Supporting Information

Nickel-Promoted C(2)-H Amidation of Quinoline N-oxides with N-Fluorobenzenesulfonimide

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1. General information

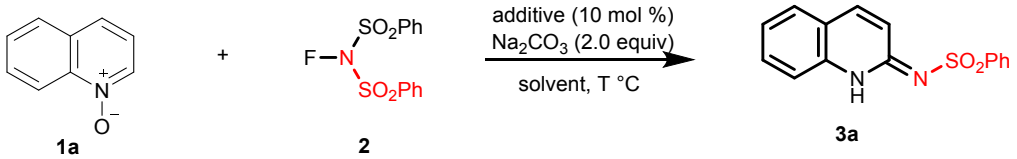
All manipulations were performed in 25 mL Schlenk tube equipped with a magnetic stir bar unless otherwise noted. Solvents and reagents were purchased from commercial sources and used as received. Flash column chromatography was performed using silica gel (60-Å pore size, 32-63 μm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Melting points were recorded by XT4A micro melting point Measurement Instruments, thermometer was unrevised. The transformation progress and mass spectra were indicated by GC (Shimadzu GC-2010 Plus) or GC-MS (Thermo Fisher Scientific DSQ II). NMR spectra were obtained on Bruker AVANCE III systems using $CDCl_3$ or DMSO-d_6 as solvent, TMS as internal standard substance, at 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, and 376 MHz for ^{19}F NMR. The high resolution mass spectrum was received via Agilent Technologies 6540 UHD Accurate-mass Q-Tof LC/MS, with ESI as ion source. X-ray analysis was performed with a single-crystal X-ray diffractometer. Preparative TLC was performed on silica gel plates and developed with ethyl acetate/hexane.

2. Preparation of substrates

All of the quinoline N-oxides were prepared from the corresponding quinolines according to the reported procedure.[1]

3. Optimization of the reaction

Table 1 Additive, base and temperature effects on the synthesis of (E)-N-(quinolin-2(1H)-ylidene)benzenesulfonamide.[a]

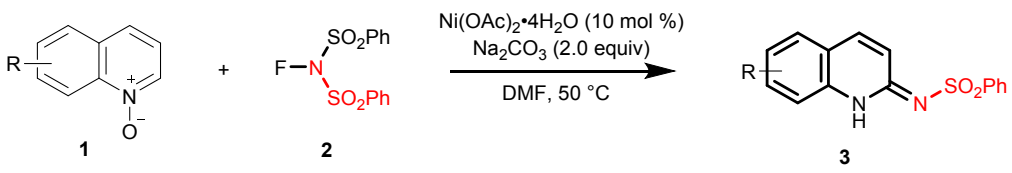


entry	additive	solvent	base	temperature (°C)	yield (%)[b]

1	$Ni(OAc)_2·4H_2O$	CH_3CN	Na_2CO_3	90	18
2	$Ni(OAc)_2·4H_2O$	DMF	Na_2CO_3	90	81
3	$Ni(OAc)_2·4H_2O$	DME	Na_2CO_3	90	40
4	$Ni(OAc)_2·4H_2O$	toluene	Na_2CO_3	90	16
5	$NiCl_2·6H_2O$	DMF	Na_2CO_3	90	27
6	$Ni(acac)_2$	DMF	Na_2CO_3	90	62
7	$Ni(OTf)_2$	DMF	Na_2CO_3	90	64
8	$Ni(PPh_3)Cl_2$	DMF	Na_2CO_3	90	15
9	CuI	DMF	Na_2CO_3	90	67
10	$FeCl_2$	DMF	Na_2CO_3	90	22
11[c]	$Ni(OAc)_2·4H_2O$	DMF	Na_2CO_3	90	77
12[d]	$Ni(OAc)_2·4H_2O$	DMF	Na_2CO_3	90	75
13	-	DMF	Na_2CO_3	90	49
14	$Ni(OAc)_2·4H_2O$	DMF	K_2CO_3	90	35
15	$Ni(OAc)_2·4H_2O$	DMF	Cs_2CO_3	90	25
16	$Ni(OAc)_2·4H_2O$	DMF	K_3PO_4	90	63
17	$Ni(OAc)_2·4H_2O$	DMF	NaOH	90	72
18	$Ni(OAc)_2·4H_2O$	DMF	-	90	nd
19	$Ni(OAc)_2·4H_2O$	DMF	Na_2CO_3	50	82 (77)
20	$Ni(OAc)_2·4H_2O$	DMF	Na_2CO_3	40	76
21	$Ni(OAc)_2·4H_2O$	DMF	Na_2CO_3	25	22
22	$FeCl_3$	DMF	Na_2CO_3	50	10
23	$MgCl_2$	DMF	Na_2CO_3	50	14
24	$ZnCl_2$	DMF	Na_2CO_3	50	22

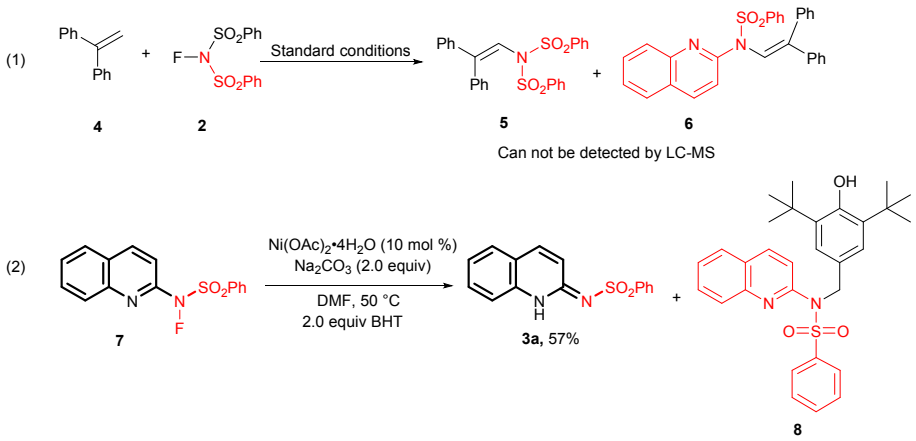
[a]Reaction conditions: **1a** (0.3 mmol), **2** (0.6 mmol), additive (10 mol %), base (2 equiv), solvent (2 mL) at 90 °C for 12 h. nd = not detected. [b]HPLC yields, isolated yields are shown in parentheses. [c]$Ni(OAc)_2·4H_2O$ (5 mol %). [d]$Ni(OAc)_2·4H_2O$ (3 mol %).

4. General procedure for the reaction

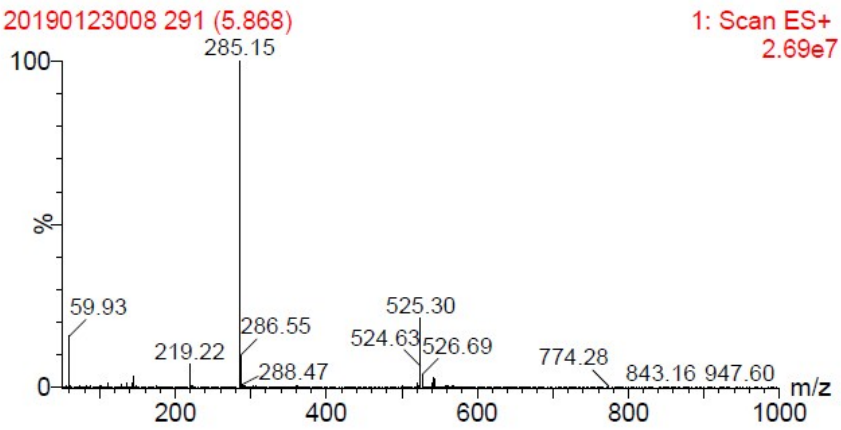


Experimental Procedure: A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with **1** (0.3 mmol, 1.0 equiv), **2** (0.6 mmol, 2.0 equiv), $Ni(OAc)_2 \cdot 4H_2O$ (10 mol %), Na_2CO_3 (2.0 equiv), DMF (2.0 mL). Subsequently, the tube was sealed and the resulting mixture was then stirred at 50 ℃ for 12 h. The crude production was diluted with ethyl acetate and H_2O and then the resulting mixture was filtered through a pad of Celite. The filtrate was extracted with ethyl acetate (3 × 10 mL). The combined organic layers dried over anhydrous Na_2SO_4, concentrated in vacuo, and purified by flash column chromatograph to give the pure products. The products were characterized by ^1H NMR, ^{13}C NMR, LC-MS.

5. Control Experiments.



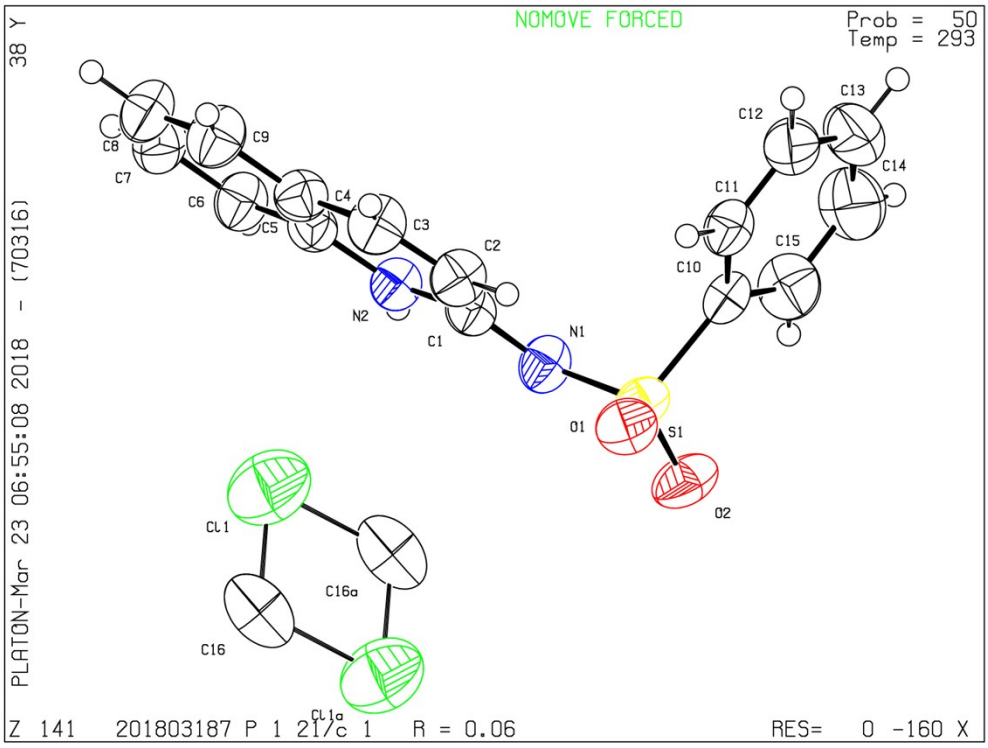
The mass of 8



6. X-Ray Crystallographic Data of 3a

The structure of **3a** (CCDC 1873672) was determined by the X-ray diffraction.

Recrystallized from CH_2Cl_2. Further information can be found in the CIF file.[1]



Bond precision: C-C = 0.0059 A Wavelength=1.54184

Cell: a=8.2400(4) b=10.3859(4) c=17.7438(8)
alpha=90 beta=95.373(4) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	1511.84(12)	1511.85(12)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	2(C15 H12 N2 O2 S), C Cl2	2(C15 H12 N2 O2 S), C Cl2
Sum formula	C31 H24 Cl2 N4 O4 S2	C31 H26 Cl2 N4 O4 S2
Mr	651.56	653.58
Dx,g cm-3	1.431	1.436
Z	2	2
Mu (mm-1)	3.589	3.589
F000	672.0	676.0
F000'	676.48	
h,k,lmax	9,12,21	9,12,21
Nref	2701	2695
Tmin,Tmax	0.570,0.627	0.684,1.000
Tmin'	0.517	

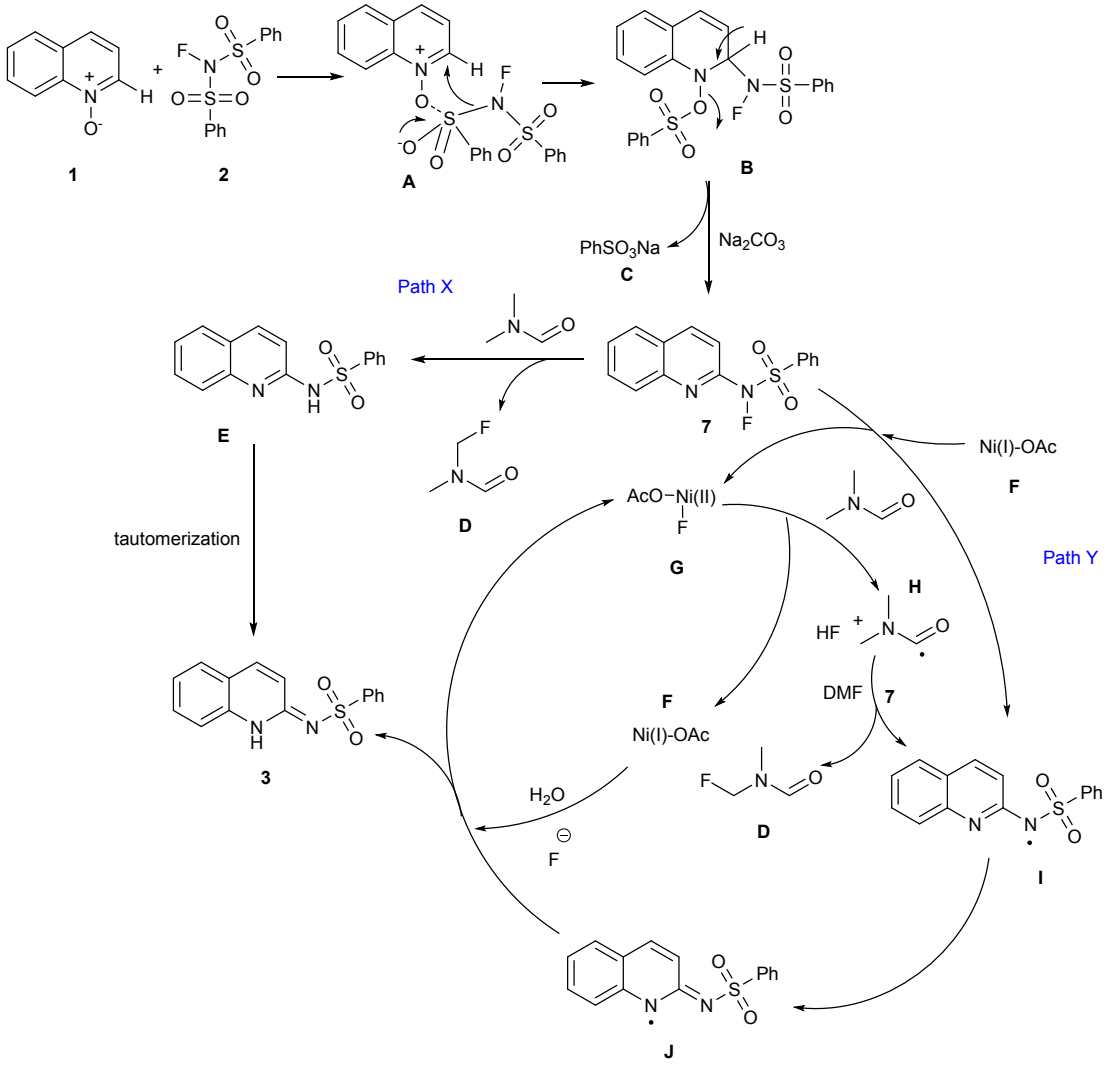
Correction method= # Reported T Limits: Tmin=0.684 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 67.054

R(reflections)= 0.0642(2193) wR2(reflections)= 0.1981(2695)

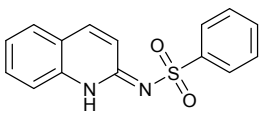
S = 1.049 Npar= 204

7. Plausible Mechanism.



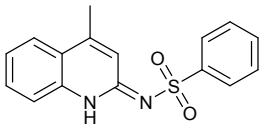
8. Characterization data of the products.

(E)-N-(quinolin-2(1H)-ylidene)benzenesulfonamidetert-butyl (3a): (65.6 mg, yield 77 %); White solid; m.p. 162-164 °C.



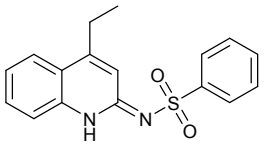
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 12.00 (s, 1H), 7.99-8.01 (m, 2H), 7.88 (d, J = 9.5 Hz, 1H), 7.59-7.62 (m, 2H), 7.42-7.53 (m, 4H), 7.32-7.36 (m, 1H), 7.07 (d, J = 9.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 154.5, 142.8, 140.9, 136.4, 132.1, 131.8, 128.8, 128.2, 126.2, 124.8, 121.4, 120.9, 117.4. HRMS (ESI): m/z calcd for $C_{15}H_{12}N_2O_2S$ $[M+H]^+$: 285.0692, found: 285.0699.

(E)-N-(4-methylquinolin-2(1H)-ylidene)benzenesulfonamide (3b): (67.9 mg, yield 76 %); White solid; m.p. 202-204 °C.



