# Supporting Information

# Pd-Catalyzed Regioselective Rollover Dual C-H Annulation Cascade: Facile Approach to phenanthrene derivatives

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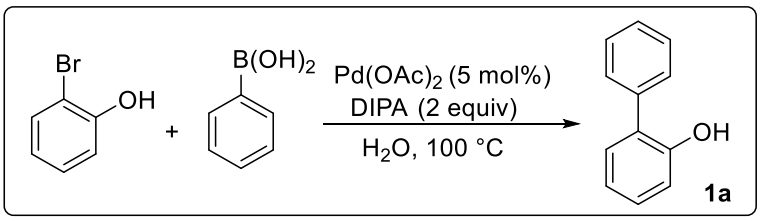
## 1. General Information and methods.

All reagents and solvents were purchased from commercial sources and used without purification. NMR spectra were recorded with a 300, 400 or 500 MHz spectrometer for $^{1}H$ NMR, 100 or 125 MHz for $^{13}C$ NMR spectroscopy. Chemical shifts are reported relative to the residual signals of tetramethylsilane in DMSO-$d_6$ or deuterated solvent DMSO-$d_6$ for $^{1}H$ and $^{13}C$ NMR spectroscopy. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of triplets (dt), triplet (t), quartet (q), multiplet (m). HRMS were recorded by using ORBITRAP and ESI mass spectrometer under positive and negative modes. Column chromatography was performed with silica gel (100–200 mesh) as the stationary phase. All reactions were monitored by using TLC. Most of the compounds HRMS was detected under negative ESI-HRMS mode.

Following the known procedure, *o*-aryl phenol and hydroxy-alkynoates were prepared (Table S1and S2). Analytical and spectral data of these compounds are exactly matching with the reported values.[1-2]

## 2. Experimental Procedures

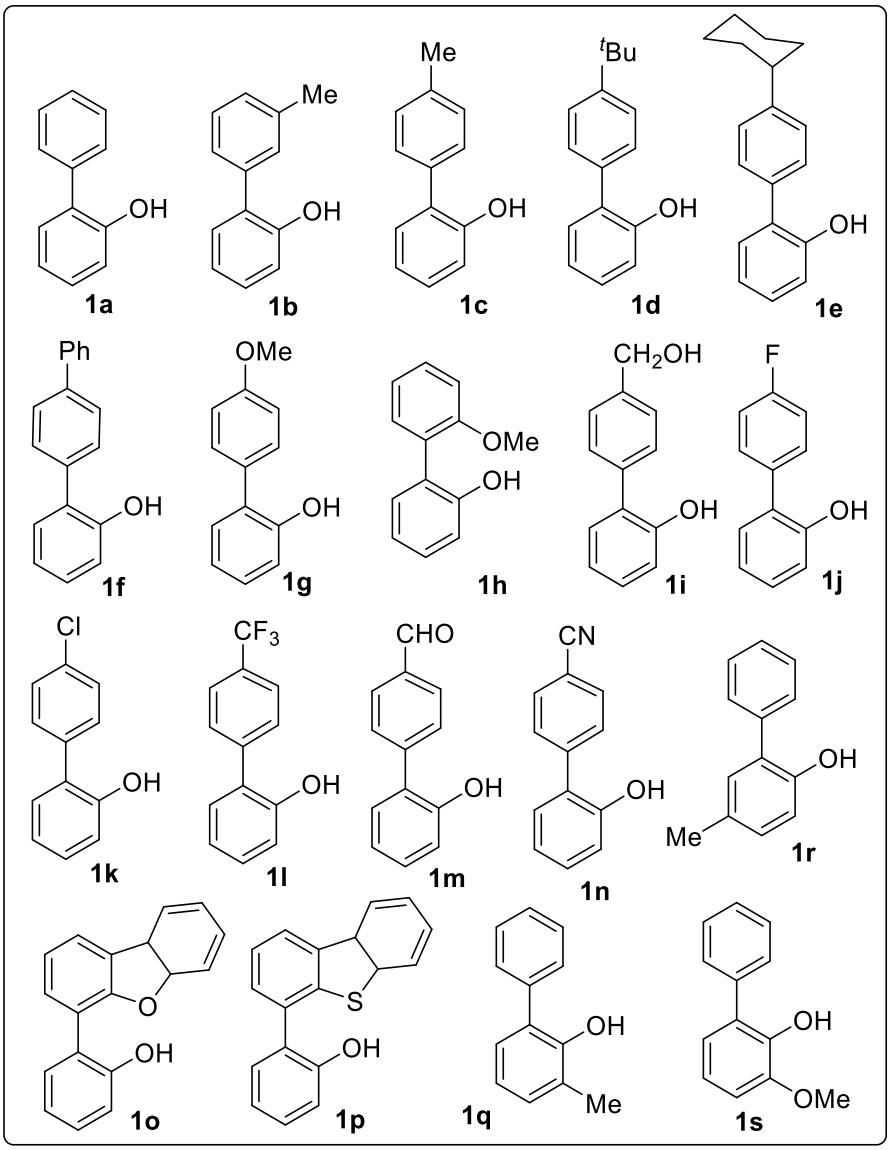
### 2.1. Preparation of *o*-aryl phenols: General Procedure (GP-1):[1]



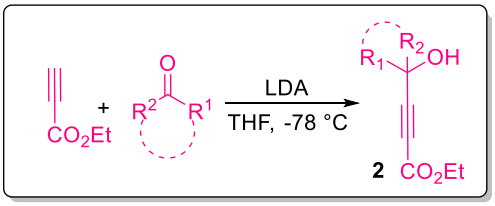

**General Procedure for the Synthesis of *o*-aryl phenols 1a-1s:**

A mixture of *o*-bromophenol (1 g, 5.78 mmol), aryl boronic acids (1.04 g, 8.67 mmol) and base (0.59 g, 11.56 mmol) in $H_2O$ (15 mL) as a solvent, $Pd(OAc)_2$ (71 mg, 5 mol%) was introduced. The contents were stirred at 100 °C for 0.5 h. The reaction mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were washed with brine, dried over sodium sulfate and concentrated under a vacuum. The crude product was purified through a short silica gel column using petroleum ether/EtOAc (20:1) as an eluent to get the corresponding *o*-aryl phenol as off-white solid **1a**.

**Table S1: List of *o*-aryl phenols.**




## 2.2. Preparation of hydroxy-alkynoates: General Procedure (GP-2):[2]

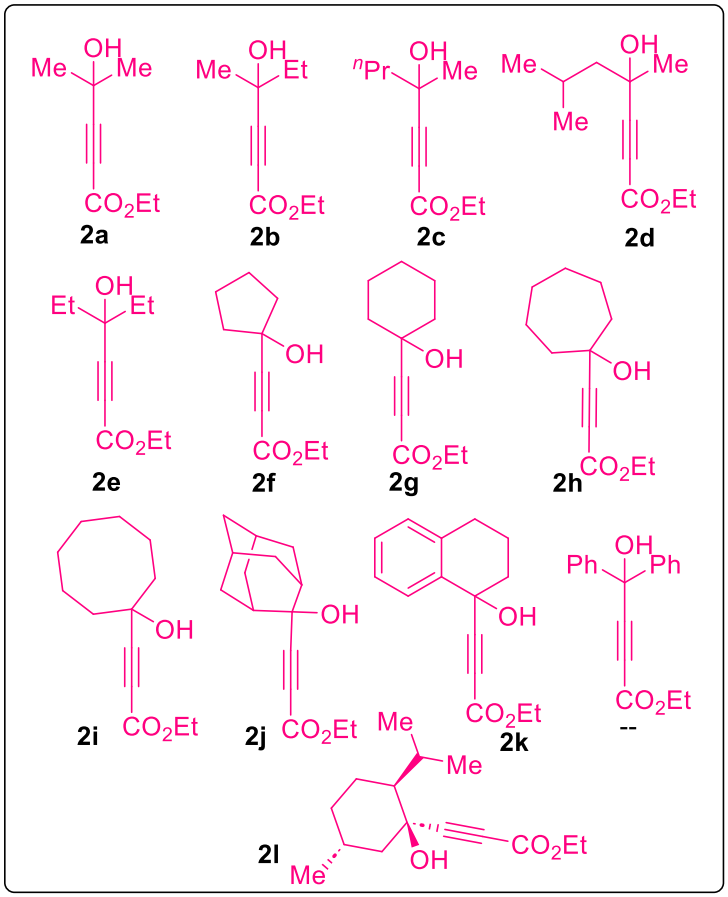



**General Procedure for the Synthesis of 2a-2l:[2]**

To a solution of ethyl propiolate (4.5 mmol) in tetrahydrofuran (20 mL), Lithium diisopropylamide (1.6 M in hexane, 4.5 mmol) was added drop wise by syringe at -78 °C. After stirring for 1 h, a solution of ketone (3 mmol) in THF (5 mL) was added drop wise and the mixture was stirred at the same temperature for 2 h. The solution was allowed to warm to room temperature, and was quenched with saturated aqueous $NH_4Cl$ before extraction with ethyl acetate. The combined organic extracts were washed with brine, dried over sodium sulfate and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (EtOAc:Hexanes) to get the expected hydroxy-alkynoates **2**.

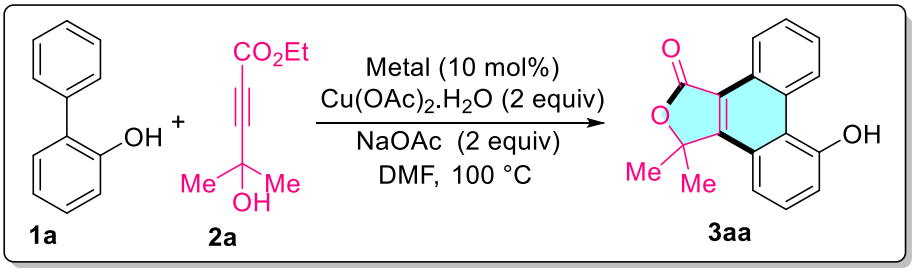
Note: Stereoselectivity of the major isomer of menthone derived propiolate was shown using previous literature.[3]

**Table S2: List of hydroxy-alkynoates**




## 3. Optimization Studies:

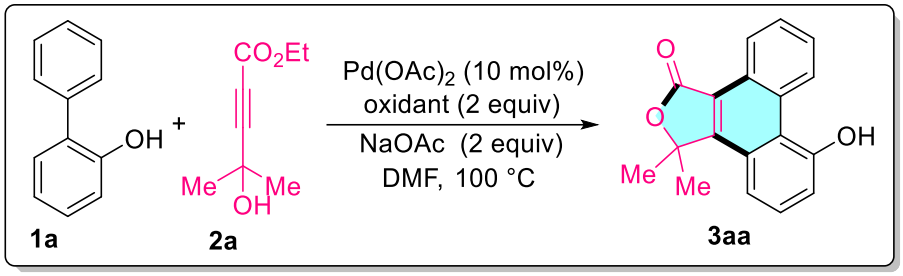
**Table S1: Optimization of Metal Catalyst.[a]**




| Entry | Metal Catalyst | Yield of **3aa**[b] |
|---|---|---|
| 1 | $[Cp^*RhCl_2]_2$ | -- |
| 2 | -- | -- |
| 3 | $[RuCl_2(p\text{-cymene})]_2$ | -- |
| **4** | **$Pd(OAc)_2$** | **80%** |
| 5 | $[Cp^*Co(CO)I_2]$ | -- |
| 6 | $MnBr(CO)_5$ | -- |
| 7 | $Co(OAc)_2$ | -- |
| 8 | $Pd_2(dba)_3$ | 35% |

[a]Reaction conditions:**1a** (0.5 mmol), **2a** (0.6 mmol), metal complex (10 mol %), NaOAc (2 equiv), $Cu(OAc)_2.H_2O$ (2 equiv), DMF, 100 °C for 3 h, $N_2$ balloon. [b]Isolated yield

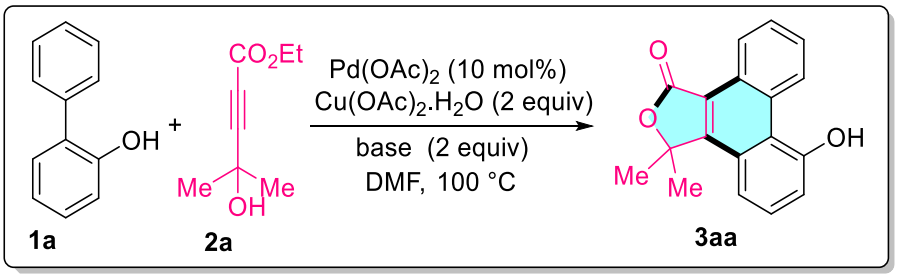
**Table S2: Optimization of Oxidant.[a]**




| Entry | Oxidant | Yield of **3aa**[b] |
|---|---|---|
| **1** | **$Cu(OAc)_2.H_2O$** | **80%** |
| 2 | AgOAc | 18% |
| 3 | $Zn(OAc)_2.2H_2O$ | n.r. |
| 4 | $Ag_2CO_3$ | 5% |
| 5 | $Ag_2O$ | trace |
| 6 | $PhI(OAc)_2$ | n.r. |

[a]Reaction conditions:**1a** (0.5 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (10 mol %), NaOAc (2 equiv), oxidant (2 equiv), DMF, 100 °C for 3 h, $N_2$ balloon. [b]Isolated yield

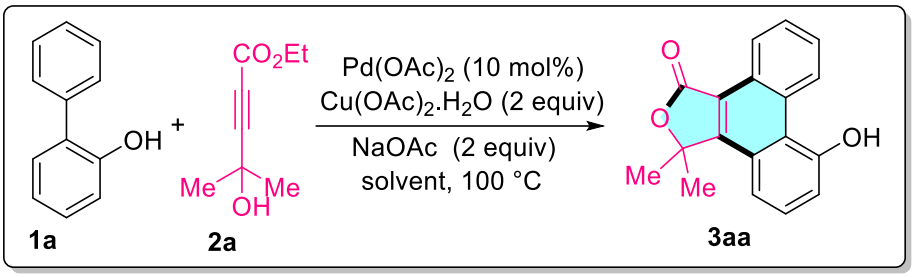
**Table S3: Optimization of base.[a]**




| Entry | base | Yield of **3aa**[b] |
|---|---|---|
| 1 | KOAc | 62% |
| 2 | CsOAc | 55% |
| **3** | **NaOAc** | **80%** |
| 4 | LiOAc | 75% |
| 5 | NaOPiv | 30% |
| 6 | $NH_4OAc$ | n.r. |

[a]Reaction conditions:**1a** (0.5 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (10 mol %), base (2 equiv), $Cu(OAc)_2.H_2O$ (2 equiv), DMF, 100 °C for 3 h, $N_2$ balloon. [b]Isolated yield

**Table S4: Optimization of Solvent.[a]**

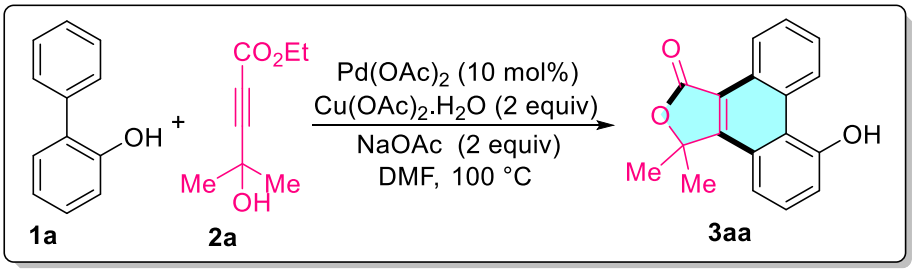



| Entry | Solvent | Yield of **3aa**[b] |
|---|---|---|
| 1 | *t*-AmOH | n.r. |
| 2 | THF | n.r. |
| 3 | MeCN | n.r. |
| 4 | Toluene | n.r. |
| 5 | MeOH | n.r. |
| **6** | **DMF** | **80%** |
| 7 | DMAc | 70% |
| 8 | 1,4-Dioxane | 8% |

[a]Reaction conditions:**1a** (0.5 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (10 mol %), NaOAc (2 equiv), $Cu(OAc)_2.H_2O$ (2 equiv), solvent, 100 °C for 3 h, $N_2$ balloon. [b]Isolated yield

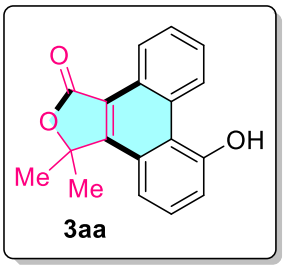
**4. General Procedure for title compounds 3 and their Characteristic data:**

**General Procedure for title compounds taking 3aa as an example:**




To a mixture of biphenol **1a** (85 mg, 0.5 mmol), 4-hydroxy-2-alkyonate **2a** (94 mg, 0.6 mmol) in DMF, $Pd(OAc)_2$ (11.2 mg, 10 mol %), $Cu(OAc)_2.H_2O$ (199.6 mg, 2 equiv) sodium acetate (82 mg, 2 equiv) were introduced and the reaction mixture was stirred at 100 °C (oil bath) for 3 hours under nitrogen balloon. After completion of the reaction, the reaction mixture was cooled to room temperature before ice water was added to it. The aqueous layer was extracted with ethyl acetate (3×10 mL), the combined organic extracts were washed with brine, dried over sodium sulfate and concentrated under reduced pressure. The crude residue was purified by column chromatography ($R_f$ = 0.50) ($SiO_2$, EtOAc:Hexane, 15:85) to get **3aa** as an off-white solid (111.2 mg, 80% yield, mp 275-280 °C).

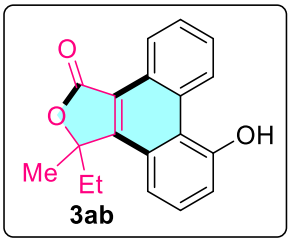
**7-Hydroxy-3,3-dimethylphenanthro[9,10-*c*]furan-1(3*H*)-one (3aa)**:



**3aa**

**$^{1}$H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.16 (s, 1H), 9.93 – 9.85 (m, 1H), 9.09 (dd, *J* = 6.3, 3.3 Hz, 1H), 7.75 (dd, *J* = 5.8, 4.4 Hz, 3H), 7.67 (t, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 1.88 (s, 6H). **$^{13}$C NMR (100 MHz, DMSO-*d*$_6$)** δ 169.2, 157.2, 155.3, 131.1, 128.7, 128.4, 127.5, 127.1, 126.5, 126.0, 122.8, 121.4, 117.9, 117.1, 116.8, 84.9, 26.6. **HRMS (ESI)** calcd for $C_{18}H_{15}O_3$ $[M+H]^+$ 279.1021, found 279.1000.

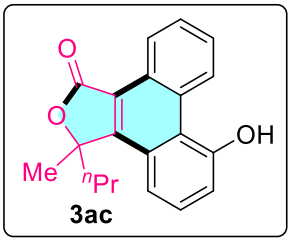
**3-Ethyl-7-hydroxy-3-methylphenanthro[9,10-*c*]furan-1(3*H*)-one (3ab):**



**3ab**

The title compound was prepared from **1a** (85 mg, 0.5 mmol) and **2b** (102 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.55, $SiO_2$, EtOAc:Hexane, 15:85) gave pure product **3ab** as a white solid (109.5 mg, 75% yield), mp 278-282 °C. **$^{1}$H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.19 (s, 1H), 9.90 (dd, *J* = 6.4, 3.4 Hz, 1H), 9.19 – 9.03 (m, 1H), 7.78 – 7.71 (m, 3H), 7.66 (t, *J* = 7.9 Hz, 1H), 7.45 (dd, *J* = 7.8, 0.9 Hz, 1H), 2.34 (dt, *J* = 20.8, 7.4 Hz, 2H), 1.86 (s, 3H), 0.53 (t, *J* = 7.3 Hz, 3H). **$^{13}$C NMR (100 MHz, DMSO-*d*$_6$)** δ 169.4, 157.2, 153.9, 131.1, 128.7, 128.5, 127.5, 127.1, 126.8, 126.0, 122.7, 121.2, 118.9, 116.9, 116.8, 87.3, 25.7, 16.7, 13.7. **HRMS (ESI)** calcd for $C_{19}H_{15}O_3$ $[M-H]^-$ 291.1021, found 291.1015.

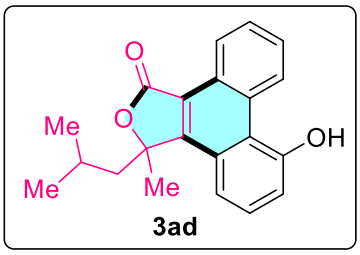
**7-Hydroxy-3-methyl-3-propylphenanthro[9,10-*c*]furan-1(3*H*)-one (3ac):**



**3ac**

The title compound was prepared from **1a** (85 mg, 0.5 mmol) and **2b** (110 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.55, $SiO_2$, EtOAc:Hexane, 15:85) gave pure product **3ac** as a white solid (108.6 mg, 71% yield), mp 283-287 °C. **$^{1}$H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.16 (s, 1H), 9.93 – 9.87 (m, 1H), 9.12 – 9.04 (m, 1H), 7.79 – 7.71 (m, 3H), 7.66 (t, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 2.29 (tt, *J* = 14.4, 7.8 Hz, 2H), 1.85 (s, 3H), 1.24 – 1.05 (m, 2H), 0.77 – 0.71 (m, 3H). **$^{13}$C NMR (100 MHz, DMSO-*d*$_6$)** δ 169.4, 157.2, 153.9, 131.1, 128.7, 128.5, 127.5, 127.1, 126.8, 126.0, 122.7, 121.2, 118.9, 116.9, 116.8, 87.3, 40.3, 25.7, 16.7, 13.7. **HRMS (ESI)** calcd for $C_{20}H_{17}O_3$ $[M-H]^-$ 305.1178, found 305.1172.

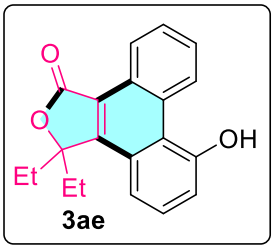
**7-Hydroxy-3-isobutyl-3-methylphenanthro[9,10-c]furan-1(3H)-one (3ad)**:



3ad

The title compound was prepared from **1a** (85 mg, 0.5 mmol) and **2d** (118.8 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.50, $SiO_2$, EtOAc:Hexane, 15:85) gave pure product **3ad** as a white solid (118.4 mg, 74% yield), mp 281-286 °C. **$^1$H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.16 (s, 1H), 9.95 – 9.85 (m, 1H), 9.13 – 9.07 (m, 1H), 7.78 – 7.70 (m, 3H), 7.66 (t, J = 7.9 Hz, 1H), 7.45 (dd, J = 7.7, 0.9 Hz, 1H), 2.31 (dd, J = 15.1, 5.8 Hz, 1H), 2.21 (dd, J = 15.2, 6.3 Hz, 1H), 1.83 (s, 3H), 1.25 (tt, J = 12.9, 6.5 Hz, 1H), 0.78 (d, J = 6.6 Hz, 3H), 0.48 (d, J = 6.7 Hz, 3H). **$^{13}$C NMR (100 MHz, DMSO-*d*$_6$)** δ 169.4, 157.2, 154.0, 131.1, 128.7, 128.4, 127.5, 127.1, 127.0, 125.9, 122.7, 121.2, 119.0, 117.0, 116.8, 87.5, 46.5, 26.8, 24.2, 23.7, 23.6. **HRMS (ESI)** calcd for $C_{21}H_{19}O_3$ $[M-H]^-$ 319.1334, found 319.1328.

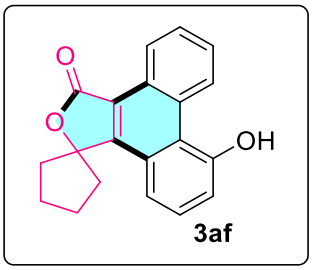
**3,3-Diethyl-7-hydroxyphenanthro[9,10-*c*]furan-1(3*H*)-one(3ae)**:



3ae

The title compound was prepared from **1a** (85 mg, 0.5 mmol) and **2e** (110 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.50, $SiO_2$, EtOAc:Hexane15:85 ) gave pure product **3ae** as a pale grey solid (132 mg, 72% yield). mp 310-314°C. **$^1$H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.17 (s, 1H), 9.96 – 9.83 (m, 1H), 9.17 – 9.06 (m, 1H), 7.81 – 7.71 (m, 3H), 7.65 (t, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 2.44 – 2.25 (m, 4H), 0.49 (t, *J* = 7.3 Hz, 6H). **$^{13}$C NMR (100 MHz, DMSO-*d*$_6$)** δ 169.9, 157.2, 151.6, 131.2, 128.8, 128.6, 127.6, 127.2, 127.0, 125.9, 122.8, 121.0, 120.5, 117.1, 116.4, 90.7, 30.5, 7.5. **HRMS (ESI)** calcd for $C_{20}H_{17}O_3$ $[M-H]^-$ 305.1178, found 305.1172.

**8'-Hydroxy-3'*H*-spiro[cyclopentane-1,1'-phenanthro[9,10-*c*]furan]-3'-one (3af)**:

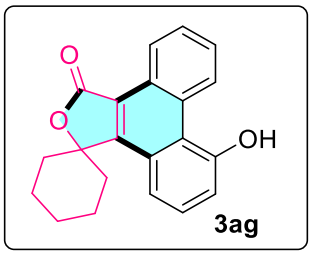


3af

The title compound was prepared from **1a** (85 mg, 0.5 mmol) and **2f** (109 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.50, $SiO_2$, EtOAc:Hexane, 15:85) gave pure product **3af** as colourless solid (107.9 mg, 71% yield). mp 340-343 °C. **$^1$H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.18 (s, 1H), 9.90 (s, 1H), 9.08

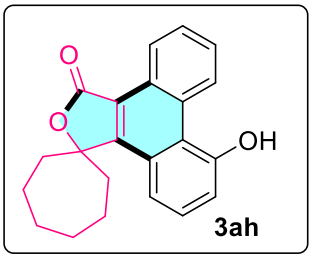
(s, 1H), 7.71 (d, *J* = 32.4 Hz, 3H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.49 (dd, *J* = 36.8, 7.3 Hz, 1H), 2.59 (s, 2H), 2.07 (s, 6H). **$^{13}$C NMR (100 MHz, DMSO-*d*$_6$)** δ 169.3, 157.4, 152.0, 131.2, 128.8, 128.5, 127.6, 127.2, 126.7, 126.0, 122.7, 121.4, 119.0, 116.8, 116.5, 94.8, 38.7, 25.5. **HRMS (ESI)** calcd for $C_{20}H_{15}O_3$ $[M-H]^-$ 303.1021, found 303.1016.

**8'-Hydroxy-3'*H*-spiro[cyclohexane-1,1'-phenanthro[9,10-*c*]furan]-3'-one (3ag)**:



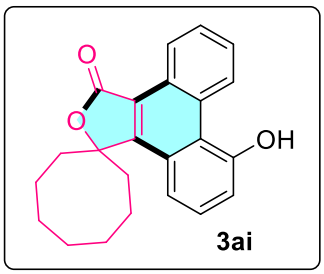

The title compound was prepared from **1a** (85 mg, 0.5 mmol) and **2g** (117.6 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.60, $SiO_2$, Hexane) gave pure product **3ag** as a colourless solid (108.1 mg, 68% yield), mp 325-328 °C. **$^1$H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.14 (s, 1H), 9.94 – 9.84 (m, 1H), 9.12 (dd, *J* = 6.3, 3.3 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 2.55 (dd, *J* = 13.3, 3.4 Hz, 2H), 1.80 (d, *J* = 21.5 Hz, 5H), 1.74 – 1.59 (m, 3H). **$^{13}$C NMR (100 MHz, DMSO-*d*$_6$)** δ 169.3, 157.3, 154.9, 131.1, 128.7, 128.3, 127.6, 127.1, 126.8, 126.2, 122.8, 121.4, 118.1, 117.2, 116.7, 86.5, 34.7, 23.9, 22.4. **HRMS (ESI)** calcd for $C_{21}H_{17}O_3$ $[M-H]^-$ 317.1178, found 317.1172.

**8'-Hydroxy-3'*H*-spiro[cycloheptane-1,1'-phenanthro[9,10-*c*]furan]-3'-one (3ah)**:



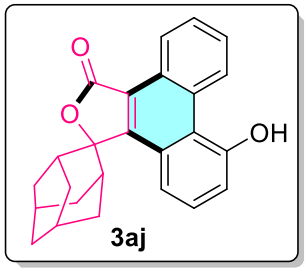

The title compound was prepared from **1a** (85 mg, 0.5 mmol) and **2h** (126 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.55, $SiO_2$, EtOAc:Hexane, 16:84) gave pure product **3ah** as a pale brown solid (106.2 mg, 64% yield), mp 312-315 °C. **$^1$H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.14 (s, 1H), 9.93 – 9.83 (m, 1H), 9.13 – 9.05 (m, 1H), 7.81 – 7.63 (m, 4H), 7.44 (d, *J* = 7.5 Hz, 1H), 2.63 – 2.53 (m, 3H), 1.96 (d, *J* = 11.8 Hz, 2H), 1.91 – 1.79 (m, 7H). **$^{13}$C NMR (100 MHz, DMSO-*d*$_6$)** δ 169.5, 157.3, 156.8, 131.0, 128.6, 128.3, 127.4, 127.1, 126.5, 126.0, 122.8, 121.5, 117.3, 116.9, 116.7, 89.2, 38.4, 27.0, 23.2. **HRMS (ESI)** calcd for $C_{22}H_{19}O_3$ $[M-H]^-$ 331.1334, found 331.1328.

**8'-Hydroxy-3'*H*-spiro[cyclooctane-1,1'-phenanthro[9,10-*c*]furan]-3'-one (3ai)**:



The title compound was prepared from **1a** (85 mg, 0.5 mmol) and **2i** (134 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.6, $SiO_2$, EtOAc:Hexane, 16:84) gave pure product **3ai** as a white solid (105.5 mg, 61% yield), mp 318-322 °C. **$^1$H NMR (500 MHz, DMSO-*d*$_6$)** δ 11.16 (s, 1H), 9.92 – 9.86 (m, 1H), 9.13 – 9.05 (m, 1H), 7.79 – 7.68 (m, 4H), 7.44 (dd, *J* = 6.6, 2.5 Hz, 1H), 2.56 (dd, *J* = 14.4, 9.6 Hz, 2H), 2.15 (dt, *J* = 16.8, 6.7 Hz, 2H), 1.94 – 1.89 (m, 1H), 1.83 (td, *J* = 14.4, 6.8 Hz, 4H), 1.68 (tt, *J* = 12.0, 6.0 Hz, 5H). **$^{13}$C NMR (125 MHz, DMSO-*d*$_6$)** δ 169.5, 157.6, 157.3, 131.0, 128.6, 128.3, 127.4, 127.1, 126.5, 126.1, 122.8, 121.5, 117.3, 117.0, 116.7, 88.2, 35.6, 27.2, 22.7, 21.4. **HRMS (ESI)** calcd for $C_{23}H_{21}O_3$ $[M-H]^-$ 345.1491, found 345.1485.

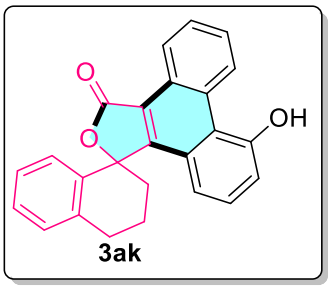
**8'-Hydroxy-3'*H*-spiro[adamantane-2,1'-phenanthro[9,10-*c*]furan]-3'-one (3aj):**



3aj

The title compound was prepared from **1a** (85 mg, 0.5 mmol) and **2j** (148.8 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.50, $SiO_2$, EtOAc:Hexane, 16:84) gave pure product **3aj** as a sticky solid (111 mg, 60% yield). **$^1$H NMR (400 MHz, DMSO-*d*$_6$)** 11.06 (s, 1H), 9.89 (d, *J* = 9.3 Hz, 1H), 9.58 – 9.28 (m, 1H), 8.45 (d, J = 8.3 Hz, 1H), 7.83 – 7.70 (m, 2H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 3.03 (d, *J* = 13.5 Hz, 2H), 2.58 (d, *J* = 11.4 Hz, 2H), 2.26 (s, 1H), 2.08 (s, 2H), 1.99 (d, *J* = 13.5 Hz, 3H), 1.92 (s, 2H), 1.82 (d, *J* = 12.0 Hz, 2H). **$^{13}$C NMR (100 MHz, DMSO-*d*$_6$)** δ 168.3, 157.1, 155.9, 130.9, 128.5, 128.2, 127.6, 127.0, 126.7, 126.3, 123.1, 122.2, 120.9, 120.7, 116.3, 94.0, 78.3, 37.6, 37.3, 33.4, 26.8, 25.4. **HRMS (ESI)** calcd for $C_{25}H_{22}O_3Na$ $[M+Na]^+$ 393.1478, found 393.1467.

**8'-Hydroxy-3,4-dihydro-2*H*,3'*H*-spiro[naphthalene-1,1'-phenanthro[9,10-*c*]furan]-3'-one (3ak)**:

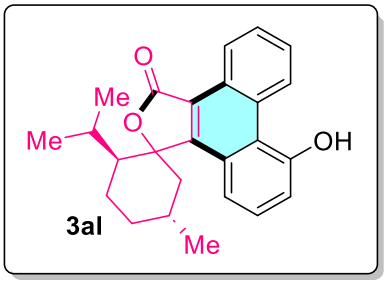


3ak

The title compound was prepared from **1a** (85 mg, 0.5 mmol) and **2k** (146 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.5, $SiO_2$, EtOAc:Hexane, 15:85) gave pure product **3ak** as a sticky solid (93 mg, 51% yield). **$^1$H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.18 (s, 1H), 9.92 (dd, *J* = 6.6, 3.3 Hz, 1H), 9.14 (dd, *J* = 6.4, 3.2 Hz, 1H), 7.86 – 7.75 (m, 2H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.38 – 7.27 (m, 3H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 7.0 Hz, 1H), 6.59 (d, *J* = 7.5 Hz, 1H), 3.15 – 3.04 (m, 2H), 2.71 (dd, *J* = 15.2, 8.2 Hz, 1H), 2.09 (d, *J* = 12.7 Hz, 3H). **$^{13}$C NMR (100 MHz, DMSO-*d*$_6$)** δ 169.4, 157.2, 153.9, 138.1, 133.3, 129.7, 129.2, 128.8, 128.1, 127.8, 127.4, 127.3, 126.9,

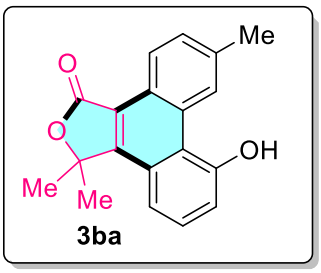
126.3, 122.9, 121.6, 119.6, 117.3, 116.6, 84.9, 36.1, 29.0, 19.8. **HRMS (ESI)** calcd for $C_{25}H_{17}O_3$ $[M-H]^-$ 365.1178, found 365.1172.

**(2S,5R)-8'-Hydroxy-2-isopropyl-5-methyl-3'*H*-spiro[cyclohexane-1,1'-phenanthro[9,10-*c*]furan]-3'-one (3al):**



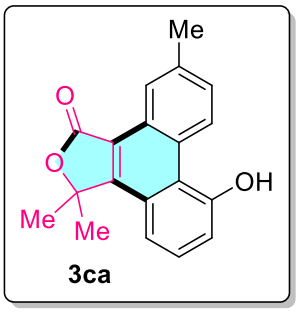

The title compound was prepared from **1a** (85 mg, 0.5 mmol) and **2l** (151.2 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.60, $SiO_2$, EtOAc:Hexane, 15:85) gave pure product **3al** as a white coloured soild (112.2 mg, 60% yield). mp 250-255°C. **$^1$H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.15 (s, 1H), 9.88 (d, *J* = 7.2 Hz, 1H), 9.22 (d, *J* = 6.1 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.68 (t, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 2.22 – 2.10 (m, 3H), 2.04 (d, *J* = 12.3 Hz, 1H), 1.94 – 1.83 (m, 2H), 1.38 (s, 1H), 1.25 (d, *J* = 11.1 Hz, 2H), 0.91 (d, *J* = 5.4 Hz, 3H), 0.78 (d, *J* = 6.6 Hz, 3H), 0.17 (d, *J* = 6.5 Hz, 3H). **$^{13}$C NMR (100 MHz, DMSO-*d*$_6$)** δ 169.3, 157.2, 155.0, 130.7, 128.5, 127.7, 127.5, 127.1, 126.2, 126.1, 122.9, 121.3, 120.6, 119.9, 116.6, 92.2, 49.6, 45.1, 33.2, 27.9, 26.1, 23.3, 23.0, 21.9, 17.9. **HRMS (ESI)** calcd for $C_{25}H_{25}O_3$ $[M-H]^-$ 373.1804, found 373.1798.

**7-Hydroxy-3,3,9-trimethylphenanthro[9,10-*c*]furan-1(3*H*)-one (3ba)**:




The title compound was prepared from **1b** (92 mg, 0.5 mmol) and **2a** (94 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.53, $SiO_2$, EtOAc:Hexane, 15:85) gave pure product **3ba** as an off-white solid (80 mg, 55% yield), mp 288-293 °C. **$^1$H NMR (500 MHz, DMSO-*d*$_6$)** δ 11.08 (s, 1H), 9.72 (s, 1H), 8.97 (d, *J* = 8.2 Hz, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.64 (t, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 2.57 (s, 3H), 1.86 (s, 6H). **$^{13}$C NMR (125 MHz, DMSO-*d*$_6$)** δ 169.3, 157.3, 154.3, 136.7, 131.3, 128.5, 128.2, 126.7, 123.9, 122.6, 121.2, 117.9, 117.1, 116.6, 84.9, 26.6, 22.3. **HRMS (ESI)** calcd for $C_{19}H_{17}O_3$ $[M+H]^+$ 293.1178, found 293.1172.

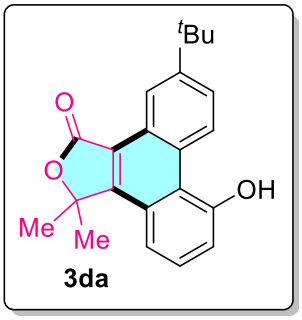
**7- Hydroxy-3,3,10-trimethylphenanthro[9,10-*c*]furan-1(3*H*)-one (3ca)**:




**3ca**

The title compound was prepared from **1c** (92 mg, 0.5 mmol) and **2a** (94 mg, 0. 6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.50, $SiO_2$, EtOAc:Hexane, 15:85) gave pure product **3ca** as an off-white solid (113.8 mg, 78% yield), mp 270-275 °C. **$^1$H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.06 (s, 1H), 9.77 (d, *J* = 8.8 Hz, 1H), 8.89 (s, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.66 – 7.55 (m, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 2.54 (s, 3H), 1.86 (s, 6H). **$^{13}$C NMR (100 MHz, DMSO-*d*$_6$)** δ 169.2, 157.0, 155.3, 136.5, 128.9, 128.6, 127.9, 126.3, 126.2, 122.4, 121.6, 117.6, 117.0, 116.6, 84.8, 26.6, 21.3. **HRMS (ESI)** calcd for $C_{19}H_{17}O_3$ $[M+H]^+$ 293.1178, found 293.1172.

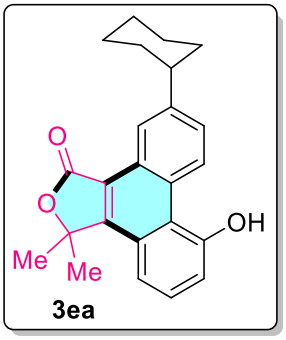
**10-(tert-Butyl)-7-hydroxy-3,3-dimethylphenanthro[9,10-*c*]furan-1(3*H*)-one (3da)**:




**3da**

The title compound was prepared from **1d** (113 mg, 0.5 mmol) and **2a** (94 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.52, $SiO_2$, EtOAc:Hexane, 15:85) gave pure product **3da** as a white solid (125.2 mg, 75% yield), mp 290-295 °C. **$^1$H NMR (400 MHz**, **DMSO-*d*$_6$)** δ 11.06 (s, 1H), 9.80 (d, *J* = 9.1 Hz, 1H), 9.14 (d, *J* = 2.2 Hz, 1H), 7.83 (dd, *J* = 9.2, 2.3 Hz, 1H), 7.72 (d, *J* = 7.3 Hz, 1H), 7.62 (t, *J* = 7.9 Hz, 1H), 7.45 – 7.39 (m, 1H), 1.87 (s, 6H), 1.41 (s, 9H).). **$^{13}$C NMR (100 MHz**, **DMSO-*d*$_6$)** δ 169.4, 157.1, 155.2, 149.4, 128.9, 128.5, 127.9, 126.3, 126.1, 125.5, 121.4, 118.5, 118.0, 117.0, 116.5, 84.8, 34.7, 31.1, 26.6. **HRMS (ESI)** calcd for $C_{22}H_{23}O_3$ $[M+H]^+$ 335.1647, found 335.1628

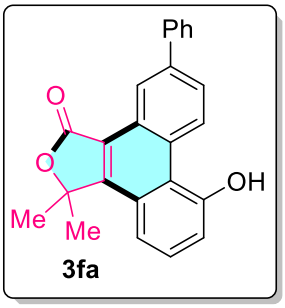
**10-Cyclohexyl-7-hydroxy-3,3-dimethylphenanthro[9,10-*c*]furan-1(3*H*)-one (3ea):**




**3ea**

The title compound was prepared from **1e** (126 mg, 0.5 mmol) and **2a** (94 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.51, $SiO_2$, EtOAc:Hexane, 15:85) gave pure product **3ea** as a white solid (122.4 mg, 68% yield), mp 270-273°C. **$^1$H NMR (500 MHz, DMSO-*d*$_6$)** δ 11.05 (s, 1H), 9.80 (s, 1H), 8.95 (d, *J* = 1.9 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.63 (dd, *J* = 13.1, 5.1 Hz, 2H), 7.41 (d, *J* = 7.7 Hz, 1H), 2.72 (dd, *J* = 21.2, 9.9 Hz, 1H), 1.94 – 1.88 (m, 2H), 1.87 (s, 6H), 1.83 (s, 1H), 1.74 (d, *J* = 11.9 Hz, 1H), 1.59 – 1.40 (m, 4H), 1.28 (dd, *J* = 25.2, 16.1 Hz, 2H). **$^{13}$C NMR (125 MHz, DMSO-*d*$_6$)** δ 169.3, 157.0, 155.3, 146.3, 129.3, 128.7, 127.9, 126.8, 126.3, 126.2, 121.5, 120.0, 117.8, 117.0, 116.5, 84.8, 43.8, 34.0, 26.6, 26.4, 25.7. **HRMS (ESI)** calcd for $C_{24}H_{23}O_3$ $[M-H]^-$ 359.1647, found 359.1641.

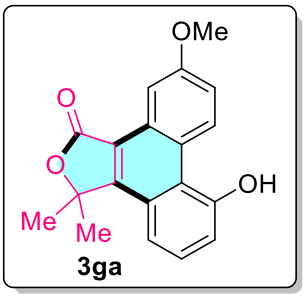
**7-Hydroxy-3,3-dimethyl-10-phenylphenanthro[9,10-*c*]furan-1(3*H*)-one (3fa)**:



**3fa**

The title compound was prepared from **1f** (123 mg, 0.5 mmol) and **2a** (94 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.51, $SiO_2$, EtOAc:Hexane, 2:8) gave pure product **3fa** as a pale grey solid (115 mg, 65% yield), mp 298-303 °C. **$^1$H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.22 (s, 1H), 9.97 (d, *J* = 9.0 Hz, 1H), 9.39 (d, *J* = 2.1 Hz, 1H), 8.09 (dd, *J* = 9.1, 2.2 Hz, 1H), 7.87 – 7.81 (m, 2H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.68 (t, *J* = 7.9 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 2H), 7.50 – 7.42 (m, 2H), 1.90 (s, 6H). **$^{13}$C NMR (100 MHz, DMSO-*d*$_6$)** δ 169.3, 157.3, 155.8, 139.6, 138.3, 130.3, 129.4, 129.3, 128.4, 128.0, 127.0, 126.6, 126.5, 126.0, 121.2, 120.2, 118.0, 117.2, 116.8, 85.0, 26.5. **HRMS (ESI)** calcd for $C_{24}H_{17}O_3$ $[M-H]^-$ 353.1178, found 353.1172.

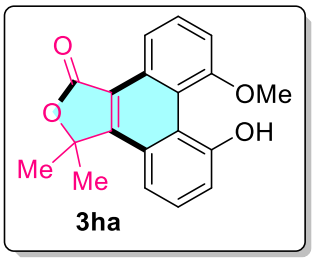
**7-Hydroxy-10-methoxy-3,3-dimethylphenanthro[9,10-c]furan-1(3H)-one (3ga)**:



**3ga**

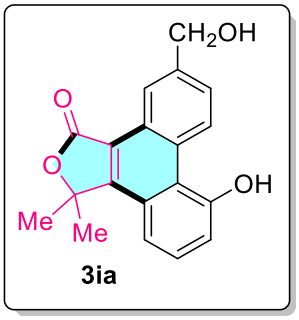
The title compound was prepared from **1g** (100 mg, 0.5 mmol) and **2a** (94 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.55, $SiO_2$, EtOAc:Hexane, 1:4) gave pure product **3ga** as a white solid (126.2 mg, 82% yield), mp 250-255 °C. **$^1$H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.03 (s, 1H), 9.82 (d, *J* = 9.5 Hz, 1H), 8.58 (d, *J* = 2.6 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.39 (dd, *J* = 11.1, 6.6 Hz, 2H), 3.92 (s, 3H), 1.86 (s, 6H). **$^{13}$C NMR (100 MHz, DMSO-*d*$_6$)** δ 169.3, 157.9, 156.4, 155.8, 130.4, 127.9, 127.2, 125.5, 125.2, 121.9, 117.3, 117.0, 116.7, 116.5, 104.1, 84.8, 55.2, 26.6. **HRMS (ESI)** calcd for $C_{19}H_{17}O_4$ $[M+H]^+$ 309.1127, found 309.1121.

