

Supporting Information

Paired electrolysis enables weak Brønsted base-promoted amination of arenes with *N,N*-dialkyl formamides as the amine source

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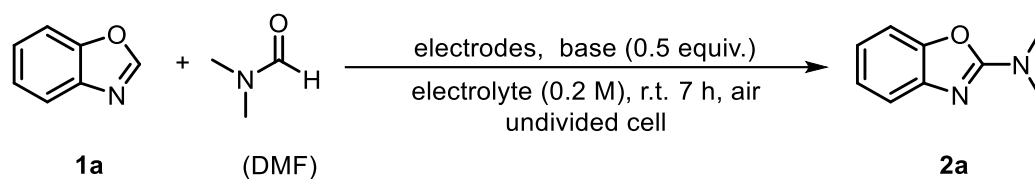
1. General Information

Chemicals were received from commercial sources without further purification or prepared by literature methods. Melting points are uncorrected and recorded on Digital Melting Point Apparatus WRS-1B. ^1H NMR and ^{13}C NMR spectra were measured on a 400 MHz Bruker spectrometer, using CDCl_3 as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, m = multiplet. Chemical shifts were reported in units (ppm) by assigning the residual protonated solvent of CDCl_3 resonance in the ^1H spectrum as 7.26 ppm and CDCl_3 resonance in the ^{13}C spectrum as 77.0 ppm. All coupling constants (J values) were reported in Hertz (Hz). Chemical shifts of common trace ^1H NMR impurities (ppm): H_2O : 1.56, CHCl_3 : 7.26. High-resolution mass spectrometry (HRMS) was performed with a TOF MS instrument with an ESI source. Column chromatography was performed using EM silica gel 60 (300–400 mesh). Reactions were monitored by thin layer chromatography (TLC). Visualization was achieved under a UV lamp (254 nm and 365 nm). Electrolysis experiments were performed using a MESTEK power supply (DP3005B). Cyclic voltammograms were obtained on a CHI 760E potentiostat.

2. Experimental Section

2.1 Optimization of conditions for 2a

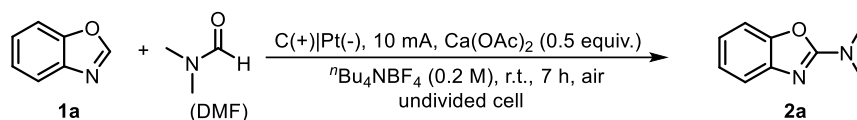
Table S1. Optimization of the reaction conditions for **2a**^a



entry	electrolyte	electrodes	base	Yield(%) ^b
1	ⁿ Bu ₄ NBF ₄	C(+) Pt(-)	Ca(OAc) ₂	86
2	ⁿ Bu ₄ NBF ₄	C(+) Pt(-)	-	n.d.
3	ⁿ Bu ₄ NBF ₄	C(+) Pt(-)	NaOH	47
4	ⁿ Bu ₄ NBF ₄	C(+) Pt(-)	^t BuOK	32
5	ⁿ Bu ₄ NBF ₄	C(+) Pt(-)	NaOEt	36
6	ⁿ Bu ₄ NBF ₄	C(+) Pt(-)	CF ₃ CO ₂ Na	0
7	ⁿ Bu ₄ NBF ₄	C(+) Pt(-)	K ₂ CO ₃	41
8	ⁿ Bu ₄ NBF ₄	C(+) Pt(-)	K ₂ HPO ₄	0
9	ⁿ Bu ₄ NBF ₄	C(+) Pt(-)	LiOAc ^c	68
10	ⁿ Bu ₄ NBF ₄	C(+) Pt(-)	NaOAc ^c	53
11	ⁿ Bu ₄ NBF ₄	C(+) Pt(-)	KOAc ^c	64
12	ⁿ Bu ₄ NBF ₄	C(+) Pt(-)	Mg(OAc) ₂	49
13	ⁿ Bu ₄ NBF ₄	C(+) Pt(-)	Ca(OAc) ^d	32
14	ⁿ Bu ₄ NBF ₄	C(+) Pt(-)	Ca(OAc) ^c	78
15	ⁿ Bu ₄ NCIO ₄	C(+) Pt(-)	Ca(OAc)	n.d.
16	ⁿ Bu ₄ NPF ₄	C(+) Pt(-)	Ca(OAc)	n.d.
17	ⁿ Bu ₄ NI	C(+) Pt(-)	Ca(OAc)	n.d.
18	ⁿ Bu ₄ NHSO ₄	C(+) Pt(-)	Ca(OAc)	n.d.
19	ⁿ Bu ₄ NBF ₄	Pt(+) Pt(-)	Ca(OAc)	73
20	ⁿ Bu ₄ NBF ₄	C(+) C(-)	Ca(OAc)	n.d.
21	ⁿ Bu ₄ NBF ₄	Pt(+) C(-)	Ca(OAc)	n.d.
22	ⁿ Bu ₄ NBF ₄	Cu(+) Pt(-)	Ca(OAc)	n.d.
23	ⁿ Bu ₄ NBF ₄	RVC(+) Pt(-)	Ca(OAc)	n.d.
24	ⁿ Bu ₄ NBF ₄	Ni(+) Pt(-)	Ca(OAc)	n.d.
25	ⁿ Bu ₄ NBF ₄	C(+) Pt(-)	Ca(OAc)	80 ^e
26	ⁿ Bu ₄ NBF ₄	C(+) Pt(-)	Ca(OAc)	n.d. ^f
27	ⁿ Bu ₄ NBF ₄	C(+) Pt(-)	Ca(OAc)	n.d. ^g

^aReaction conditions: **3a** (0.3 mmol), electrodes, 10 mA, base (1.0 equiv.), electrolyte (0.2 M), and DMF (5 mL), in an undivided cell, rt, 2 h, in air, n.d. = no detected. ^bYield of the isolated product **4a**. ^c1.0 equiv. ^d0.25 equiv. ^e15 mA. ^f5 mA. ^gno electricity.

Table S2. Optimization of DMF in different solvents for **2a**^a.



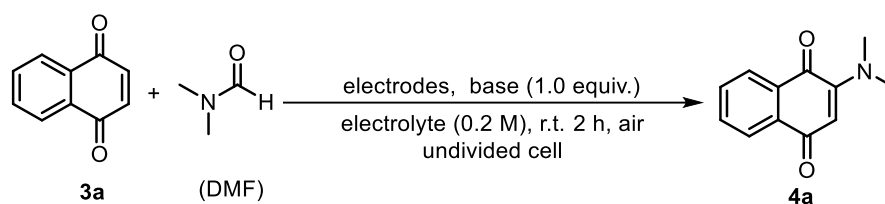
entr	solvents	yield ^b
1	CH_3CN	trace
2	MeOH	n.d.
3	DMSO	trace
4	DMA	trace

^aStandard conditions: **1a** (0.30 mmol), DMF (3 mmol), $\text{C}(+)/\text{Pt}(-)$, 10 mA, $\text{Ca}(\text{OAc})_2$ (0.5 equiv.),

^t Bu_4NBF_4 (0.2 M), solvent (5 mL), in an undivided cell, r.t., 7 h, in air. ^bn.d. = no detected.

2.2 Optimization of conditions for 4a

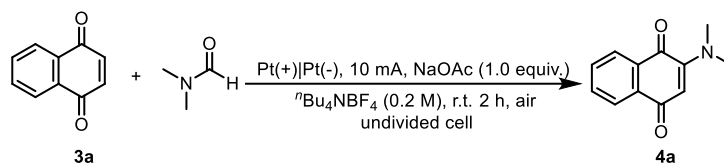
Table S3. Optimization of the reaction conditions for 4a^a



entry	electrolyte	electrodes	base	Yield(%) ^b
1	ⁿ Bu ₄ NBF ₄	Pt(+) Pt(-)	NaOAc	90
2	ⁿ Bu ₄ NBF ₄	Pt(+) Pt(-)	-	n.d.
3	ⁿ Bu ₄ NBF ₄	Pt(+) Pt(-)	NaOH	0
4	ⁿ Bu ₄ NBF ₄	Pt(+) Pt(-)	^t BuOK	0
5	ⁿ Bu ₄ NBF ₄	Pt(+) Pt(-)	NaOEt	0
6	ⁿ Bu ₄ NBF ₄	Pt(+) Pt(-)	CF ₃ CO ₂ Na	61
7	ⁿ Bu ₄ NBF ₄	Pt(+) Pt(-)	K ₂ CO ₃	32
8	ⁿ Bu ₄ NBF ₄	Pt(+) Pt(-)	K ₂ HPO ₄	0
9	ⁿ Bu ₄ NBF ₄	Pt(+) Pt(-)	LiOAc	16
10	ⁿ Bu ₄ NBF ₄	Pt(+) Pt(-)	KOAc	63
11	ⁿ Bu ₄ NBF ₄	Pt(+) Pt(-)	Ca(OAc) ₂ ^c	38
12	ⁿ Bu ₄ NBF ₄	Pt(+) Pt(-)	Mg(OAc) ₂ ^c	44
13	ⁿ Bu ₄ NBF ₄	Pt(+) Pt(-)	NaOAc ^c	45
14	ⁿ Bu ₄ NBF ₄	Pt(+) Pt(-)	NaOAc ^d	74
15	ⁿ Bu ₄ NCIO ₄	Pt(+) Pt(-)	NaOAc	n.d.
16	ⁿ Bu ₄ NPF ₄	Pt(+) Pt(-)	NaOAc	n.d.
17	ⁿ Bu ₄ NI	Pt(+) Pt(-)	NaOAc	n.d.
18	ⁿ Bu ₄ NHSO ₄	Pt(+) Pt(-)	NaOAc	n.d.
19	ⁿ Bu ₄ NBF ₄	C(+) Pt(-)	NaOAc	trace
20	ⁿ Bu ₄ NBF ₄	Ti(+) Pt(-)	NaOAc	n.d.
21	ⁿ Bu ₄ NBF ₄	Ag(+) Pt(-)	NaOAc	n.d.
22	ⁿ Bu ₄ NBF ₄	Cu(+) Pt(-)	NaOAc	trace
23	ⁿ Bu ₄ NBF ₄	RVC(+) Pt(-)	NaOAc	trace
24	ⁿ Bu ₄ NBF ₄	Al(+) Al(-)	NaOAc	72
25	ⁿ Bu ₄ NBF ₄	Pt(+) Pt(-)	NaOAc	68 ^e
26	ⁿ Bu ₄ NBF ₄	Pt(+) Pt(-)	NaOAc	61 ^f
27	ⁿ Bu ₄ NBF ₄	Pt(+) Pt(-)	NaOAc	n.d. ^g

^aReaction conditions: 3a (0.3 mmol), electrodes, 10 mA, base (1.0 equiv.), electrolyte (0.2 M), and DMF (5 mL), in an undivided cell, rt, 2 h, in air, n.d. = no detected. ^bYield of the isolated product 4a. ^c0.5 equiv. ^d2.0 equiv. ^e15 mA. ^f5 mA. ^gno electricity.

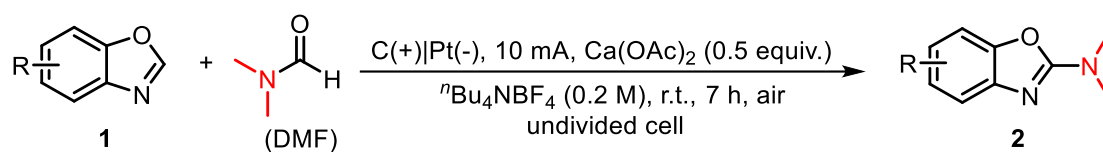
Table S4. Optimization of DMF in different solvents for **4a**^a.



entr	solvents	yield ^b
1	CH ₃ CN	n.d.
2	MeOH	n.d.
3	DMSO	trace
4	DMA	trace

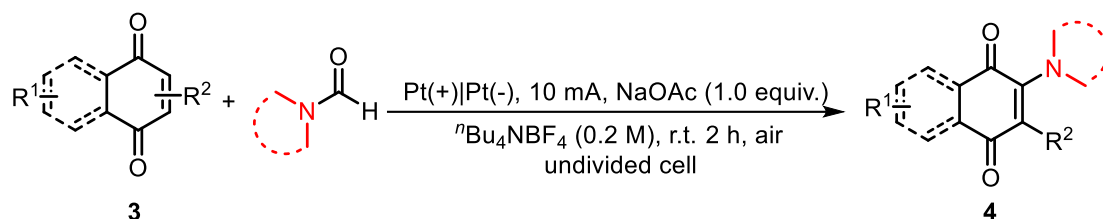
^aStandard conditions: **3a** (0.30 mmol), DMF (3 mmol), Pt(+)/Pt(-), 10 mA, NaOAc (1.0 equiv.), ^tBu₄NBF₄ (0.2 M), and solvent (5 mL), in an undivided cell, r.t., 2 h, in air. ^bn.d. = no detected.

2.3 General procedure for the synthesis of 2

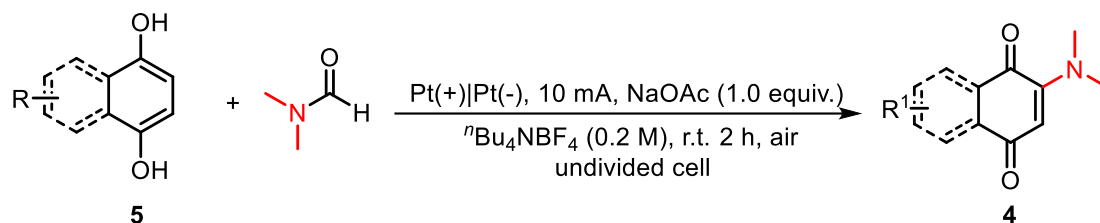


An oven-dried 25 mL three-necked round-bottomed flask with a magnetic stir bar was charged with substrate **1** (0.3 mmol), ⁿBu₄NBF₄ (1.0 mmol, 0.2 M), Ca(OAc)₂ (0.15 mmol, 0.5 equiv.). The flask was equipped with graphite rod as the anode and platinum plate as the cathode (10 mm x 10 mm x 0.1 mm). The electrolysis was carried out at r.t. in DMF (5.0 mL) using a constant current of 10 mA for 7 hours. The reaction mixture was extracted with EtOAc (15 mL × 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes to give the desired products **2**.

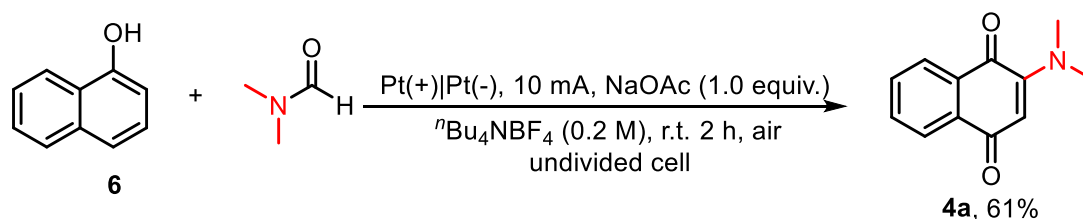
2.4 General procedure for the synthesis of 4



An oven-dried 25 mL three-necked round-bottomed flask with a magnetic stir bar was charged with substrate **3** (0.3 mmol), ⁿBu₄NBF₄ (1.0 mmol, 0.2 M), NaOAc (0.3 mmol, 1.0 equiv.). The flask was equipped with platinum plate as the anode (10 mm x 10 mm x 0.1 mm) and platinum plate as the cathode (10 mm x 10 mm x 0.1 mm). The electrolysis was carried out at r.t. in DMF (5.0 mL) using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL × 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes to give the desired products **4**.

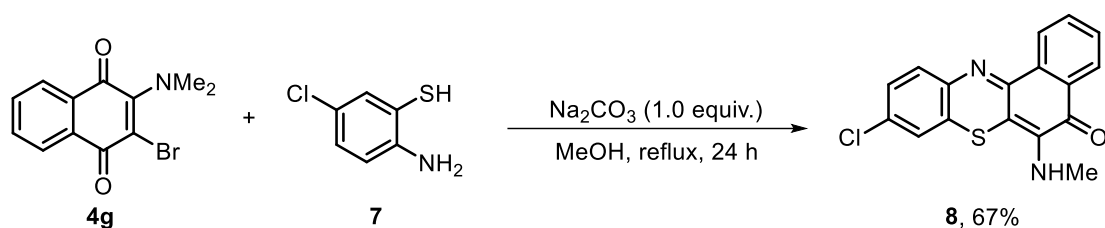


An oven-dried 25 mL three-necked round-bottomed flask with a magnetic stir bar was charged with substrate **5** (0.3 mmol), $^n\text{Bu}_4\text{NBF}_4$ (1.0 mmol, 0.2 M), NaOAc (0.3 mmol, 1.0 equiv.). The flask was equipped with platinum plate as the anode (10 mm x 10 mm x 0.1 mm) and platinum plate as the cathode (10 mm x 10 mm x 0.1 mm). The electrolysis was carried out at r.t. in DMF (5.0 mL) using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes to give the desired products **4**.



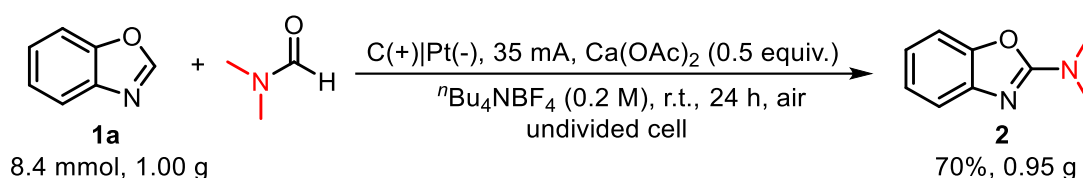
An oven-dried 25 mL three-necked round-bottomed flask with a magnetic stir bar was charged with substrate **6** (0.3 mmol), $^n\text{Bu}_4\text{NBF}_4$ (1.0 mmol, 0.2 M), NaOAc (0.3 mmol, 1.0 equiv.). The flask was equipped with platinum plate as the anode (10 mm x 10 mm x 0.1 mm) and platinum plate as the cathode (10 mm x 10 mm x 0.1 mm). The electrolysis was carried out at r.t. in DMF (5.0 mL) using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes to give the desired products **4a**.

2.5 Procedure for the synthesis of phenothiazinone 8



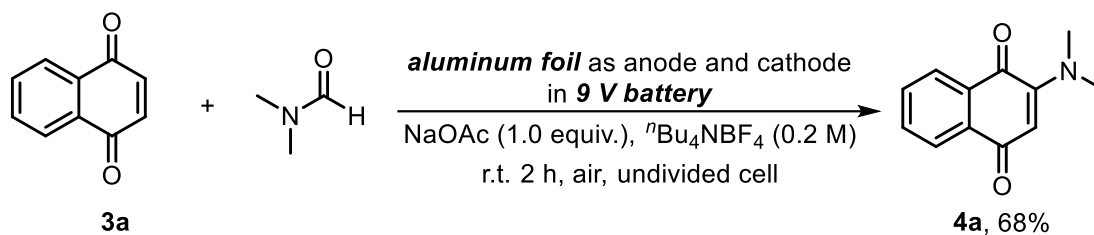
The product **4g** (0.3 mmol), 2-amino-5-chlorobenzenethiol (0.3 mmol) and Na_2CO_3 (0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of MeOH. The reaction was carried out at 65 °C for 24 hours. The organic layers were evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes to afford product **8**.

2.6. Large-scale electrochemical reaction of 1a.



An oven-dried 100 mL flask with a magnetic stir bar was charged with benzo[*d*]oxazole (1.00 g, 8.4 mmol), $^n\text{Bu}_4\text{NBF}_4$ (10.0 mmol, 0.2 M), Ca(OAc)_2 (4.2 mmol, 0.5 equiv.). The flask was equipped with graphite rod as the anode and platinum plate as the cathode (10 mm x 10 mm x 0.1 mm). The electrolysis was carried out at r.t. in DMF (50.0 mL) using a constant current of 35 mA for 24 hours. The reaction mixture was extracted with EtOAc (50 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes to give the desired products **2** (0.95 g, 70%).

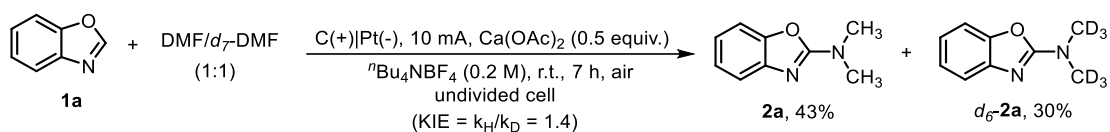
2.7. Electrochemical reaction of 3a using cost-effective and easily accessible instrument.



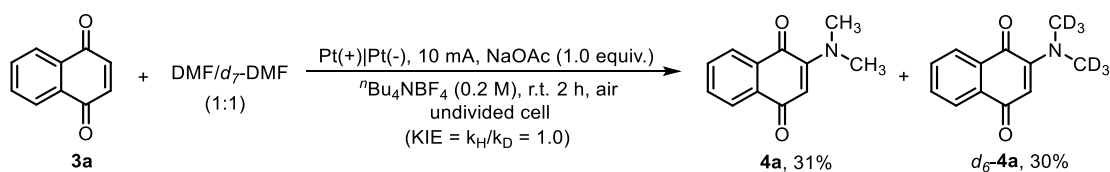
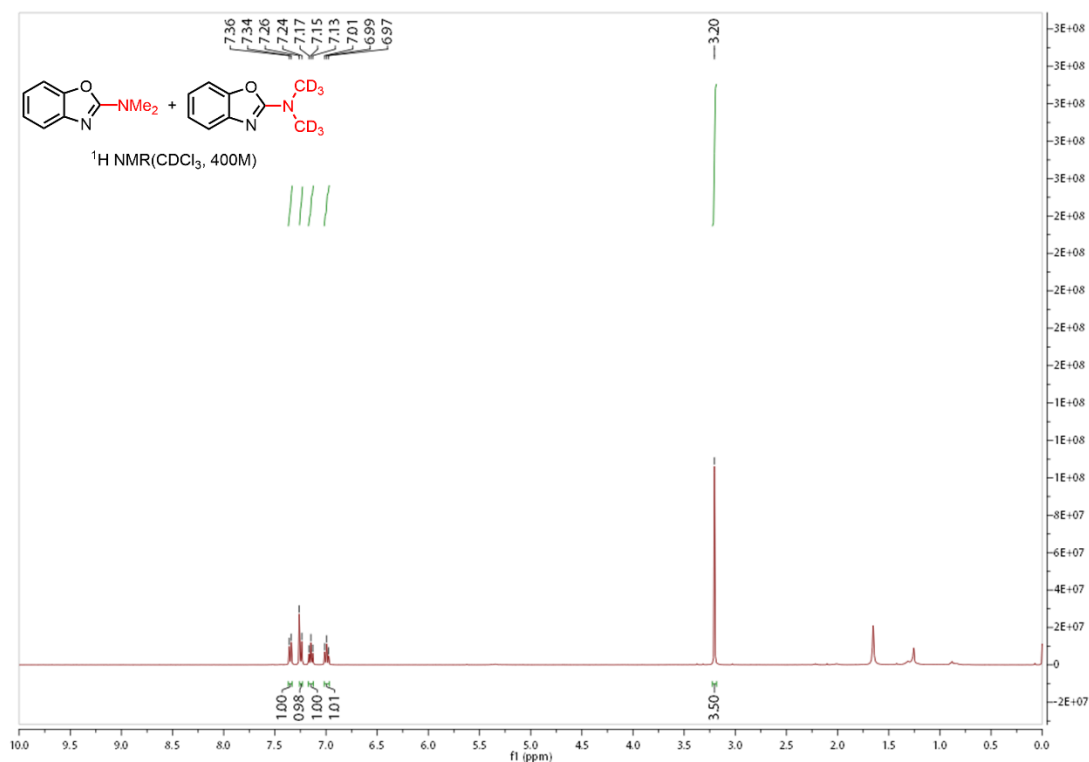
A 25 mL flask with a magnetic stir bar was charged with substrate **3a** (0.3 mmol), $t\text{Bu}_4\text{NBF}_4$ (1.0 mmol, 0.2 M), NaOAc (0.3 mmol, 1.0 equiv.). The flask was equipped with aluminum foil as the anode and aluminum foil as the cathode. The electrolysis was carried out at r.t. in DMF (5.0 mL) using 9V battery as power supply for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes to give the desired products **4a**.

3. Control experiments

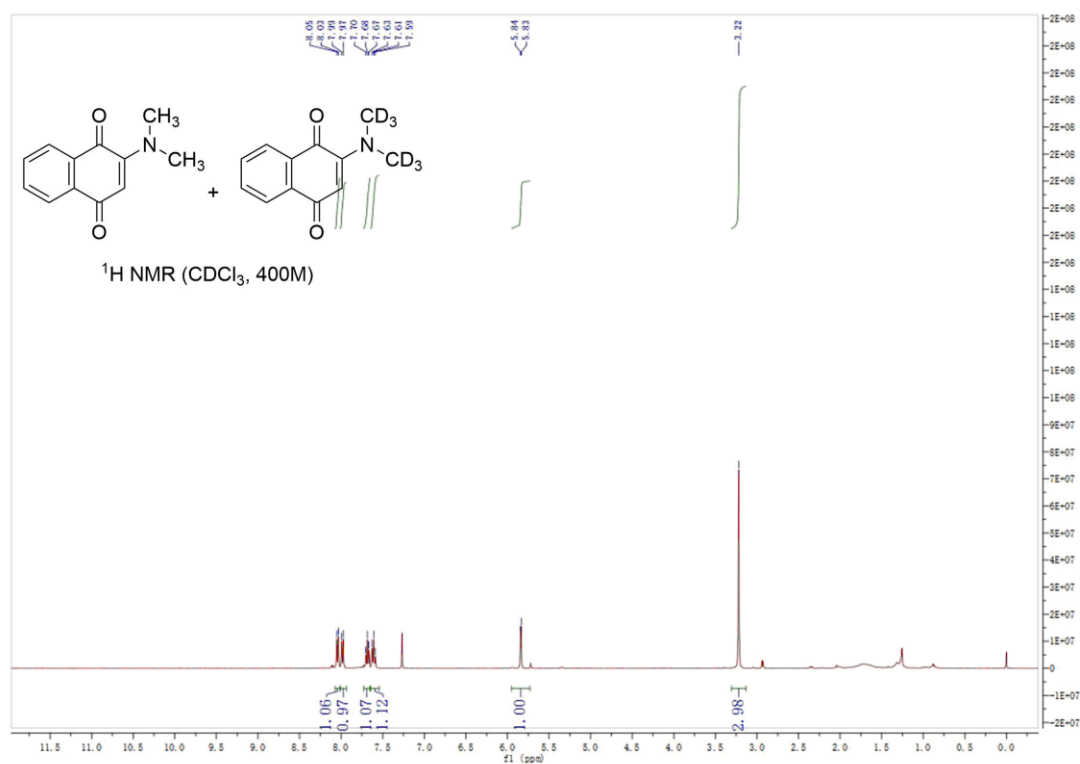
3.1 Kinetic isotope effect study



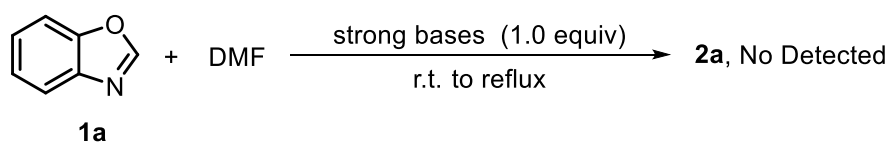
An oven-dried 25 mL three-necked round-bottomed flask with a magnetic stir bar was charged with substrate **1a** (0.3 mmol), $n\text{Bu}_4\text{NBF}_4$ (1.0 mmol, 0.2 M), $\text{Ca}(\text{OAc})_2$ (0.15 mmol, 0.5 equiv.). The flask was equipped with graphite rod as the anode and platinum plate as the cathode (10 mm x 10 mm x 0.1 mm). The electrolysis was carried out at r.t. in DMF (2.5 mL) and d_6 -DMF (2.5 mL) using a constant current of 10 mA for 7 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes to give the desired products **2a** and d_6 -**2a**.



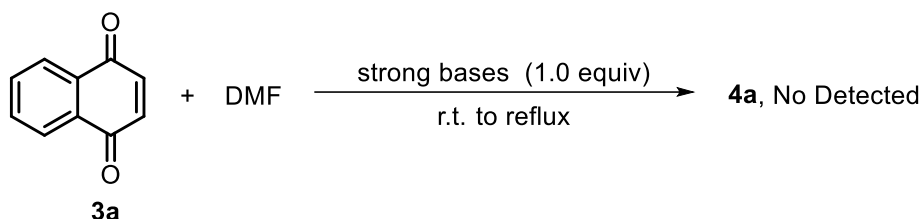
An oven-dried 25 mL three-necked round-bottomed flask with a magnetic stir bar was charged with substrate **3a** (0.3 mmol), ${}^n\text{Bu}_4\text{NBF}_4$ (1.0 mmol, 0.2 M), NaOAc (0.3 mmol, 1.0 equiv.). The flask was equipped with platinum plate as the anode (10 mm x 10 mm x 0.1 mm) and platinum plate as the cathode (10 mm x 10 mm x 0.1 mm). The electrolysis was carried out at r.t. in DMF (2.5 mL) and d_6 -DMF (2.5 mL) using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes to give the desired products **4a** and d_6 -**4a**.



3.2 1a and 3a with DMF on hydrolysis condition

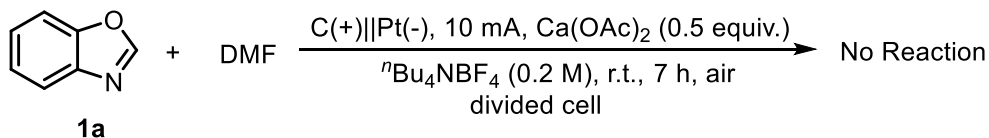


The starting material, benzo[*d*]oxazole (35.7 mg, 0.3 mmol) and strong base (0.3 mmol, 1.0 equiv.), such as KOH, NaOH and ^tBuOK, were dissolved in 5 mL of DMF. The reaction mixture was stirred gently in an oil bath at room temperature or 153 °C for 12 hours. Monitoring reaction progress via thin-layer chromatography (TLC).

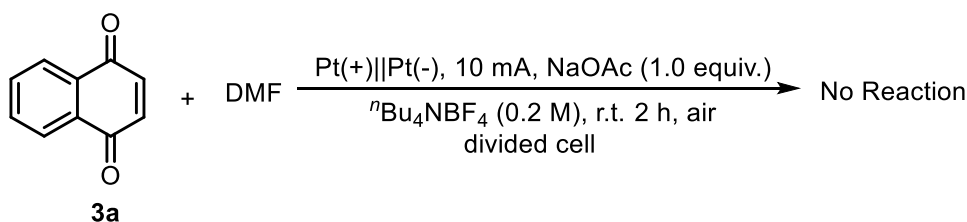


The starting material, naphthalene-1,4-dione (47.5 mg, 0.3 mmol) and strong base (0.3 mmol, 1.0 equiv.), such as KOH, NaOH and ^tBuOK, were dissolved in 5 mL of DMF. The reaction mixture was stirred gently in an oil bath at room temperature or 153 °C for 12 hours. Monitoring reaction progress via thin-layer chromatography (TLC).

3.3 Divided cell experiments

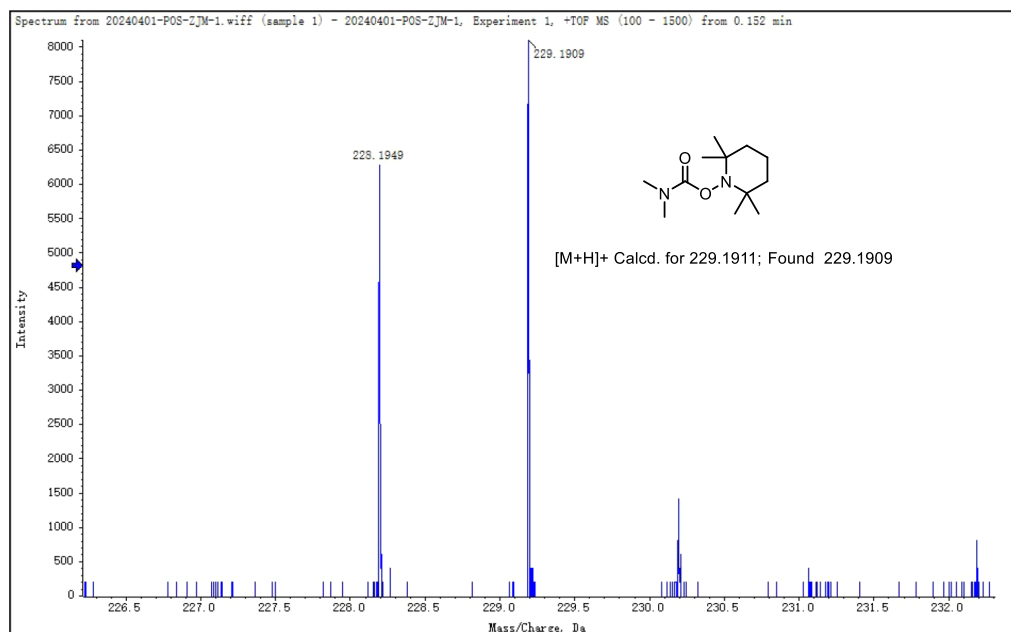
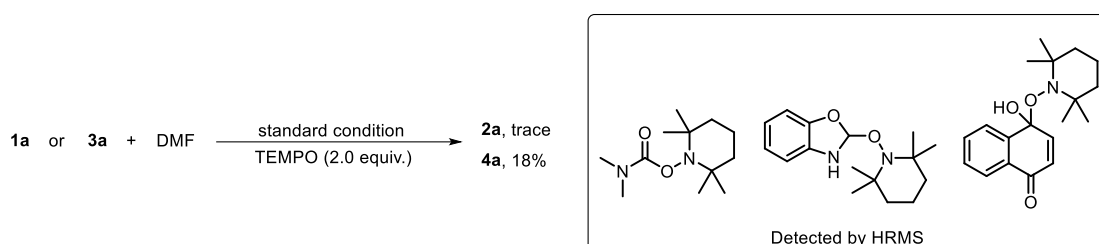


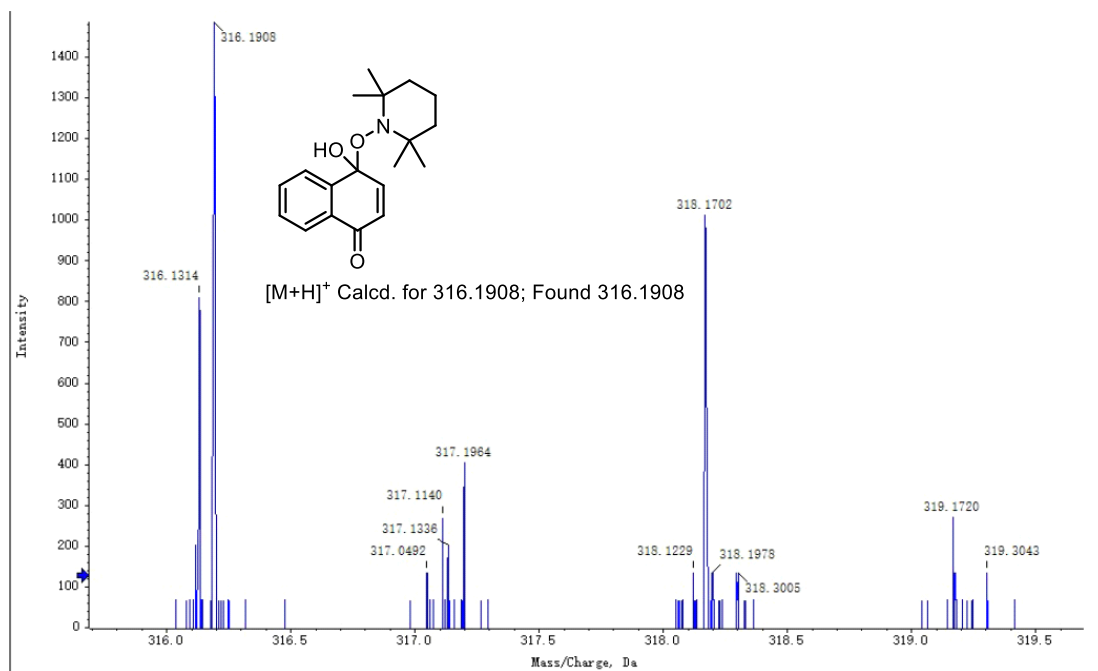
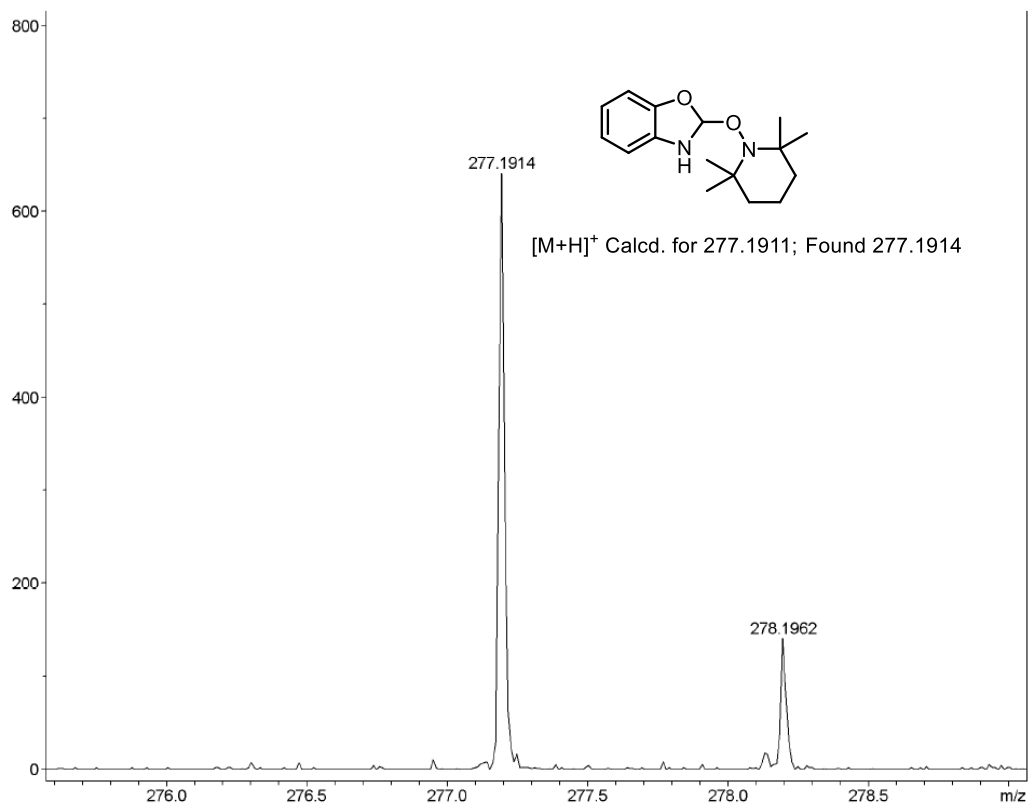
The electrolyses were carried out in a concentric cell with two compartments separated by an anionic membrane and equipped with amagnetic stirrer. The starting material, benzo[*d*]oxazole **1a** (0.3 mmol), ⁿBu₄NBF₄ (2.0 mmol, 0.2 M), Ca(OAc)₂ (0.15 mmol, 0.5 equiv.) were dissolved in 10 mL of DMF using a constant current of 10 mA for 7 hours. The flask was equipped with graphite rod as the anode and platinum plate as the cathode (10 mm x 10 mm x 0.1 mm). Monitoring reaction progress via thin-layer chromatography (TLC).



