Supporting Information

Photoinduced Arylative Formal 4-Endo-dig Cyclization of Propargyl Alcohols/Amines to Access Strained Heterocycles

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1.0. General information and methods.

All reagents and solvents were purchased from commercial sources and used without purification. NMR spectra were recorded with a 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 $CDCl_3$ or deuterated solvent $CDCl_3$ 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. Column chromatography was performed with silica gel (100–200 mesh) as the stationary phase. All reactions were monitored by using TLC.

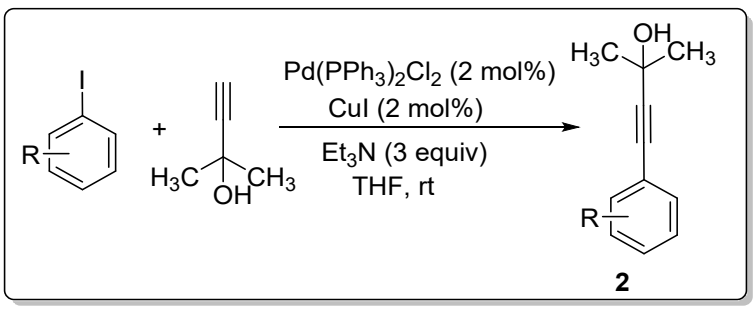
Following the known procedure, propargyl alcohols/amines[1] and ^{homo} propargyl alcohols/amines[2] were prepared (Table S1-S5). Benzoquinones were purchased from commercial sources and used after purification.

1.1. Details of light source.

All photo redox catalyzed reactions were carried out in Aldrich® Micro Photochemical Reactor, Blue LED light ranges between 435-445 nm. The reaction vial was sealed with a screw cap and kept at room temperature for 24 hours with vigorous stirring under blue light irradiation using a 12W Blue LED.

2. Experimental procedures

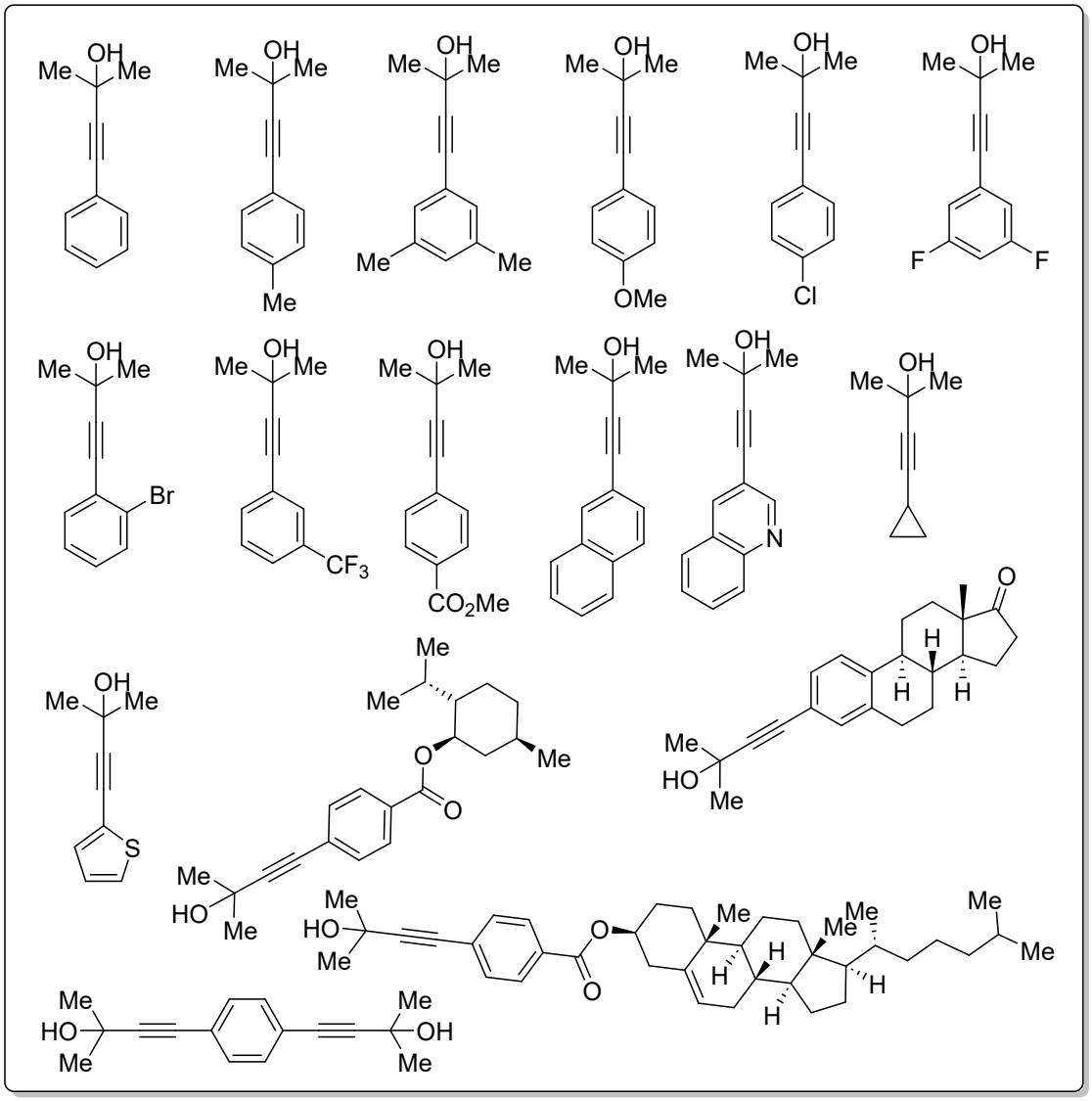
2.1. Preparation of propargyl/homo propargyl alcohols: General procedure (GP-1):[1]



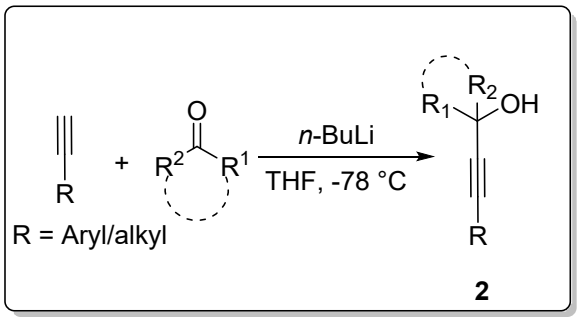
General procedure for the synthesis of PAs & HPAs:

To a mixture of aryl halide (5.00 mmol) and Et_3N (3 equiv) in THF (15 mL) were added $PdCl_2(PPh_3)_2$ (2 mol%) and CuI (2 mol%) under nitrogen atmosphere. After the reaction mixture was stirred for 5 min at room temperature, the 2-methyl but-3-yn-2-ol (6.00 mmol) was added by a syringe. The reaction mixture was stirred at room temperature until complete consumption of staring materials (monitored by TLC). The mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc:Hexanes) to get the corresponding propargyl alcohols **2**.

Table S1: List of propargyl alcohols-1.



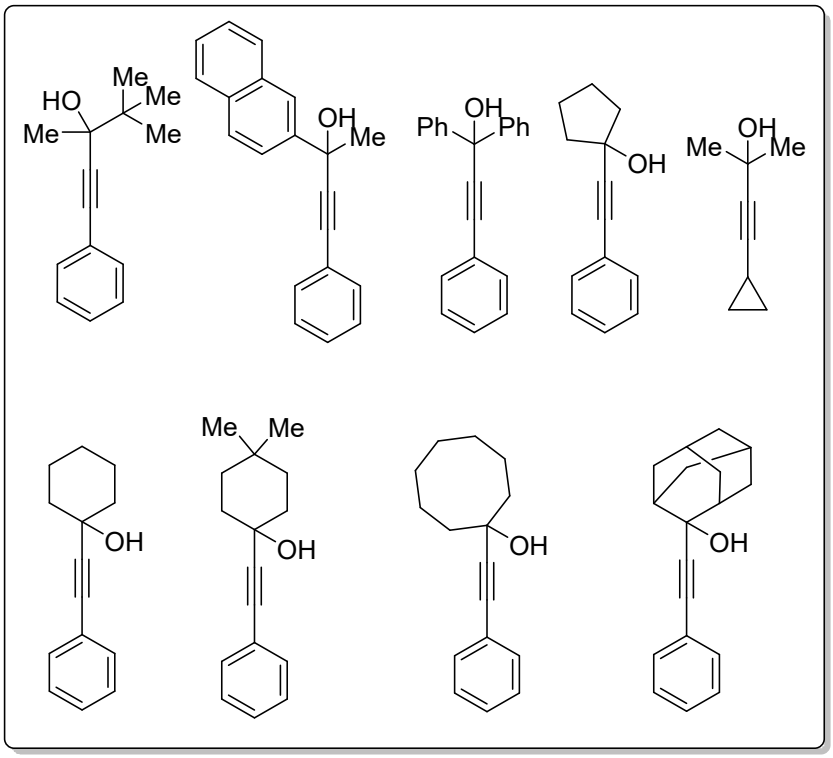
2.2. Preparation of propargyl alcohols: General procedure (GP-2):[1]



General procedure for the synthesis of PAs:

To a solution of aryl/alkyl acetylene (4.5 mmol) in tetrahydrofuran (20 mL) under nitrogen atmosphere, *n*-butyl lithium (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/aldehyde (3 mmol) in THF (5 mL) was added drop wise and the mixture was stirred at the same temperature for 2-3 h. The solution was allowed to warm to room temperature and was quenched with saturated aqueous NH_4Cl and was extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (Hexane/EtOAc) to give the expected propargyl alcohols **2**.

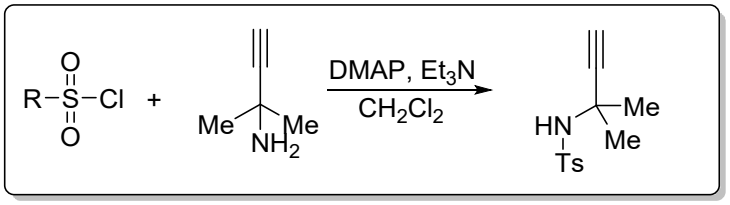
Table S2: List of propargyl alcohols-2.



2.3. Preparation of propargyl amines: General procedure (GP-3):

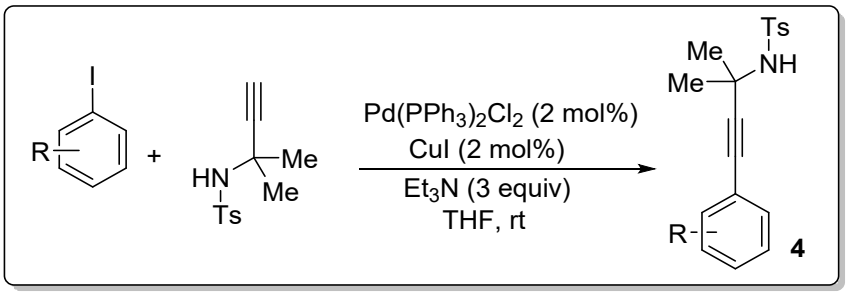
General procedure for the synthesis of propargyl amines:

Step-1: General procedure for the synthesis of benzenesulfonamides:



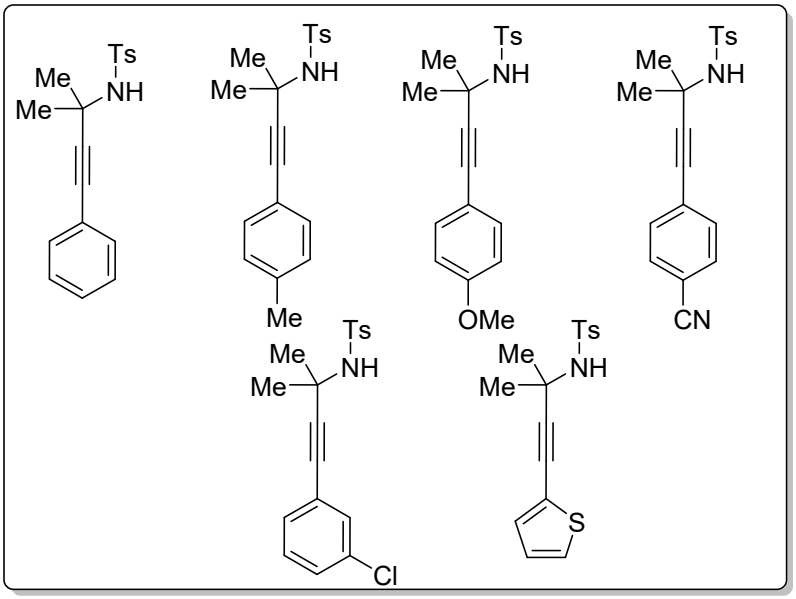
The sulfonyl chloride (1.2 equiv.) was slowly added at 0 °C to a solution of propargylamine (1 equiv.), DMAP (0.05 equiv.) and Et_3N (2 equiv.) in an anhydrous dichloromethane (0.3 M). The resulting mixture was stirred overnight at room temperature and was diluted with dichloromethane (20 mL), washed with brine (2 x 20 mL). The resultant solution was dried over Na_2SO_4, and concentrated under rotary evaporator. The crude product was purified by flash chromatography on silica gel (hexane:ethyl acetate) to give the expected tosylated products.

Step-2:



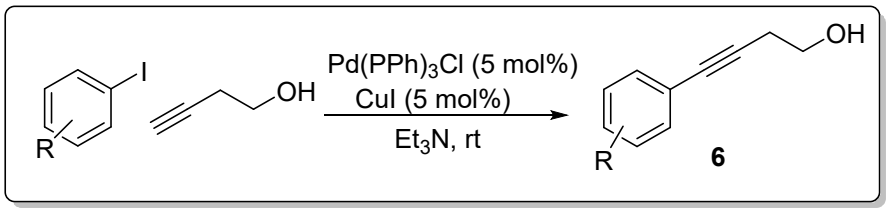
To a mixture of aryl halide (5.00 mmol) and Et_3N (3 equiv) in THF (15 mL) were added $PdCl_2(PPh_3)_2$ (2 mol%) and CuI (2 mol%) under nitrogen atmosphere. After the reaction mixture was stirred for 5 min at room temperature, the benzene sulfonamides (6.00 mmol) was added by a syringe. The reaction mixture was stirred at room temperature until the complete consumption of staring materials (monitored by TLC). The mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc:Hexanes) to get the corresponding propargyl amines **4**.

Table S3: List of propargyl amines.



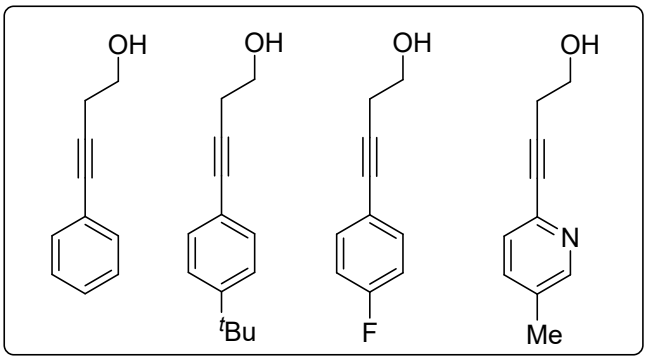
2.4. Preparation of homo propargyl amines: General procedure (GP-4):

General procedure for the synthesis of homopropargyl alcohols 6:



To a mixture of the aryl halide (5.00 mmol) in Et_3N (30 mL) was added $PdCl_2(PPh_3)_2$ (5 mol%) followed by CuI (5 mol%) under nitrogen atmosphere. After the reaction mixture was stirred for 5 min at room temperature, the terminal alkynol (6.00 mmol) was added by a syringe. The reaction mixture was then stirred at room temperature for 3-6 hours. After the completion of reaction (monitored by TLC), the mixture was concentrated under reduced pressure and purified by column chromatography on silica gel (EtOAc:Hexanes) to afford the corresponding alkynols **6**.

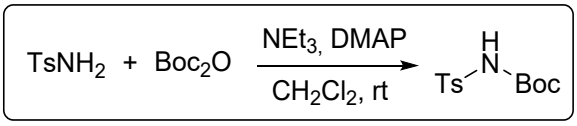
Table S4: List of homo propargyl alcohols.



2.5. Preparation of homo propargyl amines: General procedure (GP-5):

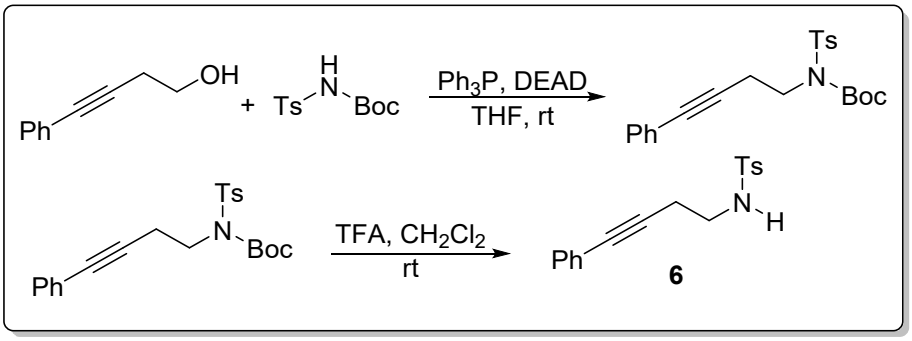
General procedure for the synthesis of propargyl amines 6:

Step-1:



To a mixture of *p*-toluenesulfonamide (1.5 mmol) in dichloromethane (3 mL), DMAP (0.1 equiv) triethylamine (1.0 equiv) were added. Subsequently, Boc anhydride (1.2 equiv) was added dropwise at 0 °C under nitrogen atmosphere and was stirred at room temperature for overnight. After the completion of reaction (monitored by TLC), the solvent was removed under reduced pressure and the product was washed with 5N HCl. The mixture was diluted with EtOAc, and the organic layer was washed with saturated $NaHCO_3$ solution, concentrated and washed with hexane to get the product as white solid.

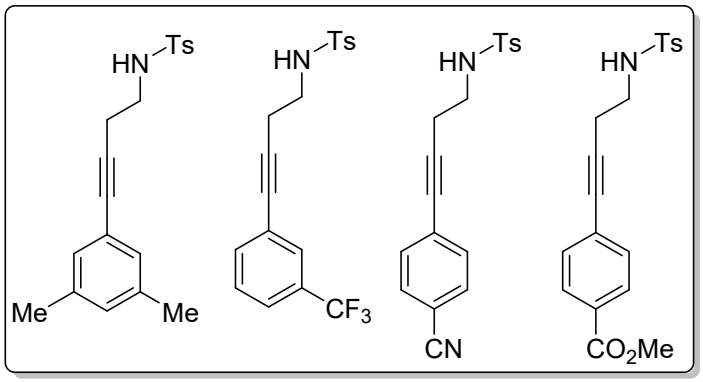
Step-2:



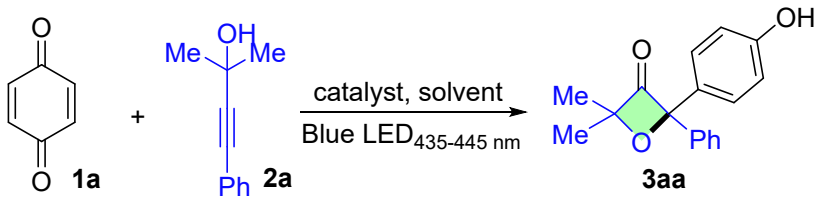
N-Boc *p*-toluenesulfonamide (1.5 mmol) was dissolved in dry THF (3 mL) and was charged with triphenylphosphine (3.0 equiv). The solution was stirred under nitrogen atmosphere and 4-phenylbut-3-yn-1-ol (1.0 equiv) followed by diethylazodicarboxylate (or DIAD) (2.5 equiv) were added at 0 °C. The mixture was stirred at room temperature for 6-10 hours, and the contents were concentrated under reduced pressure and the product was purified by flash chromatography to give tert-butyl (4-phenylbut-3-yn-1-yl) (tosyl)carbamate.

To a solution of the tert-butyl (4-phenylbut-3-yn-1-yl)(tosyl)carbamate (1.0 mmol) in CH_2Cl_2 (5 mL) was added trifluoroacetic acid (20 equiv) at 0 °C and the mixture was stirred at room temperature for 3 hours. The mixture was diluted with EtOAc, and the organic layer was washed with saturated $NaHCO_3$ solution and saturated NaCl solution, and the resultant organic layers were dried over Na_2SO_4 and concentrated to get the product **6** as white solids.

Table S5: List of homo propargyl amines.



3. Optimization studies[a]:

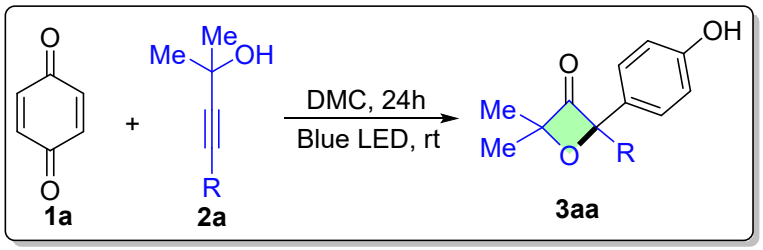


Entry	catalyst	solvent	Yield (%)[b]
1	acridinium tetrafluoroborate	CH_3CN	-
2	acridinium perchlorate	CH_3CN	-
3	$Cu(OTf)_2$	CH_3CN	-
4	$Ru(bpy)_3Cl_2$	DMC	63%
5	Eosin-Y	DMC	72%
6	Rose bengal	DMC	58%
7	*p*TSA	CH_3CN	15%
8	$Zn(OTf)_2$	CH_3CN	28%
9	-	DMSO	-
10	-	CH_2Cl_2	58%
11	-	CH_3CN:MeOH (1:1)	-
12	-	EtOH	-
13	-	^{i}PrOH	-
14	-	^{t}BuOH	52%
15	-	^{n}BuOH	15%
16	-	^{i}amyl alcohol	-
17	-	^{t}amyl alcohol	5%

[a]reaction conditions: **1a** (1.0 mmol), **2a** (1.1 mmol), catalyst (10 mol%), solvent (5 mL), rt, 24h. [b]isolated yields.

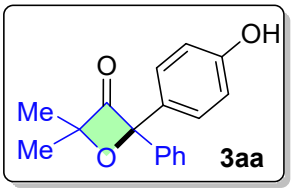
4. General procedure for the synthesis of compounds and characteristic data:

General procedure for the synthesis of title compounds taking 3aa as an example:



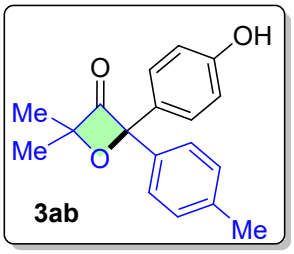
The mixture of benzoquinone **1a** (108 mg, 1 mmol) and propargyl alcohol **2a** (176 mg, 1.1 mmol) in dimethyl carbonate were taken into the reaction vial, flushed the vial with nitrogen gas and was sealed with a screw cap. The vial was vigorously stirred under blue light (435-445nm) irradiation for 24 hours. After completion of the reaction (monitored by TLC), solvent was evaporated and water was added. The contents were extracted with ethyl acetate (2×10 mL). The organic layer was evaporated and the residue was purified by column chromatography (R_f= 0.45) (SiO_2, EtOAc:Hexane, 15:85) to get **3aa** as pale green gel in 88% (236 mg) yield).

2-(4-Hydroxyphenyl)-4,4-dimethyl-2-phenyloxetan-3-one (3aa):



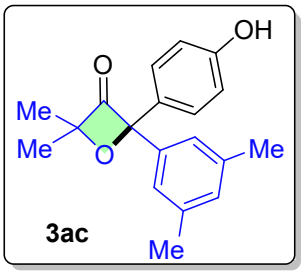
^{1}H NMR (500 MHz, DMSO-d_6) δ 9.67 (s, 1H), 7.39 (d, J = 2.9 Hz, 4H), 7.31 (d, J = 3.7 Hz, 1H), 7.16 (d, J = 8.1 Hz, 2H), 6.79 (d, J = 8.1 Hz, 2H), 1.42 (s, 3H), 1.38 (s, 3H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 206.7, 157.4, 140.2, 130.3, 128.7, 128.0, 126.5, 124.9, 115.5, 104.1, 101.0, 23.5, 23.4. **HRMS** (QToF) calcd for $C_{17}H_{15}O_3$ [M-H]$^-$ 267.1021 found 267.1015.

2-(4-Hydroxyphenyl)-4,4-dimethyl-2-(*p*-tolyl) oxetan-3-one (3ab):



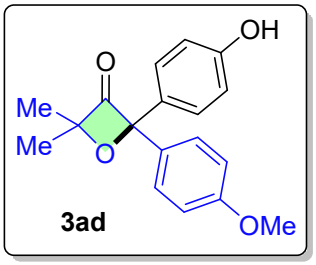
The title compound was prepared from **1a** (108 mg, 1 mmol) and **2b** (190 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.50, SiO_2, EtOAc:Hexane, 12:88) gave pure product as a pale yellow gel (240 mg, 85% yield). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.63 (s, 1H), 7.22 (q, J = 8.1 Hz, 4H), 7.12 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 8.4 Hz, 2H), 2.28 (s, 3H), 1.42 (s, 3H), 1.38 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 206.9, 157.3, 137.4, 137.3, 130.4, 129.2, 126.6, 124.9, 115.4, 104.1, 100.8, 23.6, 23.4, 20.7. **HRMS** (QToF) calcd for $C_{18}H_{17}O_3$ [M-H]$^-$ 281.1178 found 281.1172.

2-(3,5-Dimethylphenyl)-2-(4-hydroxyphenyl)-4,4-dimethyloxetan-3-one (3ac):



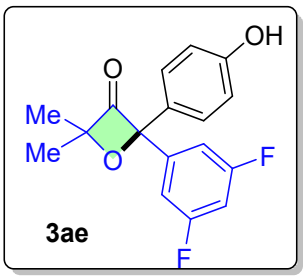
The title compound was prepared from **1a** (108 mg, 1 mmol) and **2c** (207 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.53, SiO_2, EtOAc:Hexane, 1:9) gave pure product as a pale green gel (231 mg, 78% yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 9.62 (s, 1H), 7.13 (d, J = 8.4 Hz, 2H), 6.96 (s, 2H), 6.94 (s, 1H), 6.77 (s, 1H), 6.75 (s, 1H), 2.25 (s, 6H), 1.41 (s, 3H), 1.37 (s, 3H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 206.8, 157.3, 140.2, 137.8, 130.4, 129.4, 126.4, 122.4, 115.4, 104.0, 100.7, 23.6, 23.4, 21.0. **HRMS** (QToF) calcd for $C_{19}H_{19}O_3$ [M-H]$^-$ 295.1334 found 295.1328.

2-(4-Hydroxyphenyl)-2-(4-methoxyphenyl)-4,4-dimethyloxetan-3-one (3ad):



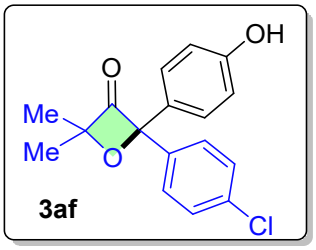
The title compound was prepared from **1a** (108 mg, 1 mmol) and **2d** (87 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.40, SiO_2, EtOAc:Hexane, 17:83) gave pure product as a yellow gel (268 mg, 90% yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 9.64 (s, 1H), 7.24 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 8.5 Hz, 2H), 6.95 (d, J = 8.7 Hz, 2H), 6.77 (d, J = 8.5 Hz, 2H), 3.73 (s, 3H), 1.41 (s, 3H), 1.39 (s, 3H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 207.1, 159.0, 157.3, 132.2, 130.4, 126.6, 126.5, 115.4, 114.1, 104.0, 100.7, 55.2, 23.6, 23.5. **HRMS** (QToF) calcd for $C_{18}H_{19}O_4$ $[M+H]^+$ 299.1283 found 299.1277.

2-(3,5-Difluorophenyl)-2-(4-hydroxyphenyl)-4,4-dimethyloxetan-3-one (3ae):



The title compound was prepared from **1a** (108 mg, 1 mmol) and **2e** (216 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.65, SiO_2, EtOAc:Hexane, 8:92) gave pure product as an off-white solid (207 mg, 68% yield) mp 120-123 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.73 (s, 1H), 7.27 – 7.12 (m, 3H), 7.04 (d, J = 5.5 Hz, 2H), 6.79 (d, J = 7.9 Hz, 2H), 1.43 (s, 3H), 1.41 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 205.1, 163.5, 163.4, 161.5, 161.4, 157.7, 144.3, 144.2, 144.2, 129.2, 126.4, 115.7, 108.1, 108.1, 108.0, 107.9, 103.9, 103.7, 103.5, 102.8, 102.1, 23.5, 23.3. **HRMS** (QToF) calcd for $C_{17}H_{13}F_2O_3$ $[M-H]^-$ 303.0833 found 303.0827.

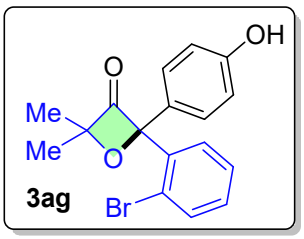
2-(4-Chlorophenyl)-2-(4-hydroxyphenyl)-4,4-dimethyloxetan-3-one (3af):



The title compound was prepared from **1a** (108 mg, 1 mmol) and **2f** (214 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.60, SiO_2, EtOAc:Hexane, 1:9) gave pure product as a pale green gel (223 mg, 74% yield). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.69 (s, 1H), 7.47 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 6.78 (d, J = 8.5 Hz, 2H), 1.43 (s, 3H), 1.39 (s, 3H). **^{13}C NMR**

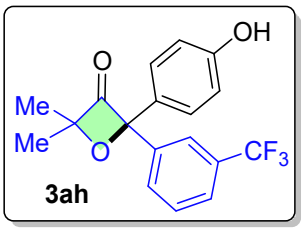
(100 MHz, DMSO-d_6) δ 206.2, 157.5, 139.0, 132.8, 129.8, 128.8, 126.8, 126.5, 115.6, 103.5, 101.5,23.5, 23.4. **HRMS** (QToF) calcd for $C_{17}H_{14}ClO_3$ [M-H]$^-$ 301.0631 found 301.0626.

2-(2-Bromophenyl)-2-(4-hydroxyphenyl)-4,4-dimethyloxetan-3-one (3ag):



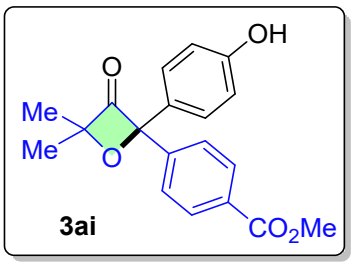
The title compound was prepared from **1a** (108 mg, 1 mmol) and **2g** (261 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.50, SiO_2, EtOAc:Hexane, 11:89) gave pure product as a pale yellow gel (225 mg, 65% yield). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.66 (s, 1H), 7.69 (d, J = 6.5 Hz, 1H), 7.63 (d, J = 7.1 Hz, 1H), 7.50 (s, 1H), 7.32 (d, J = 6.3 Hz, 1H), 7.04 (d, J = 7.0 Hz, 2H), 6.75 (d, J = 7.2 Hz, 2H), 1.51 (s, 3H), 1.33 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 205.0, 157.4, 138.3, 135.0, 130.4, 128.3, 127.5, 127.3, 121.0, 115.3, 105.2, 101.0, 23.9, 23.2. **HRMS** (QToF) calcd for $C_{17}H_{14}BrO_3$ [M-H]$^-$ 345.0126 found 345.0120.

2-(4-Hydroxyphenyl)-4,4-dimethyl-2-(3-(trifluoromethyl) phenyl) oxetan-3-one (3ah):



The title compound was prepared from **1a** (108 mg, 1 mmol) and **2h** (251 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.58, SiO_2, EtOAc:Hexane, 10:90) gave pure product as a pale green gel (208 mg, 62% yield). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.73 (s, 1H), 7.69 (t, J = 9.0 Hz, 3H), 7.64 (s, 1H), 7.16 (d, J = 8.3 Hz, 2H), 6.80 (d, J = 8.3 Hz, 2H), 1.45 (s, 3H), 1.39 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 205.8, 157.7, 141.4, 130.2, 129.6, 129.0, 126.5, 125.0, 122.6, 120.8, 120.8, 115.8, 103.2, 101.9, 23.5, 23.3. **HRMS** (QToF) calcd for $C_{18}H_{14}F_3O_3$ [M-H]$^-$ 335.0895 found 335.0889.

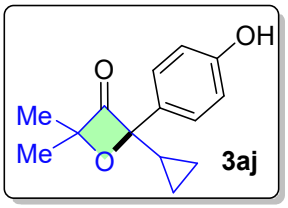
Methyl 4-(2-(4-hydroxyphenyl)-4,4-dimethyl-3-oxooxetan-2-yl) benzoate (3ai):



The title compound was prepared from **1a** (108 mg, 1 mmol) and **2i** (240 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.53, SiO_2, EtOAc:Hexane, 11:89) gave pure product as an off-white solid (225 mg, 69% yield), mp 120-123 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.71 (s, 1H), 7.99 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.3 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 6.78 (d, J = 8.6 Hz, 2H), 3.84 (s, 3H),

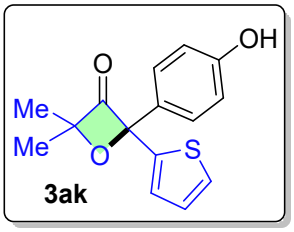
1.44 (s, 3H), 1.38 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 205.9, 165.9, 157.6, 144.9, 129.7, 129.2, 126.5, 125.1, 115.6, 103.7, 101.6, 52.3, 23.5, 23.3. **HRMS** (QToF) calcd for $C_{19}H_{17}O_5$ [M-H]$^-$ 325.1076 found 325.1070.

2-Cyclopropyl-2-(4-hydroxyphenyl)-4,4-dimethyloxetan-3-one (3aj):



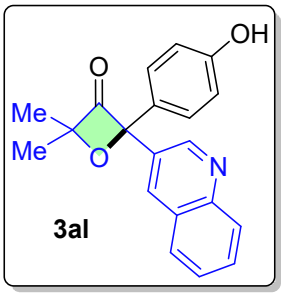
The title compound was prepared from **1a** (108 mg, 1 mmol) and **2j** (134 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.42, SiO_2, EtOAc:Hexane, 23:77) gave pure product as a colourless gel (58 mg, 25% yield). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.55 (s, 1H), 7.19 (d, J = 7.6 Hz, 2H), 6.77 (d, J = 7.6 Hz, 2H), 1.44 (s, 3H), 1.34 (s, 1H), 1.23 (s, 3H), 0.55 (d, J = 8.7 Hz, 1H), 0.49 (d, J = 5.4 Hz, 2H), 0.22 (d, J = 4.4 Hz, 1H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 208.6, 157.1, 129.8, 125.9, 115.4, 103.5, 99.9, 24.3, 22.3, 18.0, 1.9, 1.4. **HRMS** (QToF) calcd for $C_{14}H_{15}O_3$ [M-H]$^-$ 231.1021 found 231.1015.

2-(4-Hydroxyphenyl)-4,4-dimethyl-2-(thiophen-2-yl) oxetan-3-one (3ak):



The title compound was prepared from **1a** (108 mg, 1 mmol) and **2k** (182 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.55, SiO_2, EtOAc:Hexane, 10:90) gave pure product as a yellow gel (197 mg, 72% yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 9.65 (s, 1H), 7.56 (dd, J = 5.0, 3.0 Hz, 1H), 7.39 (dd, J = 2.9, 1.2 Hz, 1H), 7.18 (d, J = 8.6 Hz, 2H), 6.93 (dd, J = 5.0, 1.2 Hz, 1H), 6.79 (d, J = 8.6 Hz, 2H), 1.46 (s, 3H), 1.40 (s, 3H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 206.1, 157.4, 141.0, 129.5, 127.7, 126.3, 125.6, 122.5, 115.4, 102.32, 101.1, 23.6. **HRMS** (QToF) calcd for $C_{15}H_{13}O_3S$ [M-H]$^-$ 273.0585 found 273.0579.

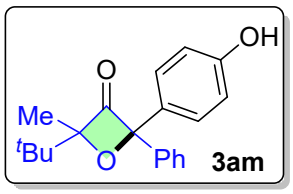
2-(4-Hydroxyphenyl)-4,4-dimethyl-2-(quinolin-3-yl) oxetan-3-one (3al):



The title compound was prepared from **1a** (108 mg, 1 mmol) and **2l** (232 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.40, SiO_2, EtOAc:Hexane, 25:75) gave pure product as an off-white solid (176 mg, 55% yield), mp 242-245 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.74 (s, 1H), 8.81 (d, J = 1.8 Hz,

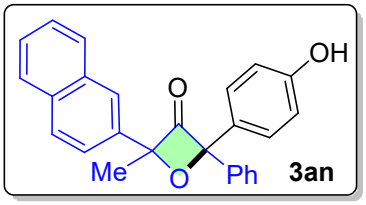
1H), 8.39 (s, 1H), 8.10 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.80 (t, *J* = 7.4 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 1.51 (s, 3H), 1.44 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 205.8, 157.7, 147.6, 147.0, 132.9, 131.4, 130.2, 129.4, 128.7, 128.6, 127.5, 126.9, 126.7, 115.8, 102.7, 102.2, 23.7, 23.5. **HRMS** (QToF) calcd for $C_{20}H_{18}NO_3$ $[M+H]^+$ 320.1287 found 320.1281.

2-(Tert-butyl)-4-(4-hydroxyphenyl)-2-methyl-4-phenyloxetan-3-one (3am):



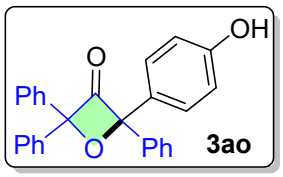
The title compound was prepared from **1a** (108 mg, 1 mmol) and **2m** (222 mg, 1.1 mmol) according to general procedure **A**. Diastereomeric ratio was 2:1. Purification using column chromatography (R_f = 0.58, SiO_2, EtOAc:Hexane, 7:93) gave pure product as an off-white solid (211 mg, 68% yield), mp 162-165 °C. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.57 (s, 1H), 9.53 (s, 0.47H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 2.2H), 7.36 (dd, *J* = 9.7, 5.0 Hz, 3.3H), 7.29 (d, *J* = 8.6 Hz, 2.5H), 7.26 – 7.23 (m, 2.4H), 6.74 (d, *J* = 8.5 Hz, 3.3H), 1.35 (s, 3H), 1.31 (s, 1.5H), 0.84 (s, 4.6H), 0.82 (s, 9H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 207.2, 207.1, 156.9, 156.7, 142.1, 140.3, 132.1, 130.5, 128.7, 128.5, 127.5, 127.4, 125.1, 125.1, 123.7, 115.4, 115.4, 108.8, 108.8, 102.6, 102.5, 35.7, 35.6, 26.4, 25.2, 25.2, 18.8, 18.8. **HRMS** (QToF) calcd for $C_{20}H_{21}O_3$ $[M-H]^-$ 309.1491 found 309.1485.

2-(4-Hydroxyphenyl)-4-methyl-4-(naphthalen-2-yl)-2-phenyloxetan-3-one (3an):



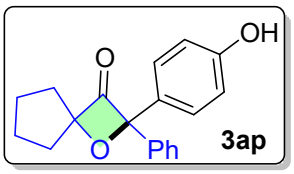
The title compound was prepared from **1a** (108 mg, 1 mmol) and **2n** (299 mg, 1.1 mmol) according to general procedure **A**. Diastereomeric ratio was 1:1. Purification using column chromatography (R_f = 0.55, SiO_2, EtOAc:Hexane, 10:90) gave pure product as a colourless gel (213 mg, 56% yield). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.74 (s, 1H), 9.62 (s, 1H), 7.91 (dd, *J* = 21.7, 8.5 Hz, 8.6H), 7.49 (dd, *J* = 19.0, 8.5 Hz, 11H), 7.42 – 7.15 (m, 8.5H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 8.0 Hz, 2H), 1.85 (s, 3H), 1.81 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 203.6, 203.5, 157.6, 157.4, 140.0, 139.4, 136.6, 136.5, 132.5, 132.4, 132.3, 130.2, 129.6, 128.8, 128.6, 128.4, 128.3, 128.1, 127.6, 126.8, 126.7, 126.5, 126.5, 125.0, 124.8, 123.2, 123.1, 122.4, 122.3, 115.6, 115.4, 105.6, 105.6, 103.8, 25.6. **HRMS** (QToF) calcd for $C_{26}H_{19}O_3$ $[M-H]^-$ 379.1334 found 379.1328.

2-(4-Hydroxyphenyl)-2,4,4-triphenyloxetan-3-one (3ao):



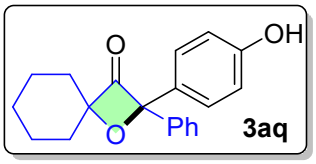
The title compound was prepared from **1a** (108 mg, 1 mmol) and **2o** (312 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.55, SiO_2, EtOAc:Hexane, 10:90) gave pure product as a white solid (286 mg, 73% yield), mp 172-175 °C. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 9.69 (s, 1H), 7.41 – 7.35 (m, 6H), 7.35 – 7.29 (m, 7H), 7.27 (d, *J* = 6.8 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.69 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 201.2, 157.5, 139.1, 139.1, 129.2, 128.8, 128.6, 128.3, 128.3, 126.8, 125.1, 124.9, 124.8, 115.4, 106.6, 105.8. **HRMS** (QToF) calcd for $C_{27}H_{19}O_3$ $[M-H]^-$ 391.1334 found 391.1328.

2-(4-Hydroxyphenyl)-2-phenyl-1-oxaspiro [3.4] octan-3-one (3ap):



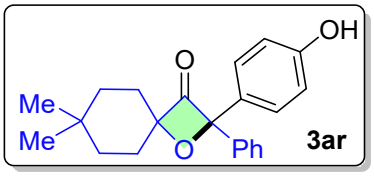
The title compound was prepared from **1a** (108 mg, 1 mmol) and **2p** (205 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.50, SiO_2, EtOAc:Hexane, 8:92) gave pure product as a pale green gel (235 mg, 80% yield). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.67 (s, 1H), 7.43 – 7.38 (m, 2H), 7.37 – 7.30 (m, 3H), 7.14 – 7.08 (m, 2H), 6.79 – 6.76 (m, 2H), 2.01 (dd, *J* = 8.7, 5.2 Hz, 2H), 1.95 (dd, *J* = 13.0, 6.1 Hz, 2H), 1.78 – 1.67 (m, 2H), 1.62 – 1.49 (m, 2H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 207.8, 157.5, 139.3, 129.6, 128.6, 128.1, 127.0, 125.3, 115.5, 109.4, 104.6, 36.5, 36.3, 24.5, 24.5. **HRMS** (QToF) calcd for $C_{19}H_{17}O_3$ $[M-H]^-$ 293.1178 found 293.1172.

2-(4-Hydroxyphenyl)-2-phenyl-1-oxaspiro [3.5] nonan-3-one (3aq):



The title compound was prepared from **1a** (108 mg, 1 mmol) and **2q** (220 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.50, SiO_2, EtOAc:Hexane, 8:92) gave pure product as a white solid (240 mg, 78% yield) mp 87-90 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.65 (s, 1H), 7.39 (d, *J* = 6.3 Hz, 4H), 7.32 (d, *J* = 6.3 Hz, 1H), 7.14 (d, *J* = 8.3 Hz, 2H), 6.77 (d, *J* = 8.3 Hz, 2H), 1.82 (d, *J* = 7.8 Hz, 1H), 1.77 – 1.61 (m, 5H), 1.46 (d, *J* = 11.8 Hz, 2H), 1.36 (d, *J* = 12.0 Hz, 2H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 206.7, 157.4, 140.3, 130.4, 128.6, 128.0, 126.6, 124.9, 115.5, 103.0, 33.1, 32.9, 24.1, 21.9. **HRMS** (QToF) calcd for $C_{20}H_{19}O_3$ $[M-H]^-$ 307.1334 found 307.1328.

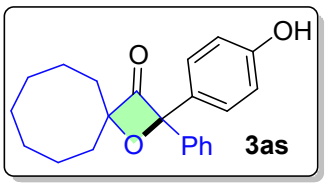
2-(4-Hydroxyphenyl)-7,7-dimethyl-2-phenyl-1-oxaspiro [3.5] nonan-3-one (3ar):



The title compound was prepared from **1a** (108 mg, 1 mmol) and **2r** (251 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.55, SiO_2, EtOAc:Hexane, 7:93) gave pure product as a colourless gel (259 mg, 77% yield). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.65 (s, 1H), 7.43 – 7.35 (m, 4H), 7.31 (dd, *J* = 8.2, 4.8

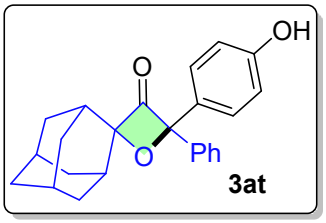
Hz, 1H), 7.14 (d, J = 8.6 Hz, 2H), 6.76 (d, J = 8.6 Hz, 2H), 1.80 (t, J = 6.0 Hz, 2H), 1.74 (t, J = 5.9 Hz, 2H), 1.47 (dd, J = 12.9, 5.0 Hz, 2H), 1.33 (dd, J = 19.6, 9.8 Hz, 2H), 0.92 (s, 3H), 0.87 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 206.8, 157.3, 140.6, 130.7, 128.7, 127.9, 126.3, 124.7, 115.5, 105.6, 103.2, 31.6, 31.6, 26.8, 26.7, 23.9, 20.8, 20.8. **HRMS** (QToF) calcd for $C_{22}H_{23}O_3$ $[M-H]^-$ 335.1647 found 335.1641.

2-(4-Hydroxyphenyl)-2-phenyl-1-oxaspiro [3.7] undecan-3-one (3as):



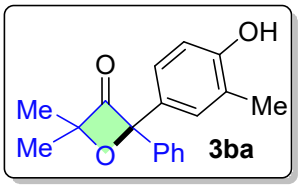
The title compound was prepared from **1a** (108 mg, 1 mmol) and **2s** (251 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.57, SiO_2, EtOAc:Hexane, 6:94) gave pure product as a colourless gel (252 mg, 75% yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 9.63 (s, 1H), 7.38 (s, 4H), 7.30 (s, 1H), 7.15 (d, J = 6.6 Hz, 2H), 6.76 (d, J = 6.5 Hz, 2H), 1.89 (dd, J = 35.1, 16.5 Hz, 4H), 1.64 (s, 2H), 1.51 (s, 8H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 206.8, 157.3, 140.6, 130.7, 128.7, 127.9, 126.3, 124.7, 115.5, 105.6, 103.2, 31.6, 31.6, 26.8, 26.7, 23.9, 20.8, 20.8. **HRMS** (QToF) calcd for $C_{22}H_{23}O_3$ $[M-H]^-$ 335.1647 found 335.1641.

4'-(4-Hydroxyphenyl)-4'-phenylspiro[adamantane-2,2'-oxetan]-3'-one (3at):



The title compound was prepared from **1a** (108 mg, 1 mmol) and **2t** (396 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.58, SiO_2, EtOAc:Hexane, 6:94) gave pure product as an off-white solid (267 mg, 74% yield), mp 172-175 °C. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 9.64 (s, 1H), 7.41 – 7.37 (m, 4H), 7.33 – 7.29 (m, 1H), 7.15 (d, J = 8.6 Hz, 2H), 6.76 (d, J = 8.6 Hz, 2H), 2.12 – 2.04 (m, 3H), 1.99 (s, 1H), 1.88 (d, J = 12.8 Hz, 1H), 1.83 (d, J = 13.3 Hz, 2H), 1.78 (s, 1H), 1.77 – 1.69 (m, 2H), 1.66 (s, 2H), 1.63 – 1.57 (m, 2H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 206.1, 157.4, 140.2, 130.4, 128.7, 128.0, 126.7, 125.0, 115.5, 106.6, 102.5, 35.8, 34.5, 34.3, 33.6, 33.6, 31.7, 31.6, 26.0, 25.6. **HRMS** (QToF) calcd for $C_{24}H_{23}O_3$ $[M-H]^-$ 359.1647 found 359.1641.

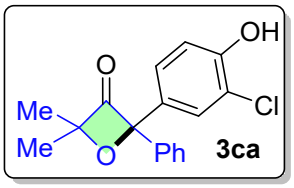
2-(4-Hydroxy-2-methylphenyl)-4,4-dimethyl-2-phenyloxetan-3-one (3ba):



The title compound was prepared from **1b** (122 mg, 1 mmol) and **2a** (176 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.50, SiO_2, EtOAc:Hexane, 12:88) gave pure product as a pale green gel (206 mg, 73% yield). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.55 (s, 1H), 7.42 – 7.34 (m, 4H), 7.34 – 7.28 (m,

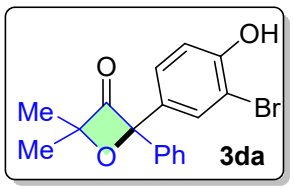
1H), 6.99 (d, J = 7.3 Hz, 2H), 6.77 (d, J = 8.5 Hz, 1H), 2.07 (s, 3H), 1.42 (s, 3H), 1.38 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 206.8, 155.4, 140.3, 130.3, 128.7, 128.0, 127.4, 124.8, 124.3, 123.6, 114.6, 104.1, 100.9, 23.5, 23.5, 16.2. **HRMS** (QToF) calcd for $C_{18}H_{17}O_3$ $[M-H]^-$ 281.1178 found 281.1172.

2-(3-Chloro-4-hydroxyphenyl)-4,4-dimethyl-2-phenyloxetan-3-one (3ca):



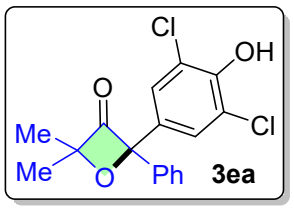
The title compound was prepared from **1c** (143 mg, 1 mmol) and **2a** (176 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.55, SiO_2, EtOAc:Hexane, 6:94) gave pure product as a pale green gel (196 mg, 65% yield). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.51 (s, 1H), 7.45 – 7.33 (m, 5H), 7.21 (d, J = 2.0 Hz, 1H), 7.16 (dd, J = 8.4, 2.0 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H), 1.43 (s, 3H), 1.39 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 206.1, 153.2, 139.7, 131.7, 129.0, 128.4, 126.4, 125.0, 124.8, 120.0, 117.0, 103.2, 101.8, 23.5, 23.5. **HRMS** (QToF) calcd for $C_{17}H_{14}ClO_3$ $[M-H]^-$ 301.0631 found 301.0626.

2-(3-bromo-4-hydroxyphenyl)-4,4-dimethyl-2-phenyloxetan-3-one (3da):



The title compound was prepared from **1d** (187 mg, 1 mmol) and **2a** (176 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.55, SiO_2, EtOAc:Hexane, 8:92) gave pure product as a pale brown gel (211 mg, 61% yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 10.61 (s, 1H), 7.43 – 7.35 (m, 5H), 7.32 (dd, J = 9.8, 4.2 Hz, 1H), 7.21 (dd, J = 8.4, 2.0 Hz, 1H), 6.99 (d, J = 8.5 Hz, 1H), 1.43 (s, 3H), 1.38 (s, 3H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 206.0, 154.2, 139.6, 132.0, 129.3, 128.9, 128.3, 125.6, 124.8, 116.7, 109.6, 103.0, 101.7, 23.5, 23.5. **HRMS** (QToF) calcd for $C_{17}H_{14}BrO_3$ $[M-H]^-$ 345.0126 found 345.0120.

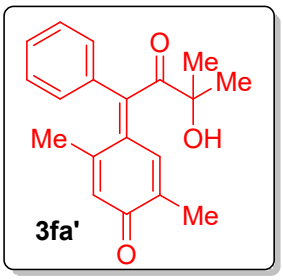
2-(3,5-Dichloro-4-hydroxyphenyl)-4,4-dimethyl-2-phenyloxetan-3-one (3ea):



The title compound was prepared from **1e** (177 mg, 1 mmol) and **2a** (176 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.55, SiO_2, EtOAc:Hexane, 8:92) gave pure product as a pale green solid (175 mg, 52% yield), mp 123-125 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.46 – 7.33 (m, 5H), 7.28 (s, 2H), 1.45 (s, 3H), 1.40 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 205.1, 149.2, 139.1, 132.5,

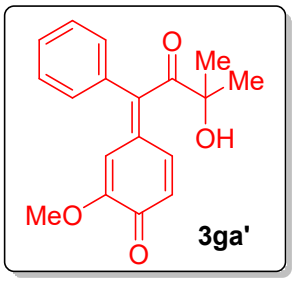
129.0, 128.5, 124.7, 124.7, 122.7, 102.4, 102.2, 23.5, 23.4. **HRMS** (QToF) calcd for $C_{17}H_{13}Cl_2O_3$ $[M-H]^-$ 335.0242 found 335.0236.

4-(3-Hydroxy-3-methyl-2-oxo-1-phenylbutylidene)-2,5-dimethylcyclohexa-2,5-dien-1-one (3fa'):



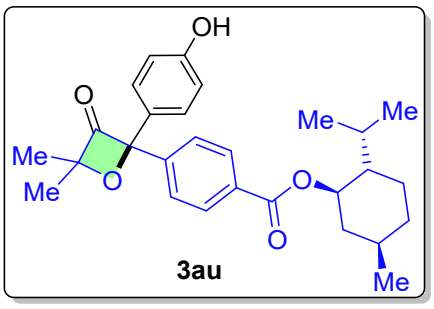
The title compound was prepared from **1d** (136 mg, 1 mmol) and **4a** (176 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.50, SiO_2, EtOAc:Hexane, 13:87) gave pure product as a pale brown gel (124 mg, 42% yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 7.58 (d, J = 7.4 Hz, 2H), 7.29 (dt, J = 30.7, 7.1 Hz, 4H), 6.53 (s, 1H), 5.08 (s, 1H), 1.92 (s, 3H), 1.51 (s, 3H), 1.27 (s, 3H), 1.12 (s, 3H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 199.5, 199.3, 150.2, 147.6, 143.7, 134.8, 132.6, 128.5, 128.0, 69.4, 56.8, 53.7, 28.3, 18.8, 16.0.

4-(3-Hydroxy-3-methyl-2-oxo-1-phenylbutylidene)-2-methoxycyclohexa-2,5-dien-1-one (3ga'):



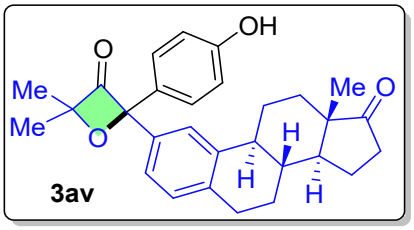
The title compound was prepared from **1d** (138 mg, 1 mmol) and **4a** (176 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.47, SiO_2, EtOAc:Hexane, 18:82) gave pure product as a pale yellow gel (158 mg, , 53% yield). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.77 (d, J = 7.0 Hz, 2H), 7.30 (dd, J = 15.8, 7.0 Hz, 4H), 6.76 (dd, J = 19.7, 10.4 Hz, 2H), 5.36 (s, 1H), 3.24 (s, 3H), 1.34 (s, 3H), 1.16 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 197.9, 196.2, 154.7, 139.7, 138.8, 138.4, 131.1, 129.1, 128.3, 127.9, 81.8, 69.7, 55.6, 52.9, 27.7. **HRMS** (QToF) calcd for $C_{18}H_{19}O_4$ $[M+H]^+$ 299.1283 found 299.1277.

(1*R*,2*R*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-(2-(4-hydroxyphenyl)-4,4-dimethyl-3-oxo oxetan-2-yl) benzoate (3au):



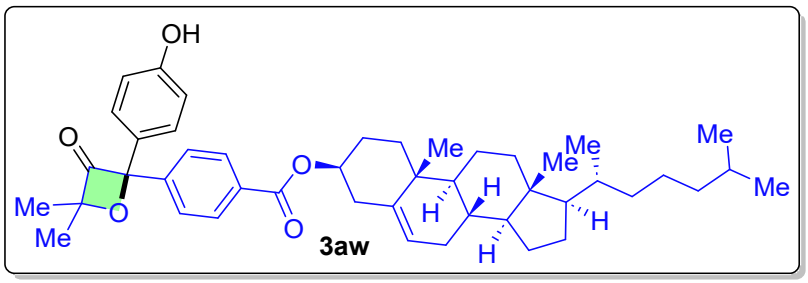
The title compound was prepared from **1a** (108 mg, 1 mmol) and **2u** (376 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.55, SiO_2, EtOAc:Hexane, 8:92) gave pure product as an off-white solid (306 mg, 68% yield), mp 87-90 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.70 (s, 1H), 7.98 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 4.83 (td, *J* = 10.8, 4.3 Hz, 1H), 1.96 (d, *J* = 11.8 Hz, 1H), 1.83 (dd, *J* = 12.8, 6.6 Hz, 1H), 1.67 (d, *J* = 12.1 Hz, 2H), 1.51 (t, *J* = 11.3 Hz, 2H), 1.45 (s, 3H), 1.38 (s, 3H), 1.13 – 1.03 (m, 2H), 0.87 (dd, *J* = 11.2, 6.8 Hz, 6H), 0.72 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 205.9, 164.9, 157.6, 145.0, 129.7, 129.6, 126.5, 125.2, 115.6, 103.7, 101.6, 74.3, 46.6, 40.5, 33.8, 30.9, 26.2, 23.5, 23.3, 23.2, 23.2, 21.9, 20.5, 16.5, 16.4. **HRMS** (QToF) calcd for $C_{28}H_{35}O_5$ $[M+H]^+$ 451.2484 found 451.2479.

2-(4-Hydroxyphenyl)-4,4-dimethyl-2-((*8R,9S,13S,14S*)-13-methyl-17-oxo-7,8,9,11,12,13, 14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-2-yl) oxetan-3-one (3av):



The title compound was prepared from **1a** (108 mg, 1 mmol) and **2b** (370 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.47, SiO_2, EtOAc:Hexane, 16:84) gave pure product as an off-white solid (267 mg, 60% yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.93 (s, 1H), 6.82 – 6.72 (m, 1H), 6.58 (d, *J* = 2.6 Hz, 2H), 6.34 (s, 1H), 6.15 (dd, *J* = 7.3, 1.5 Hz, 2H), 5.99 (s, 1H), 4.52 (d, *J* = 8.9 Hz, 1H), 2.33 – 2.25 (m, 2H), 1.62 (s, 1H), 1.56 – 1.49 (m, 1H), 1.41 (d, *J* = 8.9 Hz, 1H), 1.30 – 1.23 (m, 1H), 1.19 (dd, *J* = 16.0, 7.8 Hz, 2H), 0.94 – 0.88 (m, 1H), 0.82 (d, *J* = 9.1 Hz, 2H), 0.78 (s, 3H), 0.74 (s, 3H), 0.71 (dd, *J* = 12.5, 3.5 Hz, 1H), 0.65 (d, *J* = 15.6 Hz, 1H), 0.50 (s, 3H), 0.48 – 0.41 (m, 1H). **^{13}C NMR (125 MHz, DMSO-d_6):** δ 200.0, 169.6, 156.7, 149.8, 147.2, 140.7, 139.6, 132.0, 127.8, 127.6, 124.6, 120.9, 118.2, 115.7, 79.3, 70.5, 51.5, 46.6, 42.9, 37.5, 35.1, 30.3, 28.9, 27.2, 26.1, 25.2, 20.5, 17.6. **LC-MS** found for $C_{29}H_{33}O_4$ $[M+H]^+$ 445.

