Supporting Information

Regioselective Synthesis of 4-Arylamino-1,2-Naphthoquinones in Eutectogel as a Confined Reaction Media using LED Light

R. Vara Prasad, ‡[a] Yogendra Kumar, ‡[a] R. Arun Kumar,[a] Tohira Banoo,[a]

and Subbiah Nagarajan[a]*

Table of contents

Experimental Section

1. General materials and methods

All reagents and solvents used for the synthesis of 4-(hydroxymethyl)-1,3:2,4-dibenzylidene-D-sorbitol and 4-arylamino-1,2-napthoquinones were purchased from commercial suppliers such as Merck, Aldrich, Finar, SRL and Avra chemicals and were used without purification. For the compound purification and recrystallization, LR-grade solvents were employed. AR-grade solvents were used for the gelation studies. The pre-coated Merck silica gel plates (TLC Silica gel 60 F_{254}) were used to monitor the reaction progress and visualized the spots using any one or the combination of the following visualizing agents such as UV detection, $KMnO_4$, p-anisaldehyde, H_2SO_4 spray, or molecular iodine.

2. NMR and HRMS

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz instrument either in $CDCl_3$ or DMSO-d_6 at room temperature. Chemical shifts (δ) are reported in parts per million (ppm) with reference to the internal standard TMS and coupling constants (J) are given in Hz. Proton multiplicity is assigned using the following abbreviations: singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). High-resolution MS analysis were performed on an Agilent 6520 Q-TOF instrument by dissolving the solid sample in methanol or any other suitable solvent.

3. Gelation Studies

To a known quantity of HMDBS taken in a glass vial, an appropriate amount of solvent was added and sealed tightly, and the system was heated until the solid was completely dissolved. The homogeneous solution thus obtained is allowed to cool slowly to rt. The gelation ability of HMDBS can be observed by naked eye by inverting the test tube. In the inverted test tube, a sample exhibiting no gravitational flow is referred as gel “G”, instead it remains as solution is referred as “S”. If the compound is insoluble, it is referred as “I”. Precipitation and crystallization observed in the test tube is denoted as “P” and “Crys” respectively.

4. Morphological study

The morphology of the gels was investigated using optical microscopy and scanning electron microscopy. The gel was prepared at a critical gelation concentration and placed over a glass plate and viewed using a Carl Zeiss Axio Scope A1 fluorescent/phase-contrast microscope. The xerogel was used for SEM analysis, which

is prepared by taking a suitable quantity of eutectogel and disperse in water. DES in the 3D fibrous network is exchanged slowly with water and the resultant gel is dried and used.

5. Rheological measurements

The viscoelastic behaviour of the gels was identified using a stress-controlled rheometer (Anton Paar 302 rheometer) equipped with a steel-coated parallel plate geometry of 25 mm diameter. The rheological behaviour of the gels was investigated by keeping the gel sample over the parallel plate at 23 °C. A 1 mm gap has been maintained between the two parallel plates and the excess gel squeezing out of the parallel plate was trimmed and the measurements were done.

6. FT-IR studies

Infrared (IR) spectra were recorded from 400 – 4000 cm^{-1} using KBr in Perkin Elmer spectrum 100 spectrophotometer. Agilent Q-TOF 6230 instrument were used.

7. Formation of deep eutectic gel

Deep eutectic solvent is prepared my mixing a suitable quantity of choline chloride ChCl (HBA) and Ethylene glycol/ Glycerol/ Urea (HBD) in a round bottom flask and stirred at 70 °C till a homogeneous solution is formed. To the formed DES, HMBDS gelator is added and heated till the gelator dissolves and left to stand for the gel formation.

2 Synthesis

(a) Procedure for the synthesis of 4-hydroxymethyl benzaldehyde (2)

To a stirred solution of terepthalaldehyde **1** (1eq) in dry THF at 0 ˚C, $NaBH_4$ (0.3 eq) is added in portions. The mixture was stirred for 6h. After completion of the reaction as identified by TLC, 1N HCl is added to the mixture and further stirred for 20 min. Solvent was removed by under reduced pressure and the residue is extracted with ethyl acetate. Column chromatography was performed to obtain the pure product.[7]

(b) Procedure for the synthesis of 4-(hydroxymethyl)-1,3:2,4-dibenzylidene-D-sorbitol (4)

To a stirred solution of D-Sorbitol **3** (1 mmol) in acetonitrile (10 mL) at rt under N_2 atmosphere, 4-hydroxymethyl benzaldehyde **2** (2.1 mmol) and Dowex 50WX8 were added. The reaction mixture was stirred for about 24 h at 70 ^oC. After completion of the reaction as identified by TLC, the reaction mixture was allowed to cool down to room temperature. The formed precipitate is dissolved in hot cyrene and separate the catalyst by filtration. The cyrene solution is refrigerated for crystallization. The product is

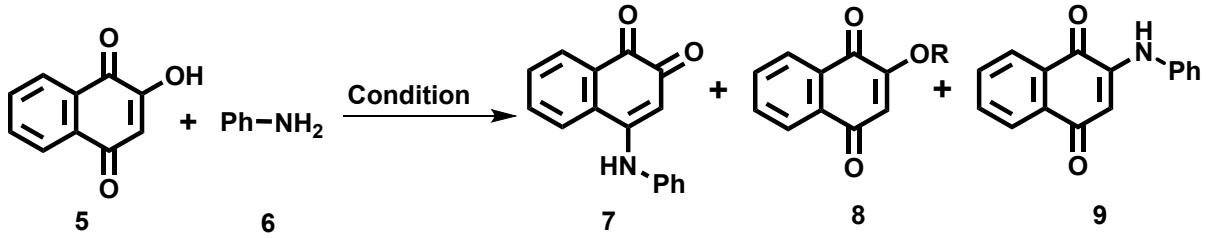
filtered, washed with water and dried under vacuum. The product was obtained as a white solid.

(c) General Procedure for the synthesis of 4-arylamino-1,2-naphthoquinones (7)

Lawsone (1 mmol) and amine (1.2 mmol) was incorporated in the HMDBS eutectogel by ether co-gelation method or cast on gel surface method. In cast on gel surface method, a complete permeation of reactant was achieved after 12h at room temperature. After incorporation of reactants, the gel vial is irradiated under blue LED for about 24 h. In order follow the reaction progress, a small piece of gel is taken, dispersed in DCM and analyzed with TCL. After completion of the reaction, the gel is placed in chloroform or hexane-chloroform or chloroform-methanol mixture to extract the product, this process is repeated 3 times. The extracted mixture is evaporated under vacuum. Brown product thus obtained is crystalized in a mixture of solvents (Hexane-Ethylacetate; Chloroform-Methanol, or a suitable solvents) and directly subjected to NMR analysis. Column chromatography is not performed..

3 Optimization studies

Table S1: Optimization studies for 4-arylamino-1,2-naphthoquinones using conventional method



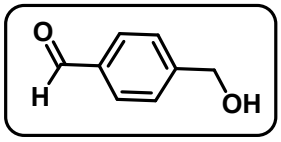
S.No	Catalyst	Condition	Solvent	Time (h)	7 (%)	8 (%)	9 (%)	observation
1.	pTSA	Reflux	MeOH	24	-	12	45	Isolated as a mixture
2.	TFA	Reflux	MeOH	12	traces	21	42	Isolated as a mixture
3.	$CuSO_4$	Reflux	MeOH/EtOH/BuOH, iPrOH	24	traces	57	traces	Isolated as a mixture*

4.	$ZnSO_4$	Reflux	MeOH	48	traces	traces	traces	-$
5.	$MgSO_4$	Reflux	MeOH	48	-	-	-	-$
6.	No catalyst	Reflux	MeOH	24	13	52	32	Isolated yield
9.	$CuSO_4$	Reflux	BuOH	48				98

* among all protic solvents MeOH rendered maximum yield, and hence yield mentioned are for MeOH in entry 3. $ multiple spots were observed in TLC and starting materials are not consumed completely even after prolonged reaction. 5 and 6a (1 mmol) were used as model substrate for the conventional reaction.

4 Characterization studies

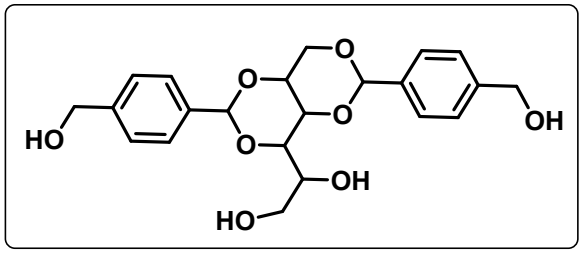
Compound 1: 4-hydroxymethyl benzaldehyde



The product was obtained as a colour less liquid with 70% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.86 (d, *J* = 1.6 Hz, 1H, OH), 7.74 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.41 (d, *J* = 7.9 Hz, 2H, Ar-H), 4.68 (s, 2H, Ar-CH_2).

Compound 2: 4-(hydroxymethyl)-1,3:2,4-dibenzylidene-D-sorbitol



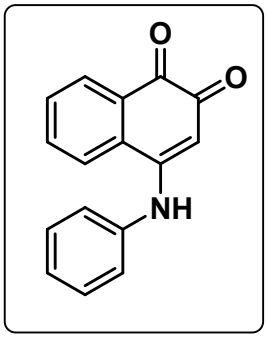
The product was obtained as a white solid with 86% yield

^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.41 (t, *J* = 8.1 Hz, 4H, Ar-H), 7.31 (dd, *J* = 8.1, 1.6 Hz, 4H, Ar-H), 5.64 (s, 2H, acetal-H), 5.21 (s, 2H, benzylic-OH), 4.83 (s, 1H, Sac-H), 4.50 (s, 4H, Ar-CH_2), 4.21 – 4.11 (m, 3H, Sac-H), 3.93 (d, *J* = 1.7 Hz, 1H, Sac-H), 3.83 (dd, *J* = 9.2, 1.7 Hz, 1H, Sac-H), 3.76 (d, *J* = 6.4 Hz, 1H, Sac-H), 3.59 (dd, *J* = 11.3, 2.3 Hz, 1H, Sac-H), 3.43 (dd, *J* = 11.2, 5.1 Hz, 2H, Sac-H).

^{13}C NMR (100 MHz, DMSO-d_6) δ: 143.39, 143.29, 137.64, 137.38, 126.40, 126.38, 126.36, 126.34, 99.84, 99.78, 78.20, 78.12, 70.55, 69.78, 68.89, 68.20, 63.12.

HRMS (ESI, m/z): $C_{22}H_{26}O_8$, $[M+H]^+$ Calculated: 419.1706; $[M+H]^+$ found: 419.1704.

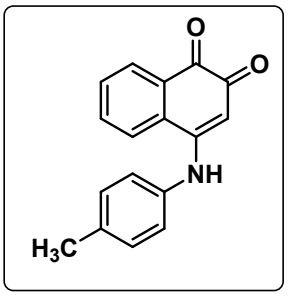
Compound 7a: 4-(phenylamino)-naphthalene-1,2-dione



The product was obtained as a brown solid with a 92% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (t, *J* = 6.3 Hz, 2H, Ar-H), 7.69 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.63 – 7.57 (m, 1H, Ar-H), 7.50 (s, 1H, NH), 7.35 (t, *J* = 7.8 Hz, 2H, Ar-H), 7.21 (dd, *J* = 8.0 Hz, 2H, Ar-H), 7.15 (t, *J* = 7.4 Hz, 1H Ar-H), 6.35 (s, 1H, Olefin-H). **^{13}C NMR (100 MHz, $CDCl_3$) δ:** 183.97, 182.09, 144.75, 137.45, 134.95, 133.24, 132.38, 130.38, 129.72, 126.55, 126.19, 125.65, 122.64, 103.41. **HRMS(ESI m/z):** $C_{16}H_{11}NO_2$, $[M+H]^+$ Calculated: 250.0868, $[M+H]^+$ Found: 250.0869**.**

Compound 7b: 4-(p-tolylamino)naphthalene-1,2-dione

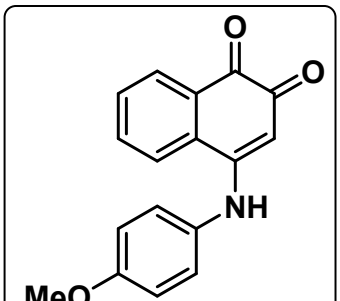


The product was obtained as a brown solid with a 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (m, *J* = 7.6, 3.0, 1.3 Hz, 2H, Ar-H), 7.75 (td, *J* = 7.6, 1.3 Hz, 1H, Ar-H), 7.65 (td, *J* = 7.5, 1.4 Hz, 1H, Ar-H), 7.52 (s, 1H, NH), 7.22 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.16 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.35 (s, 1H, Olefin-H), 2.36 (s, 3H, Ar-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.86, 182.16, 145.07, 135.66, 134.89, 134.77, 133.34, 132.26, 130.42, 130.25, 126.49, 126.16, 122.75, 103.04, 20.99.

Compound 7c: 4-((4-methoxyphenyl)amino)naphthalene-1,2-dione

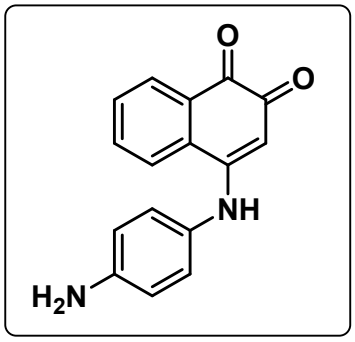


The product was obtained as a brown solid with a 86% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (m, *J* = 7.6, 4.0, 1.3 Hz, 2H, Ar-H), 7.75 (td, *J* = 7.5, 1.4 Hz, 1H, Ar-H), 7.66 (td, *J* = 7.5, 1.4 Hz, 1H, Ar-H), 7.44 (s, 1H, NH), 7.20 (d, *J* = 8.9 Hz, 2H, Ar-H), 6.95 (d, *J* = 9.0 Hz, 2H, Ar-H), 6.22 (s, 1H, Olefin-H), 3.83 (s, 3H, O-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.75, 182.19, 157.70, 145.70, 134.89, 133.42, 132.21, 130.44, 130.04, 126.45, 126.16, 124.87, 114.93, 102.55, 55.58.

Compound 7d: 4-((4-aminophenyl)amino)naphthalene-1,2-dione

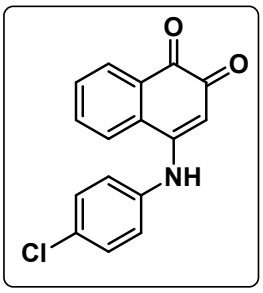


^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.03 (s, 1H, NH), 8.09 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.99 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.89 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.81 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.07 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.68 (d, *J* = 8.7 Hz, 2H, Ar-H), 5.91 (s, 1H, Olefin-H), 5.28 (s, 2H, NH_2).

^{13}C NMR (100 MHz, DMSO-d_6) δ: 182.36, 147.64, 135.20, 133.66, 132.65, 131.05, 130.44, 126.41, 125.70, 122.53, 119.77, 114.92, 101.27.

HRMS(ESI m/z): $C_{16}H_{12}N_2O_2$, $[M+H]^+$ Calculated: 265.0977, $[M+H]^+$ Found: 265.0979**.**

Compound 7e: 4-((4-chlorophenyl)amino)naphthalene-1,2-dione



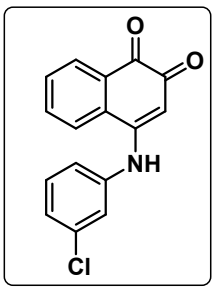
The product was obtained as a brown solid with a 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.78 (s, 1H, Ar-H), 7.69 (s, 1H, Ar-H), 7.52 (s, 1H, NH), 7.40 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.27 – 7.17 (m, 2H, Ar-H), 6.37 (s, 1H, Olefin-H).

^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6) δ: 183.26, 181.85, 146.09, 137.37, 135.01, 133.03, 132.76, 130.77, 129.73, 129.49, 126.47, 125.73, 125.28, 103.03.

HRMS(ESI m/z): $C_{16}H_{10}ClNO_2$, $[M+H]^+$ Calculated: 284.0478, $[M+H]^+$ Found: 284.0477**.**

Compound 7f: 4-((3-chlorophenyl)amino)naphthalene-1,2-dione



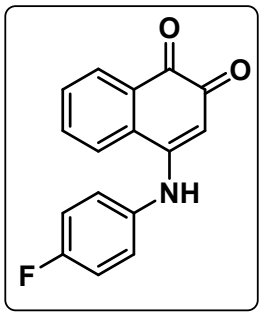
The product was obtained as a brown solid with a 93% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (m, *J* = 7.5, 4.9, 1.3 Hz, 2H, Ar-H), 7.71 (td, *J* = 7.6, 1.4 Hz, 1H, Ar-H), 7.62 (td, *J* = 7.6, 1.4 Hz, 1H, Ar-H), 7.47 (s, 1H, NH), 7.28 (t, *J* = 8.0 Hz, 1H, Ar-H), 7.22 (t, *J* = 2.1 Hz, 1H, Ar-H), 7.14 – 7.09 (m, 2H, Ar-H), 6.36 (s, 1H, Olefin-H).

^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6) δ: 181.72, 134.81, 132.96, 132.55, 130.59, 126.48, 125.79, 125.17, 124.06, 123.21, 122.27, 103.55.

HRMS(ESI m/z): $C_{16}H_{10}ClNO_2$, $[M+H]^+$ Calculated: 284.0475, $[M+H]^+$ Found: 284.0477**.**

Compound 7g: 4-((4-fluorophenyl)amino)naphthalene-1,2-dione

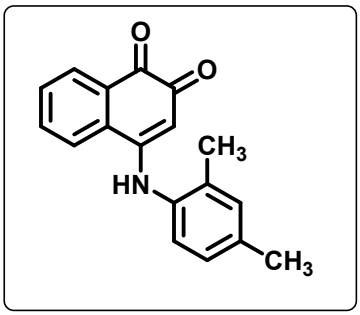


The product was obtained as a brown solid with a 84% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (t, *J* = 7.0 Hz, 2H, Ar-H), 7.72 (dt, *J* = 36.7, 7.5 Hz, 2H, Ar-H), 7.46 (s, 1H, NH), 7.29 – 7.22 (m, 2H, Ar-H), 7.13 (t, *J* = 8.4 Hz, 2H, Ar-H), 6.25 (s, 1H, Olefin-H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.86, 181.97, 145.32, 135.00, 133.22, 132.43, 130.36, 126.55, 126.24, 125.07, 124.99, 116.77, 116.55, 103.14.

Compound 7h: 4-((2,4-dimethylphenyl)amino)naphthalene-1,2-dione

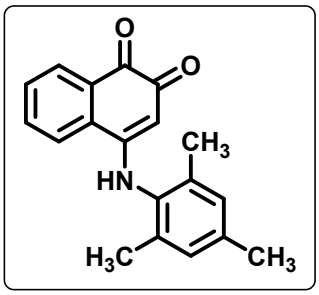


The product was obtained as a brown solid with a 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (m, *J* = 9.4, 7.7, 1.0 Hz, 2H, Ar-H), 7.75 (td, *J* = 7.5, 1.3 Hz, 1H, Ar-H), 7.66 (td, *J* = 7.5, 1.3 Hz, 1H, Ar-H),7.27(s,1H, NH) 7.17 – 7.04 (m, 3H, Ar-H), 5.90 (s, 1H, Olefin-H), 2.34 (s, 3H, Ar-CH_3), 2.24 (s, 3H, Ar-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.71, 182.24, 146.16, 136.90, 134.87, 133.49, 133.13, 132.70, 132.20, 132.05, 130.53, 127.74, 126.39, 126.18, 124.93, 102.90, 20.99, 17.67.

Compound 7i: 4-((2,4,6-trimethylphenyl)amino)naphthalene-1,2-dione

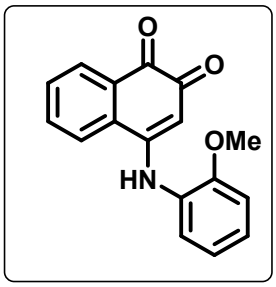


The product was obtained as a brown solid with a 92% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15 – 8.07 (m, 2H, Ar-H), 7.74 (d, *J* = 1.3 Hz, 1H, Ar-H), 7.66 (td, *J* = 7.5, 1.2 Hz, 1H, Ar-H), 7.04(s, 1H, NH), 6.95 (s, 2H, Ar-H), 5.38 (s, 1H, Olefin-H), 2.31 (s, 3H, Ar-CH_3), 2.16 (s, 6H, Ar-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.51, 182.10, 146.92, 137.93, 135.43, 134.82, 133.65, 132.13, 130.92, 130.69, 129.48, 126.30, 126.21, 102.66, 20.96, 17.92.

Compound 7j: 4-((2-methoxyphenyl)amino)naphthalene-1,2-dione

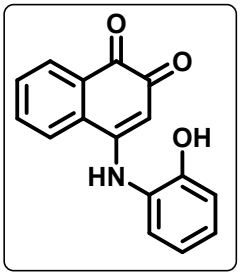


The product was obtained as a brown solid with a 86% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13 (s, 2H, Ar-H), 7.72 (dt, *J* = 36.5, 7.0 Hz, 2H, Ar-H), 7.49 – 7.39 (m, 1H, Ar-H), 7.22 – 7.11 (m, 1H, Ar-H), 7.01 (dt, *J* = 13.2, 5.7 Hz, 2H, Ar-H), 6.48 (s, 1H, Olefin-H), 3.91 (s, 3H, Ar-OCH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 184.00, 182.14, 151.18, 143.99, 134.78, 133.33, 132.30, 126.98, 126.54, 126.13, 125.48, 121.08, 120.92, 111.17, 103.63, 55.78.

Compound 7k: 4-((2-hydroxyphenyl)amino)naphthalene-1,2-dione

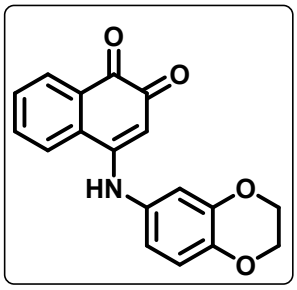


The product was obtained as a brown solid with a 62% yield.

^{1}H NMR (400 MHz, $CDCl_3$+DMSO) δ: 9.65 (s, 1H, NH), 8.15 – 8.03 (m, 3H, Ar-H), 7.81 – 7.73 (m, 1H, NH), 7.71 – 7.65 (m, 1H, Ar-H), 7.33 (d, *J* = 7.1 Hz, 1H, Ar-H), 7.07 – 6.97 (m, 2H, Ar-H), 6.93 – 6.85 (m, 1H Ar-H), 6.29 (s, 1H, Olefin-H).

^{13}C NMR (100 MHz, $CDCl_3$+DMSO) δ: 183.52, 181.97, 149.92, 144.70, 134.72, 133.29, 132.27, 130.55, 126.40, 126.04, 125.83, 125.51, 122.17, 119.71, 116.32, 102.93.

