Supporting Information

Efficient Synthesis of 3-Sulfonyl-2-sulfonylmethyl-2*H*-chromenes *via* Tandem Knoevenagel Condensation/Oxa-Michael Addition Protocol

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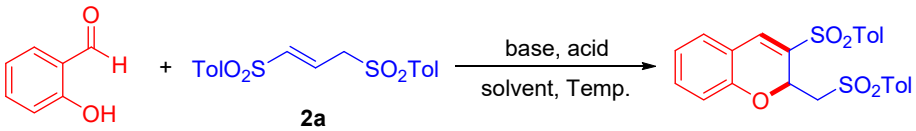
1. Further optimization of reaction conditions

Results of further optimizing reaction conditions were listed in Table S1. Exploration of catalytic amount of both the *p*-TsOH and piperidine revealed that the equimolar amounts of these two catalysts were essential to give full play to the advantages of dual-catalysis. Reducing catalytic amount of both catalysts to 20 mol% decreased the yield, whereas increasing both of them to 40 mol% showed no substantial influence on reaction efficiency (Table S1, entries 1-3). Subsequently, we took a brief examination of several representative solvents such as EtOH, THF, DCE and $PhCF_3$ (entries 4-7). Generally, the reaction proceeded better in aromatic solvents. In particular, toluene was still the preferred candidate. Lowing reaction temperature to 60 °C led to a higher yield of 88%. However, test at 50 °C could not further improve product yield (entries 8 and 9). Other adjustments including substrate concentration and adding of 4Å molecular sieves (4Å MS) as a water scavenger seemed to have no positive influence on reaction performance (entries 10-12).

Table S1. Further optimization of reaction conditions. [a]

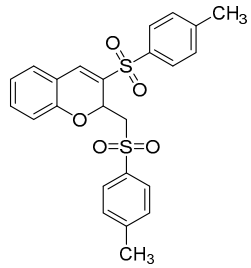


1 **2a** Tol = *p*-MeC_6H_4 **3a**

Entry	Base (mol%)	Brønsted acid (mol%)	Solvent	Temp. (°C)	Time (h)	Yield of 3a (%) [b]
1	piperidine (30)	*p*-TsOH (20)	toluene	90	5	75
2	piperidine (20)	*p*-TsOH (20)	toluene	90	5	78
3	piperidine (40)	*p*-TsOH (40)	toluene	90	3	84
4	piperidine (30)	*p*-TsOH (30)	EtOH	reflux	12	72
5	piperidine (30)	*p*-TsOH (30)	THF	reflux	12	55
6	piperidine (30)	*p*-TsOH (30)	DCE	reflux	6	74
7	piperidine (30)	*p*-TsOH (30)	$PhCF_3$	90	3	81
8	piperidine (30)	*p*-TsOH (30)	toluene	60	10	88
9	piperidine (30)	*p*-TsOH (30)	toluene	50	12	85
10 [c,d]	piperidine (30)	*p*-TsOH (30)	toluene	60	9	75
11 [c,e]	piperidine (30)	*p*-TsOH (30)	toluene	60	12	91
12 [c,f]	piperidine (30)	*p*-TsOH (30)	toluene	60	10	92

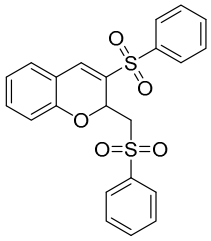
[a] Reaction conditions: unless otherwise noted, reactions were conducted with salicylaldehyde **1** (0.22 mmol), 1,3-bis(*p*-tolylsulfonyl)propene **2a** (0.2 mmol), indicated amount of base and Brønsted acid in solvent (2 mL) at indicated temperature. [b] Isolated yields. [c] 1.2 equiv. of salicylaldehyde. [d] 1 mL of solvent. [e] 4 mL of solvent. [f] 50 mg of 4Å MS.

2. Compound characterization data



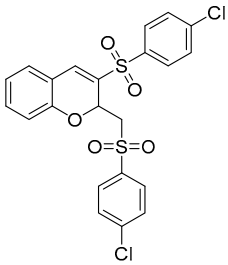
3-Tosyl-2-(tosylmethyl)-2*H*-chromene (3a)

White solid; 92% yield; m.p. 205-207 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.55 (s, 1H), 7.38-7.34 (m, 4H), 7.21-7.17 (m, 2H), 7.00-6.96 (m, 1H), 6.32 (d, *J* = 8.0 Hz, 1H), 5.46 (d, *J* = 12.0 Hz, 1H), 3.68 (dd, *J* = 16.0 Hz, 12.0 Hz, 1H), 3.41 (d, *J* = 16.0 Hz, 1H), 2.49 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 145.6, 145.0, 137.0, 135.5, 133.5, 133.0, 131.4, 130.5, 130.0, 129.4, 128.6, 128.4, 123.1, 119.2, 117.8, 68.3, 57.4, 21.9, 21.8; ESI HRMS: calcd. for $C_{24}H_{22}O_5S_2$+Na $[M+Na]^+$ 477.0806, found 477.0812.



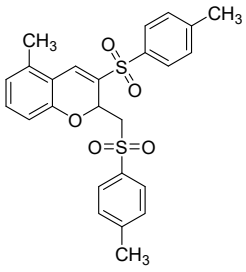
3-(Phenylsulfonyl)-2-((phenylsulfonyl)methyl)-2*H*-chromene (3b)

White solid; 90% yield; m.p. 166-167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.73-7.66(m, 2H), 7.60-7.56 (m, 5H), 7.22-7.16 (m, 2H), 7.00-6.96 (m, 1H), 6.21 (d, *J* = 8.0 Hz, 1H), 5.49 (d, *J* = 12.0 Hz, 1H), 3.72 (dd, *J* = 16.0 Hz, 12.0 Hz, 1H), 3.45 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 139.9, 138.5, 134.4, 134.0, 133.6, 130.9, 129.9, 129.5, 129.4, 128.6, 128.3, 123.2, 119.0, 117.7, 68.3, 57.3; ESI HRMS: calcd. for $C_{22}H_{18}O_5S_2$+Na $[M+Na]^+$ 449.0493, found 449.0498.



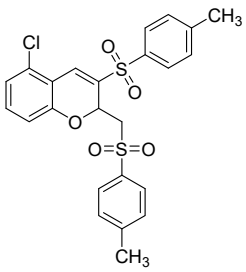
3-((4-Chlorophenyl)sulfonyl)-2-(((4-chlorophenyl)sulfonyl)methyl)-2*H*-chromene (3c)

White solid; 86% yield; m.p. 223-225 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.59 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 4H), 7.22 (d, *J* = 4.0 Hz, 2H), 7.03-6.99 (m, 1H), 6.29 (d, *J* = 8.0 Hz, 1H), 5.44 (d, *J* = 12.0 Hz, 1H), 3.73 (dd, *J* = 16.0 Hz, 12.0 Hz, 1H), 3.48 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 141.4, 140.9, 138.4, 137.0, 134.2, 134.0, 130.4, 130.3, 130.1, 129.8, 129.7, 123.4, 118.9, 117.6, 68.3, 57.5; ESI HRMS: calcd. for $C_{22}H_{16}Cl_2O_5S_2$+H $[M+H]^+$ 494.9894, found 494.9892.



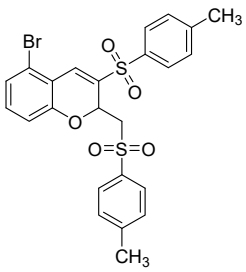
5-Methyl-3-tosyl-2-(tosylmethyl)-2*H*-chromene (3d)

White solid; 90% yield; m.p. 165-167 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.74-7.72 (m, 3H), 7.36-7.33 (m, 4H), 7.07-7.03 (m, 1H), 6.80 (d, *J* = 8.0 Hz, 1H) , 6.11 (d, *J* = 8.0 Hz, 1H), 5.42 (d, *J* = 12.0 Hz, 1H), 3.67 (dd, *J* = 16.0 Hz, 12.0 Hz, 1H), 3.36 (d, *J* = 16.0 Hz, 1H), 2.48 (s, 3H), 2.45 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 145.4, 144.9, 137.7, 137.0, 135.6, 132.8, 130.8, 130.4, 130.1, 129.9, 128.6, 128.3, 124.6, 118.1, 115.4, 67.7, 57.1, 21.8, 21.8, 18.5; ESI HRMS: calcd. for $C_{25}H_{24}O_5S_2$+Na $[M+Na]^+$ 491.0963, found 491.0966.



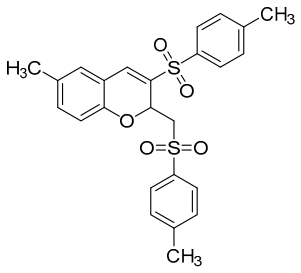
5-Chloro-3-tosyl-2-(tosylmethyl)-2*H*-chromene (3e)

White solid; 84% yield; m.p. 175-178 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 4H), 7.12-7.08 (m, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.25 (d, *J* = 8.0 Hz, 1H), 5.47 (d, *J* = 12.0 Hz, 1H), 3.64 (dd, *J* = 12.0 Hz, 12.0 Hz, 1H), 3.35 (d, *J* = 12.0 Hz, 1H), 2.47 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 145.7, 145.1, 136.6, 135.0, 133.9, 133.2, 132.5, 130.5, 129.9, 129.2, 128.4, 128.4, 123.7, 117.8, 116.3, 67.9, 57.0, 21.8, 21.7; ESI HRMS: calcd. for $C_{24}H_{21}ClO_5S_2$+H $[M+H]^+$ 489.0597, found 489.0602.



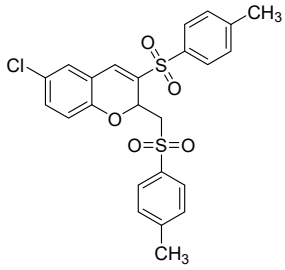
5-Bromo-3-tosyl-2-(tosylmethyl)-2*H*-chromene (3f)

White solid; 89% yield; m.p. 115-117 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.76 (d, *J* = 12.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 4H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.06-7.02 (m, 1H), 6.33 (d, *J* = 12.0 Hz, 1H), 5.47 (d, *J* = 12.0 Hz, 1H), 3.63 (dd, *J* = 12.0 Hz, 12.0 Hz, 1H), 3.35 (d, *J* = 12.0 Hz, 1H), 2.48 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 145.8, 145.1, 136.8, 135.2, 133.6, 133.0, 131.5, 130.5, 130.0, 128.5, 127.1, 124.1, 119.6, 117.1, 68.1, 57.1, 21.8, 21.8; ESI HRMS: calcd. for $C_{24}H_{21}BrO_5S_2$+Na $[M+Na]^+$ 554.9911, found 554.9915.



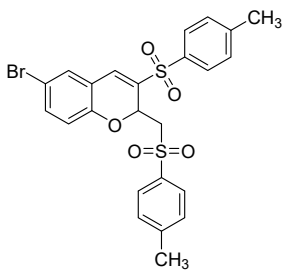
6-Methyl-3-tosyl-2-(tosylmethyl)-2*H*-chromene (3g)

White solid; 85% yield; m.p. 187-190 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.50 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.98 (s, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.14 (d, *J* = 8.0 Hz, 1H), 5.43 (d, *J* = 8.0 Hz, 1H), 3.68 (dd, *J* = 16.0 Hz, 12.0 Hz, 1H), 3.36 (d, *J* = 16.0 Hz, 1H), 2.48 (s, 3H), 2.43 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 145.5, 144.9, 136.9, 135.5, 134.1, 133.2, 132.6, 131.1, 130.4, 129.9, 129.5, 128.5, 128.3, 118.8, 117.3, 68.2, 57.1, 21.8, 21.7, 20.5; ESI HRMS: calcd. for $C_{25}H_{24}O_5S_2$+Na $[M+Na]^+$ 491.0963, found 491.0965.



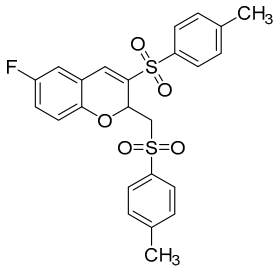
6-Chloro-3-tosyl-2-(tosylmethyl)-2*H*-chromene (3h)

White solid; 83% yield; m.p. 190-191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.47 (s, 1H), 7.37 (d, *J* = 12.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 4.0 Hz, 1H), 7.12 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 6.26 (d, *J* = 12.0 Hz, 1H), 5.48 (dd, *J* = 12.0 Hz, 4.0 Hz, 1H), 3.63 (dd, *J* = 12.0 Hz, 12.0 Hz, 1H), 3.38 (dd, *J* = 12.0 Hz, 4.0 Hz, 1H), 2.48 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 145.8, 145.1, 136.8, 135.0, 133.0, 132.9, 131.7, 130.5, 130.0, 128.6, 128.5, 128.4, 128.1, 120.3, 119.1, 68.4, 57.2, 21.8, 21.8; ESI HRMS: calcd. for $C_{24}H_{21}ClO_5S_2$+Na $[M+Na]^+$ 511.0417, found 511.0422.



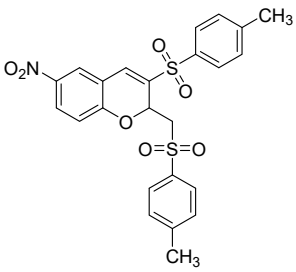
6-Bromo-3-tosyl-2-(tosylmethyl)-2*H*-chromene (3i)

White solid; 81% yield; m.p. 201-204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 12.0 Hz, 2H), 7.45 (s, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 2.4 Hz, 1H), 7.25 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 6.19 (d, *J* = 8.0 Hz, 1H), 5.48 (d, *J* = 12.0 Hz, 1H), 3.62 (dd, *J* = 16.0 Hz, 12.0 Hz, 1H), 3.36 (d, *J* = 16.0 Hz, 1H), 2.47 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 145.8, 145.1, 136.8, 135.8, 135.0, 132.9, 131.5, 131.5, 130.5, 130.0, 128.5, 128.4, 120.8, 119.4, 115.2, 68.4, 57.2, 21.8, 21.8; ESI HRMS: calcd. for $C_{24}H_{21}BrO_5S_2$+Na $[M+Na]^+$ 554.9911, found 554.9918.



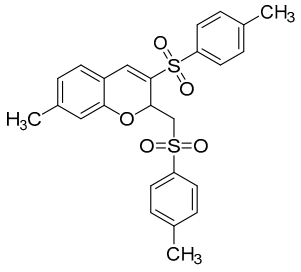
6-Fluoro-3-tosyl-2-(tosylmethyl)-2*H*-chromene (3j)

White solid; 73% yield; m.p. 186-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.48 (s, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.92 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 6.87 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 6.28 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 5.46 (dd, *J* = 12.0 Hz, 4.0 Hz, 1H), 3.64 (dd, *J* = 16.0 Hz, 12.0 Hz, 1H), 3.36 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 2.48 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9 (*J* = 250 Hz), 146.4 (*J* = 2 Hz), 145.8, 145.1, 136.8, 135.1, 133.0, 131.9 (*J* = 2 Hz), 130.5, 130.0, 128.5, 128.4, 119.9 (*J* = 23 Hz), 119.9 (*J* = 9 Hz), 119.0 (*J* = 8 Hz), 115.0 (*J* = 24 Hz), 68.3, 56.9, 21.8, 21.8; ESI HRMS: calcd. for $C_{24}H_{21}FO_5S_2$+K $[M+K]^+$ 511.0452, found 511.0458.



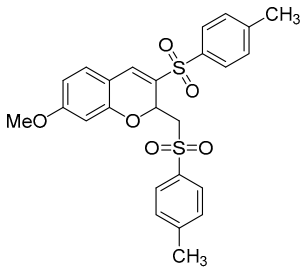
6-Nitro-3-tosyl-2-(tosylmethyl)-2*H*-chromene (3k)

White solid; 70% yield; m.p. 216-219 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 4.0 Hz, 1H), 8.10 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.56 (s, 1H), 7.40 (d, *J* = 4.0 Hz, 2H), 7.38 (d, *J* = 4.0 Hz, 2H), 6.55 (d, *J* = 8.0 Hz, 1H), 5.63 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 3.59 (dd, *J* = 16.0 Hz, 8.0 Hz, 1H), 3.48 (d, *J* = 16.0 Hz, 4.0 Hz, 1H), 2.50 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 146.3, 145.4, 143.1, 136.7, 134.7, 134.3, 131.0, 130.7, 130.2, 128.6, 128.5, 124.9, 119.2, 118.5, 69.2, 58.0, 21.9, 21.8; ESI HRMS: calcd. for $C_{24}H_{21}NO_7S_2$+Na $[M+Na]^+$ 522.0657, found 522.0663.



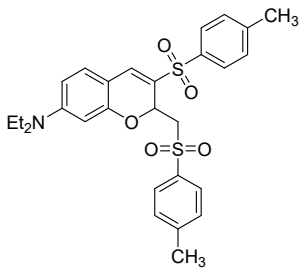
7-Methyl-3-tosyl-2-(tosylmethyl)-2*H*-chromene (3l)

White solid; 90% yield; m.p. 152-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.52 (s, 1H), 7.36 (d, *J* = 12.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 12.0 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H) , 5.93 (s, 1H), 5.44 (d, *J* = 8.0 Hz, 1H), 3.68 (dd, *J* = 16 Hz, 8.0 Hz, 1H), 3.38 (d, *J* = 16.0 Hz, 1H), 2.49 (s, 3H), 2.44 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 145.4, 144.8, 144.6, 137.3, 135.8, 133.1, 130.4, 130.0, 129.9, 129.1, 128.7, 128.3, 124.0, 118.0, 116.6, 68.4, 57.3, 21.9, 21.8, 21.8; ESI HRMS: calcd. for $C_{25}H_{24}O_5S_2$+H $[M+Na]^+$ 469.1143, found 469.1148.



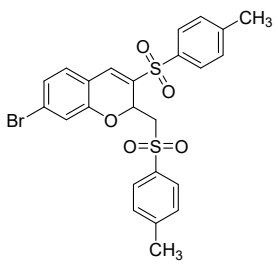
7-Methoxy-3-tosyl-2-(tosylmethyl)-2*H*-chromene (3m)

Light yellow solid; 70% yield; m.p. 209-212 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.51 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 1H) , 6.53 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 5.82 (d, *J* = 4.0 Hz, 1H), 5.46 (dd, *J* = 12.0 Hz, 4.0 Hz, 1H), 3.70 (s, 3H), 3.69 (dd, *J* = 12.0 Hz, 12.0 Hz, 1H), 3.39 (dd, *J* = 12.0 Hz, 4.0 Hz, 1H), 2.48 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 152.4, 145.3, 144.9, 137.2, 136.0, 133.2, 130.5, 130.4, 130.0, 128.7, 128.2, 127.5, 112.2, 110.1, 102.6, 68.5, 57.5, 55.7, 21.8, 21.8; ESI HRMS: calcd. for $C_{25}H_{24}O_6S_2$+Na $[M+Na]^+$ 507.0912, found 507.0918.



***N*,*N*-diethyl-3-tosyl-2-(tosylmethyl)-2*H*-chromen-7-amine (3n)**

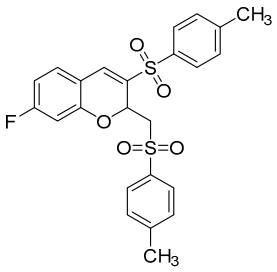
Yellow solid; 71% yield; m.p. 208-211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.46 (s, 1H), 7.36 (d, *J* = 12.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 1H) , 6.24 (d, *J* = 8.0 Hz, 1H), 5.65 (d, *J* = 4.0 Hz, 1H), 5.41 (d, *J* = 8.0 Hz, 1H), 3.74 (dd, *J* = 12.0 Hz, 8.0 Hz, 1H), 3.37 (d, *J* = 12.0 Hz, 1H), 3.26 (q, *J* = 8.0 Hz, 4H), 2.45 (s, 3H), 2.41 (s, 3H), 1.11 (t, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 152.1, 144.6, 144.5, 137.3, 136.8, 134.0, 130.8, 130.1, 129.8, 128.6, 127.9, 122.3, 107.1, 106.4, 99.0, 68.5, 57.7, 44.6, 21.8, 21.7, 12.6; ESI HRMS: calcd. for $C_{28}H_{31}KNO_5S_2$+K $[M+K]^+$ 564.1281, found 564.1285.



7-Bromo-3-tosyl-2-(tosylmethyl)-2*H*-chromene (3o)

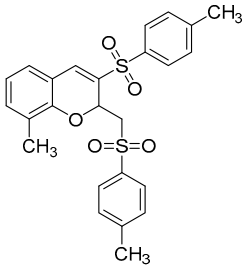
White solid; 77% yield; m.p. 227-229 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 4H), 7.49 (s, 1H), 7.39-7.36 (m, 4H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 5.95 (s, 1H), 5.47 (d, *J* = 8.0 Hz, 4.0 Hz, 1H), 3.66 (dd, *J* = 16.0 Hz, 8.0 Hz, 1H), 3.41 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 2.52 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 145.8, 145.3, 137.0, 135.1, 132.0, 131.8, 130.6, 130.1, 130.0, 128.6, 128.4, 126.6, 126.4, 120.7, 118.0, 68.8, 57.2, 21.9, 21.9; ESI HRMS: calcd. for $C_{24}H_{21}BrO_5S_2$+Na $[M+Na]^+$ 554.9911, found

554.9916.



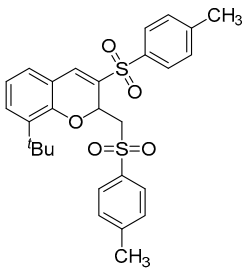
7-Fluoro-3-tosyl-2-(tosylmethyl)-2*H*-chromene (3p)

White solid; 75% yield; m.p. 153-156 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.52 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.18 (dd, *J* = 8.0 Hz, 8.0 Hz, 1H), 6.68 (ddd, *J* = 8.0 Hz, 8.0 Hz, 4.0 Hz, 1H) , 5.83 (dd, *J* = 12.0 Hz, 4.0 Hz, 1H), 5.47 (d, *J* = 12.0 Hz, 1H), 3.66 (dd, *J* = 16.0 Hz, 12.0 Hz, 1H), 3.41 (d, *J* = 16.0 Hz, 1H), 2.48 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5 (*J* = 252 Hz), 152.0 (*J* = 13 Hz), 145.6, 145.2, 136.8, 135.3, 132.2, 130.8 (*J* = 11 Hz), 130.5, 130.2 (*J* = 3 Hz), 130.0, 128.5, 128.3, 115.5 (*J* = 3 Hz), 110.7 (*J* = 22 Hz), 105.3 (*J* = 25 Hz), 68.5, 57.3, 21.8, 21.7; ESI HRMS: calcd. for $C_{24}H_{21}FO_5S_2$+Na $[M+Na]^+$ 495.0712, found 495.0717.



8-Methyl-3-tosyl-2-(tosylmethyl)-2*H*-chromene (3q)

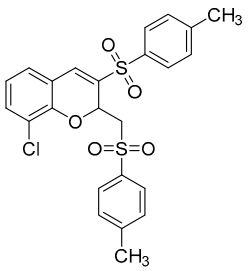
White solid; 84% yield; m.p. 163-165 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.55 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 4.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.94-6.90 (m, 1H), 5.44 (d, *J* = 12.0 Hz, 1H), 3.64 (dd, *J* = 16.0 Hz, 12.0 Hz, 1H), 3.41 (d, *J* = 16.0 Hz, 1H), 2.48 (s, 3H), 2.43 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 145.4, 145.1, 136.5, 135.4, 135.3, 133.6, 130.3, 130.3, 130.1, 128.3, 128.3, 128.2, 127.0, 122.6, 118.6, 67.7, 57.4, 21.8, 21.8, 15.5; ESI HRMS: calcd. for $C_{25}H_{24}O_5S_2$+H $[M+H]^+$ 469.1143, found 469.1145.



8-(*Tert*-butyl)-3-tosyl-2-(tosylmethyl)-2*H*-chromene (3r)

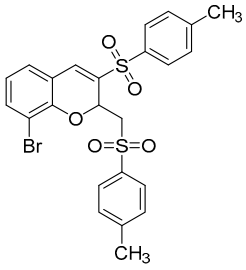
White solid; 88% yield; m.p. 159-162 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 12.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.52 (s, 1H), 7.40-7.33 (m, 5H), 7.06 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 6.96-6.92 (m, 1H), 5.67 (d, *J* = 8.0 Hz, 1H), 3.77 (dd, *J* = 12.0 Hz, 8.0 Hz, 1H), 3.64 (d, *J* = 12.0 Hz, 1H), 2.47 (s, 3H), 2.46 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 145.4, 145.1, 139.7, 137.0, 135.4, 133.8, 131.7, 130.3, 130.1, 130.0, 128.5, 128.4, 128.0,

122.4, 119.2, 67.4, 59.7, 35.0, 30.1, 21.9, 21.8; ESI HRMS: calcd. for $C_{28}H_{30}O_5S_2$+Na $[M+Na]^+$ 533.1432, found 533.1438.



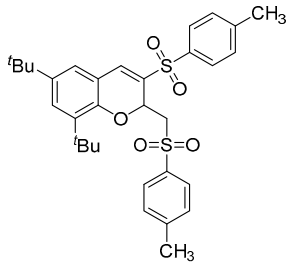
8-Chloro-3-tosyl-2-(tosylmethyl)-2*H*-chromene (3s)

White solid; 80% yield; m.p. 185-187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.54 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.14 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 6.98-6.94 (m, 1H), 5.49 (d, *J* = 8.0 Hz, 1H), 3.66 (dd, *J* = 16.0 Hz, 8.0 Hz, 1H), 3.50 (d, *J* = 16.0 Hz, 1H), 2.47 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 145.8, 145.1, 136.3, 134.8, 134.0, 132.1, 131.9, 130.4, 130.1, 128.4, 128.4, 127.8, 123.3, 123.2, 120.3, 68.7, 57.9, 21.8, 21.8; ESI HRMS: calcd. for $C_{24}H_{21}ClO_5S_2$+H $[M+H]^+$ 489.0597, found 489.0595.



8-Bromo-3-tosyl-2-(tosylmethyl)-2*H*-chromene (3t)

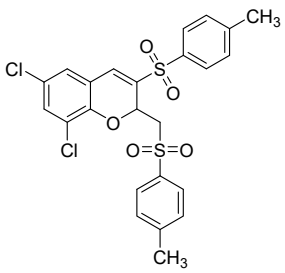
White solid; 79% yield; m.p. 175-177 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.53-7.51 (m, 2H), 7.38 (d, *J* = 12.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.18 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 6.92-6.88 (m, 1H), 5.48 (d, *J* = 12.0 Hz, 1H), 3.66 (dd, *J* = 16.0 Hz, 12.0 Hz, 1H), 3.50 (d, *J* = 16.0 Hz, 1H), 2.47 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 145.8, 145.1, 137.1, 136.3, 134.8, 132.2, 131.9, 130.4, 130.1, 128.6, 128.5, 128.4, 123.9, 120.3, 111.9, 68.8, 58.0, 21.8, 21.8; ESI HRMS: calcd. for $C_{24}H_{21}BrO_5S_2$+H $[M+H]^+$ 533.0092, found 533.0096.



6,8-Di-*tert*-butyl-3-tosyl-2-(tosylmethyl)-2*H*-chromene (3u)

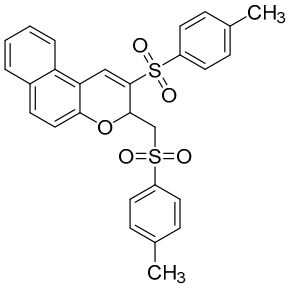
White solid; 77% yield; m.p. 210-212 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.54 (s, 1H), 7.42 (d, *J* = 4.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 2.4 Hz, 1H), 5.62 (d, *J* = 8.0 Hz, 1H), 3.80 (dd, *J* = 16.0 Hz, 8.0 Hz, 1H), 3.62 (d, *J* = 16.0 Hz, 1H), 2.48 (s, 3H), 2.46 (s, 3H), 1.39 (s, 9H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 145.3, 145.0, 144.9, 138.9, 136.9, 135.5, 134.4,

130.3, 130.1, 129.5, 129.0, 128.4, 128.4, 124.6, 118.5, 67.4, 59.6, 35.1, 34.4, 31.4, 30.1, 21.9, 21.8; ESI HRMS: calcd. for $C_{32}H_{38}O_5S_2$+Na $[M+Na]^+$ 589.2058, found 589.2064.



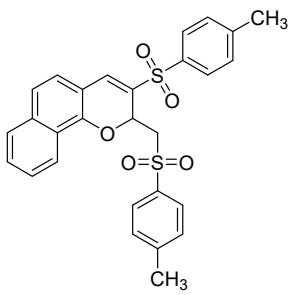
6,8-Dichloro-3-tosyl-2-(tosylmethyl)-2*H*-chromene (3v)

White solid; 88% yield; m.p. 160-163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.47 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 4.0 Hz, 2H), 7.33 (s, 1H), 7.14 (d, *J* = 4.0 Hz, 1H), 5.53 (dd, *J* = 12.0 Hz, 4.0 Hz, 1H), 3.63 (dd, *J* = 16.0 Hz, 12.0 Hz, 1H), 3.48 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 2.48 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 145.7, 145.3, 136.3, 134.5, 133.6, 133.4, 131.0, 130.6, 130.2, 128.6, 128.5, 127.9, 127.2, 124.2, 121.1, 69.0, 57.9, 21.9, 21.8; ESI HRMS: calcd. for $C_{24}H_{20}Cl_2O_5S_2$+Na $[M+Na]^+$ 545.0027, found 545.0035.



2-Tosyl-3-(tosylmethyl)-3*H*-benzo[f]chromene (3w)

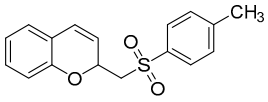
Yellow solid; 71% yield; m.p. 231-234 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.79-7.76 (m, 5H), 7.72 (d, *J* = 12.0 Hz, 1H), 7.61-7.59 (m, 1H), 7.47-7.43 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 4H), 6.56 (d, *J* = 8.0 Hz, 1H), 5.63 (d, *J* = 8.0 Hz, 1H), 3.78 (dd, *J* = 16.0 Hz, 8.0 Hz, 1H), 3.34 (d, *J* = 16.0 Hz, 1H), 2.50 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 145.5, 145.0, 137.1, 135.8, 134.3, 130.5, 130.4, 130.0, 129.8, 129.3, 129.0, 128.9, 128.5, 128.4, 128.4, 125.3, 121.4, 118.0, 112.6, 68.3, 56.8, 21.9, 21.8; ESI HRMS: calcd. for $C_{28}H_{24}O_5S_2$+Na $[M+Na]^+$ 527.0963, found 527.0970.



3-Tosyl-2-(tosylmethyl)-2*H*-benzo[h]chromene (3x)

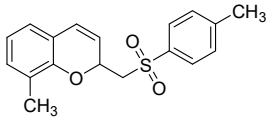
Yellow solid; 70% yield; m.p. 224-226 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.75-7.72 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.54-7.50 (m, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.44-7.40 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.27-7.25 (m, 1H), 5.75 (d, *J* = 8.0 Hz, 1H), 3.78 (dd, *J* = 16.0 Hz, 8.0 Hz, 1H), 3.44 (d, *J* = 16.0 Hz, 1H), 2.49 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 145.4,

145.1, 136.9, 136.5, 135.8, 133.7, 130.4, 130.2, 128.8, 128.6, 128.4, 128.4, 127.7, 126.6, 125.0, 124.7, 123.6, 122.8, 113.6, 68.6, 57.4, 21.9, 21.9; ESI HRMS: calcd. for $C_{28}H_{24}O_5S_2$+Na $[M+Na]^+$ 527.0963, found 527.0968.



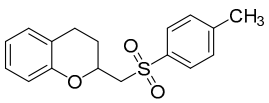
2-(Tosylmethyl)-2*H*-chromene (10a)

White solid; 85% yield; m.p. 125-127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.02-6.97 (m, 1H), 6.94 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 6.86-6.82 (m, 1H), 6.46 (d, *J* = 12.0 Hz, 1H), 6.19 (d, *J* = 8.0 Hz, 1H), 5.72 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 5.43 m, 1H), 3.66 (dd, *J* = 16.0 Hz, 8.0 Hz, 1H), 3.24 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 144.9, 137.2, 129.9, 129.7, 128.6, 126.8, 125.6, 122.3, 122.0, 121.2, 116.4, 69.7, 59.9, 21.8; ESI HRMS: calcd. for $C_{17}H_{16}O_3S$+H $[M+H]^+$ 301.0898, found 301.0904.



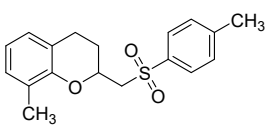
8-Methyl-2-(tosylmethyl)-2*H*-chromene (10q)

White solid; 88% yield; m.p. 103-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.82-6.75 (m, 2H), 6.46 (d, *J* = 12.0 Hz, 1H), 5.70 (dd, *J* = 12.0 Hz, 4.0 Hz, 1H), 5.47-5.43 (m, 1H), 3.65 (dd, *J* = 16.0 Hz, 8.0 Hz, 1H), 3.30 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 2.45 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 145.0, 137.0, 131.5, 130.1, 128.3, 126.1, 125.8, 124.6, 122.1, 121.4, 120.6, 69.6, 60.6, 21.7, 15.2. ESI HRMS: calcd. for $C_{18}H_{18}O_3S$+H $[M+H]^+$ 315.1055, found 315.1058.



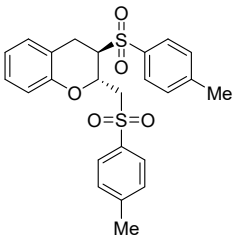
2-(Tosylmethyl)chromane (11a)

White solid; 90% yield; m.p. 112-114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.01-6.98 (m, 2H), 6.84-6.80 (m, 1H), 6.35 (d, *J* = 8.0 Hz, 1H), 4.57 (m, 1H), 3.58 (dd, *J* = 16.0 Hz, 8.0 Hz, 1H), 3.34 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 2.91-2.82 (m, 1H), 2.77-2.70 (m, 1H), 2.48 (s, 3H), 2.18-2.12 (m, 1H), 1.89-1.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 144.8, 137.3, 129.8, 129.6, 128.5, 127.8, 121.3, 120.9, 116.7, 70.5, 61.2, 27.2, 23.9, 21.8; ESI HRMS: calcd. for $C_{17}H_{18}O_3S$+Na $[M+Na]^+$ 325.0874, found 325.0878.



