Supporting Information

Metal-free, Base Catalysed sp^2 C-H Functionalization in Sulfonamidation of 1,4-Naphthoquinones

Devenderan Ramanathan,[a] Kasi Pitchumani*[a,b]

[a] *School of Chemistry, Madurai Kamaraj University, Madurai-625 021*
[b] *Centre for green chemistry Process, Madurai Kamaraj university, Madurai-625 021*

Contents

Experimental Section

General methods: All reactions were carried out under a nitrogen atmosphere, with dry, freshly distilled solvents in anhydrous conditions. All chemicals (1,4-naphthoquinone, Menadione, sulfonyl chlorides, metal salts) were used without further purification as commercially available unless otherwise noted. NMR spectra were registered on Bruker DRX spectrometer operating at 300 & 400 MHz for 1H and 75 &100 MHz for ^{13}C. All ^{1}H- and ^{13}C-NMR spectra were measured in DMSO-d_6 and $CDCl_3$ with TMS as the internal standard. HRMS-ESI was obtained by using Orbitrap mass spectrometers and ESI-MS was recorded in Thermo Scientific mass spectrometer. All the compounds were purified by column chromatography using silica gel (60-120 mesh). Sulfonyl azides,[17] were prepared according to the published methods.

General procedure for the base-mediated sulfonamidation reaction of 1,4-naphthoquinone (3):

A mixture of 1,4-naphthoquinone 1 (1.0 mmol), 4-methylbenzenesulfonyl azide 2a (1.0 mmol), K_2CO_3 (1.0 mmol) DMSO (3.0 mL) were taken in a 15 mL reaction tube under an open-air atmosphere and the reaction tube was placed in a magnetic stirrer. The reaction mixture was stirred at room temperature for 15 minutes. After completion of the reaction, the solvent was removed under vacuum and the reaction mixture was quenched with water (25 mL) and extracted with dichloromethane (15 mL × 3). The combined organic layers were dried with anhydrous Na_2SO_4 and the crude product was purified over a column of silica gel (eluent: petroleum ether/ethyl acetate = 10:5) to afford the desired product N-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-4-methylbenzenesulfonamide **3a**.

General procedure for the base mediated sulfonamidation reaction of 2-methyl-1,4-naphthoquinone (Menadione) 5: A mixture of 2-Methyl-1,4-naphthoquinone 4 (1.0 mmol), 4-methylbenzenesulfonyl azide 2a (1.0 mmol), K_2CO_3 (1.0 mmol) DMSO (3.0 mL) were taken in a 15 mL reaction tube under an open air atmosphere and the reaction tube was placed in a magnetic stirrer. The reaction mixture was stirred at room temperature for 30 minutes. After completion of the reaction, the solvent was removed under vacuum and the reaction mixture was quenched with water (25 mL) and extracted with dichloromethane (15 mL × 3). The combined organic layers were dried with anhydrous Na_2SO_4 and the crude product was purified over a column of silica gel (eluent: petroleum ether/ethyl

acetate = 10:5) to afford the desired product 4-Methyl-N-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide **5a**.

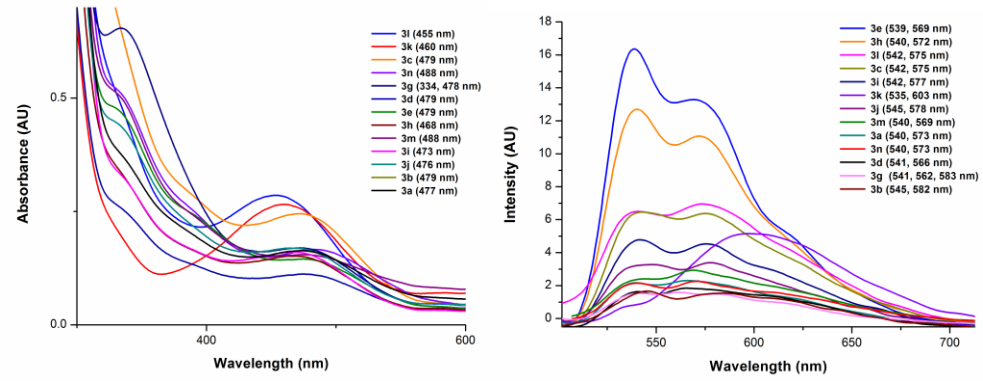


Fig.S2 Absorbance and PL spectrum of (**3a-3n**)

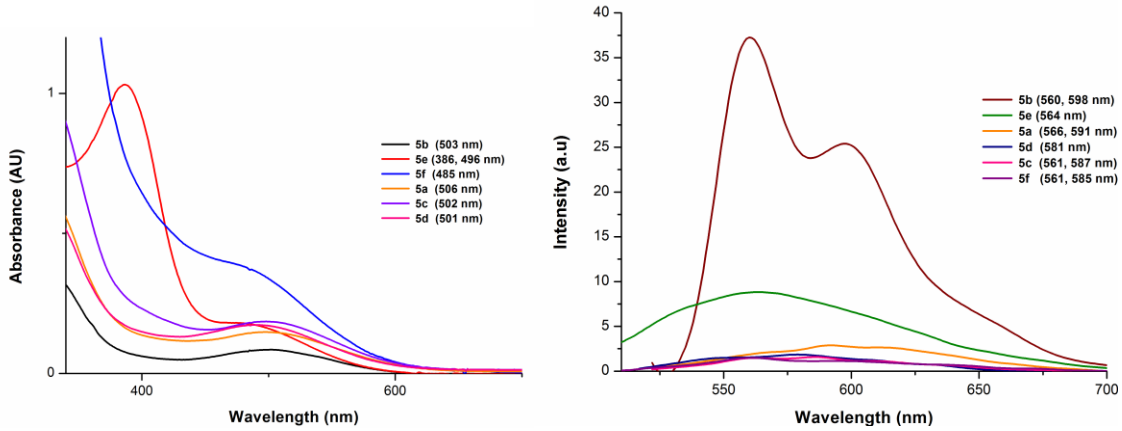


Fig.S2 Absorbance and PL spectra of (**5a-5f**)

Table S1. Absorbance and fluorescence data of sulfonamidation derivatives of menadione and 1,4-naphthoquinone.

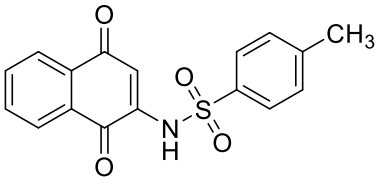
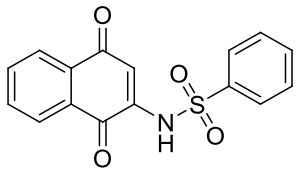
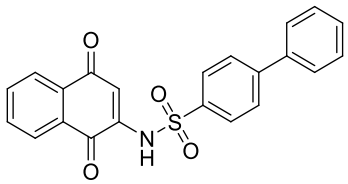
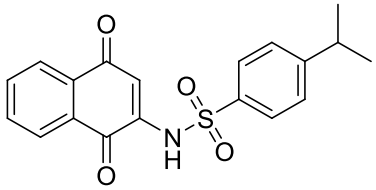
S. No	Compound	Absorption maximum (nm)	Excitation (nm) ($\lambda_{excitation}$)	Emission Maximum (nm) ($\lambda_{emission}$)
	Naphthoquinone	331	340	
1.	3a	477	485	540, 573
2.	3b	479	490	545,582
3.	3c	479	490	542,575
4.	3d	479	490	541, 566
5.	3e	479	490	539, 569
6.	3g	334, 478	490	541,562,583
7.	3h	468	480	540, 572
8.	3i	473	480	542, 577
9.	3j	476	485	545, 578
10.	3k	460	470	535, 603
11.	3l	455	465	542, 575
12.	3m	488	500	540, 569
13.	3n	488	500	540, 573
14.	Menadione	332	340	
15.	5a	506	515	566, 591
16.	5b	503	510	560, 598
17.	5c	502	510	561, 587
18.	5d	501	510	581
19.	5e	386, 496	505	564
20.	5f	485	495	561, 585
Absorbance and Pl spectrum are studied in 1 X 10^{-4}M concentration and solutions are made in DMSO as solvent.				

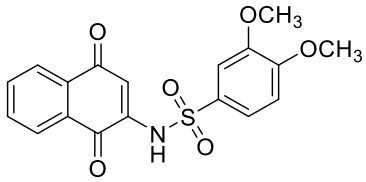
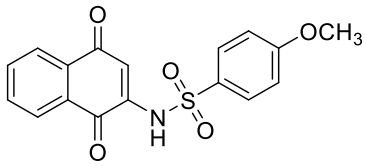
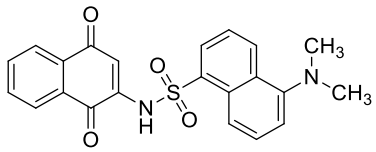
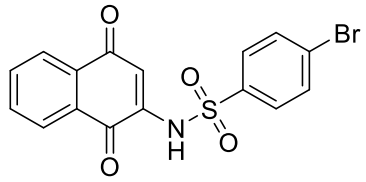
Table S2. Electrochemical data measured using cyclic voltammetry (CV) for 1,4-naphthoquinone and menadione sulfonamidation derivatives in selective.

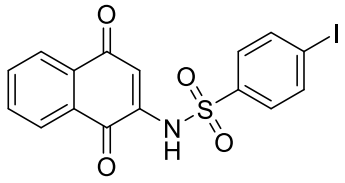
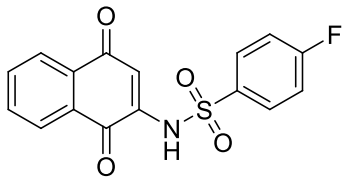
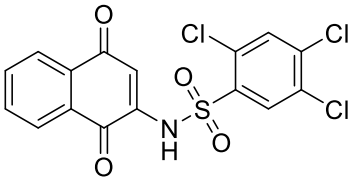
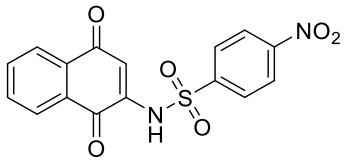
Compound	First redox wave		Second redox wave		Third redox wave	
	$E_{pc/Epa}$	$E_{1/2}$ (ΔE)	$E_{pc/Epa}$	$E_{1/2}$(ΔE)	$E_{pc/Epa}$	$E_{1/2}$(ΔE)
Naphthoquinone	-0.75/-0.41	-0.58 (343)	-1.40/-1.04	-1.22 (365)	-	-
3a	-0.82/-0.64	-0.73 (182)	-1.17/-0.93	-1.05 (241)	-1.60/-1.25	-1.42 (354)
3j	-0.81/-0.57	-0.69 (241)	-1.14/-0.93	-1.03 (210)	-1.75/-1.29	-1.52 (458)
3e	-0.80/-0.62	-0.71 (187)	-1.14/-0.97	-1.05 (168)	-1.76/-1.36	-1.56 (401)
Menadione	-0.77/-0.47	-0.62 (303)	-1.24/-0.88	-1.06 (356)	-1.44/-1.07	-1.25 (369)
5a	-0.58/-0.76	-0.67 (177)	-0.75/-1.15	-0.94 (405)	-1.00/-1.58	-1.29 (579)
5c	-0.80/-0.59	-0.69 (212)	-1.17/-0.96	-1.06 (206)	-1.53/-1.22	-1.37 (311)
5f	-0.62/-0.80	-0.71 (178)	-0.89/-1.05	-0.97 (164)	-1.30/-1.25	-1.27 (56)

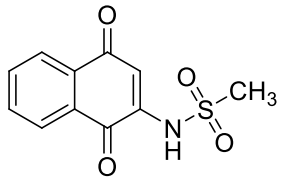
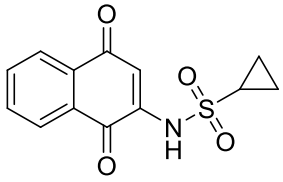
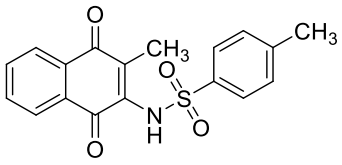
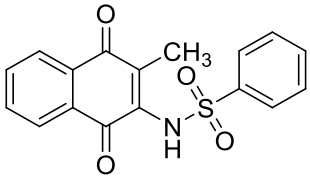
[a]DMSO; I= 0.1m n-Bu_4NClO_4. (Epc and Epa (V), E1/2= (Epc+ Epa)/2 (V). v= 200 mV s^{-1}; ΔE= E_{pa}-E_{pc} (mV); reference electrode= KCl(3m)/Ag/AgCl; working electrode= glassy carbon disk of 0.07 cm^2 area; auxiliary electrode= Pt wire.

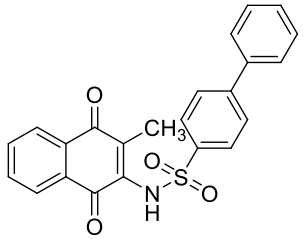
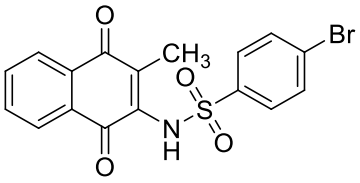
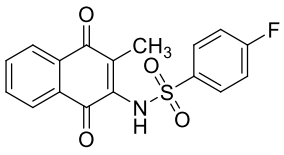
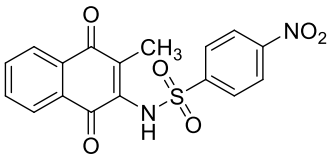
Characterization data

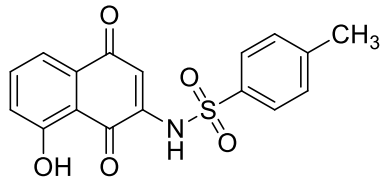
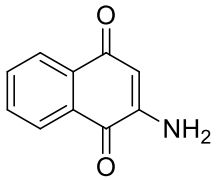
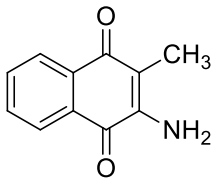
 **3a**	***N-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-4-methylbenzenesulfonamide*** (table 2, **3a**); Yellow colored solid; m.p 202 °C; yield 71%;^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.28 (s, 1H), 7.92 (d, J = 10.3 Hz, 2H), 7.81 (d, J = 8.2 Hz, 2H), 7.63 (dd, J = 10.7, 7.5 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 6.66 (s, 1H), 2.32 (s, 3H). ^{13}C-NMR (75 MHz, DMSO-d_6) δ 183.13, 179.27, 144.34, 141.44, 135.53, 134.47, 133.21, 131.15, 129.99, 129.67, 127.13, 126.14, 125.47, 113.39, 21.08; HRMS (ESI): *m/z* calculated for $C_{17}H_{14}O_4NNaS$ $[M+Na]^+$ 350.0457, found: 350.0450.
 **3b**	***N-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide*** (table 2, **3b**); yellow colored solid; m.p >240 °C; yield 70%; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 10.82 (s, 1H), 8.04 (d, J = 7.8 Hz, 2H), 8.00 (d, J = 7.0 Hz, 1H), 7.92 (d, J = 7.5 Hz, 1H), 7.80 (m,2H), 7.73 – 7.57 (m, 3H), 6.62 (s, 1H).^{13}C-NMR (75 MHz, DMSO- d_6) δ 183.18, 179.25, 141.56, 138.51, 134.53, 133.64, 133.33, 131.14, 130.10, 129.25, 127.03, 126.18, 125.47, 113.58, 79.14, 78.70, 78.26, 40.34, 40.07, 39.79, 39.51, 39.23, 38.95, 38.68; HRMS (ESI): *m/z* calculated for $C_{16}H_{11}O_4NNaS$ $[M+Na]^+$ 336.0301, found: 336.0298.
 **3c**	***N-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)biphenyl-4-sulfonamide*** (table 2, **3c**); yellow colored solid; m.p 182 °C; yield 82%;^{1}H-NMR (300 MHz, $CDCl_3$) δ 10.52 (s, 1H), 8.16 (d, 4.5 Hz, 2H), 7.97 (d, J = 6.5 Hz, 2H), 7.84 – 7.71 (m, 5H), 7.61 (d, J = 4.3 Hz, 2H), 7.48 – 7.43 (m, 2H), 6.75 (s, 1H). ^{13}C NMR (75 MHz, DMSO- d_6) δ 184.31, 180.15, 146.20, 142.73, 138.96, 138.11, 135.60, 134.51, 132.01, 131.17, 129.98, 129.62, 128.74, 128.57, 128.00, 127.86, 127.16, 126.37, 114.40; HRMS (ESI): *m/z* calculated for $C_{22}H_{16}O_4NS$ $[M+H]^+$ 390.0795, found: 390.0794.
 **3d**	***N-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-4-isopropylbenzenesulfonamide*** (table 2, **3d**); Yellow colored solid; m.p 201 °C; yield 76%; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.05 – 7.97 (m, 2H), 7.94 (d, J = 8.4 Hz, 2H), 7.75 (dd, J = 15.4, 6.6 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 6.73 (s, 1H), 2.98 (dd, J = 13.6, 6.8 Hz, 1H), 1.24 (d, J = 6.9 Hz, 6H). ^{13}C-NMR (75 MHz, DMSO-d_6) δ 184.26, 180.13, 155.75, 142.74, 136.92, 135.59, 134.48, 131.98, 131.14, 128.37, 128.22, 127.14, 126.35, 114.16, 34.28, 24.16; HRMS (ESI): *m/z* calculated for $C_{19}H_{18}O_4NS$ $[M+H]^+$ 356.0951, found: 356.0966.

 **3e**	***N-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-3,4-dimethoxybenzenesulfonamide*** (table 2, **3e**); Yellow colored solid; m.p 196 °C; yield 84%; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.54 (s, 1H), 8.05 (d, J = 7.4 Hz, 1H), 8.01 (d, J = 7.3 Hz, 1H), 7.71-7.50 (m, 4H), 6.97 (d, J = 8.6 Hz, 1H), 6.75 (s, 1H), 3.93 (s, 3H), 3.92 (s, 3H). ^{13}C-NMR (75 MHz, DMSO-d_6) δ 184.16, 180.13, 153.93, 149.73, 142.56, 135.49, 134.33, 131.96, 131.02, 130.46, 127.04, 126.28, 122.26, 114.01, 111.78, 110.56, 56.66; HRMS (ESI): *m/z* calculated for $C_{18}H_{15}NNaO_6S$ $[M+Na]^+$ 396.0512, found: 396.0529.
 **3f**	***N-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-4-methoxybenzenesulfonamide*** (table 2, **3f**); Yellow colored solid; m.p 200 °C; yield 78%; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.28 (s, 1H), 7.92 (d, J = 10.3 Hz, 2H), 7.81 (d, J = 8.2 Hz, 2H), 7.63 (dd, J = 10.7, 7.5 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 6.66 (s, 1H), 3.82 (s, 3H). ^{13}C-NMR (75 MHz, DMSO-d_6) δ 183.13, 179.27, 144.34, 141.44, 135.53, 134.47, 133.21, 131.15, 129.99, 129.67, 127.13, 126.14, 125.47, 113.39, 55.08; ESI-MS: *m/z* calculated for $C_{17}H_{14}NO_5S$ $[M+H]^+$ 344.05, found: 344.13
 **3g**	***5-(Dimethylamino)-N-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)naphthalene-1-sulfonamide*** (table 2, **3g**); Colorless solid; m.p 192-194 °C; yield 85%; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 8.44 (dd, J = 12.2, 8.7 Hz, 2H), 8.34 (d, J = 7.3 Hz, 1H), 7.82 (d, J = 8.8 Hz, 1H), 7.71 (d, J = 8.7 Hz, 1H), 7.64 (d, J = 7.7 Hz, 2H), 7.58 (dd, J = 8.0, 4.0 Hz, 2H), 7.13 (d, J = 7.6 Hz, 1H), 6.44 (s, 1H), 2.71 (s, 6H); ^{13}C-NMR (75 MHz, DMSO) δ 183.04, 179.21, 151.47, 141.58, 134.47, 133.27, 133.14, 131.18, 131.03, 130.38, 130.03, 129.16, 128.94, 128.57, 126.13, 125.40, 123.21, 118.59, 115.36, 113.58, 44.93; HRMS (ESI): *m/z* calculated for $C_{22}H_{19}O_4N_2NaS$ $[M+Na]^+$ 429.0879, found: 429.0868.
 **3h**	***N-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-4-brmobenzenesulfonamide*** (table 2, **3h**); Yellow colored solid; m.p 196 °C; yield 70%; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 10.83 (s, 1H), 7.94 (m, 4H), 7.84 – 7.37 (m, 4H), 6.66 (s, 1H). ^{13}C-NMR (75 MHz, DMSO) δ 181.65, 177.71, 139.75, 136.67, 135.97, 132.97, 131.71, 129.66, 128.51, 127.11, 125.89, 124.68, 124.02, 112.28. ESI-MS: *m/z* calculated for $C_{16}H_{11}BrNO_4S$ $[M+H]^+$ 391.9587, found: 391.9594.