Compound 7l: 4-((3,4-ethylenedioxyphenyl)amino)naphthalene-1,2-dione

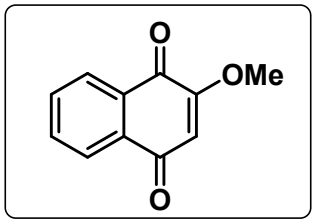


The product was obtained as a brown solid with a 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (dt, *J* = 7.5, 1.7 Hz, 2H, Ar-H), 7.75 (td, *J* = 7.6, 1.3 Hz, 1H, Ar-H), 7.65 (td, *J* = 7.6, 1.3 Hz, 1H, Ar-H), 7.40 (s, 1H, NH), 6.89 (d, *J* = 8.6 Hz, 1H, Ar-H), 6.81 (d, *J* = 2.5 Hz, 1H, Ar-H), 6.74 (dd, *J* = 8.6, 2.5 Hz, 1H, Ar-H), 6.29 (s, 1H, Olefin-H), 4.28 (s, 4H, Ar-O-CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ:183.78, 182.11, 145.38, 144.07, 141.75, 134.86, 133.35, 132.22, 130.72, 130.42, 126.45, 126.13, 118.02, 116.58, 112.47, 102.89, 64.41, 64.33.

Compound 8a: 2-methoxynaphthalene-1,4-dione



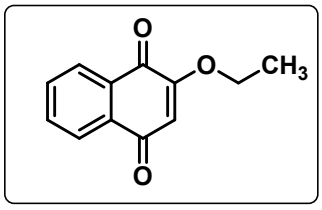
The product was obtained as a brown solid with a 92% yield.

^{1}H NMR (400 MHz, $CDCl_3$+DMSO-d_6) δ: 8.00 (dd, *J* = 17.0, 7.1 Hz, 2H, Ar-H), 7.70 (m, *J* = 7.5 Hz, 2H, Ar-H), 6.16 (s, 1H, Olefin-H), 3.85 (s, 3H, O-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6) δ: 184.58, 179.95, 160.39, 134.39, 133.40, 131.95, 130.98, 126.49, 126.00, 109.95, 56.52.

HRMS(ESI m/z): $C_{11}H_{18}O_3$, $[M+H]^+$ Calculated: 189.0551, $[M+H]^+$ Found: 189.0559**.**

Compound 8b: 2-ethoxynaphthalene-1,4-dione



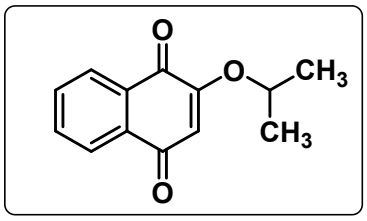
The product was obtained as a brown solid with a 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 – 7.99 (m, 2H, Ar-H), 7.70 – 7.61 (m, 2H, Ar-H), 6.08 (s, 1H, Olefin-H), 4.03 (q, *J* = 7.0 Hz, 2H, O-CH_2), 1.46 (t, *J* = 7.0 Hz, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.08, 180.21, 159.72, 134.25, 133.28, 132.01, 131.15, 126.71, 126.12, 110.21, 65.35, 13.93.

HRMS(ESI m/z): $C_{12}H_{10}O_3$, $[M+H]^+$ Calculated: 203.0708, $[M+H]^+$ Found: 203.0708**.**

Compound 8c: 2-isopropoxynaphthalene-1,4-dione

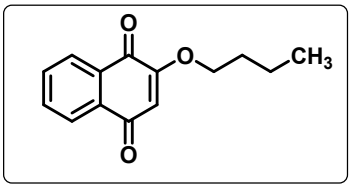


The product was obtained as a brown solid with a 78% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (m, *J* = 16.8, 7.2, 1.1 Hz, 2H, Ar-H), 7.69 – 7.61 (m, 2H, Ar-H), 6.07 (s, 1H, Olefin-H), 4.50 (m, *J* = 6.1 Hz, 1H, O-C*H*), 1.38 (d, *J* = 6.1 Hz, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.25, 180.53, 158.70, 134.18, 133.21, 131.96, 131.29, 126.70, 126.04, 110.50, 72.46, 21.18.

Compound 8d: 2-butoxynaphthalene-1,4-dione

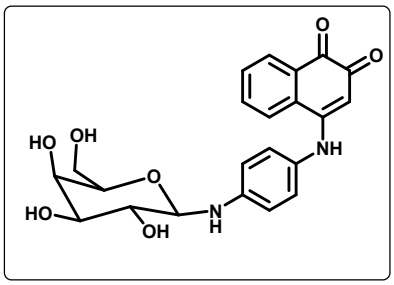


The product was obtained as a brown solid with a 98% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02 (m, *J* = 17.0, 7.2, 1.3 Hz, 2H, Ar-H), 7.69 – 7.60 (m, 2H, Ar-H), 6.08 (s, 1H, Olefin-H), 3.94 (t, *J* = 6.6 Hz, 2H, O-CH_2), 1.81 (m, *J* = 9.1, 7.8, 6.5 Hz, 2H, alkyl(CH_2)), 1.50 – 1.38 (m, 2H, Alkyl(CH_2)), 0.92 (t, *J* = 7.4 Hz, 3H, Alkyl(CH_3)).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.09, 180.16, 159.92, 134.21, 133.25, 132.02, 131.18, 126.66, 126.10, 110.17, 69.38, 30.24, 19.12, 13.70.

Compound 10: 4-((4-Phenyl-β-D-galactose)amino)naphthalene-1,2-dione



The product was obtained as a brown solid with a 92% yield.

1H NMR (400 MHz, DMSO-d_6) δ: 9.10 (s, 1H, NH), 8.10 (d, J = 7.6 Hz, 1H, Ar-H), 7.99 (d, J = 7.6 Hz, 1H, Ar-H), 7.90 (t, J = 7.5 Hz, 1H, Ar-H), 7.82 (t, J = 7.5 Hz, 1H, Ar-H), 7.16 (d, J = 8.5 Hz, 2H, Ar-H), 6.83 (d, J = 8.4 Hz, 2H, Ar-H), 5.94 (s, 1H, Olefin-H), 5.37 (dd, J = 5.5 Hz, 1H, Sac-H), 5.15 – 4.95 (m, 1H, Sac-H), 4.81 (dd, J = 5.4 Hz, 1H, Sac-H), 4.62 (dq, J = 13.4, 5.9 Hz, 1H, Sac-H), 4.46 – 4.36 (m, 1H, Sac-H), 3.93 (m, J = 6.5, 6.0 Hz, 1H, Sac-H), 3.78 (d, J = 3.9 Hz, 1H, Sac-H), 3.53 (s, 2H, Sac-H). **13C NMR (100 MHz, DMSO-d_6) δ:** 182.29, 147.46, 146.00, 135.34, 133.42, 132.80, 130.92, 127.57, 126.48, 125.70, 125.62, 113.99, 100.95, 86.00, 76.08, 74.78, 70.60, 68.91, 61.05. **HRMS(ESI m/z):** $C_{22}H_{22}N_2O_7$, $[M+H]^+$ Calculated : 427.1505, $[M+H]^+$ Found: 427.1497 .

5 Gelation studies

Table S2: Gelation studies of HMDBS in various solvents

S.No	Solvent	Gelation (CGC, % (wt/v)
1	Water	I
2	Methanol	I
3	Ethanol	I
4	Glycerol	G(0.4)
5	Ethylene glycol	G(0.6)
6	Tetrahydrofuran	S
7	Dimethyl sulfoxide	S
8	Dimethyl sulfoxide + water	G(0.4)

9	Acetone	I
10	1,4-dioxane	PS
11	Dimethyl formamide	G(0.6)
12	Polyethylene glycol	G(0.5)
13	Acetic acid	I
14	N-methyl pyrrolidone	I
15	1,2-Dichlorobenzene	I
16	pyridine	I
17	n-Butanol	G(0.4)
18	Toulene	I
19	Benzyl alcohol	G(0.4)
20	Olive oil	I
21	Linseed oil	I
22	Dimethyl carbonate	I
24	Cyrene	I

I – Insoluble, G – Gelation, S – solution, PS – Partially soluble

Table S3: Gelation studies of HMDBS in Deep eutectic solvents

S.NO	Deep Eutectic solvents	Gelation(CGC wt/v)
1	Choline Chloride + Ethylene glycol (1:4)	G(0.3)
2	Choline Chloride + Ethylene glycol (1:3)	G(0.3)
3	Choline Chloride + Ethylene glycol (1.5:2)	G(1)
4	Choline Chloride + Glycerol (1:4)	G(0.4)
5	Choline Chloride + Glycerol (1:3)	G(0.5)
6	Choline Chloride + Glycerol (1.5:2)	G(1.3)
7	Choline Chloride + Urea (1:4)	G(0.6)
8	Choline Chloride + Urea (1:3)	G(0.6)

9	Choline Chloride + Urea (1.5:2)	G(1.5)
10	Choline Chloride + Polyethylene glycol (1:4)	Dense precipitation is observed
11	Choline Chloride + Polyethylene glycol (1:3)	Dense precipitation is observed
12	Choline Chloride + Polyethylene glycol (1.5:2)	Dense precipitation is observed

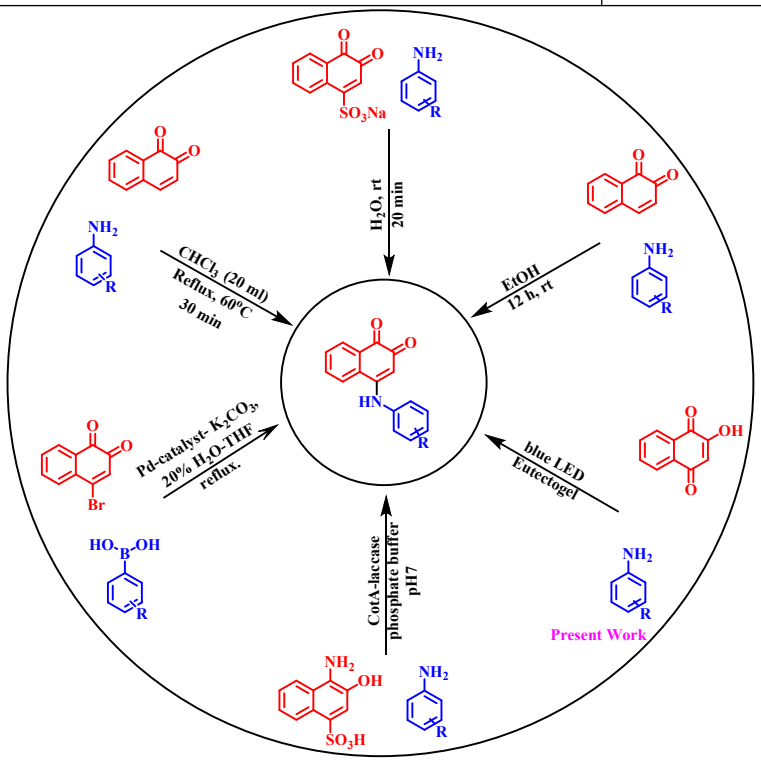


Figure S1: Various reaction conditions for the synthesis of 4-arylamino-1,2-napthoquinones present in literature[1,2,3,4,5,6]

6 NMR and HRMS spectra

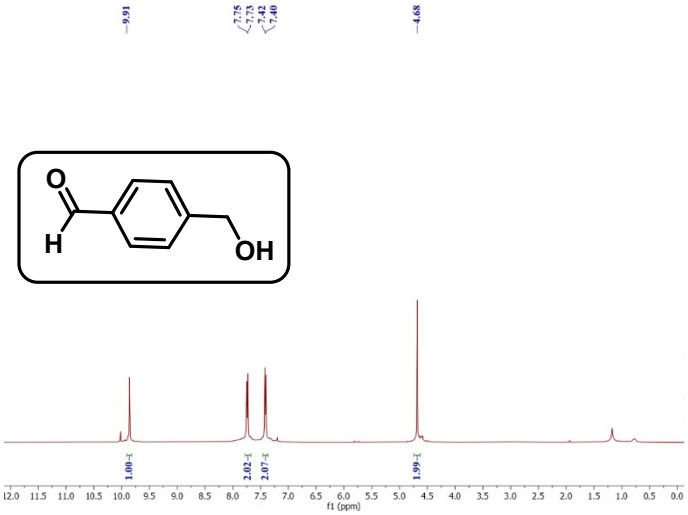


Figure S2: ^{1}H NMR (400MHz) Spectrum of HMBA **2** in $CDCl_3$ at 28 °C.

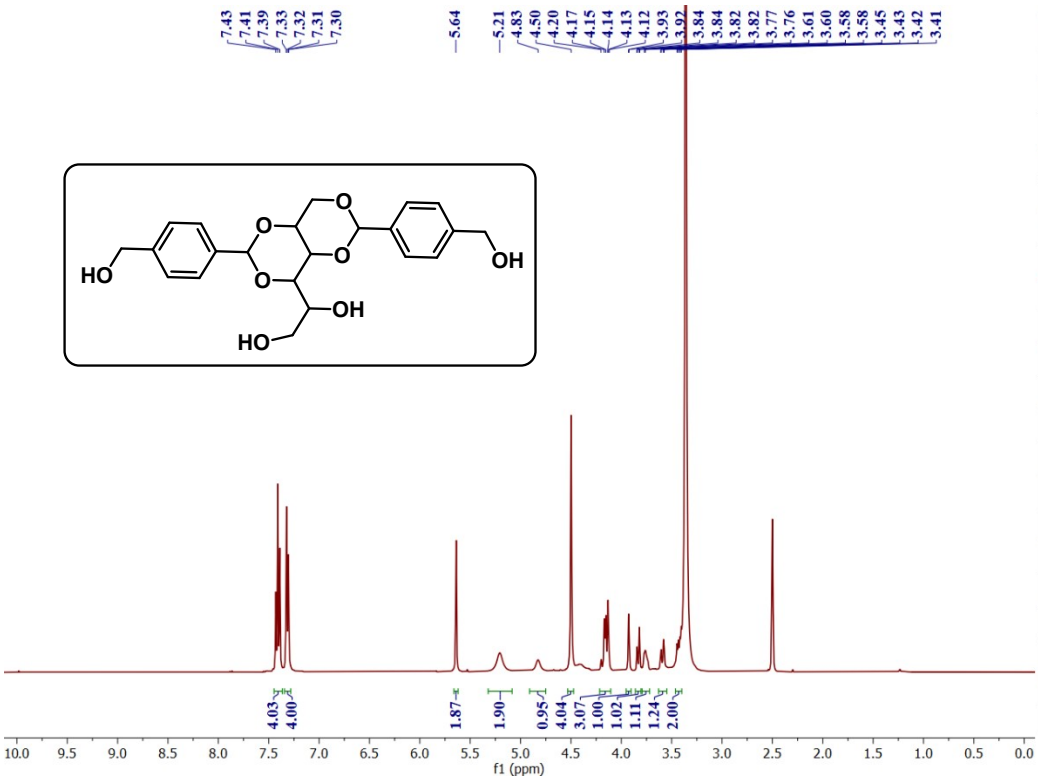


Figure S3: ^{1}H NMR (400MHz) Spectrum of HMDBS **4** in DMSO-d_6 at 28 °C.

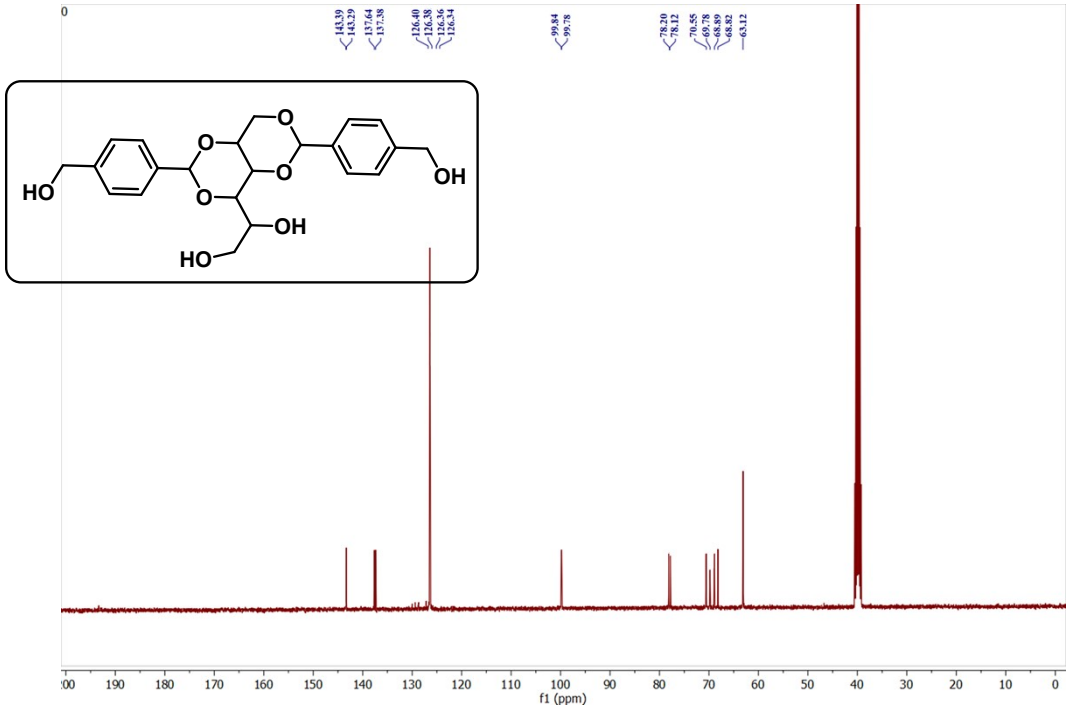


Figure S4: ^{13}C NMR (100 MHz) Spectrum HMDBS **4** in DMSO-d_6 28 °C.

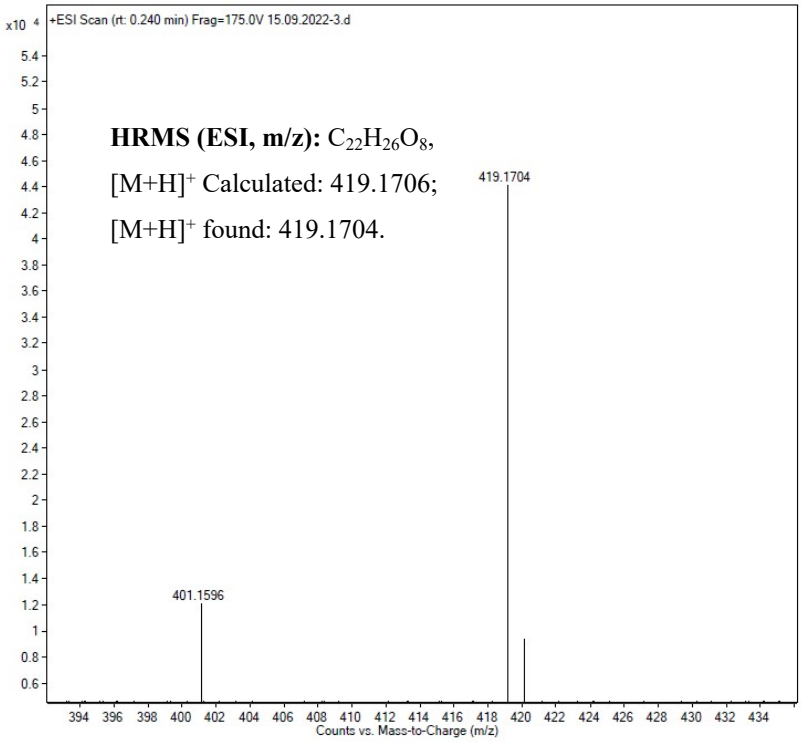


Figure S5: HRMS Spectrum of HMDBS **4**.

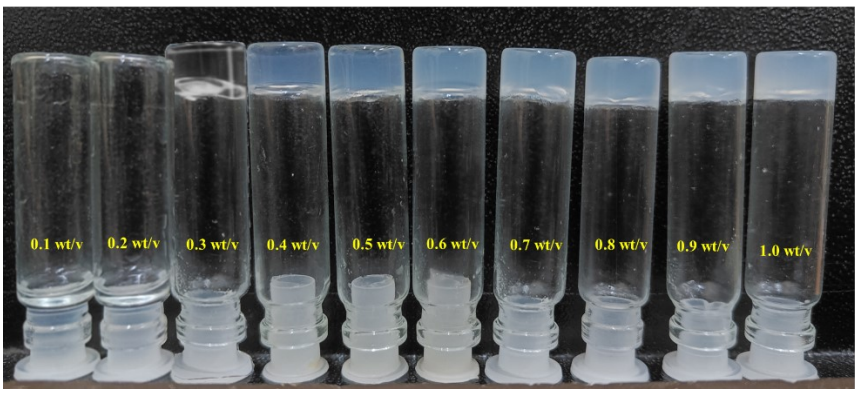
. 

Figure S6: Images of gel formed by HMDBS in ChCl:EG (1:3) ratio with increasing gelator concentration in wt/v.

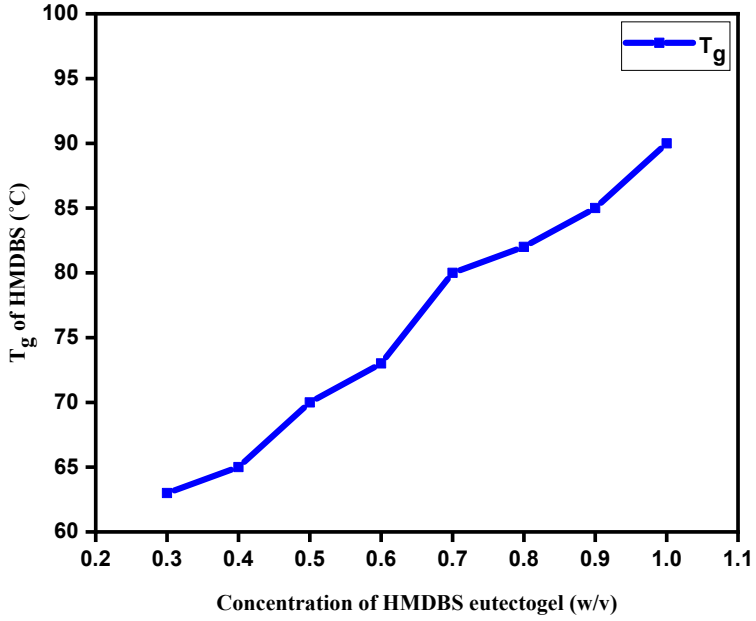


Figure S7: Transition temperature (T_g) values of HMDBS- ChCl: EG gels determined via reproducible tube inversion experiments.