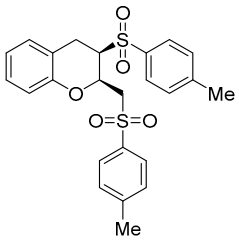
8-Methyl-2-(tosylmethyl)chromane (11q)

White solid; 90% yield; m.p. 126-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.80-6.75 (m, 2H), 6.66-6.62 (m, 1H), 4.51-4.45 (m, 1H), 3.55 (dd, *J* = 12.0 Hz, 8.0 Hz, 1H), 3.28 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 2.82-2.73 (m, 1H), 2.68-2.61 (m, 1H), 2.36 (s, 3H), 2.09-2.03 (m, 1H), 1.81-1.74 (m, 1H), 1.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 144.9, 137.1, 130.0, 128.6, 128.2, 127.0, 126.0, 120.6, 120.2, 70.5, 61.4, 27.5, 24.2, 21.7, 15.4. ESI HRMS: calcd. for $C_{18}H_{20}O_3S$+Na $[M+Na]^+$ 339.1031, found 339.1035.



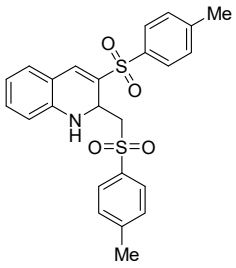
3-Tosyl-2,3-*anti*-2-(tosylmethyl)chromane ((±)-12a)

White solid; 47% yield; m.p. 152-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.99-6.93 (m, 2H), 6.87-6.83 (m, 1H), 6.19 (d, *J* = 8.0 Hz, 1H), 5.06 (d, *J* = 12.0 Hz, 1H), 4.04 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 3.62 (ddd, *J* = 8.0 Hz, 4.0 Hz, 4.0 Hz, 1H), 3.56 (dd, *J* = 16.0 Hz, 12.0 Hz, 1H), 3.11-3.08 (m, 2H), 2.47 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 145.9, 144.9, 137.2, 134.5, 130.3, 129.9, 129.5, 128.9, 128.5, 128.4, 122.1, 117.9, 117.8, 67.9, 60.0, 55.1, 22.5, 21.8, 21.8; ESI HRMS: calcd. for $C_{24}H_{24}O_5S_2$+Na $[M+Na]^+$ 479.0963, found 479.0965.



3-Tosyl-2,3-*syn*-2-(tosylmethyl)chromane ((±)-12a′)

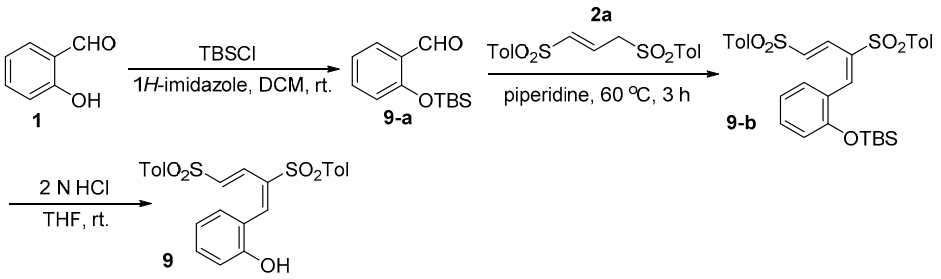
White solid; 43% yield; m.p. 151-153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 12.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.94-6.89 (m, 2H), 6.81-6.77 (m, 1H), 6.22 (d, *J* = 8.0 Hz, 1H), 5.03 (ddd, *J* = 8.0 Hz, 4.0 Hz, 4.0 Hz, 1H), 3.74 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 3.68 (ddd, *J* = 8.0 Hz, 4.0 Hz, 4.0 Hz, 1H), 3.57 (dd, *J* = 16.0 Hz, 8.0 Hz, 1H), 3.16 (dd, *J* = 16.0 Hz, 8.0 Hz, 1H), 2.98 (dd, *J* = 16.0 Hz, 8.0 Hz, 1H), 2.47 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 145.6, 145.1, 137.0, 133.7, 130.0, 129.8, 129.3, 129.0, 128.4, 127.9, 122.0, 117.9, 117.1, 68.4, 60.3, 58.8, 23.6, 21.8, 21.7; ESI HRMS: calcd. for $C_{24}H_{24}O_5S_2$+Na $[M+Na]^+$ 479.0963, found 479.0969.



3-Tosyl-2-(tosylmethyl)-1,2-dihydroquinoline (14)

Yellow solid; 78% yield; m.p. 170-172 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.86 (d, J = 12.0 Hz, 2H), 7.60 (s, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 1H), 7.14-7.11 (m, 1H), 6.67-6.64 (m, 1H), 6.52-6.49 (m, 2H), 4.44 (dd, J = 8.0 Hz, 4.0 Hz, 1H), 3.68 (dd, J = 16.0 Hz, 8.0 Hz, 1H), 2.86 (d, J = 16.0 Hz, 1H), 2.48 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 144.8, 144.7, 142.5, 136.1, 135.9, 135.4, 132.6, 130.3, 130.3, 130.0, 127.9, 126.1, 117.9, 116.9, 114.7, 57.9, 45.8, 21.1, 21.1; ESI HRMS: calcd. for $C_{24}H_{23}NO_4S_2$+Na $[M+Na]^+$ 476.0966, found 476.0975.

3. Synthetic procedure of substrate 9 for reaction mechanistic investigation



TBS-protection of phenolic hydroxyl group (step 1): To a suspension of salicylaldehydes **1** (5.0 g, 40.94 mmol) and *t*-butyldimethylchlorosilane (TBSCl, 6.79 g, 45.03 mmol) in DCM (50 mL) was added 1*H*-imidazole (3.35 g, 49.13 mmol). The reaction was stirred at 25 °C for 12 h. The reaction mixture was successively washed with citric acid solution (2 N) and saturated aqueous NaCl, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give the crude TBS-protected salicylaldehyde **9-a** (9.10 g, 94% crude yield) as pale yellow liquid, which was used without further purification for the next step.

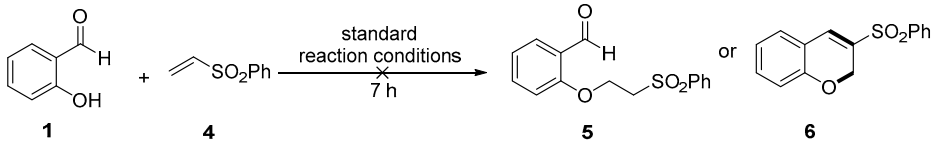
Knoevenagel Condensation (step 2): To a suspension of **9-a** (2.84 g, 12.0 mmol) and 1,3-bis(*p*-tolylsulfonyl)propene **2a** (3.50 g, 10.0 mmol) in toluene (60 mL) was added piperidine (0.20 mL, 2.0 mmol). The reaction was stirred at 60 °C for 5 h. The reaction mixture was washed successively with water and brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography over silica gel (eluent: petroleum ether/ethyl acetate = 5:1) to afford pure Knoevenagel adduct **9-b**. Pale yellow oil; 5.00 g, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ_{major} 8.38 (s, 1H), 7.61 (d, J

= 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.33-7.20 (m, 5H), 7.12-7.07 (m, 3H), 6.96-6.92 (m, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 2.43 (s, 3H), 2.33 (s, 3H), 1.05 (s, 9H), 0.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{major} 155.7, 144.7, 144.6, 142.3, 137.4, 136.4, 134.6, 133.9, 133.1, 131.7, 131.3, 130.1, 129.8, 128.1, 127.9, 124.2, 121.6, 119.4, 29.8, 25.8, 21.8, 21.7, 18.4.

Deprotection of TBS ethers (step 3): **9-b** (1.0 g, 1.76 mmol) was dissolved in THF (15 mL) and 2N hydrochloric acid (3 mL) was then added, and the solution was stirred at room temperature for 5 h. The reaction was quenched by dilution with ethyl acetate and organic layer was collected. The aqueous phase was extracted with ethyl acetate (10 mL× 2). The combined organic fractions were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash chromatography over silica gel (eluent: petroleum ether/ethyl acetate = 5:1) to afford compound **9**. Pale yellow oil; 0.75 g, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.62-7.58 (m, 4H), 7.35 (br.s, 1H), 7.32-7.23 (m, 5H), 7.13-7.09 (m, 3H), 6.90-6.86 (m, 2H), 2.45 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 144.8, 144.6, 142.2, 136.9, 136.1, 133.9, 133.4, 133.1, 131.5, 131.3, 130.1, 129.9, 127.9, 127.8, 120.6, 119.8, 116.4, 21.8, 21.7. ESI HRMS: calcd. for $C_{24}H_{22}O_5S_2$+Na $[M+Na]^+$ 477.0806, found 477.0808.

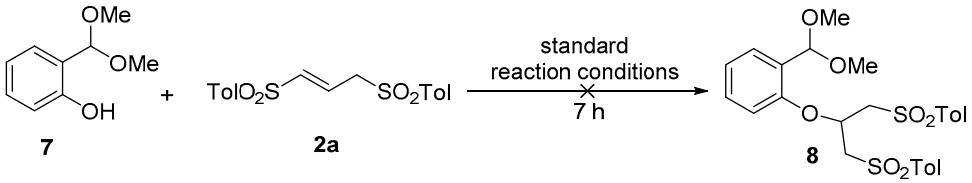
4. Experimental procedures for mechanistic investigation

4.1 Procedure for Scheme 3, Eq. 1



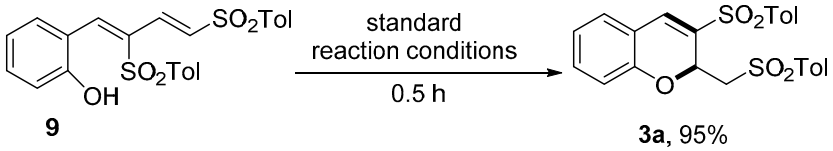
To a suspension of salicylaldehyde **1** (25.6 μL, 0.24 mmol) and phenyl vinyl sulfone **4** (28.6 μL, 0.20 mmol) in dry toluene (2 mL) was added piperidine (6.0 μL, 0.06 mmol) and *p*-TsOH (10.3 mg, 0.06 mmol). The reaction mixture was stirred at 60 °C for 7 h. The ^{1}H NMR spectrum of the crude reaction mixture shows no oxa-Michael adduct **5** or annulation product **6** was formed.

4.2 Procedure for Scheme 3, Eq. 2



To a solution of salicylaldehyde dimethyl acetal **7** (40.4 mg, 0.24 mmol) in dry toluene (2 mL) was added 1,3-bis(p-tolylsulfonyl)propene **2a** (70.1 mg, 0.20 mmol), piperidine (6.0 μL, 0.06 mmol) and *p*-TsOH (10.3 mg, 0.06 mmol). The reaction mixture was stirred at 60 °C for 7 h. The ^{1}H NMR spectrum of the crude reaction mixture shows no oxa-Michael adduct **8** was formed.

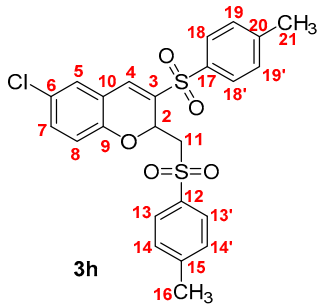
4.3 Procedure for Scheme 3, Eq. 3



To a solution of phenol derivative **9** (90.9 mg, 0.20 mmol) in dry toluene (2 mL) was added piperidine (6.0 μL, 0.06 mmol) and *p*-TsOH (10.3 mg, 0.06 mmol). The reaction mixture was stirred at 60 °C for 0.5 h. After completion (monitored by TLC), the reaction mixture was purified by flash chromatography over silica gel (eluent: petroleum ether/ethyl acetate = 5:1) to give the pure product **3a** (86.4 mg, 95% yield).

5. Detailed NMR spectroscopic analysis of product 3h

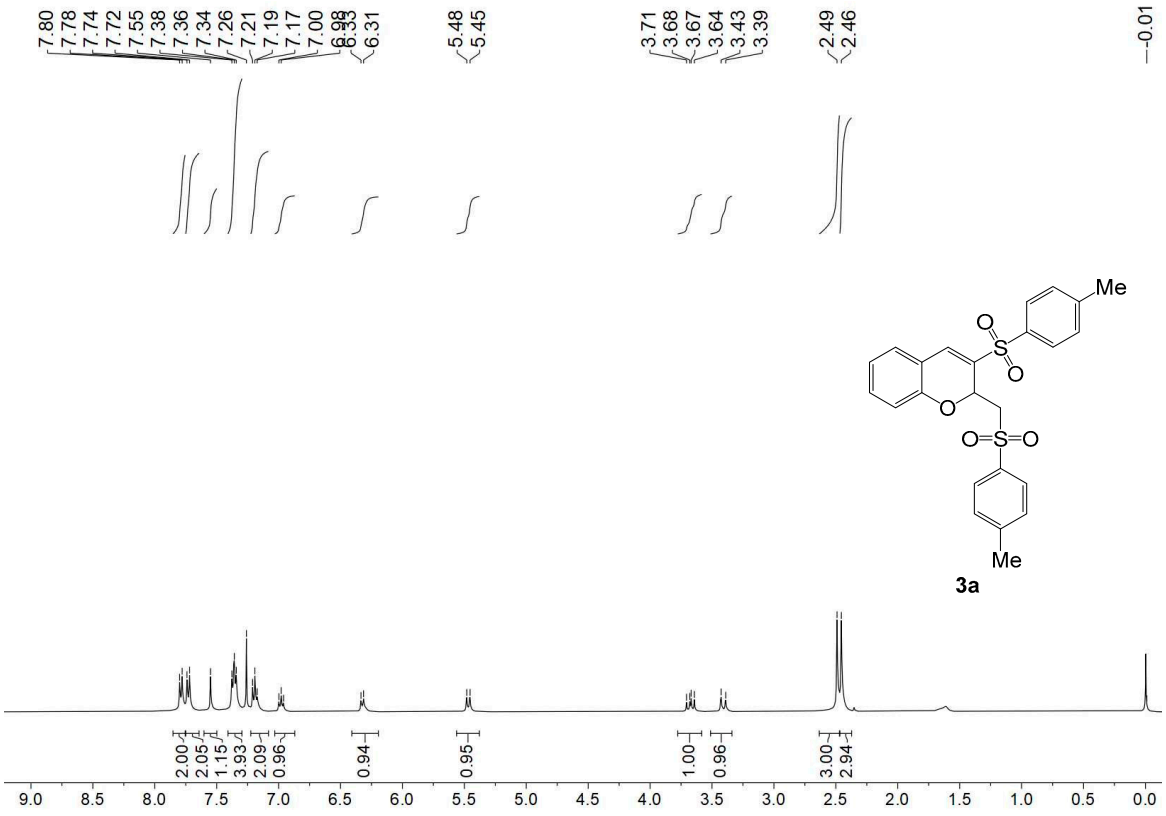
Table S2. ^{1}H and ^{13}C NMR (400 and 100 MHz, $CDCl_3$) spectroscopic data of **3h**



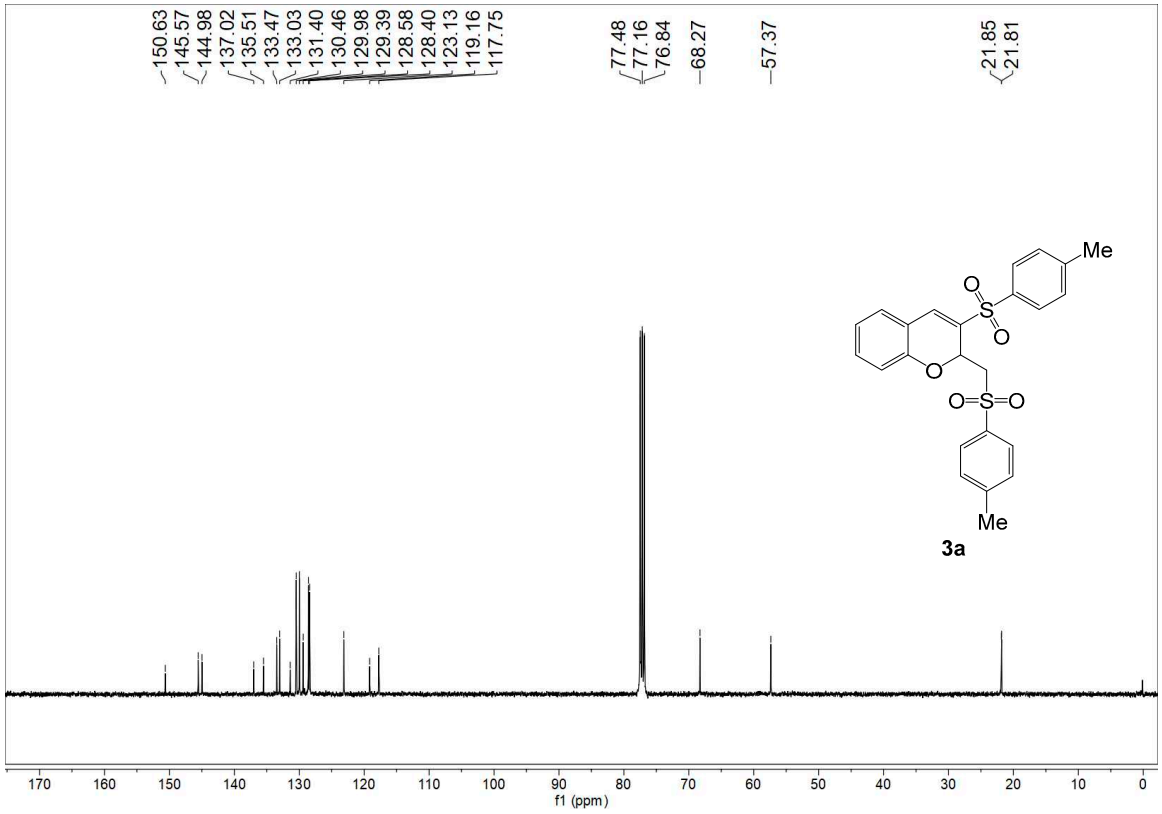
3h

Position	^{1}H [*m*, *J* (Hz)]	^{13}C	HMBC (C→H)
2	5.48 (dd, *J* = 12.0 Hz, 4.0 Hz, 1H)	68.4	4-H, 11-H
3	/	132.9	2-H, 4-H
4	7.47 (s, 1H)	131.7	/
5	7.18 (d, *J* = 4.0 Hz, 1H)	128.6	4-H, 7-H
6	/	128.1	8-H
7	7.12 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H)	133.0	5-H
8	6.26 (d, *J* = 12.0 Hz, 1H)	119.1	/
9	/	149.0	2-H, 4-H, 5-H, 7-H, 8-H
10	/	120.3	4-H, 8-H
11	3.63 (dd, *J* = 12.0 Hz, 12.0 Hz, 1H) 3.38 (dd, *J* = 12.0 Hz, 4.0 Hz, 1H)	57.2	2-H
12/17	/	136.8, 135.0	14/14'-H, 19/19'-H
13/13' 18/18'	7.77 (d, *J* = 8.0 Hz, 2H) 7.72 (d, *J* = 8.0 Hz, 2H)	128.5, 128.4	/
14/14' 19/19'	7.37 (d, *J* = 12.0 Hz, 2H) 7.36 (d, *J* = 8.0 Hz, 2H)	130.5, 130.0	16-H, 21-H
15/20	/	145.8, 145.1	13/13'-H, 18/18'-H, 16-H, 21-H
16/21	2.48 (s, 3H), 2.45 (s, 3H)	21.8, 21.8	14/14'-H, 19/19'-H

