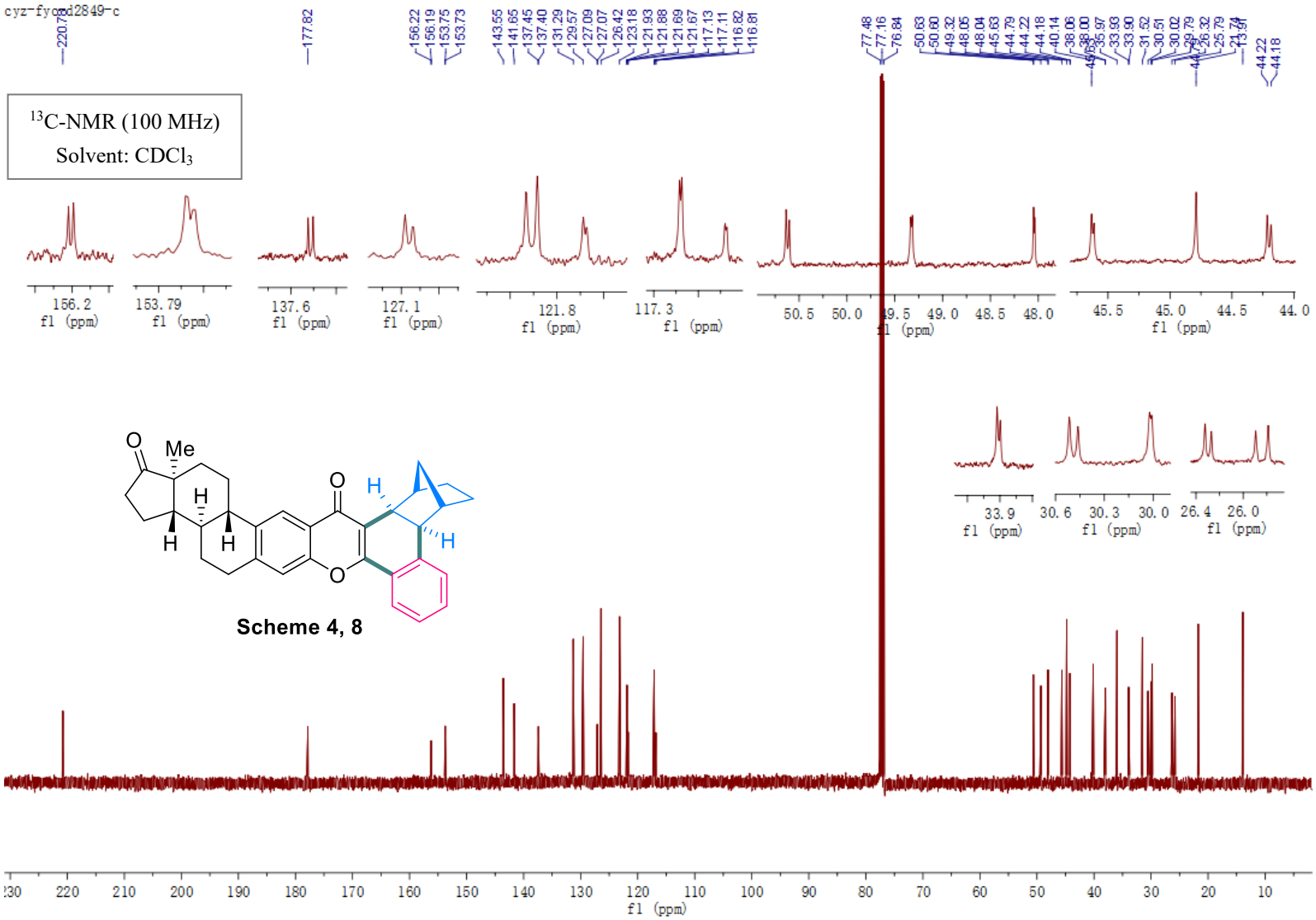

cyz-fyc-542a-h
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$
MeO
Scheme 3, 6c'
f1 (ppm)