**7-Hydroxy-8-methoxy-3,3-dimethylphenanthro[9,10-*c*]furan-1(3*H*)-one (3ha)**:



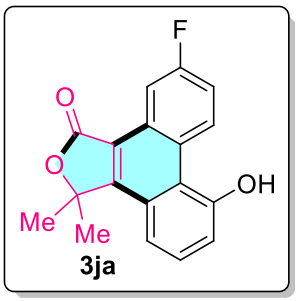

The title compound was prepared from **1h** (100 mg, 0.5 mmol) and **2a** (94 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.55, $SiO_2$, EtOAc:Hexane, 1:4) gave pure product **3ha** as a white solid (104.7 mg, 68% yield), mp 250-260°C. **$^1$H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.80 (s, 1H), 8.64 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.76 – 7.62 (m, 3H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.31 (dd, *J* = 7.6, 1.3 Hz, 1H), 4.04 (s, 3H), 1.85 (s, 6H). **$^{13}$C NMR (100 MHz, DMSO-*d*$_6$)** δ 168.9, 156.2, 156.1, 155.9, 128.5, 128.4, 127.7, 126.4, 120.8, 119.4, 117.6, 117.3, 116.1, 115.1, 110.9, 84.6, 56.6, 26.5. **HRMS (ESI)** calcd for $C_{19}H_{17}O_4$ $[M+H]^+$ 309.1127, found 309.1121.

**7-Hydroxy-10-(hydroxymethyl)-3,3-dimethylphenanthro[9,10-*c*]furan-1(3*H*)-one (3ia)**:




The title compound was prepared from **1i** (100 mg, 0.5 mmol) and **2a** (94 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.50 $SiO_2$, EtOAc:Hexane, 22:78) gave pure product **3ia** as a colourless gel (80 mg, 52% yield). **$^1$H NMR (500 MHz, DMSO-*d*$_6$)** δ 11.11 (s, 1H), 9.84 (d, *J* = 8.9 Hz, 1H), 9.07 (s, 1H), 7.75 – 7.63 (m, 3H), 7.43 (d, *J* = 7.7 Hz, 1H), 5.47 (s, 1H), 4.74 (d, *J* = 5.5 Hz, 2H), 1.87 (s, 6H). **$^{13}$C NMR (125 MHz, DMSO-*d*$_6$)** δ 169.2, 157.1, 155.3, 141.4, 129.9, 128.5, 128.0, 126.3, 126.1, 121.6, 120.1, 117.9, 117.1, 116.6, 84.8, 62.9, 26.6. **HRMS (ESI)** calcd for $C_{19}H_{17}O_3$ $[M+H]^+$ 309.1127, found 309.1121.

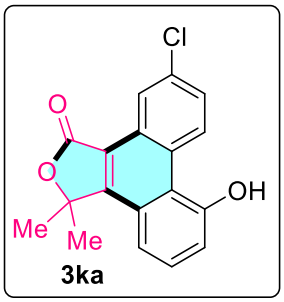
**10-Fluoro-7-hydroxy-3,3-dimethylphenanthro[9,10-*c*]furan-1(3*H*)-one (3ja)**:




The title compound was prepared from **1j** (94 mg, 0.5 mmol) and **2a** (94 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.50, $SiO_2$, EtOAc:Hexane 15:85) gave pure product **3ja** as a off-white solid (94.7 mg, 64%

yield), mp 290-295 °C. **$^1$H NMR (500 MHz, DMSO-*d*$_6$)** δ 11.36 (s, 1H), 9.83 (dd, *J* = 9.6, 6.0 Hz, 1H), 8.58 (dd, *J* = 10.1, 3.0 Hz, 1H), 7.68 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.63 (t, *J* = 7.9 Hz, 1H), 7.53 – 7.45 (m, 1H), 7.38 (dd, *J* = 7.7, 1.1 Hz, 1H), 1.81 (s, 6H). **$^{13}$C NMR (125 MHz, DMSO-*d*$_6$)** δ 170.0, 162.4, 159.9, 157.4, 157.2, 132.2, 132.1, 129.1, 128.5, 128.3, 128.2, 126.6, 121.8, 118.0, 117.8, 116.5, 116.3, 114.6, 108.2, 107.9, 86.2, 27.0. **$^{19}$F NMR (376 MHz, DMSO)** δ -112.49. (s, 1F). **HRMS (ESI)** calcd for $C_{18}H_{12}FO_3$ $[M-H]^-$ 295.0770, found 295.0765.

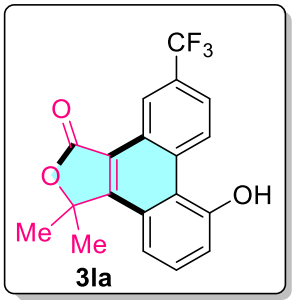
**10-Chloro-7-hydroxy-3,3-dimethylphenanthro[9,10-*c*]furan-1(3*H*)-one (3ka)**:



**3ka**

The title compound was prepared from **1k** (102 mg, 0.5 mmol) and **2a** (94 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.50, $SiO_2$, EtOAc:Hexane, 15:85) gave pure product **3ka** as a white solid (96.7 mg, 62% yield), mp 379-383 °. **$^1$H NMR (500 MHz, DMSO-*d*$_6$)** δ 11.31 (s, 1H), 9.89 (d, *J* = 9.3 Hz, 1H), 9.05 (d, *J* = 2.5 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.70 (t, *J* = 7.9 Hz, 1H), 7.47 (dd, *J* = 7.9, 1.0 Hz, 1H), 1.88 (s, 6H). **$^{13}$C NMR (100 MHz, DMSO-*d*$_6$)** δ 168.9, 157.1, 156.5, 131.9, 130.7, 129.69, 128.8, 127.5, 127.3, 126.4, 121.7, 120.8, 117.3, 117.1, 117.0, 85.2, 26.4. **HRMS (ESI)** calcd for $C_{18}H_{12}ClO_3$ $[M-H]^-$ 311.0475, found 311.0469.

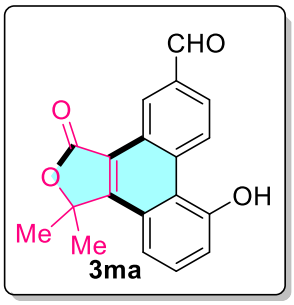
**7-Hydroxy-3,3-dimethyl-10-(trifluoromethyl)phenanthro[9,10-*c*]furan-1(3*H*)-one (3la)**:



**3la**

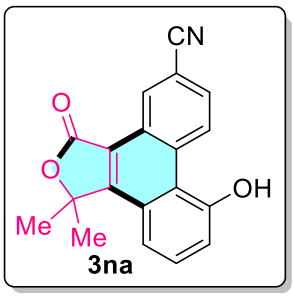
The title compound was prepared from **1l** (119 mg, 0.5 mmol) and **2a** (94 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.50, $SiO_2$, EtOAc:Hexane, 16:84) gave pure product **3la** as a pale greyish solid (96.8 mg, 56% yield), mp 310-313 °C. **$^1$H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.47 (s, 1H), 10.09 (d, *J* = 9.1 Hz, 1H), 9.41 (s, 1H), 8.06 (dd, *J* = 9.1, 2.0 Hz, 1H), 7.83 (d, *J* = 7.0 Hz, 1H), 7.77 (t, *J* = 7.9 Hz, 1H), 7.52 (dd, *J* = 7.7, 0.8 Hz, 1H), 1.90 (s, 6H). **$^{13}$C NMR (100 MHz, DMSO-*d*$_6$)** δ 168.9, 157.7, 156.8, 133.6, 129.8, 129.8, 127.2, 127.0, 126.7, 125.8, 125.68, 123.1, 120.3, 119.5, 117.7, 117.4, 117.4, 85.4, 26.3. **$^{19}$F NMR (376 MHz, DMSO-*d*$_6$)** δ -60.83. **HRMS (ESI)** calcd for $C_{19}H_{14}F_3O_3$ $[M+H]^+$ 347.0895, found 347.0941.

**8-hydroxy-1,1-dimethyl-3-oxo-1,3-dihydrophenanthro[9,10-*c*]furan-5-carbaldehyde (3ma)**:



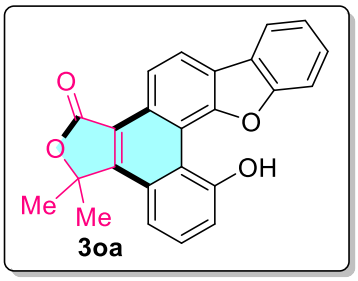

The title compound was prepared from **1m** (99 mg, 0.5 mmol) and **2a** (94 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.50, $SiO_2$, EtOAc:Hexane, 3:7) gave pure product **3ma** as a pale yellow solid (48.9 mg, 32% yield), mp 340-343 °C. **$^1$H NMR (500 MHz, DMSO-*d*$_6$)** δ 11.46 (s, 1H), 10.23 (s, 1H), 10.05 (d, *J* = 8.9 Hz, 1H), 9.58 (s, 1H), 8.19 (d, *J* = 8.9 Hz, 1H), 7.85 – 7.74 (m, 2H), 7.51 (d, *J* = 7.7 Hz, 1H), 1.90 (s, 6H). **$^{13}$C NMR (125 MHz, DMSO-*d*$_6$)** δ 193.1, 168.9, 157.9, 156.4, 135.2, 133.7, 130.0, 129.3, 127.4, 126.0, 125.9, 125.6, 120.6, 118.2, 117.4, 117.4, 85.3, 26.4. **HRMS (ESI)** calcd for $C_{19}H_{13}O_4$ $[M-H]^-$ 305.0814, found 305.0808.

**8-hydroxy-1,1-dimethyl-3-oxo-1,3-dihydrophenanthro[9,10-*c*]furan-5-carbonitrile (3na)**:




The title compound was prepared from **1n** (97.5 mg, 0.5 mmol) and **2a** (94 mg, 0.6 mmol) according to general procedure **A**. Only traces of the product (**3na**) formation was observed (<5% yield). **HRMS (ESI)** calcd for $C_{19}H_{12}NO_3[M-H]^-$ 302.0817, found 302.0811.

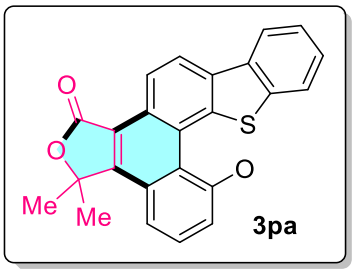
**23-Hydroxy-17,17-dimethyl-3,16-dioxahexacyclo[11.11.0.0$^{2,10}$.0$^{4,9}$.0$^{14,18}$.0$^{19,24}$]tetracosa-1(13), 2(10), 4, 6, 8, 11, 14(18), 19(24), 20, 22-decaen-15-one (3oa)**:




The title compound was prepared from **1o** (130 mg, 0.5 mmol) and **2a** (94 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.55, $SiO_2$, EtOAc:Hexane, 20:80) gave pure product **3oa** as a pale brown solid (88.3 mg, 48 % yield), mp 210-220 °C. **$^1$H NMR (400 MHz, CDCl$_3$)** δ 9.64 (s, 1H), 9.46 (d, *J* = 8.4 Hz, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 7.5 Hz, 1H), 7.83 – 7.75 (m, 2H), 7.72 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.52 (dd, *J* = 10.9, 4.1 Hz, 1H), 1.99 (s, 6H). **$^{13}$C NMR (100 MHz, CDCl$_3$)** δ 169.7, 155.6, 155.3, 154.1, 149.7, 129.3, 128.0, 127.5, 127.5, 124.7,

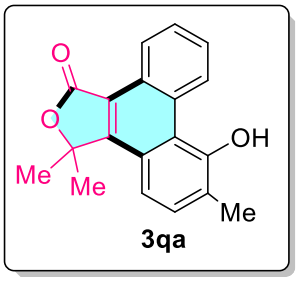
124.0, 123.2, 121.2, 120.9, 120.6, 120.5, 120.0, 118.9, 118.0, 116.2, 111.7, 84.9, 27.2 . **HRMS (ESI)** calcd for $C_{24}H_{17}O_4$ $[M+H]^+$ 369.1127, found 369.1121. *note: IUPAC name of* **3ma** *was obtained from Marvin Sketch software.*

**1-Hydroxy-5,5-dimethylbenzo[4',5']thieno[3',2':3,4]phenanthro[9,10-*c*]furan-7(5*H*)-one (3pa)**:



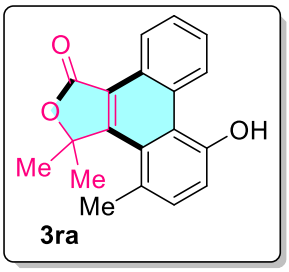

The title compound was prepared from **1p** (138 mg, 0.5 mmol) and **2a** (94 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.50, $SiO_2$, EtOAc:Hexane, 1:4) gave pure product **3pa** as a sticky solid (80.6 mg, 42% yield). **$^1$H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.60 (s, 1H), 9.25 (d, *J* = 8.5 Hz, 1H), 8.80 (d, *J* = 8.6 Hz, 1H), 8.52 (dd, *J* = 5.3, 3.7 Hz, 1H), 8.07 (dd, *J* = 5.2, 3.6 Hz, 1H), 7.83 – 7.77 (m, 2H), 7.57 – 7.52 (m, 2H), 7.49 (dd, *J* = 6.0, 2.9 Hz, 1H), 1.90 (s, 6H). **$^{13}$C NMR (100 MHz, DMSO-*d*$_6$)** δ 169.0, 154.9, 154.6, 140.3, 137.2, 134.1, 134.0, 129.2, 127.0, 126.7, 126.5, 126.1, 124.4, 122.2, 121.9, 121.6, 120.7, 119.0, 118.4, 116.2, 115.6, 84.6, 26.6. **HRMS (ESI)** calcd for $C_{24}H_{15}O_3S$ $[M-H]^-$ 383.0742, found 383.0736.

**7-Hydroxy-3,3,6-trimethylphenanthro[9,10-*c*]furan-1(3*H*)-one (3qa):**



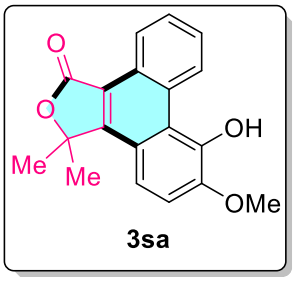

The title compound was prepared from **1q** (92 mg, 0.5 mmol) and **2a** (94 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.50, $SiO_2$, EtOAc:Hexane, 15:85) gave pure product **3qa** as a off-white solid (105.1 mg, 72% yield), mp 278-283 °C. **$^1$H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.00 (dd, *J* = 6.6, 3.1 Hz, 1H), 9.72 (s, 1H), 9.08 (dd, *J* = 6.5, 2.9 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 3H), 7.62 (d, *J* = 8.2 Hz, 1H), 2.52 (s, 3H), 1.87 (s, 6H). **$^{13}$C NMR (101 MHz, DMSO-*d*$_6$)** δ 169.2, 155.55, 154.3, 131.1, 130.7, 128.9, 127.4, 127.2, 127.1, 126.4, 124.8, 122.8, 117.7, 117.04, 84.7, 79.2, 26.6, 17.8. **HRMS (ESI)** calcd for $C_{19}H_{17}O_3$ $[M+H]^+$ 293.1178, found 293.1172.

**7-Hydroxy-3,3,4-trimethylphenanthro[9,10-c]furan-1(3H)-one (3ra):**



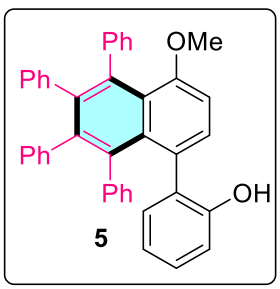

The title compound was prepared from **1r** (92 mg, 0.5 mmol) and **2a** (94 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.55, $SiO_2$, EtOAc:Hexane, 15:85) gave pure product **3ra** as a white solid (91.9 mg, 63% yield), mp 265-268 °C. **$^1$H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.78 (s, 1H), 9.76 – 9.72 (m, 1H), 9.18 – 9.14 (m, 1H), 7.72 – 7.65 (m, 2H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 2.83 (s, 3H), 1.96 (s, 6H). **$^{13}$C NMR (100 MHz, DMSO-*d*$_6$)** δ 168.9, 155.4, 155.0, 132.6, 131.3, 128.4, 127.7, 127.1, 127.0, 125.5, 124.6, 123.4, 122.5, 119.3, 116.4, 87.0, 28.0, 25.8. **HRMS (ESI)** calcd for $C_{19}H_{17}O_3$ $[M+H]^+$ 293.1178, found 293.1172.

**7-Hydroxy-6-methoxy-3,3-dimethylphenanthro[9,10-*c*]furan-1(3*H*)-one (3sa):**




The title compound was prepared from **1s** (100 mg, 0.5 mmol) and **2a** (94 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.50, $SiO_2$, EtOAc:Hexane, 1:4) gave pure product **3sa** as a white solid (103.1 mg, 67% yield) mp 260-270°C. **$^1$H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.05 (s, 1H), 9.89 (dd, *J* = 6.3, 3.4 Hz, 1H), 9.04 (dd, *J* = 6.1, 3.3 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.72 (dd, *J* = 6.3, 3.4 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 1H), 4.05 (s, 3H), 1.86 (s, 6H). **$^{13}$C NMR (100 MHz, DMSO-*d*$_6$)** δ 169.2, 156.0, 148.2, 145.2, 130.9, 128.8, 127.2, 127.1, 126.4, 122.8, 121.3, 119.7, 117.6, 115.6, 112.74, 84.55, 56.7, 26.7. **HRMS (ESI)** calcd for $C_{19}H_{17}O_4$ $[M+H]^+$ 309.1127, found 309.1121.

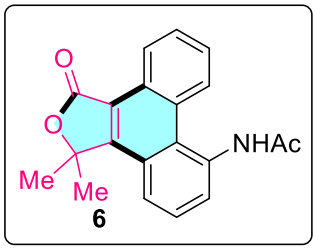
**2-(4-Methoxy-5,6,7,8-tetraphenylnaphthalen-1-yl)phenol (5):**




The title compound was prepared from **1g** (100 mg, 0.5 mmol) and **4a** (94 mg, 0.6 mmol) according to general procedure **A**. Purification using column chromatography ($R_f$ = 0.50, $SiO_2$, EtOAc:Hexane, 30:70) gave pure product **5** as a white solid (124.6 mg, 45% yield), mp 230-234 °C. **$^1$H NMR (500 MHz, CDCl$_3$)** δ 7.28 (d, *J* = 1.7 Hz, 1H), 7.11 (dd, *J* =

3.3, 2.3 Hz, 4H), 7.05 (dd, *J* = 8.8, 3.9 Hz, 1H), 6.88 (dd, *J* = 7.7, 3.9 Hz, 2H), 6.84 – 6.80 (m, 4H), 6.77 – 6.72 (m, 6H), 6.66 (dd, *J* = 9.0, 4.3 Hz, 2H), 6.62 (ddd, *J* = 9.9, 3.8, 1.7 Hz, 4H), 6.57 (d, *J* = 1.1 Hz, 1H), 6.45 – 6.42 (m, 1H), 3.43 (s, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$)** δ 157.5, 151.6, 144.1, 141.7, 140.4, 140.3, 140.1, 138.0, 137.0, 132.9, 132.3, 132.2, 131.7, 131.4, 131.4, 131.1, 131.0, 130.6, 130.2, 129.8, 127.9, 126.8, 126.5, 126.3, 126.2, 125.6, 125.6, 125.13, 125.0 124.9, 119.6, 114.7, 106.4, 55.7. **HRMS (ESI)** calcd for $C_{41}H_{31}O_2$ $[M+H]^+$ 555.2324, found 555.2317.

**N-(3,3-dimethyl-1-oxo-1,3-dihydrophenanthro[9,10-*c*]furan-7-yl)acetamide (6):**



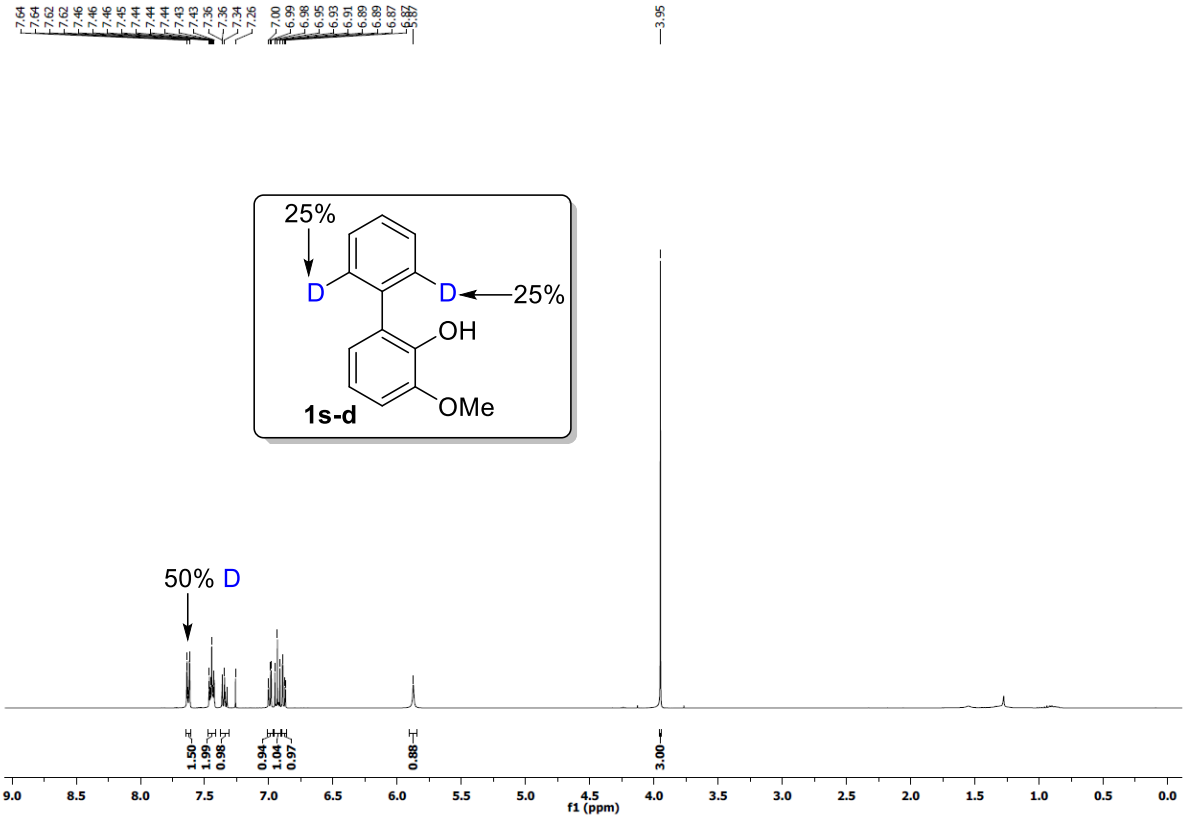

**6**

The title compound was prepared from **1u** (106 mg, 0.5 mmol) and **2a** (94 mg, 0.6 mmol) according to general procedure A. Purification using column chromatography ($R_f$ = 0.50, $SiO_2$, EtOAc:Hexane, 1:4) gave regioisomeric mixture **6** as a white colour solid (71.7 mg, 45% yield). mp 210-214°C. **$^1$H NMR (400 MHz, DMSO-$d_6$)** δ 10.48 (s, 1H), 10.43 (s, 0.24H), 9.38 (d, J = 8.4 Hz, 0.25H), 9.27 (d, J = 8.1 Hz, 1H), 9.09 (d, J = 7.8 Hz, 1H), 9.06 (s, 0.17H), 8.30 (d, J = 8.0 Hz, 0.26H), 8.20 (d, J = 5.8 Hz, 1H), 7.92 – 7.69 (m, 5H), 7.64 (d, J = 7.4 Hz, 0.27H), 2.21 (s, 3.7H), 1.91 (s, 7.68H). **$^{13}$C NMR (100 MHz, DMSO-$d_6$)** δ 169.0, 168.9, 155.3, 155.2, 154.3, 136.1, 135.4, 133.1, 131.2, 130.4, 129.4, 129.3, 129.0, 128.0, 127.8, 127.4, 127.3, 126.6, 126.4, 126.0, 125.9, 124.8, 124.5, 123.2, 121.8, 117.9, 117.7, 85.0, 84.5, 79.2, 26.6, 23.5. **HRMS (ESI)** calcd for $C_{20}H_{16}NO_3$ $[M-H]^-$ 318.1130, found 318.1124.

**5. Labelling and KIE studies:**

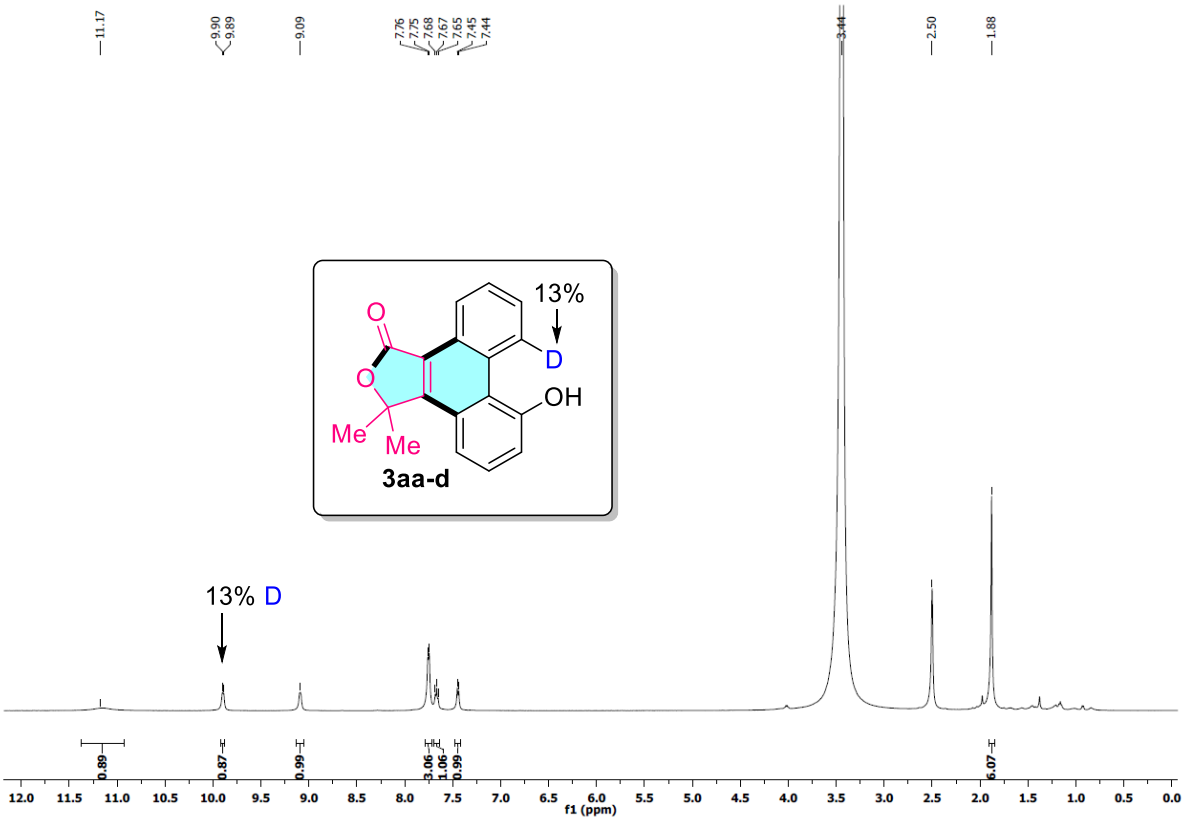
**EXP. I: H/D exchange experiment:**

To a solution of biphenol **1s** (100 mg, 0.5 mmol) in DMF, $Pd(OAc)_2$ (11.2 mg, 10 mol %), $Cu(OAc)_2.H_2O$ (199.6 mg, 2 equiv) sodium acetate (82 mg, 2 equiv) were introduced. Later deuterium oxide (50 mg, 5 equiv) and methanol-$d_4$ (90 mg, 5 equiv) were added to the contents and the resultant reaction mixture was stirred at 100 °C (oil bath) for 2 hours under nitrogen balloon. The reaction mixture was cooled to room temperature before ice water was added to it. The aqueous layer was extracted with ethyl acetate (3×10 mL), the combined organic extracts were washed with brine, dried over sodium sulfate and concentrated under reduced pressure. The crude residue was purified by column chromatography ($R_f$ = 0.50) ($SiO_2$, EtOAc:Hexane, 1:4) to get **1s-*d*** as off-white solid.

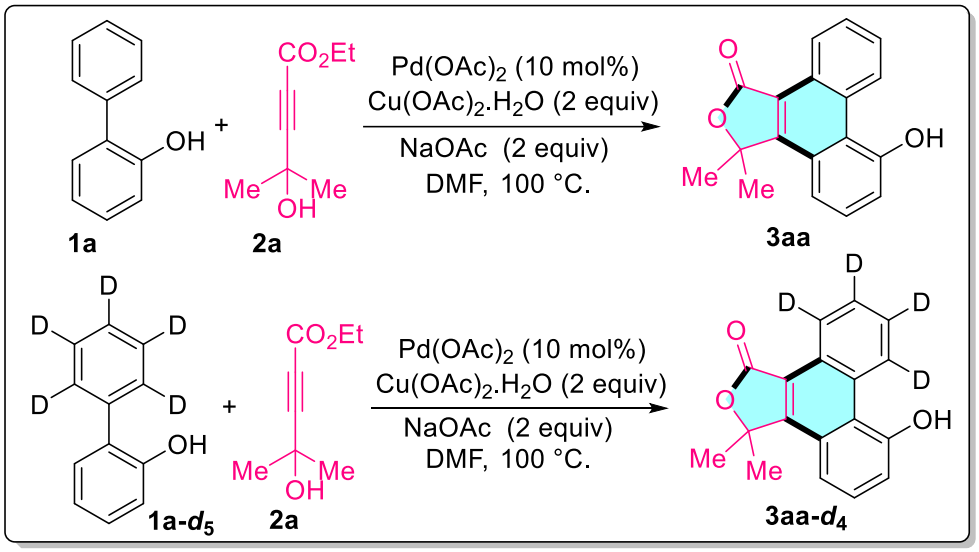



**EXP. II: Deuterium insertion experiment:**

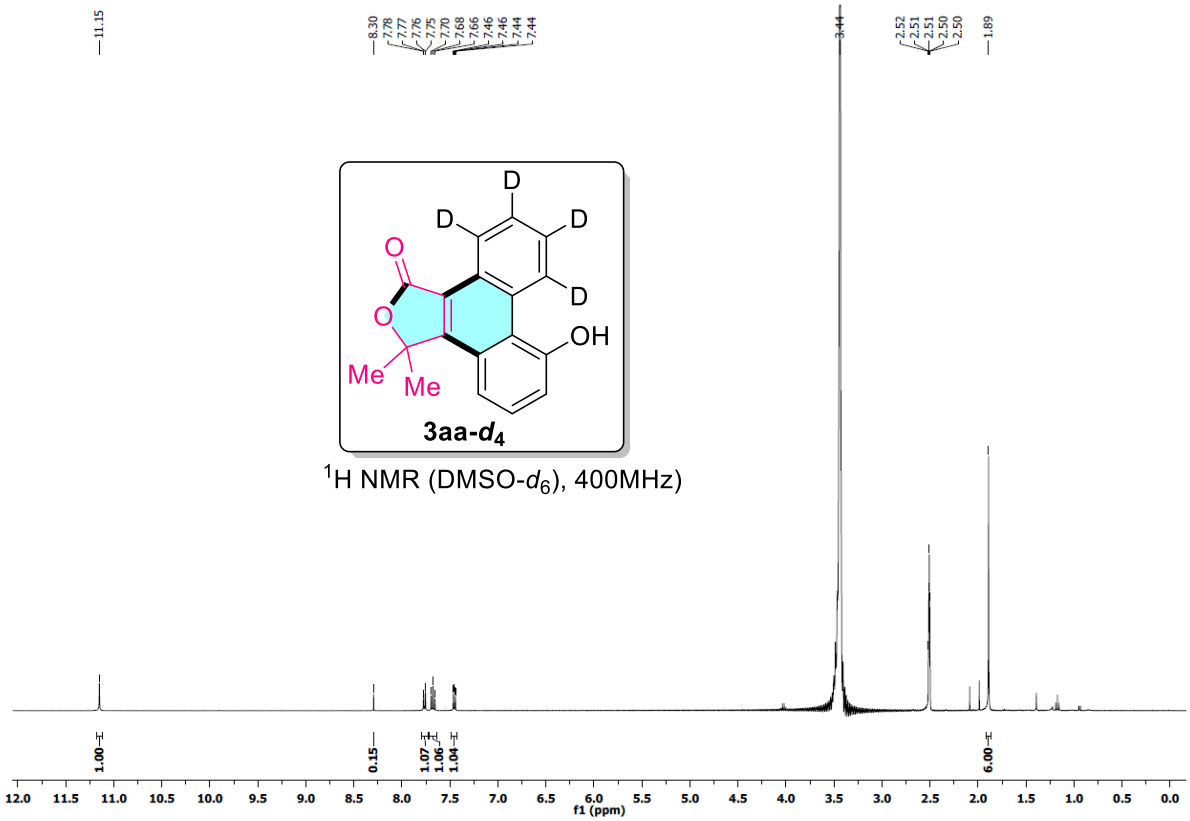
To a solution of biphenol **1a** (85 mg, 0.5 mmol), 4-hydroxy-2-alkyonate **2a** (94 mg, 0.6 mmol) in DMF, $Pd(OAc)_2$ (11.2 mg, 10 mol %), $Cu(OAc)_2.H_2O$ (199.6 mg, 2 equiv) sodium acetate (82 mg, 2 equiv) were introduced. Later deuterium oxide (50 mg, 5 equiv) and methanol-$d_4$ (90 mg, 5 equiv) were added to the contents and the resultant reaction mixture was stirred at 100 °C (oil bath) for 2 hours under nitrogen balloon. The reaction mixture was cooled to room temperature before ice water was added to it. The aqueous layer was extracted with ethyl acetate (3×10 mL), the combined organic extracts were washed with brine, dried over sodium sulfate and concentrated under reduced pressure. The crude residue was purified by column chromatography ($R_f$ = 0.50) ($SiO_2$, EtOAc:Hexane, 15:85) to get **3aa-*d*** as off-white solid.



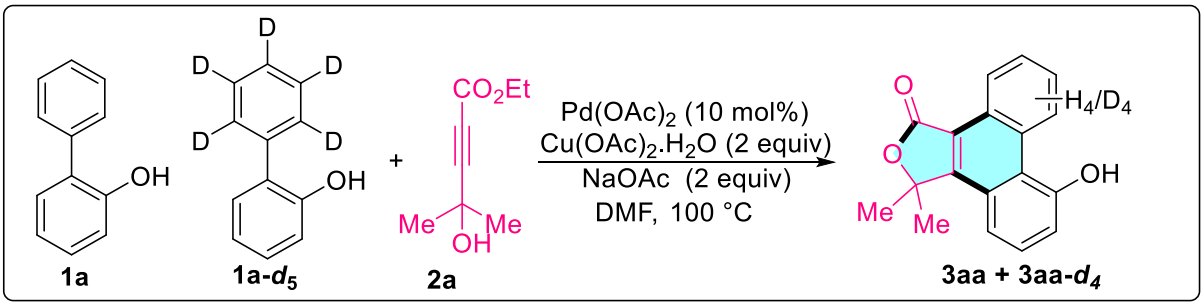

**Exp-III. KIE determined from two parallel reactions:**



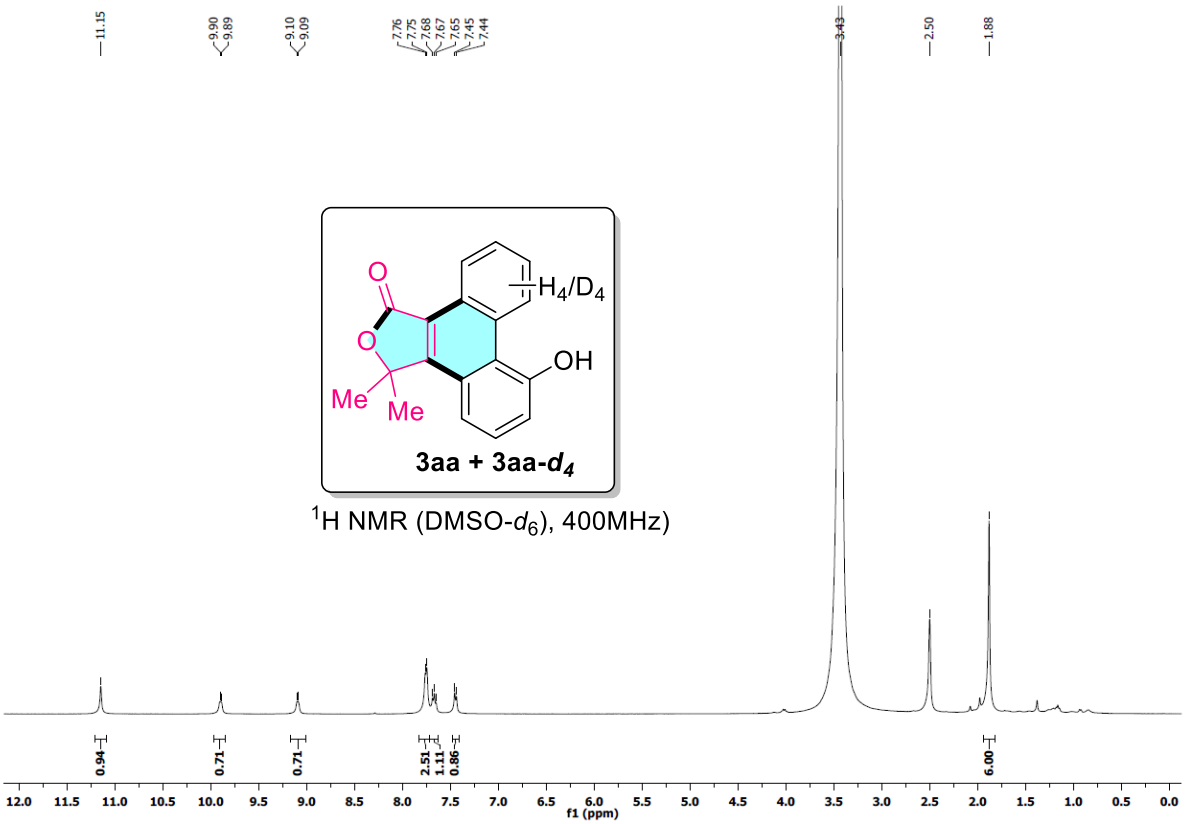

To a mixture of biphenol **1a** (85 mg, 0.5 mmol) or **1a-*d*$_5$** (87.5 mg, 0.5 mmol) and 4-hydroxy-2-alkyonate **2a** (94 mg, 0.6 mmol) in DMF, $Pd(OAc)_2$ (11.2 mg, 10 mol%), $Cu(OAc)_2.H_2O$ (199.6 mg, 2 equiv) sodium acetate (82 mg, 2 equiv) were introduced and the reaction mixture was stirred at 100 °C (oil bath) for 1 hour under nitrogen balloon. The reaction mixture was cooled to room temperature before ice water was added to it. The aqueous layer was extracted with ethyl acetate (3×10 mL), the combined organic extracts were washed with brine, dried over sodium sulfate and concentrated under reduced pressure. The crude residue was purified by column chromatography ($R_f$ = 0.50) ($SiO_2$, EtOAc:Hexane, 15:85) to get **3aa** (58.3 mg, 42%) or **3aa-*d*$_4$** (22.5 mg, 16%) as off-white solids. The $k_H/k_D$ value was determined to be 2.62 by the isolated yield.




**Exp. IV: KIE determined from an intermolecular competition**:

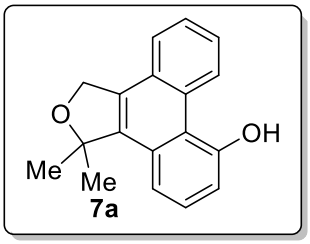



To a mixture of biphenol **1a** (85 mg, 0.5 mmol), **1a-*d*$_5$** (87.5 mg, 0.5 mmol) and 4-hydroxy-2-alkyonate **2a** (78.3 mg, 0.5 mmol) in DMF, $Pd(OAc)_2$ (11.2 mg, 10 mol %), $Cu(OAc)_2.H_2O$ (199.6 mg, 2 equiv) sodium acetate (82 mg, 2 equiv) were introduced and the reaction mixture was stirred at 100 °C (oil bath) for 1 hour under nitrogen balloon. The reaction mixture was cooled to room temperature before ice water was added to it. The aqueous layer was extracted with ethyl acetate (3×10 mL), the combined organic extracts were washed with brine, dried over sodium sulfate and concentrated under reduced pressure. The crude residue was purified by column chromatography ($R_f$ = 0.50) ($SiO_2$, EtOAc:Hexane, 15:85) to get **3aa+3aa-*d*$_4$**. The $k_H/k_D$ value of **3aa+3aa-*d*$_4$** was determined to be 2.45 by $^1$H NMR.



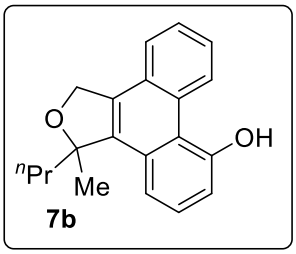

**6. General Procedure and Characteristic Data of Synthetic Transformations.**

**3,3-Dimethyl-1,3-dihydrophenanthro[9,10-*c*]furan-7-ol (7a):**




To a round-bottomed flask, compound **3aa** (50 mg, 0.18 mmol) was dissolved in $CH_2Cl_2$ before the addition of DIBAL-H (0.45 mL, 0.54 mmol, 1.2 M in toluene) at 0 °C. The mixture was stirred at room temperature until the complete consumption of starting materials (monitored by TLC). The solvent was evaporated using a rotary evaporator, and the residue was added to 3 M NaOH. The aqueous layer was extracted with ethyl acetate (2 × 10 mL), the organic layer was evaporated, and the residue was purified by column chromatography, $R_f$ = 0.50 ($SiO_2$, EtOAc:hexane, 1:4), to get **7a** as colourless solid in 85% (40.3 mg) yield, mp 245-248 °C. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 9.75 (d, *J* = 8.4 Hz, 1H), 7.69 – 7.59 (m, 4H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 5.53 (s, 2H), 1.85 (s, 6H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 155.3, 138.6, 133.6, 130.7, 129.6, 129.3, 127.2, 126.8, 126.5, 126.5, 124.1, 120.3, 116.8, 113.1, 89.5, 71.1, 28.3. **HRMS Mass (ESI)** calcd for $C_{18}H_{15}O_2$ $[M-H]^-$ 263.1072, found 263.1067.

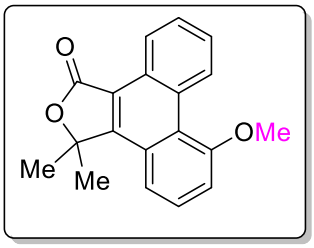
**3-Methyl-3-propyl-1,3-dihydrophenanthro[9,10-*c*]furan-7-ol (7b):**




**7b**

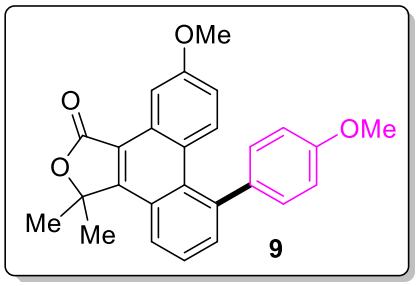
The title compound was prepared from **3ac** (50 mg, 0.16 mmol) using DIBAL-H (0.41 mL, 0.49 mmol, 1.2 M in toluene) following the above procedure. Purification using column chromatography ($R_f$ = 0.50, $SiO_2$, EtOAc:Hexane, 1:4) gave pure product **7b** as a off-white solid (38.7 mg, 83% yield), mp 248-251 °C. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 9.75 (d, *J* = 8.4 Hz, 1H), 7.70 – 7.56 (m, 4H), 7.47 (t, *J* = 7.9 Hz, 1H), 7.02 (dd, *J* = 7.7, 0.8 Hz, 1H), 6.05 (s, 1H), 5.53 (d, J = 1.6 Hz, 2H), 2.28 (ddd, J = 14.4, 12.0, 4.7 Hz, 1H), 2.07 (ddd, J = 14.4, 11.8, 4.5 Hz, 1H), 1.79 (s, 3H), 1.42 (ddd, J = 12.9, 7.4, 2.8 Hz, 1H), 1.03 – 0.89 (m, 1H), 0.82 (t, J = 7.3 Hz, 3H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 155.4, 136.9, 134.5, 130.8, 129.9, 129.3, 127.2, 126.8, 126.53, 126.4, 124.0, 120.1, 116.5, 113.1, 92.5, 72.0, 43.8, 27.7, 17.8, 14.4. **HRMS Mass (ESI)** calcd for $C_{20}H_{19}O_2$ $[M-H]^-$ 291.1385, found 291.1380.

**7-Methoxy-3,3-dimethylphenanthro[9,10-*c*]furan-1(3*H*)-one (8):**




A round-bottomed flask was charged with compound **3aa** (0.18 mmol, 50 mg) and $K_2CO_3$ (0.27 mmol, 37.2 mg) in acetone. Methyl iodide (0.17 mmol, 38.3 mg) was added drop wise at 0 °C, and the reaction mixture was stirred at room temperature for overnight. The solvent was removed before 10 mL of water was added. The aqueous layer was extracted with ethyl acetate (2 × 10 mL), the organic layer was evaporated, and the residue was purified by column chromatography. A colorless solid **8** was obtained in 86% (45.2 mg) yield. $R_f$ = 0.50 ($SiO_2$, EtOAc:hexane, 5:95), mp 180–186 °C. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 9.77 – 9.70 (m, 1H), 9.35 – 9.27 (m, 1H), 7.76 – 7.71 (m, 2H), 7.71 – 7.67 (m, 2H), 7.37 (dd, *J* = 6.1, 3.1 Hz, 1H), 4.18 (s, 3H), 1.95 (s, 6H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 170.0, 159.6, 154.7, 131.1, 128.9, 127.7, 127.6, 127.2, 124.3, 124.0, 119.5, 118.0, 111.5, 84.8, 56.1, 27.19. **HRMS(ESI)** calcd for $C_{19}H_{17}O_3$ $[M+H]^+$ 293.1178, found 293.1190.