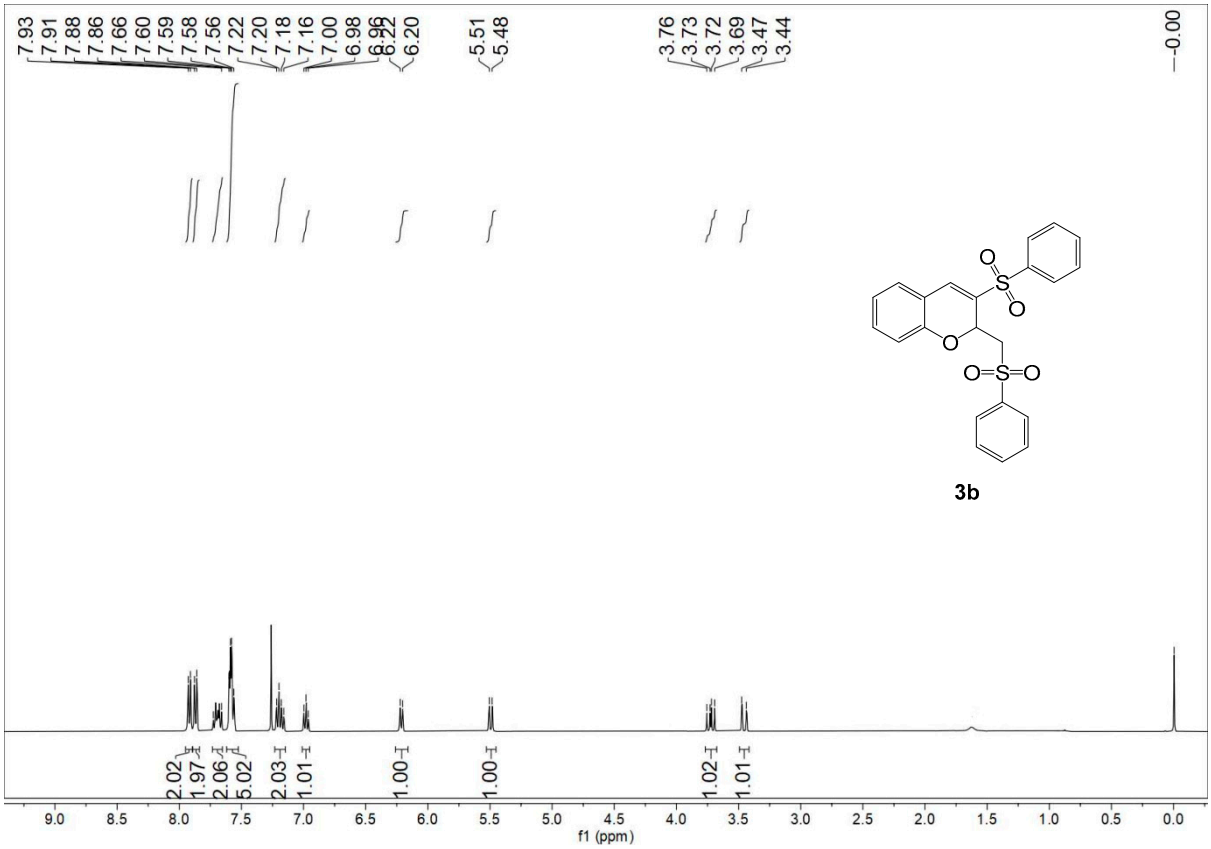
6. Copies of NMR spectra



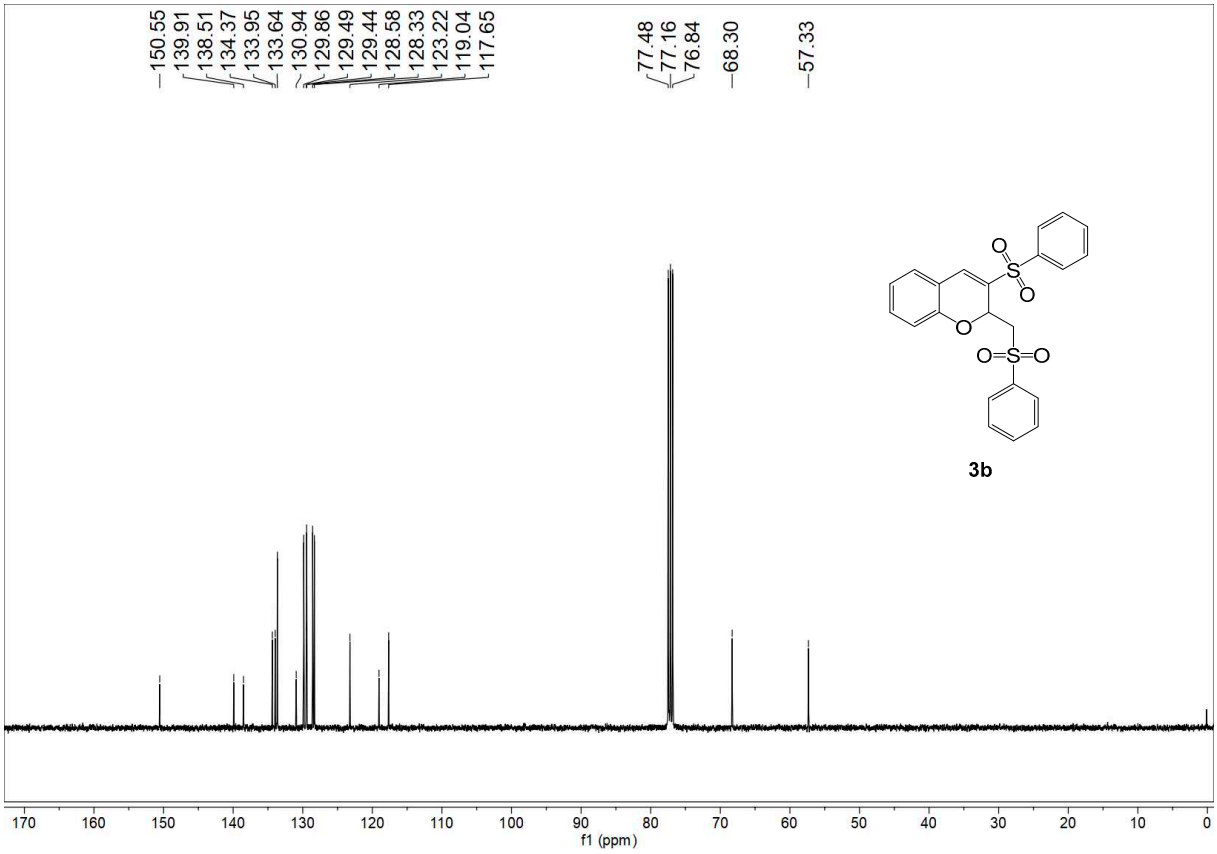
^{1}H NMR spectrum of **3a**



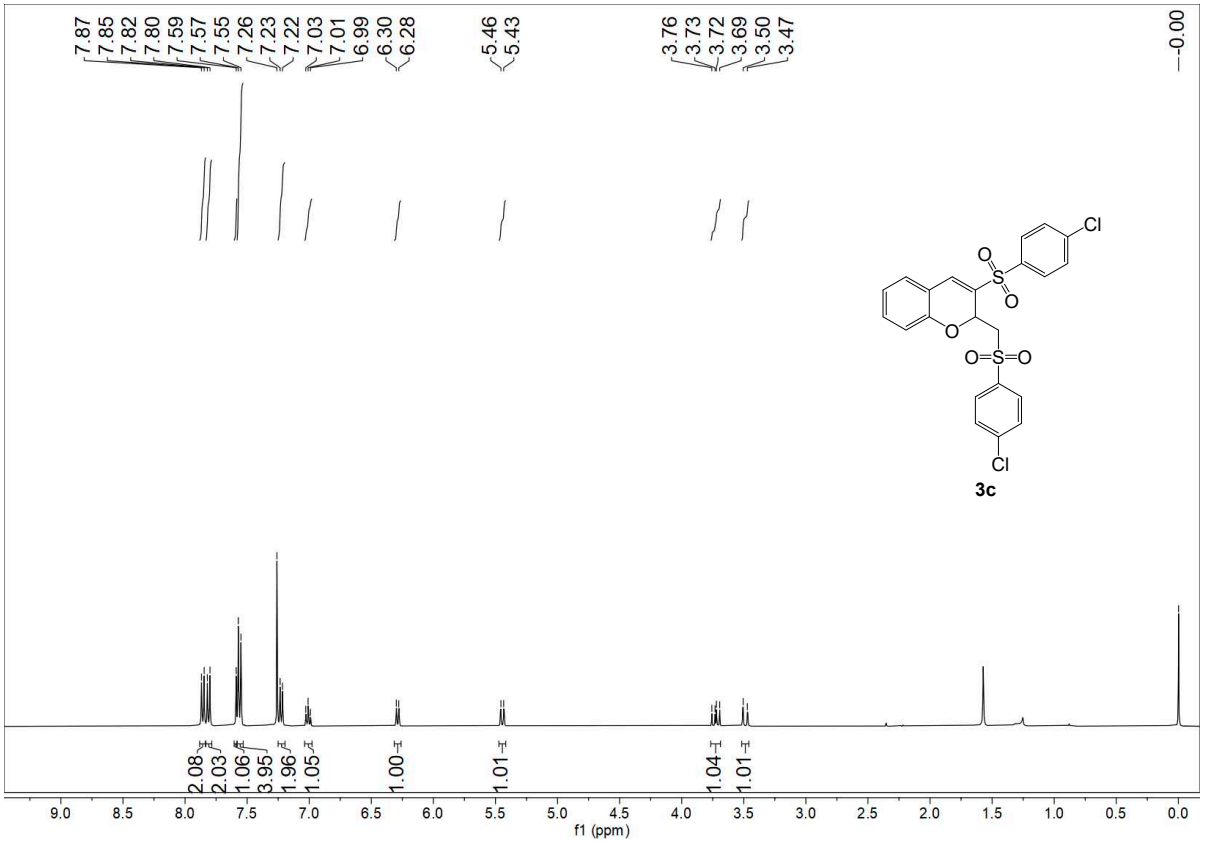
^{13}C NMR spectrum of **3a**



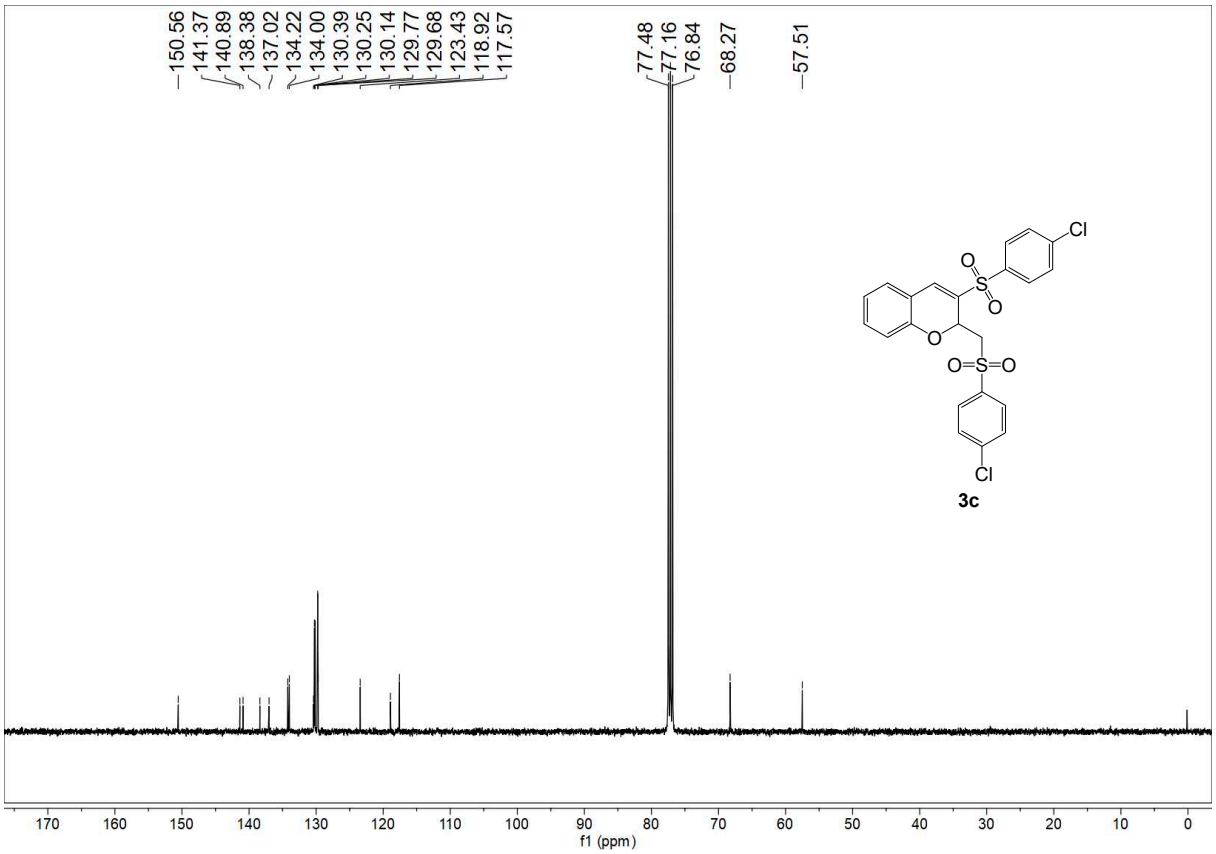
^{1}H NMR spectrum of **3b**



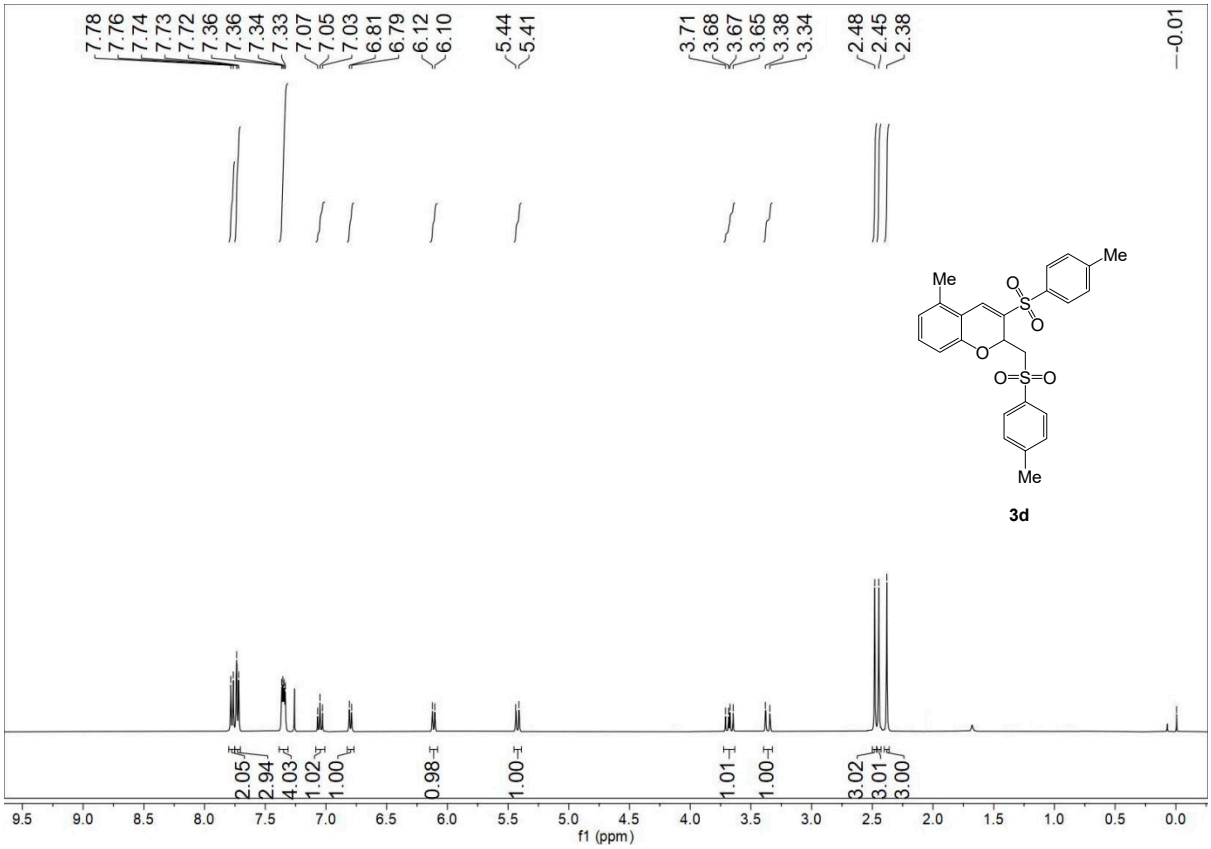
^{13}C NMR spectrum of **3b**



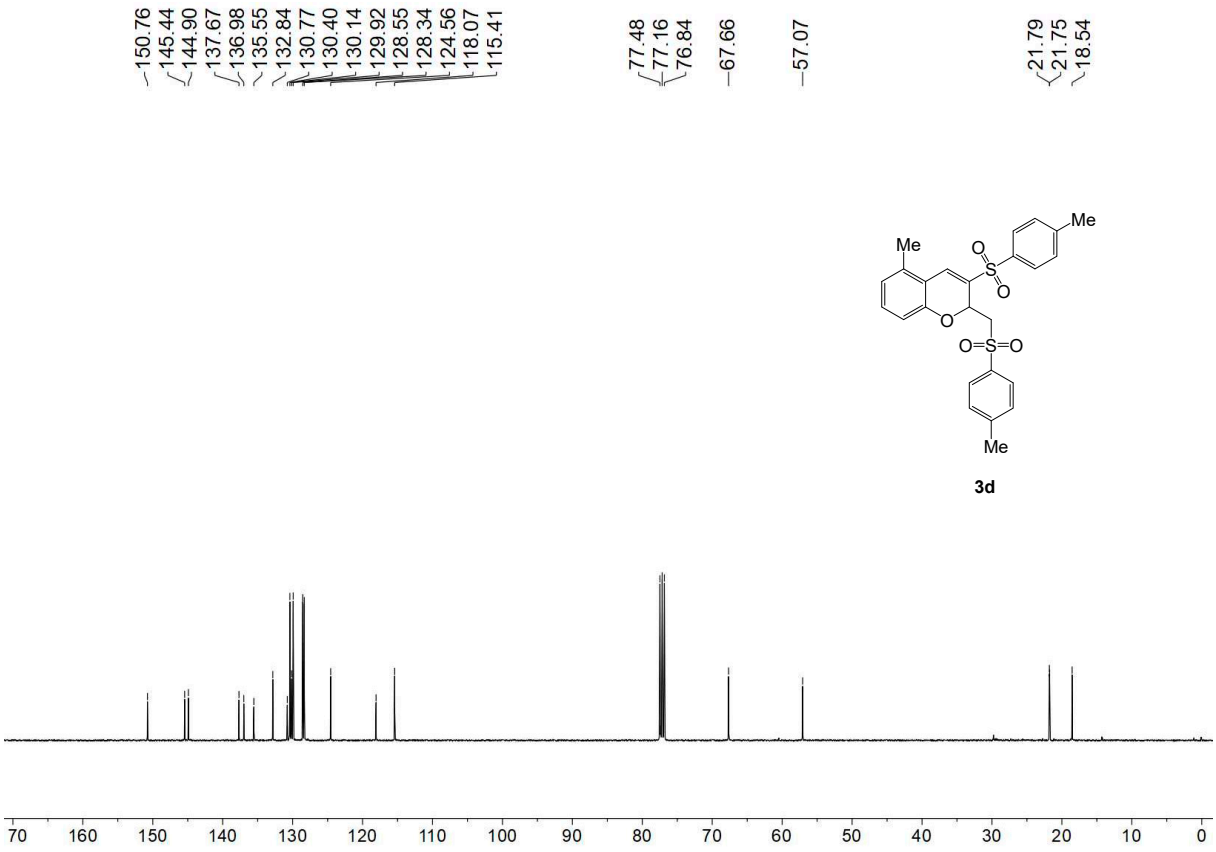
^{1}H NMR spectrum of **3c**



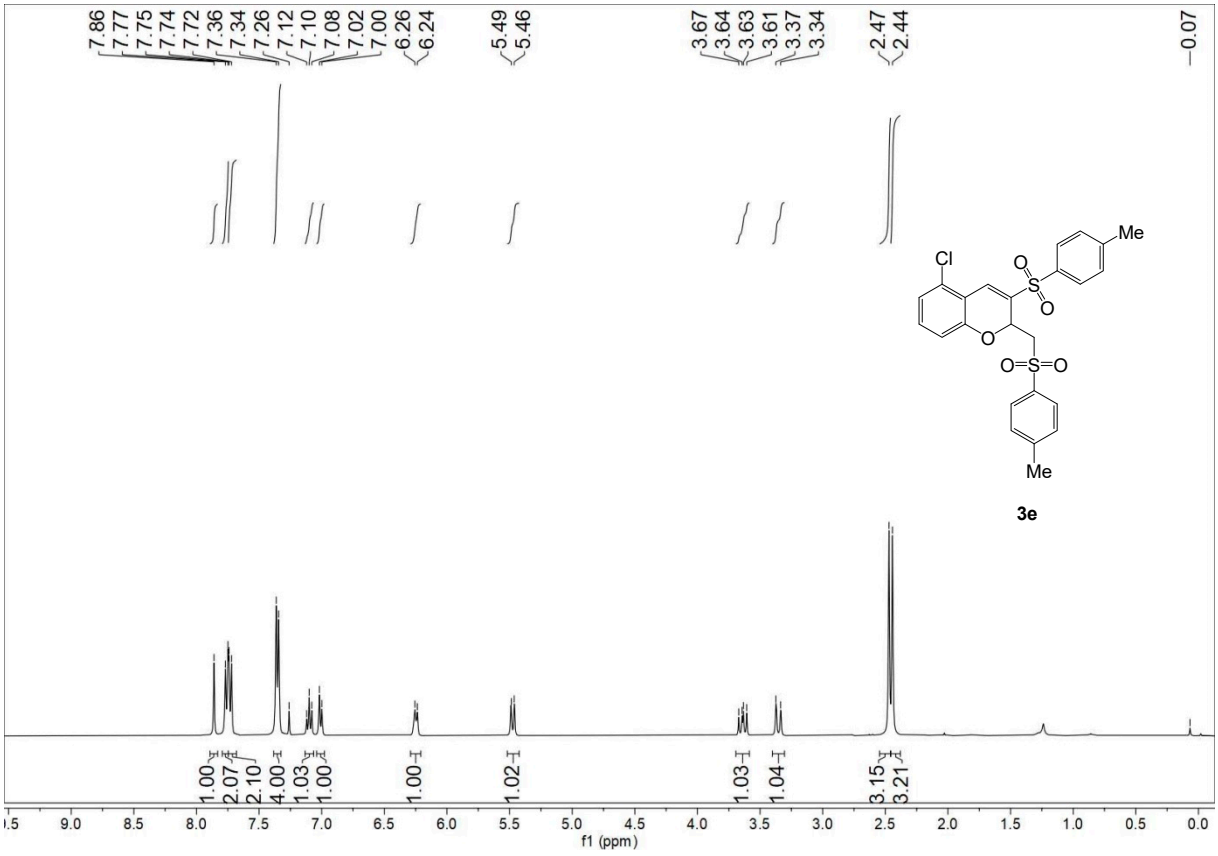
^{13}C NMR spectrum of **3c**



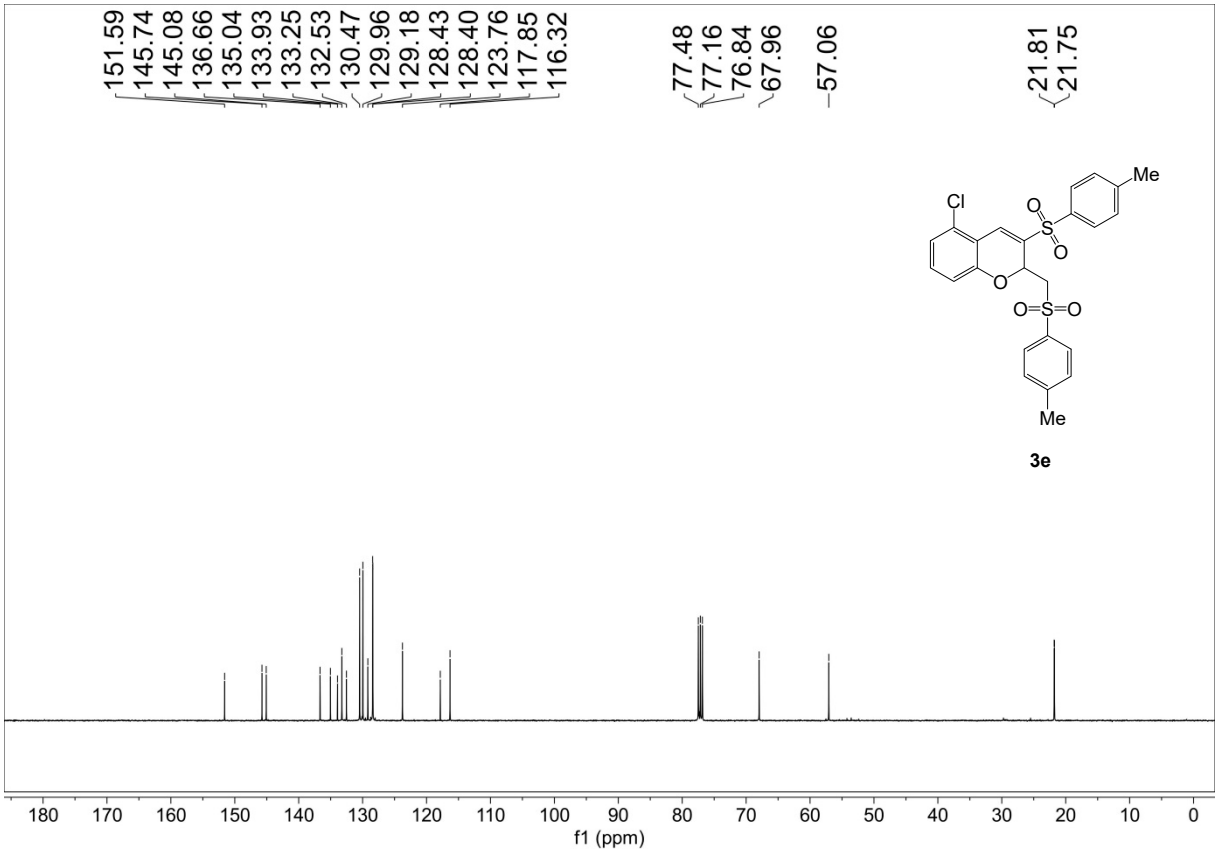
^{1}H NMR spectrum of **3d**



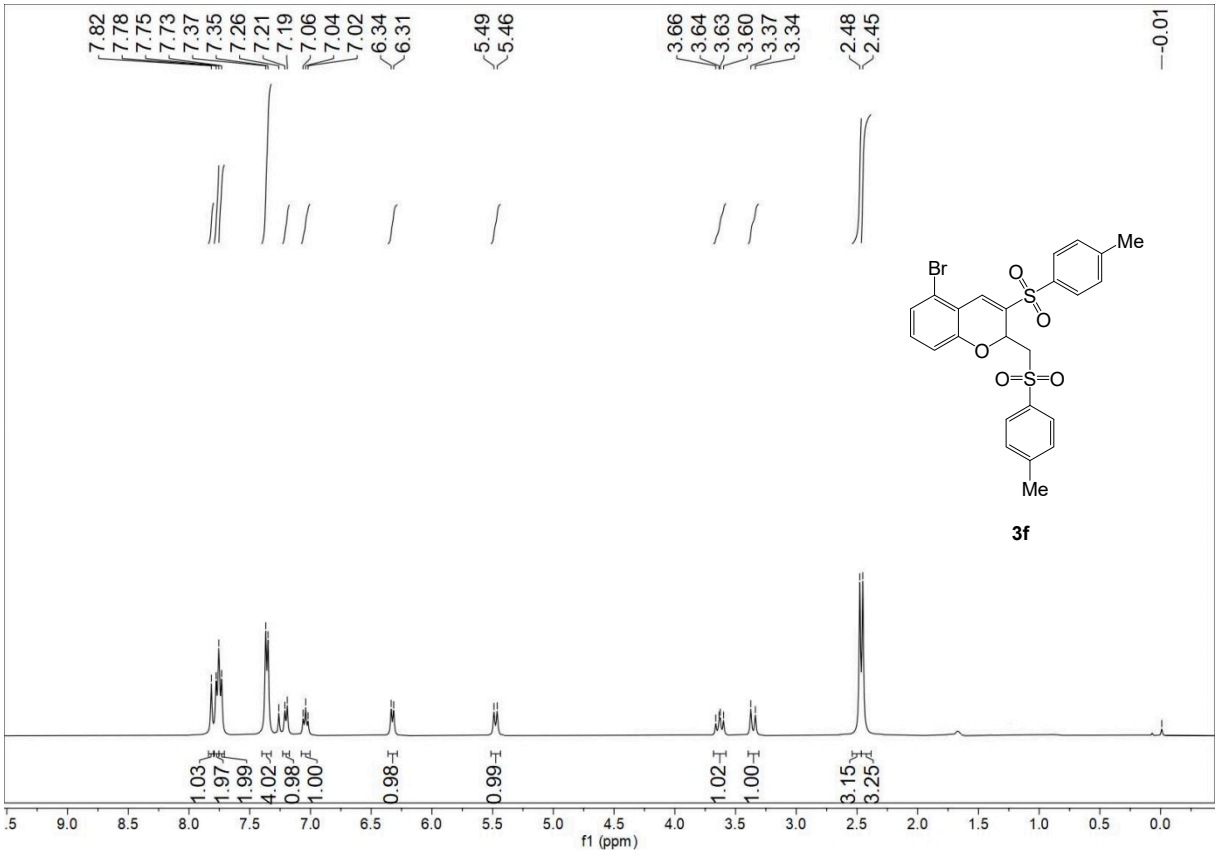
^{13}C NMR spectrum of **3d**



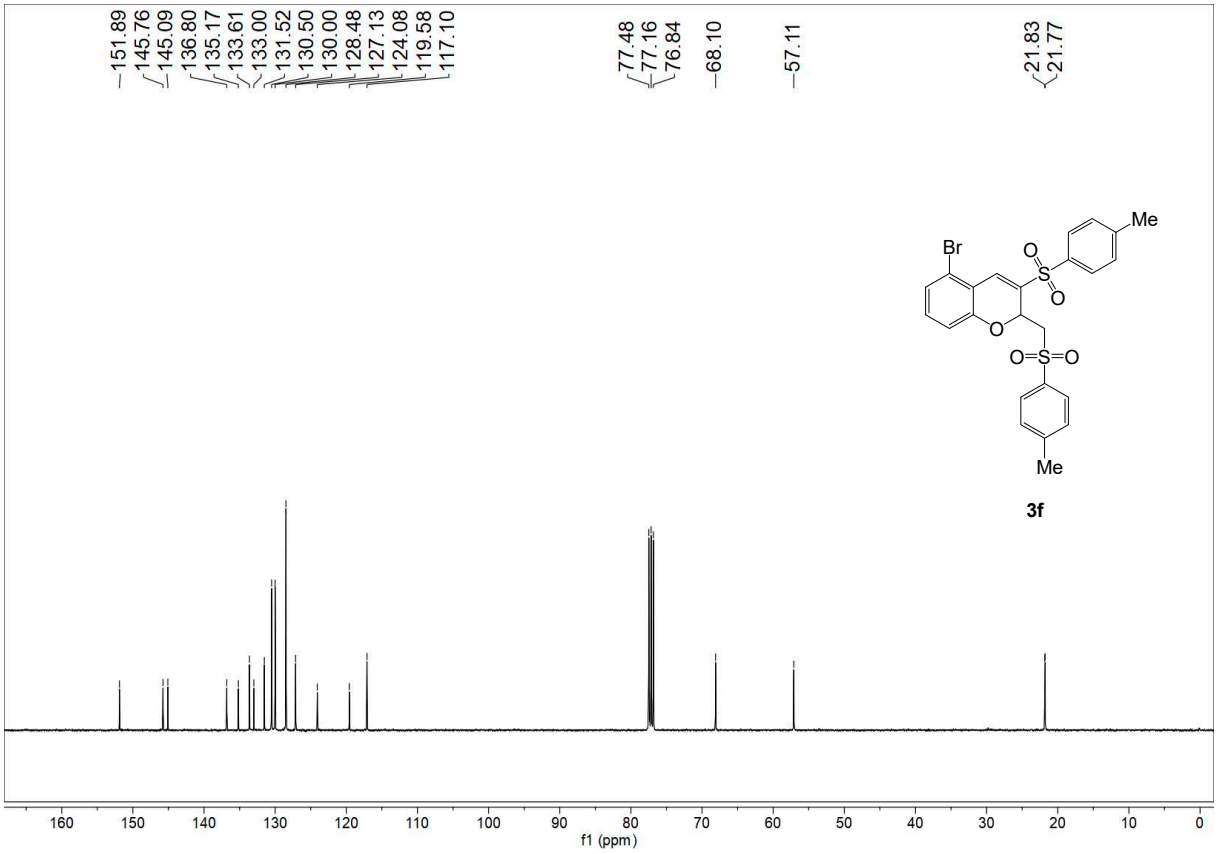
^{1}H NMR spectrum of **3e**



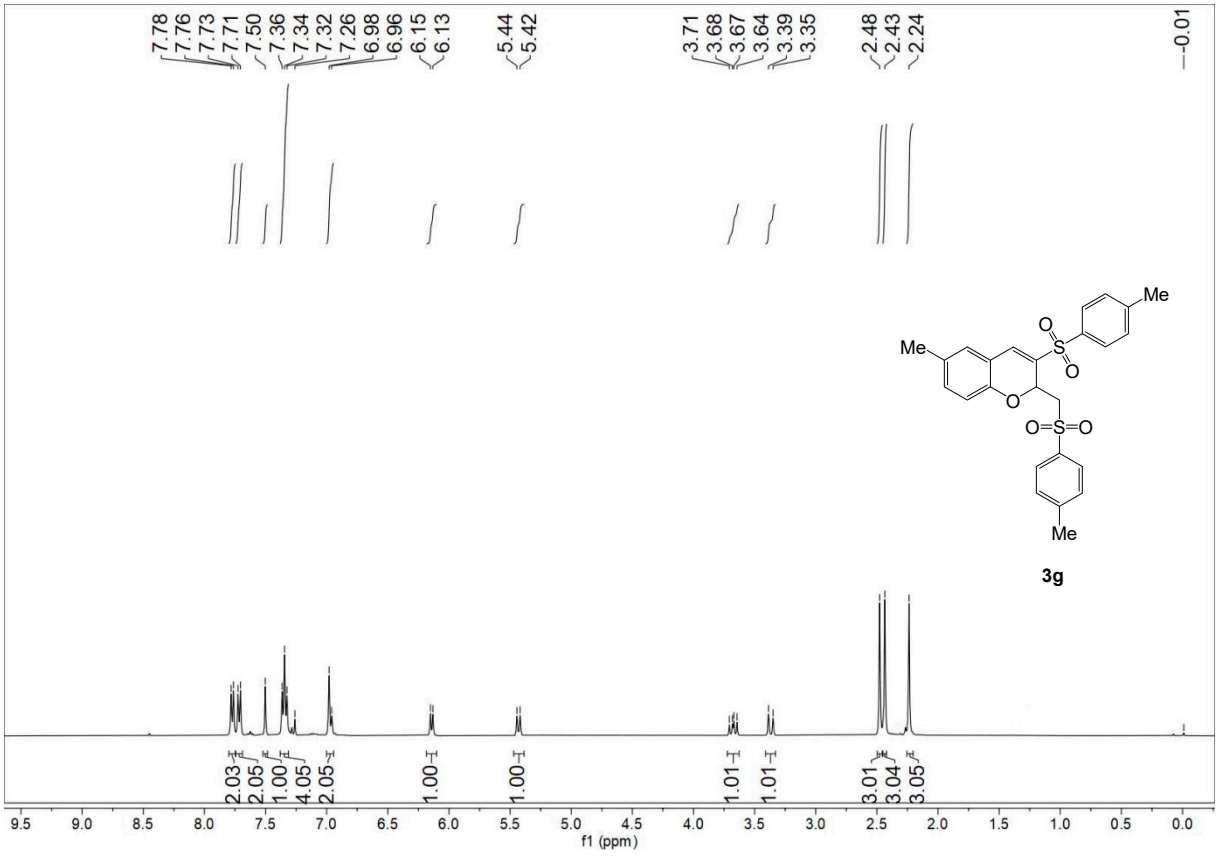
^{13}C NMR spectrum of **3e**



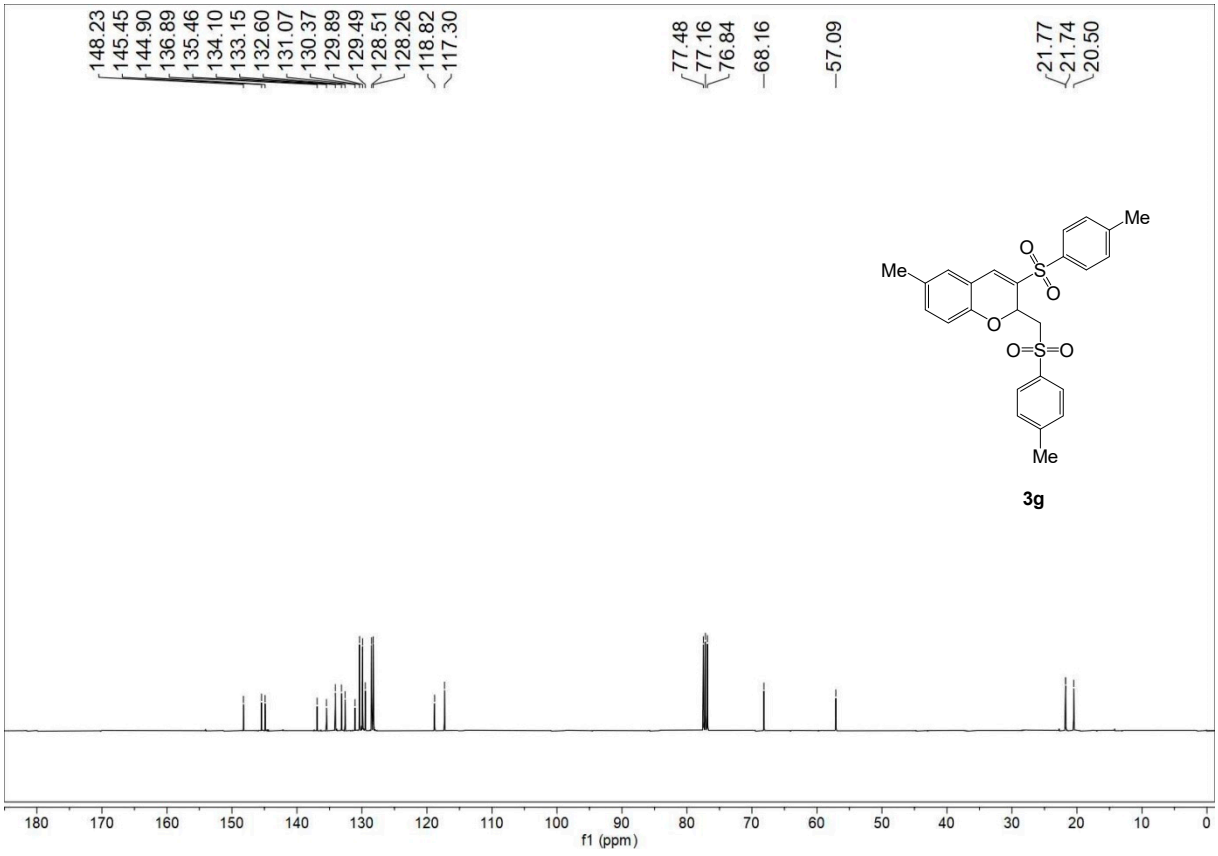
