

Supporting Information for

Synthesis of 7-Hydroxy-6,7-dihydro-indole and 6',7'-Dihydro-3,7'-biindole Derivatives from Domino Reactions of Arylglyoxals or Methyl Ketones with Enamines†

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Table of contents

General information	S2
Synthetic procedures	S2-S3
Table S1: The Optimization of reaction conditions for the reactions of 6a and 2a	S4
Table S2. Synthesis of 7-hydroxy-6,6-dimethyl-6,7-dihydro-1 <i>H</i> -indol-4(5 <i>H</i>)-one 3 from different acetophenone and enamines	S5
Characterization Data of Compounds compounds 3 , 5 and 8	S5-S13
Copies of ¹ HNMR and ¹³ C NMR spectra of compounds 3 , 5 and 8	S14-S34
X-ray structure of 3a	S35
¹ HNMR spectrum comparison of 3b and the deuterated product 3b'	S36

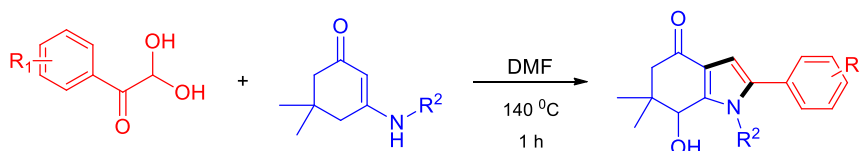
I. General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out in air and using undistilled solvent, without any precautions to exclude air and moisture unless otherwise noted. Melting points were recorded on an Electrothermal digital melting point apparatus and were uncorrected. IR spectra were recorded on a spectrophotometer using KBr optics. ¹HNMR and ¹³CNMR spectra were recorded on a 400 MHz (¹HNMR) and 100 MHz (¹³CNMR) spectrometer using CDCl₃, DMSO-d₆ as solvent and TMS as internal standard. High resolution mass spectra were obtained using a high resolution ESI-TOF mass.

II. Synthetic procedures

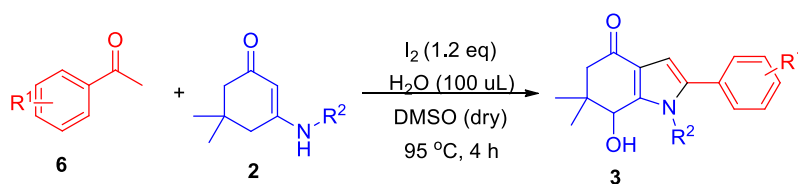
General procedure for the preparation of the 7-hydroxy-6,6-dimethyl-2-phenyl-1-(p-tolyl)-6,7-dihydro-1*H*-indol-4(5*H*)-one derivatives **3 (3a as an example):**

A mixture of arylglyoxal **1a** (0.5 mmol) and enamine **2a** (0.75 mmol) was heated at 140 °C in DMF (2.5 mL) for 1 h and the reaction was monitored by TLC. After completion of the reaction, the resulting mixture was diluted with 10 mL of ethyl acetate and washed with 10 mL of brine. The aqueous layer was extracted with ethyl acetate (10 mL x 2). The organic layer was combined and dried over Na₂SO₄ and concentrated. The resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc=10:1) to yield the desired product **3a** as a yellow solid (143 mg, 83% yield)



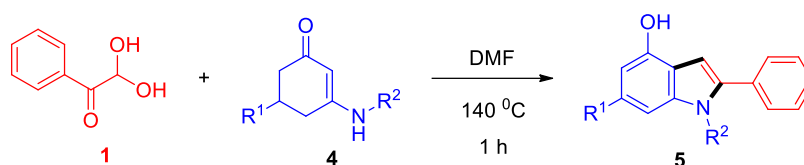
General procedure for the preparation of the 7-hydroxy-6,6-dimethyl-2-phenyl-1-(p-tolyl)-6,7-dihydro-1*H*-indol-4(5*H*)-one derivatives from different substituted aryl methyl ketones and enamionone (3a as an example):

A mixture of acetophenone **6a** (0.5 mmol) and I₂ (0.6 mmol) was heated at 95 °C in DMSO (2 mL) for 2 h. After cooling to the room temperature, H₂O (100 uL), enamionone **2a** (0.6 mmol) were added and further heated at 95 °C for 2 h. Then the resulting mixture was diluted with 10 mL of ethyl acetate and washed with 10 mL of sodium thiosulfate saturated solution. The aqueous layer was extracted with ethyl acetate (10 mL x 2). The organic layer was combined and dried over Na₂SO₄ and concentrated. The resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc=10:1) to yield the desired product **3a** as a yellow solid (100 mg, 58% yield).



General procedure for the preparation of the 1,2-diphenyl-1H-indol-4-ol derivatives 5 (5a as an example):

A mixture of arylglyoxal **1a** (0.5 mmol) and enamine **4a** (0.75 mmol) was heated at 140 °C in DMF (2.5 mL) for 1 h and the reaction was monitored by TLC. After completion of the reaction, the resulting mixture was diluted with 10 mL of ethyl acetate and washed with 10 mL of brine. The aqueous layer was extracted with ethyl acetate (10 mL x 2). The organic layer was combined and dried over Na_2SO_4 and concentrated. The resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc=20:1) to yield the desired product **5a** as a purple solid (70 mg, 47% yield).



General procedure for the preparation of the 1,6,6'-trimethyl-2'-phenyl-1'-(p-tolyl)-6',7'-dihydro-1H,1'H-[3,7'-biindol]-4'(5'H)-one derivatives 8 (8a as an example):

A mixture of arylglyoxal **1a** (0.5 mmol) and enamine **2a** (0.75 mmol) was heated at 140 °C in DMF (2.5 mL) for 1 h. The reaction mixture was then cooled to room temperature, followed by addition of 1-methyl-1H-indole **7** (0.75 mmol) and PTSA (0.5 mmol). Then, the mixture was stirred for 8 h at 100 °C monitored by TLC. The resulting mixture was diluted with 10 mL of ethyl acetate and washed with 10 mL of brine. The aqueous layer was extracted with ethyl acetate (10 mL x 2). The organic layer was combined and dried over Na_2SO_4 and concentrated. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc=8:1) to yield the desired product **8a** as a yellow solid (144 mg, 63% yield).

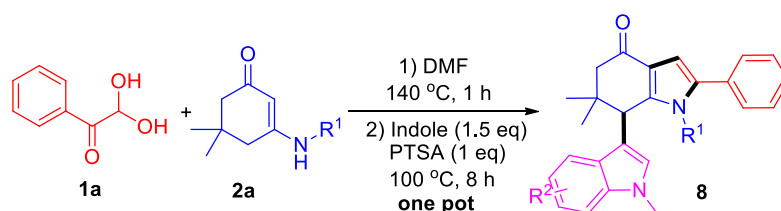
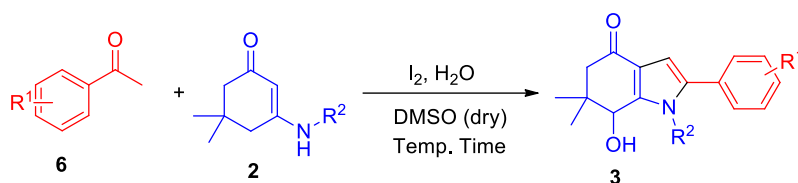
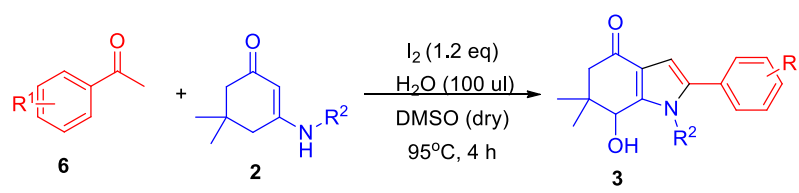


Table S1: The Optimization of reaction conditions for the reactions of **6a** and **2a**

Entry	Cat.(eq)	Time1 (h) ^b	Time 2 (h) ^c	T (°C)	Solvent (dry)	H ₂ O (uL)	Yield (%) ^d
1	I ₂ (1.2)	2	2	95	DMSO	-	N.R.
2	I ₂ (1.2)	2	2	95	DMSO	20	50
3	I ₂ (1.2)	2	2	95	DMSO	50	61
4	I ₂ (1.2)	2	2	95	DMSO	100	66(58 ^e)
5	I ₂ (1.2)	2	2	95	DMSO	200	64
6	I ₂ (1.5)	2	2	95	DMSO	100	65
7	I ₂ (1.0)	2	2	95	DMSO	100	62
8	I ₂ (0.8)	2	2	95	DMSO	100	58
9	I ₂ (1.2)	2	2	40	DMSO	100	43
10	I ₂ (1.2)	2	2	60	DMSO	100	58
11	I ₂ (1.2)	2	2	80	DMSO	100	59
12	I ₂ (1.2)	2	2	100	DMSO	100	38
13	I ₂ (1.2)	2	2	120	DMSO	100	16
14	I ₂ (1.2)	2	0.5	95	DMSO	100	57
15	I ₂ (1.2)	2	1	95	DMSO	100	63
16	I ₂ (1.2)	2	3	95	DMSO	100	58
17	I ₂ (1.2)	2	4	95	DMSO	100	57
18	I ₂ (1.2)	2	6	95	DMSO	100	44
19	I ₂ (1.2)	2	12	95	DMSO	100	31

^aReaction conditions: **6a** (0.5 mmol), **2a** (0.6 mmol), solvent (2 mL). ^bThe first step of the reaction time (2h). ^cThe second step of the reaction time. ^dYields were determined by LC analysis with biphenyl (0.5 mmol) as the internal standard. ^eIsolated yield.

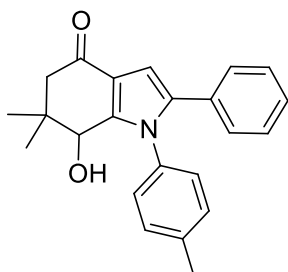
Table S2. Synthesis of 7-hydroxy-6,6-dimethyl-6,7-dihydro-1*H*-indol-4(5*H*)-one **3** from different acetophenone and enamines^{a,b}



entry	R ¹	R ²	3	yield (%)
1	H (6a)	4-MeC ₆ H ₄ - (2a)	3a	58
2	H (6a)	4-BrC ₆ H ₄ - (2b)	3b	41
3	H (6a)	4-OMeC ₆ H ₄ - (2d)	3d	36
4	H (6a)	2-naphthalen- (2g)	3g	47
5	4-BrC ₆ H ₄ - (6b)	4-MeC ₆ H ₄ - (2a)	3h	34
6	4-ClC ₆ H ₄ - (6c)	4-MeC ₆ H ₄ - (2a)	3i	50
7	3-ClC ₆ H ₄ - (6d)	4-MeC ₆ H ₄ - (2a)	3j	48
8	4-OMeC ₆ H ₄ - (6e)	4-MeC ₆ H ₄ - (2a)	3k	46
9	4-MeC ₆ H ₄ - (6f)	4-MeC ₆ H ₄ - (2a)	3l	45
10	2-MeC ₆ H ₄ - (6g)	4-MeC ₆ H ₄ - (2a)	3m	38

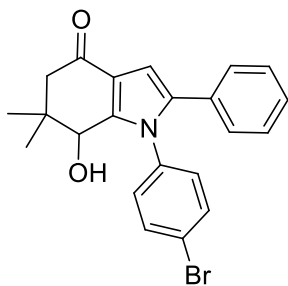
^aReaction conditions: **6a** (0.5 mmol), **2a** (0.6 mmol), I₂ (0.6 mmol), and H₂O (100 μL) in DMSO (2 mL) at 95 °C for 4 hours. ^bIsolated yield.

III.Characterization Data of Compounds **3**, **5** and **8** :



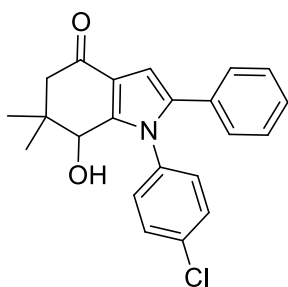
7-hydroxy-6,6-dimethyl-2-phenyl-1-(p-tolyl)-6,7-dihydro-1*H*-indol-4(5*H*)-one(3a):

yellow solid. m. p.: 178-180 °C. **IR** (neat, v, cm⁻¹): 3065, 2961, 2878, 1714, 1606, 745, 726, 693 cm⁻¹. ¹HNMR (400 MHz, DMSO) δ 7.30 – 7.15 (m, 6H), 7.11 (d, *J* = 6.9 Hz, 3H), 6.63 (s, 1H), 5.39 (d, *J* = 7.3 Hz, 1H), 3.84 (d, *J* = 7.1 Hz, 1H), 2.78 (d, *J* = 16.4 Hz, 1H), 2.35 (s, 3H), 1.98 (d, *J* = 16.4 Hz, 1H), 1.03 (s, 3H), 0.87 (s, 3H). ¹³CNMR (101 MHz, DMSO) δ 193.4, 146.0, 138.4, 136.8, 134.9, 132.1, 130.2, 128.7, 128.5, 128.2, 127.5, 119.5, 105.2, 68.0, 47.2, 26.4, 25.9, 21.1. **HRMS (ESI-TOF)** Calcd for C₂₃H₂₄NO₂⁺ ([M+H]⁺) 346.1807. Found 346.1811.



