Supporting Information

Synergistic silver/scandium catalysis for divergent synthesis of skeletally diverse chromene derivatives

Shuai Liu,[a] Ke Chen,[a] Xin-Chan Lan,[a] Wen-Juan Hao,*[,a] Guigen Li,[b] Shu-Jiang Tu,*[,a] and Bo Jiang*[,a]

[a]School of Chemistry & Materials Science, Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou 221116, P. R. China. Email: wjhaol@jsnu.edu.cn (WJH); laotu@jsnu.edu.cn (SJT); jiangchem@jsnu.edu.cn (BJ) Fax: +8651683500065; Tel: +8651683500065

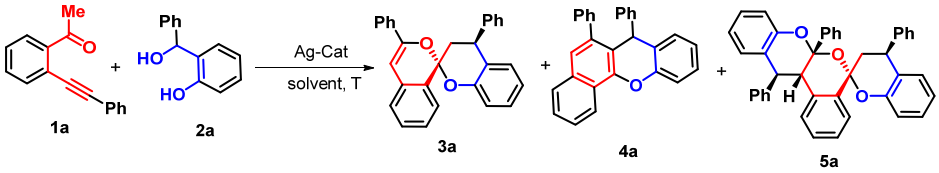
[b]Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061, United States.

Context

General Information

^{1}H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in DMSO-d_6 ($CDCl_3$, or Acetone-d_6) with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. HRMS (ESI) was determined by using microTOF-QII HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

Table 1. Optimization of Reaction Conditions



Entry	Co-Catalyst (mol %)	Solvent	T (°C)	Yield[b] (%)		
				3a	**4a**	**5a**
1[a]	AgTFA (10)	Toluene	50	trace	trace	trace
2[a]	AgTFA (10)/$BiNPO_4H$ (10)	Toluene	50	35	trace	trace
3[a]	AgOAc (10)/$BiNPO_4H$ 10)	Toluene	50	ND[c]	trace	trace
4[a]	AgOTf (10)/$BiNPO_4H$ (10)	Toluene	50	33	trace	trace
5[a]	$AgNO_3$ (10)/$BiNPO_4H$ (10)	Toluene	50	22	trace	trace
6[a]	AgTFA (10)/TFA (10)	Toluene	50	23	trace	trace
7[a]	AgTFA (10)/$Sc(OTf)_3$ (10)	Toluene	50	68	trace	trace
8[a]	AgTFA (10)/$Sn(OTf)_2$ (10)	Toluene	50	trace	trace	trace
9[a]	AgTFA (10)/$Zn(OTf)_2$ (10)	Toluene	50	41	trace	trace
10[a]	$PdCl_2$ (10)/$Sc(OTf)_3$ (10)	Toluene	50	trace	trace	trace
11[a]	$Cu(OTf)_2$ (10)/$Sc(OTf)_3$ (10)	Toluene	50	trace	trace	trace
12[a]	AgTFA (5)/ $Sc(OTf)_3$ (10)	Toluene	50	53	trace	trace
13[a]	AgTFA (10)/$Sc(OTf)_3$ (10)	CH_3CN	50	58	trace	trace
14[a]	AgTFA (10)/$Sc(OTf)_3$ (10)	1,4-Dioxane	50	trace	trace	trace
15[a]	AgTFA (10)/$Sc(OTf)_3$ (10)	THF	50	trace	trace	trace
16[a]	AgTFA (10)/$Sc(OTf)_3$ (10)	DCE	50	trace	trace	trace
17[a]	AgTFA (10)/$Sc(OTf)_3$ (10)	Toluene	r.t.	43	trace	trace
18[a]	AgTFA (10)/$Sc(OTf)_3$ (10)	Toluene	70	33	25	12
19[a]	AgTFA (10)/$Sc(OTf)_3$ (10)	Toluene	80	12	63	15
20[a]	AgTFA (10)/$Sc(OTf)_3$ (10)	Toluene	90	trace	65	13
21[a]	AgTFA (10)/$Sc(OTf)_3$ (10)	Toluene	100	ND	68	trace
22[a]	AgTFA (10)/$Sc(OTf)_3$ (10)	Toluene	110	ND	65	trace
23[a]	AgTFA (10)/$Sc(OTf)_3$ (20)	Toluene	100	ND	78	trace
24[a]	AgTFA (10)/$Sc(OTf)_3$ (30)	Toluene	100	ND	72	trace
25[d]	AgTFA (10)/$Sc(OTf)_3$ (10)	Toluene	80	trace	trace	72

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), Ag-catalyst (x mol%), Lewis acid/ catalyst (y mol%), solvent (3.0 mL), under air conditions.

[b]Isolated yield based on substrate **2a**. [c]Not detected (ND). [d] Using **1a** (0.2 mmol) and **2a** (0.6 mmol); isolated yield based on substrate **1a**.

Our initial investigation was started with the treatment of β-alkynyl ketone **1a** and *o*-hydroxybenzyl alcohol **2a** in a 1.5:1 mole ratio under air conditions in toluene at 50 °C using silver trifluoroacetate

(AgTFA, 10 mol %) as a catalyst, but the transformation did not proceed (Table S1, entry S1). Merging AgTFA with 1,1'-Binaphthyl-2,2'-diyl hydrogen phosphate ($BiNPO_4H$, 10 mol %) as co-catalytic system delivered the desired spiro[chromane-2,1'-isochromene] **3a**, albeit with a low 35% yield (entry S2). Screening followed by several others silver salts often used in the catalytic transformations such as AgOAc, silver trifluormethanesulfonate (AgOTf) and silver nitrate ($AgNO_3$) showed that all these attempted silver catalysts showed a lower catalytic capability and gave unsatisfactory results as compared with AgTFA (entries S3-S5). Exchanging $BiNPO_4H$ for trifluoroacetic acid (TFA, 10 mol %) as a Brønsted acid catalyst led to a poor yield of 23% (entry S6), indicating that Brønsted acid catalyst may disfavor this transformation. Next, we considered using Lewis acid catalyst to explore this bicyclization cascade. To our delight, the combination of AgTFA and $Sc(OTf)_3$ as a dual catalyst system makes these transformations work well, furnishing the desired 6,6-dibenzannulated spiroketal **3a** in 68% yield (entry S7). The use of AgTFA/$Sn(OTf)_2$ or AgTFA/$Zn(OTf)_2$ as a co-catalytic system resulted in a very inferior outcome (entries S8-S9). When $PdCl_2$/$Sc(OTf)_3$ or $Cu(OTf)_2$/$Sc(OTf)_3$ was used as a bimetallic catalyst, the reaction did not work (entries S10-S11), indicating that silver catalyst is critical for this transformation. Employment of a lower loading of AgTFA resulted in a relatively lower yield of **3a** (entry S12). The investigation of the solvent effect revealed that the use of solvents including acetonitrile (CH_3CN), 1,4-dioxane, tetrahydrofuran (THF), and 1,2-dichloroethane (DCE) has no positive effect on the yield of **3a** (entries S13-S16). Lower conversion of **3a** was observed with the reaction temperature being at room temperature (entry S17). Surprisingly, elevating the reaction temperature to 70 ^oC provided product **3a** in 33% yield, along with two unexpected products, benzo[*c*]xanthenes **4a** and spiro[chromane-2,5'-isochromeno[3,4-*b*] chromene] **5a** (entry S18). Next, our endeavor aimed at improving the generation of products **4a** and **5a** was made by adjusting reaction conditions. It is found that the selectivity of reaction shows an important dependency on temperature (entries S19-S22). For instance, elevating the reaction temperature from 70 ^oC to 100 ^oC facilitated the formation of **4a** (68%) and simultaneously suppressed the formation of **5a** without observation of **3a**. After carful optimizations, we found that the reaction in the presence of 10 mol % of AgTFA and 20 mol % of $Sc(OTf)_3$ worked more efficiently and offered a 78% yield of **4a** (entry S23), whereas adjusting substrate ratio to 1:3 gave product **5a** in 72% yield with use of 10 mol % of AgTFA and 10 mol % of $Sc(OTf)_3$ at 80 ^oC in the current catalytic tricyclization (entry S25).

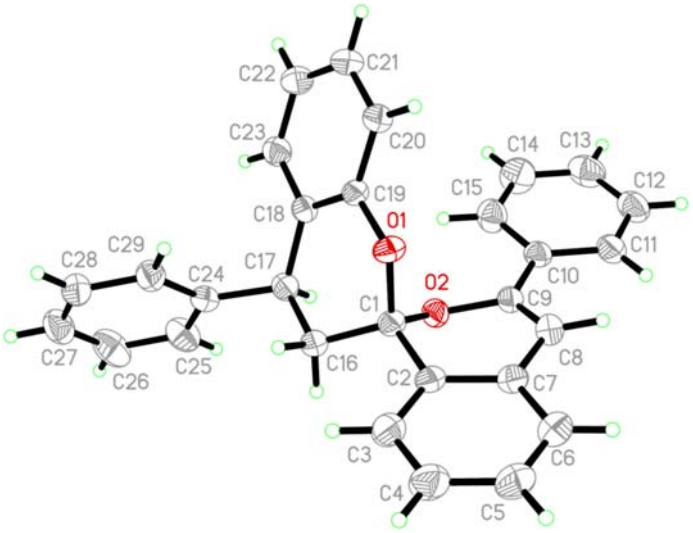


Figure 1. The ORTEP Drawing of **3a**

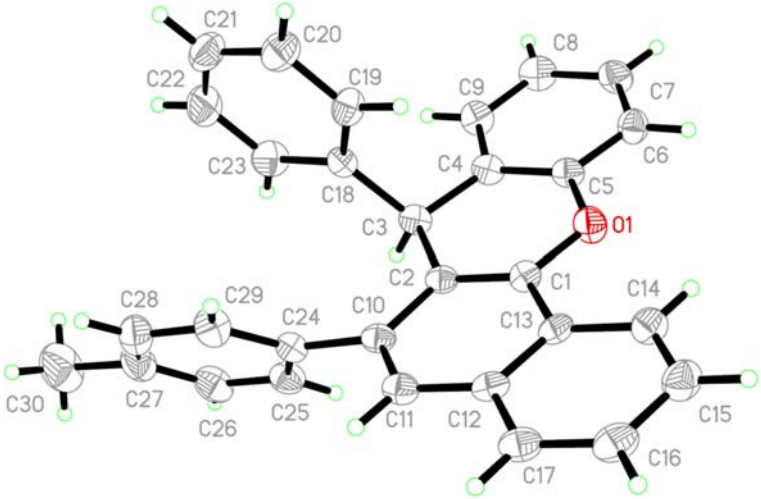


Figure 2. The ORTEP Drawing of **4b**

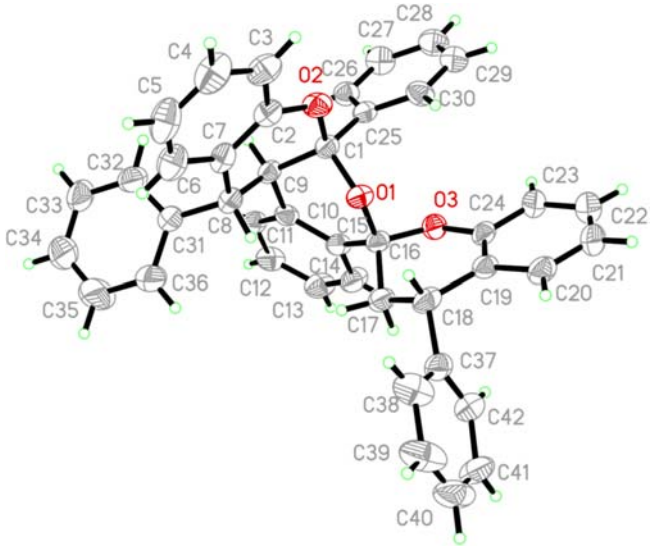
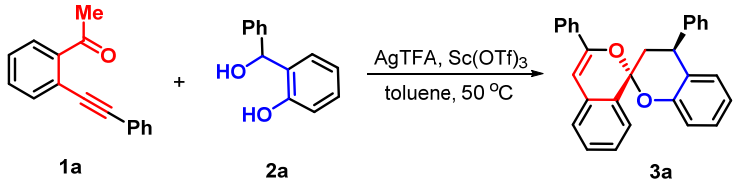


Figure 3. The ORTEP Drawing of **5a**

General procedure for the synthesis of compounds 3

Example for the synthesis of **3a**:

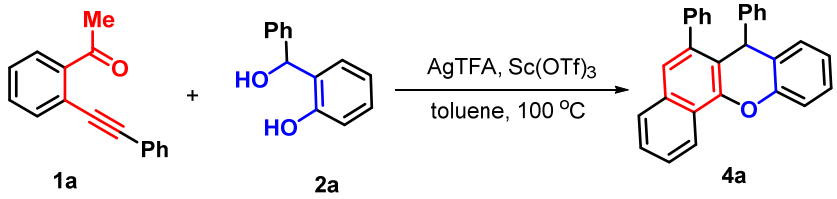


1a **2a** **3a**

A mixture of 1-(2-(phenylethynyl)phenyl)ethanone (**1a**, 0.3 mmol, 66.0 mg), 2-(hydroxy(phenyl)methyl)phenol (**2a**, 0.2 mmol, 40.0 mg), $Sc(OTf)_3$ (10 mol%, 9.8 mg) and AgTFA (10 mol%, 4.4 mg) were added in a 25-mL reaction vial, which was sealed and heated at 50 °C until TLC (petroleum ether: ethyl acetate= 12:1) revealed that conversion of the starting material **2a** was completed. Then the reaction mixture was concentrated by vacuum distillation and was purified by flash column chromatography (silica gel, mixtures of petroleum ether / acetic ester, 50:1, v/v) to afford the desired pure products (**3a**, 54.7 mg, 68% yield) as white solid.

General procedure for the synthesis of compounds 4

Example for the synthesis of **4a**

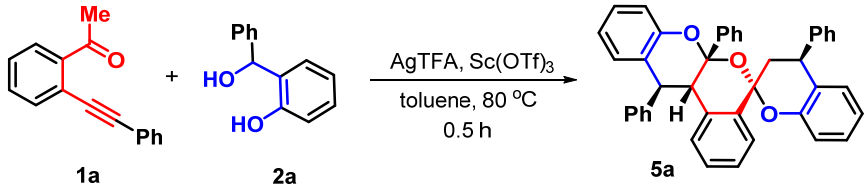


1a **2a** **4a**

A mixture of 1-(2-(phenylethynyl)phenyl)ethanone (**1a**, 0.3 mmol, 66.0 mg), 2-(hydroxy(phenyl)methyl)phenol (**2a**, 0.2 mmol, 40.0 mg), $Sc(OTf)_3$ (20 mol%, 19.6 mg) and AgTFA (10 mol%, 4.4 mg) were added in a 25-mL reaction vial, which was sealed and heated at 100 °C until TLC (petroleum ether: ethyl acetate= 12:1) revealed that conversion of the starting material **2a** was completed. Then the reaction mixture was concentrated by vacuum distillation and was purified by flash column chromatography (silica gel, petroleum ether) to afford the desired pure products (**4a**, 59.9 mg, 78% yield) as white solid.

General procedure for the synthesis of compounds 5

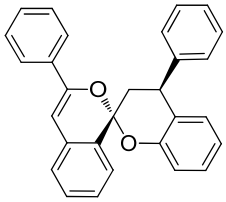
Example for the synthesis of **5a**



1a **2a** **5a**

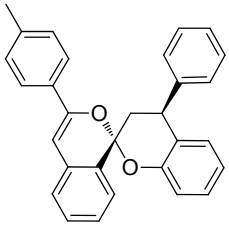
A mixture of 1-(2-(phenylethynyl)phenyl)ethanone (**1a**, 0.2 mmol, 66.0 mg), 2-(hydroxy(phenyl)methyl)phenol (**2a**, 0.6 mmol, 40.0 mg), $Sc(OTf)_3$ (10 mol%, 9.8 mg) and AgTFA (10 mol%, 4.4 mg) were added in a 25-mL reaction vial. The solution was stirred at 80 °C for 30 min, the reaction mixture was concentrated by vacuum distillation and was purified by flash column chromatography (silica gel, petroleum ether / ethylacetate = 50/1, v/v) to afford the desired pure products (**5a**, 84.1 mg, 72% yield) as white solid.

3',4-diphenylspiro[chroman-2,1'-isochromene] (3a)



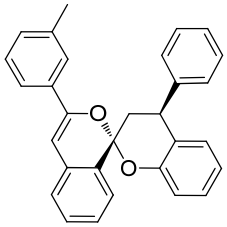
54.7 mg, 68%; white solid, mp 181-182 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.54-7.48 (m, 3H), 7.46-7.39 (m, 5H), 7.37-7.31 (m, 6H), 7.16-7.11 (m, 1H), 6.97-6.90 (m, 2H), 6.85 (d, J = 8.0 Hz, 1H), 6.68 (s, 1H), 4.90-4.84 (m, 1H), 2.97-2.89 (m, 1H), 2.88-2.82 (m, 1H) ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 152.3, 149.5, 144.2, 134.4, 130.8, 129.6, 129.3(8), 129.3(5), 129.1, 128.8(3), 128.8(0), 128.5, 128.0, 127.1, 127.0, 125.5, 125.2, 125.1, 123.7, 121.5, 117.6, 101.3, 98.6, 39.1, 39.0. IR (film, ν, cm^{-1}). 3022, 1787, 1499, 1254, 1045, 1003, 883, 749. HR-MS (APCI) m/z calcd for $C_{29}H_{23}O_2$ $[M+H]^+$ 403.1698, found 403.1703.

4-phenyl-3'-(p-tolyl)spiro[chroman-2,1'-isochromene] (3b)



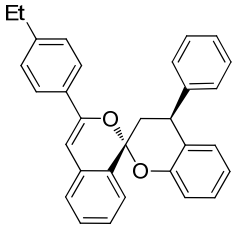
51.6 mg, 62%; white solid, mp 188-189 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.49 (d, J = 7.6 Hz, 1H), 7.44-7.38 (m, 5H), 7.38-7.28 (m, 5H), 7.11 (d, J = 8.0 Hz, 3H), 6.97-6.88 (m, 2H), 6.82 (d, J = 8.0 Hz, 1H), 6.61 (s, 1H), 4.89-4.80 (m, 1H), 2.94-2.86 (m, 1H), 2.86-2.77 (m, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 152.3, 149.7, 144.3, 138.9, 131.7, 131.0, 129.5, 129.3, 129.2, 129.1, 128.8, 128.0, 126.9(4), 126.9(0), 125.5, 125.1, 125.0, 123.7, 121.4, 117.6, 100.6, 98.5, 39.1, 39.0, 21.3. IR (film, ν, cm^{-1}). 3027, 1484, 1454, 1228, 1050, 1008, 879, 762. HR-MS (APCI) m/z calcd for $C_{30}H_{25}O_2$ $[M+H]^+$ 417.1855, found 417.1854.

4-phenyl-3'-(p-tolyl)spiro[chroman-2,1'-isochromene] (3c)



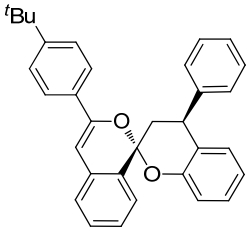
50.8 mg, 61%; white solid, mp 160-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.50 (d, J = 7.2 Hz, 1H), 7.44-7.39 (m, 5H), 7.35-7.29 (m, 4H), 7.19 (d, J = 7.2 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.97-6.92 (m, 2H), 6.83 (d, J = 8.0 Hz, 1H), 6.64 (s, 1H), 4.90-4.83 (m, 1H), 2.96-2.89 (m, 1H), 2.86-2.80 (m, 1H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 152.4, 149.8, 144.4, 138.0, 134.5, 130.9, 129.7, 129.6, 129.3, 129.1, 128.8, 128.4, 128.0, 127.1, 127.0, 126.1, 125.7, 125.1, 123.7, 122.4, 121.6, 117.7, 101.4, 98.5, 39.1, 21.5. IR (film, ν, cm^{-1}) 3023, 1484, 1450, 1257, 1051, 1006, 872, 741. HR-MS (APCI) m/z calcd for $C_{30}H_{25}O_2$ $[M+H]^+$ 417.1855, found 417.1861.

3'-(4-ethylphenyl)-4-phenylspiro[chroman-2,1'-isochromene] (3d)



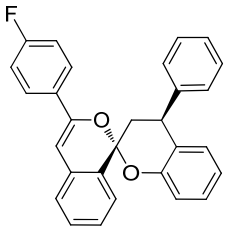
54.2 mg, 63%; white solid, mp 184-185 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.48 (d, J = 7.6 Hz, 1H), 7.44-7.37 (m, 7H), 7.34-7.28 (m, 3H), 7.14-7.08 (m, 3H), 6.93-6.87 (m, 2H), 6.82 (d, J = 8.4 Hz, 1H), 6.60 (s, 1H), 4.86-4.81 (m, 1H), 293-2.86 (m, 1H), 2.84-2.79 (m, 1H), 2.63 (m, 2H), 1.24-1.19 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 152.3, 149.7, 145.3, 144.3, 131.9, 131.0, 129.5, 129.3, 129.1(4), 129.1(7), 128.8, 128.0, 126.9(4), 126.9(9), 125.5, 125.3, 125.0, 123.7, 121.4, 117.6, 100.6, 98.5, 39.1, 39.0, 28.7, 15.4. IR (film, ν, cm^{-1}) 3024, 1512, 1452, 1226, 1052, 1009, 913, 762. HR-MS (APCI) m/z calcd for $C_{31}H_{27}O_2$ $[M+H]^+$ 431.2011, found 431.2009.

3'-(4-(tert-butyl)phenyl)-4-phenylspiro[chroman-2,1'-isochromene] (3e)



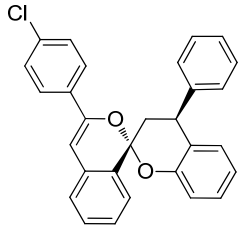
48.5 mg, 53%; white solid, mp 201-202 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.48 (d, J = 7.6 Hz, 2H), 7.44-7.42 (m, 2H), 7.40-7.38 (m, 4H), 7.35-7.30 (m, 5H), 7.14-7.09 (m, 1H), 6.95-6.89 (m, 2H), 6.82 (d, J = 8.0 Hz, 1H), 6.61 (s, 1H), 4.89-4.83 (m, 1H), 2.95-2.88 (m, 1H), 2.84-2.78 (m, 1H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 152.3, 152.1, 149.7, 144.3, 131.7, 131.0, 129.5, 129.3, 129.1, 128.8, 128.0, 127.0, 126.9, 125.5, 125.4, 125.1, 125.0, 123.7, 121.5, 117.0, 100.6, 98.4, 39.1, 39.0, 34.7, 31.2. IR (film, ν, cm^{-1}) 3028, 1485, 1451, 1231, 1107, 1005, 879, 749. HR-MS (APCI) m/z calcd for $C_{33}H_{30}O_2$ $[M+H]^+$ 459.2324, found 459.2328.

3'-(4-fluorophenyl)-4-phenylspiro[chroman-2,1'-isochromene] (3f)



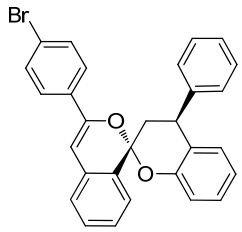
48.7 mg, 58%; white solid, mp 181-182 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.49 (d, J = 7.2 Hz, 1H), 7.45-7.40 (m, 4H), 7.39-7.36 (m, 3H), 7.34-7.30 (m, 3H), 7.13-7.09 (m, 1H), 7.00-6.95 (m, 2H), 6.93-6.88 (m, 2H), 6.83-6.80 (m, 1H), 6.58 (s, 1H), 4.84-4.78 (m, 1H), 2.94-2.87 (m, 1H), 2.84-2.79 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 163.1($^1J_{CF}$ = 243.7 Hz), 152.2, 148.7, 144.1, 130.7, 130.6($^4J_{CF}$ = 3.2 Hz), 129.5($^3J_{CF}$ = 8.6 Hz), 129.1, 129.0, 128.8, 128.1, 127.2, 127.1, 127.0(1), 127.0(0), 125.5, 125.1, 123.7, 121.6, 117.6, 115.5($^2J_{CF}$ = 21.7 Hz), 101.1, 98.6, 39.0. IR (film, ν, cm^{-1}) 3022, 1507, 1482, 1227, 1044, 1008, 881, 763. HR-MS (APCI) m/z calcd for $C_{29}H_{22}FO_2$ $[M+H]^+$ 421.1604, found 421.1602.

3'-(4-chlorophenyl)-4-phenylspiro[chroman-2,1'-isochromene] (3g)



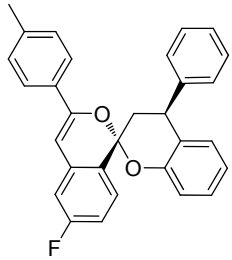
37.5 mg, 43%; white solid, mp 230-231 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.48 (d, J = 7.2 Hz, 1H), 7.45-7.39 (m, 2H), 7.38-7.35 (m, 5H), 7.34-7.29 (m, 3H), 7.26-7.23 (m, 2H), 7.12-7.08 (m, 1H), 6.93-6.87 (m, 2H), 6.81-6.78 (m, 1H), 6.63 (s, 1H), 4.81-4.76 (m, 1H), 2.93-2.86 (m, 1H), 2.84-2.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 152.1, 148.5, 144.1, 134.6, 132.9, 130.5, 129.6, 129.3, 129.0, 128.8, 128.7, 128.1, 127.4, 127.0, 126.4, 125.4, 125.2, 123.7, 121.6, 117.5, 101.8, 98.6, 39.0. IR (film, ν, cm^{-1}) 3025, 1491, 1453, 1227, 1048, 1009, 881, 766. HR-MS (APCI) m/z calcd for $C_{29}H_{22}ClO_2$ $[M+H]^+$ 437.1308, found 437.1306.

3'-(4-bromophenyl)-4-phenylspiro[chroman-2,1'-isochromene] (3h)



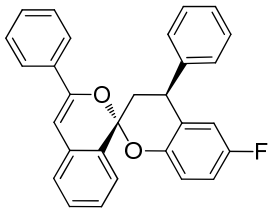
43.2 mg, 45%; white solid, mp 233-234 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.48 (d, J = 7.6 Hz, 1H), 7.44-7.41 (m, 2H), 7.40-7.37 (m, 4H), 7.35 (d, J = 5.2 Hz, 1H), 7.33-7.28 (m, 5H), 7.12-7.08 (m, 1H), 6.92-6.87 (m, 2H), 6.79 (d, J = 8.0 Hz, 1H), 6.64 (s, 1H), 4.80-4.75 (m, 1H), 2.93-2.86 (m, 1H), 2.83-2.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) IR (film, ν, cm^{-1}). 152.1, 148.5, 144.1, 133.3, 131.6, 130.5, 129.6, 129.3, 129.0, 128.8, 128.1, 127.4, 127.0, 126.6, 125.4, 125.2, 123.8, 122.9, 121.6, 117.5, 101.8, 98.6, 39.0. IR (film, ν, cm^{-1}) 3022, 1489,1452, 1227, 1071, 1006, 880, 765. HR-MS (APCI) m/z calcd for $C_{29}H_{22}BrO_2$ $[M+H]^+$ 481.0803, found 481.0799.

6'-fluoro-4-phenyl-3'-(p-tolyl)spiro[chroman-2,1'-isochromene] (3j)



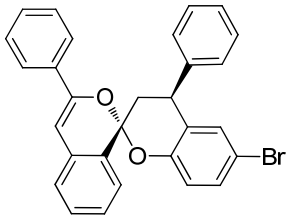
50.3 mg, 58%; white solid, mp 244-245 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.47-7.43 (m, 1H), 7.42-7.37 (m, 3H), 7.37-7.30 (m, 4H), 7.13-7.09 (m, 3H), 7.00-6.95 (m, 2H), 6.94-6.88 (m, 2H), 6.83-6.79 (m, 1H), 6.55 (s, 1H), 4.85-4.79 (m, 1H), 2.89-2.83 (m, 1H), 2.83-2.78 (m, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 163.4($^{1}J_{CF}$ = 245.5 Hz), 152.2, 150.9, 144.1, 139.4, 133.5 ($^{4}J_{CF}$ = 9.2 Hz), 131.2, 129.3, 129.2, 129.0, 128.8, 128.1, 127.0, 125.8($^{5}J_{CF}$ =9.0 Hz), 125.4, 125.3, 125.2($^{6}J_{CF}$ = 2.6Hz), 121.6, 117.5, 113.6($^{2}J_{CF}$ = 22.3Hz), 111.1($^{3}J_{CF}$ = 22.3Hz), 99.9, 98.4, 39.2, 39.0, 21.3. IR (film, ν, cm^{-1}) 3026, 1611, 1511, 1205, 1050, 1009, 878, 762. HR-MS (APCI) m/z calcd for $C_{30}H_{24}FO_2$ $[M+H]^+$ 435.1760, found 435.1762.

6-fluoro-3',4-diphenylspiro[chroman-2,1'-isochromene] (3k)



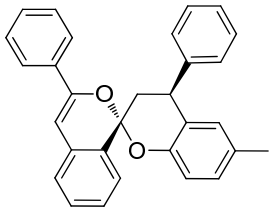
48.7 mg, 58%; white solid, mp 185-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.50-7.38 (m, 6H), 7.38-7.32 (m, 4H), 7.32-7.27 (m, 4H), 6.84- 6.74 (m, 2H), 6.66 (s, 1H), 6.65-6.61 (m, 1H), 4.84-4.77 (m, 1H), 2.93-2.86 (m, 1H), 2.84-2.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 157.5($^{1}J_{CF}$ = 237.4Hz), 149.4, 148.2, 143.4, 134.3, 130.8, 129.7, 129.0(0), 129.0(6), 128.9, 128.5, 127.2 ($^{4}J_{CF}$ = 9.4Hz), 126.9, 126.8, 125.1($^{6}J_{CF}$ = 2.4Hz), 123.7, 118.6($^{5}J_{CF}$ = 8.1Hz), 115.3($^{2}J_{CF}$ = 23.4Hz), 114.9($^{3}J_{CF}$ = 23.1Hz), 101.4, 98.5, 39.2, 38.6. IR (film, ν, cm^{-1}) 3023, 1484, 1453, 1256, 1046, 1008, 818, 759. HR-MS (APCI) m/z calcd for $C_{29}H_{22}FO_2$ $[M+H]^+$ 421.1604, found 421.1607.

6-bromo-3',4-diphenylspiro[chroman-2,1'-isochromene] (3l)



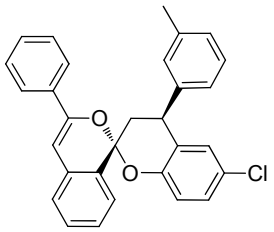
49.9 mg, 52%; white solid, mp 212-213 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.50-7.46 (m, 3H), 7.45-7.40 (m, 3H), 7.36 (d, J = 8.0 Hz, 3H), 7.35-7.30 (m, 5H), 7.23-7.19 (m, 1H), 7.05 (d, J = 1.2 Hz, 1H), 6.70 (d, J = 8.8 Hz, 1H), 6.66 (s, 1H), 4.87-4.78 (m, 1H), 2.93-2.85 (m, 1H), 2.84-2.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 151.4, 149.3, 143.2, 134.2, 131.8, 131.1, 130.7, 129.7, 129.0(3), 129.0(6), 128.7, 128.6, 127.7, 127.3, 127.2, 125.2, 125.1, 123.7, 119.5, 113.8, 101.3, 98.6, 39.0, 38.7. IR (film, ν, cm^{-1}) 3029, 1471, 1453, 1229, 1074, 1005, 885, 776. HR-MS (APCI) m/z calcd for $C_{29}H_{22}BrO_2$ $[M+H]^+$ 481.0803, found 481.0805.

6-methyl-3',4-diphenylspiro[chroman-2,1'-isochromene](3m)



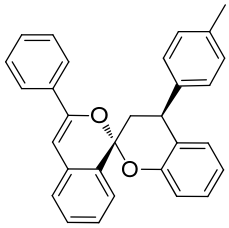
59.9 mg, 72%; white solid, mp 188-189 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.50-7.46 (m, 3H), 7.43-7.37 (m, 5H), 7.34-7.28 (m, 6H), 6.92-6.88 (m, 1H), 6.71 (d, J = 8.0 Hz, 2H), 6.64 (s, 1H), 4.82-4.76 (m, 1H), 2.89-2.82 (m, 1H), 2.81-2.76 (m, 1H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.1, 149.6, 144.3, 134.5, 130.8, 130.6, 129.5, 129.4, 129.4, 129.1, 128.8, 128.7, 128.4, 127.1, 126.9, 125.2, 125.0(3), 125.0(9), 123.7, 117.3, 101.2, 98.5, 39.2, 39.0, 20.7. IR (film, ν, cm^{-1}) 3029, 1492, 1452, 1230, 1061, 1003, 872, 760. HR-MS (APCI) m/z calcd for $C_{30}H_{25}O_2$ $[M+H]^+$ 417.1855, found 417.1851.

6-chloro-3'-phenyl-4-(m-tolyl)spiro[chroman-2,1'-isochromene] (3n)



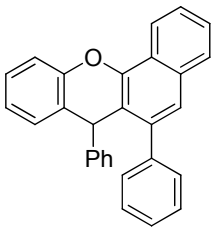
54.0 mg, 60%; white solid, mp 199-200 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.50-7.45 (m, 3H), 7.45-7.41 (m, 1H), 7.36-7.29 (m, 6H), 7.15 (d, J = 8.0 Hz, 3H), 7.07-7.03 (m, 1H), 6.92-6.89 (m, 1H), 6.74 (d, J = 8.8 Hz, 1H), 6.65 (s, 1H), 4.78-4.73 (m, 1H), 2.92-2.85 (m, 1H), 2.81-2.76 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.9, 149.4, 143.1, 138.7, 134.2, 130.7, 129.7, 128.9(4), 128.9(9), 128.9(8), 128.8, 128.5, 128.1, 127.3, 127.2, 126.3, 126.0, 125.1(4), 125.1(8), 123.7, 119.0, 101.3, 98.6, 38.9, 38.6, 21.5. IR (film, ν, cm^{-1}) 3024, 1489, 1454, 1228, 1047, 1007, 890, 752. HR-MS (APCI) m/z calcd for $C_{30}H_{24}ClO_2$ $[M+H]^+$ 451.1465, found 451.1466.

3'-phenyl-4-(p-tolyl)spiro[chroman-2,1'-isochromene] (3o)



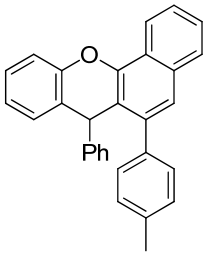
45.8 mg, 55%; white solid, mp 186-187 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.51-7.45 (m, 3H), 7.45-7.40 (m, 1H), 7.32 (d, J = 7.6 Hz, 2H), 7.30-7.26 (m, 5H), 7.21 (d, J = 7.6 Hz, 2H), 7.12-7.07 (m, 1H), 6.94 (d, J = 7.6 Hz, 1H), 6.91-6.86 (m, 1H), 6.81 (d, J = 8.0 Hz, 1H), 6.65 (s, 1H), 4.85-4.78 (m, 1H), 2.93-2.85 (m, 1H), 2.83-2.77 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 152.2, 149.5, 141.2, 136.6, 134.4, 130.8, 129.5(4), 129.5(0), 129.3, 128.9, 128.8, 128.4, 127.9, 127.1, 125.7, 125.2, 125.1, 123.7, 121.5, 117.5, 101.3, 98.6, 39.1, 38.5, 21.1. IR (film, ν, cm^{-1}) 3029, 1483, 1453, 1253, 1045, 1008, 881, 752. HR-MS (APCI) m/z calcd for $C_{30}H_{25}O_2$ $[M+H]^+$ 417.1855, found 417.1856.

6,7-diphenyl-7H-benzo[c]xanthene (4a)



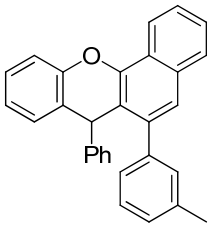
59.9 mg, 78%; white solid, mp 191-192 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.57 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.64-7.54 (m, 2H), 7.43 (s, 1H), 7.41-7.31 (m, 4H), 7.24 (d, J = 7.2 Hz, 1H), 7.16 (d, J = 7.6 Hz, 1H), 7.11-6.96 (m, 6H), 6.75-6.69 (m, 2H), 5.37 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.7, 147.0, 146.3, 140.5, 140.3, 133.0, 129.5, 129.1, 128.2, 127.9, 127.6, 127.5(0), 127.5(7), 127.1, 126.7, 126.1, 126.0, 125.7, 123. 8, 123.7, 121.9, 117.4, 116.7, 42.9. IR (film, ν, cm^{-1}) 3023, 1487, 1387, 1234, 1090, 887, 750. HR-MS (APCI) m/z calcd for $C_{29}H_{21}O$ $[M+H]^+$ 385.1592, found 385.1594.

7-phenyl-6-(p-tolyl)-7H-benzo[c]xanthene (4b)



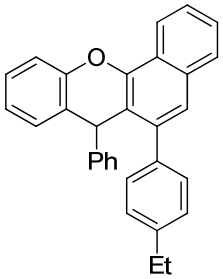
70.0 mg, 88%; white solid, mp 185-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.56 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.63-7.52 (m, 2H), 7.42 (s, 1H), 7.34-7.31 (m, 1H), 7.25-7.20 (m, 1H), 7.18-7.11 (m, 3H), 7.06-6.99 (m, 4H), 6.96 (d, J = 6.8 Hz, 2H), 6.77-6.73 (m, 2H), 5.37 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.8, 147.0, 146.3, 140.3, 137.6, 136.8, 133.0, 129.4, 129.0, 128.6, 128.2, 127.6, 127.5(7), 127.5(5), 126.6, 126.1, 126.0, 125.9, 123.9, 123.7(1), 123.7(6), 121.8, 117.6, 116.7, 43.0, 21.3. IR (film, ν, cm^{-1}) 3024, 1487, 1387, 1234, 1090, 814, 749. HR-MS (APCI) m/z calcd for $C_{30}H_{23}O$ $[M+H]^+$ 399.1749, found 399.1750.

7-phenyl-6-(m-tolyl)-7H-benzo[c]xanthene (4c)



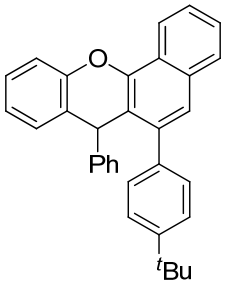
70.0 mg, 88%; white solid, mp 185-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.57 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.64-7.60 (m, 1H), 7.58-7.53 (m, 1H), 7.42 (s, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.24-7.15 (m, 4H), 7.05-6.99 (m, 4H), 6.90 (s, 1H), 6.81-6.71 (m, 3H), 5.31 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.7, 146.9, 146.5, 140.5, 140.4, 137.4, 133.0, 130.4, 129.0, 128.2, 127.8, 127.7, 127.6, 127.5(2), 127.5(8), 126.7, 126.4, 126.1, 125.9, 125.8, 123.7, 123.6, 121.8, 117.5, 116.7, 43.1, 21.4. IR (film, ν, cm^{-1}) 3021, 1487, 1390, 1242, 1090, 883,750. HR-MS (APCI) m/z calcd for $C_{30}H_{23}O$ $[M+H]^+$ 399.1749, found 399.1754.

6-(4-ethylphenyl)-7-phenyl-7H-benzo[c]xanthene (4d)



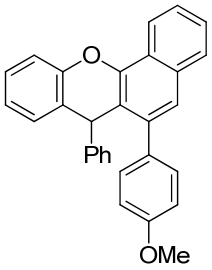
66.7 mg, 81%; white solid, mp 156-157 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.56 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.64-7.54 (m, 2H), 7.43 (s, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.25-7.21 (m, 1H), 7.17 (d, J = 7.6 Hz, 3H), 7.05-6.94 (m, 6H), 6.75-6.70 (m, 2H), 5.39 (s, 1H), 2.77-2.71 (m, 2H), 1.33 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.7, 146.9, 146.4, 143.3, 140.3, 137.8, 133.0, 129.4, 129.1, 128.2, 127.6, 127.5, 127.4, 126.7, 126.0, 125.9, 123.8, 123.7, 123.6, 121.8, 117.6, 116.7, 42.9, 28.7, 15.9. IR (film, ν, cm^{-1}) 3026,.1487, 1383, 1235, 1090, 852, 751. HR-MS (APCI) m/z calcd for $C_{31}H_{25}O$ $[M+H]^+$ 413.1905, found 413.1909.

6-(4-(tert-butyl)phenyl)-7-phenyl-7H-benzo[c]xanthene (4e)



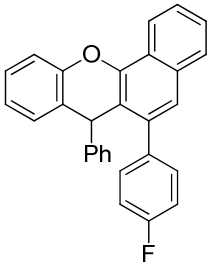
69.5 mg, 79%; white solid, mp 202-203 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.57 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.64-7.60 (m, 1H), 7.57-7.53 (m, 1H), 7.45 (s, 1H), 7.38-7.32 (m, 3H), 7.25-7.21 (m, 1H), 7.17-7.15 (m, 1H), 7.03-6.97 (m, 6H), 6.71-6.67 (m, 2H), 5.42 (s, 1H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.6, 150.1, 146.8, 146.4, 140.3, 137.6, 133.0, 129.2, 129.1, 128.1, 127.6(7), 127.6(5), 127.5, 126.6, 126.0, 125.8, 125.7, 124.8, 123.7(2), 123.7(9), 123.6, 121.8, 117.6, 116.6, 42.8, 34.6, 31.5. IR (film, ν, cm^{-1}) 3023, 1485, 1389, 1256, 1087, 830, 747. HR-MS (APCI) m/z calcd for $C_{33}H_{29}O$ $[M+H]^+$ 441.2218, found 441.2220.

6-(4-methoxyphenyl)-7-phenyl-7H-benzo[c]xanthene (4f)



52.2 mg, 63%; white solid, mp 196-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.57 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.65-7.53 (m, 2H), 7.42 (s, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.26-7.17 (m, 2H), 7.06-6.96 (m, 6H), 6.88 (d, J = 8.0 Hz, 2H), 6.77 (d, J = 6.8 Hz, 2H), 5.37 (s, 1H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 158.9, 150.8, 147.0, 146.4, 140.0, 133.0(2), 133.0(8), 130.6, 129.0, 128.3, 127.6, 127.5, 126.7, 126.1, 125.9(8), 125.9(5), 124.0, 123.7(9), 123.7(6), 121.8, 117.8, 116.7, 113.3, 55.4, 43.0. IR (film, ν, cm^{-1}) 3026, 1487, 1388, 1254, 1091, 825. 744. HR-MS (APCI) m/z calcd for $C_{30}H_{23}O_2$ $[M+H]^+$ 415.1698, found 415.1703.