 **3i**	***N-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-4-iodobenzenesulfonamide*** (table 2, **3i**);Yellow colored solid; m.p 204-206 °C; yield 68%; ^{1}H-NMR (300 MHz, DMSO) δ 8.05 – 7.90 (m, 4H), 7.79 (d, J = 7.8 Hz, 4H), 6.65 (s, 1H). ^{13}C-NMR (75 MHz, DMSO-d_6) δ 181.58, 177.68, 139.82, 136.32, 132.92, 131.69, 130.77, 129.72, 128.56, 127.38, 126.45, 124.63, 123.96, 112.45. HRMS (ESI): *m/z* calculated for $C_{16}H_{11}INO_4S$ $[M+H]^+$ 439.9448, found: 439.9452.
 **3j**	***N-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-4-fluorobenzenesulfonamide*** (table 2, **3j**); Yellow colored solid; m.p 190 °C; yield 68%; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 10.88 – 10.40 (m, 1H), 8.10 (dd, J = 8.7, 5.0 Hz, 2H), 8.02 (d, J = 7.4 Hz, 1H), 7.96 (d, J = 8.7 Hz, 1H), 7.83 – 7.70 (m, 2H), 7.32 (t, J = 8.6 Hz, 2H), 6.69 (s, 1H). ^{13}C-NMR (75 MHz, DMSO-d_6) δ 184.26, 180.19, 142.78, 135.61, 134.51, 132.11, 131.20, 127.17, 126.39, 117.79, 117.49, 114.67; HRMS (ESI): *m/z* calculated for $C_{16}H_{11}FNO_4S$ $[M + H]^+$ 332.0387, found: 332.0378.
 **3k**	***2,4,5-Trichloro-N-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide*** (table 2, **3k**); Brown colored solid; m.p 186 °C; yield 55%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 – 8.26 (m, 1H), 8.06 – 8.01 (m, 2H), 7.96 (d, J = 8.3 Hz, 1H), 7.82 (s, 1H), 7.77 (t, J = 6.7 Hz, 2H), 6.59 (s, 1H).^{13}C-NMR (101 MHz, DMSO) δ 181.56, 178.93, 173.04, 143.62, 139.20, 135.96, 134.98, 133.87, 132.83, 131.61, 131.22, 129.94, 128.87, 128.64, 128.21, 124.53, 123.69, 118.31, 112.27; HRMS(ESI): *m/z* calculated for $C_{16}H_9Cl_3NO_4S$ $[M+H]^+$ 415.9312, found: 415.9319.
 **3l**	***N-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-4-nitrobenzenesulfonamide*** (table 2, **3l**); Yellow colored solid; m.p 194 °C; yield 43%; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 10.88 – 10.40 (m, 1H), 8.10 (dd, J = 8.7, 5.0 Hz, 2H), 8.02 (d, J = 7.4 Hz, 1H), 7.96 (d, J = 8.7 Hz, 1H), 7.83 – 7.70 (m, 2H), 7.32 (t, J = 8.6 Hz, 2H), 6.69 (s, 1H). ^{13}C-NMR (75 MHz, DMSO-d_6) δ 184.26, 180.19, 142.78, 135.61, 134.51, 132.11, 131.20, 127.17, 126.39, 117.79, 117.49, 114.67; ESI-MS: *m/z* calculated for $C_{16}H_{10}N_2O_6NaS$ $[M + Na]^+$ 381.0152, found: 381.0160.

 **3m**	***N-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)methanesulfonamide*** (table 2, **3m**); Yellow colored solid; m.p 178 °C; yield 58%; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 8.04 (d, J = 7.1 Hz, 1H), 7.98 (d, J = 7.3 Hz, 1H), 7.81 (dd, J = 15.2, 7.4 Hz, 2H), 6.80 (s, 1H), 3.26 (s, 3H). ^{13}C-NMR (75 MHz, DMSO-d_6) δ 182.03, 178.10, 140.52, 133.15, 132.92, 131.81, 130.11, 128.77, 125.60, 124.89, 124.24, 112.10, 77.44, 77.00, 76.56, 39.17, 38.89, 38.81, 38.61, 38.33, 38.05, 37.78, 37.49; HRMS (ESI): *m/z* calculated for $C_{11}H_{10}O_4NS$ $[M + H]^+$ 252.0325, found: 252.0324.
 **3n**	***N-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)cyclopropanesulfonamide*** (table 2, **3n**); Yellow colored solid; m.p 172 °C; yield 59%; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.08 (d, J = 7.2 Hz, 1H), 8.01 (d, J = 6.7 Hz, 1H), 7.80 (dd, J = 14.5, 7.5 Hz, 2H), 6.85 (s, 1H), 2.94 (dd, J = 8.4, 3.9 Hz, 1H), 1.27 (dd, J = 6.5, 4.1 Hz, 2H), 1.09 (dd, J = 12.2, 6.6 Hz, 2H). ^{13}C-NMR (75 MHz, DMSO-d_6) δ 184.55, 180.49, 143.33, 135.71, 134.55, 132.19, 131.24, 127.24, 126.41, 114.44, 31.36, 6.37; HRMS (ESI): *m/z* calculated for C_{13} $H_{12}O_4NS$ $[M+H]^+$ 278.0482, found: 278.0494.
 **5a**	***4-Methyl-N-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide*** (table 3, **5a**); Yellow colored solid; m.p 207-210 °C; yield 76%; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.05 (d, J = 5.0 Hz, 1H), 7.90 (d, J = 4.3 Hz, 2H), 7.71 (dd, J = 14.7, 5.1 Hz, 5H), 2.41 (d, J = 4.5 Hz, 3H), 2.24 (d, J = 4.8 Hz, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 185.48, 180.98, 143.99, 142.34, 139.76, 139.21, 135.15, 134.93, 132.38, 131.36, 130.28, 127.51, 126.91, 21.91, 14.27; HRMS (ESI): *m/z* calculated for C_{18} $H_{15}O_4NNaS$ $[M+Na]^+$ 364.0614, found: 364.0614.
 **5b**	***N-(3-Methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide*** (table 3, **5b**); Yellow colored solid; m.p 186 °C; yield 74%; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.88 (s, 1H), 8.00 (d, J = 6.9 Hz, 1H), 7.86 (d, J = 7.8 Hz, 3H), 7.81 – 7.73 (m, 2H), 7.61 (d, J = 7.0 Hz, 1H), 7.53 (t, J = 7.3 Hz, 2H), 2.13 (s, 3H). ^{13}C-NMR (75 MHz, DMSO-d_6) δ 182.68, 178.21, 139.70, 139.26, 137.11, 132.25, 132.00, 130.83, 129.74, 128.67, 126.97, 124.78, 124.20, 11.59; HRMS (ESI): *m/z* calculated for $C_{17}H_{13}NNaO_4S$ $[M+Na]^+$ 350.0463, found: 350.0469.

 **5c**	***N-(3-Methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)biphenyl-4-sulfonamide***(table 3, **5c**); Yellow colored solid; m.p 211 °C; yield 88%; ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.10 (s, 1H), 7.97 (d, *J* = 8.3 Hz, 3H), 7.89 (d, *J* = 8.7 Hz, 3H), 7.85 – 7.78 (m, 2H), 7.75 (d, *J* = 7.4 Hz, 2H), 7.48 (dd, *J* = 14.5, 6.9 Hz, 3H), 2.16 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.40, 180.99, 144.98, 142.23, 140.88, 139.77, 139.18, 135.12, 134.88, 132.36, 131.36, 129.97, 129.39, 128.16, 128.00, 127.92, 127.87, 127.17, 126.88, 14.22; HRMS (ESI): *m/z* calculated for $C_{23}H_{17}O_4NNaS$ $[M+Na]^+$ 426.0770, found: 426.0789.
 **5d**	***4-Bromo-N-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide*** (table 3, **5d**); Yellow colored solid; m.p 208 °C; yield 78%; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.09 (d, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 6.3 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.38 (s, 1H), 2.30 (s, 3H).^{13}C-NMR (75 MHz, DMSO-d_6) δ 182.62, 178.24, 139.99, 138.69, 136.91, 132.30, 132.05, 130.04, 129.73, 128.65, 126.75, 124.80, 124.22, 11.53;HRMS (ESI): *m/z* calculated for $C_{17}H_{13}BrNO_4S$$[M+H]^+$405.9743, found:405.9755.
 **5e**	***4-Fluoro-N-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide*** (table 3, **5e**); Yellow colored solid; m.p 193 °C; yield 51%; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.12 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 6.3 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.7 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.40 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.56, 180.14, 165.40, 163.40, 142.06, 138.76, 137.50, 134.21, 133.97, 131.63, 130.54, 129.87, 129.79, 129.72, 126.16, 126.01, 116.10, 115.92, 13.43; HRMS (ESI): *m/z* calculated for $C_{17}H_{13}O_4NFS$ $[M+H]^+$ 346.0544, found: 346.0561.
 **5f**	***N-(3-Methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)-4-nitrobenzenesulfonamide*** (table 3, **5e**);. Yellow colored solid; m.p 190 °C; yield 63%; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.36 (d, *J* = 8.3 Hz, 2H), 8.13 (d, *J* = 8.2 Hz, 2H), 8.03 (d, *J* = 7.4 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 7.3 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 6.59 (s, 1H), 6.32 (s, 1H), 2.24 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.00, 178.76, 148.22, 145.74, 140.56, 137.40, 132.64, 132.31, 130.31, 129.18, 126.76, 124.77, 124.66, 122.46, 111.10, 11.87; HRMS (ESI): *m/z* calculated for $C_{17}H_{13}N_2O_6S$ $[M+H]^+$ 373.0489, found: 373.0495.

 **7**	***N-(8-Hydroxy-1,4-dioxo-1,4-dihydronaphthalen-2-yl)-4-methylbenzenesulfonamide***(table 2, **7):** Yellow solid; yield 76%;^{1}H NMR (300 MHz, $CDCl_3$):δ 11.81 (s, 1H), 7.75 (d, J = 12.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 12 Hz, 2H), 7.19 (d, J = 8.0 Hz, 1H), 6.86 (s, 2H), 2.39 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 190.19, 184.13, 161.32, 146.12, 139.48, 138.54, 136.46, 135.42, 131.66, 130.19, 127.43, 124.37, 119.03, 114.06, 21.15; ESI-MS: *m/z* calculated for $C_{17}H_{14}NO_5S$ $[M+H]^+$ 344.05, found: 344.15.
 **8**	***2-Aminonaphthalene-1,4-dione*** **(**Scheme 1**, 8):** Orange colored solid; yield (56%)^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 11.5, 2H), 7.72 (d, *J* = 7.6, 1H), 7.63 (d, *J* = 7.6, 1H), 6.01 (s, 1H), 5.32 (s, 2H);^{13}C NMR (126 MHz, $CDCl_3$) δ 183.49, 182.01, 149.11, 134.40, 133.45, 131.95, 130.53, 126.03, 125.86, 104.21; (ESI): *m/z* calculated for $C_{10}H_7NO_2$ $[M+H]^+$ 173.04, found:174.10.
 **9**	***2-Amino-3-methylnaphthalene-1,4-dione***(Scheme 1, **9):** Orange colored solid; yield (60%)^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6, 1H), 8.01 (d, *J* = 7.6, Hz, 1H), 7.68 (t, *J* = 7.6, 1H), 7.59 (t, *J* = 7.5, 1H), 5.03 (s, 2H), 2.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.83, 181.13, 145.32, 134.17, 131.97, 126.15, 125.72, 113.12, 9.17; HRMS (ESI): *m/z* calculated for $C_{17}H_{13}N_2O_6S[M+H]^+$ 373.0489, found: 373.0495.

^{1}H- and ^{13}C-NMR spectra and Mass analysis

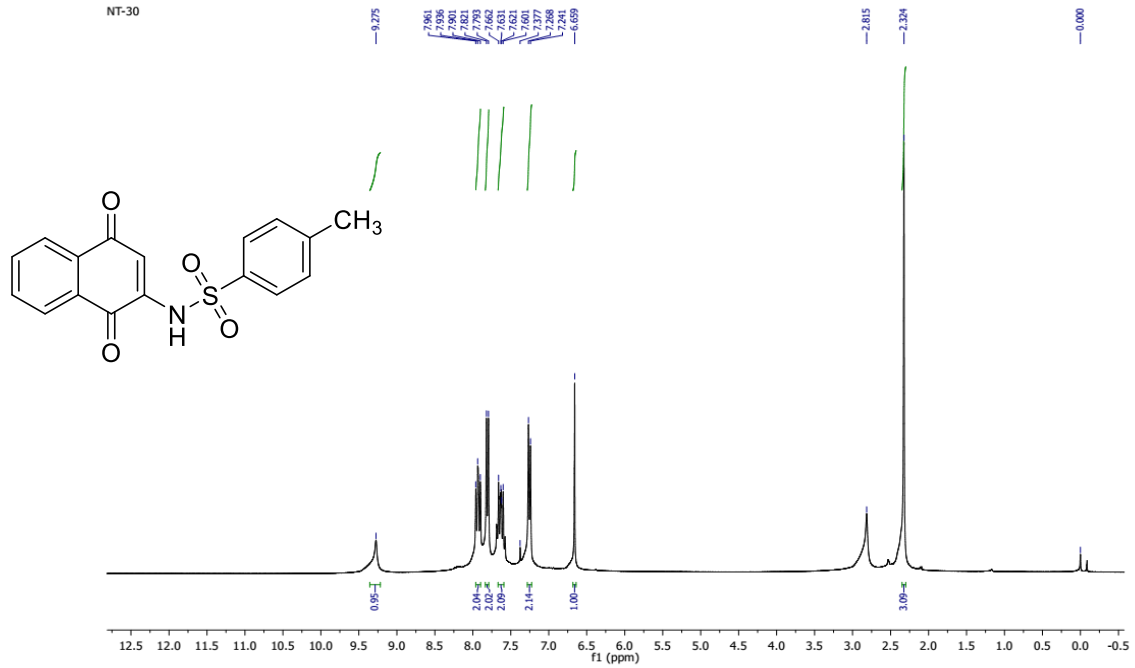


Fig. 1. ^{1}H-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-4-methylbenzenesulfonamide (Table 2, **3a**).

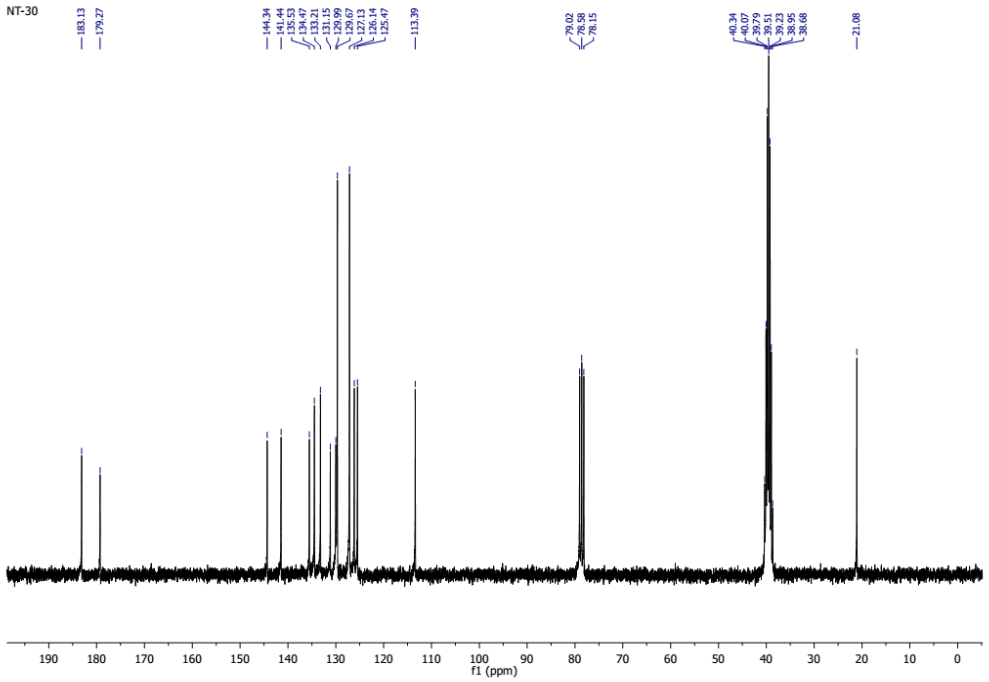


Fig. 2. ^{13}C-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-4-methylbenzenesulfonamide (Table 2, **3a**).

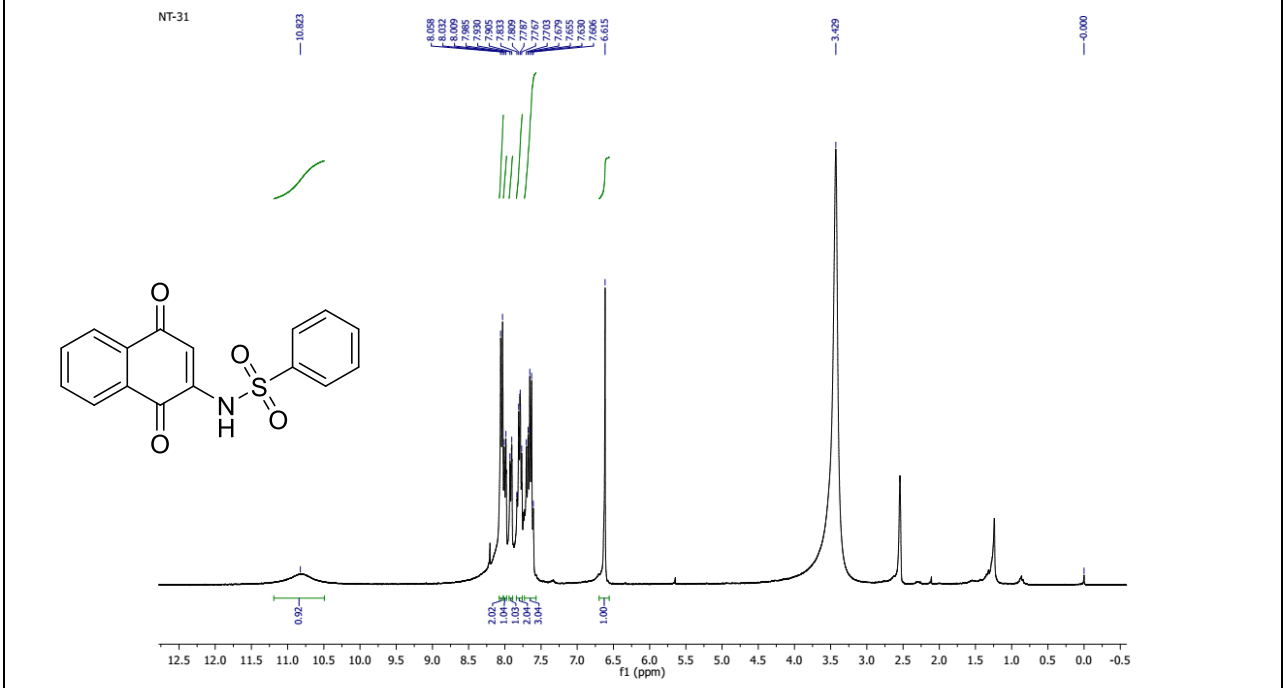


Fig. 3. ^{1}H-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide (Table 2, **3b**).