^{1}H NMR spectrum of **3f**



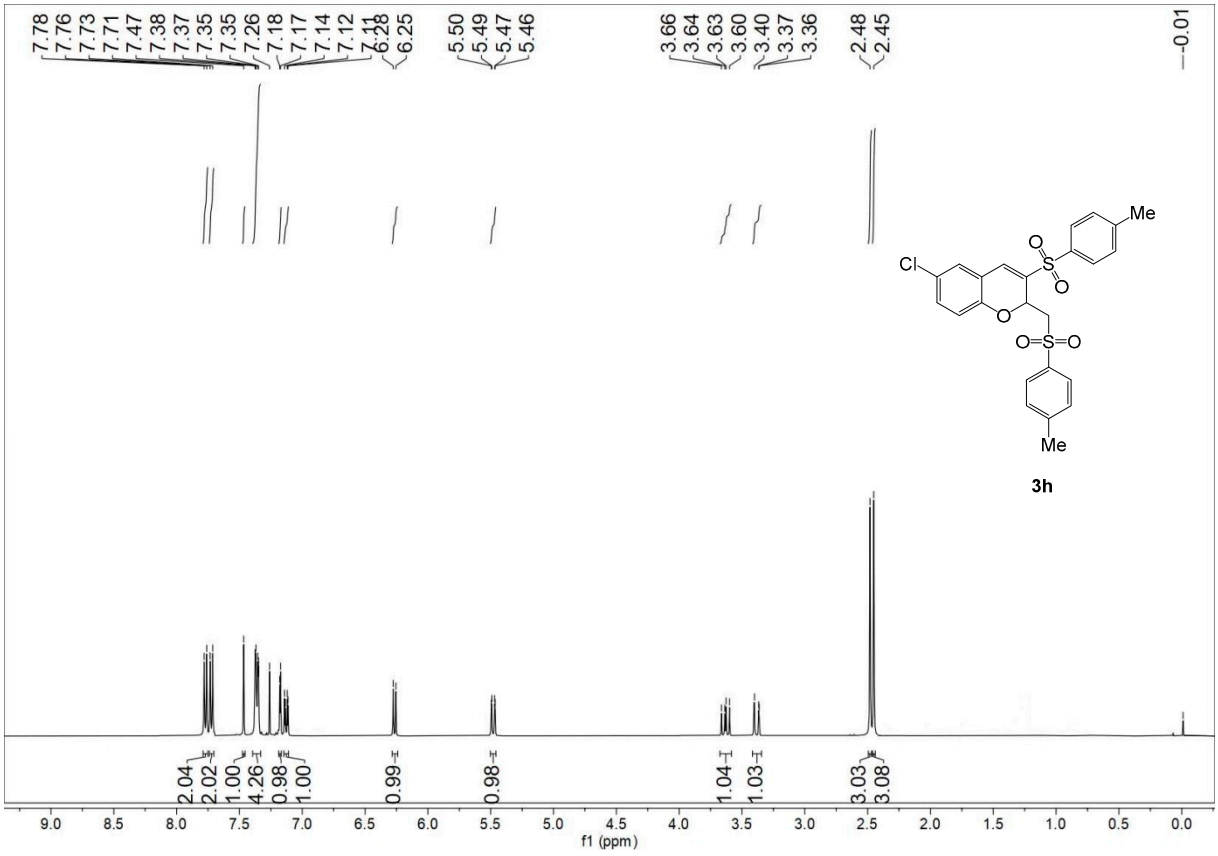
^{13}C NMR spectrum of **3f**



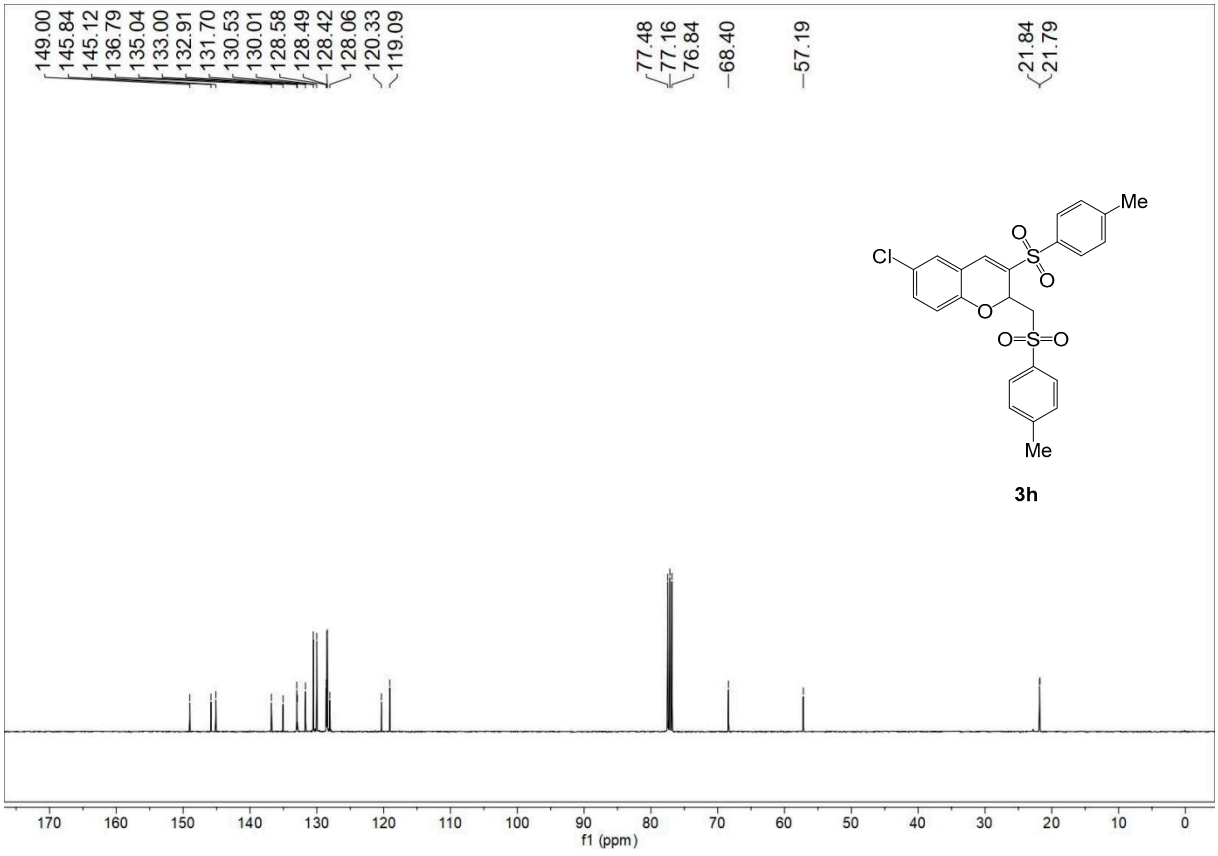
^{1}H NMR spectrum of **3g**



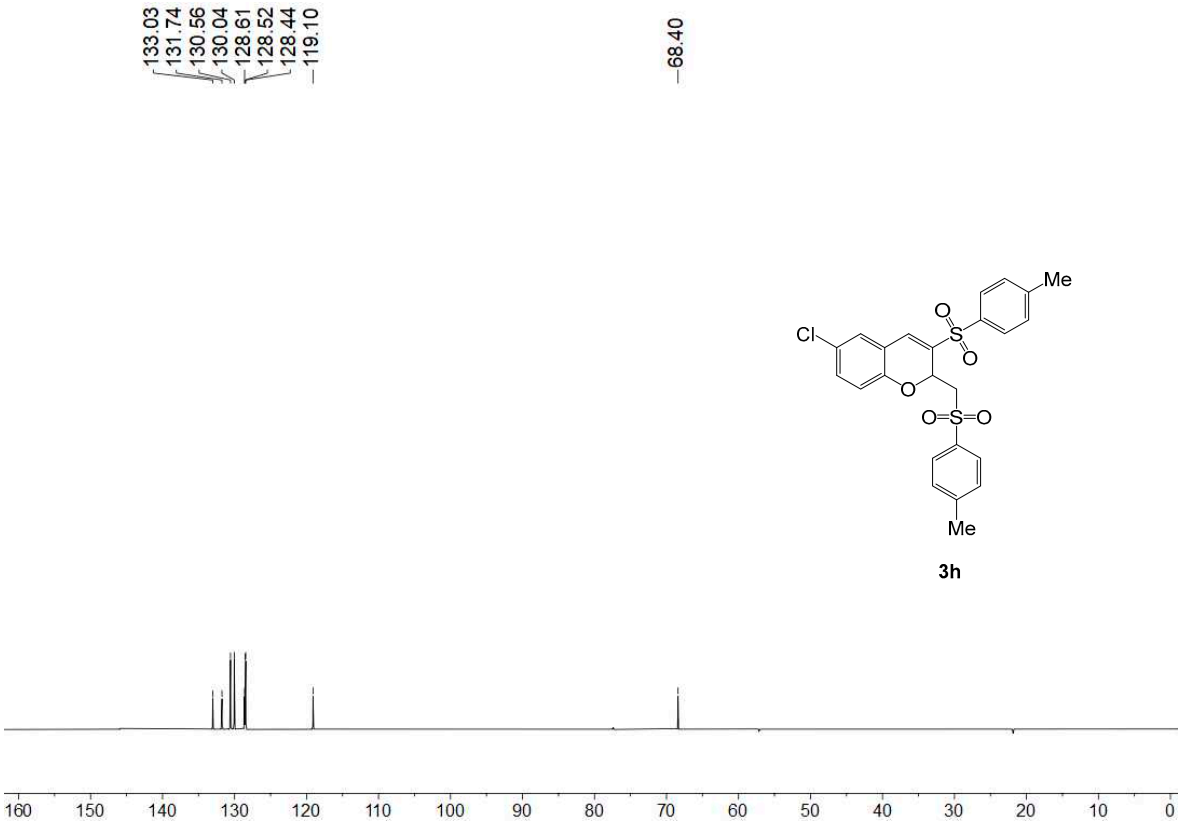
^{13}C NMR spectrum of **3g**



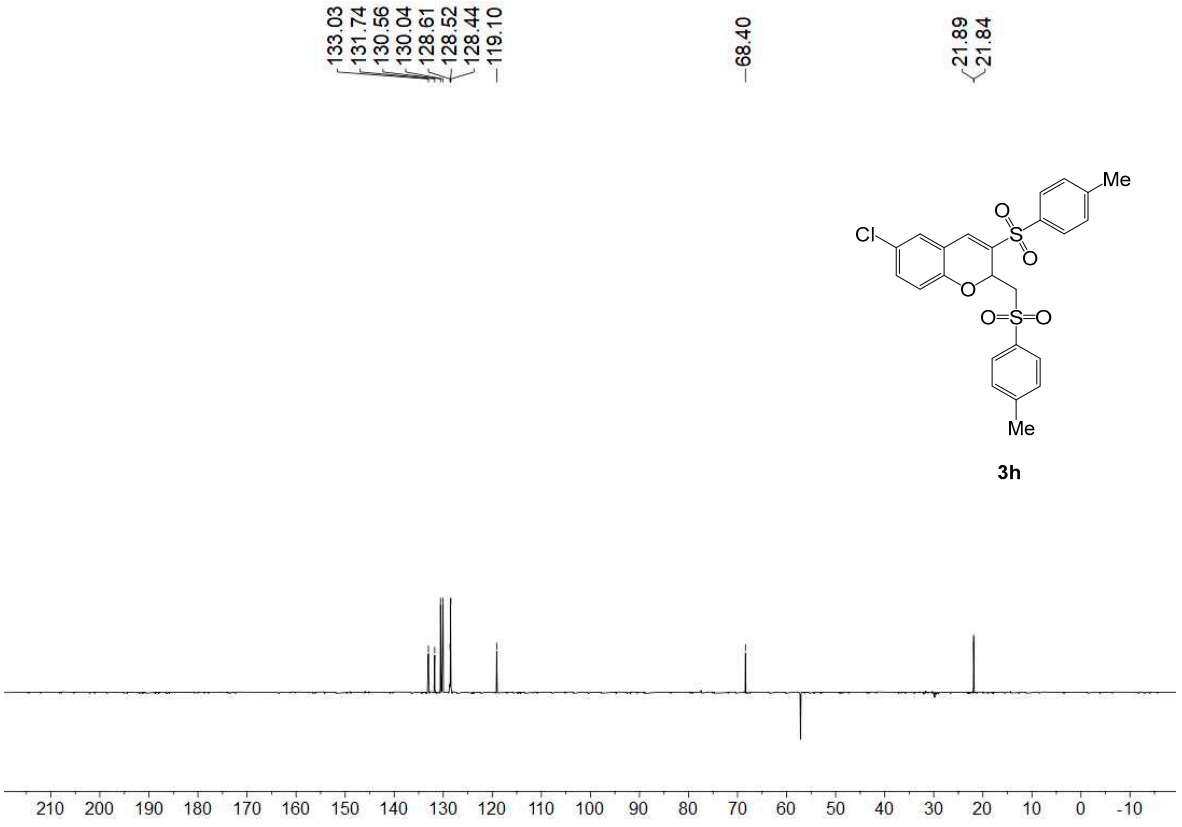
^{1}H NMR spectrum of **3h**



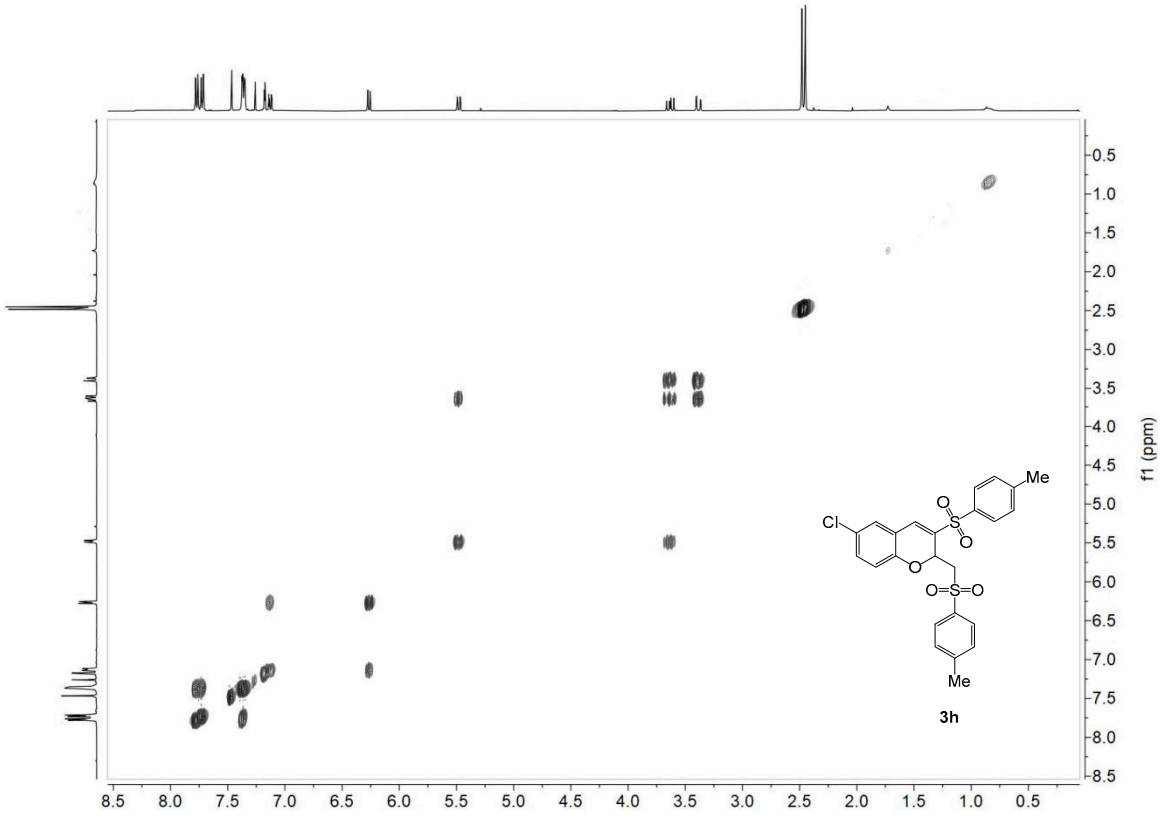
^{13}C NMR spectrum of **3h**



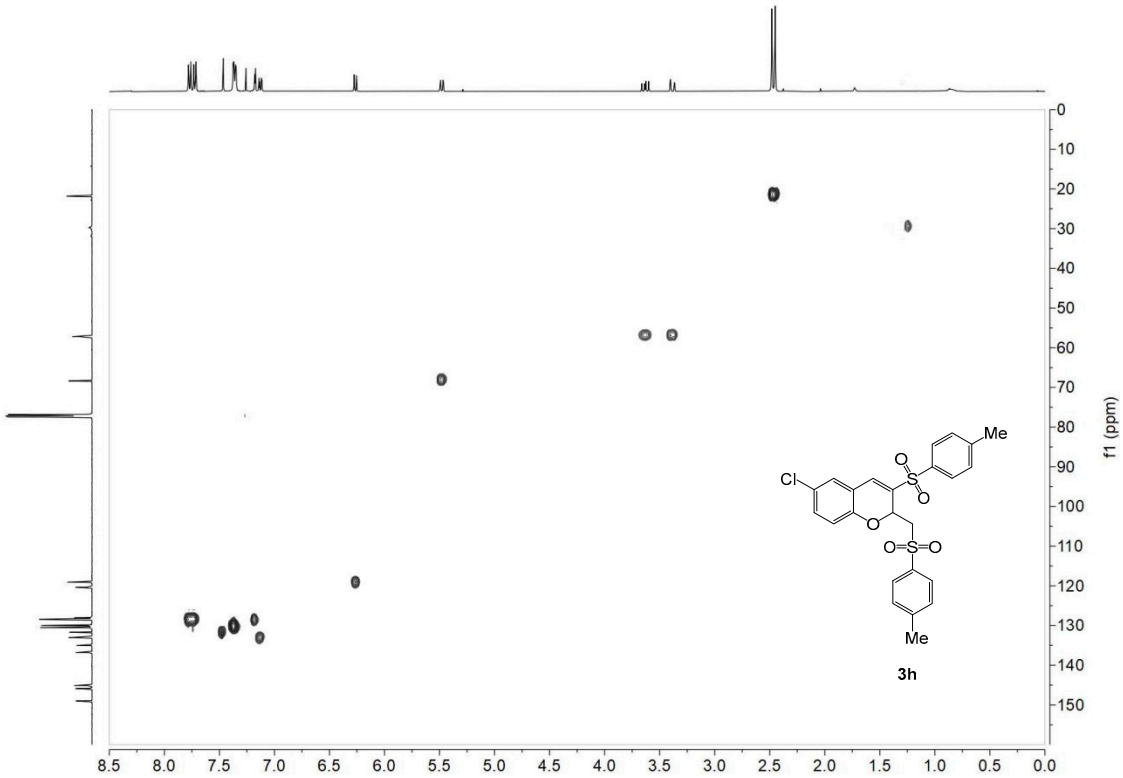
DEPT-90 spectrum of **3h**



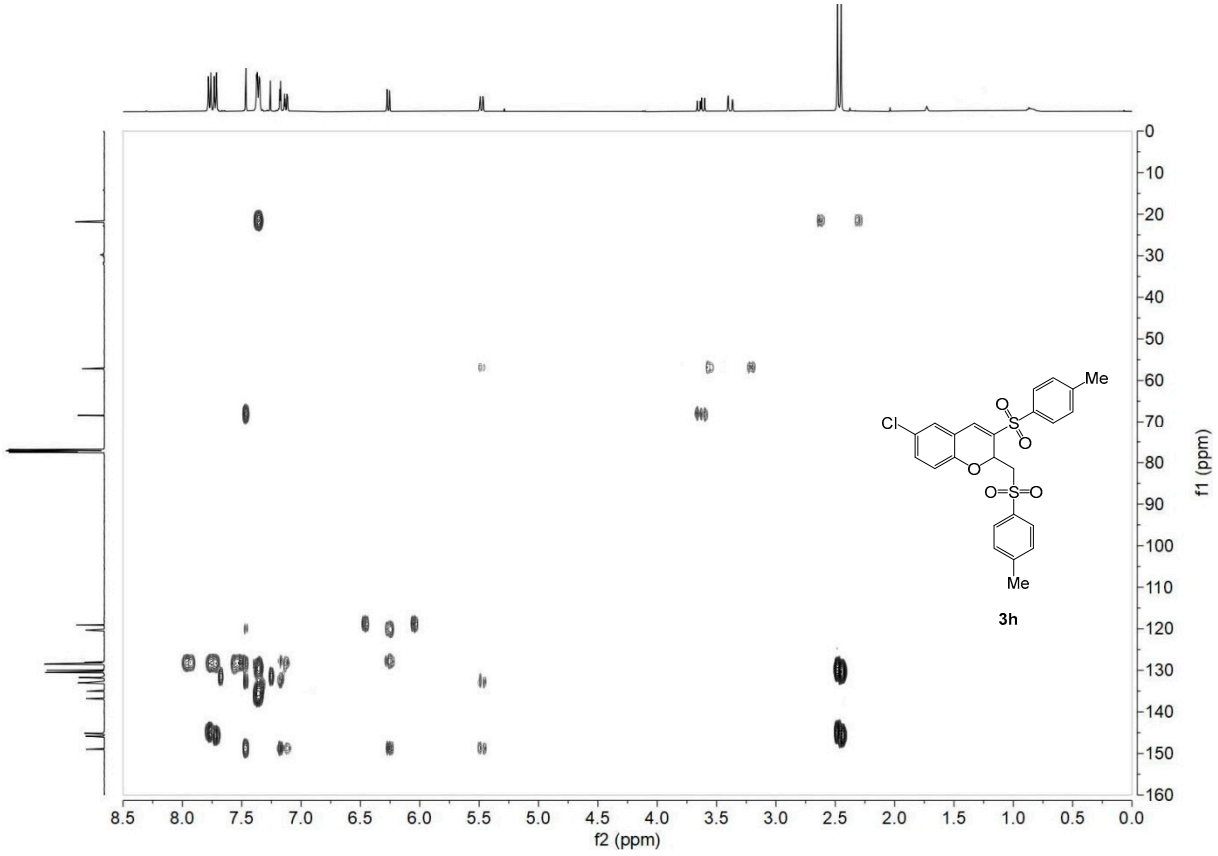
DEPT-135 spectrum of **3h**



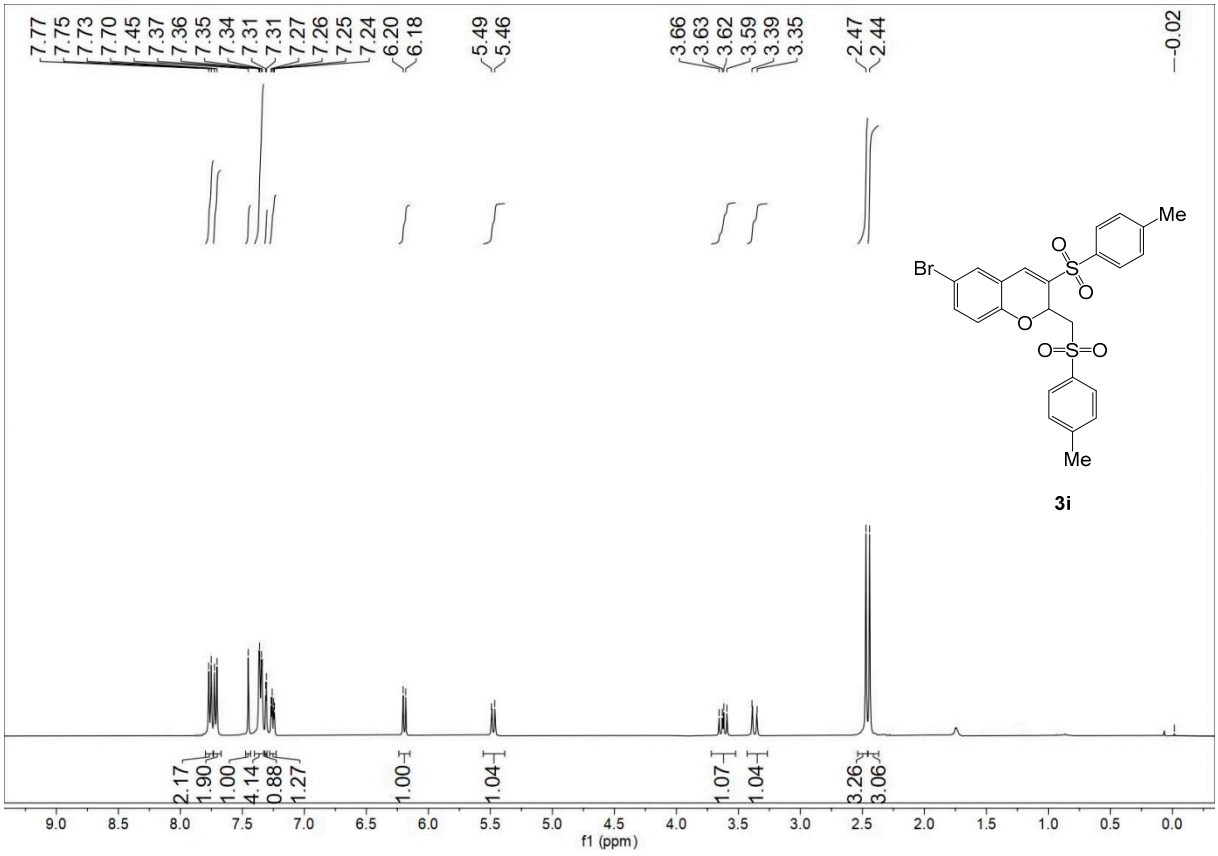
^{1}H-^{1}H COSY spectrum of **3h**



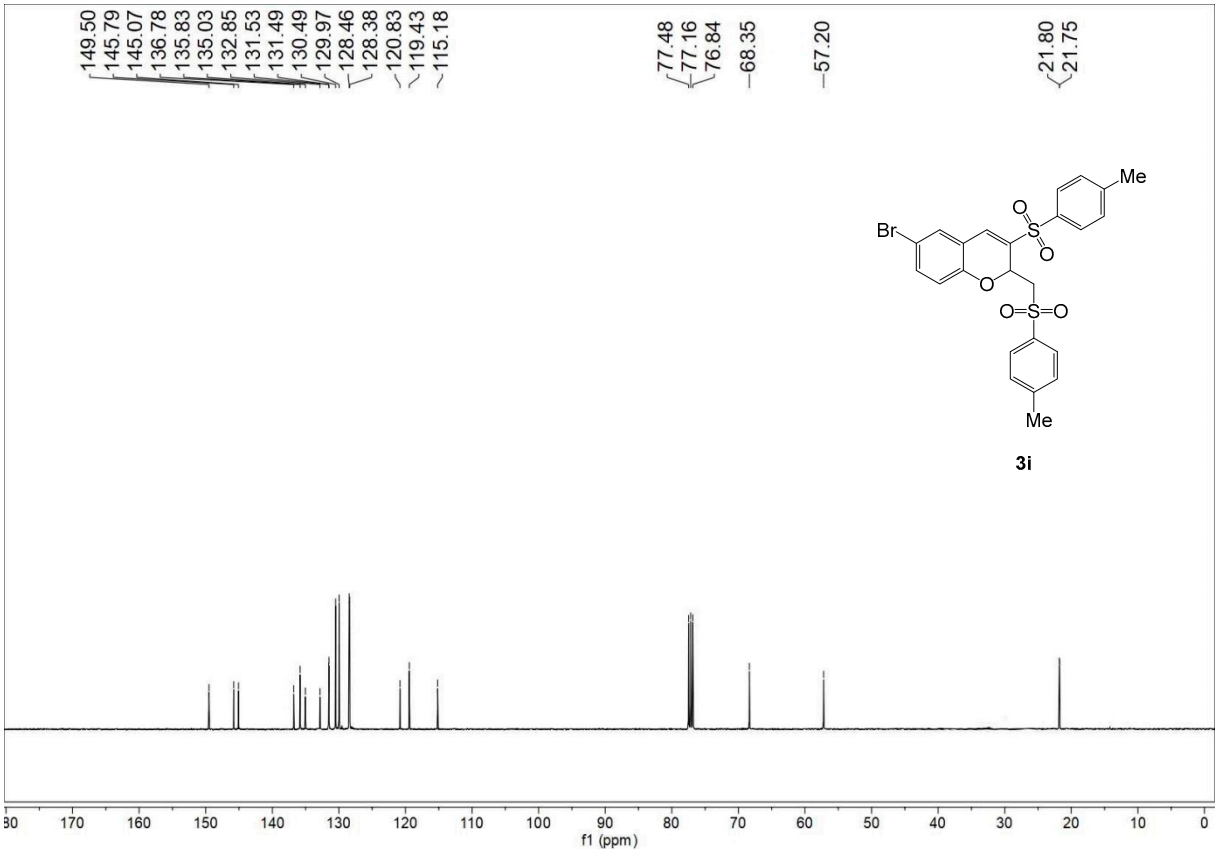
HSQC spectrum of **3h**



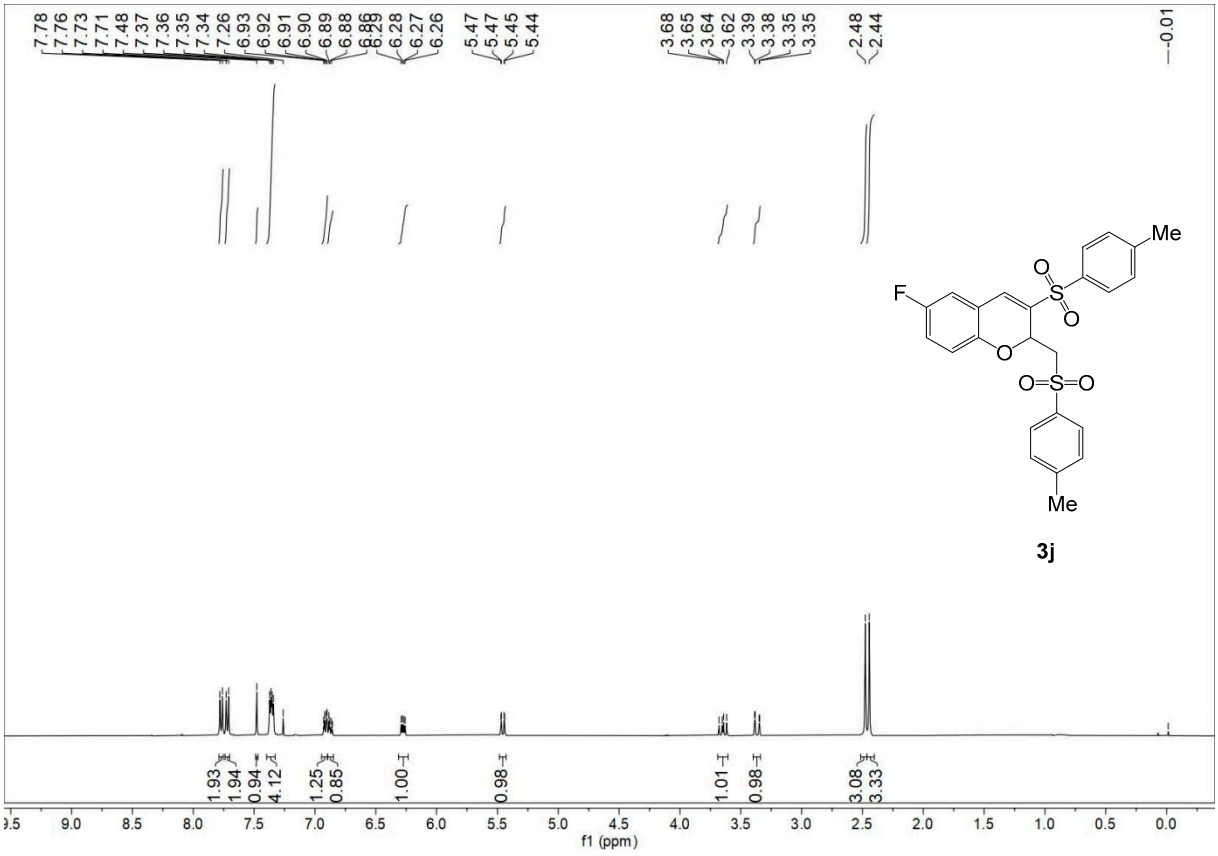
HMBC spectrum of **3h**



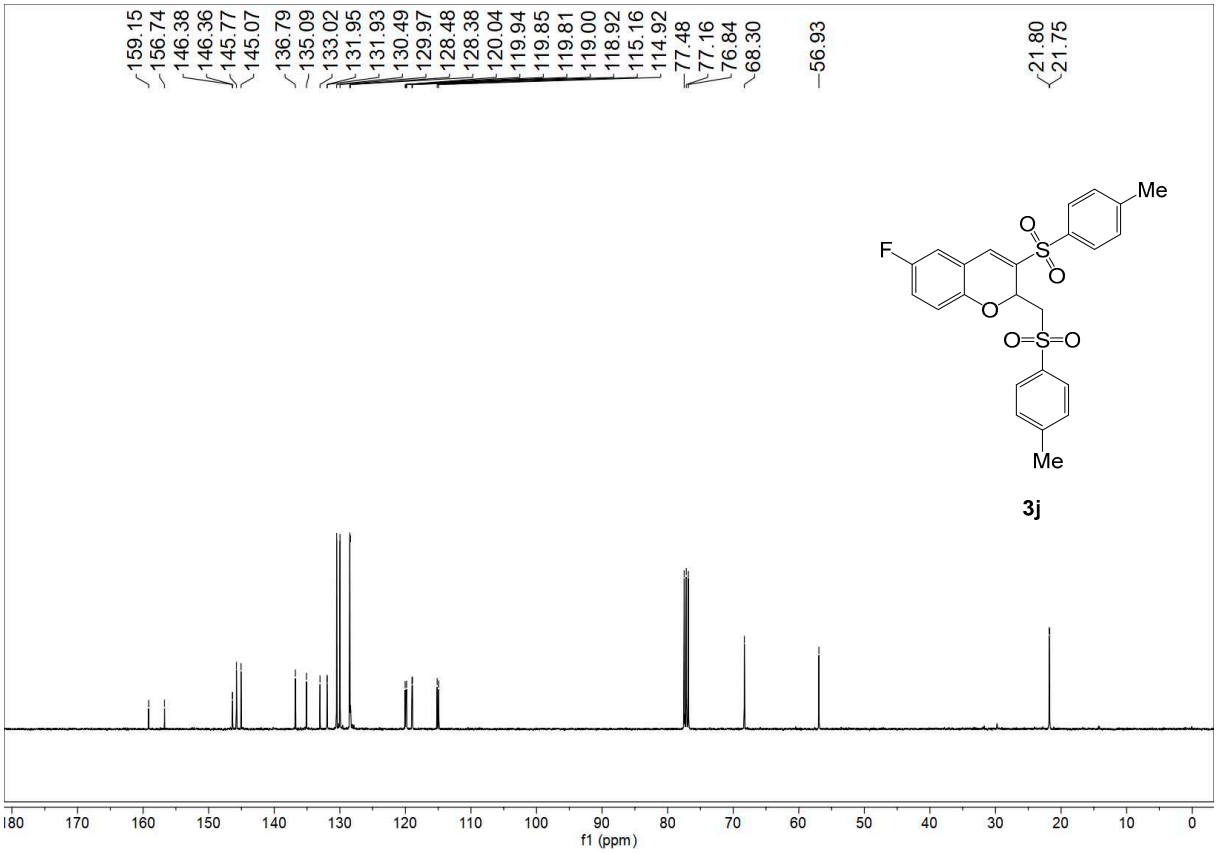
^{1}H NMR spectrum of **3i**