**10-Methoxy-7-(4-methoxyphenyl)-3,3-dimethylphenanthro[9,10-*c*]furan-1(3*H*)-one (9):**

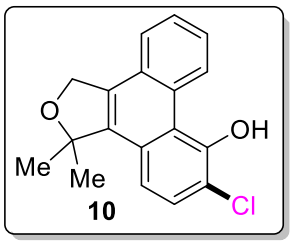



A round-bottomed flask was charged with compound **3ga** (0.16 mmol, 50 mg), pyridine (0.32 mmol, 25.65 mg) in dichlromethane, triflic anhydride ( 0.32 mmol, 92 mg) was added drop wise at 0 °C, and the reaction mixture was stirred at room temperature for 3 hours. The solvent was removed before 10 mL of water was added. The aqueous layer was extracted with ethyl acetate (2 × 10 mL), the organic layer was concentrated, and the residue was purified by column chromatography. A colorless solid (53 mg) was obtained.

This triflated adduct (53 mg, 0.12) in 1,4-dioxane, para methoxy phenyl boronic acid (27 mg, 0.18 mmol), potassium phosphate (77 mg, 0.36 mmol), $Pd(PPh_3)_4$ (10 mol%) were added and the mixture was stirred at 90 °C for 5 h under nitrogen atmosphere. After completion of the reaction, brine solution was added (10 mL) at room temperature and was extracted with ethyl acetate (3 × 10 mL). The solvent was removed under vacuum and the product was purified through a short silica gel column using EtOAc:Hexanes (1:9) as the eluent to get product **9** as a colorless solid (40 mg, 62 % yield), mp 205-208 °C.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.64 (d, *J* = 2.9 Hz, 1H), 7.99 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.74 (d, *J* = 9.5 Hz, 1H), 7.68 – 7.60 (m, 2H), 7.32 – 7.27 (m, 2H), 7.04 – 6.97 (m, 2H), 6.82 (dd, *J* = 9.5, 2.9 Hz, 1H), 3.97 (s, 3H), 3.91 (s, 3H), 1.99 (s, 6H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 170.1, 159.2, 158.8, 155.5, 141.1, 137.2, 133.8, 132.9, 130.3, 130.0, 129.7, 125.5, 125.3, 125.3, 124.6, 118.6, 116.5, 114.8, 104.1, 84.8, 55.6, 55.5, 27.3. **HRMS(ESI)** calcd for $C_{26}H_{23}O_4$ $[M+H]^+$ 399.1596, found 399.1590.

**6-Chloro-3,3-dimethyl-1,3-dihydrophenanthro[9,10-*c*]furan-7-ol (8):**

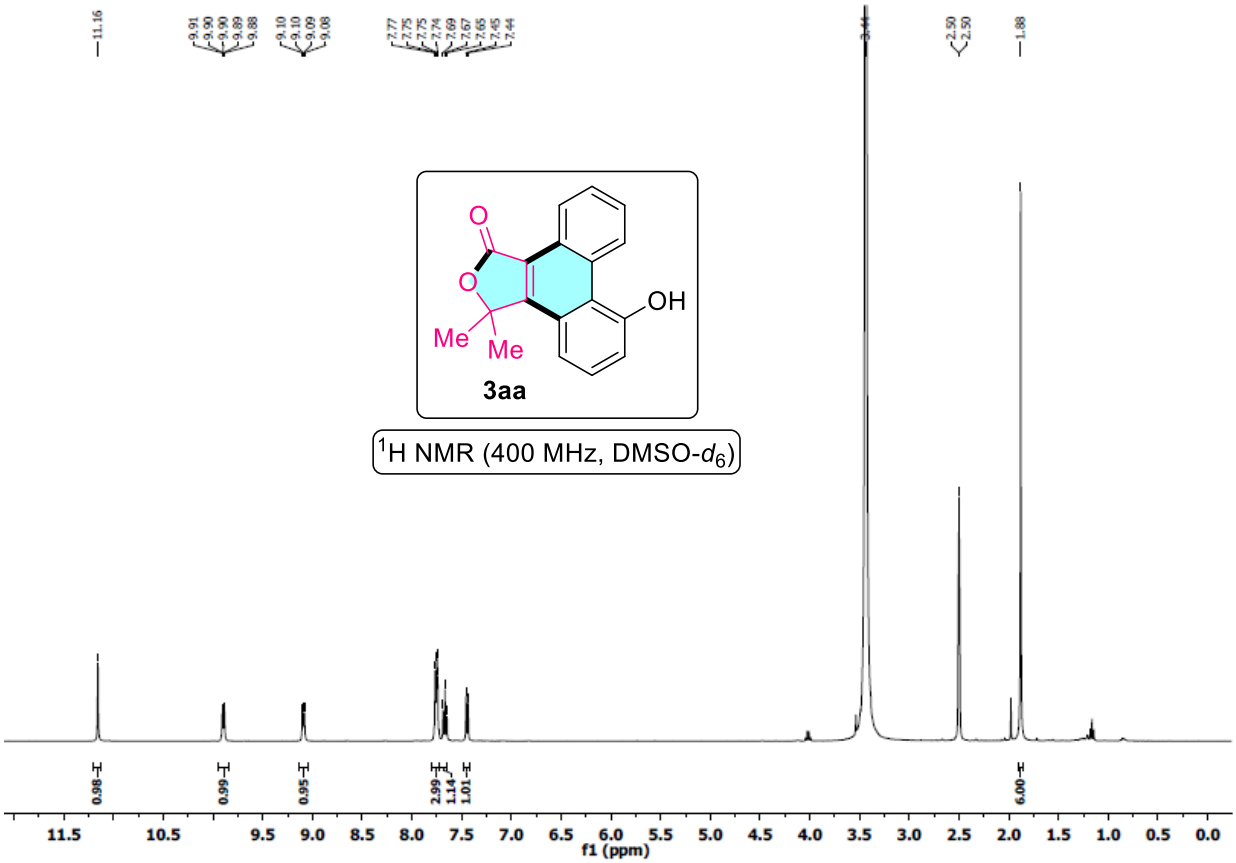



A round-bottomed flask was charged with compound **7a** (0.19 mmol, 50 mg) in 1:4 ratio of water and ethyl acetate mixture as solvents, sodium chloride (0.38 mmol, 22 mg), oxone (0.09 mmol, 28 mg) were added and the reaction mixture was stirred at room temperature for overnight. Water was added to the reaction mixture and the aqueous layer was extracted with ethyl acetate (2 × 10 mL). The organic layer was concentrated, and the residue was purified by column chromatography. A pale brown color solid **10** was obtained in 65% (36.6 mg) yield. $R_f$ = 0.55 ($SiO_2$, EtOAc:hexane, 5:95), mp 170-173 °C.

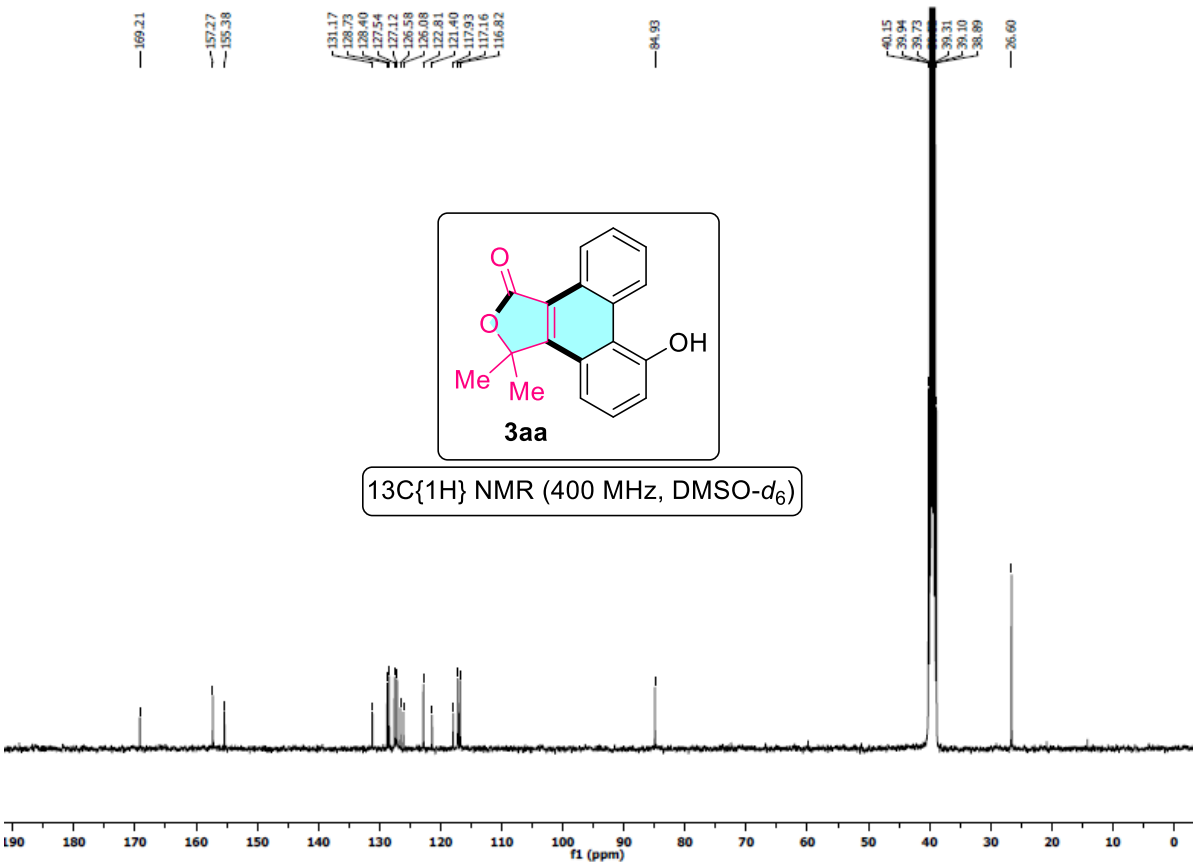
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 9.75 (d, *J* = 8.1 Hz, 1H), 7.87 – 7.44 (m, 5H), 6.83 (s, 1H), 5.51 (s, 2H), 1.82 (s, 6H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 150.4, 138.4, 134.2, 130.3,

129.3, 128.3, 127.5, 127.1, 126.9, 126.5, 124.2, 117.5, 116.6, 89.2, 71.0, 28.3. **HRMS(ESI)** calcd for $C_{18}H_{14}ClO_2$ $[M-H]^-$ 297.0682, found 297.0677.

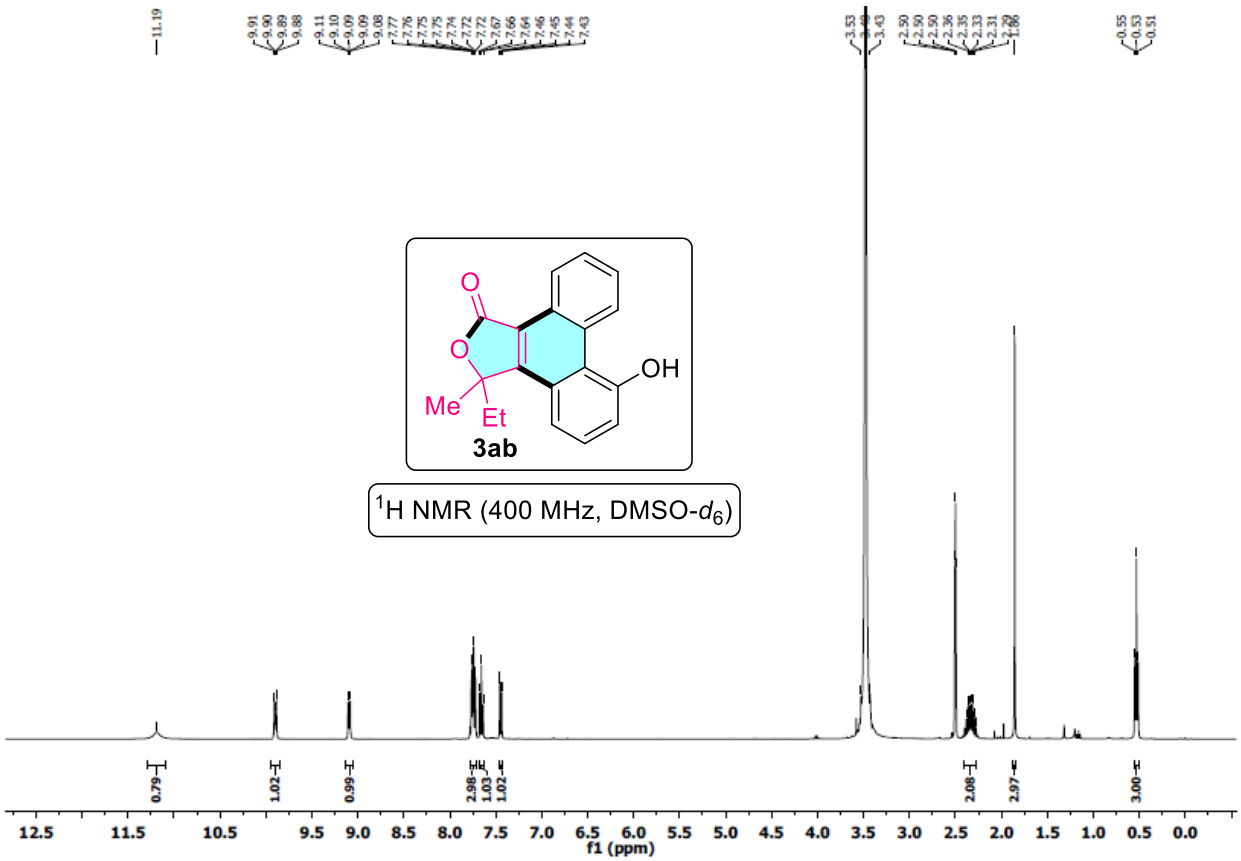
## 7. Copies of $^{1}H$, $^{13}C$, $^{19}F$ NMR spectra:



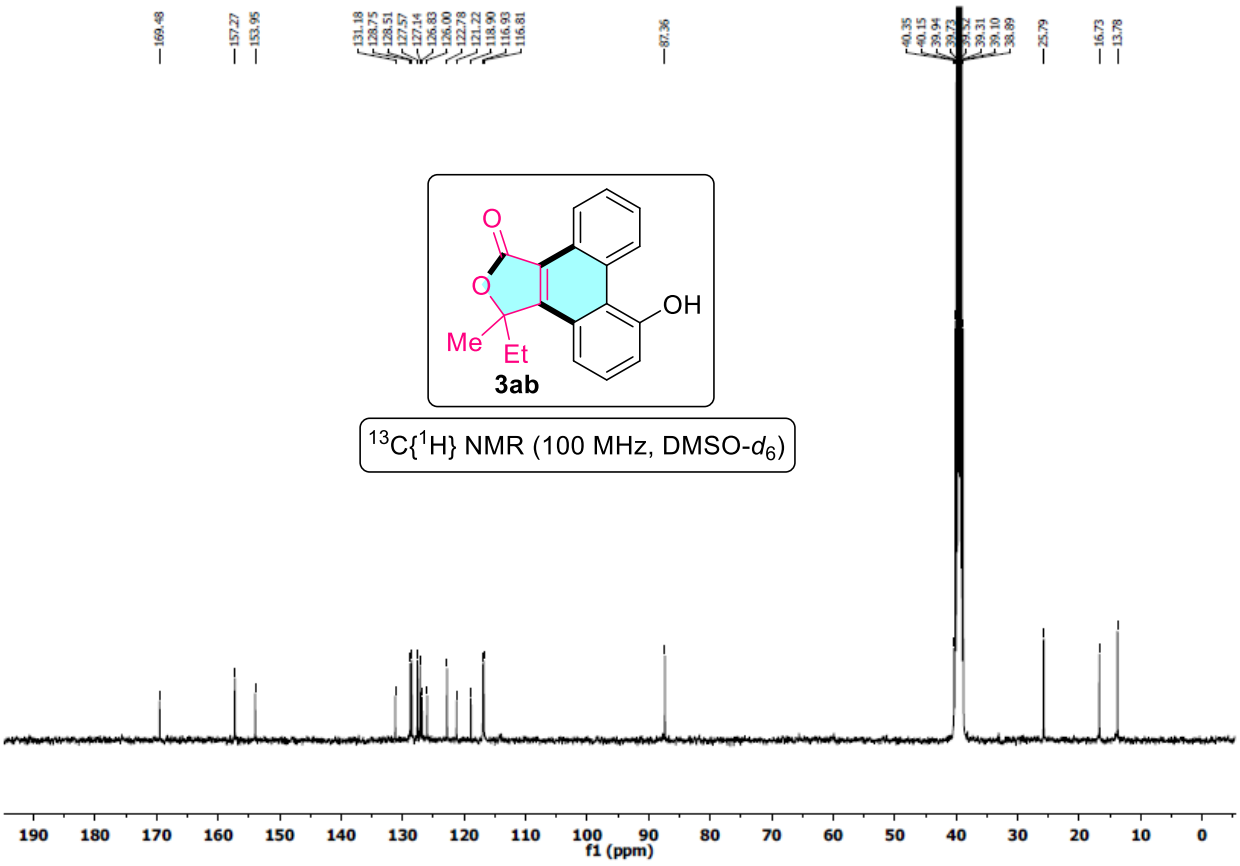

$^{1}H$ NMR (400 MHz, DMSO-$d_6$)



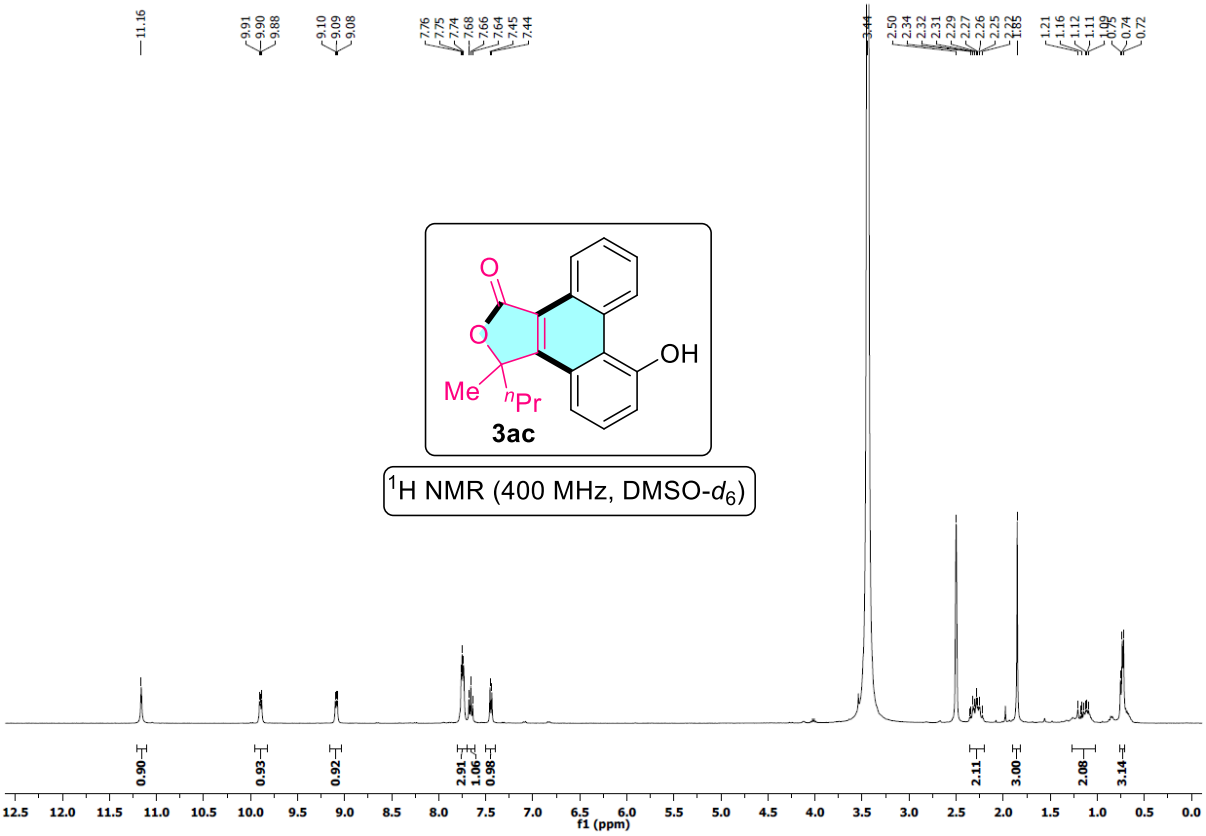

13C{1H} NMR (400 MHz, DMSO-$d_6$)

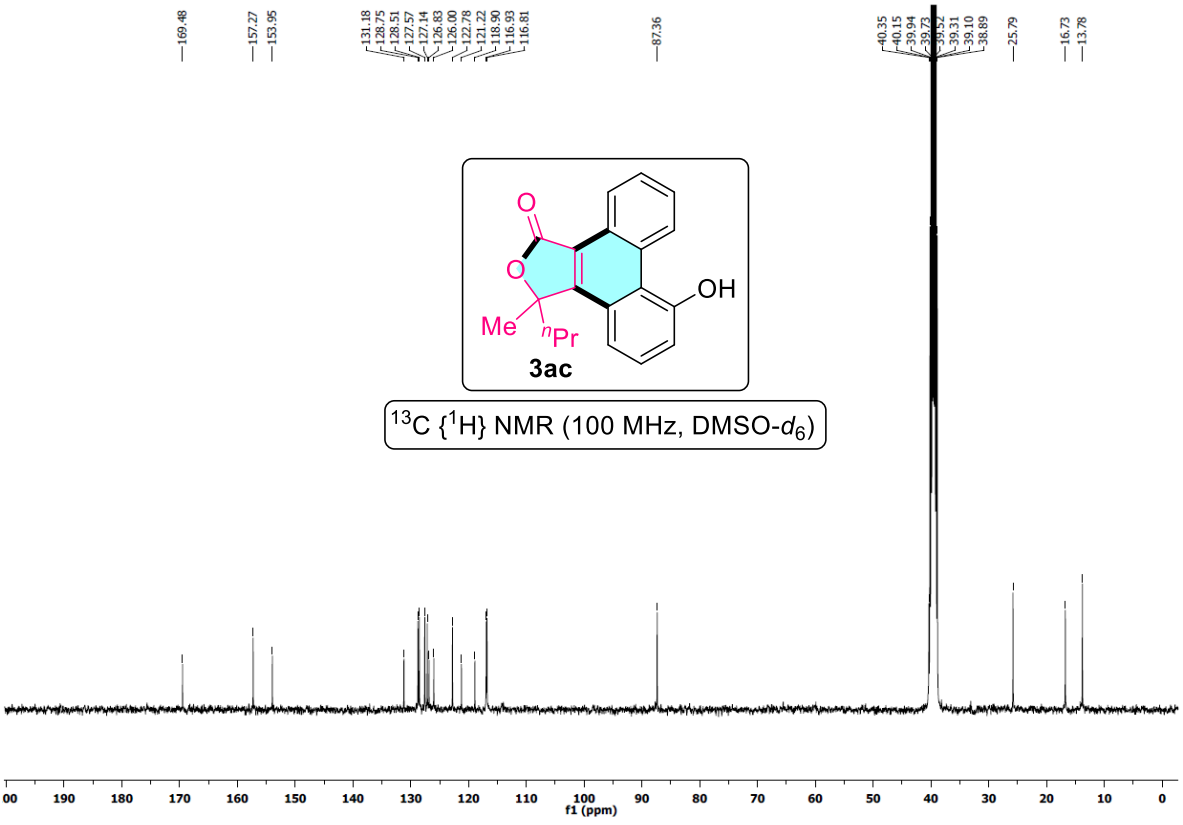


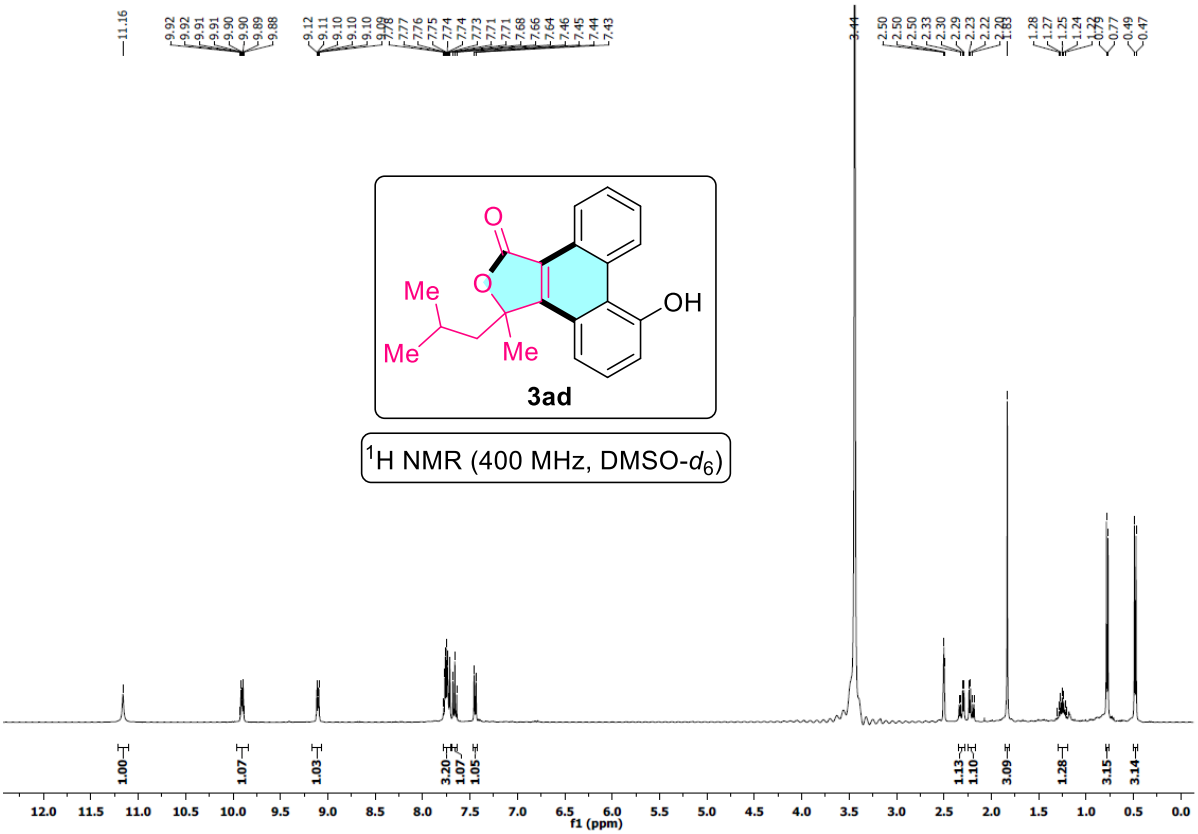

$^{1}$H NMR (400 MHz, DMSO-$d_6$)

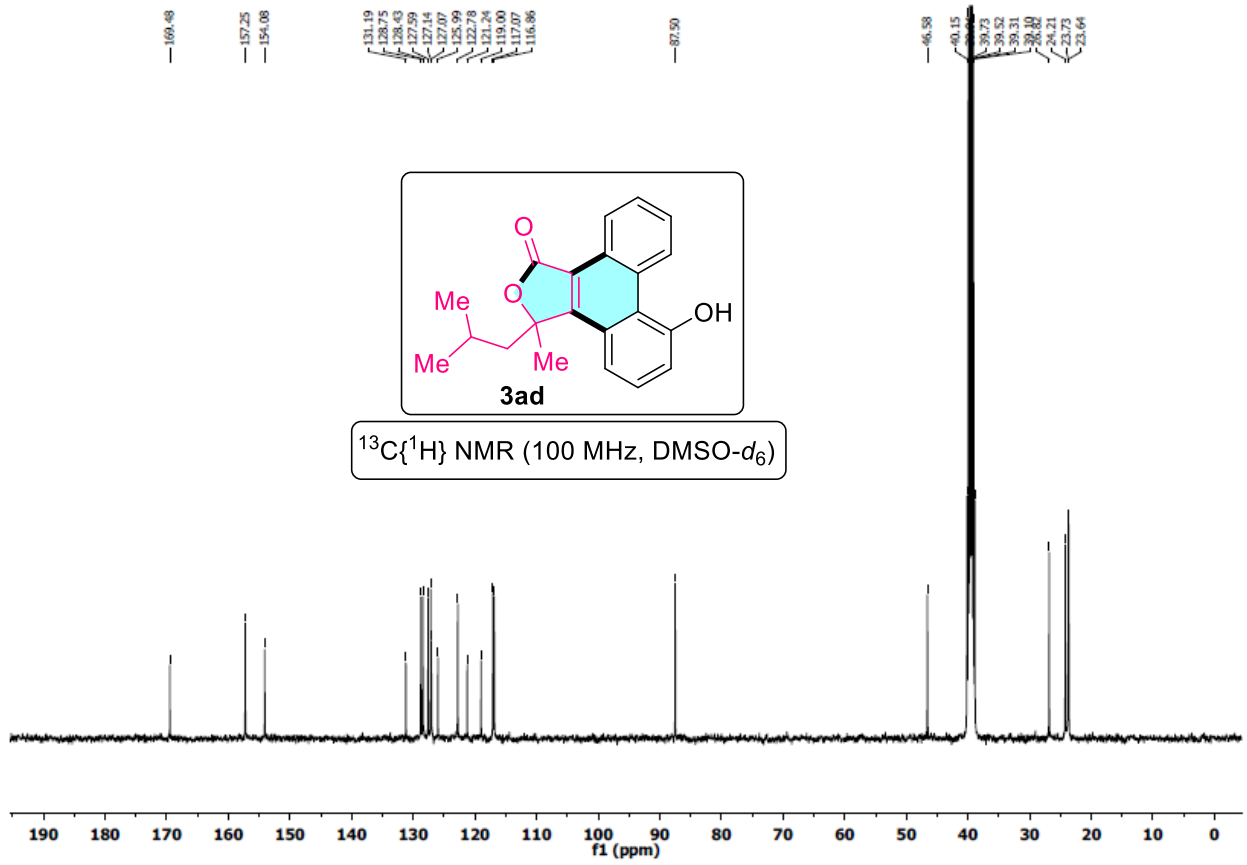


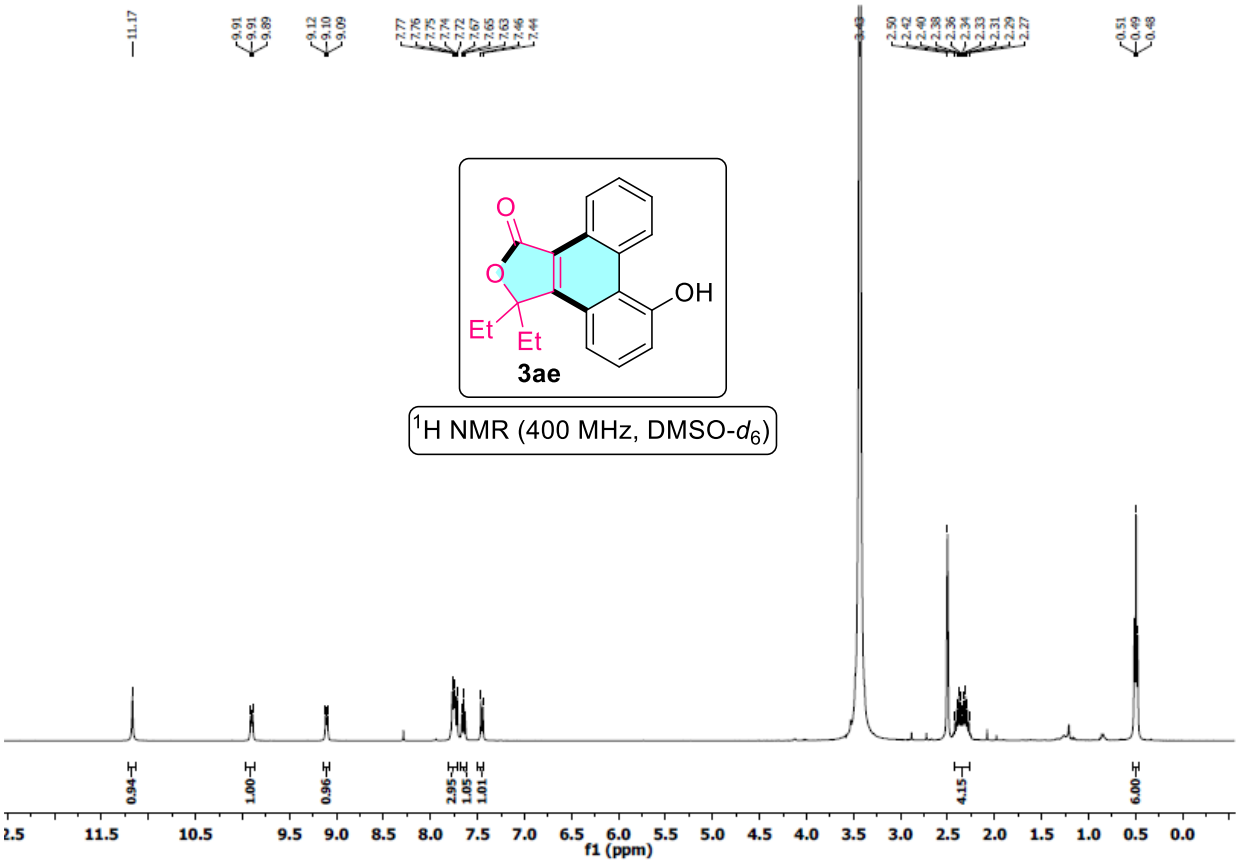

$^{13}$C{$^{1}$H} NMR (100 MHz, DMSO-$d_6$)


11.16
9.91
9.90
9.88
9.10
9.09
9.08
7.76
7.75
7.74
7.68
7.66
7.64
7.45
7.44
3.44
2.50
2.34
2.32
2.31
2.29
2.27
2.26
2.25
2.23
1.85
1.21
1.16
1.12
1.11
1.09
0.75
0.74
0.72
O
O
OH
Me
nPr
3ac
1H NMR (400 MHz, DMSO-d6)
0.90
0.93
0.92
2.91
1.06
0.98
2.11
3.00
2.08
3.14
f1 (ppm)

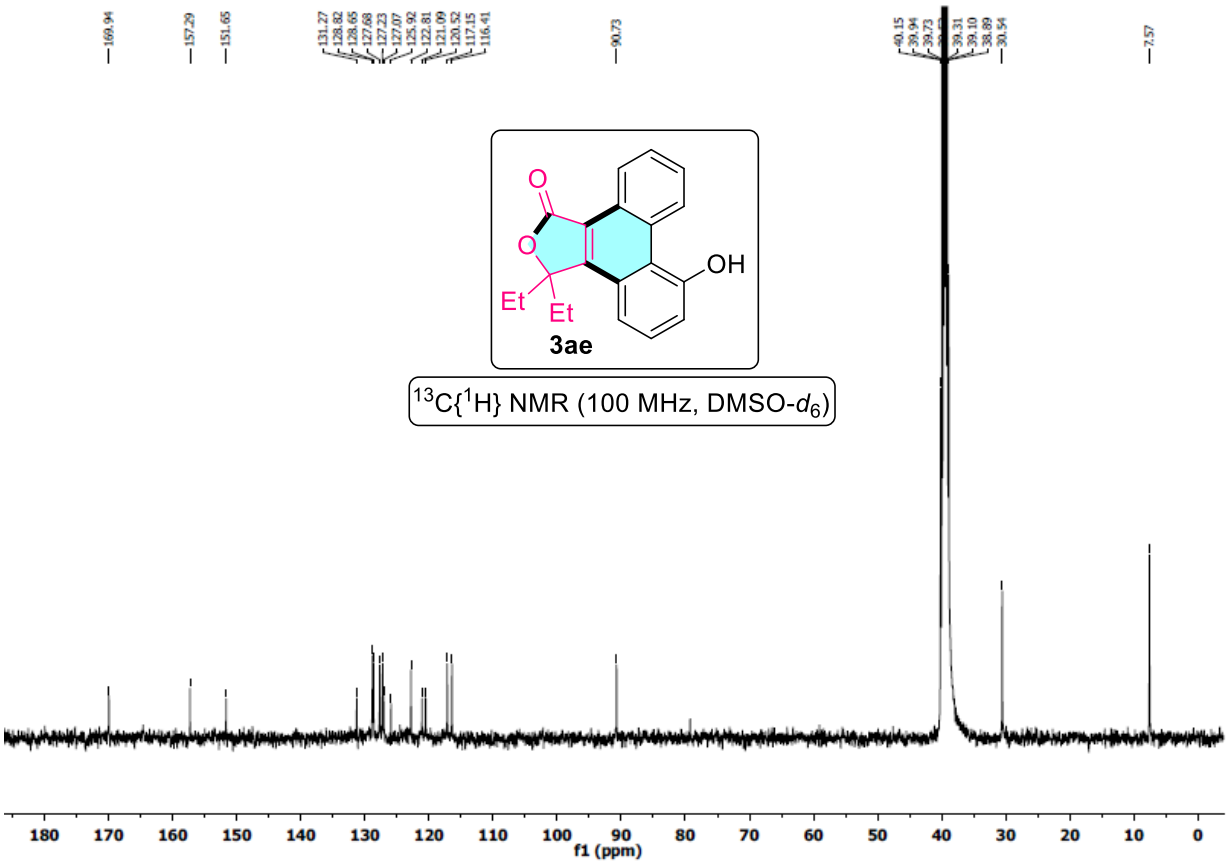

169.48
157.27
153.95
131.18
128.75
128.51
127.57
127.14
126.83
126.00
122.78
121.22
118.90
116.93
116.81
87.36
40.35
40.15
39.94
39.73
39.52
39.31
39.10
38.89
25.79
16.73
13.78
O
O
OH
Me
nPr
3ac
13C {1H} NMR (100 MHz, DMSO-d6)
f1 (ppm)


O
O
Me
Me
Me
OH
3ad
$^1$H NMR (400 MHz, DMSO-$d_6$)
f1 (ppm)

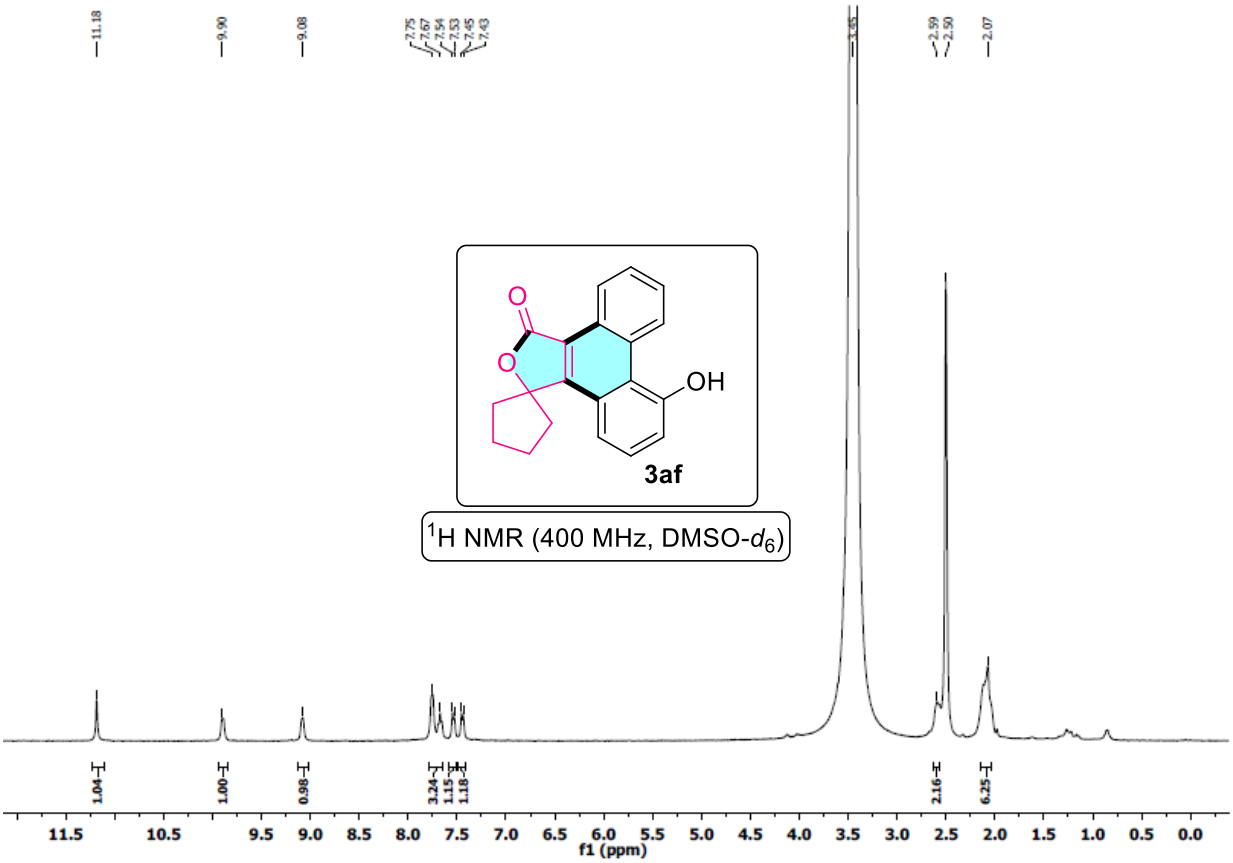

O
O
Me
Me
Me
OH
3ad
$^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$)
f1 (ppm)



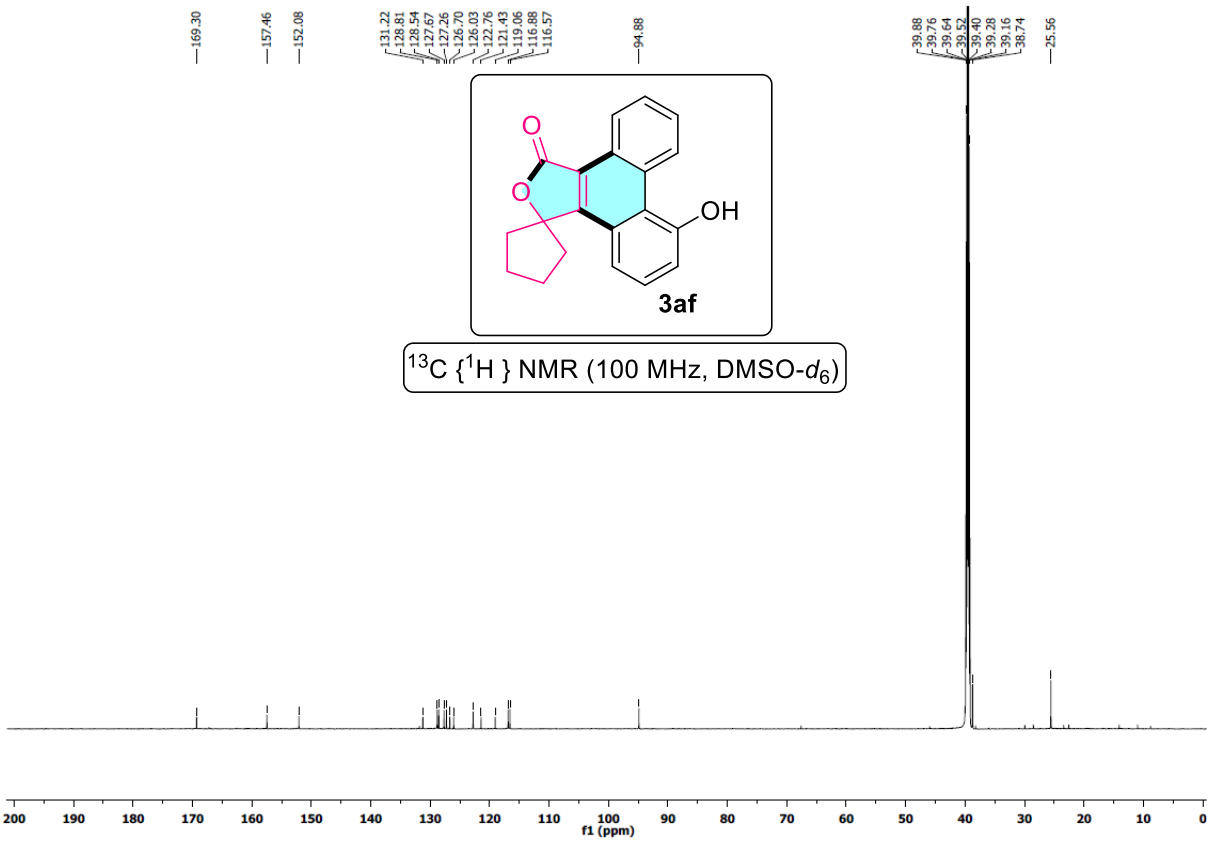

$^{1}$H NMR (400 MHz, DMSO-$d_6$)



