Supporting Information

Olefin skeletal rearrangement enabling access to multiarylated *N*-sulfonyl amidines

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Contents

General information

EtOAc refers to ethyl acetate, PE refers to Petroleum Ethers (60-90 ºC), DCM refers to dichloromethane, THF refers to tetrahydrofuran, DMF refers to *N*,*N*-dimethylformamide. Unless otherwise stated, all other starting materials and solvents were commercially available and used without further purification. Dried THF was delivered from an Innovation Technology solvent system. ^{1}HNMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, 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.

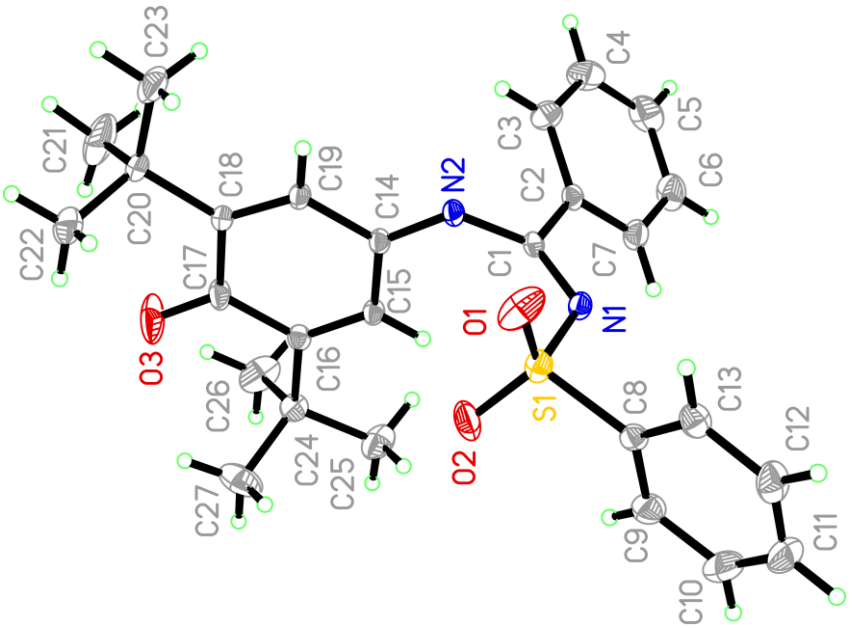


Figure S1. X-Ray Structure of **3a** (CCDC 2310727)

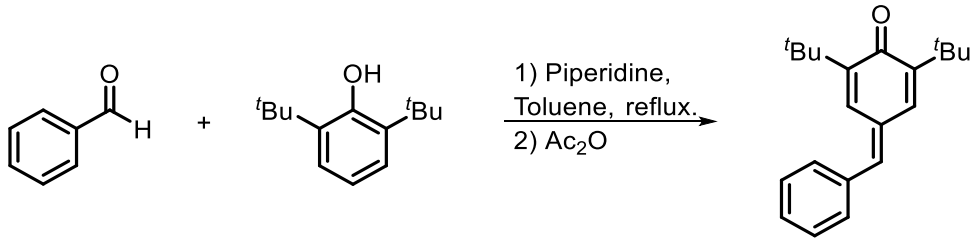
A single crystal **3a** was obtained by slowly evaporating the mixed solvent of dichloromethane and hexane (V/V 1:10) at room temperature under air conditions. Its dimensions of 0.31 mm × 0.22 mm × 0.14 mm was mounted on a Siemens P1 diffractometer equipped with a graphite mono-chromated MoKa (λ = 0.71073 Å) radiation at 298(2) K. A total of 42129 reflections were collected in the 2.52 <θ< 35.08 º range by using an ω scan mode and 11291 were independent (R_{int} = 0.0356), of which 8080 with $I > 2\sigma(I)$ were observed. The calculations were performed with SHELXS-97 and SHELXS-97 programs and corrections for *Lp* factors and absorptions were applied. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were determined by theoretical calculations. The final cycle of refinement gave R = 0.0630 and wR = 0.1617 (w = $1/[\sigma^2(F_o^2)+(0.1038\,P)^2+0.2838P]$, where $P = (F_o^2+2F_c^2)/3$). S = 1.074, $(\triangle/\sigma)_{max}$ = 0.000, $(\triangle\rho)_{min}$ = 0.378 e/Å^3 and $(\triangle\rho)_{max}$ = -0.372 e/Å^3.

The crystal of compound **3a** belongs to Orthorhombic, space group *P2(1)2(1)2(1)* with a = 9.7941(9) Å, b = 11.2385(11) Å, c = 23.348(2) Å, $\alpha = \beta = \gamma = 90^o$, V = 2569.9(4) Å^3, Mr = 462.59, Z = 4, Dc = 1.196 g/cm^3, μ(Mo$K\alpha$) = 0.155 mm^{-1}, F(000) = 984, the final R = 0.0630 and wR = 0.1617.

General information

General procedure for the synthesis of compounds 1[1]:

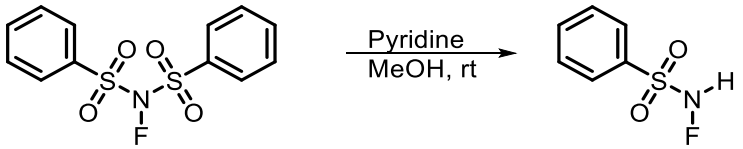
General Procedure for **1a-1r**:



In a Dean−Stark apparatus, a mixture of aldehyde (25.0 mmol, 1.0 equiv) and 2,6-di-*tert*-butylphenol (25.0 mmol, 1.0 equiv) in toluene (100 mL) was placed and refluxed. Piperidine (50.0 mmol, 4.94 mL) was added to this reaction mixture in a dropwise manner within an hour, and the resultant mixture was stirred at reflux temperature for 12 h. The reaction mixture was cooled to 100 °C, and after acetic anhydride (50.0 mmol, 2.55 g) was added, the resulting solution was stirred for 30 minutes at the same temperature. The reaction mixture was then cooled to room temperature, poured into ice-cold water (500 mL), and extracted with dichloromethane (DCM) (200 mL × 3). The combined organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to obtain pure p-quinone methides (PE/EtOAc).

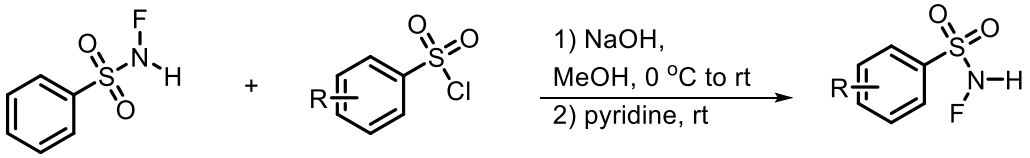
General procedure for the synthesis of compounds 2[2]:

General Procedure for **2**:



A 100 mL flask was charged with NFSI (15.8 g, 50 mmol) and MeOH (30 mL). Pyridine (4.9 mL, 60 mmol) was added via a syringe with stirring. The reaction mixture was stirred at room temperature until the insoluble NFSI was dissolved completely. The solution was diluted with EtOAc. The organic phase was washed with 2 M HCl (2 × 30 mL), water, and brine successively, and dried over anhydrous Na_2SO_4. The organic solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EtOAc = 5:1) to give product 1 as a pale yellow oil (7.26 g, 83% yield).

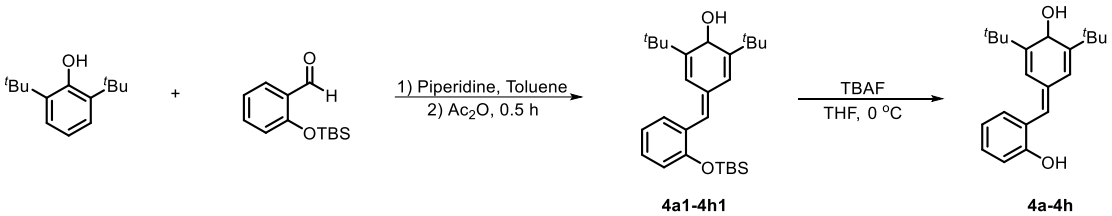
General Procedure for **2a, 2b**:



To the solution of $PhSO_2NHF$ (876 mg, 5 mmol) in MeOH (2 mL), the solution of NaOH (200 mg, 5 mmol) in MeOH (3 mL) was added at 0 °C slowly. The solution was stirred at 0 °C for 30 min, followed by adding $ArSO_2Cl$ (6 mmol) slowly. Precipitate formed quickly, and the reaction was stirred for 4 h at room temperature. Then, pyridine (0.8 mL, 10 mmol) was added and stirred overnight. EtOAc and water was added for dilution. The organic phase was washed with 2 M HCl (2 × 5 mL), water and brine successively, and dried over anhydrous Na_2SO_4. The organic solvent was removed under reduced pressure. The residues were purified by column chromatography on silica gel (PE/EtOAc) to obtain *N*-fluoroarenesulfonamides (**2a-b**) as white or pale yellow solid.

General procedure for the synthesis of compounds 4[3]:

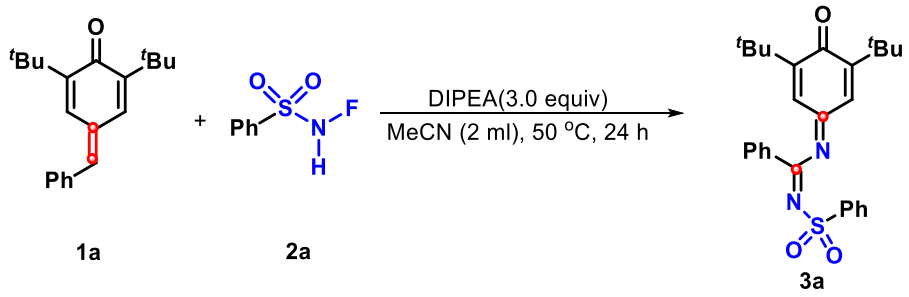
General Procedure for **4a-4h:**



4a1-4h1 **4a-4h**

A solution of phenols (1.1 equiv.) and aldehydes (1.0 equiv.) in toluene (5 mL/mmol substrate) was placed in a Dean-Stark apparatus which was heated to reflux. Piperidine (2.0 equiv.) was added dropwise slowly. Then, the temperature was raised to 140 ºC and stirred for 12 h. After that, the reaction mixture was cooled to 120 ºC and acetic anhydride (2.0 equiv.) was dropwise added. The stirring was continued for 30 min and the solution was poured on ice-water and extracted with CH_2Cl_2 (3 × 50 mL). The organic phases were combined, washed with brine and dried over anhydrous Na_2SO_4. Then the solvent was evaporated under reduced pressure and the corresponding products **4a1-4h1** were obtained after flash column chromatography (pentane/Et_2O = 100/1 to 30/1). To a solution of **4a1-4h1** (1.0 equiv.) in THF (10 mL/mmol substrate) at 0 ºC was added tetrabutylammonium fluoride trihydrate (1.1 equiv.). The reaction mixture was stirred for 10 min and a saturated NH_4Cl solution was added dropwise to quench the reaction. The resulting solution was extracted with Et_2O (3 × 20 mL). Then the combined organic phases were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed to give the crude product which was purified by flash column chromatography (pentane/Et_2O = 10/1 to 4/1) to afford the desired compounds **4a-4h**.

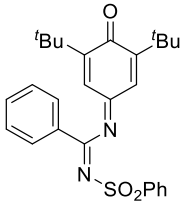
General procedure for the synthesis of compounds 3 and 5:



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

Add 4-benzylidene-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **1a** (0.2 mmol, 59 mg), *N*-fluorobenzenesulfonamide **2a** (0.6 mmol, 105 mg), DIPEA (0.6 mmol, 77 mg), and MeCN (4 mL) to a 10-mL reaction tube, and then the reaction system was stirred at 50 ºC (oil bath) for 24 hours. After the reaction was complete (monitored by TLC), the reaction system was concentrated by vacuum filtration, and the crude product was purified by flash silica gel column chromatography (PE/EtOAc = 25:1) to obtain pure product **3a** (77 mg, 85 %).

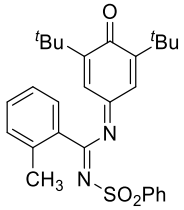
(Z)-N-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-N'-(phenylsulfonyl)benzimidamide (3a)



Orange solid; 77 mg, 85% yield; m.p. 83-85 ˚C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.61-7.55 (m, 2H), 7.54-7.48 (m, 2H), 7.47-7.41 (m, 2H), 6.64 (s, 2H), 1.26 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 186.3, 168.9, 157.6, 156.5, 141.2, 134.0, 132.8, 132.2, 129.1, 129.0, 128.8, 128.3, 127.6, 36.1,

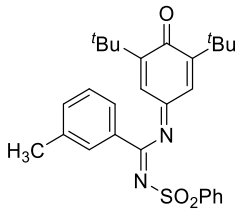
29.5. **IR** (KBr, *v*, cm^{-1}): 3307, 2961, 1644, 1518, 1293, 1056, 825. **HRMS** (ESI) m/z calcd for $C_{27}H_{31}N_2O_3S$ $[M+H]^+$ 463.2055, found 463.2042.

(Z)-N-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-2-methyl-N'-(phenylsulfonyl)benzimidamide (3b)



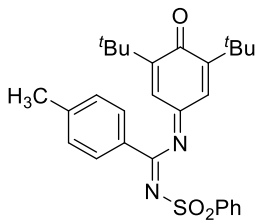
Orange solid; 19 mg, 21% yield; m.p. 87-89 ˚C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.55-7.46 (m, 3H), 7.40-7.33 (m, 1H), 7.27-7.19 (m, 4H), 6.70 (s, 2H), 2.56 (s, 3H), 1.27 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 186.1, 171.2, 156.2, 141.2, 133.6, 132.8, 132.2, 132.0, 130.0, 128.8, 128.5, 127.4, 126.2, 36.0, 29.4, 21.9. **IR** (KBr, *v*, cm^{-1}): 3318, 2961, 1654, 1538, 1267, 1086, 822, 578. **HRMS** (ESI) m/z calcd for $C_{28}H_{33}N_2O_3SNa$ $[M+Na]^+$ 499.2031, found 499.2025.

(Z)-N-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-3-methyl-N'-(phenylsulfonyl)benzimidamide (3c)



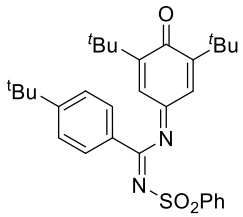
Orange solid; 76 mg, 81% yield; m.p. 83-85 ˚C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.72 (s, 1H), 7.55 (d, *J* = 7.1 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 3H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 6.62 (s, 2H), 2.37 (s, 3H), 1.26 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 186.3, 169.2, 157.4, 156.4, 141.1, 139.0, 135.0, 132.8, 132.0, 129.4, 128.8, 128.8, 128.3, 127.6, 126.5, 36.1, 29.5, 21.5. **IR** (KBr, *v*, cm^{-1}): 3064, 2870, 1655, 1536, 1321, 1107, 823, 589. **HRMS** (ESI) m/z calcd for $C_{28}H_{33}N_2O_3S$ $[M+H]^+$ 477.2212, found 477.2216.

(Z)-N-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-methyl-N'-(phenylsulfonyl)benzimidamide (3d)



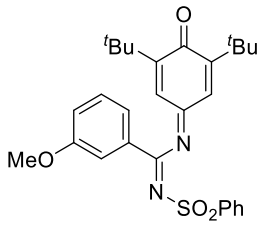
Orange solid; 56 mg, 59% yield; m.p. 87-89 ˚C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.58-7.53 (m, 1H), 7.51-7.46 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.62 (s, 2H), 2.40 (s, 3H), 1.25 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 186.3, 169.0, 157.4, 156.3, 145.2, 141.2, 132.7, 129.7, 129.2, 128.7, 128.3, 127.5, 36.0, 29.5, 21.8. **IR** (KBr, *v*, cm^{-1}): 3416, 2871, 1655, 1520, 1408, 1210, 1085, 854, 689. **HRMS** (ESI) m/z calcd for $C_{28}H_{33}N_2O_3S$ $[M+H]^+$ 477.2212, found 477.2205.

(Z)-4-(tert-butyl)-N-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-N'-(phenylsulfonyl)benzimidamide (3e)



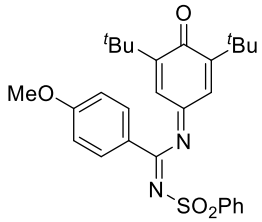
Orange solid; 70mg, 67% yield; m.p. 94-96 ˚C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.58-7.53 (m, 1H), 7.51-7.43 (m, 4H), 6.64 (s, 2H), 1.31 (s, 9H), 1.26 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 186.3, 168.9, 158.1, 157.3, 156.2, 141.2, 132.7, 129.2, 129.0, 129.0, 128.7, 128.3, 127.5, 125.9, 36.0, 35.3, 31.0, 29.5. **IR** (KBr, *v*, cm^{-1}): 3417, 2963, 1655, 1525, 1485, 1101, 905, 597. **HRMS** (ESI) m/z calcd for $C_{31}H_{39}N_2O_3S$ $[M+H]^+$ 519.2681, found 519.2678.

(Z)-N-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-3-methoxy-N'-(phenylsulfonyl)benzimidamide-(3f)



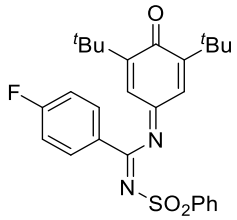
Orange solid; 70mg, 72% yield; m.p. 76-78 ˚C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.58-7.53 (m, 1H), 7.51-7.45 (m, 2H), 7.41 (s, 1H), 7.32-7.26 (m, 2H), 7.11-7.07 (m, 1H), 6.61 (s, 2H), 3.81 (s, 3H), 1.25 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 186.2, 168.8, 159.9, 157.4, 156.4, 141.0, 133.4, 132.8, 129.9, 128.7, 128.2, 127.5, 121.6, 119.8, 113.9, 55.6, 36.0, 29.4. **IR** (KBr, *v*, cm^{-1}): 3358, 2961, 1597, 1458, 1363, 1102, 905, 776. **HRMS** (ESI) m/z calcd for $C_{28}H_{34}N_2O_4S$ $[M+H]^+$ 493.2161, found 493.2165.

(Z)-N-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-methoxy-N'-(phenylsulfonyl)benzimidamide (3g)



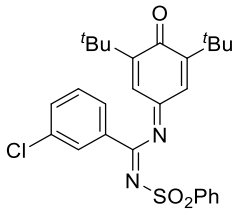
Orange solid; 69 mg, 69% yield; m.p. 100-102 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.55-7.50 (m, 1H), 7.49-7.43 (m, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.60 (s, 2H), 3.83 (s, 3H), 1.24 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 186.3, 168.8, 164.6, 157.5, 156.2, 141.4, 132.7, 131.5, 128.7, 128.3, 127.5, 123.9, 114.4, 55.7, 36.0, 29.5. **IR** (KBr, *v*, cm^{-1}): 3001, 2871, 1640, 1500, 1311, 1087, 786, 549. **HRMS** (ESI) m/z calcd for $C_{28}H_{34}N_2O_4S$ $[M+H]^+$ 493.2161, found 493.2160.

(Z)-N-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-fluoro-N'-(phenylsulfonyl)benzimidamide (3h)



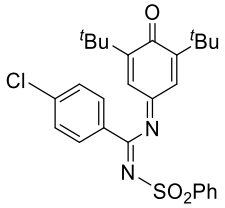
Orange solid; 53 mg, 55% yield; m.p. 140-142 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.86-7.81 (m, 2H), 7.59-7.54 (m, 1H), 7.51-7.46 (m, 2H), 7.13-7.08 (m, 2H), 6.62 (s, 2H), 1.25 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 186.1, 166.3 ($^{4}J_{CF}$ = 257.6 Hz), 157.8, 156.6, 141.0, 132.8, 131.7 ($^{2}J_{CF}$ = 9.4 Hz), 128.2 ($^{1}J_{CF}$ = 2.9 Hz), 127.5, 116.3 ($^{3}J_{CF}$ = 22 Hz), 36.0, 29.4. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -103.32. **IR** (KBr, *v*, cm^{-1}): 3417, 2952, 1654, 1523, 1345, 1176, 822, 618. **HRMS** (ESI) m/z calcd for $C_{27}H_{30}FN_2O_3S$ $[M+H]^+$ 481.1961, found 481.1966.

(Z)-3-chloro-N-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-N'-(phenylsulfonyl)benzimidamide (3i)



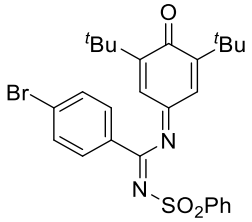
Orange solid; 43 mg, 45% yield; m.p. 148-150 ˚C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.85 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.55-7.49 (m, 3H), 7.40-7.36 (m, 1H), 6.64 (s, 2H), 1.28 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 186.1, 167.3, 158.0, 156.8, 140.8, 135.2, 134.0, 133.8, 132.9, 130.2, 128.8, 128.1, 127.5, 127.2, 36.1, 29.5. **IR** (KBr, *v*, cm^{-1}): 3068, 2871, 1655, 1534, 1365, 1161, 822, 553. **HRMS** (ESI) m/z calcd for $C_{27}H_{30}ClN_2O_3S$ $[M+H]^+$ 497.1666, found 497.1680.

(Z)-4-chloro-N-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-N'-(phenylsulfonyl)benzimidamide (3j)



Orange solid; 76 mg, 77% yield; m.p. 153-155 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 14.4 Hz, 1H), 7.53-7.47 (m, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 6.62 (s, 2H), 1.26 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 186.2, 167.7, 157.9, 156.7, 141.0, 140.7, 133.0, 130.6, 130.4, 130.4, 129.4, 128.8, 128.1, 127.6, 36.1, 29.5. **IR** (KBr, *v*, cm^{-1}): 3510, 2956, 1654, 1528, 1355, 1085, 878, 566. **HRMS** (ESI) m/z calcd for $C_{27}H_{30}ClN_2O_3S$ $[M+H]^+$ 497.1666, found 497.1636.

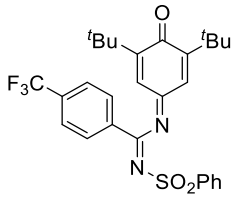
(Z)-4-bromo-N-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-N'-(phenylsulfonyl)benzimidamide (3k)



Orange solid; 71 mg, 66% yield; m.p. 189-191 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.59-7.52 (m, 3H), 7.51-7.45 (m, 2H), 6.61 (s, 2H), 1.24 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 186.1, 167.8, 157.8, 156.6, 140.9, 132.9, 132.3, 131.0, 130.4, 129.4, 128.8, 128.1, 127.5, 36.0, 29.5. **IR** (KBr, *v*, cm^{-1}): 2995, 1655, 1521, 1394, 1276, 1087, 849, 577. **HRMS** (ESI) m/z calcd for $C_{27}H_{30}BrN_2O_3S$ $[M+H]^+$ 541.1161, found 541.1162.

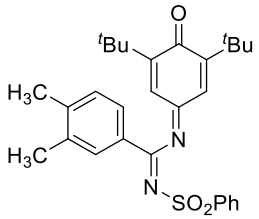
(Z)-N-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-N'-(phenylsulfonyl)-4-(trifluoromethyl)benzimidamide

(3l)



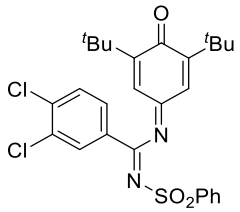
Orange solid; 55 mg, 51% yield; m.p. 115-117 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.98-7.93 (m, 4H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.61-7.57 (m, 1H), 7.54-7.49 (m, 2H), 6.65 (s, 2H), 1.27 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 186.1, 167.1, 158.1, 157.0, 140.7, 135.7, 135.7, 135.7, 135.2, 134.9, 133.1, 128.9, 128.5 ($^{4}J_{CF}$ = 184.1 Hz) 128.1, 126.0 ($^{2}J_{CF}$ = 7.9 Hz), 125.9 ($^{3}J_{CF}$ = 11.8 Hz), 125.9 ($^{1}J_{CF}$ = 3.9 Hz), 36.1, 29.5. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.18. **IR** (KBr, *v*, cm^{-1}): 3502, 2963, 1654, 1539, 1409, 1277, 1087, 823, 577. **HRMS** (ESI) m/z calcd for $C_{28}H_{30}F_3N_2O_3S$ $[M+H]^+$ 531.1929, found 531.1957.

(Z)-N-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-3,4-dimethyl-N'-(phenylsulfonyl)benzimidamide (3m)



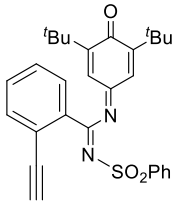
Orange solid; 76 mg, 79% yield; m.p. 101-103 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.67 (s, 1H), 7.56-7.51 (m, 1H), 7.49-7.44 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.61 (s, 2H), 2.27 (d, *J* = 6.8 Hz, 6H), 1.25 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 186.4, 169.4, 157.3, 156.2, 144.2, 144.2, 141.2, 141.2, 141.2, 141.2, 137.7, 132.8, 130.2, 129.9, 129.4, 128.7, 128.4, 127.6, 127.0, 36.0, 29.5, 20.3, 19.9. **IR** (KBr, *v*, cm^{-1}): 3063, 2870, 1655, 1525, 1321, 1103, 931, 689. **HRMS** (ESI) m/z calcd for $C_{29}H_{35}N_2O_3S$ $[M+H]^+$ 491.2368, found 491.2369.

(Z)-3,4-dichloro-N-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-N'-(phenylsulfonyl)benzimidamide (3n)



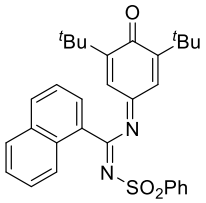
Orange solid; 79 mg, 74% yield; m.p. 122-124 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.0 Hz, 3H), 7.59-7.54 (m, 2H), 7.51-7.46 (m, 3H), 6.61 (s, 2H), 1.25 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 186.1, 166.4, 158.3, 156.9, 140.7, 138.6, 133.7, 133.1, 132.1, 131.0, 130.6, 128.9, 128.1, 128.0, 127.6, 36.2, 29.5. **IR** (KBr, *v*, cm^{-1}): 3281, 2870, 1640, 1529, 1324, 1108, 815, 462. **HRMS** (ESI) m/z calcd for $C_{27}H_{28}Cl_2N_2O_3SNa$ $[M+Na]^+$ 553.1095, found 553.1095.

(Z)-N-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-2-ethynyl-N'-(phenylsulfonyl)benzimidamide (3o)



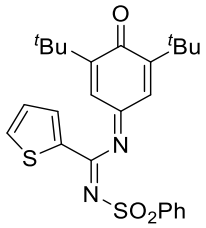
Orange solid; 35 mg, 36% yield; m.p. 90-92 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.61-7.56 (m, 2H), 7.55-7.50 (m, 2H), 7.47-7.38 (m, 2H), 6.77 (s, 2H), 3.20 (s, 1H), 1.27 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 186.2, 157.1, 156.2, 141.1, 136.1, 135.3, 132.8, 131.9, 130.0, 129.0, 128.9, 128.8, 128.1, 127.6, 83.8, 81.4, 36.1, 29.5. **IR** (KBr, *v*, cm^{-1}): 3258, 2961, 2362, 1751, 1595, 1482, 1321, 1124, 881, 612. **HRMS** (ESI) m/z calcd for $C_{29}H_{31}N_2O_3S$ $[M+H]^+$ 487.2055, found 487.2064.

(Z)-N-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-N'-(phenylsulfonyl)-1-naphthimidamide (3p)



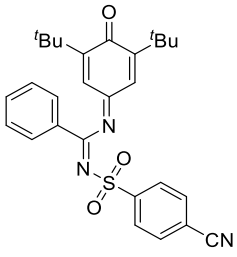
Orange solid; 72 mg, 70% yield; m.p. 80-82 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.31 (s, 1H), 8.02 (d, *J* = 7.3 Hz, 2H), 7.94-7.82 (m, 4H), 7.60-7.53 (m, 2H), 7.53-7.46 (m, 3H), 6.72 (s, 2H), 1.26 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 186.3, 169.2, 169.2, 157.8, 156.5, 156.5, 141.2, 136.0, 132.9, 132.6, 131.3, 129.7, 129.4, 129.3, 129.0, 128.9, 128.9, 128.4, 128.0, 127.6, 127.3, 124.2, 36.1, 29.5. **IR** (KBr, *v*, cm^{-1}): 3308, 2831, 1605, 1517, 1389, 1157, 775, 582. **HRMS** (ESI) m/z calcd for $C_{31}H_{33}N_2O_3S$ $[M+H]^+$ 513.2212, found 513.2210.

(Z)-N-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-N'-(phenylsulfonyl)thiophene-2-carboximidamide (3q)



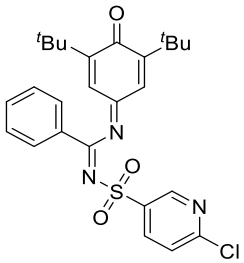
Orange solid; 70 mg, 74% yield; m.p. 73-75 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.70 (d, *J* = 5.2 Hz, 1H), 7.58-7.53 (m, 1H), 7.51-7.46 (m, 2H), 7.44 (d, *J* = 3.6 Hz, 1H), 7.13-7.08 (m, 1H), 6.66 (s, 2H), 1.26 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 186.3, 164.5, 158.6, 156.6, 141.1, 136.8, 135.8, 134.3, 132.8, 128.8, 128.8, 128.2, 127.6, 36.1, 29.5. **IR** (KBr, *v*, cm^{-1}): 2962, 1655, 1528, 1412, 1286, 1087, 828, 584. **HRMS** (ESI) m/z calcd for $C_{25}H_{29}N_2O_3S_2$ $[M+H]^+$ 469.1620, found 469.1620.

(Z)-N'-((4-cyanophenyl)sulfonyl)-N-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzimidamide (3r)



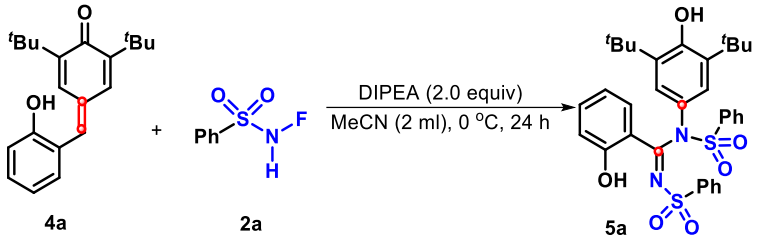
Orange solid; 77 mg, 80% yield; m.p. 151-153 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.0 Hz, 2H), 7.84-7.78 (m, 4H), 7.64-7.58 (m, 1H), 7.49-7.43 (m, 2H), 6.67 (s, 2H), 1.27 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 186.2, 169.8, 157.8, 157.1, 145.4, 134.5, 132.7, 131.7, 129.2, 129.1, 128.1, 128.1, 117.6, 116.4, 36.2, 29.5. **IR** (KBr, *v*, cm^{-1}): 2961, 2870, 2232, 1654, 1525, 877, 857, 822. **HRMS** (ESI) m/z calcd for $C_{28}H_{29}N_3O_3SNa$ $[M+Na]^+$ 510.1827, found 510.1826.

(Z)-N'-((6-chloropyridin-3-yl)sulfonyl)-N-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzimidamide (3s)



Orange solid; 74 mg, 76% yield; m.p. 129-130 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.95 (s, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.64-7.58 (m, 1H), 7.50-7.43 (m, 3H), 6.67 (s, 2H), 1.27 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 186.1, 169.8, 157.9, 157.2, 155.5, 148.9, 137.7, 136.7, 134.6, 131.6, 129.3, 129.1, 128.1, 124.5, 36.2, 29.5. **IR** (KBr, *v*, cm^{-1}): 3064, 2956, 1653, 1520, 1277, 861, 738, 683. **HRMS** (ESI) m/z calcd for $C_{25}H_{28}ClN_3O_3S$ [M-H]$^+$ 496.1462, found 496.1488.

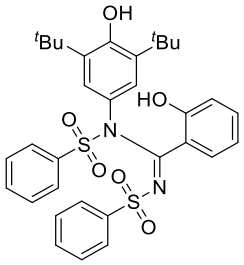
Example for the synthesis of **5a**:



4a 2a 5a

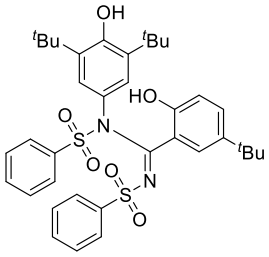
Add 2,6-di-*tert*-butyl-4-(2-hydroxybenzylidene)cyclohexa-2,5-dien-1-one **4a** (0.2 mmol, 62 mg), *N*-fluorobenzenesulfonamide **2a** (0.6 mmol, 105 mg), DIPEA (0.4 mmol, 52 mg), and MeCN (4 mL) to a 10-mL reaction tube, and then the reaction system was stirred at 0 °C for 24 hours. After the reaction was complete (monitored by TLC), the reaction system was concentrated by vacuum filtration, and the crude product was purified by flash silica gel column chromatography (PE/EtOAc = 10:1) to obtain pure product **5a** (89 mg, 73%).