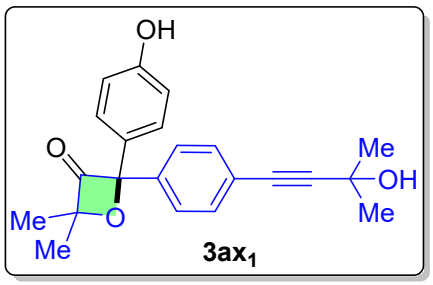
(3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2, 3, 4, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17-tetradecahydro-1H-cyclopenta[*a*]phenanthren-3-yl 4-(2-(4-hydroxyphenyl)-4,4-dimethyl-3-oxooxetan-2-yl)benzoate (3aw):



The title compound was prepared from **1a** (108 mg, 1 mmol) and **2b** (629 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.55, SiO_2, EtOAc:Hexane, 8:92) gave pure product as an off-white solid (374 mg, 55% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.28

(d, J = 8.7 Hz, 2H), 6.81 (d, J = 8.7 Hz, 2H), 5.41 (s, 1H), 4.90 – 4.79 (m, 1H), 4.28 – 4.16 (m, 1H), 2.43 (d, J = 7.6 Hz, 2H), 2.08 – 1.87 (m, 6H), 1.74 – 1.64 (m, 2H), 1.51 (s, 3H), 1.45 (s, 3H), 1.43 – 1.40 (m, 2H), 1.34 – 1.27 (m, 6H), 1.25 (s, 3H), 1.12 (d, J = 8.9 Hz, 3H), 1.06 (s, 3H), 1.02 – 0.97 (m, 2H), 0.93 (d, J = 3.8 Hz, 2H), 0.91 (d, J = 2.9 Hz, 2H), 0.90 (d, J = 2.4 Hz, 1H), 0.87 (d, J = 1.8 Hz, 3H), 0.86 (d, J = 1.8 Hz, 3H), 0.68 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 205.6, 167.9, 165.8, 156.0, 144.9, 139.7, 132.5, 131.9, 131.0, 130.4, 129.9, 128.9, 126.9, 125.0, 122.9, 115.7, 104.4, 102.1, 74.9, 68.3, 56.8, 56.2, 50.1, 42.4, 39.8, 39.6, 38.8, 38.3, 37.1, 36.7, 36.3, 35.9, 32.0, 32.0, 30.5, 29.8, 29.5, 29.0, 28.3, 28.1, 28.0, 24.4, 23.9, 23.8, 23.8, 23.1, 22.9, 22.8, 22.7, 21.1, 19.5, 18.8, 14.2, 14.2, 12.0, 11.1. **HRMS** (QToF) calcd for $C_{45}H_{59}O_5$ $[M-H]^-$ 679.4363 found 679.4357.

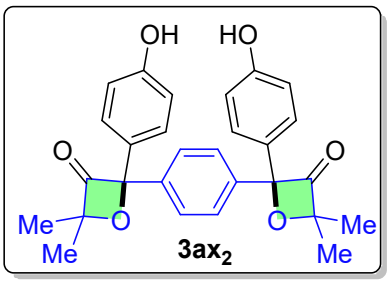
2-(4-(3-Hydroxy-3-methylbut-1-yn-1-yl)phenyl)-2-(4-hydroxyphenyl)-4,4-dimethyl oxetan-3-one ($3ax_1$):



$3ax_1$

The title compound was prepared from **1a** (108 mg, 1 mmol) and **2x** (266 mg, 1.1mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.48, SiO_2, EtOAc:Hexane, 13:87) gave pure product as a pale green gel (157 mg, 45% yield). **^{1}H NMR (400 MHz, DMSO-d_6)** 9.71 (s, 1H), 7.41 (s, 2H), 7.36 (s, 2H), 7.13 (d, J = 6.6 Hz, 2H), 6.78 (d, J = 7.1 Hz, 2H), 5.52 (s, 1H), 1.44 (s, 9H), 1.38 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 196.6, 147.8, 130.3, 121.9, 120.2, 116.9, 115.5, 112.7, 105.9, 94.1, 91.7, 87.1, 70.3, 54.0, 21.9, 13.9, 13.7. **HRMS** (QToF) calcd for $C_{22}H_{21}O_4$ $[M-H]^-$ 349.1440 found 349.1434.

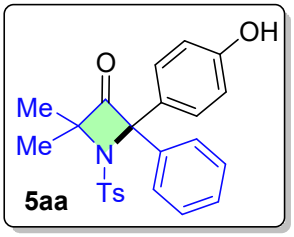
2-(4-Hydroxyphenyl)-2-(4-(2-(4-hydroxyphenyl)-4,4-dimethyl-3-oxooxetan-2-yl)phenyl)-4,4-dimethyloxetan-3-one ($3ax_2$):



$3ax_2$

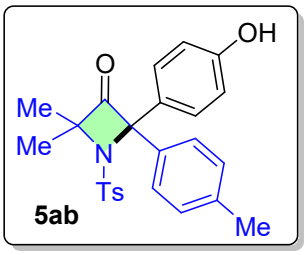
The title compound was prepared from **1a** (108 mg, 1 mmol) and **2x** (266 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.45, SiO_2, EtOAc:Hexane, 20:80) gave pure product as a yellow gel (147 mg, 32% yield). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.67 (d, J = 12.9 Hz, 2H), 7.41 (s, 4H), 7.14 (d, J = 6.1 Hz, 4H), 6.77 (d, J = 6.6 Hz, 4H), 1.40 (s, 6H), 1.37 (s, 3H), 1.32 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 206.4, 204.5, 157.4, 157.2, 139.8, 130.1, 129.5, 126.4, 125.2, 118.3, 115.6, 115.3, 114.8, 103.8, 101.3, 87.9, 76.1, 26.4, 23.6, 22.7. **HRMS** (QToF) calcd for $C_{28}H_{25}O_6$ $[M-H]^-$ 457.1651 found 457.1645.

2-(4-Hydroxyphenyl)-4,4-dimethyl-2-phenyl-1-tosylazetidin-3-one (5aa):



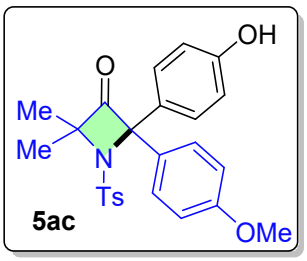
The title compound was prepared from **1a** (108 mg, 1 mmol) and **4a** (344 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.42, SiO_2, EtOAc:Hexane, 18:82) gave pure product as an off-white solid (379 mg, 90% yield) mp 157-160 °C. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.87 (s, 1H), 7.42 (s, 3H), 7.38 (s, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.97 (dd, *J* = 11.3, 8.5 Hz, 4H), 6.76 (d, *J* = 8.3 Hz, 2H), 2.29 (s, 3H), 1.42 (s, 3H), 1.40 (s, 3H). **^{13}C NMR (125 MHz, DMSO-*d*$_6$)** δ 204.6, 158.2, 143.1, 138.6, 137.6, 130.0, 129.2, 128.7, 128.6, 127.7, 127.1, 127.0, 115.4, 97.1, 86.2, 23.5, 22.0, 21.0. **HRMS** (QToF) calcd for $C_{24}H_{22}NO_4S$ $[M-H]^-$ 420.1270 found 420.1264.

2-(4-Hydroxyphenyl)-4,4-dimethyl-2-(p-tolyl)-1-tosylazetidin-3-one (5ab):



The title compound was prepared from **1a** (108 mg, 1 mmol) and **4b** (360 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.45, SiO_2, EtOAc:Hexane, 15:85) gave pure product as a pale brown gel (400 mg, 92% yield). **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 9.89 (s, 1H), 7.23 – 7.18 (m, 4H), 7.05 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 2.32 (s, 3H), 2.28 (s, 3H), 1.42 (s, 3H), 1.39 (s, 3H). **^{13}C NMR (125 MHz, DMSO-*d*$_6$)** δ 204.8, 158.2, 143.1, 138.7, 138.4, 134.7, 129.9, 129.2, 127.8, 127.4, 127.1, 115.4, 97.1, 86.2, 23.3, 22.3, 21.1, 20.8. **HRMS** (QToF) calcd for $C_{25}H_{24}NO_4S$ $[M-H]^-$ 434.1426 found 434.1420.

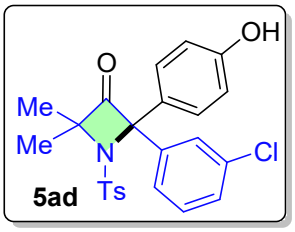
2-(4-Hydroxyphenyl)-2-(4-methoxyphenyl)-4,4-dimethyl-1-tosylazetidin-3-one (5ac):



The title compound was prepared from **1a** (108 mg, 1 mmol) and **4c** (377 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.42, SiO_2, EtOAc:Hexane, 20:80) gave pure product as a pale yellow puffy solid (428 mg, 95% yield) mp 177-180 °C. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.84 (s, 1H), 7.20 (d, *J* = 8.8 Hz, 2H), 7.05 (t, *J* = 8.5 Hz, 4H), 6.98 – 6.94 (m, 4H), 6.76 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 3H),

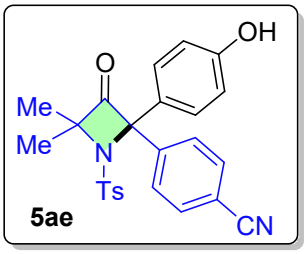
2.29 (s, 3H), 1.42 (s, 3H), 1.40 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 204.8, 159.5, 158.0, 143.0, 138.7, 129.6, 129.3, 129.1, 127.4, 127.0, 115.7, 115.3, 113.9, 96.8, 85.9, 79.2, 55.4, 23.0, 22.5, 21.0. **HRMS** (QToF) calcd for $C_{25}H_{24}NO_5S$ $[M-H]^-$ 450.1375 found 450.1369.

2-(3-Chlorophenyl)-2-(4-hydroxyphenyl)-4,4-dimethyl-1-tosylazetidin-3-one (5ad):



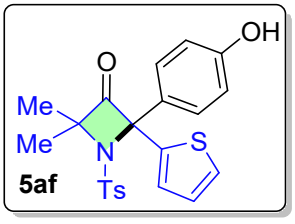
The title compound was prepared from **1a** (108 mg, 1 mmol) and **4d** (382 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.50, SiO_2, EtOAc:Hexane, 15:85) gave pure product as a pale green puffy solid (309 mg, 68% yield) mp 98-102 °C. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 9.95 (s, 1H), 7.52 – 7.44 (m, 2H), 7.38 (s, 1H), 7.33 (d, J = 6.6 Hz, 1H), 7.09 (d, J = 8.1 Hz, 2H), 7.00 (d, J = 8.2 Hz, 2H), 6.93 (d, J = 8.5 Hz, 2H), 6.76 (d, J = 8.5 Hz, 2H), 2.30 (s, 3H), 1.46 (s, 3H), 1.41 (s, 3H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 203.9, 158.5, 143.3, 140.0, 138.2, 133.3, 130.6, 130.2, 129.2, 128.7, 127.1, 127.0, 126.3, 126.1, 115.6, 96.1, 86.8, 23.9, 21.6, 21.0. **HRMS** (QToF) calcd for $C_{24}H_{23}NO_4SCl$ $[M+H]^+$ 456.1036 found 456.1030.

4-(2-(4-Hydroxyphenyl)-4,4-dimethyl-3-oxo-1-tosylazetidin-2-yl) benzonitrile (5ae):



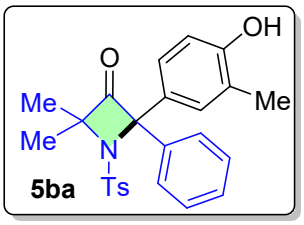
The title compound was prepared from **1a** (108 mg, 1 mmol) and **4e** (372 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.45, SiO_2, EtOAc:Hexane, 18:82) gave pure product as a pale green puffy solid (268 mg, 60% yield) mp 177-180 °C. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 9.99 (s, 1H), 7.93 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 8.3 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 7.00 (d, J = 8.2 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 6.75 (d, J = 8.6 Hz, 2H), 2.30 (s, 3H), 1.45 (s, 3H), 1.40 (s, 3H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 203.6, 158.6, 143.4, 142.9, 138.1, 132.6, 130.4, 129.2, 128.1, 127.1, 126.0, 118.5, 115.7, 115.6, 111.3, 96.4, 86.9, 24.2, 21.2, 21.0. **HRMS** (QToF) calcd for $C_{25}H_{21}N_2O_4S$ $[M-H]^-$ 445.1222 found 445.1216.

2-(4-Hydroxyphenyl)-4,4-dimethyl-2-(thiophen-2-yl)-1-tosylazetidin-3-one (5af):



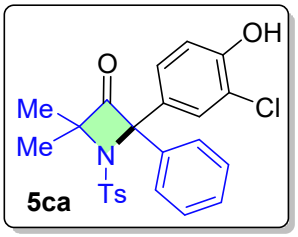
The title compound was prepared from **1a** (108 mg, 1 mmol) and **4f** (351 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.50, SiO_2, EtOAc:Hexane, 15:85) gave pure product as a pale green puffy solid (269 mg, 63% yield) mp 173-177 °C. **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 9.91 (s, 1H), 7.65 (d, *J* = 4.5 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.13 (dd, *J* = 17.0, 7.8 Hz, 4H), 7.08 – 7.04 (m, 1H), 6.96 (s, 1H), 6.81 (d, *J* = 8.2 Hz, 2H), 2.31 (s, 3H), 1.46 (s, 3H), 1.41 (s, 3H). **^{13}C NMR (125 MHz, DMSO-*d*$_6$)** δ 203.0, 158.3, 143.3, 140.4, 138.5, 129.3, 129.1, 128.8, 128.3, 127.2, 127.0, 126.8, 115.3, 93.2, 86., 23.0, 22.9, 21.0. **HRMS** (QToF) calcd for $C_{22}H_{20}NO_4S_2$ [M-H]$^-$ 426.0834 found 426.0828.

2-(4-Hydroxy-3-methylphenyl)-4,4-dimethyl-2-phenyl-1-tosylazetidin-3-one (5ba):



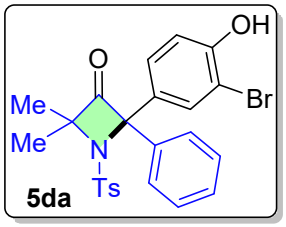
The title compound was prepared from **1b** (122 mg, 1 mmol) and **4a** (344 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.49, SiO_2, EtOAc:Hexane, 16:84) gave pure product as a pale green puffy solid (313 mg, 72% yield) mp 97-100 °C. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.77 (s, 1H), 7.41 (s, 5H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.94 (d, *J* = 7.8 Hz, 2H), 6.81 – 6.71 (m, 3H), 2.29 (s, 3H), 1.99 (s, 3H), 1.43 (s, 6H).**^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 204.7, 156.3, 143.0, 138.5, 137.6, 130.8, 129.0, 128.6, 128.5, 127.6, 127.4, 127.0, 126.8, 124.2, 114.4, 97.1, 86.3, 23.8, 21.8, 21.0, 16.1. **HRMS** (QToF) calcd for $C_{25}H_{24}NO_4S$ [M-H]$^-$ 434.1426 found 434.1420.

2-(3-chloro-4-hydroxyphenyl)-4,4-dimethyl-2-phenyl-1-tosylazetidin-3-one (5ca):



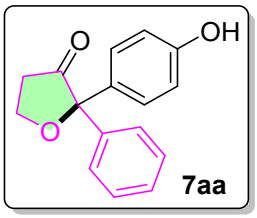
The title compound was prepared from **1c** (143 mg, 1 mmol) and **4a** (344 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.50, SiO_2, EtOAc:Hexane, 15:85) gave pure product as pale green puffy solid (355 mg, 78% yield), mp 98-102 °C. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.72 (s, 1H), 7.44 (s, 3H), 7.34 (s, 2H), 7.12 – 7.04 (m, 3H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.96 (s, 2H), 2.30 (s, 3H), 1.46 (s, 3H), 1.43 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 203.9, 153.9, 143.4, 138.2, 136.8, 129.7, 129.2, 129.1, 128.8, 128.4, 128.2, 127.8, 127.0, 119.9, 116.7, 96.0, 86.9, 23.2, 22.4, 21.0. **HRMS** (QToF) calcd for $C_{24}H_{23}NO_4SCl$ [M+H]$^+$ 456.1036 found 456.1030.

2-(3-Bromo-4-hydroxyphenyl)-4,4-dimethyl-2-phenyl-1-tosylazetidin-3-one (5da):



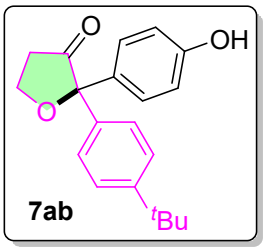
The title compound was prepared from **1d** (187 mg, 1 mmol) and **4a** (344 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.47, SiO_2, EtOAc:Hexane, 18:82) gave pure product as a pale brown gel (399 mg, 80% yield). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.80 (s, 1H), 7.43 (d, *J* = 2.3 Hz, 3H), 7.35 (d, *J* = 2.8 Hz, 2H), 7.19 (s, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.01 (s, 1H), 6.98 (d, *J* = 5.0 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 1H), 2.30 (s, 3H), 1.46 (s, 3H), 1.43 (s, 3H).**^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 203.9, 155.0, 143.3, 138.2, 136.8, 132.7, 129.2, 129.0, 128.8, 128.8, 128.7, 127.8, 127.0, 116.3, 109.5, 95.9, 86.9, 79.2, 23.3, 22.3, 21.0. **HRMS** (QToF) calcd for $C_{24}H_{23}NO_4SBr$ $[M+H]^+$ 500.0531 found 500.0525.

2-(4-Hydroxyphenyl)-2-phenyldihydrofuran-3(2*H*)-one (7aa):



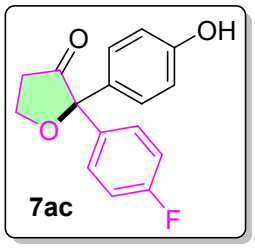
The title compound was prepared from **1a** (108 mg, 1 mmol) and **6a** (161 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.52, SiO_2, EtOAc:Hexane, 10:90) gave pure product as a pale green gel (211 mg, 83% yield). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.58 (s, 1H), 7.34 (s, 4H), 7.29 (s, 1H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.74 (d, *J* = 7.9 Hz, 2H), 4.14 (d, *J* = 4.8 Hz, 2H), 2.74 (t, *J* = 6.6 Hz, 2H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 213.4, 157.1, 139.7, 129.5, 128.3, 128.0, 127.8, 126.6, 115.2, 85.3, 62.1, 36.5. **HRMS** (QToF) calcd for $C_{16}H_{13}O_3$ $[M-H]^-$ 253.0865 found 253.0859.

2-(4-(Tert-Butyl) phenyl)-2-(4-hydroxyphenyl) dihydrofuran-3(2*H*)-one (7ab):



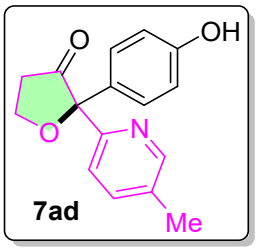
The title compound was prepared from **1a** (108 mg, 1 mmol) and **6b** (222 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.55, SiO_2, EtOAc:Hexane, 10:90) gave pure product as a pale yellow solid (202 mg, 65% yield) mp 78-80 °C. **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 9.56 (s, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.74 (d, *J* = 8.3 Hz, 2H), 4.12 (dt, *J* = 16.3, 8.1 Hz, 2H), 2.72 (t, *J* = 7.1 Hz, 2H), 1.24 (s, 9H). **^{13}C NMR (125 MHz, DMSO-*d*$_6$)** δ 213.5, 157.1, 150.1, 136.7, 129.6, 127.9, 126.3, 125.1, 115.1, 85.1, 62.0, 36.5, 34.3, 31.1. **HRMS** (QToF) calcd for $C_{20}H_{23}O_3$ $[M+H]^+$ 311.1647 found 311.1641.

2-(4-Fluorophenyl)-2-(4-hydroxyphenyl) dihydrofuran-3(2*H*)-one (7ac):



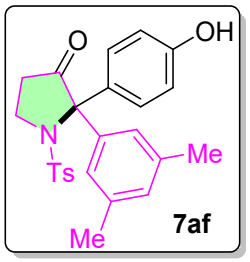
The title compound was prepared from **1a** (108 mg, 1 mmol) and **6c** (180 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.53, SiO_2, EtOAc:Hexane, 11:89) gave pure product as a pale yellow gel (158 mg, 58% yield). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.60 (s, 1H), 7.35 (d, *J* = 5.4 Hz, 2H), 7.17 (t, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 7.9 Hz, 2H), 4.13 (dt, *J* = 23.7, 7.7 Hz, 2H), 2.75 (t, *J* = 6.6 Hz, 2H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 213.3, 162.9, 160.5, 157.2, 136.0, 129.2, 128.8, 128.7, 128.0, 115.3, 115.2, 115.0, 84.9, 62.1, 36.4. **HRMS** (QToF) calcd for $C_{16}H_{12}FO_3$ $[M-H]^-$ 271.0770 found 271.0765.

2-(4-Hydroxyphenyl)-2-(5-methylpyridin-2-yl) dihydrofuran-3(2*H*)-one (7ad):



The title compound was prepared from **1a** (108 mg, 1 mmol) and **6d** (177 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.40, SiO_2, EtOAc:Hexane, 28:72) gave pure product as a pale green solid (97 mg, 36% yield). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.53 (s, 1H), 8.35 (s, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 8.3 Hz, 2H), 4.22 (dd, *J* = 14.5, 7.8 Hz, 1H), 4.18 – 4.10 (m, 1H), 2.69 (dd, *J* = 16.2, 7.6 Hz, 2H), 2.26 (s, 3H).**^{13}C NMR (100 MHz, DMSO-d_6)** δ 212.1, 157.6, 157.1, 148.8, 137.5, 132.4, 127.9, 127.7, 121.7, 114.9, 85.8, 62.5, 36.5, 17.6. **HRMS** (QToF) calcd for $C_{16}H_{16}NO_3$ $[M+H]^+$ 270.1130 found 270.1124.

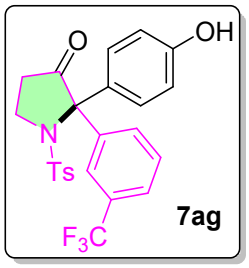
2-(3,5-Dimethylphenyl)-2-(4-hydroxyphenyl)-1-tosylpyrrolidin-3-one (7af):



The title compound was prepared from **1a** (108 mg, 1 mmol) and **6f** (360 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.45, SiO_2, EtOAc:Hexane, 22:88) gave pure product as an off-white solid (366 mg, 84% yield), mp 157-160 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.65 (s, 1H), 7.06 (dd, *J* = 11.3, 8.5 Hz, 4H), 6.91 (s, 1H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.72 (s, 2H), 6.68 (d, *J* = 8.7 Hz, 2H),

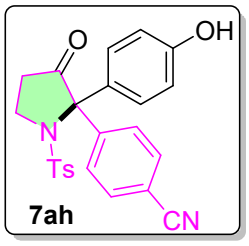
3.90 – 3.82 (m, 2H), 2.84 (dd, J = 7.5, 6.8 Hz, 2H), 2.30 (s, 3H), 2.14 (s, 6H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 211.0, 157.1, 142.5, 138.2, 136.8, 136.6, 130.8, 129.2, 128.9, 127.9, 127.5, 126.4, 114.5, 76.7, 43.4, 35.3, 21.0, 20.9. **HRMS** (QToF) calcd for $C_{25}H_{26}NO_4S$ $[M+H]^+$ 436.1583 found 436.1577.

2-(4-Hydroxyphenyl)-1-tosyl-2-(3-(trifluoromethyl) phenyl) pyrrolidin-3-one (7ag):



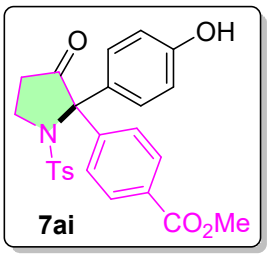
The title compound was prepared from **1a** (108 mg, 1 mmol) and **6f** (404 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.45, SiO_2, EtOAc:Hexane, 28:72) gave pure product as a pale green solid (361 mg, 76% yield), mp 222-225 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.75 (s, 1H), 7.68 (d, J = 6.3 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.47 (s, 1H), 7.07 (d, J = 7.8 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 7.9 Hz, 2H), 6.69 (d, J = 8.4 Hz, 2H), 3.95 (dd, J = 15.7, 8.2 Hz, 1H), 3.85 (dd, J = 16.4, 8.4 Hz, 1H), 2.94 (t, J = 6.6 Hz, 2H), 2.29 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 210.6, 157.5, 143.0, 139.7, 136.5, 133.9, 130.8, 129.1, 128.8, 127.6, 126.3, 126.0, 124.8, 114.8, 76.3, 43.5, 35.4, 21.0. **HRMS** (QToF) calcd for $C_{24}H_{19}F_3NO_4S$ $[M-H]^-$ 474.0987 found 474.0981.

4-(2-(4-Hydroxyphenyl)-3-oxo-1-tosylpyrrolidin-2-yl) benzonitrile (7ah):



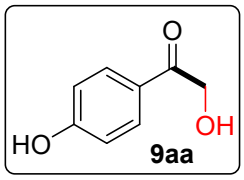
The title compound was prepared from **1a** (108 mg, 1 mmol) and **6h** (356 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.40, SiO_2, EtOAc:Hexane, 30:70) gave pure product as an off-white solid (324 mg, 75% yield), mp 127-130 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.75 (s, 1H), 7.79 (d, J = 5.8 Hz, 2H), 7.47 (d, J = 5.9 Hz, 2H), 7.09 (s, 2H), 6.91 (s, 4H), 6.66 (s, 2H), 3.95 (d, J = 6.5 Hz, 2H), 2.93 (s, 2H), 2.31 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 210.4, 157.5, 143.8, 143.0, 136.3, 131.6, 131.1, 130.4, 129.1, 127.6, 126.5, 118.7, 114.7, 110.7, 76.5, 43.5, 35.5, 21.0. **HRMS** (QToF) calcd for $C_{24}H_{19}N_2O_4S$ $[M-H]^-$ 431.1066 found 431.1060.

Methyl-4-(2-(4-hydroxyphenyl)-3-oxo-1-tosylpyrrolidin-2-yl) benzoate (7ai):



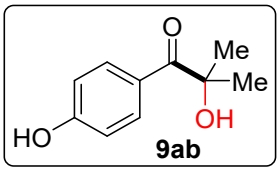
The title compound was prepared from **1a** (108 mg, 1 mmol) and **6i** (393 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.40, SiO_2, EtOAc:Hexane, 32:68) gave pure product as a pale yellow solid (335 mg, 72% yield), mp 127-130 °C. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.70 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.2 Hz, 2H), 6.66 (d, *J* = 8.7 Hz, 2H), 3.94 (dd, *J* = 16.3, 8.1 Hz, 1H), 3.87 (s, 3H), 3.85 – 3.77 (m, 1H), 2.91 (dd, *J* = 10.7, 4.8 Hz, 2H), 2.29 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 210.5, 166.1, 157.4, 143.6, 142.9, 136.5, 131.1, 129.8, 129.1, 128.4, 127.8, 126.4, 114.6, 76.6, 52.3, 43.4, 35.5, 21.0. **HRMS** (QToF) calcd for $C_{25}H_{22}NO_6S$ $[M-H]^-$ 464.1168 found 464.1162.

2-Hydroxy-1-(4-hydroxyphenyl) ethan-1-one (9aa):



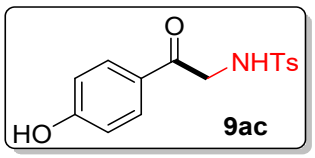
The title compound was prepared from **1a** (108 mg, 1 mmol) and **8a** (62 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.45, SiO_2, EtOAc:Hexane, 22:88) gave pure product as an off-white solid (31 mg, 20% yield). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 7.80 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 4.90 (s, 1H), 4.69 (s, 2H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 197.2, 162.3, 130.2, 126.1, 115.4, 64.8. **HRMS** (QToF) calcd for $C_8H_7O_3$ $[M-H]^-$ 151.0395 found 151.0389.

2-hydroxy-1-(4-hydroxyphenyl)-2-methylpropan-1-one (9ab):



The title compound was prepared from **1a** (108 mg, 1 mmol) and **8b** (92 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.40, SiO_2, EtOAc:Hexane, 25:75) gave pure product as an off-white solid (50 mg, 28% yield), mp 135-138 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.04 – 7.99 (m, 2H), 6.93 – 6.87 (m, 2H), 1.66 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 202.6, 160.4, 132.8, 116.3, 115.4, 76.0, 28.8. **HRMS** (QToF) calcd for $C_{10}H_{11}O_3$ $[M-H]^-$ 179.0708 found 179.0702.

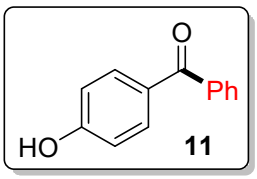
***N*-(2-(4-Hydroxyphenyl)-2-oxoethyl)-4-methylbenzenesulfonamide (9ac)**:



The title compound was prepared from **1a** (108 mg, 1 mmol) and **2c** (220 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.46, SiO_2, EtOAc:Hexane, 22:88) gave pure product as an off-white solid (107 mg, 35% yield), mp 157-160 °C. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.51 (s, 1H), 7.82 (t, *J* = 5.6 Hz, 1H), 7.77 (d, *J* = 8.6 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.29 (d, *J* = 5.7 Hz, 2H), 2.36 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 192.0,

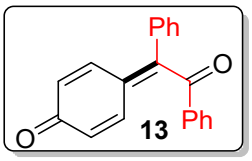
162.5, 142.7, 137.8, 131.6, 130.6, 129.6, 126.7, 126.1, 115.4, 115.2, 48.5, 21.0. **HRMS** (QToF) calcd for $C_{15}H_{16}NO_4S$ $[M+H]^+$ 306.0800 found 306.0794.

(4-Hydroxyphenyl) (phenyl)methanone (11):



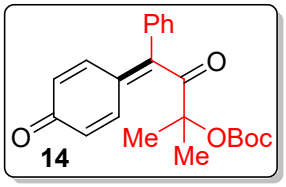
The title compound was prepared from **1a** (108 mg, 1 mmol) and **10a-10c** (145, 160, 313 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.53, SiO_2, EtOAc:Hexane, 15:85) gave pure product as a white solid, mp 127-130 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.50 (s, 1H), 7.63 (dd, *J* = 15.3, 7.6 Hz, 5H), 7.53 (t, *J* = 7.3 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 194.5, 162.1, 138.1, 132.6, 132.0, 129.2, 128.5, 128.0, 115.4. **HRMS** (QToF) calcd for $C_{13}H_{11}O_2$ $[M+H]^+$ 199.0759 found 199.0753.

4-(2-Oxo-1,2-diphenylethylidene) cyclohexa-2,5-dien-1-one (13):



The title compound was prepared from **1a** (108 mg, 1 mmol) and **12** (87 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.50, SiO_2, EtOAc:Hexane, 15:85) gave pure product as a yellow gel (214 mg, 75% yield). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.94 (d, *J* = 7.4 Hz, 2H), 7.69 (t, *J* = 7.3 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 2H), 7.54 – 7.47 (m, 6H), 7.15 (dd, *J* = 10.0, 2.5 Hz, 1H), 6.50 (dd, *J* = 10.1, 1.7 Hz, 1H), 6.37 (dd, *J* = 9.9, 1.7 Hz, 1H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 195.7, 185.9, 154.3, 137.2, 137.0, 135.2, 133.2, 130.6, 130.5, 129.9, 129.7, 129.6, 129.4, 129.0, 40.0, 39.8, 39.6, 39.5, 39.3, 39.1, 39.0. **HRMS** (QToF) calcd for $C_{20}H_{15}O_2$ $[M+H]^+$ 287.1072 found 287.1066.

Tert-butyl (2-methyl-3-oxo-4-(4-oxocyclohexa-2,5-dien-1-ylidene)-4-phenylbutan-2-yl) carbonate (14):

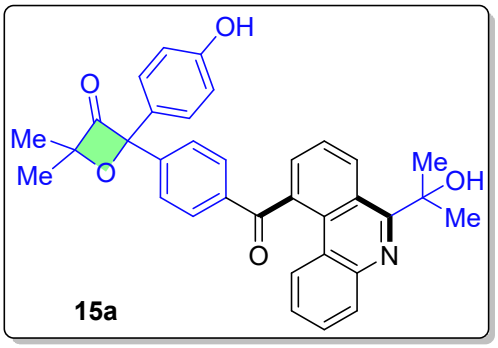


The title compound was prepared from **1a** (108 mg, 1 mmol) and **2y** (286 mg, 1.1 mmol) according to general procedure **A**. Purification using column chromatography (R_f = 0.60, SiO_2, EtOAc:Hexane, 5:95) gave pure product as a yellow gel (258 mg, 70% yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 7.58 – 7.54 (m, 3H), 7.47 (dd, *J* = 10.1, 2.6 Hz, 1H), 7.31 (dd, *J* = 6.3, 2.8 Hz, 2H), 7.10 (dd, *J* = 10.1, 2.6 Hz, 1H), 6.44 (dd, *J* = 10.1, 1.9 Hz, 1H), 6.37 (dd, *J* = 10.1, 1.9 Hz, 1H), 1.35 (s, 9H), 1.28 (s, 6H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 204.6, 186.1, 154.4, 151.7, 137.9, 136.6, 132.8, 130.9, 130.4, 130.3, 129.7, 129.1, 85.5, 82.7, 27.3, 25.5. **HRMS** (QToF) calcd for $C_{19}H_{19}O_3$ $[M+H+Na]^+$ 392.1660 found 392.1557.

When we added triflouroacetic acid (3 equivalents) to compound **14** at room temperature, it delivered the compound **3aa**.

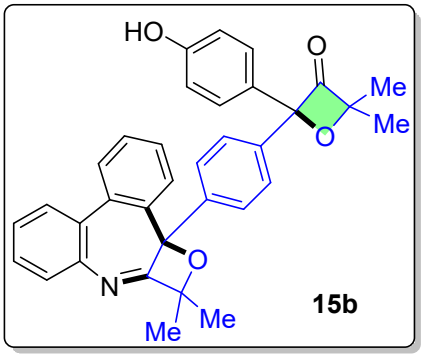
5. General procedure for the synthesis of derivatives and their characteristic data:

2-(4-Hydroxyphenyl)-2-(4-(6-(2-hydroxypropan-2-yl)phenanthridine-10-carbonyl) phenyl)-4,4-dimethyloxetan-3-one (15a):



A round-bottomed flask was charged with biphenyl amine **15** (60 mg, 0.35 mmol) and propargyl alcohol **3ax$_1$** (122 mg, 0.35 mmol) in DMSO (5 mL) was added $Pd(OAc)_2$ (8 mg, 10 mol%), $Cu(OAc)_2.H_2O$ (28.3 mg, 0.4 equiv) and 4 equivalent of water (26 mg), and the reaction mixture was stirred at 100 °C (oil bath) for 12-18hours under air balloon. After completion of the reaction, the reaction mixture was cooled to rt before water was added to it. The aqueous layer was extracted with ethyl acetate (2×10 mL), the organic layer was evaporated and the residue was purified by column chromatography (Rf = 0.50) (SiO2, EtOAc:Hexane, 25:75) to get product 15a as as an off-white solid (103 mg, 55 % yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 9.95 – 9.66 (m, 1H), 9.49 (d, *J* = 6.2 Hz, 1H), 8.03 (s, 1H), 7.82 (d, *J* = 13.1 Hz, 5H), 7.65 (d, *J* = 6.5 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.37 (s, 1H), 7.25 – 7.11 (m, 2H), 6.77 (s, 2H), 5.97 (s, 1H), 1.81 (s, 6H), 1.35 (s, 3H), 1.22 (s, 3H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 198.4, 174.8, 167.2, 165.1, 158.4, 146.7, 142.9, 137.1, 136.9, 132.1, 131.84, 131.5, 131.1, 130.6, 130.3, 129.2, 128.8, 127.4, 126.6, 126.5, 126.2, 126.0, 125.6, 124.6, 121.8, 115.8, 115.4, 107.8, 77.9, 75.6, 31.1, 24.8, 24.6. **HRMS** (QToF) calcd for $C_{34}H_{30}NO_5$ $[M+H]^+$ 532.2124 found 532.2118.

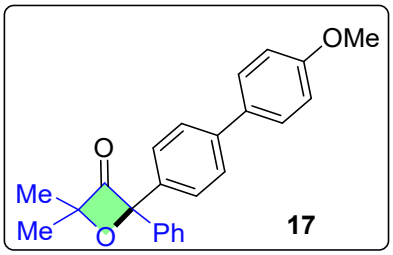
2-(4-(6,6-Dimethyldibenzo[*b,d*]oxeto[*2,3-f*]azepin-4*b*(6*H*)-yl)phenyl)-2-(4-hydroxy phenyl)-4,4-dimethyloxetan-3-one (15b):



To an oven-dried 25 mL round bottom flask, a mixture of biphenyl amine **15** (60 mg, 0.35 mmol) and propargyl alcohol **3ax$_1$** (120 mg, 0.35 mmol) in anhydrous DMF (5 mL), $Pd(OAc)_2$ (8 mg, 10 mol%) was added $Cu(OAc)_2$ (282 mg, 4 eq) and 4 Å molecular sieves, and the reaction mixture was stirred at 100 °C (oil bath) for 12 hours under nitrogen

atmosphere. After completion of the reaction, reaction mixture was cooled to rt before ice water was added to it. 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, 15:85) to get product 15b as as an off-white solid (83mg, 45 % yield). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.72 (s, 1H), 8.14 (d, 2H), 7.72 (dd, 2H), 7.48 (m, *J* = 23.9 Hz, 7H), 7.26 (m, 1H), 7.16 (d, 2H), 6.78 (d, 2H), 1.59 (s, 3H), 1.49 (s, 3H), 1.43 (s, 3H), 1.39 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 206.3, 157.5, 146.4, 142.6, 139.9, 136.1, 132.5, 131.2, 130.0, 129.7, 129.4, 129.3, 128.6, 128.3, 127.9, 127.7, 127.5, 126.6, 125.4, 124.8, 115.6, 103.9, 101.5, 23.6, 23.4, 21.5, 19.7. **HRMS** (QToF) calcd for $C_{34}H_{30}O_4N$ $[M+H]^+$ 516.2169 found 516.2169.

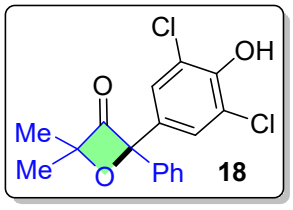
2-(4'-Methoxy-[1,1'-biphenyl]-4-yl)-4,4-dimethyl-2-phenyloxetan-3-one (17):



A round-bottomed flask was charged with compound **3aa** (1 mmol, 268 mg), pyridine (2 mmol, 158 mg) in dichloromethane, triflic anhydride (2 mmol, 564 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 (280 mg) was obtained.

To this triflated adduct (80 mg, 0.2 mmol) in 1,4-dioxane, para methoxy phenyl boronic acid (51 mg, 0.33 mmol), potassium phosphate (141 mg, 0.66 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 the contents were 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 (6:94) as the eluent to get product 17 as a white solid (49 mg, 68 % yield), mp 123-125 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 – 7.50 (m, 7H), 7.49 (s, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 2H), 3.84 (s, 3H), 1.54 (s, 3H), 1.51 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 206.1, 159.2, 139.9, 139.7, 138.2, 131.8, 128.9, 128.3, 127.9, 126.6, 125.4, 124.7, 114.5, 103.8, 101.7, 55.3, 23.5, 23.5. **HRMS** (QToF) calcd for $C_{24}H_{23}O_3$ $[M+H]^+$ 359.1647 found 359.1641.

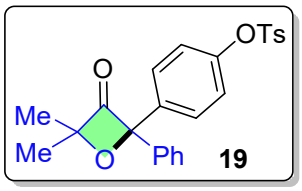
2-(3,5-Dichloro-4-hydroxyphenyl)-4,4-dimethyl-2-phenyloxetan-3-one (18):



A round-bottomed flask was charged with compound **3aa** (0.19 mmol, 50 mg) in 1:4 ratio of water and ethyl acetate, and the contents were added with sodium chloride (0.42

mmol, 25 mg), oxone (0.19 mmol, 60 mg). 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 theresidue was purified by column chromatography (R_f = 0.58, SiO_2, EtOAc:Hexane, 5:95) gave pure product as a pale green solid (42mg, 65% yield), mp 123-125 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 (t, *J* = 1.8 Hz, 1H), 7.44 – 7.43 (m, 1H), 7.40 – 7.37 (m, 3H), 7.34 – 7.31 (m, 1H), 5.91 (s, 1H), 1.52 (s, 3H), 1.47 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 204.8, 147.7, 139.3, 133.8, 128.9, 128.5, 125.1, 125.0, 121.5, 103.0, 102.7, 23.9, 23.9. **HRMS** (QToF) calcd for $C_{17}H_{13}Cl_2O_3$ $[M-H]^-$ 335.0242 found 335.0236.

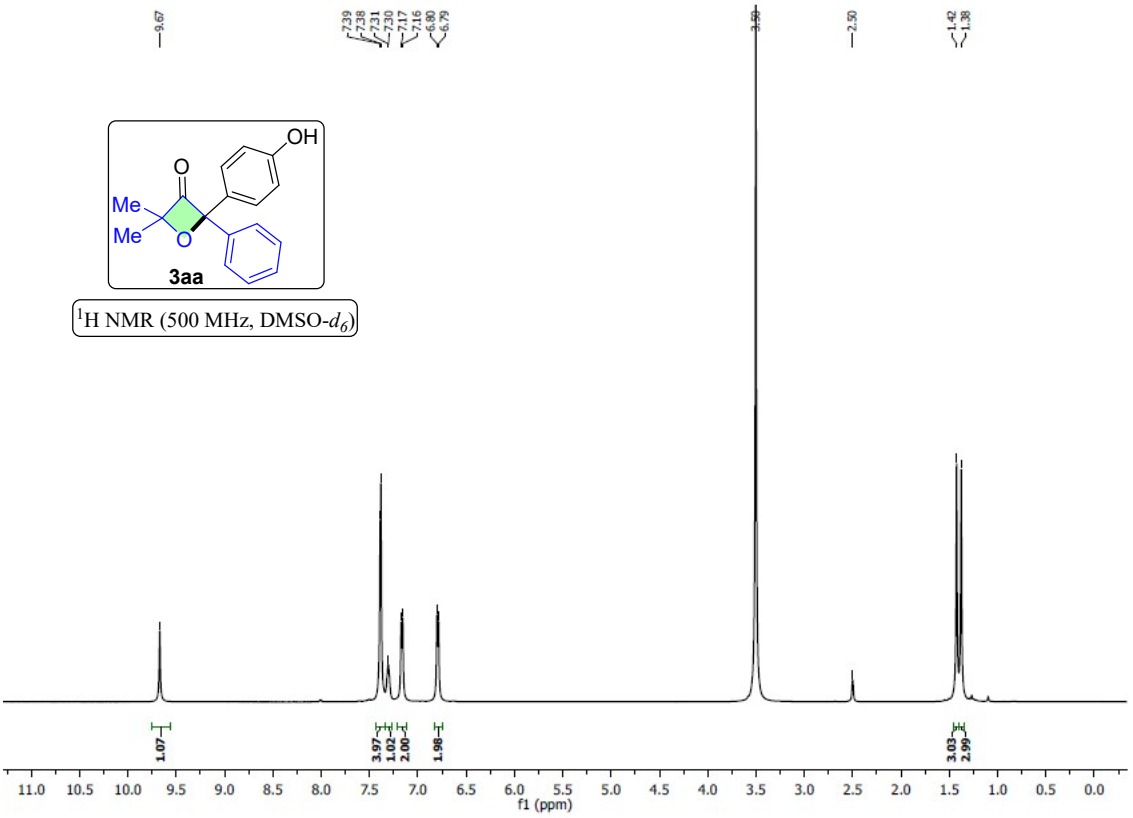
4-(4,4-dimethyl-3-oxo-2-phenyloxetan-2-yl) phenyl 4-methylbenzenesulfonate (19):



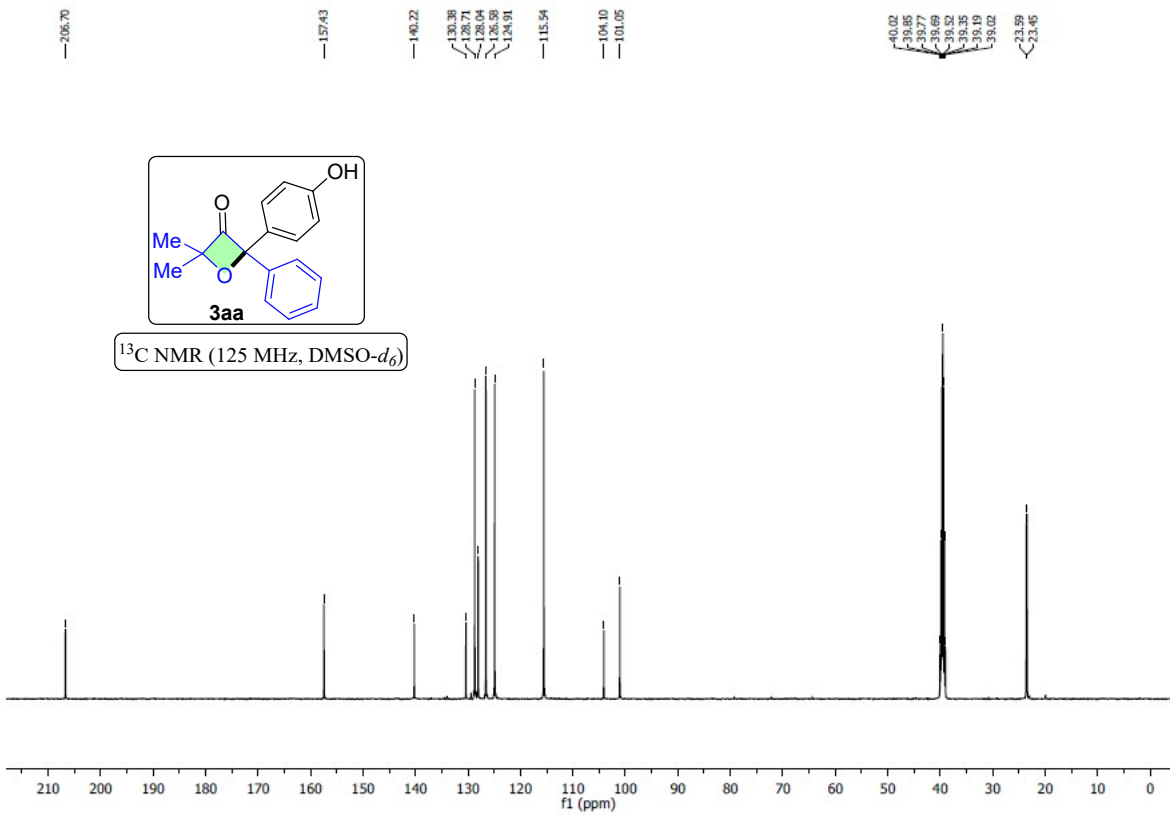
19

A round-bottomed flask was charged with compound **3aa** (0.19 mmol, 50 mg), pyridine (0.56 mmol, 44 mg) in dichloromethane. Tosyl chloride (0.28 mmol, 53 mg) was added and the contents and the reaction mixture was stirred at room temperature for 3h. 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 theresidue was purified by column chromatography (R_f= 0.58, SiO_2, EtOAc:Hexane, 5:95) gave pure product as a white solid (54mg, 68% yield), mp 147-150 °C.**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.72 – 7.68 (m, 2H), 7.43 (t, *J* = 1.8 Hz, 1H), 7.43 – 7.41 (m, 2H), 7.41 (d, *J* = 2.1 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.30 (dq, *J* = 3.8, 1.4 Hz, 3H), 7.00 – 6.96 (m, 2H), 2.44 (s, 3H), 1.47 (s, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 205.3, 149.3, 145.5, 139.7, 139.0, 132.5, 129.9, 128.8, 128.6, 128.3, 126.5, 125.0, 122.6, 104.0, 102.3, 23.9, 23.9, 21.8. **HRMS** (QToF) calcd for $C_{24}H_{23}O_5S$ $[M+H]^+$ 423.1266 found 423.1261.

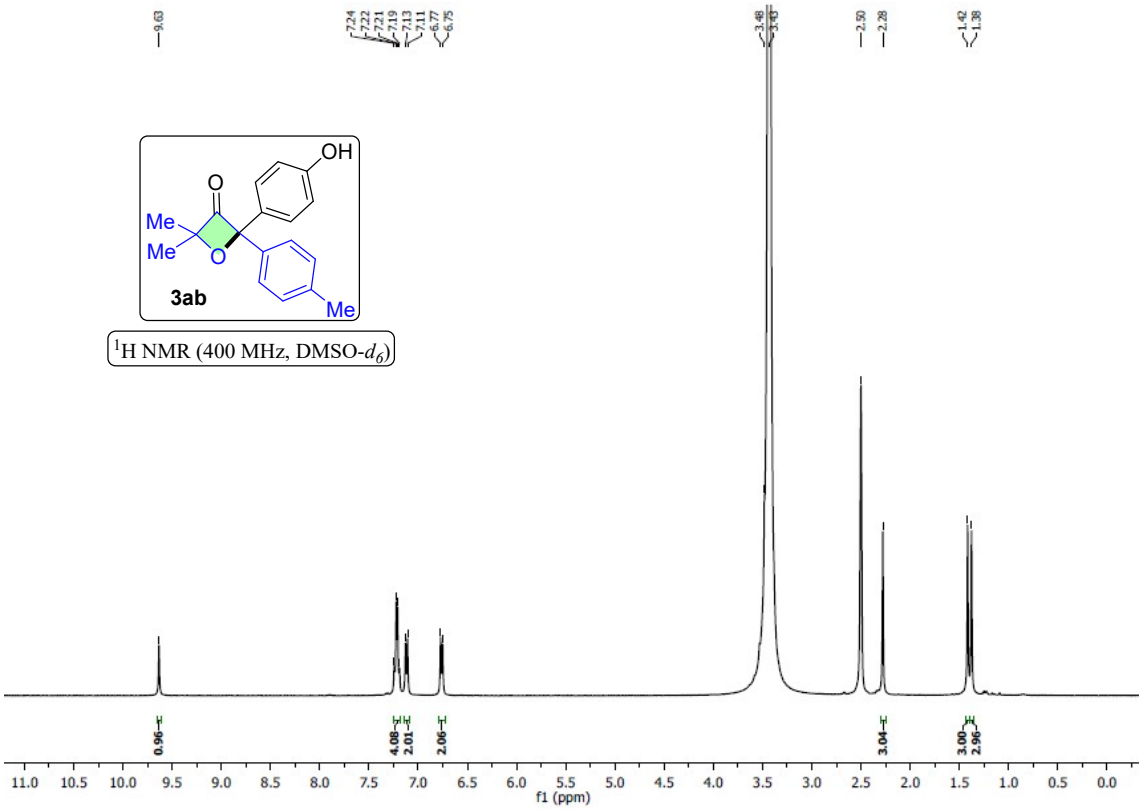
6. Copies of ^{1}H and ^{13}C NMR spectra:



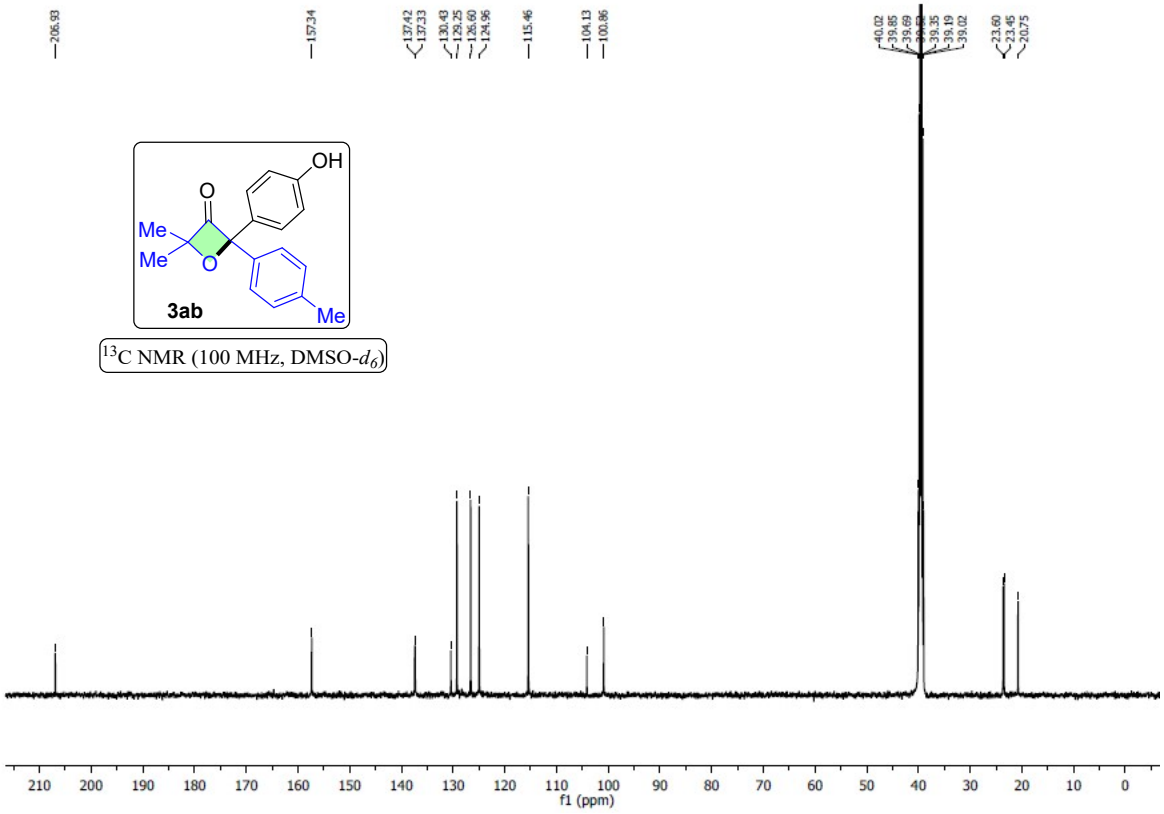
^{1}H NMR (500 MHz, DMSO-d_6)



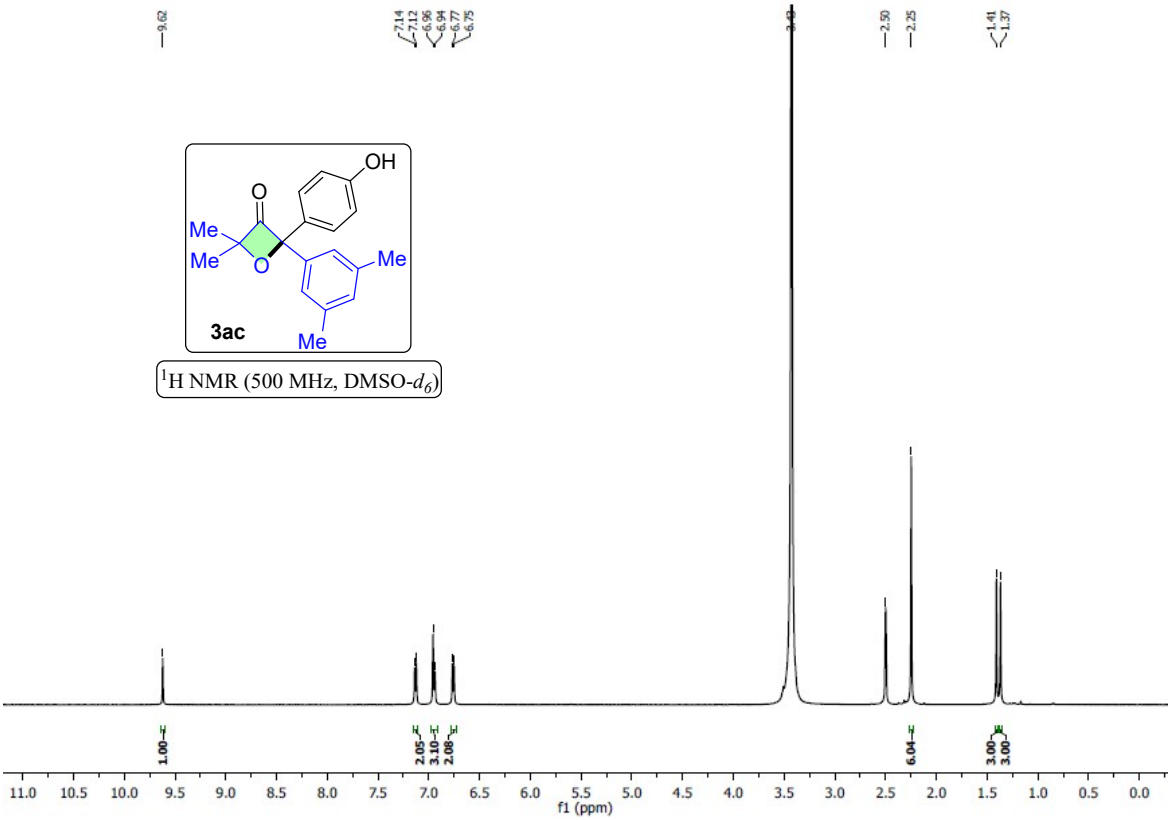
^{13}C NMR (125 MHz, DMSO-d_6)