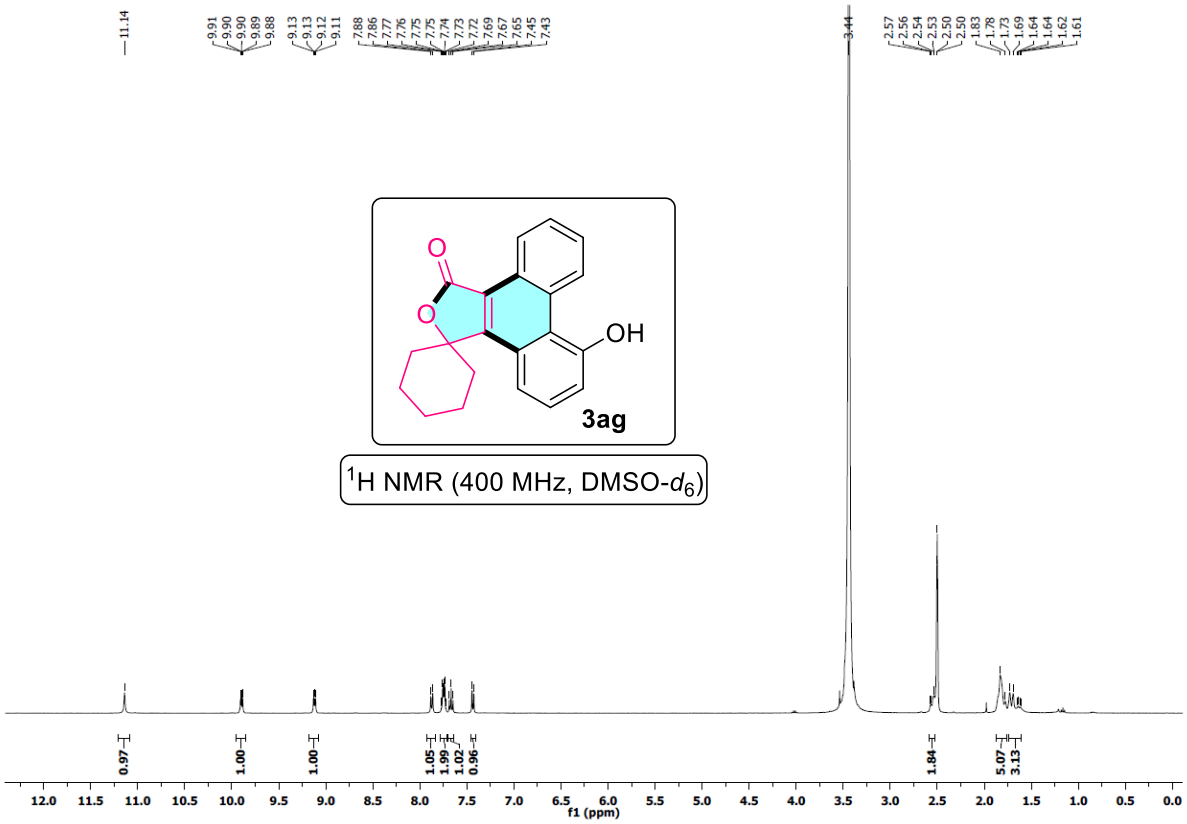

$^{13}$C{$^{1}$H} NMR (100 MHz, DMSO-$d_6$)



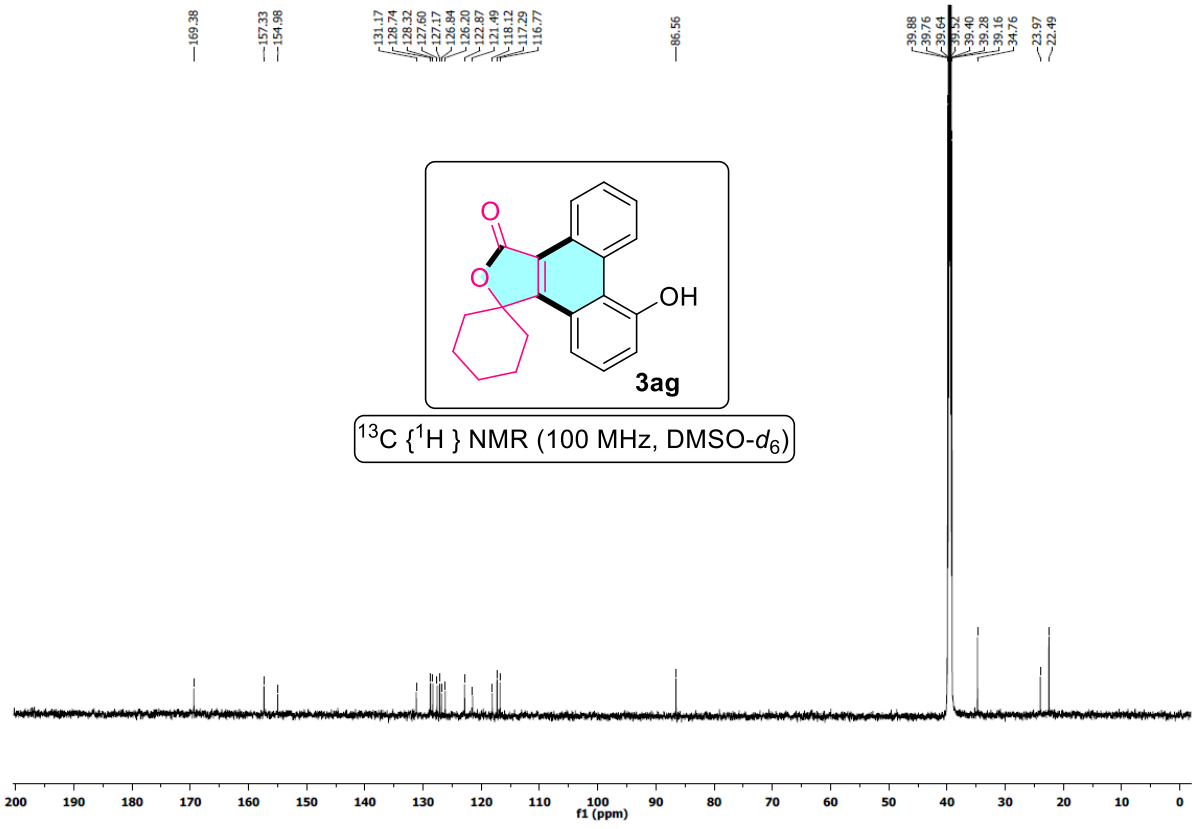

$^{1}$H NMR (400 MHz, DMSO-$d_6$)



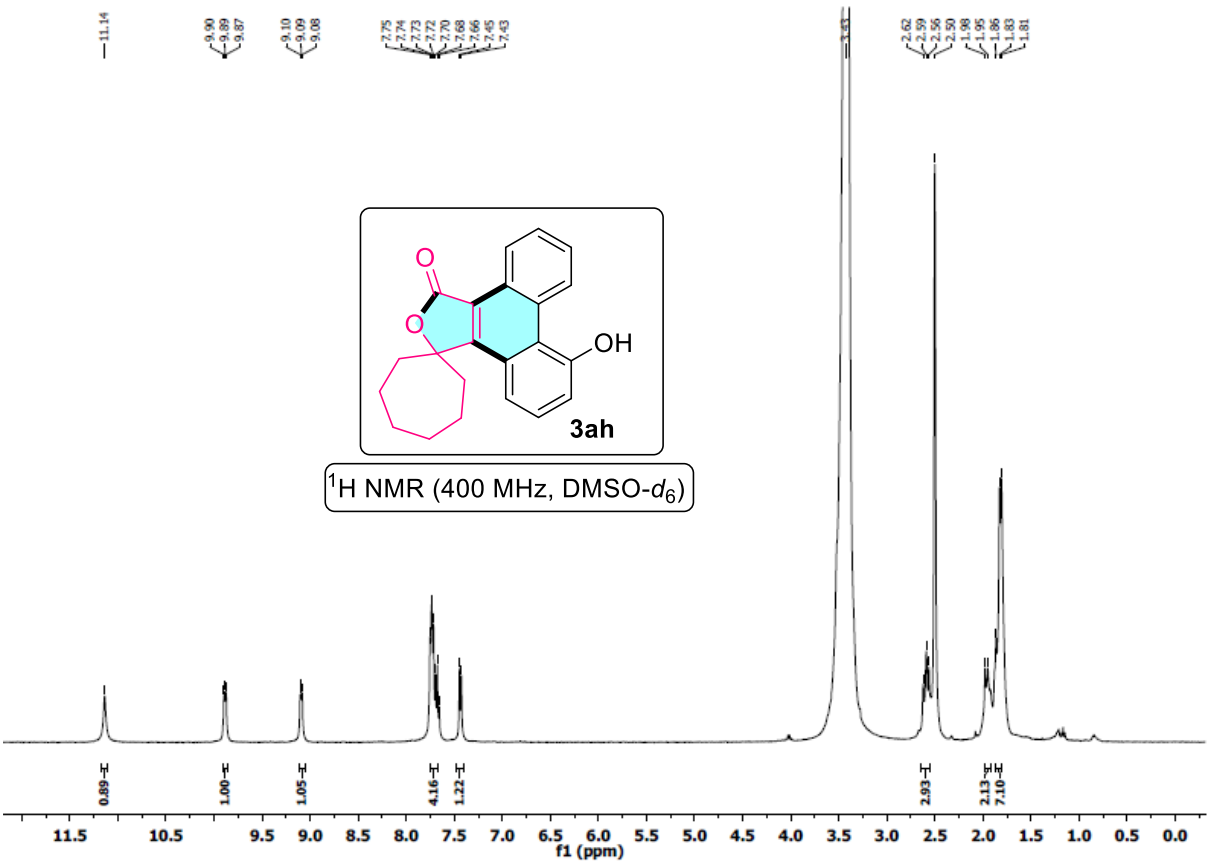

$^{13}$C {$^{1}$H } NMR (100 MHz, DMSO-$d_6$)

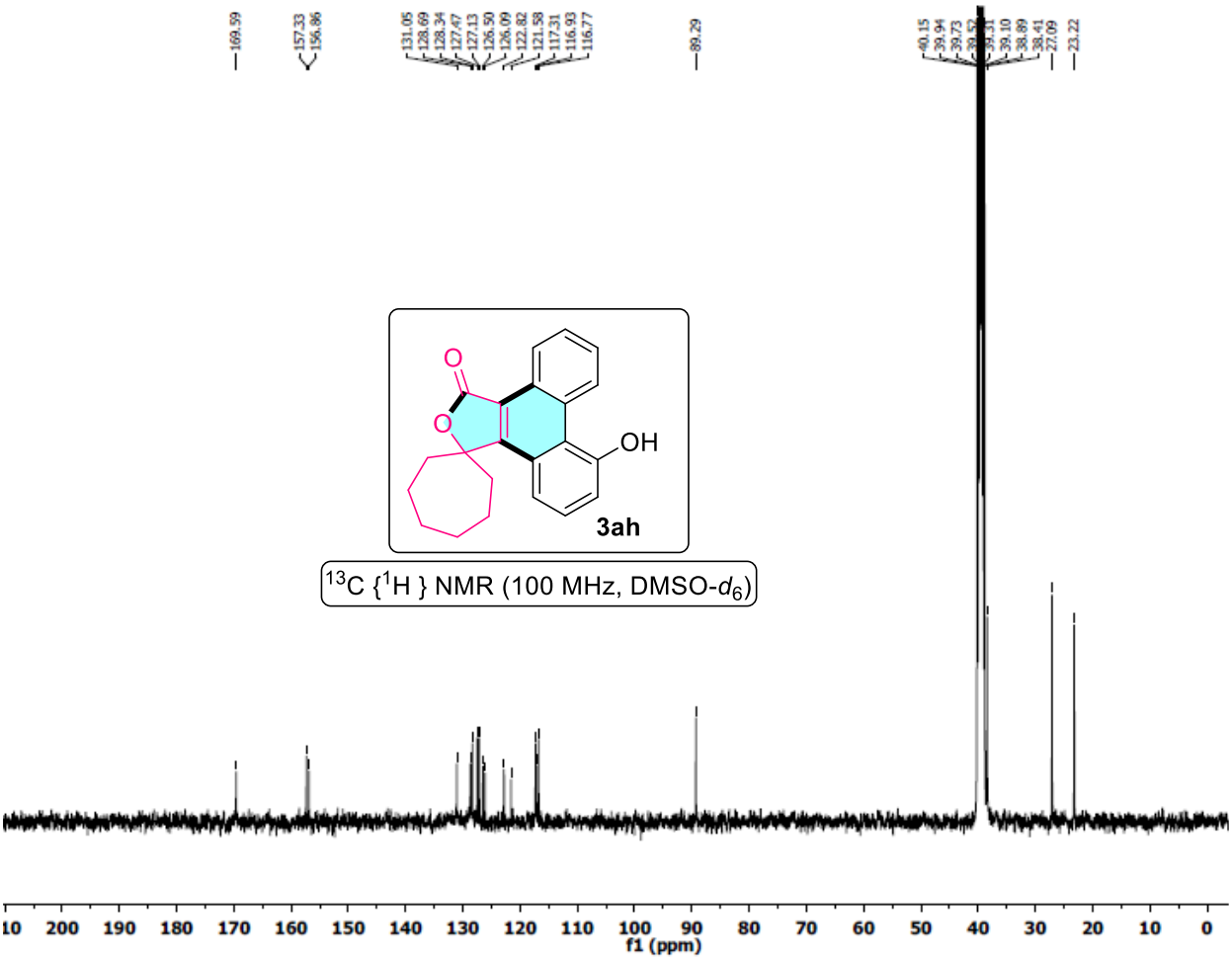


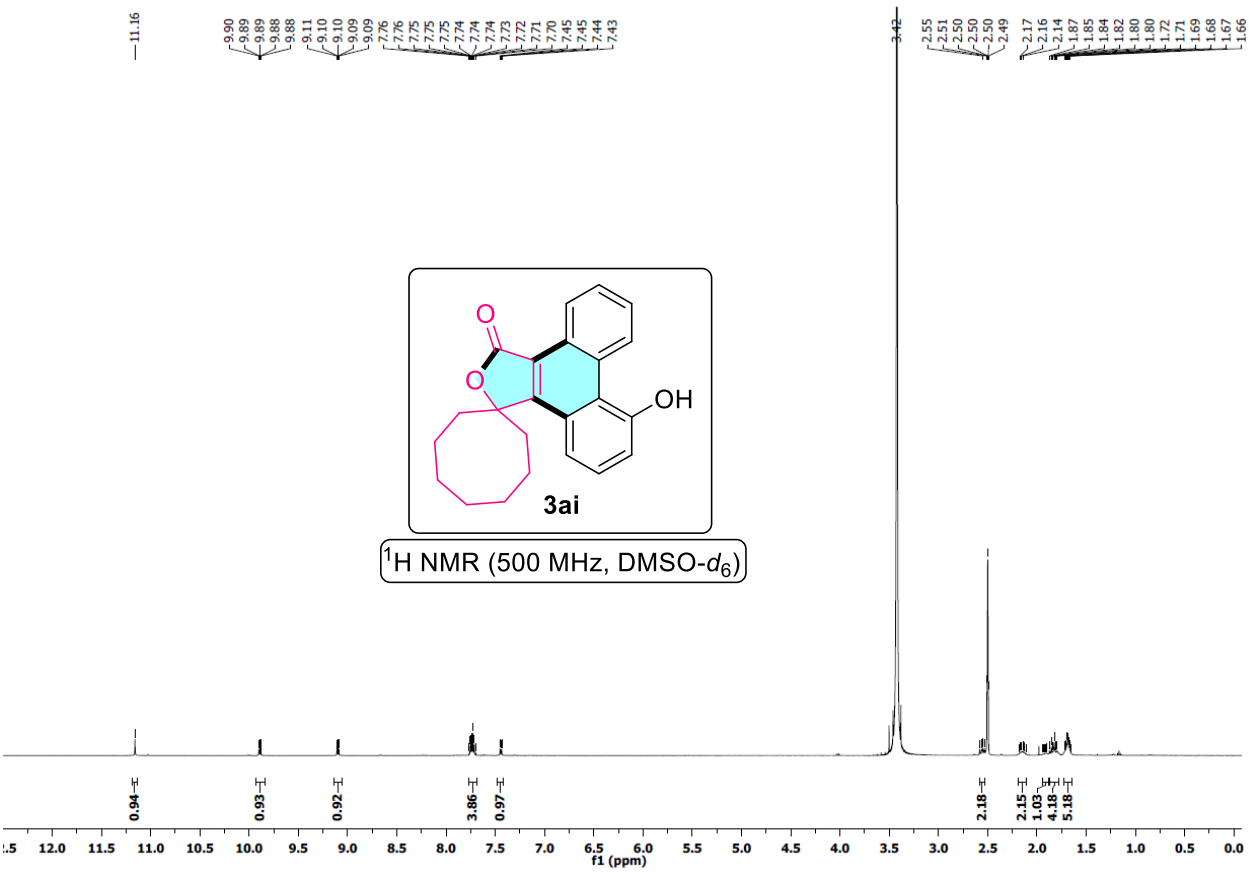

$^{1}$H NMR (400 MHz, DMSO-$d_6$)

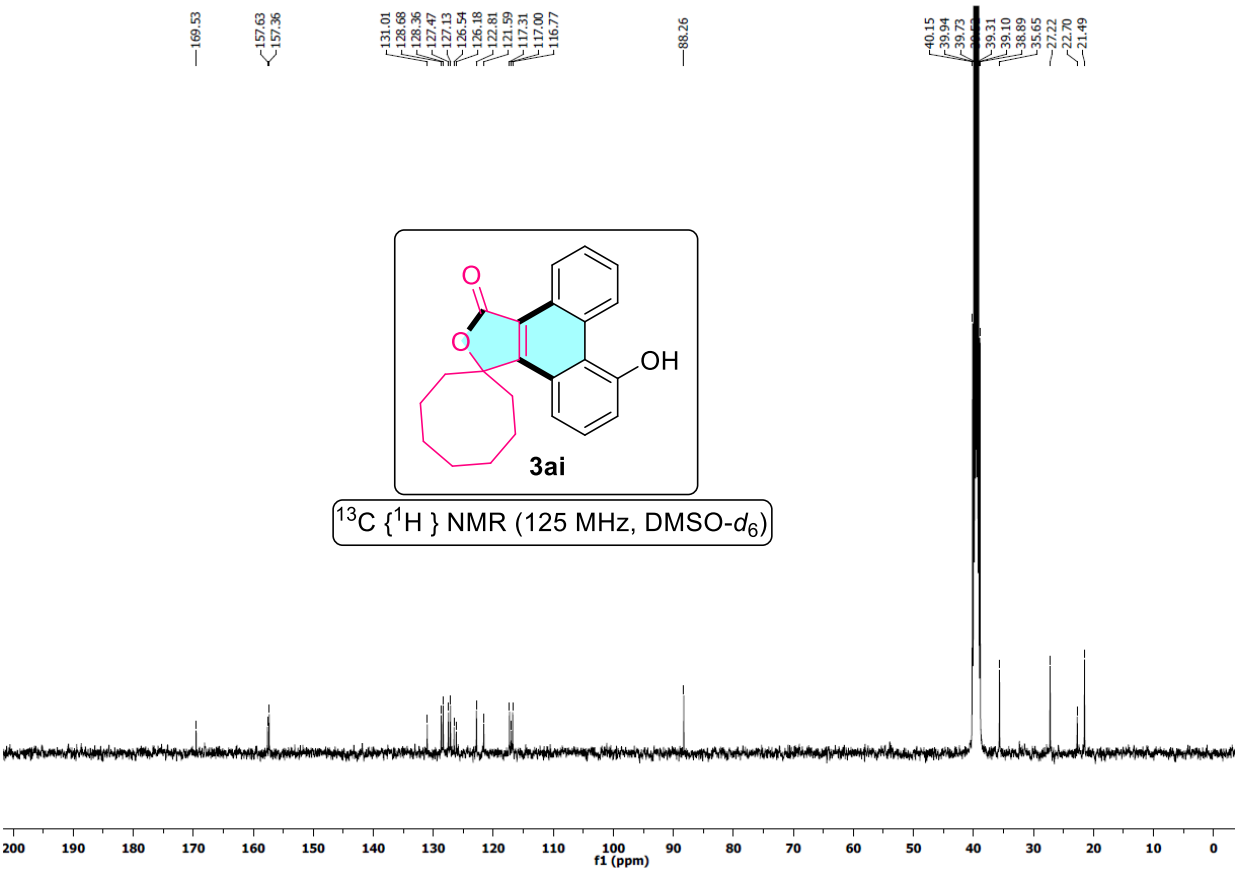


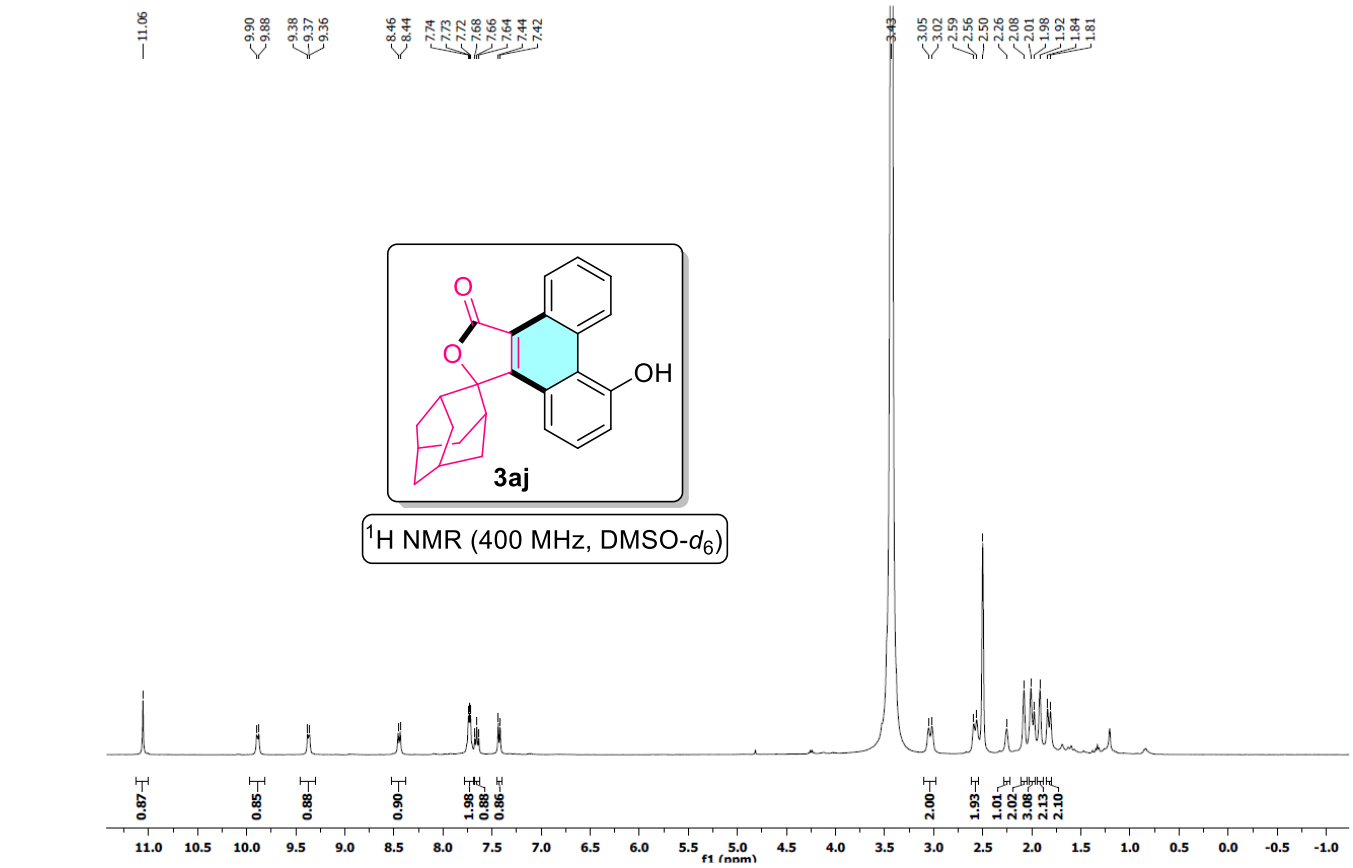

$^{13}$C {$^{1}$H } NMR (100 MHz, DMSO-$d_6$)


OH
3ah
1H NMR (400 MHz, DMSO-d6)
f1 (ppm)


OH
3ah
13C {1H } NMR (100 MHz, DMSO-d6)
f1 (ppm)


3ai
1H NMR (500 MHz, DMSO-d6)
f1 (ppm)


3ai
13C {1H } NMR (125 MHz, DMSO-d6)
f1 (ppm)

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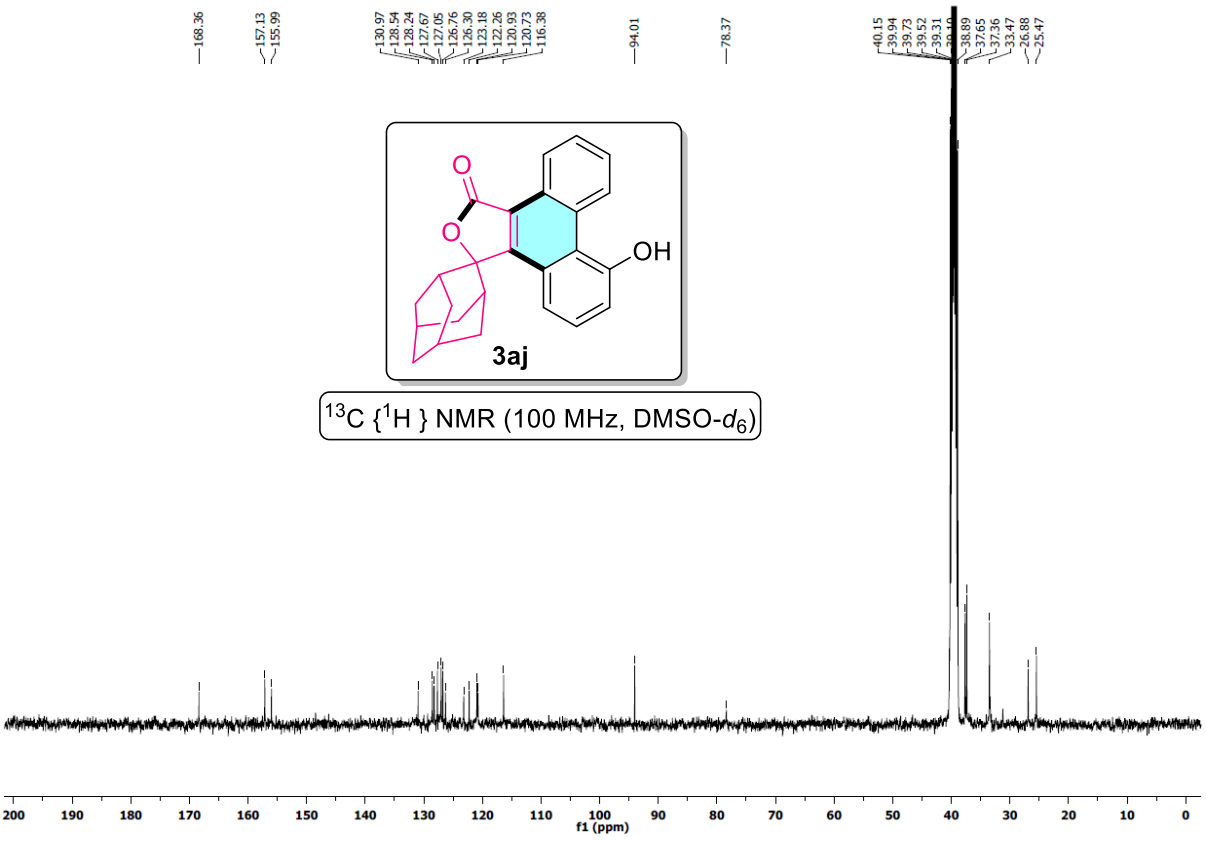
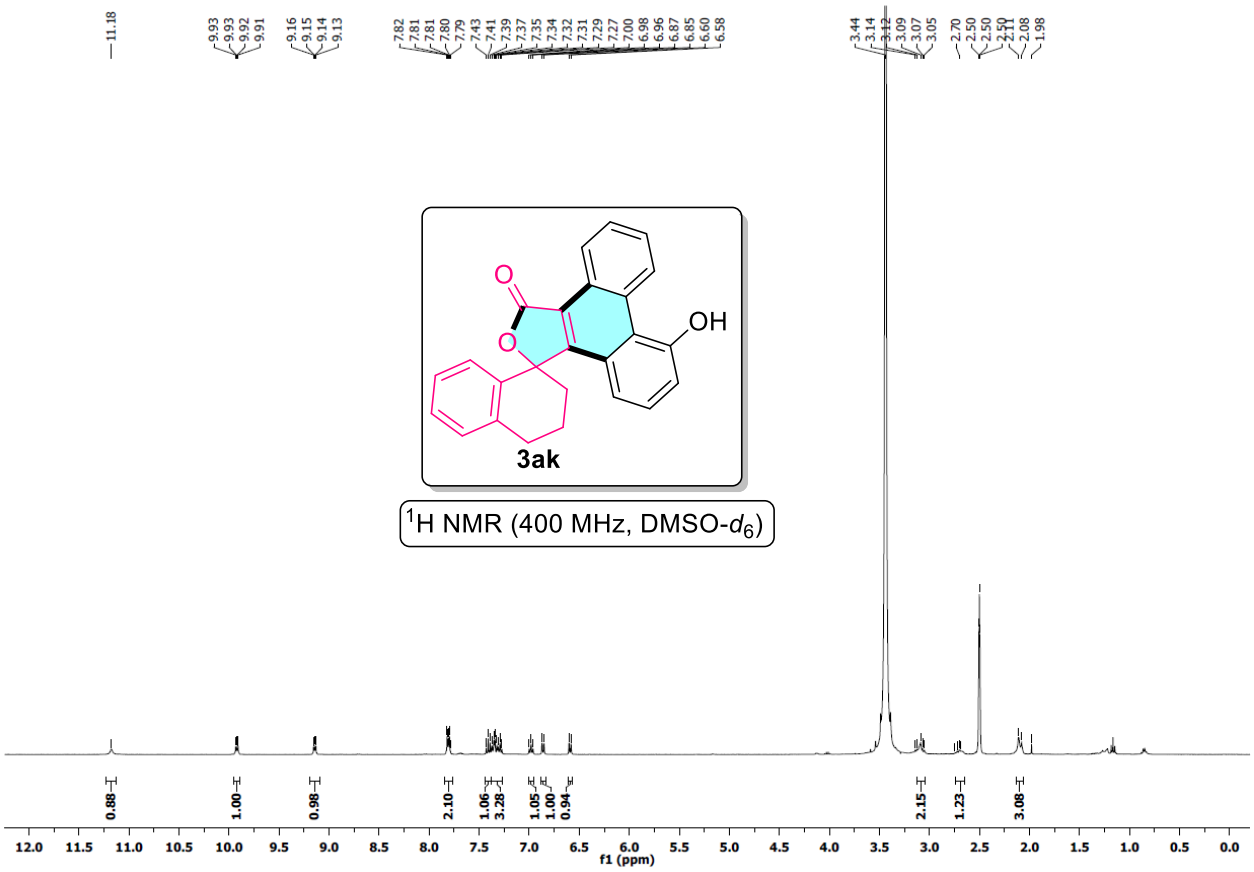
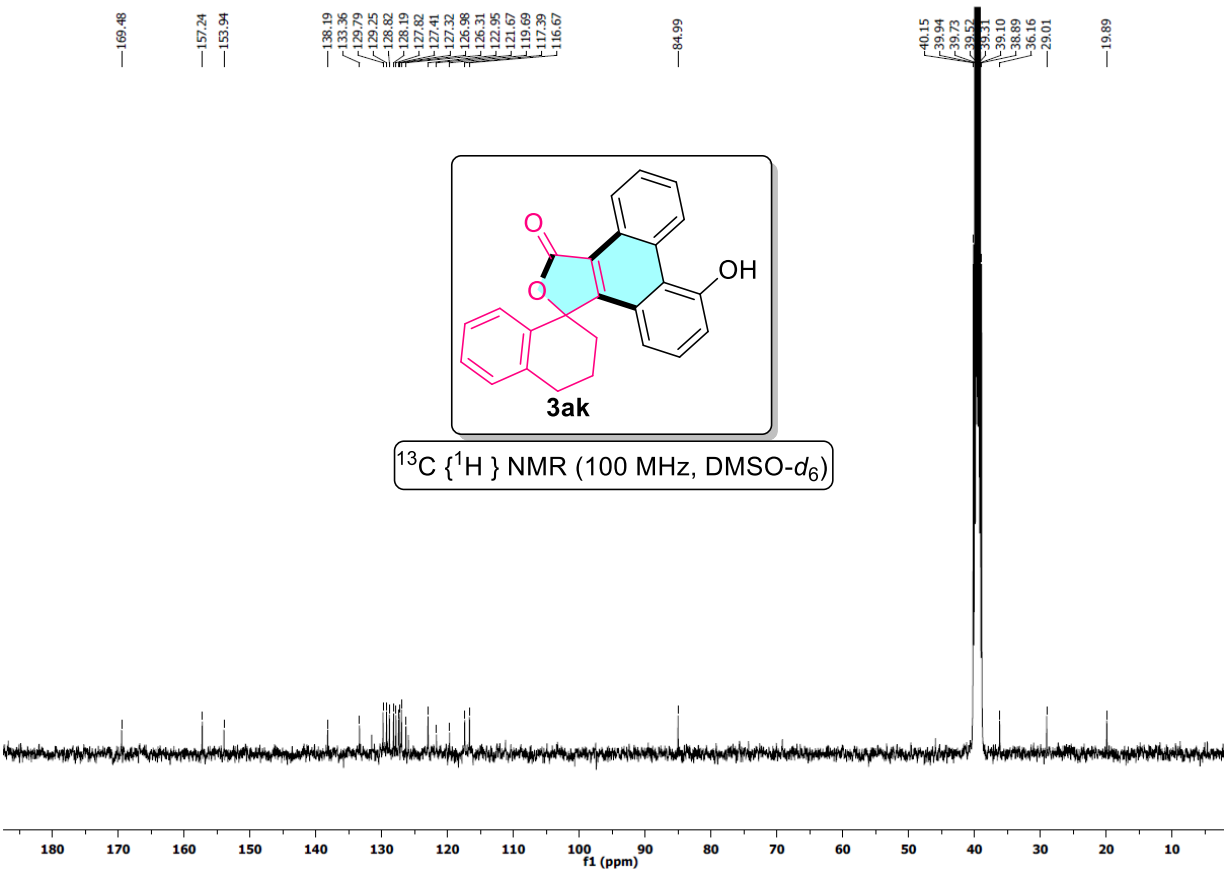


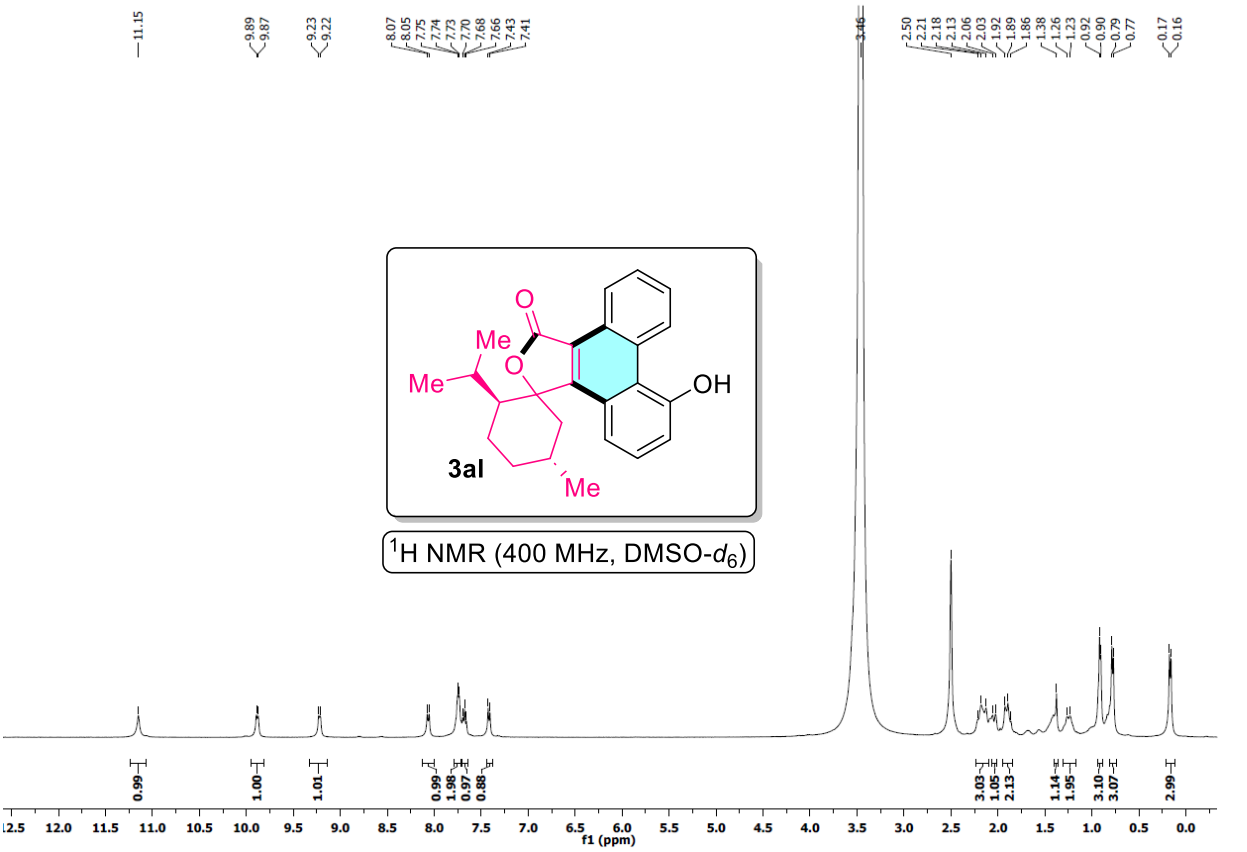

$^{13}$C {$^{1}$H } NMR (100 MHz, DMSO-$d_6$)




$^{1}$H NMR (400 MHz, DMSO-$d_6$)



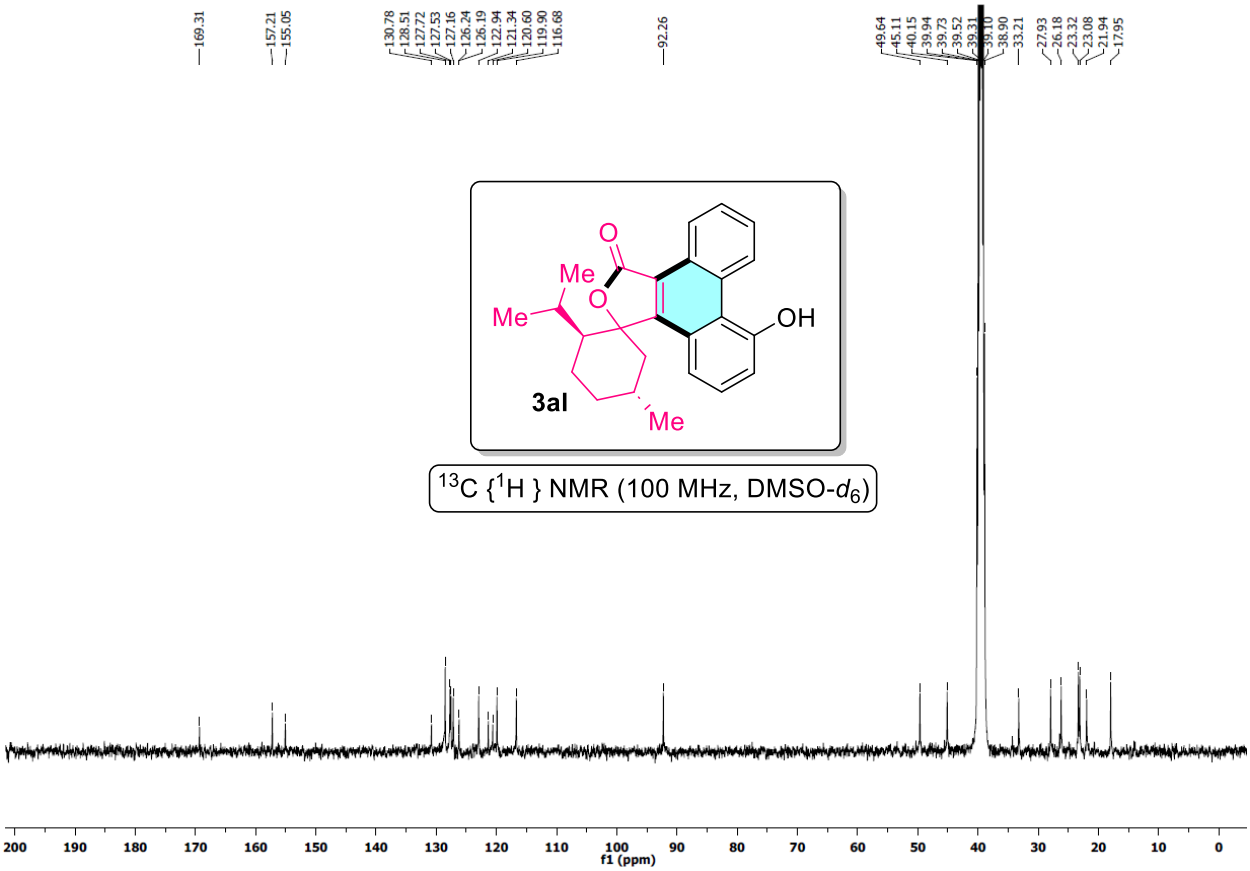

$^{13}$C {$^{1}$H } NMR (100 MHz, DMSO-$d_6$)







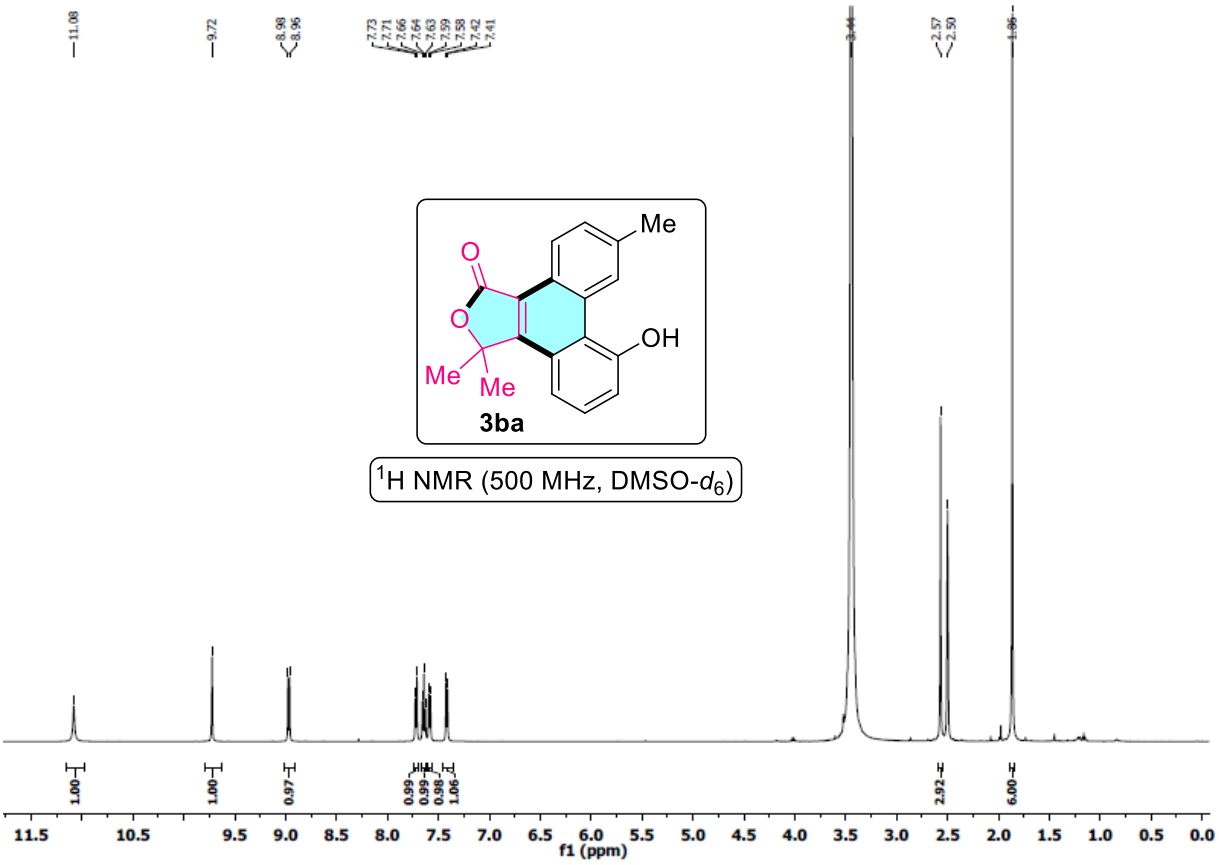
$^{1}$H NMR (400 MHz, DMSO-$d_6$)