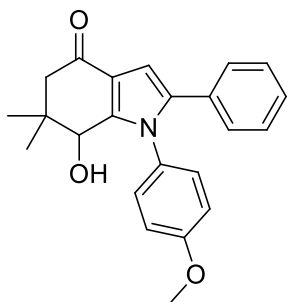
1-(4-bromophenyl)-7-hydroxy-6,6-dimethyl-2-phenyl-6,7-dihydro-1H-in

dol-4(5H)-one(3b): yellow solid. m. p.: 153-155 °C. **IR** (neat, v, cm⁻¹): 3372, 2958, 1649, 1600, 1522, 763, 696, 673 cm⁻¹. ¹HNMR (400 MHz, DMSO) δ 7.66 (d, *J* = 5.1 Hz, 2H), 7.33 – 7.17 (m, 4H), 7.12 (d, *J* = 6.8 Hz, 3H), 6.64 (s, 1H), 5.45 (d, *J* = 7.3 Hz, 1H), 3.89 (d, *J* = 7.1 Hz, 1H), 2.76 (d, *J* = 16.3 Hz, 1H), 2.00 (d, *J* = 16.0 Hz, 1H), 1.03 (s, 3H), 0.89 (s, 3H). ¹³CNMR (101 MHz, DMSO) δ 193.4, 145.8, 136.8, 132.7, 131.7, 130.6, 128.9, 128.6, 127.7, 122.0, 119.8, 105.5, 68.0, 47.3, 26.2, 25.9. **HRMS (ESI-TOF)** Calcd for C₂₂H₂₁BrNO₂⁺ ([M+H]⁺) 410.0756. Found 410.0760.



1-(4-chlorophenyl)-7-hydroxy-6,6-dimethyl-2-phenyl-6,7-dihydro-1H-in

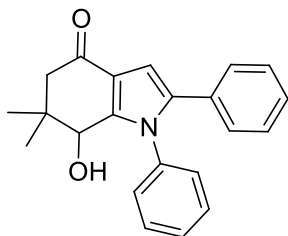
dol-4(5H)-one(3c): yellow solid. m. p.: 139-141 °C. **IR** (neat, v, cm⁻¹): 2955, 2852, 1726, 1633, 1556, 762, 695, 638 cm⁻¹. ¹HNMR (400 MHz, DMSO) δ 7.66 (d, *J* = 5.1 Hz, 2H), 7.35 – 7.01 (m, 7H), 6.64 (s, 1H), 5.45 (d, *J* = 7.3 Hz, 1H), 3.89 (d, *J* = 7.1 Hz, 1H), 2.76 (d, *J* = 16.3 Hz, 1H), 2.00 (d, *J* = 16.0 Hz, 1H), 1.03 (s, 3H), 0.89 (s, 3H). ¹³CNMR (101 MHz, CDCl₃) δ 194.1, 144.0, 137.6, 135.8, 134.4, 131.3, 129.5, 129.2, 128.5, 128.4, 127.5, 120.1, 105.9, 69.3, 46.8, 39.5, 29.7, 25.8, 16.3. **HRMS (ESI-TOF)** Calcd for C₂₂H₂₁ClNO₂⁺ ([M+H]⁺) 366.1261. Found 366.1262.



7-hydroxy-1-(4-methoxyphenyl)-6,6-dimethyl-2-phenyl-6,7-dihydro-1H-

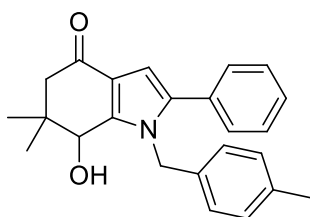
indol-4(5H)-one(3d): yellow solid. m. p.: 149-151 °C. **IR** (neat, v, cm⁻¹): 3068, 2963, 2873, 1719, 1606, 741, 724, 691 cm⁻¹. ¹HNMR (400 MHz, DMSO) δ 7.29 – 7.15 (m, 4H), 7.12 (d, *J* = 6.7 Hz, 2H), 7.00 (s, 3H), 6.62 (s, 1H), 5.37 (d, *J* = 7.4 Hz, 1H), 3.83 (d, *J* = 7.3 Hz, 1H), 3.79 (s, 3H), 2.76

(d, $J = 16.4$ Hz, 1H), 1.98 (d, $J = 16.3$ Hz, 1H), 1.03 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 193.4, 159.3, 146.1, 136.9, 132.1, 130.1, 129.7, 128.7, 128.4, 127.5, 119.3, 114.8, 104.9, 68.0, 55.8, 47.2, 26.4, 25.9. **HRMS (ESI-TOF)** Calcd for $\text{C}_{23}\text{H}_{24}\text{NO}_3^+$ ($[\text{M}+\text{H}]^+$) 362.1756. Found 362.1758.



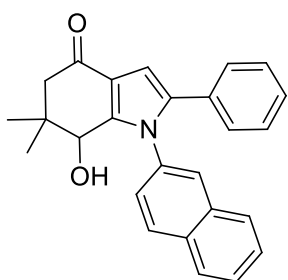
7-hydroxy-6,6-dimethyl-1,2-diphenyl-6,7-dihydro-1H-indol-4(5H)-one(3e):

yellow solid. m. p.: 162-163 °C. **IR** (neat, v, cm^{-1}): 3298, 2972, 2956, 2887, 1716, 1698, 1684, 1576, 737, 665 cm^{-1} . ^1H NMR (400 MHz, DMSO) δ 7.45 (s, 4H), 7.20 (d, $J = 6.5$ Hz, 4H), 7.09 (d, $J = 6.6$ Hz, 2H), 6.64 (s, 1H), 5.43 (d, $J = 7.3$ Hz, 1H), 3.85 (d, $J = 7.1$ Hz, 1H), 2.77 (d, $J = 16.4$ Hz, 1H), 1.99 (d, $J = 16.3$ Hz, 1H), 1.03 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 193.4, 145.9, 137.4, 136.8, 132.0, 129.7, 128.9, 128.7, 128.5, 128.5, 127.6, 119.5, 105.3, 68.1, 47.2, 26.4, 25.9. **HRMS (ESI-TOF)** Calcd for $\text{C}_{22}\text{H}_{22}\text{NO}_2^+$ ($[\text{M}+\text{H}]^+$) 332.1651. Found 332.1658.



7-hydroxy-6,6-dimethyl-1-(4-methylbenzyl)-2-phenyl-6,7-dihydro-1H-indol-4(5H)-one(3f):

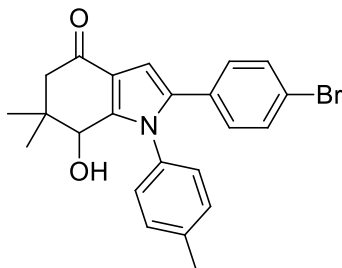
yellow solid. m. p.: 163-164 °C. **IR** (neat, v, cm^{-1}): 2957, 2921, 2869, 1644, 1607, 1561, 760, 718, 677 cm^{-1} . ^1H NMR (400 MHz, DMSO) δ 7.34 (dt, $J = 10.7, 6.9$ Hz, 5H), 7.10 (d, $J = 7.8$ Hz, 2H), 6.78 (d, $J = 7.9$ Hz, 2H), 6.46 (s, 1H), 5.56 (d, $J = 7.2$ Hz, 1H), 5.35 (d, $J = 17.1$ Hz, 1H), 5.24 (d, $J = 17.1$ Hz, 1H), 4.07 (d, $J = 7.0$ Hz, 1H), 2.70 (d, $J = 16.2$ Hz, 1H), 2.24 (s, 3H), 2.04 – 1.94 (m, 1H), 1.03 (s, 3H), 0.84 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 193.0, 144.8, 137.0, 136.7, 135.5, 132.2, 129.6, 129.1, 129.1, 128.3, 125.8, 119.3, 105.0, 68.3, 47.6, 47.4, 26.3, 26.0, 21.1. **HRMS (ESI-TOF)** Calcd for $\text{C}_{24}\text{H}_{26}\text{NO}_2^+$ ($[\text{M}+\text{H}]^+$) 360.1964. Found 360.1967.



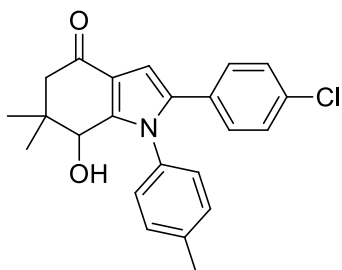
7-hydroxy-6,6-dimethyl-1-(naphthalen-2-yl)-2-phenyl-6,7-dihydro-1H-indol-4(5H)-one(3g):

yellow solid. m. p.: 101-102 °C. **IR** (neat, v, cm^{-1}): 2955, 2922, 2863, 1644, 1599, 1556, 752, 696, 660 cm^{-1} . ^1H NMR (400 MHz, DMSO) δ 7.99 (s, 4H), 7.60 (s, 3H), 7.16 (s,

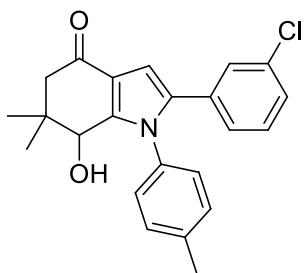
5H), 6.71 (s, 1H), 5.47 (s, 1H), 3.97 (d, $J = 35.0$ Hz, 1H), 2.80 (d, $J = 16.3$ Hz, 1H), 2.02 (d, $J = 16.9$ Hz, 1H), 0.97 (d, $J = 42.4$ Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 193.5, 146.2, 135.0, 133.1, 132.7, 132.0, 129.4, 128.8, 128.4, 128.2, 127.6, 127.5, 127.4, 126.9, 126.6, 119.7, 105.4, 68.1, 47.3, 45.7, 26.3, 25.9. **HRMS (ESI-TOF)** Calcd for $\text{C}_{26}\text{H}_{24}\text{NO}_2^+$ ($[\text{M}+\text{H}]^+$) 382.1807. Found 382.1834.



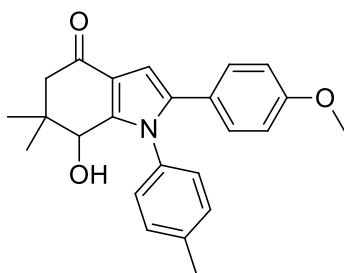
2-(4-bromophenyl)-7-hydroxy-6,6-dimethyl-1-(p-tolyl)-6,7-dihydro-1H-indol-4(5H)-one(3h): yellow solid. m. p.: 179-181 °C. **IR** (neat, v, cm^{-1}): 3354, 2963, 2934, 1672, 1644, 1545, 743, 708, 661 cm^{-1} . ^1H NMR (400 MHz, DMSO) δ 7.49 – 7.18 (m, 5H), 7.05 (d, $J = 8.1$ Hz, 3H), 6.69 (s, 1H), 5.42 (d, $J = 6.6$ Hz, 1H), 3.85 (s, 1H), 2.78 (d, $J = 16.4$ Hz, 1H), 2.36 (s, 3H), 1.99 (d, $J = 16.4$ Hz, 1H), 1.03 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 193.4, 146.3, 138.5, 135.5, 134.6, 131.7, 131.3, 130.4, 130.3, 128.2, 120.9, 119.6, 105.7, 68.0, 47.2, 26.4, 25.8, 21.2. **HRMS (ESI-TOF)** Calcd for $\text{C}_{23}\text{H}_{23}\text{BrNO}_2^+$ ($[\text{M}+\text{H}]^+$) 424.0912. Found 424.0902



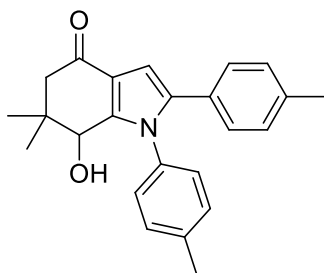
2-(4-chlorophenyl)-7-hydroxy-6,6-dimethyl-1-(p-tolyl)-6,7-dihydro-1H-indol-4(5H)-one(3i): yellow solid. m. p.: 187-189 °C. **IR** (neat, v, cm^{-1}): 3264, 2963, 1673, 1645, 1555, 749, 720, 657 cm^{-1} . ^1H NMR (400 MHz, DMSO) δ 7.28 (d, $J = 8.5$ Hz, 5H), 7.11 (d, $J = 8.5$ Hz, 3H), 6.68 (s, 1H), 5.41 (d, $J = 7.3$ Hz, 1H), 3.84 (d, $J = 7.2$ Hz, 1H), 2.77 (d, $J = 16.4$ Hz, 1H), 2.36 (s, 3H), 1.99 (d, $J = 16.4$ Hz, 1H), 1.03 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 193.4, 146.2, 138.5, 135.5, 134.6, 132.3, 131.0, 130.3, 130.1, 128.8, 128.2, 119.5, 105.7, 68.0, 47.2, 26.4, 25.8, 21.2. **HRMS (ESI-TOF)** Calcd for $\text{C}_{23}\text{H}_{23}\text{ClNO}_2^+$ ($[\text{M}+\text{H}]^+$) 380.1417. Found 380.1419.



2-(3-chlorophenyl)-7-hydroxy-6,6-dimethyl-1-(p-tolyl)-6,7-dihydro-1H-indol-4(5H)-one(3j): yellow solid. m. p.: 165-167 °C. **IR** (neat, v, cm⁻¹): 2957, 2931, 1639, 1597, 1567, 726, 690, 663 cm⁻¹. ¹HNMR (400 MHz, DMSO) δ 7.23 (dd, *J* = 26.7, 21.4 Hz, 7H), 7.03 (d, *J* = 4.3 Hz, 1H), 6.75 (s, 1H), 5.43 (d, *J* = 7.3 Hz, 1H), 3.86 (d, *J* = 7.2 Hz, 1H), 2.78 (d, *J* = 16.4 Hz, 1H), 2.36 (s, 3H), 2.00 (d, *J* = 16.4 Hz, 1H), 1.03 (s, 3H), 0.88 (s, 3H). ¹³CNMR (101 MHz, DMSO) δ 193.4, 146.4, 138.6, 135.1, 134.6, 134.1, 133.4, 130.5, 130.3, 128.2, 128.0, 127.3, 126.9, 119.5, 106.1, 89.4, 68.0, 47.2, 26.4, 25.8, 21.2, 15.9. **HRMS (ESI-TOF)** Calcd for C₂₃H₂₃ClNO₂⁺ ([M+H]⁺) 380.1417. Found 380.1419.