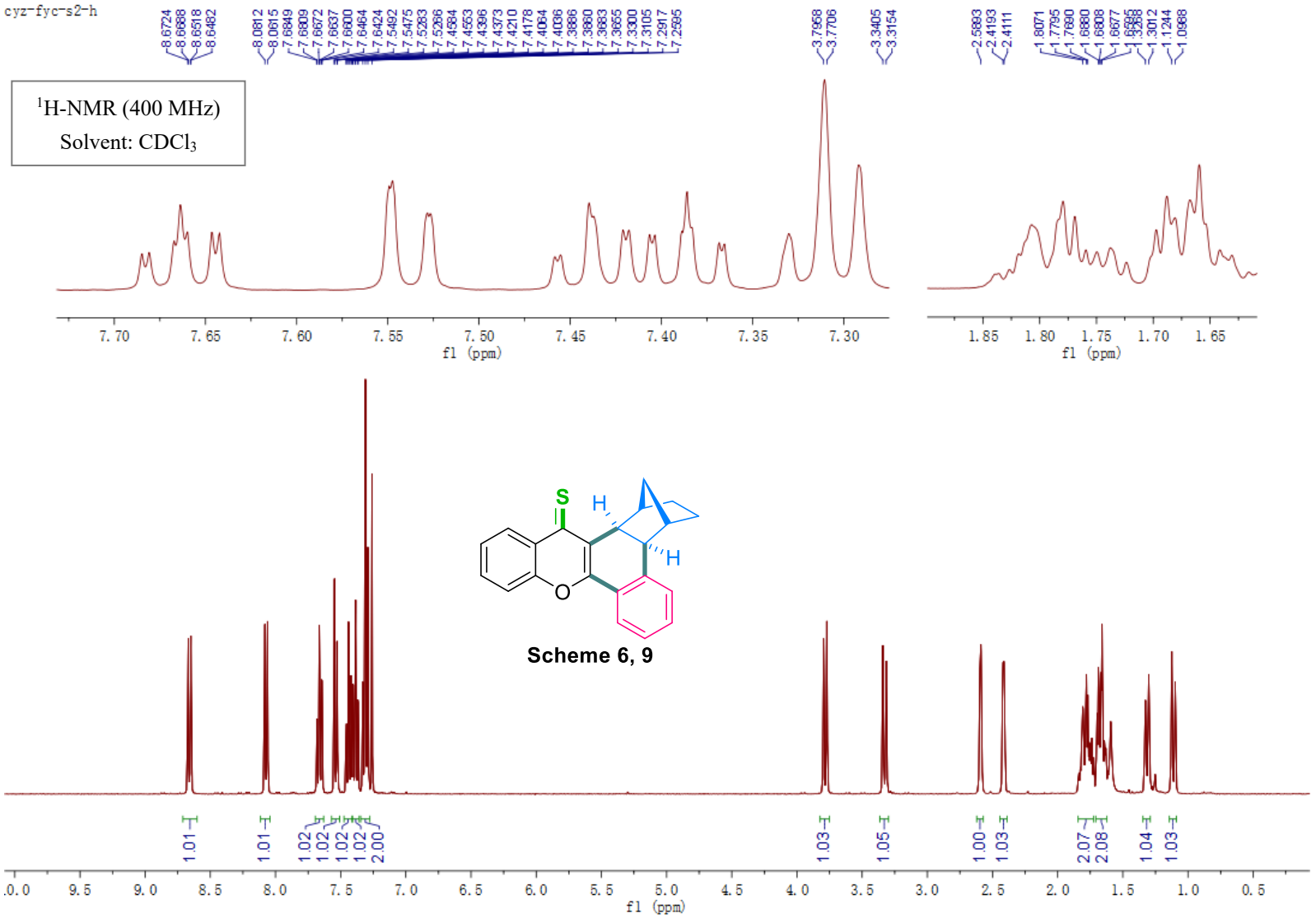

fyc-542a-c
178.95
158.24
155.72
151.94
148.59
141.86
139.33
134.55
132.81
130.75
128.36
126.67
123.73
122.29
120.80
117.80
115.82
114.52
112.93
77.48
77.16
76.84
55.59
48.83
44.01
40.84
28.39
27.38
26.25
26.16
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$
O
O
MeO
29.5
28.5
27.5
26.5
25.5
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

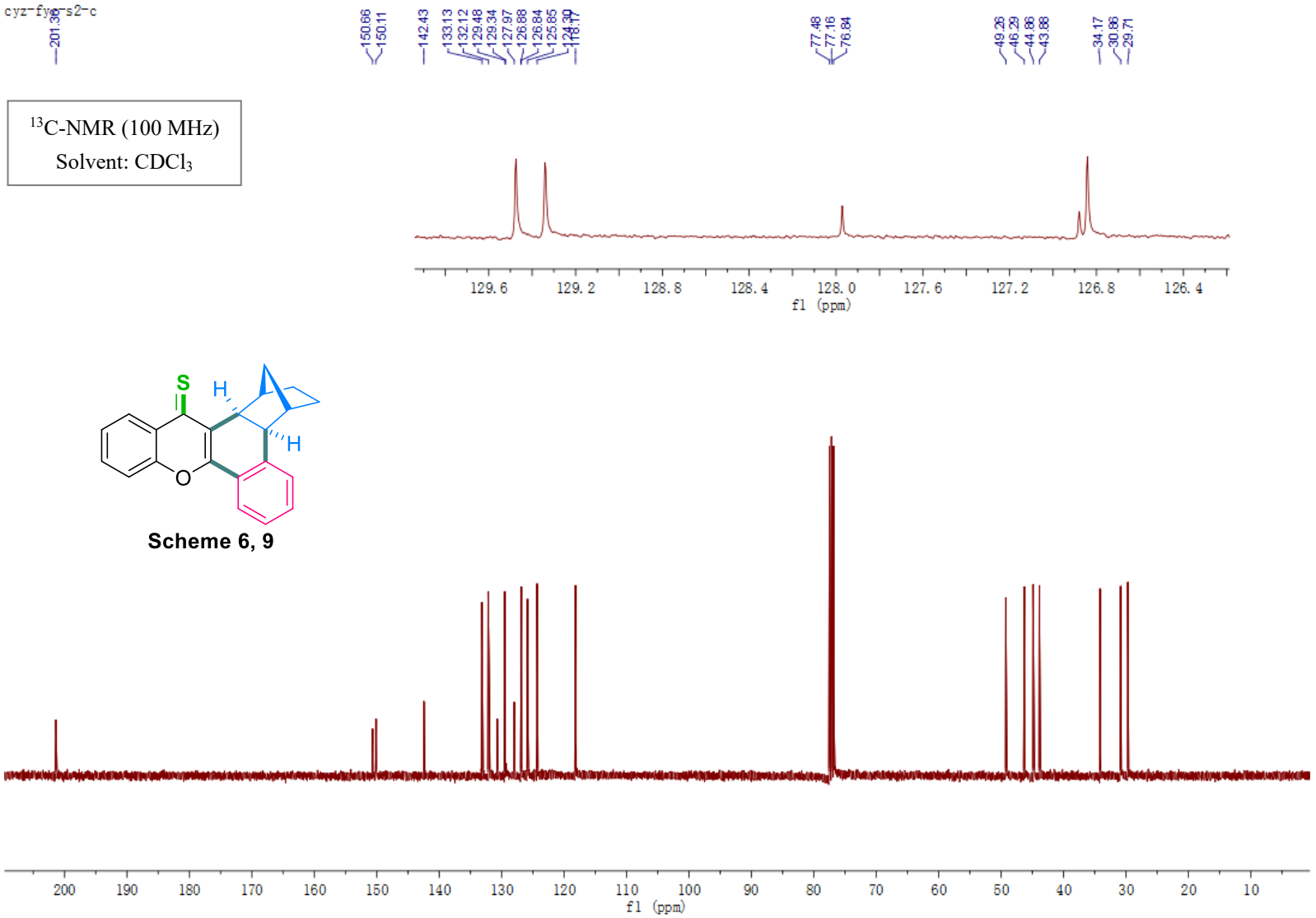
Scheme 3, 6c'