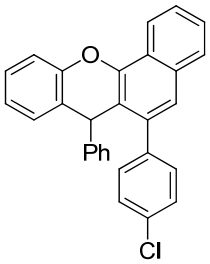
6-(4-fluorophenyl)-7-phenyl-7H-benzo[c]xanthene (4g)



66.7 mg, 83%; white solid, mp 184-185 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.57 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.65-7.54 (m, 2H), 7.39 (s, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.25-7.21 (m, 1H), 7.16 (d, J = 7.6 Hz, 1H), 7.01-6.94 (m, 8H), 6.76-6.72 (m, 2H), 5.29 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 162.2($^{1}J_{CF}$ = 244.4Hz), 150.5, 147.0, 146.3, 139.3, 136.5($^{4}J_{CF}$ = 3.3Hz), 132.9, 131.1($^{3}J_{CF}$ = 7.9Hz), 129.1, 128.3, 127.7, 127.5, 126.8, 126.2, 126.1, 125.4, 123.9, 123.8, 123.7, 121. 9, 117.3, 116.7, 114.7($^{2}J_{CF}$ = 21.2 Hz), 43.0. IR

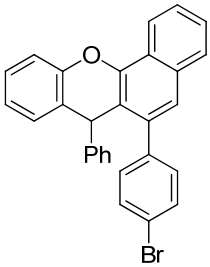
(film, ν, cm^{-1}) 3030, 1487, 1386, 1232, 1092, 830, 748. HR-MS (APCI) m/z calcd for $C_{29}H_{20}FO$ $[M+H]^+$ 403.1498, found 403.1497.

6-(4-chlorophenyl)-7-phenyl-7H-benzo[c]xanthene (4h)



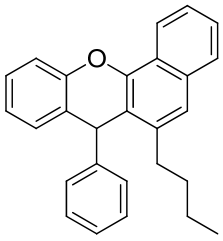
63.5 mg, 76%; white solid, mp 196-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.56 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.65-7.54 (m, 2H), 7.38 (s, 1H), 7.34-7.27 (m, 3H), 7.25-7.20 (m, 1H), 7.18-7.14 (m, 1H), 7.07-6.92 (m, 6H), 6.78-6.73 (m, 2H), 5.28 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.5, 147.0, 146.2, 139.0, 133.2, 132.9, 130.8, 129.0, 128.4, 128.0, 127.7, 127.5(8), 127.5(5), 126.9, 126.3, 126.2, 125.4, 123.9, 123.8(0), 123.8(6), 121.9, 117.1, 116.7, 43.0. IR (film, ν, cm^{-1}) 3028, 1487, 1386, 1233, 1087, 848, 747. HR-MS (APCI) m/z calcd for $C_{29}H_{20}ClO$ $[M+H]^+$ 419.1203, found 419.1208.

6-(4-bromophenyl)-7-phenyl-7H-benzo[c]xanthene (4i)



72.1 mg, 78%; white solid, mp 192-193 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm). 8.54-8.50 (m, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.65-7.60 (m, 1H), 7.58-7.53 (m, 1H), 7.43 (s, 1H), 7.40-7.32 (m, 3H), 7.31-7.27 (m, 2H), 7.21 (d, J = 8.4 Hz, 1H), 7.08-6.97 (m, 5H), 6.70-6.66 (m, 2H), 5.31 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) IR (film, ν, cm^{-1}). 149.8, 146.6, 145.6, 140.2, 140.1, 133.0, 131.7, 130.6, 129.4, 128.4, 128.0, 127.8, 127.6, 127.4, 127.3, 126.9, 126.4, 126.1, 124.1, 123.6, 121.7, 118.5, 116.8, 115.8, 42.8. IR (film, ν, cm^{-1}) 3041, 1487, 1385, 1234, 1092, 827, 755. HR-MS (APCI) m/z calcd for $C_{29}H_{20}BrO$ $[M+H]^+$ 463.0698, found 463.0691.

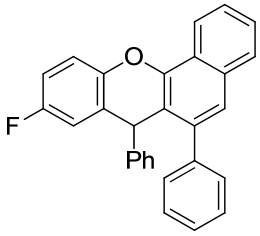
6-butyl-7-phenyl-7H-benzo[c]xanthene (4j)



35.7 mg,49%; white solid, mp 140-141 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm). 8.51-8.48 (m, 1H), 7.78-7.74 (m, 1H), 7.57-7.49 (m, 2H), 7.40-7.35 (m, 2H), 7.31-7.27 (m, 1H), 7.24-7.17 (m, 5H), 7.13-7.08 (m, 1H), 7.07-7.03 (m, 1H), 5.46 (s, 1H), 2.81-2.73 (m, 1H), 2.61-2.52 (m, 1H), 1.66-1.57 (m, 1H), 1.42-1.34 (m, 3H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.6, 147.1, 146.2, 139.1, 133.4, 128.9, 128.8, 127.6, 127.4, 126.9, 126.5, 126.3, 125.7, 125.1, 123.5, 123.0, 122.2, 121.8, 117.8, 116.7, 42.8, 32.8, 32.2, 22.8,

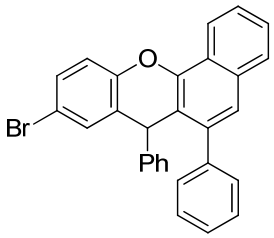
14.0. IR (film, ν, cm^{-1}) 3021, 1487, 1394, 1258, 1098, 848, 750. HR-MS (APCI) m/z calcd for $C_{27}H_{25}O$ $[M+H]^+$ 365.1905, found 365.1907.

9-fluoro-6,7-diphenyl-7H-benzo[c]xanthene (4l)



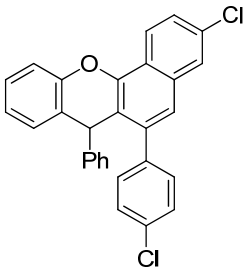
57.9 mg, 72%; white solid, mp 164-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm). 8.56-8.52 (m, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.64-7.60 (m, 1H), 7.59-7.54 (m, 1H), 7.43 (s, 1H), 7.38-7.27 (m, 4H), 7.08-6.99 (m, 5H), 6.95-6.90 (m, 1H), 6.86-6.83 (m, 1H), 6.71-6.67 (m, 2H), 5.32 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 158.7($^1J_{CF}$ = 239.9Hz), 146.8($^6J_{CF}$ = 2.1Hz), 145.7, 140.4, 140.1, 133.0, 129.4, 128.3, 127.9, 127.5, 127.4, 127.2, 127.0($^5J_{CF}$ = 7.5Hz), 126.8, 126.4, 126.1, 123.9, 123.6, 121.8, 117.8($^4J_{CF}$ = 8.3Hz), 116.4, 115.0($^3J_{CF}$ = 23.1Hz), 114.6($^2J_{CF}$ = 23.5Hz), 43.14. IR (film, ν, cm^{-1}) 3023, 1490, 1394, 1214, 1026, 852, 766. HR-MS (APCI) m/z calcd for $C_{29}H_{20}FO$ $[M+H]^+$ 403.1498, found 403.1497.

9-bromo-6,7-diphenyl-7H-benzo[c]xanthene (4m)



55.4 mg, 60%; white solid, mp 209-210 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm). 8.57 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.66-7.62 (m, 1H), 7.59-7.55 (m, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.39 (s, 1H), 7.35-7.31 (m, 1H), 7.25-7.21 (m, 1H), 7.18-7.15 (m, 1H), 7.06-7.01 (m, 4H), 6.92 (d, J = 5.6 Hz, 2H), 6.78-6.75 (m, 2H), 5.29 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.5, 147.1, 146.2, 139.5, 139.0, 132.9, 131.2, 131.0, 129.0, 128.4, 127.7, 127.5(0), 127.5(6), 126.9, 126.3, 126.2, 125.4, 123.9, 123.8(8), 123.8(5), 121.9, 121.4, 117.0, 116.7, 43.0. IR (film, ν, cm^{-1}) 3056, 1492, 1394, 1254, 1091, 850, 757. HR-MS (APCI) m/z calcd for $C_{29}H_{20}BrO$ $[M+H]^+$ 463.0698, found 463.0693.

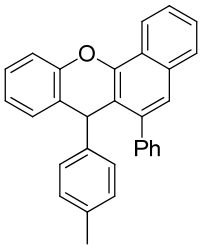
3-chloro-6-(4-chlorophenyl)-7-phenyl-7H-benzo[c]xanthene (4n)



55.1 mg, 61%; white solid, mp 196-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm). 8.55 (d, J = 2.0 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.54-7.50 (m, 1H), 7.38-7.30 (m, 4H), 7.28-7.24 (m, 1H), 7.19-7.16 (m, 1H), 7.09-7.03 (m, 4H), 6.98 (s, 2H), 6.78-6.73 (m, 2H), 5.29 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.7, 146.9, 146.4, 143.3, 140.3, 137.8, 133.0, 129.4, 129.1, 128.2, 127.6, 127.5, 127.4, 126.7, 126.0, 125.9, 123.8, 123.7, 123.6,

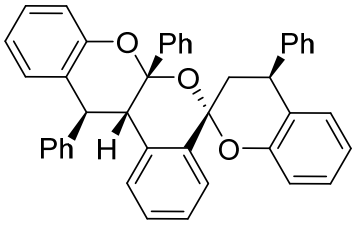
121.8, 117.6, 116.7, 42.9, 28.7, 15.9. IR (film, ν, cm^{-1}) 3014, 1493, 1382, 1250, 1098, 887, 748. HR-MS (APCI) m/z calcd for $C_{29}H_{19}Cl_2O$ $[M+H]^+$ 453.0813, found 453.0819.

6-phenyl-7-(p-tolyl)-7H-benzo[c]xanthene (4o)



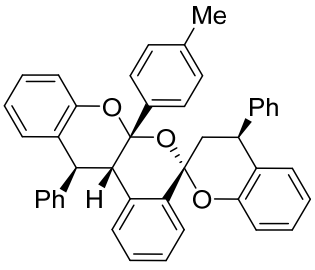
60.5 mg, 76%; white solid, mp 160-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm). 8.56 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.63-7.59 (m, 1H), 7.56-7.53 (m, 1H), 7.43 (s, 1H), 7.38-7.30 (m, 4H), 7.23-7.19 (m, 1H), 7.16-7.14 (m, 1H), 7.09 (s, 2H), 7.02-6.98 (m, 1H), 6.81 (d, J = 8.0 Hz, 2H), 6.60 (d, J = 8.0 Hz, 2H), 5.31 (s, 1H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.8, 147.0, 143.4, 140.6, 140.3, 135.6, 132.9, 129.5, 128.9(4), 128.9(2), 127.9, 127.5, 127.2, 127.1, 126.6, 126.1, 125.9, 123.8, 123.7, 121.8, 117.6, 116.6, 42.5, 20.9. IR (film, ν, cm^{-1}) 3021, 1485, 1391, 1238, 1088, 820, 752. HR-MS (APCI) m/z calcd for $C_{30}H_{23}O$ $[M+H]^+$ 399.1749, found 399.1740.

4,6a',12'-triphenyl-12',12a'-dihydro-6a'H-spiro[chroman-2,5'-isochromeno[3,4-b]chromene] (5a)



84.1 mg,72%; white solid, mp 182-183 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm). 7.38 (d, J = 7.2 Hz, 2H), 7.33-7.29 (m, 6H),7.27-7.23 (m, 3H), 7.21-7.13 (m, 5H), 7.04-6.93 (m, 5H), 6.89-6.85 (m, 2H), 6.81-6.73 (m, 2H), 6.46 (d, J = 8.0 Hz, 1H), 6.30 (d, J = 7.6 Hz, 1H), 4.57-4.51 (m, 1H), 4.15 (d, J = 10.8 Hz, 1H), 3.93 (d, J = 10.4 Hz, 1H), 2.47 (d, J = 10.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 152.6, 151.9, 143.9, 141.9, 140.5, 135.7, 134.9, 130.2, 129.2(0), 129.2(5), 129.1, 128.6(3), 128.6(5), 128.5, 128.3, 128.0, 127.9, 127.8, 127.6, 127.5(9), 127.5(5), 127.2, 126.9, 126.8, 125.9, 124.3, 121.3, 120.9, 117.9, 117.1, 99.3, 99.1, 48.0, 45.3, 45.2, 38.8. IR (film, ν, cm^{-1}) 3022, 1487, 1455, 1227, 1003, 884, 750. HR-MS (APCI) m/z calcd for $C_{42}H_{33}O_3$ $[M+H]^+$ 585.2430, found 585.2433.

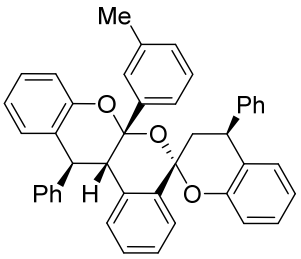
4,12'-diphenyl-6a'-(p-tolyl)-12',12a'-dihydro-6a'H-spiro[chroman-2,5'-isochromeno[3,4-b]chromene] (5b)



63.4 mg, 53%; white solid, mp 227-228 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm). 7.34-7.26 (m, 9H), 7.24 (s, 2H), 7.20-7.14 (m, 3H), 7.04-6.98 (m, 5H), 6.96-6.92 (m, 1H), 6.89-6.84 (m, 2H), 6.80 (d, J = 7.6 Hz, 1H), 6.73 (d, J = 7.6 Hz, 1H), 6.53-6.49 (m, 1H), 6.29 (d, J = 7.2 Hz, 1H), 4.57-4.50 (m, 1H), 4.15 (d, J = 10.8 Hz, 1H),

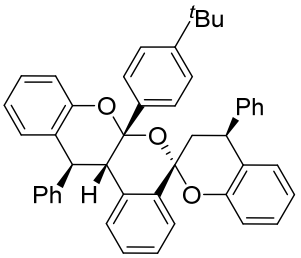
3.92 (d, J = 10.4 Hz, 1H), 2.52-2.45 (m, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.5, 149.8, 144.1, 142.1, 140.7, 135.7, 135.0, 130.4, 130.2, 130.0, 129.4, 129.3, 129.1, 128.6, 128.5, 128.4, 128.2, 128.2, 127.9, 127.7, 127.6, 127.4, 127.1, 126.9, 126.7, 125.5, 123.9, 117.7, 116.9, 99.2, 99.1, 48.1, 45.7, 45.4, 38.8, 20.7. IR (film, ν, cm^{-1}) 3028, 1486, 1451, 1230, 1005, 823, 758. HR-MS (APCI) m/z calcd for $C_{44}H_{35}O_3$ $[M+H]^+$ 599.2586, found 599.2587.

4,12'-diphenyl-6a'-(m-tolyl)-12',12a'-dihydro-6a'H-spiro[chroman-2,5'-isochromeno[3,4-b]chromene] (5c)



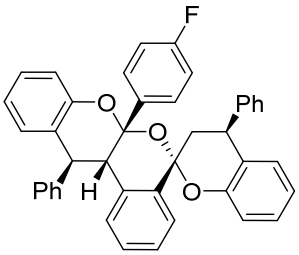
76.5 mg, 64%; white solid, mp 254-255 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm). 7.34-7.31 (m, 2H), 7.30-7.28 (m, 3H), 7.26-7.23 (m, 5H), 7.20-7.13 (m, 3H), 7.08-7.04 (m, 3H), 7.02-6.97 (m, 3H), 6.96-6.93 (m, 1H), 6.88-6.84 (m, 2H), 6.80 (d, J = 7.6 Hz, 1H), 6.72 (d, J = 7.6 Hz, 1H), 6.46-6.43 (m, 1H), 6.29 (d, J =7.2 Hz, 1H), 4.57-4.51 (m, 1H), 4.14 (d, J = 10.8 Hz, 1H), 3.92 (d, J = 10.8 Hz, 1H), 2.52-2.45 (m, 2H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 152.7, 151.9, 143.9, 141.9, 140.3, 136.9, 135.7, 134.8, 130.2, 129.3, 129.2, 129.1(1), 129.1(7), 129.0, 128.6, 128.5, 128.4, 128.0, 127.9, 127.7, 127.4, 127.2, 127.1, 126.9, 126.8, 125.9, 124.3, 123.9, 121.2, 120.9, 118.0, 117.1, 108.1, 99.3, 99.1, 48.0, 45.3, 45.2, 38.8, 21.5. IR (film, ν, cm^{-1}) 3026, 1486, 1449, 1234, 1007, 890, 750. HR-MS (APCI) m/z calcd for $C_{44}H_{35}O_3$ $[M+H]^+$ 599.2586, found 599.2583.

6a'-(4-(tert-butyl)phenyl)-4,12'-diphenyl-12',12a'-dihydro-6a'H-spiro[chroman-2,5'-isochromeno[3,4-b]chromene] (5d)



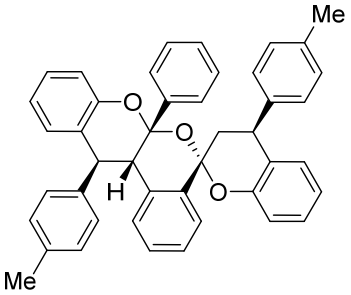
70.4 mg, 55%; white solid, mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm). 7.38-7.34 (m, 3H), 7.34-7.32 (m, 4H), 7.30 (s, 2H), 7.26 (s, 2H), 7.25-7.20 (m, 4H), 7.18 (d, J = 7.6 Hz, 1H), 7.05-7.01 (m, 3H), 6.99 (d, J = 8.0 Hz, 1H), 6.91-6.88 (m, 2H), 6.82 (d, J = 7.6 Hz, 1H), 6.75 (d, J = 7.6 Hz, 1H), 6.42 (d, J = 8.0 Hz, 1H), 6.34 (d, J = 7.6 Hz, 1H), 4.58-4.52 (m, 1H), 4.15 (d, J = 10.4 Hz, 1H), 3.94 (d, J = 10.4 Hz, 1H), 2.54-2.47 (m, 2H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 152.7, 151.9, 150.8, 144.0, 142.1, 137.6, 136.0, 134.9, 130.2, 129.2, 129.1, 128.6, 128.5(0), 128.5(5), 128.3, 127.9(3), 127.9(5), 127.6, 127.4, 127.1(2), 127.1(8), 126.9, 126.8, 125.9, 124.4, 124.3, 121.2, 120.8, 118.0, 117.1, 99.2, 99.1, 48.1, 45.5, 45.1, 38.8, 34.5, 31.3, 31.2. IR (film, ν, cm^{-1}) 3028, 1487, 1453, 1228, 1109, 891, 768. HR-MS (APCI) m/z calcd for $C_{46}H_{41}O_3$ $[M+H]^+$ 641.3056, found 641.3060.

6a'-(4-fluorophenyl)-4,12'-diphenyl-12',12a'-dihydro-6a'H-spiro[chroman-2,5'-isochromeno[3,4-b]chromene] (5e)

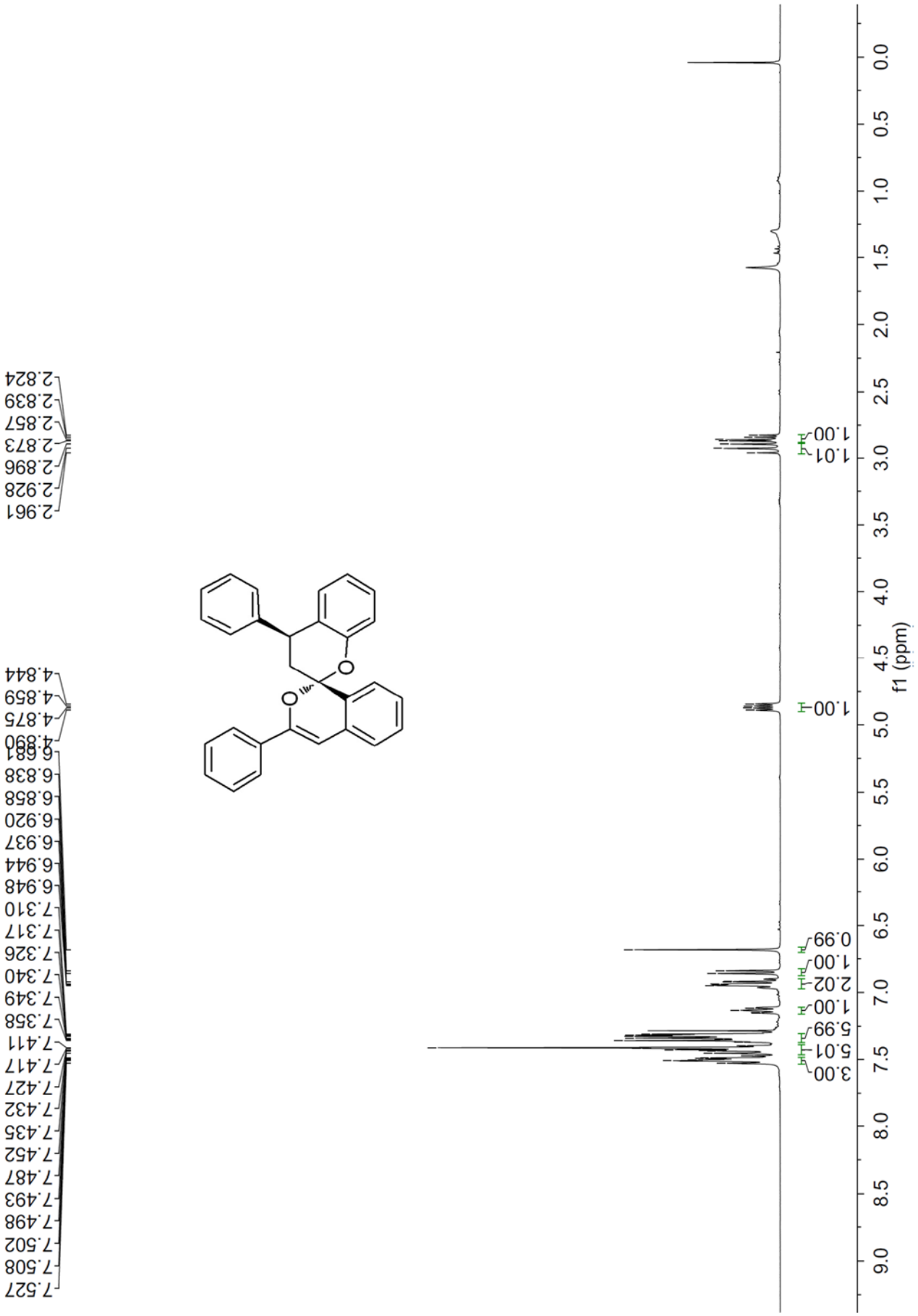


69.8 mg, 58%; white solid, mp 285-286 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm). 7.37-7.27 (m, 9H), 7.25-7.20 (m, 3H), 7.19-7.14 (m, 2H), 7.03-6.98 (m, 3H), 6.95-6.92 (m, 1H), 6.90-6.84 (m, 4H), 6.80 (d, J = 8.0 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 6.50-6.46 (m, 1H), 6.29 (d, J = 7.2 Hz, 1H), 4.56-4.49 (m, 1H), 4.14 (d, J = 10.8 Hz, 1H), 3.88 (d, J = 10.8 Hz, 1H), 2.52-2.43 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 162.4($^{1}J_{CF}$ = 239.9Hz), 152.5, 151.8, 143.8, 141.7, 136.5 ($^{4}J_{CF}$ = 3.3Hz), 135.4, 134.8, 130.2, 129.6, 129.5($^{3}J_{CF}$ = 8.3Hz), 129.3, 129.2, 129.1, 128.7, 128.5, 128.1, 128.0, 127.9, 127.6, 127.3, 127.0, 126.9, 125.9, 124.2, 121.4, 121.0, 117.7, 117.0, 114.3($^{2}J_{CF}$ = 21.3), 99.3, 98.7, 47.9, 45.4, 45.2, 38.7. IR (film, ν, cm^{-1}) 3028, 1488, 1449, 1231, 1040, 918, 747. HR-MS (APCI) m/z calcd for $C_{42}H_{32}FO_3$ $[M+H]^+$ 603.2335, found 603.2343.

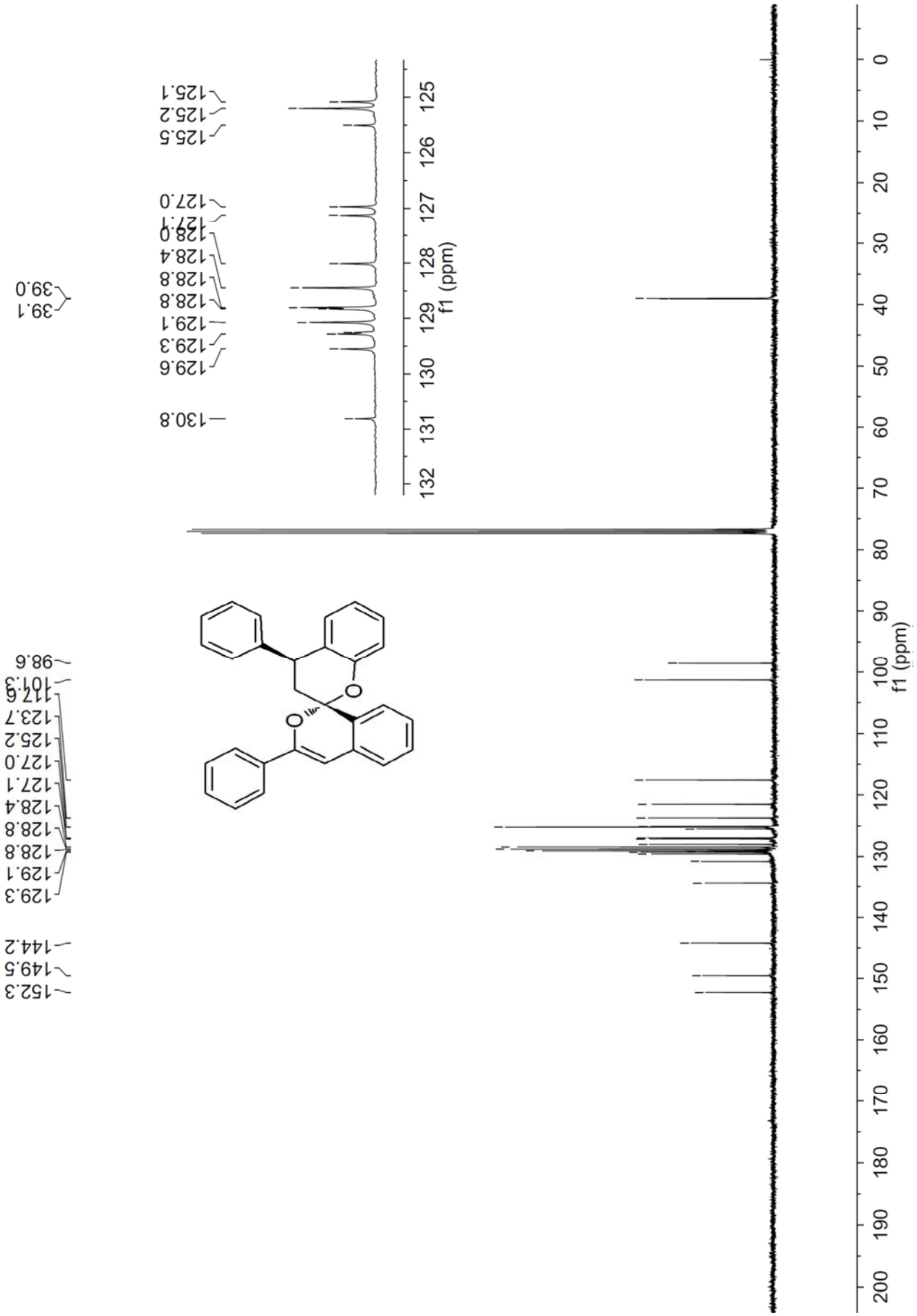
6a'-phenyl-4,12'-di-p-tolyl-12',12a'-dihydro-6a'H-spiro[chroman-2,5'-isochromeno[3,4-b]chromene] (5e)



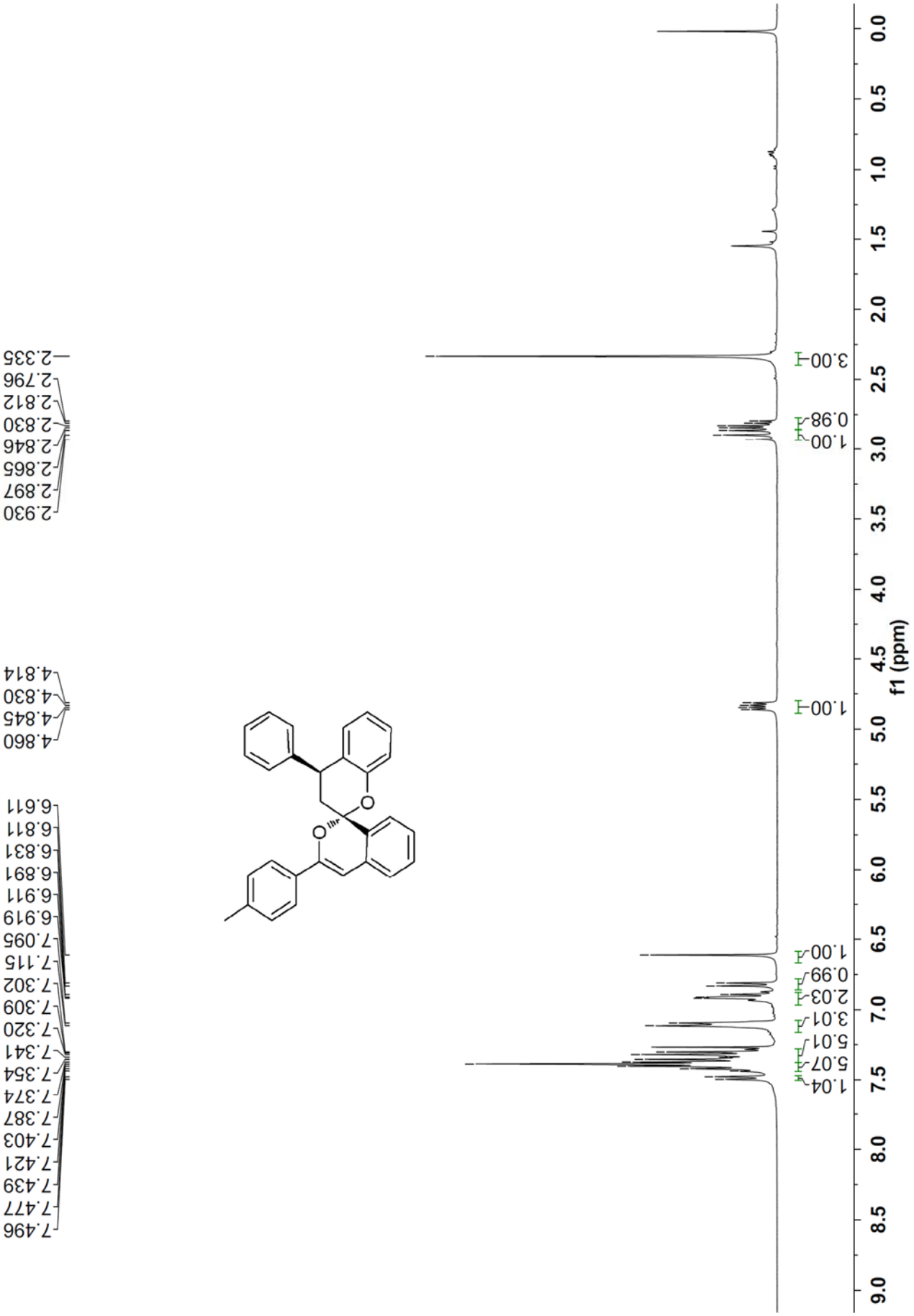
77.1 mg, 63%; white solid, mp 234-235 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.38 (d, J = 7.2 Hz, 2H), 7.33-7.29 (m, 6H), 7.25-7.22 (m, 3H), 7.21-7.15 (m, 4H), 7.02-6.94 (m, 5H), 6.83 (d, J = 8.0 Hz, 1H), 6.55 (d, J = 26.4 Hz, 2H), 6.37 (d, J = 8.4 Hz, 1H), 6.28 (d, J = 8.0 Hz, 1H), 4.49-4.44 (m, 1H), 4.09 (d, J = 10.4Hz, 1H),, 3.89 (d, J = 10.8 Hz, 1H), 2.47-2.41 (m, 2H), 2.19 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 150.5, 149.8, 144.1, 142.1, 140.7, 135.7, 135.0, 130.4, 130.2, 130.0, 129.4, 129.3, 129.1, 128.6, 128.5, 128.4, 128.3, 128.2(3), 128.2(9), 127.9, 127.7, 127.6, 127.4, 127.3, 127.1, 126.9, 126.7, 125.5, 123.9, 117.7, 116.9, 99.2, 99.1, 48.1, 45.7, 45.4, 38.8, 20.7. IR (film, ν, cm^{-1}) 3025, 1485, 1450, 1232, 1004, 912, 754. HR-MS (APCI) m/z calcd for $C_{44}H_{37}O_3$ $[M+H]^+$ 613.2743, found 613.2749.