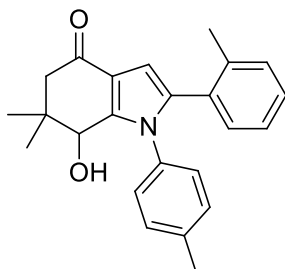


7-hydroxy-2-(4-methoxyphenyl)-6,6-dimethyl-1-(p-tolyl)-6,7-dihydro-1H-indol-4(5H)-one(3k): yellow solid. m. p.: 198-200 °C. **IR** (neat, v, cm⁻¹): 3414, 2969, 1634, 1613, 1560, 732, 691, 675 cm⁻¹. ¹HNMR (400 MHz, DMSO) δ 7.25 (s, 3H), 7.04 (d, *J* = 8.5 Hz, 3H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.53 (s, 1H), 5.36 (d, *J* = 7.3 Hz, 1H), 3.83 (d, *J* = 7.2 Hz, 1H), 3.69 (s, 3H), 2.77 (d, *J* = 16.4 Hz, 1H), 2.35 (s, 3H), 1.97 (d, *J* = 16.0 Hz, 1H), 1.02 (s, 3H), 0.87 (s, 3H). ¹³CNMR (101 MHz, DMSO) δ 193.4, 158.8, 145.5, 138.3, 136.7, 135.0, 130.2, 129.9, 128.3, 124.5, 119.3, 114.2, 104.3, 68.1, 55.5, 47.2, 26.4, 25.9, 21.2. **HRMS (ESI-TOF)** Calcd for C₂₄H₂₆NO₃⁺ ([M+H]⁺) 376.1913. Found 376.1914.

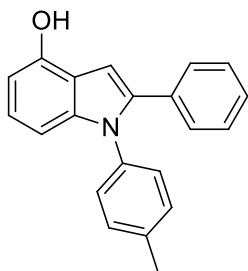


7-hydroxy-6,6-dimethyl-1,2-di-p-tolyl-6,7-dihydro-1H-indol-4(5H)-one(3l): yellow solid. m. p.: 180-182 °C. **IR** (neat, v, cm⁻¹): 3372, 2958, 1649, 1600, 1555, 763, 637 cm⁻¹. ¹HNMR (400 MHz, DMSO) δ 7.25 (s, 3H), 7.01 (d, *J* = 2.6 Hz, 5H), 6.58 (s, 1H), 5.38 (s, 1H), 3.84 (s, 1H), 2.77 (d, *J* = 16.4 Hz, 1H), 2.35 (s, 3H), 2.22 (s, 3H), 1.98 (d, *J* = 16.4 Hz, 1H), 1.03 (s, 3H), 0.87 (s, 3H). ¹³CNMR (101 MHz, DMSO) δ 193.4, 145.8, 138.3, 136.9, 134.9, 130.2,

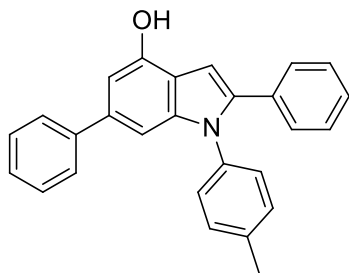
129.3, 129.3, 128.4, 128.2, 119.4, 104.71, 68.1, 47.2, 26.4, 25.9, 21.1, 21.1. **HRMS (ESI-TOF)** Calcd for $C_{24}H_{26}NO_2^+$ ($[M+H]^+$) 360.1964. Found 360.1960.



7-hydroxy-6,6-dimethyl-2-(o-tolyl)-1-(p-tolyl)-6,7-dihydro-1H-indol-4(5H)-one(3m): yellow solid. m. p.: 95-96 °C. **IR** (neat, v, cm^{-1}): 3332, 2956, 1642, 1557, 761, 681, 638 cm^{-1} . 1H NMR (400 MHz, DMSO) δ 7.18 – 7.02 (m, 8H), 6.42 (s, 1H), 5.41 (d, $J = 7.5$ Hz, 1H), 3.88 (d, $J = 7.5$ Hz, 1H), 2.79 (d, $J = 16.5$ Hz, 1H), 2.27 (s, 3H), 2.07 (s, 3H), 1.99 (d, $J = 16.4$ Hz, 1H), 1.04 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 193.5, 144.6, 137.9, 137.6, 135.8, 134.6, 132.0, 131.7, 130.3, 129.8, 128.7, 128.6, 127.7, 125.8, 119.1, 105.7, 68.2, 47.3, 39.7, 26.4, 25.9, 21.0, 20.5. **HRMS (ESI-TOF)** Calcd for $C_{24}H_{26}NO_2^+$ ($[M+H]^+$) 360.1964. Found 360.1960.

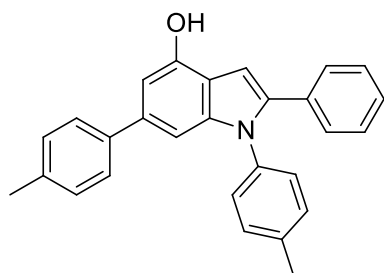


2-phenyl-1-(p-tolyl)-1H-indol-4-ol (5a): purple solid. m. p.: 125-127 °C. **IR** (neat, v, cm^{-1}): 2970, 2925, 2869, 1660, 1603, 1555, 753, 711, 655 cm^{-1} . 1H NMR (400 MHz, DMSO) δ 9.64 (s, 1H), 7.34 – 7.19 (m, 7H), 7.13 (d, $J = 8.2$ Hz, 2H), 6.91 (dd, $J = 20.5, 12.6$ Hz, 2H), 6.59 (d, $J = 8.2$ Hz, 1H), 6.49 (d, $J = 7.6$ Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 151.1, 141.2, 138.7, 137.3, 136.2, 130.4, 128.8, 128.8, 128.1, 127.6, 123.9, 118.3, 105.2, 102.2, 101.3, 100.4, 21.1. **HRMS (ESI-TOF)** Calcd for $C_{21}H_{18}NO^+$ ($[M+H]^+$) 300.1388. Found 300.1393.

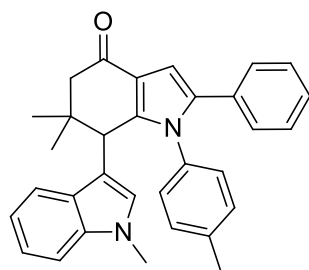


2,6-diphenyl-1-(p-tolyl)-1H-indol-4-ol(5b): green solid. m. p.: 136-138 °C. **IR** (neat, v, cm^{-1}): 3450, 3120, 1586, 1571, 761, 658 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 2H), 7.38 (dd, $J = 10.4, 4.8$ Hz, 2H), 7.30 – 7.21 (m, 8H), 7.18 – 7.13 (m, 2H), 7.06 (s, 1H), 6.85 – 6.83 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 142.1, 141.4, 140.4, 137.3, 137.1, 135.8, 132.5, 130.0, 128.8, 128.6, 128.2, 127.8, 127.4, 127.3, 126.75, 117.1,

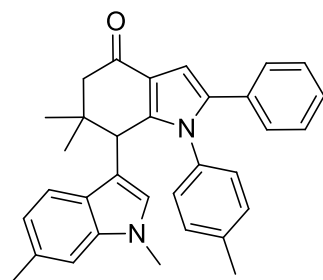
104.9, 102.7, 99.4, 21.2. **HRMS (ESI-TOF)** Calcd for $C_{27}H_{22}NO^+$ ($[M+H]^+$) 376.1701. Found 376.1701.



2-phenyl-1,6-di-p-tolyl-1H-indol-4-ol(5c): green solid. m. p.: 200-201 °C. **IR** (neat, v, cm^{-1}): 3540, 3103, 2875, 1585, 1515, 761, 725, 650 cm^{-1} . 1H NMR (400 MHz, DMSO) δ 9.82 (s, 1H), 7.41 (d, $J = 7.9$ Hz, 2H), 7.33 – 7.13 (m, 11H), 6.91 (s, 1H), 6.80 (d, $J = 2.0$ Hz, 2H), 2.35 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 151.3, 141.7, 139.3, 139.1, 137.4, 136.6, 136.3, 136.1, 132.6, 130.5, 129.8, 128.8, 128.7, 128.1, 127.7, 126.9, 117.7, 104.5, 101.3, 100.3, 21.2, 21.1. **HRMS (ESI-TOF)** Calcd for $C_{28}H_{24}NO^+$ ($[M+H]^+$) 390.1858. Found 390.1848.

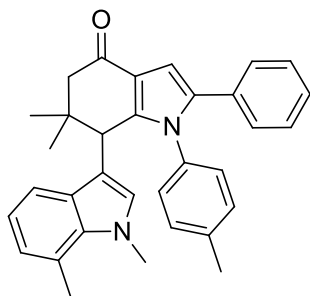


1,6,6'-trimethyl-2'-phenyl-1'-(p-tolyl)-6',7'-dihydro-1H,1'H-[3,7'-biindol]-4'(5'H)-one (8a): yellow solid. m. p.: 198-199 °C. **IR** (neat, v, cm^{-1}): 2951, 2926, 1656, 1604, 761, 641 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 7.12 (dd, $J = 20.7, 13.4$ Hz, 4H), 7.07 – 6.89 (m, 8H), 6.79 (s, 2H), 6.55 (s, 1H), 3.72 (s, 1H), 3.63 (s, 3H), 2.83 – 2.64 (m, 1H), 2.13 (s, 3H), 2.06 (d, $J = 17.1$ Hz, 1H), 1.17 (s, 3H), 0.73 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 192.5, 169.5, 140.6, 138.9, 138.0, 134.3, 133.3, 131.6, 130.6, 130.2, 129.7, 129.0, 128.7, 128.6, 128.4, 128.1, 127.9, 121.1, 105.1, 69.0, 60.2, 48.2, 39.1, 26.0, 25.364, 21.172, 20.8. **HRMS (ESI-TOF)** Calcd for $C_{32}H_{31}N_2O^+$ ($[M+H]^+$) 459.2436. Found 459.2438.



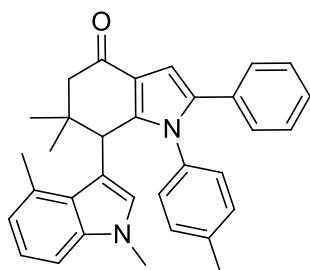
1,6,6',6'-tetramethyl-2'-phenyl-1'-(p-tolyl)-6',7'-dihydro-1H,1'H-[3,7'-biindol]-4'(5'H)-one(8b): yellow solid. m. p.: 227-228 °C. **IR** (neat, v, cm^{-1}): 2956, 2921, 1661, 1602, 1550, 760, 642 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 6.99 (dt, $J = 5.9, 5.4$ Hz, 9H), 6.83 –

6.71 (m, 3H), 6.47 (s, 2H), 3.68 (s, 1H), 3.58 (s, 3H), 2.77 (d, $J = 17.1$ Hz, 1H), 2.40 (s, 3H), 2.14 (s, 3H), 2.04 (d, $J = 15.8$ Hz, 1H), 1.15 (s, 3H), 0.72 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.7, 137.8, 137.3, 136.4, 134.9, 132.0, 131.3, 129.4, 128.1, 127.9, 127.8, 127.5, 127.2, 126.7, 125.8, 120.8, 118.9, 113.0, 109.1, 105.2, 60.4, 39.3, 32.8, 28.5, 28.4, 21.9, 21.1, 14.2. **HRMS (ESI-TOF)** Calcd for $\text{C}_{33}\text{H}_{33}\text{N}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$) 473.2593. Found 473.2588.



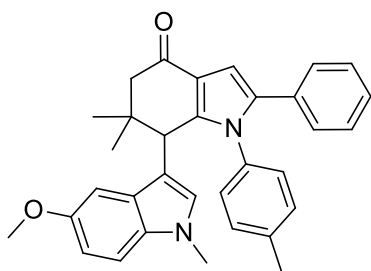
1,6,6',7'-tetramethyl-2'-phenyl-1'-(p-tolyl)-6',7'-dihydro-1H,1'H-[3,7'-

biindol]-4'(5'H)-one(8c): purple solid. m. p.: 183-185 °C. **IR** (neat, v, cm^{-1}): 2951, 2925, 1660, 1602, 759, 642 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.01 (dt, $J = 7.2, 4.4$ Hz, 8H), 6.78 (t, $J = 6.5$ Hz, 5H), 6.45 (s, 1H), 3.91 (s, 3H), 3.68 (s, 1H), 2.78 (d, $J = 17.1$ Hz, 1H), 2.69 (s, 3H), 2.16 (s, 3H), 2.05 (d, $J = 17.1$ Hz, 1H), 1.15 (s, 3H), 0.72 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 193.0, 137.8, 136.0, 135.4, 134.9, 132.1, 129.8, 129.0, 128.6, 128.1, 127.2, 124.0, 121.3, 119.1, 117.1, 111.8, 105.3, 48.2, 36.6, 31.4, 28.3, 28.1, 22.5, 21.0, 19.7, 14.4. **HRMS (ESI-TOF)** Calcd for $\text{C}_{33}\text{H}_{33}\text{N}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$) 473.2593. Found 473.2591.