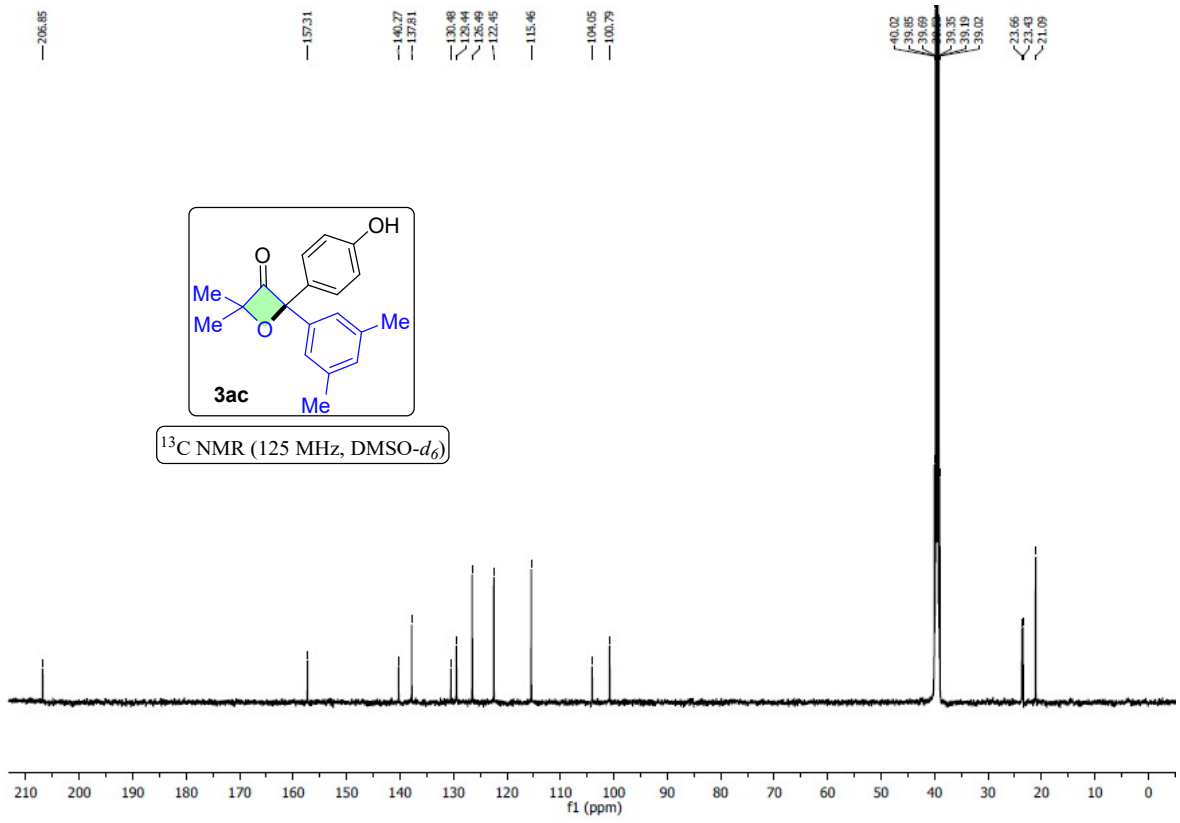
^{1}H NMR (400 MHz, DMSO-d_6)



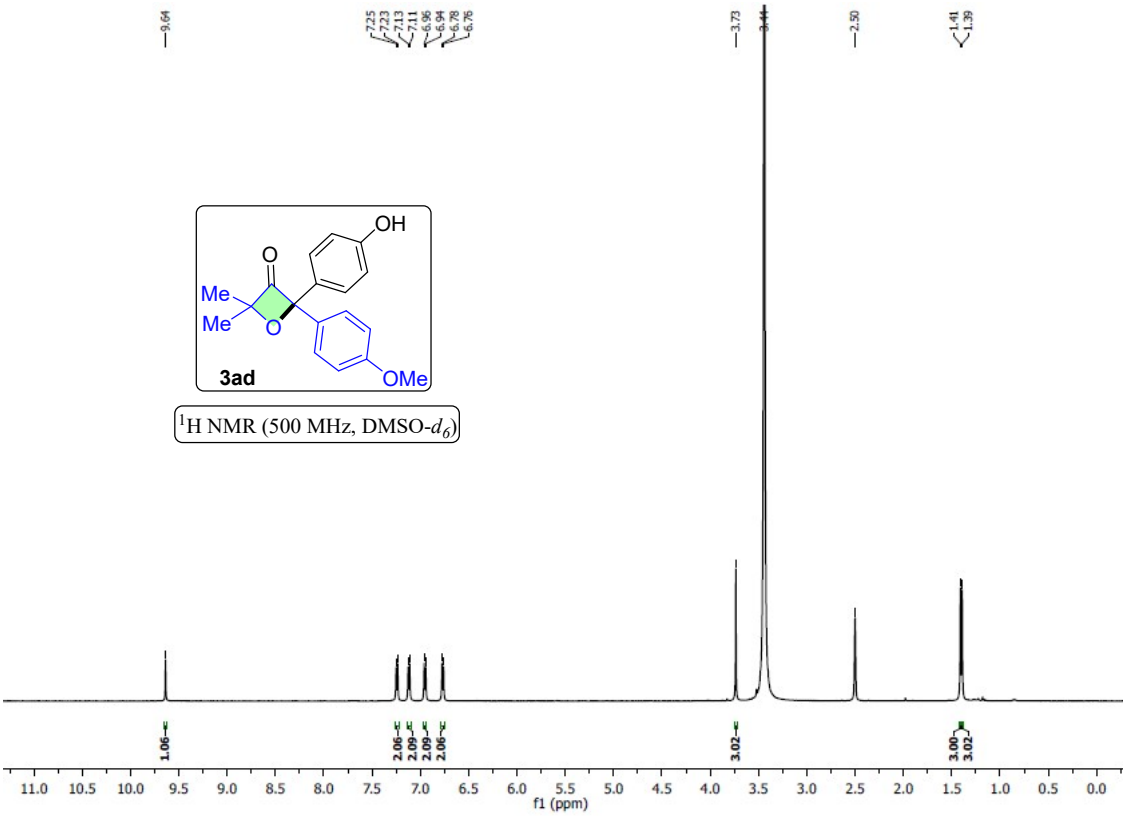
^{13}C NMR (100 MHz, DMSO-d_6)



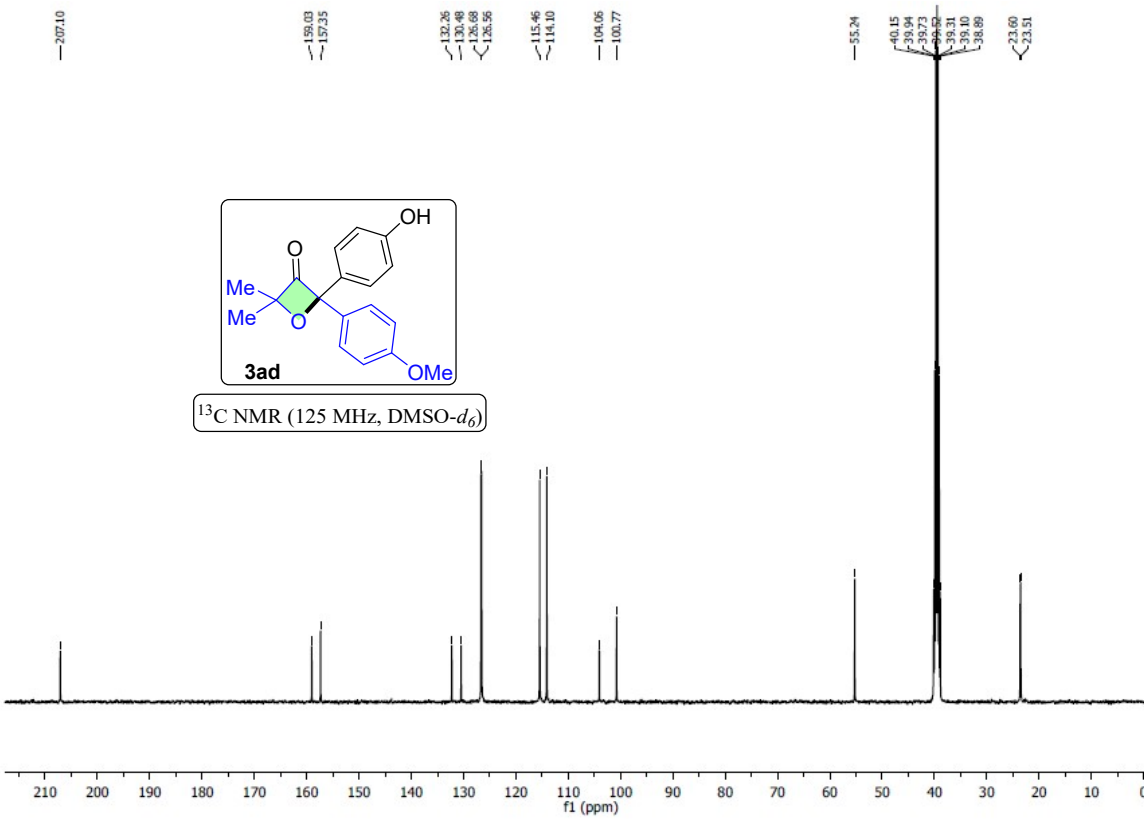
^{1}H NMR (500 MHz, DMSO-d_6)



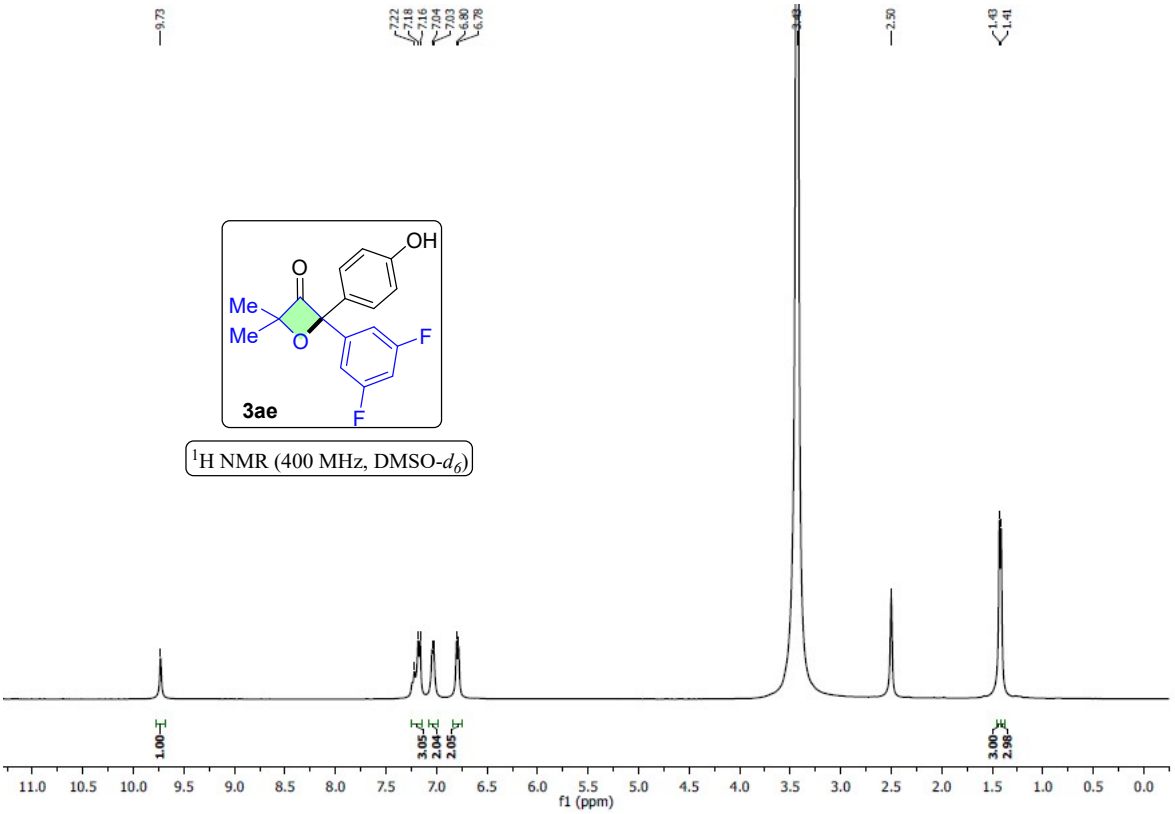
^{13}C NMR (125 MHz, DMSO-d_6)



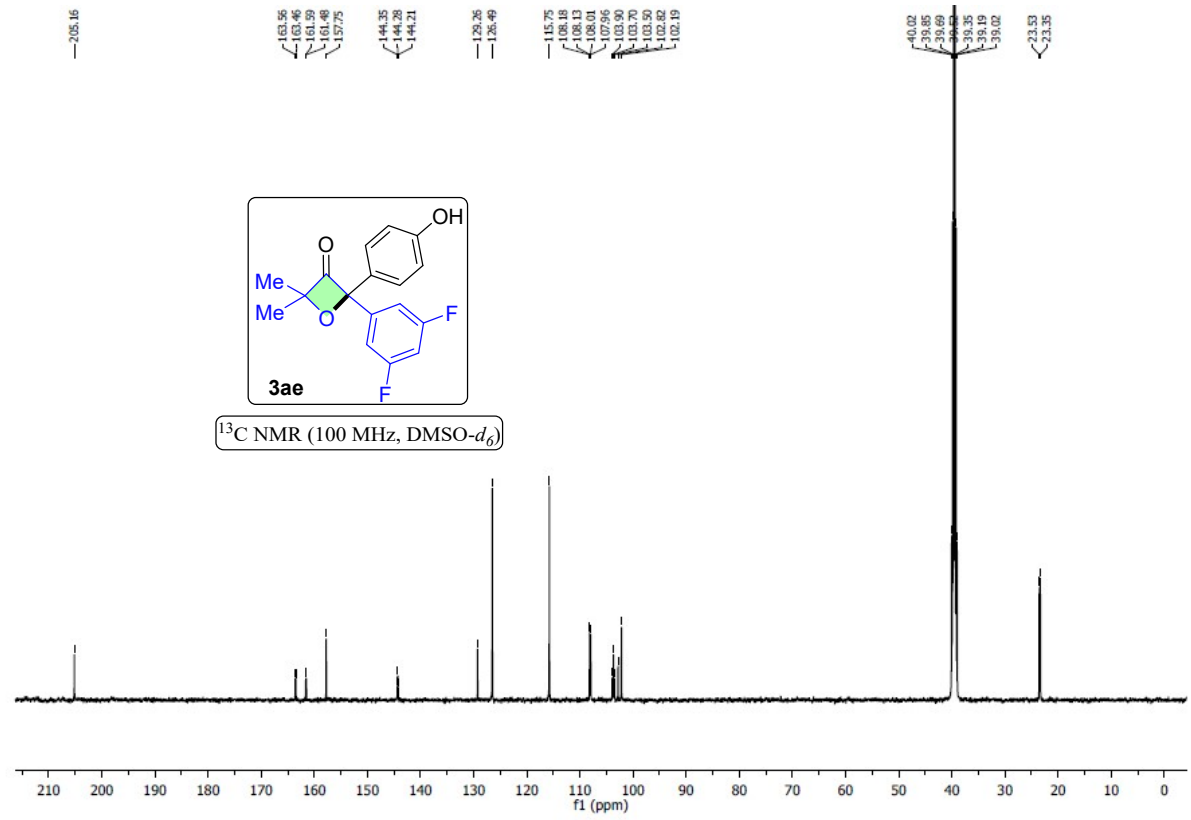
^{1}H NMR (500 MHz, DMSO-d_6)



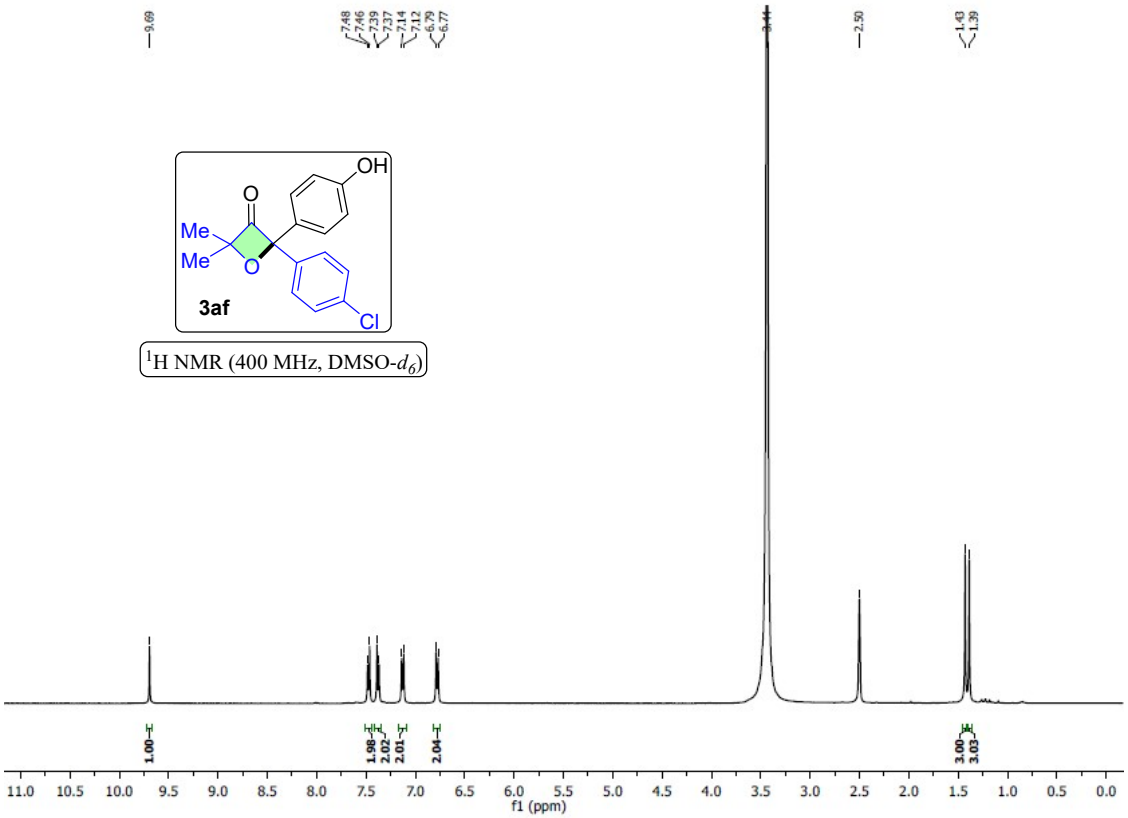
^{13}C NMR (125 MHz, DMSO-d_6)



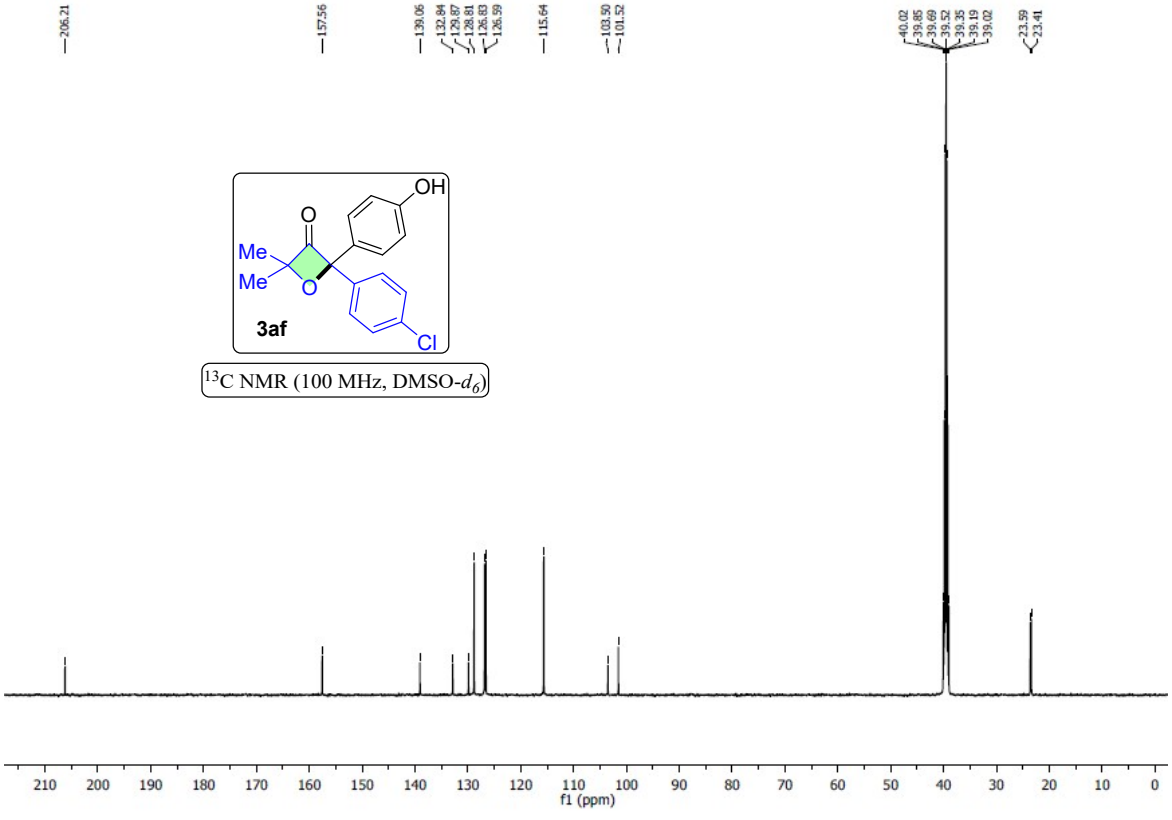
^{1}H NMR (400 MHz, DMSO-d_6)



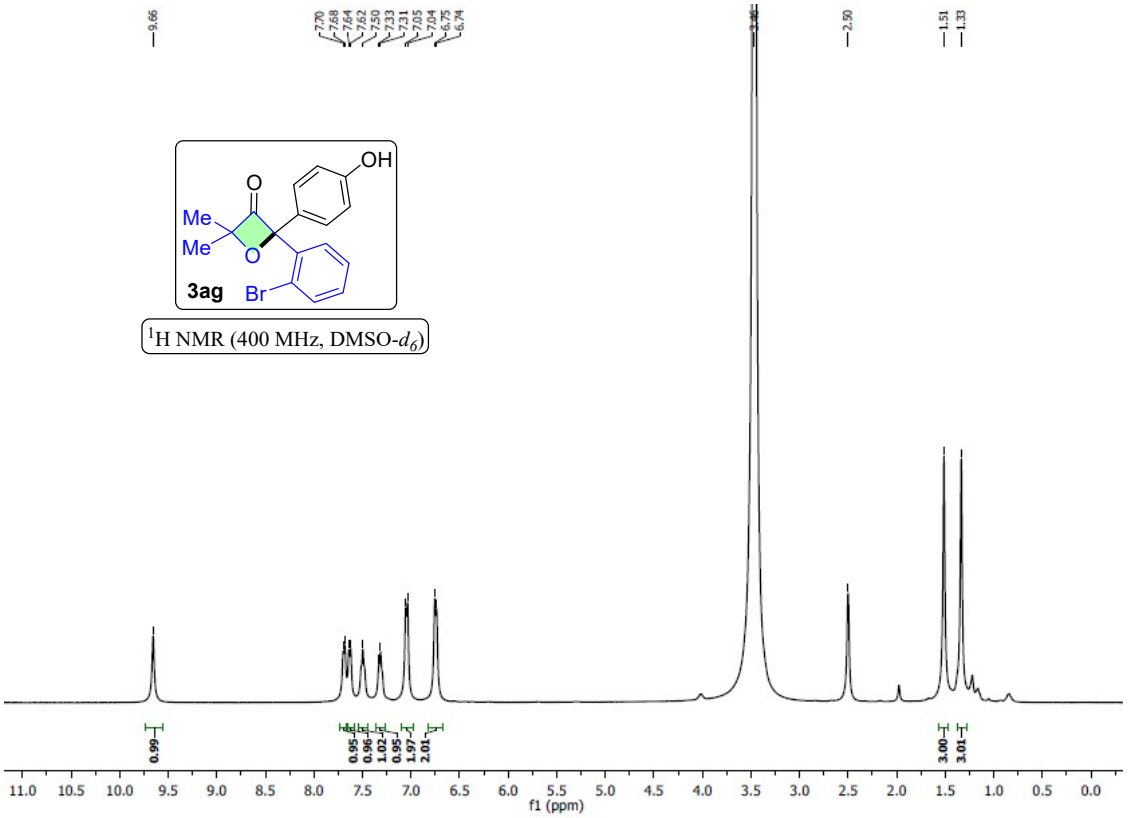
^{13}C NMR (100 MHz, DMSO-d_6)



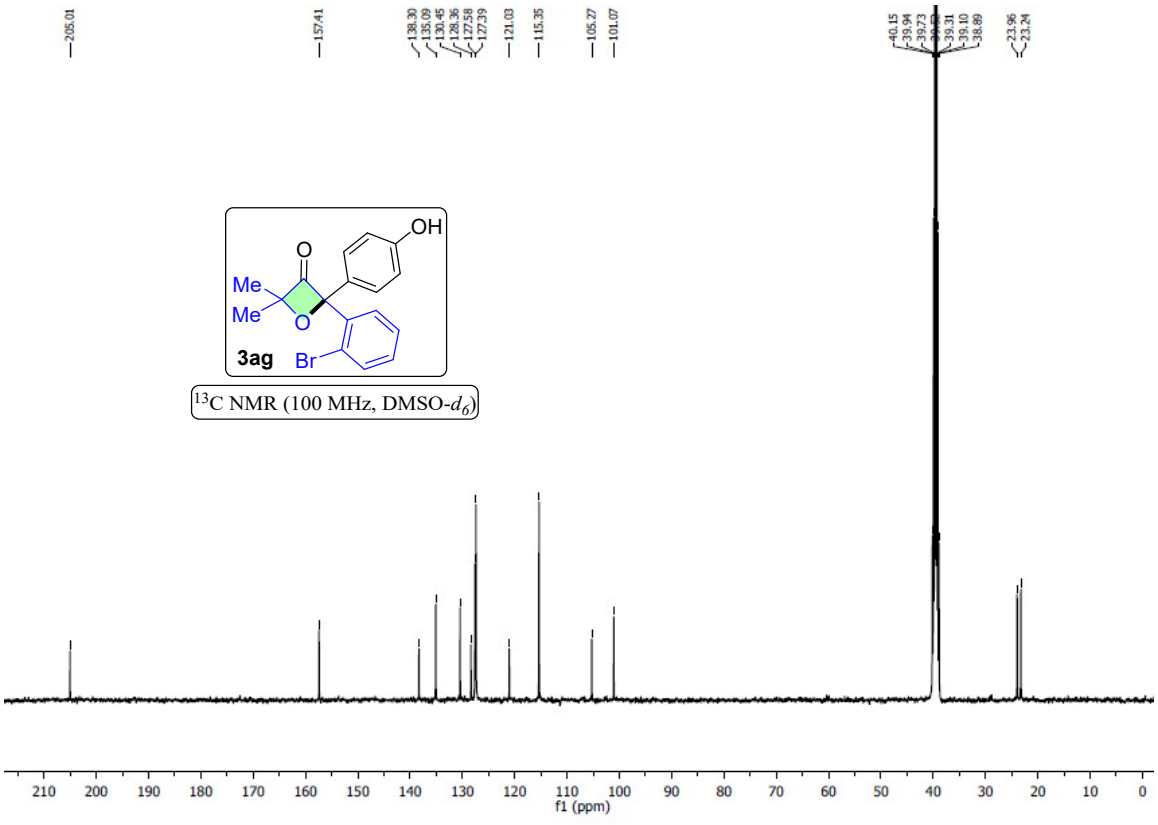
[1]H NMR (400 MHz, DMSO-d_6)



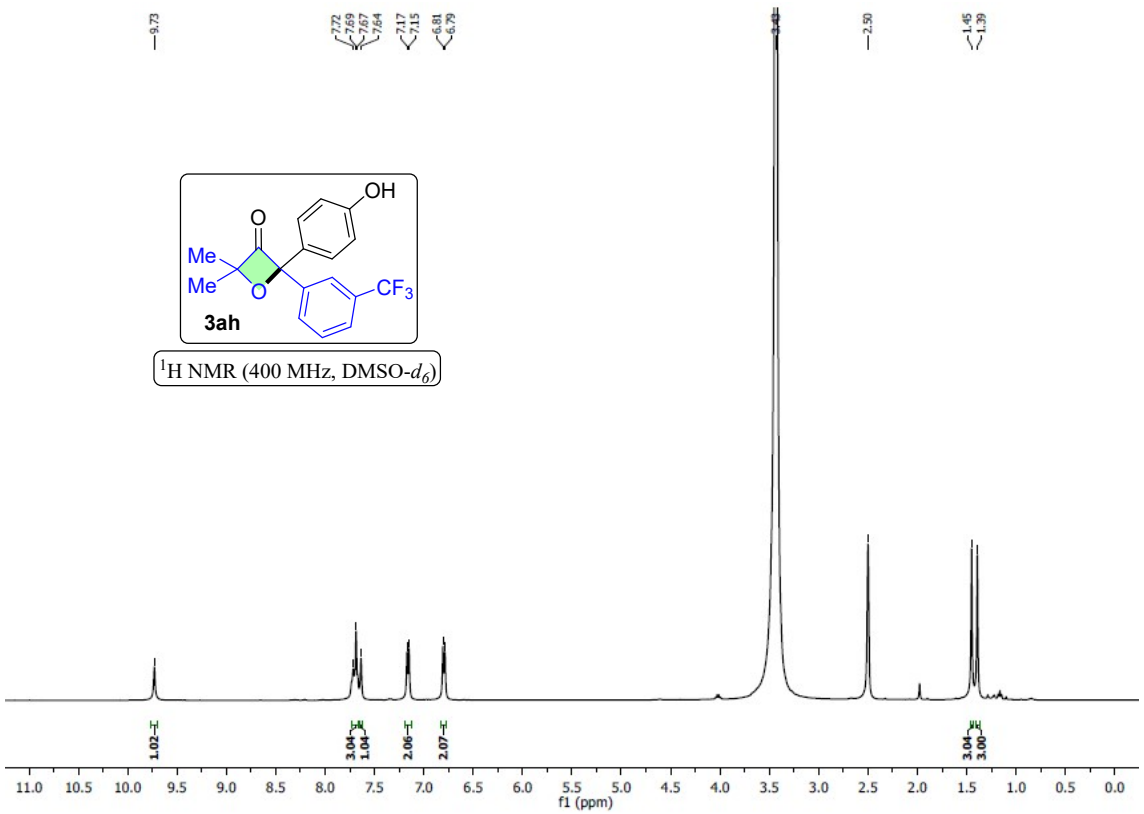
[13]C NMR (100 MHz, DMSO-d_6)



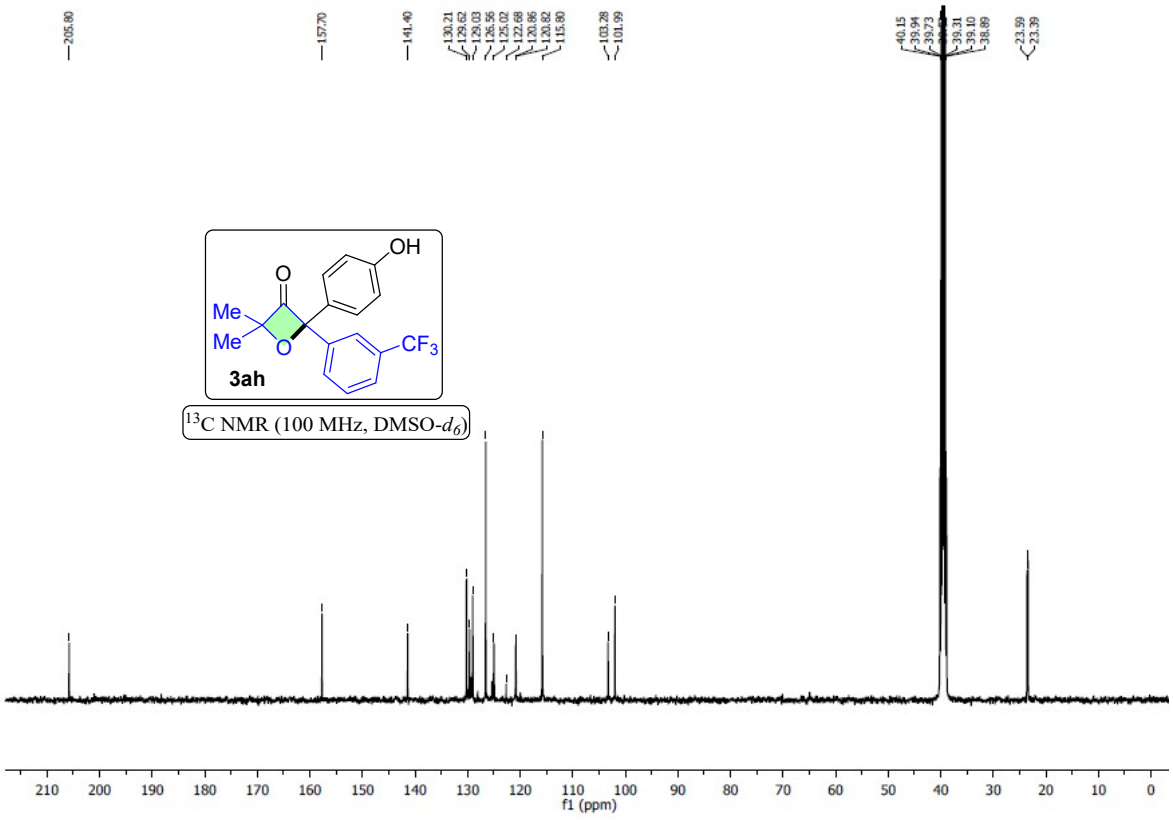
^{1}H NMR (400 MHz, DMSO-d_6)



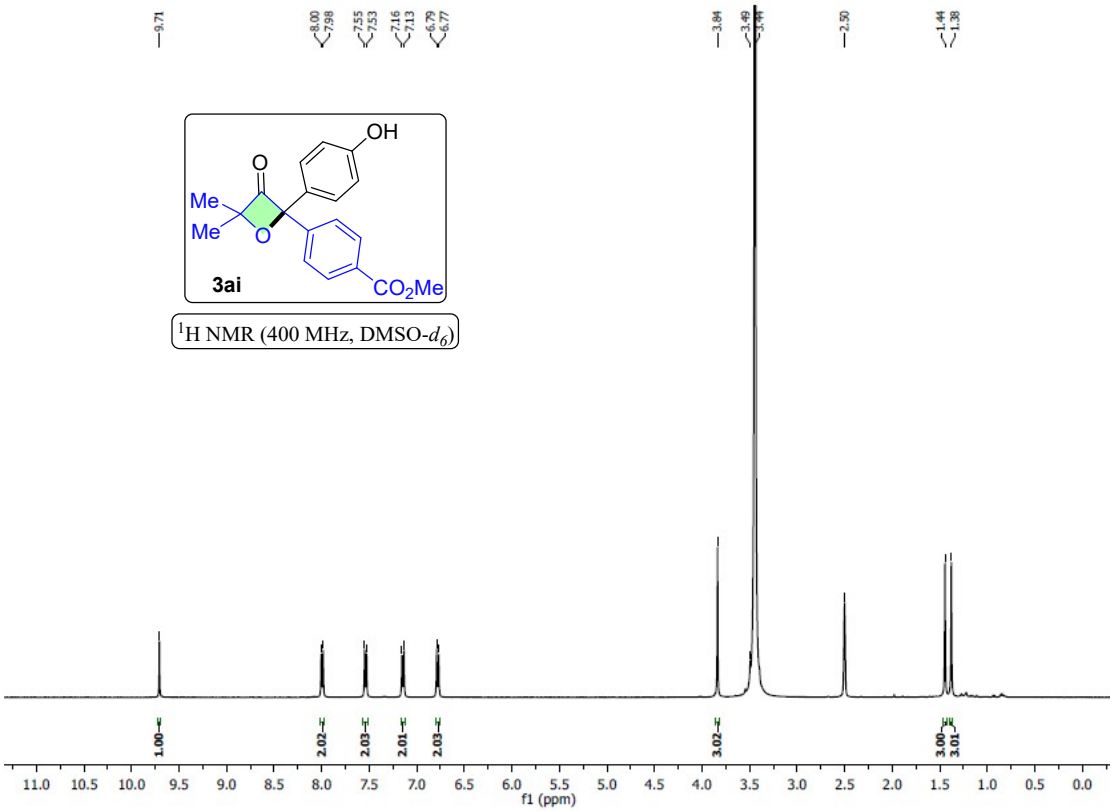
^{13}C NMR (100 MHz, DMSO-d_6)



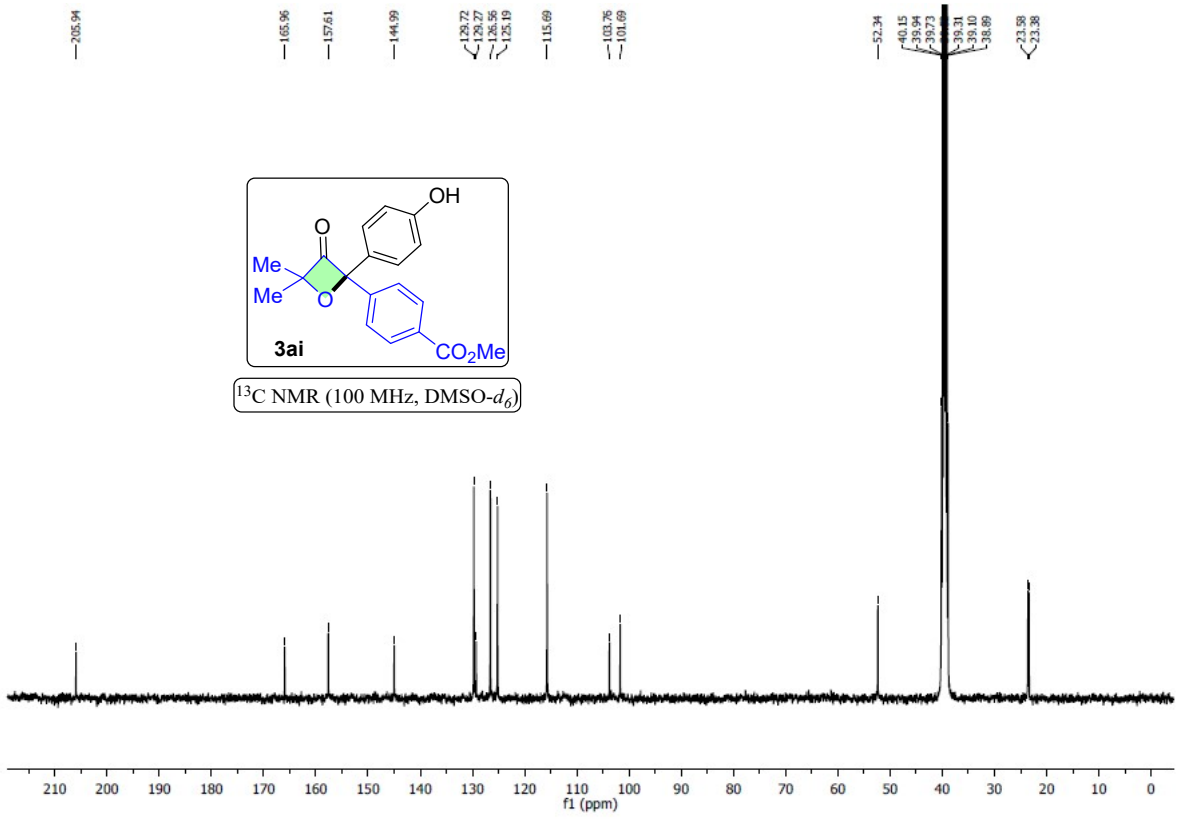
^{1}H NMR (400 MHz, DMSO-d_6)



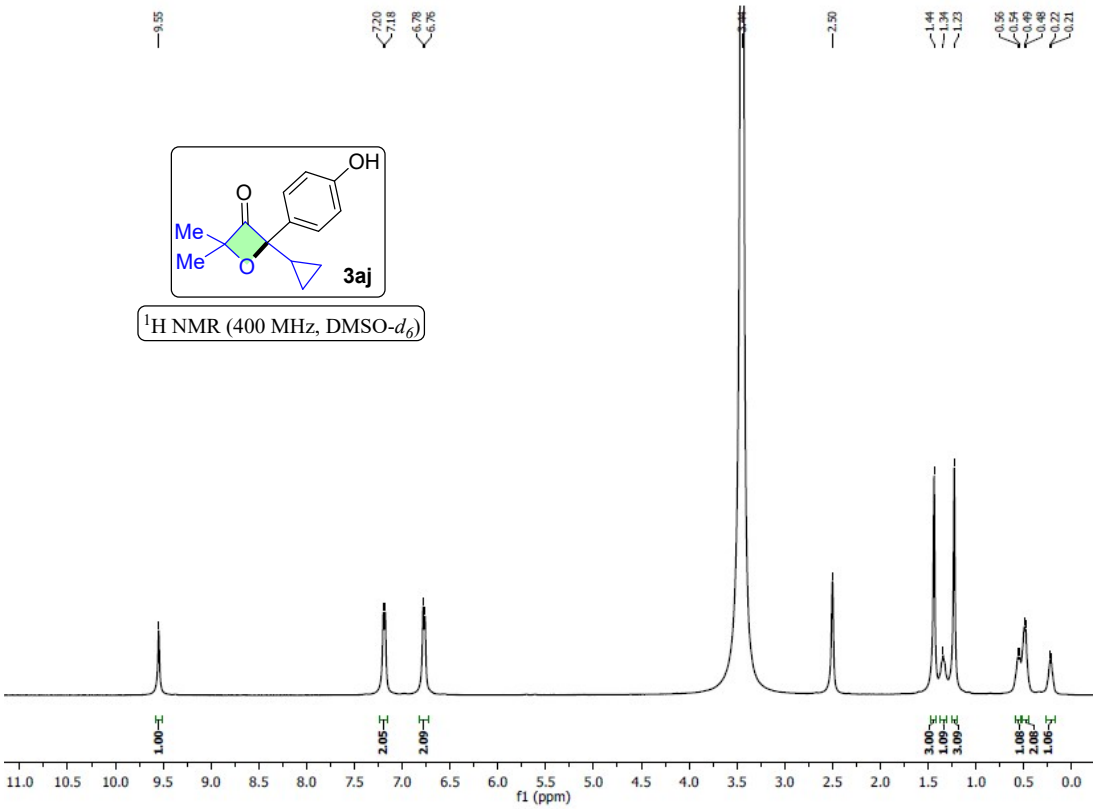
^{13}C NMR (100 MHz, DMSO-d_6)



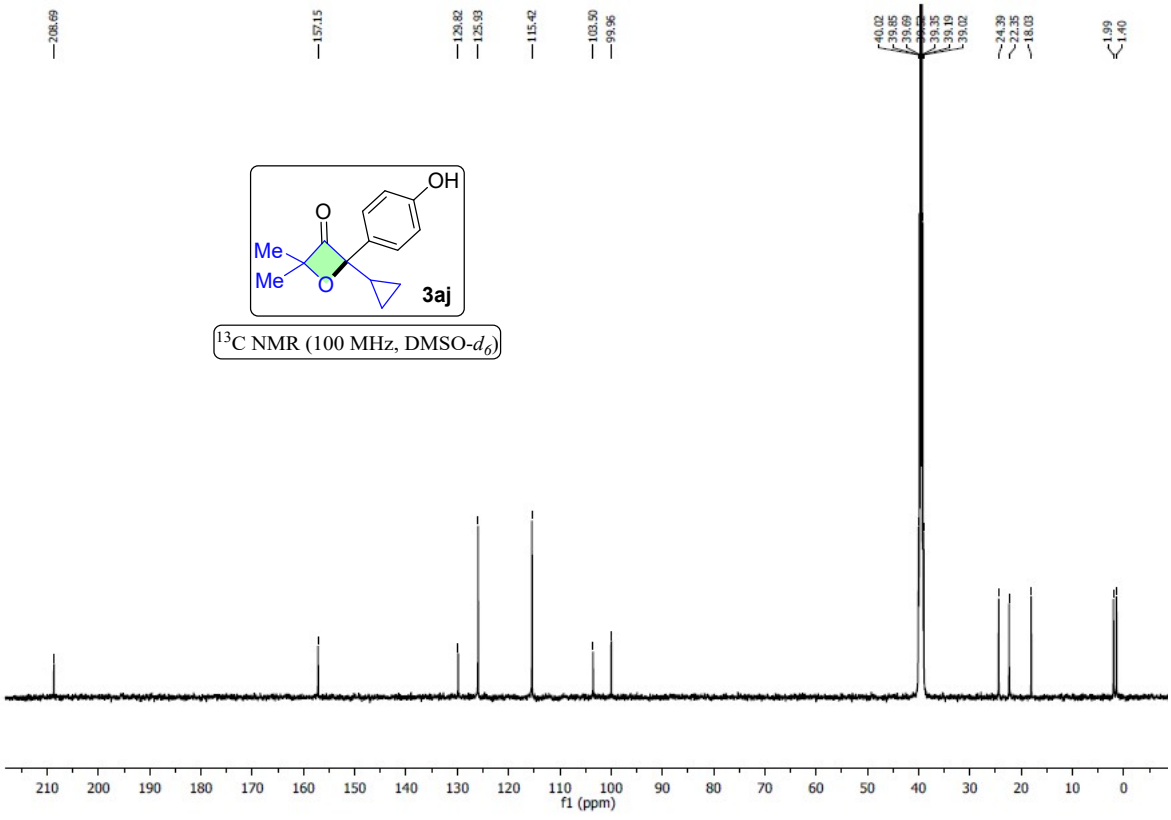
^{1}H NMR (400 MHz, DMSO-d_6)



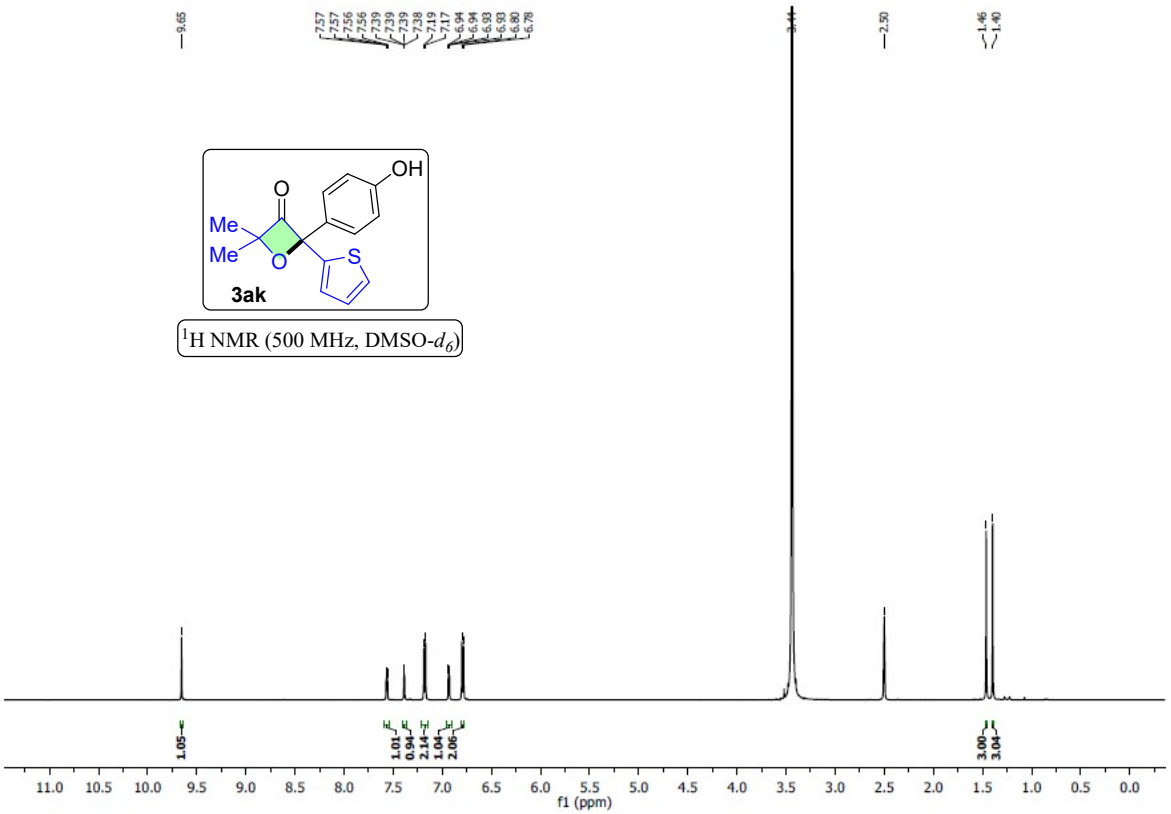
^{13}C NMR (100 MHz, DMSO-d_6)



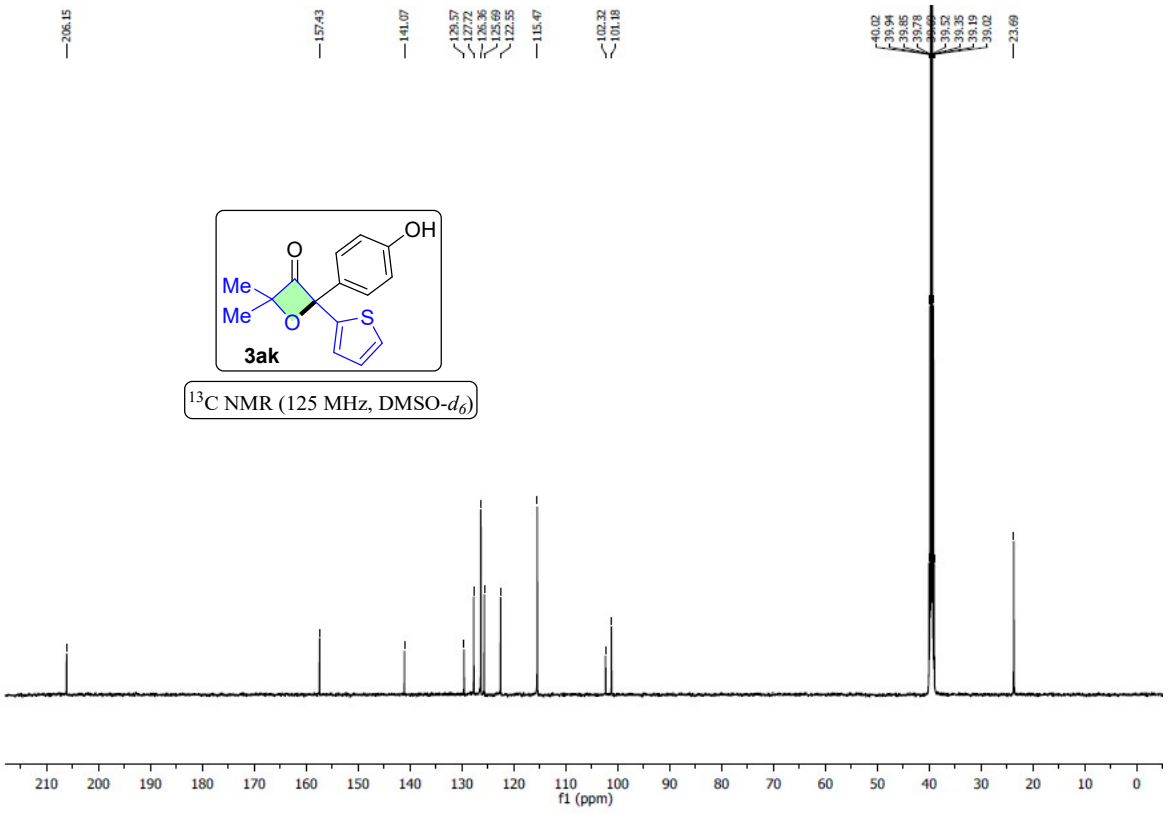
^{1}H NMR (400 MHz, DMSO-d_6)



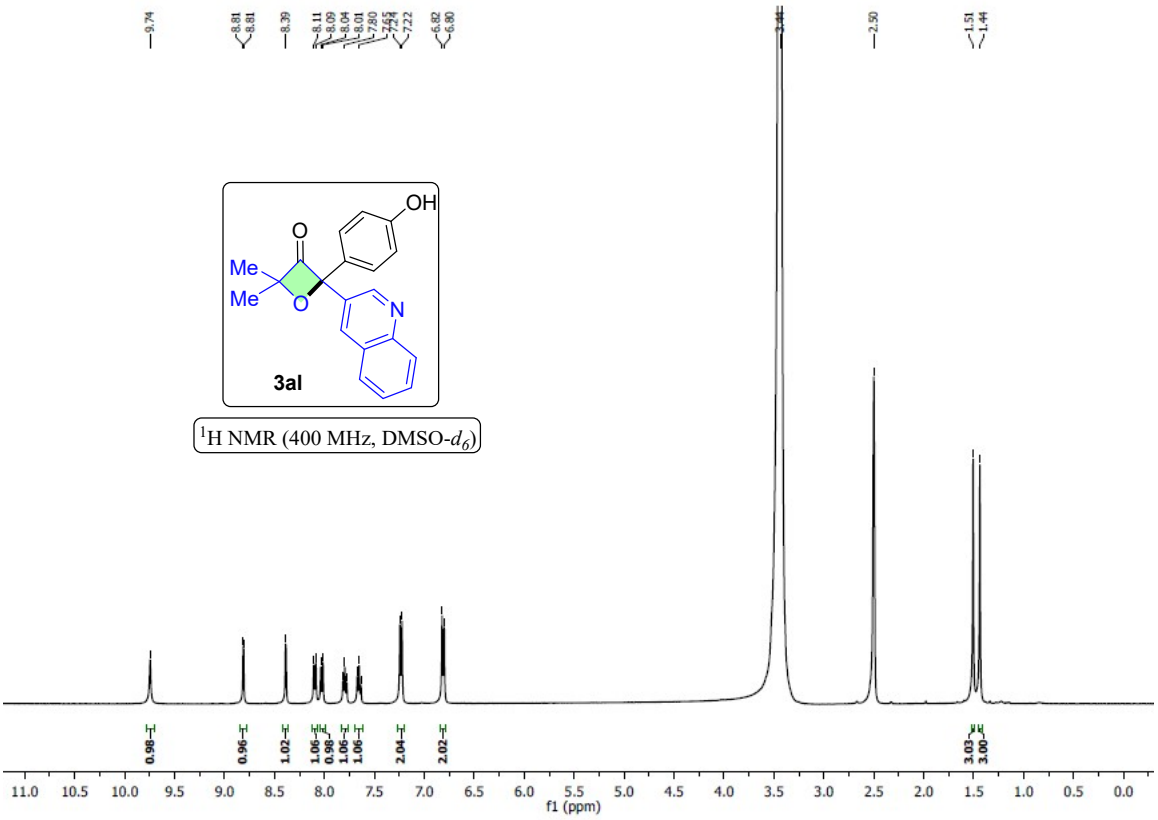
^{13}C NMR (100 MHz, DMSO-d_6)



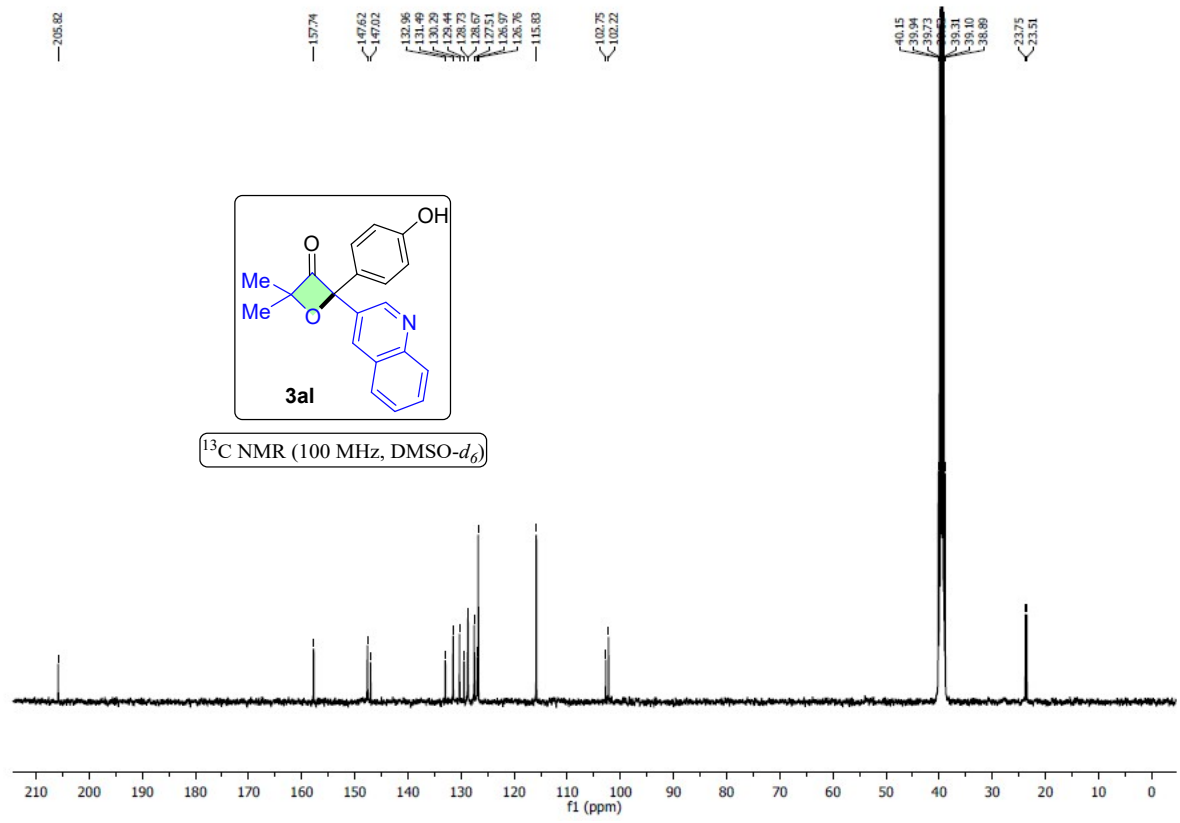
^{1}H NMR (500 MHz, DMSO-d_6)