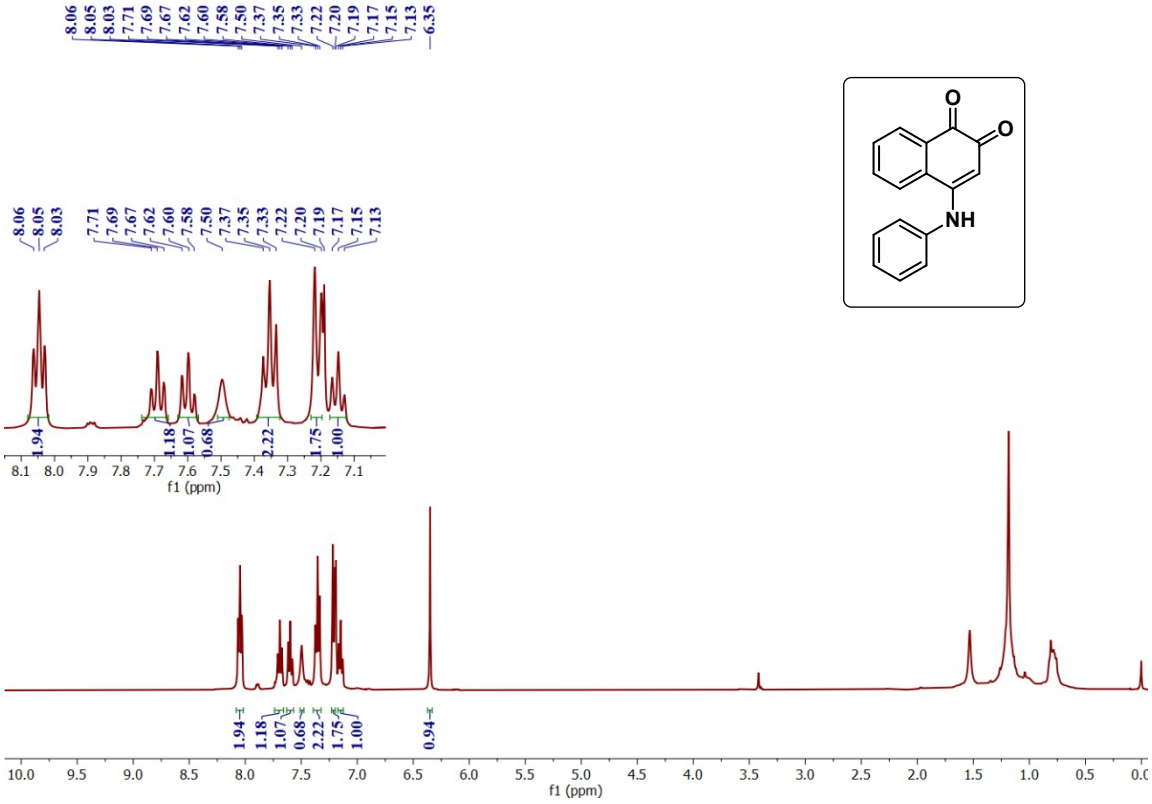


Figure S8: ^{1}H NMR (400MHz) Spectrum of **7a** in $CDCl_3$ at 28 °C.

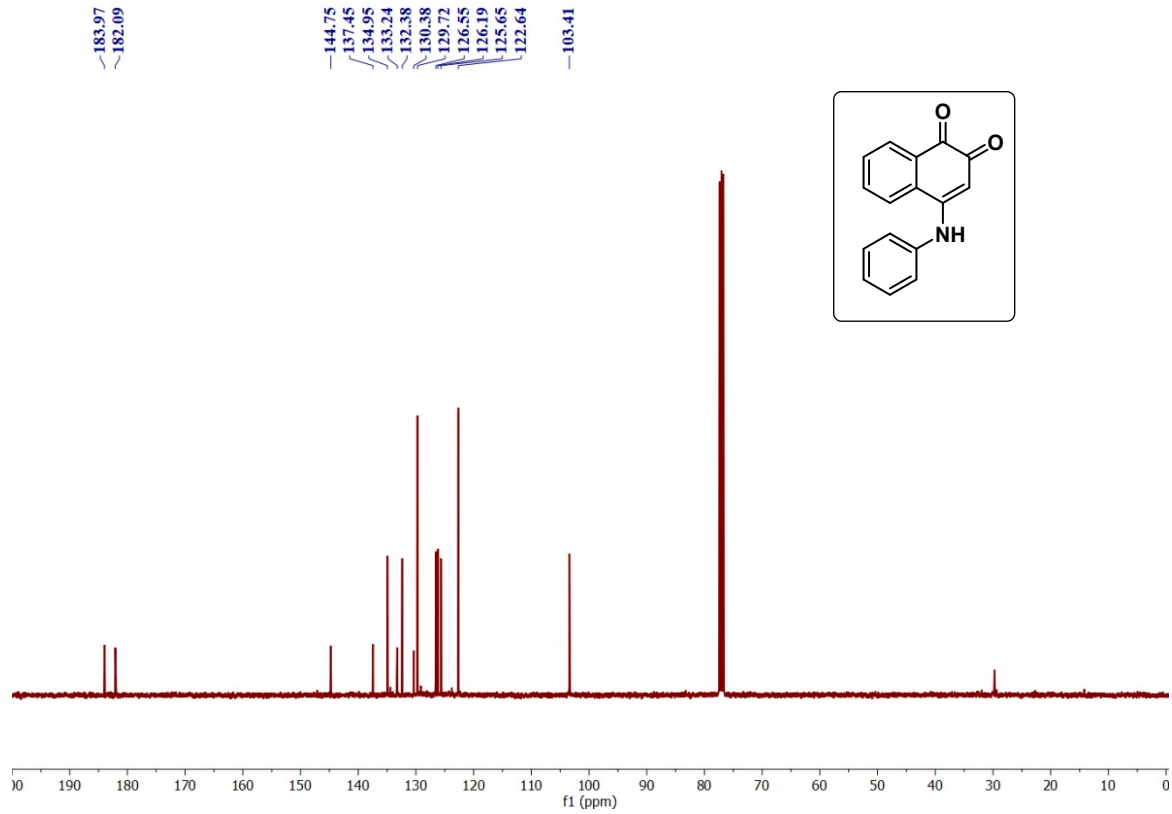


Figure S9: ^{13}C NMR (100 MHz) Spectrum of **7a** in $CDCl_3$ at 28 °C.

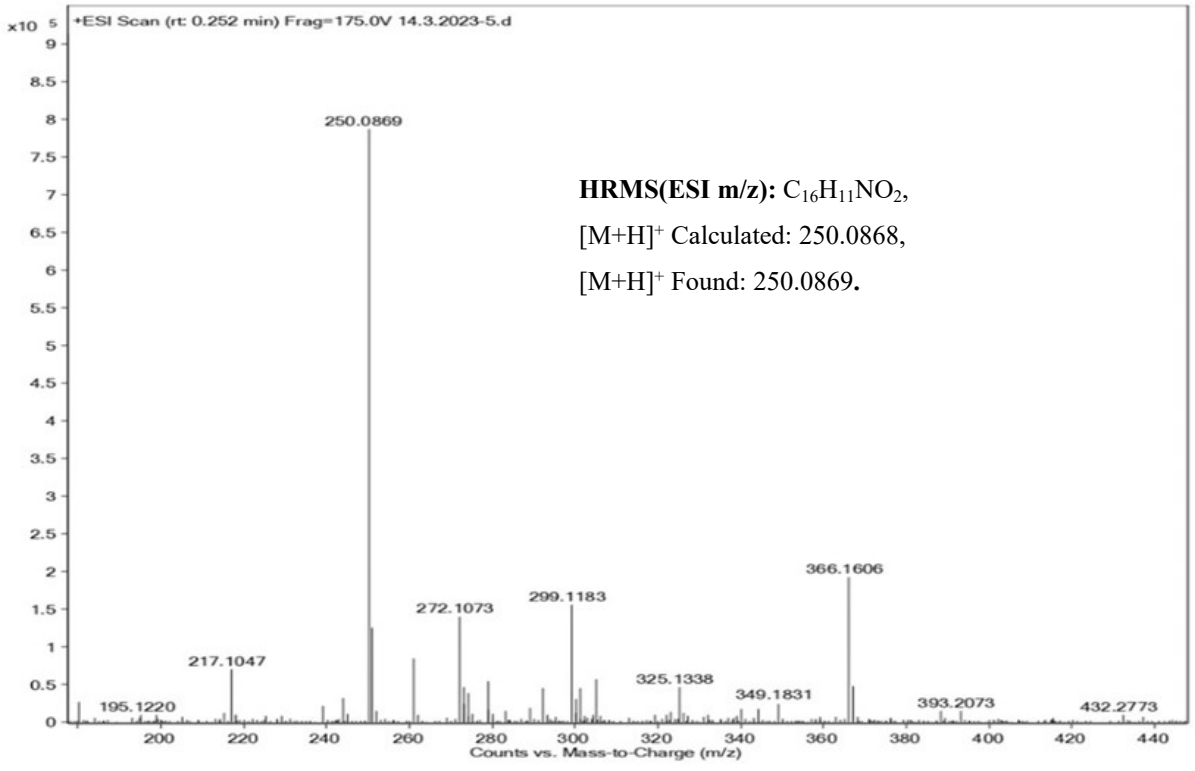


Figure S10: HRMS Spectrum of **7a**.

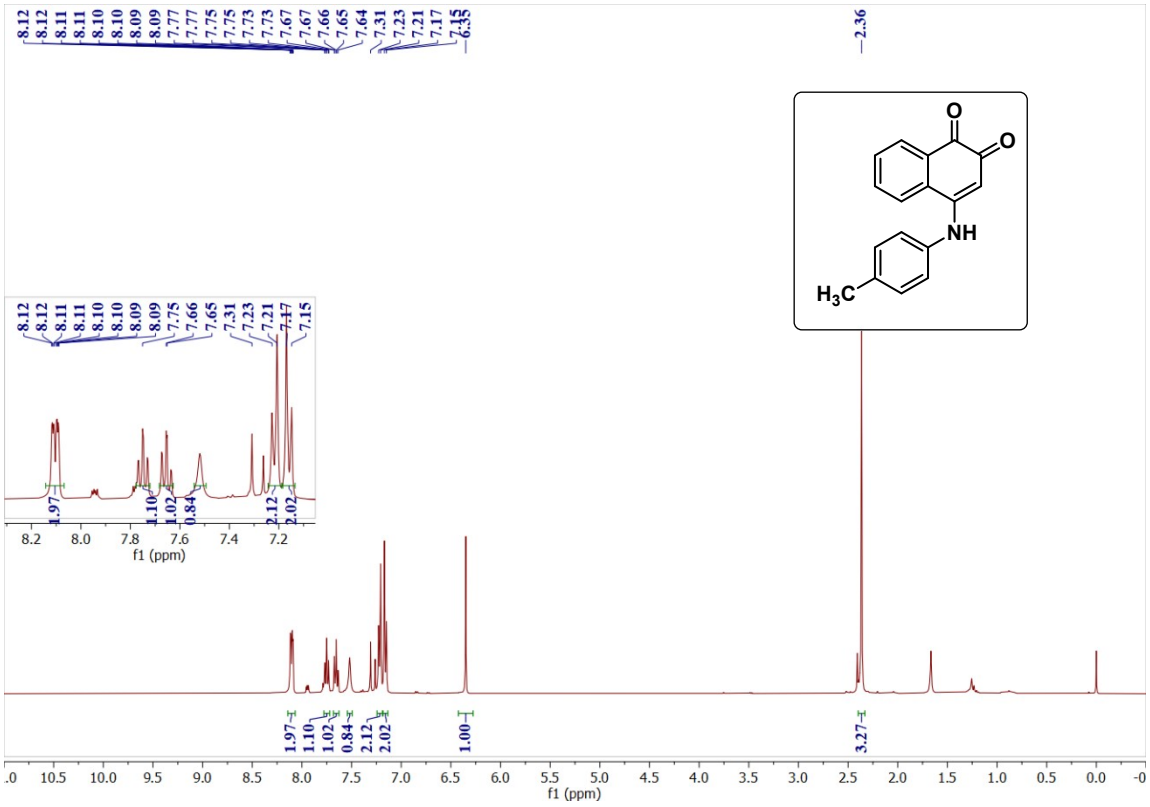


Figure S11: ^{1}H NMR (400MHz) Spectrum of **7b** in $CDCl_3$ at 28 °C.

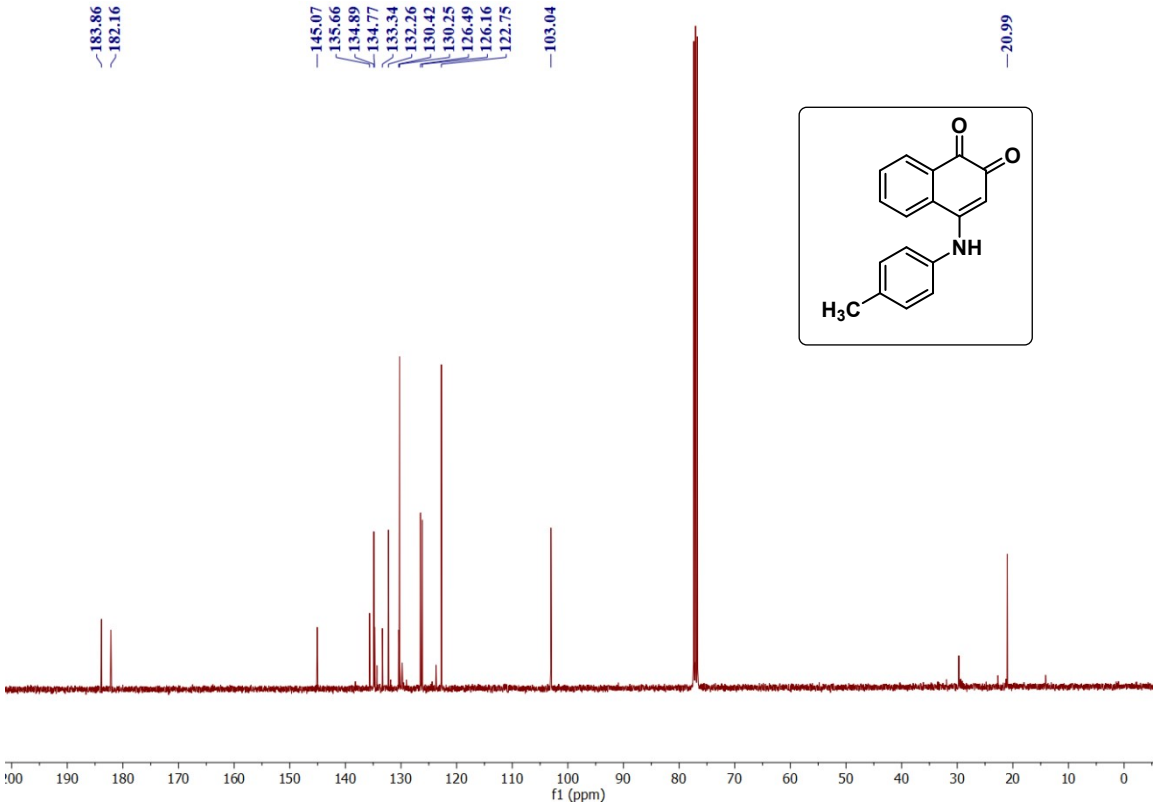


Figure S12: ^{13}C NMR (100 MHz) Spectrum of **7b** in $CDCl_3$ at 28 °C.

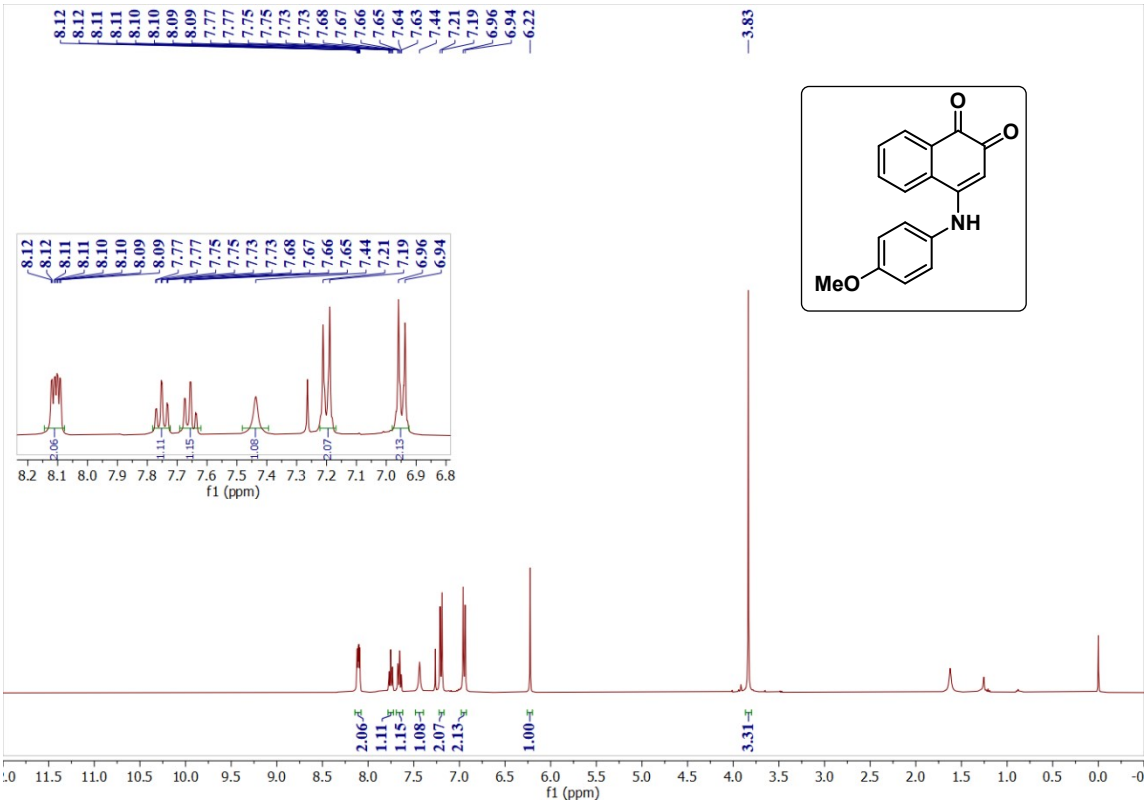


Figure S13: ^{1}H NMR (400MHz) Spectrum of **7c** in $CDCl_3$ at 28 °C.

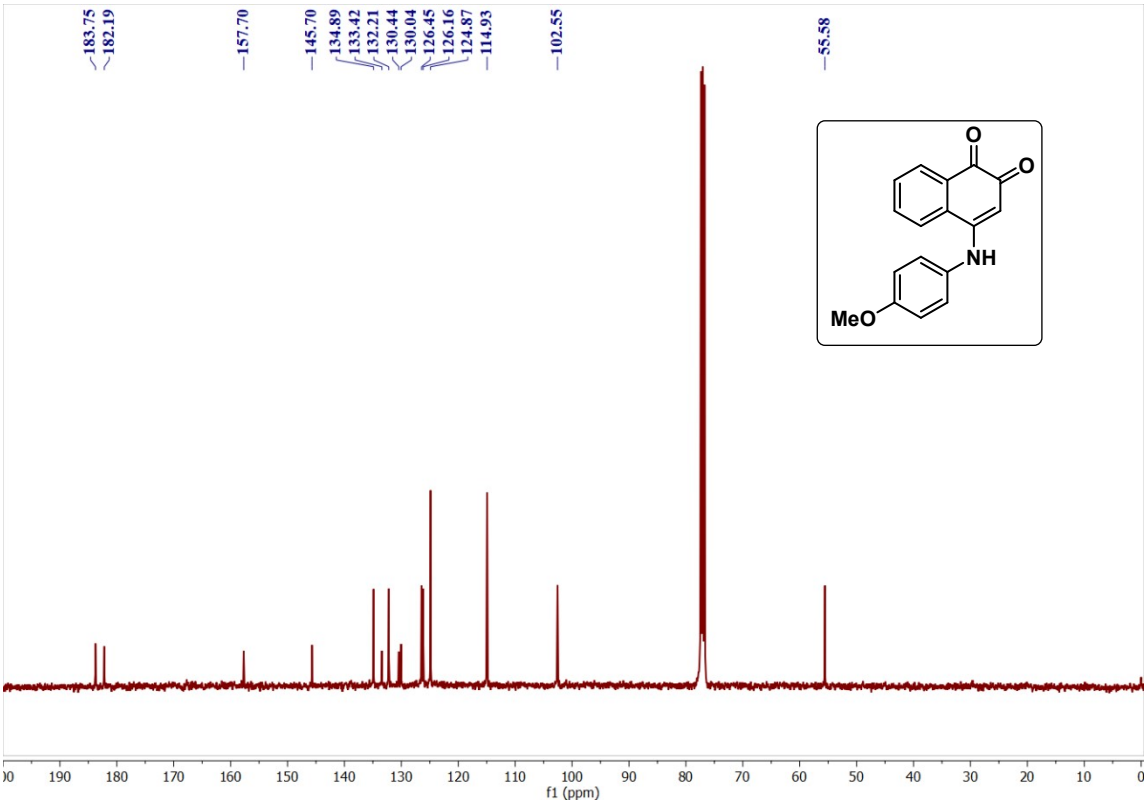


Figure S14: ^{13}C NMR (100 MHz) Spectrum of **7c** in $CDCl_3$ at 28 °C.

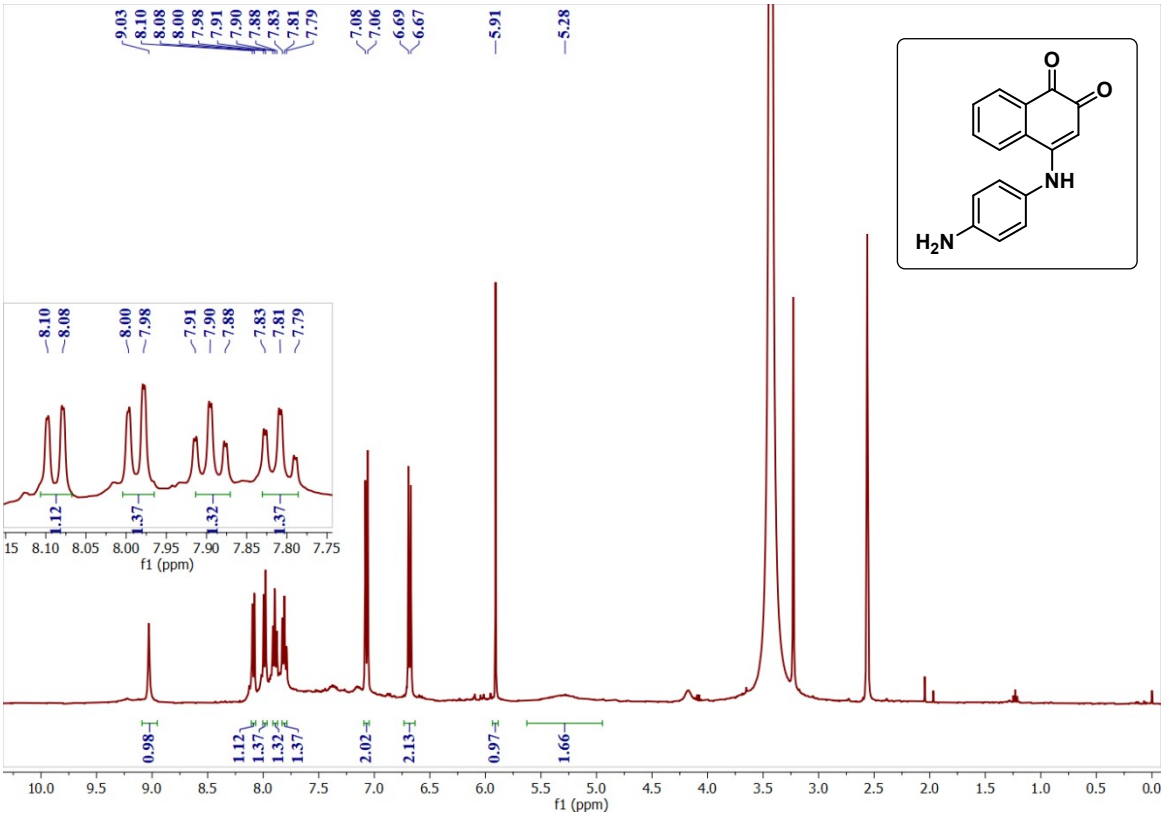


Figure S15: ^{11}H NMR (400MHz) Spectrum of **7d** in DMSO-d_6 at 80 °C.

