Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Visible-light-promoted iron catalyzed C–H functionalization of 1,4-naphthoquinones via oxidative coupling with sulfoximines

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Content

General experimental section:

All reactions were performed in oven-dried glass apparatus. Solvents were distilled in the standard way, and commercial reagents were used without any purification. Analytical TLC was performed on 60 F254 plates, and visualized by exposure to ultraviolet light (UV-254 nm). Column chromatography was carried out with silica (60-120, 100-200 mesh). NMR spectra for characterization of compounds were recorded on Bruker Advance DPX FT-NMR 400 MHz instrument (^{1}H, 2D, ^{1}H-^{1}H-COSY and ^{1}H-^{13}C HMBC, HMQC, and NOESY) at 400 MHz and (^{13}C) at 100 MHz respectively. ^{19}F NMR were recorded at 376 MHz. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (δH = 7.26 and δC = 77.16 ppm) and DMSO-d6 (δH = 2.50 and δC = 39.52 ppm) as internal reference and coupling constants (J) are given in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-Resolution Mass Spectra (HRMS) were recorded using Waters XEVO-G2-XS-Q-TOF mass spectrometer. Analytical and semi-preparative HPLC (Thermofisher) purifications were carried out on reversed-phase columns connected to a binary pump and monitored using a photodiode array detector. The Microwave assisted reactions were performed on CHEM Discover Microwave system. Melting points were recorded on BUCHI melting point M-560.

General Procedure for the synthesis of naphthoquinone-sulfoximine derivatives

To a 10 mL vial equipped with a magnetic stir bar was added 1,4-naphthoquinone (0.32 mmol, 1 equiv), sulfoximine (0.47 mmol, 1.5 equiv), $FeCl_3$ (12 mol %) and 2 mL of EtOH. The reaction mixture was stirred at room temperature under a 60 W blue LED in air for 12 h. After the indicated reaction time, the reaction mixture was extracted with EtOAc twice. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The resulting crude residue was subjected to silica gel column-chromatography by using EtOAc/hexane to afford the desired coloured products.

General Procedure for the synthesis of benzoquinone-sulfoximine derivatives

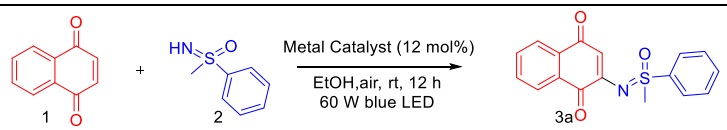
To a solution of substituted benzoquinone (1 mmol, 1 equiv), $FeCl_3$ (0.12 mmol, 0.12 equiv) and sulfoximine (1.5 equiv) in ethanol. The reaction was carried out under microwave irradiation at 100 W at 100 ^oC for 10 min. The reaction mixture was cooled to room temperature and diluted with EtOAc. Then the whole mixture was transferred into separatory funnel and washed with H_2O. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The resulting crude residue was subjected to silica gel column-chromatography by using EtOAc/hexane to afford the desired coloured products.

General Procedure for the synthesis of sulfoximines

The sulfide (1 equiv), phenyliodine(III)diacetate (PIDA) (2.5 equiv) and ammonium carbamate (2.0 equiv) were added to a flask containing a stirrer bar. MeOH was used as solvent and the reaction was stirred at 25 ^oC for 3 h. After the indicated reaction time, solvent was removed under reduced pressure and purified by column chromatography which afforded the sulfoximine product.[1]

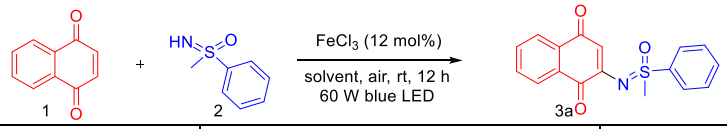
Optimization of the Reaction Conditions

a) Table S1: Examination of Metal Catalysts other than Iron



S No.	Metal Catalyst	Isolated Yield (%) of 3a
1	$Pd(OAc)_2$,	52
2	$Co(OAc)_2$	34
3	$Mn(OAc)_3$	64
4	$Ni(C_5HF_6O_2)_2.xH_2O$	28
5	Cu-Mn spinel	68
6	$Cu(OAc)_2.H_2O$	67

b) Table S2: Examination of Different Solvents



S No.	Metal Catalyst	Solvent	Isolated Yield (%) of 3a
1	$FeCl_3$	THF	trace
2	$FeCl_3$	DMSO	trace
3	$FeCl_3$	DMF	trace
4	$FeCl_3$	MeOH	75
5	$FeCl_3$	EtOH: Water (1:1)	36
6	$FeCl_3$	EtOH	78
7	$FeCl_3$	Water	0
8	$FeCl_3$	Acetone	trace

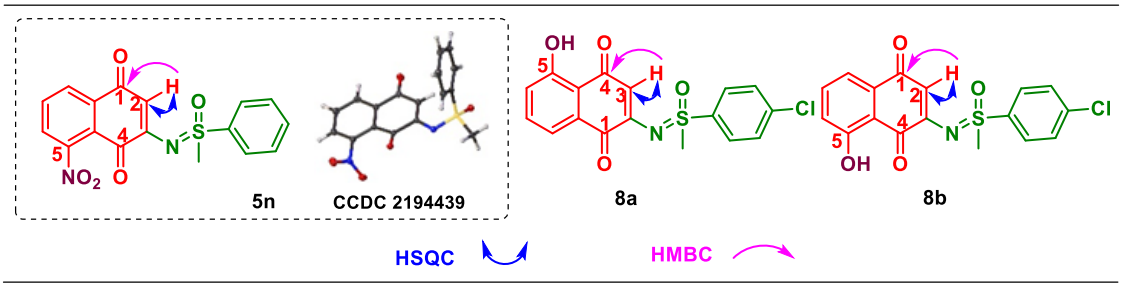
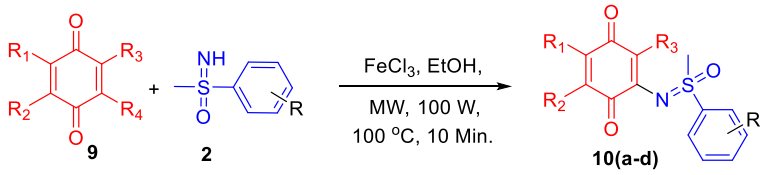


Figure S1: HSQC and HMBC correlation of 5n, 8a and 8b

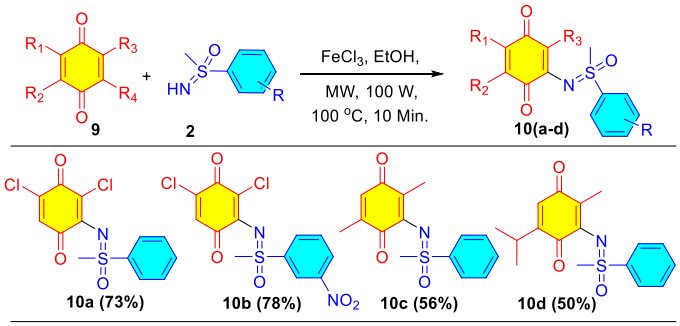
Table S3: Optimization studies for Microwave assisted addition of sulfoximine to benzoquinone



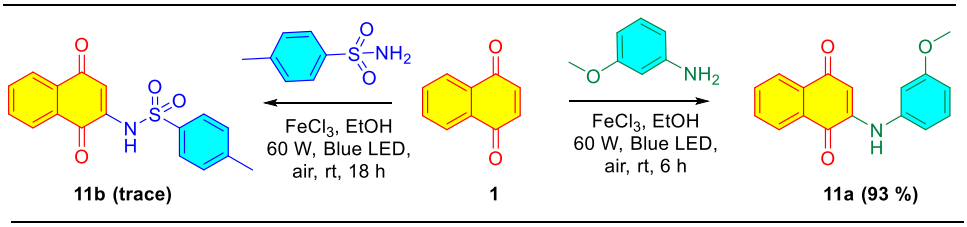
Yields 50 - 78%
10a = 73%; 10b = 78%; 10c = 56%; 10d = 50%

Entry	Power (W)	Temperature (° C)	Time (Min)	Isolated yield of 10b (%)
1	50	100	10	57
2	80	100	10	63
3	100	100	10	78
4	100	100	15	77
5	120	100	10	75

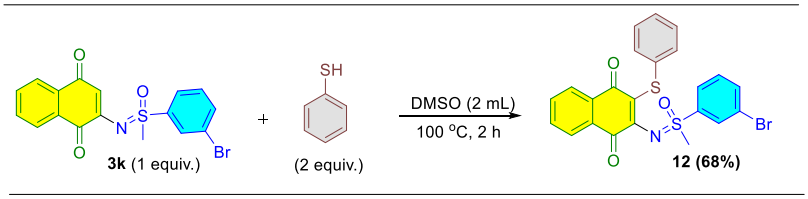
Scheme S1: Sulfoximine addition on benzoquinones



Scheme S2: *m*-Anisidine and *p*-toluenesulfonamide addition on 1,4-naphthoquinones



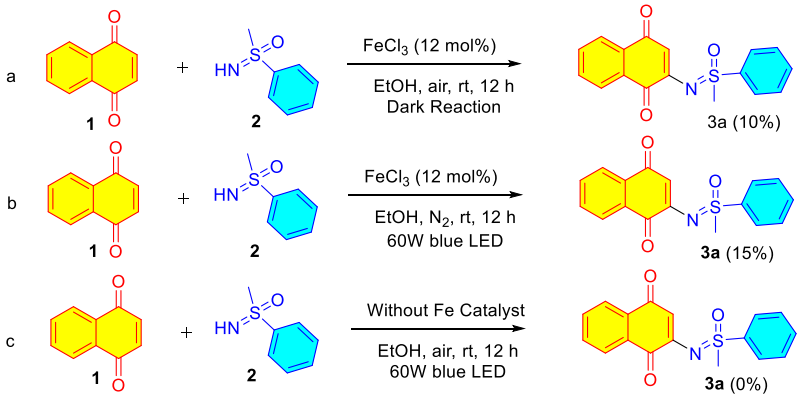
Scheme S3: Late – stage functionalization of the sulfoximinated naphthoquinone product



General Procedure for the synthesis of 12

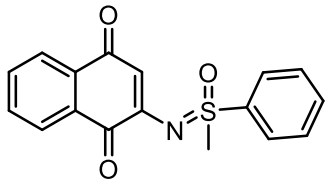
A mixture of **3k** (1 equiv), thiophenol (2 equiv) and DMSO (2 mL) was placed in a reaction vial with a magnetic stirrer bar. The tube was then placed into an oil bath and the reaction was conducted at 100 °C for 2 h. After the reaction was finished the resulting suspension was diluted with water (2.0 mL) and extracted with ethyl acetate (6.5 mL x 3). Then the organic layer was washed with brine and dried over Na_2SO_4 and the solvents were removed under reduced vacuum. The resultant crude residue was purified by column chromatography using EtOAc/hexane to give the desired product **12**.[2]

Scheme S4. Control Experiments



Physical and Spectroscopic Characterization Data of Compounds:

2-((METHYL(OXO)(PHENYL)-Λ^6-SULFANYLIDENE)AMINO)NAPHTHALENE-1,4-DIONE (3a)



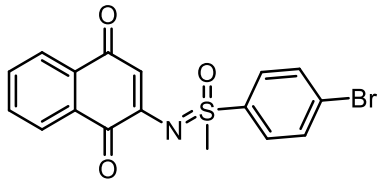
The compound **3a** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 3/7), 76.93 mg, 78% yield; yellow solid; m.p. = 158 - 160 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 5.3, 3.7 Hz, 1H), 7.92 – 7.89 (m, 3H), 7.61 – 7.51 (m, 5H), 6.27 (s, 1H), 3.34 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 183.8, 181.8, 150.0, 136.8, 133.1, 132.8, 131.7, 131.4, 130.5, 129.0, 126.8, 125.7, 124.8, 118.4, 46.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{14}NO_3S$: 312.0694; found: 312.0707.

2-(((4-BROMOPHENYL)(METHYL)(OXO)-Λ^6-SULFANYLIDENE)AMINO) NAPHTHALENE-1,4-DIONE (3b)



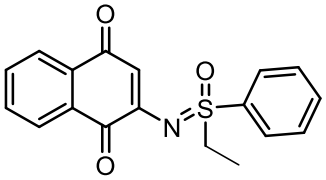
The compound **3b** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 1/3), 98.50 mg, 80% yield; yellow solid; m.p. = 151 - 153 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 7.2 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.66 (dd, *J* = 9.2, 7.5 Hz, 2H), 6.37 (s, 1H), 3.40 (s, 3H)

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 185.0, 182.9, 150.8, 137.5, 134.1, 133.4, 133.0, 132.5, 131.5, 129.6, 129.4, 126.9, 126.0, 120.2, 47.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{13}NO_3SBr$: 389.9800; found: 389.9805

2-((ETHYL(OXO)(PHENYL)-Λ^6-SULFANYLIDENE)AMINO)NAPHTHALENE-1,4-DIONE (3c)



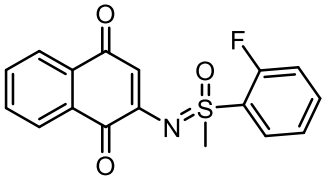
The compound **3c** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 3/7), 85.59 mg, 83% yield; yellow solid; m.p. = 124 - 126 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.01 – 7.97 (m, 1H), 7.91 – 7.86 (m, 3H), 7.62 – 7.52 (m, 5H), 6.31 (s, 1H), 3.55 – 3.38 (m, 2H), 1.31 (t, *J* = 7.4 Hz, 3H).

^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ 184.7, 182.9, 151.5, 135.6, 134.1, 133.7, 132.7, 132.4, 131.6, 129.9, 128.6, 126.6, 125.7, 119.2, 53.0, 7.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{18}H_{16}NO_3S$: 326.0851; found: 326.0852.

2-(((2-FLUOROPHENYL)(METHYL)(OXO)-Λ^6-SULFANYLIDENE)AMINO) NAPHTHALENE-1,4-DIONE (3d)



The compound **3d** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 3/7), 88.81 mg, 85% yield; yellow solid; m.p. = 133-135 ^{o}C.

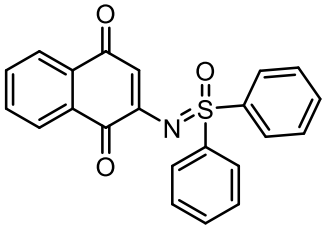
^{1}H NMR (400 MHz, CDCl$_3$): δ 8.06 – 8.01 (m, 1H), 7.98 – 7.95 (m, 1H), 7.92 – 7.88 (m, 1H), 7.62 – 7.57 (m, 3H), 7.37-7.32 (m, 1H), 7.19 – 7.13 (m, 1H), 6.31 – 6.30 (m, 1H), 3.48 (d, *J* = 2.8 Hz, 3H).

^{19}F NMR (377 MHz, CDCl$_3$): δ -108.14 – -108.27 (m).

^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ 185.1, 182.6, 160.1, 157.6, 150.8, 136.6 (d, *J* = 8.4 Hz), 134.0, 132.9, 132.5, 131.6 (d, *J* = 4.3 Hz), 127.0, 125.9 (d, *J* = 5.0 Hz) 125.3 (d, *J* = 3.7 Hz), 119.6, 117.8 (d, *J* = 23.2 Hz), 46.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{13}NO_3FS$: 330.0600; found: 330.0598.

2-((OXODIPHENYL-Λ^6-SULFANYLIDENE)AMINO)NAPHTHALENE-1,4-DIONE (3E)



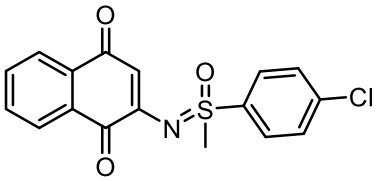
The compound **3e** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 3/7), 95.75 mg, 81% yield; yellow solid; m.p. = 172 - 174 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.04 – 8.01 (m, 5H), 7.94 – 7.91 (m, 1H), 7.62 – 7.58 (m, 2H), 7.51 – 7.44 (m, 6H), 6.45 (s, 1H).

^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ 185.0, 183.0, 151.0, 139.9, 133.9, 133.7, 132.9, 132.7, 131.9, 129.9, 129.7, 128.3, 127.7, 126.8, 126.0, 120.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{22}H_{16}NO_3S$: 374.0851; found: 374.0859.

2-(((4-CHLOROPHENYL)(METHYL)(OXO)-Λ^{6}-SULFANYLIDENE)AMINO) NAPHTHALENE-1,4-DIONE (3f)



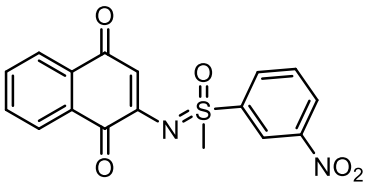
The compound **3f** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 3/7), 84.33 mg, 77% yield; yellow solid; m.p. = 158 - 160 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.99 – 7.96 (m, 1H), 7.93 – 7.90 (m, 1H), 7.87 – 7.84 (m, 2H), 7.62 – 7.55 (m, 2H), 7.51 – 7.48 (m, 2H), 6.30 (s, 1H), 3.33 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ 184.9, 182.9, 150.8, 141.0, 136.8, 134.1, 132.9, 132.5, 131.5, 130.4, 129.3, 126.9, 125.9, 120.1, 47.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{14}NO_3SCl$: 346.0305; found: 346.0292.

2-((METHYL(3-NITROPHENYL)(OXO)-Λ^{6}-SULFANYLIDENE)AMINO) NAPHTHALENE-1,4-DIONE (3g)



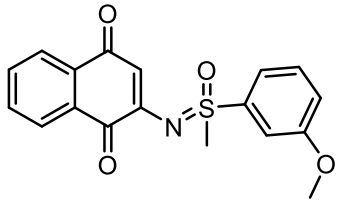
The compound **3g** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 3/7), 84.73 mg, 75% yield; Yellow solid; m.p. = 230 - 232 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (t, *J* = 1.9 Hz, 1H), 8.46 – 8.43 (m, 1H), 8.28 – 8.25 (m, 1H), 7.94 – 7.90 (m, 2H), 7.77 (t, *J* = 8.0 Hz, 1H), 7.64 – 7.55 (m, 2H), 6.40 (s, 1H), 3.37 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 185.0, 182.4, 150.0, 148.8, 142.4, 134.2, 132.9, 132.8, 132.3, 131.2, 131.1, 128.1, 126.9, 125.9, 122.7, 121.2, 47.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{13}N_2O_5S$: 357.0545; found: 357.0551.

2-(((3-METHOXYPHENYL)(METHYL)(OXO)-Λ^{6}-SULFANYLIDENE)AMINO) NAPHTHALENE-1,4-DIONE (3h)



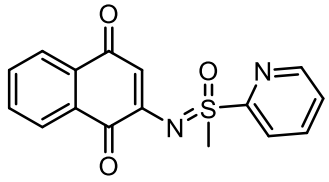
The compound **3h** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 3/7), 79.04 mg, 73% yield; yellow solid; m.p. = 130 - 132 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.98 (m, 1H), 7.91 – 7.89 (m, 1H), 7.60 – 7.56 (m, 2H), 7.47 – 7.39 (m, 3H), 7.10 (d, *J* = 7.9 Hz, 1H), 6.27 (s, 1H), 3.79 (s, 3H), 3.34 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 184.9, 183.0, 160.7, 151.2, 139.1, 133.9, 132.9, 132.5, 131.6, 131.2, 126.9, 125.9, 120.5, 119.8, 119.6, 112.6, 55.9, 47.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{18}H_{16}NO_4S$:342.0800; found: 342.0803.

2-((METHYL(OXO)(PYRIDIN-2-YL)-Λ^{6}-SULFANYLIDENE)AMINO) NAPHTHALENE-1,4-DIONE (3i)



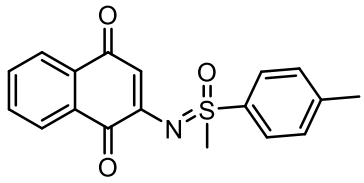
The compound **3i** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 3/7), 69.28 mg, 70% yield; orange coloured solid; m.p. = 133 - 134 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.7 Hz, 1H), 8.27 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.99 – 7.90 (m, 3H), 7.61 – 7.47 (m, 3H), 6.45 (s, 1H), 3.42 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 185.3, 182.5, 157.6, 150.8, 150.4, 138.6, 134.1, 132.8, 132.6, 11.3, 127.4, 126.9, 125.9, 123.1, 120.4, 44.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{16}H_{13}N_2O_3S$: 313.0647; found: 313.0644.

2-((METHYL(OXO)(P-TOLYL)-Λ^6-SULFANYLIDENE)AMINO)NAPHTHALENE-1,4-DIONE (3j)



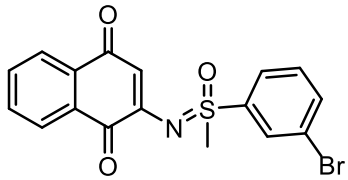
The compound **3j** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 3/7), 79.43 mg, 77% yield; yellow solid; m.p. = 128 - 130 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.05 (m, 1H), 7.96 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.86 – 7.83 (m, 2H), 7.66 – 7.62 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.32 (s, 1H), 3.40 (s, 3H), 2.44 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 184.8, 183.1, 151.3, 145.5, 134.5, 133.8, 132.8, 132.5, 131.7, 130.8, 128.0, 126.8, 125.8, 119.3, 47.3, 21.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{18}H_{16}NO_3S$: 326.0851; found: 326.0864.

2-(((3-BROMOPHENYL)(METHYL)(OXO)-Λ^6-SULFANEYLIDENE)AMINO) NAPHTHALENE-1,4-DIONE (3k)



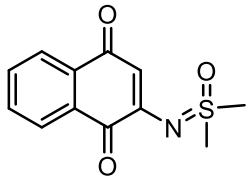
The compound **3k** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 3/7), 98.90 mg, 81% yield; yellow solid; m.p. = 175 - 177 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 8.05 – 8.01 (m, 1H), 7.99 – 7.95 (m, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.69 – 7.61 (m, 2H), 7.46 (t, J = 8.0 Hz, 1H), 6.37 (s, 1H), 3.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 185.0, 182.7, 150.6, 140.6, 137.2, 134.1, 133.0, 132.4, 131.5, 131.4, 130.6, 126.9, 126.2, 125.9, 124.1, 120.2, 47.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{13}NO_3SBr$: 389.9800; found: 389.9798.

2-((DIMETHYL(OXO)-Λ^6-SULFANEYLIDENE)AMINO)NAPHTHALENE-1,4-DIONE (3l)



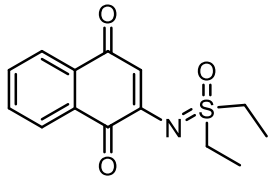
The compound **3l** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 1/1), 56.96 mg, 72 % yield; yellow solid; m.p. = 169 - 171 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.07 (m, 2H), 7.74 – 7.65 (m, 2H), 6.53 (s, 1H), 3.40 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 185.2, 183.3, 151.5, 134.2, 132.9, 132.6, 131.6, 126.9, 126.0, 118.8, 44.1 (2C).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{12}H_{12}NO_3S$: 250.0538; found: 250.0546.

2-((DIETHYL(OXO)-Λ^6-SULFANEYLIDENE)AMINO)NAPHTHALENE-1,4-DIONE (3m)



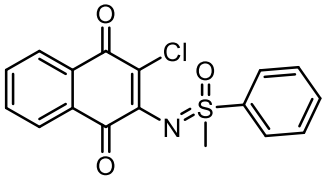
The compound **3m** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 2/3), 58.96 mg, 67% yield; yellow solid; m.p. = 155 - 157 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.00 – 7.94 (m, 2H), 7.64 – 7.55 (m, 2H), 6.51 (s, 1H), 3.39 – 3.32 (m, 4H), 1.40 (t, J = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 185.0, 183.2, 152.3, 133.9, 132.7, 132.6 131.6, 126.7, 125.8, 118.0, 47.4 (2C), 7.4 (2C).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{14}H_{16}NO_3S$: 278.0851; found: 278.0833.

2-CHLORO-3-((METHYL(OXO)(PHENYL)- Λ^6-SULFANYLIDENE)AMINO) NAPHTHALENE-1,4-DIONE (5a)



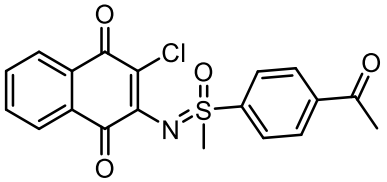
The compound **5a** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 2/8), 72.08 mg, 80% yield; Orange Coloured solid; m.p. = 209 - 211 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.11 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.06 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.94 (d, *J* = 1.3 Hz, 1H), 7.71 – 7.59 (m, 5H), 3.44 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ 179.6, 178.4, 147.6, 141.7, 134.3, 133.2, 133.1, 132.0, 130.2, 129.7, 127.8, 127.2, 126.7, 126.7, 49.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{13}NO_3SCl$: 346.0305; found: 346.0313.

2-(((4-ACETYLPHENYL)(METHYL)(OXO)-Λ^6-SULFANYLIDENE)AMINO)-3-CHLORONAPHTHALENE-1,4-DIONE (5b)



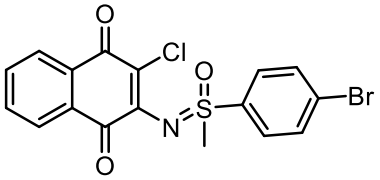
The compound **5b** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 2/8), 74.77 mg, 74% yield; Yellow solid; m.p. = 225 - 227 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.09 (s, 3H), 8.05 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.86 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.63 (td, *J* = 7.6, 1.4 Hz, 1H), 7.54 (td, *J* = 7.6, 1.3 Hz, 1H), 3.38 (s, 3H), 2.60 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ 196.6, 178.6, 177.3, 146.0, 144.6, 139.4, 133.4, 132.2, 130.9, 129.0, 128.4, 127.2, 126.2, 126.0, 125.8, 47.8, 26.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{19}H_{15}NO_4SCl$: 388.0410; found: 388.0417.

2-(((4-BROMOPHENYL)(METHYL)(OXO)-Λ^6-SULFANYLIDENE)AMINO)-3-CHLORONAPHTHALENE-1,4-DIONE (5c)



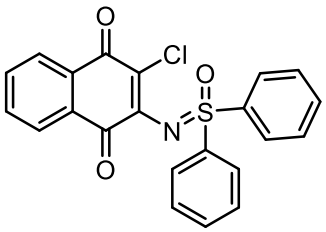
The compound **5c** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 2/8), 95.52 mg, 87% yield; Orange solid; m.p. = 236 - 238 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.12 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.97 – 7.91 (m, 3H), 7.76 – 7.73 (m, 2H), 7.69(dd, *J* = 7.6, 1.4 Hz, 1H), 7.65 – 7.61 (m, 1H), 3.43 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ 179.6, 178.4, 147.2, 140.8, 134.4, 133.2, 132.9, 131.9, 130.1, 128.4, 128.3, 128.1, 127.3, 126.8, 48.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{12}NO_3SClBr$: 423.9410; found: 423.9423.

2-CHLORO-3-((OXODIPHENYL-Λ^6-SULFANYLIDENE)AMINO)NAPHTHALENE-1,4-DIONE (5d)



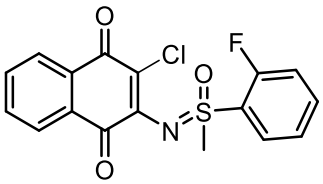
The compound **5d** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 2/8), 88.95 mg, 84% yield; Orange solid; m.p. = 202 - 204 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.15 – 8.09 (m, 5H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.62 – 7.57 (m, 1H), 7.55 – 7.49 (m, 6H).

^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$) δ 178.9, 178.5, 147.5, 142.6, 134.2, 133.1, 132.8, 132.0, 130.2, 129.5, 128.7, 127.5, 127.3, 126.7, 124.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{22}H_{15}NO_3SCl$: 408.0461; found: 408.0449.

2-CHLORO-3-(((2-FLUOROPHENYL)(METHYL)(OXO)-Λ^6-SULFANYLIDENE) AMINO)NAPHTHALENE-1,4-DIONE (5e)



The compound **5e** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 2/8), 77.48 mg, 82% yield; Orange solid; m.p. = 221 - 222 ^{o}C.

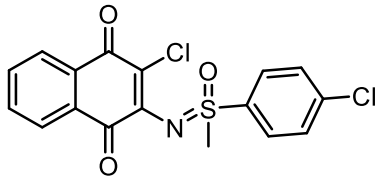
^{1}H NMR (400 MHz, CDCl$_3$): δ 8.21 – 8.20 (m, 1H), 8.06 – 8.03 (m, 1H), 7.89 – 7.87 (m, 1H), 7.62 – 7.54 (m, 3H), 7.37 – 7.33 (m, 1H), 7.19 – 7.14 (m, 1H), 3.53 (s, 3H).

^{19}F NMR (377 MHz, CDCl$_3$): δ -108.20 – -108.24 (m).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 178.5, 177.5, 158.8, 156.3, 146.0, 134.5 (d, *J* = 8.3 Hz), 133.3, 132.1, 130.9, 129.6, 129.4 (d, *J* = 48.4 Hz) 128.2 (d, *J* = 14.1 Hz), 126.2, 125.7, 123.9 (d, *J* = 3.8 Hz), 116.4, (d, *J* = 22.2 Hz), 47.0 (d, *J* = 2.4 Hz).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{12}NO_3SClF$: 364.0210; found: 364.0217.

2-CHLORO-3-(((4-CHLOROPHENYL)(METHYL)(OXO)-Λ^6-SULFANYLIDENE) AMINO)NAPHTHALENE-1,4-DIONE (5f)



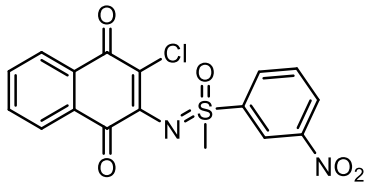
The compound **5f** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 2/8), 87.56 mg, 89% yield; Orange solid; m.p. = 240 - 242 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (dd, *J* = 7.6, 1.0 Hz, 1H), 8.03 – 7.98 (m, 2H), 7.96 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.70 (td, *J* = 7.5, 1.4 Hz, 1H), 7.63 (td, *J* = 7.5, 1.3 Hz, 1H), 7.59 – 7.56 (m, 2H), 3.44 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 179.6, 178.4, 147.2, 140.2, 139.9, 134.4, 133.2, 131.9, 130.1, 130.0, 128.2, 128.1, 127.3, 126.8, 49.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{12}NO_3SCl_2$: 379.9915; found: 379.9920.

2-CHLORO-3-((METHYL(3-NITROPHENYL)(OXO)-Λ^6-SULFANYLIDENE) AMINO)NAPHTHALENE-1,4-DIONE (5g)



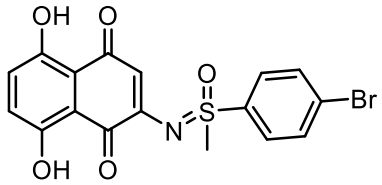
The compound **5g** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 3/7), 86.28 mg, 85% yield; Orange solid; m.p. = 211 - 212 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.94 (t, *J* = 1.9 Hz, 1H), 8.52 – 8.50 (m, 1H), 8.43 – 8.40 (m, 1H), 8.13 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.94 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.85 (t, *J* = 8.0 Hz, 1H), 7.72 (td, *J* = 7.6, 1.4 Hz, 1H), 7.64 (td, *J* = 7.5, 1.3 Hz, 1H), 3.50(s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 179.7, 178.3, 148.7, 146.6, 144.5, 134.6, 133.4, 132.2, 131.8, 131.0, 130.0, 128.9, 127.6, 127.3, 126.9, 122.2, 48.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{12}N_2O_5SCl$: 391.0155; found: 391.0143.

2-(((4-BROMOPHENYL)(METHYL)(OXO)-Λ^6-SULFANYLIDENE)AMINO)-5,8-DIHYDROXYNAPHTHALENE-1,4-DIONE (5h)



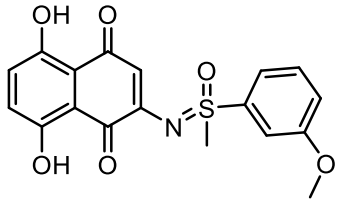
The compound **5h** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 4/6), 60.93 mg, 55% yield; crimson red solid; m.p. = 197 - 199 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$): δ 12.76 (s, 1H), 12.30 (s, 1H), 7.85 – 7.83 (m, 2H), 7.77 – 7.75 (m, 2H), 7.19 (dd, *J* = 26.8, 9.4 Hz, 2H), 6.32 (s, 1H), 3.42 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ 187.9, 185.4, 158.4, 156.8, 151.7, 136.6, 133.6, 130.5, 130.1, 129.5, 127.9, 119.9, 111.9, 111.4, 47.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{13}NO_5SBr$: 421.9698; found: 421.9694.

5,8-DIHYDROXY-2-(((3-METHOXYPHENYL)(METHYL)(OXO)-Λ^6-SULFANYLIDENE)AMINO)NAPHTHALENE-1,4-DIONE (5i)



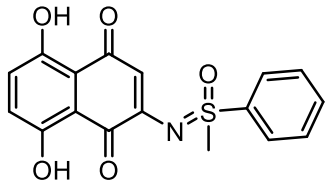
The compound **5i** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 4/6), 57.07 mg, 58% yield; Dark red solid; m.p. = 169 - 171 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$): δ 12.77 (s, 1H), 12.36 (s, 1H), 7.52 – 7.47 (m, 3H), 7.22 – 7.14 (m, 3H), 6.30 (s, 1H), 3.88 (s, 3H), 3.43 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ 187.9, 185.7, 160.7, 158.1, 156.5, 151.9, 138.2, 131.2, 130.2, 127.6, 120.6, 119.8, 119.3, 112.7, 112.0, 111.3, 55.9, 47.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{18}H_{16}NO_6S$: 374.0698; found: 374.0708.

5,8-DIHYDROXY-2-((METHYL(OXO)(PHENYL)-Λ^6-SULFANYLIDENE) AMINO)NAPHTHALENE-1,4-DIONE (5j)



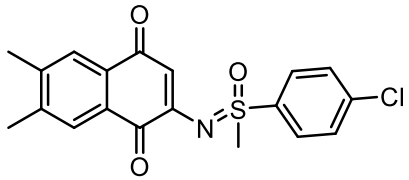
The compound **5j** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 4/6), 46.19 mg, 51% yield; Dark red solid; m.p. = 160 - 162 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$): δ 12.70 (s, 1H), 12.29 (s, 1H), 7.92 – 7.90 (m, 2H), 7.63 (d, *J* = 7.4 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.15 - 7.07 (m, 2H), 6.22 (s, 1H), 3.36 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ 188.0, 185.8, 158.2, 156.6, 152.1, 149.2, 137.2, 134.6, 130.4, 130.3, 128.0, 127.8, 119.4, 112.1, 47.2.

HRMS (ESI) m/z: [M+H] $^{+}$ Calcd. For $C_{17}H_{14}NO_5S$: 344.0593; found: 344.0580.

2-(((4-CHLOROPHENYL)(METHYL)(OXO)-Λ^{6}-SULFANYLIDENE)AMINO)-6,7-DIMETHYLNAPHTHALENE-1,4-DIONE (5k)



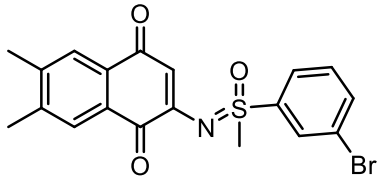
The compound **5k** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 2/8), 53.27 mg, 53% yield; yellow solid; m.p. = 212 - 214 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.78 (s, 1H), 7.72(s, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 6.30 (s, 1H), 3.39 (s, 3H), 2.35 (s, 6H).

^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ 185.4, 183.0, 150.7, 143.9, 142.5, 140.9, 137.1, 130.5, 130.4, 129.3, 129.1, 128.0, 127.0, 120.0, 47.5, 20.3, 20.1.

HRMS (ESI) m/z: [M+H]$^{+}$ Calcd. For $C_{19}H_{17}NO_3SCl$: 374.0618; found: 374.0625.

2-(((3-BROMOPHENYL)(METHYL)(OXO)-Λ^{6}-SULFANYLIDENE)METHYL)-6,7-DIMETHYLNAPHTHALENE-1,4-DIONE (5l)



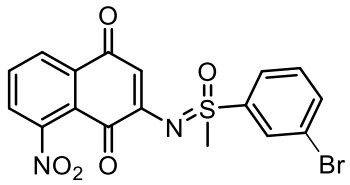
The compound **5l** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 2/8), 57.30 mg, 51% yield; yellow solid; m.p. = 169 - 171 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.11 (t, *J* = 1.8 Hz, 1H), 7.90 – 7.88 (m, 1H), 7.77 – 7.76 (m, 2H), 7.72 (s, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 6.31 (s, 1H), 3.37 (s, 3H), 2.34 (s, 6H).

^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ 185.5, 182.8, 150.5, 144.0, 142.5, 140.9, 137.1, 131.5, 130.6, 130.5, 129.4, 128.0, 127.0, 126.2, 124.1, 120.2, 47.6, 20.3, 20.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{19}H_{17}NO_3SBr$: 418.0113; found: 418.0122.

2-(((3-BROMOPHENYL)(METHYL)(OXO)-Λ^6-SULFANYLIDENE)AMINO)-8-NITRONAPHTHALENE-1,4-DIONE (5m)



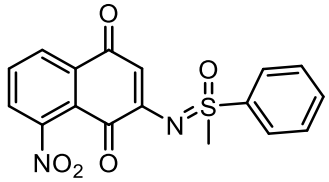
The compound **5m** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 4/6), 91.93 mg, 86% yield; Orange solid; m.p. = 142 - 145 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.19 – 8.16 (m, 1H), 8.11 (t, *J* = 1.9 Hz, 1H), 7.90 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.82 – 7.77 (m, 2H), 7.63 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.51 – 7.46 (m, 1H), 6.36 (s, 1H), 3.42 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ 182.2, 179.5, 151.2, 148.7, 139.3, 137.7, 134.7, 133.5, 131.7, 130.8, 128.5, 126.7, 126.5, 124.3, 122.9, 118.7, 47.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{12}N_2O_5SBr$: 434.9650; found: 434.9640.

2-((METHYL(OXO)(PHENYL)-Λ^6-SULFANYLIDENE)AMINO)-8-NITRONAPHTHALENE-1,4-DIONE (5n)



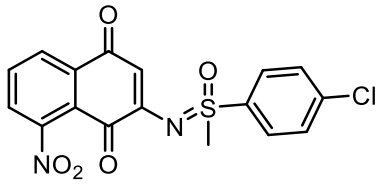
The compound **5n** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 4/6), 72.98 mg, 83% yield; yellow solid; m.p. = 217 - 219 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.11 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.93 – 7.90 (m, 2H), 7.72 (t, *J* = 7.9 Hz, 1H), 7.67 – 7.62 (m, 1H), 7.58 – 7.53 (m, 3H), 6.28 (s, 1H), 3.35 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 182.1, 179.8, 151.7, 148.7, 137.0, 134.7, 134.5, 133.6, 130.3, 128.5, 128.1, 126.6, 122.9, 118.2, 46.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{13}N_2O_5S$: 357.0545; found: 357.0560.

2-(((4-CHLOROPHENYL)(METHYL)(OXO)-Λ^6-SULFANYLIDENE)AMINO)-8-NITRONAPHTHALENE-1,4-DIONE (5o)



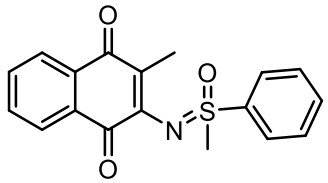
The compound **5o** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 4/6), 77.04 mg, 80% yield; Yellow Solid; m.p. = 147 - 149 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.88 – 7.84 (m, 2H), 7.73 (t, *J* = 7.9 Hz, 1H), 7.57 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.53 – 7.50 (m, 2H), 6.28 (s, 1H), 3.36 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 182.1, 179.6, 151.3, 148.6, 141.5, 135.6, 134.7, 133.5, 130.6, 129.5, 128.5, 126.6, 122.8, 118.5, 46.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{12}N_2O_5SCl$: 391.0155; found: 391.0145.

2-METHYL-3-((METHYL(OXO)(PHENYL)-Λ^6-SULFANYLIDENE)AMINO) NAPHTHALENE-1,4-DIONE (7a)



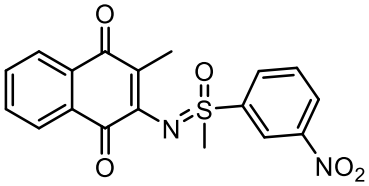
The compound **7a** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 1/9), 45.48 mg, 48% yield; orange coloured solid; m.p. = 164 - 166 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.3 Hz, 1H), 7.92 (dd, *J* = 7.5, 1.1 Hz, 2H), 7.83 (d, *J* = 7.3 Hz, 1H), 7.51 (m, 5H), 3.28 (s, 3H), 2.19 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 186.4, 181.1, 147.4, 142.7, 133.8, 132.8, 132.7, 132.5, 130.9 (2C), 129.6, 126.7, 126.5, 126.0, 49.4, 11.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{18}H_{16}NO_3S$: 326.0851; found: 326.0843.

2-METHYL-3-((METHYL(3-NITROPHENYL)(OXO)-Λ^6-SULFANYLIDENE) AMINO)NAPHTHALENE-1,4-DIONE (7b)



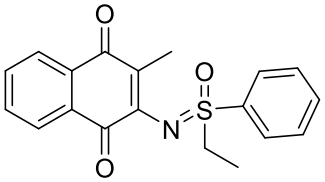
The compound **7b** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 1/9), 56.02 mg, 52% yield; yellow solid; m.p. = 210 - 212 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.76 (t, *J* = 1.9 Hz, 1H), 8.42 - 8.39 (m, 1H), 8.28 - 8.26 (m, 1H), 7.98 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.80 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.75 (t, *J* = 8.0 Hz, 1H), 7.58 (td, *J* = 7.5, 1.4 Hz, 1H), 7.49 (td, *J* = 7.5, 1.3 Hz, 1H), 3.33 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (101 MHz, CDCl3): δ 185.3, 181.2, 148.8, 146.3, 145.5, 134.1, 132.8, 132.7, 132.1, 131.9, 131.0, 130.6, 127.3, 126.7, 126.2, 121.9, 49.1, 12.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{18}H_{15}N_2O_5S$: 371.0702; found: 371.0691.

2-((ETHYL(OXO)(PHENYL)-Λ^6-SULFANYLIDENE)AMINO)-3-METHYLNAPHTHALENE-1,4-DIONE (7c)



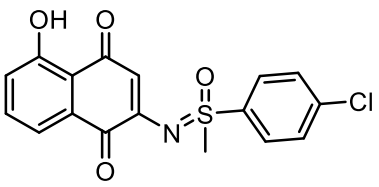
The compound **7c** was purified by column chromatography silica gel (Eluent: EtOAc/Hexane = 1/9), 54.36 mg, 55% yield; yellow solid; m.p. = 132-134 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.96 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.85 – 7.78 (m, 3H), 7.56 – 7.44 (m, 5H), 3.33 (q, *J* = 7.3 Hz, 2H), 2.22 (s, 3H), 1.28 (t, *J* = 7.4 Hz, 3H).

^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ 186.4, 181.0, 147.6, 140.6, 133.7, 132.8, 132.5, 130.9, 130.6, 129.5, 127.2, 126.7, 126.0, 55.2, 11.8, 8.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{19}H_{18}NO_3S$: 340.1007; found: 340.0990.

2-(((4-CHLOROPHENYL)(METHYL)(OXO)-Λ^6-SULFANYLIDENE)AMINO)-5-HYDROXYNAPHTHALENE-1,4-DIONE (8a)



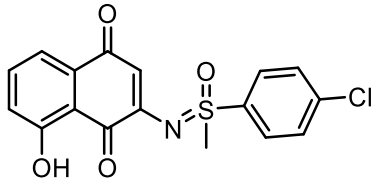
The compound **8a** was purified by semipreparative RP-HPLC using a Purospher STAR C_{18} column, an acetonitrile-water (15% to 65%) gradient with a flow of 2.0 mL/min, and monitoring at 210 nm, 254 nm, 280 nm and 300 nm, 8.73 mg of compound in 10% yield was reported as yellow solid; m.p. = 169 - 171 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 11.84 (s, 1H), 7.86 – 7.83 (m, 2H), 7.54 – 7.43 (m, 5H), 7.11 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.22 (s, 1H), 3.35 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 188.0, 184.0, 161.8, 150.5, 141.3, 136.8, 135.9, 132.4, 130.5, 129.4, 123.4, 120.2, 118.5, 114.7, 47.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{13}NO_4SCl$: 362.0254; found: 362.0260.

2-(((4-CHLOROPHENYL)(METHYL)(OXO)-Λ^{6}-SULFANYLIDENE)AMINO)-8-HYDROXYNAPHTHALENE-1,4-DIONE (8b)



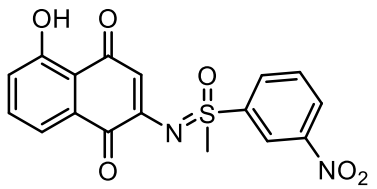
The compound **8b** was purified by semipreparative RP-HPLC using a Purospher STAR C_{18} column, an acetonitrile-water (15% to 65%) gradient with a flow of 2.0 mL/min, and monitoring at 210 nm, 254 nm, 280 nm and 300 nm, 78.56 mg, 90% yield; Orange coloured solid; m.p. = 178 - 180 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 12.28 (s, 1H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.53 – 7.50 (m, 3H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.15 – 7.12 (m, 1H), 6.23 (s, 1H), 3.33 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 190.5, 182.0, 160.8, 151.8, 141.0, 136.6, 134.9, 131.3, 130.4, 129.1, 124.7, 119.6, 119.1, 114.7, 47.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{13}NO_4SCl$: 362.0254; found: 362.0247.

5-HYDROXY-2-((METHYL(3-NITROPHENYL)(OXO)-Λ^{6}-SULFANYLIDENE) AMINO)NAPHTHALENE-1,4-DIONE (8c)



The compound **8c** was purified by semipreparative RP-HPLC using a Purospher STAR C_{18} column, an acetonitrile-water (15% to 65%) gradient with a flow of 2.0 mL/min, and

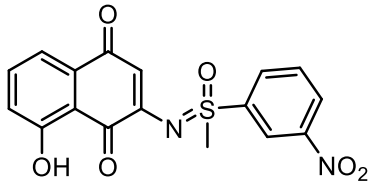
monitoring at 210 nm, 254 nm, 280 nm and 300 nm, 7.20 mg, 8% yield; Orange Coloured solid; m.p. = 176 - 177 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 11.64 (s, 1H), 8.77 (t, *J* = 1.9 Hz, 1H), 8.49 – 8.46 (m, 1H), 8.28 – 8.25 (m, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.11(dd, *J* = 8.2, 1.4 Hz, 1H), 6.31 (s, 1H), 3.40 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 187.4, 184.1, 161.8, 149.9, 141.4, 137.1, 133.2, 132.5, 131.6, 128.7, 123.6, 123.2, 121.5, 118.8, 47.4

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{13}N_2O_6S$: 373.0494; found: 373.0503.

8-HYDROXY-2-((METHYL(3-NITROPHENYL)(OXO)-Λ^{6}-SULFANYLIDENE) AMINO)NAPHTHALENE-1,4-DIONE (8d)



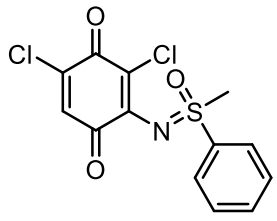
The compound **8d** was purified by semipreparative RP-HPLC using a Purospher STAR C_{18} column, an acetonitrile-water (15% to 65%) gradient with a flow of 2.0 mL/min, and monitoring at 210 nm, 254 nm, 280 nm and 300 nm, 77.28 mg, 92% yield; Orange Coloured solid; m.p. = 215 - 217 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 12.25 (s, 1H), 8.76 (t, *J* = 1.9 Hz, 1H), 8.47 – 8.44 (m, 1H), 8.27 – 8.24 (m, 1H), 7.78 (t, *J* = 8.0 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.14 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.34 (s, 1H), 3.36 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 190.8, 181.8, 161.0, 151.2, 149.0, 142.4, 136.2, 132.8, 131.4, 131.1, 128.3, 125.1, 122.7, 120.0, 114.8, 47.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{13}N_2O_6S$: 373.0494; found: 373.0497.

3,5-DICHLORO-2-((METHYL(OXO)(PHENYL)-Λ^{6}-SULFANYLIDENE)AMINO) CYCLOHEXA-2,5-DIENE-1,4-DIONE (10a)



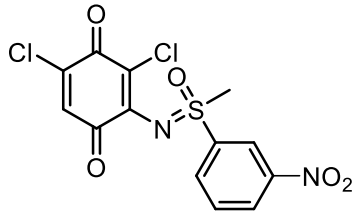
The compound **10a** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 1/9), 67.88 mg, 73% yield; dark red solid; m.p. = 165 - 167 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 – 7.91 (m, 2H), 7.60 – 7.52 (m, 3H), 6.70 (s, 1H), 3.33 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 179.4, 173.1, 146.1, 145.1, 141.0, 133.6, 130.4, 129.8, 126.7, 123.9, 48.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{13}H_{10}NO_3SCl_2$: 329.9758; found: 329.9761.

3,5-DICHLORO-2-((METHYL(3-NITROPHENYL)(OXO)-Λ^{6}-SULFANYLIDENE) AMINO)CYCLOHEXA-2,5-DIENE-1,4-DIONE (10b)



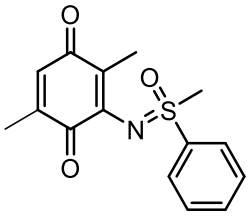
The compound **10b** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 1/9), 82.45 mg, 78% yield; dark red solid; m.p. = 170 - 173 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (s, 1H), 8.47 – 8.42 (m, 1H), 8.31 – 8.26 (m, 1H), 7.78 (t, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 0.6 Hz, 1H), 3.40 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 178.4, 171.9, 147.6, 144.2, 144.0, 142.8, 131.1, 130.1, 129.2, 126.8, 124.0, 121.1, 47.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{13}H_9N_2O_5SCl_2$: 374.9609; found: 374.9597.

2,5-DIMETHYL-3-((METHYL(OXO)(PHENYL)-Λ^{6}-SULFANYLIDENE)AMINO) CYCLOHEXA-2,5-DIENE-1,4-DIONE (10c)



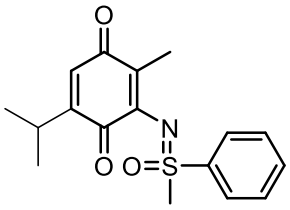
The compound **10c** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 1/9), 64.16 mg, 56% yield; orange coloured solid; m.p. = 133 - 135 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 – 7.86 (m, 2H), 7.56 – 7.48 (m, 3H), 6.36 (d, *J* = 1.6 Hz, 1H), 3.23 (s, 3H), 2.01 (s, 3H), 1.83 (d, *J* = 1.6 Hz, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 187.2, 182.6, 155.0, 141.5, 141.3, 132.9, 131.7, 128.4, 126.8, 125.5, 48.0, 14.6, 9.9.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{15}H_{15}NO_3NaS$: 312.0670; found: 312.0675.

2-ISOPROPYL-5-METHYL-3-((METHYL(OXO)(PHENYL)-Λ^6-SULFANYLIDENE) AMINO)CYCLOHEXA-2,5-DIENE-1,4-DIONE (10d)



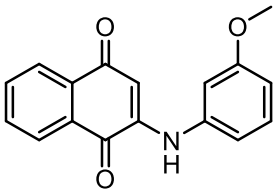
The compound **10d** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 1/9), 48.45 mg, 50% yield; dark orange coloured solid; m.p. = 128 - 130 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.54 – 7.47 (m, 3H), 6.29 (d, *J* = 1.2 Hz, 1H), 3.24 (s, 3H), 2.01 (s, 3H), 0.96 (d, *J* = 6.9 Hz, 3H), 0.84 (d, *J* = 6.9 Hz, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 187.6, 181.9, 150.6, 144.6, 141.2, 131.6, 129.8, 128.4, 126.2, 125.5, 47.9, 25.5, 20.3 (2C), 9.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{20}NO_3S$: 318.1164; found: 318.1149.

2-((3-METHOXYPHENYL)AMINO)NAPHTHALENE-1,4-DIONE (11a)



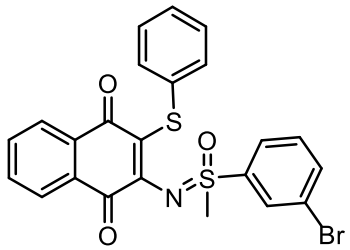
The compound **11a** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 1/9), 82.4 mg, 93% yield; red solid; m.p. = 163 - 165 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 – 8.02 (m, 2H), 7.71 – 7.66 (m, 1H), 7.61 – 7.57 (m, 1H), 7.49 (s, 1H), 7.24 (t, J = 8.1 Hz, 1H), 6.80 (dd, J = 7.9, 1.9 Hz, 1H), 6.73 (t, J = 2.2 Hz, 1H), 6.69 – 6.67 (m, 1H), 6.38 (s, 1H), 3.75 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 184.1, 182.2, 160.7, 144.7, 138.7, 135.1, 133.3, 132.5, 130.5, 130.4, 126.7, 126.3, 114.9, 111.1, 108.6, 103.9, 55.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{14}NO_3$: 280.0974; found: 280.0990.

2-(((3-BROMOPHENYL)(METHYL)(OXO)-Λ^6-SULFANEYLIDENE)AMINO)-3-(PHENYLTHIO)NAPHTHALENE-1,4-DIONE (12)



The compound **12** was purified by column chromatography on silica gel (Eluent: EtOAc/Hexane = 1/9), 43.52 mg, 68% yield; red solid; m.p. = 207 - 210 ^{o}C.

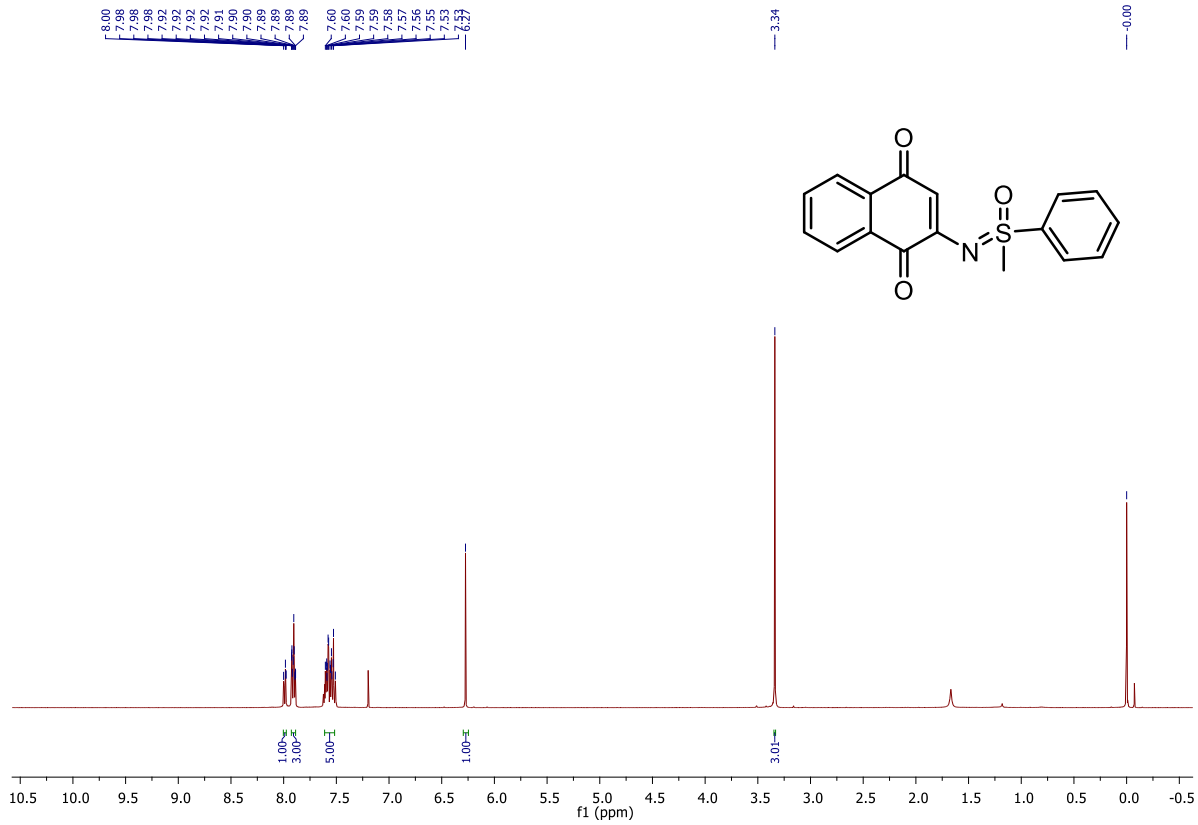
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.10 (dd, J = 7.7, 0.9 Hz, 1H), 7.92 (dd, J = 7.6, 1.0 Hz, 1H), 7.82 (t, J = 1.8 Hz, 1H), 7.70 – 7.63 (m, 3H), 7.60 (td, J = 7.5, 1.3 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.38 (t, J = 7.9 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.23 – 7.21 (m, 1H), 2.91 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 182.0, 179.3, 149.0, 143.6, 135.9, 135.5, 134.2, 133.0, 132.8, 130.9, 130.6, 130.3, 129.0, 128.8, 128.2, 127.1, 126.8, 126.4, 124.9, 123.4, 48.3.

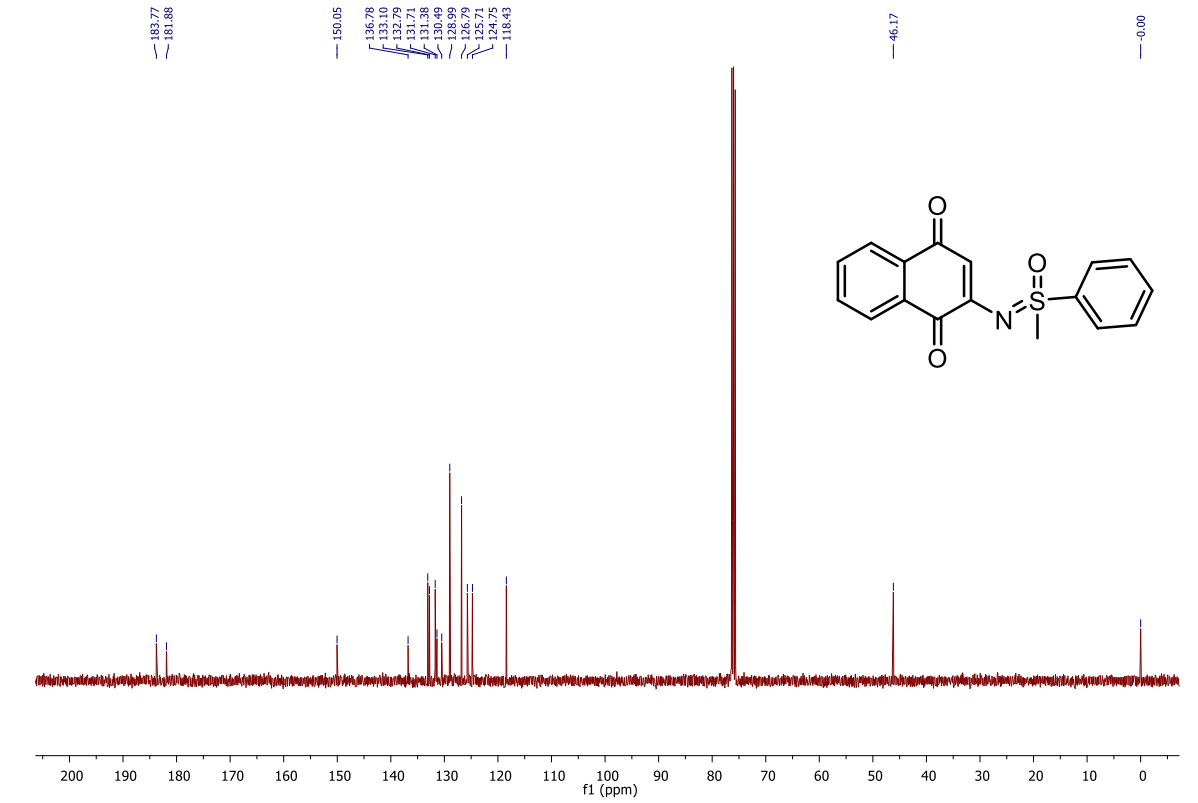
HRMS (ESI) m/z: $[M+H]^+$ Calcd. For $C_{23}H_{17}NO_3S_2Br$: 497.9833; found: 497.9828.