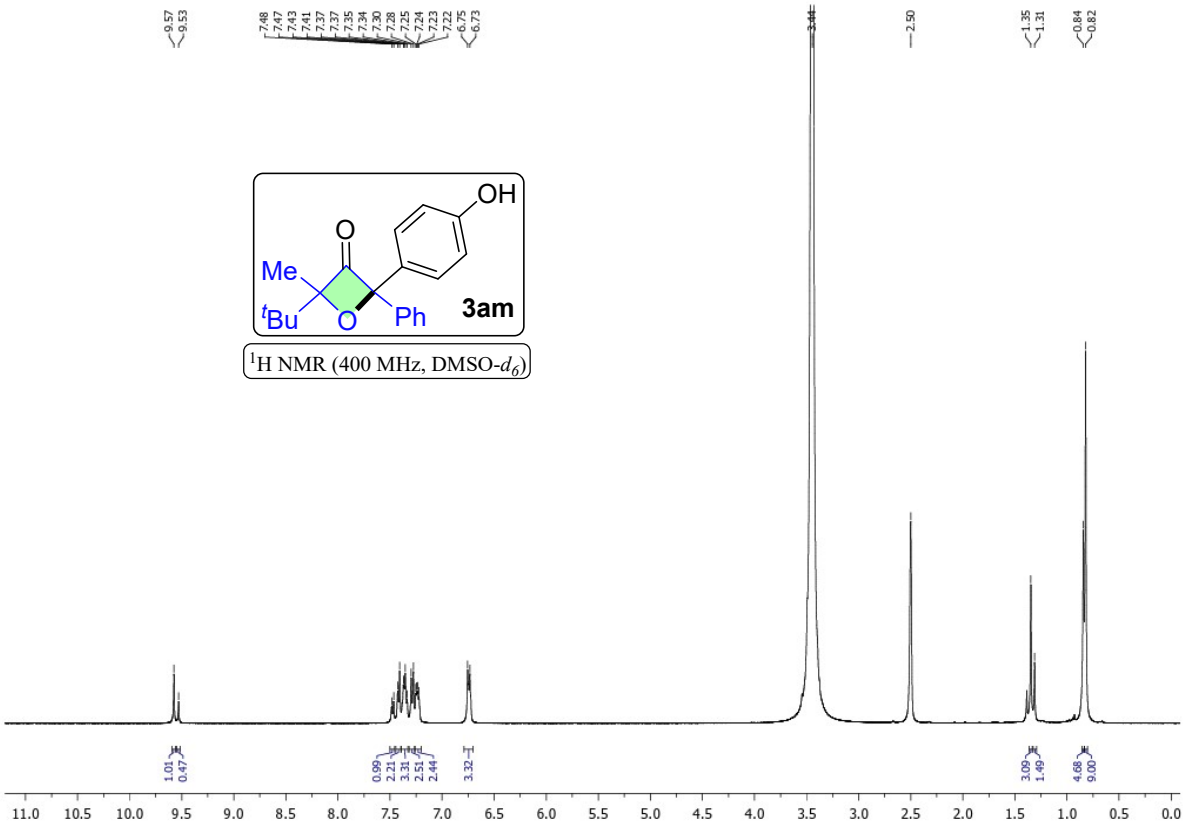
^{13}C NMR (125 MHz, DMSO-d_6)



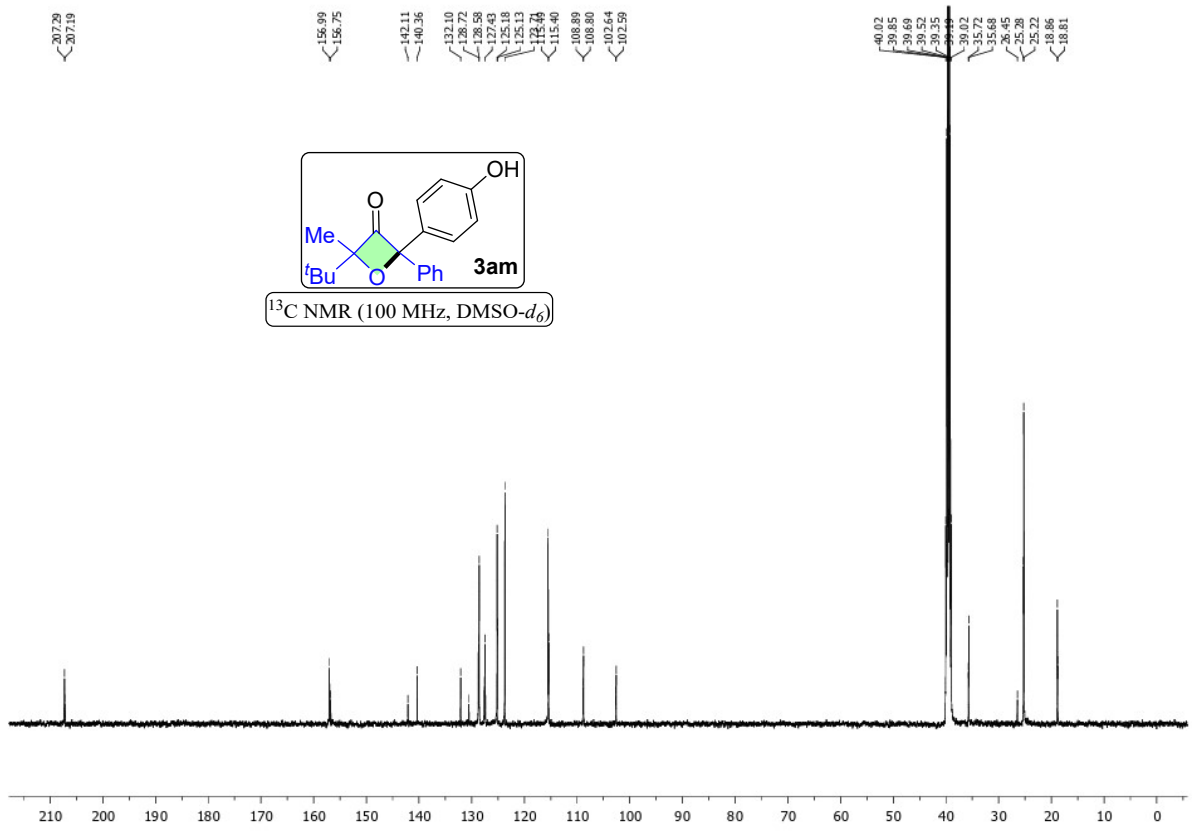
^{1}H NMR (400 MHz, DMSO-d_6)



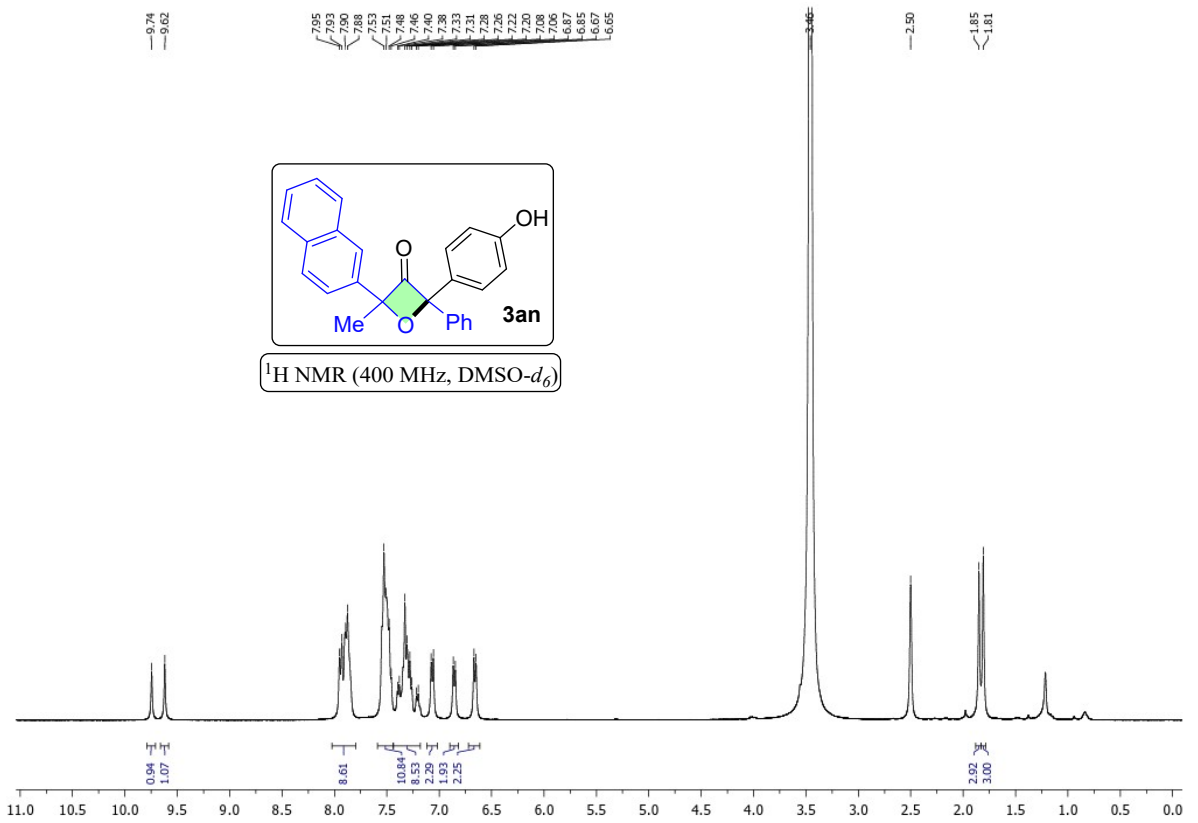
^{13}C NMR (100 MHz, DMSO-d_6)



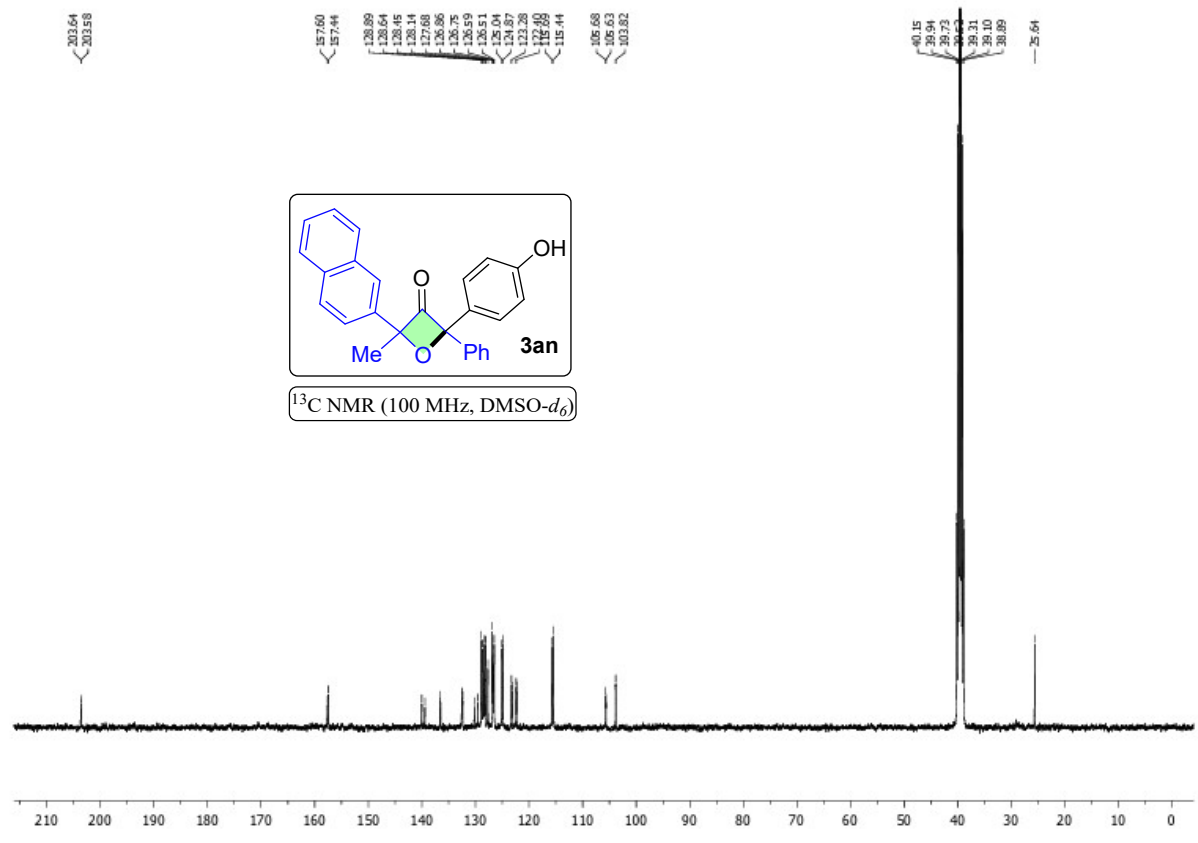
^{1}H NMR (400 MHz, DMSO-d_6)



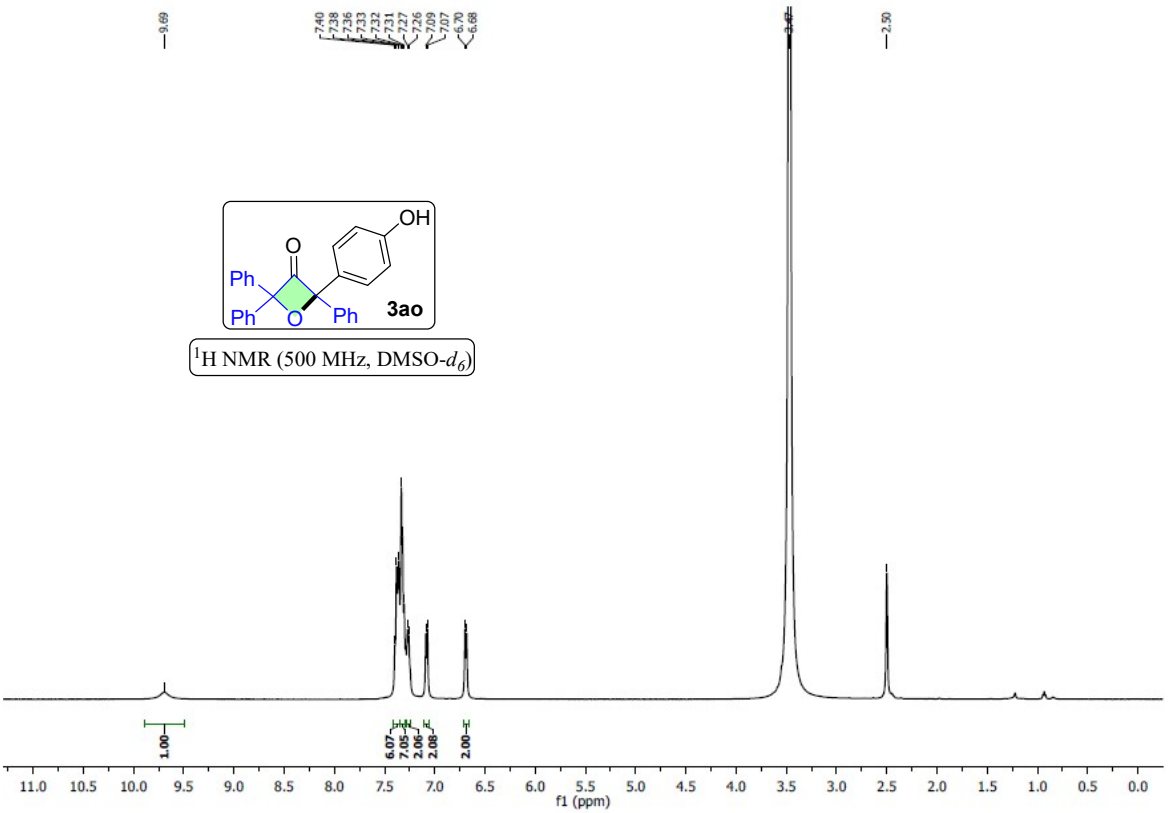
^{13}C NMR (100 MHz, DMSO-d_6)



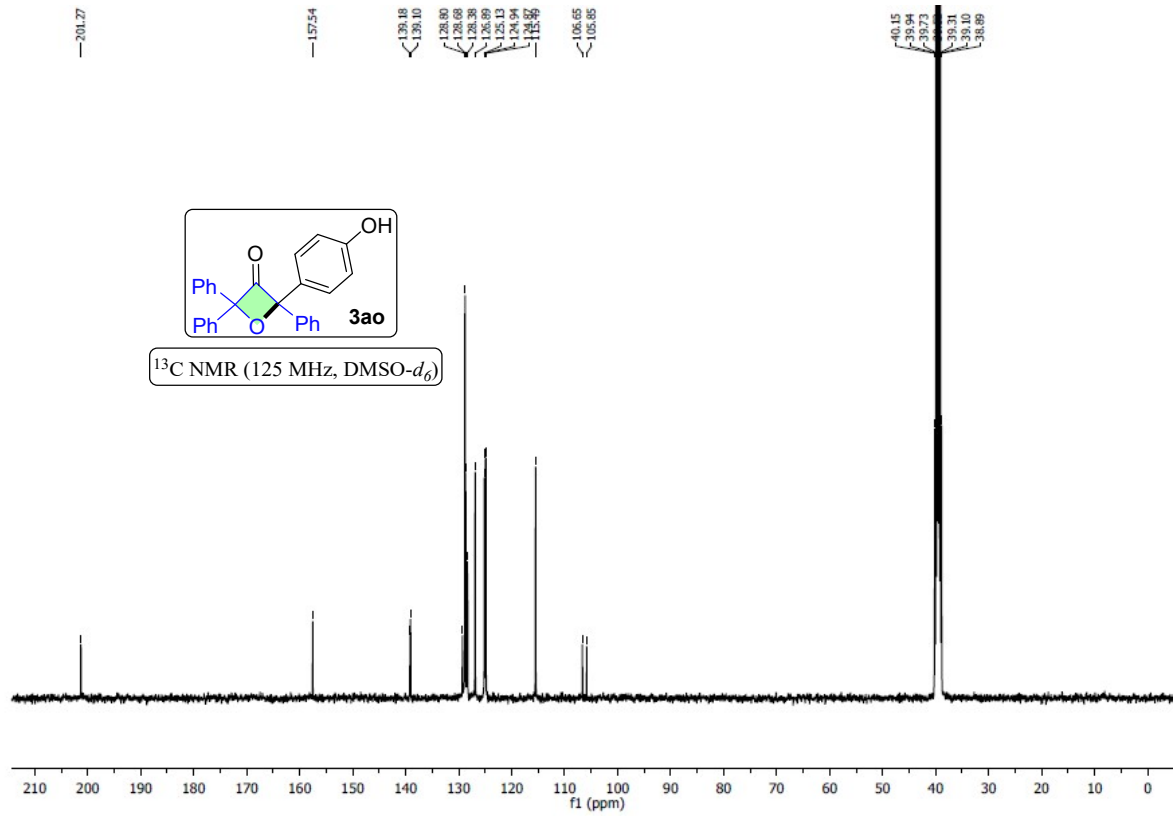
^{1}H NMR (400 MHz, DMSO-d_6)



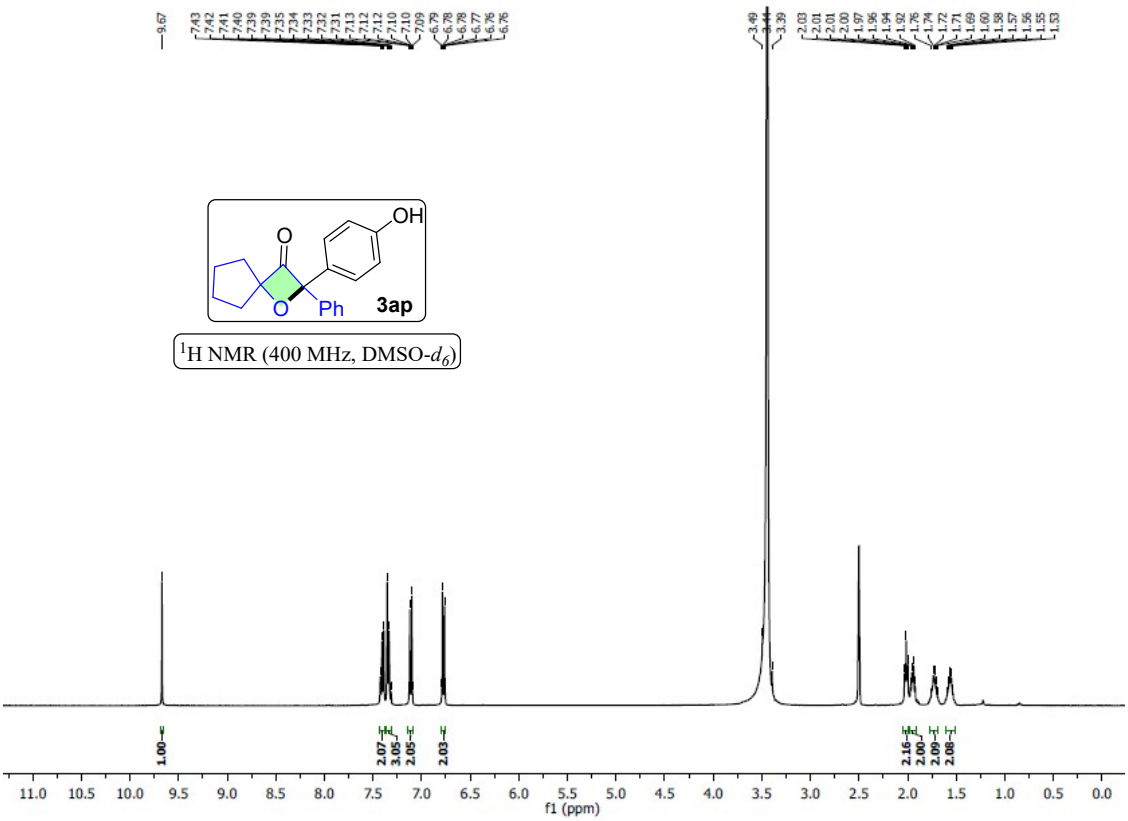
^{13}C NMR (100 MHz, DMSO-d_6)



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



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



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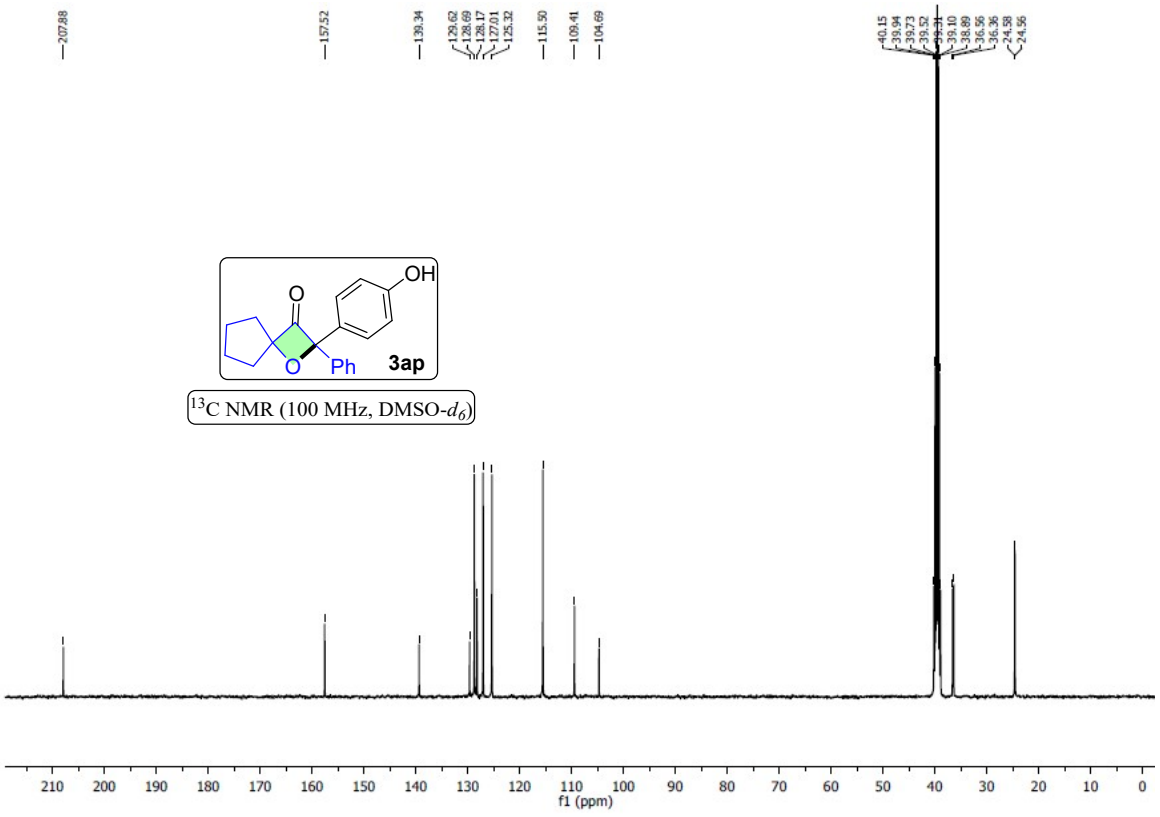
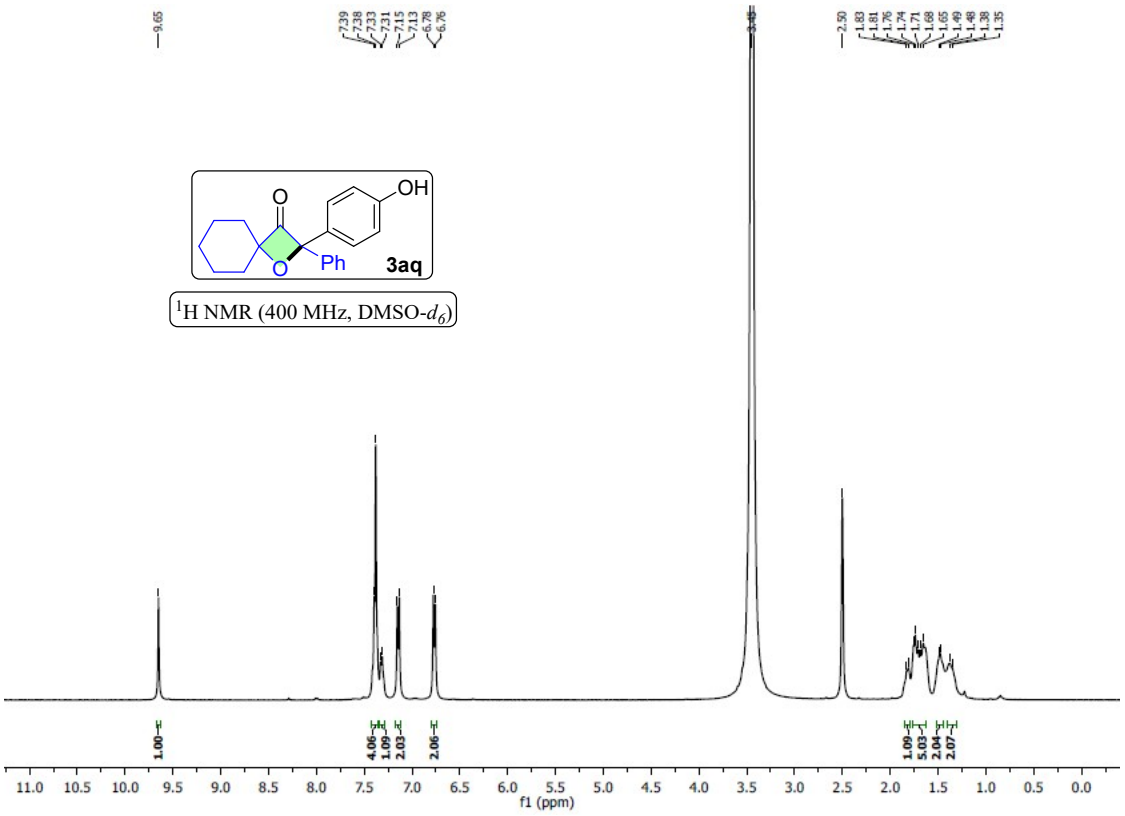
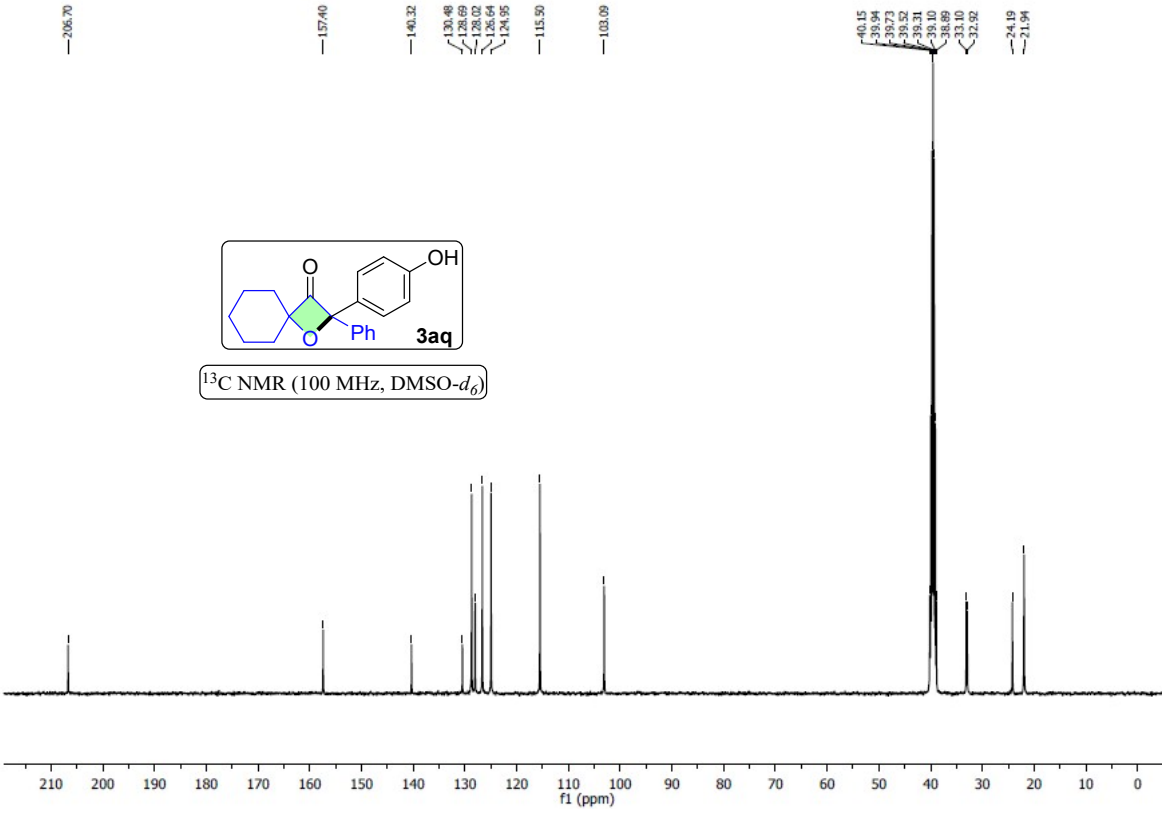


^{13}C NMR (100 MHz, DMSO-d_6)



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



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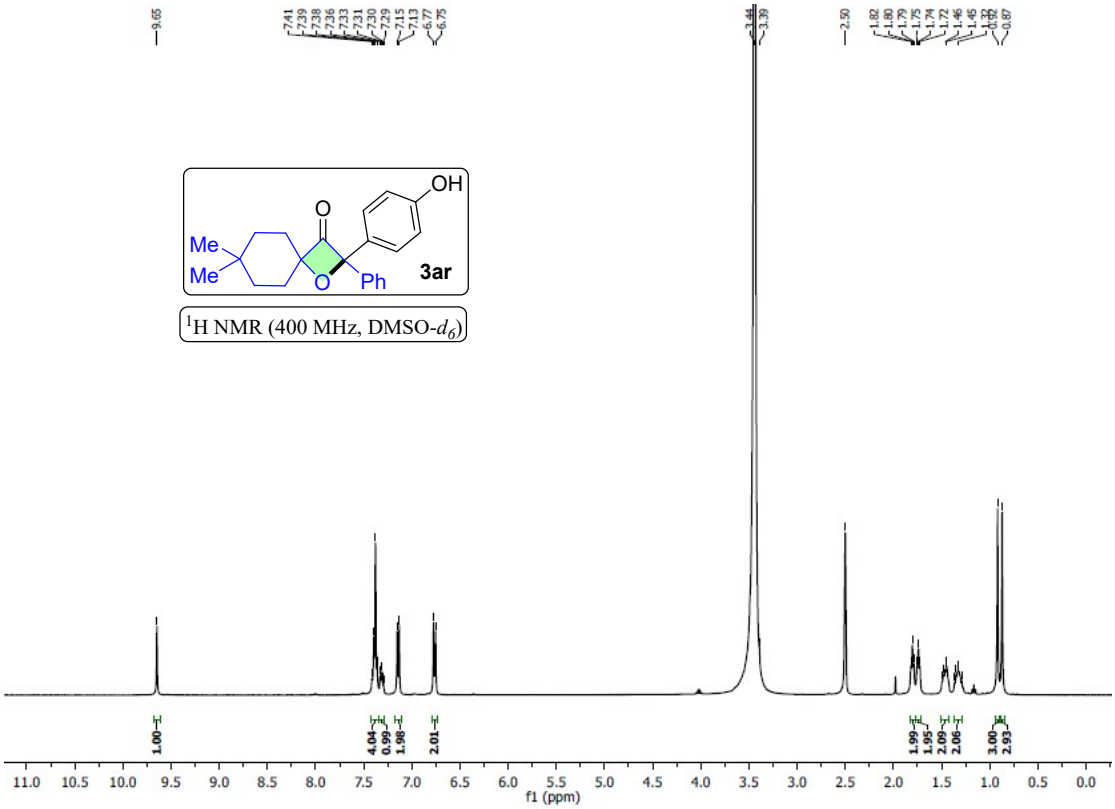
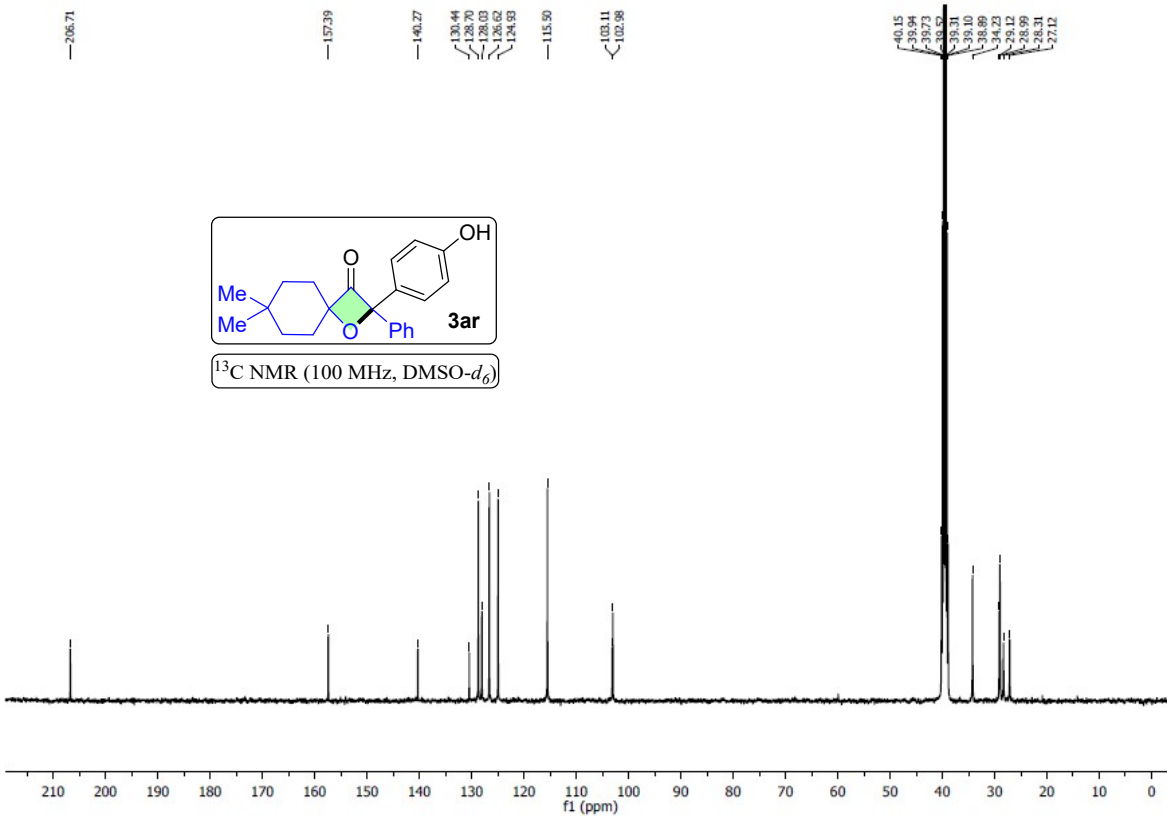
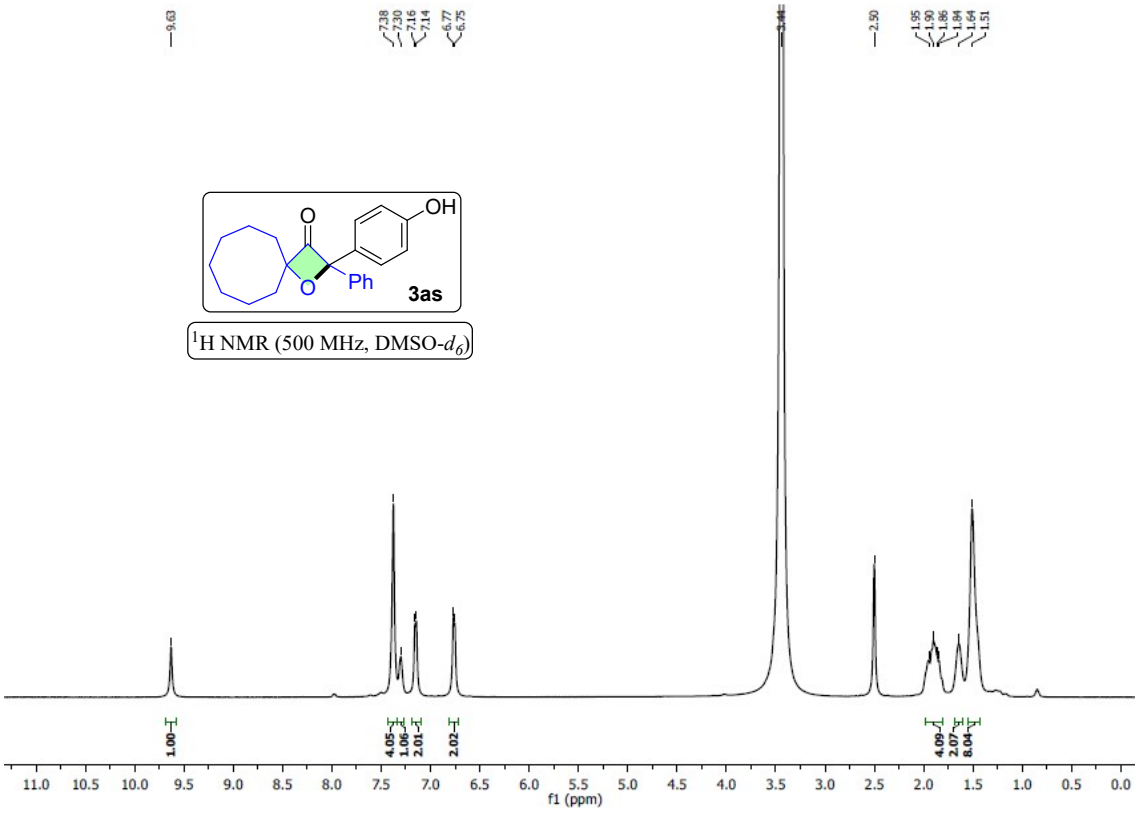


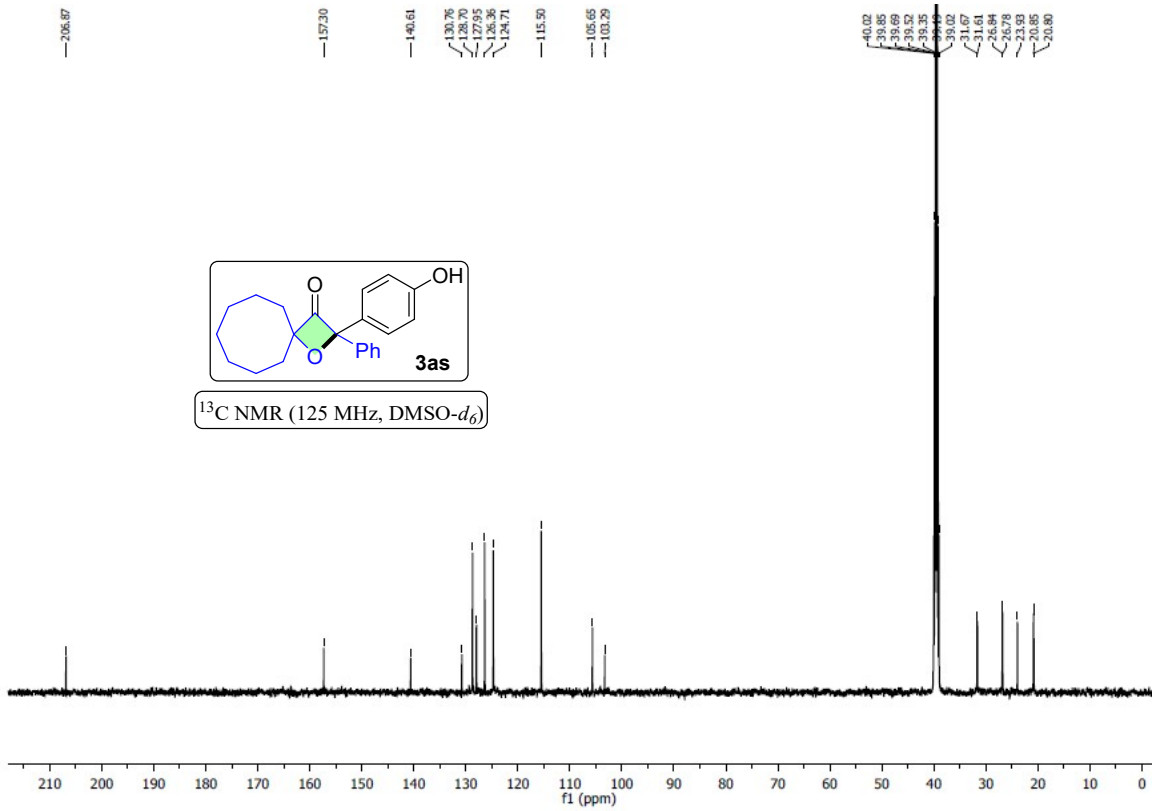
^{1}H NMR (400 MHz, DMSO-d_6)



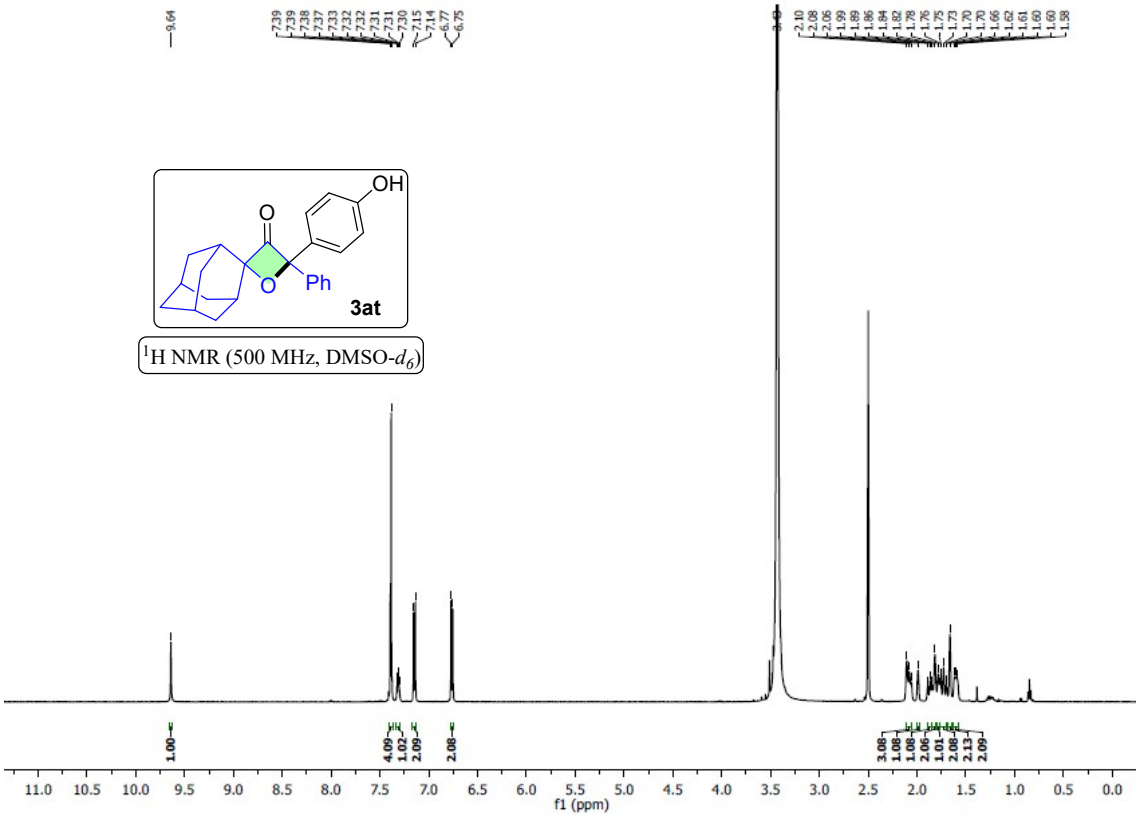
^{13}C NMR (100 MHz, DMSO-d_6)



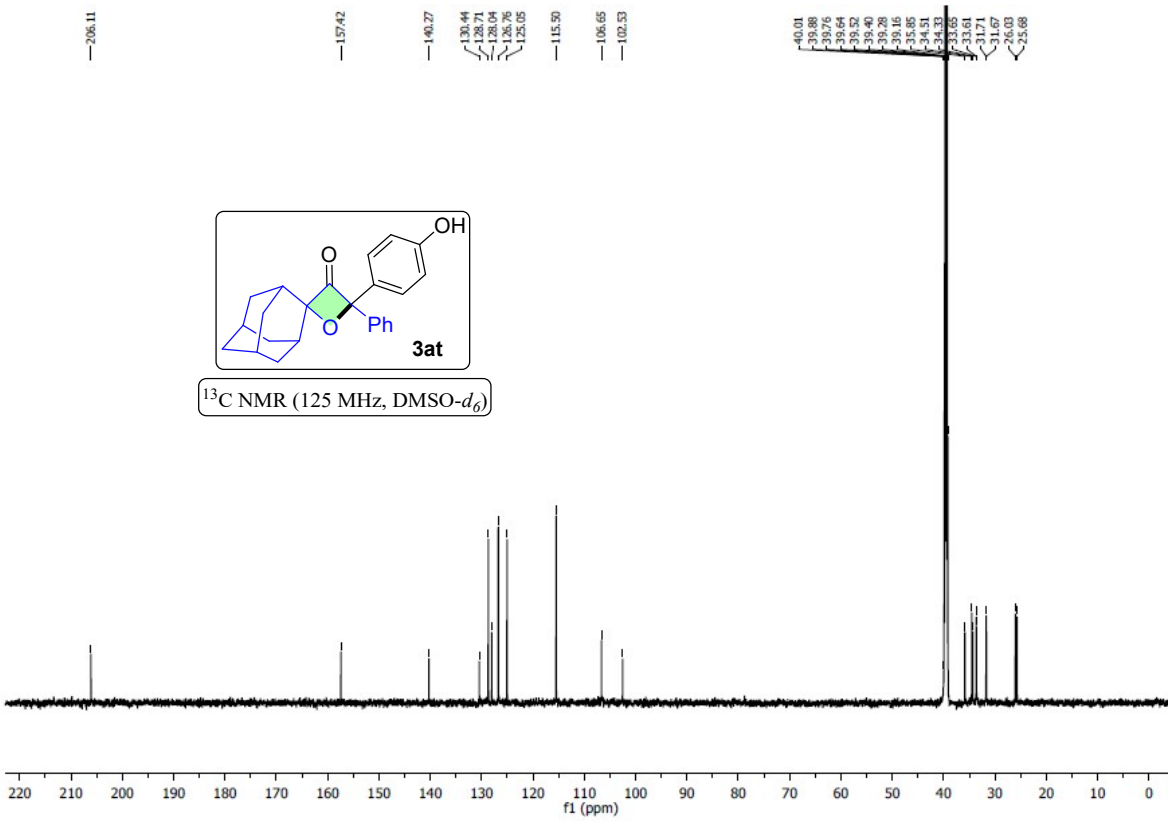
^{1}H NMR (500 MHz, DMSO-d_6)



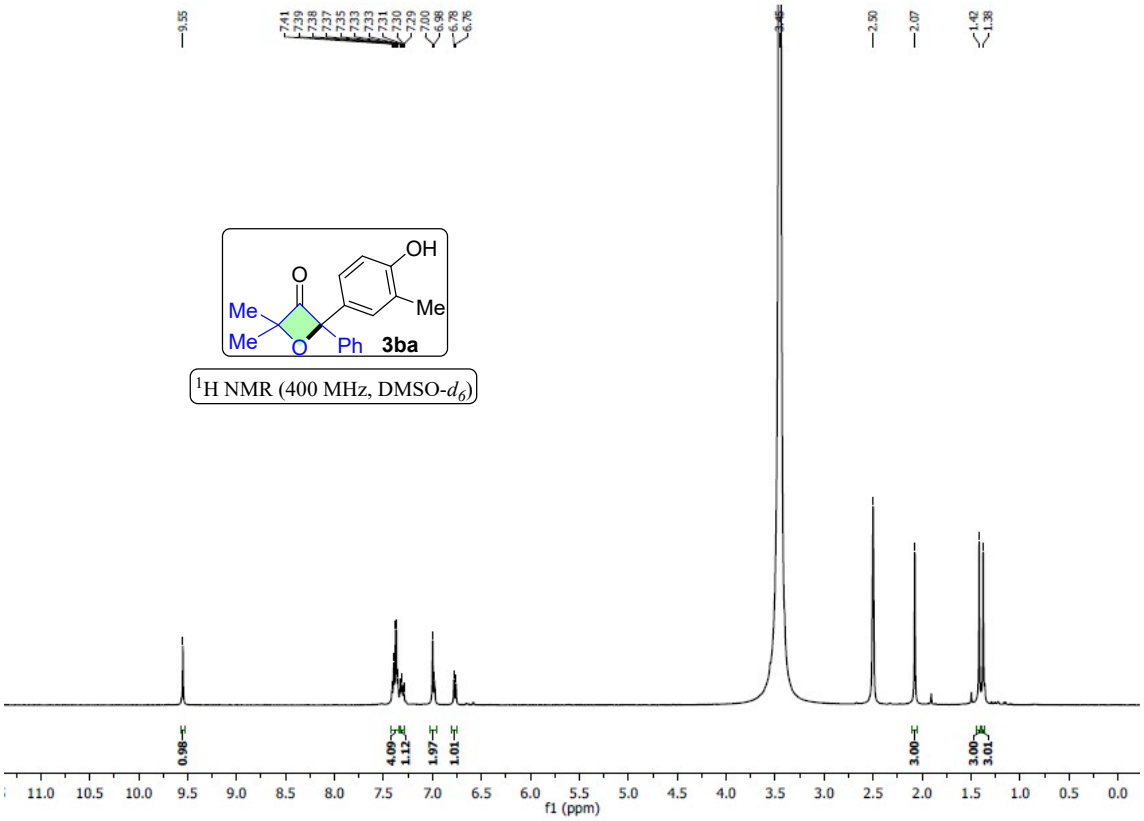
^{13}C NMR (125 MHz, DMSO-d_6)



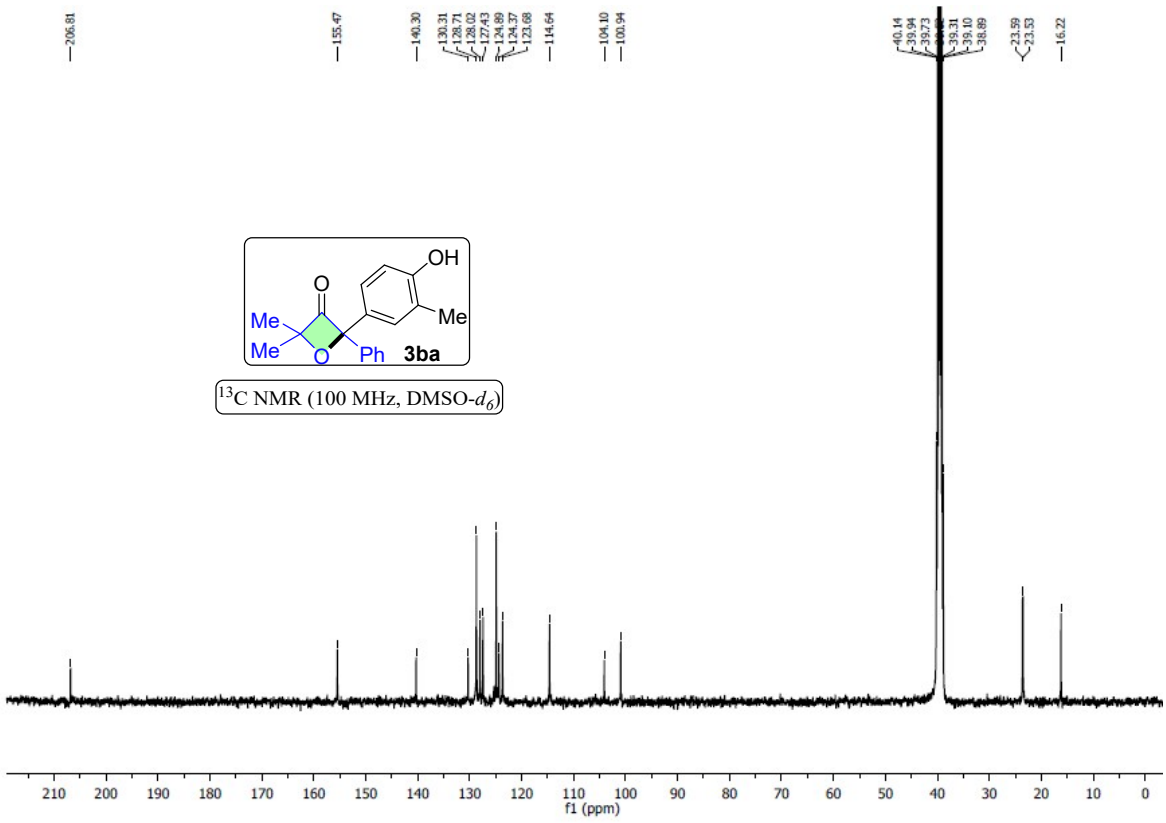
^{1}H NMR (500 MHz, DMSO-d_6)



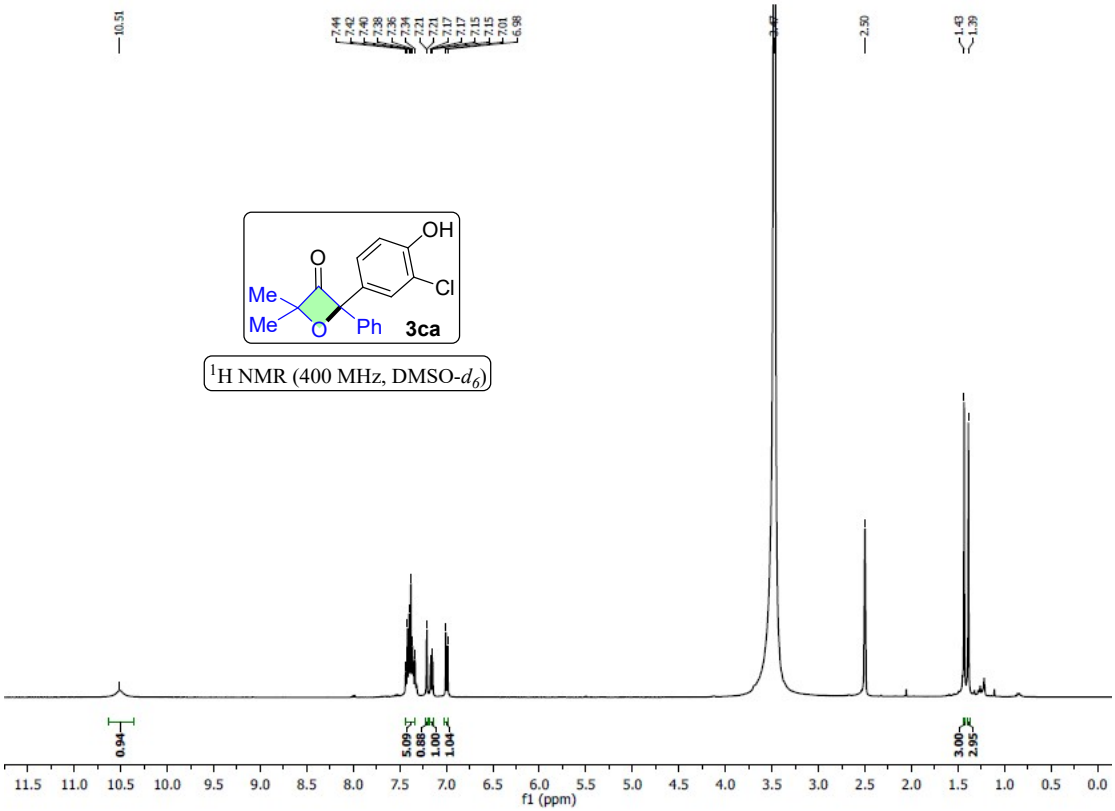
^{13}C NMR (125 MHz, DMSO-d_6)



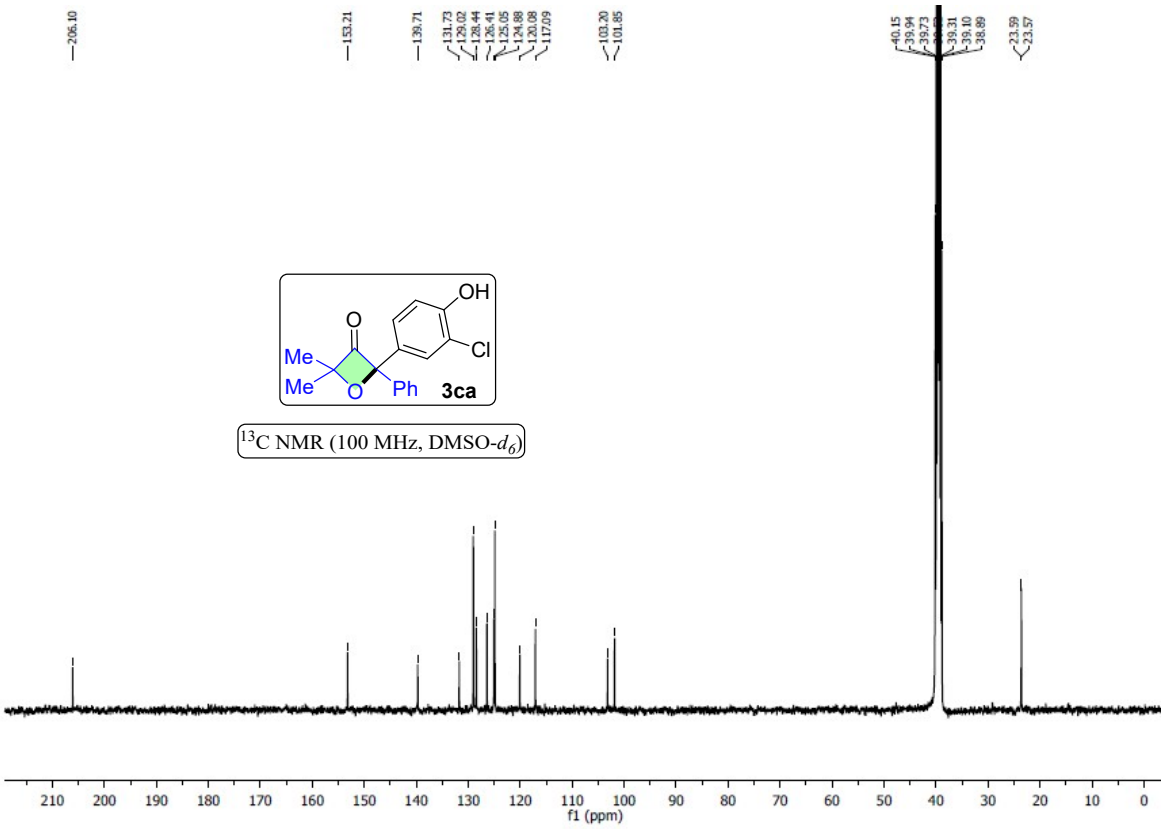
^{1}H NMR (400 MHz, DMSO-d_6)