(Z)-N-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-hydroxy-N,N'-bis(phenylsulfonyl)benzimidamide (5a)



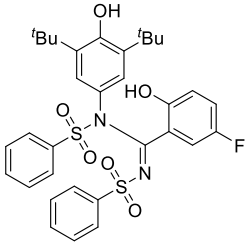
White solid; 89 mg, 73% yield; m.p. 192-194 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.91 (s, 1H), 7.84 (d, *J* = 7.2 Hz, 1H), 7.78-7.70 (m, 3H), 7.67 (s, 1H), 7.60-7.52 (m, 6H), 7.35 (s, 1H), 7.15 (s, 1H), 6.98-6.93 (m, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 6.55-6.49 (m, 1H), 6.44 (d, *J* = 8.4 Hz, 1H), 1.25 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 164.6, 154.6, 152.4, 141.2, 138.5, 136.1, 134.0, 132.8, 131.8, 129.5, 129.2, 128.8, 128.6, 127.6, 127.1, 126.5, 121.8, 119.8, 117.8, 34.3, 29.9. **IR** (KBr, *v*, cm^{-1}): 2958, 1611, 1563, 1364, 1157, 890, 787, 729. **HRMS** (ESI) m/z calcd for $C_{33}H_{37}N_2O_6S_2$ [M+H]$^+$ 621.2093, found 621.2090.

(Z)-5-(tert-butyl)-N-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-hydroxy-N,N'-bis(phenylsulfonyl)benzimidamide (5b)



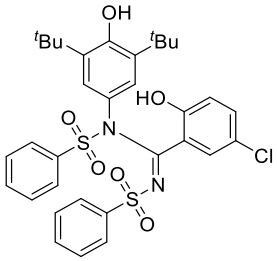
White solid; 94 mg, 69% yield; m.p. 201-203 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.72 (s, 1H), 7.84 (d, J = 7.2 Hz, 1H), 7.80-7.72 (m, 3H), 7.66-7.60 (m, 1H), 7.60-7.55 (m, 3H), 7.52-7.47 (m, 3H), 7.35 (s, 1H), 7.15 (s, 1H), 6.99 (d, J = 8.4 Hz, 1H), 6.71 (s, 1H), 6.38 (d, J = 8.8 Hz, 1H), 1.24 (s, 18H), 1.06 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-d) δ 165.0, 154.6, 150.3, 143.7, 140.7, 138.3, 134.1, 132.8, 129.8, 129.3, 129.2, 128.7, 128.5, 127.9, 124.6, 122.6, 119.2, 34.3, 34.0, 31.3, 30.0. **IR** (KBr, v, cm^{-1}): 2962, 2386, 1729, 1557, 1365, 1152, 785, 729. **HRMS** (ESI) m/z calcd for $C_{37}H_{45}N_2O_6S_2$ $[M+H]^+$ 677.2719, found 677.2718.

(Z)-N-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-fluoro-2-hydroxy-N,N'-bis(phenylsulfonyl)benzimidamide (5c)



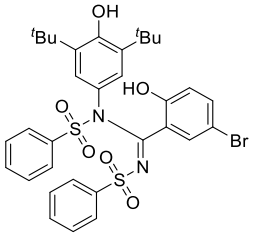
White solid; 75 mg, 59% yield; m.p. 212-214 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.94 (s, 1H), 7.78-7.72 (m, 3H), 7.71-7.65 (m, 1H), 7.62-7.55 (m, 5H), 7.56-7.49 (m, 3H), 7.20 (s, 1H), 6.80 (d, J = 8.4 Hz, 2H), 6.46-6.40 (m, 1H), 1.26 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-d) δ 162.6, 156.1 ($^{1}J_{CF}$ = 240.3 Hz), 154.8, 148.6, 140.7, 138.2, 134.2, 132.9, 129.6, 129.3, 128.9, 128.6, 127.4, 127.1, 126.5, 123.4 ($^{4}J_{CF}$ = 7.9 Hz), 120.2 ($^{5}J_{CF}$ = 7.4 Hz), 118.5 ($^{3}J_{CF}$ = 22.9 Hz), 114.7 ($^{2}J_{CF}$ = 25.3 Hz), 34.3, 29.9. **^{19}F NMR** (376 MHz, DMSO-d_6) δ -127.50. **IR** (KBr, v, cm^{-1}): 2959, 2667, 1568, 1447, 1308, 1155, 898, 782, 728. **HRMS** (ESI) m/z calcd for $C_{33}H_{36}FN_2O_6S_2$ $[M+H]^+$ 639.1999, found 639.2002.

(Z)-5-chloro-N-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-hydroxy-N,N'-bis(phenylsulfonyl)benzimidamide (5d)



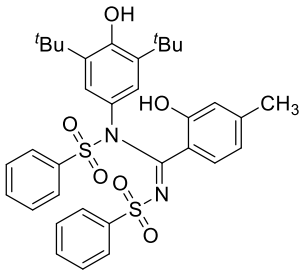
White solid; 83 mg, 64% yield; m.p. 218-220 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.25 (s, 1H), 7.79-7.73 (m, 3H), 7.72-7.65 (m, 1H), 7.62-7.54 (m, 5H), 7.55-7.49 (m, 2H), 7.21 (s, 1H), 6.99 (d, J = 8.8 Hz, 2H), 6.91 (s, 1H), 6.46 (d, J = 8.8 Hz, 1H), 1.27 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-d) δ 162.6, 154.8, 151.3, 140.7, 138.2, 134.2, 133.0, 131.6, 129.6, 128.9, 128.7, 127.9, 127.4, 127.1, 125.1, 123.4, 119.7, 34.3, 29.9. **IR** (KBr, v, cm^{-1}): 2957, 2663, 1430, 1365, 1158, 897, 785, 728. **HRMS** (ESI) m/z calcd for $C_{33}H_{36}ClN_2O_6S_2$ $[M+H]^+$ 655.1703, found 655.1700.

(Z)-5-bromo-N-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-hydroxy-N,N'-bis(phenylsulfonyl)benzimidamide (5e)



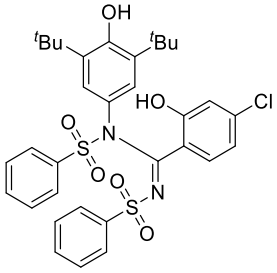
White solid; 102 mg, 73% yield; m.p. 207-209 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.28 (s, 1H), 7.79-7.73 (m, 3H), 7.72-7.65 (m, 1H), 7.60-7.55 (m, 6H), 7.55-7.51 (m, 2H), 7.21 (s, 1H), 7.10 (d, J = 8.8 Hz, 1H), 6.99 (s, 1H), 6.41 (d, J = 8.8 Hz, 1H), 1.27 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 162.5, 154.8, 151.7, 140.6, 138.2, 134.5, 134.3, 133.1, 132.9, 130.7, 129.7, 129.3, 128.9, 128.7, 127.5, 127.2, 126.5, 124.2, 120.5, 112.3, 34.3, 29.9. **IR** (KBr, *v*, cm^{-1}): 2958, 2658, 1611, 1491, 1307, 1157, 895, 785, 728. **HRMS** (ESI) m/z calcd for $C_{33}H_{36}BrN_2O_6S_2$ $[M+H]^+$ 699.1198, found 699.1194.

(Z)-N-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-hydroxy-4-methyl-N,N'-bis(phenylsulfonyl)benzimidamide (5f)



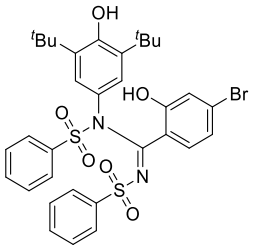
White solid; 70 mg, 55% yield; m.p. 197-199 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.80 (s, 1H), 7.76-7.69 (m, 3H), 7.68-7.62 (m, 1H), 7.61-7.53 (m, 5H), 7.53-7.48 (m, 2H), 7.15 (s, 1H), 6.89 (s, 1H), 6.72 (d, J = 7.6 Hz, 1H), 6.35 (d, J = 7.6 Hz, 1H), 6.26 (s, 1H), 2.04 (s, 3H), 1.25 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 164.9, 154.5, 152.3, 142.7, 141.1, 138.5, 136.1, 134.0, 132.7, 129.5, 128.8, 128.6, 128.4, 127.8, 127.2, 121.0, 119.6, 118.8, 34.3, 29.9, 21.3. **IR** (KBr, *v*, cm^{-1}): 2958, 1619, 1447, 1365, 1156, 1082, 805, 729, 609. **HRMS** (ESI) m/z calcd for $C_{34}H_3N_2O_6S_2$ $[M+H]^+$ 635.2250, found 635.2249.

(Z)-4-chloro-N-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-hydroxy-N,N'-bis(phenylsulfonyl)benzimidamide (5g)



White solid; 65 mg, 49% yield; m.p. 192-194 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.47 (s, 1H), 7.74 (d, J = 7.6 Hz, 3H), 7.71-7.65 (m, 1H), 7.61-7.54 (m, 5H), 7.54-7.48 (m, 2H), 7.23 (s, 1H), 6.93 (d, J = 8.4 Hz, 2H), 6.60 (d, J = 8.4 Hz, 1H), 6.47 (s, 1H), 1.26 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 163.6, 154.8, 153.3, 141.0, 138.2, 137.4, 136.3, 134.2, 133.0, 129.5, 129.4, 128.9, 128.6, 127.4, 127.1, 120.5, 120.2, 117.9, 34.3, 29.9. **IR** (KBr, *v*, cm^{-1}): 3764, 3272, 2959, 2766, 1747, 1430, 1365, 1083, 878, 729. **HRMS** (ESI) m/z calcd for $C_{33}H_{36}ClN_2O_6S_2$ $[M+H]^+$ 655.1703, found 655.1702.

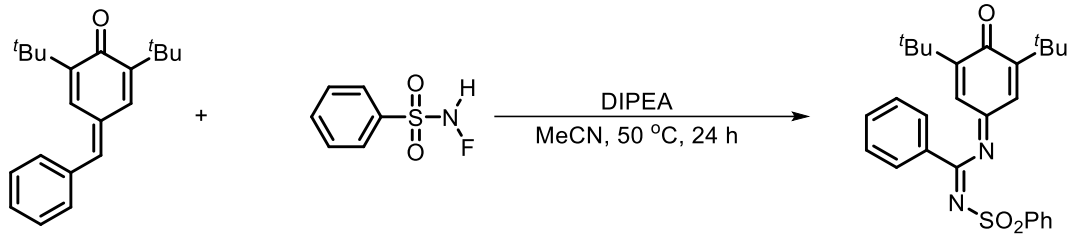
(Z)-4-bromo-N-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-hydroxy-N,N'-bis(phenylsulfonyl)benzimidamide (5h)



White solid; 77 mg, 56% yield; m.p. 183-185 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.46 (s, 1H), 7.74 (d, J = 7.2 Hz, 3H), 7.71-7.65 (m, 1H), 7.57 (d, J = 4.8 Hz, 4H), 7.55-7.50 (m, 2H), 7.23 (s, 1H), 6.86 (d, J = 8.8 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 6.62 (s, 1H), 1.27 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-d) δ 163.5, 154.8, 153.2, 140.9, 138.2, 136.4, 134.2, 133.0, 129.5, 128.9, 128.6, 127.4, 127.1, 125.5, 123.3, 121.2, 34.3, 29.9. **IR** (KBr, v, cm^{-1}): 2957, 1604, 1447, 1365, 1155, 1082, 805, 729. **HRMS** (ESI) m/z calcd for $C_{33}H_{36}BrN_2O_6S_2$ $[M+H]^+$ 699.1198, found 699.1195.

Application of Product 3a:

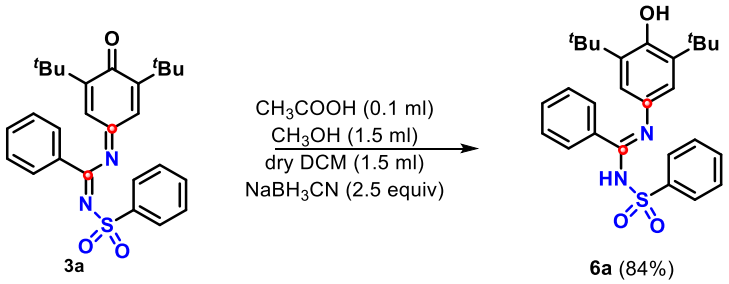
Gram scale reaction:



1a (1.5 mmol) **2a** (4.5 mmol) **3a** (0.56 g, 80%)

Add 4-benzylidene-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **1a** (1.5 mmol, 441 mg), *N*-fluorobenzenesulfonamide (4.5 mmol, 787.5 mg), DIPEA (4.5 mmol, 580.5 mg), and MeCN (15 mL) to a 25-ml reaction tube, and then the reaction system was stirred at 50 °C for 24 hours. After the reaction was complete (monitored by TLC), the reaction system was concentrated by vacuum filtration, and the crude product was purified by flash silica gel column chromatography (PE/EtOAc = 25:1) to obtain pure product **3a** (0.56 g)

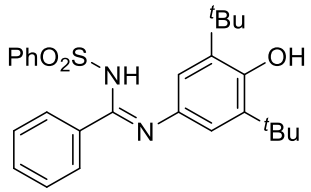
Procedure for Synthesis of 6a:



3a **6a** (84%)

Add **3a** (0.1 mmol, 46.3 mg) to the reaction tube equipped with a magnetic stirrer, followed by acetic acid (0.1 mL), methanol (1.5 mL), dry DCM (0.15 mL), and sodium cyanide borohydride (0.2 mmol, 12.6 mg). After the reaction was complete (monitored by TLC), the reaction system was concentrated by vacuum filtration, and the crude product was purified by flash silica gel column chromatography (PE/EtOAc = 5:1) to obtain pure product **6a** (19 mg, 84 % yield).

(Z)-N'-(3,5-di-tert-butyl-4-hydroxyphenyl)-N-(phenylsulfonyl)benzimidamide (6a)



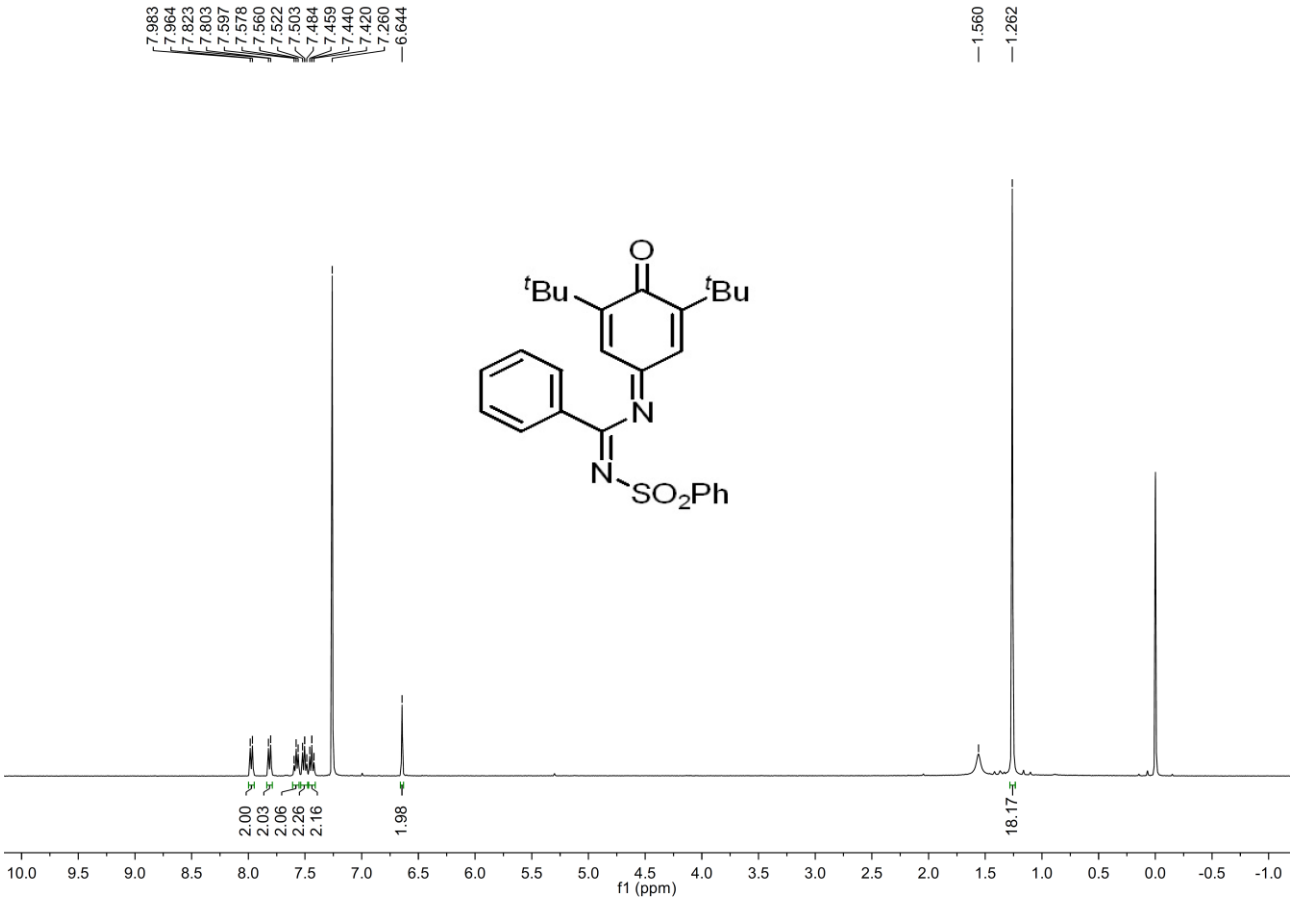
White solid; 40mg, 84% yield; m.p. 187-189 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.07 (s, 1H), 8.06 (d, *J* = 7.6 Hz, 2H), 7.61-7.46 (m, 4H), 7.31 (d, *J* = 7.6 Hz, 3H), 7.25-7.16 (m, 2H), 6.59 (s, 2H), 5.13 (s, 1H), 1.25 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 162.6, 151.3, 135.9, 132.6, 131.6, 130.1, 128.7, 128.5, 128.0, 127.2, 125.8, 120.9, 33.5, 29.2. **IR** (KBr, *v*, cm^{-1}): 3005, 2989, 1646, 1436, 1275, 1260, 1145, 1085, 749. **HRMS** (ESI) m/z calcd for $C_{27}H_{33}N_2O_3S$ $[M+H]^+$ 464.2134, found 464.2143.

References

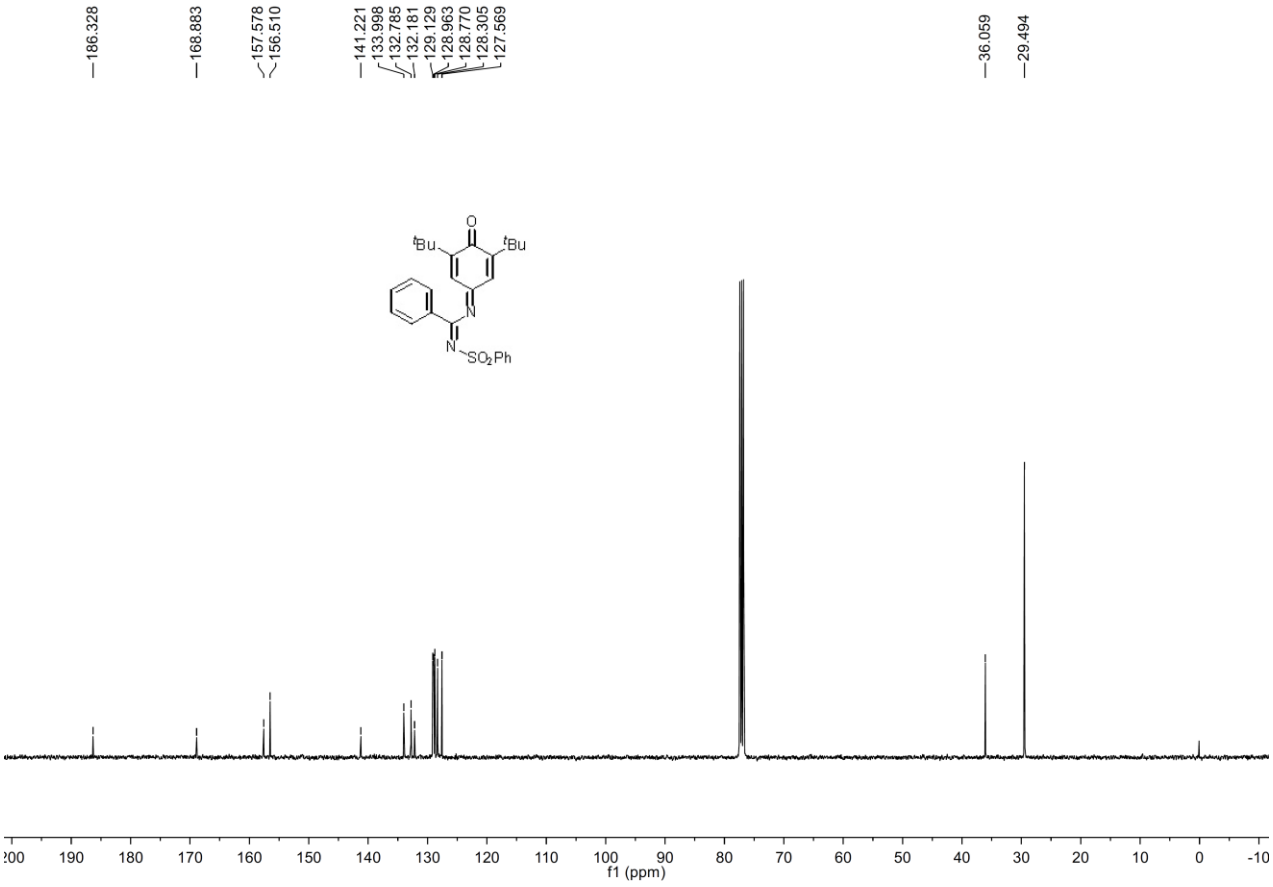
[1] W. D. Chu, L. F. Zhang, X. Bao, X. H. Zhao, C. Zeng, J. Y. Du, G. B. Zhang, F. X. Wang, X. Y. Ma and C. A. Fan, *Angew. Chem. Int. Ed.*, 2013, **52**, 9229.

[2] Y.Y. Zhang, X. H. Xu and F. L. Qing, *Chin. J. Chem.,* 2022, **40**, 2956.

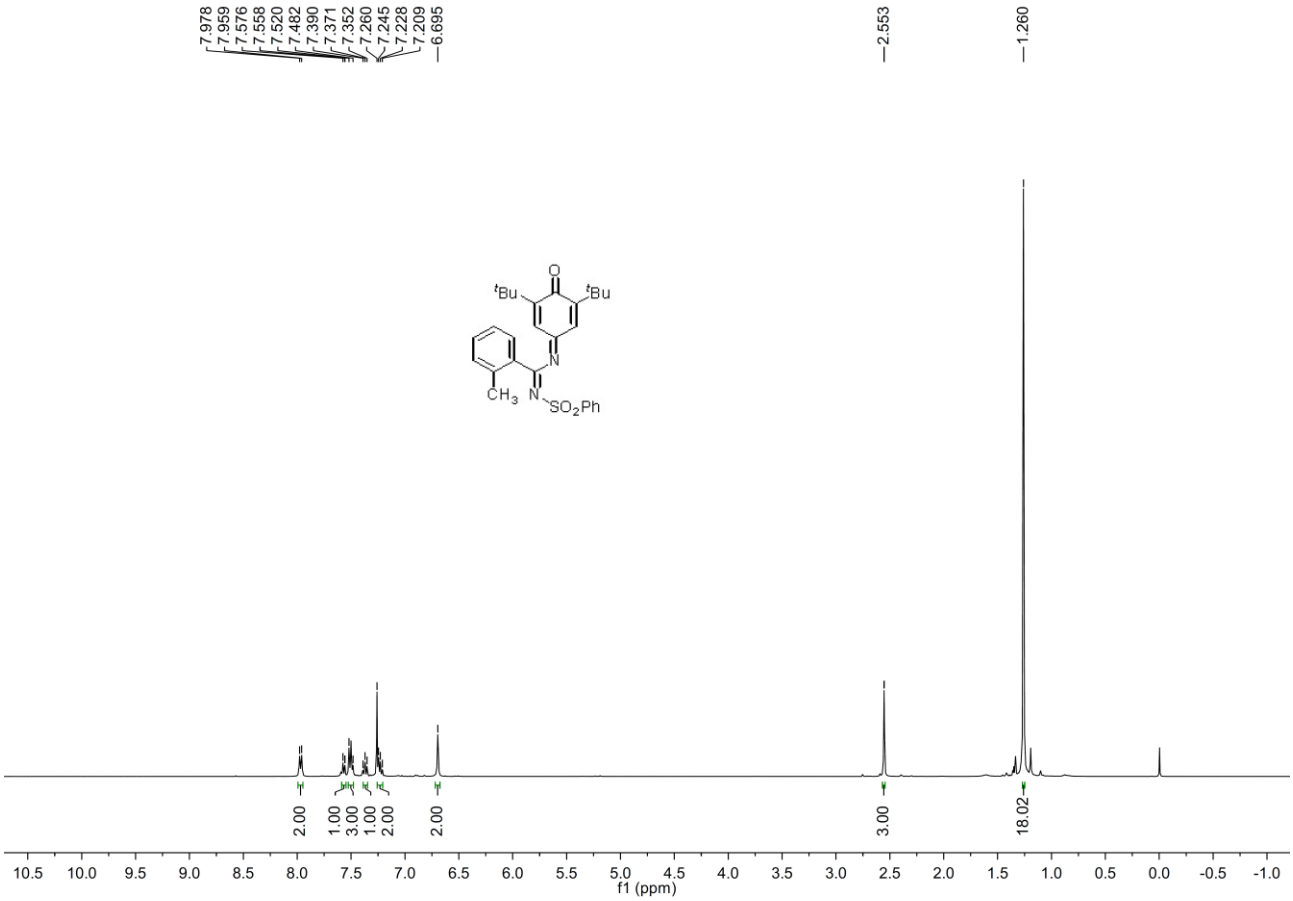
[3] K. Zhao, Y. Zhi, T. Shu, A. Valkonen, K. Rissanen and D. Enders, *Angew. Chem. Int. Ed.,* 2016, **55**, 12104.



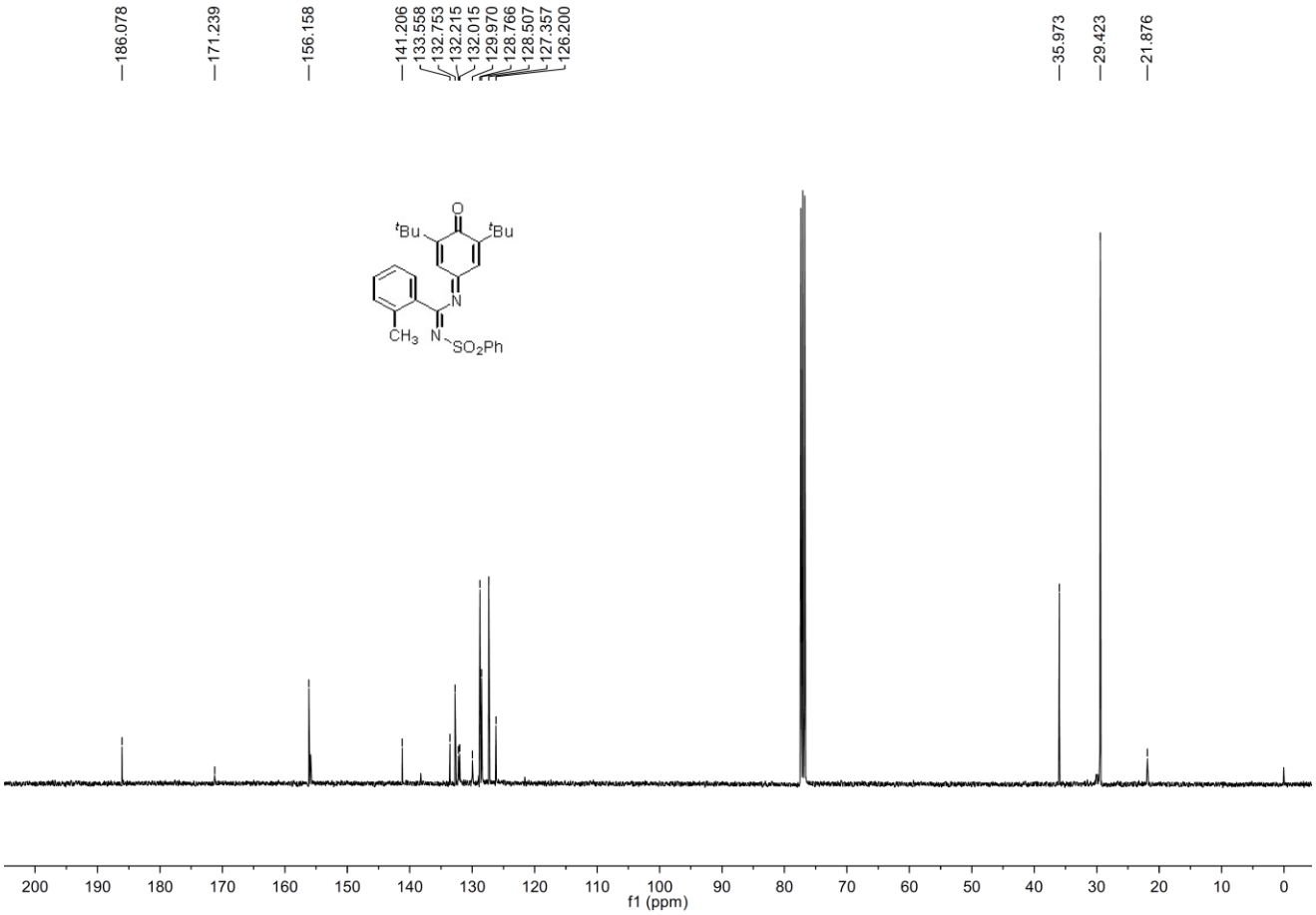
^{1}H NMR Spectrum of Compound 3a (400 MHz, $CDCl_3$)



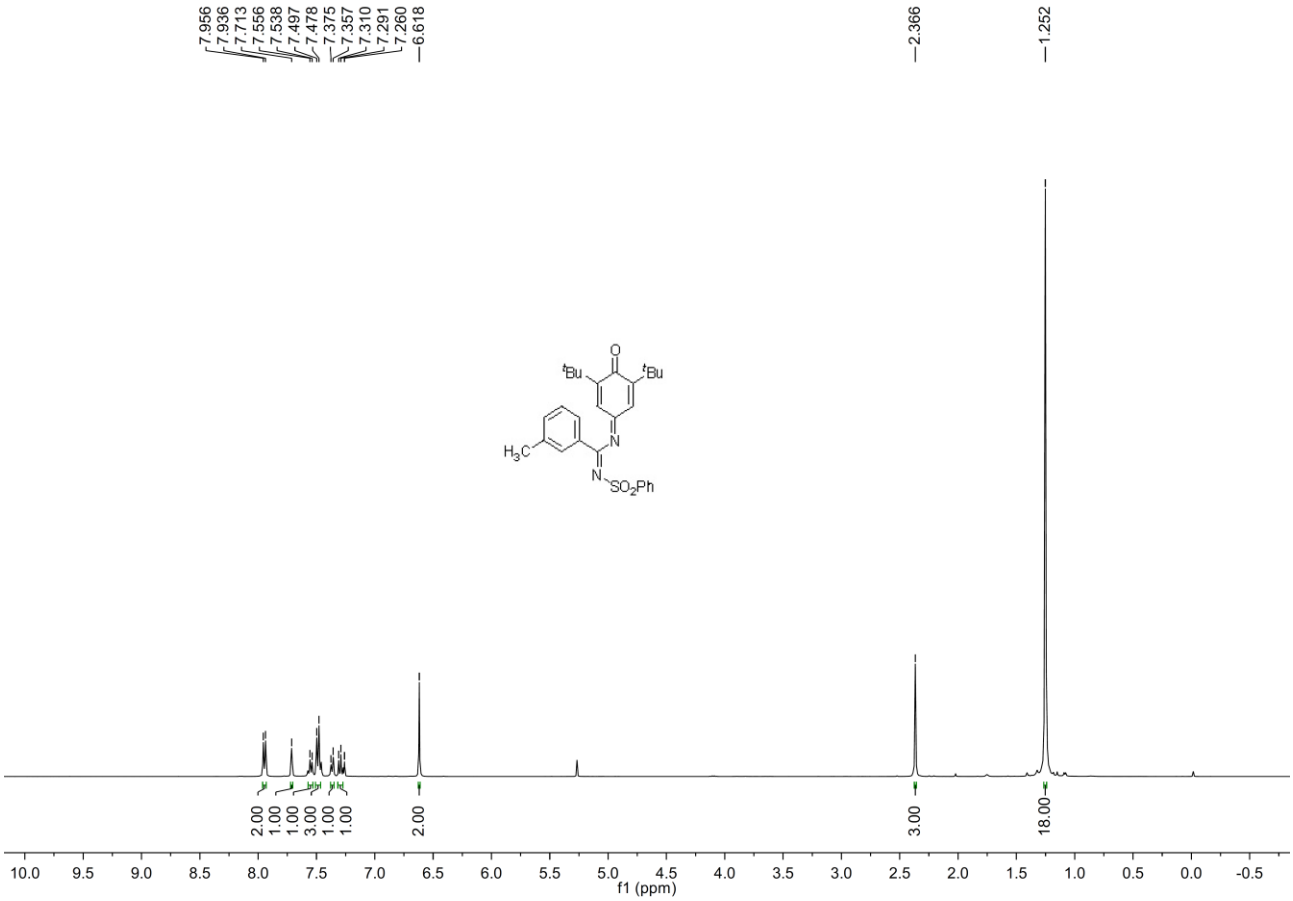
^{13}C NMR Spectrum of Compound 3a (100 MHz, $CDCl_3$)