^{1}H and ^{13}C {^{1}H} NMR and HRMS Spectra

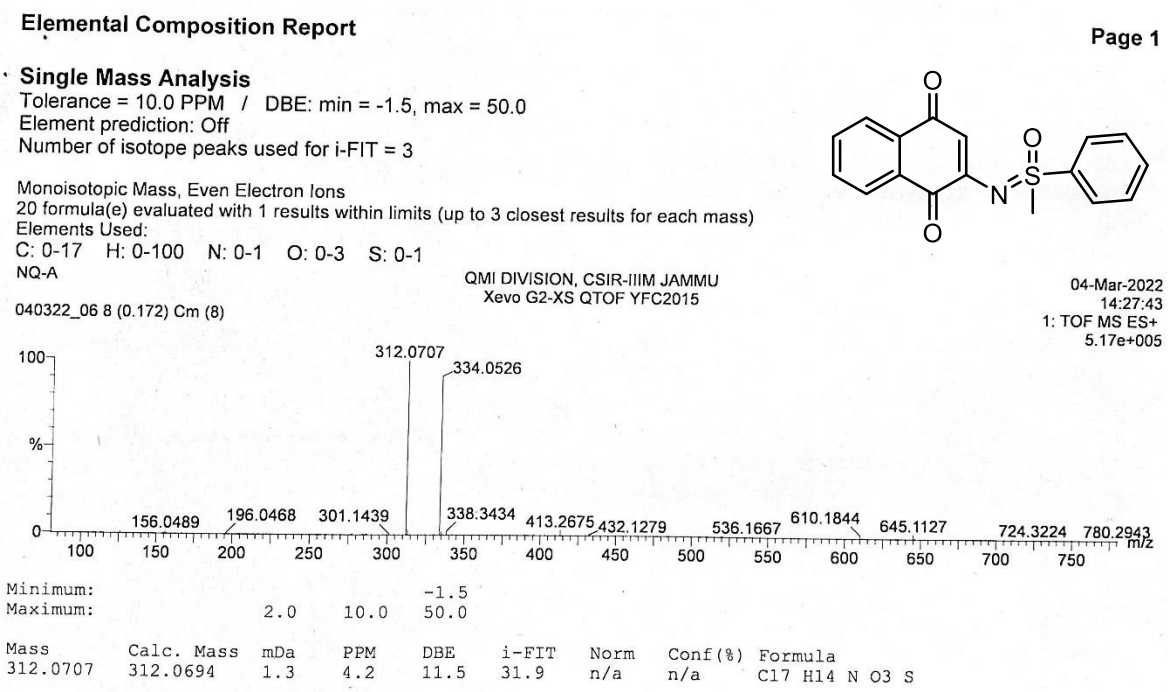
^{1}H NMR (400 MHz) of 3a in $CDCl_3$



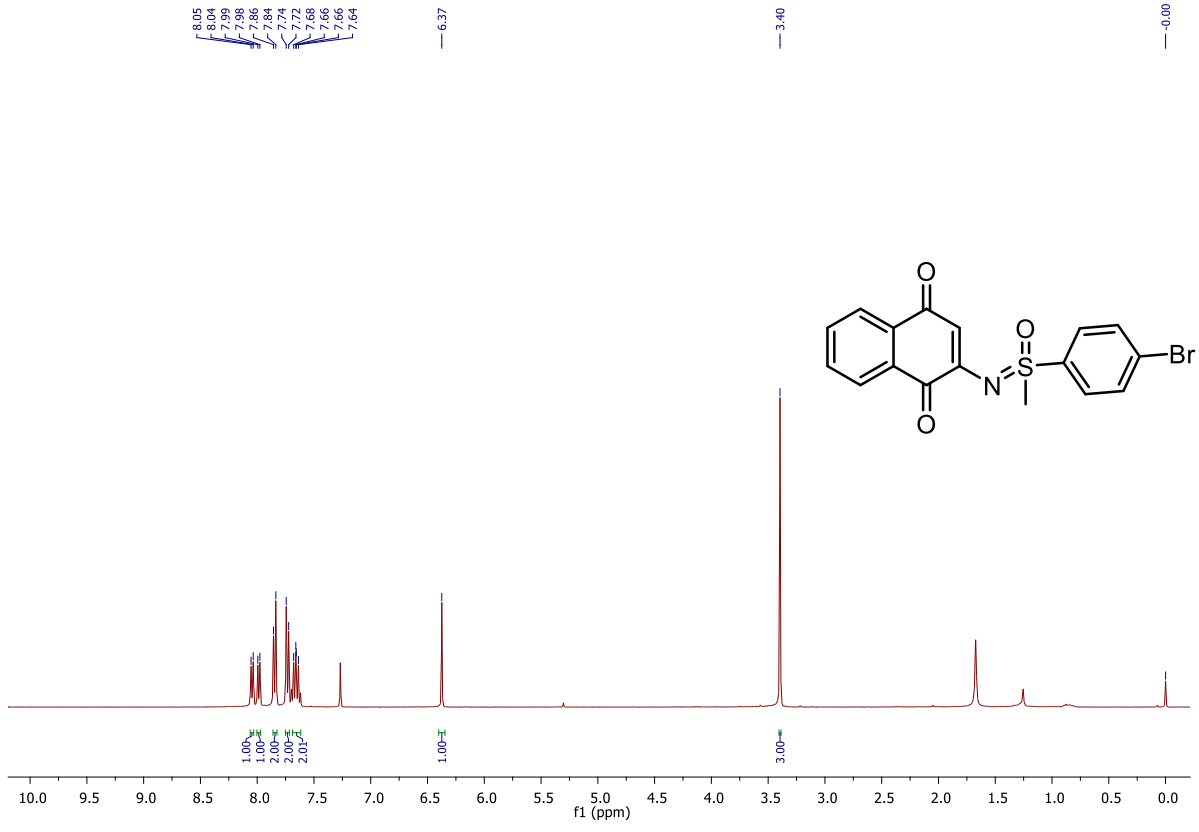
^{13}C {^{1}H} NMR (101 MHz) of 3a in $CDCl_3$



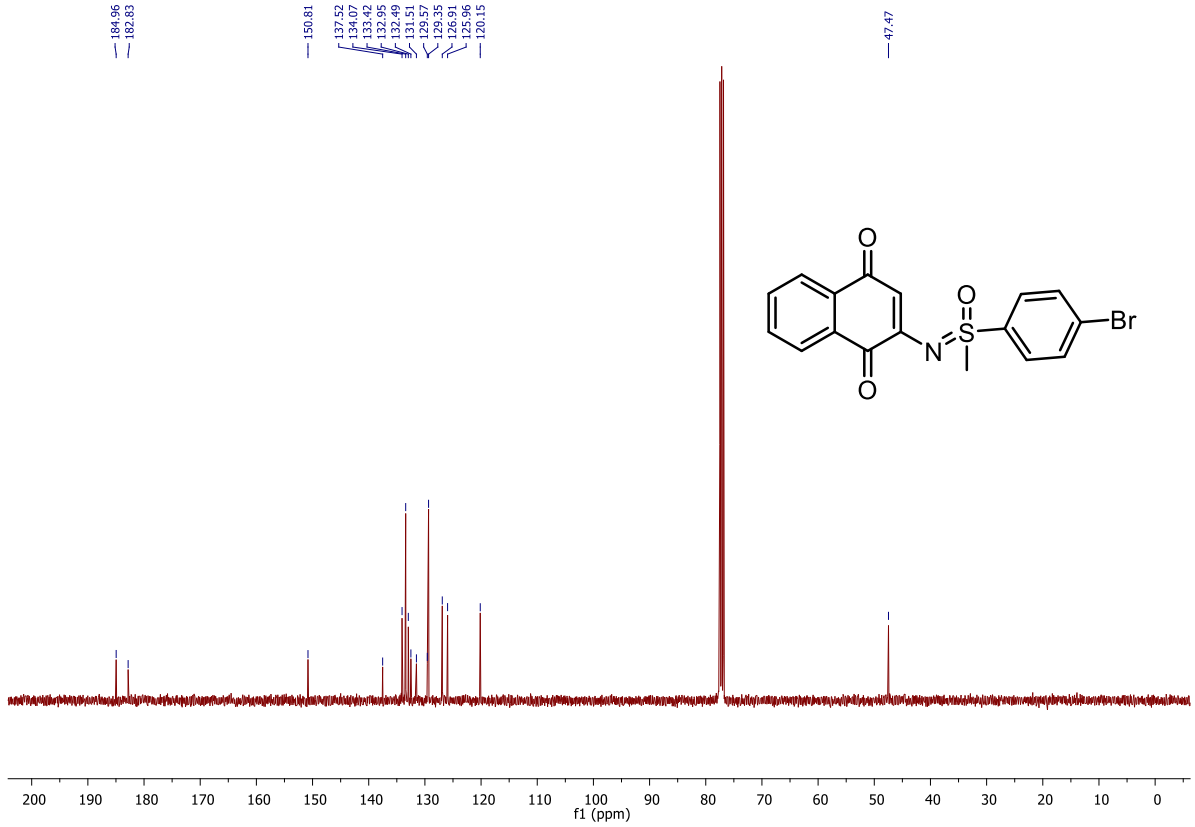
HRMS of 3a



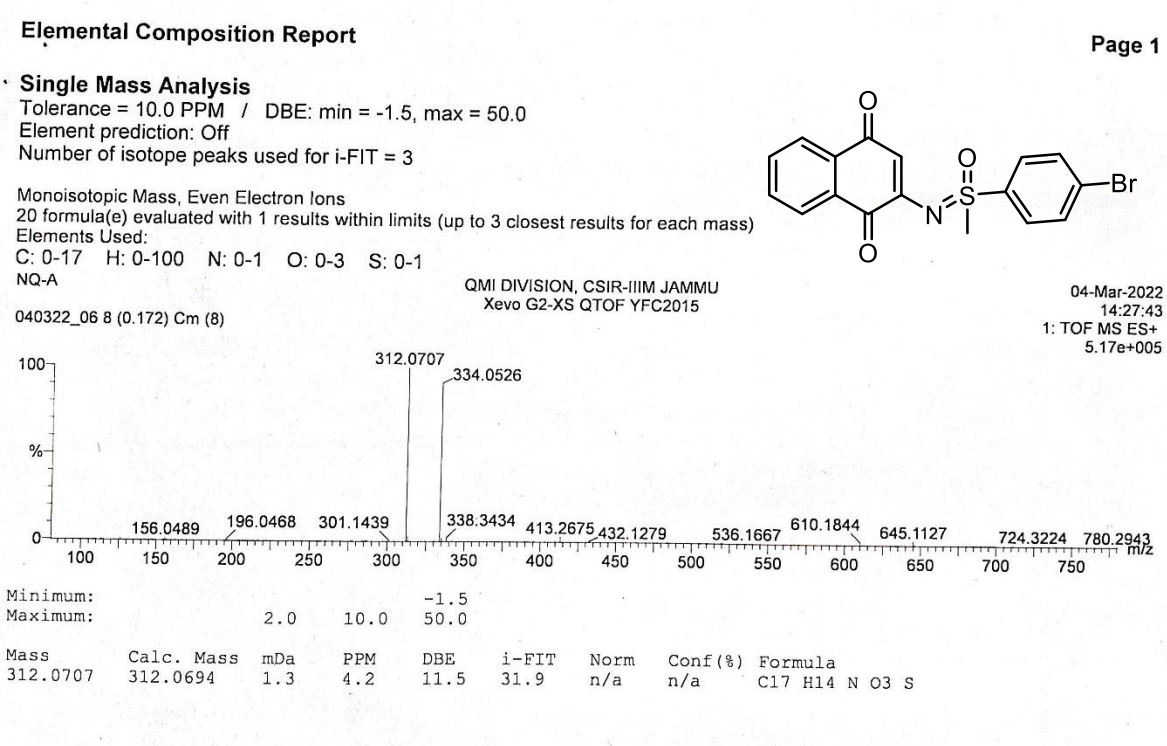
^{1}H NMR (400 MHz) of 3b in $CDCl_3$



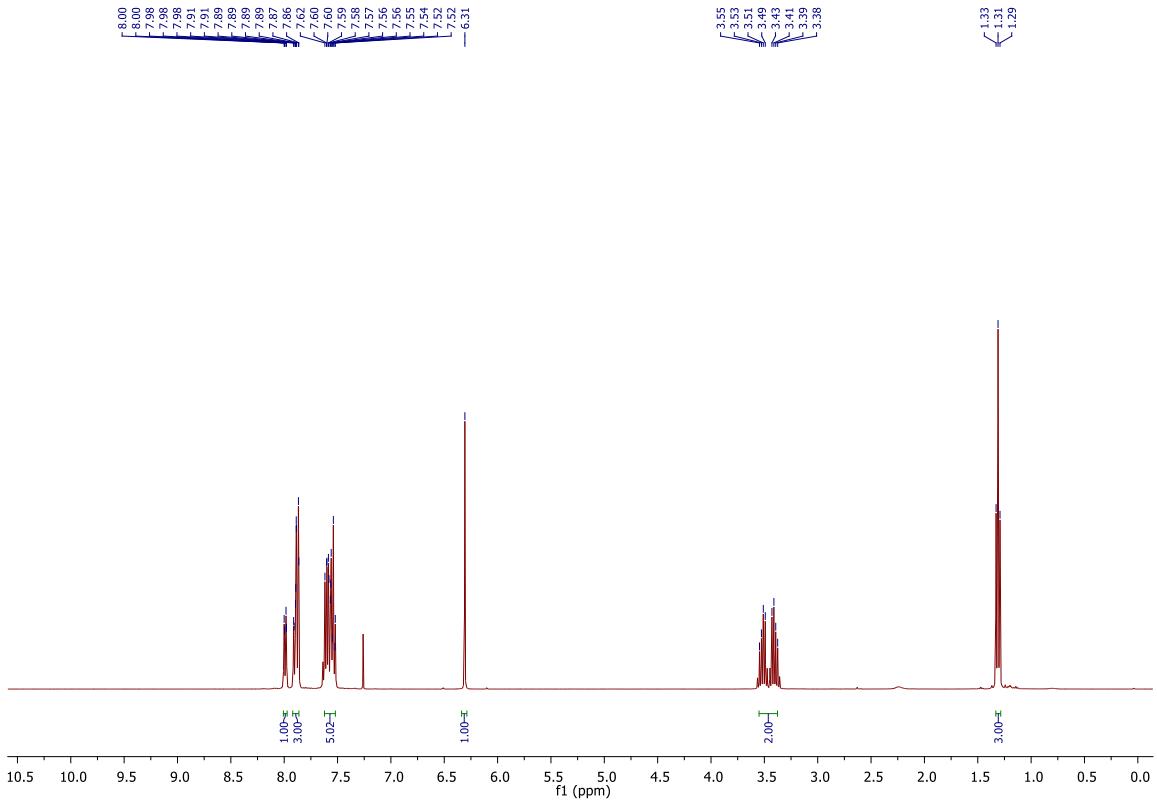
^{13}C {^{1}H} NMR (101 MHz) of 3b in $CDCl_3$



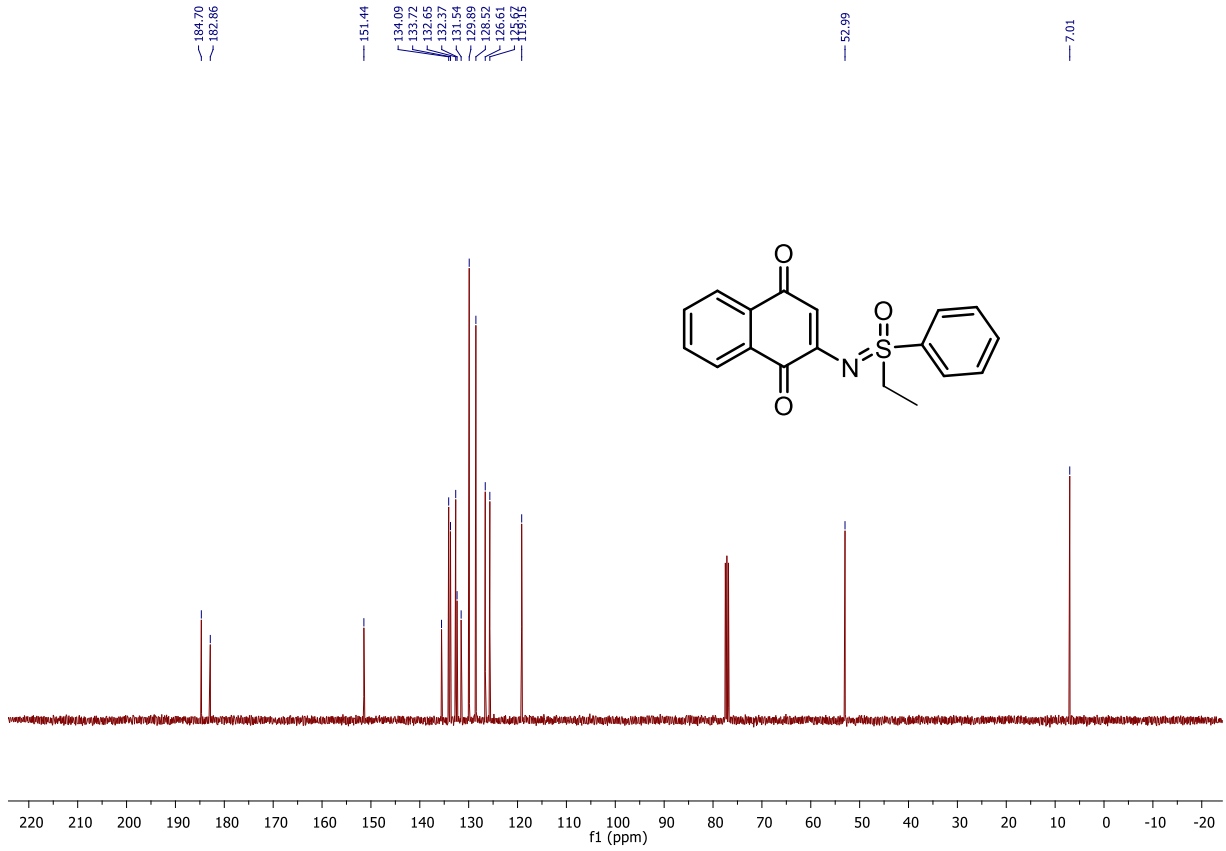
HRMS Spectra of 3b



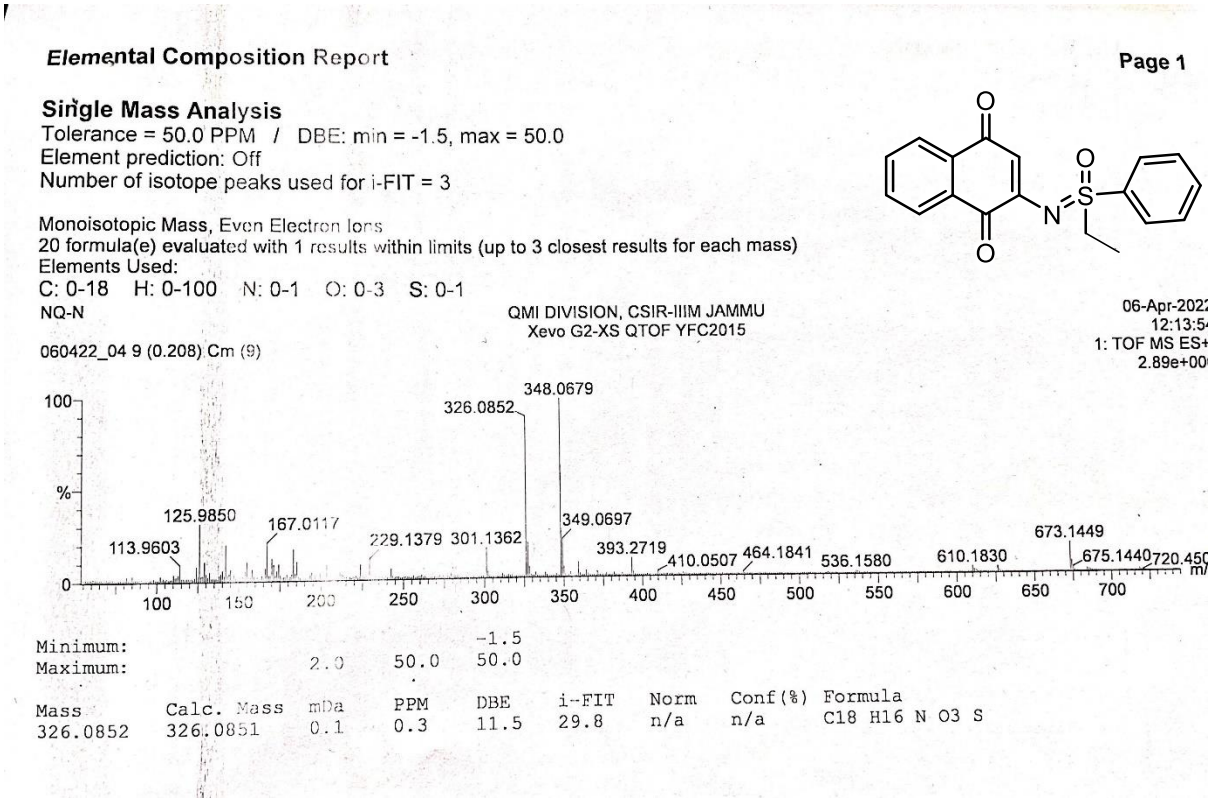
^{1}H NMR (400 MHz) of 3c in $CDCl_3$



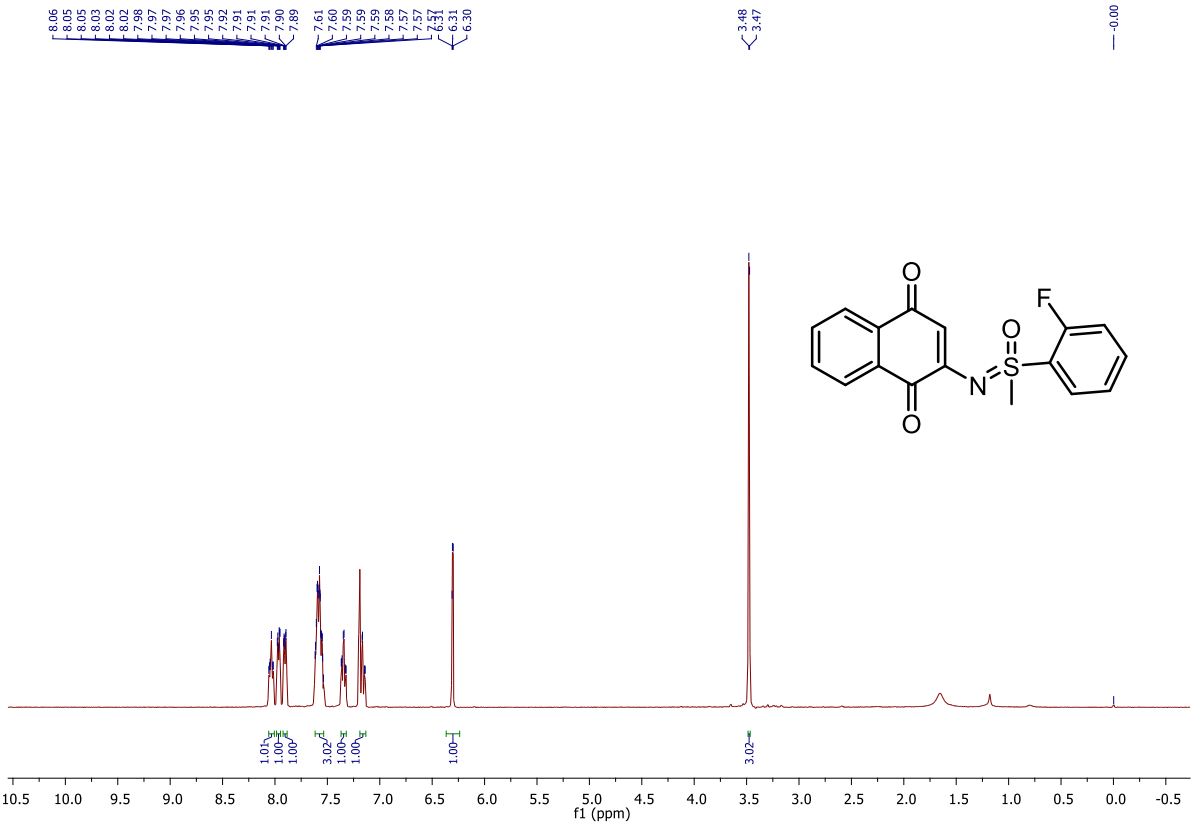
^{13}C {^{1}H} NMR (101 MHz) of 3c in $CDCl_3$



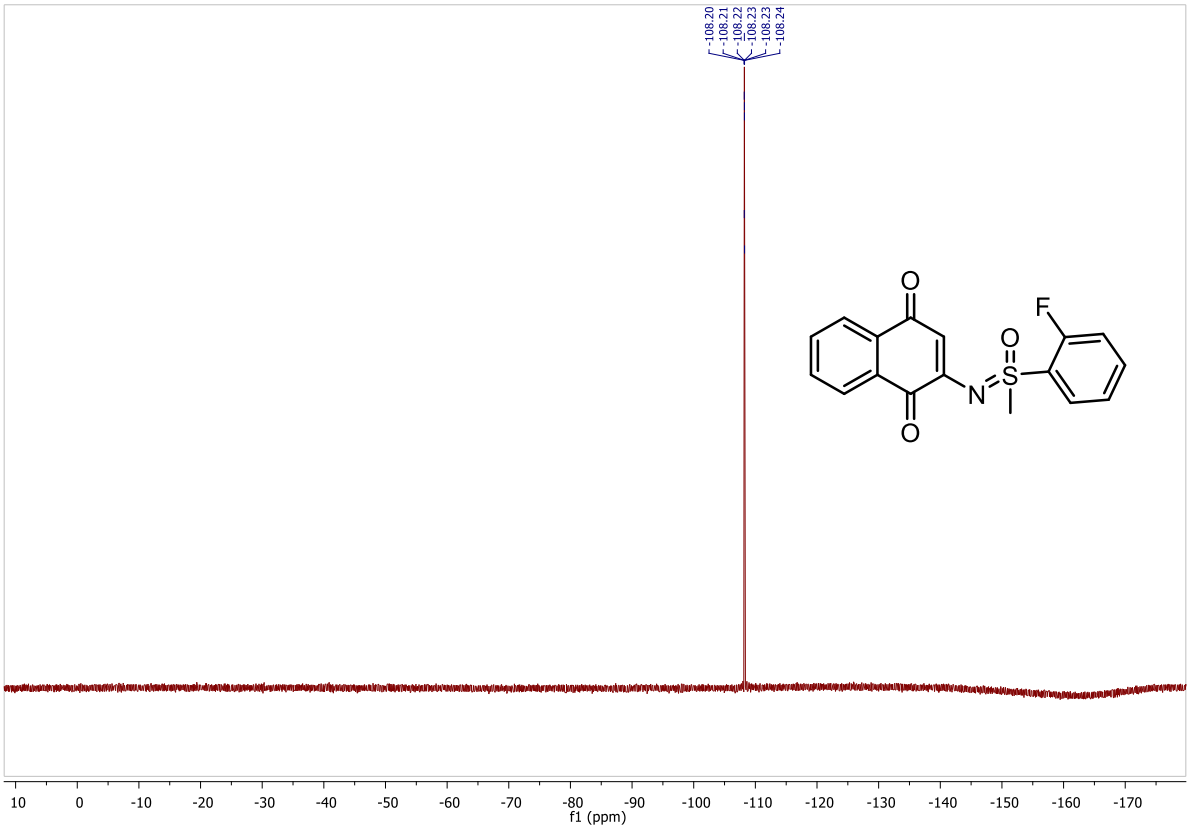
HRMS of 3c



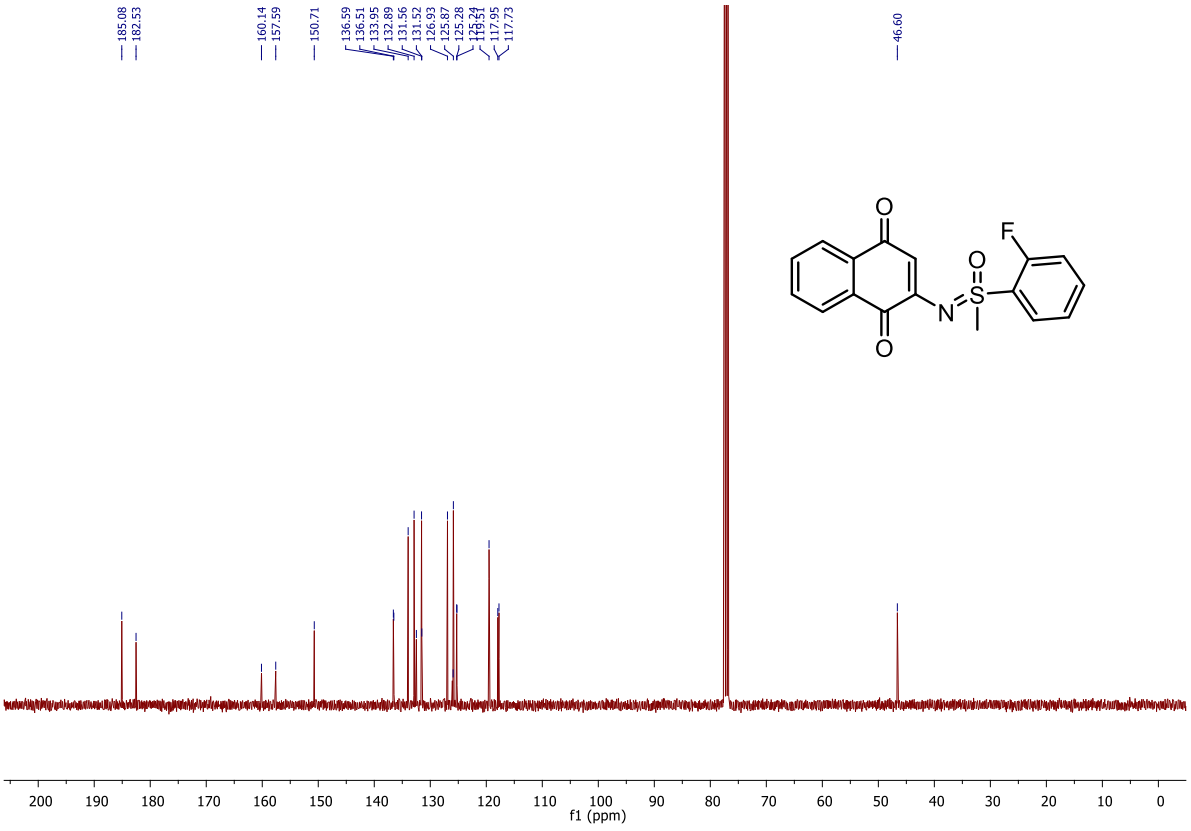
^{1}H NMR (400 MHz) of 3d in $CDCl_3$



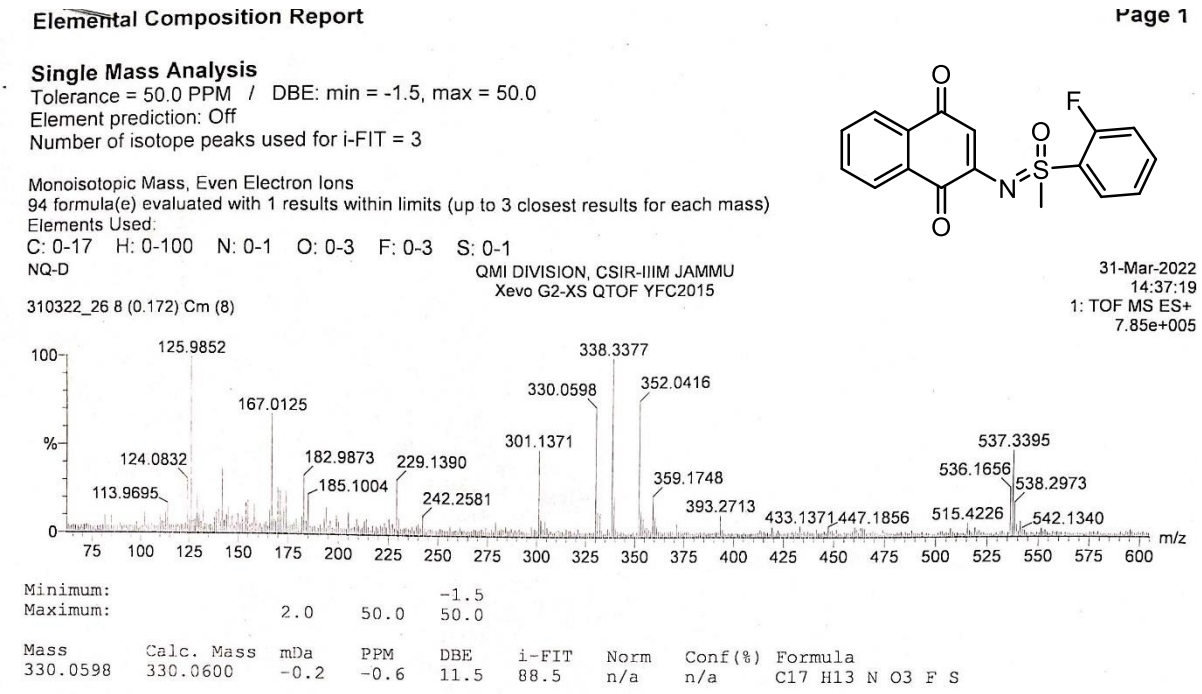
^{19}F NMR (377 MHz) of 3d in $CDCl_3$



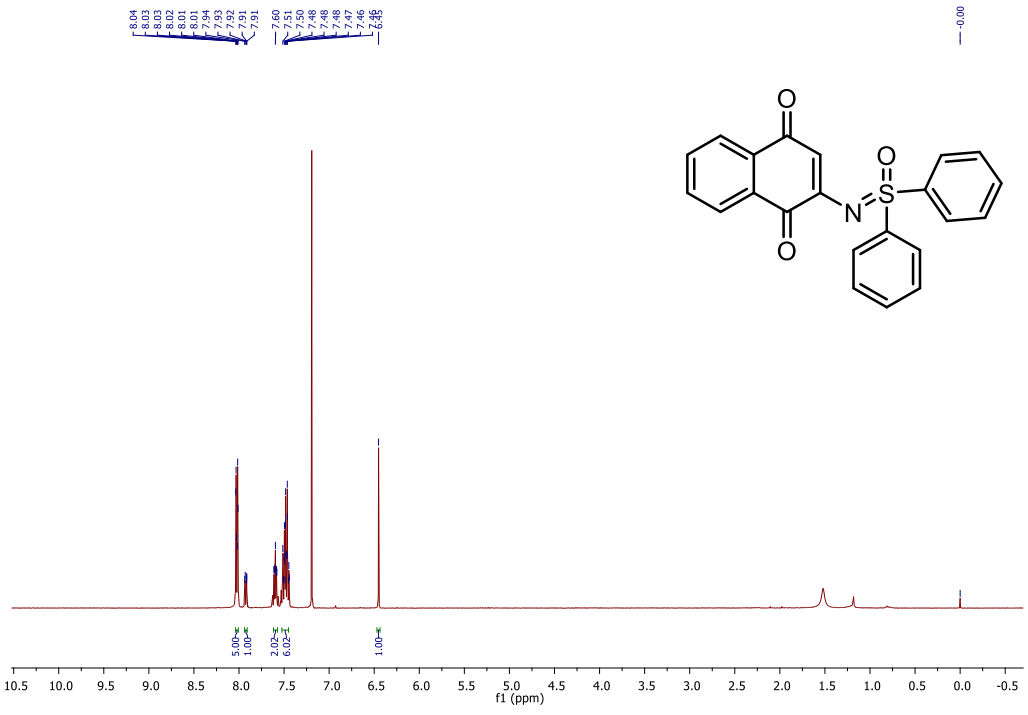
^{13}C {^{1}H} NMR (101 MHz) of 3d in $CDCl_3$



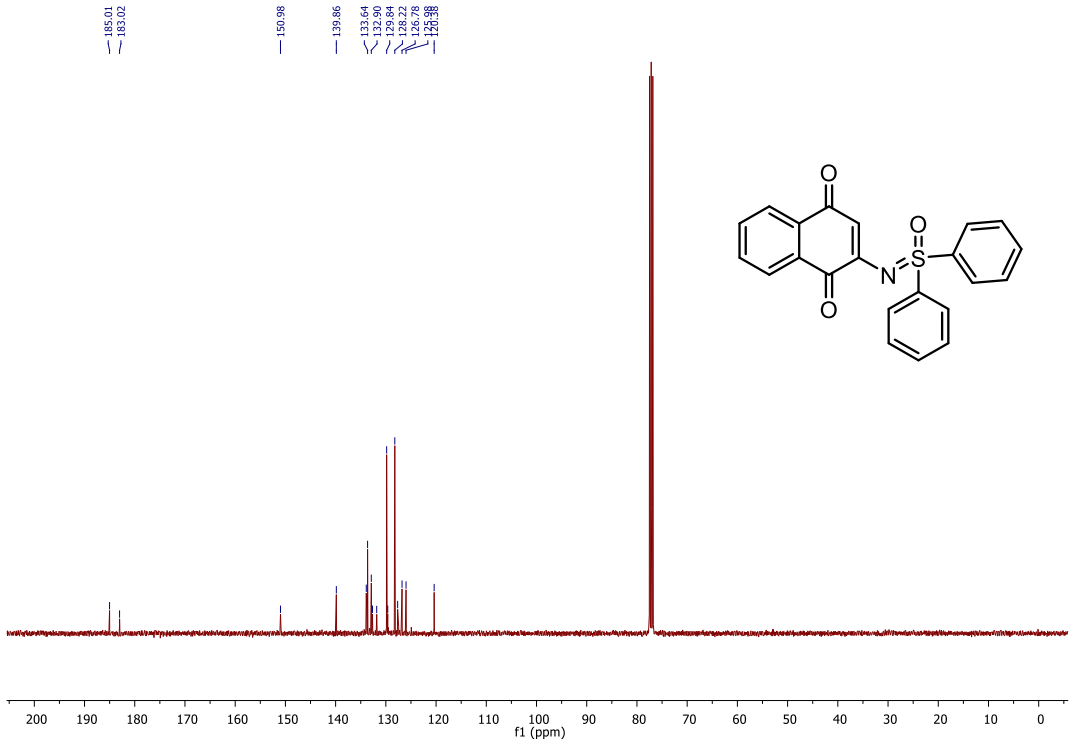
HRMS of 3d



^{1}H NMR (400 MHz) of 3e in $CDCl_3$



^{13}C {^{1}H} NMR (101 MHz) of 3e in $CDCl_3$



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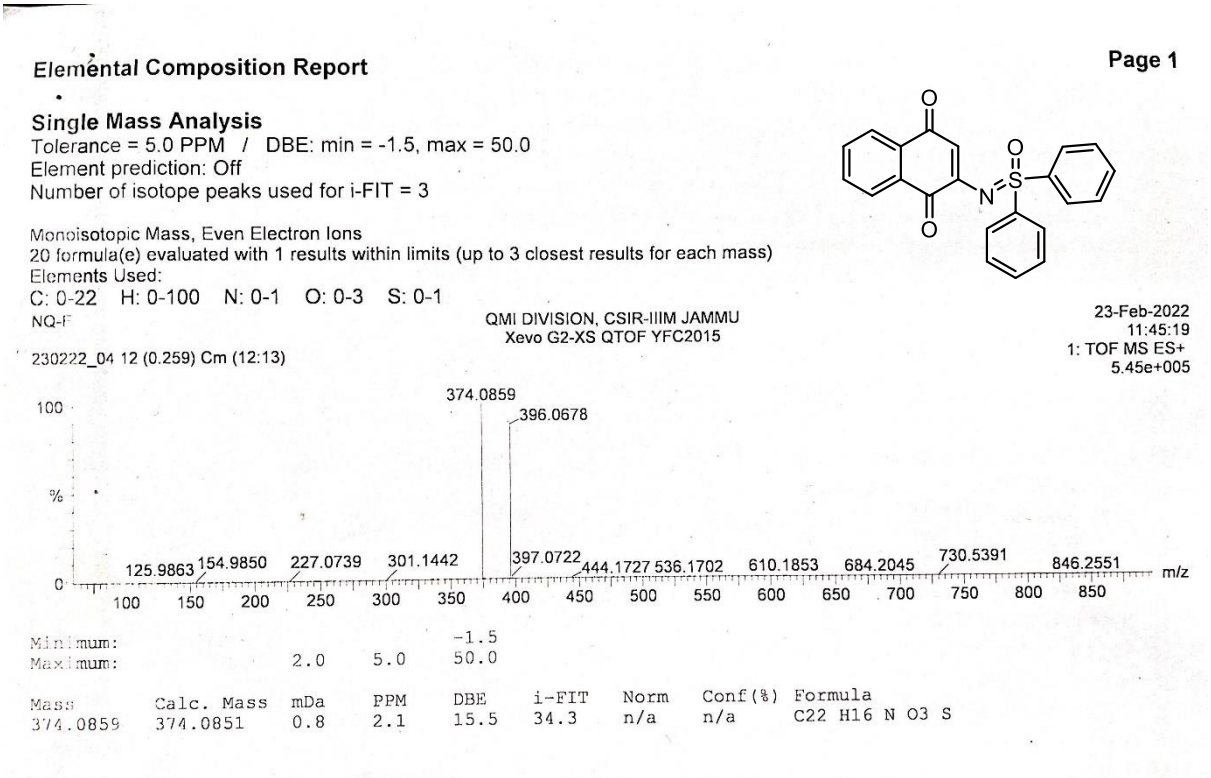
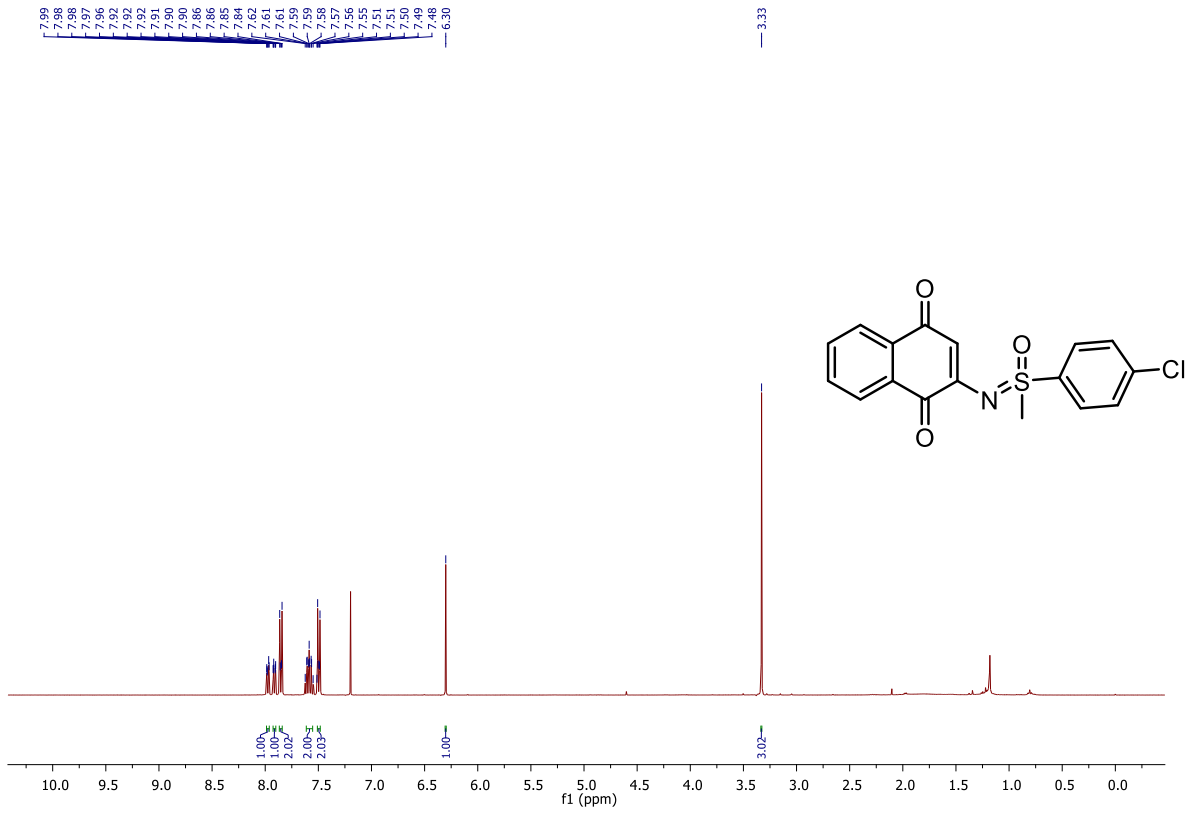
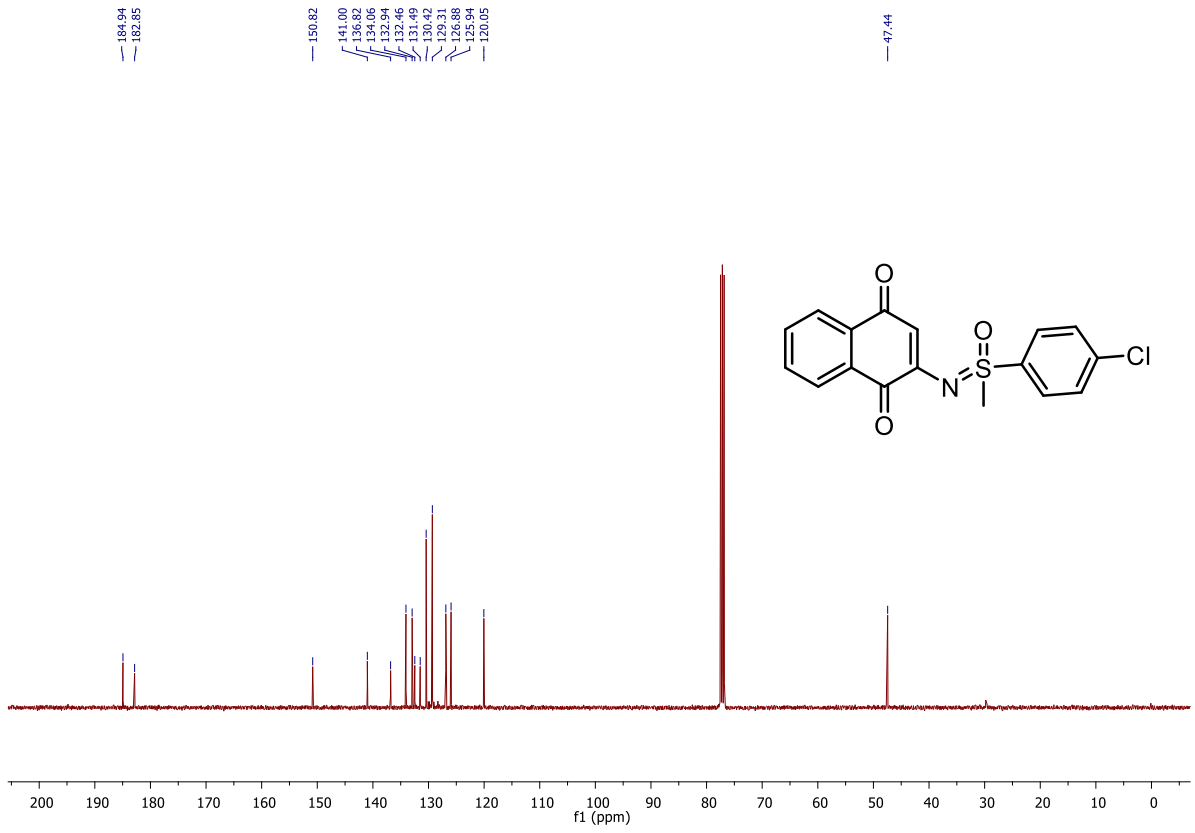


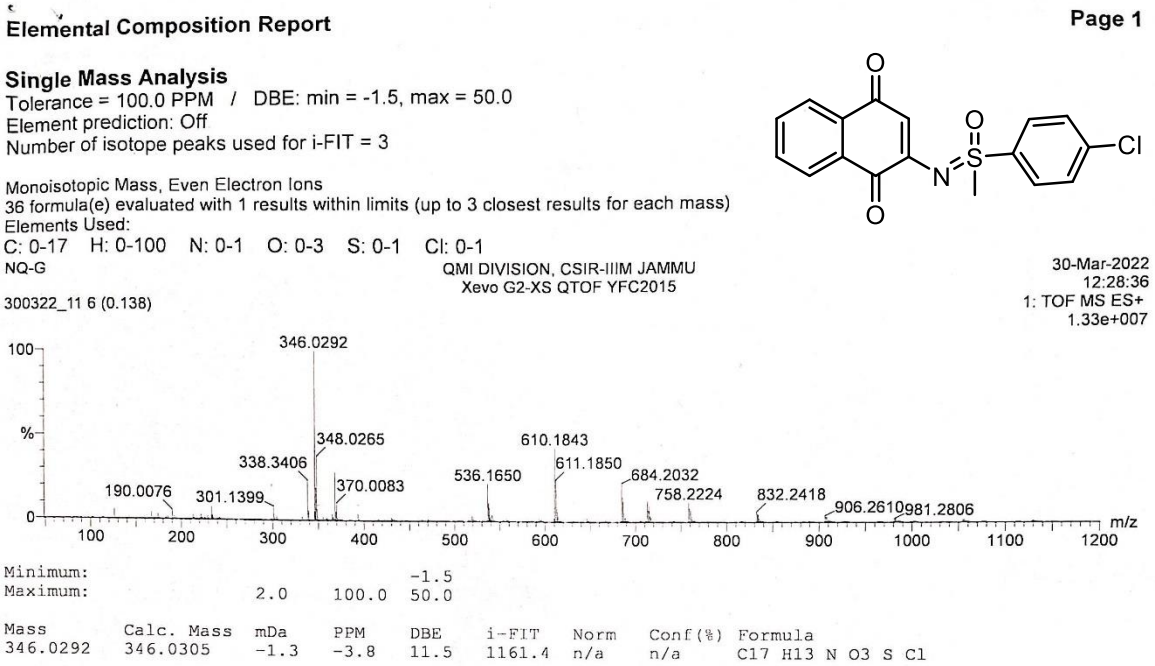
^{1}H NMR (400 MHz) of 3f in $CDCl_3$



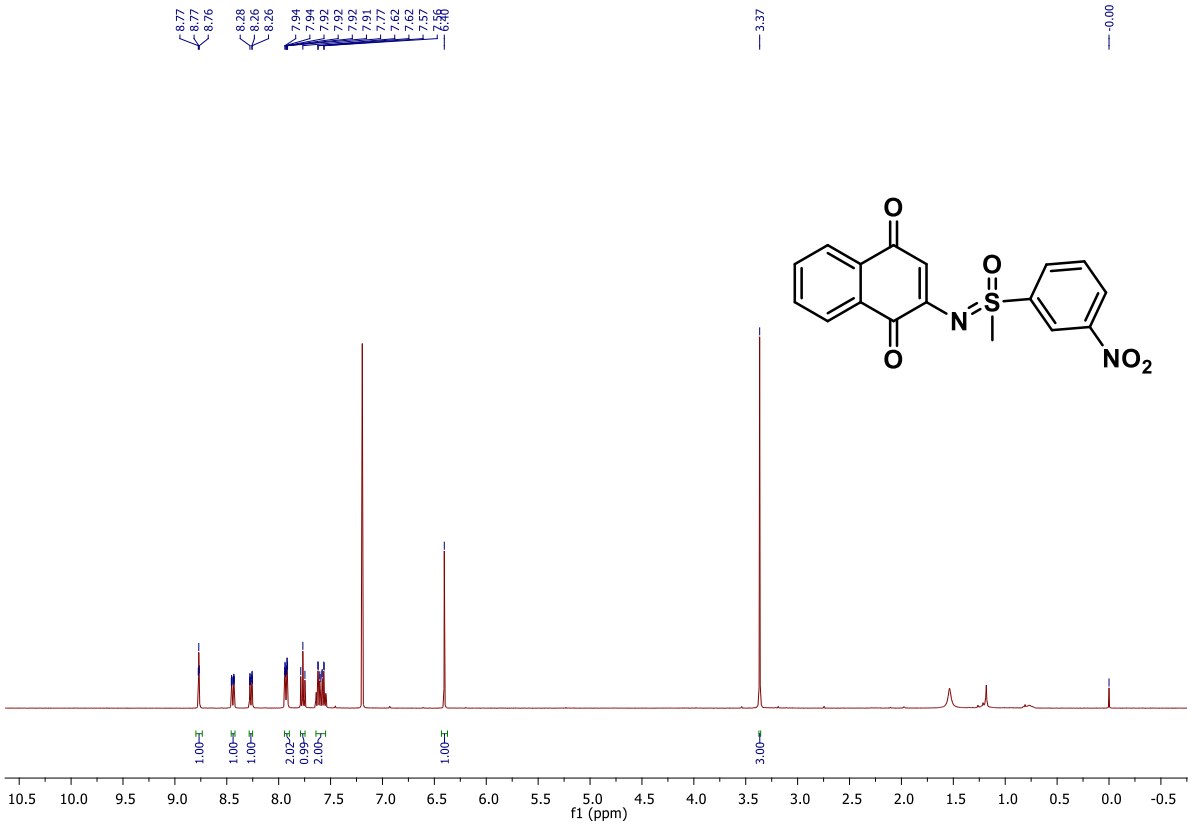
^{13}C {^{1}H} NMR (101 MHz) of 3f in $CDCl_3$



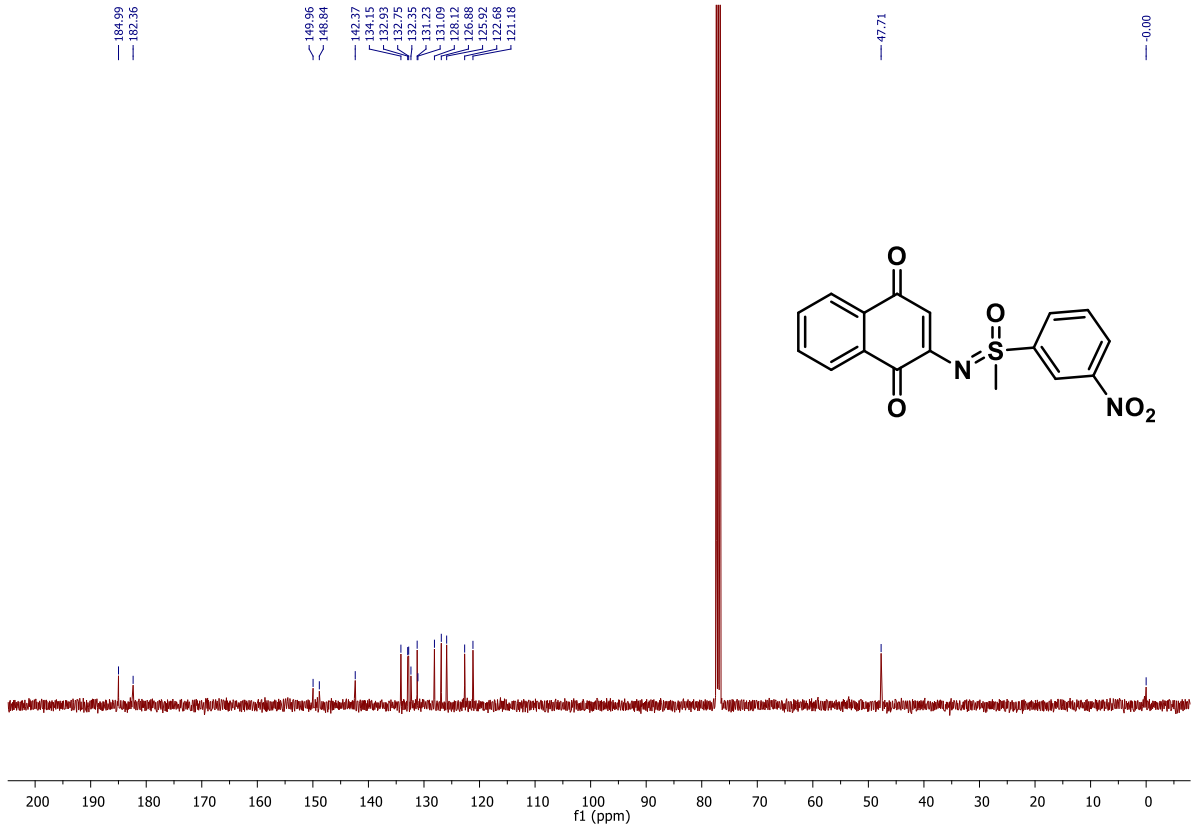
HRMS of 3f



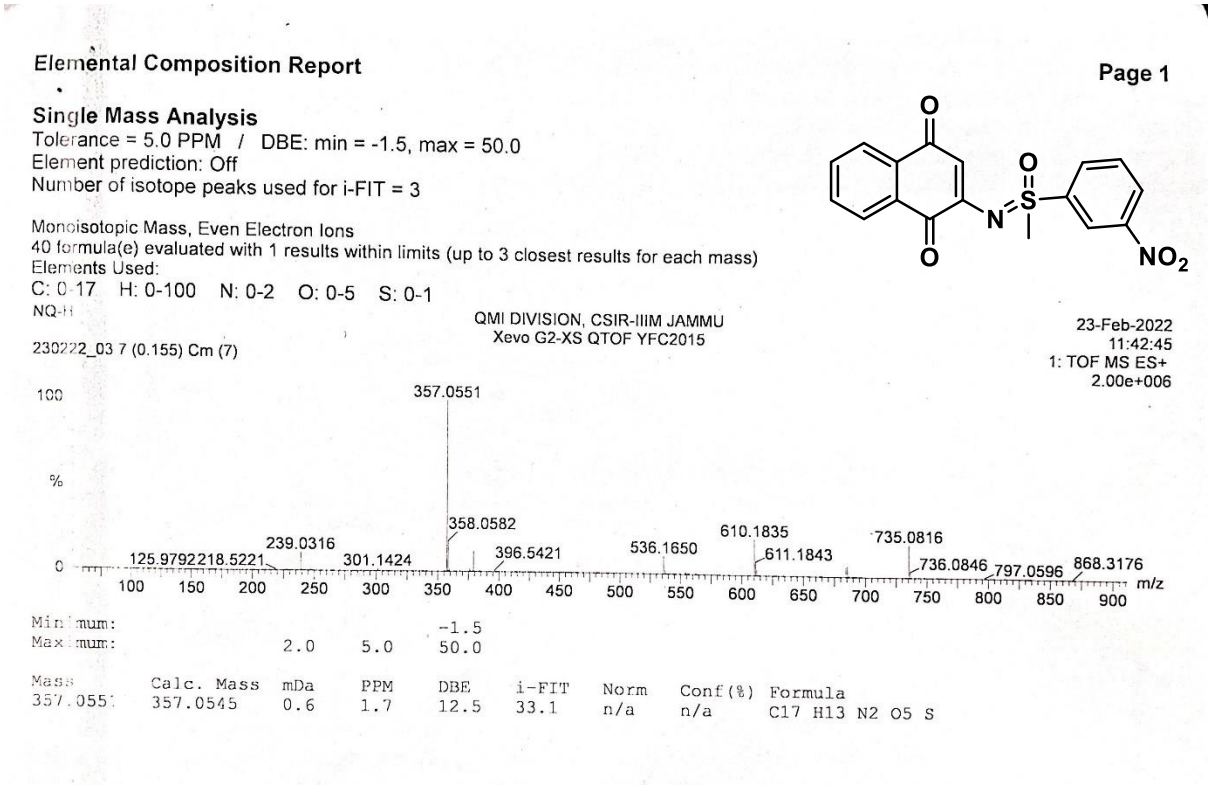
^{1}H NMR (400 MHz) of 3g in $CDCl_3$



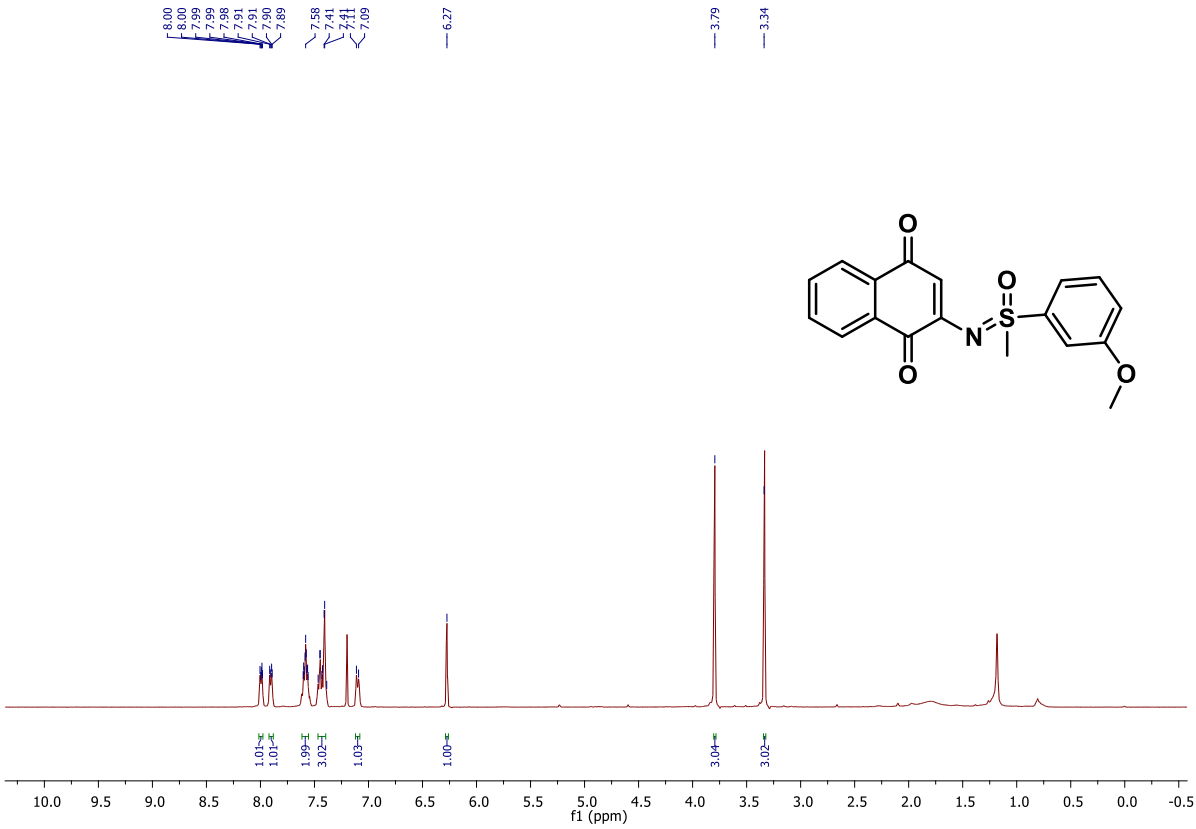
^{13}C {^{1}H} NMR (101 MHz) of 3g in $CDCl_3$