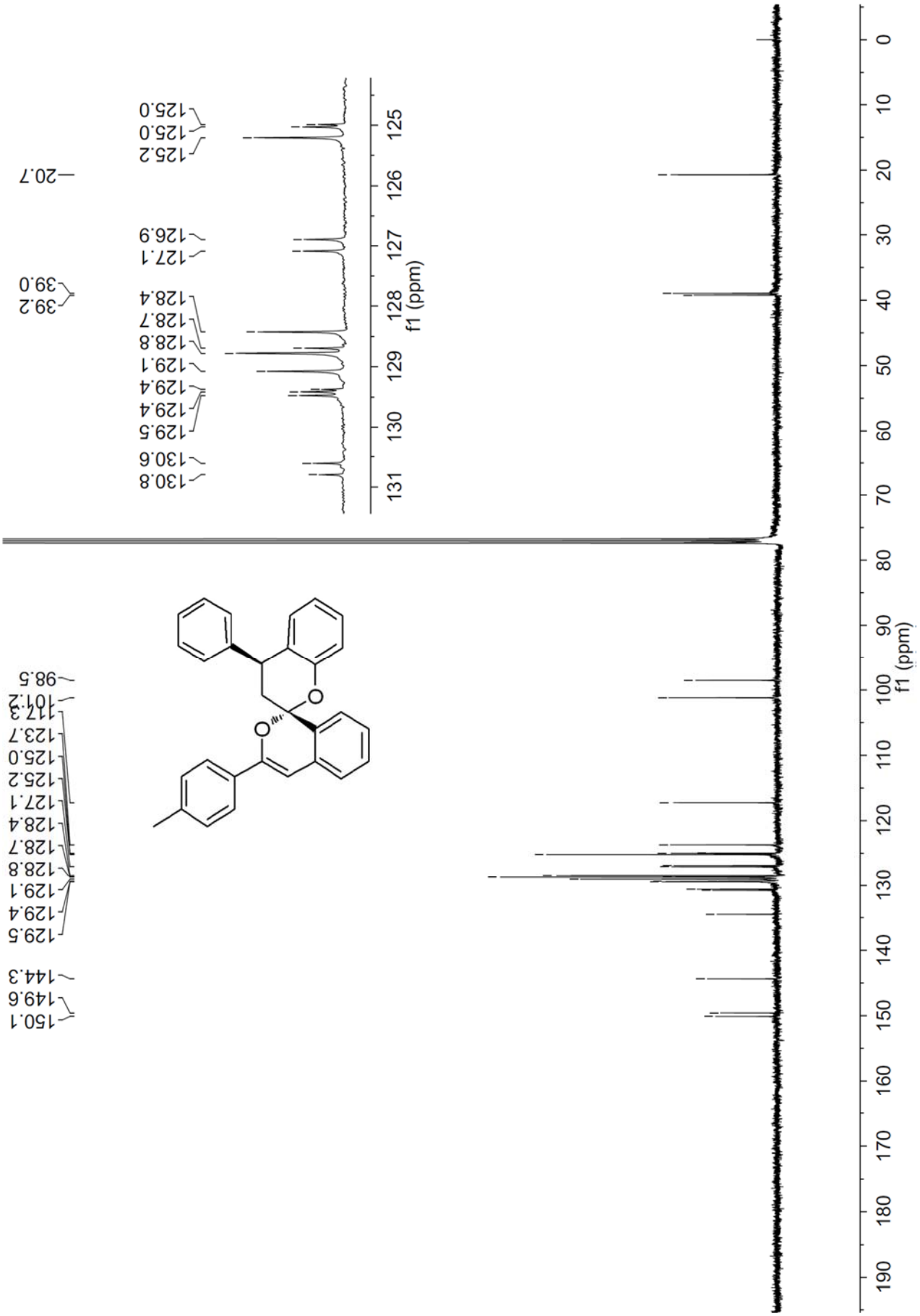
^{1}H NMR Spectrum of Compound 3a



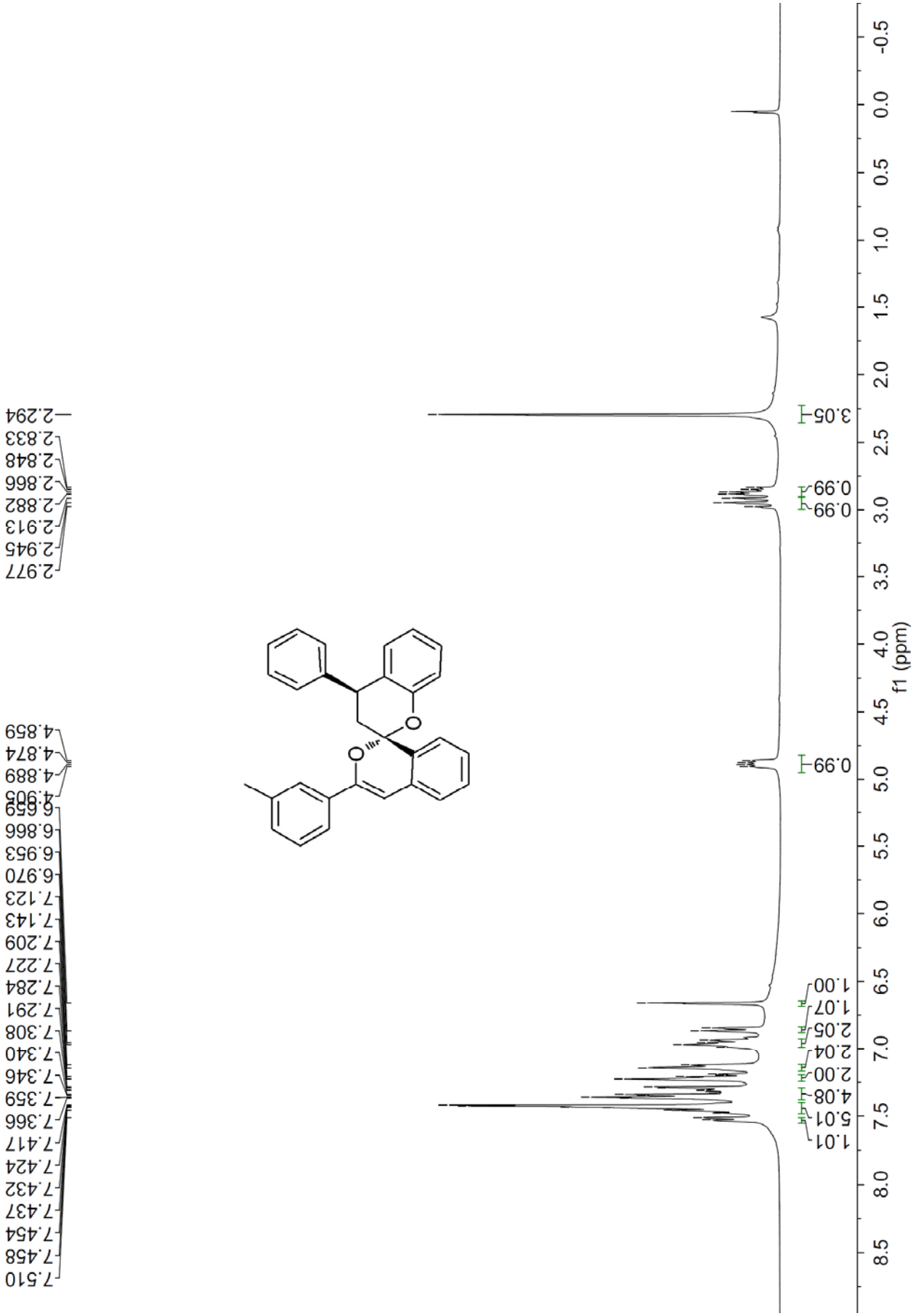
^{13}C NMR Spectrum of Compound 3a



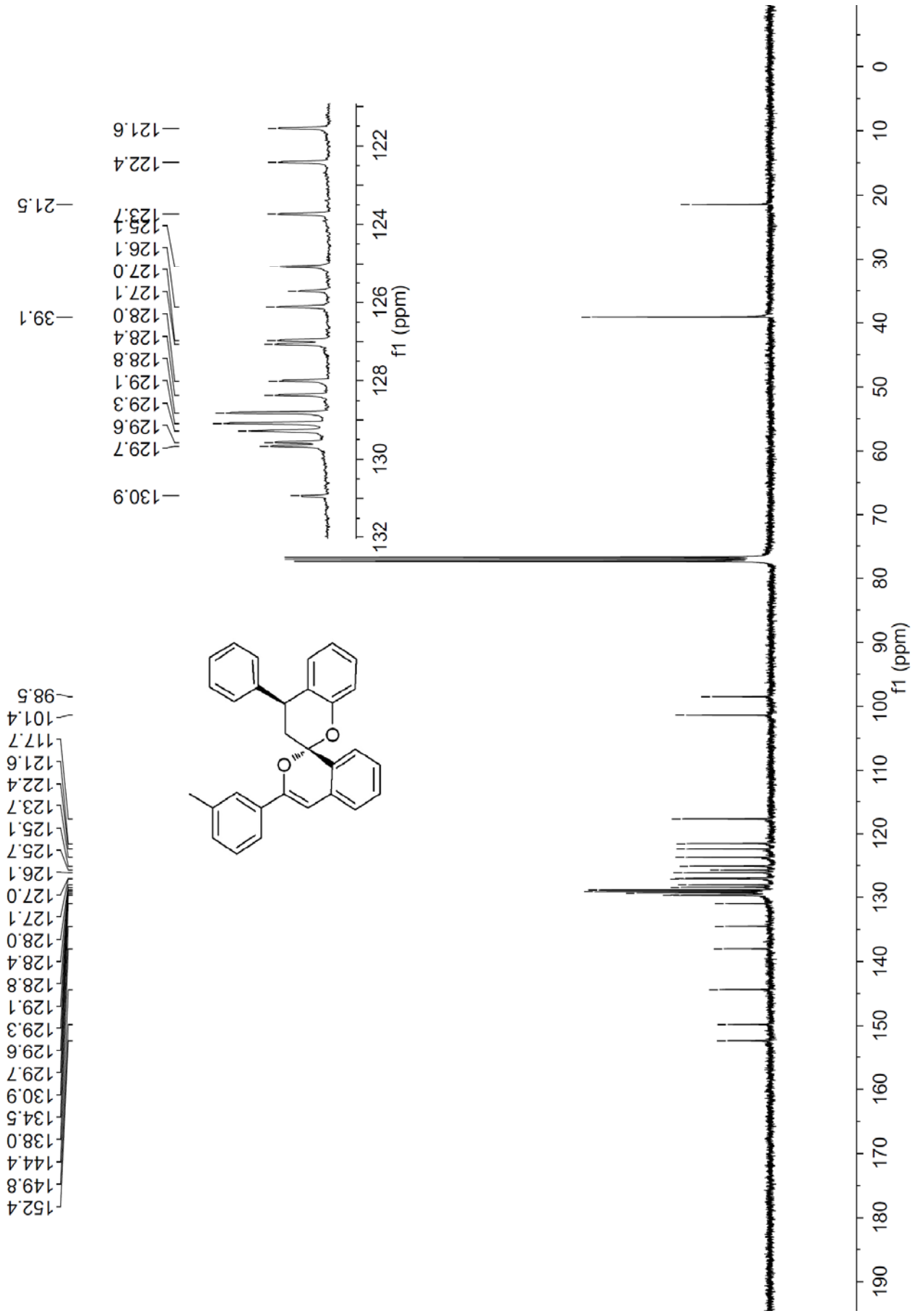
^{1}H NMR Spectrum of Compound 3b



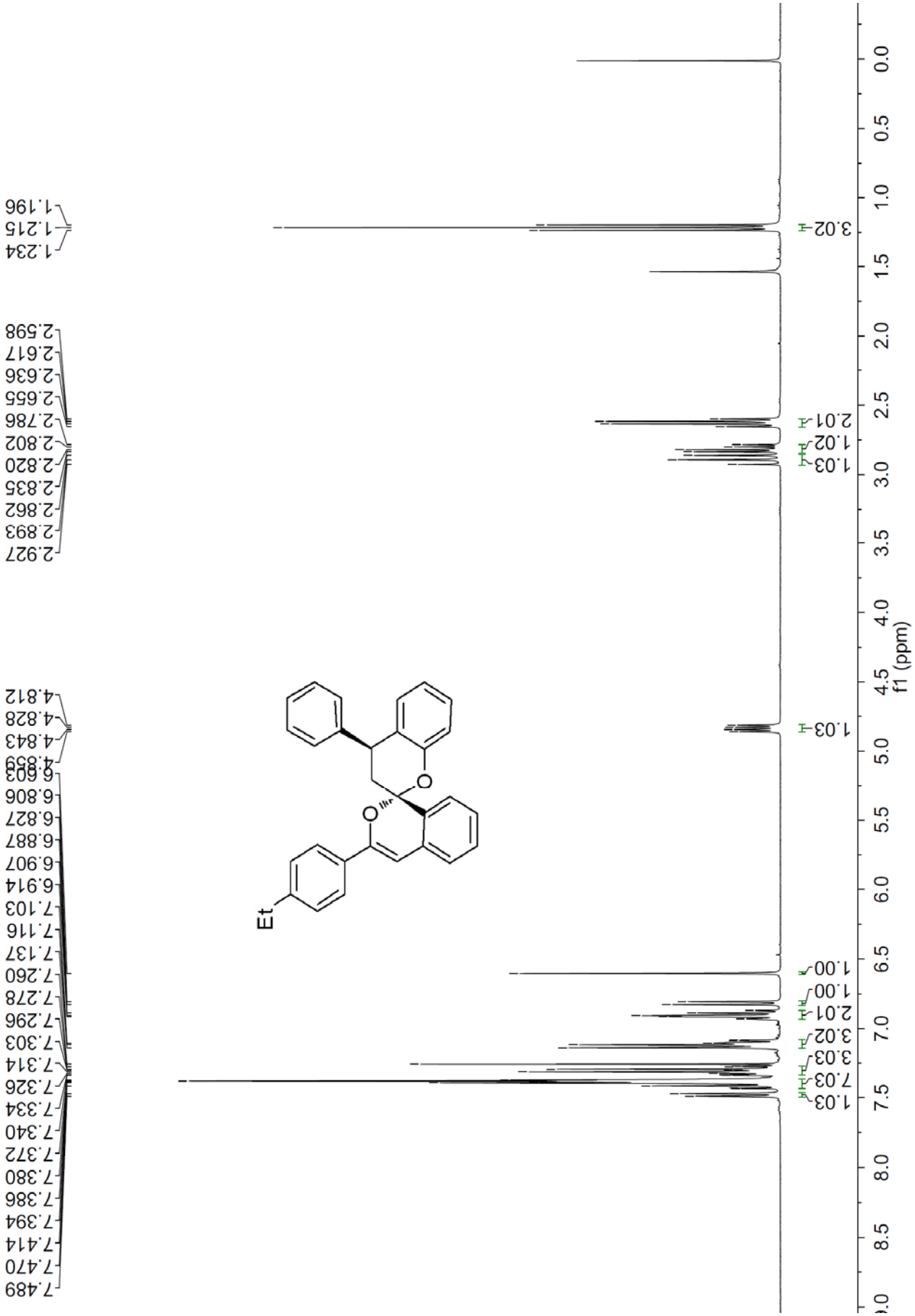
^{13}C NMR Spectrum of Compound 3b



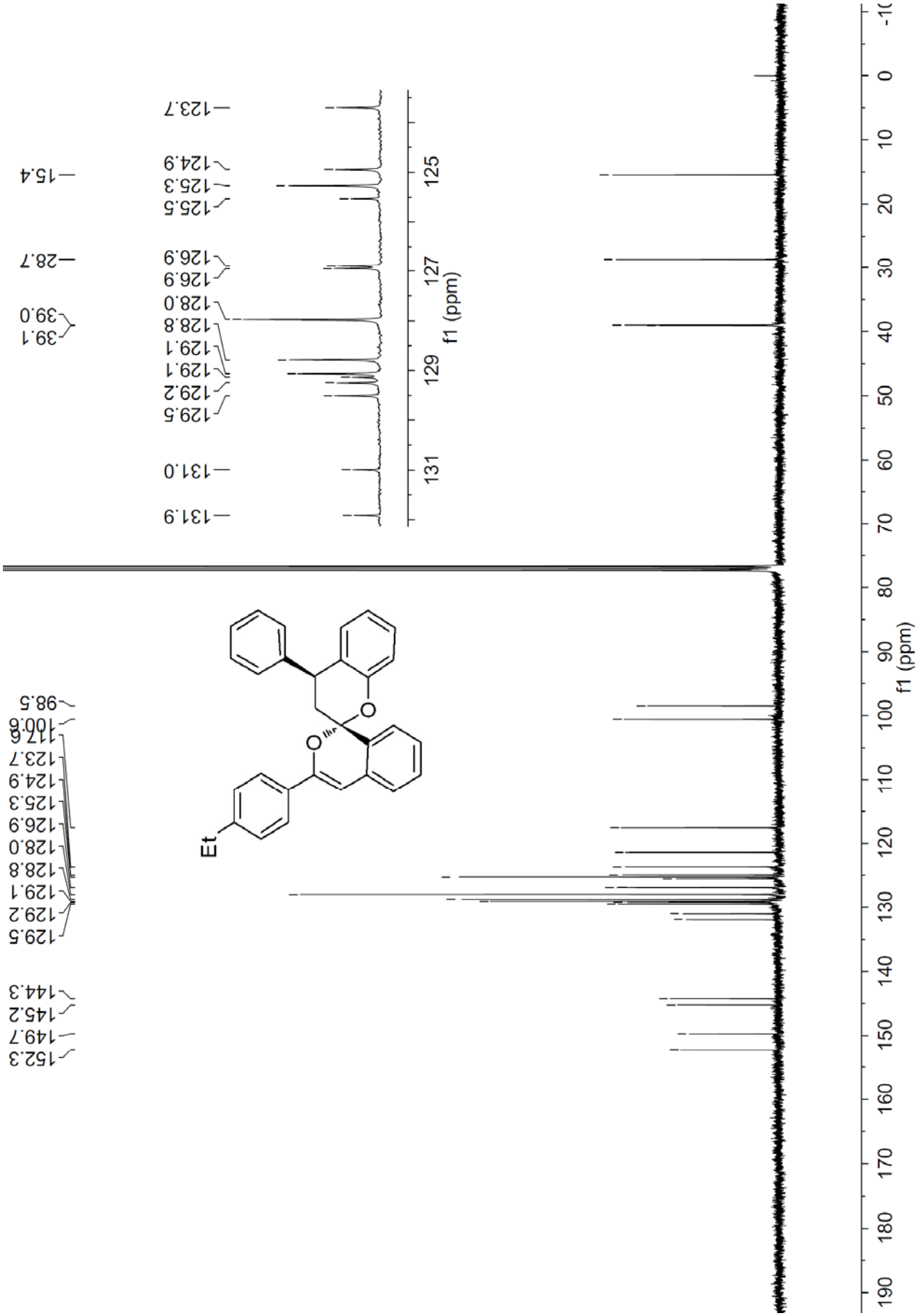
^{1}H NMR Spectrum of Compound 3c



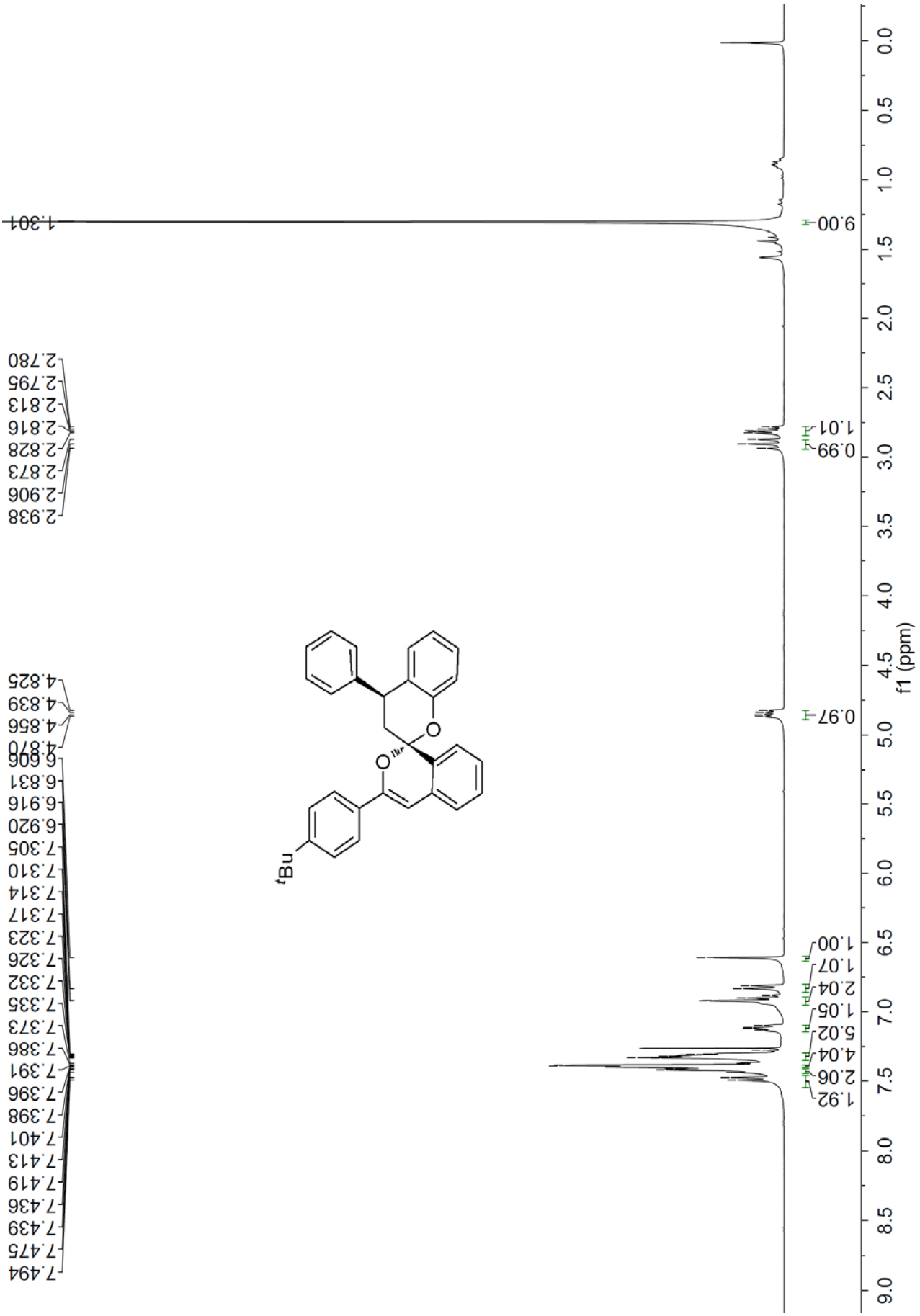
^{13}C NMR Spectrum of Compound 3c



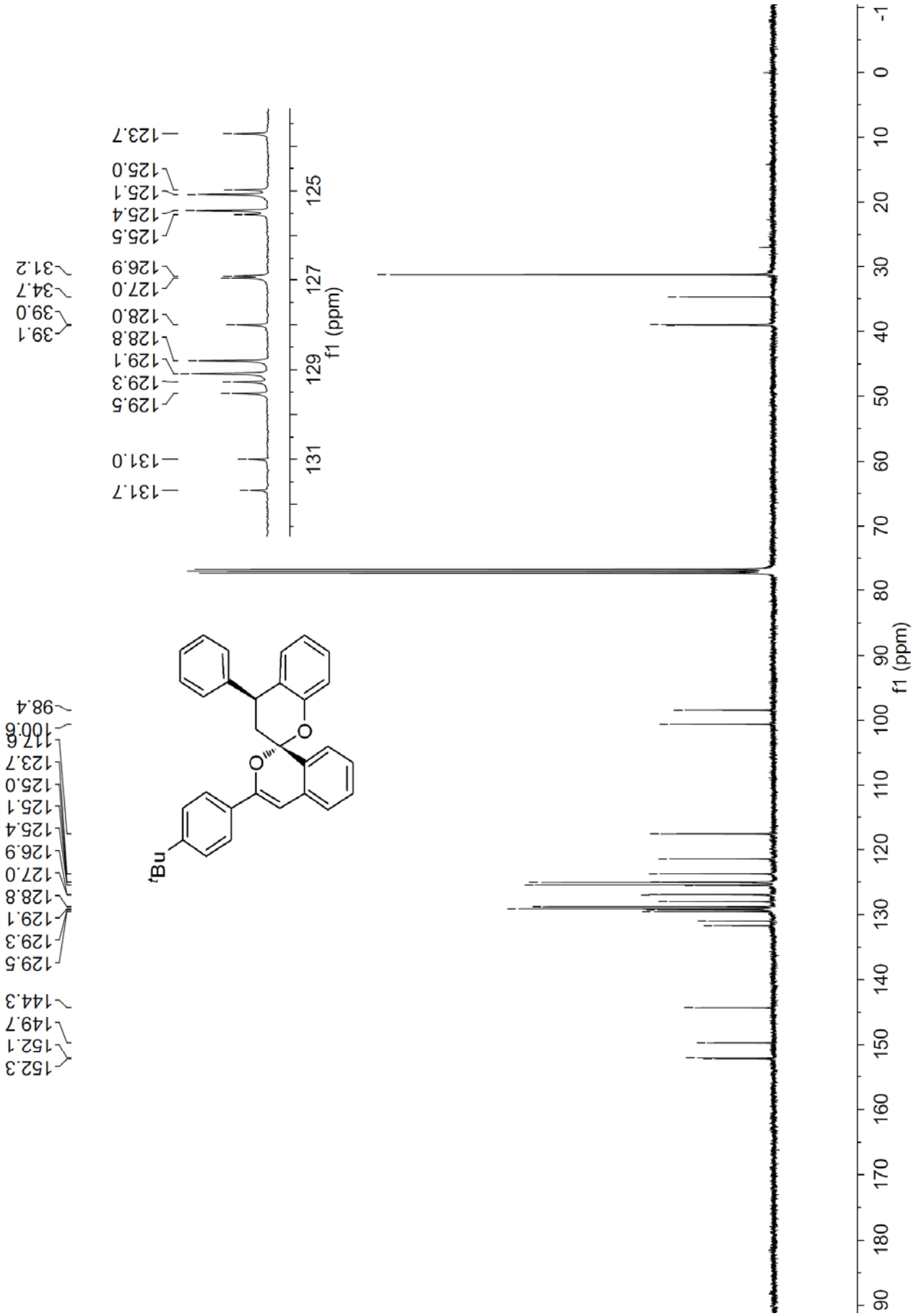
^{1}H NMR Spectrum of Compound 3d



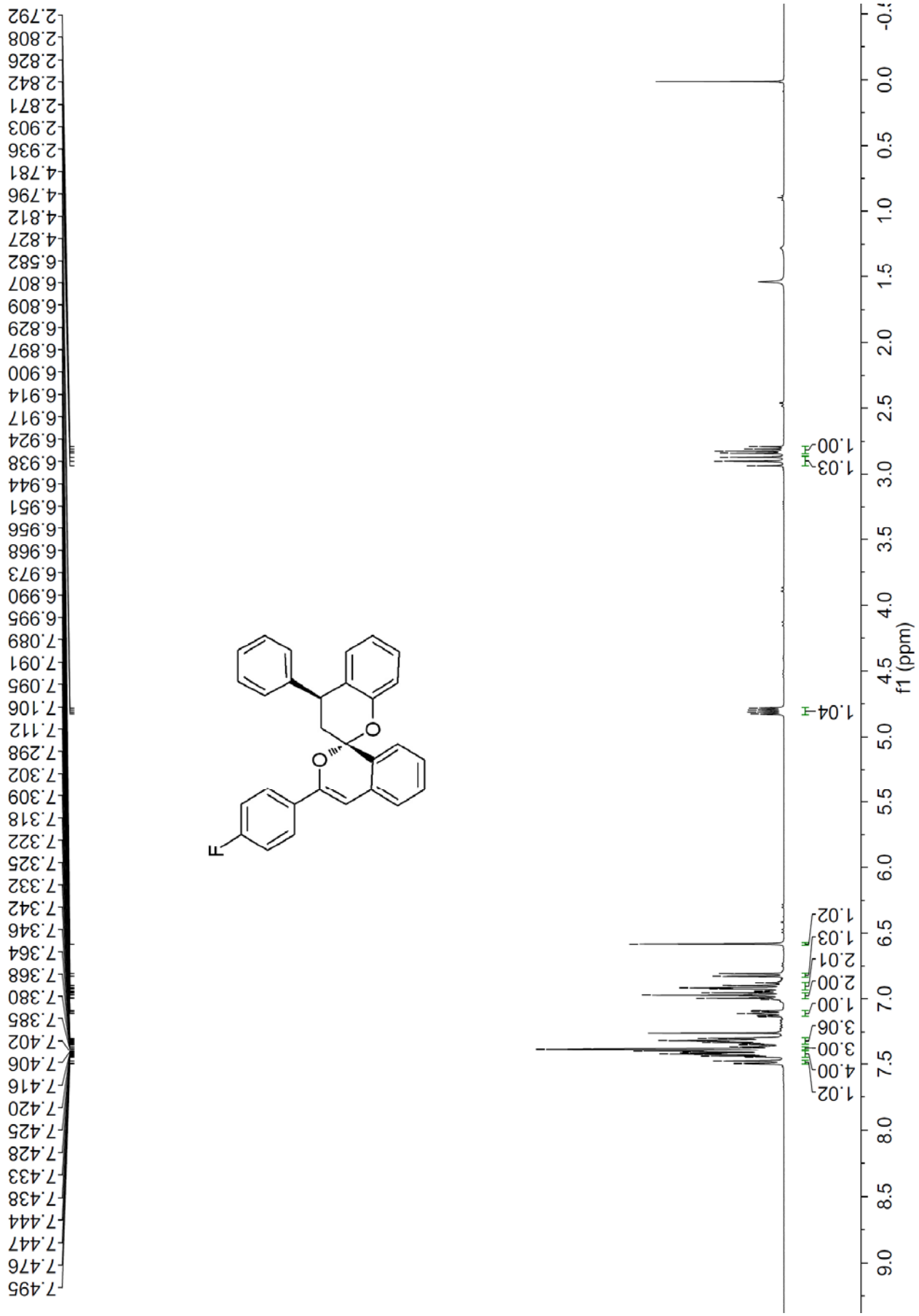
^{13}C NMR Spectrum of Compound 3d



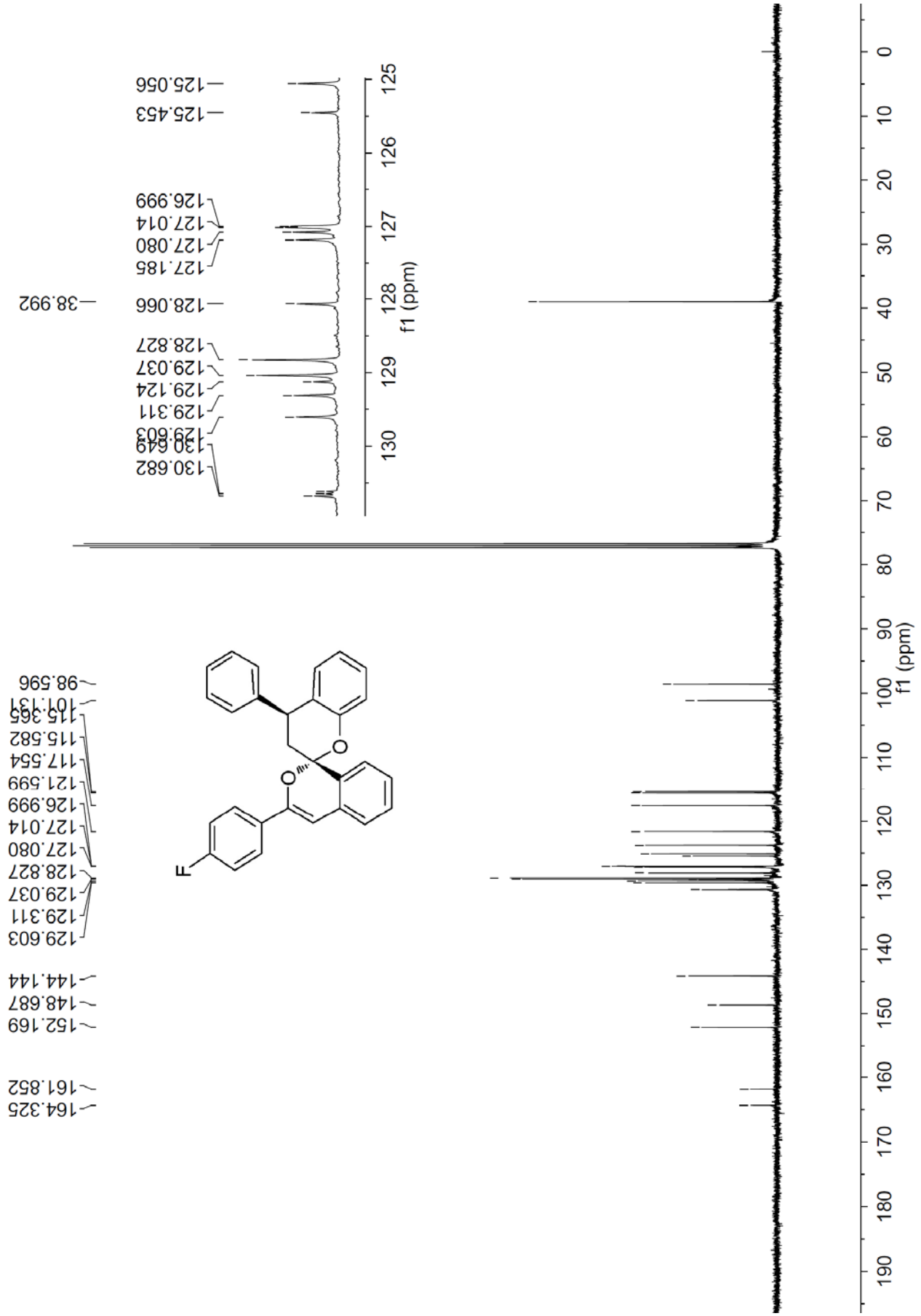
^{1}H NMR Spectrum of Compound 3e



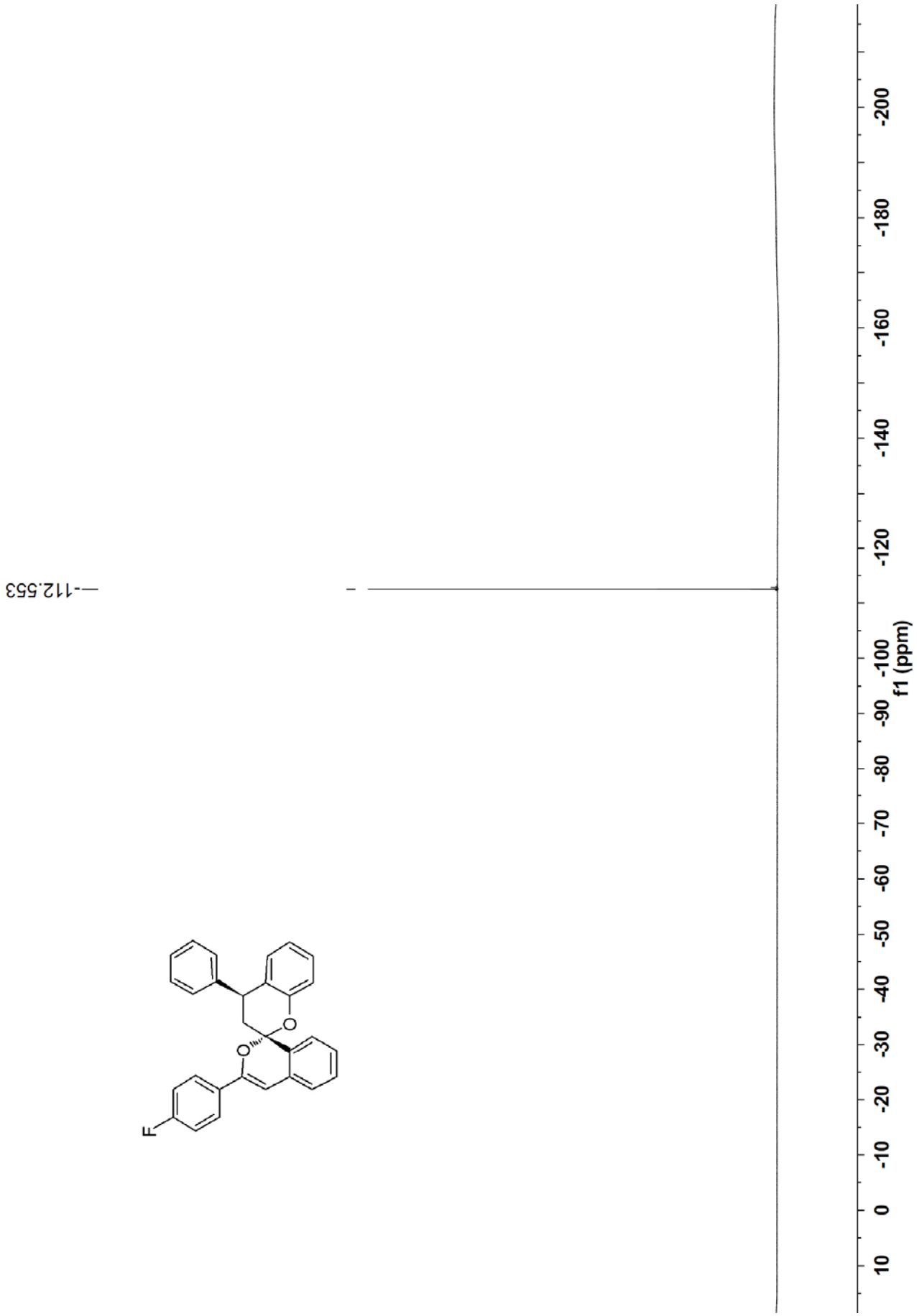
^{13}C NMR Spectrum of Compound 3e



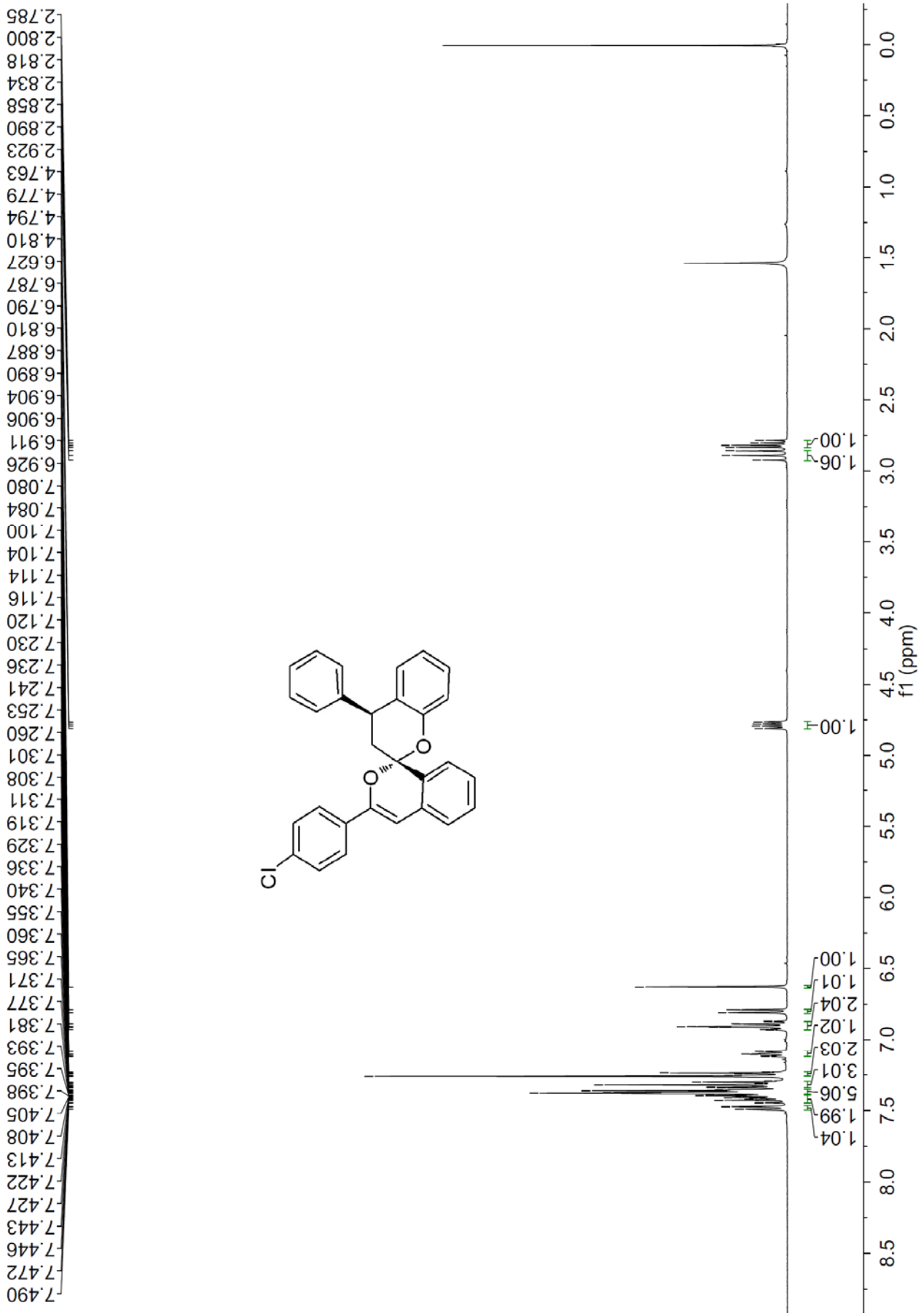
^{1}H NMR Spectrum of Compound 3f



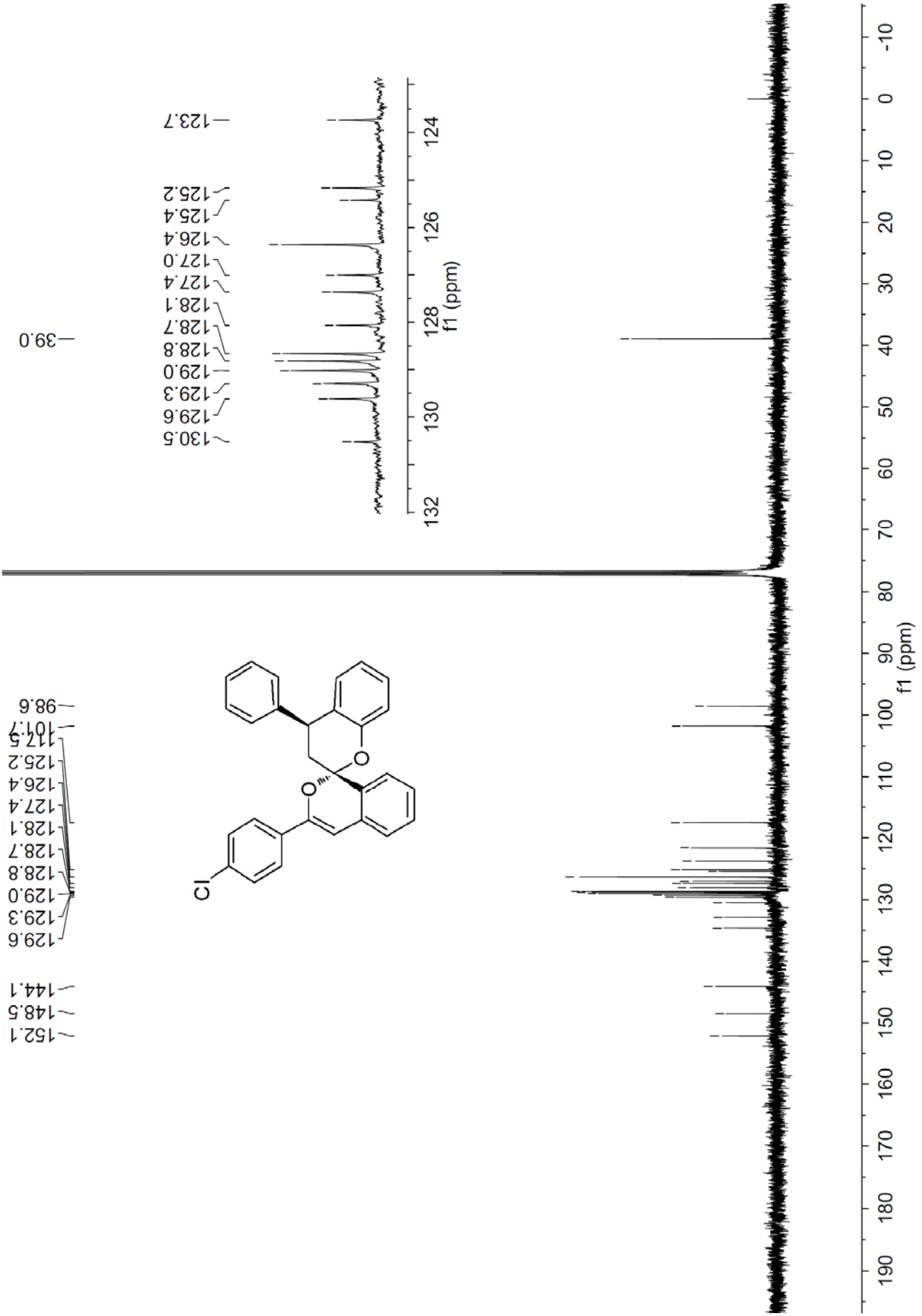
^{13}C NMR Spectrum of Compound 3f