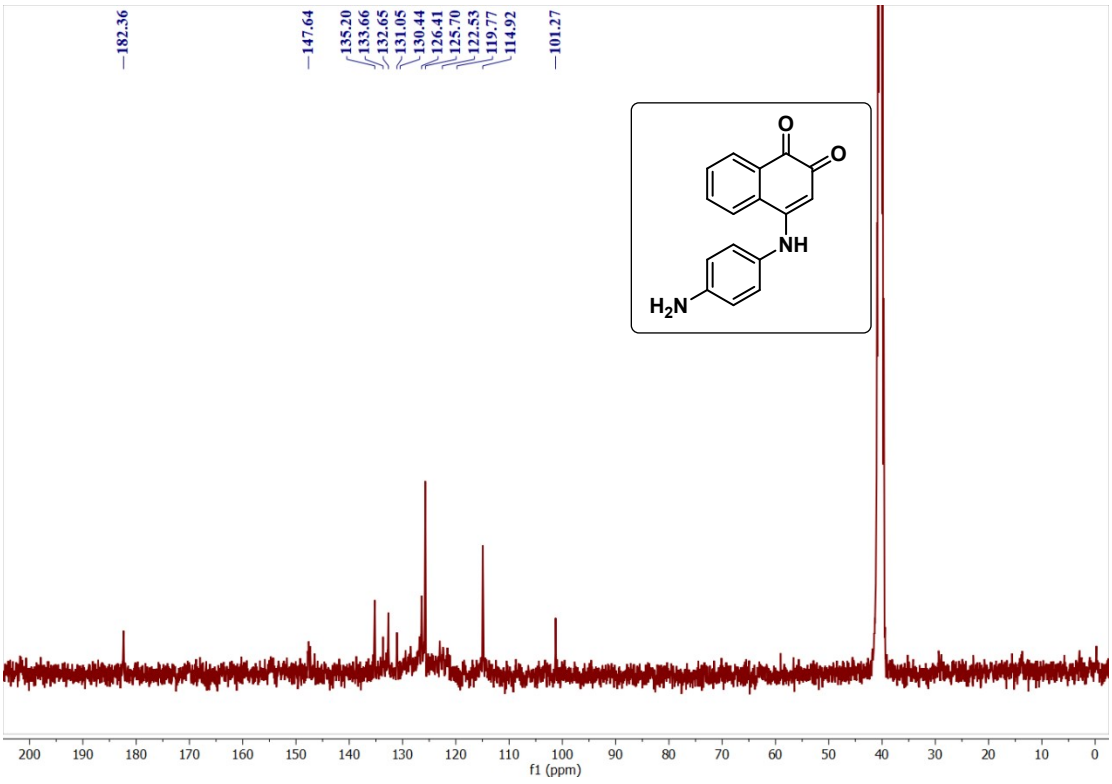


Figure S16: ^{13}C NMR (100 MHz) Spectrum of **7d** in DMSO-d_6 at 80 °C.

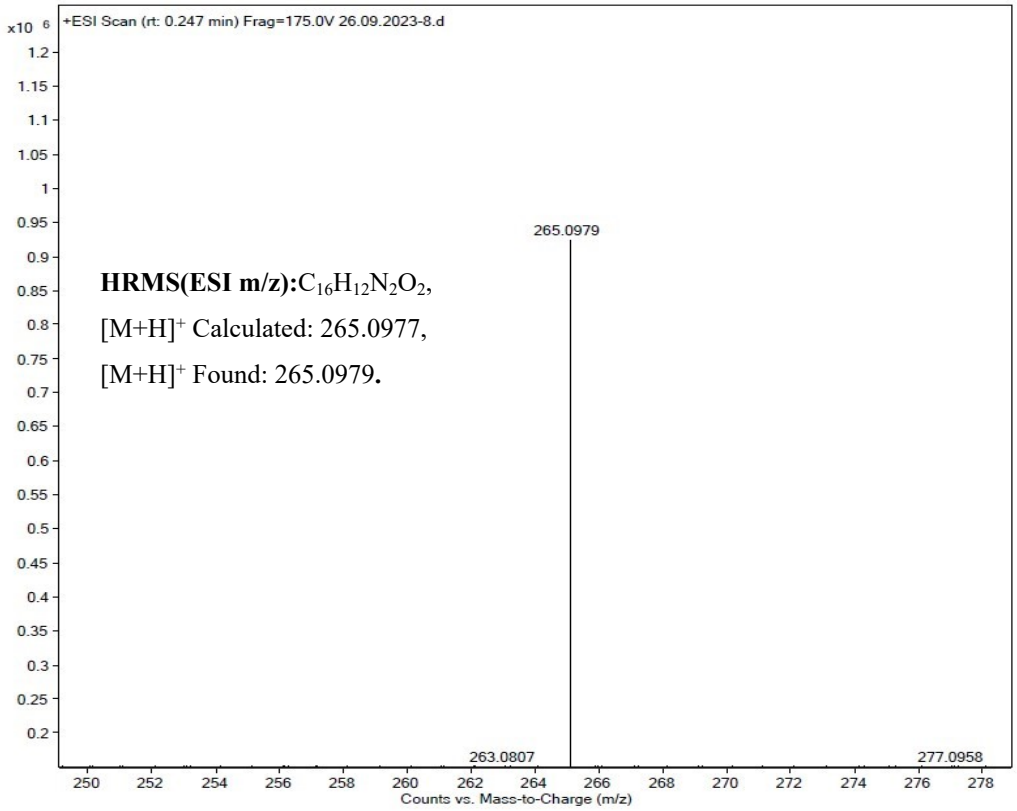


Figure S17: HRMS Spectrum of **7d**.

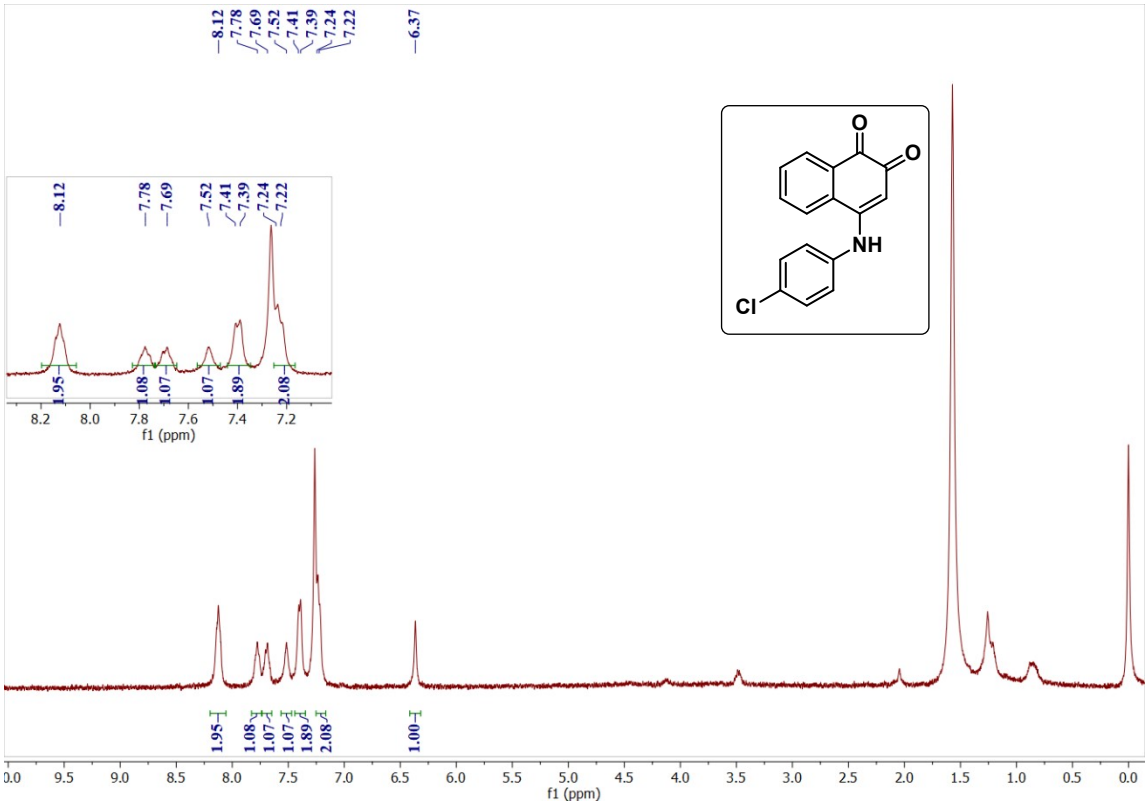


Figure S18: ^{1}H NMR (400MHz) Spectrum of **7e** in $CDCl_3$ at 28 °C.

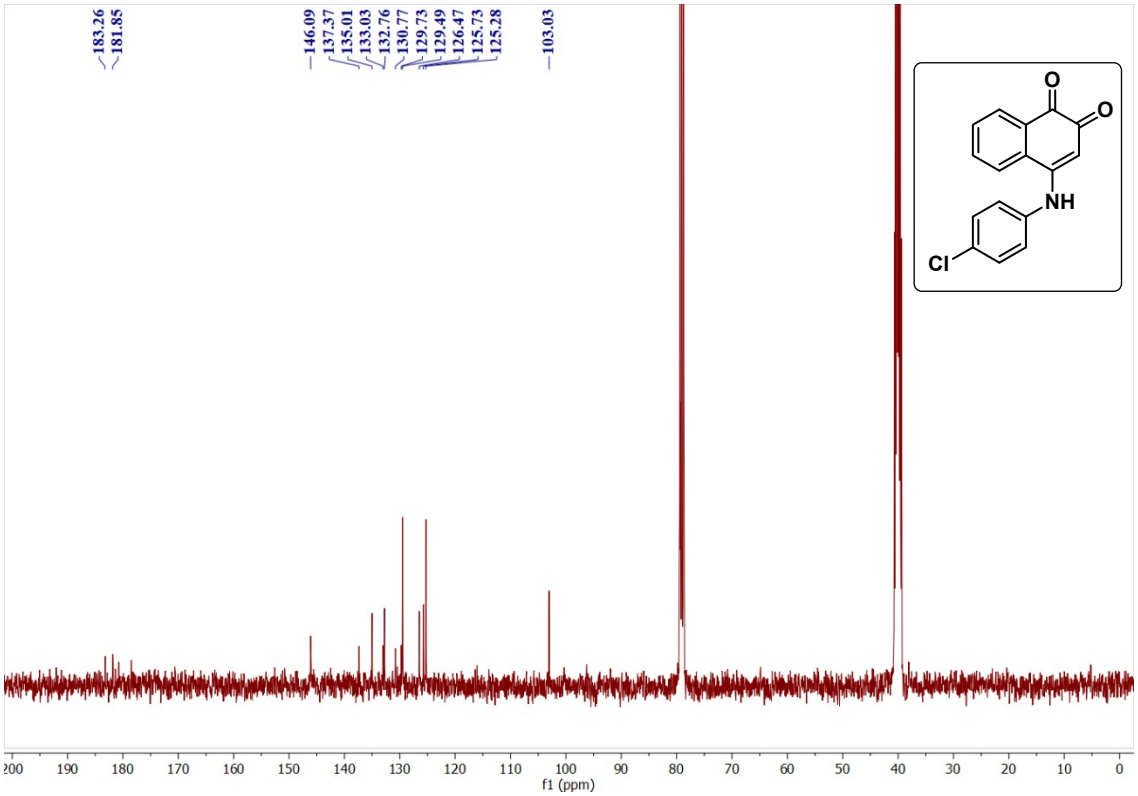


Figure S19: ^{13}C NMR (100 MHz) Spectrum of **7e** in $CDCl_3$+DMSO-d_6 at 28 °C.

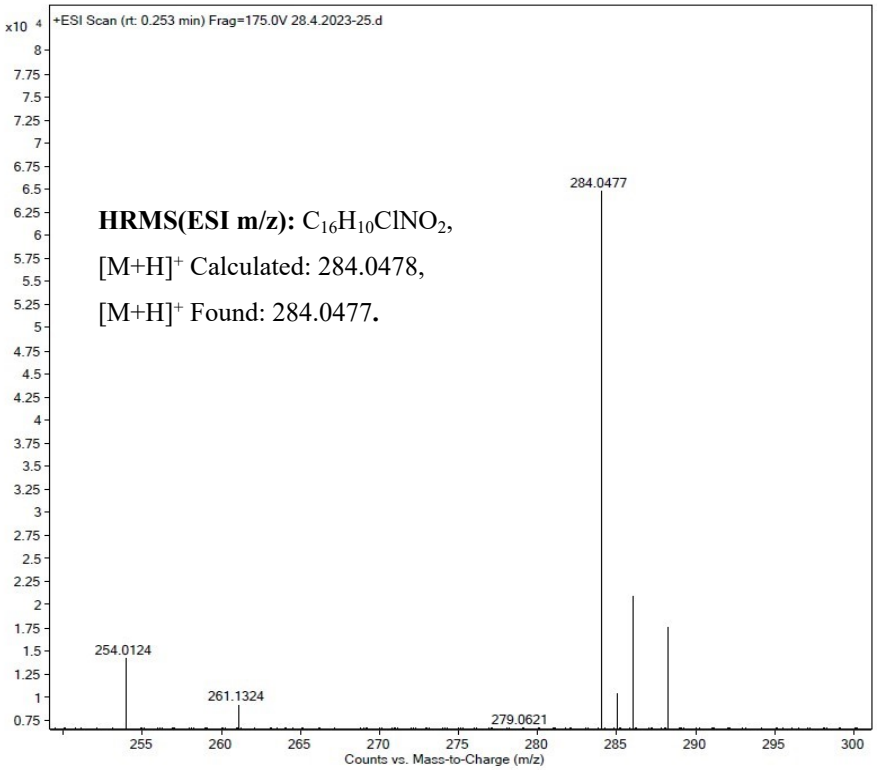


Figure S20: HRMS Spectrum of **7e**.

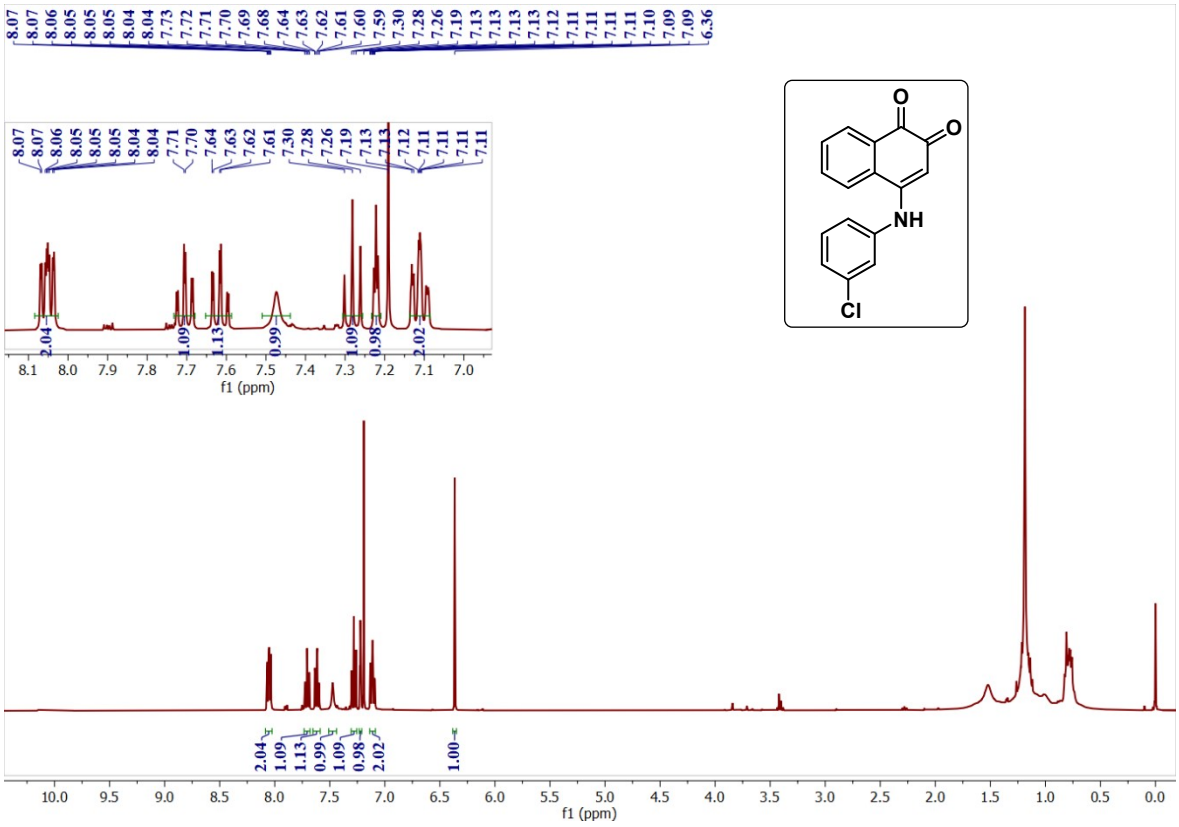


Figure S21: ^{1}H NMR (400MHz) Spectrum of **7f** in $CDCl_3$ at 28 °C.

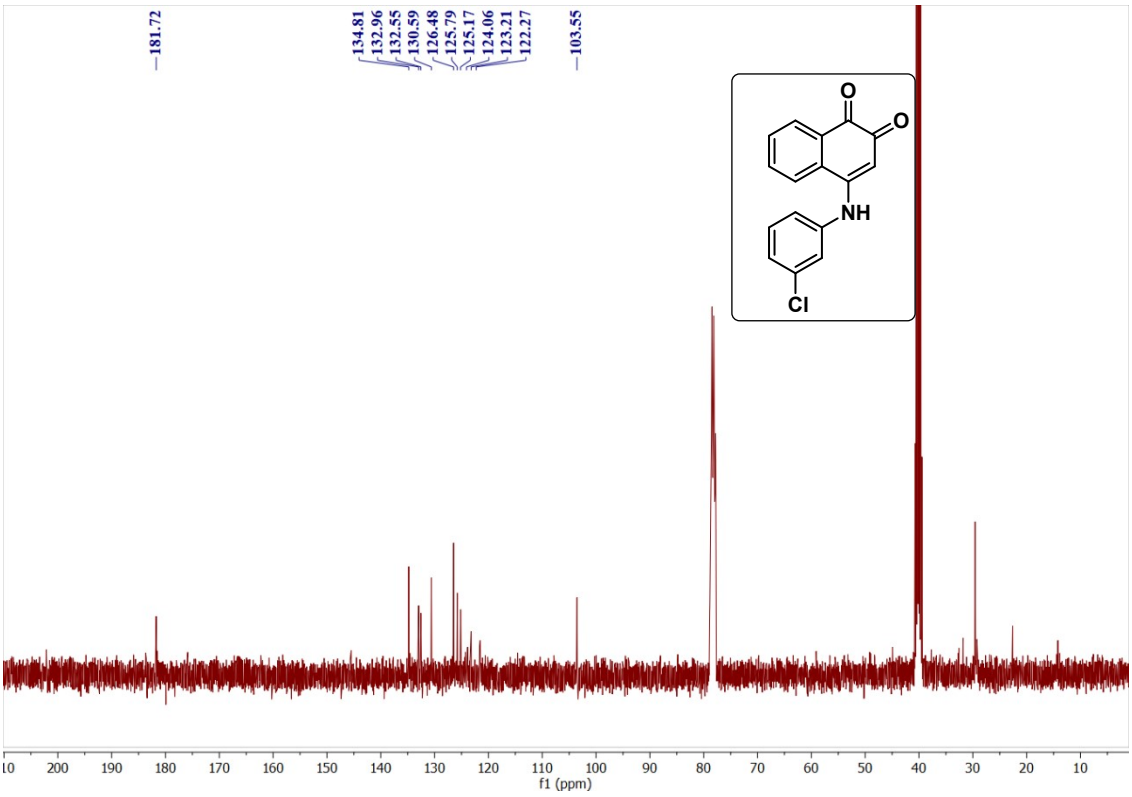


Figure S22: ^{13}C NMR (100 MHz) Spectrum of **7f** in $CDCl_3$+DMSO-d_6 at 28 °C.

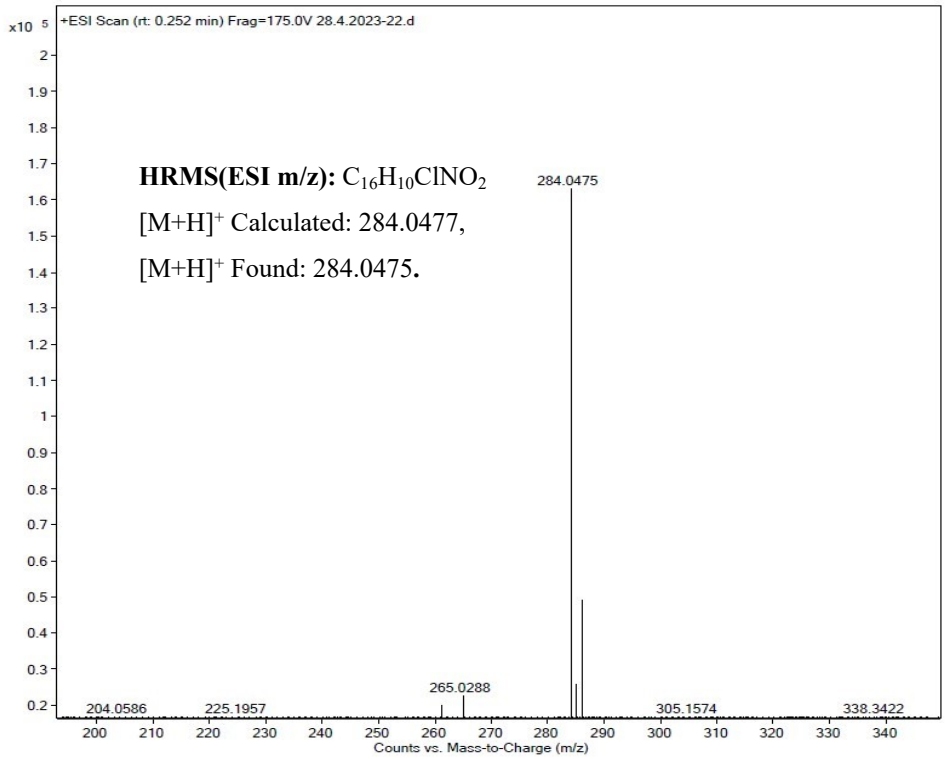


Figure S23: HRMS Spectrum of **7f**.