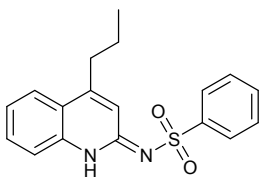
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 11.84 (s, 1H), 7.99-8.01 (m, 2H), 7.76 (d, J = 8.1 Hz, 1H), 7.60-7.64 (m, 1H), 7.43-7.52 (m, 4H), 7.37-7.41 (m, 1H), 6.82 (s, 1H); 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 154.2, 150.2, 143.1, 136.1, 131.9, 131.6, 128.8, 126.2, 124.6, 122.0, 119.8, 117.7, 19.3. HRMS (ESI): m/z calcd for $C_{16}H_{14}N_2O_2S$ $[M+H]^+$: 299.0849, found: 299.0854.

(E)-N-(4-ethylquinolin-2(1H)-ylidene)benzenesulfonamide (3c): (48.7 mg, yield 52 %); White solid; m.p. 192-193 °C.



^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 11.90 (s, 1H), 8.00-8.02 (m, 2H), 7.79 (d, J = 8.2 Hz, 1H), 7.59-7.63 (m, 1H), 7.44-7.50 (m, 4H), 7.35-7.40 (m, 1H), 6.84 (s, 1H); 2.93 (t, J = 7.3 Hz, 2H), 1.33 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 155.3, 154.3, 143.1, 136.2, 131.9, 131.4, 128.8, 126.2, 124.6, 124.2, 121.3, 118.2, 117.8, 25.3, 12.8. HRMS (ESI): m/z calcd for $C_{17}H_{16}N_2O_2S$ $[M+H]^+$: 313.1005, found: 313.1010.

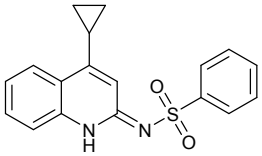
(E)-N-(4-propylquinolin-2(1H)-ylidene)benzenesulfonamide (3d): (52.8 mg, yield 54 %); White solid; m.p. 210-211 °C.



^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 11.88 (s, 1H), 8.00-8.02 (m, 2H), 7.79 (d, J = 8.1 Hz, 1H), 7.59-7.63 (t, 1H), 7.44-7.53 (m, 4H), 7.36-7.39 (m, 1H), 6.80 (s, 1H); 2.86 (t, J = 7.4 Hz, 2H), 1.69-1.78 (m, 2H), 1.03 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz,

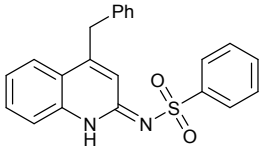
$CDCl_3$, ppm) δ: 154.2, 154.0, 143.1, 136.4, 131.9, 131.4, 128.8, 126.2, 124.6, 124.4, 121.4, 119.0, 118.0, 34.4, 22.1, 14.0. HRMS (ESI): m/z calcd for $C_{18}H_{18}N_2O_2S$ $[M+H]^+$: 327.1162, found: 327.1166.

(E)-N-(4-cyclopropylquinolin-2(1H)-ylidene)benzenesulfonamide (3e): (58.3 mg, yield 60 %); yellow solid; m.p. 204-206 °C.



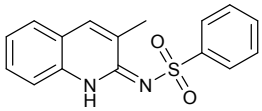
^1H NMR (400 MHz, $CDCl_3$, ppm) δ: 11.83 (s, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.98-8.00 (m, 2H), 7.60-7.64 (m, 1H), 7.38-7.52 (m, 5H), 6.56 (s, 1H), 2.18-2.25 (m, 1H), 1.13-1.18 (m, 2H), 0.81-0.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 155.3, 154.4, 143.1, 136.0, 131.9, 131.5, 128.8, 126.2, 124.8, 124.6, 122.4, 117.6, 116.1, 12.6, 8.2. HRMS (ESI): m/z calcd for $C_{18}H_{16}N_2O_2S$ $[M+H]^+$: 325.1005, found: 325.1009.

(E)-N-(4-benzylquinolin-2(1H)-ylidene)benzenesulfonamide (3f): (65.1 mg, yield 58 %); White solid; m.p. 219-220 °C.



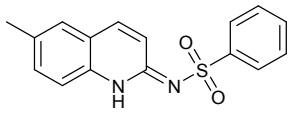
^1H NMR (400 MHz, $CDCl_3$, ppm) δ: 11.85 (s, 1H), 7.96-7.98 (m, 2H), 7.81 (d, J = 8.0 Hz, 1H), 7.58-7.62 (m, 1H), 7.43-7.53 (m, 4H), 7.24-7.36 (m, 4H), 7.18-7.19 (like d, 2H), 6.64 (s, 1H), 4.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 154.0, 152.1, 142.9, 136.5, 136.3, 132.0, 131.5, 129.1, 129.0, 128.8, 127.2, 126.2, 124.7, 121.3, 121.0, 117.7, 38.5. HRMS (ESI): m/z calcd for $C_{22}H_{18}N_2O_2S$ $[M+H]^+$: 375.1162, found: 375.1165.

(E)-N-(3-methylquinolin-2(1H)-ylidene)benzenesulfonamide (3g): (59.0 mg, yield 66 %); White solid; m.p. 160-162 °C.



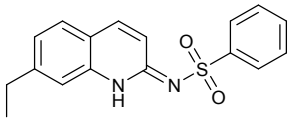
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 12.12 (s, 1H), 8.01-8.03 (m, 2H), 7.73 (s, 1H), 7.44-7.56 (m, 5H), 7.30-7.36 (m, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 154.1, 143.3, 138.4, 135.0, 132.0, 130.5, 130.1, 128.7, 127.3, 126.0, 124.6, 121.3, 116.5, 18.0. HRMS (ESI): m/z calcd for $C_{16}H_{14}N_2O_2S$ $[M+H]^+$: 299.0849, found: 299.0854.

(E)-N-(6-methylquinolin-2(1H)-ylidene)benzenesulfonamide (3h): (68.8 mg, yield 77 %); White solid; m.p. 175-177 °C.



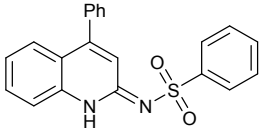
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 11.92 (s, 1H), 7.99-8.01 (m, 2H), 7.81 (d, J = 9.3 Hz, 1H), 7.36-7.52 (m, 6H), 6.94 (d, J = 9.4 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 154.3, 143.0, 140.8, 134.8, 134.6, 133.4, 132.0, 128.8, 127.6, 126.2, 121.5, 120.5, 117.2, 21.0. HRMS (ESI): m/z calcd for $C_{16}H_{14}N_2O_2S$ $[M+H]^+$: 299.0849, found: 299.0852.

(E)-N-(7-ethylquinolin-2(1H)-ylidene)benzenesulfonamide (3i): (65.5 mg, yield 70 %); White solid; m.p. 139-141 °C.



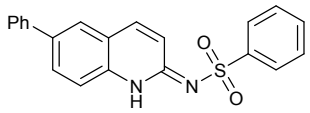
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 12.08 (s, 1H), 8.00-8.02 (m, 2H), 7.86 (d, J = 9.3 Hz, 1H), 7.53 (d, J = 8.2 Hz, 2H), 7.42-7.49 (m, 3H), 7.37 (s, 1H), 7.2 (dd, J_1 = 1.2 Hz, J_2 = 8.2, 1H); 7.03 (d, J = 9.3 Hz, 1H), 2.78 (q, J = 7.6 Hz, 2H), 1.29 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 154.8, 149.3, 143.1, 141.0, 136.7, 132.0, 128.8, 127.9, 126.2, 125.5, 119.6, 119.2, 116.0, 29.1, 15.1. HRMS (ESI): m/z calcd for $C_{17}H_{16}N_2O_2S$ $[M+H]^+$: 313.1005, found: 313.1013.

(E)-N-(4-phenylquinolin-2(1H)-ylidene)benzenesulfonamide (3j): (86.4 mg, yield 80 %); White solid; m.p. 200-202 °C.



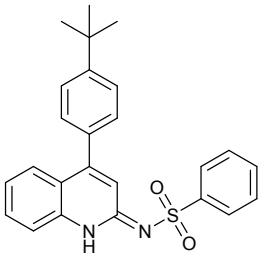
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 11.98 (s, 1H), 8.02-8.04 (m, 2H), 7.61-7.66 (m, 2H), 7.45-7.54 (m, 7H), 7.40-7.43 (m, 2H), 7.29-7.33 (m, 1H), 6.92 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 153.8, 153.6, 143.0, 136.8, 136.2, 132.0, 131.7, 129.4, 128.9, 128.8, 127.1, 126.3, 124.6, 121.0, 120.6, 117.7. HRMS (ESI): m/z calcd for $C_{21}H_{16}N_2O_2S$ $[M+H]^+$: 361.1005, found: 361.1013.

(E)-N-(6-phenylquinolin-2(1H)-ylidene)benzenesulfonamide (3k): (49.7 mg, yield 46 %); White solid; m.p. 180-182 °C.



^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 12.02 (s, 1H), 8.01-8.03 (m, 2H), 7.94 (d, J = 9.4 Hz, 1H), 7.85-7.88 (m, 1H), 7.80-7.81 (like d, 1H), 7.57-7.62 (m, 3H), 7.45-7.52 (m, 5H), 7.38-7.42 (m, 1H), 7.06 (d, J = 9.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 154.4, 142.8, 141.0, 139.3, 138.1, 135.8, 132.1, 131.1, 129.1, 128.8, 127.9, 127.1, 126.3, 126.0, 121.8, 121.0, 117.9. HRMS (ESI): m/z calcd for $C_{21}H_{16}N_2O_2S$ $[M+H]^+$: 361.1005, found: 361.1010.

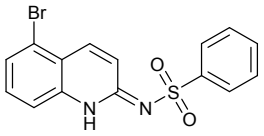
(E)-N-(4-(4-(tert-butyl)phenyl)quinolin-2(1H)-ylidene)benzenesulfonamide (3l): (91.1 mg, yield 73 %); White solid; m.p. 214-216 °C.



^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 11.93 (s, 1H), 8.02-8.04 (m, 2H), 7.72 (d, J = 8.2 Hz, 1H), 7.61-7.65 (m, 1H), 7.45-7.53 (m, 6H), 7.35-7.37 (like d, 2H), 7.29-7.33 (m, 1H), 6.89 (s, 1H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 154.2, 153.9, 152.7, 143.1, 137.0, 133.3, 132.0, 131.7, 128.8, 128.7, 127.2, 126.3, 125.8, 124.6, 121.1, 120.0, 117.8, 34.8, 31.3. HRMS (ESI): m/z calcd for $C_{25}H_{24}N_2O_2S$ $[M+H]^+$: 417.1631, found: 417.1641.

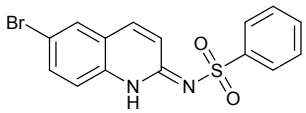
(E)-N-(5-bromoquinolin-2(1H)-ylidene)benzenesulfonamide (3m): (54.3 mg, yield

50 %); White solid; m.p. 185-187 °C.



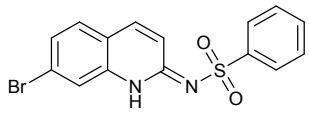
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 11.77 (s, 1H), 8.24 (d, J = 9.7 Hz, 1H), 8.00-8.02 (m, 2H), 7.58-7.60 (m, 1H), 7.42-7.55 (m, 5H), 7.12 (d, J = 9.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 153.9, 142.3, 139.6, 138.3, 132.4, 132.0, 128.9, 128.7, 126.4, 122.9, 121.5, 121.0, 117.7. HRMS (ESI): m/z calcd for $C_{15}H_{11}BrN_2O_2S$ $[M+H]^+$: 362.9797, found: 362.9800.

(E)-N-(6-bromoquinolin-2(1H)-ylidene)benzenesulfonamide (3n): (82.5 mg, yield 76 %); White solid; m.p. 186-188 °C.



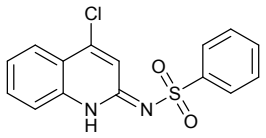
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 11.81 (s, 1H), 7.98-8.00 (m, 2H), 7.77-7.80 (m, 2H), 7.68-7.70 (m, 1H), 7.45-7.55 (m, 3H), 7.40 (d, J = 8.8 Hz, 1H), 7.04 (d, J = 9.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 154.1, 142.3, 139.5, 135.9, 134.7, 132.3, 130.3, 128.9, 126.4, 122.9, 121.3, 119.6, 117.7. HRMS (ESI): m/z calcd for $C_{15}H_{11}BrN_2O_2S$ $[M+H]^+$: 362.9797, found: 362.9799.

(E)-N-(7-bromoquinolin-2(1H)-ylidene)benzenesulfonamide (3o): (79.3 mg, yield 73 %); White solid; m.p. 173-174 °C.



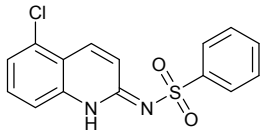
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 11.72 (s, 1H), 7.99-8.01 (like d, 2H), 7.83 (d, J = 9.4 Hz, 1H), 7.69 (s, 1H), 7.52-7.46 (m, 5H), 7.06 (d, J = 9.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 154.2, 142.3, 140.3, 137.8, 132.3, 129.2, 128.9, 128.2, 126.4, 126.0, 120.6, 120.4, 120.3. HRMS (ESI): m/z calcd for $C_{15}H_{11}BrN_2O_2S$ $[M+H]^+$: 362.9797, found: 362.9799..

(E)-N-(4-chloroquinolin-2(1H)-ylidene)benzenesulfonamide (3p): (58.2 mg, yield 61 %); White solid; m.p. 160-162 °C.



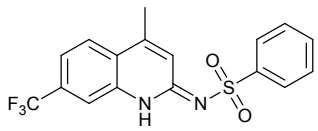
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 11.85 (s, 1H), 7.98-8.01 (m, 3H), 7.66-7.70 (m, 1H), 7.51-7.55 (m, 2H), 7.42-7.49 (m, 3H), 7.24 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 153.6, 147.0, 142.5, 137.2, 132.9, 132.3, 128.9, 126.3, 125.3, 125.3, 120.2, 119.0, 118.1. HRMS (ESI): m/z calcd for $C_{15}H_{11}ClN_2O_2S$ $[M+H]^+$: 319.0303, found: 319.0307.

(E)-N-(5-chloroquinolin-2(1H)-ylidene)benzenesulfonamide (3q): (57.2 mg, yield 60 %); White solid; m.p. 184-186 °C.



^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 11.93 (s, 1H), 8.26 (d, J = 9.7 Hz, 1H), 7.98-8.01 (m, 2H), 7.43-7.53 (m, 5H), 7.38 (dd, J_1 = 1.6 Hz, J_2 = 7.1 Hz, 1H), 7.19 (d, J = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 154.0, 142.3, 138.1, 137.1, 132.7, 132.4, 131.8, 128.9, 126.4, 125.1, 121.4, 119.6, 116.9. HRMS (ESI): m/z calcd for $C_{15}H_{11}ClN_2O_2S$ $[M+H]^+$: 319.0303, found: 319.0307.

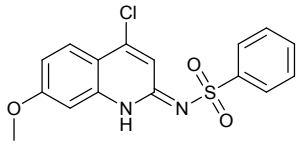
(E)-N-(4-methyl-7-(trifluoromethyl)quinolin-2(1H)-ylidene)benzenesulfonamide (3t): (68.1 mg, yield 62 %); White solid; m.p. 185-187 °C.



^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 11.72 (s, 1H), 7.98-8.00 (like d, 2H), 7.86 (d, J = 8.4 Hz, 1H), 7.76 (s, 1H), 7.57 (d, J = 8.4 Hz, 1H), 7.43-7.52 (m, 3H), 6.99 (s, 1H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 154.0, 149.1, 142.4, 136.5, 133.0 (q, J = 32.8 Hz), 132.3, 128.8, 126.3, 125.7, 124.2, 123.2 (q, J = 273.5 Hz), 121.7, 120.7 (q, J = 3.1 Hz), 115.6 (q, J = 4.2 Hz), 19.2. HRMS (ESI): m/z calcd for $C_{17}H_{13}F_3N_2O_2S$ $[M+H]^+$: 367.0723, found: 367.0726.

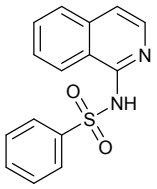
(E)-N-(4-chloro-7-methoxyquinolin-2(1H)-ylidene)benzenesulfonamide (3v):

(57.4 mg, yield 55 %); White solid; m.p. 188-190 °C.



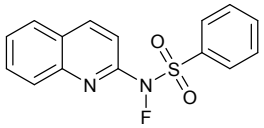
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 11.44 (s, 1H), 7.98-7.99 (m, 2H), 7.86 (d, J = 9.1 Hz, 1H), 7.49-7.53 (m, 1H), 7.41-7.46 (m, 3H), 7.33 (d, J = 1.9 Hz, 1H), 7.00 (dd, J_1 = 2.2 Hz, J_2 = 9.1 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 163.8, 154.9, 147.7, 142.7, 139.5, 132.1, 128.9, 126.6, 126.3, 116.5, 114.7, 114.6, 99.6, 56.4. HRMS (ESI): m/z calcd for $C_{16}H_{13}ClN_2O_3S$ $[M+H]^+$: 349.0408, found: 349.0411.