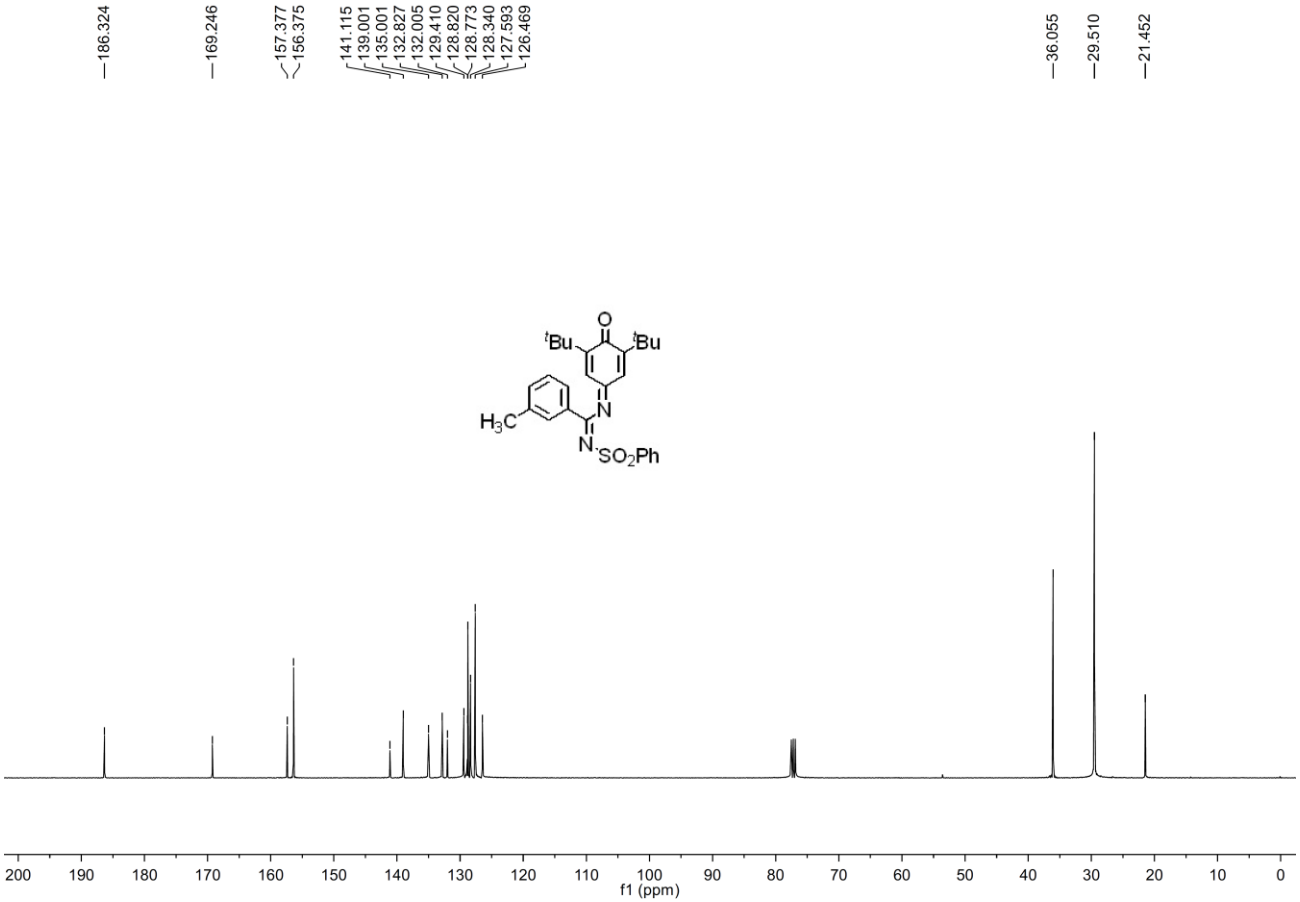
^{1}H NMR Spectrum of Compound 3b (400 MHz, $CDCl_3$)



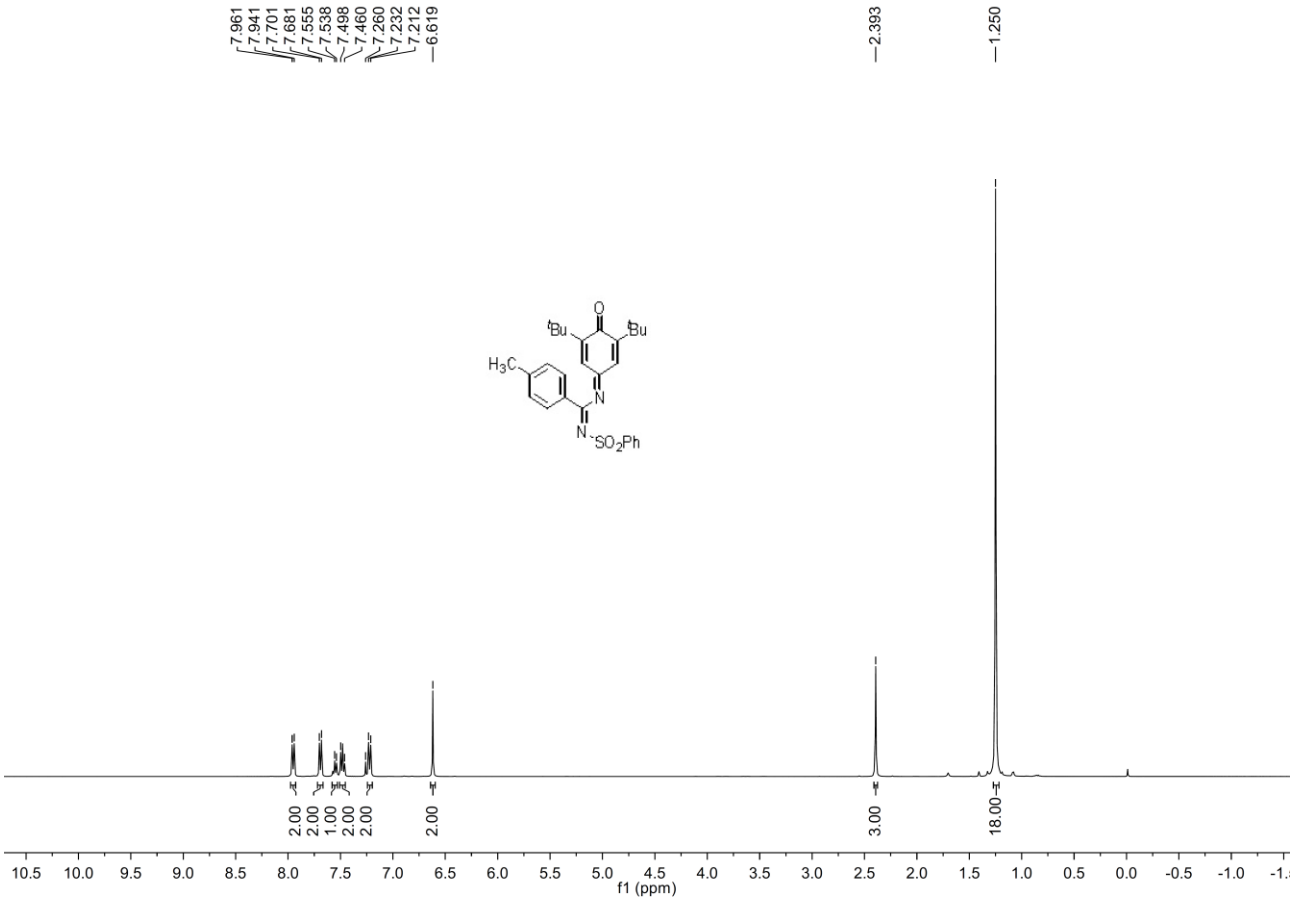
^{13}C NMR Spectrum of Compound 3b (100 MHz, $CDCl_3$)



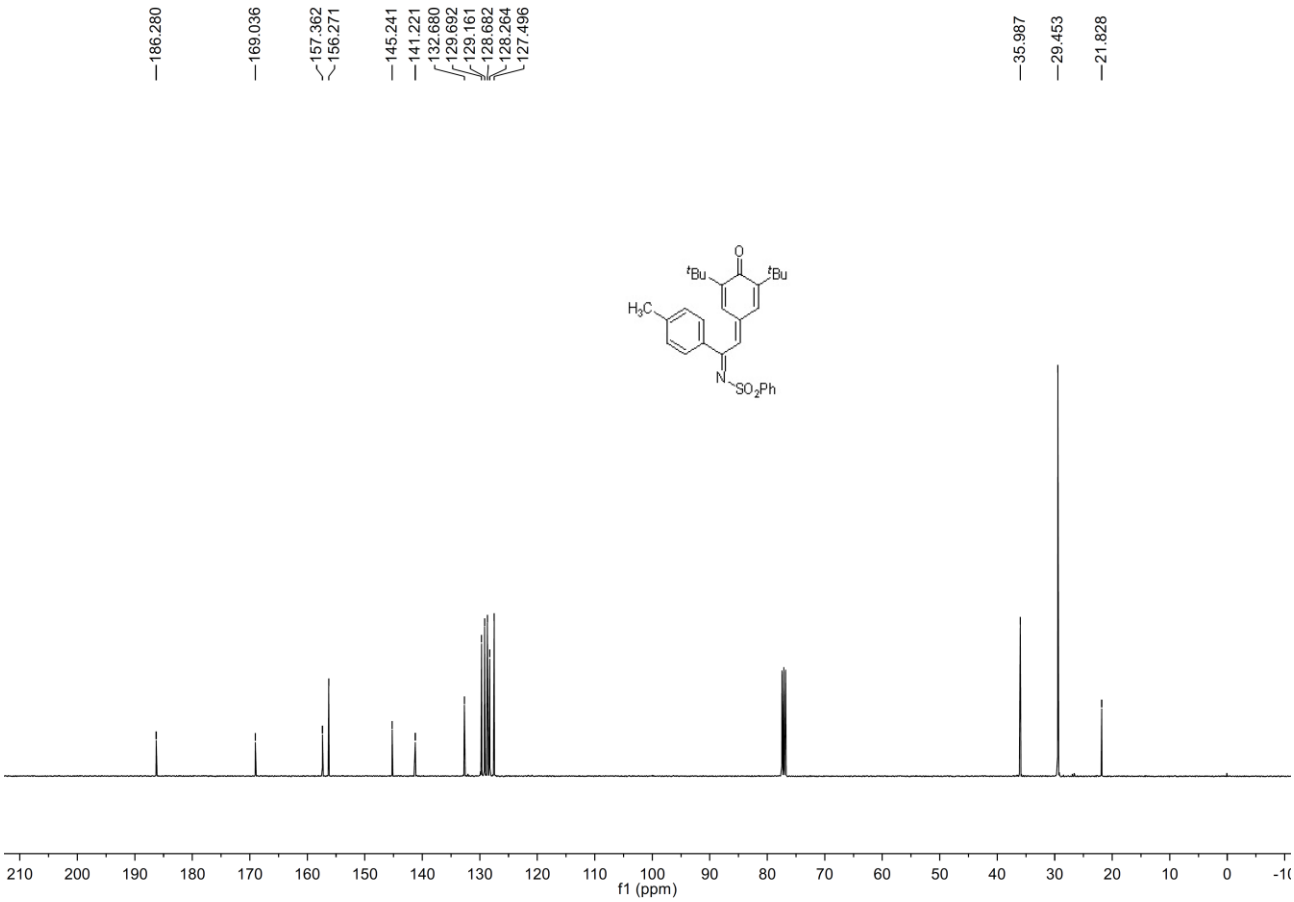
^{1}H NMR Spectrum of Compound 3c (400 MHz, $CDCl_3$)



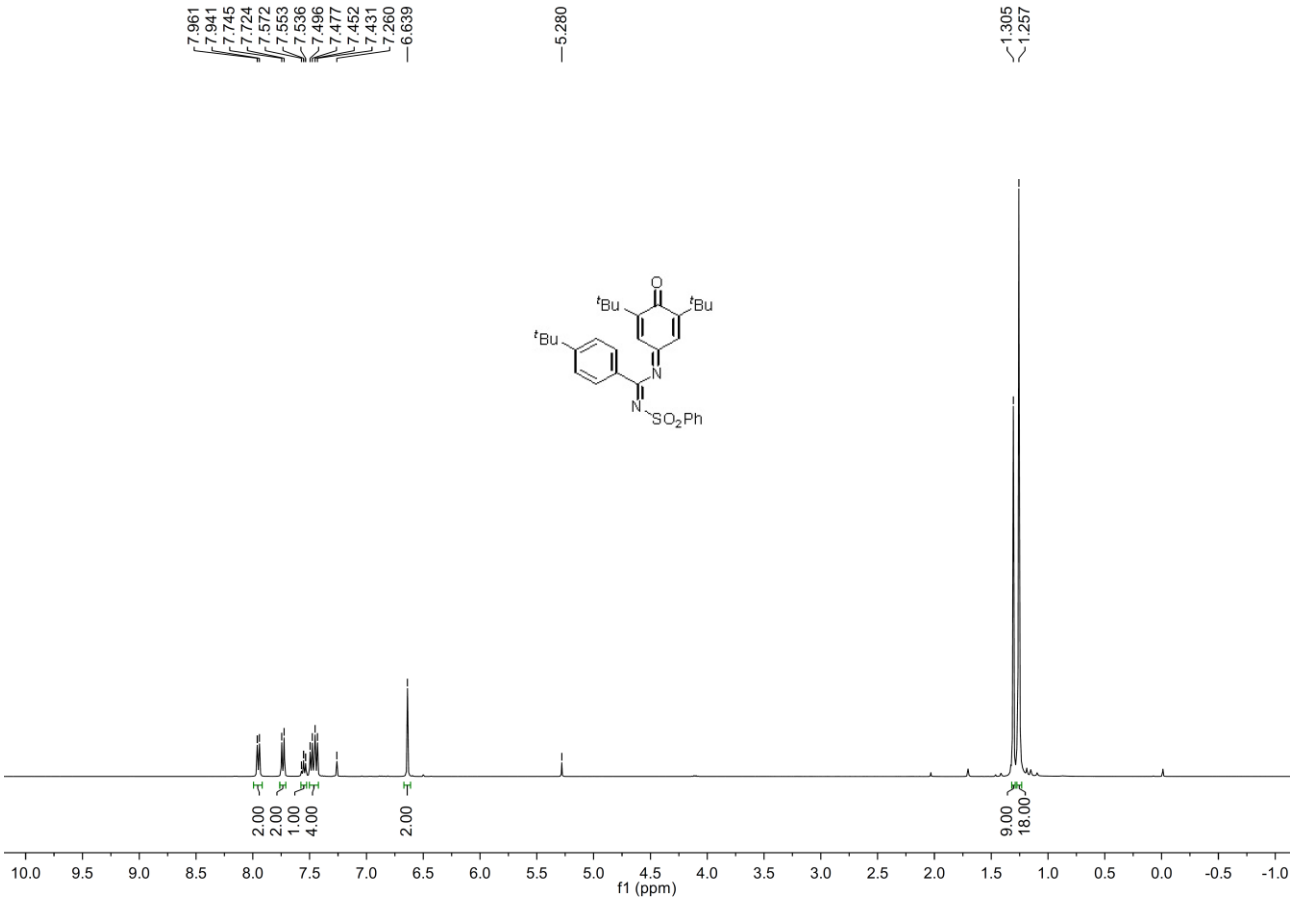
^{13}C NMR Spectrum of Compound 3c (100 MHz, $CDCl_3$)



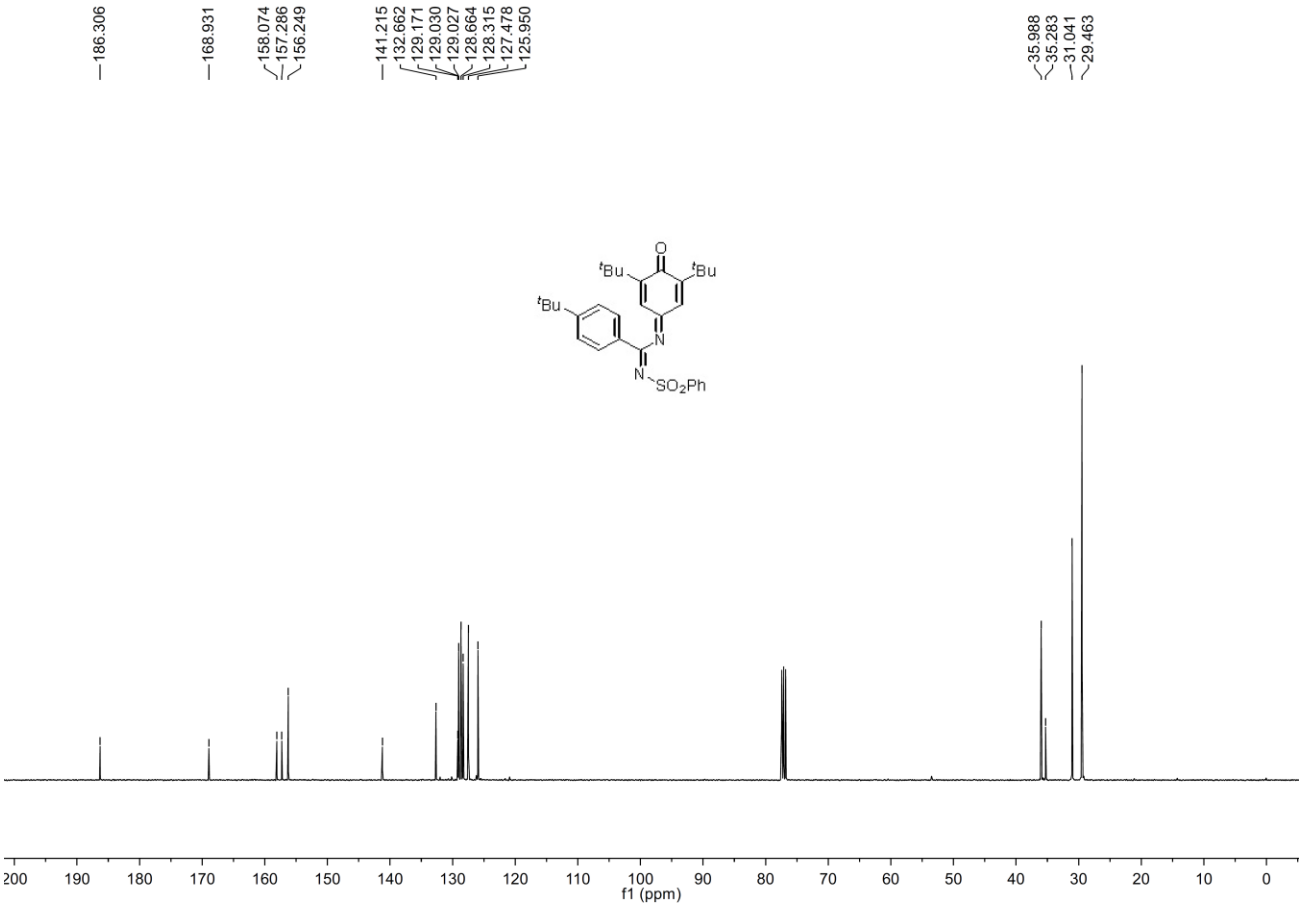
^{1}H NMR Spectrum of Compound 3d (400 MHz, $CDCl_3$)



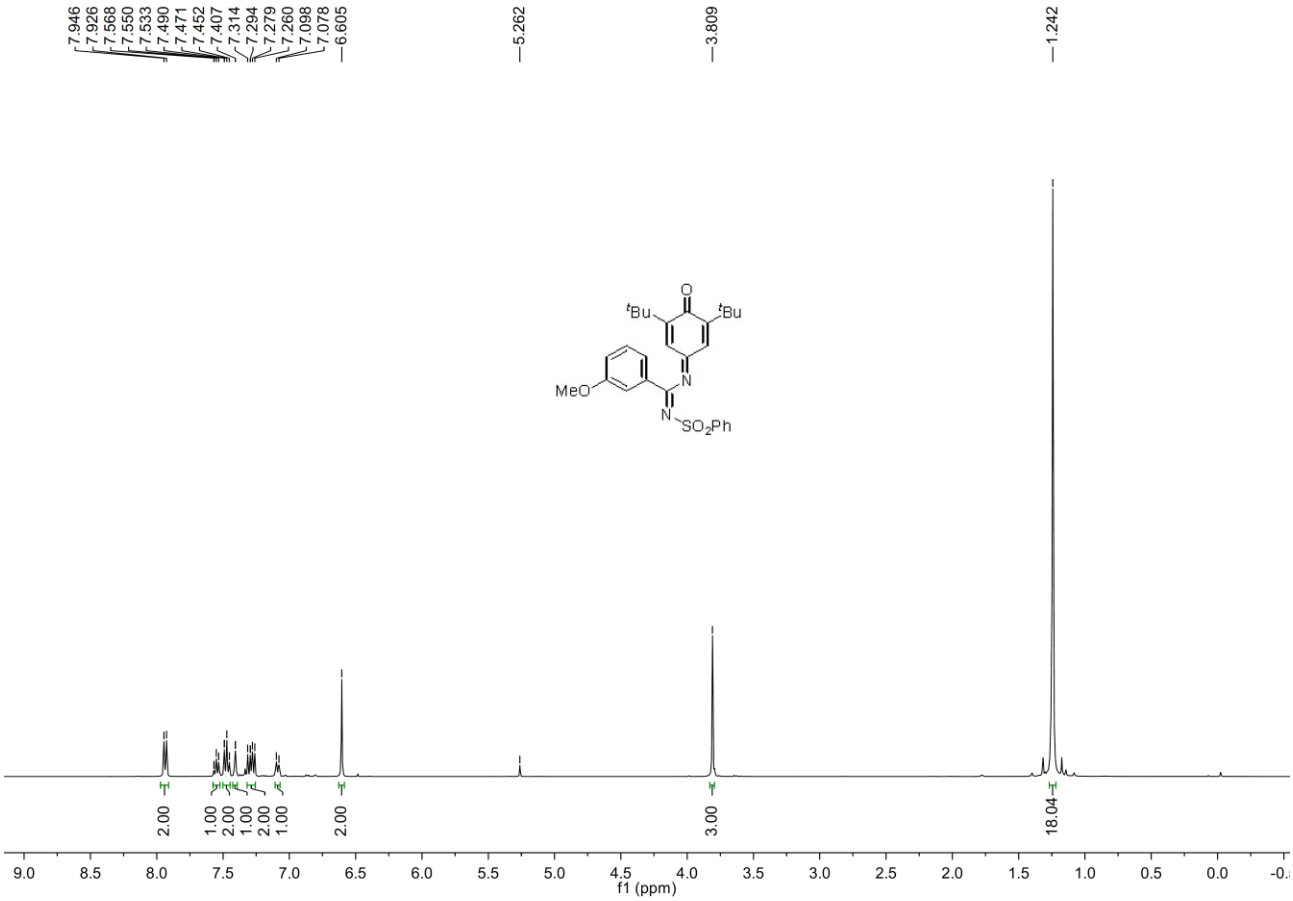
^{13}C NMR Spectrum of Compound 3d (100 MHz, $CDCl_3$)



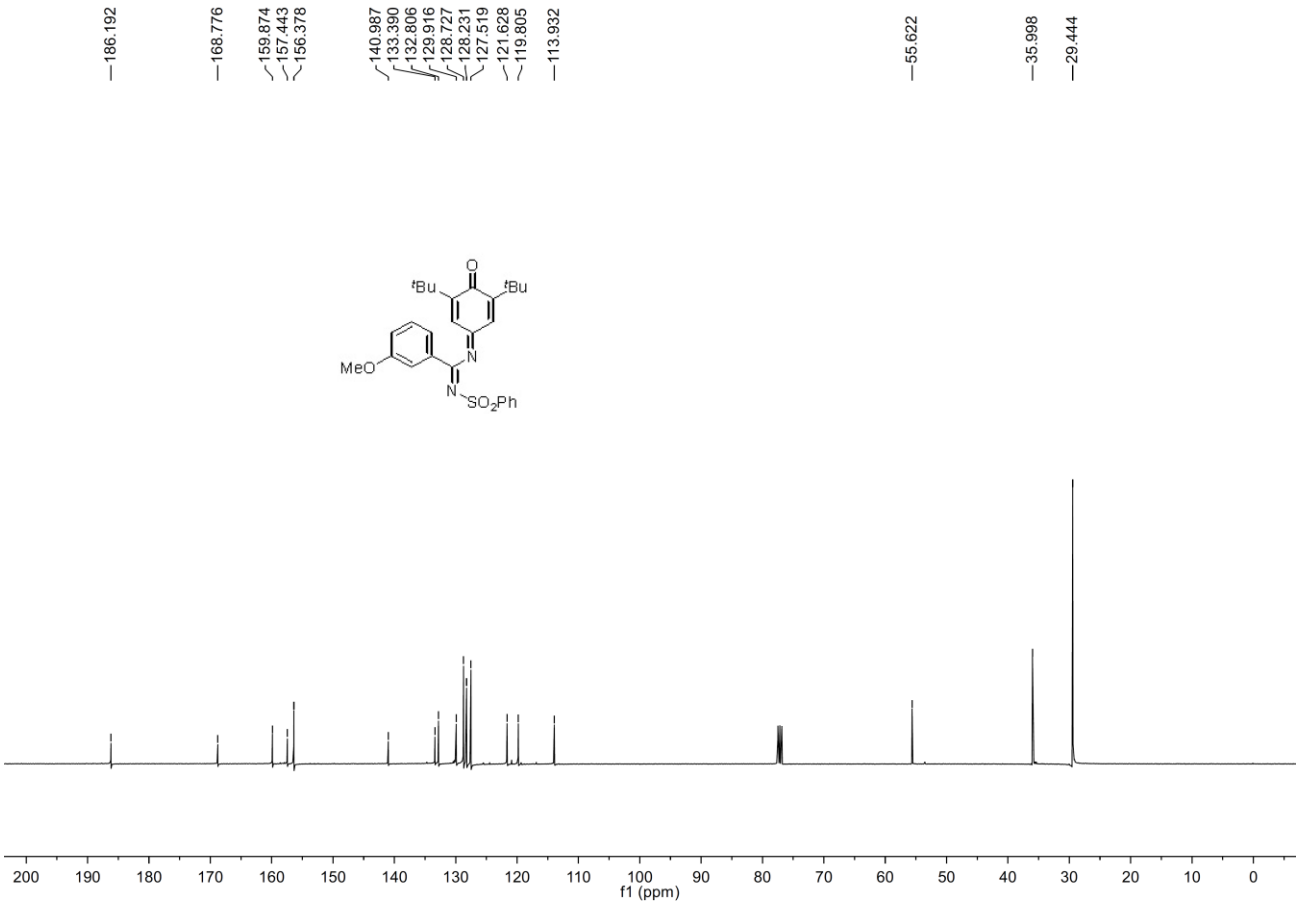
^{1}H NMR Spectrum of Compound 3e (400 MHz, $CDCl_3$)



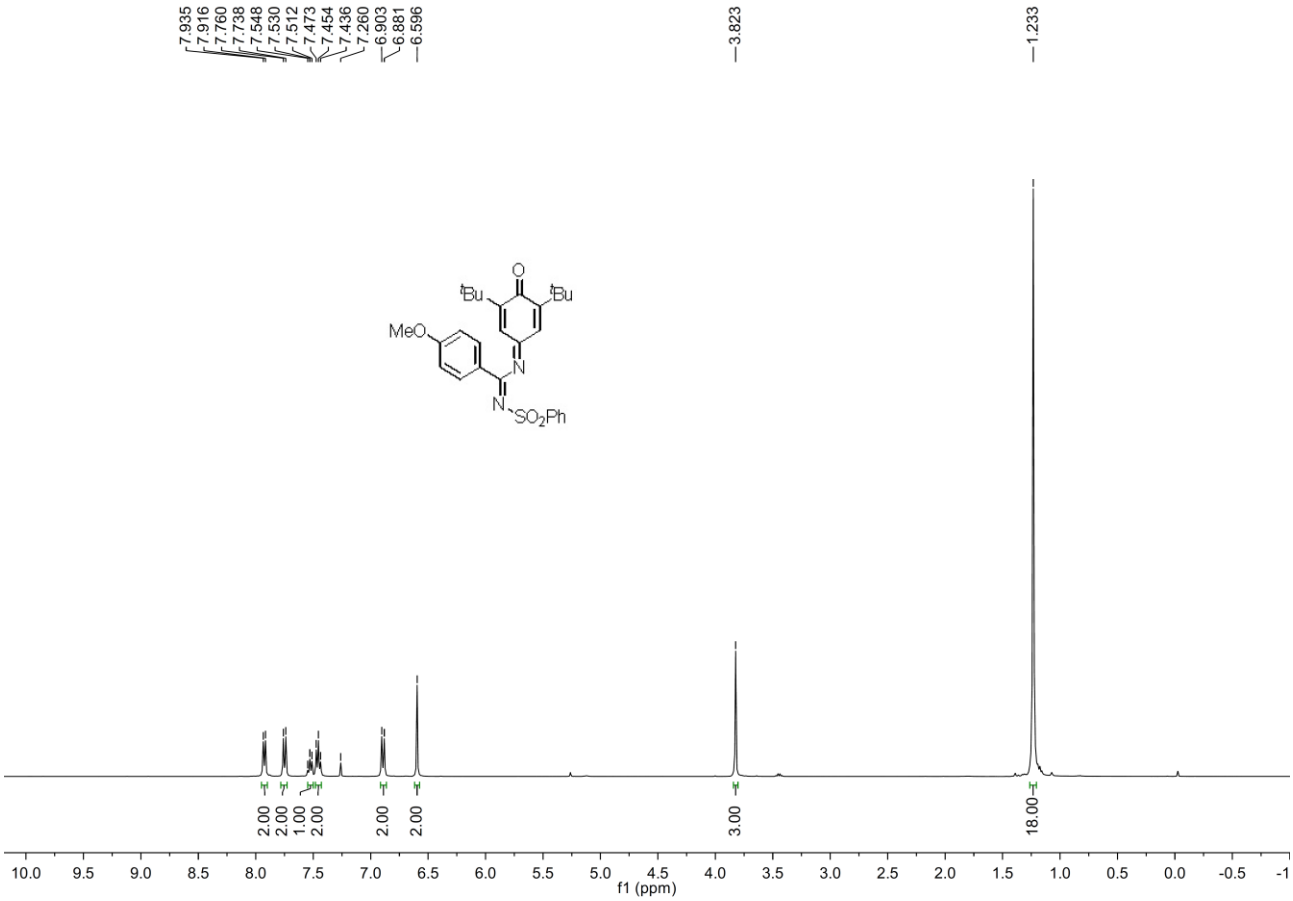
^{13}C NMR Spectrum of Compound 3e (100 MHz, $CDCl_3$)



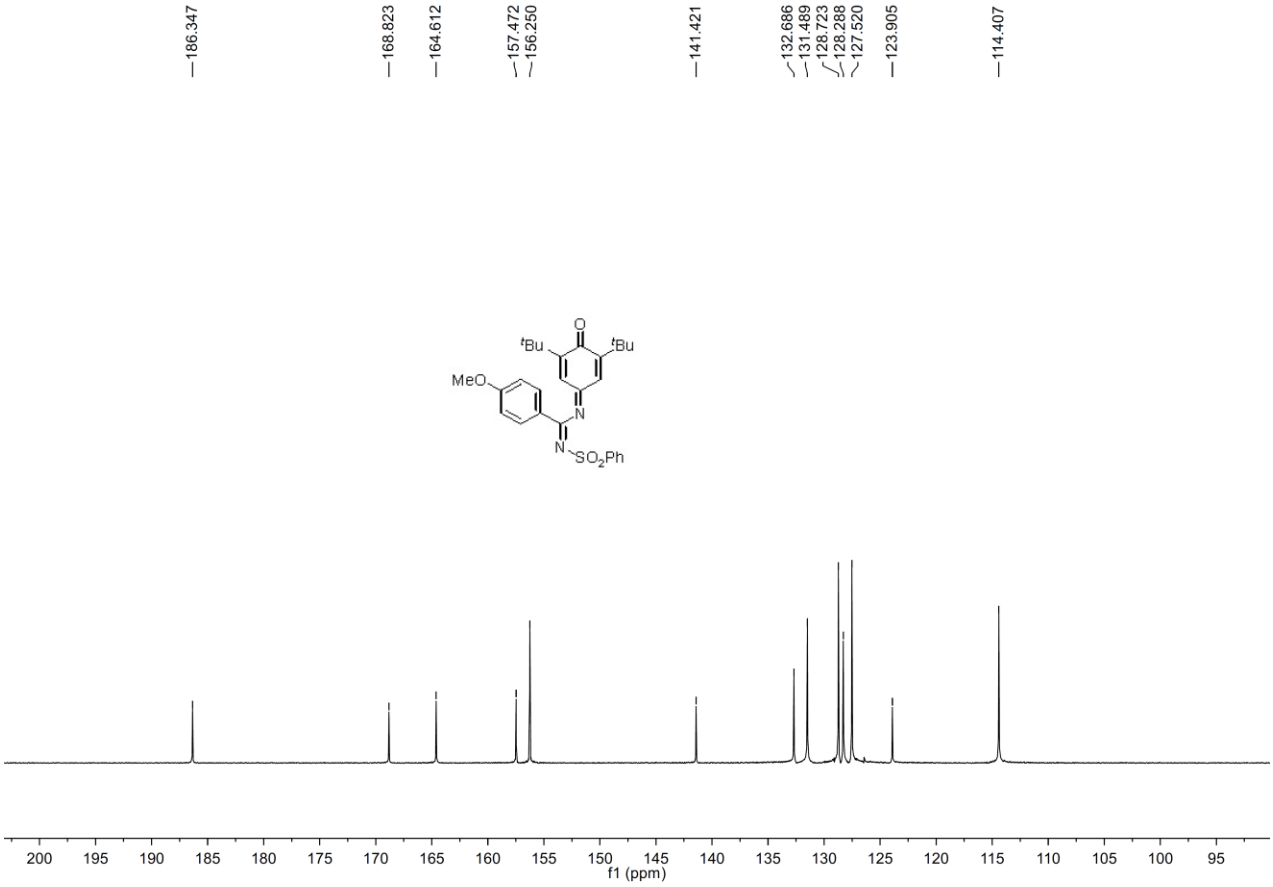
^{1}H NMR Spectrum of Compound 3f (400 MHz, $CDCl_3$)