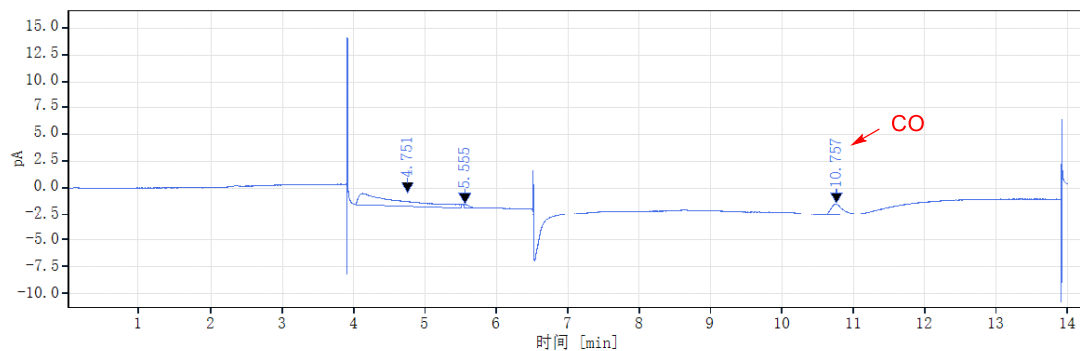
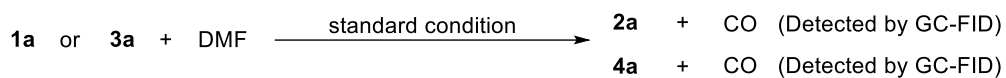
The electrolyses were carried out in a concentric cell with two compartments separated by an anionic membrane and equipped with amagnetic stirrer. The starting material, naphthalene-1,4-dione **3a** (0.3 mmol), ${}^n\text{Bu}_4\text{NBF}_4$ (2.0 mmol, 0.2 M), NaOAc (0.3 mmol, 1.0 equiv.) were dissolved in 10 mL of DMF using a constant current of 10 mA for 2 hours. The flask was equipped with platinum plate as the anode (10 mm x 10 mm x 0.1 mm) and platinum plate as the cathode (10 mm x 10 mm x 0.1 mm). Monitoring reaction progress via thin-layer chromatography (TLC).

3.4 Reaction intermediate investigation

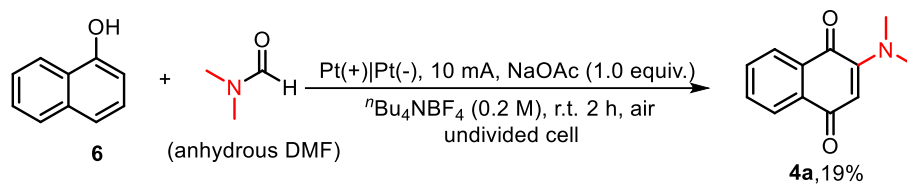




3.5 Detect CO by GC-FID.



3.6 Amination of naphthalen-1-ol with anhydrous DMF



The anhydrous DMF as solvent led to poor reaction performance, delivering product **4a** in 19% yield.

4. Cyclic voltammetry (CV) experiments.

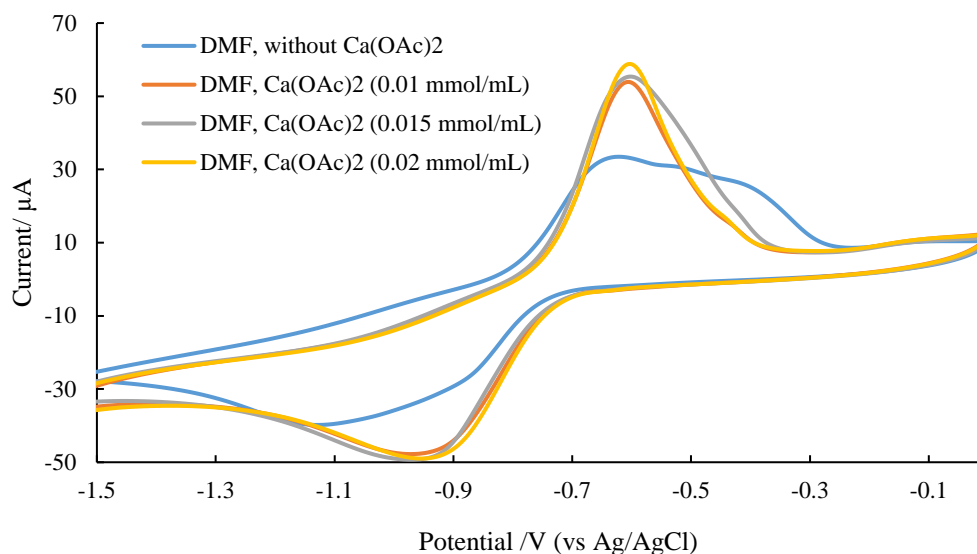


Figure S1. CV tests of DMF with different amount of Ca(OAc)₂.

The cyclic voltammograms were recorded in an electrolyte of ⁿBu₄NBF₄ (0.2 M) in DMF using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and a SCE reference electrode. The scan rate is 100 mV/s. (blue line) DMF, ⁿBu₄NBF₄ (0.2 M); (orange line) DMF, ⁿBu₄NBF₄ (0.2 M), Ca(OAc)₂ (0.01 M); (gray line) DMF, ⁿBu₄NBF₄ (0.2 M), Ca(OAc)₂ (0.015 M); (yellow line) DMF, ⁿBu₄NBF₄ (0.2 M), Ca(OAc)₂ (0.02 M).

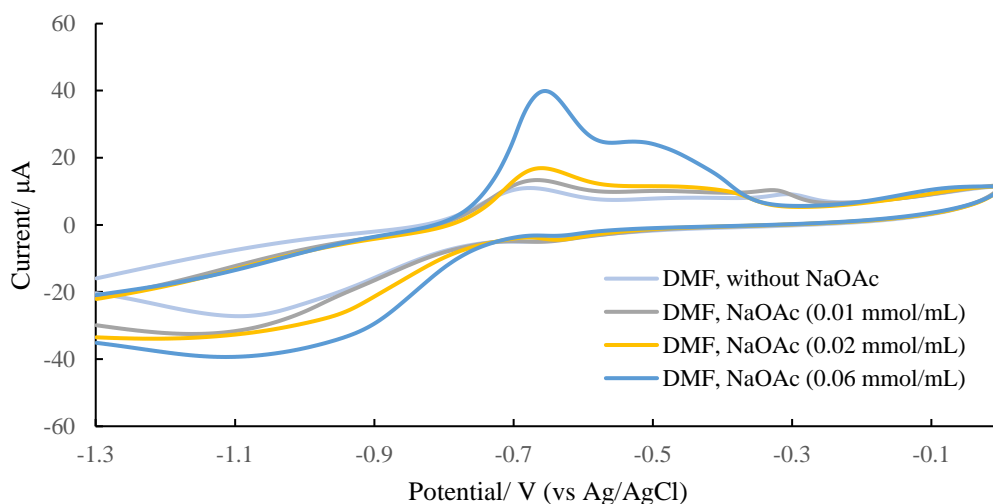


Figure S2. CV tests of DMF with different amount of NaOAc.

The cyclic voltammograms were recorded in an electrolyte of ⁿBu₄NBF₄ (0.2 M) in DMF using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary

electrode and a SCE reference electrode. The scan rate is 100 mV/s. (bluish line) DMF, $n\text{Bu}_4\text{NBF}_4$ (0.2 M); (gray line) DMF, $n\text{Bu}_4\text{NBF}_4$ (0.2 M), NaOAc (0.01 M); (yellow line) DMF, $n\text{Bu}_4\text{NBF}_4$ (0.2 M), NaOAc (0.02 M); (blue line) DMF, $n\text{Bu}_4\text{NBF}_4$ (0.2 M), NaOAc (0.06 M).

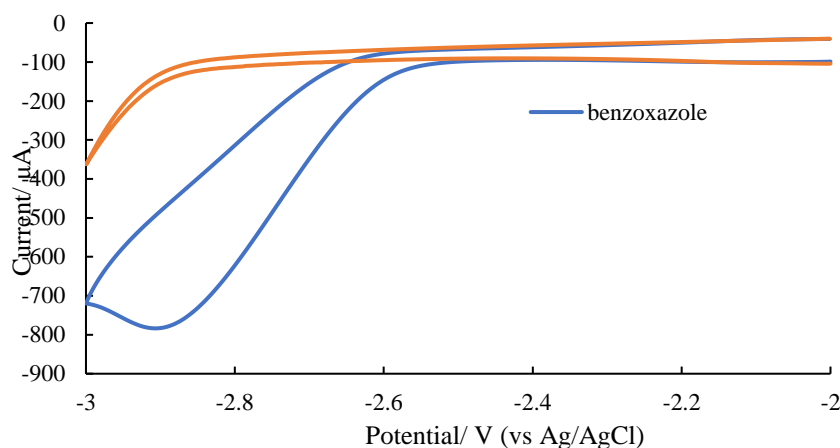


Figure S3. Reduction potential of benzoxazole.

The cyclic voltammograms were recorded in an electrolyte of $n\text{Bu}_4\text{NBF}_4$ (0.2 M) in acetonitrile using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and a SCE reference electrode. The scan rate is 100 mV/s. (organe line) acetonitrile, $n\text{Bu}_4\text{NBF}_4$ (0.2 M); (blue line) acetonitrile, $n\text{Bu}_4\text{NBF}_4$ (0.2 M), benzoxazole (0.006 M).

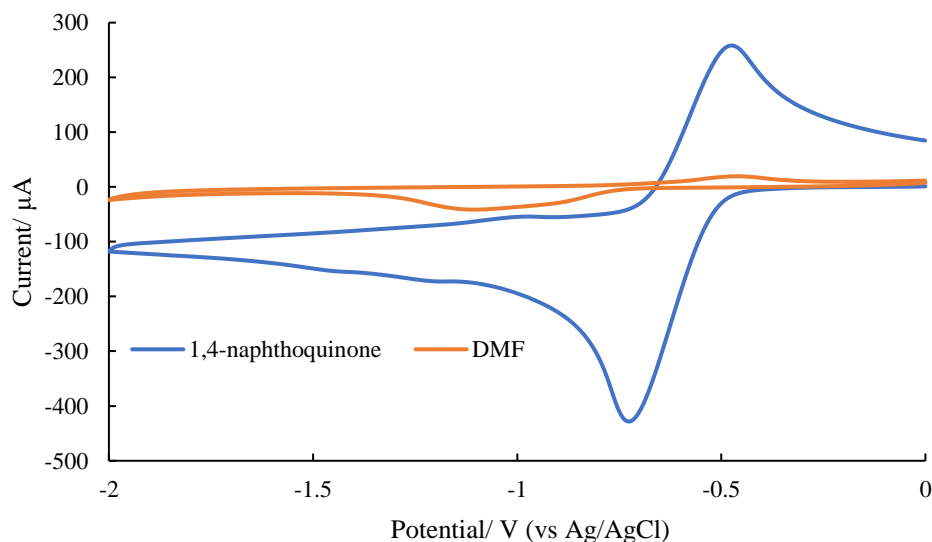


Figure S4. Reduction potential of 1,4-naphthoquinone.

The cyclic voltammograms were recorded in an electrolyte of $n\text{Bu}_4\text{NBF}_4$ (0.2 M) in DMF using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and a SCE reference electrode. The scan rate is 100 mV/s. (organe line) DMF,

ⁿBu₄NBF₄ (0.2 M); (blue line) DMF, ⁿBu₄NBF₄ (0.2 M), 1,4-naphthoquinone (0.006 M).

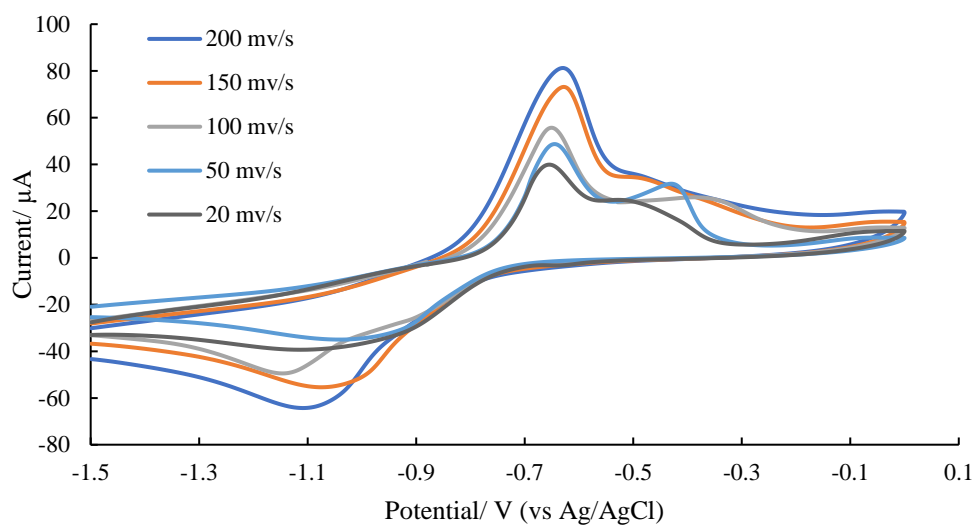


Figure S5. CV tests with different scan rates of DMF.

The cyclic voltammograms were recorded in an electrolyte of ⁿBu₄NBF₄ (0.2 M) in DMF using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and a SCE reference electrode. (purple line) 20 mV/s; (bluish line) 50 mV/s; (gray line) 100 mV/s; (orange line) 150 mV/s; (blue line) 200 mV/s.

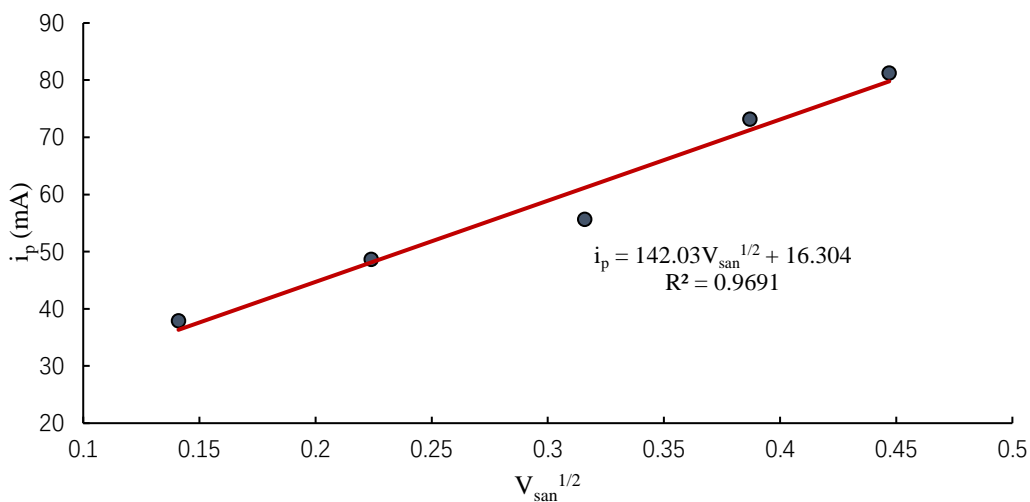
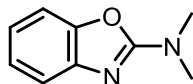


Figure S6. linear fit analysis.

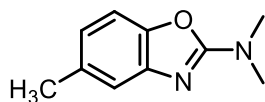
5. Analytical data for products



N,N-dimethylbenzo[*d*]oxazol-2-amine (**2a**)

The starting material, benzo[*d*]oxazole (35.7 mg, 0.3 mmol), $n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), $\text{Ca}(\text{OAc})_2$ (23.7 mg, 0.15 mmol, 0.5 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with graphite rod as the anode and platinum plate as the cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 7 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (10:1) to afford 41.8 mg yellow solid product **2a** in 86% yield.

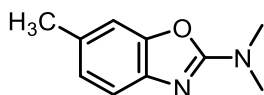
m.p. 73.3-81.8 °C. ^1H NMR (400MHz, CDCl_3) δ 7.35 (d, $J=7.8$ Hz, 1H), 7.24 (d, $J=9.6$ Hz, 1H), 7.13-7.17 (m, 1H), 6.98-7.02 (m, 1H), 3.20 (s, 6H). ^{13}C NMR (100MHz, CDCl_3) δ 163.1, 149.1, 143.6, 123.9, 120.2, 116.0, 108.6, 37.7. The ^1H and ^{13}C NMR data match the reported values^[1].



N,N,5-trimethylbenzo[*d*]oxazol-2-amine (**2b**)

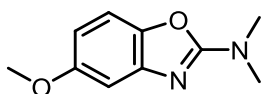
The starting material, 5-methylbenzo[*d*]oxazole (39.9 mg, 0.3 mmol), $n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), $\text{Ca}(\text{OAc})_2$ (23.7 mg, 0.15 mmol, 0.5 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with graphite rod as the anode and platinum plate as the cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 7 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (10:1) to afford 39.1 mg yellow liquid product **2b** in 74% yield.

^1H NMR (400MHz, CDCl_3) δ 7.15 (s, 1H), 7.11 (d, $J=8.1$ Hz, 1H), 6.79 (d, $J=8.0$ Hz, 1H), 3.19 (s, 6H), 2.38 (s, 3H). ^{13}C NMR (100MHz, CDCl_3) δ 163.3, 147.2, 143.7, 133.5, 120.8, 116.4, 107.9, 37.7, 21.5. The ^1H and ^{13}C NMR data match the reported values^[2].



***N,N,6*-trimethylbenzo[*d*]oxazol-2-amine (**2c**)**

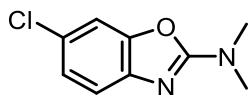
The starting material, 6-methylbenzo[*d*]oxazole (39.9 mg, 0.3 mmol), ⁿBu₄NBF₄ (322.4 mg, 1.0 mmol), Ca(OAc)₂ (23.7 mg, 0.15 mmol, 0.5 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with graphite rod as the anode and platinum plate as the cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 7 hours. The reaction mixture was extracted with EtOAc (15 mL × 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (10:1) to afford 38.1 mg brown solid product **2c** in 72% yield. m.p. 45.9-54.5 °C. ¹H NMR (400MHz, CDCl₃) δ 7.22 (d, *J*=7.9 Hz, 1H), 7.07 (s, 1H), 6.96 (d, *J*=7.9 Hz, 1H), 3.18 (s, 6H), 2.39 (s, 3H). ¹³C NMR (100MHz, CDCl₃) δ 162.9, 149.3, 141.2, 130.2, 124.6, 115.4, 109.2, 37.7, 21.4. The ¹H and ¹³C NMR data match the reported values^[3].



5-methoxy-*N,N*-dimethylbenzo[*d*]oxazol-2-amine (2d**)**

The starting material, 5-methoxybenzo[*d*]oxazole (44.7 mg, 0.3 mmol), ⁿBu₄NBF₄ (322.4 mg, 1.0 mmol), Ca(OAc)₂ (23.7 mg, 0.15 mmol, 0.5 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with graphite rod as the anode and platinum plate as the cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 7 hours. The reaction mixture was extracted with EtOAc (15 mL × 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (10:1) to afford 36.9 mg yellow liquid product **2d** in 64% yield.

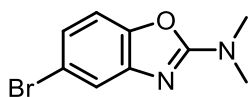
¹H NMR (400MHz, CDCl₃) δ 7.11 (d, *J*=8.6 Hz, 1H), 6.92 (d, *J*=2.5 Hz, 1H), 6.56 (dd, *J*₁=8.7 Hz, *J*₂=2.6 Hz, 1H), 3.80 (s, 3H), 3.19 (s, 6H). ¹³C NMR (100MHz, CDCl₃) δ 163.8, 157.0, 144.5, 143.6, 108.4, 106.6, 101.2, 55.9, 37.7. The ¹H and ¹³C NMR data match the reported values^[1].



6-chloro-*N,N*-dimethylbenzo[*d*]oxazol-2-amine (2e)

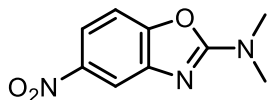
The starting material, 6-chlorobenzo[*d*]oxazole (46.1 mg, 0.3 mmol), $n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), $\text{Ca}(\text{OAc})_2$ (23.7 mg, 0.15 mmol, 0.5 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with graphite rod as the anode and platinum plate as the cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 7 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (10:1) to afford 43.6 mg yellow solid product **2e** in 74% yield.

m.p. 71.3-78.9 °C. ^1H NMR (400MHz, CDCl_3) δ 7.29(d, $J=2.0$ Hz, 1H), 7.13 (d, $J=8.4$ Hz, 1H), 6.95 (dd, $J_1=8.4$ Hz, $J_2=2.0$ Hz, 1H), 3.20 (s, 6H). ^{13}C NMR (100MHz, CDCl_3) δ 163.8, 147.7, 144.9, 129.2, 120.0, 116.1, 109.1, 37.7. The ^1H and ^{13}C NMR data match the reported values^[4].



5-bromo-*N,N*-dimethylbenzo[*d*]oxazol-2-amine (2f)

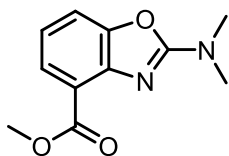
The starting material, 5-bromobenzo[*d*]oxazole (59.4 mg, 0.3 mmol), $n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), $\text{Ca}(\text{OAc})_2$ (23.7 mg, 0.15 mmol, 0.5 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with graphite rod as the anode and platinum plate as the cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 7 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (10:1) to afford 39.8 mg red liquid product **2f** in 55% yield. ^1H NMR (400MHz, CDCl_3) δ 7.44 (s, 1H), 7.09 (s, 2H), 3.19 (s, 6H). ^{13}C NMR (100MHz, CDCl_3) δ 163.5, 148.1, 145.4, 122.7, 118.9, 116.5, 109.6, 37.6. The ^1H and ^{13}C NMR data match the reported values^[5].



***N,N*-dimethyl-5-nitrobenzo[*d*]oxazol-2-amine (2g)**

The starting material, 5-nitrobenzo[*d*]oxazole (49.2 mg, 0.3 mmol), ⁿBu₄NBF₄ (322.4 mg, 1.0 mmol), Ca(OAc)₂ (23.7 mg, 0.15 mmol, 0.5 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with graphite rod as the anode and platinum plate as the cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 7 hours. The reaction mixture was extracted with EtOAc (15 mL × 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (10:1) to afford 46.6 mg yellow solid product **2g** in 75% yield.

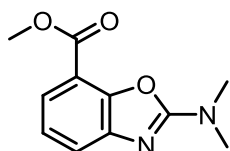
m.p. 160.1-166.3 °C. ¹H NMR (400MHz, CDCl₃) δ 8.15 (d, *J* = 2.2 Hz, 1H), 7.98 (d, *J*₁ = 8.7 Hz, *J*₂ = 2.2 Hz 1H), 7.30 (d, *J*=8.7 Hz, 1H), 3.25 (s, 6H). ¹³C NMR (100MHz, CDCl₃) δ 164.5, 153.0, 145.2, 144.6, 116.8, 111.5, 108.2, 37.7. The ¹H and ¹³C NMR data match the reported values^[1].



methyl 2-(dimethylamino)benzo[*d*]oxazole-4-carboxylate (2h)

The starting material, methyl benzo[*d*]oxazole-4-carboxylate (53.2 mg, 0.3 mmol), ⁿBu₄NBF₄ (322.4 mg, 1.0 mmol), Ca(OAc)₂ (23.7 mg, 0.15 mmol, 0.5 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with graphite rod as the anode and platinum plate as the cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 7 hours. The reaction mixture was extracted with EtOAc (15 mL × 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (10:1) to afford 42.9 mg brown solid product **2h** in 65% yield.

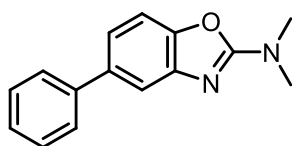
m.p. 85.7-94.1 °C. ¹H NMR (400MHz, CDCl₃) δ 7.81 (d, *J*=8.0 Hz, 1H), 7.38 (d, *J*=7.8 Hz, 1H), 7.01 (dd, *J*₁=8.0 Hz, *J*₂=7.9 Hz, 1H), 3.98 (s, 3H), 3.27 (s, 6H). ¹³C NMR (100MHz, CDCl₃) δ 166.3, 164.3, 150.0, 144.6, 126.0, 119.2, 117.5, 112.3, 52.1, 37.8. HRMS (ESI) *m/z*: [M+H]⁺ Calcd. for C₁₁H₁₂N₂O₃ 221.0921; Found 221.0918.



methyl 2-(dimethylamino)benzo[d]oxazole-7-carboxylate (2i)

The starting material, methyl benzo[d]oxazole-7-carboxylate (53.2 mg, 0.3 mmol), ${}^n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), $\text{Ca}(\text{OAc})_2$ (23.7 mg, 0.15 mmol, 0.5 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with graphite rod as the anode and platinum plate as the cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 7 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (10:1) to afford 47.6 mg brown solid product **2i** in 72% yield.

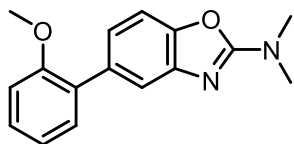
m.p. 102.8-108.1 °C. ${}^1\text{H}$ NMR (400MHz, CDCl_3) δ 7.59 (d, $J=7.9$, 1H), 7.51 (d, $J=7.8$, 1H), 7.20 (dd, $J_1=7.9$ Hz, $J_2=7.8$ Hz, 1H), 3.97 (s, 3H), 3.26 (s, 6H). ${}^{13}\text{C}$ NMR (100MHz, CDCl_3) δ 165.1, 163.6, 148.3, 145.0, 123.6, 121.8, 120.3, 113.0, 52.1, 37.7. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_3$ 221.0921; Found 221.0918.



***N,N*-dimethyl-5-phenylbenzo[d]oxazol-2-amine (2j)**

The starting material, 5-phenylbenzo[d]oxazole (58.6 mg, 0.3 mmol), ${}^n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), $\text{Ca}(\text{OAc})_2$ (23.7 mg, 0.15 mmol, 0.5 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with graphite rod as the anode and platinum plate as the cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 7 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (10:1) to afford 20.7 mg yellow solid product **2j** in 29% yield.

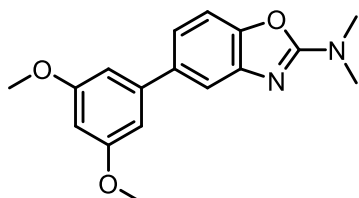
m.p. 113.6-118.9 °C. ${}^1\text{H}$ NMR (400 MHz, CDCl_3) δ 7.60-7.57 (m, 3H), 7.45-7.41 (m, 2H), 7.34-7.28 (m, 2H), 7.22 (dd, $J_1=8.2$ Hz, $J_2=1.6$ Hz, 1H), 3.23 (s, 6H). ${}^{13}\text{C}$ NMR (100 MHz, CDCl_3) δ 163.5, 148.7, 144.2, 141.7, 137.7, 128.7, 127.3, 126.8, 119.6, 114.7, 108.5, 37.7. The ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR data match the reported values^[2].



5-(2-methoxyphenyl)-*N,N*-dimethylbenzo[*d*]oxazol-2-amine (**2k**)

The starting material, 5-(3-methoxyphenyl)benzo[*d*]oxazole (67.6 mg, 0.3 mmol), ${}^n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), $\text{Ca}(\text{OAc})_2$ (23.7 mg, 0.15 mmol, 0.5 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with graphite rod as the anode and platinum plate as the cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 7 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (10:1) to afford 20.1 mg brown solid product **2k** in 25% yield.

m.p. 120.7-128.3 °C. ${}^1\text{H}$ NMR (400MHz, CDCl_3) δ 7.54 (s, 1H), 7.34-7.27 (m, 3H), 7.15 (d, $J = 6.5$ Hz, 1H), 7.04-6.97 (m, 2H), 3.80 (s, 3H), 3.21 (s, 6H). ${}^{13}\text{C}$ NMR (100MHz, CDCl_3) δ 163.3, 156.4, 148.3, 143.3, 134.4, 131.1, 131.1, 128.3, 121.9, 120.8, 117.4, 111.2, 108.0, 55.5, 37.7. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$ 269.1285; Found 269.1288.

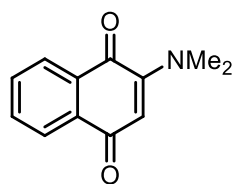


5-(3,5-dimethoxyphenyl)-*N,N*-dimethylbenzo[*d*]oxazol-2-amine (**2l**)

The starting material, 5-(3,5-dimethoxyphenyl)benzo[*d*]oxazole (76.6 mg, 0.3 mmol), ${}^n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), $\text{Ca}(\text{OAc})_2$ (23.7 mg, 0.15 mmol, 0.5 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with graphite rod as the anode and platinum plate as the cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 7 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (10:1) to afford 22.4 mg brown liquid product **2l** in 25% yield.

${}^1\text{H}$ NMR (400MHz, CDCl_3) δ 7.56 (s, 1H), 7.27 (d, $J = 9.7$ Hz, 1H), 7.21 (d, $J = 8.2$ Hz, 1H), 6.74 (s, 1H), 6.45 (s, 1H), 3.84 (s, 6H), 3.22 (s, 6H). ${}^{13}\text{C}$ NMR (100 MHz, CDCl_3) δ 163.5, 160.9, 148.9, 144.1, 143.9, 137.6, 119.6, 114.7, 108.5, 105.5, 99.0,

55.4, 37.7. HRMS (ESI) m/z : $[M+H]^+$ Calcd. for $C_{17}H_{18}N_2O_3$ 299.1391; Found 299.1390.



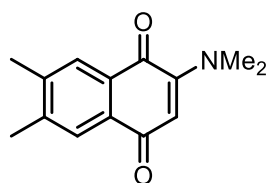
2-(dimethylamino)naphthalene-1,4-dione (**4a**)

The starting material, naphthalene-1,4-dione (47.5 mg, 0.3 mmol), ${}^n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (2:1) to afford 54.3 mg red solid product **4a** in 90% yield.

The starting material, naphthalene-1,4-diol (48.1 mg, 0.3 mmol), ${}^n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (2:1) to afford 45.9 mg red solid product **4a** in 76% yield.

The starting material, naphthalen-1-ol (43.2 mg, 0.3 mmol), ${}^n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (2:1) to afford 36.8 mg red solid product **4a** in 61% yield.

m.p. 102-108 °C. ${}^1\text{H}$ NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 7.5$ Hz, 1H), 7.99 (d, $J = 7.5$ Hz, 1H), 7.69 (dd, $J_1 = 11.6$ Hz, $J_2 = 4.2$ Hz, 1H), 7.62 (dd, $J_1 = 10.8$ Hz, $J_2 = 4.2$ Hz, 1H), 5.85 (s, 1H), 3.22 (s, 6H). ${}^{13}\text{C}$ NMR (100 MHz, CDCl_3) δ 183.4, 182.7, 152.4, 133.8, 132.7, 132.4, 131.9, 126.4, 125.3, 106.8, 42.5. The ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR data match the reported values^[6].

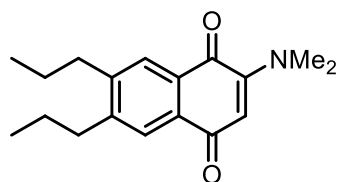


2-(dimethylamino)-6,7-dimethylnaphthalene-1,4-dione (**4b**)

The starting material, 6,7-dimethylnaphthalene-1,4-dione (55.8 mg, 0.3 mmol), $n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (2:1) to afford 44.7 mg red solid product **4b** in 65% yield.

The starting material, 6,7-dimethylnaphthalene-1,4-diol (56.4 mg, 0.3 mmol), $n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (2:1) to afford 31.0 mg red solid product **4b** in 45% yield.

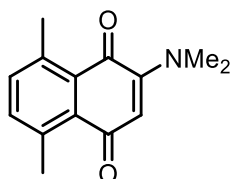
m.p. 153-156 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.77 (s, 1H), 7.71 (s, 1H), 5.76 (s, 1H), 3.19 (s, 6H), 2.36 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 183.6, 183.3, 152.6, 143.6, 141.3, 130.7, 130.4, 127.5, 126.4, 106.9, 42.5, 20.1, 19.9. HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{14}\text{H}_{15}\text{NO}_2$ 230.1176; Found 230.1173.



2-(dimethylamino)-6,7-dipropylnaphthalene-1,4-dione (**4c**)

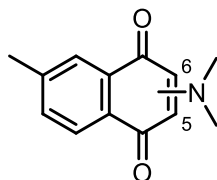
The starting material, 6,7-dipropylnaphthalene-1,4-dione (72.6 mg, 0.3 mmol), $n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected

organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (2:1) to afford 29.9 mg red solid product **4c** in 35% yield. m.p. 78-80 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (s, 1H), 7.76 (s, 1H), 5.79 (s, 1H), 3.21 (s, 6H), 2.72-2.66 (m, 4H), 1.72-1.62 (m, 4H), 1.04-0.99 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 183.6, 183.3, 152.7, 147.5, 145.1, 130.5, 130.3, 127.2, 126.1, 106.9, 42.5, 34.9, 34.6, 23.8, 14.1, 14.1. HRMS (ESI) m/z: [M+H]⁺ Calcd. for C₁₈H₂₃NO₂ 286.1802; Found 286.1805.



2-(dimethylamino)-5,8-dimethylnaphthalene-1,4-dione (**4d**)

The starting material, 5,8-dimethylnaphthalene-1,4-dione (55.8 mg, 0.3 mmol), ⁿBu₄NBF₄ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL × 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (2:1) to afford 26.1 mg red solid product **4d** in 38% yield. m.p. 86-91 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.23 (m, 2H), 5.66 (s, 1H), 3.10 (s, 6H), 2.70 (s, 3H), 2.58 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 186.5, 185.9, 154.4, 137.8, 137.6, 136.9, 134.8, 132.7, 131.4, 106.4, 41.4, 22.8, 22.1. HRMS (ESI) m/z: [M+H]⁺ Calcd. for C₁₄H₁₅NO₂ 230.1176; Found 230.1175.

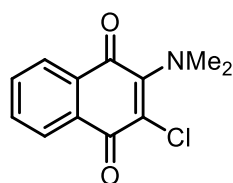


2-(dimethylamino)-7-methylnaphthalene-1,4-dione and 2-(dimethylamino)-6-methylnaphthalene-1,4-dione (**4e**)

The starting material, 6-methylnaphthalene-1,4-dione (51.6 mg, 0.3 mmol), ⁿBu₄NBF₄ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The

reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (2:1) to afford 43.9 mg orange solid product **4e** in 68% yield (isomeric mixture of C6/C5 = 1:1).

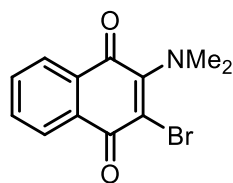
m.p. 85-91 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.93-7.86 (m, 1H), 7.83-7.76 (m, 1H), 7.48-7.38 (m, 1H), 5.79 (s, 1H), 3.20 (s, 6H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 183.8, 183.3, 183.0, 182.9, 152.5, 145.0, 142.6, 134.5, 132.7, 132.6, 132.4, 130.5, 130.2, 126.8, 126.7, 125.8, 125.5, 107.0, 106.8, 42.5, 42.4, 21.8, 21.5. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{13}\text{H}_{13}\text{NO}_2$ 216.1020; Found 216.1018.