Scheme 4, 8

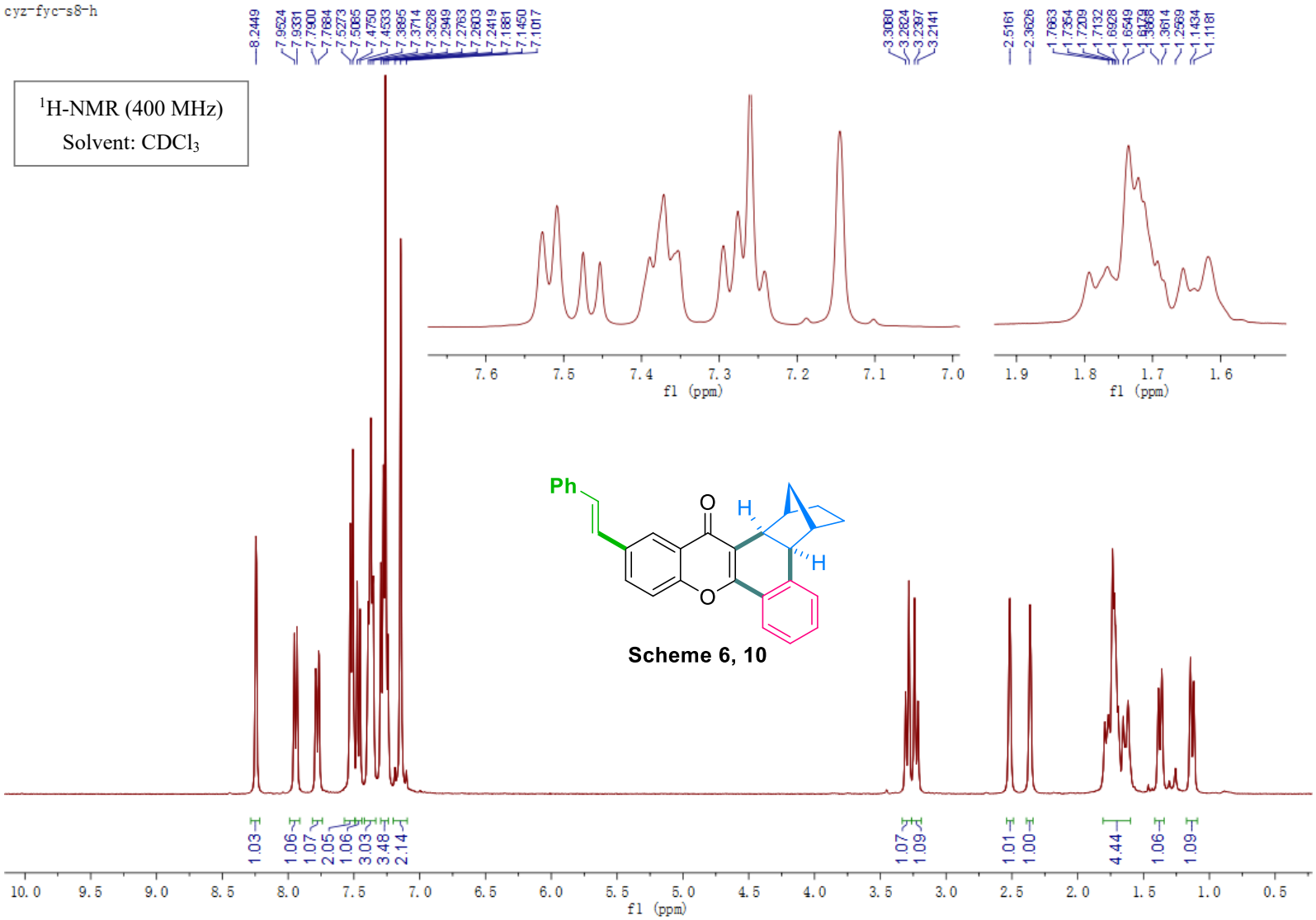

cyz-fyc-sd2849-c
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$
Me
H
O
Scheme 4, 8
f1 (ppm)