N-(isoquinolin-1-yl)benzenesulfonamide (3w): (6.0 mg, yield 7 %); White solid; m.p. 62-63 °C.



^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 11.92 (s, 1H), 8.58 (d, J = 8.3 Hz, 1H), 8.02-8.05 (m, 2H), 7.71-7.75 (m, 1H), 7.44-7.59 (m, 5H), 7.21-7.24 (m, 1H), 6.83 (d, J = 7.0 Hz 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 154.1, 143.3, 136.8, 133.7, 131.9, 128.8, 128.0, 127.9, 126.4, 126.1, 126.0, 124.8, 110.6. HRMS (ESI): m/z calcd for $C_{15}H_{12}N_2O_2S$ $[M+H]^+$: 285.0692, found: 285.0694.

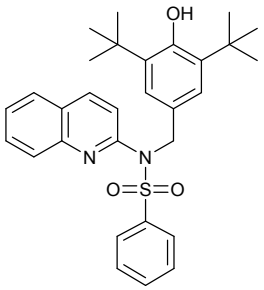
N-fluoro-N-(quinolin-2-yl)benzenesulfonamide (7): (47.1 mg, yield 52 %); faint yellow solid; m.p. 187-189 °C.



^{1}H NMR (400 MHz, MeOD, ppm) δ: 8.35 (d, J = 8.8 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.69-7.75 (m, 2H), 7.65 (d, J = 7.5 Hz, 2H), 7.60 (t, J = 7.2 Hz, 1H), 7.47-7.51 (m, 2H), 7.35 (d, J = 8.5 Hz, 1H); ^{13}C NMR (100 MHz, MeOD, ppm) δ: 152.8 (d, J = 8.7 Hz), 147.4, 140.5 (d, J = 2.6 Hz), 136.7, 133.3, 132.1, 131.0, 130.4, 129.5, 129.2, 129.1, 129.0, 116.4 (d, J = 5.2 Hz). ^{19}F NMR (376 MHz, MeOD,

ppm) δ = -49.0; HRMS (ESI): m/z calcd for $C_{15}H_{11}FN_2O_2S$ $[M+H]^+$: 303.0598, found: 303.0599.

N-(3,5-di-tert-butyl-4-hydroxybenzyl)-N-(quinolin-2-yl)benzenesulfonamide (8): White solid; m.p. 67-69 °C.



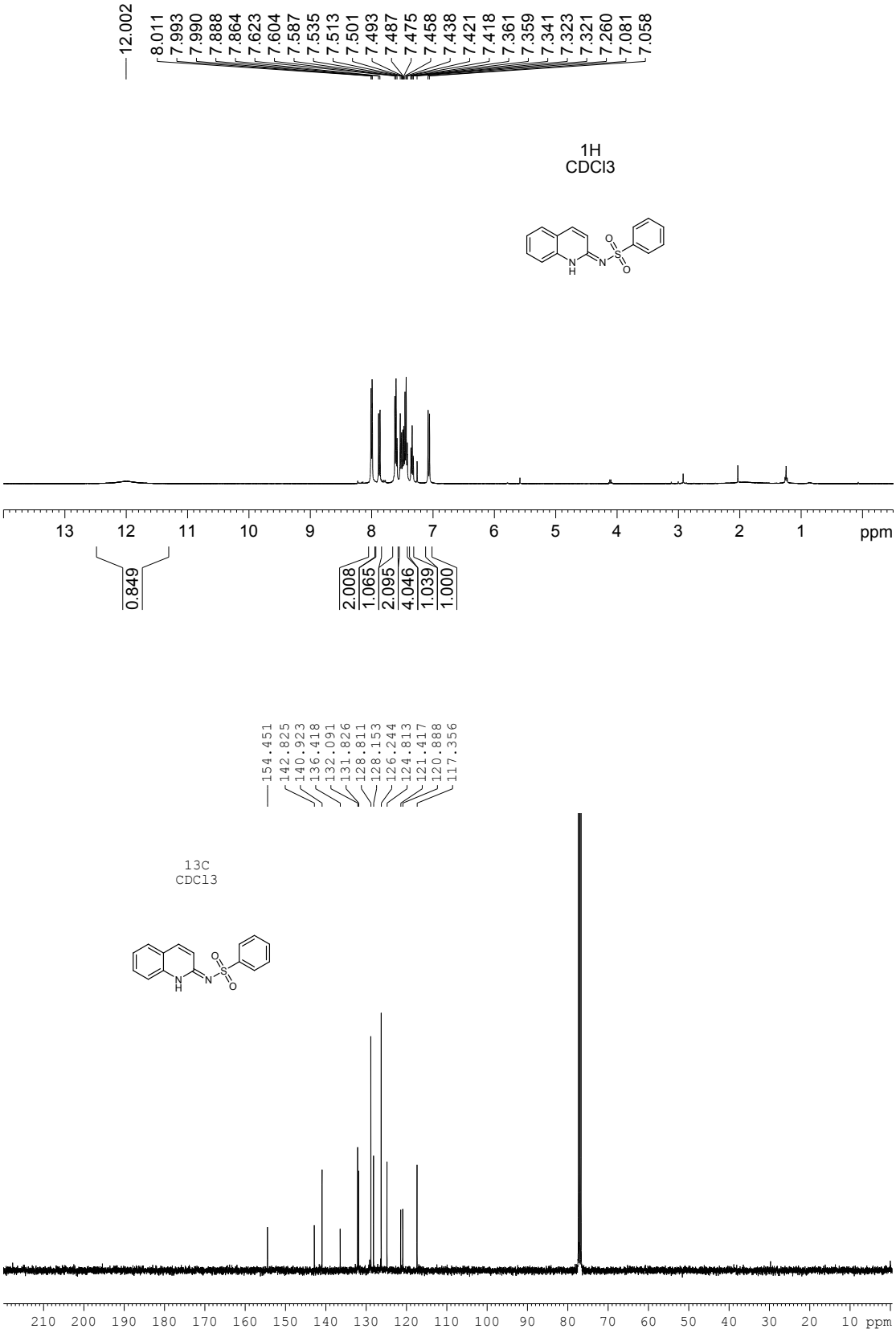
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.00 (d, J = 9.6 Hz, 1H), 7.91 (d, J = 7.4 Hz, 2H), 7.86 (d, J = 9.6 Hz, 1H), 7.57-7.67 (m, 3H), 7.32-7.46 (m, 4H), 7.02 (s, 2H), 5.68 (s, 2H), 5.16 (s, 1H), 1.33 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 156.1, 153.2, 143.8, 139.6, 139.0, 136.2, 131.9, 131.4, 129.2, 128.5, 126.3, 125.6, 123.9, 123.8, 122.1, 117.4, 116.5, 49.1, 34.3, 30.2. LC-MS (ESI, m/z): $[M+Na]^+$ 525.3.

9. References

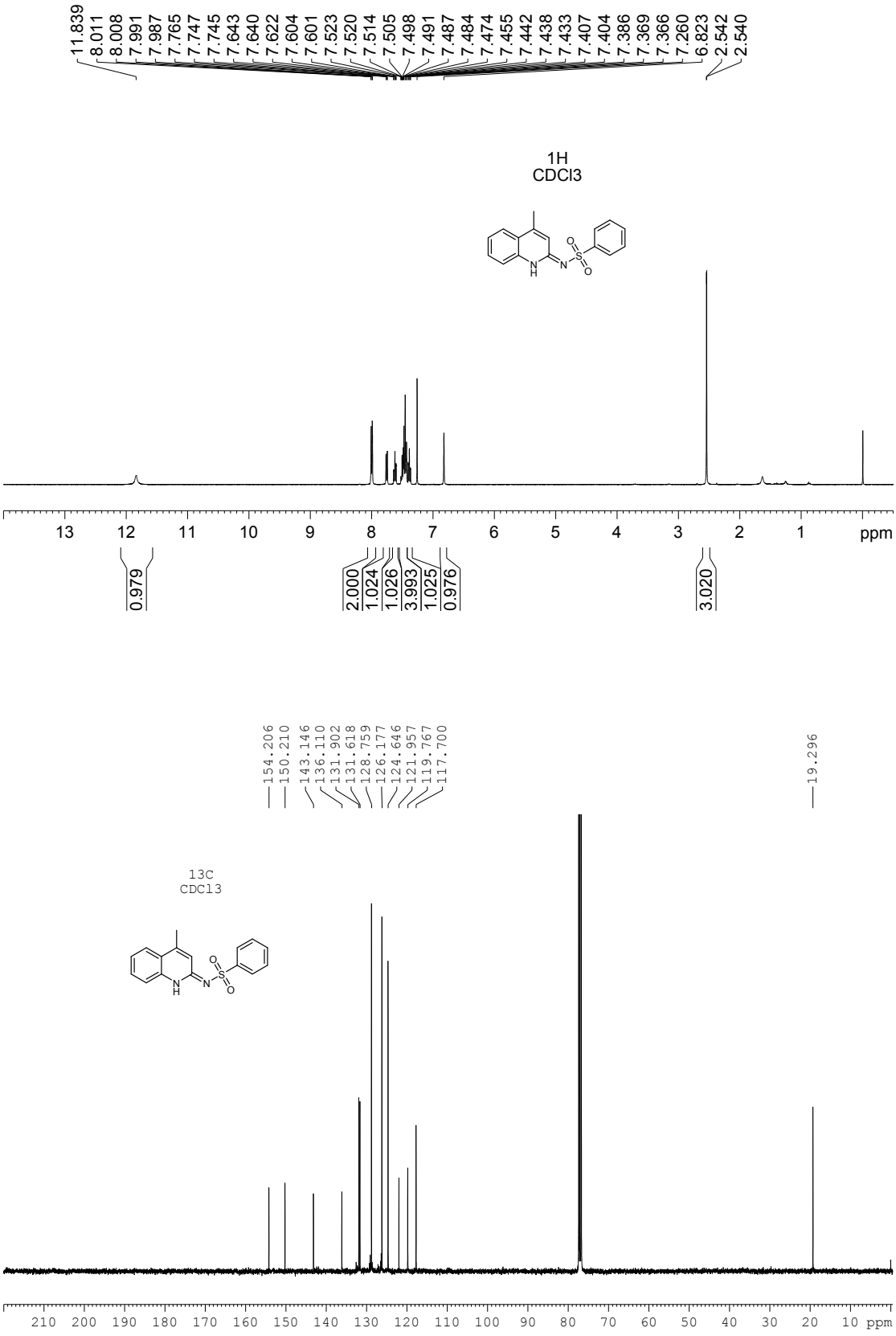
1. (a) A. Londregan, K. Burford, E. Conn, K. Hesp, *Org. Lett.* **2014**, *16*, 3336-3339. (b) A. Biswas, U. Karmakar, S. Nandi, R. Samanta, *J. Org. Chem.* **2017***, 82,* 8933-8942.

10. ^{1}H NMR and ^{13}C NMR spectra of the products

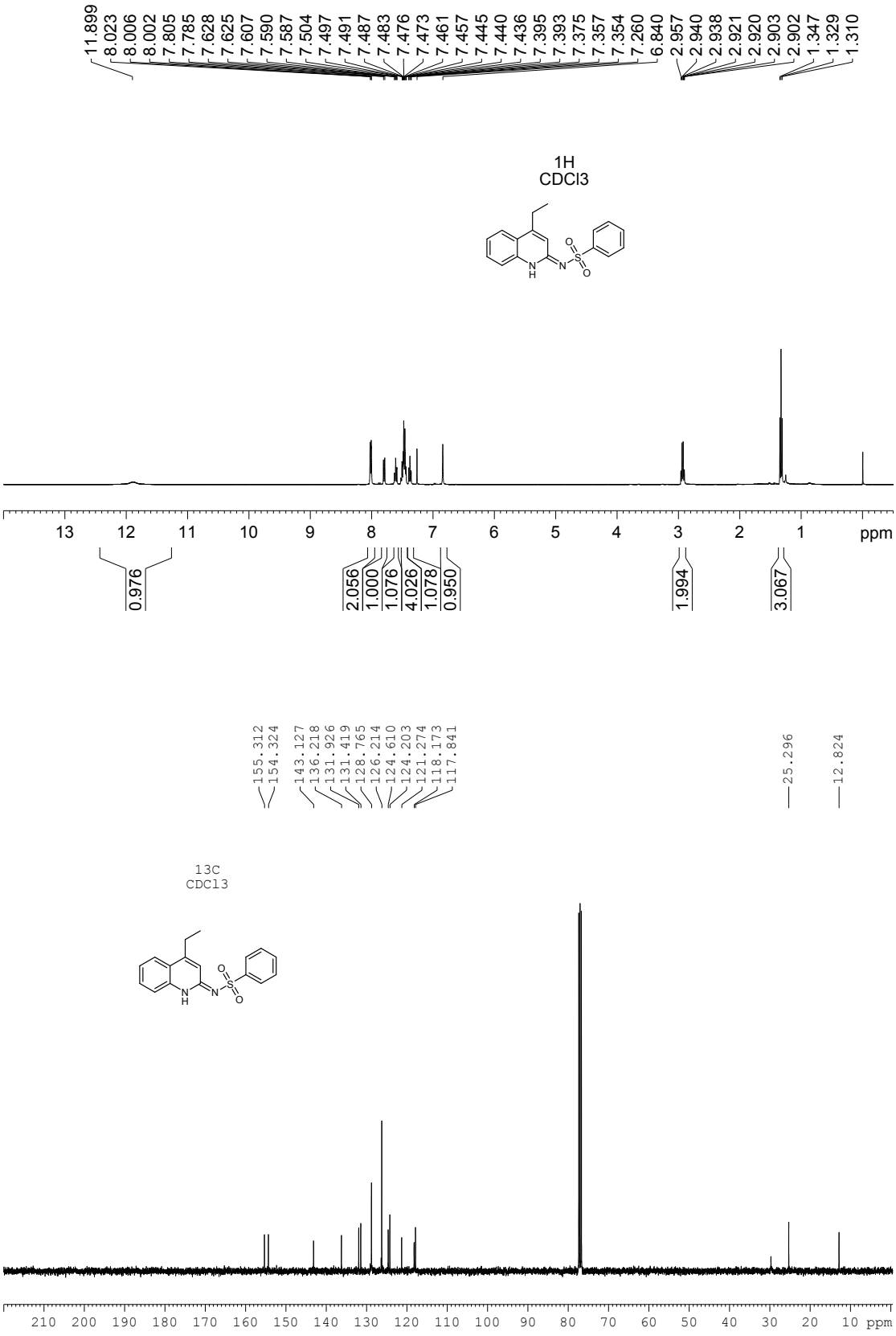
^{1}H NMR and ^{13}C NMR of compound **3a**



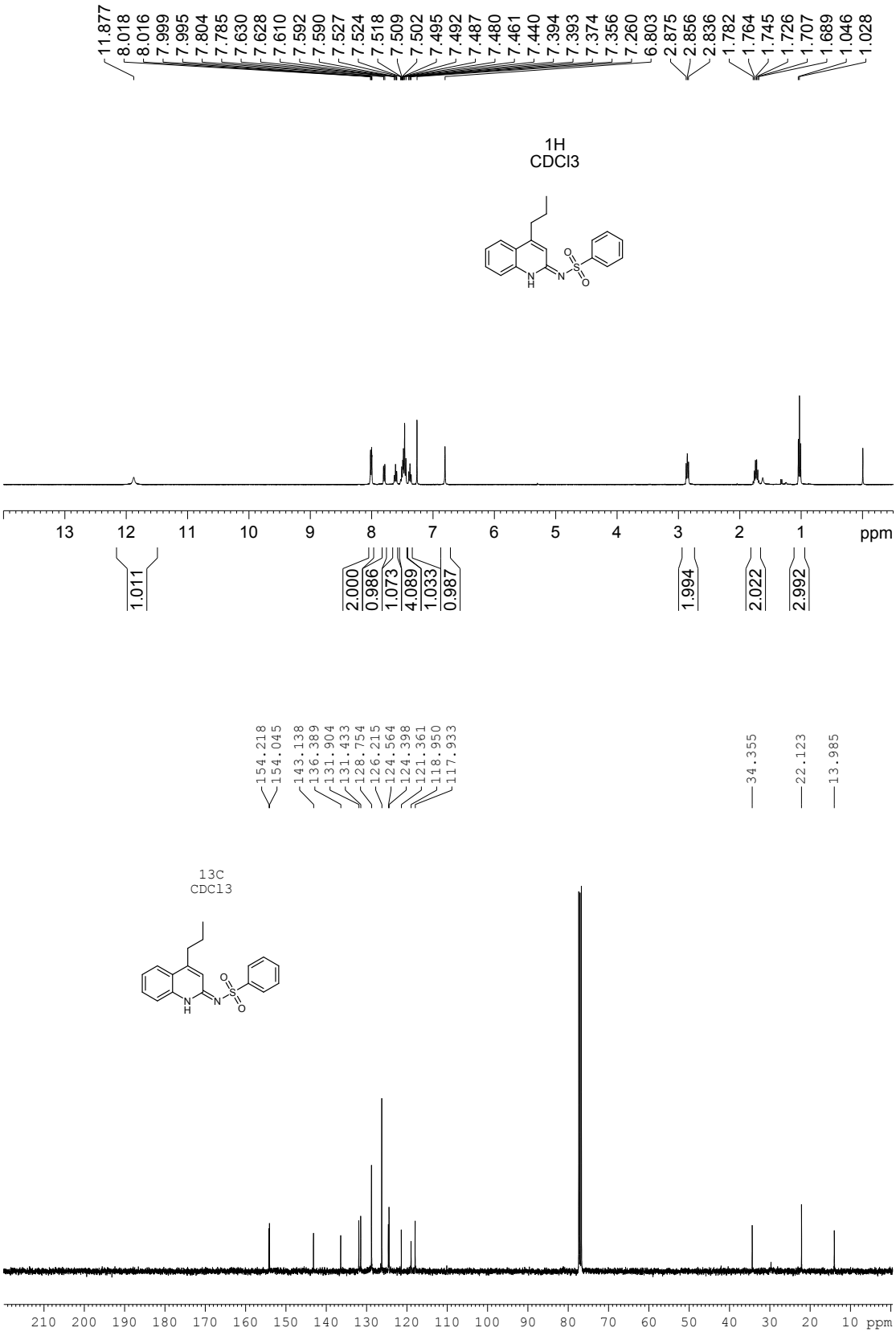
^{1}H NMR and ^{13}C NMR of compound **3b**