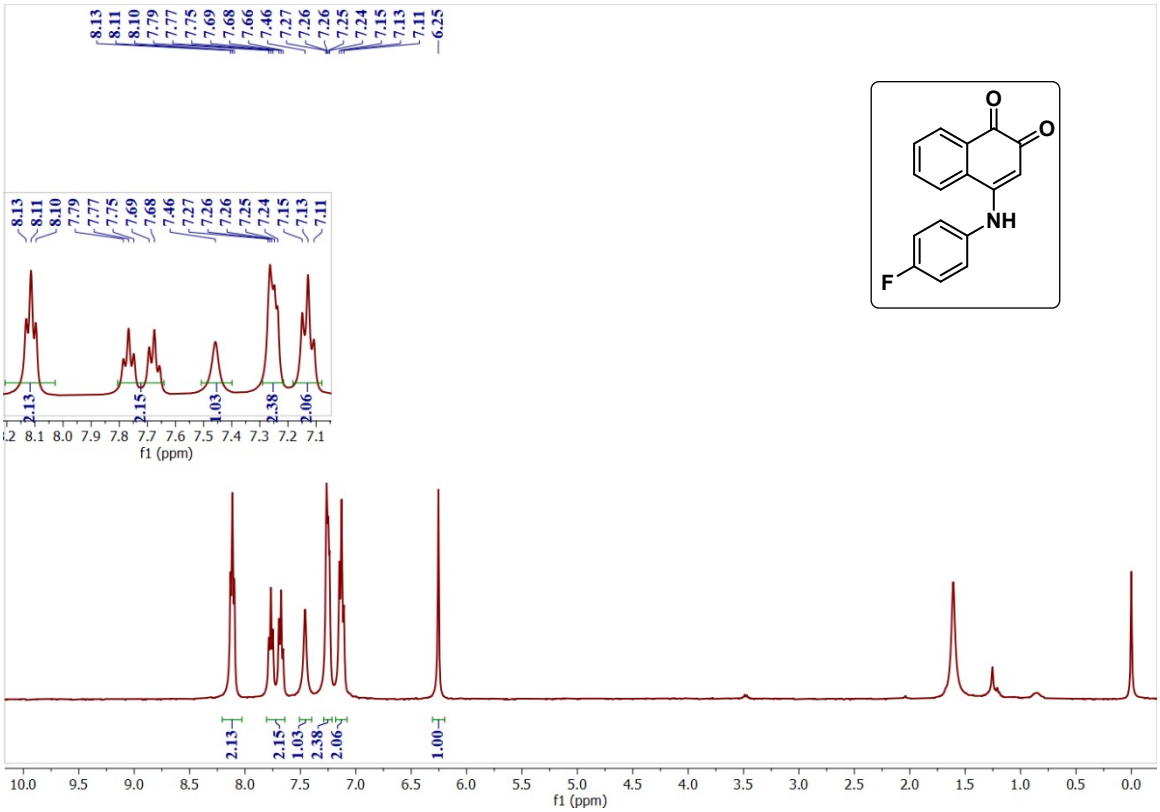


Figure S24: ^{1}H NMR (400MHz) Spectrum of **7g** in $CDCl_3$ at 28 °C.

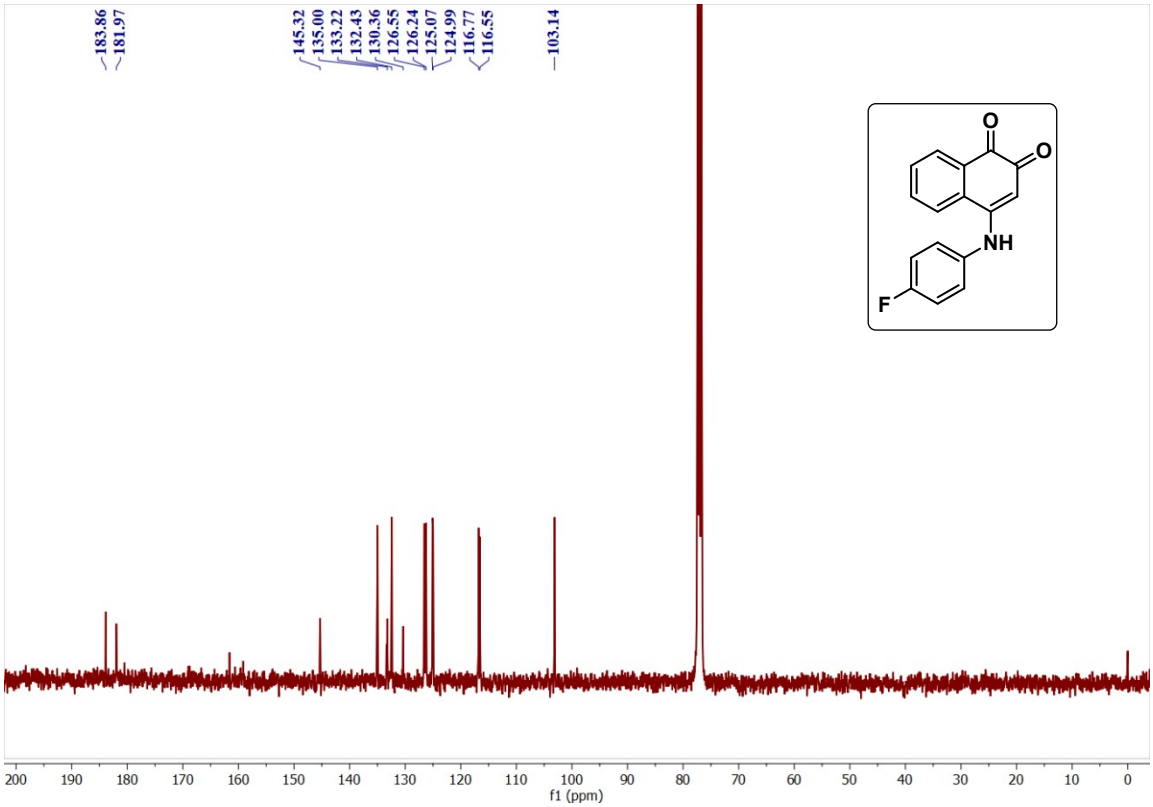


Figure S25: ^{13}C NMR (100 MHz) Spectrum of **7g** in $CDCl_3$ at 28 °C.

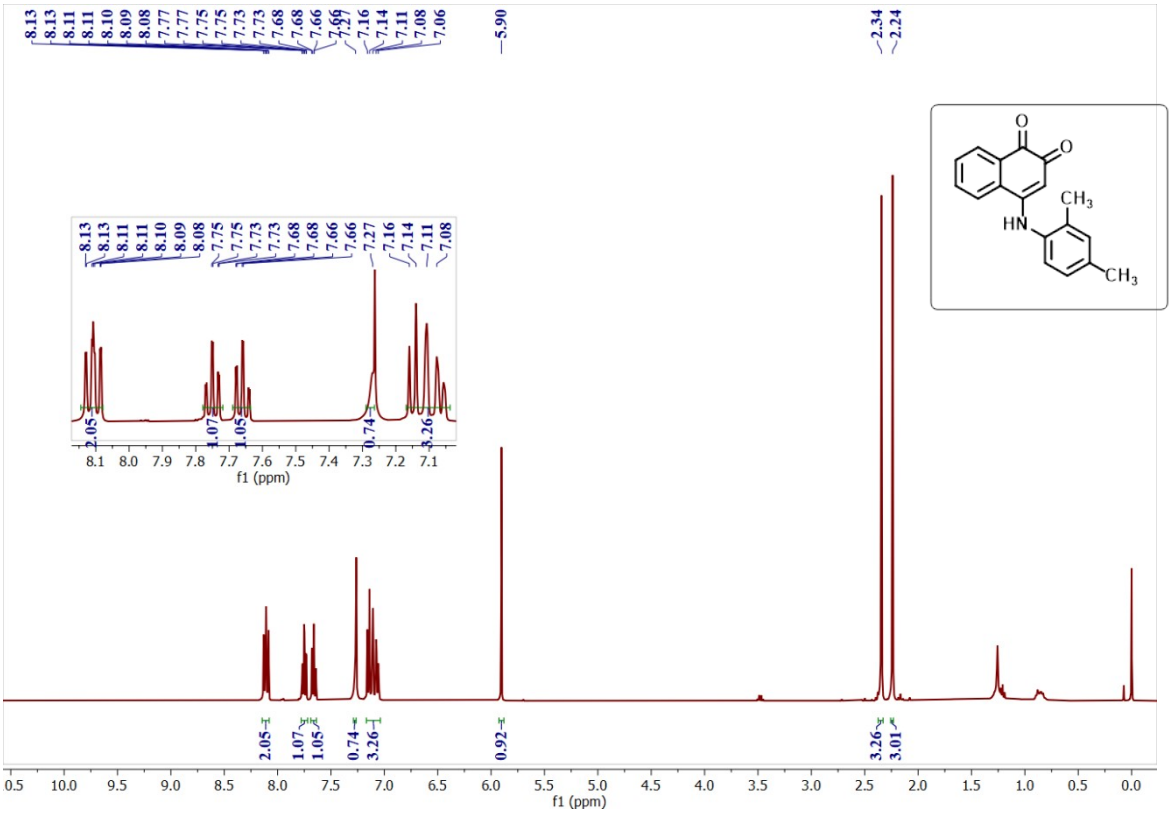


Figure S26: ^{1}H NMR (400MHz) Spectrum of 7h in $CDCl_3$ at 28 °C.

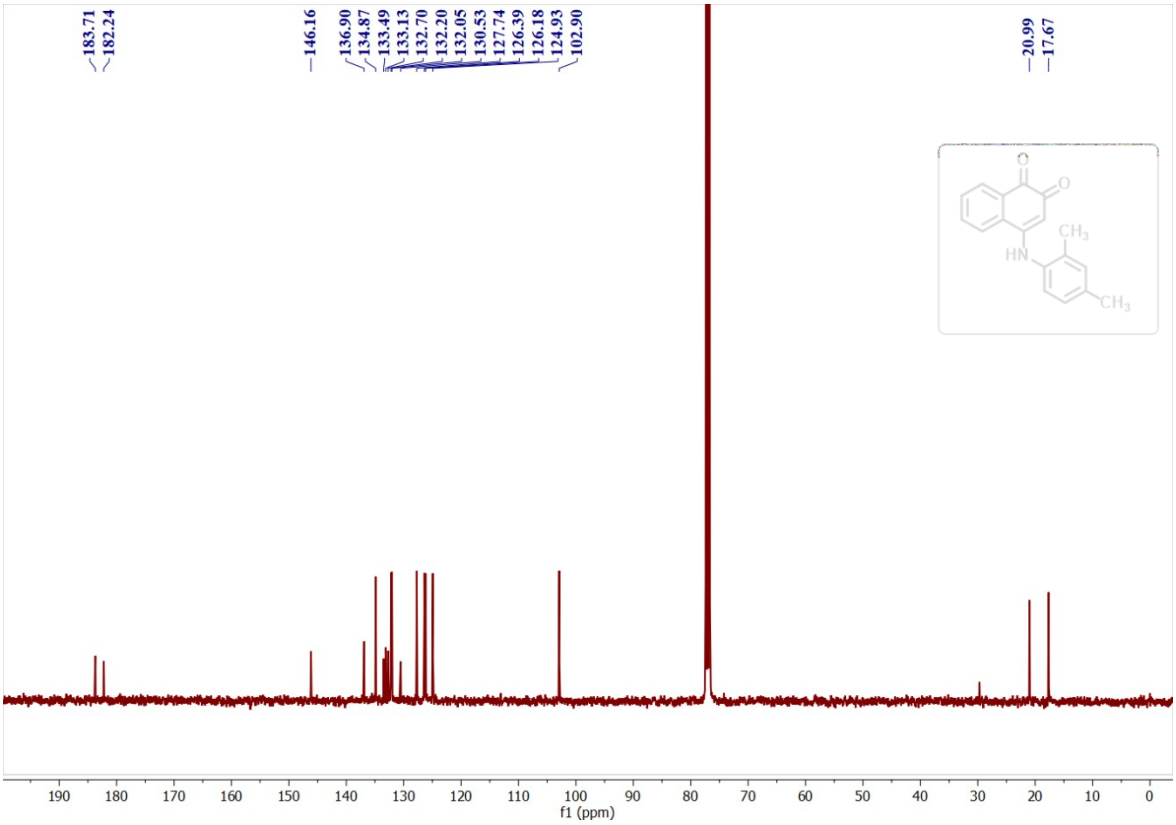


Figure S27: ^{13}C NMR (100 MHz) Spectrum 7h in $CDCl_3$ at 28 °C.

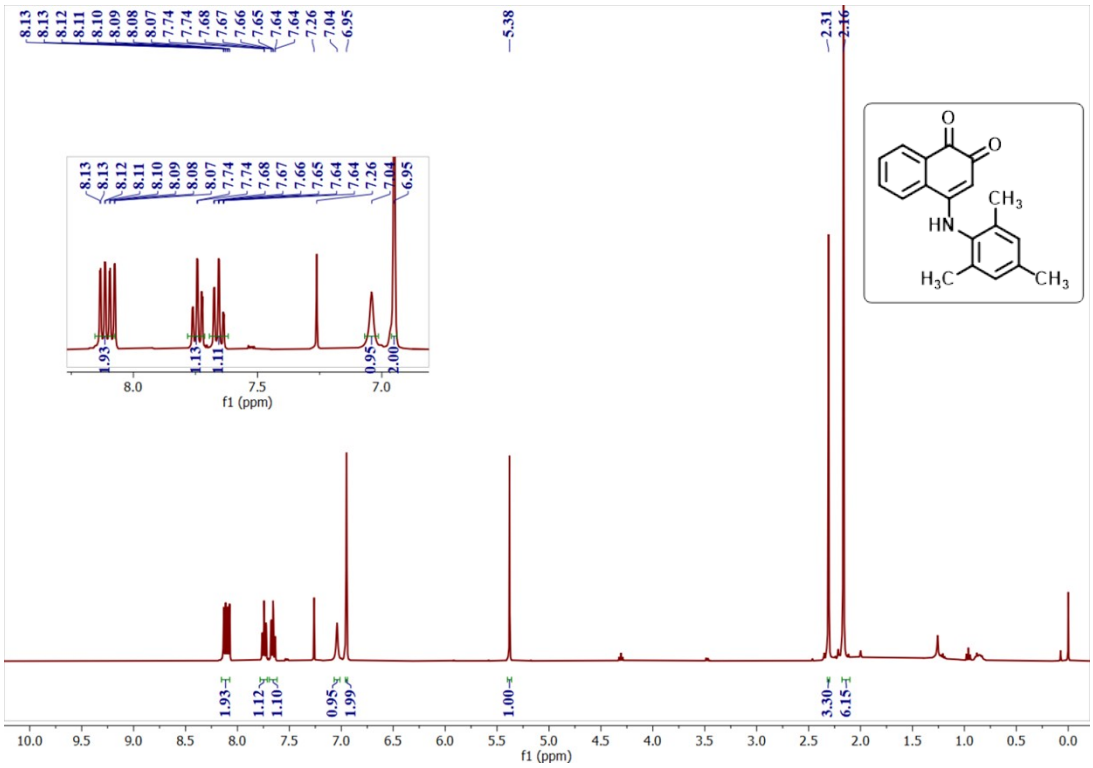


Figure S28: ^{1}H NMR (400MHz) Spectrum of 7i in $CDCl_3$ at 28 °C.

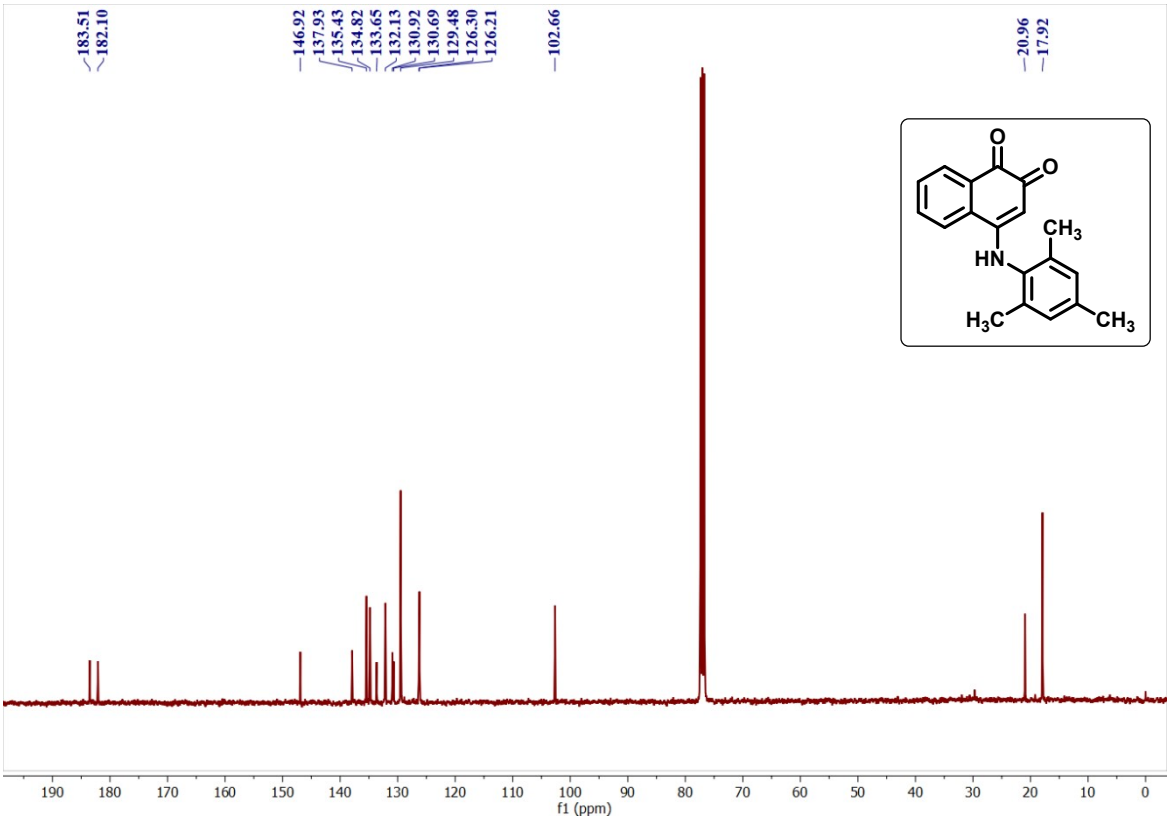


Figure S29: ^{13}C NMR (100 MHz) Spectrum 7i in $CDCl_3$ at 28 °C.

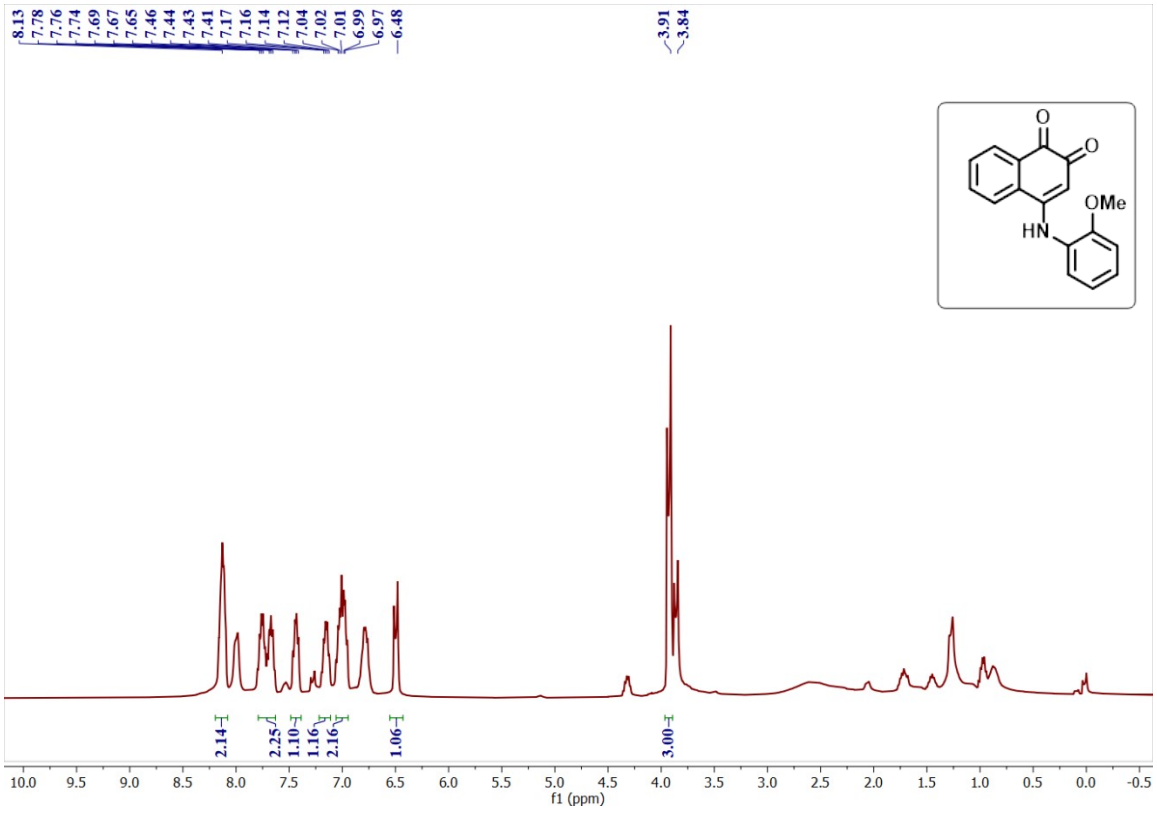


Figure S30: ^{1}H NMR (400MHz) Spectrum of 7j in $CDCl_3$ at 28 °C.

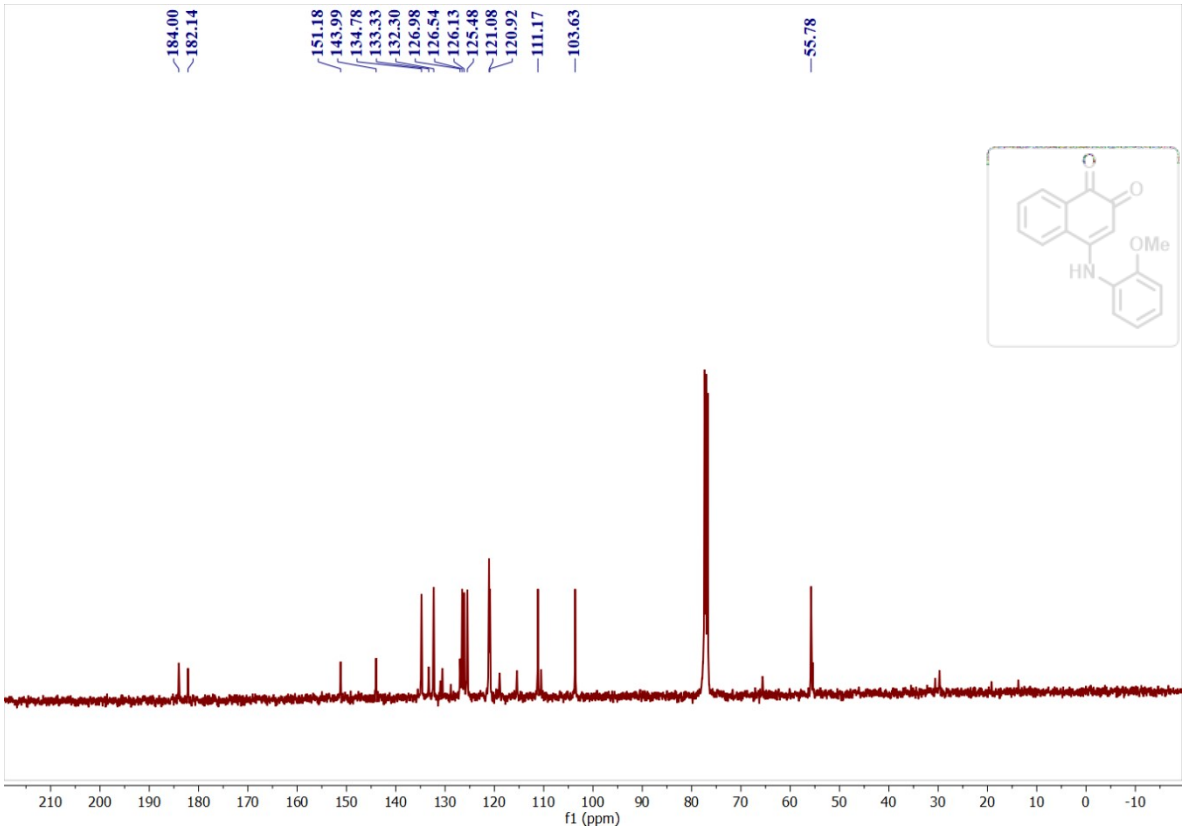


Figure S31: ^{13}C NMR (100 MHz) Spectrum 7j in $CDCl_3$ at 28 °C.

