Synthesis of chromone-containing polycyclic compounds *via* palladium-catalyzed [2+2+1] annulation

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Electronic Supplementary Information

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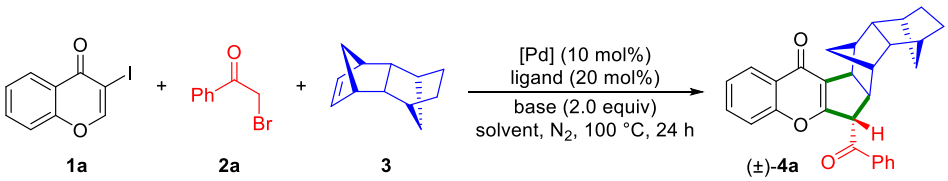
1. General experimental information

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

3-Iodochromones (**1**) was prepared according to the reported procedures.[1] α-Bromoacetophenones (**2**) and TCD (**3**) were purchased from commercial suppliers.

(1) D. A. Vasselin, A. D. Westwell, C. S. Matthews, T. D. Bradshaw and M. F. G. Stevens, *J. Med. Chem.*, 2006, **49**, 3973.

2. Optimization of the reaction conditions[a]



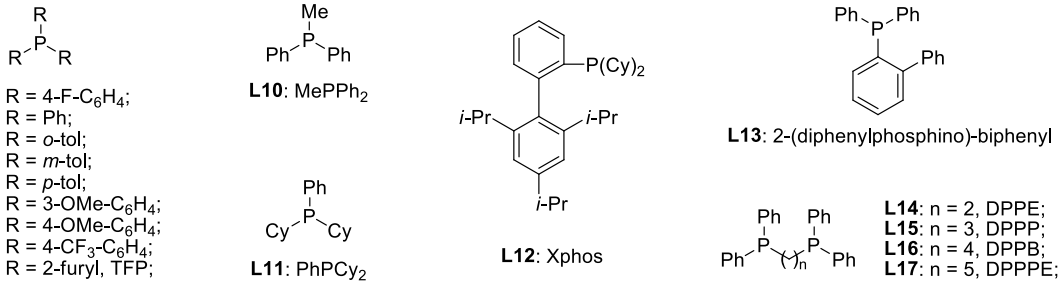
1a **2a** **3** (±)-**4a**

Entry	Catalyst	Ligand	Base	Solvent	Yield (%)[b]	dr[c]
1	$Pd(OPiv)_2$	**L1**	K_3PO_4	mesitylene	35	99:1
2	$Pd(OAc)_2$	**L1**	K_3PO_4	mesitylene	48	99:1
3	$Pd(TFA)_2$	**L1**	K_3PO_4	mesitylene	47	99:1
4	$[(\pi\text{-cinnamyl})PdCl]_2$	**L1**	K_3PO_4	mesitylene	19	99:1
5	$PdCl_2[PPh(t\text{-Bu})_2]_2$	**L1**	K_3PO_4	mesitylene	11	99:1
6	$Pd(DIPHOS)_2$	**L1**	K_3PO_4	mesitylene	13	99:1
7	$[Pd(dppf)Cl_2]_2\cdot$DCM	**L1**	K_3PO_4	mesitylene	21	99:1
8	$PdCl_2$(dppe)	**L1**	K_3PO_4	mesitylene	12	99:1
9	$PdCl_2$(dppb)	**L1**	K_3PO_4	mesitylene	27	99:1

10	$[PdCl(C_3H_5)]_2$	**L1**	K_3PO_4	mesitylene	13	99:1
11	$Pd(PPh_3)_4$	**L1**	K_3PO_4	mesitylene	22	99:1
12	$Pd_2(dba)_3$	**L1**	K_3PO_4	mesitylene	31	99:1
13	$Pd(OAc)_2$	**L2**	K_3PO_4	mesitylene	26	99:1
14	$Pd(OAc)_2$	**L3**	K_3PO_4	mesitylene	40	99:1
15	$Pd(OAc)_2$	**L4**	K_3PO_4	mesitylene	44	99:1
16	$Pd(OAc)_2$	**L5**	K_3PO_4	mesitylene	40	99:1
17	$Pd(OAc)_2$	**L6**	K_3PO_4	mesitylene	50	99:1
18	$Pd(OAc)_2$	**L7**	K_3PO_4	mesitylene	37	99:1
19	$Pd(OAc)_2$	**L8**	K_3PO_4	mesitylene	37	99:1
20	$Pd(OAc)_2$	**L9**	K_3PO_4	mesitylene	18	99:1
21	$Pd(OAc)_2$	**L10**	K_3PO_4	mesitylene	21	99:1
22	$Pd(OAc)_2$	**L11**	K_3PO_4	mesitylene	36	99:1
23	$Pd(OAc)_2$	**L12**	K_3PO_4	mesitylene	32	99:1
24	$Pd(OAc)_2$	**L13**	K_3PO_4	mesitylene	18	99:1
25	$Pd(OAc)_2$	**L14**	K_3PO_4	mesitylene	4	–
26	$Pd(OAc)_2$	**L15**	K_3PO_4	mesitylene	2	–
27	$Pd(OAc)_2$	**L16**	K_3PO_4	mesitylene	29	99:1
28	$Pd(OAc)_2$	**L17**	K_3PO_4	mesitylene	18	99:1
29	$Pd(OAc)_2$	**L6**	Cs_2CO_3	mesitylene	16	99:1
30	$Pd(OAc)_2$	**L6**	Na_2CO_3	mesitylene	16	99:1
31	$Pd(OAc)_2$	**L6**	K_2CO_3	mesitylene	53	99:1
32	$Pd(OAc)_2$	**L6**	$NaHCO_3$	mesitylene	13	99:1
33	$Pd(OAc)_2$	**L6**	NaOAc	mesitylene	4	–
34	$Pd(OAc)_2$	**L6**	KOAc	mesitylene	35	99:1
35	$Pd(OAc)_2$	**L6**	NaOPiv	mesitylene	10	99:1
36	$Pd(OAc)_2$	**L6**	*t*-BuOK	mesitylene	12	99:1
37	$Pd(OAc)_2$	**L6**	*t*-BuONa	mesitylene	11	99:1
38	$Pd(OAc)_2$	**L6**	CsF	mesitylene	31	99:1
39	$Pd(OAc)_2$	**L6**	KF	mesitylene	18	99:1
40	$Pd(OAc)_2$	**L6**	K_2CO_3	toluene	54	99:1
41	$Pd(OAc)_2$	**L6**	K_2CO_3	*o*-xylene	62	99:1
42	$Pd(OAc)_2$	**L6**	K_2CO_3	*m*-xylene	57	99:1
43	$Pd(OAc)_2$	**L6**	K_2CO_3	*p*-xylene	60	99:1
44	$Pd(OAc)_2$	**L6**	K_2CO_3	$PhCF_3$	12	99:1
45	$Pd(OAc)_2$	**L6**	K_2CO_3	1,4-dioxane	43	99:1
46	$Pd(OAc)_2$	**L6**	K_2CO_3	DCE	14	99:1
47	$Pd(OAc)_2$	**L6**	K_2CO_3	NMP	2	–
48	$Pd(OAc)_2$	**L6**	K_2CO_3	DMSO	3	–
49	$Pd(OAc)_2$	**L6**	K_2CO_3	DMF	2	–
50[d]	$Pd(OAc)_2$	**L6**	K_2CO_3	*o*-xylene	65	99:1

51[e]	$Pd(OAc)_2$	**L6**	K_2CO_3	*o*-xylene	69	99:1
52[f]	$Pd(OAc)_2$	**L6**	K_2CO_3	*o*-xylene	69	99:1
53[e,g]	$Pd(OAc)_2$	**L6**	K_2CO_3	*o*-xylene	67	99:1
54[e,h]	$Pd(OAc)_2$	**L6**	K_2CO_3	*o*-xylene	69	99:1
55[e,i]	$Pd(OAc)_2$	**L6**	K_2CO_3	*o*-xylene	75	99:1
65[e,i,j]	$Pd(OAc)_2$	**L6**	K_2CO_3	*o*-xylene	81	99:1
66[e,i,k]	$Pd(OAc)_2$	**L6**	K_2CO_3	*o*-xylene	71	99:1
67[e,i,l]	$Pd(OAc)_2$	**L6**	K_2CO_3	*o*-xylene	70	99:1
68[e,i,j,m]	$Pd(OAc)_2$	**L6**	K_2CO_3	*o*-xylene	62	99:1
69[e,i,j,n]	$Pd(OAc)_2$	**L6**	K_2CO_3	*o*-xylene	76	99:1
70[e,i,j,o]	$Pd(OAc)_2$	**L6**	K_2CO_3	*o*-xylene	69	99:1

Phosphine ligands examined in this work:



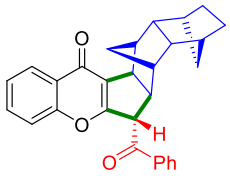
[a] Unless otherwise noted, all reactions were performed with **1a** (0.2 mmol, 1.0 equiv), **2a** (0.2 mmol, 1.0 equiv), **3** (0.4 mmol, 2.0 equiv), Pd-catalyst (10 mol%), ligand (20 mol%), base (0.4 mmol, 2.0 equiv) in 2.0 mL of solvent under N_2 atmosphere at 100 °C for 24 h. [b] Isolated yield based on **1a**. [c] The dr values were determined by ^1H NMR analysis. [d] 3.0 equiv of **3** was used. [e] 4.0 equiv of **3** was used. [f] 5.0 equiv of **3** was used. [g] 1.0 equiv of K_2CO_3 was used. [h] 3.0 equiv of K_2CO_3 was used. [i] 4.0 equiv of K_2CO_3 was used. [j] 1.2 equiv of **2a** was used. [k] 1.4 equiv of **2a** was used. [l] 1.6 equiv of **2a** was used. [m] 4.0 mL of *o*-xylene was used. [n] 1.3 mL of *o*-xylene was used. [o] 1.0 mL of *o*-xylene was used.

3. Representative procedure for the synthesis of compound (±)-4a.

A 4 mL flame-dried vial with a stir bar was charged with 3-iodochromone (**1a**, 54.4 mg, 0.2 mmol), α-bromoacetophenone (**2a**, 47.8 mg, 0.24 mmol), TCD (**3**, 128.2 mg, 0.8mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), P(3-OMe-C_6H_4)$_3$ (14.1mg, 0.04 mmol), and K_2CO_3 (110.6 mg, 0.8 mmol) in 2.0 mL of dry *o*-xylene under nitrogen atmosphere at 100 °C for 24 h. After the completion of the reaction detected by thin layer chromatography (TLC), the mixture was cooled to room temperature and purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1–1:1) to afford the desired product (±)-**4a** as a light yellow solid (68.4 mg, 81%, 99:1 dr).

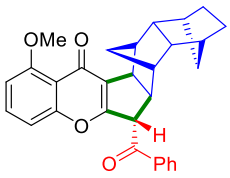
4. Characterization data of compounds (±)-4a−af

Scheme 2, 4a



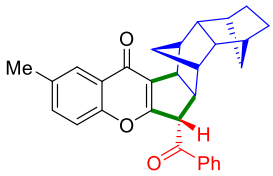
(±)-6-Benzoyl-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*]chromen-13 (6*H*)-one (4a). Light yellow solid, 68.4 mg, 81% yield, mp 235.4–237.2 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 8.4 Hz, 2H), 7.66 (td, J = 7.2, 1.6 Hz, 1H), 7.59–7.53 (m, 3H), 7.39–7.29 (m, 2H), 4.51–4.47 (m, 1H), 3.67 (d, J = 7.2 Hz, 1H), 2.81–2.72 (m, 2H), 2.43 (d, J = 4.6 Hz, 1H), 2.40 (d, J = 3.6 Hz, 1H), 2.06 (d, J = 3.6 Hz, 1H), 1.86 (dd, J = 10.0, 4.8 Hz, 1H), 1.77 (dd, J = 10.0, 4.8 Hz, 1H), 1.61 (d, J = 11.4 Hz, 1H), 1.51–1.41 (m, 3H), 1.24 (d, J = 10.8 Hz, 1H), 1.03–0.93 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 176.2, 165.7, 157.1, 135.9, 134.0, 133.1, 129.0, 129.0, 125.9, 125.1, 124.9, 124.5, 118.2, 59.2, 50.2, 50.1, 47.9, 44.9, 43.8, 42.7, 36.4, 36.3, 35.3, 31.4, 31.3. HRMS (ESI-TOF): calcd. for $C_{29}H_{27}O_3$ $[M + H]^+$ 423.1955; found 423.1951.

Scheme 2, 4b



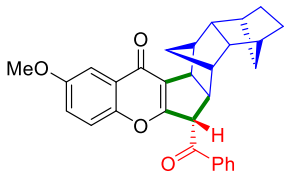
(±)-6-Benzoyl-1-methoxy-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*] chromen-13(6*H*)-one (4b). Light yellow solid, 56.8 mg, 63% yield, mp 220.7–222.5 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.4 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.4 Hz, 2H), 7.43 (t, J = 8.4 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 6.76 (d, J = 8.4 Hz, 1H), 4.42 (s, 1H), 3.94 (s, 3H), 3.59 (d, J = 7.0 Hz, 1H), 2.80–2.69 (m, 2H), 2.40–2.34 (m, 2H), 2.03 (s, 1H), 1.85–1.80 (m, 1H), 1.76–1.73 (m, 1H), 1.60 (d, J = 11.2 Hz, 1H), 1.49–1.37 (m, 3H), 1.21 (d, J = 10.4 Hz, 1H), 1.01–0.90 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 176.2, 163.2, 160.4, 159.4, 135.9, 133.9, 133.0, 129.0, 128.4, 126.0, 115.2, 110.4, 106.6, 59.0, 56.5, 50.4, 50.2, 50.1, 47.8, 45.0, 43.7, 42.8, 41.0, 36.3, 36.2, 35.3, 31.4. HRMS (ESI-TOF): calcd. for $C_{30}H_{29}O_4$ $[M + H]^+$ 453.2060; found 453.2067.

Scheme 2, 4c



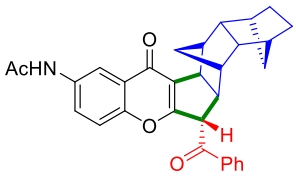
(±)-6-Benzoyl-2-methyl-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*] chromen-13(6*H*)-one (4c). Light yellow solid, 61.1 mg, 70% yield, mp 126.5–128.2 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.6 Hz, 2H), 7.99 (s, 1H), 7.64 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H), 7.36 (dd, J = 8.4, 2.4 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H), 4.47 (s, 1H), 3.65 (d, J = 7.2 Hz, 1H), 2.78–2.70 (m, 2H), 2.41–2.38 (m, 5H), 2.04 (s, 1H), 1.85 (dd, J = 10.0, 4.8 Hz, 1H), 1.75 (dd, J = 10.0, 4.8 Hz, 1H), 1.61 (d, J = 11.2 Hz, 1H), 1.50–1.38 (m, 3H), 1.21 (d, J = 10.4 Hz, 1H), 1.03–0.91 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 176.2, 165.6, 155.4, 135.8, 134.9, 134.2, 133.9, 129.0, 128.9, 125.2, 124.6, 124.1, 117.9, 59.1, 50.1, 50.1, 47.8, 44.8, 43.8, 42.7, 36.3, 36.2, 35.3, 31.4, 31.3, 21.0. HRMS (ESI-TOF): calcd. for $C_{30}H_{29}O_3$ $[M + H]^+$ 437.2111; found 437.2113.

Scheme 2, 4d



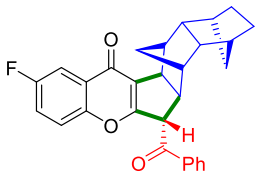
(±)-6-Benzoyl-2-methoxy-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*] chromen-13(6*H*)-one (4d). Light yellow solid, 66.1 mg, 73% yield, mp 121.7–123.4 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08–8.02 (m, 2H), 7.67–7.61 (m, 1H), 7.60–7.52 (m, 3H), 7.26–7.22 (m, 1H), 7.17–7.14 (m, 1H), 4.48 (dd, *J* = 3.6, 2.0 Hz, 1H), 3.90–3.86 (m, 3H), 3.66 (d, *J* = 5.6 Hz, 1H), 2.80–2.71 (m, 2H), 2.41 (t, *J* = 5.6 Hz, 2H), 2.05 (s, 1H), 1.88–1.83 (m, 1H), 1.78–1.74 (m, 1H), 1.61 (d, *J* = 11.2 Hz, 1H), 1.51–1.38 (m, 3H), 1.26–1.19 (m, 1H), 1.03–0.93 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 176.0, 165.6, 156.9, 151.9, 135.9, 133.9, 129.1, 129.0, 125.1, 124.2, 122.9, 119.5, 105.2, 59.1, 56.0, 50.2, 50.1, 47.9, 44.8, 43.8, 42.8, 36.4, 36.3, 35.3, 31.4, 31.3. HRMS (ESI-TOF): calcd. for $C_{30}H_{29}O_4$ $[M + H]^+$ 453.2060; found 453.2058.

Scheme 2, 4e



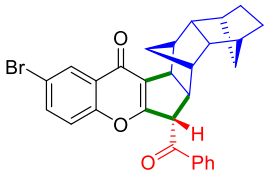
(±)-6-Benzoyl-13-oxo-6,6a,7,7a,8,9,10,11,11a,12,12a,13-dodecahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*] chromen-2-yl)acetamide (4e). Light yellow solid, 29.7 mg, 31% yield, mp 207.8–209.4 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (br s, 1H), 8.50 (d, *J* = 9.0 Hz, 1H), 8.06 (d, *J* = 7.6 Hz, 2H), 8.01 (s, 1H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 9.0 Hz, 1H), 4.52 (s, 1H), 3.65 (d, *J* = 7.2 Hz, 1H), 2.79 (dd, *J* = 7.6, 3.4 Hz, 1H), 2.71 (d, *J* = 4.4 Hz, 1H), 2.44 (d, *J* = 4.4 Hz, 1H), 2.36 (s, 3H), 2.30 (s, 1H), 2.07 (d, *J* = 3.4 Hz, 1H), 1.88–1.84 (m, 1H), 1.79 (dd, *J* = 10.0, 4.8 Hz, 1H), 1.60 (d, *J* = 10.8 Hz, 1H), 1.50–1.42 (m, 2H), 1.25 (d, *J* = 10.0 Hz, 1H), 1.04–0.94 (m, 3H), 0.91–0.80 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 176.4, 169.6, 166.7, 153.5, 136.5, 135.8, 134.1, 129.1, 129.0, 126.5, 124.3, 124.2, 118.9, 114.8, 59.0, 50.1, 50.0, 47.8, 44.9, 43.8, 42.7, 36.4, 36.3, 35.3, 31.3, 24.9. HRMS (ESI-TOF): calcd. for $C_{31}H_{30}NO_4$ $[M + H]^+$ 480.2169; found 480.2163.

Scheme 2, 4f



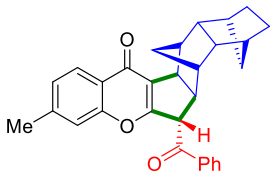
(±)-6-Benzoyl-2-fluoro-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*] chromen-13(6*H*)-one (4f). Light yellow solid, 44.1 mg, 50% yield, mp 254.3–256.1 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.6 Hz, 2H), 7.85 (dd, J = 8.4, 2.6 Hz, 1H), 7.66 (t, J = 7.4 Hz, 1H), 7.56 (t, J = 7.6 Hz, 2H), 7.36–7.27 (m, 2H), 4.49 (s, 1H), 3.65 (d, J = 7.2 Hz, 1H), 2.77 (dd, J = 7.4, 3.4 Hz, 1H), 2.72 (d, J = 4.6 Hz, 1H), 2.44 (d, J = 4.6 Hz, 1H), 2.39 (s, 1H), 2.05 (s, 1H), 1.86 (dd, J = 10.0, 4.6 Hz, 1H), 1.78 (dd, J = 10.0, 4.6 Hz, 1H), 1.59 (d, J = 11.2 Hz, 1H), 1.47–1.40 (m, 2H), 1.29–1.21 (m, 2H), 1.04–0.93 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 175.3, 166.2, 159.6 (d, J = 246.2 Hz, 1C), 153.3 (d, J = 1.8 Hz, 1C), 135.8, 134.1, 129.0 (d, J = 9.7 Hz, 1C), 125.8 (d, J = 7.0 Hz, 1C), 124.5, 121.1 (d, J = 25.5 Hz, 1C), 120.20 (d, J = 8.0 Hz, 1C), 110.8 (d, J = 23.7 Hz, 1C), 59.1, 50.2, 50.1, 47.8, 44.8, 43.8, 42.8, 36.3, 36.2, 35.3, 31.4, 31.3. HRMS (ESI-TOF): calcd. for $C_{29}H_{26}FO_3$ $[M + H]^+$ 441.1860; found 441.1851.

Scheme 2, 4g



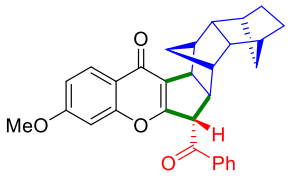
(±)-6-Benzoyl-2-bromo-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*] chromen-13(6*H*)-one (4g). Light yellow solid, 78.2 mg, 78% yield, mp 229.8–231.5 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.04 (d, J = 6.8 Hz, 2H), 7.70–7.62 (m, 2H), 7.56 (t, J = 6.4 Hz, 2H), 7.21 (dd, J = 8.8, 2.4 Hz, 1H), 4.48 (s, 1H), 3.65 (d, J = 7.0 Hz, 1H), 2.81–2.67 (m, 2H), 2.44 (s, 1H), 2.39 (s, 1H), 2.05 (s, 1H), 1.90–1.83 (m, 1H), 1.80–1.74 (m, 1H), 1.58 (d, J = 11.0 Hz, 1H), 1.51–1.37 (m, 3H), 1.26–1.23 (m, 1H), 1.05–0.91 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 174.8, 166.1, 155.9, 136.0, 135.7, 134.1, 129.1, 129.0, 128.6, 125.9, 125.2, 120.2, 118.5, 59.1, 50.2, 50.1, 47.9, 44.9, 43.8, 42.8, 36.3, 36.2, 35.3, 31.4, 31.3. HRMS (ESI-TOF): calcd. for $C_{29}H_{26}BrO_3$ $[M + H]^+$ 501.1060; found 501.1051.

Scheme 2, 4h



(±)-6-Benzoyl-3-methyl-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimetha nobenzo[5,6]indeno[2,1-*b*] chromen-13(6*H*)-one (4h). Light yellow solid, 61.1 mg, 70% yield, mp 192.4–194.2 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13–8.08 (m, 1H), 8.08–8.03 (m, 2H), 7.69–7.62 (m, 1H), 7.59–7.51 (m, 2H), 7.20–7.14 (m, 1H), 7.10 (s, 1H), 4.47–4.45 (m, 1H), 3.65 (d, *J* = 7.0 Hz, 1H), 2.78–2.74 (m, 2H), 2.43–2.39 (m, 5H), 2.08–2.03 (m, 1H), 1.86 (dd, *J* = 10.0, 4.6 Hz, 1H), 1.77 (dd, *J* = 10.0, 4.6 Hz, 1H), 1.61 (d, *J* = 11.0 Hz, 1H), 1.49–1.42 (m, 3H), 1.23 (d, *J* = 9.8 Hz, 1H), 1.04–0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 176.2, 165.4, 157.3, 144.3, 135.9, 133.9, 129.1, 129.0, 126.5, 125.7, 124.7, 122.2, 118.0, 59.2, 50.2, 50.1, 47.9, 44.9, 43.9, 42.7, 36.4, 36.3, 35.3, 31.4, 31.4, 21.8. HRMS (ESI-TOF): calcd. for $C_{30}H_{29}O_3$ $[M + H]^+$ 437.2111; found 437.2113.

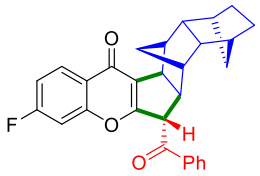
Scheme 2, 4i



(±)-6-Benzoyl-3-methoxy-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimeth anobenzo[5,6]indeno[2,1-*b*] chromen-13(6*H*)-one (4i). Light yellow solid, 72.4 mg, 80% yield, mp 164.9–166.7 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.8 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 6.91 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.70 (d, *J* = 2.4 Hz, 1H), 4.45 (dd, *J* = 3.6, 2.0 Hz, 1H), 3.80 (s, 3H), 3.62 (d, *J* = 6.8 Hz, 1H), 2.73 (t, *J* = 5.2 Hz, 2H), 2.41 (d, *J* = 4.6 Hz, 1H), 2.37 (d, *J* = 3.8 Hz, 1H), 2.03 (d, *J* = 3.8 Hz, 1H), 1.84 (dd, *J* = 10.0, 4.8 Hz, 1H), 1.75 (dd, *J* = 10.0, 4.8 Hz, 1H), 1.58 (d, *J* = 11.2 Hz, 1H), 1.49–1.41 (m, 3H), 1.24–1.19 (m, 1H), 1.03–0.91 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 175.7, 165.1, 163.6, 158.8, 135.8, 133.9, 129.0, 128.9, 127.1, 124.7, 118.3, 114.1, 100.6, 59.1, 55.8, 50.1, 50.1, 47.8, 44.7, 43.8, 42.8, 36.3, 36.2,

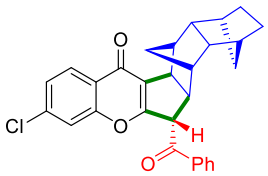
35.3, 31.3, 31.2. HRMS (ESI-TOF): calcd. for $C_{30}H_{29}O_4$ $[M + H]^+$ 453.2060; found 453.2057.

Scheme 2, 4j



(±)-6-Benzoyl-3-fluoro-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*] chromen-13(6*H*)-one (4j). Light yellow solid, 66.1 mg, 75% yield, mp 213.6–215.0 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, J = 8.8, 6.4 Hz, 1H), 8.04 (d, J = 7.6 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.6 Hz, 2H), 7.09 (td, J = 8.4, 2.4 Hz, 1H), 7.00 (dd, J = 9.2, 2.4 Hz, 1H), 4.48 (s, 1H), 3.63 (d, J = 7.1 Hz, 1H), 2.79–2.69 (m, 2H), 2.44 (d, J = 4.6 Hz, 1H), 2.38 (s, 1H), 2.04 (s, 1H), 1.86 (dd, J = 10.0, 4.6 Hz, 1H), 1.77 (dd, J = 10.0, 4.6 Hz, 1H), 1.58 (d, J = 11.2 Hz, 1H), 1.51–1.41 (m, 3H), 1.24 (d, J = 10.2 Hz, 1H), 1.03–0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 175.3, 165.9, 165.3 (d, J = 254.1 Hz, 1C), 158.0 (d, J = 13.2 Hz, 1C), 135.7, 134.1, 130.6, 129.0 (d, J = 10.4 Hz, C), 128.3 (d, J = 10.6 Hz, 1C), 125.1, 121.3 (d, J = 2.3 Hz, 1C), 113.7 (d, J = 22.7 Hz, 1C), 104.9 (d, J = 25.4 Hz, 1C), 59.0, 50.2, 50.1, 47.8, 44.8, 43.8, 42.9, 36.3, 36.3, 35.3, 31.4, 31.3. HRMS (ESI-TOF): calcd. for $C_{29}H_{26}FO_3$ $[M + H]^+$ 441.1860; found 441.1852.

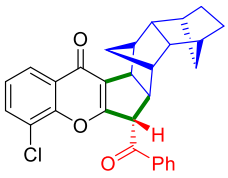
Scheme 2, 4k



(±)-6-Benzoyl-3-chloro-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*] chromen-13(6*H*)-one (4k). Light yellow solid, 74.0 mg, 81% yield, mp 197.9–199.9 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dt, J = 9.2, 1.6 Hz, 1H), 8.05 (d, J = 7.2 Hz, 2H), 7.69–7.63 (m, 1H), 7.59–7.52 (m, 2H), 7.36–7.30 (m, 2H), 4.48 (dd, J = 3.6, 2.0 Hz, 1H), 3.64 (d, J = 7.2 Hz, 1H), 2.79–2.74 (m, 1H), 2.72 (d, J = 4.4 Hz, 1H), 2.44 (d, J = 4.6 Hz, 1H), 2.38 (s, 1H), 2.05 (s, 1H), 1.86 (dd, J = 10.2, 4.4 Hz, 1H), 1.77 (dd, J = 10.2, 4.4 Hz, 1H), 1.59 (d, J = 11.2 Hz, 1H), 1.50–1.39 (m, 3H), 1.25 (d, J =

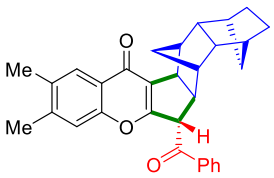
10.2 Hz, 1H), 1.04–0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 175.3, 165.9, 157.2, 139.1, 135.7, 134.1, 129.1, 129.0, 127.2, 125.9, 125.3, 123.0, 118.3, 59.0, 50.1, 50.0, 47.8, 44.8, 43.8, 42.8, 36.3, 36.2, 35.3, 31.4, 31.3. HRMS (ESI-TOF): calcd. for $C_{29}H_{26}ClO_3$ $[M + H]^+$ 457.1565; found 457.1557.

Scheme 2, 4l



(±)-6-Benzoyl-4-chloro-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*] chromen-13(6*H*)-one (4l). Light yellow solid, 56.7 mg, 62% yield, mp 249.3–251.0 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15–8.03 (m, 3H), 7.68–7.58 (m, 2H), 7.54 (t, J = 7.6 Hz, 2H), 7.30–7.24 (m, 1H), 4.57 (s, 1H), 3.64 (d, J = 7.2 Hz, 1H), 2.93–2.85 (m, 1H), 2.70 (d, J = 4.6 Hz, 1H), 2.38 (s, 2H), 2.07 (s, 1H), 1.85 (dd, J = 10.0, 4.6 Hz, 1H), 1.76 (dd, J = 10.0, 4.6 Hz, 1H), 1.65 (d, J = 11.2 Hz, 1H), 1.49–1.40 (m, 3H), 1.23 (d, J = 10.4 Hz, 1H), 1.03–0.95 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 175.5, 165.6, 152.8, 135.9, 134.0, 133.5, 129.2, 129.0, 125.9, 125.1, 125.1, 124.6, 123.3, 59.0, 50.2, 50.1, 47.8, 44.7, 43.8, 42.2, 36.4, 36.3, 35.3, 31.4. HRMS (ESI-TOF): calcd. for $C_{29}H_{26}ClO_3$ $[M + H]^+$ 457.1565; found 457.1563.

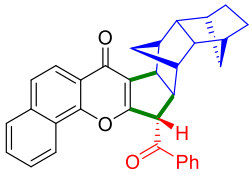
Scheme 2, 4m



(±)-6-Benzoyl-2,3-dimethyl-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*] chromen-13(6*H*)-one (4m). White solid, 63.1 mg, 70% yield, mp 161.3–162.9 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.6 Hz, 2H), 7.91 (s, 1H), 7.63 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.06 (s, 1H), 4.44 (s, 1H), 3.63 (d, J = 7.2 Hz, 1H), 2.77–2.69 (m, 2H), 2.38 (s, 2H), 2.30 (s, 3H), 2.29 (s, 3H), 2.03 (t, J = 4.8 Hz, 1H), 1.83 (dd, J = 10.0, 4.8 Hz, 1H), 1.74 (dd, J = 10.0, 4.8 Hz, 1H), 1.60 (d, J = 11.2 Hz, 1H), 1.47–1.38 (m, 3H), 1.20 (d, J = 10.4 Hz, 1H), 1.00–0.89 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 176.3, 165.3, 155.7, 143.4, 136.0, 134.2, 133.9, 129.0,

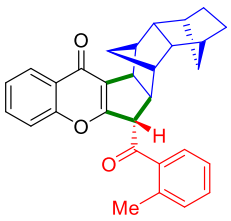
125.5, 124.6, 122.3, 118.3, 59.3, 50.2, 50.1, 47.9, 44.9, 43.9, 42.7, 36.4, 36.3, 35.3, 31.4, 31.3, 20.4, 19.4. HRMS (ESI-TOF): calcd. for $C_{31}H_{31}O_3$ $[M + H]^+$ 451.2268; found 451.2279.

Scheme 2, 4n



(±)-14-Benzoyl-8,8a,9,10,11,12,12a,13,13a,14-decahydro-8,13:9,12-dimethanobenzo[h]benzo[5,6]indeno[2,1-b] chromen-7(7b*H*)-one (4n). Light yellow solid, 39.7 mg, 42% yield, mp 144.2–146.0 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17–8.12 (m, 3H), 8.04 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.73–7.68 (m, 2H), 7.62–7.59 (m, 3H), 7.50–7.45 (m, 1H), 4.66 (s, 1H), 3.74–3.70 (m, 1H), 3.02–2.93 (m, 1H), 2.80 (s, 1H), 2.43 (s, 2H), 2.11 (s, 1H), 1.88 (dd, J = 10.0, 4.8 Hz, 1H), 1.79 (dt, J = 9.8, 4.6 Hz, 1H), 1.69 (d, J = 11.2 Hz, 1H), 1.51–1.45 (m, 3H), 1.25 (d, J = 10.4 Hz, 1H), 1.06–0.96 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 176.1, 164.6, 154.4, 136.1, 135.7, 134.0, 129.1, 129.0, 128.9, 128.0, 126.9, 126.0, 125.1, 124.1, 122.2, 121.0, 120.6, 59.1, 50.2, 50.2, 47.9, 44.8, 43.8, 42.2, 36.4, 35.3, 31.4. HRMS (ESI-TOF): calcd. for $C_{33}H_{29}O_3$ $[M + H]^+$ 473.2111; found 473.2102.

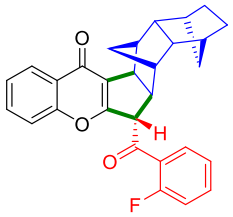
Scheme 2, 4o



(±)-6-(2-Methylbenzoyl)-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*] chromen-13(6*H*)-one (4o). Light yellow solid, 64.3 mg, 74% yield, mp 179.3–180.8 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, J = 8.0, 1.6 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.61–7.55 (m, 1H), 7.46 (t, J = 7.4 Hz, 1H), 7.40–7.30 (m, 4H), 4.39 (dd, J = 3.8, 2.0 Hz, 1H), 3.64 (d, J = 7.2 Hz, 1H), 2.77 (dd, J = 7.2, 3.4 Hz, 1H), 2.72 (d, J = 4.6 Hz, 1H), 2.52 (s, 3H), 2.40 (s, 1H), 2.31 (d, J = 4.6 Hz, 1H), 2.06 (s, 1H), 1.85 (dd, J = 10.0, 4.8 Hz, 1H), 1.74 (dd, J = 10.0, 4.8 Hz, 1H), 1.64 (d, J = 11.2 Hz, 1H),

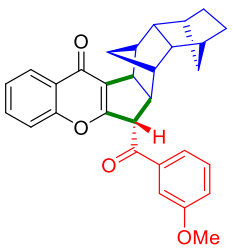
1.56–1.41 (m, 2H), 1.37 (dd, *J* = 10.4, 1.6 Hz, 1H), 1.20 (d, *J* = 10.4 Hz, 1H), 1.05–0.95 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 176.2, 165.8, 157.1, 139.5, 136.7, 133.1, 132.4, 132.1, 128.8, 125.9, 125.1, 124.9, 124.5, 118.2, 61.7, 50.2, 50.1, 47.8, 44.7, 43.8, 42.6, 36.4, 36.3, 36.2, 35.3, 31.4, 31.3, 21.6; HRMS (ESI-TOF): calcd. for $C_{30}H_{29}O_3$ $[M + H]^+$ 437.2111; found 437.2118.

Scheme 2, 4p



(±)-6-(2-Fluorobenzoyl)-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*] chromen-13(6*H*)-one (4p). Light yellow solid, 37.8 mg, 43% yield, mp 207.9–209.6 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.0 Hz, 1H), 7.84 (td, *J* = 7.6, 1.8 Hz, 1H), 7.62–7.53 (m, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.31–7.18 (m, 3H), 4.49 (s, 1H), 3.60 (d, *J* = 7.2 Hz, 1H), 2.77 (dd, *J* = 7.2, 3.4 Hz, 1H), 2.68 (d, *J* = 4.6 Hz, 1H), 2.37 (s, 2H), 2.05 (s, 1H), 1.82 (dd, *J* = 10.0, 4.8 Hz, 1H), 1.72 (dd, *J* = 10.0, 4.8 Hz, 1H), 1.61 (d, *J* = 11.2 Hz, 1H), 1.45 (td, *J* = 7.6, 4.2 Hz, 2H), 1.34 (d, *J* = 10.4 Hz, 1H), 1.17 (d, *J* = 10.4 Hz, 1H), 10.02–0.93 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2 (d, *J* = 4.1 Hz, 1C), 176.3, 165.5, 161.8 (d, *J* = 254.9 Hz, 1C), 157.1, 135.4 (d, *J* = 9.1 Hz, 1C), 133.1, 131.4 (d, *J* = 2.4 Hz, 1C), 125.9, 125.2 (d, *J* = 12.4 Hz, 1C), 125.0, 124.9 (d, *J* = 3.4 Hz, 1C), 124.8, 124.5, 118.2, 116.9 (d, *J* = 23.6 Hz, 1C), 62.6 (d, *J* = 6.8 Hz, 1C), 50.2, 50.1, 47.7 (d, *J* = 2.5 Hz, 1C), 44.8, 43.6, 42.4, 36.4 (d, *J* = 1.6 Hz, 1C), 36.2, 35.3, 31.4, 31.3. HRMS (ESI-TOF): calcd. for $C_{29}H_{26}FO_3$ $[M + H]^+$ 441.1860; found 441.1864.

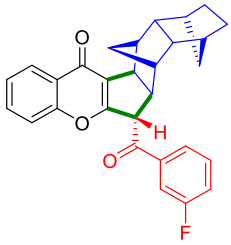
Scheme 2, 4q



(±)-6-(3-Methoxybenzoyl)-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*] chromen-13(6*H*)-one (4q). White solid, 49.8 mg, 55%

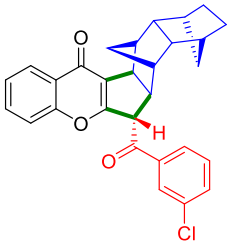
yield, mp 218.3–219.3 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, J = 8.0, 1.6 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 6.4 Hz, 2H), 7.46 (t, J = 8.0 Hz, 1H), 7.38–7.31 (m, 2H), 7.20 (dd, J = 8.2, 2.4 Hz, 1H), 4.46 (s, 1H), 3.88 (s, 3H), 3.66 (d, J = 7.2 Hz, 1H), 2.75 (t, J = 5.2 Hz, 2H), 2.44–2.37 (m, 2H), 2.06 (s, 1H), 1.86 (dd, J = 10.0, 4.8 Hz, 1H), 1.77 (dd, J = 10.0, 4.8 Hz, 1H), 1.61 (d, J = 11.2 Hz, 1H), 1.45 (dd, J = 18.4, 7.0 Hz, 3H), 1.23 (d, J = 10.4 Hz, 1H), 1.03–0.93 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 176.2, 165.7, 160.2, 157.1, 137.2, 133.1, 130.0, 125.9, 125.0, 124.9, 124.5, 121.5, 120.5, 118.2, 113.2, 59.3, 55.6, 50.2, 50.1, 47.9, 44.9, 43.8, 42.9, 36.4, 36.3, 35.3, 31.4, 31.3. HRMS (ESI-TOF): calcd. for $C_{30}H_{29}O_4$ $[M + H]^+$ 453.2060; found 453.2051.