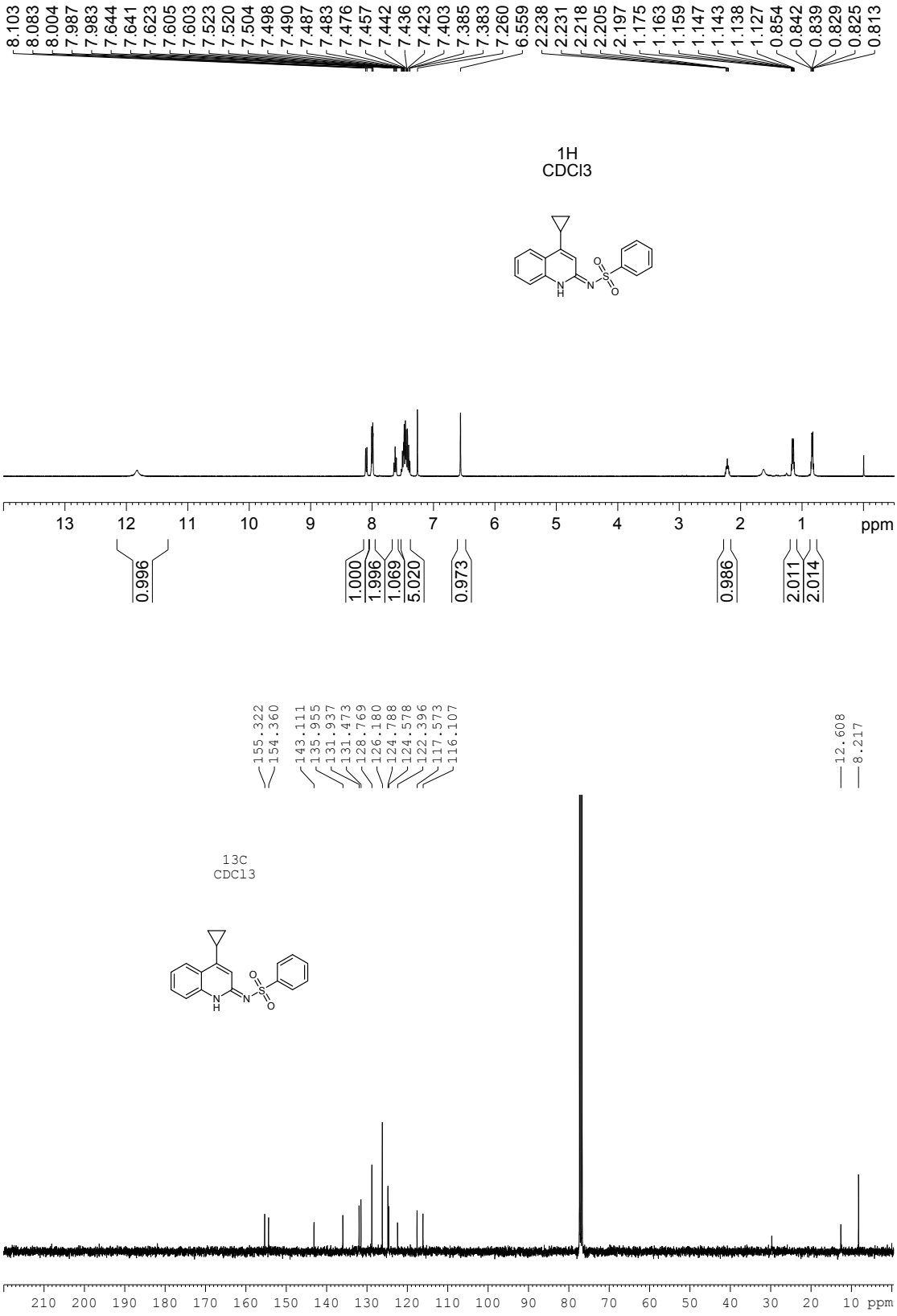
^{1}H NMR and ^{13}C NMR of compound **3c**



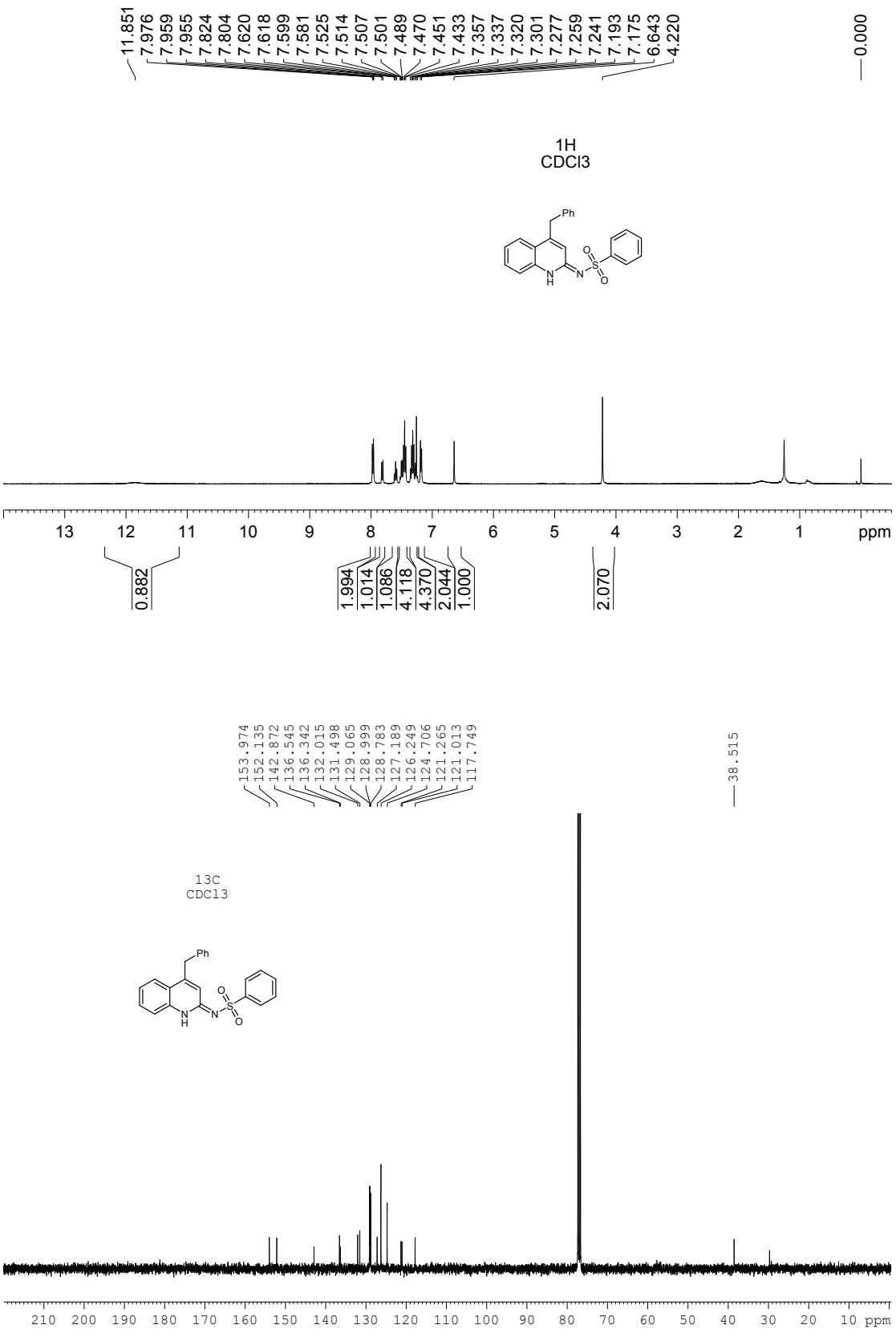
^{1}H NMR and ^{13}C NMR of compound **3d**



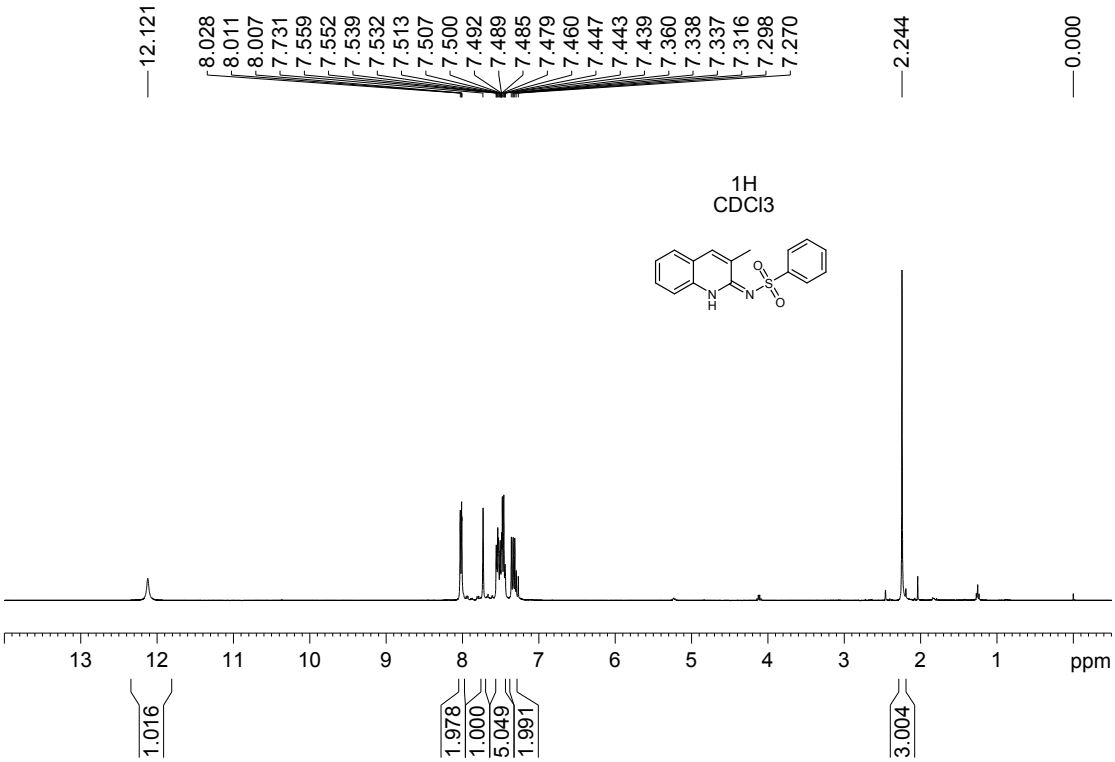
^{1}H NMR and ^{13}C NMR of compound **3e**