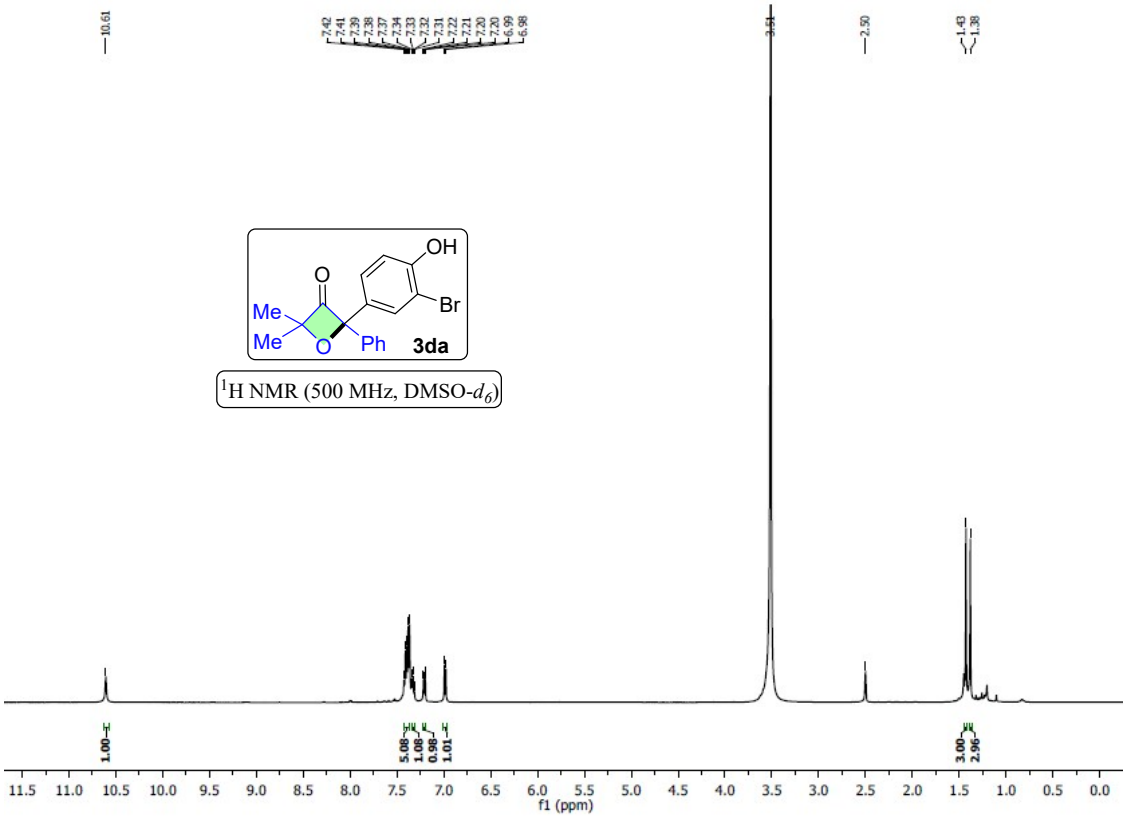
^{13}C NMR (100 MHz, DMSO-d_6)



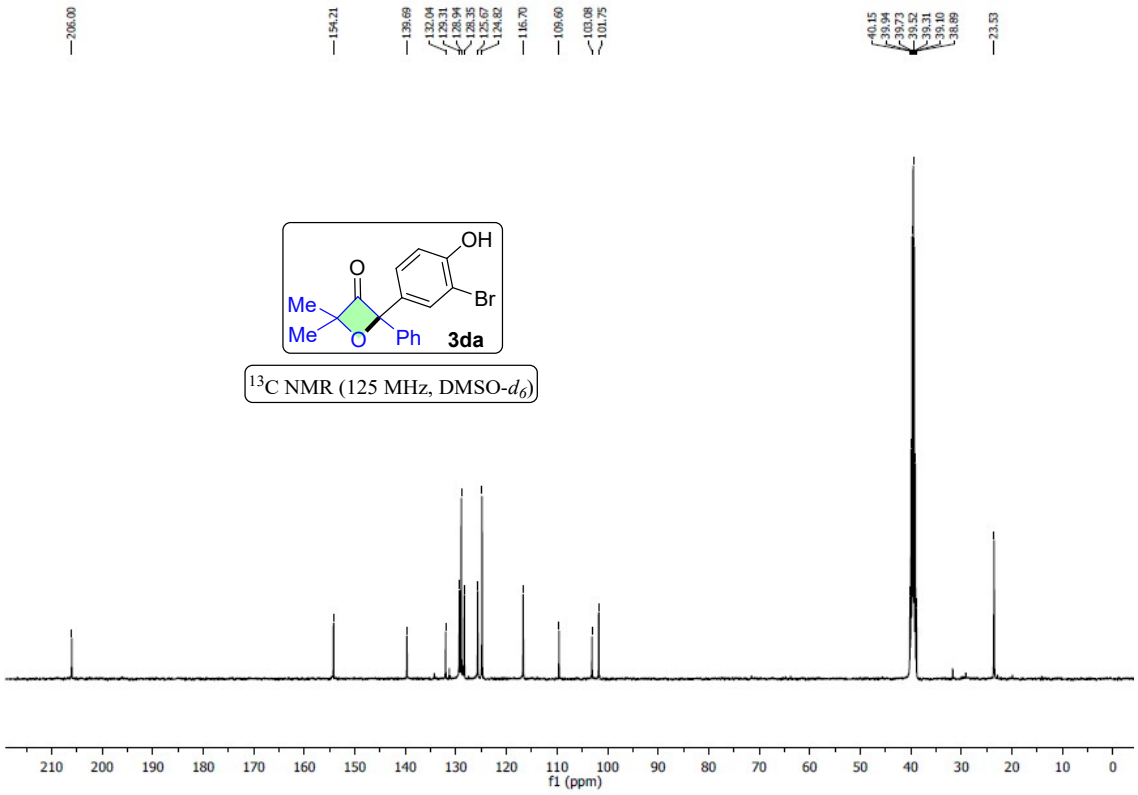
^{1}H NMR (400 MHz, DMSO-d_6)



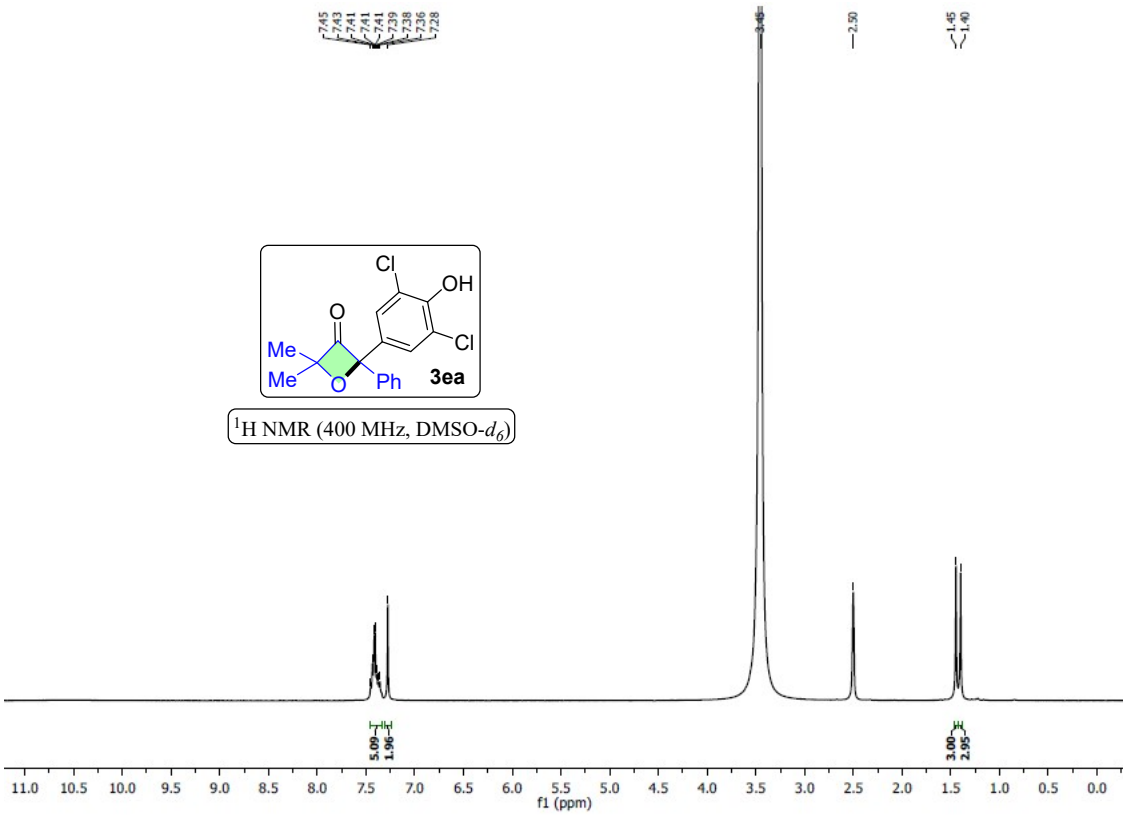
^{13}C NMR (100 MHz, DMSO-d_6)



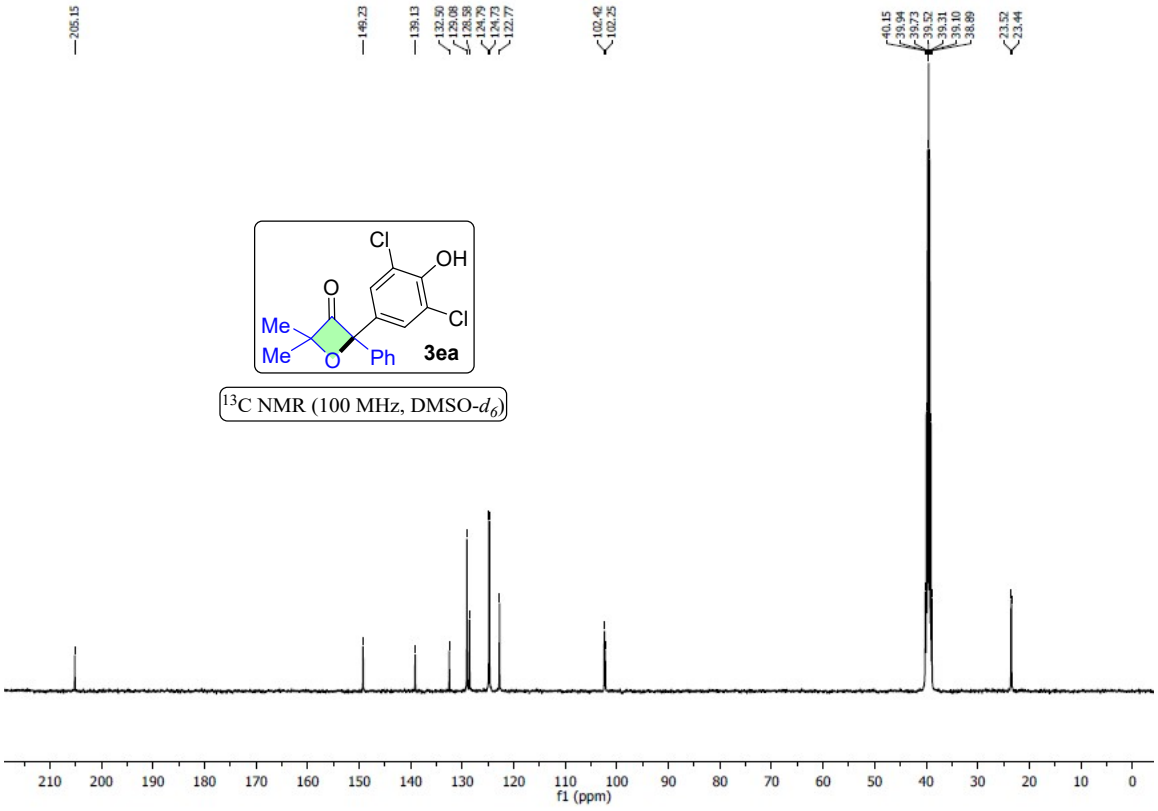
^{1}H NMR (500 MHz, DMSO-d_6)



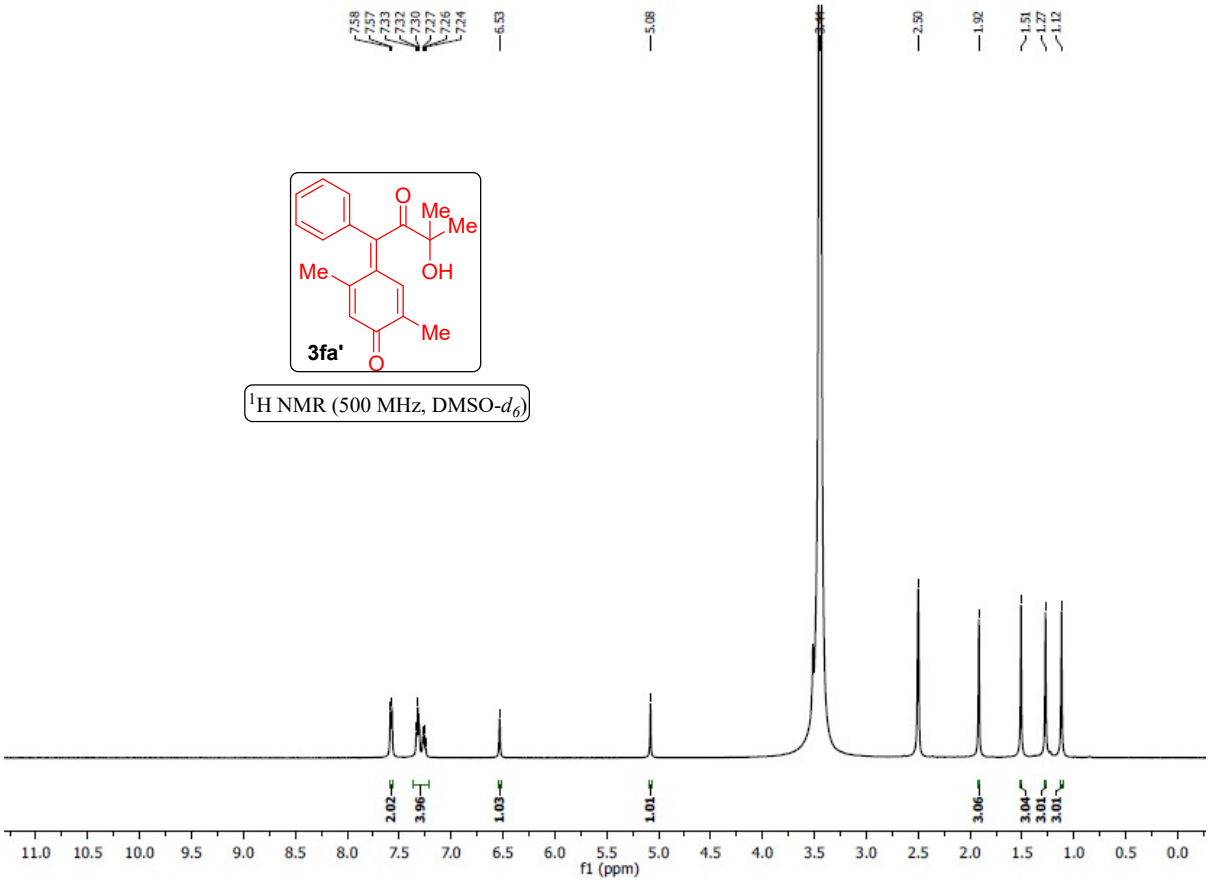
^{13}C NMR (125 MHz, DMSO-d_6)



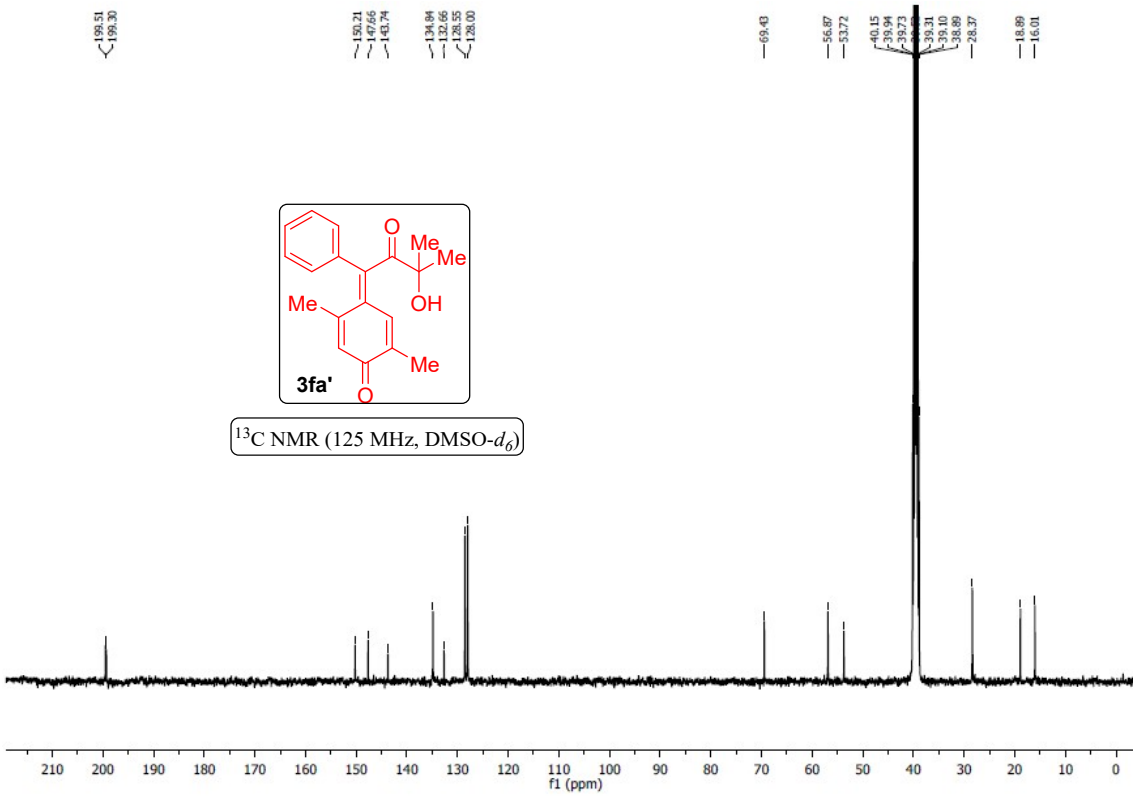
^{1}H NMR (400 MHz, DMSO-d_6)



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



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



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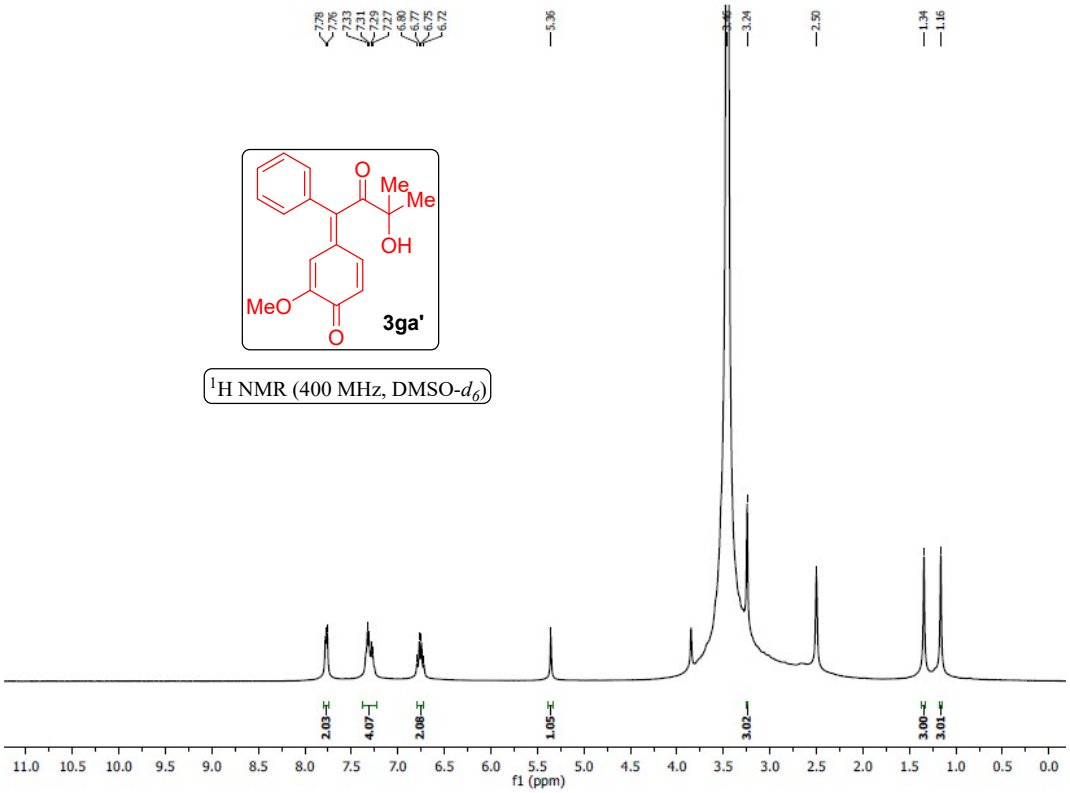

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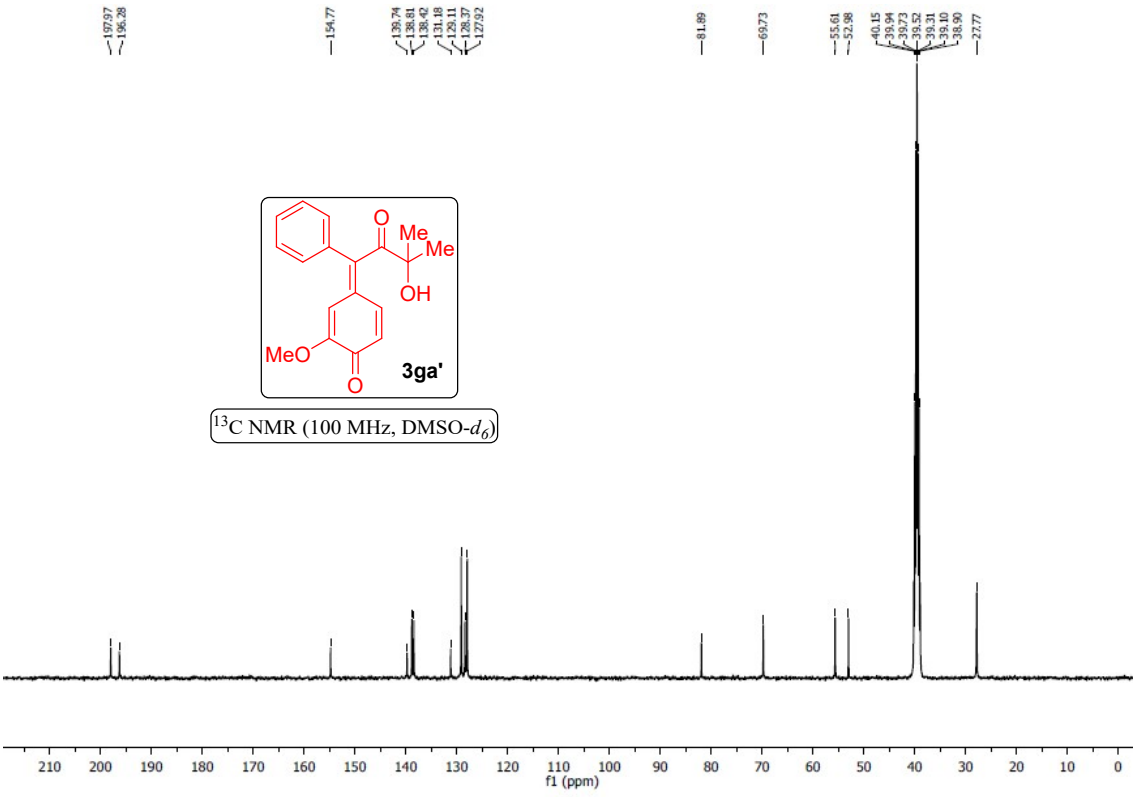

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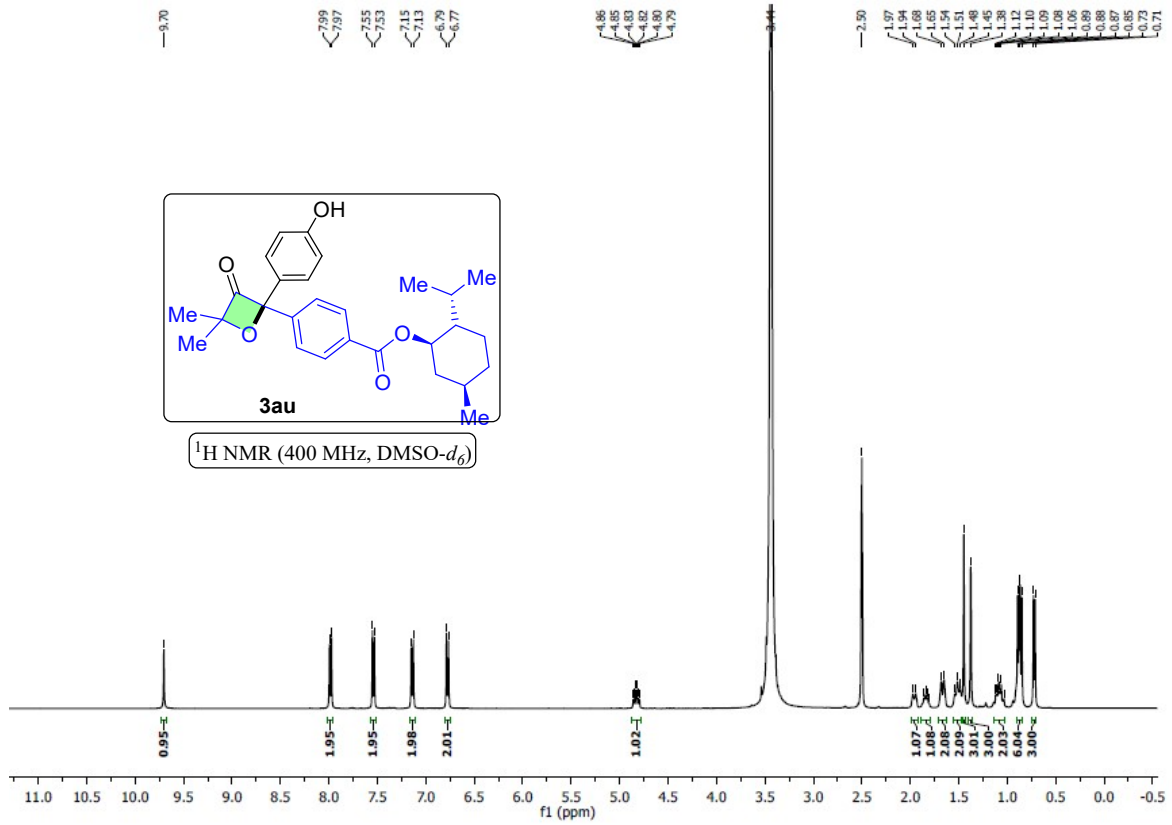

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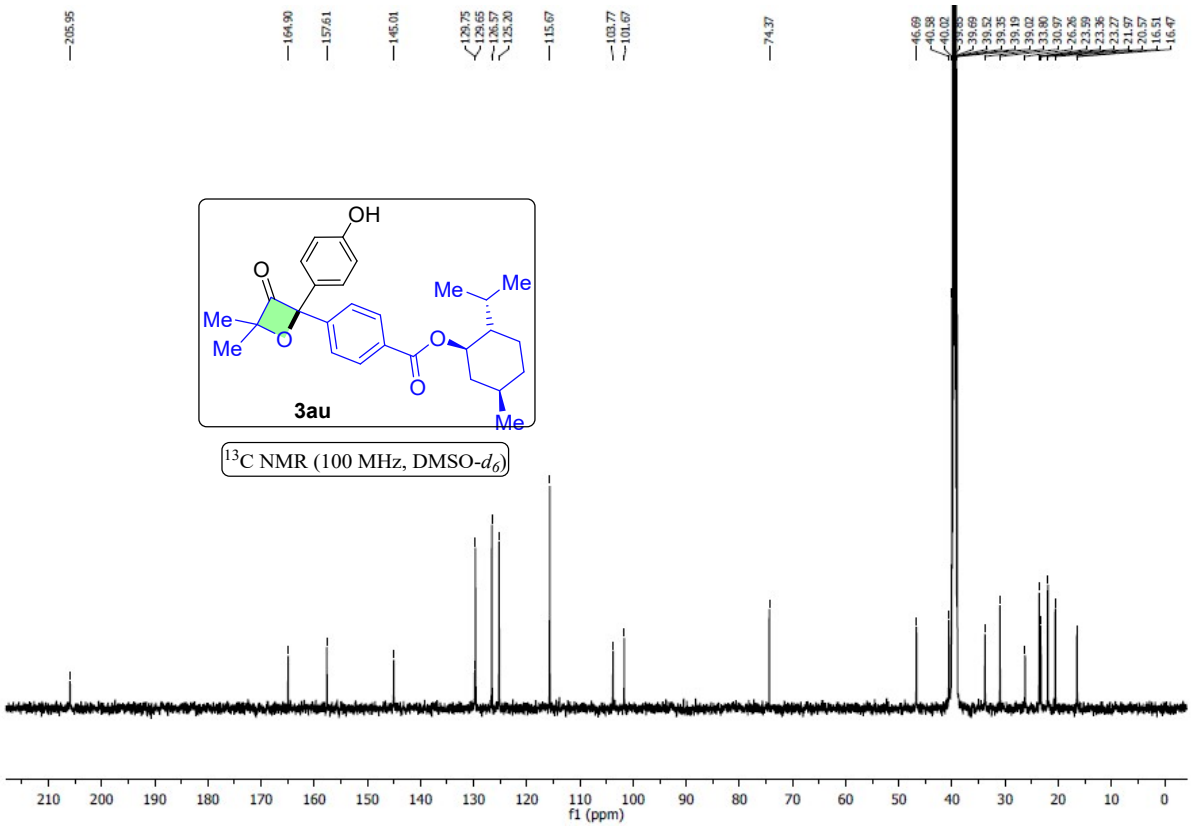
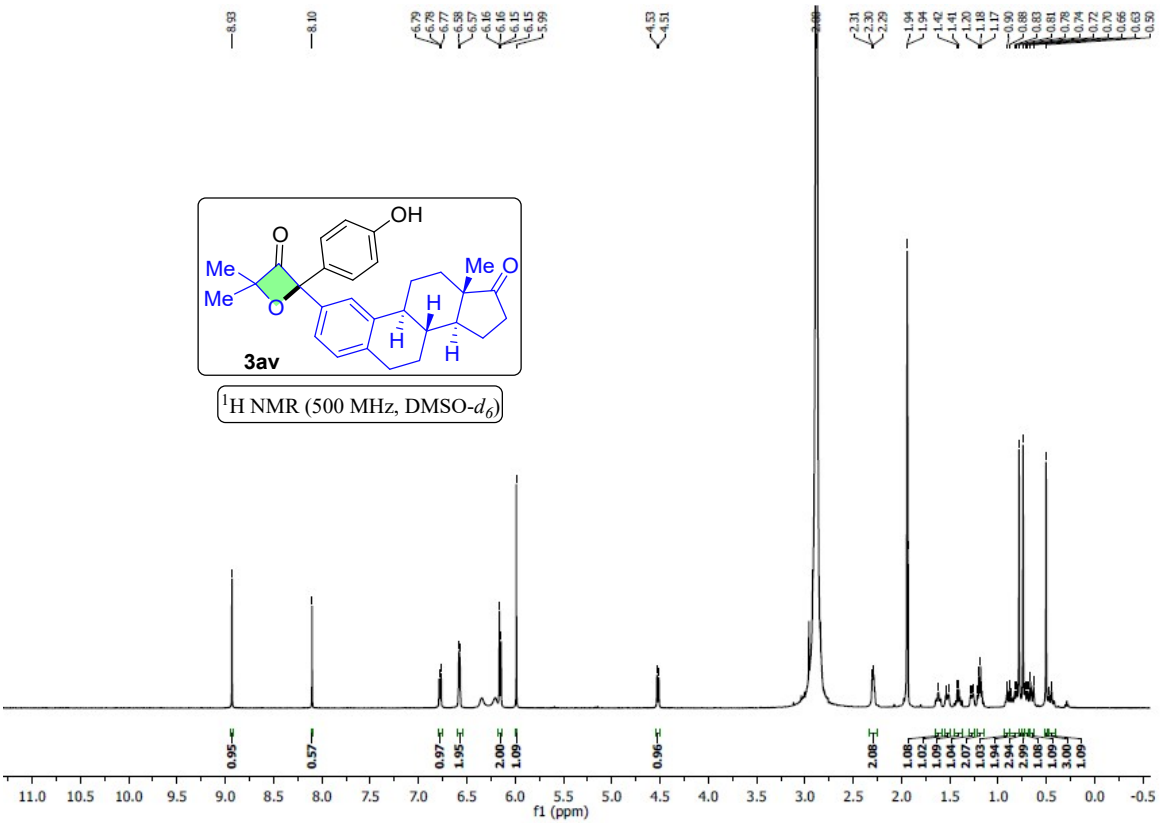


^{13}C NMR (100 MHz, DMSO-d_6)



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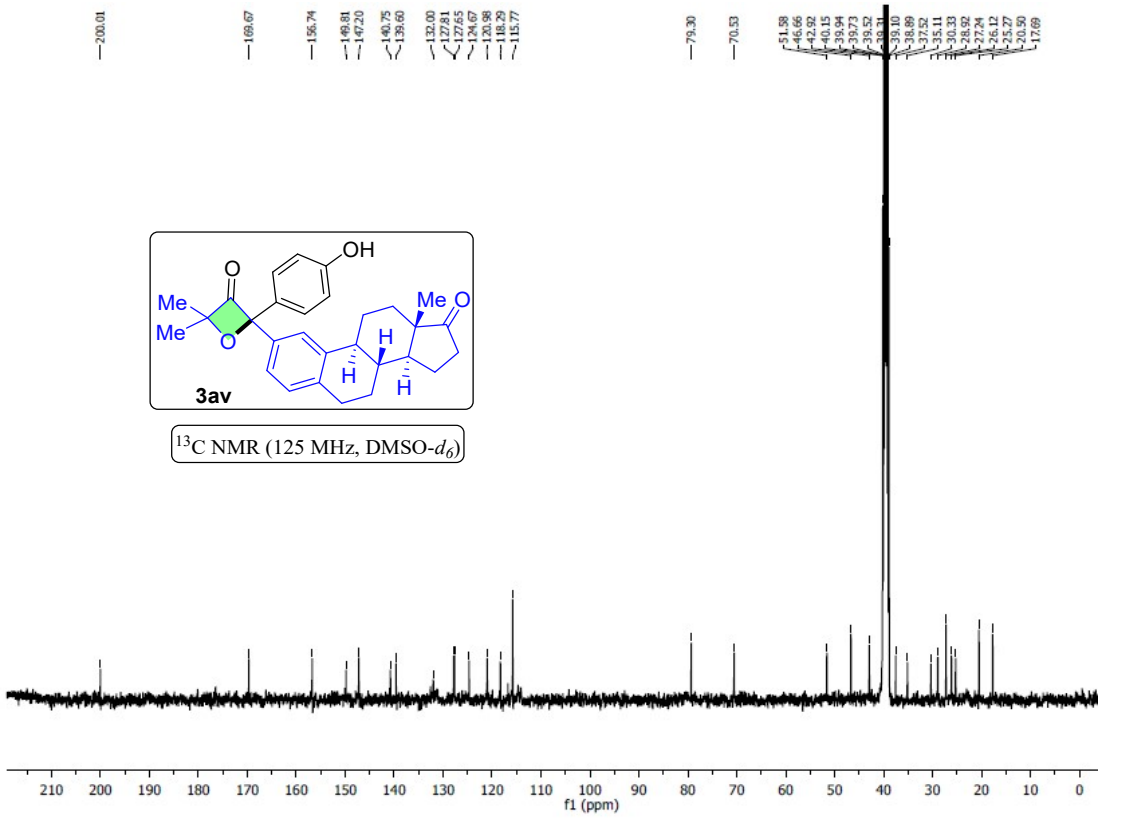
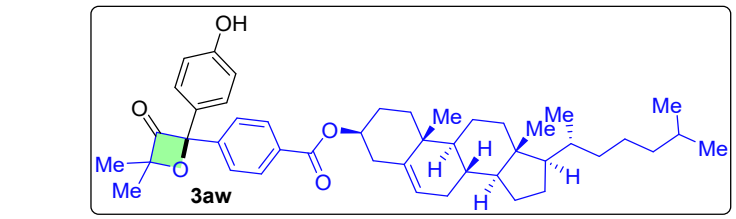
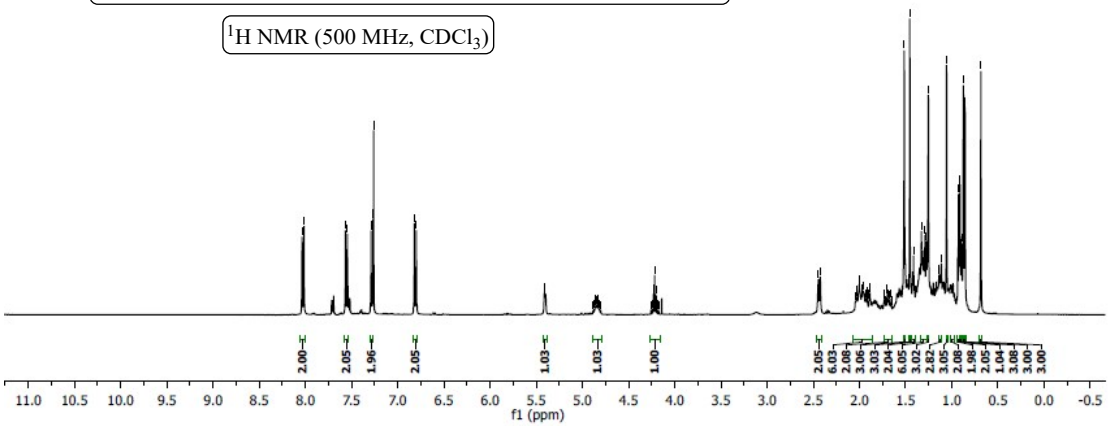
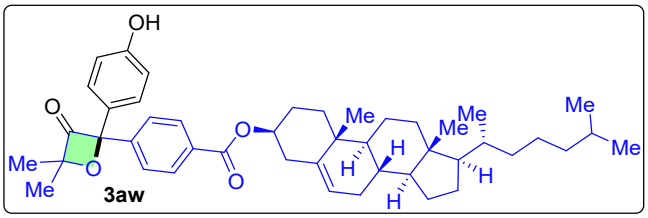


^{13}C NMR (125 MHz, DMSO-d_6)

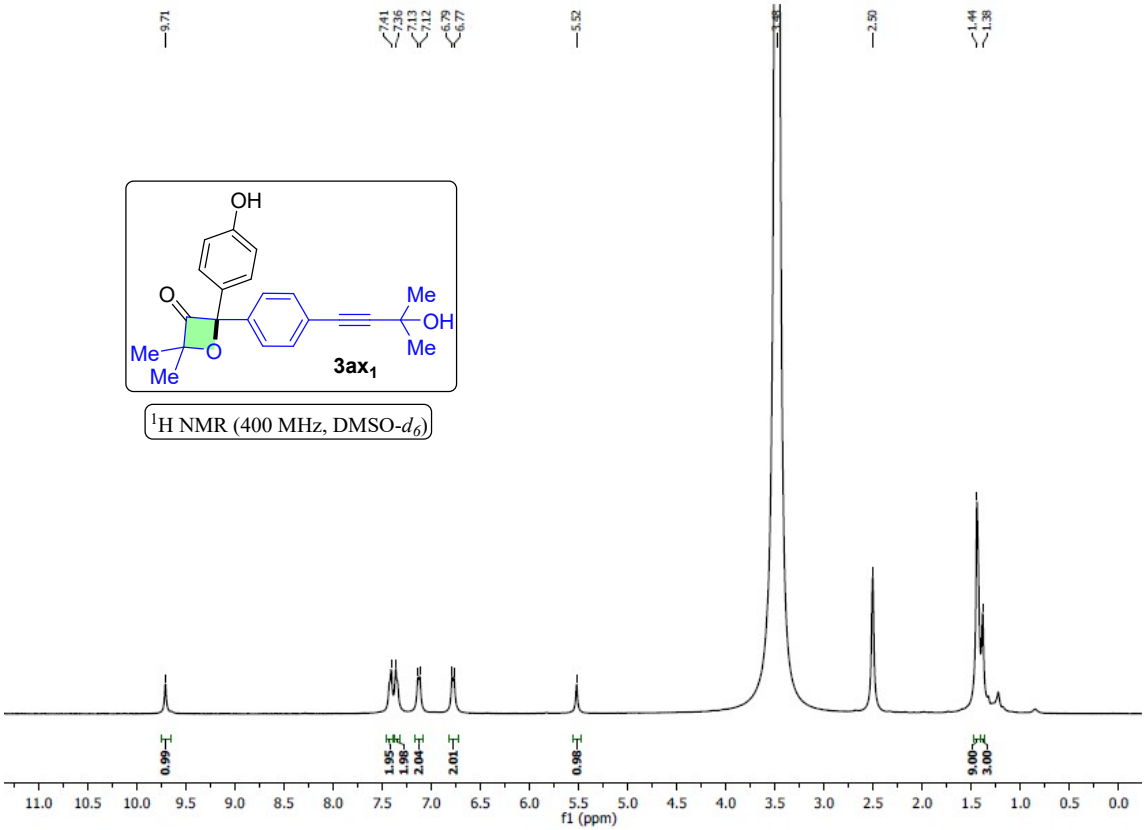


^{1}H NMR (500 MHz, $CDCl_3$)

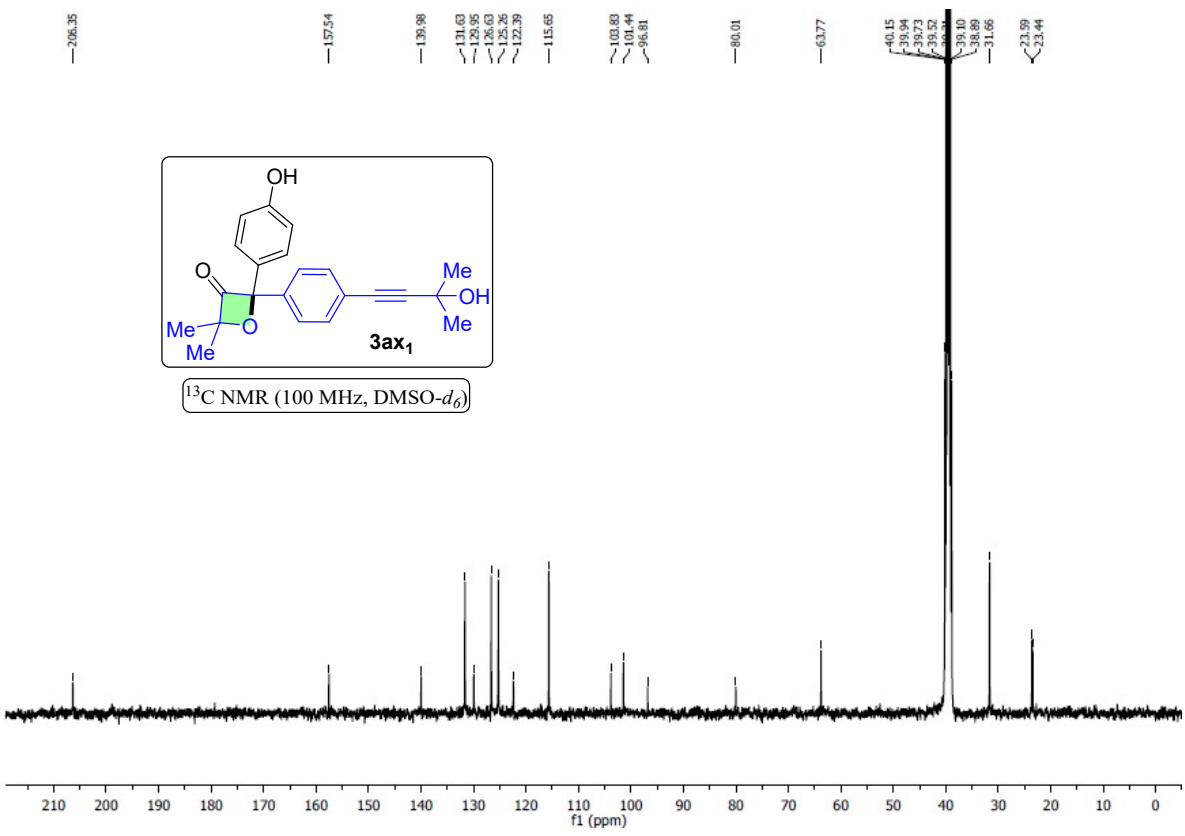




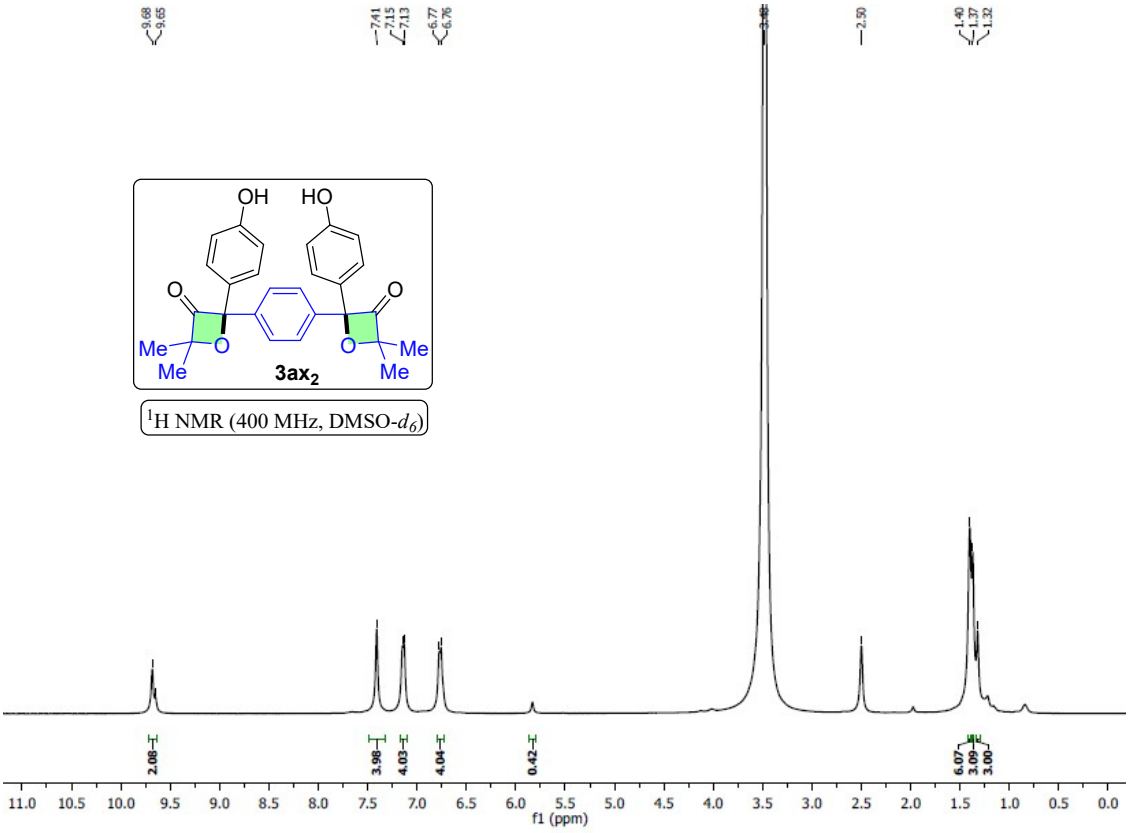
^{13}C NMR (125MHz,$CDCl_3$)

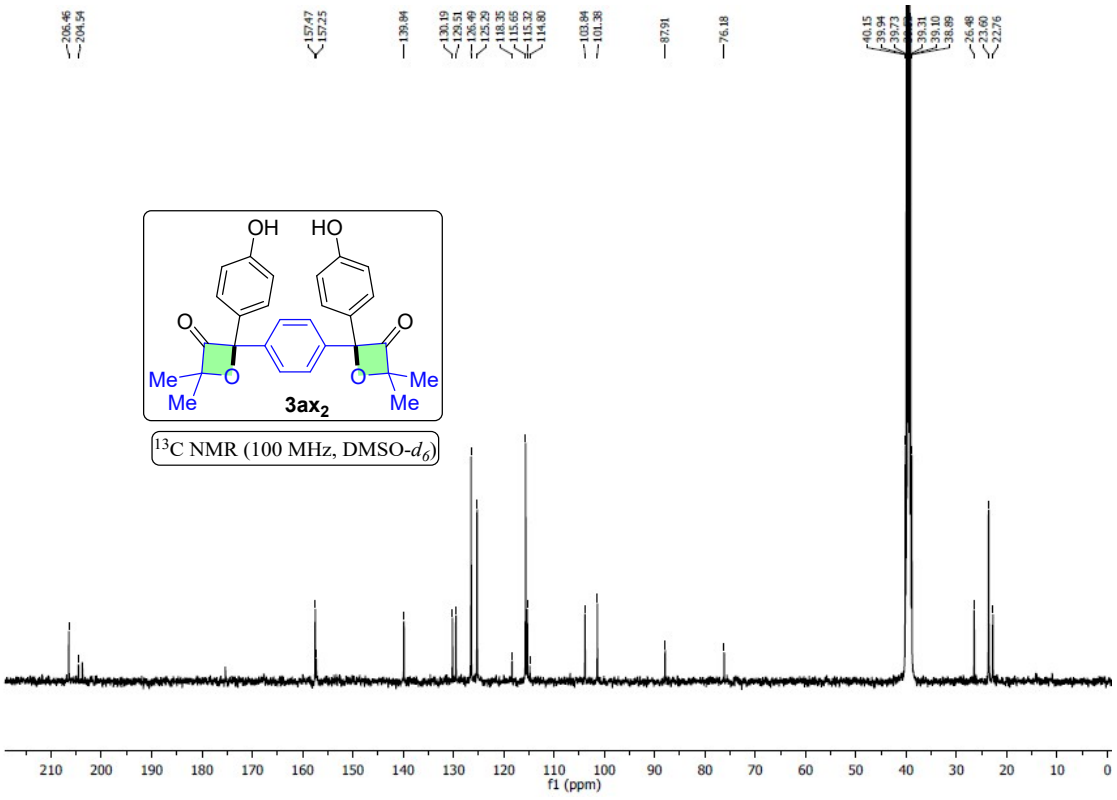


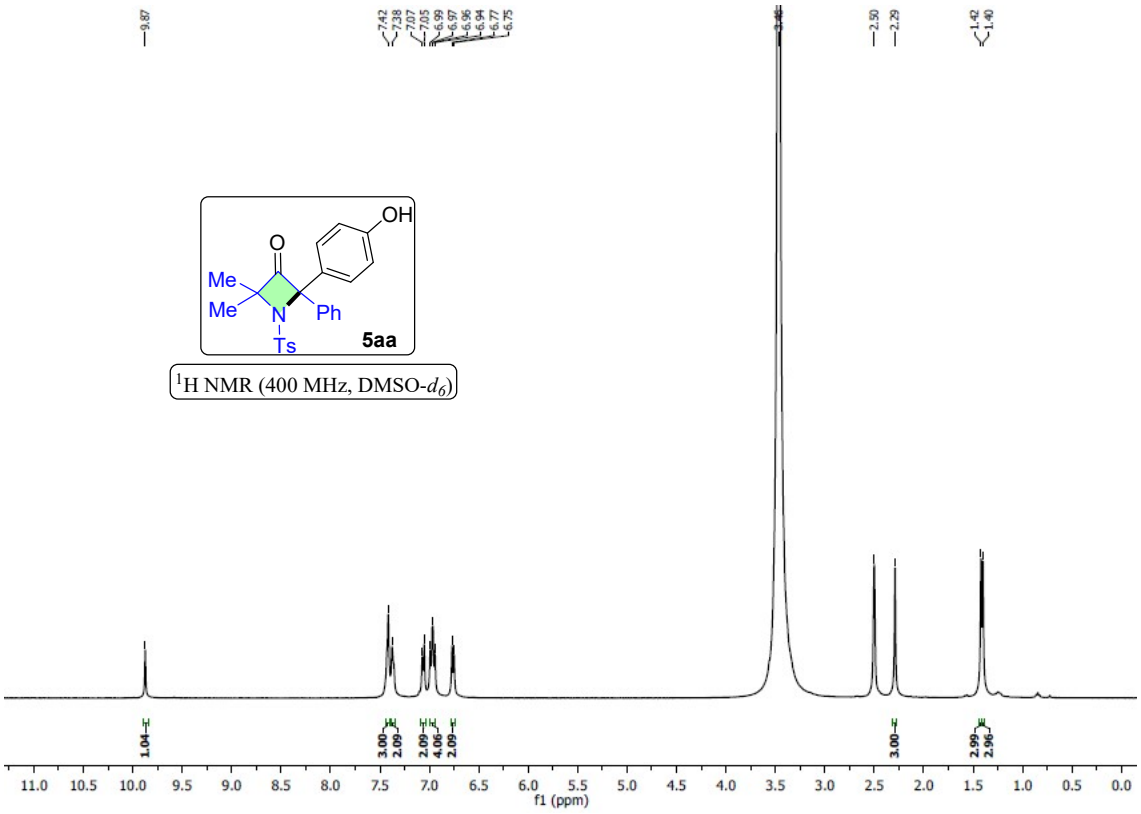
^{1}H NMR (400 MHz, DMSO-d_6)



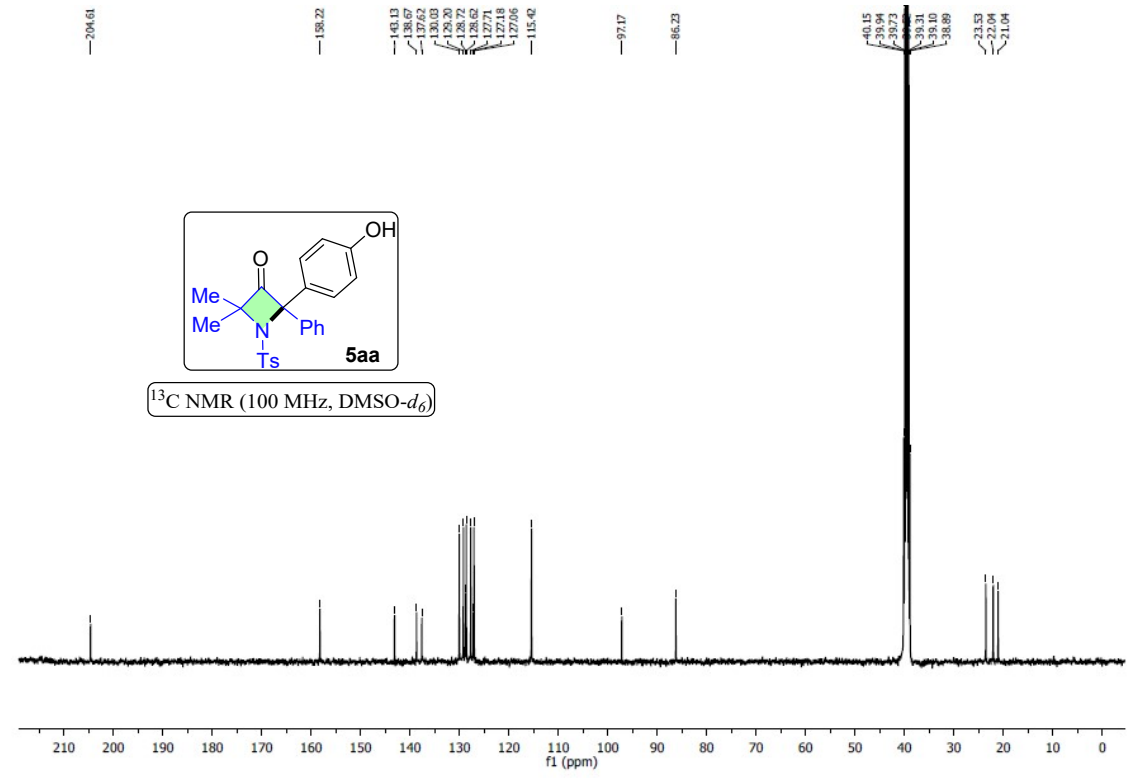
^{13}C NMR (100 MHz, DMSO-d_6)


OH
HO
O
O
Me
O
Me
Me
O
Me
Me
3ax2
1H NMR (400 MHz, DMSO-d6)
f1 (ppm)