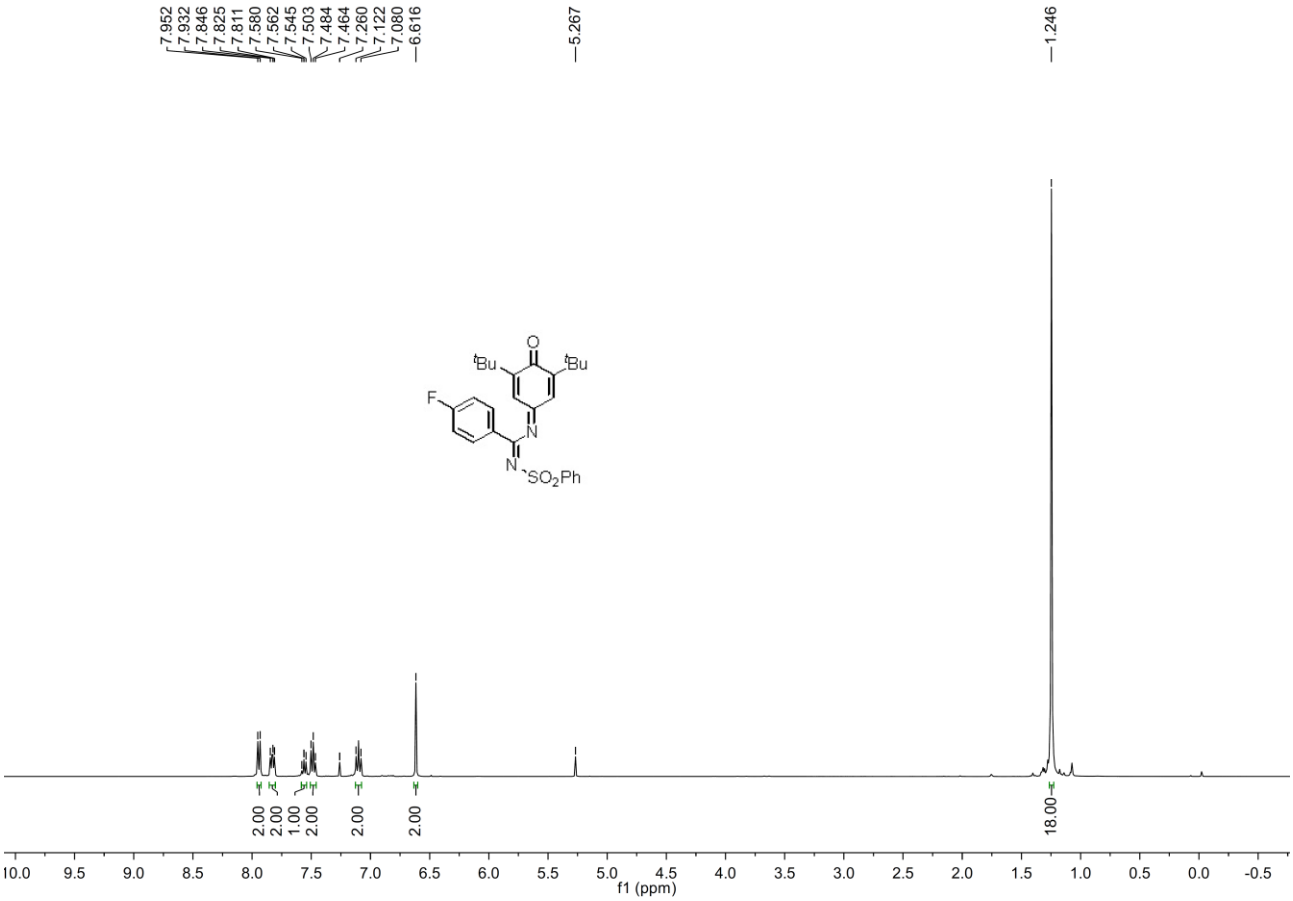
^{13}C NMR Spectrum of Compound 3f (100 MHz, $CDCl_3$)



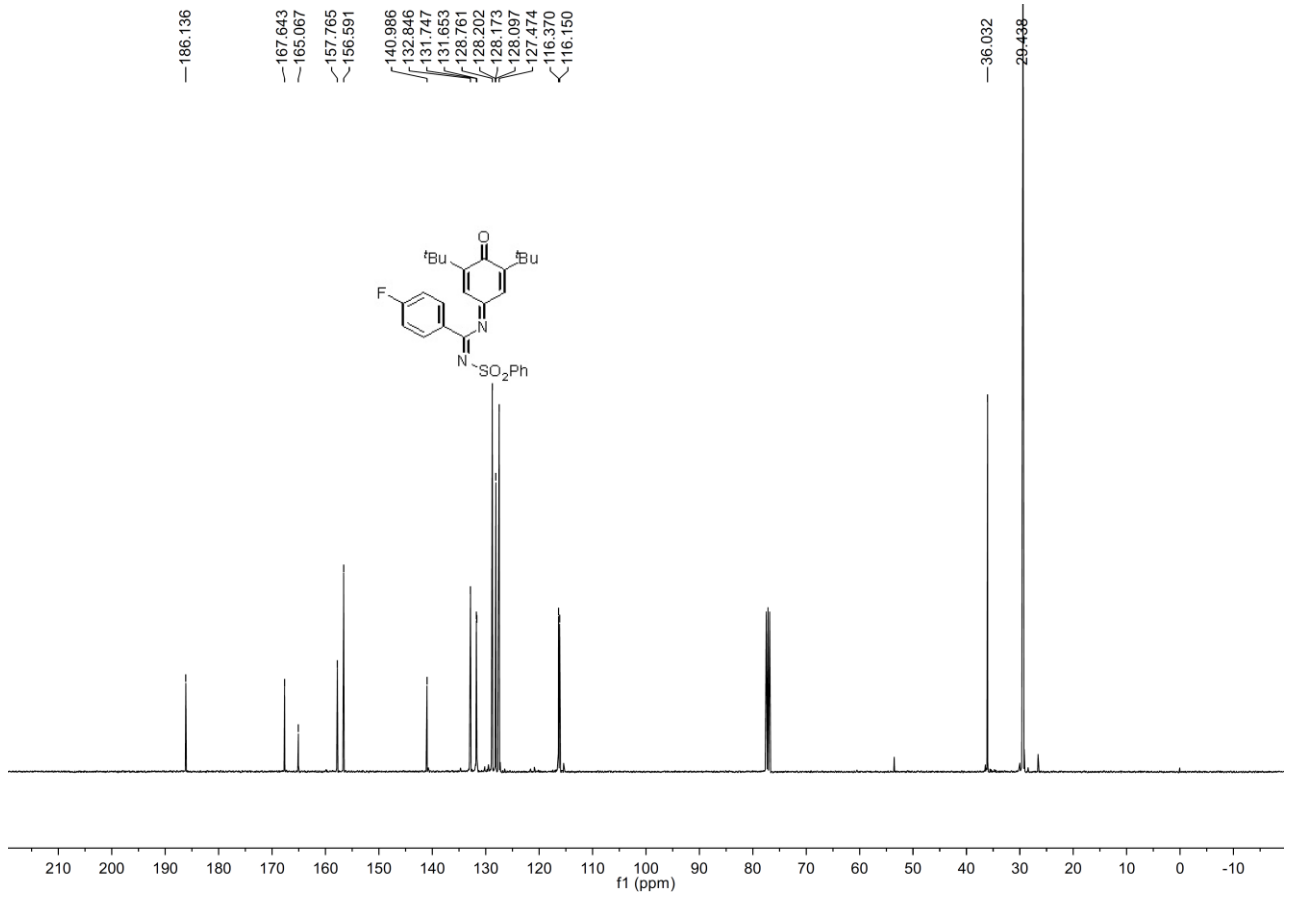
^{1}H NMR Spectrum of Compound 3g (400 MHz, $CDCl_3$)



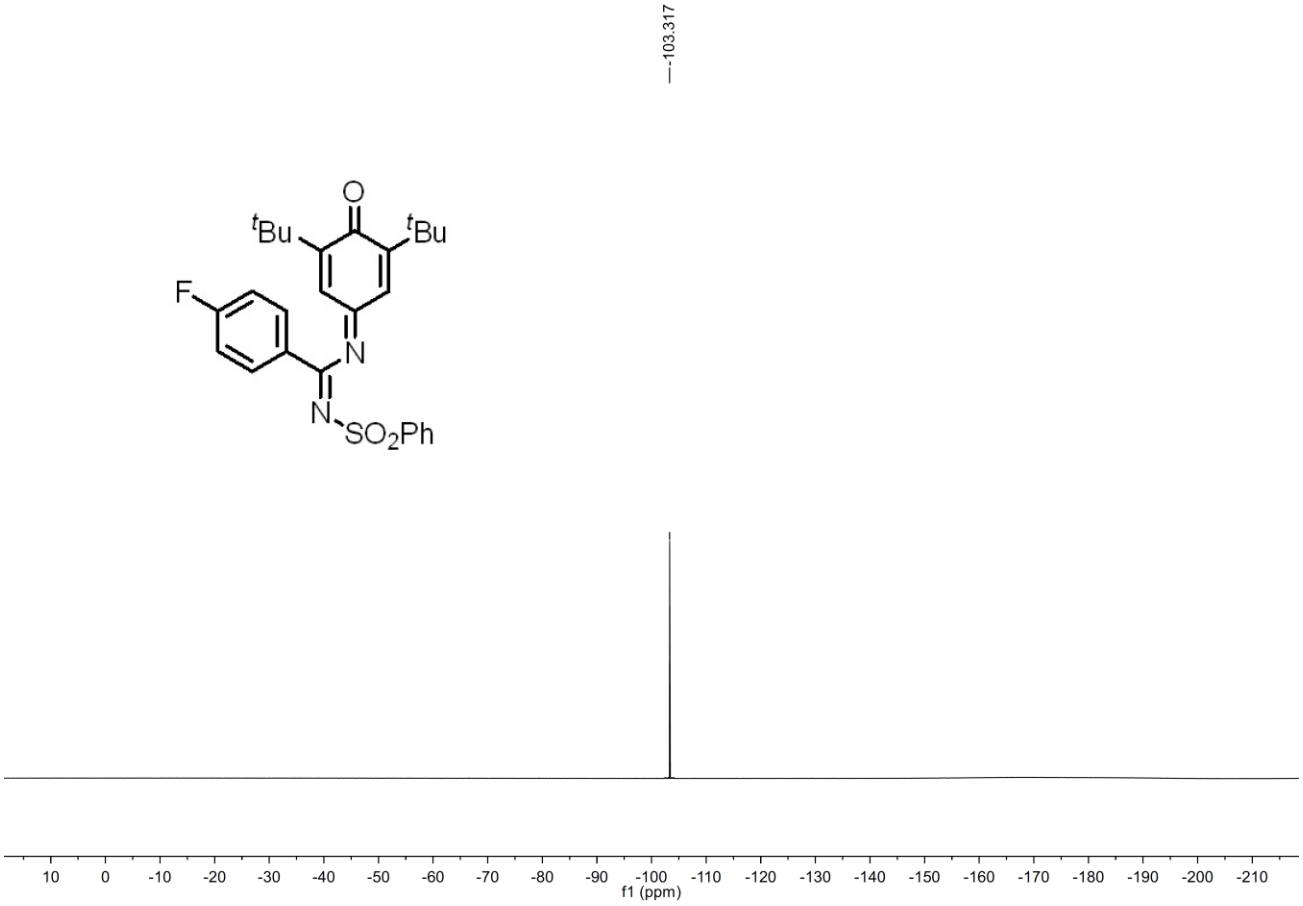
^{13}C NMR Spectrum of Compound 3g (100 MHz, $CDCl_3$)



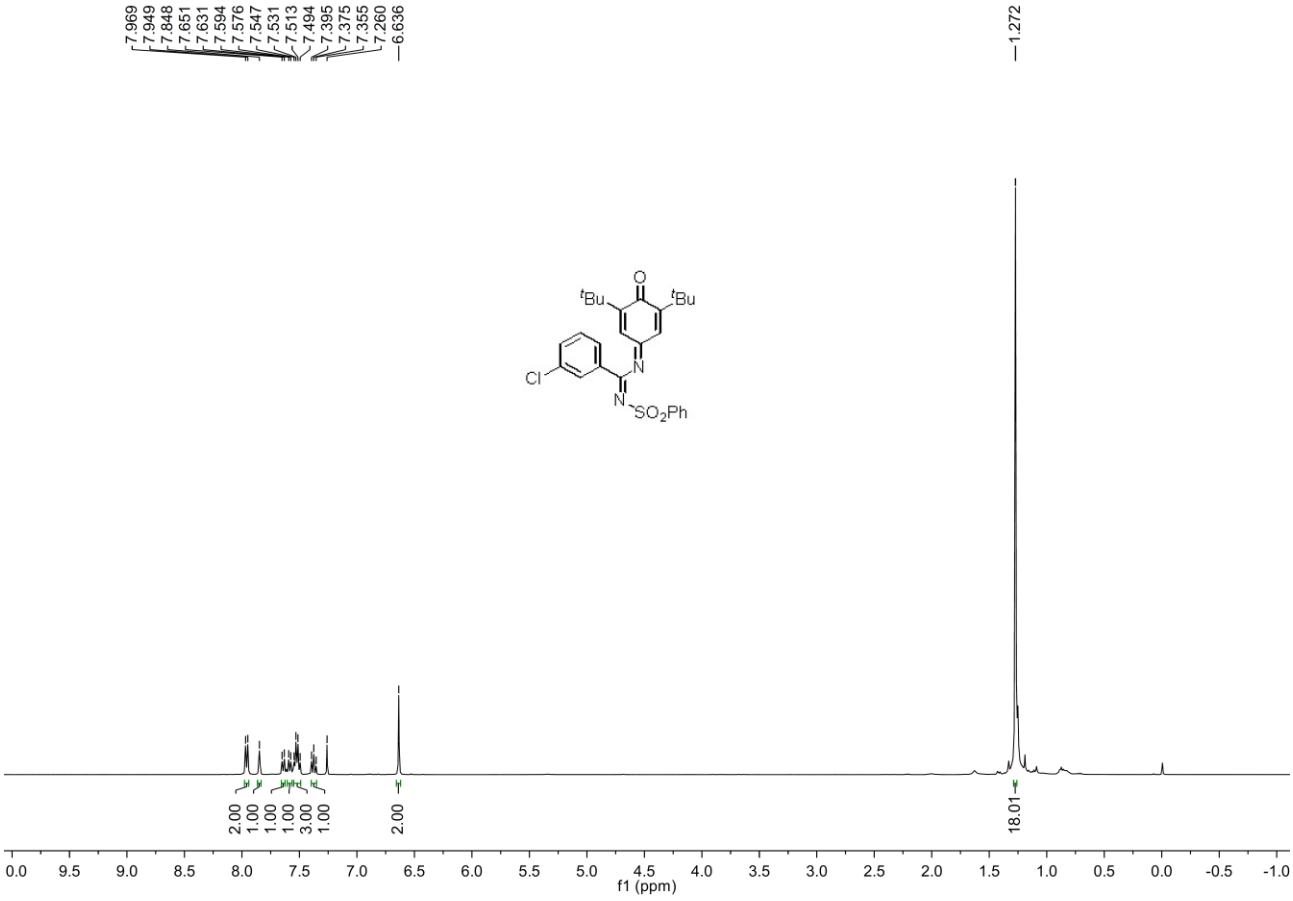
^{1}H NMR Spectrum of Compound 3h (400 MHz, $CDCl_3$)



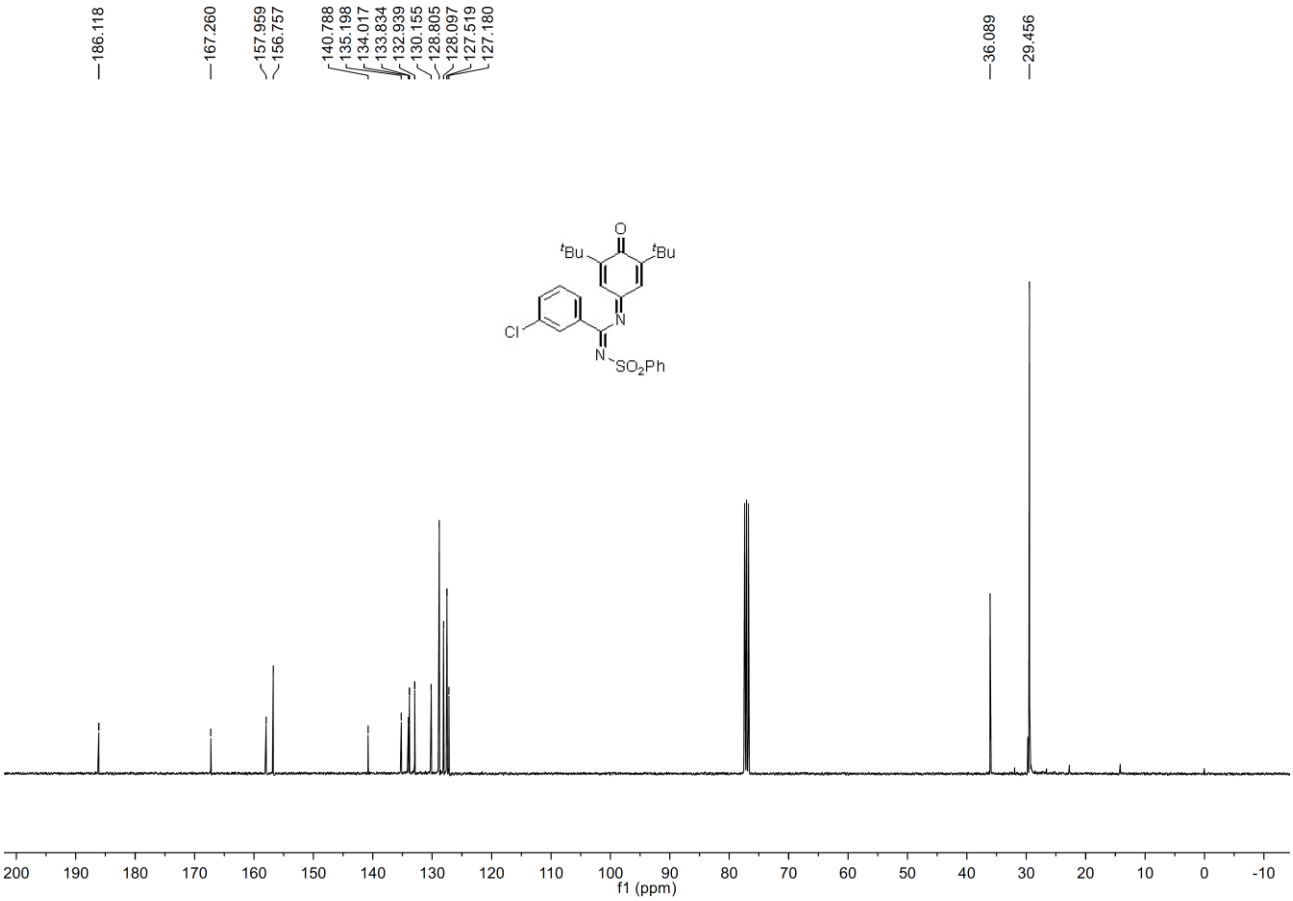
^{13}C NMR Spectrum of Compound 3h (100 MHz, $CDCl_3$)



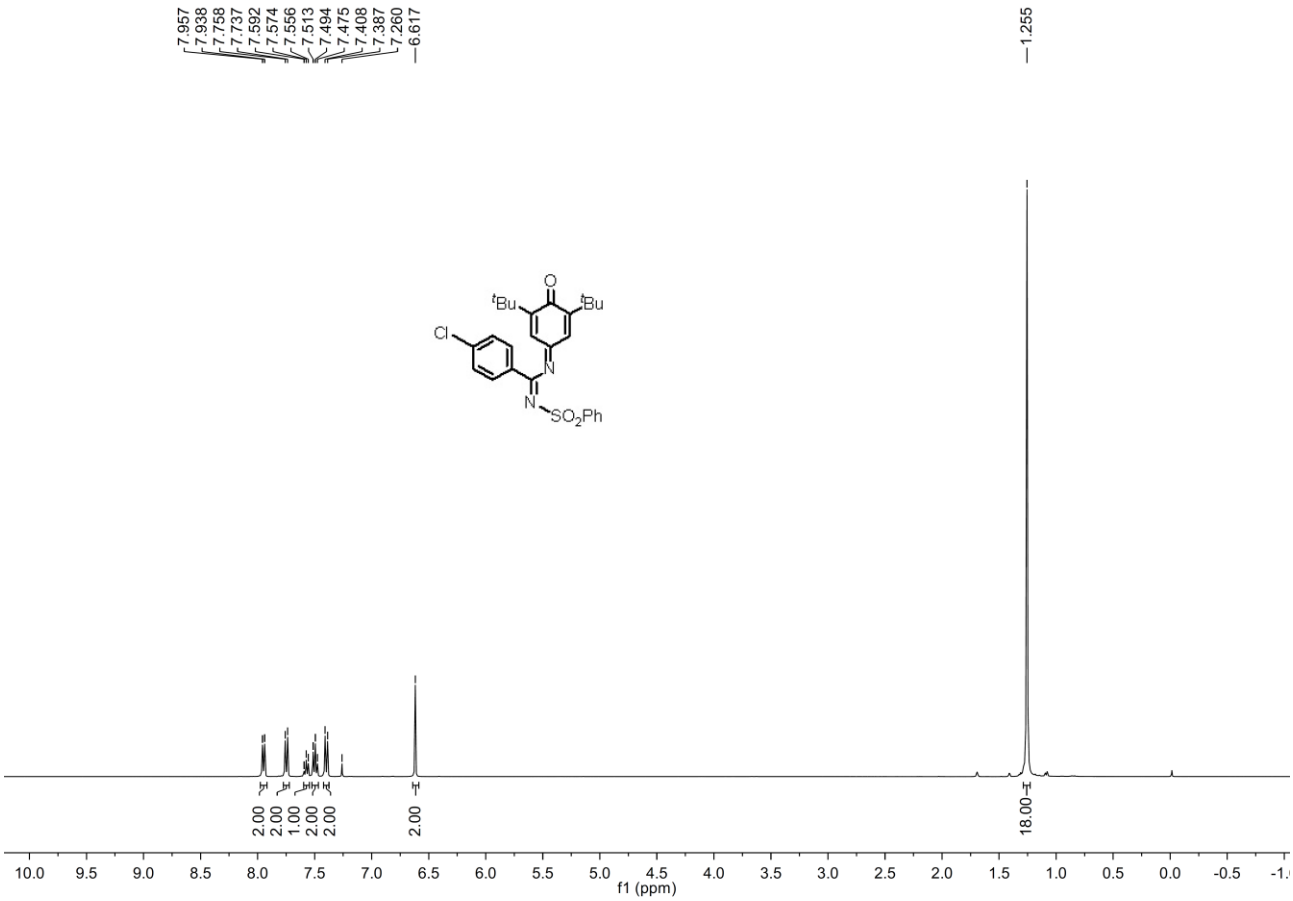
^{19}F NMR Spectrum of Compound 3h (376 MHz, $CDCl_3$)



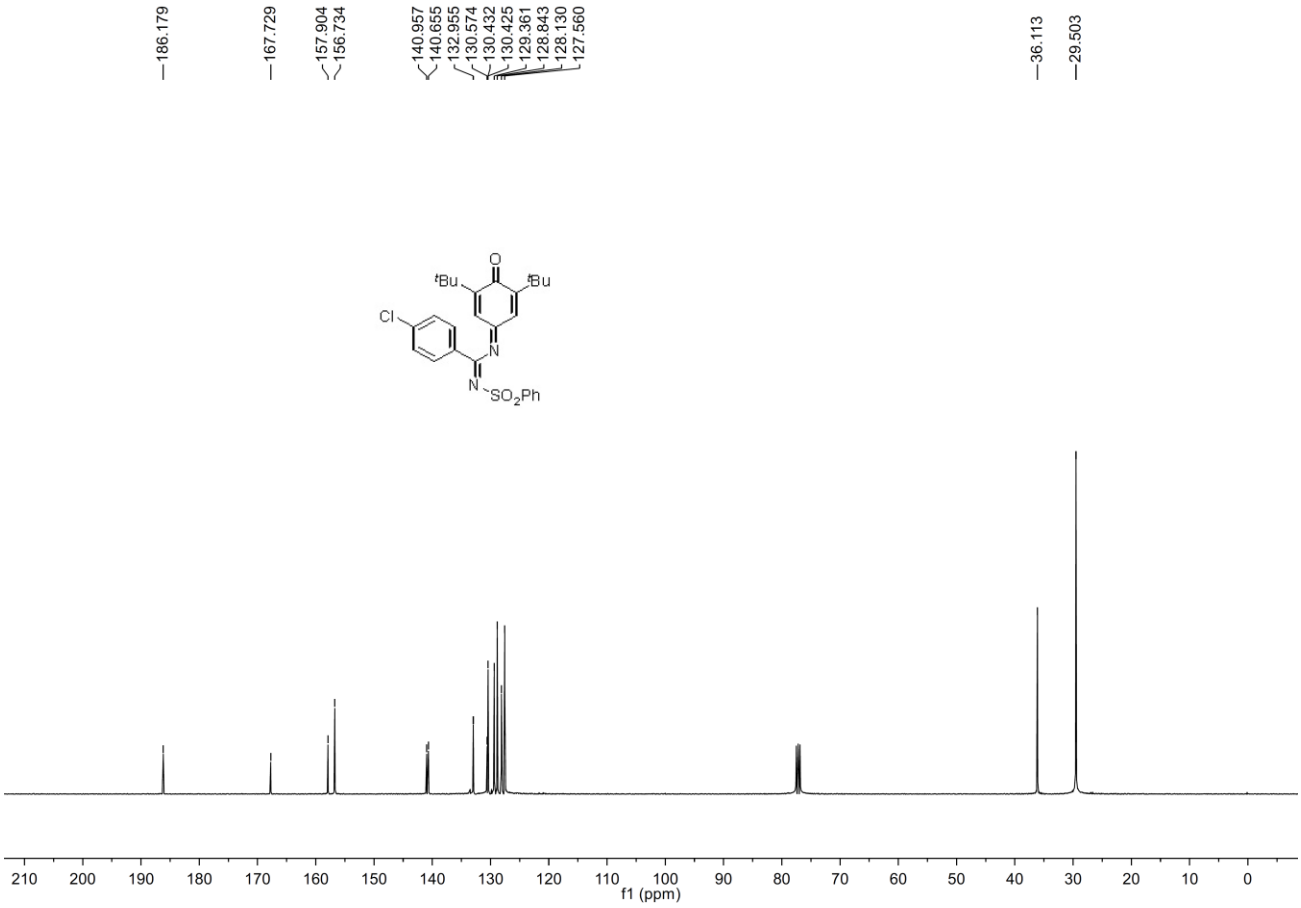
^{1}H NMR Spectrum of Compound 3i (400 MHz, $CDCl_3$)



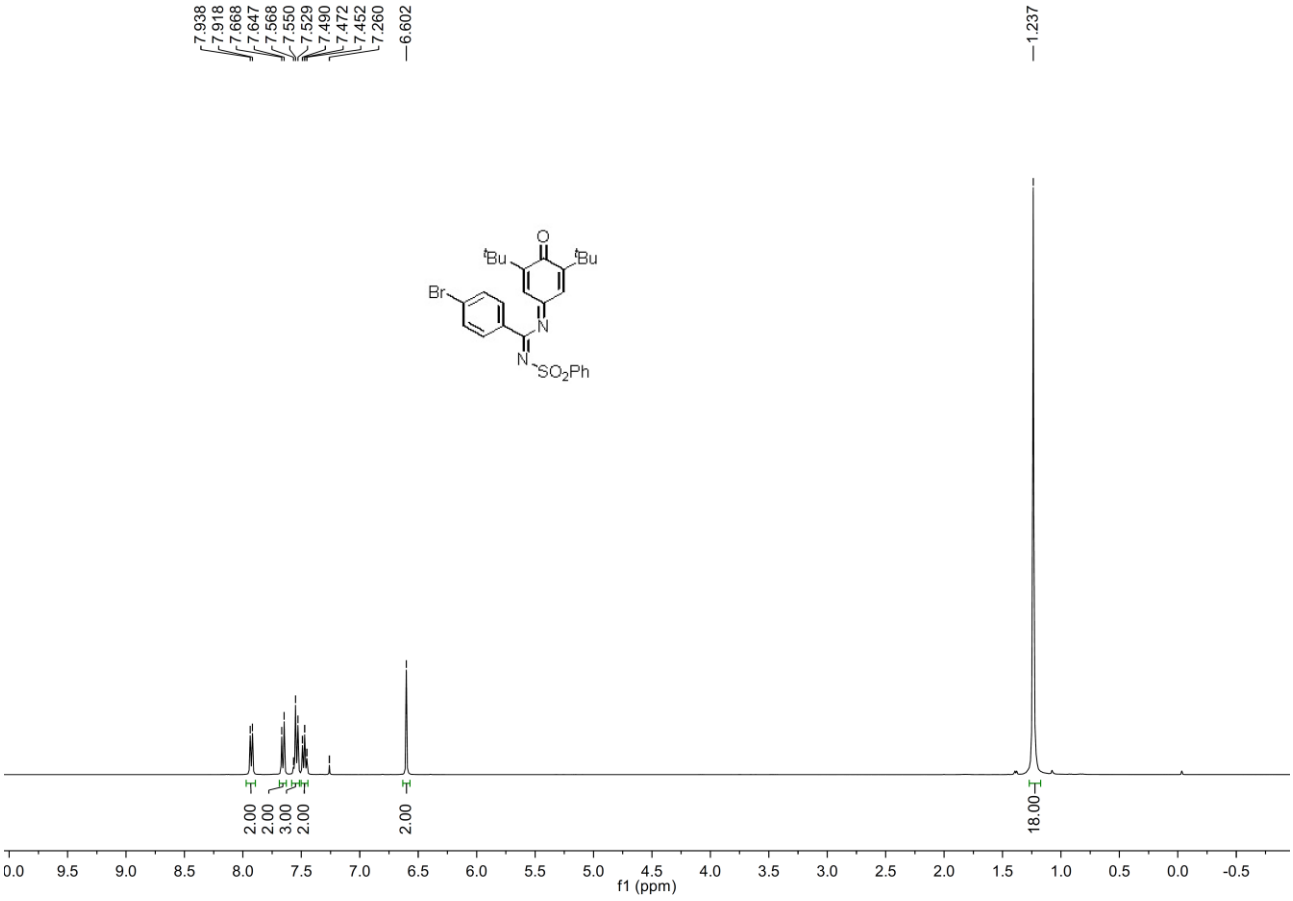
^{13}C NMR Spectrum of Compound 3i (100 MHz, $CDCl_3$)



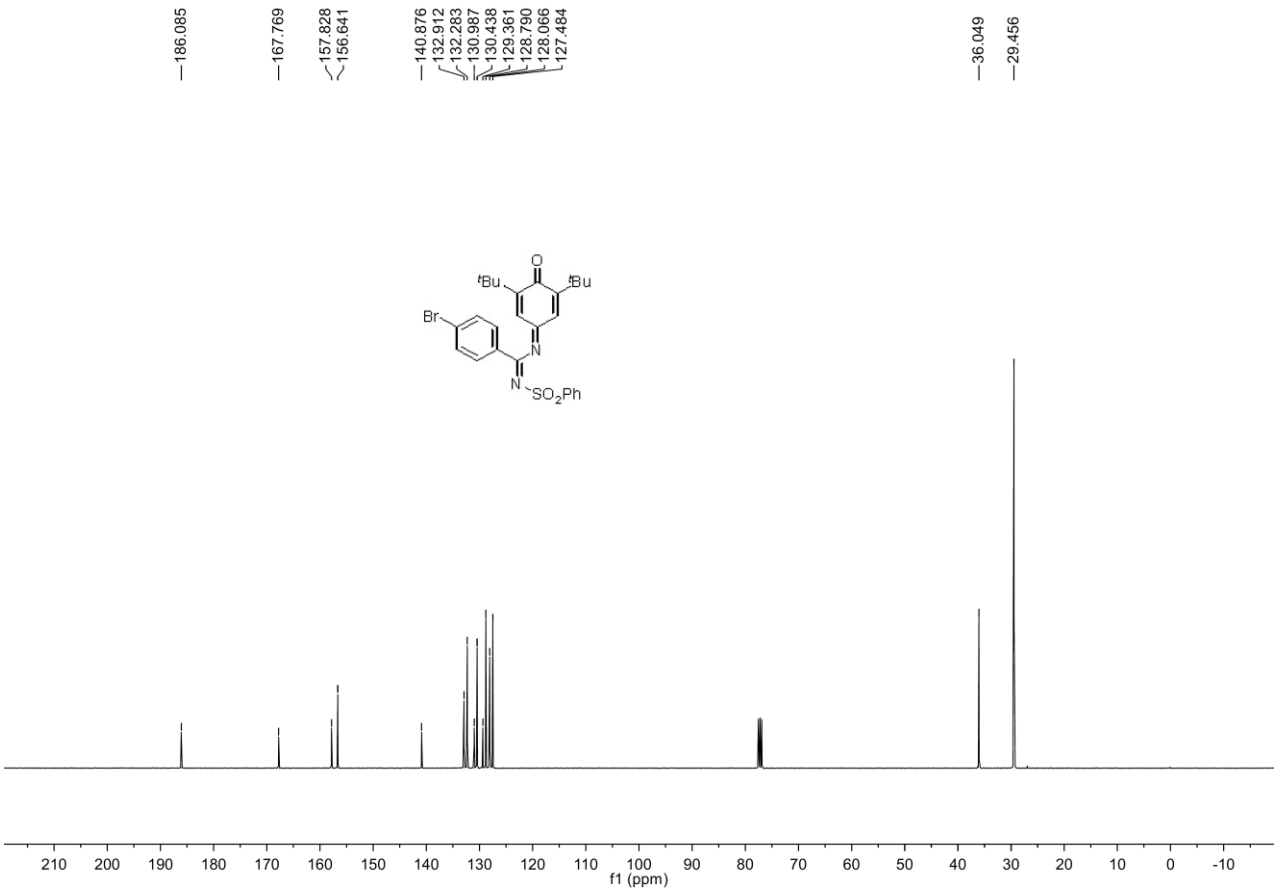
^{1}H NMR Spectrum of Compound 3j (400 MHz, $CDCl_3$)