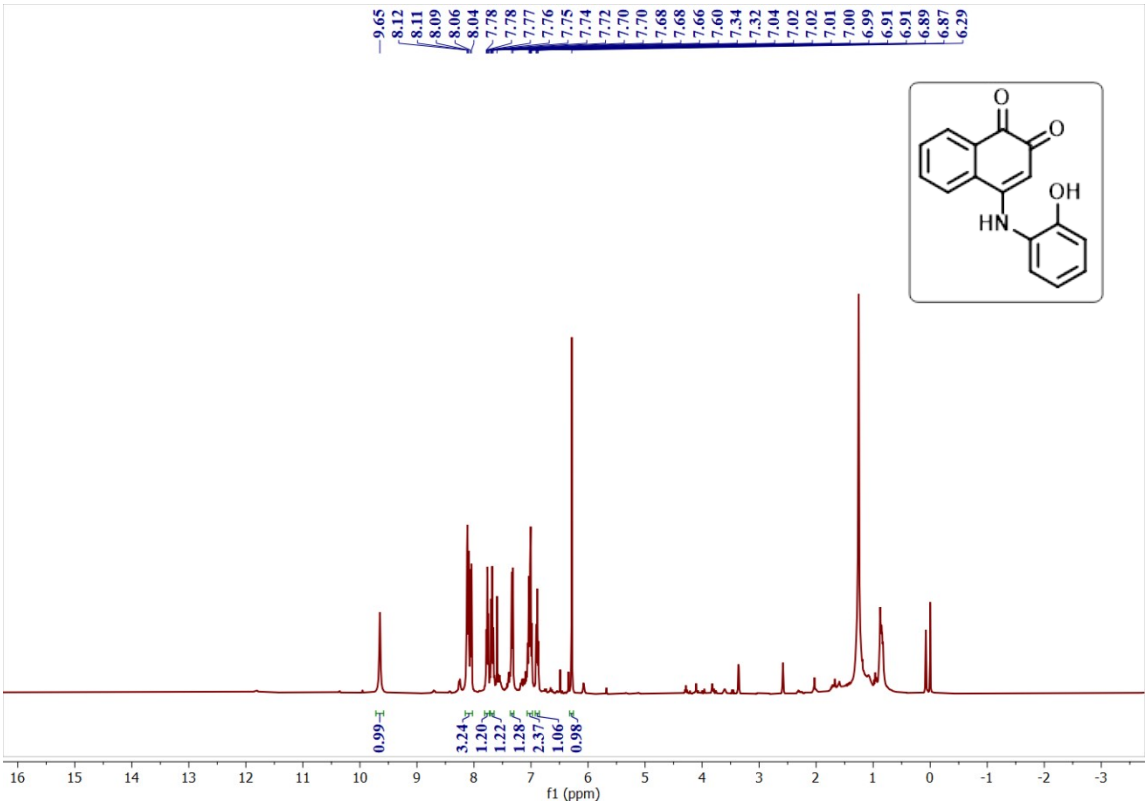


Figure S32: ^{1}H NMR (400MHz) Spectrum of 7k in $CDCl_3$ + DMSO at 28 °C.

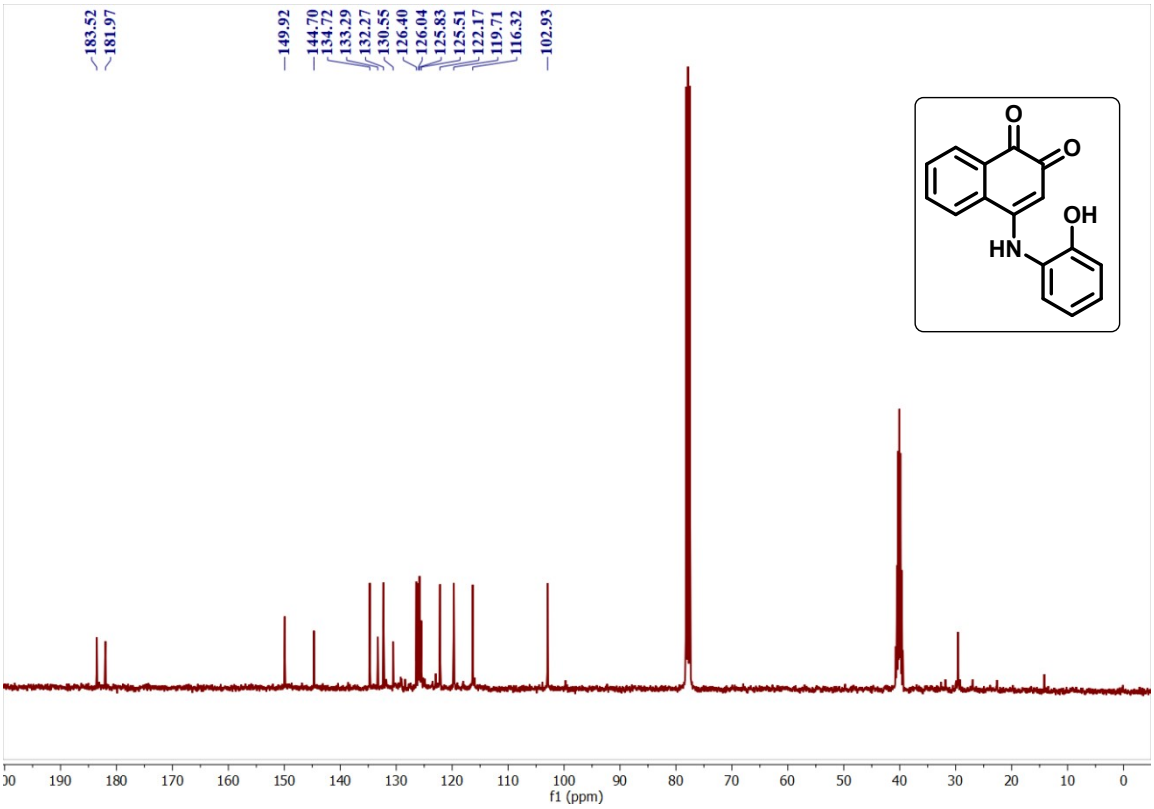


Figure S33: ^{13}C NMR (100 MHz) Spectrum 7k in $CDCl_3$ + DMSO at 28 °C.

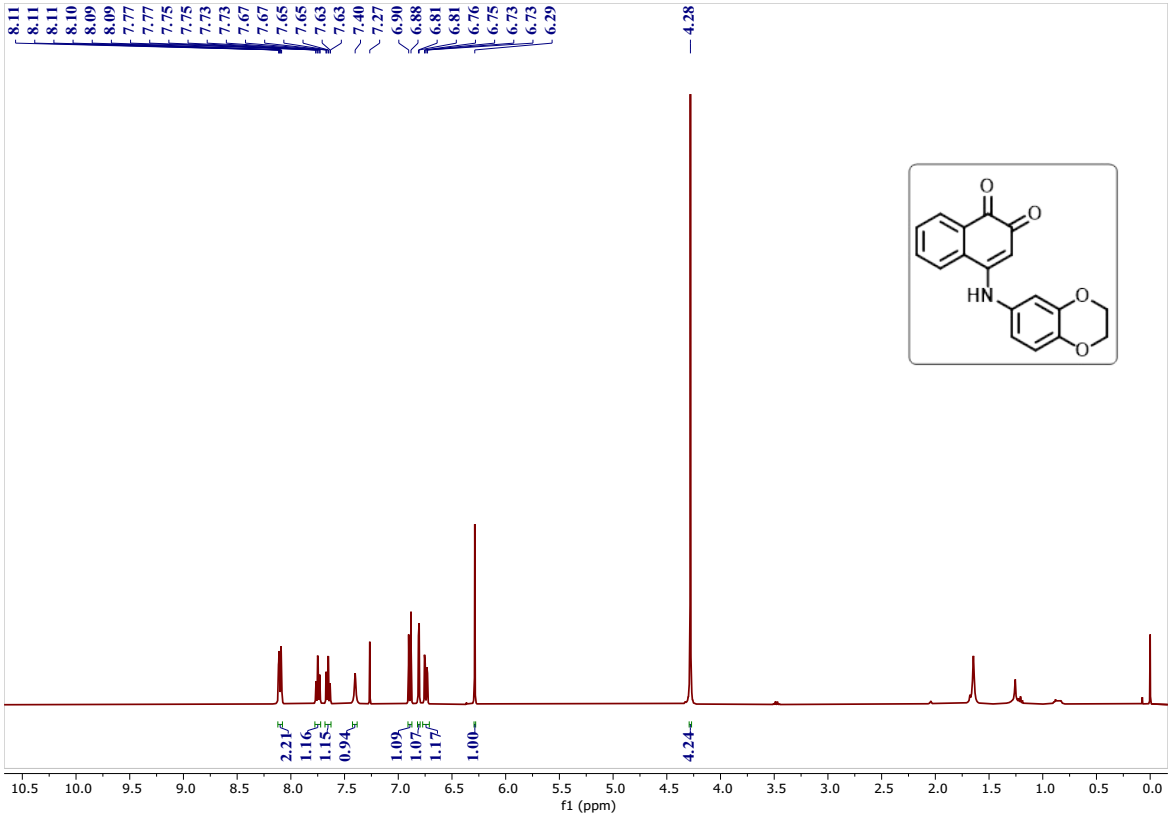


Figure S34: ^{1}H NMR (400MHz) Spectrum of 7l in $CDCl_3$ at 28 °C.

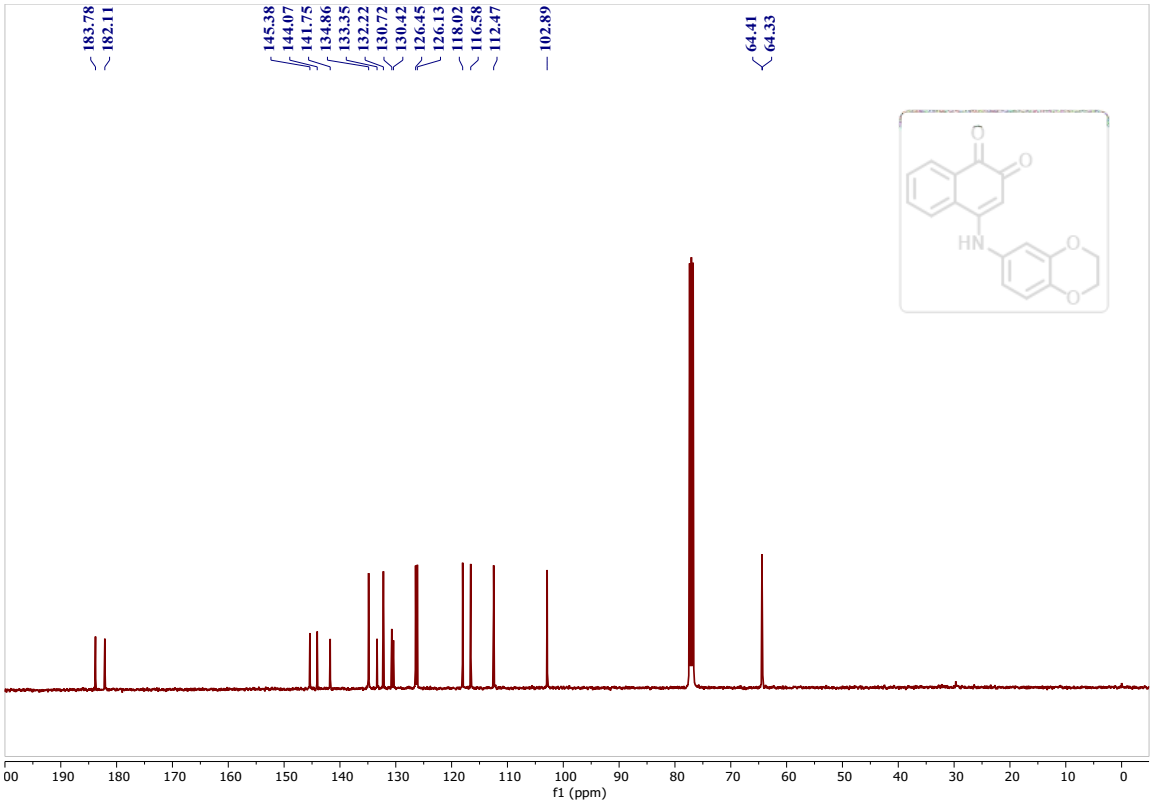


Figure S35: ^{13}C NMR (100 MHz) Spectrum 7l in $CDCl_3$ at 28 °C.

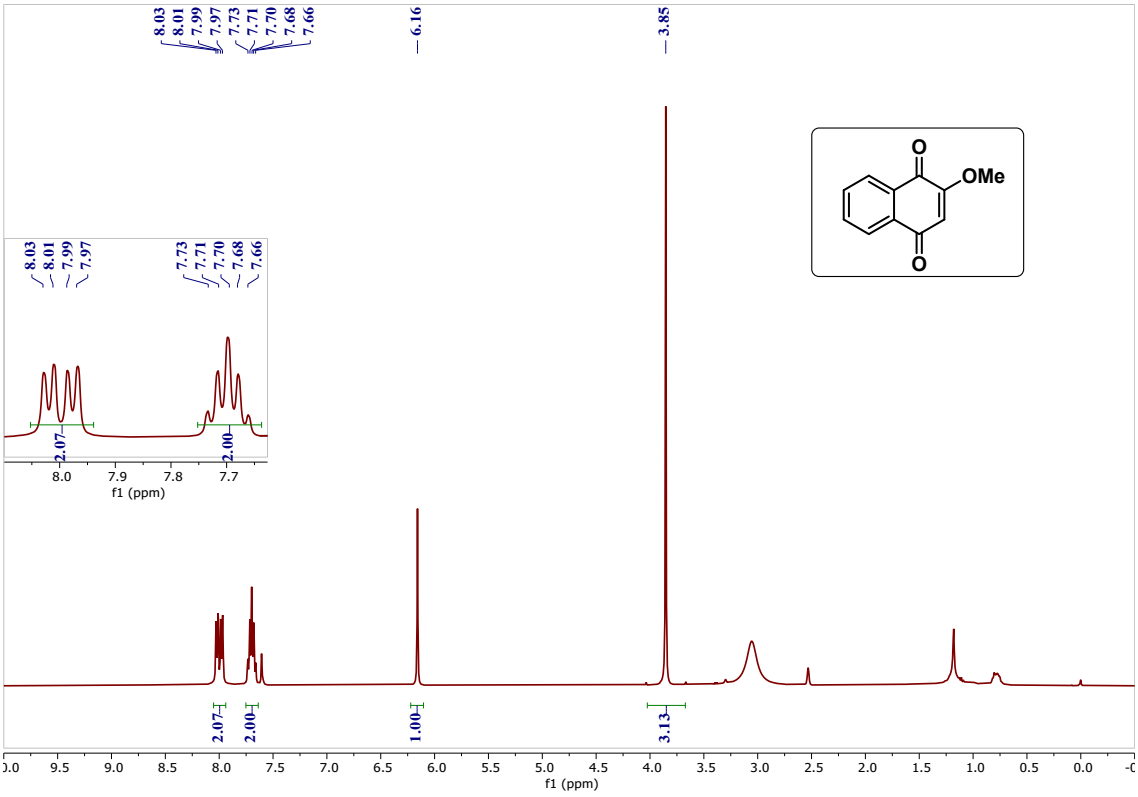


Figure S36: ^{1}H NMR (400MHz) Spectrum of **8a** in $CDCl_3$+DMSO-d_6 at 28 °C.

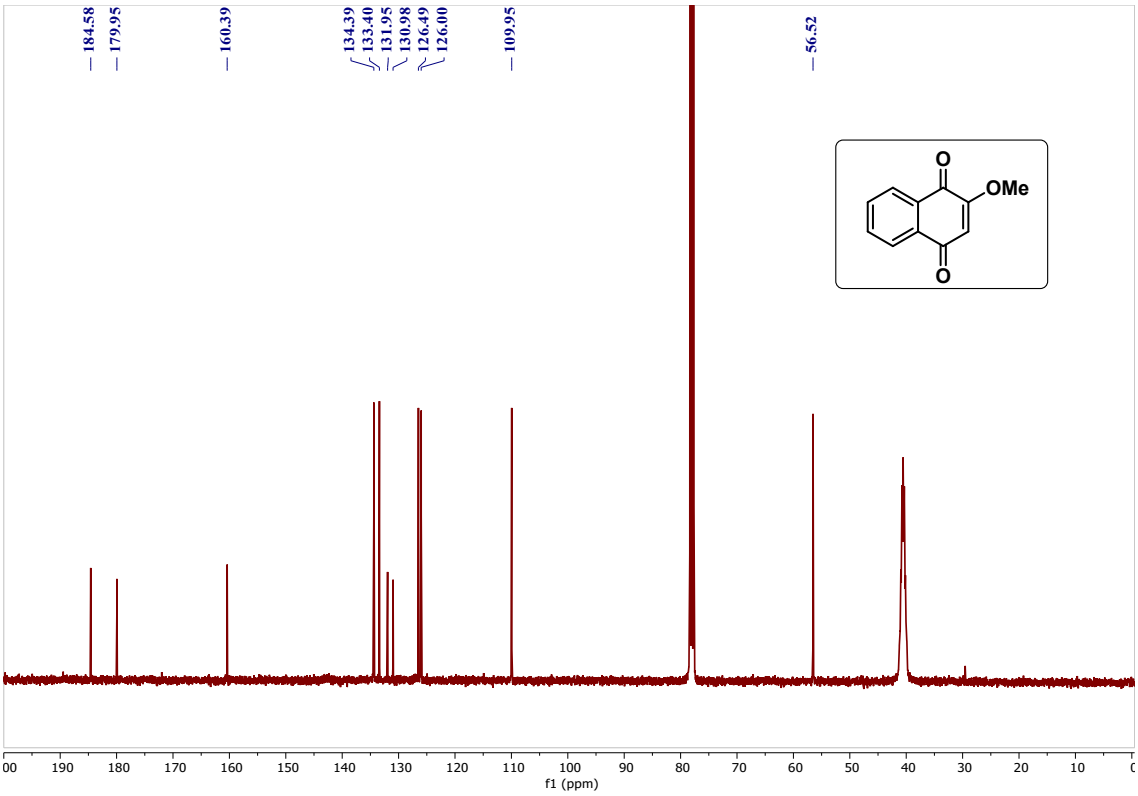


Figure S37: ^{13}C NMR (100 MHz) Spectrum of **8a** in $CDCl_3$+DMSO-d_6 at 28 °C.

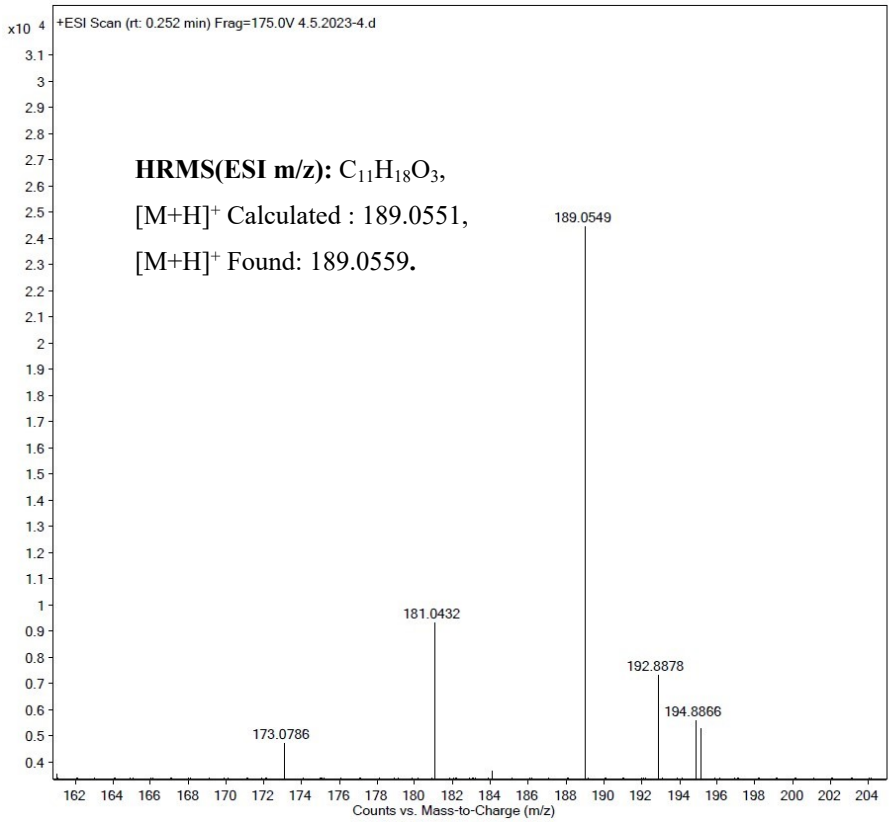


Figure S27: HRMS Spectrum of **8a**.

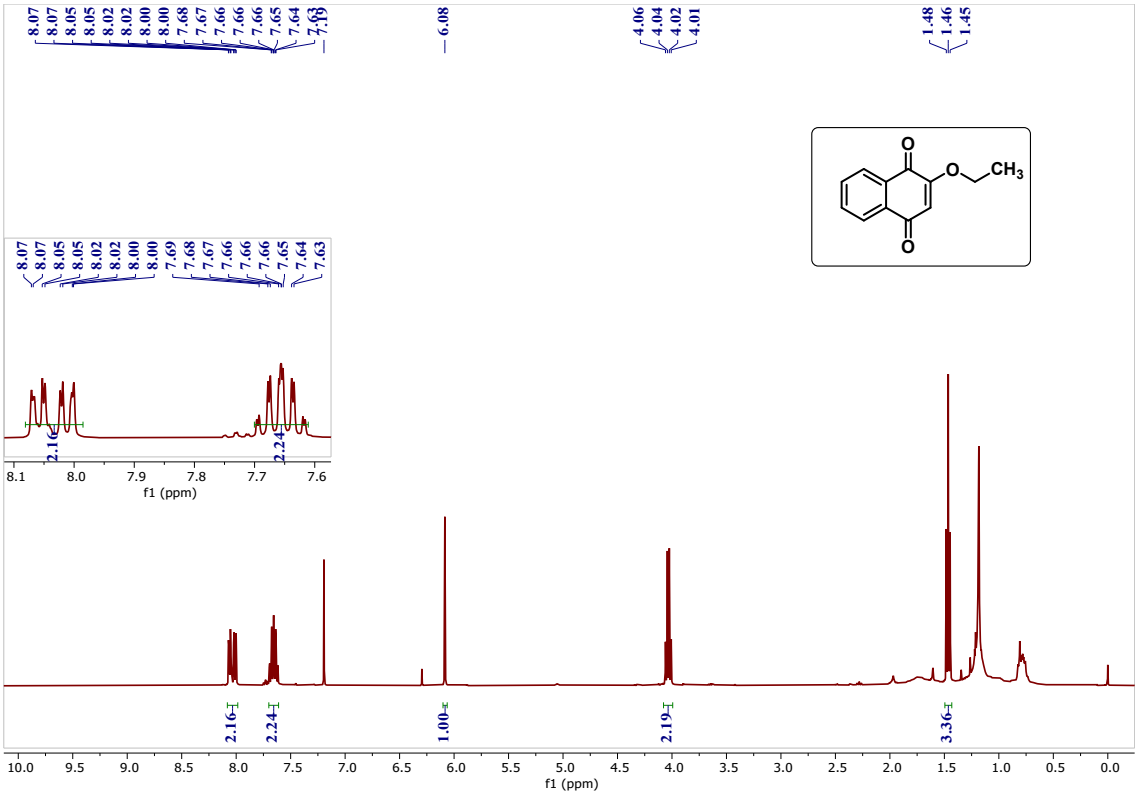


Figure S38: ^{1}H NMR (400MHz) Spectrum of **8b** in $CDCl_3$ at 28 °C.