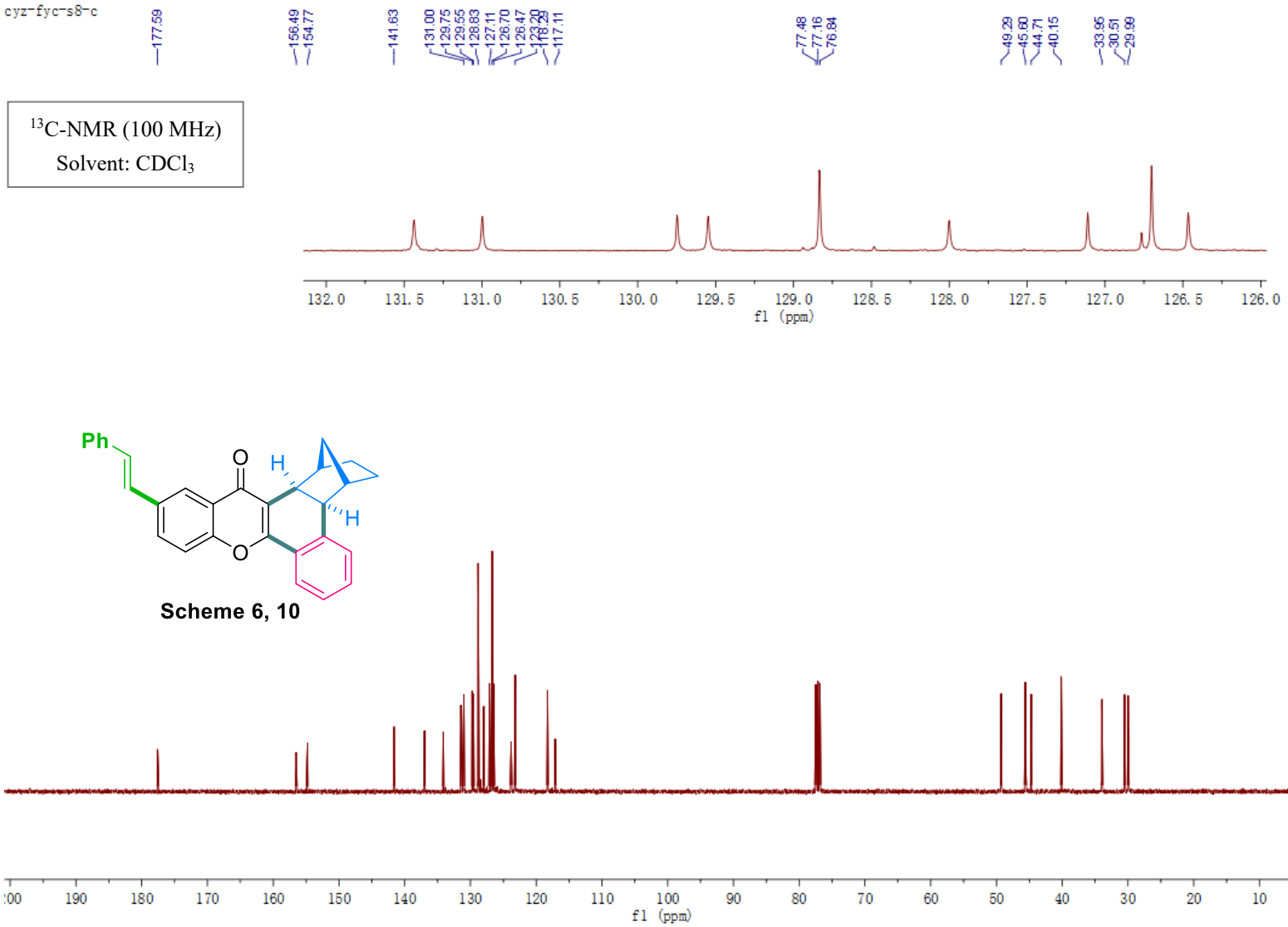

cyz-fyc-s2-h
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$
S
H
H
O
Scheme 6, 9
f1 (ppm)