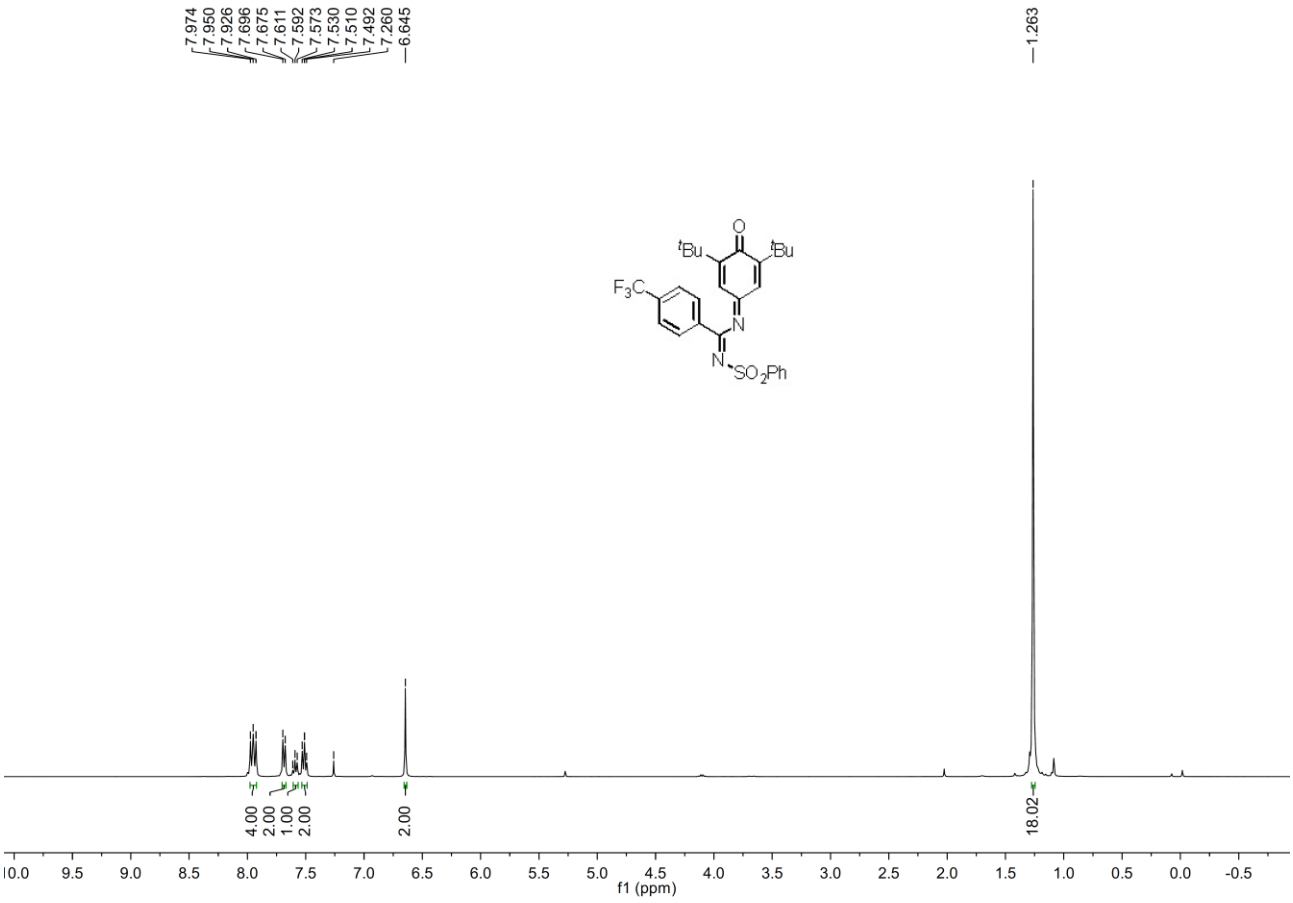
^{13}C NMR Spectrum of Compound 3j (100 MHz, $CDCl_3$)



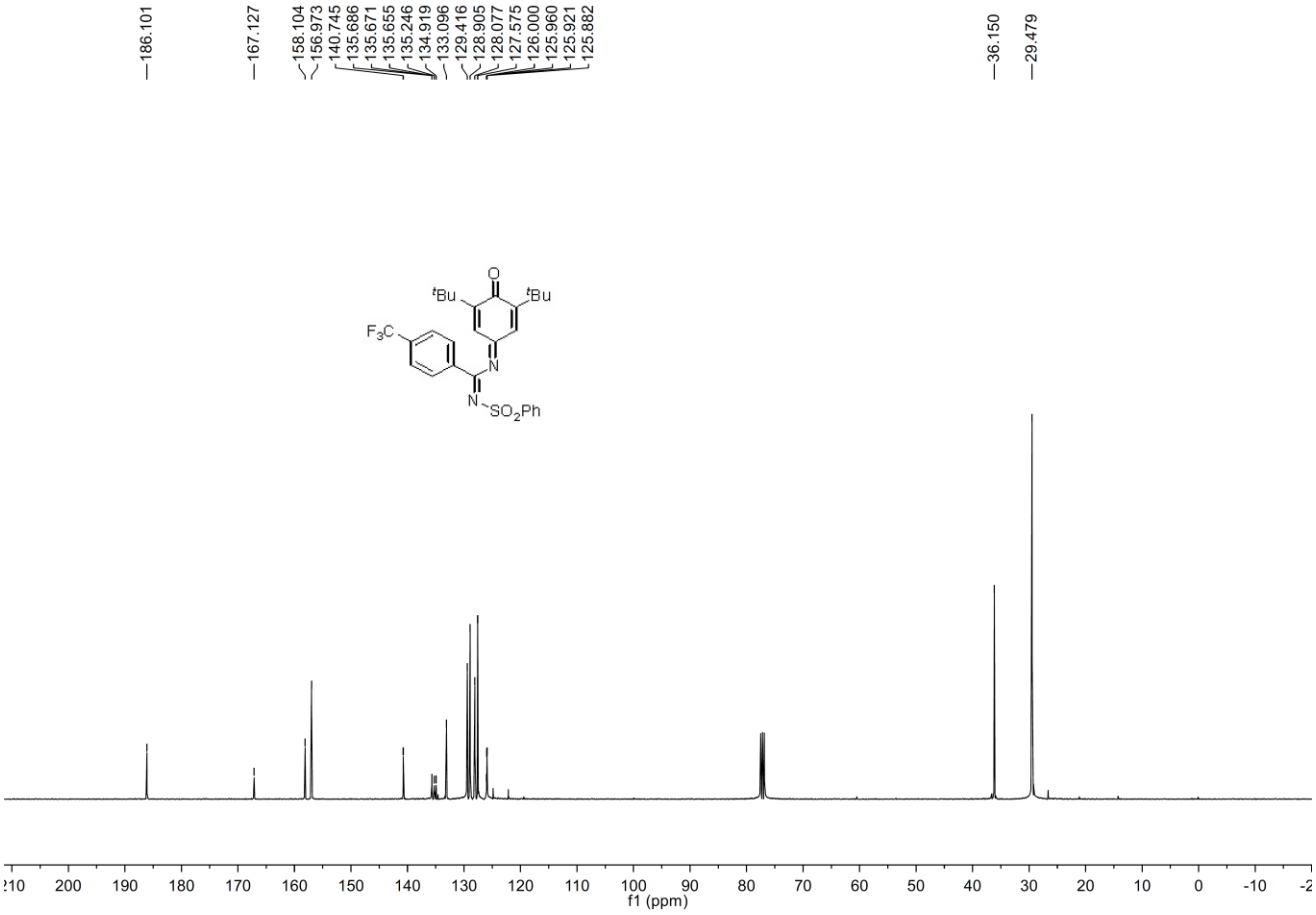
^{1}H NMR Spectrum of Compound 3k (400 MHz, $CDCl_3$)



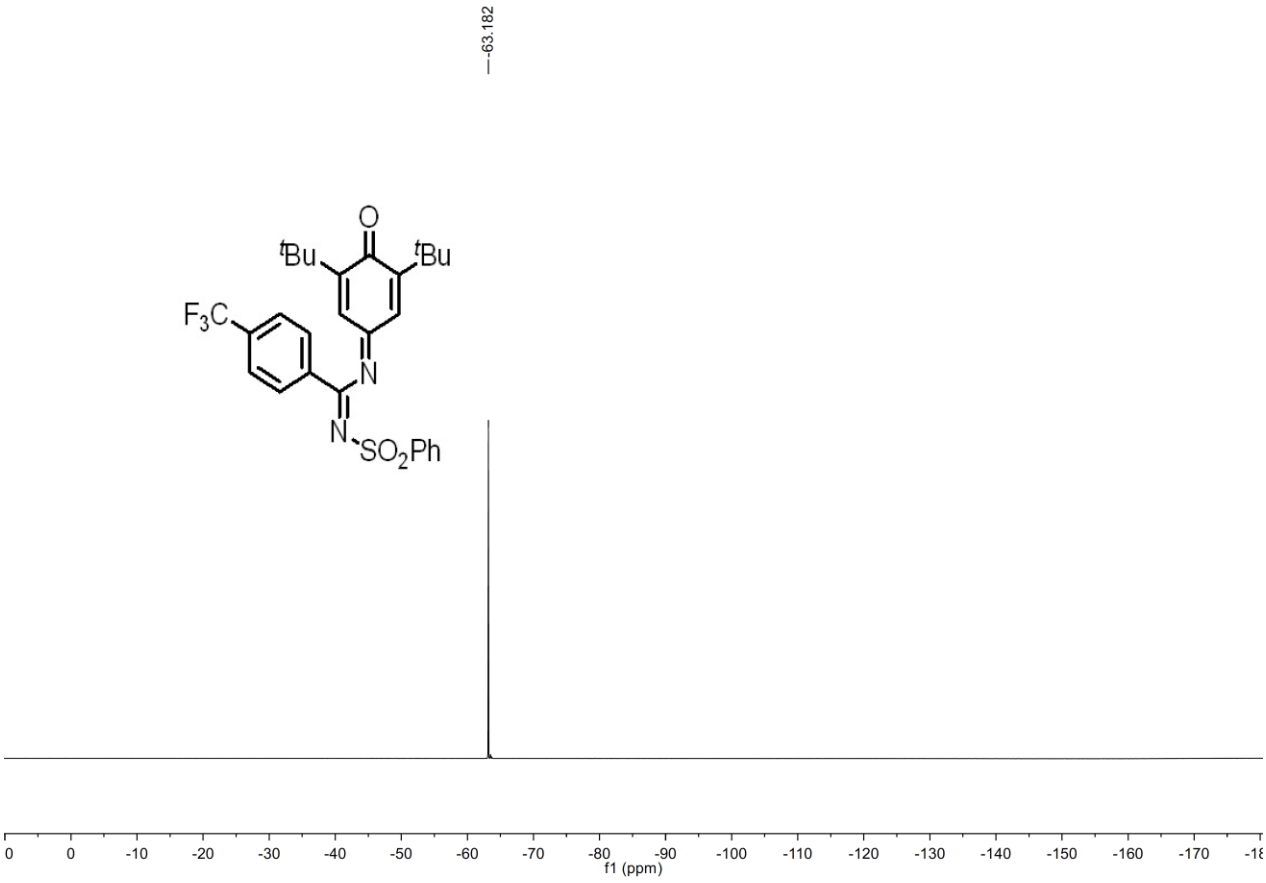
^{13}C NMR Spectrum of Compound 3k (100 MHz, $CDCl_3$)



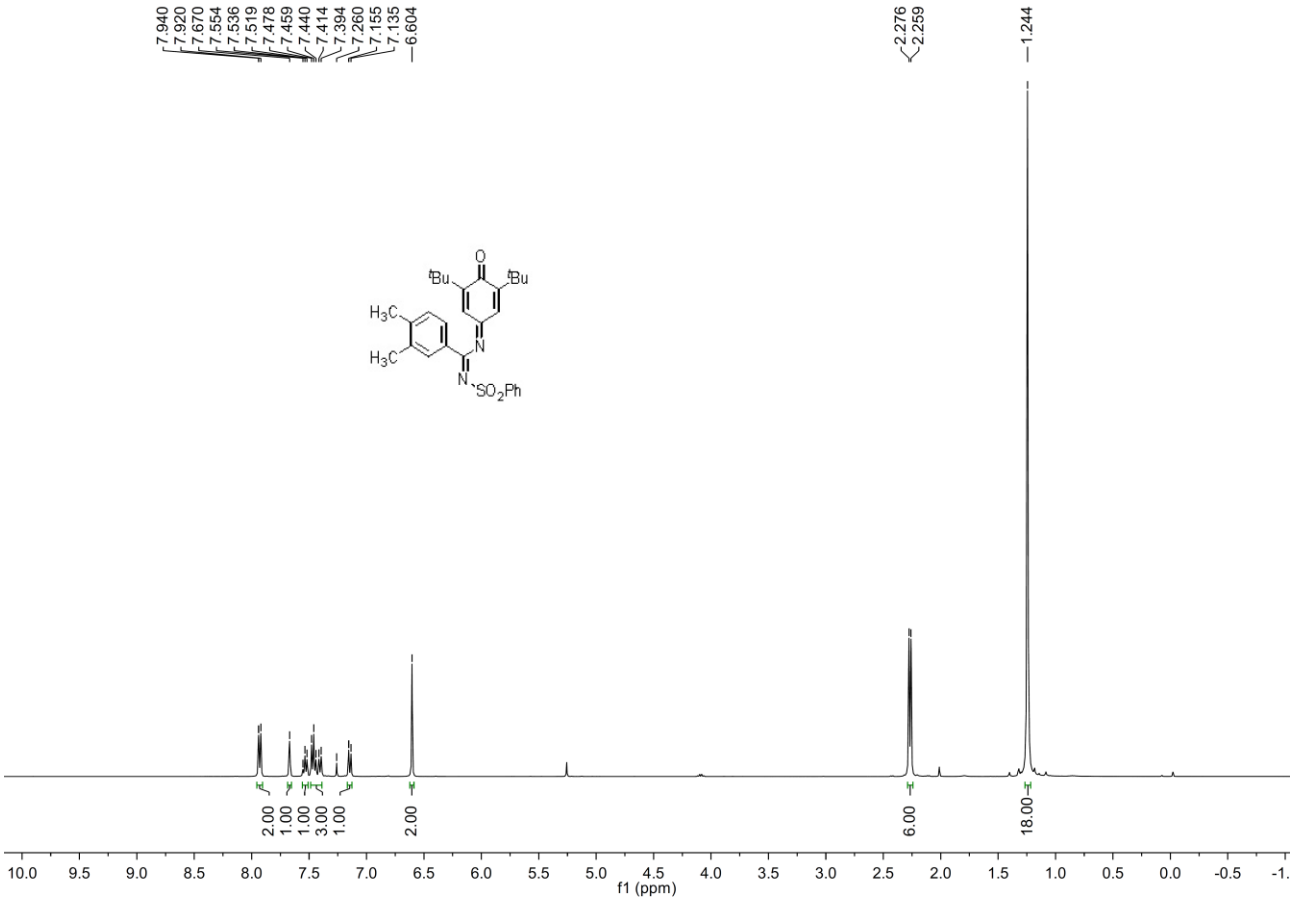
^{1}H NMR Spectrum of Compound 3l (400 MHz, $CDCl_3$)



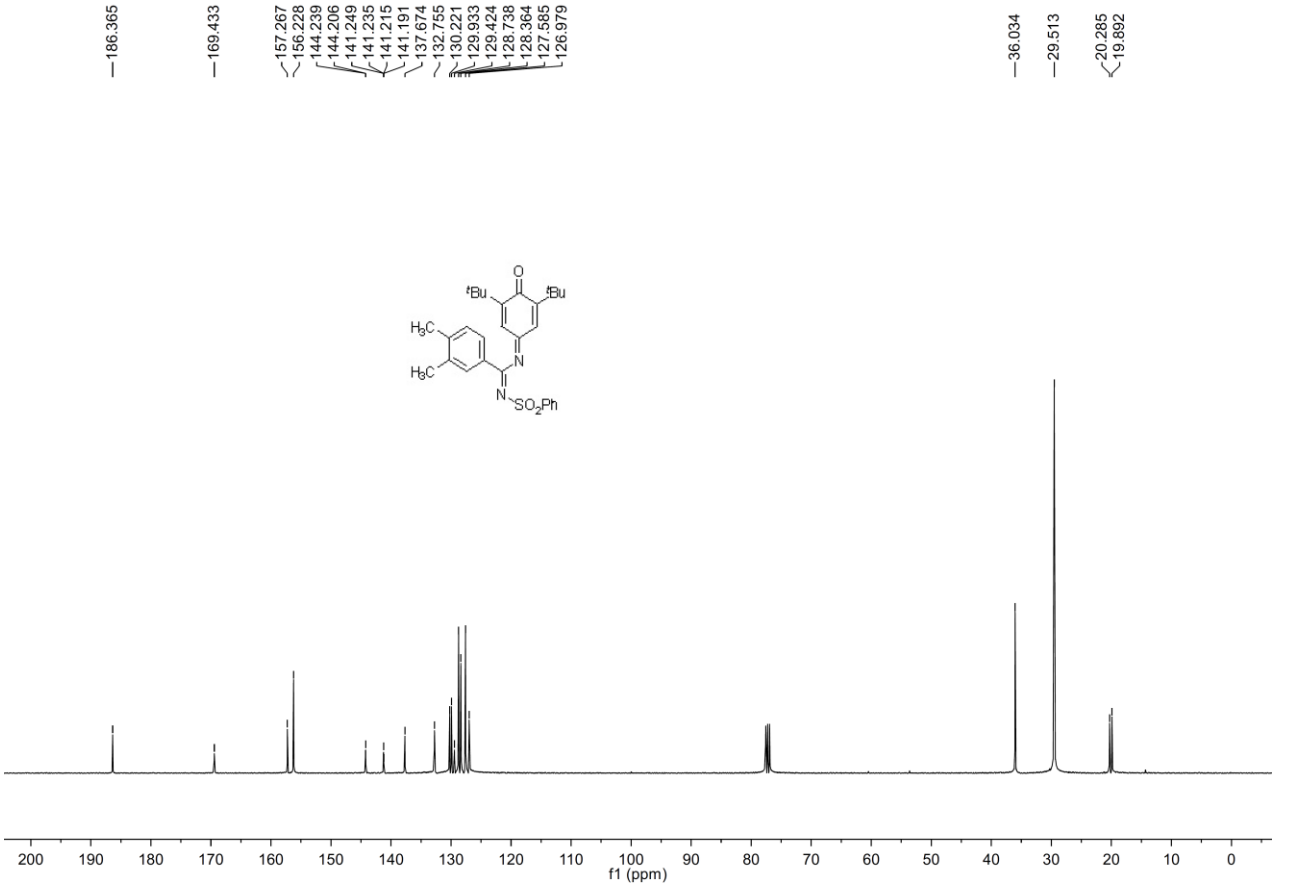
^{13}C NMR Spectrum of Compound 3l (100 MHz, $CDCl_3$)



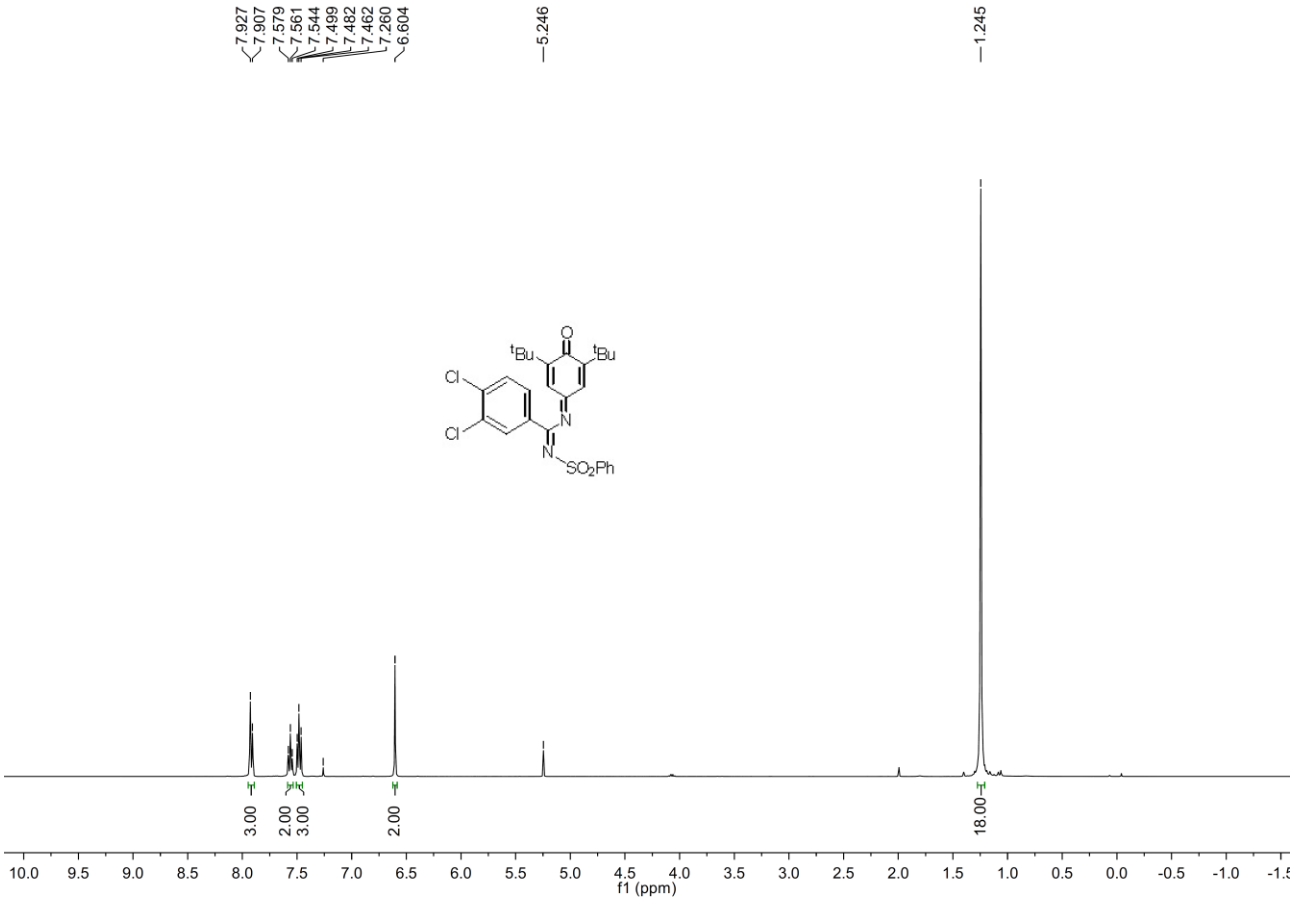
^{19}F NMR Spectrum of Compound 3l (376 MHz, $CDCl_3$)



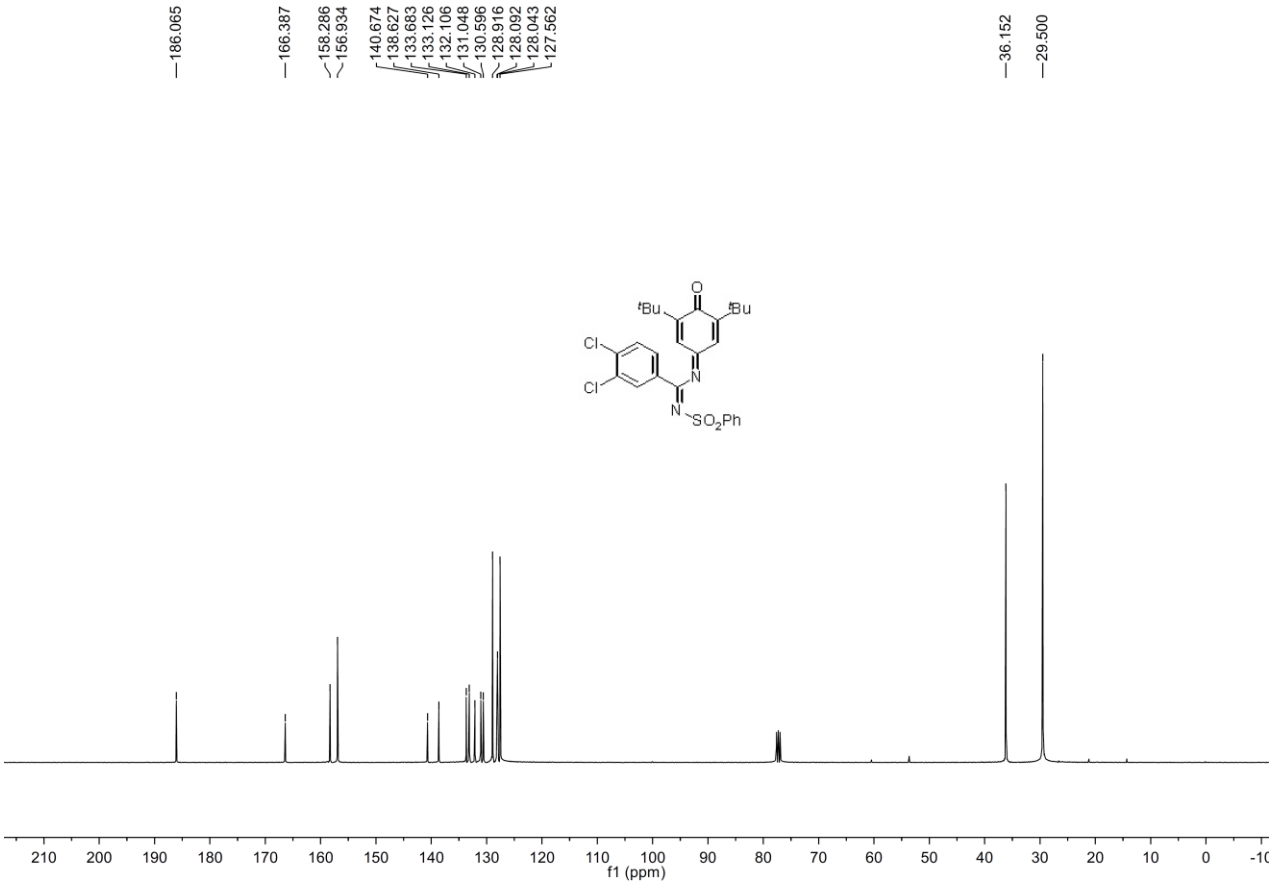
^{1}H NMR Spectrum of Compound 3m (400 MHz, $CDCl_3$)



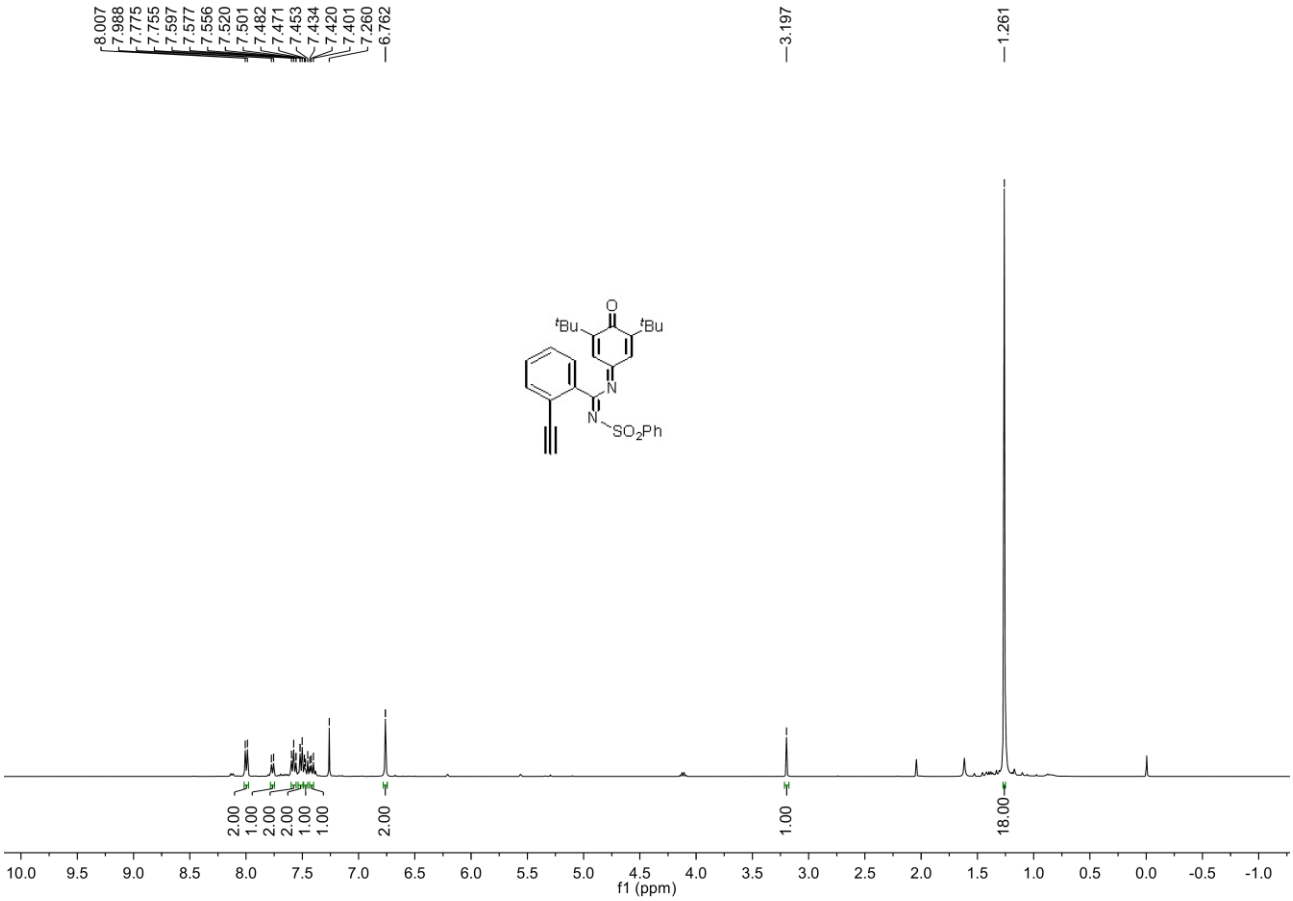
^{13}C NMR Spectrum of Compound 3m (100 MHz, $CDCl_3$)



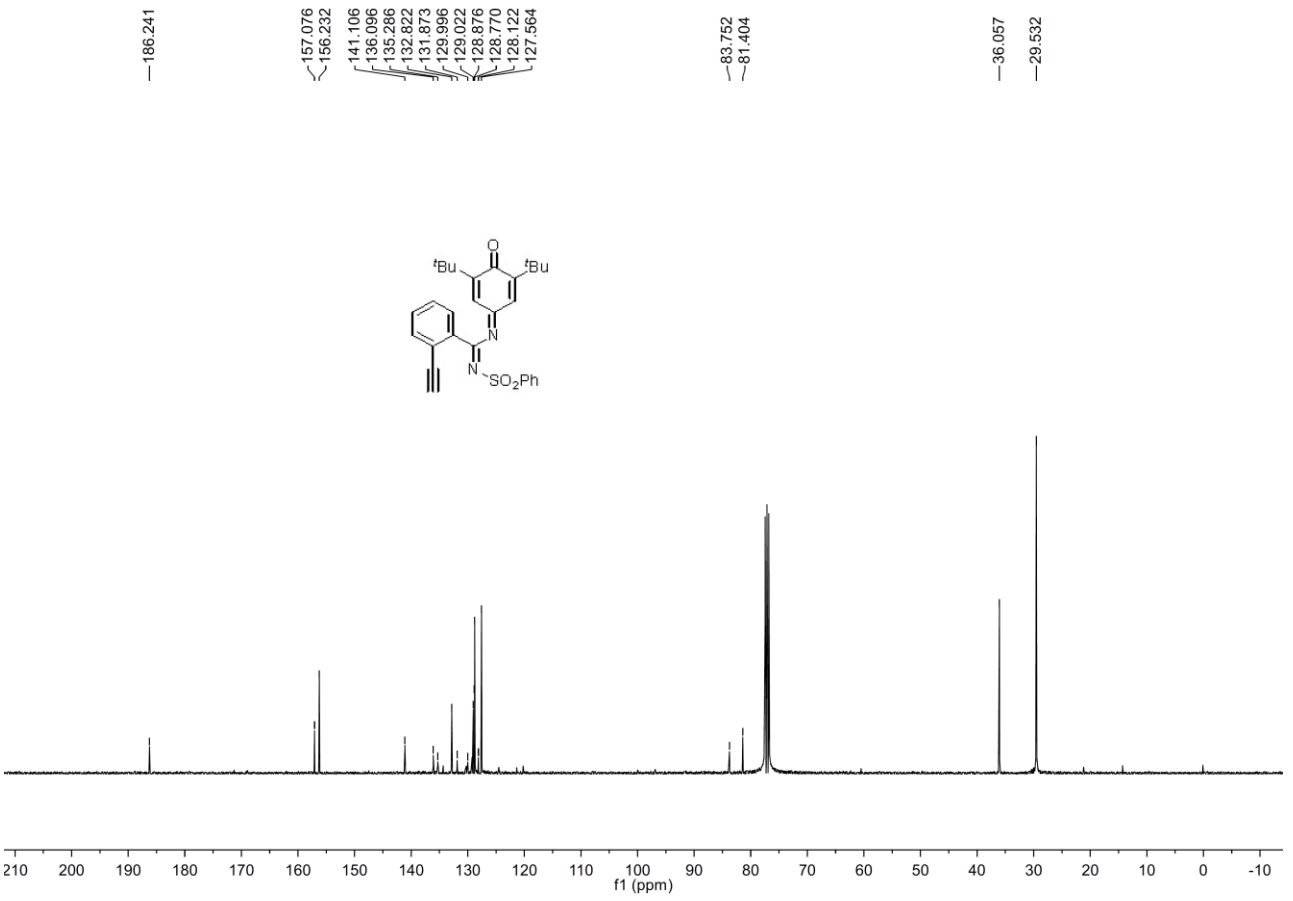
^{1}H NMR Spectrum of Compound 3n (400 MHz, $CDCl_3$)