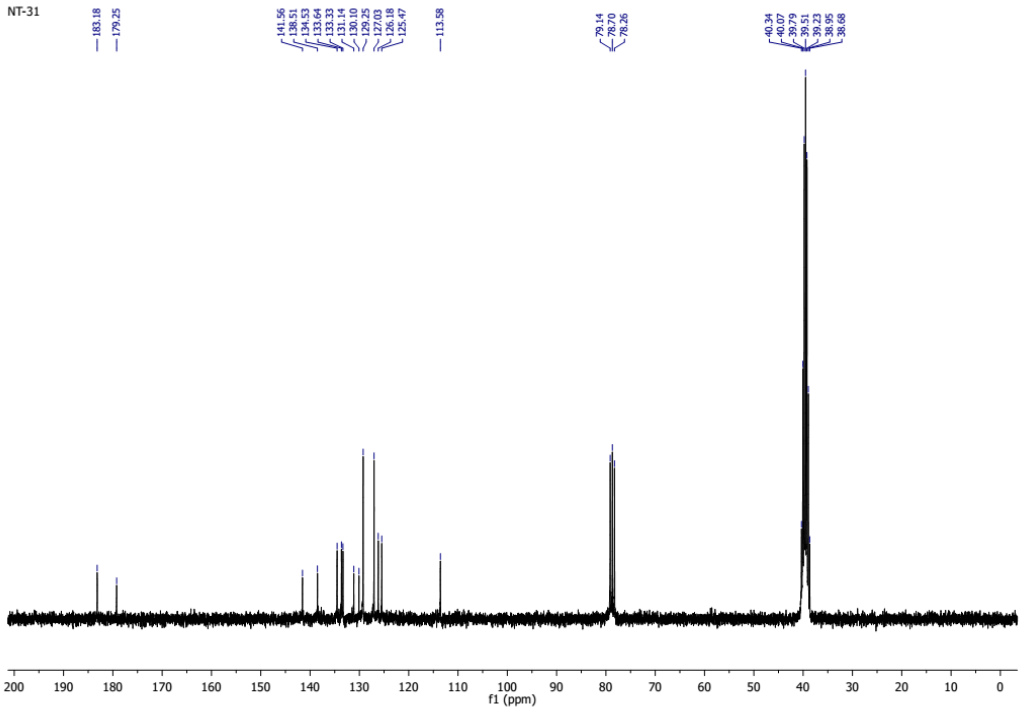


Fig. 4. ^{13}C-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide (Table2, **3b**).

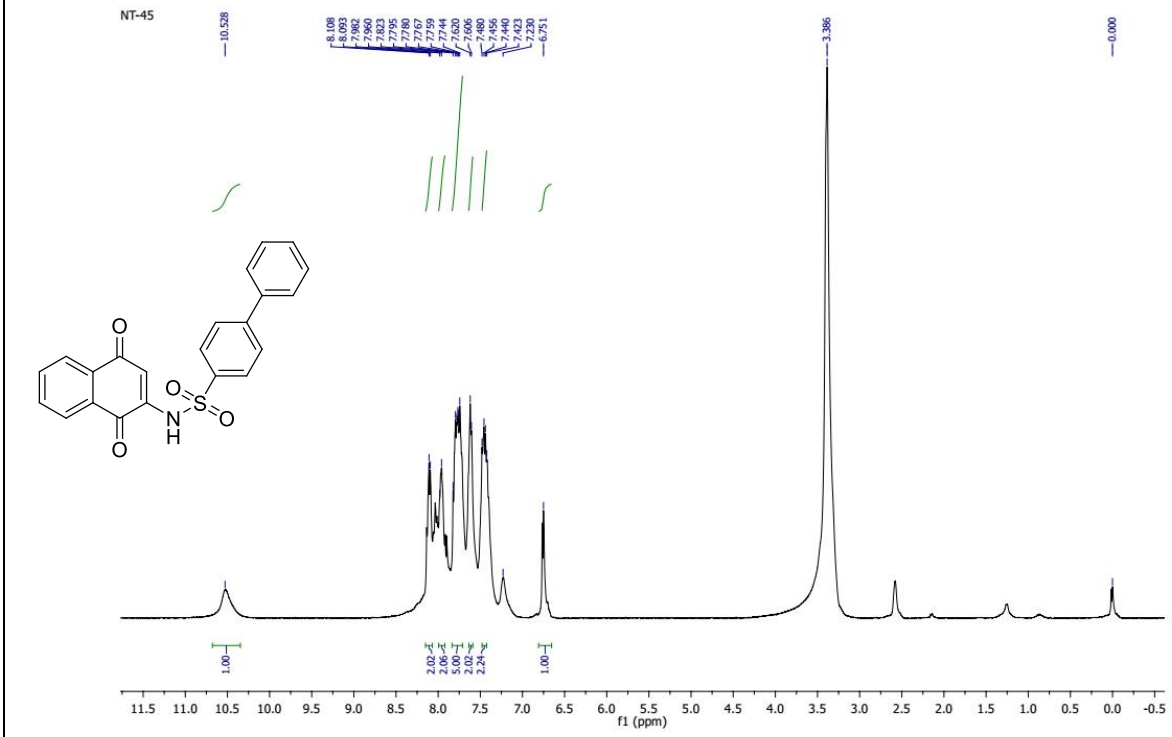


Fig. 5. ^{1}H-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)biphenyl-4-sulfonamide (Table 2, **3c**).

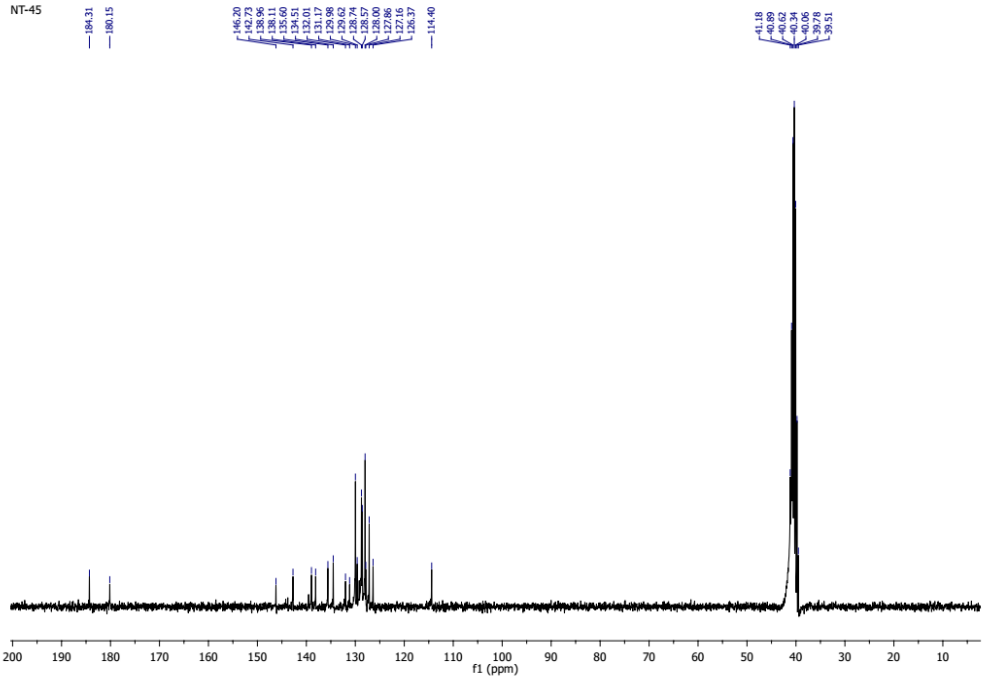


Fig. 6. ^{13}C-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)biphenyl-4-sulfonamide (Table 2, **3c**).

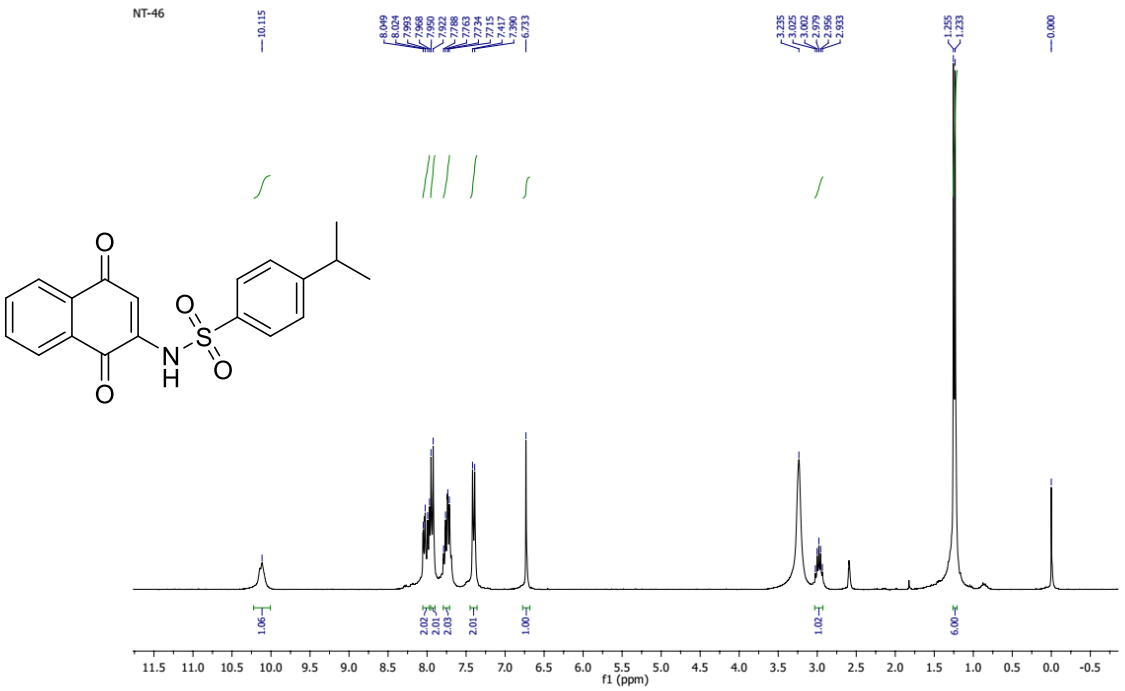


Fig. 7. ^{1}H-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-4-isopropylbenzenesulfonamide (Table 2, **3d**).

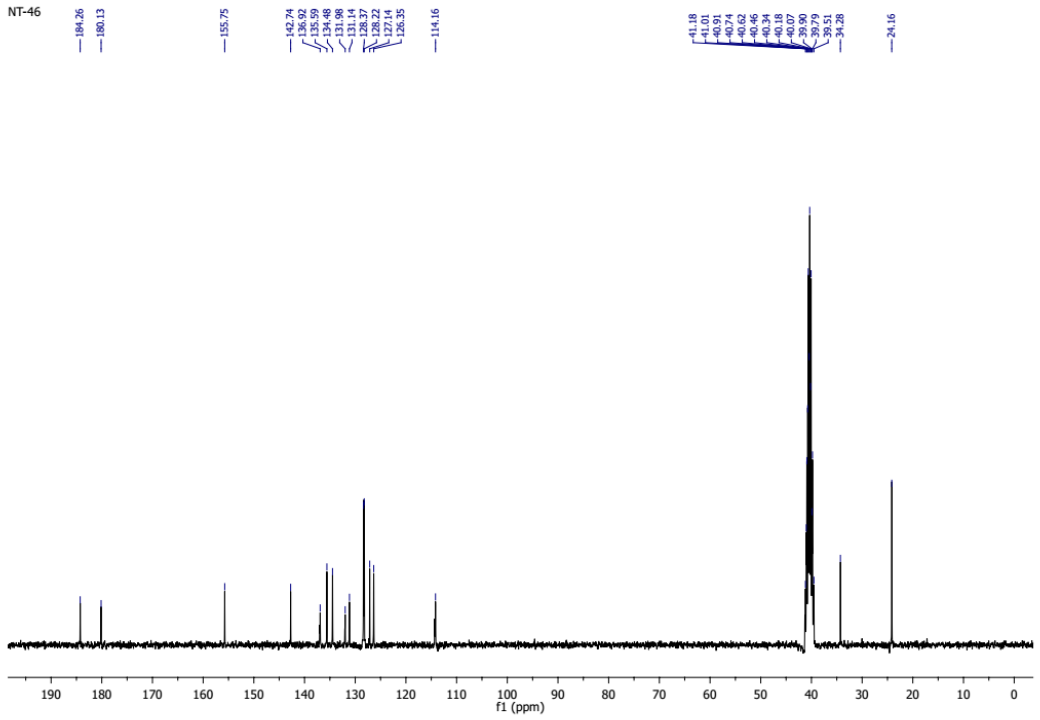


Fig. 8. ^{13}C-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-4-isopropylbenzenesulfonamide (Table2, **3d**).

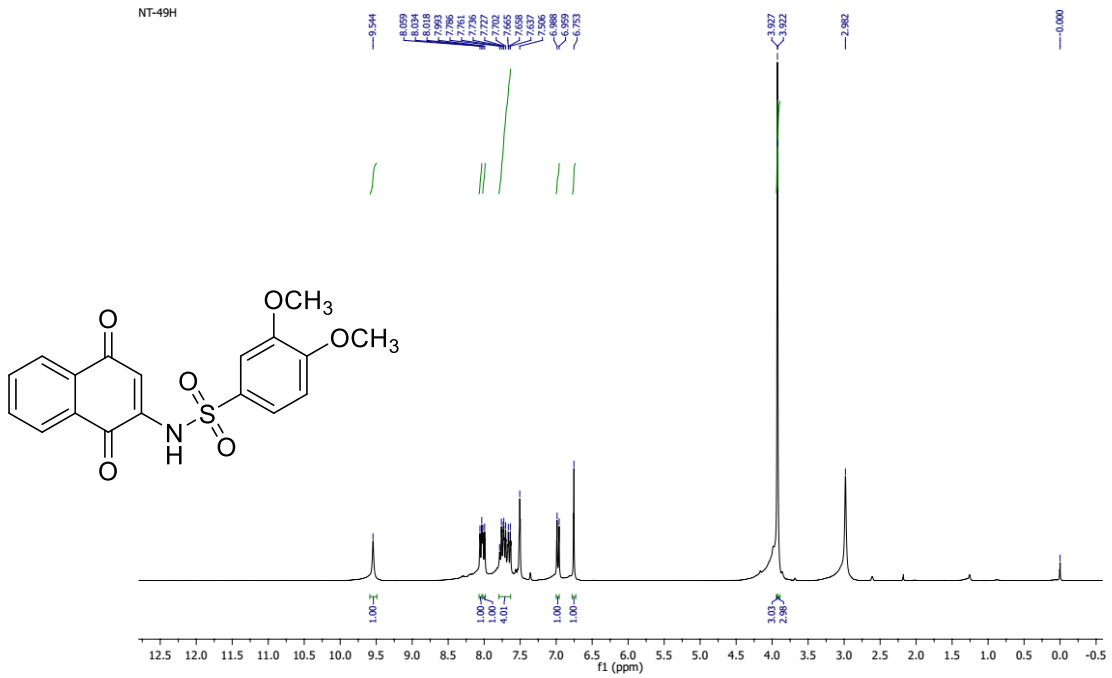


Fig. 9. ^{1}H-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-3,4-dimethoxybenzenesulfonamide (Table 2, **3e**).

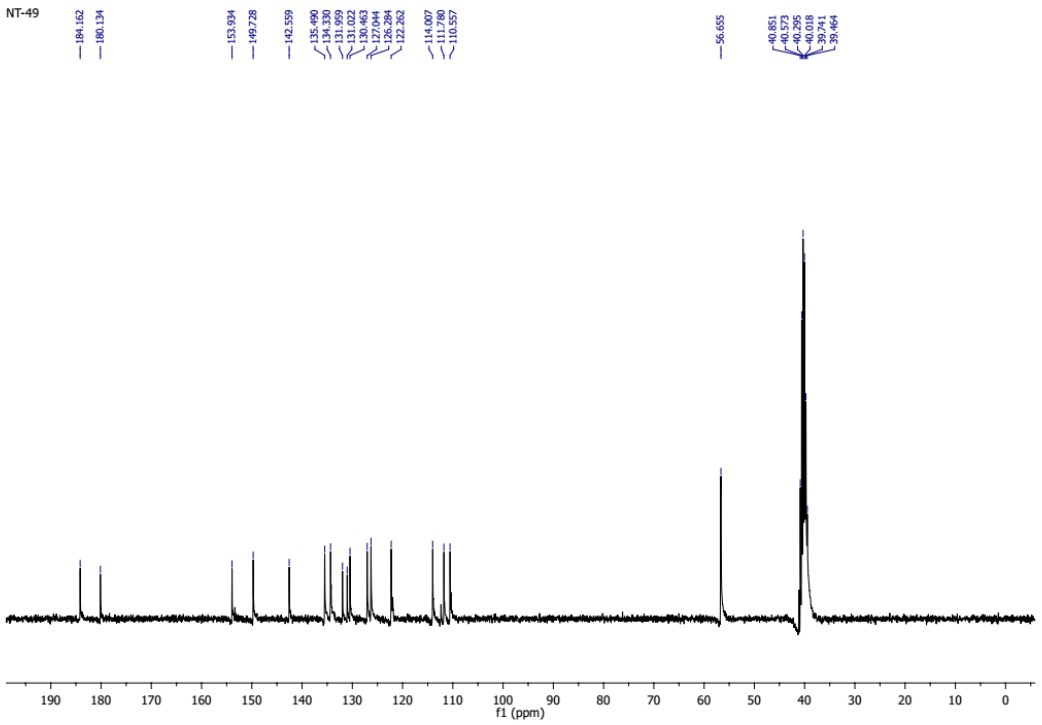


Fig. 10. ^{13}C-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-3,4-dimethoxybenzenesulfonamide (Table 2, **3e**).

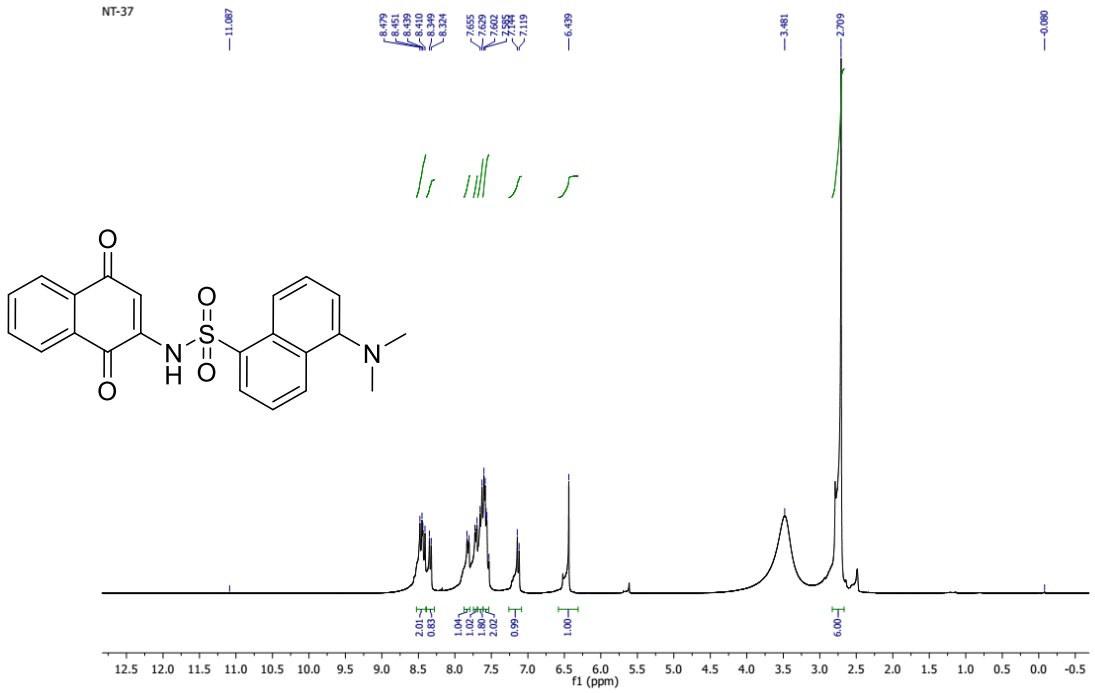


Fig. 11. ^{1}H-NMR spectrum of 5-(Dimethylamino)-*N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)naphthalene-1-sulfonamide (Table 2, **3g**).