2-chloro-3-(dimethylamino)naphthalene-1,4-dione (**4f**)

The starting material, 2,3-dichloronaphthalene-1,4-dione (68.1 mg, 0.3 mmol), $^n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (10:1) to afford 27.6 mg red solid product **4f** in 39% yield.

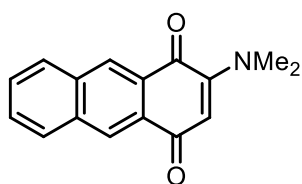
m.p. 73-75 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, $J = 7.7$ Hz, 1H), 8.00 (d, $J = 7.5$ Hz, 1H), 7.71-7.63 (m, 2H), 3.25 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 182.2, 177.9, 151.0, 134.0, 132.8, 131.7, 131.4, 126.8, 126.4, 120.2, 44.4. The ^1H and ^{13}C NMR data match the reported values^[7].



2-bromo-3-(dimethylamino)naphthalene-1,4-dione (**4g**)

The starting material, 2,3-dibromonaphthalene-1,4-dione (94.8 mg, 0.3 mmol), $^n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with platinum plates as the anode

and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (10:1) to afford 39.5 mg red solid product **4g** in 47% yield. m.p. 59-63 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.09 (dd, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 1H), 7.97 (dd, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 1H), 7.69-7.61 (m, 2H), 3.25 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 181.8, 177.9, 153.5, 133.9, 132.7, 131.3, 131.2, 126.7, 126.6, 112.9, 44.7. The ^1H and ^{13}C NMR data match the reported values^[8].

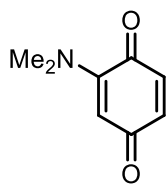


2-(dimethylamino)anthracene-1,4-dione (**4h**)

The starting material, anthracene-1,4-dione (62.5 mg, 0.3 mmol), $^t\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (2:1) to afford 55.8 mg red solid product **4h** in 74% yield.

The starting material, anthracene-1,4-diol (63.1 mg, 0.3 mmol), $^t\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (2:1) to afford 35.4 mg red solid product **4h** in 47% yield.

m.p. 81-90 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.49 (d, $J = 11.2$ Hz, 2H), 7.99 (d, $J = 1.9$ Hz, 2H), 7.61 (s, 2H), 5.95 (s, 1H), 3.24 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 183.0, 182.4, 153.4, 135.1, 134.1, 129.8, 129.7, 129.6, 129.2, 129.1, 128.9, 128.4, 126.6, 108.7, 42.5. The ^1H and ^{13}C NMR data match the reported values^[9].

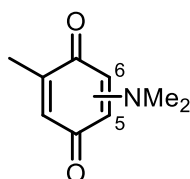


2-(dimethylamino)cyclohexa-2,5-diene-1,4-dione (**4i**)

The starting material, benzoquinone (32.4 mg, 0.3 mmol), ${}^n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (4:1) to afford 24.9 mg red solid product **4i** in 55% yield.

The starting material, hydroquinone (33.0 mg, 0.3 mmol), ${}^n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (4:1) to afford 40.8 mg red solid product **4i** in 90% yield.

m.p. 124-128 °C. ${}^1\text{H}$ NMR (400 MHz, CDCl_3) δ 6.63 (d, $J = 9.9$ Hz, 1H), 6.53 (d, $J = 9.9$ Hz, 1H), 5.61 (s, 1H), 3.17 (s, 6H). ${}^{13}\text{C}$ NMR (100 MHz, CDCl_3) δ 185.3, 185.2, 150.4, 137.9, 134.2, 104.4, 42.3. The ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR data match the reported values^[10].



The starting material, 2-methylcyclohexa-2,5-diene-1,4-dione (36.6 mg, 0.3 mmol), ${}^n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (4:1) to afford 49.5 mg red solid product **4j** in 99% yield

(C6/C5 = 1:1).

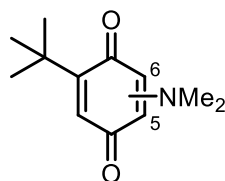
The starting material, 2-methylbenzene-1,4-diol (37.2 mg, 0.3 mmol), $n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (4:1) to afford 29.7 mg red solid product **4j** in 60% yield (C6/C5 = 1:1).

2-(dimethylamino)-5-methylcyclohexa-2,5-diene-1,4-dione (4j, 6-NMe₂)

m.p. 126-129 °C. ^1H NMR (400 MHz, CDCl_3) δ 6.44 (d, J = 1.6 Hz, 1H), 5.53 (d, J = 2.2 Hz, 1H), 3.11 (s, 6H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 185.9, 185.6, 151.2, 142.7, 134.5, 104.5, 42.3, 15.8.

2-(dimethylamino)-6-methylcyclohexa-2,5-diene-1,4-dione (4j, 5-NMe₂)

m.p. 130-132 °C. ^1H NMR (400 MHz, CDCl_3) δ 6.35 (s, 1H), 5.56 (s, 1H), 3.12 (s, 6H), 2.02 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 185.4, 185.4, 150.7, 147.4, 131.1, 104.33, 42.33, 15.7. The ^1H and ^{13}C NMR data match the reported values^[11].



The starting material, 2-(tert-butyl)cyclohexa-2,5-diene-1,4-dione (49.3 mg, 0.3 mmol), $n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (4:1) to afford 37.3 mg orange solid product **4k** in 60% yield (C6/C5 = 7:1).

The starting material, 2-(tert-butyl)benzene-1,4-diol (49.9 mg, 0.3 mmol), $n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers

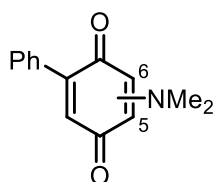
were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (10:1) to afford 53.5 mg orange solid product **4k** in 86% yield (C6/C5 = 7:1).

2-(tert-butyl)-5-(dimethylamino)cyclohexa-2,5-diene-1,4-dione (4k, 6-NMe₂)

m.p. 99-102 °C. ¹H NMR (400 MHz, CDCl₃) δ 6.43 (d, *J* = 2.4 Hz, 1H), 5.50 (d, *J* = 1.9 Hz, 1H), 3.07 (s, 6H), 1.27 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 186.0, 185.7, 153.6, 153.5, 132.8, 103.1, 42.1, 35.0, 29.2. The ¹H and ¹³C NMR data match the reported values^[12].

2-(tert-butyl)-6-(dimethylamino)cyclohexa-2,5-diene-1,4-dione (4k, 5-NMe₂)

m.p. 100-102 °C. ¹H NMR (400 MHz, CDCl₃) δ 6.33 (s, 1H), 5.50 (s, 1H), 3.09 (s, 6H), 1.29 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 186.4, 185.6, 157.0, 149.5, 129.6, 106.7, 41.9, 35.1, 29.5. The ¹H and ¹³C NMR data match the reported values^[7].



The starting material, [1,1'-biphenyl]-2,5-dione (55.3 mg, 0.3 mmol), ⁿBu₄NBF₄ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL × 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (4:1) to afford 50.5 mg red solid product **4l** in 74% yield (C6/C5 = 3:1). The starting material, [1,1'-biphenyl]-2,5-diol (55.9 mg, 0.3 mmol), ⁿBu₄NBF₄ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL × 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (4:1) to afford 28.6 mg red solid product **4l** in 42% yield (C6/C5 = 3:1).

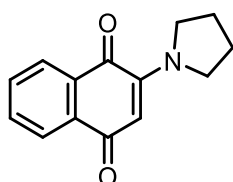
2-(dimethylamino)-5-methylcyclohexa-2,5-diene-1,4-dione (4l, 6-NMe₂)

m.p. 98-100 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.42 (s, 5H), 6.71 (d, *J* = 2.6 Hz, 1H), 5.65 (d, *J* = 2.4 Hz, 1H), 3.15 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 185.1, 151.8,

144.1, 134.1, 133.5, 129.4, 128.9, 128.4, 104.2, 42.4. HRMS (ESI) m/z : $[M+H]^+$ Calcd. for $C_{14}H_{13}NO_2$ 228.1020; Found 228.1022.

2-(dimethylamino)-6-methylcyclohexa-2,5-diene-1,4-dione (**4l**, 5-NMe₂)

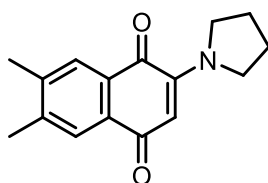
m.p. 103-105 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.51 (dd, $J_1 = 6.7$ Hz, $J_2 = 3.0$ Hz, 2H), 7.42-7.41 (m, 3H), 6.61 (s, 1H), 5.69 (s, 1H), 3.18 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 185.5, 184.2, 150.3, 146.6, 133.5, 130.9, 129.7, 129.6, 129.5, 128.2, 104.8, 42.3. HRMS (ESI) m/z : $[M+H]^+$ Calcd. for $C_{14}H_{13}NO_2$ 228.1020; Found 228.1022.



2-(pyrrolidin-1-yl)naphthalene-1,4-dione (**4m**)

The starting material, naphthalene-1,4-dione (47.5 mg, 0.3 mmol), ⁿBu₄NBF₄ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of pyrrolidine-1-carbaldehyde. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (2:1) to afford 27.3 mg orange solid product **4m** in 40% yield.

m.p. 143-146 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, $J = 7.6$ Hz, 1H), 8.01 (d, $J = 7.7$ Hz, 1H), 7.69 (dd, $J_1 = 7.6$ Hz, $J_2 = 7.2$ Hz, 1H), 7.60 (dd, $J_1 = 7.6$ Hz, $J_2 = 7.2$ Hz, 1H), 5.75 (s, 1H), 3.90-3.47 (m, 4H), 2.02-1.98 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 183.3, 182.4, 149.0, 134.0, 133.2, 131.8, 131.6, 126.3, 125.4, 104.7, 51.0, 29.7. The ¹H and ¹³C NMR data match the reported values^[13].

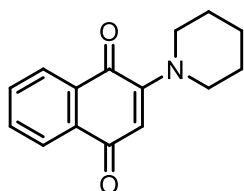


6,7-dimethyl-2-(pyrrolidin-1-yl)naphthalene-1,4-dione (**4n**)

The starting material, 6,7-dimethylnaphthalene-1,4-dione (55.8 mg, 0.3 mmol), ⁿBu₄NBF₄ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of pyrrolidine-1-carbaldehyde. The flask was equipped with platinum

plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (2:1) to afford 25.3 mg red solid product **4n** in 33% yield.

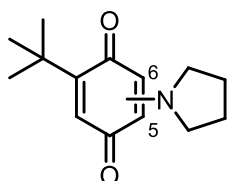
m.p. 70-77 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.80 (s, 1H), 7.74 (s, 1H), 5.67 (s, 1H), 3.92-3.43 (m, 4H), 2.37 (s, 3H), 2.35 (s, 3H), 2.00-1.97 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 183.4, 182.9, 149.1, 143.8, 140.9, 131.1, 129.7, 127.4, 126.5, 104.5, 50.8, 29.7, 20.1, 19.9. HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{16}\text{H}_{17}\text{NO}_2$ 256.1333; Found 256.1329.



2-(piperidin-1-yl)naphthalene-1,4-dione (**4o**)

The starting material, naphthalene-1,4-dione (47.5 mg, 0.3 mmol), $^n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of piperidine-1-carbaldehyde. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (2:1) to afford 15.2 mg red solid product **4o** in 21% yield.

m.p. 98-105 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 7.3$ Hz, 1H), 7.98 (d, $J = 7.1$ Hz, 1H), 7.68 (dd, $J_1 = 8.0$ Hz, $J_2 = 6.9$ Hz, 1H), 7.62 (dd, $J = 8.0, 7.0$ Hz, 1H), 6.02 (s, 1H), 3.50-3.48 (m, 4H), 1.74-1.72 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 183.5, 183.4, 154.1, 133.7, 133.0, 132.6, 132.2, 126.6, 125.4, 110.4, 50.4, 25.7, 24.3. The ^1H and ^{13}C NMR data match the reported values^[13].



The starting material, 2-(tert-butyl)cyclohexa-2,5-diene-1,4-dione (49.3 mg, 0.3 mmol), $^n\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were

dissolved in 5 mL of pyrrolidine-1-carbaldehyde. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (2:1) to afford 50.4 mg red liquid product **4p** in 72% yield (C6/C5 = 3:1).

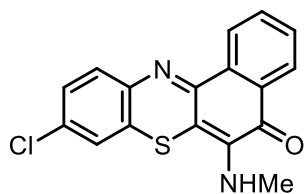
The starting material, 2-(tert-butyl)benzene-1,4-diol (49.9 mg, 0.3 mmol), $t\text{Bu}_4\text{NBF}_4$ (322.4 mg, 1.0 mmol), NaOAc (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of DMF. The flask was equipped with platinum plates as the anode and cathode. The electrolysis was carried out at r.t. using a constant current of 10 mA for 2 hours. The reaction mixture was extracted with EtOAc (15 mL \times 3). The collected organic layers were dried, evaporated and chromatographed through silica gel eluting with ethyl acetate/hexanes (2:1) to afford 39.9 mg red liquid product **4p** in 57% yield (C6/C5 = 3:1).

2-(tert-butyl)-6-(pyrrolidin-1-yl)cyclohexa-2,5-diene-1,4-dione (4p, 6-NMe₂)

¹H NMR (400 MHz, CDCl₃) δ 6.47 (d, J = 1.6 Hz, 1H), 5.42 (d, J = 1.8 Hz, 1H), 3.67-3.39 (m, 4H), 1.98-1.94 (m, 4H), 1.27 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ . 185.4, 151.8, 149.3, 133.7, 100.9, 50.8, 34.9, 29.4, 29.22. HRMS (ESI) m/z : [M+H]⁺ Calcd. for C₁₄H₁₉NO₂ 234.1489; Found 234.1486.

2-(tert-butyl)-5-(pyrrolidin-1-yl)cyclohexa-2,5-diene-1,4-dione (4p, 5-NMe₂)

¹H NMR (400 MHz, CDCl₃) δ 6.33 (s, 1H), 5.40 (s, 1H), 3.48-3.43 (m, 4H), 1.96-1.93 (m, 4H), 1.30 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 186.3, 185.1, 157.8, 146.3, 128.5, 104.3, 50.3, 35.3, 29.6, 29.1. HRMS (ESI) m/z : [M+H]⁺ Calcd. for C₁₄H₁₉NO₂ 234.1489; Found 234.1490.



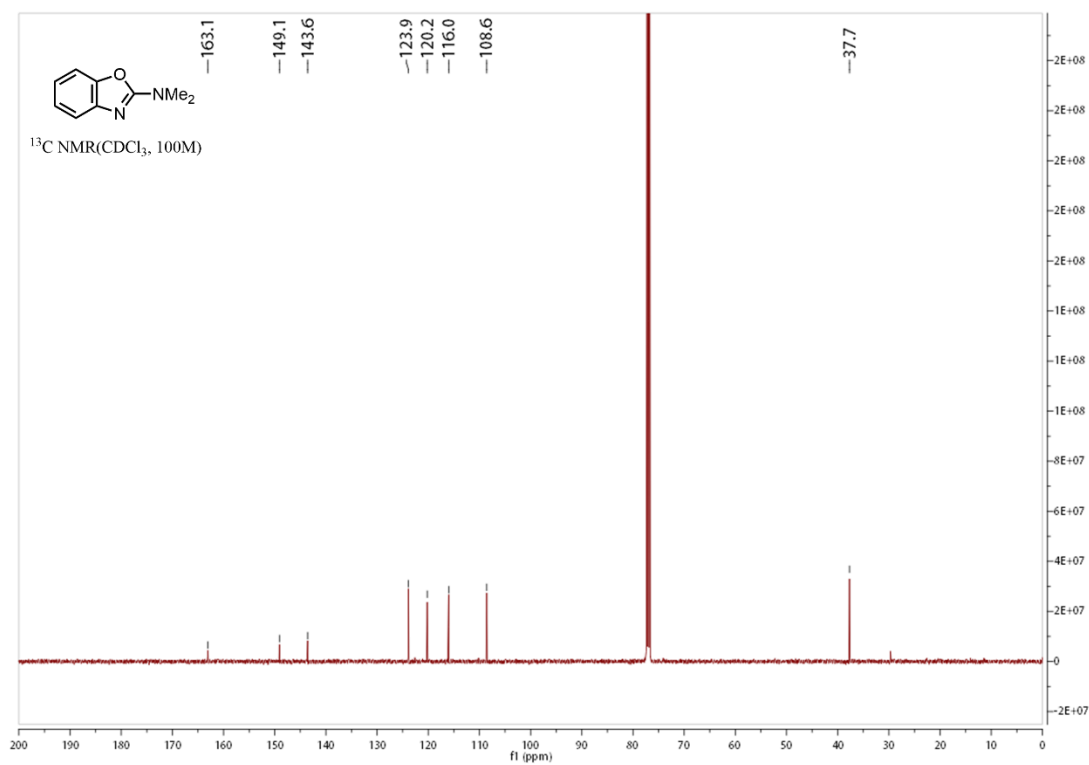
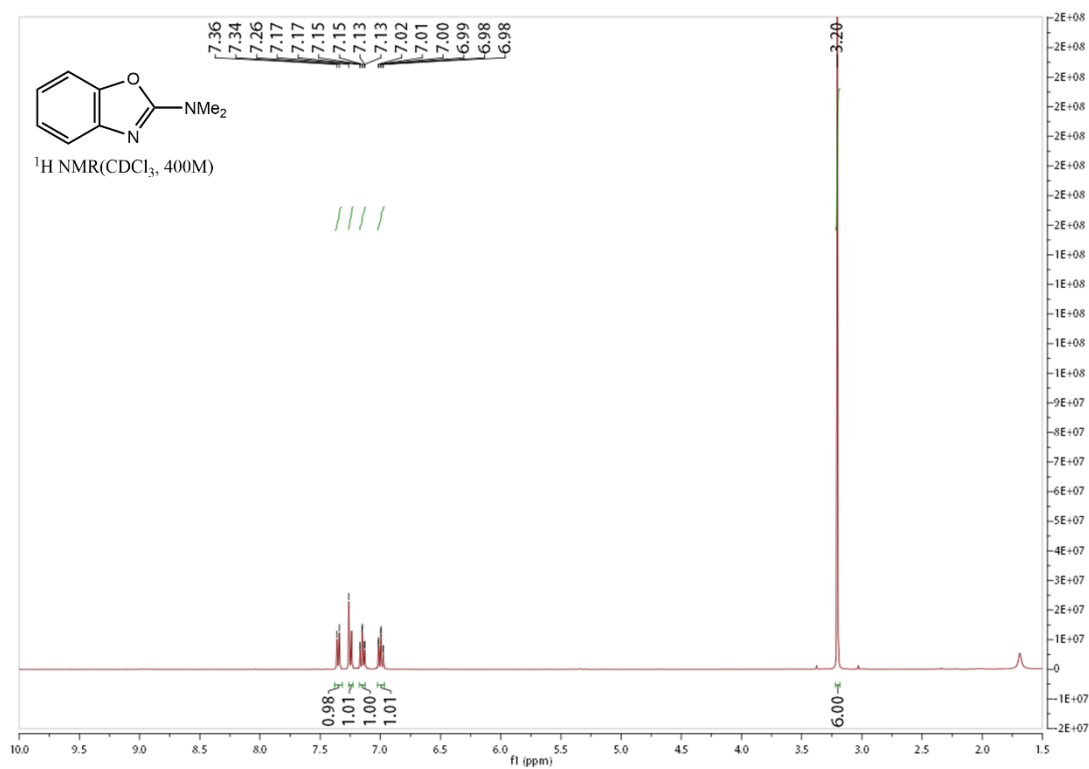
9-chloro-6-(methylamino)-5H-benzo[a]phenothiazin-5-one(8)

The starting material, 2-bromo-3-(dimethylamino)naphthalene-1,4-dione (84.0 mg, 0.3 mmol), 2-amino-5-chlorobenzenethiol (47.9 mg, 0.3 mmol), Na₂CO₃ (24.6 mg, 0.3 mmol, 1.0 equiv.) were dissolved in 5 mL of MeOH. The reaction was carried out at 65 °C. for 24 hours. The organic layers were evaporated and chromatographed through

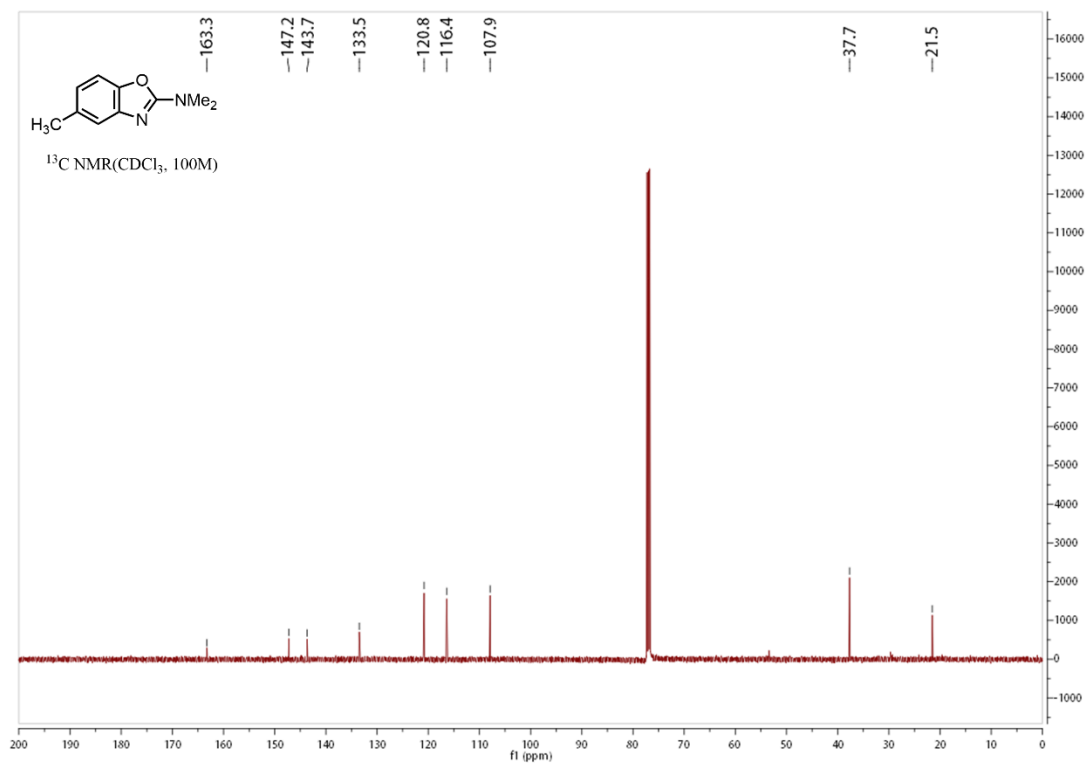
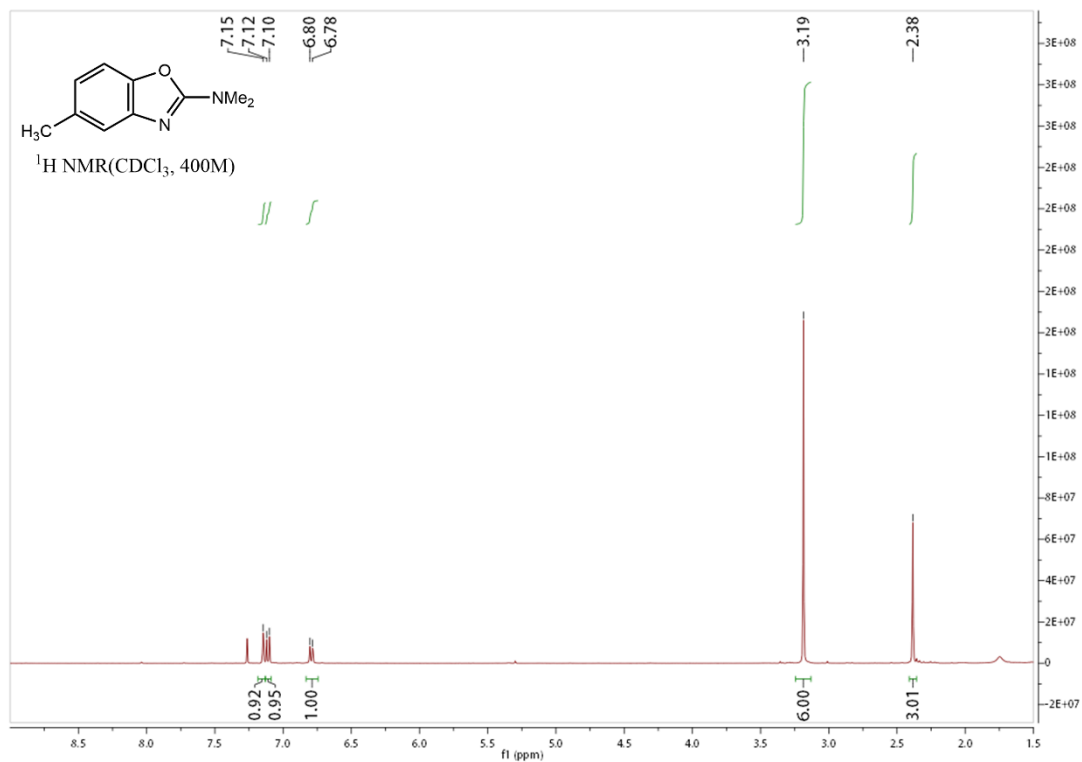
silica gel eluting with ethyl acetate/hexanes (10:1) to afford 65.7 mg red solid product **8** in 67% yield.

m.p. 185-189°C. ¹H NMR (400MHz, CDCl₃) δ 8.80-8.78 (m, 1H), 8.30-8.27 (m, 1H), 7.78-7.70 (m, 3H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.36 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.0 Hz, 1H), 4.20 (s, 3H). ¹³C NMR (100MHz, CDCl₃) δ 175.4, 145.6, 145.5, 137.5, 135.2, 133.9, 133.5, 132.3, 131.6, 131.4, 128.0, 125.9, 125.4, 125.0, 124.9, 123.0, 60.2. HRMS (ESI) *m/z*: [M+H]⁺ Calcd. for C₁₇H₁₁ClN₂OS 327.0354, 329.0324; Found 327.0355, 329.0326.

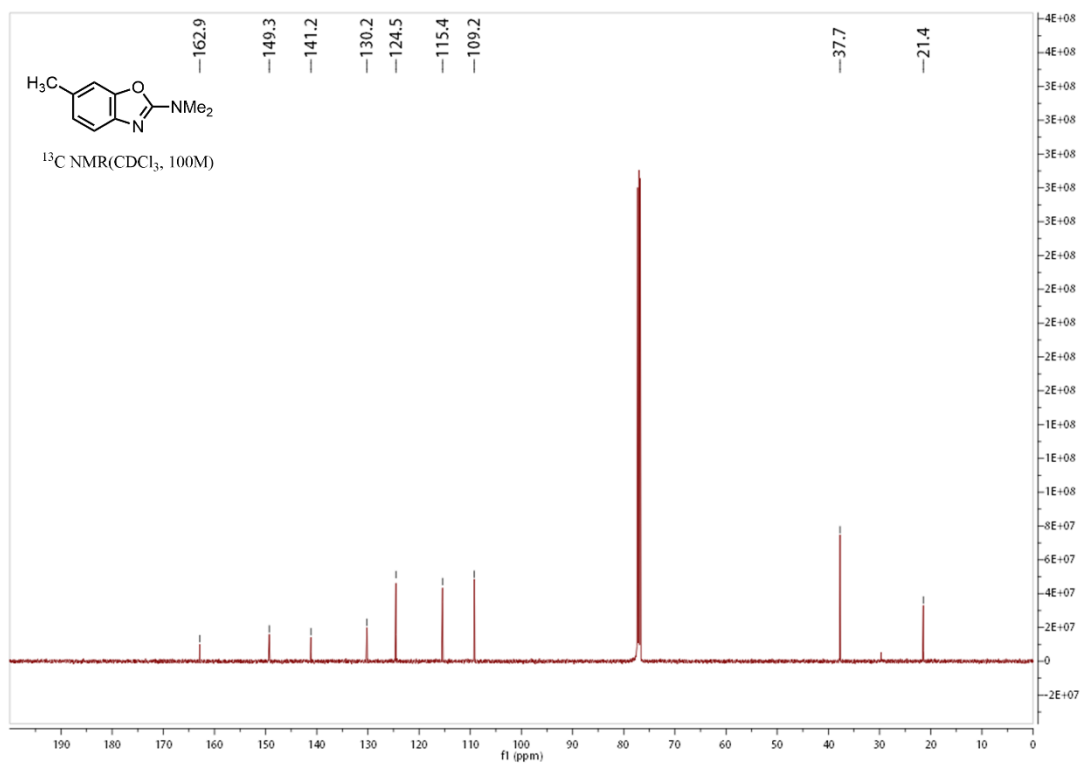
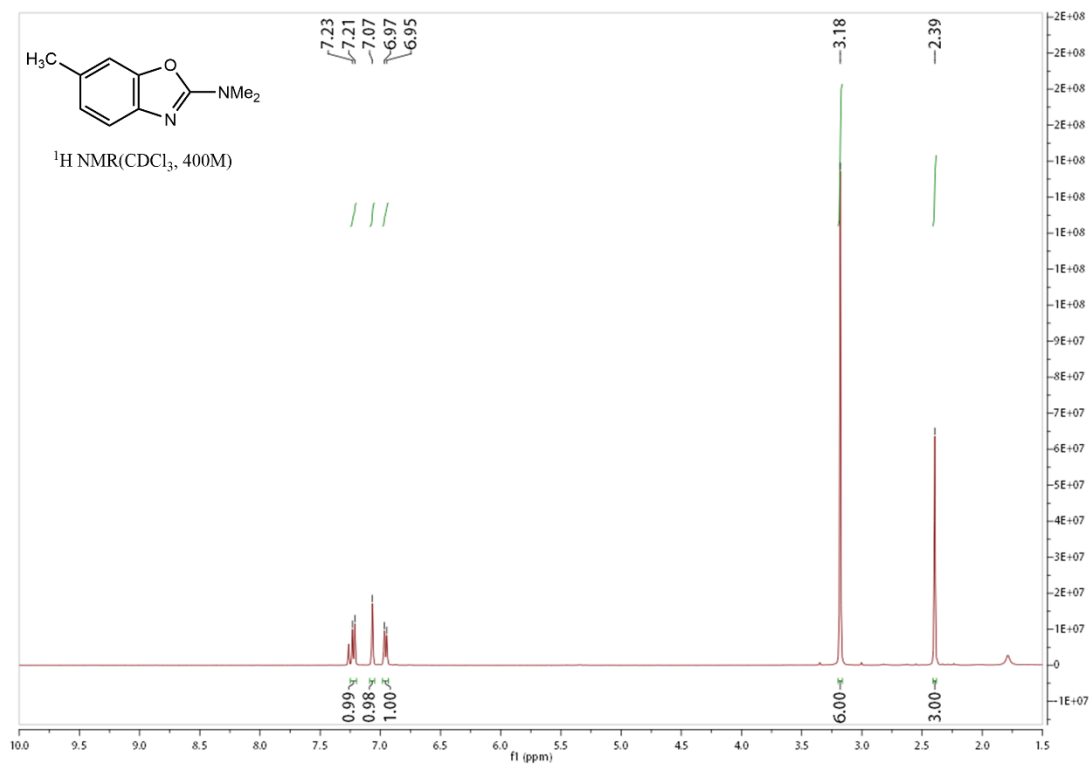
6. NMR spectra for products



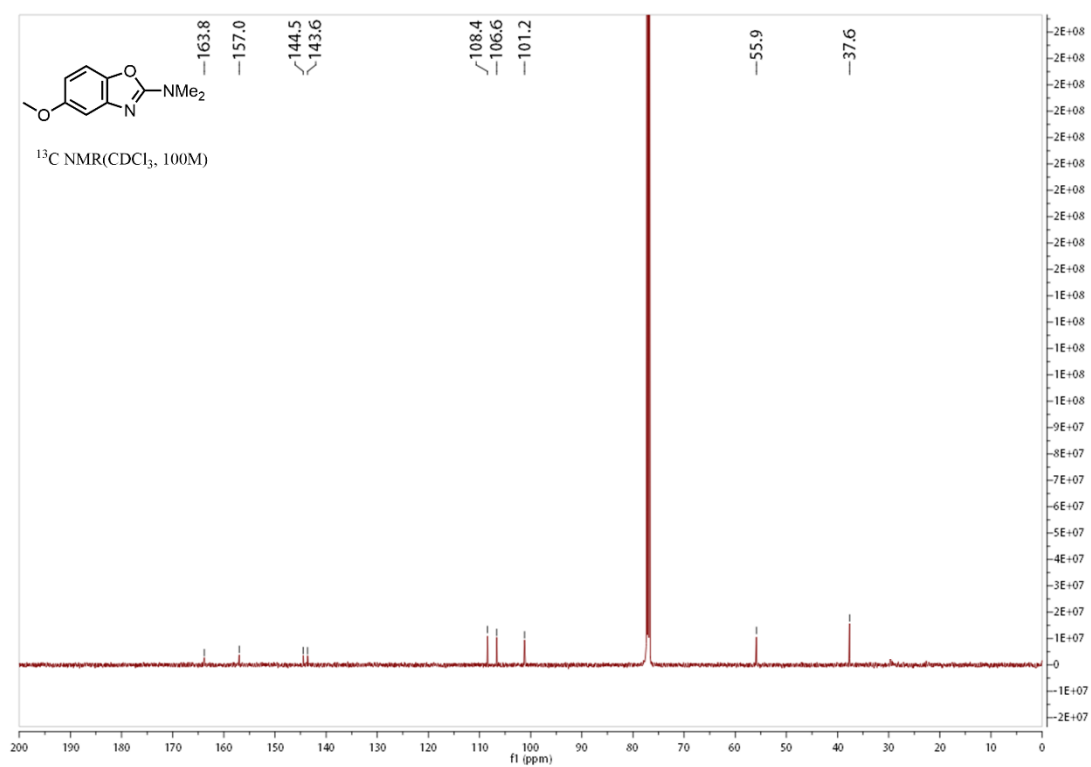
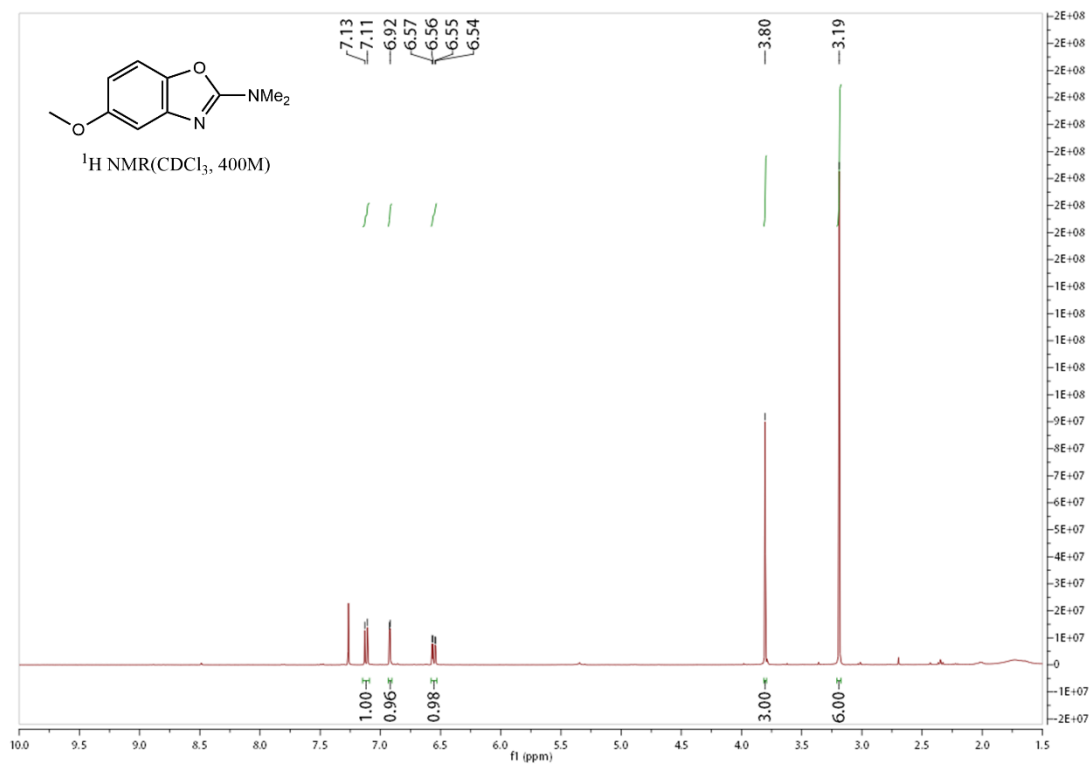
¹H NMR of **2a** (400 MHz, CDCl₃) and ¹³C NMR of **2a** (100 MHz, CDCl₃)