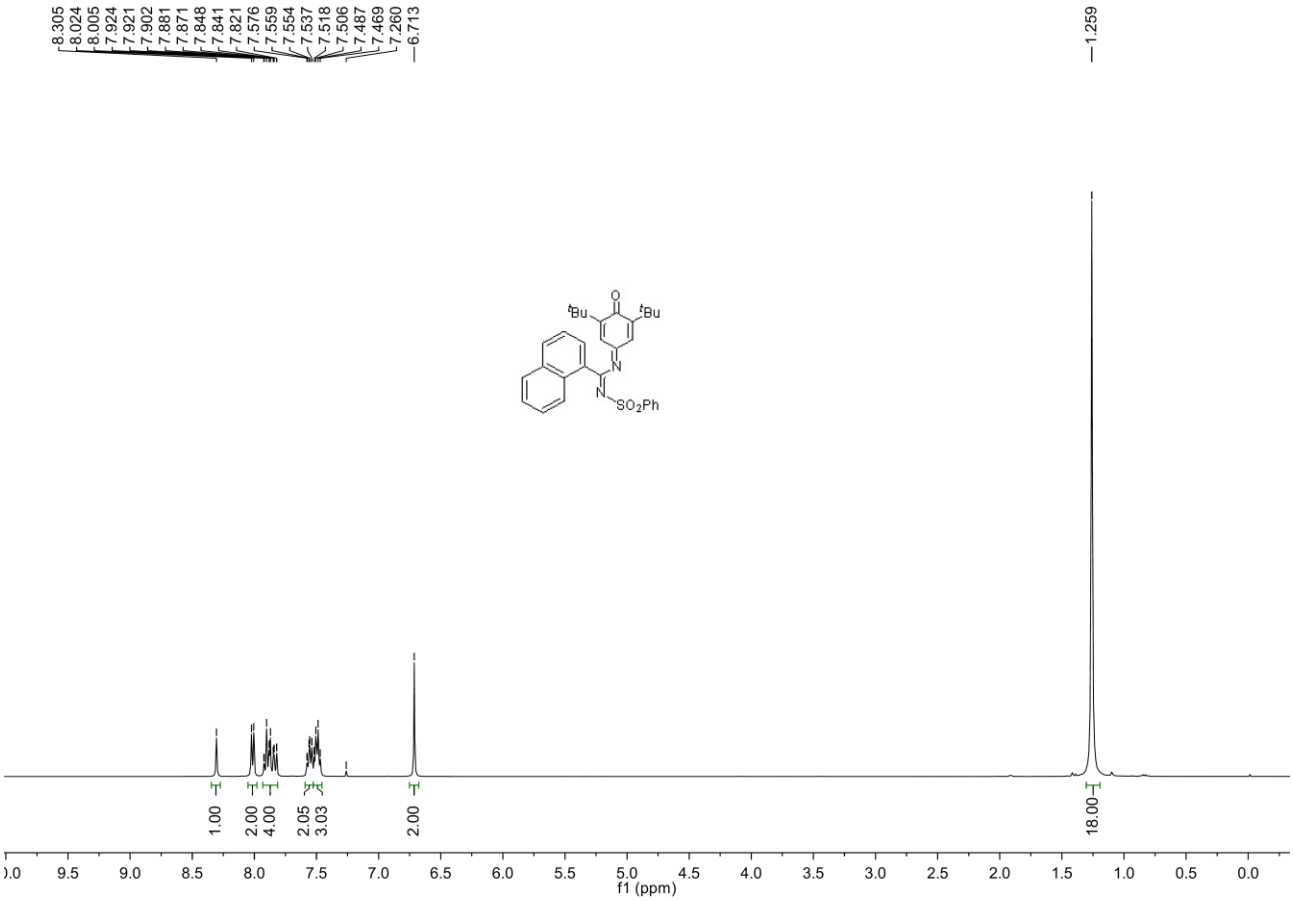
^{13}C NMR Spectrum of Compound 3n (100 MHz, $CDCl_3$)



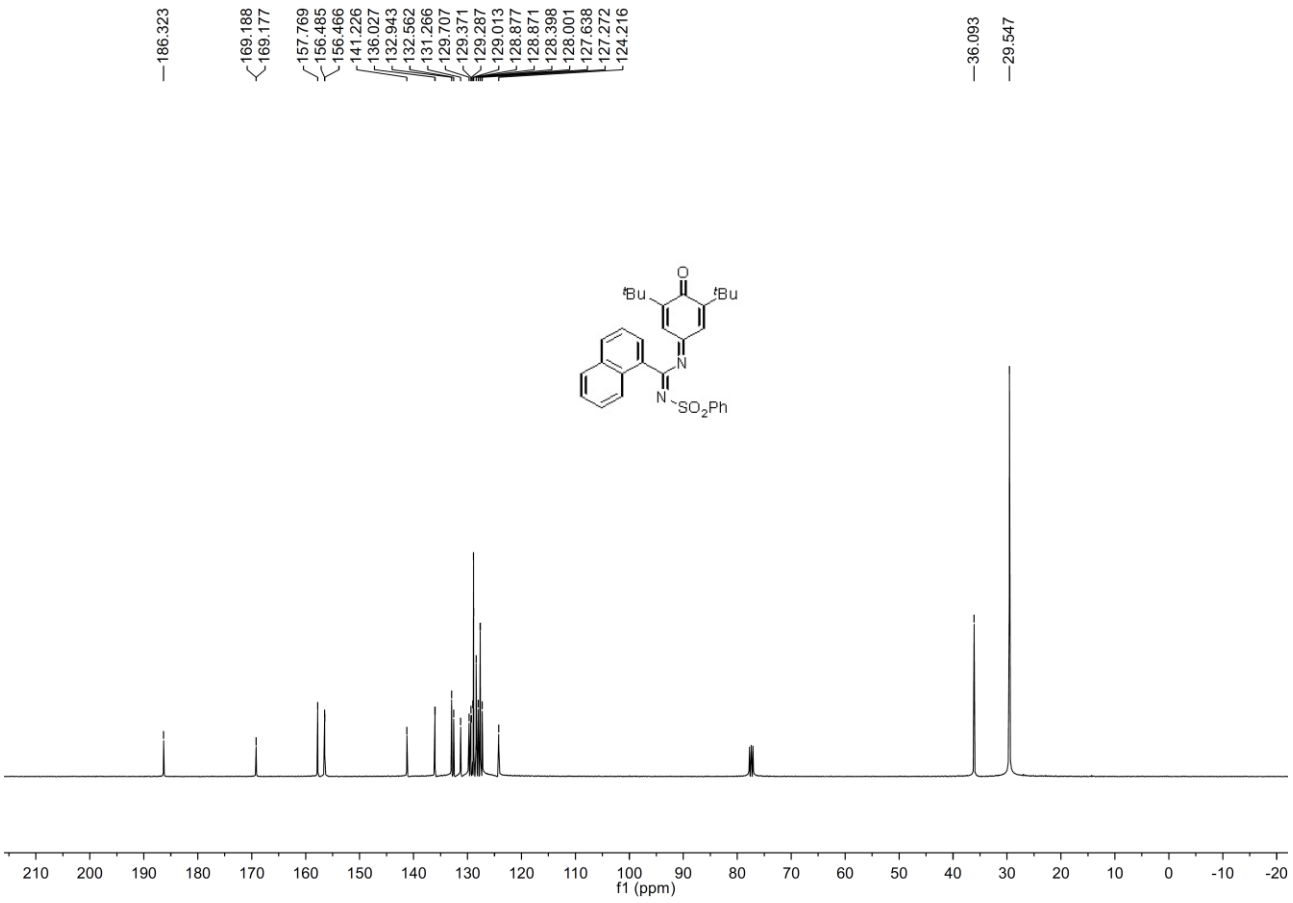
^{1}H NMR Spectrum of Compound 3o



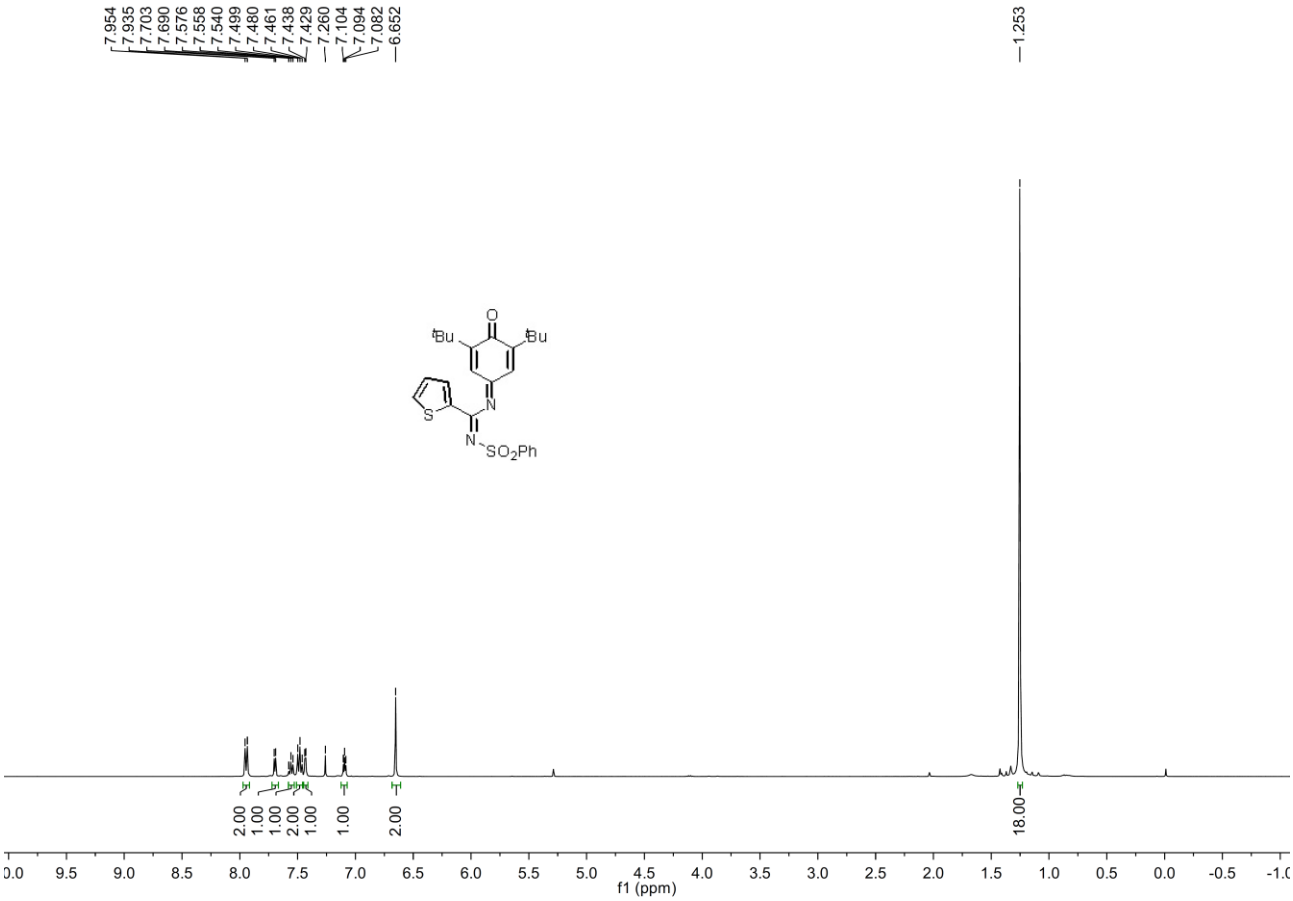
^{13}C NMR Spectrum of Compound 3o (100 MHz, $CDCl_3$)



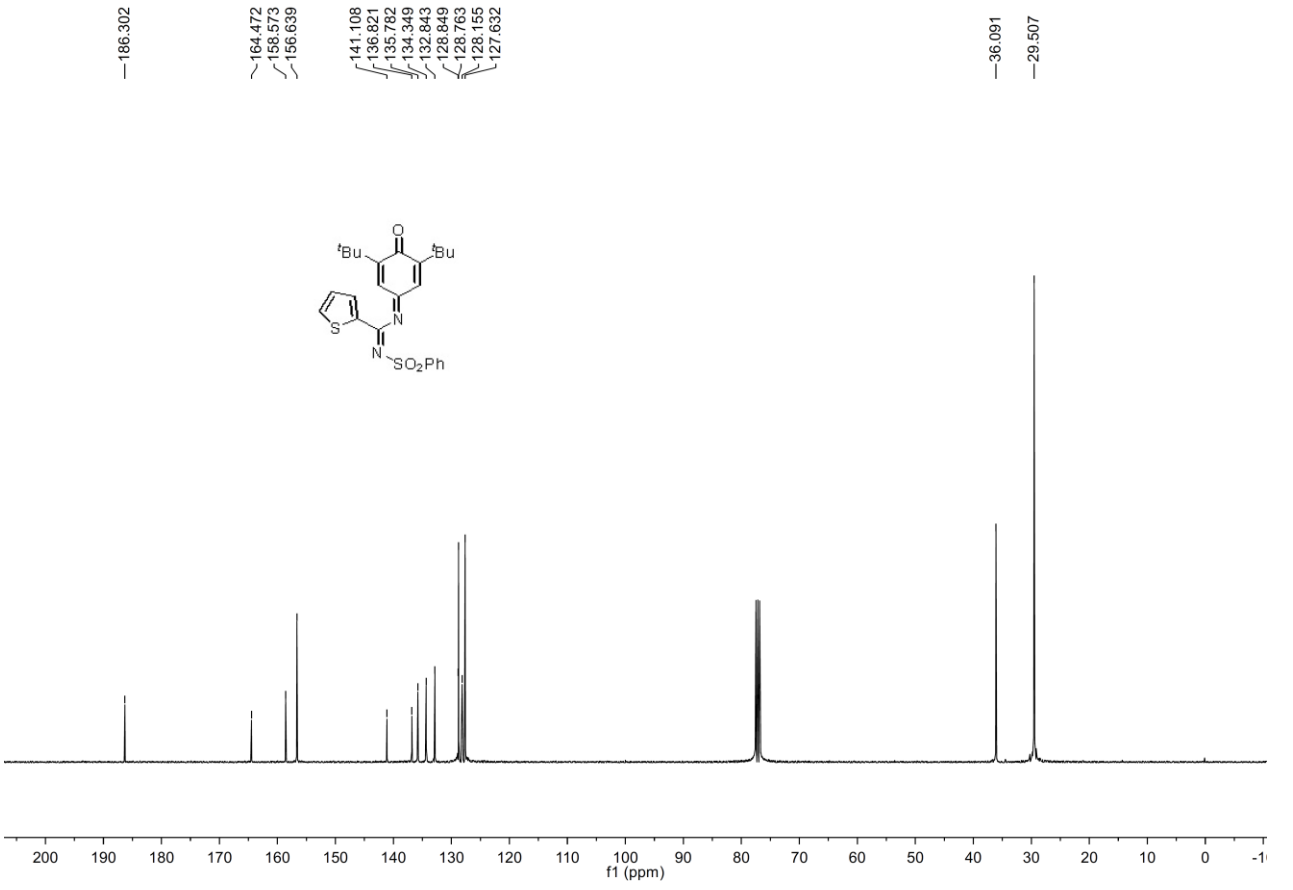
^{1}H NMR Spectrum of Compound 3p (400 MHz, $CDCl_3$)



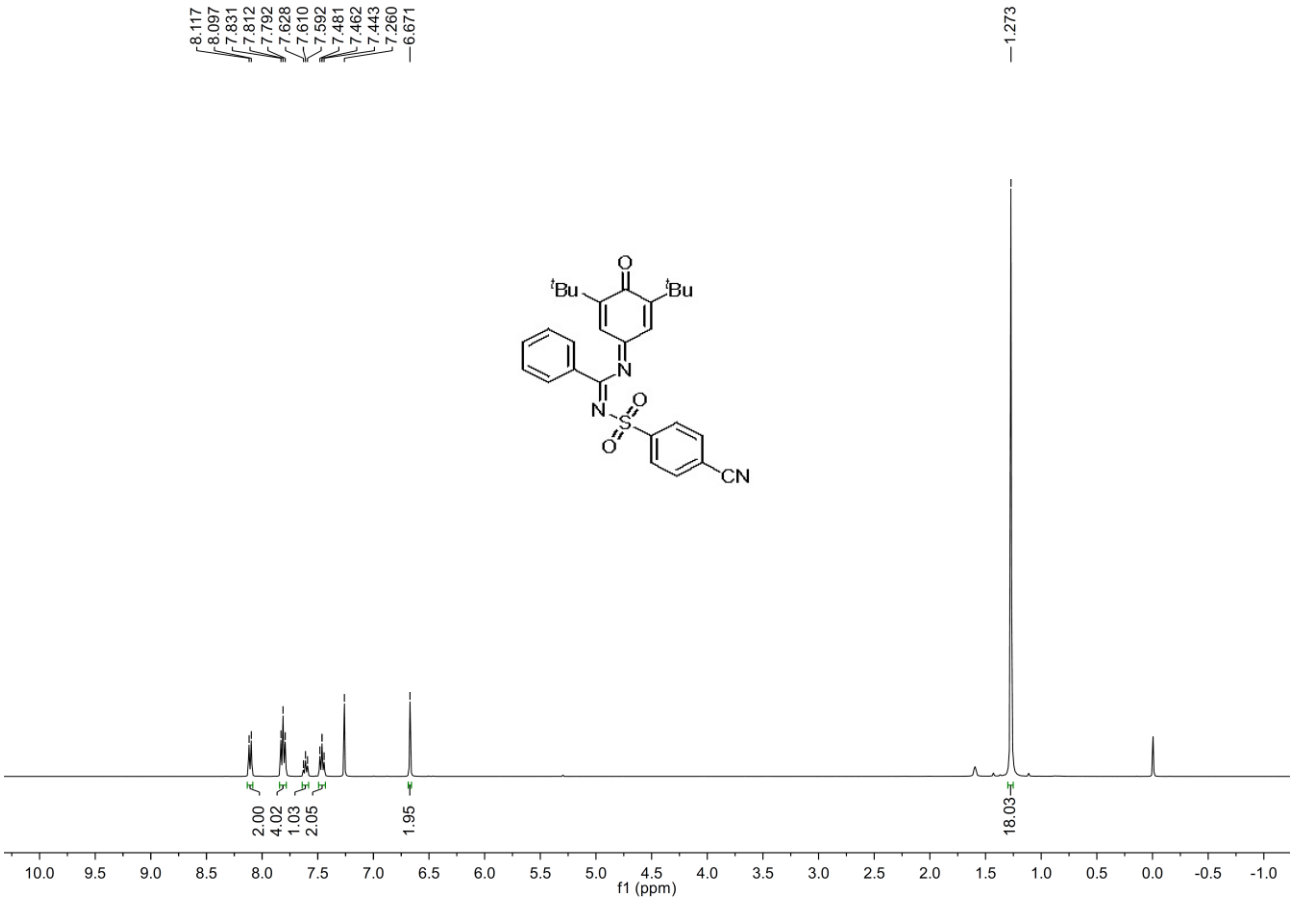
^{13}C NMR Spectrum of Compound 3p (100 MHz, $CDCl_3$)



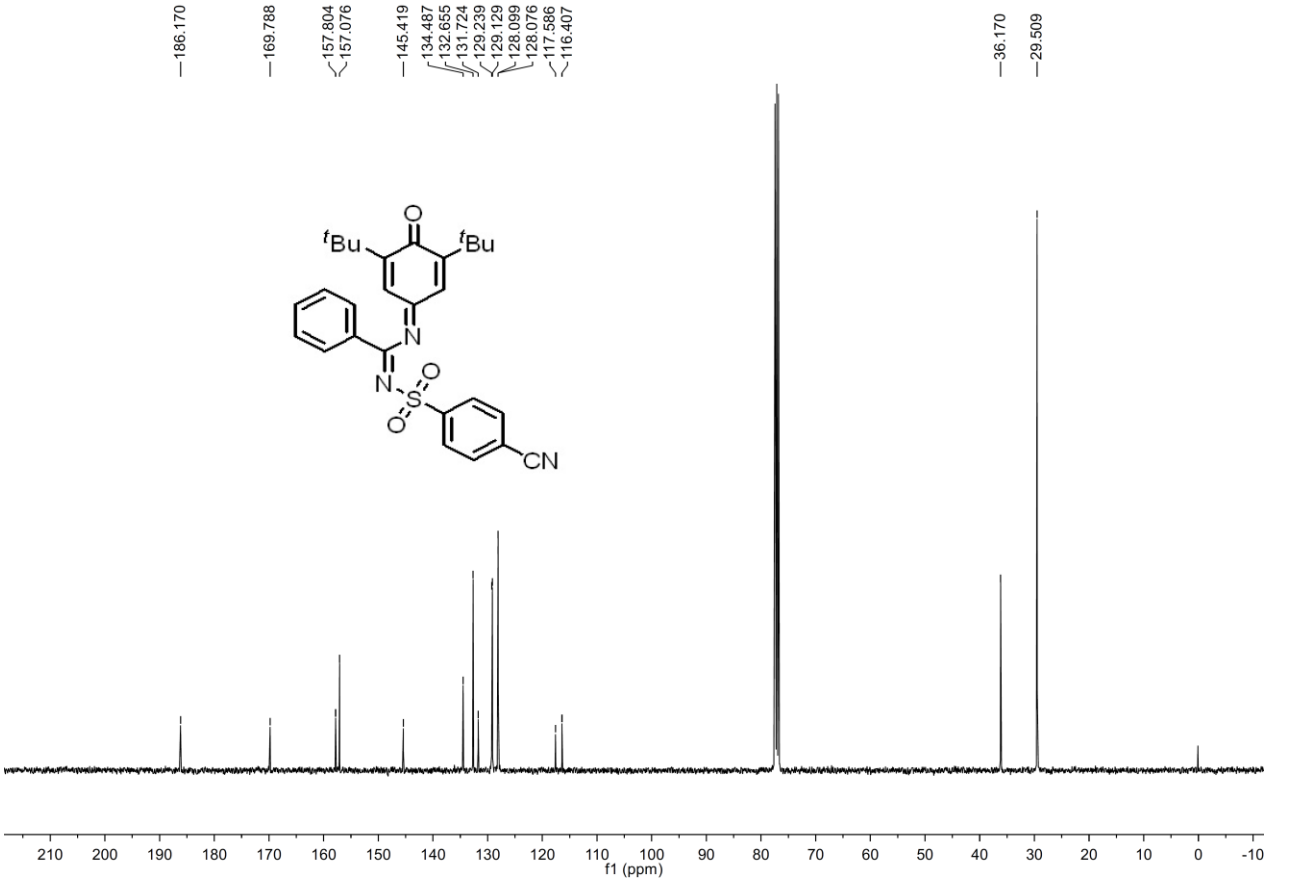
^{1}H NMR Spectrum of Compound 3q (400 MHz, $CDCl_3$)



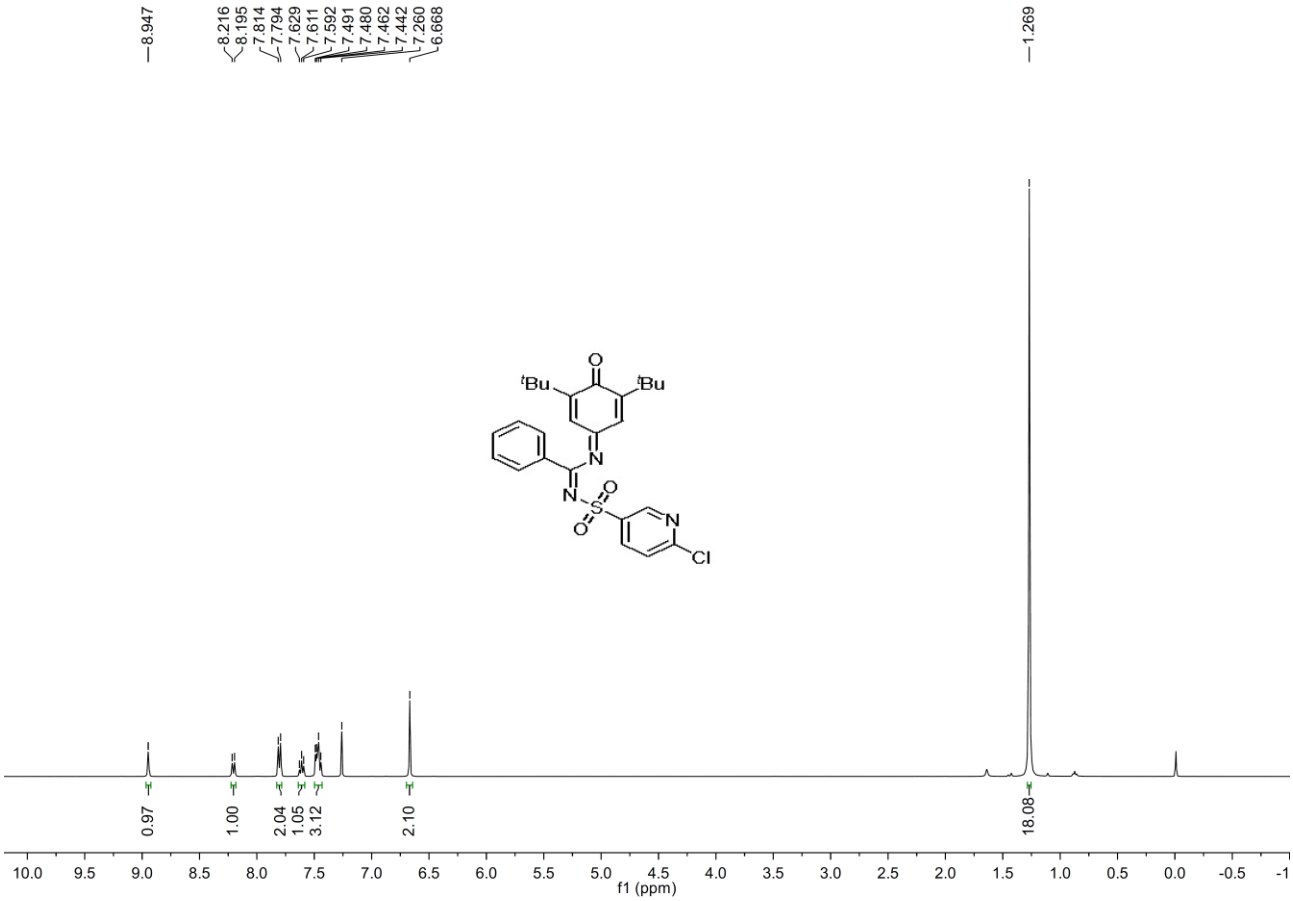
^{13}C NMR Spectrum of Compound 3q (100 MHz, $CDCl_3$)



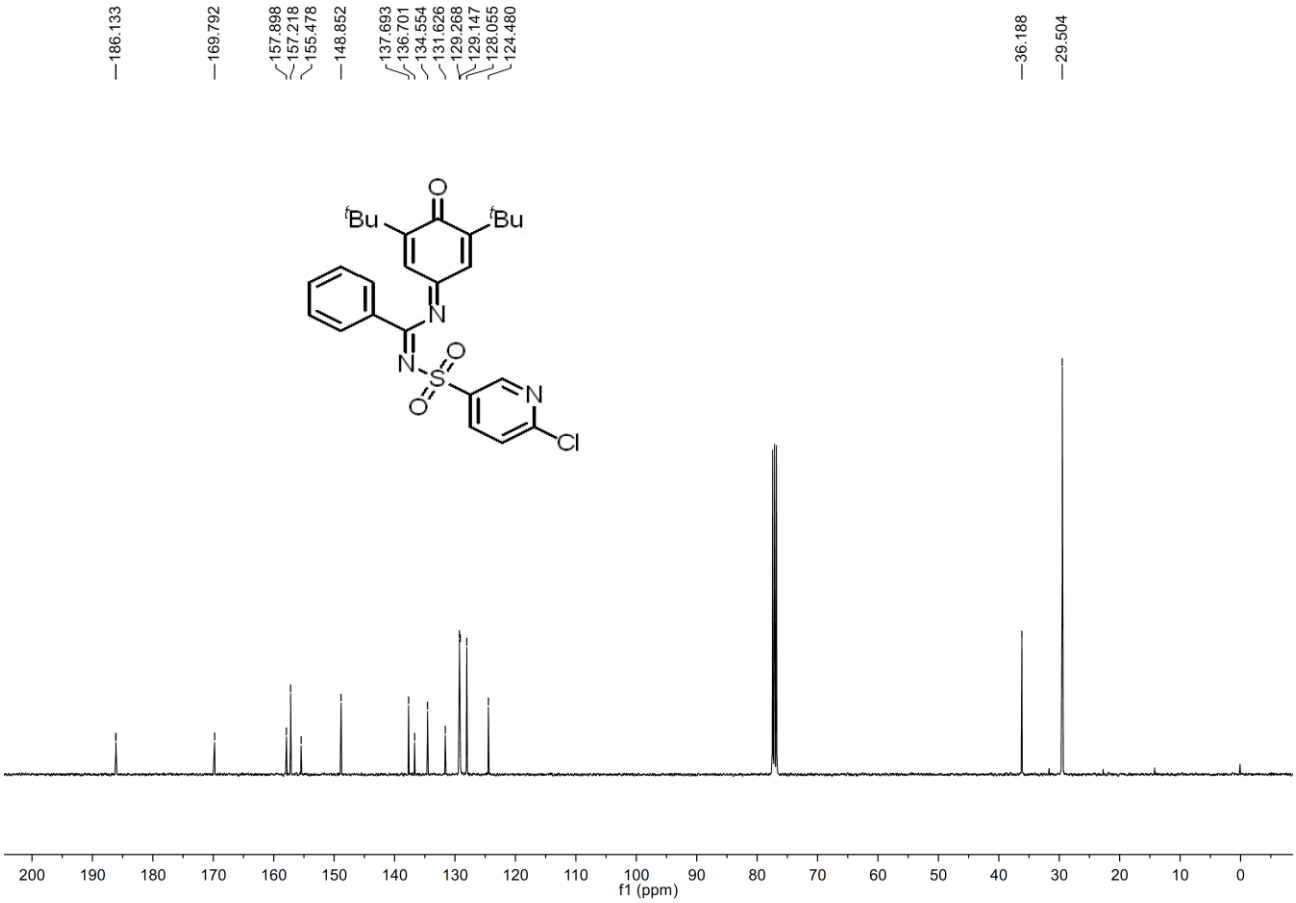
^{1}H NMR Spectrum of Compound 3r (400 MHz, $CDCl_3$)