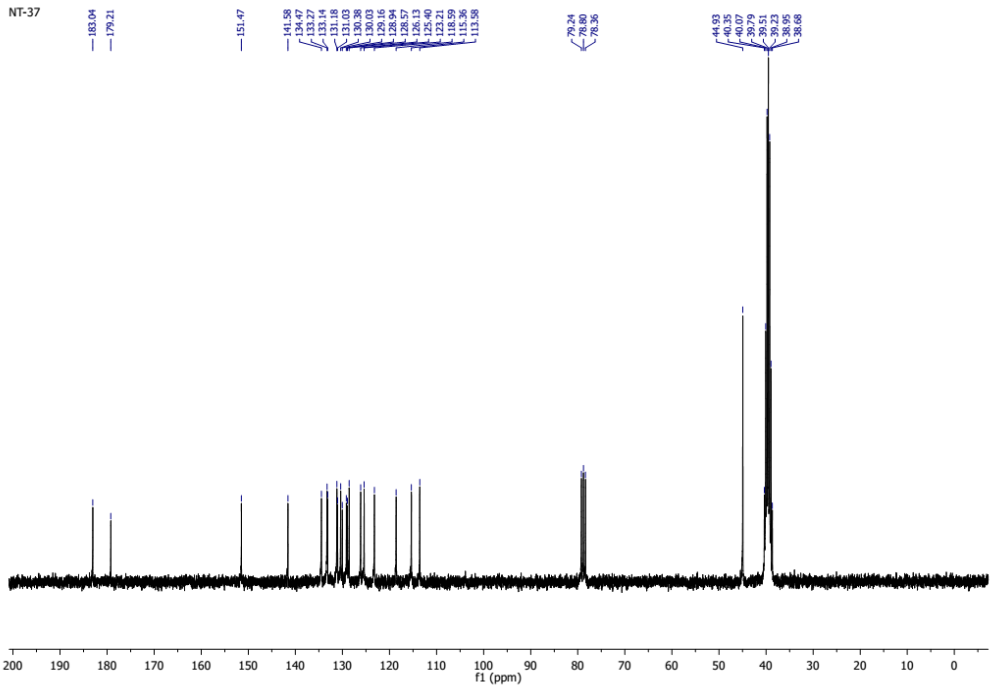


Fig. 12. ^{13}C-NMR spectrum of 5-(dimethylamino)-*N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)naphthalene-1-sulfonamide (Table 2, **3g**).

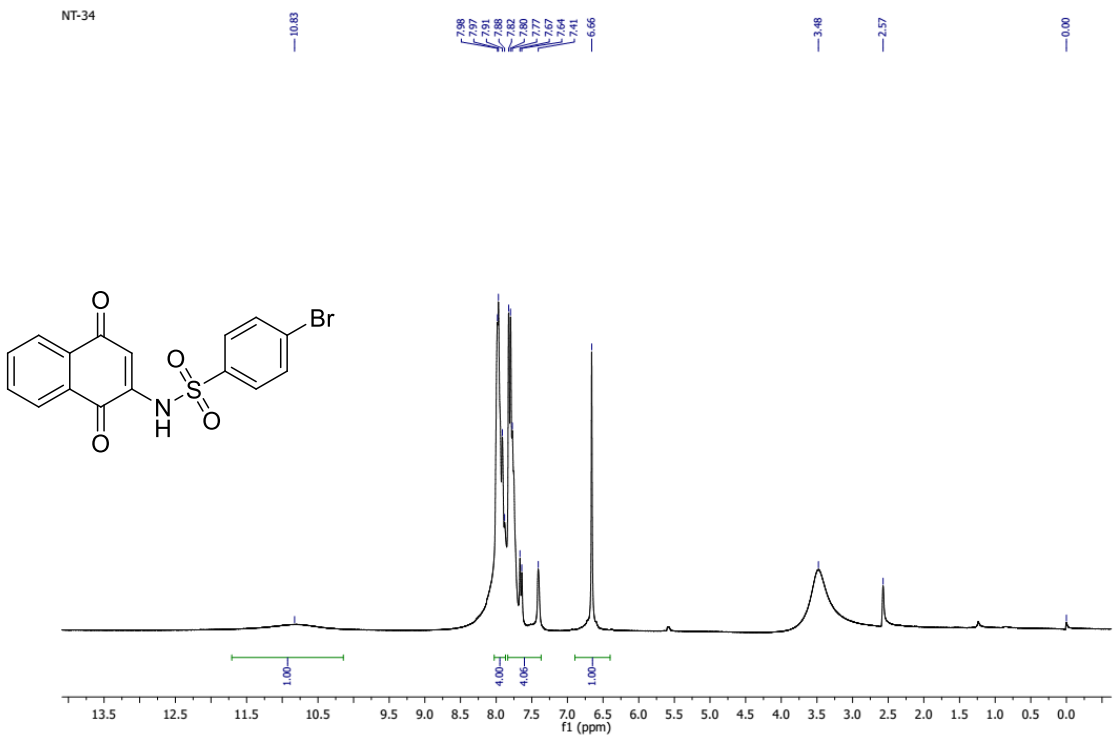


Fig. 13. ^{1}H-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-4-bromobenzenesulfonamide (Table 2, **3h**).

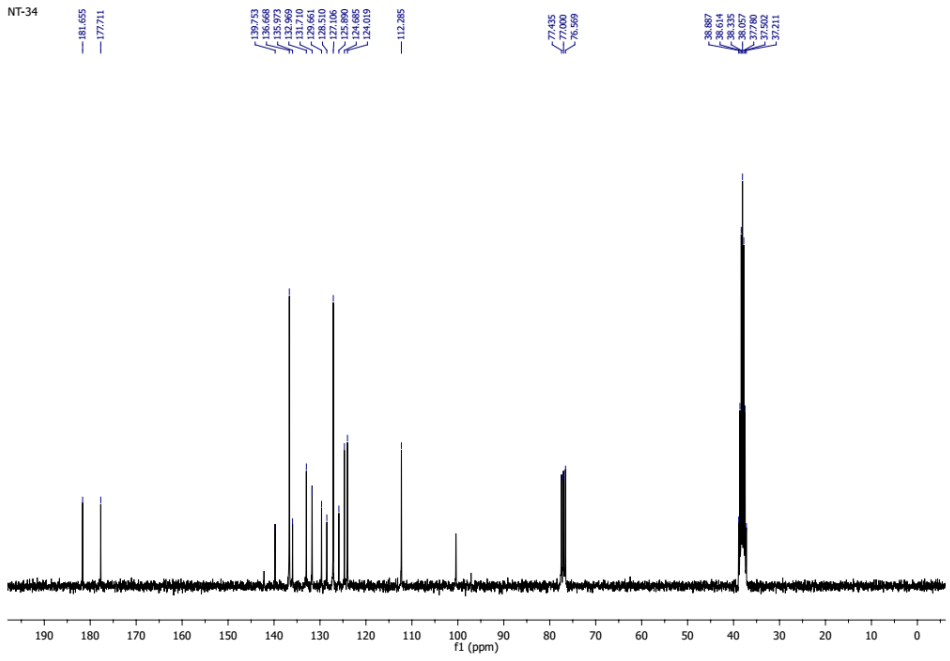


Fig. 14. ^{13}C-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-4-bromobenzenesulfonamide (Table 2, **3h**).

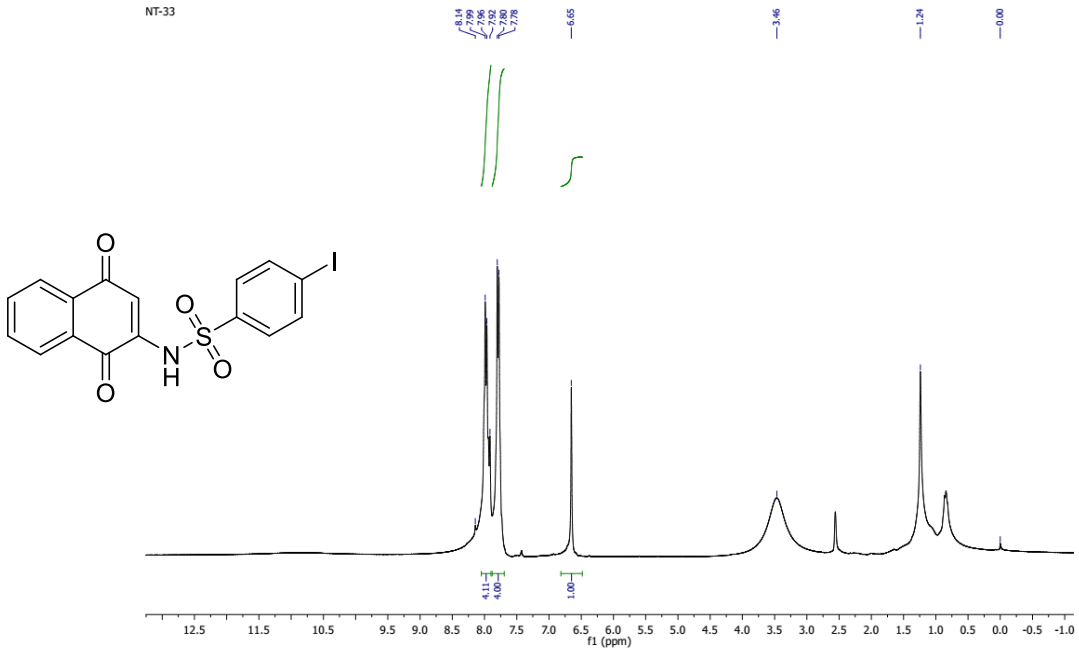


Fig. 15. ^{1}H-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-4-iodobenzenesulfonamide (Table 2, **3i**).

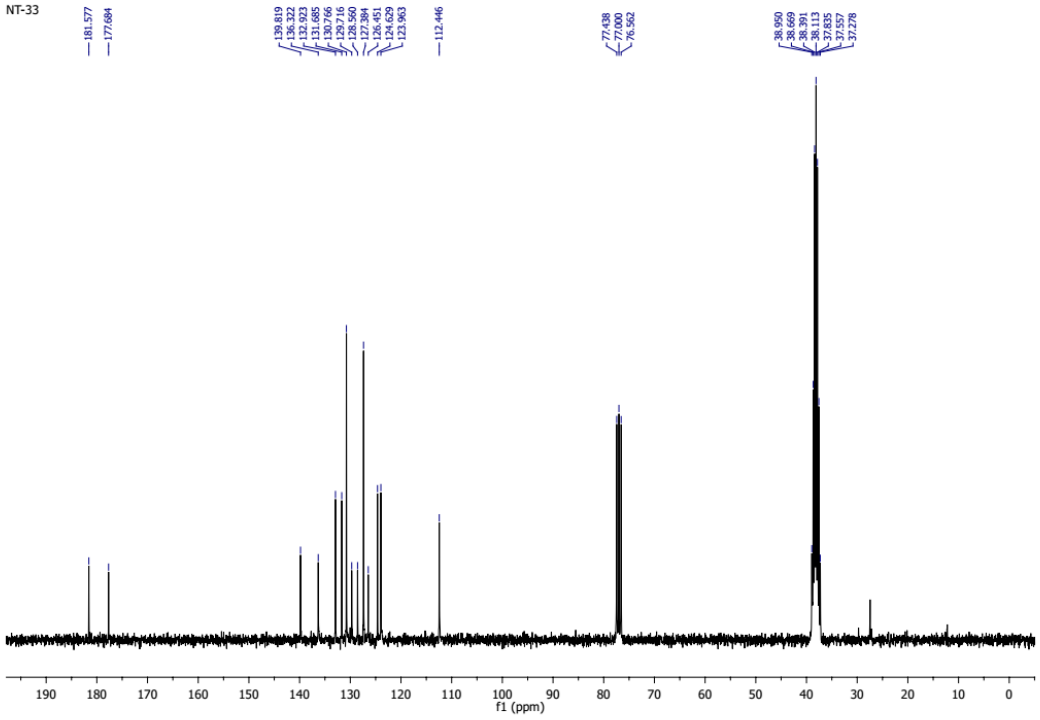


Fig. 16. ^{13}C-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-4-iodobenzenesulfonamide (Table 2, **3i**).

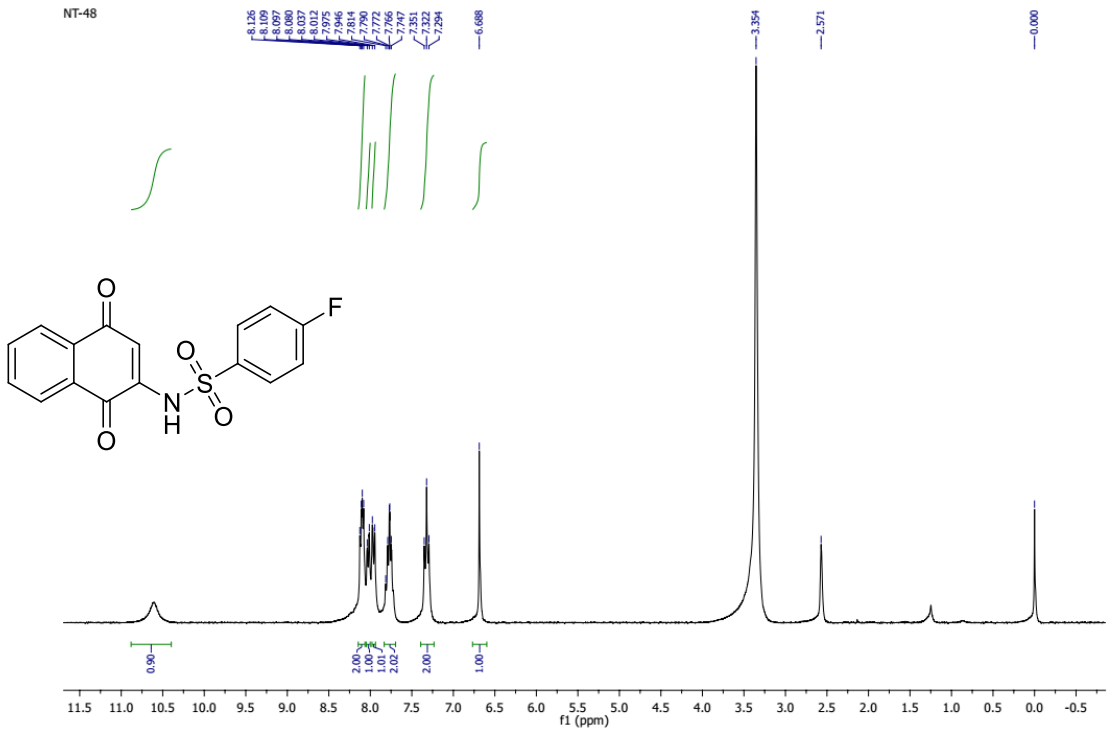


Fig. 17. ^{1}H-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-4-fluorobenzenesulfonamide (Table 2, **3j**).

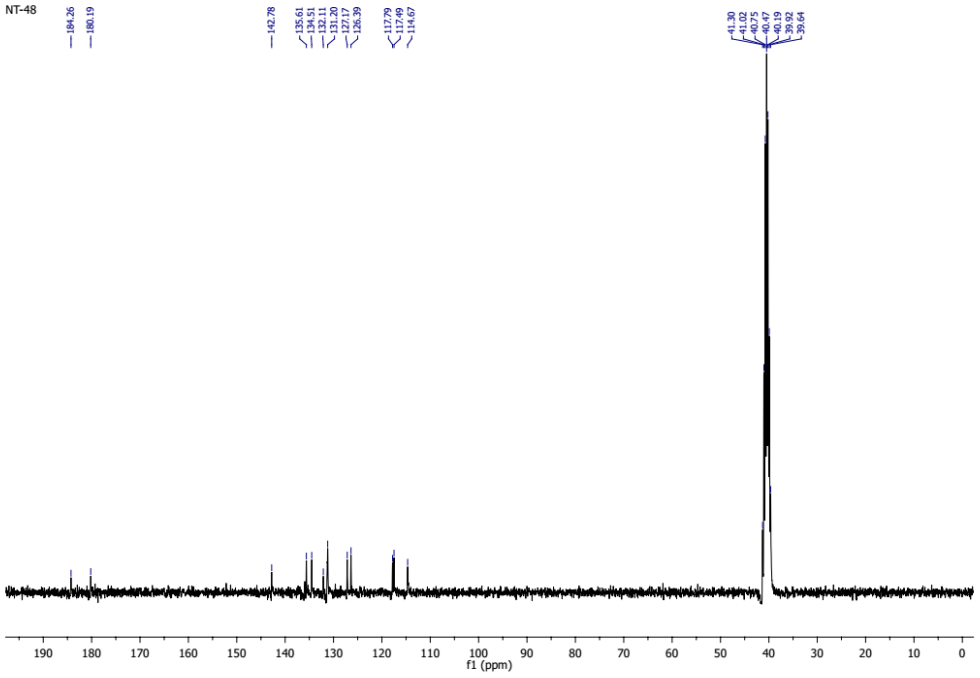


Fig. 18. ^{13}C-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-4-fluorobenzenesulfonamide (Table 2, **3j**).

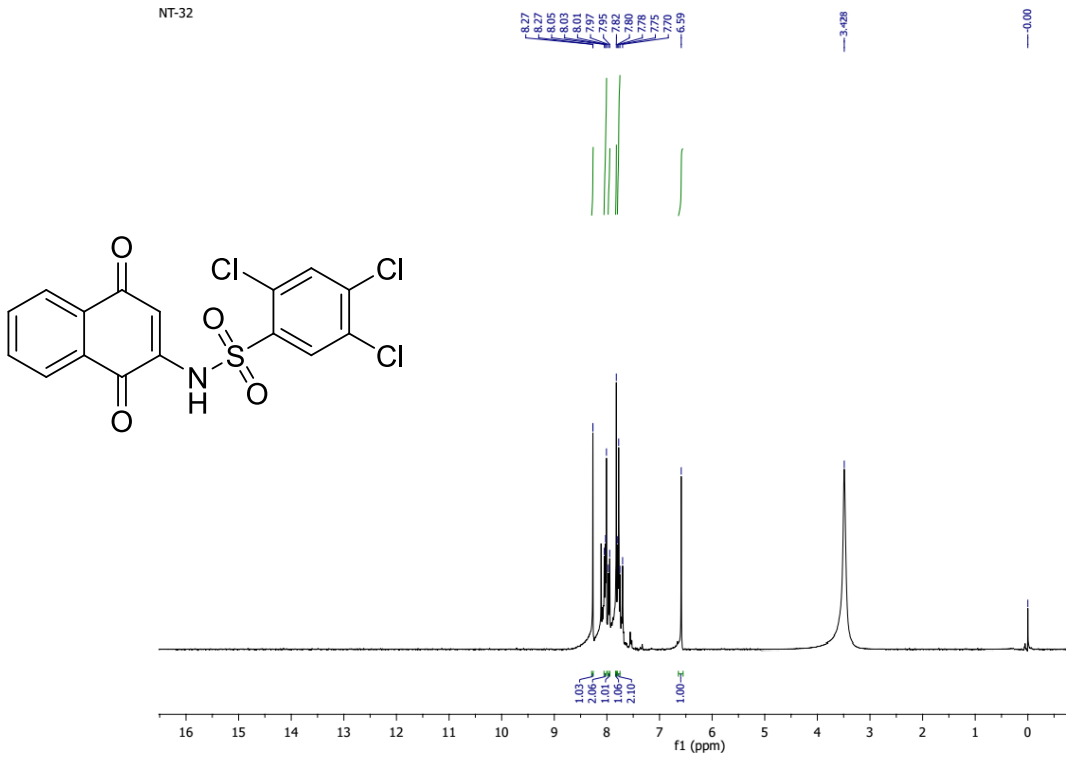


Fig. 19. ^{1}H-NMR spectrum of 2,4,5-trichloro-*N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide (Table 2, **3k**).

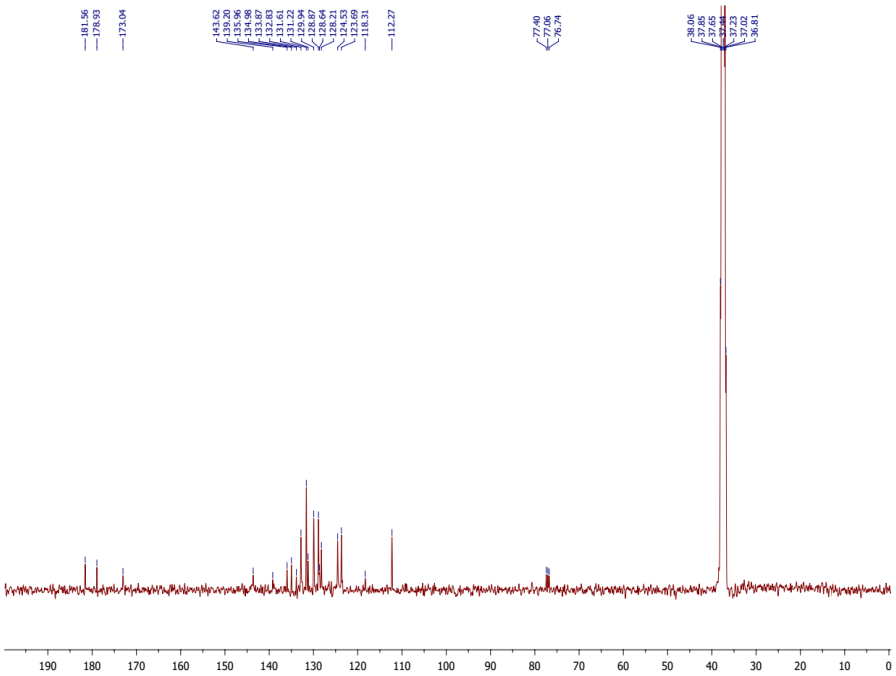


Fig. 20. ^{13}C-NMR spectrum of 2,4,5-trichloro-*N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide (Table 2, **3k**).