Scheme 2, 4r



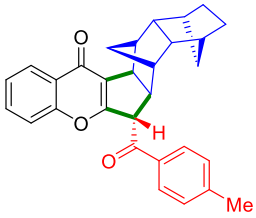
(±)-6-(3-Fluorobenzoyl)-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*]chromen-13(6*H*)-one (4r). Yellow solid, 41.2 mg, 47% yield, mp 241.2–243.1 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.74 (d, J = 9.2 Hz, 1H), 7.60–7.51 (m, 2H), 7.38–7.30 (m, 3H), 4.44 (t, J = 2.8 Hz, 1H), 3.66 (d, J = 7.2 Hz, 1H), 2.78–2.71 (m, 2H), 2.42–2.39 (m, 2H), 2.06 (s, 1H), 1.88–1.84 (m, 1H), 1.77 (dd, J = 10.0, 4.8 Hz, 1H), 1.60 (d, J = 11.0 Hz, 1H), 1.50–1.41 (m, 3H), 1.24 (d, J = 10.2 Hz, 1H), 1.04–0.94 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 176.2, 165.2, 163.1 (d, J = 248.7 Hz, 1C), 157.1, 138.0 (d, J = 6.1 Hz, 1C), 133.2, 130.7 (d, J = 7.6 Hz, 1C), 126.0, 125.1, 125.0, 124.7 (d, J = 3.1 Hz, 1C), 124.5, 121.0 (d, J = 21.4 Hz, 1C), 118.2, 115.8 (d, J = 22.4 Hz, 1C), 59.3, 50.1 (d, J = 7.4 Hz, 1C), 47.9, 44.9, 43.8, 42.7, 36.4, 36.3, 35.3, 31.6, 31.4 (d, J = 3.2 Hz, 1C), 30.3, 29.8. HRMS (ESI-TOF): calcd. for $C_{29}H_{26}FO_3$ $[M + H]^+$ 441.1860; found 441.1869.

Scheme 2, 4s



(±)-6-(3-Chlorobenzoyl)-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*] chromen-13(6*H*)-one (4s). Light yellow solid, 39.9 mg, 44% yield, mp 179.8–181.5 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, J = 8.0, 1.6 Hz, 1H), 8.04 (s, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.65–7.56 (m, 2H), 7.50 (t, J = 8.0 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 4.44 (dd, J = 3.6, 2.0 Hz, 1H), 3.66 (d, J = 7.2 Hz, 1H), 2.79–2.71 (m, 2H), 2.40 (s, 2H), 2.07 (s, 1H), 1.87 (dd, J = 10.0, 4.8 Hz, 1H), 1.78 (dd, J = 10.0, 4.8 Hz, 1H), 1.60 (d, J = 11.2 Hz, 1H), 1.52–1.40 (m, 3H), 1.25 (d, J = 10.4 Hz, 1H), 1.05–0.94 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 176.2, 165.1, 157.1, 137.5, 135.5, 133.9, 133.2, 130.3, 129.1, 127.0, 126.0, 125.2, 125.0, 124.4, 118.2, 59.2, 50.2, 50.1, 47.8, 44.9, 43.8, 42.6, 42.4, 36.4, 36.3, 35.3, 31.4, 31.3. HRMS (ESI-TOF): calcd. for $C_{29}H_{26}ClO_3$ $[M + H]^+$ 457.1565; found 457.1562.

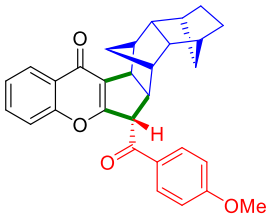
Scheme 2, 4t



(±)-6-(4-Methylbenzoyl)-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*] chromen-13(6*H*)-one (4t). Light yellow solid, 66.4 mg, 76% yield, mp 190.3–192.1 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, J = 8.0, 1.6 Hz, 1H), 7.95 (d, J = 8.0 Hz, 2H), 7.59–7.53 (m, 1H), 7.38–7.27 (m, 4H), 4.46 (s, 1H), 3.66 (d, J = 7.2 Hz, 1H), 2.78–2.71 (m, 2H), 2.45 (s, 3H), 2.40 (dd, J = 12.0, 4.2 Hz, 2H), 2.05 (d, J = 3.6 Hz, 1H), 1.87–1.83 (m, 1H), 1.76 (dd, J = 10.0, 4.7 Hz, 1H), 1.61 (d, J = 11.2 Hz, 1H), 1.51–1.38 (m, 3H), 1.22 (d, J = 10.4 Hz, 1H), 1.04–0.90 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 176.2, 166.0, 157.1, 145.0, 133.4, 133.0, 129.7, 129.1, 125.9, 125.0,

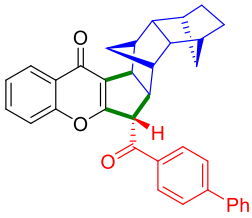
124.9, 124.5, 118.2, 59.1, 50.2, 50.1, 47.8, 44.8, 43.8, 42.8, 36.3, 36.2, 35.3, 31.3, 21.9. HRMS (ESI-TOF): calcd. for $C_{30}H_{29}O_3$ $[M + H]^+$ 437.2111; found 437.2109.

Scheme 2, 4u



(±)-6-(4-Methoxybenzoyl)-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*]chromen-13(6*H*)-one (4u). White solid, 72.4 mg, 80% yield, mp 232.6–234.4 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, J = 8.0, 1.8 Hz, 1H), 8.03 (d, J = 8.8 Hz, 2H), 7.55 (ddd, J = 8.8, 7.2, 1.8 Hz, 1H), 7.36–7.29 (m, 2H), 7.01 (d, J = 8.8 Hz, 2H), 4.44 (dd, J = 3.6, 2.0 Hz, 1H), 3.90 (s, 3H), 3.65 (d, J = 7.2 Hz, 1H), 2.75 (dt, J = 12.4, 4.0 Hz, 2H), 2.39 (dd, J = 9.6, 4.0 Hz, 2H), 2.06 (d, J = 3.6 Hz, 1H), 1.84 (dd, J = 10.0, 4.8 Hz, 1H), 1.75 (dd, J = 10.0, 4.8 Hz, 1H), 1.61 (d, J = 11.2 Hz, 1H), 1.49–1.39 (m, 3H), 1.21 (d, J = 10.2 Hz, 1H), 1.02–0.91 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 176.1, 166.1, 164.2, 157.0, 133.0, 131.3, 128.8, 125.8, 124.9, 124.8, 124.4, 118.2, 114.2, 58.9, 55.7, 50.1, 50.0, 47.8, 44.8, 43.8, 42.8, 36.3, 36.2, 35.3, 31.3. HRMS (ESI-TOF): calcd. for $C_{30}H_{29}O_4$ $[M + H]^+$ 453.2060; found 453.2056.

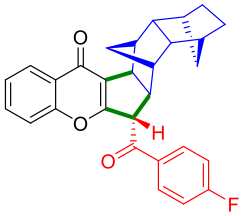
Scheme 2, 4v



(±)-6-([1,1'-Biphenyl]-4-carbonyl)-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*]chromen-13(6*H*)-one (4v). Light yellow solid, 53.9 mg, 54% yield, mp 204.6–206.1 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.0 Hz, 1H), 8.14 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 7.6 Hz, 2H), 7.59 (t, J = 7.8 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.44 (t, J = 7.2 Hz, 1H), 7.40–7.32 (m, 2H), 4.52 (s, 1H), 3.70 (d, J = 7.2 Hz, 1H), 2.82 (dd, J = 7.4, 3.6 Hz, 1H), 2.77 (d, J = 4.6 Hz, 1H), 2.47 (d, J = 4.6 Hz, 1H), 2.42 (d, J = 3.6 Hz, 1H), 2.09 (d, J = 3.6 Hz, 1H), 1.88 (dd, J =

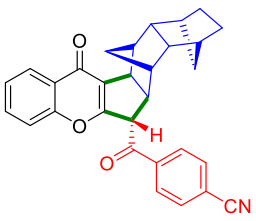
10.0, 4.6 Hz, 1H), 1.79 (dd, *J* = 10.0, 4.6 Hz, 1H), 1.64 (d, *J* = 11.2 Hz, 1H), 1.47 (dd, *J* = 11.2, 6.8 Hz, 3H), 1.26 (d, *J* = 10.2 Hz, 1H), 1.06–0.95 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 176.2, 165.8, 157.1, 146.6, 139.7, 134.5, 133.1, 129.6, 129.2, 128.6, 127.6, 127.4, 125.9, 125.1, 124.9, 124.5, 118.2, 59.3, 50.2, 50.1, 47.9, 44.9, 43.8, 42.8, 36.4, 36.3, 35.3, 31.4, 31.3. HRMS (ESI-TOF): calcd. for $C_{35}H_{31}O_3$ $[M + H]^+$ 499.2268; found 499.2263.

Scheme 2, 4w



(±)-6-(4-Fluorobenzoyl)-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*] chromen-13(6*H*)-one (4w). Light yellow solid, 43.7 mg, 50% yield, mp 210.4–212.0 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.8 Hz, 1H), 8.09 (dd, *J* = 8.6, 5.2 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 1H), 7.27–7.19 (m, 2H), 4.45 (s, 1H), 3.66 (d, *J* = 7.0 Hz, 1H), 2.79–2.72 (m, 2H), 2.39 (s, 2H), 2.06 (s, 1H), 1.88–1.84 (m, 1H), 1.77 (dd, *J* = 10.0, 4.4 Hz, 1H), 1.61 (d, *J* = 11.2 Hz, 1H), 1.50–1.39 (m, 3H), 1.23 (d, *J* = 10.4 Hz, 1H), 1.03–0.93 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 176.1, 165.4, 166.3 (d, *J* = 256.6 Hz, 1C), 157.0, 133.1, 132.3 (d, *J* = 2.9 Hz, 1C), 131.7 (d, *J* = 9.4 Hz, 1C), 125.9, 125.1, 124.9, 124.4, 118.2, 116.2 (d, *J* = 22.0 Hz, 1C), 59.1, 50.1, 50.0, 47.8, 44.8, 43.8, 42.6, 36.3, 36.2, 35.3, 31.3, 31.2. HRMS (ESI-TOF): calcd. for $C_{29}H_{26}FO_3$ $[M + H]^+$ 441.1860; found 441.1858.

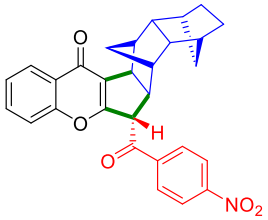
Scheme 2, 4x



(±)-13-Oxo-6,6a,7,7a,8,9,10,11,11a,12,12a,13-dodecahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*] chromene-6-carbonyl)benzonitrile (4x). Yellow solid, 36.7 mg, 41% yield, mp 157.9–159.5 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 8.0,

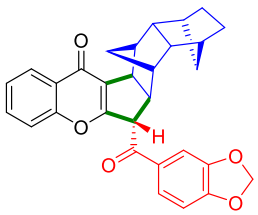
2.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.59–7.53 (m, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.28–7.24 (m, 1H), 4.45 (t, *J* = 2.4 Hz, 1H), 3.63 (d, *J* = 7.2 Hz, 1H), 2.75–2.70 (m, 2H), 2.36 (t, *J* = 5.2 Hz, 2H), 2.02 (s, 1H), 1.85–1.81 (m, 1H), 1.75 (dd, *J* = 10.0, 4.4 Hz, 1H), 1.55 (d, *J* = 11.2 Hz, 1H), 1.47–1.37 (m, 3H), 1.22 (d, *J* = 10.4 Hz, 1H), 1.01–0.91 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 176.0, 164.6, 157.0, 138.8, 133.3, 132.8, 129.3, 125.9, 125.2, 125.0, 124.3, 118.1, 117.8, 117.1, 59.3, 50.1, 50.0, 47.8, 44.9, 43.7, 42.4, 36.4, 36.3, 36.2, 35.2, 31.3, 31.2. HRMS (ESI-TOF): calcd. for $C_{30}H_{26}NO_3$ $[M + H]^+$ 448.1907; found 441. 448.1901.

Scheme 2, 4y



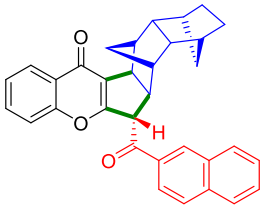
(±)-6-(4-Nitrobenzoyl)-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*] chromen-13(6*H*)-one (4y). Yellow solid, 39.3 mg, 42% yield, mp 234.6–236.1 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.4 Hz, 2H), 8.23–8.21 (m, 3H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 4.49 (t, *J* = 2.8 Hz, 1H), 3.67 (d, *J* = 7.2 Hz, 1H), 2.79 (dd, *J* = 7.6, 3.6 Hz, 1H), 2.75 (d, *J* = 4.4 Hz, 1H), 2.40 (d, *J* = 4.8 Hz, 2H), 2.06 (d, *J* = 3.6 Hz, 1H), 1.88 (dd, *J* = 10.0, 4.6 Hz, 1H), 1.79 (dd, *J* = 10.0, 4.6 Hz, 1H), 1.59 (d, *J* = 11.2 Hz, 1H), 1.50–1.40 (m, 3H), 1.26 (d, *J* = 10.4 Hz, 1H), 1.04–0.96 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 176.1, 164.5, 157.0, 150.8, 140.3, 133.3, 130.0, 126.0, 125.3, 125.1, 124.4, 124.2, 118.1, 59.6, 50.1, 50.0, 47.9, 44.9, 43.8, 42.4, 36.4, 36.3, 35.3, 31.3, 31.2. HRMS (ESI-TOF): calcd. for $C_{29}H_{26}NO_5$ $[M + H]^+$ 468.1805; found 468.1801.

Scheme 2, 4z



(±)-6-(Benzo[d][1,3]dioxole-5-carbonyl)-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7, 12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*]chromen-13(6*H*)-one (4z). Light yellow solid, 67.2 mg, 72% yield, mp 219.6–221.5 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.58 (dd, *J* = 8.4, 6.8 Hz, 1H), 7.51 (s, 1H), 7.38–7.30 (m, 2H), 6.94 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.10 (s, 2H), 4.42–4.38 (m, 1H), 3.65 (d, *J* = 7.2 Hz, 1H), 2.74 (d, *J* = 4.8 Hz, 2H), 2.40 (d, *J* = 4.0 Hz, 2H), 2.08 (d, *J* = 3.6 Hz, 1H), 1.86 (dd, *J* = 10.0, 4.6 Hz, 1H), 1.77 (dd, *J* = 10.0, 4.6 Hz, 1H), 1.62 (d, *J* = 11.2 Hz, 1H), 1.51–1.39 (m, 3H), 1.23 (d, *J* = 10.2 Hz, 1H), 1.04–0.94 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 176.2, 165.9, 157.1, 152.6, 148.7, 133.1, 130.7, 125.9, 125.5, 125.0, 124.8, 124.4, 118.2, 108.6, 108.2, 102.2, 58.9, 50.2, 50.1, 47.8, 44.8, 43.8, 42.9, 36.3, 36.2, 35.3, 31.4, 31.3. HRMS (ESI-TOF): calcd. for $C_{30}H_{27}O_5$ $[M + H]^+$ 467.1853; found 467.1851.

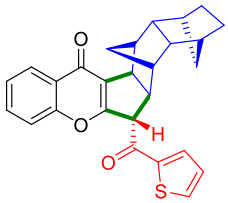
Scheme 2, 4aa



(±)-6-(2-Naphthoyl)-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanob enzo[5,6]indeno[2,1-*b*] chromen-13(6*H*)-one (4aa). Light yellow solid, 69.9 mg 74% yield, mp 157.4–159.2 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 1.8 Hz, 1H), 8.24 (dd, *J* = 8.0, 1.8 Hz, 1H), 8.11 (dd, *J* = 8.8, 1.8 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.69–7.54 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 4.67 (dd, *J* = 3.6, 2.0 Hz, 1H), 3.71 (d, *J* = 7.2 Hz, 1H), 2.86 (dd, *J* = 7.6, 3.6 Hz, 1H), 2.78 (d, *J* = 4.6 Hz, 1H), 2.51 (d, *J* = 4.6 Hz, 1H), 2.40 (d, *J* = 4.0 Hz, 1H), 2.04 (d, *J* = 4.2 Hz, 1H), 1.88 (dd, *J* = 10.0, 4.8 Hz, 1H), 1.79 (dd, *J* = 10.0, 4.8 Hz, 1H), 1.63 (d, *J* = 11.2 Hz, 1H), 1.51–1.40 (m, 3H), 1.28 (d, *J* = 10.4 Hz, 1H), 1.04–0.92 (m,

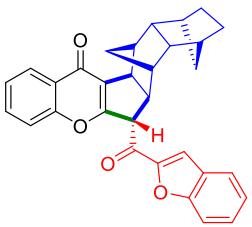
3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 176.2, 165.8, 157.1, 136.0, 133.2, 133.1, 132.6, 131.1, 129.9, 129.2, 129.0, 128.0, 127.2, 125.9, 125.0, 124.9, 124.5, 124.4, 118.2, 59.1, 50.2, 50.1, 47.9, 44.9, 43.8, 42.9, 36.4, 36.3, 35.3, 31.3. HRMS (ESI-TOF): calcd. for $C_{33}H_{29}O_3$ $[M + H]^+$ 473.2111; found 473.2110.

Scheme 2, 4ab



(±)-6-(Thiophene-2-carbonyl)-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*]chromen-13(6*H*)-one (4ab). Light yellow solid, 65.1 mg, 76% yield, mp 174.9–176.8 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, J = 8.0, 1.6 Hz, 1H), 7.85 (d, J = 4.0 Hz, 1H), 7.75 (d, J = 5.0 Hz, 1H), 7.60–7.54 (m, 1H), 7.40–7.29 (m, 2H), 7.21 (t, J = 4.4 Hz, 1H), 4.28 (t, J = 2.8 Hz, 1H), 3.67 (d, J = 7.1 Hz, 1H), 2.84 (dd, J = 7.6, 3.6 Hz, 1H), 2.72 (d, J = 4.6 Hz, 1H), 2.39 (t, J = 4.0 Hz, 2H), 2.11 (d, J = 3.6 Hz, 1H), 1.93–1.81 (m, 2H), 1.76 (dd, J = 10.0, 4.8 Hz, 1H), 1.62 (d, J = 11.2 Hz, 1H), 1.53–1.45 (m, 1H), 1.38 (d, J = 10.4 Hz, 1H), 1.22 (d, J = 10.4 Hz, 1H), 1.05–0.93 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 176.2, 165.2, 157.0, 143.1, 135.2, 133.2, 133.1, 128.6, 125.9, 125.1, 125.0, 124.4, 118.2, 60.8, 50.1, 50.0, 48.0, 44.9, 43.8, 43.2, 36.4, 36.3, 36.2, 35.3, 31.3. HRMS (ESI-TOF): calcd. for $C_{27}H_{25}O_3S$ $[M + H]^+$ 429.1519; found 429.1512.

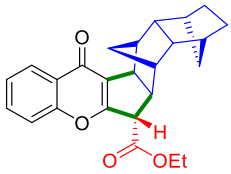
Scheme 2, 4ac



(±)-6-(Benzofuran-2-carbonyl)-6a,7,7a,8,9,10,11,11a,12,12a-decahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*]chromen-13(6*H*)-one (4ac). Yellow solid, 40.7 mg, 44% yield, mp 199.7–201.3 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.66–7.62 (m, 2H), 7.59–7.52 (m, 2H), 7.40–7.28 (m, 3H),

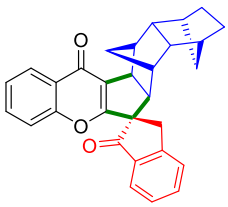
4.46–4.41 (m, 1H), 3.70 (d, *J* = 7.2 Hz, 1H), 2.87 (dd, *J* = 7.2, 3.8 Hz, 1H), 2.75 (d, *J* = 4.6 Hz, 1H), 2.49 (d, *J* = 4.6 Hz, 1H), 2.40 (d, *J* = 3.6 Hz, 1H), 2.09 (d, *J* = 3.6 Hz, 1H), 1.87 (dd, *J* = 10.0, 4.6 Hz, 1H), 1.78 (dd, *J* = 10.0, 4.6 Hz, 1H), 1.63 (d, *J* = 11.2 Hz, 1H), 1.50–1.42 (m, 3H), 1.27–1.23 (m, 1H), 1.06–0.93 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.0, 176.2, 164.8, 157.1, 156.1, 151.7, 133.2, 129.0, 127.1, 125.9, 125.2, 125.1, 124.5, 124.4, 123.7, 118.2, 114.7, 112.7, 60.1, 50.2, 50.1, 48.0, 44.9, 43.9, 43.0, 36.4, 36.3, 36.2, 35.3, 31.4. HRMS (ESI-TOF): calcd. for $C_{31}H_{27}O_4$ $[M + H]^+$ 463.1904; found 463.1898.

Scheme 2, 4ad



(±)-Ethyl-13-oxo-6,6a,7,7a,8,9,10,11,11a,12,12a,13-dodecahydro-7,12:8,11-dimethanobenzo[5,6]indeno[2,1-*b*] chromene-6-carboxylate (4ad). Light yellow solid, 60.9 mg, 78% yield, mp 132.6–134.3 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.64–7.58 (m, 1H), 7.44–7.35 (m, 2H), 4.23 (qd, *J* = 7.2, 2.0 Hz, 2H), 3.60 (d, *J* = 7.3 Hz, 1H), 3.56–3.49 (m, 1H), 2.80 (dd, *J* = 7.4, 3.8 Hz, 1H), 2.66 (d, *J* = 4.6 Hz, 1H), 2.39 (s, 1H), 2.26 (d, *J* = 4.6 Hz, 1H), 2.22 (s, 1H), 1.84 (dd, *J* = 10.0, 4.8 Hz, 1H), 1.75 (dd, *J* = 10.0, 4.8 Hz, 1H), 1.66 (d, *J* = 11.0 Hz, 1H), 1.50 (d, *J* = 6.8 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.23 (d, *J* = 10.6 Hz, 1H), 1.15 (d, *J* = 10.6 Hz, 1H), 1.02 (d, *J* = 9.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 171.2, 164.3, 157.1, 133.2, 125.9, 125.1, 124.5, 124.4, 118.2, 61.7, 56.8, 50.1, 50.0, 47.9, 44.5, 43.6, 42.6, 36.5, 36.4, 36.0, 35.3, 31.4, 31.3, 14.3. HRMS (ESI-TOF): calcd. for $C_{25}H_{27}O_4$ $[M + H]^+$ 391.1904; found 391.1906.

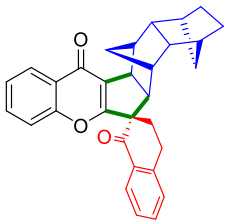
Scheme 3, 4ae



(±)-6a',7',7a',8',9',10',11',11a',12',12a'-Decahydro-13'H-spiro[indene-2,6'-[7,12:8,11]dimethanobenzo[5,6]indeno[2,1-*b*]chromene]-1,13'(3*H*)-dione (4ae). Light yellow solid, 36.5 mg, 42% yield, mp 222.2–224.0 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ

8.21 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.54–7.45 (m, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 3.82 (d, *J* = 7.2 Hz, 1H), 3.53 (q, *J* = 17.6 Hz, 2H), 2.81 (d, *J* = 7.2 Hz, 1H), 2.75 (d, *J* = 4.4 Hz, 1H), 2.44 (d, *J* = 3.6 Hz, 1H), 2.29 (d, *J* = 4.8 Hz, 1H), 2.07–2.02 (m, 1H), 1.85–1.76 (m, 3H), 1.51–1.43 (m, 2H), 1.27 (d, *J* = 10.0 Hz, 1H), 1.19 (d, *J* = 10.0 Hz, 1H), 1.06–0.93 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.4, 176.1, 167.7, 156.9, 153.3, 135.7, 134.8, 133.0, 128.2, 126.5, 125.9, 125.1, 125.0, 124.5, 123.9, 118.1, 64.4, 50.2, 49.9, 45.5, 44.7, 43.4, 43.0, 37.0, 36.4, 36.3, 35.5, 33.1, 31.5, 31.4. HRMS (ESI-TOF): calcd. for $C_{30}H_{27}O_3$ $[M + H]^+$ 435.1955; found 435.1953.

Scheme 3, 4af

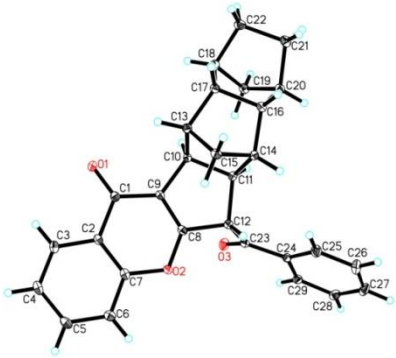


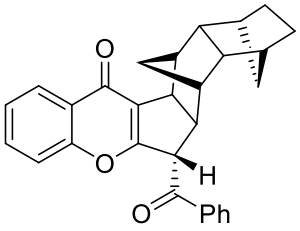
(±)-3,4,6a',7',7a',8',9',10',11',11a',12',12a'-Dodecahydro-1*H*,13'*H*-spiro[naphthalene-2,6'-[7,12:8,11]dimethanobenzo[5,6]indeno[2,1-*b*]chromene]-1,13'-dione (4af). Yellow solid, 26.9 mg, 30% yield, mp 234.9–236.0 °C; 99:1 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.35–7.29 (m, 3H), 7.24 (s, 1H), 3.69 (d, *J* = 7.0 Hz, 1H), 3.25–3.20 (m, 2H), 2.77–2.63 (m, 3H), 2.48–2.35 (m, 3H), 2.03 (t, *J* = 4.0 Hz, 1H), 1.82 (dd, *J* = 10.0, 4.4 Hz, 1H), 1.76 (dd, *J* = 10.0, 4.8 Hz, 1H), 1.70 (d, *J* = 11.2 Hz, 1H), 1.48–1.42 (m, 2H), 1.34 (d, *J* = 10.0 Hz, 1H), 1.16 (d, *J* = 10.0 Hz, 1H), 1.00–0.93 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 176.2, 168.3, 156.9, 143.9, 134.1, 132.9, 130.8, 128.9, 128.7, 127.1, 126.0, 125.0, 124.7, 124.1, 118.2, 60.4, 50.3, 50.2, 45.1, 44.9, 43.0, 42.1, 37.8, 36.4, 36.2, 35.5, 31.5, 31.4, 26.2, 25.6. HRMS (ESI-TOF): calcd. for $C_{31}H_{29}O_3$ $[M + H]^+$ 449.2111; found 449.2102.

5. Preparative-scale experiment of compound (±)-4a.

A 150 mL flame-dried vial with a stir bar was charged with 3-iodochromone (**1a**, 1.36 g, 5.0 mmol), α-bromoacetophenone (**2a**, 1.19 g, 6.0 mmol), TCD (**3**, 3.21 g, 20.0 mmol), $Pd(OAc)_2$ (112.3 mg, 0.5 mmol), $P(3\text{-}OMe\text{-}C_6H_4)_3$ (352.4 mg, 1.0 mmol), and K_2CO_3 (2.76 g, 20.0 mmol) in 50 mL of dry *o*-xylene under nitrogen atmosphere at 100 °C for 24 h. After the completion of the reaction detected by thin layer chromatography (TLC), the mixture was cooled to room temperature and purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1–1:1) to afford the desired product (±)-**4a** as a light yellow solid (1.10 g, 52%, 99:1 dr).

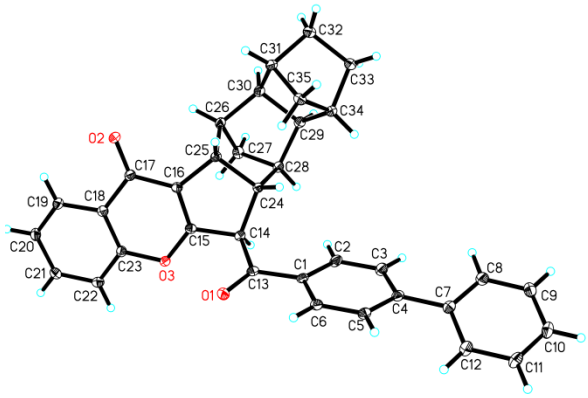
6. X-ray crystal data for compounds (±)-**4a**, (±)-**4v**, (±)-**4z**, (±)-**4ad**, and (±)-**4af**

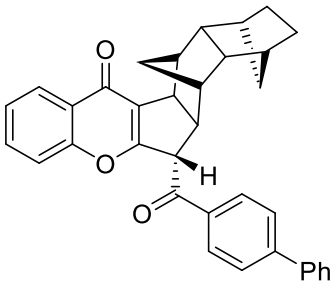




(±)-**4a** (CCDC: 1826874)

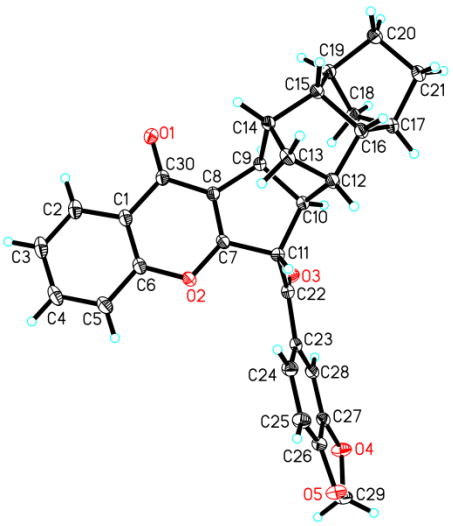
Compound	(±)-**4a**
Empirical formula	$C_{29}H_{26}O_3$
Formula weight	422.50
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	Cc
a/Å	16.1406(8)
b/Å	12.8442(6)
c/Å	10.0734(5)
α/°	90
β/°	97.501(4)
γ/°	90
Volume/Å^3	2070.48(18)
Z	4
ρ_{calc}g/cm^3	1.355
μ/mm^{-1}	0.086
F(000)	896.0
Crystal size/mm^3	0.2 × 0.16 × 0.11
Radiation	MoKα (λ = 0.71073)
θ range for data collection/°	3.772 to 29.490
Index ranges	-21 ≤ h ≤ 15, -17 ≤ k ≤ 16, -11 ≤ l ≤ 13
Reflections collected	5224
Independent reflections	3244 [R_{int} = 0.0259, R_{sigma} = 0.0388]
Data/restraints/parameters	3244/2/289
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0348, wR_2 = 0.0900
Final R indexes [all data]	R_1 = 0.0360, wR_2 = 0.0912
Largest diff. peak/hole/e Å^{-3}	0.24/-0.20

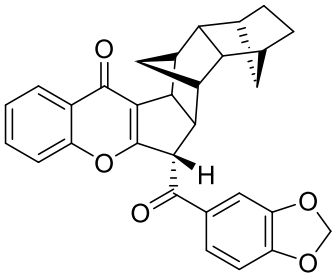




(±)-**4v** (CCDC: 1826875)

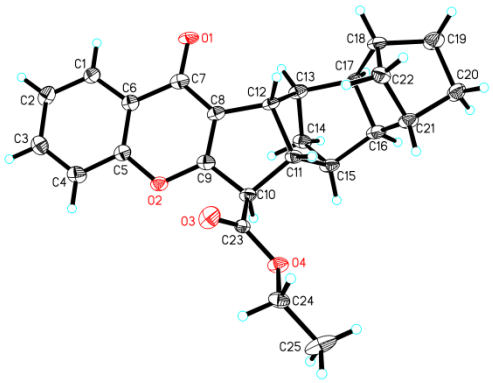
Compound	(±)-**4v**
Empirical formula	$C_{35}H_{30}O_3$
Formula weight	498.59
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.8871(3)
b/Å	12.0988(4)
c/Å	18.3739(7)
α/°	92.252(3)
β/°	102.556(3)
γ/°	100.001(3)
Volume/Å^3	2531.96(15)
Z	4
ρ_{calc}g/cm^3	1.308
μ/mm^{-1}	0.082
F(000)	1056.0
Crystal size/mm^3	0.15 × 0.13 × 0.12
Radiation	MoKα (λ = 0.71073)
2θrange for data collection/°	6.268 to 59.14
Index ranges	-16 ≤ h ≤ 14, -16 ≤ k ≤ 15, -21 ≤ l ≤ 24
Reflections collected	25396
Independent reflections	11996 [R_{int} = 0.0322, R_{sigma} = 0.0558]
Data/restraints/parameters	11996/0/685
Goodness-of-fit on F^2	1.004
Final R indexes [I>=2σ (I)]	R_1 = 0.0553, wR_2 = 0.1243
Final R indexes [all data]	R_1 = 0.0749, wR_2 = 0.1389
Largest diff. peak/hole/e Å^{-3}	0.32/-0.27

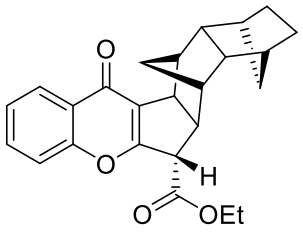




(±)-**4z** (CCDC: 1826876)

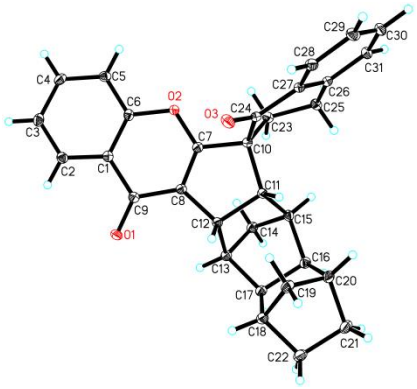
Compound	(±)-**4z**
Empirical formula	$C_{30}H_{26}O_5$
Formula weight	466.51
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.3416(4)
b/Å	11.0113(3)
c/Å	14.5008(4)
α/°	90
β/°	105.056(3)
γ/°	90
Volume/Å^3	2211.35(11)
Z	4
ρ_{calc}g/cm^3	1.401
μ/mm^{-1}	0.766
F(000)	984.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	CuKα (λ = 1.54184)
2θrange for data collection/°	7.724 to 147.358
Index ranges	-17 ≤ h ≤ 16, -13 ≤ k ≤ 13, -12 ≤ l ≤ 18
Reflections collected	14548
Independent reflections	4387 [R_{int} = 0.0327, R_{sigma} = 0.0263]
Data/restraints/parameters	4387/0/316
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0457, wR_2 = 0.1227
Final R indexes [all data]	R_1 = 0.0500, wR_2 = 0.1268
Largest diff. peak/hole/e Å^{-3}	0.28/-0.23

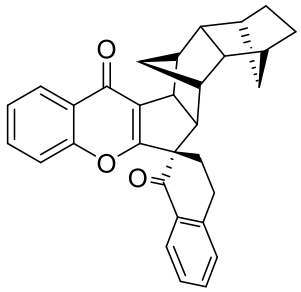




(±)-**4ad** (CCDC: 1826878)

Compound	(±)-**4ad**
Empirical formula	$C_{25}H_{26}O_4$
Formula weight	390.46
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	6.28259(10)
b/Å	18.0959(3)
c/Å	34.9828(9)
α/°	89.6453(18)
β/°	89.8577(16)
γ/°	83.5587(15)
Volume/Å^3	3951.98(14)
Z	8
ρ_{calc}g/cm^3	1.312
μ/mm^{-1}	0.088
F(000)	1664.0
Crystal size/mm^3	0.15 × 0.13 × 0.11
Radiation	MoKα (λ = 0.71073)
2θrange for data collection/°	4.152 to 50
Index ranges	-7 ≤ h ≤ 7, -21 ≤ k ≤ 21, -41 ≤ l ≤ 41
Reflections collected	90171
Independent reflections	13935 [R_{int} = 0.1317, R_{sigma} = 0.0724]
Data/restraints/parameters	13935/7/1049
Goodness-of-fit on F^2	1.100
Final R indexes [I>=2σ (I)]	R_1 = 0.1744, wR_2 = 0.3943
Final R indexes [all data]	R_1 = 0.1921, wR_2 = 0.4025
Largest diff. peak/hole/e Å^{-3}	0.70/-0.74





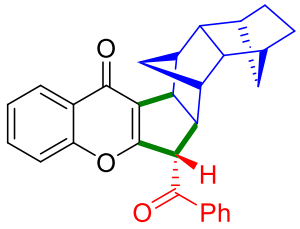
(±)-**4af** (CCDC: 1826880)