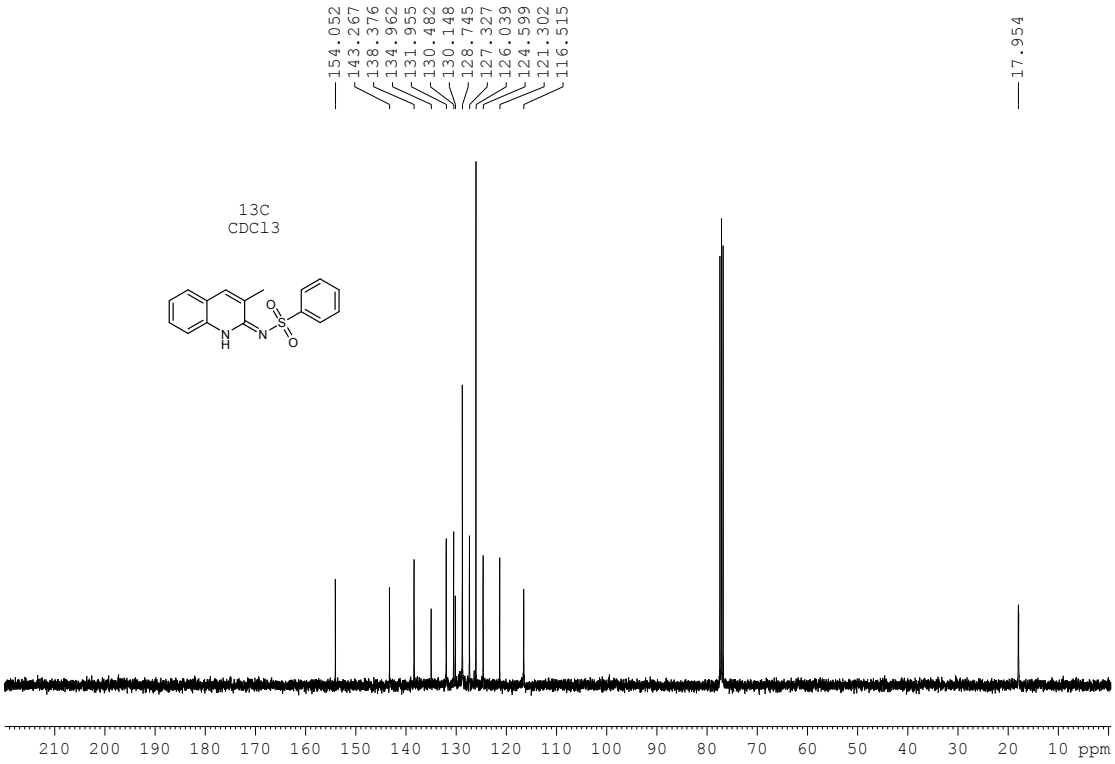


^{1}H NMR and ^{13}C NMR of compound **3f**

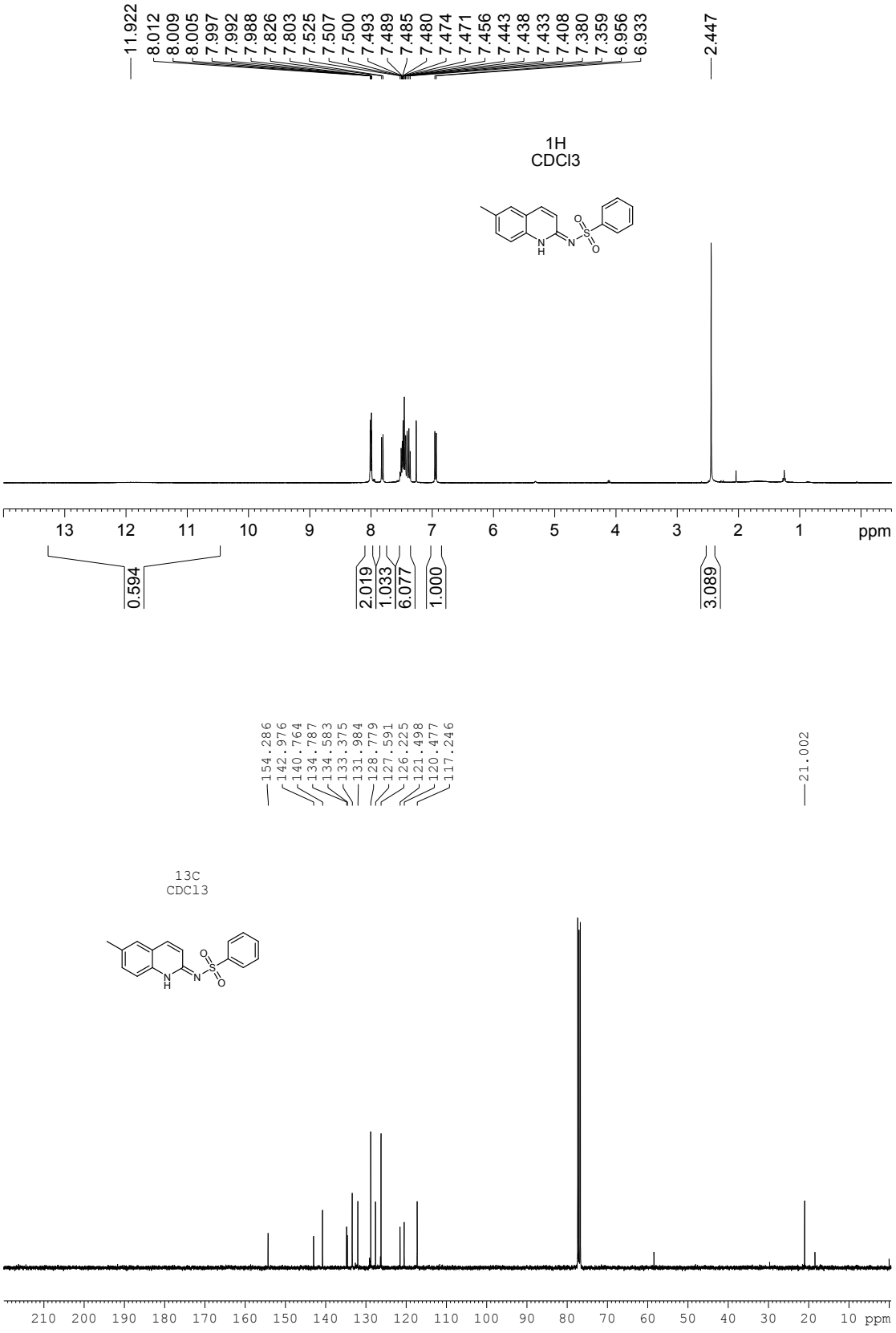


^{1}H NMR and ^{13}C NMR of compound **3g**

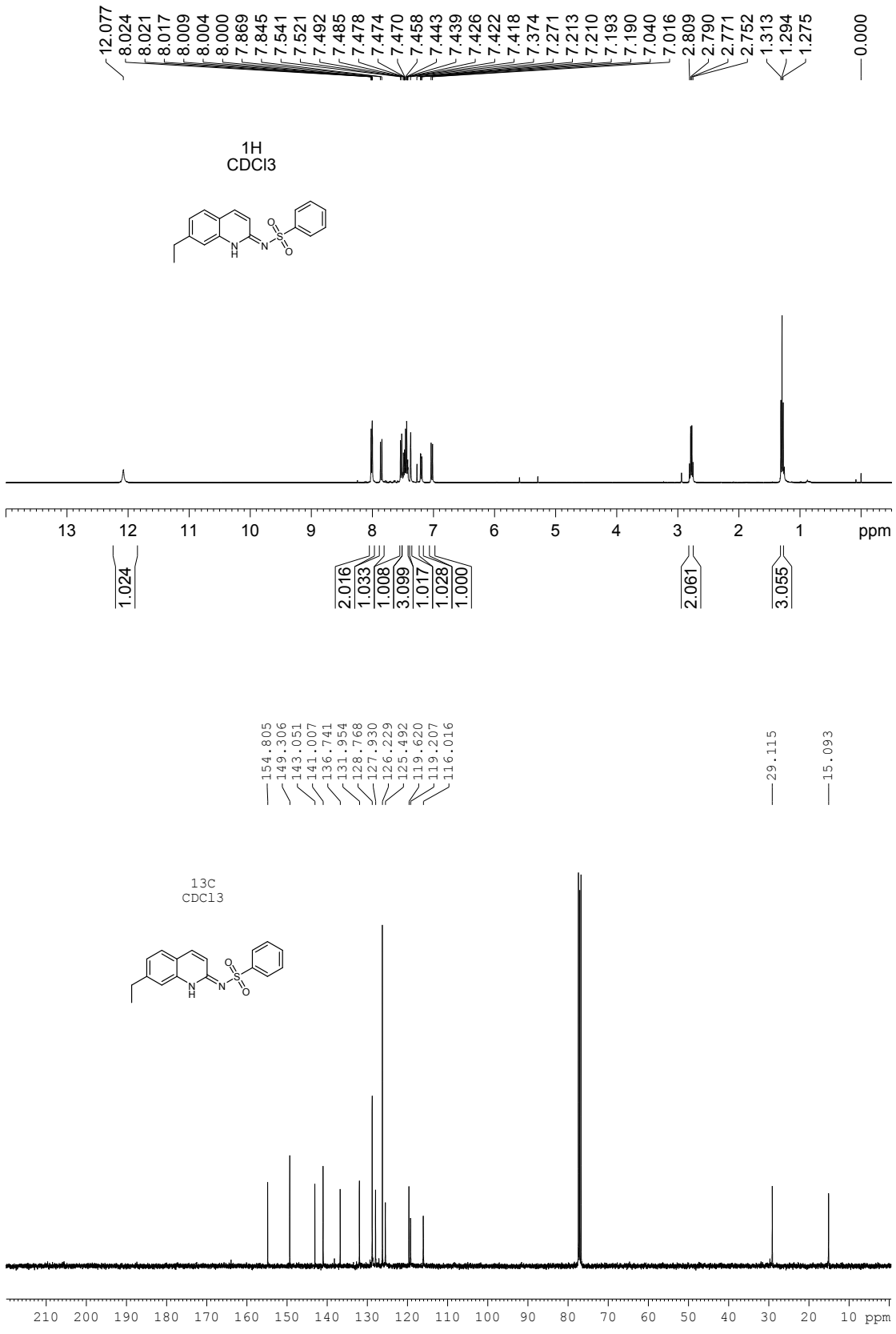




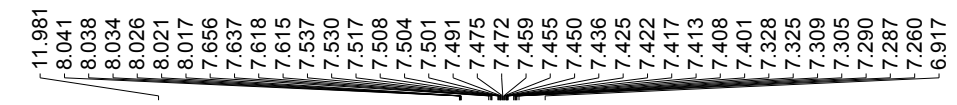
^{1}H NMR and ^{13}C NMR of compound **3h**

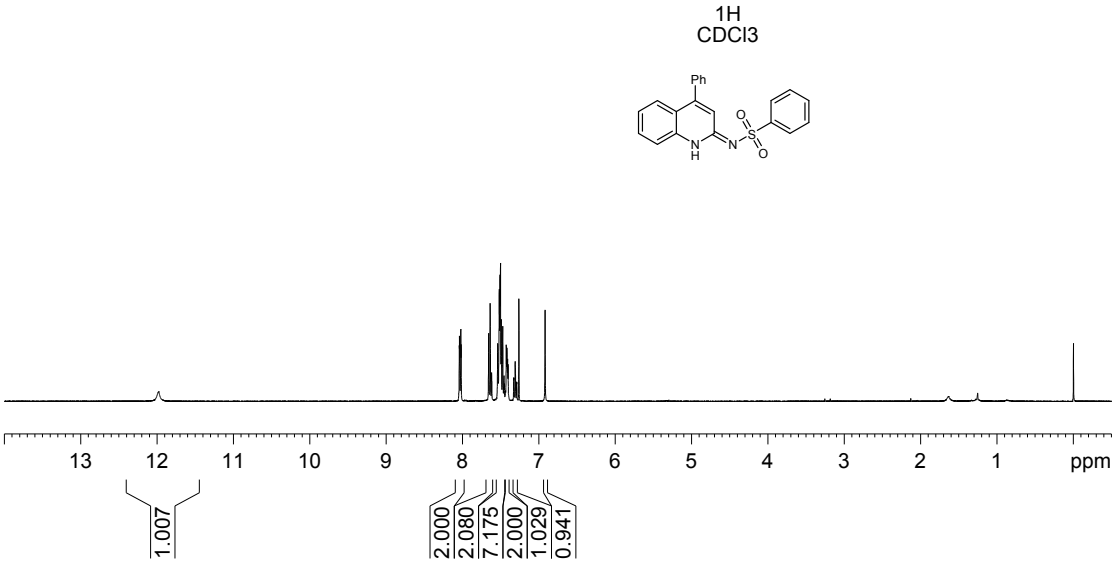


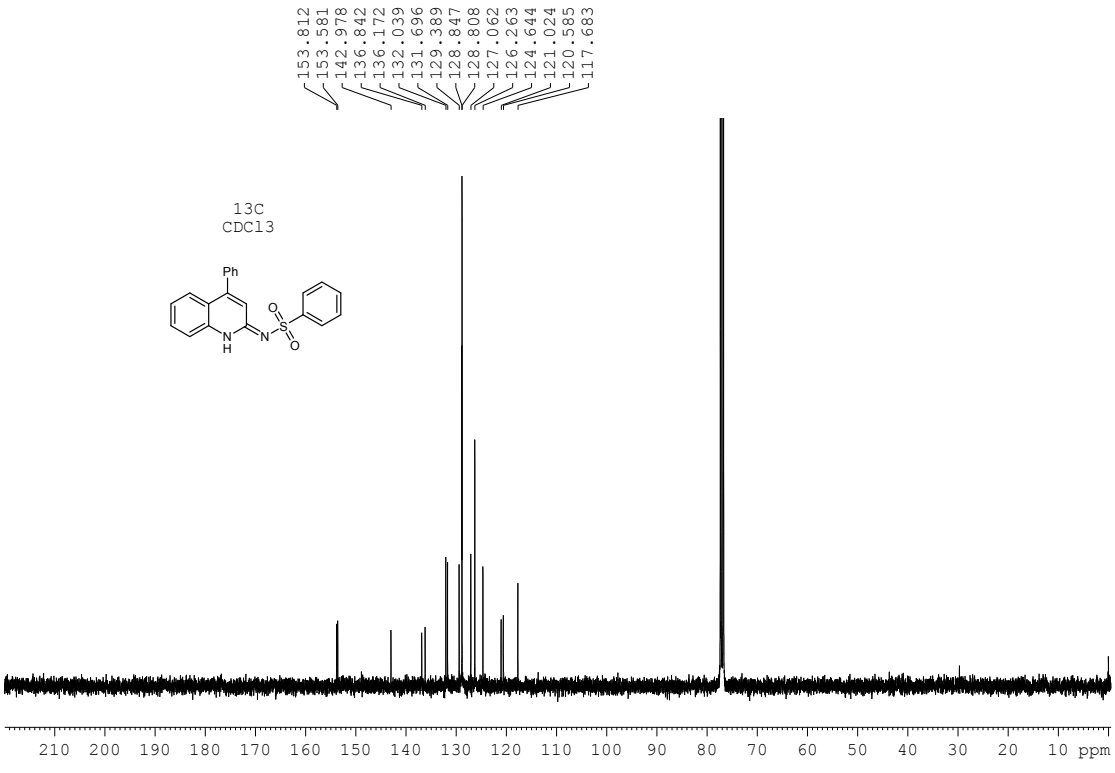
^{1}H NMR and ^{13}C NMR of compound **3i**



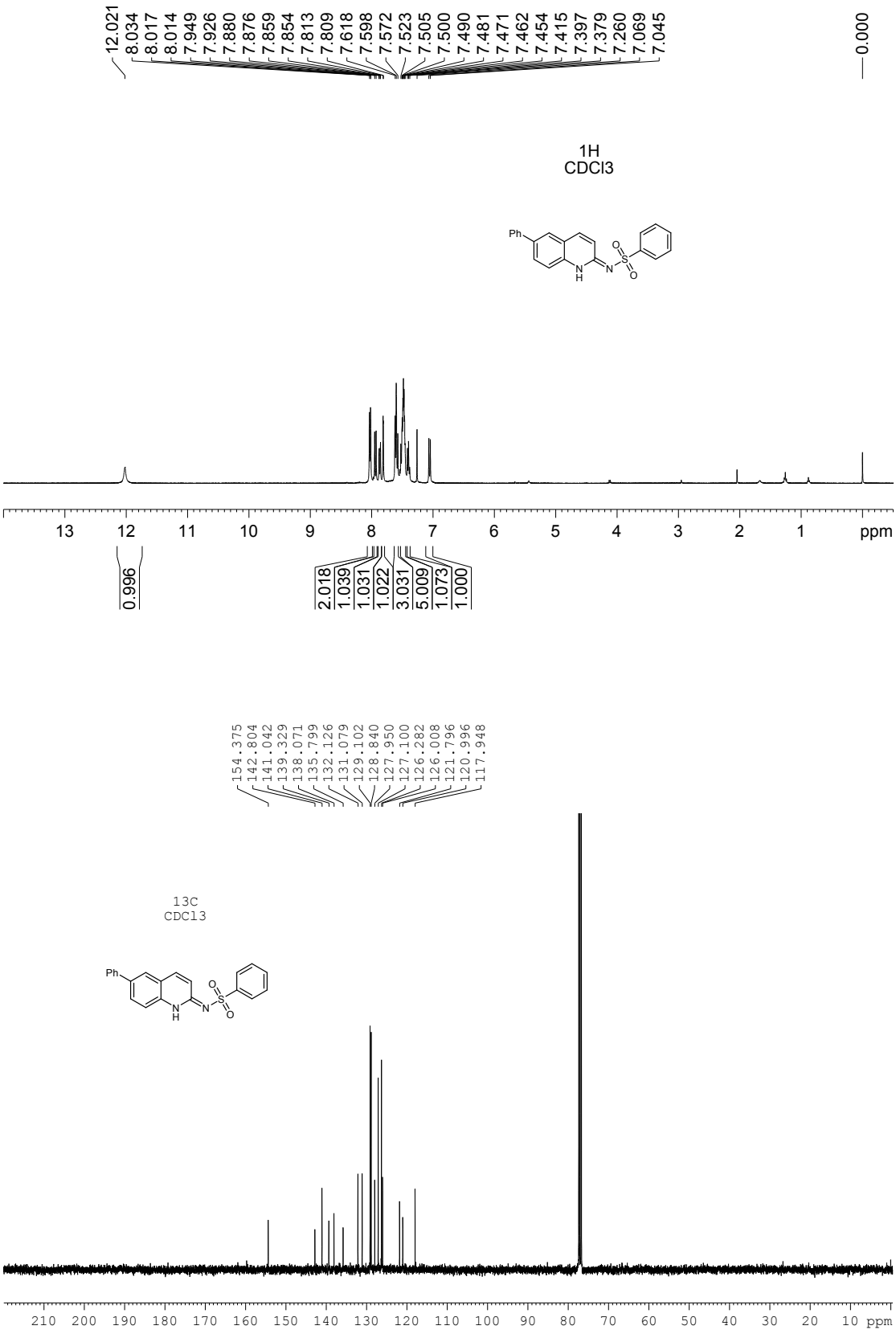
^{1}H NMR and ^{13}C NMR of compound **3j**