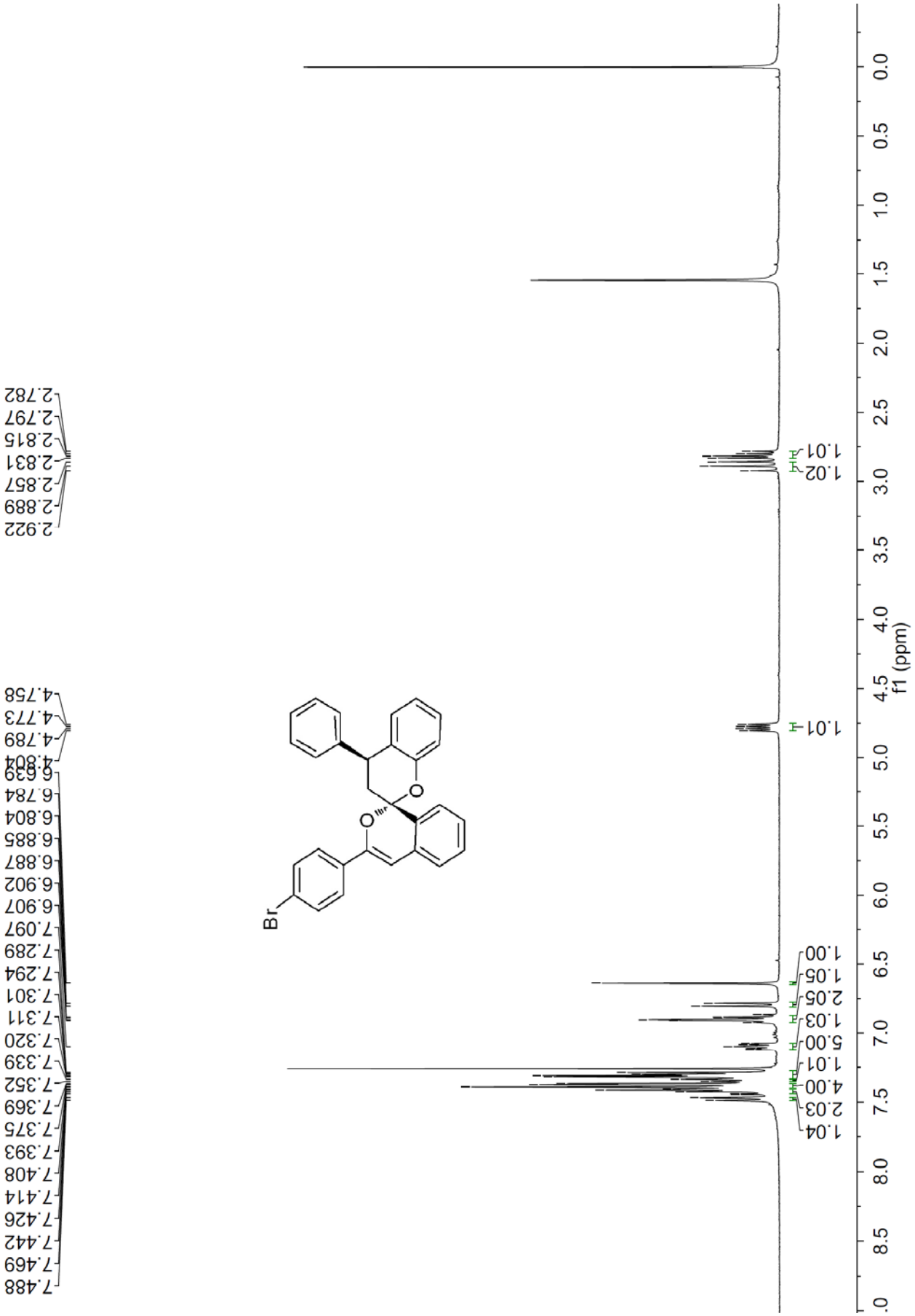
^{19}F NMR Spectrum of Compound 3f



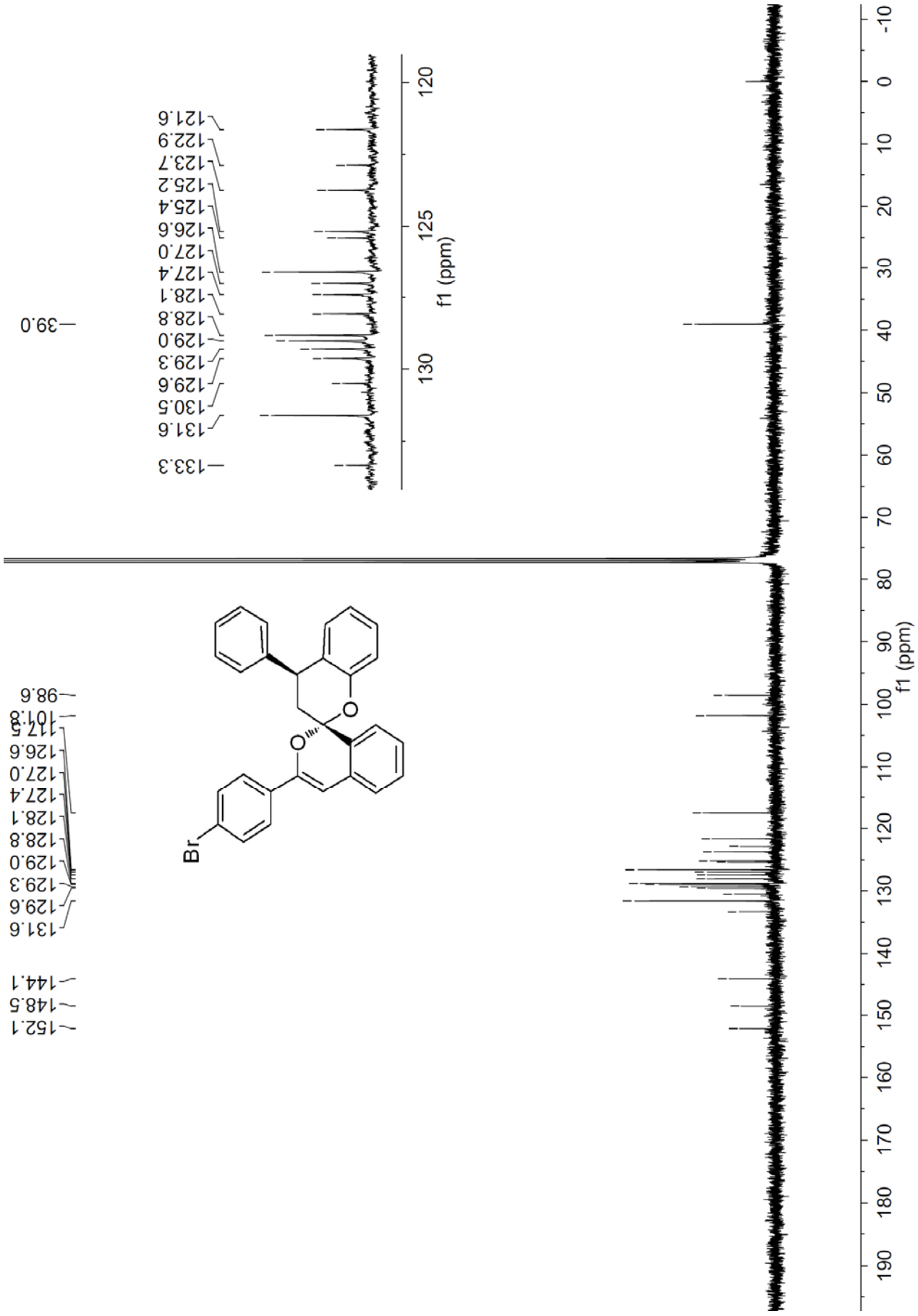
^{1}H NMR Spectrum of Compound 3g



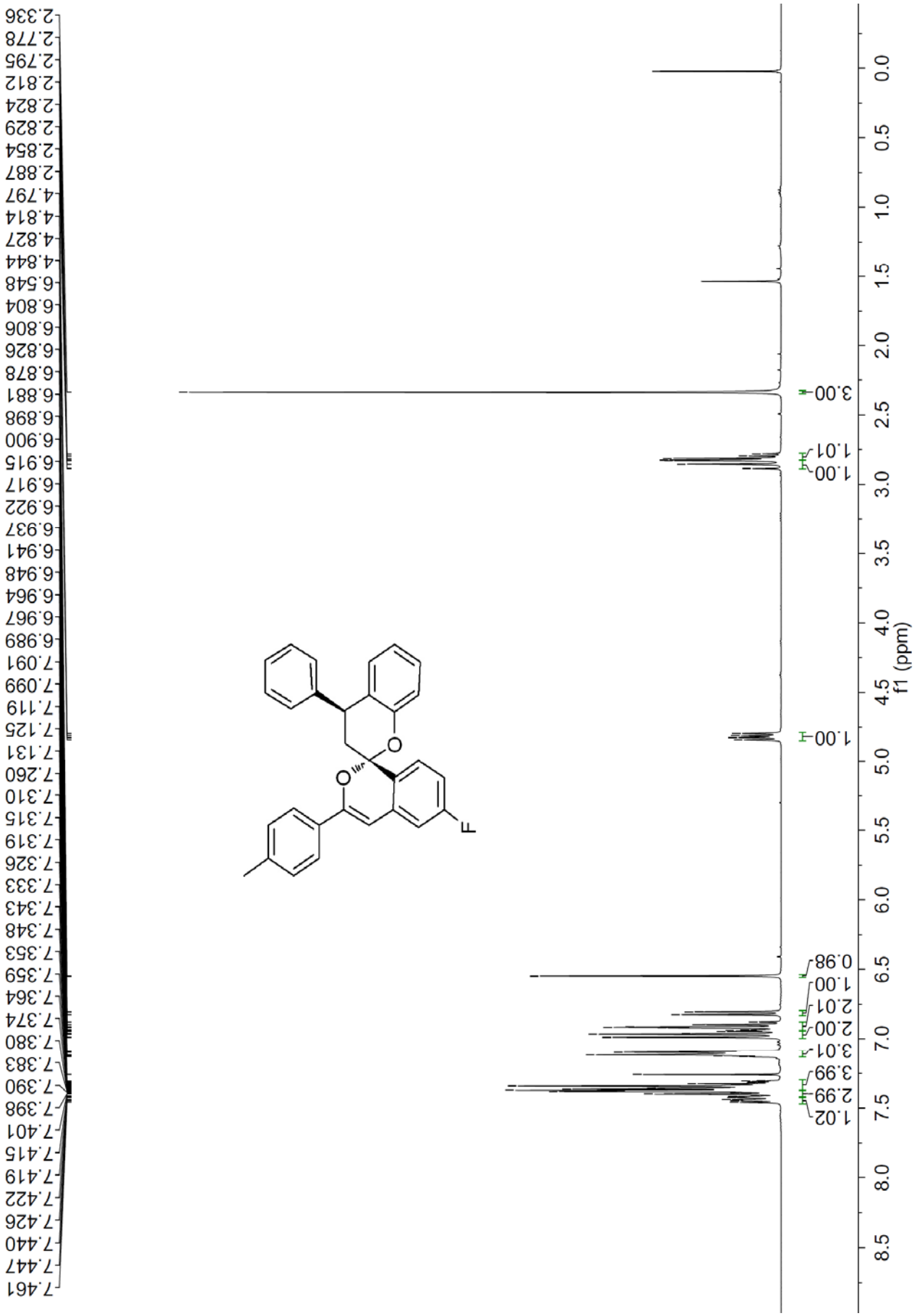
^{13}C NMR Spectrum of Compound 3g



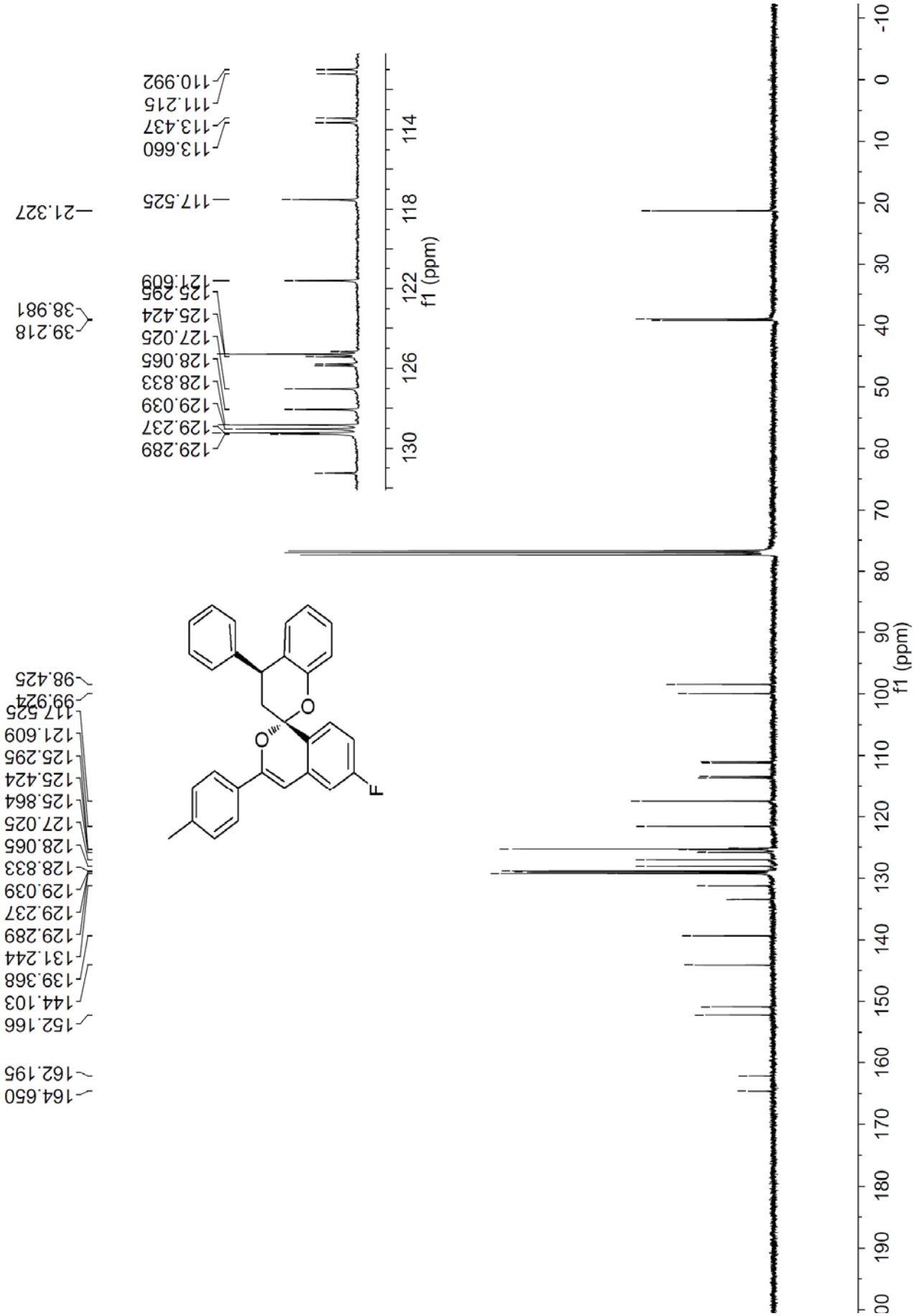
^{1}H NMR Spectrum of Compound 3h



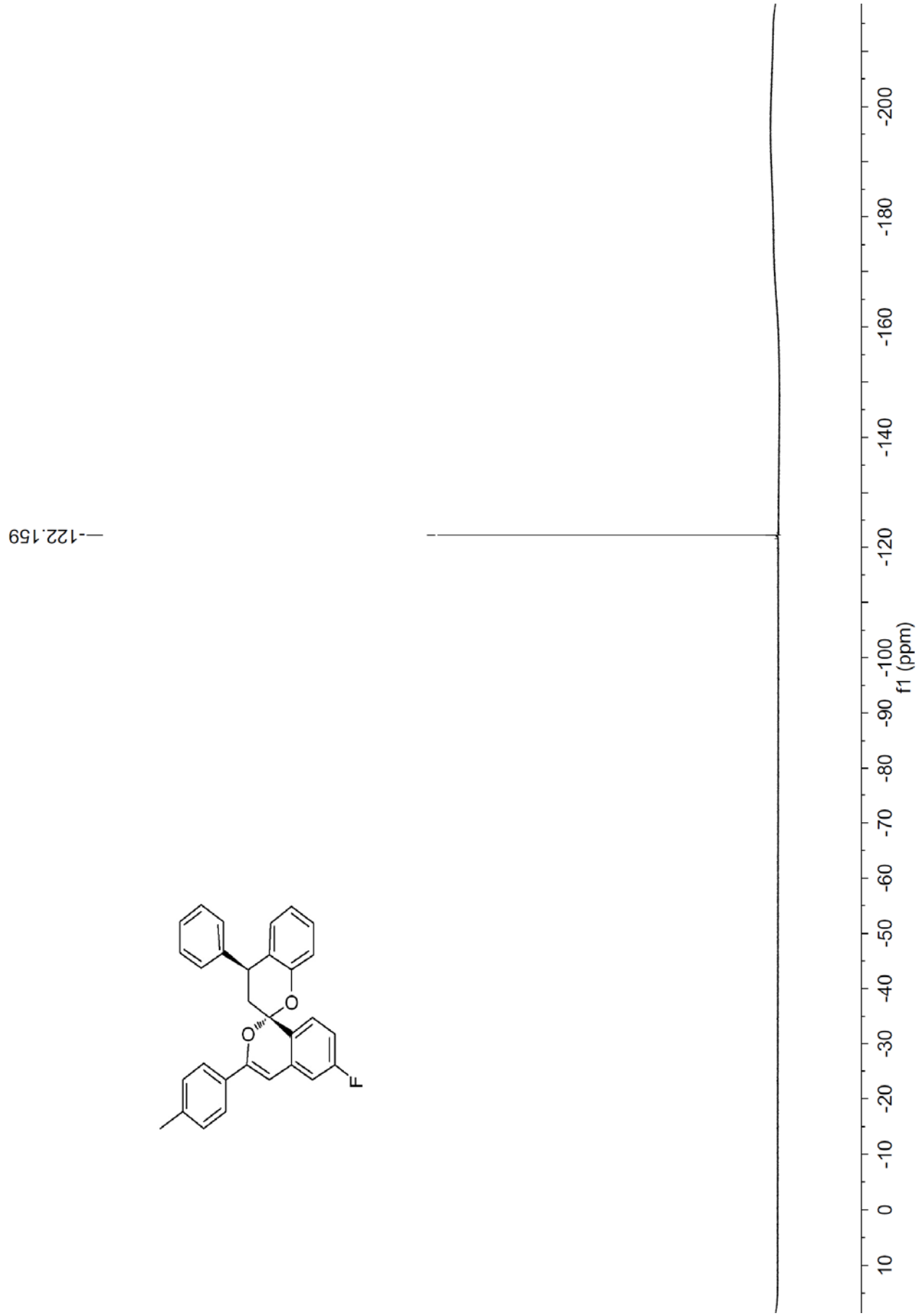
^{13}C NMR Spectrum of Compound 3h



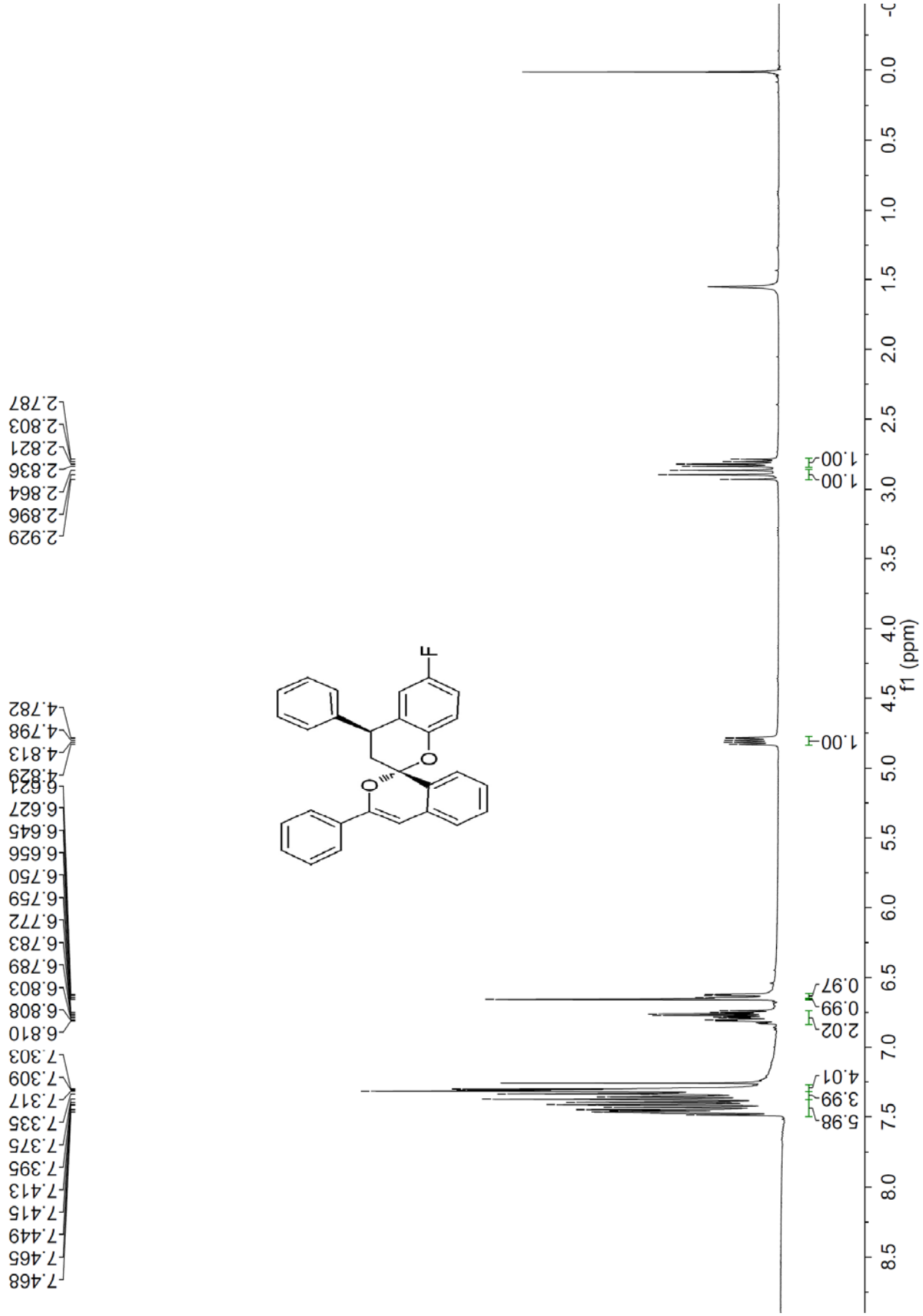
^{1}H NMR Spectrum of Compound 3j



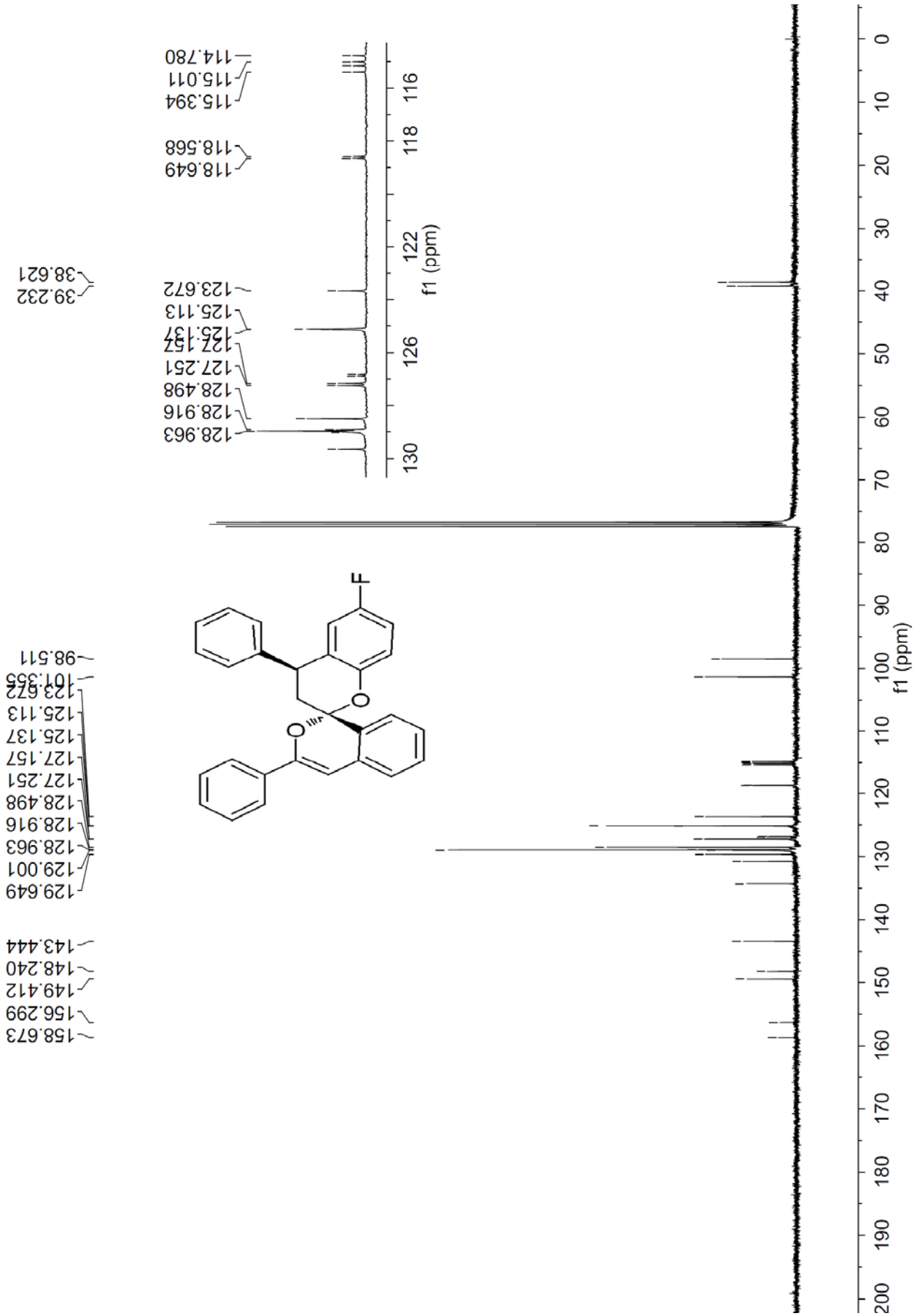
^{13}C NMR Spectrum of Compound 3j



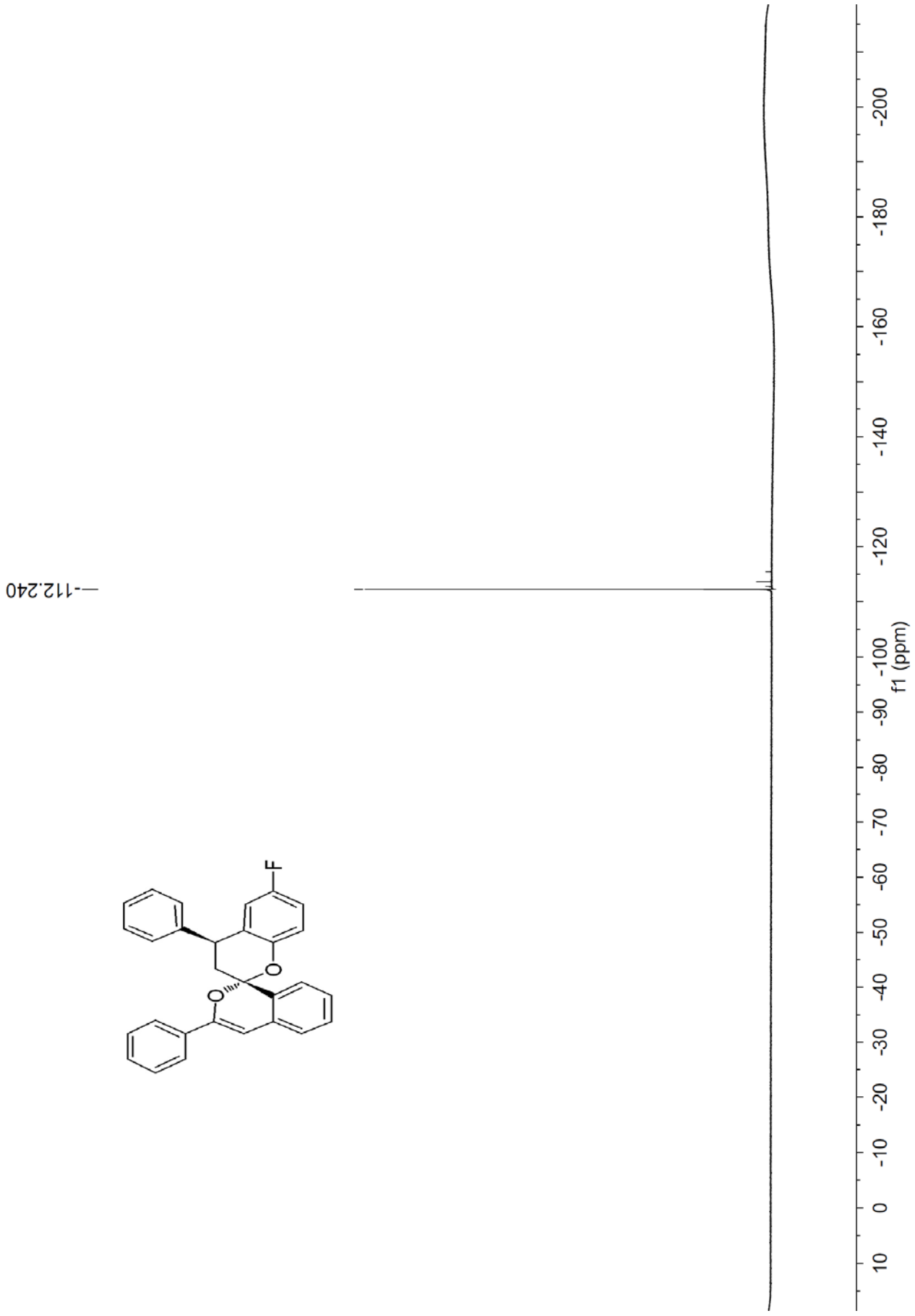
^{19}F NMR Spectrum of Compound 3j



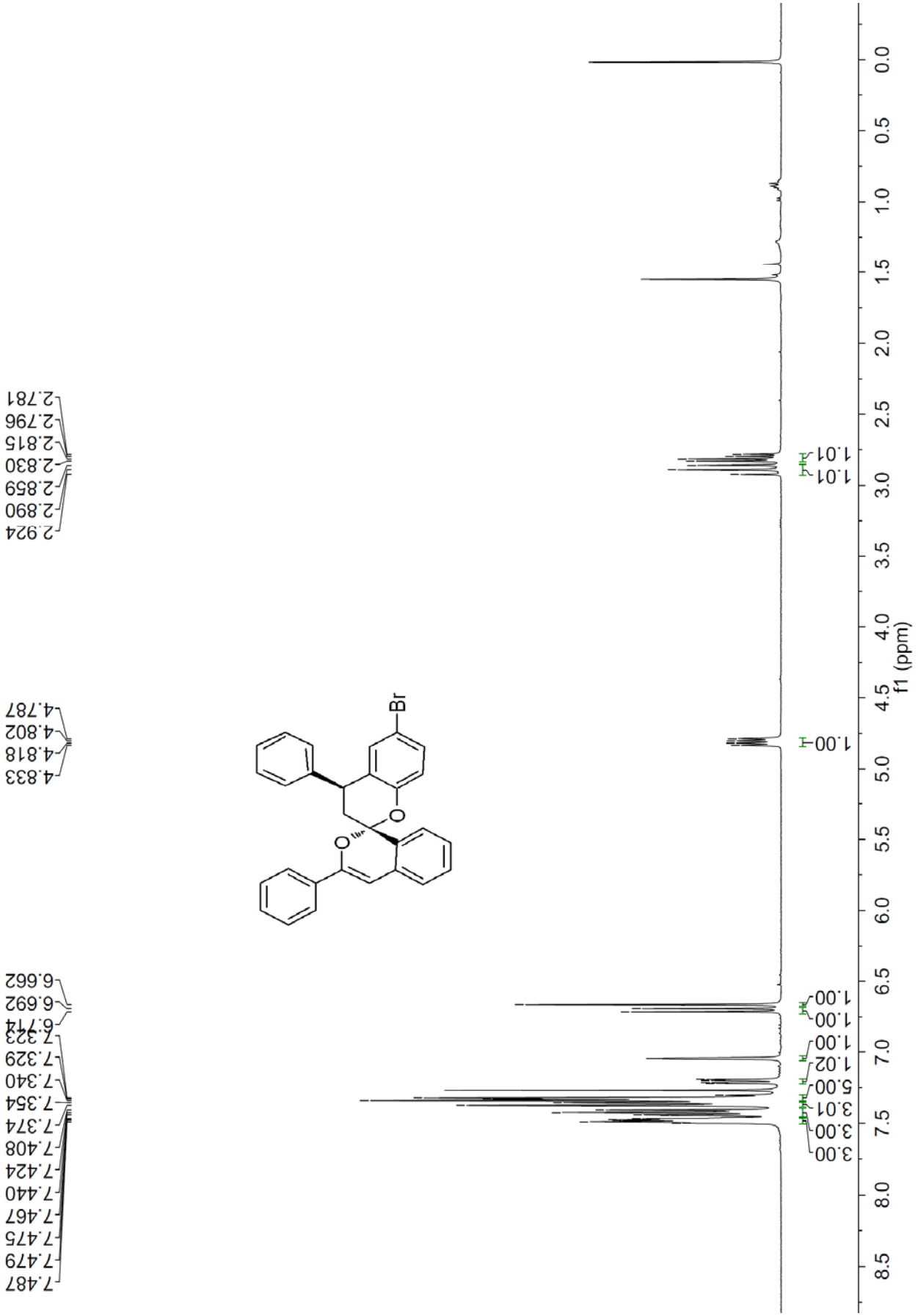
^{1}H NMR Spectrum of Compound 3k



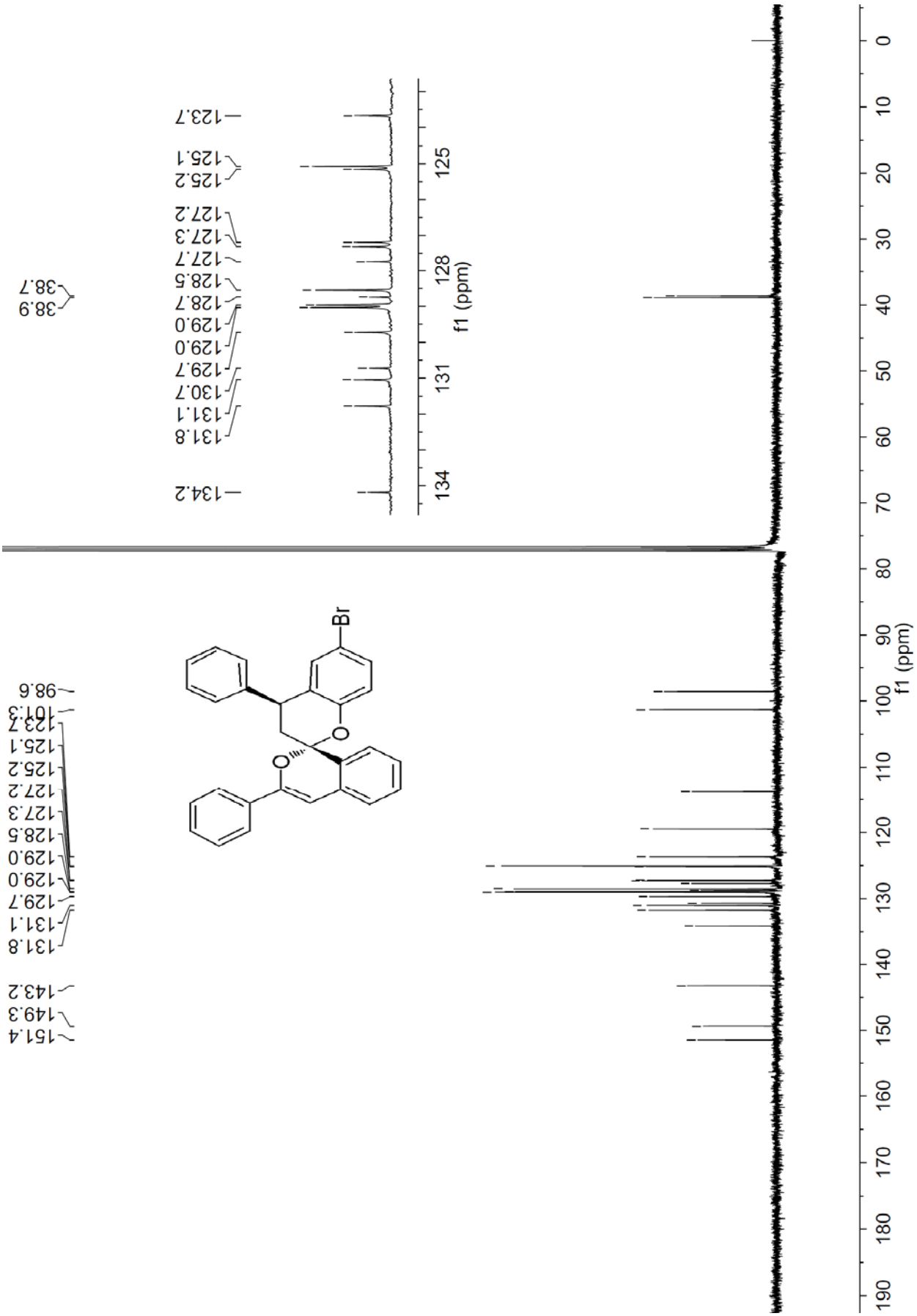
^{13}C NMR Spectrum of Compound 3k



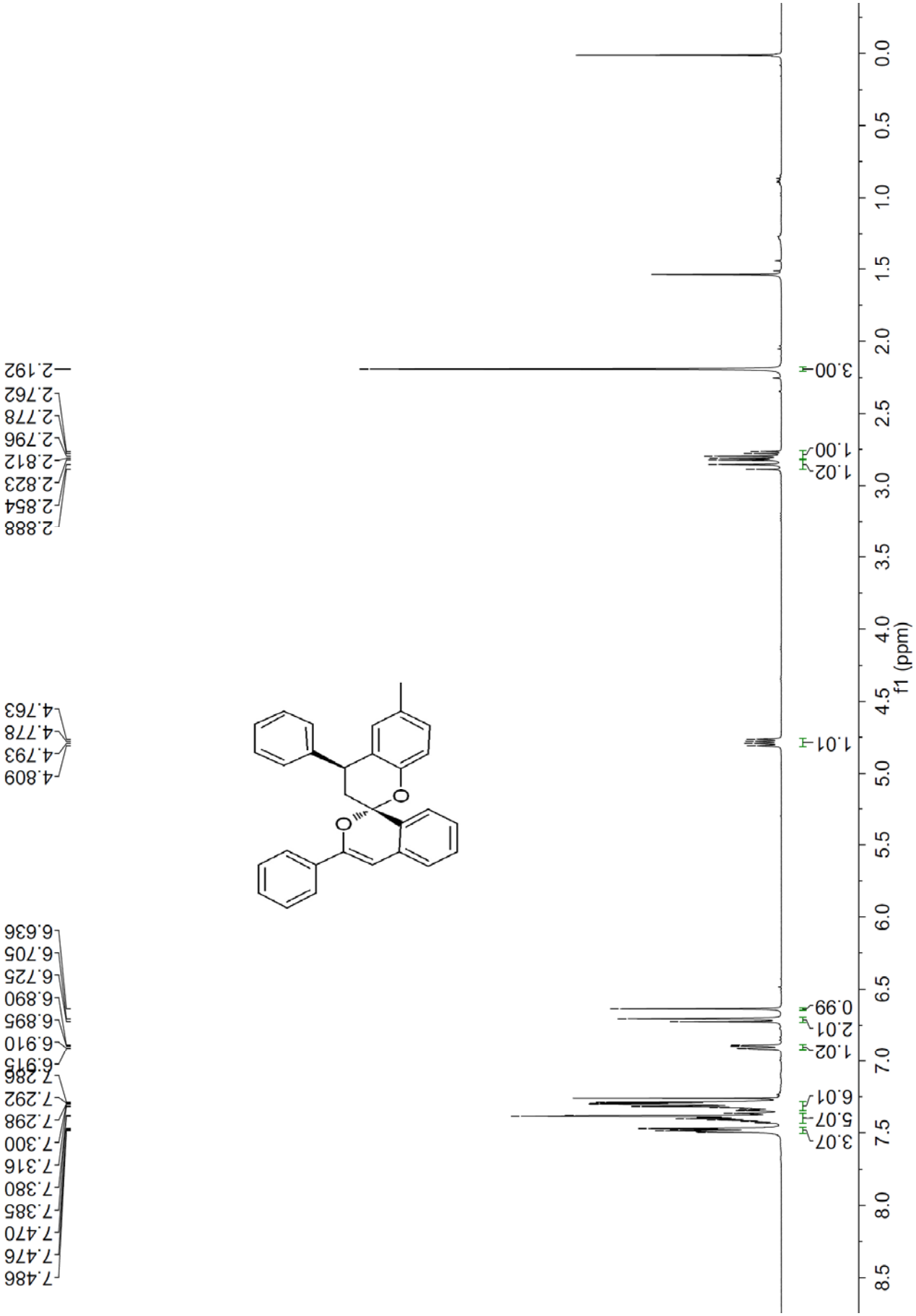
^{19}F NMR Spectrum of Compound 3k



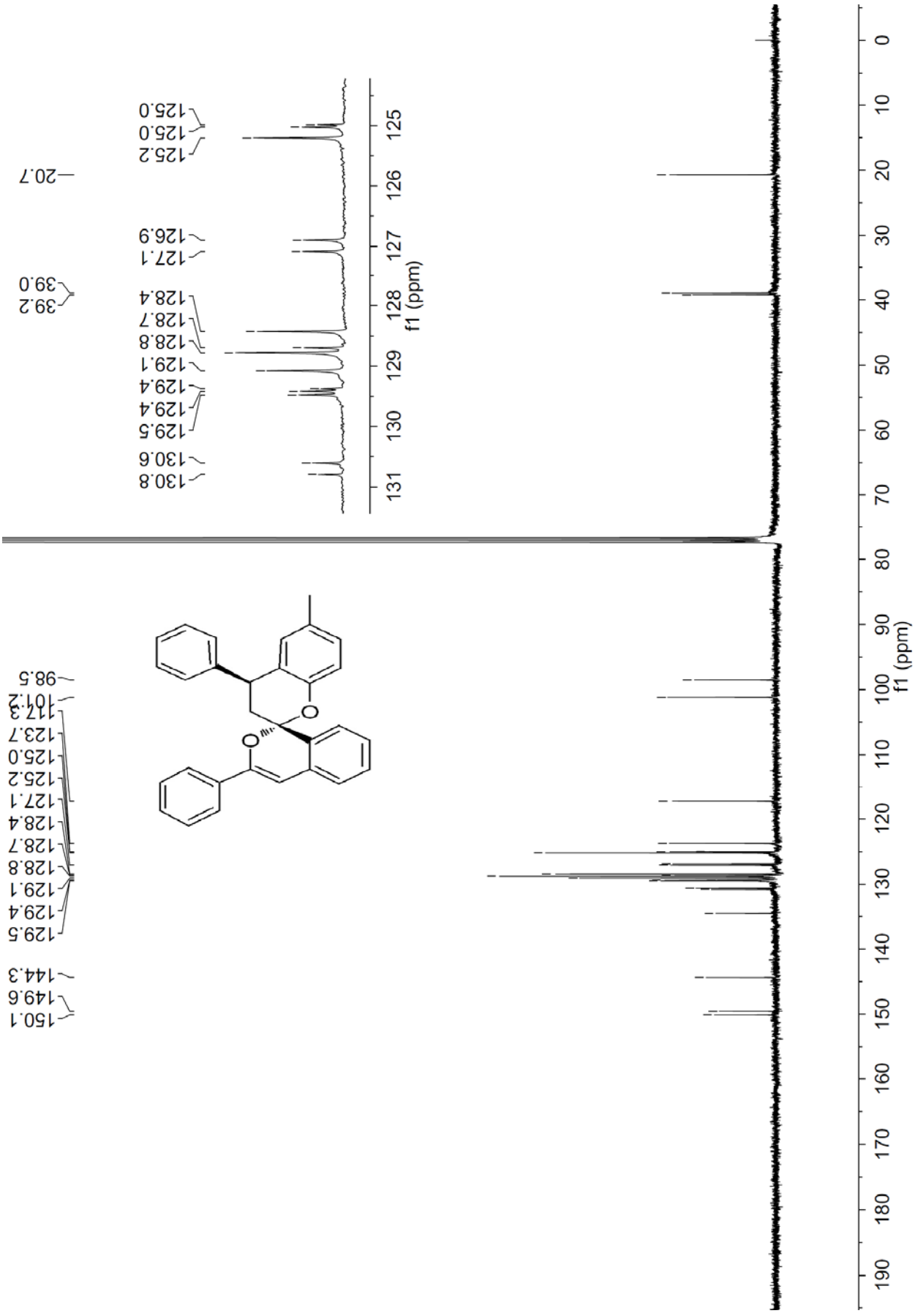
^{1}H NMR Spectrum of Compound 3l