^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

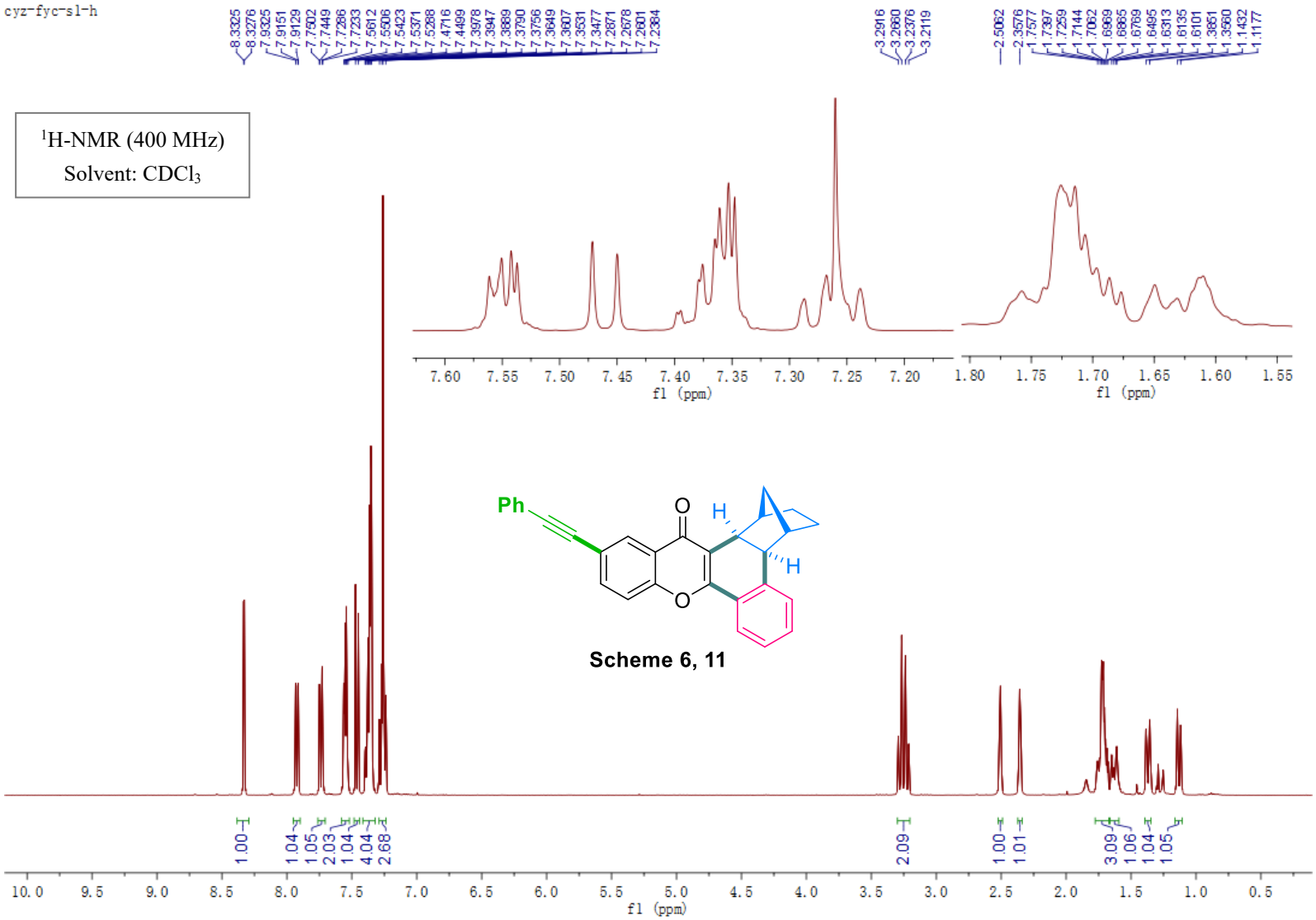
Scheme 6, 9

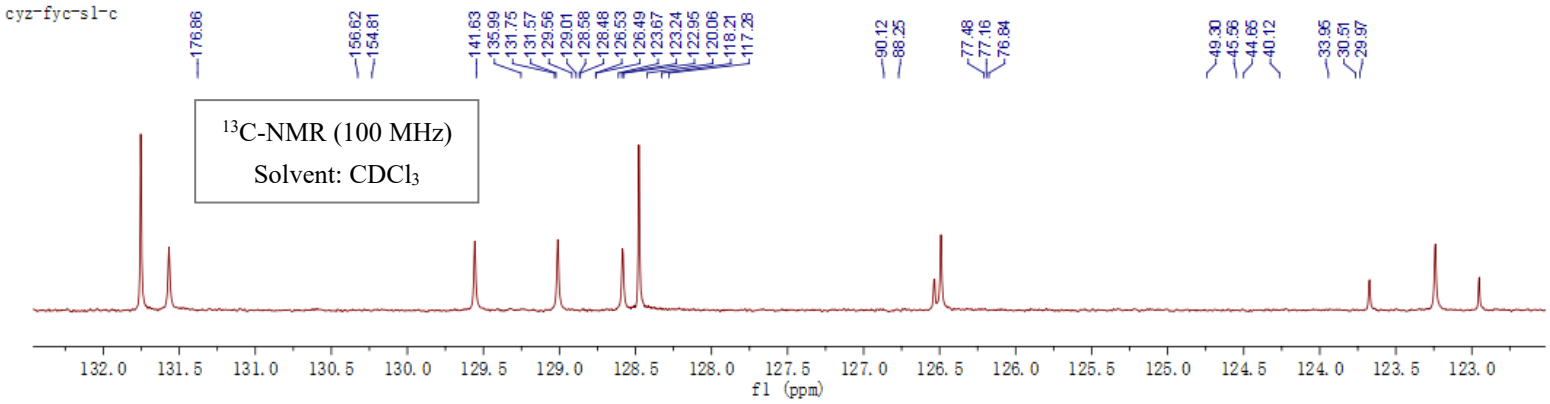

cyz-fyc-s8-h
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$
Ph
O
H
H
O
Scheme 6, 10
f1 (ppm)

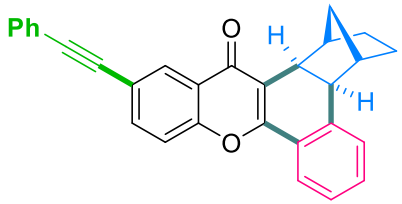


^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$

Scheme 6, 10

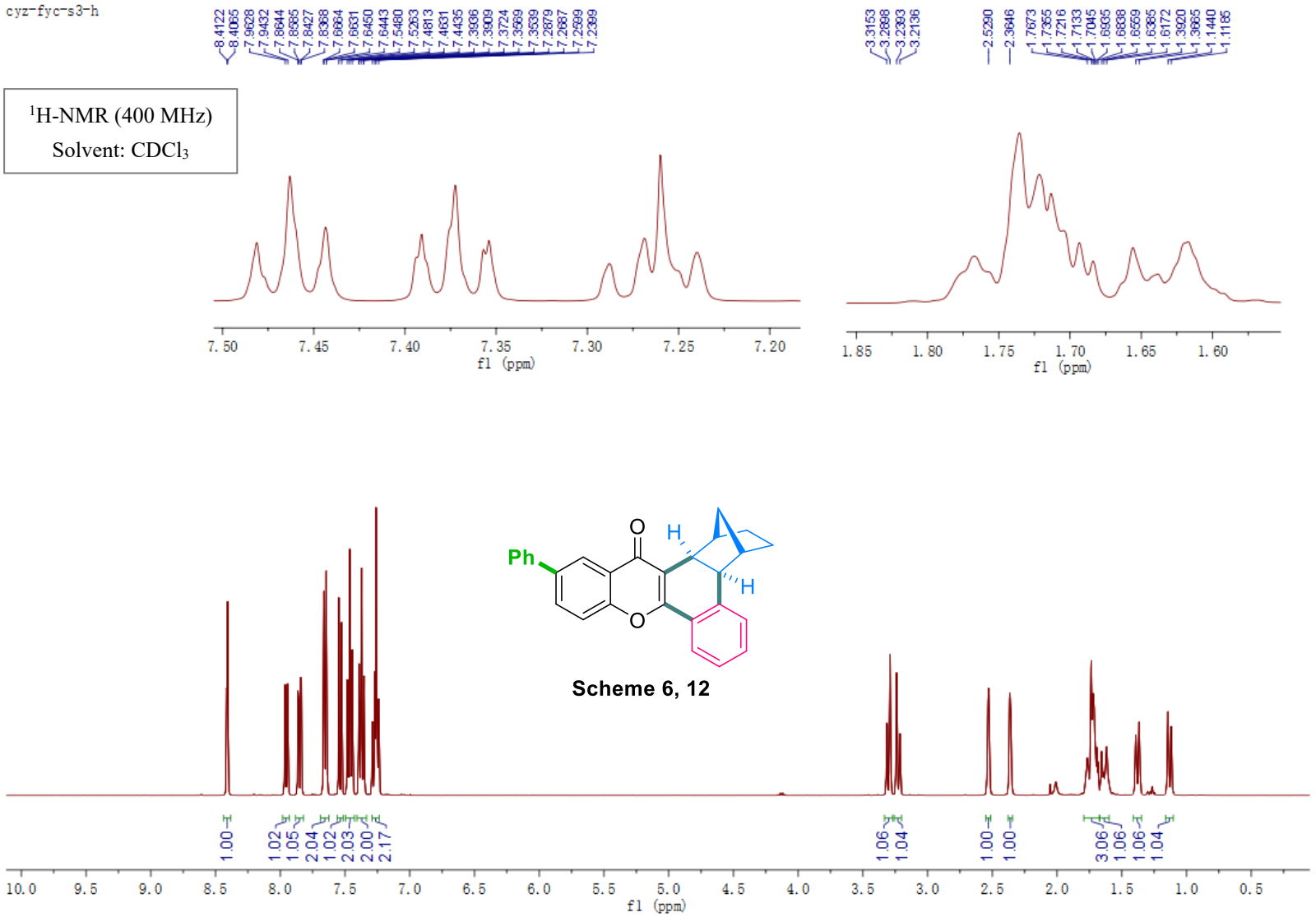

cyz-fyc-sl-h
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$
Ph
O
H
H
O
Scheme 6, 11
f1 (ppm)