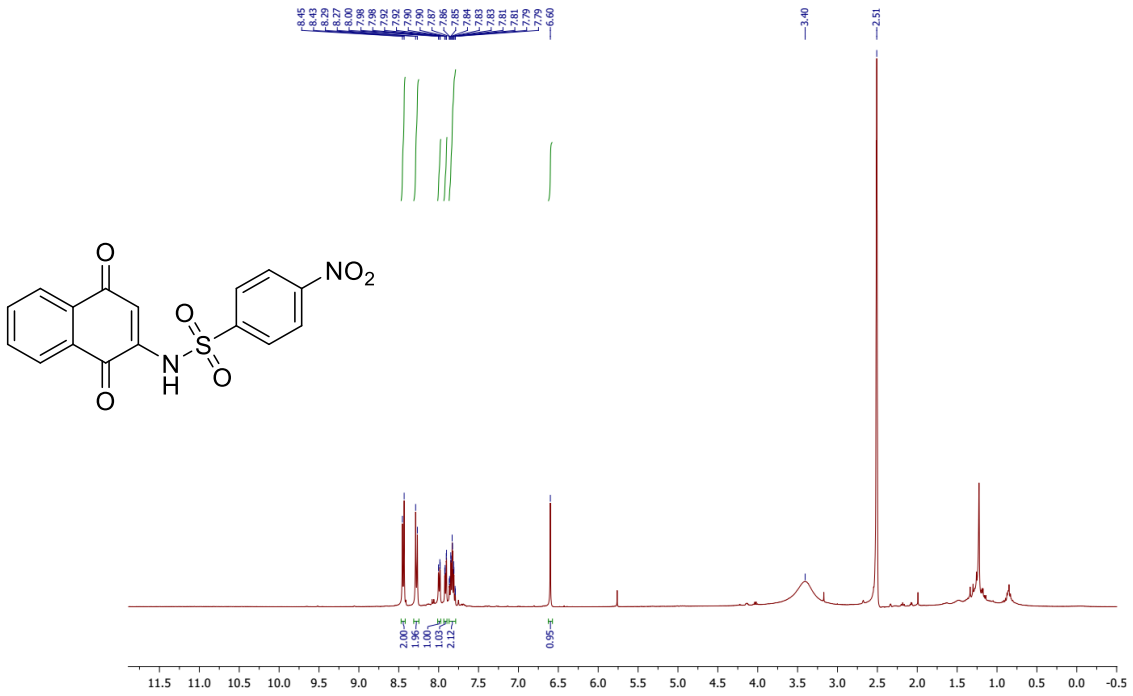


Fig. 21. ^{1}H-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-4-nitrobenzenesulfonamide (Table 2, **3l**).

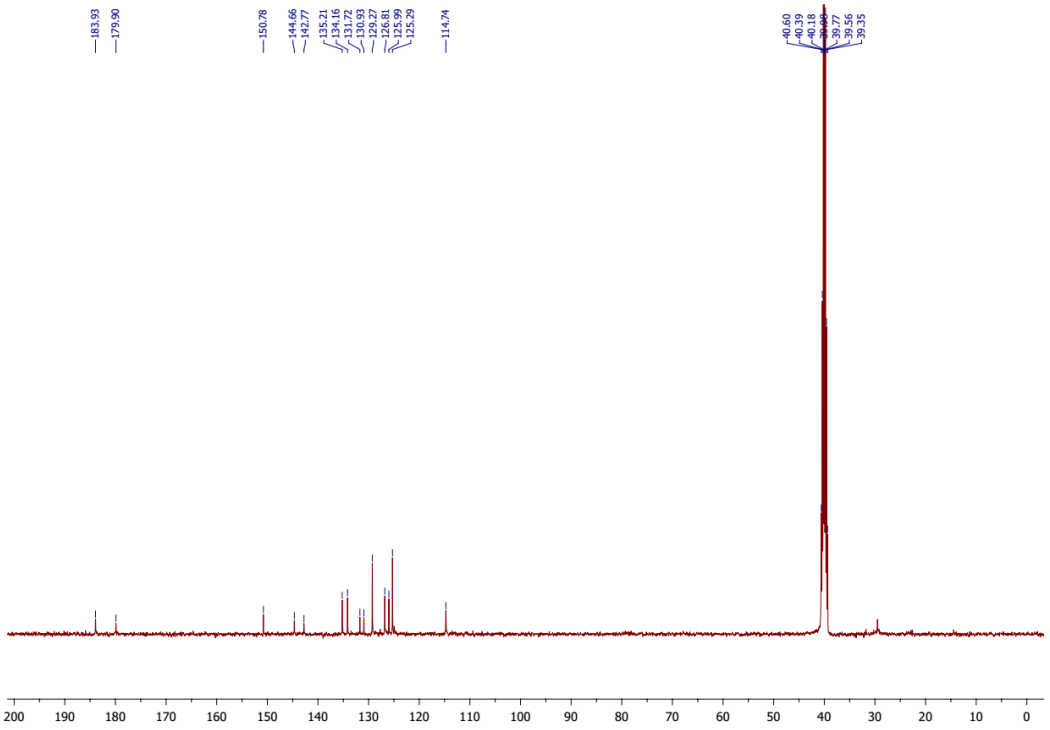


Fig. 22. ^{13}C-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-4-nitrobenzenesulfonamide (Table 2, **3l**).

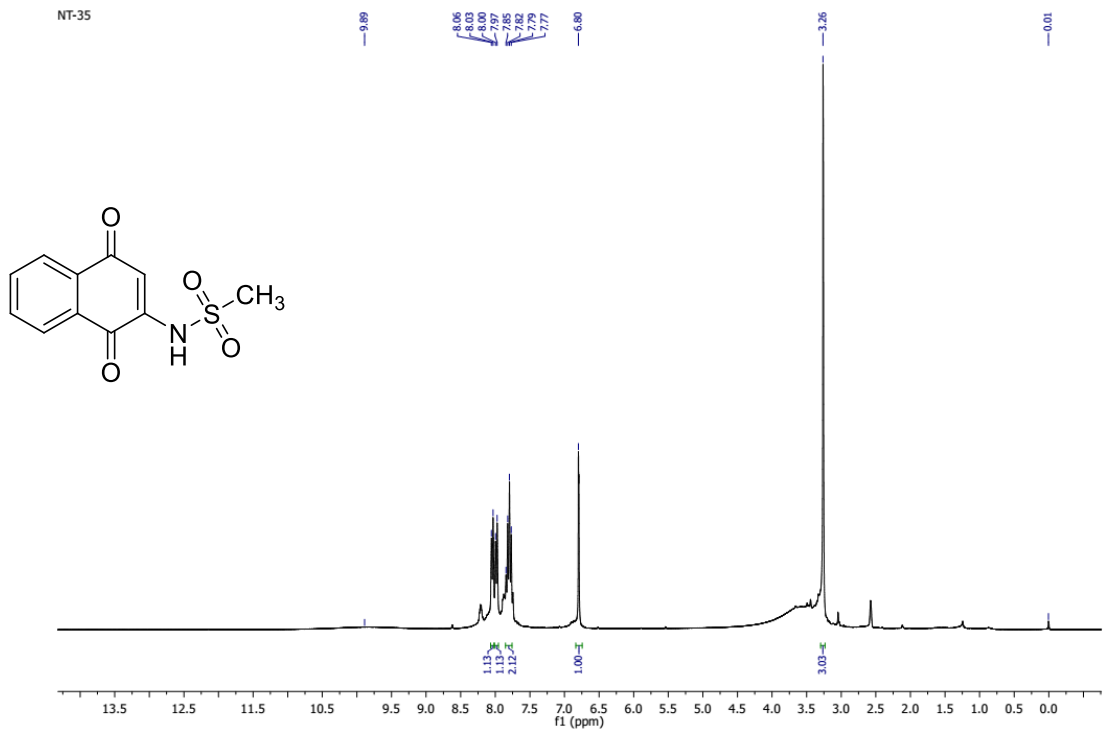


Fig. 23. ^{1}H-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)methanesulfonamide (Table 2, **3m**).

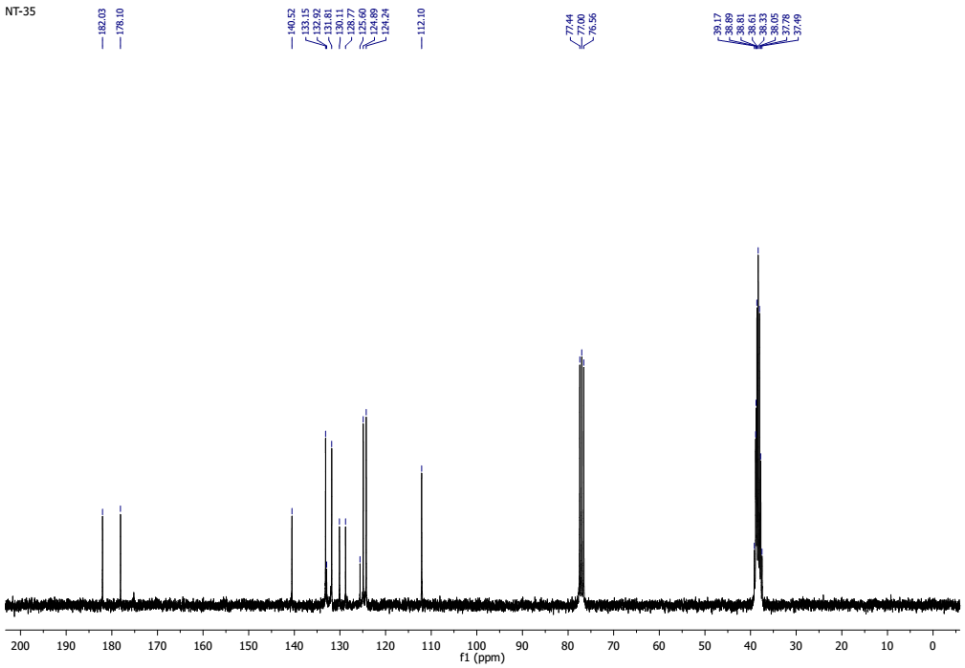


Fig. 24. ^{13}C-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)methanesulfonamide (Table 2, **3m**).

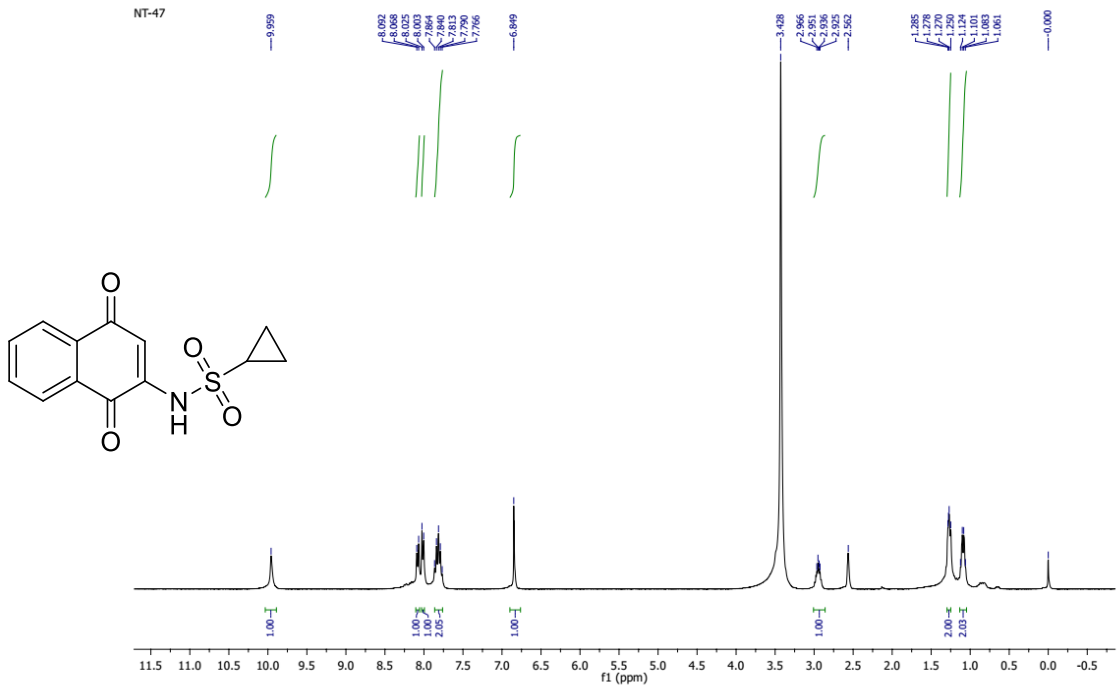


Fig. 25. ^{1}H-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)cyclopropanesulfonamide (Table 2, **3n**).

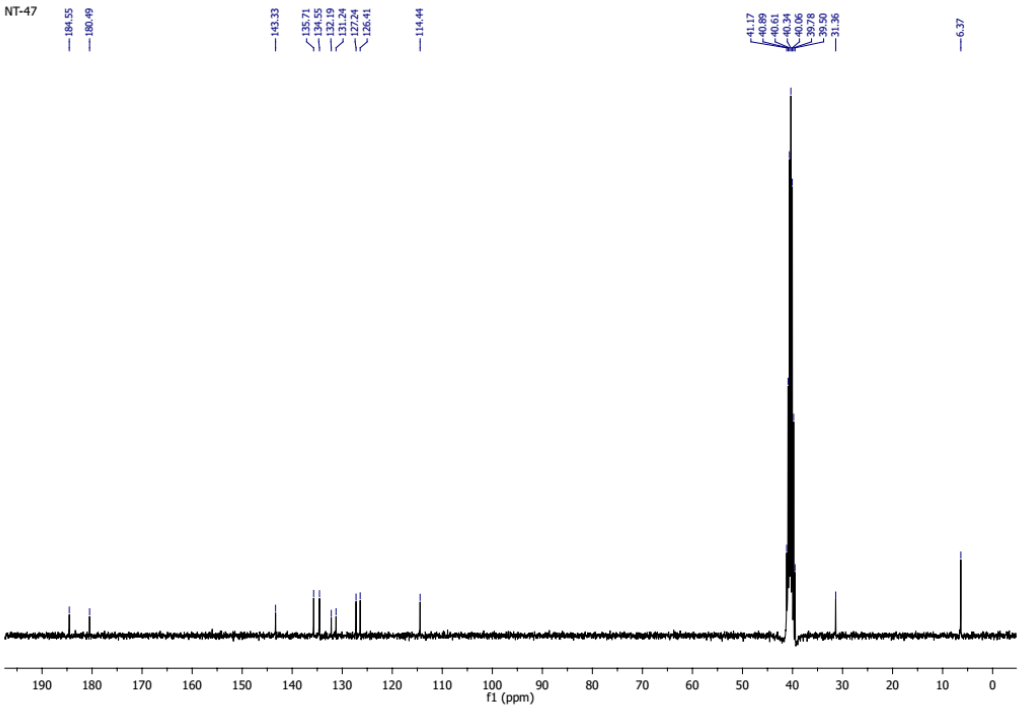


Fig. 26. ^{13}C-NMR spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)cyclopropanesulfonamide (Table 2, **3n**).

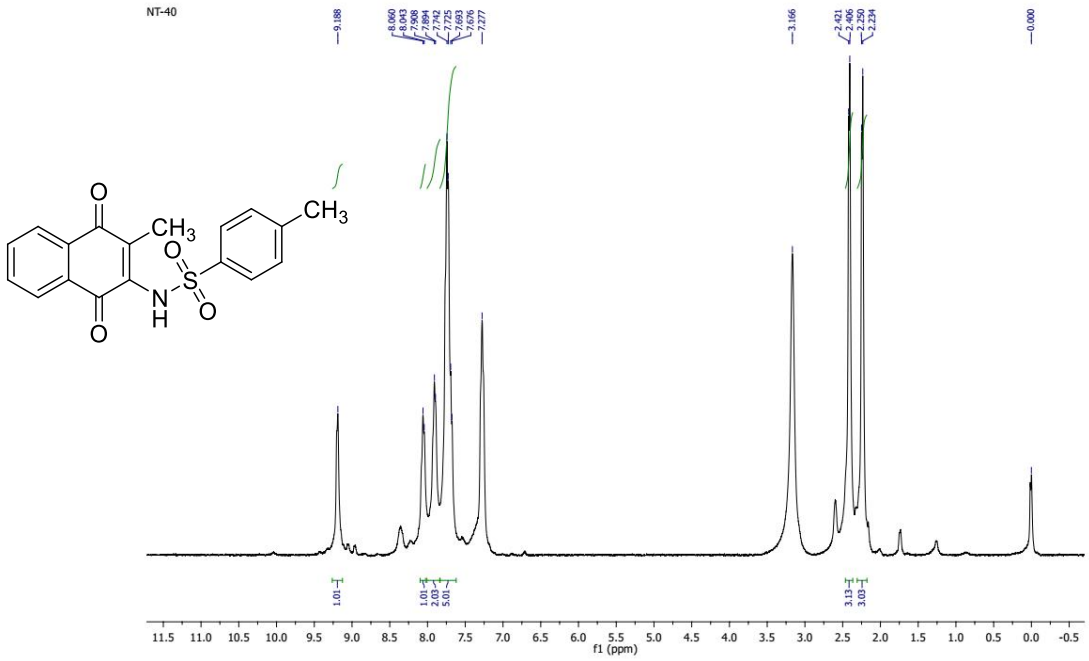


Fig. 27. ^{1}H-NMR spectrum of 4-Methyl-*N*-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide (Table 3, **5a**).

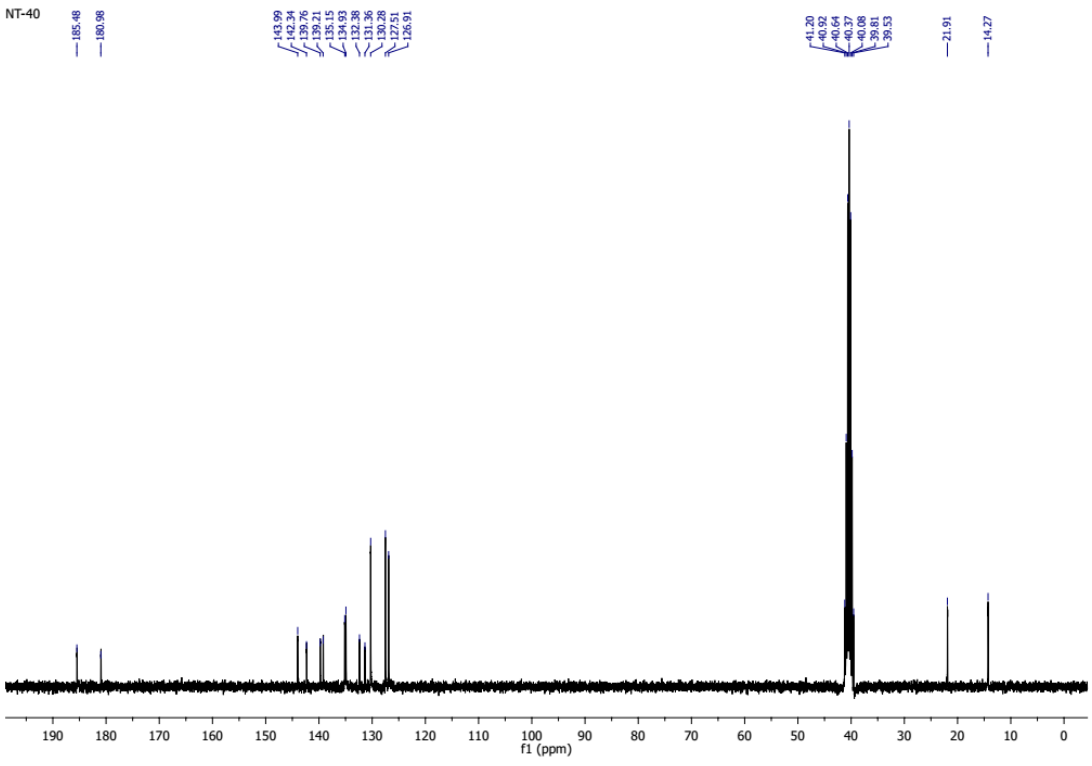


Fig. 28. ^{13}C-NMR spectrum of 4-Methyl-*N*-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide (Table 3, **5a**).