1,4,6,6'-tetramethyl-2'-phenyl-1'-(p-tolyl)-6',7'-dihydro-1H,1'H-[3,7'-

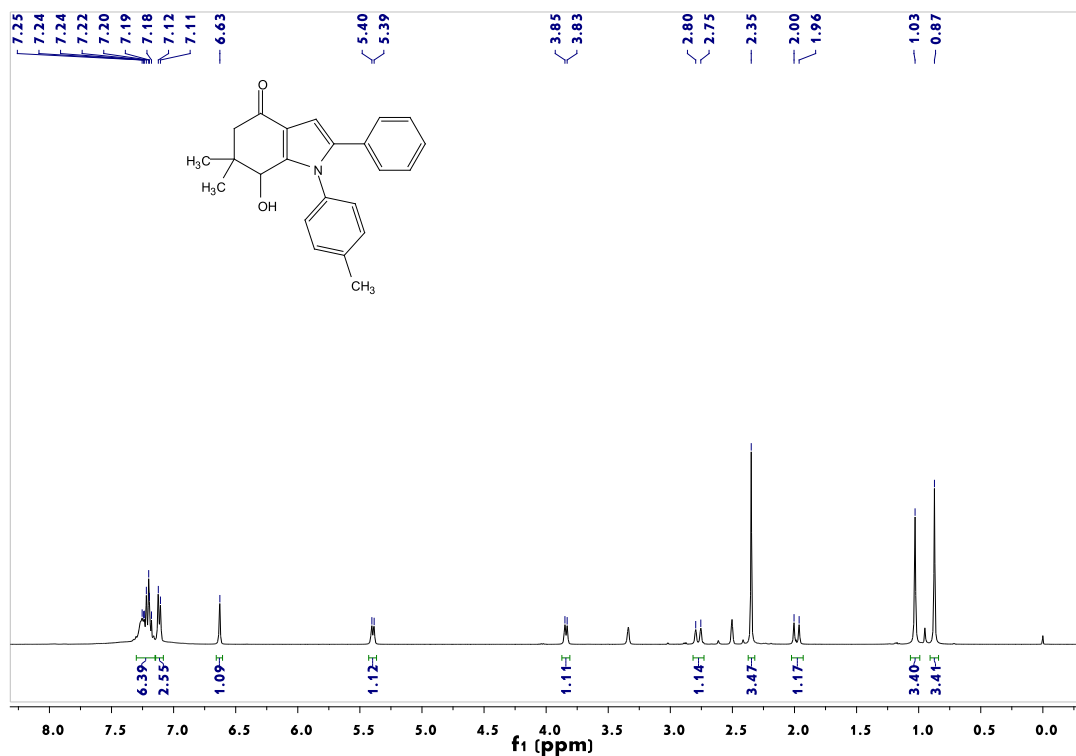
biindol]-4'(5'H)-one(8d): purple solid. m. p.: 184-186 °C. **IR** (neat, v, cm^{-1}): 2851, 1657, 1600, 1552, 738, 671 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.09 – 6.92 (m, 9H), 6.77 (s, 2H), 6.68 – 6.60 (m, 2H), 6.46 (s, 1H), 4.11 (s, 1H), 3.63 (s, 3H), 2.83 (d, $J = 17.3$ Hz, 1H), 2.33 (s, 1H), 2.17 (s, 3H), 2.00 (s, 3H), 1.18 (s, 3H), 0.70 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.5, 150.2, 138.3, 137.1, 136.4, 135.1, 132.0, 130.4, 128.4, 128.1, 128.0, 127.9, 127.8, 126.7, 126.1, 121.4, 121.4, 118.8, 113.8, 107.3, 104.8, 48.0, 41.2, 39.1, 33.0, 28.6, 27.7, 21.0, 20.7. **HRMS (ESI-TOF)** Calcd for $\text{C}_{33}\text{H}_{33}\text{N}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$) 473.2593. Found 473.2602.



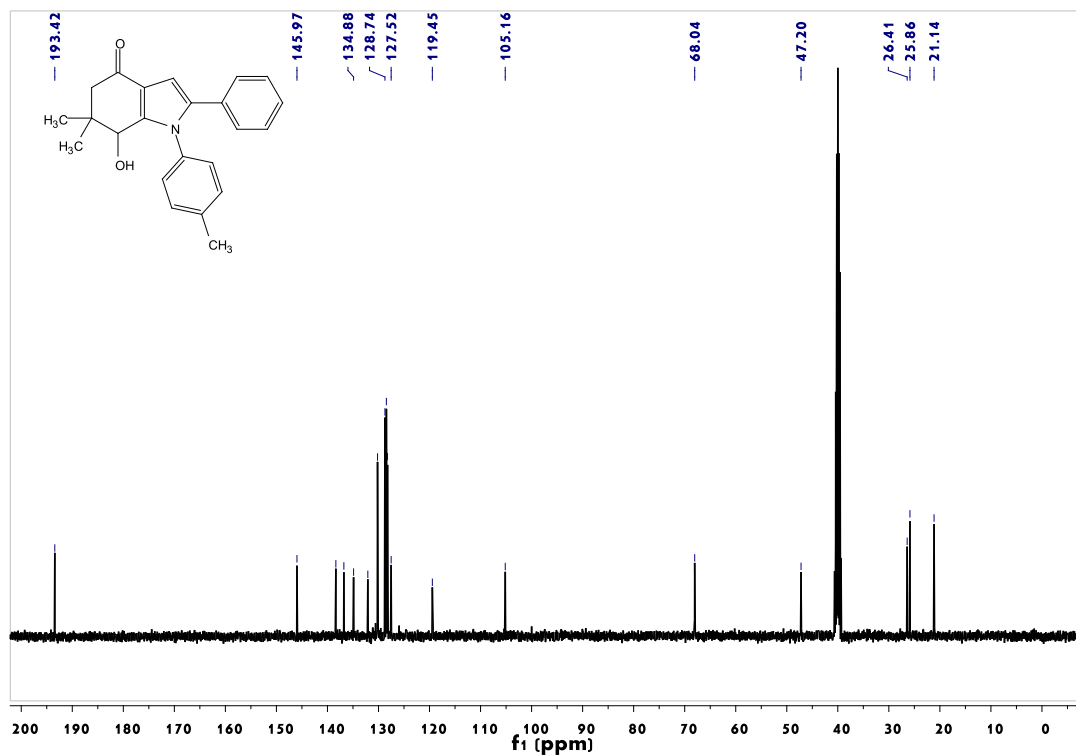
5-methoxy-1,6',6'-trimethyl-2'-phenyl-1'-(p-tolyl)-6',7'-dihydro-1

***H,1'H*-[3,7'-biindol]-4'(5'*H*)-one(8e):** purple solid. m. p.: 158-160 °C. **IR** (neat, ν , cm^{-1}): 2951, 2942, 1658, 1511, 1420, 769, 643 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.24 – 7.00 (m, 8H), 6.89 (s, 3H), 6.63 (d, $J = 20.0$ Hz, 3H), 3.87 – 3.62 (m, 7H), 2.89 (d, $J = 17.1$ Hz, 1H), 2.34 – 2.02 (m, 4H), 1.29 (s, 3H), 0.85 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.6, 153.8, 149.7, 137.8, 136.4, 134.9, 132.2, 132.0, 129.4, 128.2, 128.1, 127.9, 127.8, 127.6, 126.7, 118.9, 112.7, 111.8, 109.8, 105.1, 100.8, 55.9, 47.9, 41.2, 39.3, 33.0, 28.4, 28.2, 21.0. **HRMS (ESI-TOF)** Calcd for $\text{C}_{33}\text{H}_{33}\text{N}_2\text{O}_2^+$ ($[\text{M}+\text{H}]^+$) 489.2542 . Found 489.2540.

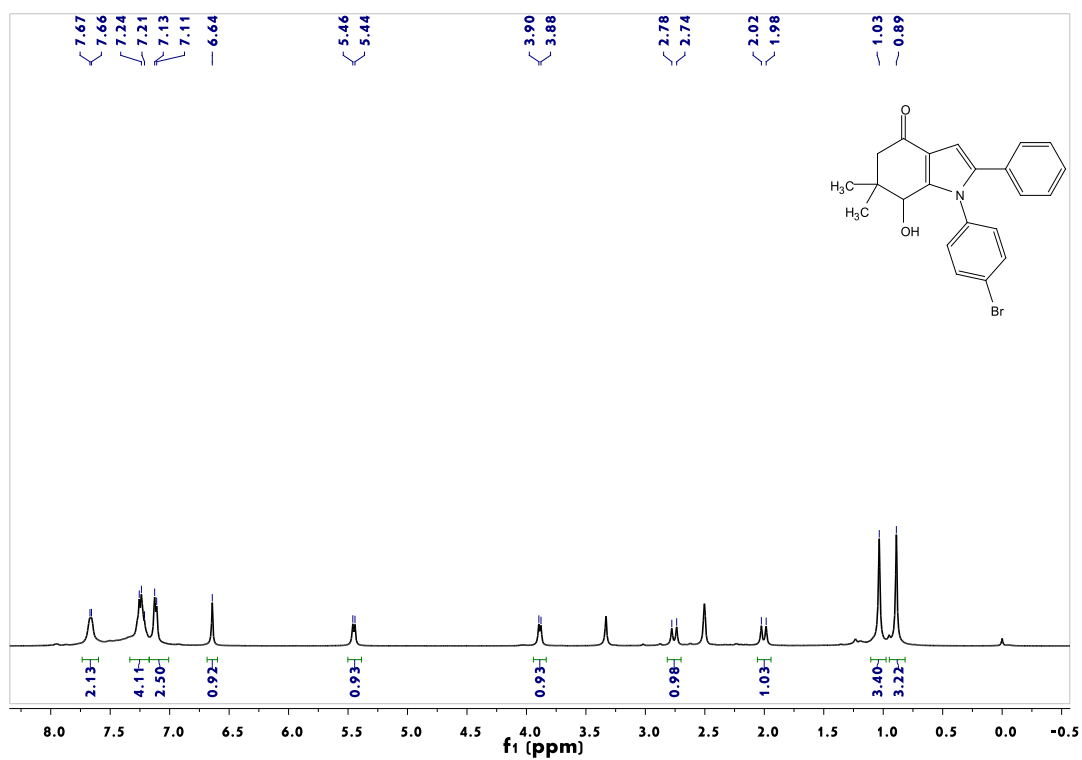
v. Copies of ^1H and ^{13}C NMR Spectra for Compounds