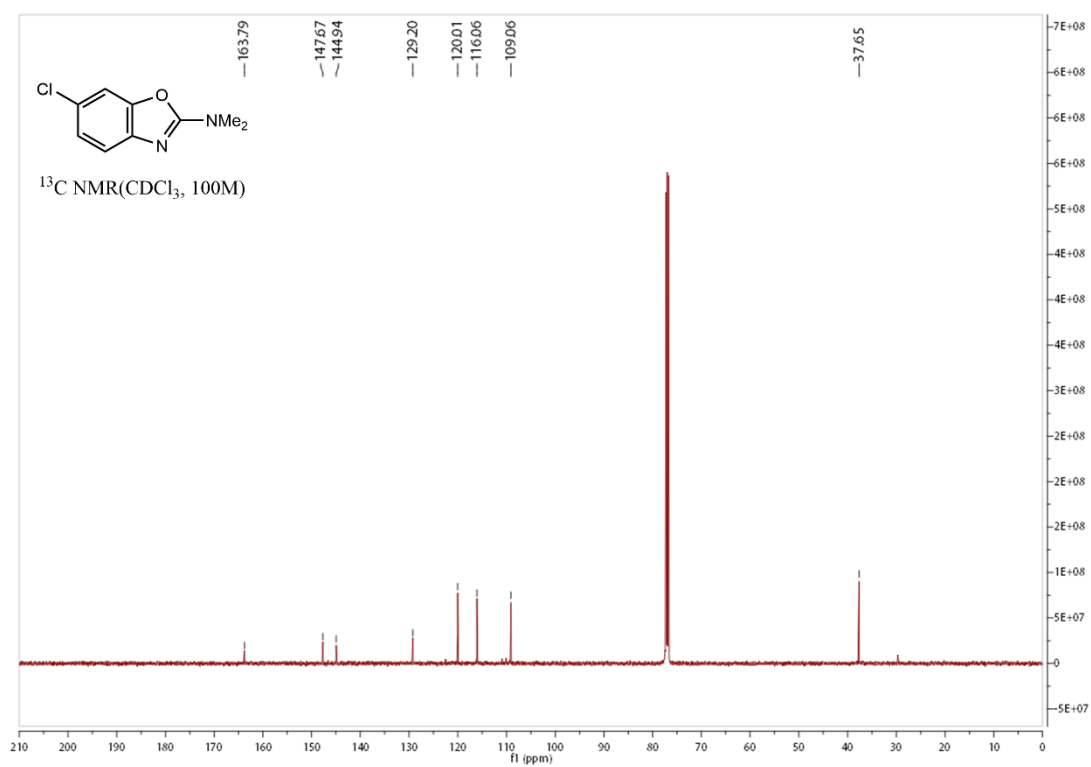
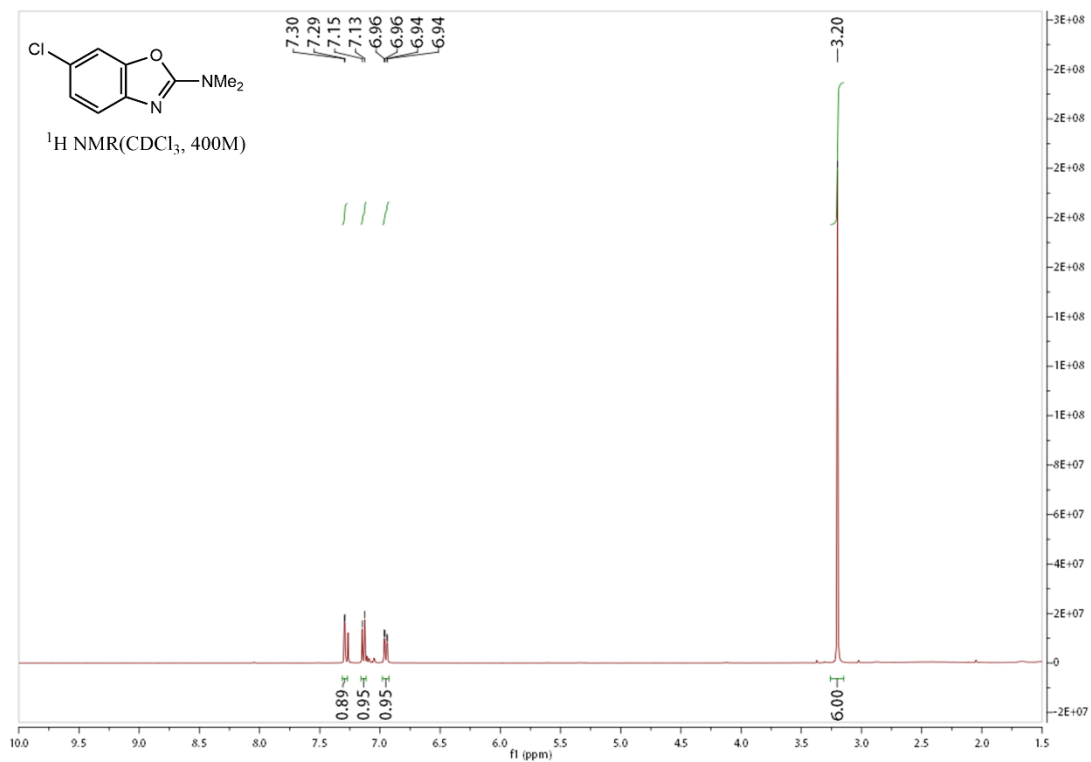
¹H NMR of **2b** (400 MHz, CDCl₃) and ¹³C NMR of **2b** (100 MHz, CDCl₃)



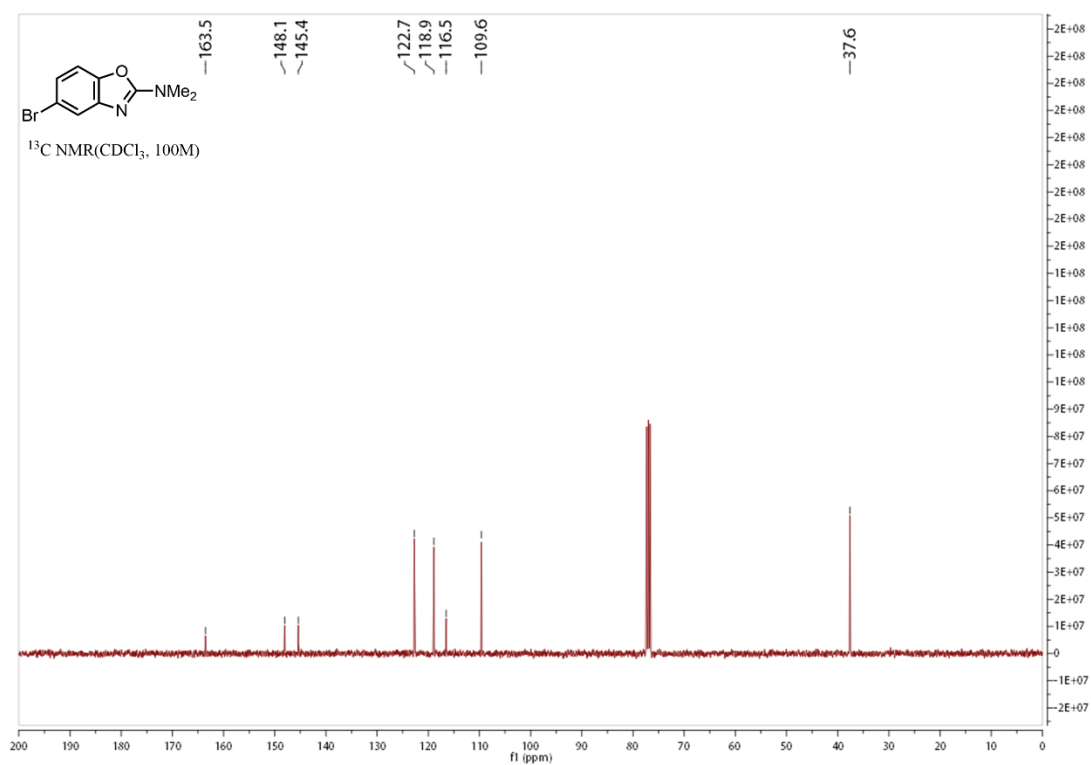
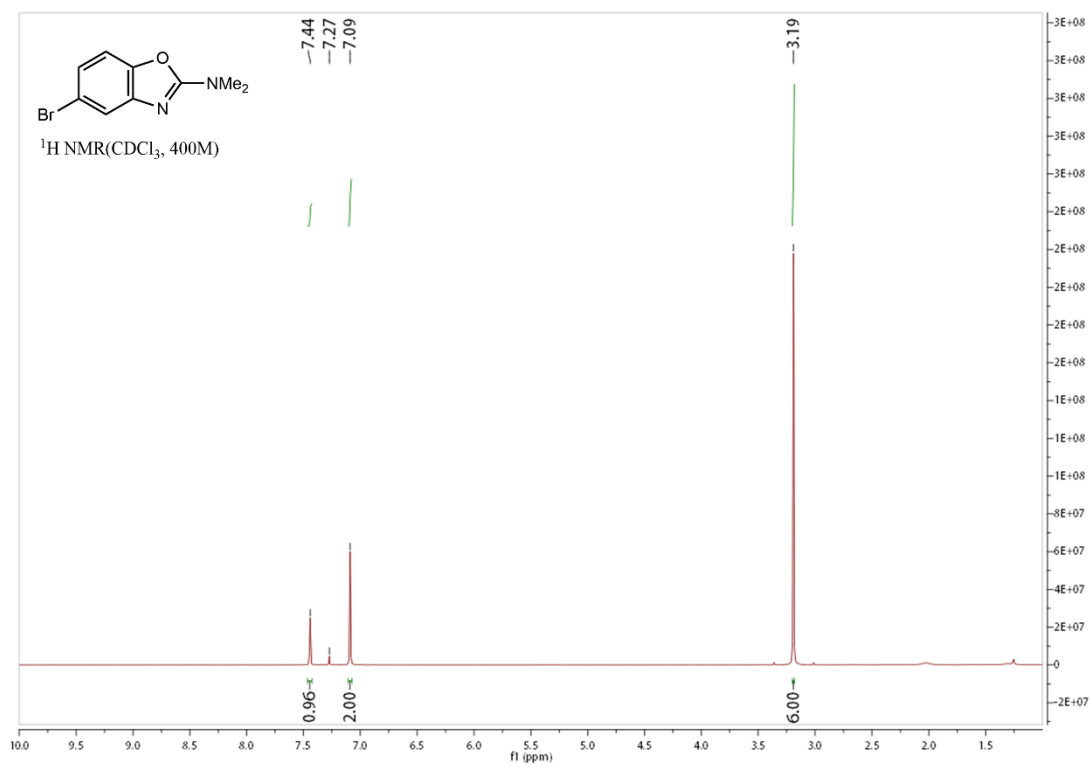
¹H NMR of **2c** (400 MHz, CDCl₃) and ¹³C NMR of **2c** (100 MHz, CDCl₃)



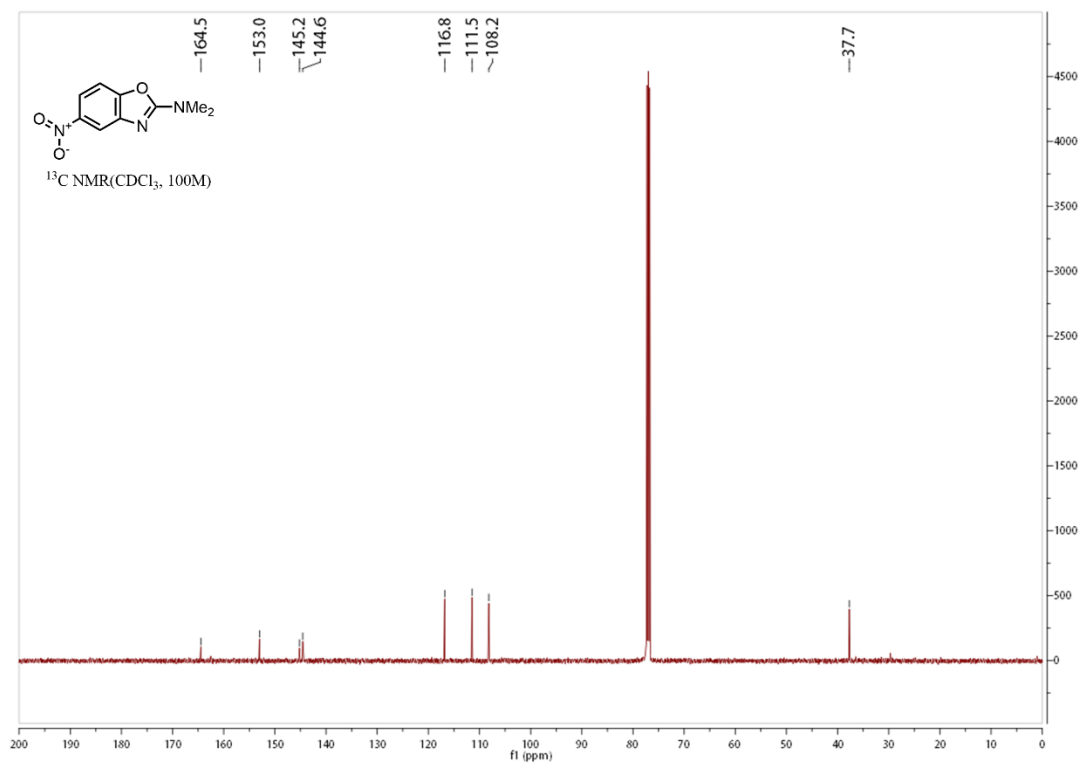
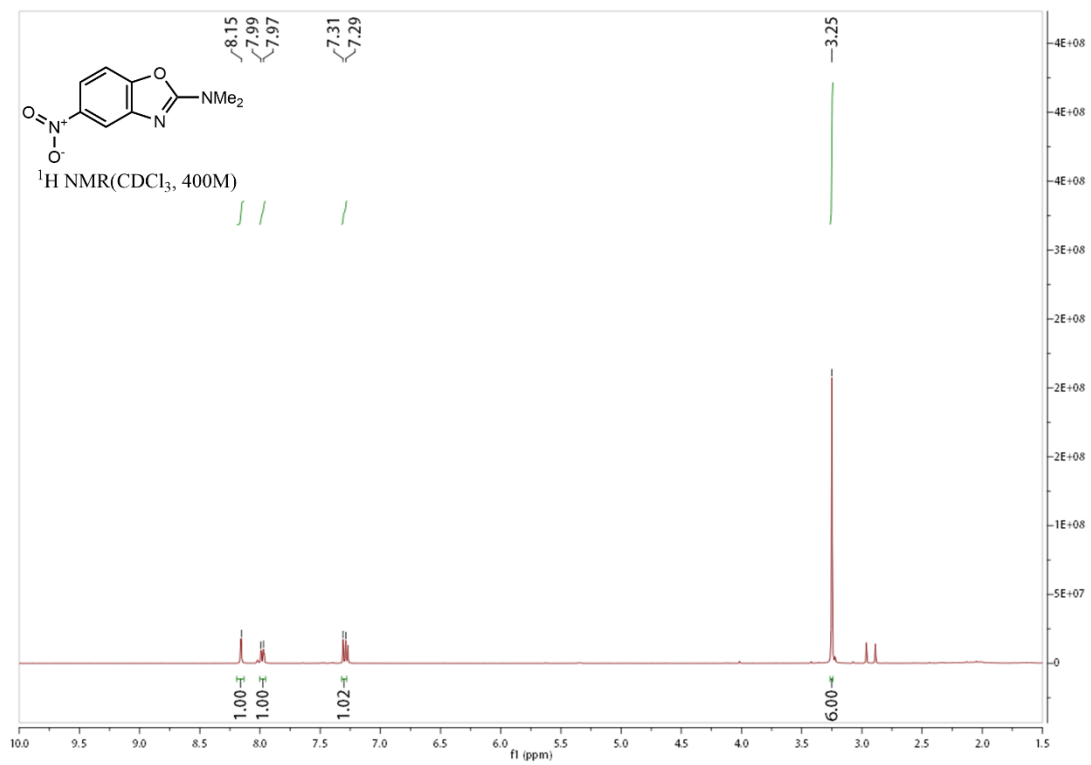
¹H NMR of **2d** (400 MHz, CDCl₃) and ¹³C NMR of **2d** (100 MHz, CDCl₃)



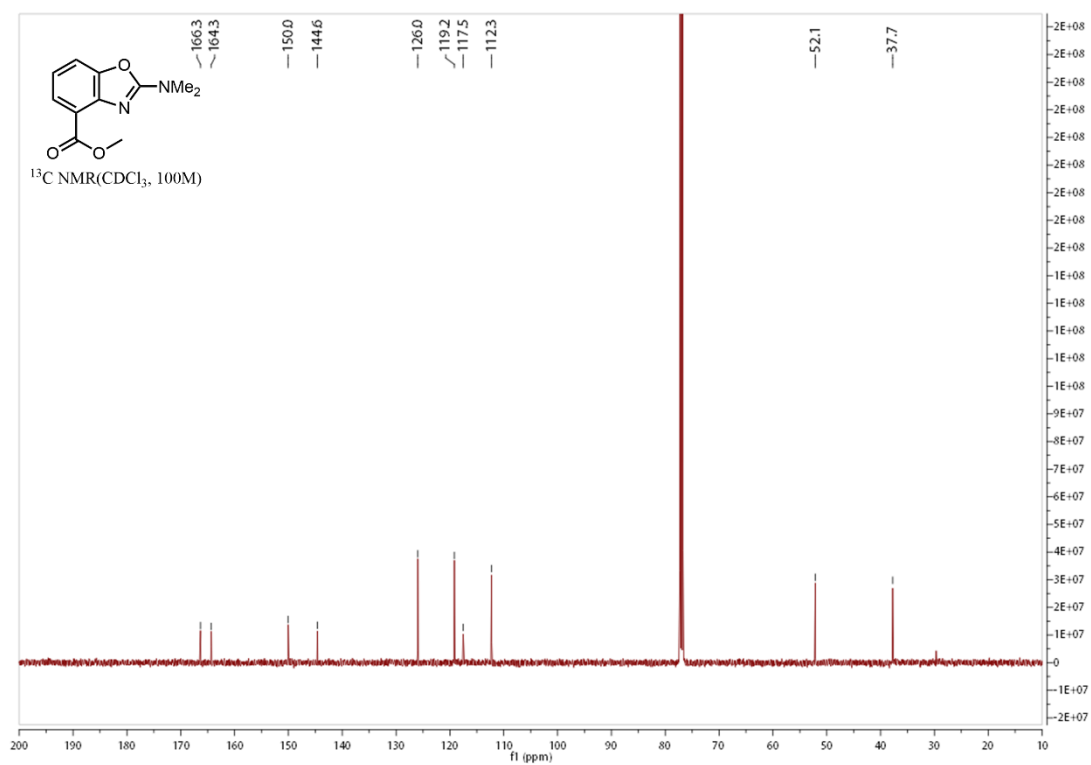
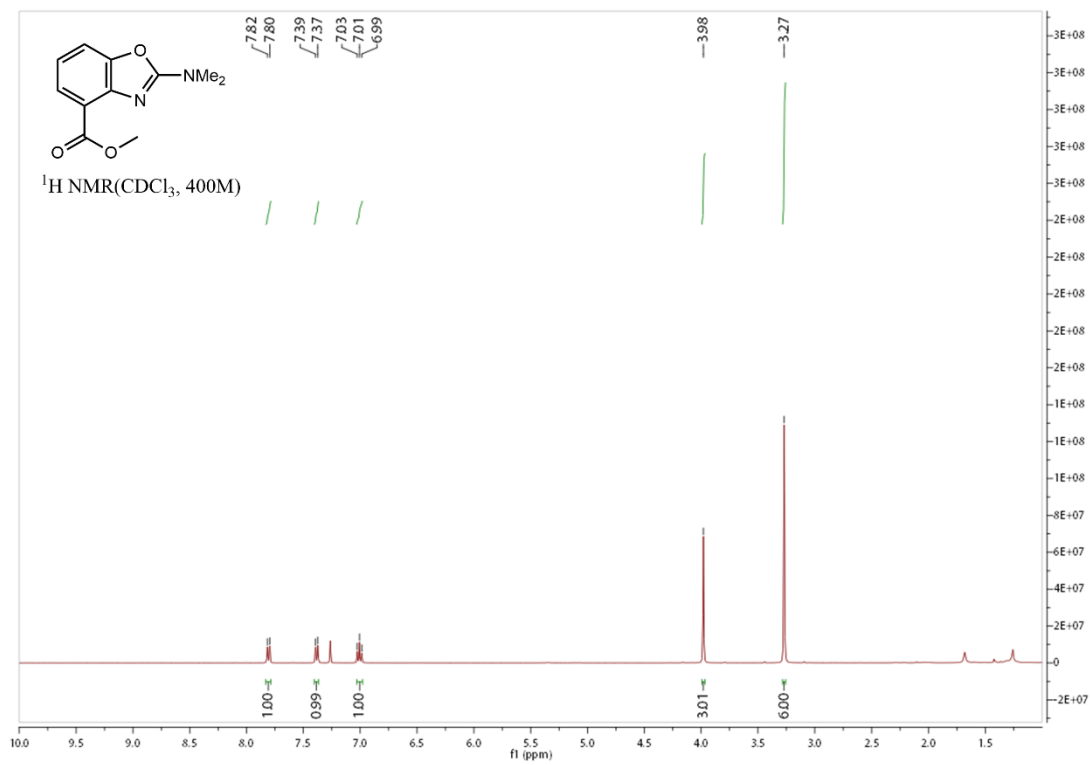
¹H NMR of **2e** (400 MHz, CDCl₃) and ¹³C NMR of **2e** (100 MHz, CDCl₃)



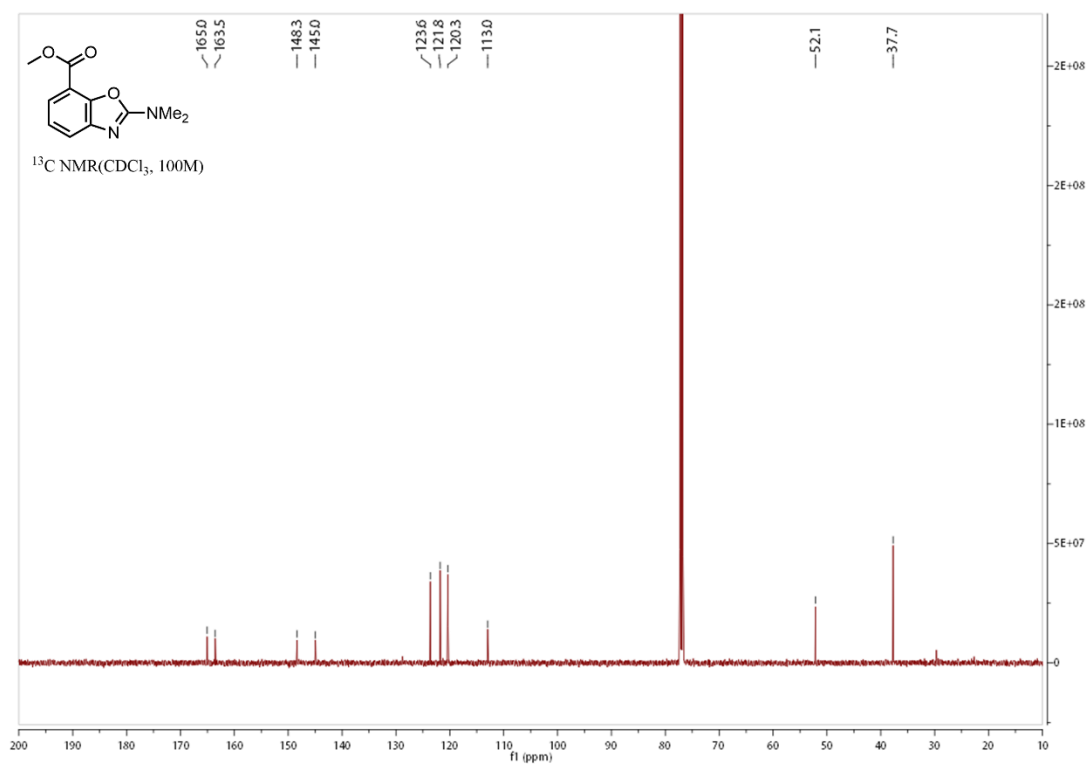
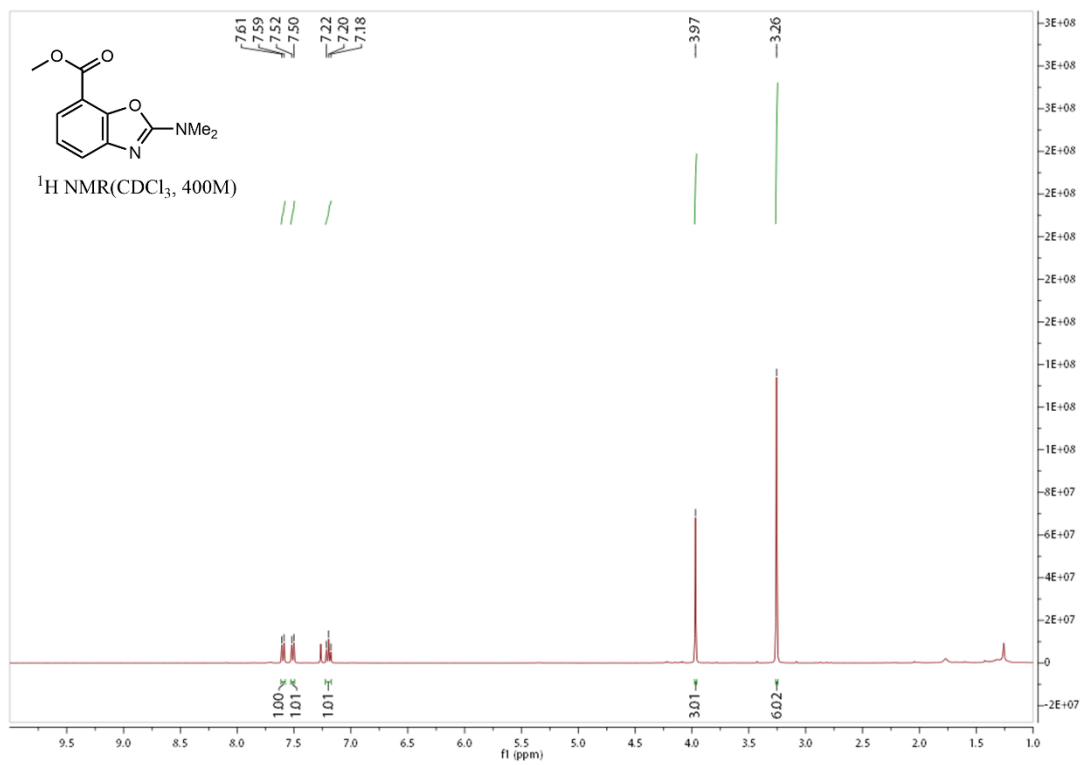
¹H NMR of **2f** (400 MHz, CDCl₃) and ¹³C NMR of **2f** (100 MHz, CDCl₃)



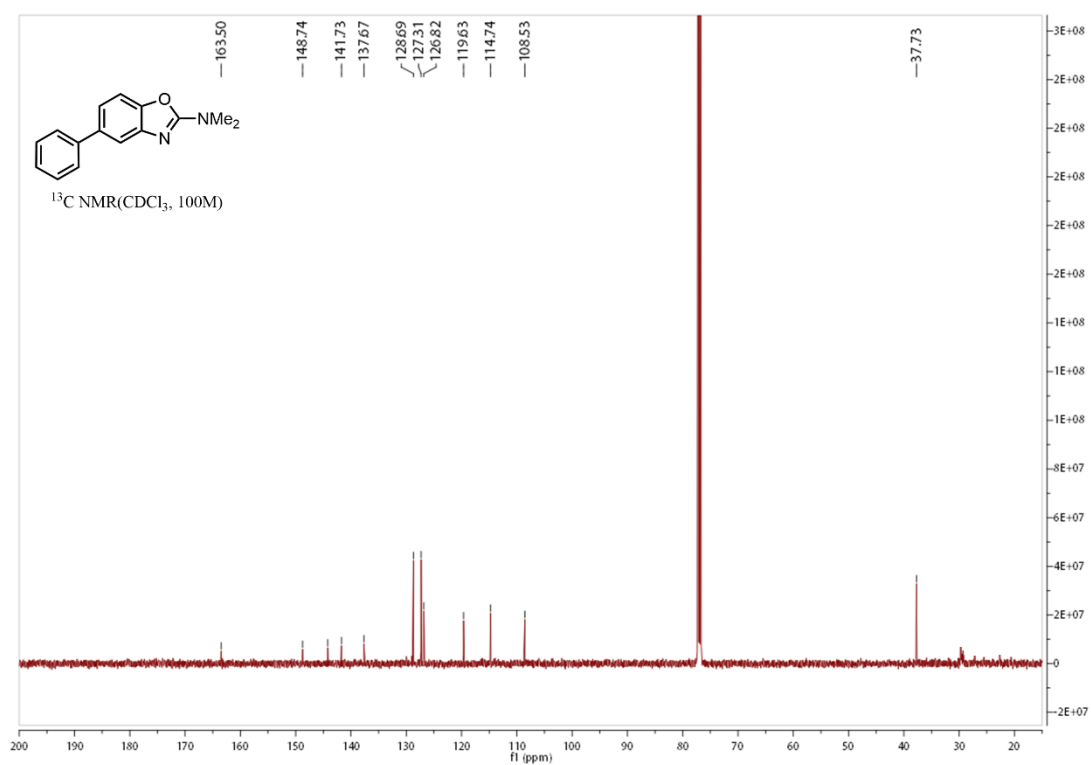
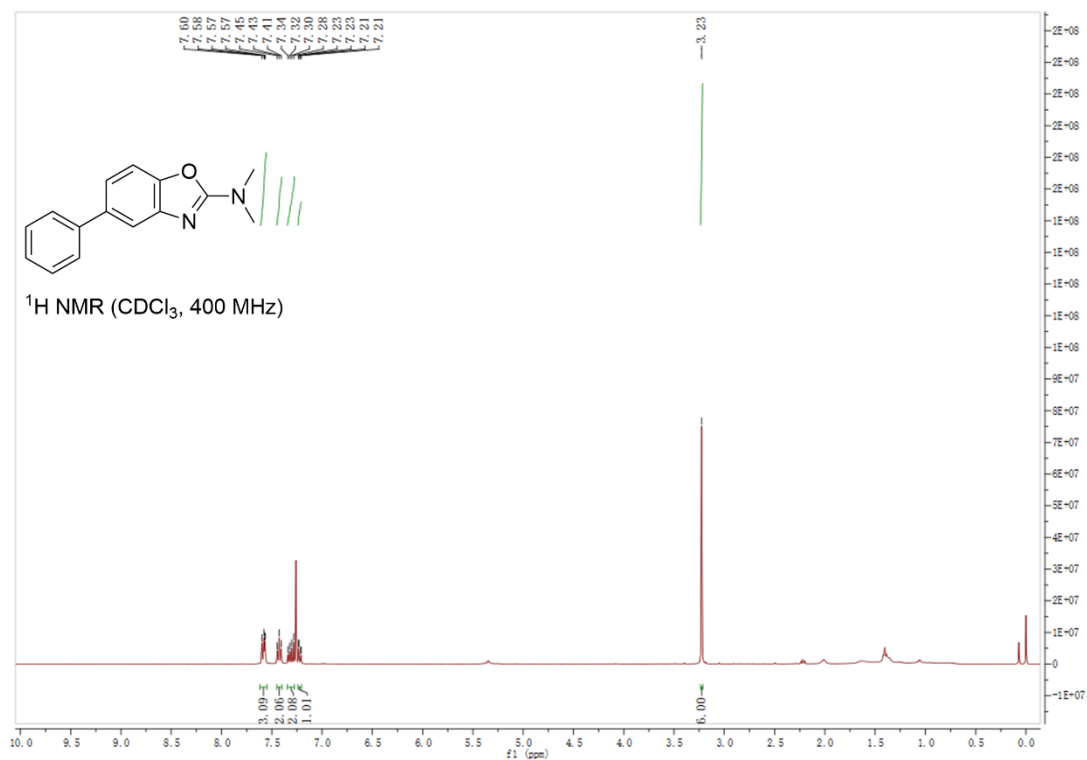
$^1\text{H NMR}$ of **2g** (400 MHz, CDCl_3) and $^{13}\text{C NMR}$ of **2g** (100 MHz, CDCl_3)



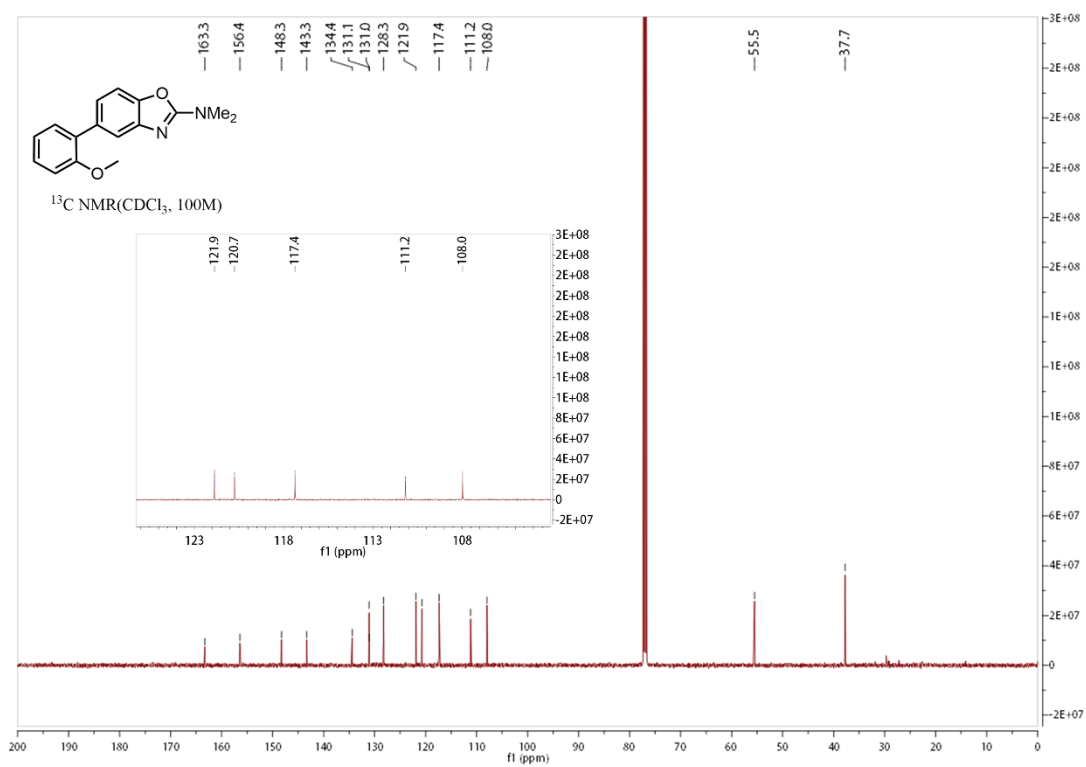
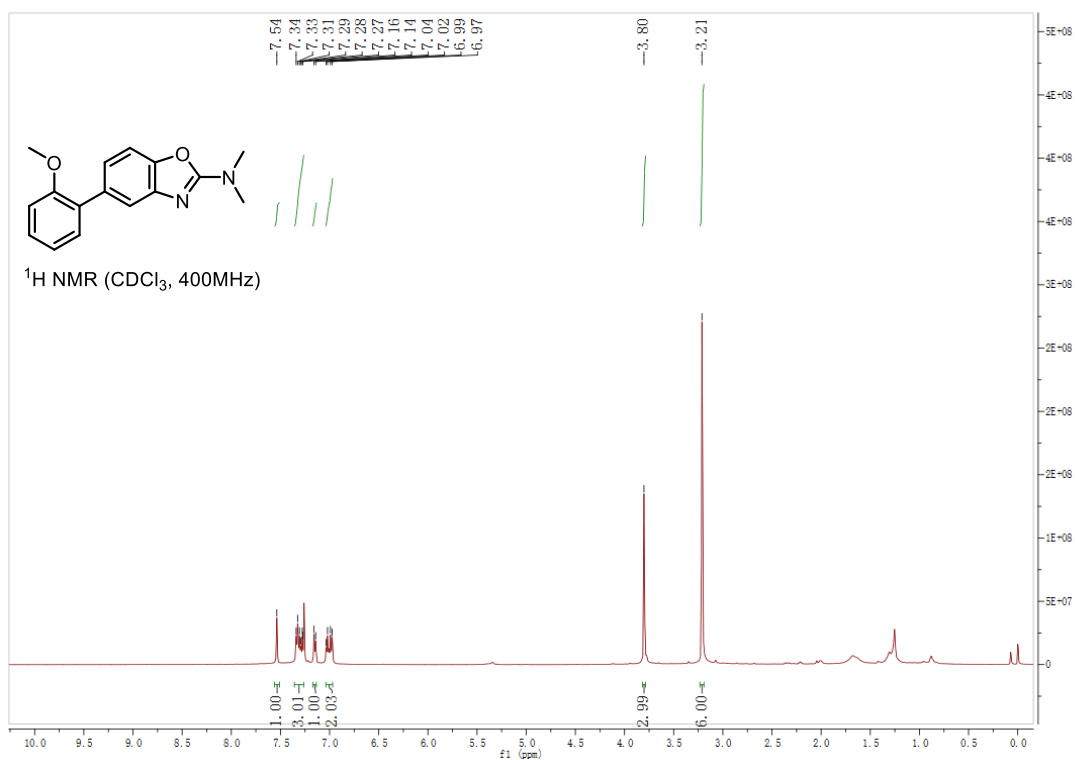
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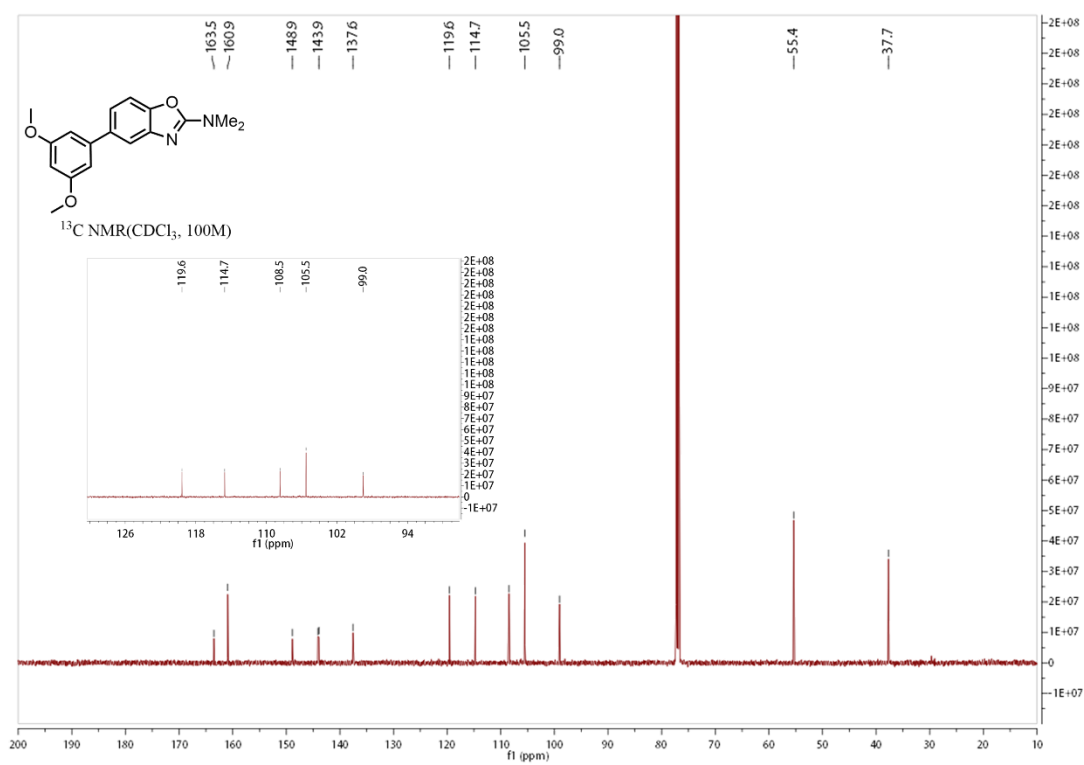
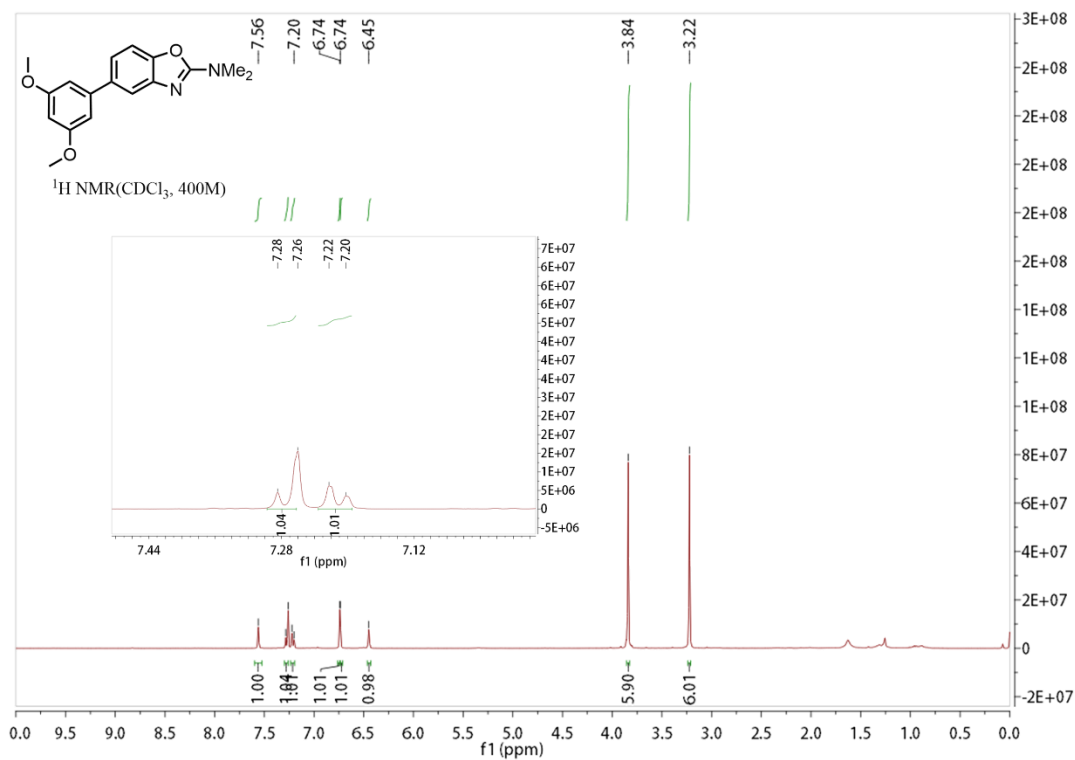
¹H NMR of **2i** (400 MHz, CDCl₃) and ¹³C NMR of **2i** (100 MHz, CDCl₃)