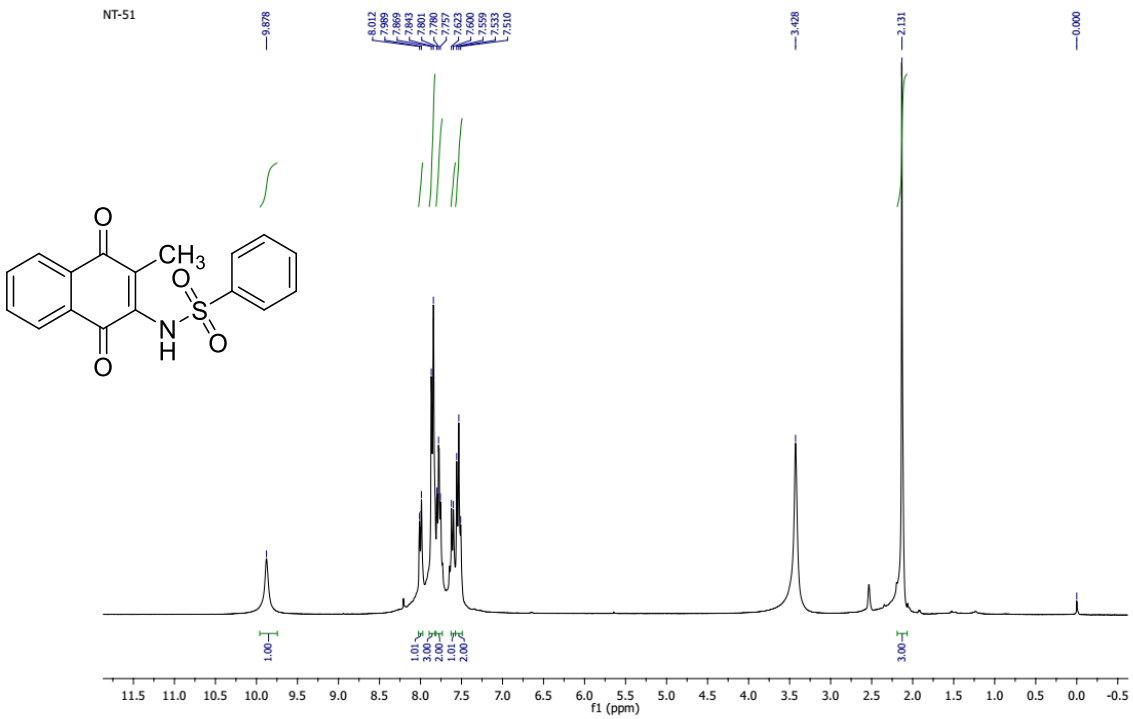


Fig. 29. ^{1}H-NMR spectrum of *N*-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide (Table 3, **5b**).

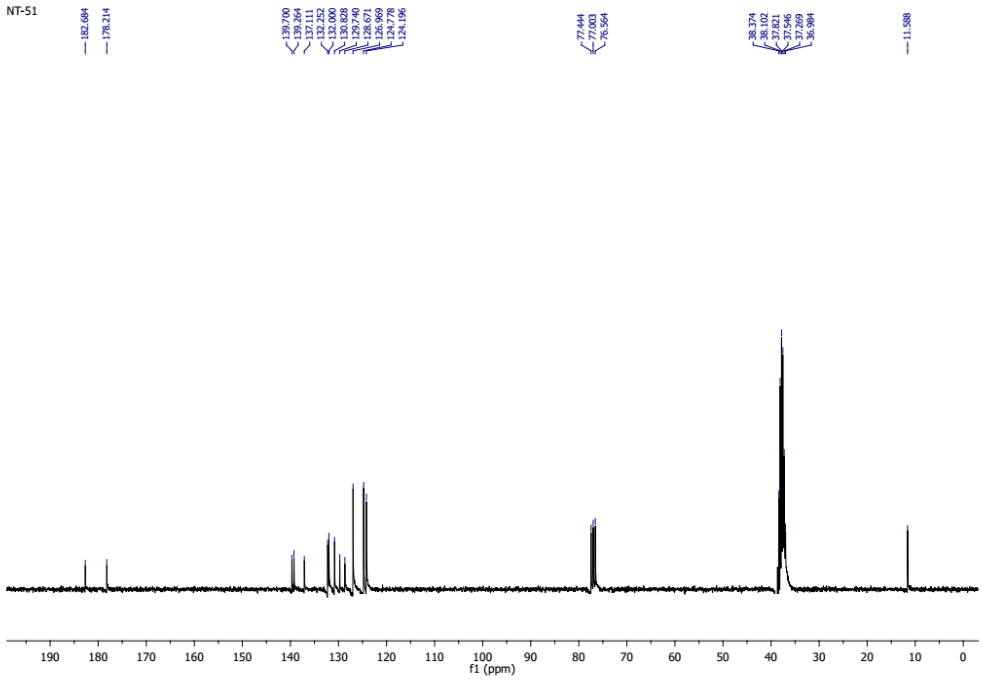


Fig. 30. ^{13}C-NMR spectrum of *N*-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide (Table 3, **5b**).

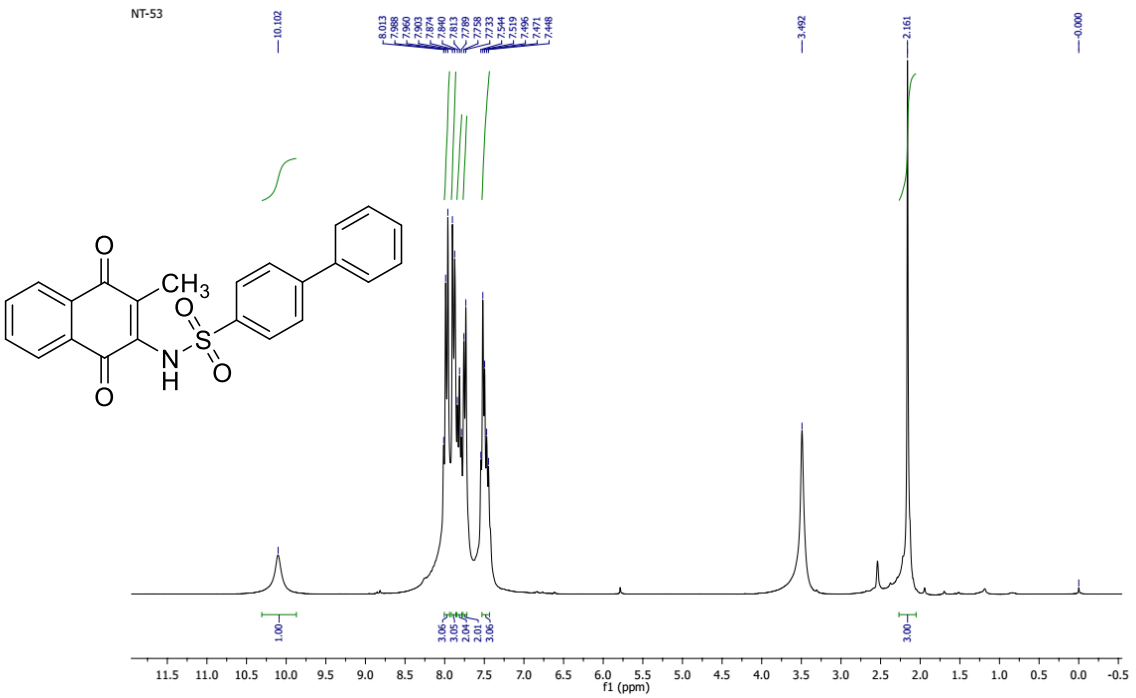


Fig. 31. ^{1}H-NMR spectrum of *N*-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)biphenyl-4-sulfonamide (Table 3, **5c**).

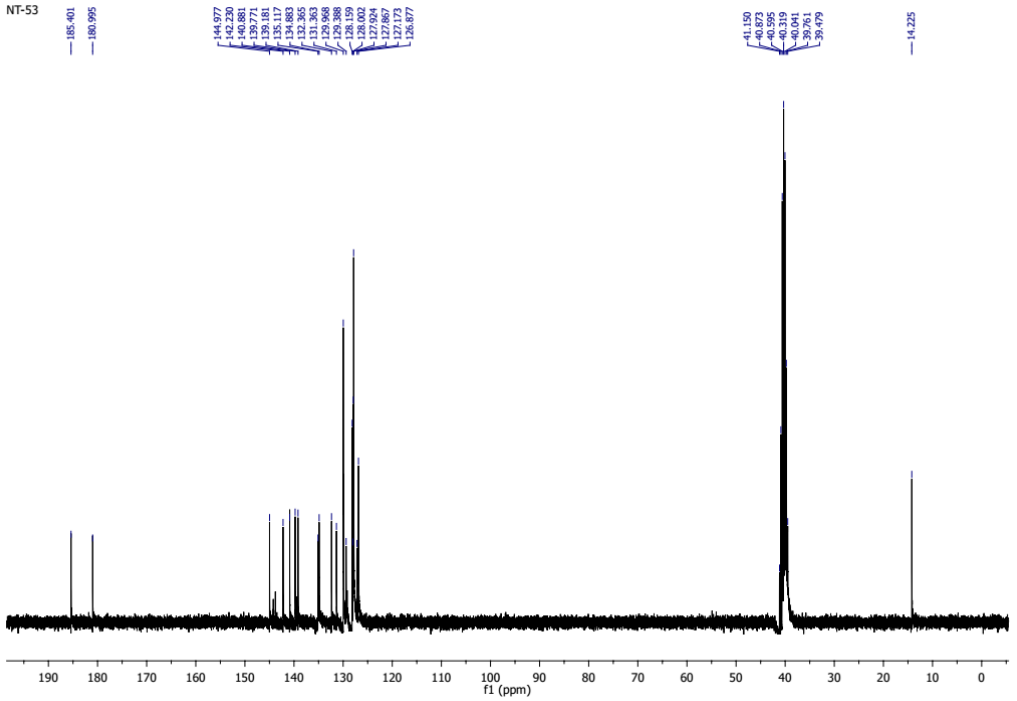


Fig. 32. ^{13}C-NMR spectrum of *N*-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)biphenyl-4-sulfonamide (Table 3, **5c**).

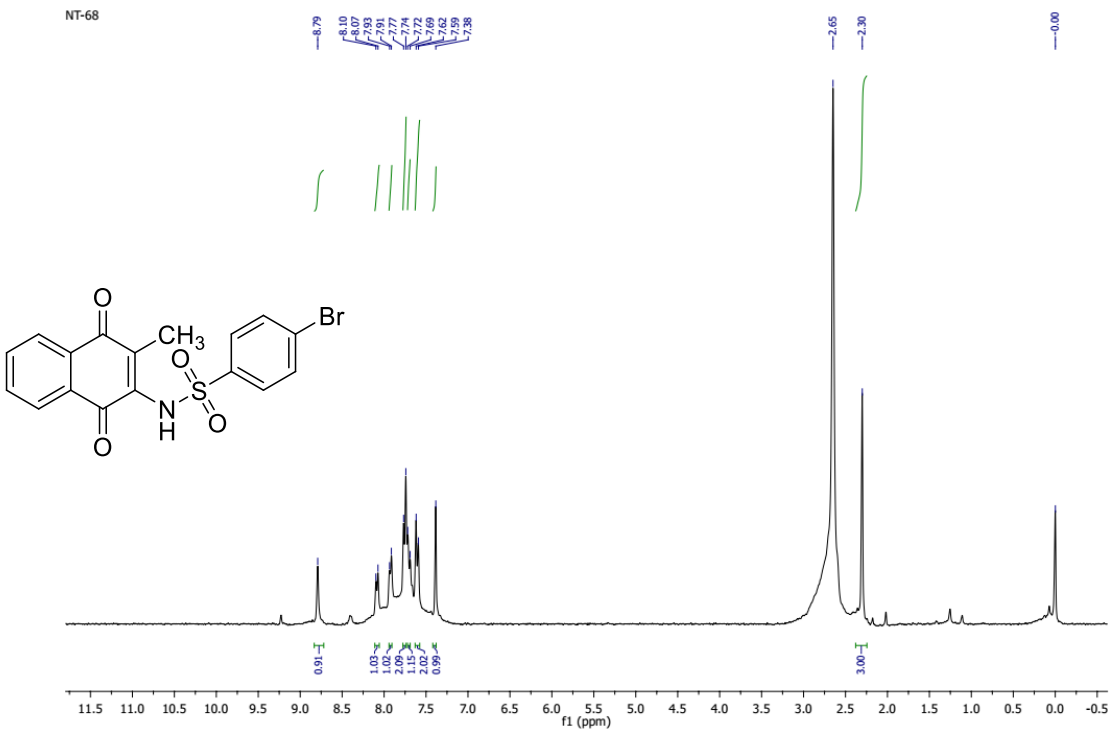


Fig. 33. ^{1}H-NMR spectrum of 4-Bromo-*N*-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide (Table 3, **5d**).

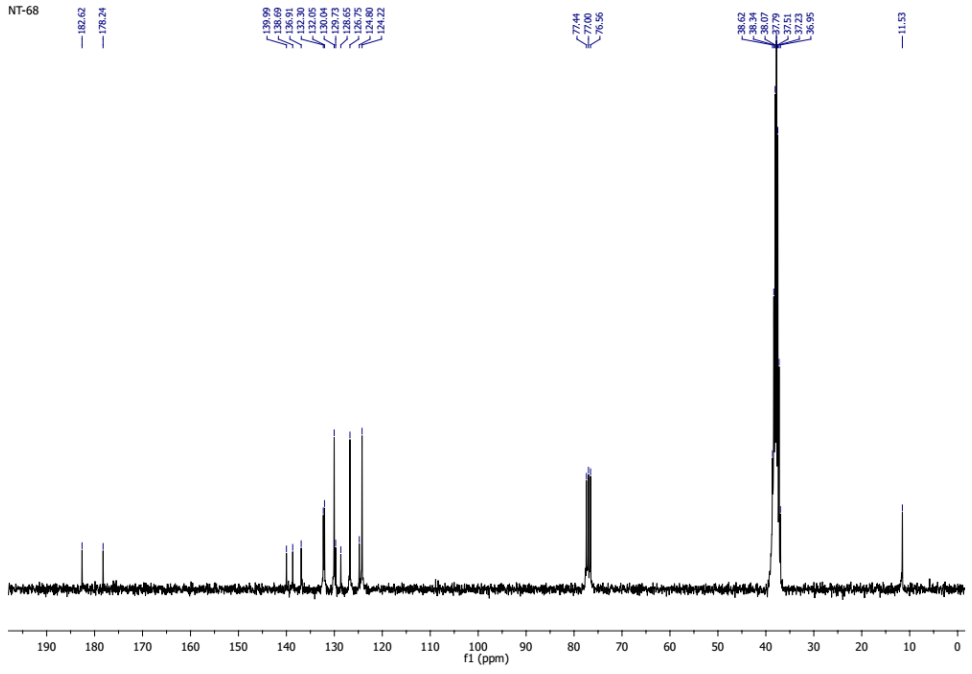


Fig. 34. ^{13}C-NMR spectrum of 4-Bromo-*N*-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide (Table 3, **5d**).

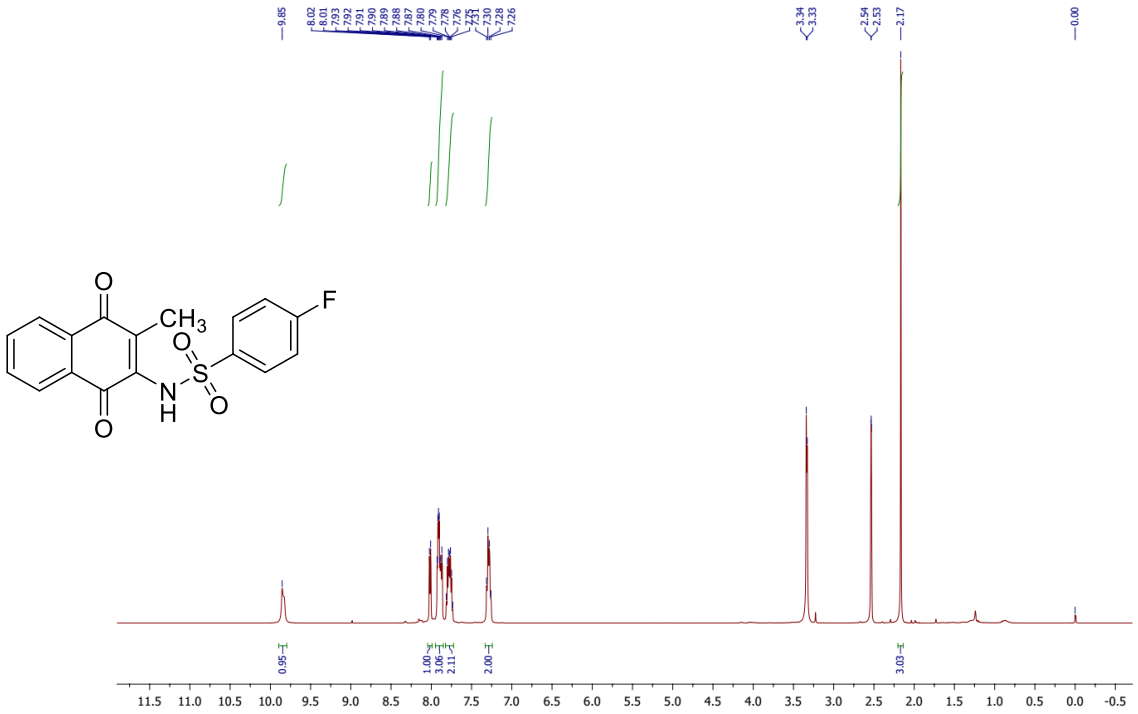


Fig. 35. ^{1}H-NMR spectrum of 4-Fluoro-*N*-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide (Table 3, **5e**).

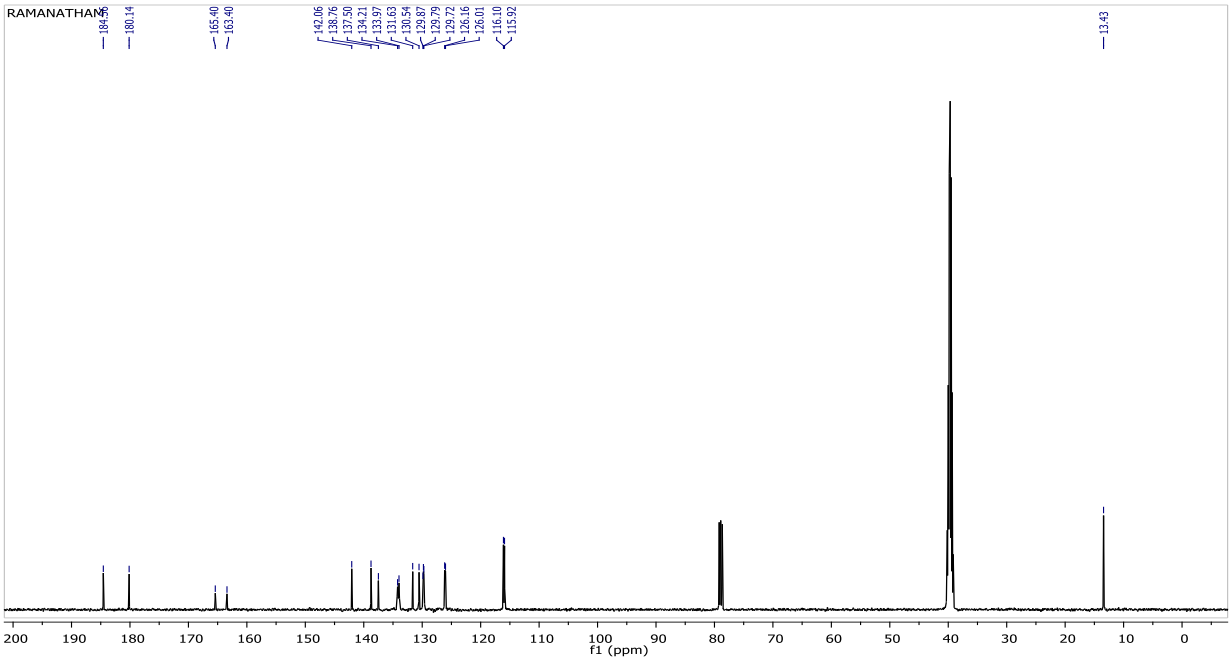


Fig. 36. ^{13}C-NMR spectrum of 4-Fluoro-*N*-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide (Table 3, **5e**)

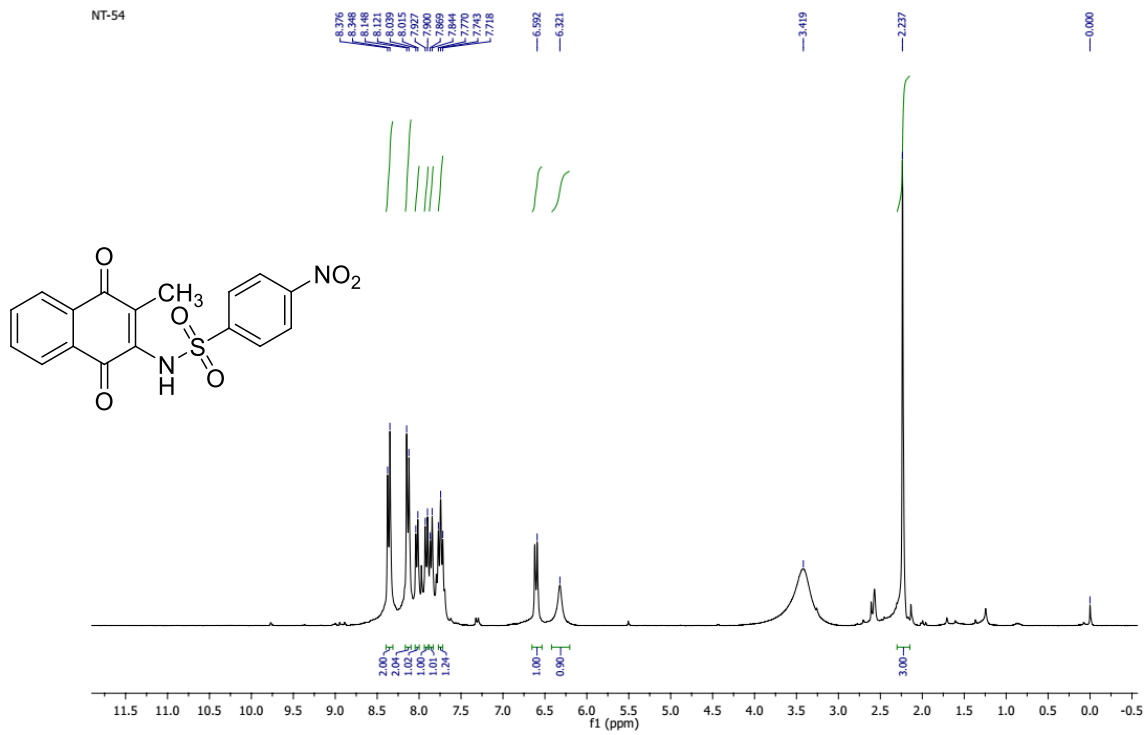


Fig. 37. ^{1}H-NMR spectrum of *N*-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)-4-nitrobenzenesulfonamide (Table 3, **5f**).