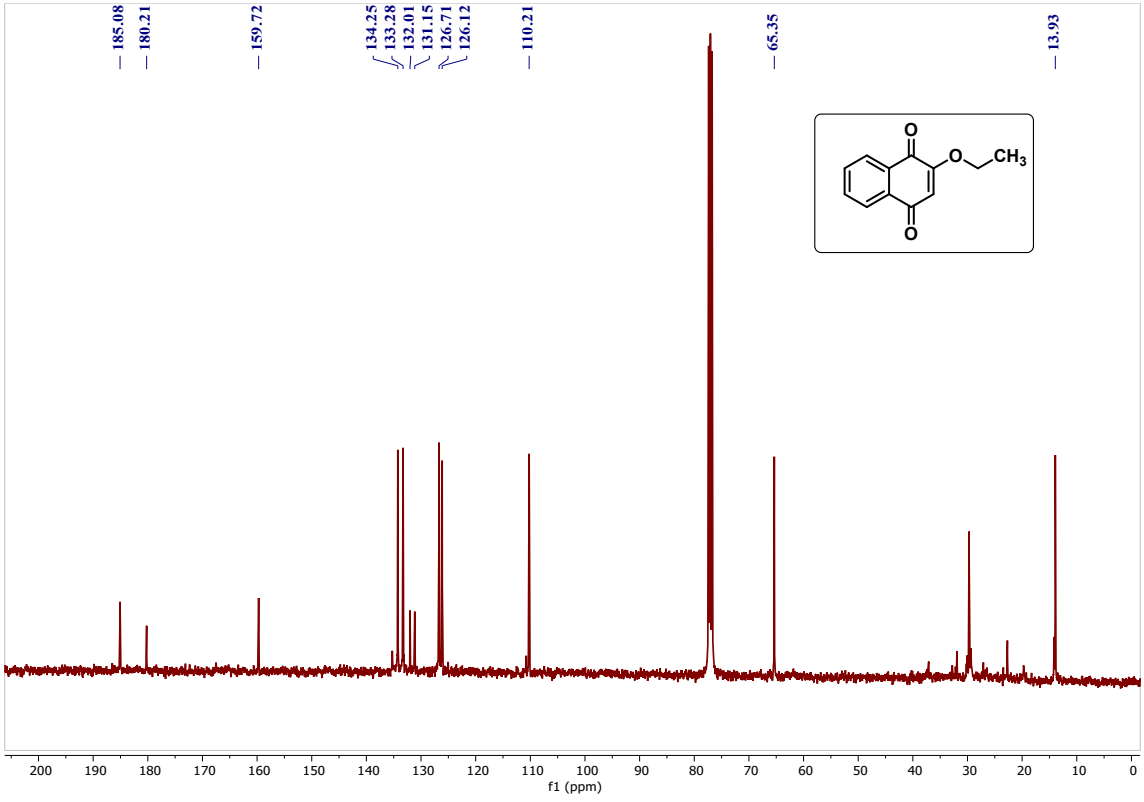


Figure S39: ^{13}C NMR (100 MHz) Spectrum of **8b** in $CDCl_3$ at 28 °C.

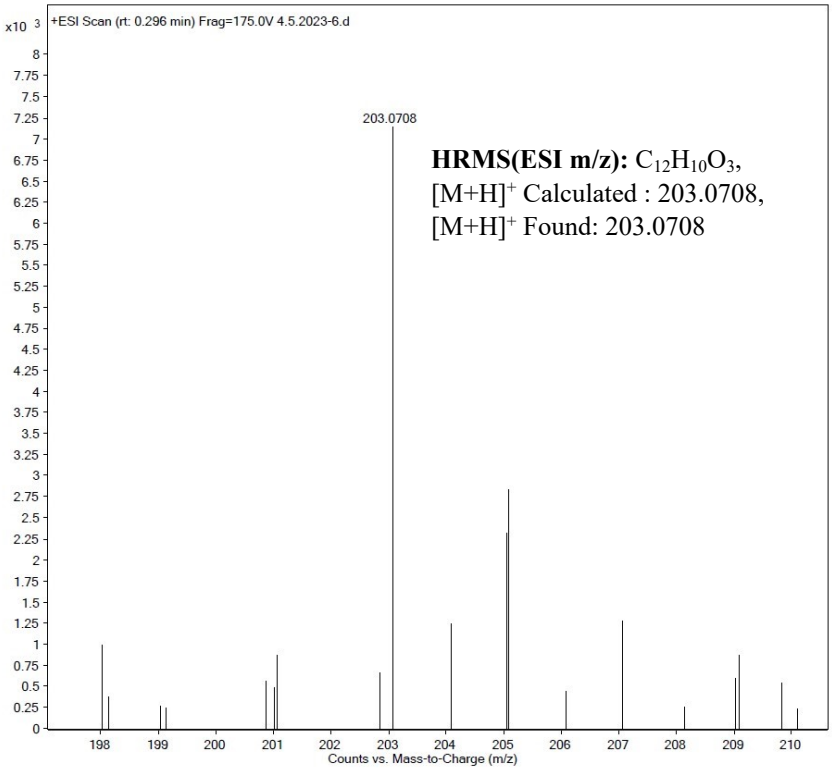


Figure S40: HRMS Spectrum of **8b**.

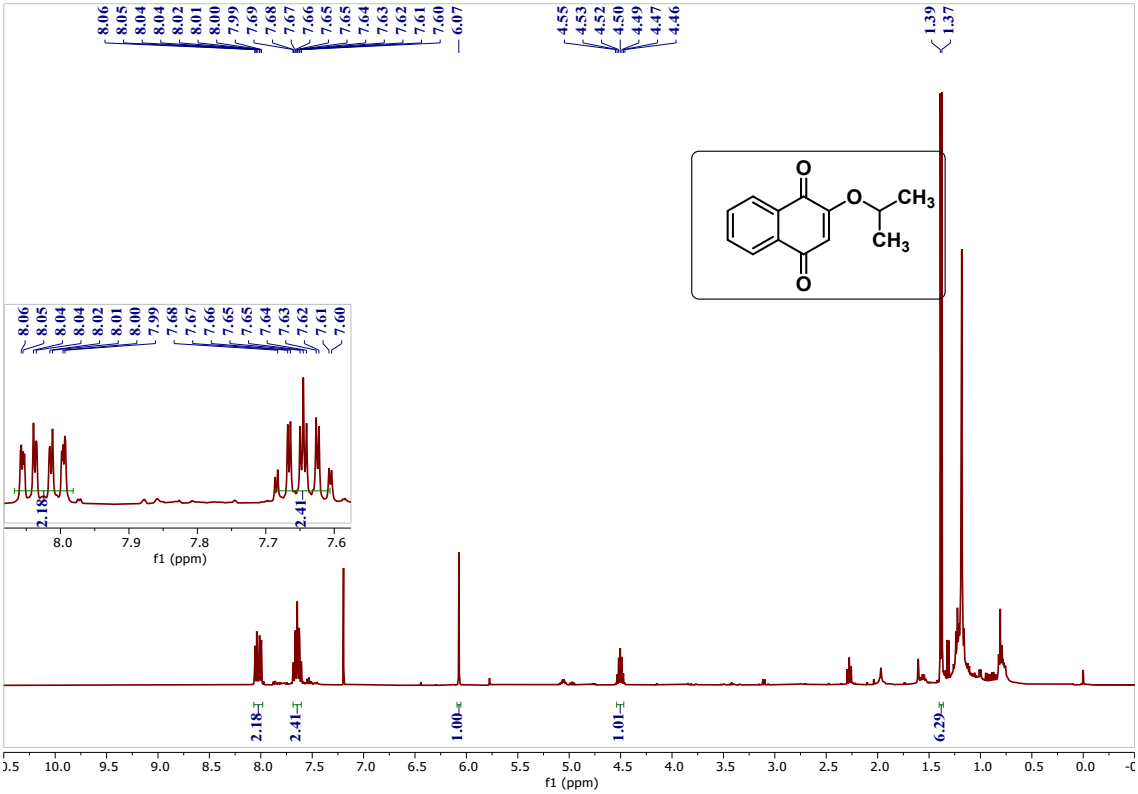


Figure S41: ^{1}H NMR (400MHz) Spectrum of **8c** in $CDCl_3$ at 28 °C.

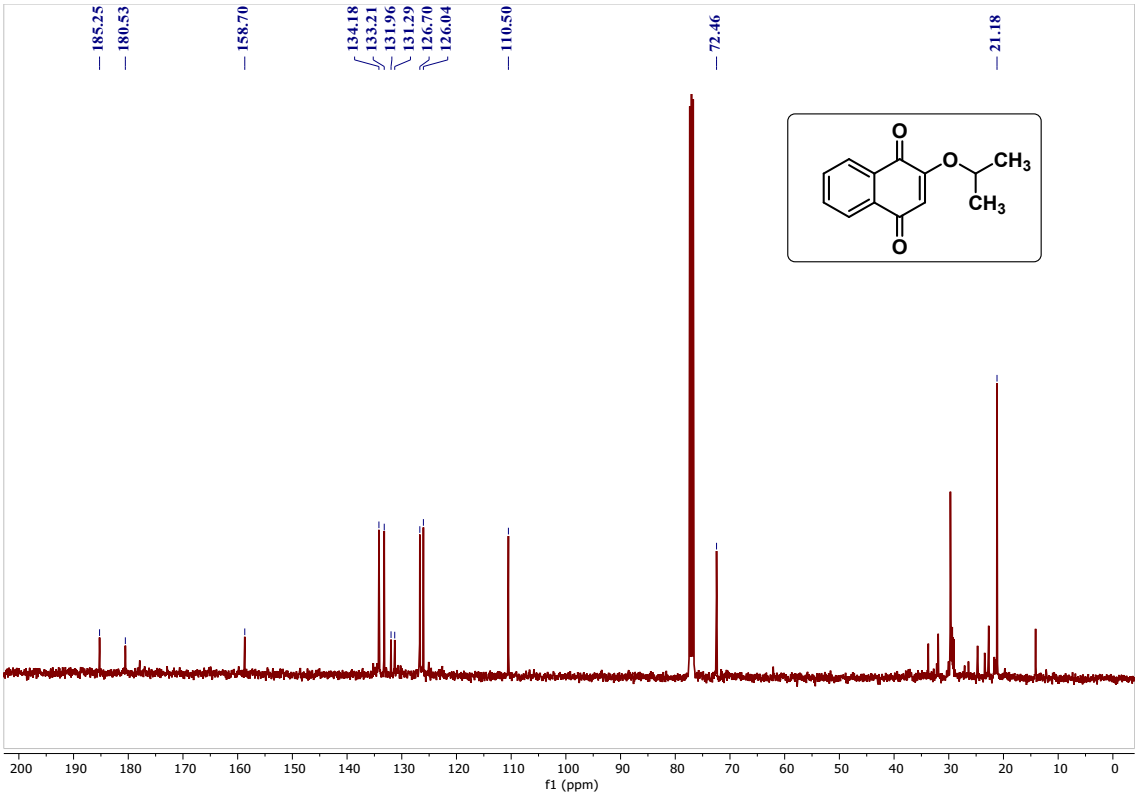


Figure S42: ^{13}C NMR (100 MHz) Spectrum of **8c** in $CDCl_3$ at 28 °C.

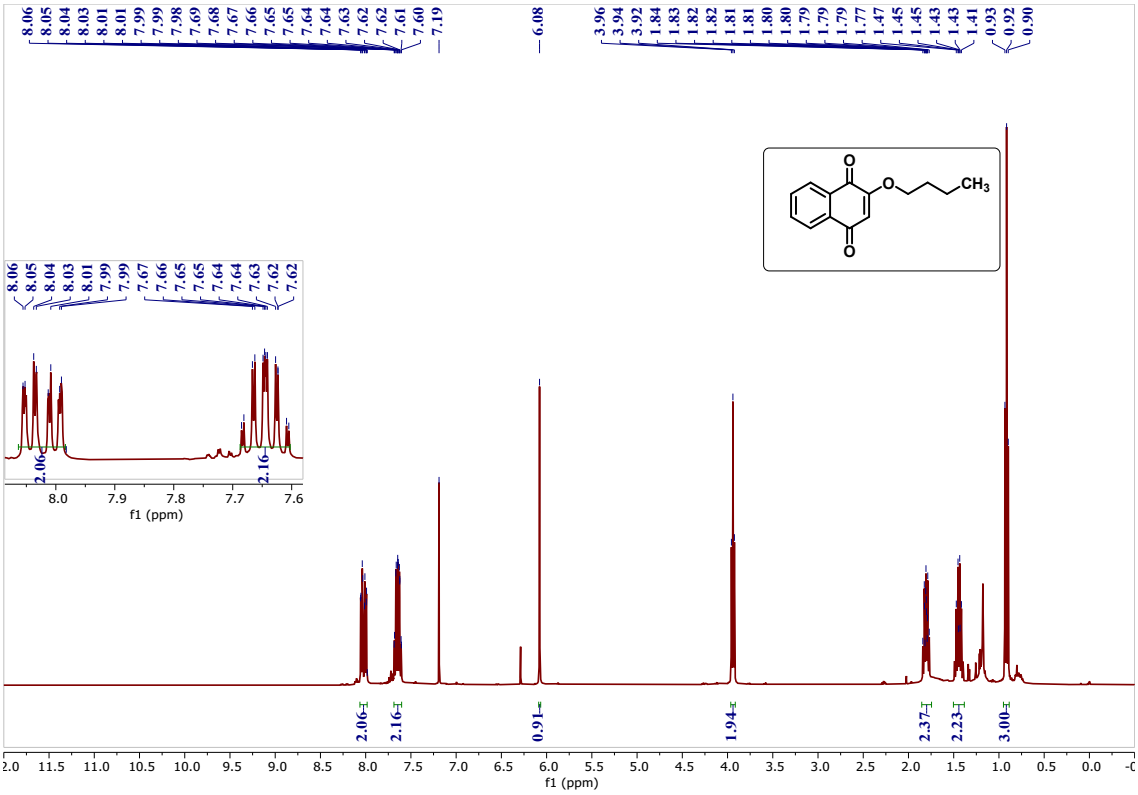


Figure S43: ^{1}H NMR (400MHz) Spectrum of **8d** in $CDCl_3$ at 28 °C.

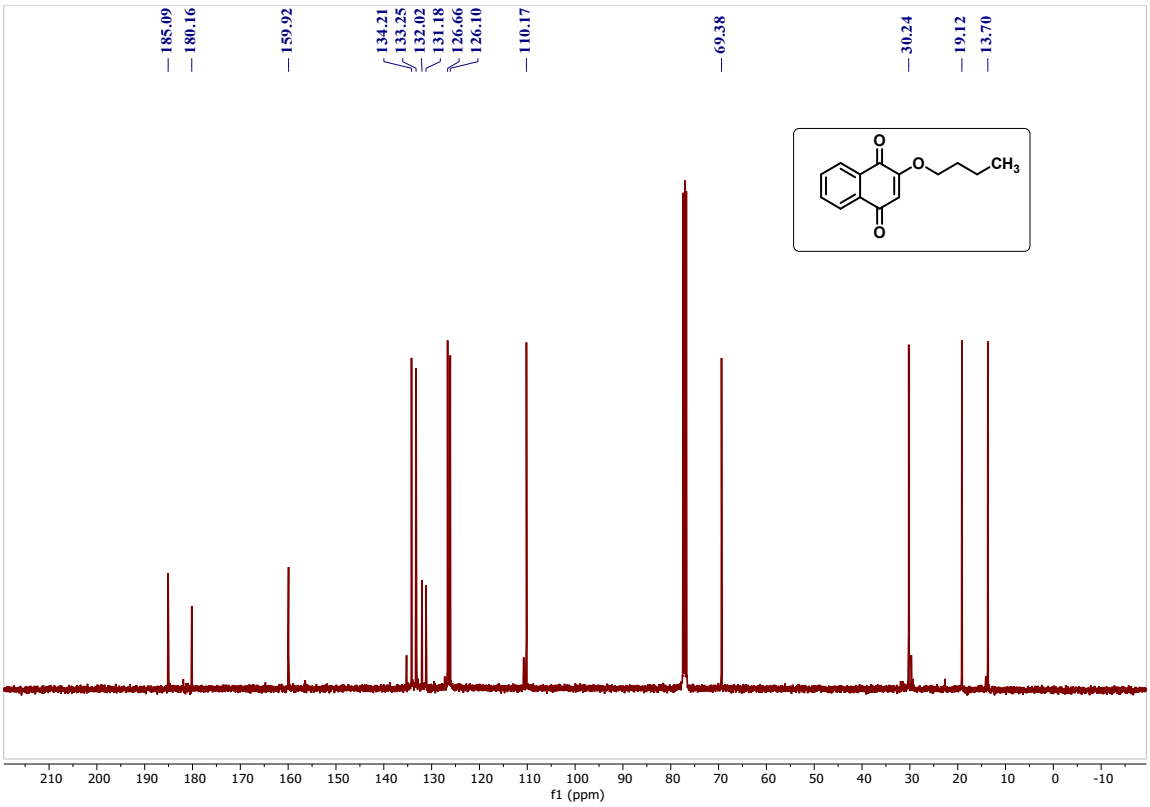


Figure S44: ^{13}C NMR (100 MHz) Spectrum of **8d** in $CDCl_3$ at 28 °C.

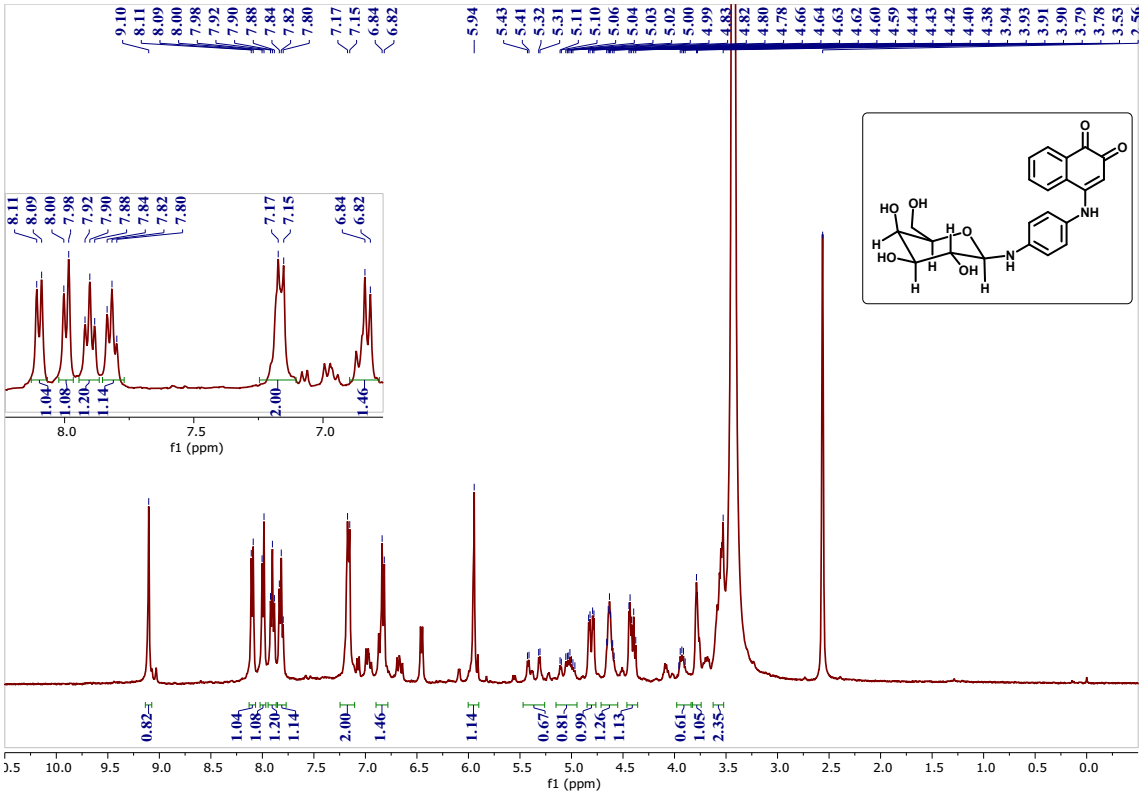


Figure S45: ^{1}H NMR (400MHz) Spectrum of **10** in DMSO-d_6 at 28 °C.

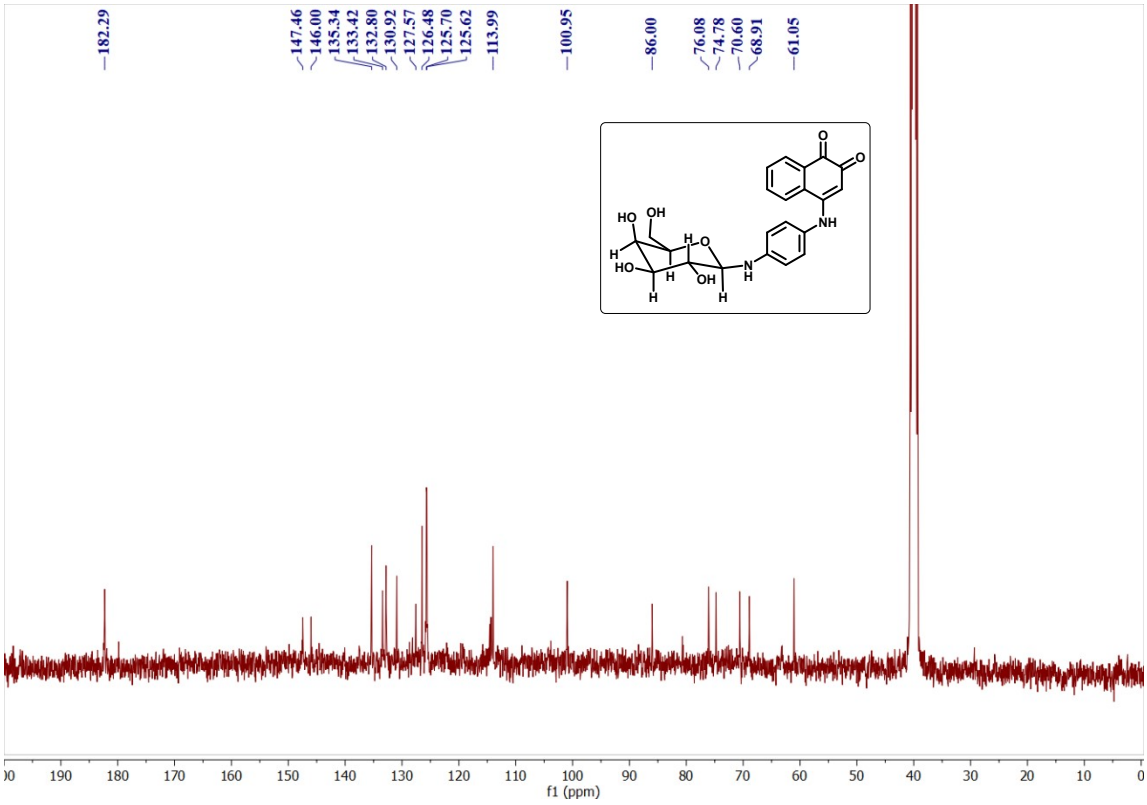


Figure S46: ^{13}C NMR (100 MHz) Spectrum of **10** in DMSO-d_6 at 28 °C.