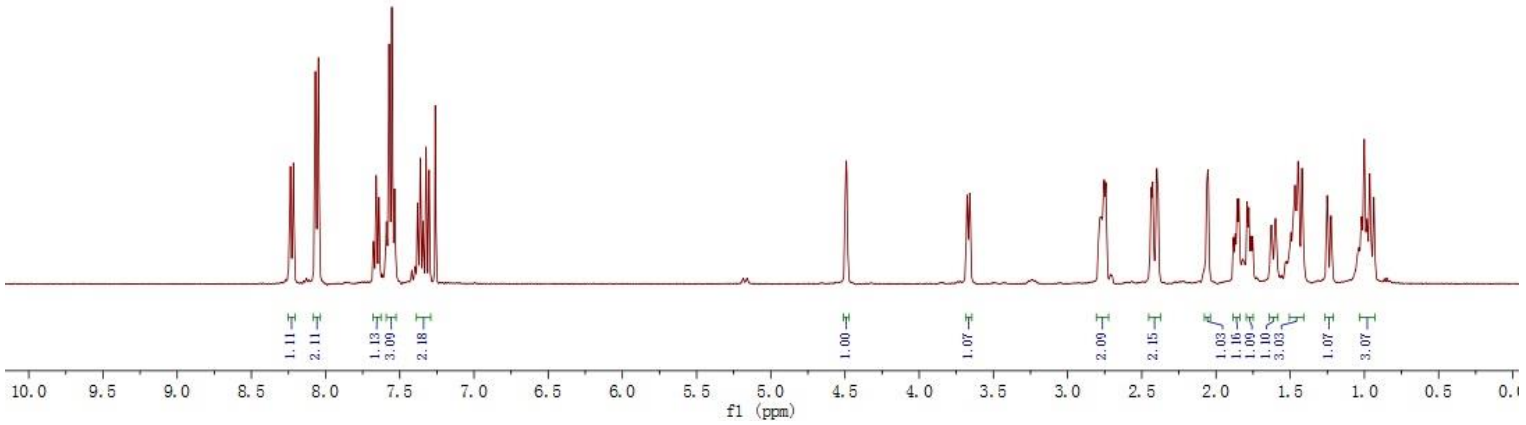
Compound	(±)-**4af**
Empirical formula	$C_{31}H_{28}O_3$
Formula weight	448.53
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.7710(5)
b/Å	12.5336(5)
c/Å	17.4579(7)
α/°	90
β/°	106.903(5)
γ/°	90
Volume/Å^3	2255.00(17)
Z	4
ρ_{calc}g/cm^3	1.321
μ/mm^{-1}	0.084
F(000)	952.0
Crystal size/mm^3	0.16 × 0.13 × 0.12
Radiation	MoKα (λ = 0.71073)
2θrange for data collection/°	6.944 to 59.014
Index ranges	$-11 \le h \le 14$, $-16 \le k \le 15$, $-23 \le l \le 17$
Reflections collected	13506
Independent reflections	5335 [R_{int} = 0.0342, R_{sigma} = 0.0481]
Data/restraints/parameters	5335/0/307
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0514, wR_2 = 0.1114
Final R indexes [all data]	R_1 = 0.0685, wR_2 = 0.1217
Largest diff. peak/hole/e Å^{-3}	0.29/-0.26

7. ^{1}H and ^{13}C NMR spectra of (±)-4a−af

ysy-162-H

Scheme 2, 4a

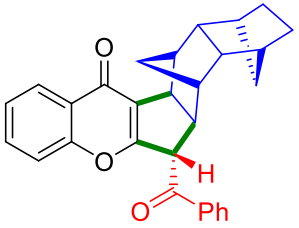


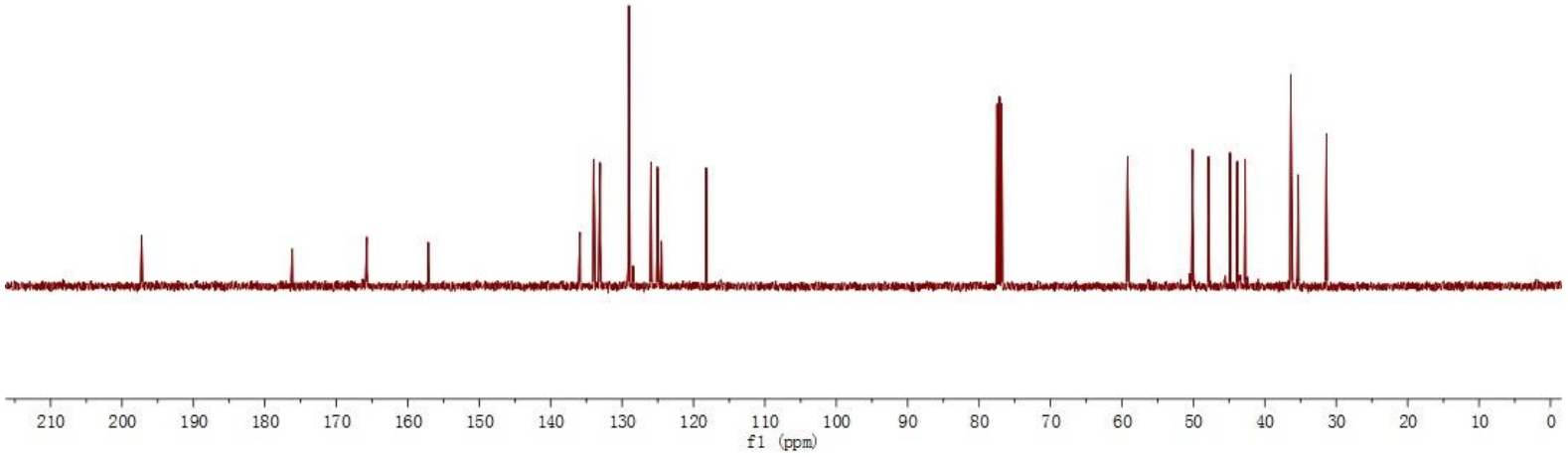


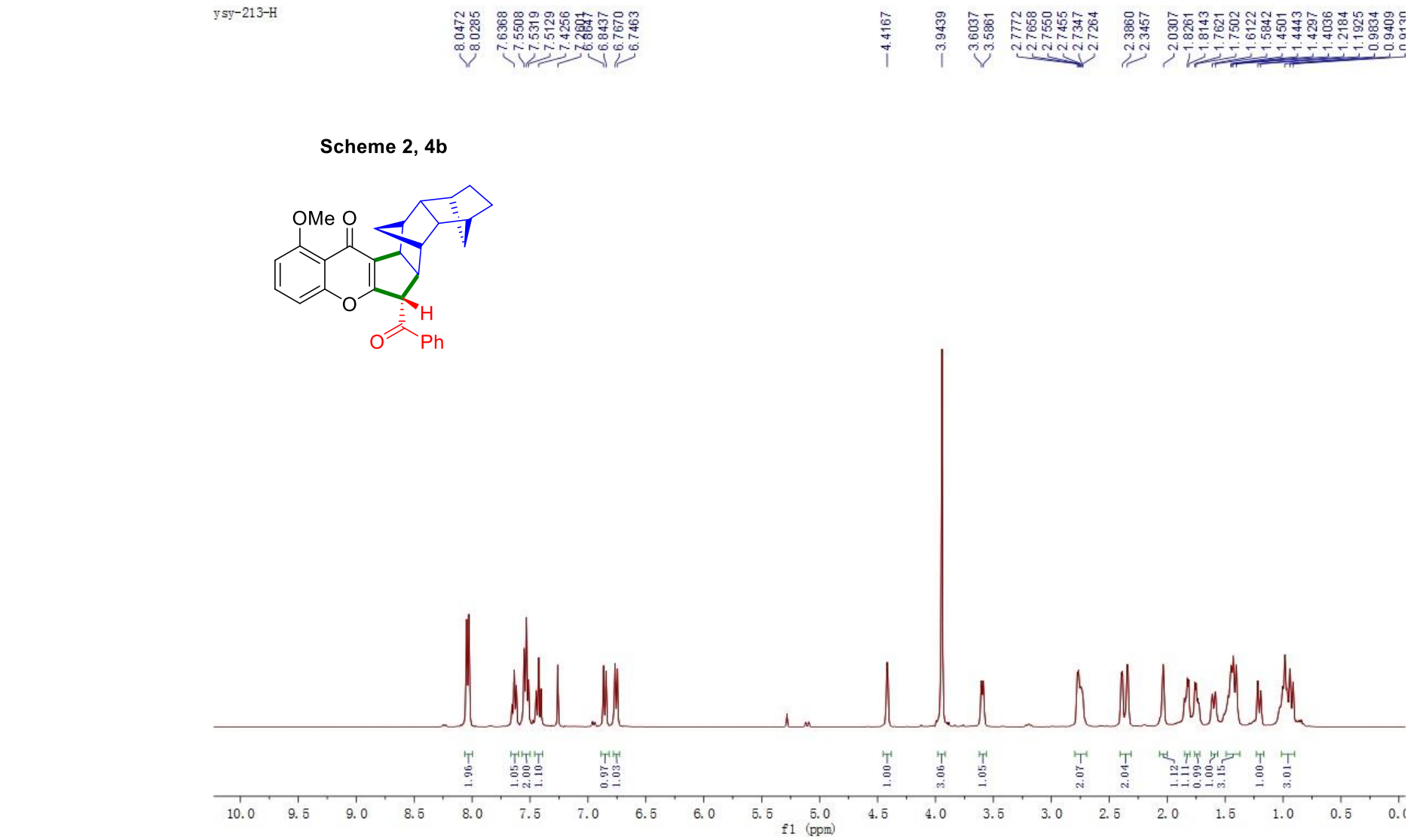
ysy-162-C

197.2506
176.1833
165.7431
157.1208
135.8972
133.9634
133.0829
129.0415
129.0068
125.9415
125.0534
124.9316
124.4910
118.2330
77.4782
77.1597
76.8420
59.2165
50.1941
50.1257
47.8567
44.8851
43.8399
42.7462
36.3678
36.2894
35.3306
31.3778
31.3585

Scheme 2, 4a





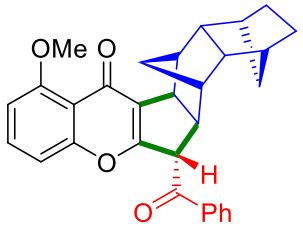

ysy-213-H
8.0472
8.0285
7.6368
7.5508
7.5319
7.5129
7.4256
7.2601
6.8647
6.8437
6.7670
6.7463
4.4167
3.9439
3.6037
3.5861
2.7772
2.7658
2.7550
2.7455
2.7347
2.7264
2.3860
2.3457
2.0307
1.8261
1.8143
1.7621
1.7502
1.6122
1.5842
1.4501
1.4443
1.4297
1.4036
1.2184
1.1925
0.9834
0.9409
1.96
1.05
2.00
1.10
0.97
1.03
1.00
3.06
1.05
2.07
2.04
1.12
1.11
0.99
1.00
3.15
1.00
3.01
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)

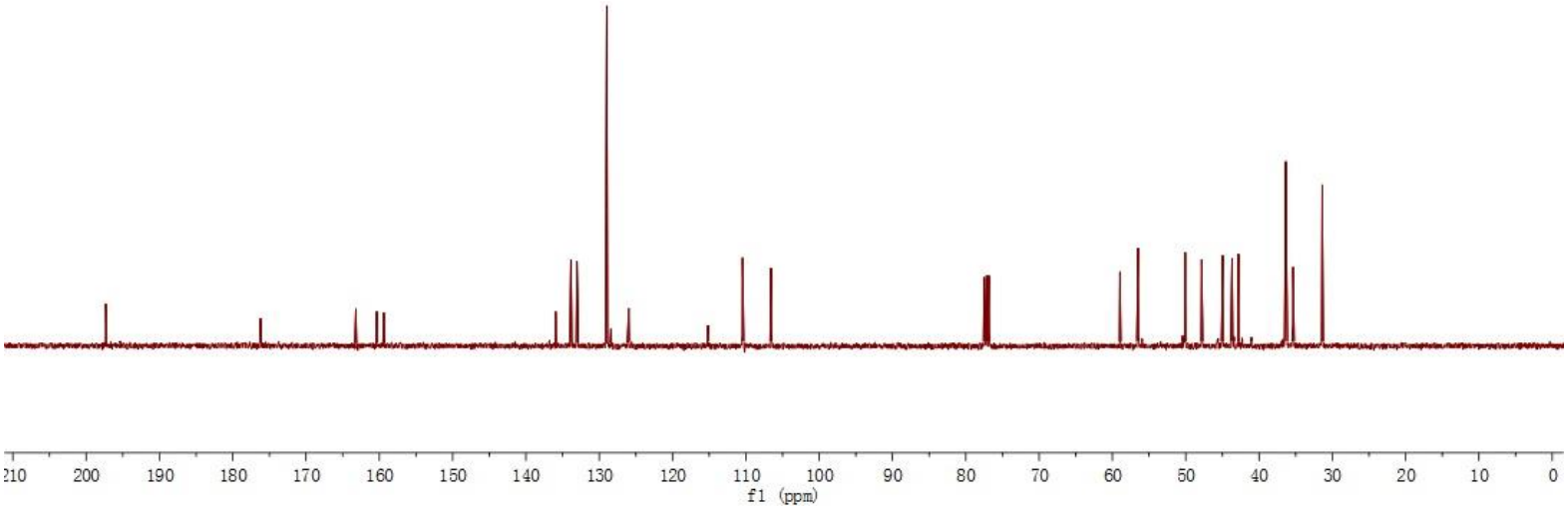
Scheme 2, 4b

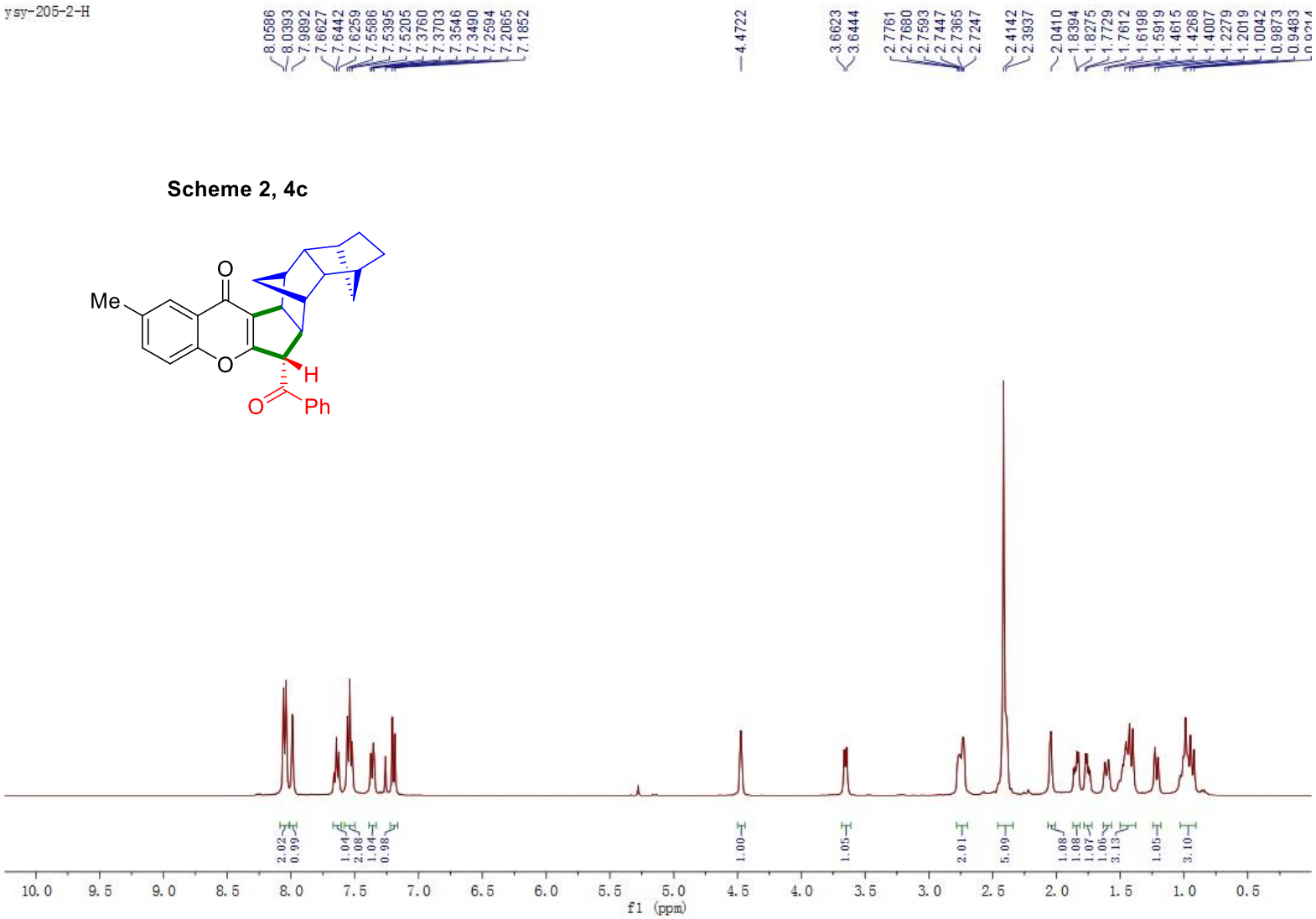
OMe
O
O
H
O
Ph


ysy-213-C
197.2869
176.2027
163.1999
160.3634
159.3967
135.9422
133.8619
133.0386
128.9760
128.4018
125.9799
115.1688
110.4343
106.5661
77.4816
77.1632
76.8450
58.9621
56.5097
50.4305
50.1875
50.0756
47.8221
44.9627
43.6885
42.8126
41.0296
36.3408
36.2277
35.3353
31.3722

Scheme 2, 4b


OMe
O
O
H
O
Ph

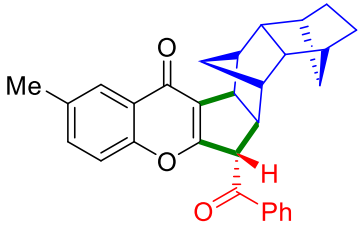

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

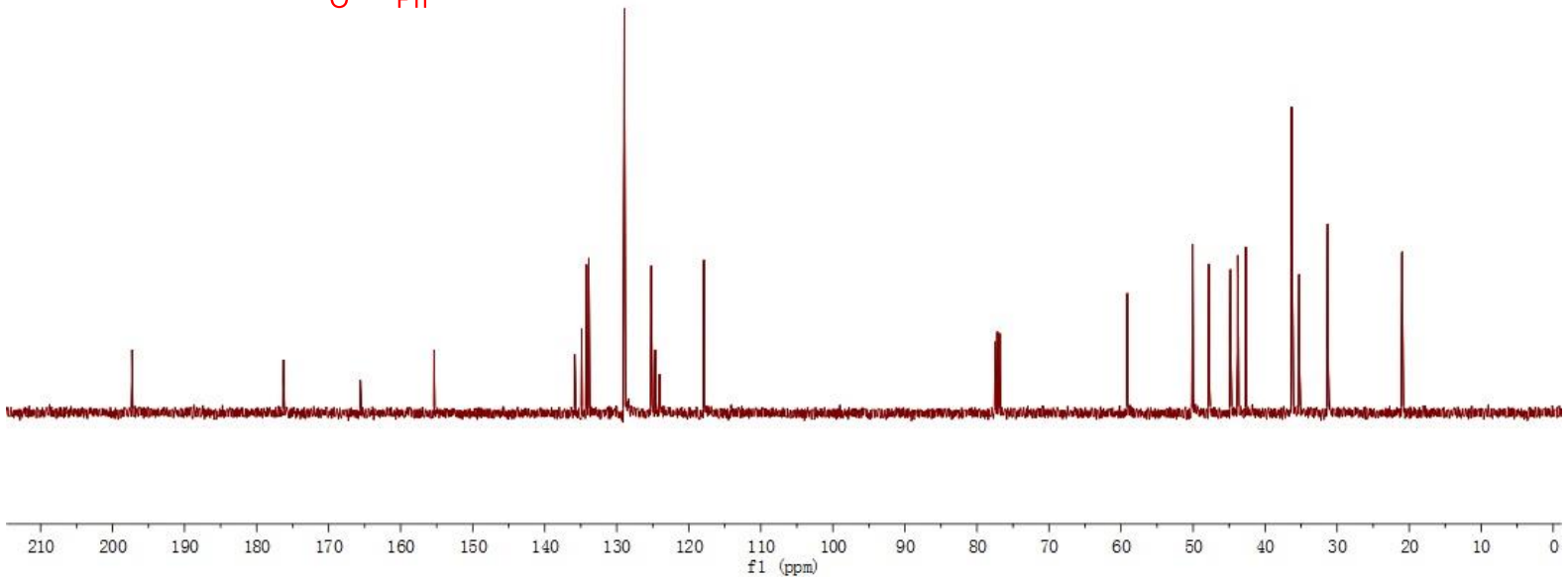

ysy-205-2-H
8.0586
8.0393
7.9892
7.6627
7.6442
7.6259
7.5586
7.5395
7.5205
7.3760
7.3703
7.3546
7.3490
7.2594
7.2065
7.1852
4.4722
3.6623
3.6444
2.7761
2.7680
2.7593
2.7447
2.7365
2.7247
2.4142
2.3937
2.0410
1.8394
1.8275
1.7729
1.7612
1.6198
1.5919
1.4615
1.4268
1.4007
1.2279
1.2019
1.0042
0.9873
0.9483
Me
O
O
H
O
Ph
2.02
0.99
1.04
2.08
1.04
0.98
1.00
1.05
2.01
5.09
1.08
1.08
1.07
1.06
3.13
1.05
3.10
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, 4c


ysy-205-2-C
197.2699
176.2360
165.6239
155.3585
135.8426
134.8855
134.2228
133.8892
128.9712
128.9473
125.2062
124.6388
124.0508
117.8895
77.4787
77.1615
76.8407
59.1192
50.1231
50.0684
47.7863
44.7981
43.7839
42.6802
36.3064
36.2233
35.2701
31.3238
31.3014
20.9609

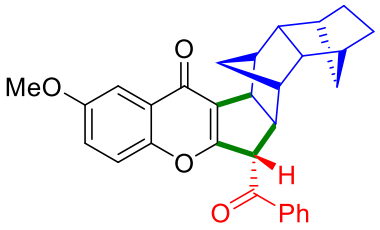
Scheme 2, 4c

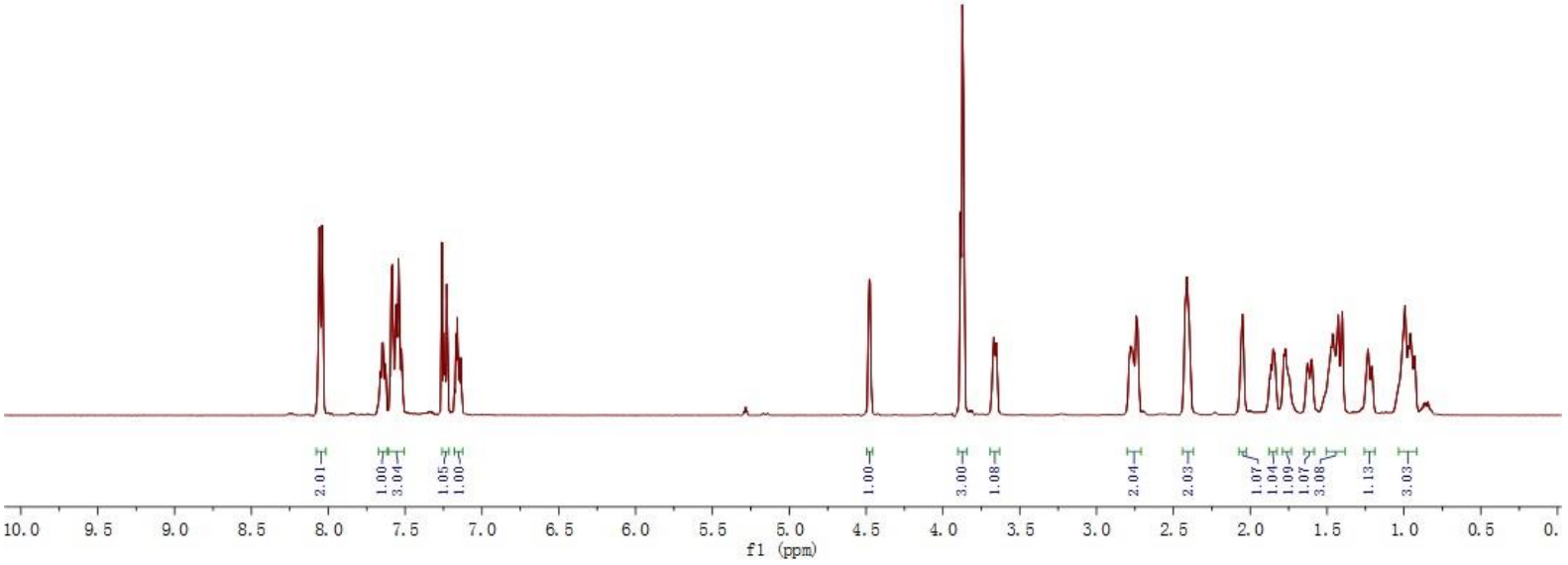

Me
O
O
H
O
Ph


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


ysy-207-H
8.0581
8.0405
8.0363
7.6585
7.6439
7.6303
7.6271
7.5984
7.5895
7.5820
7.5625
7.5561
7.5425
7.5386
7.5241
7.5203
7.2600
7.2512
7.2388
7.2288
7.2235
7.1684
7.1607
7.1555
7.1453
4.4785
4.4740
4.4692
3.8853
3.8730
3.8664
3.8630
3.8592
3.6672
3.6534
2.7885
2.7760
2.7601
2.7432
2.4233
2.4109
2.0477
1.8646
1.8511
1.8400
1.7813
1.7702
1.6274
1.5994
1.4675
1.4280
1.4022
1.2326
1.2148
1.0029
0.9576
0.9519

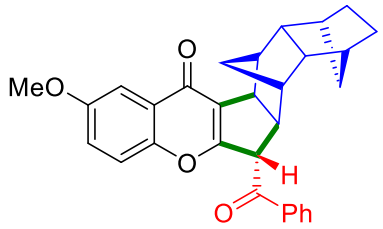
Scheme 2, 4d

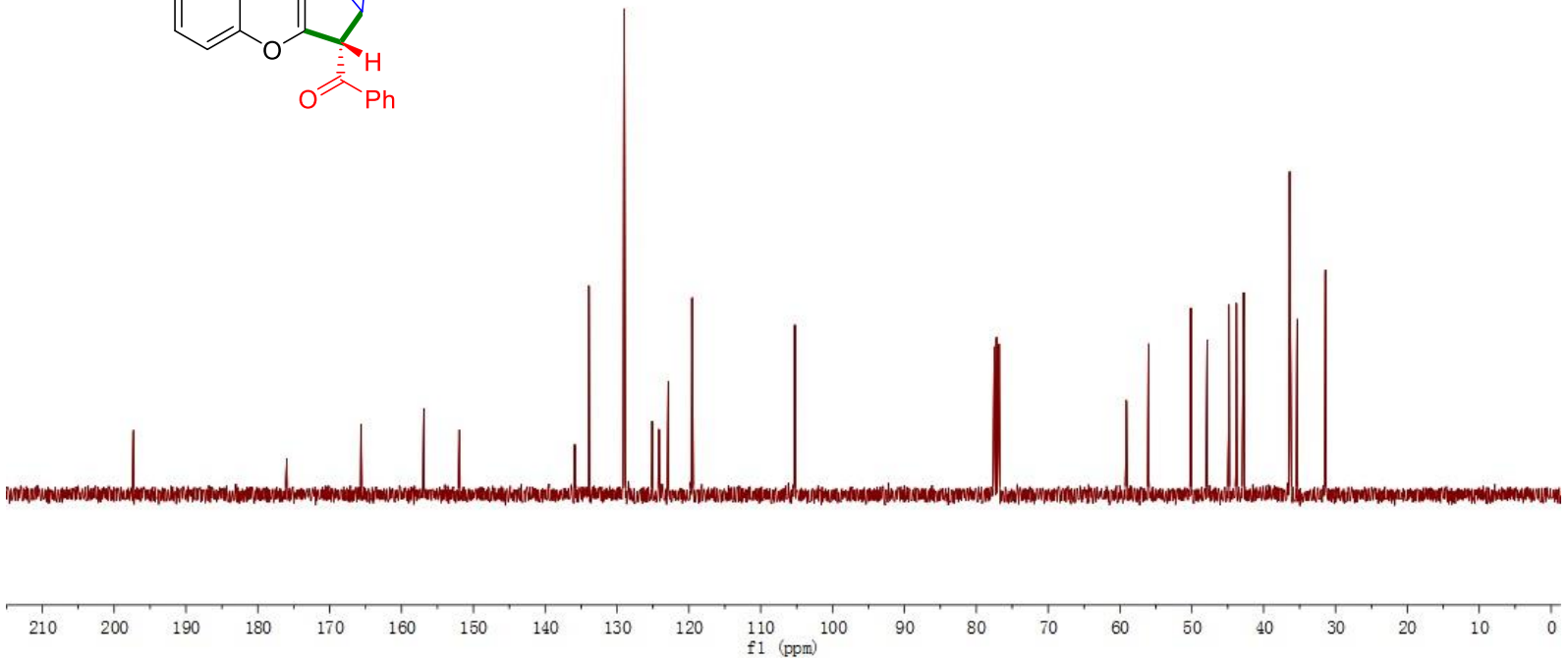

MeO
O
O
H
O
Ph


2.01
1.00
3.04
1.05
1.00
1.00
3.00
1.08
2.04
2.03
1.07
1.04
1.09
1.07
3.08
1.13
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


ysy-207-C
197.3013
175.9710
165.6349
156.8845
151.9348
135.8898
133.9486
129.0269
129.0013
125.1005
124.1785
122.8717
119.5315
105.2420
77.4810
77.1633
76.8457
59.1418
56.0144
50.1815
50.1244
44.8363
43.8264
42.3813
36.3714
36.2929
35.3304
31.3759
31.3543

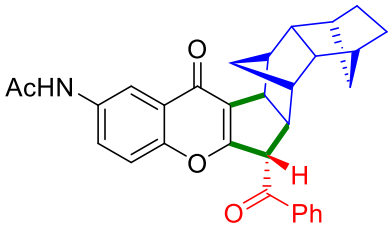
Scheme 2, 4d

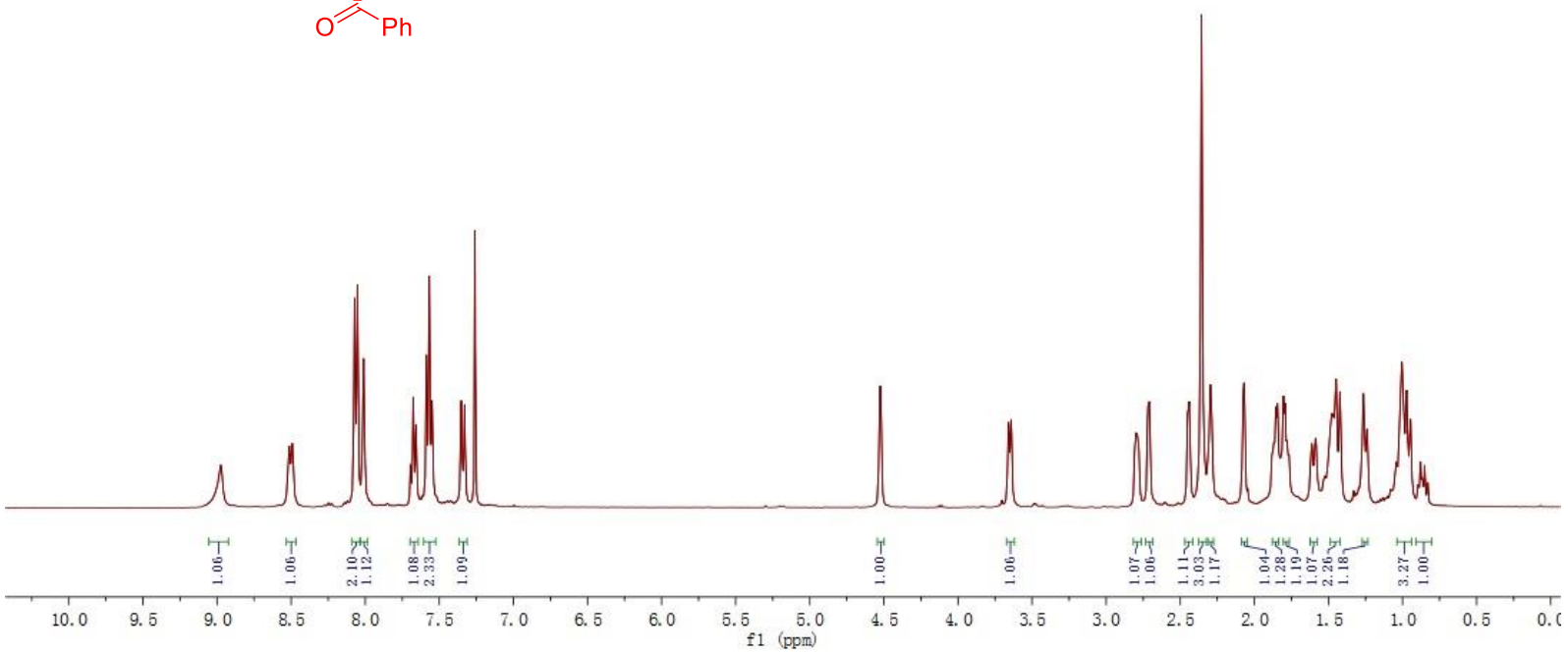

MeO
O
O
H
O
Ph


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


8.9742
8.5142
8.4915
8.0723
8.0531
8.0113
7.6946
7.6760
7.6576
7.5871
7.5680
7.5490
7.3519
7.3295
7.2601
4.5229
3.6590
3.6414
2.7983
2.7883
2.7798
2.7184
2.7073
2.4497
2.4384
2.3569
2.2932
2.0765
2.0678
1.8554
1.8435
1.8035
1.7918
1.6134
1.5861
1.4790
1.4672
1.4475
1.4221
1.2644
1.2395
1.0042
0.9724

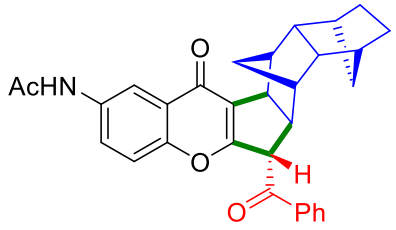
Scheme 2, 4e

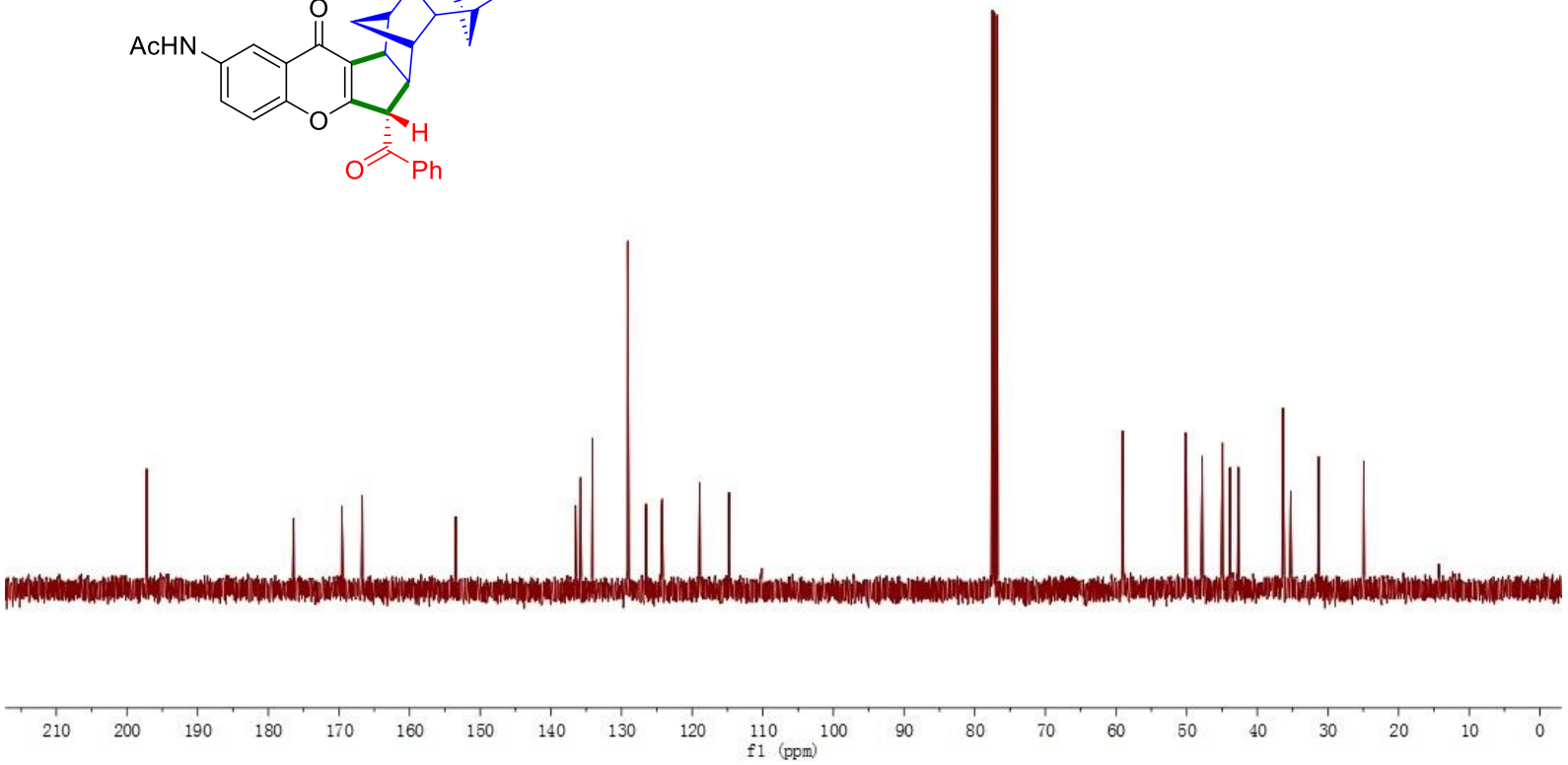

AcHN
O
O
H
O
Ph


1.06
1.06
2.10
1.12
1.08
2.33
1.09
1.00
1.06
1.07
1.06
1.11
3.03
1.17
1.04
1.28
1.19
1.07
2.26
1.18
3.27
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

197.2154
176.4263
169.5835
166.7093
153.4531
136.5204
135.7880
134.1032
129.0938
129.0271
126.5244
124.3071
124.2330
118.9165
114.7555
77.4776
77.1601
76.8428
59.0338
50.1471
50.0374
47.7987
44.9410
43.8476
42.6904
36.3625
36.3278
35.2713
31.3217
24.9342