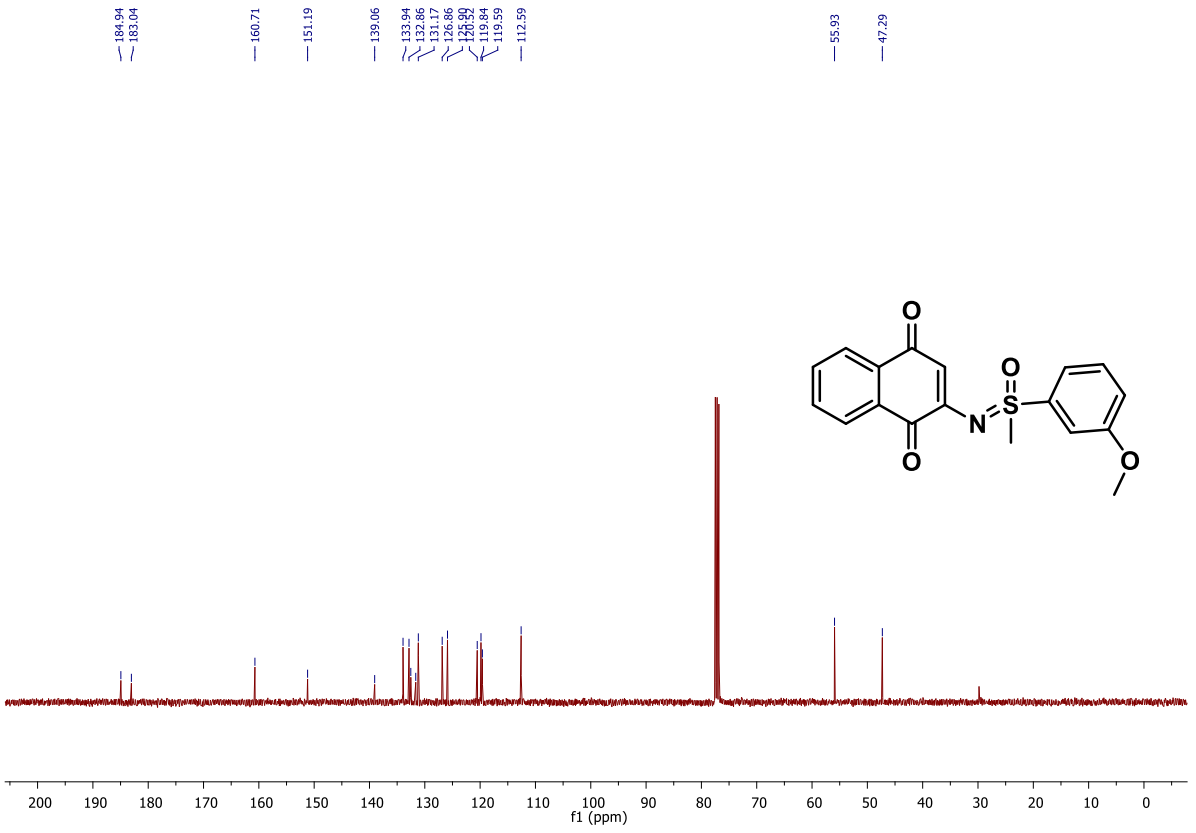
HRMS of 3g



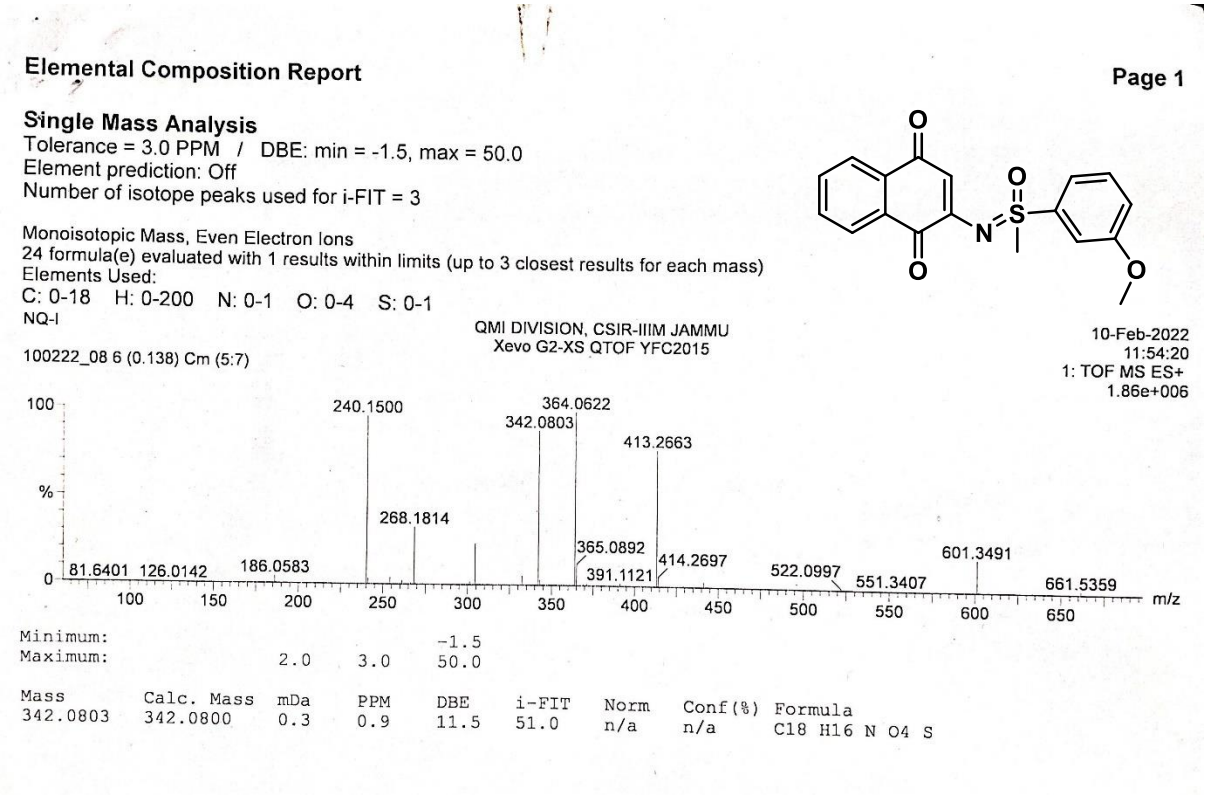
^{1}H NMR (400 MHz) of 3h in $CDCl_3$



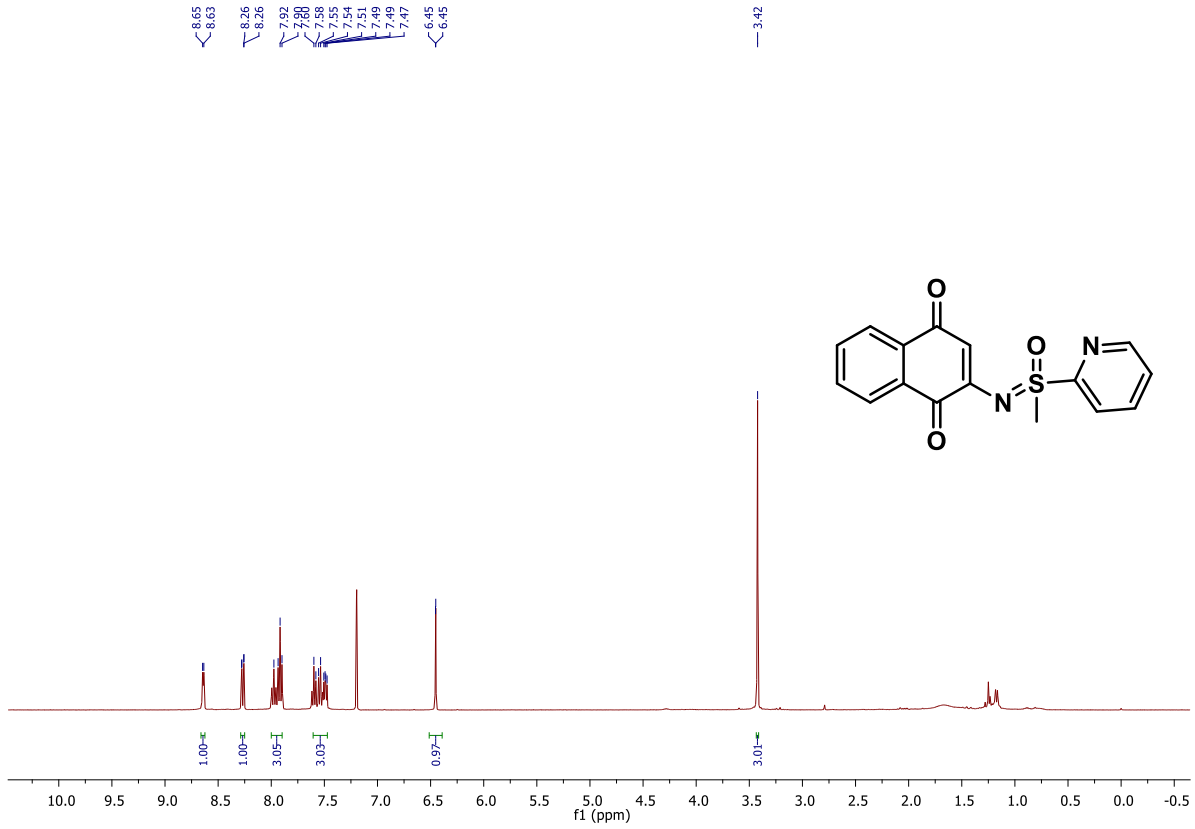
^{13}C {^{1}H} NMR (101 MHz) of 3h in $CDCl_3$



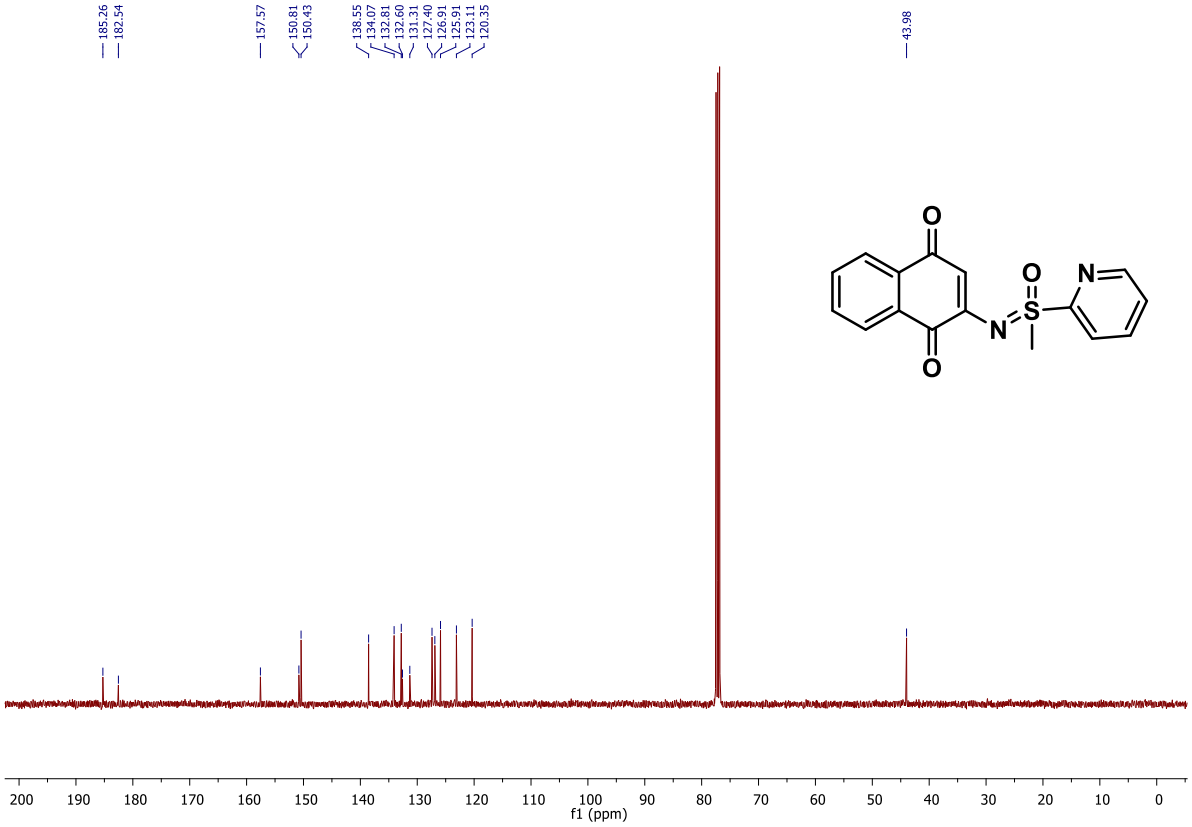
HRMS of 3h



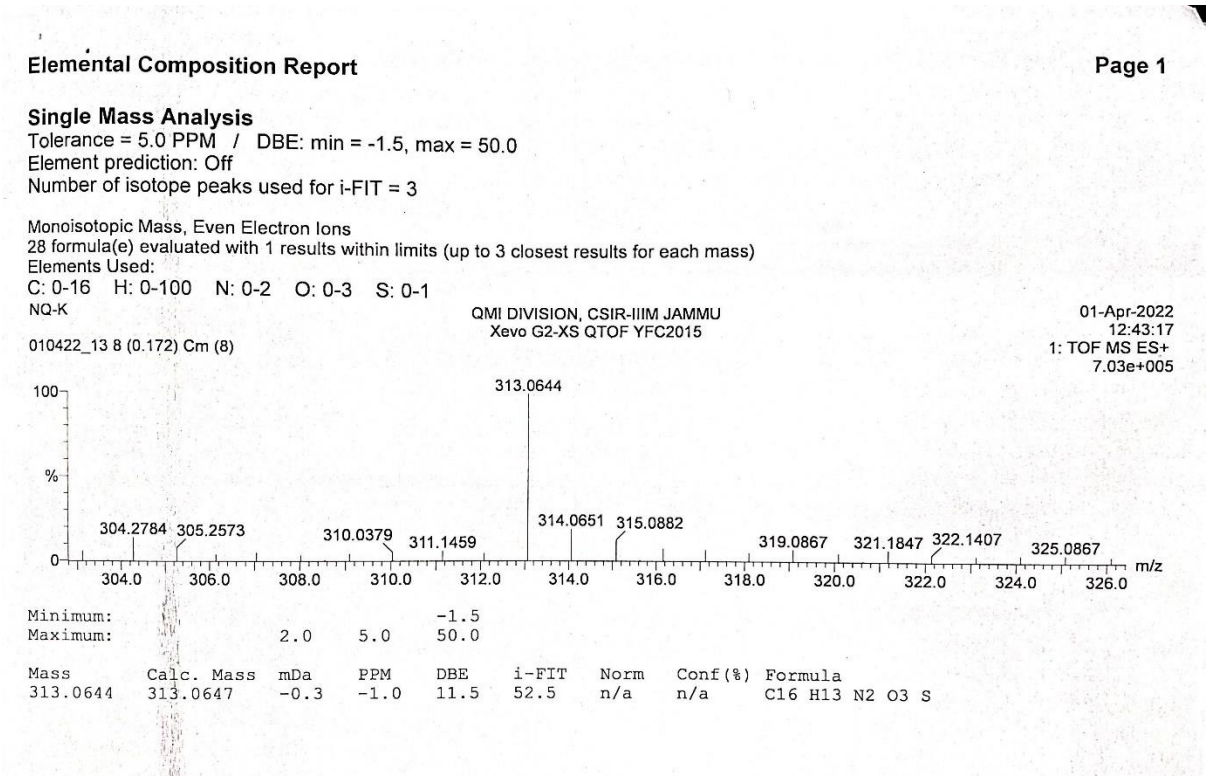
^{1}H NMR (400 MHz) of 3i in $CDCl_3$



^{13}C {^{1}H} NMR (101 MHz) of 3i in $CDCl_3$



HRMS of 3i



Elemental Composition Report Page 1

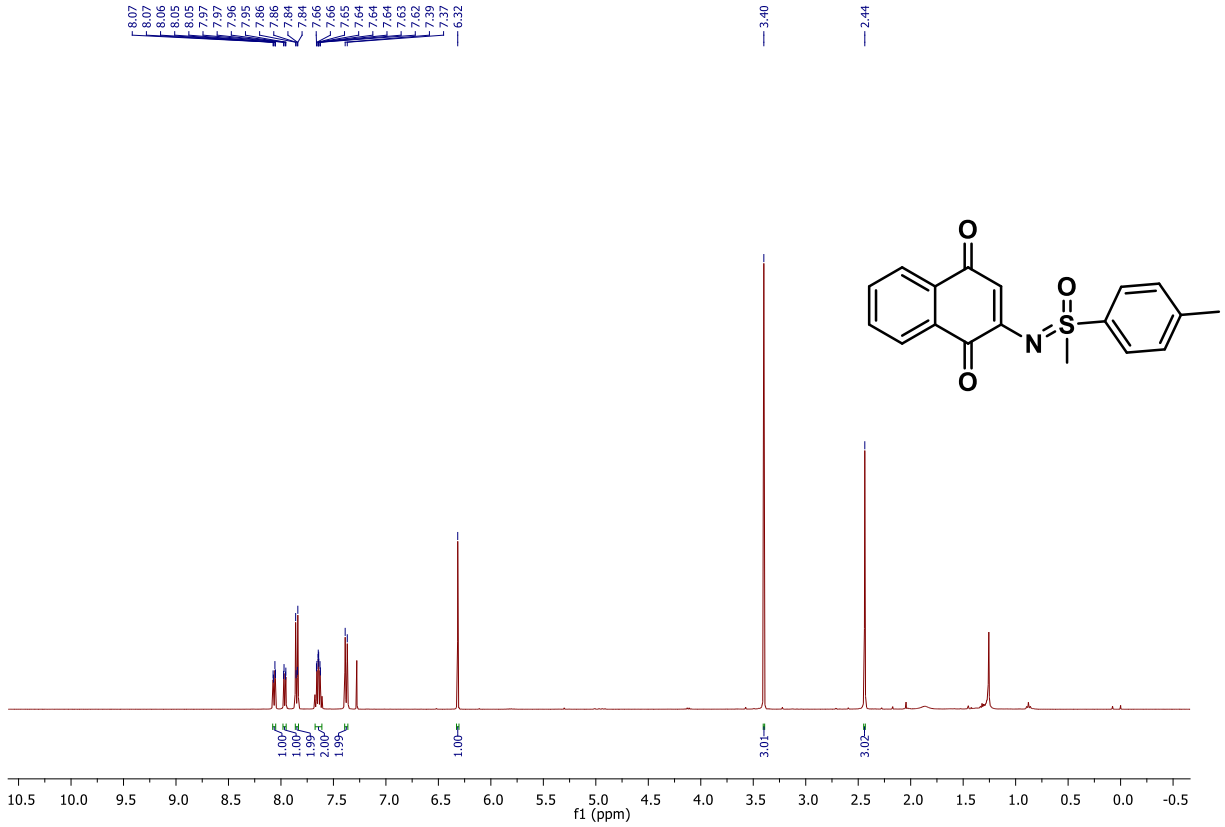
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
28 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-16 H: 0-100 N: 0-2 O: 0-3 S: 0-1

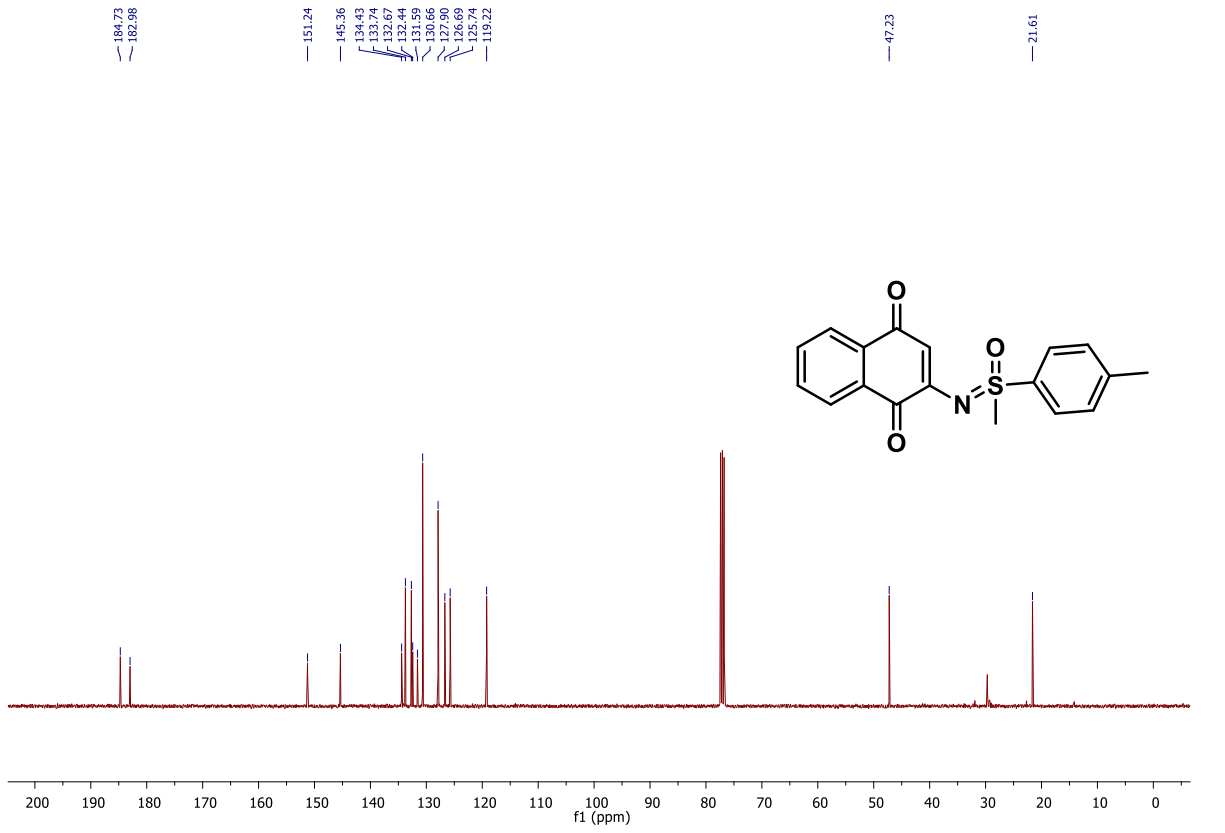
NQ-K
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015
01-Apr-2022
12:43:17
010422_13 8 (0.172) Cm (8)
1: TOF MS ES+
7.03e+005

Minimum:				-1.5				
Maximum:		2.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
313.0644	313.0647	-0.3	-1.0	11.5	52.5	n/a	n/a	C16 H13 N2 O3 S

^{1}H NMR (400 MHz) of 3j in $CDCl_3$



^{13}C {^{1}H} NMR (101 MHz) of 3j in $CDCl_3$



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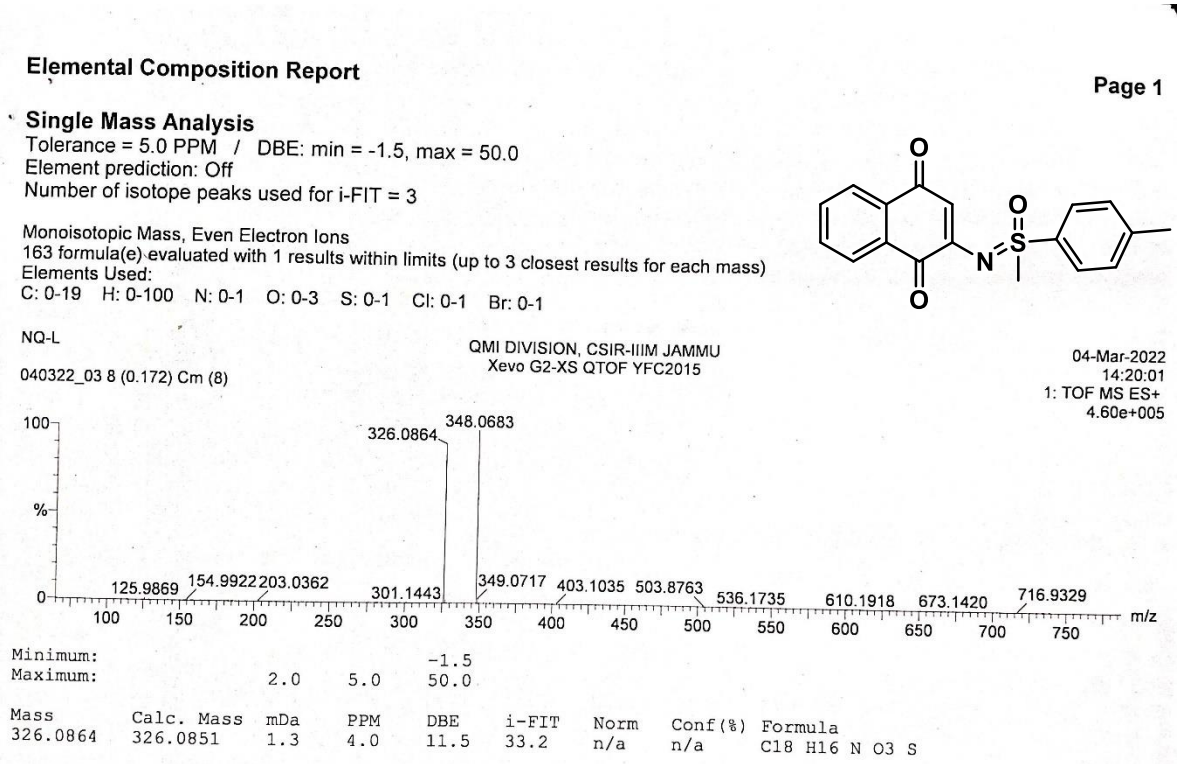
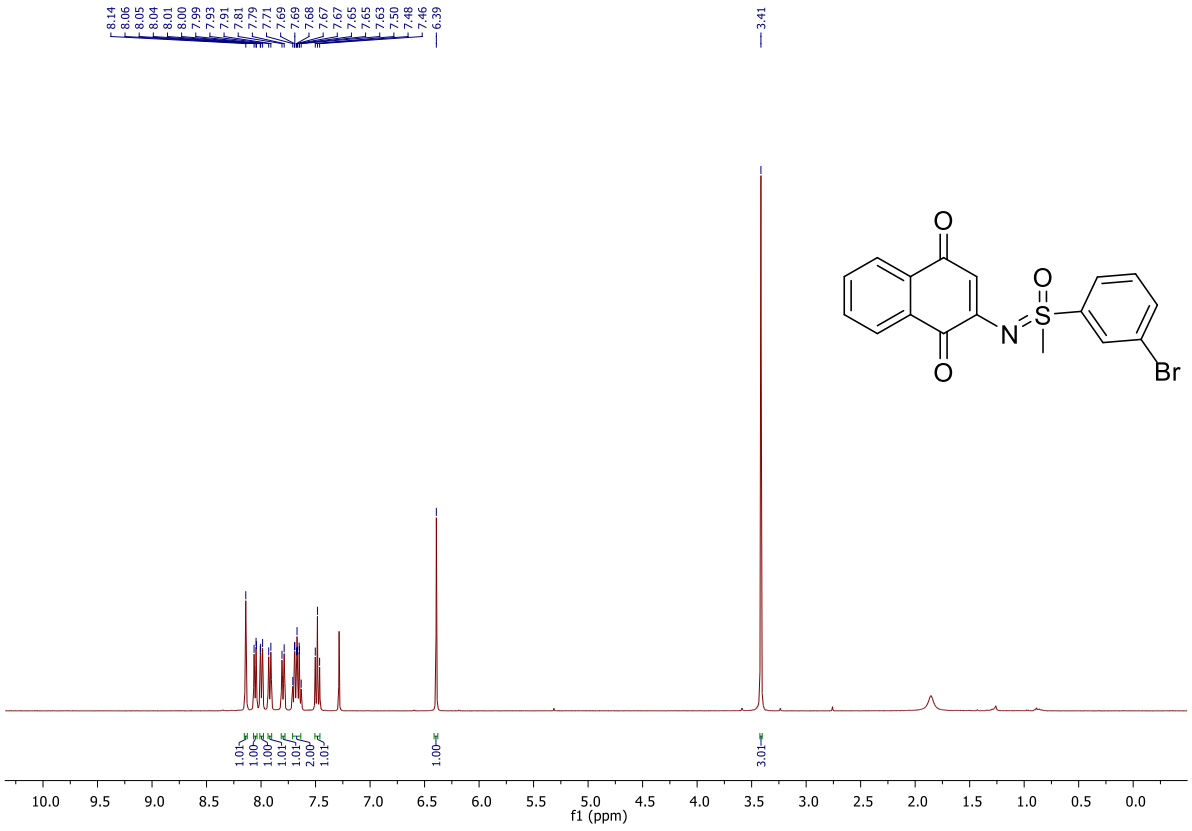
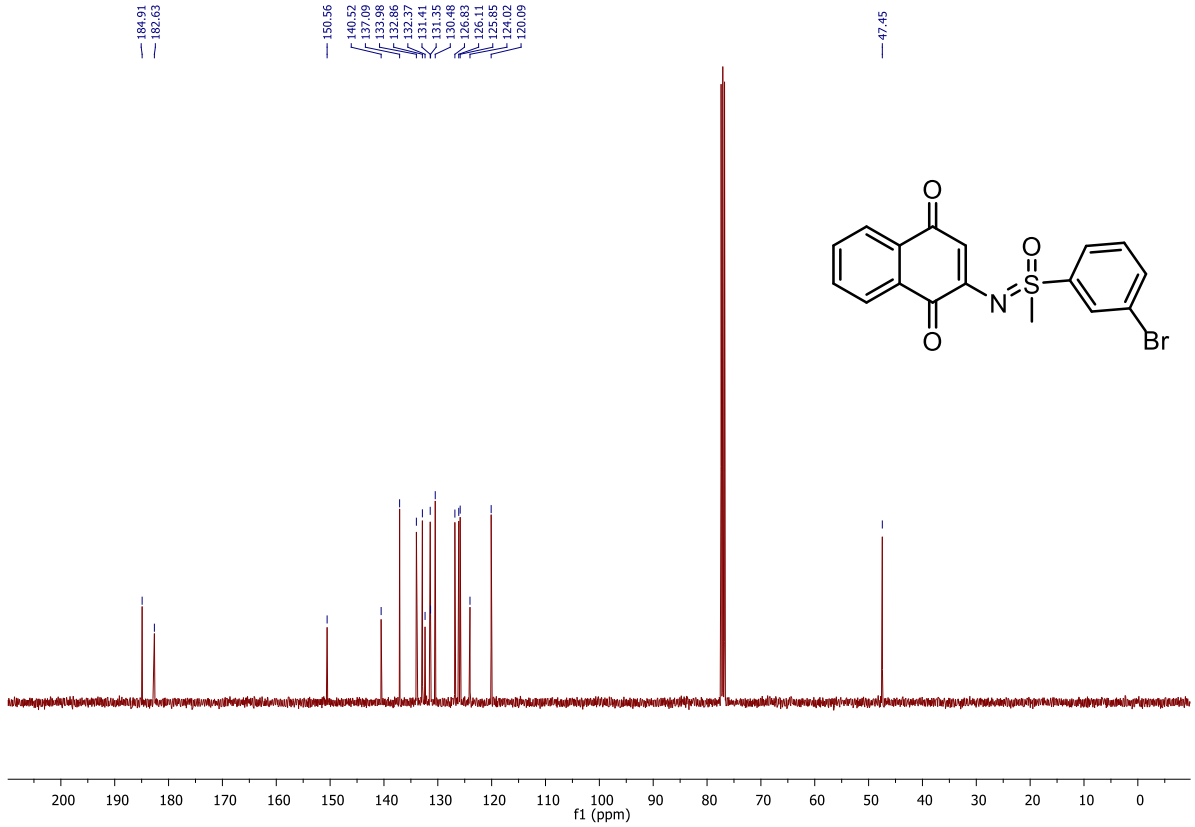


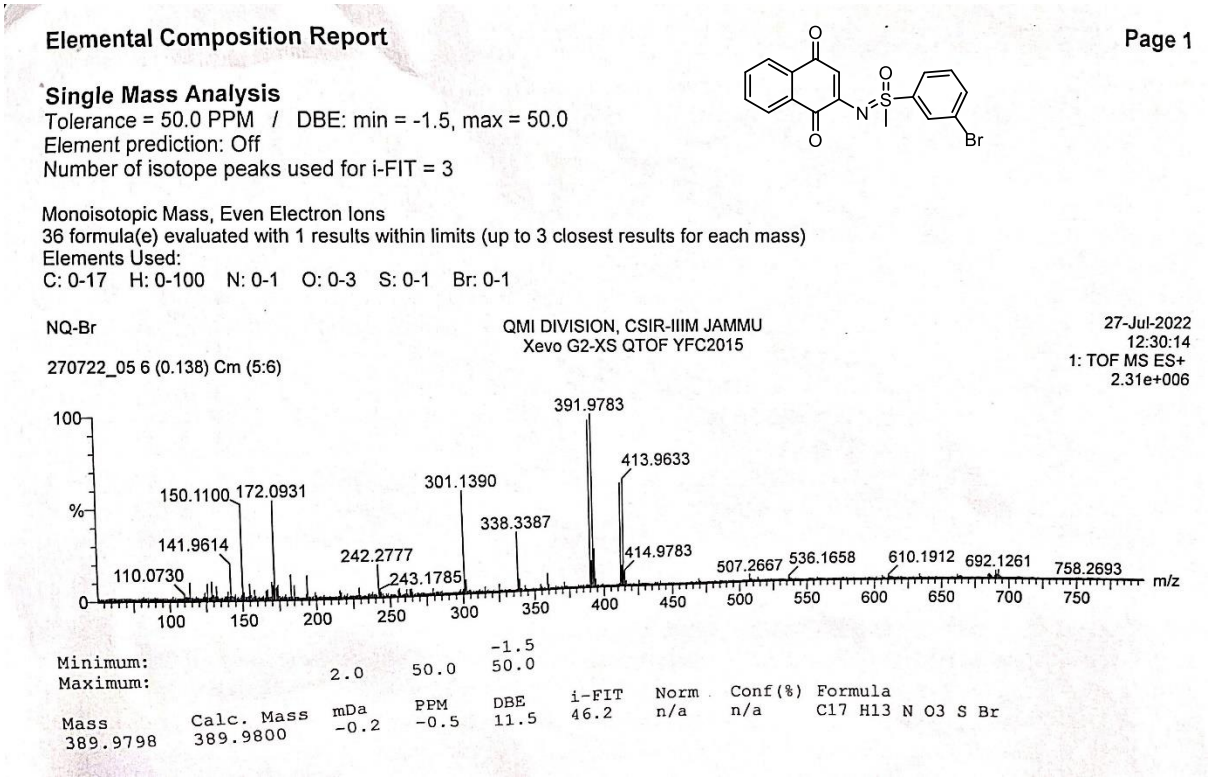
^{1}H NMR (400 MHz) of 3k in $CDCl_3$



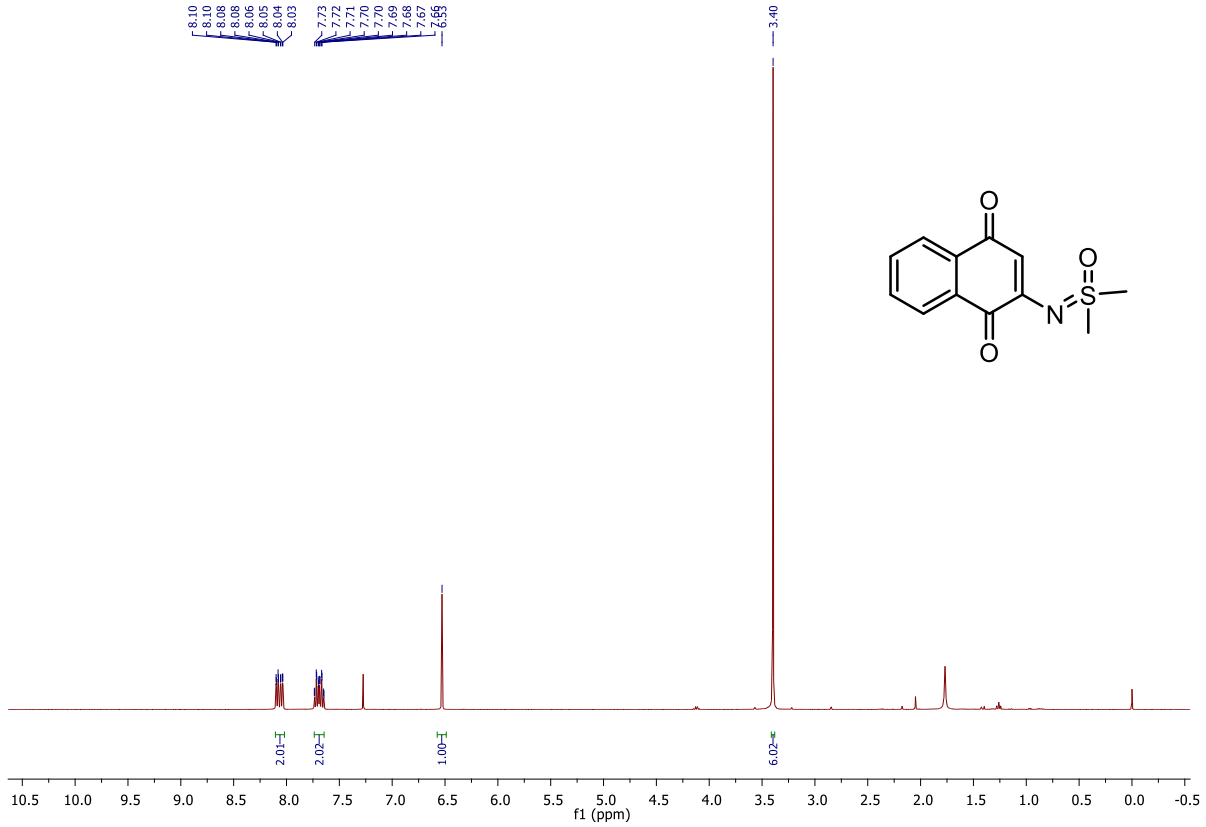
^{13}C {^{1}H} NMR (101 MHz) of 3k in $CDCl_3$



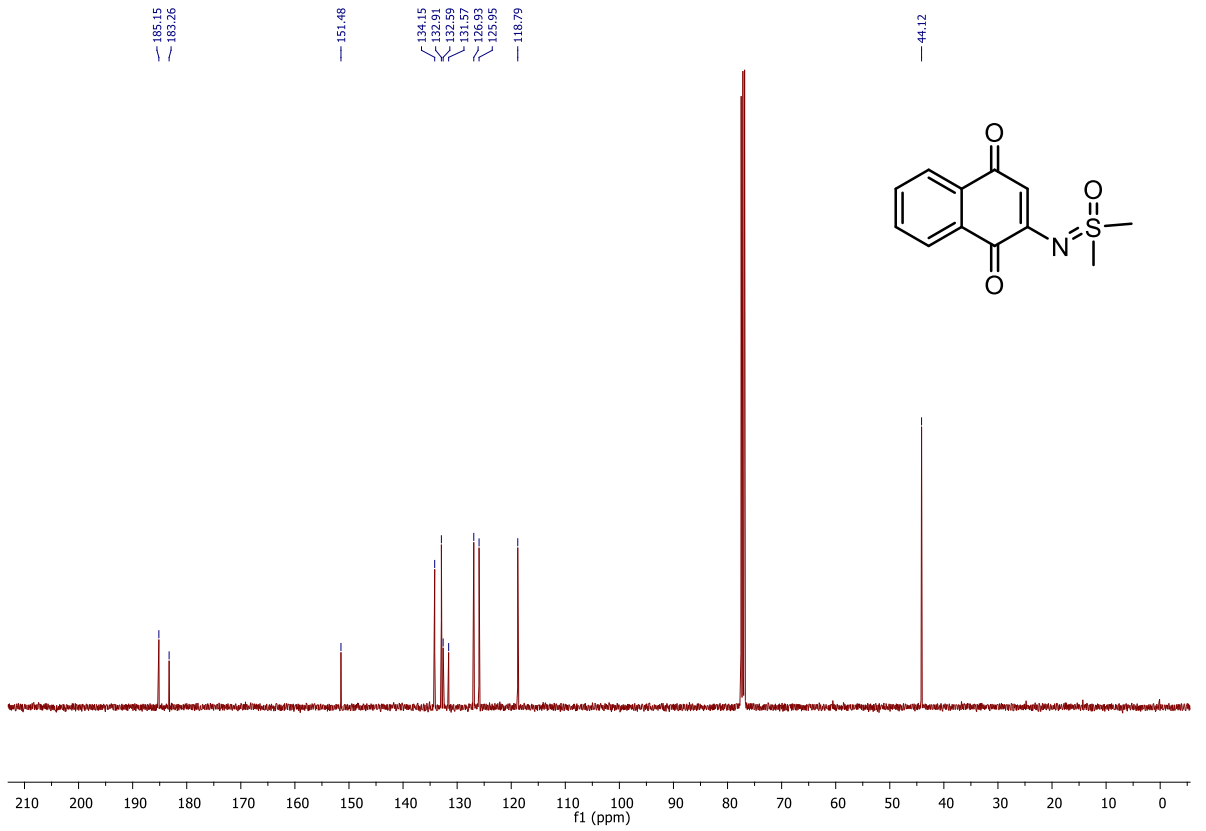
HRMS of 3k



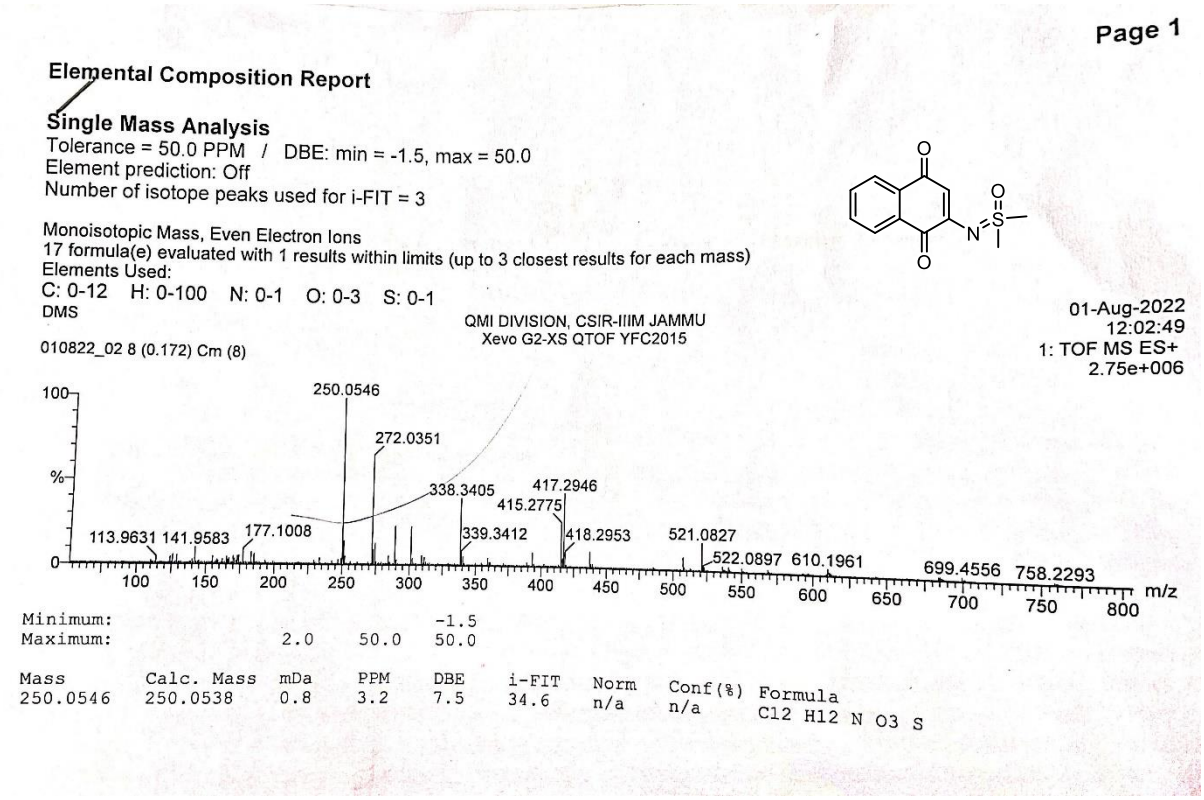
^{1}H NMR (400 MHz) of 3l in $CDCl_3$



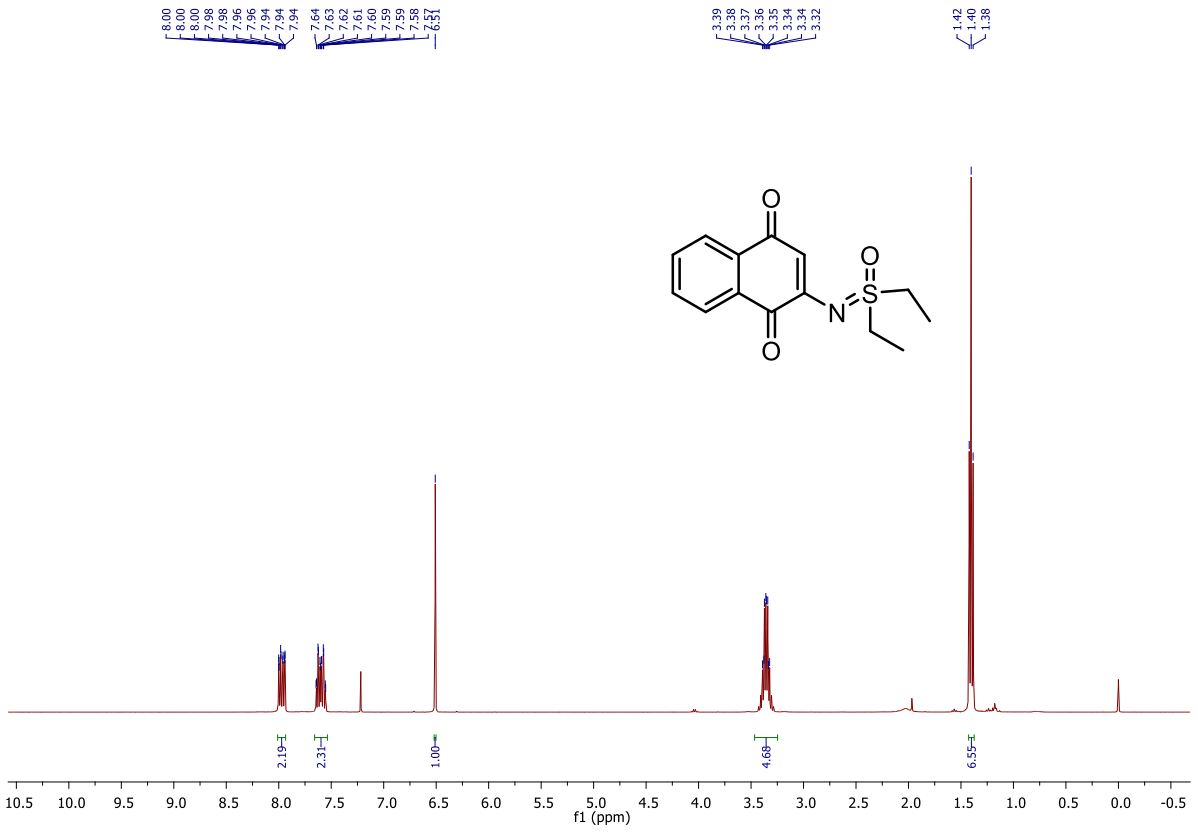
^{13}C {^{1}H} NMR (101 MHz) of 3l in $CDCl_3$



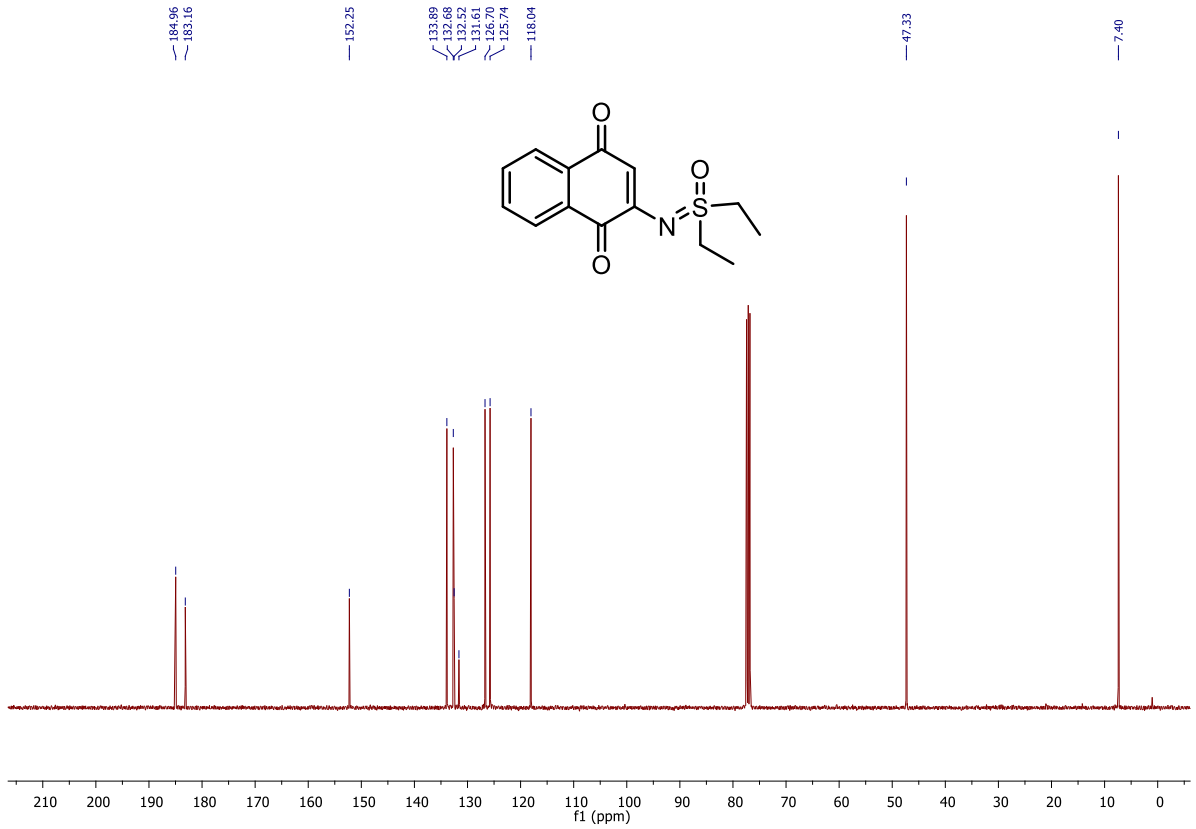
HRMS of 3l



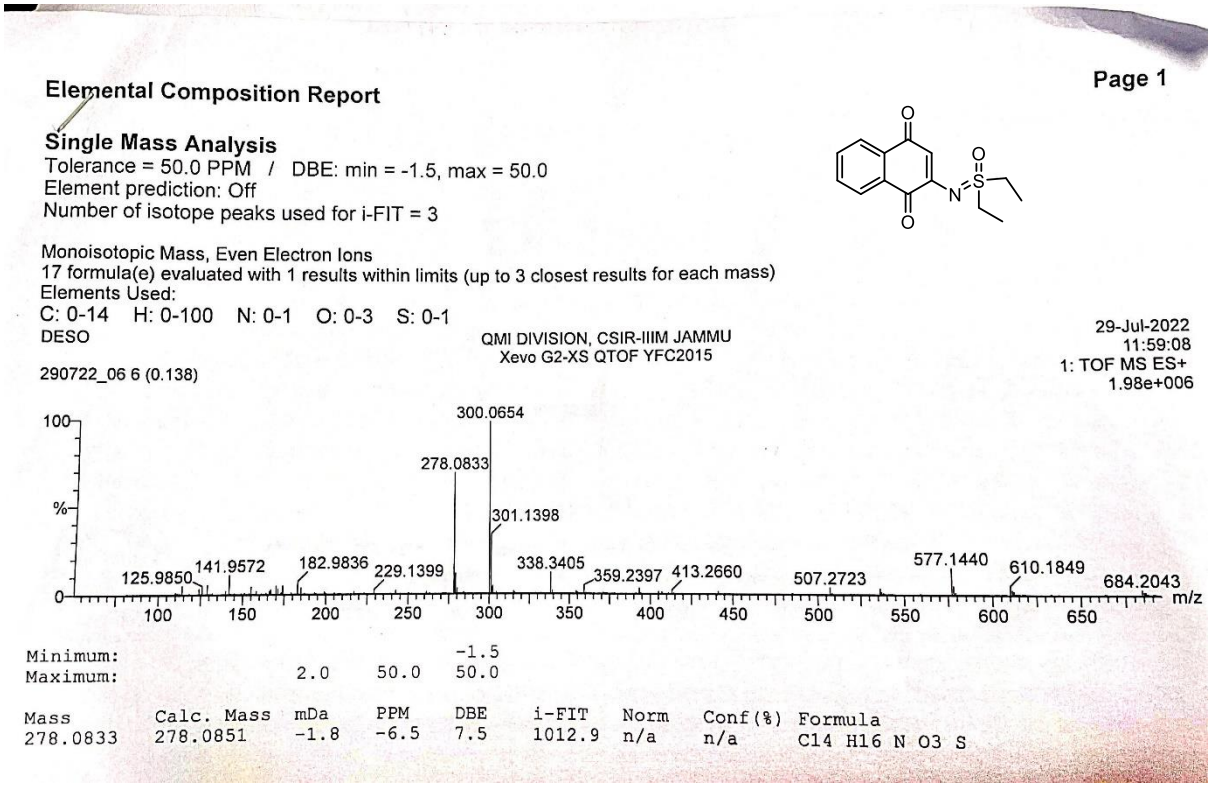
^{1}H NMR (400 MHz) of 3m in $CDCl_3$



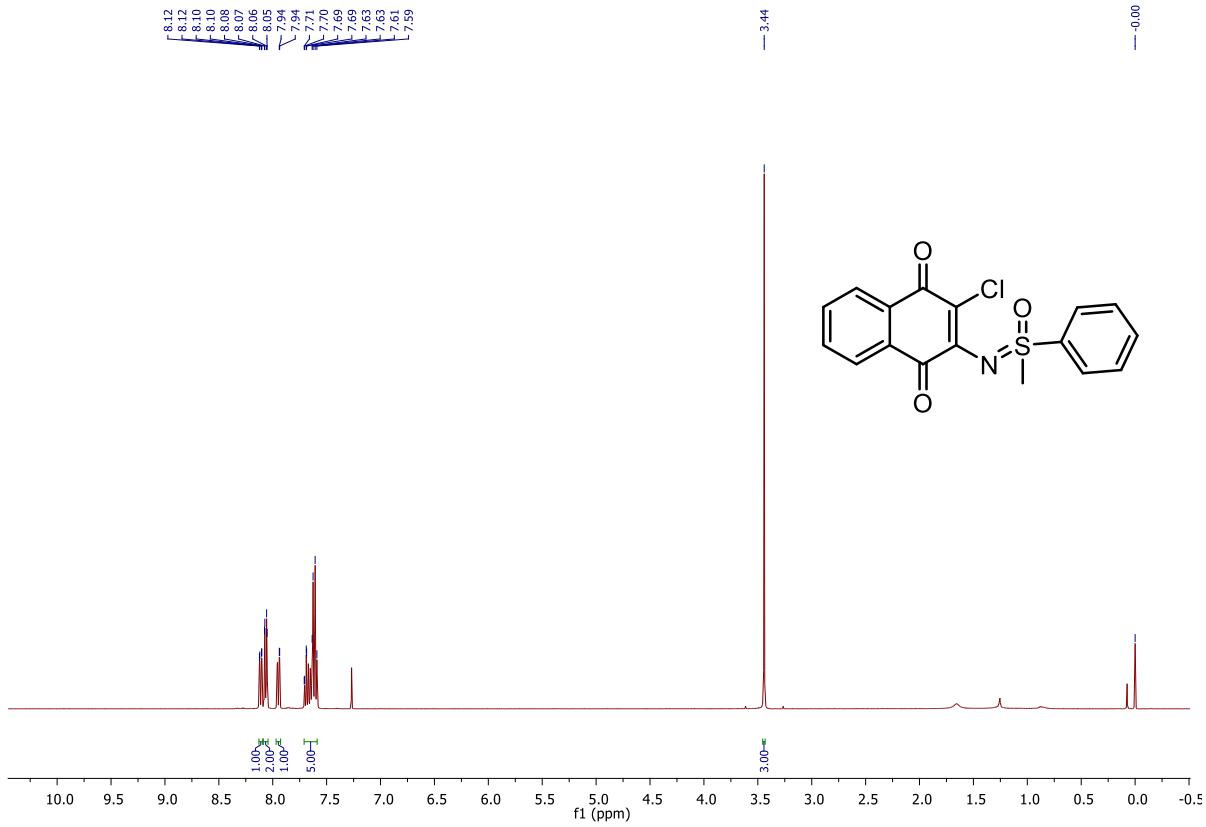
^{13}C {^{1}H} NMR (101 MHz) of 3m in $CDCl_3$