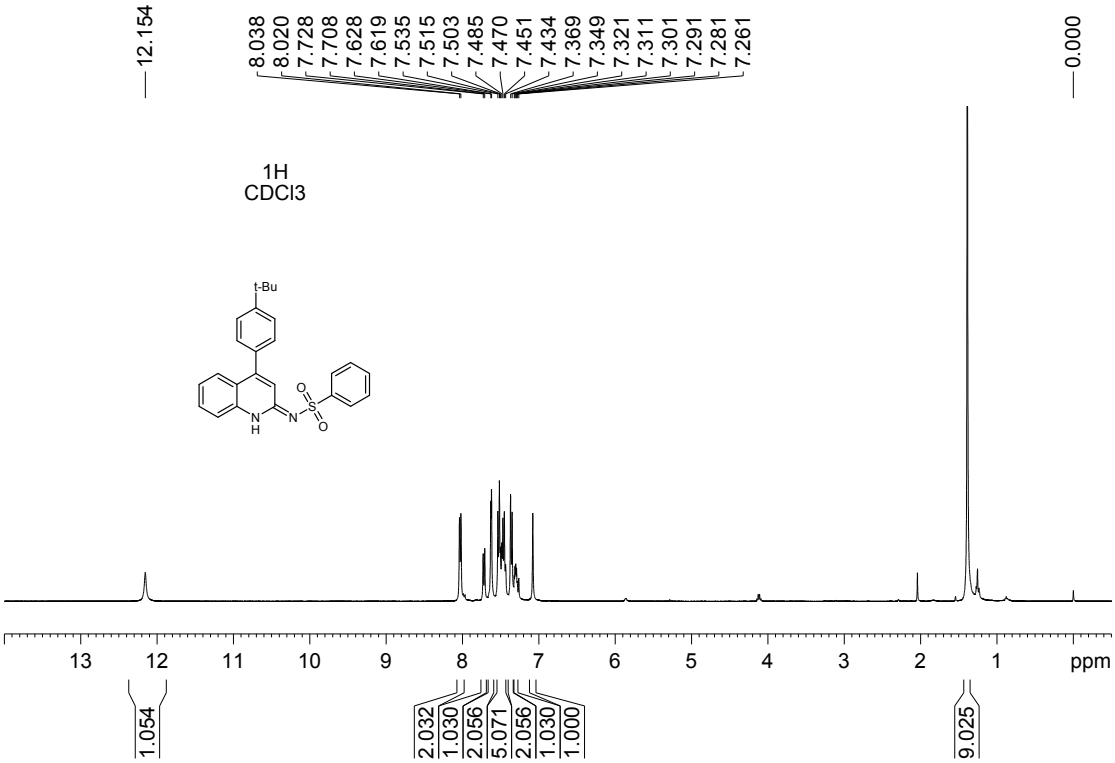


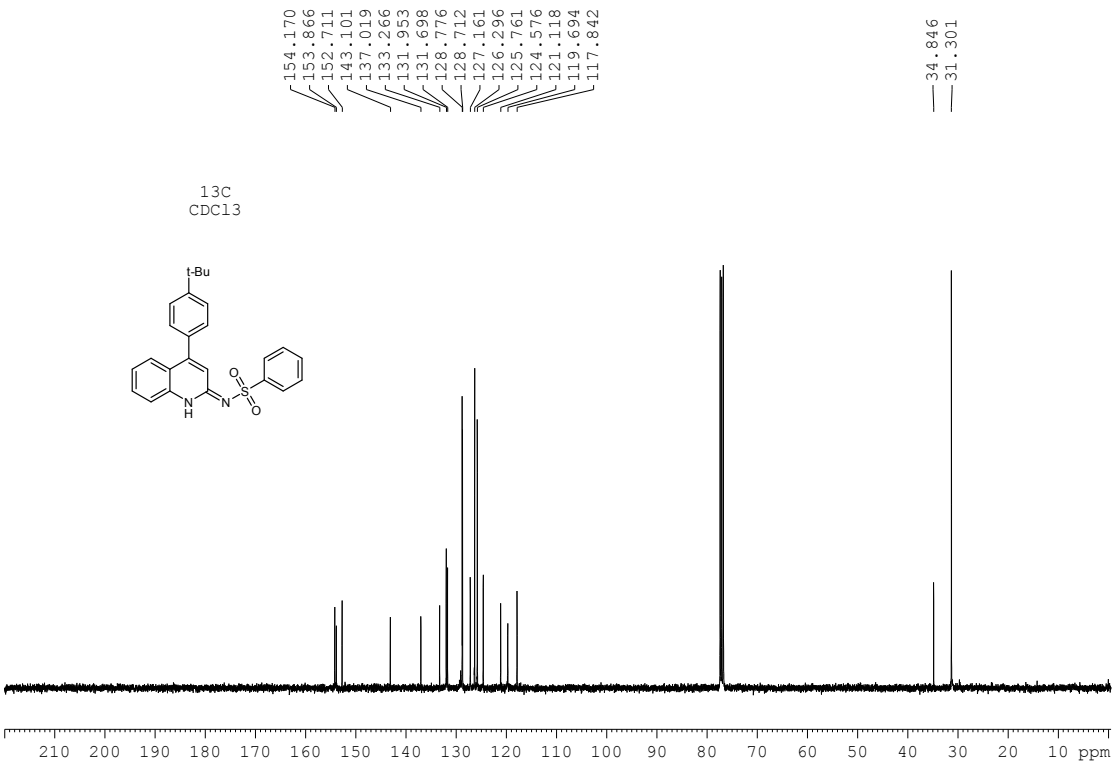


^{1}H NMR and ^{13}C NMR of compound **3k**

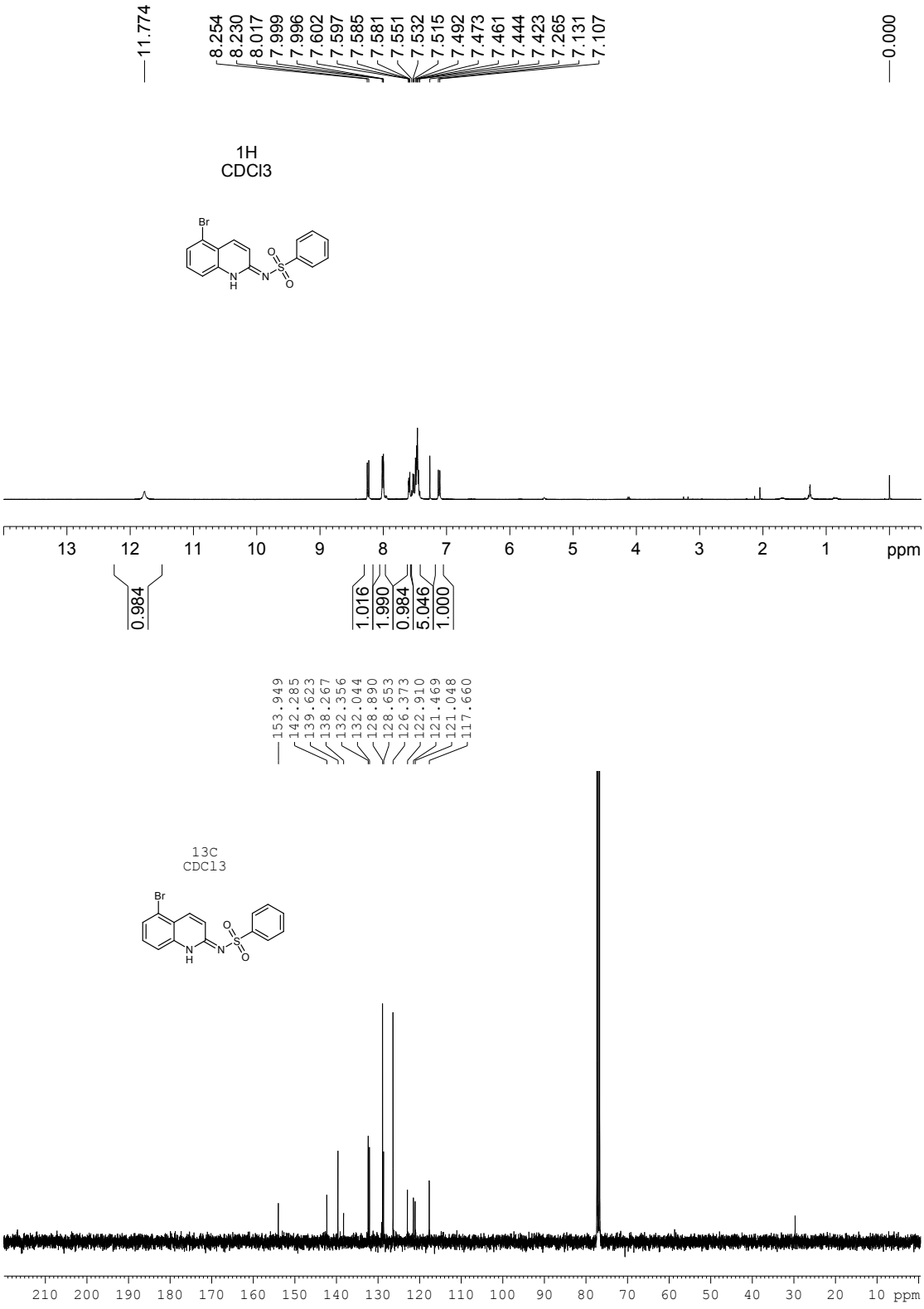


^{1}H NMR and ^{13}C NMR of compound **3l**

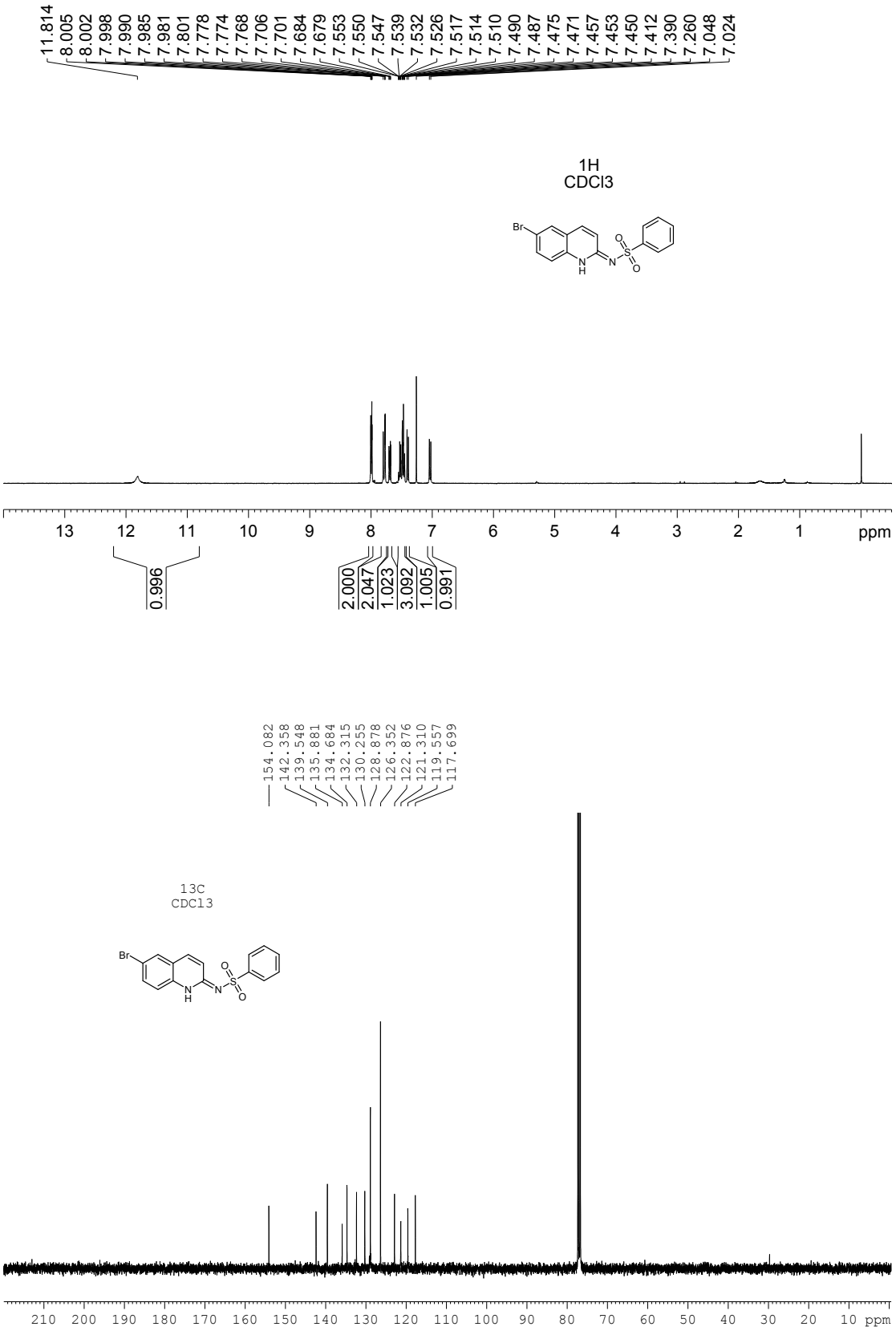




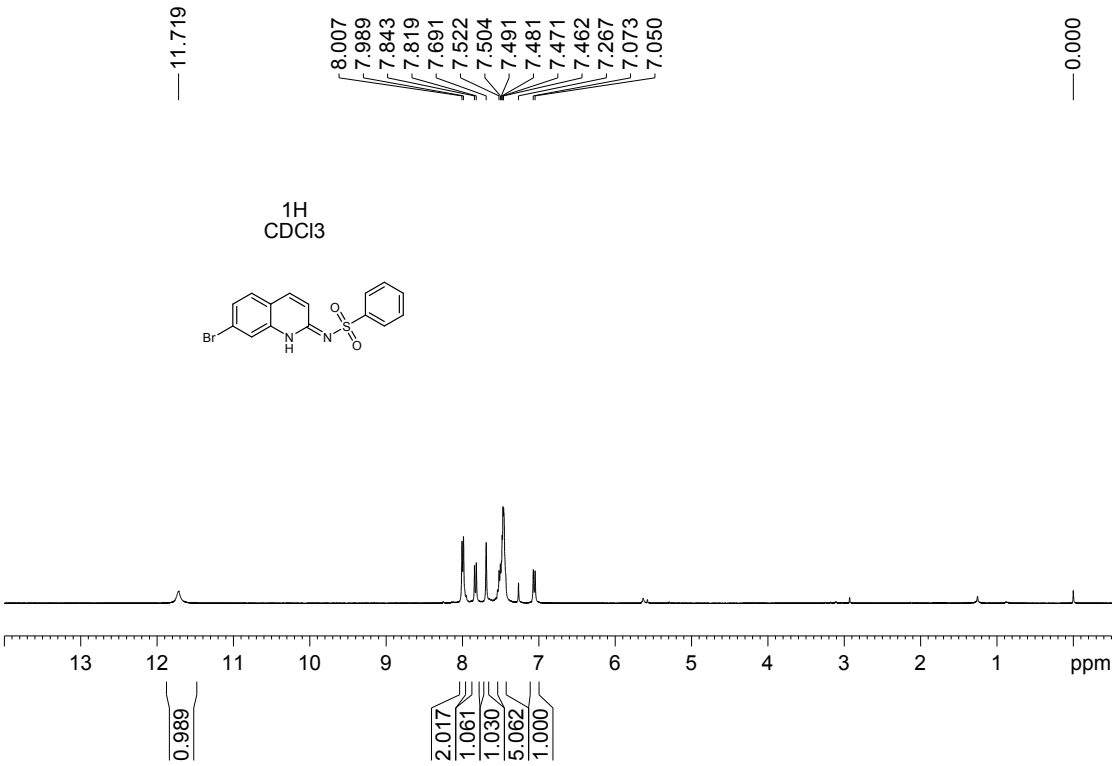
^{1}H NMR and ^{13}C NMR of compound **3m**