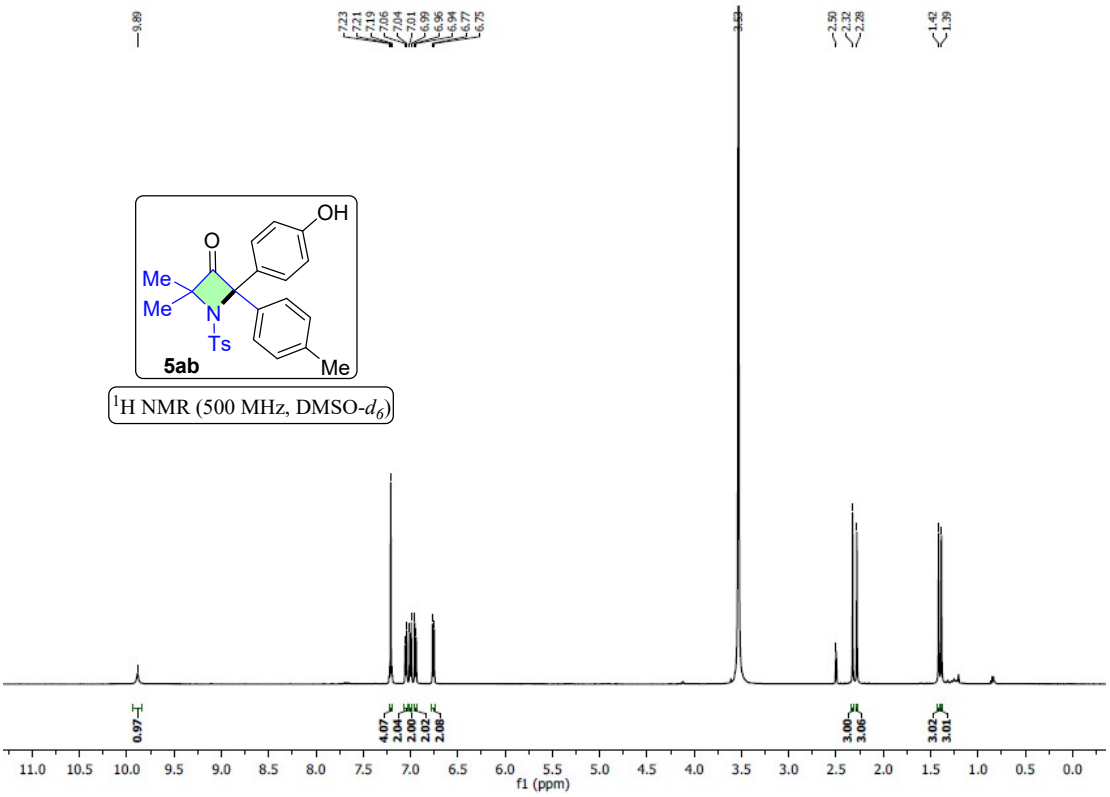

OH
HO
O
O
Me
O
Me
Me
O
Me
Me
3ax2
13C NMR (100 MHz, DMSO-d6)
f1 (ppm)



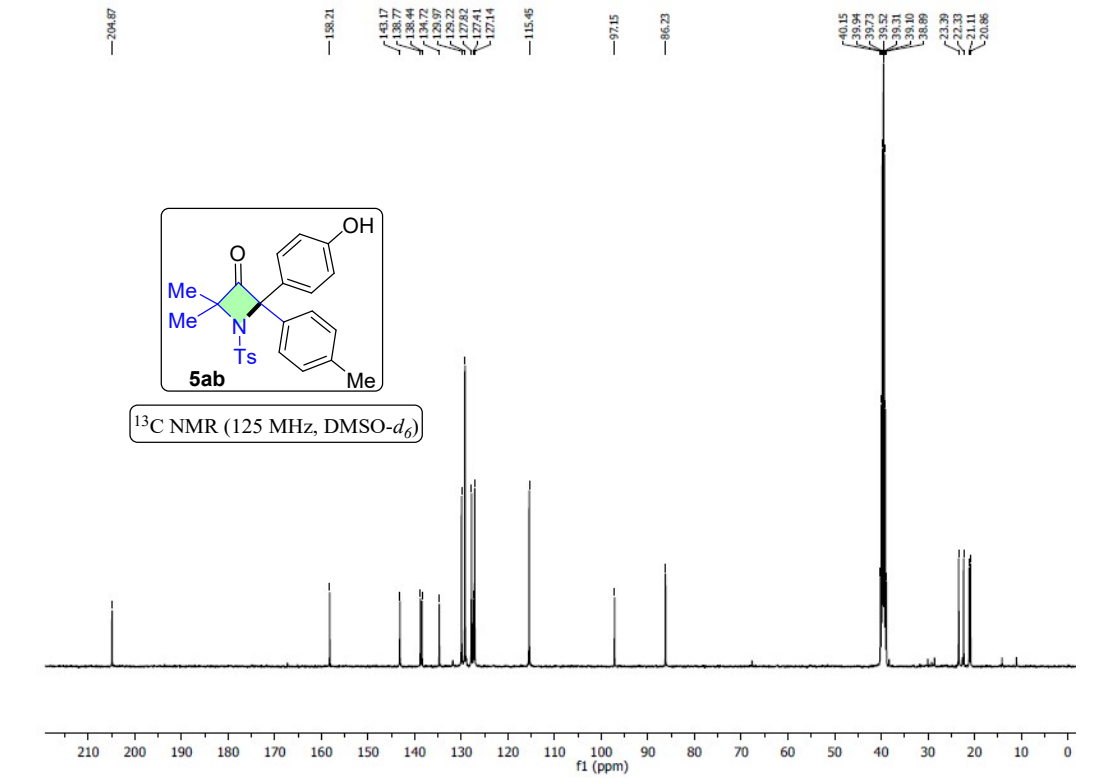
^{1}H NMR (400 MHz, DMSO-d_6)



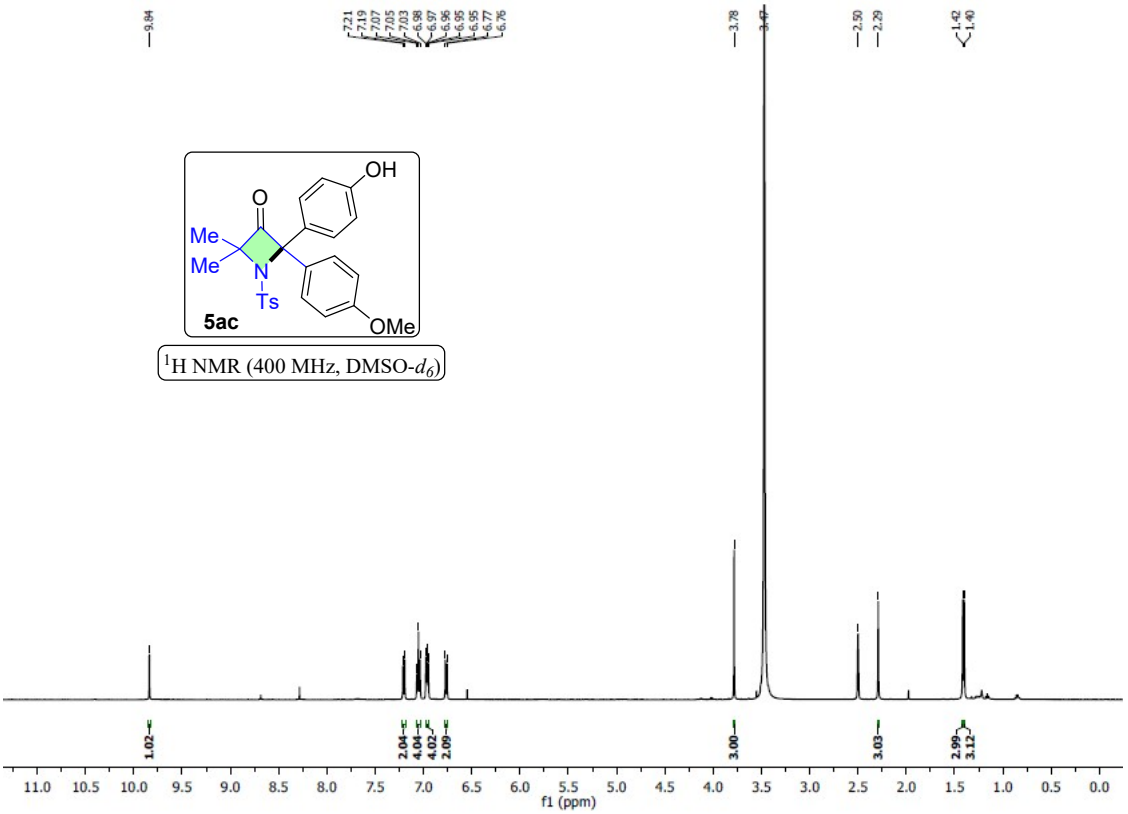
^{13}C NMR (100 MHz, DMSO-d_6)



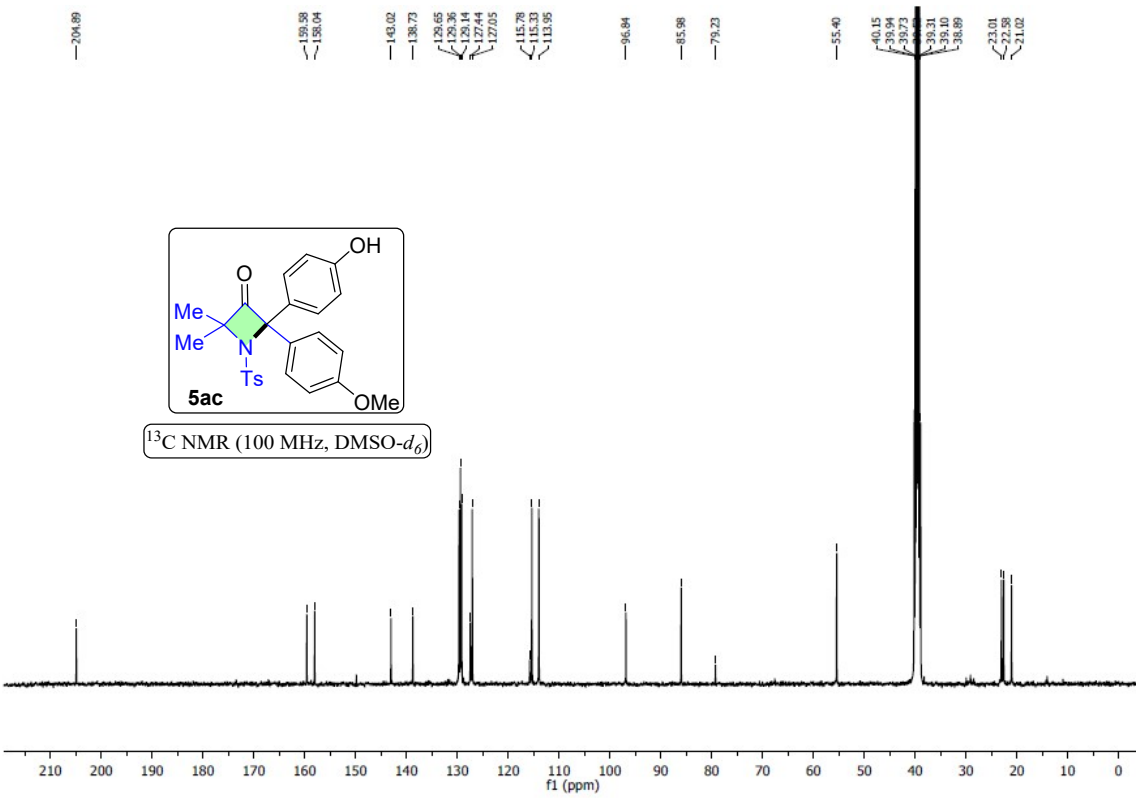
^{1}H NMR (500 MHz, DMSO-d_6)



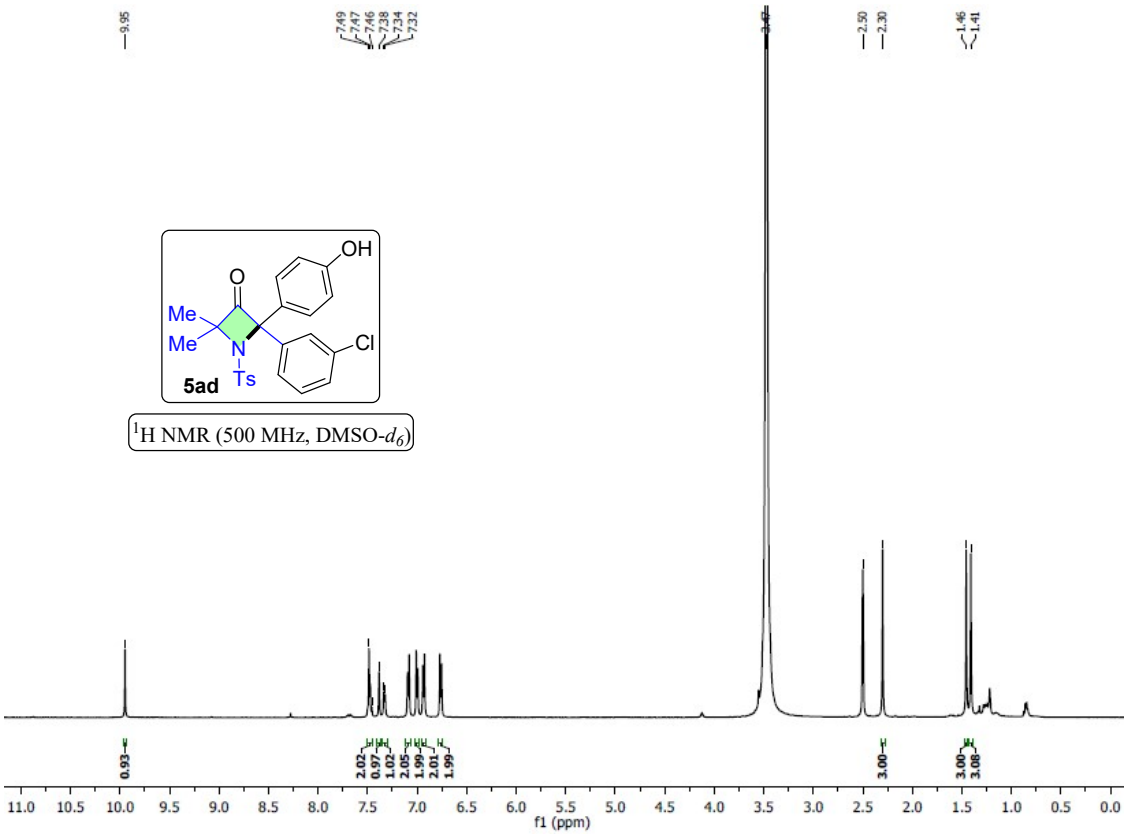
^{13}C NMR (125 MHz, DMSO-d_6)



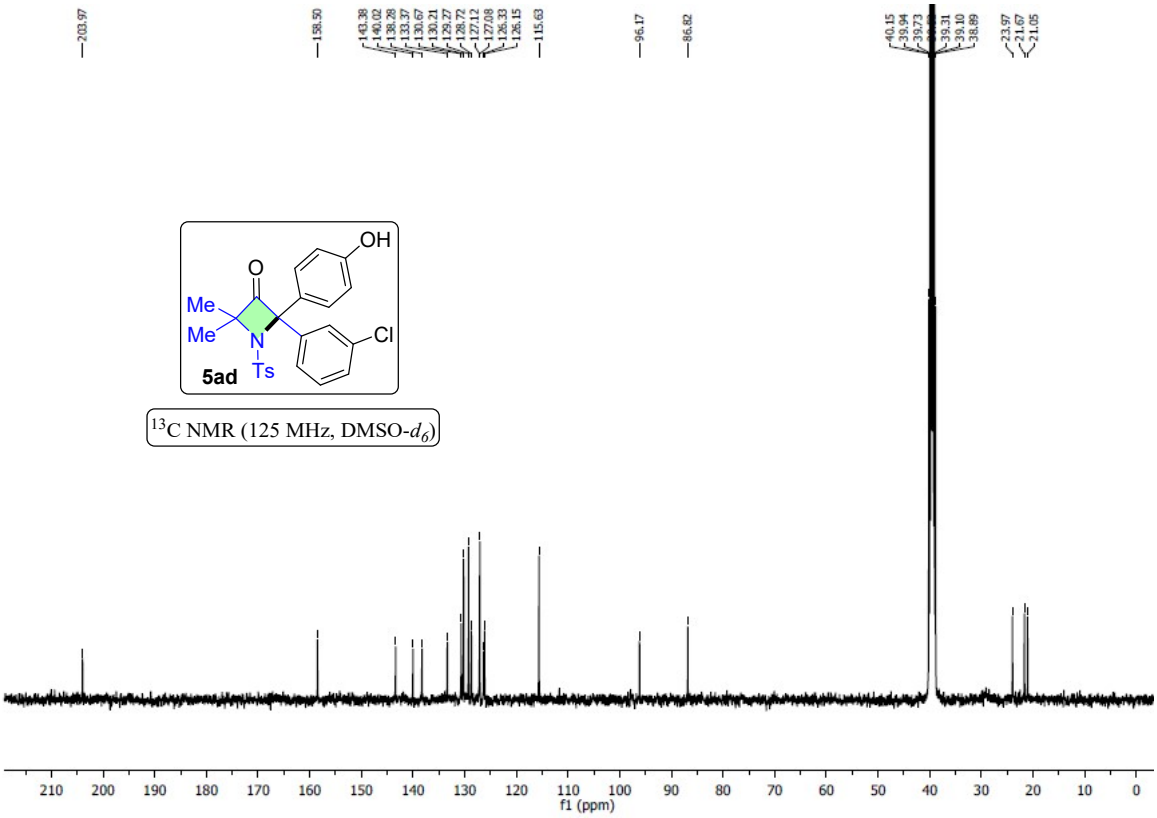
^{1}H NMR (400 MHz, DMSO-d_6)



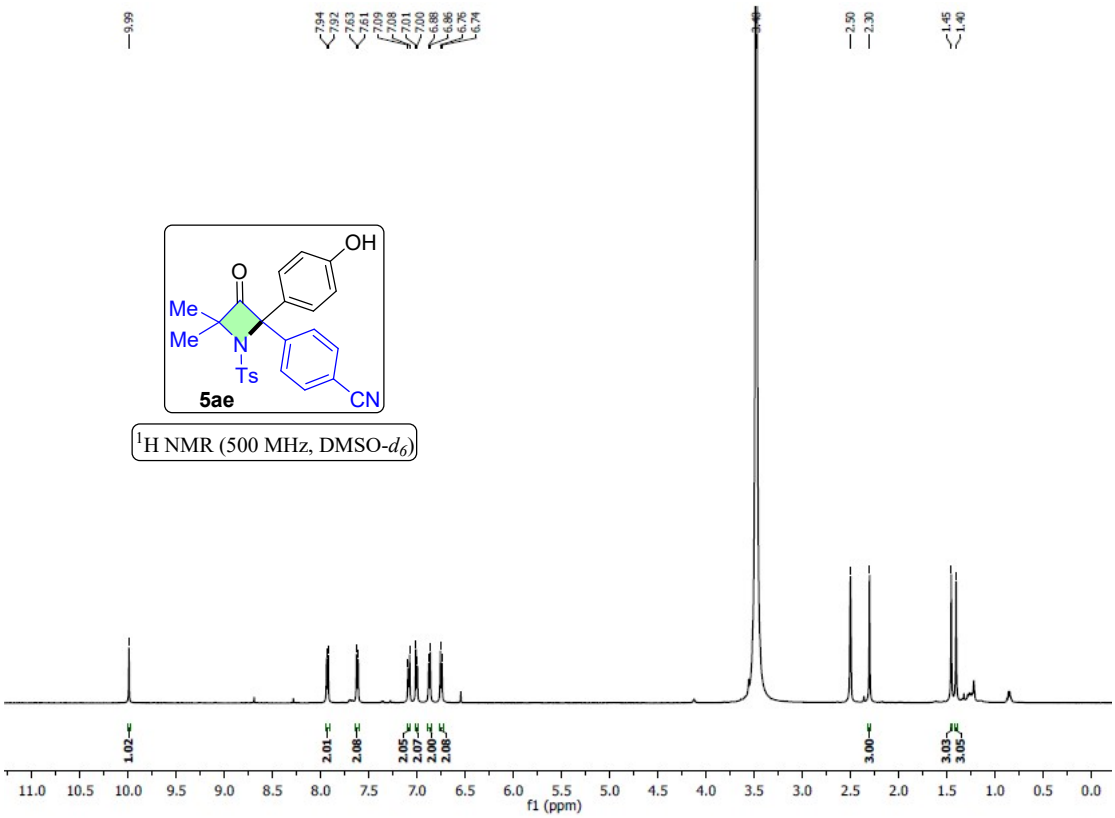
^{13}C NMR (100 MHz, DMSO-d_6)



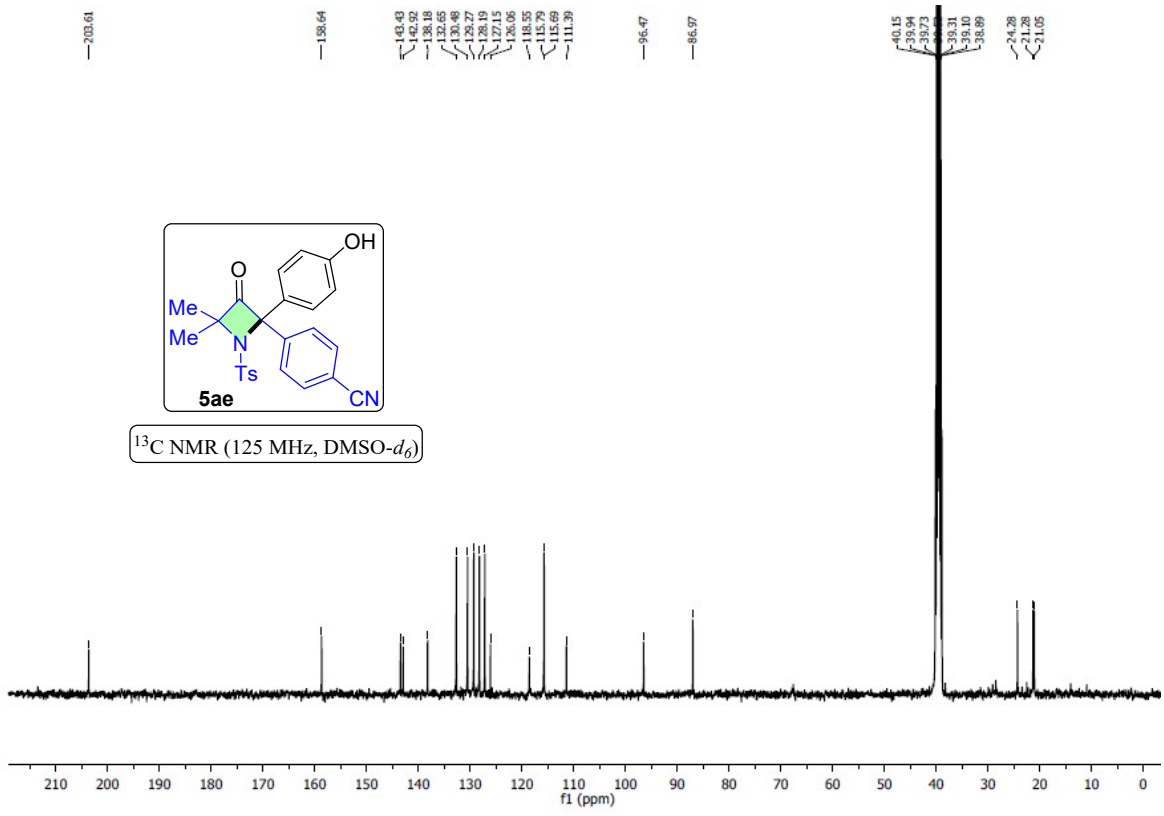
^{1}H NMR (500 MHz, DMSO-d_6)



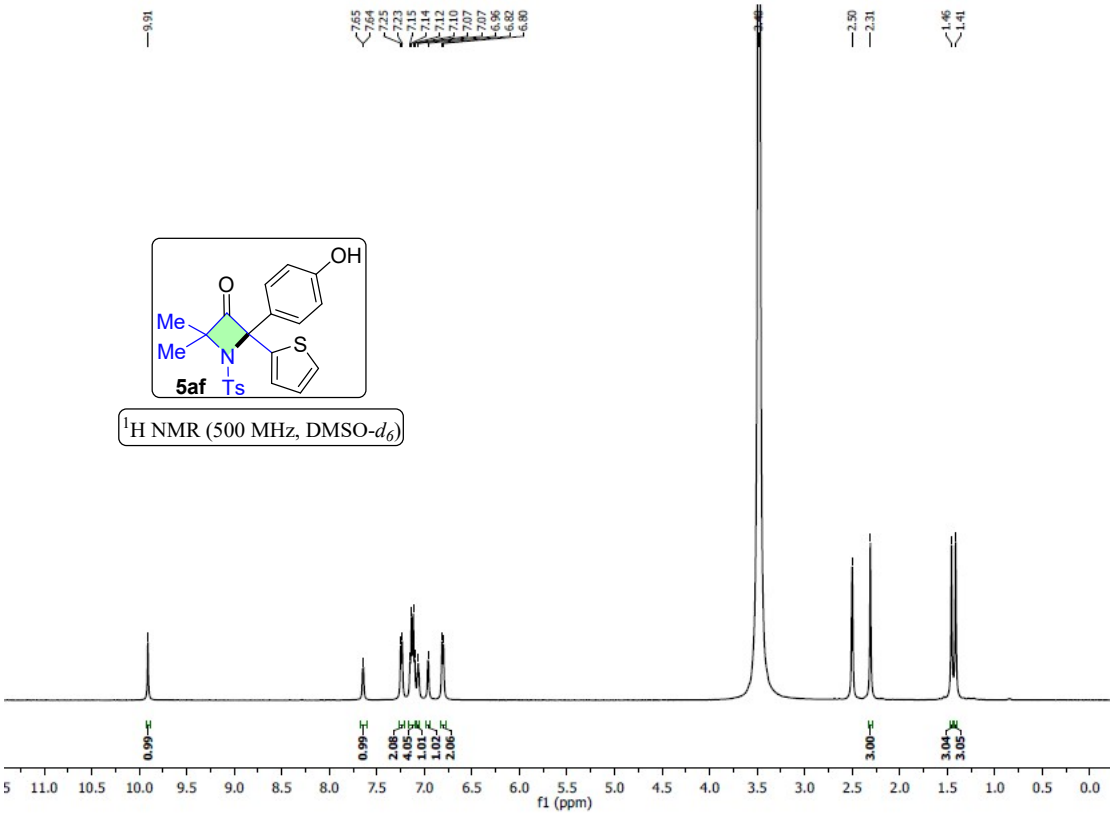
^{13}C NMR (125 MHz, DMSO-d_6)



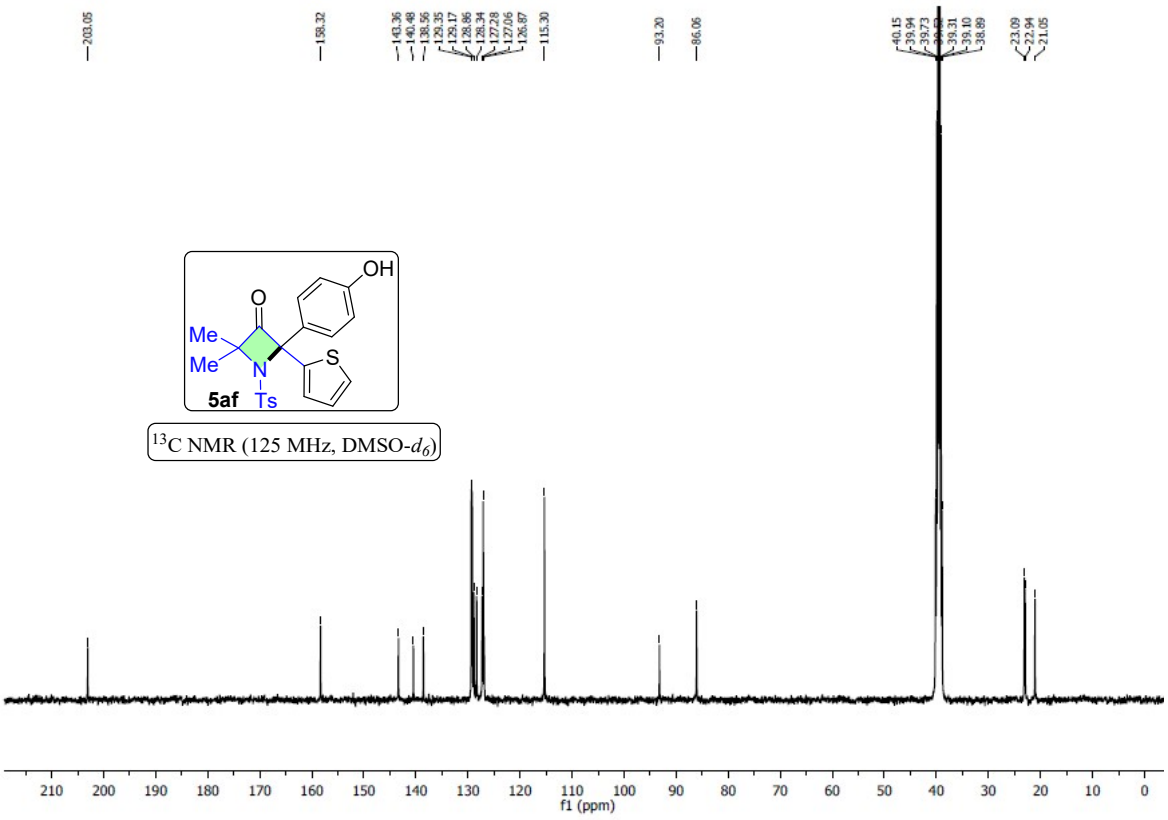
^{1}H NMR (500 MHz, DMSO-d_6)



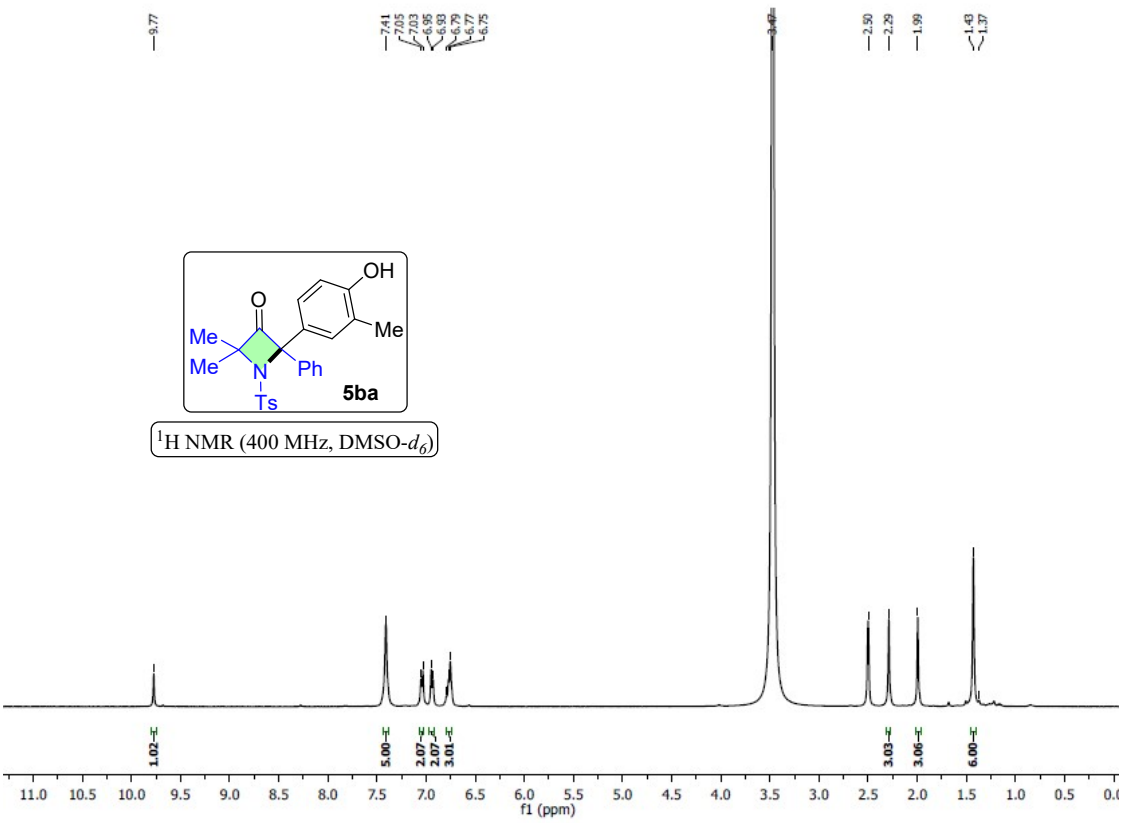
^{13}C NMR (125 MHz, DMSO-d_6)



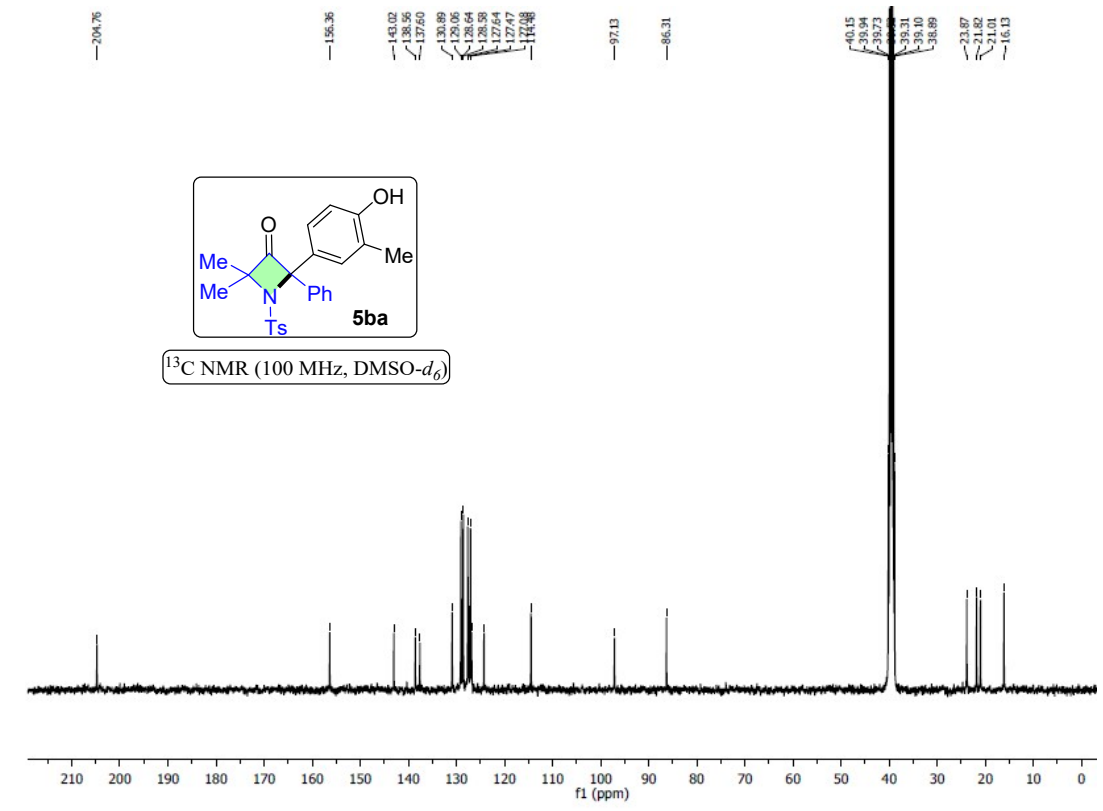
^{1}H NMR (500 MHz, DMSO-d_6)



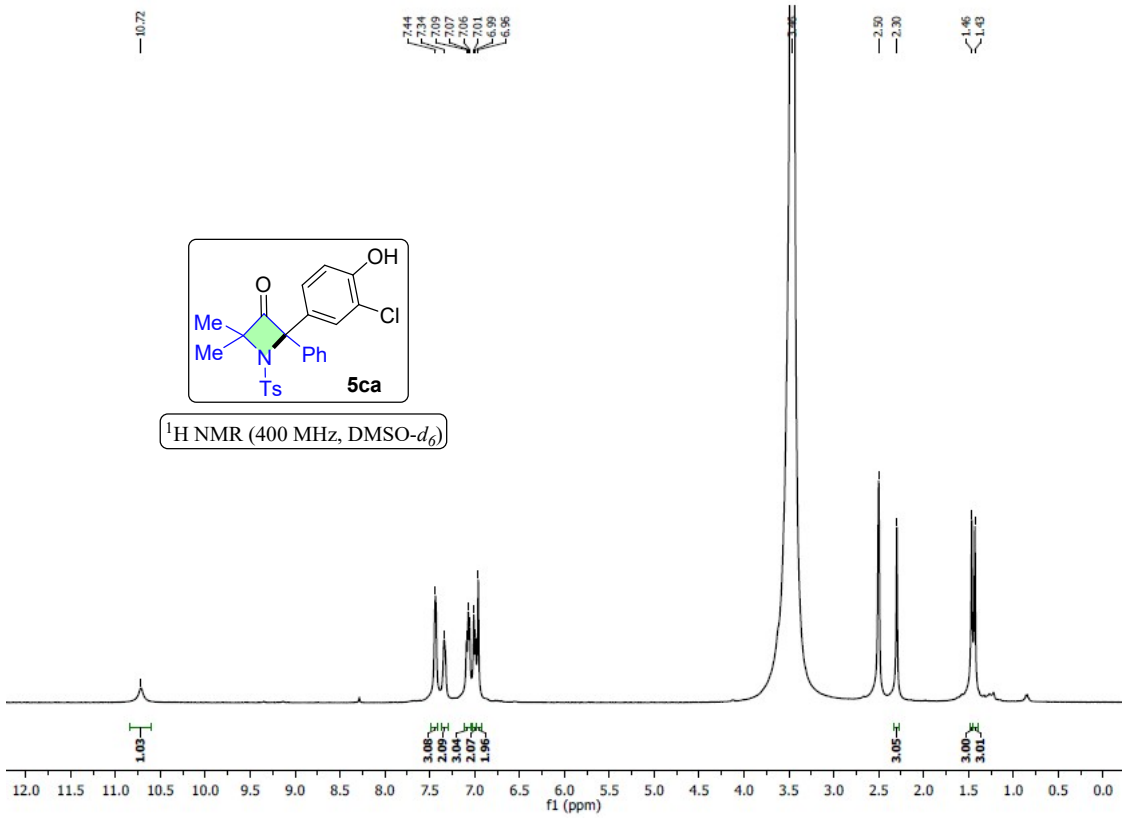
^{13}C NMR (125 MHz, DMSO-d_6)



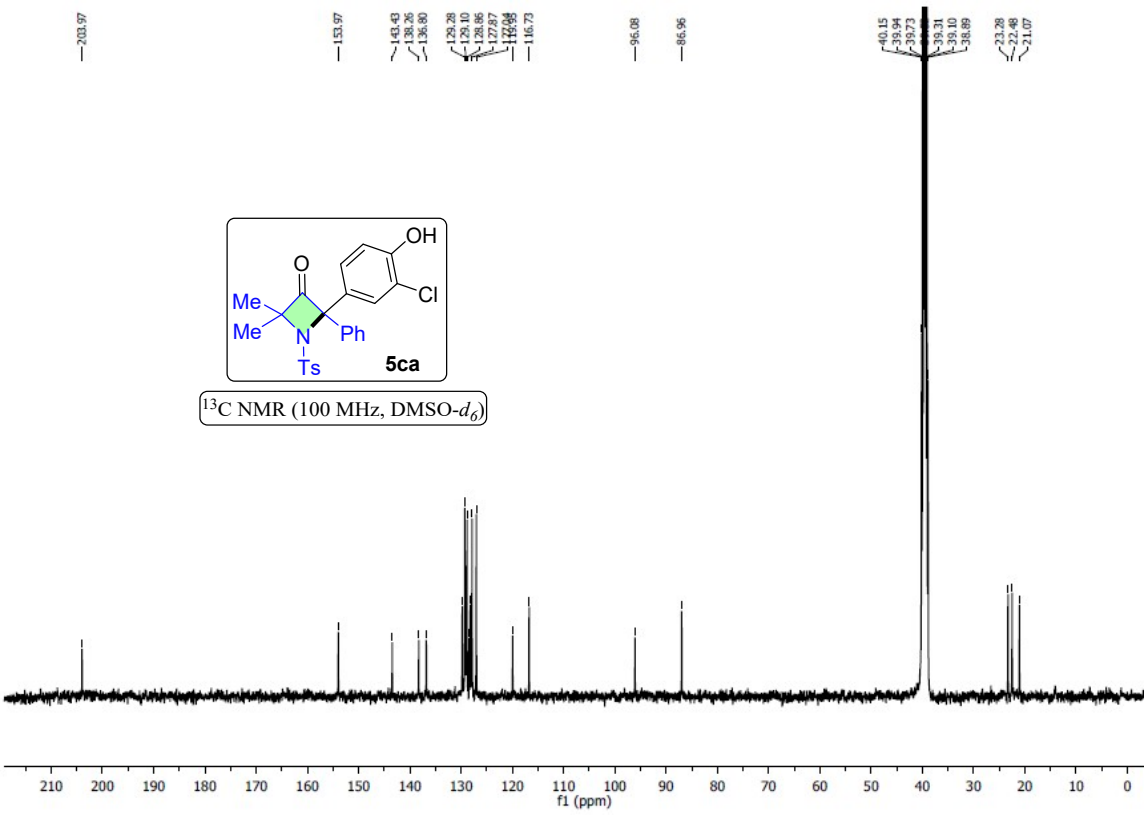
^{1}H NMR (400 MHz, DMSO-d_6)



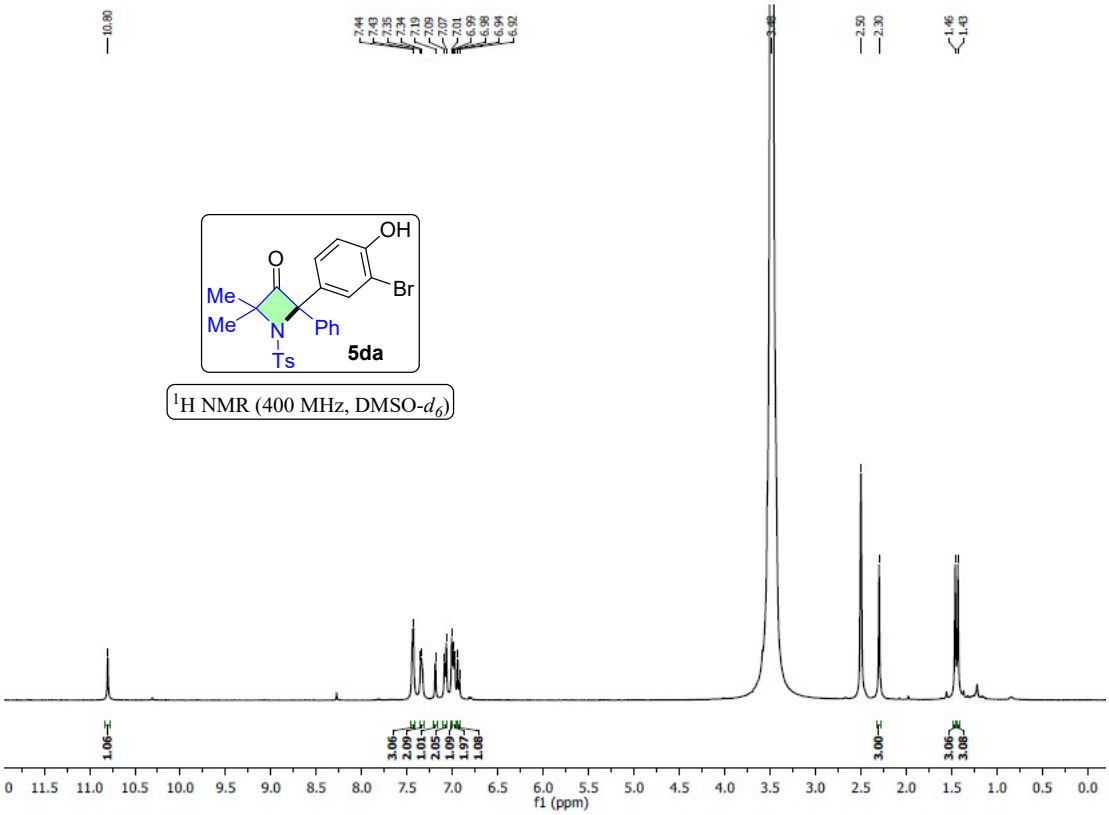
^{13}C NMR (100 MHz, DMSO-d_6)



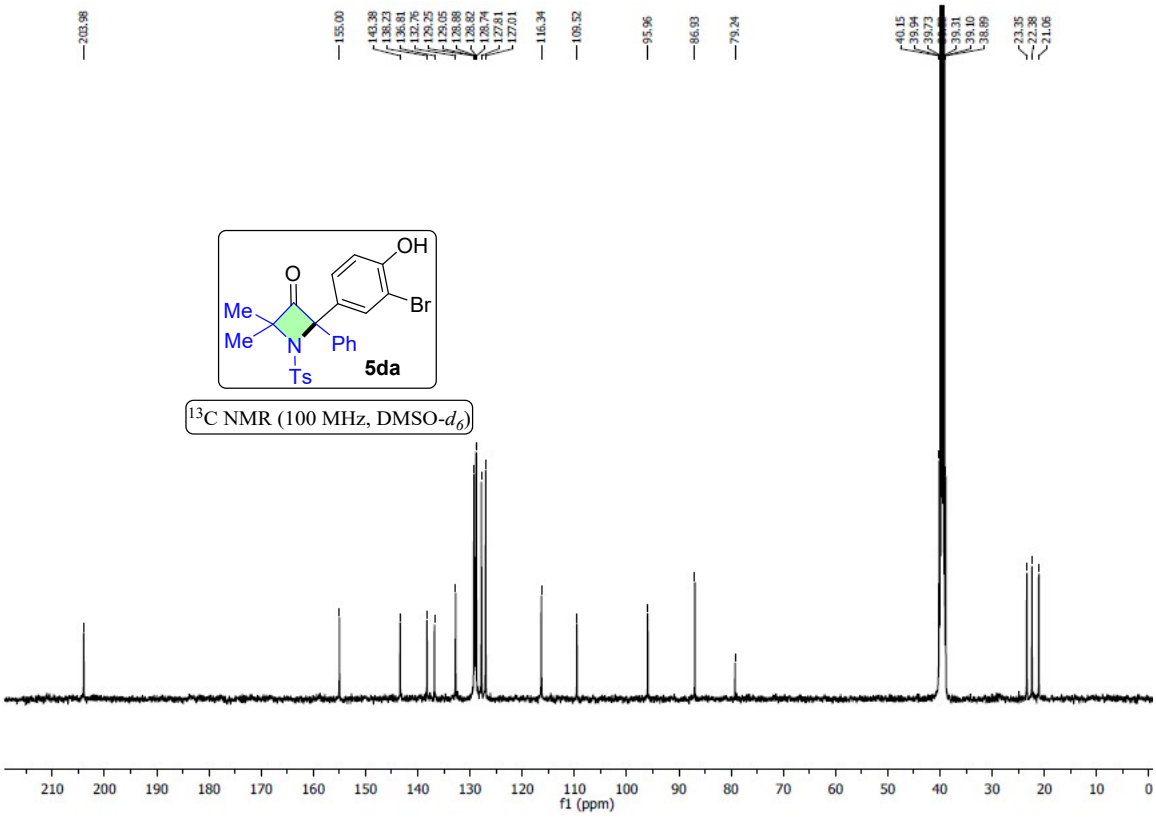
^{1}H NMR (400 MHz, DMSO-d_6)



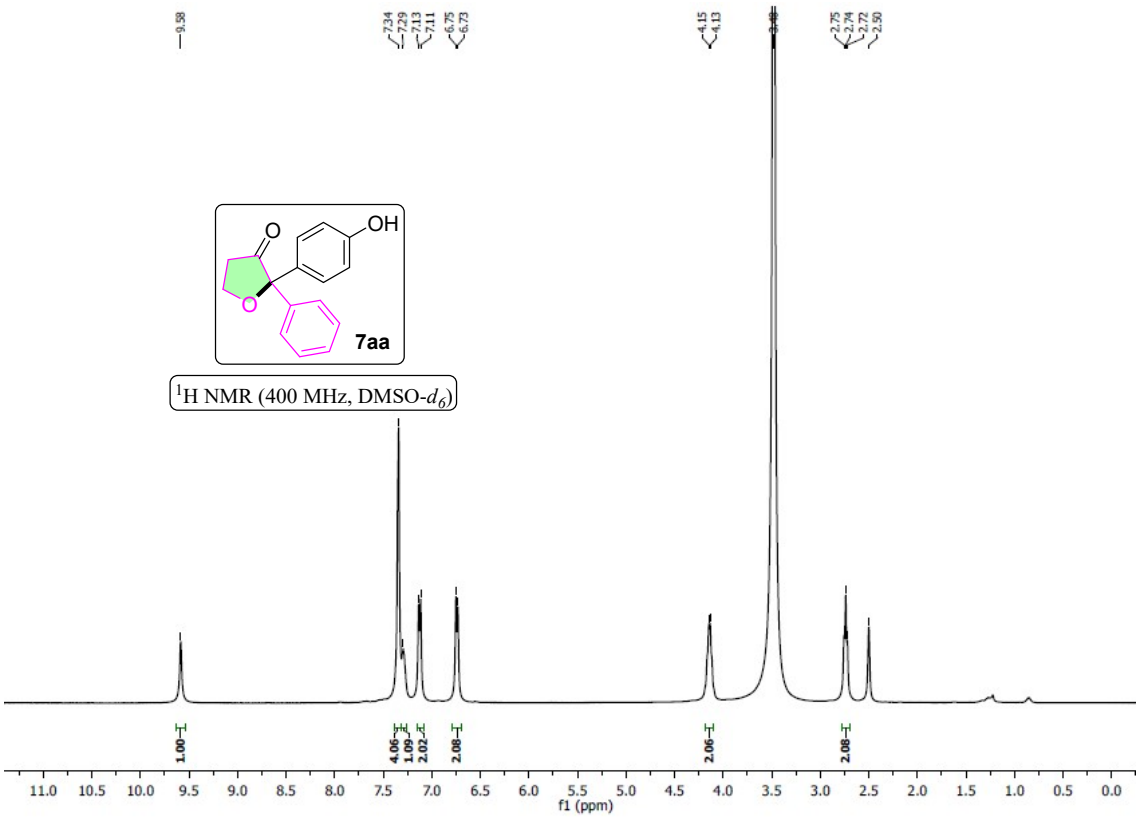
^{13}C NMR (100 MHz, DMSO-d_6)



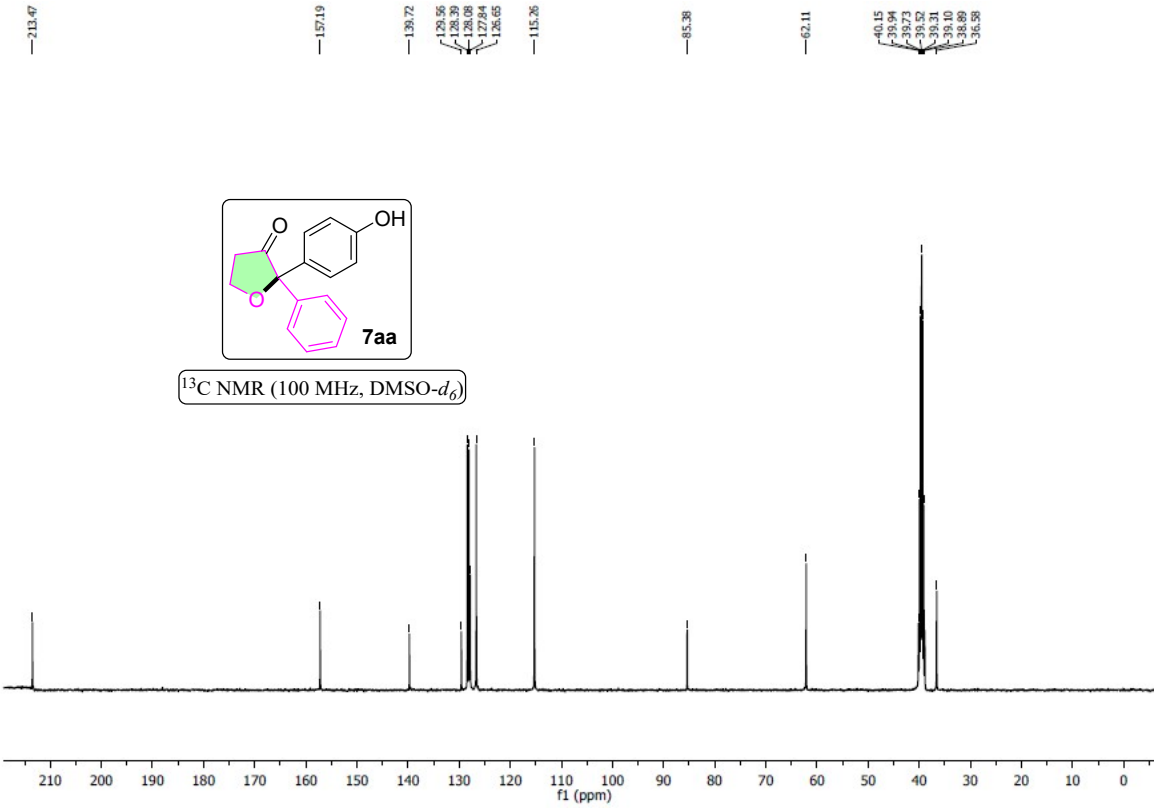
^{1}H NMR (400 MHz, DMSO-d_6)



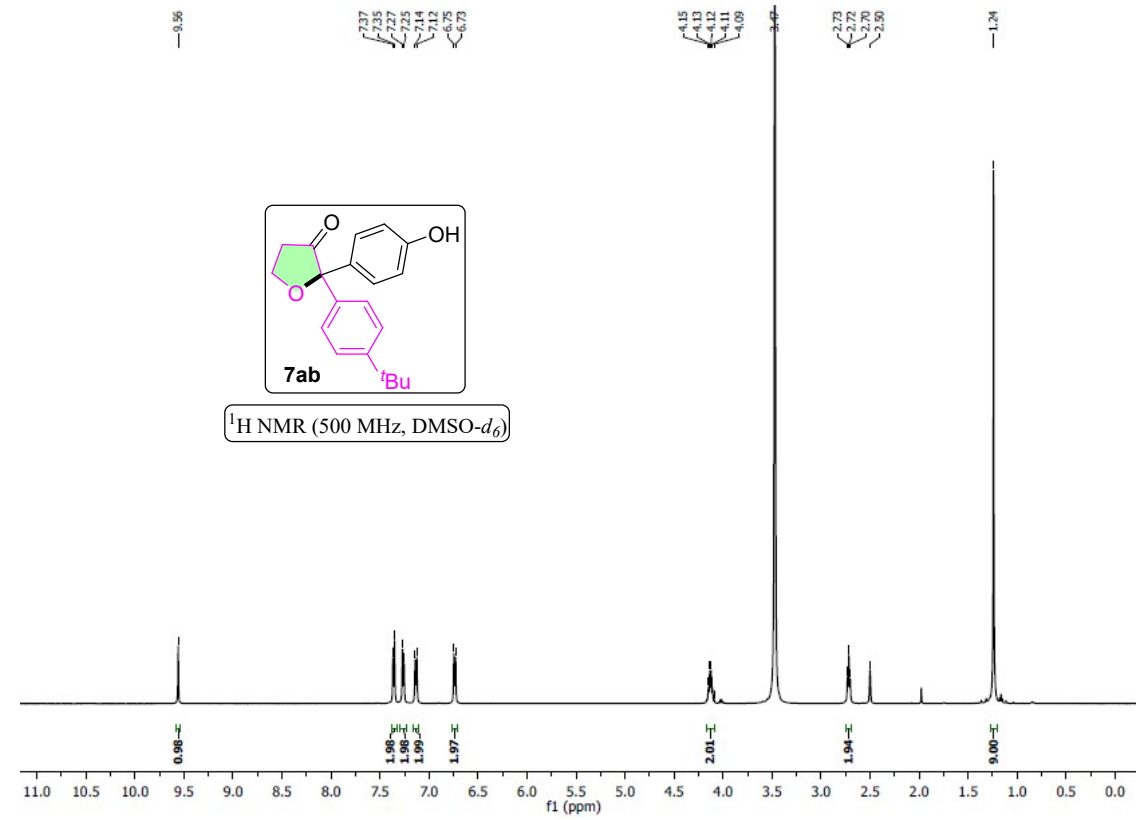
^{13}C NMR (100 MHz, DMSO-d_6)



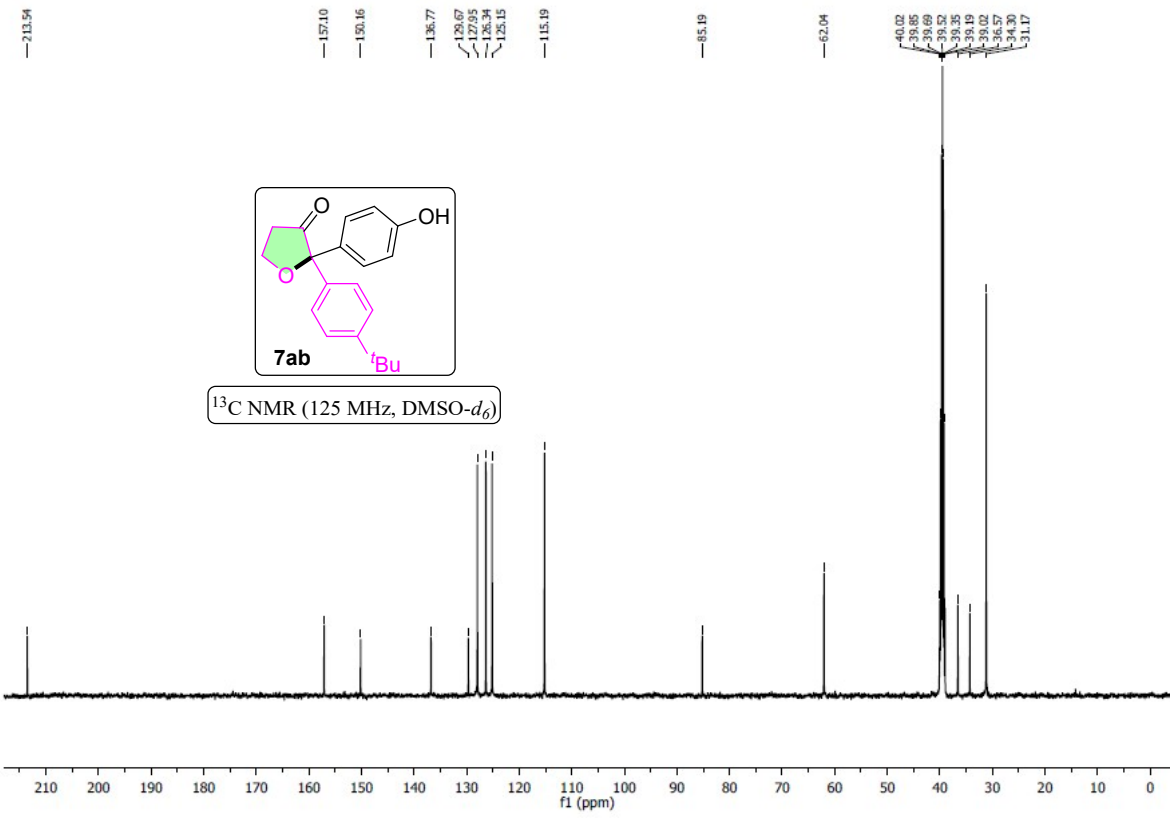
^{1}H NMR (400 MHz, DMSO-d_6)