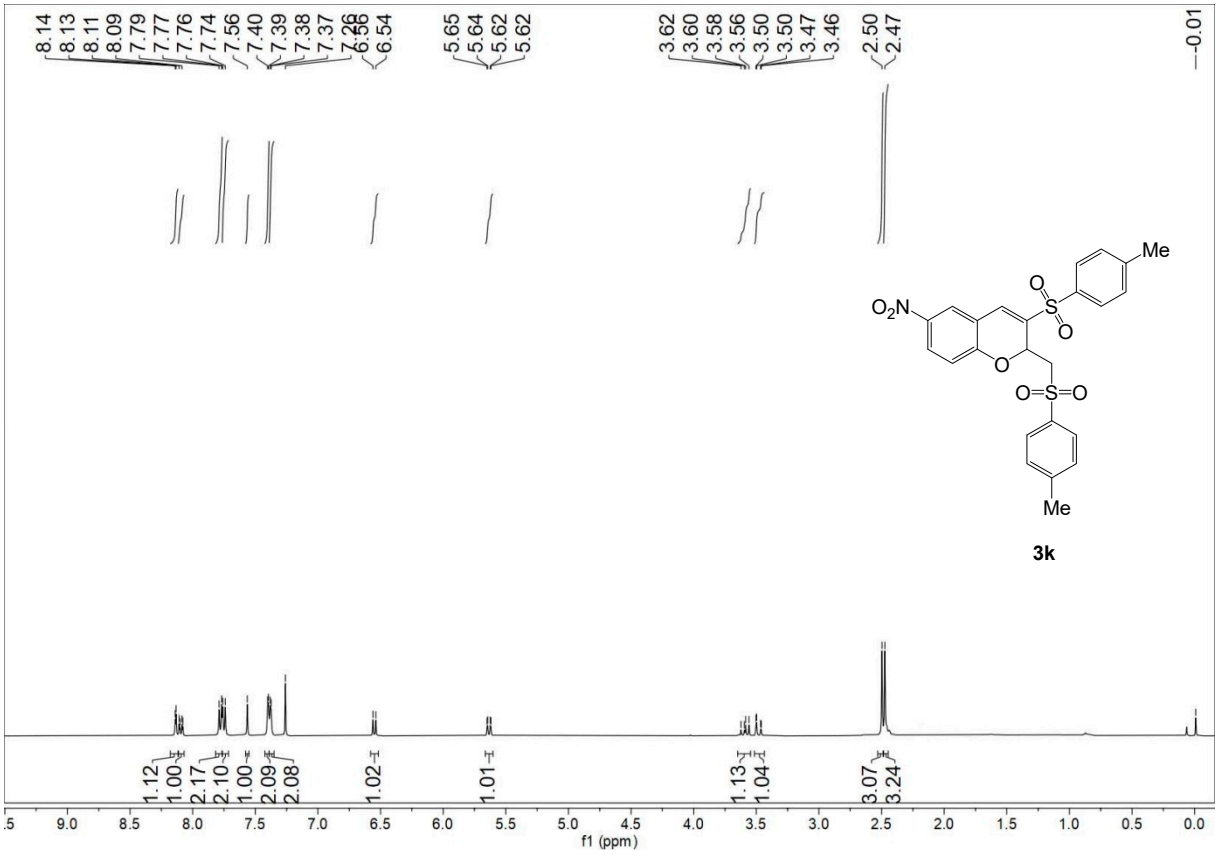
^{13}C NMR spectrum of **3i**



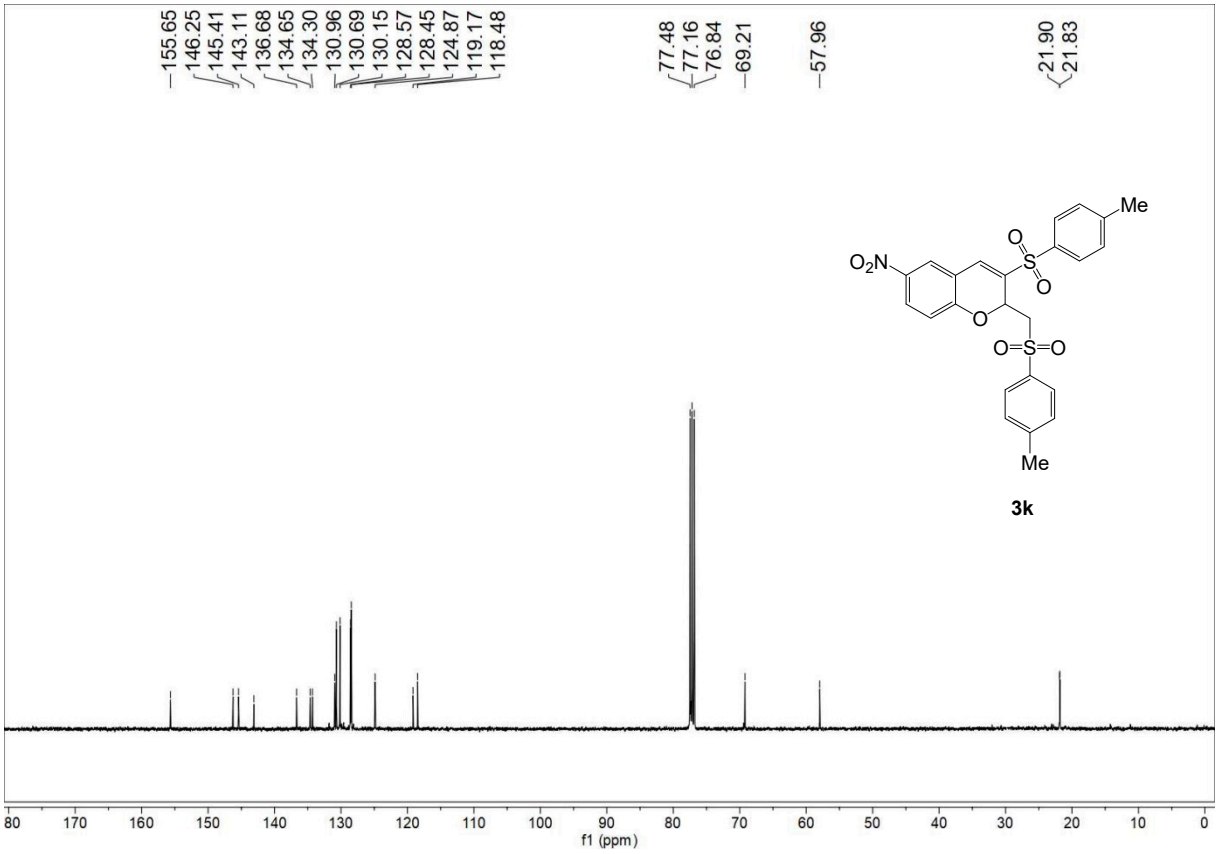
^{1}H NMR spectrum of **3j**



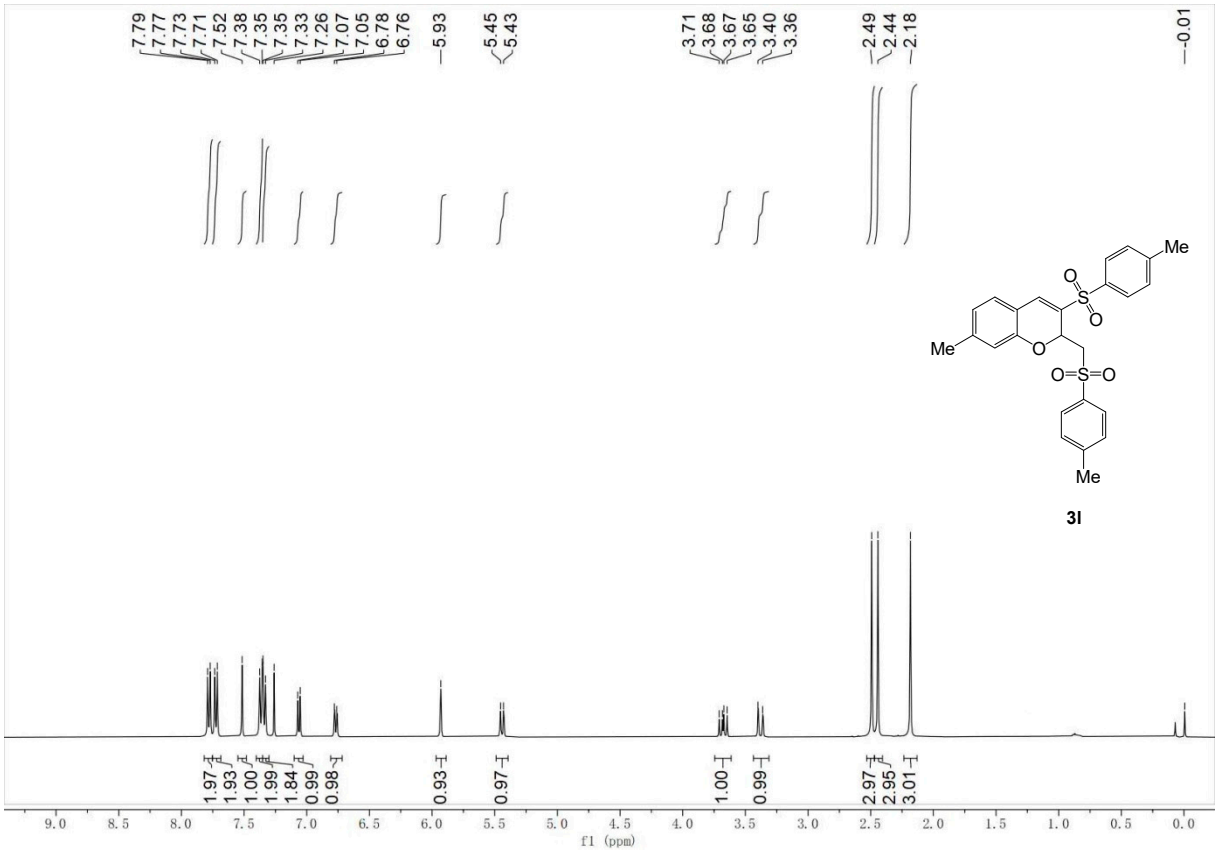
^{13}C NMR spectrum of **3j**



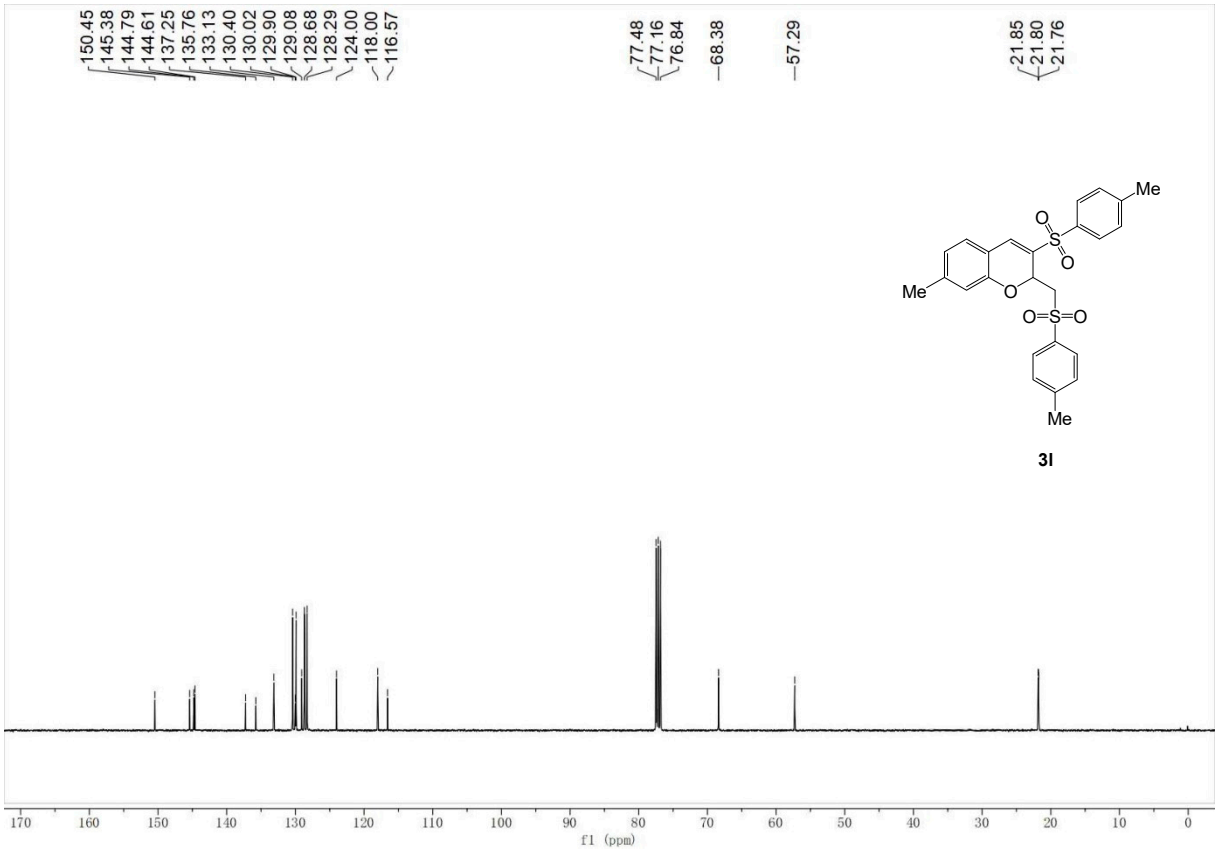
^{1}H NMR spectrum of **3k**



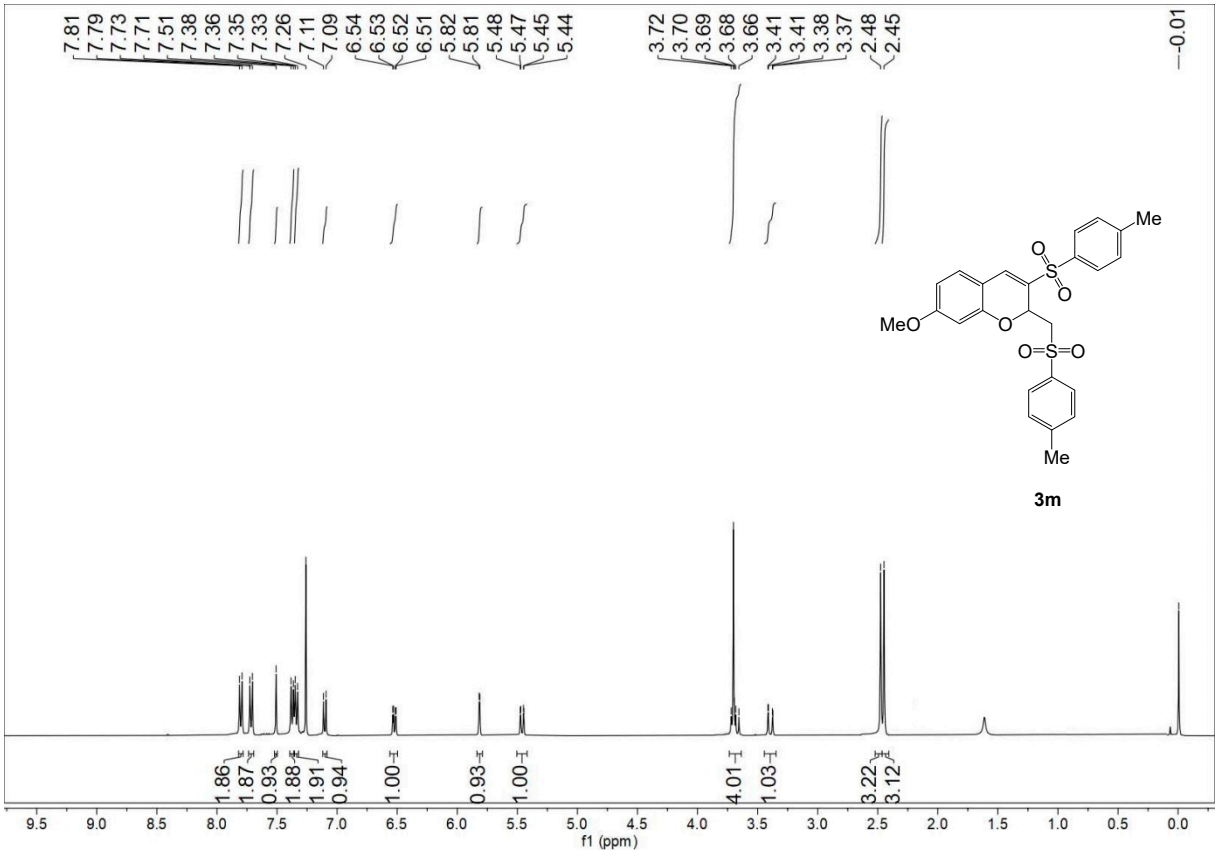
^{13}C NMR spectrum of **3k**



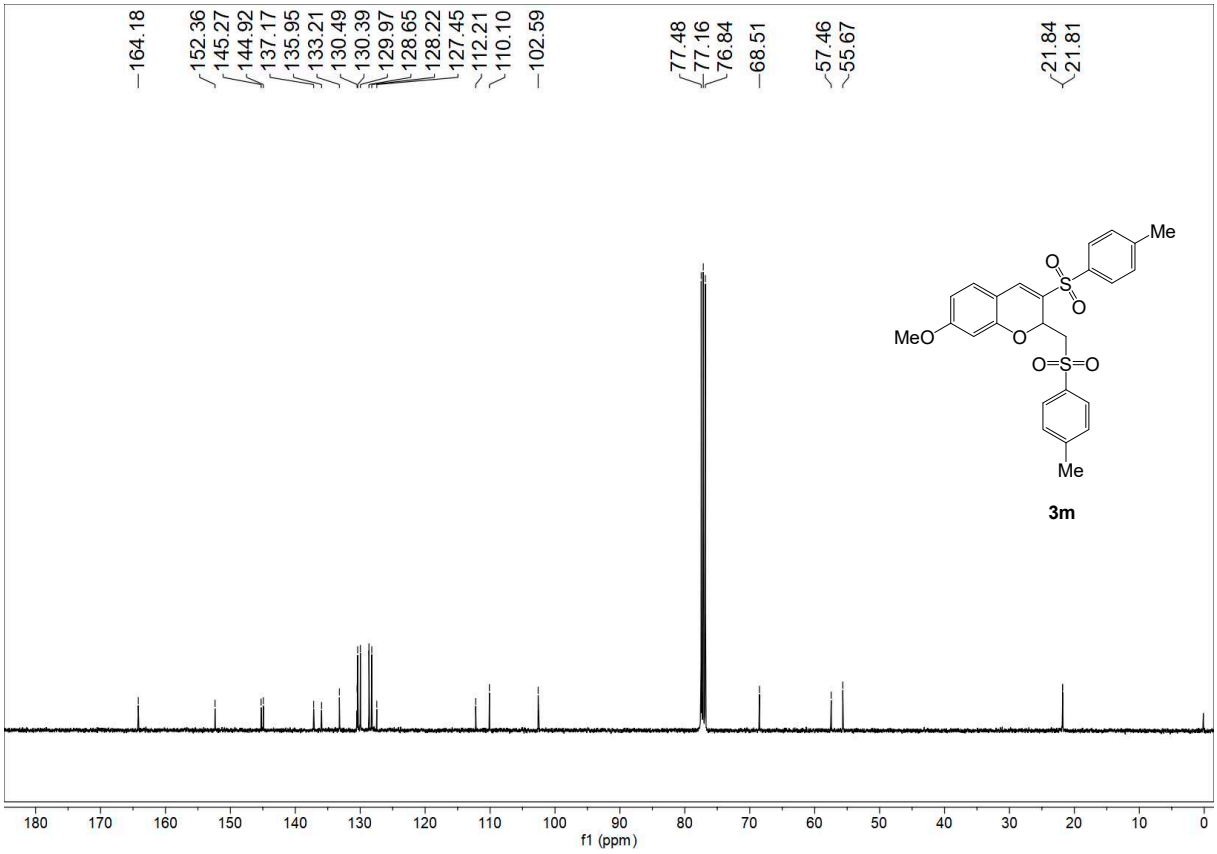
^{1}H NMR spectrum of **3l**



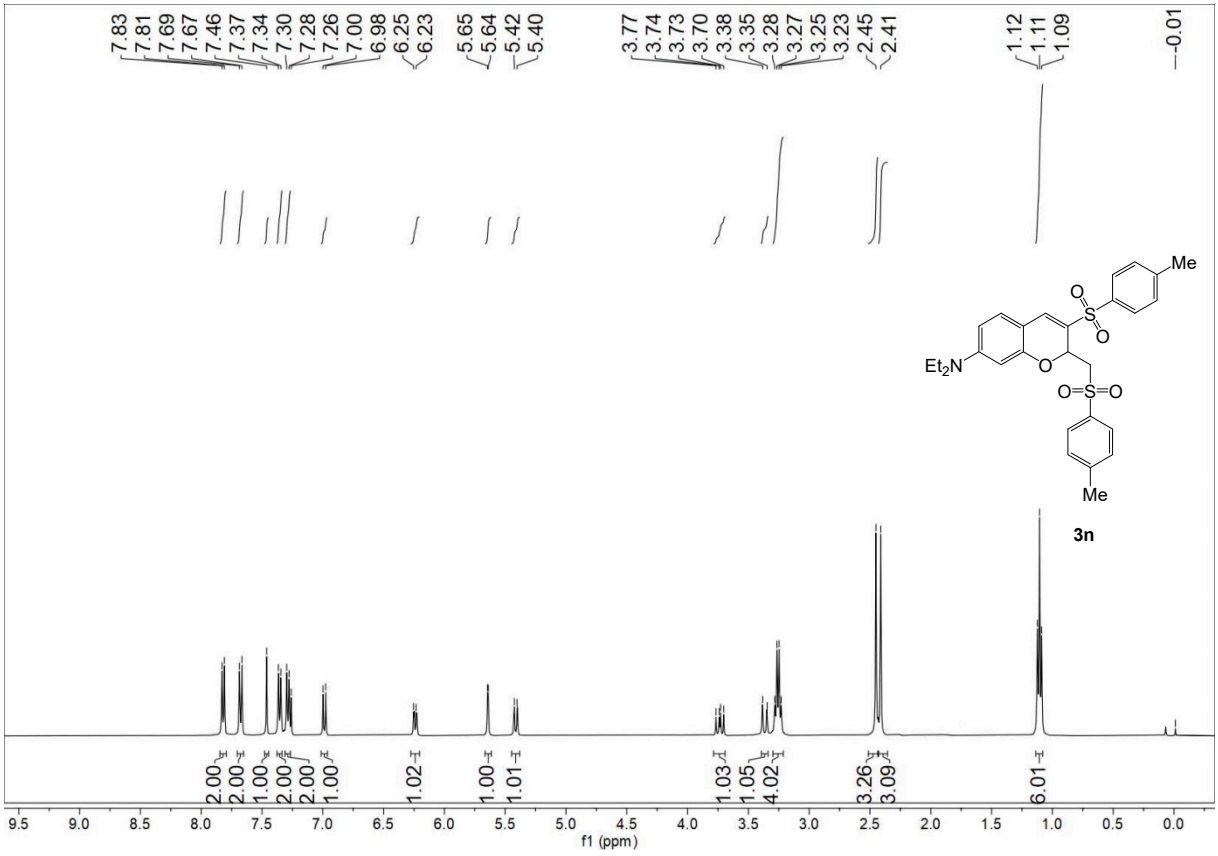
^{13}C NMR spectrum of **3l**



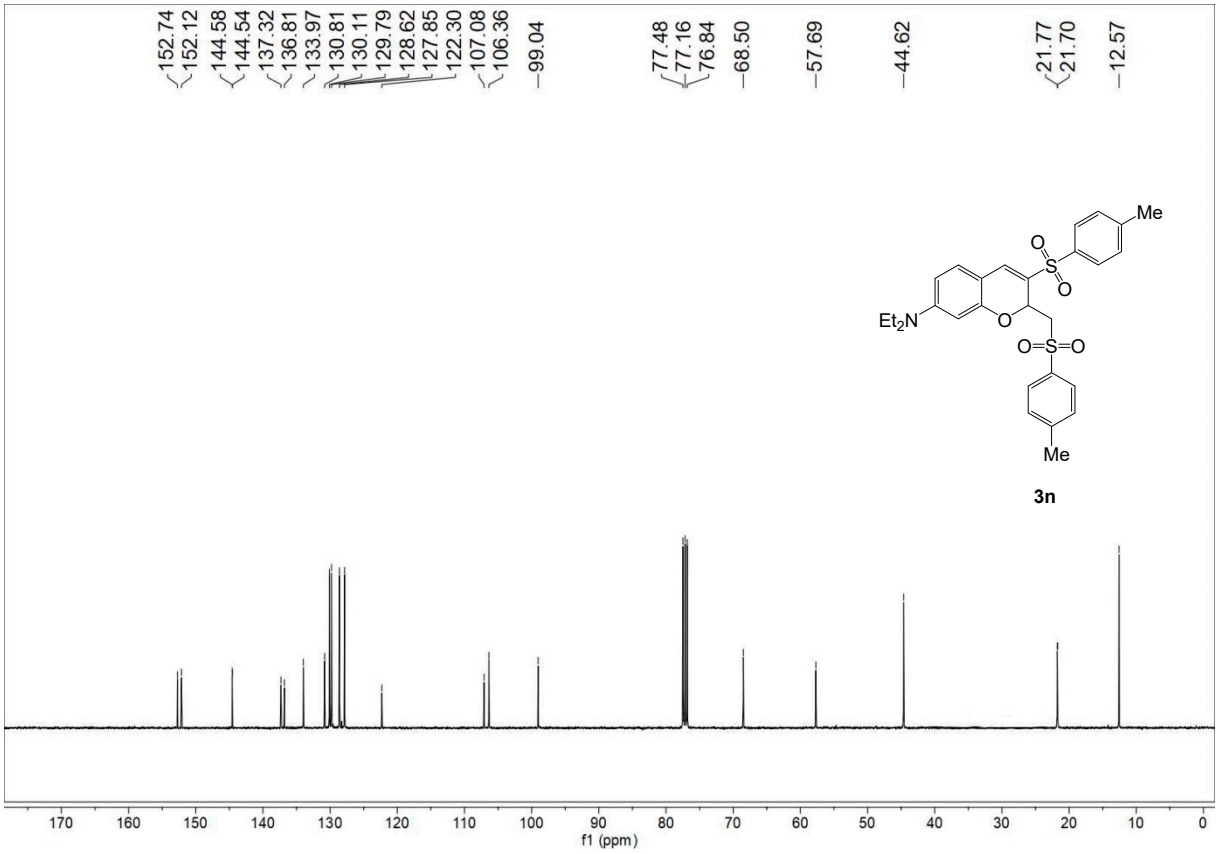
^{1}H NMR spectrum of **3m**



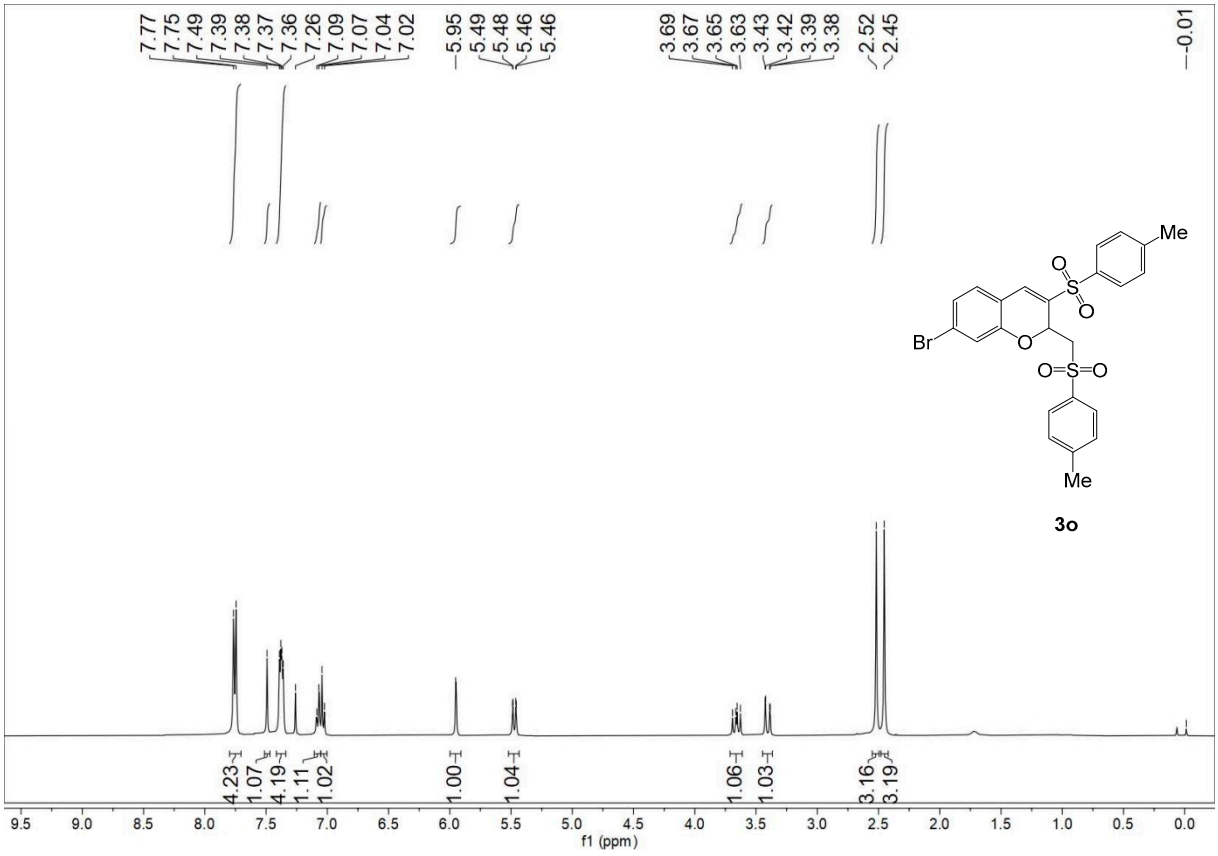
^{13}C NMR spectrum of **3m**



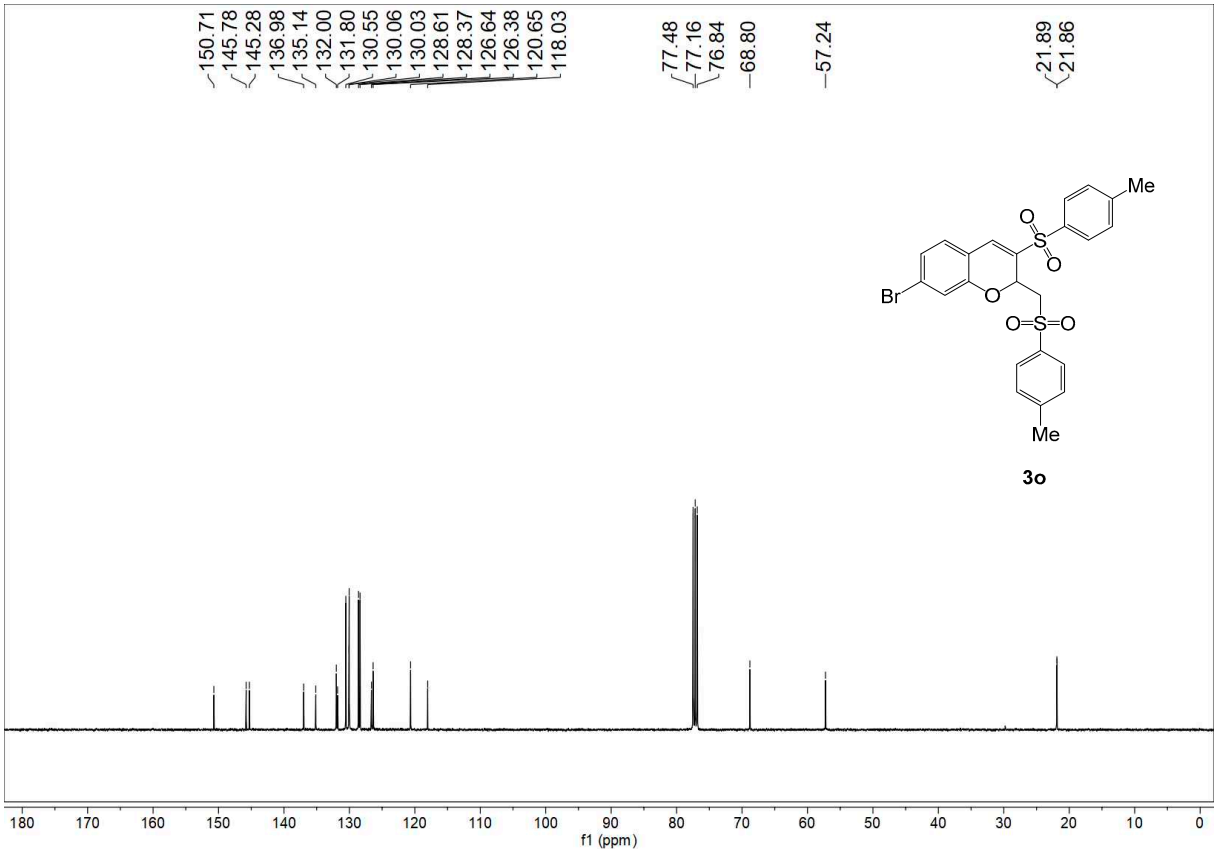
^{1}H NMR spectrum of **3n**



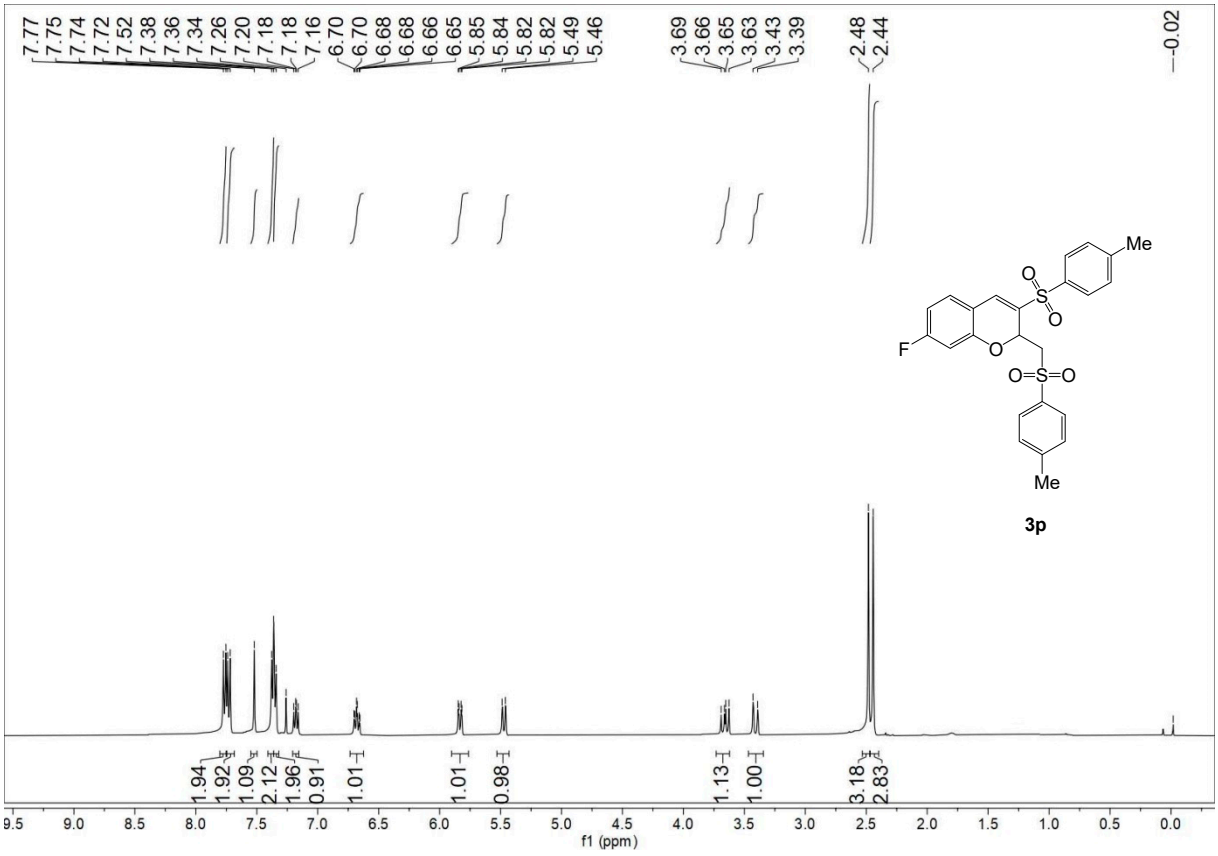
^{13}C NMR spectrum of **3n**



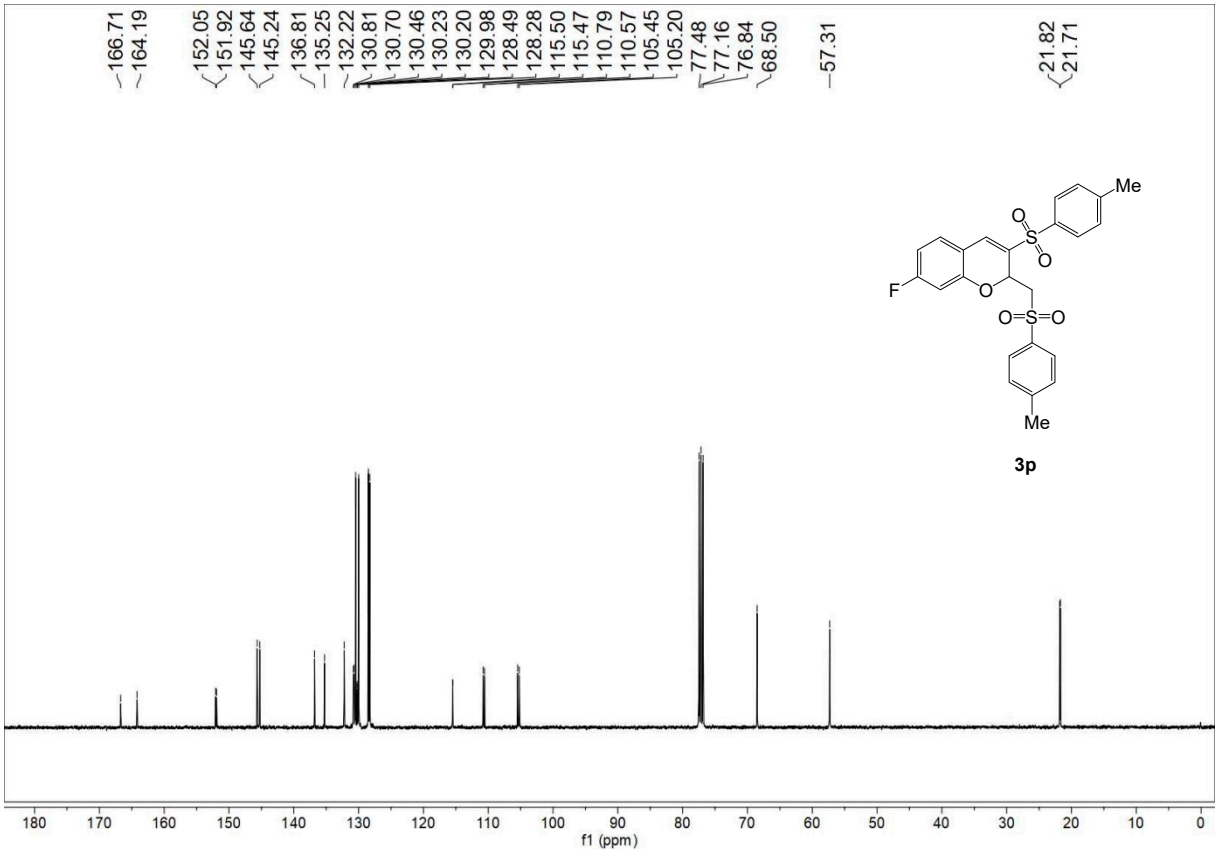