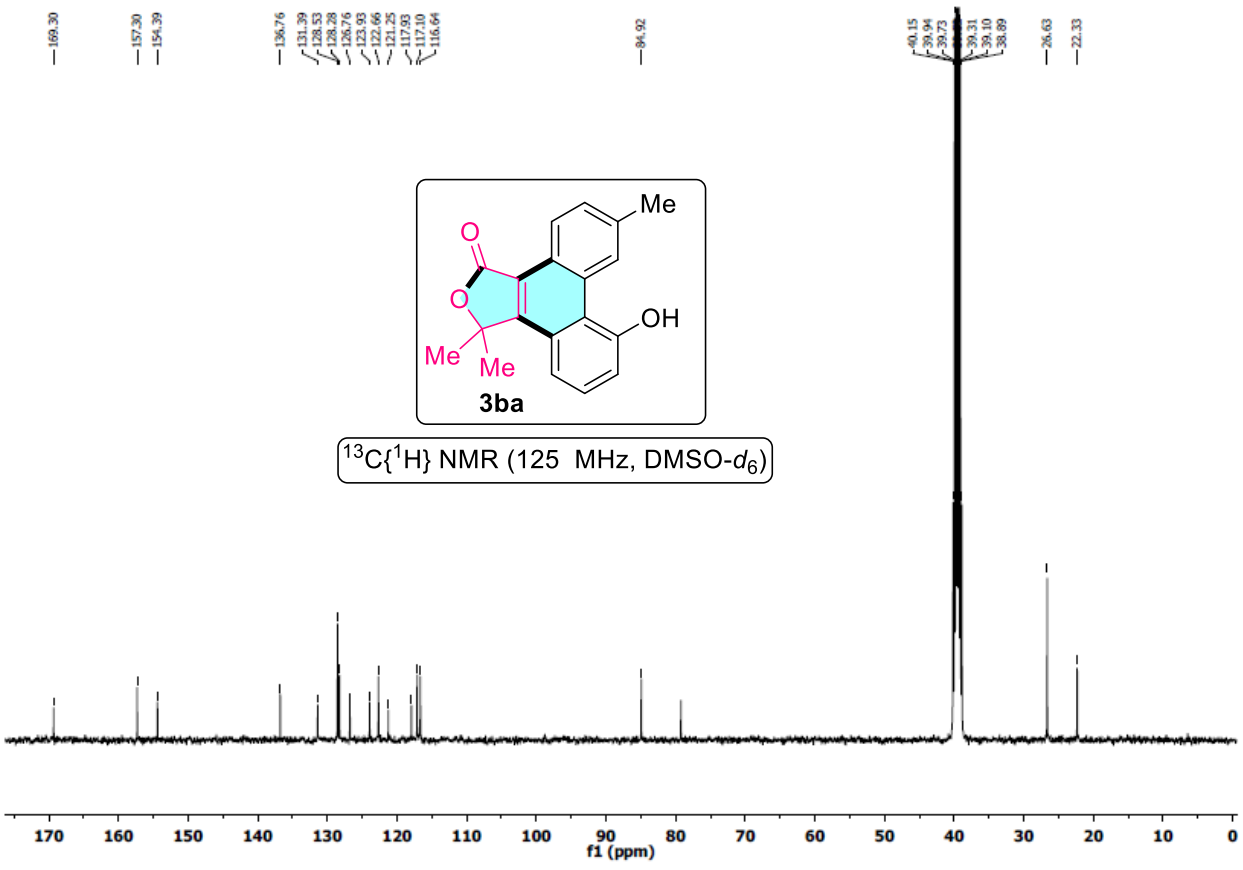




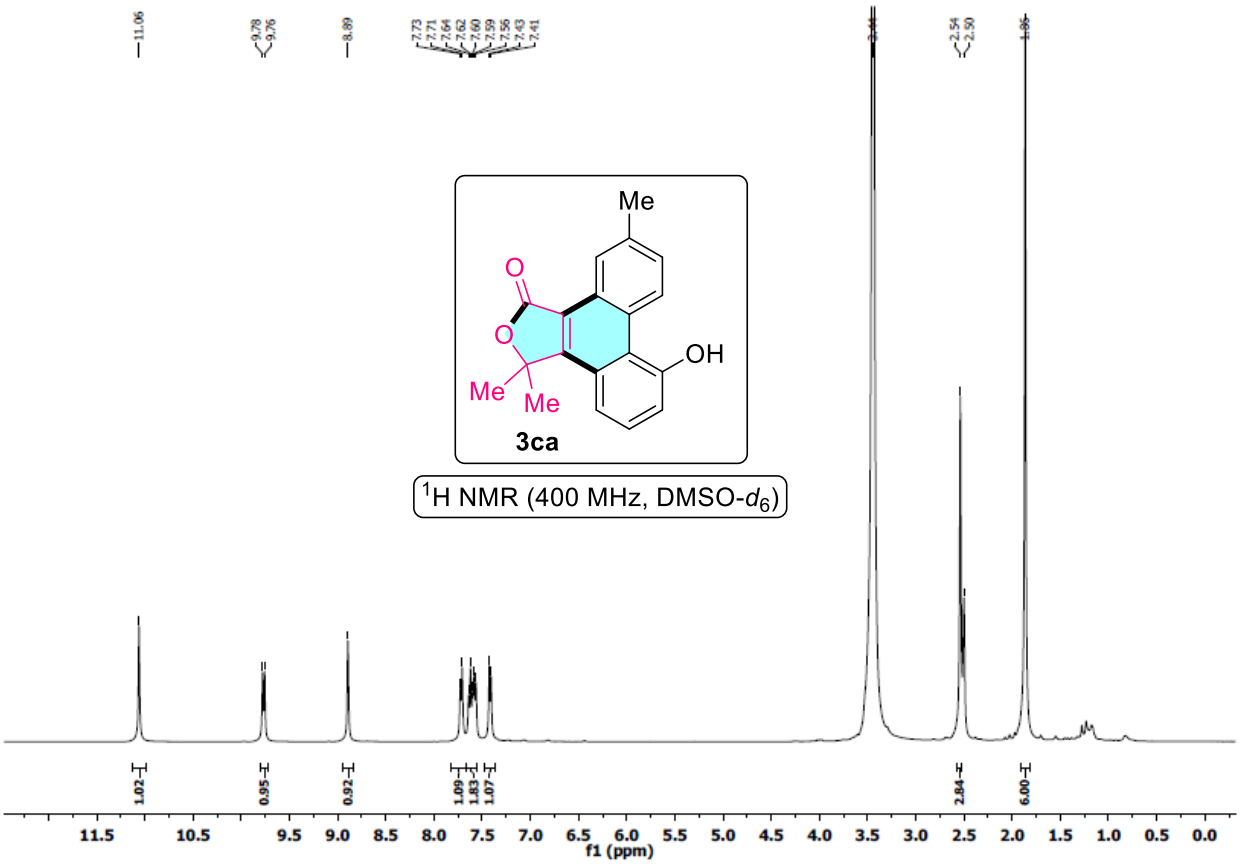
$^{13}$C {$^{1}$H } NMR (100 MHz, DMSO-$d_6$)

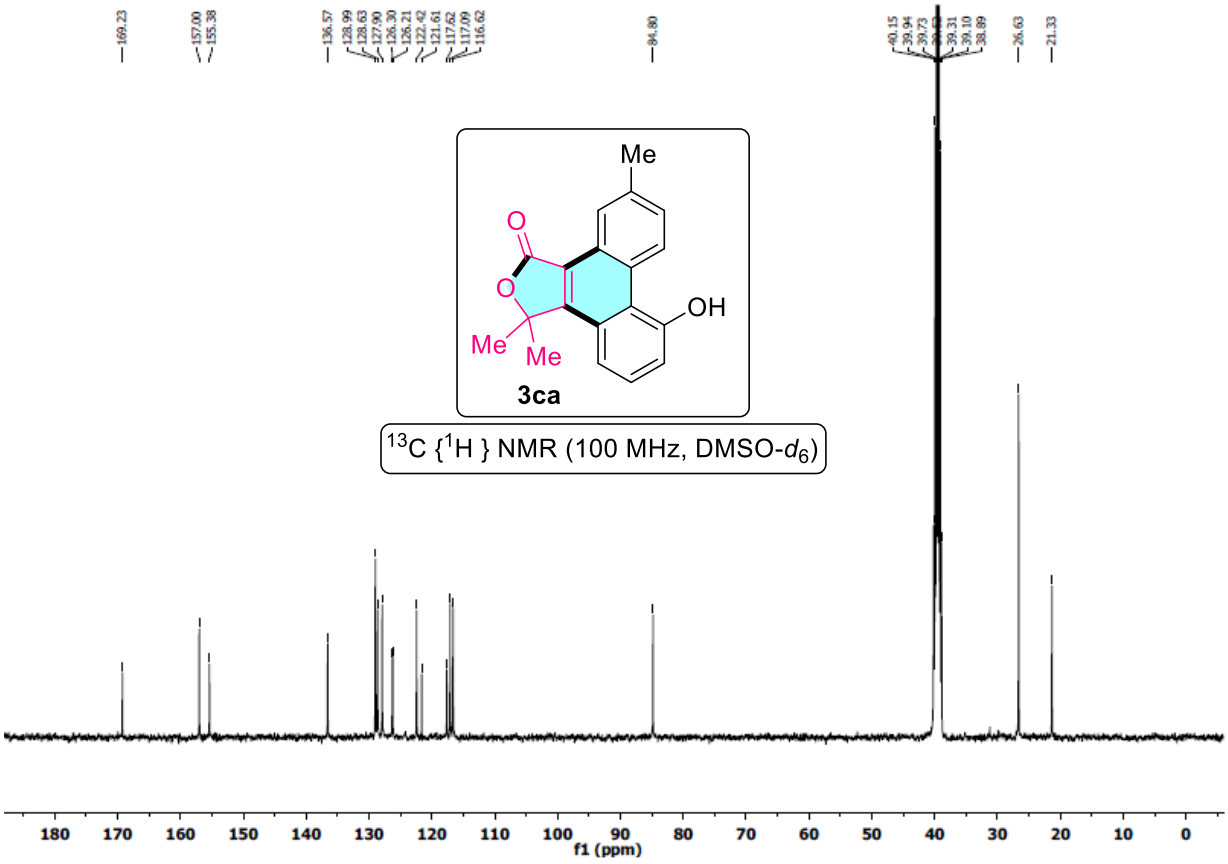


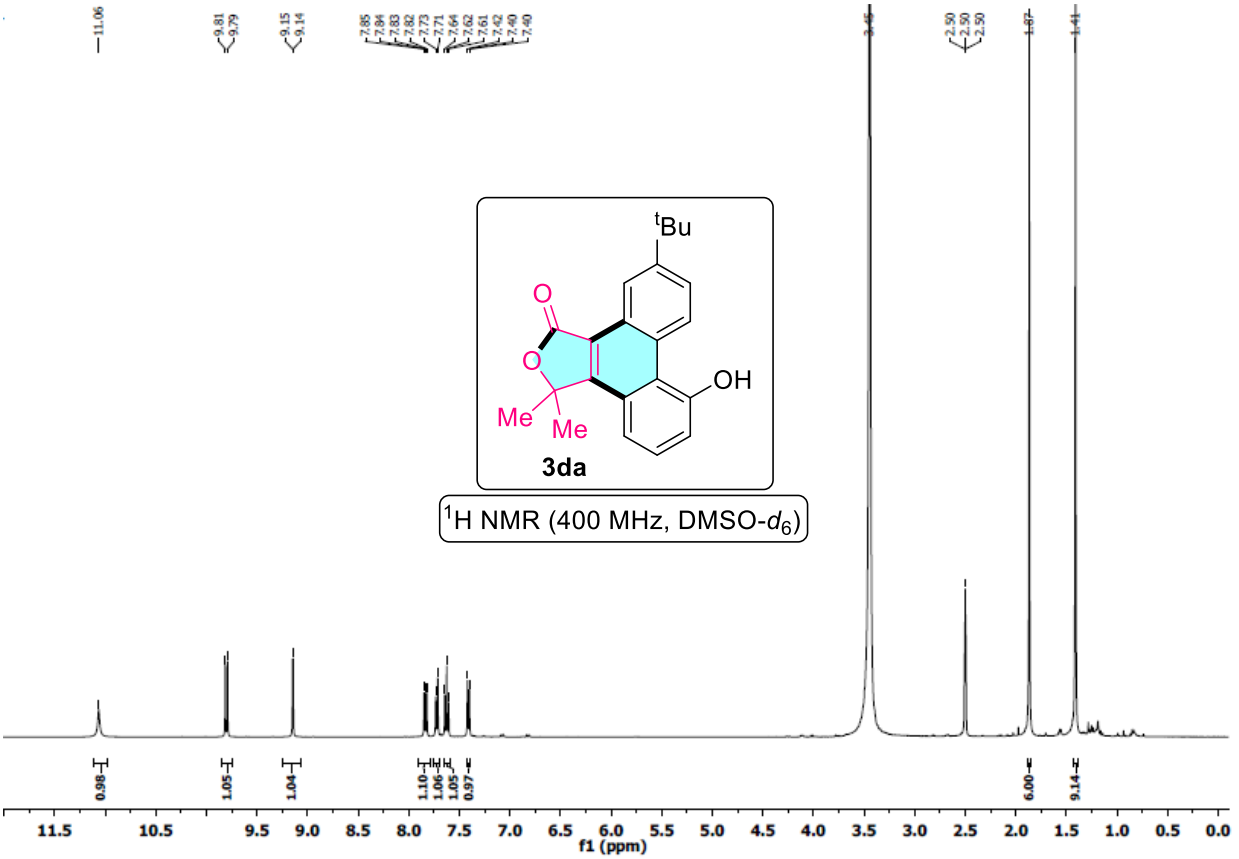

$^{1}$H NMR (500 MHz, DMSO-$d_6$)

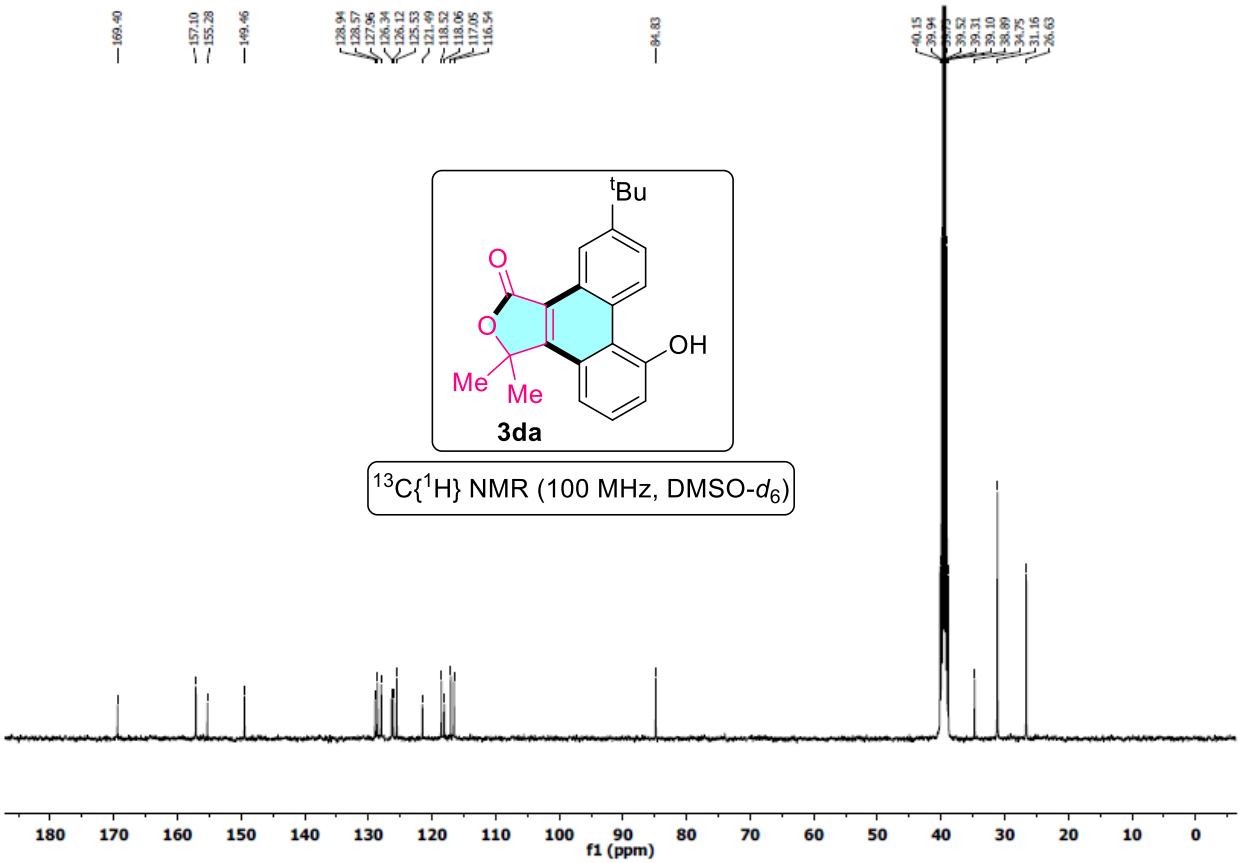


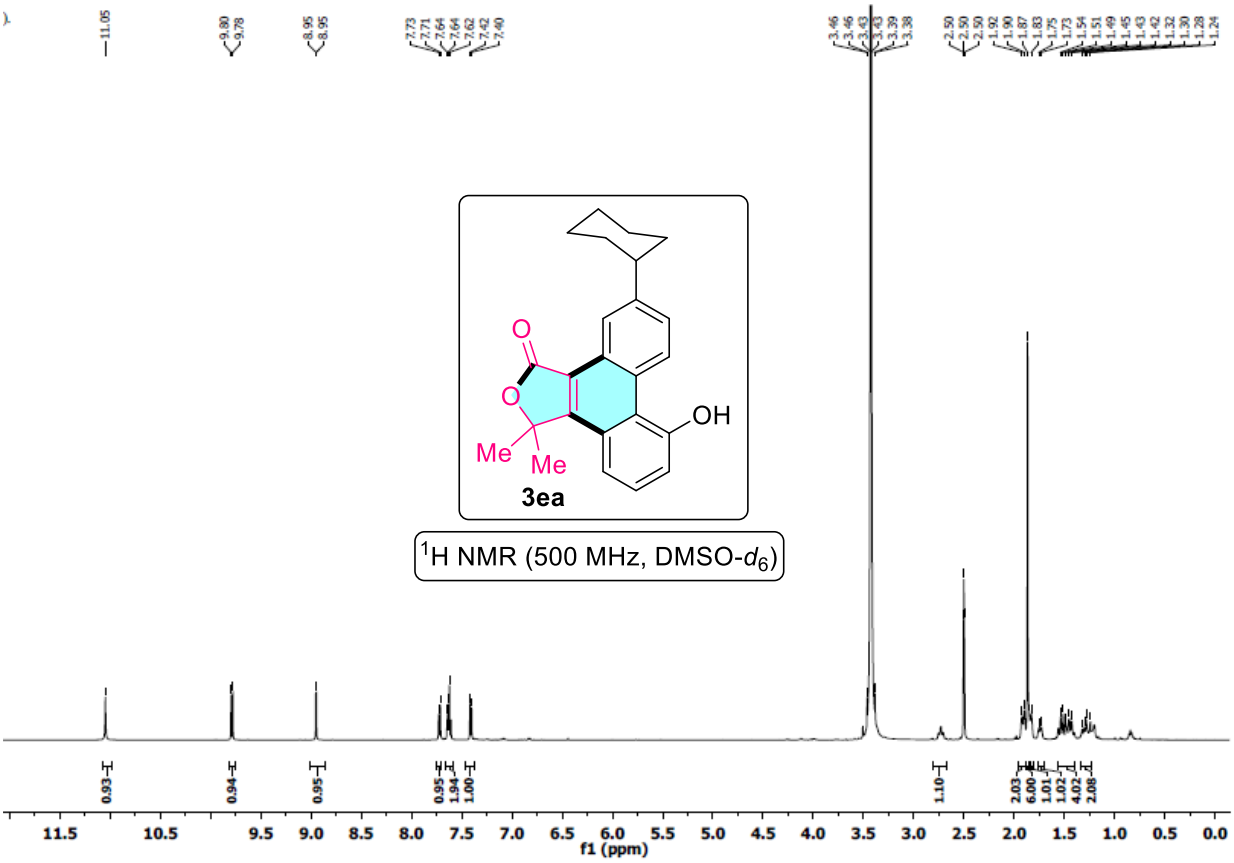

$^{13}$C{$^{1}$H} NMR (125 MHz, DMSO-$d_6$)

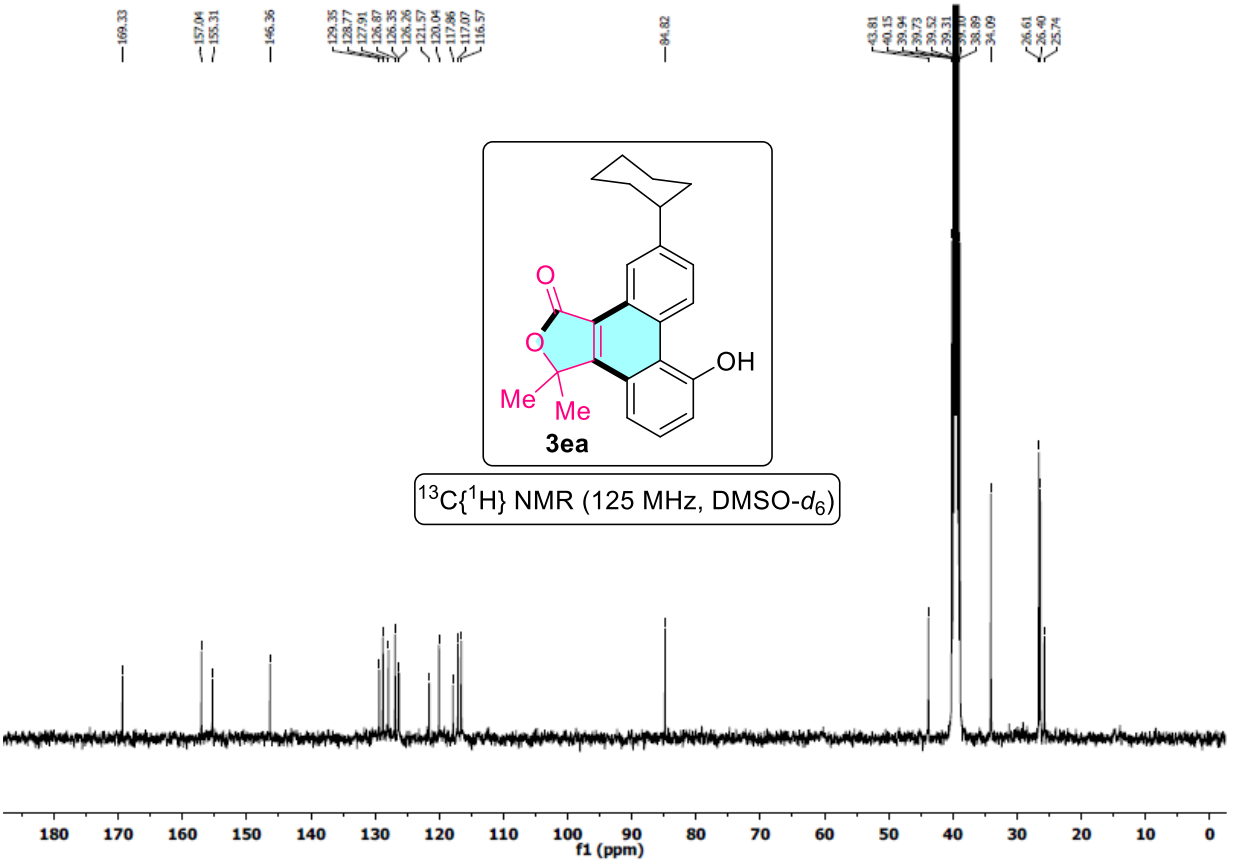

Me
O
O
OH
Me
Me
3ca
$^{1}$H NMR (400 MHz, DMSO-$d_6$)
f1 (ppm)

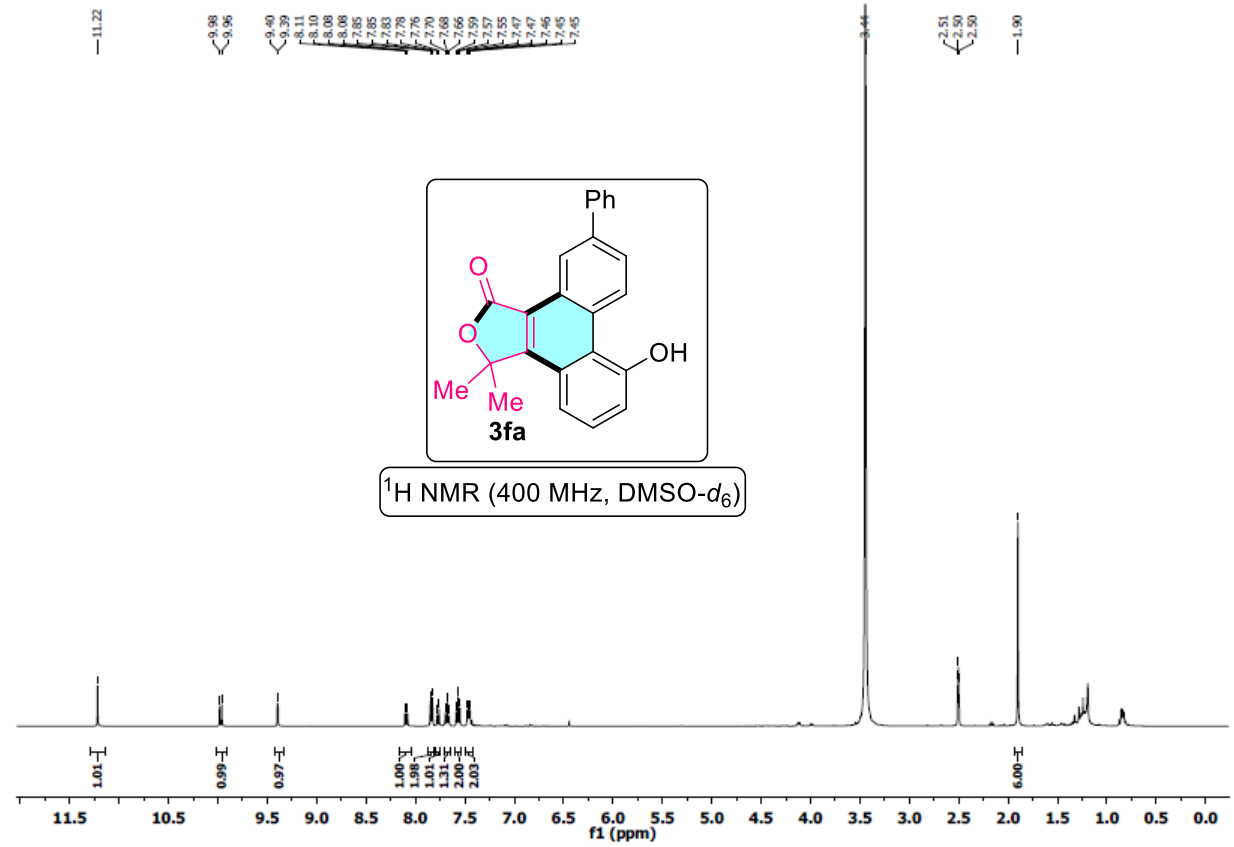

Me
O
O
OH
Me
Me
3ca
$^{13}$C {$^{1}$H } NMR (100 MHz, DMSO-$d_6$)
f1 (ppm)


tBu
O
O
OH
Me
Me
3da
1H NMR (400 MHz, DMSO-d6)
f1 (ppm)

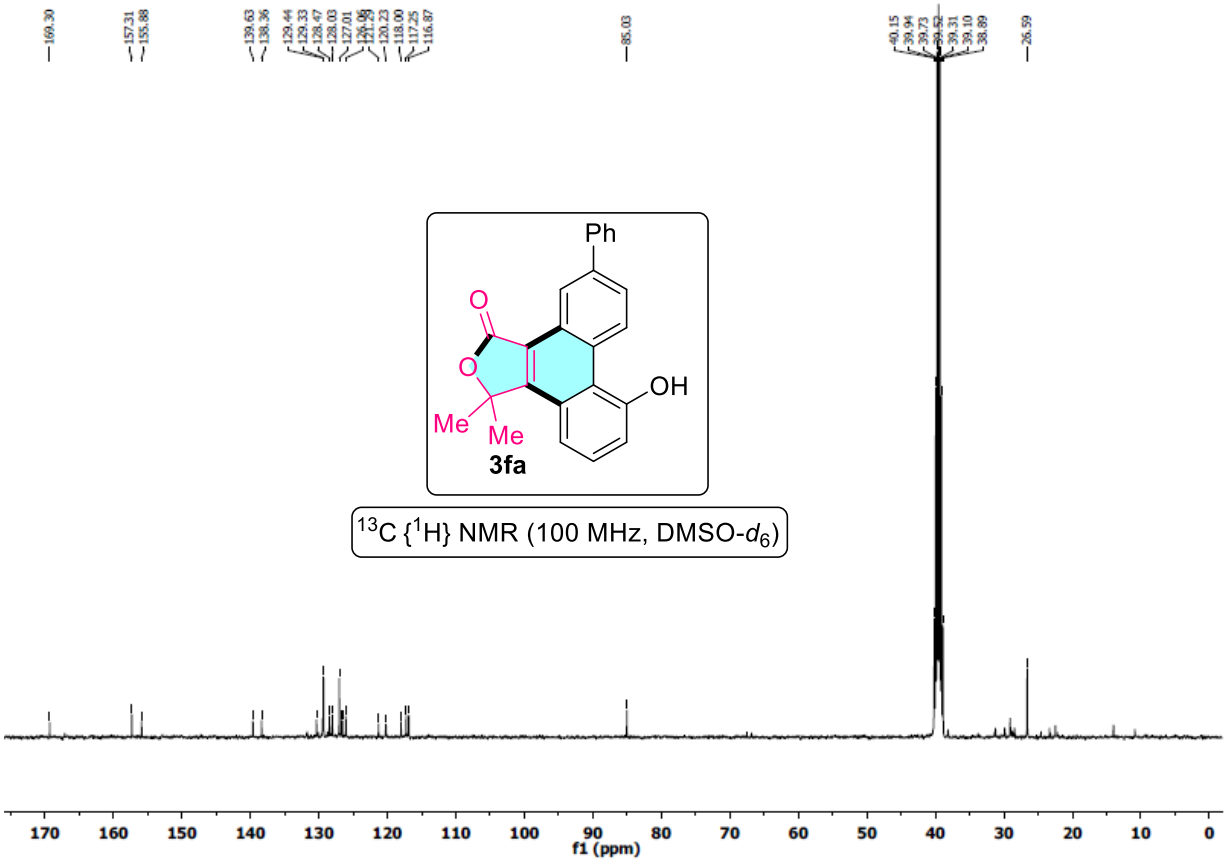

tBu
O
O
OH
Me
Me
3da
13C{1H} NMR (100 MHz, DMSO-d6)
f1 (ppm)


O
O
OH
Me
Me
3ea
$^1$H NMR (500 MHz, DMSO-$d_6$)
f1 (ppm)

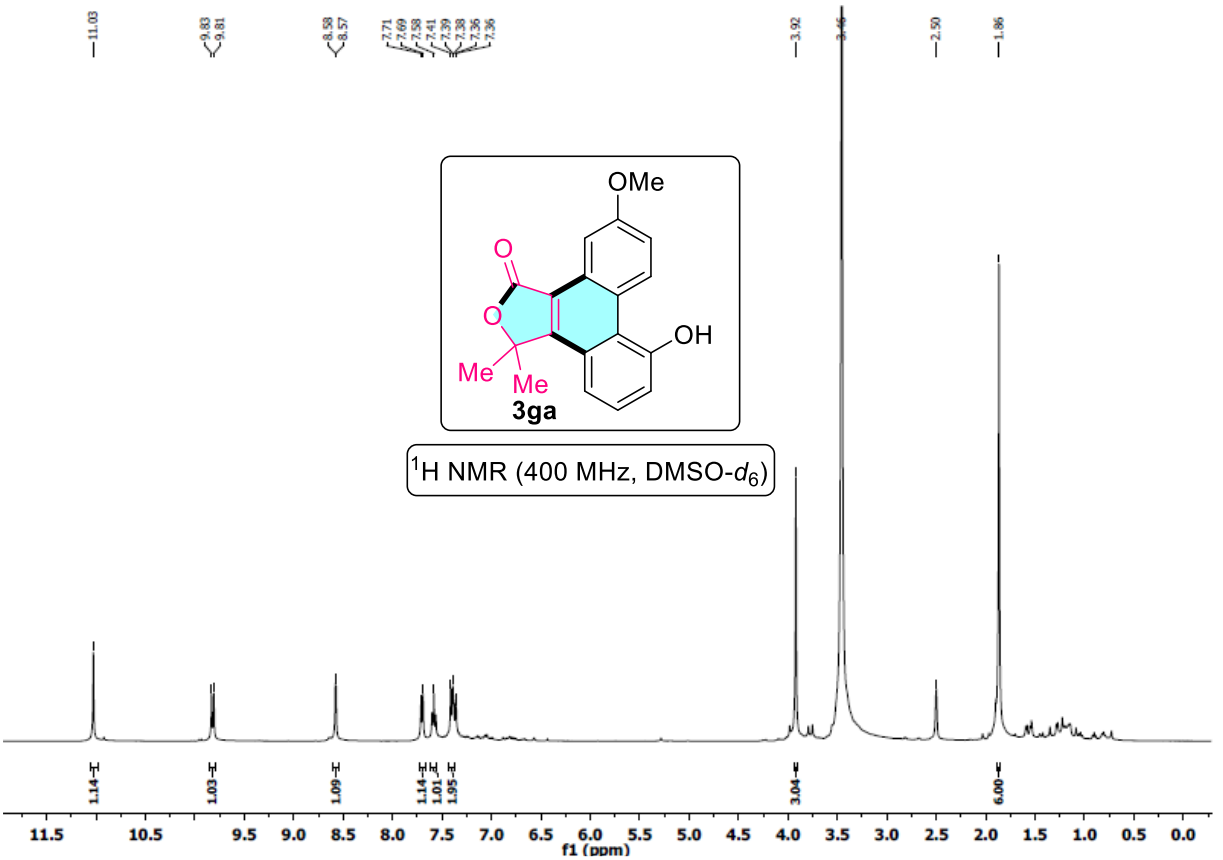

O
O
OH
Me
Me
3ea
$^{13}$C{$^1$H} NMR (125 MHz, DMSO-$d_6$)
f1 (ppm)

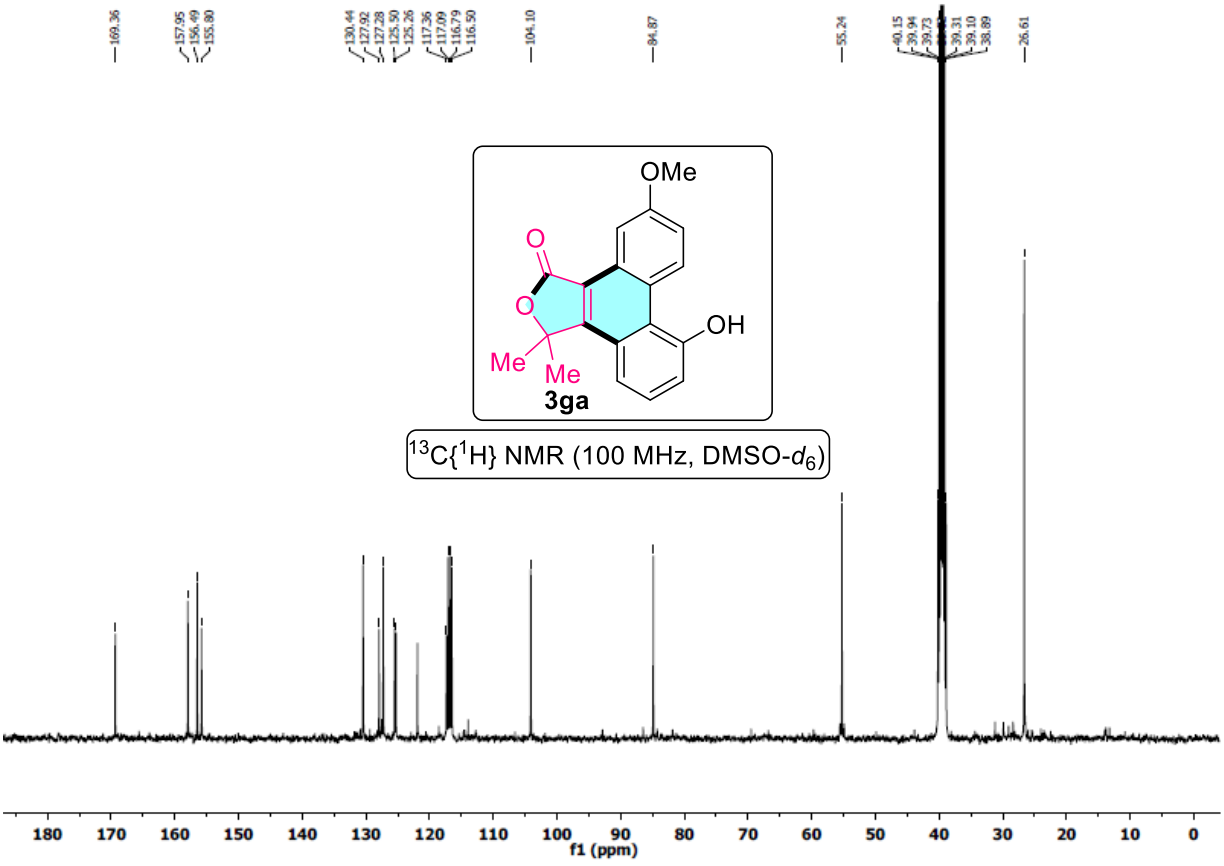


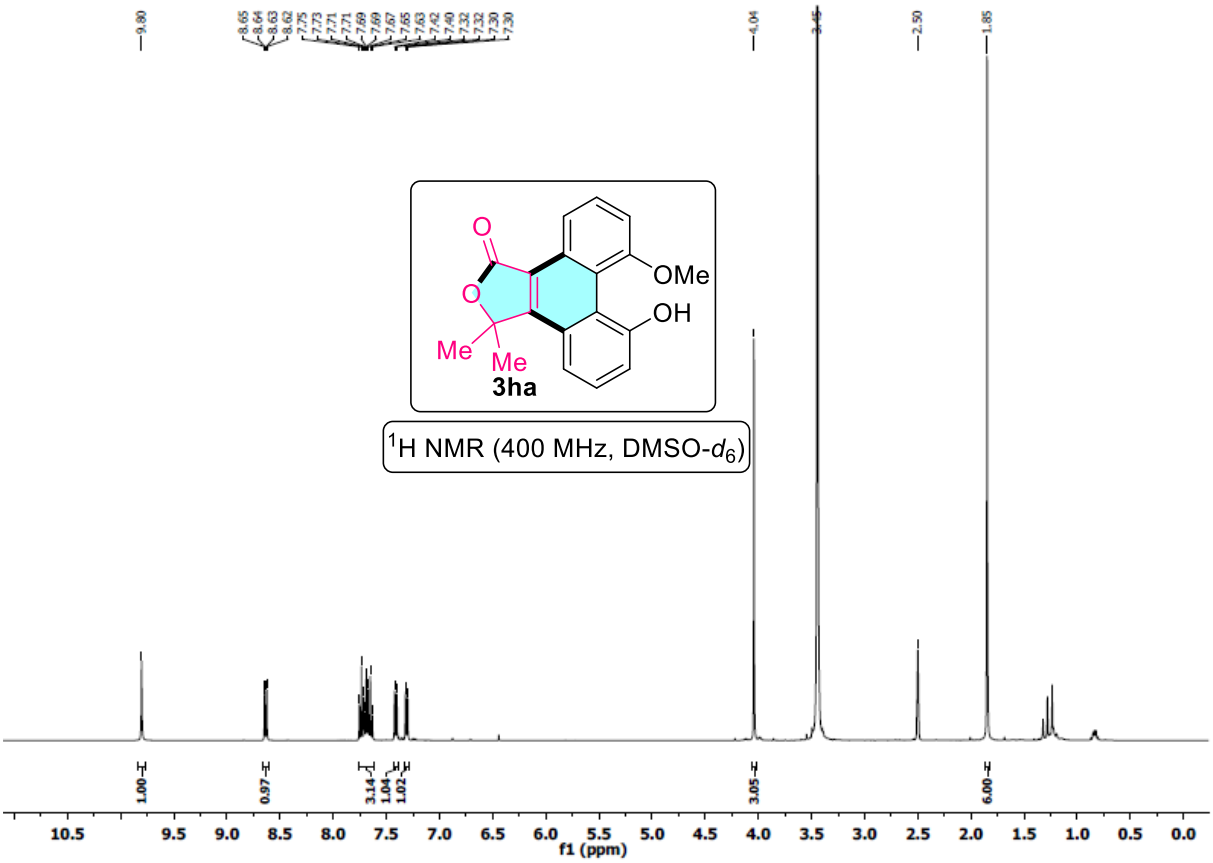

$^{1}$H NMR (400 MHz, DMSO-$d_6$)



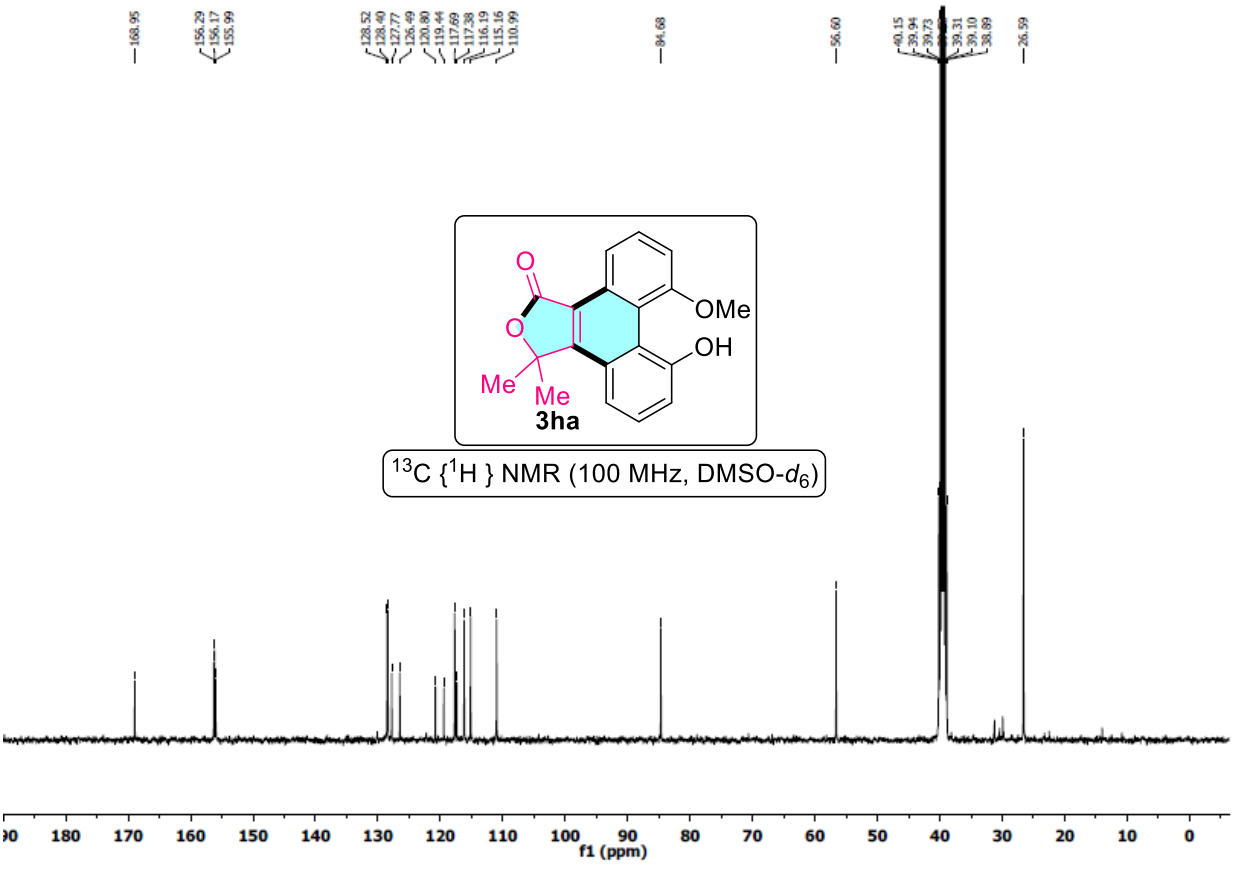

$^{13}$C {$^{1}$H} NMR (100 MHz, DMSO-$d_6$)


OMe
O
O
OH
Me
Me
3ga
1H NMR (400 MHz, DMSO-d6)
f1 (ppm)

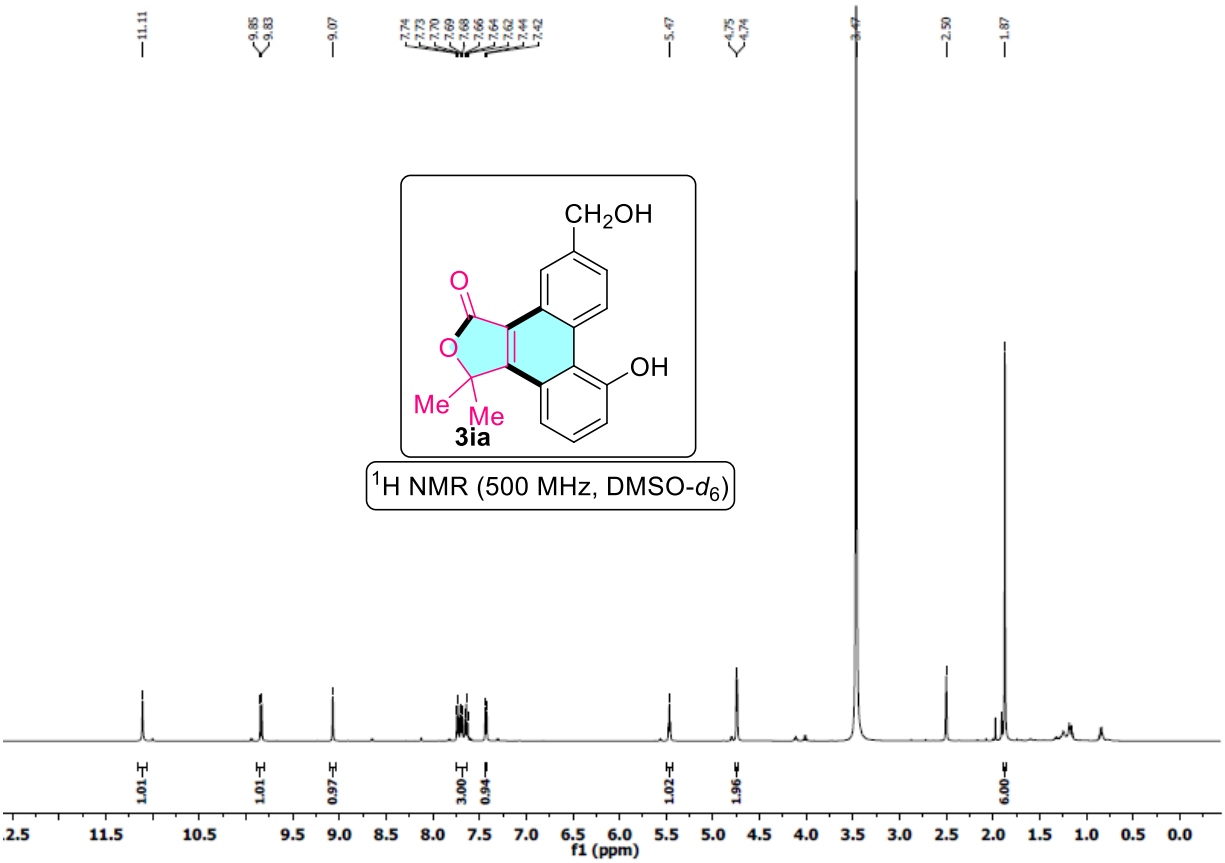

OMe
O
O
OH
Me
Me
3ga
13C{1H} NMR (100 MHz, DMSO-d6)
f1 (ppm)