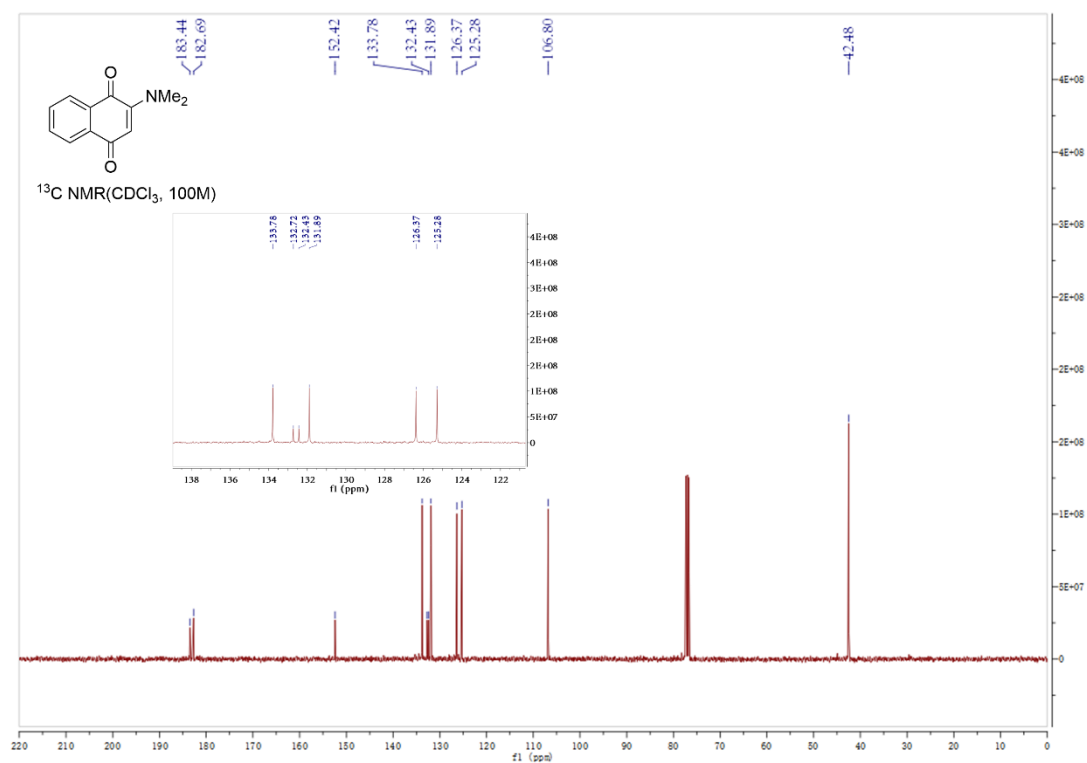
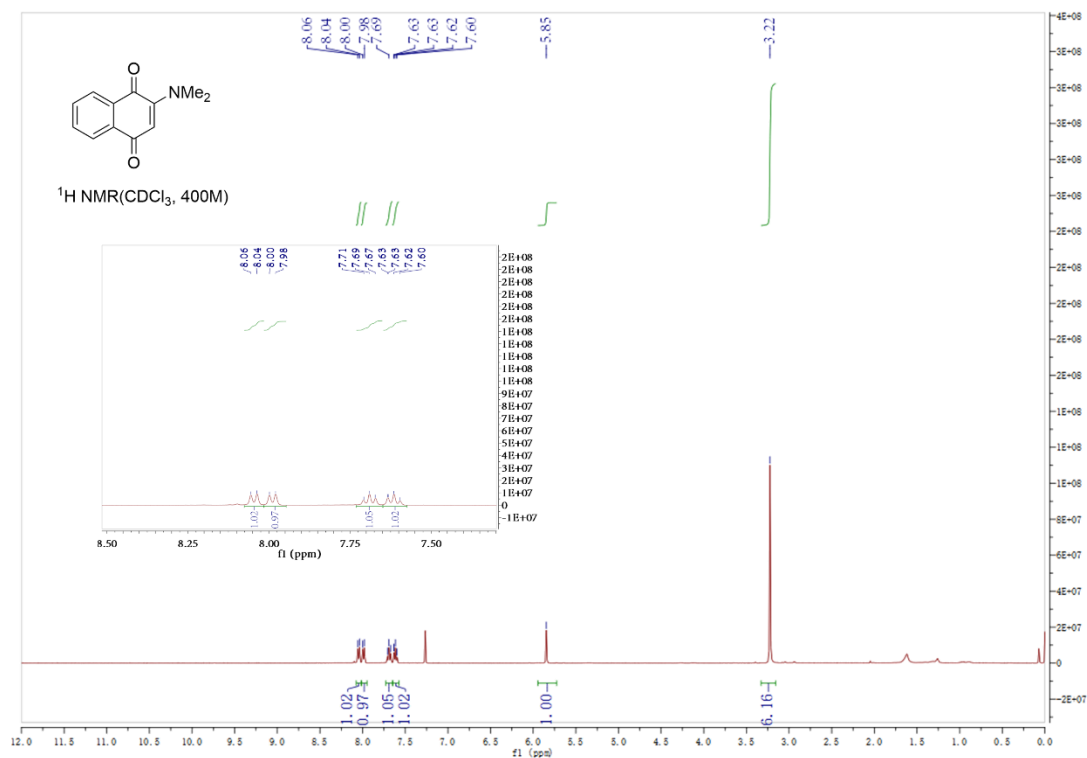
¹H NMR of **2j** (400 MHz, CDCl₃) and ¹³C NMR of **2j** (100 MHz, CDCl₃)



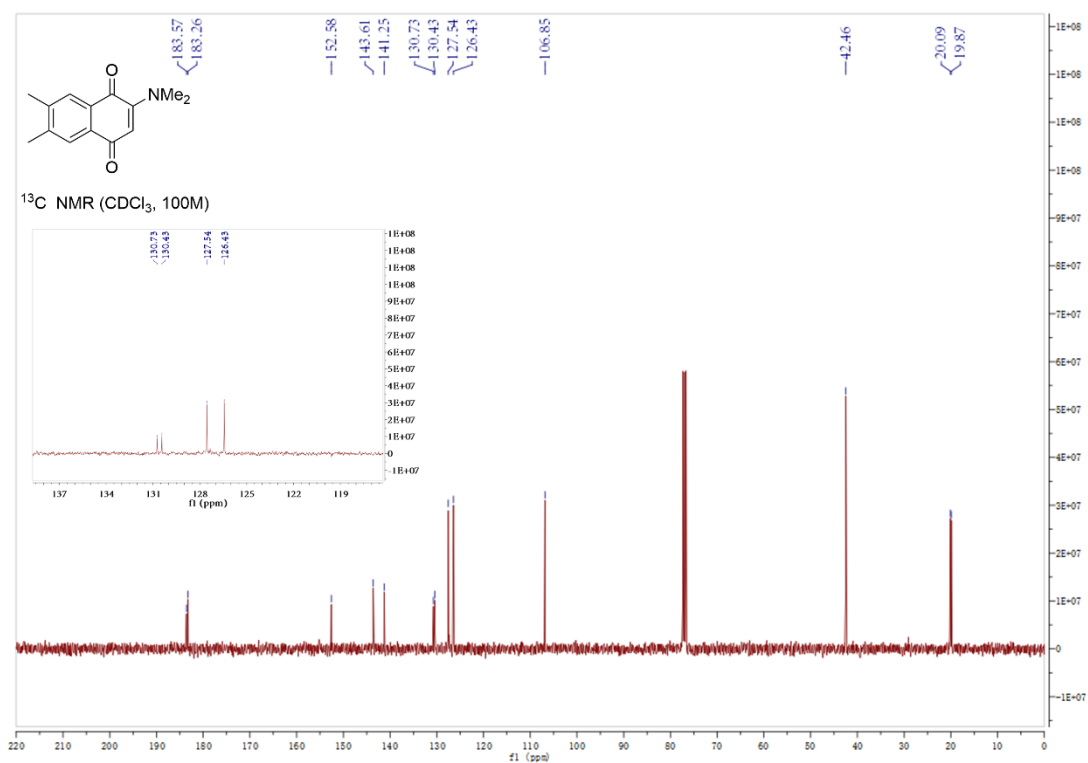
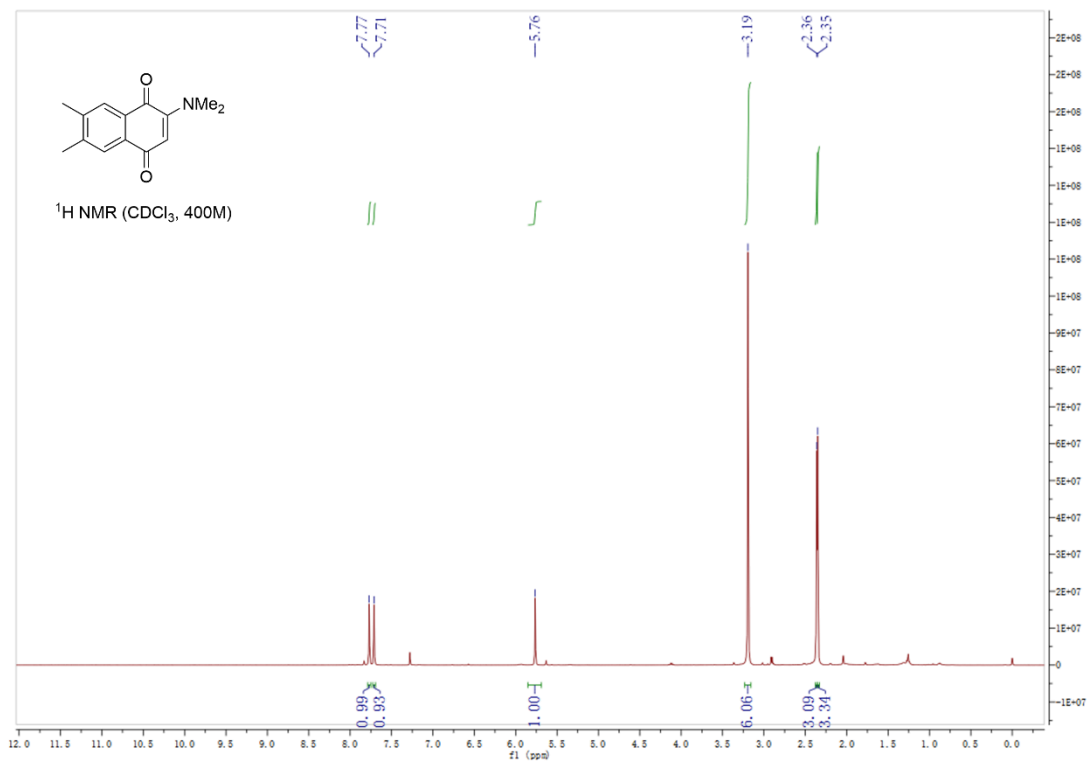
¹H NMR of **2k** (400 MHz, CDCl₃) and ¹³C NMR of **2k** (100 MHz, CDCl₃)



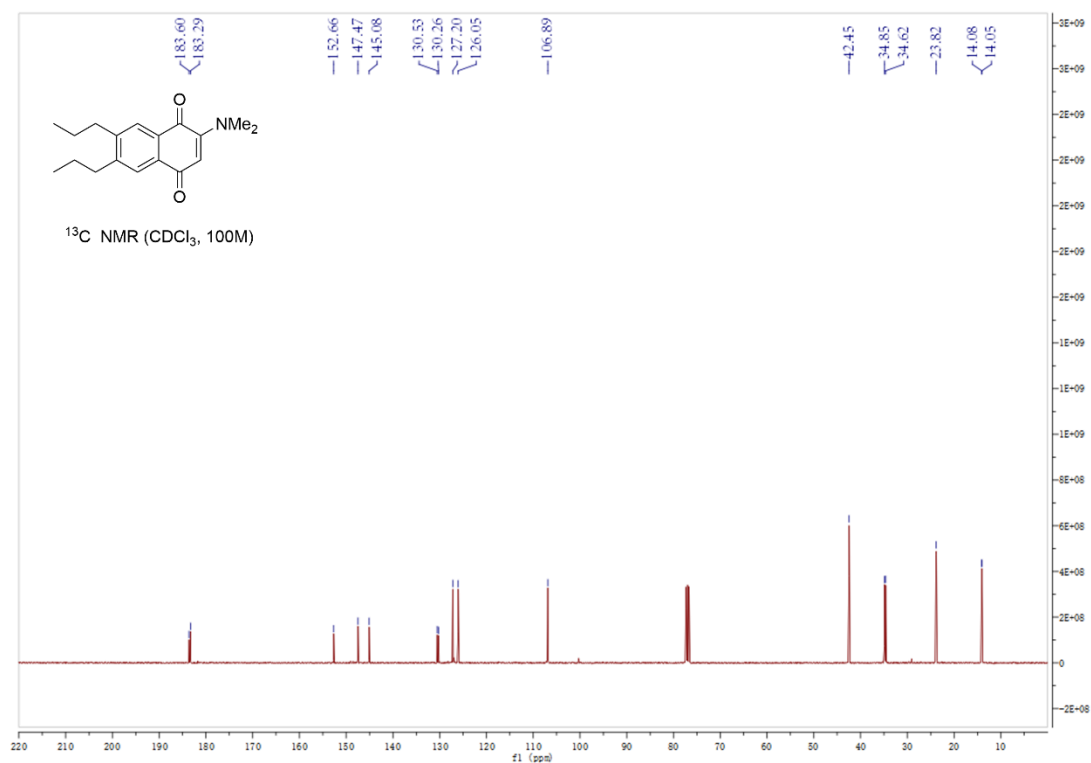
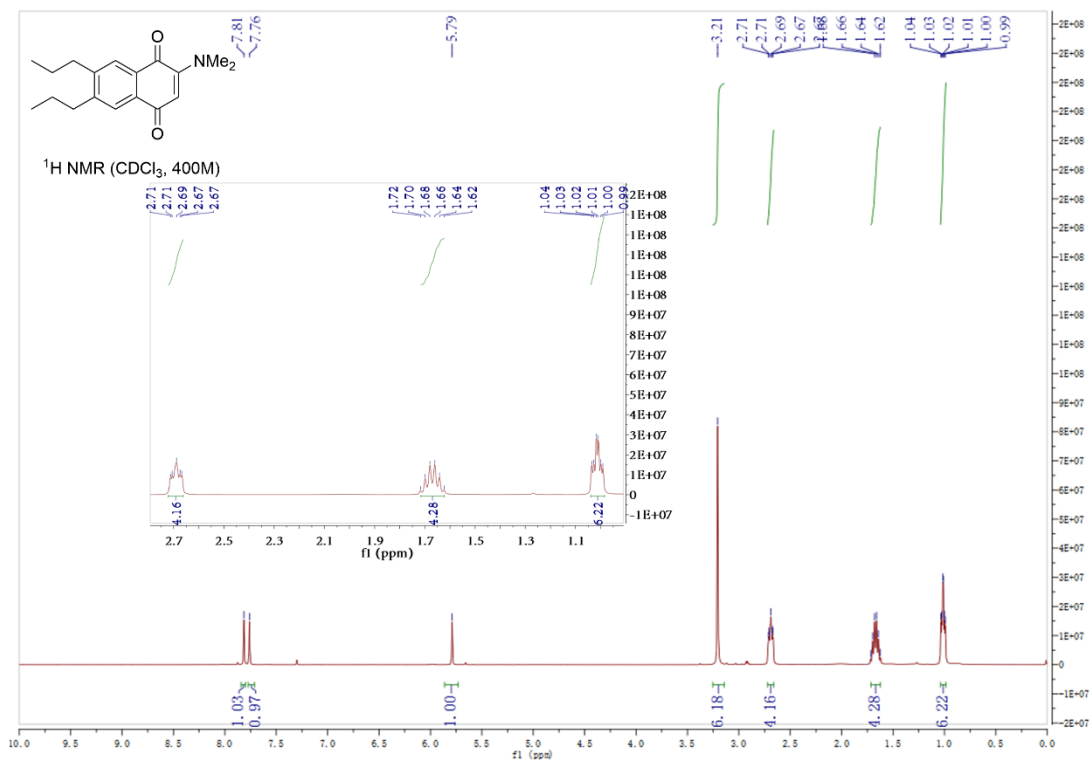
¹H NMR of **21** (400 MHz, CDCl₃) and ¹³C NMR of **21** (100 MHz, CDCl₃)



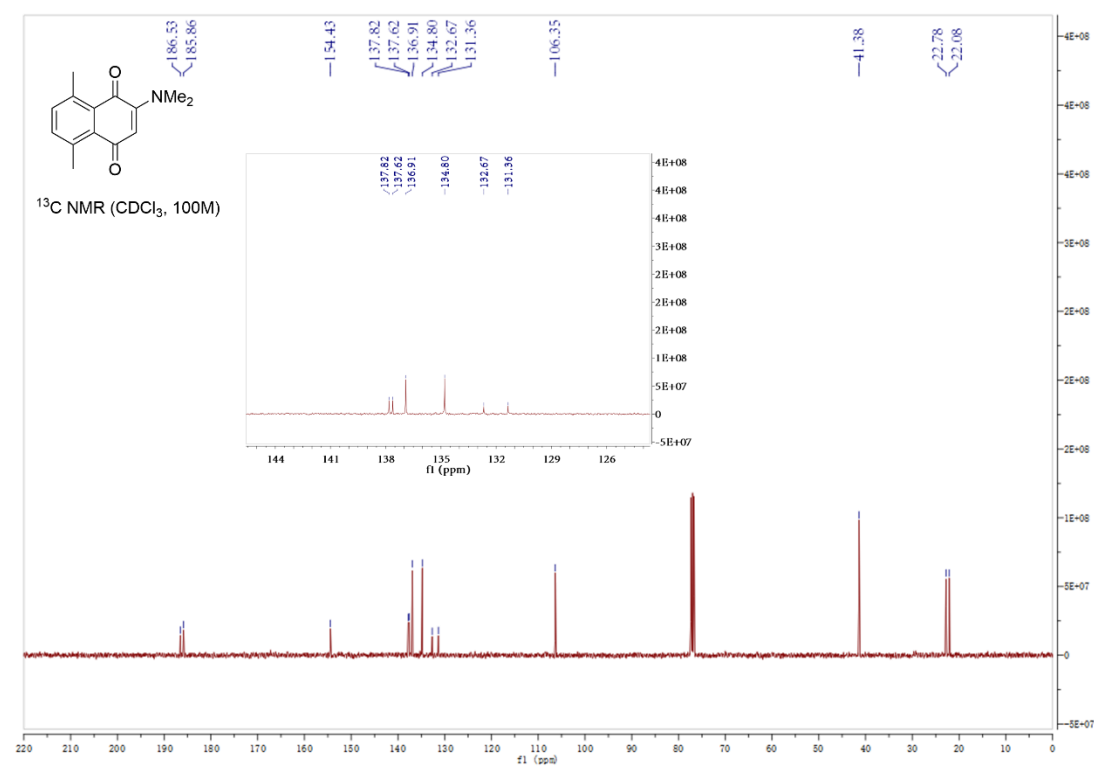
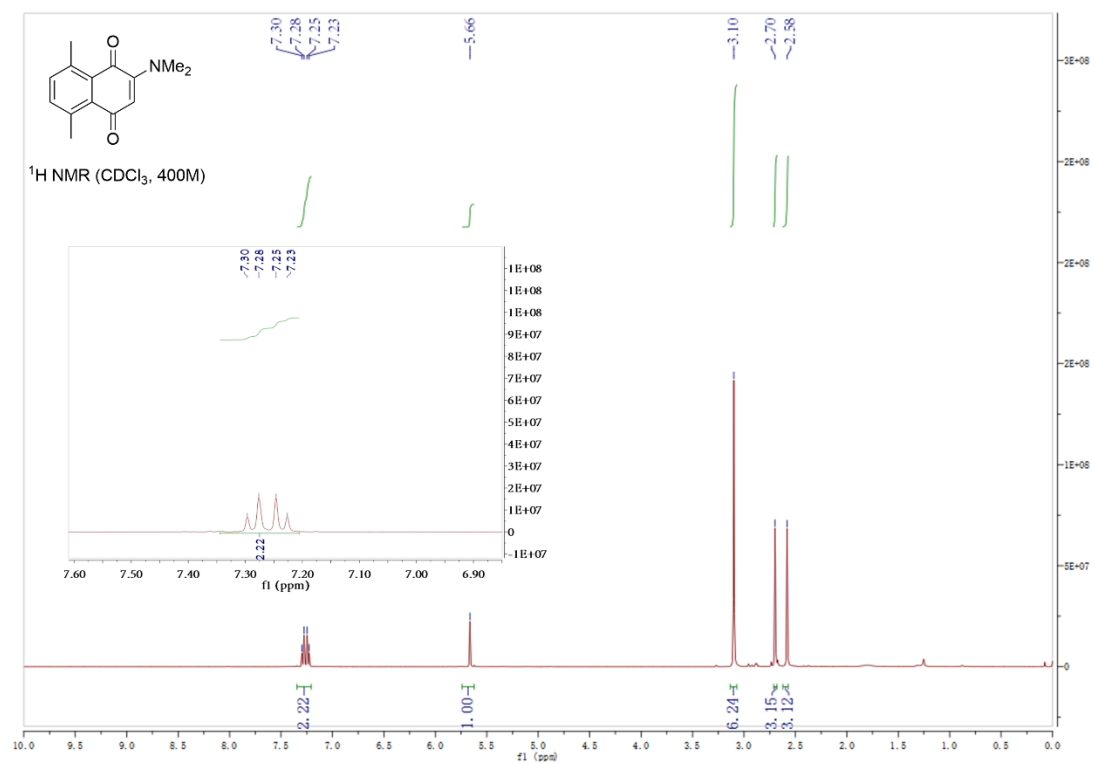
¹H NMR of **4a** (400 MHz, CDCl₃) and ¹³C NMR of **4a** (100 MHz, CDCl₃)



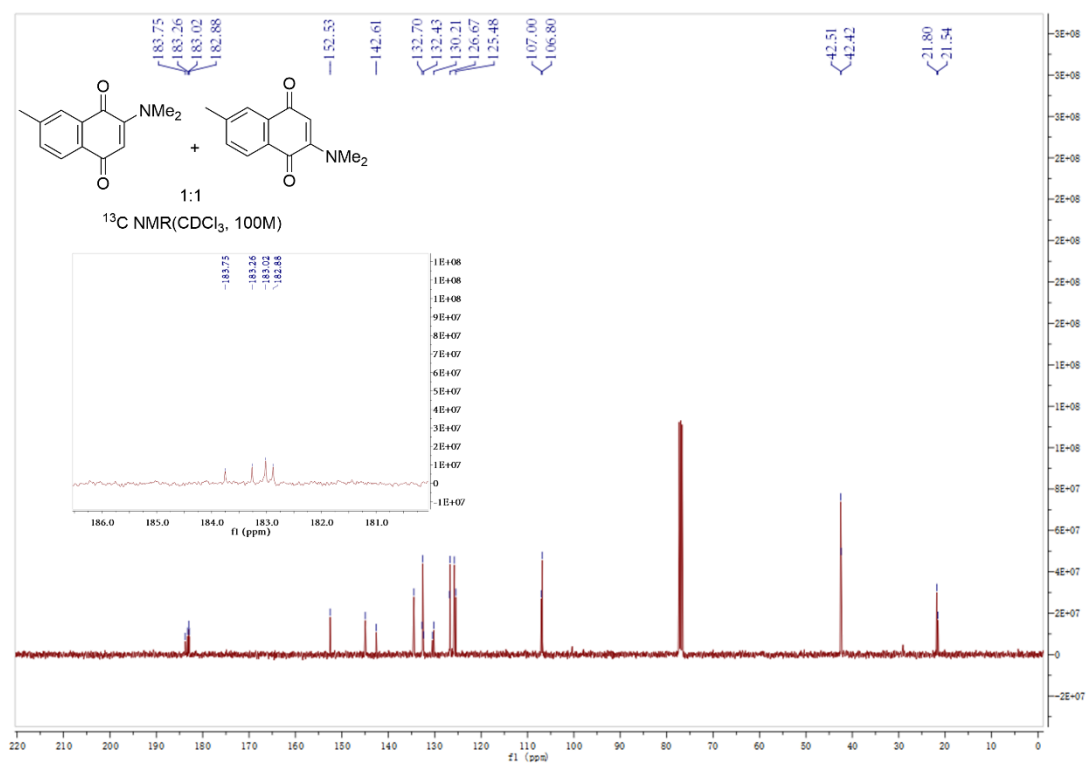
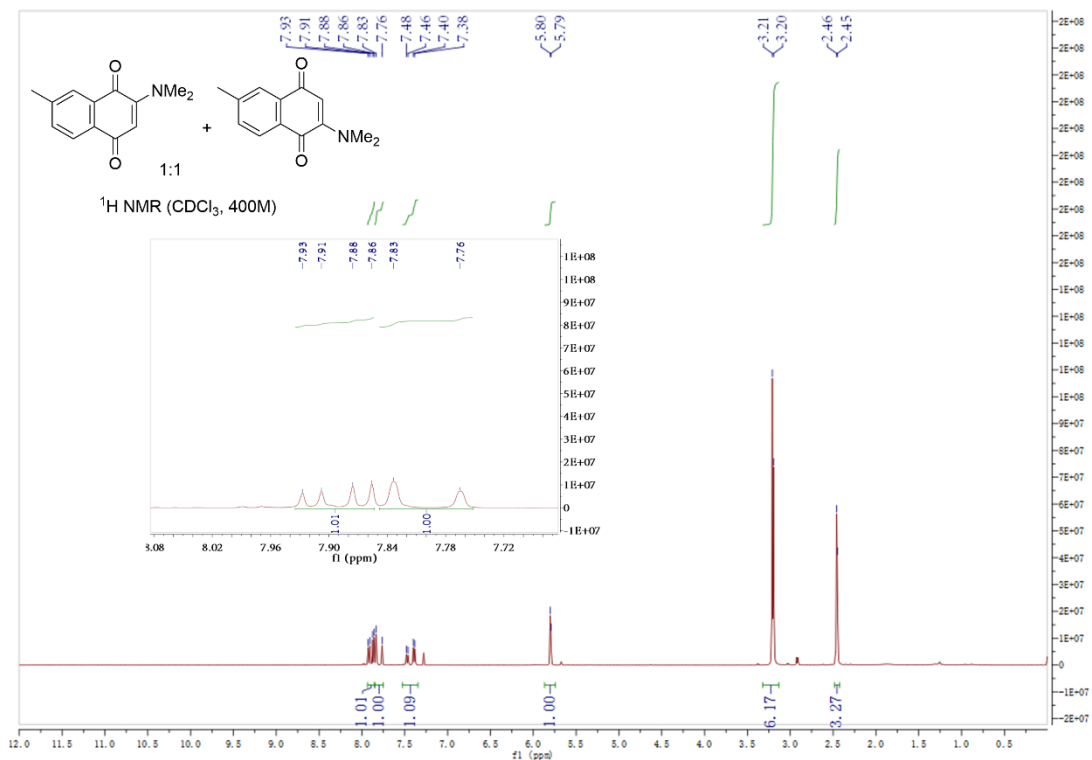
¹H NMR of **4b** (400 MHz, CDCl₃) and ¹³C NMR of **4b** (100 MHz, CDCl₃)



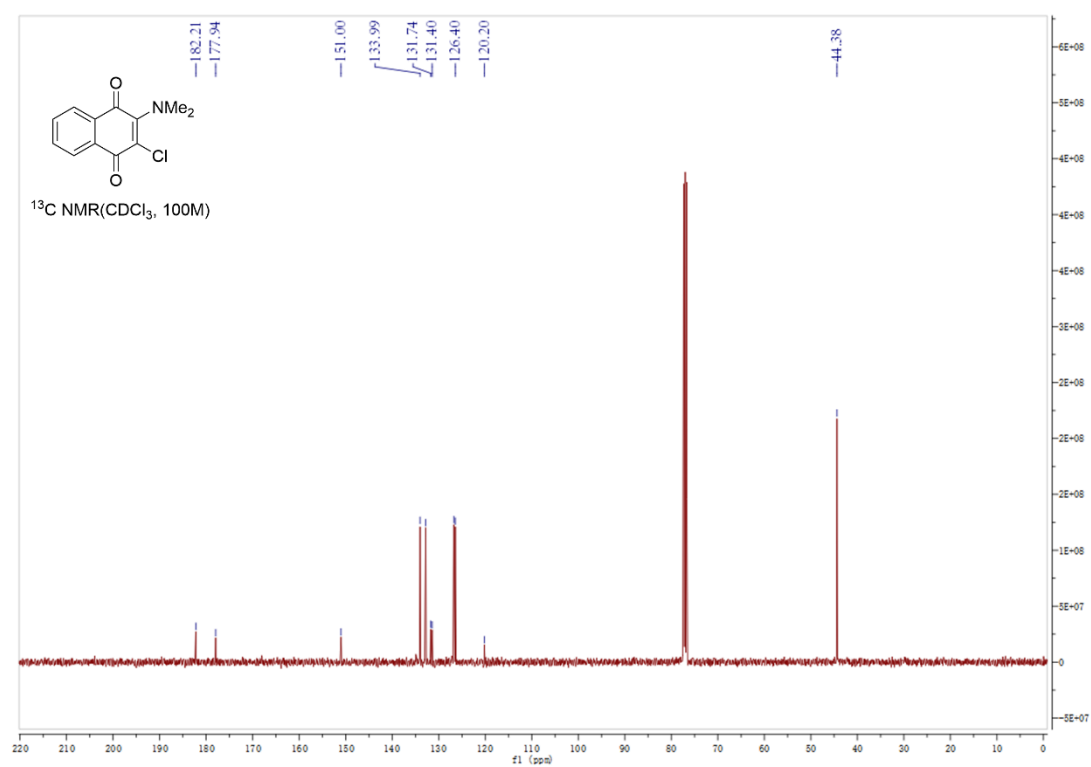
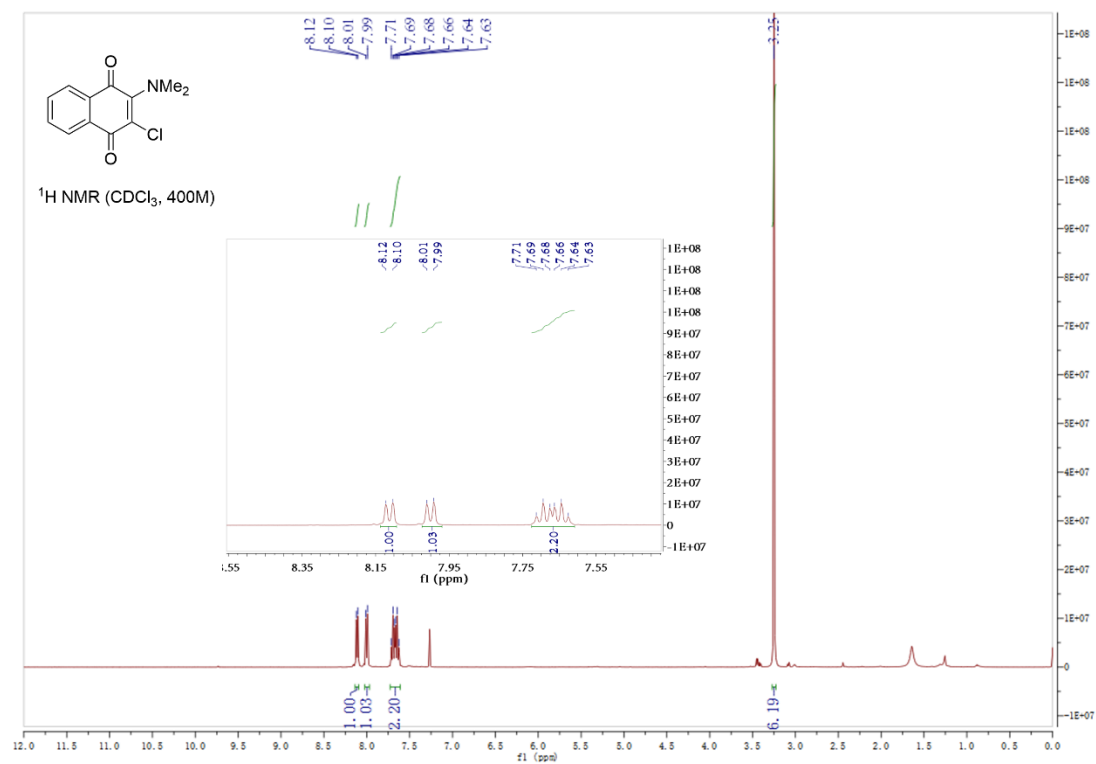
¹H NMR of **4c** (400 MHz, CDCl₃) and ¹³C NMR of **4c** (100 MHz, CDCl₃)