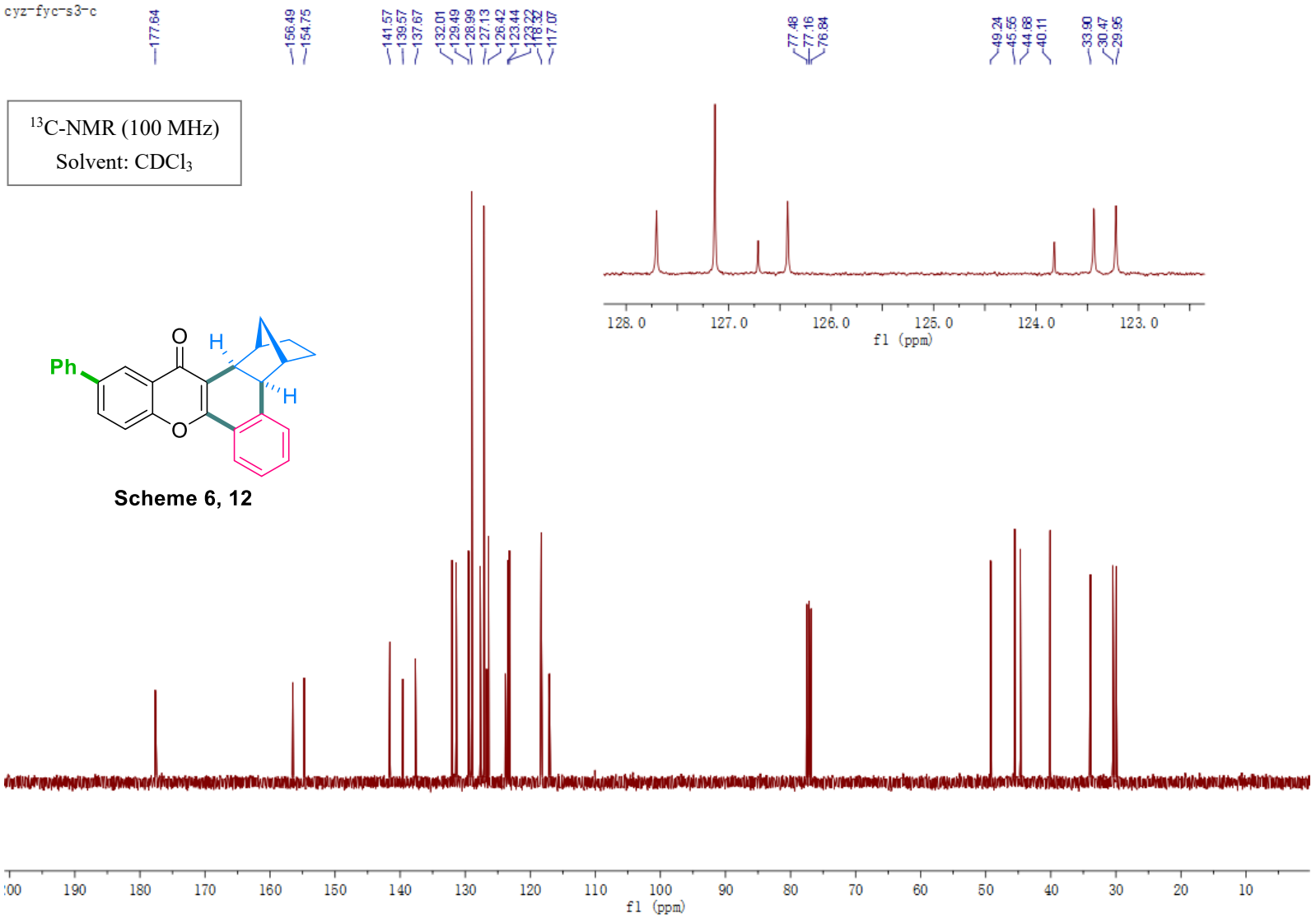

cyz-fyc-sl-c
176.86
156.62
154.81
141.63
135.99
131.75
131.57
129.56
129.01
128.58
128.48
126.53
126.49
123.67
123.24
122.95
120.06
118.21
117.28
90.12
88.25
77.48
77.16
76.84
49.30
45.56
44.65
40.12
33.95
30.51
29.97
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$
132.0 131.5 131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0 125.5 125.0 124.5 124.0 123.5 123.0
f1 (ppm)