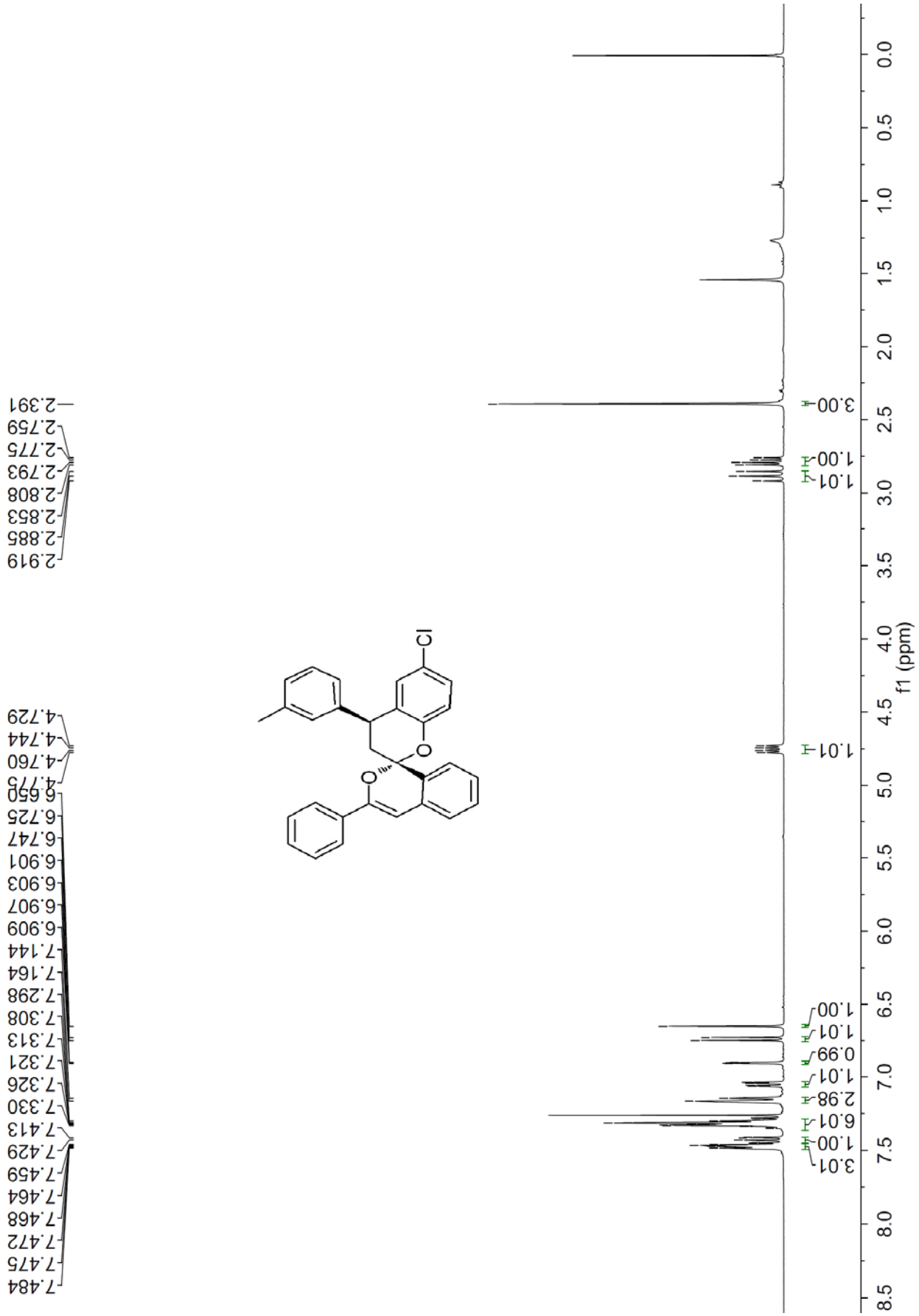
^{13}C NMR Spectrum of Compound 3l



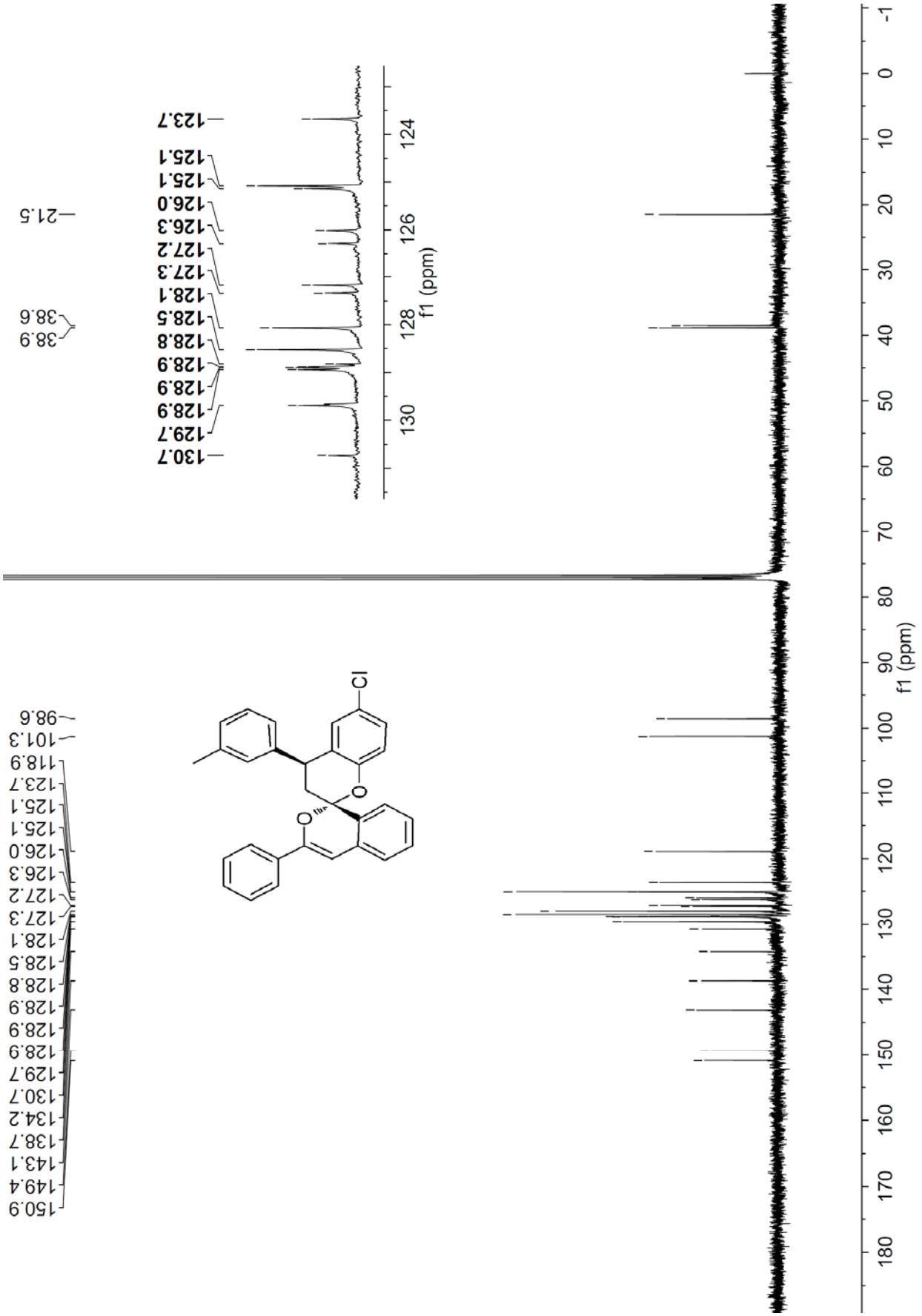
[1]H NMR Spectrum of Compound 3m



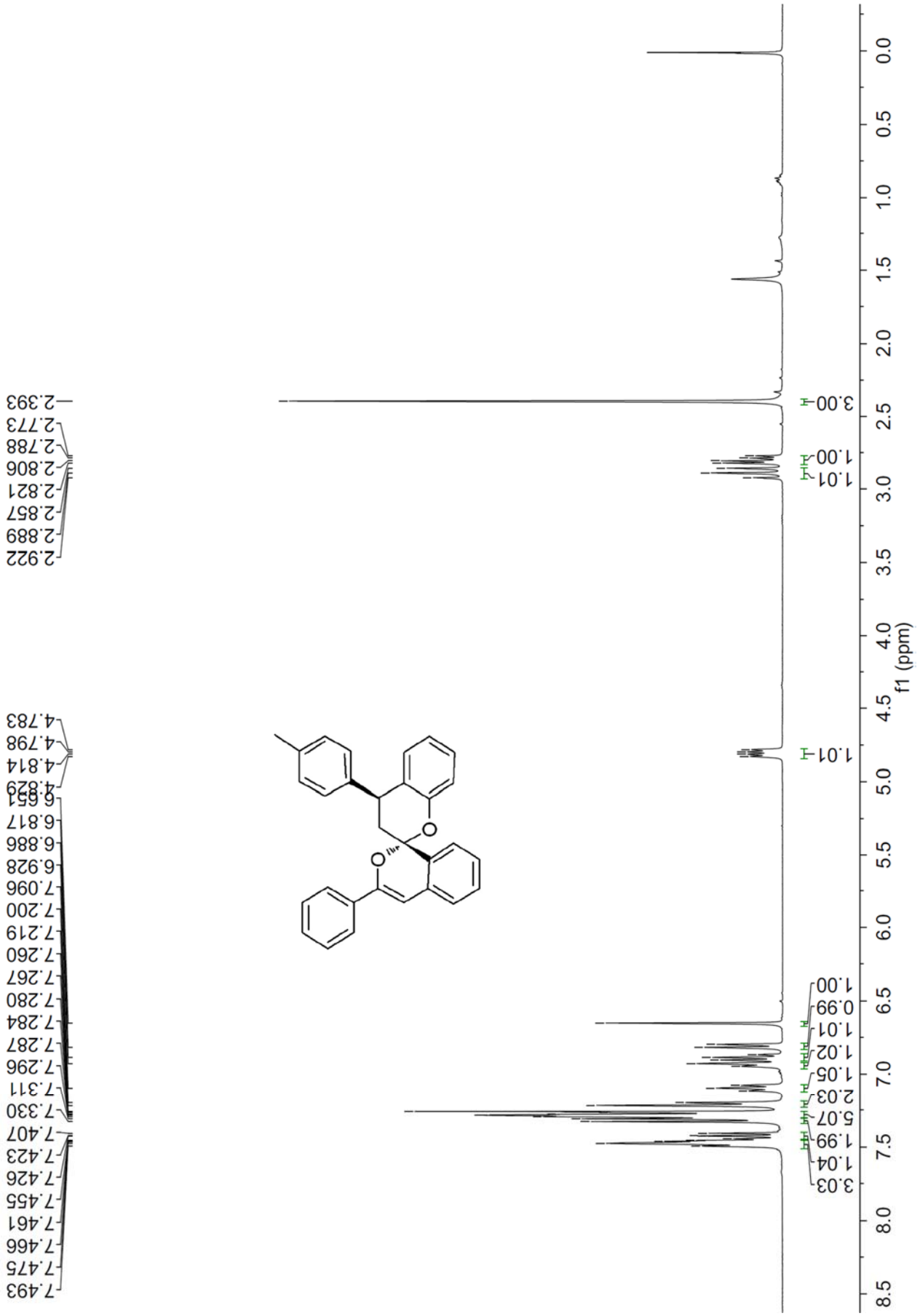
^{13}C NMR Spectrum of Compound 3m



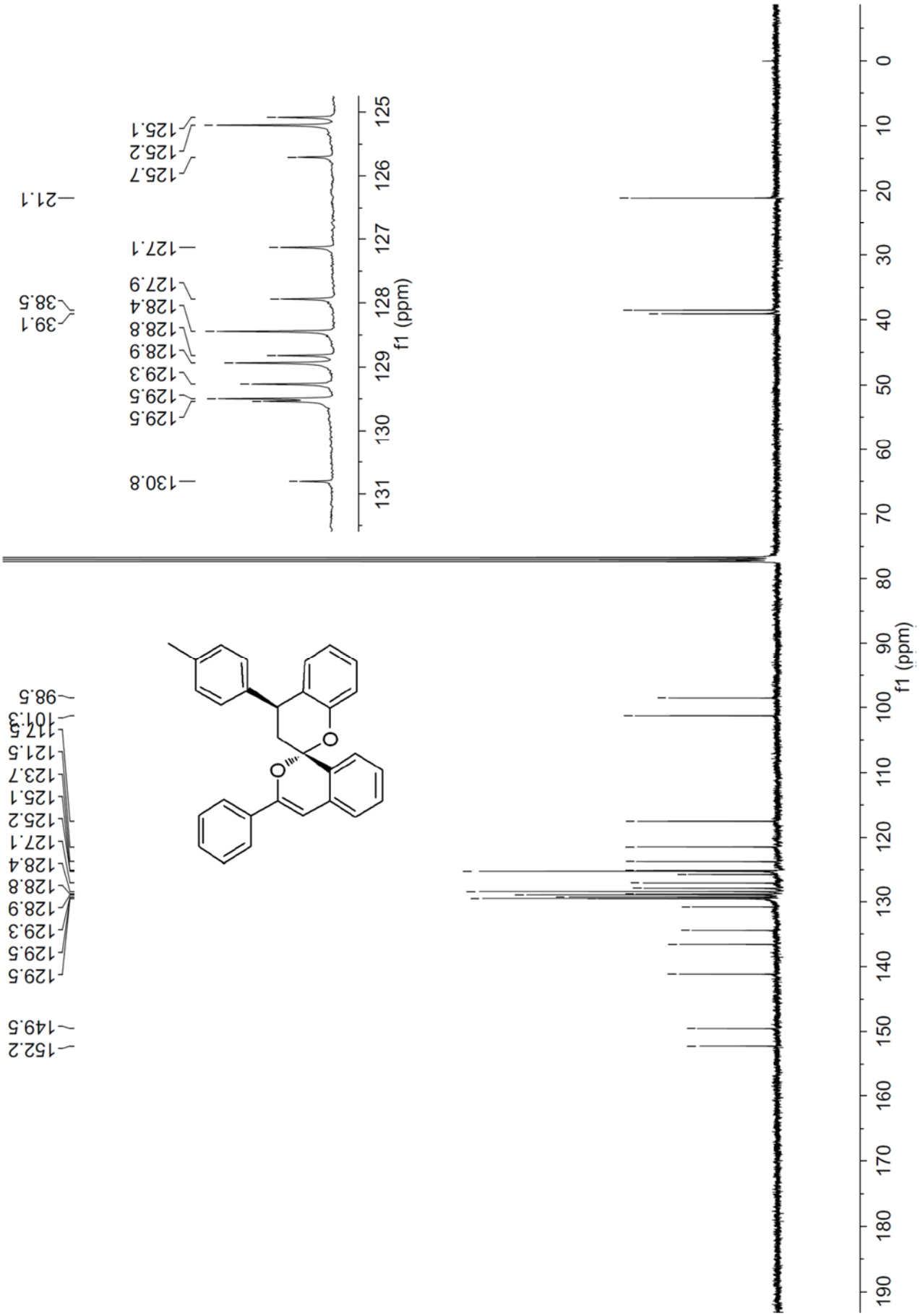
^{1}H NMR Spectrum of Compound 3n



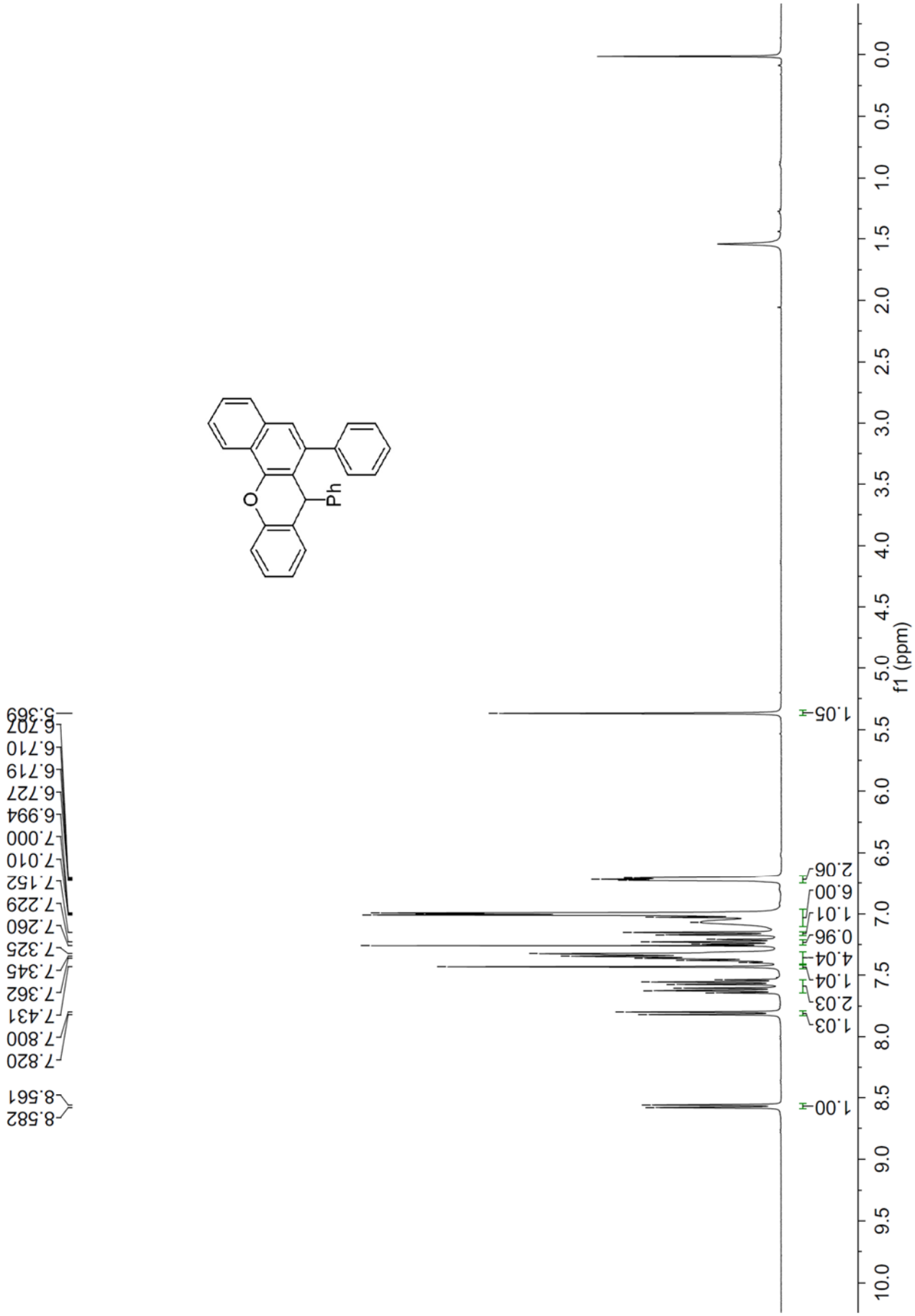
^{13}C NMR Spectrum of Compound 3n



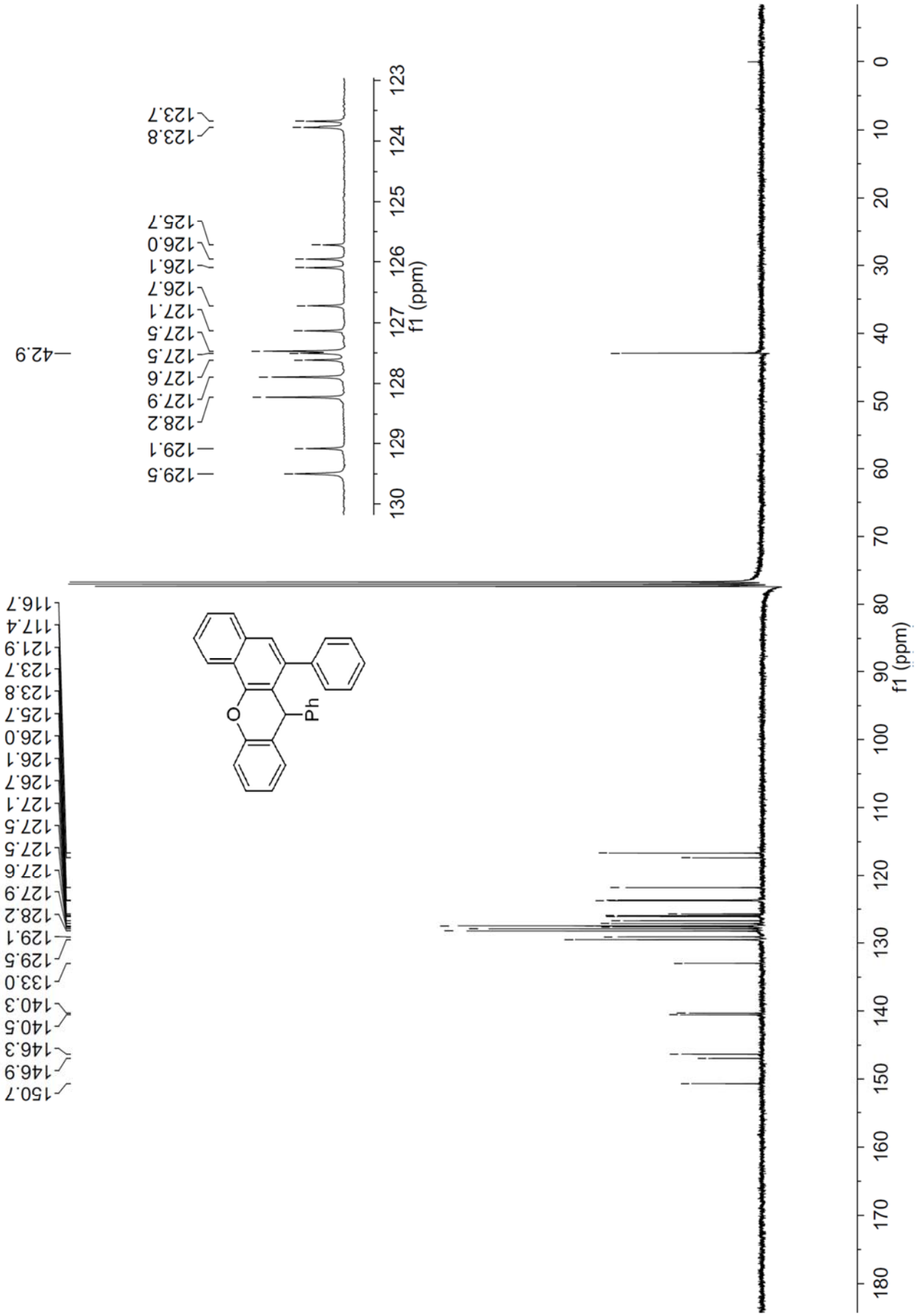
^{1}H NMR Spectrum of Compound 3o



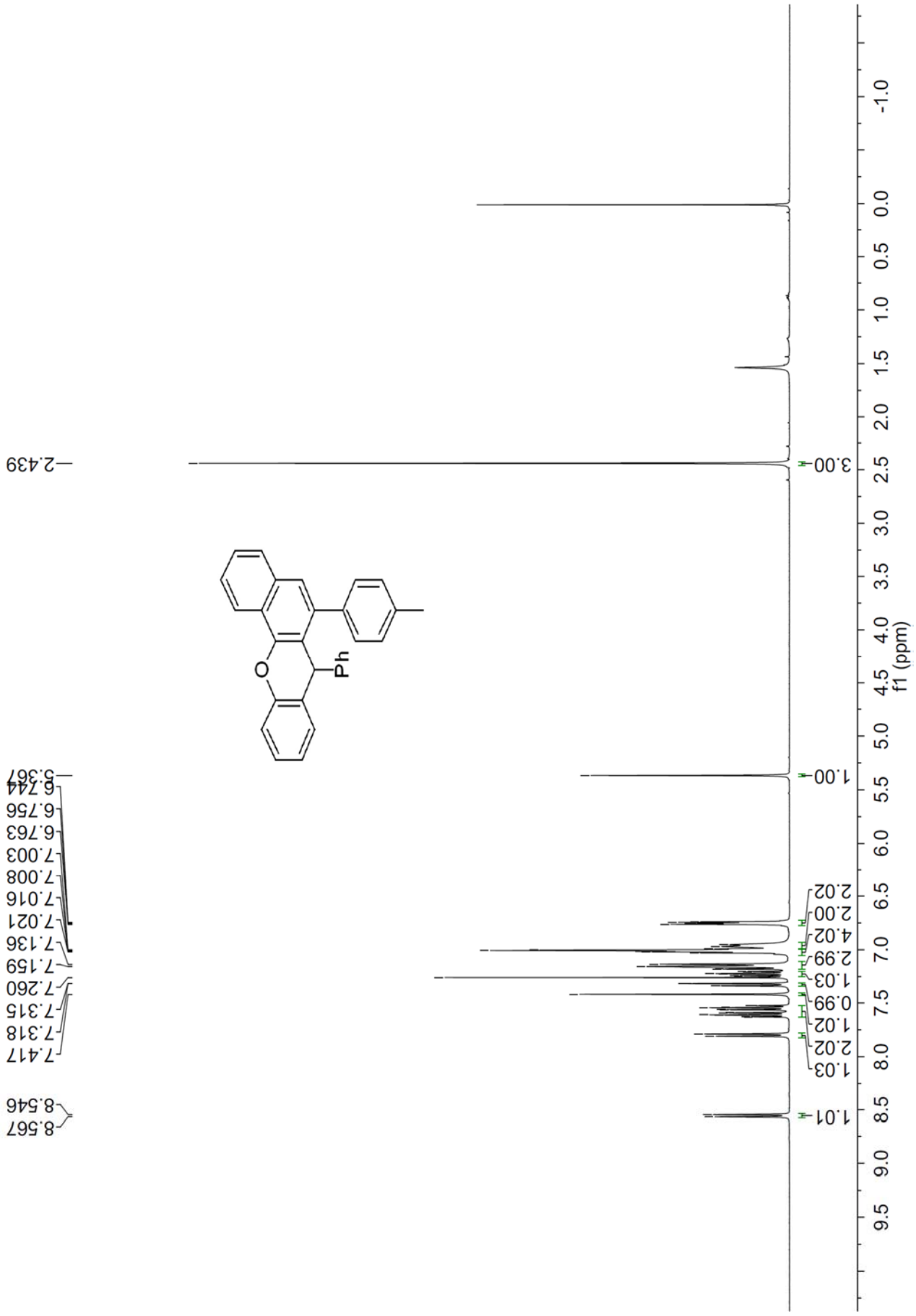
^{13}C NMR Spectrum of Compound 3o



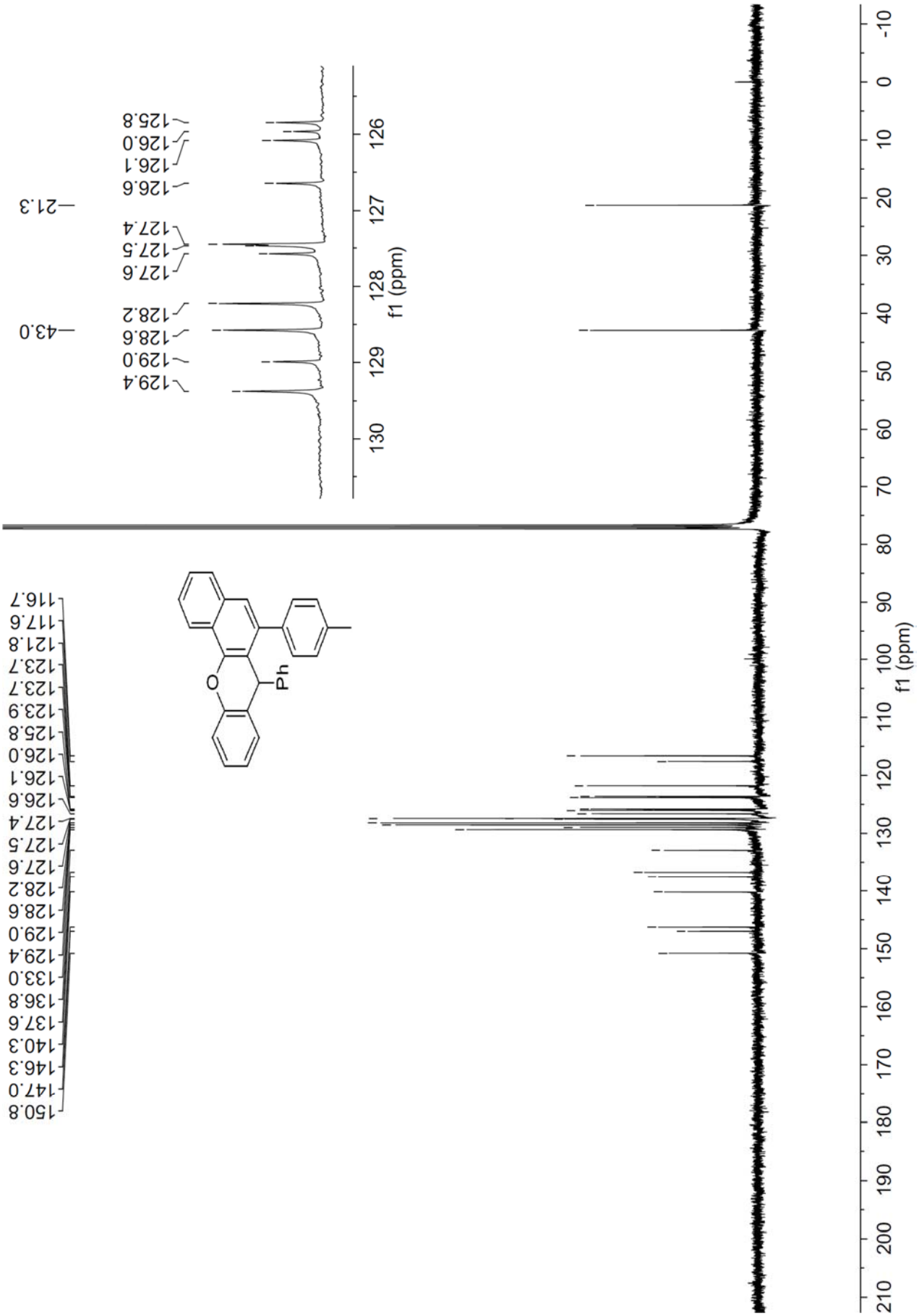
^{1}H NMR Spectrum of Compound 4a



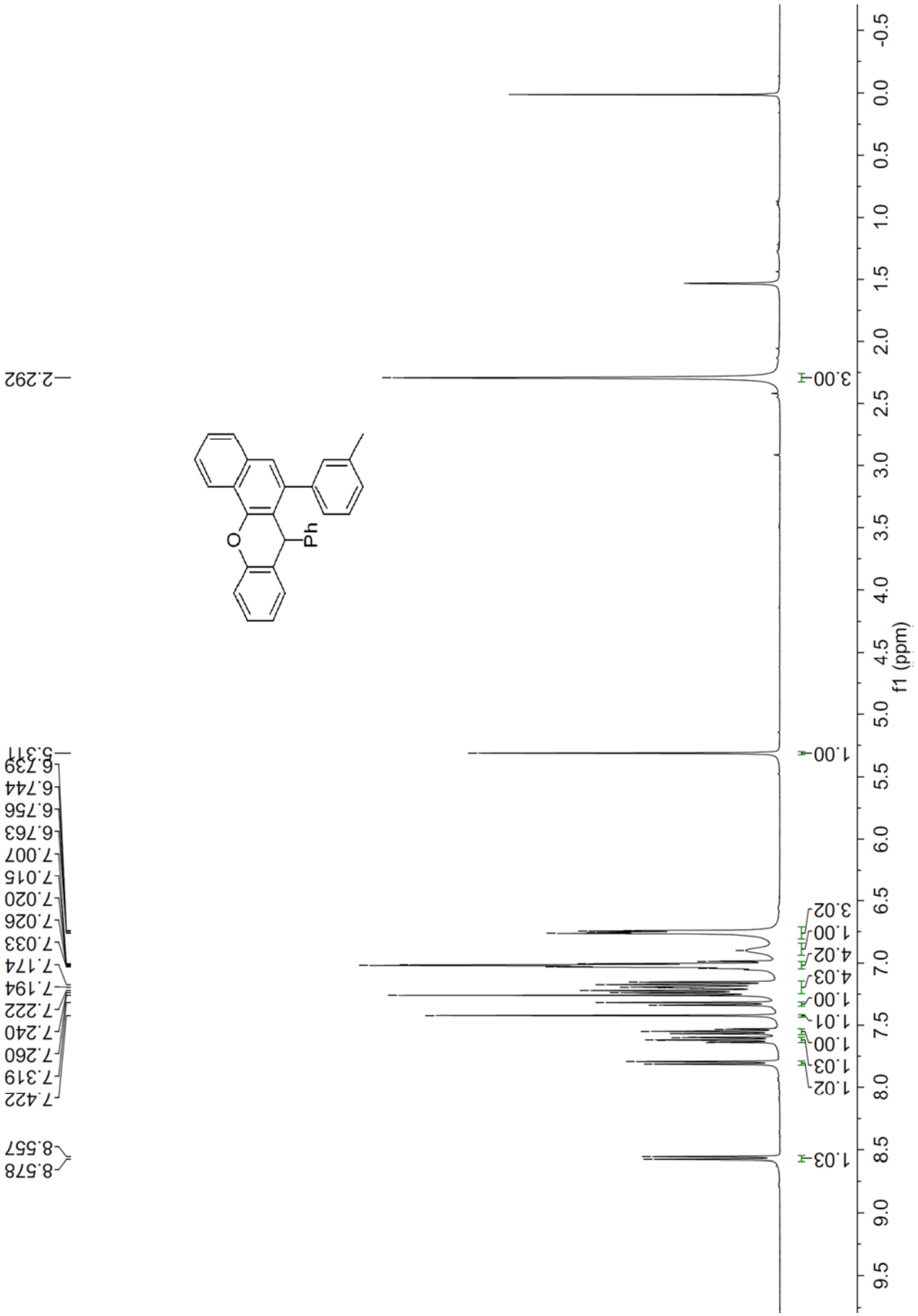
^{13}C NMR Spectrum of Compound 4a



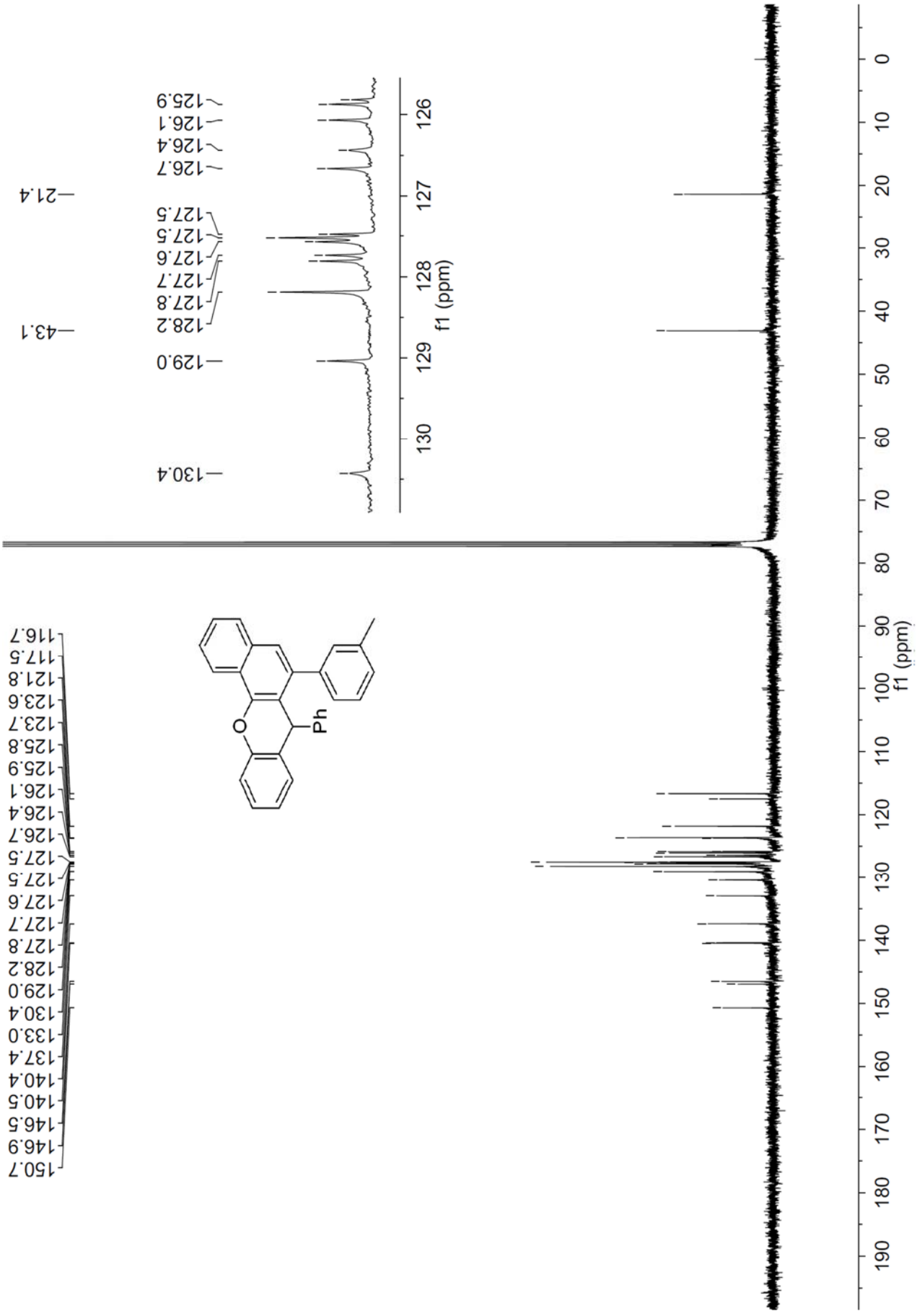
^{1}H NMR Spectrum of Compound 4b



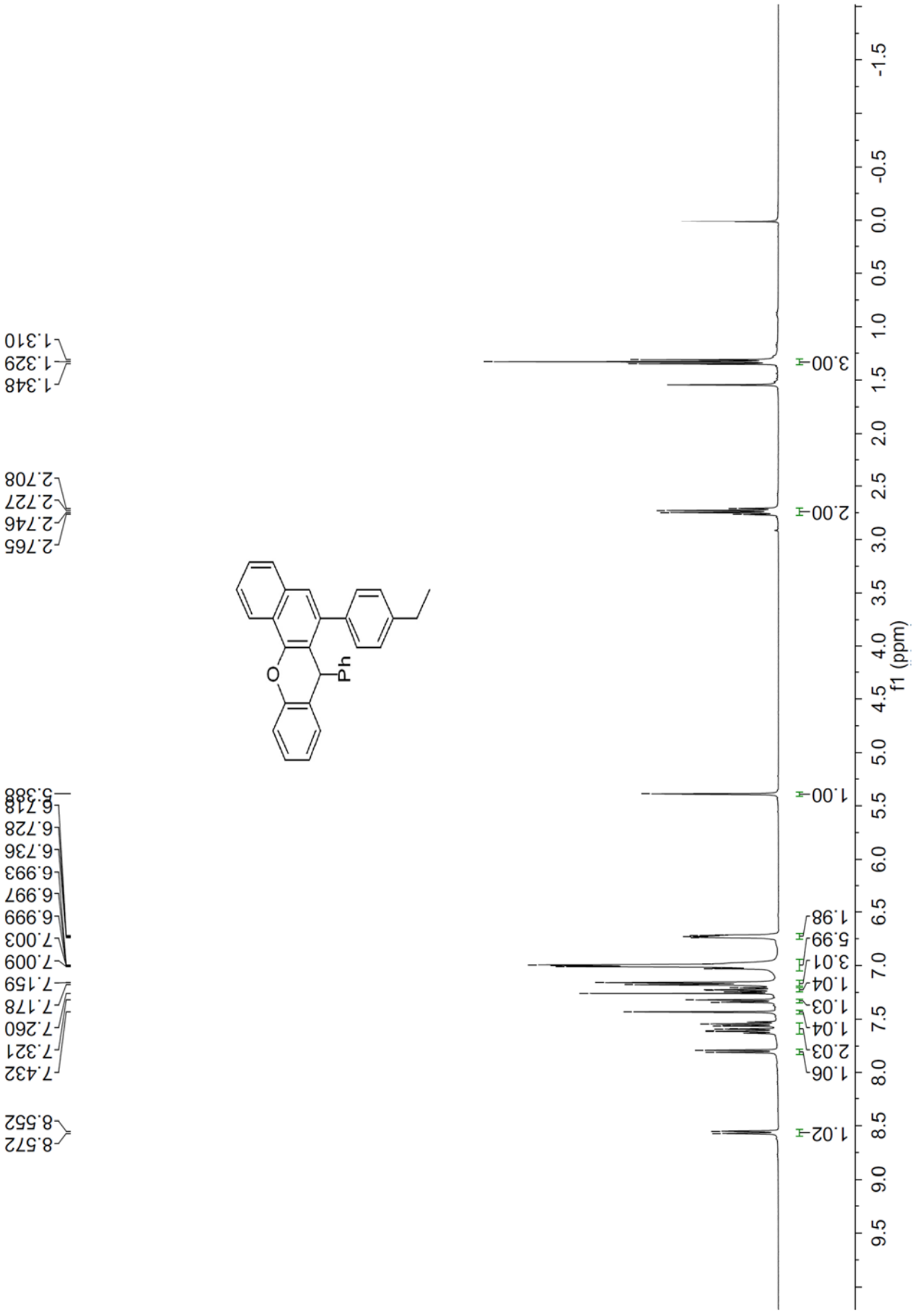
^{13}C NMR Spectrum of Compound 4b



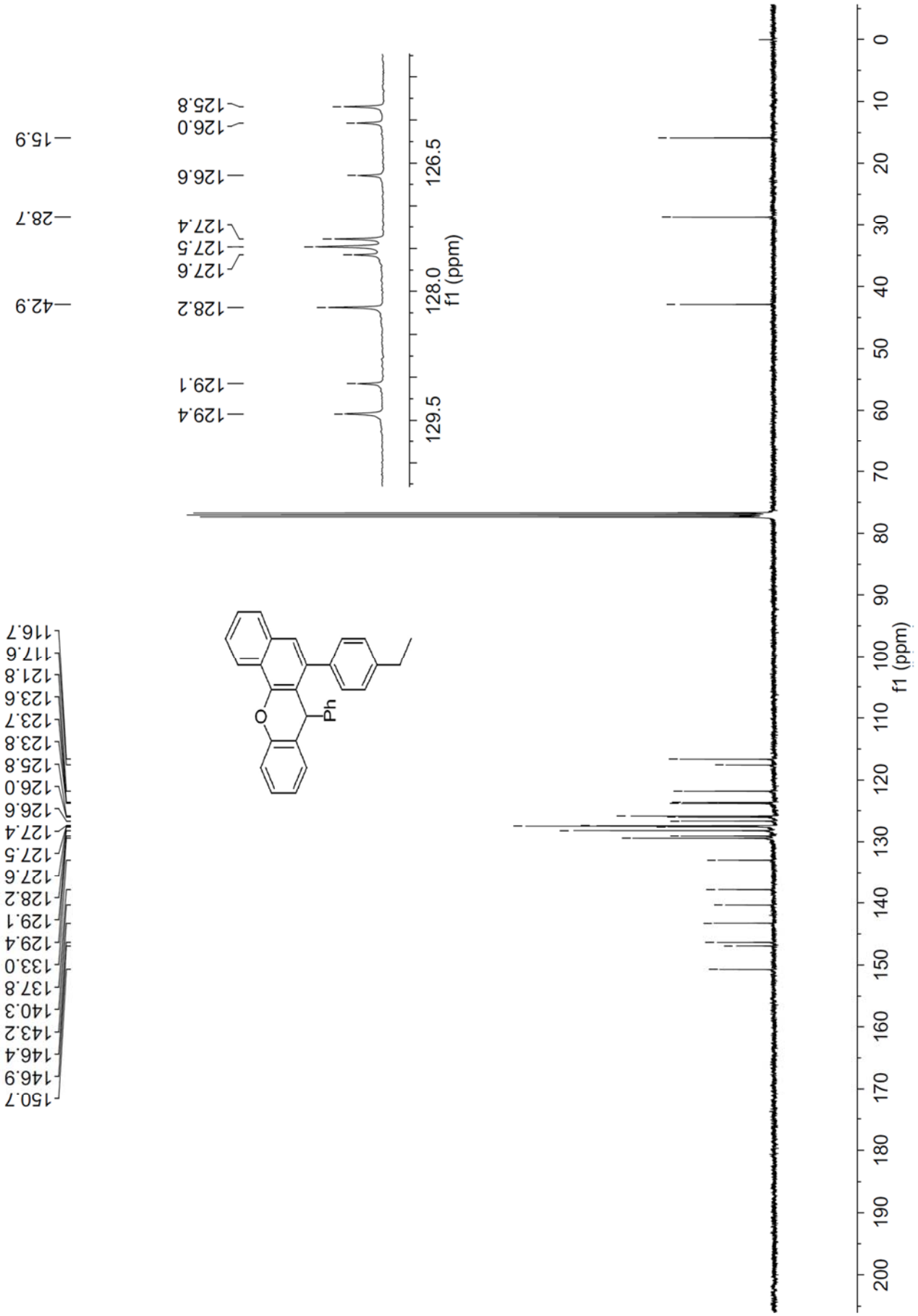
^{1}H NMR Spectrum of Compound 4c