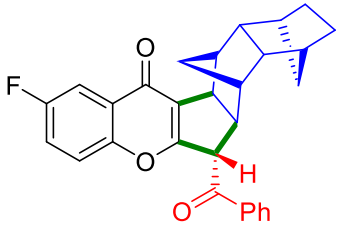
Scheme 2, 4e

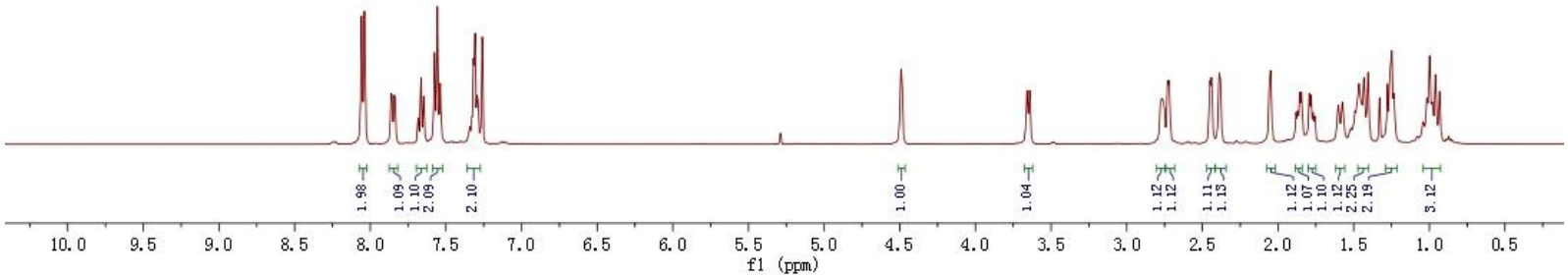


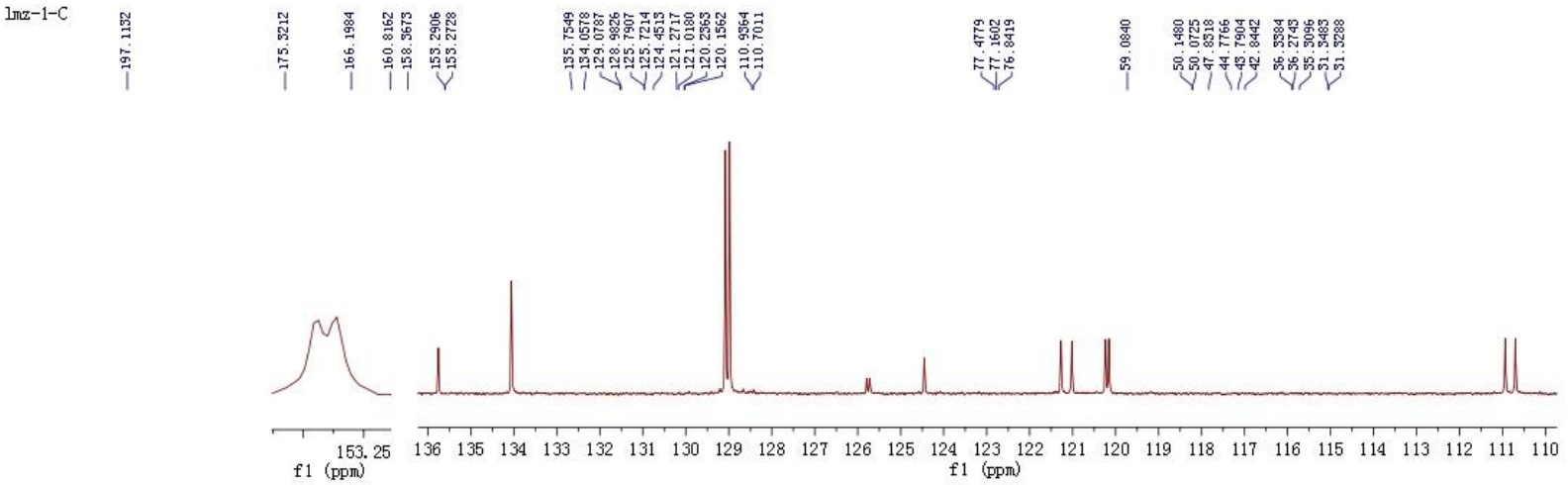


lmz-1-H

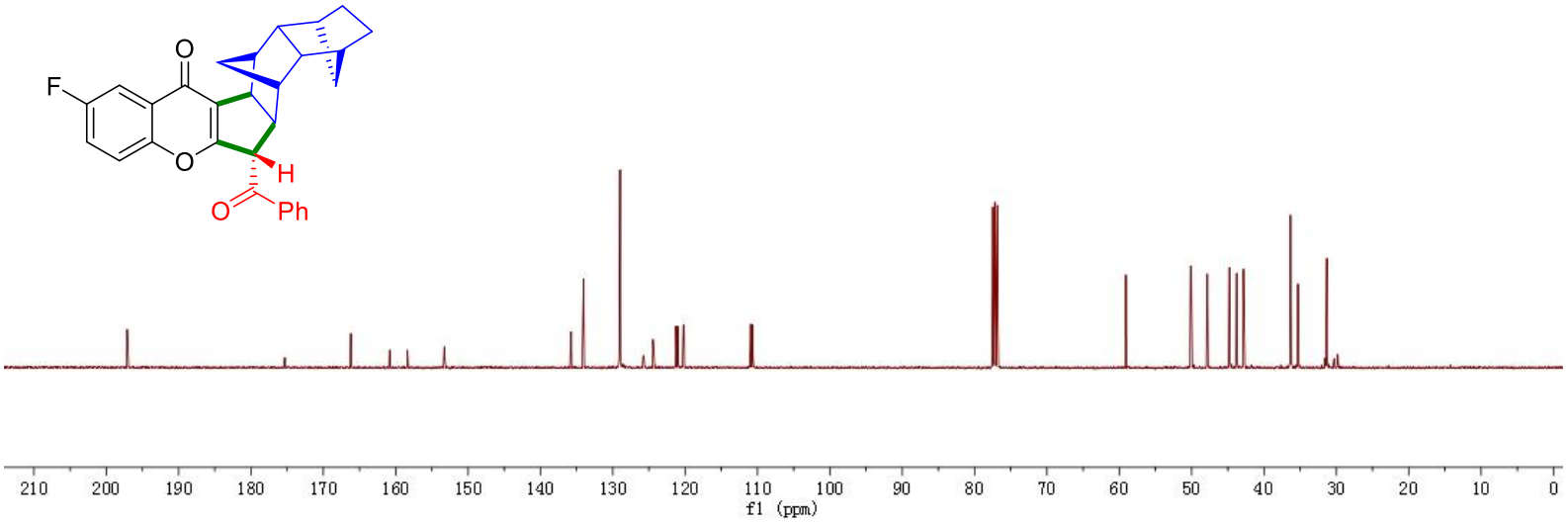
Scheme 2, 4f



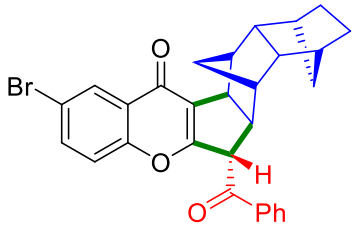


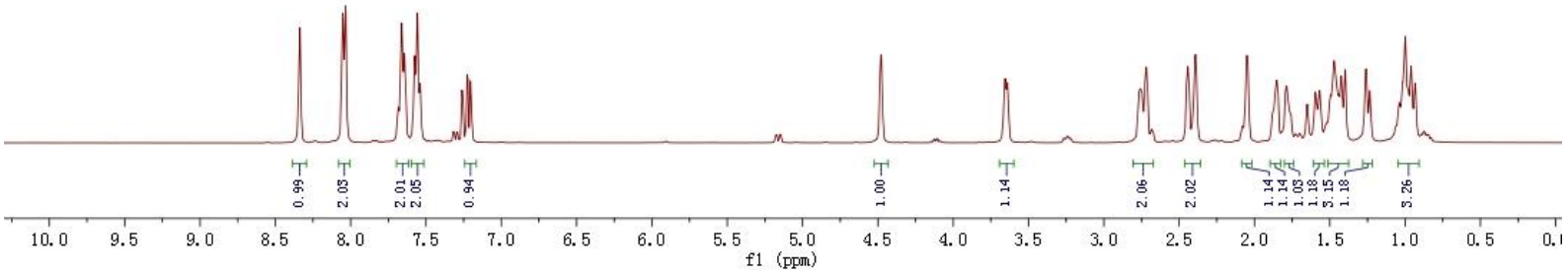

lmz-1-C
197.1132
175.5212
166.1984
160.8162
158.3673
153.2906
153.2728
135.7549
134.0578
129.0787
128.9826
125.7907
125.7214
124.4513
121.2717
121.0180
120.2363
120.1562
110.9564
110.7011
77.4779
77.1602
76.8419
59.0840
50.1480
50.0725
47.8518
44.7766
43.7904
42.8442
36.3384
36.2743
35.3096
31.5483
31.3288
153.25
f1 (ppm)
f1 (ppm)

Scheme 2, 4f


O
F
O
H
O
Ph
f1 (ppm)

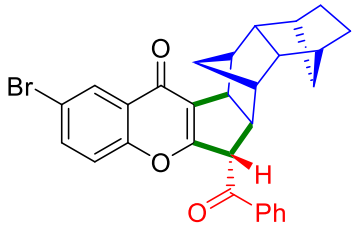
Scheme 2, 4g

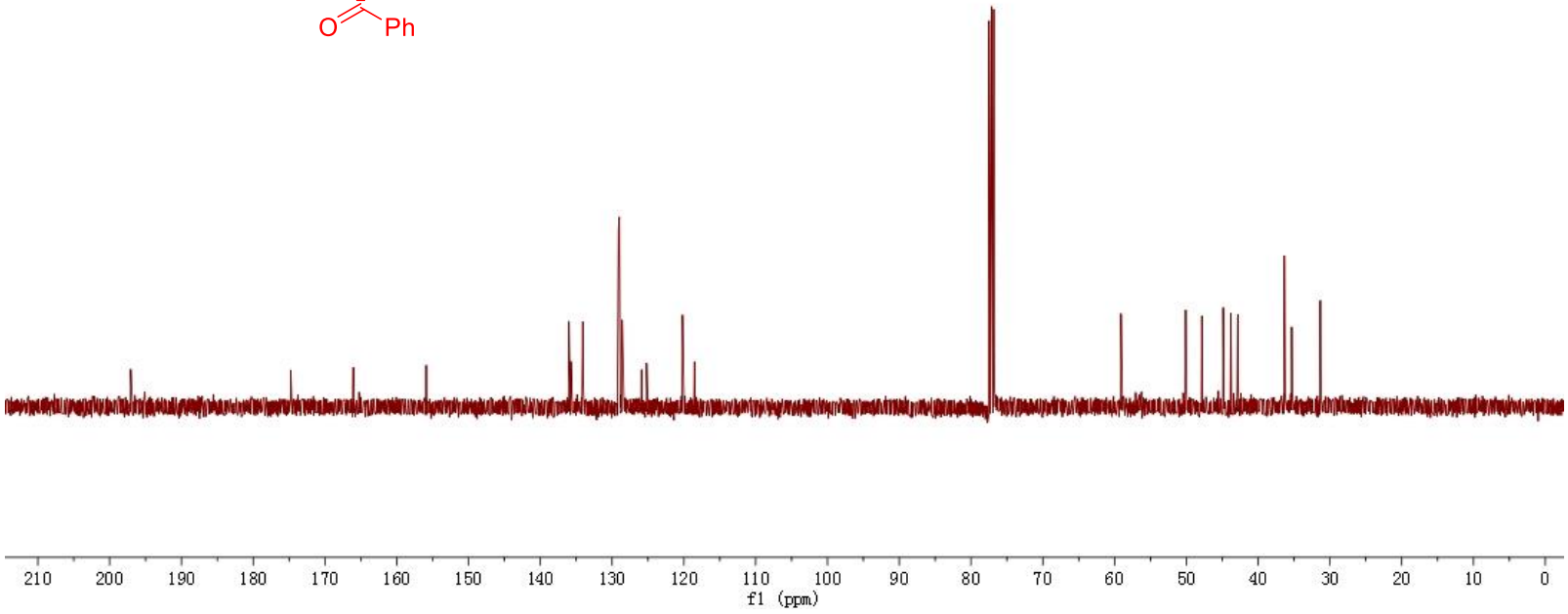




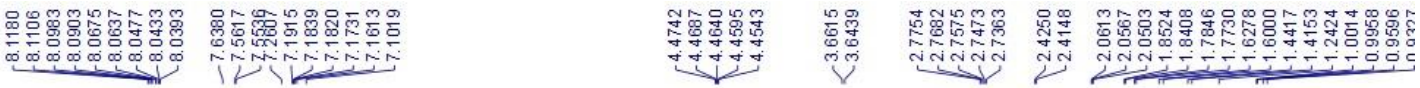

lmz-2-C
197.0602
174.7606
166.0548
155.8979
136.0056
135.7387
134.0895
129.1030
128.9934
128.6047
125.9058
125.1904
120.1797
118.5131
77.4775
77.1593
76.8413
59.0988
50.1549
50.0924
47.8478
44.8788
43.7860
42.8317
36.3492
36.2826
35.3213
31.3608
31.3370

Scheme 2, 4g

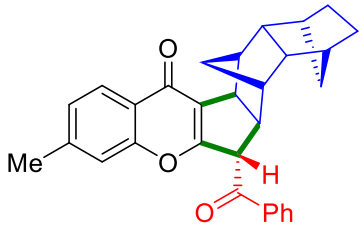

Br
O
O
H
O
Ph

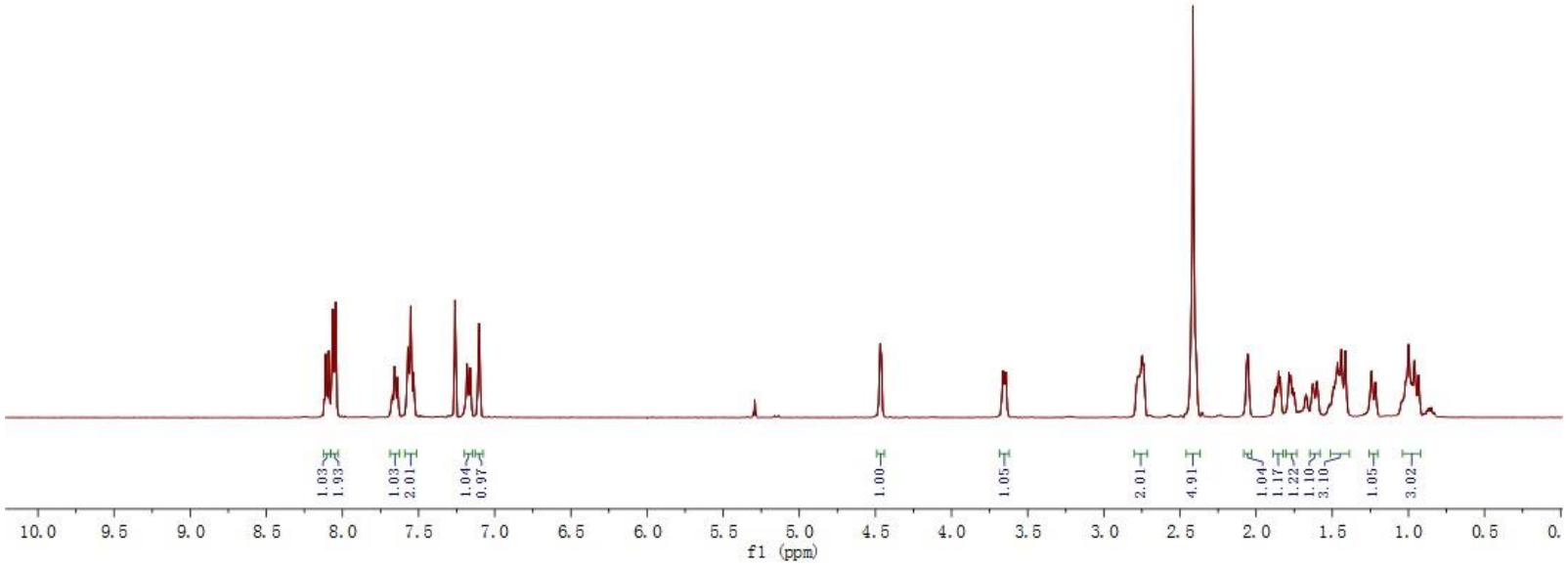

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

ysy-204-H



Scheme 2, 4h

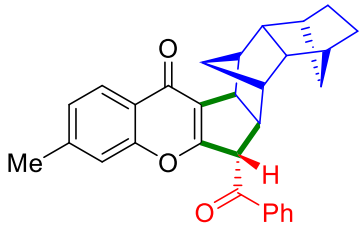


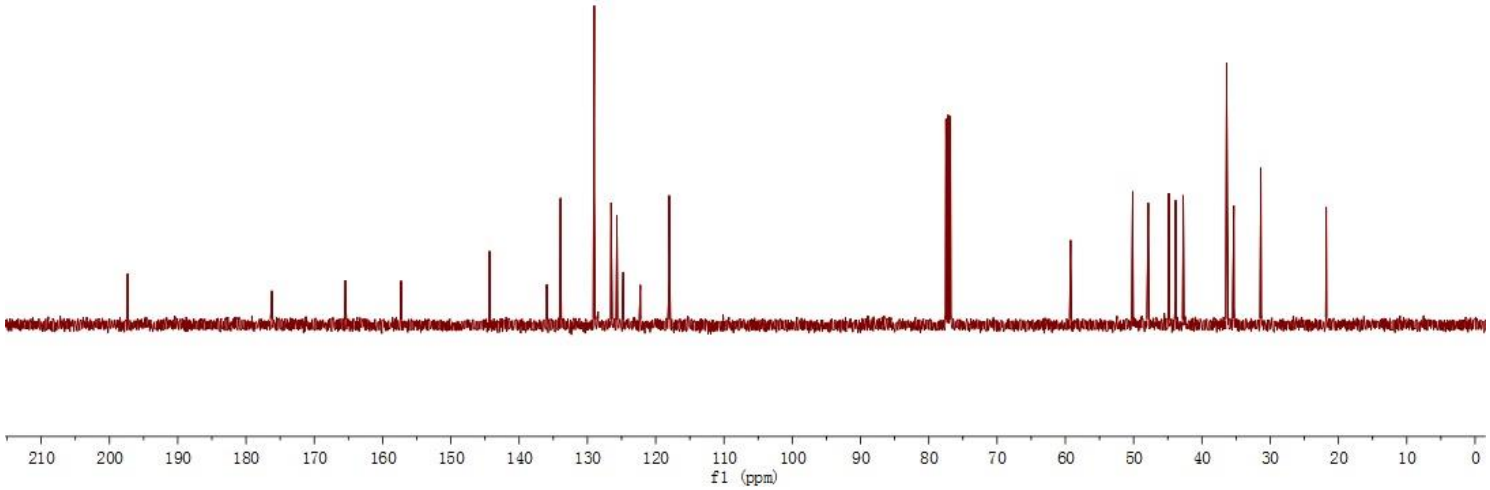


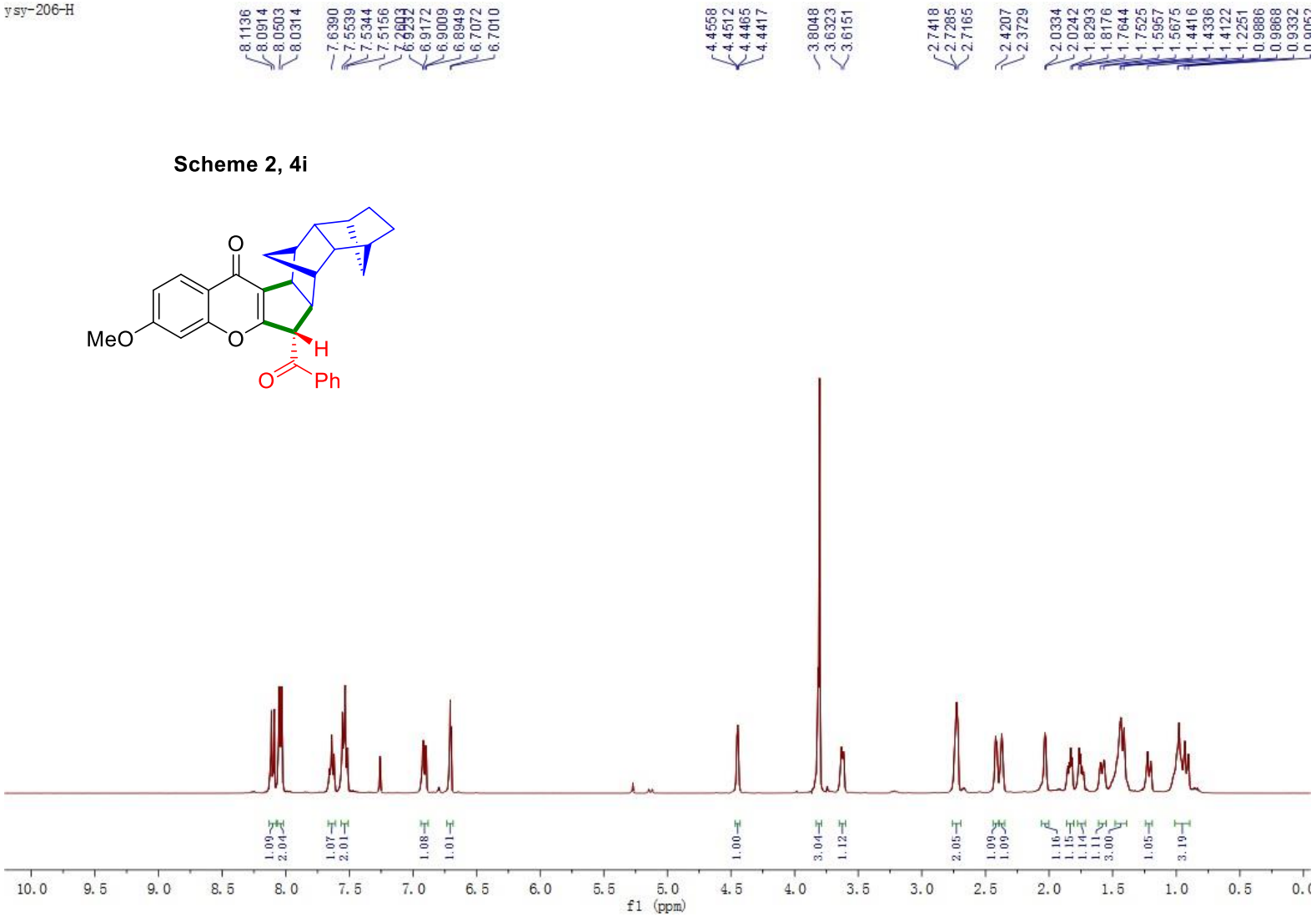
ysy-204-C

197.3331
176.1986
165.4263
157.2818
144.3472
135.9445
133.9329
129.0368
129.0176
126.5261
125.6788
124.7454
122.2497
118.0295
77.4795
77.1621
76.8445
59.2376
50.2087
50.1432
47.8682
44.8625
43.8614
42.7343
36.3800
36.2947
35.3361
31.3937
31.3720
21.7945

Scheme 2, 4h

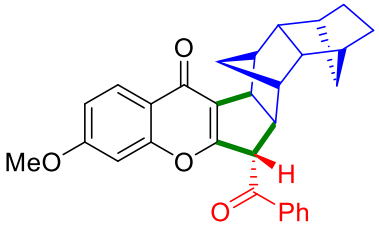


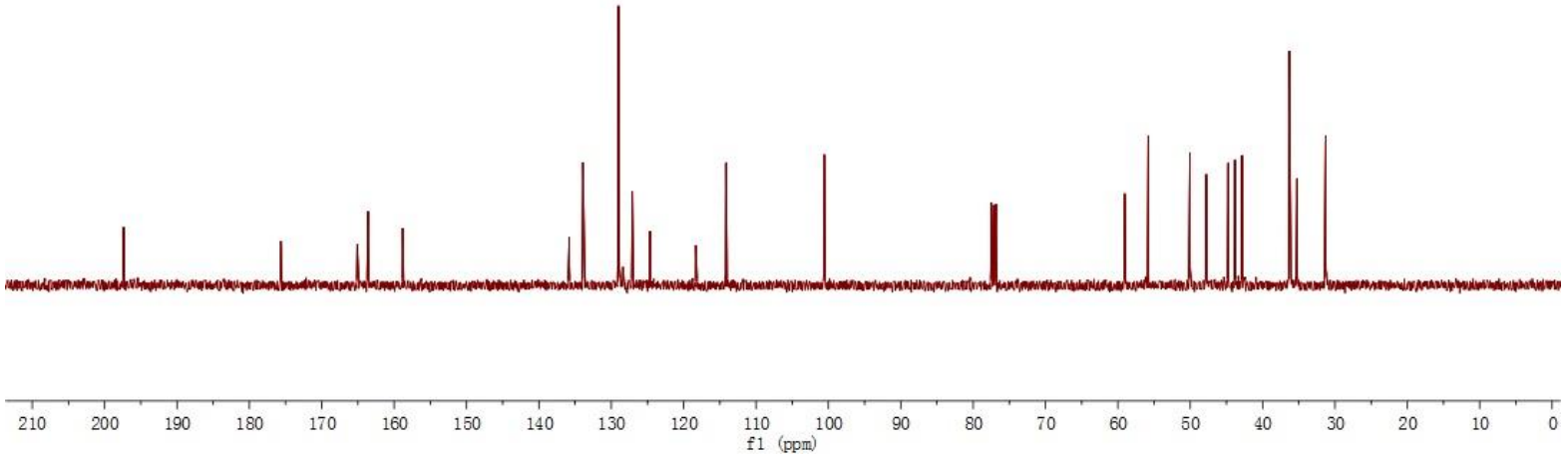



ysy-206-H
8.1136
8.0914
8.0503
8.0314
7.6390
7.5539
7.5344
7.5156
6.9232
6.9172
6.9009
6.8949
6.7072
6.7010
4.4558
4.4512
4.4465
4.4417
3.8048
3.6323
3.6151
2.7418
2.7285
2.7165
2.4207
2.3729
2.0334
2.0242
1.8293
1.8176
1.7644
1.7525
1.5957
1.5675
1.4416
1.4336
1.4122
1.2251
0.9886
0.9868
0.9332
Scheme 2, 4i
O
MeO
O
H
O
Ph
1.09
2.04
1.07
2.01
1.08
1.01
1.00
3.04
1.12
2.05
1.09
1.09
1.16
1.15
1.14
1.11
3.00
1.05
3.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


ysy-206-C
197.3815
175.6784
165.0863
163.6011
158.8128
135.8013
133.8972
128.9868
128.9232
127.0935
124.6575
118.2986
114.1260
100.5735
77.4761
77.1538
76.8398
59.0672
55.8042
50.1114
50.0571
44.7553
43.7956
36.1995
35.2611
31.3163
31.2949

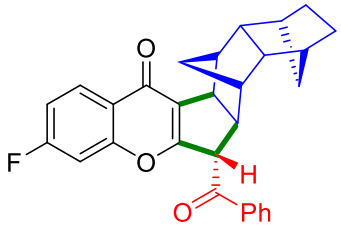
Scheme 2, 4i

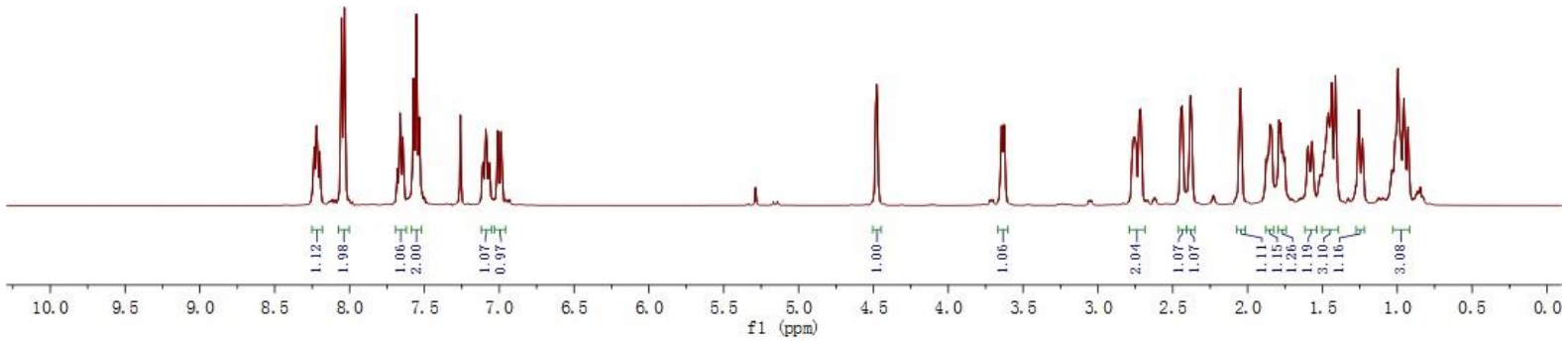

O
MeO
O
H
O
Ph

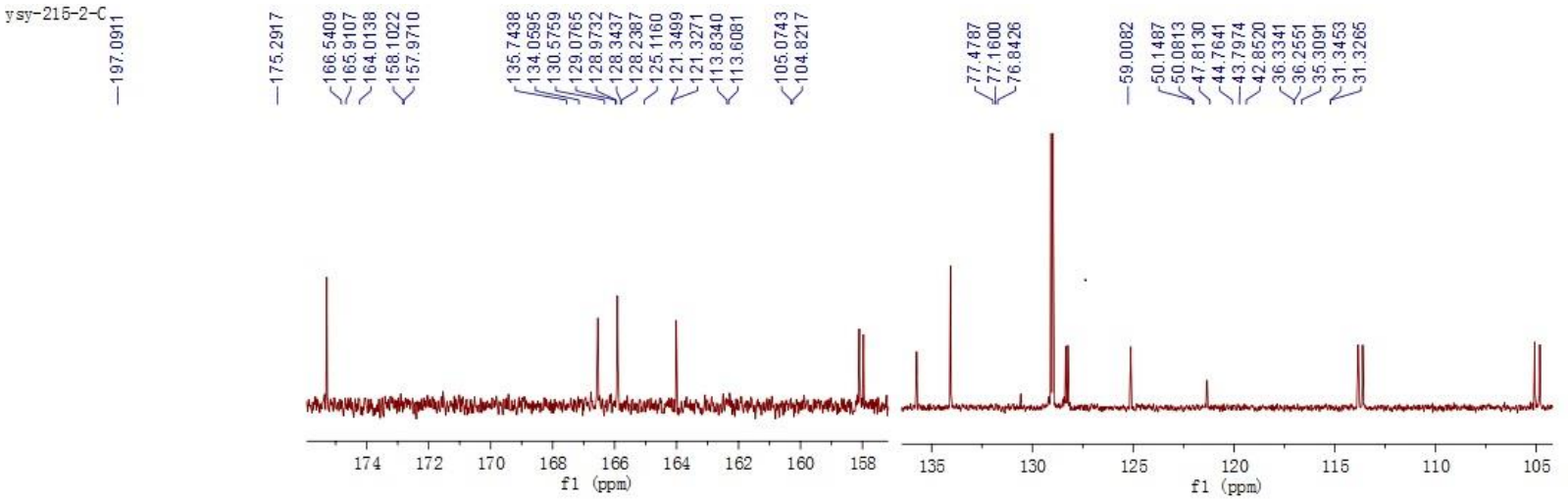

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


ysy-215-2-H
8.2363
8.2206
8.2141
8.1984
8.0534
8.0341
7.6616
7.5727
7.5539
7.5397
7.1123
7.1065
7.0911
7.0852
7.0697
7.0639
7.0111
7.0053
6.9883
6.9825
4.4787
3.6437
3.6260
2.7709
2.7622
2.7522
2.7437
2.7229
2.7117
2.4463
2.4348
2.3833
2.0439
1.8511
1.8392
1.7894
1.7775
1.5963
1.5683
1.4671
1.4611
1.4382
1.4126
1.2571
1.2314
1.0138
0.9948
0.9547

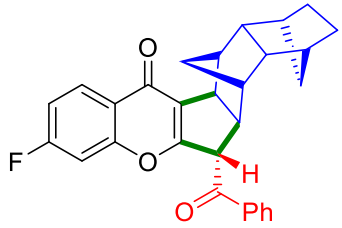
Scheme 2, 4j

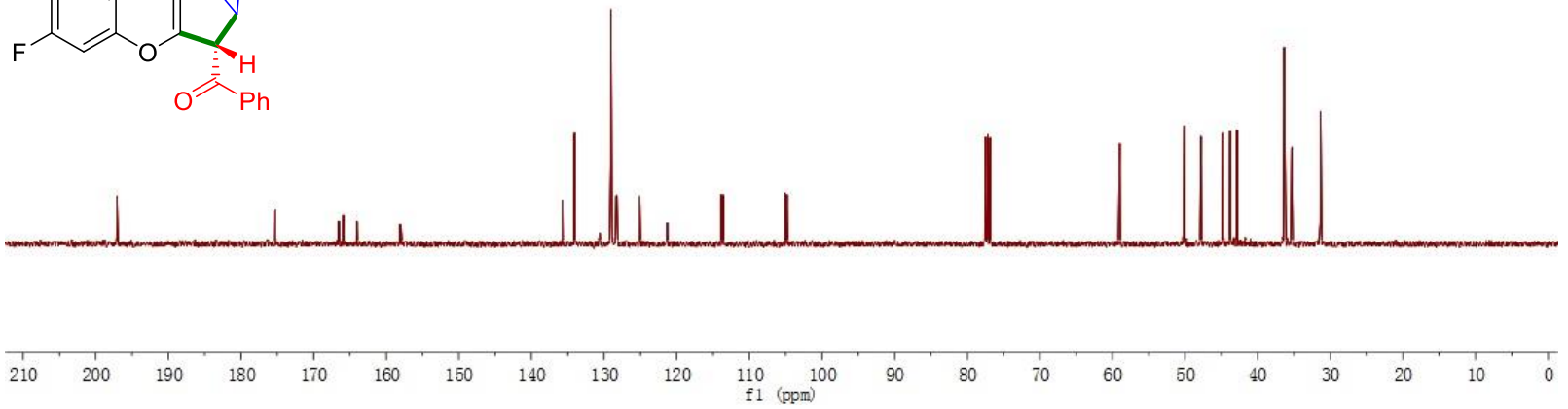

O
F
O
H
O
Ph


1.12
1.98
1.06
2.00
1.07
0.97
1.00
1.06
2.04
1.07
1.07
1.11
1.15
1.26
1.19
3.10
1.16
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


ysy-215-2-C
197.0911
175.2917
166.5409
165.9107
164.0138
158.1022
157.9710
135.7438
134.0595
130.5759
129.0765
128.9732
128.3437
128.2387
125.1160
121.3499
121.3271
113.8340
113.6081
105.0743
104.8217
77.4787
77.1600
76.8426
59.0082
50.1487
50.0813
47.8130
44.7641
43.7974
42.8520
36.3341
36.2551
35.3091
31.3453
31.3265
f1 (ppm)
f1 (ppm)

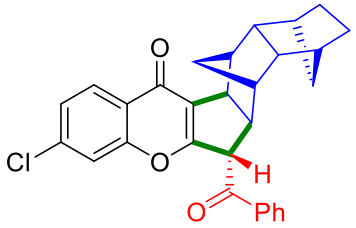
Scheme 2, 4j

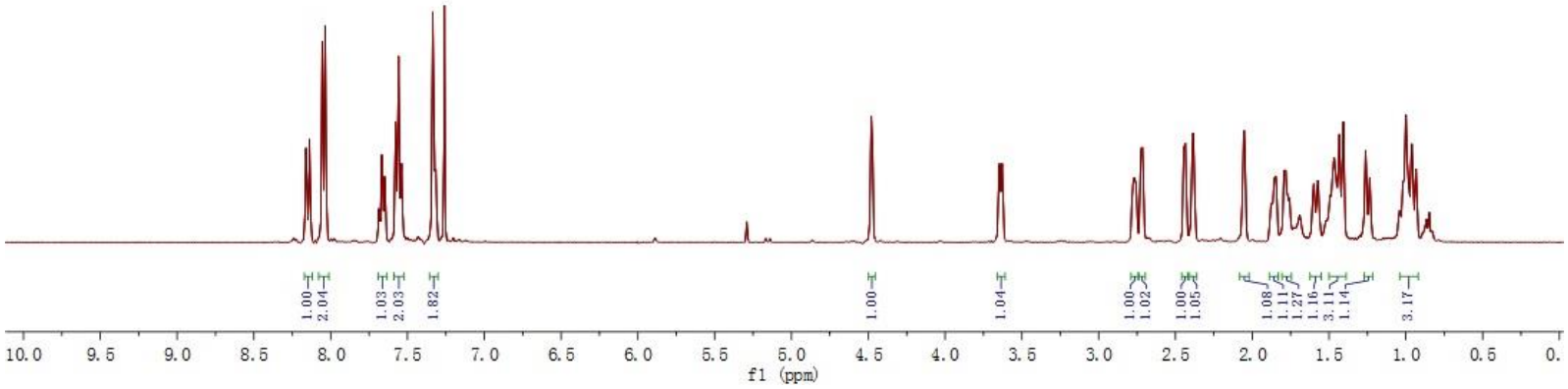

O
F
O
H
O
Ph


f1 (ppm)


ysy-208-2-H
8.1654
8.1606
8.1570
8.1506
8.1428
8.1379
8.1341
8.0542
8.0359
7.6858
7.6825
7.6723
7.6662
7.6526
7.6491
7.6459
7.6433
7.5826
7.5778
7.5742
7.5623
7.5572
7.5440
7.5383
7.3415
7.3362
7.3312
7.3215
7.3151
7.2594
4.4855
4.4805
4.4761
4.4713
3.6465
3.6287
2.7803
2.7709
2.7599
2.7527
2.7242
2.7132
2.4339
2.3849
2.0498
1.8560
1.8443
1.7928
1.7814
1.6006
1.5725
1.4659
1.4369
1.4324
1.4109
1.4058
1.2629
1.0059
0.9991
0.9608

Scheme 2, 4k

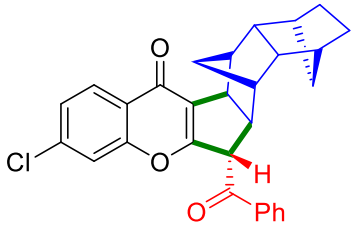

O
Cl
O
H
O
Ph

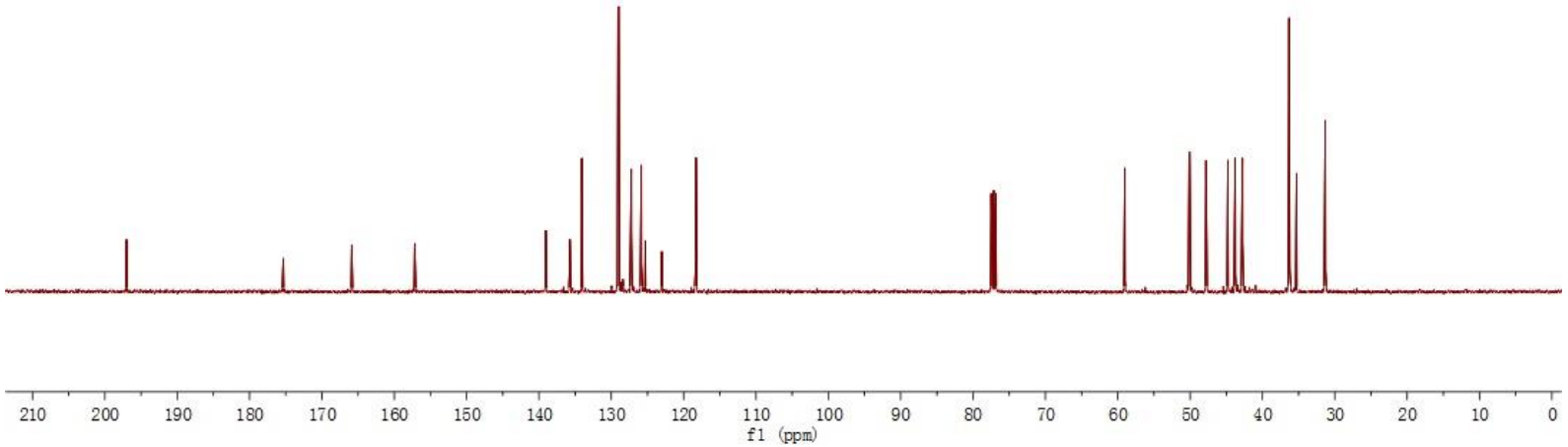

1.00
2.04
1.03
2.03
1.82
1.00
1.04
1.00
1.02
1.00
1.05
1.08
1.11
1.27
1.16
3.11
1.14
3.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