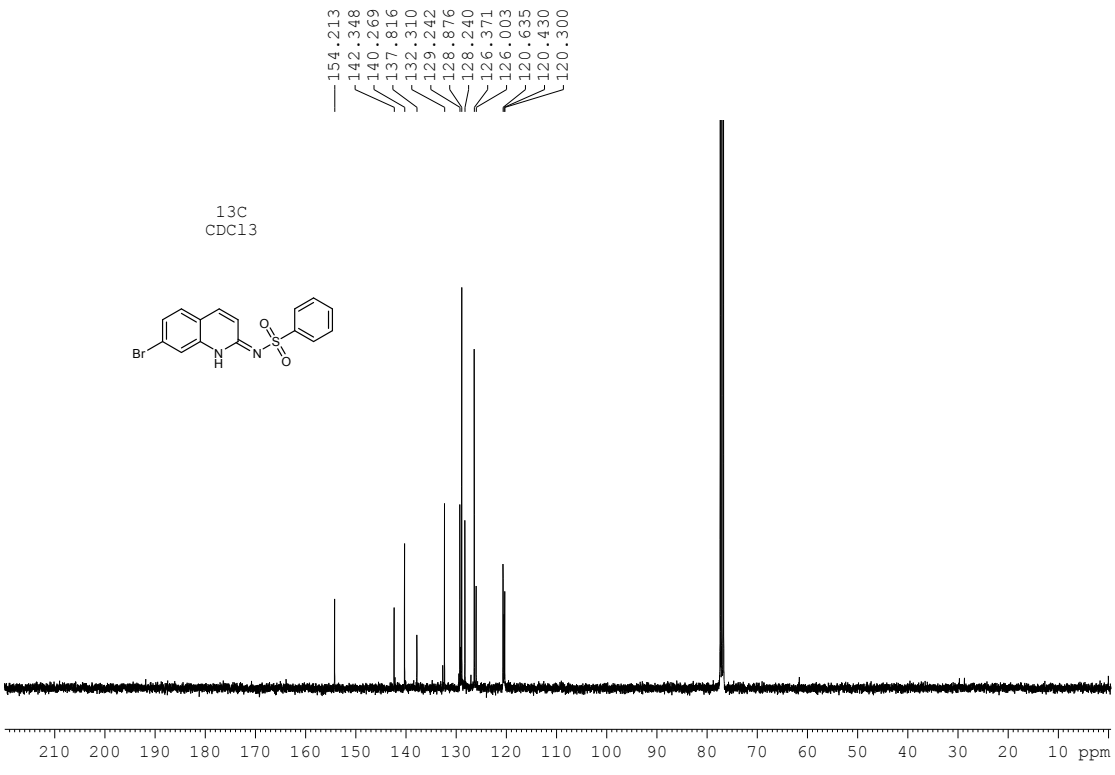


^{1}H NMR and ^{13}C NMR of compound **3n**

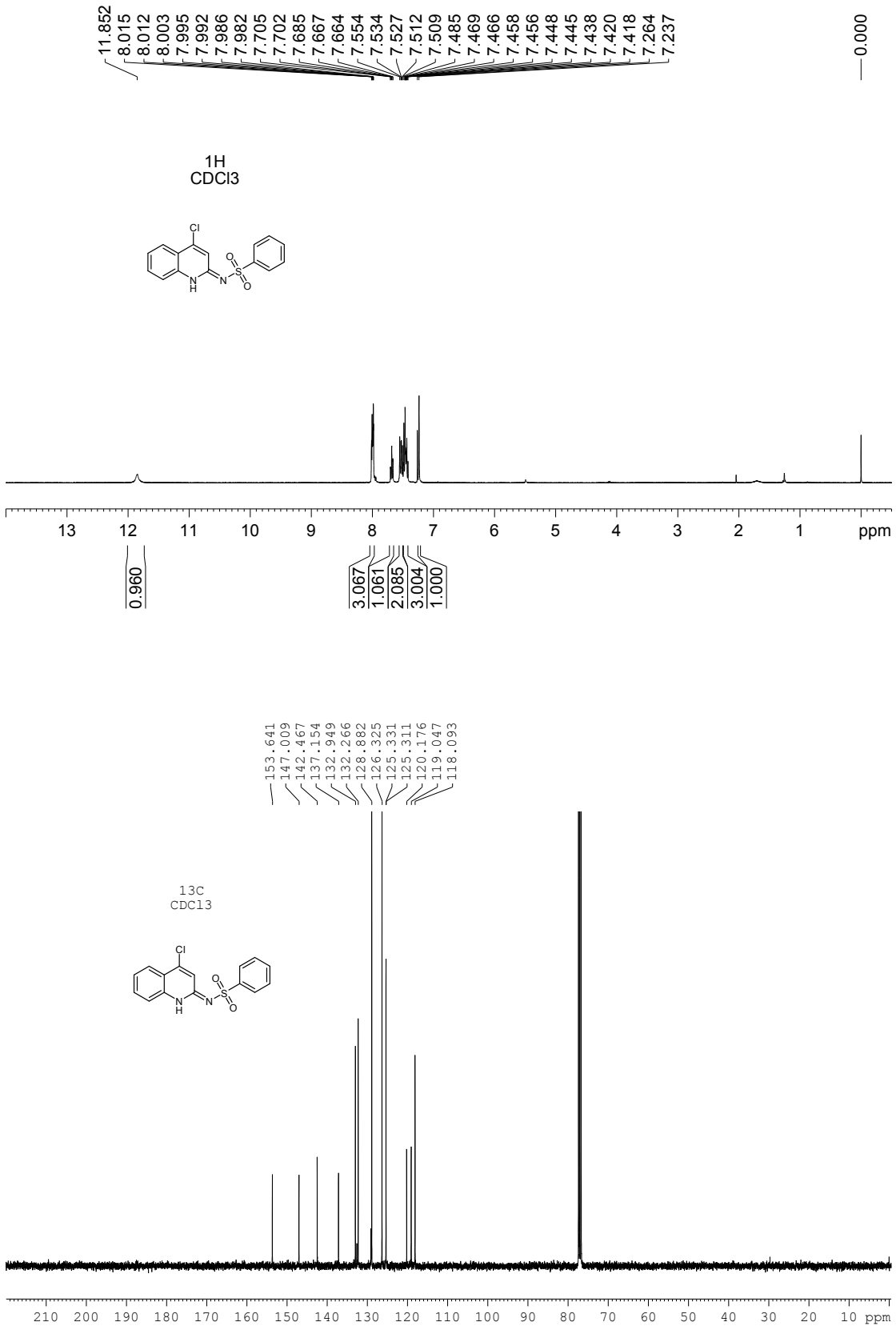


^{1}H NMR and ^{13}C NMR of compound **3o**

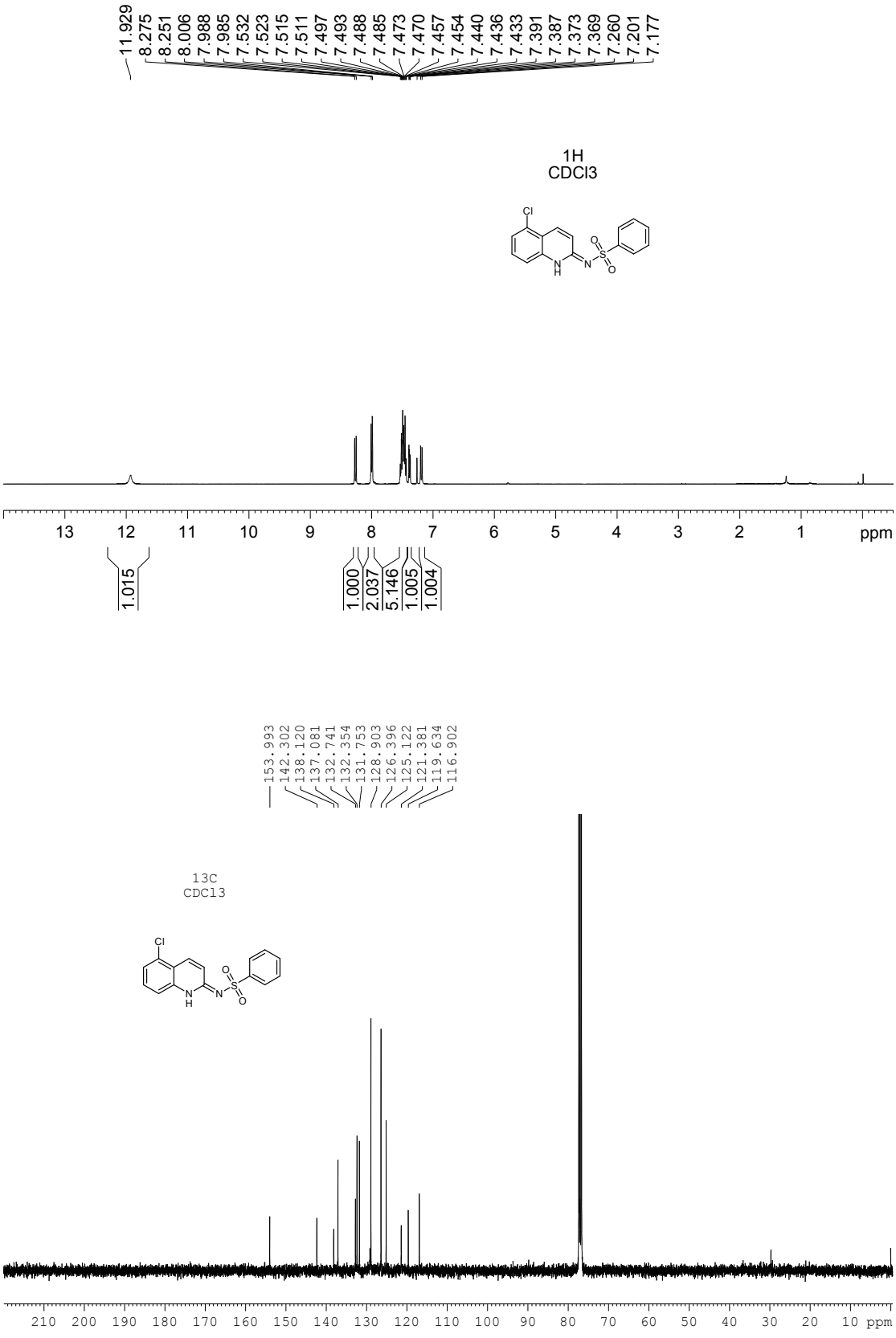




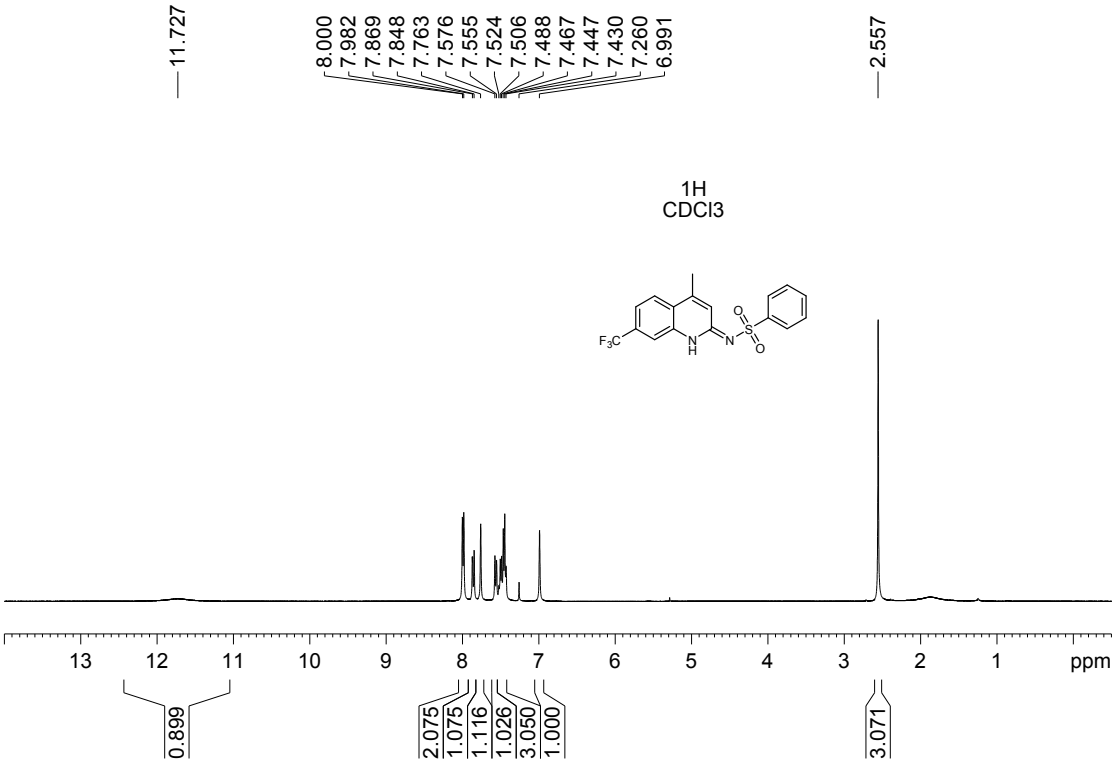
^{1}H NMR and ^{13}C NMR of compound **3p**

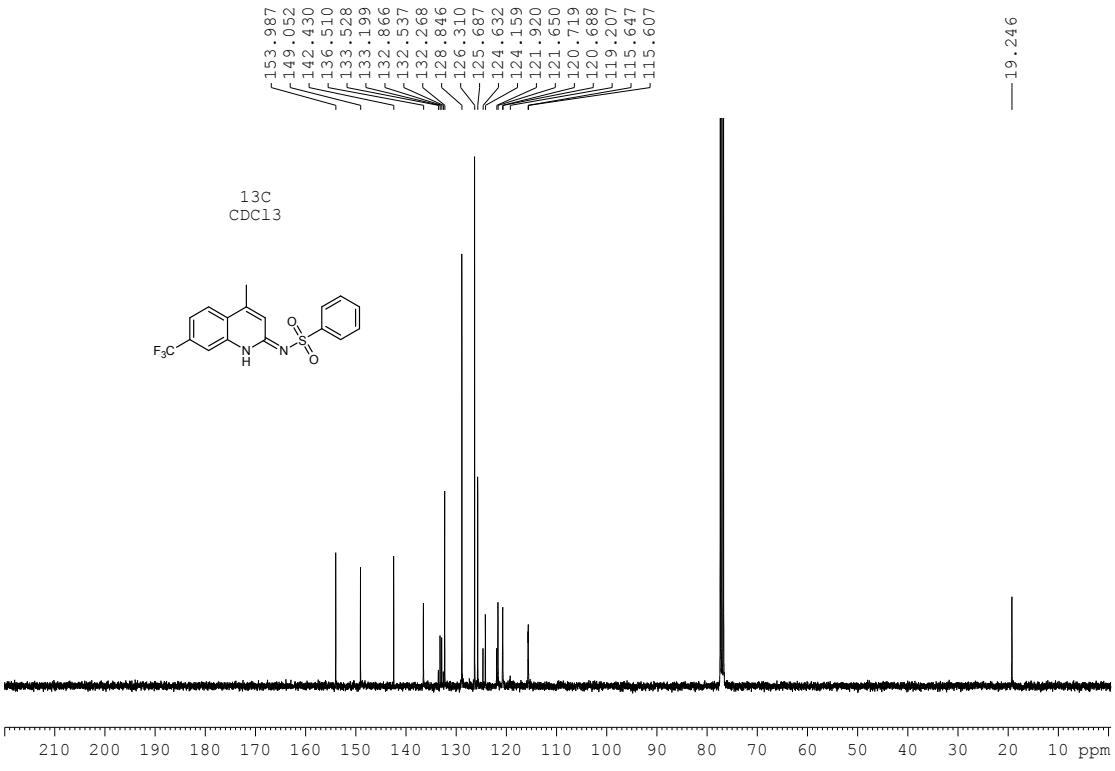


^{1}H NMR and ^{13}C NMR of compound **3q**

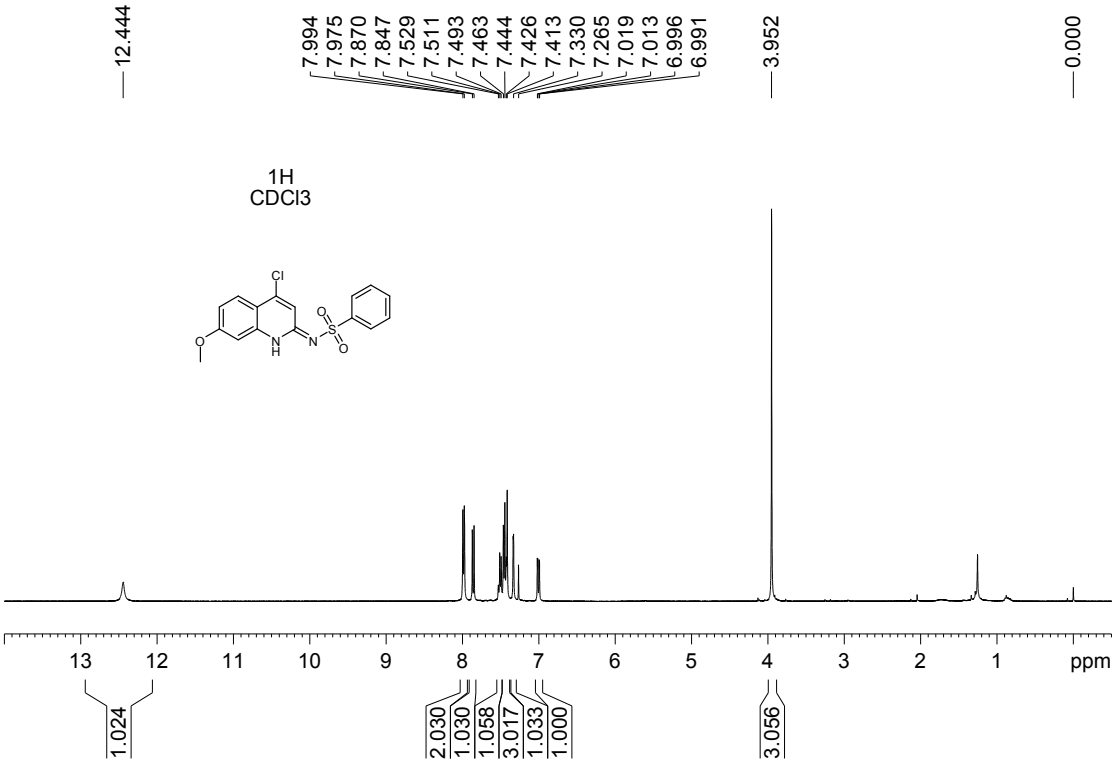


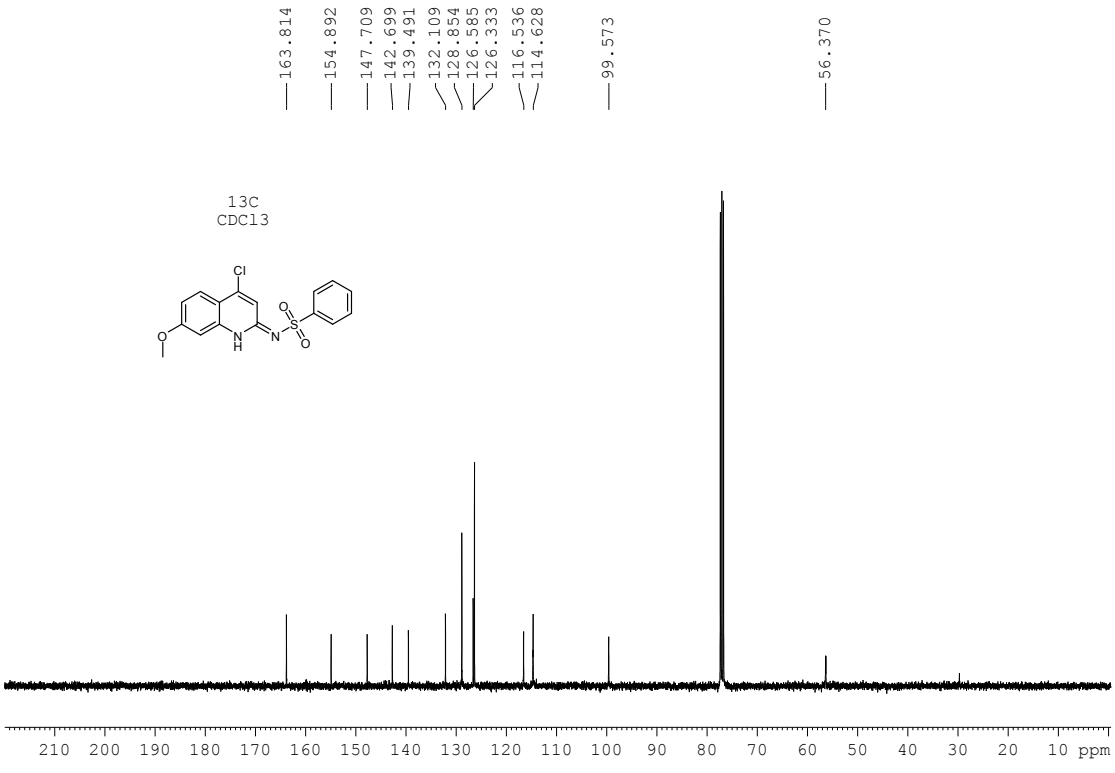
^{1}H NMR and ^{13}C NMR of compound **3t**