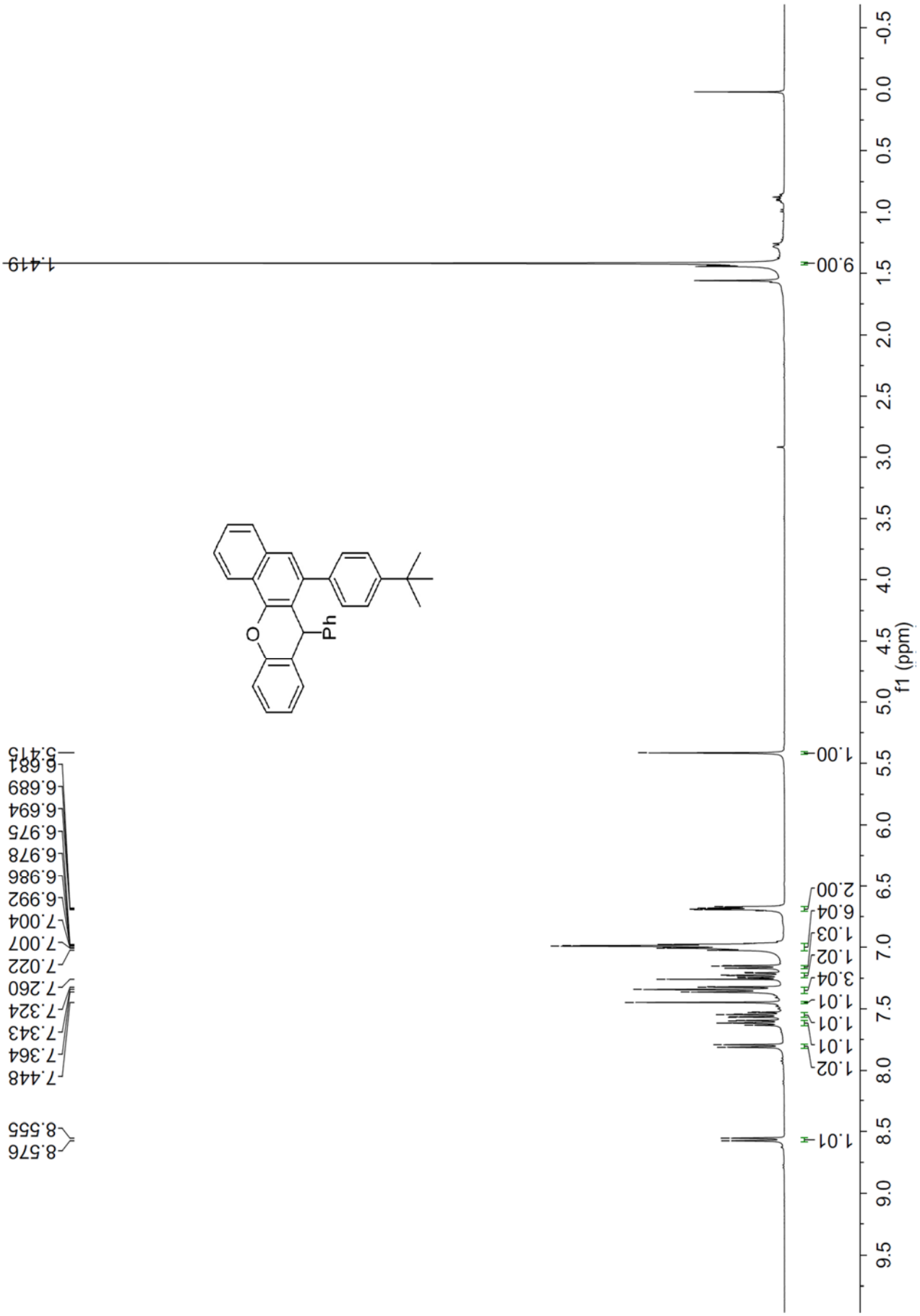
^{13}C NMR Spectrum of Compound 4c



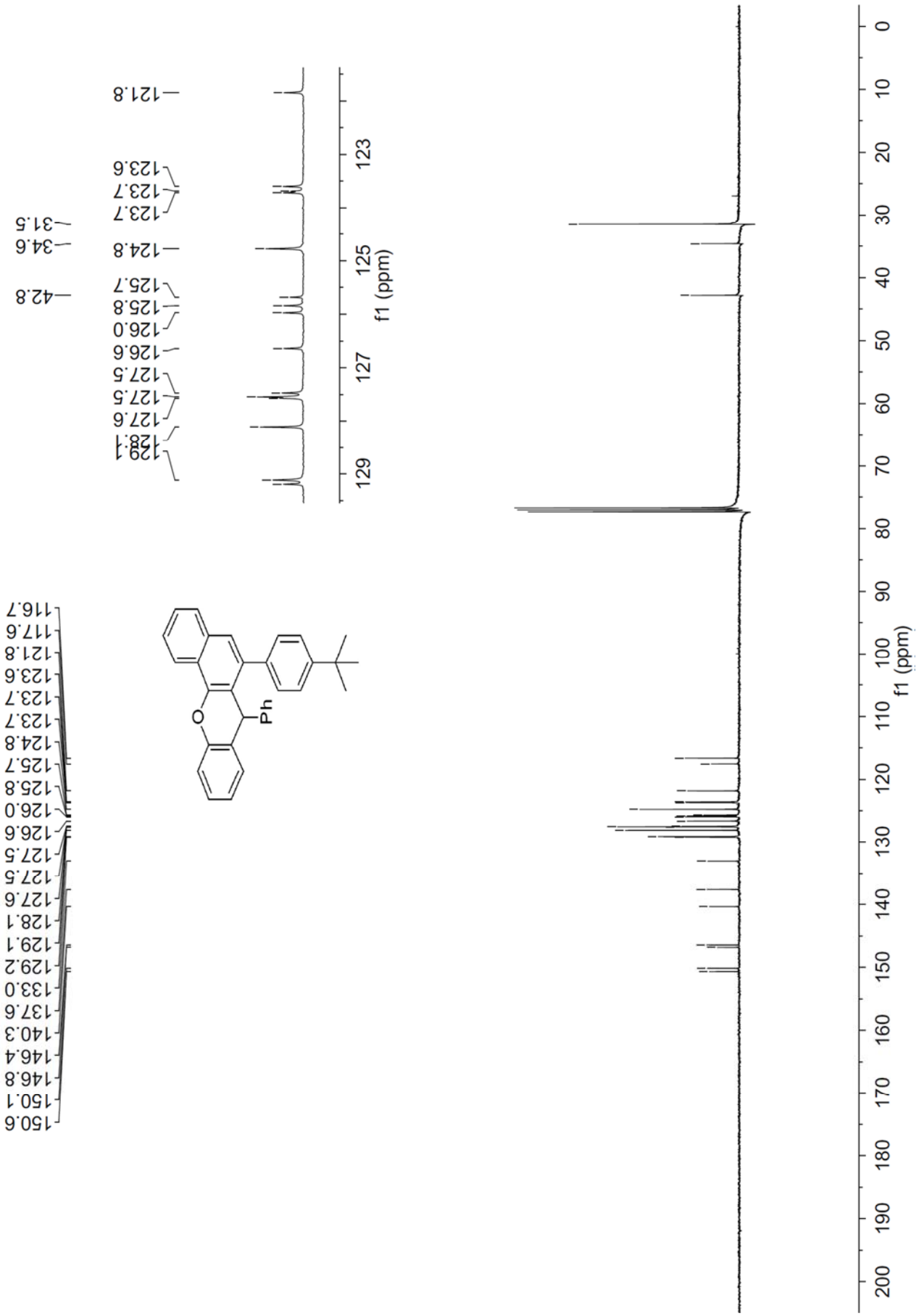
[1]H NMR Spectrum of Compound 4d



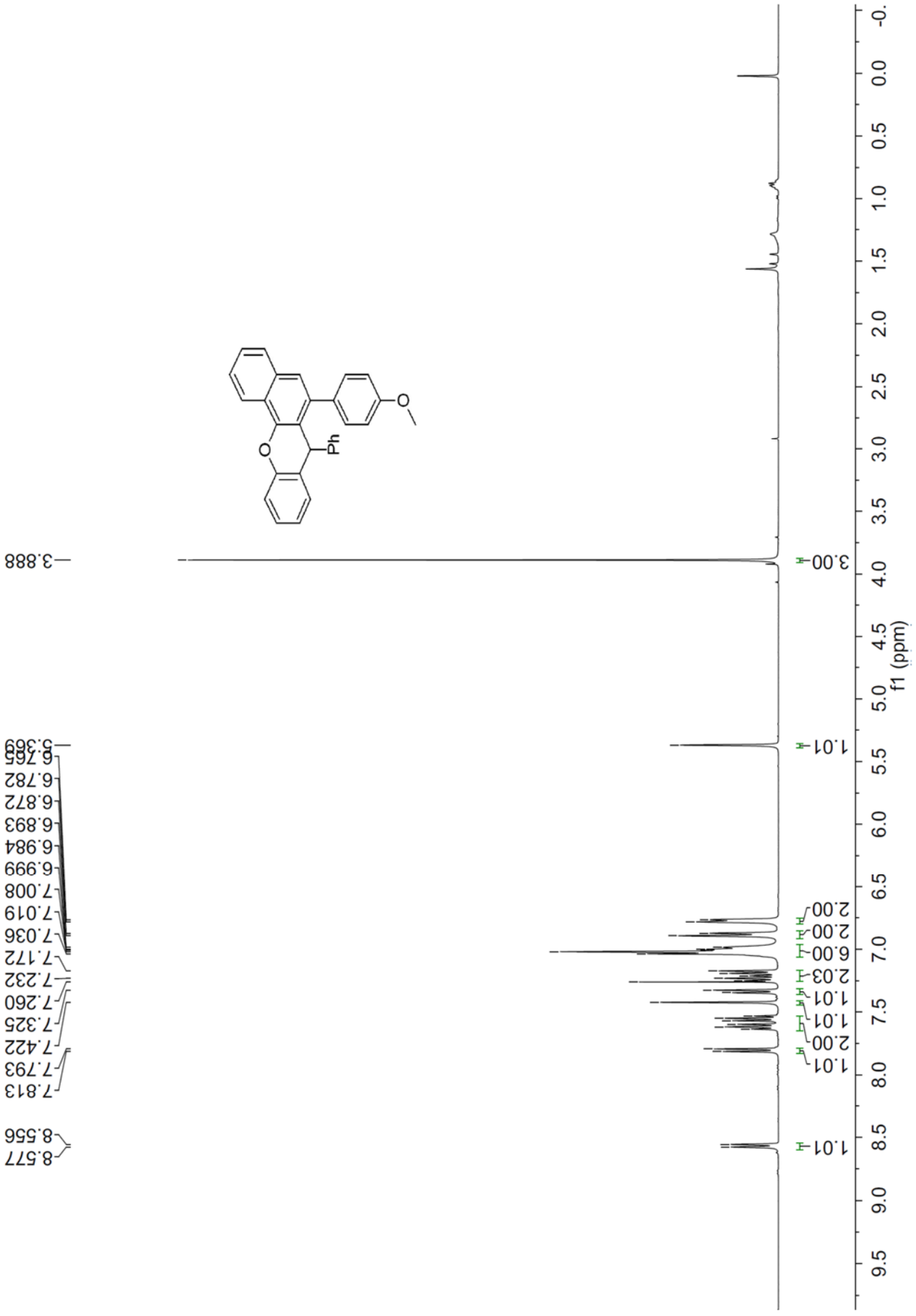
^{13}C NMR Spectrum of Compound 4d



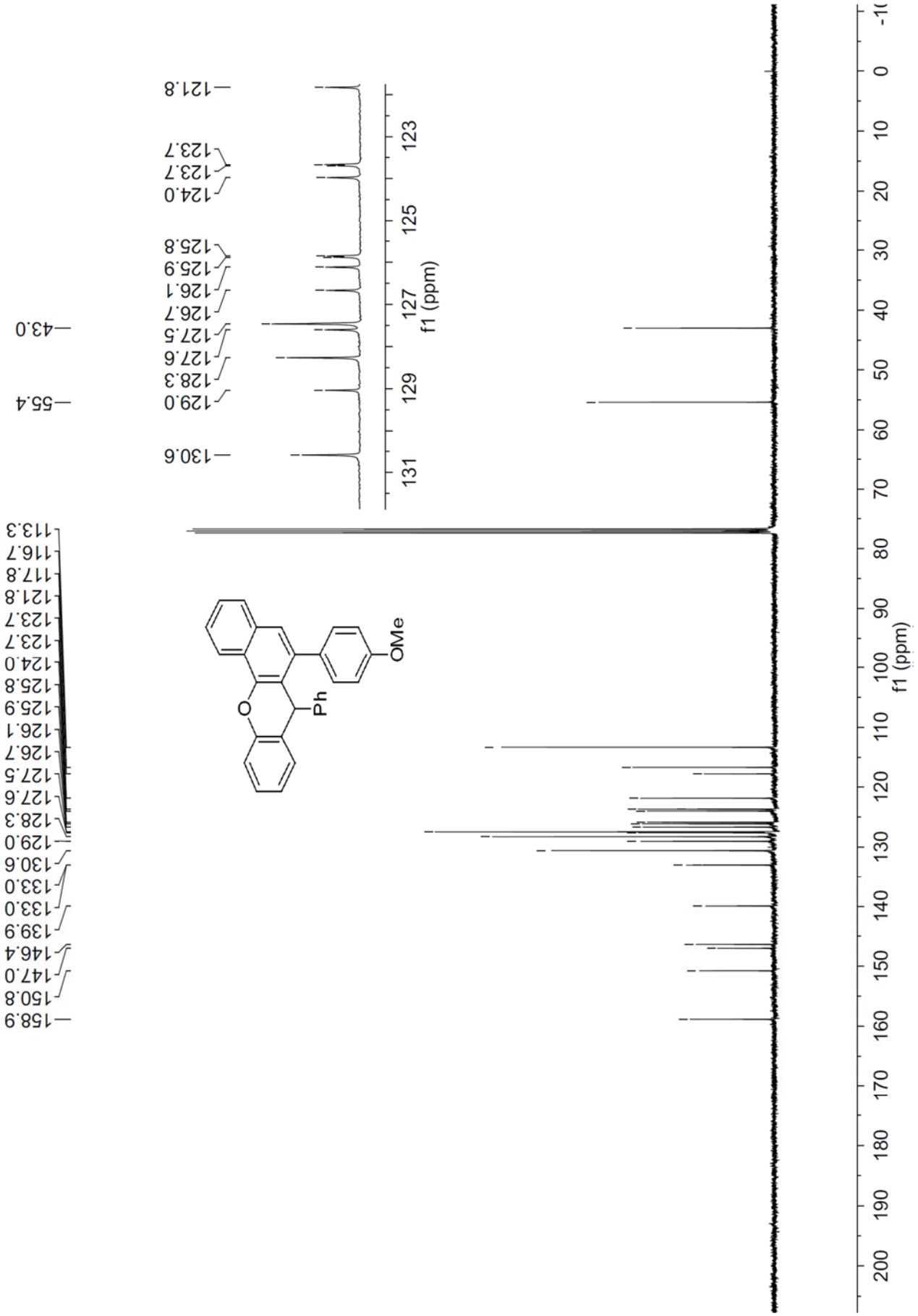
^{1}H NMR Spectrum of Compound 4e



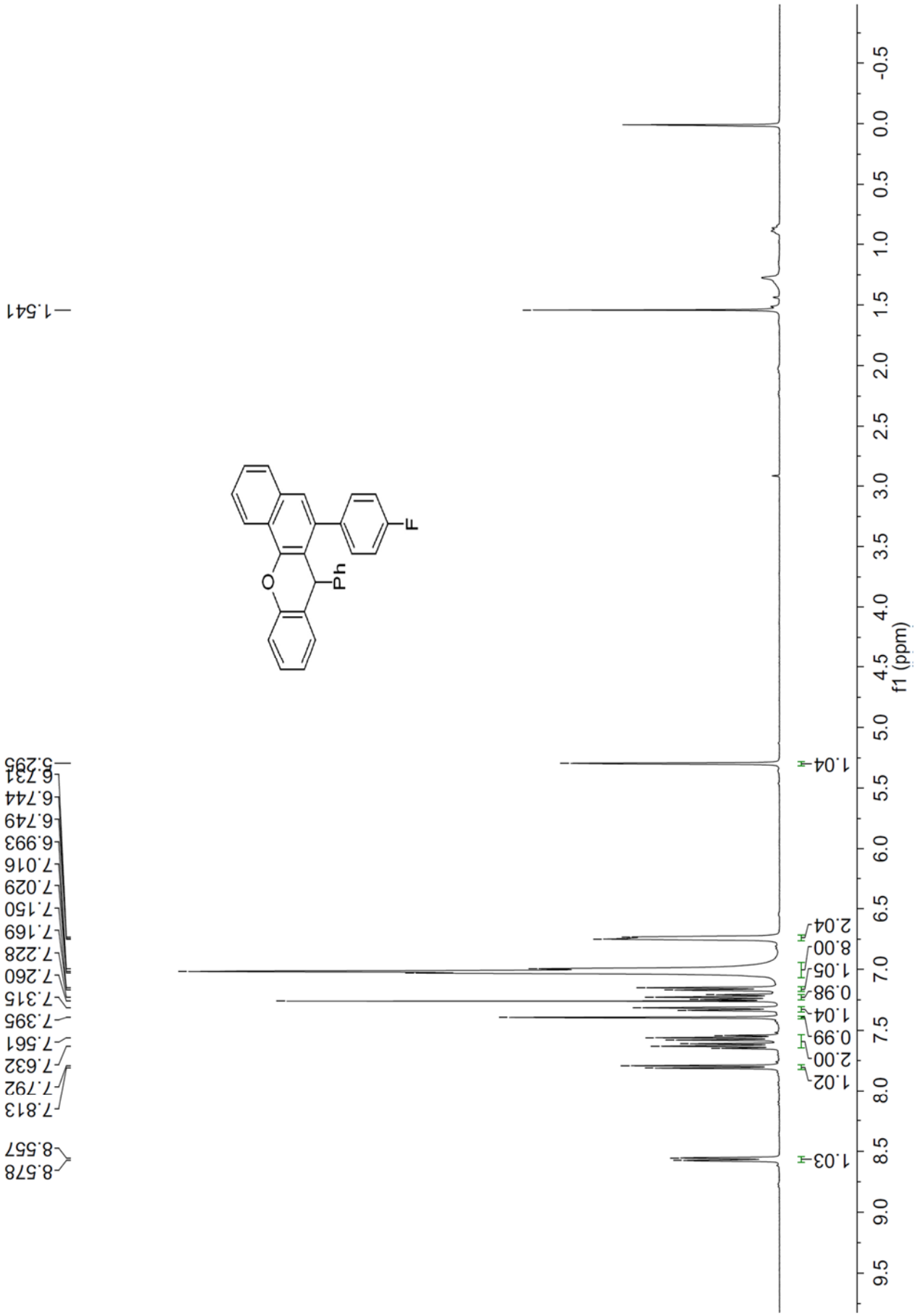
^{13}C NMR Spectrum of Compound 4e



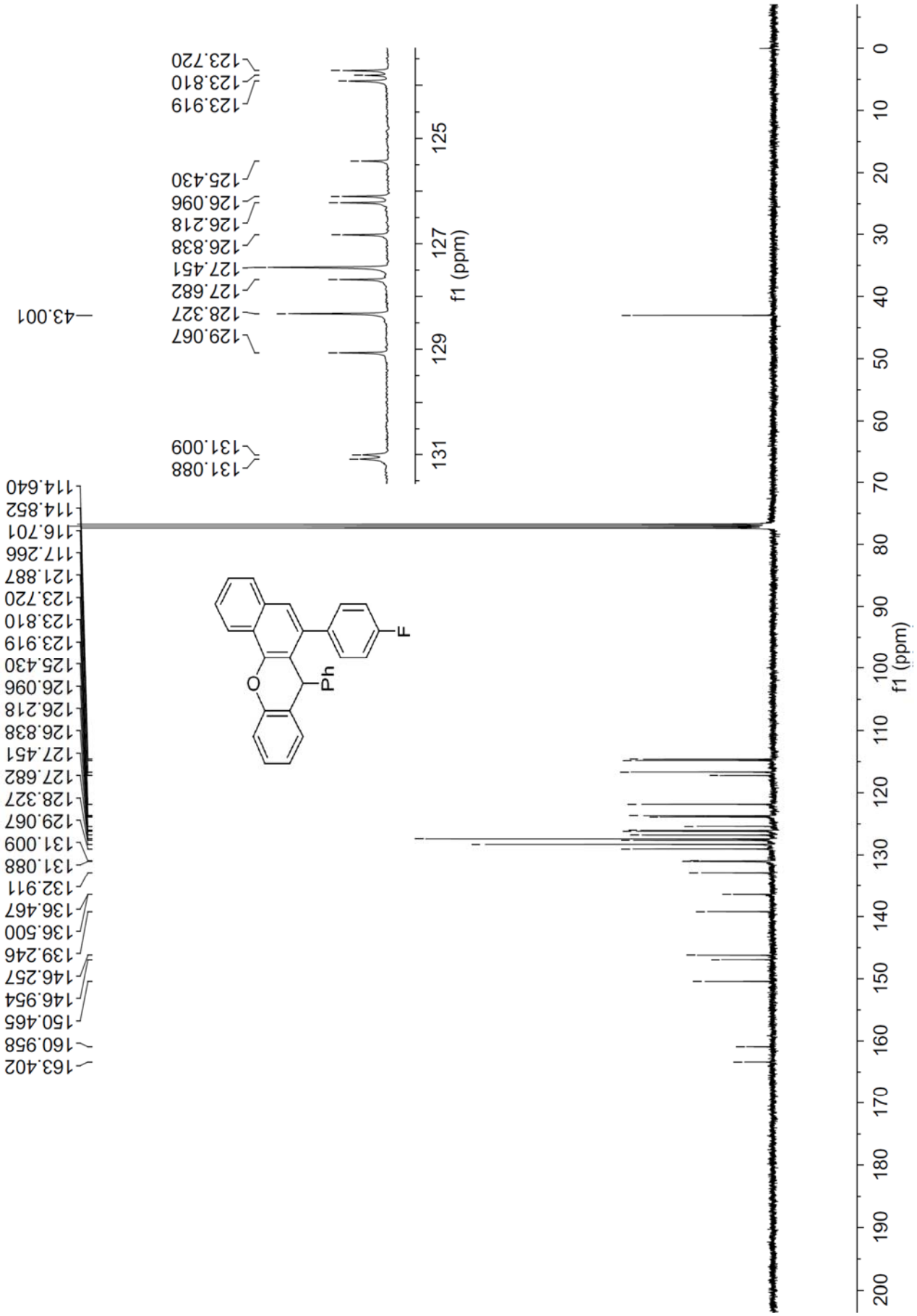
^{1}H NMR Spectrum of Compound 4f



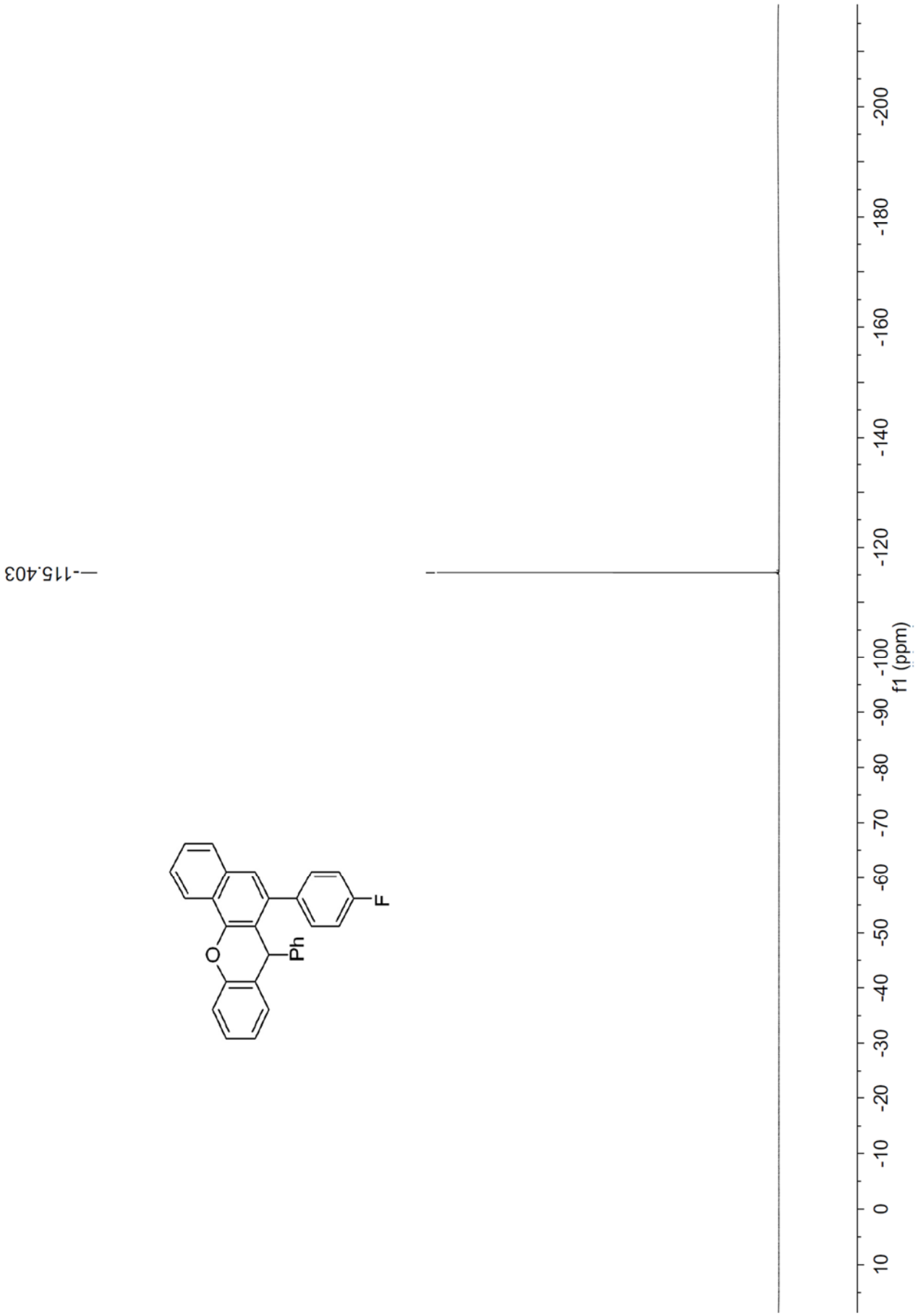
^{13}C NMR Spectrum of Compound 4f



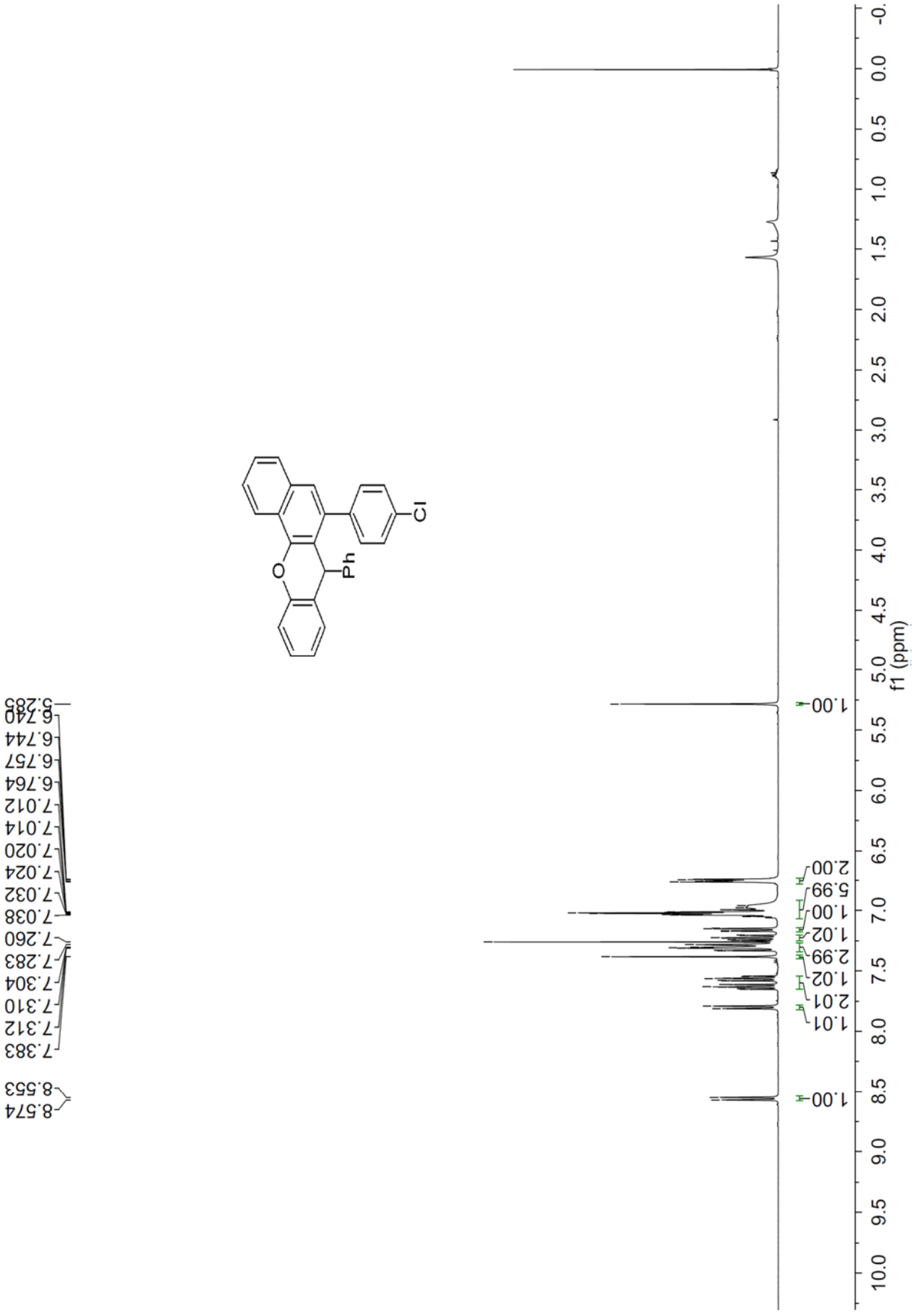
^{1}H NMR Spectrum of Compound 4g



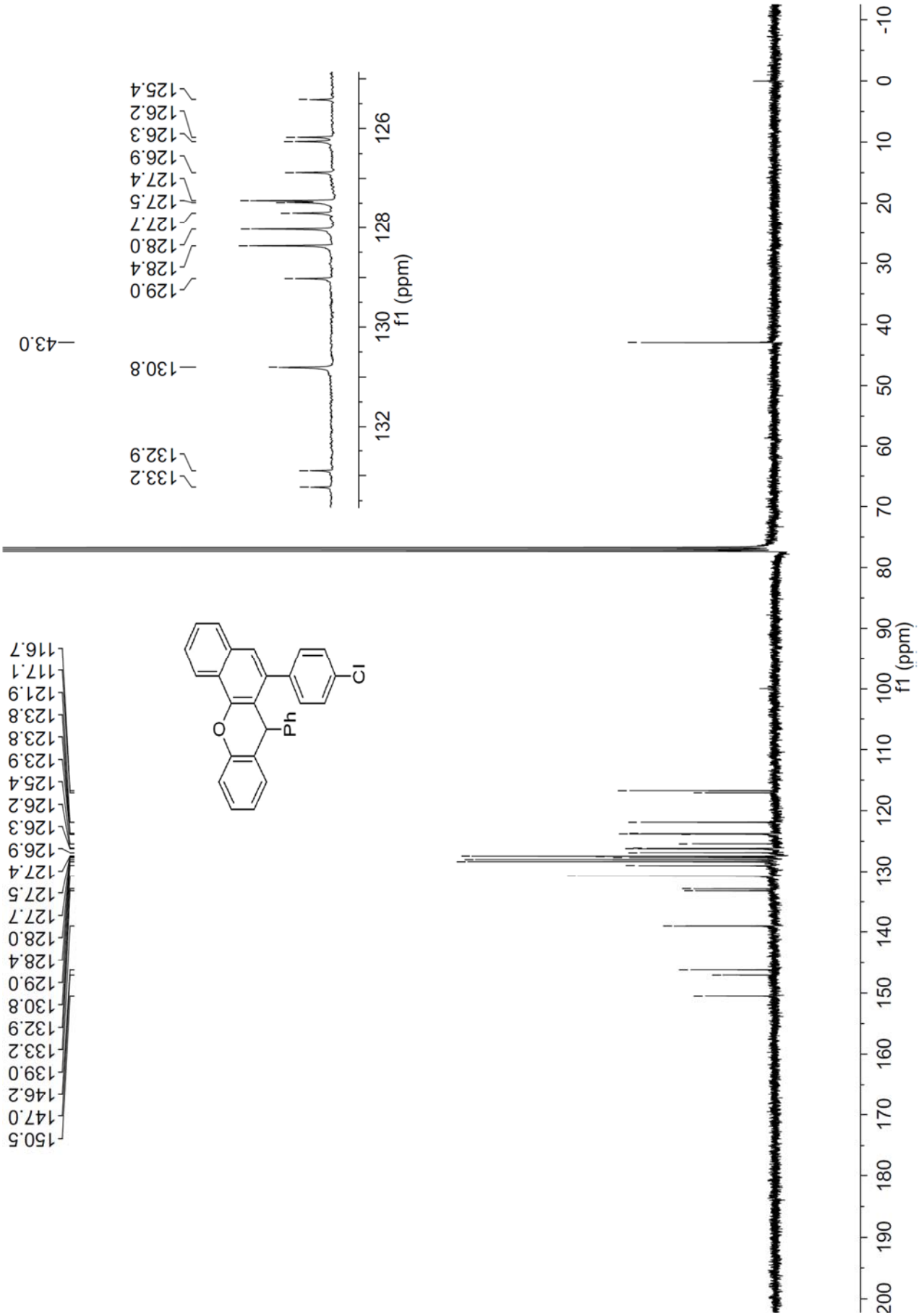
^{13}C NMR Spectrum of Compound 4g



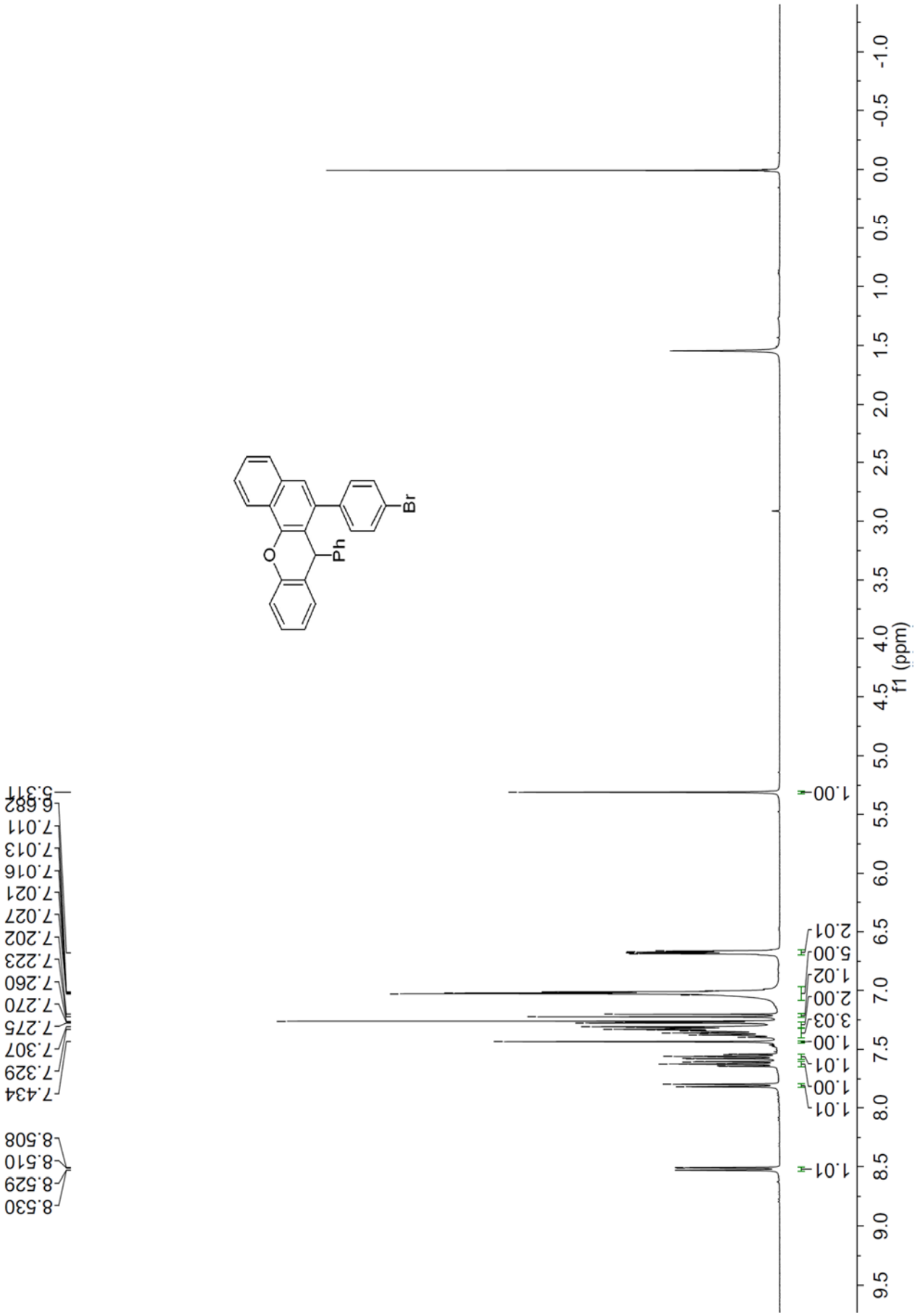
^{19}F NMR Spectrum of Compound 4g



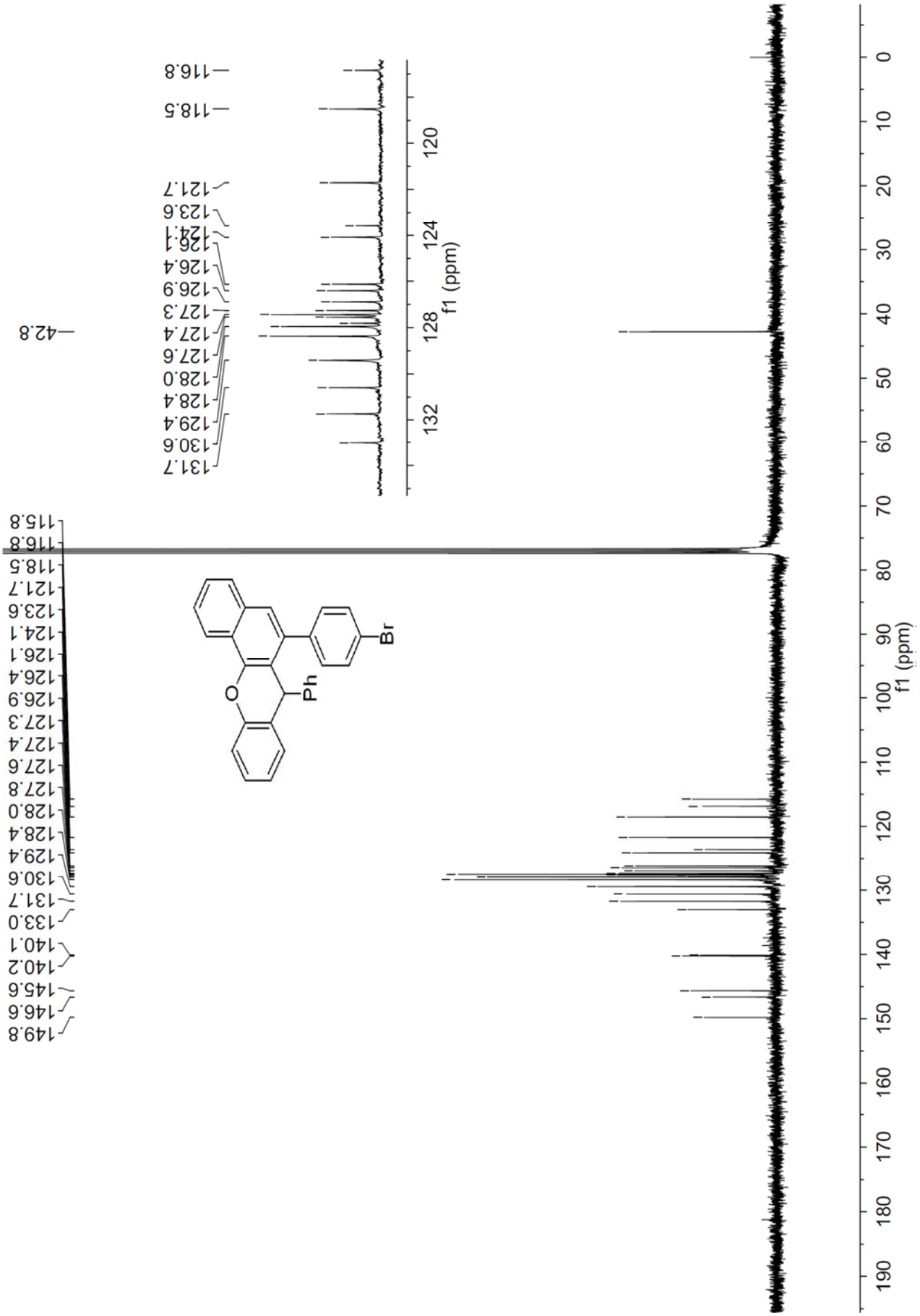
^{1}H NMR Spectrum of Compound 4h



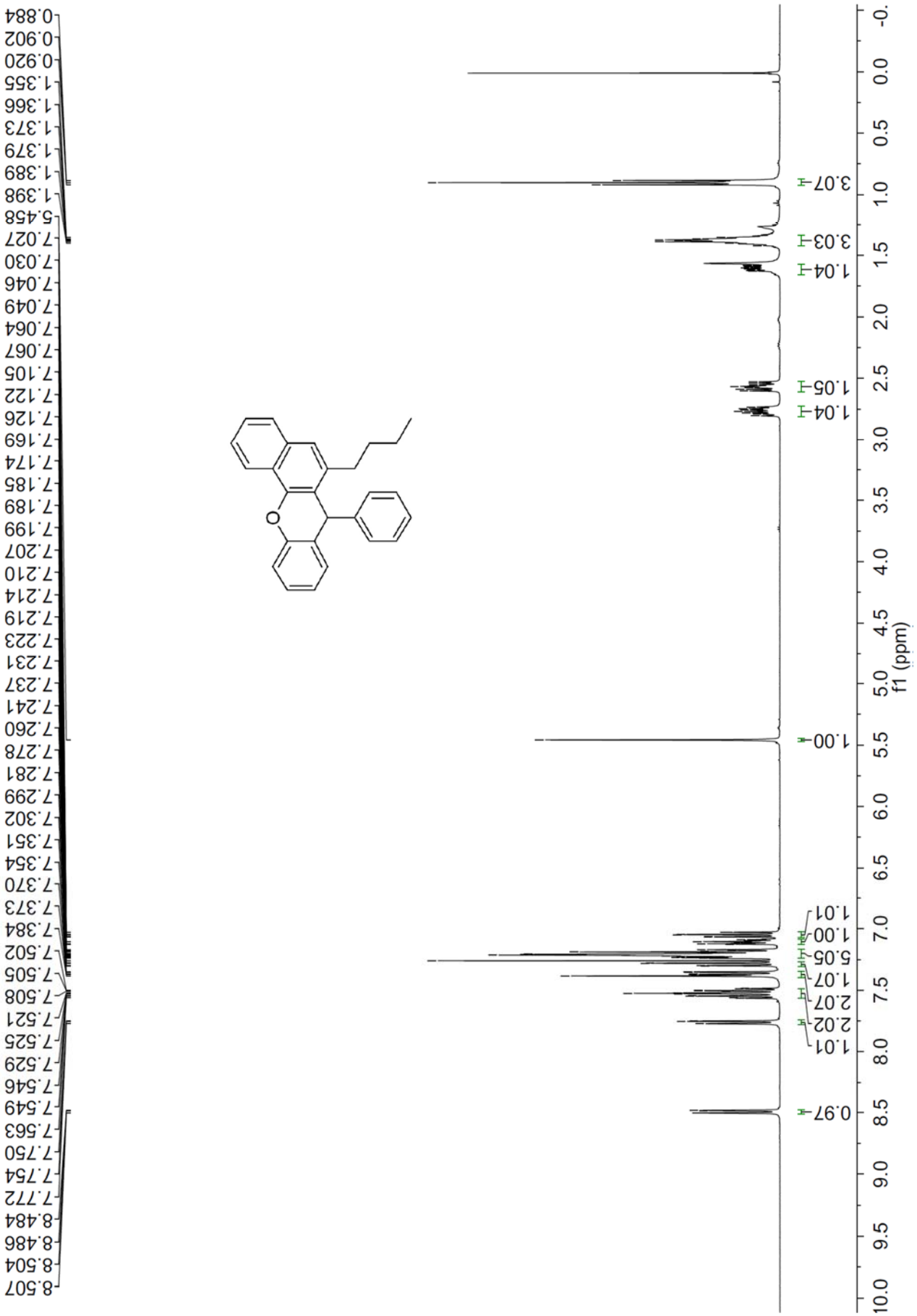
^{13}C NMR Spectrum of Compound 4h