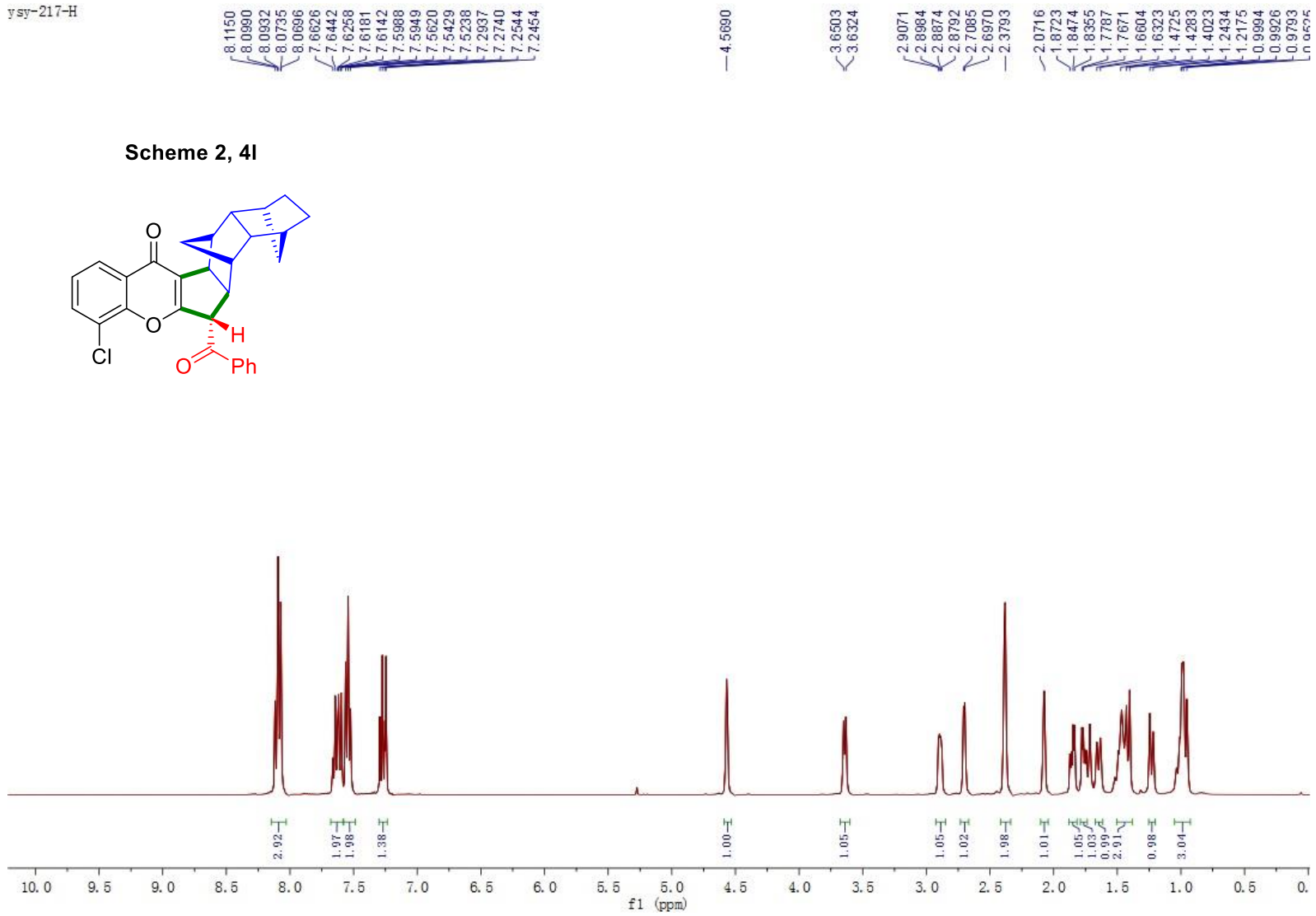
ysy-208-2-C

196.9987
175.3316
165.8660
157.1592
139.0620
135.7258
134.0635
129.0718
128.9651
127.2354
125.8589
125.2880
123.0196
118.3071
77.4784
77.1600
76.8439
59.0116
50.1321
50.0669
47.7974
44.7854
43.7733
42.7721
36.3216
36.2573
35.2945
31.3326
31.3154

Scheme 2, 4k





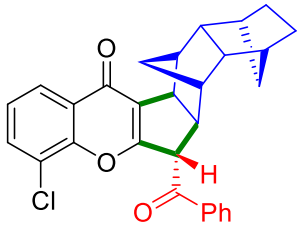

ysy-217-H
8.1150
8.0990
8.0932
8.0735
8.0696
7.6626
7.6442
7.6258
7.6181
7.6142
7.5988
7.5949
7.5620
7.5429
7.5238
7.2937
7.2740
7.2544
7.2454
4.5690
3.6503
3.6324
2.9071
2.8984
2.8874
2.8792
2.7085
2.6970
2.3793
2.0716
1.8723
1.8474
1.8355
1.7787
1.7671
1.6604
1.6323
1.4725
1.4283
1.4023
1.2434
1.2175
0.9994
0.9926
0.9793
2.92
1.97
1.98
1.38
1.00
1.05
1.05
1.02
1.98
1.01
1.05
1.03
0.99
2.91
0.98
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

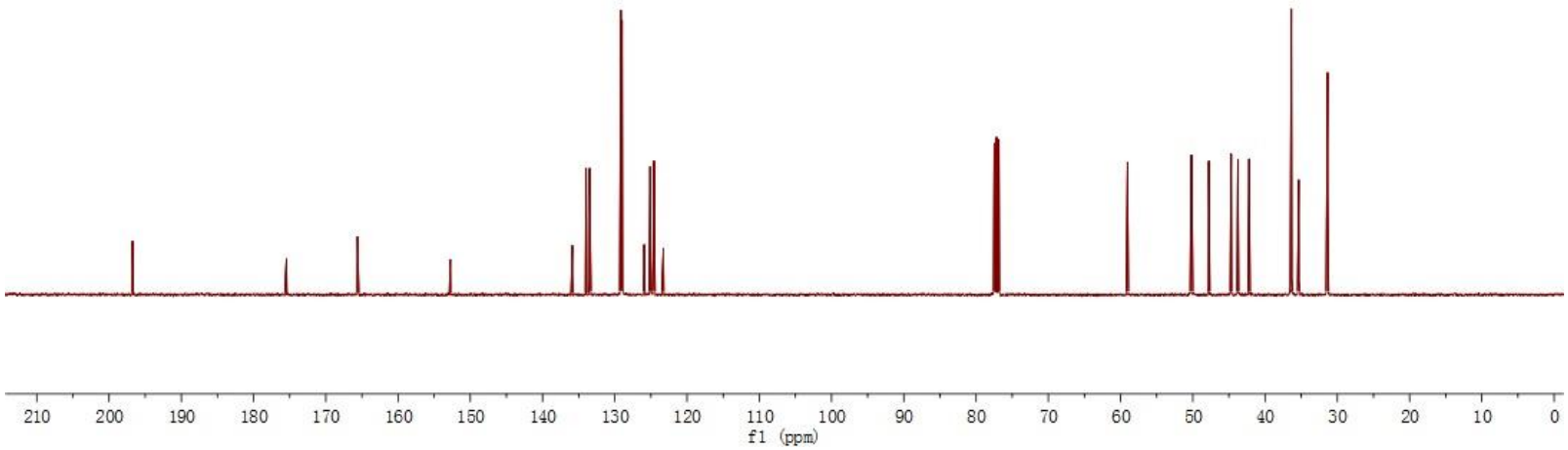
Scheme 2, 4l

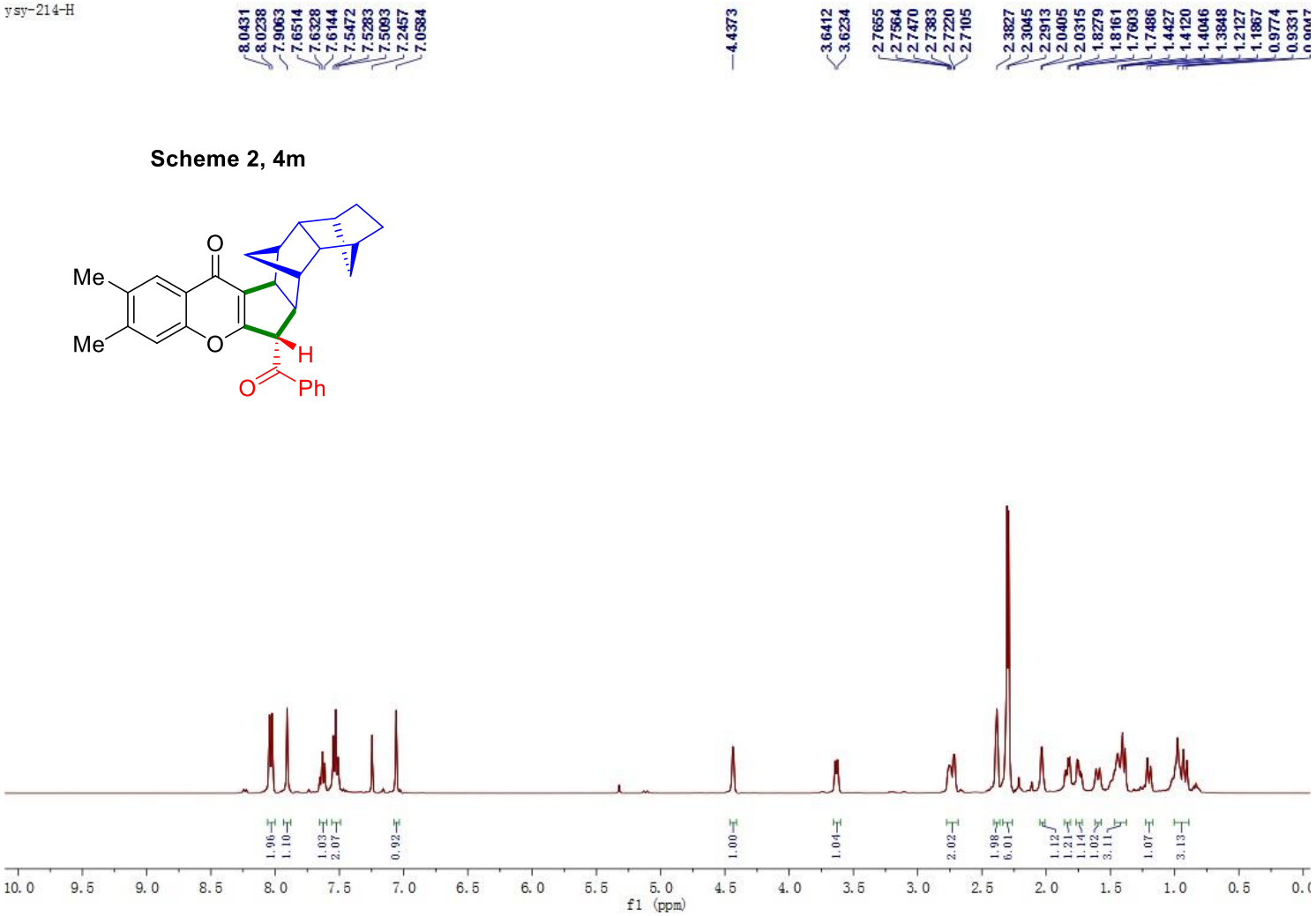
O
O
Cl
H
O
Ph


ysy-217-C
196.7500
175.4526
165.5929
152.7834
135.8954
133.9734
133.4788
129.1766
129.0005
125.9282
125.1089
125.0514
124.5741
123.2773
77.4792
77.1610
76.8423
59.0372
50.2141
50.1411
47.7770
44.6935
43.7565
42.2034
36.3706
36.3384
35.3453
31.3616

Scheme 2, 4l


O
O
H
Cl
O
Ph

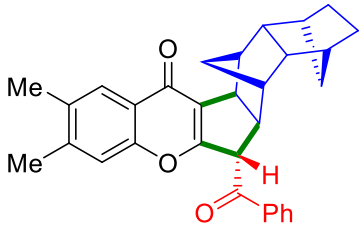

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

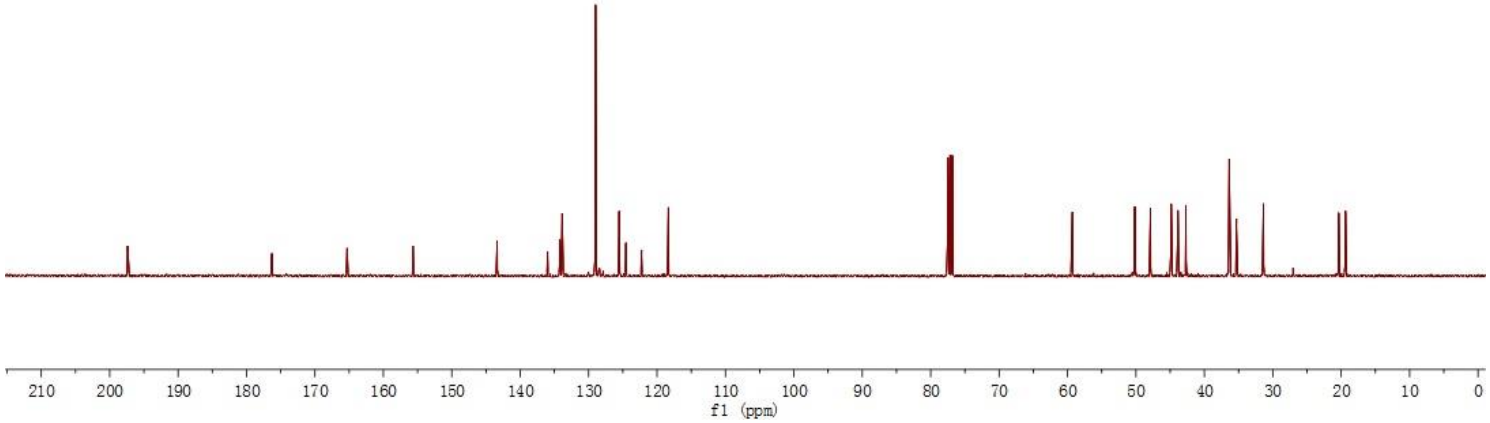

ysy-214-H
8.0431
8.0238
7.9063
7.6514
7.6328
7.6144
7.5472
7.5283
7.5093
7.2457
7.0584
4.4373
3.6412
3.6234
2.7655
2.7564
2.7470
2.7383
2.7220
2.7105
2.3827
2.3045
2.2913
2.0405
2.0315
1.8279
1.8161
1.7603
1.7486
1.4427
1.4120
1.4046
1.3848
1.2127
1.1867
0.9774
0.9331
Scheme 2, 4m
Me
Me
O
O
H
O
Ph
1.96
1.10
1.03
2.07
0.92
1.00
1.04
2.02
1.98
6.01
1.12
1.21
1.14
1.02
3.11
1.07
3.13
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)

ysy-214-C

197.3746
176.2870
165.2999
155.6715
143.3597
135.9908
134.1881
133.8664
128.8944
125.5293
124.5358
122.2608
118.3364
77.4772
77.1603
76.8423
59.2748
50.2070
50.1517
47.8712
44.8538
43.8638
42.6902
36.3705
36.2708
35.3162
31.3847
31.3589
20.3692
19.3789

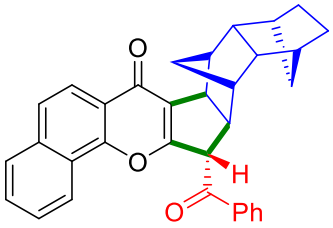
Scheme 2, 4m

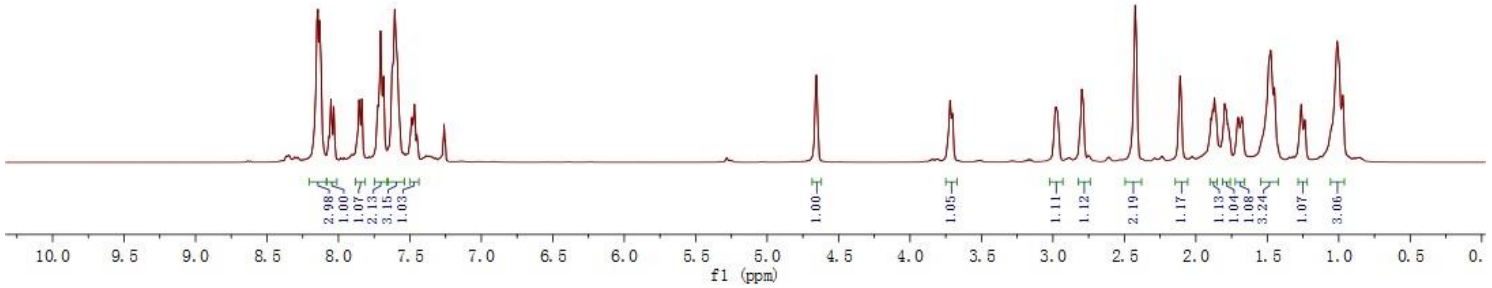


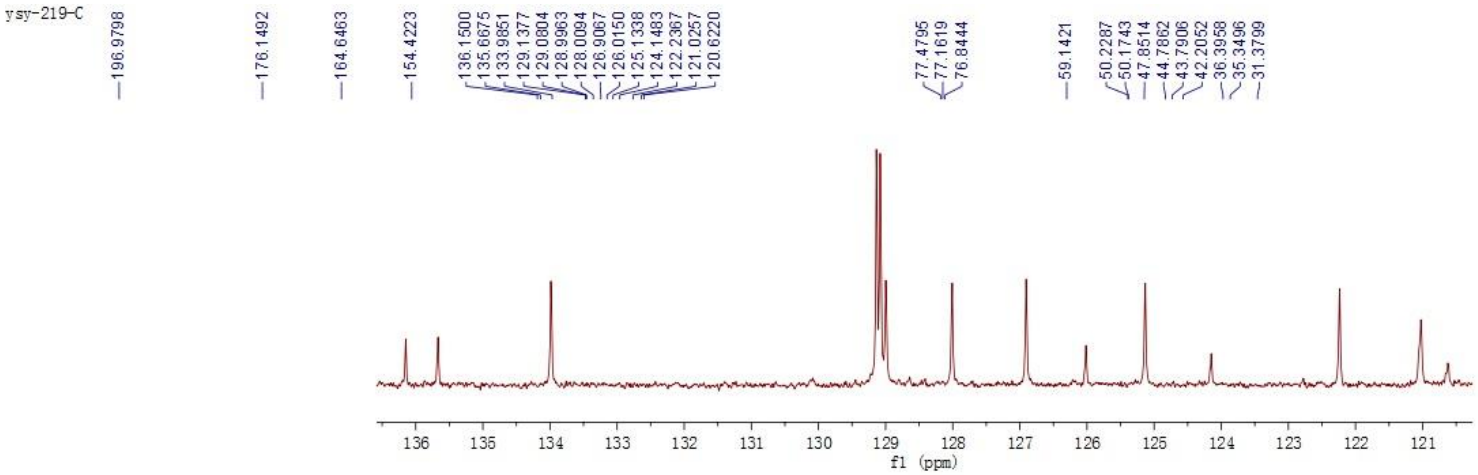



ysy-219-H
8.1709
8.1520
8.1435
8.1314
8.1218
8.0679
8.0518
8.0317
7.8556
7.8359
7.7252
7.7051
7.6839
7.6237
7.6066
7.5973
7.5875
7.4997
7.4873
7.4681
7.4489
7.2610
4.6562
3.7358
3.7198
3.7027
2.9902
2.9816
2.9718
2.9628
2.7983
2.4260
2.1096
1.8823
1.8693
1.8571
1.7994
1.7870
1.7049
1.6769
1.4896
1.4748
1.4489
1.2631
1.2370
1.0272
1.0118
0.9974

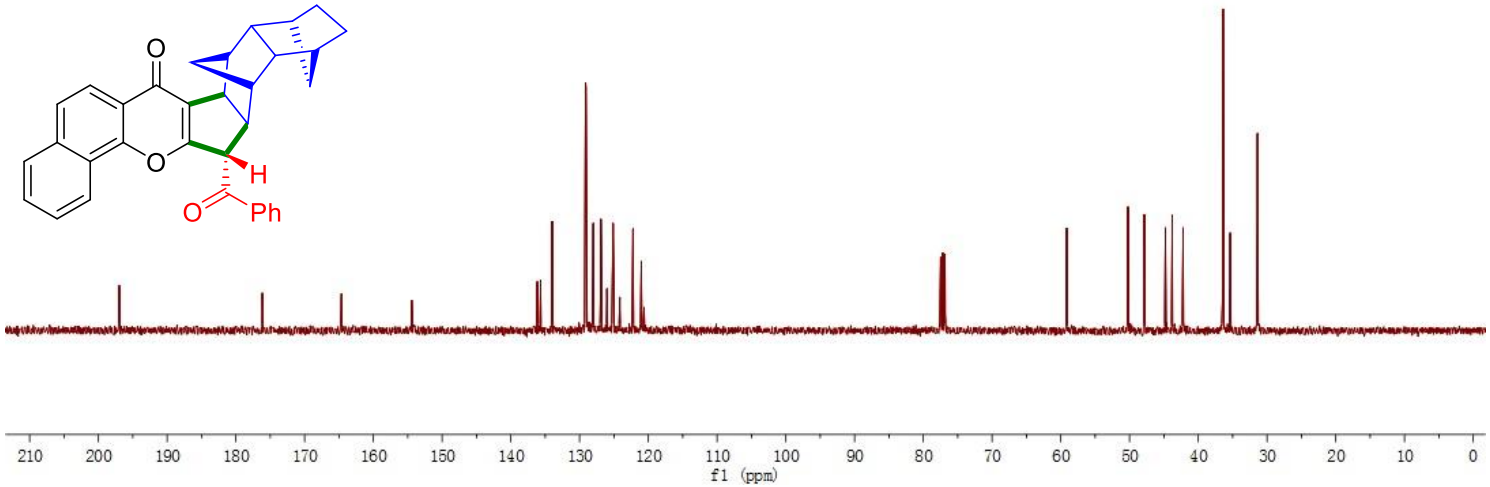
Scheme 2, 4n

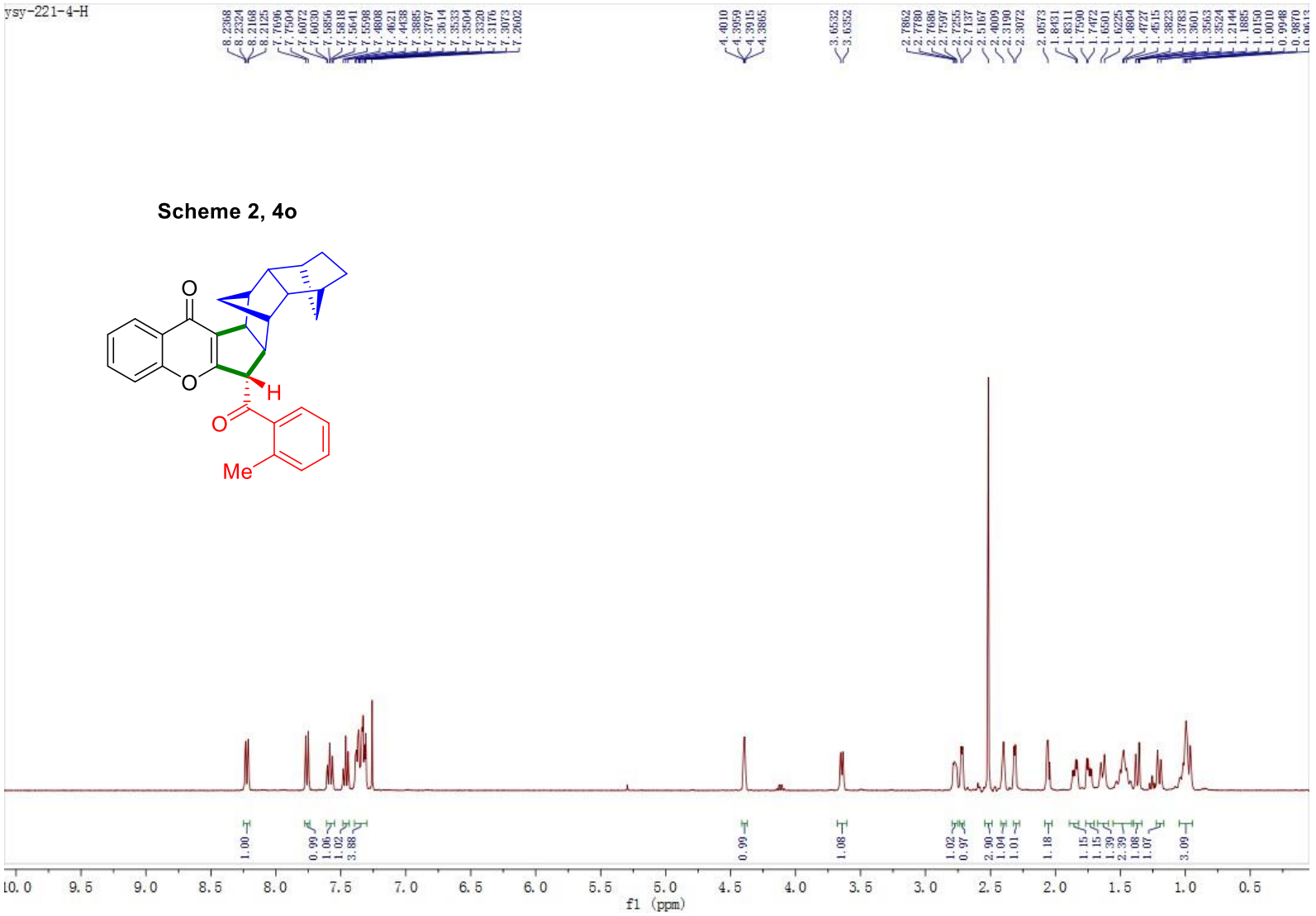

O
O
H
O
Ph

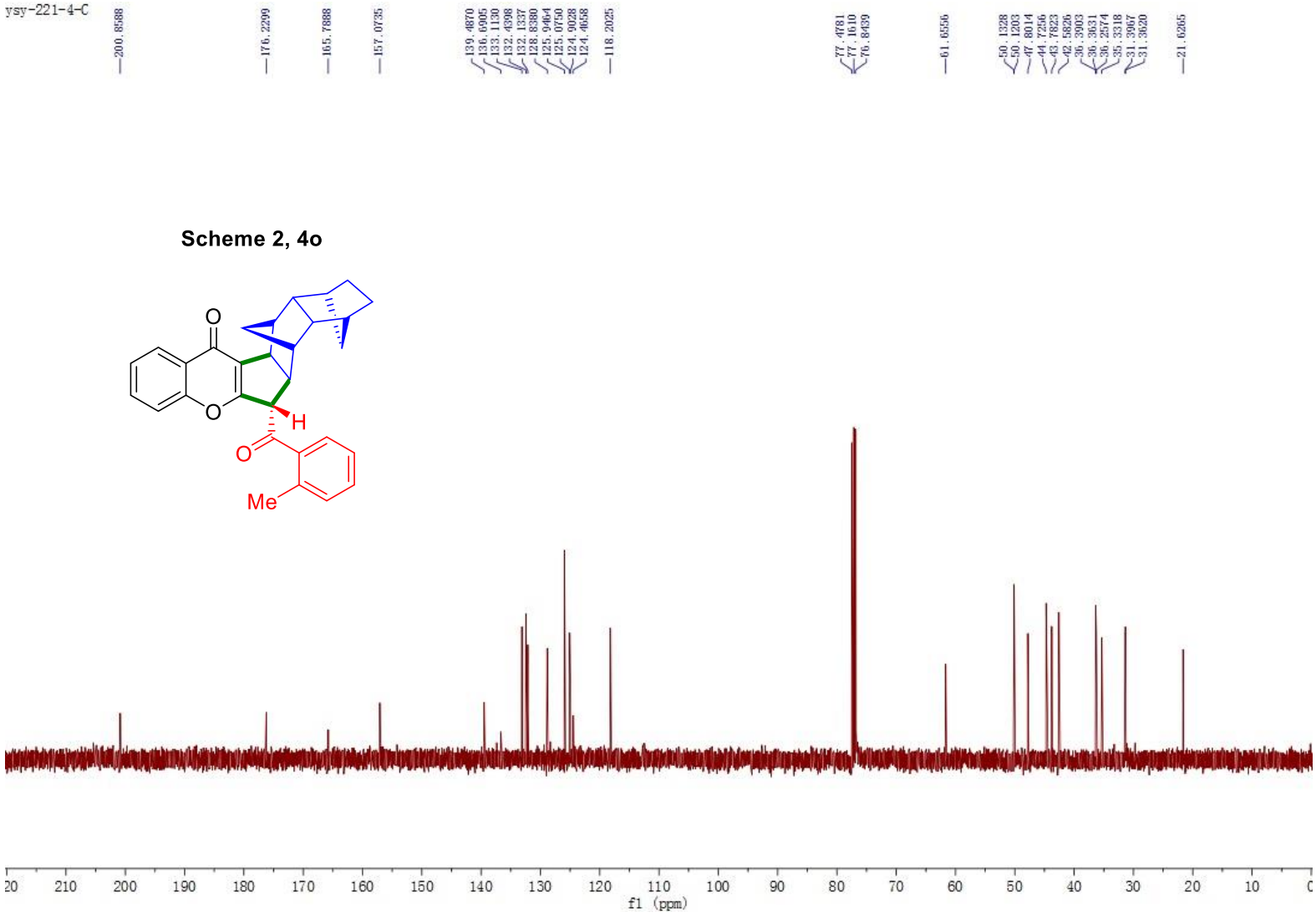

2.98
1.00
1.07
2.13
3.15
1.03
1.00
1.05
1.11
1.12
2.19
1.17
1.13
1.04
1.08
3.24
1.07
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


ysy-219-C
196.9798
176.1492
164.6463
154.4223
136.1500
135.6675
133.9851
129.1377
129.0804
128.9963
128.0094
126.9067
126.0150
125.1338
124.1483
122.2367
121.0257
120.6220
77.4795
77.1619
76.8444
59.1421
50.2287
50.1743
47.8514
44.7862
43.7906
42.2052
36.3958
35.3496
31.3799
136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121
f1 (ppm)

Scheme 2, 4n

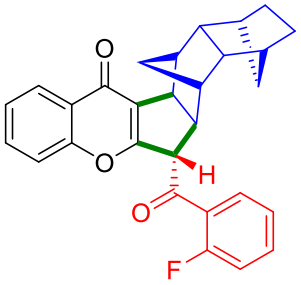

O
O
H
O
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

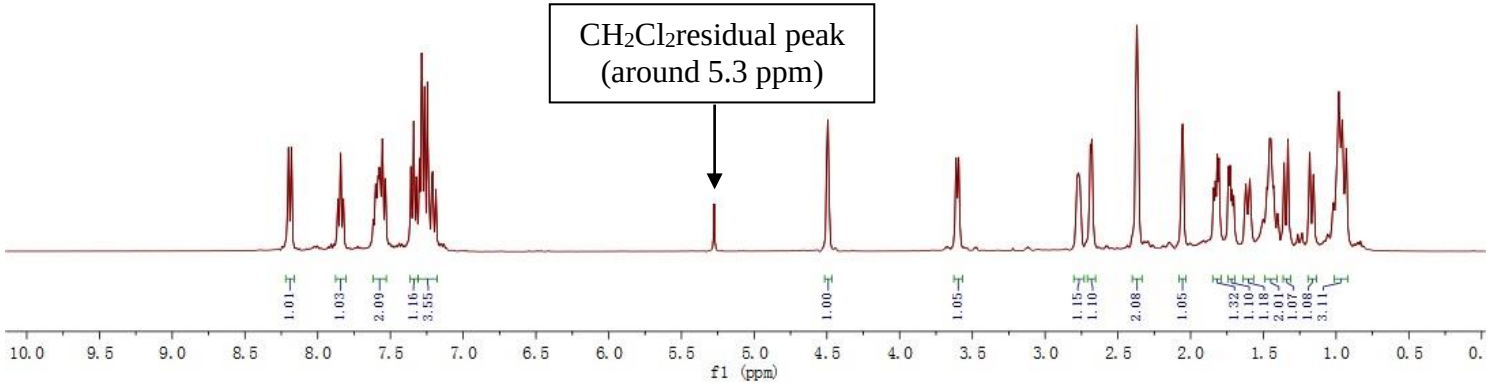

ysy-221-4-H
Scheme 2, 4o
O
O
H
O
Me
f1 (ppm)


ysy-221-4-C
200.8588
176.2299
165.7888
157.0735
139.4870
136.6905
133.1130
132.4398
132.1337
128.8380
125.9464
125.0750
124.9028
124.4658
118.2025
77.4781
77.1610
76.8439
61.6556
50.1328
50.1203
47.8014
44.7256
43.7823
42.5826
36.3903
36.3631
36.2574
35.3318
31.3967
31.3620
21.6265
Scheme 2, 4o
O
O
H
O
Me
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

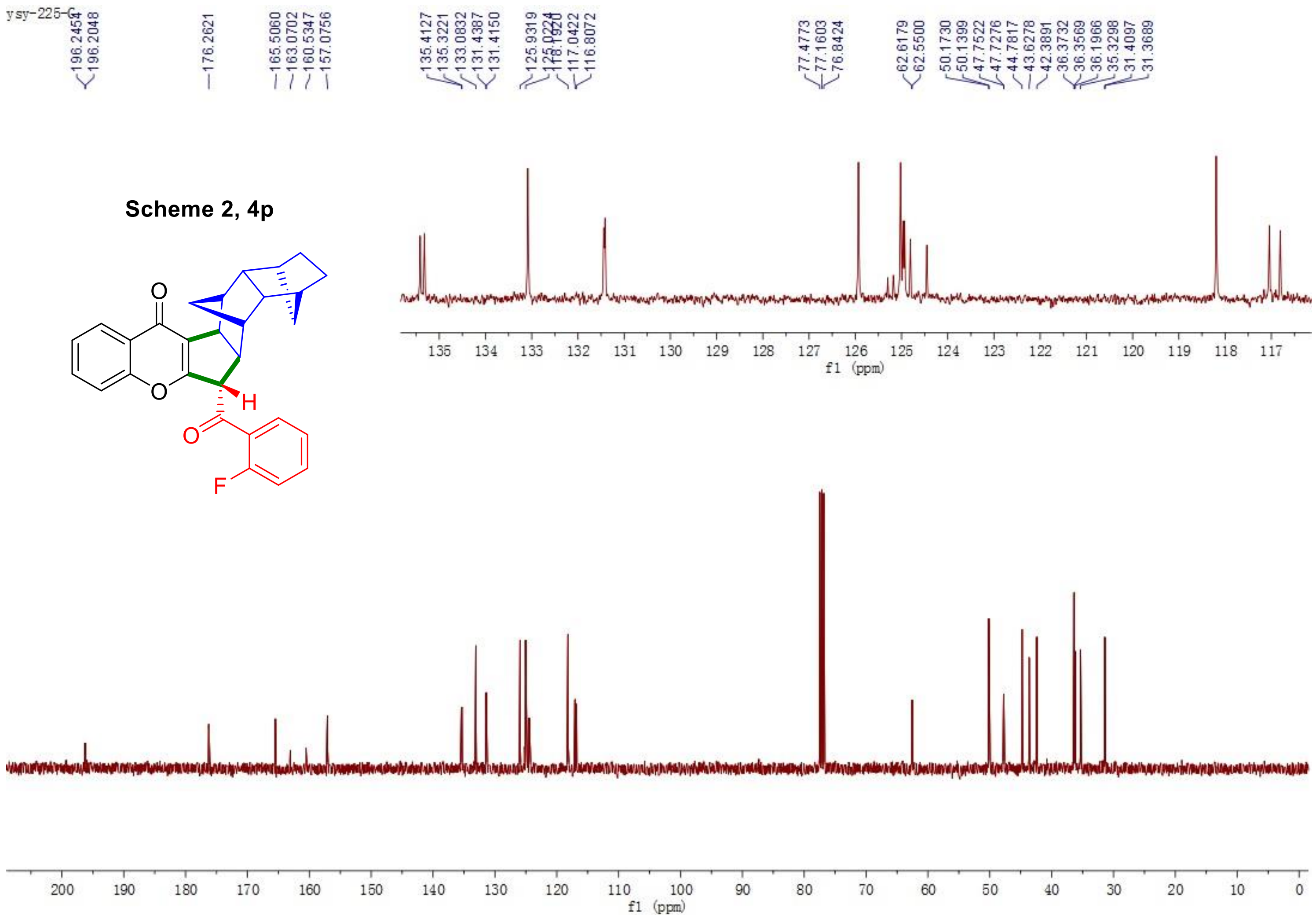

ysy-225-H
8.2008
8.1810
7.8642
7.8596
7.8453
7.8408
7.8263
7.8218
7.6033
7.5895
7.5842
7.5768
7.5713
7.5551
7.5375
7.5334
7.3590
7.3400
7.3211
7.3007
7.2868
7.2817
7.2651
7.2458
7.2371
7.2165
7.2091
3.6119
3.5943
2.7832
2.7747
2.7653
2.7569
2.6899
2.6783
2.3732
2.0526
1.8297
1.8166
1.8047
1.7398
1.7281
1.6212
1.5933
1.4576
1.4476
1.3575
1.3315
1.1817
1.1558
0.9811
0.9581