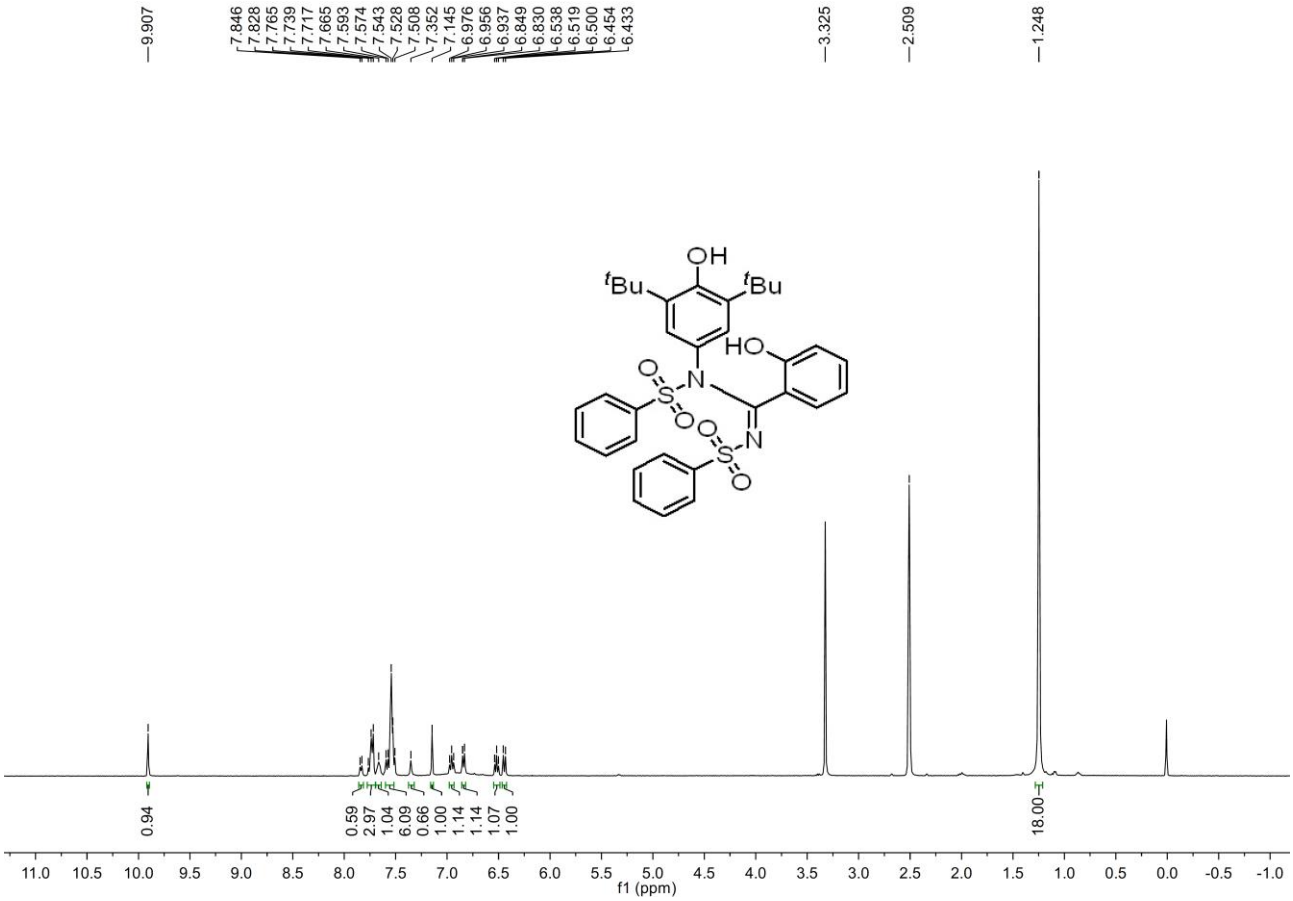
^{13}C NMR Spectrum of Compound 3r (100 MHz, $CDCl_3$)



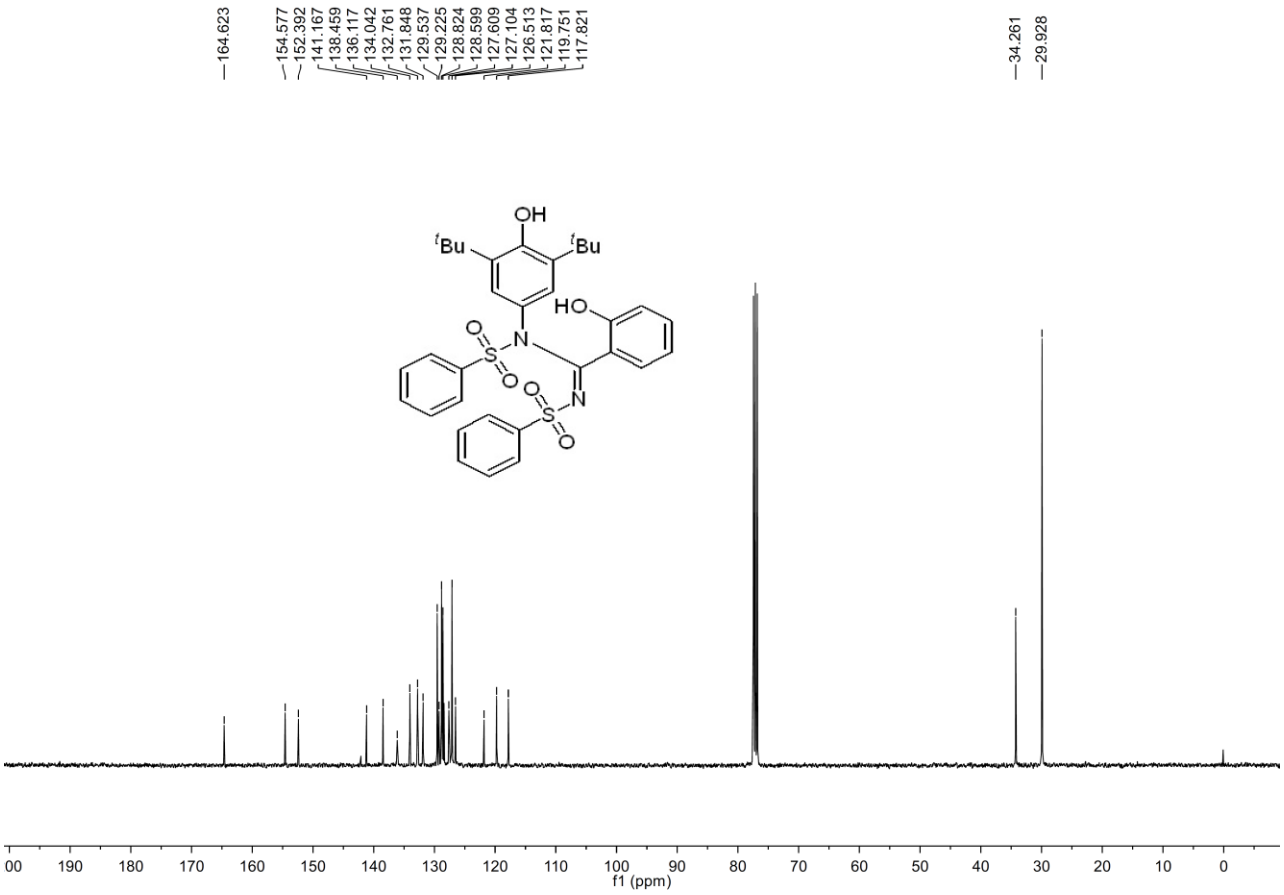
^{1}H NMR Spectrum of Compound 3s (400 MHz, $CDCl_3$)



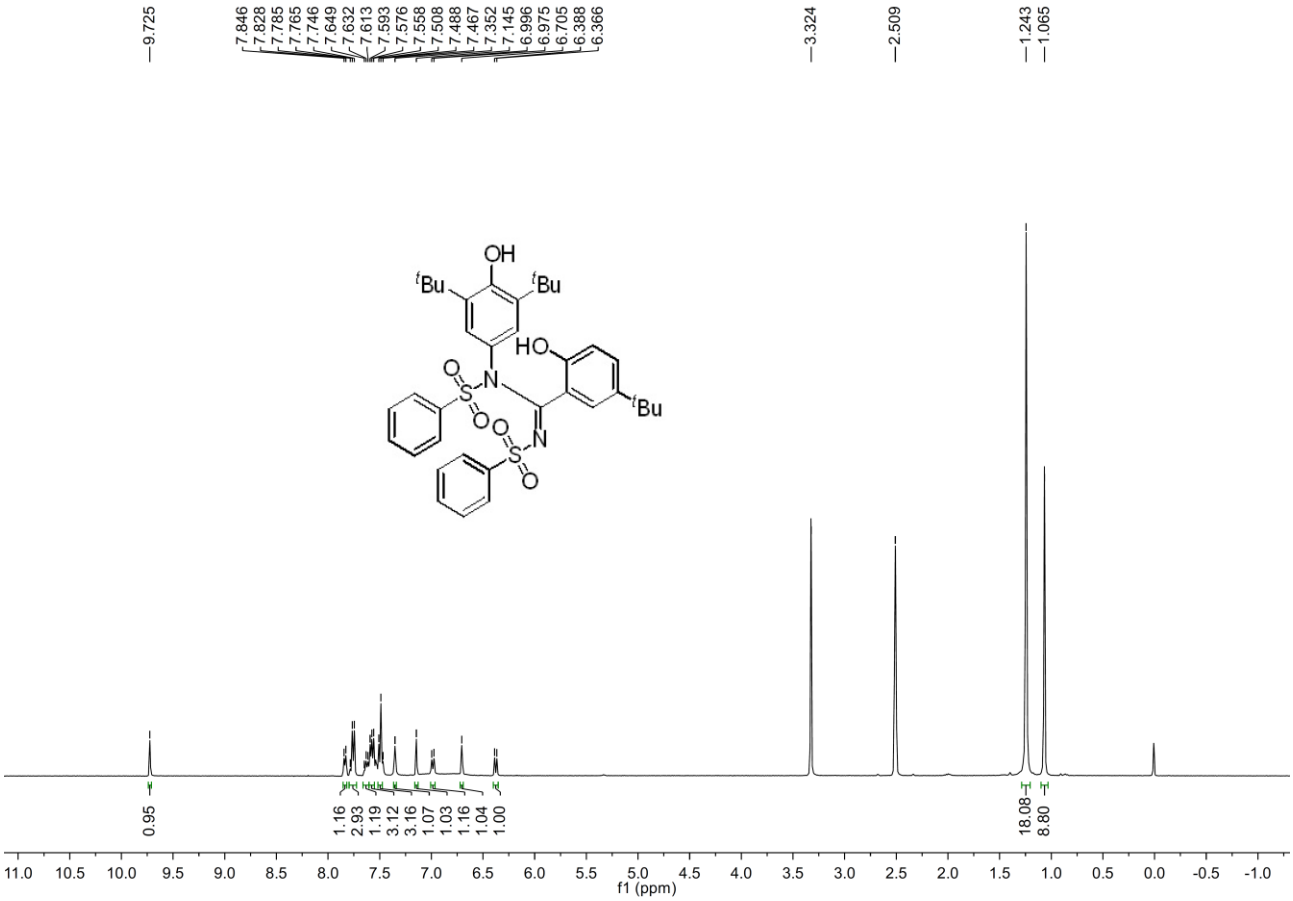
^{13}C NMR Spectrum of Compound 3s (100 MHz, $CDCl_3$)



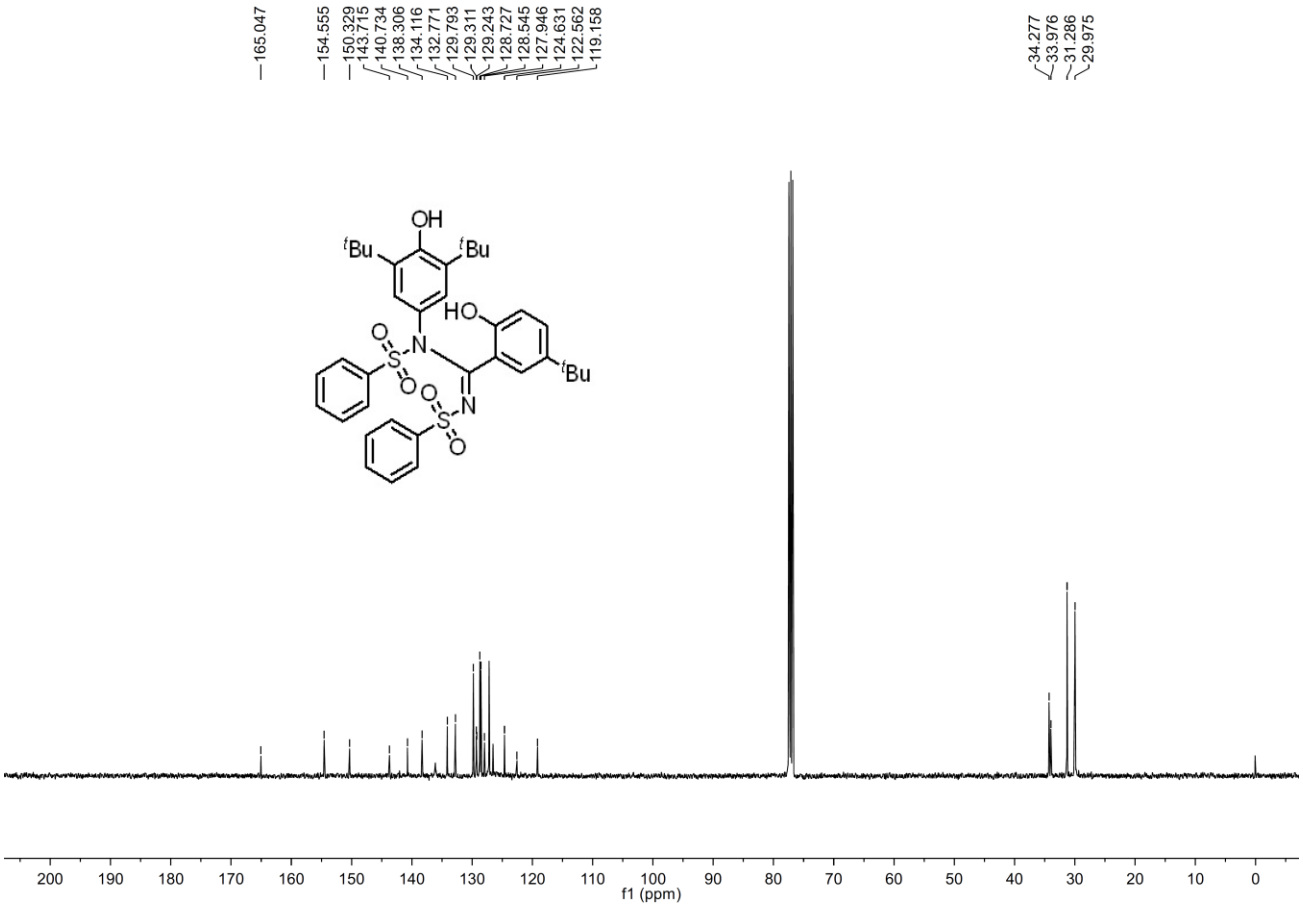
^{1}H NMR Spectrum of Compound 5a (400 MHz, DMSO-d_6)



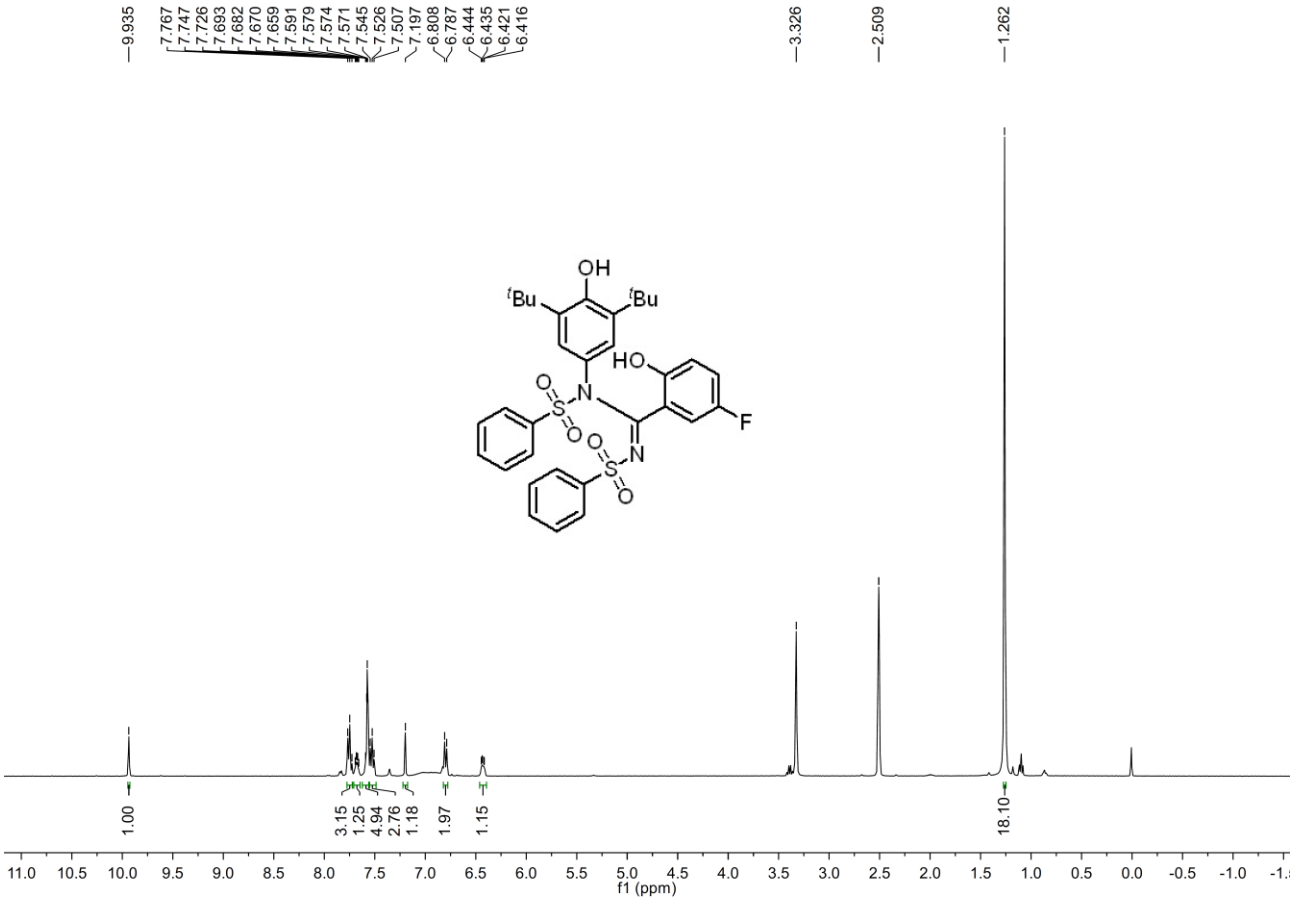
^{13}C NMR Spectrum of Compound 5a (100 MHz, $CDCl_3$)



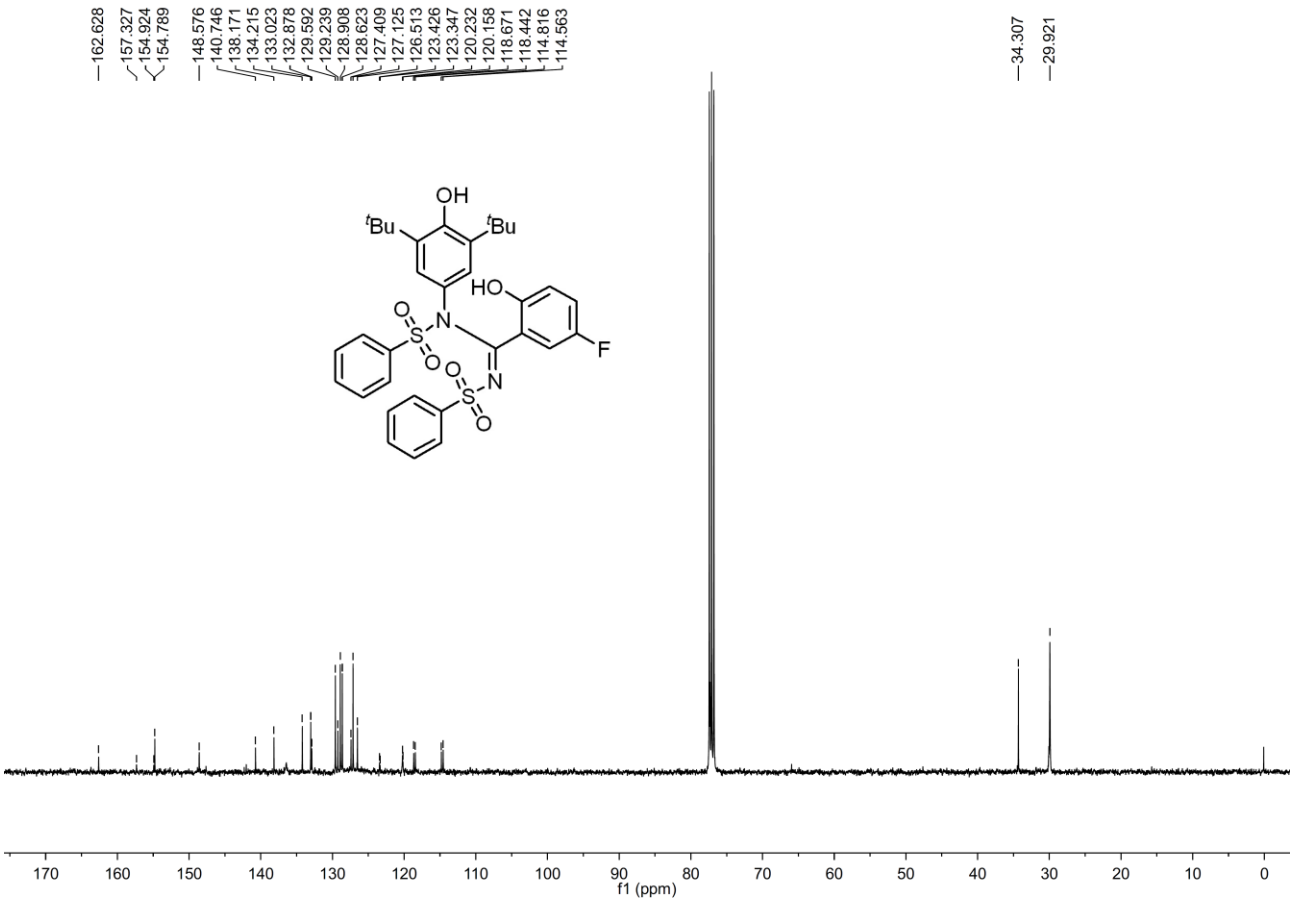
^{1}H NMR Spectrum of Compound 5b (400 MHz, DMSO-d_6)



^{13}C NMR Spectrum of Compound 5b (100 MHz, $CDCl_3$)

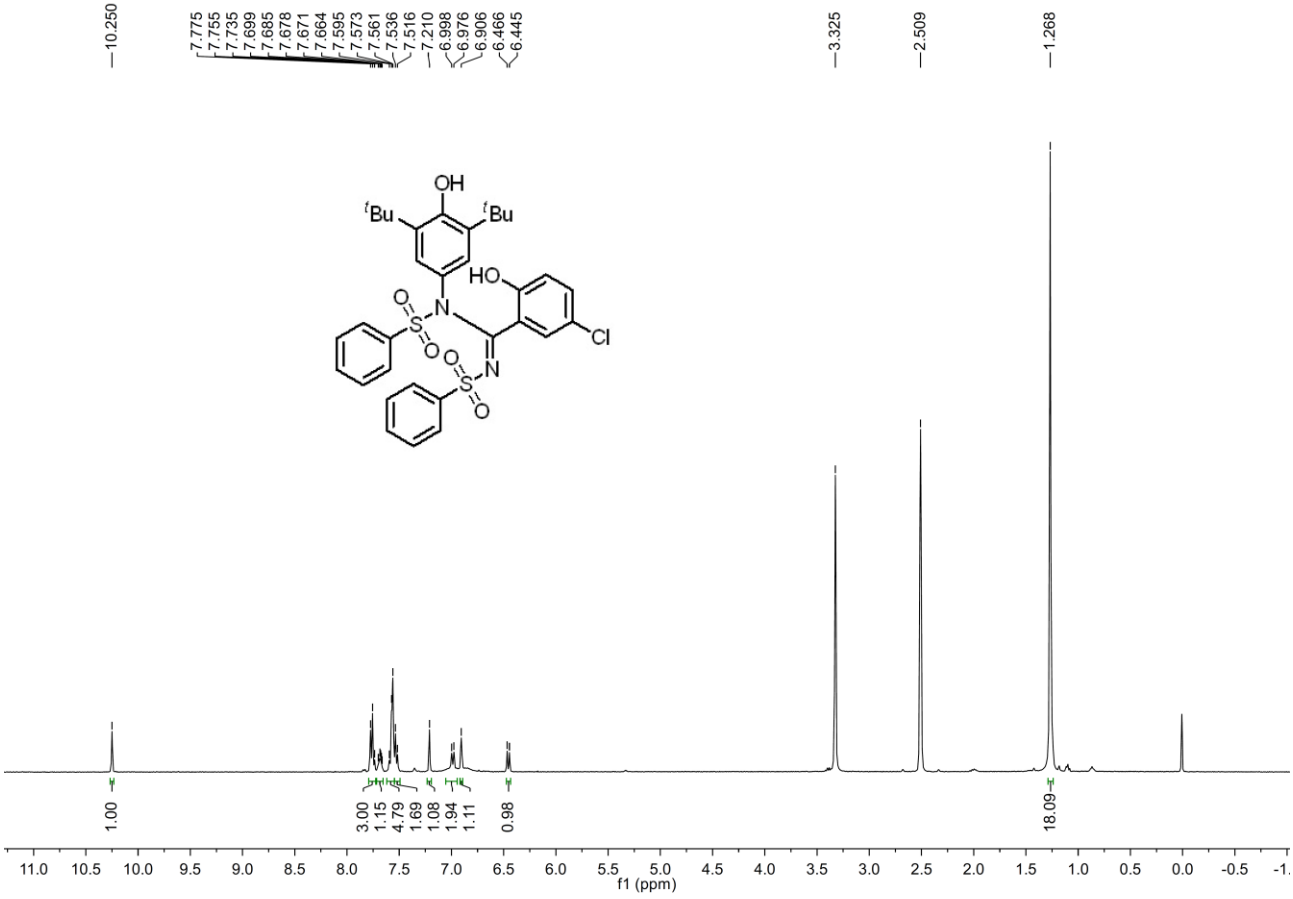


^{1}H NMR Spectrum of Compound 5c (400 MHz, DMSO-d_6)

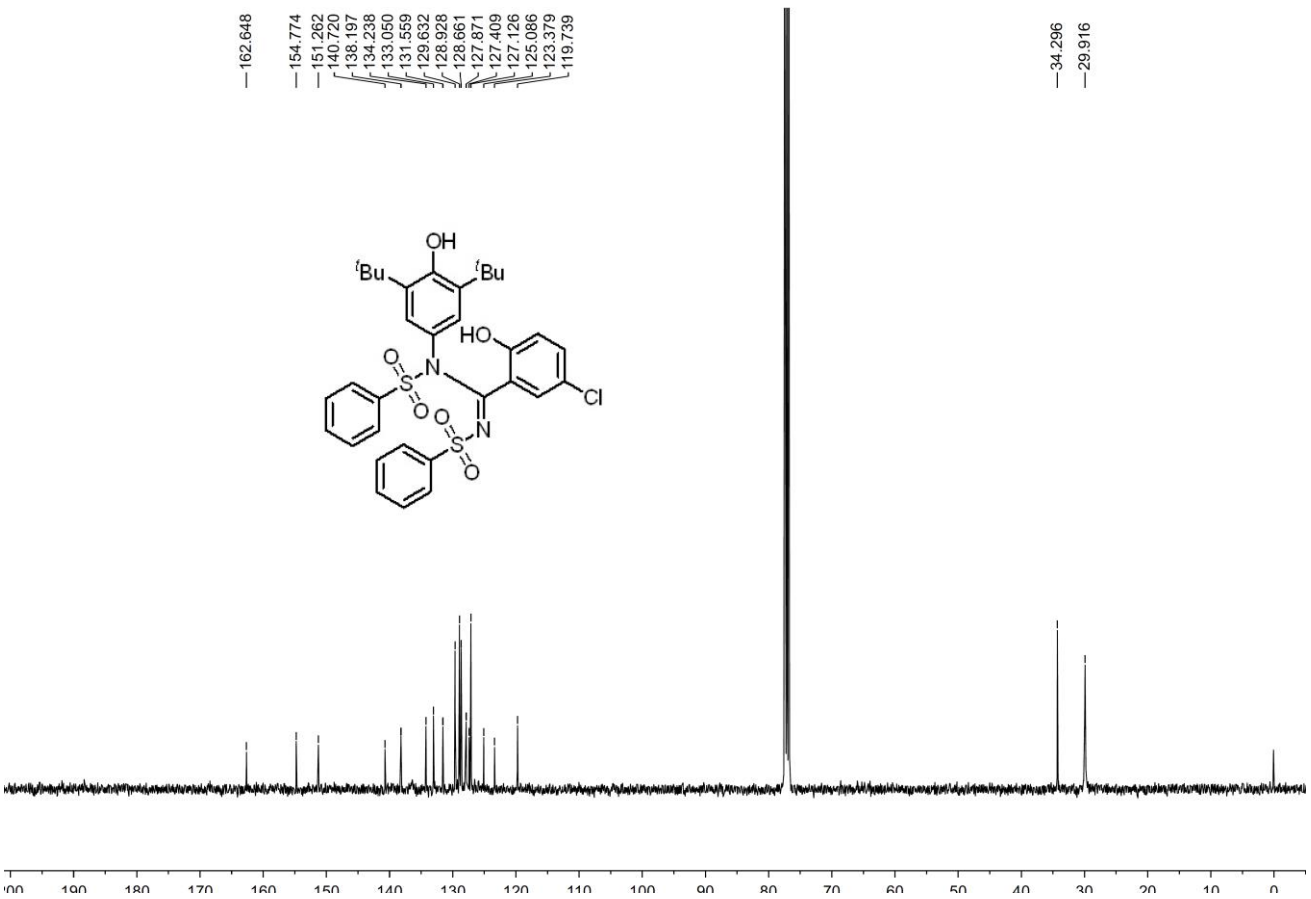


^{13}C NMR Spectrum of Compound 5c (100 MHz, $CDCl_3$)

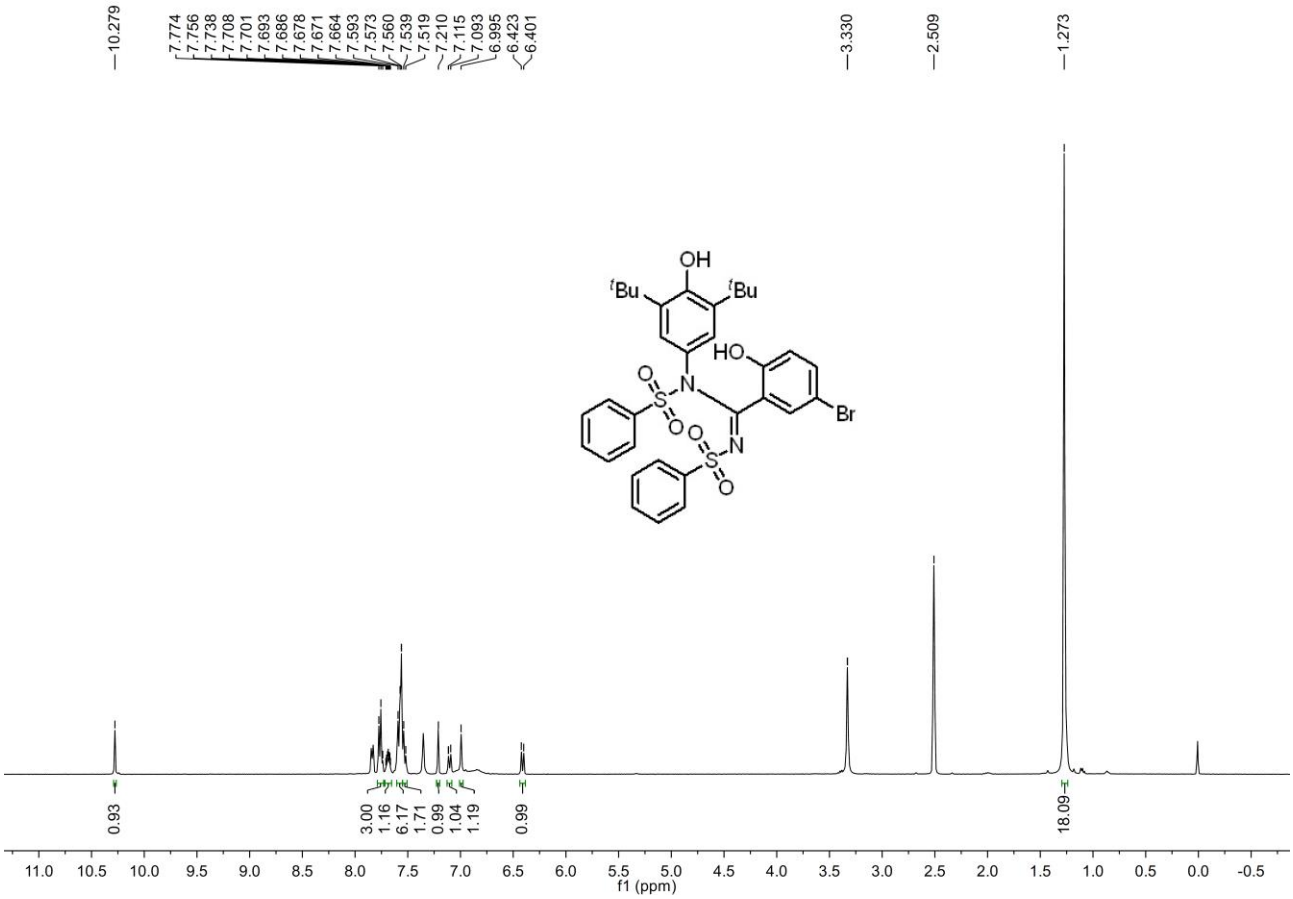
^{19}F NMR Spectrum of Compound 5c (376 MHz, DMSO-d_6)