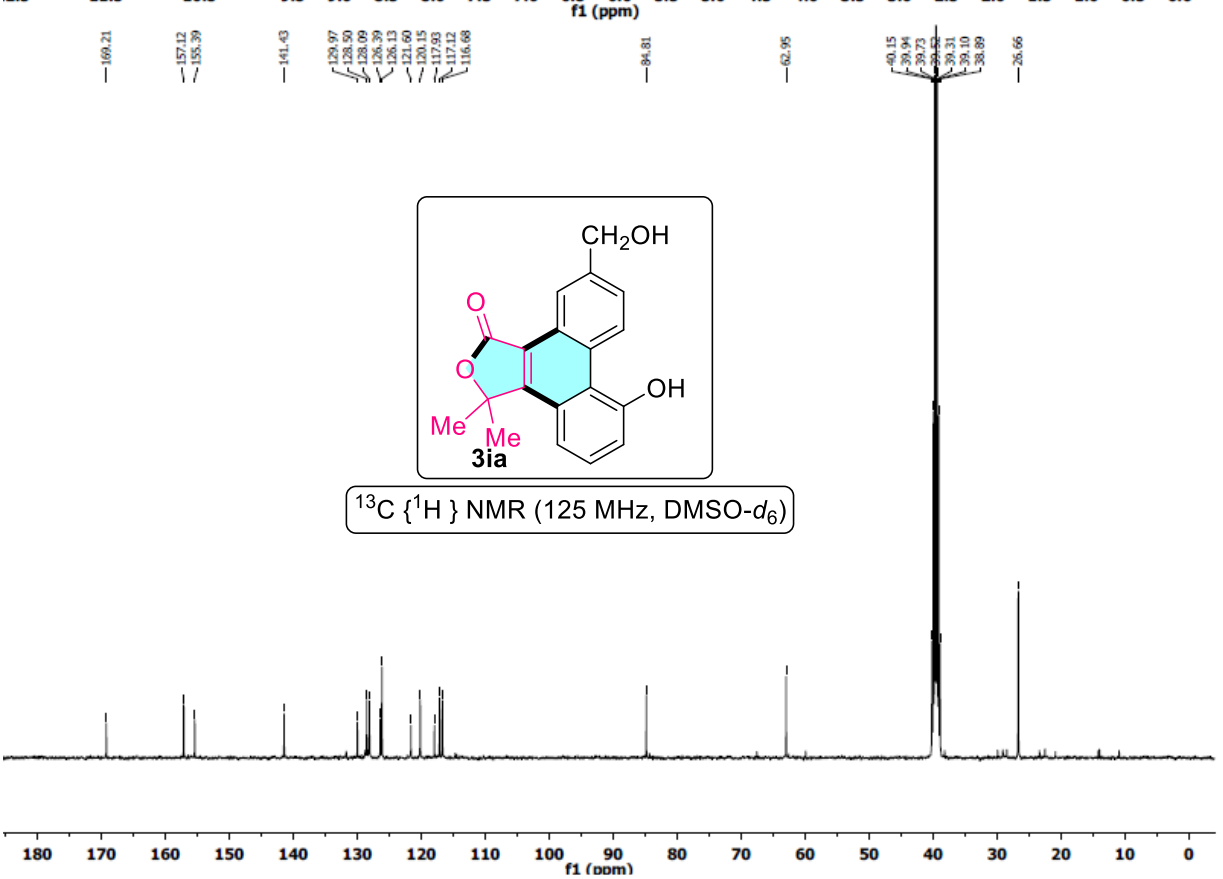

$^{1}$H NMR (400 MHz, DMSO-$d_6$)



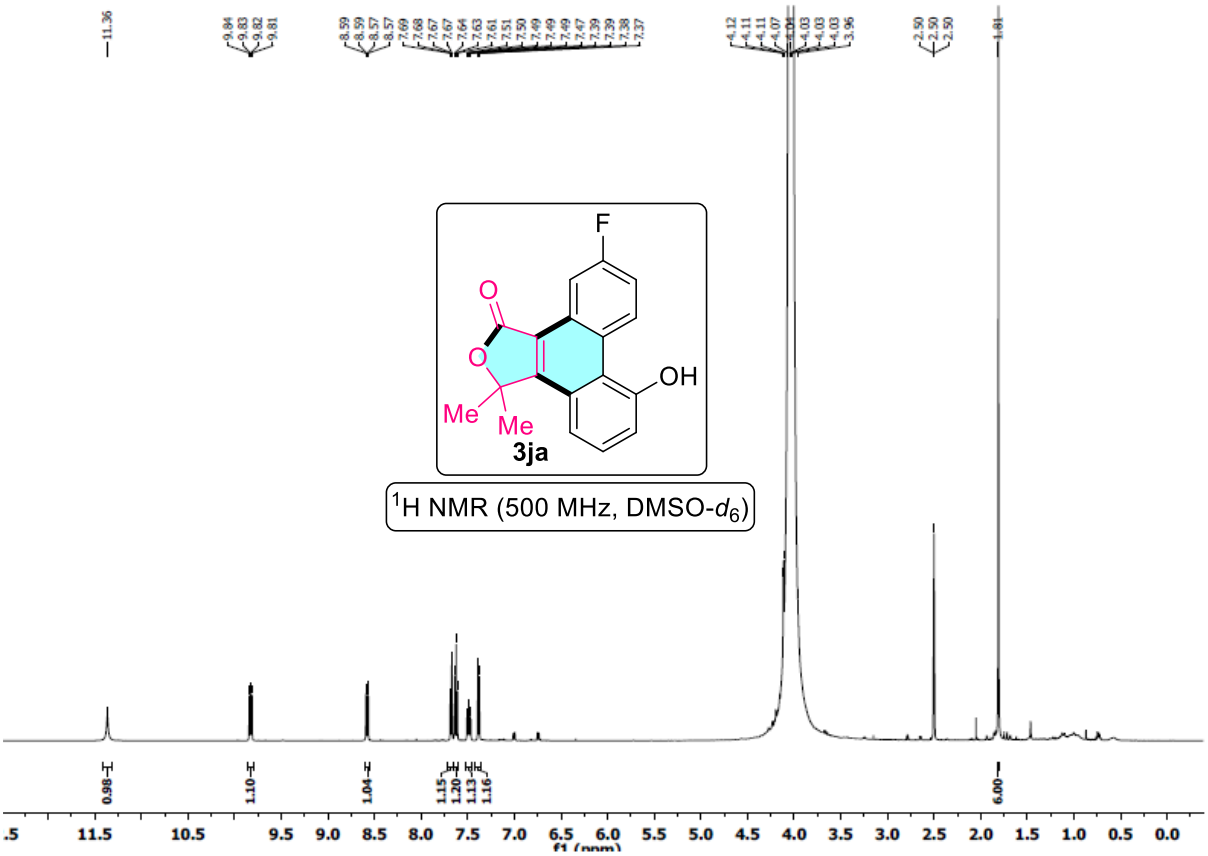

$^{13}$C {$^{1}$H } NMR (100 MHz, DMSO-$d_6$)

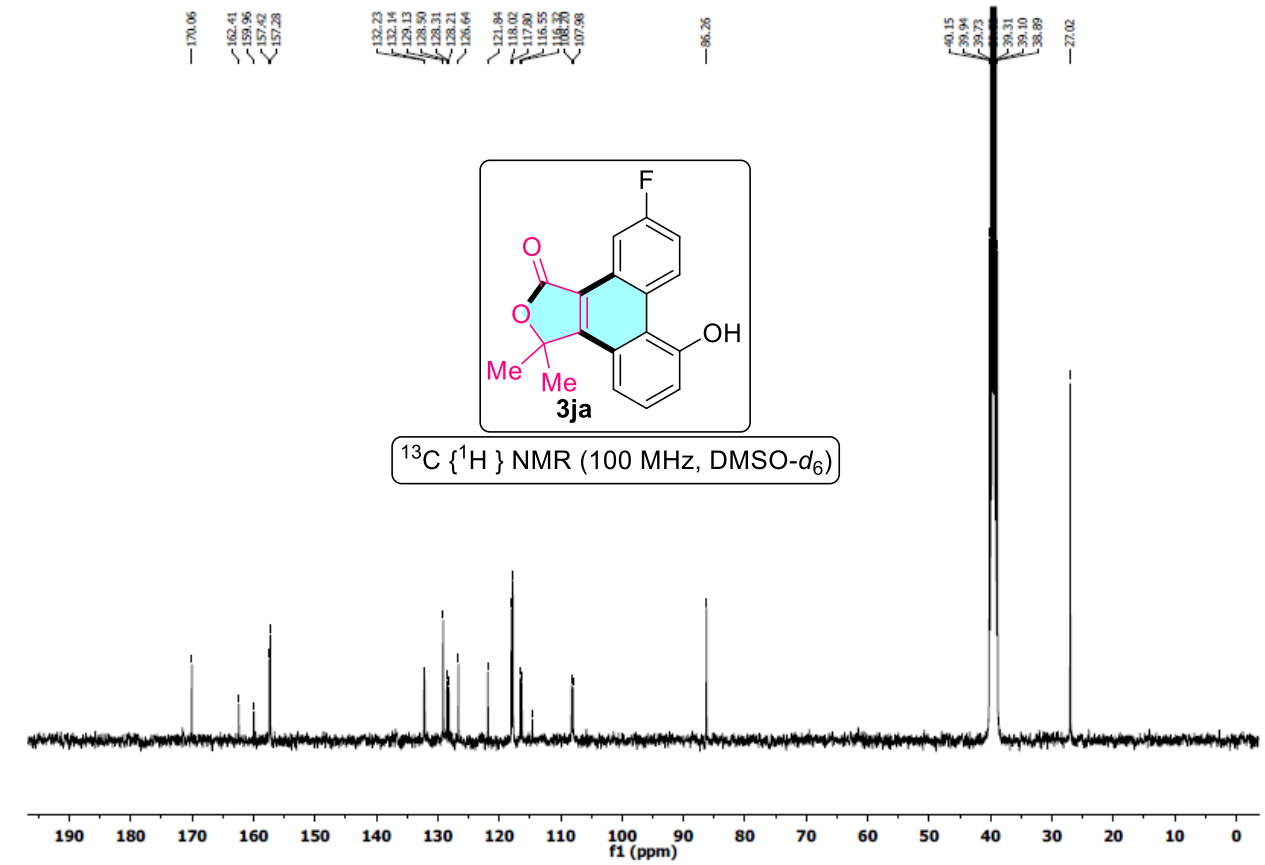


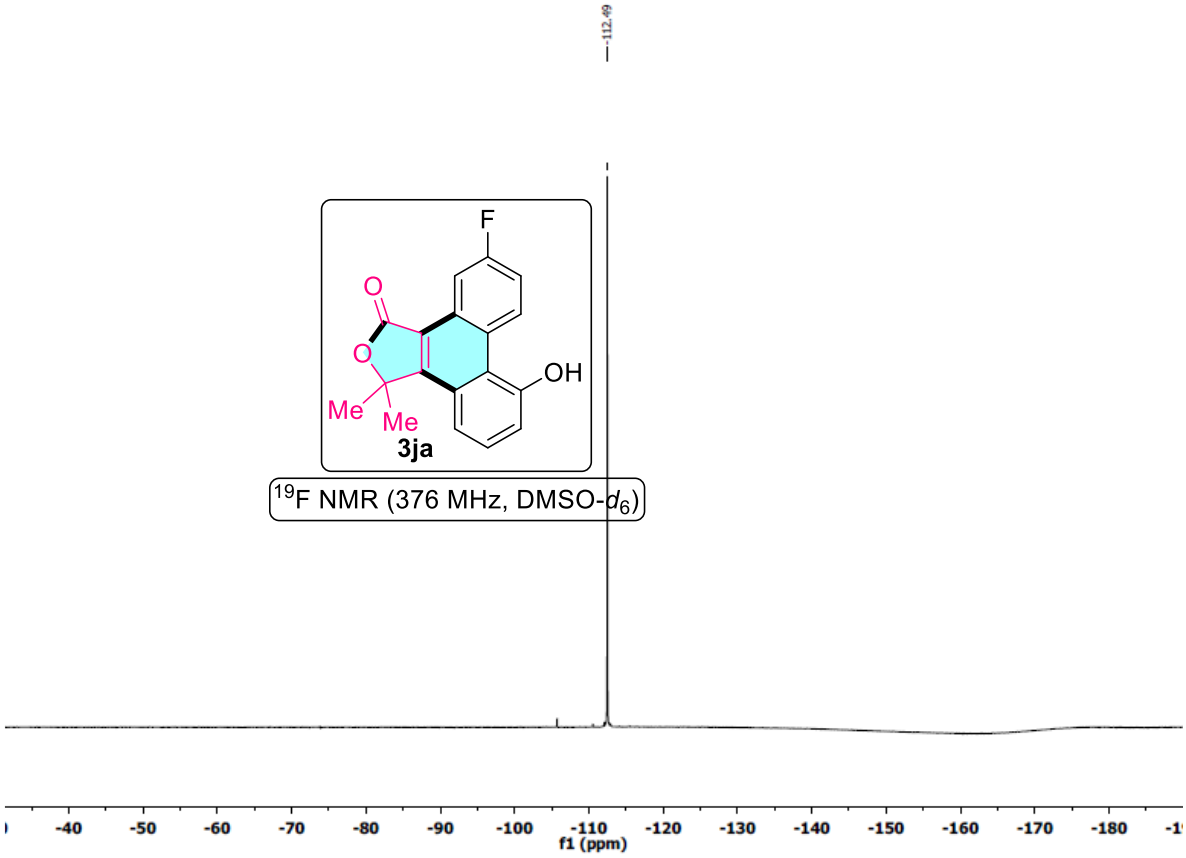

$^{1}$H NMR (500 MHz, DMSO-$d_6$)



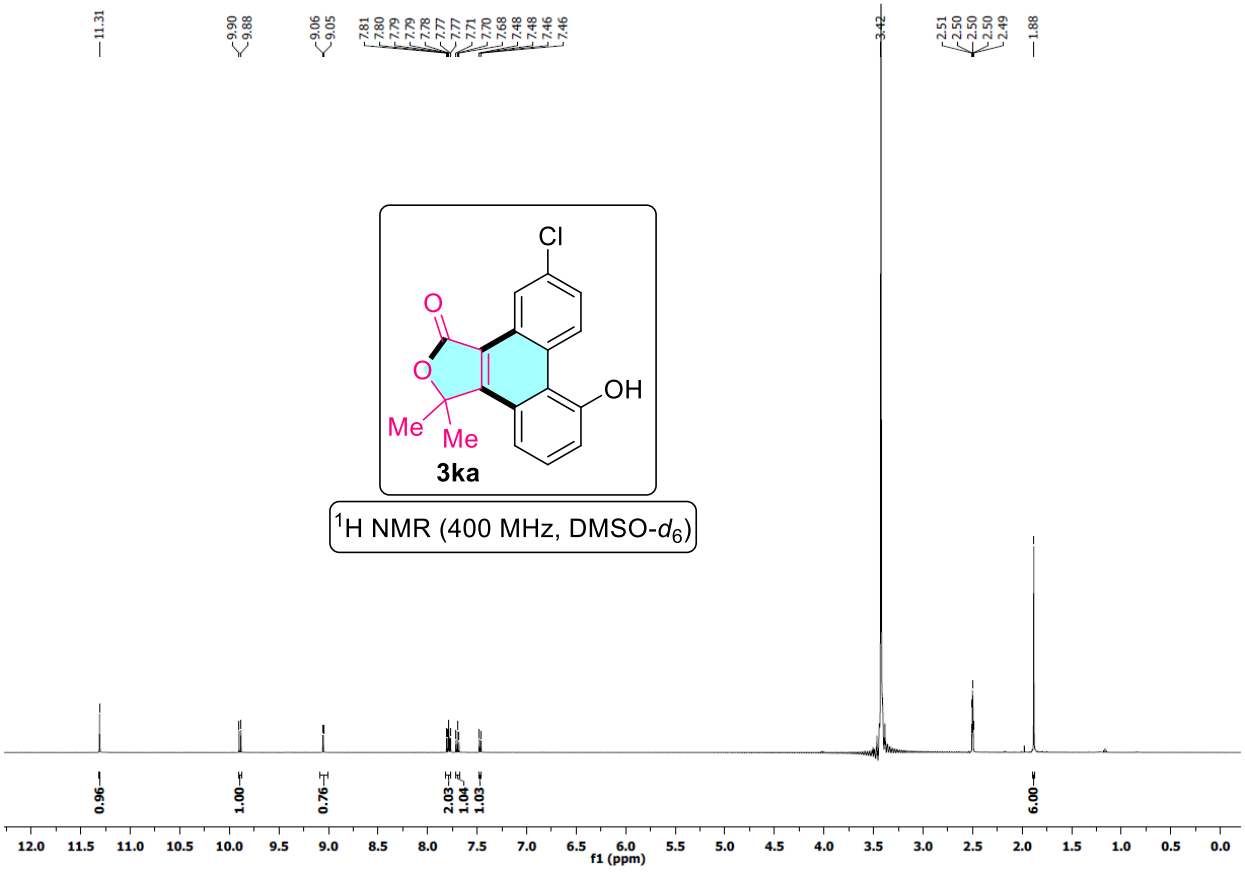

$^{13}$C {$^{1}$H } NMR (125 MHz, DMSO-$d_6$)


F
O
O
OH
Me
Me
3ja
$^{1}$H NMR (500 MHz, DMSO-$d_6$)

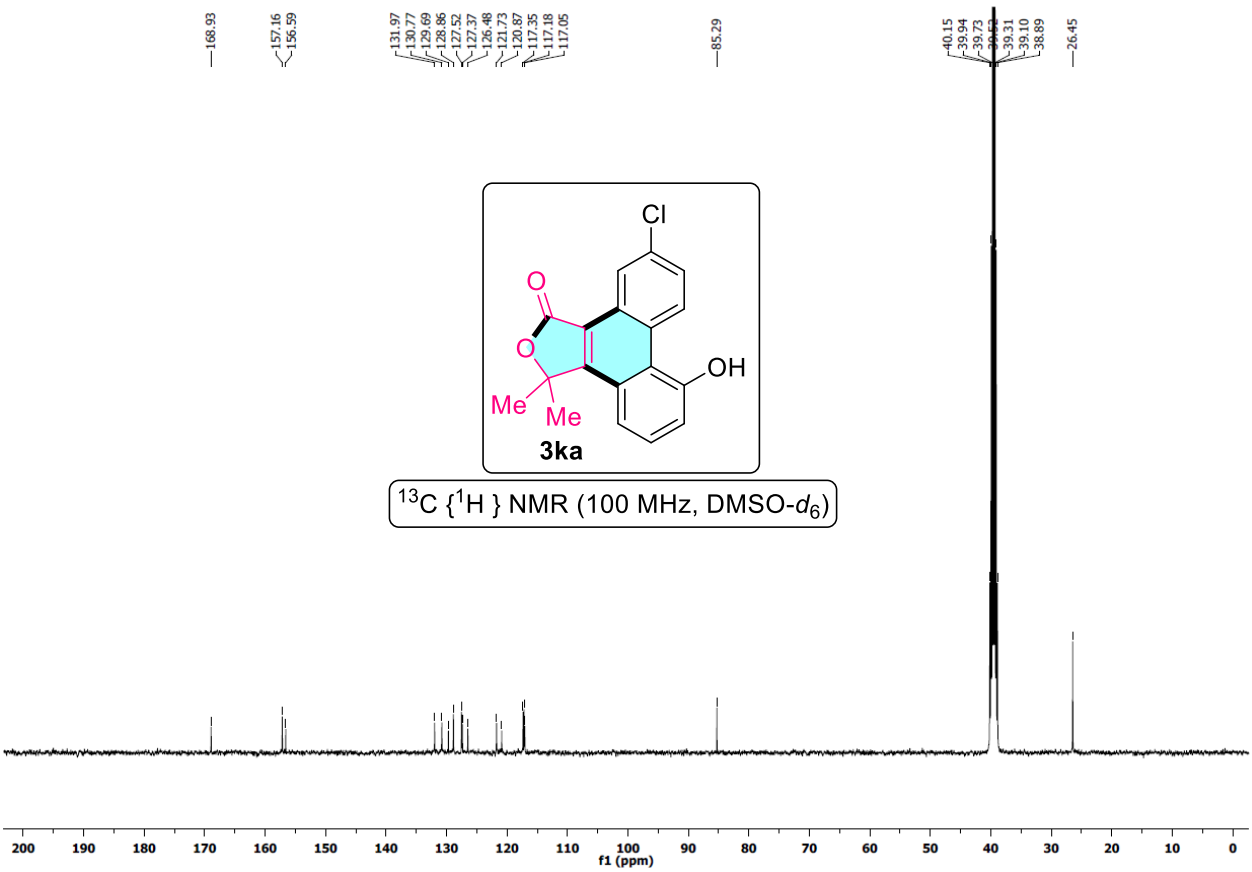

F
O
O
OH
Me
Me
3ja
$^{13}$C {$^{1}$H } NMR (100 MHz, DMSO-$d_6$)
f1 (ppm)



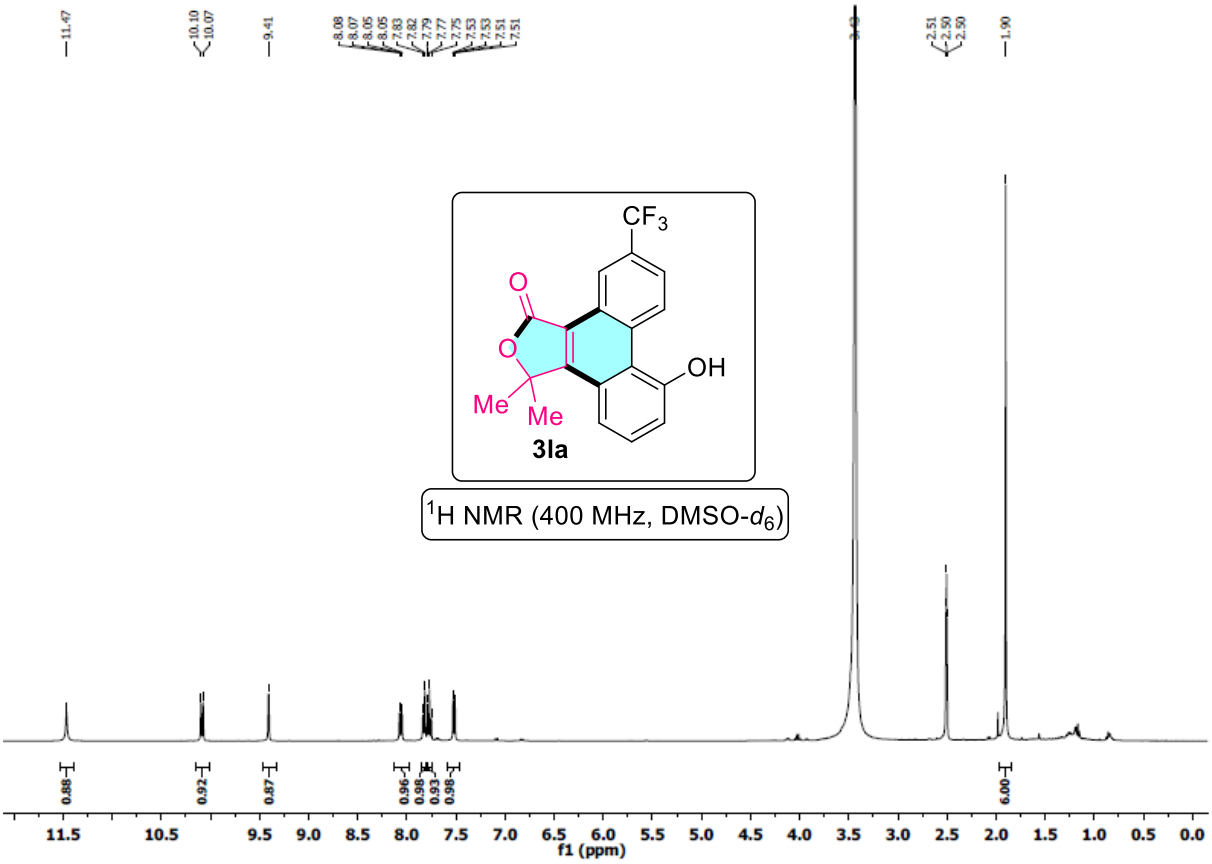

$^{19}$F NMR (376 MHz, DMSO-$d_6$)



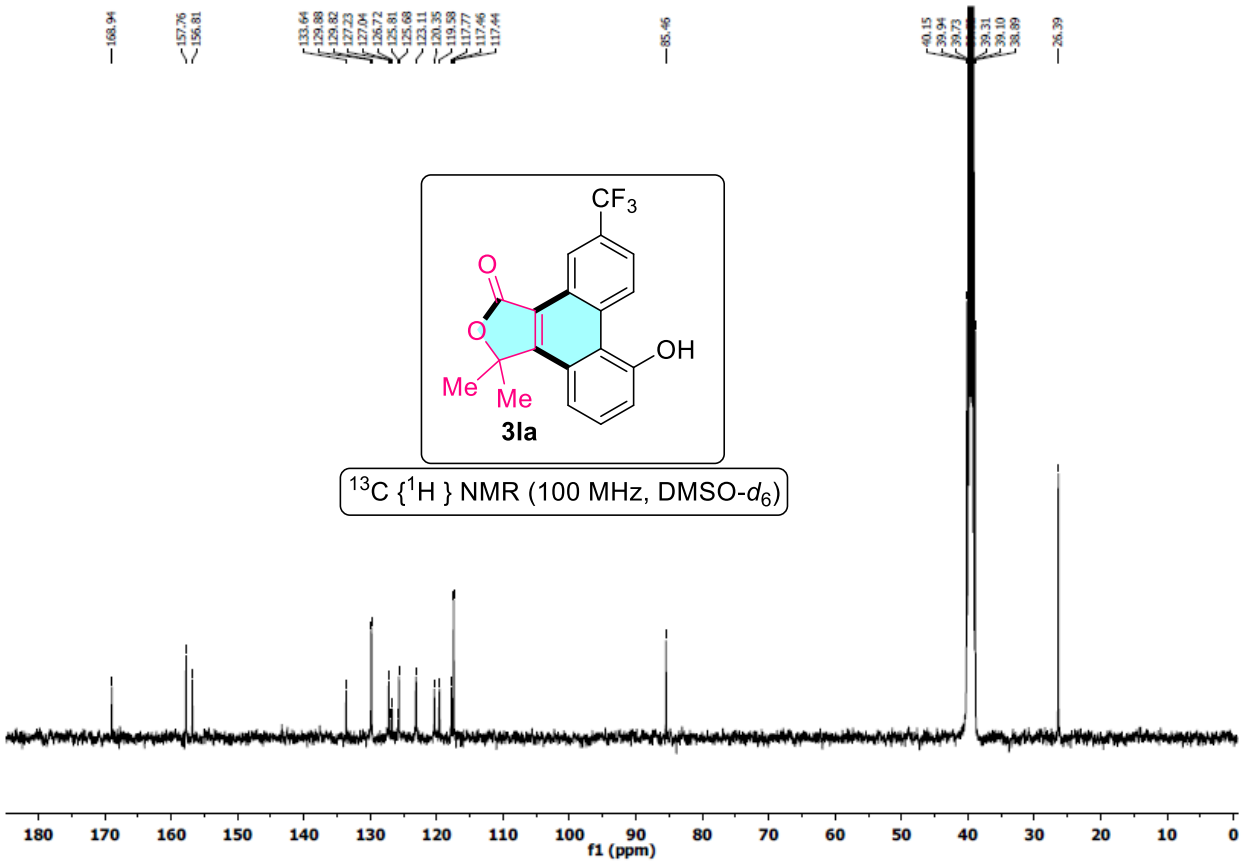

$^{1}$H NMR (400 MHz, DMSO-$d_6$)



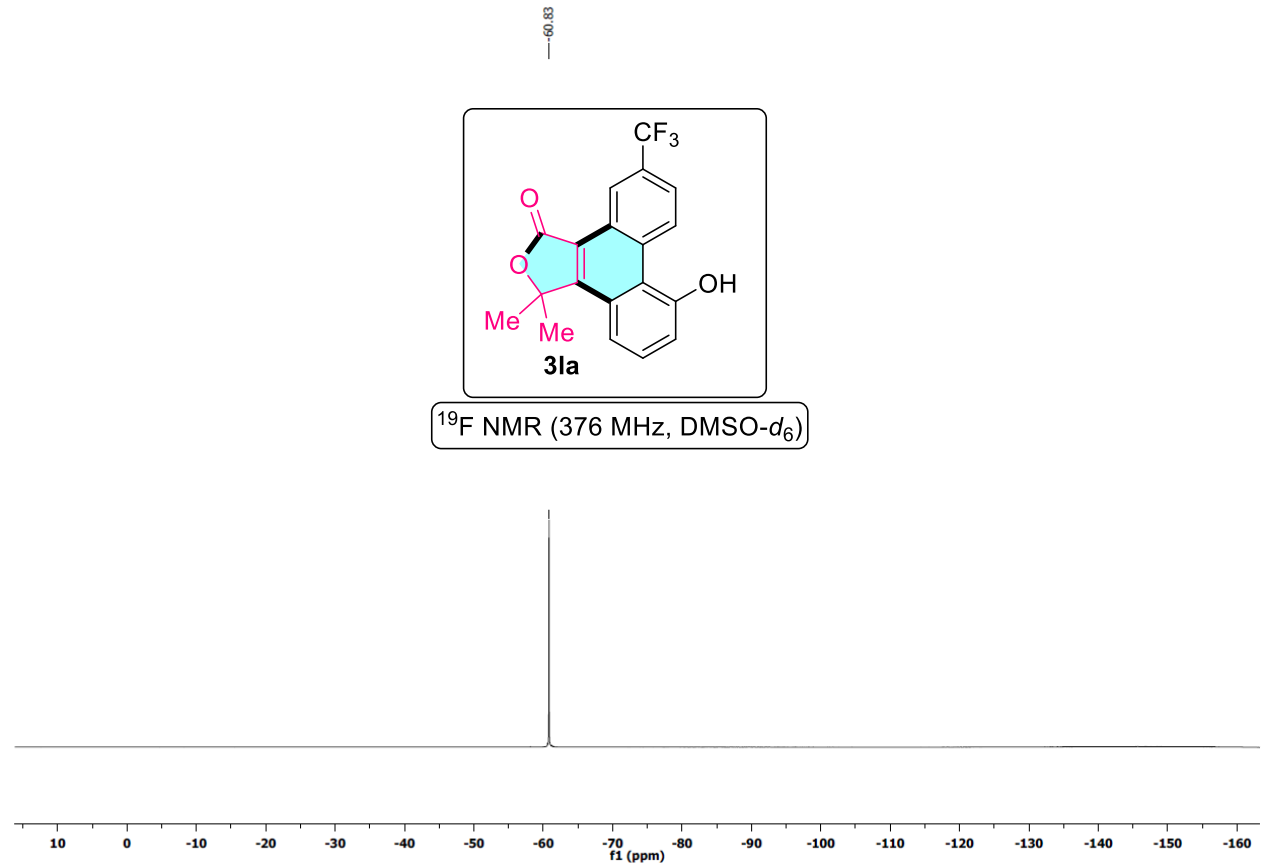

$^{13}C$ {$^{1}H$ } NMR (100 MHz, DMSO-$d_6$)



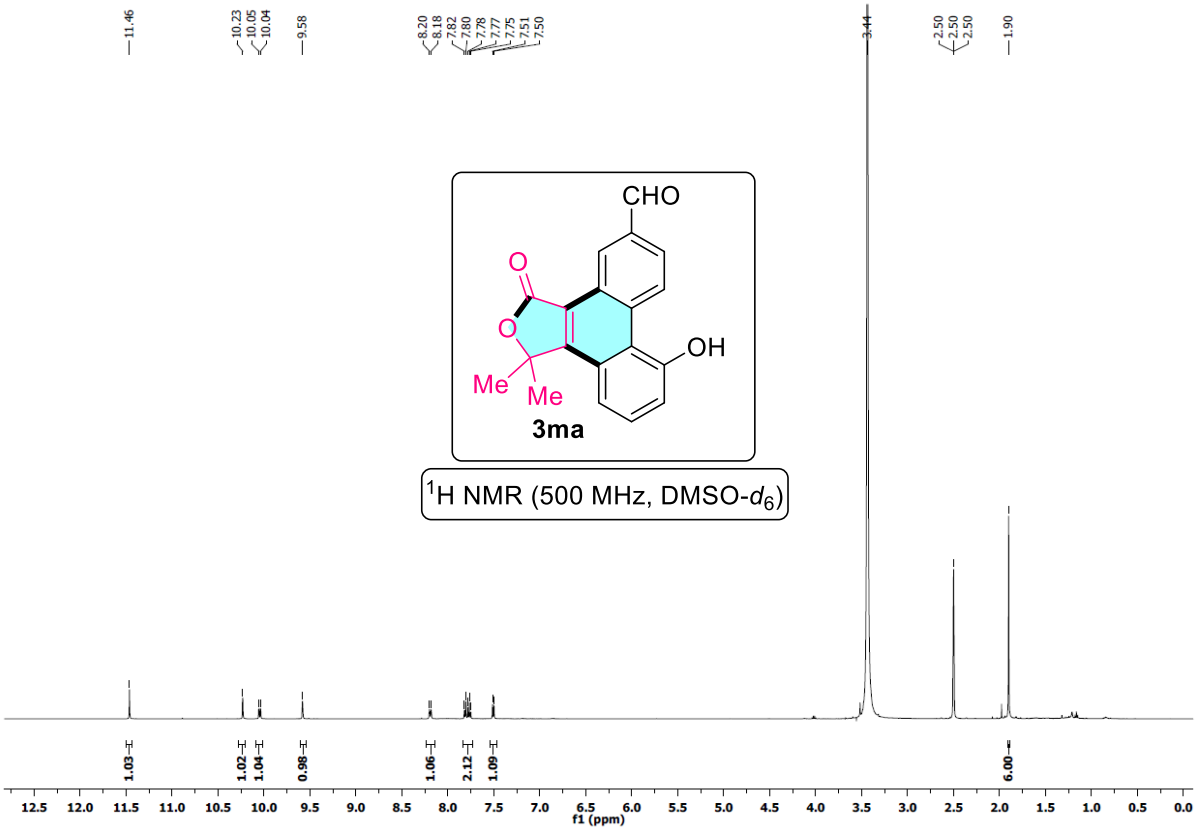

$^{1}H$ NMR (400 MHz, DMSO-$d_6$)

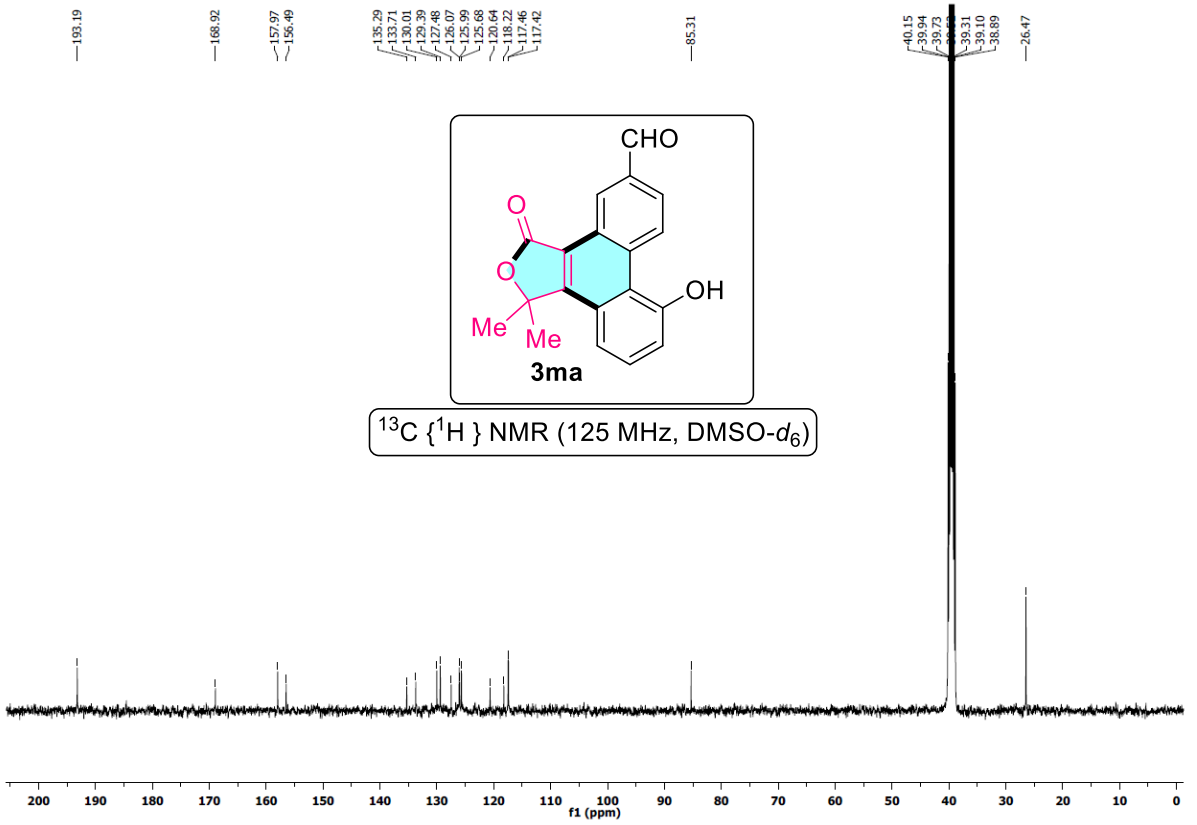


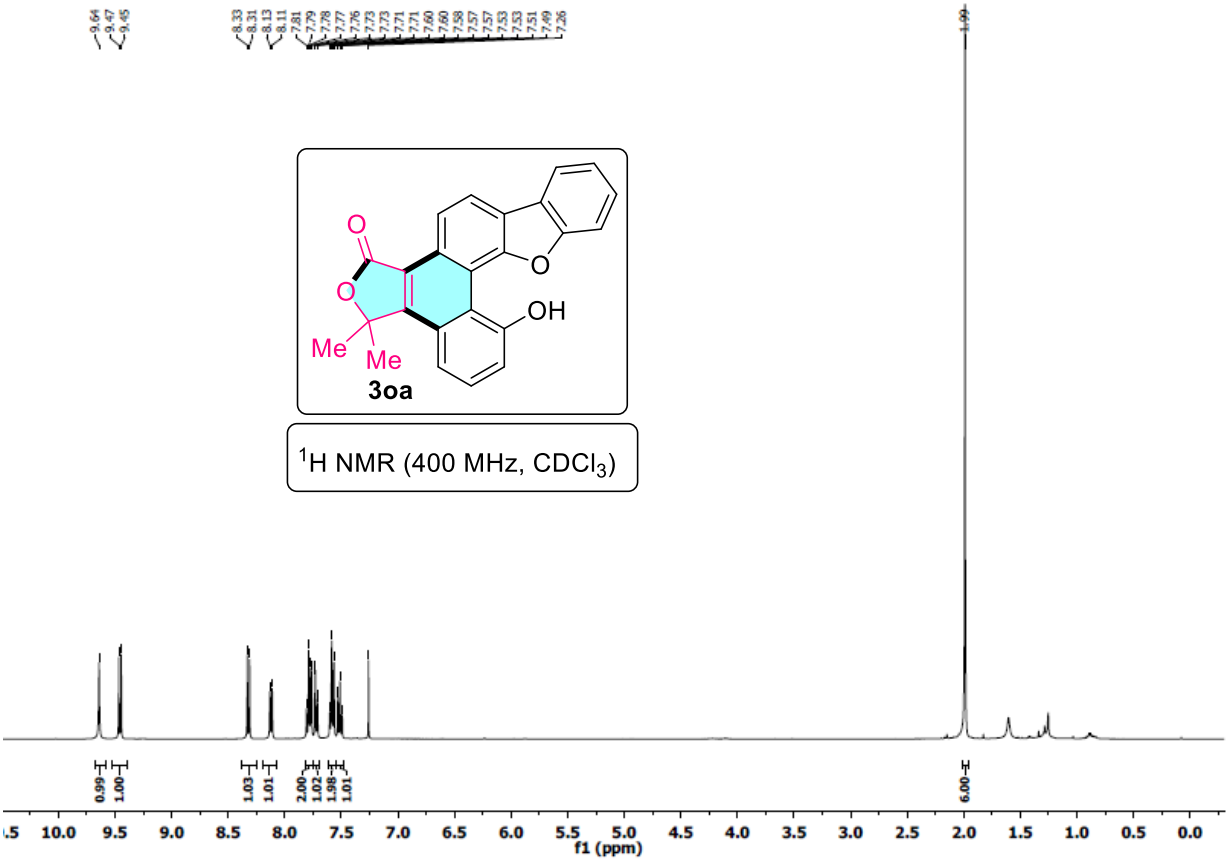

$^{13}C$ {$^{1}H$ } NMR (100 MHz, DMSO-$d_6$)

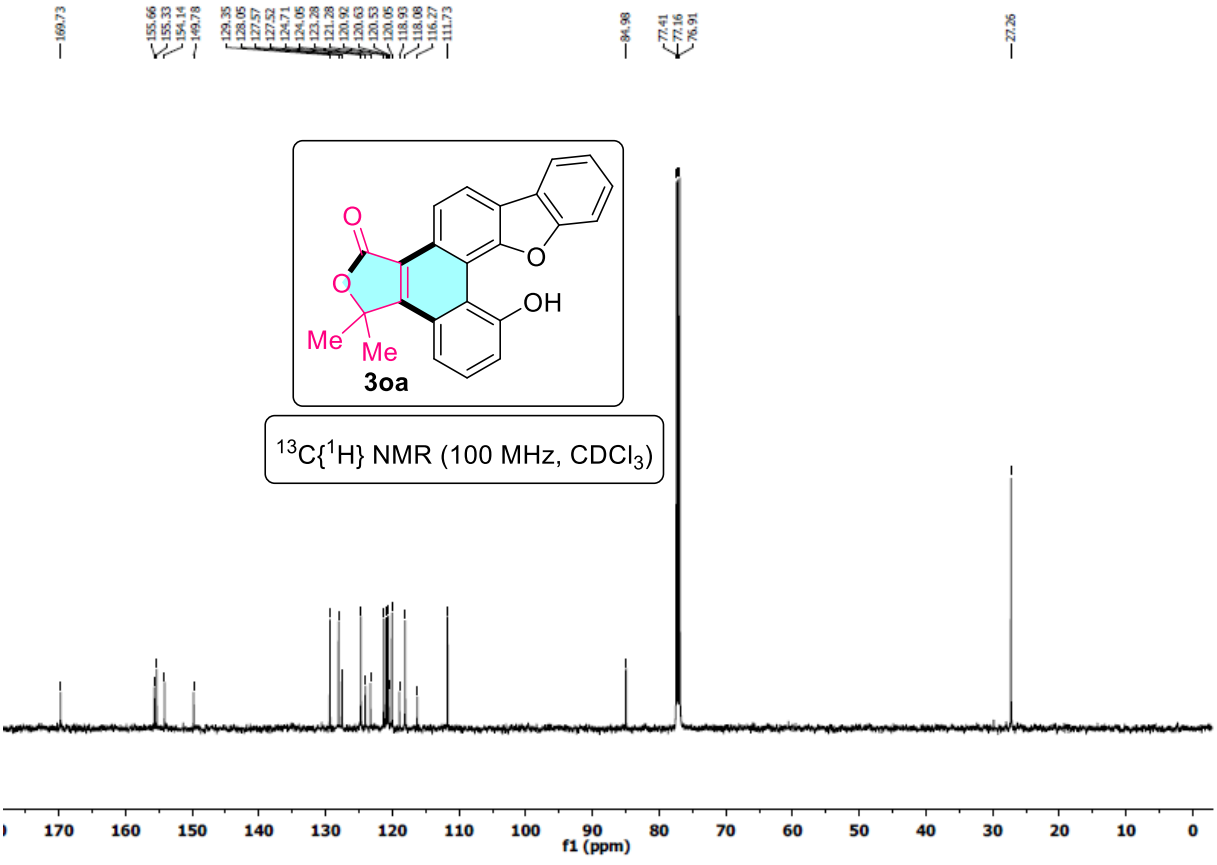


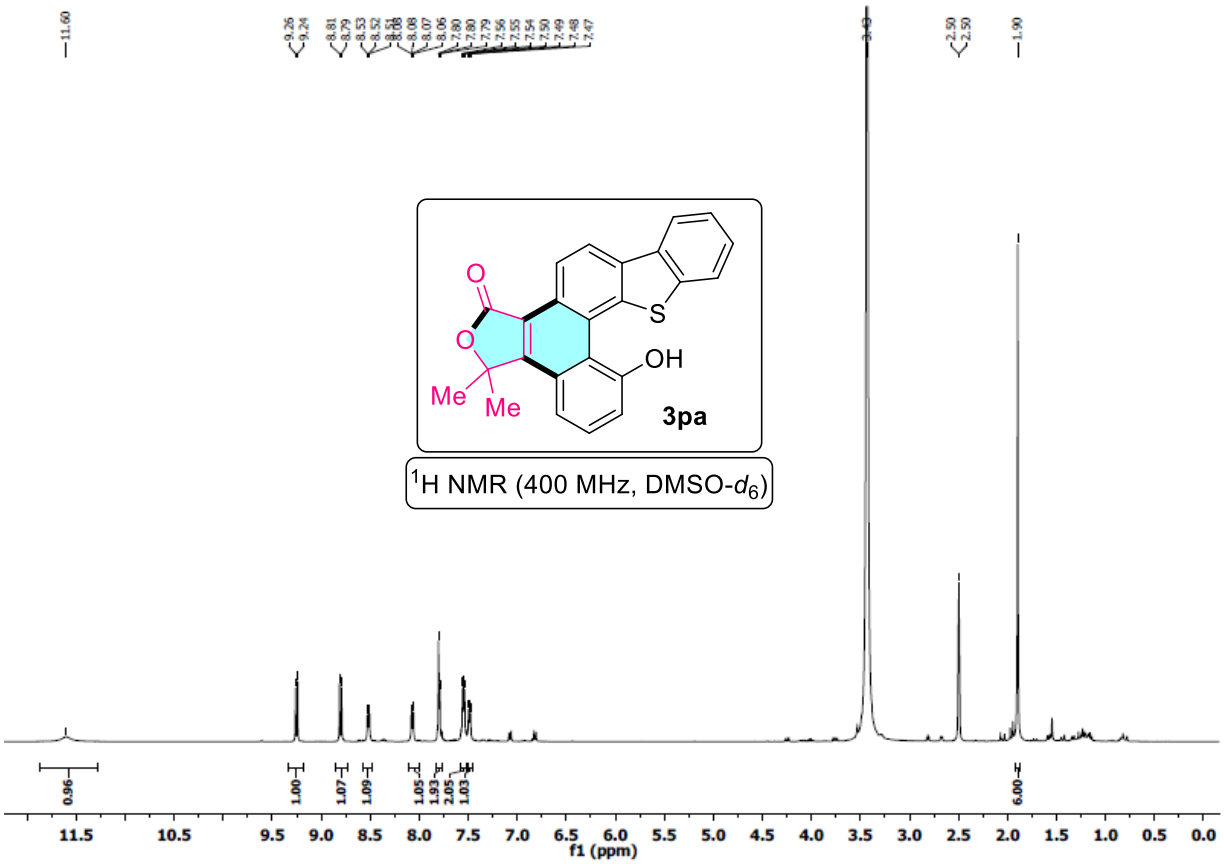

$^{19}F$ NMR (376 MHz, DMSO-$d_6$)