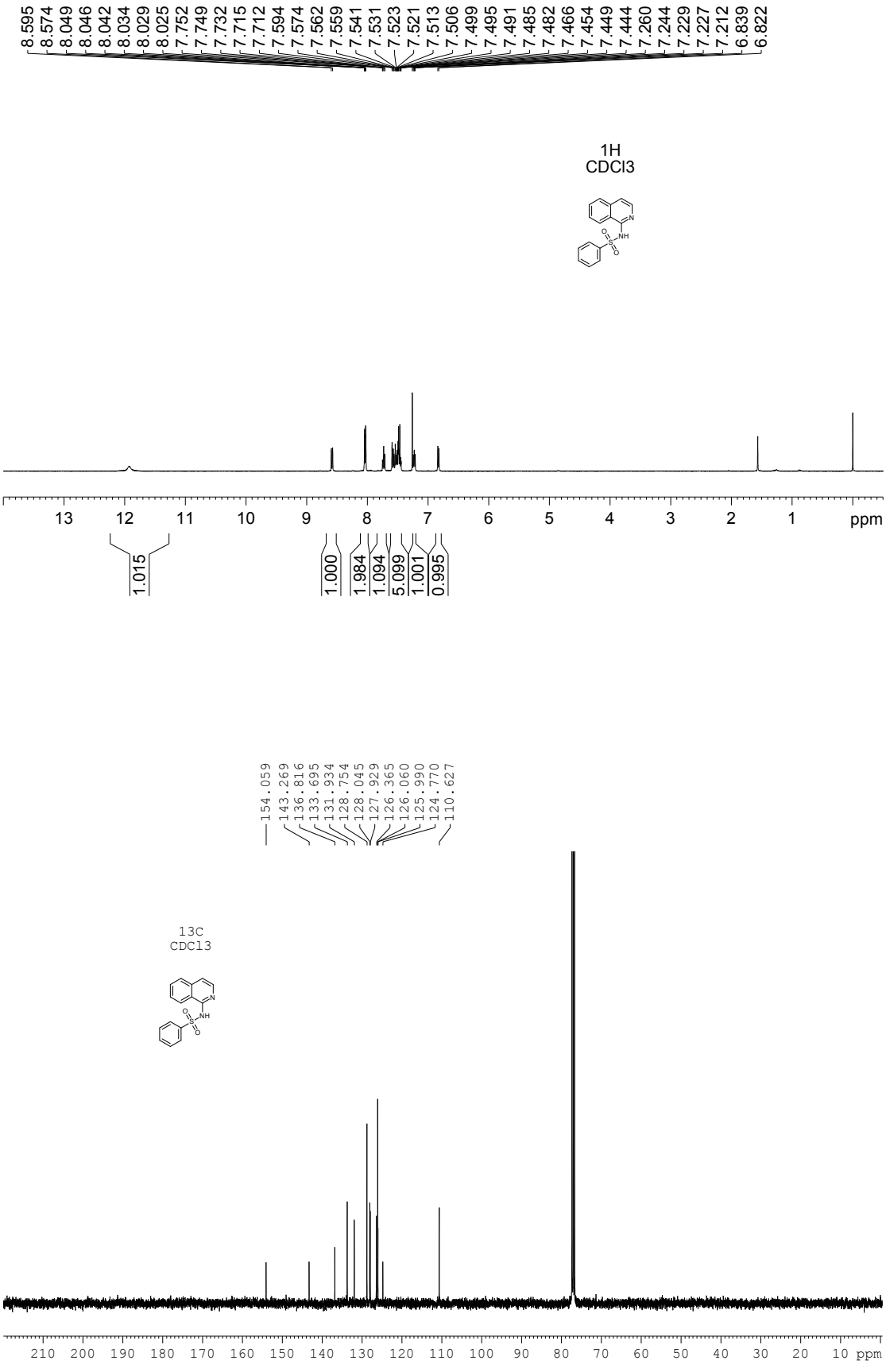


^{1}H NMR and ^{13}C NMR of compound **3v**

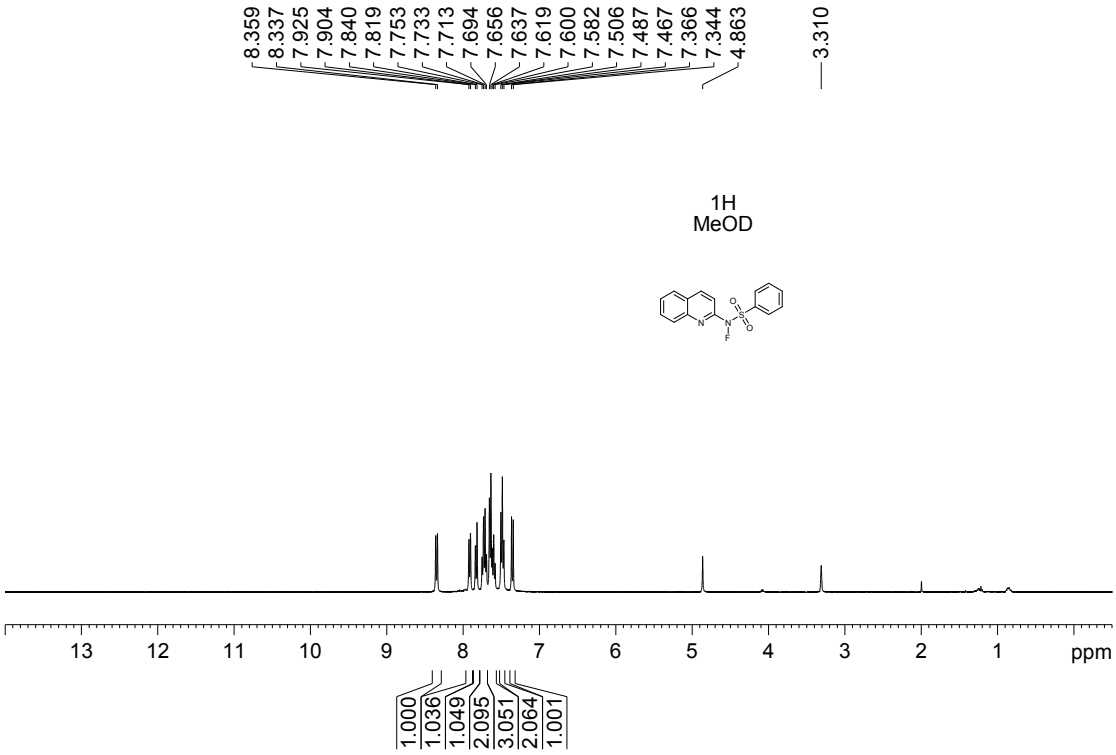


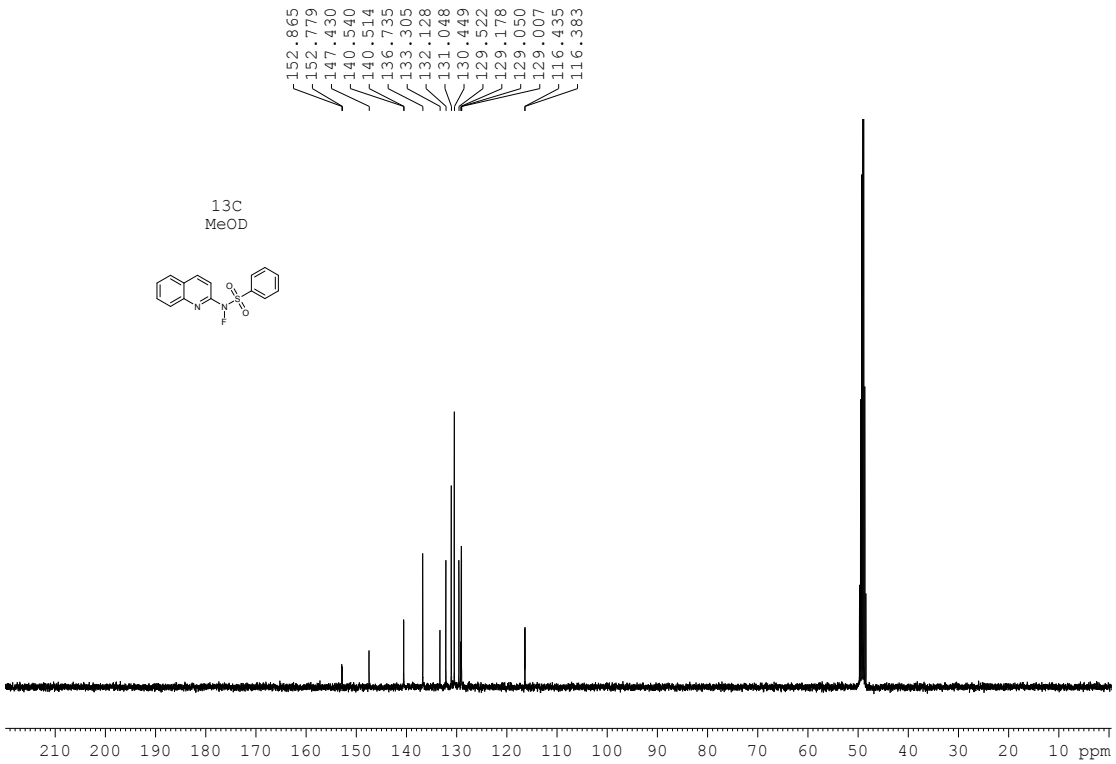


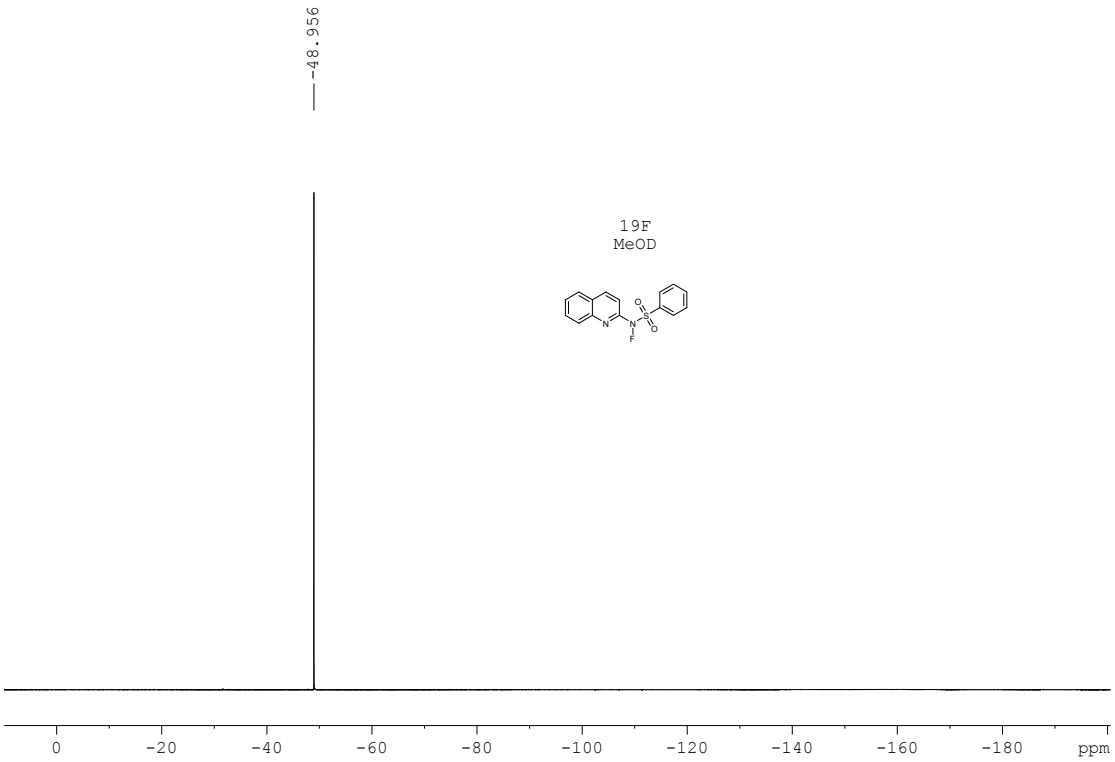
^{1}H NMR and ^{13}C NMR of compound **3w**



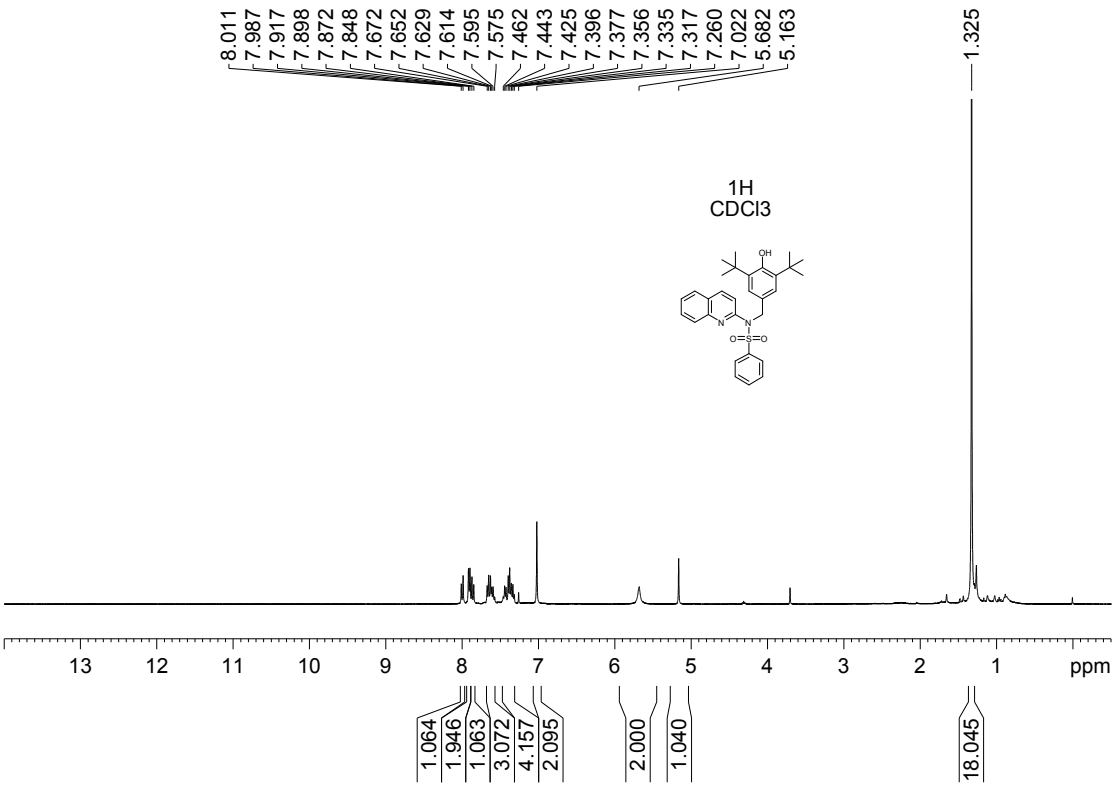
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of compound **7**

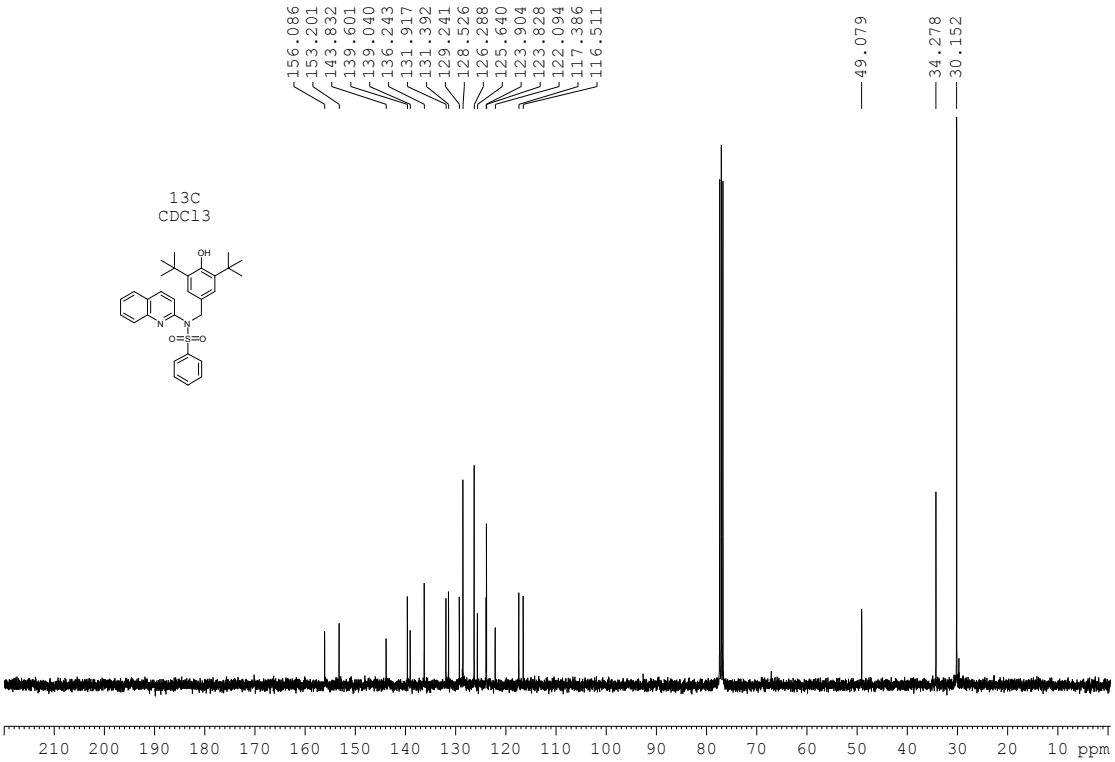






^{1}H NMR and ^{13}C NMR of compound **8**

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116.511
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13C
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