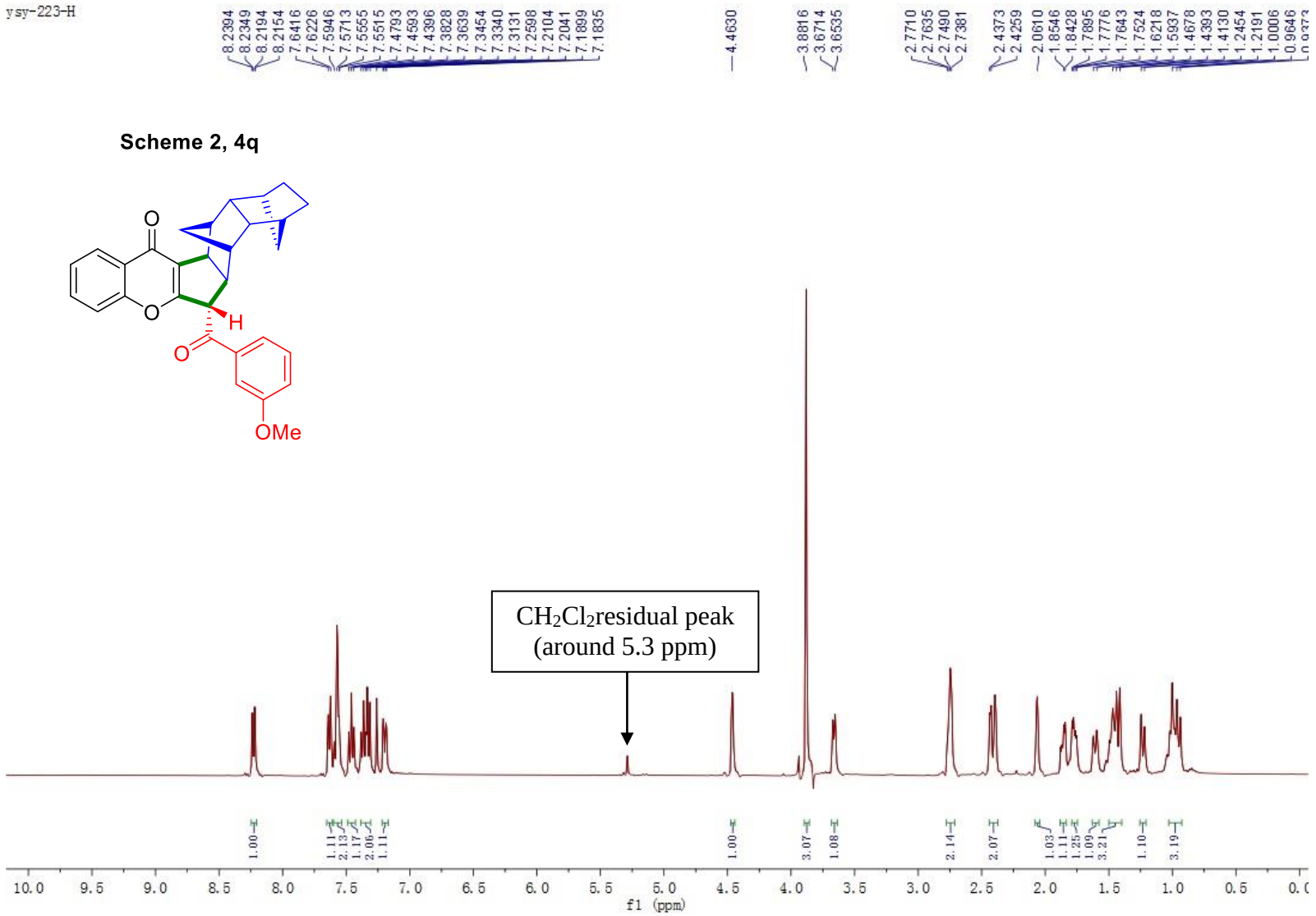
Scheme 2, 4p


O
O
H
O
F


CH2Cl2residual peak
(around 5.3 ppm)
1.01
1.03
2.09
1.16
3.55
1.00
1.05
1.15
1.10
2.08
1.05
1.32
1.10
1.18
2.01
1.07
1.08
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

Scheme 2, 4p

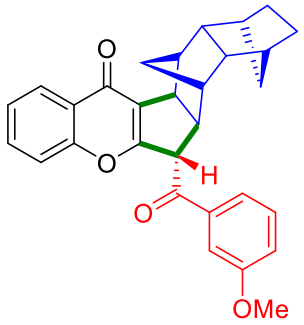

ysy-225-C
196.2454
196.2048
176.2621
165.5060
163.0702
160.5347
157.0756
135.4127
135.3221
133.0832
131.4387
131.4150
125.9319
125.0224
118.1920
117.0422
116.8072
77.4773
77.1603
76.8424
62.6179
62.5500
50.1730
50.1399
47.7522
47.7276
44.7817
43.6278
42.3891
36.3732
36.3569
36.1966
35.3298
31.4097
31.3689
O
O
H
O
F
f1 (ppm)
f1 (ppm)

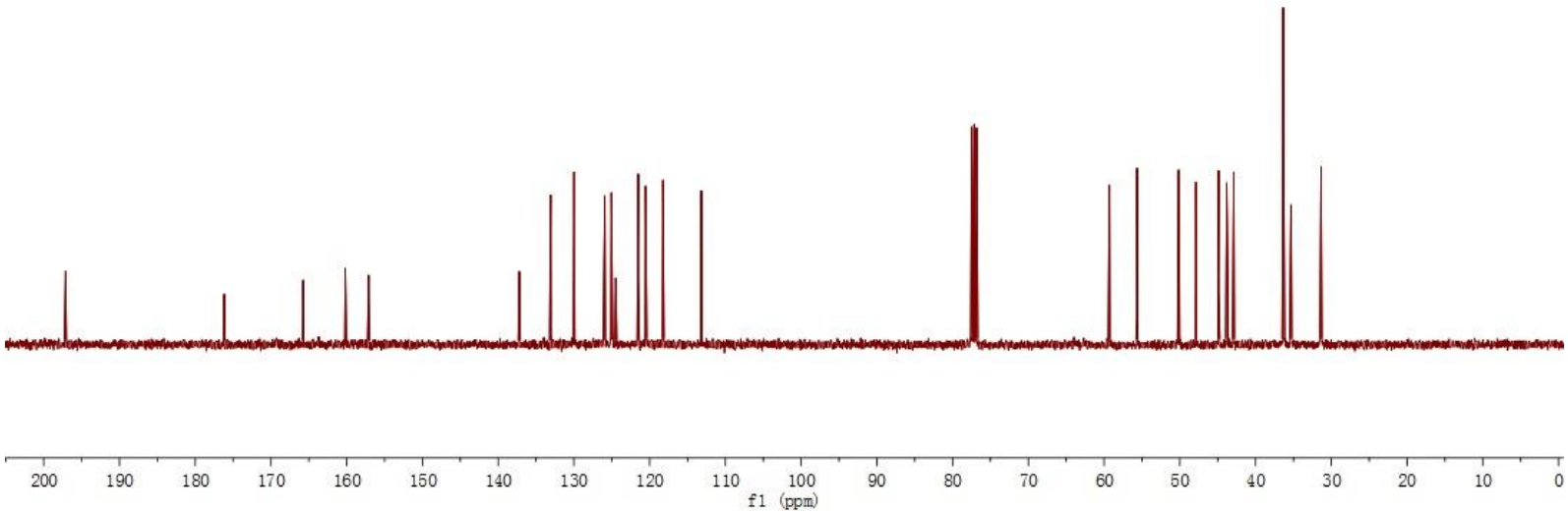

ysy-223-H
8.2394
8.2349
8.2194
8.2154
7.6416
7.6226
7.5946
7.5713
7.5555
7.5515
7.4793
7.4593
7.4396
7.3828
7.3639
7.3454
7.3340
7.3131
7.2598
7.2104
7.2041
7.1899
7.1835
4.4630
3.8816
3.6714
3.6535
2.7710
2.7635
2.7490
2.7381
2.4373
2.4259
2.0610
1.8546
1.8428
1.7895
1.7776
1.7643
1.7524
1.6218
1.5937
1.4678
1.4393
1.4130
1.2454
1.2191
1.0006
0.9646
Scheme 2, 4q
O
O
H
O
OMe
CH2Cl2residual peak
(around 5.3 ppm)
1.00
1.11
2.13
1.17
2.06
1.11
1.00
3.07
1.08
2.14
2.07
1.03
1.11
1.25
1.09
3.21
1.10
3.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

ysy-223-C

197.1176
176.1773
165.7408
160.1816
157.1137
137.2111
133.0840
129.9687
125.9268
125.0453
124.9238
124.4754
121.5153
120.5186
118.2334
113.1755
77.4791
77.1608
76.8421
59.3145
55.6410
50.1757
50.1002
47.8569
43.8181
42.8806
36.3583
36.2640
35.3211
31.3712
31.3495

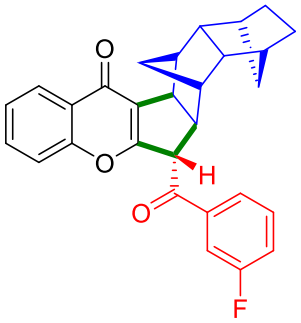
Scheme 2, 4q

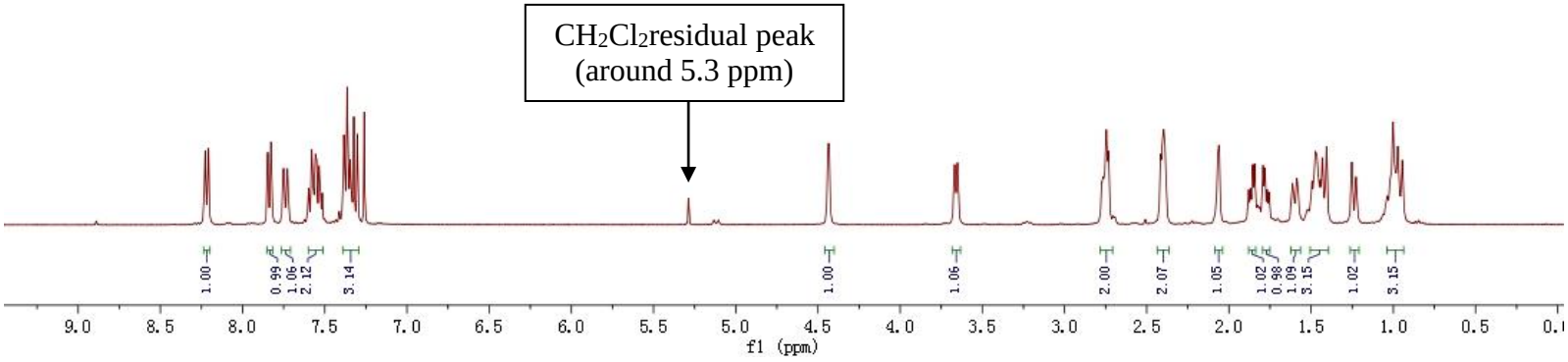


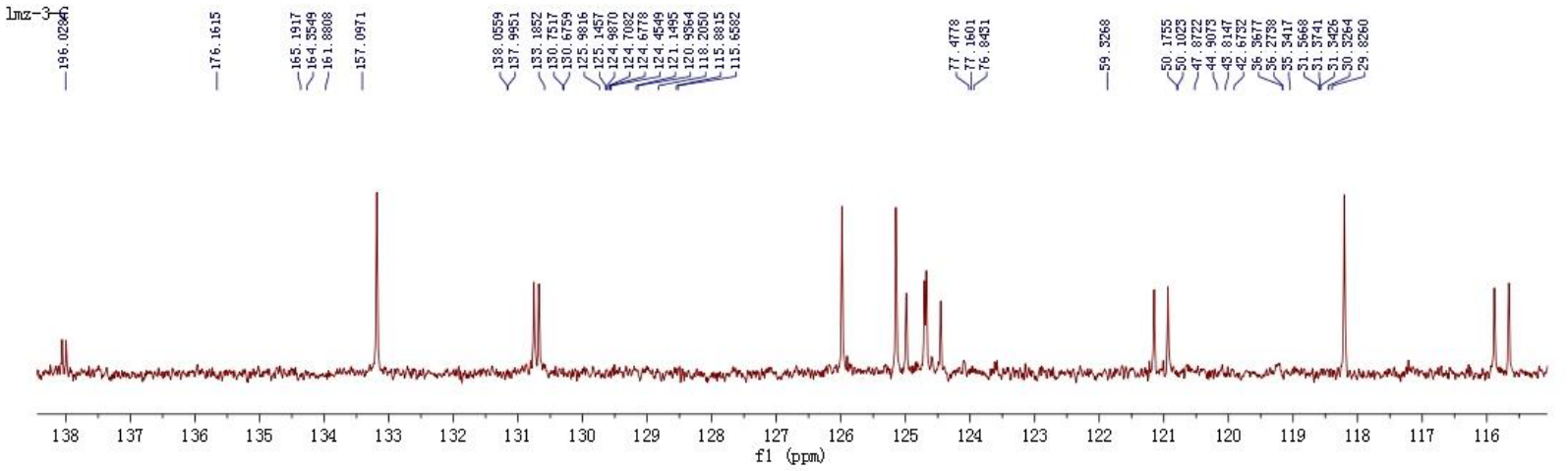



lmz-3-H
8.2270
8.2071
7.8478
7.8283
7.7503
7.7270
7.6003
7.5968
7.5824
7.5793
7.5759
7.5684
7.5561
7.5482
7.5151
7.3856
7.3640
7.3231
7.3021
7.2599
4.4428
4.4357
4.4290
3.6685
3.6507
2.7749
2.7660
2.7573
2.7453
2.7323
2.4161
2.4038
2.3947
2.3859
2.0599
1.8803
1.8686
1.8554
1.8435
1.7929
1.7812
1.7677
1.7560
1.6131
1.5857
1.4946
1.4705
1.4445
1.4320
1.4065
1.2524
1.2265
1.0428
1.0353
1.0194
1.0014
0.9727
0.9452

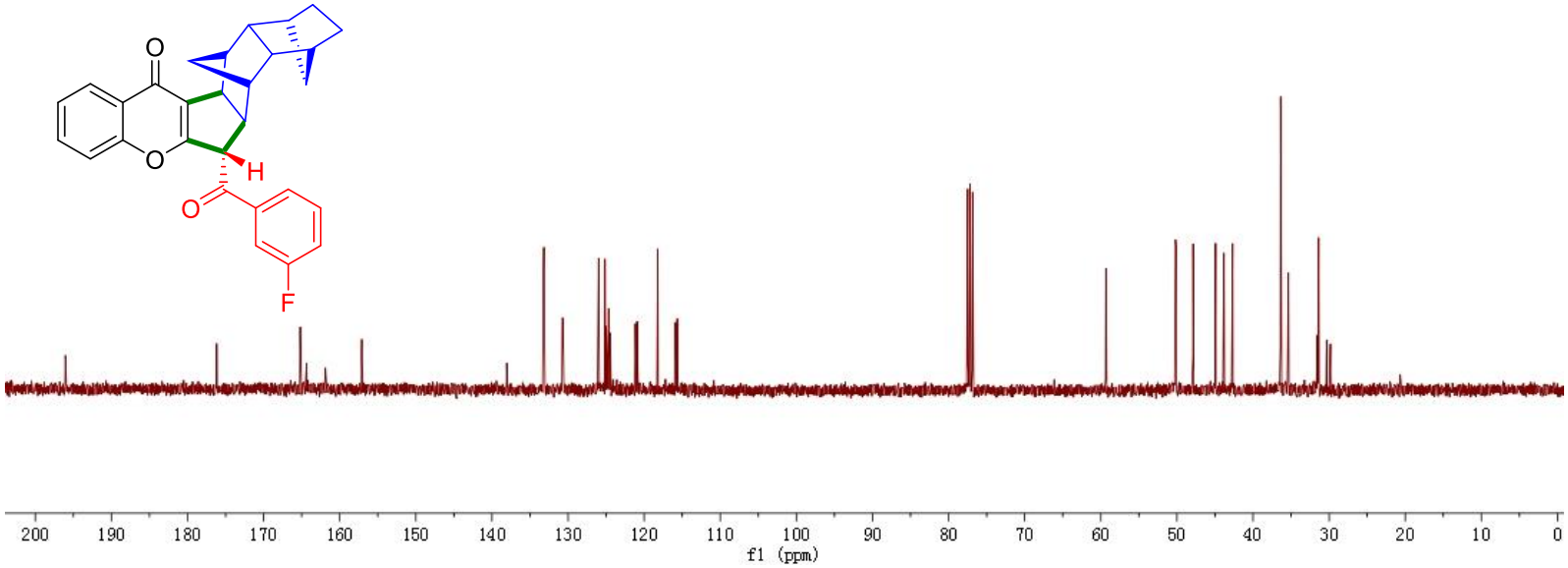
Scheme 2, 4r


O
O
H
O
F


CH2Cl2residual peak
(around 5.3 ppm)
1.00
0.99
1.06
2.12
3.14
1.00
1.06
2.00
2.07
1.05
1.02
0.98
1.09
3.15
1.02
3.15
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

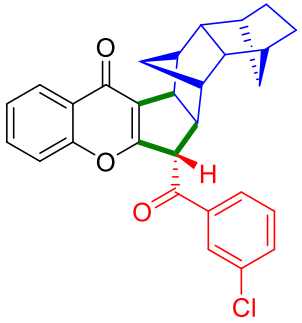

lmz-3-c
196.0284
176.1615
165.1917
164.3549
161.8808
157.0971
138.0559
137.9951
133.1852
130.7517
130.6759
125.9816
125.1457
124.9870
124.7082
124.6778
124.4549
121.1495
120.9564
118.2050
115.8815
115.6582
77.4778
77.1601
76.8431
59.3268
50.1755
50.1023
47.8722
44.9073
43.8147
42.6732
36.3677
36.2738
35.3417
31.5668
31.3741
31.1426
30.3264
29.8260
138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116
f1 (ppm)

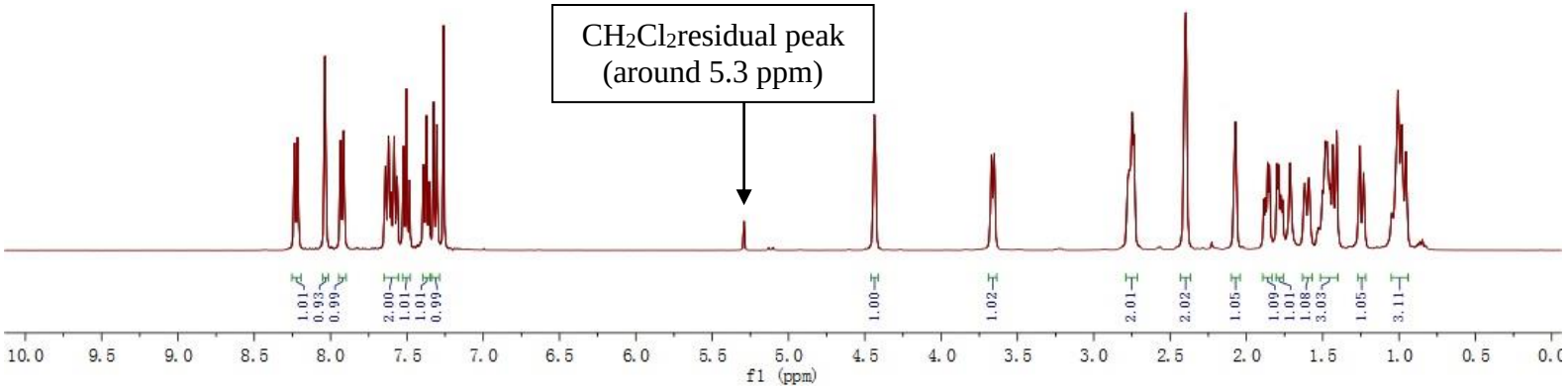
Scheme 2, 4r

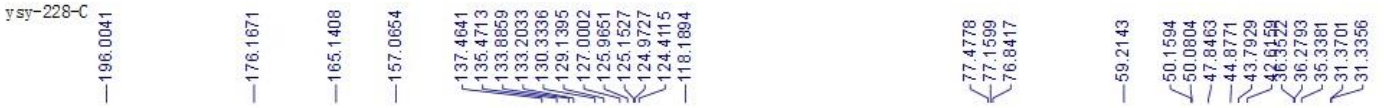

O
O
H
O
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


ysy-228-H
8.2376
8.2333
8.2175
8.2132
8.0368
7.9342
7.9147
7.6432
7.6380
7.6234
7.6183
7.6056
7.6013
7.5879
7.5839
7.5801
7.5665
7.5622
7.5225
7.5028
7.4830
7.3911
7.3722
7.3534
7.3245
7.3035
7.2594
4.4432
4.4382
4.4341
4.4292
3.6703
3.6526
2.7808
2.7721
2.7631
2.7488
2.7356
2.3951
2.0689
1.8860
1.8610
1.8492
1.7988
1.7871
1.6185
1.5906
1.4819
1.4722
1.4342
1.4090
1.2581
1.2321
1.0244
1.0079
0.9814

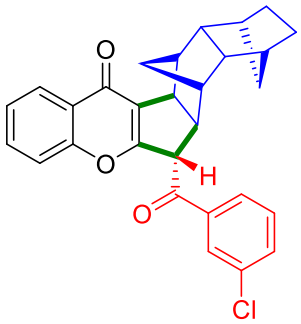
Scheme 2, 4s

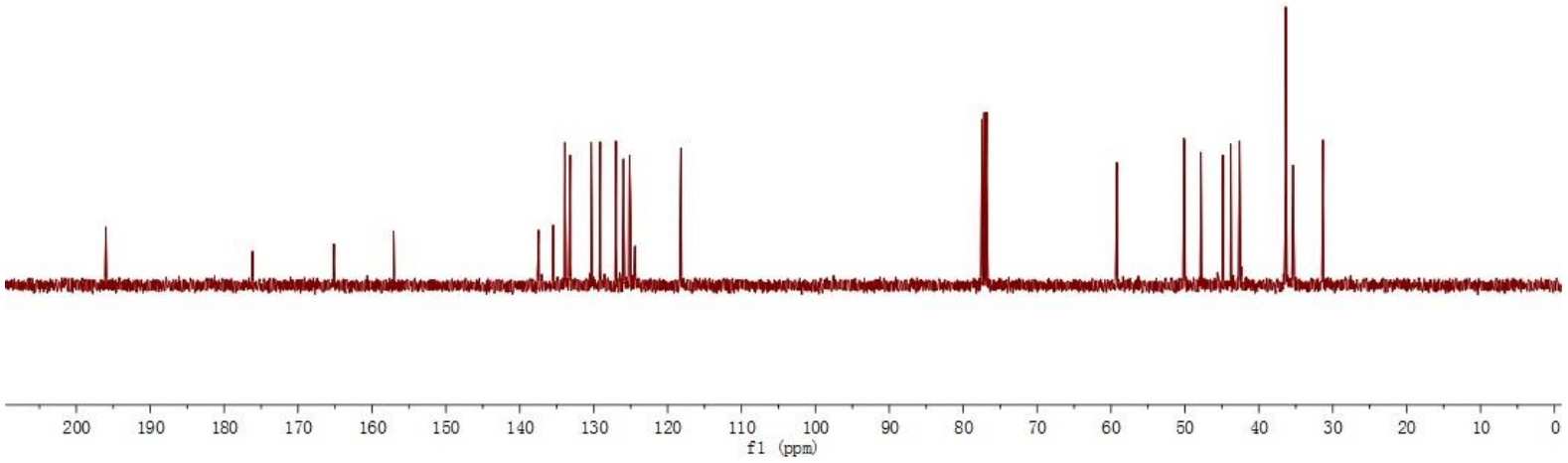

O
O
H
O
Cl

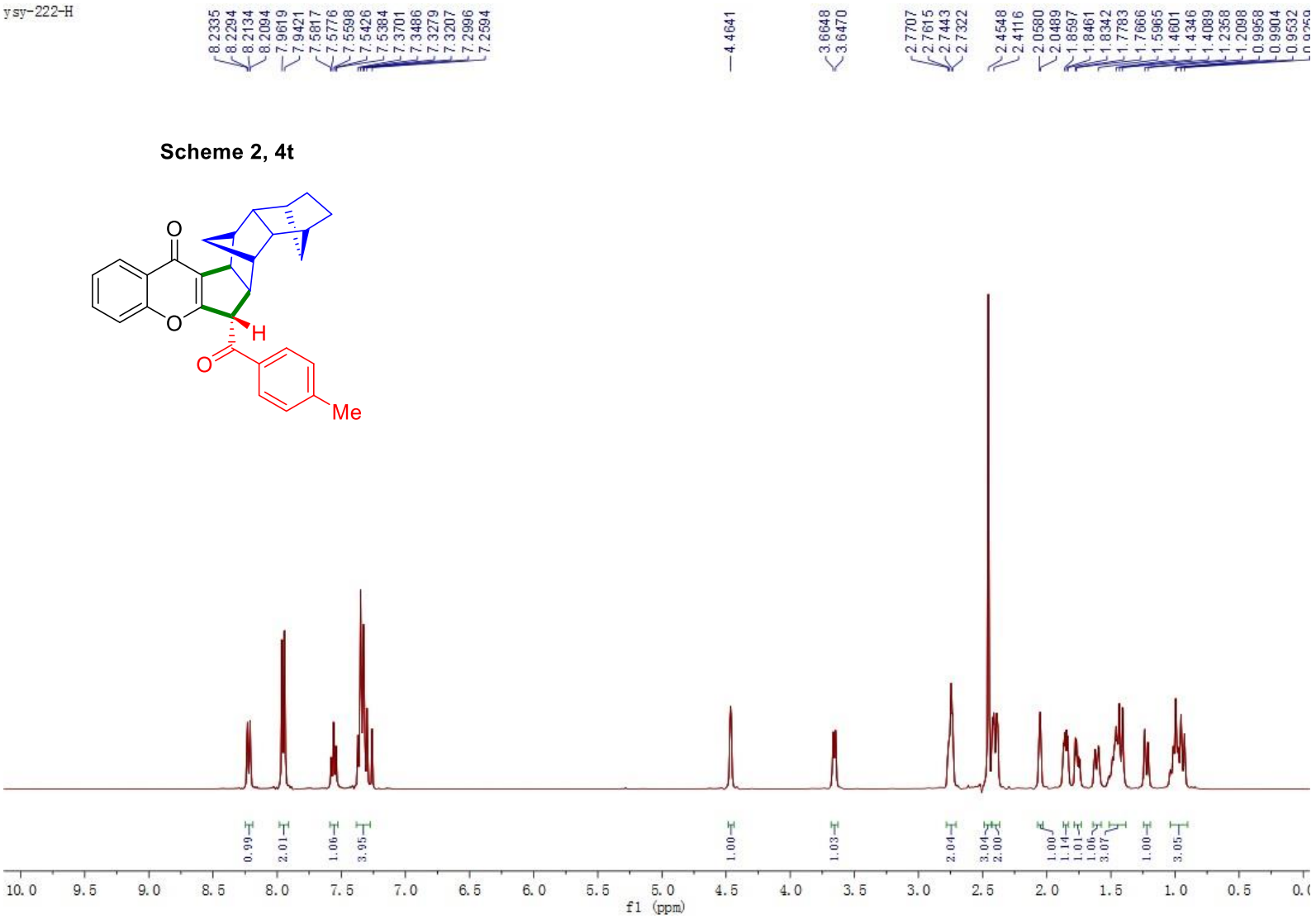

CH2Cl2residual peak
(around 5.3 ppm)
1.01
0.93
0.99
2.00
1.01
1.01
0.99
1.00
1.02
2.01
2.02
1.05
1.09
1.01
1.08
3.03
1.05
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


ysy-228-C
196.0041
176.1671
165.1408
157.0654
137.4641
135.4713
133.8859
133.2033
130.3336
129.1395
127.0002
125.9651
125.1527
124.9727
124.4115
118.1894
77.4778
77.1599
76.8417
59.2143
50.1594
50.0804
47.8463
44.8771
43.7929
42.6159
36.3522
36.2793
35.3381
31.3701
31.3356

Scheme 2, 4s


O
O
H
O
Cl


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

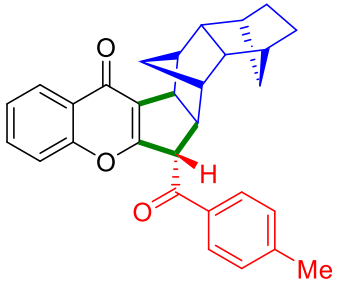

ysy-222-H
8.2335
8.2294
8.2134
8.2094
7.9619
7.9421
7.5817
7.5776
7.5598
7.5426
7.5384
7.3701
7.3486
7.3279
7.3207
7.2996
7.2594
4.4641
3.6648
3.6470
2.7707
2.7615
2.7443
2.7322
2.4548
2.4116
2.0580
2.0489
1.8597
1.8461
1.8342
1.7783
1.7666
1.5965
1.4601
1.4346
1.4089
1.2358
1.2098
0.9958
0.9904
0.9532
O
O
H
O
Me
0.99
2.01
1.06
3.95
1.00
1.03
2.04
3.04
2.00
1.00
1.14
1.01
1.06
3.07
1.00
3.05
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)

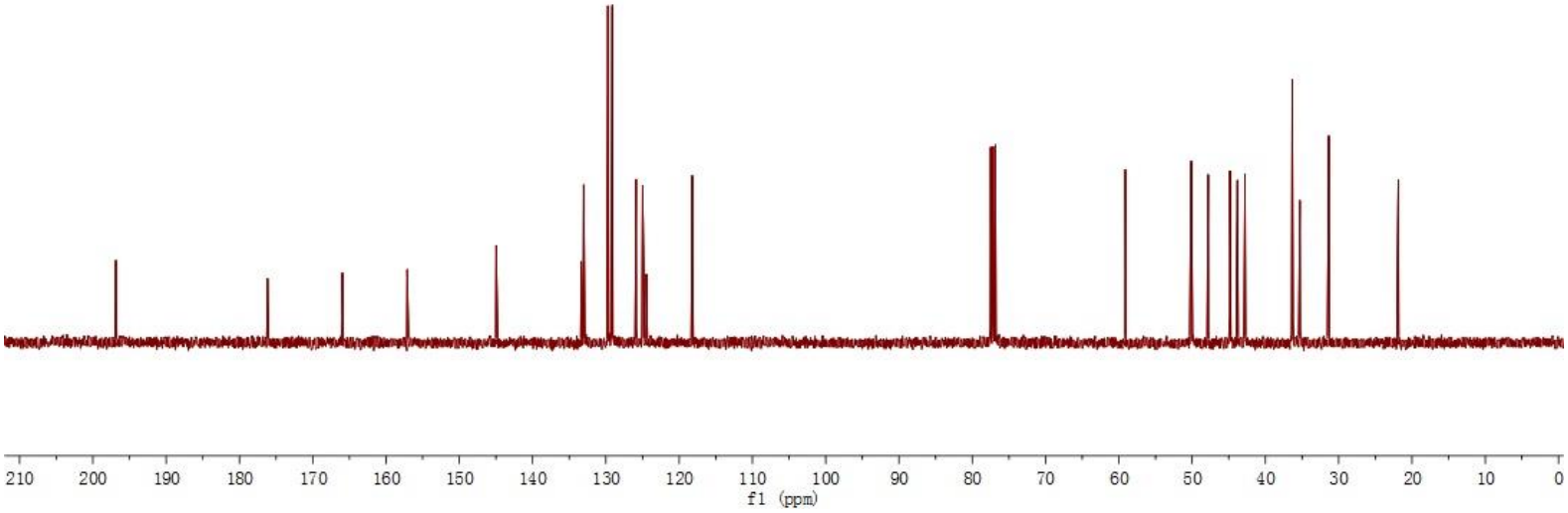
Scheme 2, 4t

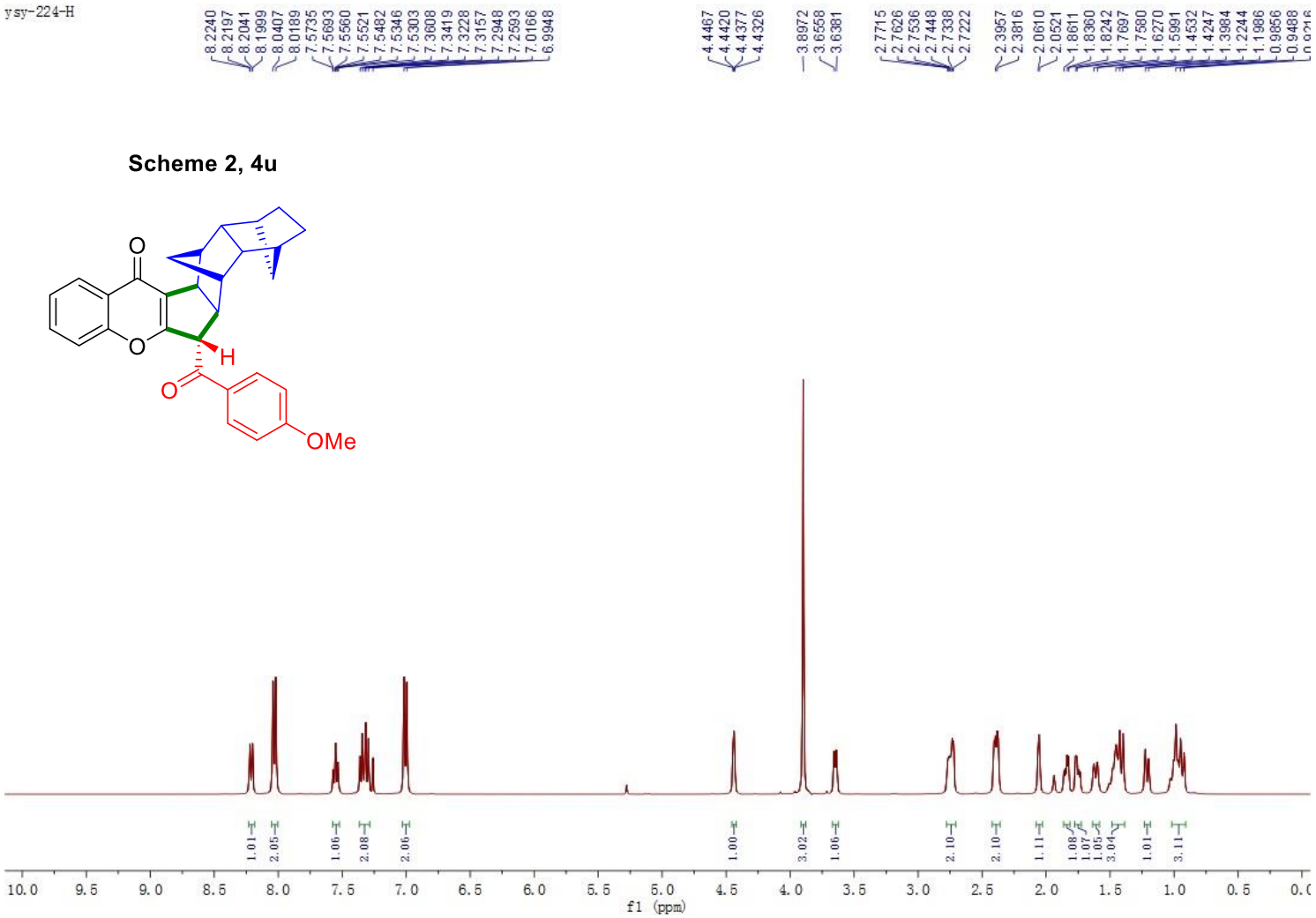
ysy-222-C

196.8480
176.1729
165.9532
157.0959
144.9582
133.3512
133.0184
129.7141
129.1222
125.8840
124.9890
124.8555
124.4670
118.2238
77.4778
77.1600
76.8427
59.0987
50.1635
50.1013
47.8127
44.8293
43.8096
42.7844
36.3445
36.2652
35.3002
31.3453
21.8660

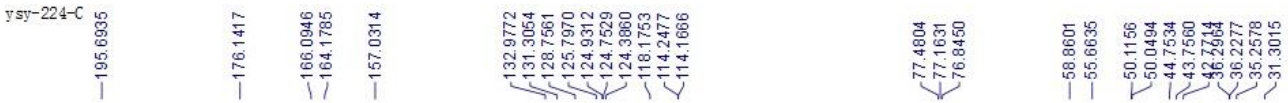
Scheme 2, 4t



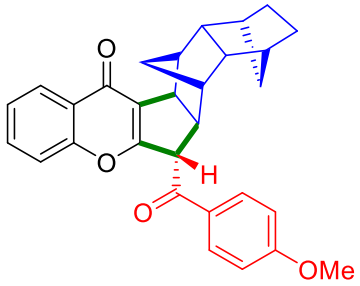


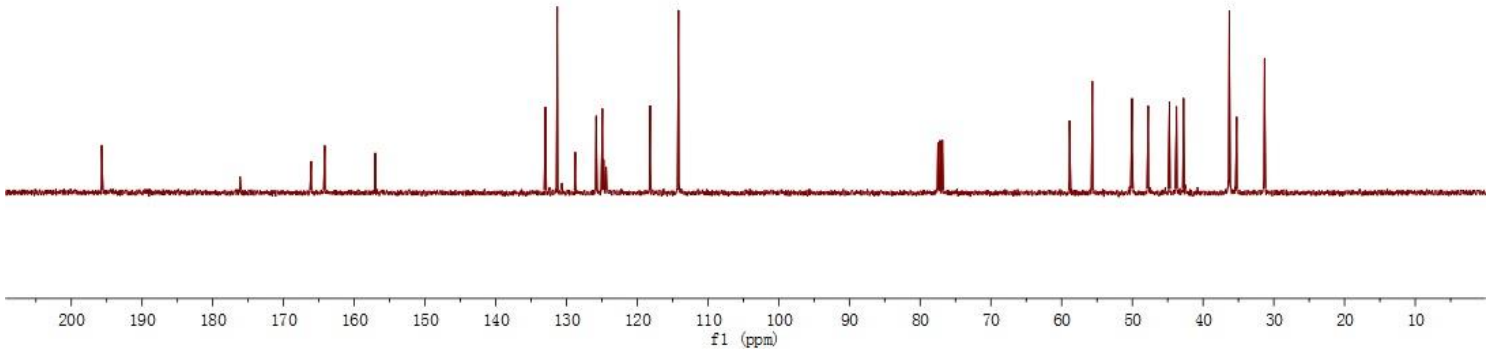

ysy-224-H
8.2240
8.2197
8.2041
8.1999
8.0407
8.0189
7.5735
7.5693
7.5560
7.5521
7.5482
7.5346
7.5303
7.3608
7.3419
7.3228
7.3157
7.2948
7.2593
7.0166
6.9948
4.4467
4.4420
4.4377
4.4326
3.8972
3.6558
3.6381
2.7715
2.7626
2.7536
2.7448
2.7338
2.7222
2.3957
2.3816
2.0610
2.0521
1.8611
1.8360
1.8242
1.7697
1.7580
1.6270
1.5991
1.4532
1.4247
1.3984
1.2244
1.1986
0.9856
0.9488
O
O
H
O
OMe
1.01
2.05
1.06
2.08
2.06
1.00
3.02
1.06
2.10
2.10
1.11
1.08
1.07
1.05
3.04
1.01
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