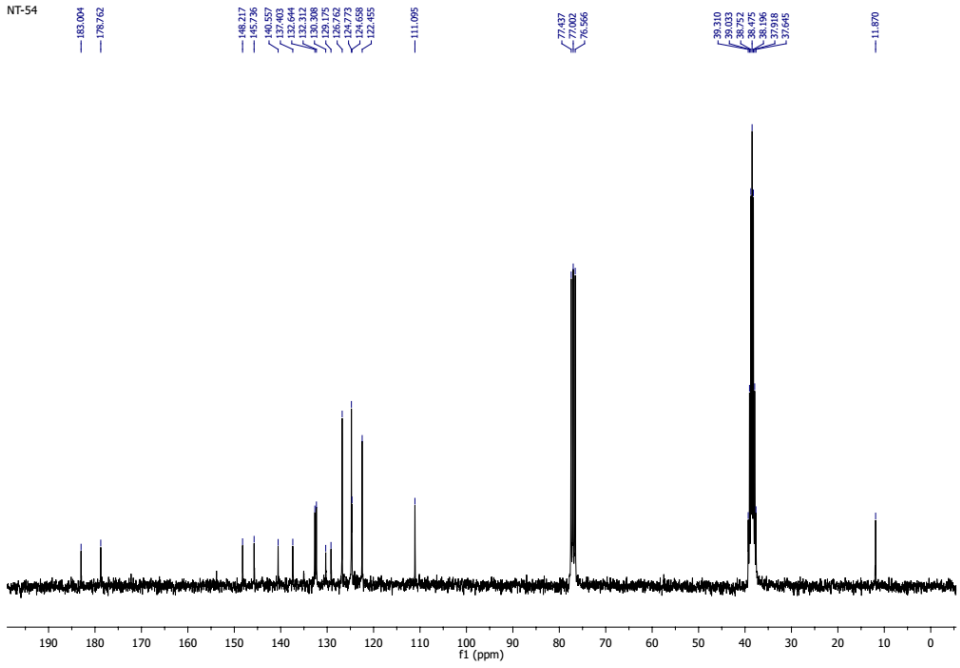


Fig. 38. ^{13}C-NMR spectrum of *N*-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)-4-nitrobenzenesulfonamide (Table 3, **5f**).

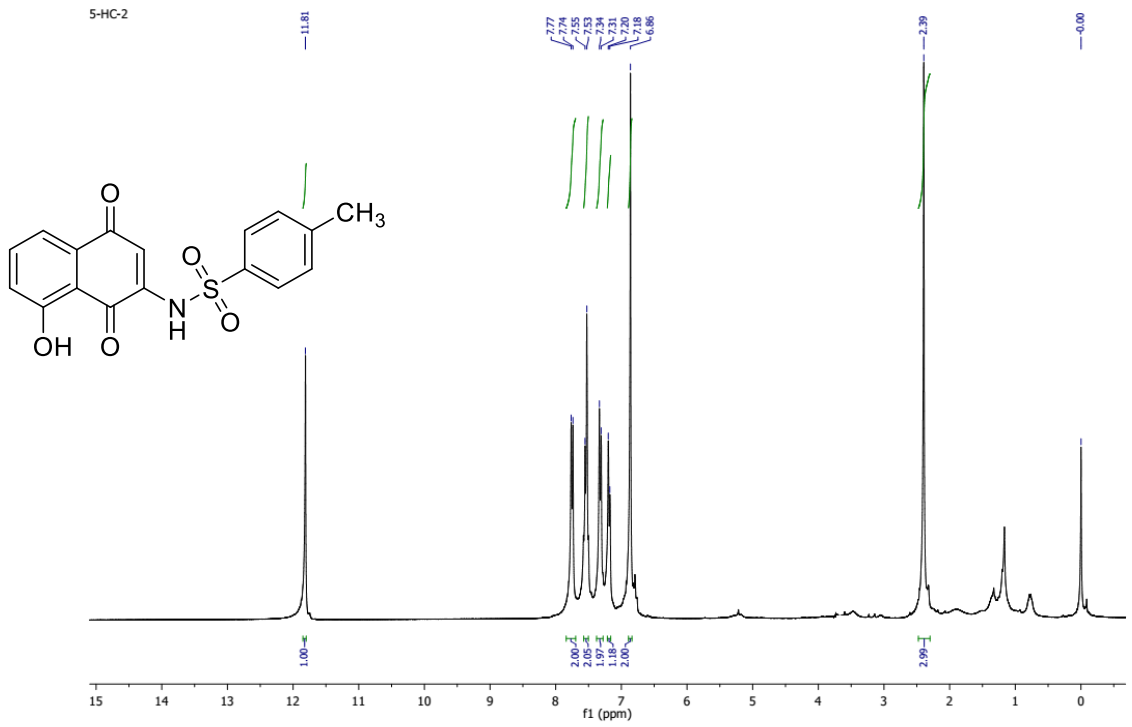


Fig. 39. ^{1}H-NMR spectrum of *N*-(8-hydroxy-1,4-dioxo-1,4-dihydronaphthalen-2-yl)-4-methylbenzenesulfonamide (Table 2, **7**).

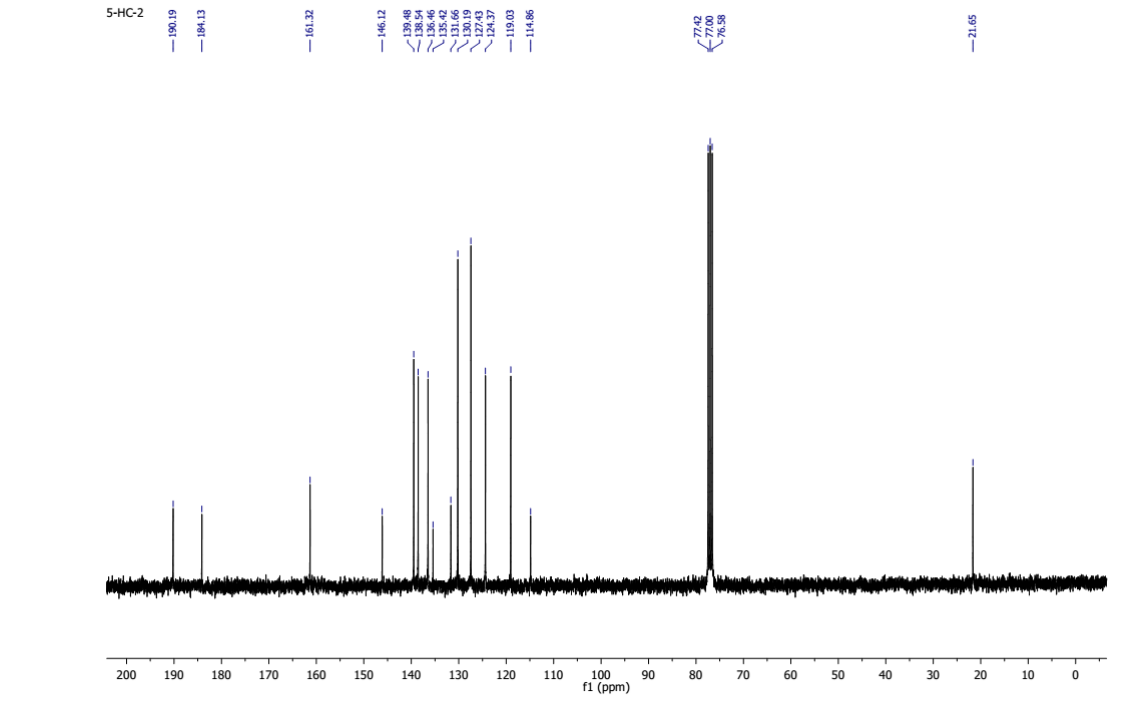


Fig. 40. ^{13}C-NMR spectrum of *N*-(8-Hydroxy-1,4-dioxo-1,4-dihydronaphthalen-2-yl)-4-methylbenzenesulfonamide (Table 2, **7**)

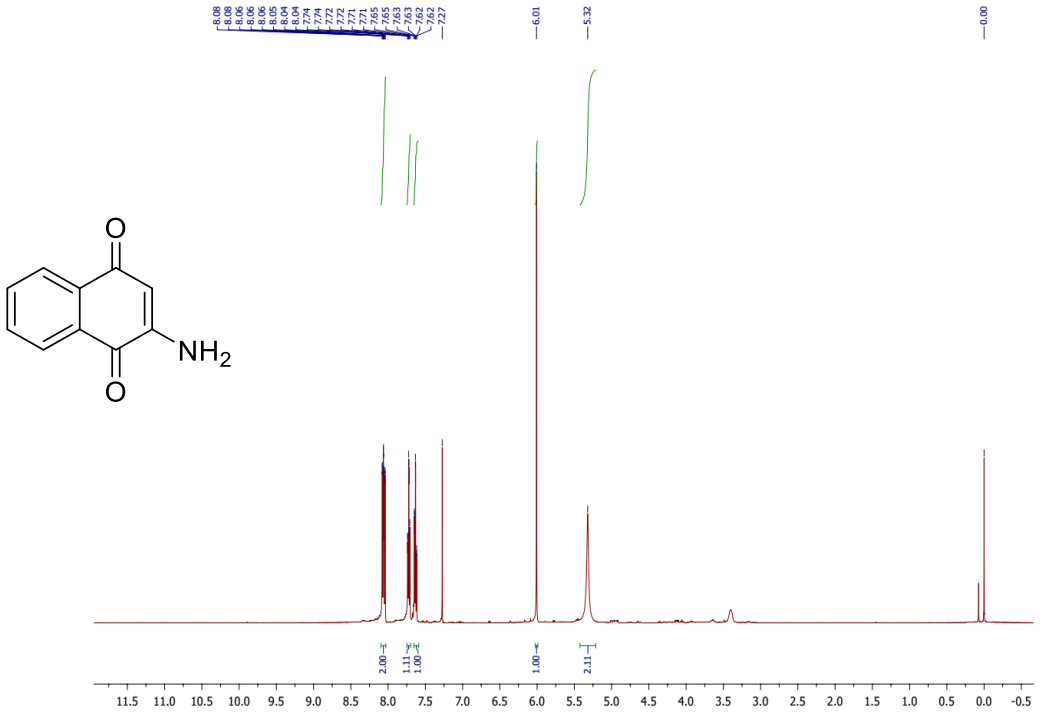


Fig. 41. ^{1}H-NMR spectrum of 2-Aminonaphthalene-1,4-dione (Scheme 1, **8**).

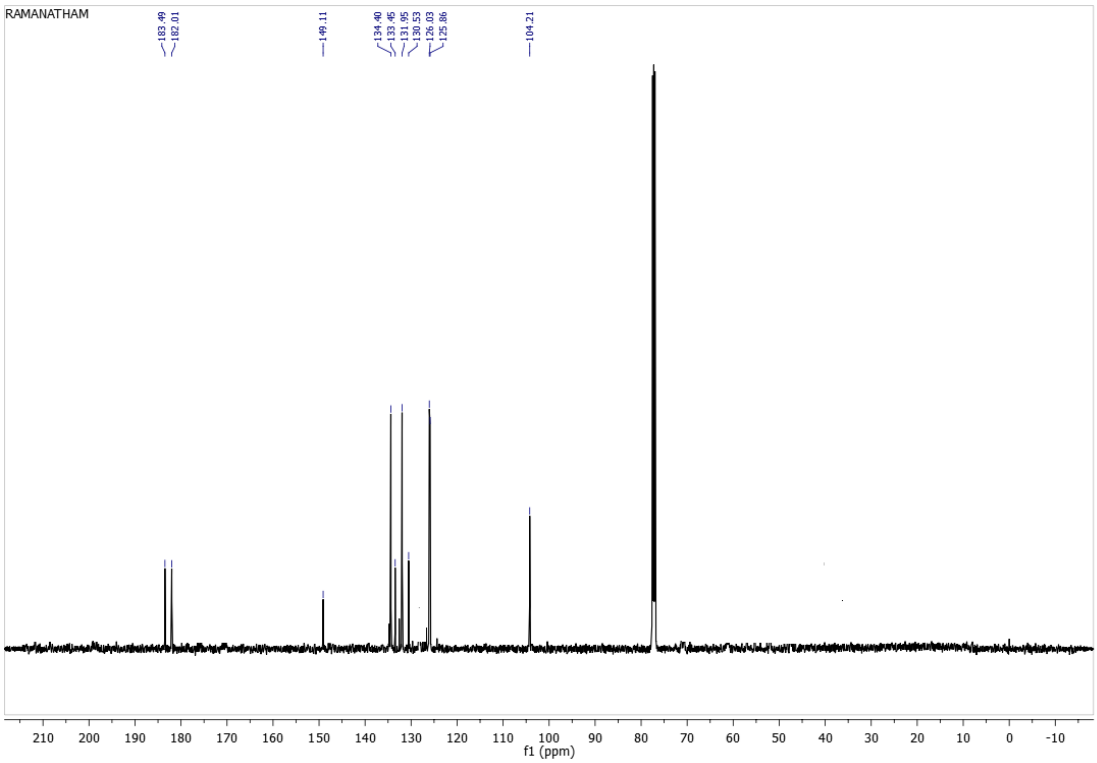


Fig. 42. ^{13}C-NMR spectrum of 2-Aminonaphthalene-1,4-dione (Scheme 1, **8**).

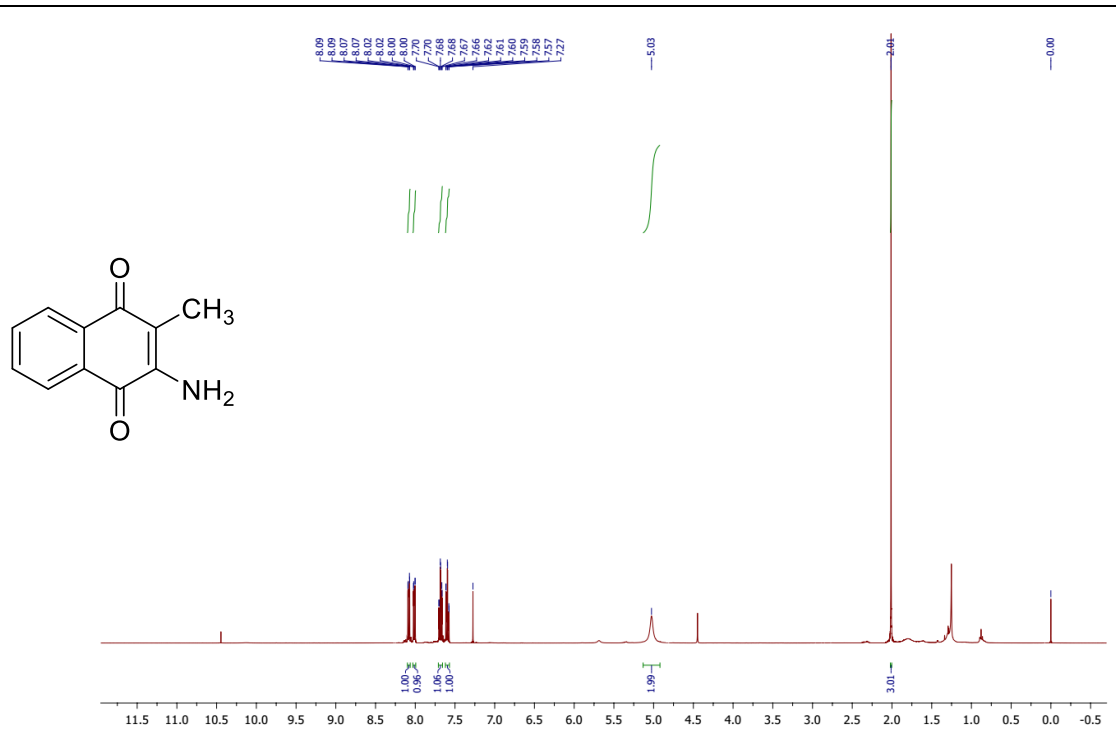


Fig. 43. ^{1}H-NMR spectrum of 2-Amino-3-methylnaphthalene-1,4-dione (Scheme 1, **9**).

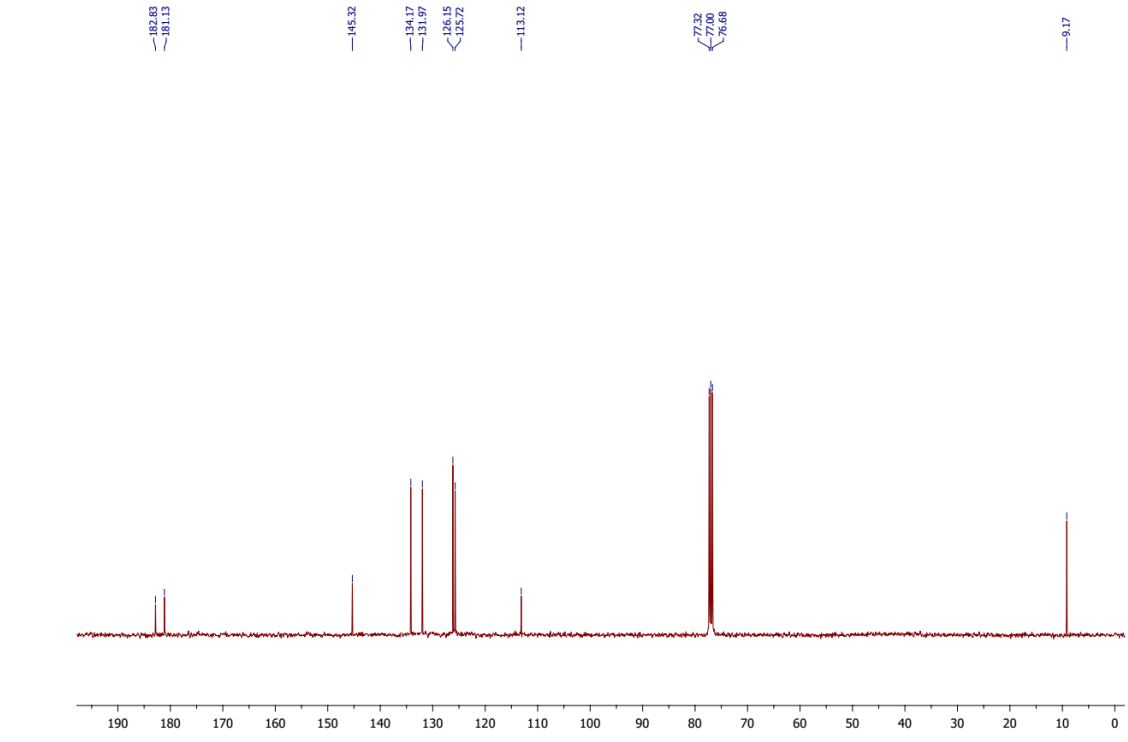


Fig. 44. ^{13}C-NMR spectrum of 2-Amino-3-methylnaphthalene-1,4-dione (Scheme 1, **9**).