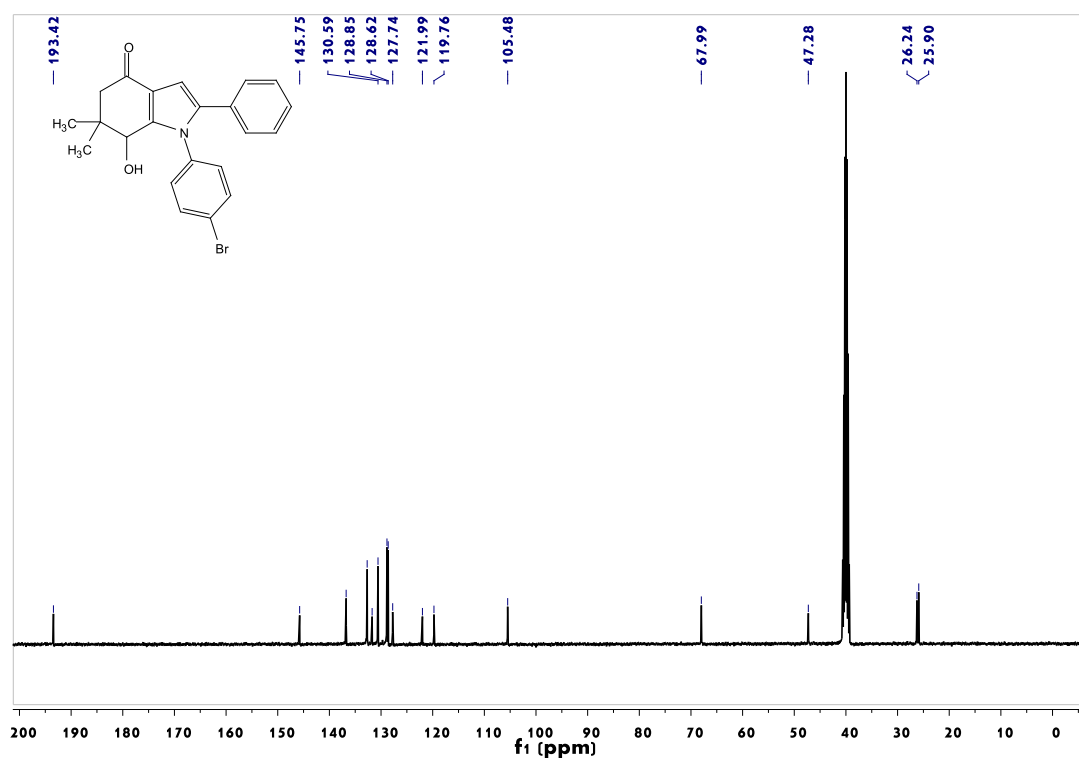
^1H NMR (400 MHz, DMSO) for 3a



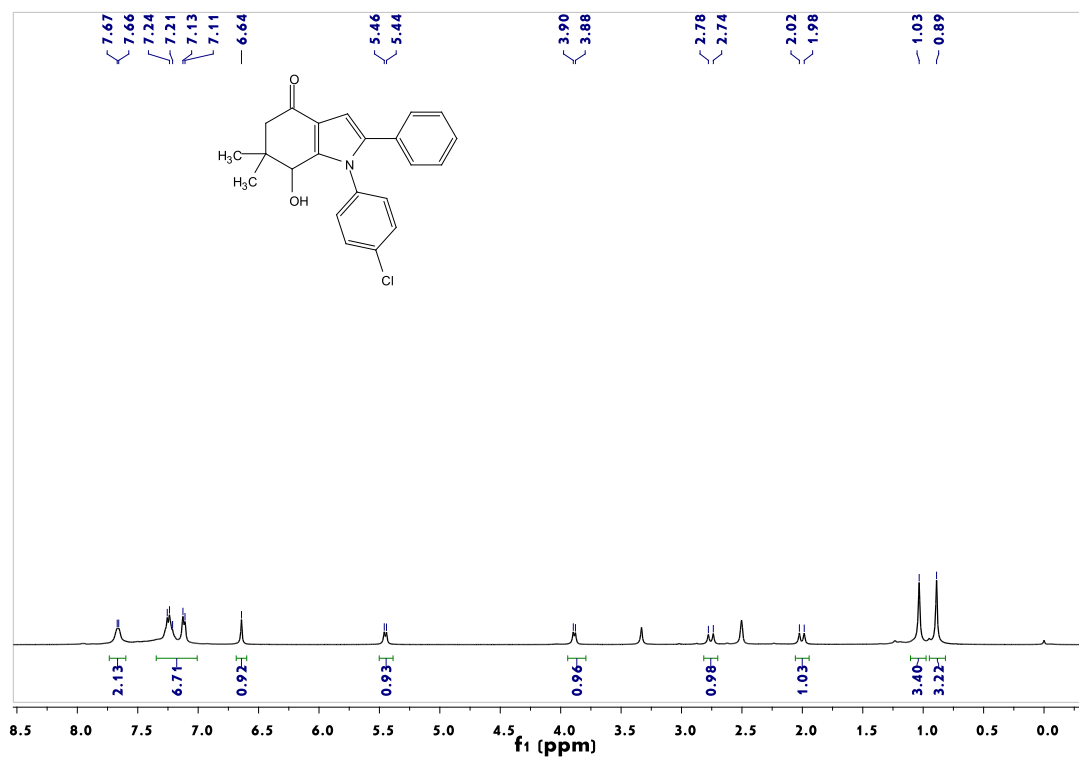
^{13}C NMR (400 MHz, DMSO) for 3a



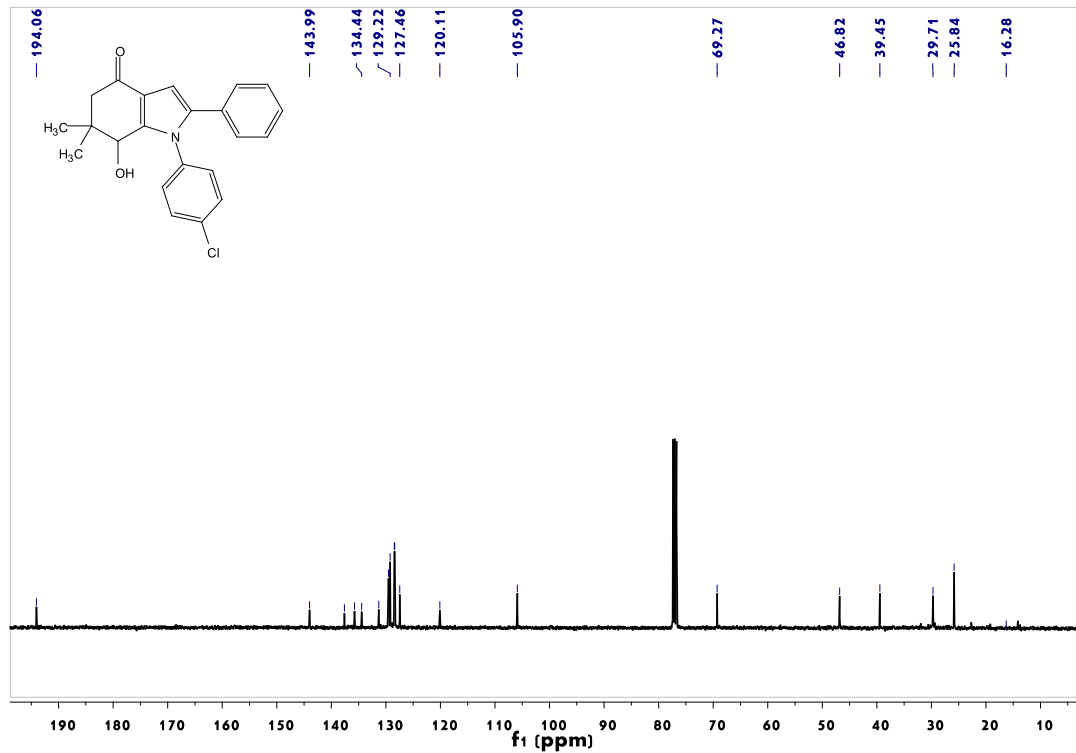
¹H NMR (400 MHz, DMSO) for 3b



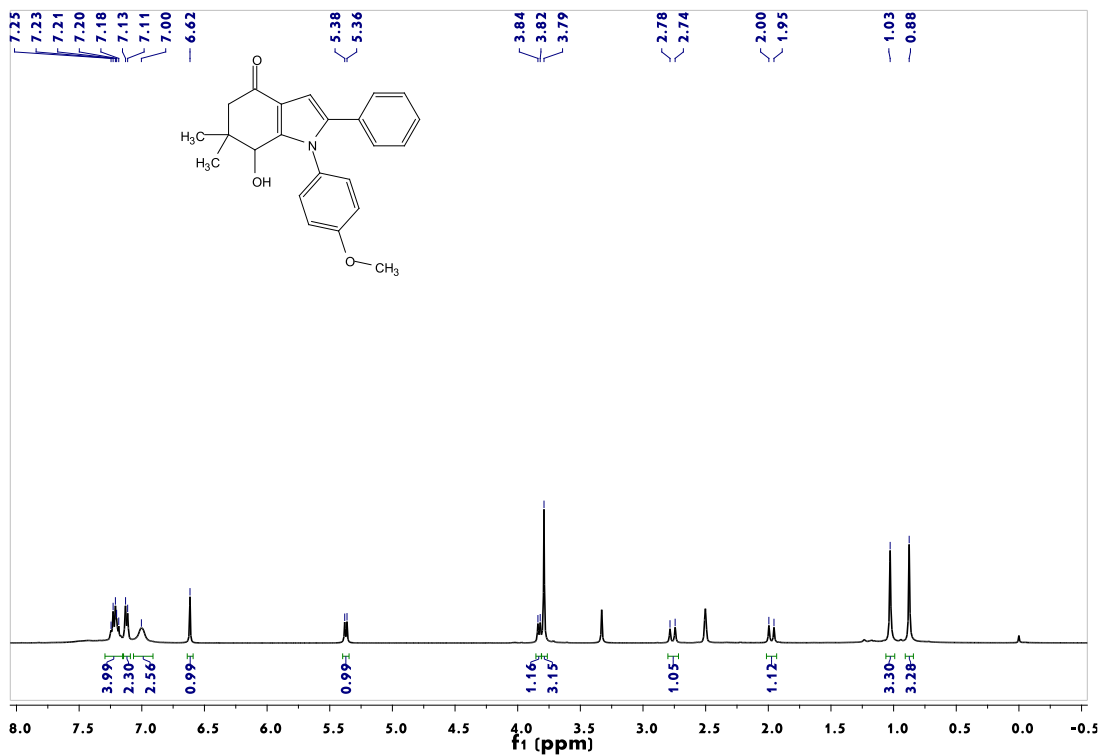
¹³C NMR (400 MHz, DMSO) for 3b



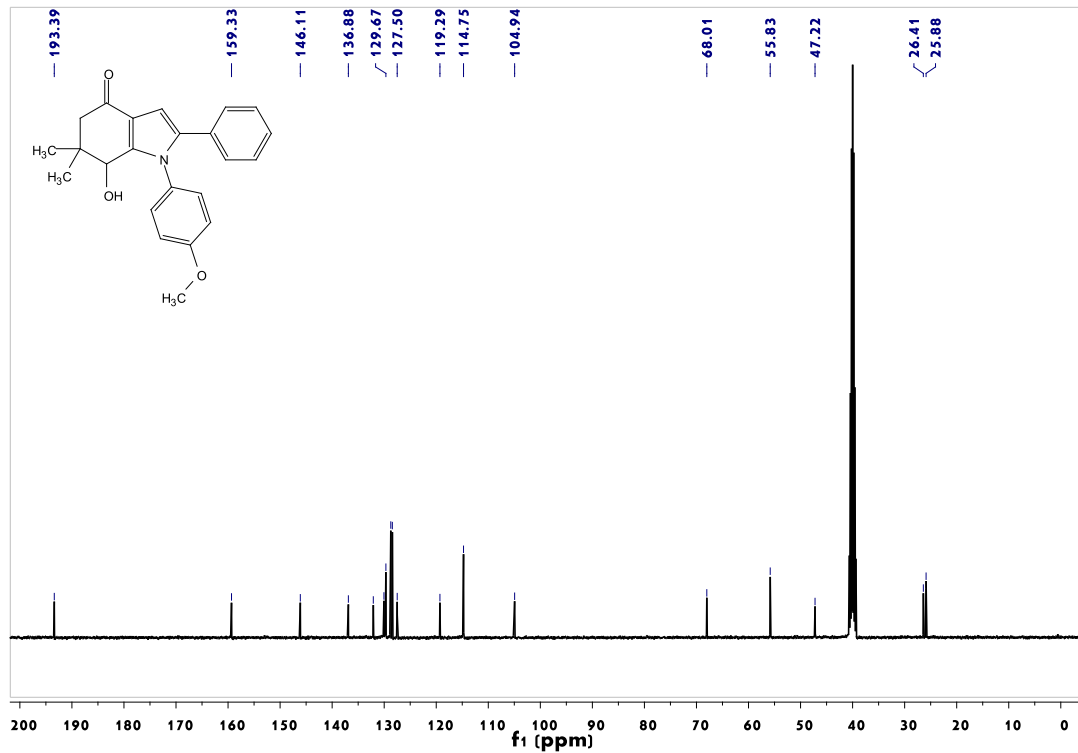
¹H NMR (400 MHz, DMSO) for 3c



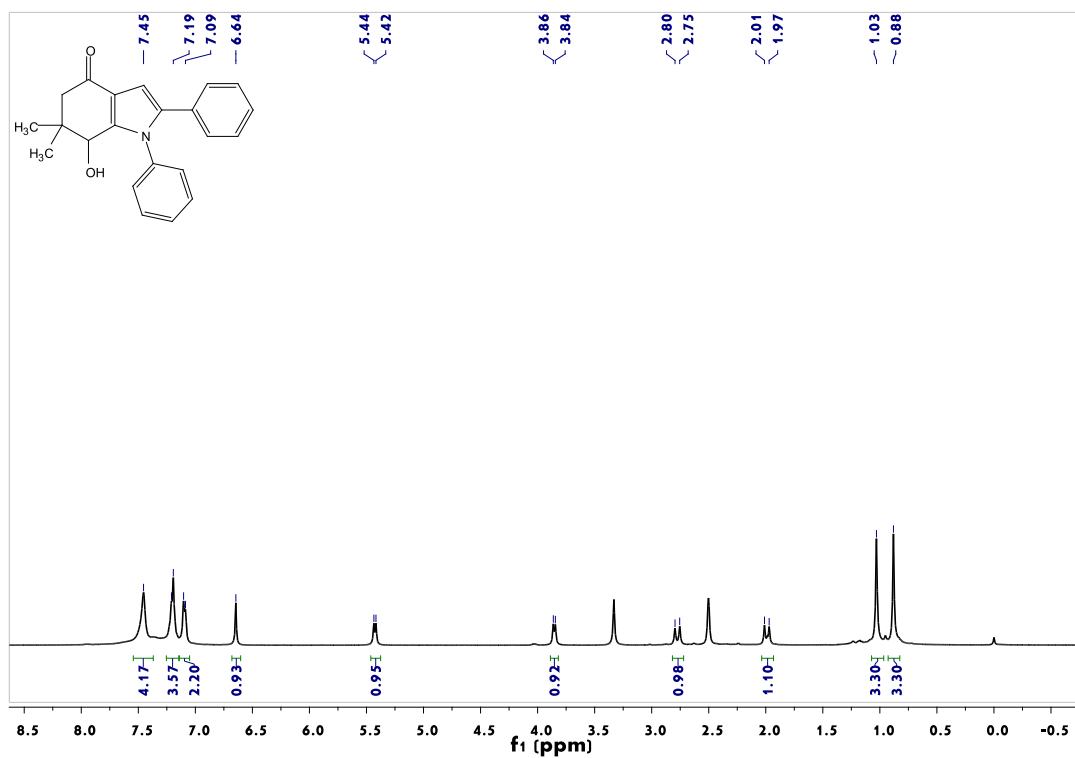