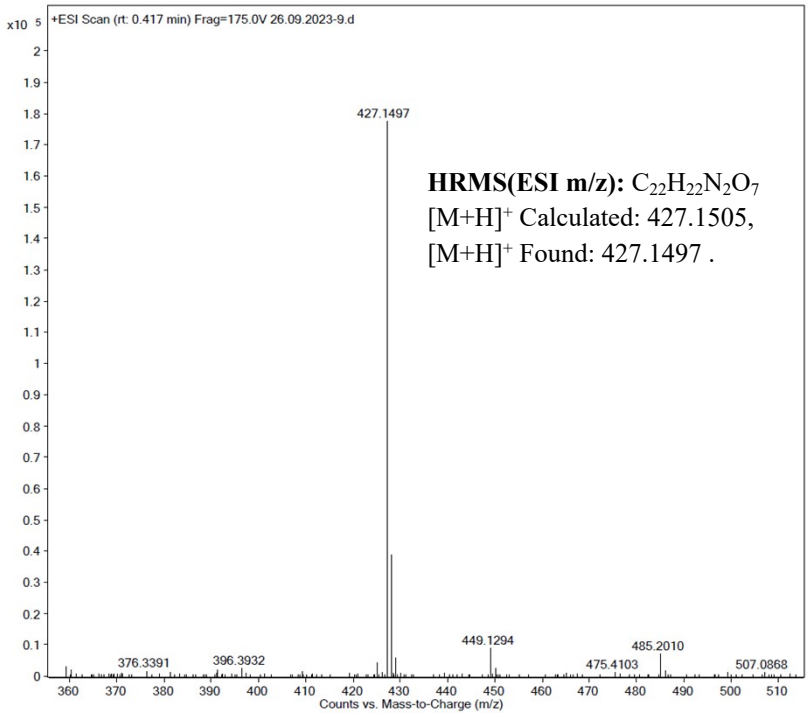


Figure S47: HRMS Spectrum of **10**.

7 IR

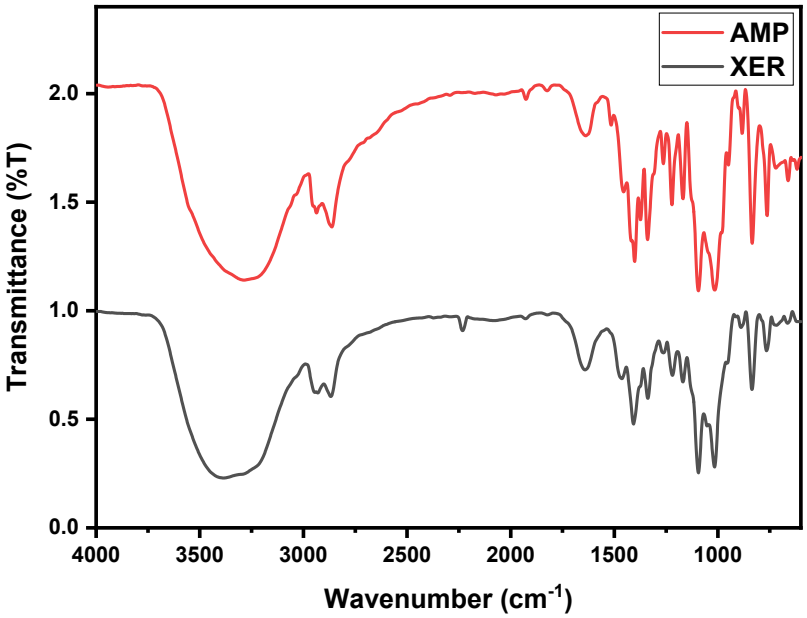


Figure S48: Comparison of IR spectrum of amorphous HMDBS and xerogel of HMDBS Eutectogels.

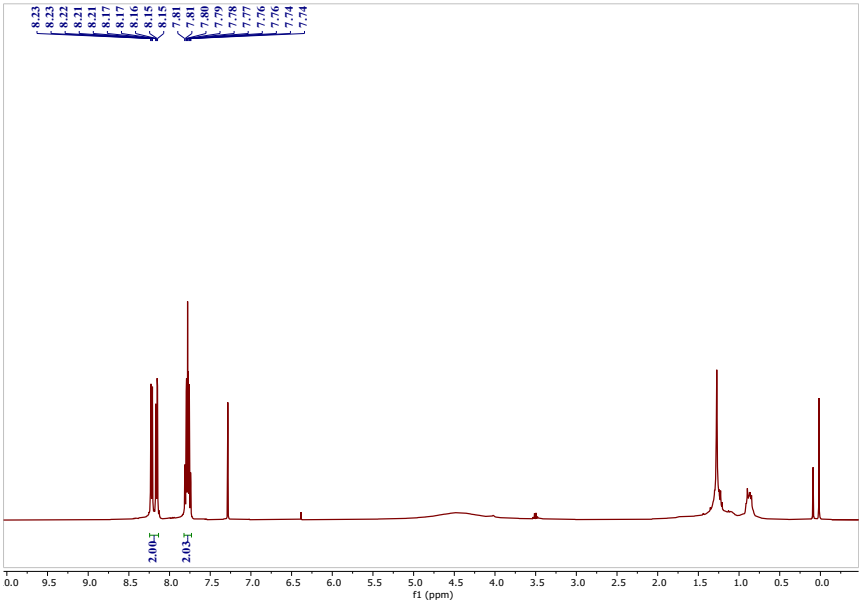


Figure S49: ^{1}H-NMR Spectra of compound 8a in $CDCl_3$ (400 MHz).[8]

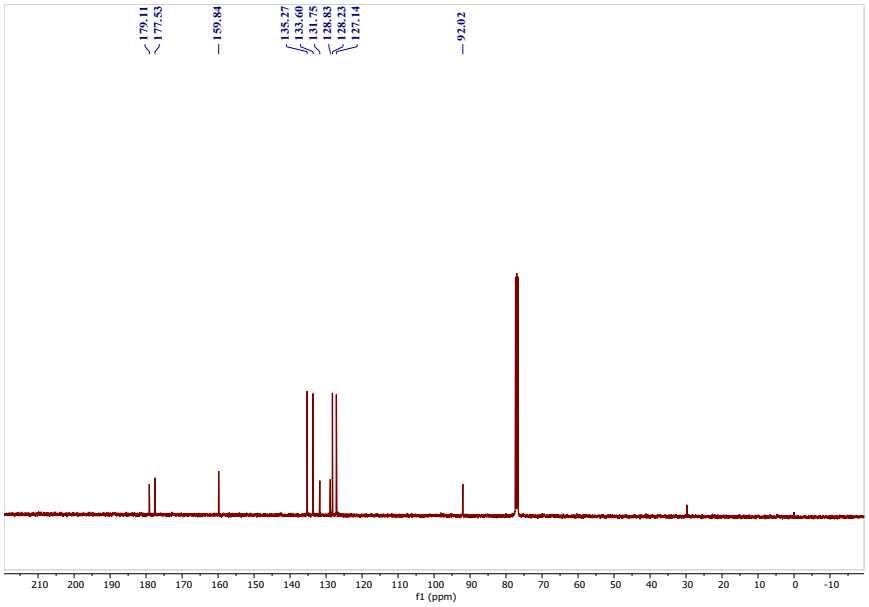


Figure S50. ^{13}C-NMR Spectra of 8a in $CDCl_3$ (100 MHz)[8]

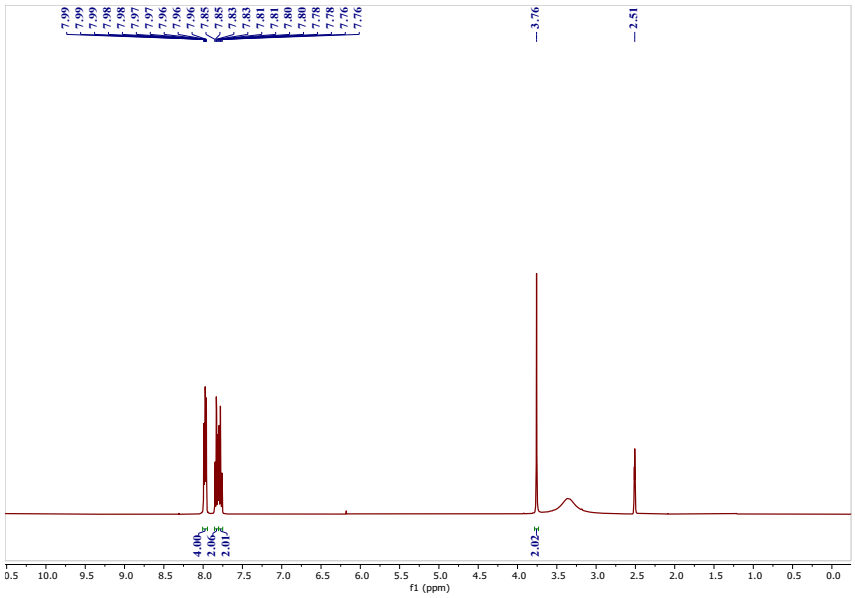


Figure S51: ^{1}H NMR spectra of Compound 8b in DMSO-d_6 (400 MHz).[9]

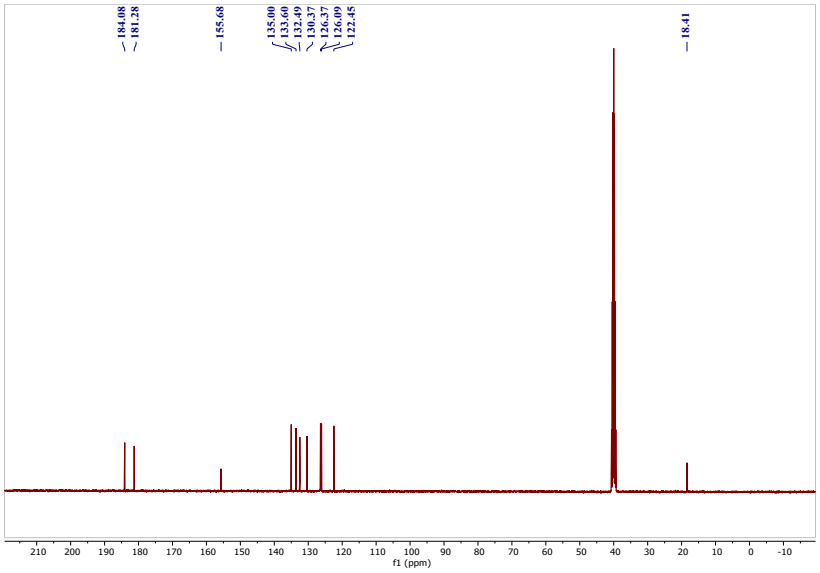


Figure S52. ^{13}C-NMR Spectra of **8b** in DMSO-d_6 (100 MHz).[9]

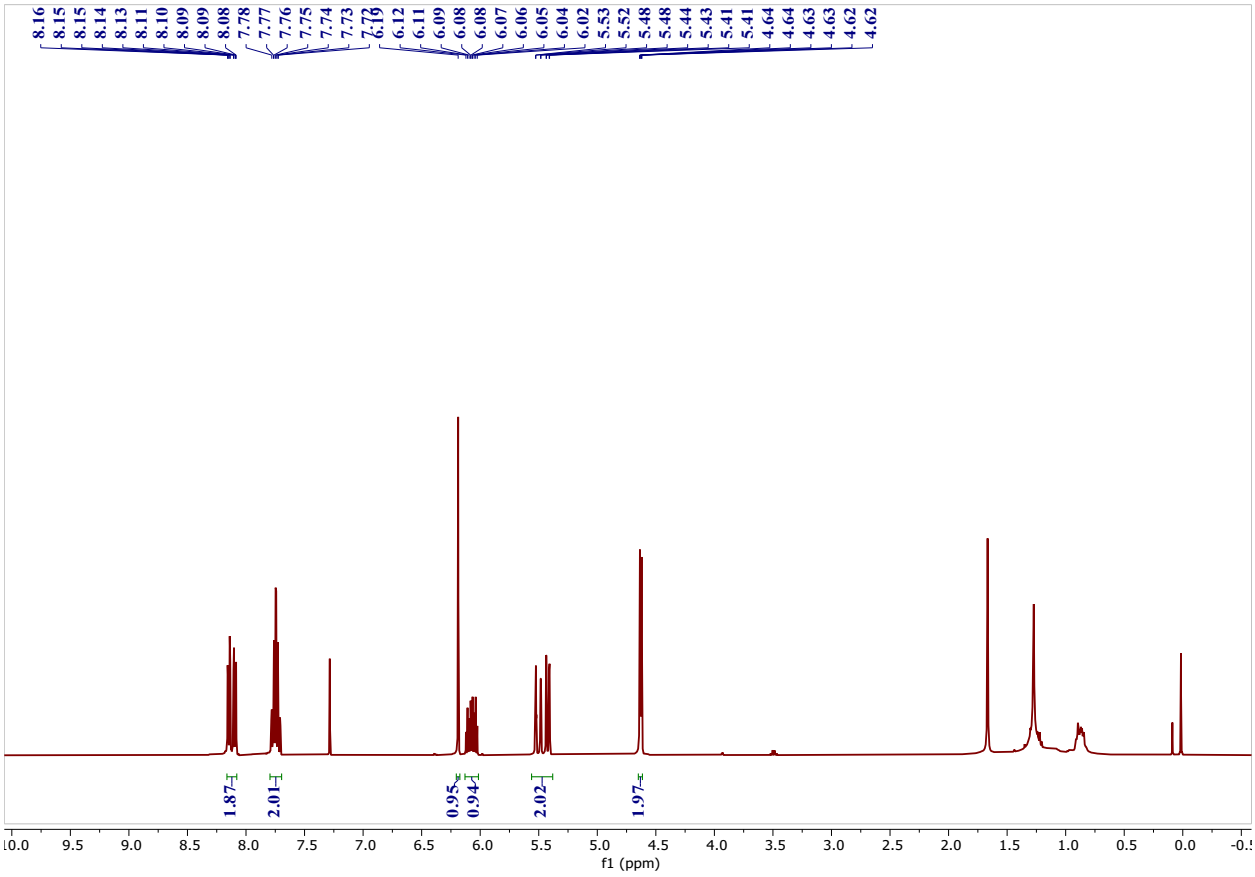


Figure S53 ^{1}H-NMR Spectra of 8c in $CDCl_3$ (400 MHz).[10]

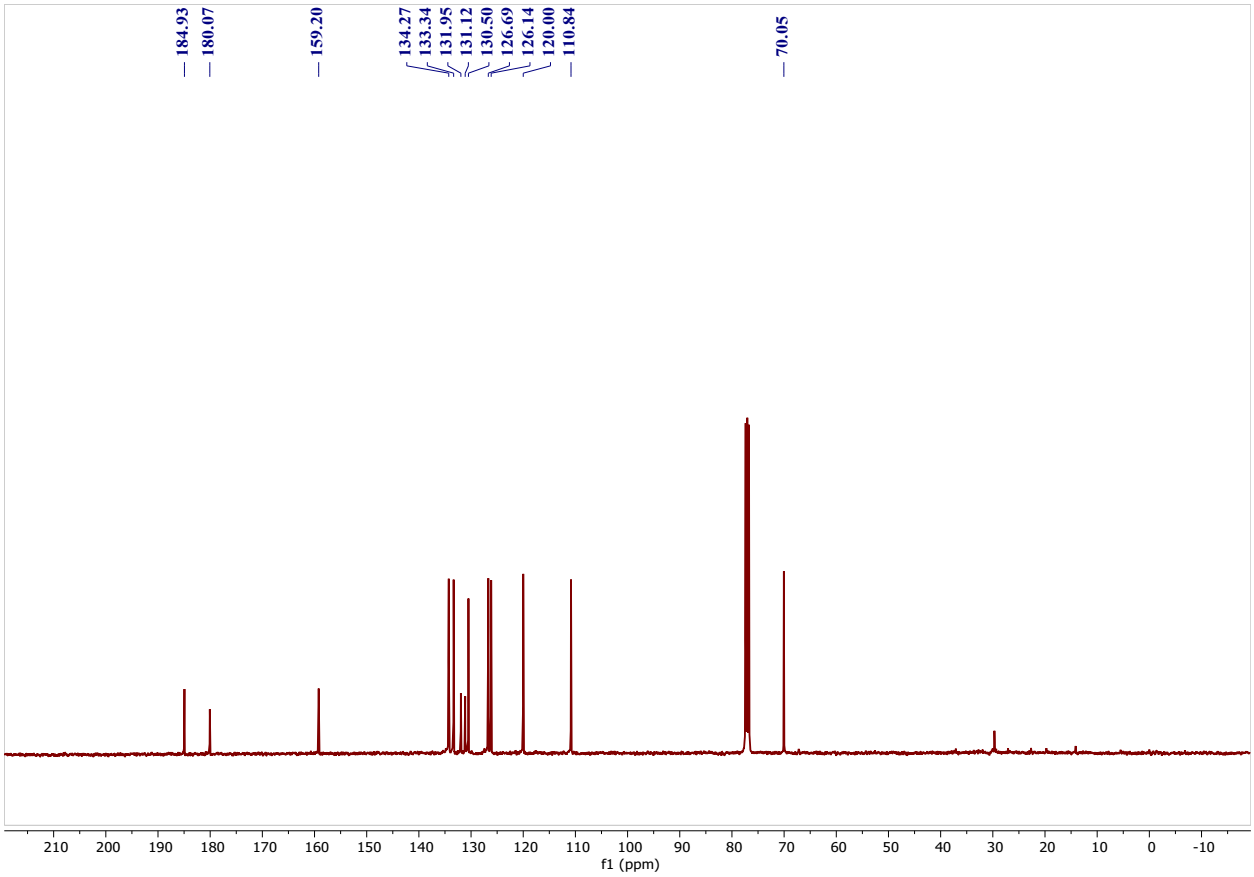


Figure S54. ^{13}C-NMR Spectra of 8c in $CDCl_3$ (100 MHz).[10]

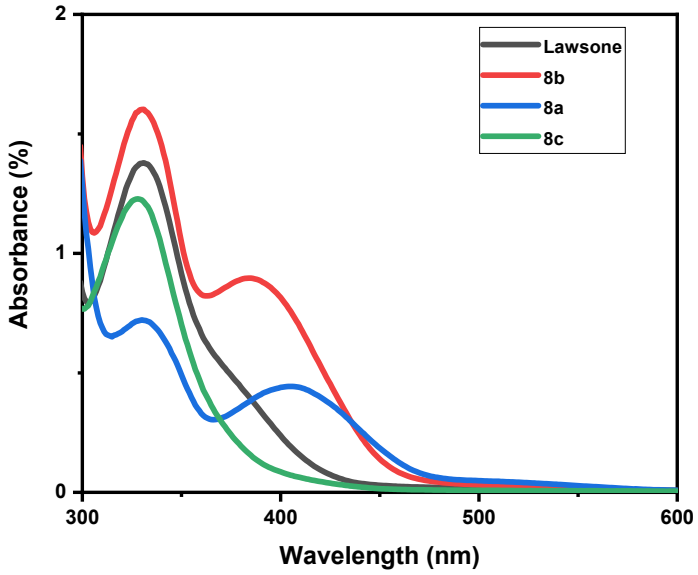


Figure S55. UV-vis spectra of lawsone, compound 8a, 8b, and 8c in THF.

References

(1) Tseng, C. H.; Lin, C. K.; Chen, Y. L.; Tseng, C. K.; Lee, J. Y.; Lee, J. C. Discovery of Naphtho[1,2-d]Oxazole Derivatives as Potential Anti-HCV Agents through Inducing Heme Oxygenase-1 Expression. *Eur. J. Med. Chem.* **2018**, *143*, 970–982. https://doi.org/10.1016/j.ejmech.2017.12.006.

(2) Tseng, C. H.; Cheng, C. M.; Tzeng, C. C.; Peng, S. I.; Yang, C. L.; Chen, Y. L. Synthesis and Anti-Inflammatory Evaluations of β-Lapachone Derivatives. *Bioorganic Med. Chem.* **2013**, *21* (2), 523–531. https://doi.org/10.1016/j.bmc.2012.10.047.

(3) Singh, P.; Baheti, A.; Thomas, K. R. J. Synthesis and Optical Properties of Acidochromic Amine-Substituted Benzo[a]Phenazines. *J. Org. Chem.* **2011**, *76* (15), 6134–6145. https://doi.org/10.1021/jo200857p.

(4) Urbanek, R. A.; Suchard, S. J.; Steelman, G. B.; Knappenberger, K. S.; Sygowski, L. A.; Veale, C. A.; Chapdelaine, M. J. Potent Reversible Inhibitors of the Protein Tyrosine Phosphatase CD45. *J. Med. Chem.* **2001**, *44* (11), 1777–1793. https://doi.org/10.1021/jm000447i.

(5) Gornostaev, L. M.; Rukovets, T. A.; Arnold, E. V.; Khalyavina, Y. G.; Gatilov, Y. V. Oximation of 2-(R1-Amino)-4-(R2-Imino)Naphthalen-1(4H)-Ones. *Russ. J. Org. Chem.* **2018**, *54* (1), 78–86. https://doi.org/10.1134/S1070428018010062.

(6) Sousa, A. C.; Santos, I.; Piedade, M. F. M. M.; Martins, L. O.; Robalo, M. P. Synthesis of Substituted 4-Arylamino-1,2-Naphthoquinones in One-Pot Reactions Using CotA-Laccase as Biocatalyst. *Adv. Synth. Catal.* **2020**, *362* (16), 3380–3387. https://doi.org/10.1002/adsc.202000082.

(7) Moser, H.; Lu, Q.; Patten, P. A.; Wang, D.; Kasar, R.; Kaldor, S.; Patterson, B. D. Preparation of Antibacterial Agents. WO 2008/154642, 2008.

(8) Costa, D. C. S.; da S. M. Forezi, L.; Lessa, M. D.; Delarmelina, M.; Matuck, B. V. A.; Freitas, M. C. R.; Ferreira, V. F.; Jackson, J. A. L.; José, J. W.; de C. da Silva, F. A Stereoselective, Base-Free, Palladium-Catalyzed Heck Coupling Between 3-Halo-1,4-Naphthoquinones and Vinyl-1H-1,2,3-Triazoles. *ChemistrySelect* **2022**, 7 (24). https://doi.org/10.1002/slct.202201334.

(9) Liu, Z.; Yin, S.; Zhang, R.; Zhu, W.; Fu, P. High-Efficiency Synthesis of Carbon-Bridged Dimers via Bioinspired Green Dimerization Involving Aldehydes. *ACS*

Sustain. Chem. Eng. **2022**, 10 (1), 655–661. https://doi.org/10.1021/acssuschemeng.1c07635.

(10) Yu, J.; Li, S.; Zeng, X.; Song, J.; Hu, S.; Cheng, S.; Chen, C.; Luo, H.; Pan, W. Design, Synthesis, and Evaluation of Proliferation Inhibitory Activity of Novel L-Shaped Ortho-Quinone Analogs as Anticancer Agents. *Bioorg. Chem*. **2021**, 117 (September), 105383. https://doi.org/10.1016/j.bioorg.2021.105383.