^{1}H NMR spectrum of **3o**



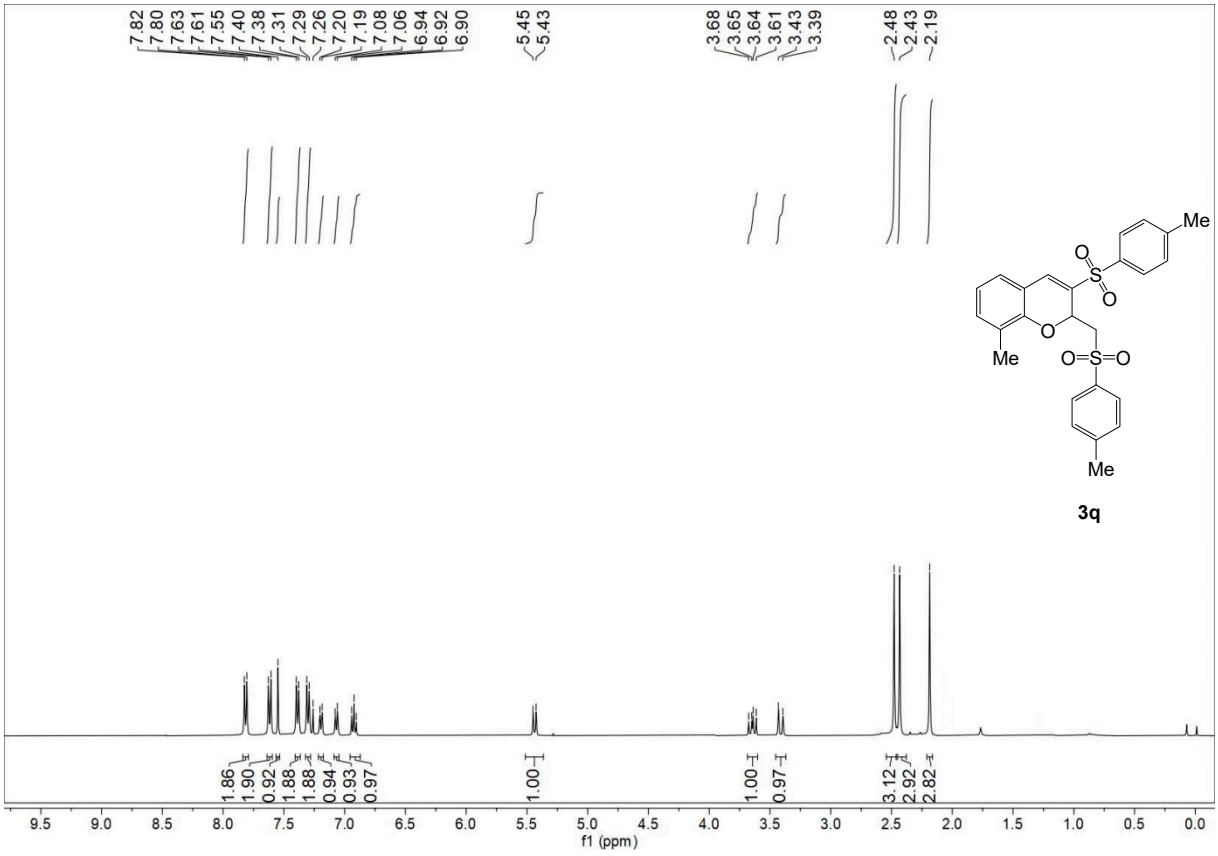
^{13}C NMR spectrum of **3o**



^{1}H NMR spectrum of **3p**

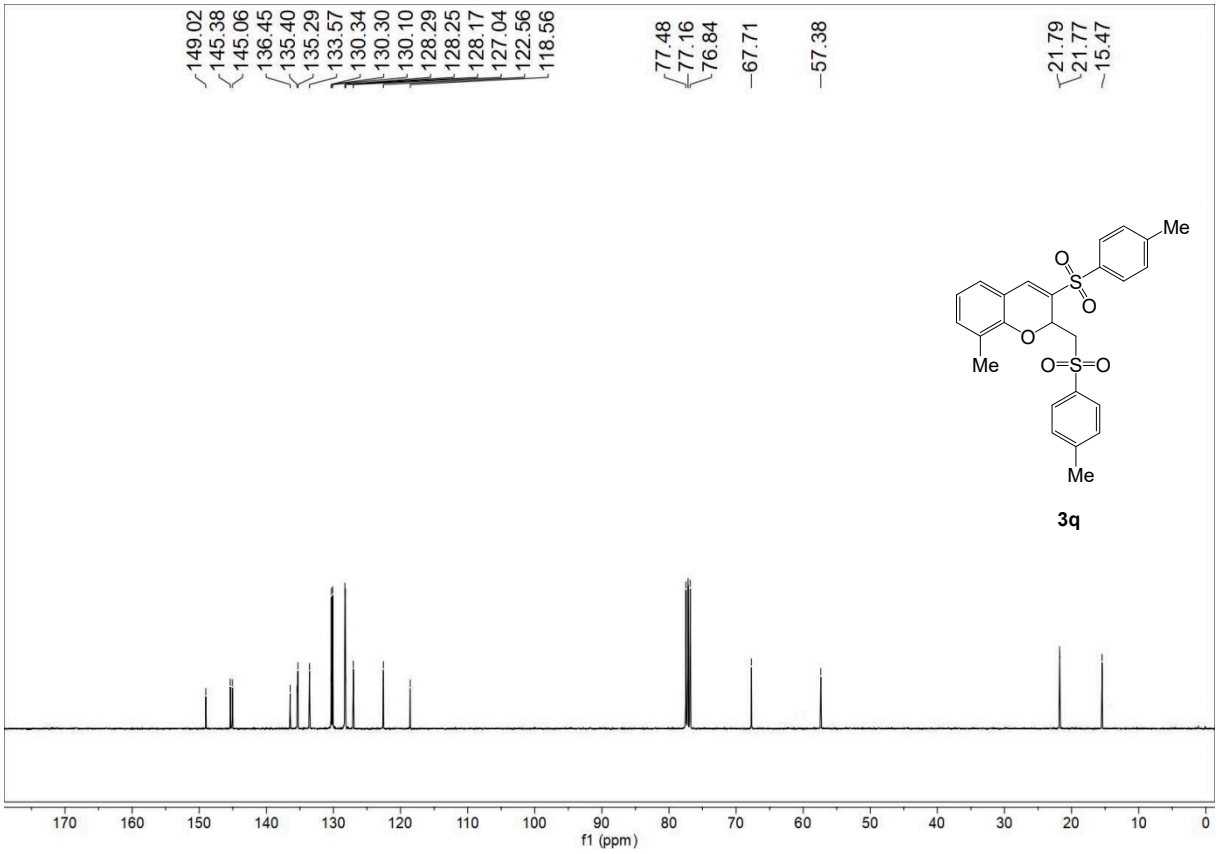


^{13}C NMR spectrum of **3p**



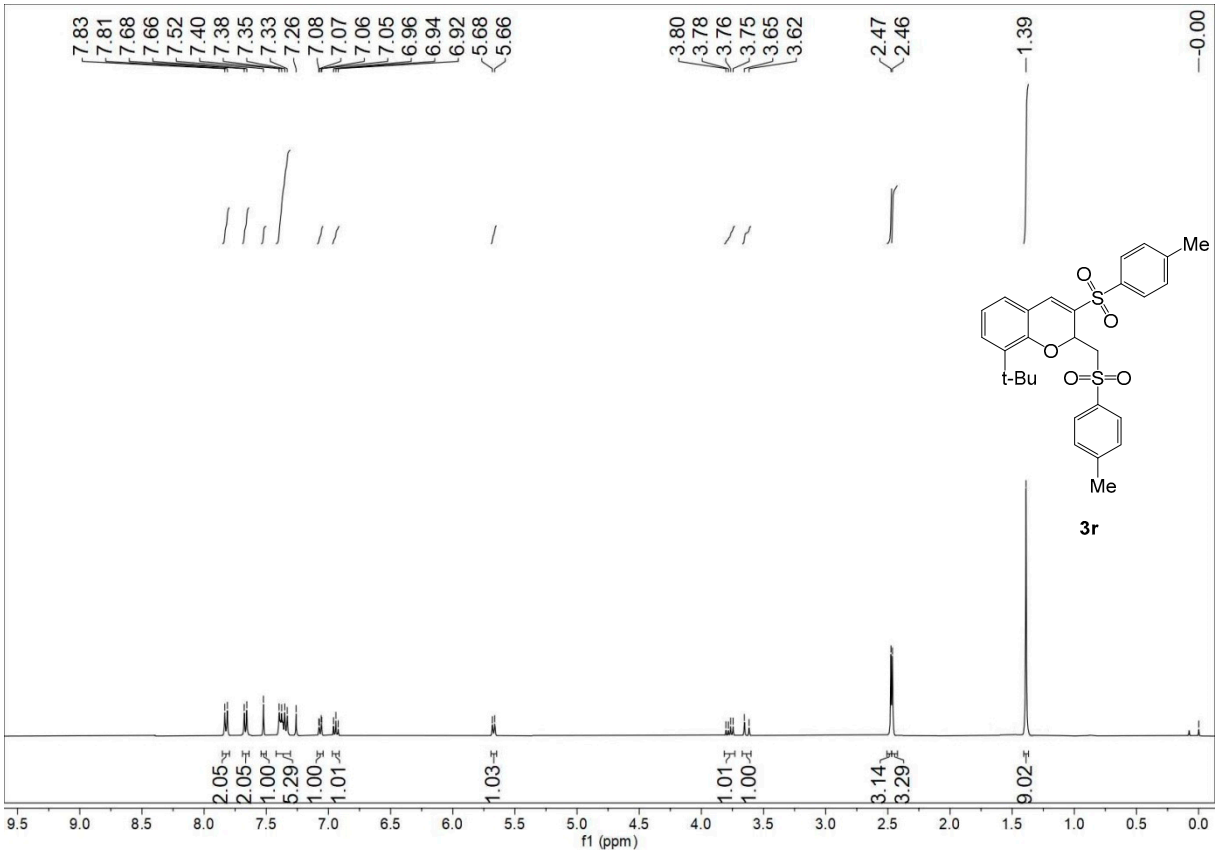
3q

^{1}H NMR spectrum of **3q**

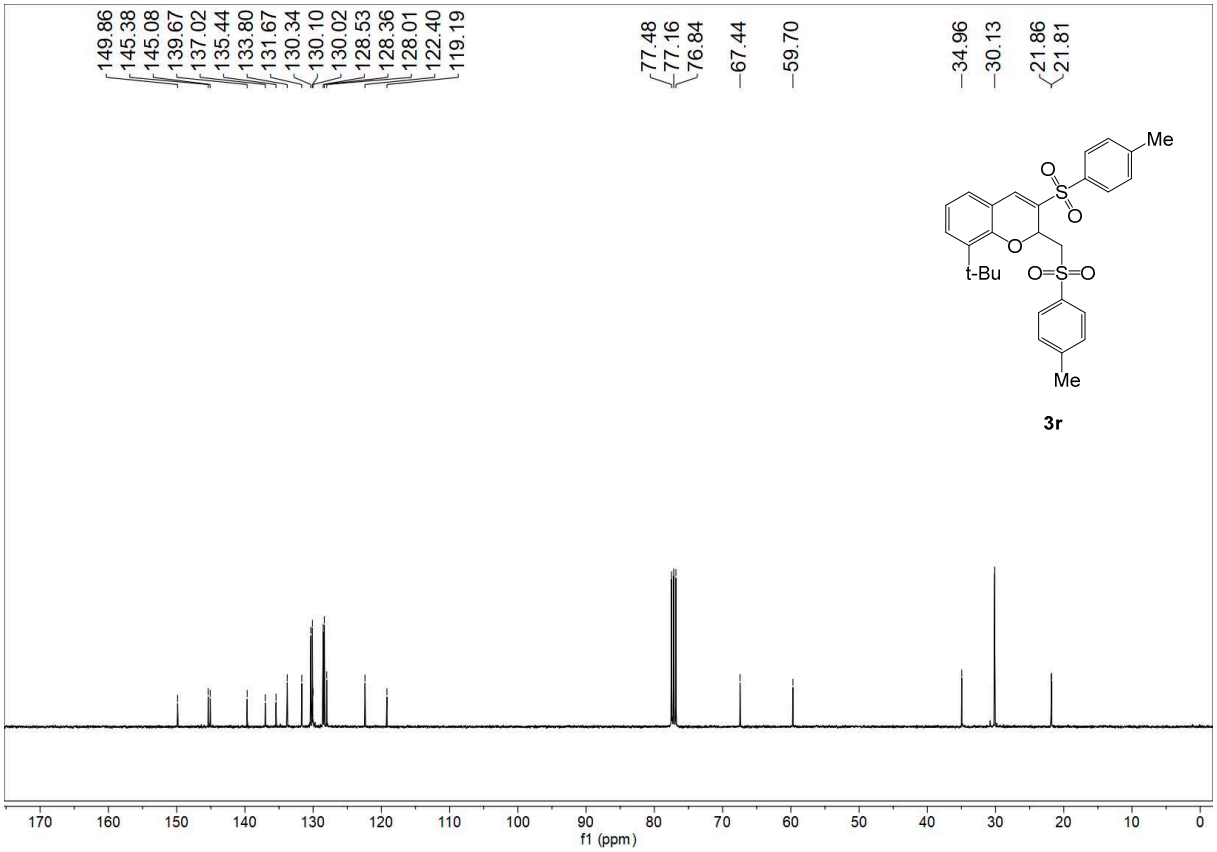


3q

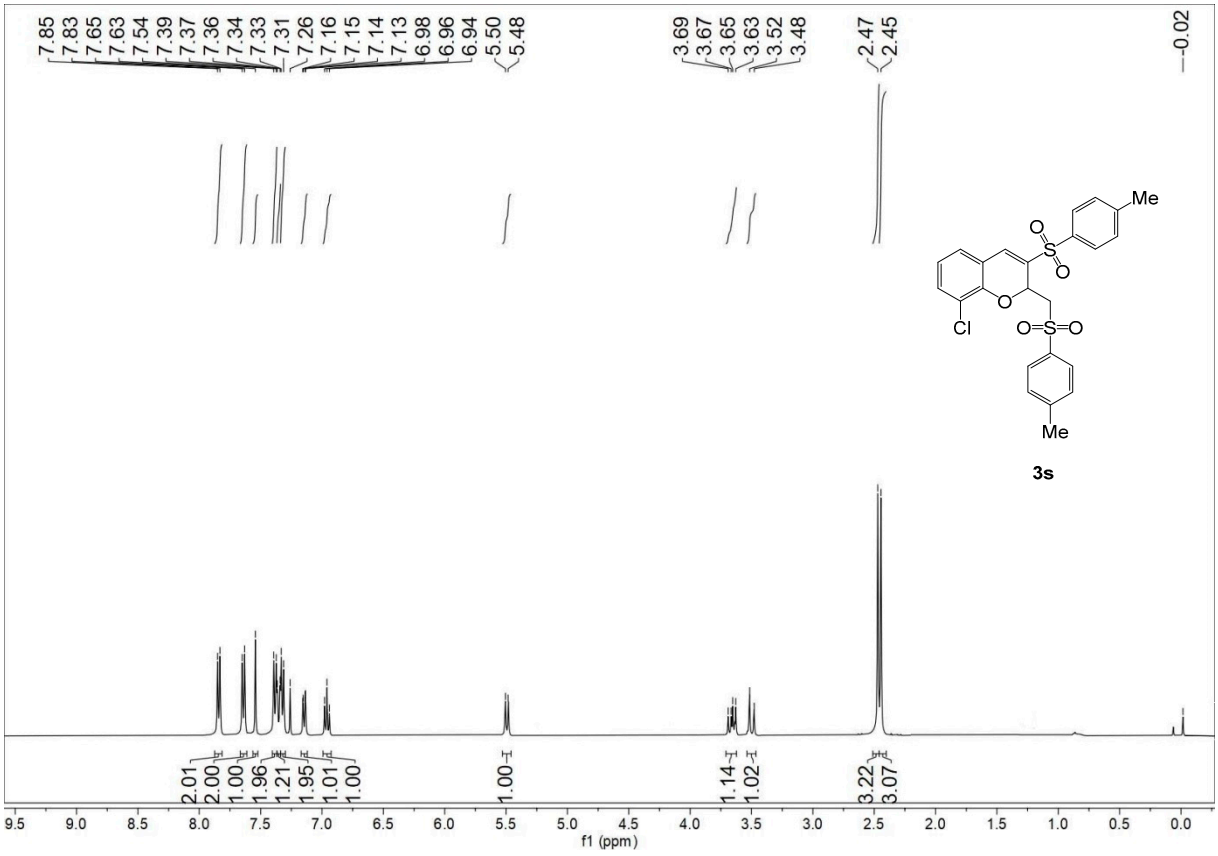
^{13}C NMR spectrum of **3q**



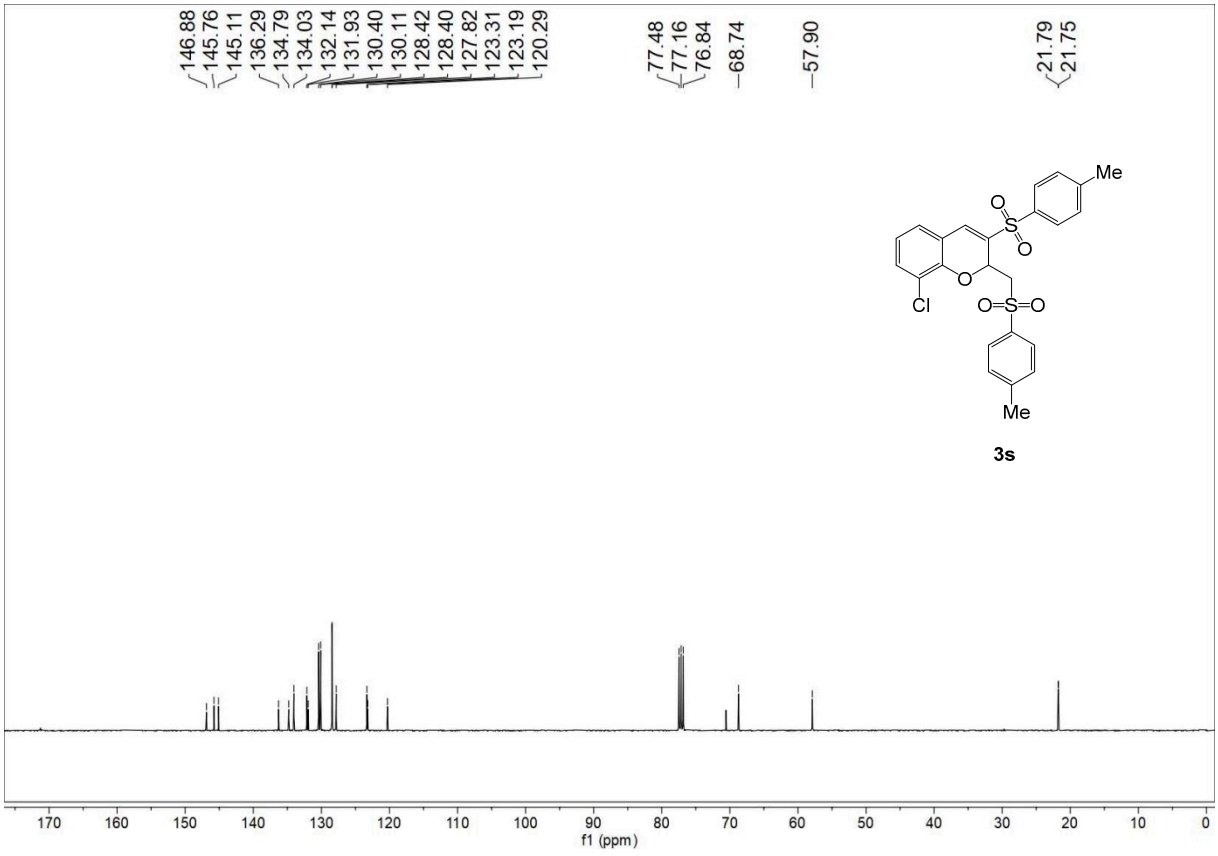
^{1}H NMR spectrum of **3r**



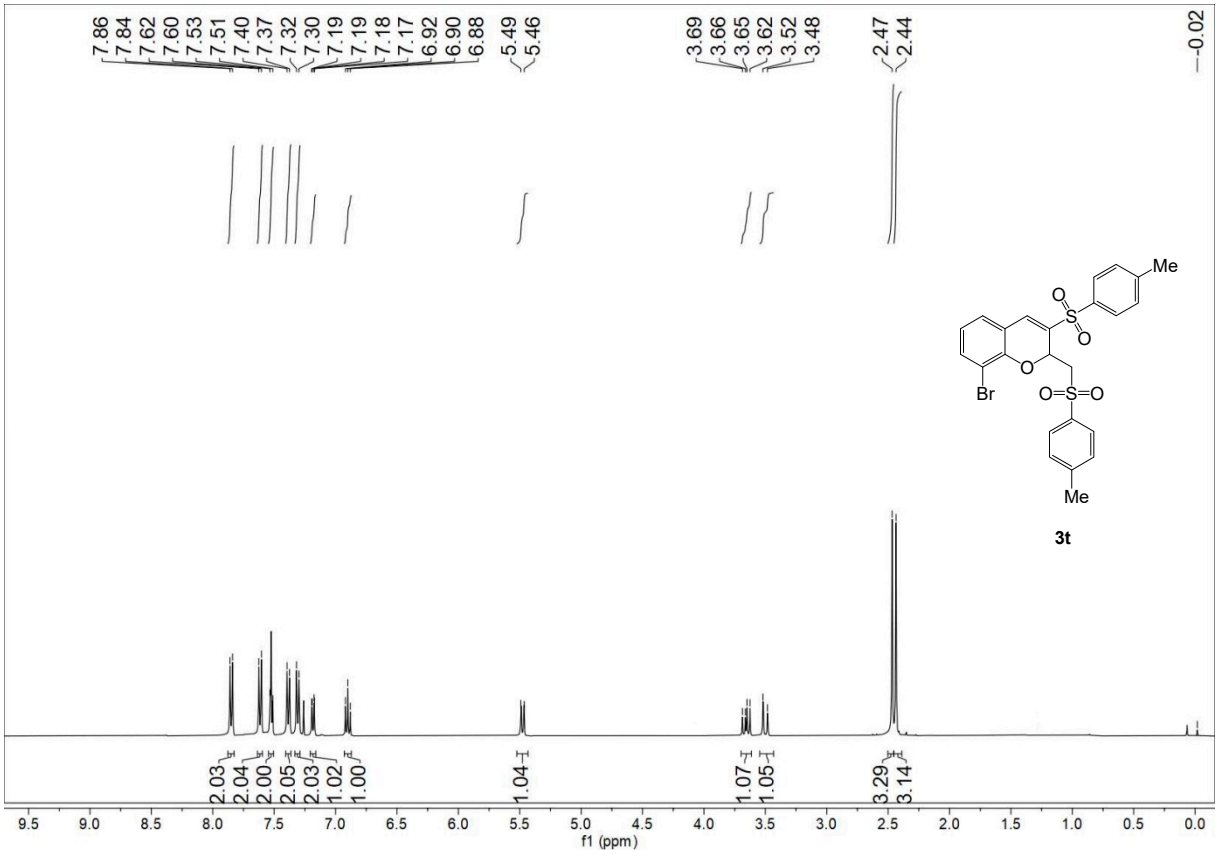
^{13}C NMR spectrum of **3r**



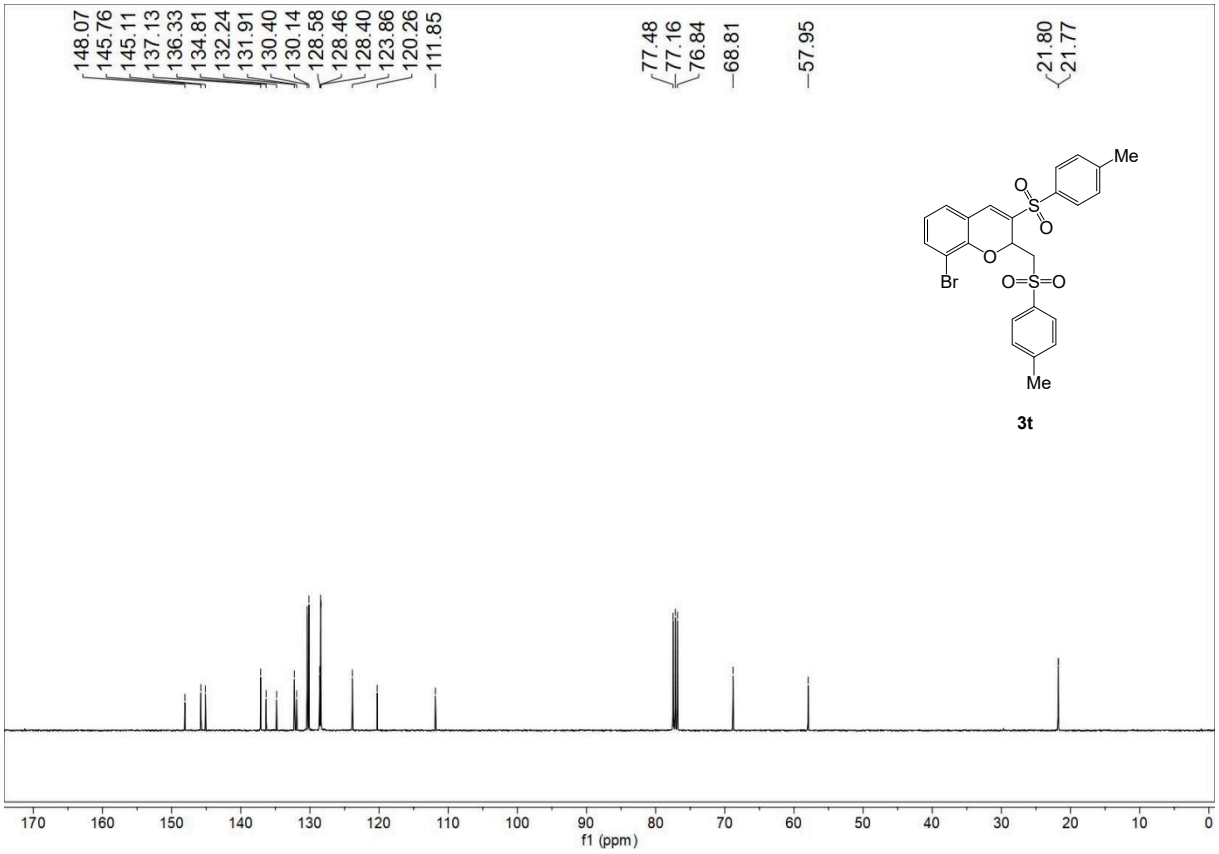
^{1}H NMR spectrum of **3s**



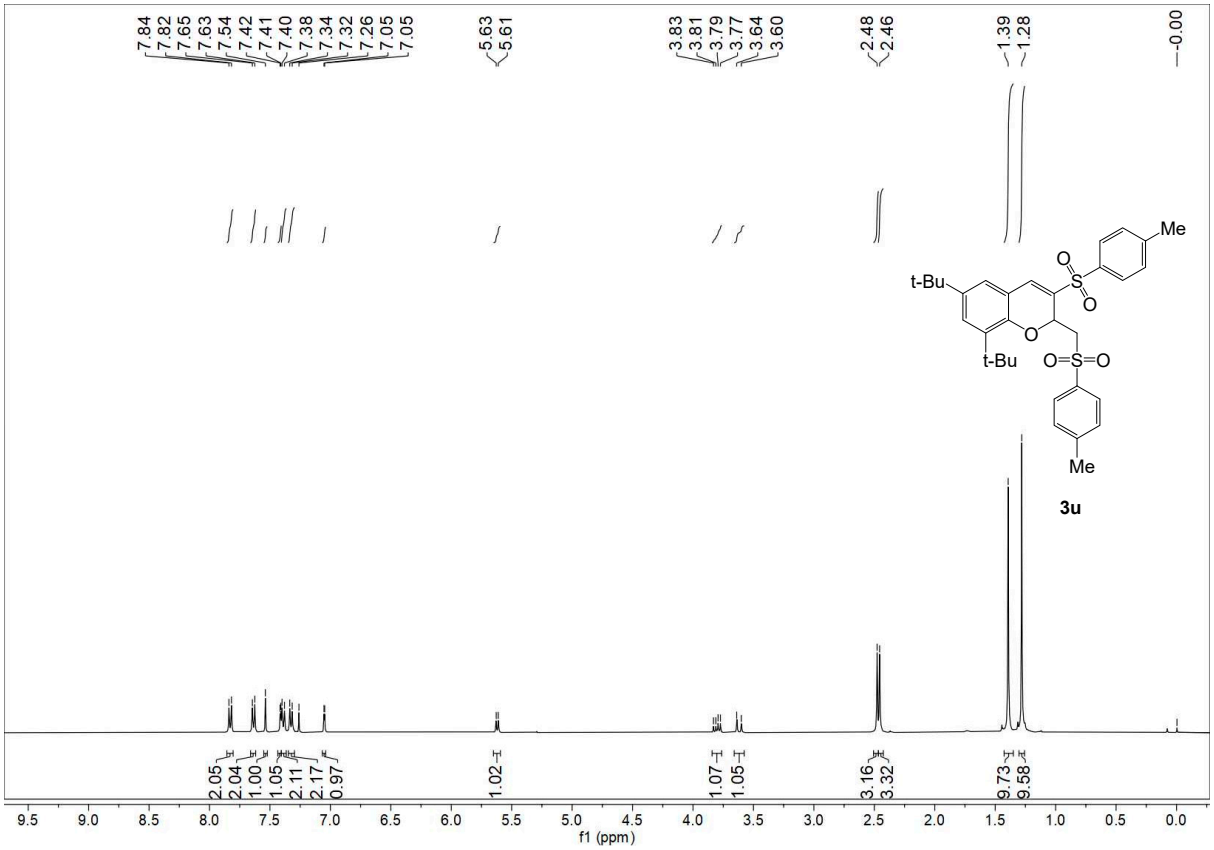
^{13}C NMR spectrum of **3s**



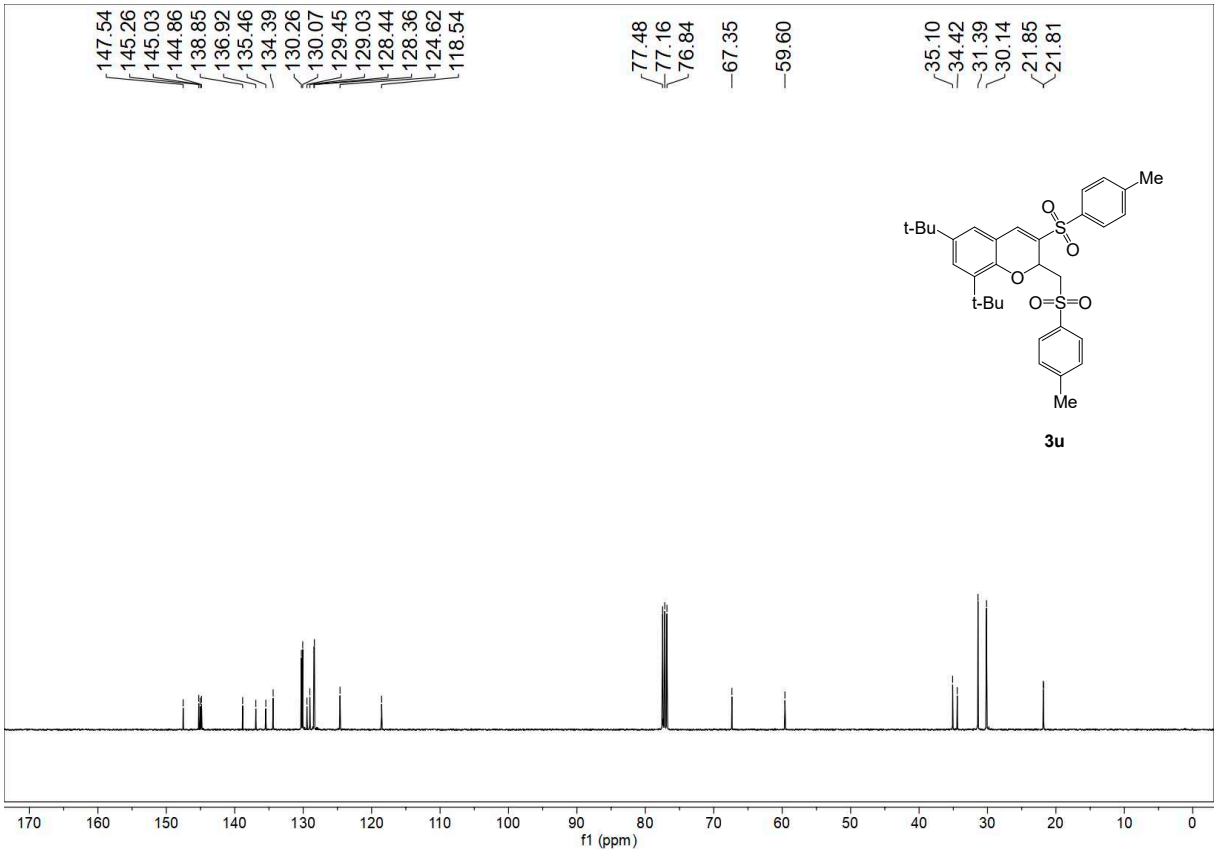
^{1}H NMR spectrum of **3t**



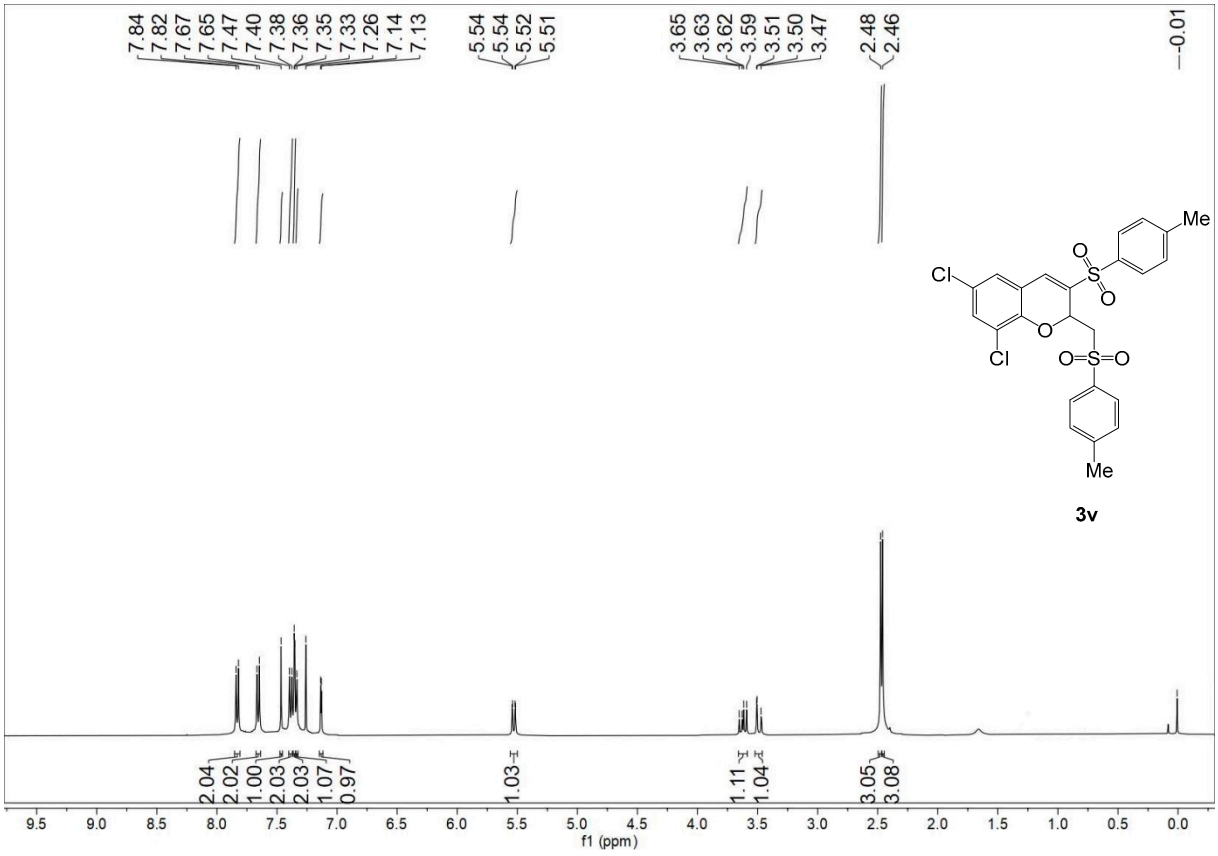
^{13}C NMR spectrum of **3t**