¹³C NMR (400 MHz, CDCl₃) for 3c



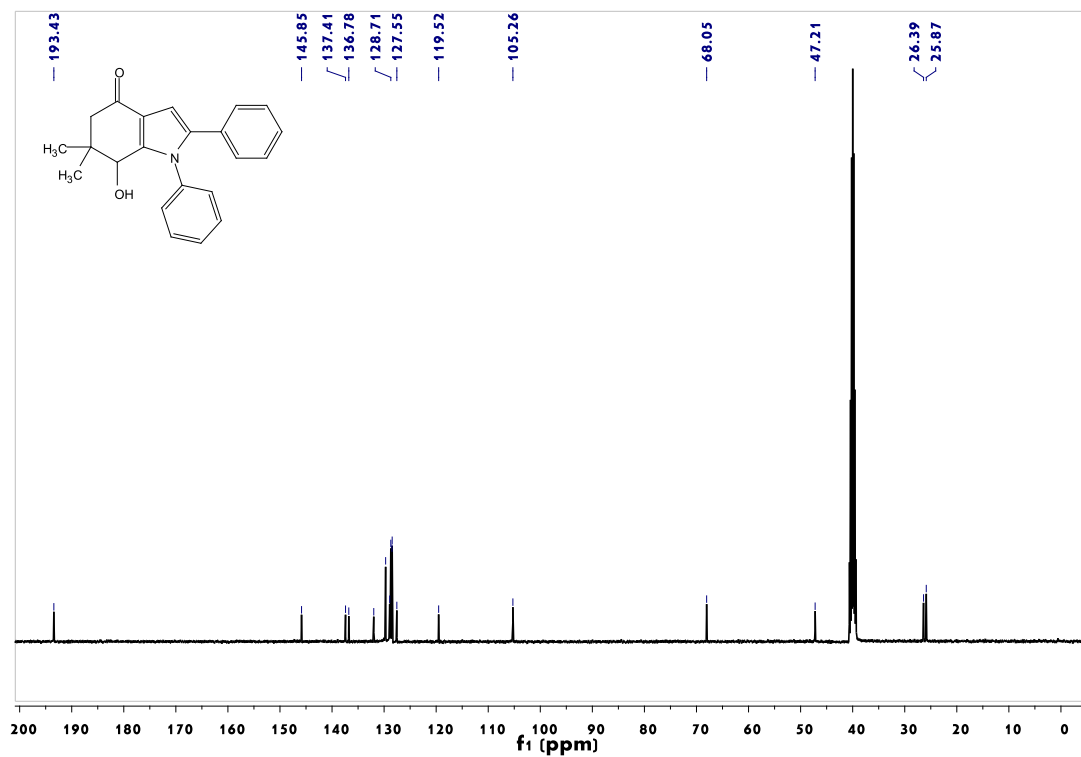
¹H NMR (400 MHz, DMSO) for 3d



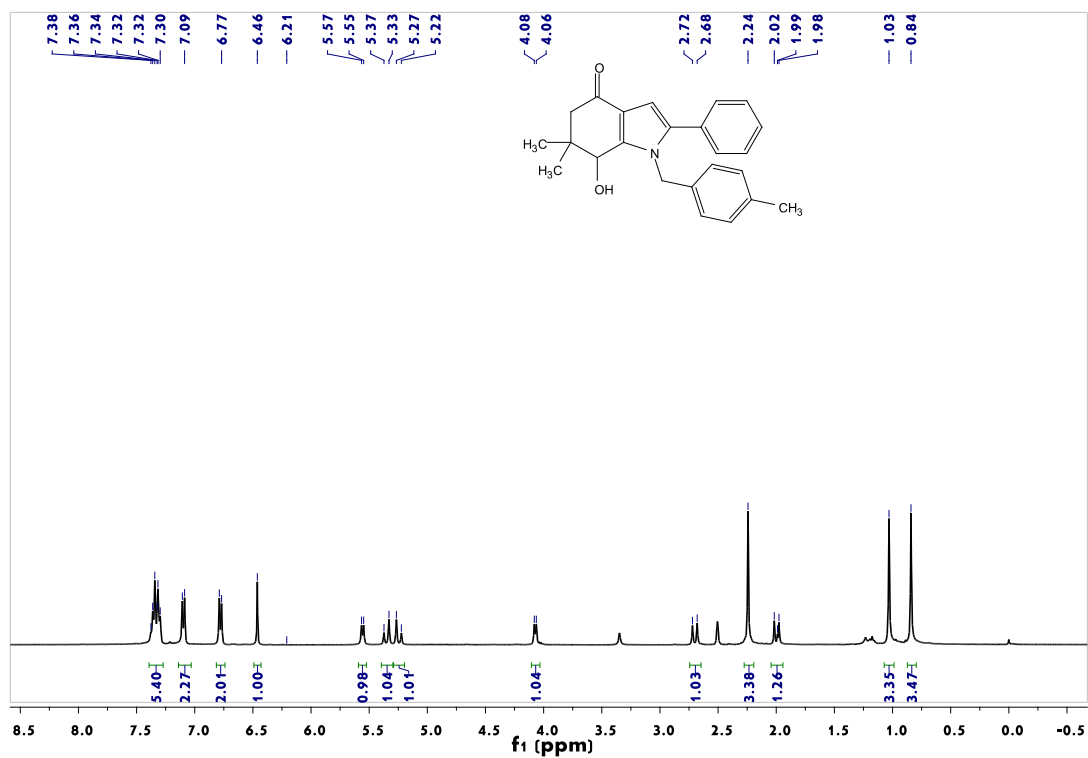
¹³C NMR (400 MHz, DMSO) for 3d



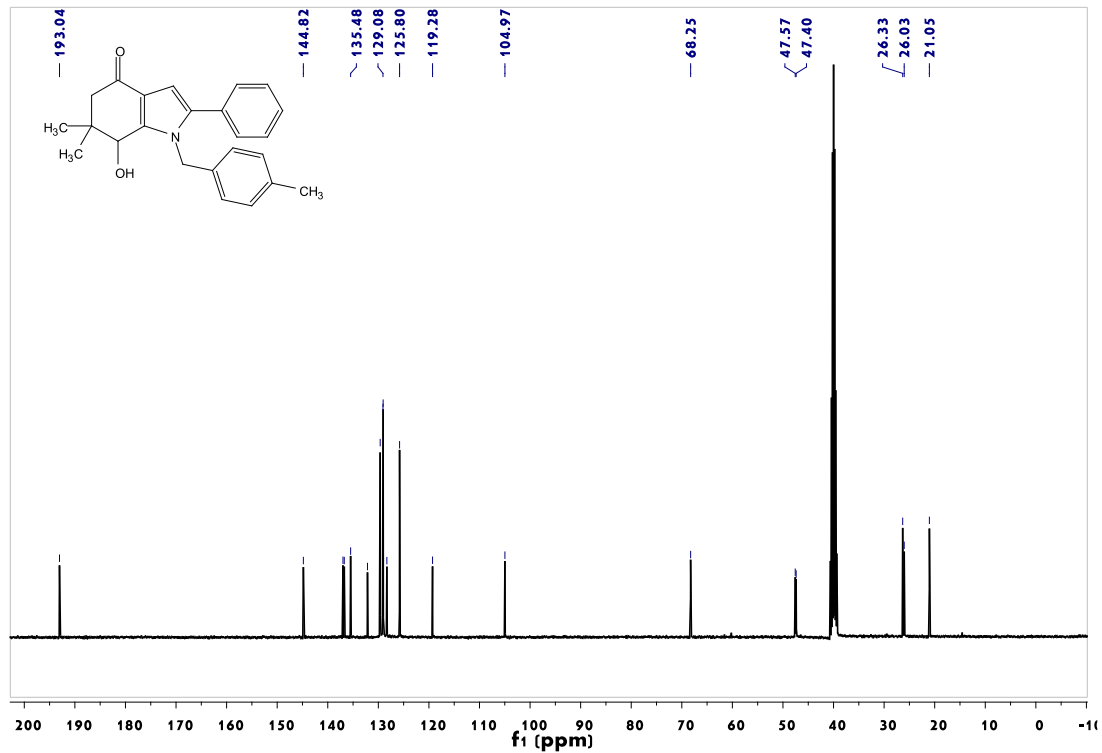
¹H NMR (400 MHz, DMSO) for 3e



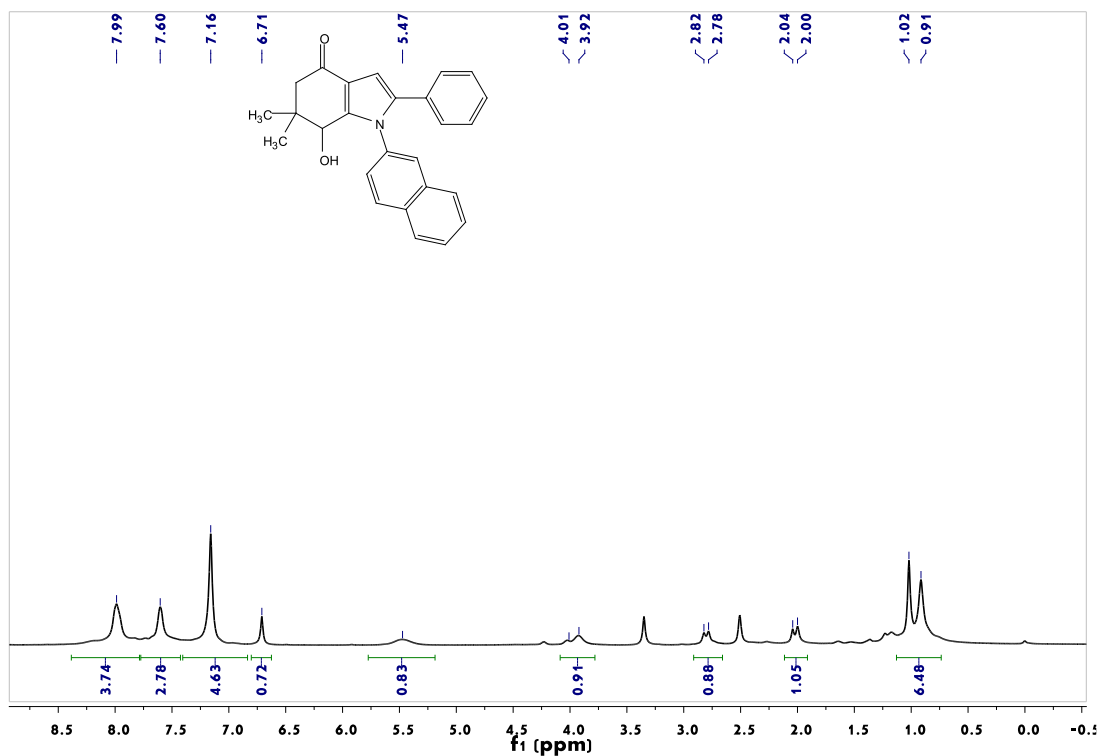
¹³C NMR (400 MHz, DMSO) for 3e



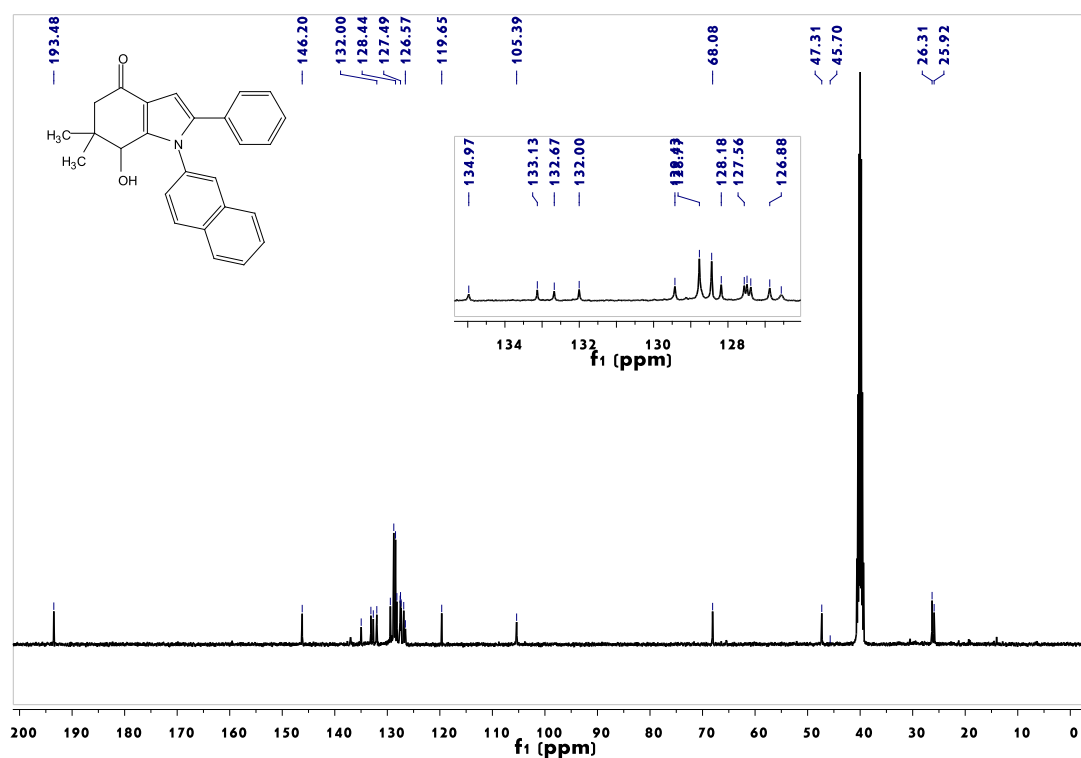
¹H NMR (400 MHz, DMSO) for 3f