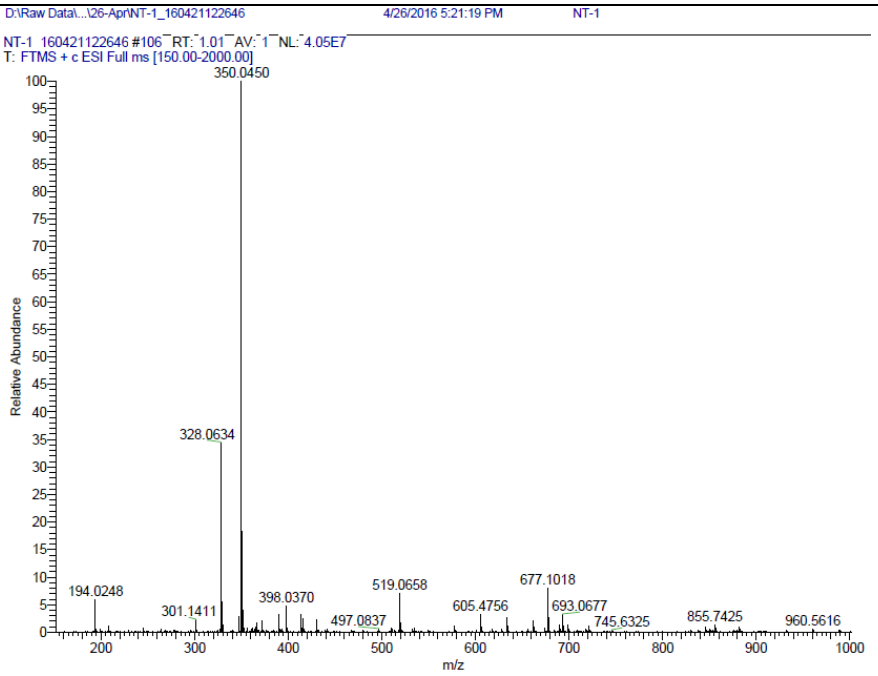


Fig. 45. HRMS (ESI)-spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-4-methylbenzenesulfonamide (Table 2, **3a**).

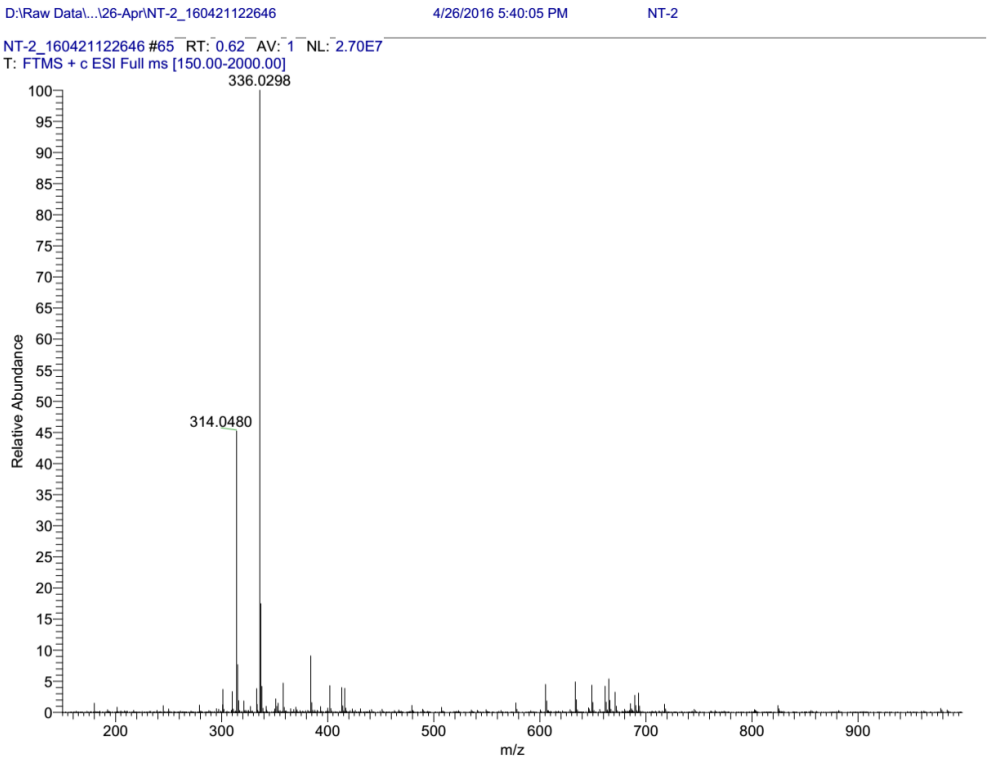


Fig. 46. HRMS (ESI)-spectrum of *N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide (Table 2, **3b**).

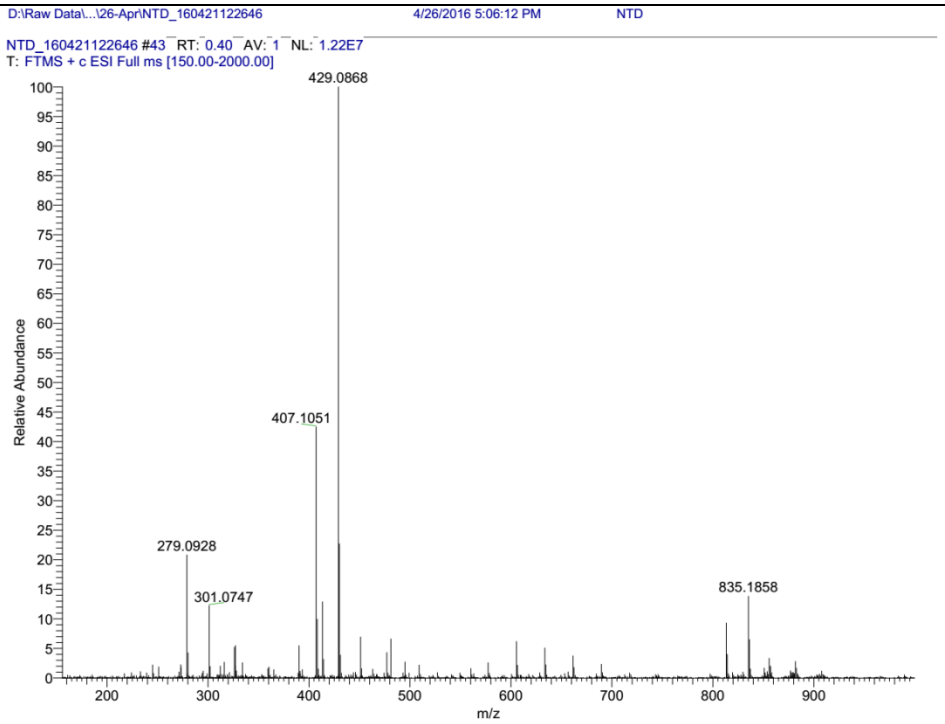


Fig. 47. HRMS (ESI)-spectrum of 5-(Dimethylamino)-*N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)naphthalene-1-sulfonamide (Table 2, **3g**).

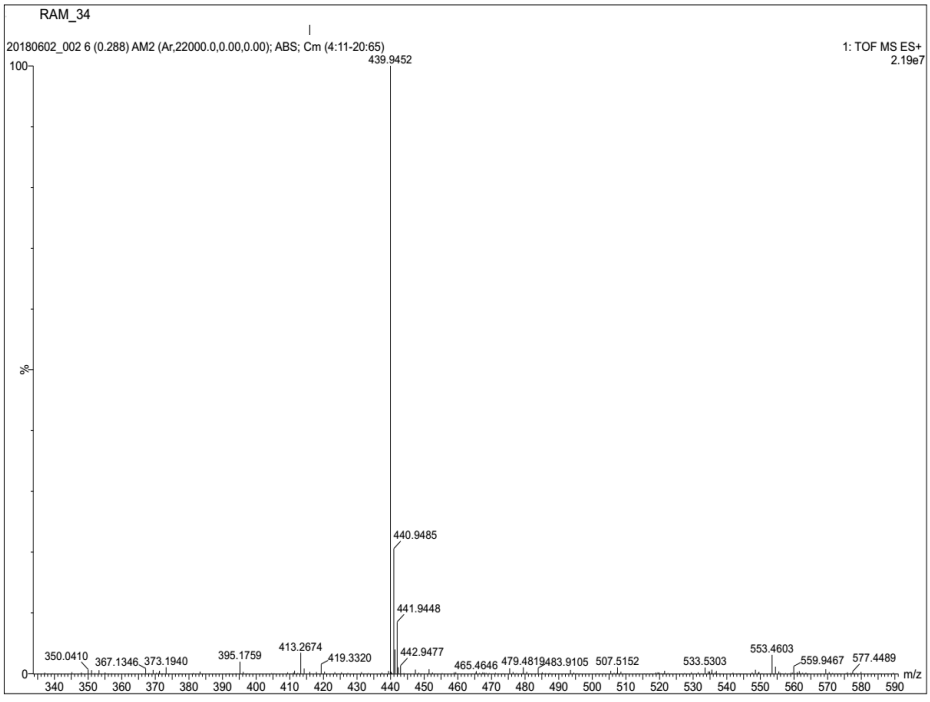


Fig. 48. HRMS (ESI)-spectrum of *N*-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-4-iodobenzenesulfonamide (Table 2, **3i**).

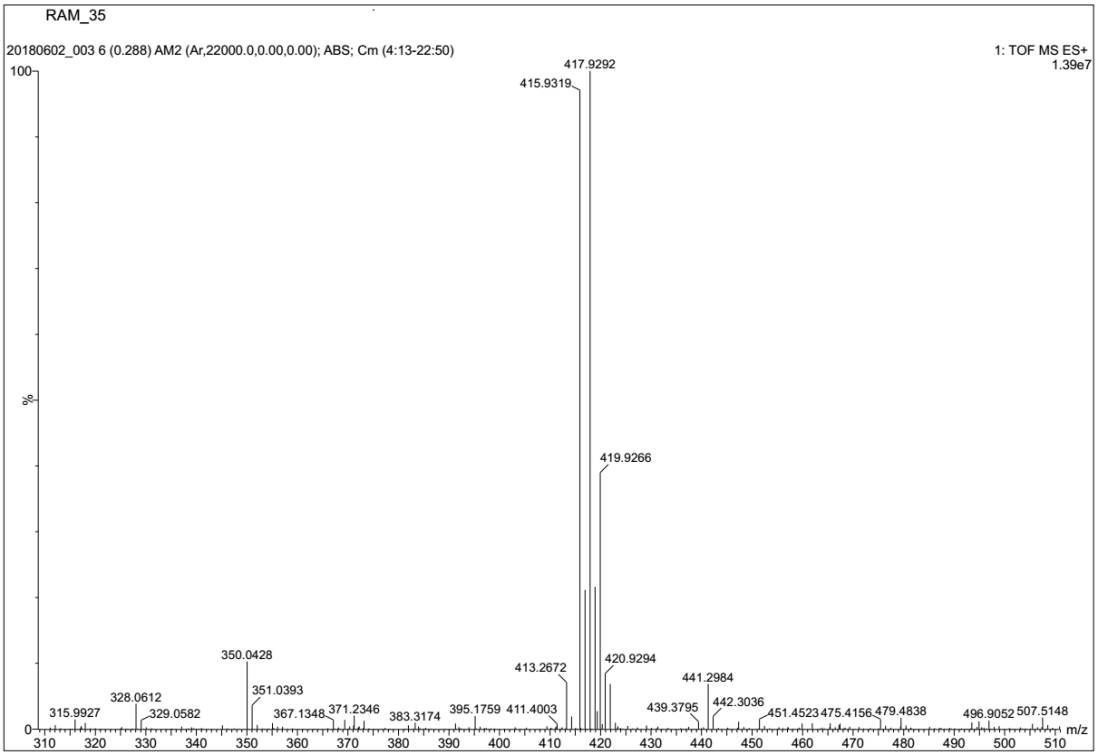


Fig. 49. HRMS (ESI)-spectrum of 2,4,5-Trichloro-*N*-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide (Table 2, **3k**).

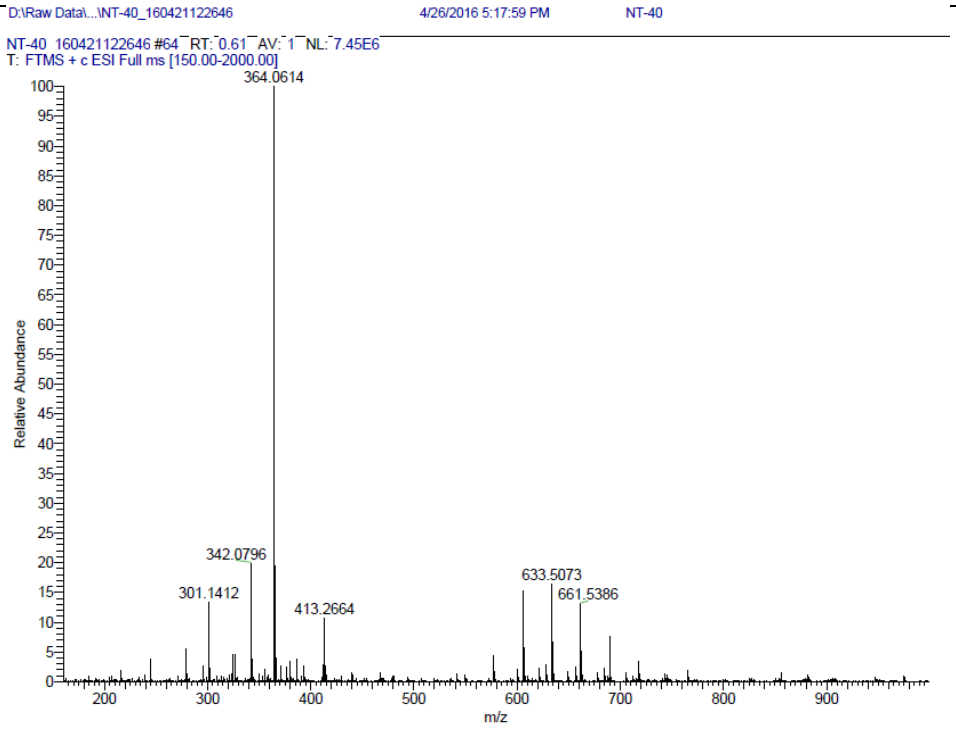


Fig. 50. HRMS (ESI)-spectrum of 4-Methyl-*N*-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide(Table 3, **5a**).

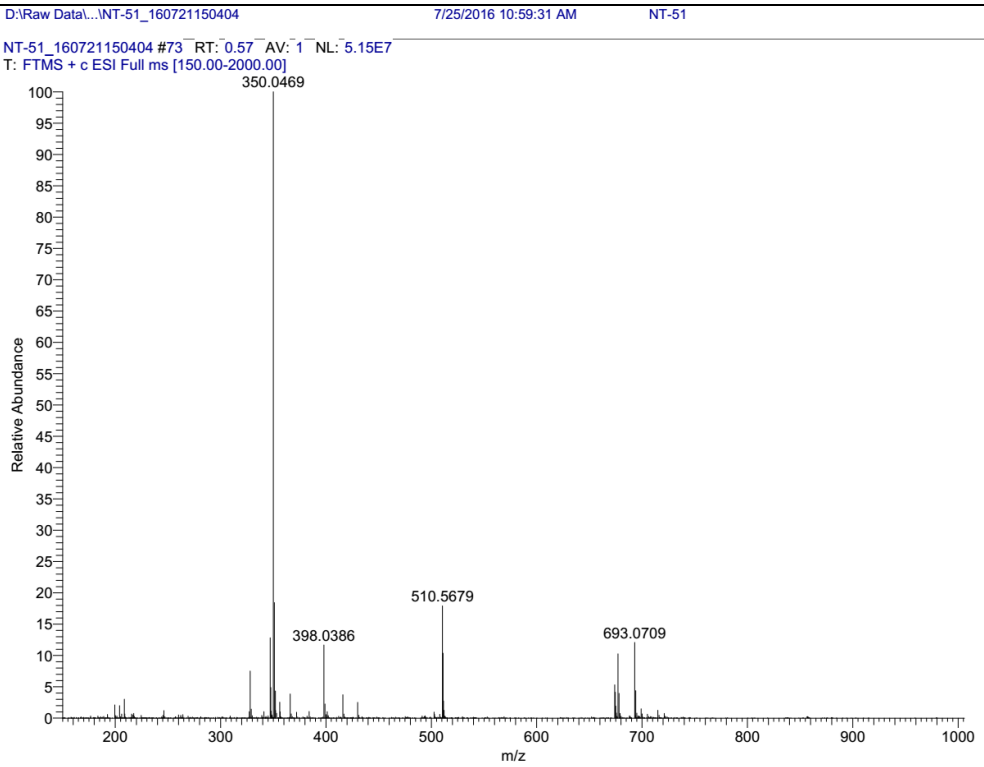


Fig. 51. HRMS (ESI)-spectrum of *N*-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)benzenesulfonamide (Table 3, **5b**).

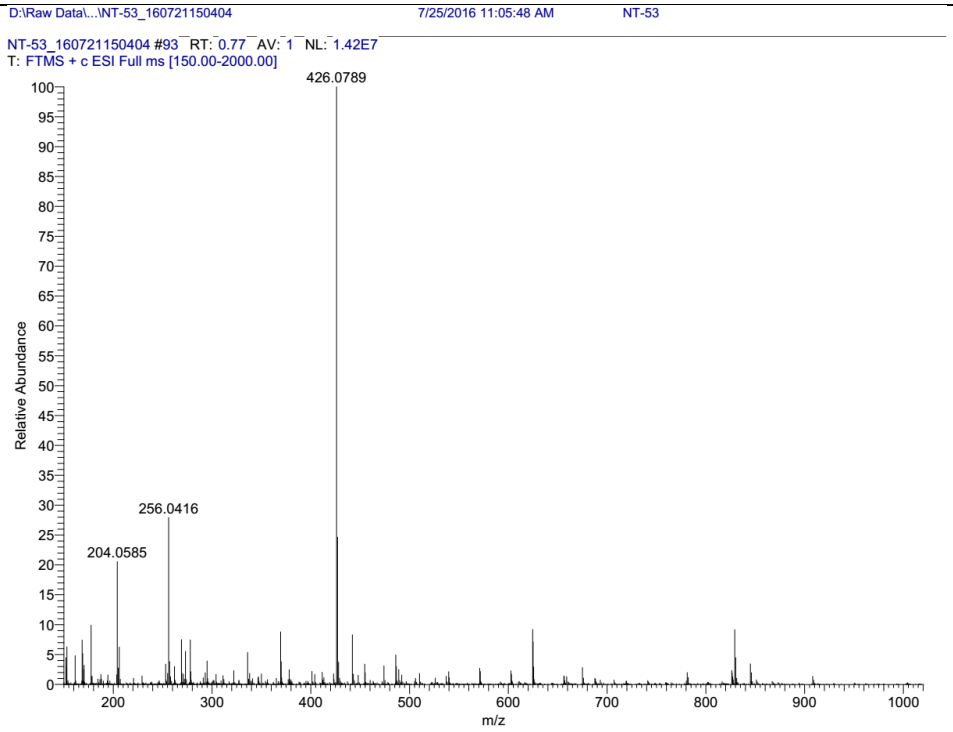


Fig. 52. HRMS (ESI)-spectrum of *N*-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)biphenyl-4-sulfonamide (Table 3, **5c**).

References

1 a) R. A. Abramovitch, T. Chellathurai, D. W. Holcomb, T. I. McMaster and D. P. Vanderpool, *J. Org. Chem*.**1977**, *42*, 2920; b) R. L. Danheiser, R. F. Miller, R. G. Brisbois and S. Z. Park, *J. Org. Chem*.**1990**, *55*, 1959.