CHO
O
O
OH
Me
Me
3ma
1H NMR (500 MHz, DMSO-d6)
f1 (ppm)

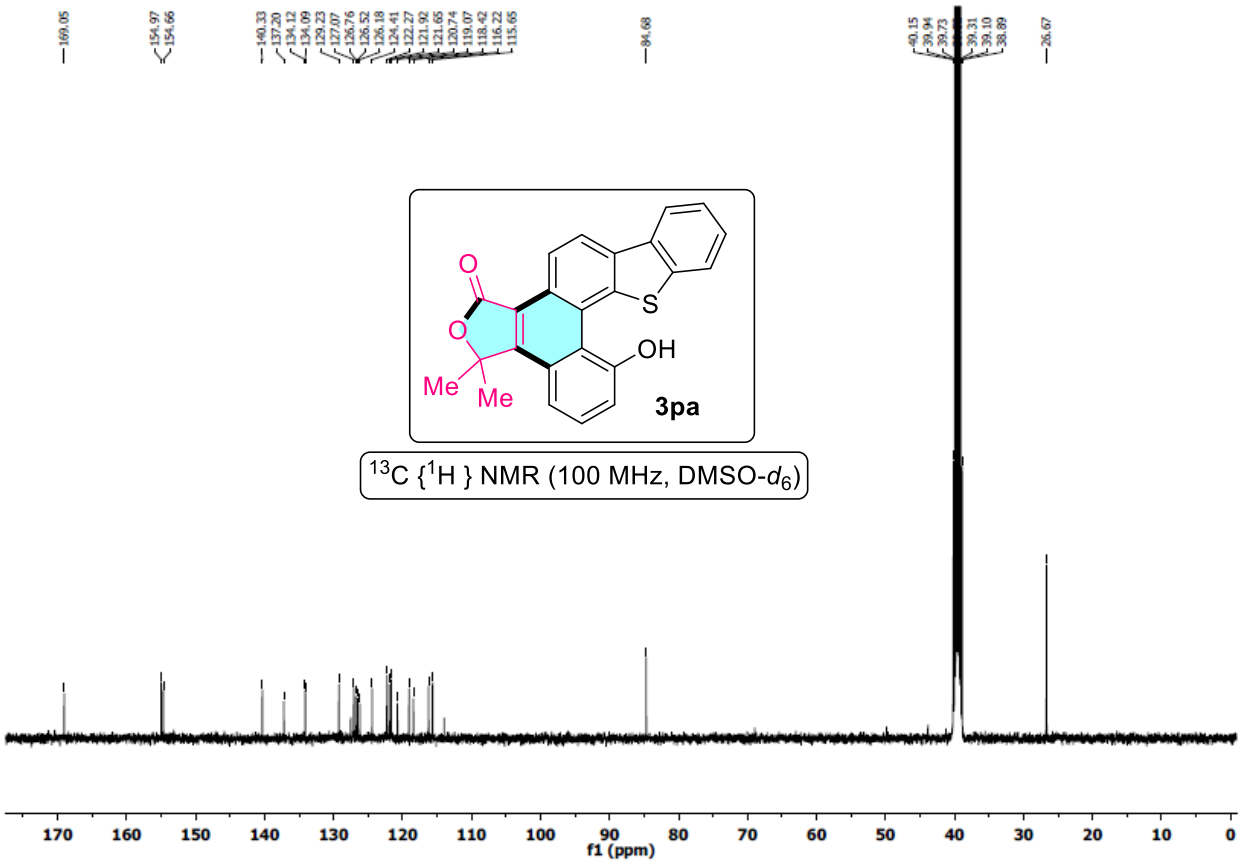

CHO
O
O
OH
Me
Me
3ma
13C {1H } NMR (125 MHz, DMSO-d6)
f1 (ppm)


O
O
OH
Me
Me
3oa
1H NMR (400 MHz, CDCl3)
f1 (ppm)

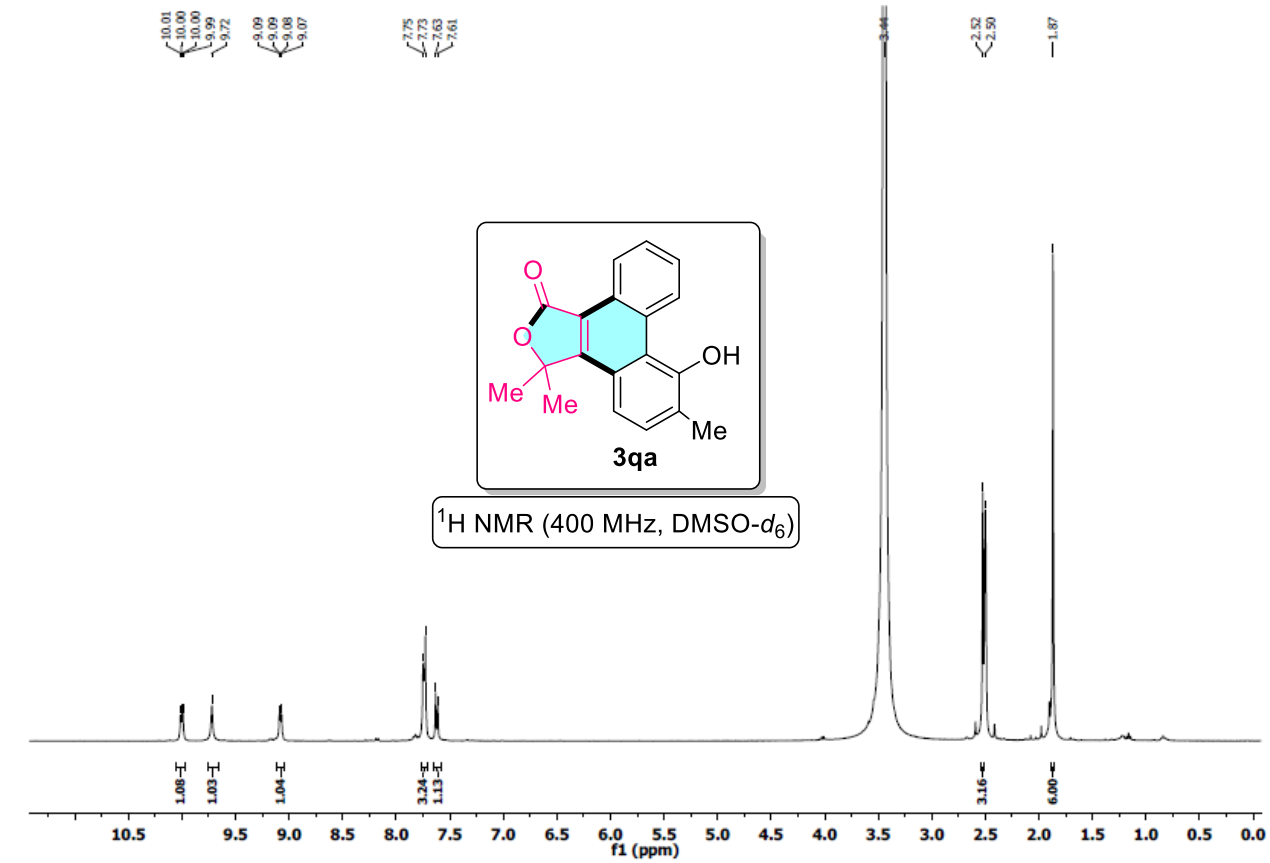

O
O
OH
Me
Me
3oa
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

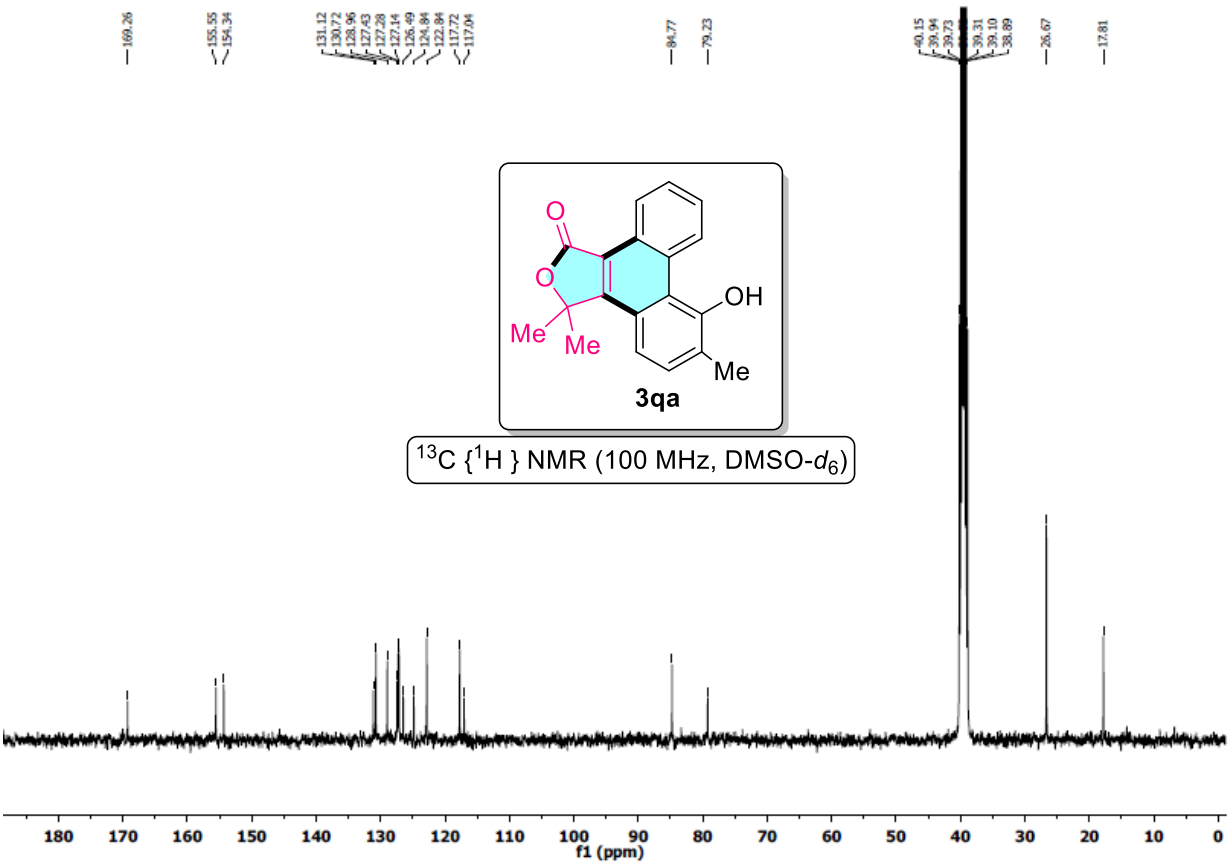


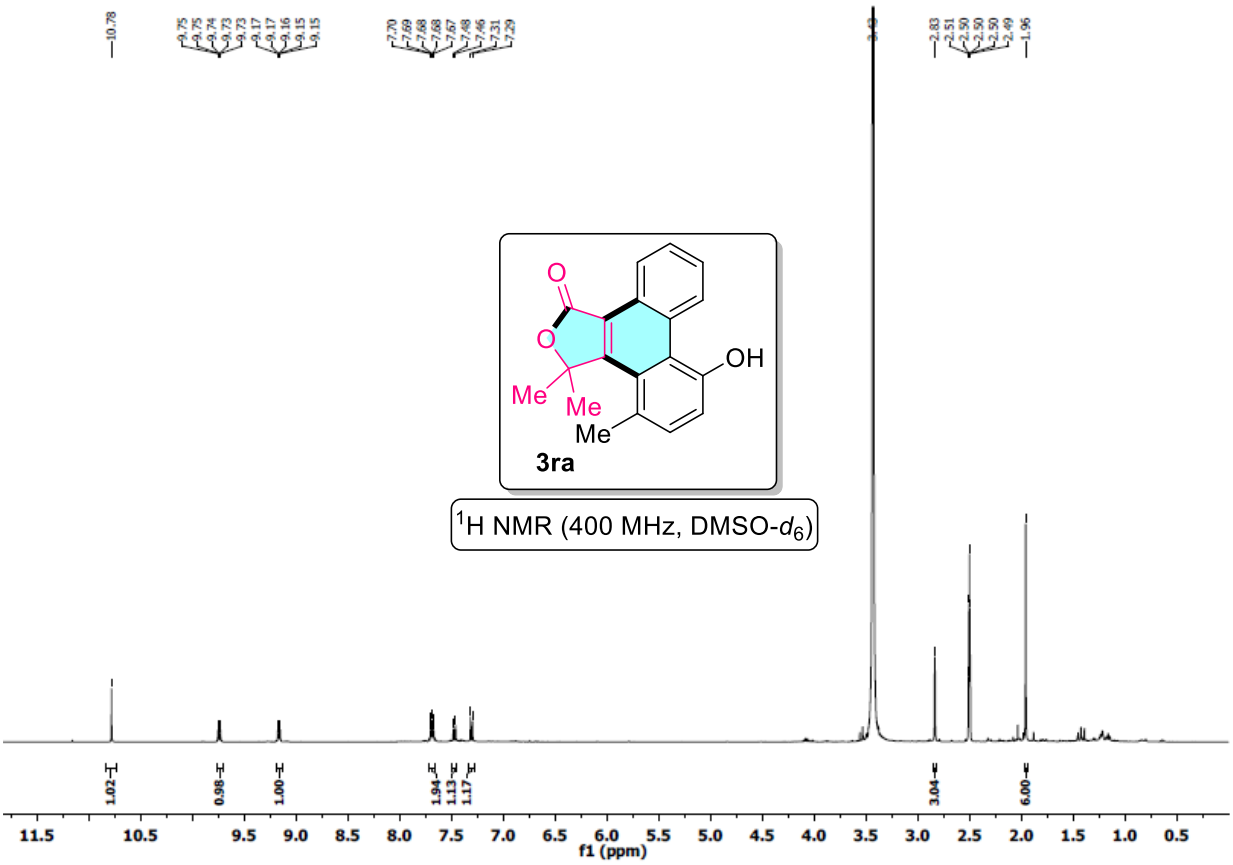

$^{1}$H NMR (400 MHz, DMSO-$d_6$)

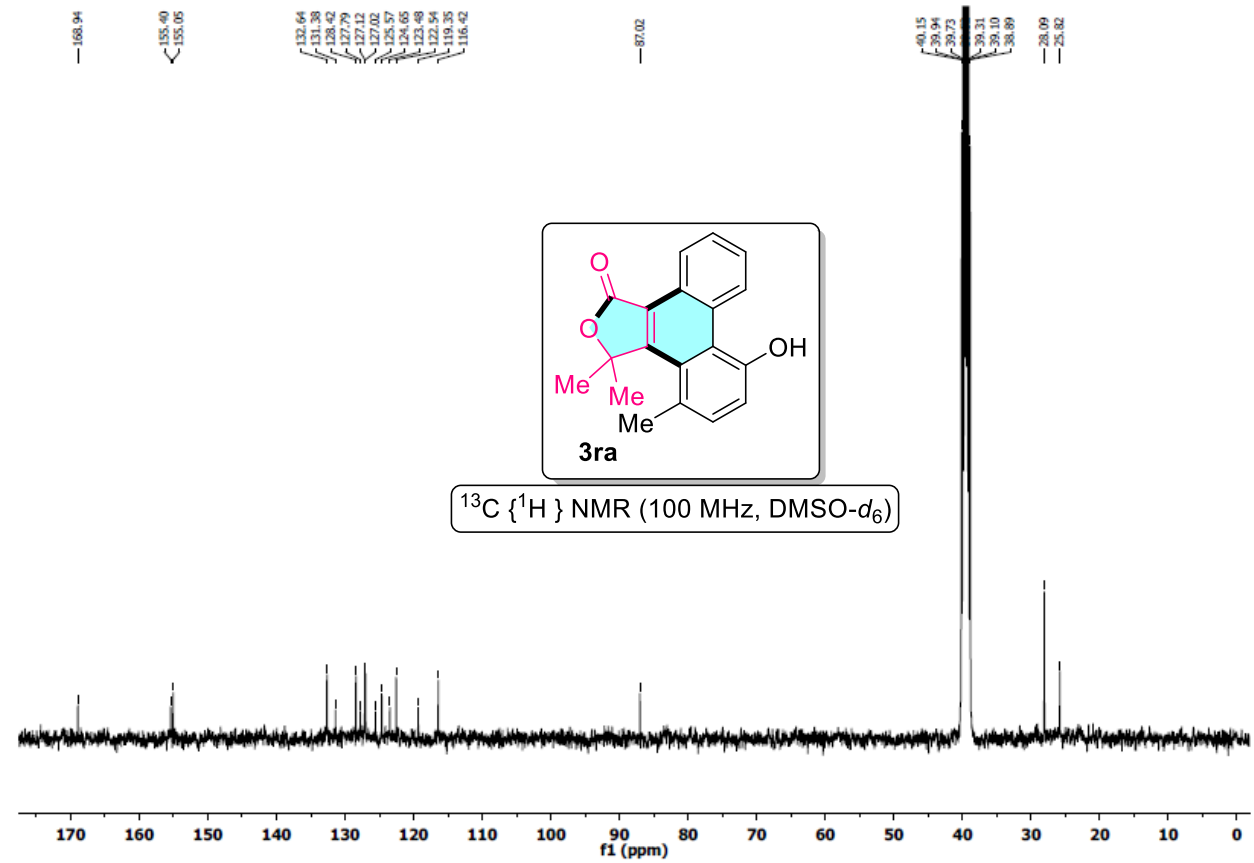


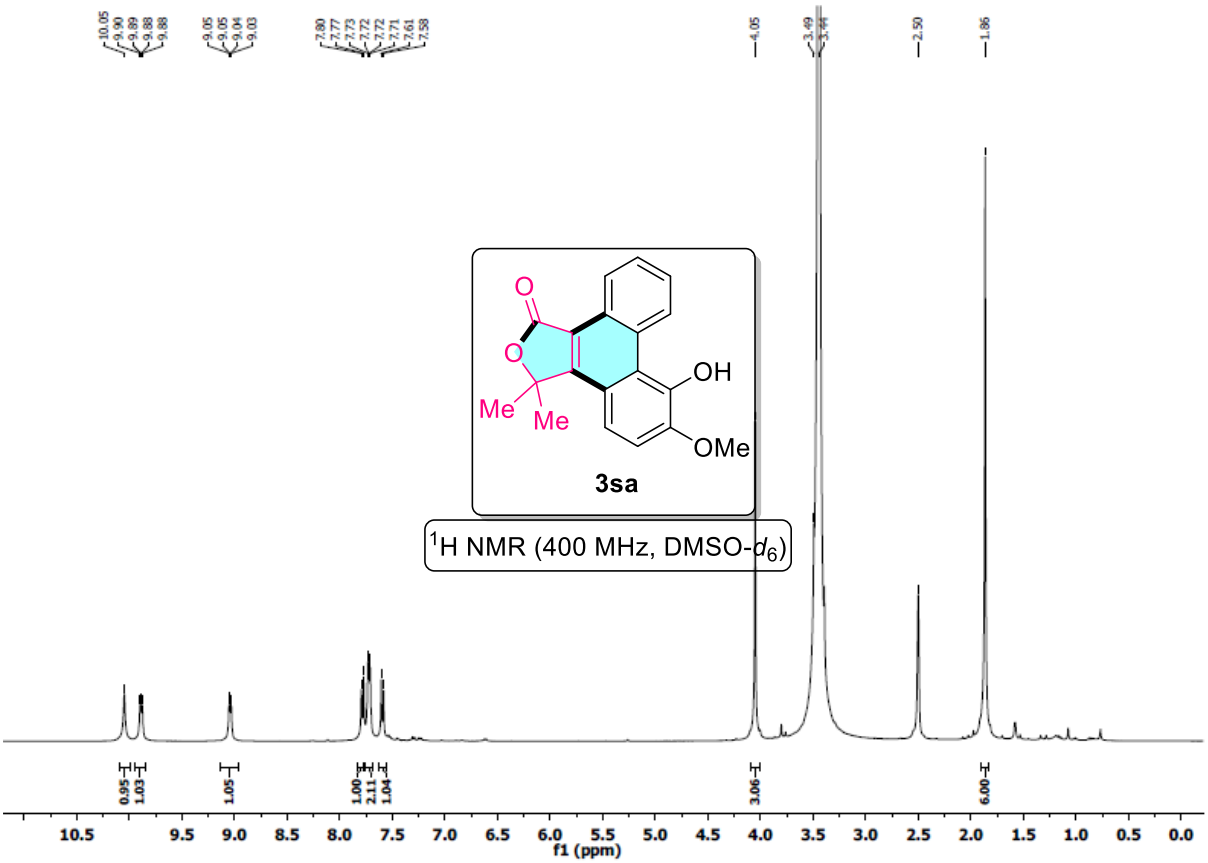

$^{13}$C {$^{1}$H } NMR (100 MHz, DMSO-$d_6$)

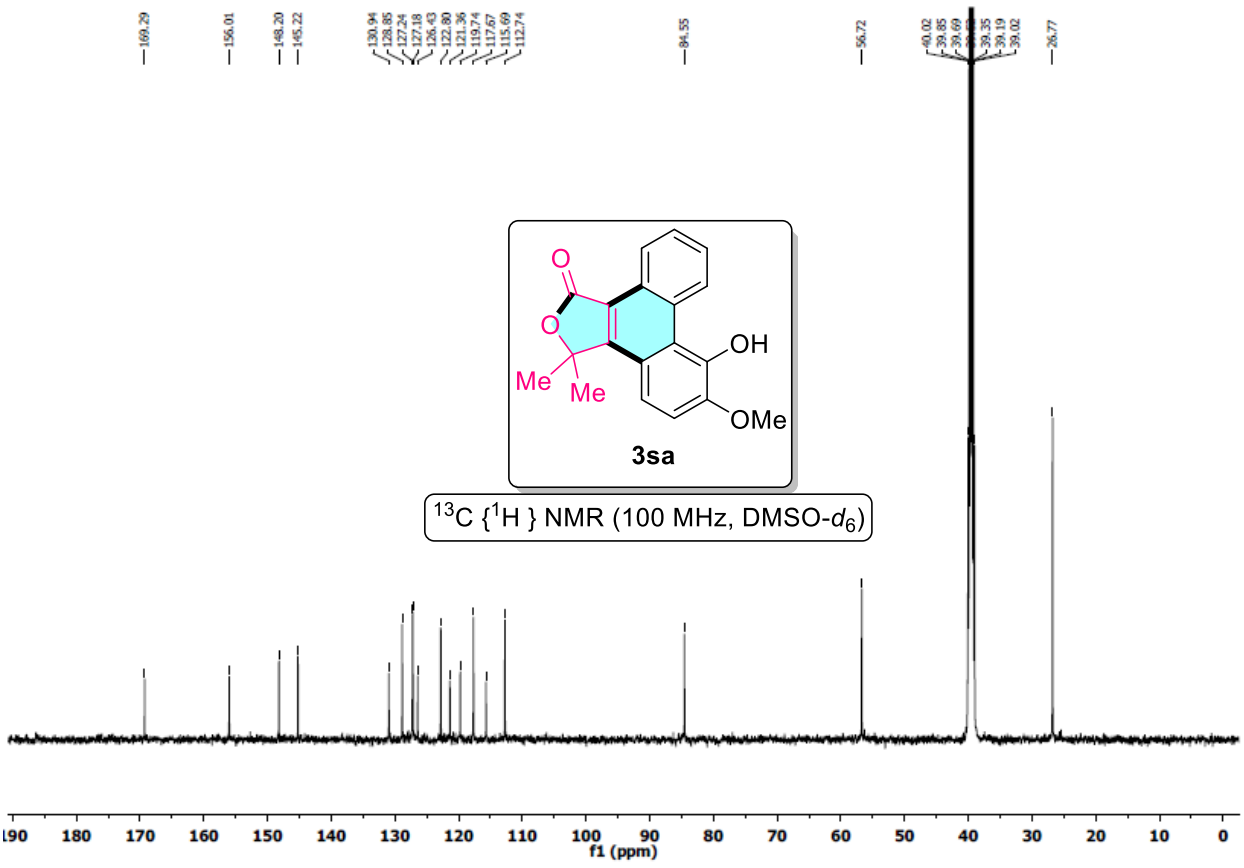

3qa
$^{1}$H NMR (400 MHz, DMSO-$d_6$)
f1 (ppm)

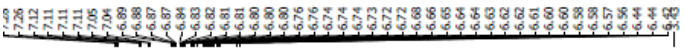

3qa
$^{13}$C {$^{1}$H } NMR (100 MHz, DMSO-$d_6$)
f1 (ppm)

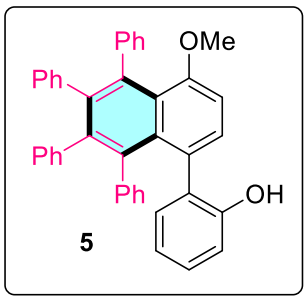

O
O
OH
Me
Me
Me
3ra
$^1$H NMR (400 MHz, DMSO-$d_6$)
f1 (ppm)


O
O
OH
Me
Me
Me
3ra
$^{13}$C {$^1$H } NMR (100 MHz, DMSO-$d_6$)
f1 (ppm)

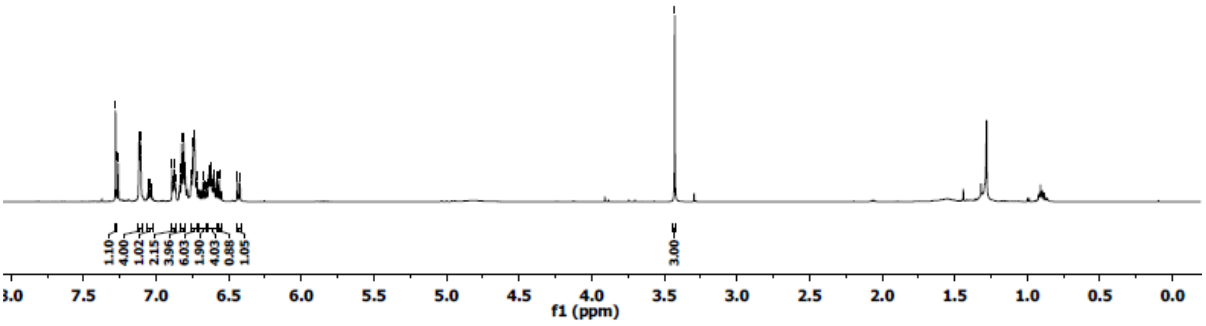

O
O
Me
Me
OH
OMe
3sa
$^1$H NMR (400 MHz, DMSO-$d_6$)
f1 (ppm)

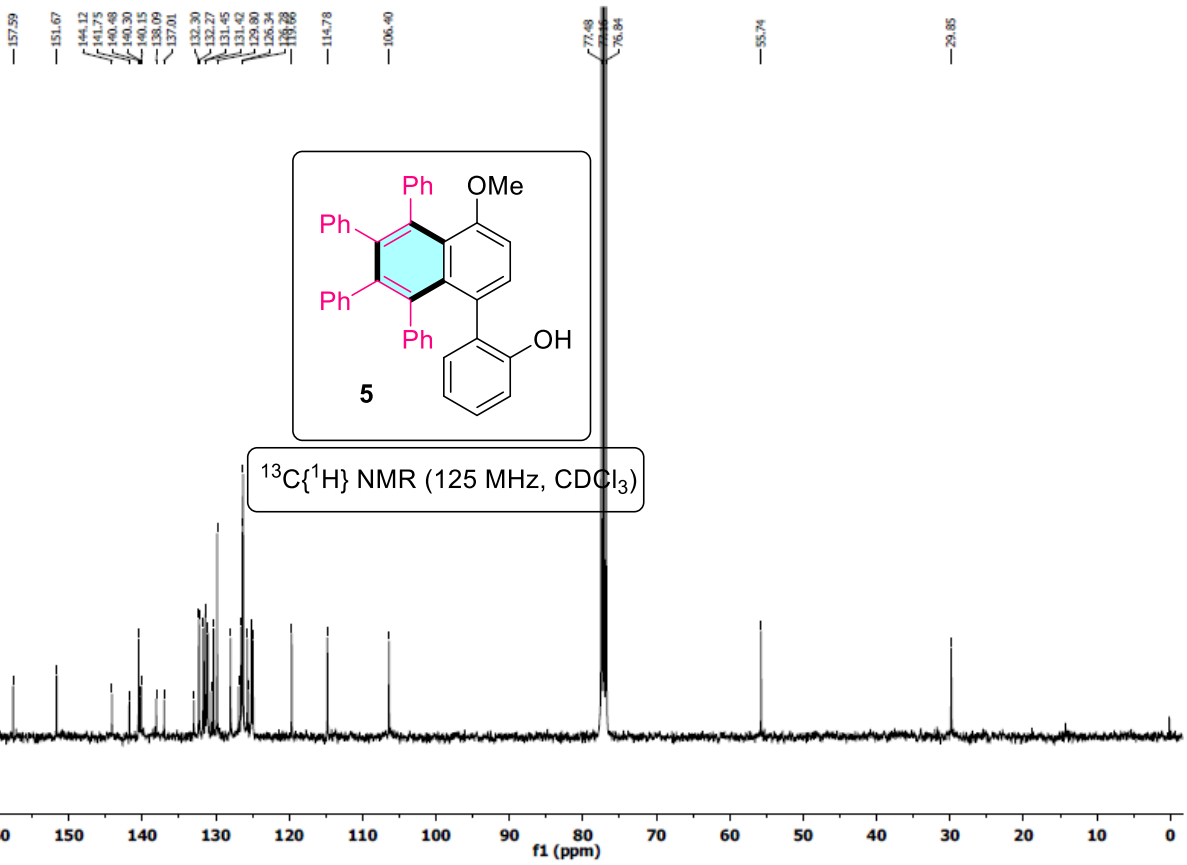

O
O
Me
Me
OH
OMe
3sa
$^{13}$C {$^1$H } NMR (100 MHz, DMSO-$d_6$)
f1 (ppm)



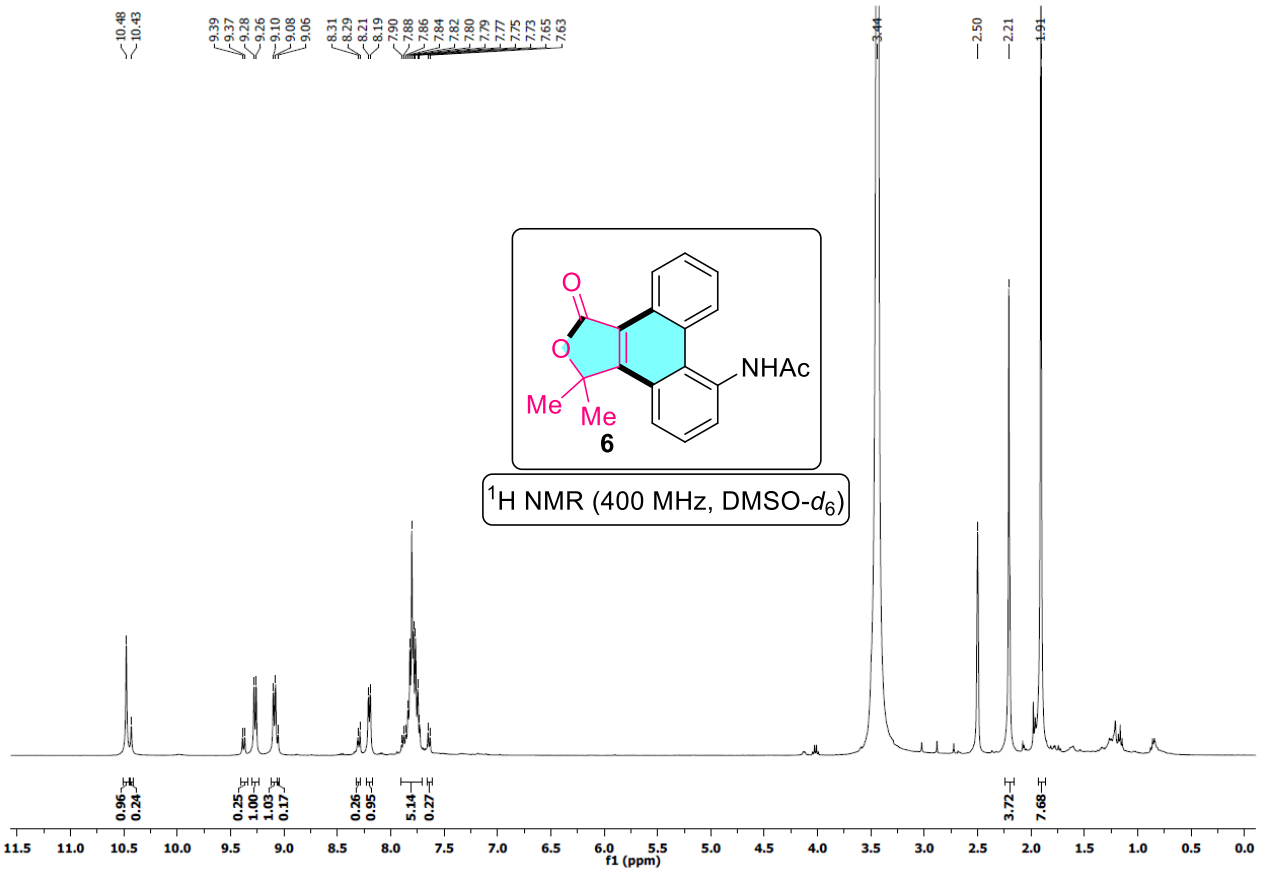



$^{1}$H NMR (500 MHz, $CDCl_3$)

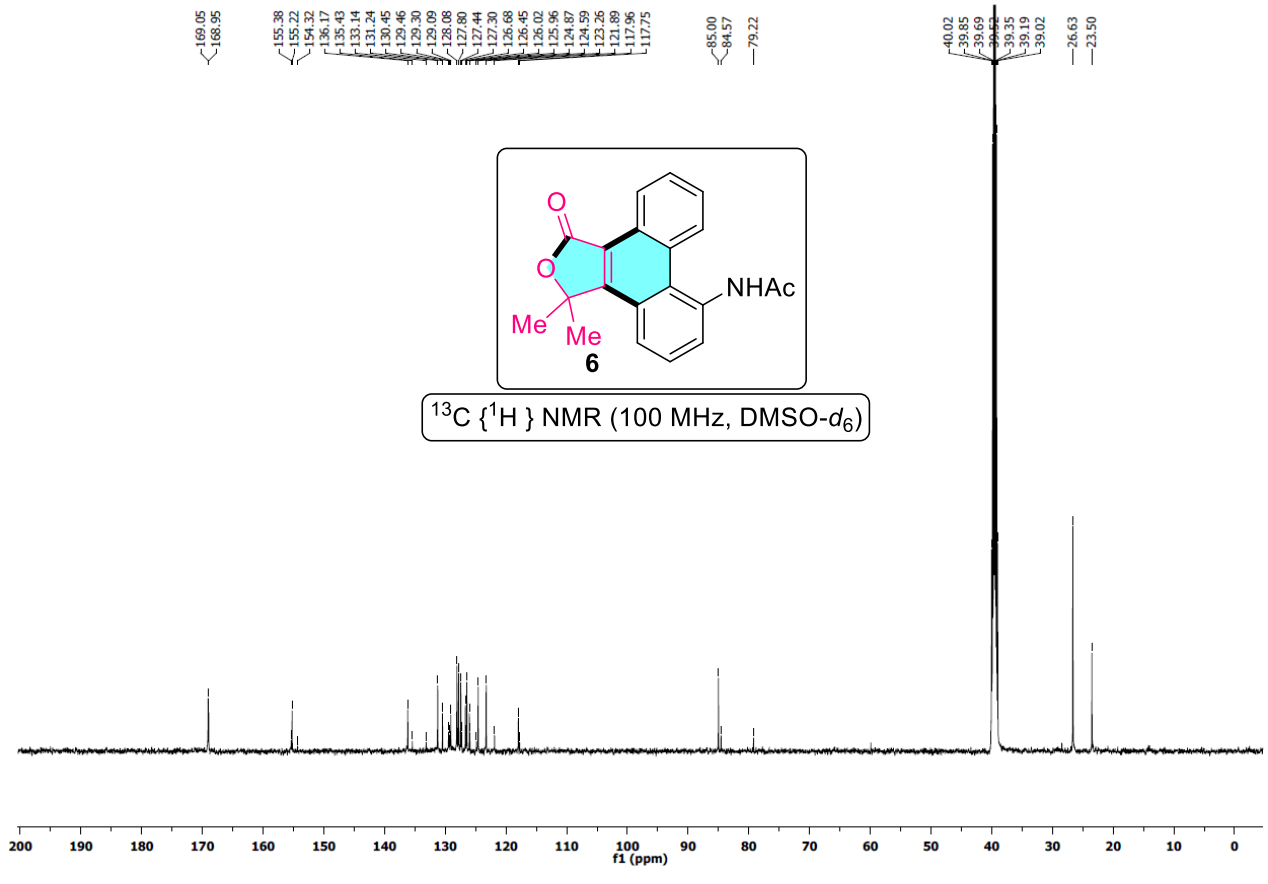


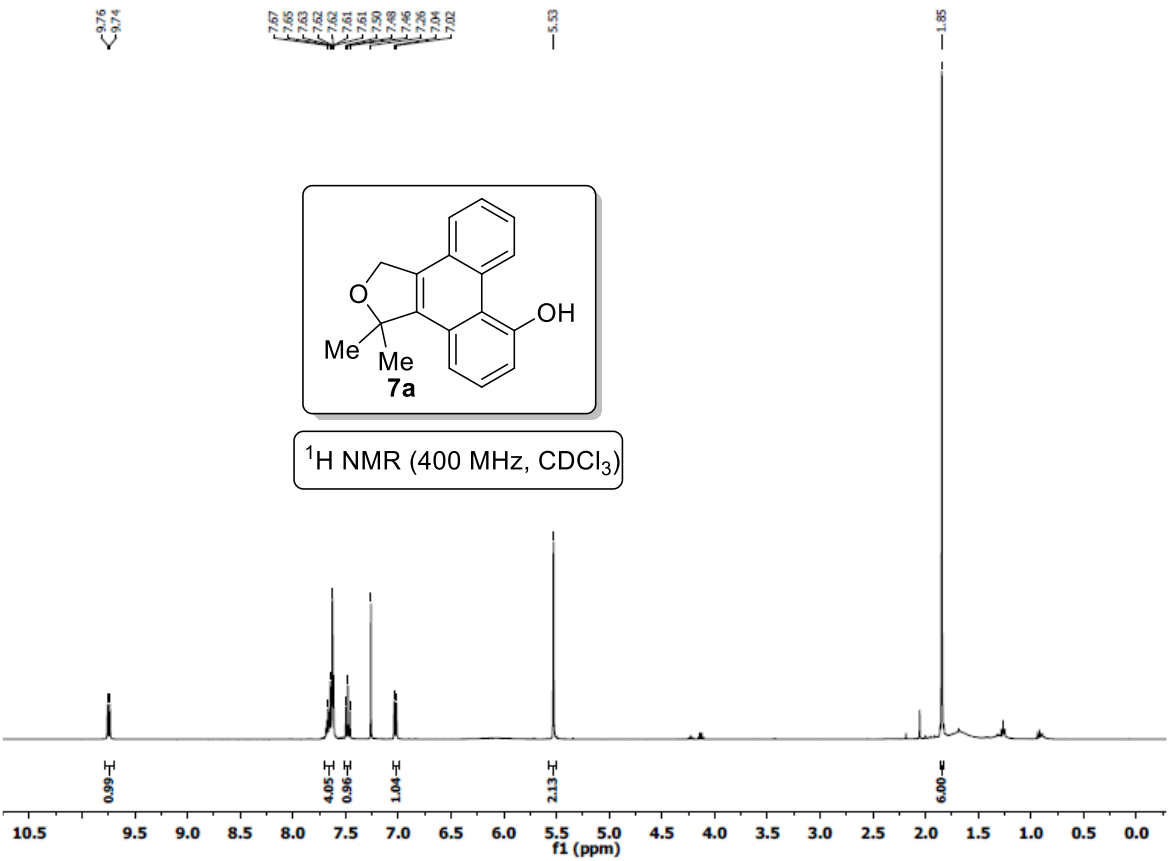

$^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$)



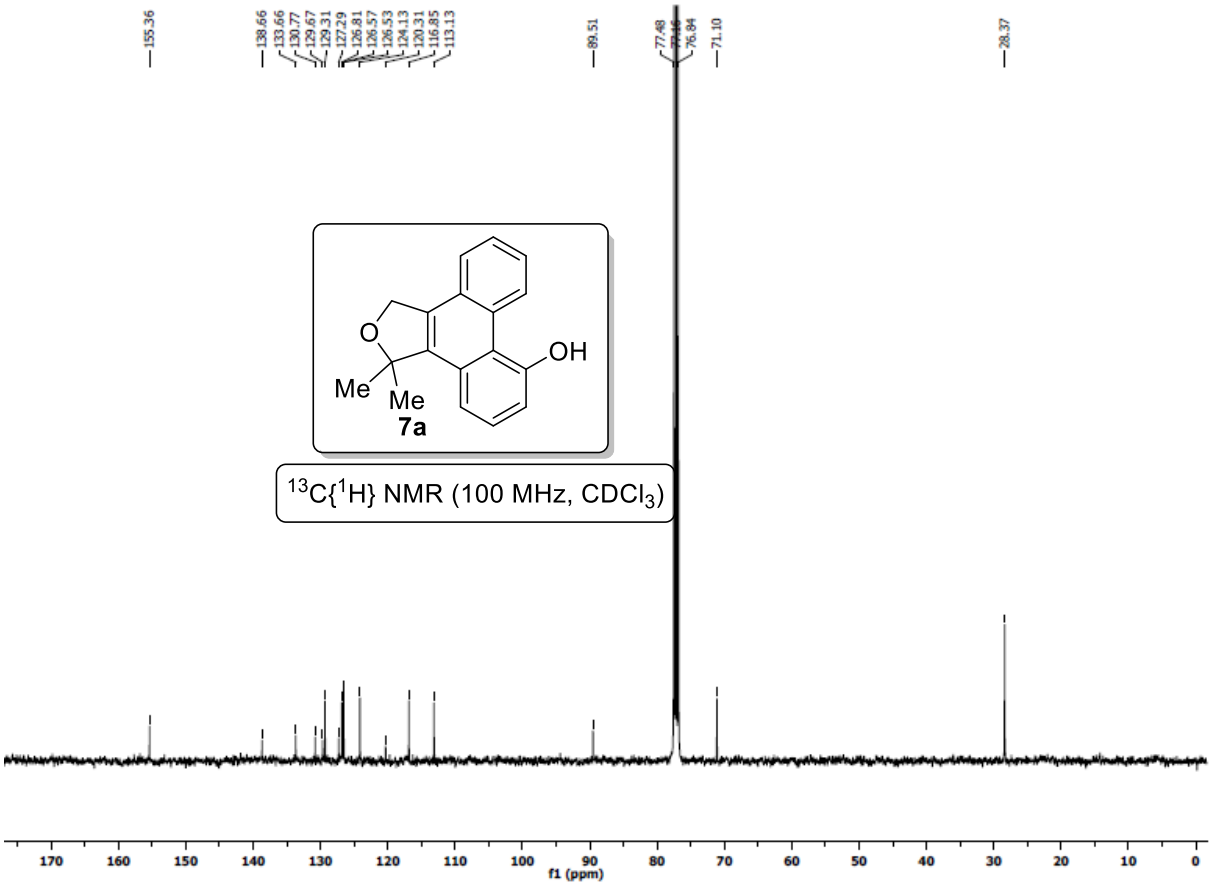

$^{1}$H NMR (400 MHz, DMSO-$d_6$)