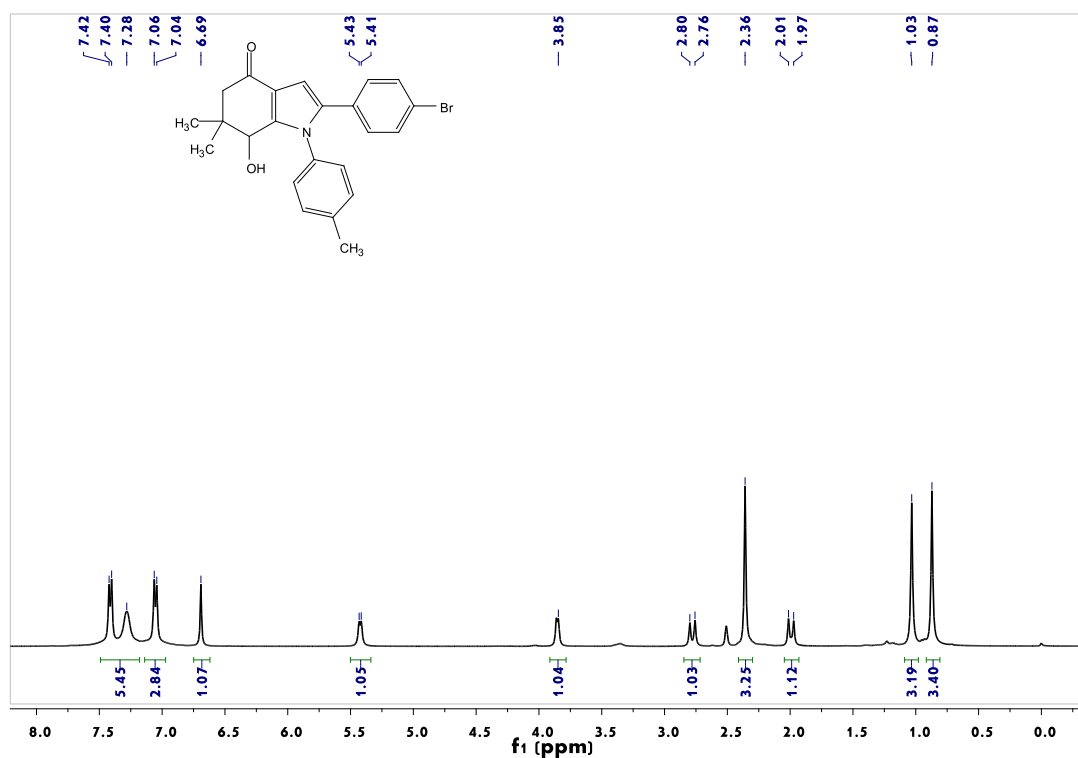
¹³C NMR (400 MHz, DMSO) for 3f



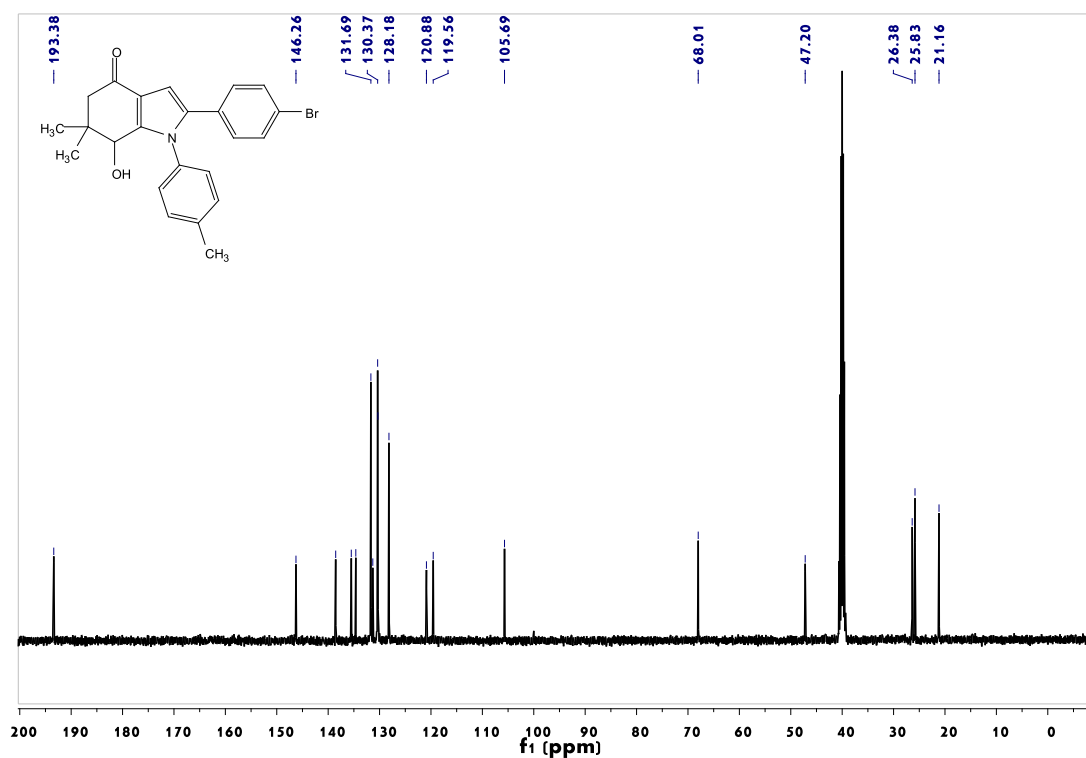
¹H NMR (400 MHz, DMSO) for 3g



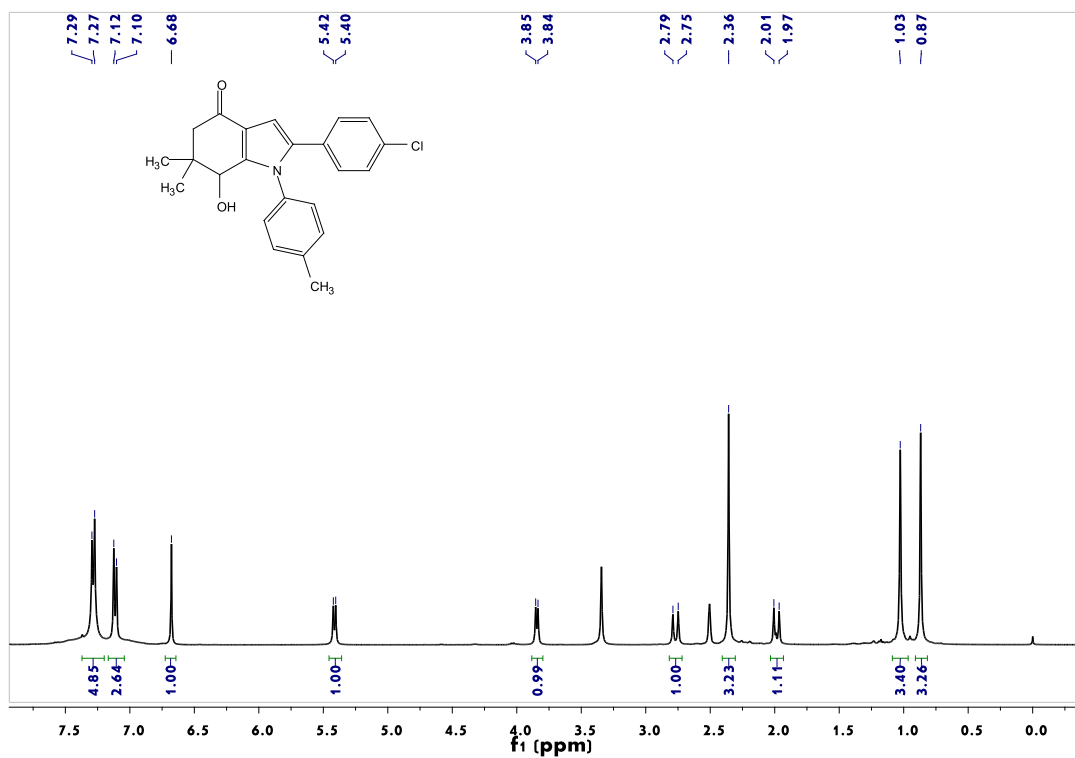
¹³C NMR (400 MHz, DMSO) for 3g



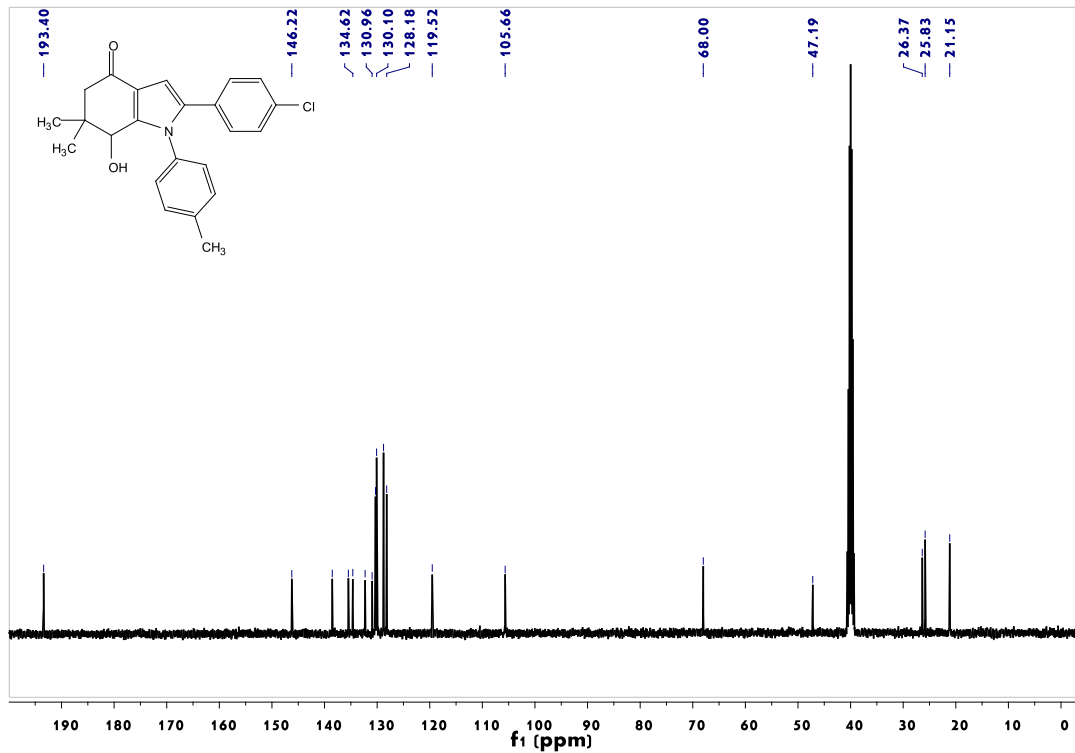
¹H NMR (400 MHz, DMSO) for 3h



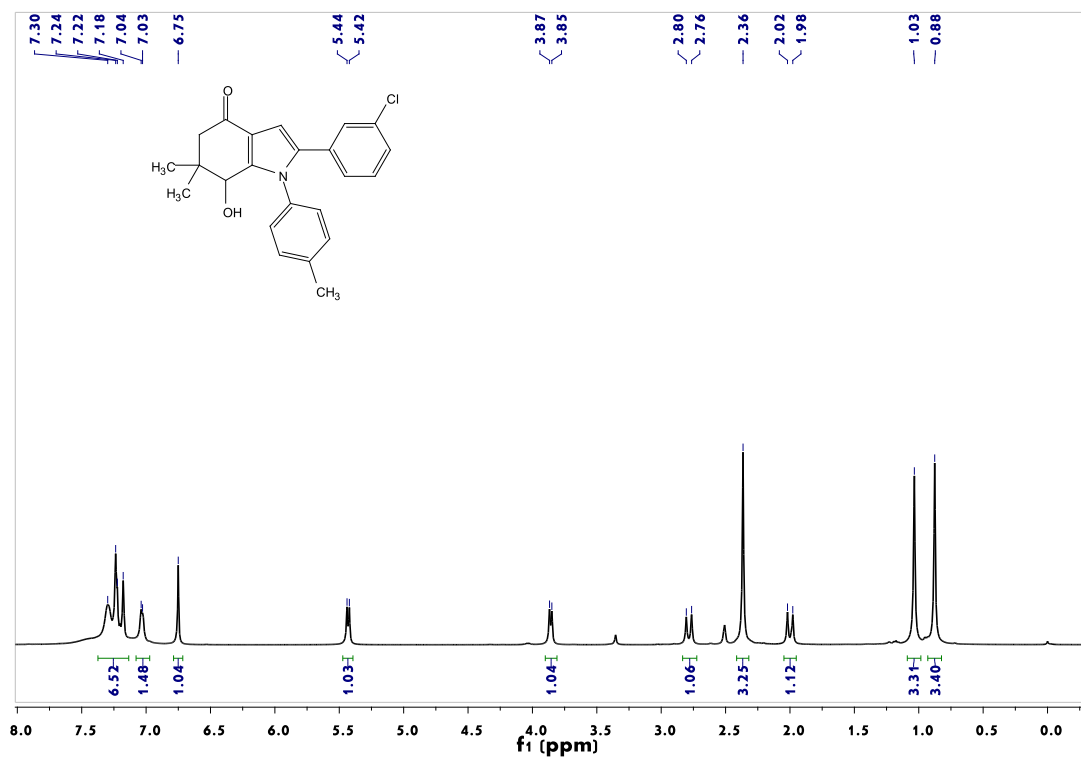
¹³C NMR (400 MHz, DMSO) for 3h



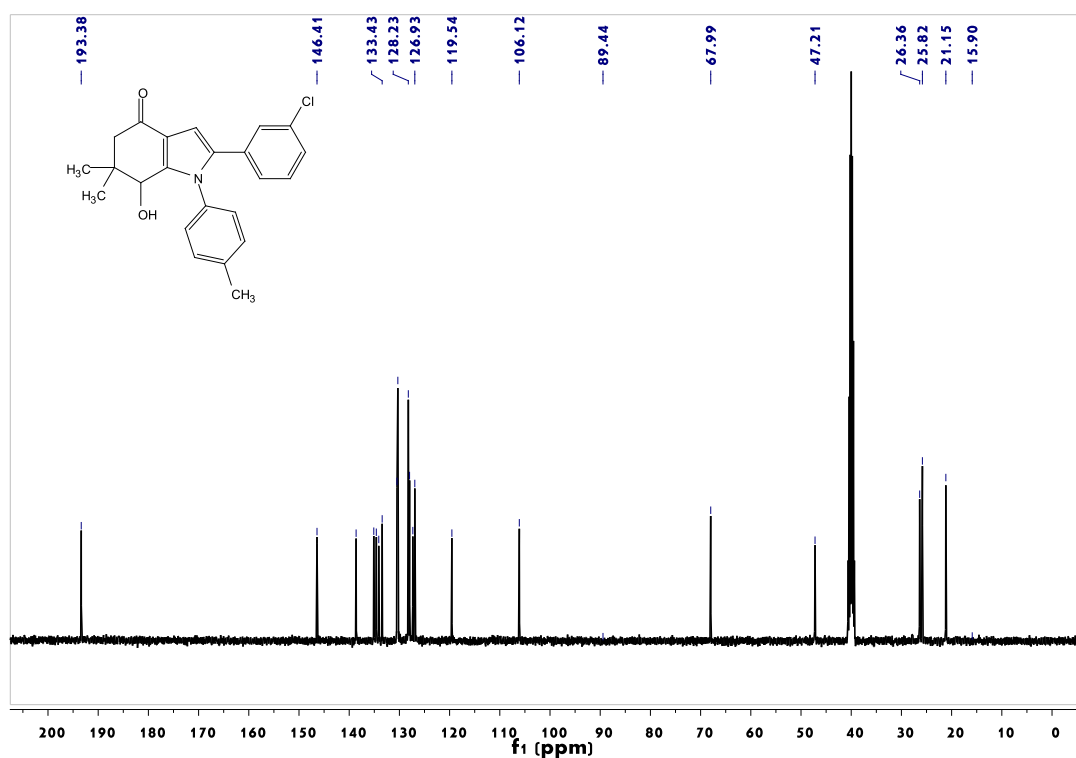