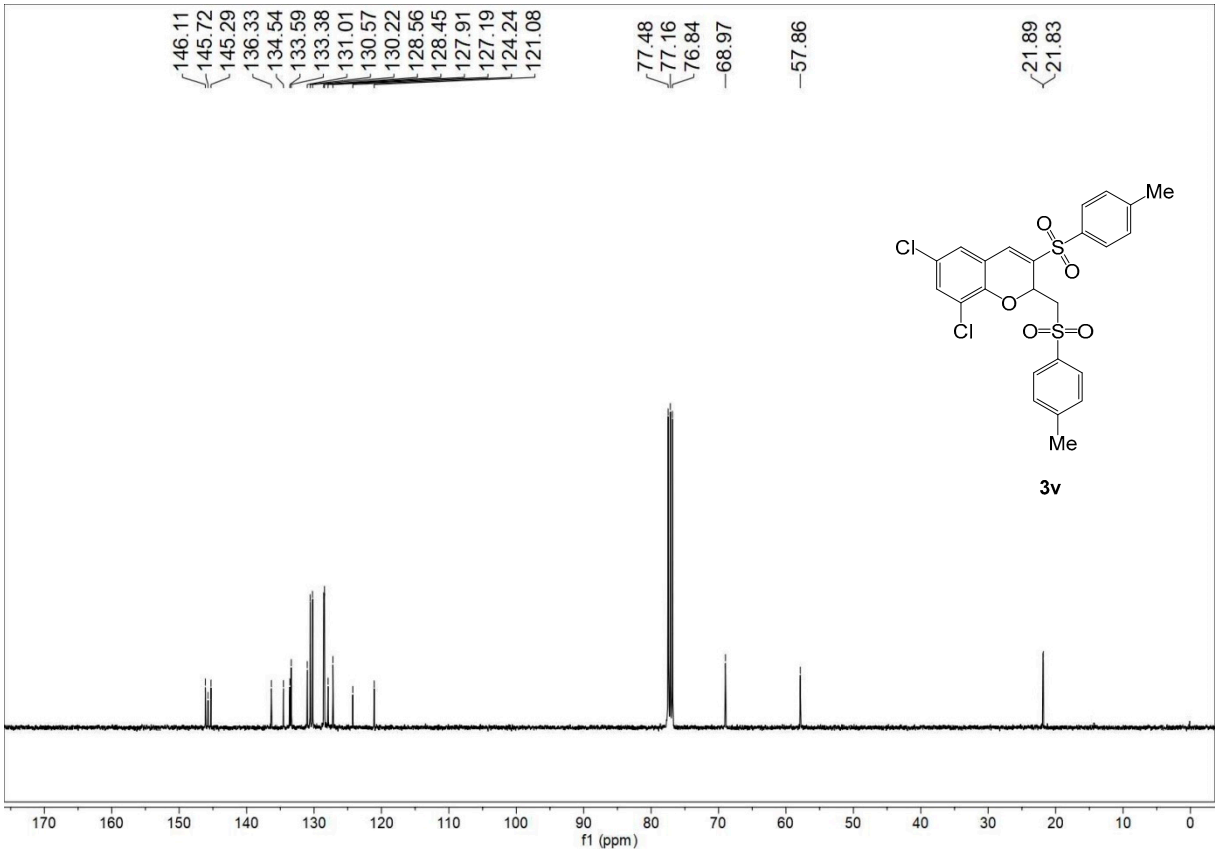
^{1}H NMR spectrum of **3u**



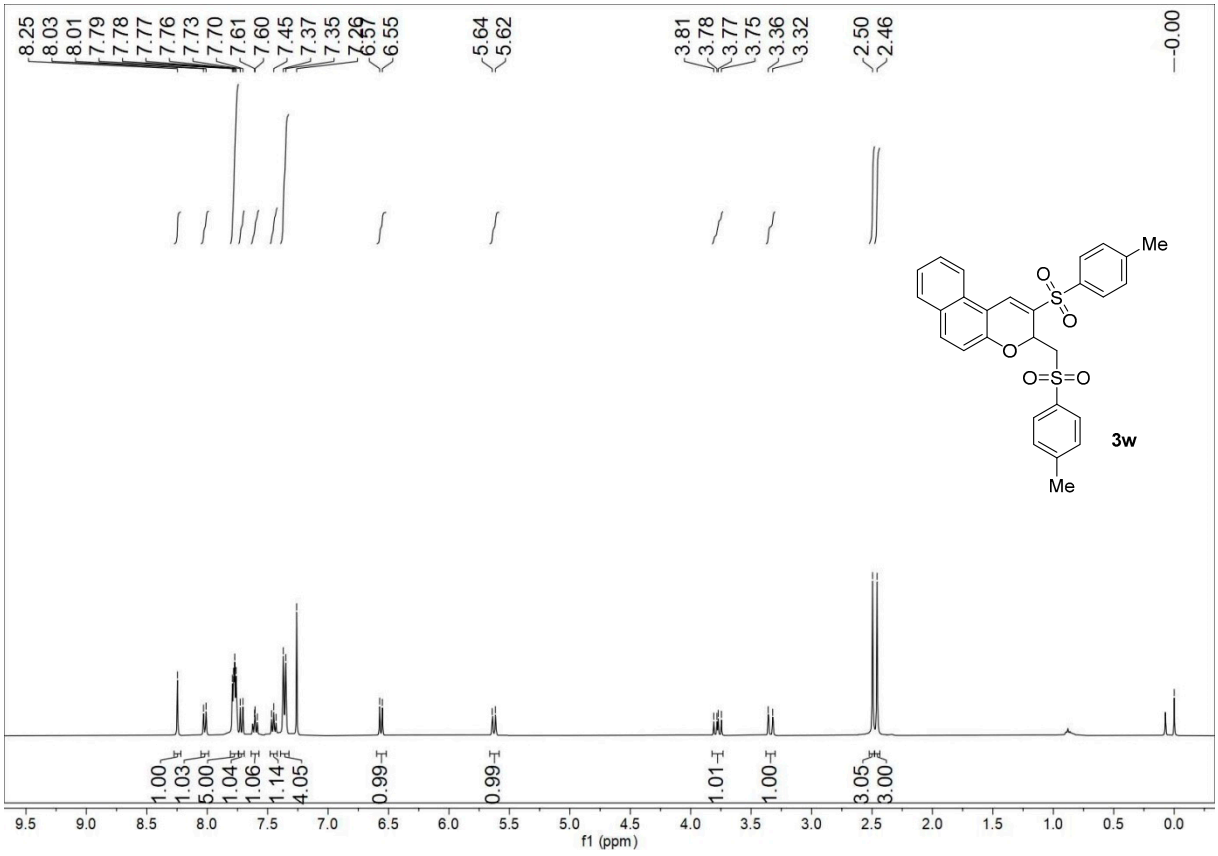
^{13}C NMR spectrum of **3u**



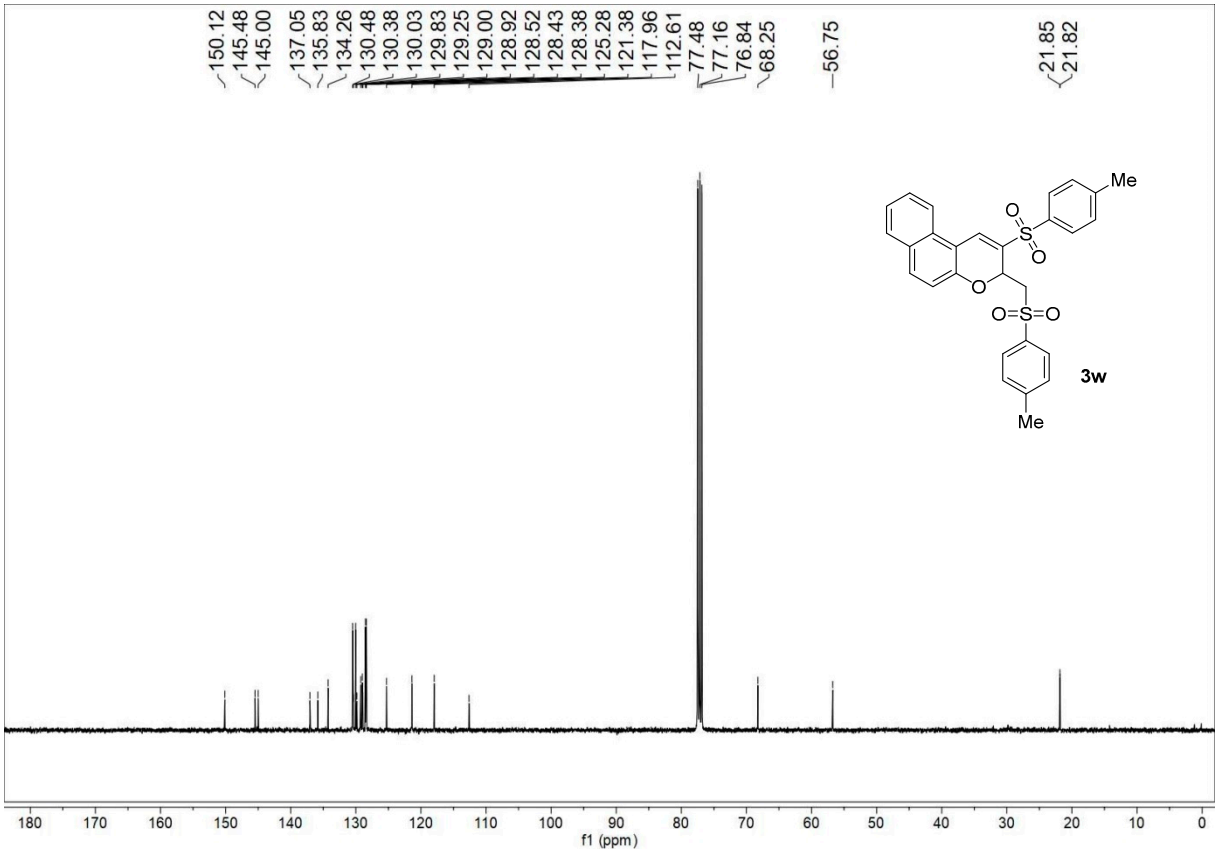
^{1}H NMR spectrum of **3v**



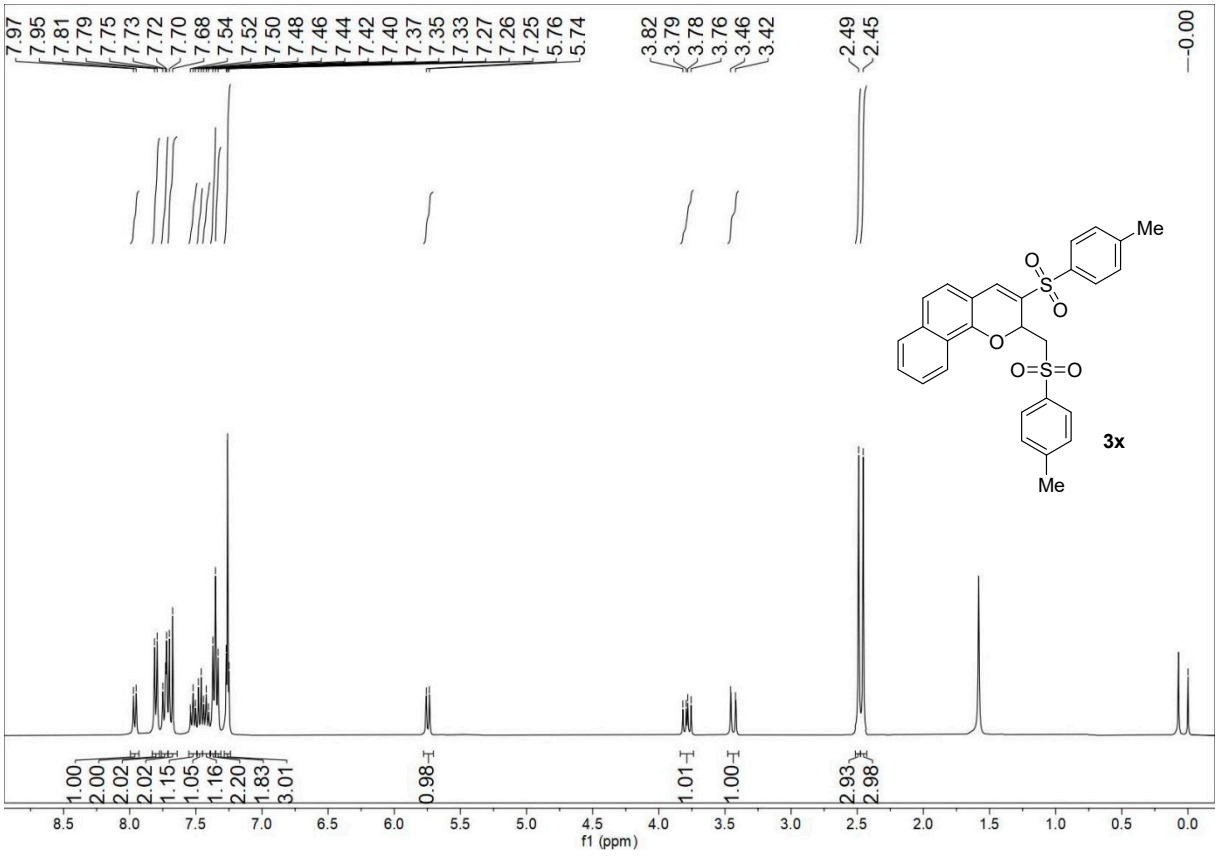
^{13}C NMR spectrum of **3v**



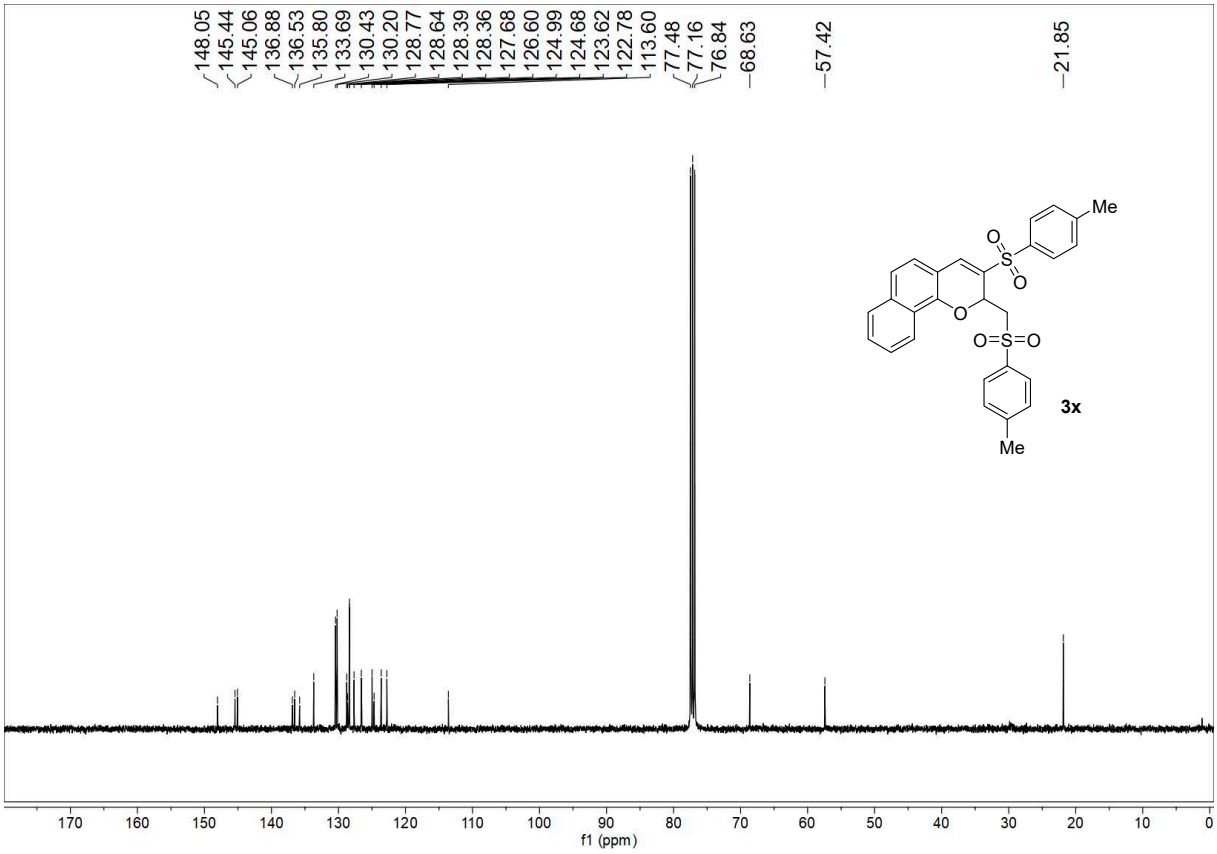
^{1}H NMR spectrum of **3w**



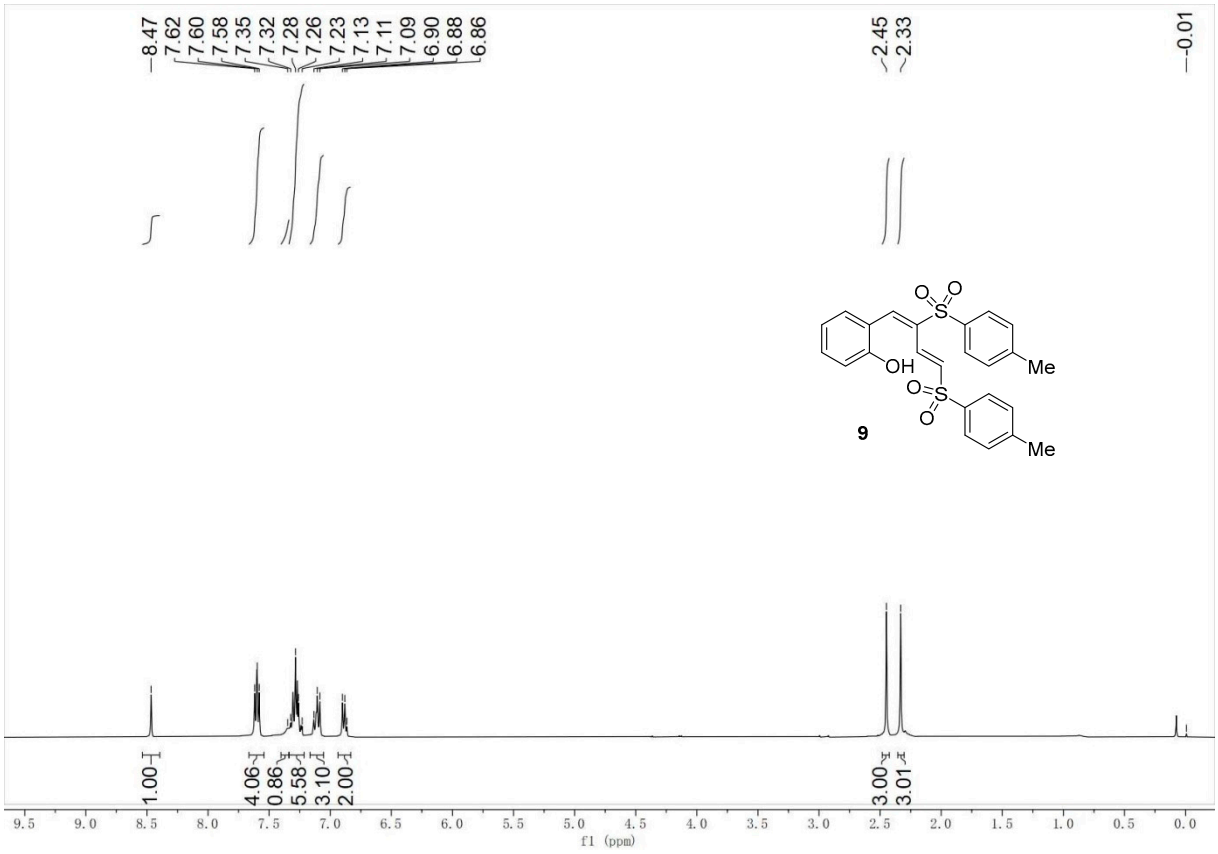
^{13}C NMR spectrum of **3w**



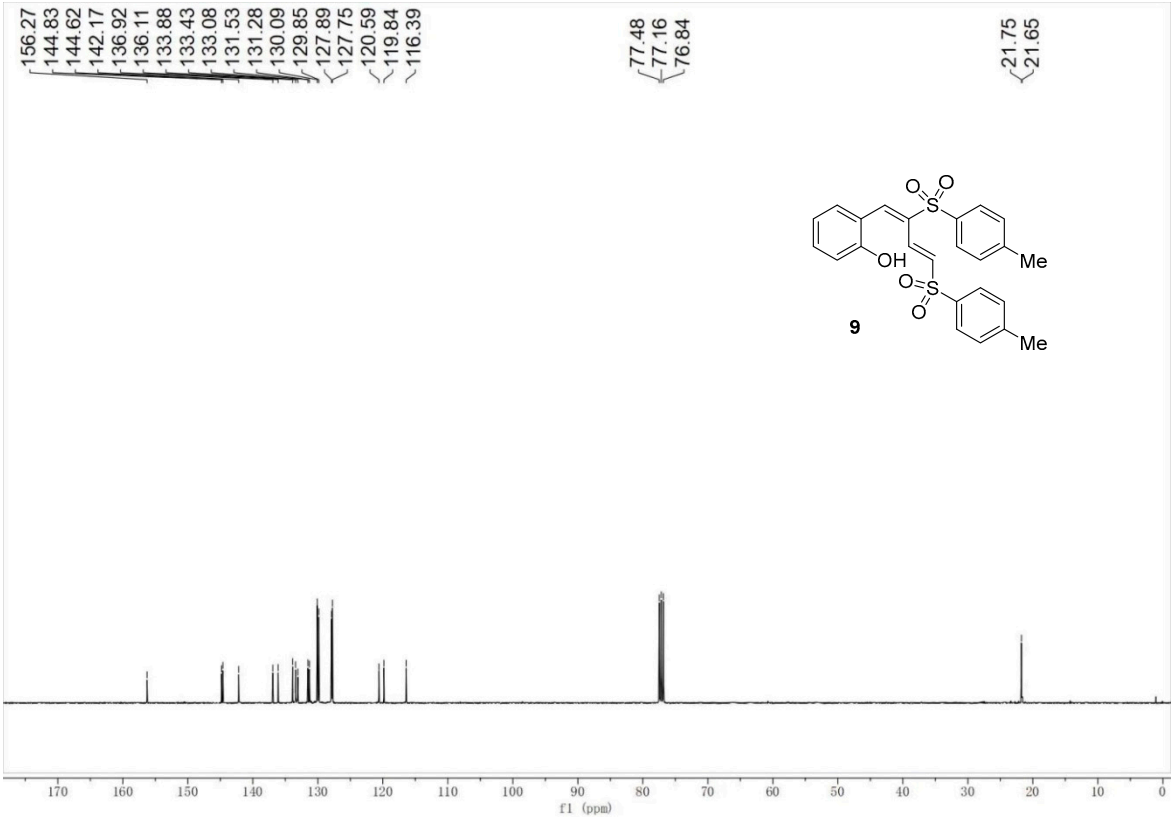
^{1}H NMR spectrum of **3x**



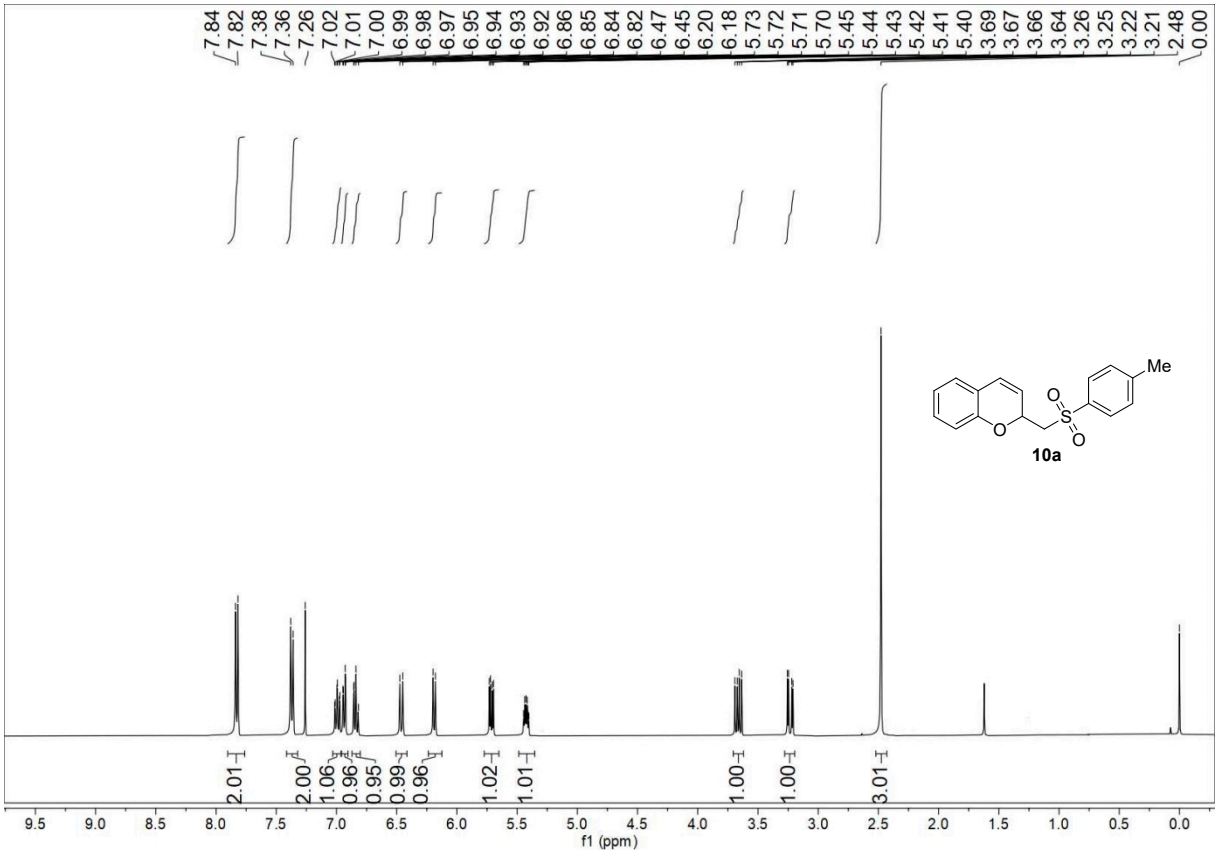
^{13}C NMR spectrum of **3x**



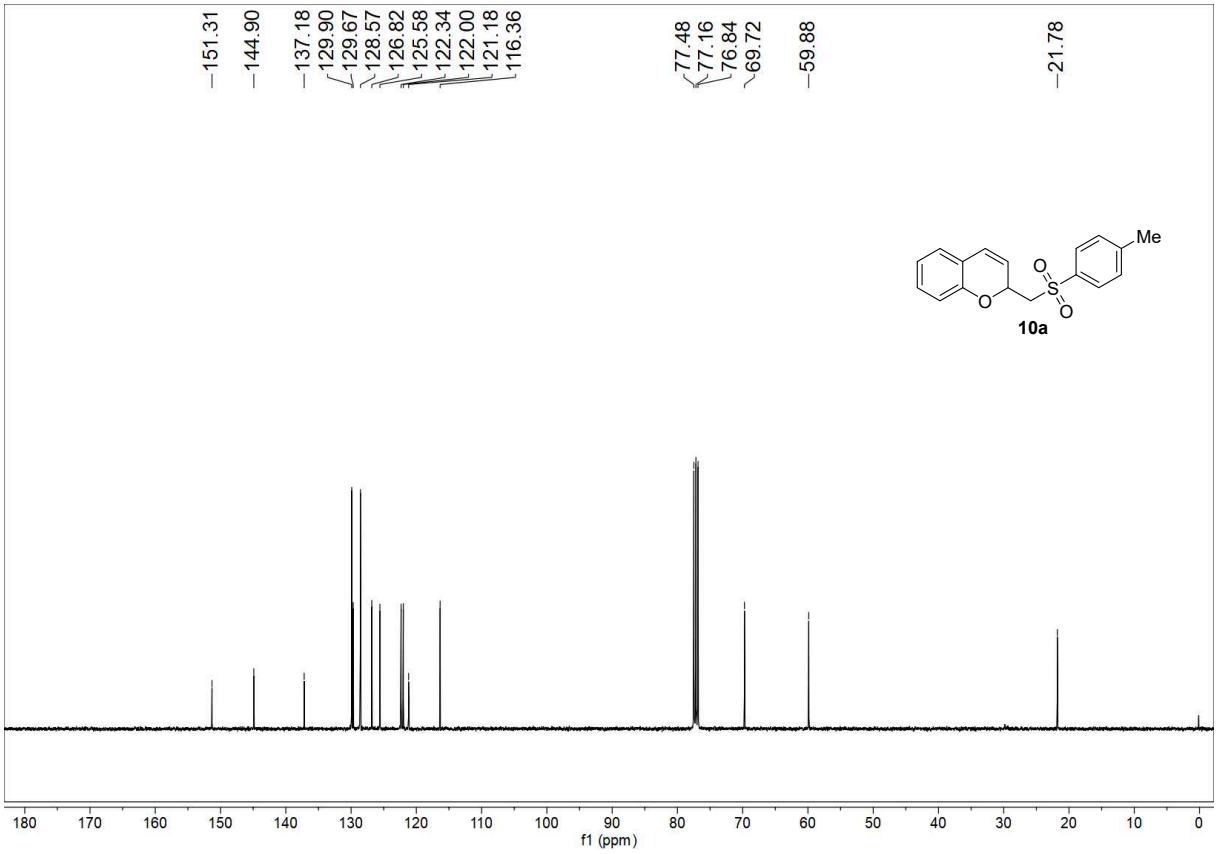
^{1}H NMR spectrum of compound **9**



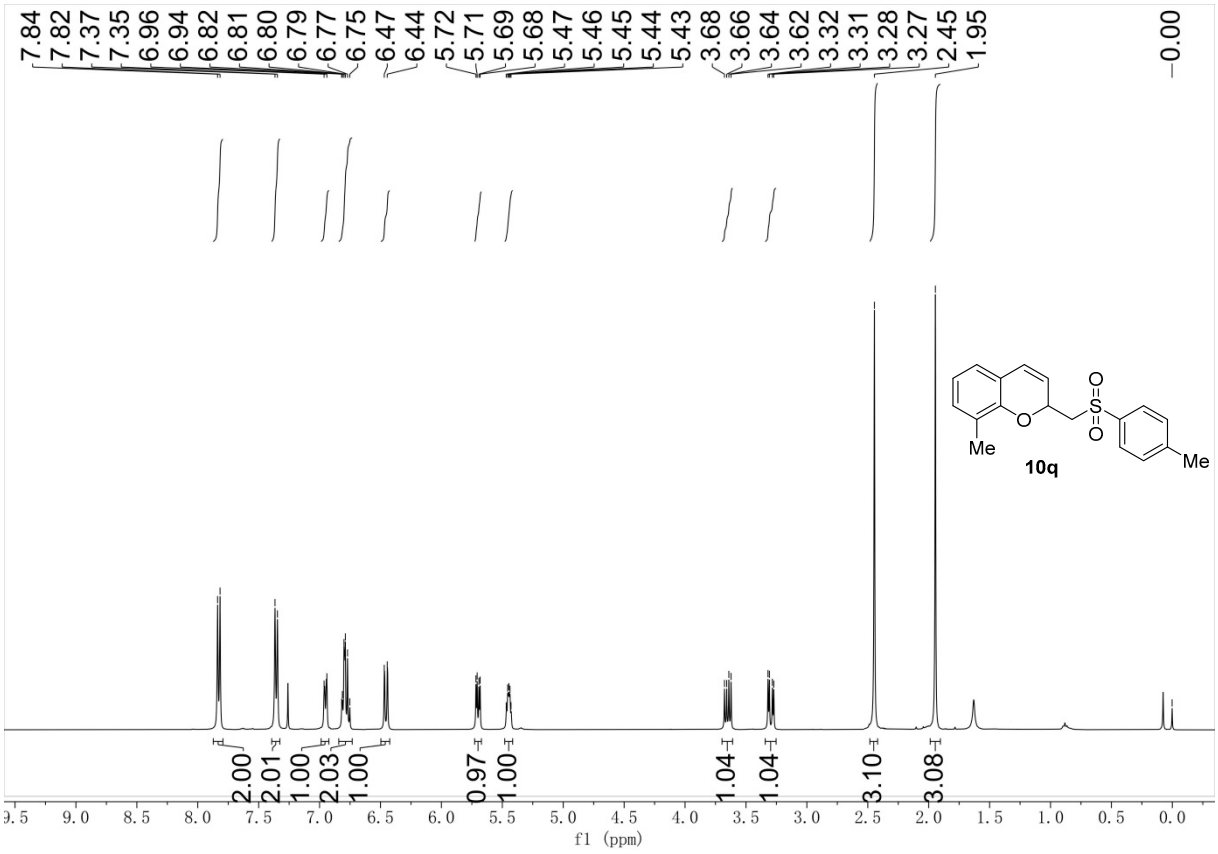
^{13}C NMR spectrum of compound **9**



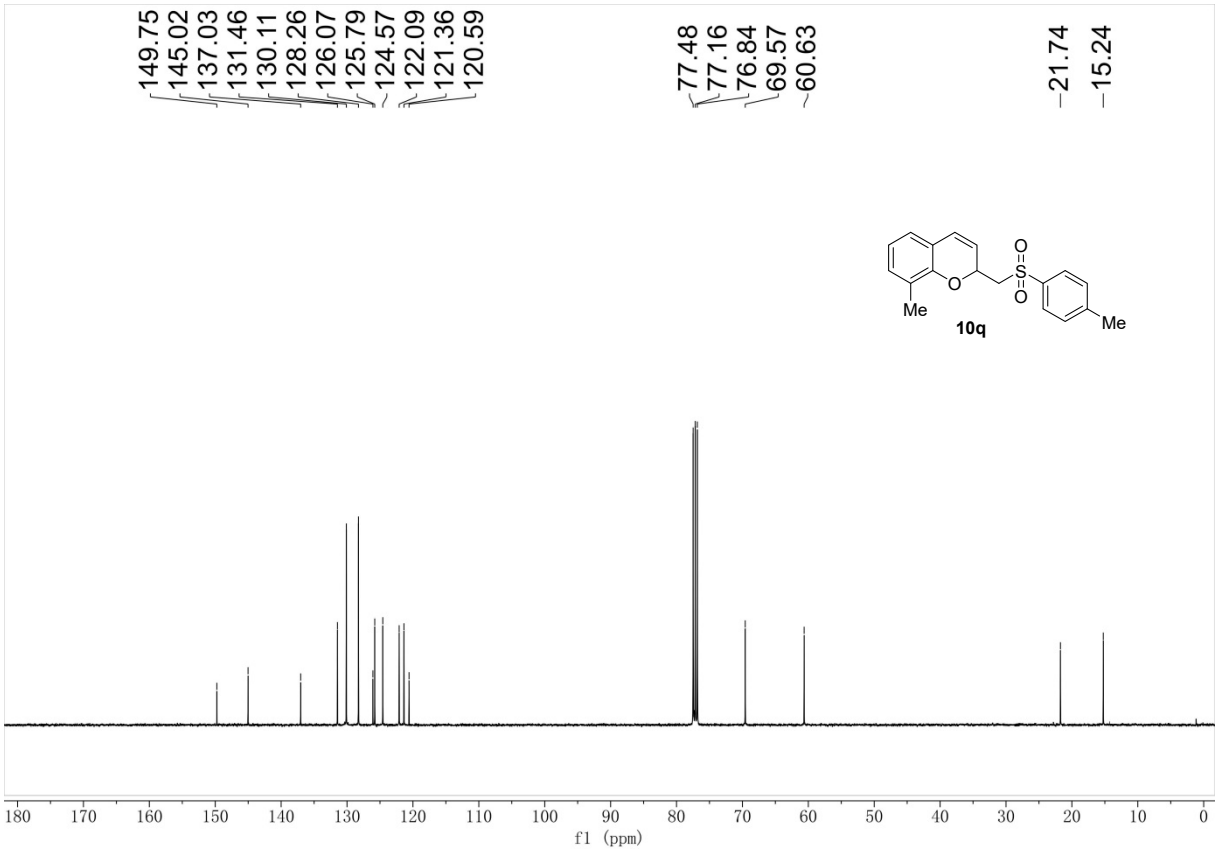
^{1}H NMR spectrum of **10a**



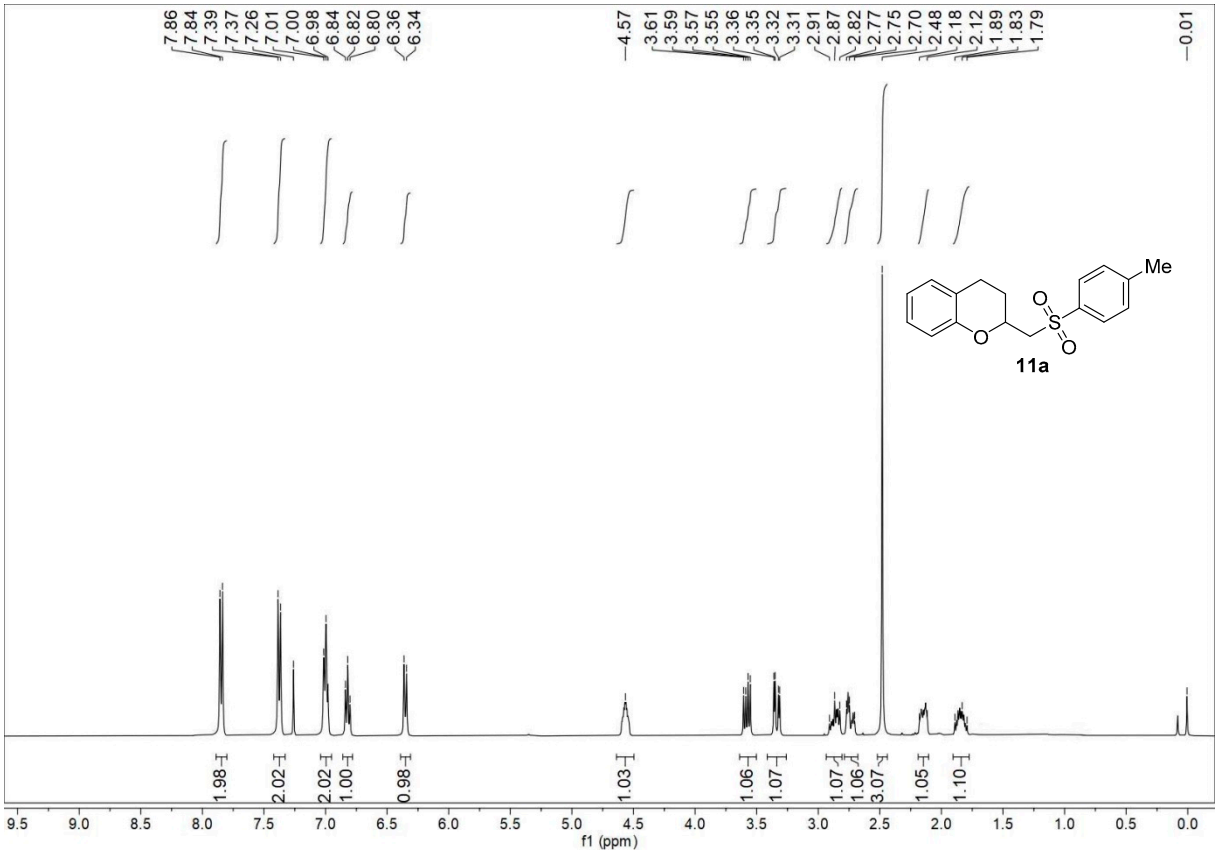