Scheme 2, 4u

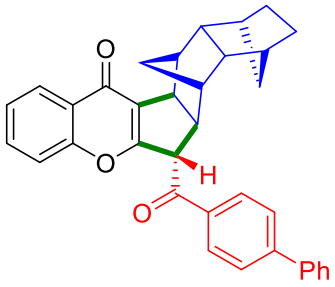

ysy-224-C
195.6935
176.1417
166.0946
164.1785
157.0314
132.9772
131.3054
128.7561
125.7970
124.9312
124.7529
124.3860
118.1753
114.2477
114.1666
77.4804
77.1631
76.8450
58.8601
55.6635
50.1156
50.0494
44.7534
43.7560
36.2277
35.2578
31.3015

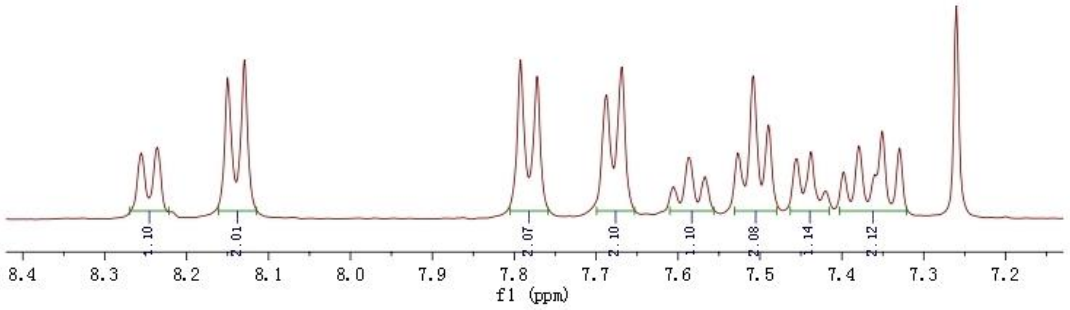
Scheme 2, 4u

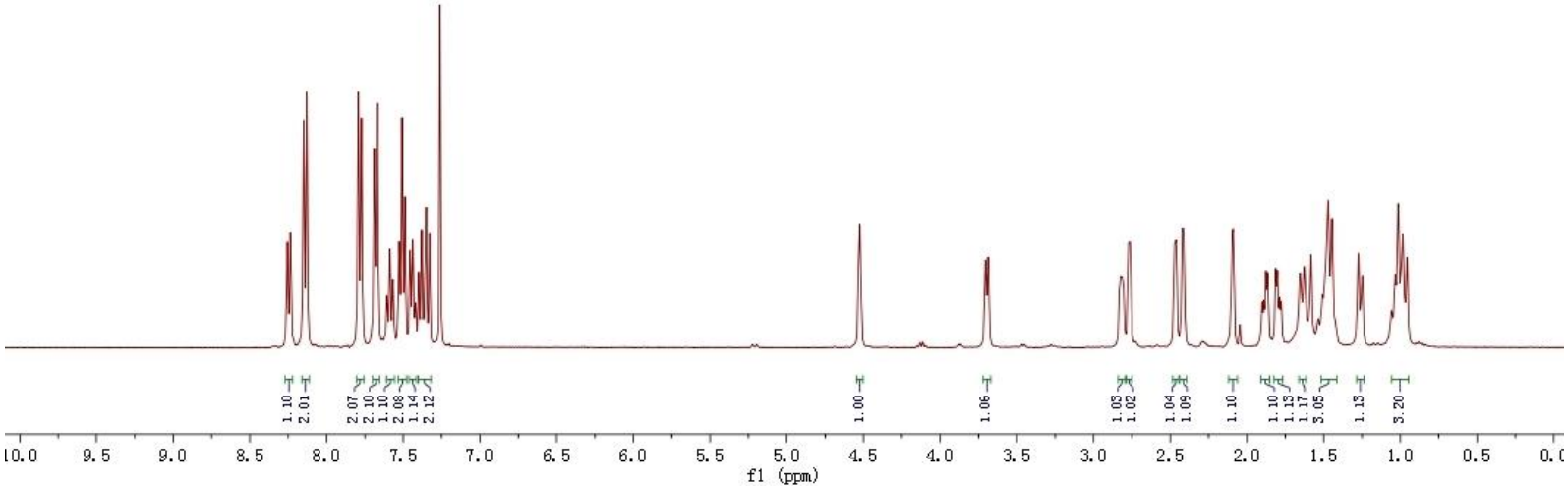

O
O
H
O
OMe

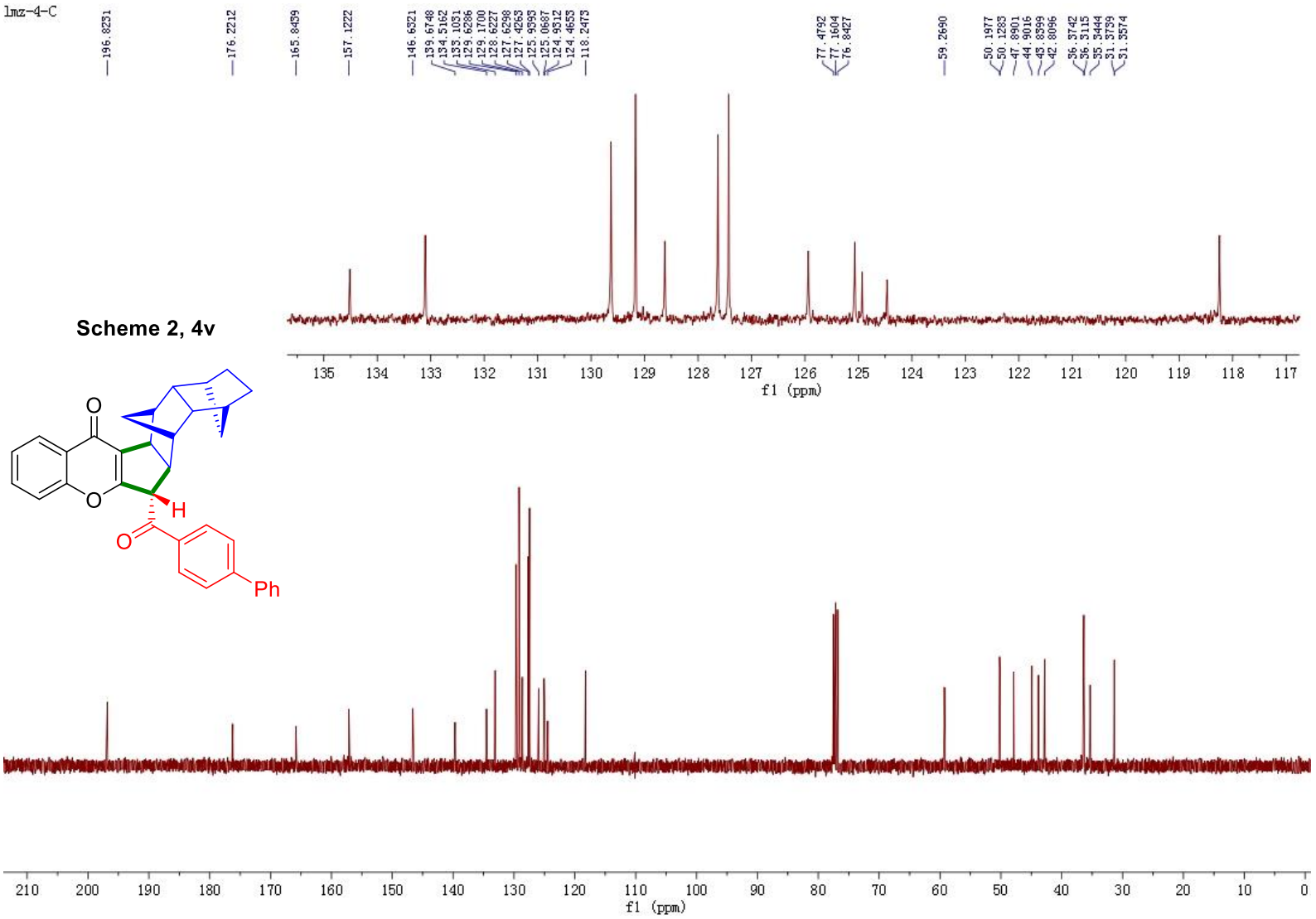

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Scheme 2, 4v





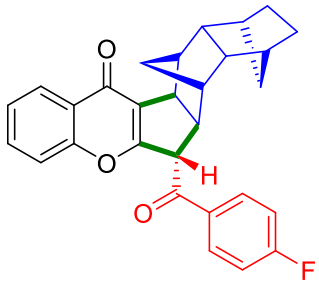


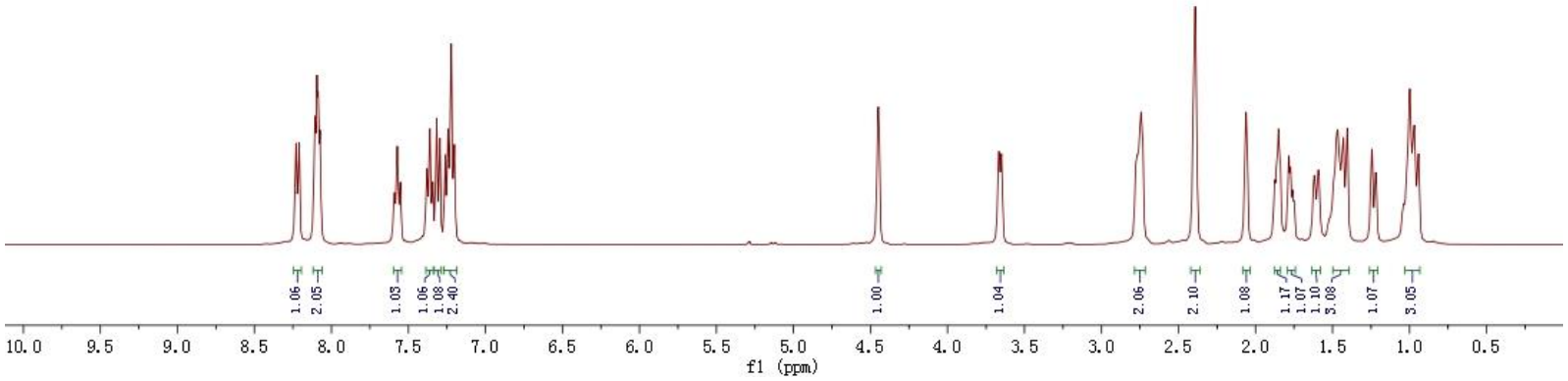

lmz-4-C
196.8231
176.2212
165.8459
157.1222
146.6321
139.6748
134.5162
133.1031
129.6286
129.1700
128.6227
127.6298
127.4263
125.9993
125.0687
124.9312
124.4653
118.2473
77.4792
77.1604
76.8427
59.2690
50.1977
50.1283
47.8901
44.9016
43.8399
42.8096
36.5742
36.3115
35.3444
31.3799
31.3574
f1 (ppm)
O
O
H
O
Ph

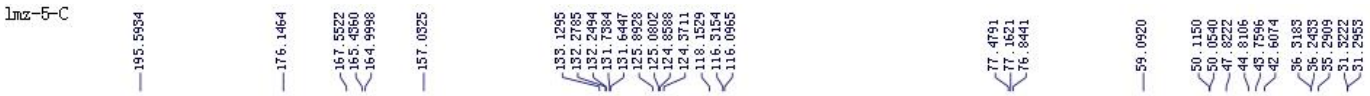
Scheme 2, 4v


lmz-5-H
8.2295
8.2102
8.1075
8.0941
8.0854
8.0733
7.5914
7.5721
7.5523
7.3792
7.3606
7.3414
7.3165
7.2952
7.2607
7.2428
7.2296
7.2217
7.2007
4.4474
3.6664
3.6490
2.7783
2.7652
2.7443
2.7309
2.3905
2.0644
1.8757
1.8626
1.8505
1.8389
1.7844
1.7726
1.7589
1.7482
1.6192
1.5913
1.4926
1.4685
1.4593
1.4293
1.4047
1.2453
1.2193
1.0155
0.9979
0.9779
0.9680

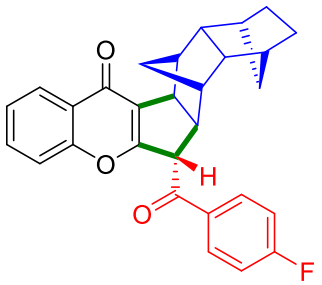
Scheme 2, 4w

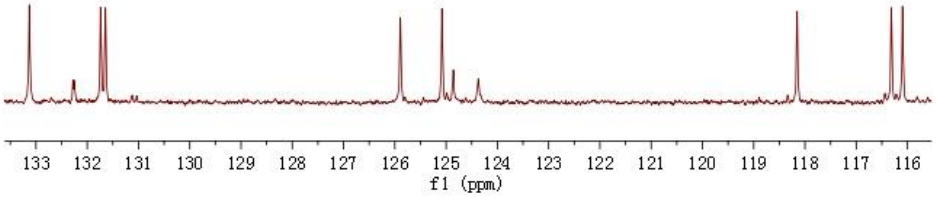

O
O
H
O
F

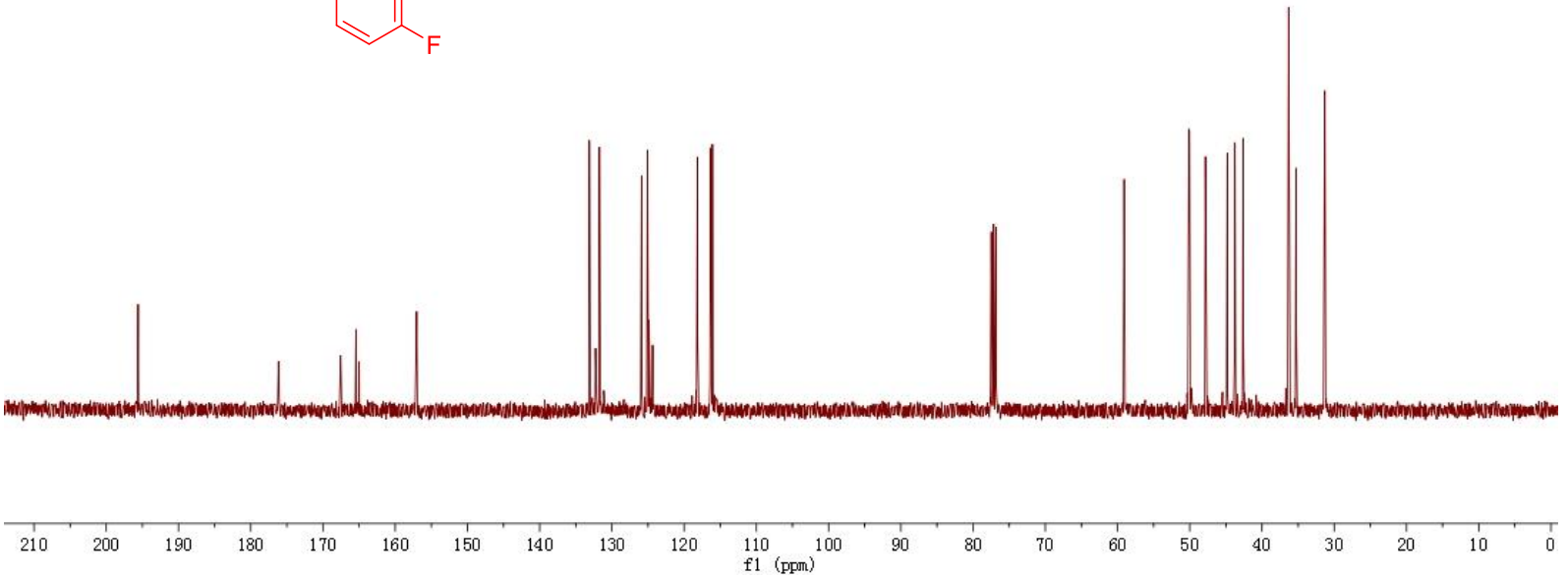

1.06
2.05
1.03
1.06
1.08
2.40
1.00
1.04
2.06
2.10
1.08
1.17
1.07
1.10
3.08
1.07
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


lmz-5-C
195.5934
176.1464
167.5522
165.4560
164.9998
157.0325
133.1295
132.2785
132.2494
131.7384
131.6447
125.8928
125.0802
124.8588
124.3711
118.1529
116.3154
116.0965
77.4791
77.1621
76.8441
59.0920
50.1150
50.0540
47.8222
44.8106
43.7596
42.6074
36.3183
36.2493
35.2909
31.3222
31.2953

Scheme 2, 4w

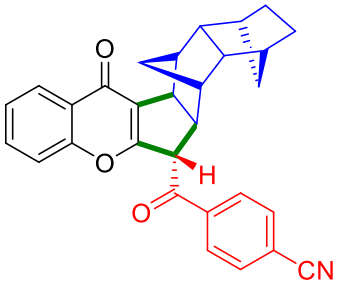

O
O
H
O
F

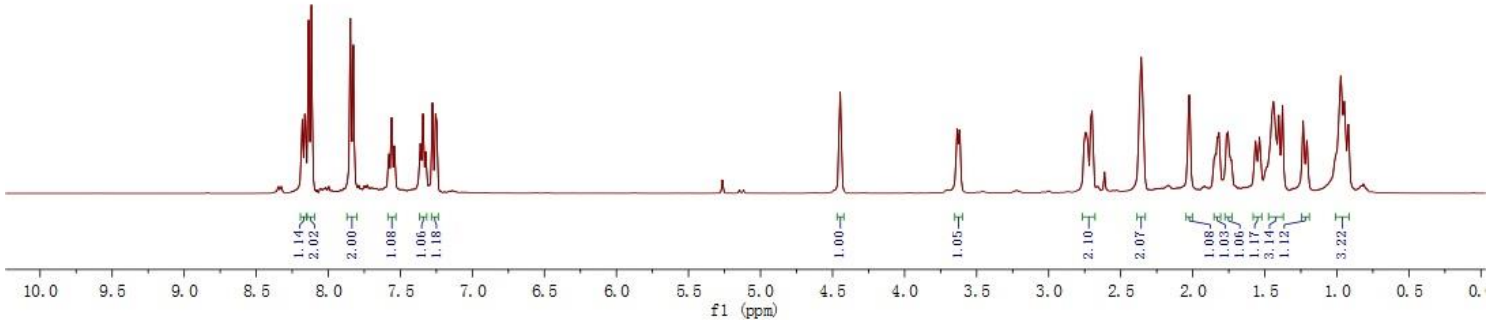

133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116
f1 (ppm)


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


ysy-232-H
8.1842
8.1795
8.1639
8.1593
8.1367
8.1166
7.8461
7.8259
7.5820
7.5774
7.5601
7.5429
7.5383
7.3616
7.3426
7.3232
7.2770
7.2558
7.2459
4.4538
4.4473
4.4411
3.6360
3.6183
2.7475
2.7370
2.7282
2.7075
2.6968
2.3714
2.3580
2.0214
1.8287
1.8170
1.7671
1.7557
1.5647
1.5365
1.4485
1.4379
1.4028
1.3774
1.2340
1.2080
0.9737
0.9474

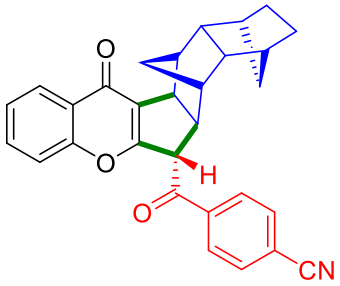
Scheme 2, 4x

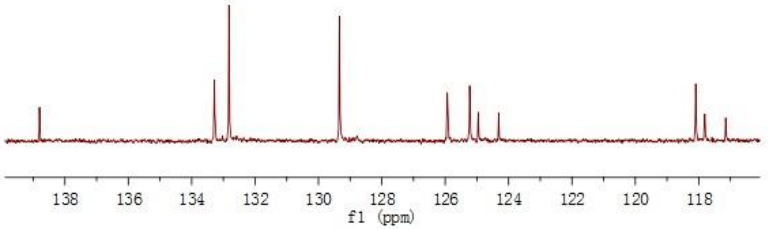

O
O
H
O
CN

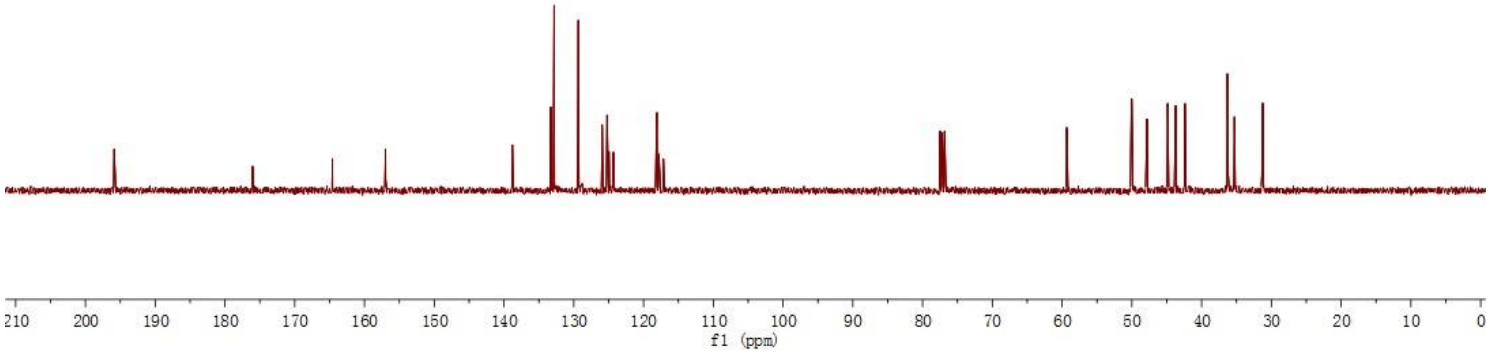

1.14
2.02
2.00
1.08
1.06
1.18
1.00
1.05
2.10
2.07
1.08
1.03
1.06
1.17
3.14
1.12
3.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


ysy-232-C
195.8805
176.0411
164.6074
156.9761
138.8028
133.2817
132.8233
129.3385
125.9330
117.8088
117.1493
77.4806
77.1620
76.8466
59.3209
50.0595
50.0023
47.8293
44.8605
43.7198
42.3954
36.3053
36.2894
36.2183
35.2871
31.2865
31.2507

Scheme 2, 4x

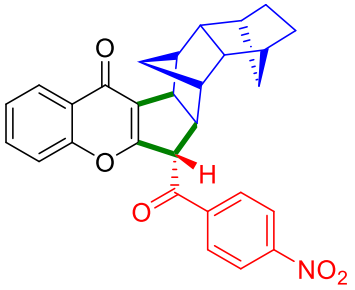

O
O
H
O
CN

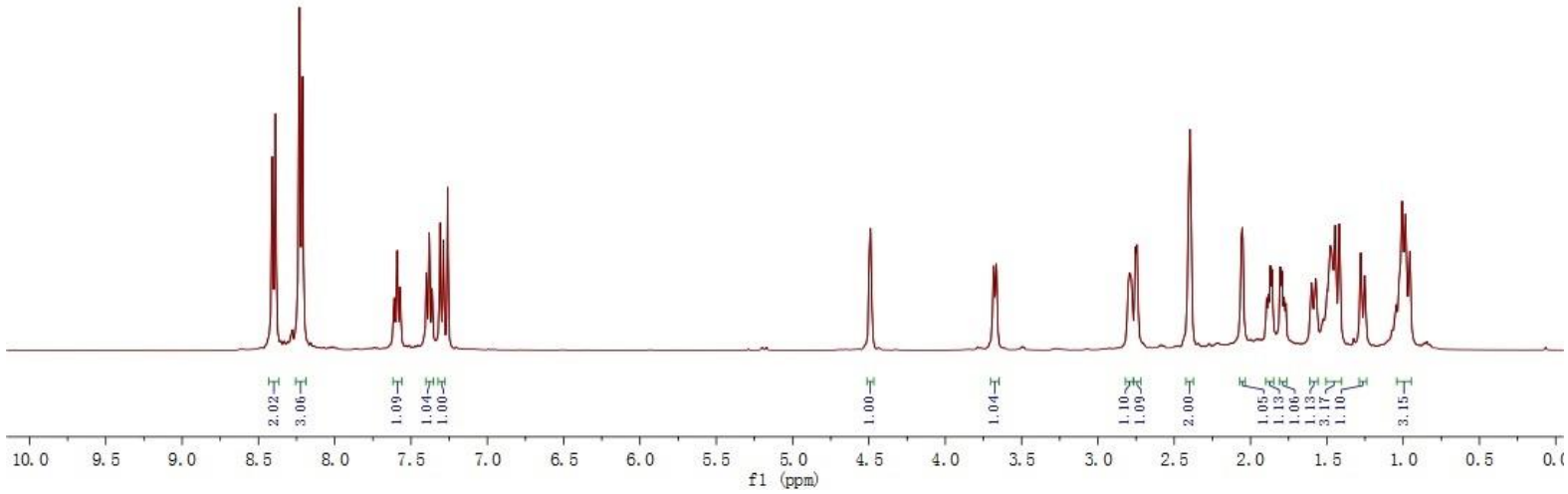

138
136
134
132
130
128
126
124
122
120
118
f1 (ppm)


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


ysy-233-H
8.4094
8.3883
8.2321
8.2156
8.2105
7.6090
7.5909
7.5727
7.3994
7.3806
7.3617
7.3090
7.2880
7.2596
4.4972
4.4903
4.4839
3.6835
3.6656
2.8036
2.7946
2.7850
2.7759
2.7542
2.7428
2.4085
2.3966
2.0801
2.0510
1.8950
1.8898
1.8380
1.8046
1.7928
1.6002
1.5725
1.4791
1.4690
1.4453
1.4177
1.2779
1.2518
1.0241
1.0064
0.9846

Scheme 2, 4y

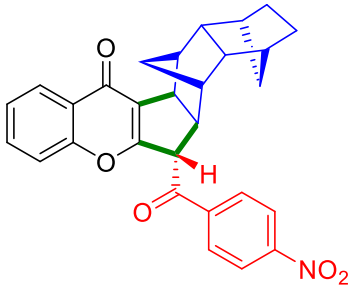

O
O
H
O
NO2

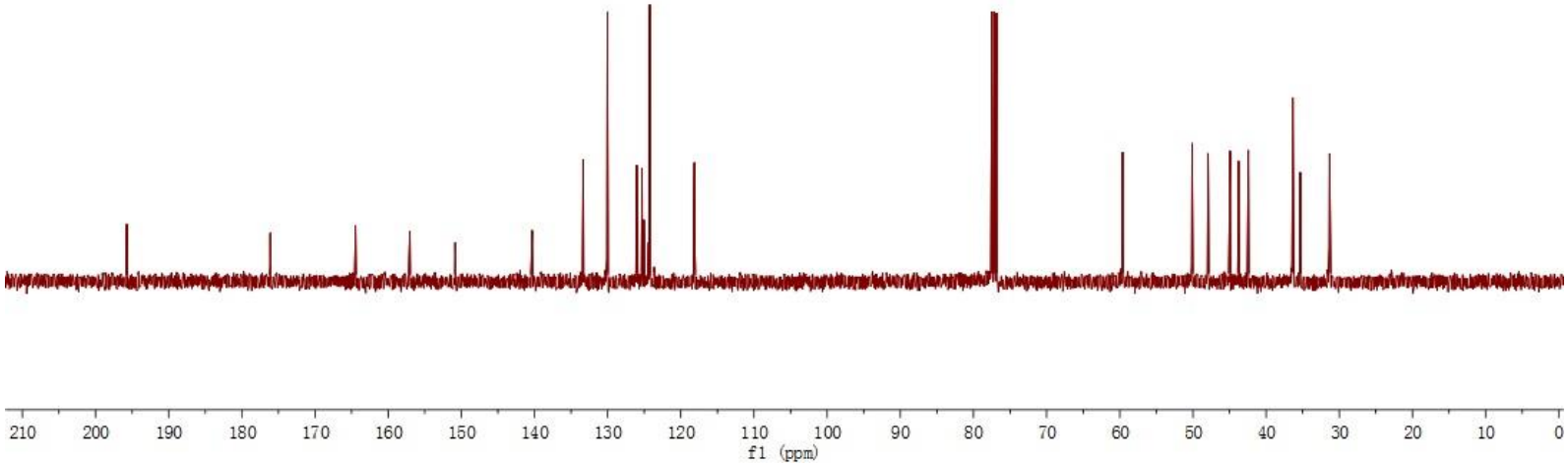

2.02
3.06
1.09
1.04
1.00
1.00
1.04
1.10
1.09
2.00
1.05
1.13
1.06
1.13
3.17
1.10
3.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

ysy-233-C

195.7213
176.0953
164.4657
157.0370
150.8304
140.3314
133.3454
130.0330
126.0322
125.3044
125.0512
124.3939
124.2244
118.1362
77.4791
77.1604
76.8417
59.6273
50.1179
50.0661
47.9329
44.9408
43.7719
42.4366
36.3601
36.2812
35.3417
31.3349
31.2939

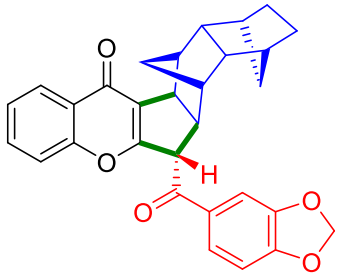
Scheme 2, 4y

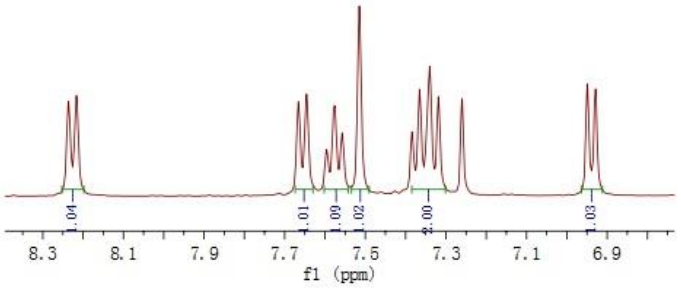


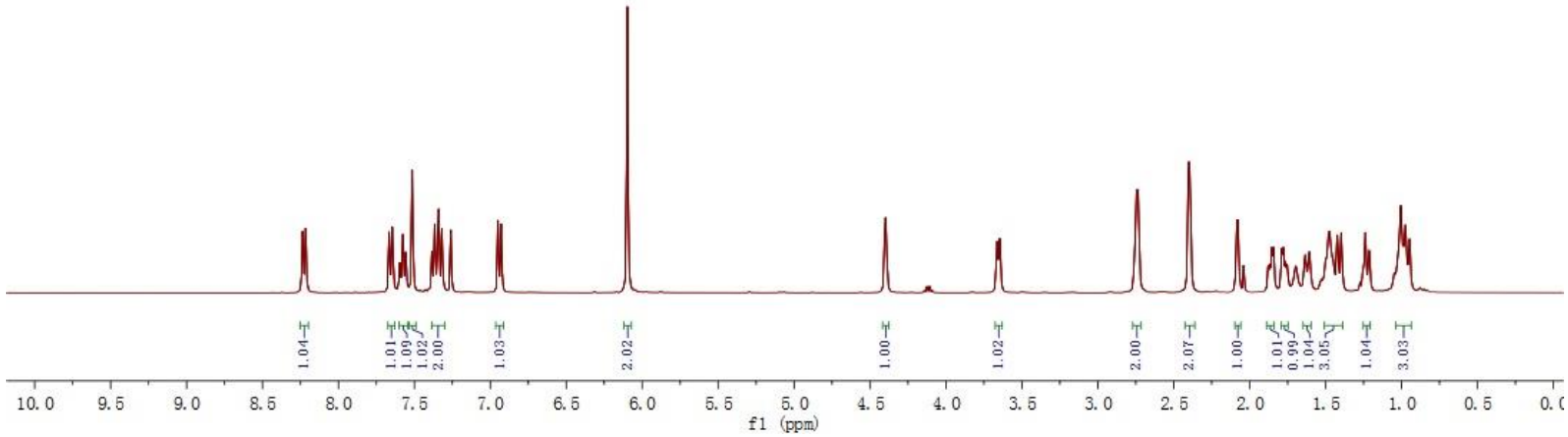



ysy-238-1-2-H
8.2361
8.2162
7.6662
7.6457
7.5148
7.3653
7.3401
7.3184
6.9475
6.9306
6.9272
6.0981
4.4034
4.3976
4.3923
3.6633
3.6456
2.7588
2.7450
2.7330
2.4030
2.3928
2.0859
2.0771
1.8548
1.8429
1.7889
1.7773
1.6351
1.6072
1.4818
1.4715
1.4227
1.3968
1.2387
1.2131
1.0057
0.9743

Scheme 2, 4z


O
O
H
O
O

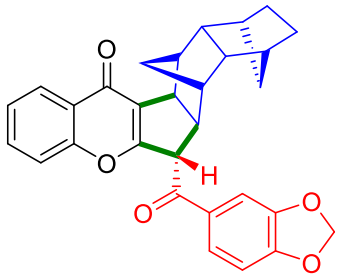

1.04
1.01
1.09
1.02
2.00
1.03
8.3
8.1
7.9
7.7
7.5
7.3
7.1
6.9
f1 (ppm)

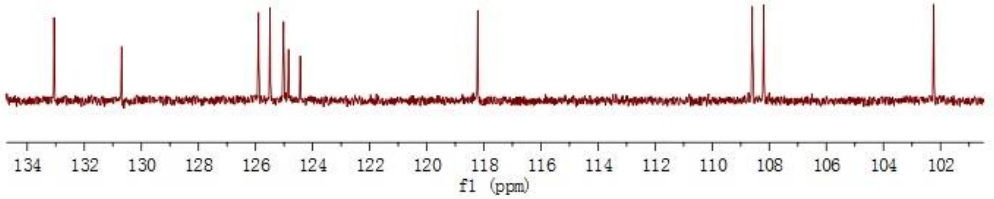

1.04
1.01
1.09
1.02
2.00
1.03
2.02
1.00
1.02
2.00
2.07
1.00
1.01
0.99
1.04
3.05
1.04
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

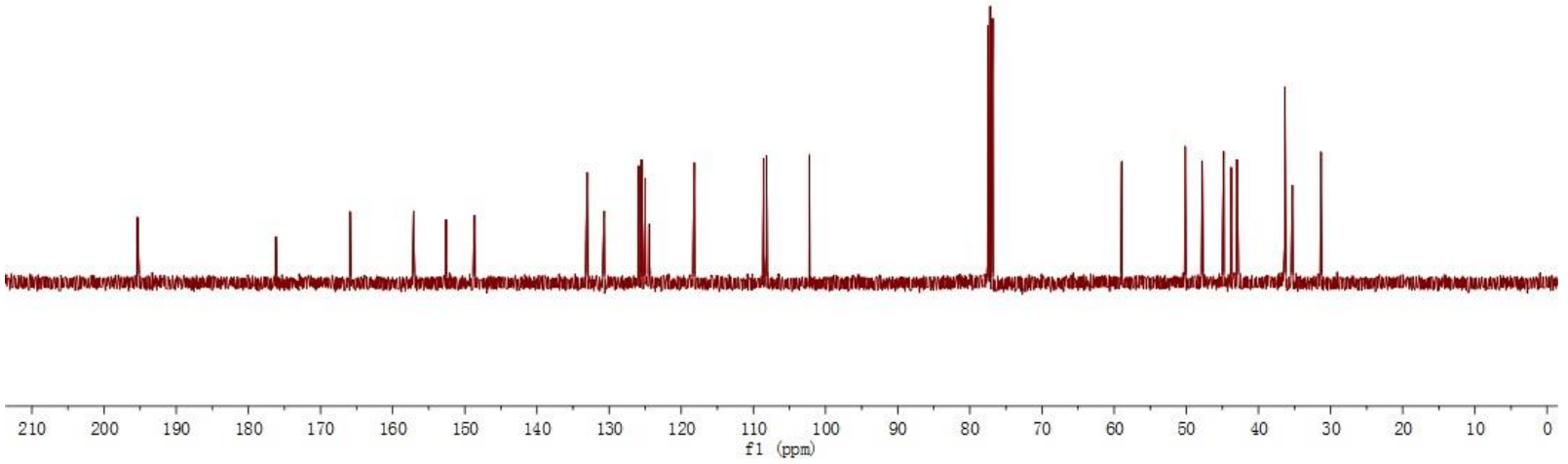
ysy-238-1-C
y1

195.3630
176.1929
165.9074
157.0783
152.6178
148.6866
133.0559
130.6897
125.8945
125.4909
125.0179
124.8423
124.4320
118.2143
108.5947
108.1902
102.2361
77.4788
77.1602
76.8415
58.9473
50.1605
50.0795
47.8017
44.8177
43.7914
42.9484
36.3470
36.2553
35.3071
31.3531
31.3341