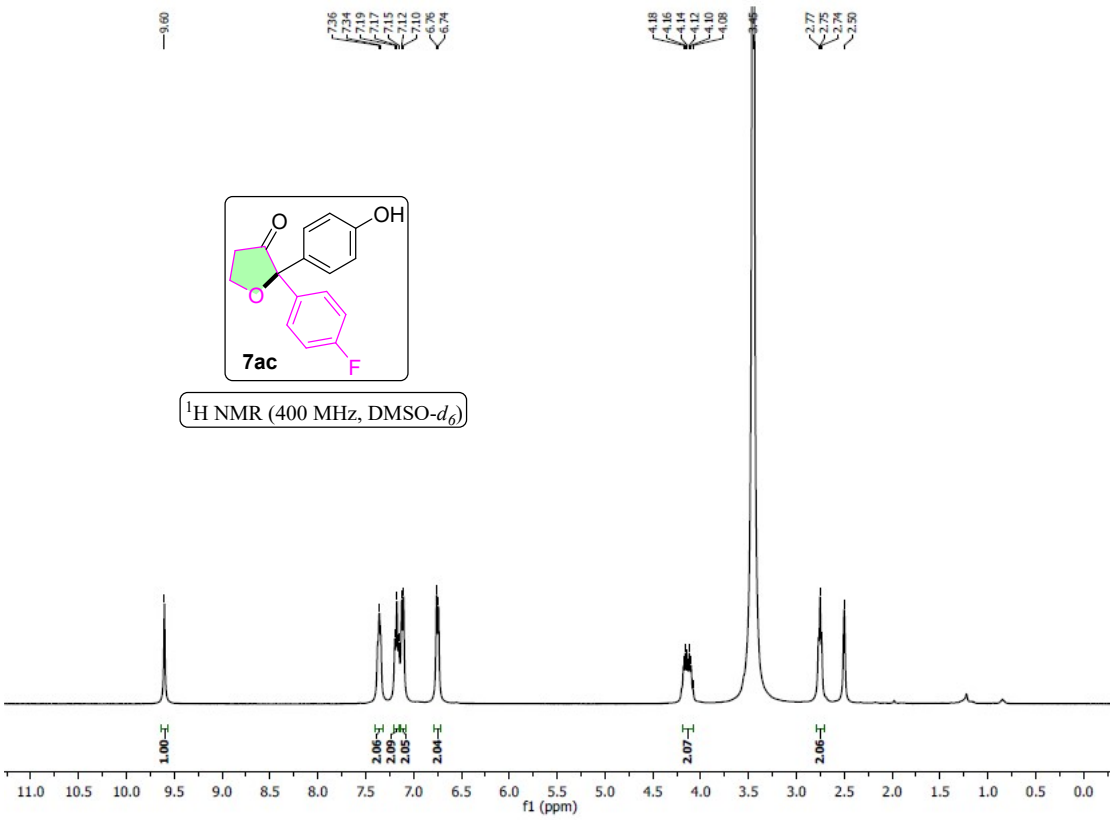
^{13}C NMR (100 MHz, DMSO-d_6)



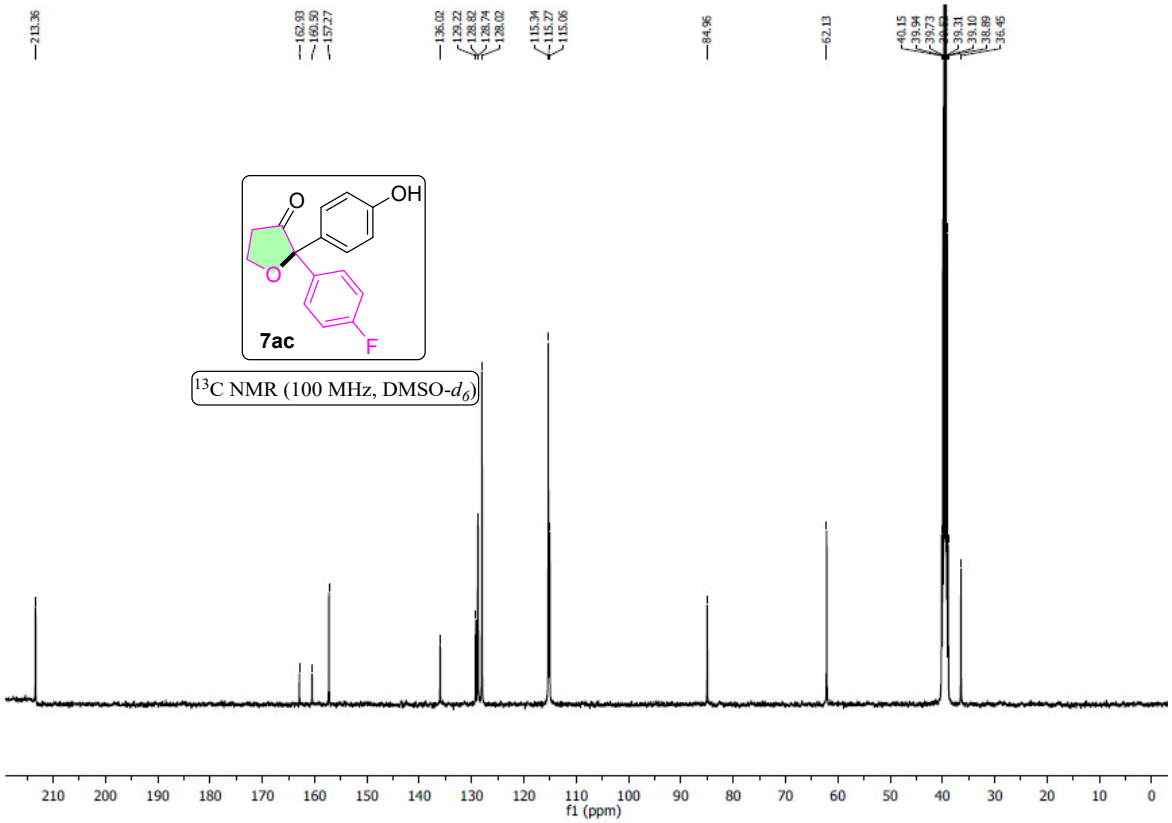
[1]H NMR (500 MHz, DMSO-d_6)



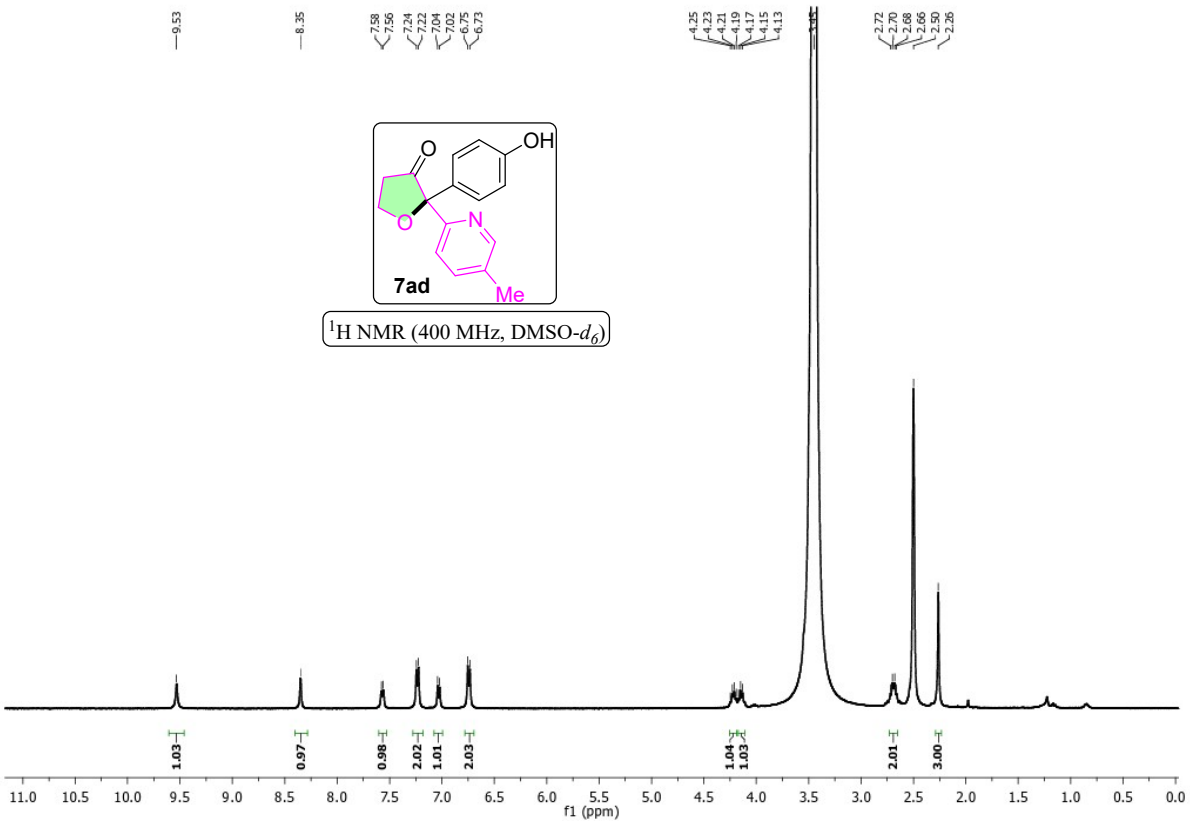
[13]C NMR (125 MHz, DMSO-d_6)



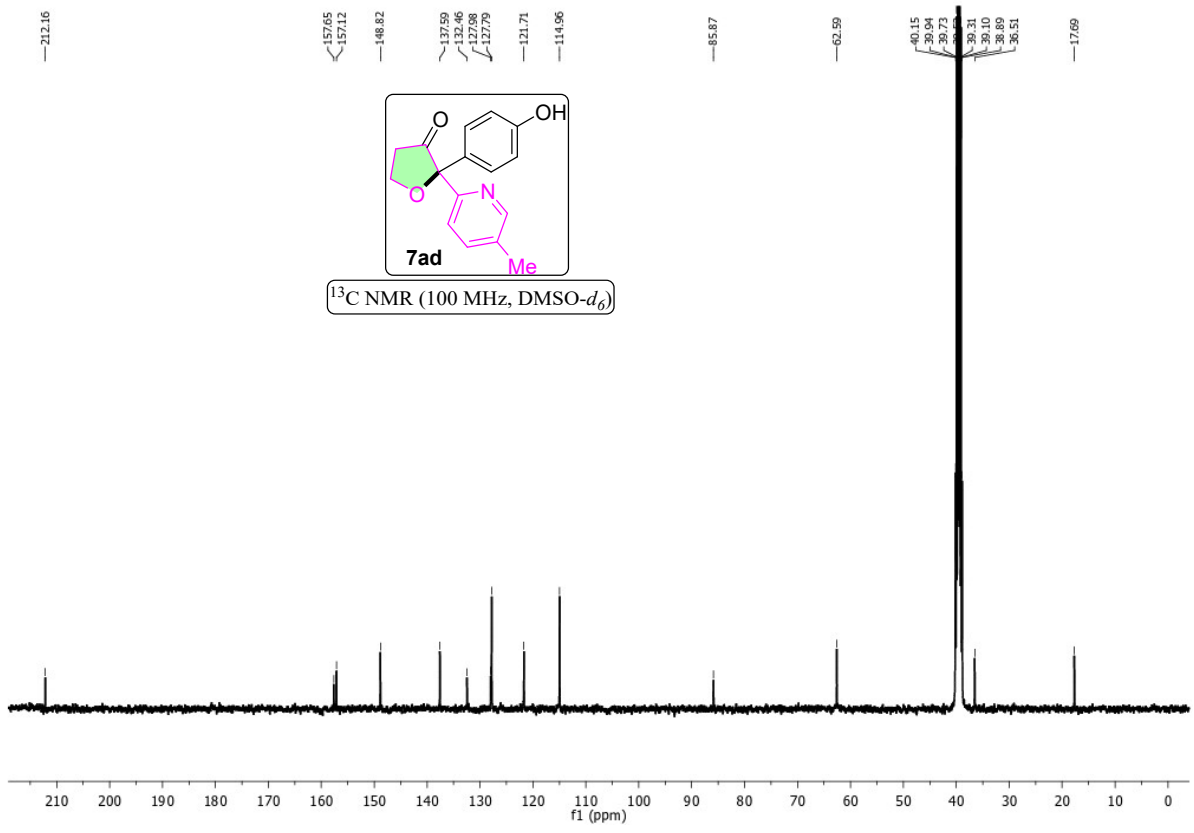
^{1}H NMR (400 MHz, DMSO-d_6)



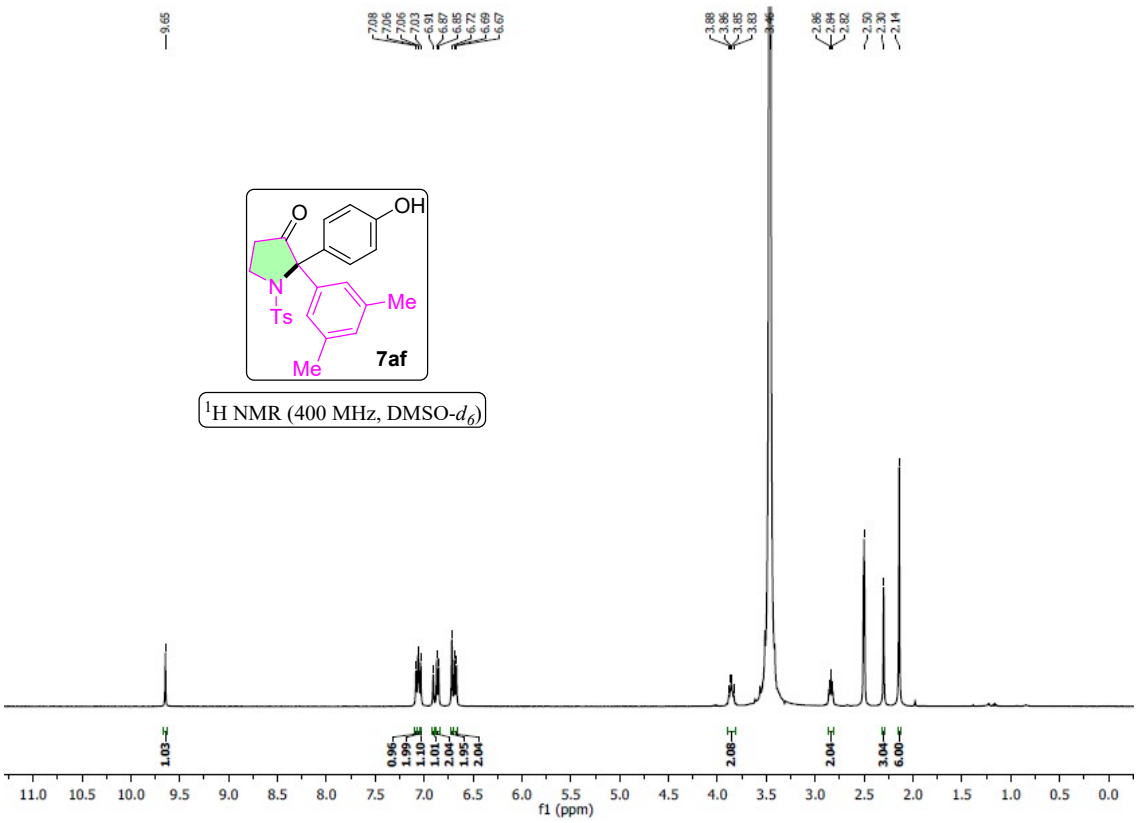
^{13}C NMR (100 MHz, DMSO-d_6)



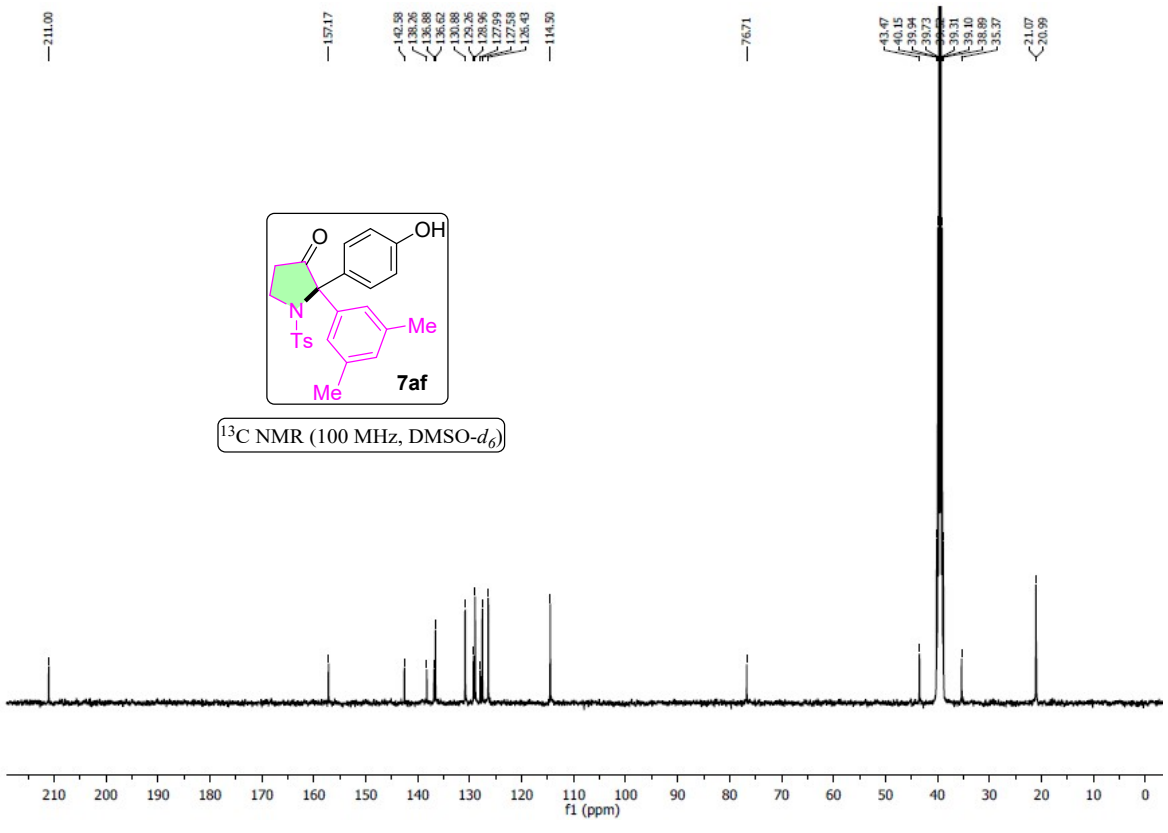
^{1}H NMR (400 MHz, DMSO-d_6)



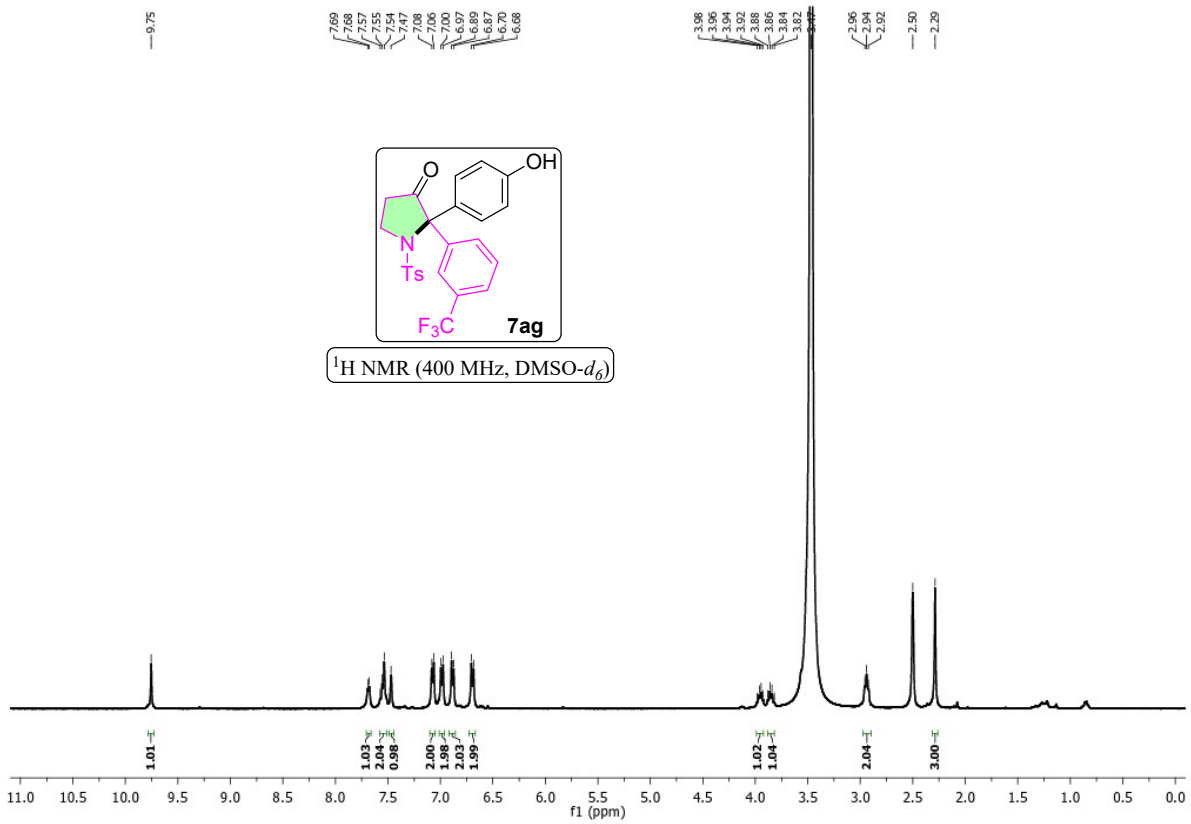
^{13}C NMR (100 MHz, DMSO-d_6)



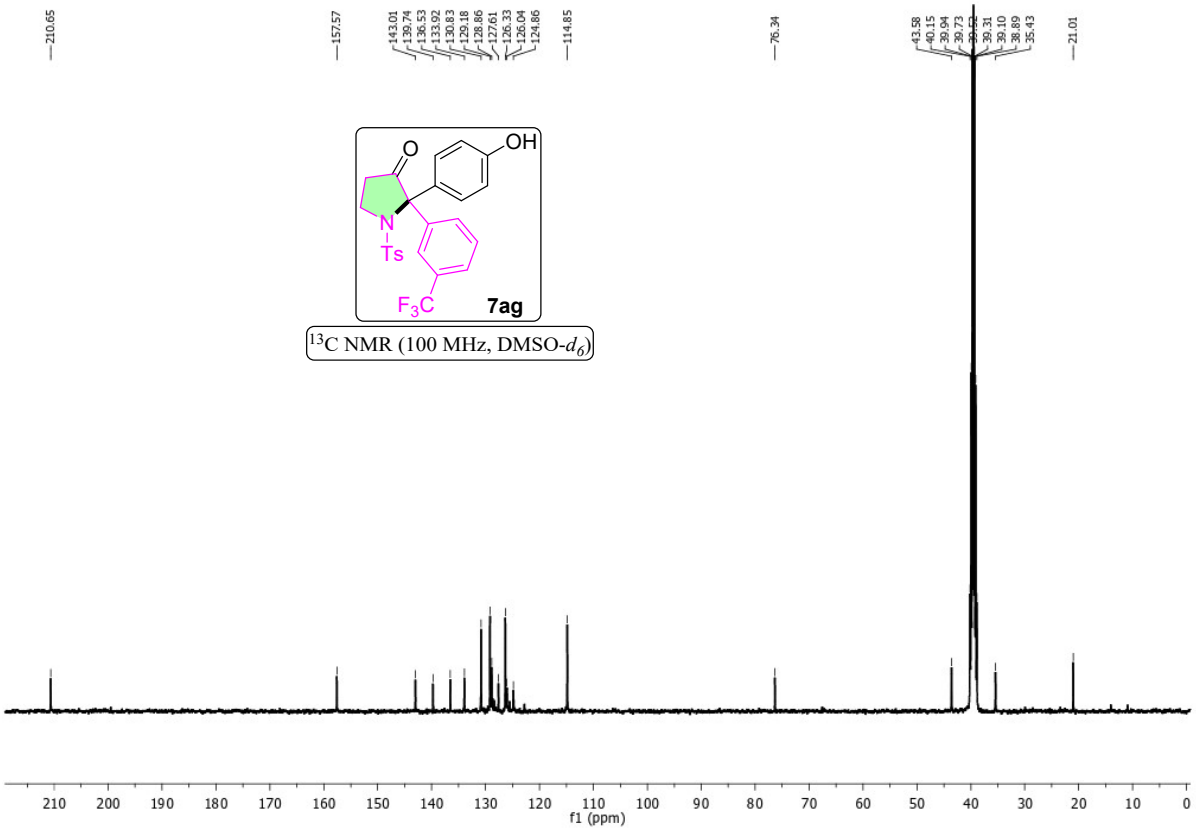
^{1}H NMR (400 MHz, DMSO-d_6)



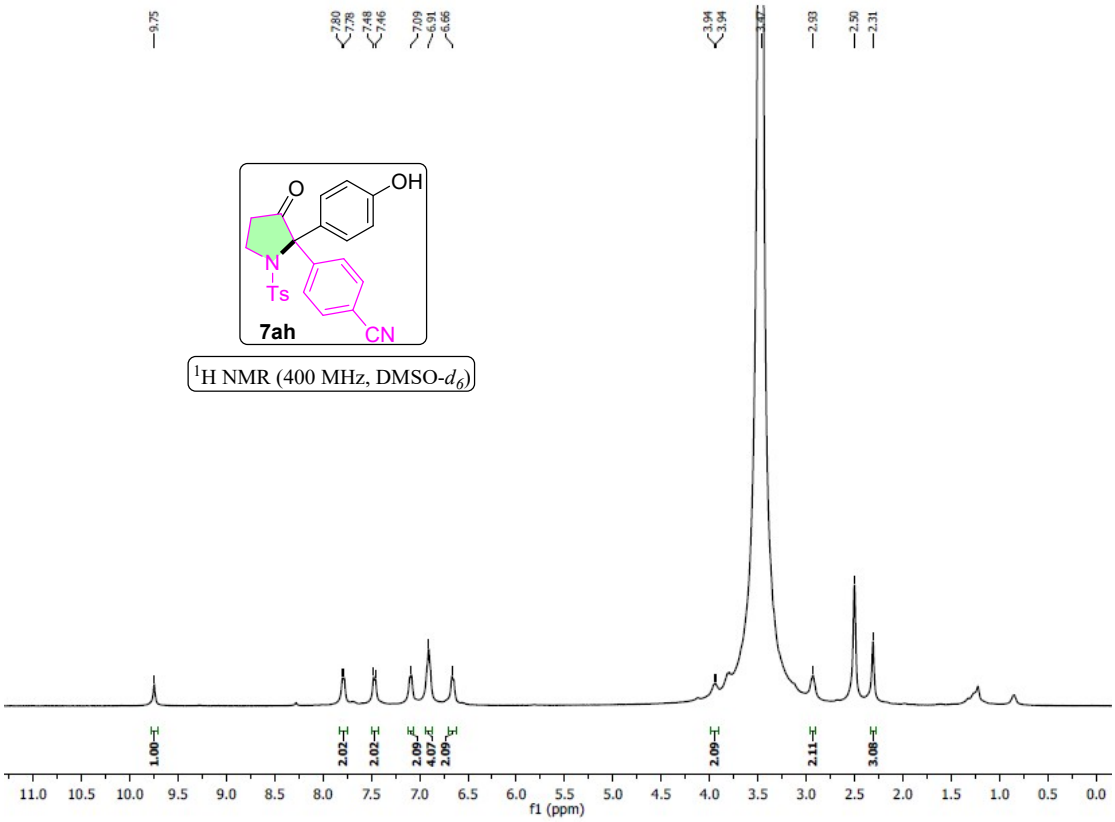
^{13}C NMR (100 MHz, DMSO-d_6)



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



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



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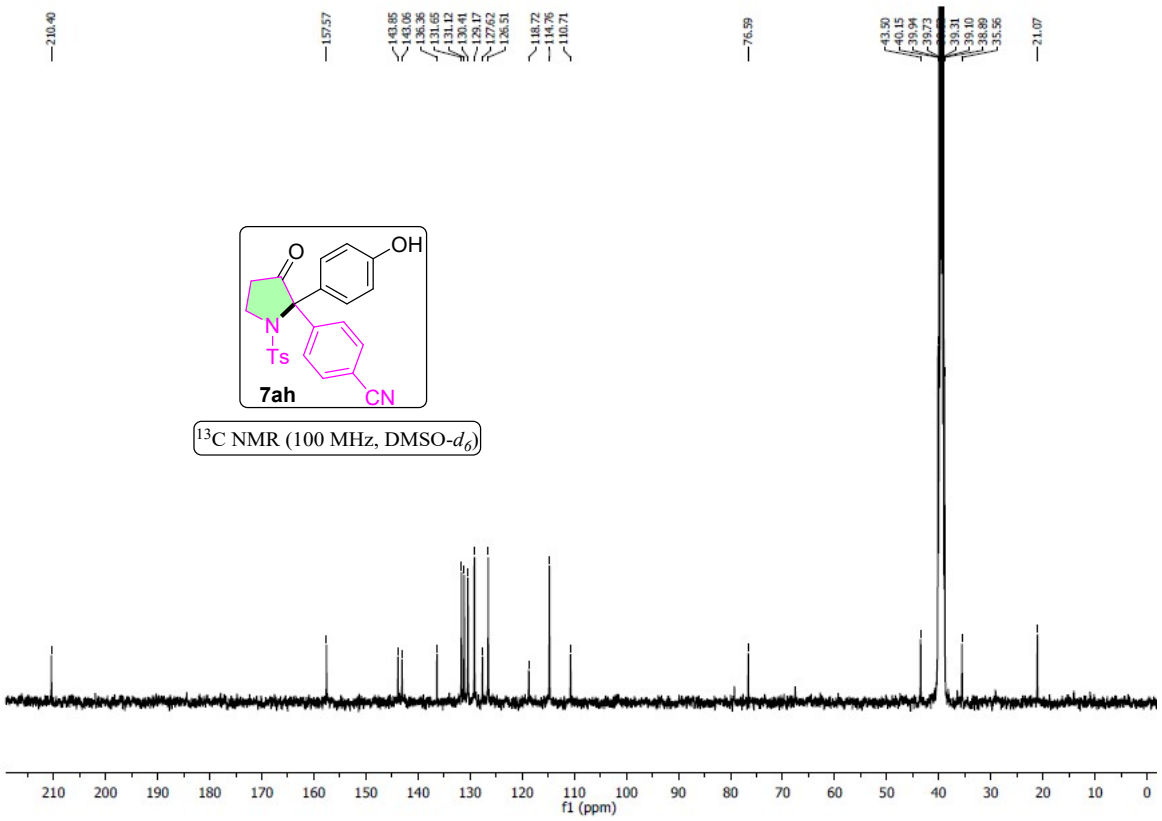

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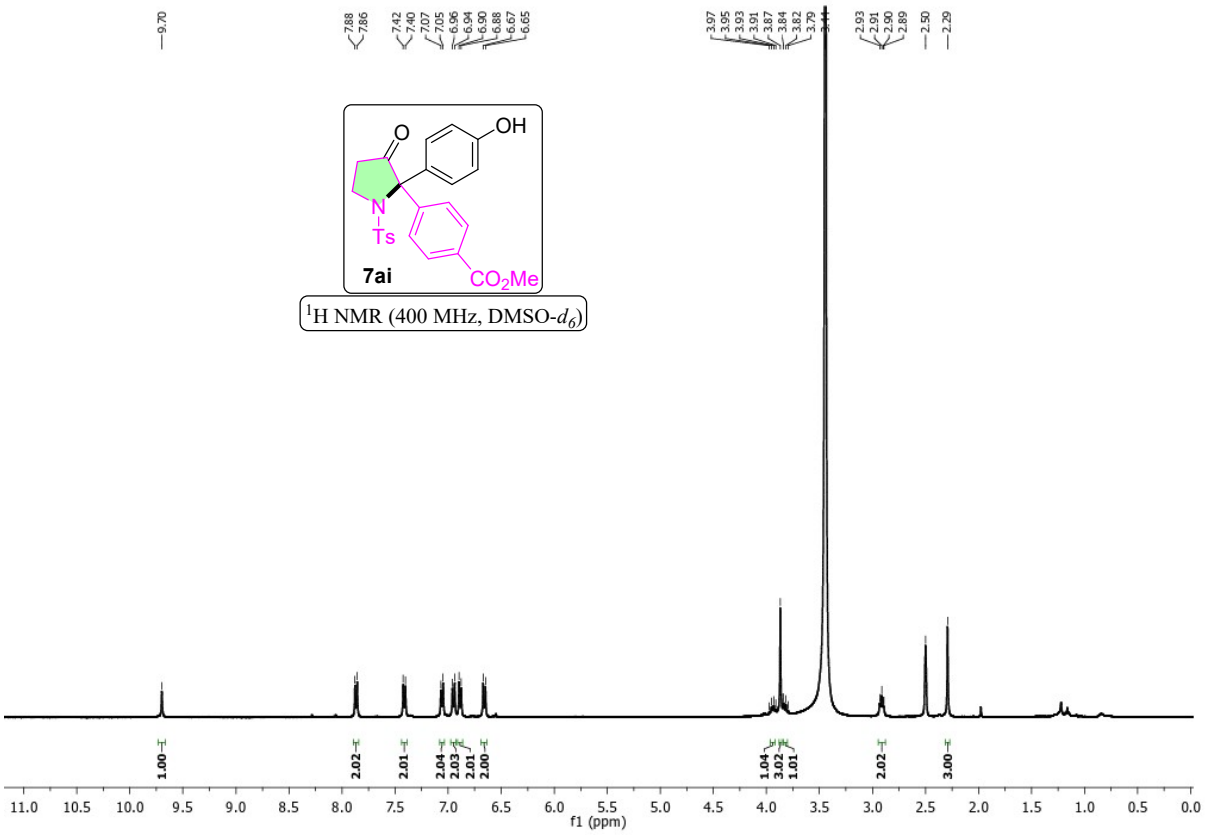
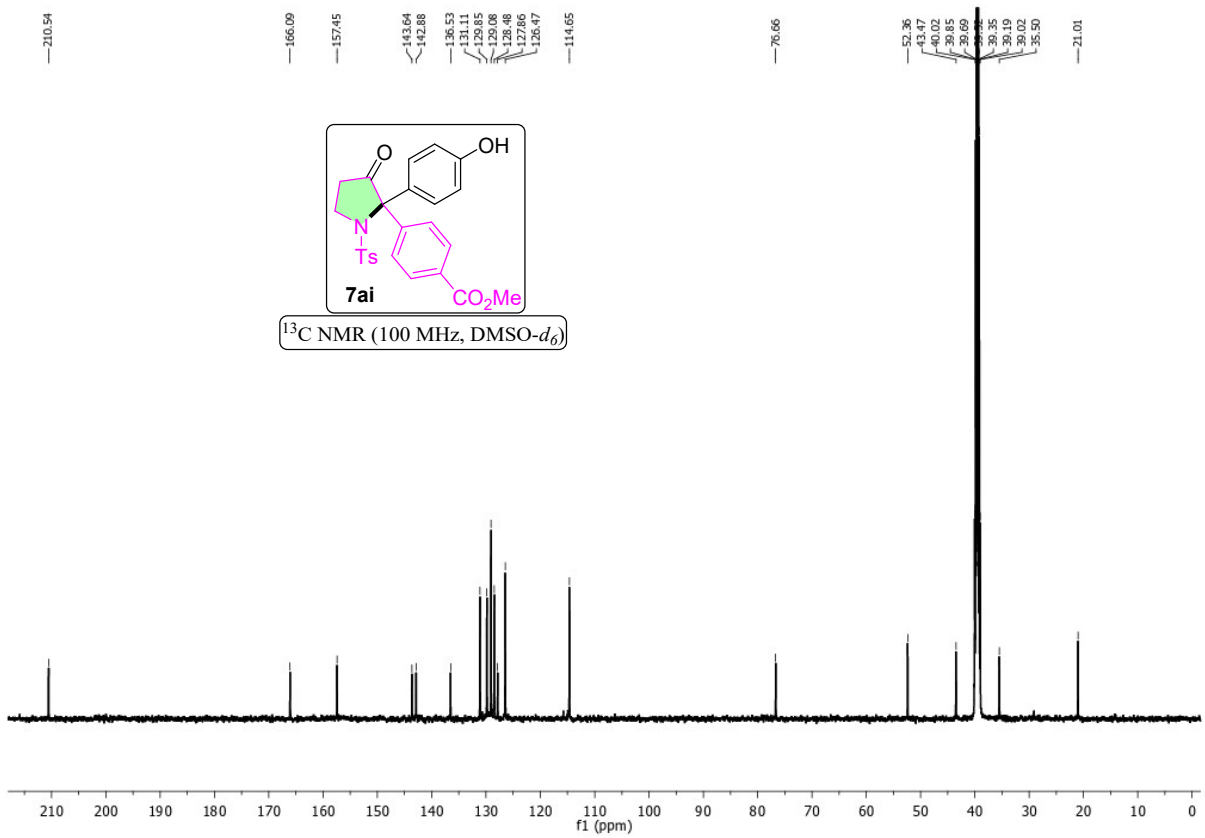
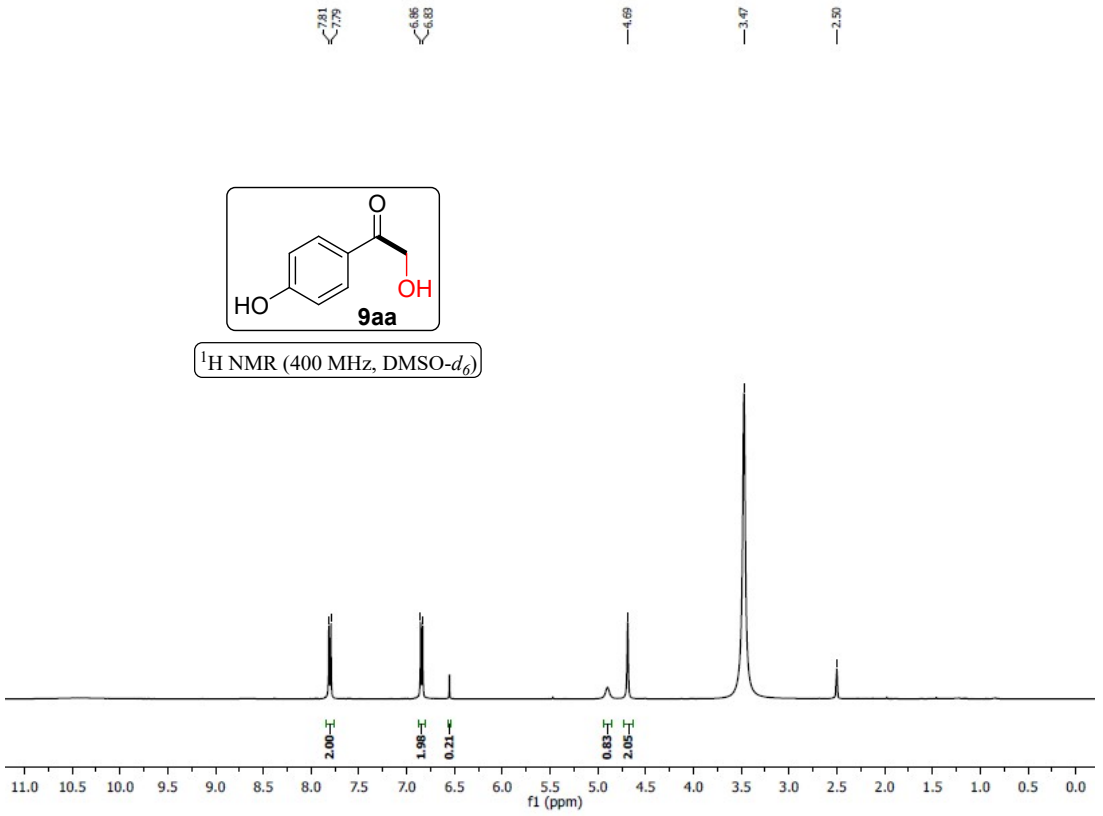


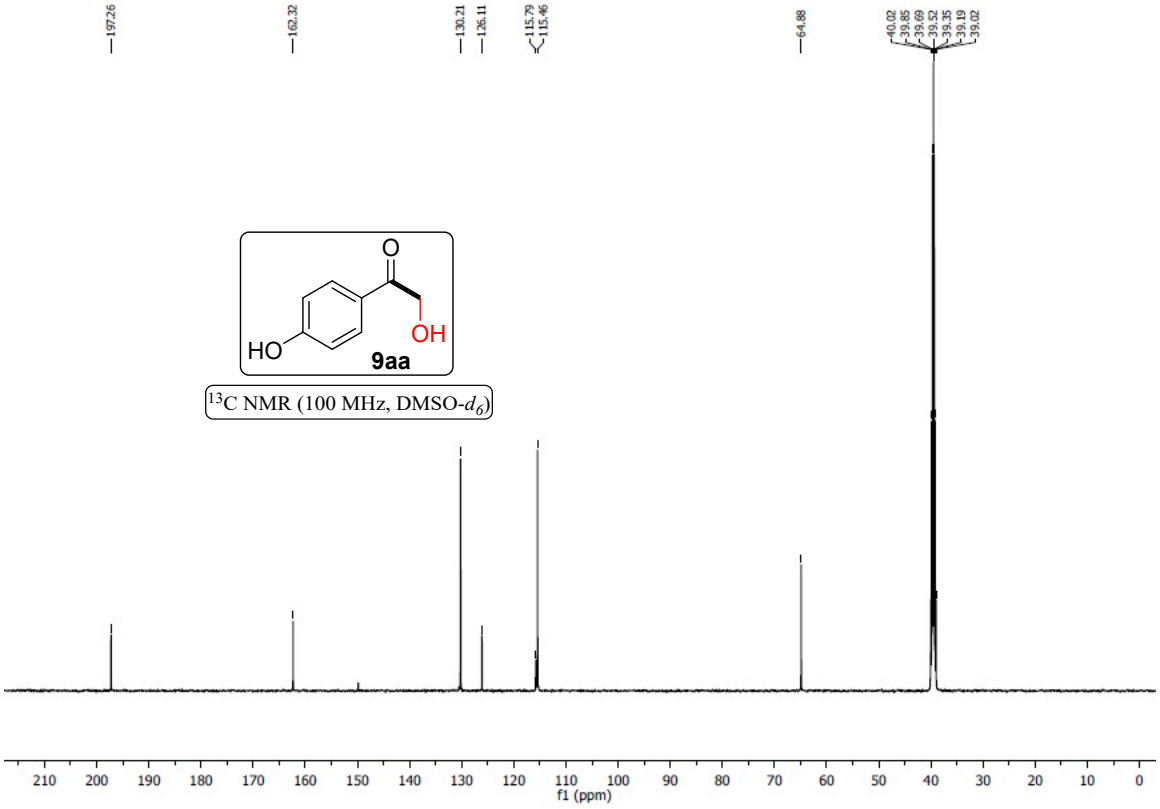
^{1}H NMR (400 MHz, DMSO-d_6)



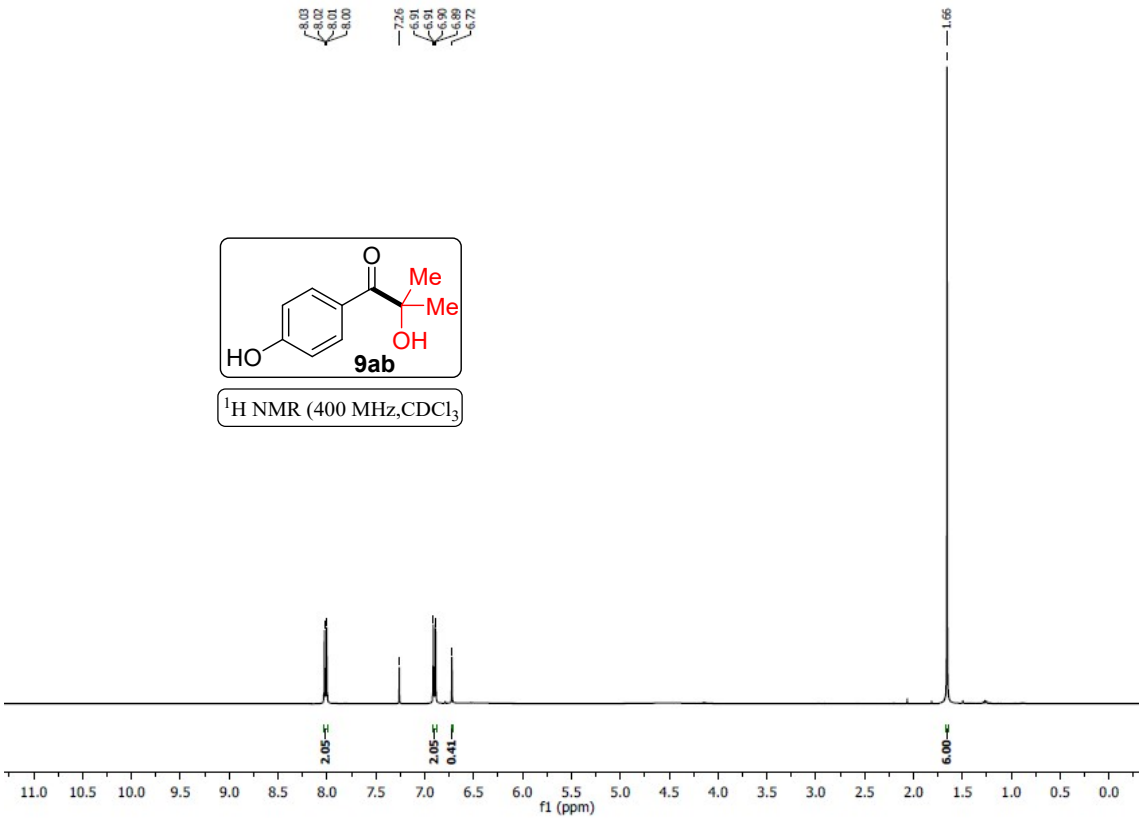
^{13}C NMR (100 MHz, DMSO-d_6)



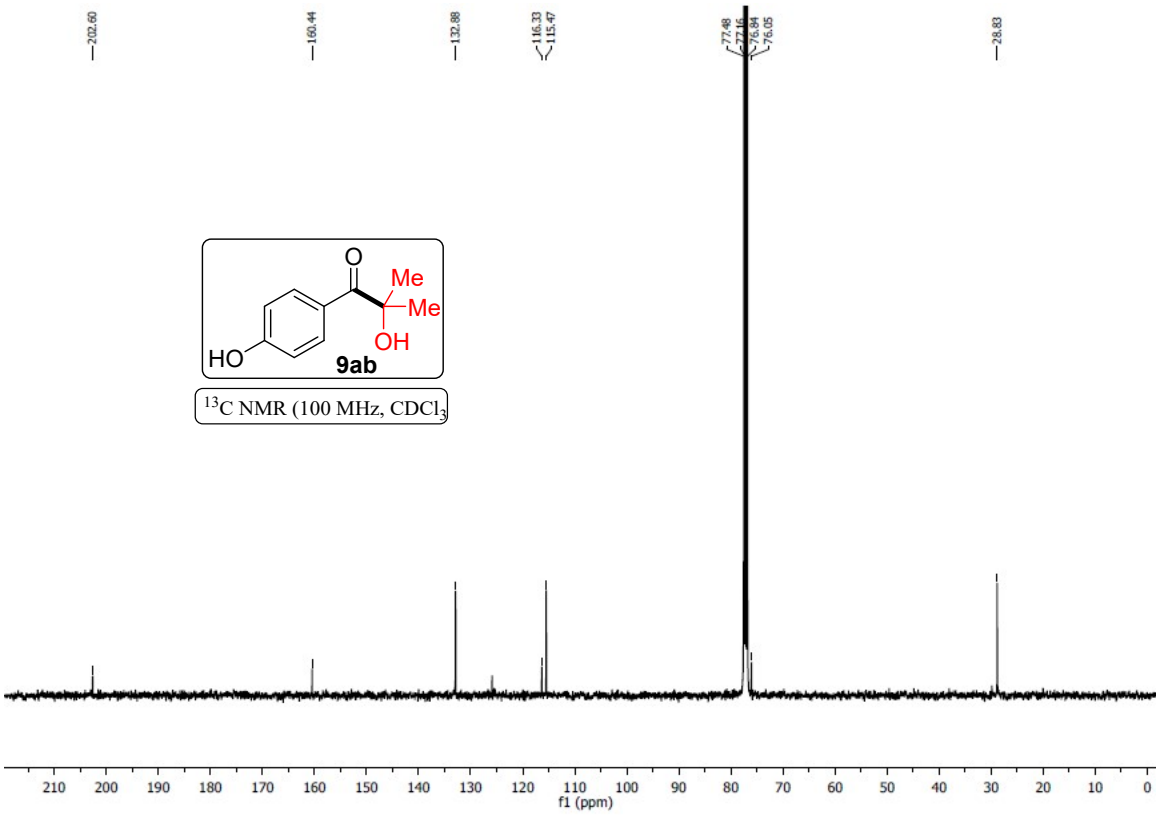
^{1}H NMR (400 MHz, DMSO-d_6)



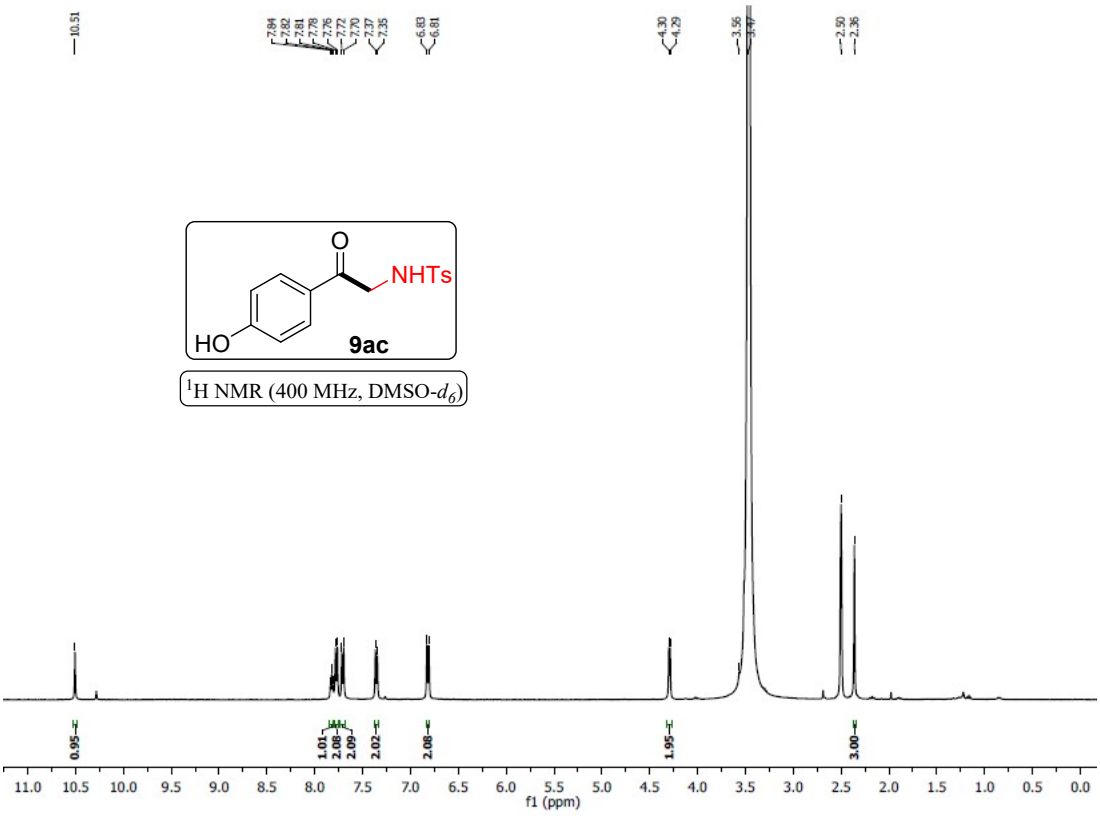
^{13}C NMR (100 MHz, DMSO-d_6)



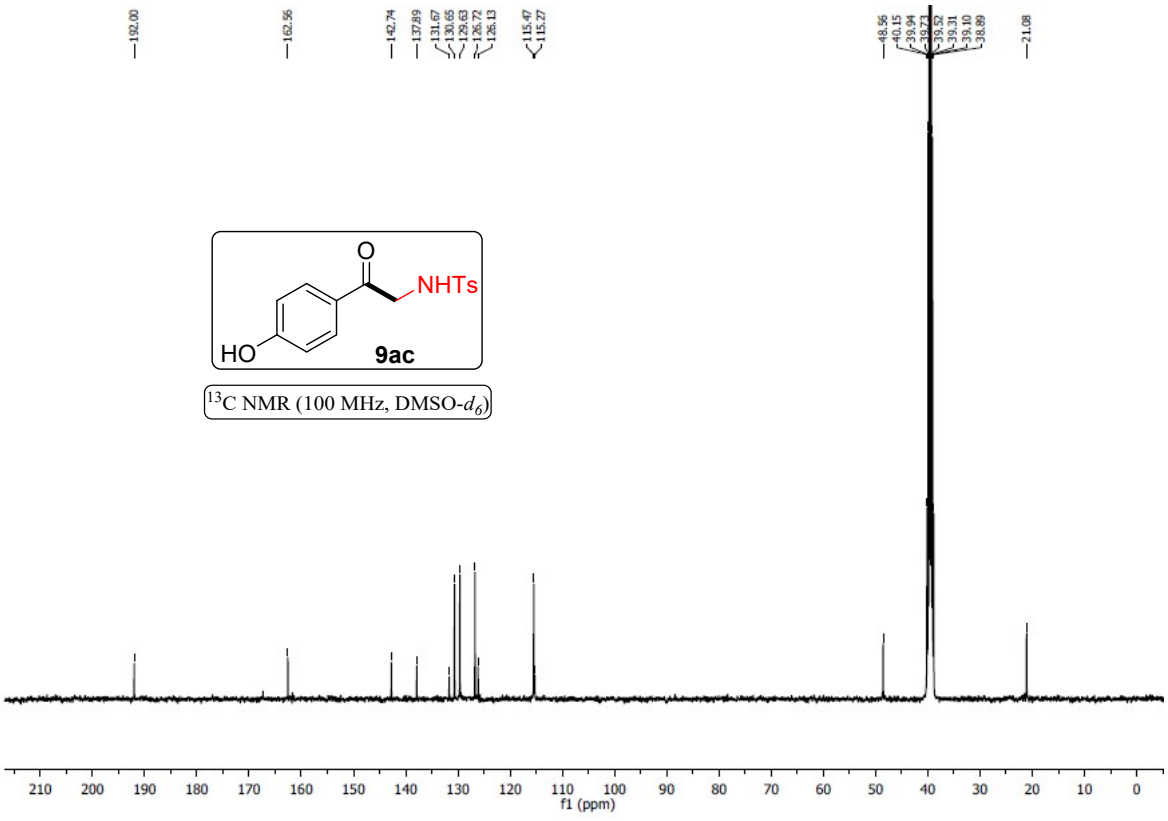
^{1}H NMR (400 MHz,$CDCl_3$)



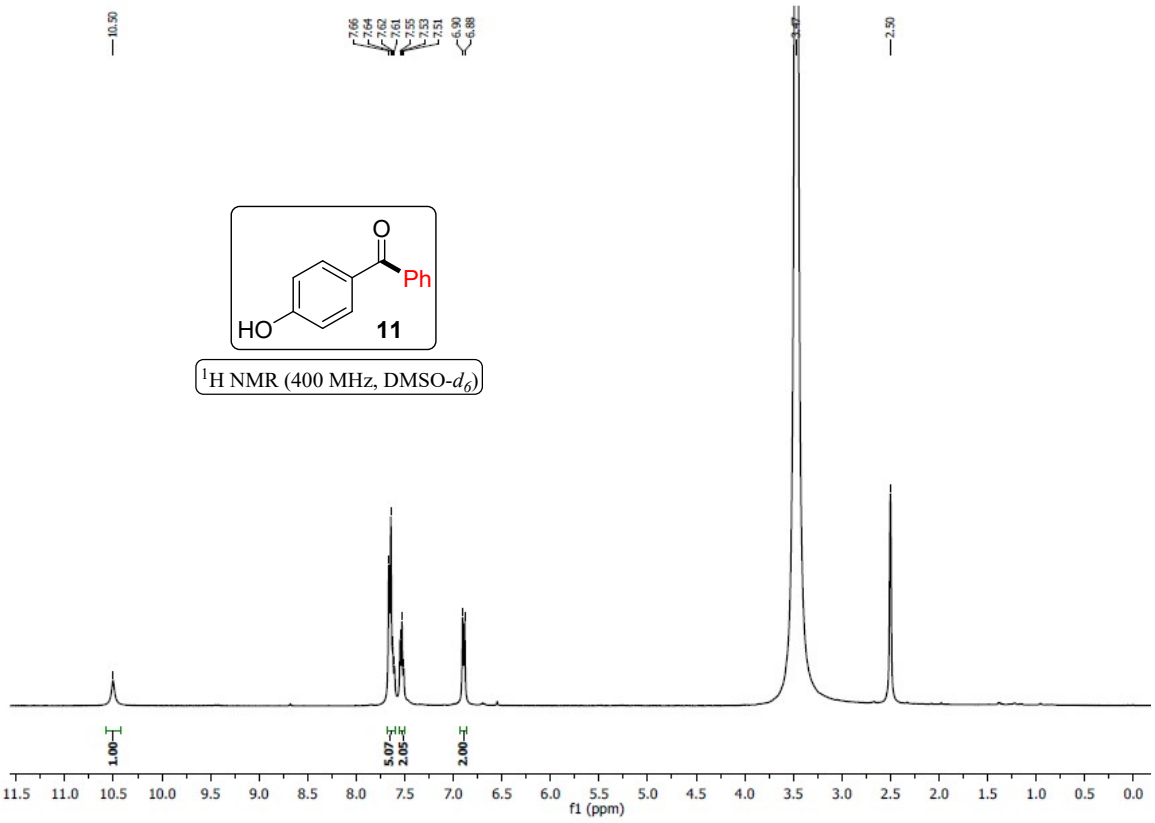
^{13}C NMR (100 MHz, $CDCl_3$)