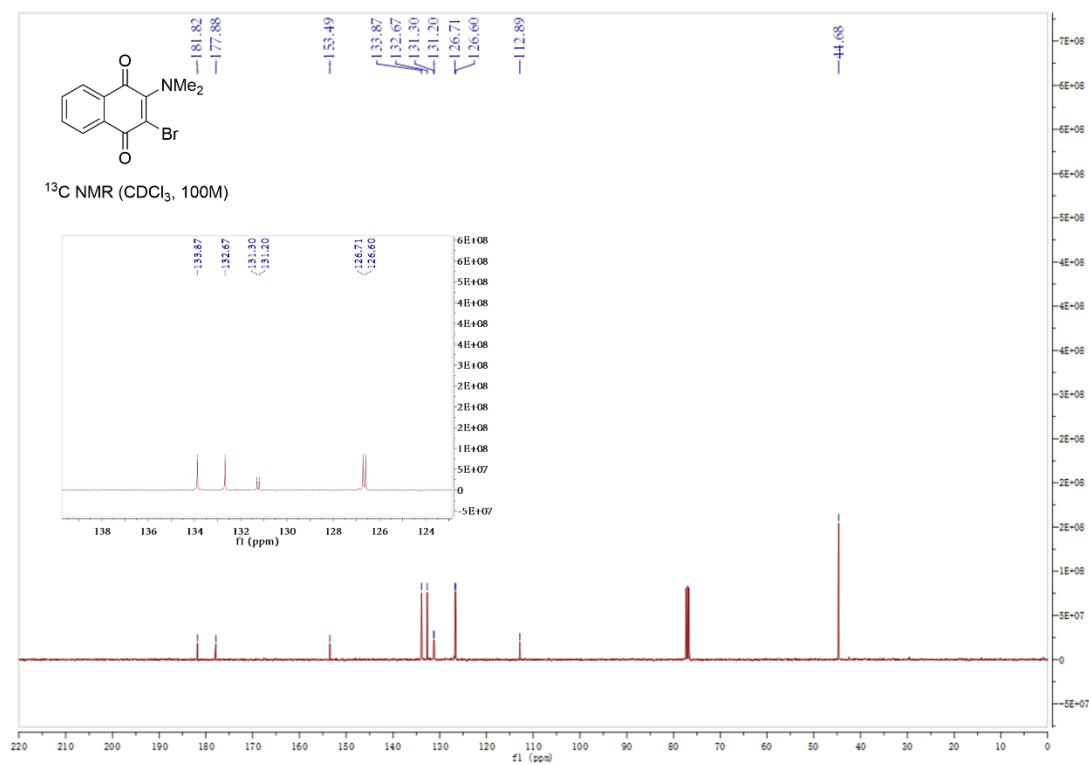
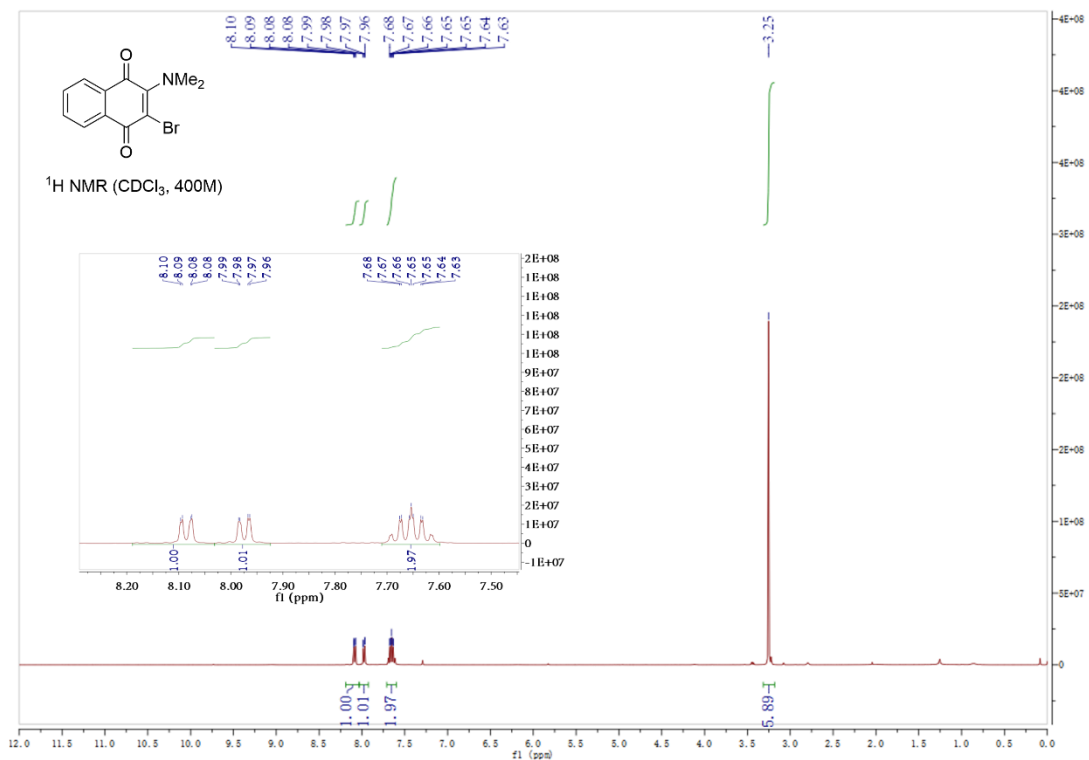
¹H NMR of **4d** (400 MHz, CDCl₃) and ¹³C NMR of **4d** (100 MHz, CDCl₃)



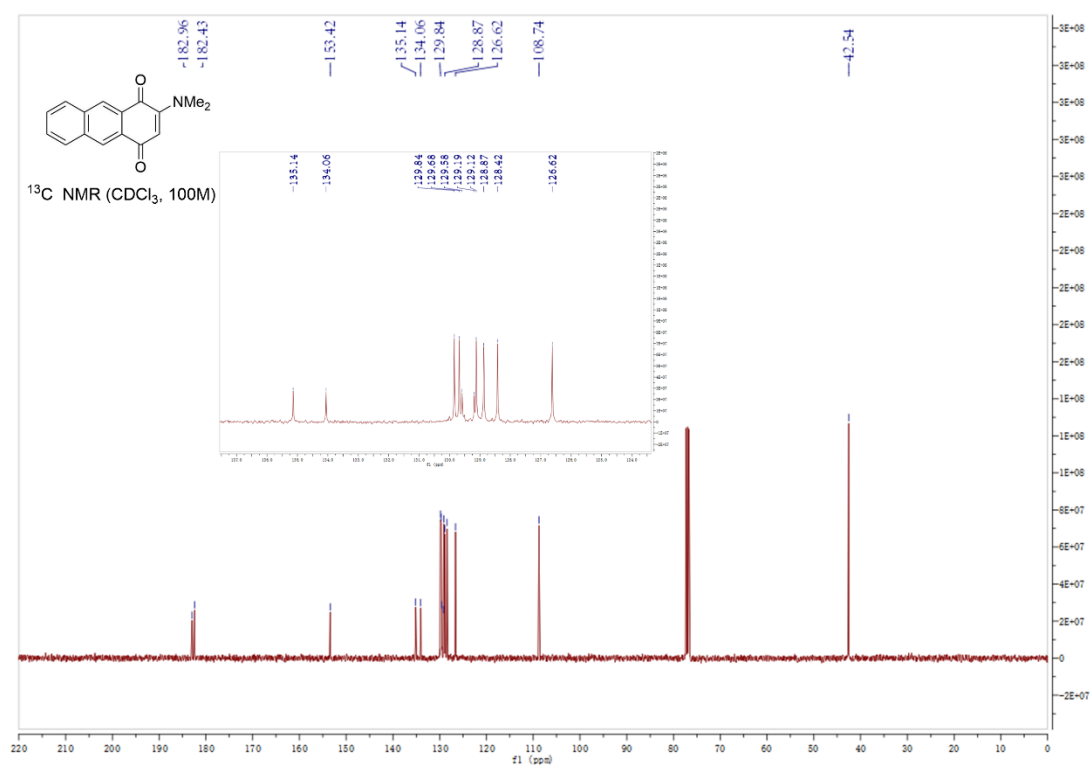
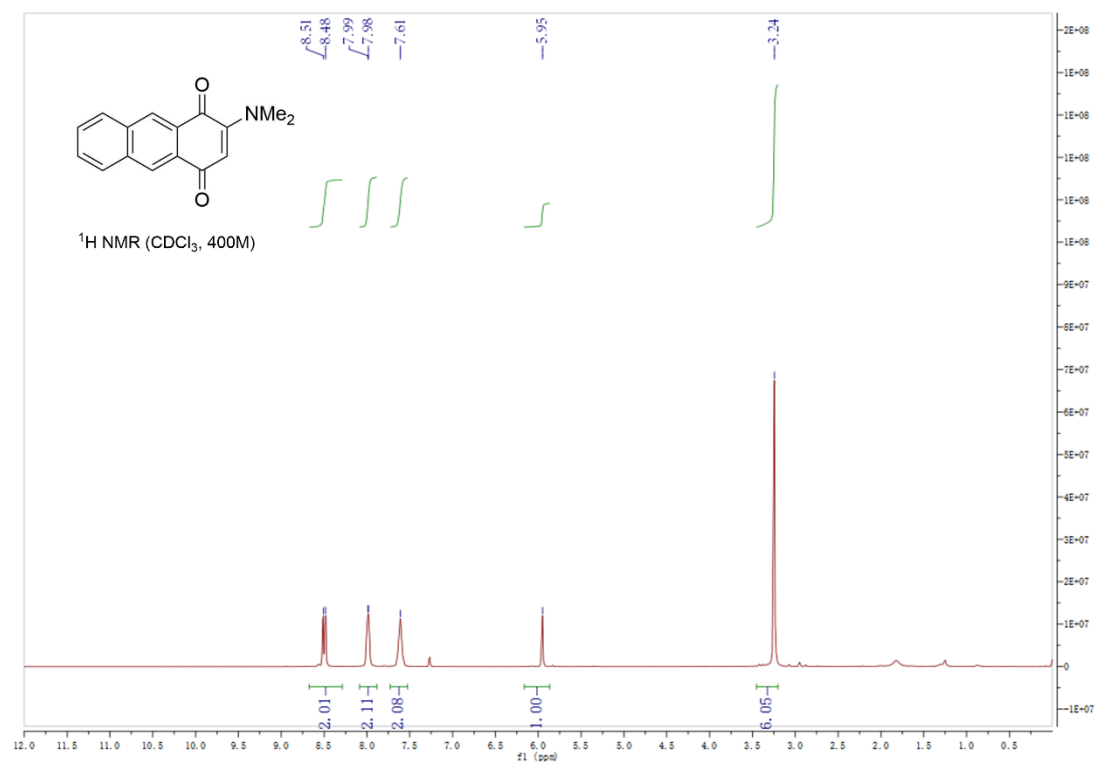
¹H NMR of **4e** (400 MHz, CDCl₃) and ¹³C NMR of **4e** (100 MHz, CDCl₃)



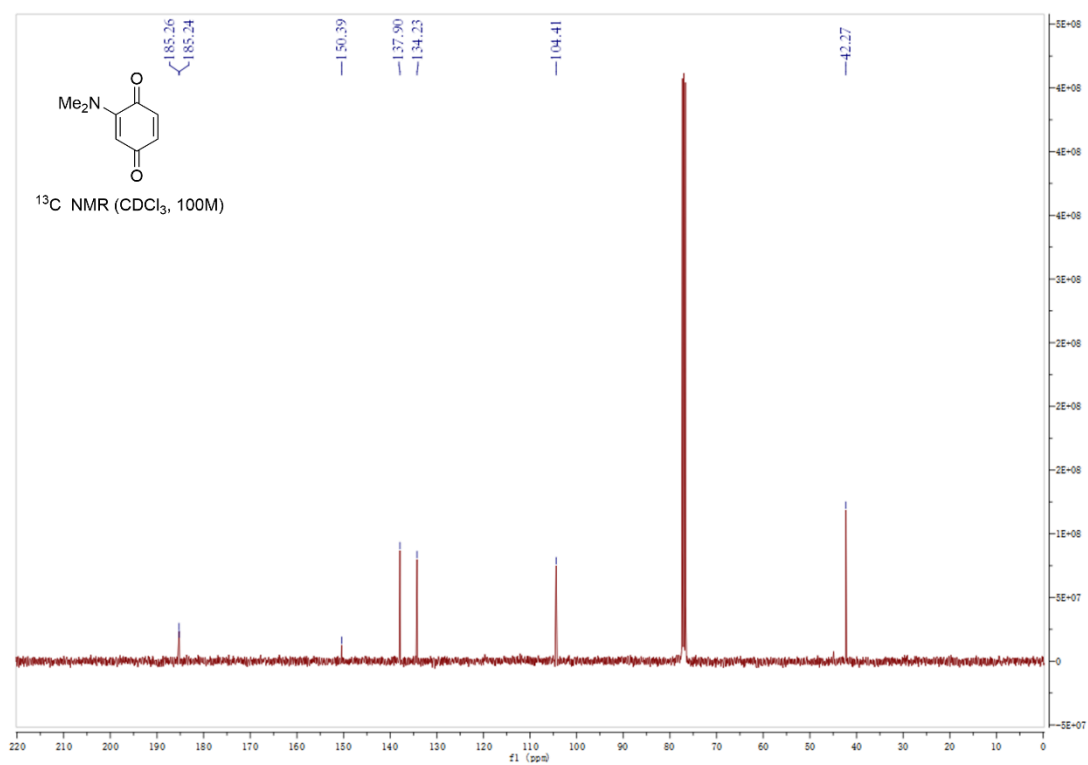
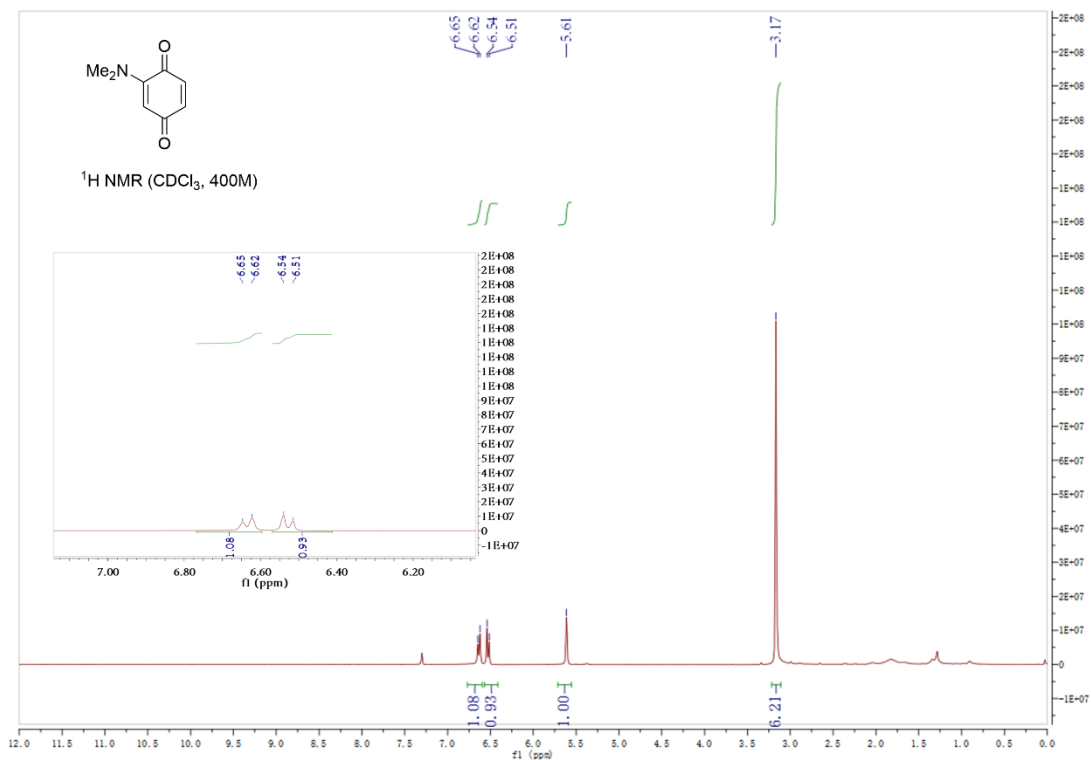
¹H NMR of **4f** (400 MHz, CDCl₃) and ¹³C NMR of **4f** (100 MHz, CDCl₃)



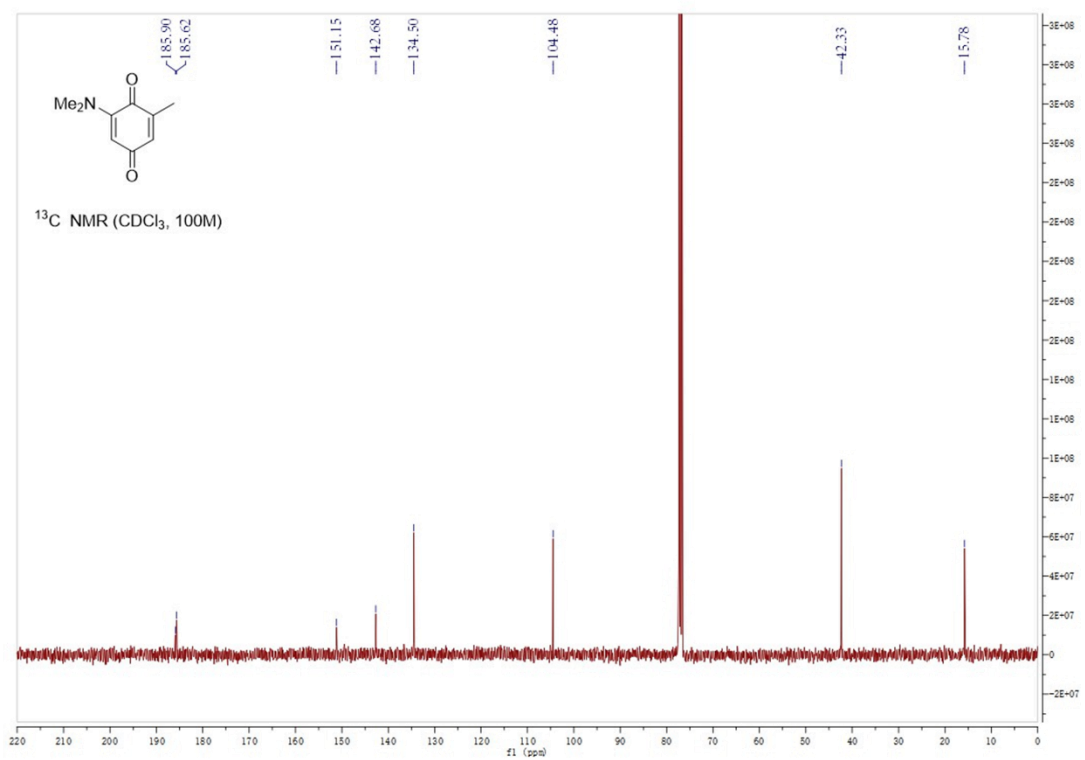
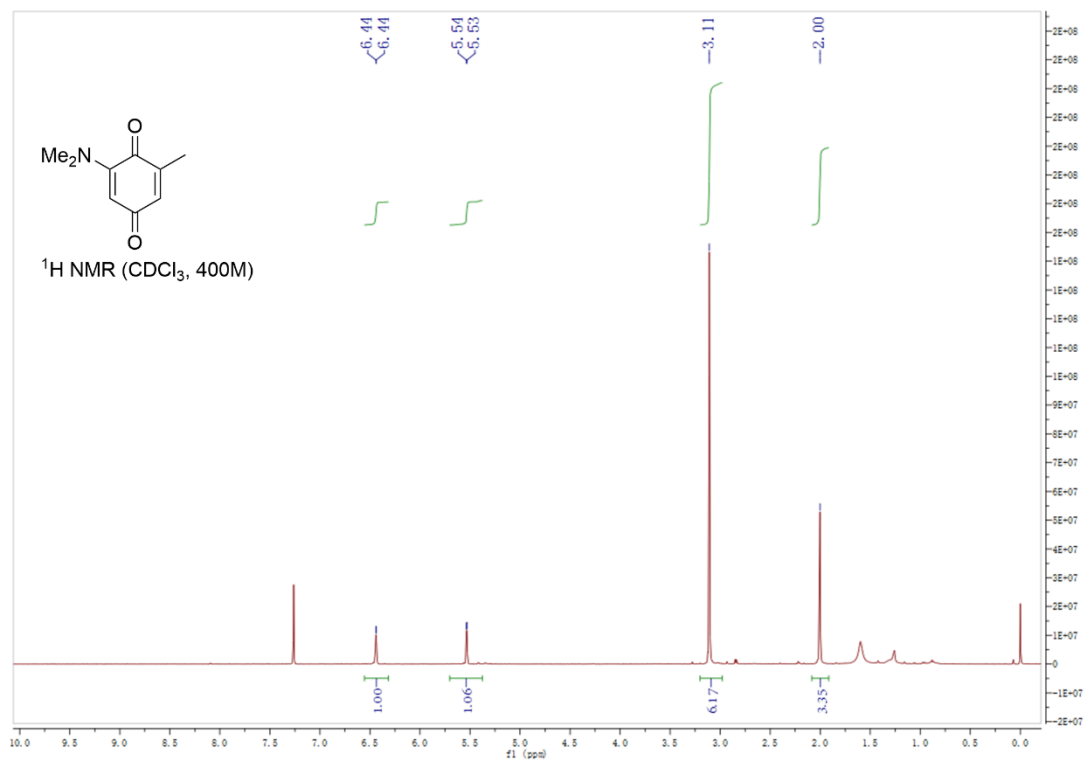
¹H NMR of **4g** (400 MHz, CDCl₃) and ¹³C NMR of **4g** (100 MHz, CDCl₃)



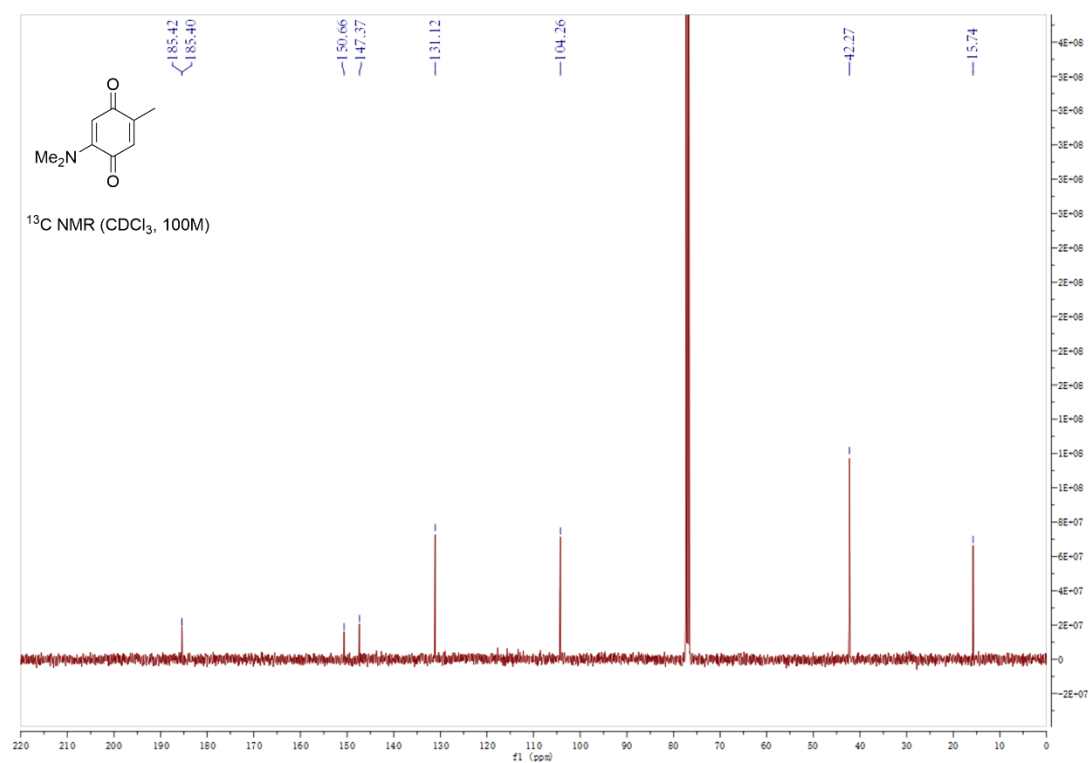
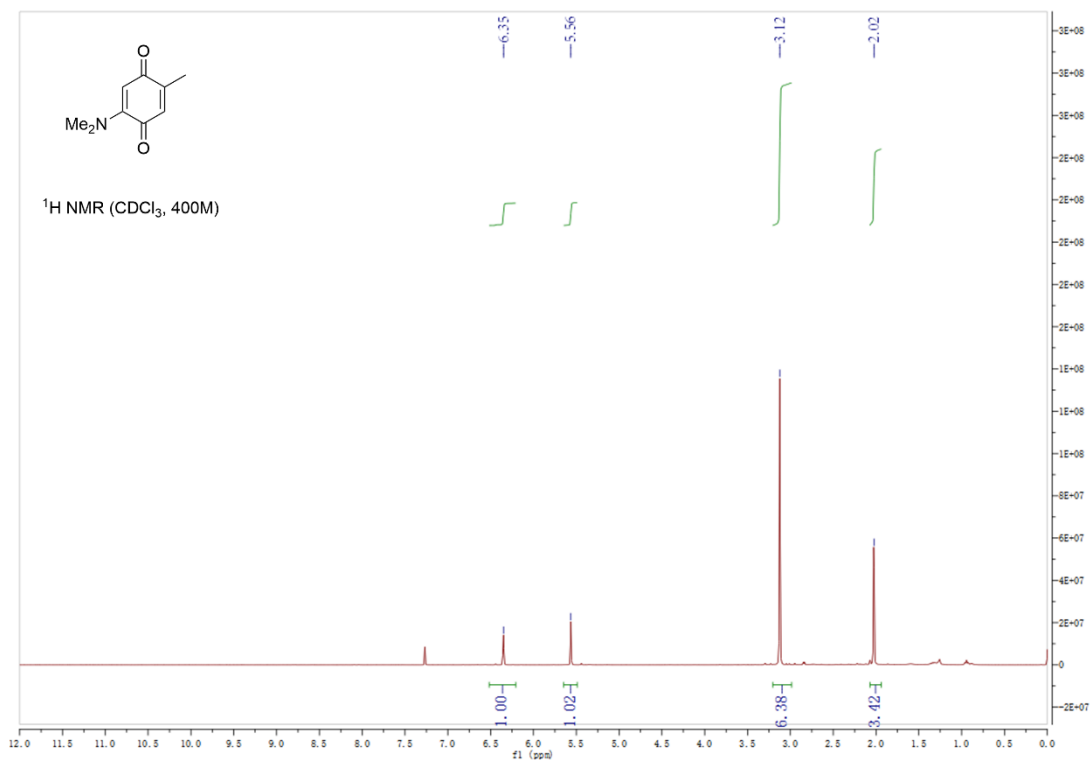
¹H NMR of **4h** (400 MHz, CDCl₃) and ¹³C NMR of **4h** (100 MHz, CDCl₃)



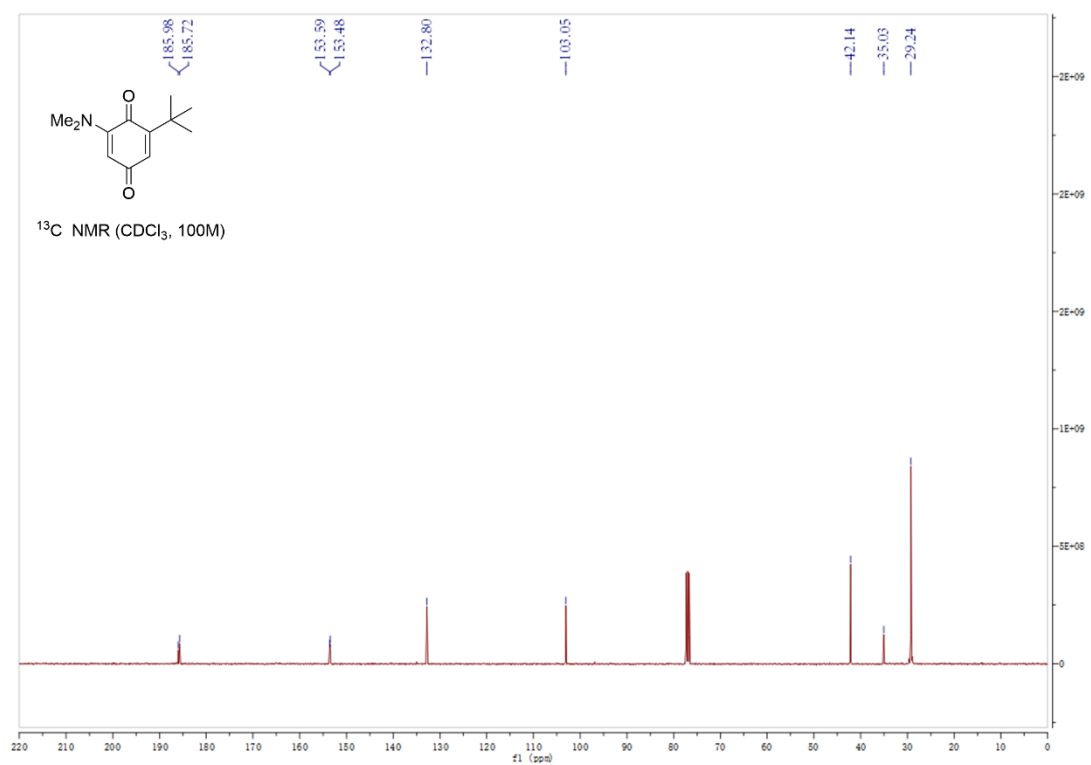
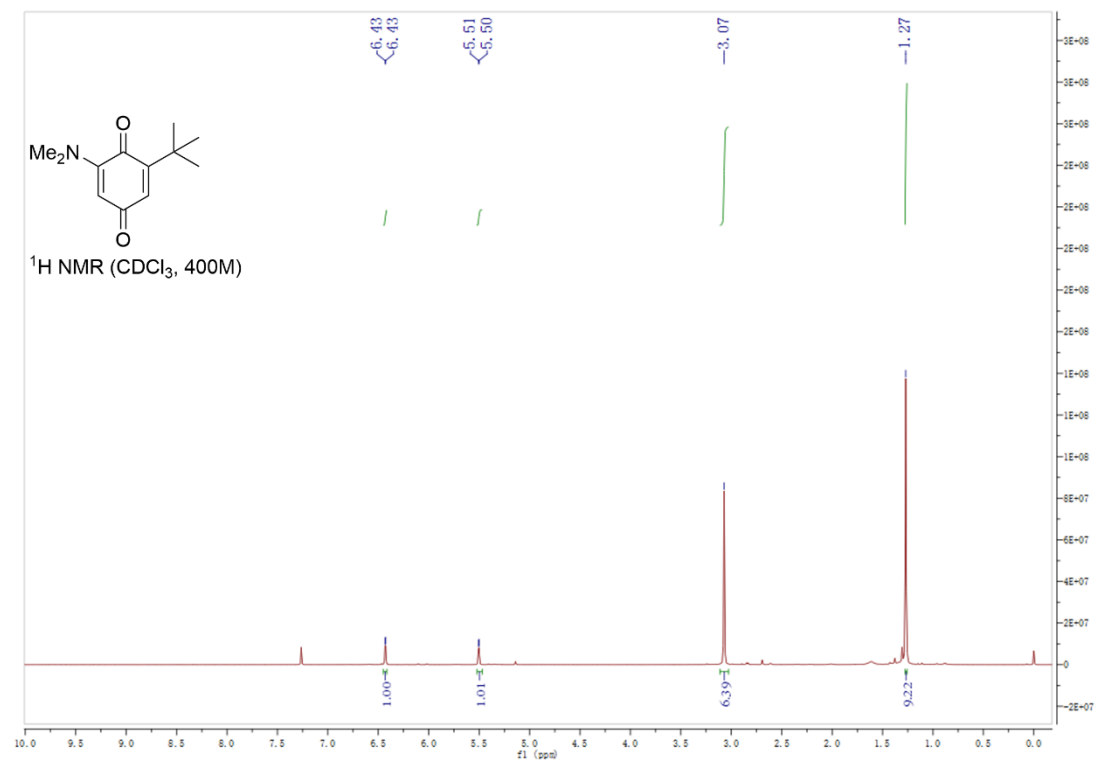
¹H NMR of **4i** (400 MHz, CDCl₃) and ¹³C NMR of **4i** (100 MHz, CDCl₃)



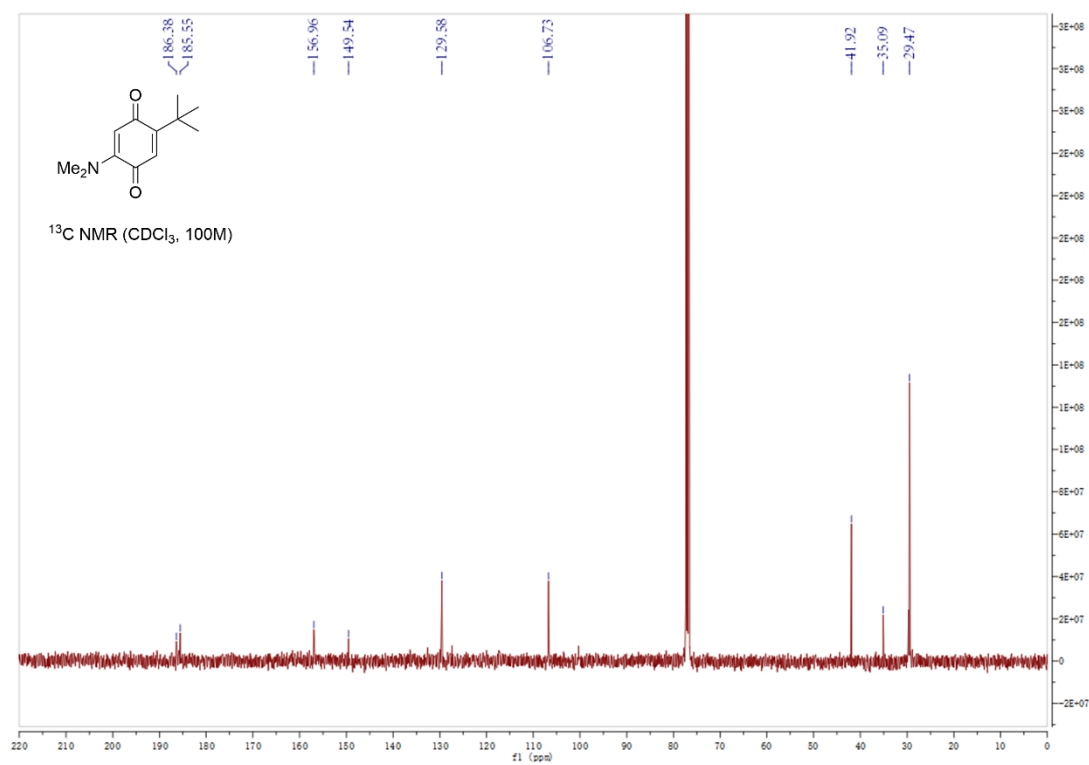
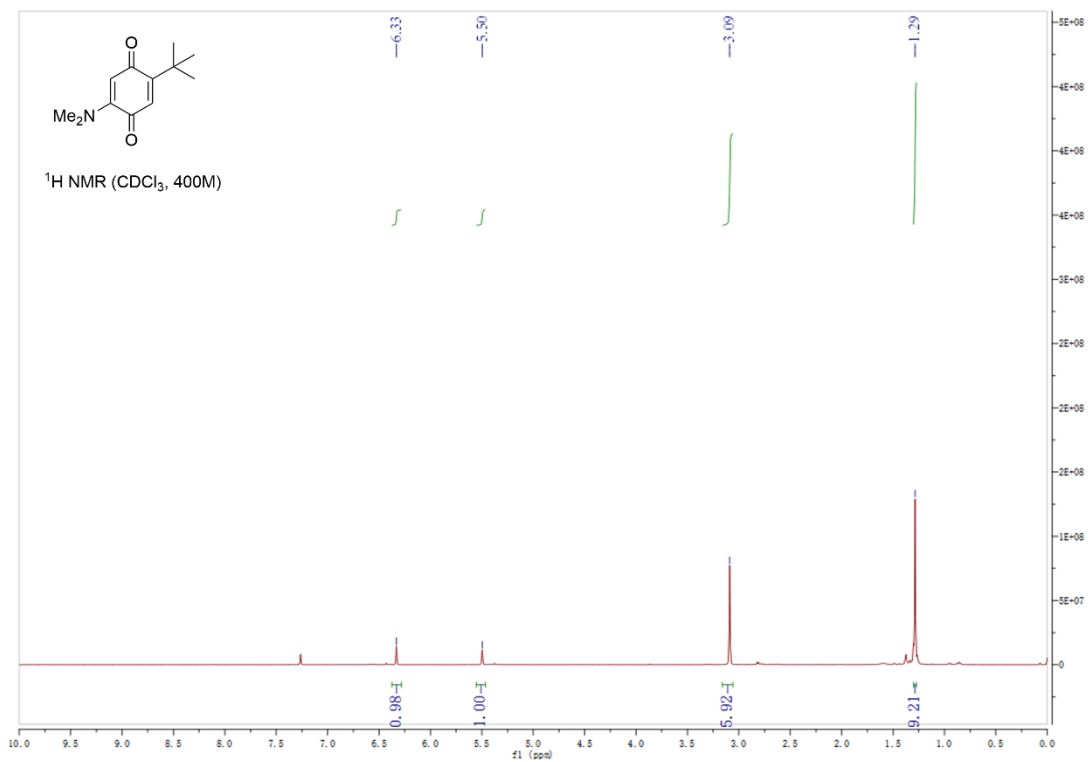
¹H NMR of **4j** (6-NMe₂) (400 MHz, CDCl₃) and ¹³C NMR of **4j** (6-NMe₂) (100 MHz, CDCl₃)