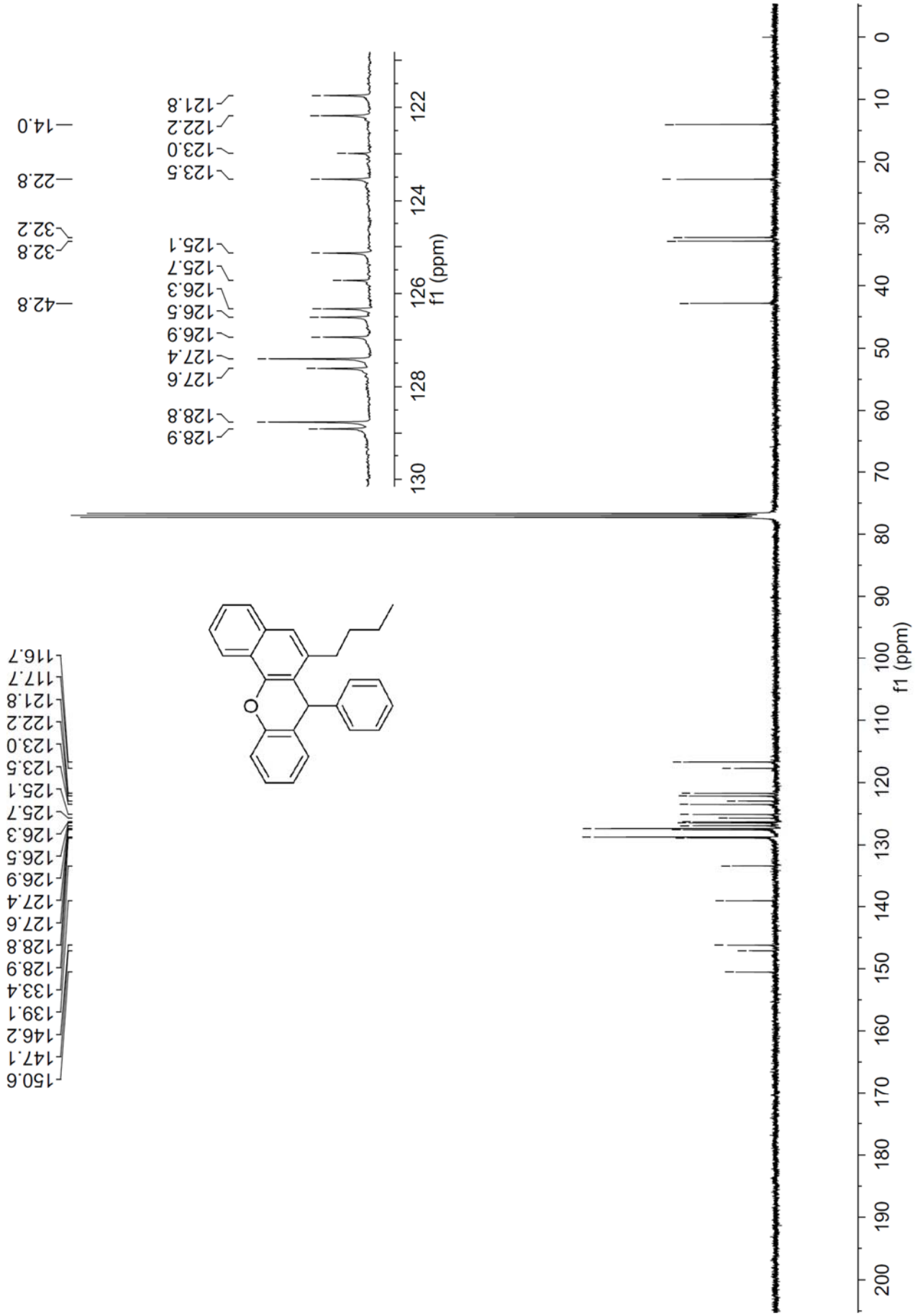
^{1}H NMR Spectrum of Compound 4i



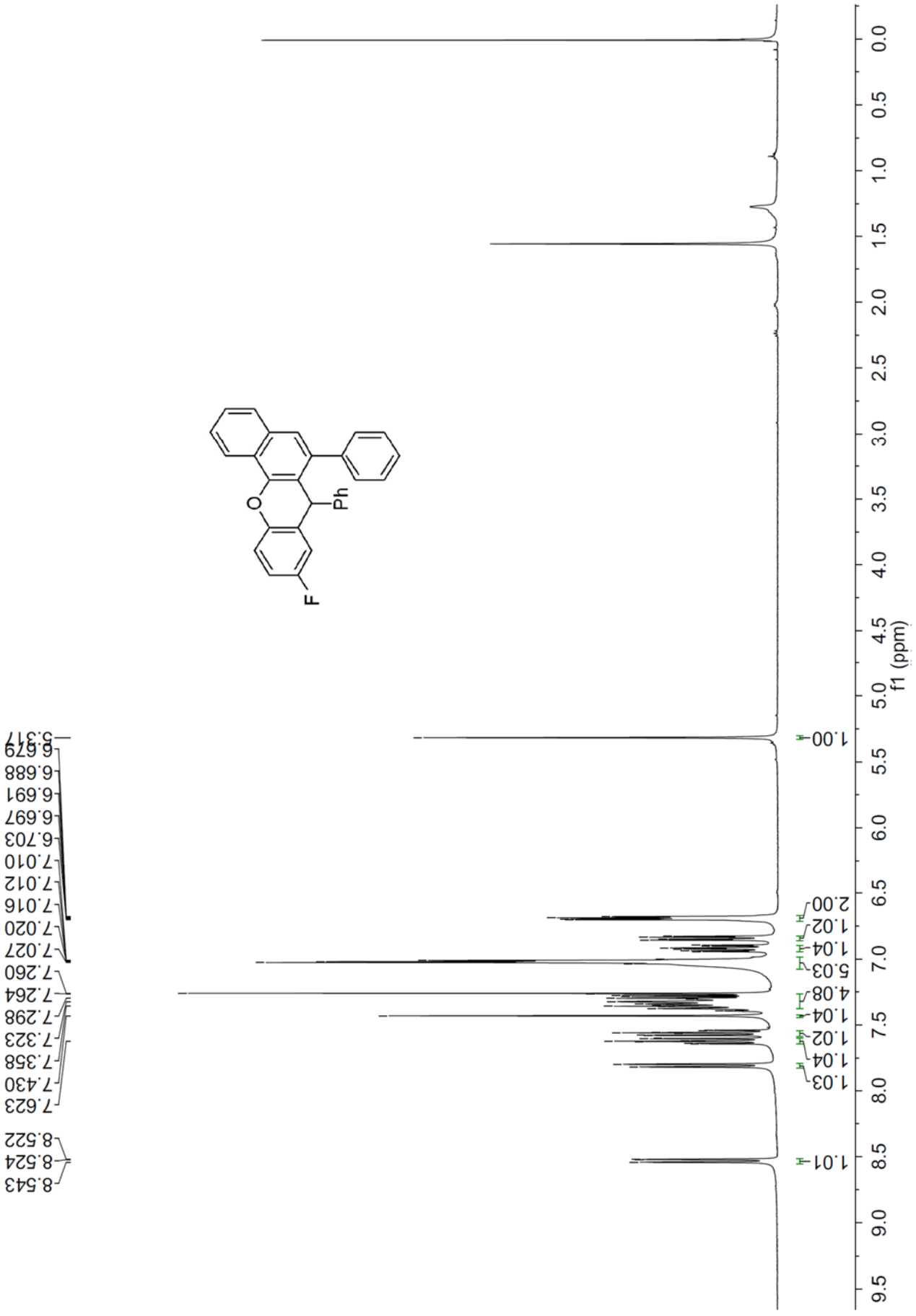
^{13}C NMR Spectrum of Compound 4i



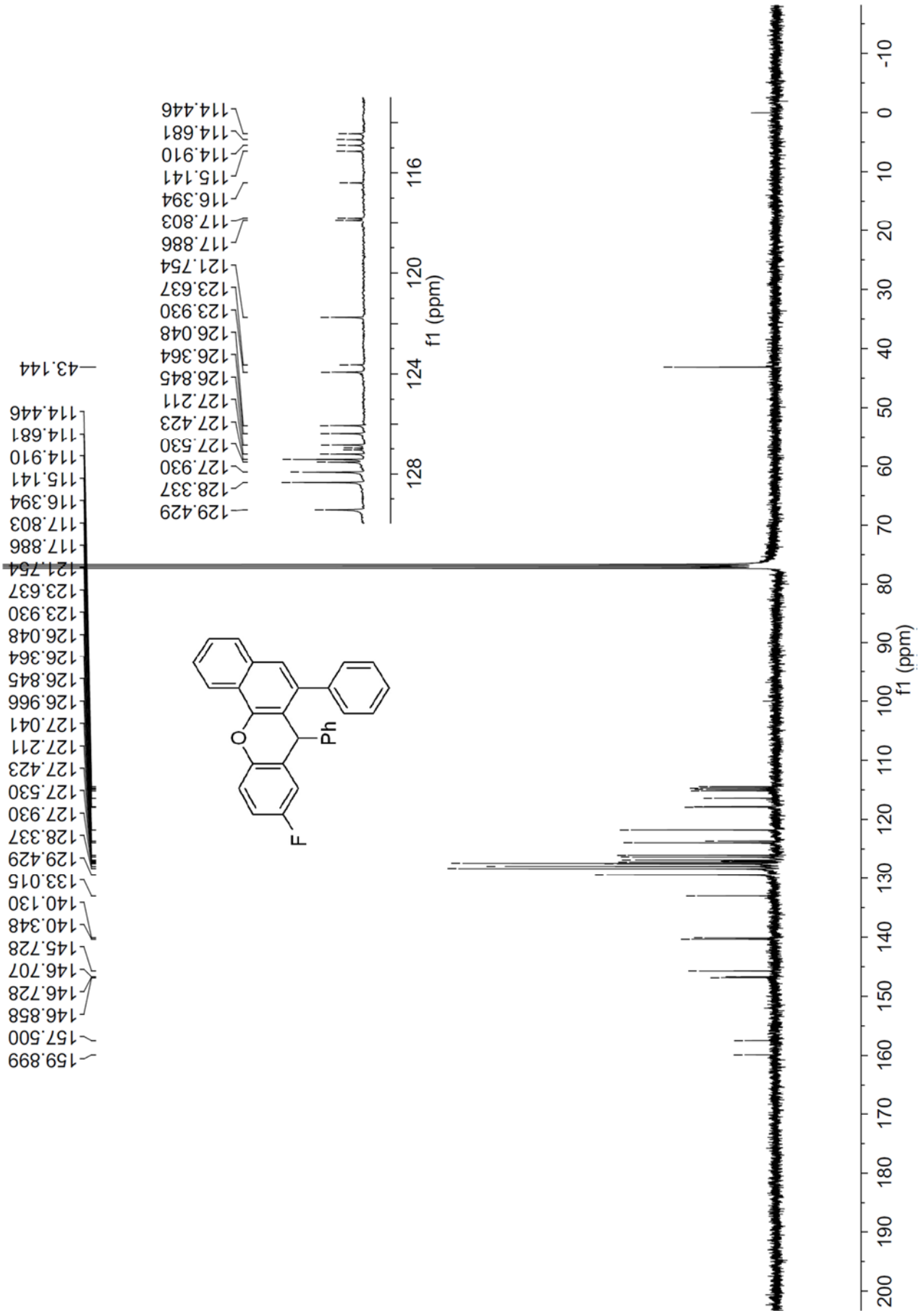
^{1}H NMR Spectrum of Compound 4j



^{13}C NMR Spectrum of Compound 4j

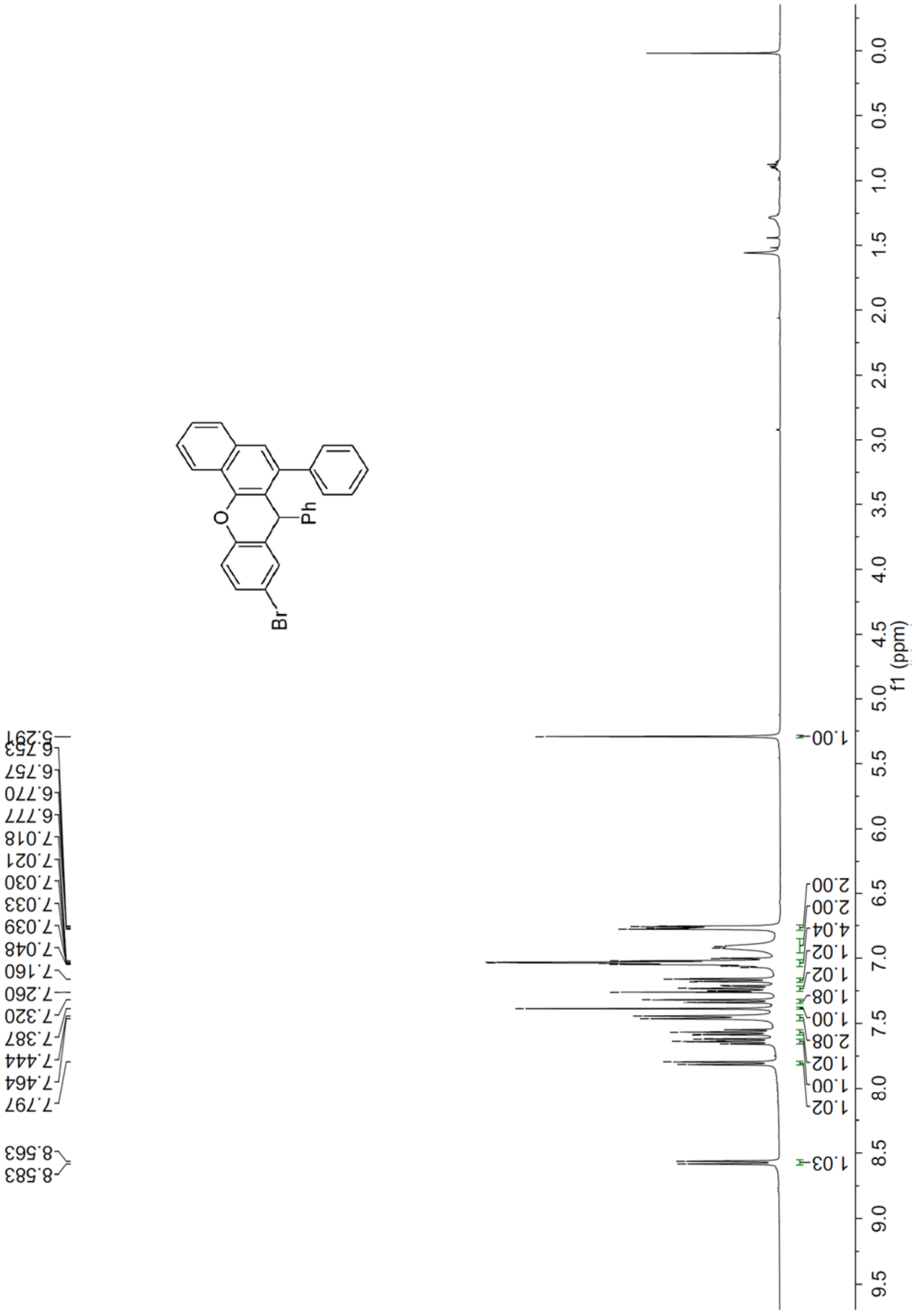


^{1}H NMR Spectrum of Compound 4l

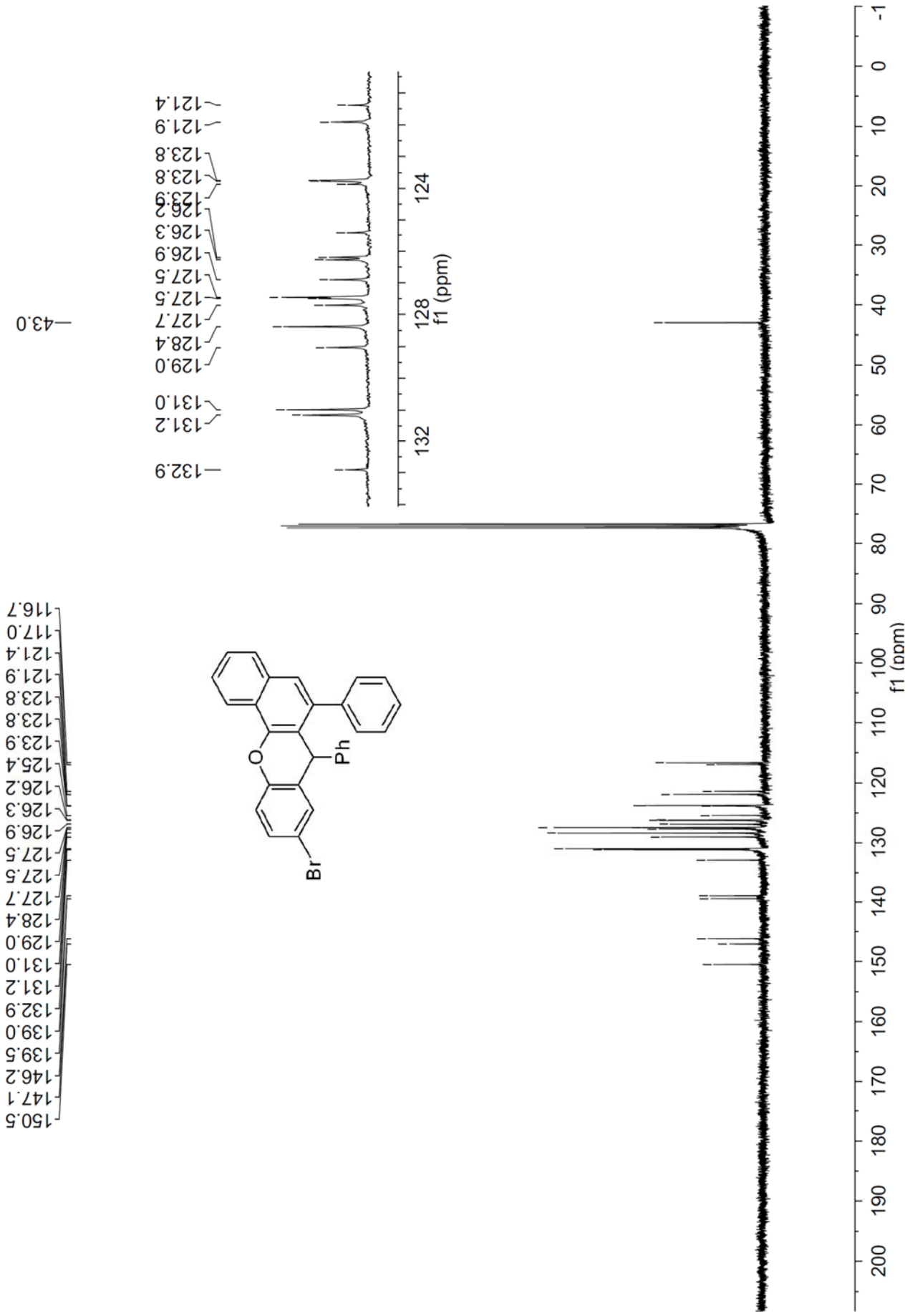


^{13}C NMR Spectrum of Compound 4l

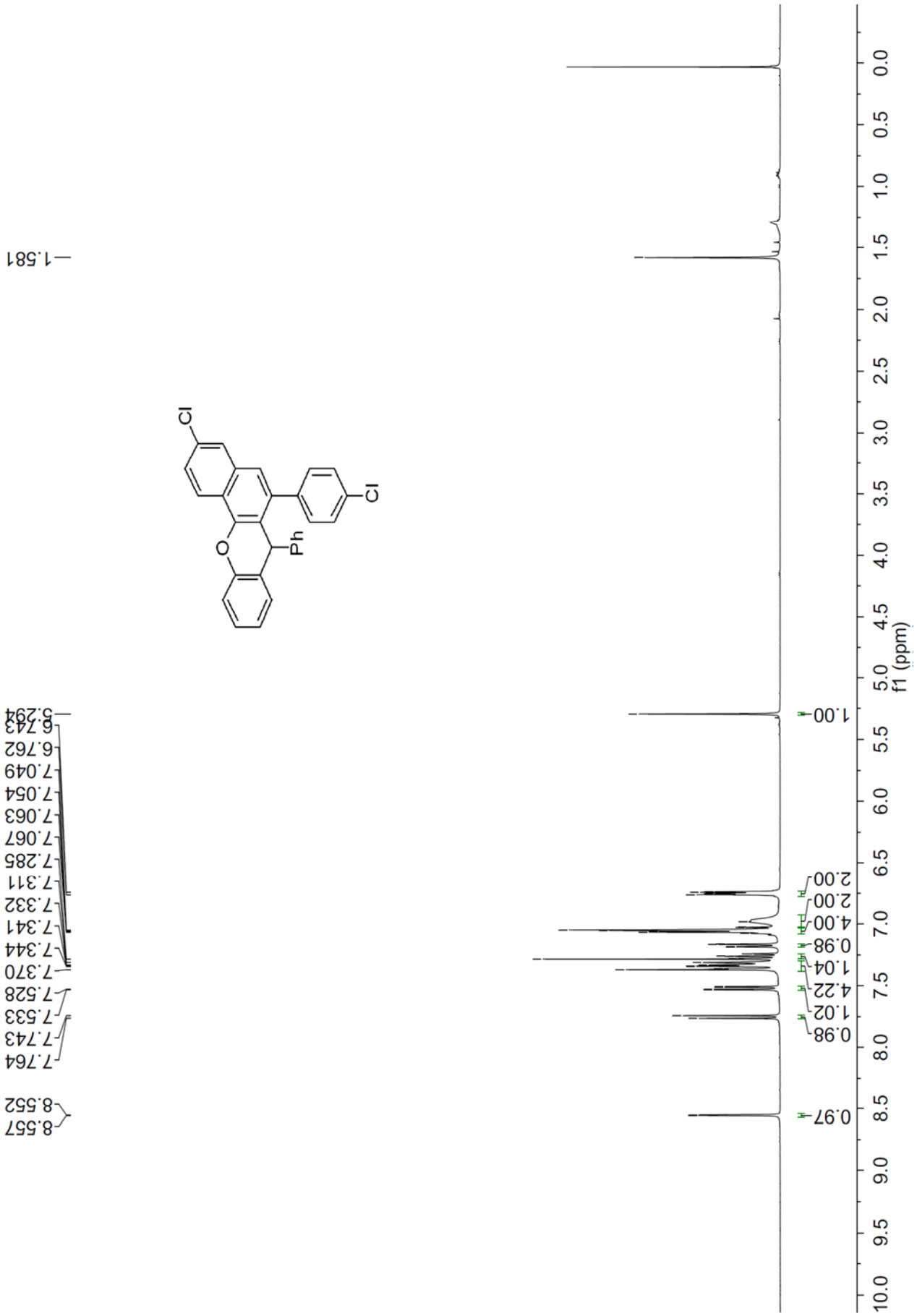
^{19}F NMR Spectrum of Compound 4l



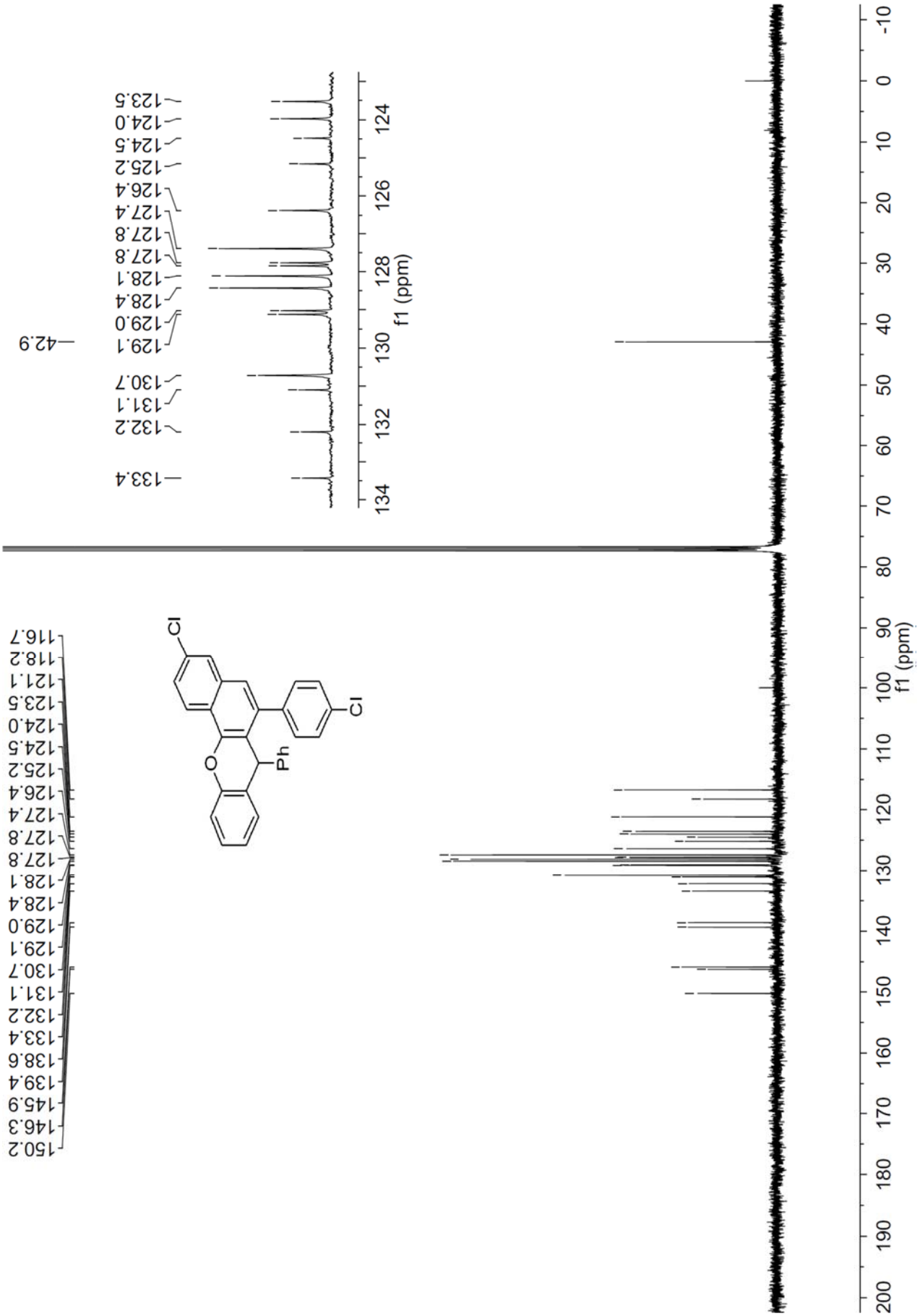
^{1}H NMR Spectrum of Compound 4m



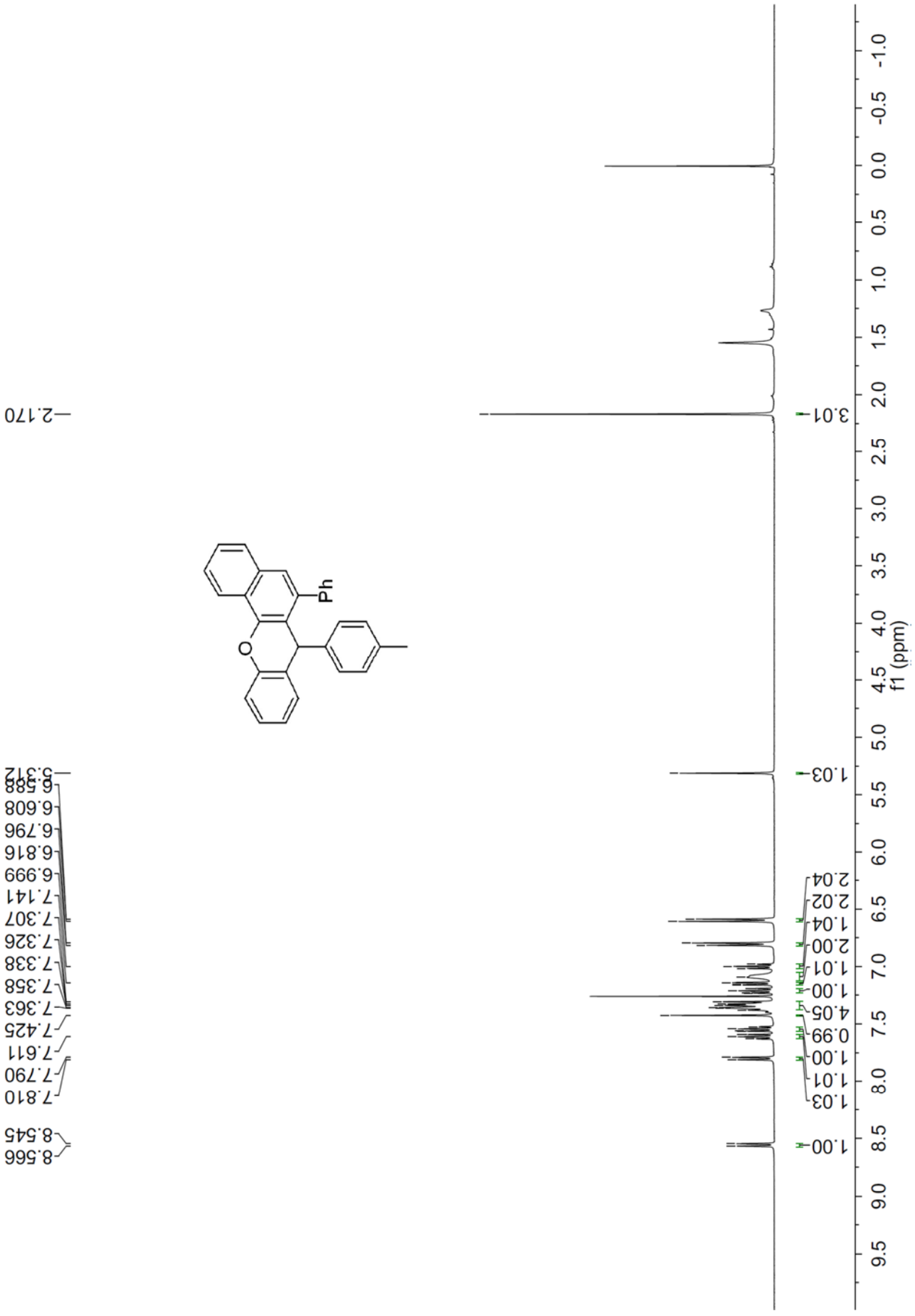
^{13}C NMR Spectrum of Compound 4m



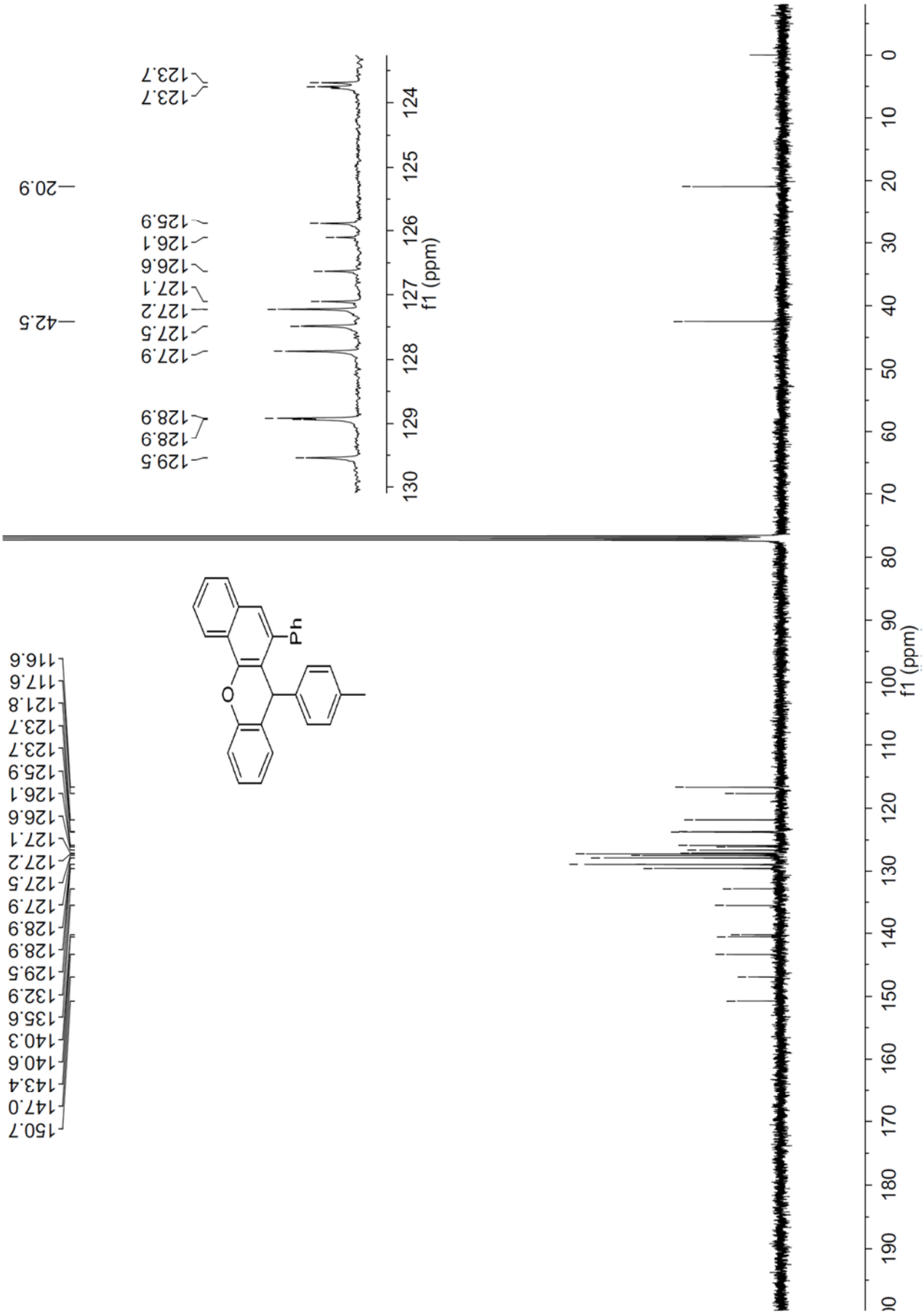
^{1}H NMR Spectrum of Compound 4n



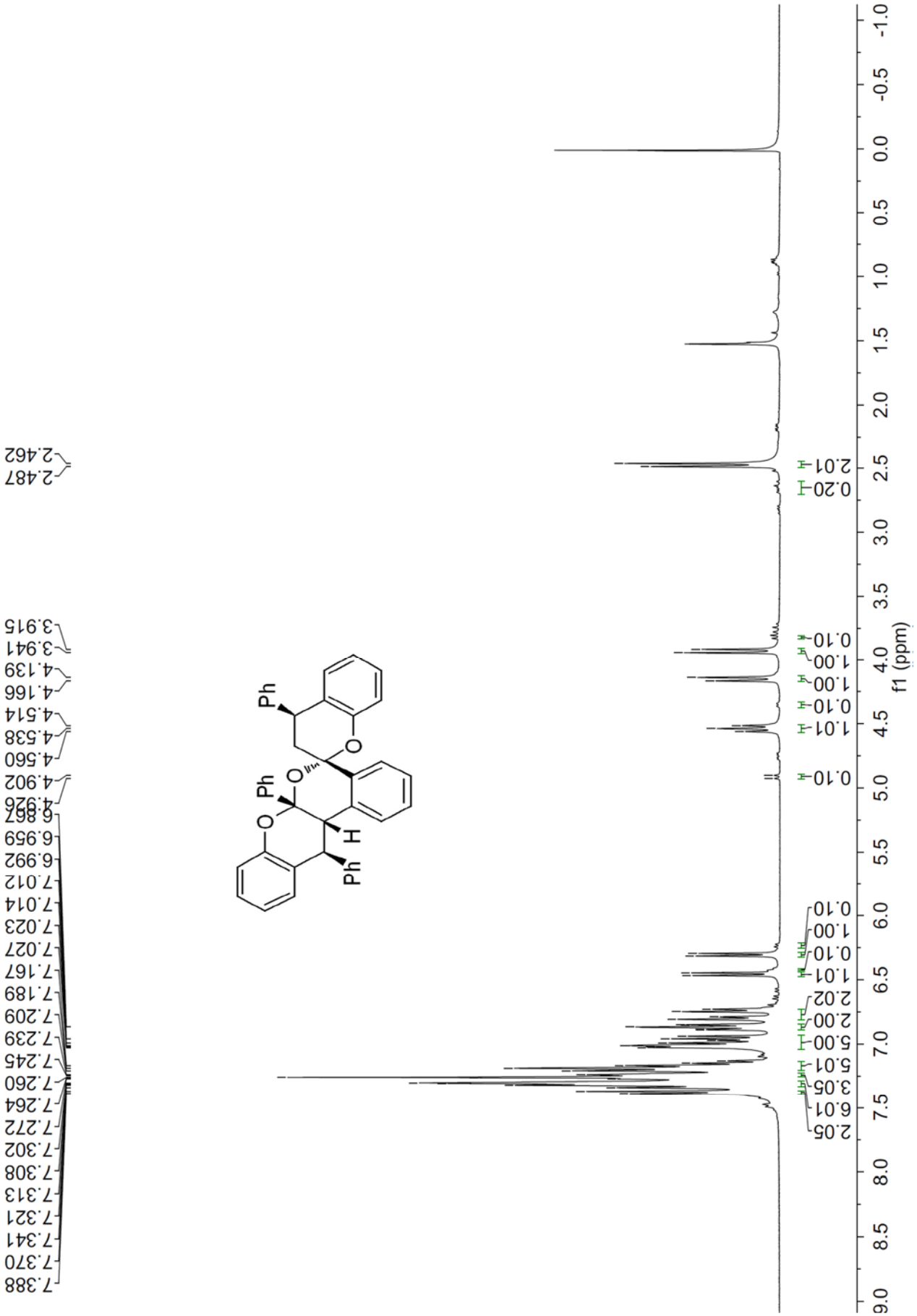
^{13}C NMR Spectrum of Compound 4n



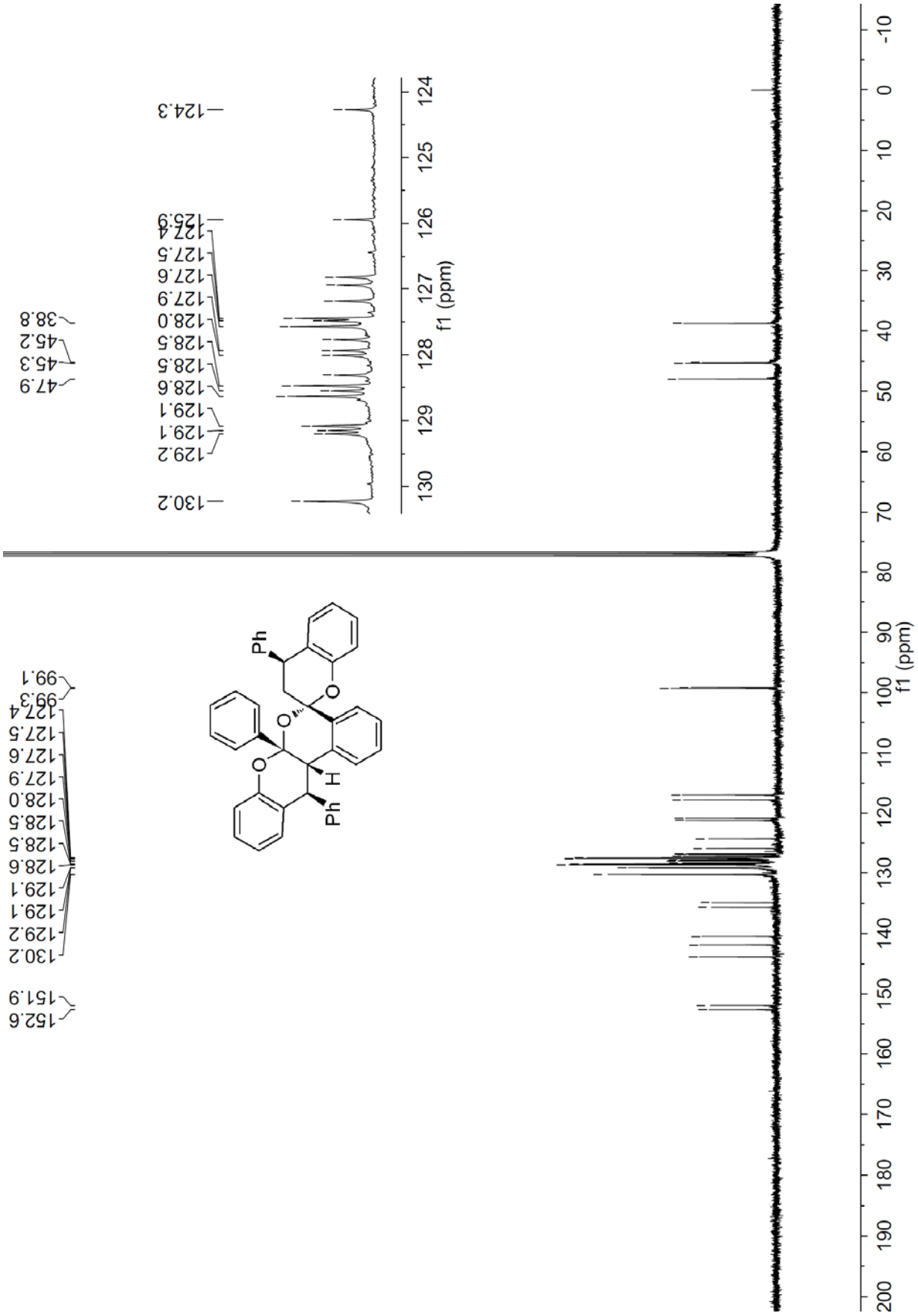
[1]H NMR Spectrum of Compound 4o



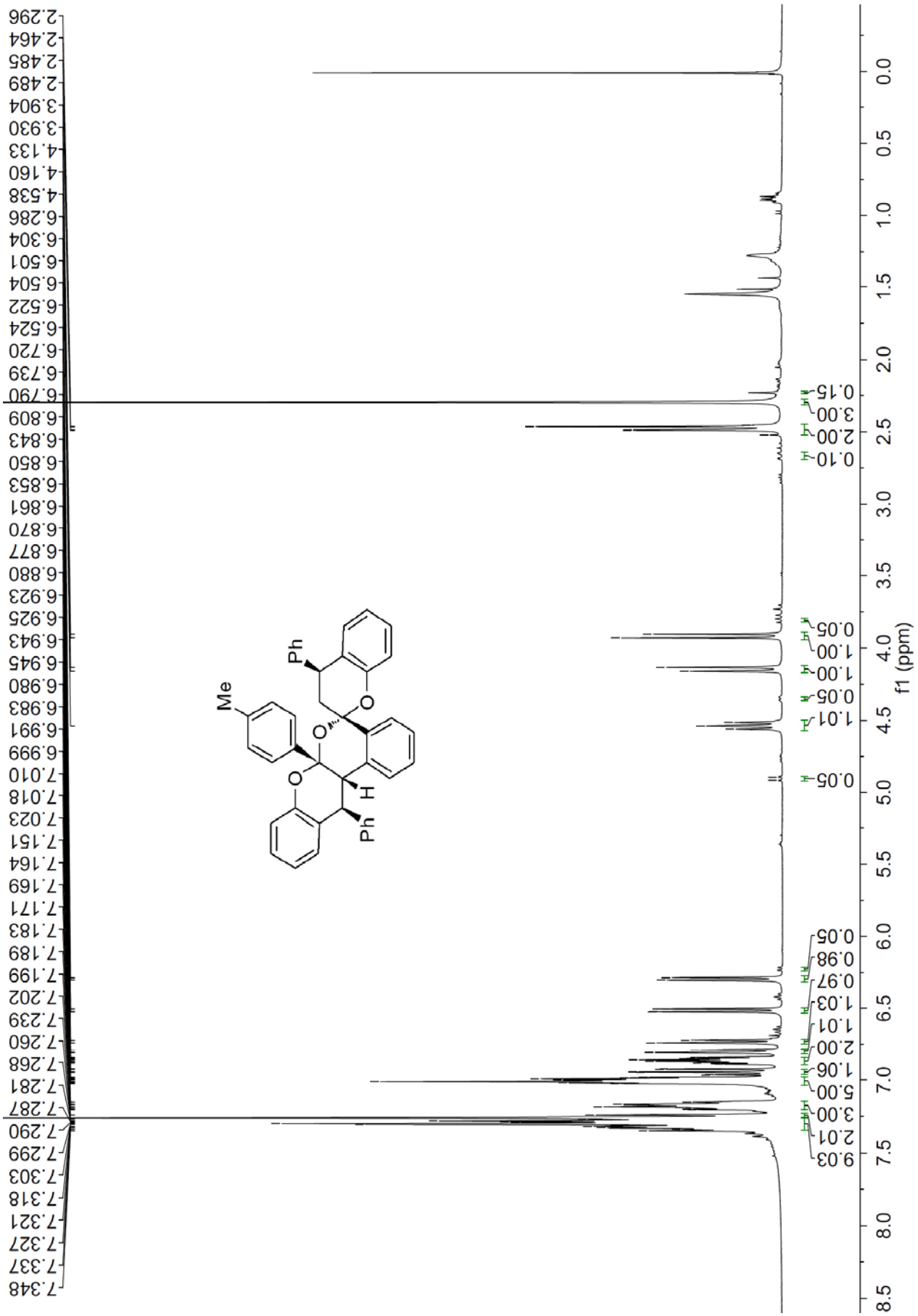