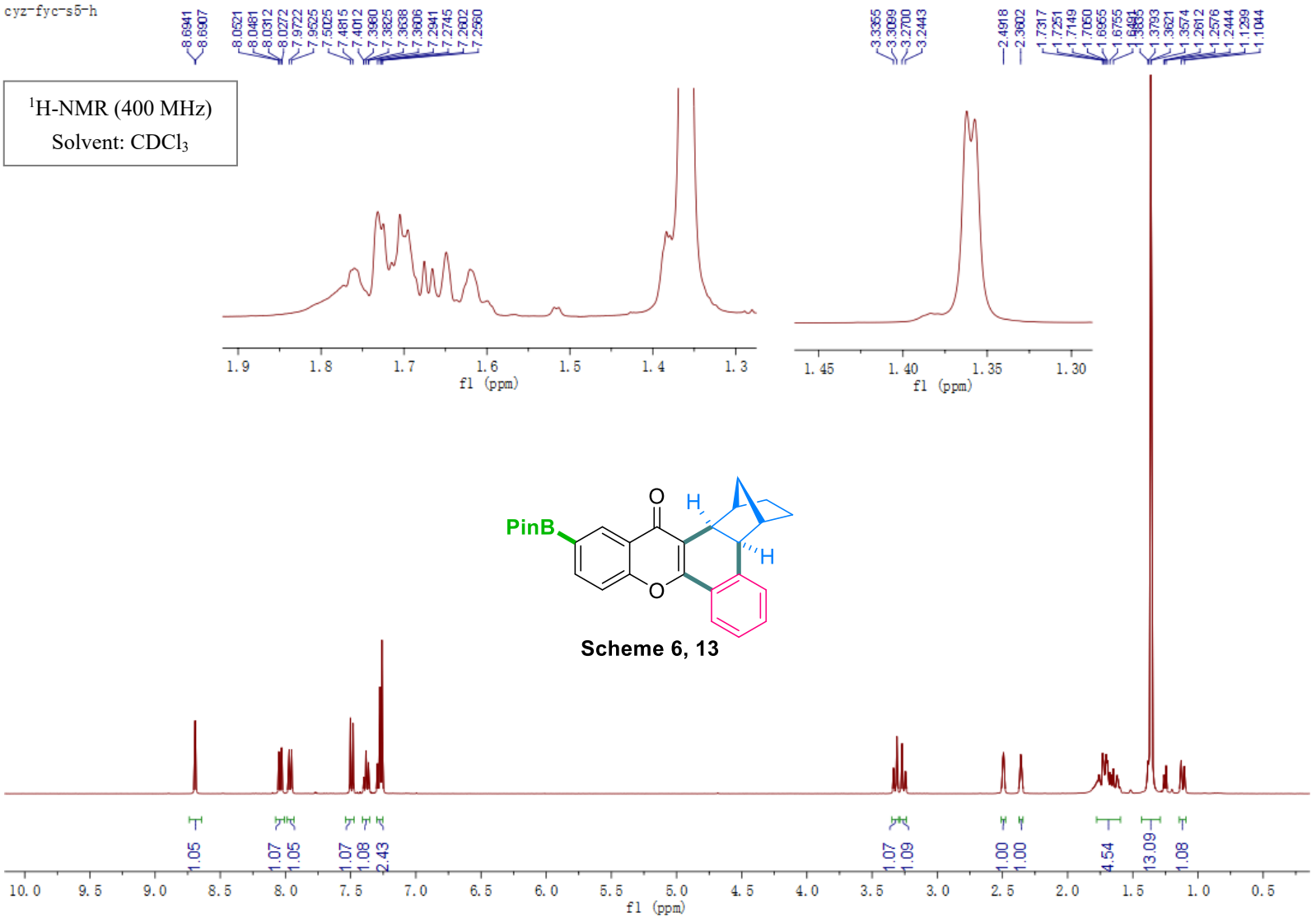

Ph
O
H
H
O

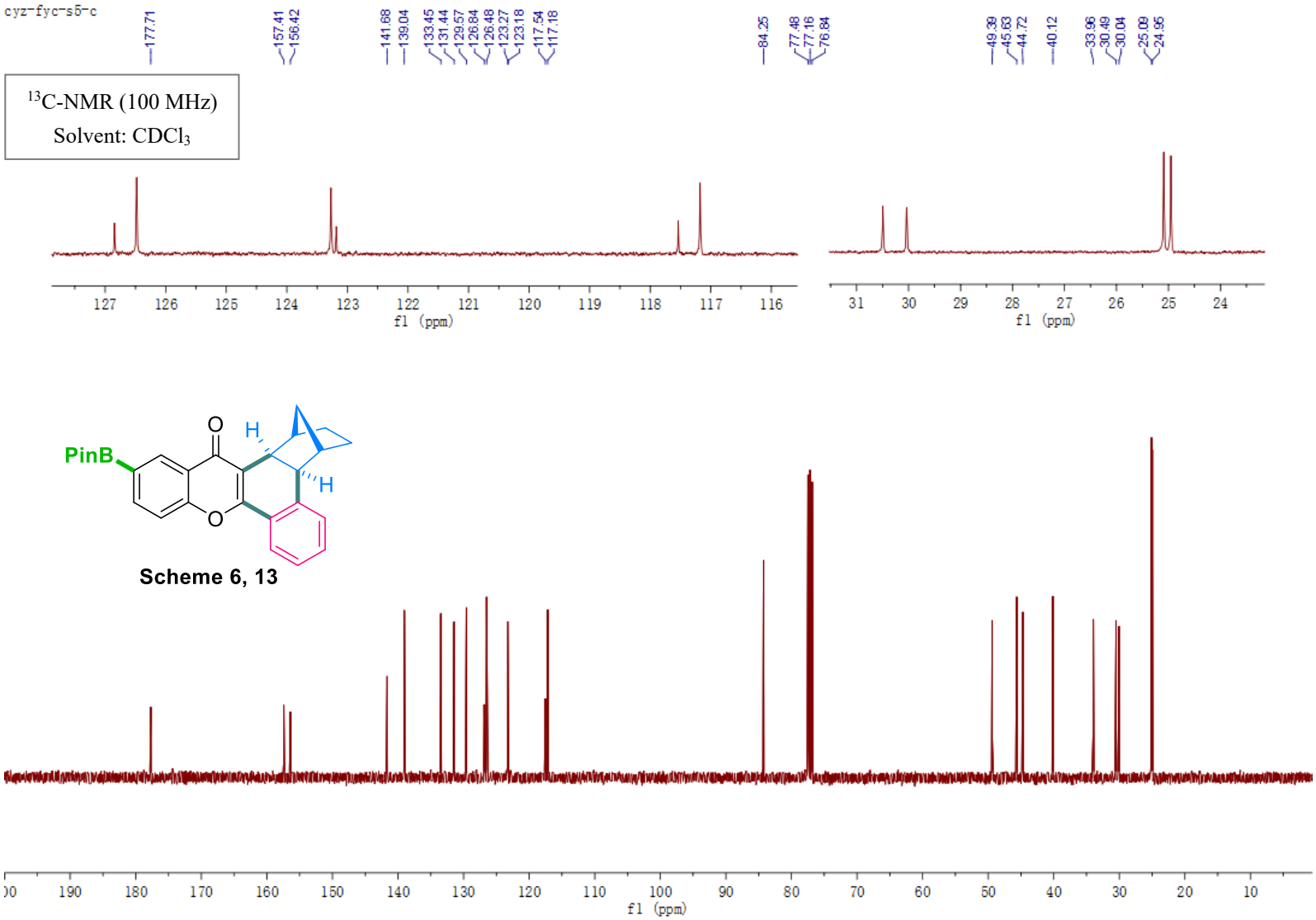
Scheme 6, 11

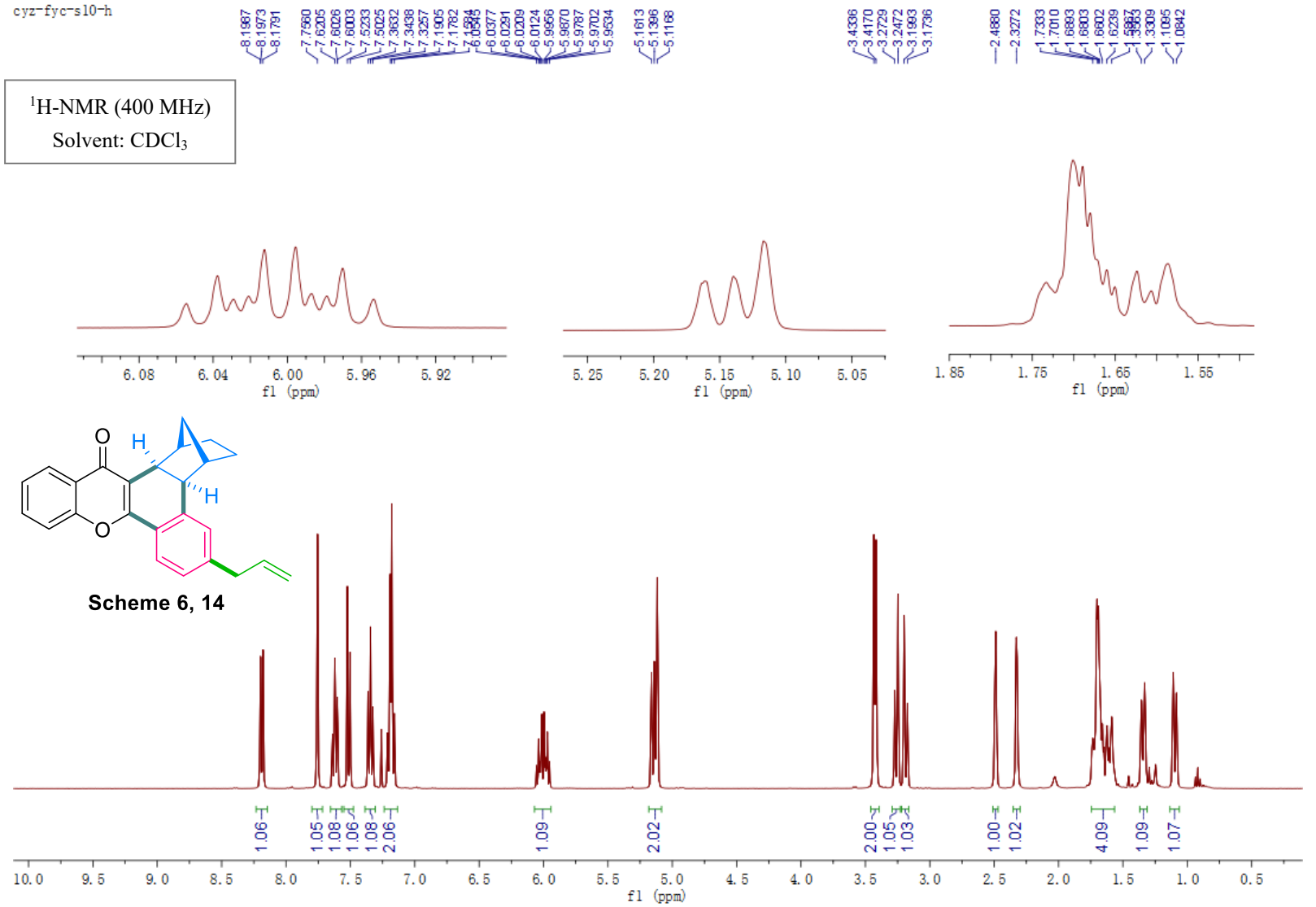
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


cyz-fyc-s3-h
1H-NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)
Ph
O
H
H
O
Scheme 6, 12


cyz-fyc-s3-c
177.64
156.49
154.75
141.57
139.57
137.67
132.01
129.49
128.99
127.13
126.42
123.44
118.22
117.07
77.48
77.16
76.84
49.24
45.55
44.68
40.11
33.90
30.47
29.95
^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$
Ph
O
H
H
O
Scheme 6, 12
128.0
127.0
126.0
125.0
124.0
123.0
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


cyz-fyc-s5-h
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$