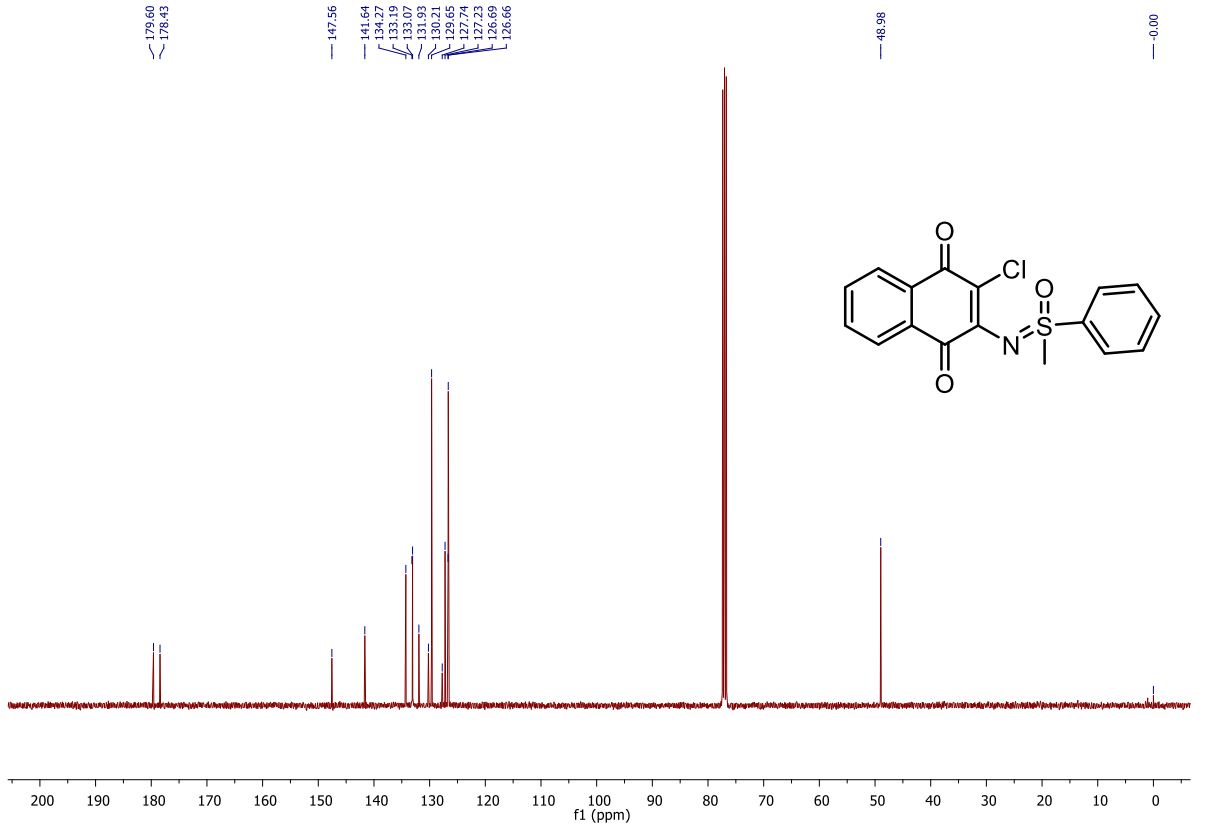
HRMS of 3m



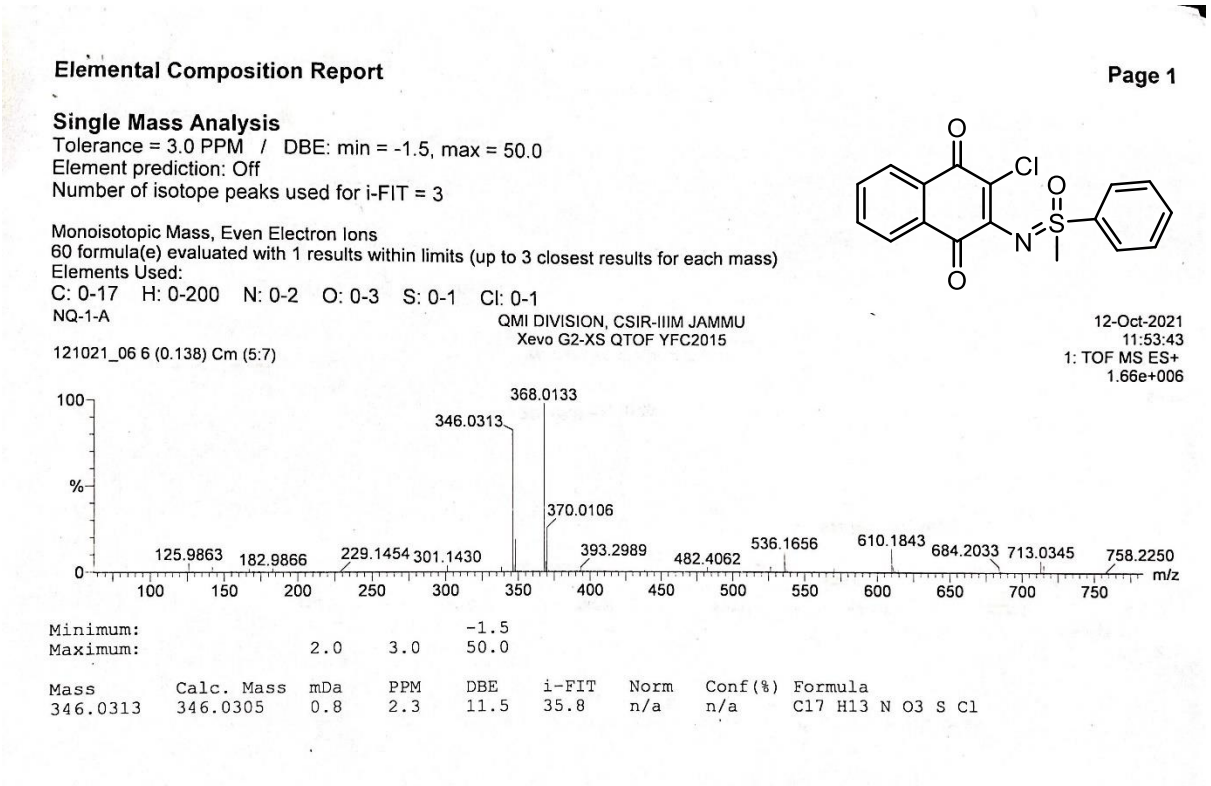
^{1}H NMR (400 MHz) of 5a in $CDCl_3$



^{13}C {^{1}H} NMR (101 MHz) of 5a in $CDCl_3$



HRMS of 5a



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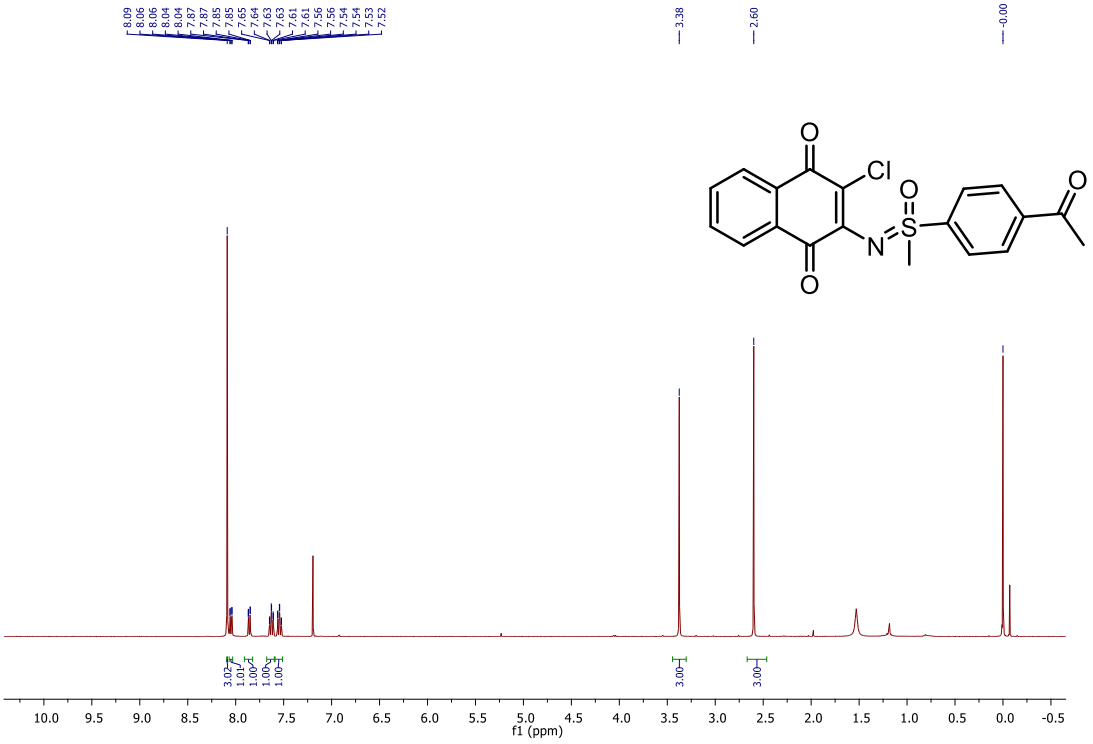

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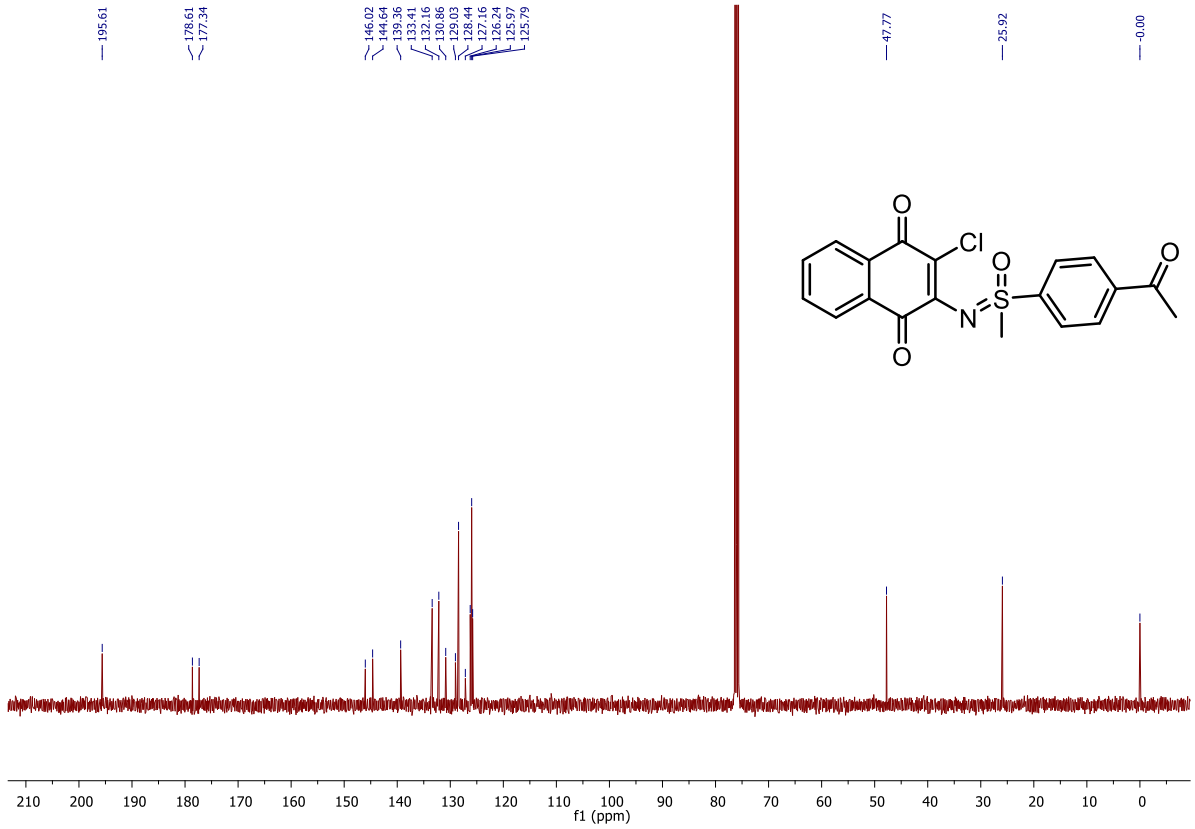

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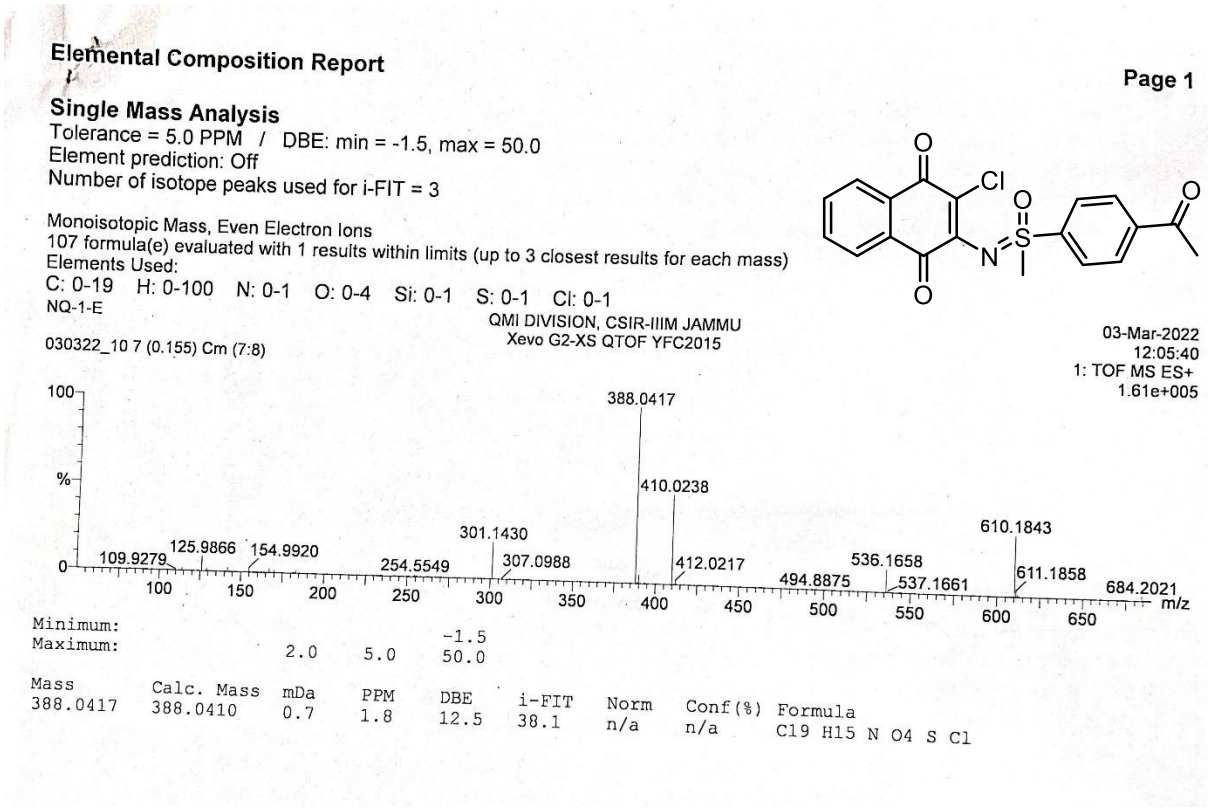

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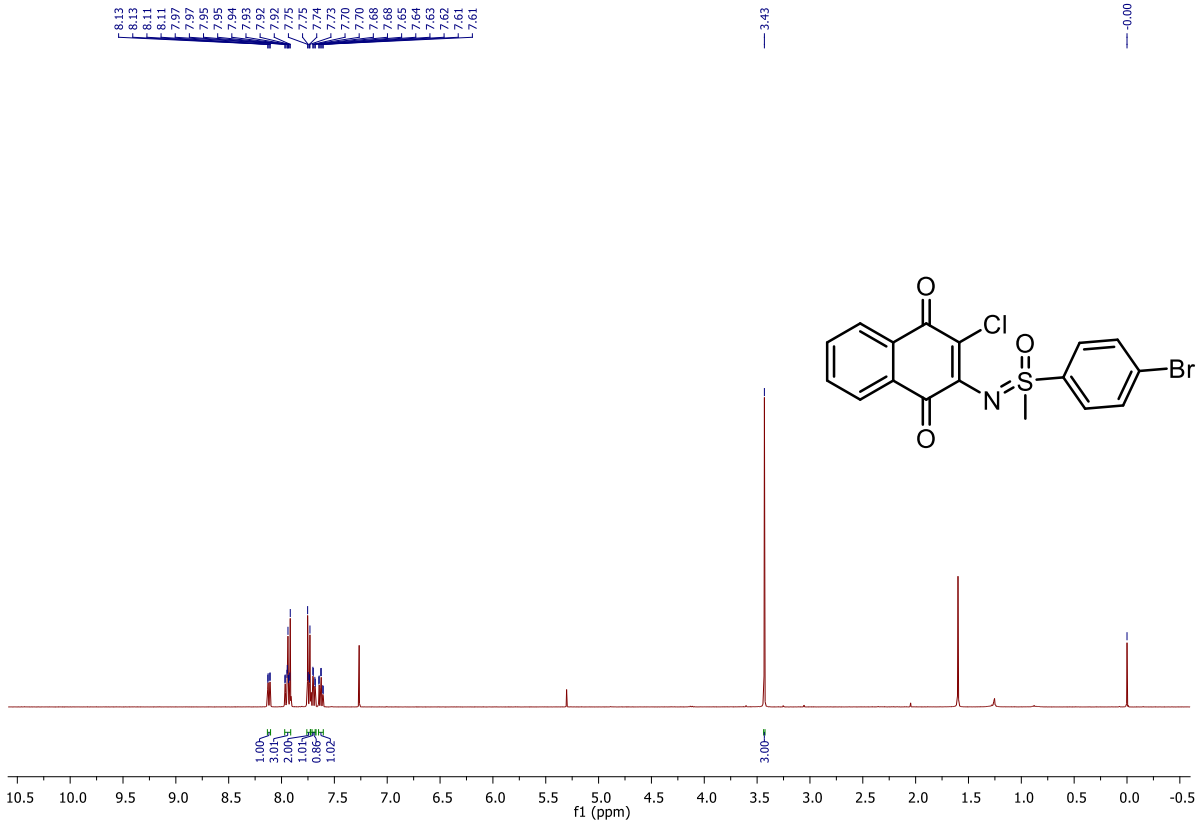
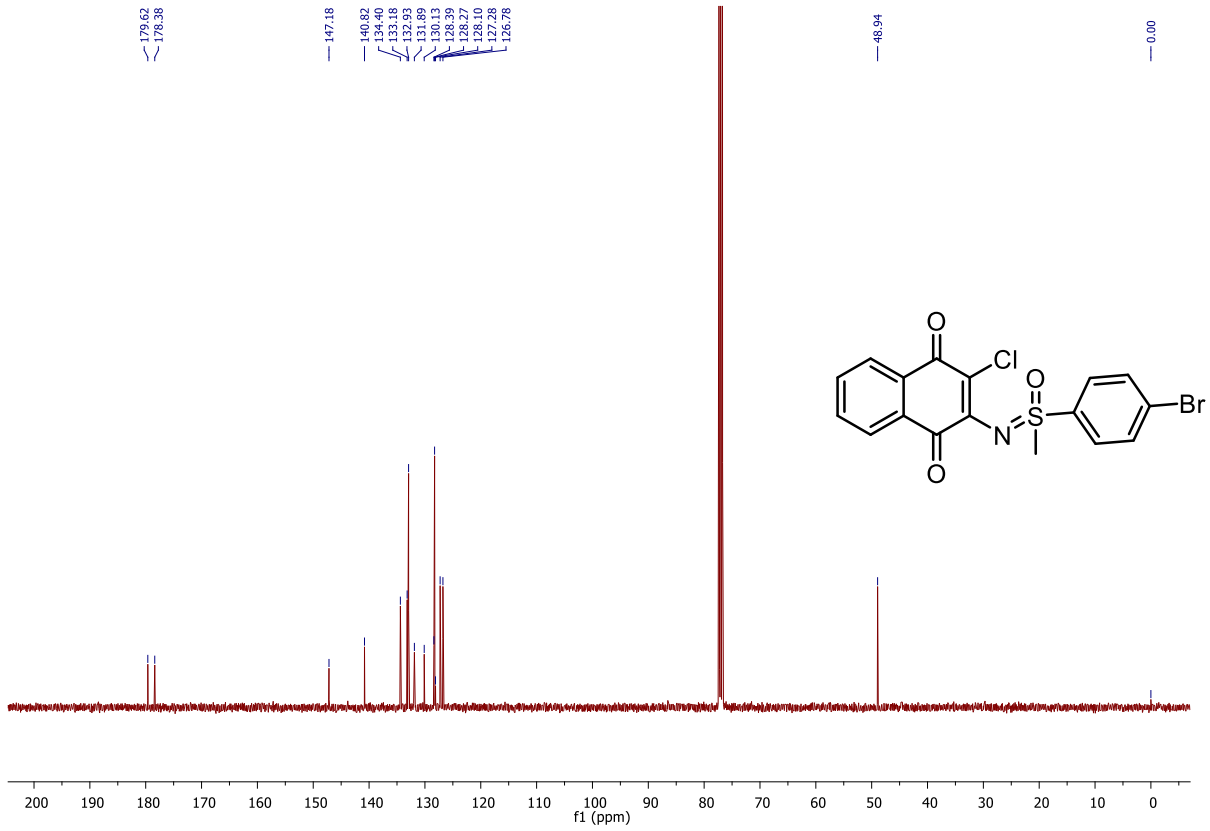


^{13}C {^{1}H} NMR (101 MHz) of 5c in $CDCl_3$



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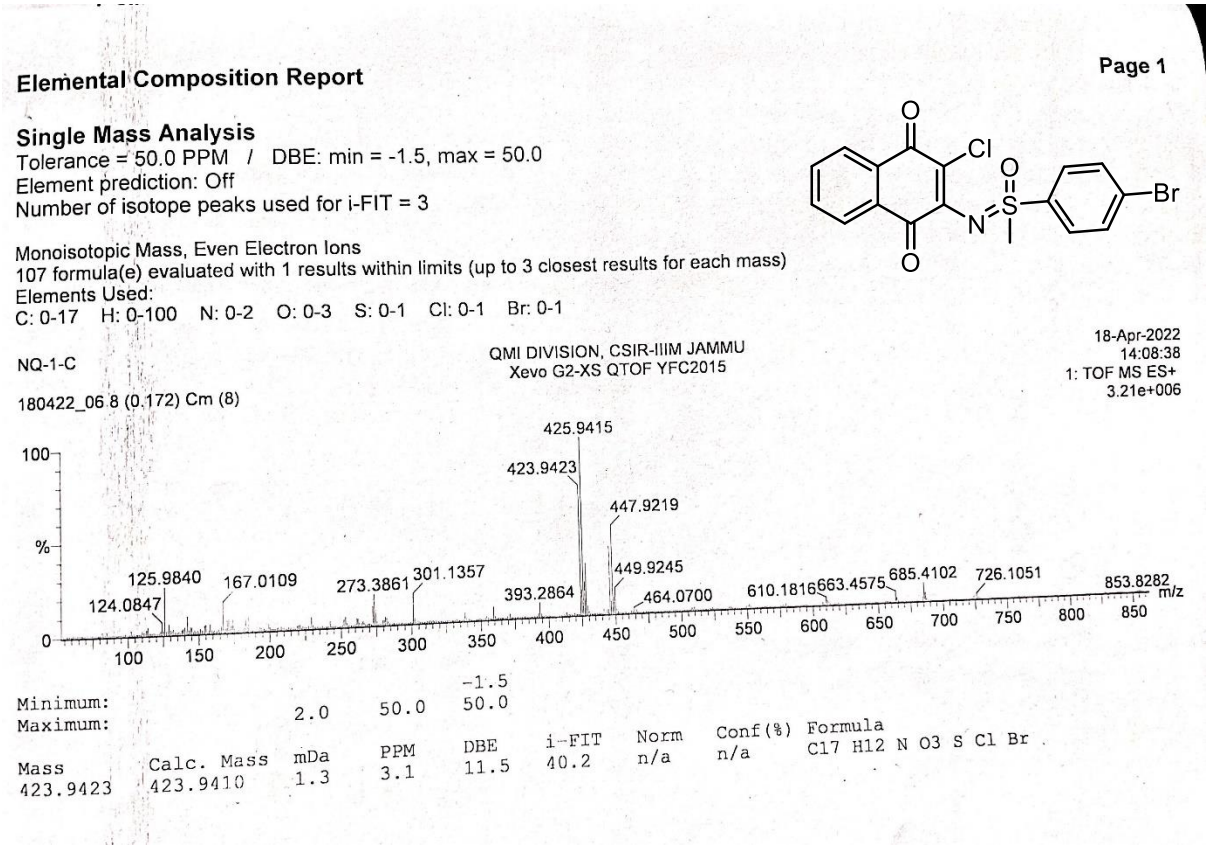
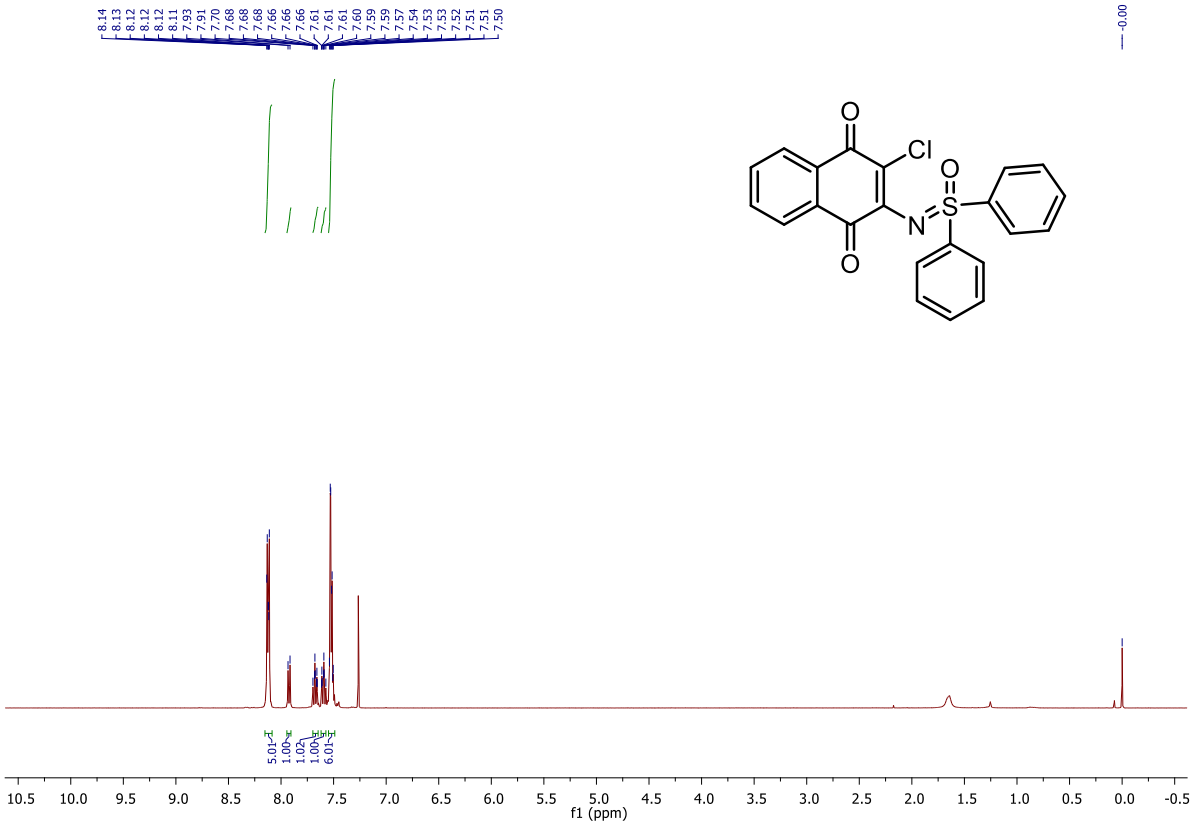
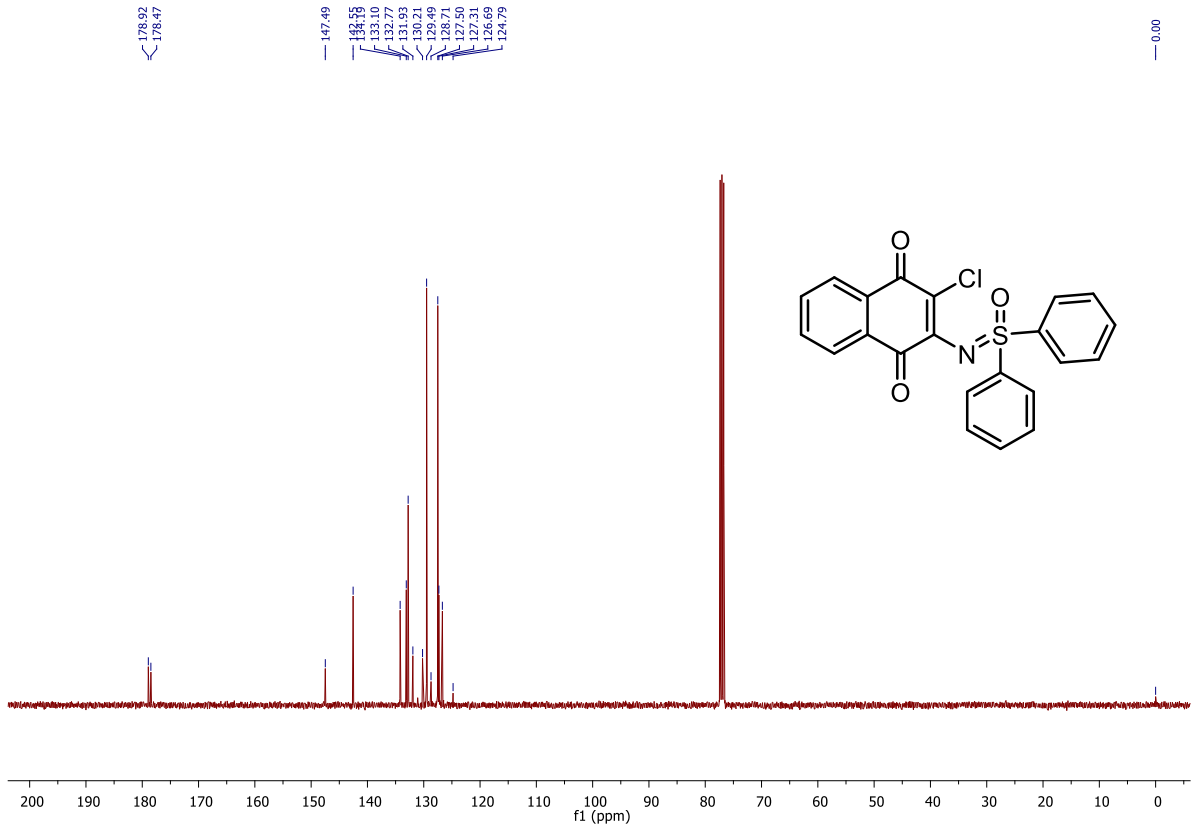


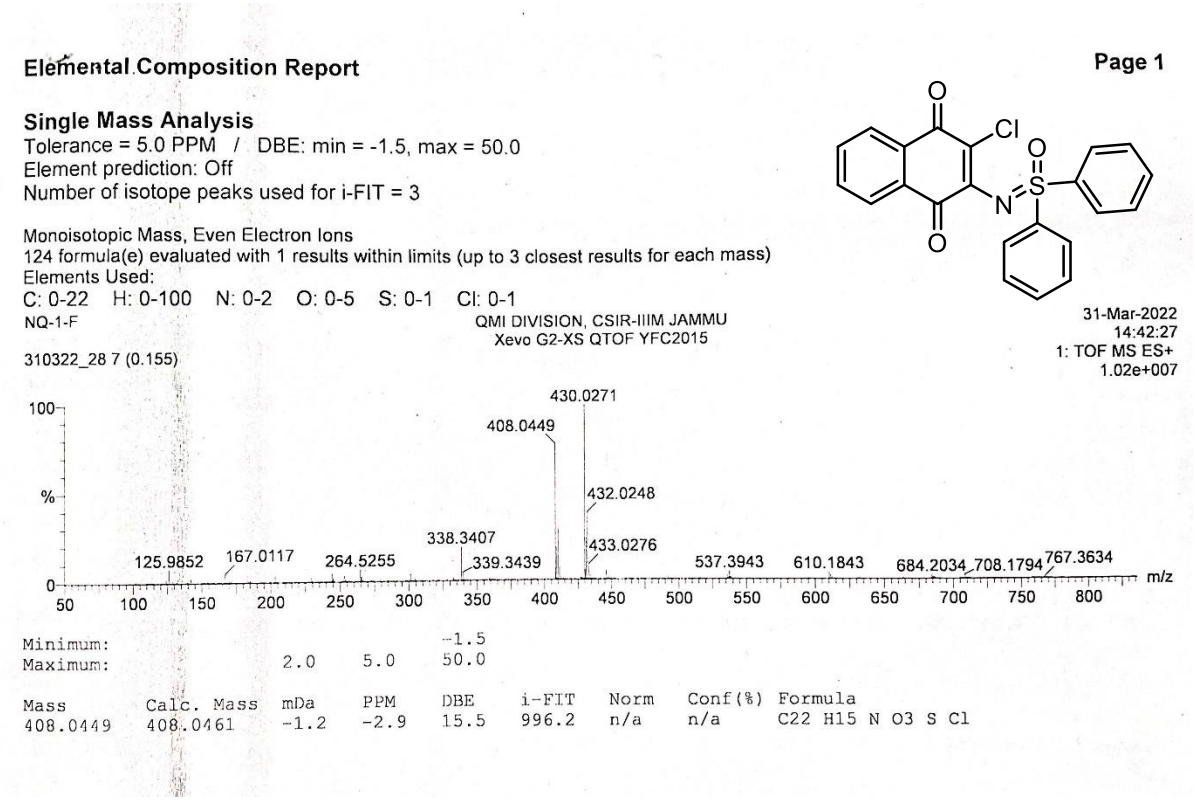
^{1}H NMR (400 MHz) of 5d in $CDCl_3$



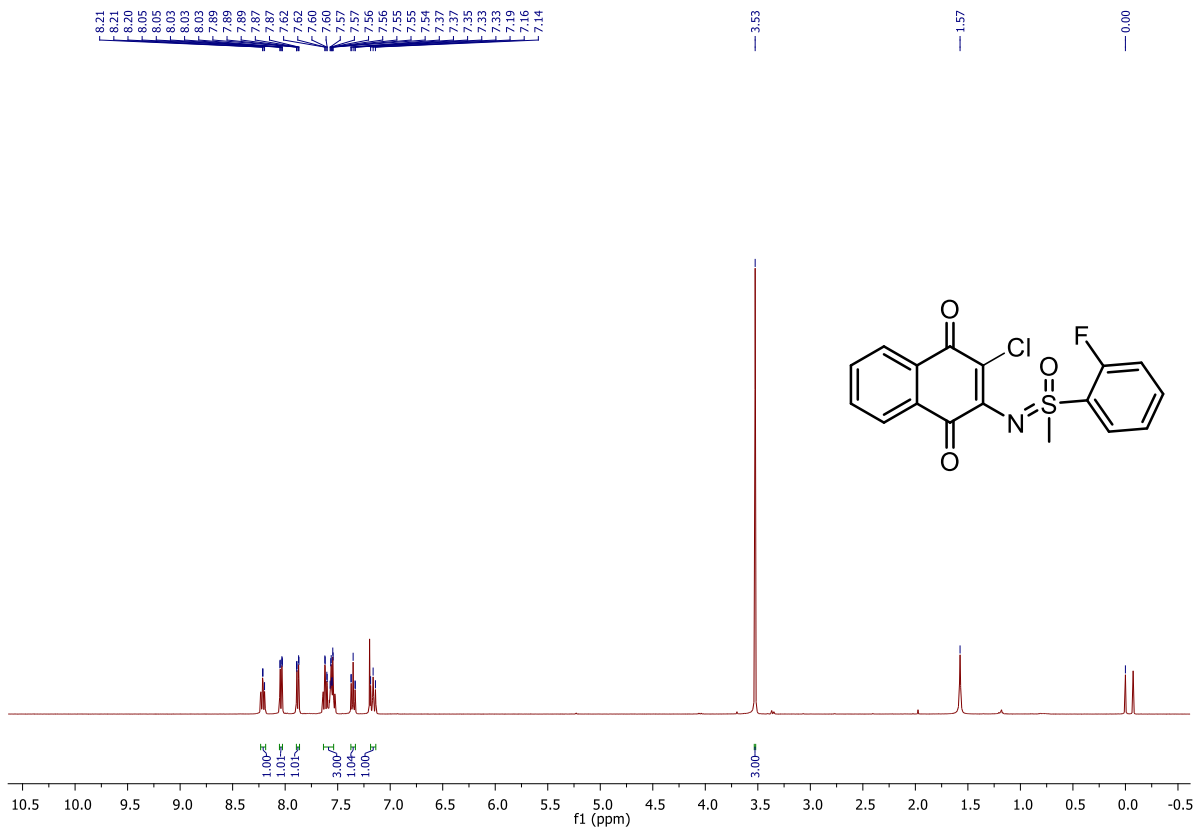
^{13}C {^{1}H} NMR (101 MHz) of 5d in $CDCl_3$



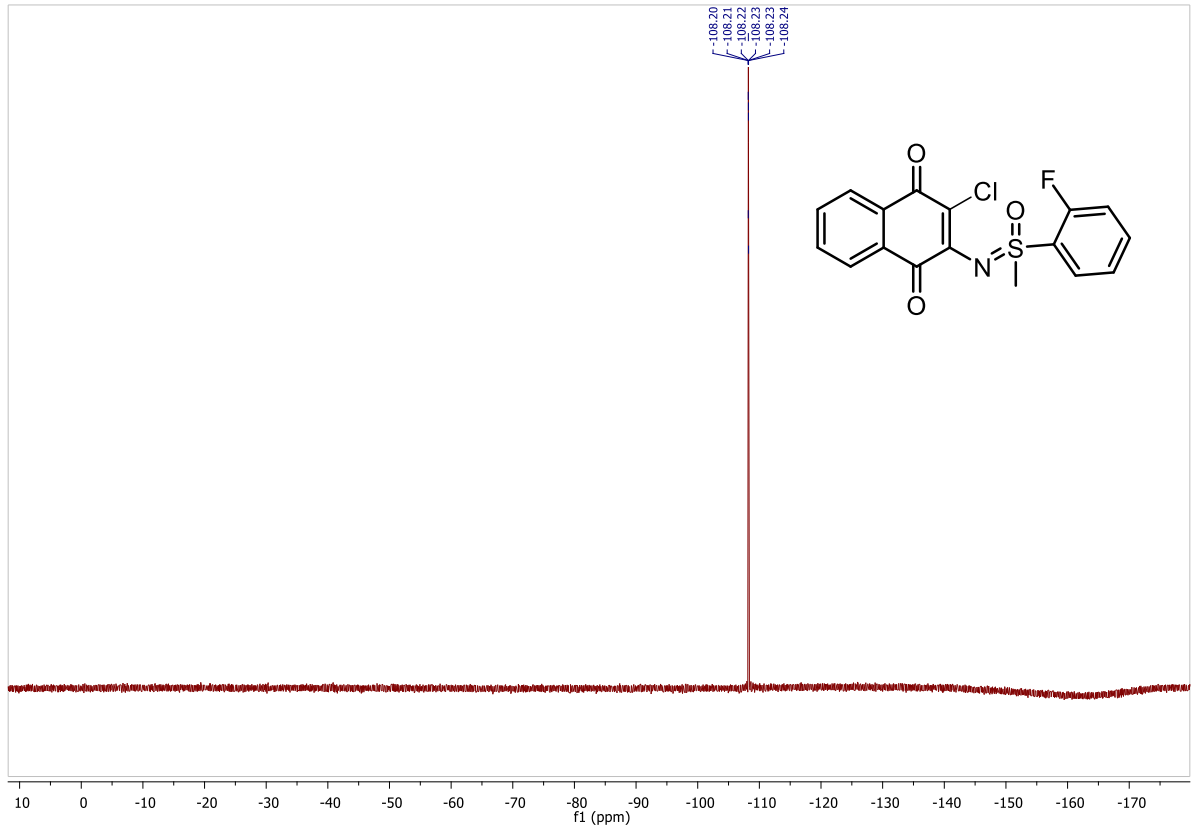
HRMS of 5d



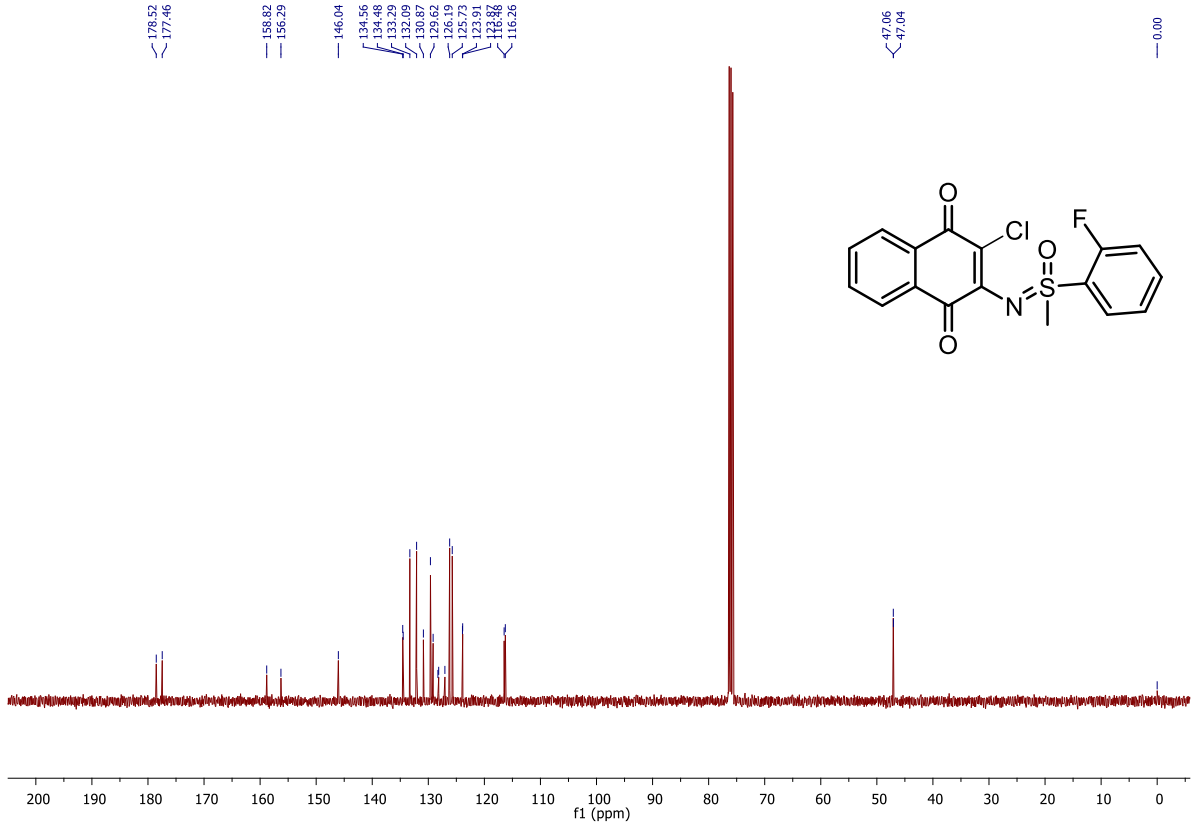
^{1}H NMR (400 MHz) of 5e in $CDCl_3$



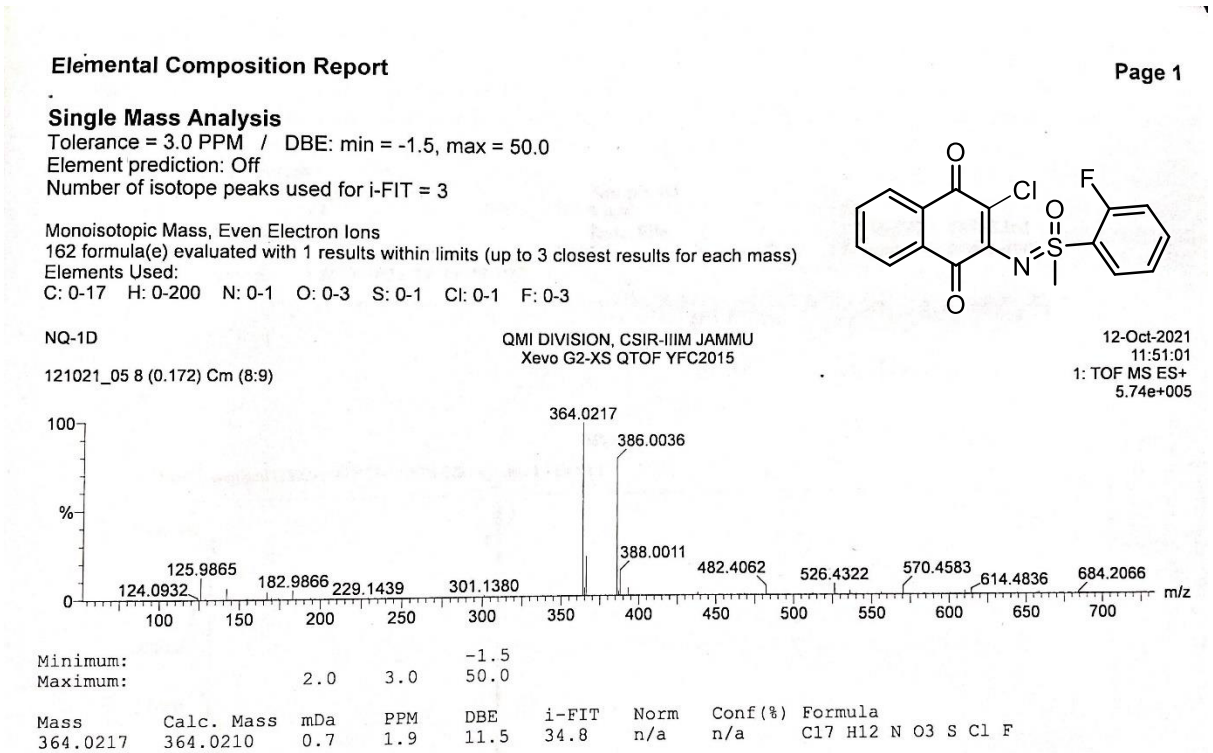
^{19}F NMR (377 MHz) of 5e in $CDCl_3$



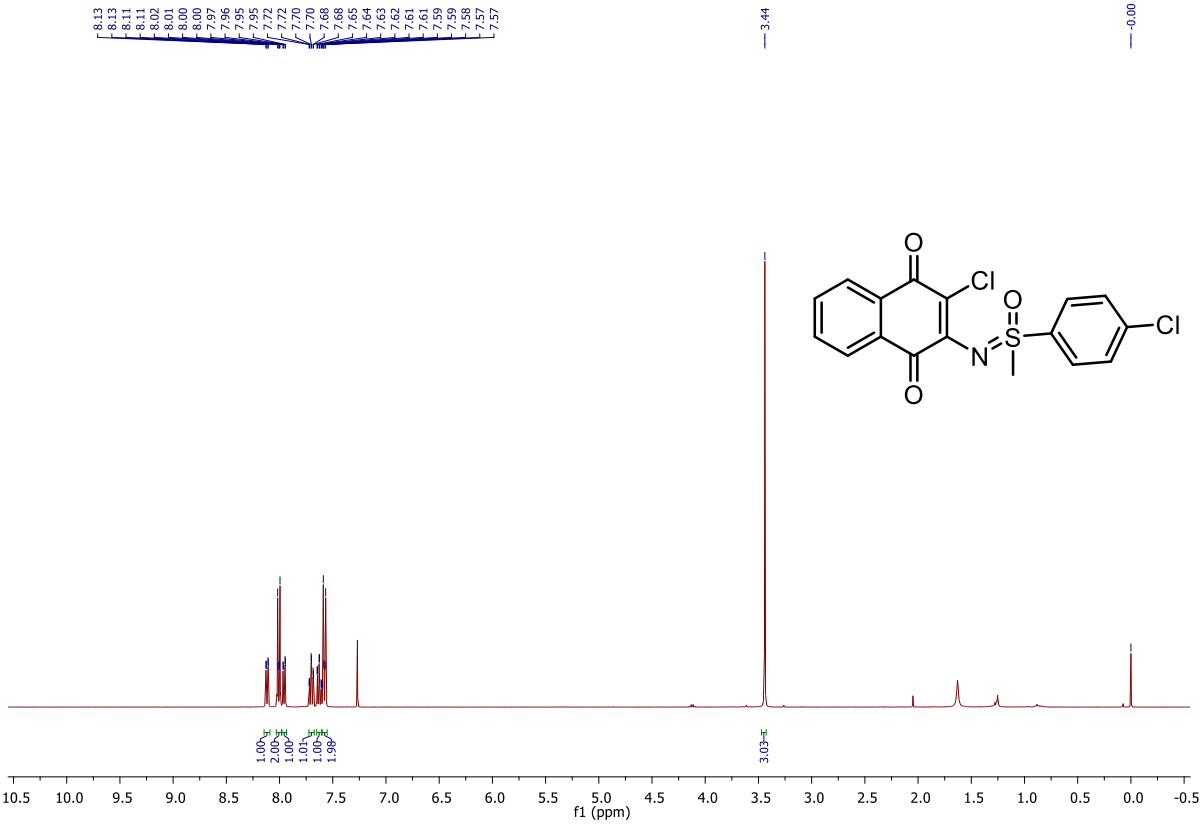
^{13}C {^{1}H} NMR (101 MHz) of 5e in $CDCl_3$



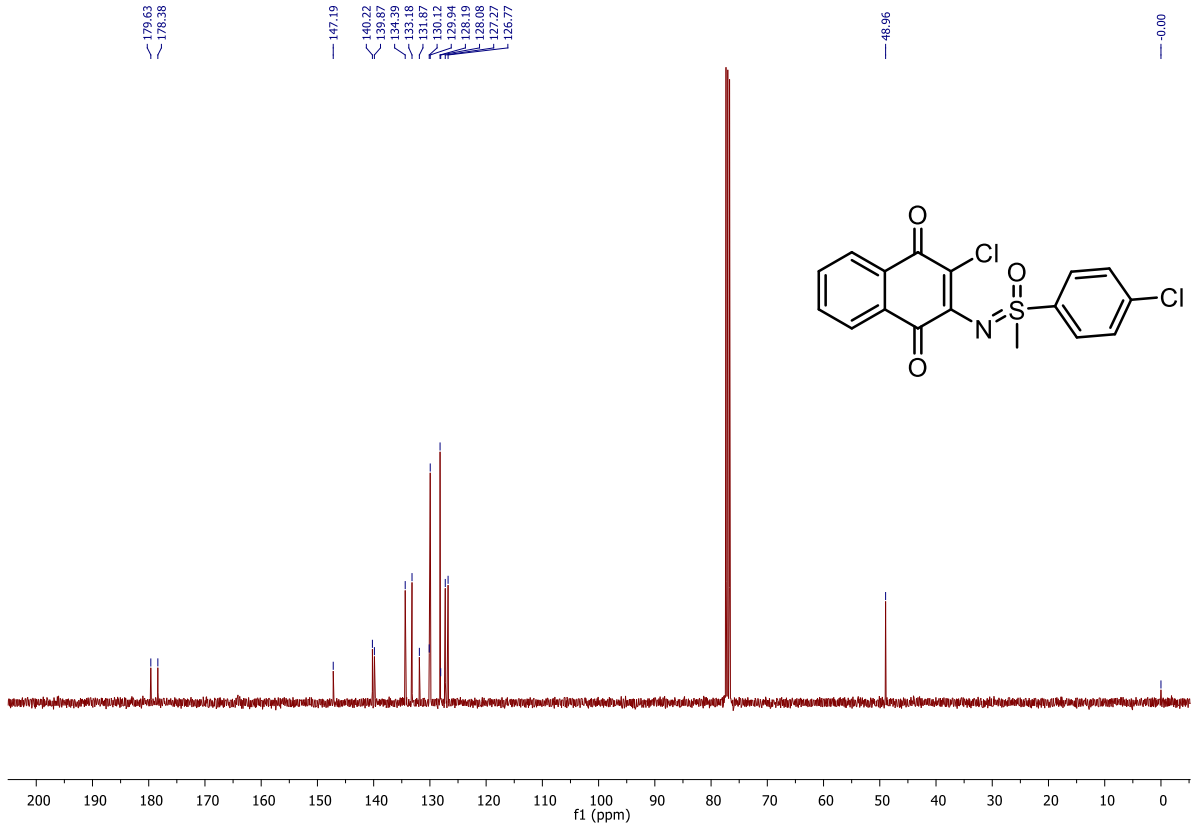
HRMS of 5e



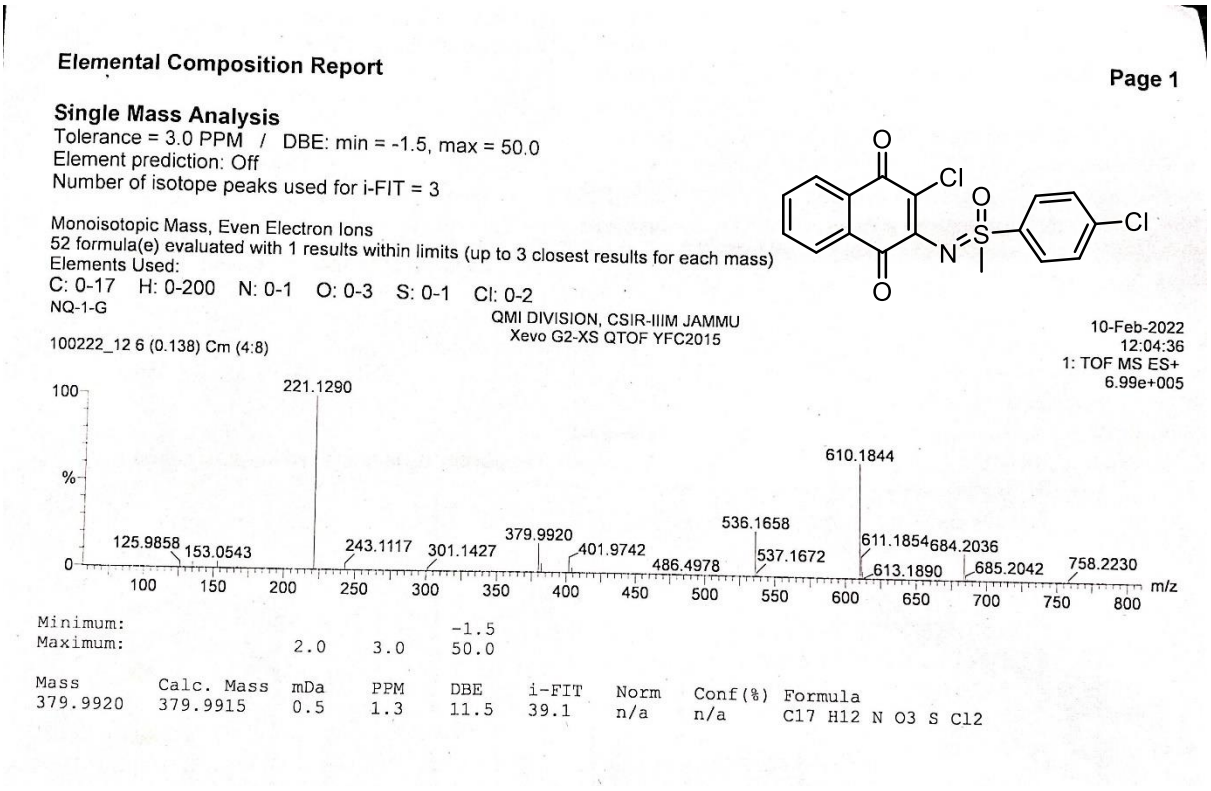
^{1}H NMR (400 MHz) of 5f in $CDCl_3$



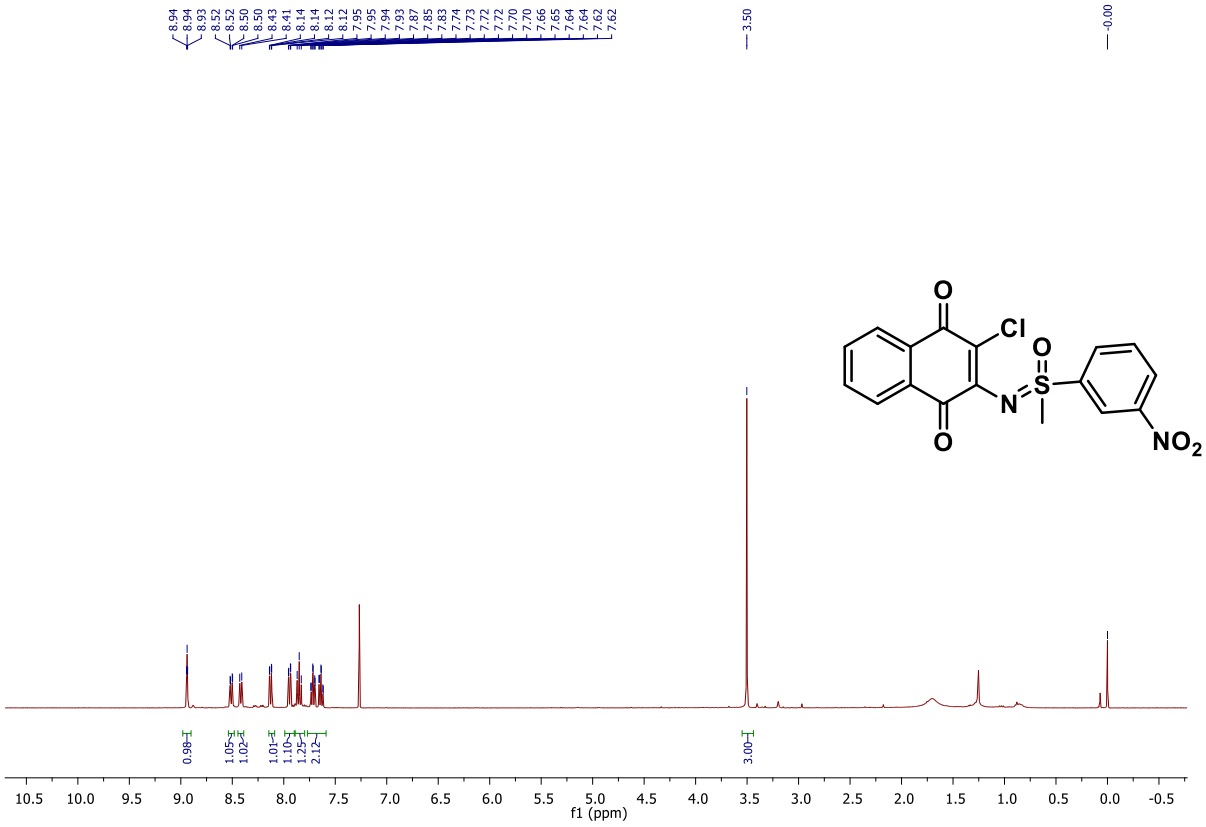
^{13}C {^{1}H} NMR (101 MHz) of 5f in $CDCl_3$