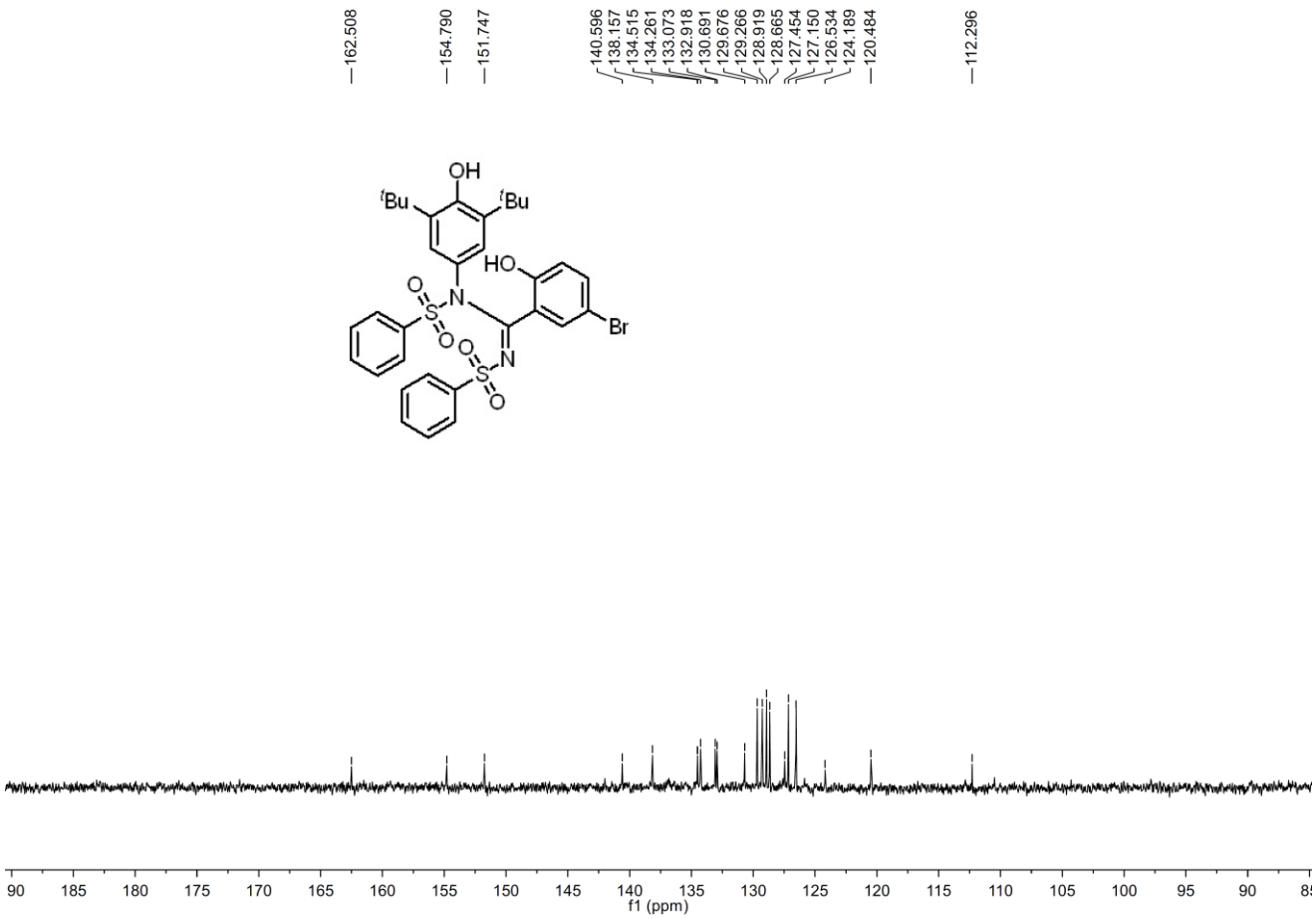
^{1}H NMR Spectrum of Compound 5d (400 MHz, DMSO-d_6)



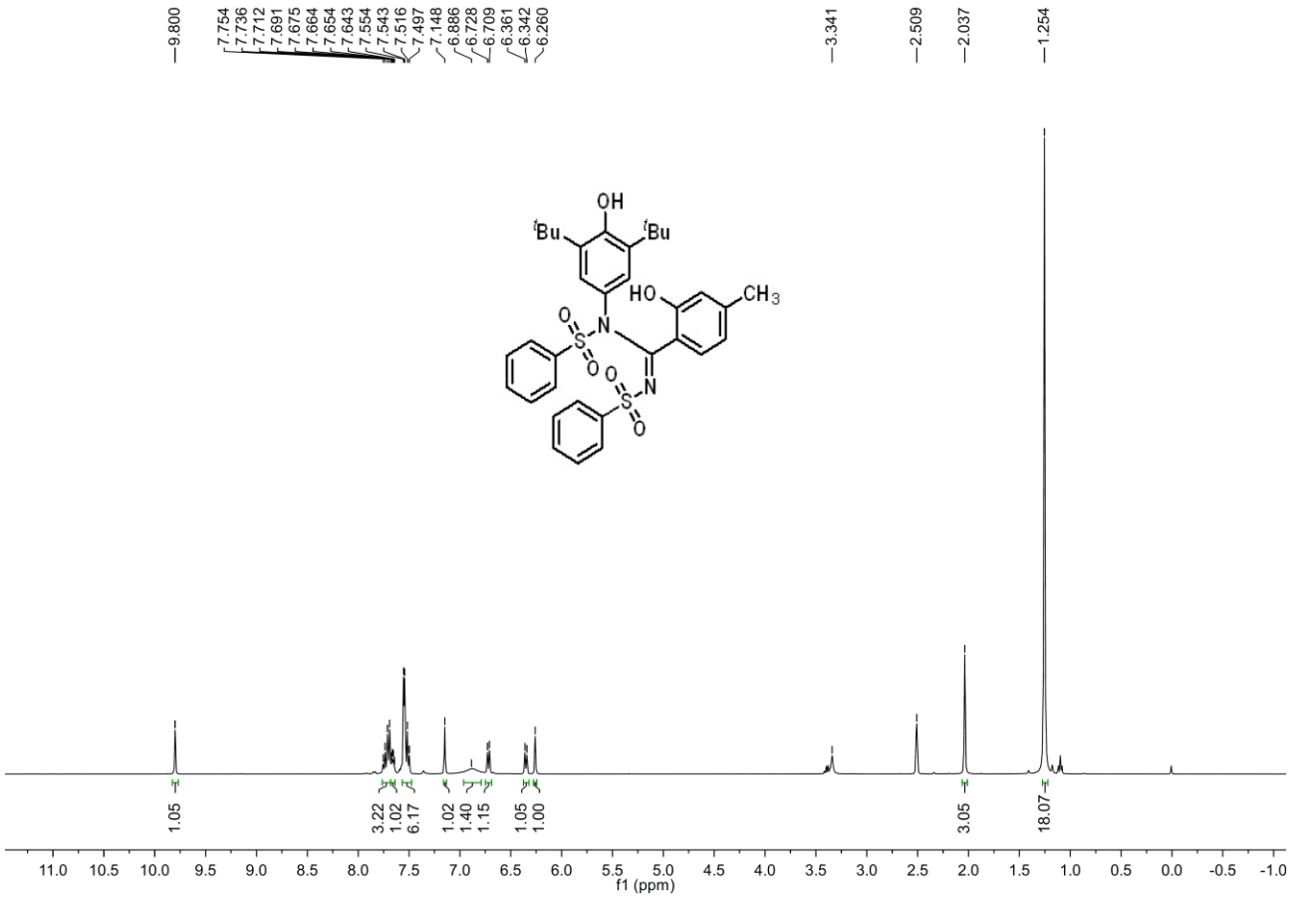
^{13}C NMR Spectrum of Compound 5d (100 MHz, $CDCl_3$)



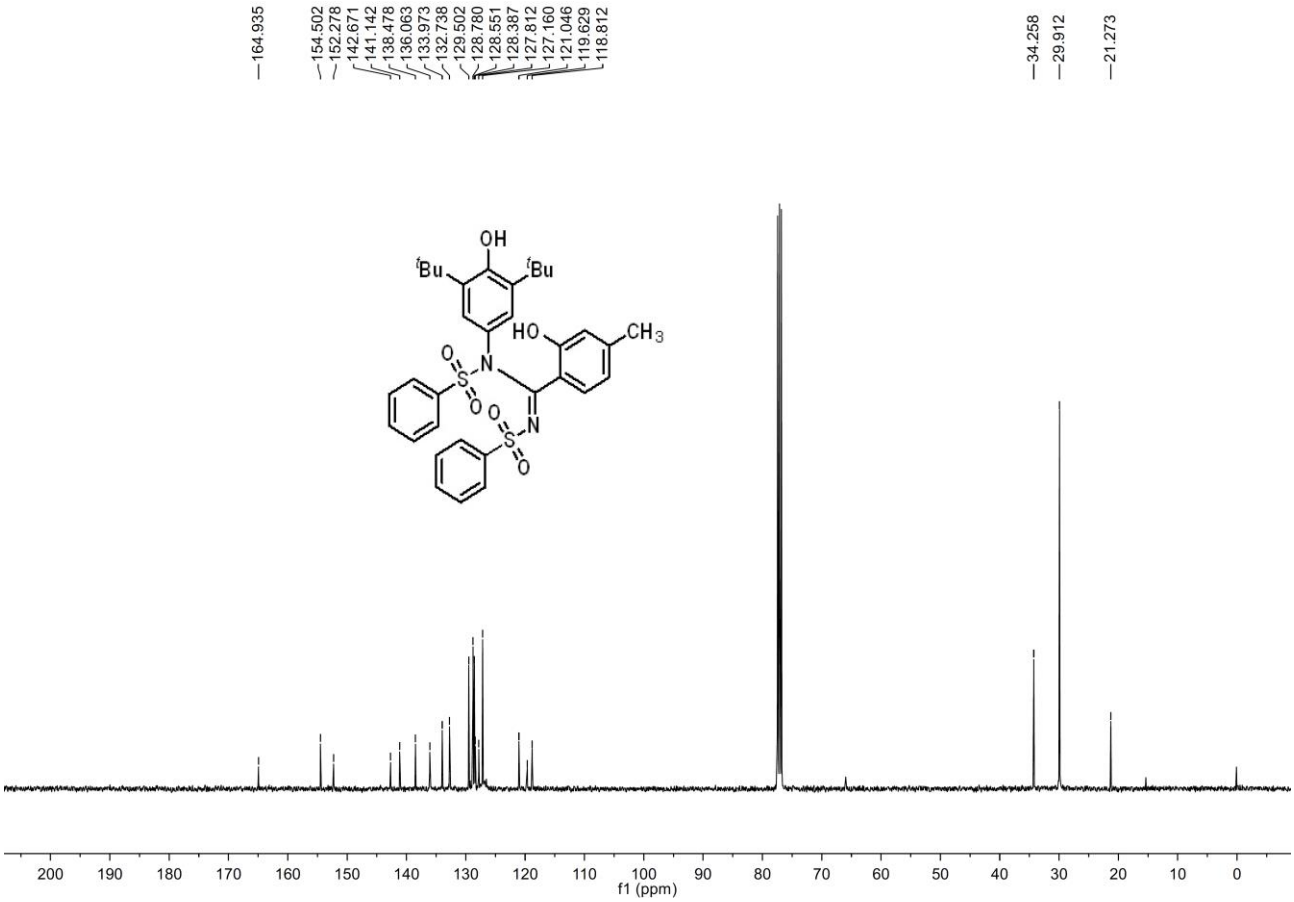
^{1}H NMR Spectrum of Compound 5e (400 MHz, DMSO-d_6)



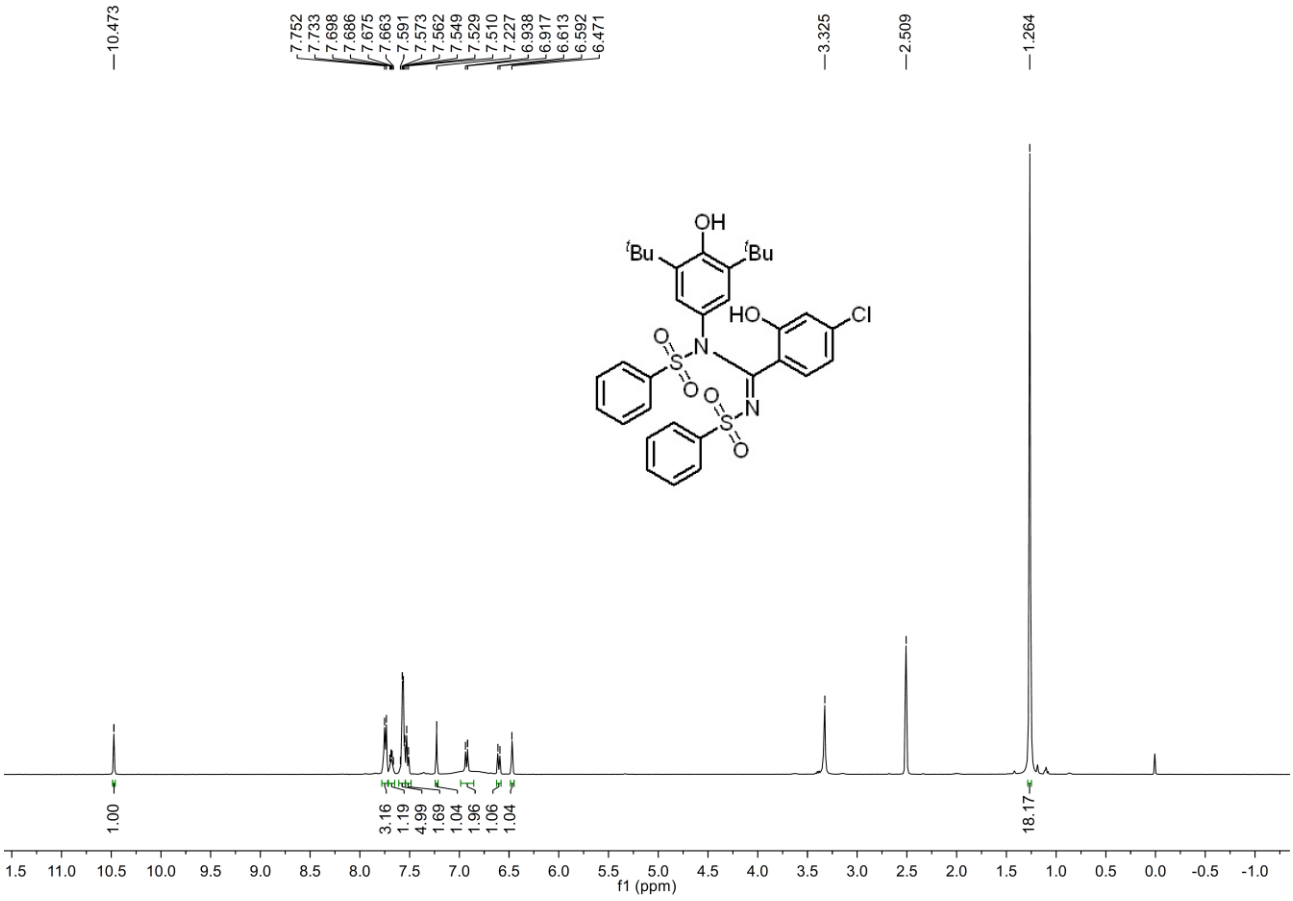
^{13}C NMR Spectrum of Compound 5e (100 MHz, $CDCl_3$)



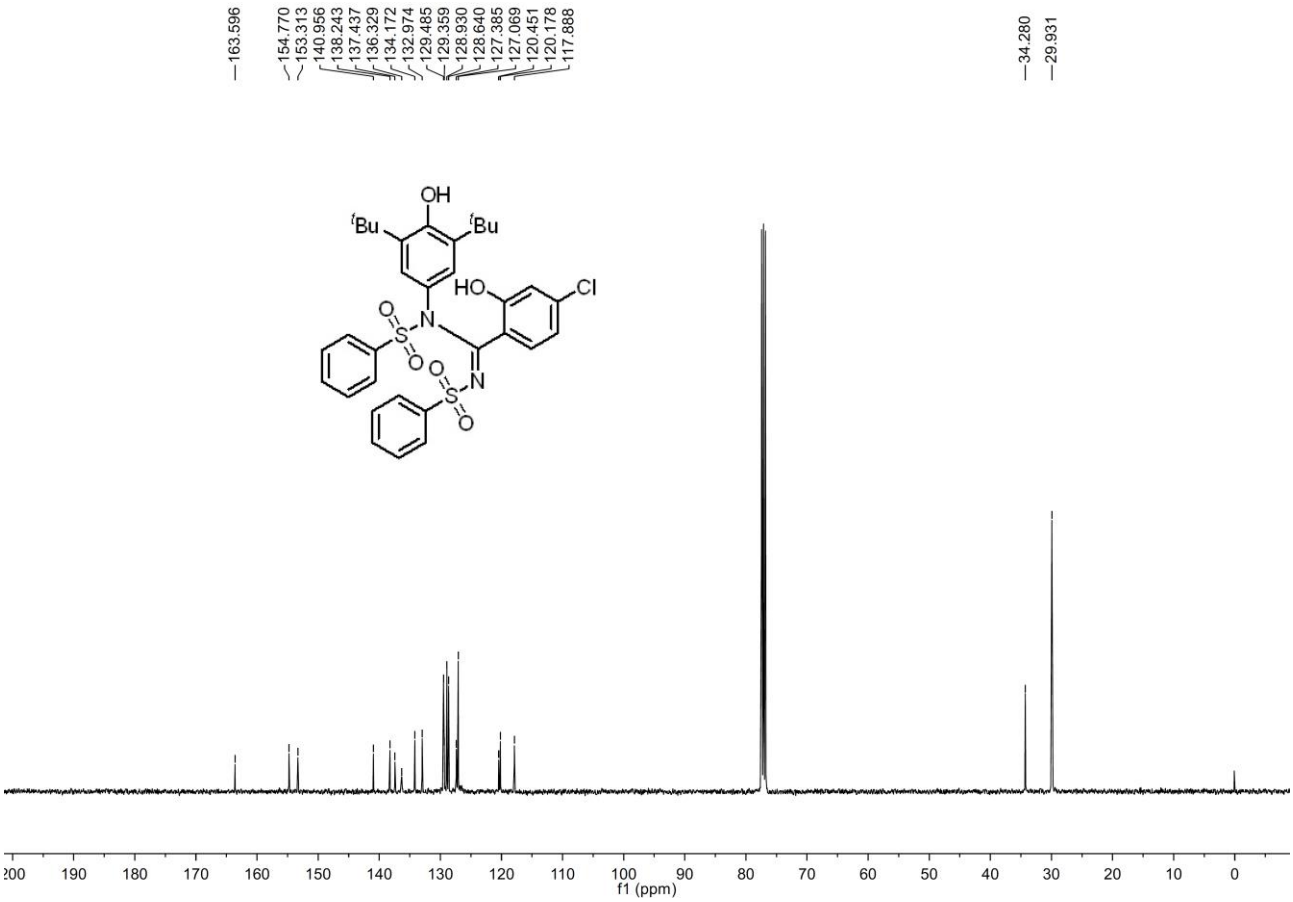
^{1}H NMR Spectrum of Compound 5f (400 MHz, DMSO-d_6)



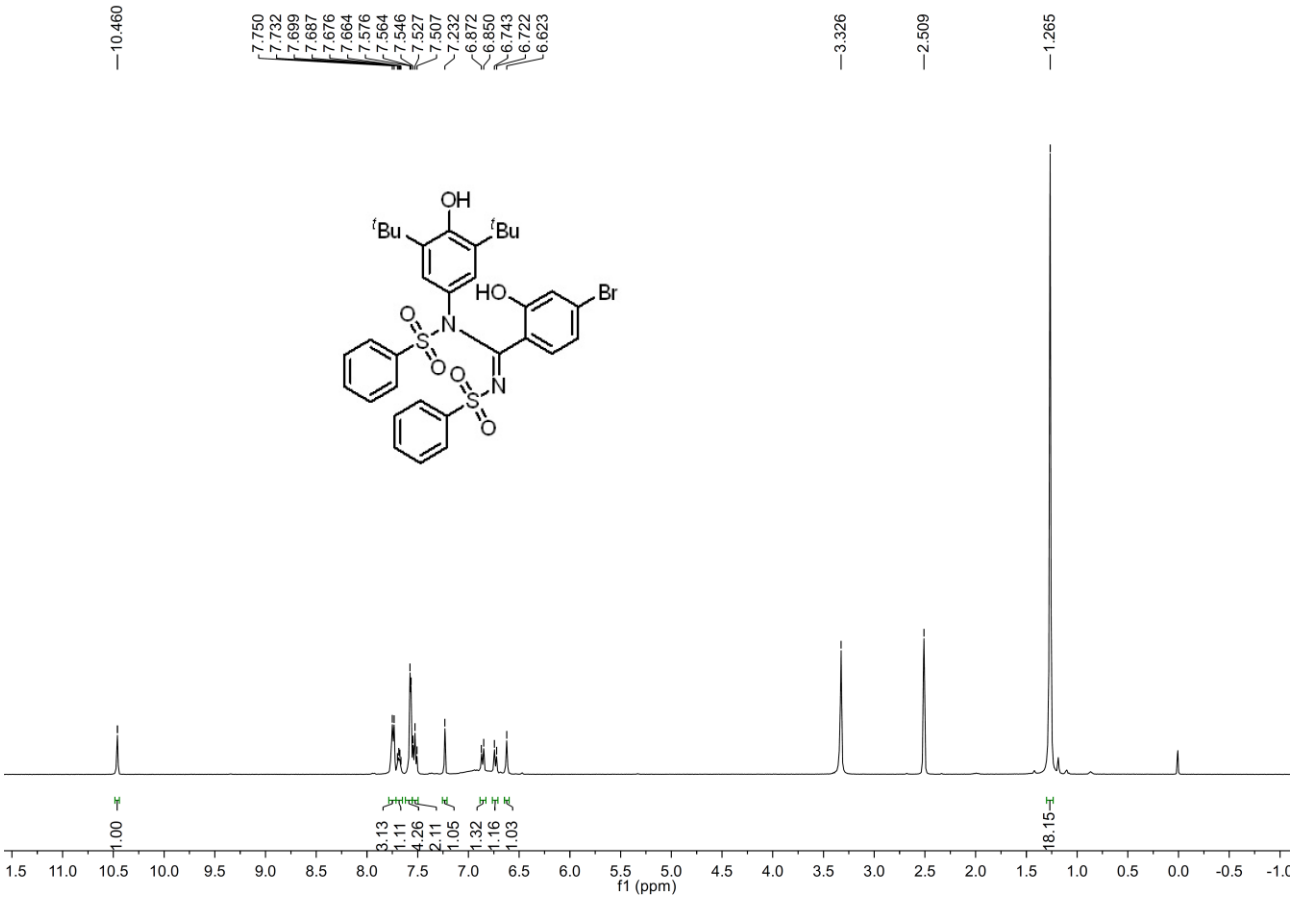
^{13}C NMR Spectrum of Compound 5f (100 MHz, $CDCl_3$)



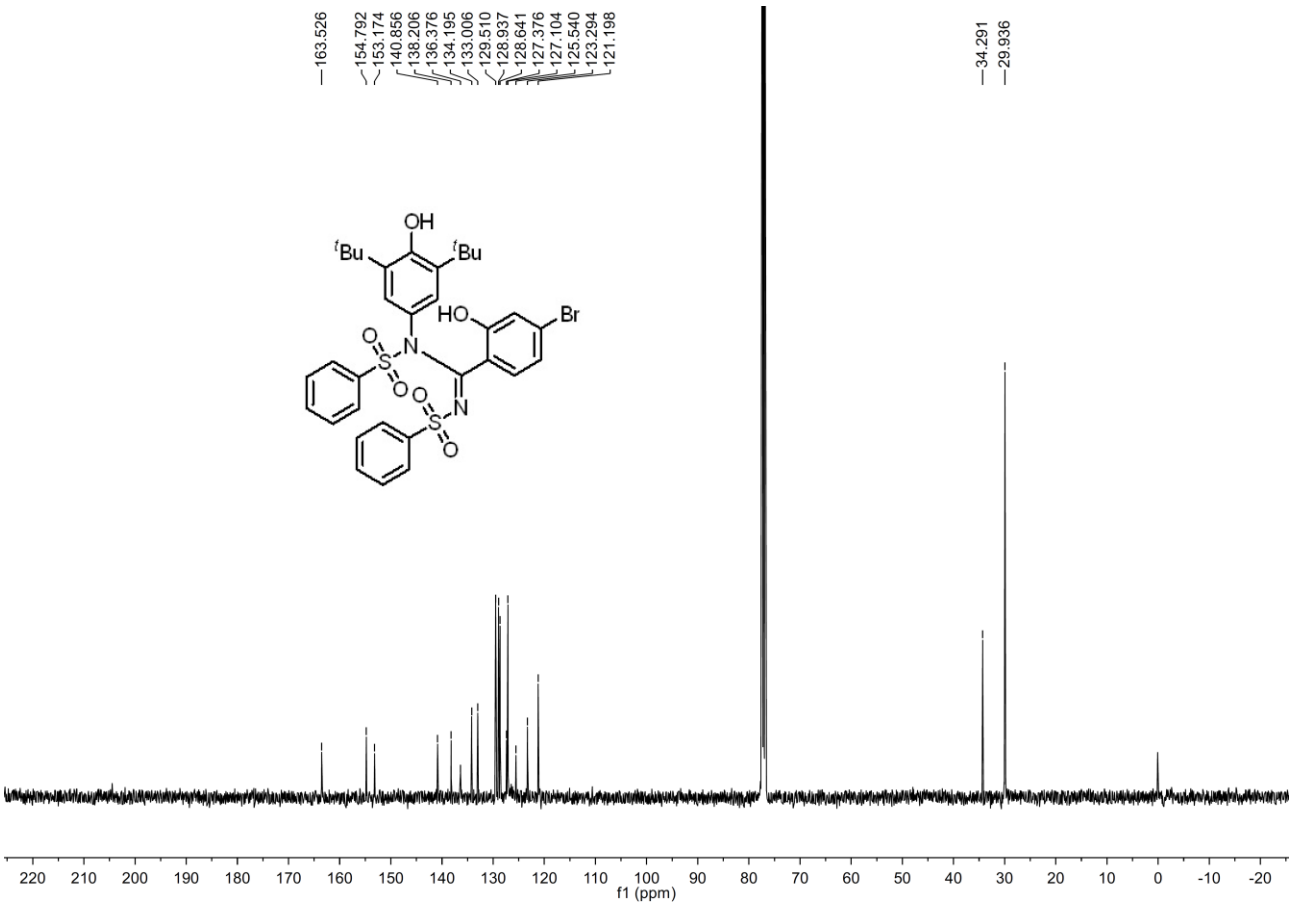
^{1}H NMR Spectrum of Compound 5g (400 MHz, DMSO-d_6)



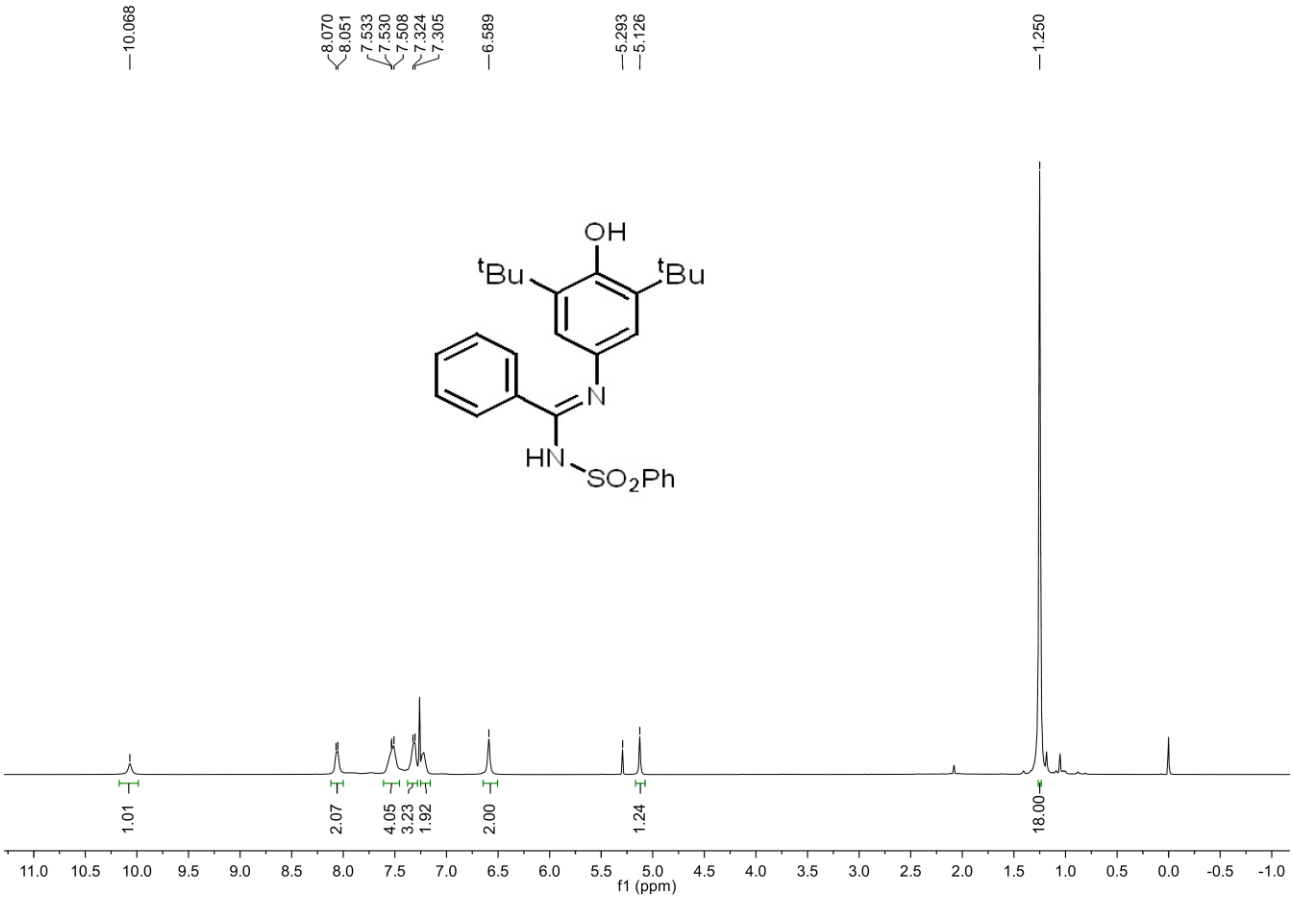
^{13}C NMR Spectrum of Compound 5g (100 MHz, $CDCl_3$)



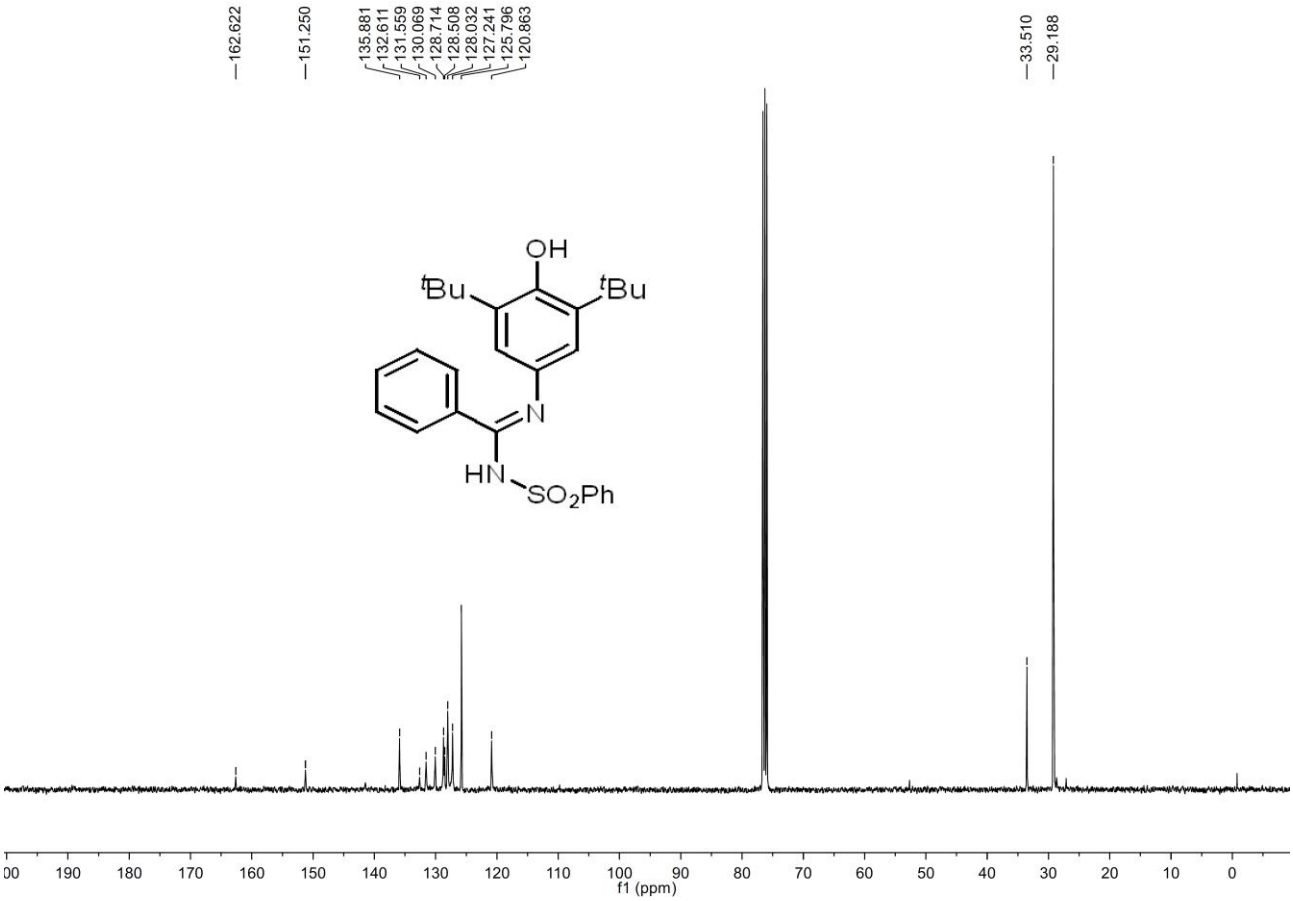
^{1}H NMR Spectrum of Compound 5h (400 MHz, DMSO-d_6)



^{13}C NMR Spectrum of Compound 5h (100 MHz, $CDCl_3$)



^{1}H NMR Spectrum of Compound 6a (400 MHz, $CDCl_3$)



^{13}C NMR Spectrum of Compound 6a (100 MHz, $CDCl_3$)