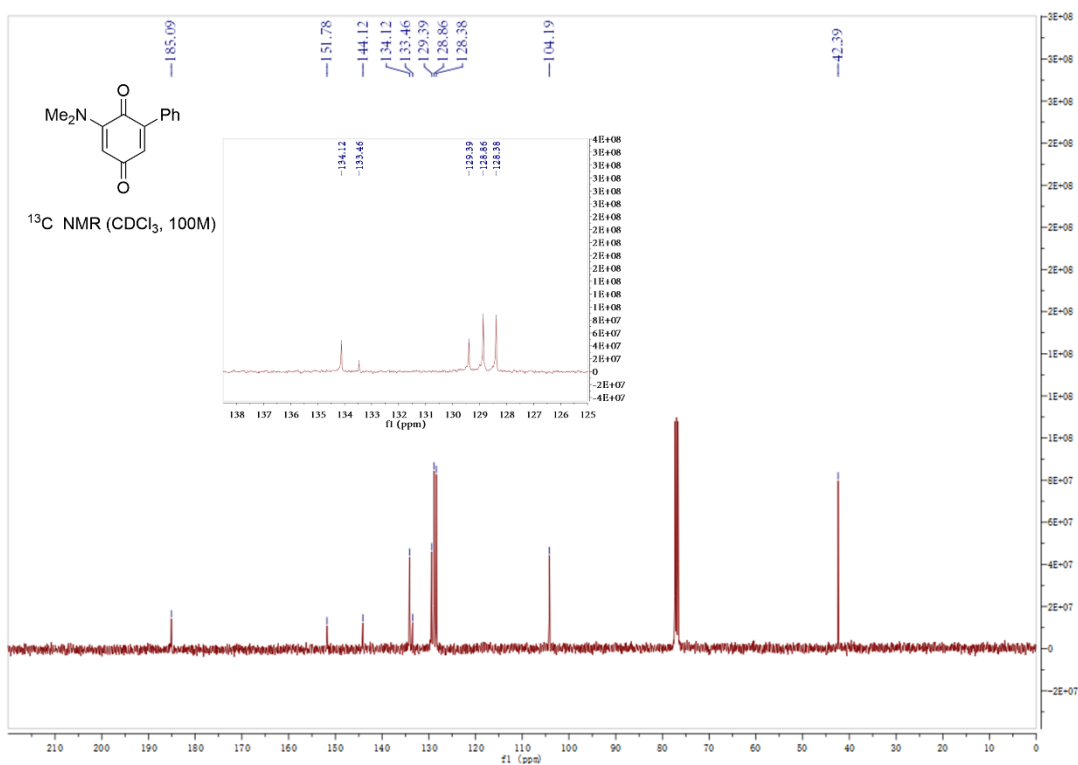
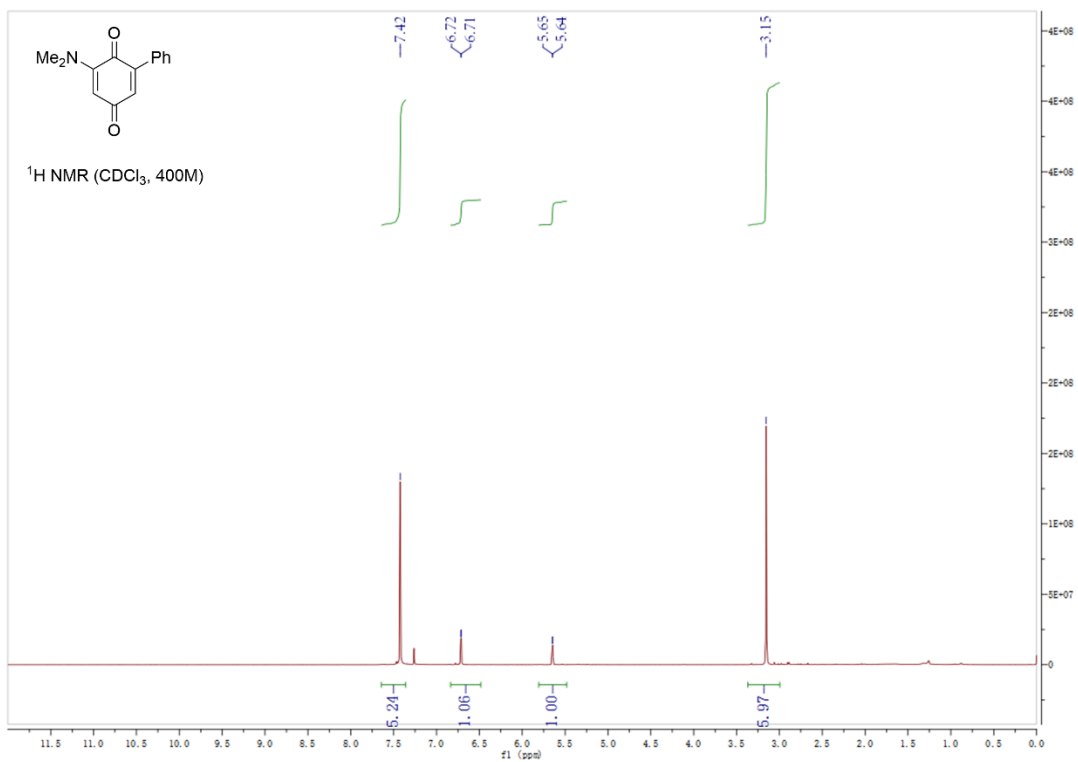
$^1\text{H NMR}$ of **4j** (5-NMe₂) (400 MHz, CDCl_3) and $^{13}\text{C NMR}$ of **4j** (5-NMe₂) (100 MHz, CDCl_3)



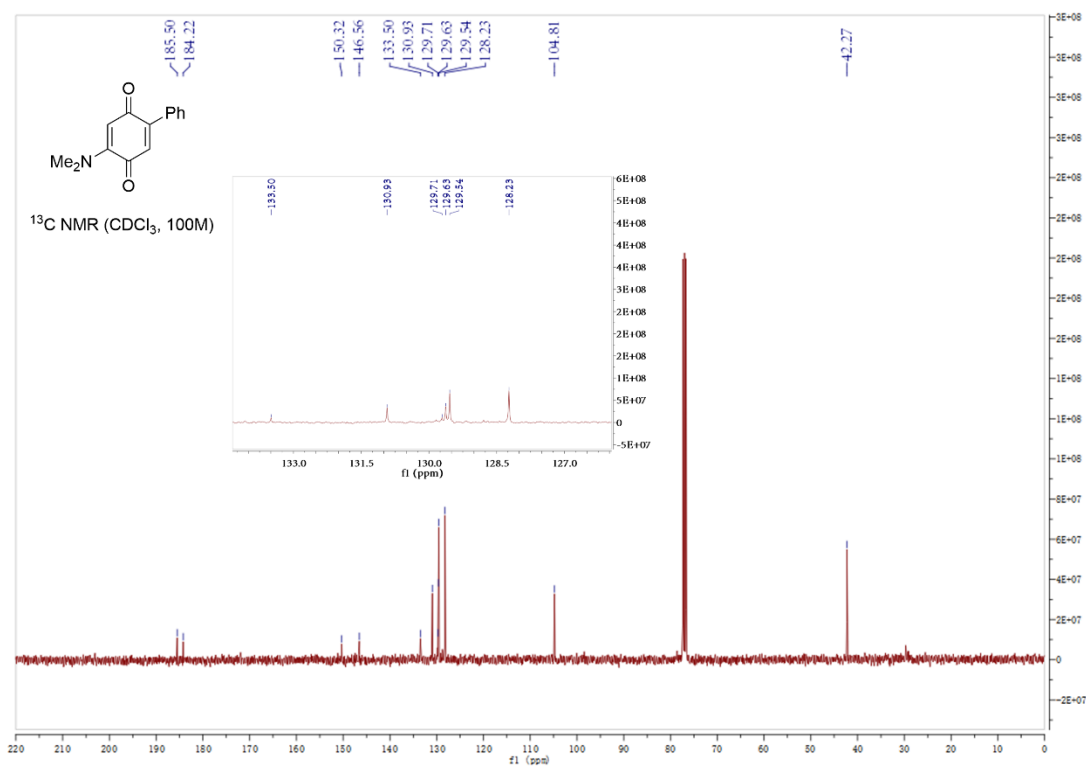
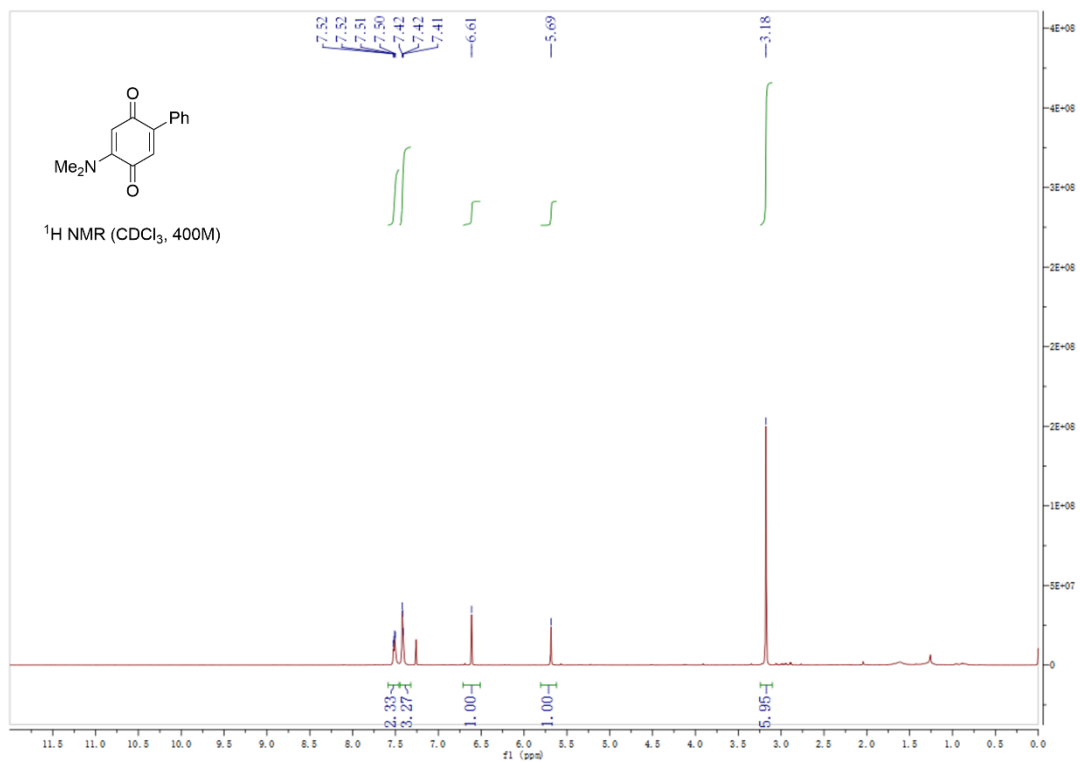
¹H NMR of **4k** (6-NMe₂) (400 MHz, CDCl₃) and ¹³C NMR of **4k** (6-NMe₂) (100 MHz, CDCl₃)



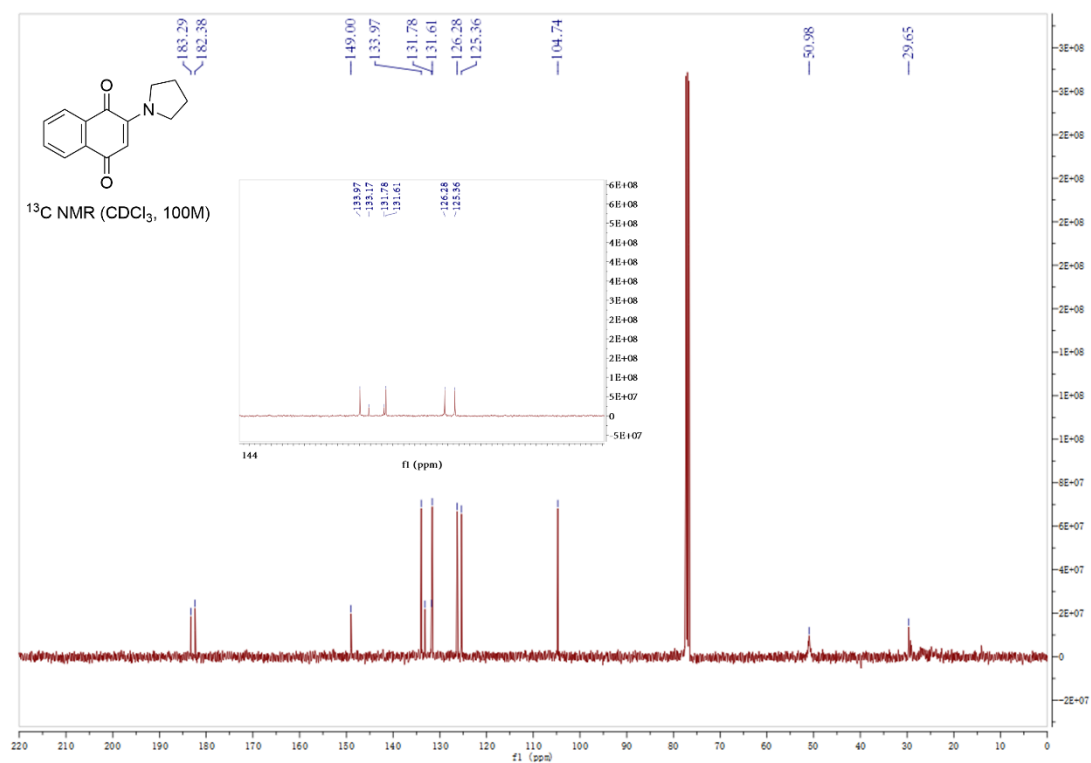
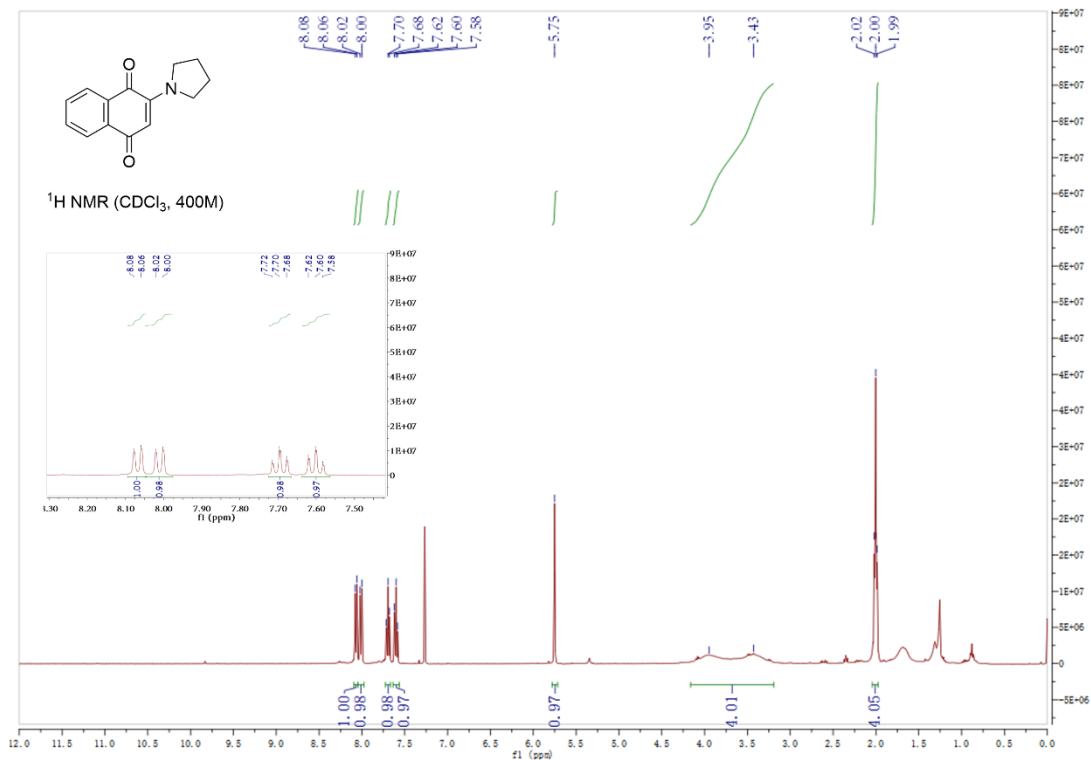
¹H NMR of **4k** (**5-NMe₂**) (400 MHz, CDCl₃) and ¹³C NMR of **4k** (**5-NMe₂**) (100 MHz, CDCl₃)



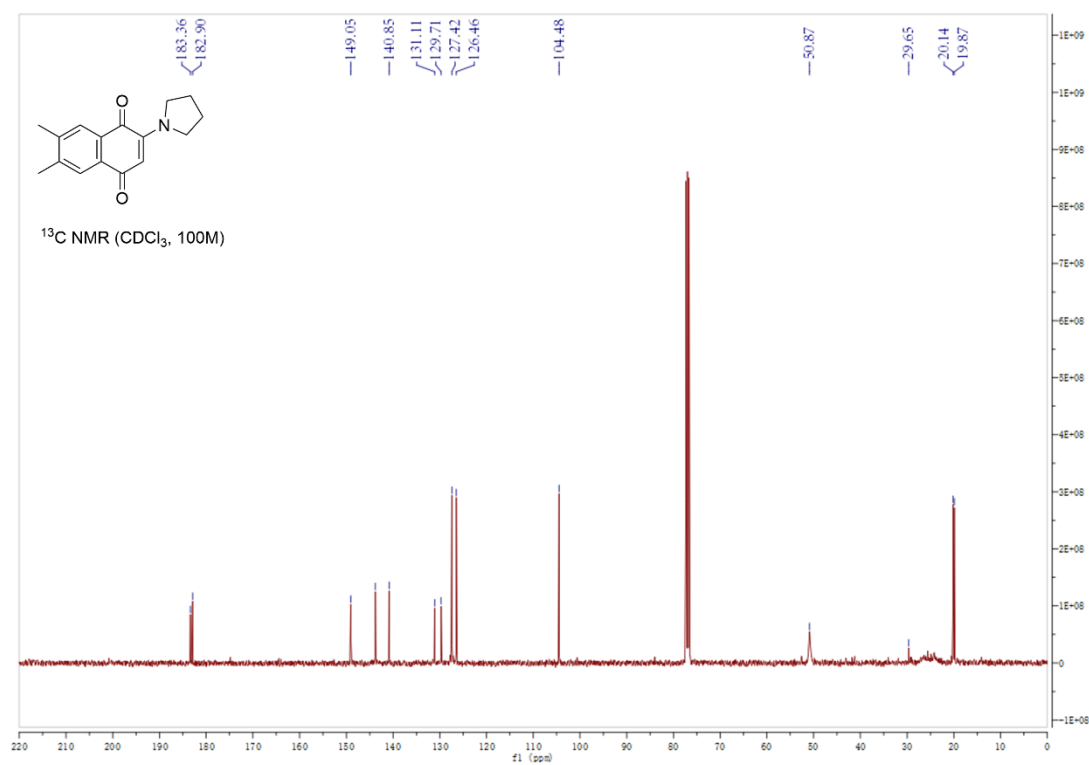
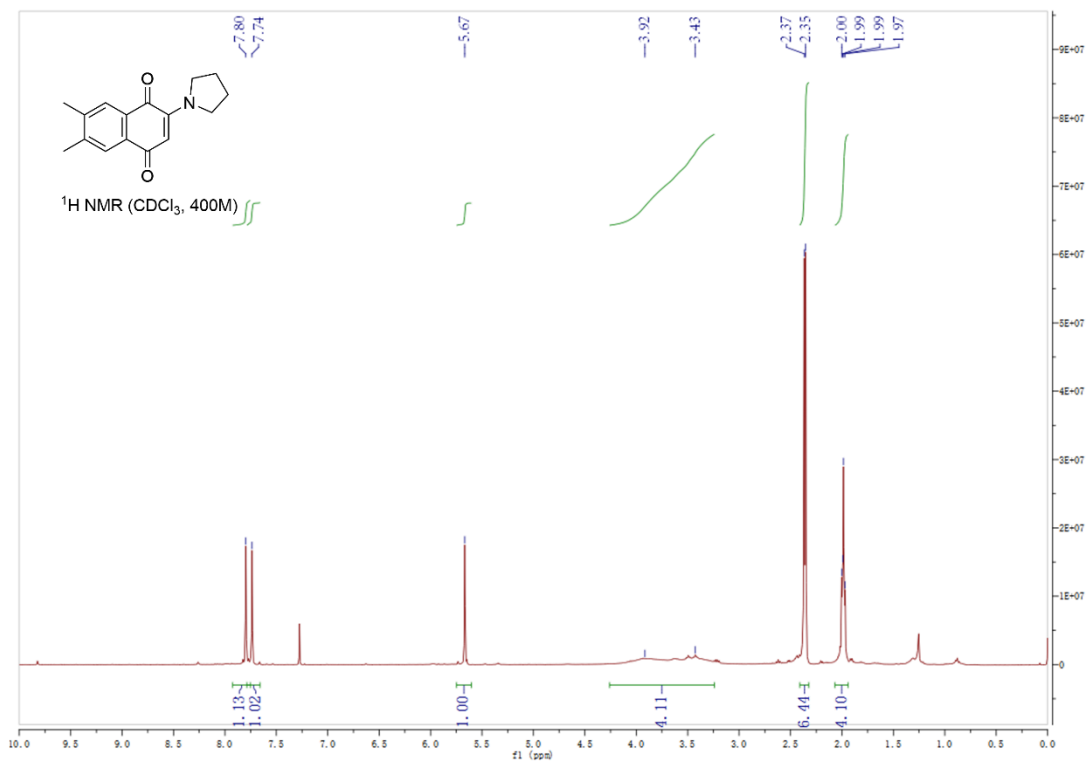
¹H NMR of **4l** (6-NMe₂) (400 MHz, CDCl₃) and ¹³C NMR of **4l** (6-NMe₂) (100 MHz, CDCl₃)



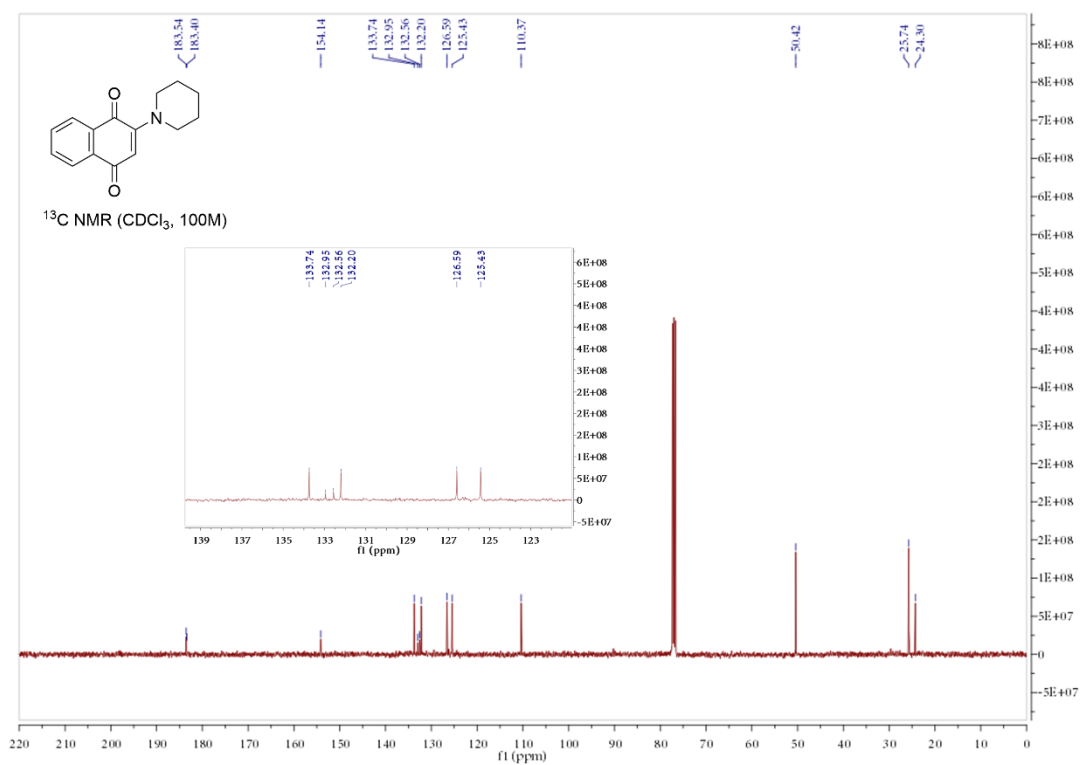
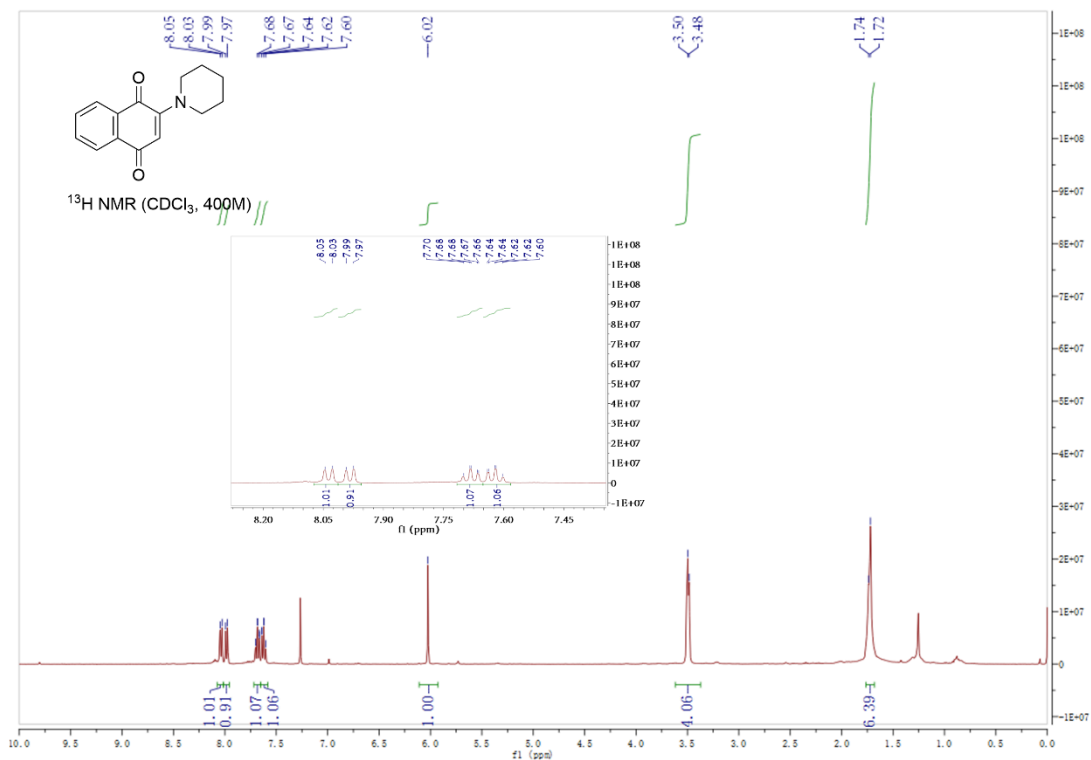
¹H NMR of **4I** (5-NMe₂) (400 MHz, CDCl₃) and ¹³C NMR of **4I** (5-NMe₂) (100 MHz, CDCl₃)



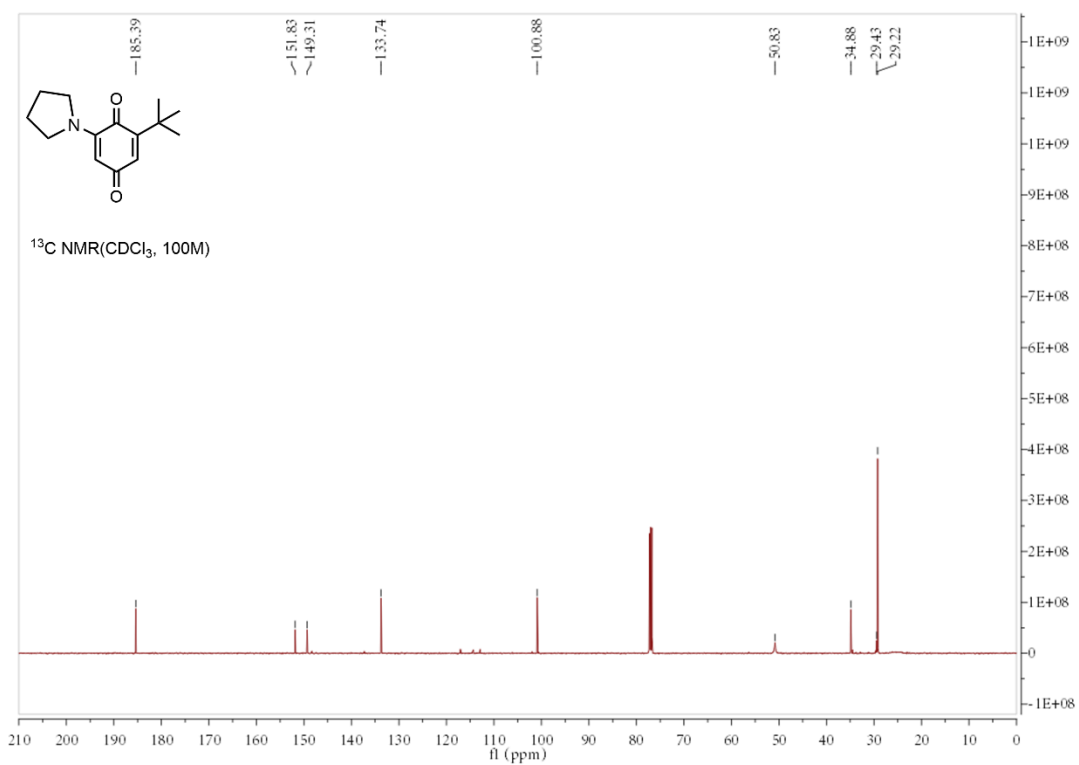
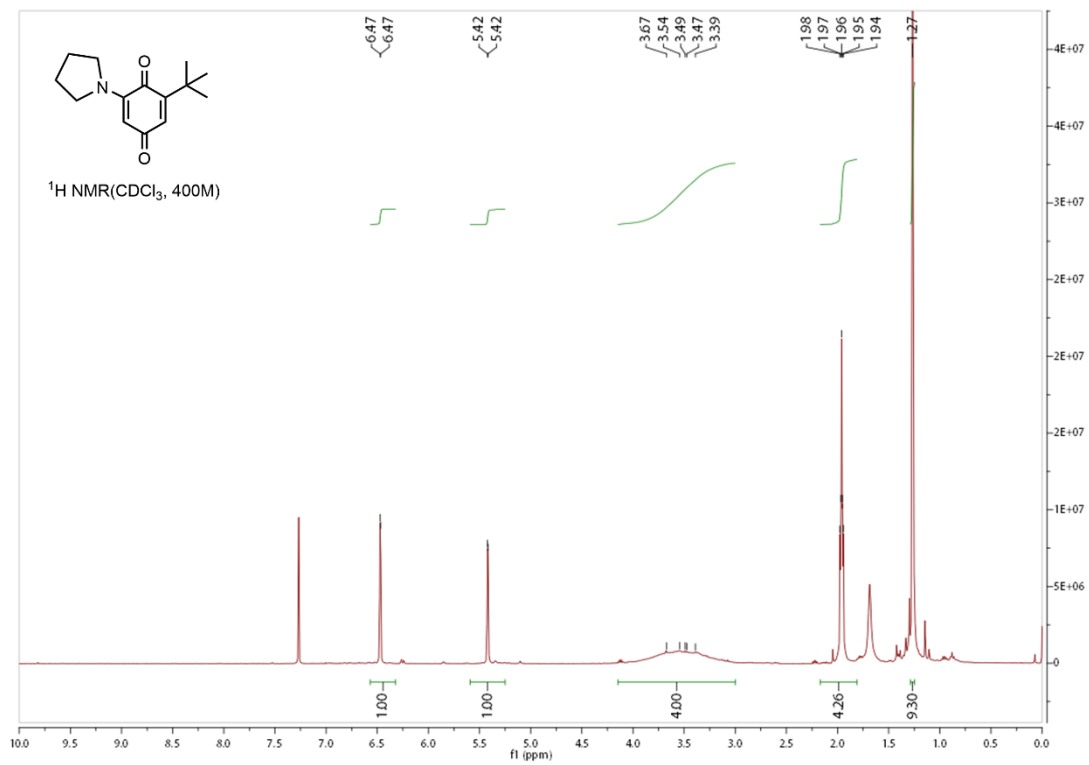
¹H NMR of **4m** (400 MHz, CDCl₃) and ¹³C NMR of **4m** (100 MHz, CDCl₃)



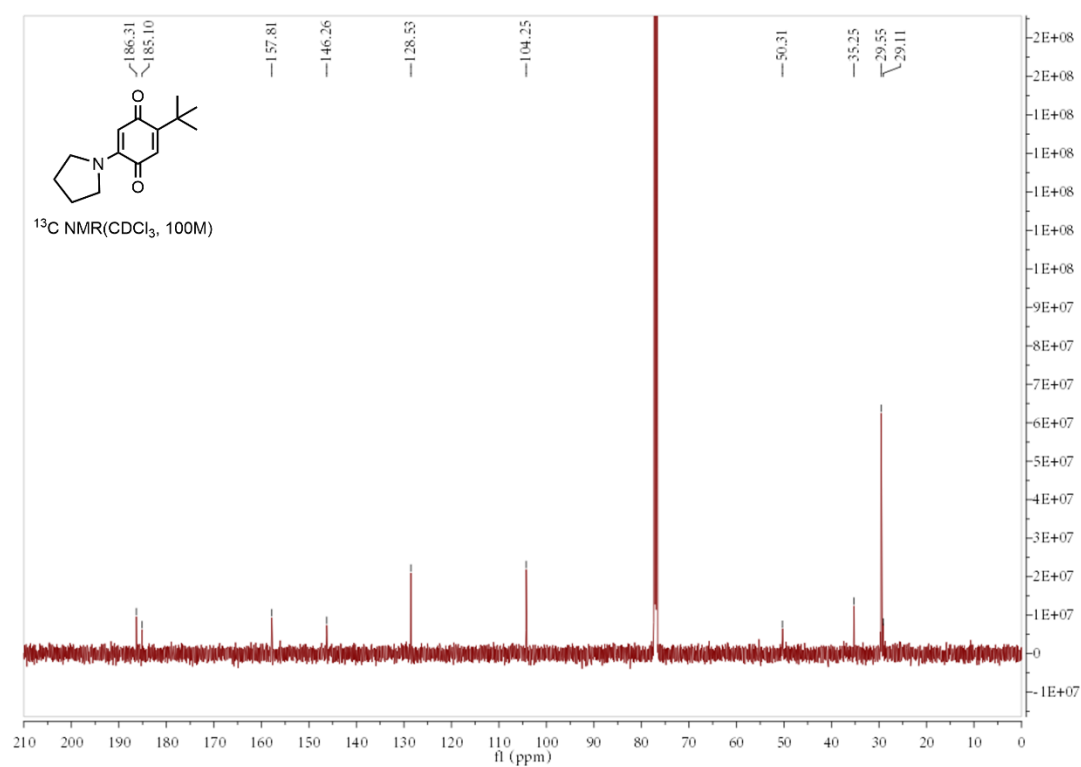
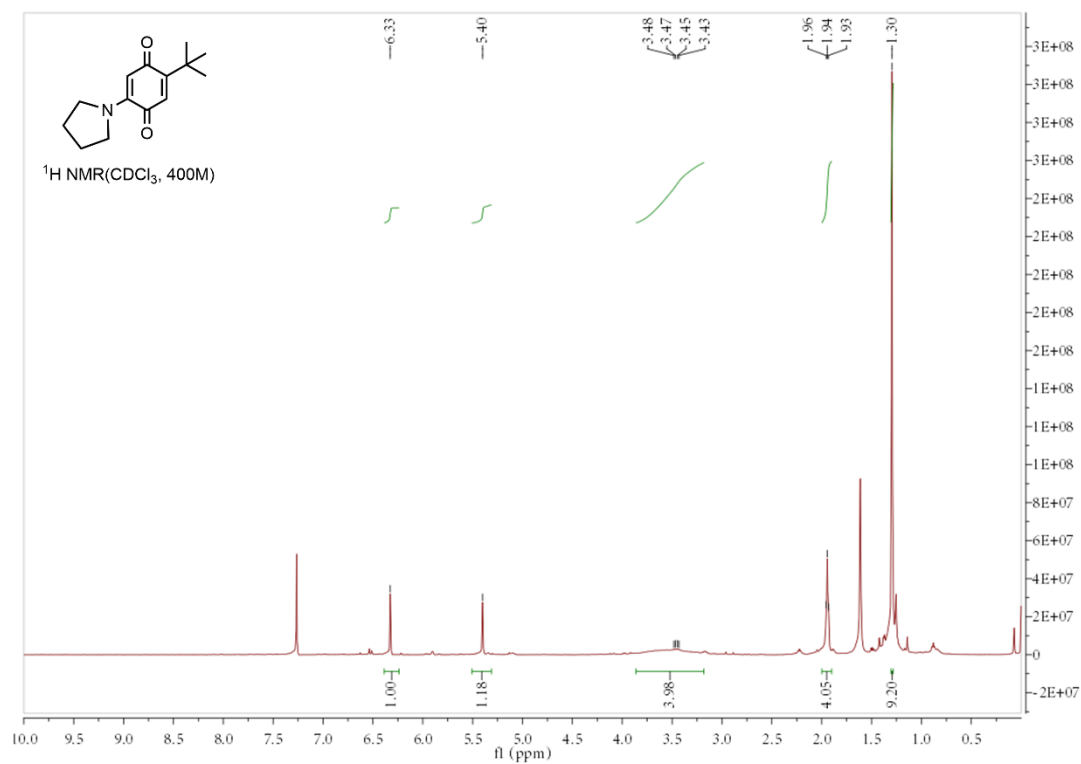
¹H NMR of **4n** (400 MHz, CDCl₃) and ¹³C NMR of **4n** (100 MHz, CDCl₃)