Scheme 2, 4z

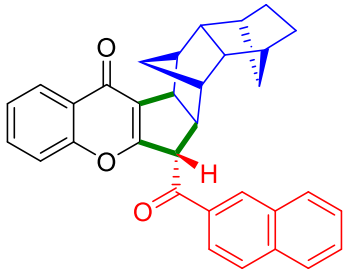


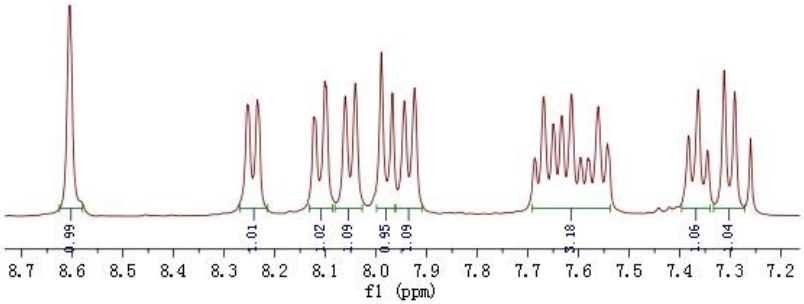


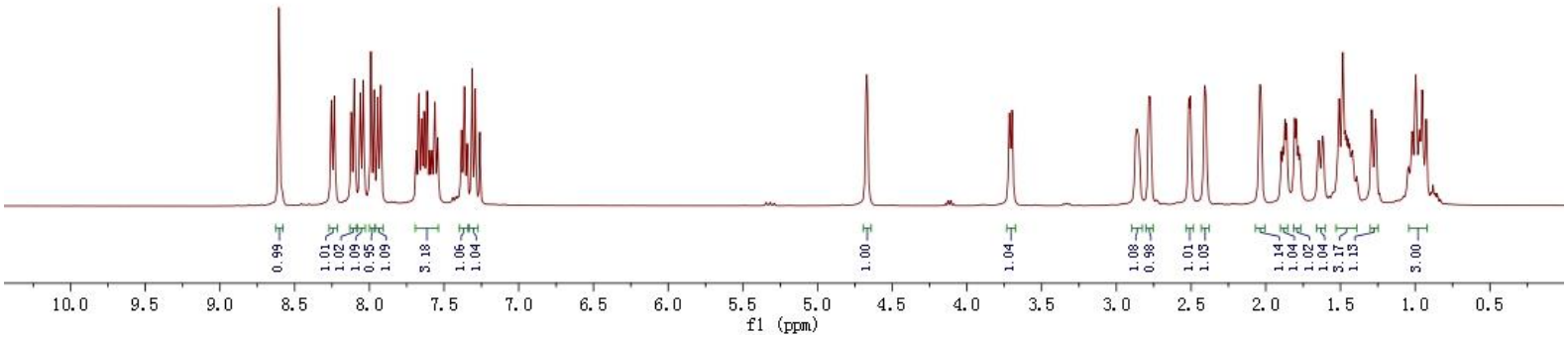



lmz-6-H
8.6072
8.6028
8.2554
8.2510
8.2353
8.2311
8.1237
8.1191
8.1019
8.0974
8.0609
8.0408
7.9896
7.9679
7.9441
7.9239
7.6668
7.6629
7.6497
7.6353
7.6141
7.5959
7.5824
7.5781
7.5613
7.5434
7.5391
7.3830
7.3640
7.3451
7.3124
7.2913
7.2601
4.6784
4.6736
4.6696
4.6647
3.7159
3.6982
2.8738
2.8645
2.8546
2.8461
2.7830
2.7716
2.5151
2.5055
2.4091
2.3994
2.0418
2.0314
1.8963
1.8843
1.8713
1.8596
1.8072
1.7954
1.7823
1.7705
1.6457
1.6180
1.5097
1.4840
1.4674
1.4579
1.4481
1.4385
1.4284
1.4184
1.2906
1.2907
1.2647
1.0508
1.0441
1.0209
0.9961
0.9714
0.9530
0.9258

Scheme 2, 4aa

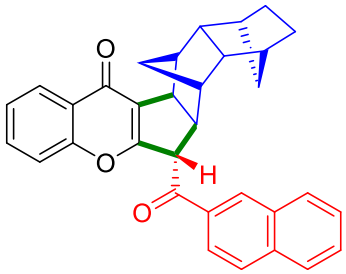

O
O
H
O

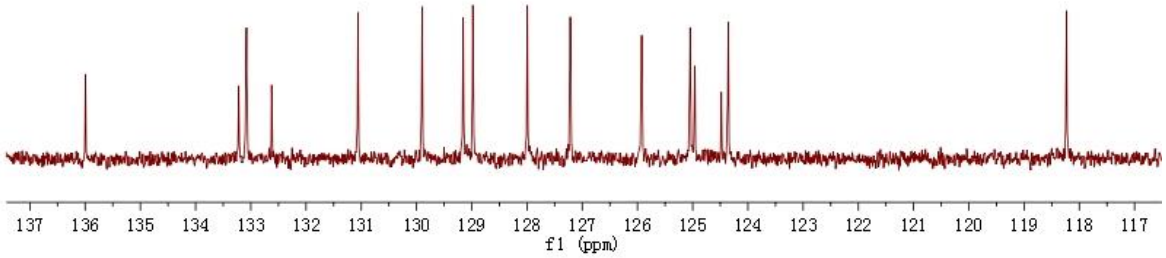

0.99
1.01
1.02
1.09
0.95
1.09
3.18
1.06
1.04
8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)

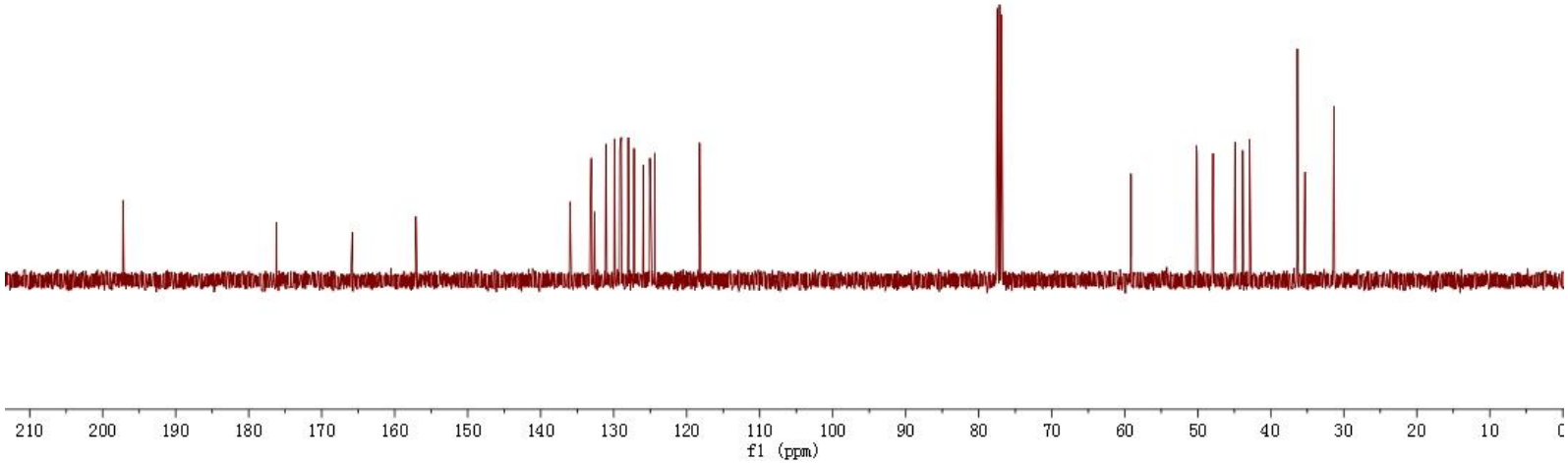

0.99
1.01
1.02
1.09
0.95
1.09
3.18
1.06
1.04
1.00
1.04
1.08
0.98
1.01
1.03
1.14
1.04
1.02
1.04
3.17
1.13
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


lmz-6-C
197.2247
176.2038
165.7896
157.1030
135.9927
133.2171
133.0803
132.6225
131.0600
129.8999
129.1561
128.9805
127.9943
127.2166
125.9240
125.0471
124.9594
124.4803
124.3578
118.2523
77.4765
77.1598
76.8416
59.1468
50.1897
50.1058
47.9128
44.9043
43.8379
42.9020
36.3562
36.3272
35.3126
31.3447

Scheme 2, 4aa


O
O
H
O


137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117
f1 (ppm)

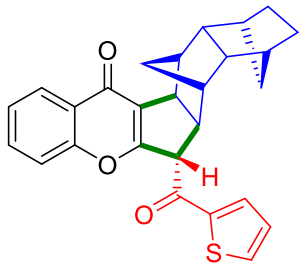

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

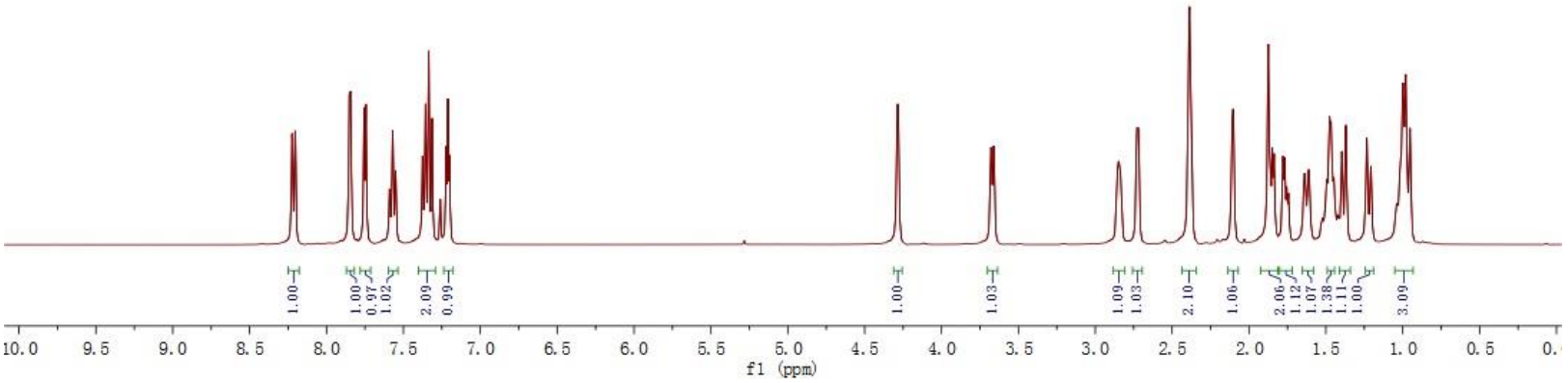
ysy-242-1-

8.2255
8.2215
8.2058
8.2016
7.8522
7.8426
7.7558
7.7434
7.5915
7.5874
7.5701
7.5525
7.5483
7.3757
7.3568
7.3355
7.3135
7.2599
7.2212
7.2103
7.1992

4.2915
4.2850
4.2777
3.6781
3.6603
2.8593
2.8498
2.8396
2.8311
2.7297
2.7182
2.3946
2.3860
2.1103
2.1014
1.8745
1.8484
1.8364
1.7794
1.7677
1.6108
1.4764
1.4669
1.3959
1.3699
1.2336
1.2075
0.9984
0.9799

Scheme 2, 4ab

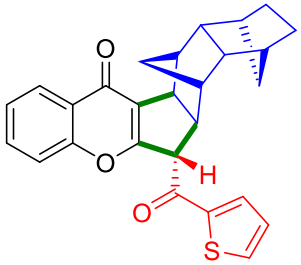


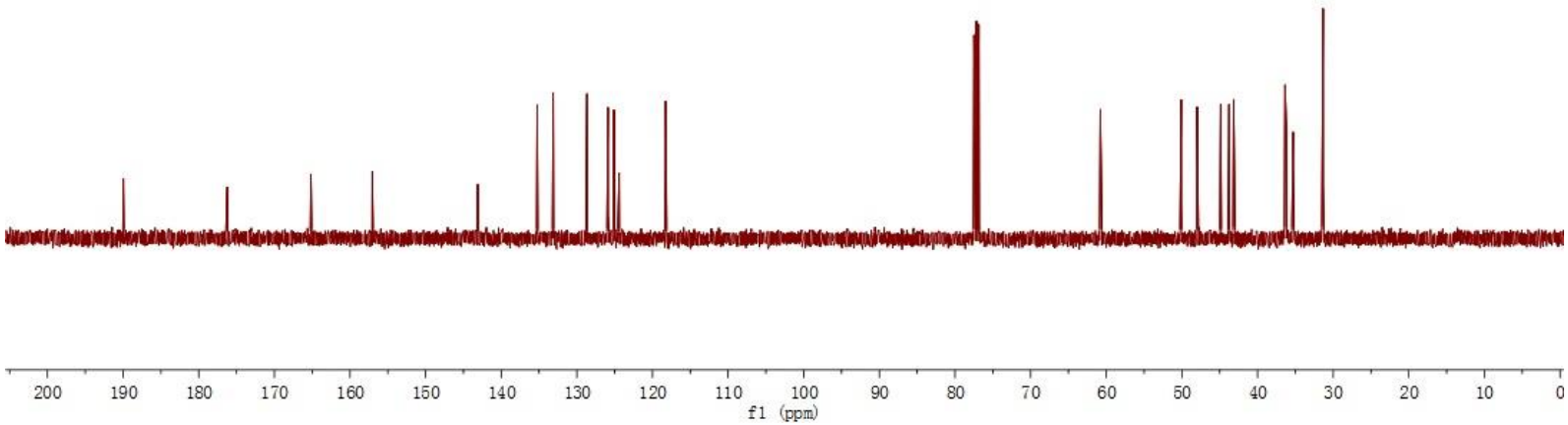


ysy-242-1-C
y1

189.9635
176.2228
165.1568
157.0490
143.1070
135.2435
133.1565
133.1278
128.6495
125.8874
125.0940
125.0077
124.4036
118.2415
77.4792
77.1606
76.8428
60.7871
50.1498
50.0908
47.9797
44.8781
43.7574
43.1535
36.3630
36.3427
36.1926
35.3057
31.3394

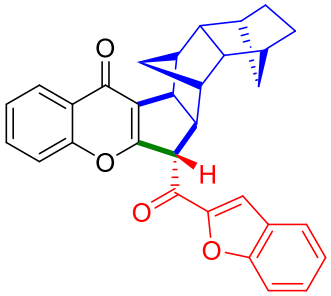
Scheme 2, 4ab

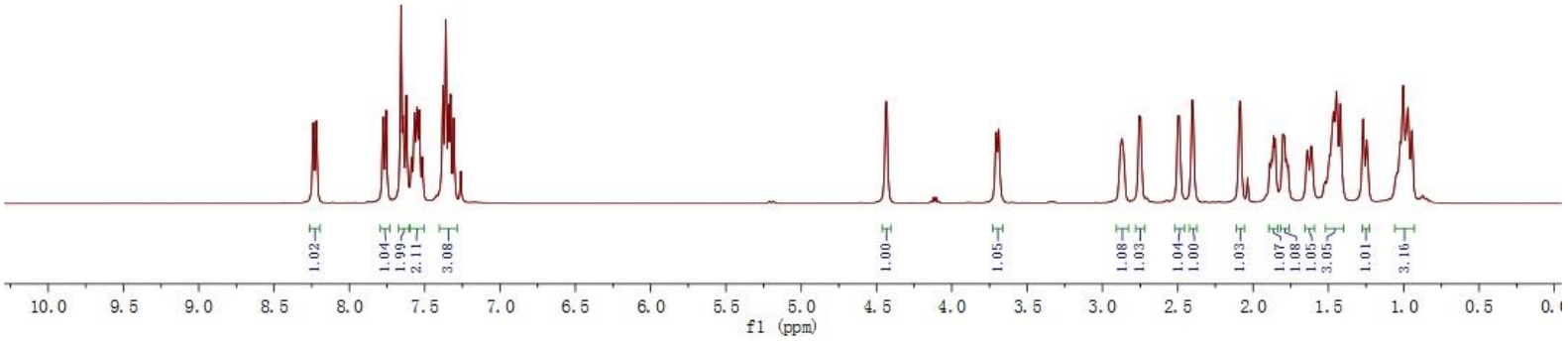




ysy-241-1-H

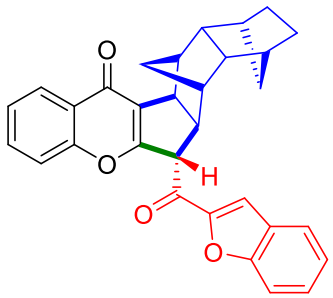
Scheme 2, 4ac

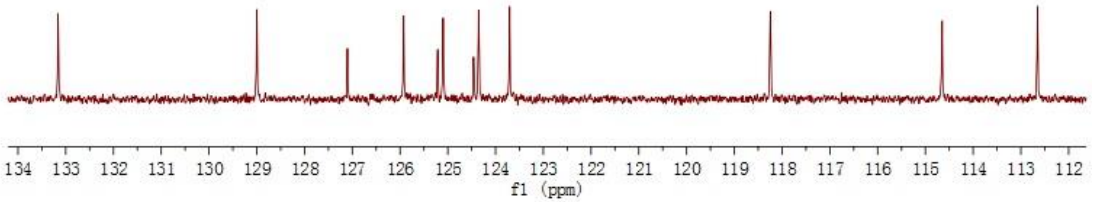


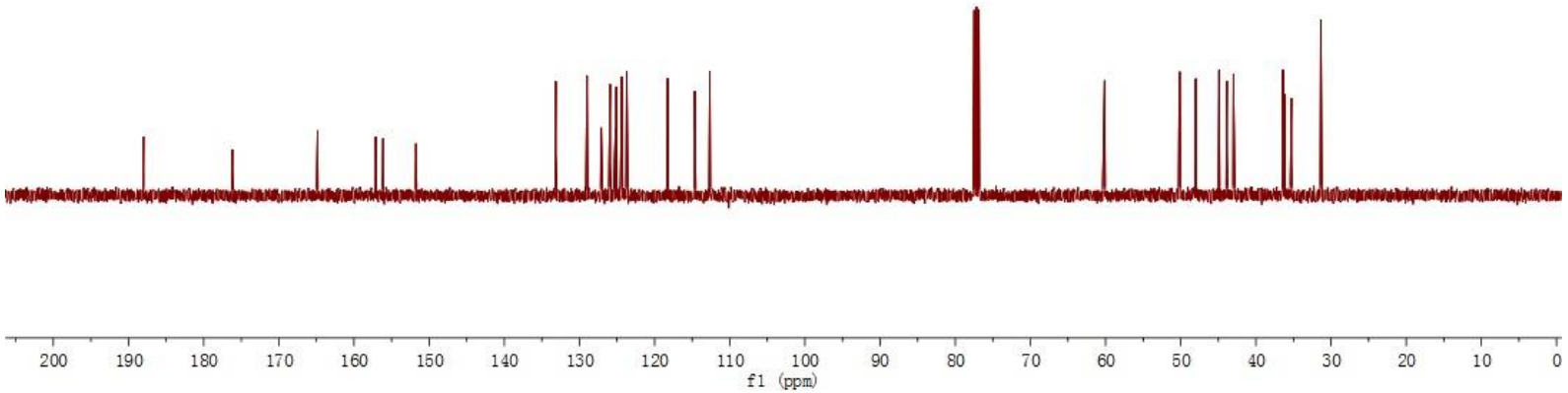



ysy-241-1-C
y1
188.0093
176.1899
164.8420
157.0941
156.1188
151.7438
133.1596
128.9983
127.1007
125.9250
125.2114
125.0984
124.4610
124.3538
123.7064
118.2460
114.6503
112.6527
77.4770
77.1595
76.8418
60.1291
50.1796
50.1083
47.9874
44.9029
43.8556
42.9920
36.4033
36.3372
36.1861
35.2856
31.3578

Scheme 2, 4ac


O
O
H
O
O


134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115 114 113 112
f1 (ppm)


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

ysy-261-H

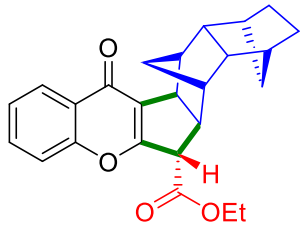
8.2283
8.2241
8.2083
8.2041
7.6355
7.6313
7.6138
7.5964
7.5922
7.4316
7.4105
7.3955
7.3766
7.3578
7.2601

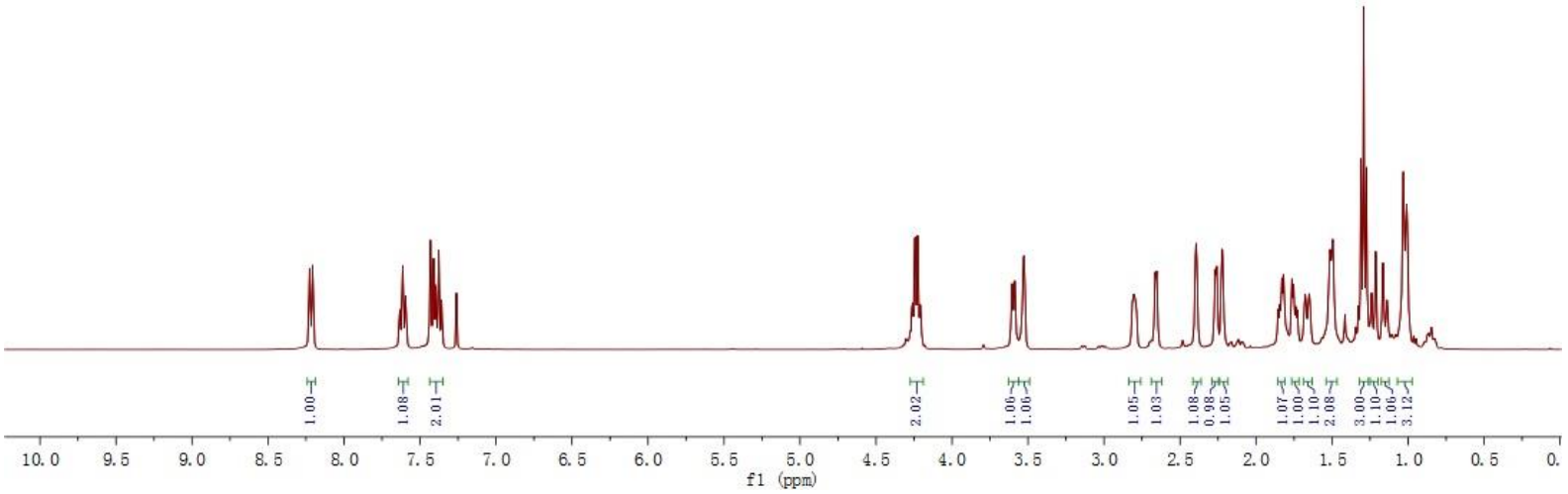
4.2639
4.2588
4.2458
4.2412
4.2277
4.2231
4.2100
4.2052
3.6052
3.5870
3.5346
3.5270
3.5204

2.8052
2.7960
2.6636
2.6521
2.3946
2.2692
2.2578
2.2225

1.8302
1.8181
1.7644
1.7526
1.6495
1.5119
1.4948
1.3093
1.2916
1.2738
1.2395
1.2130
1.1646
1.0311

Scheme 2, 4ad

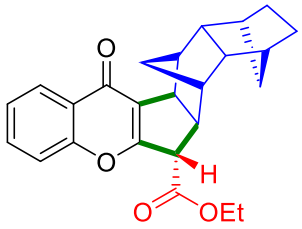


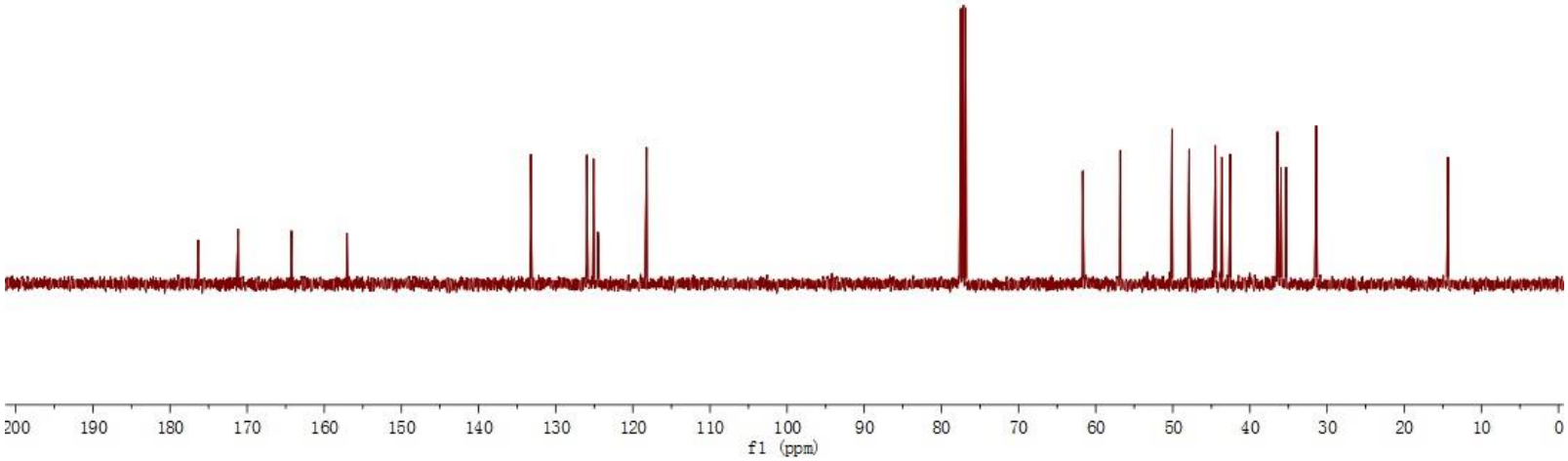


ysy-261-C
y1

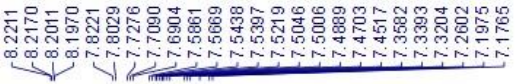
176.3436
171.1730
164.2601
157.0657
133.2076
125.9454
125.0985
124.5441
124.4211
118.2280
77.4779
77.1592
76.8417
61.6598
56.8108
50.1076
50.0839
47.8842
44.4865
43.6235
42.5698
36.4360
36.4027
35.9766
35.3013
31.4085
31.3879
14.3256

Scheme 2, 4ad

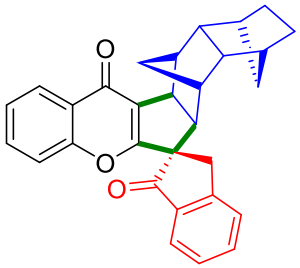


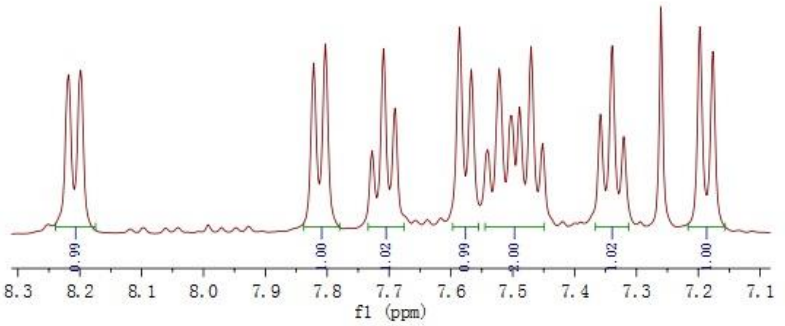


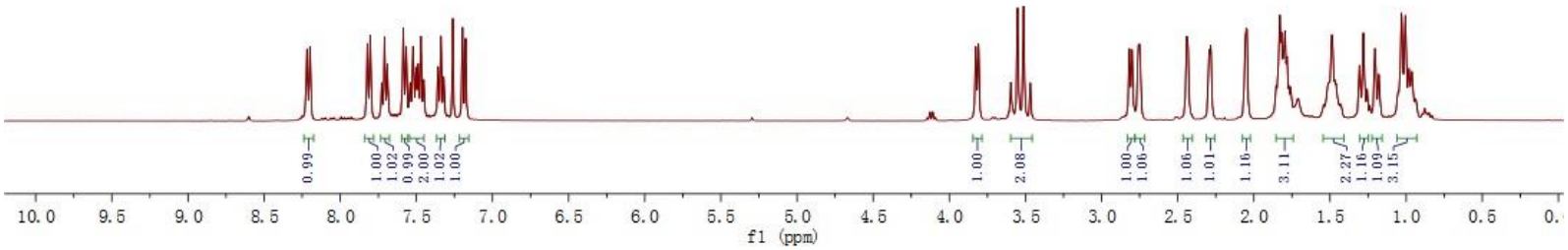
ysy-239-1-2-H

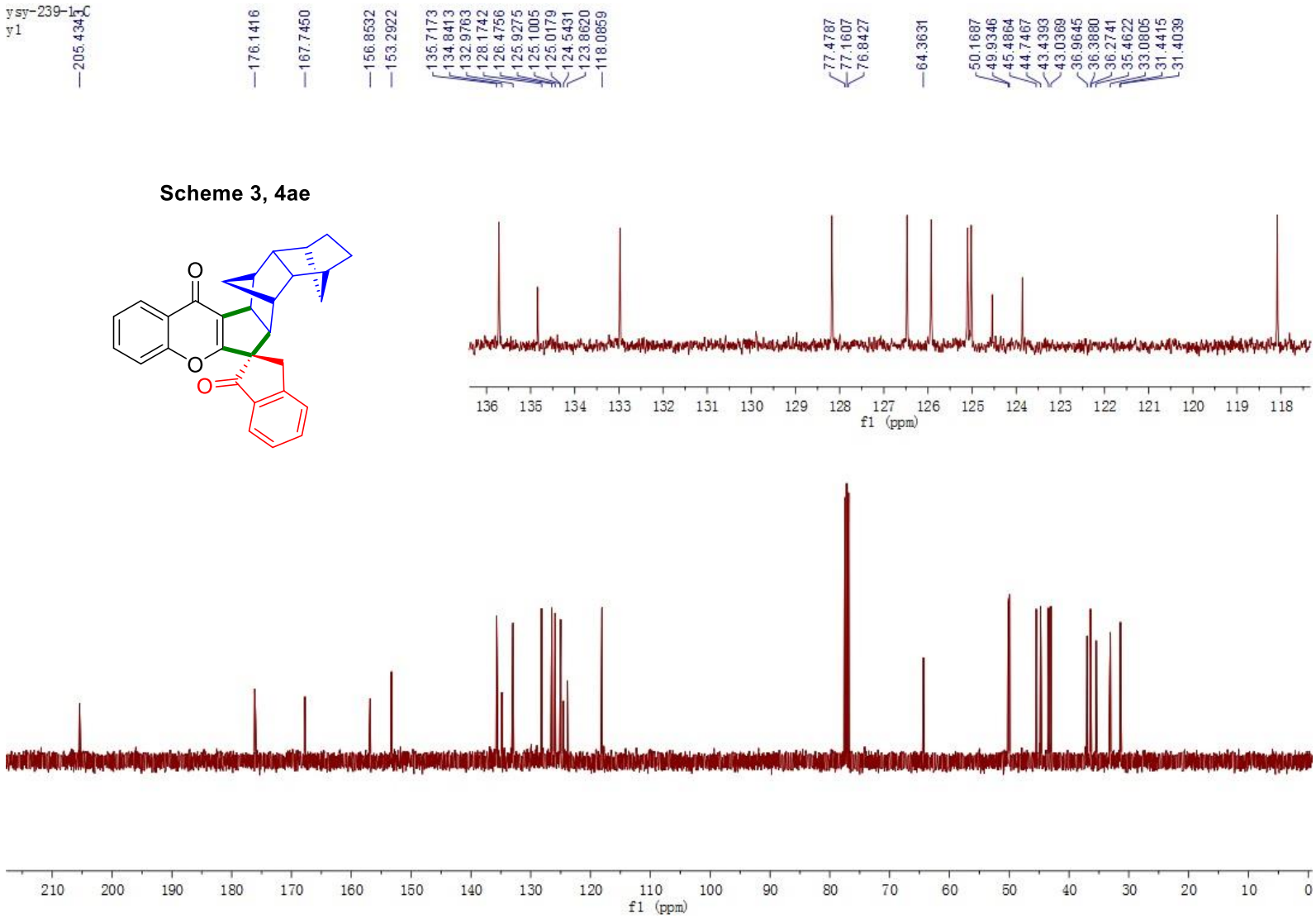


Scheme 3, 4ae








ysy-239-1-C
yl
205.4343
176.1416
167.7450
156.8532
153.2922
135.7173
134.8413
132.9763
128.1742
126.4756
125.9275
125.1005
125.0179
124.5431
123.8620
118.0859
77.4787
77.1607
76.8427
64.3631
50.1687
49.9346
45.4864
44.7467
43.4393
43.0369
36.9645
36.3880
36.2741
35.4622
33.0805
31.4415
31.4039
O
O
O
136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118
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)

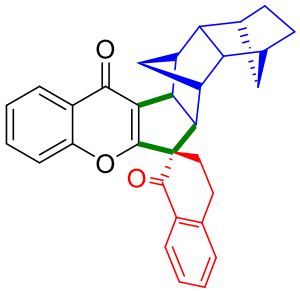
Scheme 3, 4ae

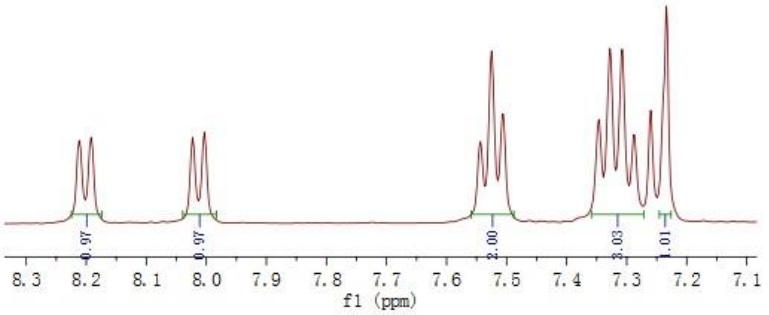
ysy-240-2-1-H

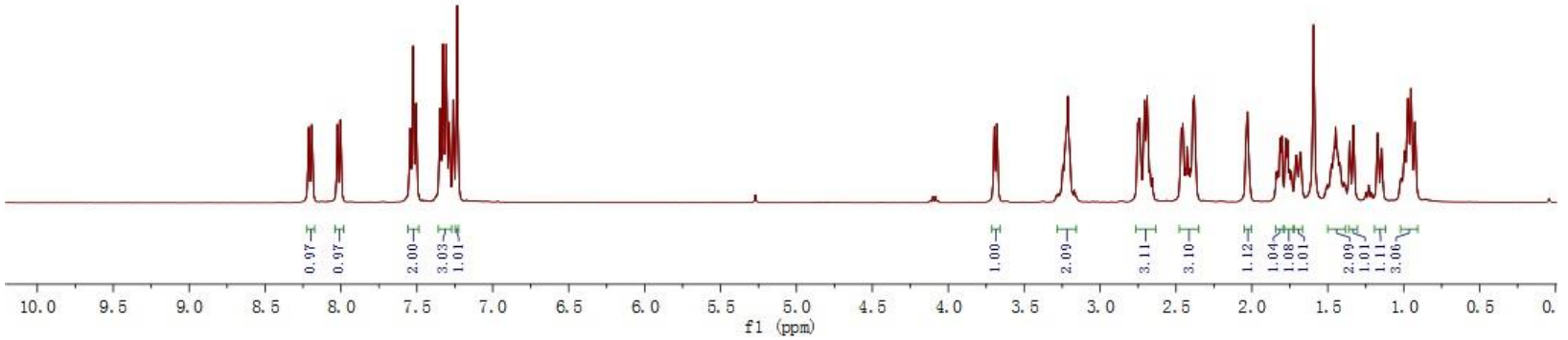
8.2115
8.1918
8.0228
8.0033
7.5440
7.5251
7.5061
7.3468
7.3279
7.3077
7.2875
7.2601
7.2396
7.2336

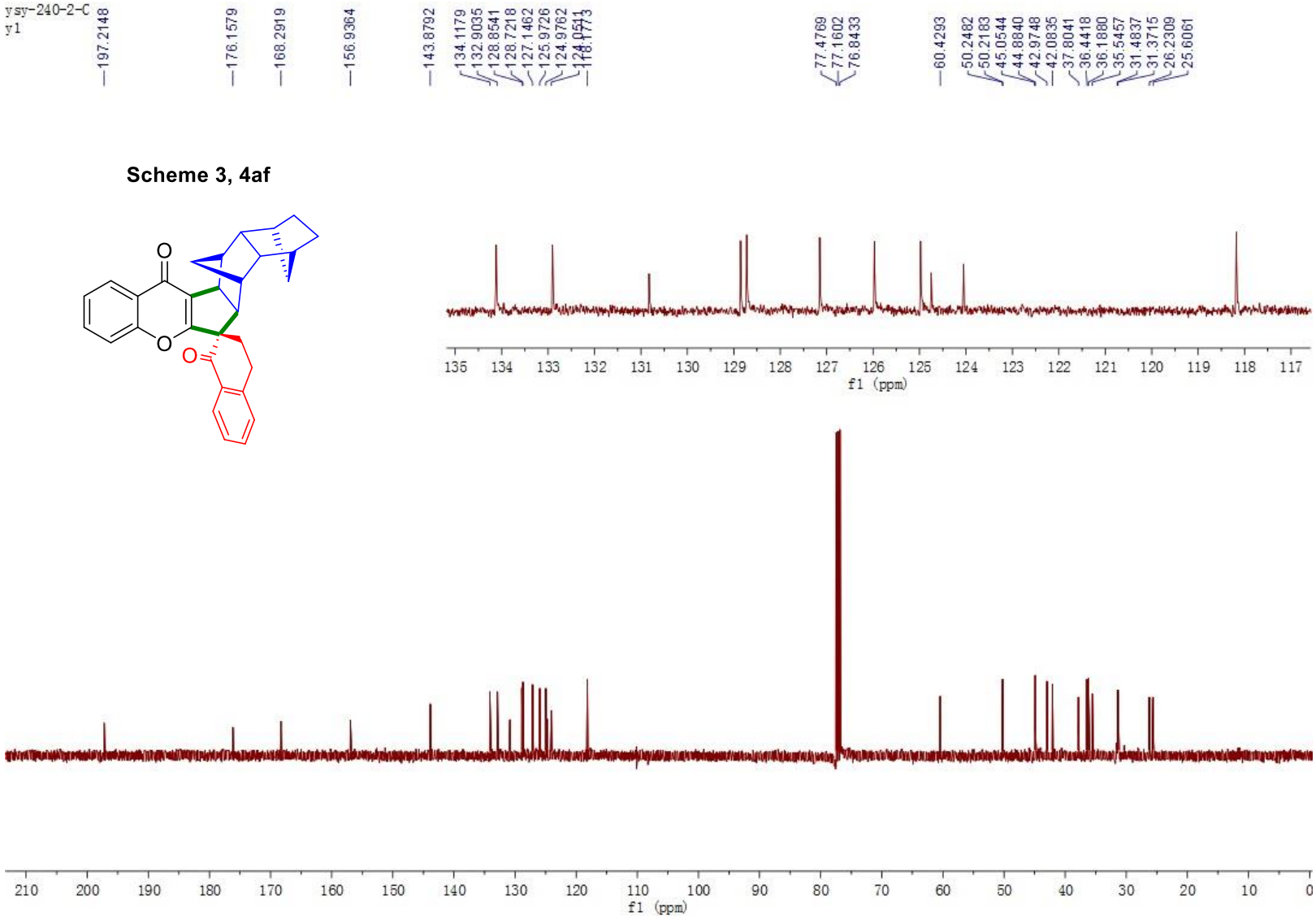
3.6972
3.6797
3.2466
3.2237
3.2115
3.1989
2.7411
2.7072
2.6906
2.3885
2.3780
2.0369
2.0278
1.8142
1.8030
1.7770
1.7648
1.6811
1.5937
1.4485
1.3565
1.3312
1.1714
1.1461
0.9734
0.9529

Scheme 3, 4af








ysy-240-2-C
y1
197.2148
176.1579
168.2919
156.9364
143.8792
134.1179
132.9035
128.8541
128.7218
127.1462
125.9726
124.9762
77.4769
77.1602
76.8433
60.4293
50.2482
50.2183
45.0544
44.8840
42.9748
42.0835
37.8041
36.4418
36.1880
35.5457
31.4837
31.3715
26.2309
25.6061
f1 (ppm)
f1 (ppm)

Scheme 3, 4af