^{13}C NMR Spectrum of Compound 4o



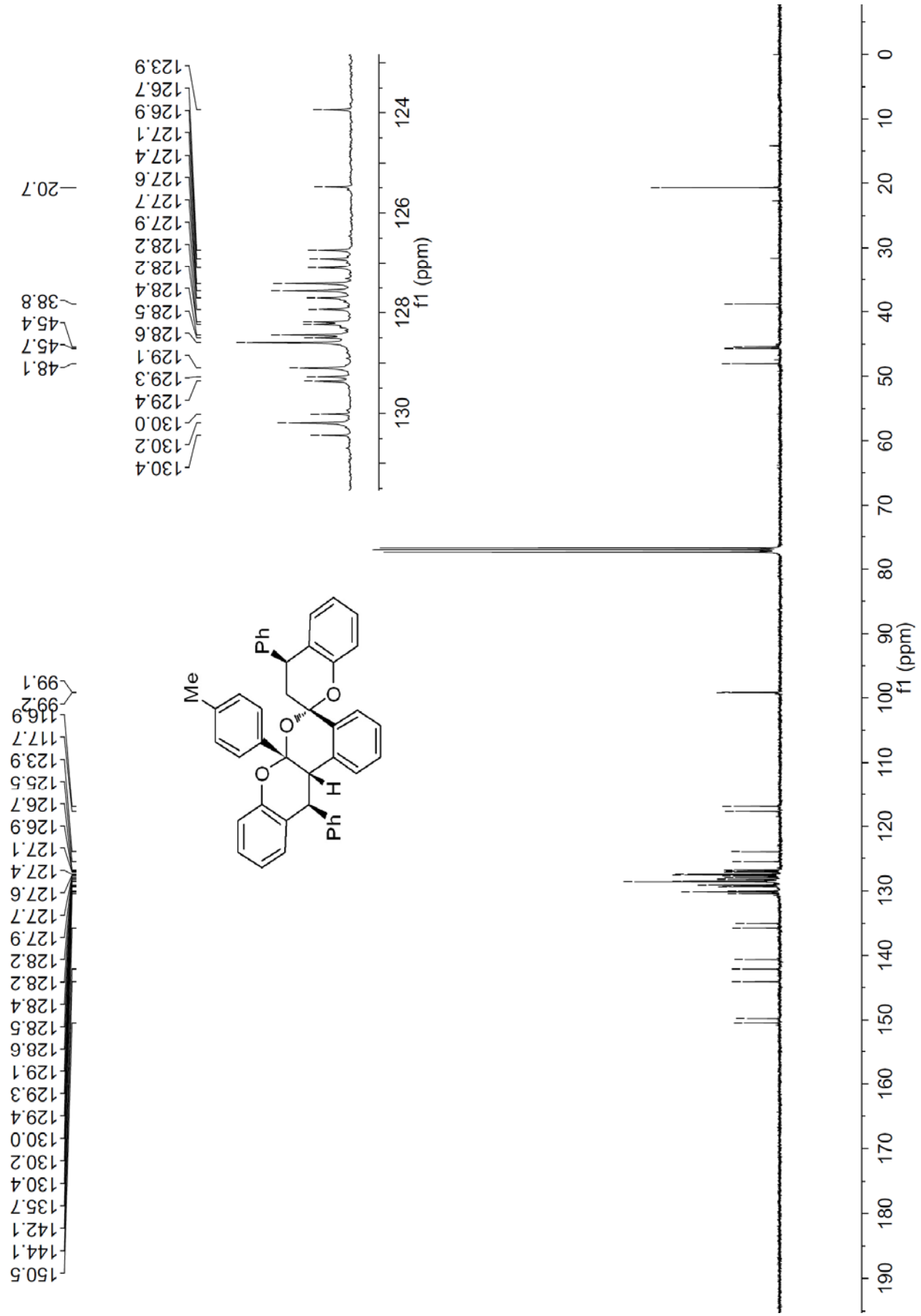
^{1}H NMR Spectrum of Compound 5a



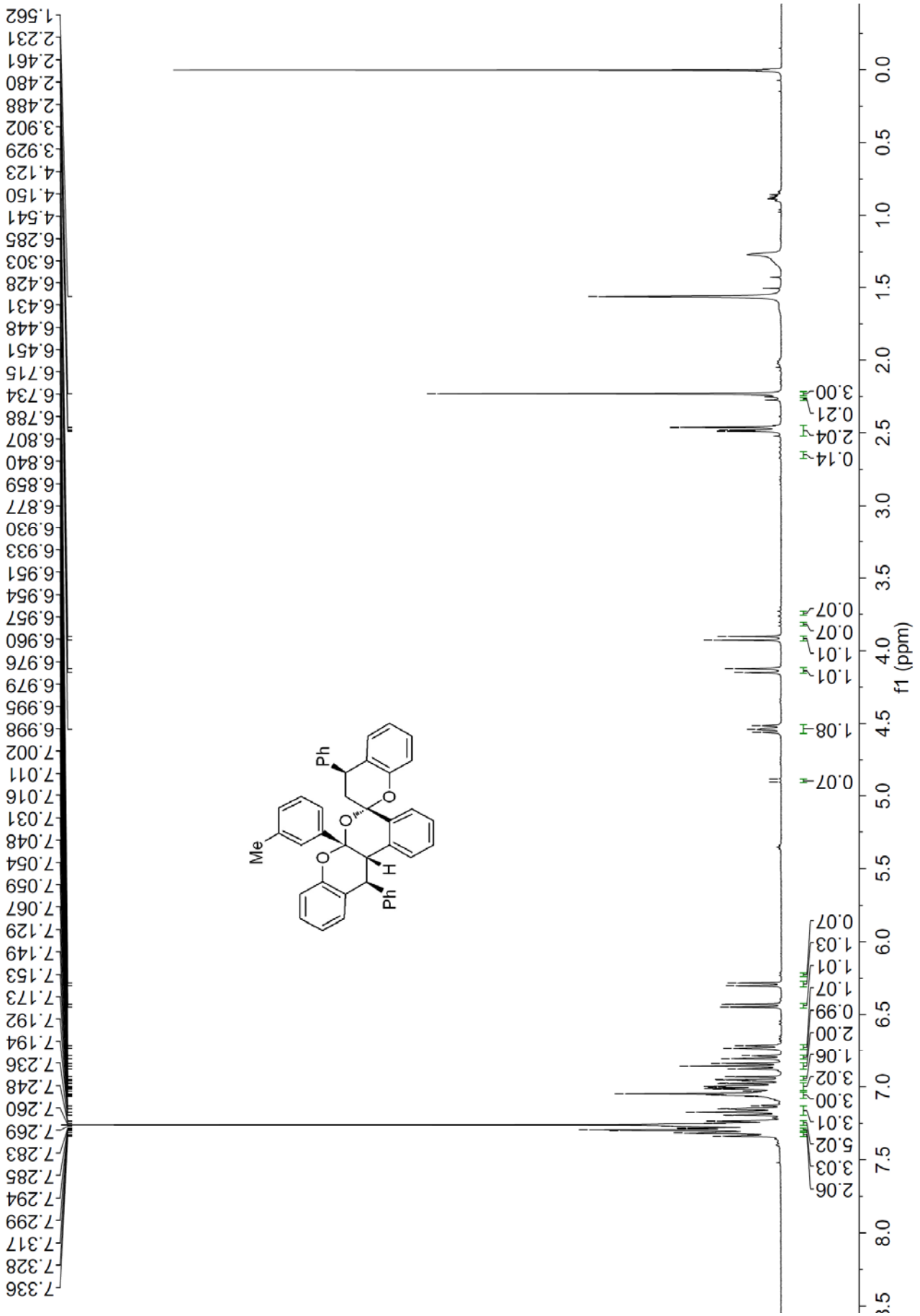
^{13}C NMR Spectrum of Compound 5a



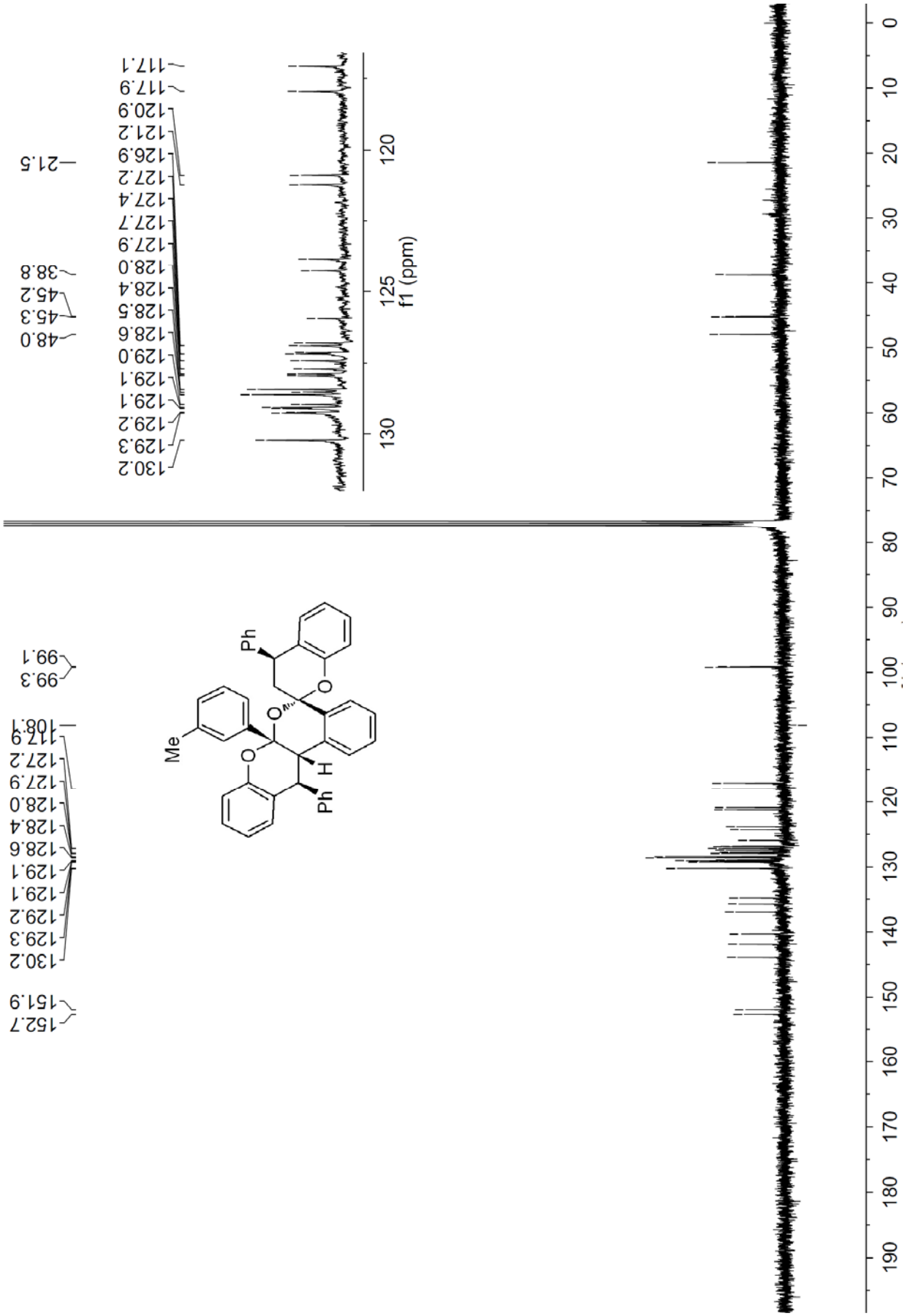
^{1}H NMR Spectrum of Compound 5b



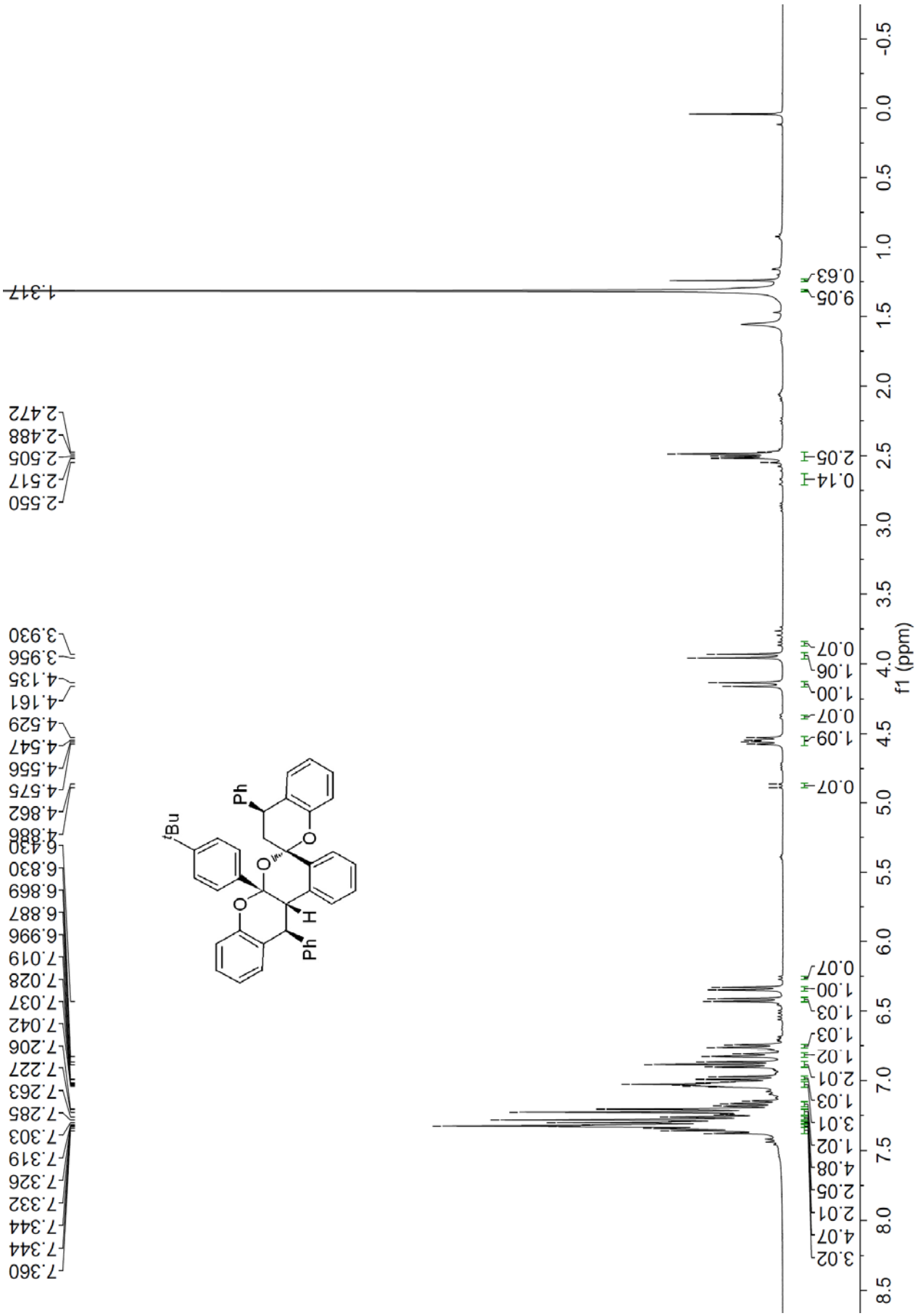
^{13}C NMR Spectrum of Compound 5b



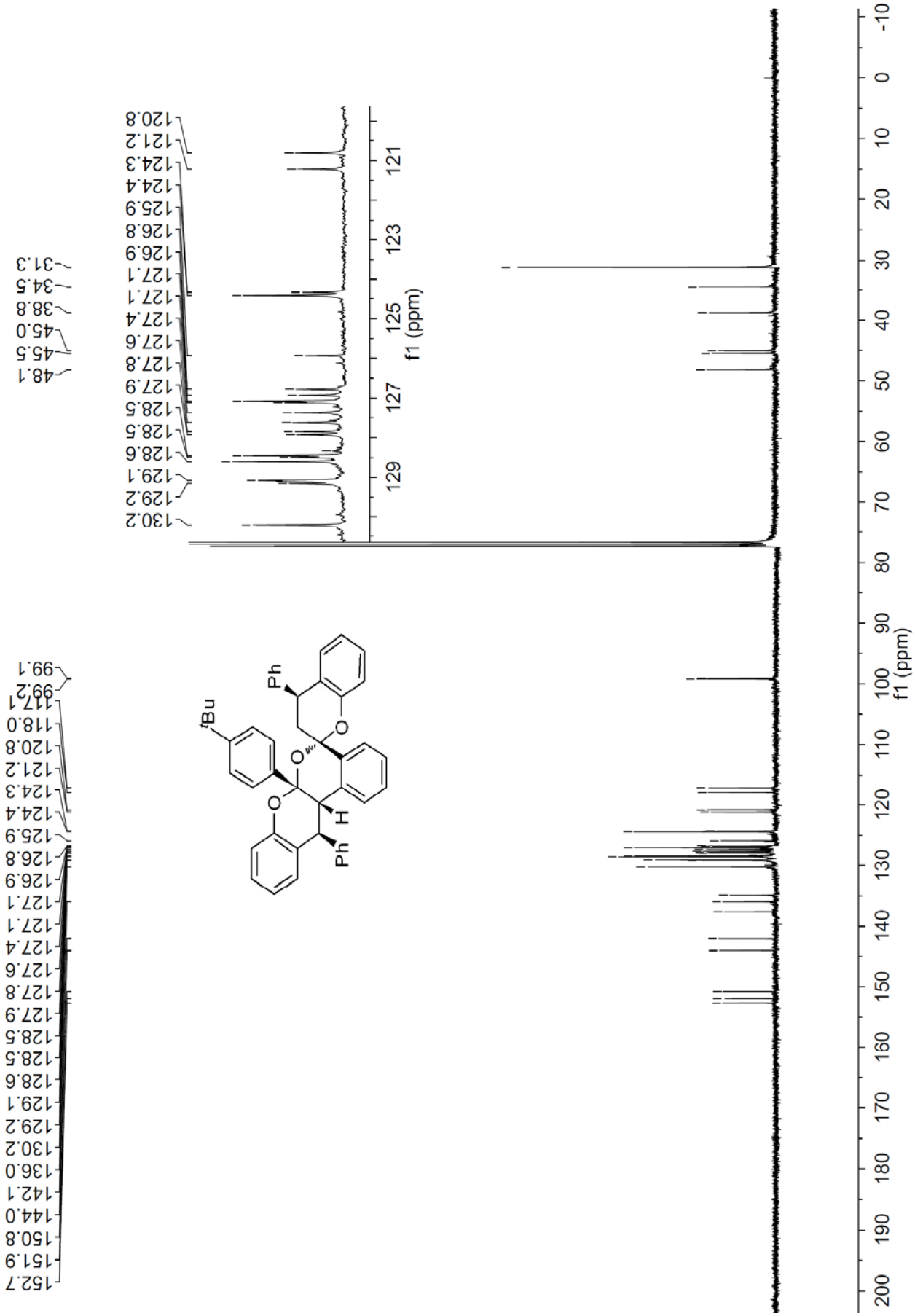
^{1}H NMR Spectrum of Compound 5c



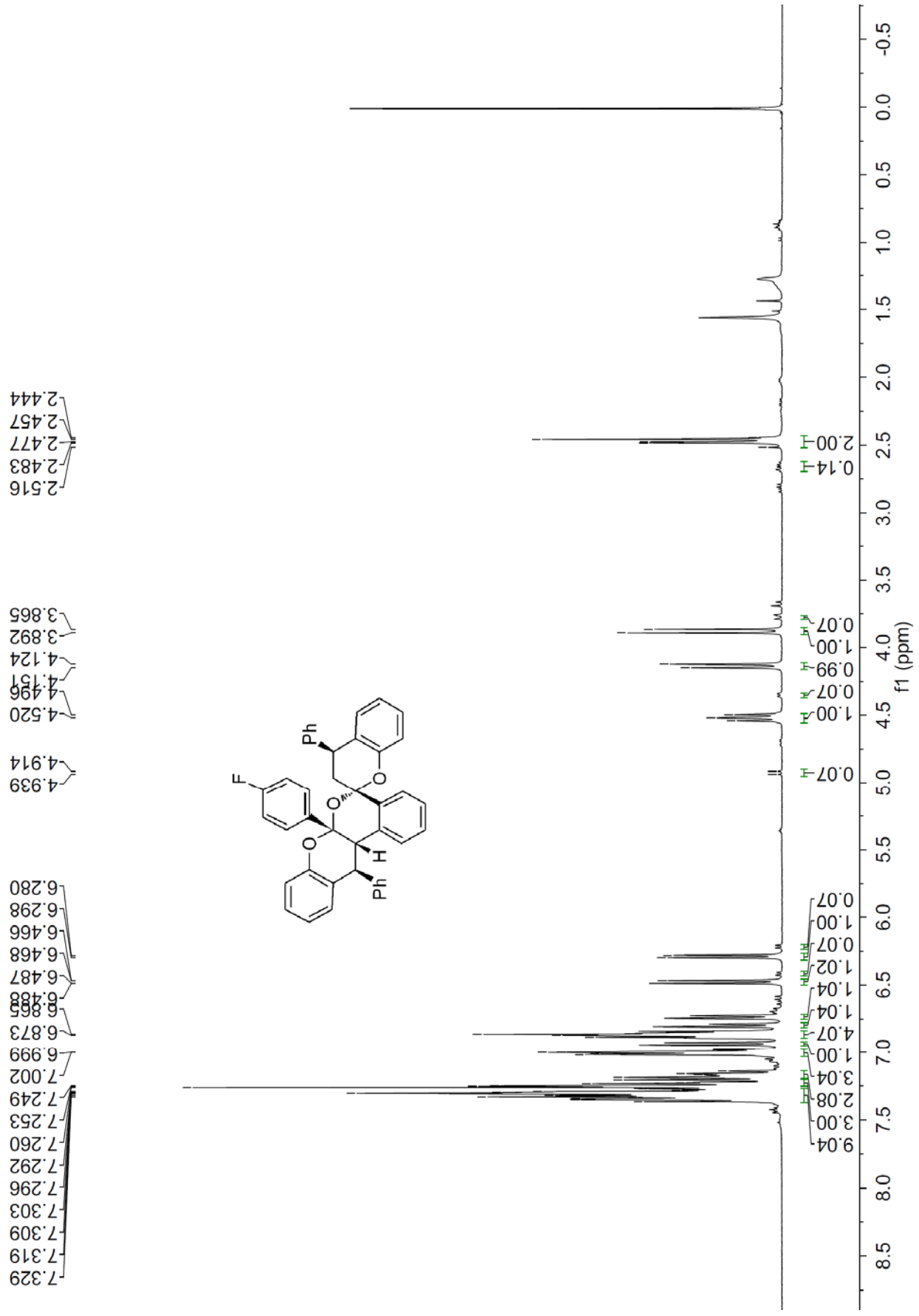
^{13}C NMR Spectrum of Compound 5c



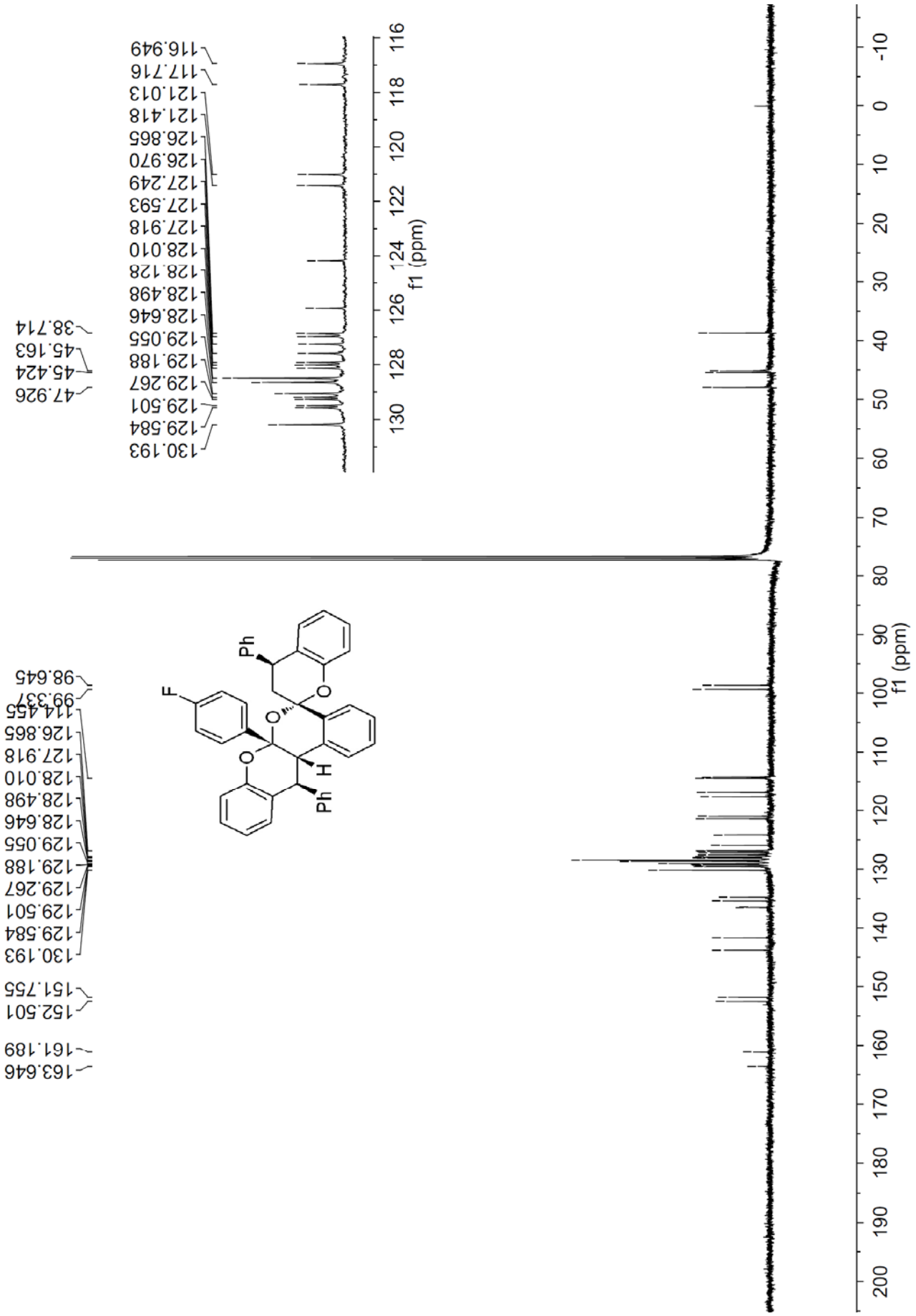
^{1}H NMR Spectrum of Compound 5d



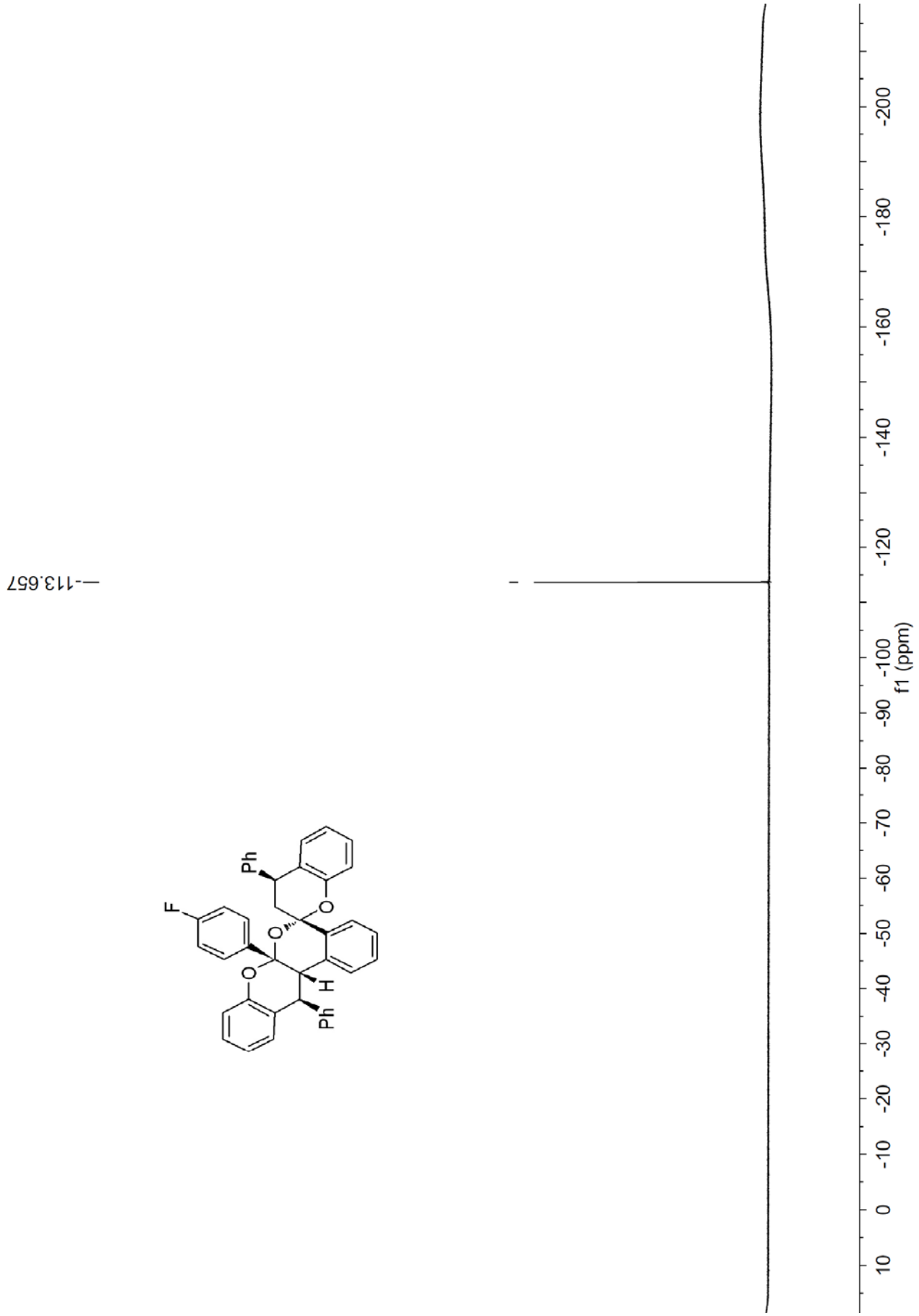
^{13}C NMR Spectrum of Compound 5d



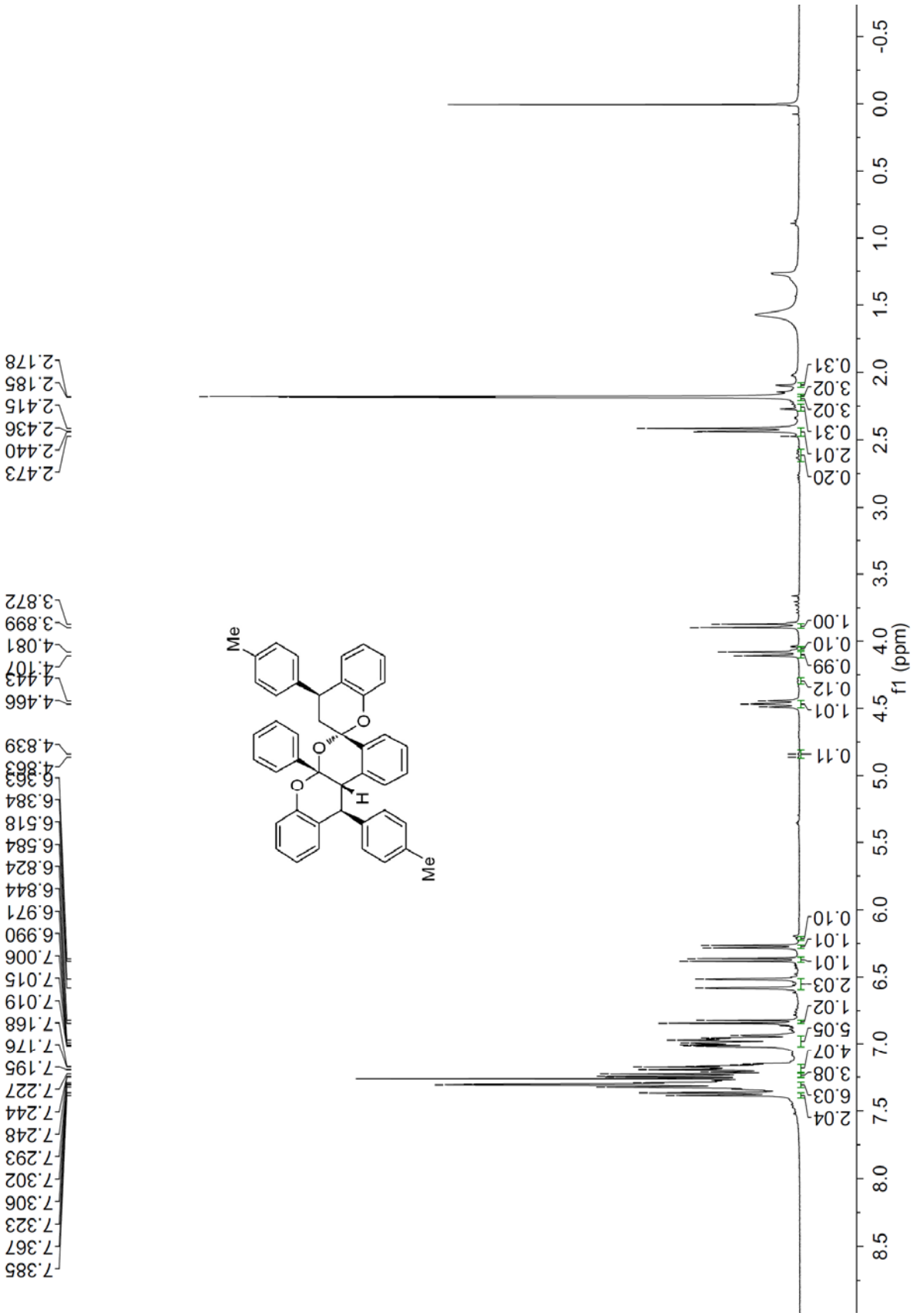
^{1}H NMR Spectrum of Compound 5e



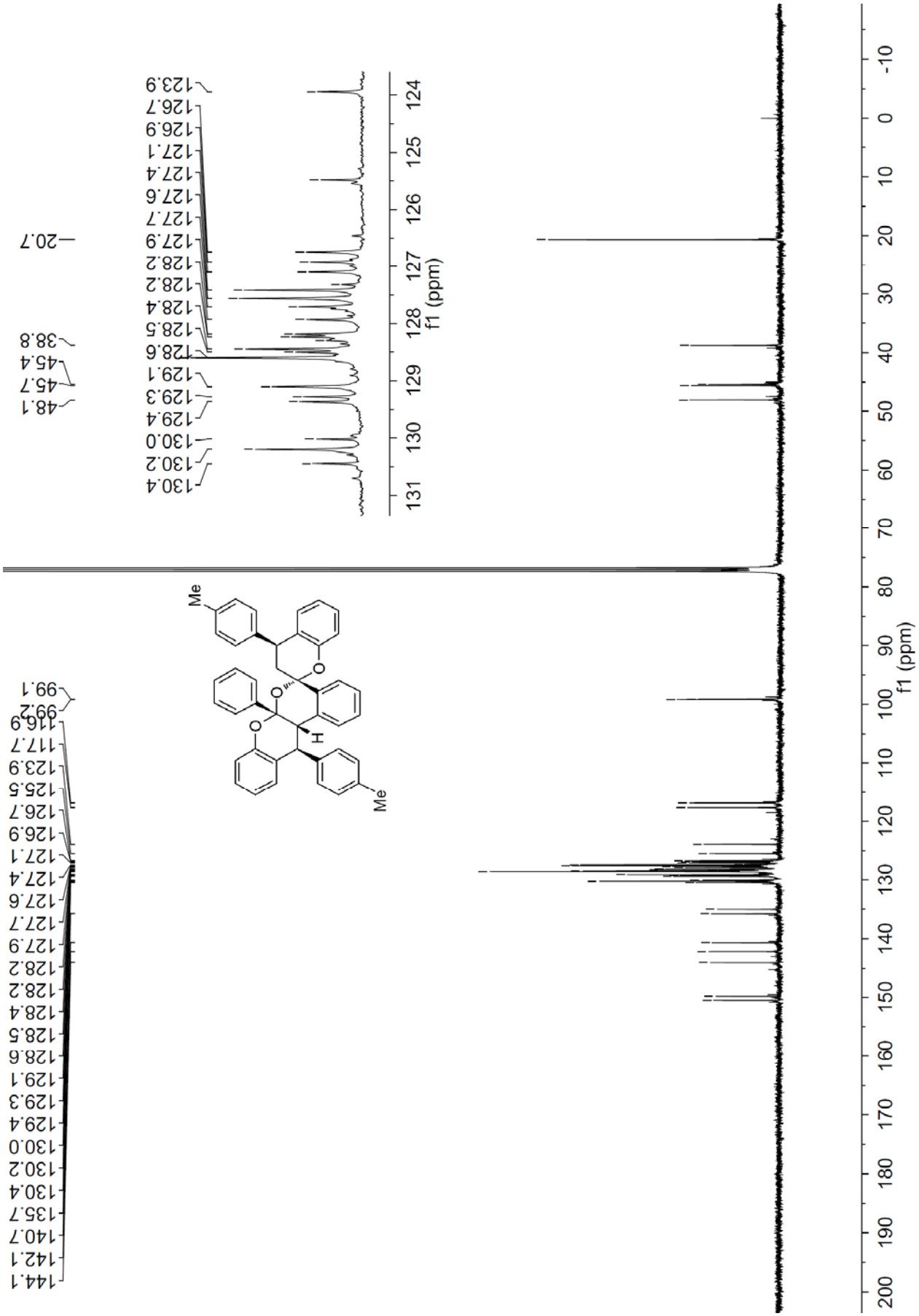
^{13}C NMR Spectrum of Compound 5e



^{19}F NMR Spectrum of Compound 5e



^{1}H NMR Spectrum of Compound 5f



^{13}C NMR Spectrum of Compound 5f