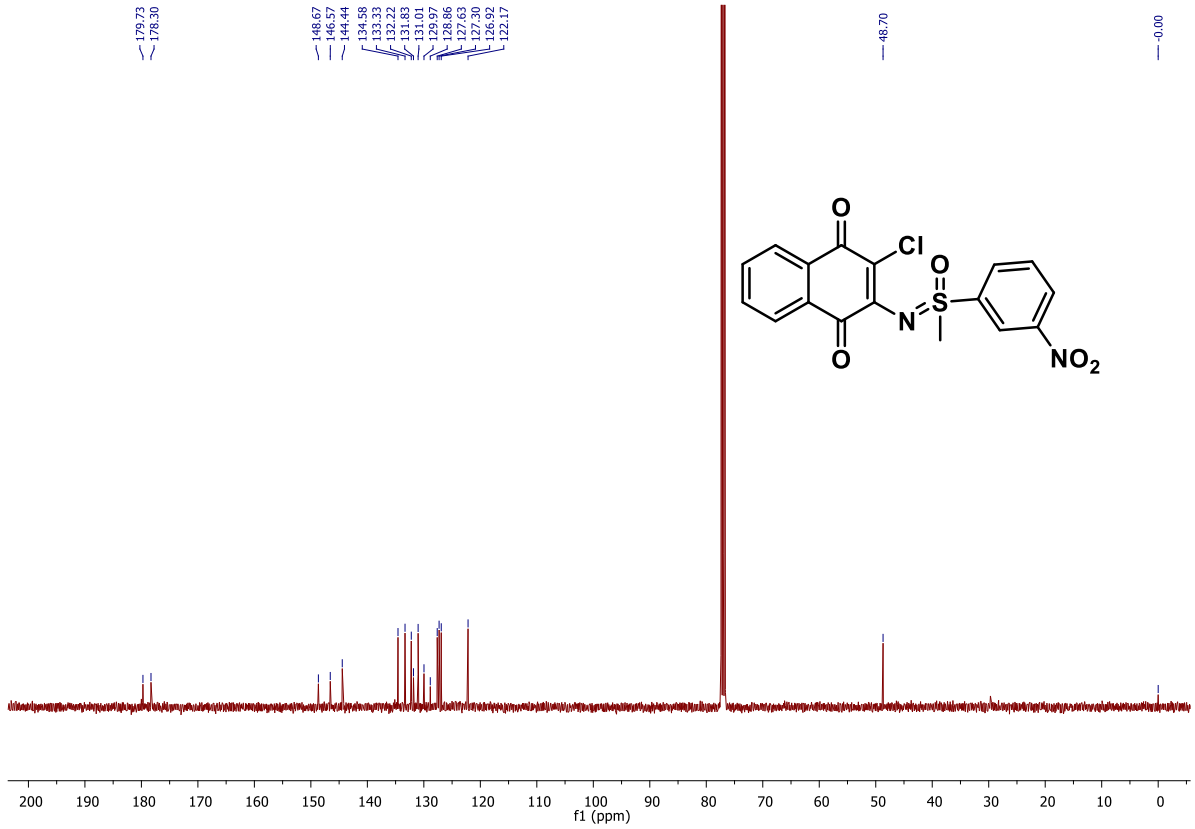
HRMS of 5f



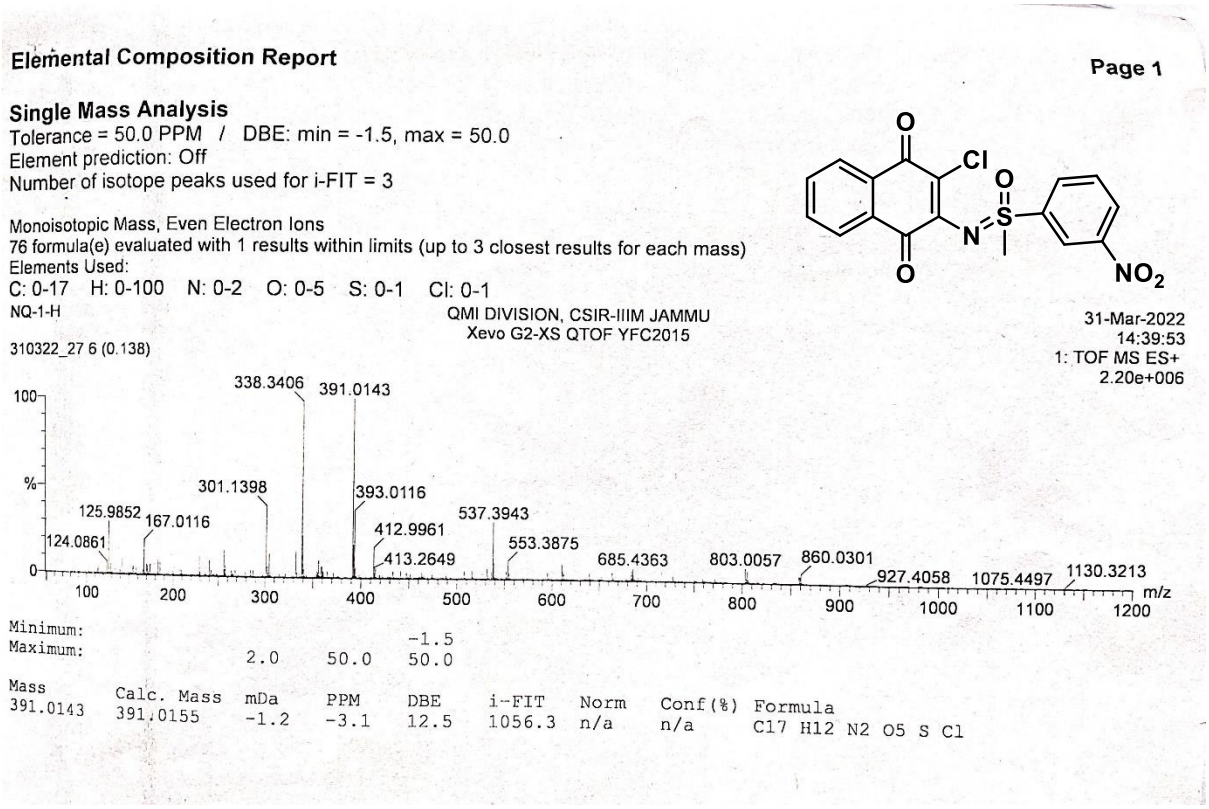
^{1}H NMR (400 MHz) of 5g in $CDCl_3$



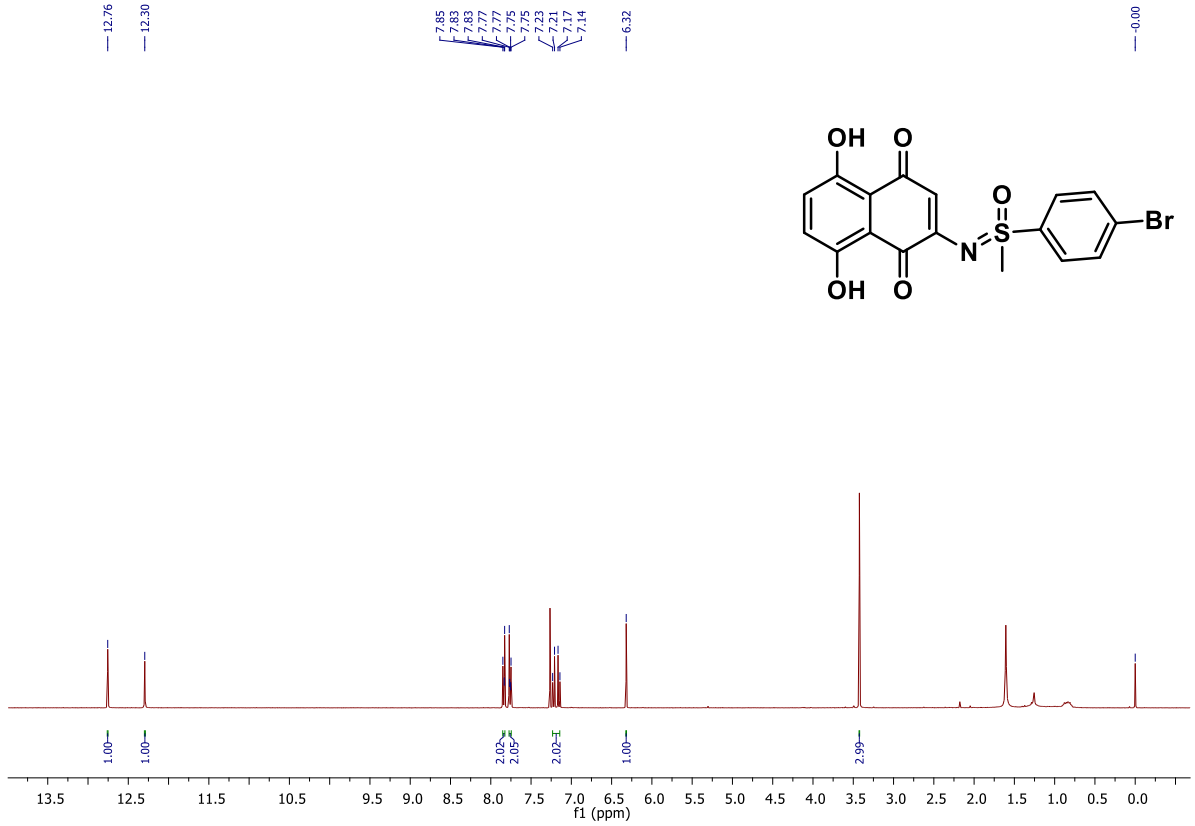
^{13}C {^{1}H} NMR (101 MHz) of 5g in $CDCl_3$



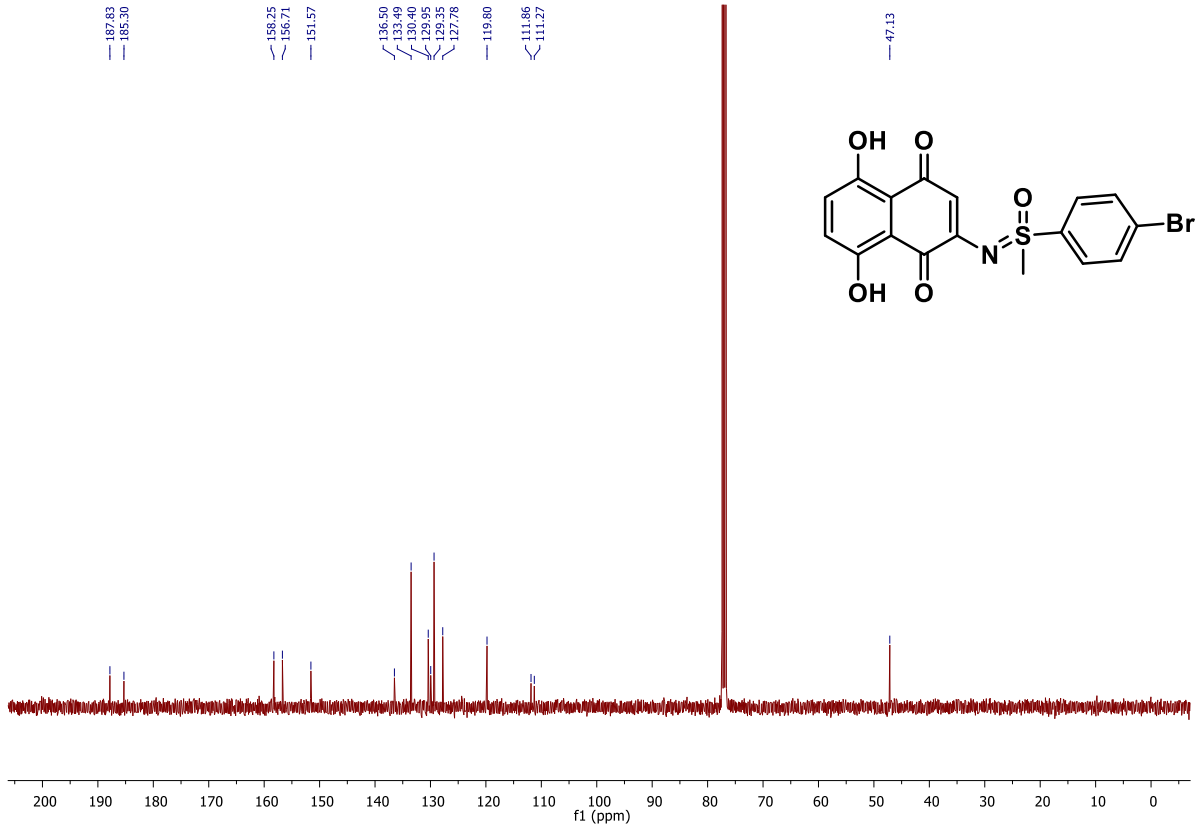
HRMS of 5g



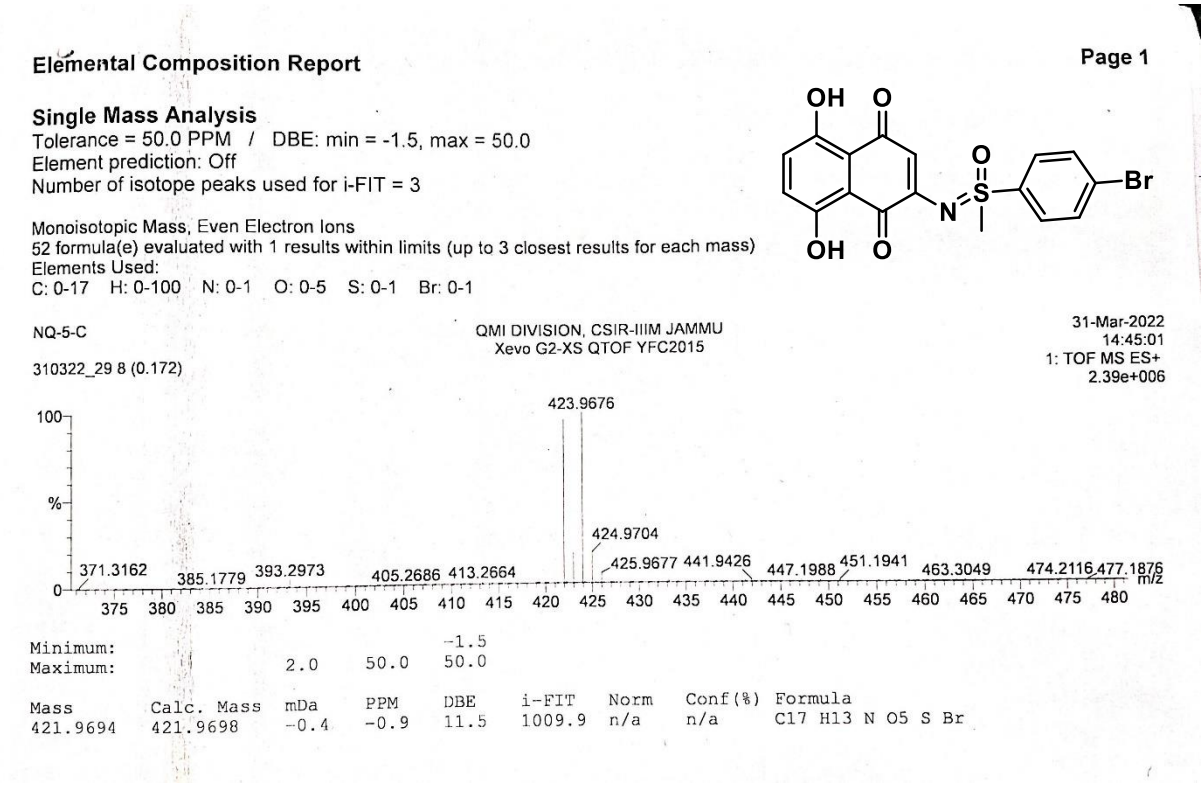
^{1}H NMR (400 MHz) of 5h in $CDCl_3$



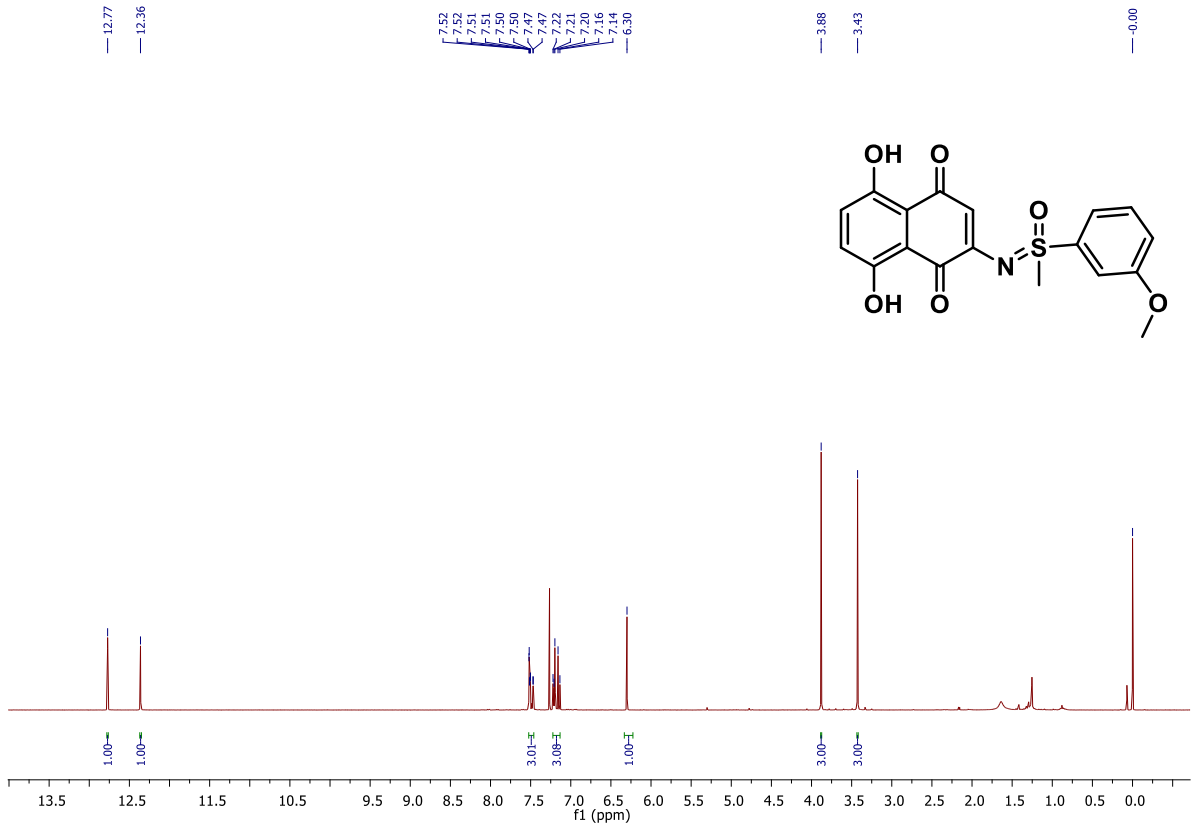
^{13}C {^{1}H} NMR (101 MHz) of 5h in $CDCl_3$



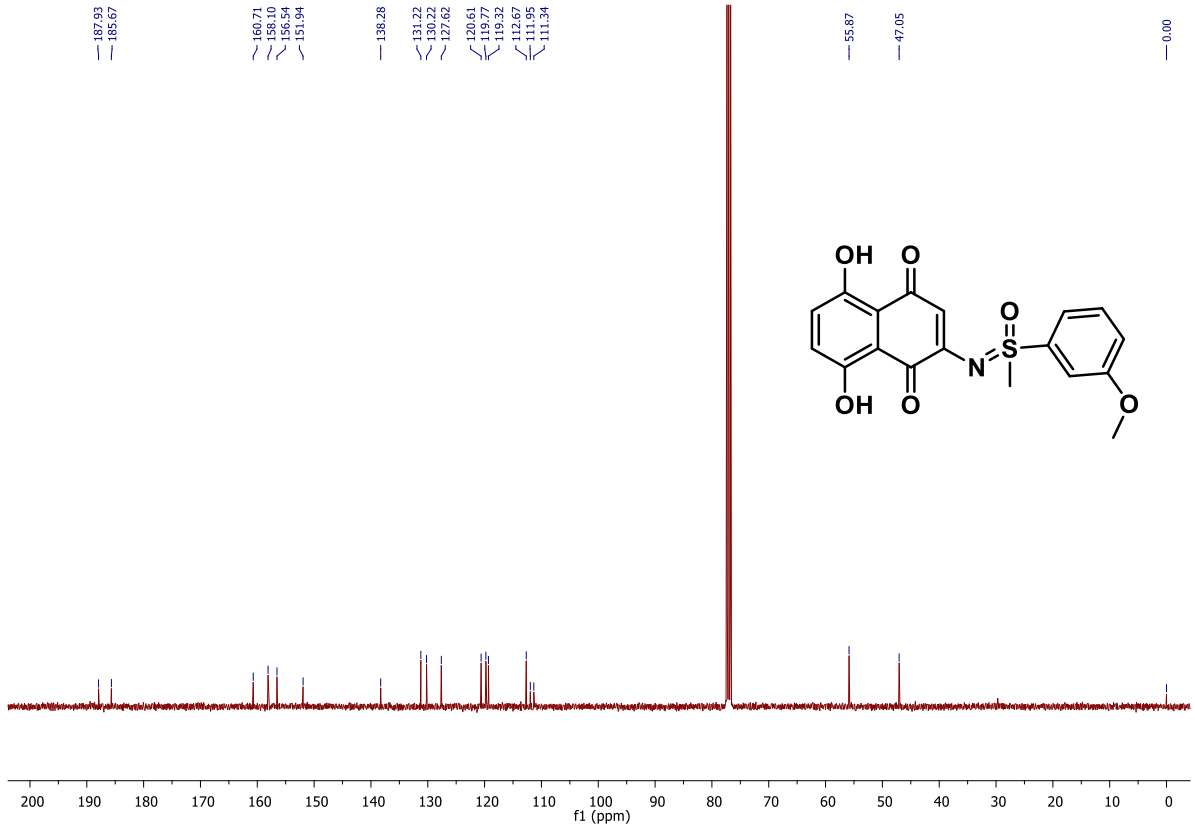
HRMS of 5h



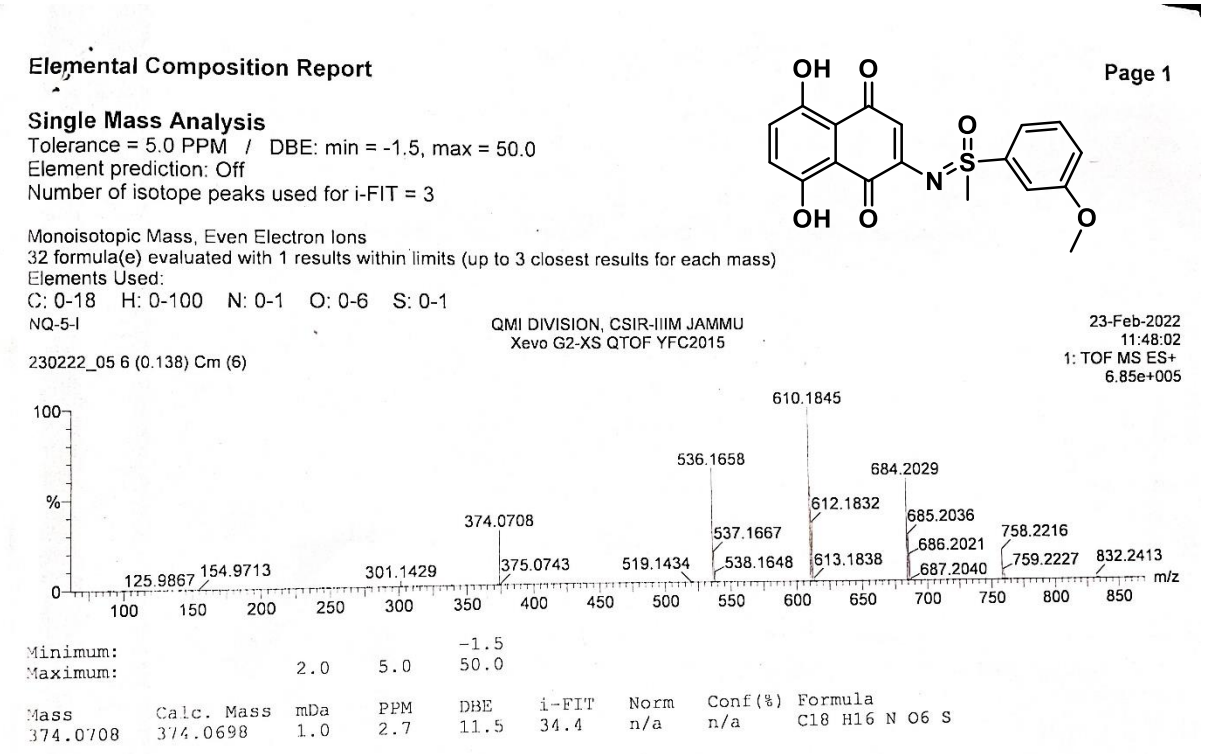
^{1}H NMR (400 MHz) of 5i in $CDCl_3$



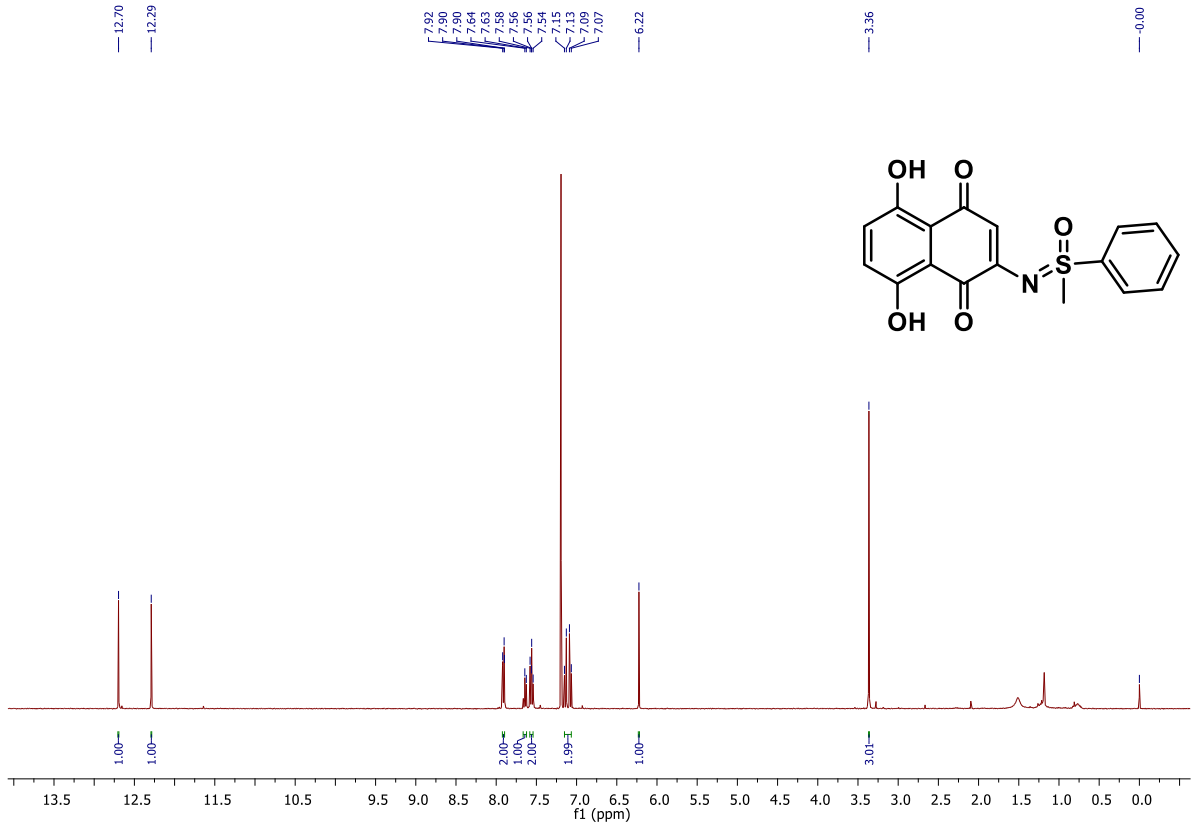
^{13}C {^{1}H} NMR (101 MHz) of 5i in $CDCl_3$



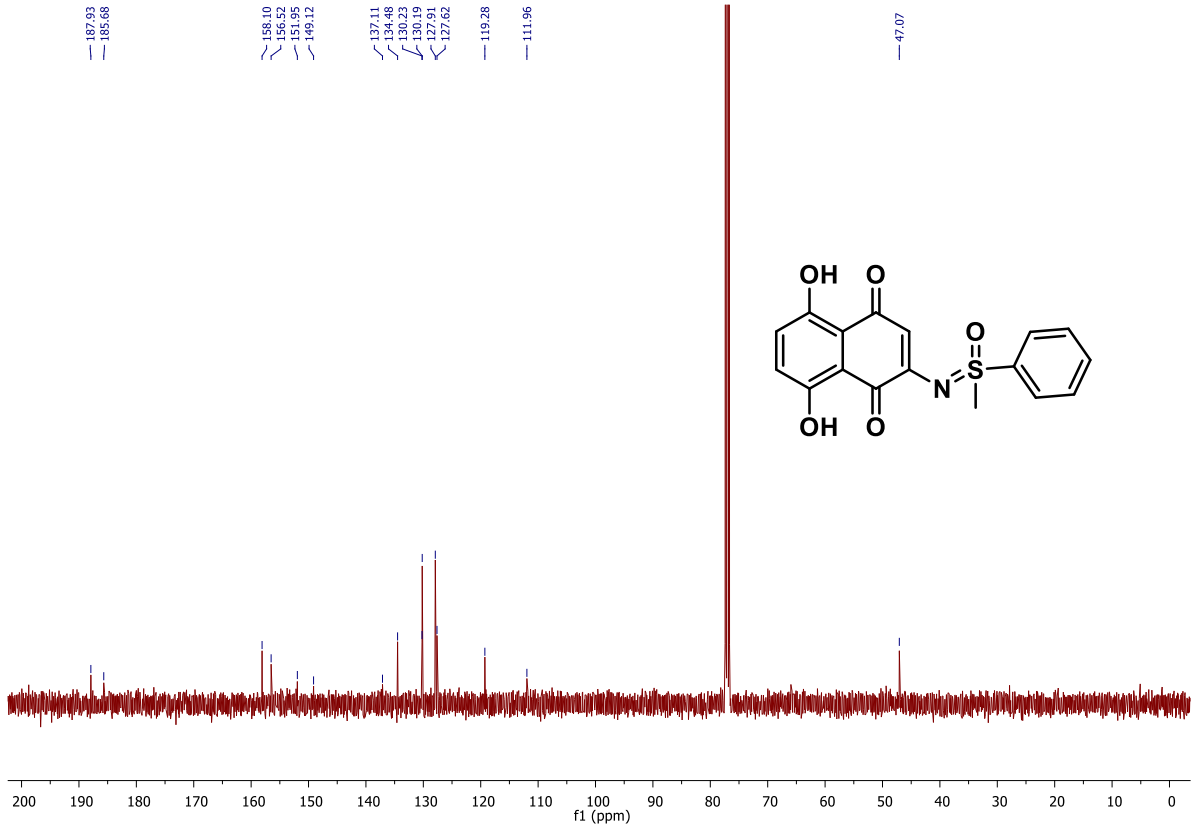
HRMS of 5i



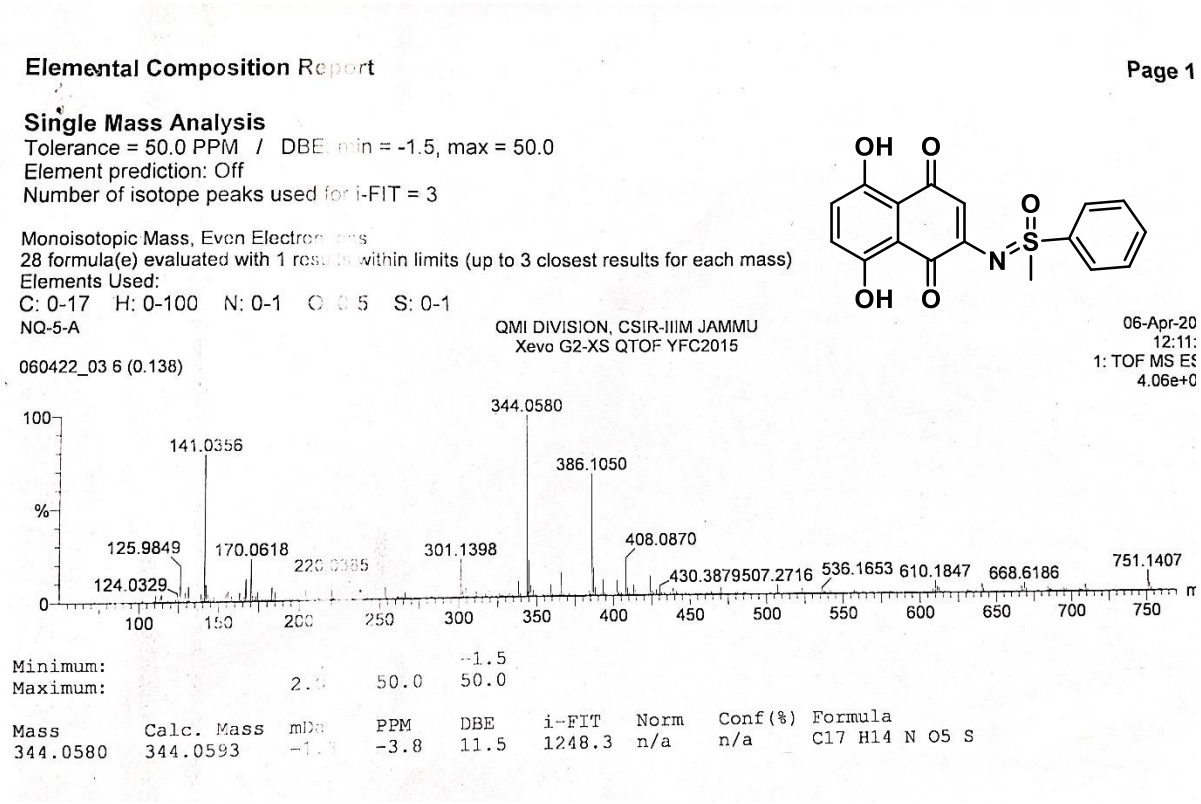
^{1}H NMR (400 MHz) of 5j in $CDCl_3$



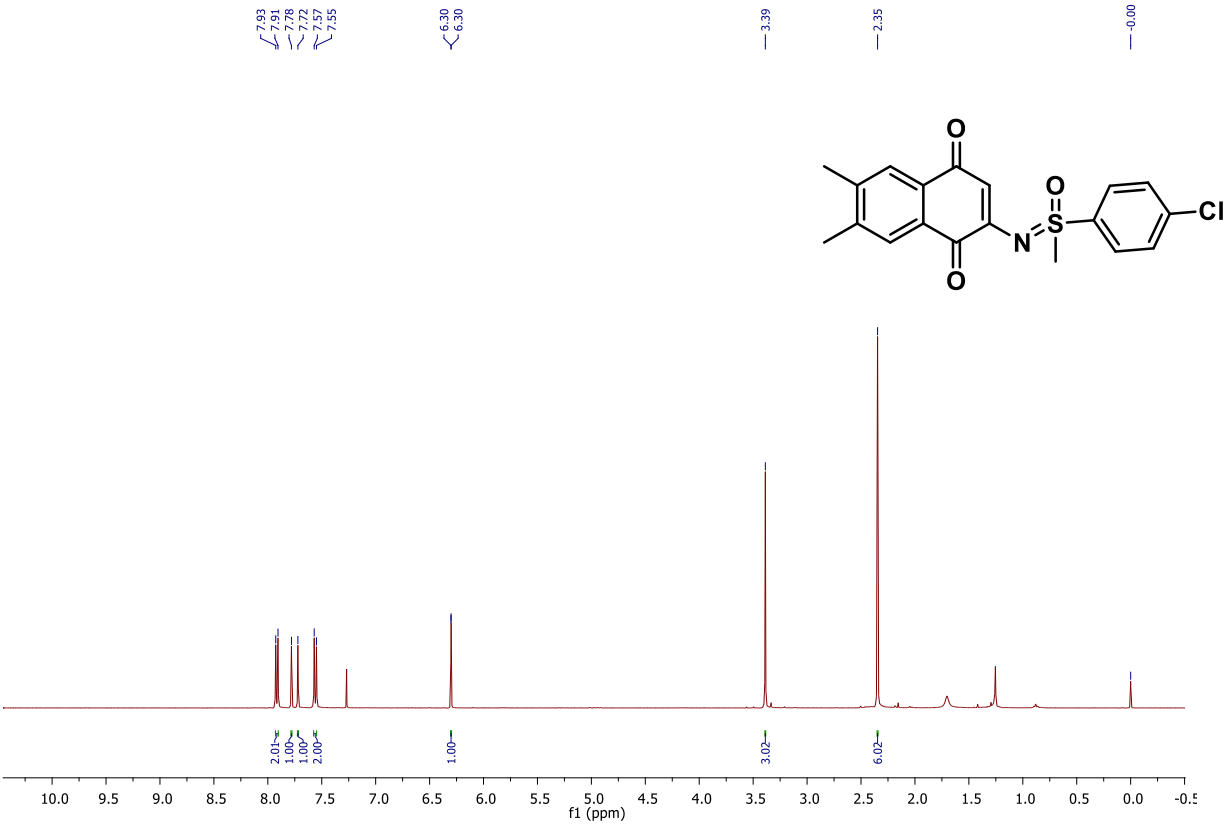
^{13}C {^{1}H} NMR (101 MHz) of 5j in $CDCl_3$



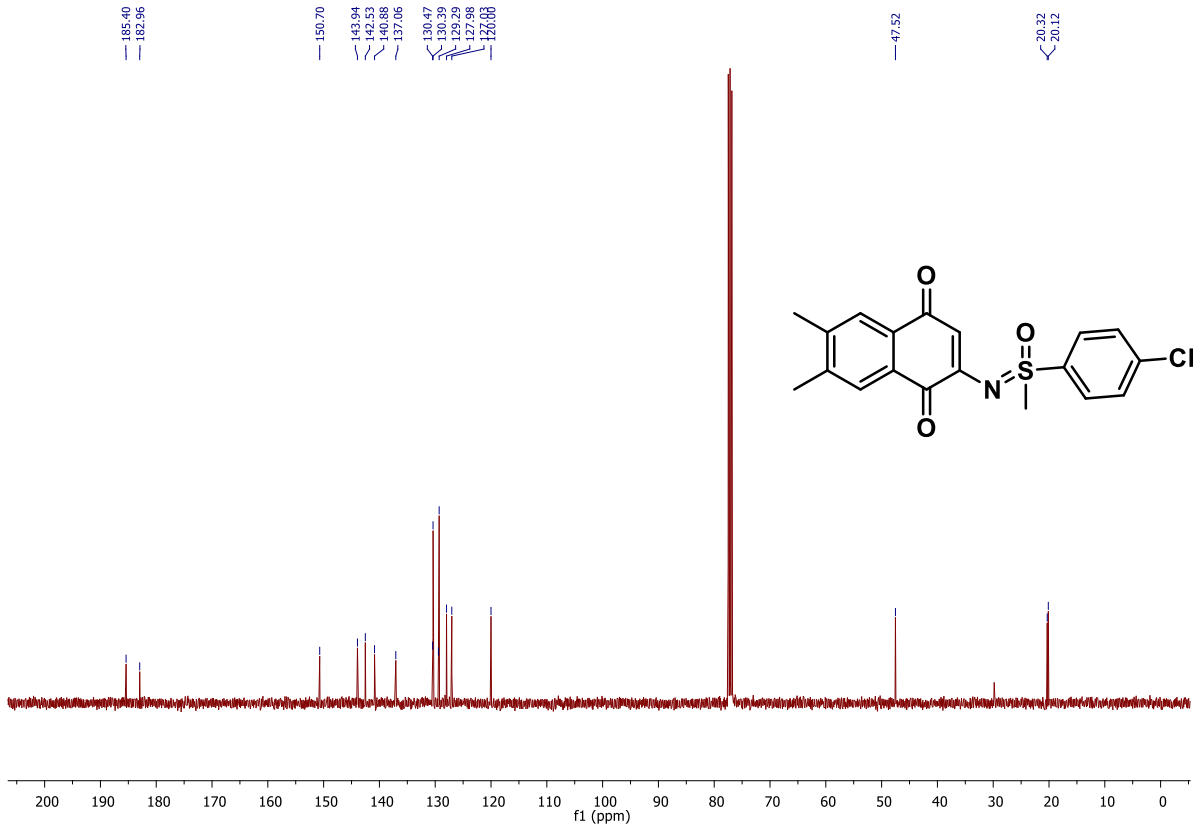
HRMS of 5j



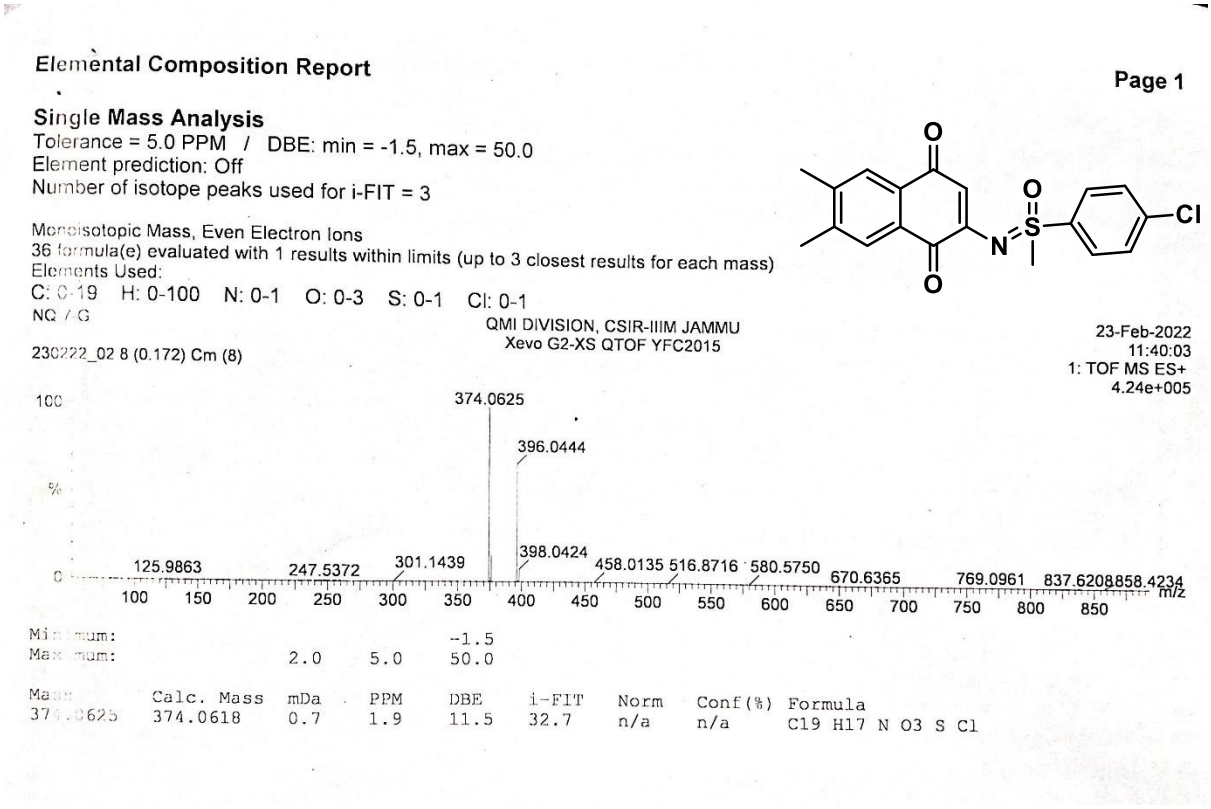
^{1}H NMR (400 MHz) of 5k in $CDCl_3$



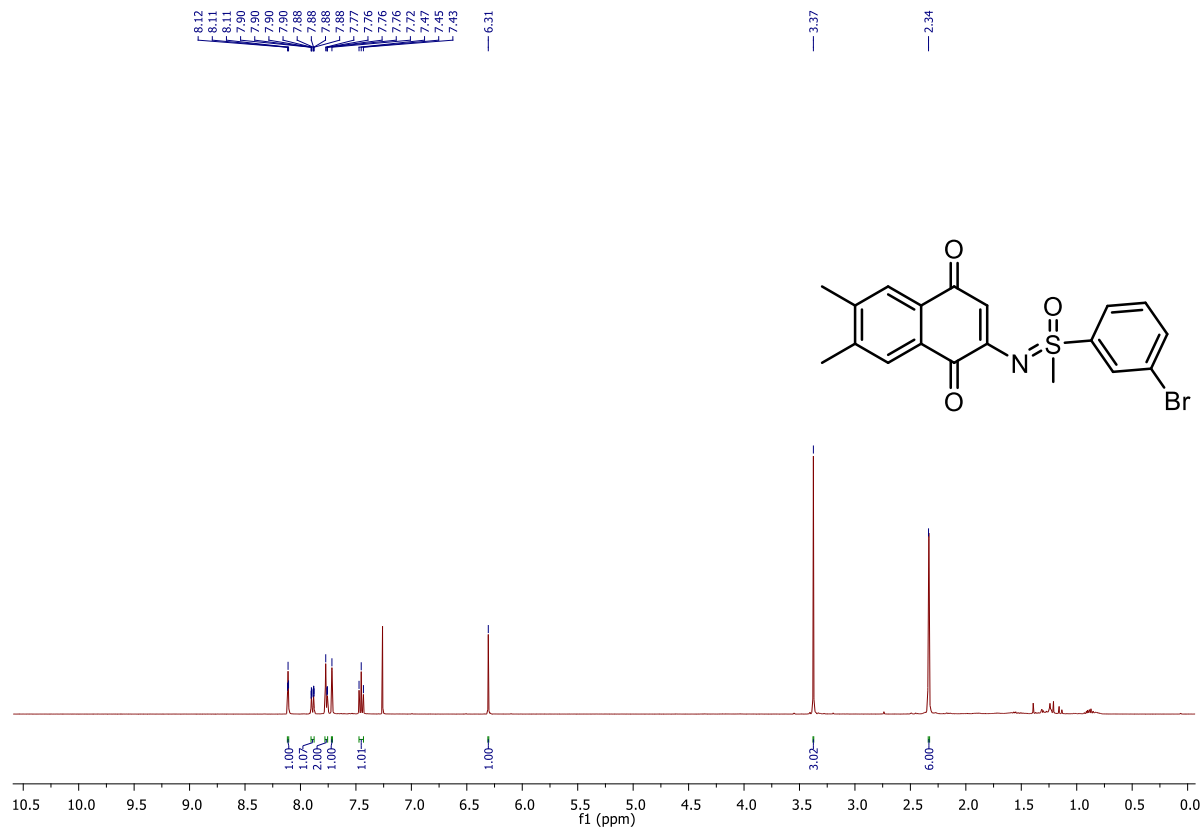
^{13}C {^{1}H} NMR (101 MHz) of 5k in $CDCl_3$



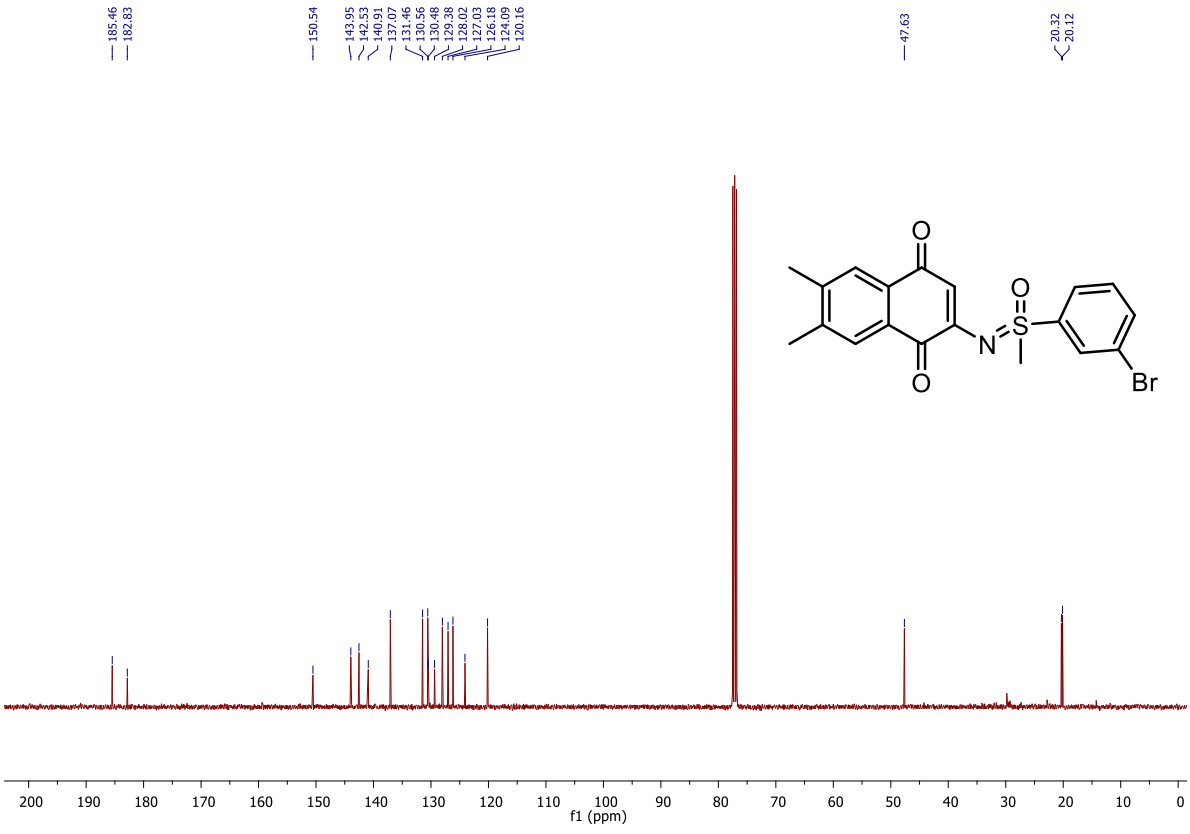
HRMS of 5k



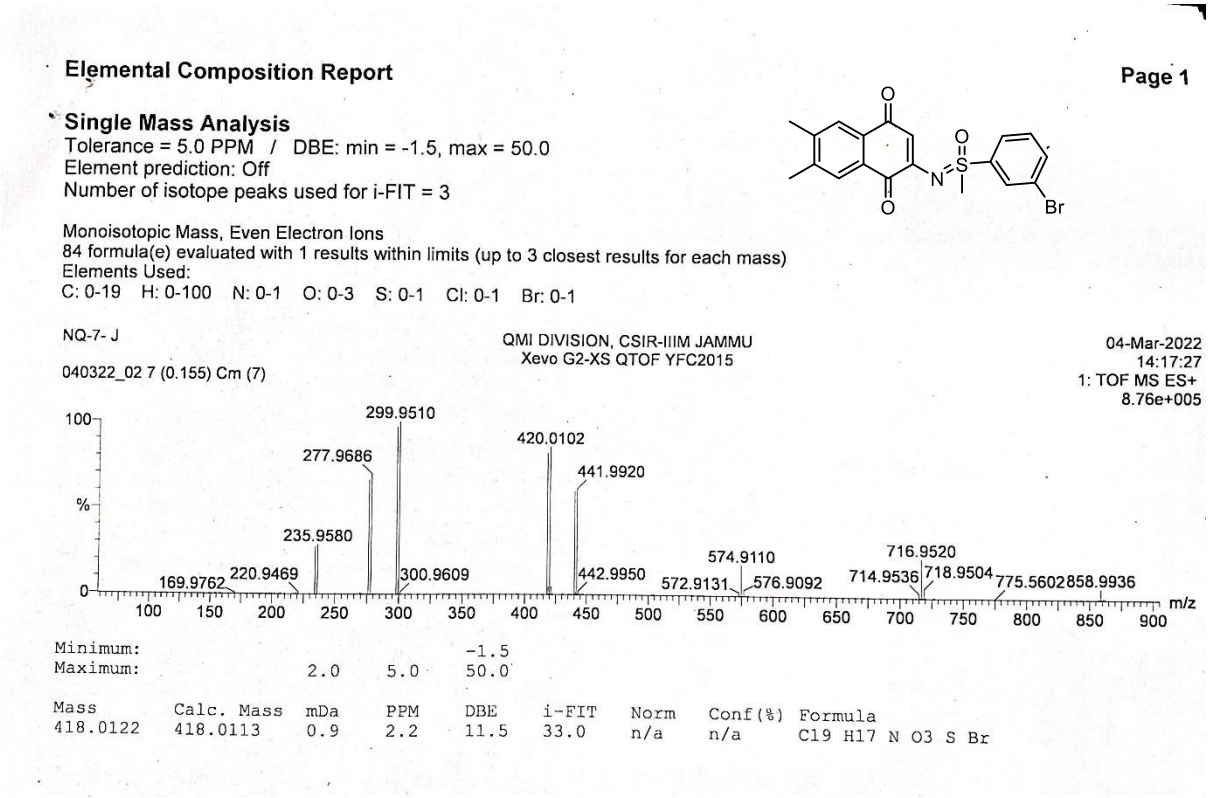
^{1}H NMR (400 MHz) of 5l in $CDCl_3$



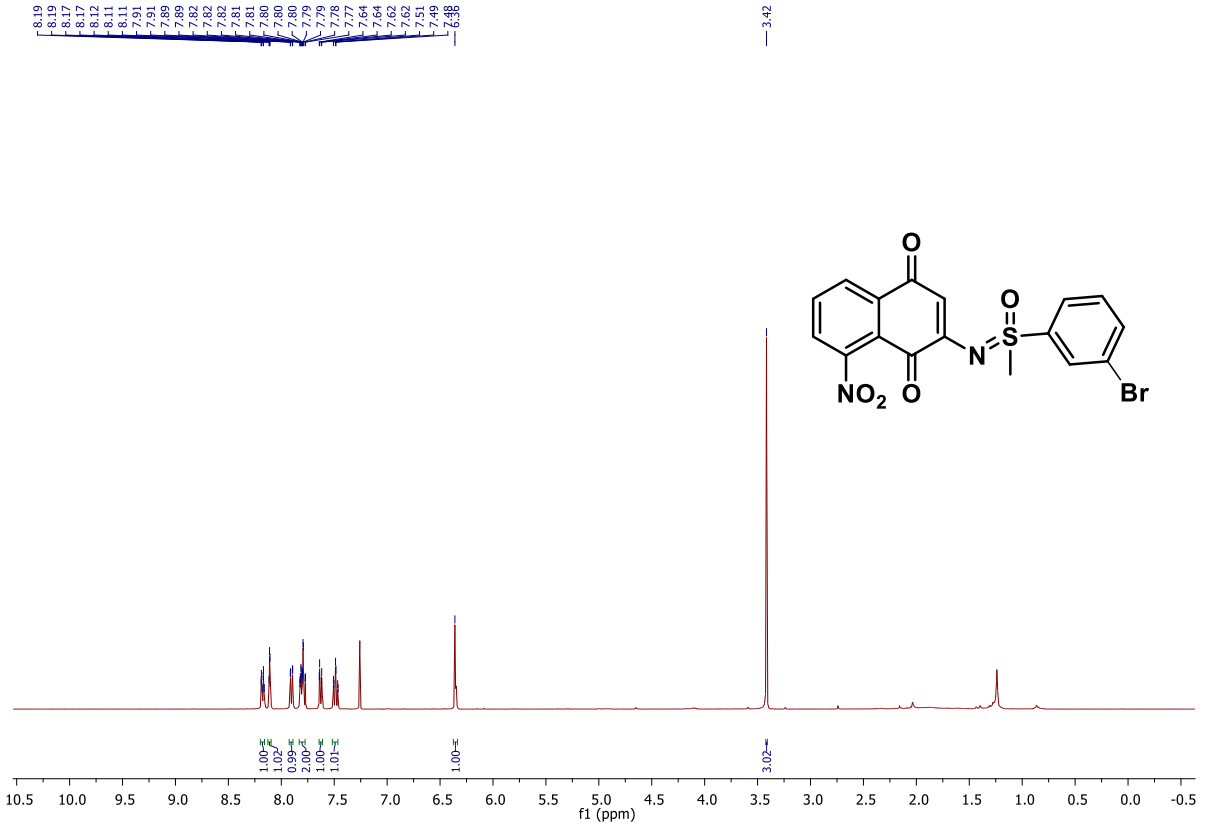
^{13}C {^{1}H} NMR (101 MHz) of 5l in $CDCl_3$