PinB
O
H
H
O
Scheme 6, 13
f1 (ppm)

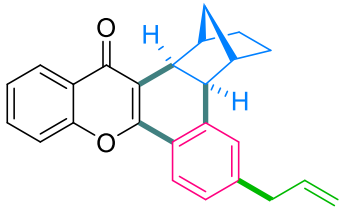

cyz-fyc-sb-c
177.71
157.41
156.42
141.68
139.04
133.45
131.44
129.57
126.84
126.48
123.27
123.18
117.54
117.18
84.25
77.48
77.16
76.84
49.39
45.63
44.72
40.12
33.96
30.49
30.04
25.09
24.95
13C-NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)
PinB
O
H
H
O
Scheme 6, 13


cyz-fyc-s10-h
^{1}H-NMR (400 MHz)
Solvent: $CDCl_3$
f1 (ppm)
Scheme 6, 14

cyz-fyc-s10-c

177.66
156.56
155.33
139.43
138.21
137.11
133.12
131.78
129.60
126.75
125.62
124.64
123.74
123.17
117.85
117.18
116.30
77.48
77.16
76.84
49.13
45.23
44.64
40.11
39.91
33.87
30.48
29.87

^{13}C-NMR (100 MHz)
Solvent: $CDCl_3$



Scheme 6, 14