^{13}C NMR spectrum of **10a**



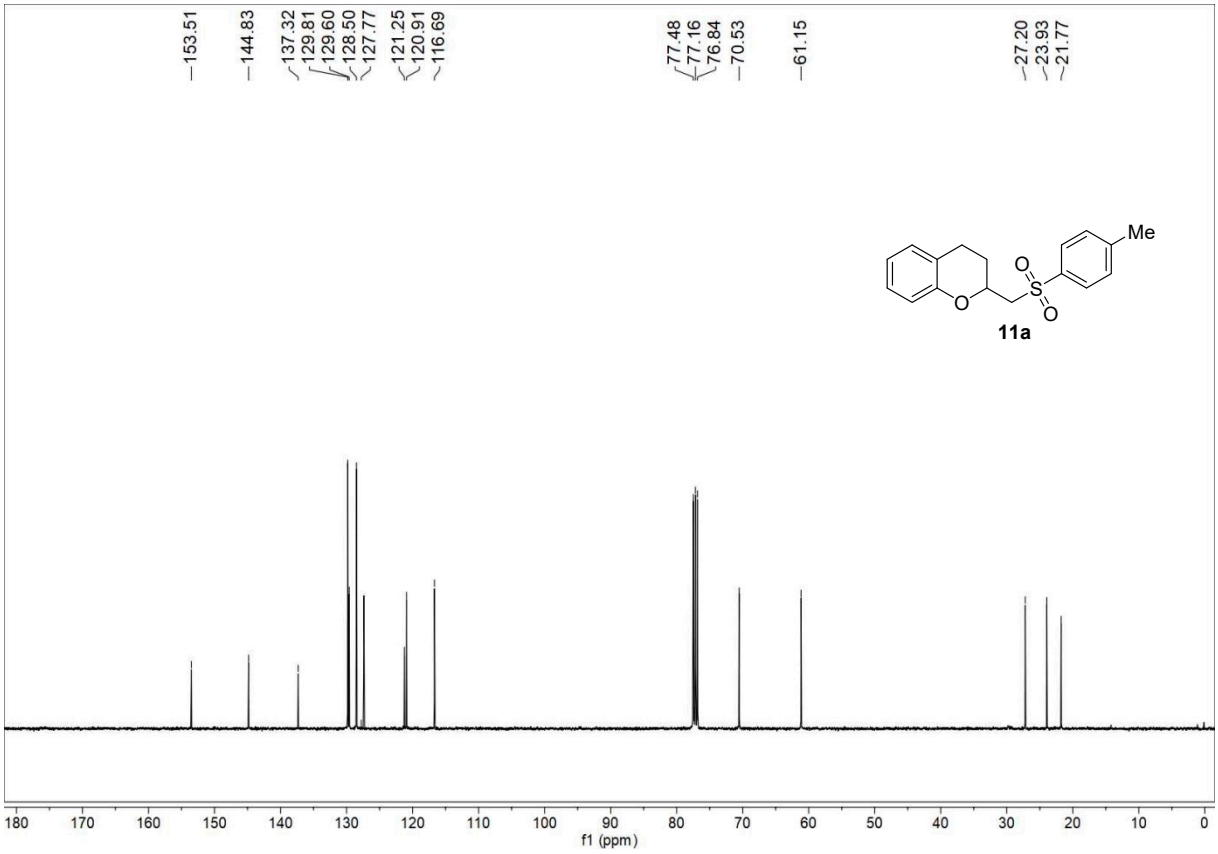
^{1}H NMR spectrum of **10q**



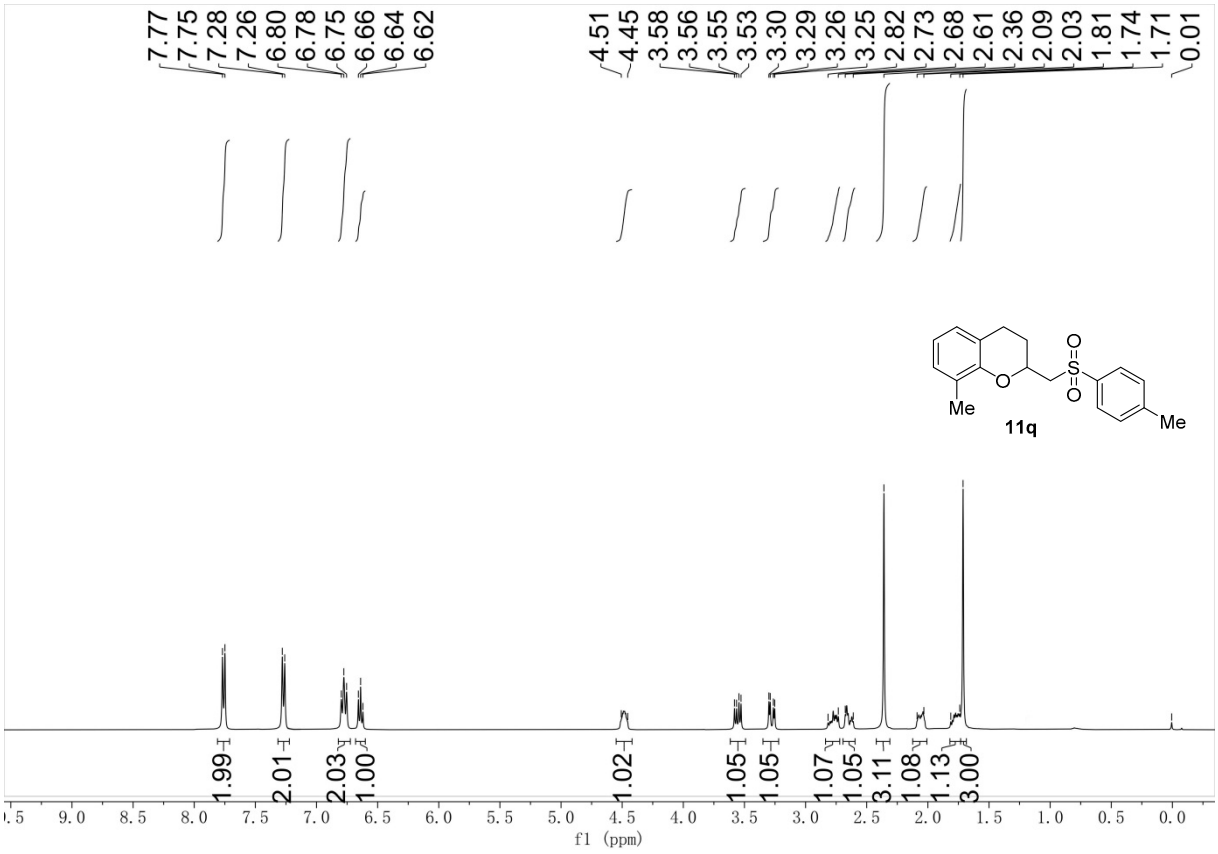
^{13}C NMR spectrum of **10q**



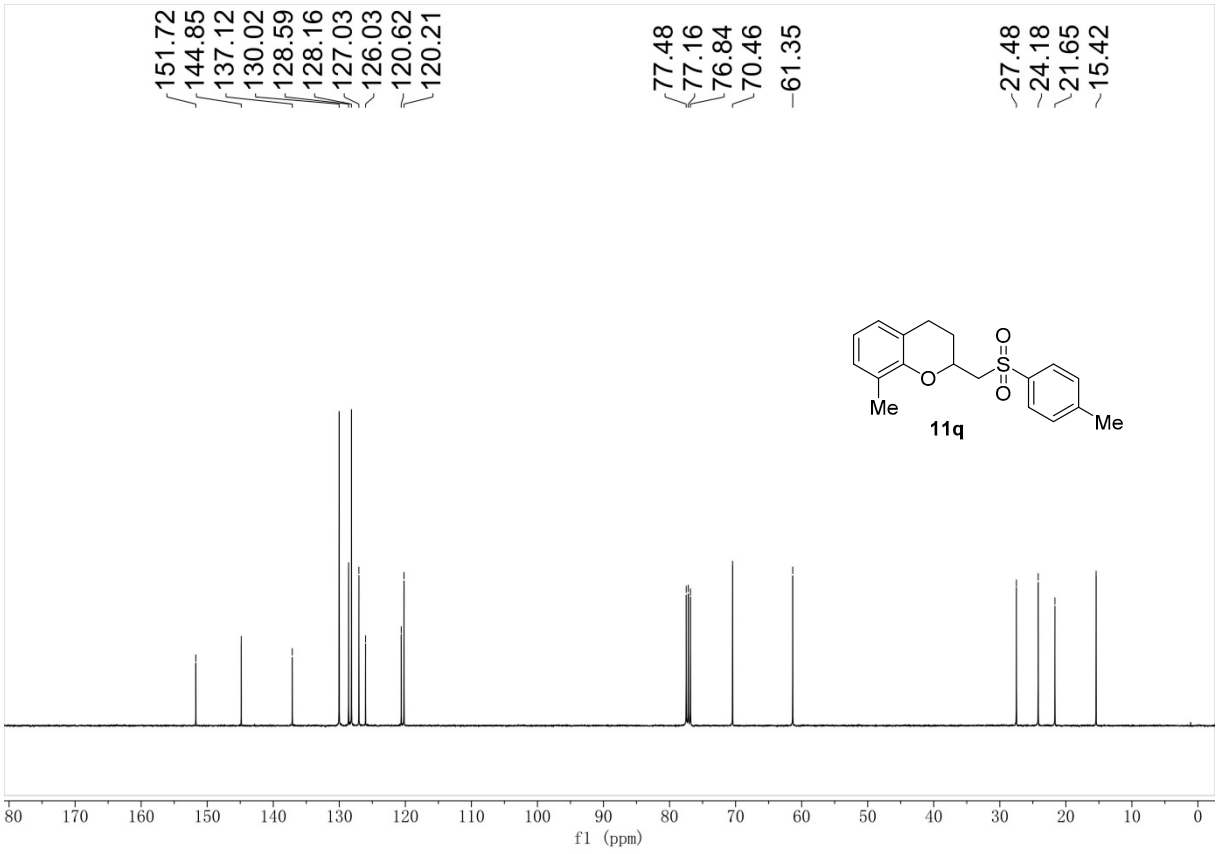
^{1}H NMR spectrum of **11a**



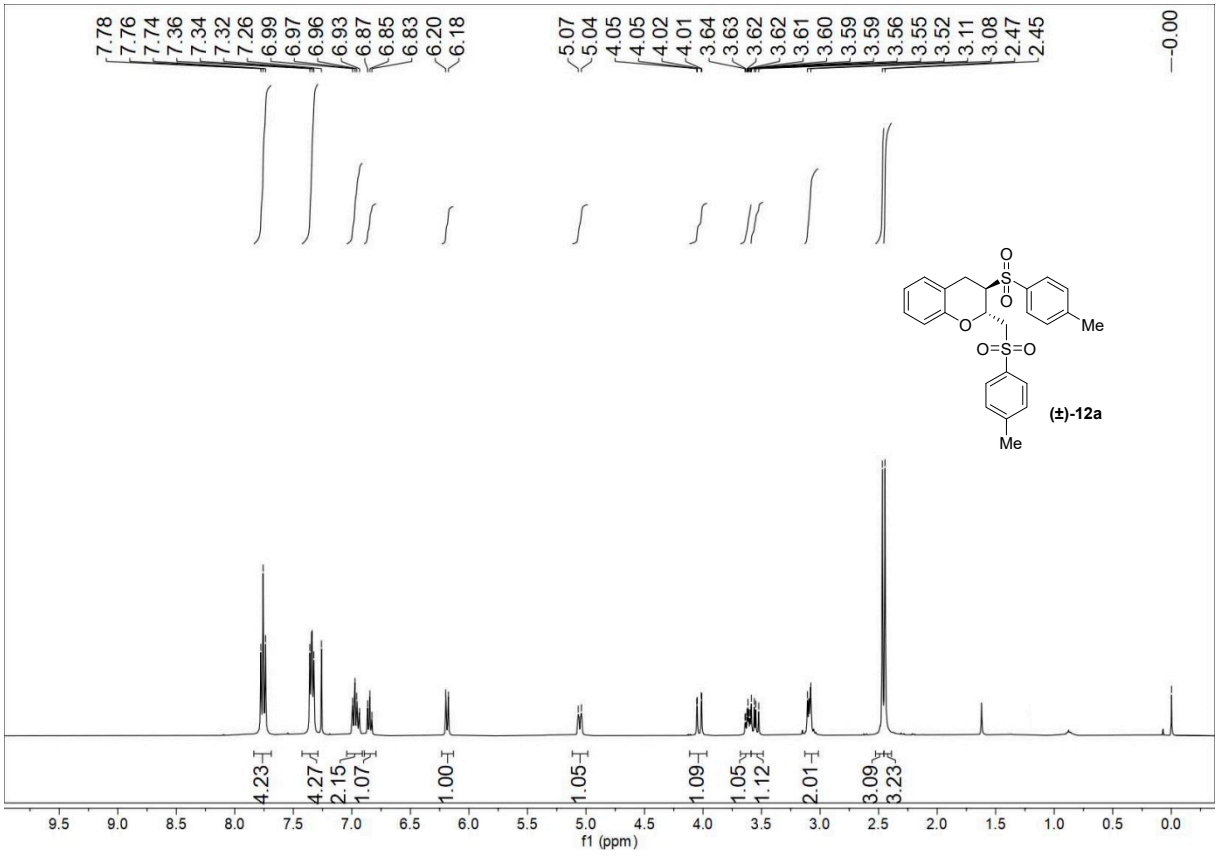
^{13}C NMR spectrum of **11a**



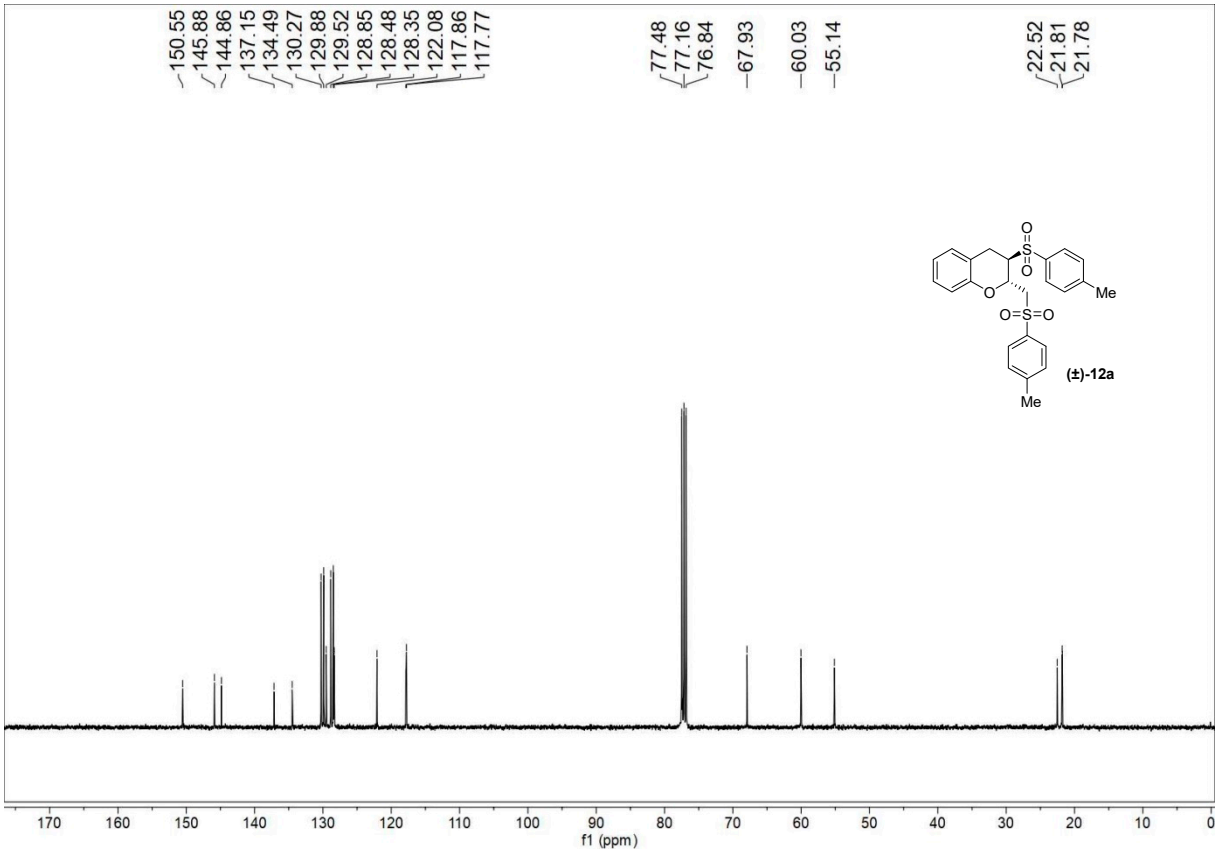
^{1}H NMR spectrum of **11q**



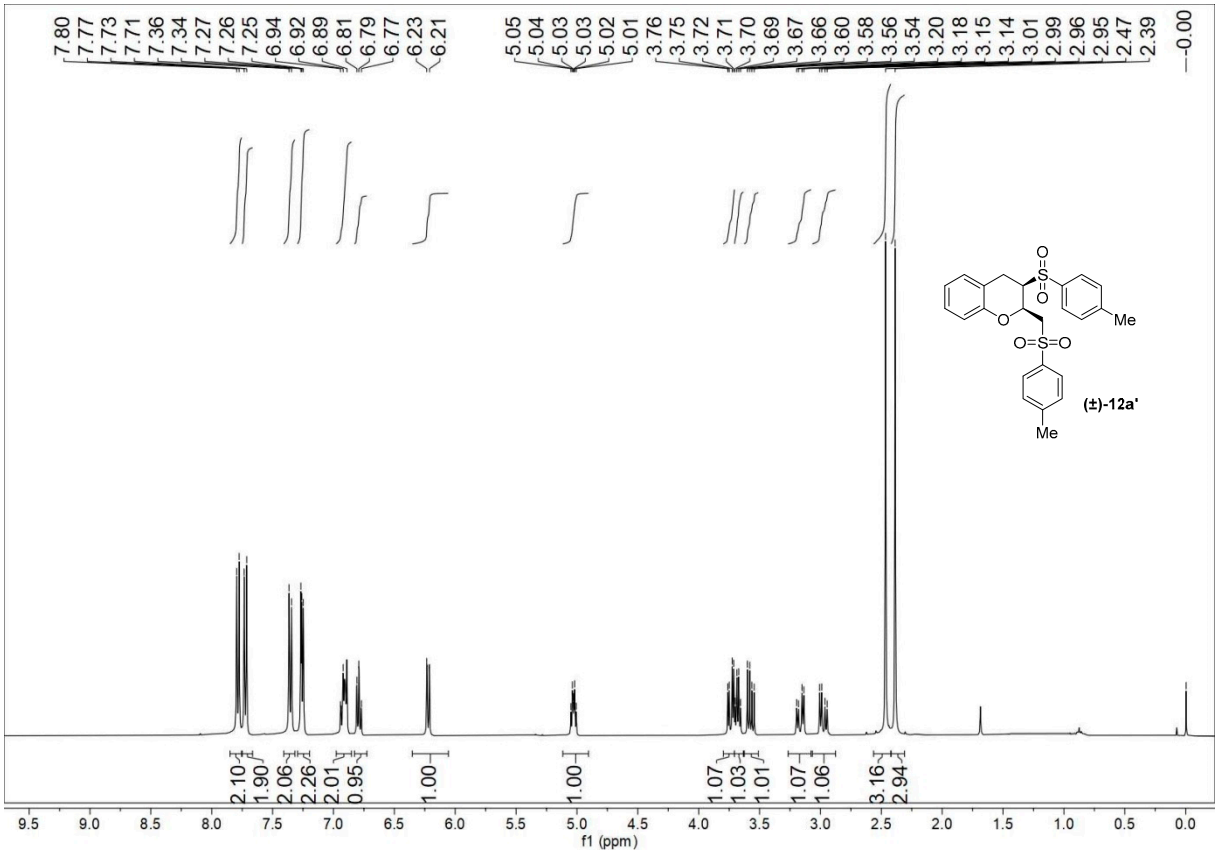
^{13}C NMR spectrum of **11q**



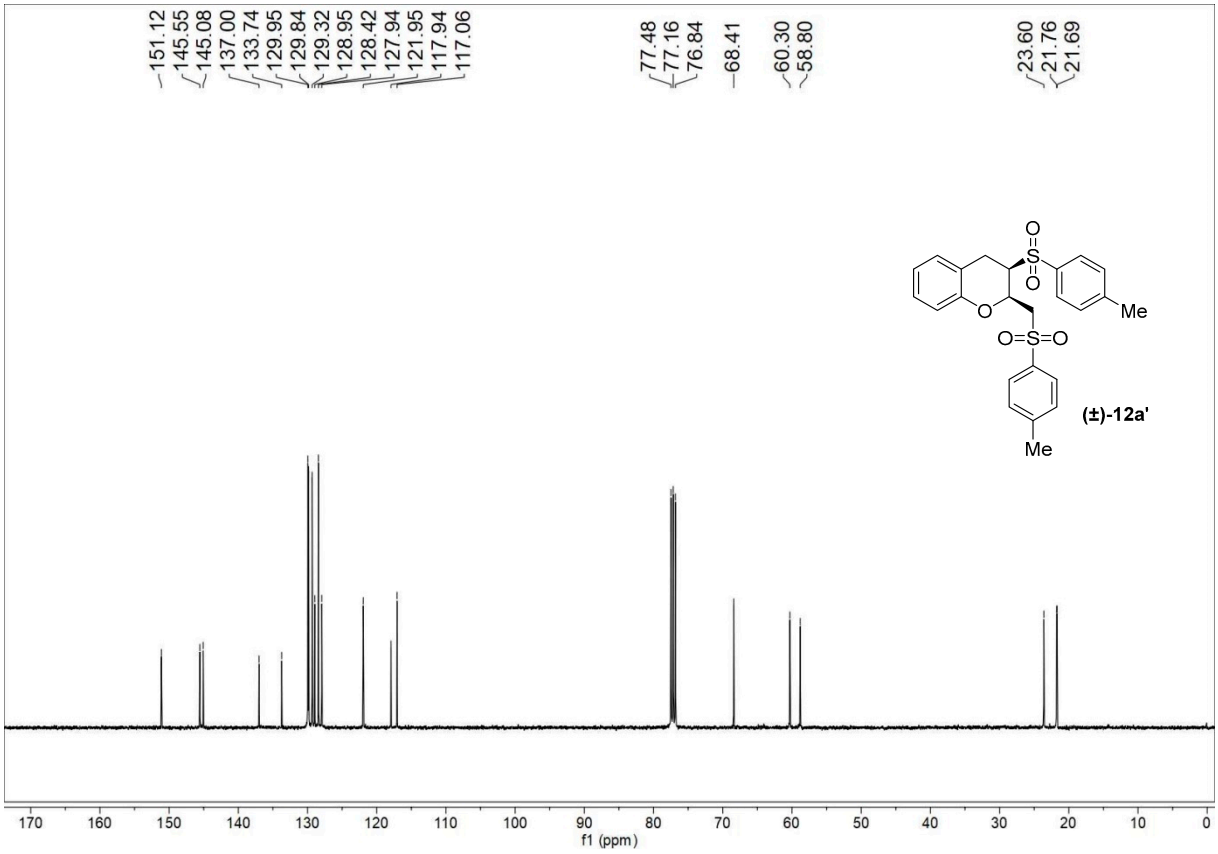
^{1}H NMR spectrum of (±)-**12a**



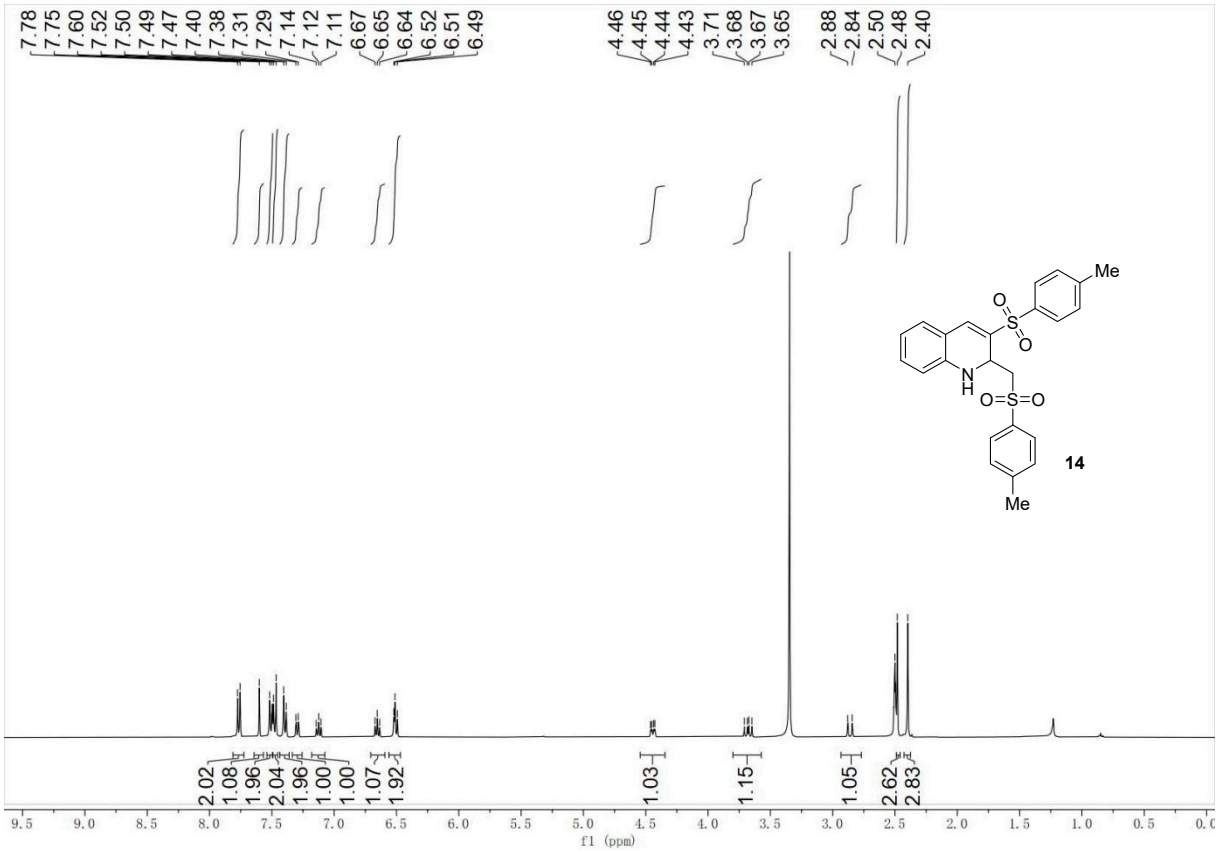
^{13}C NMR spectrum of (±)-**12a**



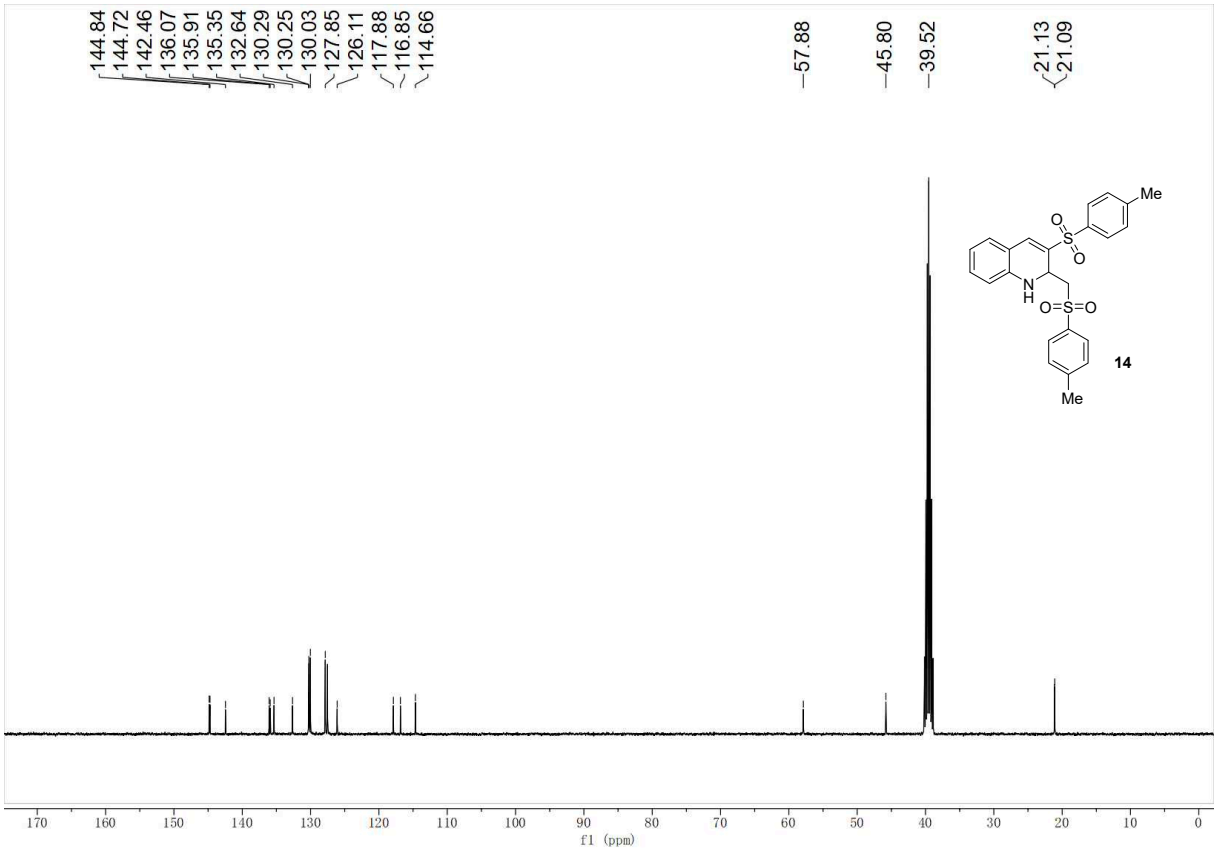
^{1}H NMR spectrum of (±)-**12a′**



^{13}C NMR spectrum of (±)-**12a′**



^{1}H NMR spectrum of compound **14**



^{13}C NMR spectrum of compound **14**