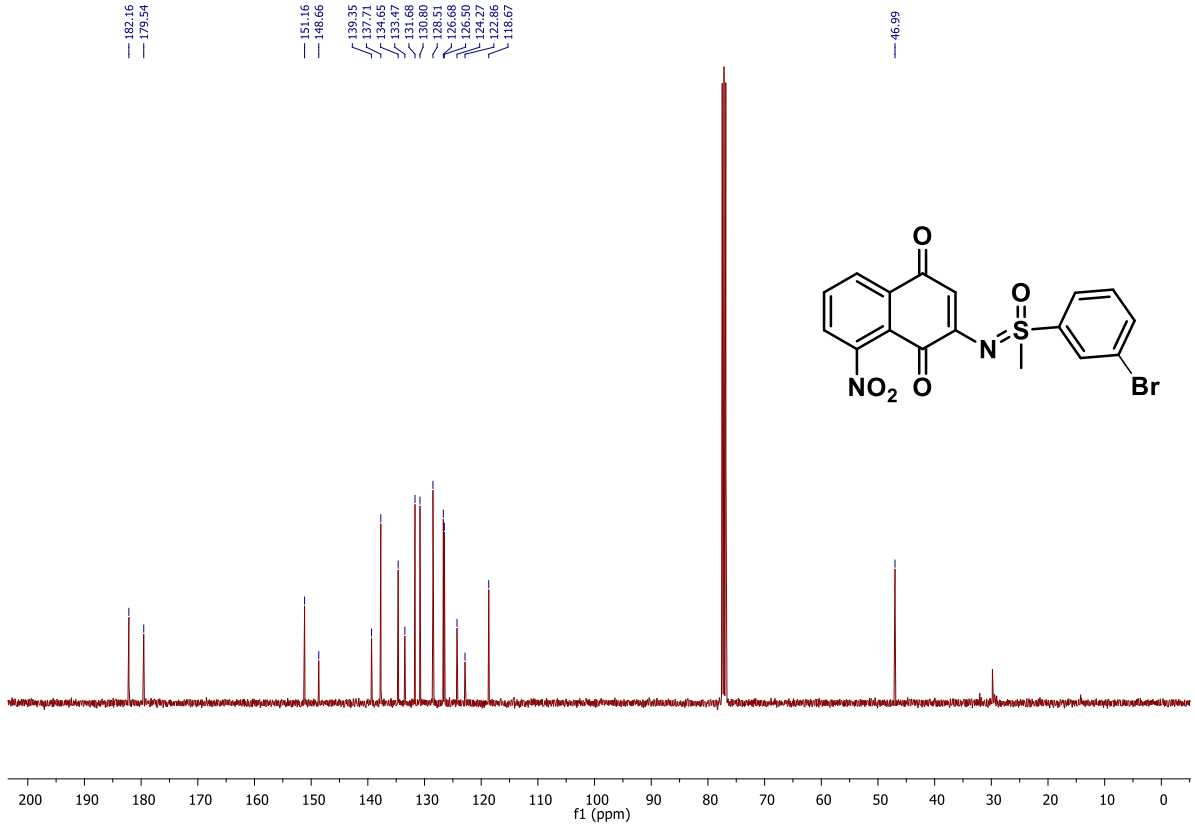
HRMS of 5l



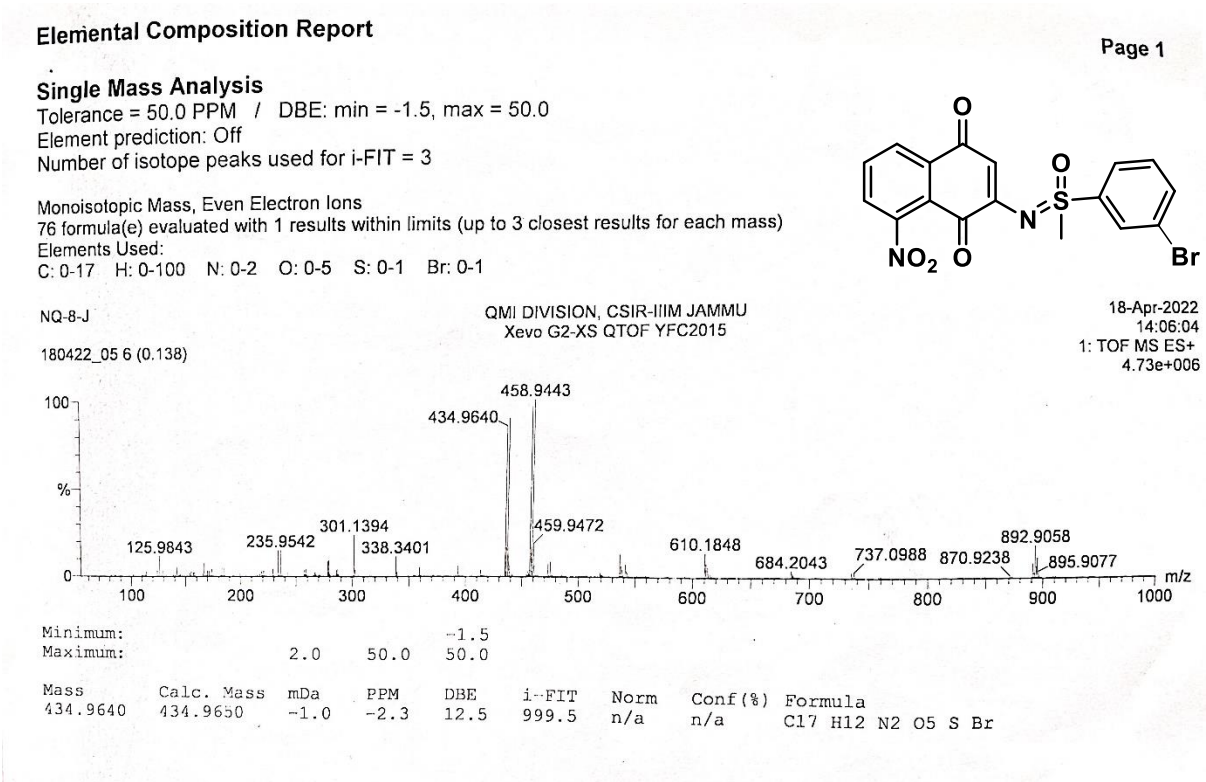
^{1}H NMR (400 MHz) of 5m in $CDCl_3$



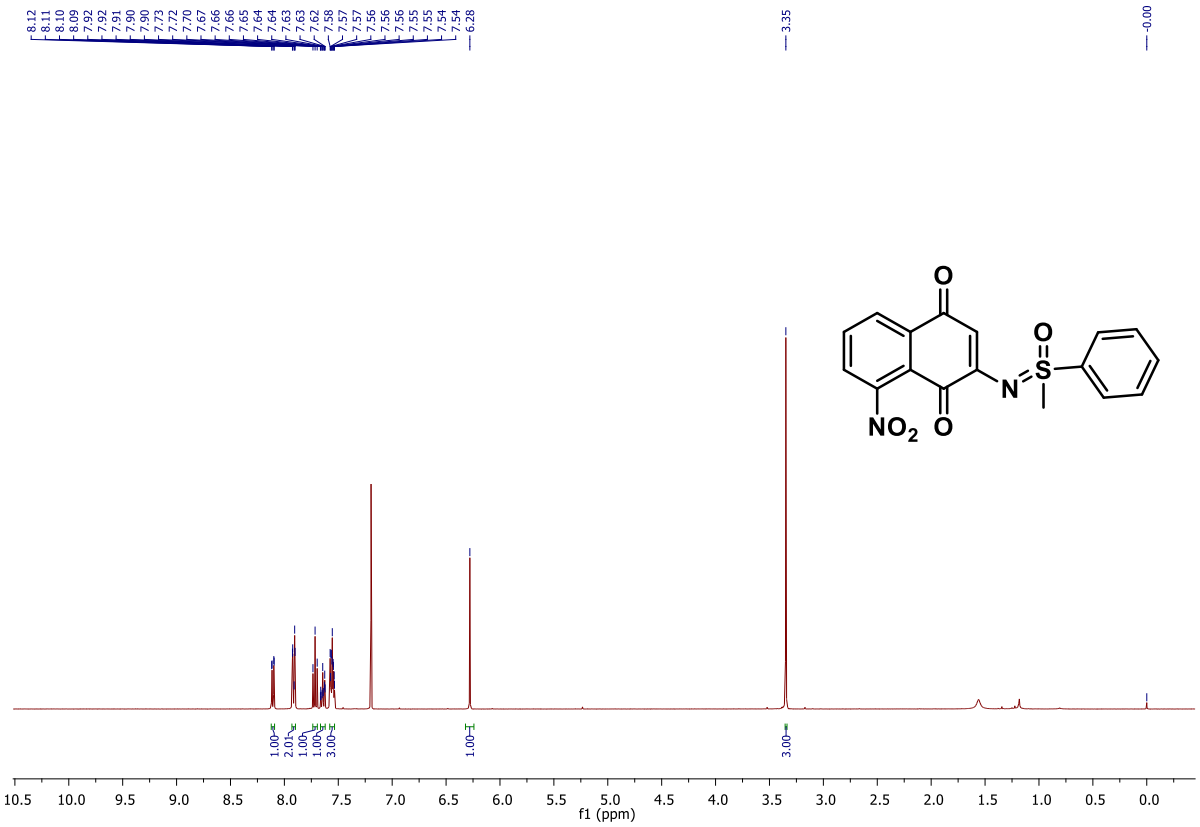
^{13}C {^{1}H} NMR (101 MHz) of 5m in $CDCl_3$



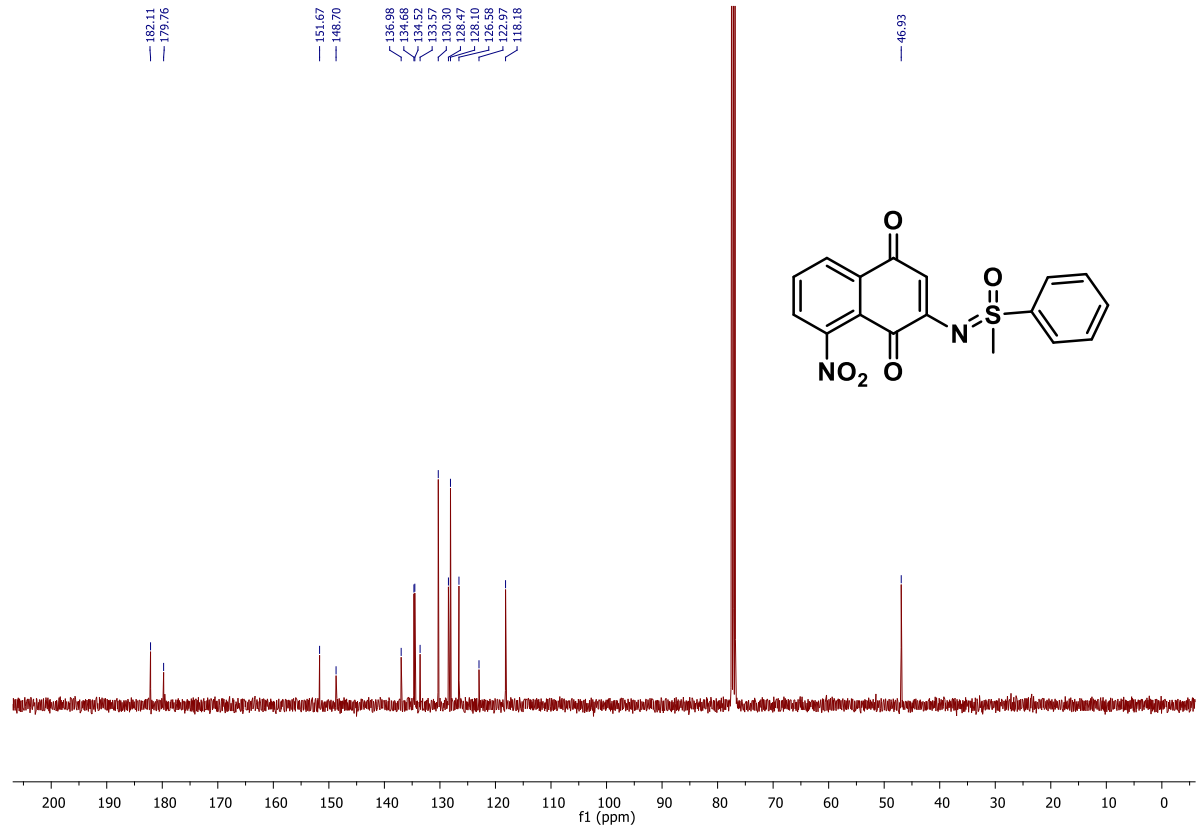
HRMS of 5m



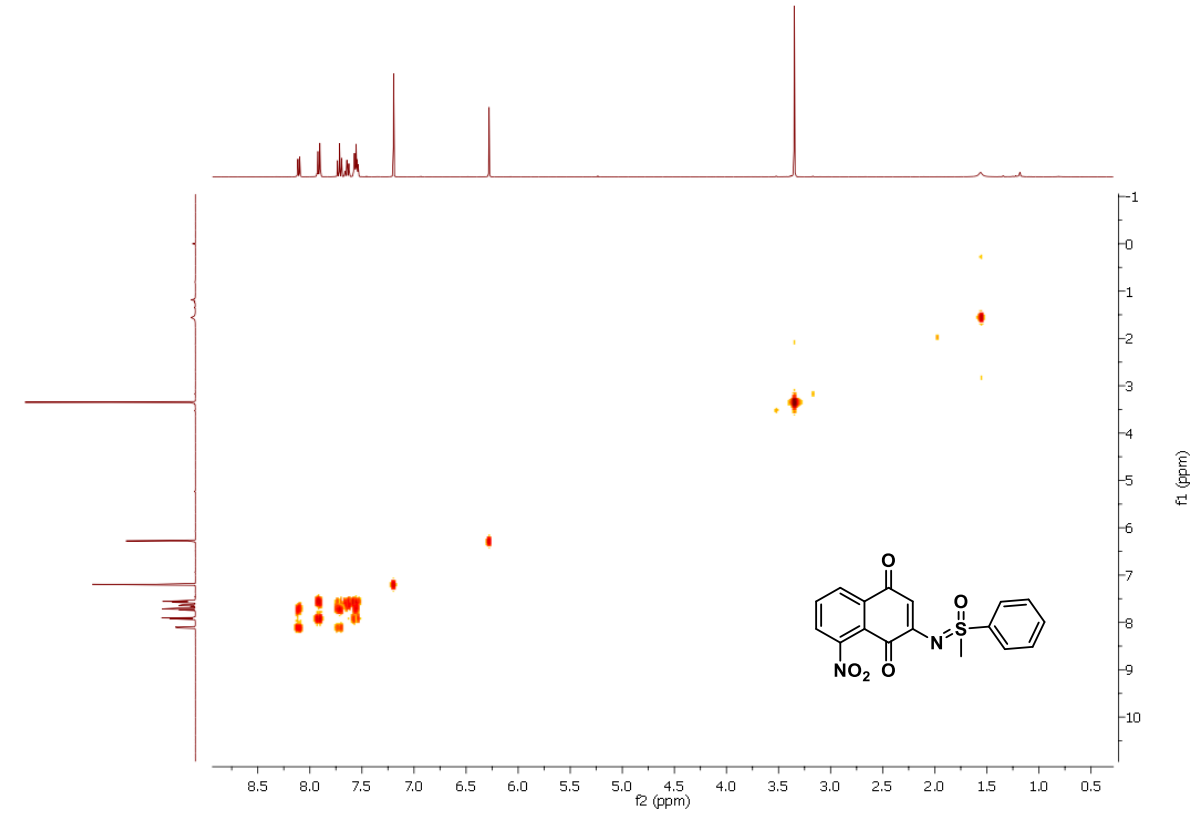
^{1}H NMR (400 MHz) of 5n in $CDCl_3$



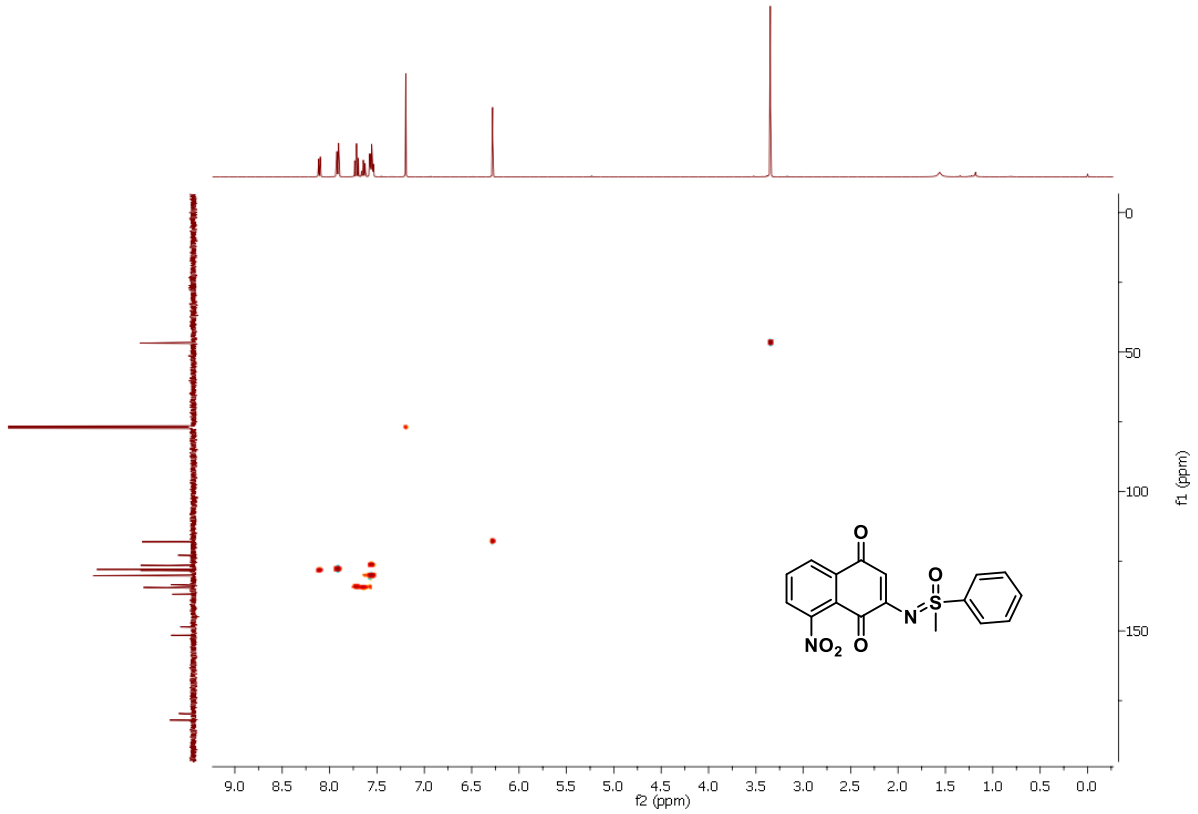
^{13}C {^{1}H} NMR (101 MHz) of 5n in $CDCl_3$



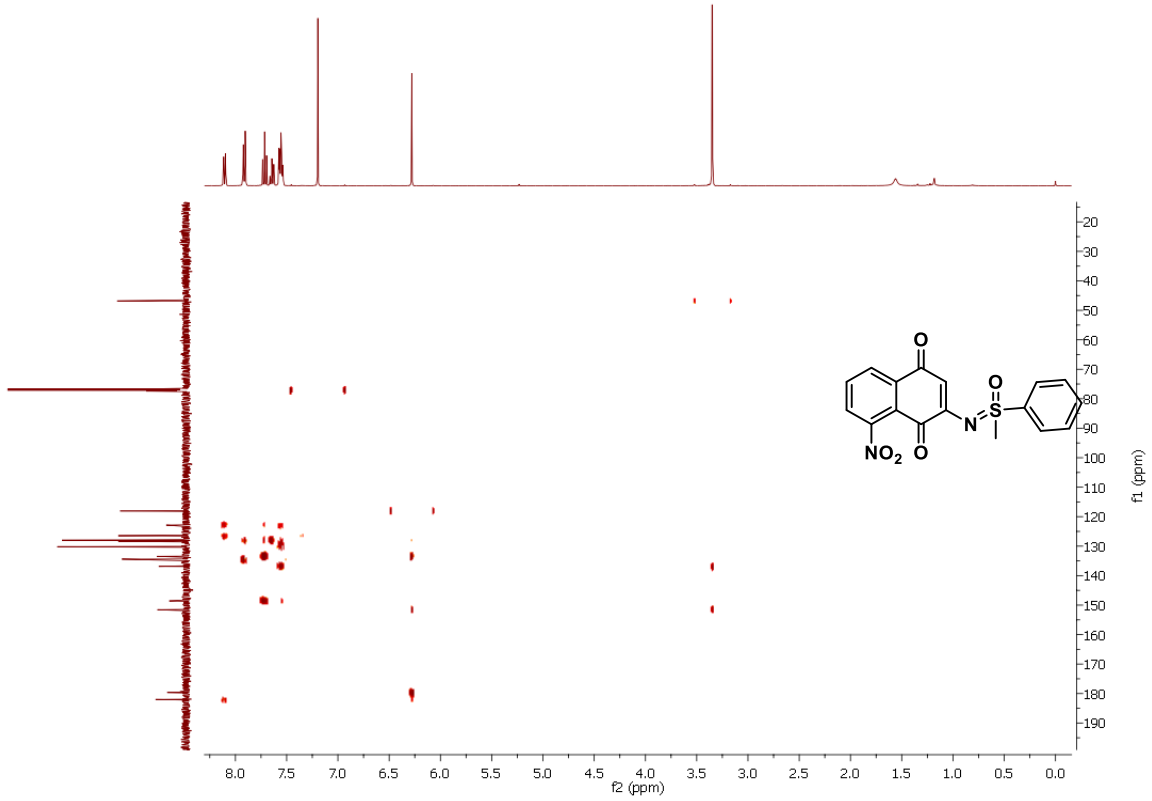
2D NMR (COSY) Spectra of 5n in $CDCl_3$



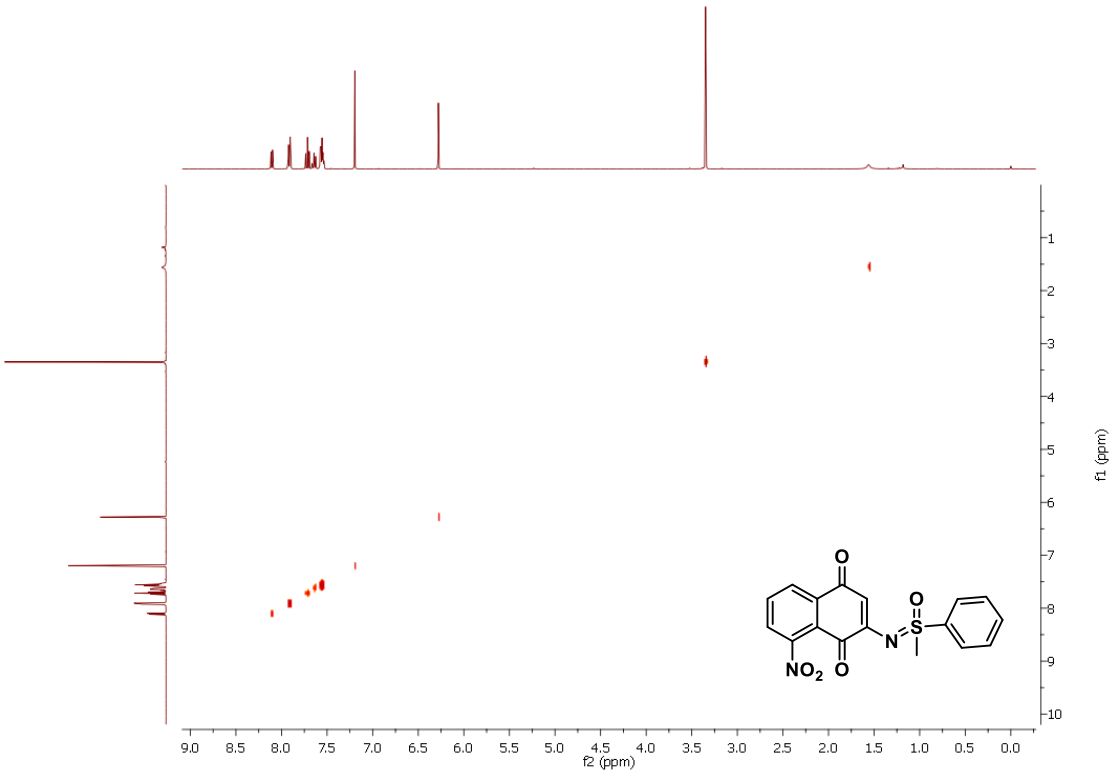
HSQC Spectra of 5n in $CDCl_3$



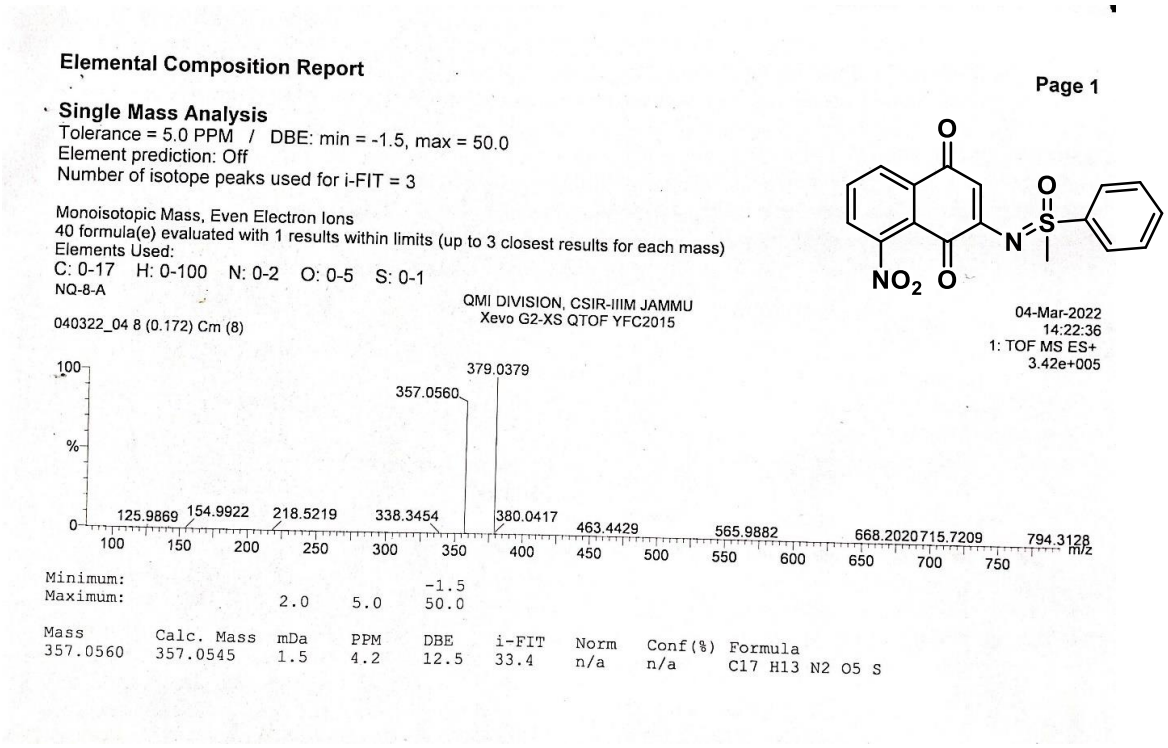
HMBC Spectra of 5n in $CDCl_3$



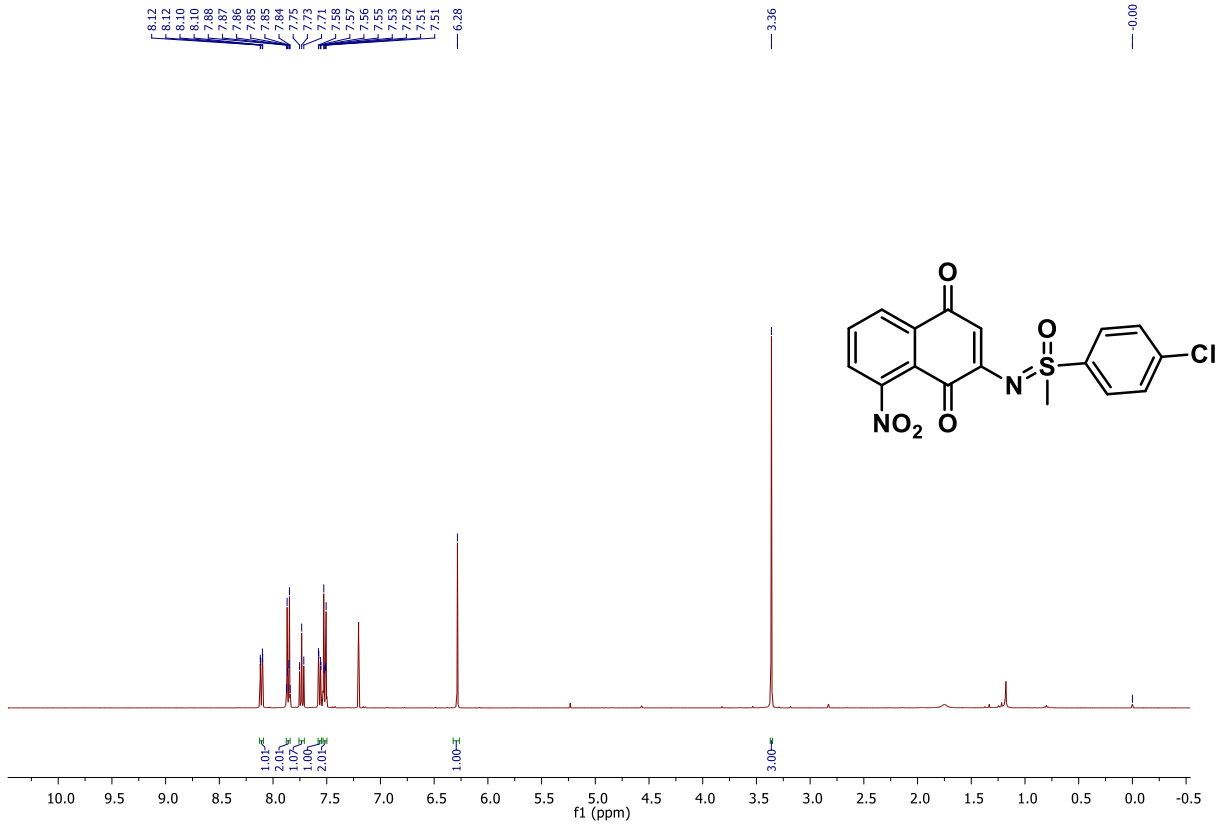
NOESY Spectra of 5n in $CDCl_3$



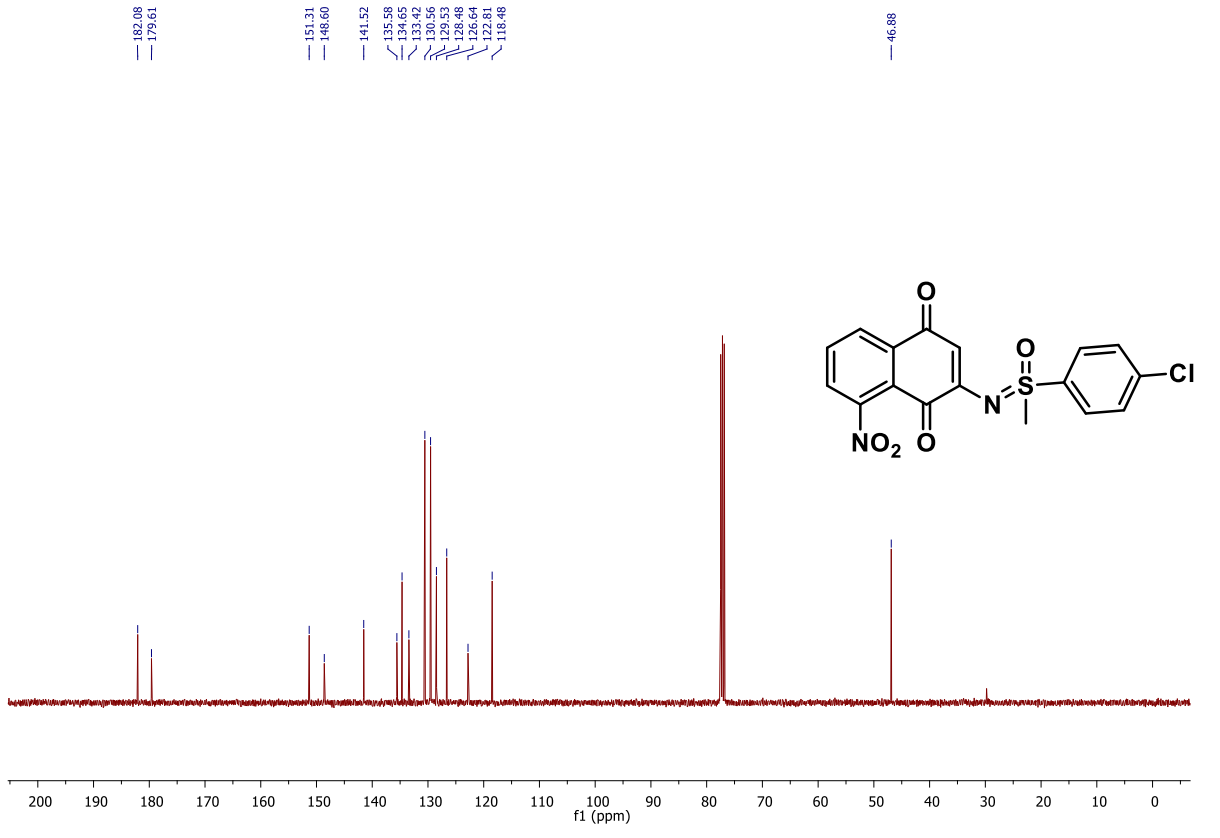
HRMS of 5n



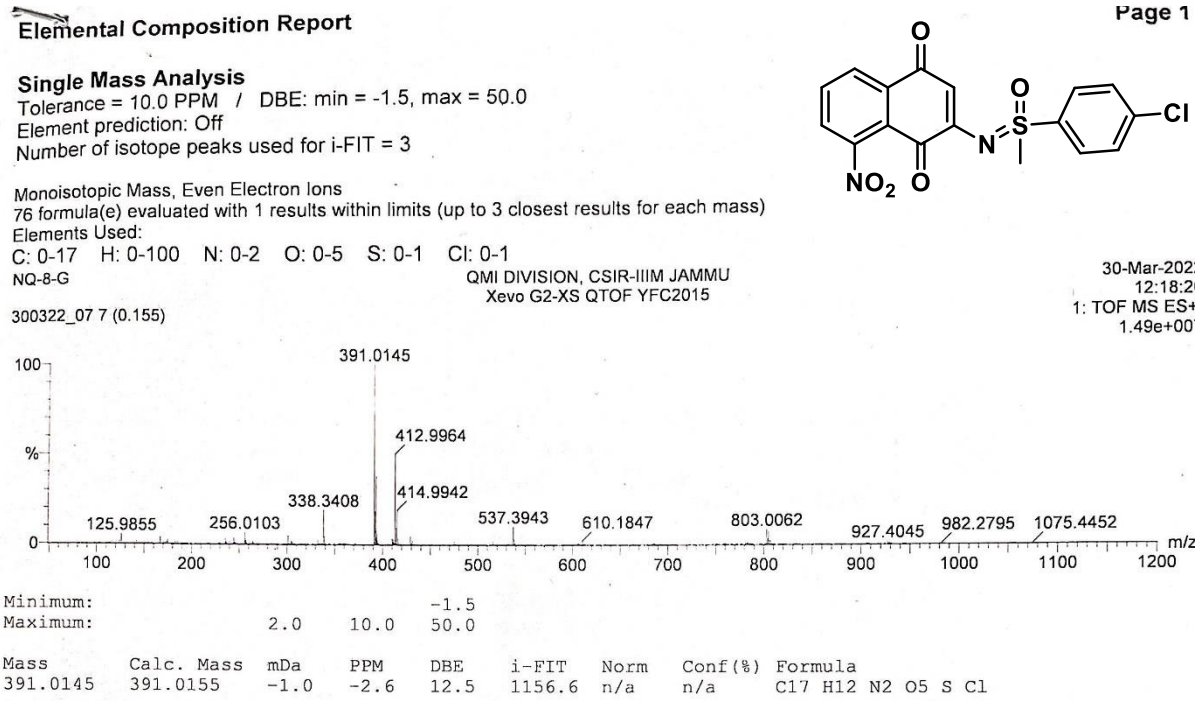
^{1}H NMR (400 MHz) of 5o in $CDCl_3$



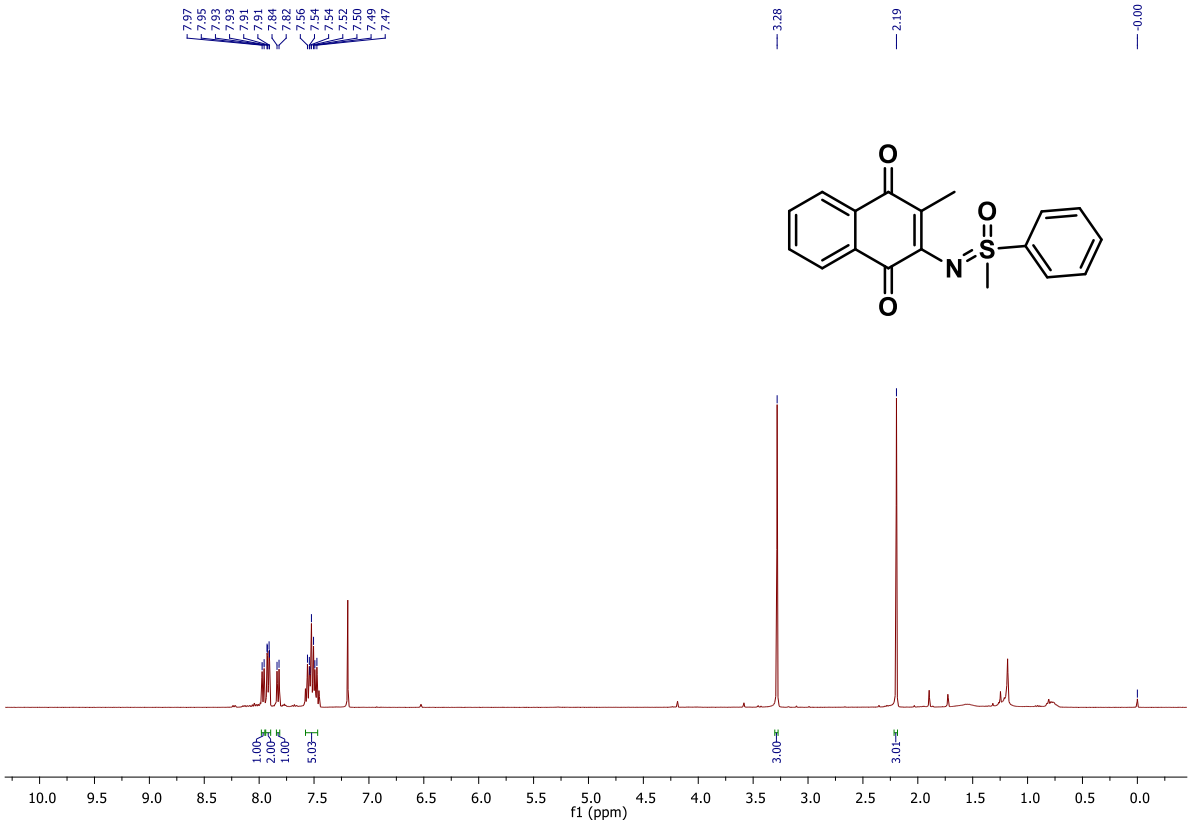
^{13}C {^{1}H} NMR (101 MHz) of 5o in $CDCl_3$



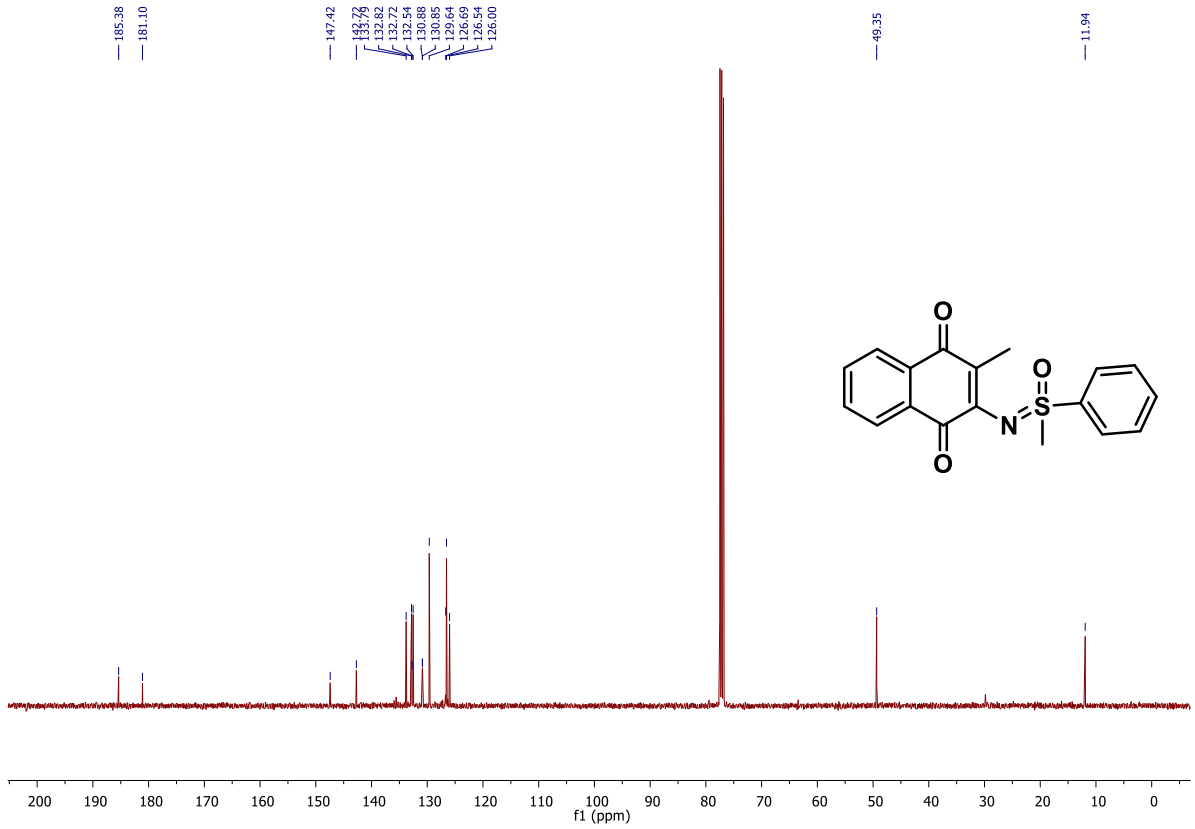
HRMS of 5o



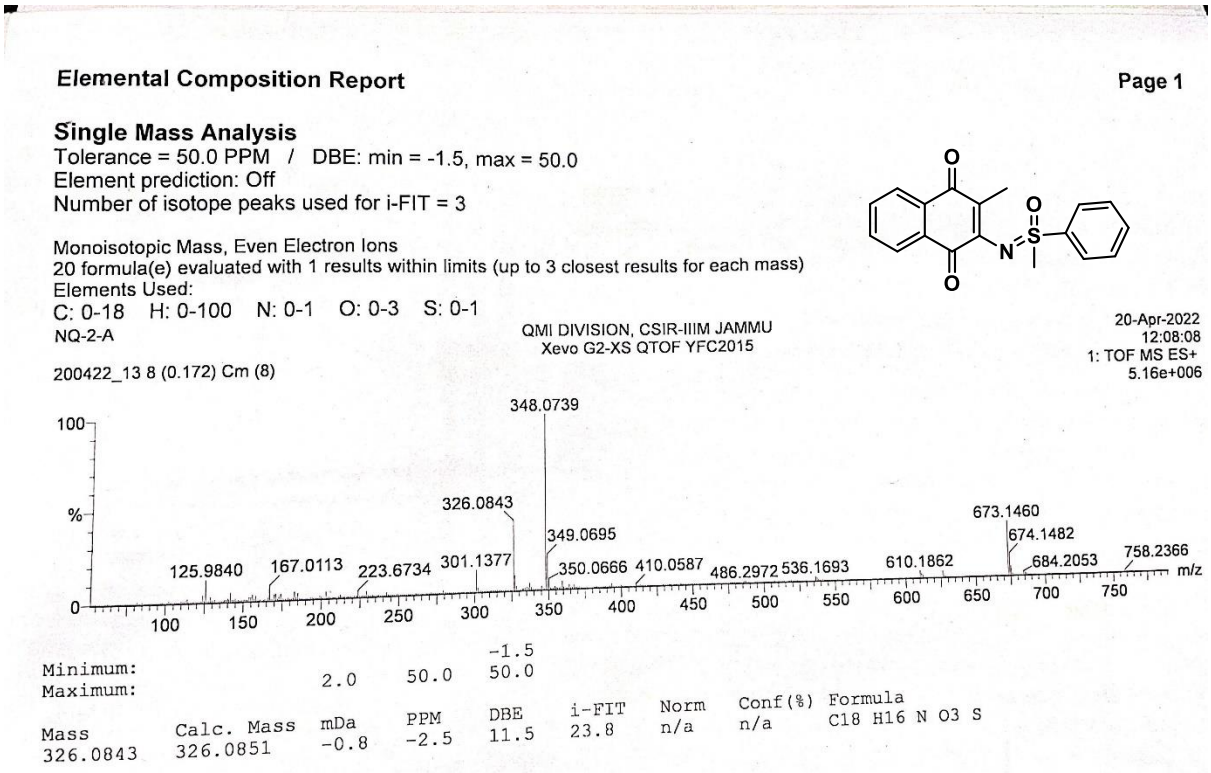
^{1}H NMR (400 MHz) of 7a in $CDCl_3$



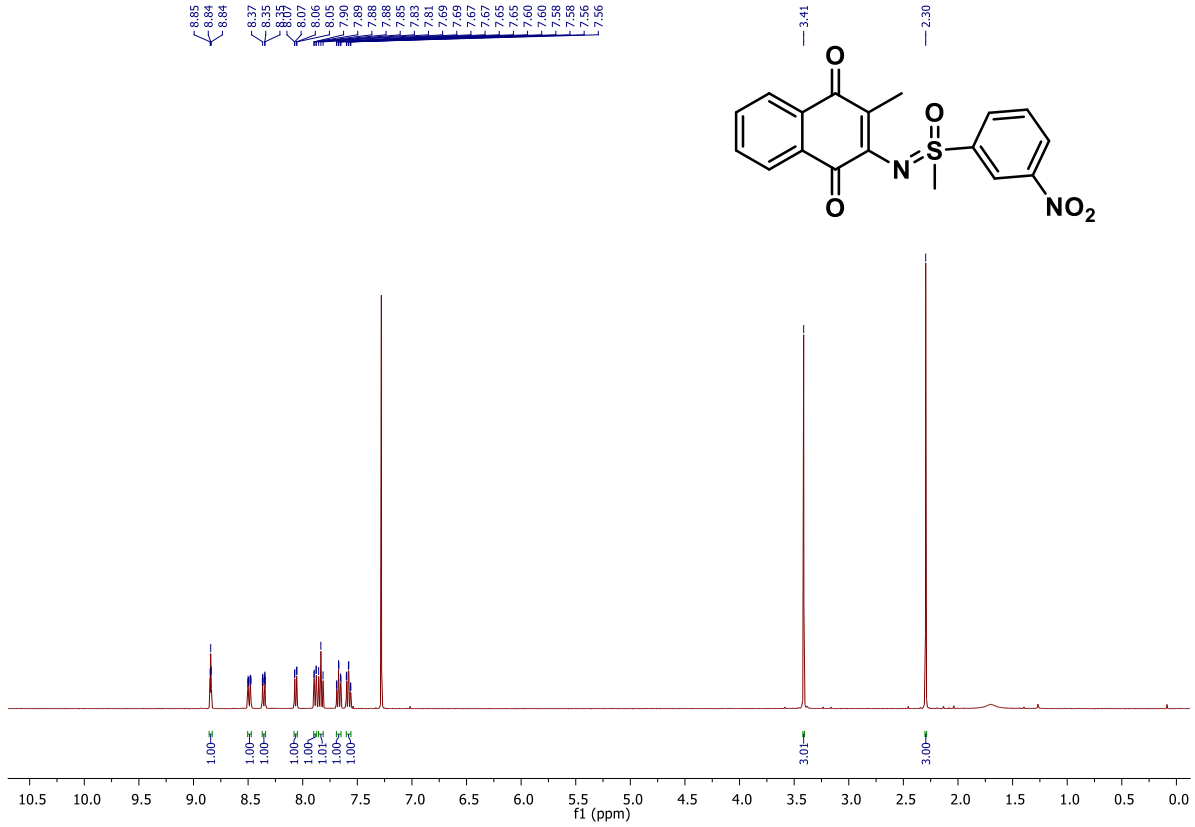
^{13}C {^{1}H} NMR (101 MHz) of 7a in $CDCl_3$



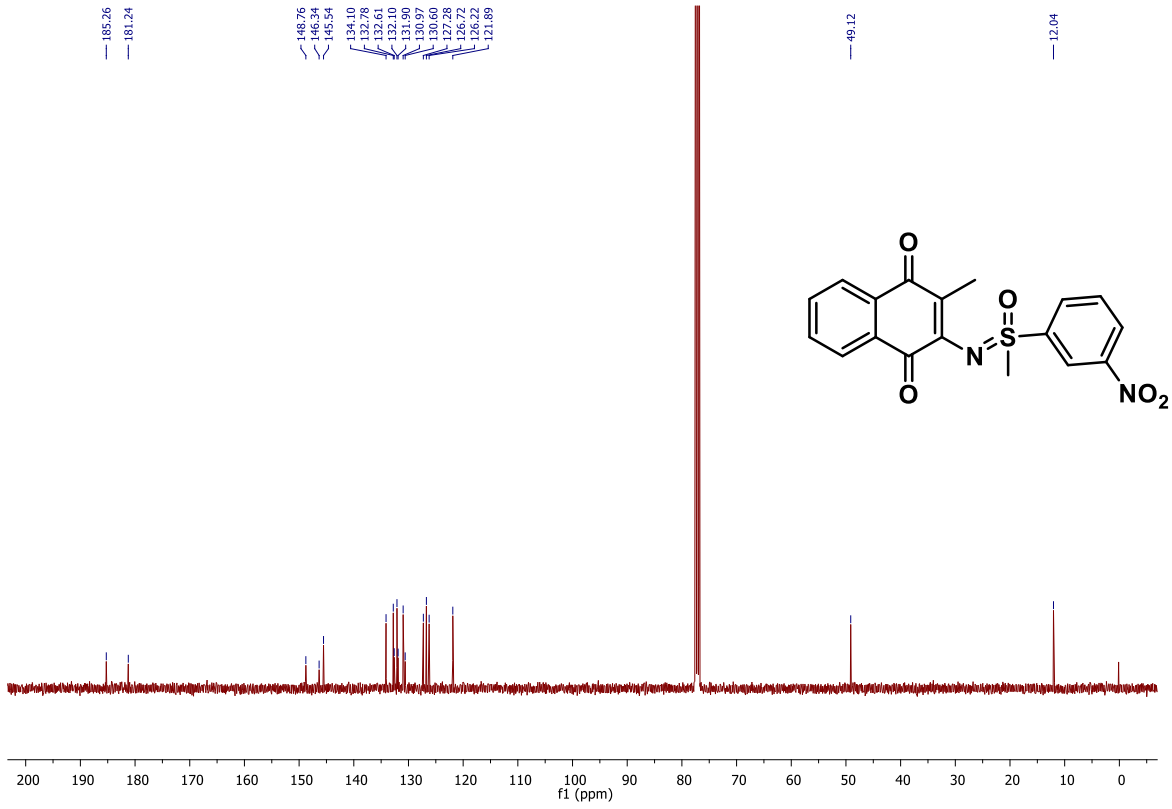
HRMS of 7a



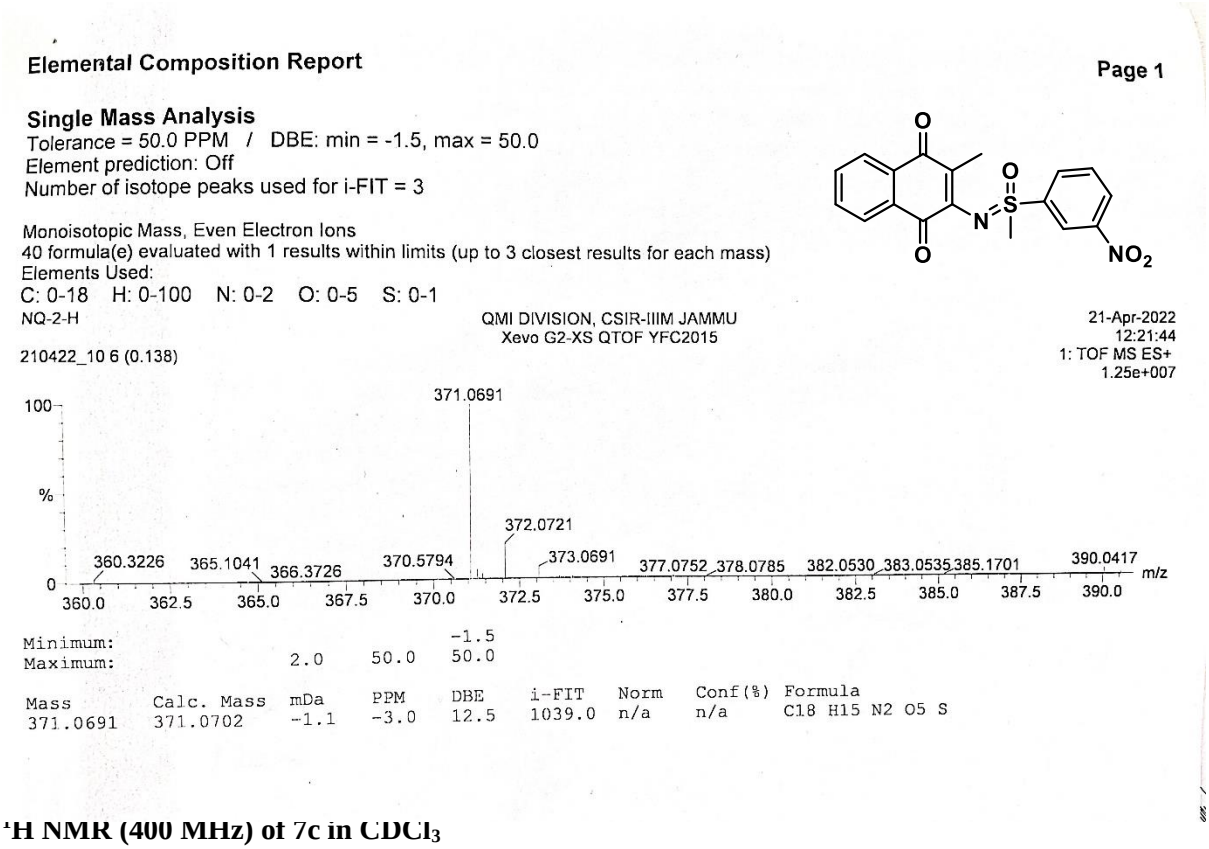
^{1}H NMR (400 MHz) of 7b in $CDCl_3$



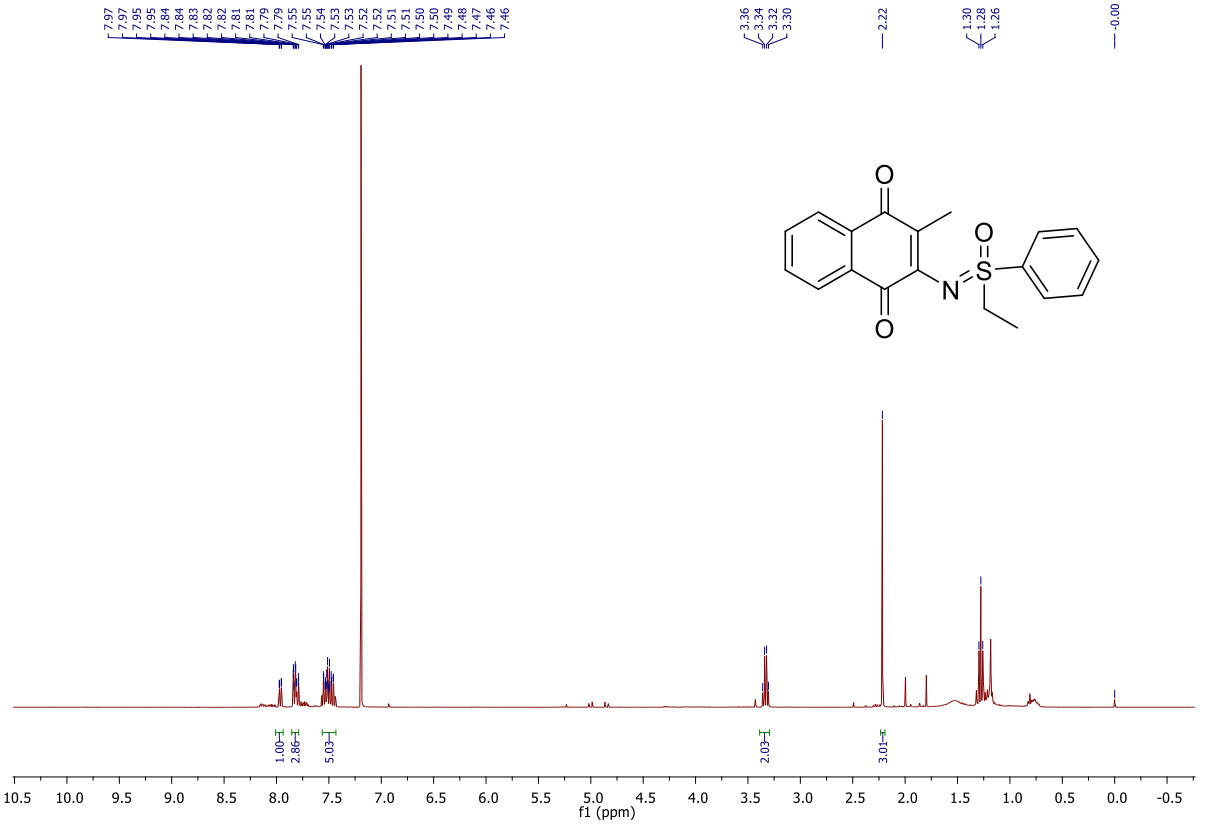
^{13}C {^{1}H} NMR (101 MHz) of 7b in $CDCl_3$



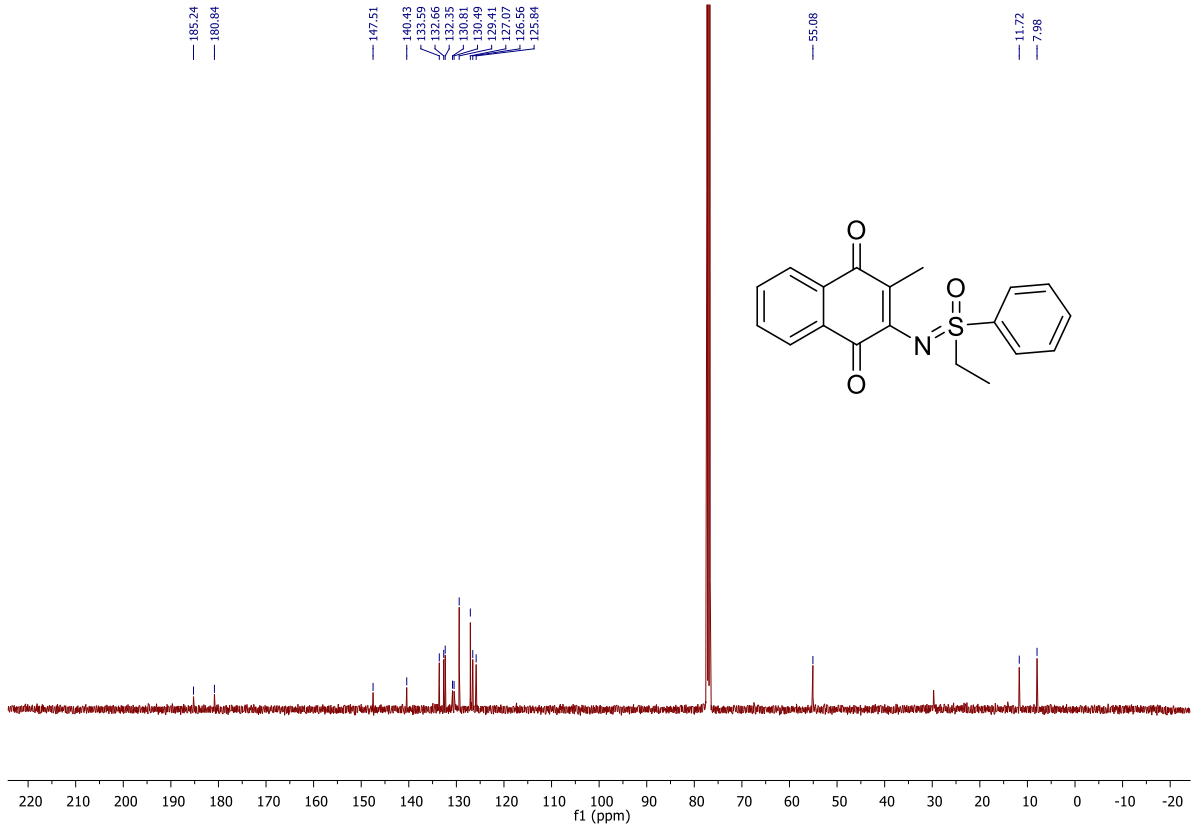
HRMS of 7b



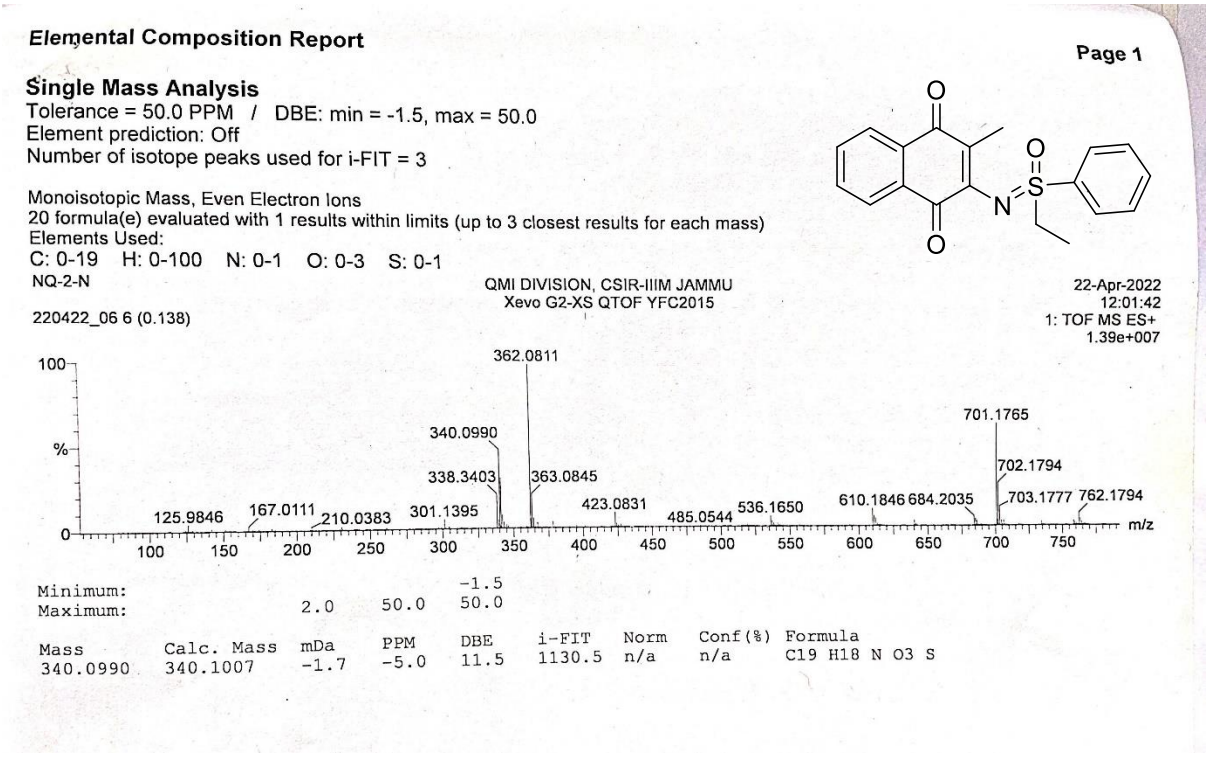
^{1}H NMR (400 MHz) of 7c in $CDCl_3$



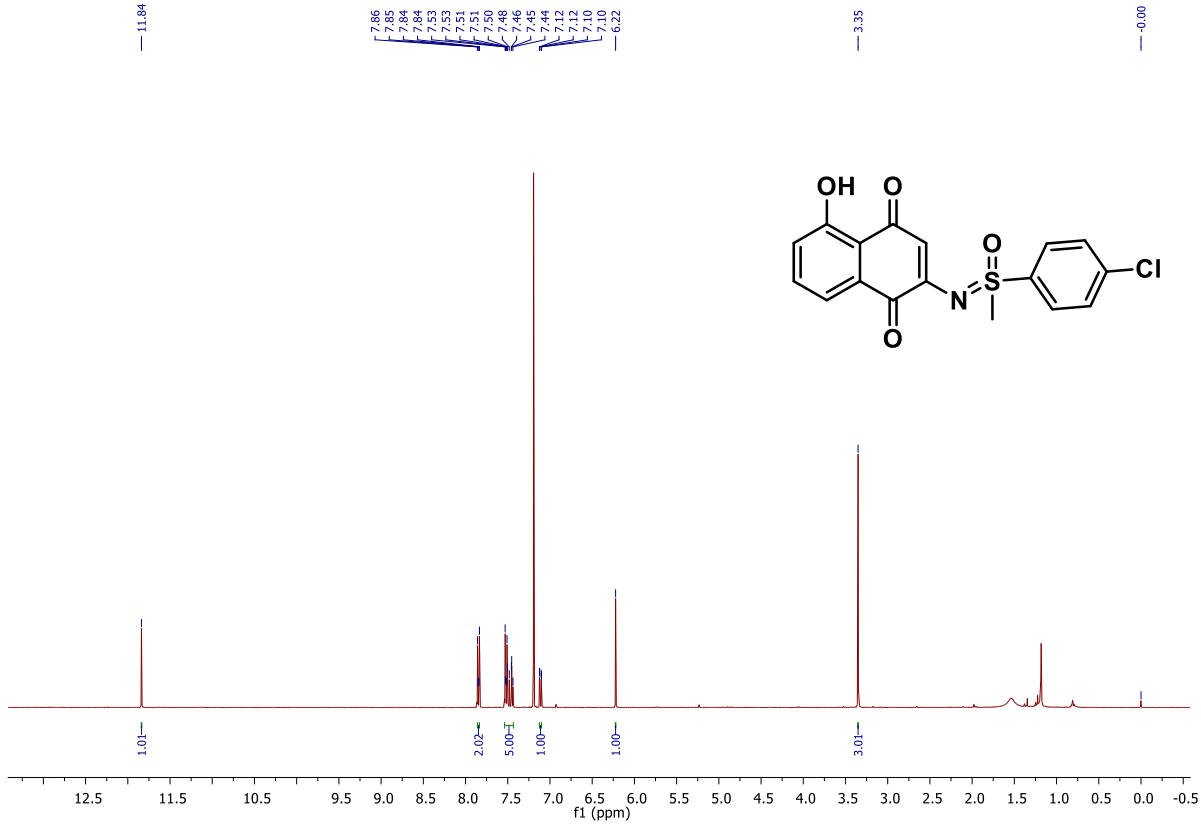
^{13}C {^{1}H} NMR (101 MHz) of 7c in $CDCl_3$