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



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



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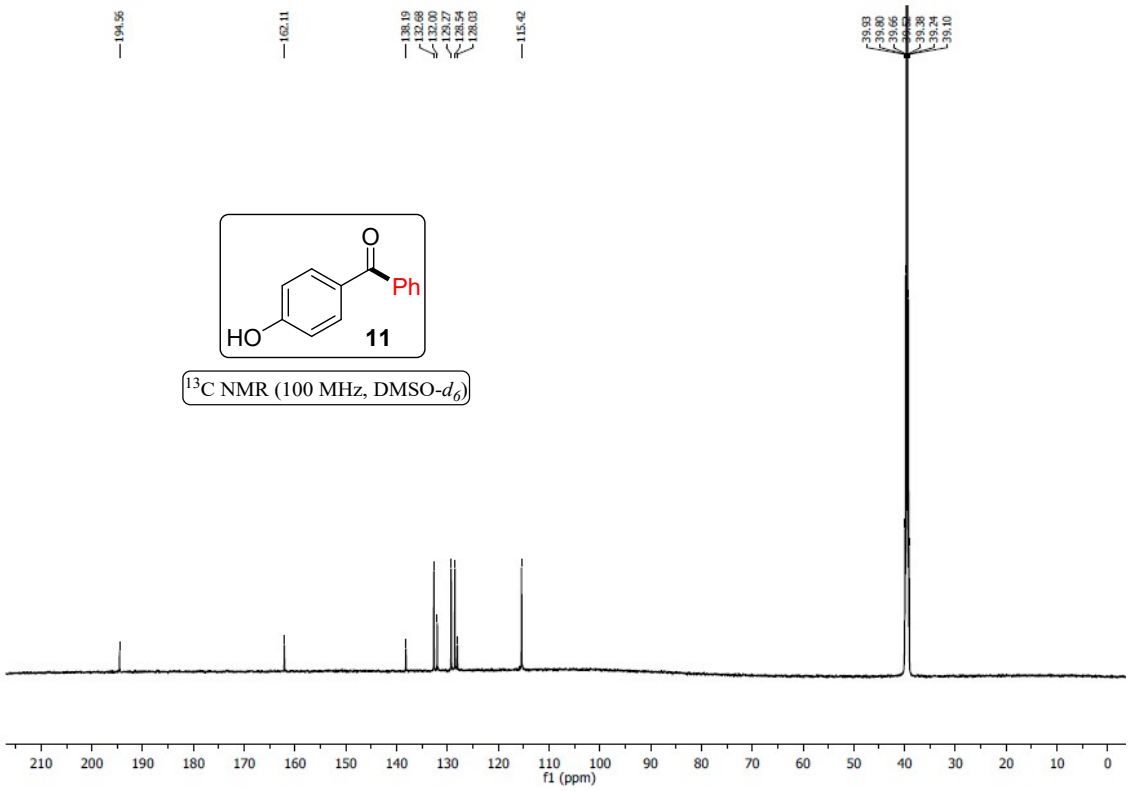
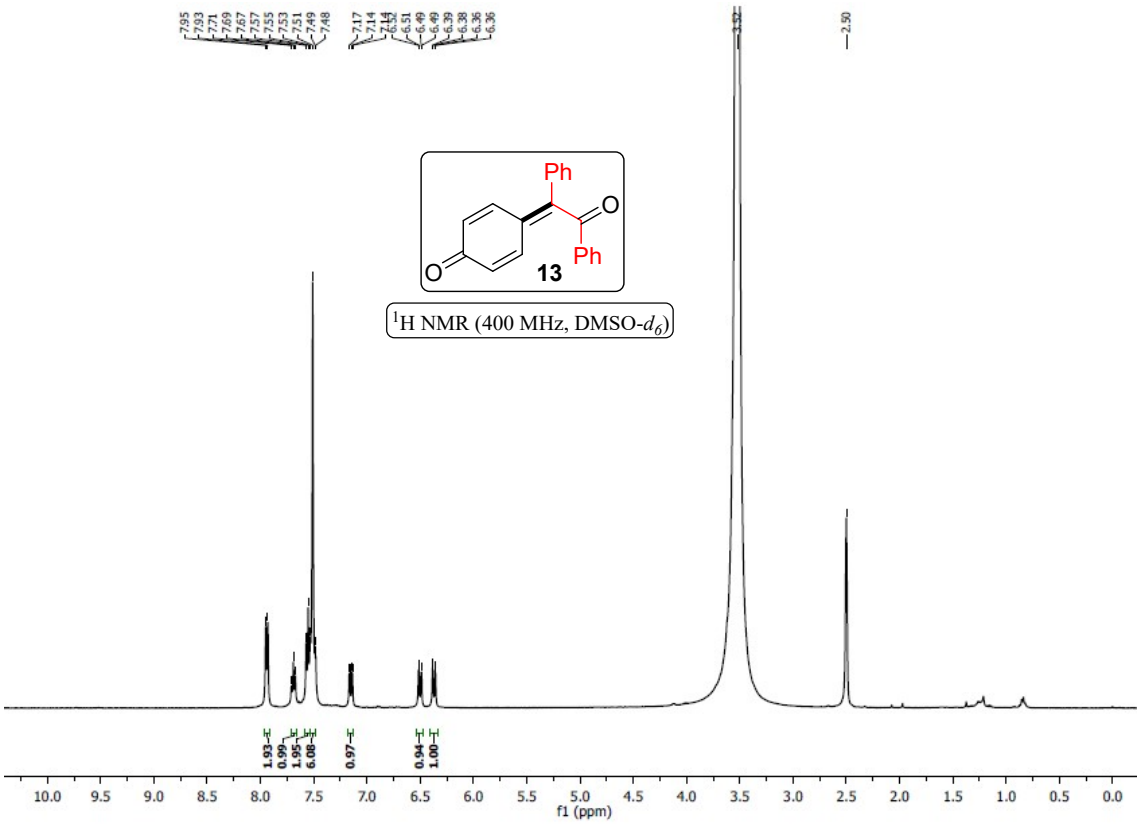
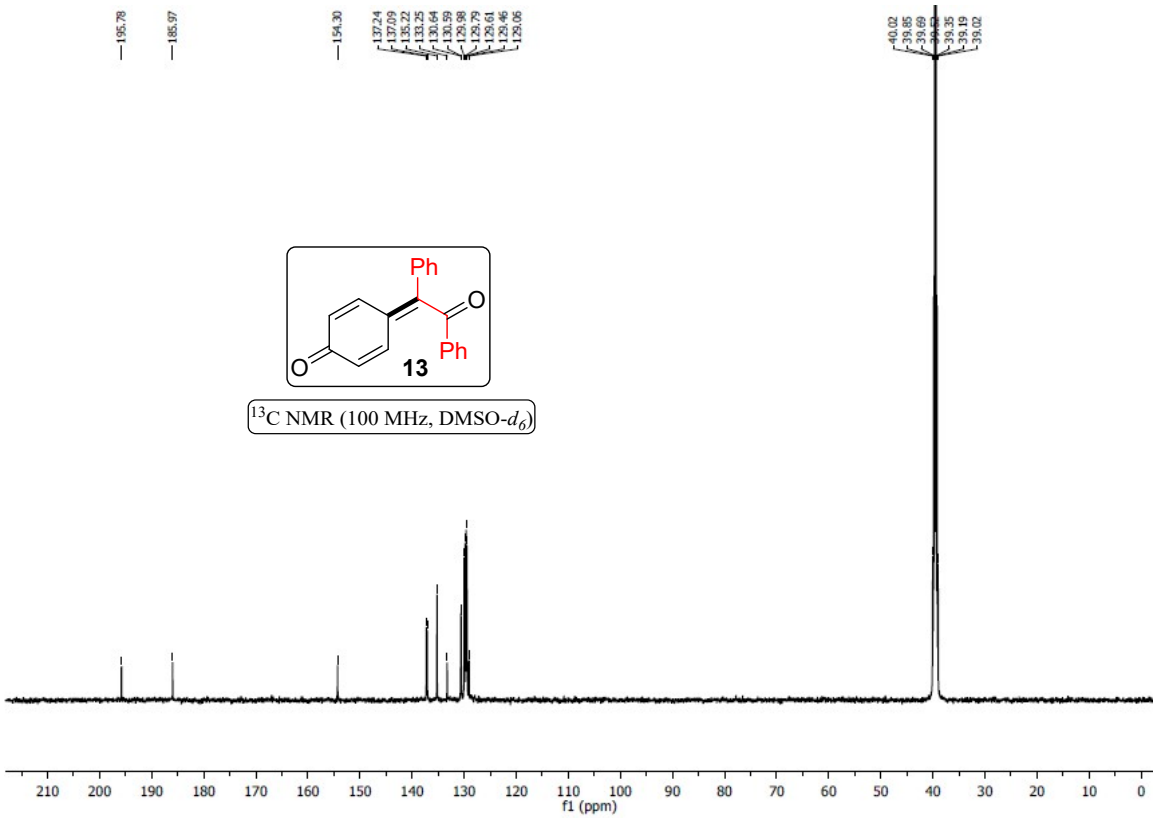
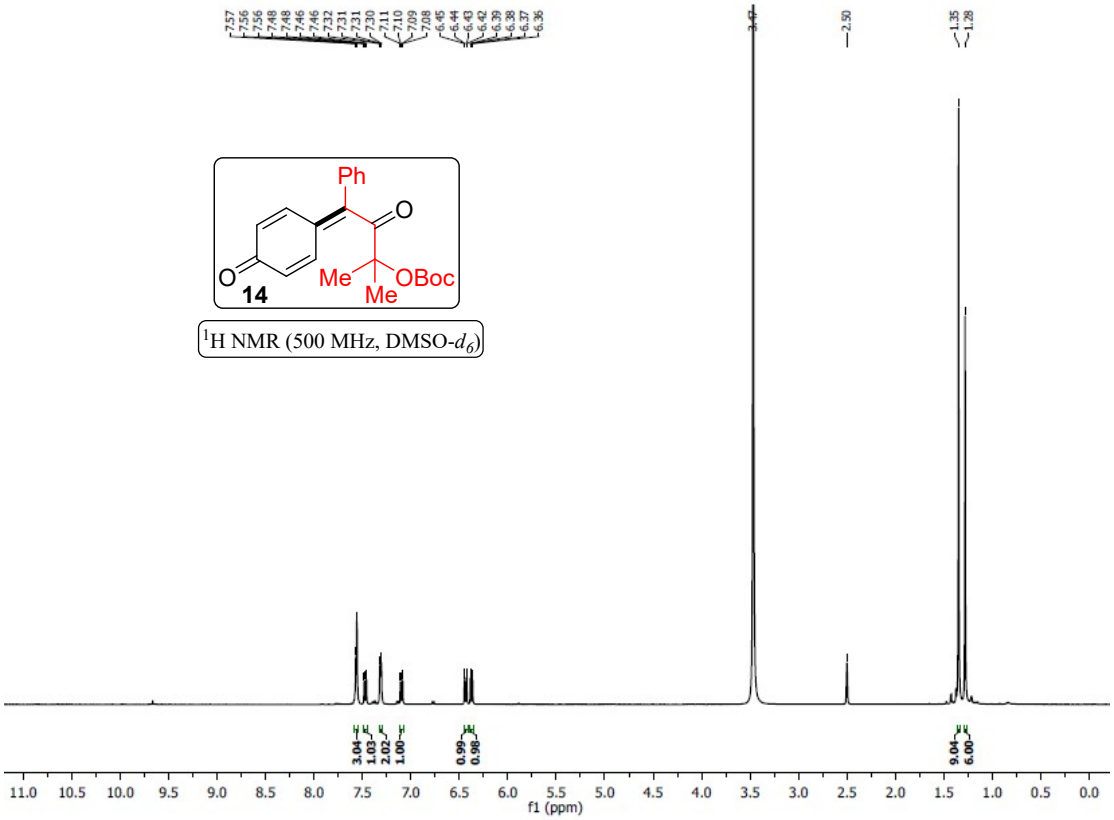


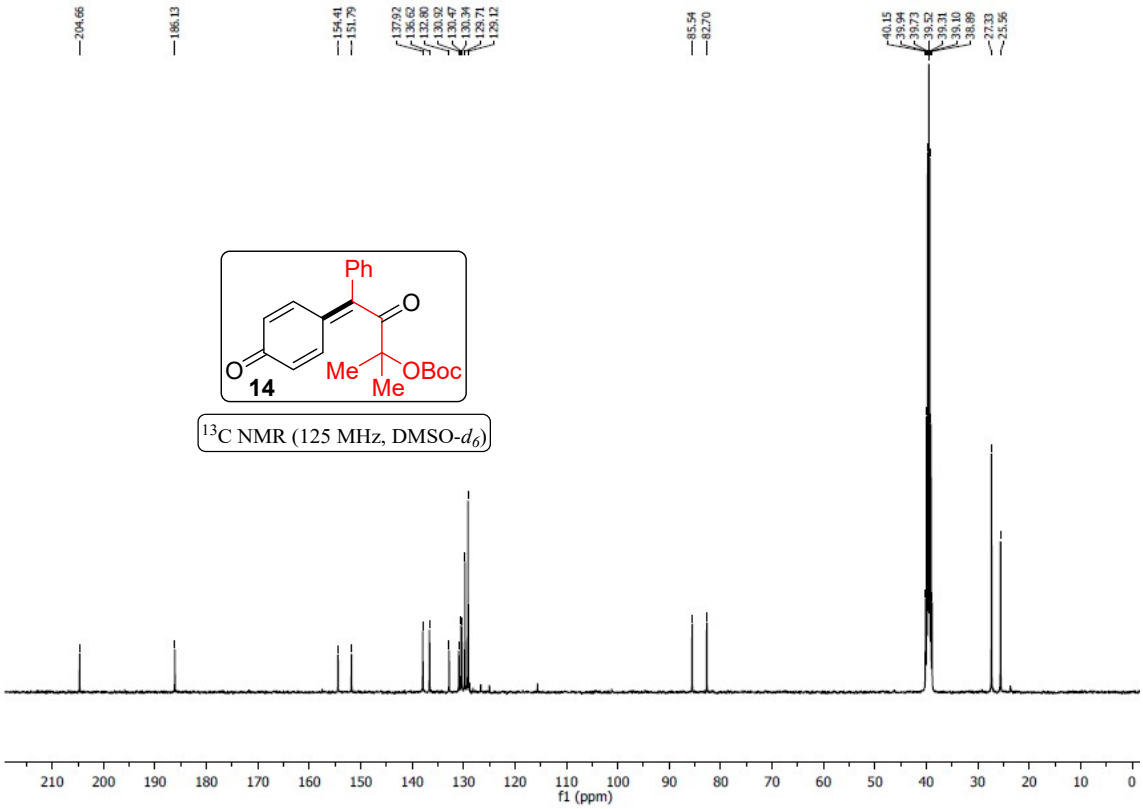
^{13}C NMR (100 MHz, DMSO-d_6)


Ph
O
O
Ph
13
1H NMR (400 MHz, DMSO-d6)
f1 (ppm)

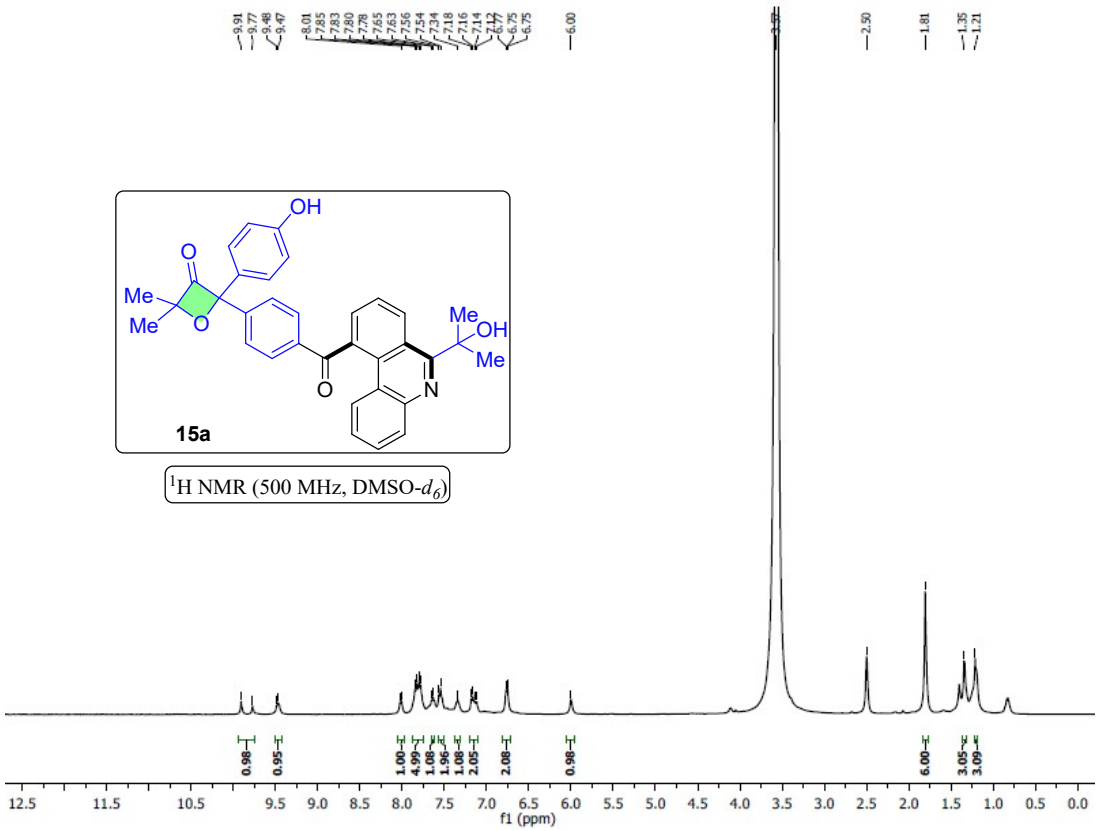

Ph
O
O
Ph
13
13C NMR (100 MHz, DMSO-d6)
f1 (ppm)



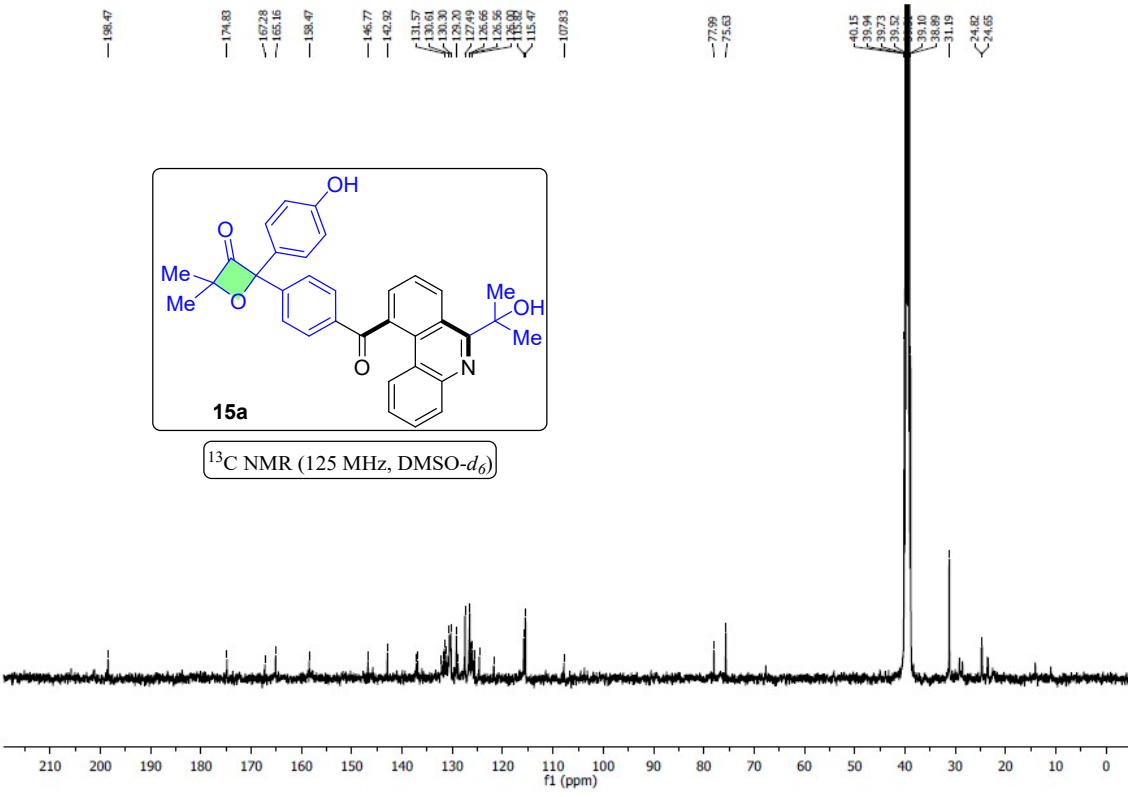
^{1}H NMR (500 MHz, DMSO-d_6)



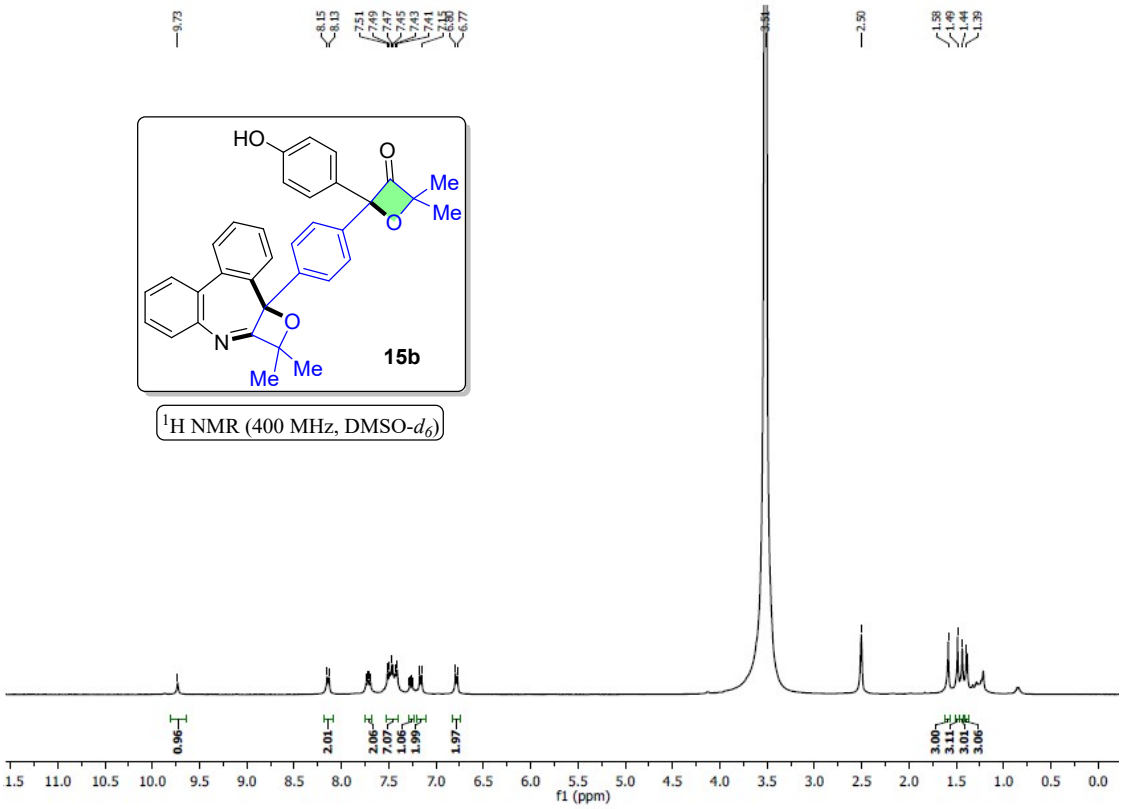
^{13}C NMR (125 MHz, DMSO-d_6)



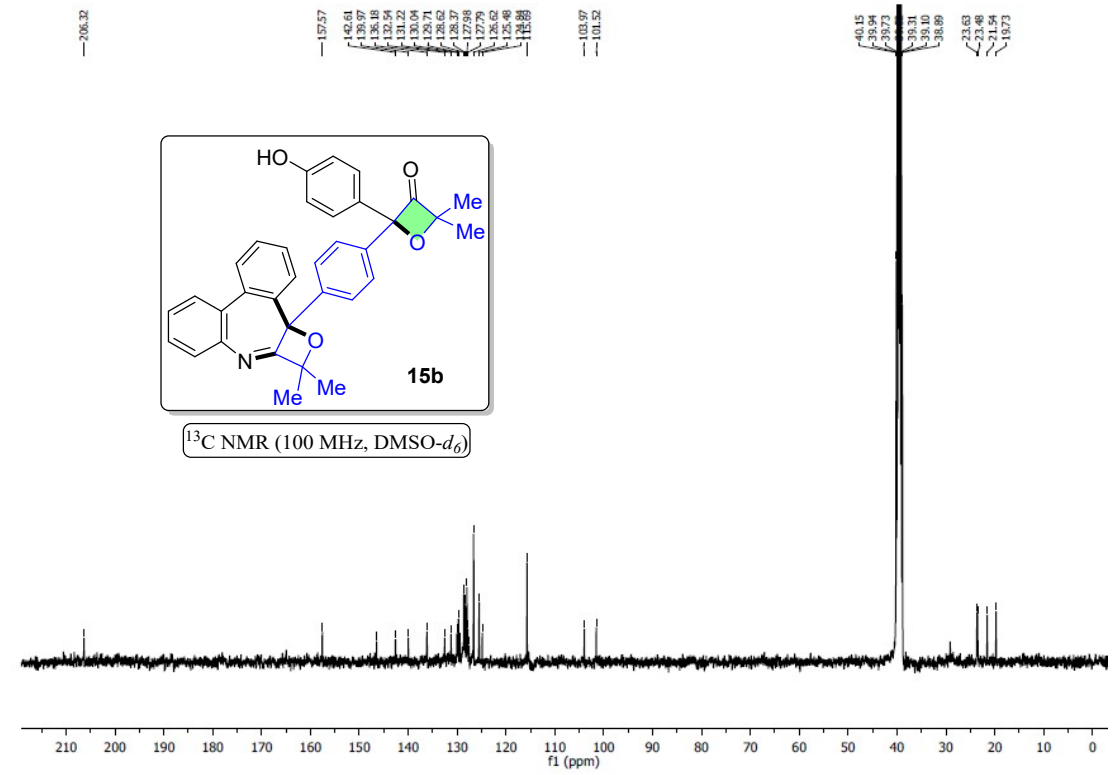
^{1}H NMR (500 MHz, DMSO-d_6)



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



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



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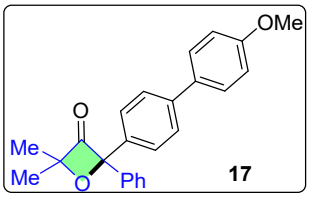
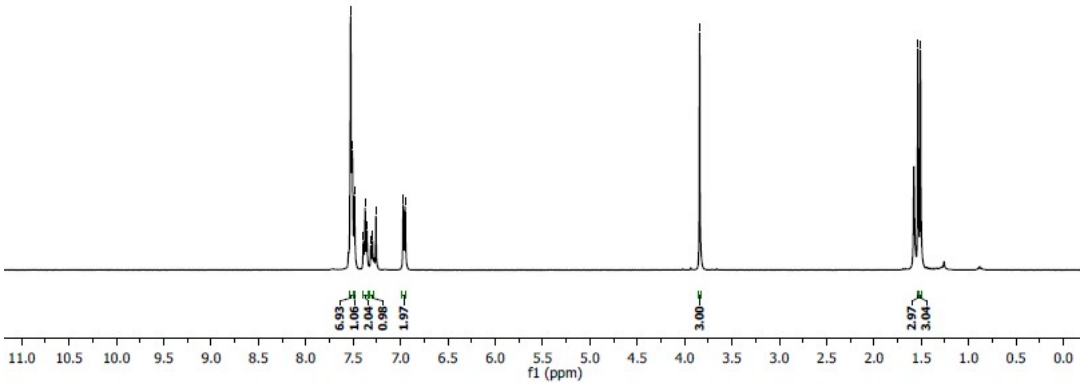
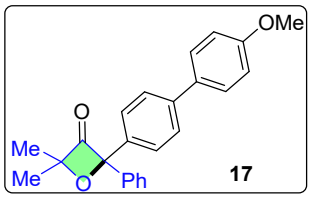
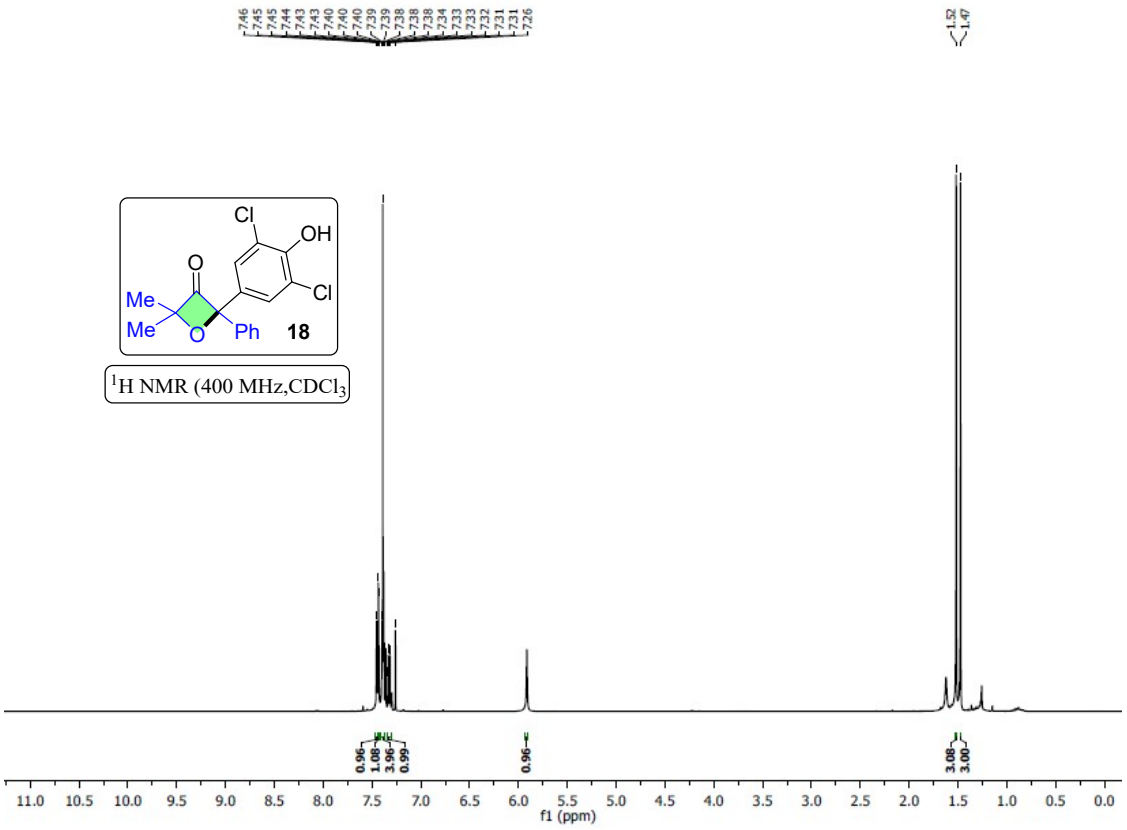


^{1}H NMR (400 MHz,$CDCl_3$)

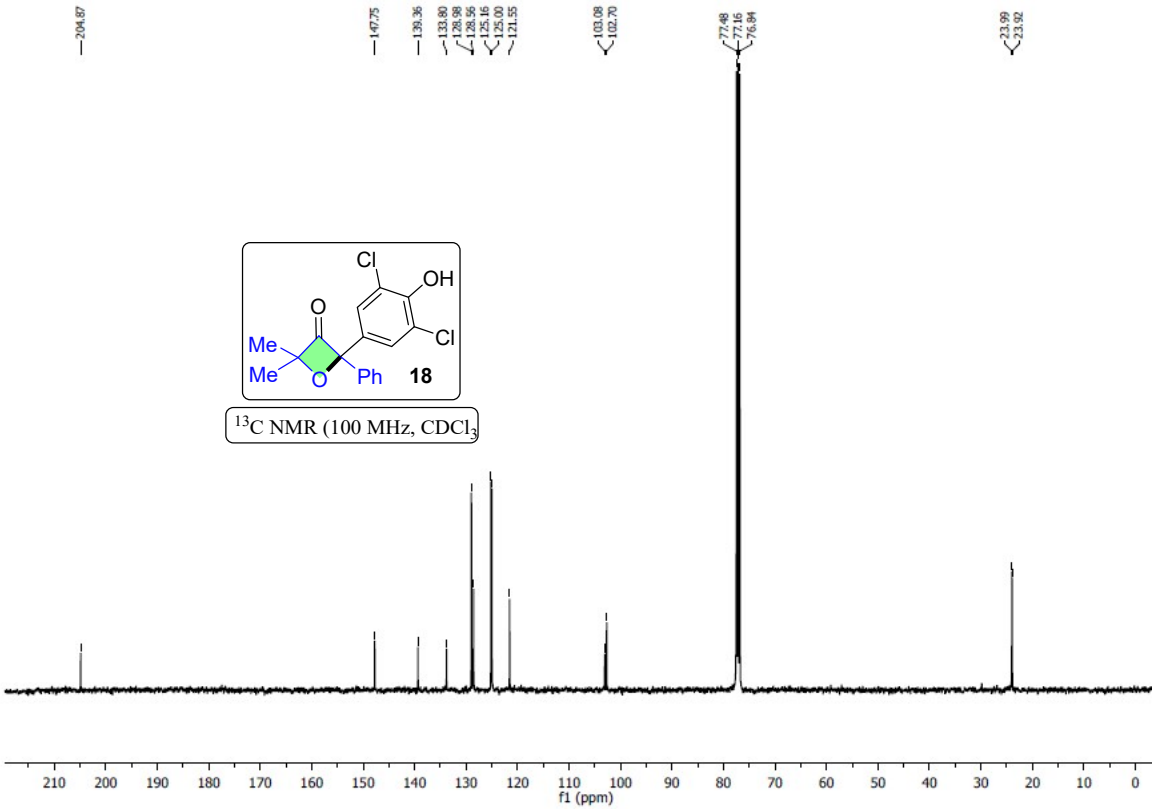




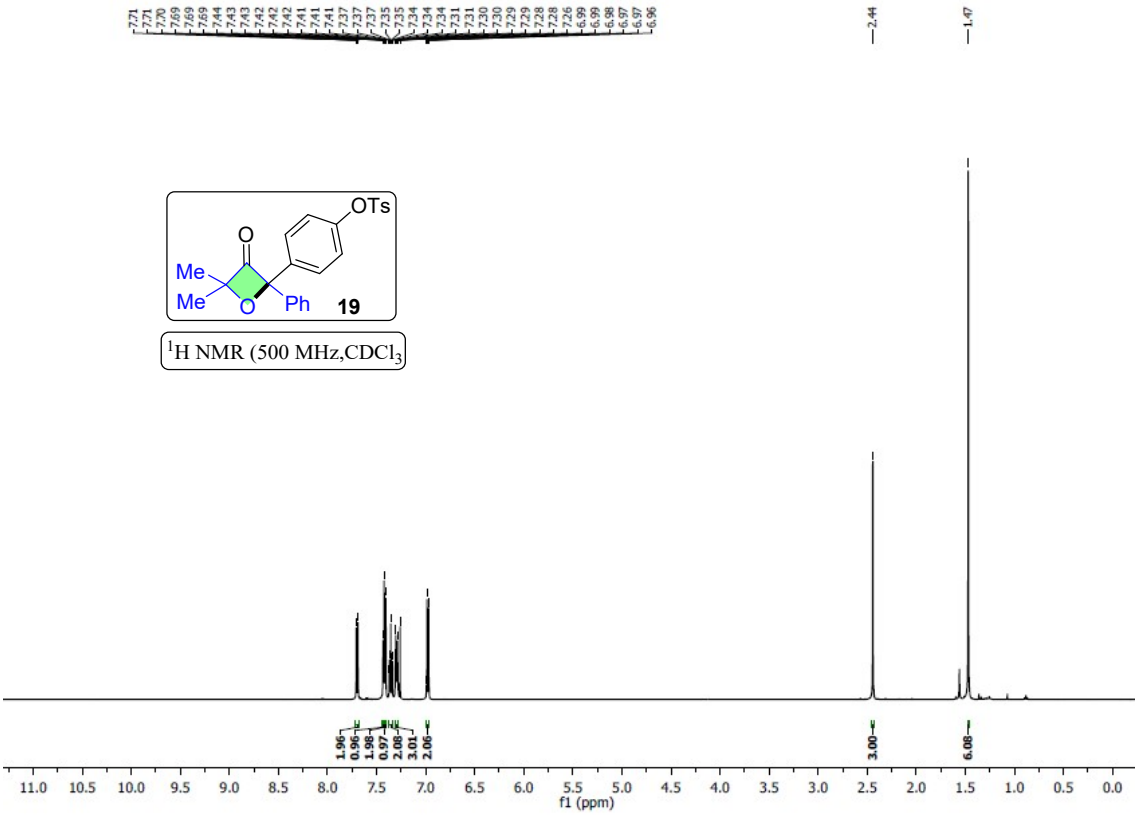
^{13}C NMR (100 MHz, $CDCl_3$)

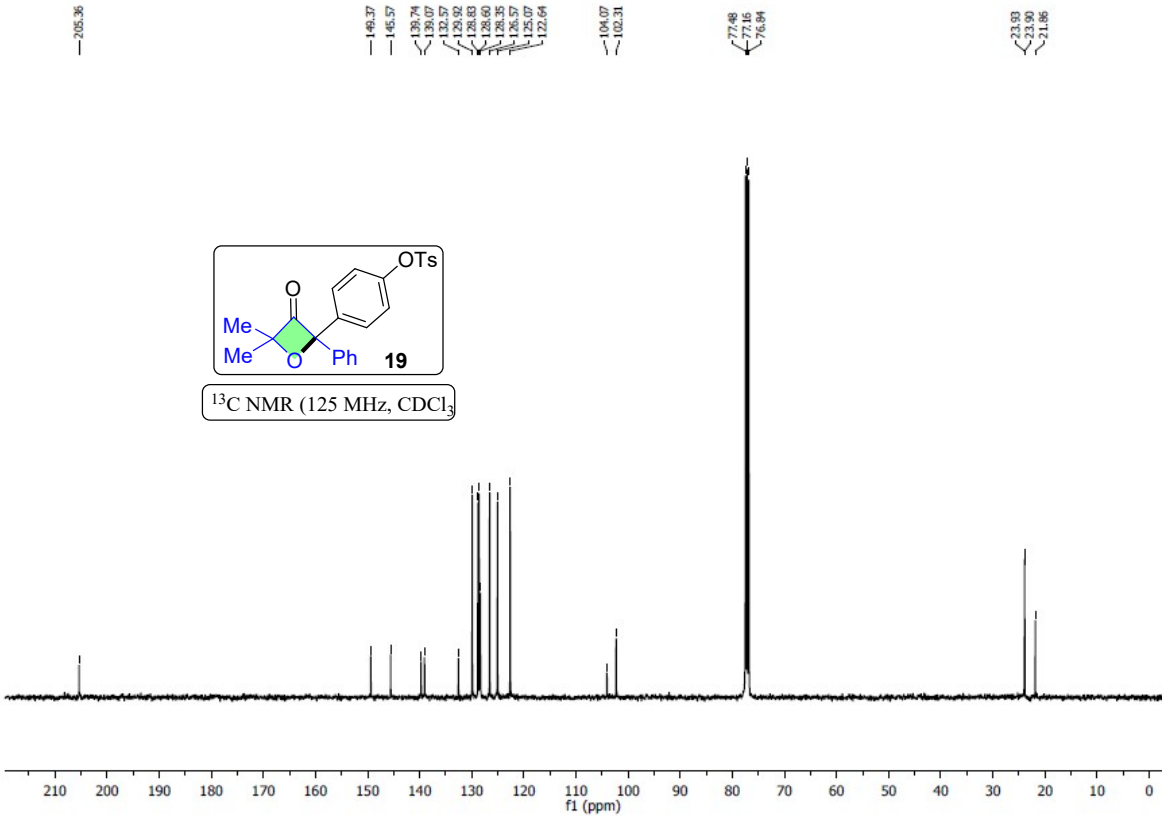


^{1}H NMR (400 MHz,$CDCl_3$)



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


OTs
O
Me
Me
O
Ph
19
1H NMR (500 MHz,CDCl3
f1 (ppm)


OTs
O
Me
Me
O
Ph
19
13C NMR (125 MHz, CDCl3
f1 (ppm)

7. X-ray crystallography data:

Sample Preparation for Crystal Growth: The compound **3al** was dissolved in acetonitrile 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.

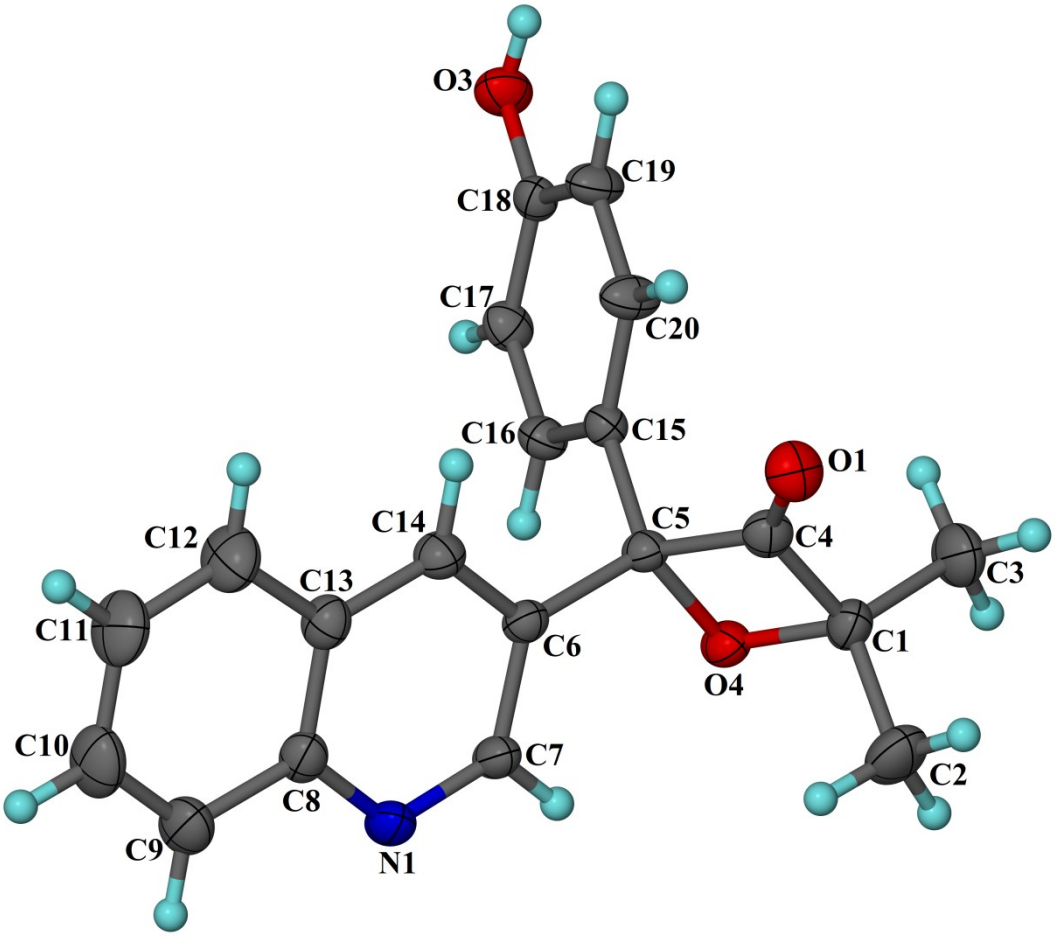


Figure 1. ORTEP diagram of KB892 (**3al**) compound with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

Crystal data for KB892 (3al): $C_{20}H_{17}NO_3$, M = 319.35, Orthorhombic, Space group *Pbca* (No.61), a = 10.9720(5)Å, b = 10.3056(5)Å, c = 29.8407(14)Å, α = 90°, β = 90°, γ = 90°, V = 3374.2(3)Å^3, Z = 8, D_c = 1.257 g/cm^3, F_{000} = 1344, Bruker D8 QUEST PHOTON III C7 HPAD detector, Mo-Kα radiation, λ = 0.71073 Å, T = 294(2)K, $2\theta_{max}$ = 55º, μ = 0.085 mm^{-1}, 25287 reflections collected, 3874 unique (R_{int} = 0.0607), 230 parameters, *R1* = 0.0454, *wR2* = 0.1073, *R* indices based on 2411 reflections with I > 2σ(I) (refinement on F^2), Final

GooF = 1.024, largest difference hole and peak = -0.144 and 0.163 e.Å^{-3}. The **CCDC deposition number 2295367** contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) KB892_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: KB892_0m

Bond precision: C-C = 0.0026 A Wavelength=0.71073

Cell: a=10.9720(5) b=10.3056(5) c=29.8407(14)
alpha=90 beta=90 gamma=90
Temperature: 294 K

	Calculated	Reported
Volume	3374.2(3)	3374.2(3)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C20 H17 N O3	C20 H17 N O3
Sum formula	C20 H17 N O3	C20 H17 N O3
Mr	319.35	319.35
Dx,g cm-3	1.257	1.257
Z	8	8
Mu (mm-1)	0.085	0.085
F000	1344.0	1344.0
F000'	1344.64	
h,k,lmax	14,13,38	14,13,38
Nref	3883	3874
Tmin,Tmax	0.978,0.981	0.671,0.746
Tmin'	0.978	

Correction method= # Reported T Limits: Tmin=0.671 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 27.499

R(reflections)= 0.0454(2411) wR2(reflections)= 0.1269(3874)

S = 1.024 Npar= 230

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

PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 8 Report
PLAT913_ALERT_3_C Missing # of Very Strong Reflections in FCF .... 6 Note

Alert level G

PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 1 Report
PLAT168_ALERT_4_G The CIF-Embedded .res File Contains EXYZ Records 2 Report
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records 2 Report
PLAT301_ALERT_3_G Main Residue Disorder .....(Resd 1) 13% Note
PLAT367_ALERT_2_G Long? C(sp?)-C(sp?) Bond C5 - C6 . 1.52 Ang.
PLAT367_ALERT_2_G Long? C(sp?)-C(sp?) Bond C5 - C15 . 1.51 Ang.
PLAT398_ALERT_2_G Deviating C-O-C Angle From 120 for O4 . 93.5 Degree
PLAT398_ALERT_2_G Deviating C-O-C Angle From 120 for O4D . 90.2 Degree
PLAT432_ALERT_2_G Short Inter X...Y Contact O1D ..C2 . 3.01 Ang.
1/2+x,y,3/2-z = 8_657 Check
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). 1 Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File 1 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. 4 Info

0 **ALERT level A** = Most likely a serious problem - resolve or explain
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14 **ALERT level G** = General information/check it is not something unexpected

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

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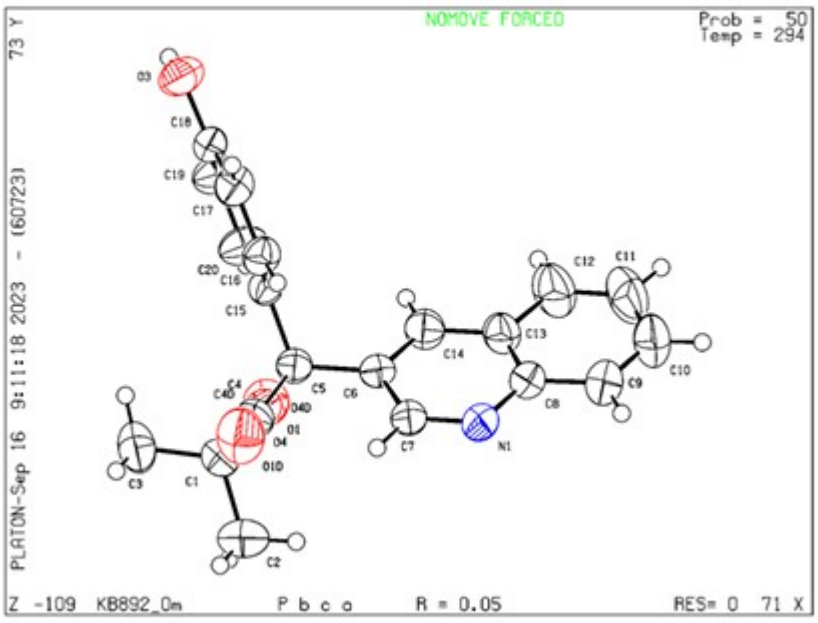
Publication of your CIF in other journals

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

PLATON version of 06/07/2023; check.def file version of 30/06/2023



Sample Preparation for Crystal Growth: The compound **9ab** was dissolved in acetonitrile 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.

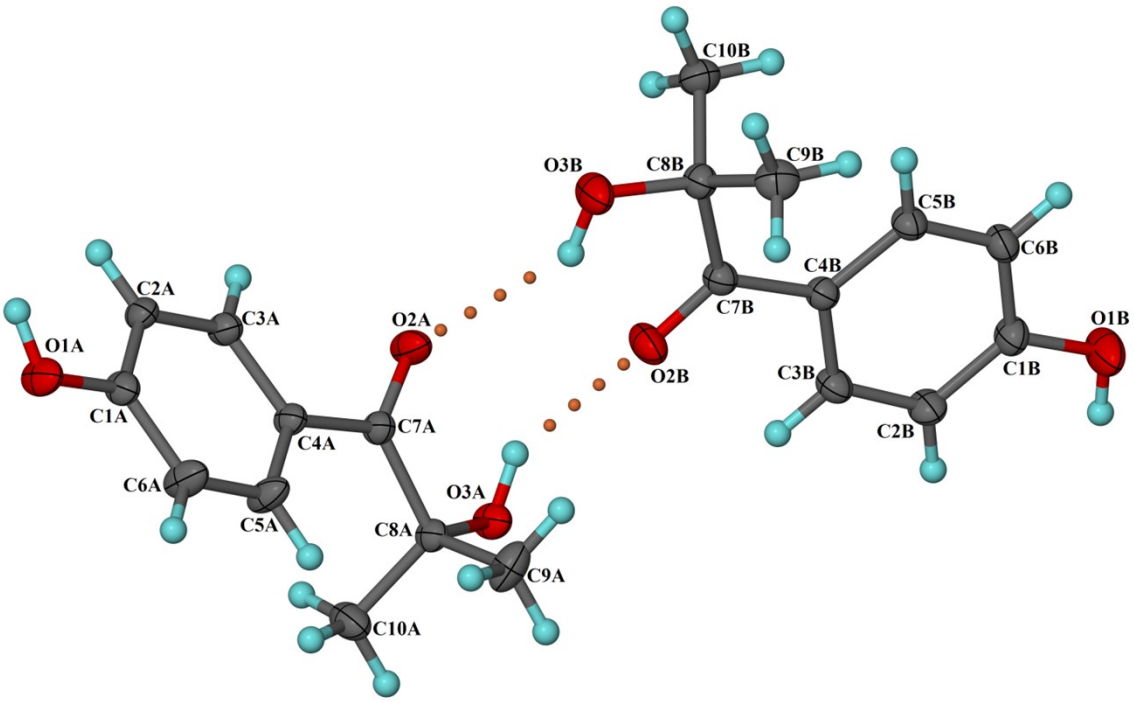


Figure 2. ORTEP diagram of KB950 (**9ab**) compound with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

Crystal data for KB950 (9ab): $C_{10}H_{12}O_3$, M = 180.20, Monoclinic, Space group $P2_1/n$ (No.14), a = 8.8036(2)Å, b = 21.7067(4)Å, c = 9.8524(2)Å, α = 90°, β = 95.1478(8)°, γ = 90°, V = 1875.17(7)Å^3, Z = 8, D_c = 1.277 g/cm^3, F_{000} = 768, Bruker D8 QUEST PHOTON III C7 HPAD detector, Mo-Kα radiation, λ = 0.71073 Å, T = 294(2)K, $2\theta_{max}$ = 55°, μ = 0.094 mm^{-1}, 31550 reflections collected, 5603 unique (R_{int} = 0.0349), 255 parameters, $R1$ = 0.0482, $wR2$ = 0.1200, R indices based on 3636 reflections with I > 2σ(I) (refinement on F^2), Final $GooF$ = 1.051, largest difference hole and peak = -0.174 and 0.240 e.Å^{-3}. The **CCDC deposition number 2295368** 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:

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 **CCDC deposition numbers 2295367-2295368** contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) KB950_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: KB950_0m

```
Bond precision:   C-C = 0.0019 A          Wavelength=0.71073

Cell:             a=8.8036(2)     b=21.7067(4)         c=9.8524(2)
                  alpha=90        beta=95.1478(8)      gamma=90
Temperature:      294 K

                 Calculated                Reported
Volume           1875.17(7)                1875.17(7)
Space group      P 21/n                    P 21/n
Hall group       -P 2yn                    -P 2yn
Moiety formula   C10 H12 O3                C10 H12 O3
Sum formula      C10 H12 O3                C10 H12 O3
Mr               180.20                    180.20
Dx,g cm-3        1.277                     1.277
Z                8                         8
Mu (mm-1)        0.094                     0.094
F000             768.0                     768.0
F000'            768.44
h,k,lmax         12,30,14                  12,30,13
Nref             5698                      5603
Tmin,Tmax        0.976,0.980               0.655,0.746
Tmin'            0.976

Correction method= # Reported T Limits: Tmin=0.655 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.983           Theta(max)= 30.468

R(reflections)= 0.0482( 3636)                    wR2(reflections)=
                                                 0.1382( 5603)
S = 1.051                 Npar= 255
```

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

PLAT250_ALERT_2_C	Large U3/U1 Ratio for Average U(i,j) Tensor	2.2 Note
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.600	16 Report
PLAT913_ALERT_3_C	Missing # of Very Strong Reflections in FCF	8 Note

Alert level G

PLAT002_ALERT_2_G	Number of Distance or Angle Restraints on AtSite	2 Note
PLAT172_ALERT_4_G	The CIF-Embedded .res File Contains DFIX Records	1 Report
PLAT720_ALERT_4_G	Number of Unusual/Non-Standard Labels	10 Note
PLAT860_ALERT_3_G	Number of Least-Squares Restraints	1 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).	1 Note
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L= 0.600	73 Note
PLAT933_ALERT_2_G	Number of HKL-OMIT Records in Embedded .res File	3 Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	19 Info

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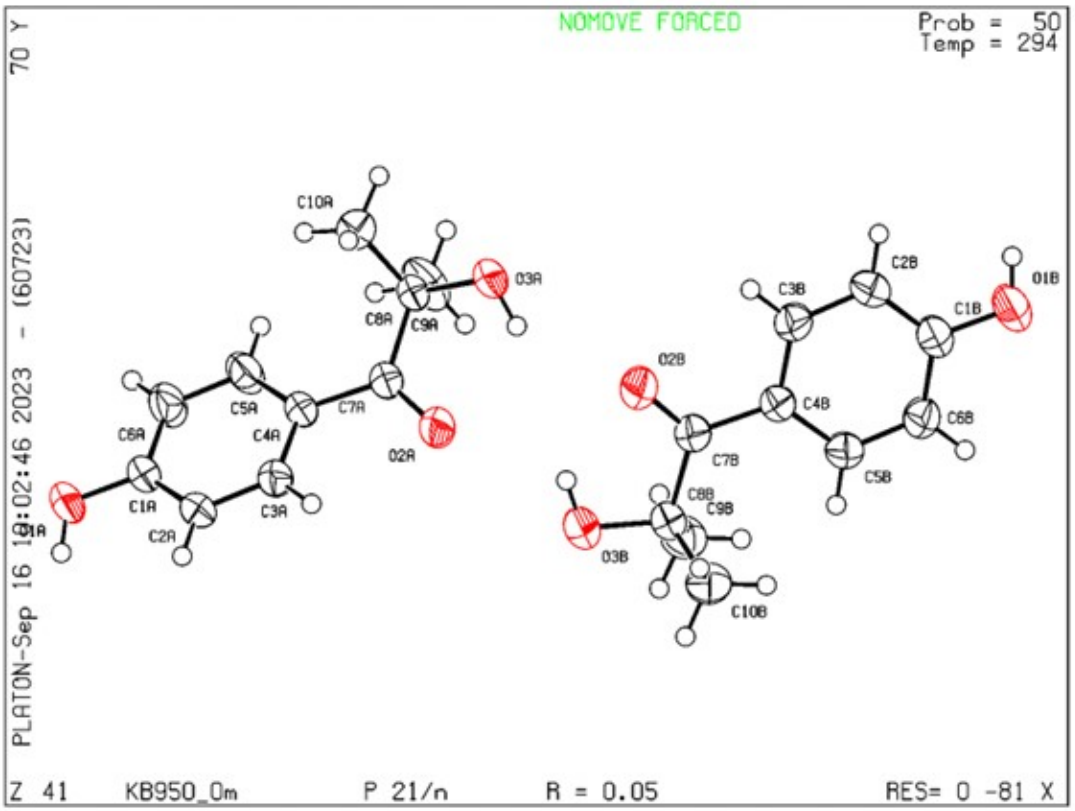
PLATON version of 06/07/2023; check.def file version of 30/06/2023

Datablock KB950_0m - ellipsoid plot



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.

8. References:

1. (a) T.-T. Wang, H.-S. Jin, M.-M. Cao, R.-B. Wan and L.-M. Zhao, *Org. Lett*., **2021**, *23,* 5952-5957; (b) J. Ren, C. Pi, X. Cui and Y. Wu, *Org. Lett.*, **2021**, *23*, 6628-6632; (c) X. Song, B. N. D. Doan, X. Zhang, R. Lee and X. Fan, *Org. Lett.*, **2020,** *22*, 46-51; (d) L. Zhang, J. Zhao, Y. Jiang, X. Zhang and X. Fan, *Org. Chem. Front.,* **2021**, *8*, 3734-3739. (e) M. K. Tiwari, L. Yadav, B. R. K. Shyamlal and S. Chaudhary, *Asian J. Org. Chem.,* **2019**, *8,* 2257-2268

2. (a) M.-B. Zhou, R. Pi, M. Hu, Y. Yang, R.-J. Song, Y. Xia, J.-H. Li, *Angew. Chem., Int. Ed.,* **2014**, *53*, 11338-11341; (b) R. Pi, M.-B. Zhou, Y. Yang, C. Gao, R.-J. Song, J.-H. Li, *Chem. Commun*., **2015**, *51*, 13550-13553.