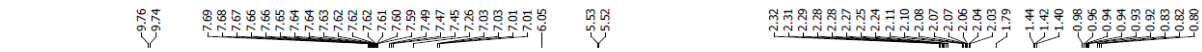

$^{13}$C {$^{1}$H } NMR (100 MHz, DMSO-$d_6$)

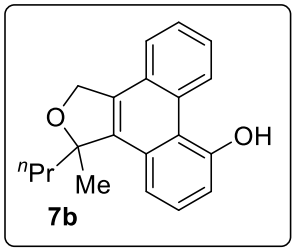



$^{1}H$ NMR (400 MHz, $CDCl_3$)

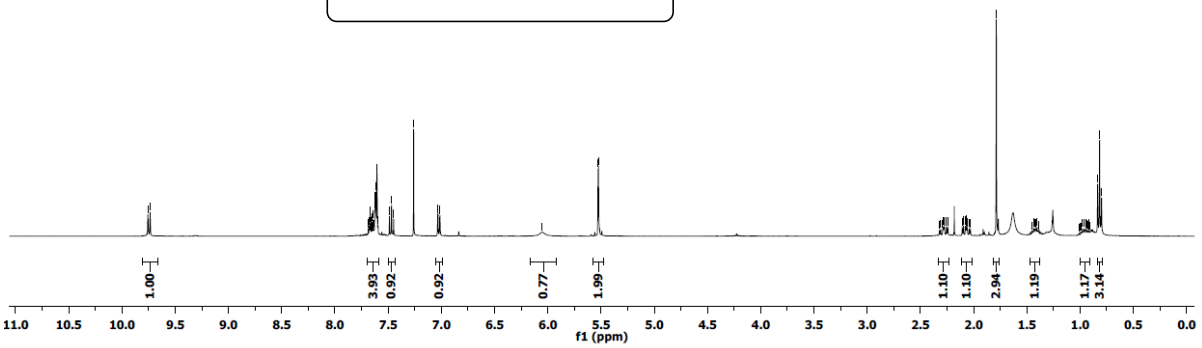


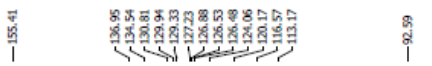

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

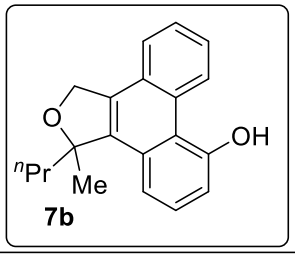


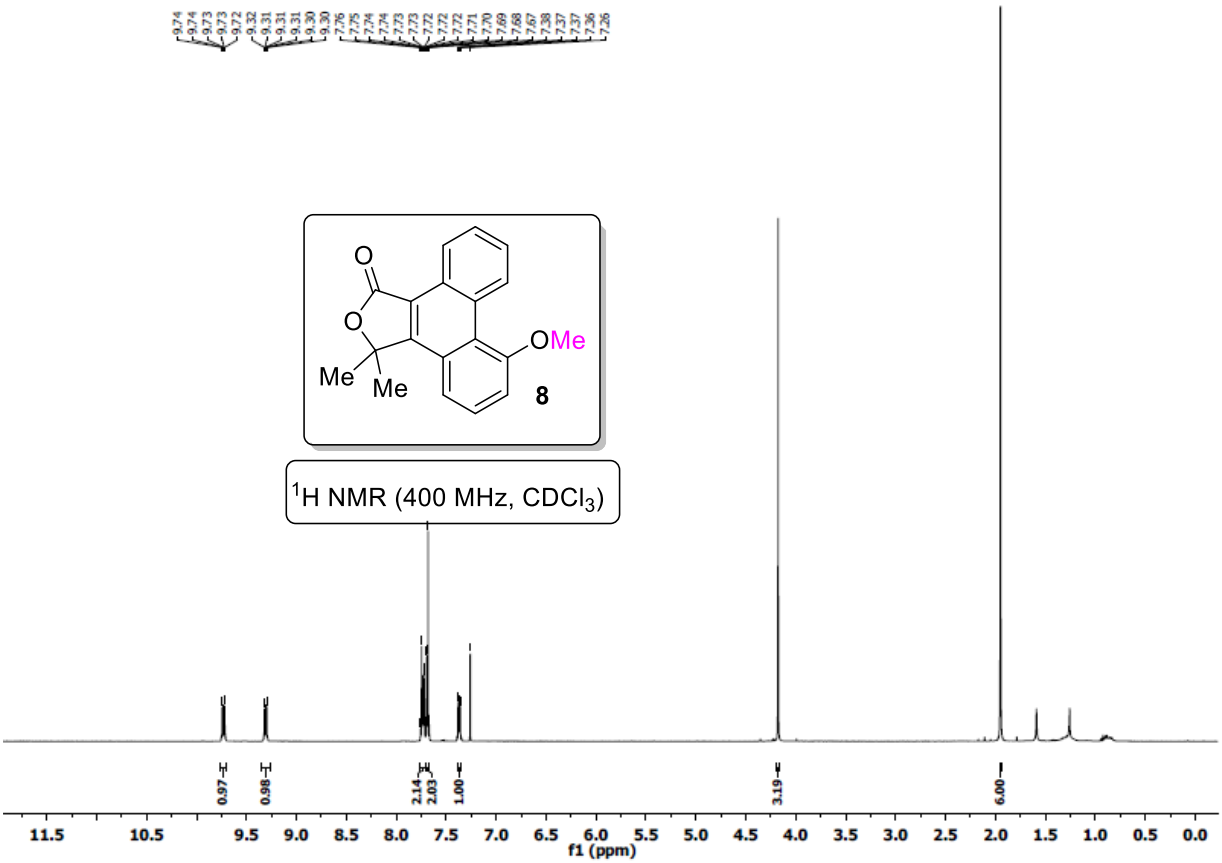

$^{1}$H NMR (400 MHz, $CDCl_3$)

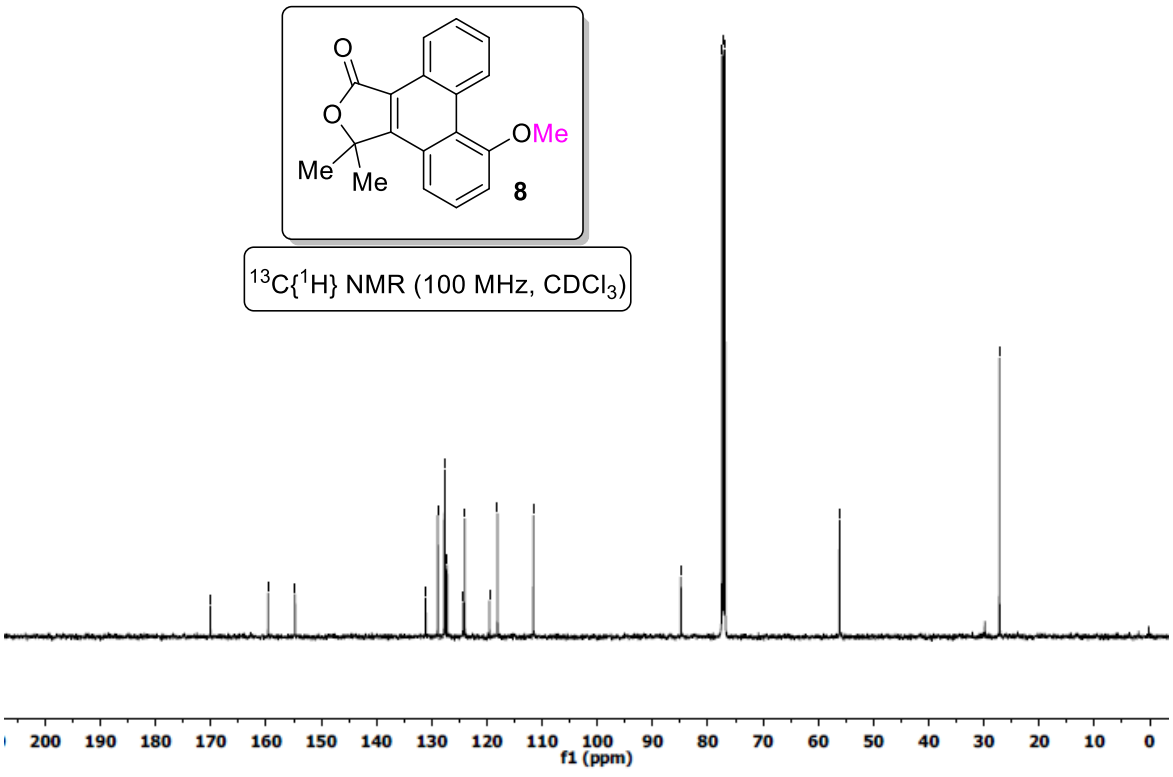


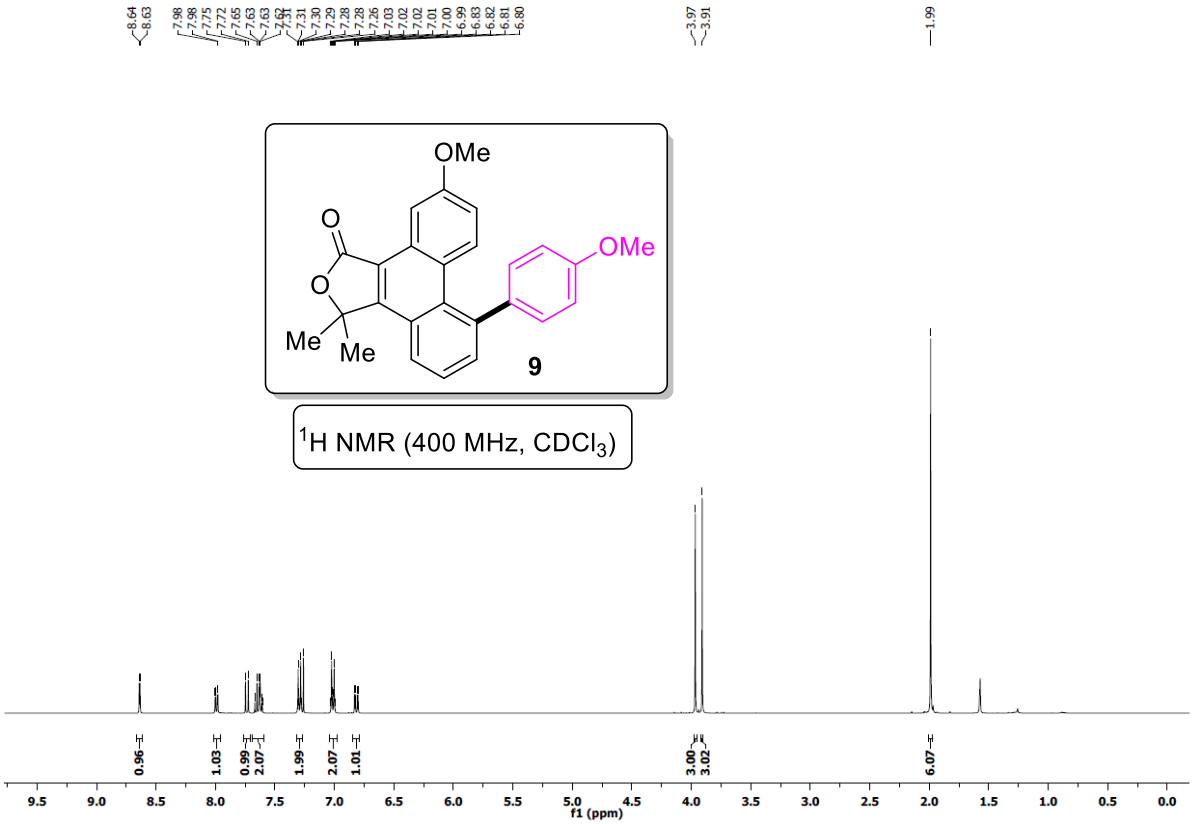



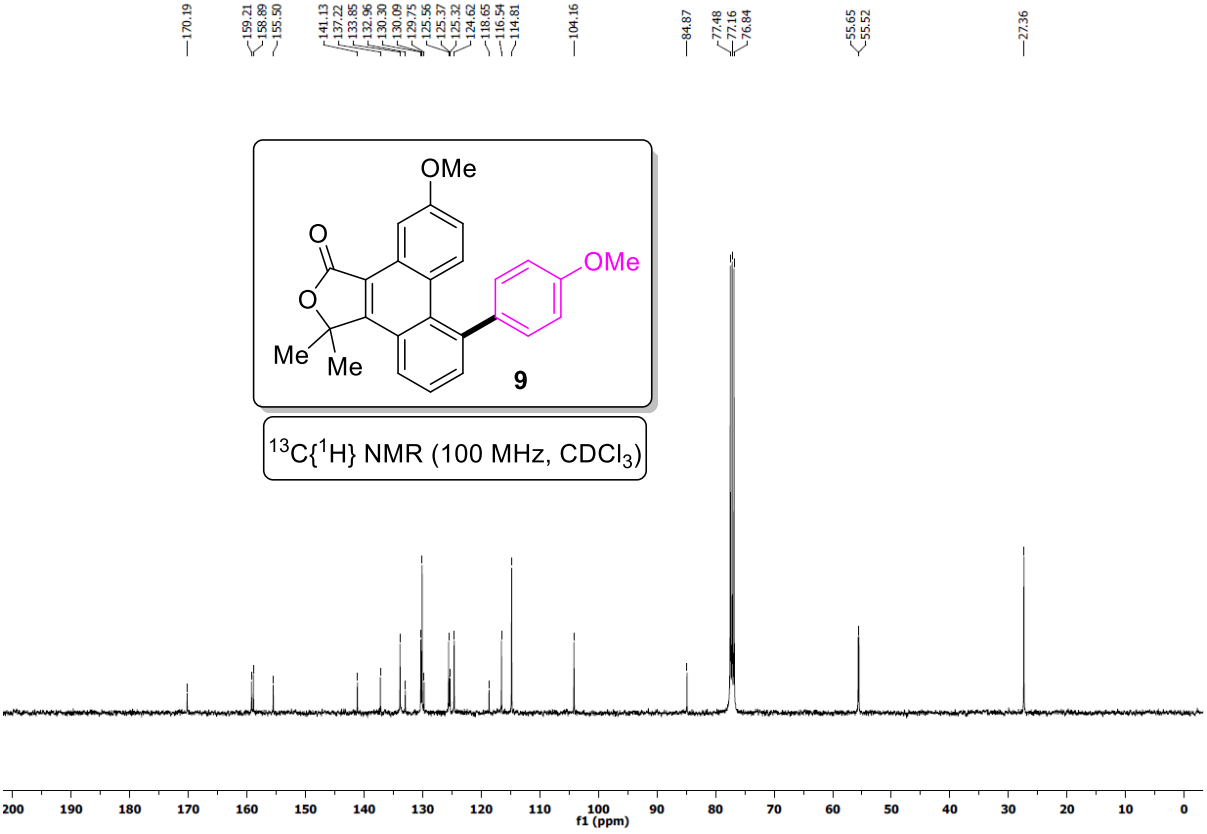



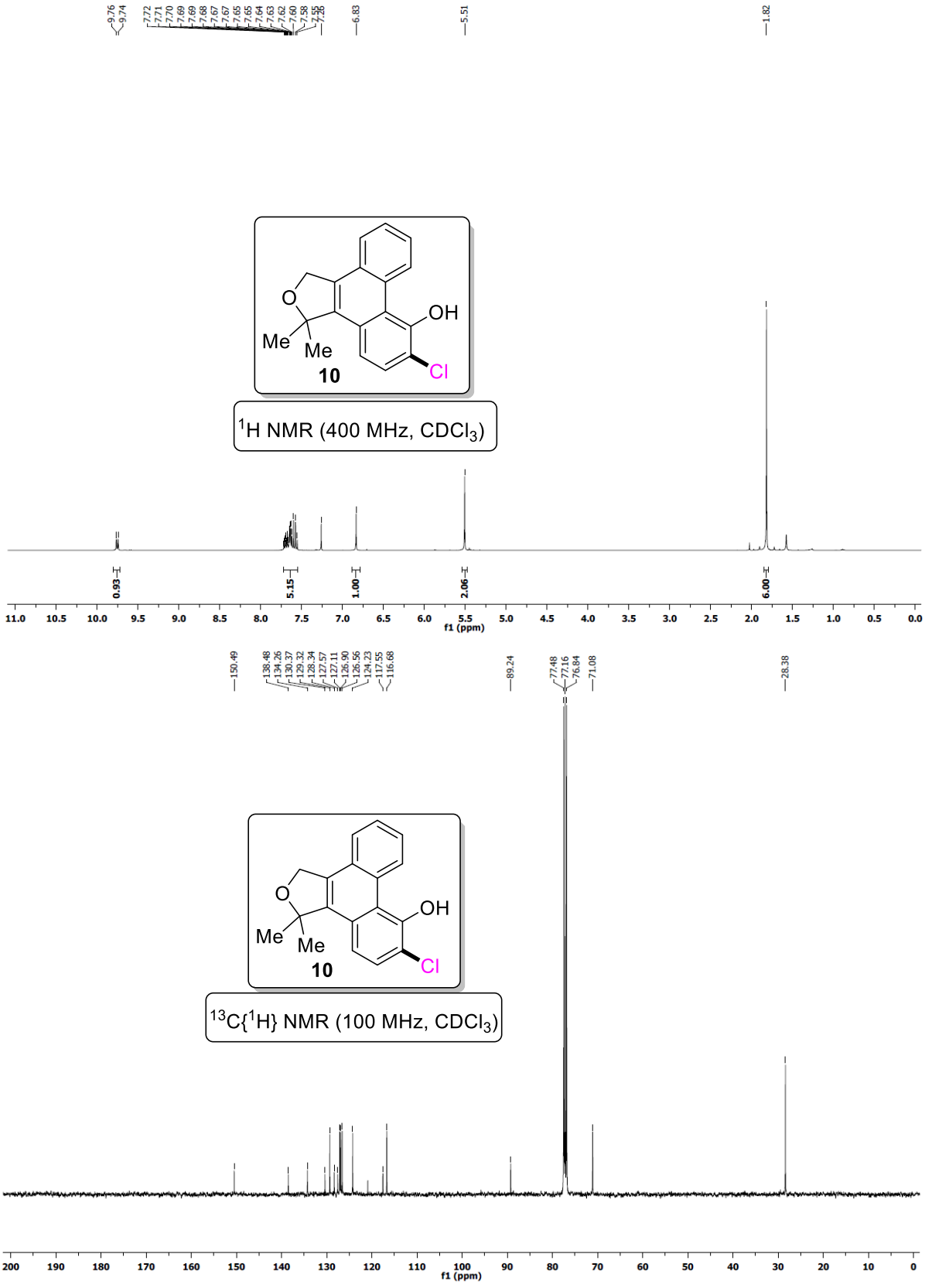

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$)


O
O
Me
Me
OMe
8
$^1$H NMR (400 MHz, CDCl$_3$)
0.97
0.98
2.14
2.03
1.00
3.19
6.00
f1 (ppm)

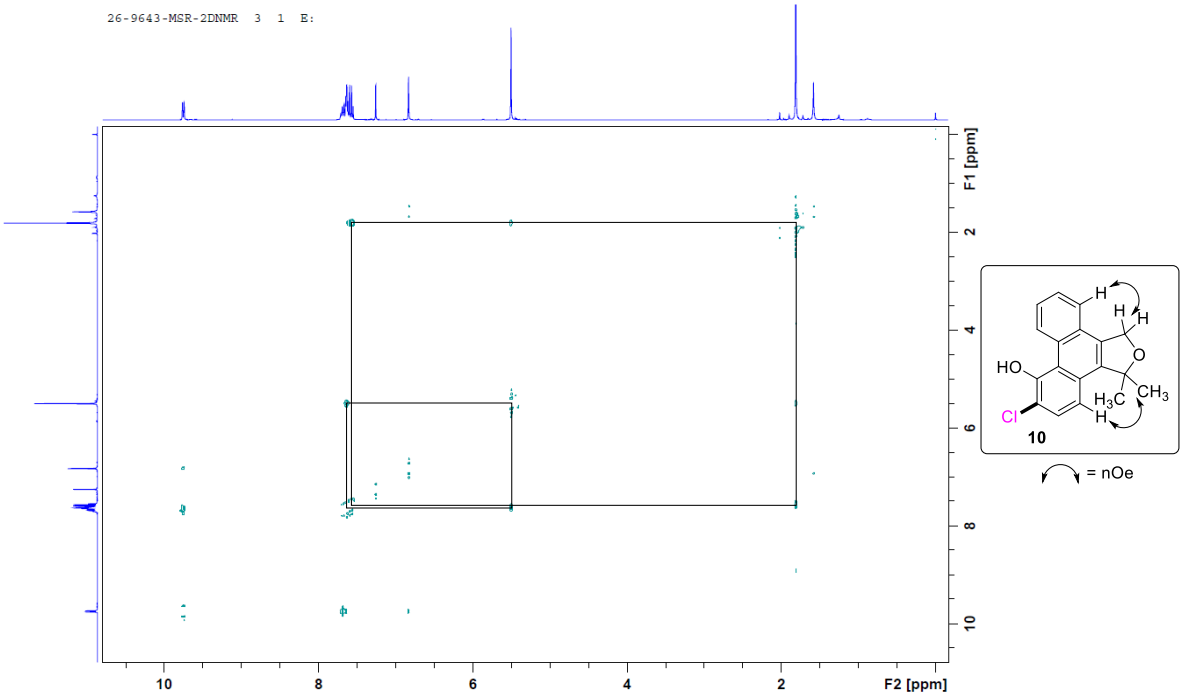

O
O
Me
Me
OMe
8
$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$)
f1 (ppm)


OMe
O
O
OMe
Me
Me
9
1H NMR (400 MHz, CDCl3)
f1 (ppm)


OMe
O
O
OMe
Me
Me
9
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)


9.76
9.74
7.72
7.71
7.70
7.69
7.69
7.68
7.67
7.67
7.65
7.65
7.64
7.63
7.62
7.60
7.58
7.55
7.26
6.83
5.51
1.82
O
OH
Me
Me
Cl
10
1H NMR (400 MHz, CDCl3)
0.93
5.15
1.00
2.06
6.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
150.49
138.48
134.26
130.37
129.32
128.34
127.57
127.11
126.90
126.56
124.23
117.55
116.68
89.24
77.48
77.16
76.84
71.08
28.38
O
OH
Me
Me
Cl
10
13C{1H} NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

## 8. 2D NMR Spectra:




## 9. X-ray crystallography data:

### Crystallography data of 3aa:

**Sample Preparation for Crystal Growth:** The compound **3aa** was dissolved in acetone in a beaker and kept for slow evaporation at room temperature. Formation of needle shape crystals was observed after three days. The single crystals were then subjected to X-ray diffraction analysis.

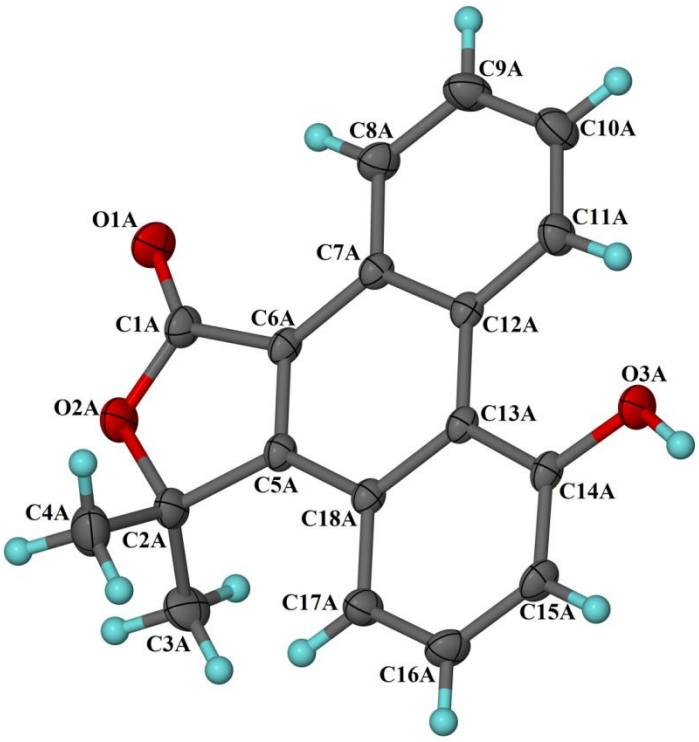


**Figure 1.** ORTEP diagram of KB693 compound with the atom-numbering. Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as small spheres of arbitrary radius. There are two molecules of KB693 (labelled A and B) and a molecule of acetone with 0.5 site occupancy in the asymmetric unit of the crystal (refer Figure 2). Only molecule A is shown in figure 1 for clarity.

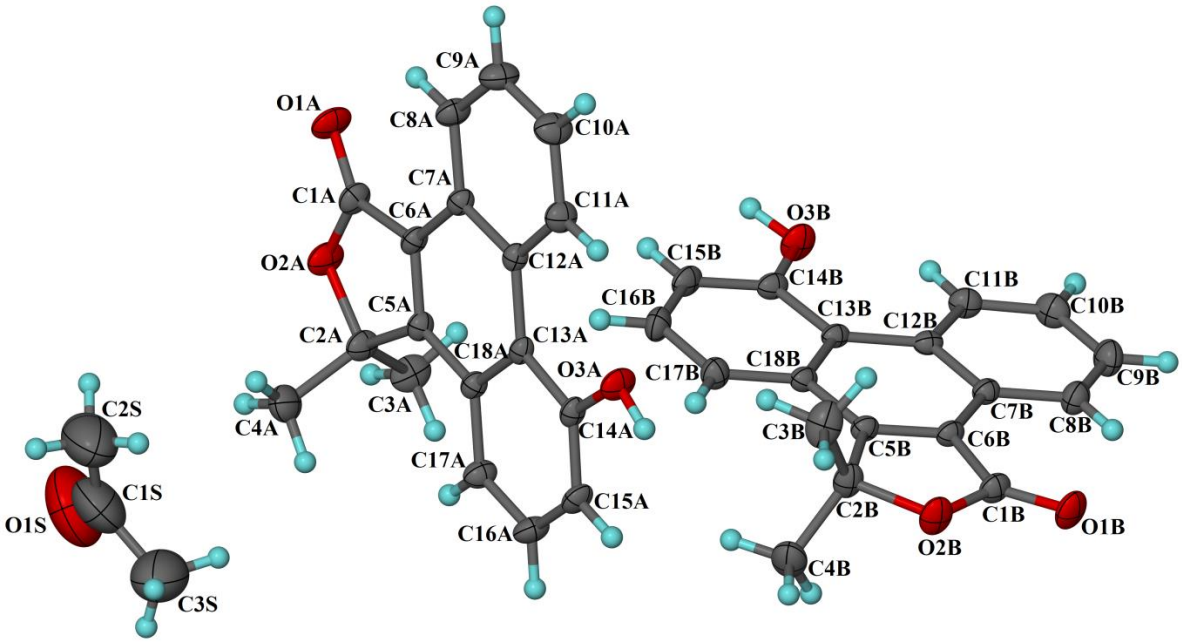



**Figure 2**. ORTEP diagram of KB693 compound with the atom-numbering. Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as small spheres of arbitrary radius. There are two molecules of KB693 (labelled A and B) with full site occupancy and acetone solvent with 0.5 site occupancy in the asymmetric unit of the crystal (the stoichiometry of compound: solvent is 2:0.5 or 4:1).

**Crystal data for KB693**: $4(C_{18}H_{14}O_3).(C_3H_6O)$, $M$ = 1171.24, Triclinic, Space group $P$-1(No.2), $a$ = 10.0982(19)Å, $b$ = 11.617(3)Å, $c$ = 13.448(3)Å, $\alpha$ = 86.075(6)°, $\beta$ = 79.905(4)°, $\gamma$ = 71.038(4)°, $V$ = 1468.8(5)Å$^3$, $Z$ = 1, $D_c$ = 1.324 g/cm$^3$, $F_{000}$ = 616, Bruker D8 QUEST PHOTON III C7 HPAD detector, Mo-Kα radiation, λ = 0.71073 Å, $T$ = 293(2)K, $2\theta_{max}$ = 55º, μ = 0.090 mm$^{-1}$, 36590 reflections collected, 6612 unique ($R_{int}$ = 0.0362), 425 parameters, *R1* = 0.0525, *wR2* = 0.1296, *R* indices based on 5106 reflections with I > 2σ(I) (refinement on $F^2$), Final *GooF* = 1.050, largest difference hole and peak = -0.189 and 0.375 e.Å$^{-3}$. **CCDC deposition number 2254681** contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

**Data collection and Structure solution details for KB693**:

X-ray data for the compound were collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 Å) and a PHOTON-III C7 HPAD detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [1]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [2-4] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms]. **CCDC deposition number 2254681** contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/


1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.
2. G. M. Sheldrick, Acta Crystallogr., 2015, C71: 3-8.
3. C. B. Hübschle, G. M. Sheldrick and B. Dittrich, ShelXle: a Qt graphical user interface for SHELXL, *J. Appl. Cryst.*, 2011, 44, 1281-1284.
4. Muller, P, Herbst-Imer, R, Spek, A. L, Schneider, T. R, and Sawaya, M. R. Crystal Structure Refinement: A Crystallographer's Guide to SHELXL. Muller, P. Ed. 2006 Oxford University Press: Oxford, New York, pp. 57–91.

# checkCIF/PLATON report

Structure factors have been supplied for datablock(s) KB693_0m

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

## Datablock: KB693_0m

---

```
Bond precision:   C-C = 0.0023 A          Wavelength=0.71073

Cell:           a=10.0982(19)      b=11.617(3)       c=13.448(3)
                alpha=86.075(6)    beta=79.905(4)    gamma=71.038(4)
Temperature:    293 K

                Calculated                Reported
Volume          1468.8(6)                 1468.8(5)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  4(C18 H14 O3), C3 H6 O    4(C18 H14 O3), C3 H6 O
Sum formula     C75 H62 O13               C75 H62 O13
Mr              1171.25                   1171.24
Dx,g cm-3       1.324                     1.324
Z               1                         1
Mu (mm-1)       0.090                     0.090
F000            616.0                     616.0
F000'           616.31
h,k,lmax        13,15,17                  13,15,17
Nref            6740                      6612
Tmin,Tmax       0.975,0.987               0.689,0.746
Tmin'           0.975

Correction method= # Reported T Limits: Tmin=0.689 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.981           Theta(max)= 27.500

R(reflections)= 0.0525( 5106)                wR2(reflections)=
                                             0.1447( 6612)
S = 1.030                 Npar= 425
```

The following ALERTS were generated. Each ALERT has the format
**test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

### Alert level C

```
PLAT260_ALERT_2_C Large Average Ueq of Residue Including       O1S      0.184 Check
PLAT767_ALERT_4_C INS Embedded LIST 6 Instruction Should be LIST 4     Please Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600       126 Report
PLAT913_ALERT_3_C Missing # of Very Strong Reflections in FCF ....        37 Note
```

### Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         4 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         4 Report
PLAT019_ALERT_1_G _diffrn_measured_fraction_theta_full/*_max < 1.0     0.995 Report
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records         3 Report
PLAT174_ALERT_4_G The CIF-Embedded .res File Contains FLAT Records         1 Report
PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records         1 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records         1 Report
PLAT188_ALERT_3_G A Non-default SIMU Restraint Value has been used    0.0100 Report
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)       293 Check
PLAT200_ALERT_1_G Reported   _diffrn_ambient_temperature ..... (K)       293 Check
PLAT300_ALERT_4_G Atom Site Occupancy of O1S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C1S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C2S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C3S        Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H2SA       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H2SB       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H2SC       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H3SA       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H3SB       Constrained at       0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H3SC       Constrained at       0.5 Check
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  3  )       100% Note
PLAT333_ALERT_2_G Large Aver C6-Ring C-C Dist C5A      -C18A     .      1.42 Ang.
PLAT333_ALERT_2_G Large Aver C6-Ring C-C Dist C5B      -C18B     .      1.42 Ang.
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........        18 Note
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group  #       10 Check
PLAT860_ALERT_3_G Number of Least-Squares Restraints ............       28 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .    Please Do !
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).        3 Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File       12 Note
PLAT967_ALERT_5_G Note: Two-Theta Cutoff Value in Embedded .res ..      55.0 Degree
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.       18 Info
PLAT992_ALERT_5_G Repd & Actual _reflns_number_gt Values Differ by        2 Check
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
  4 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 32 ALERT level G = General information/check it is not something unexpected

  4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
```

```
  7 ALERT type 2 Indicator that the structure model may be wrong or deficient
  5 ALERT type 3 Indicator that the structure quality may be low
 18 ALERT type 4 Improvement, methodology, query or suggestion
  2 ALERT type 5 Informative message, check
```

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It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

**Publication of your CIF in IUCr journals**

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

**Publication of your CIF in other journals**

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

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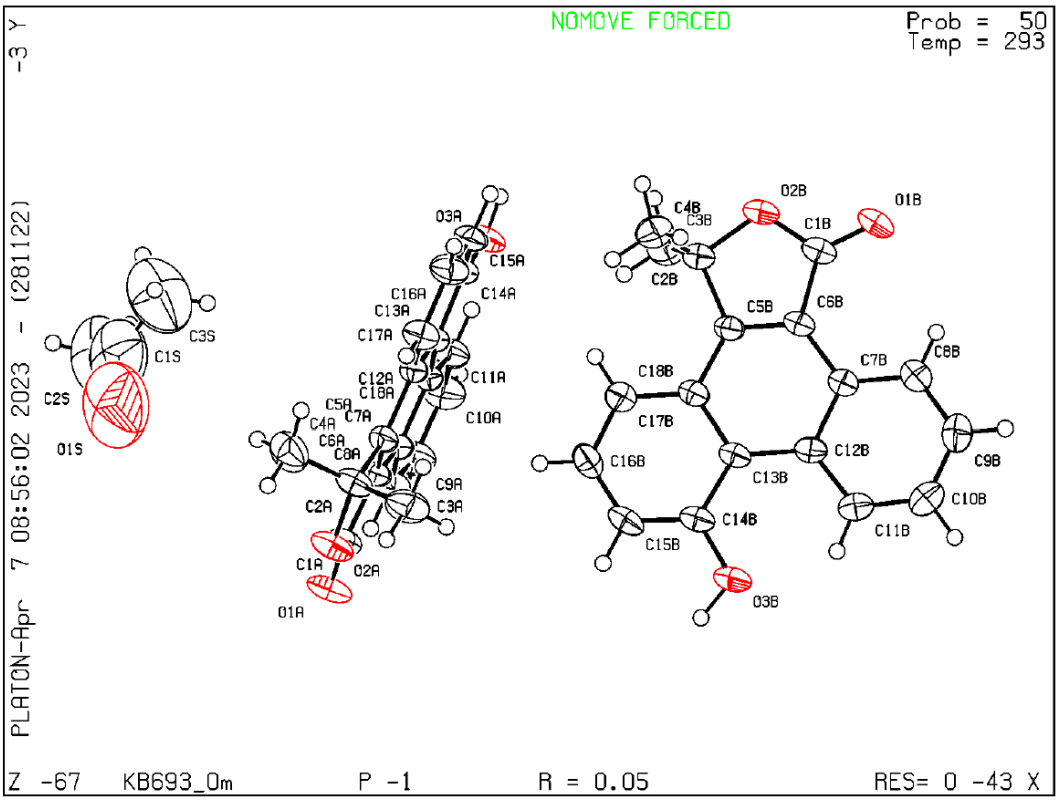
**PLATON version of 28/11/2022; check.def file version of 28/11/2022**

Datablock KB693_0m - ellipsoid plot




**Crystallography data of 7a:**

**Sample Preparation for Crystal Growth:** The compound **7a** was dissolved in $CDCl_3$ in a beaker and kept for slow evaporation at room temperature. Formation of needle shape crystals was observed after two days. The single crystals were then subjected to X-ray diffraction analysis.

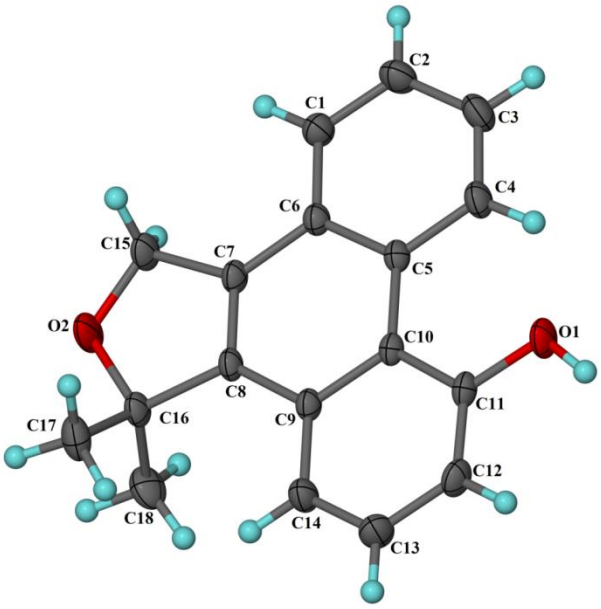


**Figure 1.** ORTEP diagram of KB887 compound with the atom-numbering. Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as small spheres of arbitrary radius.

**Crystal data for KB887**: $C_{18}H_{16}O_2$, $M$ = 264.31, Monoclinic, Space group $P2_1/c$(No.14), $a$ = 9.6943(4)Å, $b$ = 14.0544(6)Å, $c$ = 10.9983(5)Å, $\alpha$ = 90°, $\beta$ = 116.2955(18)°, $\gamma$ = 90°, $V$ = 1343.43(10)Å$^3$, $Z$ = 4, $D_c$ = 1.307 g/cm$^3$, $F_{000}$ = 560, Bruker D8 QUEST PHOTON III C7 HPAD detector, Mo-Kα radiation, λ = 0.71073 Å, $T$ = 294(2)K, $2\theta_{max}$ = 55º, μ = 0.084 mm$^{-1}$, 14510 reflections collected, 3056 unique ($R_{int}$ = 0.0284), 187 parameters, *R1* = 0.0463, *wR2* = 0.1193, *R* indices based on 2464 reflections with I > 2σ(I) (refinement on $F^2$), Final *GooF* = 1.054, largest difference hole and peak = -0.143 and 0.246 e.Å$^{-3}$. **CCDC deposition number 2257234** contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

**Data collection and Structure solution details for KB887**:

X-ray data for the compound were collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 Å) and a PHOTON-III C7 HPAD detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [1]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [2-4] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms]. The O bound H atom was located in the difference Fourier map and its positional coordinates were refined. **CCDC deposition number 2257234** contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/


1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.
2. G. M. Sheldrick, Acta Crystallogr., 2015, C71: 3-8.
3. C. B. Hübschle, G. M. Sheldrick and B. Dittrich, ShelXle: a Qt graphical user interface for SHELXL, *J. Appl. Cryst.*, 2011, 44, 1281-1284.

4. Muller, P, Herbst-Imer, R, Spek, A. L, Schneider, T. R, and Sawaya, M. R. Crystal Structure Refinement: A Crystallographer's Guide to SHELXL. Muller, P. Ed. 2006 Oxford University Press: Oxford, New York, pp. 57–91.

## checkCIF/PLATON report

Structure factors have been supplied for datablock(s) KB887_0m

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

## Datablock: KB887_0m

Bond precision: C-C = 0.0020 A Wavelength=0.71073

Cell: a=9.6943(4) b=14.0544(6) c=10.9983(5)
alpha=90 beta=116.2955(18) gamma=90
Temperature: 294 K

| | Calculated | Reported |
|---|---|---|
| Volume | 1343.43(10) | 1343.43(10) |
| Space group | P 21/c | P 21/c |
| Hall group | -P 2ybc | -P 2ybc |
| Moiety formula | C18 H16 O2 | C18 H16 O2 |
| Sum formula | C18 H16 O2 | C18 H16 O2 |
| Mr | 264.31 | 264.31 |
| Dx,g cm-3 | 1.307 | 1.307 |
| Z | 4 | 4 |
| Mu (mm-1) | 0.084 | 0.084 |
| F000 | 560.0 | 560.0 |
| F000' | 560.26 | |
| h,k,lmax | 12,18,14 | 12,18,14 |
| Nref | 3089 | 3056 |
| Tmin,Tmax | 0.978,0.985 | 0.672,0.746 |
| Tmin' | 0.978 | |

Correction method= # Reported T Limits: Tmin=0.672 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.989 Theta(max)= 27.499

R(reflections)= 0.0463( 2464) wR2(reflections)= 0.1290( 3056)

S = 1.054 Npar= 187

The following ALERTS were generated. Each ALERT has the format
**test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

### Alert level C

```
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of         O2 Check
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....        2.1 Note
PLAT767_ALERT_4_C INS Embedded LIST 6 Instruction Should be LIST 4     Please Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600        31 Report
PLAT913_ALERT_3_C Missing # of Very Strong Reflections in FCF ....        20 Note
```

### Alert level G

```
PLAT019_ALERT_1_G _diffrn_measured_fraction_theta_full/*_max < 1.0      0.997 Report
PLAT128_ALERT_4_G Alternate Setting for Input Space Group  P21/c        P21/n Note
PLAT333_ALERT_2_G Large Aver C6-Ring C-C Dist C5       -C10      .       1.42 Ang.
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          3 Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File          5 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        4.7 Low
PLAT967_ALERT_5_G Note: Two-Theta Cutoff Value in Embedded .res ..       55.0 Degree
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         17 Info
```

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
5 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
9 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
5 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

**Publication of your CIF in IUCr journals**

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

**Publication of your CIF in other journals**

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

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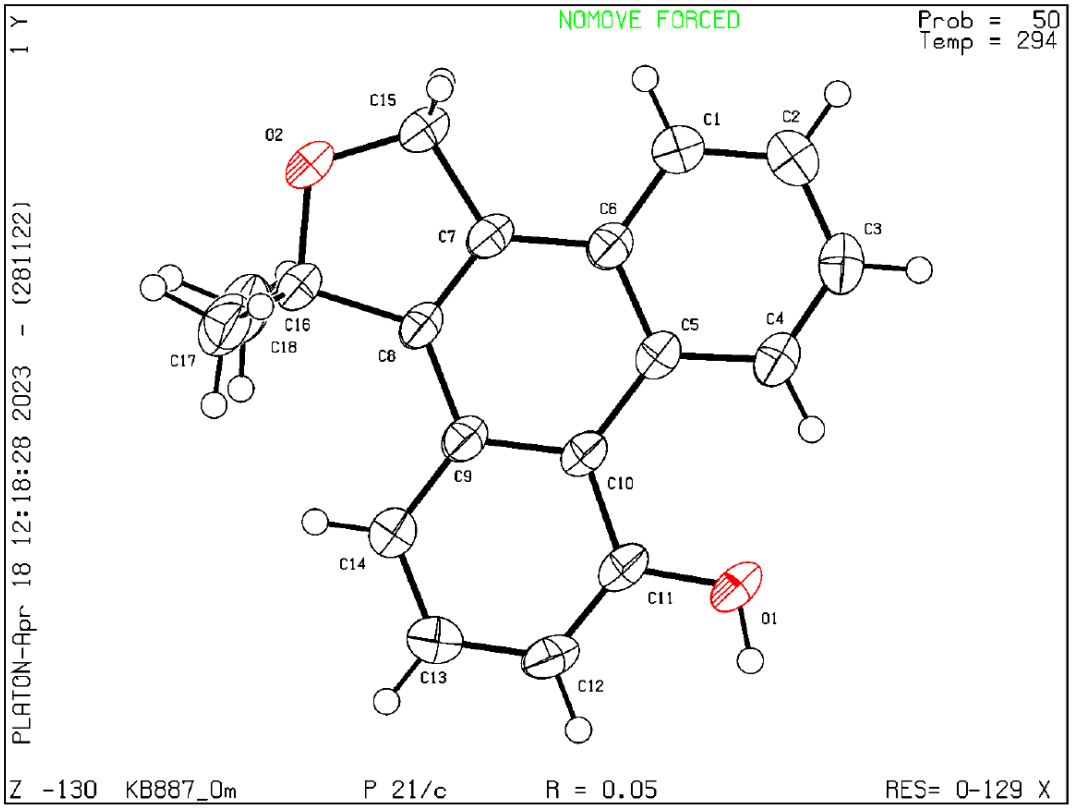
**PLATON version of 28/11/2022; check.def file version of 28/11/2022**

**Datablock KB887_0m** - ellipsoid plot




## 10. References:

1. (a) Luo, S.; Luo, F.-X.; Zhang, X.-S.; Shi, Z.-J. *Angew. Chem. Int. Ed.* **2013**, *52*, 10598-10601. (b) Fu, L.; Li, S.; Cai, Z.; Ding, Y.; Guo, X.-Q.; Zhou, L.-P.; Yuan, D.; Sun, Q.-F.; Li, G. *Nature Catalysis* **2018**, *1*, 469-478. (c) Inamoto, K.; Kadokawa, J.; Kondo,Y. *Org. lett.* **2013**, *15*, 3962-3965.
2. (a) Liao, G.; Song, H.; Yin, X.; Shi, B. *Chem. Commun*. **2017**, *53*, 7824-7827. (b) Xu, Y.; Li, B.; Zhang, X.; Fan, X. *Adv. Synth. Catal.* **2018**, *360*, 2613-2620.
3. Spino, C.; Beaulieu, C. *J. Am. Chem. Soc*. **1998**, *120*, 11832-11833.