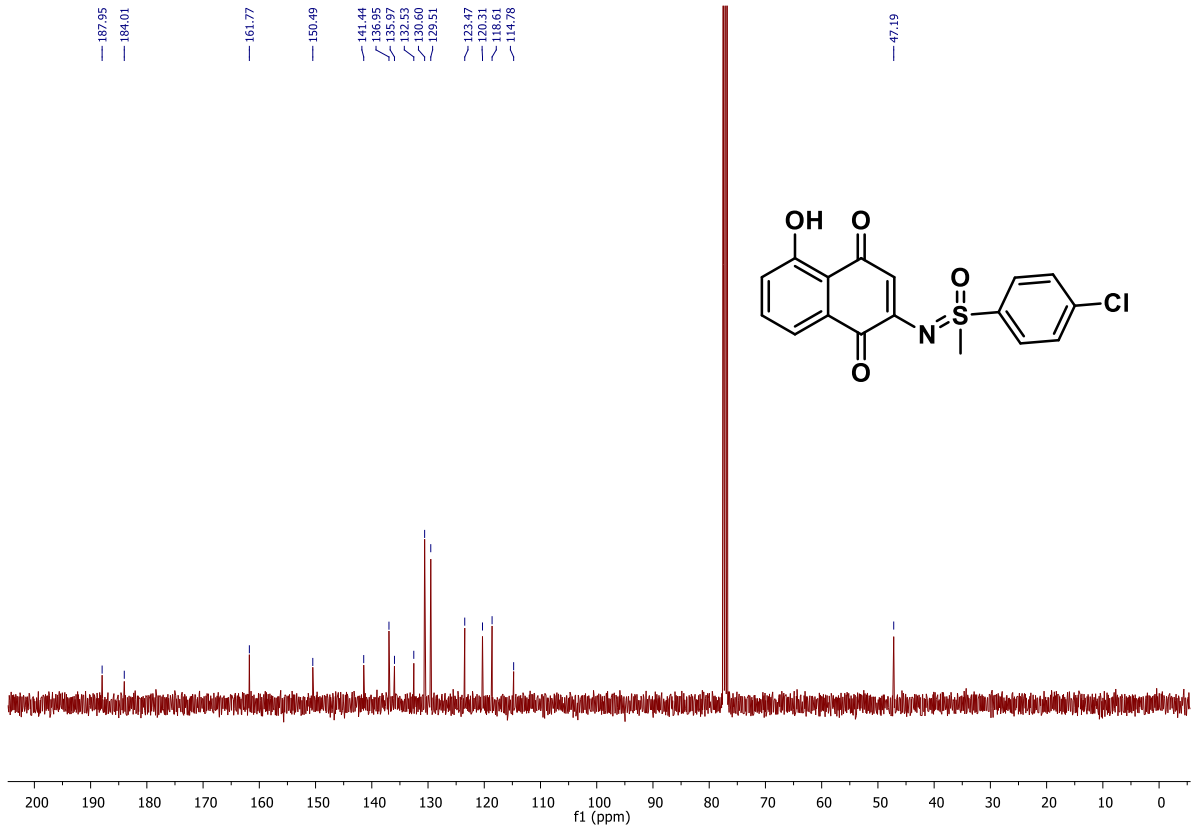
HRMS of 7c



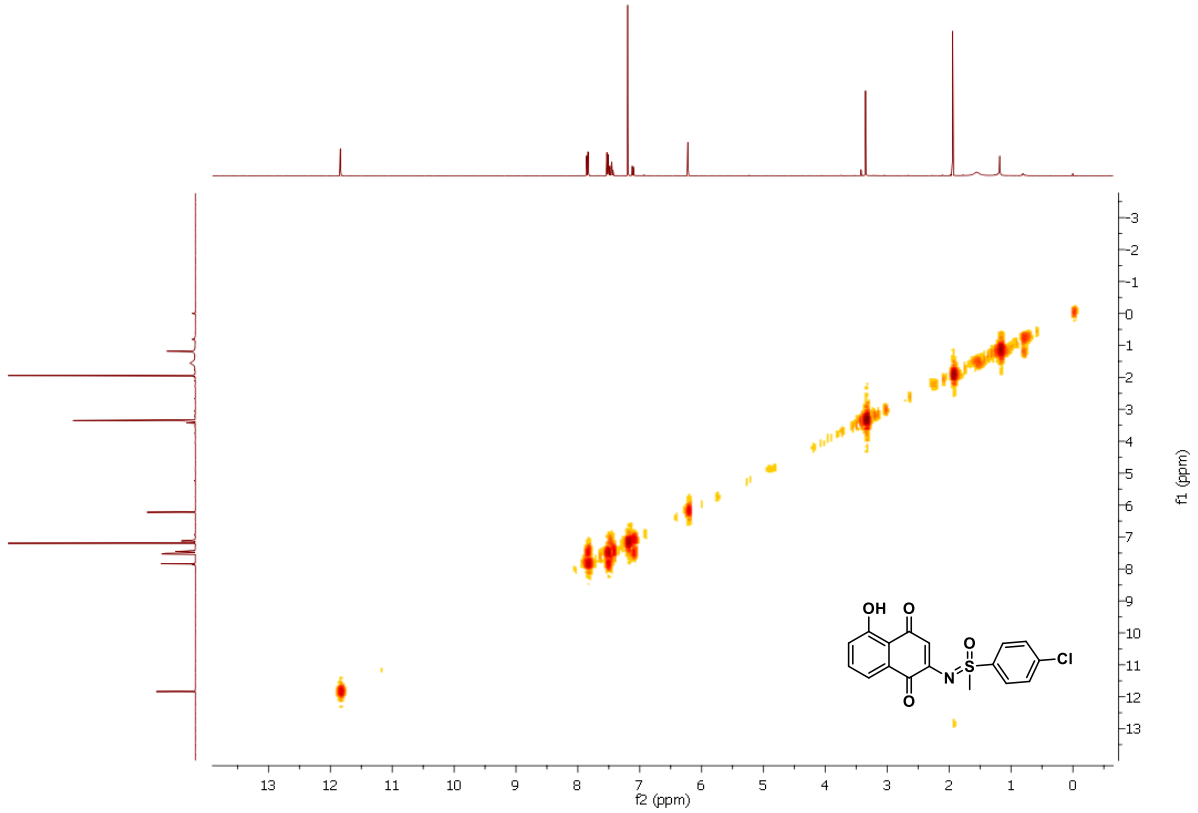
^{1}H NMR (400 MHz) of 8a in $CDCl_3$



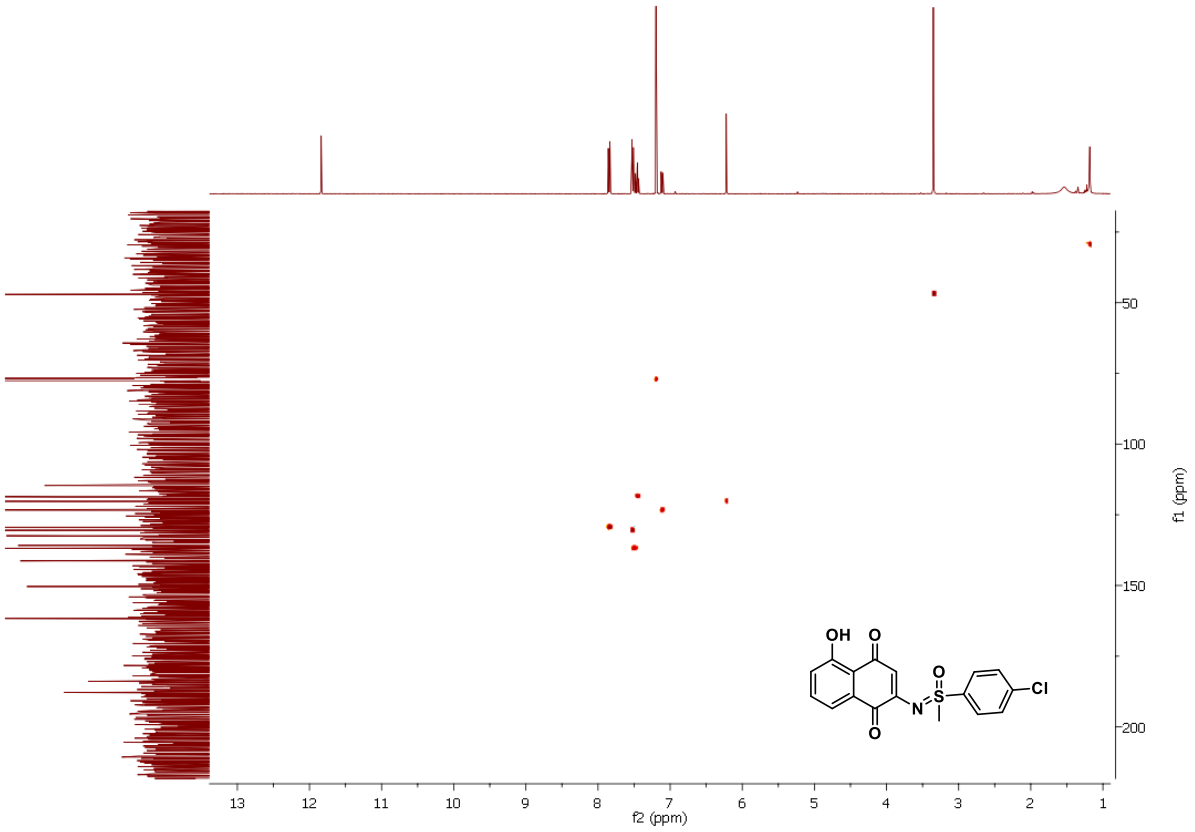
^{13}C {^{1}H} NMR (101 MHz) of 8a in $CDCl_3$



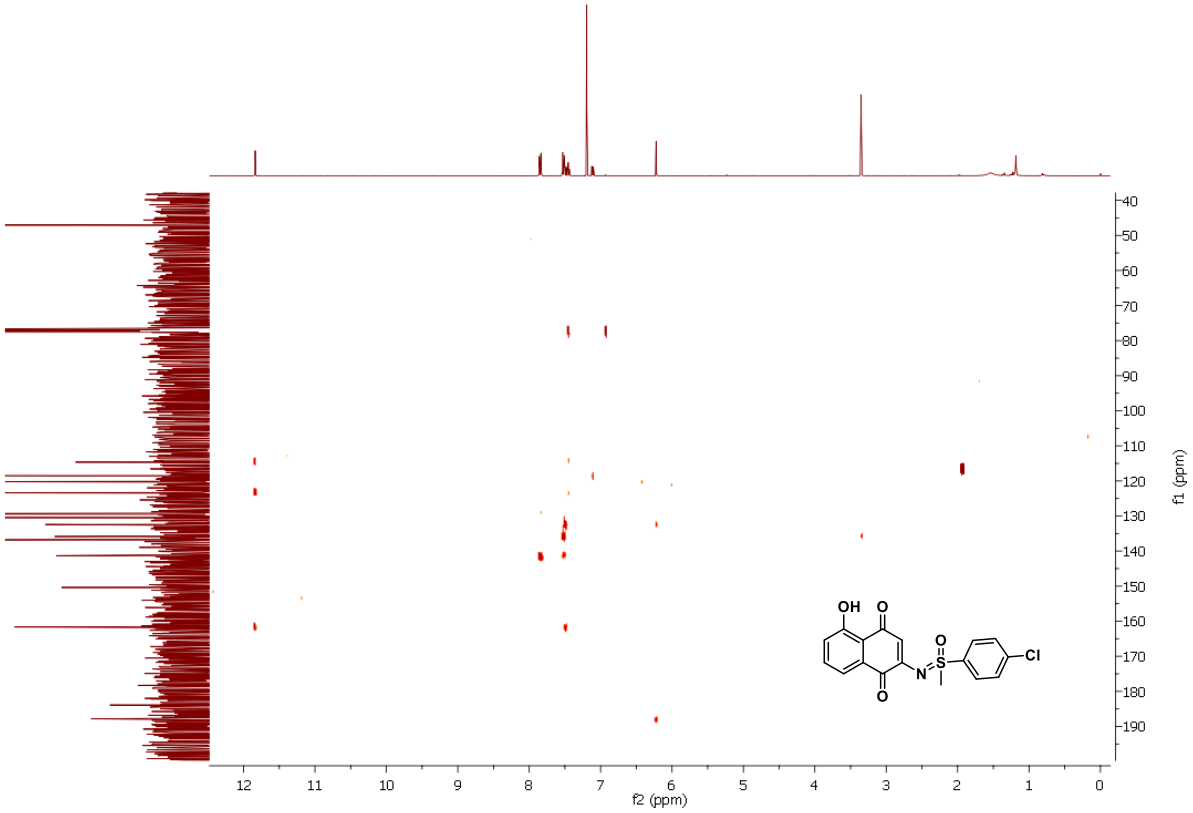
2D NMR (COSY) Spectra of 8a in $CDCl_3$



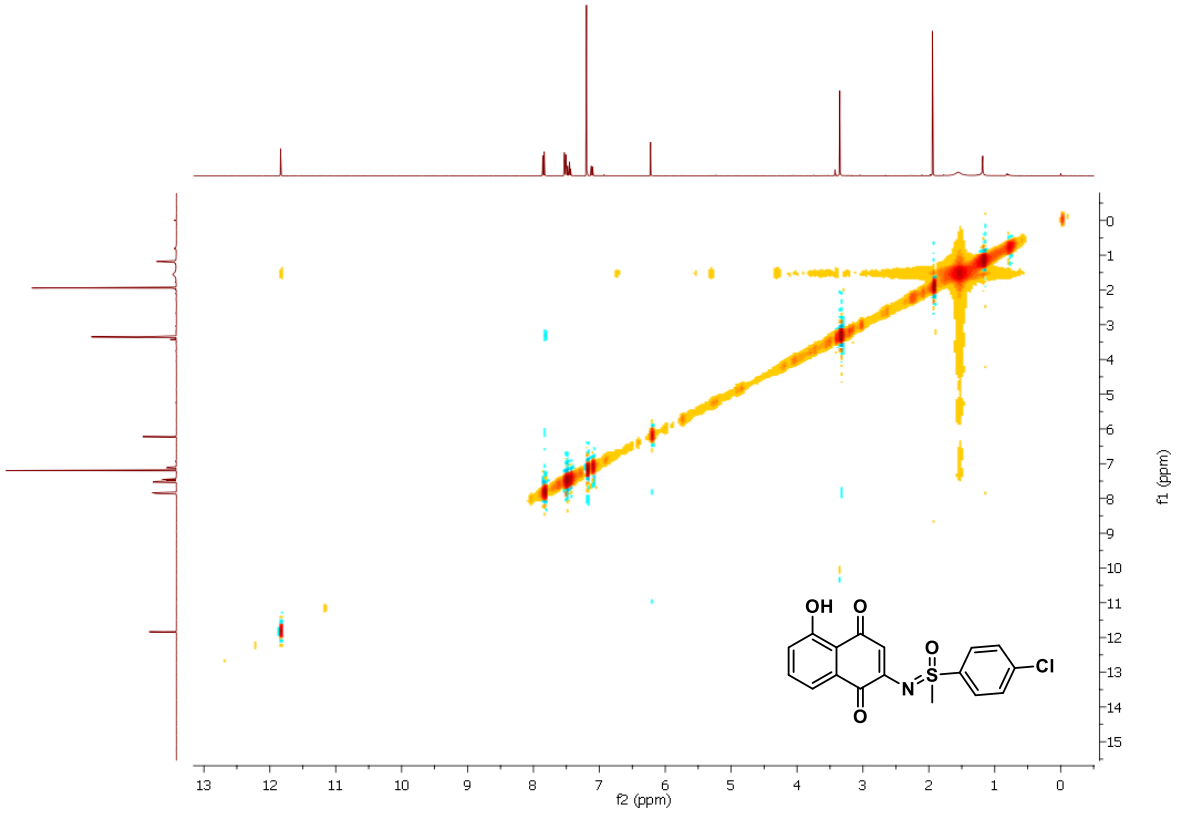
HSQC Spectra of 8a in $CDCl_3$


OH
O
O
O
N
S
O
Cl
13
12
11
10
9
8
7
6
5
4
3
2
1
f2 (ppm)
50
100
150
200
f1 (ppm)

HMBC Spectra of 8a in $CDCl_3$



NOESY Spectra of 8a in $CDCl_3$


OH
O
O
N
S
O
Cl
f2 (ppm)
f1 (ppm)

HRMS of 8a

Elemental Composition Report Page 1

Single Mass Analysis
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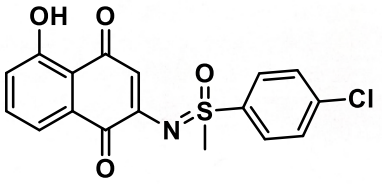
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

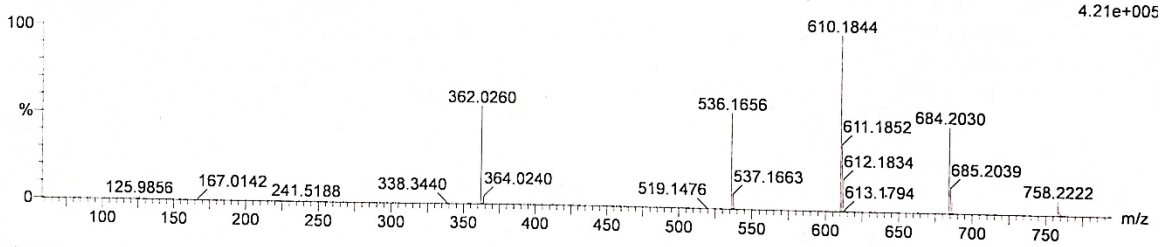


Monoisotopic Mass, Even Electron Ions
44 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-17 H: 0-200 N: 0-1 O: 0-4 S: 0-1 Cl: 0-1
NQ-6-G

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

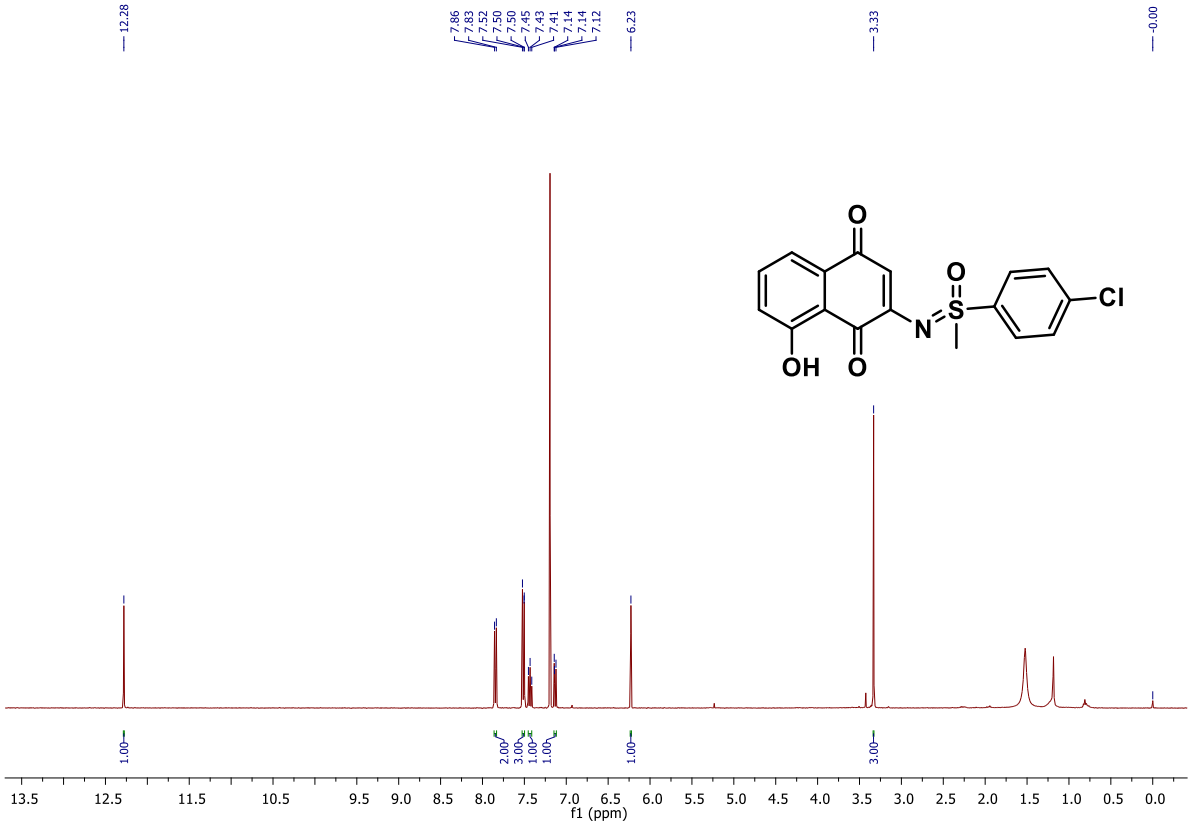
10-Feb-2022
11:56:55
1: TOF MS ES+
4.21e+005

100222_09 8 (0.172) Cm (8)

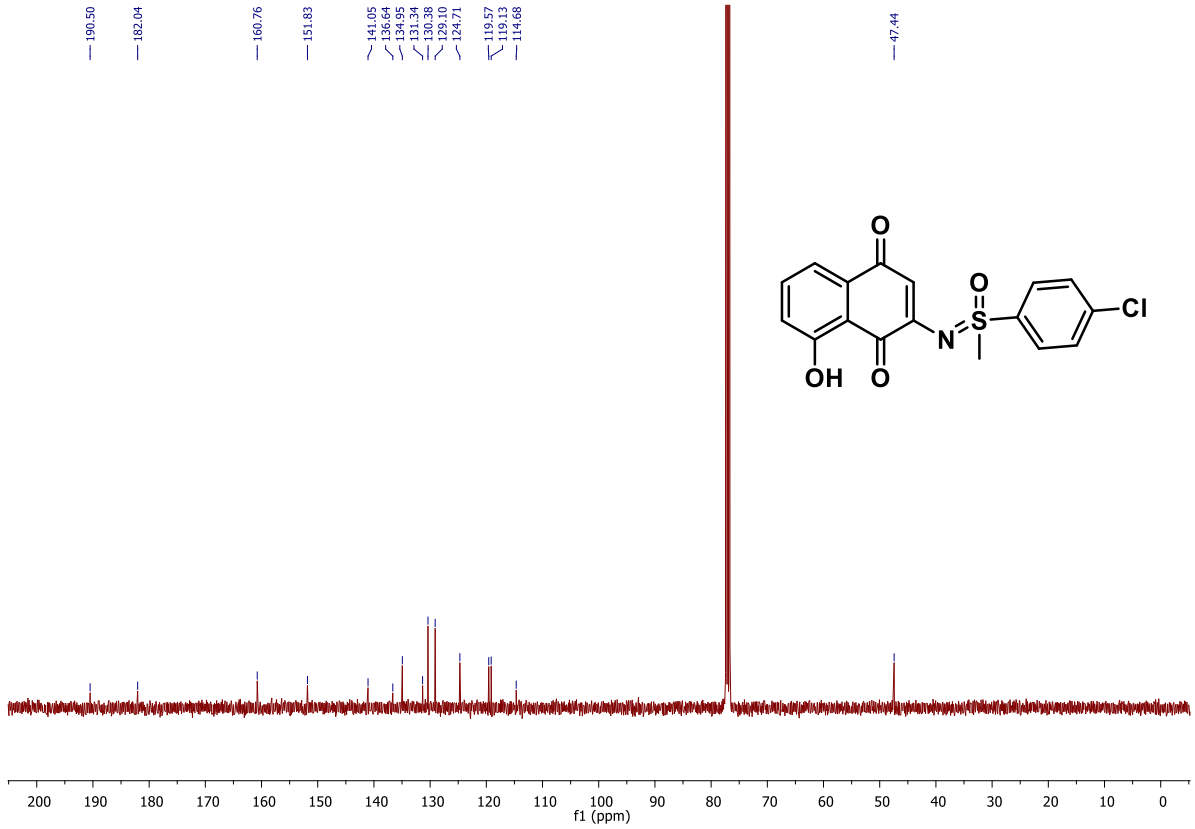


Minimum:				-1.5				
Maximum:		2.0	3.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
362.0260	362.0254	0.6	1.7	11.5	31.3	n/a	n/a	C17 H13 N O4 S Cl

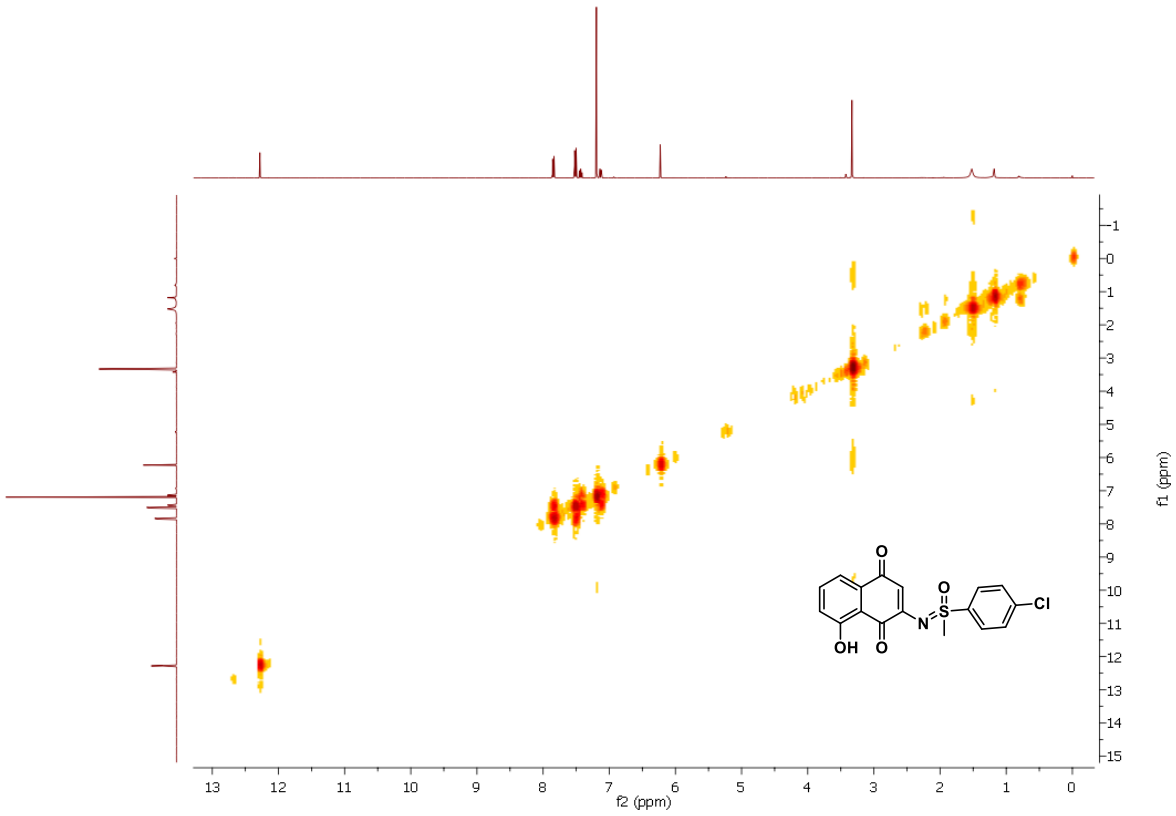
^{1}H NMR (400 MHz) of 8b in $CDCl_3$



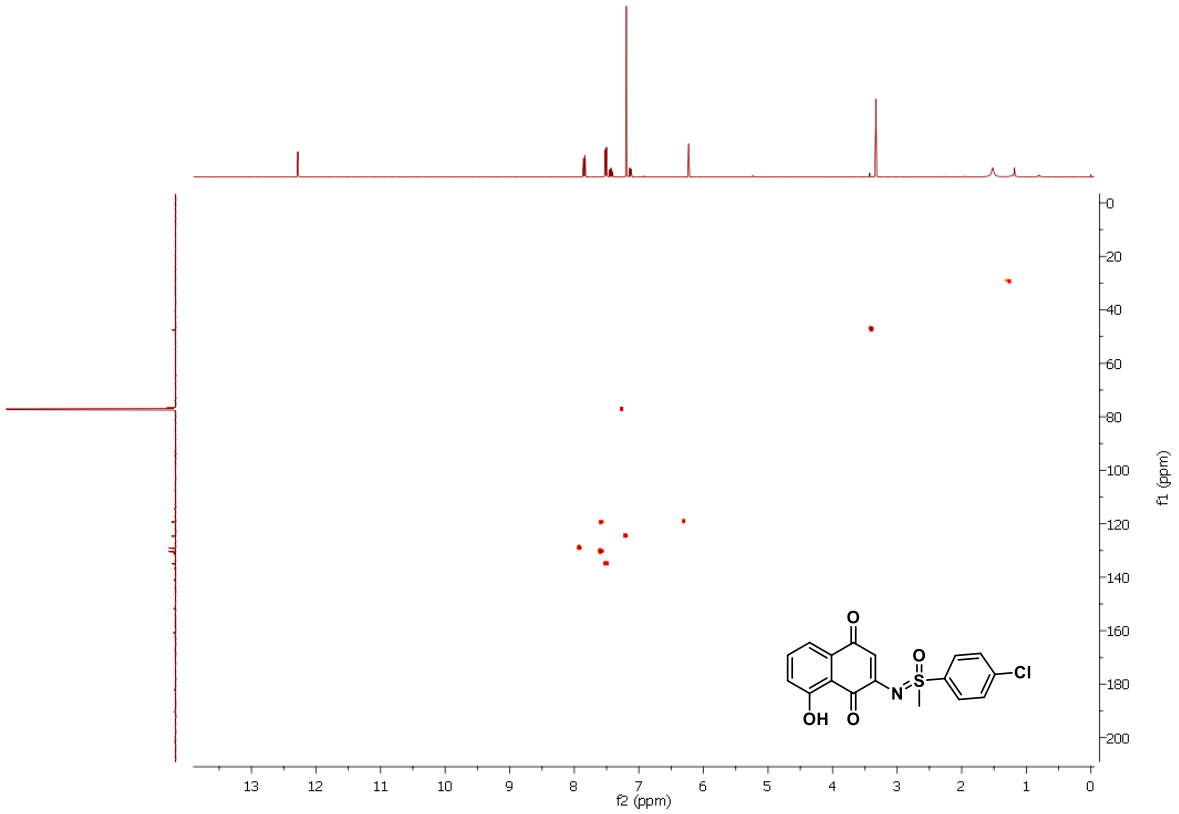
^{13}C {^{1}H} NMR (101 MHz) of 8b in $CDCl_3$



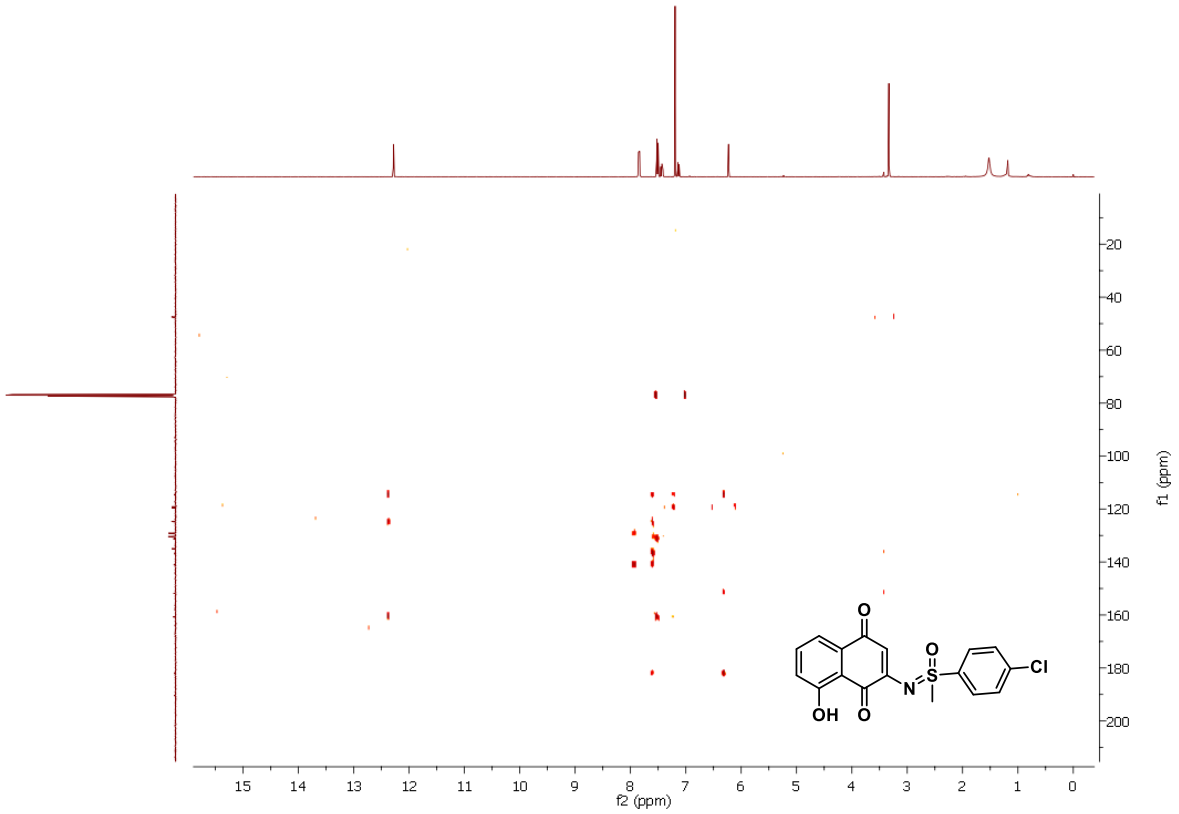
2D NMR (COSY) Spectra of 8b in $CDCl_3$



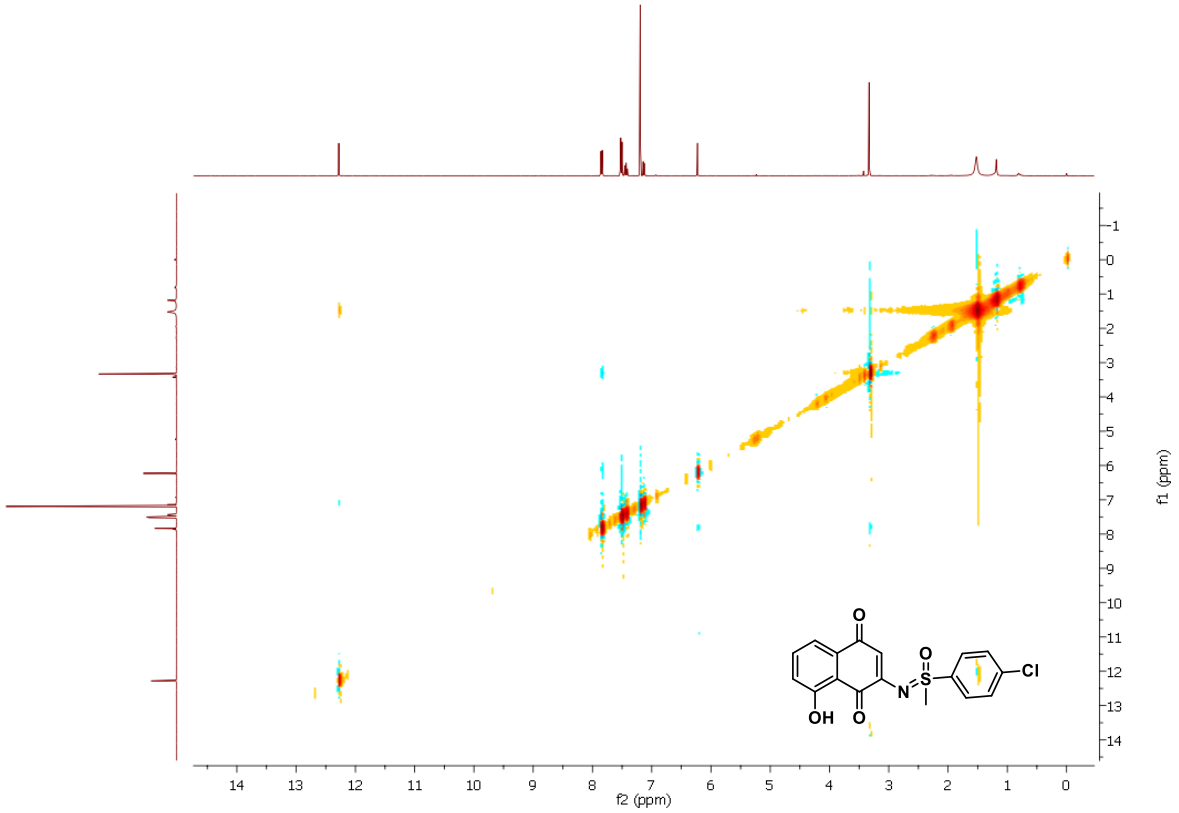
HSQC Spectra of 8b in $CDCl_3$



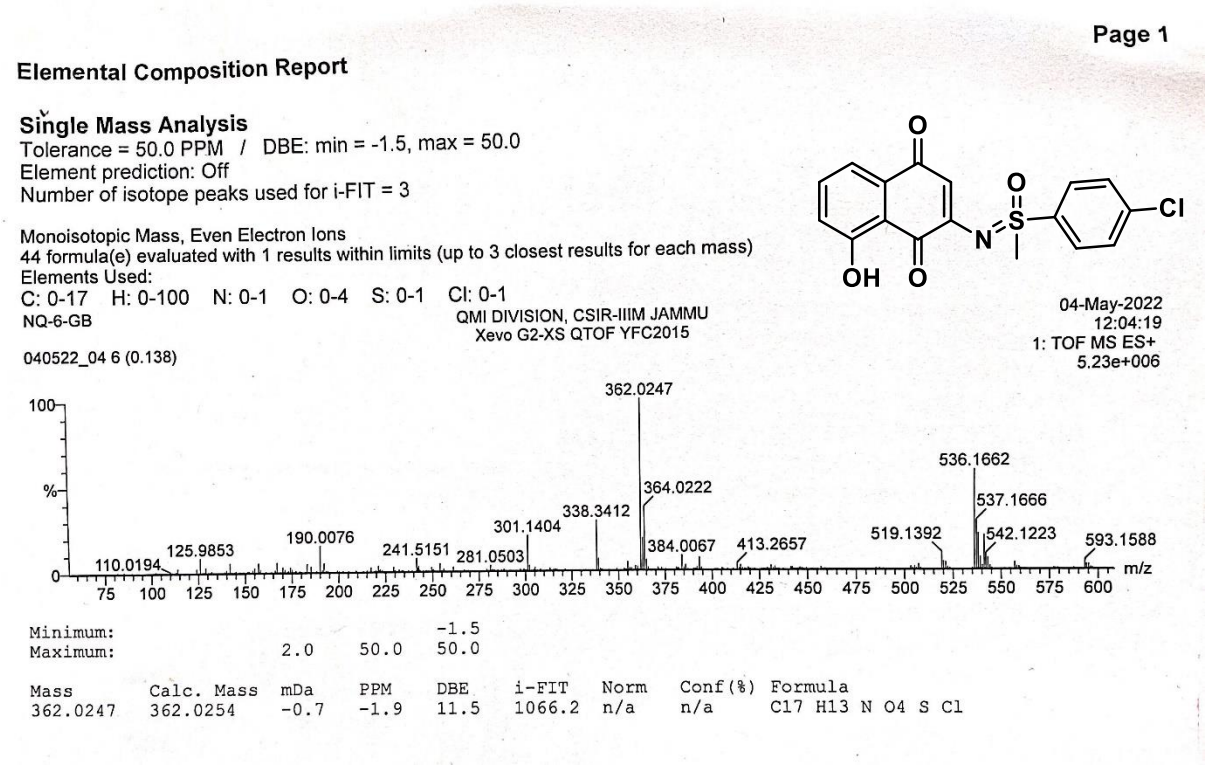
HMBC Spectra of 8b in $CDCl_3$



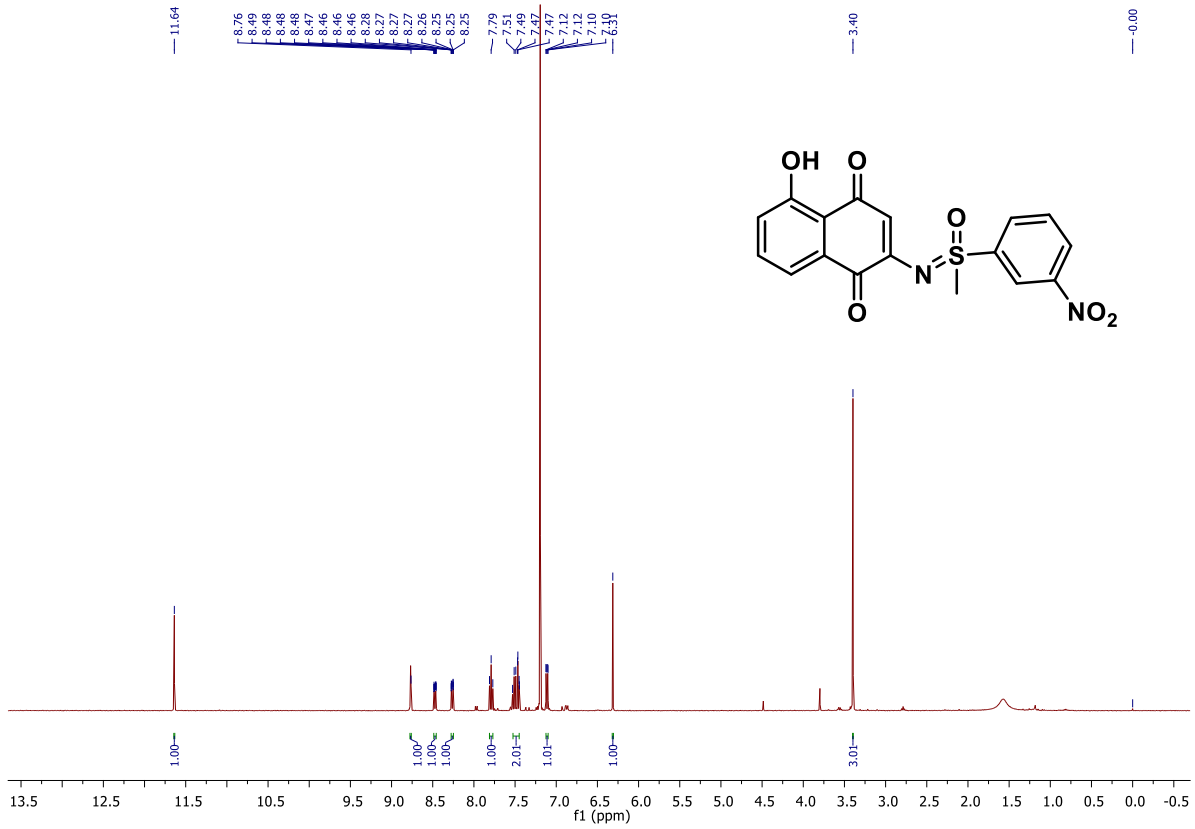
NOESY Spectra of 8b in $CDCl_3$



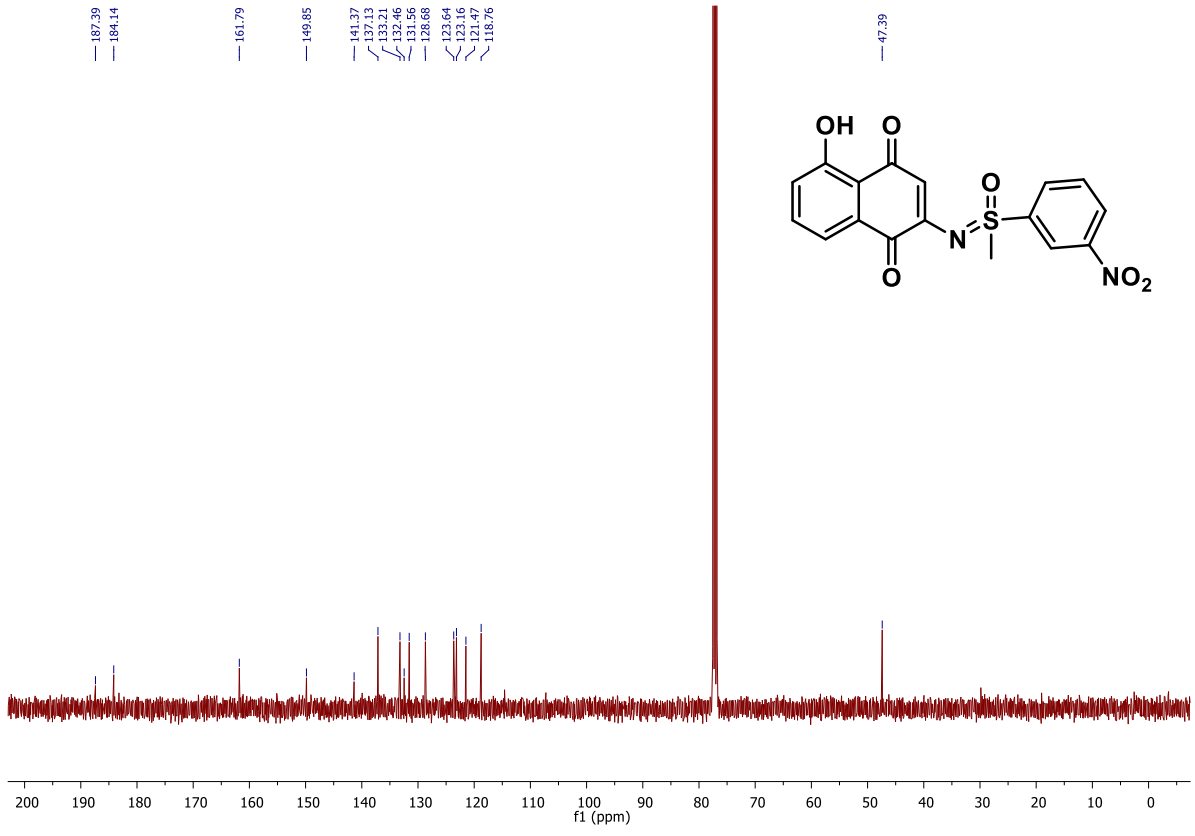
HRMS of 8b



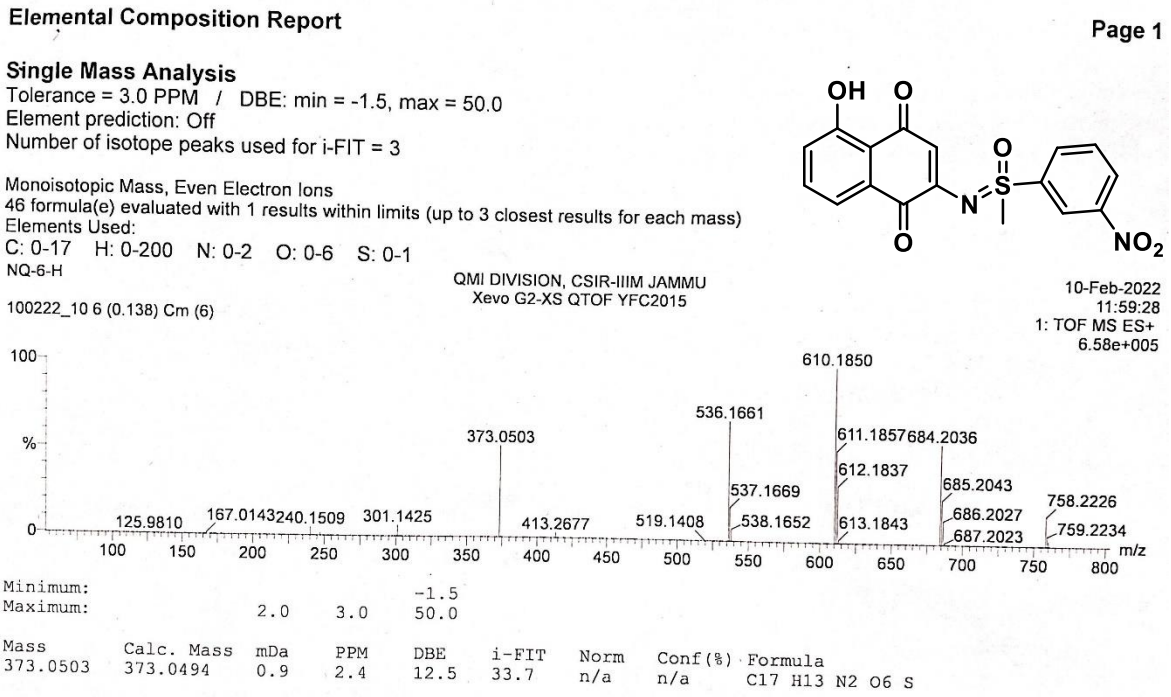
^{1}H NMR (400 MHz) of 8c in $CDCl_3$



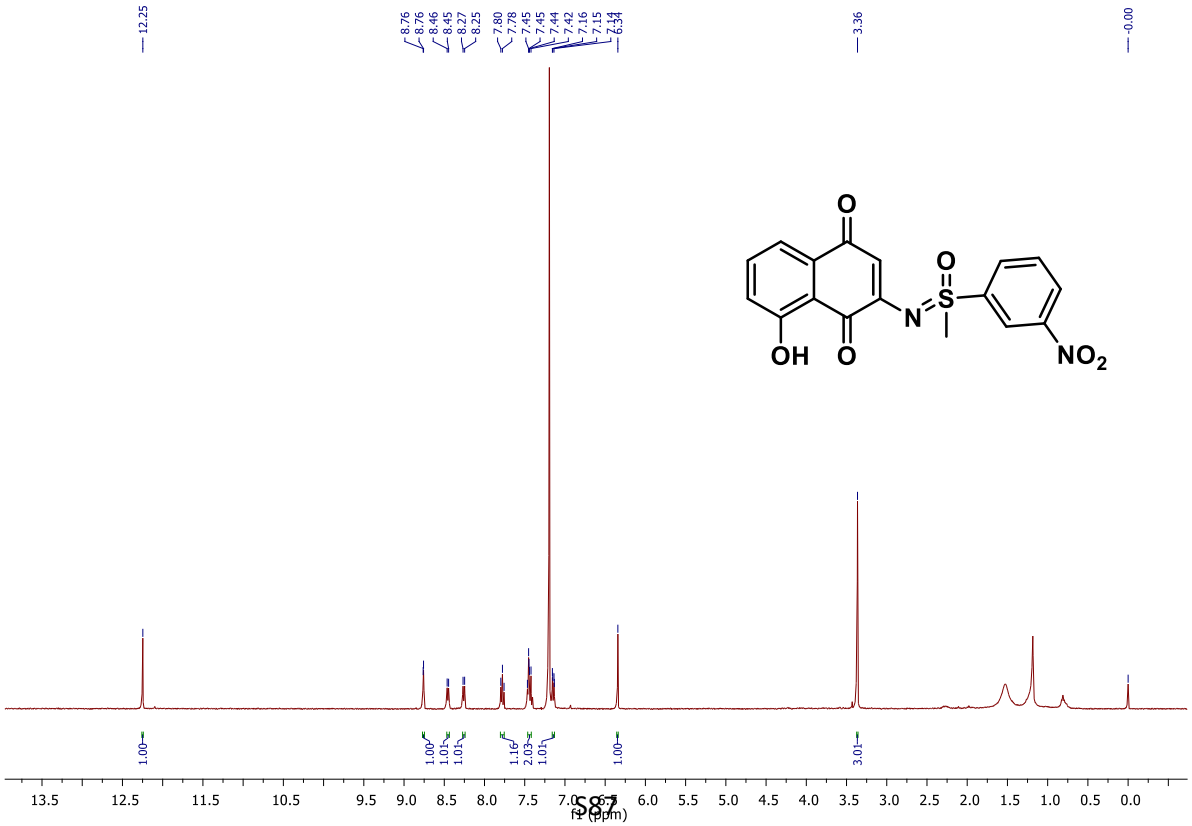
^{13}C {^{1}H} NMR (101 MHz) of 8c in $CDCl_3$