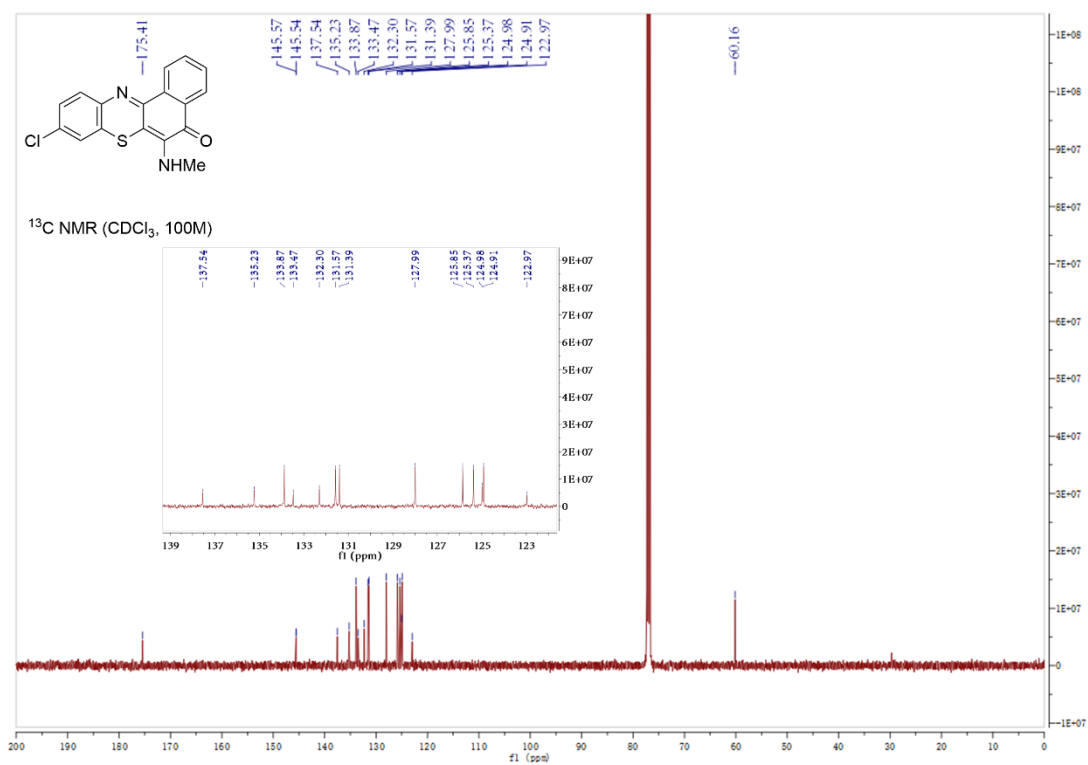
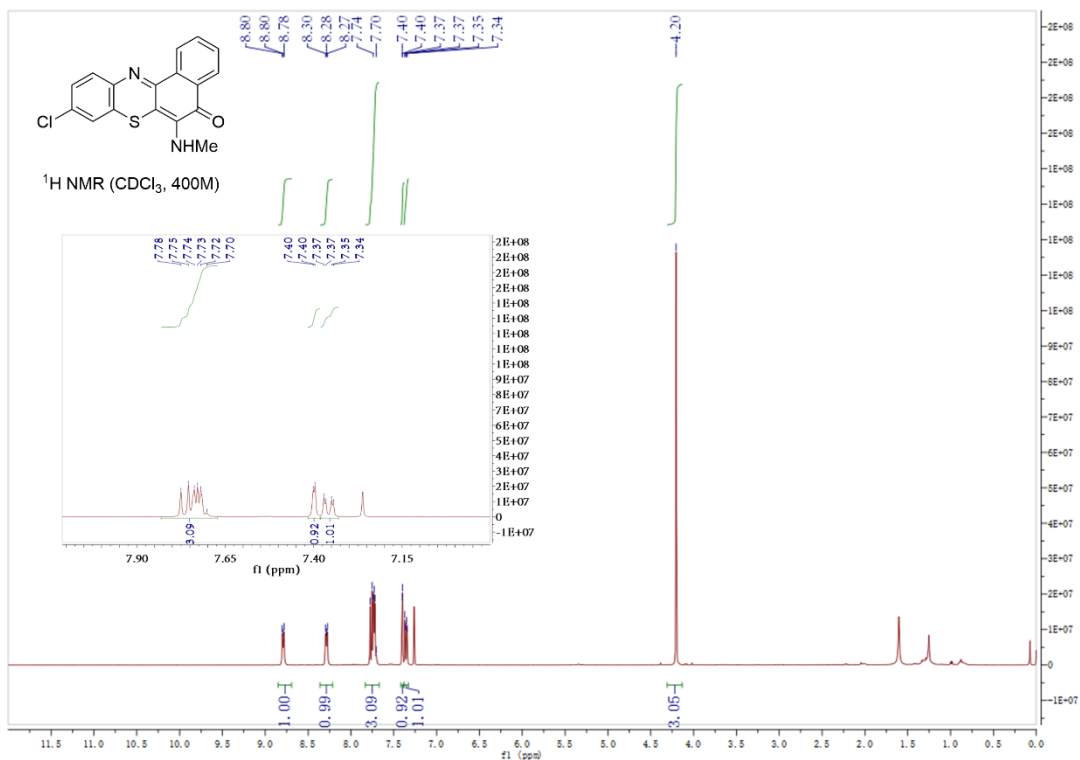
¹H NMR of **4o** (400 MHz, CDCl₃) and ¹³C NMR of **4o** (100 MHz, CDCl₃)



¹H NMR of **4p (6-NMe₂)** (400 MHz, CDCl₃) and ¹³C NMR of **4p (6-NMe₂)** (100 MHz, CDCl₃)



¹H NMR of **4p** (**5-NMe₂**) (400 MHz, CDCl₃) and ¹³C NMR of **4p** (**5-NMe₂**) (100 MHz, CDCl₃)



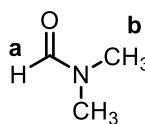
¹H NMR of **8** (400 MHz, CDCl₃) and ¹³C NMR of **8** (100 MHz, CDCl₃)

7. DFT calculations

7.1 Computational Details

All the DFT calculations were carried out with the Gaussian 09 suite of computational programs.^[14] The geometries of all stationary points were optimized using the B3LYP hybrid functional^[15] and D3 version of Grimme's dispersion corrections^[16] with Becke-Johnson damping^[17] in DMF, at 6-31g(d)^[18] basis set by using the Solvation Model based on Density (SMD)^[19] with keyword in the Gaussian code route section "SCRF = (SMD, Solvent = DMF)". Frequencies were analytically computed at the same level of theory to obtain the Gibbs free energies and to confirm whether the structures are minima (no imaginary frequency) or transition states (only one imaginary frequency). The M06L functional^[20,21] in combination with the 6-311+g(d,p) basis set^[18] was used to calculate the solvation single point energies to give more accurate energy information. The solvent effects were considered with an SMD solvation model in the DMF solvent. All transition state structures were confirmed to connect the proposed reactants and products by intrinsic reaction coordinate (IRC) calculations. All the energies given in the text are relative free energies corrected with solvation effects.

7.2 Additional Computational Results



The chemical structure shows N,N-dimethylacetamide (CH₃C(=O)N(CH₃)₂). The C-H bond of the methyl group attached to the carbonyl carbon is labeled 'a'. The C-H bond of the methyl group attached to the nitrogen atom is labeled 'b'.

C-H bond:	a	b
CBS-QB3/M052X/6-31G*		
//M052X/6-311+G(d,p)/SMD:	38.21	52.97
HCOOH		
CBS-QB3/M052X/6-31G*		
//M052X/6-311+G(d,p)/SMD:	4.33	(experimental value 3.76)

Figure S7 Calculated pKa values of different C–H bonds (CBS-QB3/M052X/6-31G*//M052X/6-311+G(d,p)/SMD)

The data were calculated for the standard state of 298 K and 1 atm in the solvent DMF.

The calculation result is calibrated by formic acid.

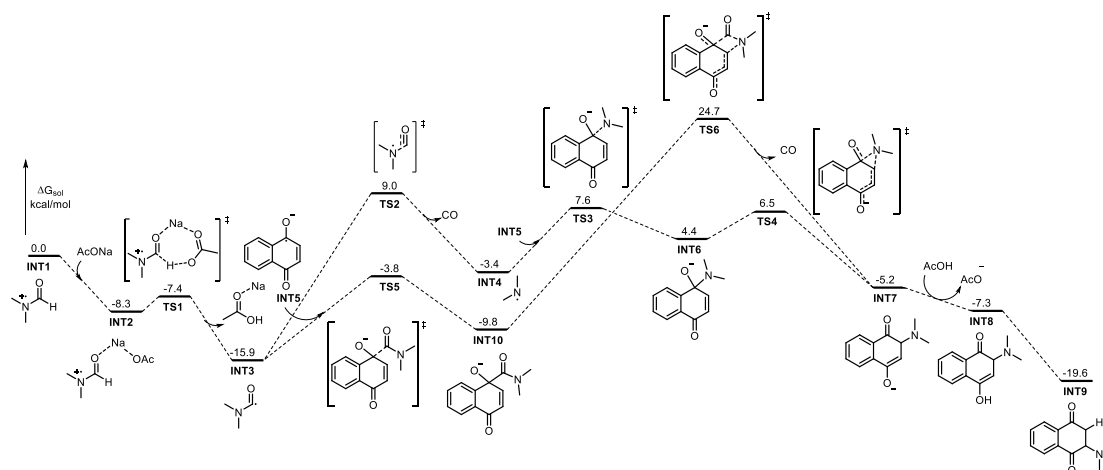


Figure S8 Energy profile for the electrooxidative amination using 4a as arene (M06L/6-311+G(d,p)-SMD(DMF)//B3LYP-D3(BJ)/6-31G(d)-SMD(DMF))

7.3 Calculated Energy Values

Table S5. Energies (in Hartree) calculated by M06L/6-311+G(d,p)-SMD(DMF)//B3LYP-D3(BJ)/6-31G(d)-SMD(DMF) level.

Species	G ₂₉₈ ^a	E ₂₉₈ ^b	E _{sol} ^c	Imaginary Frequency
INT1	-248.237277	-248.3071426	-248.324571669	
AcONa	-390.846577	-390.8672767	-390.896382669	
INT2	-639.104153	-639.2117033	-639.251223896	
TS1	-639.098111	-639.2061086	-639.250154153	-234.4332
AcOHNa	-391.287702	-391.3185937	-391.348775304	
INT3	-247.8147160	-247.8749760	-247.898098881	
TS2	-247.774111	-247.8281301	-247.852182093	-374.6619
CO	-113.319634	-113.3055241	-113.325592813	
INT4	-134.471024	-134.5216060	-134.528793453	
INT5	-535.191725	-535.2888828	-535.335776221	
TS3	-669.648522	-669.8218838	-669.872656833	-170.0418
INT6	-669.654142	-669.8296757	-669.879910835	
TS4	-669.649035	-669.8215984	-669.873564721	-94.0919
INT7	-669.671813	-669.8475015	-669.895461850	
AcOH	-229.063235	-229.0979480	-229.138666891	
AcO ⁻	-228.574318	-228.5969248	-228.654520666	
INT8	-670.160163	-670.3502693	-670.385275542	
INT9	-670.183024	-670.3732338	-670.404908621	
TS5	-782.988482	-783.1697411	-783.238462493	-247.8498
INT10	-782.996543	-783.1799835	-783.250186534	
TS6	-782.945306	-783.1269078	-783.193300703	-295.9557

^aSum of electronic and thermal free energies. ^bSum of electronic energies. ^cSingle point energies calculated in DMF solution.

7.4 Cartesian Coordinates for All Species

INT1

N	-2.58381700	1.17392000	-0.01717700
C	-2.76266900	1.86816700	1.22158400
H	-2.75517600	1.20549600	2.09408500
O	-2.89497500	3.06855800	1.23850800
C	-2.54029700	1.90540000	-1.25547700
H	-1.47780200	2.05251500	-1.51330900
H	-2.99879500	1.30032400	-2.04150500
H	-3.01904500	2.87572700	-1.13532900
C	-2.41760100	-0.25269400	-0.01658300
H	-2.25699700	-0.62069300	0.99605500
H	-3.33450100	-0.69604300	-0.43968300
H	-1.59162400	-0.51483500	-0.68748600

AcONa

N	-2.58381700	1.17392000	-0.01717700
C	-2.76266900	1.86816700	1.22158400
H	-2.75517600	1.20549600	2.09408500
O	-2.89497500	3.06855800	1.23850800
C	-2.54029700	1.90540000	-1.25547700
H	-1.47780200	2.05251500	-1.51330900
H	-2.99879500	1.30032400	-2.04150500
H	-3.01904500	2.87572700	-1.13532900
C	-2.41760100	-0.25269400	-0.01658300
H	-2.25699700	-0.62069300	0.99605500
H	-3.33450100	-0.69604300	-0.43968300
H	-1.59162400	-0.51483500	-0.68748600

INT2

N	-2.44423500	1.09120300	-0.36922900
C	-3.11243300	1.40967200	0.73972800
H	-3.05714000	0.64466800	1.52586900
O	-3.75166100	2.46746000	0.90860800
C	-2.41717100	1.97586700	-1.52617500
H	-1.38127200	2.23643300	-1.76821800
H	-2.86419000	1.47089500	-2.38948600
H	-2.97977300	2.88046100	-1.29873900
C	-1.72986500	-0.17259800	-0.48759700
H	-1.82334000	-0.73834300	0.44165800
H	-2.14589800	-0.76242500	-1.31170600
H	-0.66974200	0.01546200	-0.68866800
C	-6.27372000	1.14531200	6.06681200
H	-7.16830500	0.64675500	5.67653300

H	-6.58970600	1.87601700	6.81990300
H	-5.60209600	0.41039200	6.51689600
C	-5.60162000	1.85760300	4.96139300
O	-4.40504500	1.65812500	4.58161200
O	-6.11770100	2.76585900	4.24157700
Na	-4.91275300	3.48751400	2.39545000

TS1

N	-2.84354000	1.28410300	0.15357300
C	-3.63001900	2.01465000	0.91255100
H	-3.95448000	1.46682700	1.94200800
O	-4.07103700	3.15004100	0.72114300
C	-2.36132900	1.78862600	-1.13771500
H	-1.26779200	1.80793500	-1.12492000
H	-2.70376800	1.11755500	-1.93066000
H	-2.74961900	2.79212800	-1.30638600
C	-2.40917100	-0.06050400	0.53534900
H	-2.81255700	-0.32606800	1.51149500
H	-2.76097900	-0.77712400	-0.21228600
H	-1.31644700	-0.08477100	0.57319200
C	-5.45933300	0.81503700	5.17251000
H	-6.54713500	0.68763200	5.13783700
H	-5.21275600	1.46779300	6.01585400
H	-4.98374100	-0.15847600	5.30252100
C	-5.02809100	1.50356000	3.89706600
O	-4.29771300	0.74212200	3.12884300
O	-5.35849400	2.66389400	3.63056100
Na	-5.28386600	4.32437200	2.22288300

AcOHNa

H	-3.88498900	0.50534600	2.69612800
C	-5.66116900	1.15975400	5.28400000
H	-6.54290600	0.53062700	5.11373000
H	-5.97985600	2.11704300	5.70011400
H	-5.01012000	0.63769100	5.99044400
C	-4.96219400	1.36588800	3.97820100
O	-4.28570100	0.29582500	3.56670300
O	-4.99896100	2.39407700	3.30480800
Na	-5.91837000	4.36579000	3.36975400

INT3

C	-4.22754300	1.30181700	0.16757400
H	-4.40651600	2.36584200	0.33351000
H	-4.90551400	0.93743600	-0.61320900

H	-4.43454400	0.75193900	1.09339000
C	-2.39958600	-0.26332700	-0.48880500
H	-3.02142600	-0.71711500	-1.26856500
H	-1.35925000	-0.24753600	-0.81532000
H	-2.48800200	-0.86070600	0.42593200
N	-2.84155000	1.11063600	-0.23595700
C	-2.01699900	2.15005600	-0.34130400
O	-0.84431900	2.20408000	-0.65041000

TS2

C	-4.07036600	1.20430200	0.44528400
H	-4.33480700	2.26176600	0.54059300
H	-4.97144500	0.64919700	0.14288000
H	-3.76037500	0.81293900	1.42598600
C	-2.56226900	-0.32575200	-0.65325400
H	-1.67679700	-0.36383100	-1.29465700
H	-2.31779600	-0.75162900	0.33120700
H	-3.34368400	-0.95769100	-1.10069500
N	-3.06581900	1.03237700	-0.58888200
C	-1.56287100	2.19111400	-0.10602800
O	-1.70896600	3.32642300	-0.27165200

CO

C	-1.88033000	2.45307200	-0.64556100
O	-1.12257400	2.48166400	-1.49368900

INT4

C	-4.17838600	1.28237500	0.15083700
H	-4.42739600	2.32331600	0.38230600
H	-4.84822100	0.93403100	-0.65486700
H	-4.40418200	0.65711400	1.03179600
C	-2.42519300	-0.20811400	-0.46740500
H	-3.07863800	-0.68963800	-1.21546000
H	-1.38738200	-0.27629200	-0.80996000
H	-2.52953900	-0.79775500	0.46002600
N	-2.79756300	1.16714300	-0.24716500

INT5

C	0.22636800	-2.55277400	-0.72628600
C	-1.06429300	-1.91985400	-0.69826700
C	-1.06842900	-0.50354200	-0.28150800
C	0.13665900	0.16850800	0.06324400
C	1.44015600	-0.52313900	0.02067500
C	1.39687800	-1.90015900	-0.39040200

H	-3.19248500	-0.32901800	-0.49408500
H	0.24727500	-3.59754200	-1.03202200
C	-2.28576100	0.20434800	-0.22467200
C	0.07779500	1.52091700	0.45510300
H	2.34950900	-2.42589900	-0.42832800
C	-1.12934700	2.19964000	0.50635500
C	-2.32341300	1.53457900	0.16226300
H	1.01150700	2.01110600	0.71480900
H	-1.15775500	3.24294700	0.81128600
H	-3.27109600	2.06620700	0.20143000
O	2.51393200	0.06856900	0.32691900
O	-2.13091100	-2.52383900	-1.00573800

TS3

C	-1.31825800	6.06702300	-1.94300900
C	-2.62477800	5.73996900	-1.32902300
C	-3.05757300	6.71616100	-0.26430500
C	-2.24974800	7.80571300	0.11478600
C	-0.92530300	8.04443800	-0.53407400
C	-0.52981800	7.10886300	-1.57995700
H	-4.91893900	5.71418300	0.02267000
H	-1.00833000	5.39591600	-2.74153300
C	-4.30527600	6.54873000	0.34745700
C	-2.69728500	8.69605300	1.10527400
H	0.43347800	7.29033200	-2.05167000
C	-3.93141000	8.51142400	1.71553200
C	-4.73957900	7.42993500	1.33180700
H	-2.05423800	9.52756600	1.37721200
H	-4.27196100	9.20203200	2.48249600
H	-5.70861700	7.28492800	1.80334000
O	-0.20693100	8.99714300	-0.19580600
O	-3.50514600	5.13250100	-2.01041700
C	-1.55475600	3.25118000	-0.91093500
H	-2.31626100	3.21306200	-1.70221600
H	-0.55132200	3.22067900	-1.38668600
H	-1.64410800	2.32191700	-0.31625800
C	-0.67766500	4.80277600	0.68783800
H	0.27413400	4.92189800	0.12687100
H	-0.87242700	5.75352000	1.20022100
H	-0.47785200	4.05384700	1.47749700
N	-1.81123400	4.41895500	-0.10816200

INT6

C	-1.78871000	5.23300400	-1.57706700
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C	-3.03834200	5.27904000	-0.71824000
C	-3.06270900	6.55563900	0.14502500
C	-2.11241400	7.58430900	0.01296500
C	-0.95384200	7.44900700	-0.92166000
C	-0.88549400	6.22893500	-1.71951000
H	-4.86700000	5.94915000	1.12118600
H	-1.71436000	4.34363100	-2.20030400
C	-4.13507700	6.74523700	1.02692300
C	-2.24520700	8.76977500	0.75672700
H	-0.07795000	6.18179600	-2.44858600
C	-3.30926000	8.94076000	1.63279100
C	-4.26014400	7.91725400	1.76617300
H	-1.49289000	9.54244800	0.62997400
H	-3.40667400	9.85769900	2.20805600
H	-5.09765800	8.04196700	2.44877000
O	-0.10691300	8.34735900	-1.02633800
O	-4.05723300	5.25736200	-1.57855700
C	-3.35187800	2.84688100	-0.40614400
H	-4.12930400	3.04322200	-1.14820900
H	-2.47886900	2.39867600	-0.92388700
H	-3.71170300	2.10384600	0.31957000
C	-1.88339300	4.00124900	1.10467100
H	-1.69038500	4.95979600	1.59855400
H	-2.04482400	3.24853000	1.88849200
H	-0.96173600	3.71323300	0.56097900
N	-3.06089800	4.10218000	0.26043400

TS4

C	-2.33409700	5.40417900	-1.29526500
C	-3.63471800	5.98597400	-0.96005800
C	-3.56990100	7.23983500	-0.14634400
C	-2.33548500	7.87634500	0.09721600
C	-1.04499500	7.31261600	-0.42216900
C	-1.13495600	6.05480700	-1.11400800
H	-5.69029600	7.31374700	0.11714300
H	-2.37288700	4.47600400	-1.85936800
C	-4.75198800	7.81500700	0.33435900
C	-2.31382700	9.07299400	0.82933400
H	-0.20121000	5.60137300	-1.43782600
C	-3.49094400	9.62783900	1.31966900
C	-4.71722600	8.99444100	1.07158900
H	-1.35324400	9.54883100	1.00028700
H	-3.46184100	10.55223400	1.89073400
H	-5.63898100	9.42643700	1.45288400

O	0.02688100	7.92391600	-0.23550800
O	-4.70235600	5.61295500	-1.48418000
C	-3.64963400	3.26797500	0.18549100
H	-4.39616200	3.42209800	-0.60689600
H	-2.83171500	2.63634000	-0.22248100
H	-4.14027200	2.66398300	0.97561200
C	-2.01247000	4.50328300	1.42780600
H	-1.21051200	3.88054100	0.97688300
H	-1.60452900	5.51620800	1.55371600
H	-2.18003200	4.10704300	2.44897300
N	-3.23371100	4.54832000	0.68324000

INT7

C	-2.33491400	4.32089400	-0.04902200
C	-3.57967300	5.02235000	0.48114600
C	-3.54983900	6.50909700	0.40697700
C	-2.30236100	7.16094200	0.46333800
C	-1.01258200	6.38055400	0.65047600
C	-1.11486200	5.00141300	0.49682200
H	-5.68503000	6.71314100	0.31800100
H	-2.38098500	3.27028200	0.29334200
C	-4.73721500	7.24368000	0.33733200
C	-2.27675600	8.55690800	0.43758700
H	-0.21634200	4.40178800	0.63277600
C	-3.45993000	9.29199300	0.33024200
C	-4.69503900	8.63778500	0.27964200
H	-1.31030000	9.04426800	0.52031300
H	-3.42231400	10.37837800	0.29727300
H	-5.61583400	9.20964800	0.20231700
O	0.02154100	7.04441400	0.97157600
O	-4.55159800	4.41727900	0.92283300
C	-1.20087800	3.95988600	-2.19886100
H	-0.40111700	4.63440100	-1.88551600
H	-0.88488200	2.92259500	-1.96696700
H	-1.32000100	4.03690300	-3.28593600
C	-3.52806700	3.46946500	-2.00998800
H	-4.48314600	3.77792200	-1.57597000
H	-3.61442900	3.53314800	-3.10080800
H	-3.36632700	2.40533700	-1.74441800
N	-2.44918400	4.33609100	-1.55094200

AcOH

C	-3.46812700	0.41974300	0.03338500
H	-3.07329400	-0.47558900	0.52503800

H	-3.17252100	1.30953000	0.59053100
H	-3.04007200	0.45787400	-0.97442300
C	-4.96722500	0.34558000	-0.05191800
O	-5.74966400	1.16539000	0.38413400
O	-5.37664200	-0.77204800	-0.69645300
H	-6.35463500	-0.74262000	-0.71500900

AcO⁻

C	-3.47176400	0.41045300	0.04112900
H	-3.00929300	-0.52084600	0.39187600
H	-3.18918300	1.23062600	0.71205900
H	-3.04082000	0.62635000	-0.94786900
C	-5.01799800	0.26405000	-0.08465600
O	-5.69766200	1.28318900	0.20619400
O	-5.42432000	-0.85230300	-0.50317600

INT8

C	1.37337000	-0.82209500	-0.52890300
C	0.12609200	-1.65559000	-0.20190700
C	-1.14912100	-0.94616000	0.06480800
C	-1.28055800	0.42580000	-0.24619800
C	-0.13166600	1.15330500	-0.80478000
C	1.08065900	0.59024200	-0.93985800
H	-2.10233800	-2.70235400	0.82968100
H	1.87732000	-1.34121800	-1.35346800
C	-2.23177300	-1.64885200	0.60401300
C	-2.50562200	1.06237500	-0.01165000
H	1.91773800	1.17025600	-1.32287000
C	-3.57572400	0.35078700	0.53060700
C	-3.44312400	-1.00580400	0.84234000
H	-2.61718800	2.11318900	-0.25206500
H	-4.51898200	0.85893200	0.70992100
H	-4.27960100	-1.55449300	1.26472000
O	-0.42143000	2.44163400	-1.15461200
O	0.21371600	-2.87663900	-0.10995100
N	2.33760200	-0.83268300	0.59809800
H	0.39236300	2.86198700	-1.48598000
C	1.79051700	-0.33411800	1.85618600
H	1.08702200	-1.03535500	2.34012700
H	2.61443500	-0.15446400	2.55595100
H	1.27198600	0.61373300	1.68721300
C	3.02202900	-2.10578500	0.78512700
H	2.37380200	-2.90462800	1.18067500
H	3.43660800	-2.44588700	-0.16974800

H 3.84922200 -1.95813300 1.48991100

INT9

C -1.86886600 4.67972700 -1.07836400
C -3.16091900 5.49789100 -1.15514500
C -3.23612300 6.65829500 -0.22318500
C -2.06280500 7.18156000 0.36008400
C -0.72342900 6.63555900 -0.01226300
C -0.70486500 5.67767200 -1.18659200
H -5.37131200 6.80727900 -0.36738300
H -1.85993500 3.98588400 -1.93543300
C -4.47745300 7.22076700 0.08801300
C -2.15349800 8.24782200 1.25859500
H -0.83117400 6.26399900 -2.10727900
C -3.39594600 8.79470200 1.57372400
C -4.55808200 8.28282500 0.98660200
H -1.24211300 8.64392700 1.69415300
H -3.46109900 9.62301600 2.27309200
H -5.52494000 8.71132100 1.23335300
O 0.29608400 6.97377900 0.57232300
O -4.06694600 5.21771700 -1.92511600
C -2.97656200 3.07245600 0.35692900
H -3.91185800 3.63930500 0.33896100
H -3.02510500 2.30400500 -0.43614000
H -2.91156600 2.56376100 1.32331400
C -0.58356100 3.22141700 0.39384000
H -0.39341600 2.49390000 -0.41627600
H 0.27192700 3.89737400 0.45967400
H -0.64248400 2.67184300 1.33811700
N -1.82869800 3.96638500 0.20884600
H 0.26670900 5.18532700 -1.24707300

TS5

C 0.25022500 -0.78528300 -0.37606000
C -1.20267300 -0.97453800 -0.12199500
C -1.77807000 0.06008000 0.81605300
C -1.01248500 1.14102100 1.30518200
C 0.43237300 1.27092900 0.96759400
C 1.00052700 0.23179000 0.11610900
H -3.72454700 -0.81245200 0.71150400
H 0.68599600 -1.51270700 -1.05975700
C -3.14279400 -0.00063100 1.13788600
C -1.61181900 2.10522800 2.13643700
H 2.05927000 0.32799800 -0.11668300

C	-2.95483700	2.01308500	2.47203600
C	-3.72445500	0.95110100	1.96488300
H	-0.99425900	2.91881700	2.50514300
H	-3.41224200	2.75901800	3.11667400
H	-4.78020000	0.88120000	2.21627700
O	1.11526100	2.21495800	1.39756000
O	-1.94370200	-1.37858100	-1.08390200
C	0.33797900	-1.54918700	2.93022700
H	-0.14421000	-0.61350400	2.66769200
H	0.20784400	-1.70331600	4.00836800
H	1.41570900	-1.46976400	2.72780700
C	-0.06266500	-3.96803800	2.81911400
H	-0.58907000	-4.04897800	3.78015200
H	-0.44005100	-4.72978200	2.13756400
H	1.00705800	-4.13592500	3.00182500
N	-0.27228100	-2.65411200	2.21710300
C	-0.95547100	-2.53800700	1.03648300
O	-1.48004500	-3.50683200	0.50437500

INT10

C	0.53091000	-0.72093800	-0.08797600
C	-0.89684500	-1.08638100	0.19519500
C	-1.60873600	-0.01056600	1.02957400
C	-1.03390200	1.25690800	1.24548300
C	0.35407600	1.57404500	0.77143200
C	1.06870600	0.51865100	0.08366700
H	-3.35635400	-1.22349400	1.32176500
H	1.09022800	-1.49431600	-0.60935800
C	-2.90790600	-0.24859700	1.49530000
C	-1.75919700	2.24880100	1.92194400
H	2.04619100	0.77783200	-0.31819900
C	-3.04798000	1.99954500	2.38289100
C	-3.62356800	0.74116000	2.16627800
H	-1.28440200	3.21282000	2.07705200
H	-3.60287000	2.77312200	2.90704300
H	-4.63046700	0.53505300	2.52123100
O	0.84008400	2.70249600	0.95640800
O	-1.34999900	-1.12195500	-1.07921600
C	0.47879900	-1.75119200	2.79971900
H	0.30475900	-0.73366500	2.46415700
H	0.27595400	-1.79094800	3.87713700
H	1.53933400	-1.99543600	2.64529600
C	-0.47433600	-4.00151500	2.75355400
H	-0.89790300	-3.91490100	3.76315000

H	-1.11039400	-4.64469900	2.14704900
H	0.52432600	-4.45114000	2.84217600
N	-0.39165500	-2.69520400	2.12011600
C	-1.05065500	-2.47358800	0.93403900
O	-1.77553000	-3.33920900	0.44074500

TS6

C	0.47443000	-1.11790300	0.93649800
C	-1.01726900	-1.01460600	0.44437300
C	-1.85939600	-0.09236600	1.30694700
C	-1.25006400	0.90988000	2.08344900
C	0.25515900	1.09664800	2.13790400
C	1.02842200	0.11485500	1.51266700
H	-3.70322900	-0.94698100	0.62305300
H	1.05138900	-1.49779800	0.08916900
C	-3.25377400	-0.18064500	1.25028800
C	-2.06543300	1.79433500	2.80533400
H	2.11079600	0.24152100	1.51738500
C	-3.45377100	1.68569600	2.76976800
C	-4.05436000	0.69125900	1.98734900
H	-1.56938000	2.56826000	3.38328100
H	-4.07108100	2.37337100	3.34347800
H	-5.13744300	0.60154000	1.95193100
O	0.69602500	2.13563100	2.71527900
O	-1.26714900	-1.04910800	-0.79432900
C	1.40763400	-3.39608600	1.64140100
H	1.43946800	-3.64112400	0.57799200
H	2.38602500	-3.01948000	1.95858200
H	1.16508700	-4.29745100	2.21014400
C	0.21592900	-2.07425600	3.30630000
H	1.11526900	-1.58938500	3.69337500
H	-0.63640600	-1.40878500	3.44439300
H	0.03621700	-3.01086700	3.84055600
N	0.37661300	-2.37649400	1.87429500
C	-1.14924400	-2.71854200	1.21088800
O	-1.39820800	-3.84564600	0.93899400

8. References

- [1] S. H. Cho, J. Y. Kim, S. Y. Lee, S. Chang, *Angew. Chem., Int. Ed.* **2009**, *48*, 9127.
- [2] G. Li, H. Li, Z. Lu, B. Yu, *Org. Biomol. Chem.*, **2022**, *20*, 5125.
- [3] G. Lahm, T. Opatz, *Org. Lett.* **2014**, *16*, 4201.
- [4] L. P. Long, X. Li, Y. Wang, X. Su, L. Qiao, W. J. Luo, Z. Chen, *J. Org. Chem.*, **2023**, *88*, 7571.
- [5] J. Wang, J. T. Hou, J. Wen, J. Zhang, X. Q. Yu, *Chem. Commun.*, **2011**, *47*, 3652.
- [6] Jha, R. K.; Batabyal, M.; Kumar S. Blue Light Irradiated Metal-, Oxidant-, and Base-Free Cross-Dehydrogenative Coupling of C(sp²)-H and N-H Bonds: Amination of Naphthoquinones with Amines. *J. Org. Chem.* **2023**, *88*, 7401-7424.
- [7] Varricchio, C.; Pascale Aeschlimann, K. B.; Heard, C.; Rozanowska, M.; Votruba, M.; Brancale, A. Discovery of Novel 2-Aniline-1,4-naphthoquinones as Potential New Drug Treatment for Leber's Hereditary Optic Neuropathy (LHON). *J. Med. Chem.* **2020**, *63*, 13638-13655.
- [8] Ueda, K.; Yamashita, M.; Sakaguchi, K.; Tokuda, H.; Iida, A. Concise Synthesis of Heterocycle-Fused Naphthoquinones by Employing Sonogashira Coupling and Tandem Addition-Elimination/Intramolecular Cyclization. *Chem. Pharm. Bull.* **2013**, *61*, 648-654.
- [9] Dong, Y.; Peng, Z.; Chen, Y.; Lin, Y.; Lan, M.; Wu, C.; Shi, Z.; Deng, G.; He, B. Copper-catalyzed direct oxidative amination of maleimides and quinones with formamides in the presence of an oxidant KIO₃. *Tetrahedron.* **2024**, *155*, 133916.
- [10] Wunderer, H. Darstellung und Eigenschaften von Jodamino-*p*-benzochinonen. *Chemische Berichte.* **1972**, *105*, 3479-3490.
- [11] Johnson-Ajinwo, O. R.; Imran Ullah, I.; Mbye, H.; Richardson, A.; Horrocks, P.; Li, W. The synthesis and evaluation of thymoquinone analogues as anti-ovarian cancer and antimalarial agents. *Bioorg. Med. Chem. Lett.* **2018**, *28*, 1219-1222.
- [12] Hewgill, F. R.; Mullings, L. R. Nucleophilic substitution of Bromo-*p*-benzoquinones by dimethylamine. *Aust. J. Chem.* **1975**, *28*, 2561-2566.
- [13] Koharazawa, R.; Hayakawa, M.; Takeda, K.; Miyazaki, K.; Tode, C.; Hirota, Y.; Suhara, Y. Exploring 2-methyl-substituted vitamin K₃ derivatives with potent inhibitory activity against the 3CL protease of SARS-CoV-2. *Bioorg. Med. Chem. Lett.* **2024**, *100*, 129642.
- [14] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.
- [15] (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (d) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.
- [16] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
- [17] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456-1465.

- [18] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Phys. Chem.* **1980**, *72*, 650-654.
- [19] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378-6396.
- [20] (a) Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215. (b) Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* **2008**, *41*, 157.
- [21] (a) L. Szentpály, P. Fuentealba, H. Preuss, H. Stoll, *Chem. Phys. Lett.* **1982**, *93*, 555. (b) M. Dolg, U. Wedig, H. Stoll, H. Preuss, *J. Chem. Phys.* **1987**, *86*, 866. (c) P. Schwerdtfeger, M. Dolg, W. H. E. Schwarz, G. A. Bowmaker, P. D. W. Boyd, *J. Chem. Phys.* **1989**, *91*, 1762.