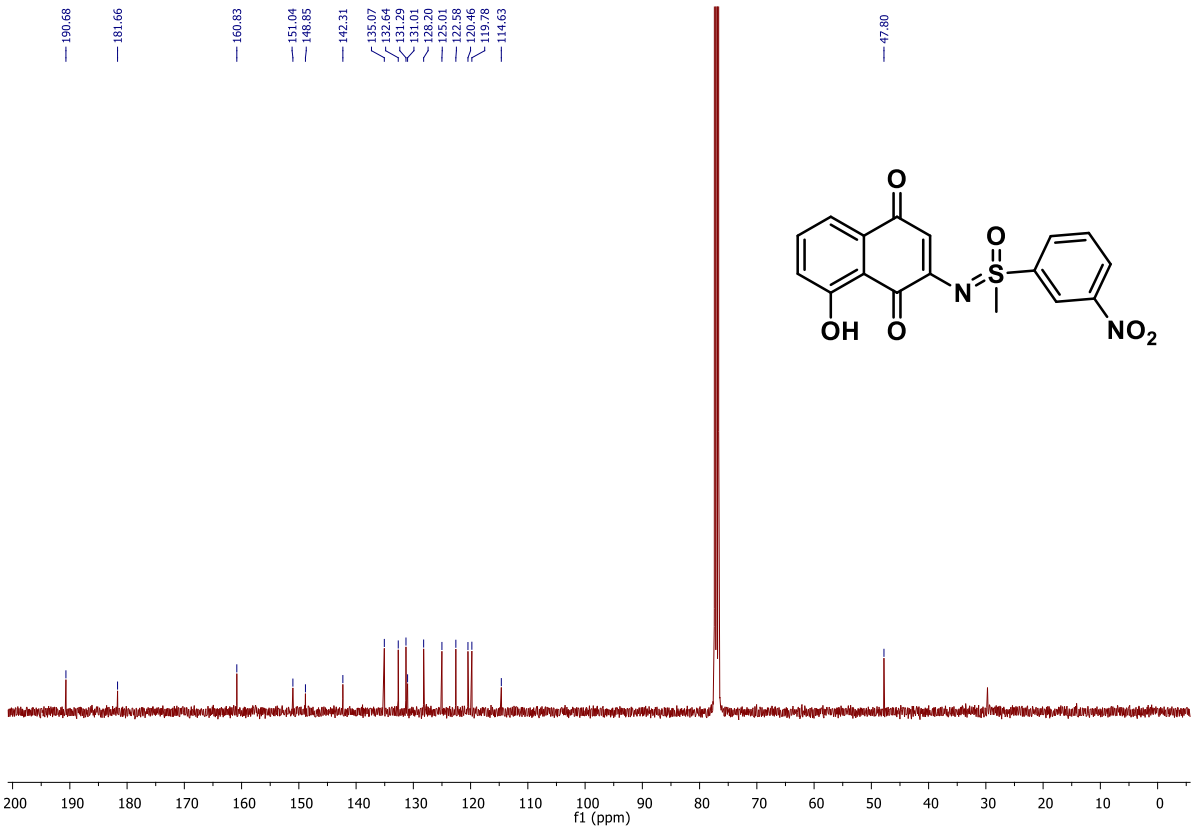
HRMS of 8c



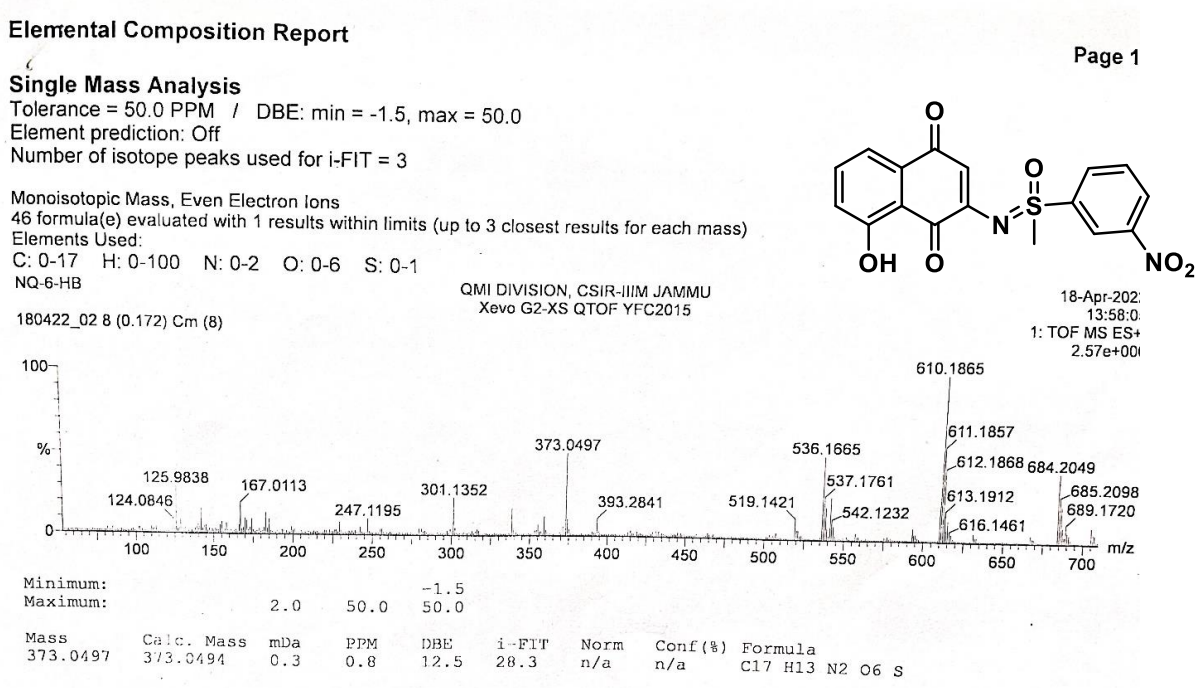
^{1}H NMR (400 MHz) of 8d in $CDCl_3$



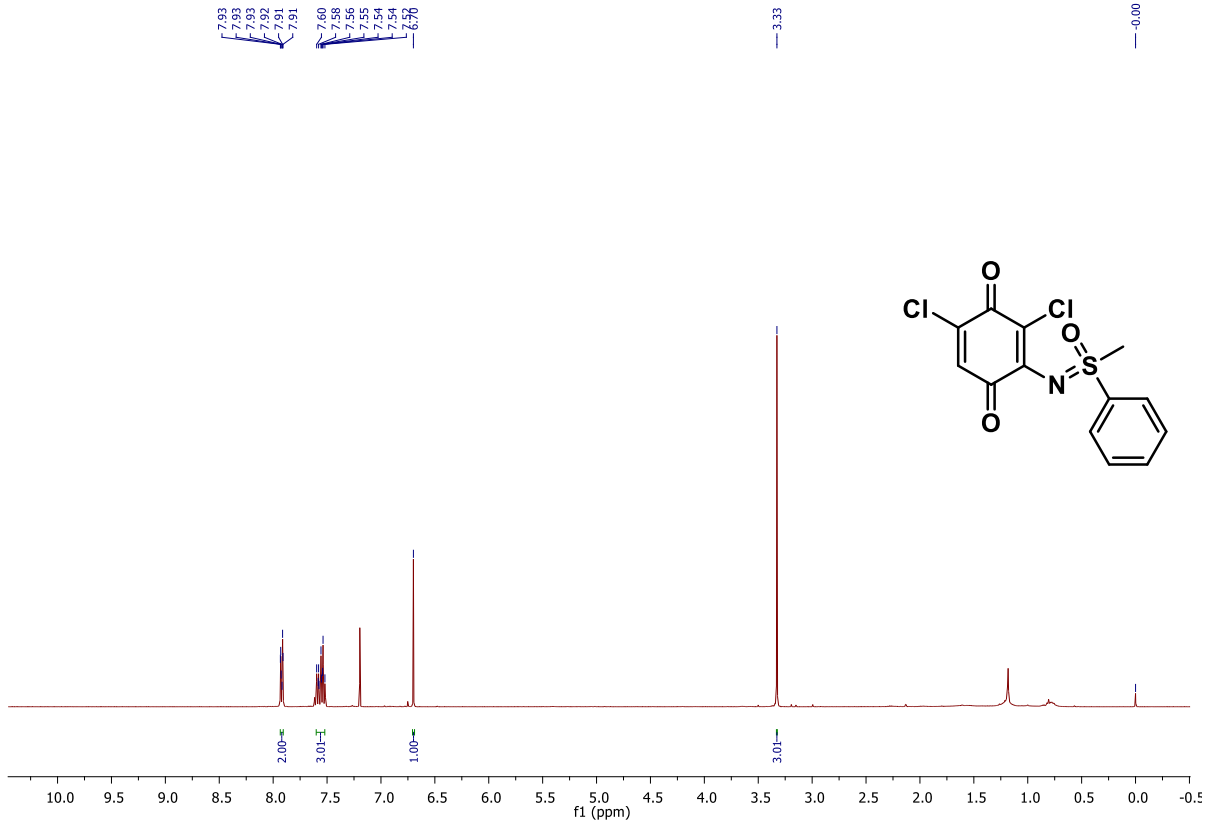
^{13}C {^{1}H} NMR (101 MHz) of 8d in $CDCl_3$



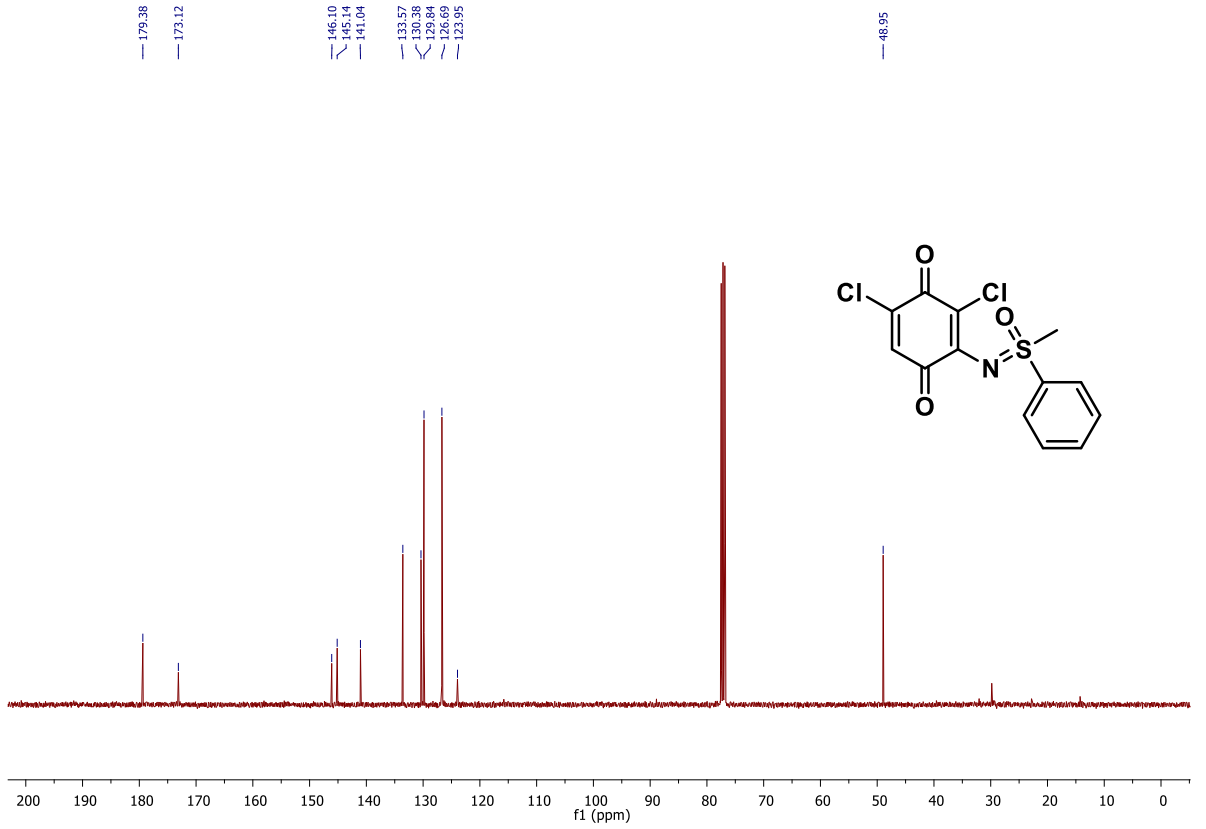
HRMS of 8d



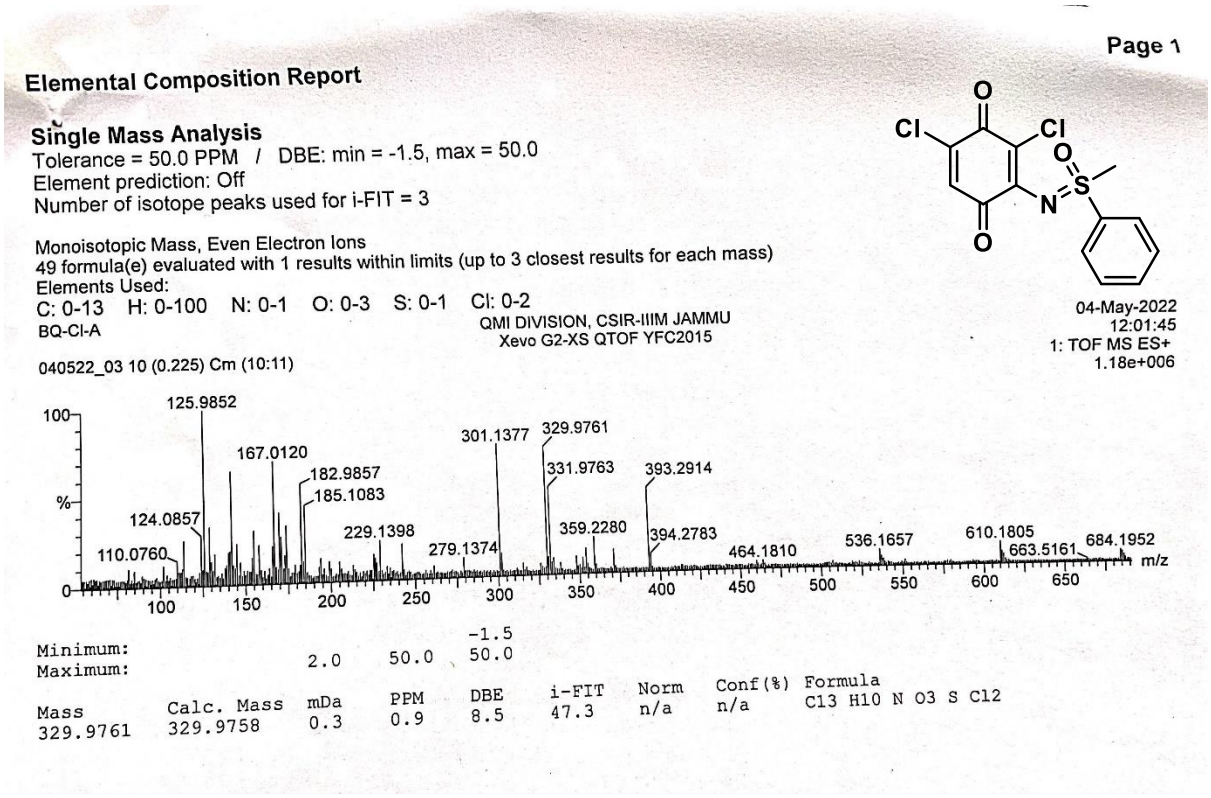
^{1}H NMR (400 MHz) of 10a in $CDCl_3$



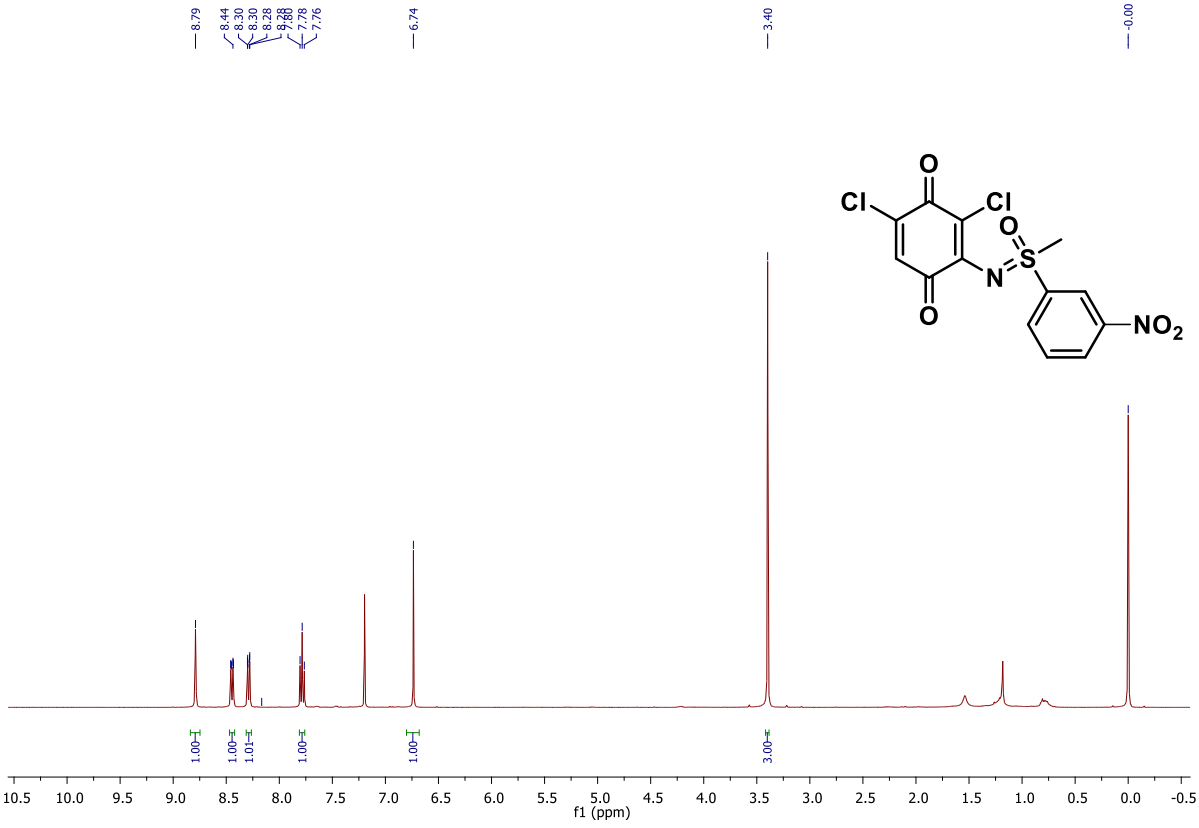
^{13}C {1H} NMR (101 MHz) of 10a in $CDCl_3$



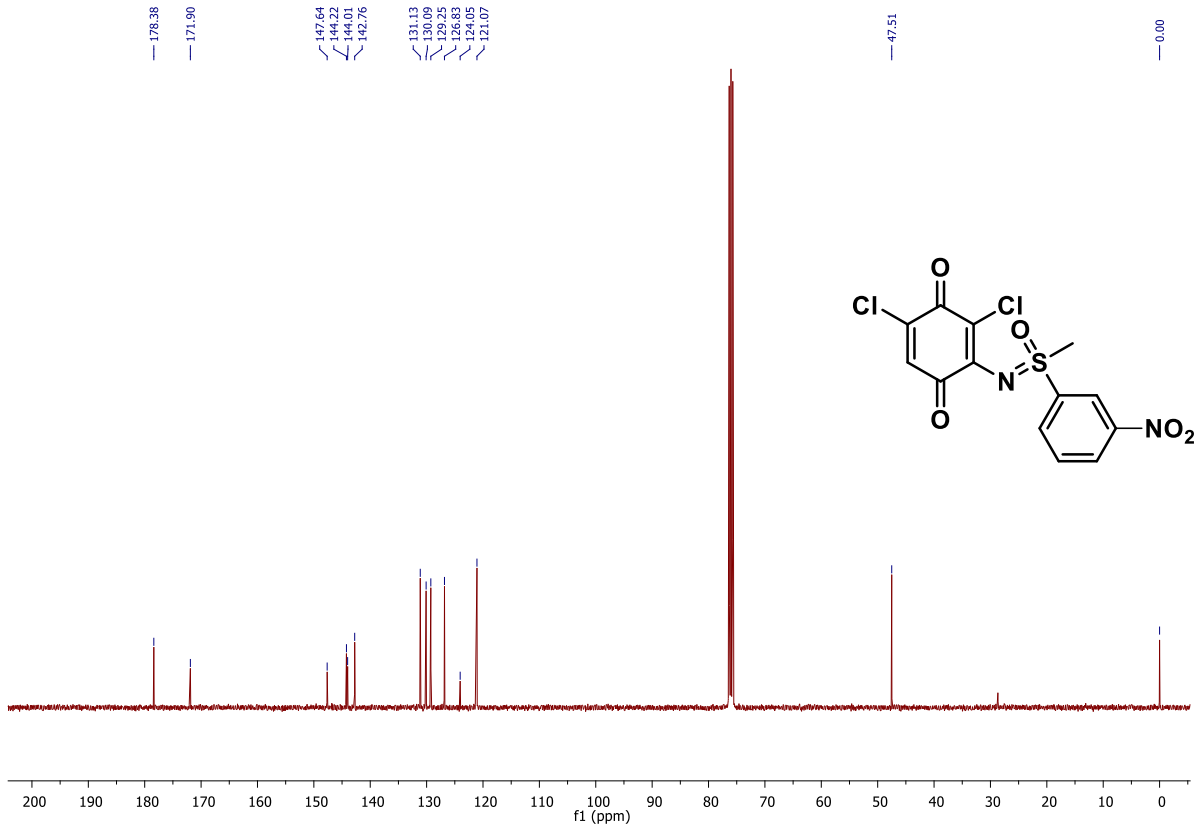
HRMS of 10a



^{1}H NMR (400 MHz) of 10b in $CDCl_3$



^{13}C {1H} NMR (101 MHz) of 10b in $CDCl_3$



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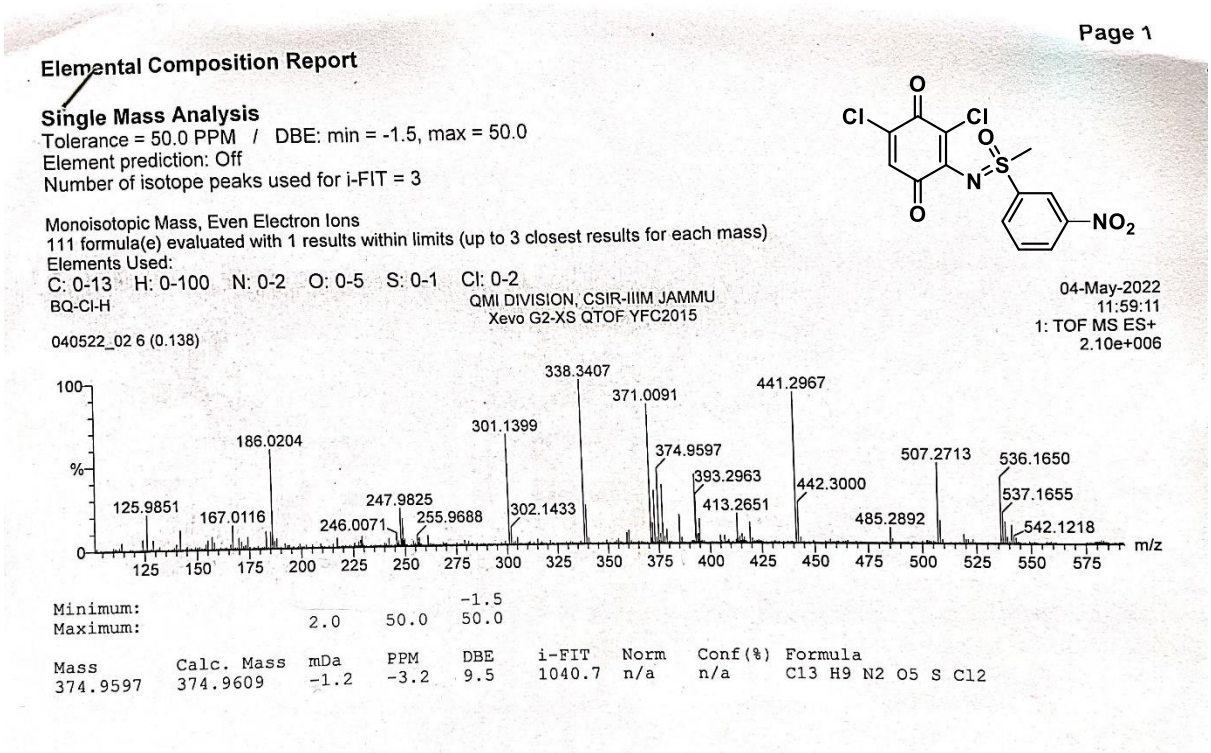
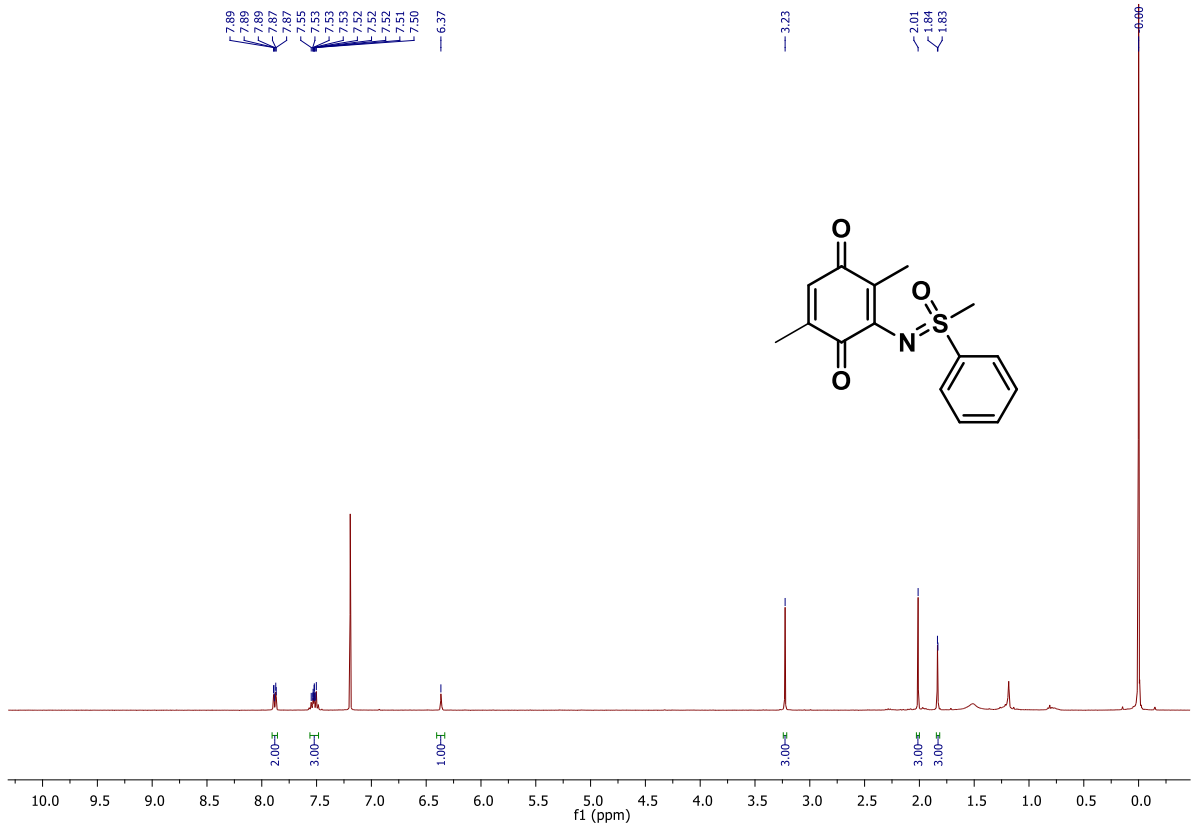
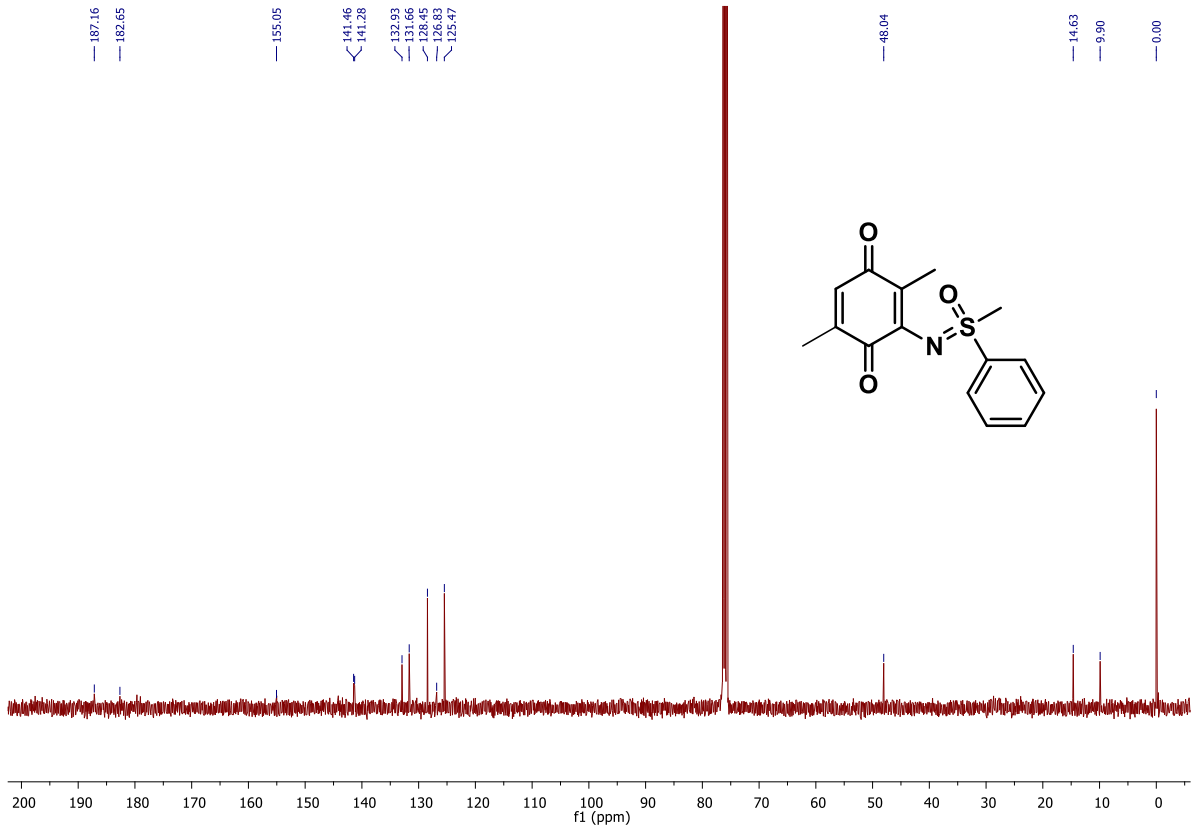


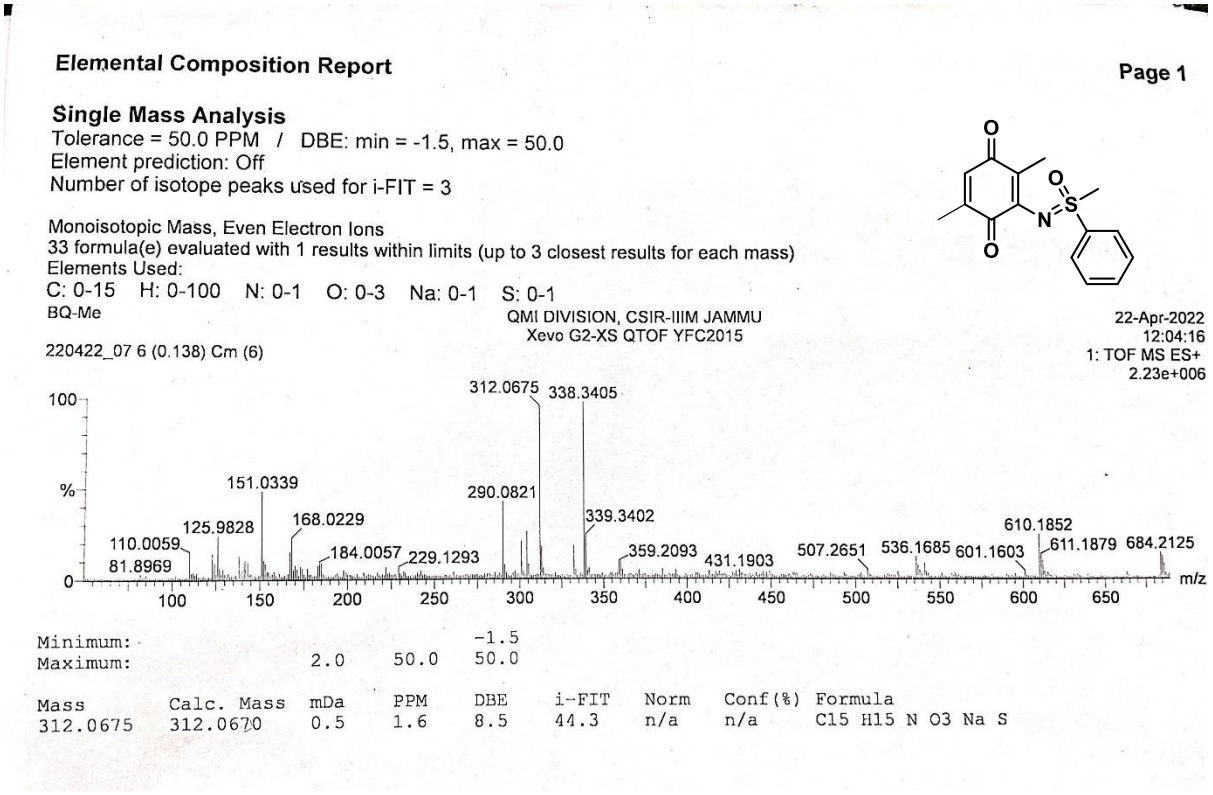
^{1}H NMR (400 MHz) of 10c in $CDCl_3$



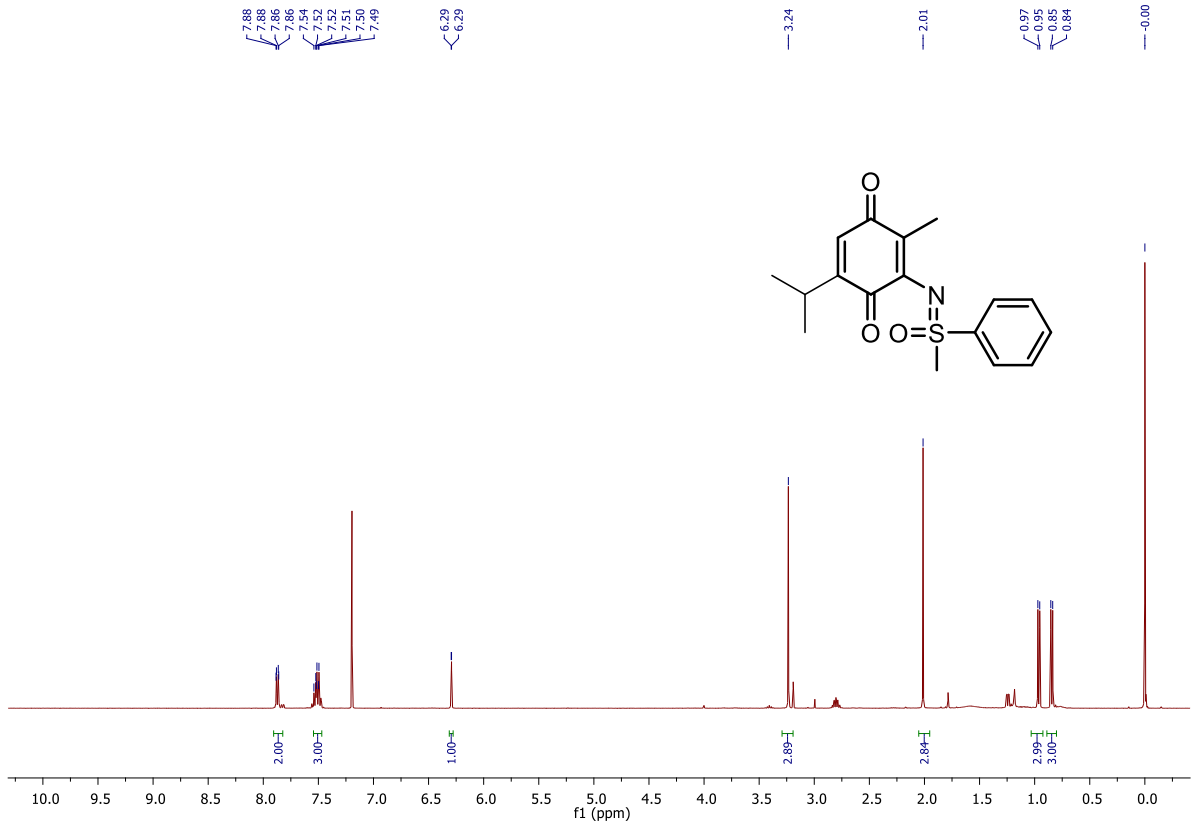
^{13}C {^{1}H} NMR (101 MHz) of 10c in $CDCl_3$



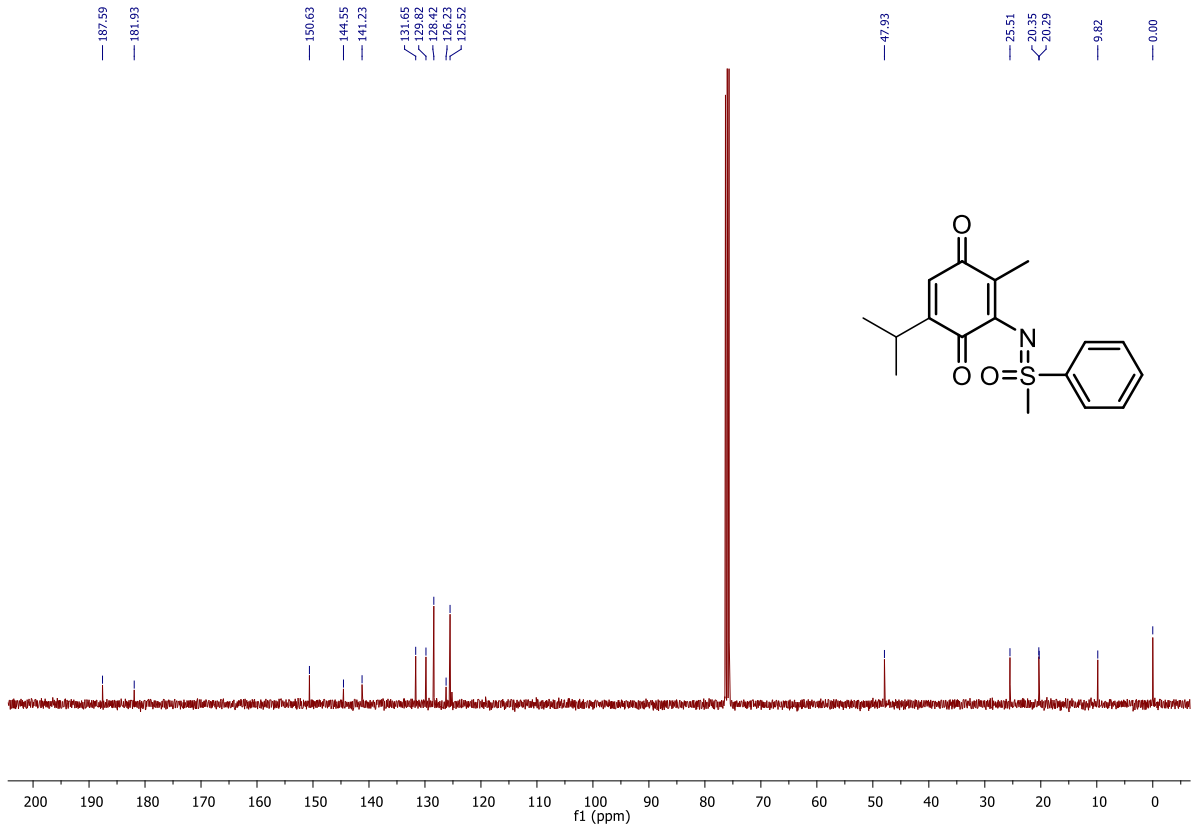
HRMS of 10c



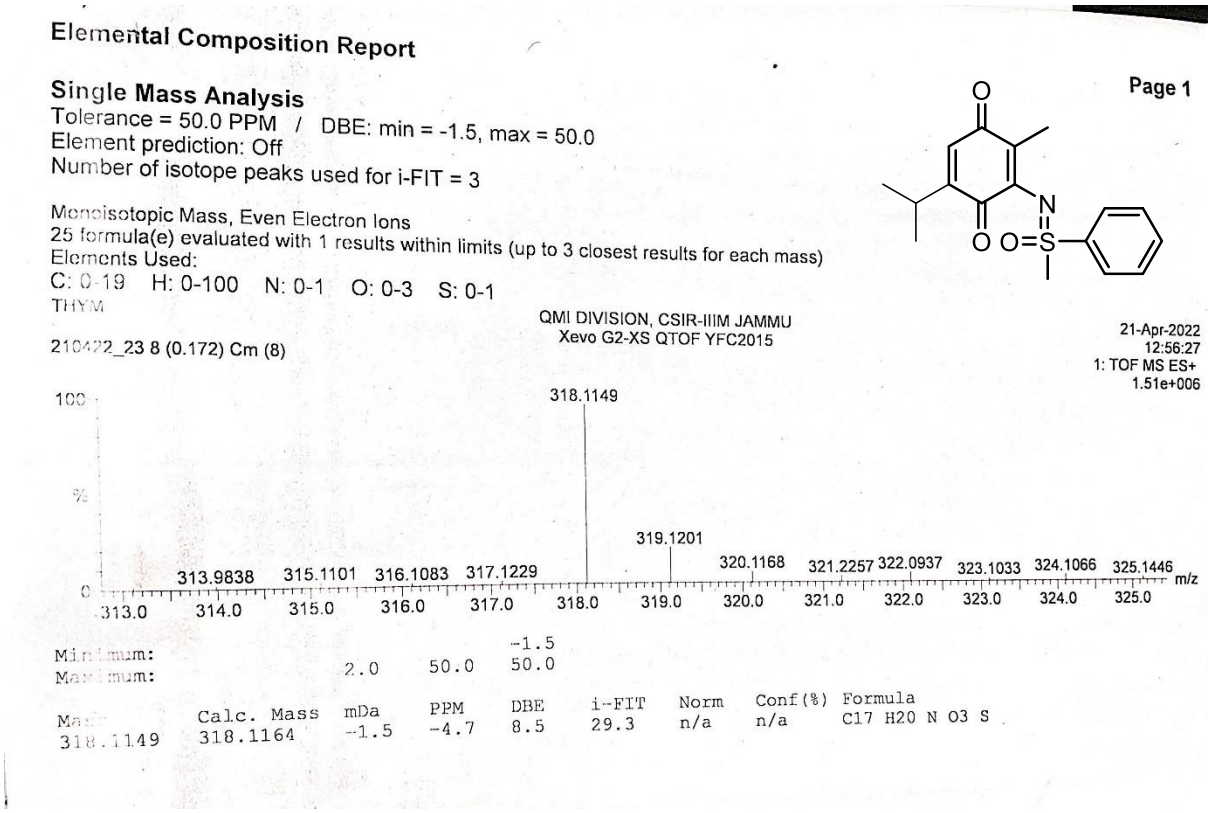
^{1}H NMR (400 MHz) of 10d in $CDCl_3$



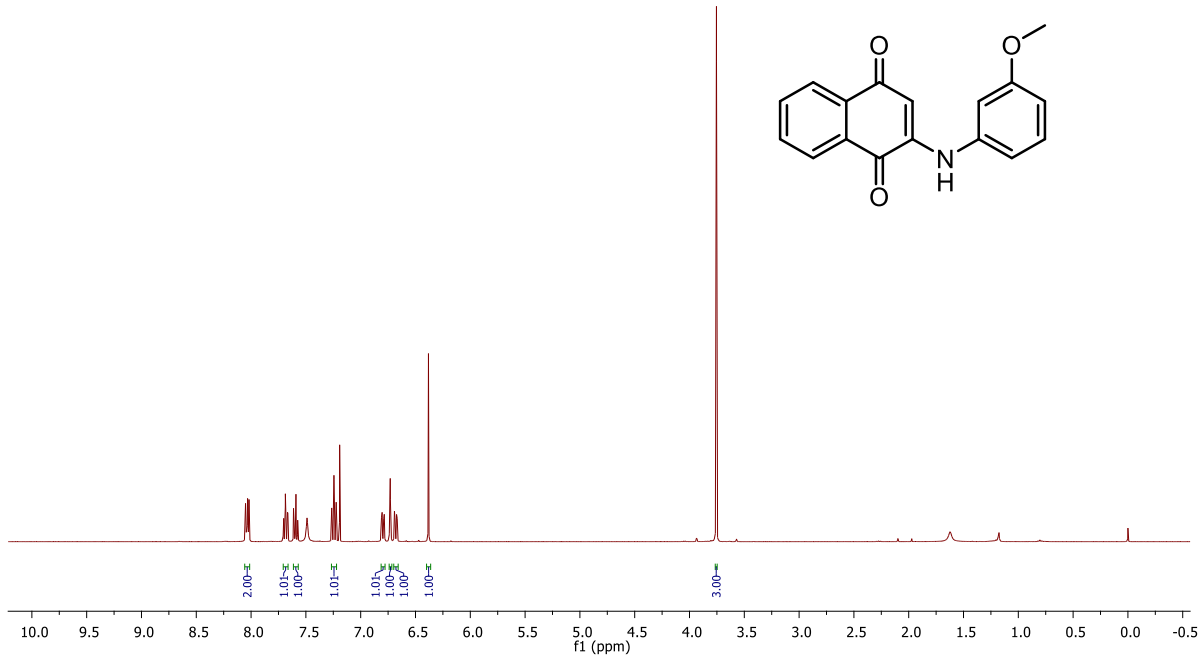
^{13}C {1H} NMR (101 MHz) of 10d in $CDCl_3$



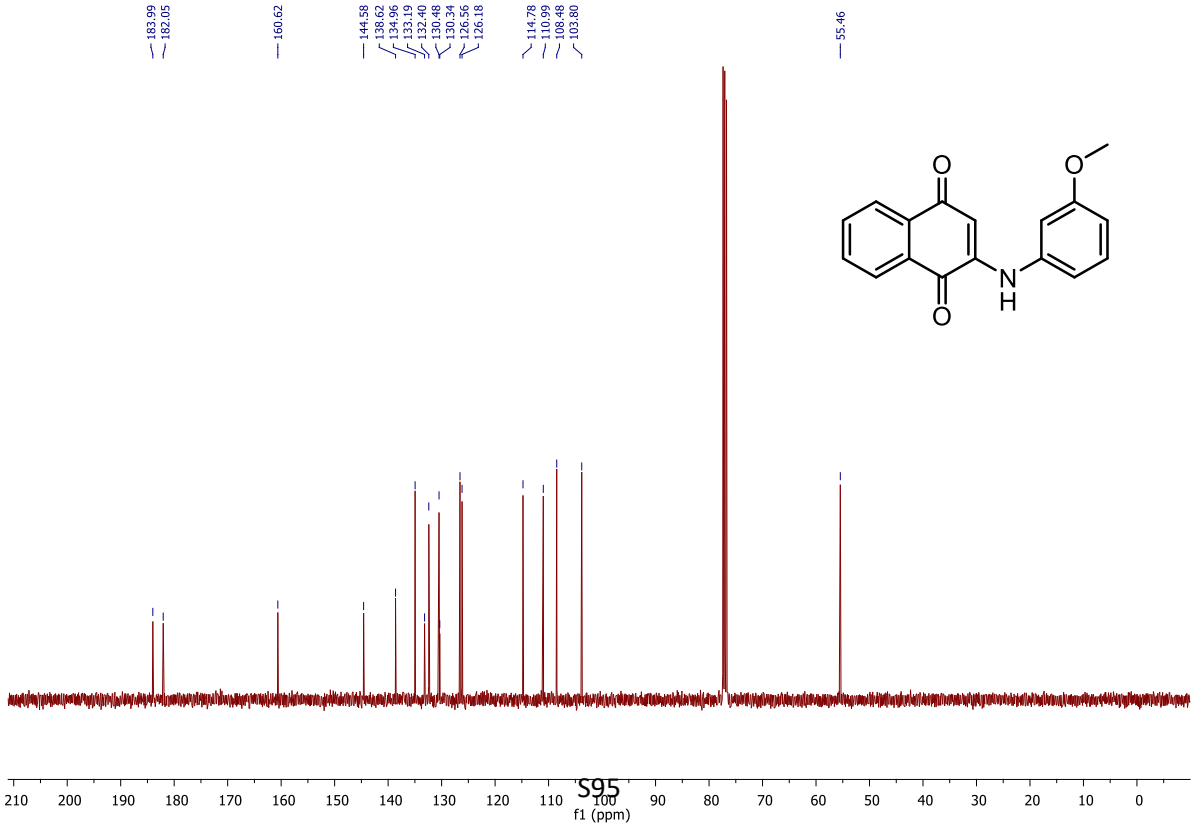
HRMS of 10d



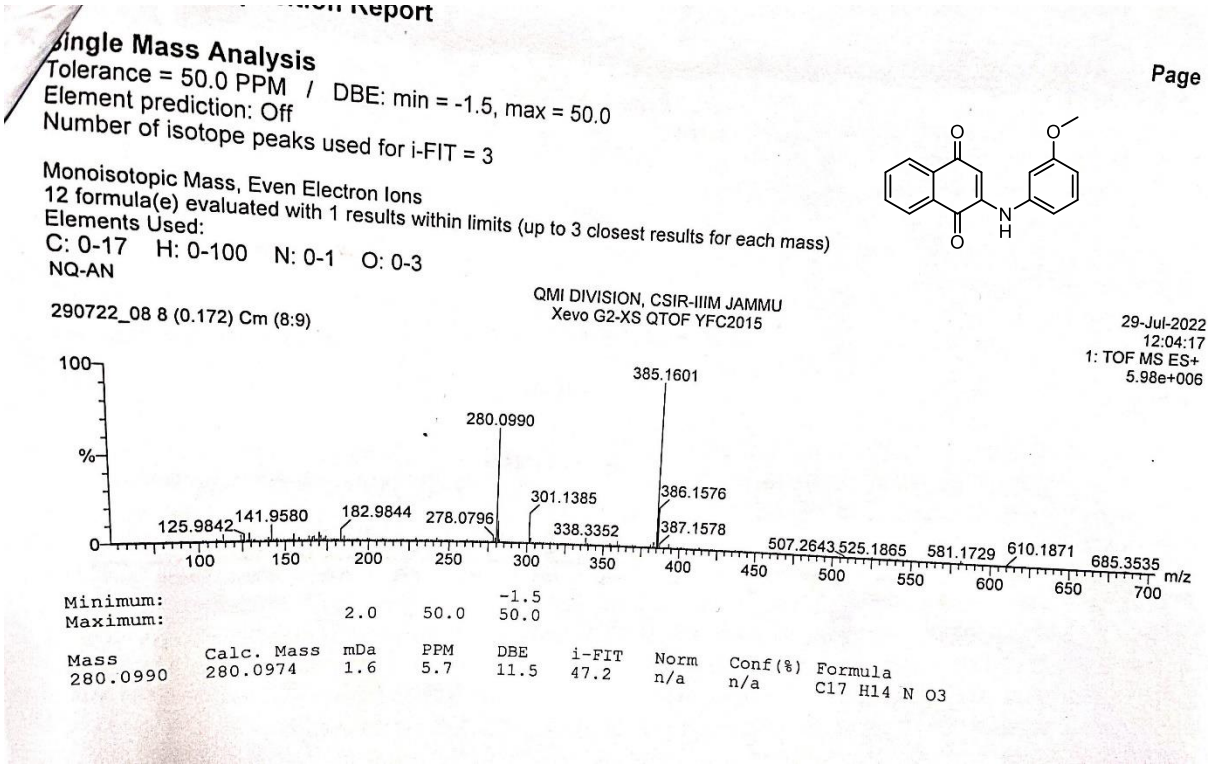
^{1}H NMR (400 MHz) of 11a in $CDCl_3$



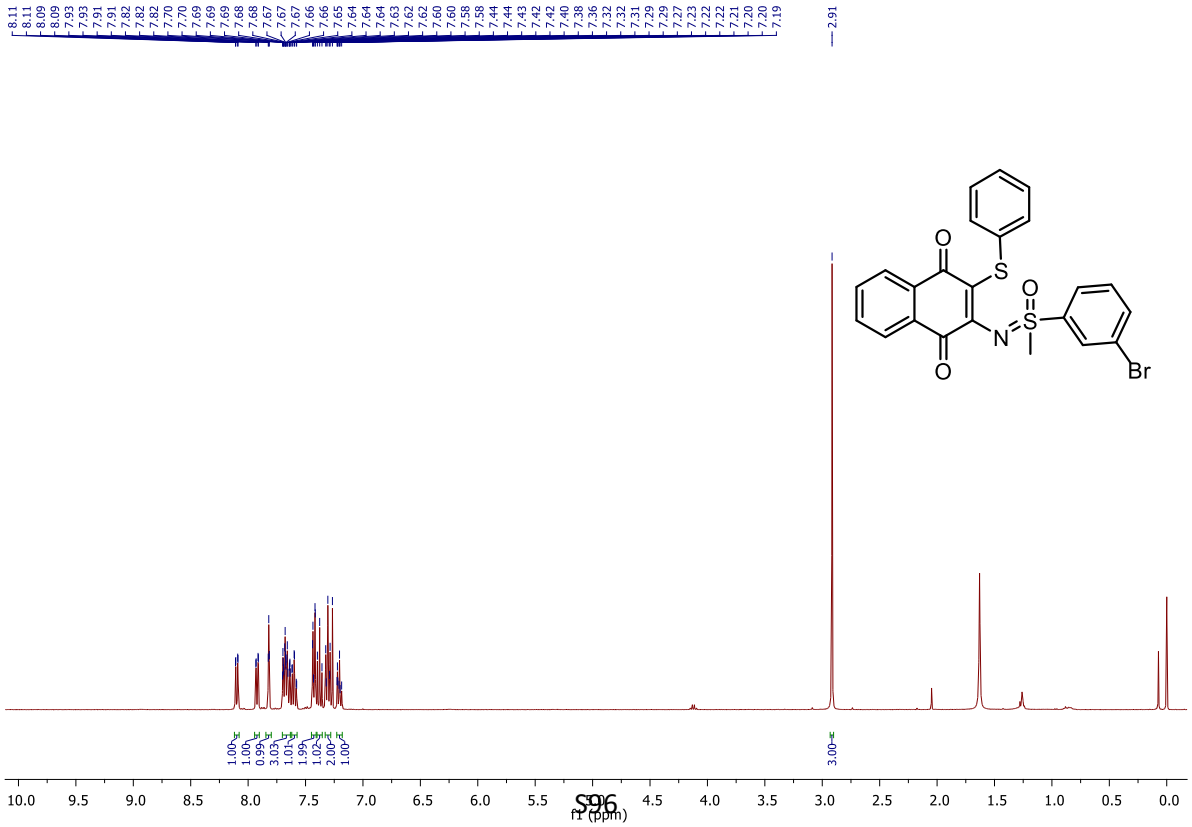
^{13}C {1H} NMR (101 MHz) of 11a in $CDCl_3$



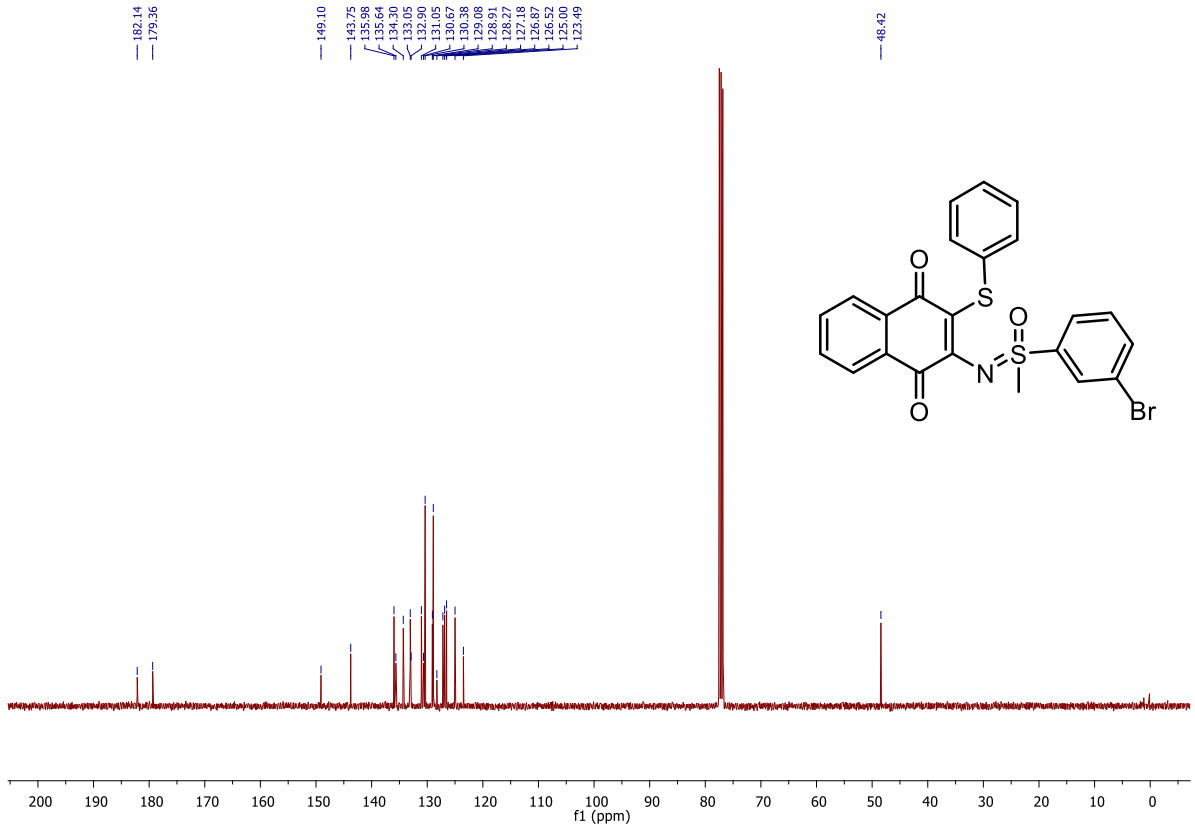
HRMS of 11a



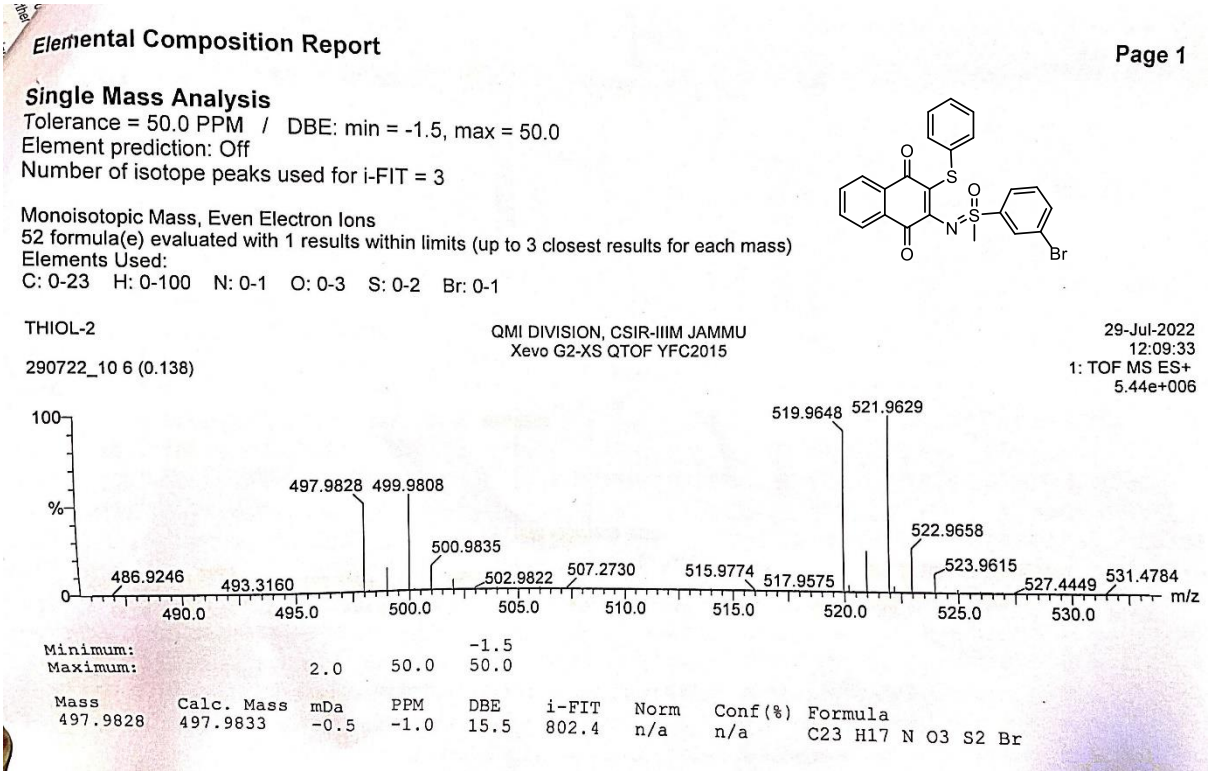
^{1}H NMR (400 MHz) of 12 in $CDCl_3$



^{13}C {1H} NMR (101 MHz) of 12 in $CDCl_3$



HRMS of 12



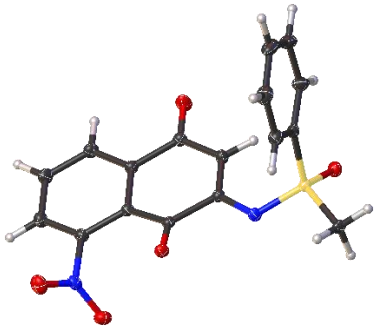
REFERENCE

1. A. Tota, M. Zenzola, S. J. Chawner, S. S. John-Campbell, C. Carlucci, G. Romanazzi, L. Degennaro, J. A. Bull and R. Luisi, *Chem comm*, 2016, **53 2**, 348-351.

2. X. Huang, J. Li, X. Li, J. Wang, Y. Peng and G. Song, *RSC Adv.*, 2019, **9**, 26419-26424.

X-ray Crystallography Data

Table S4. Crystal data and structure refinement for 5n



Compound 5n (CCDC 2194439)

Identification code	**5n**
CCDC Number	**2194439**
Empirical formula	$C_{17}H_{12}N_2O_5S$
Formula weight	356.35
Temperature/K	108.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.173(3)
b/Å	5.3337(15)
c/Å	25.755(7)
α/°	90.00
β/°	95.565(10)
γ/°	90.00
Volume/Å^3	1527.6(7)
Z	4
ρ_{calc}g/cm^3	1.549
μ/mm^{-1}	0.245
F(000)	736.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.62 to 56.7
Index ranges	$-14 \leq h \leq 14$, $-7 \leq k \leq 7$, $-34 \leq l \leq 34$
Reflections collected	43547
Independent reflections	3797 [R_{int} = 0.0636, R_{sigma} = 0.0299]
Data/restraints/parameters	3797/0/227
Goodness-of-fit on F^2	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0372, wR_2 = 0.0940
Final R indexes [all data]	R_1 = 0.0412, wR_2 = 0.0966
Largest diff. peak/hole / e Å^{-3}	0.41/-0.42