¹H NMR (400 MHz, DMSO) for **3i**



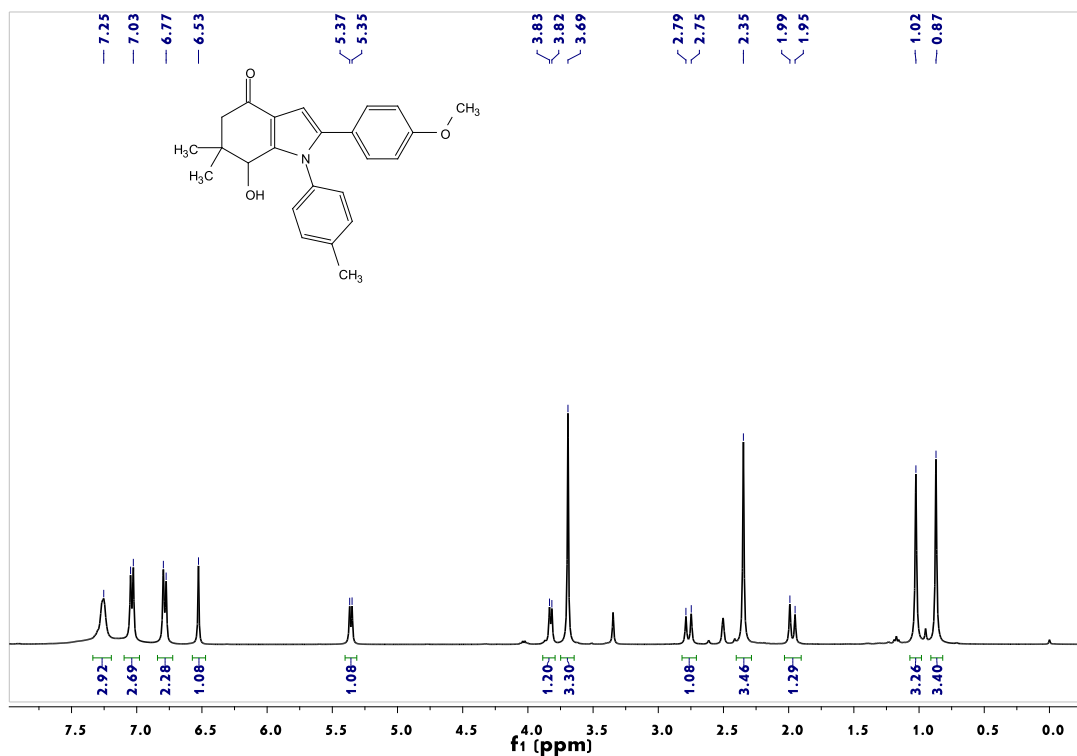
¹³C NMR (400 MHz, DMSO) for **3i**



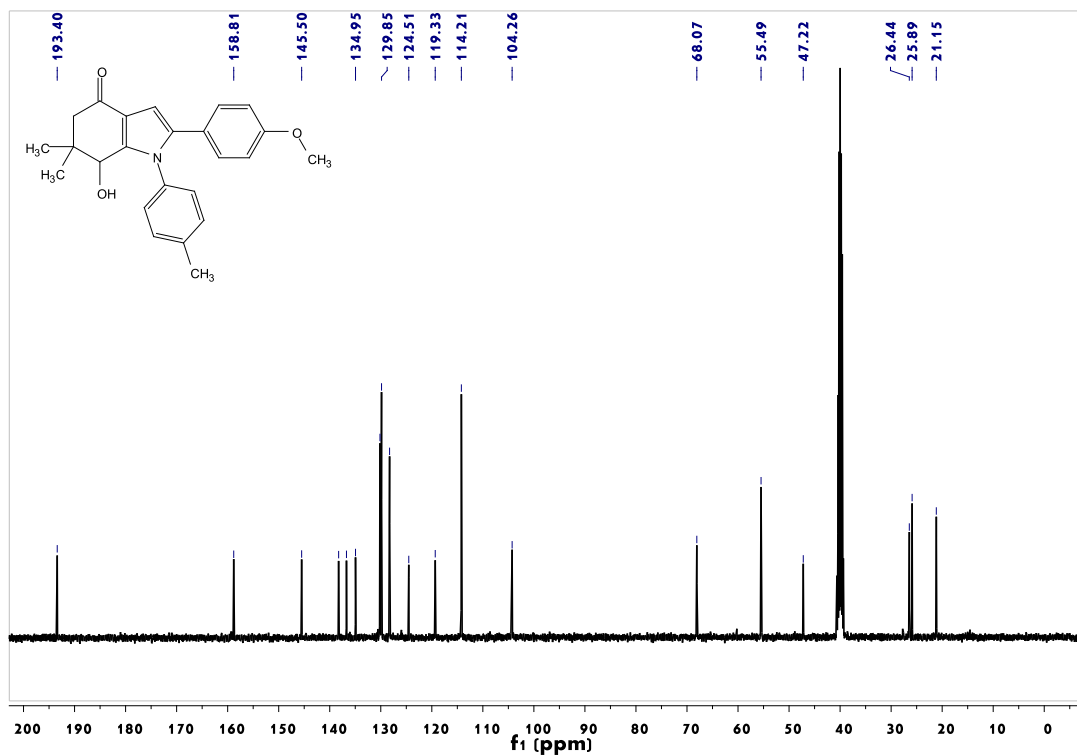
¹H NMR (400 MHz, DMSO) for 3j



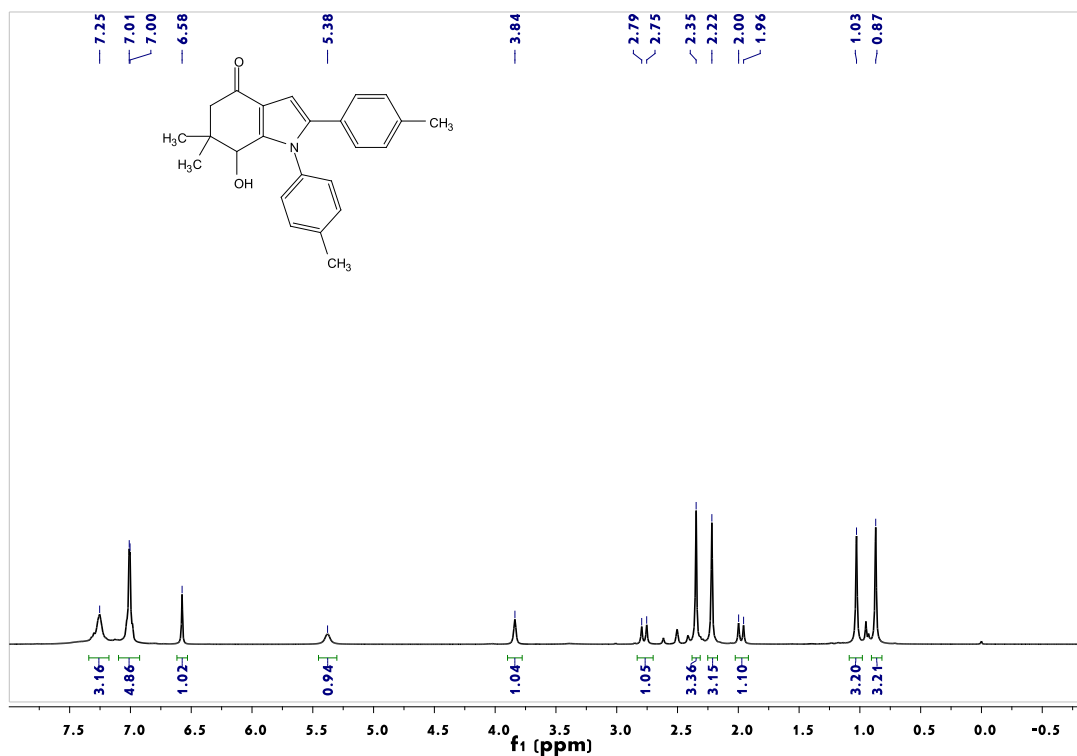
¹³C NMR (400 MHz, DMSO) for 3j



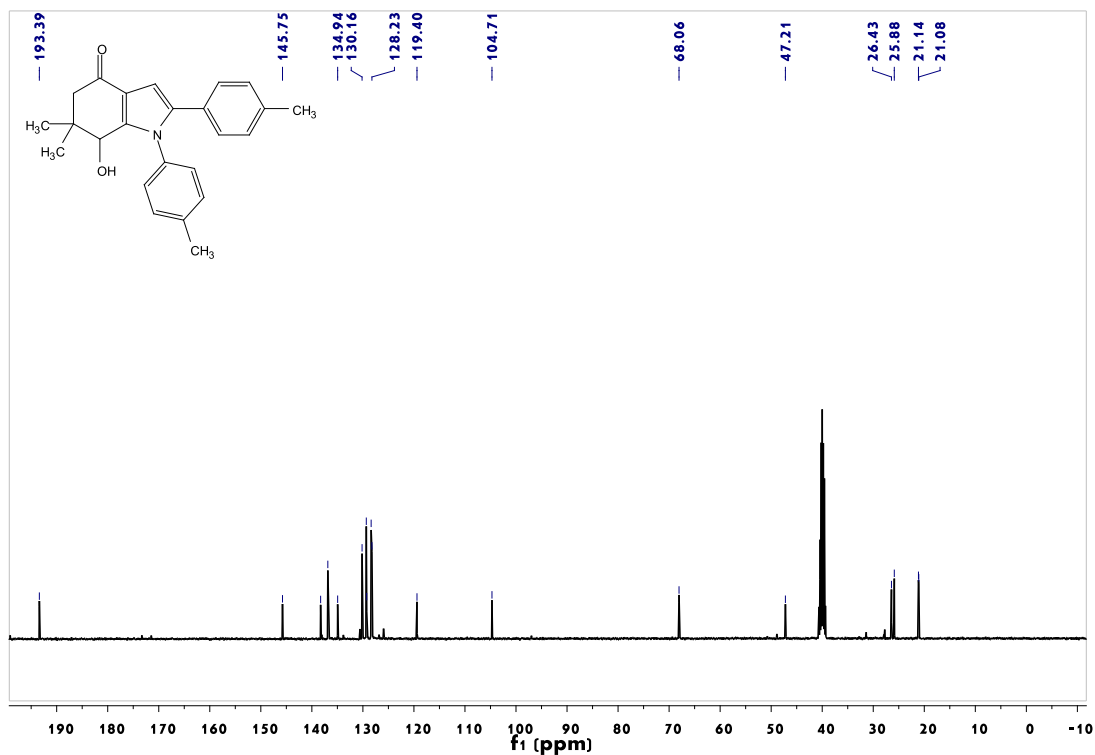
¹H NMR (400 MHz, DMSO) for 3k



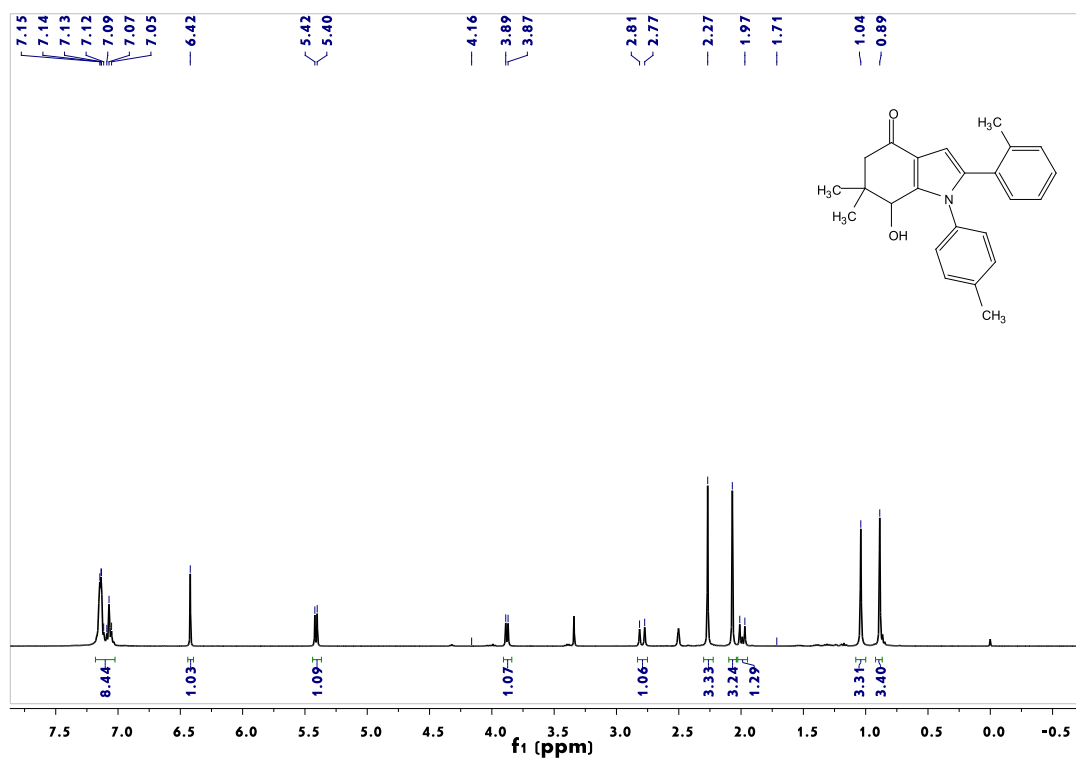
¹³C NMR (400 MHz, DMSO) for 3k



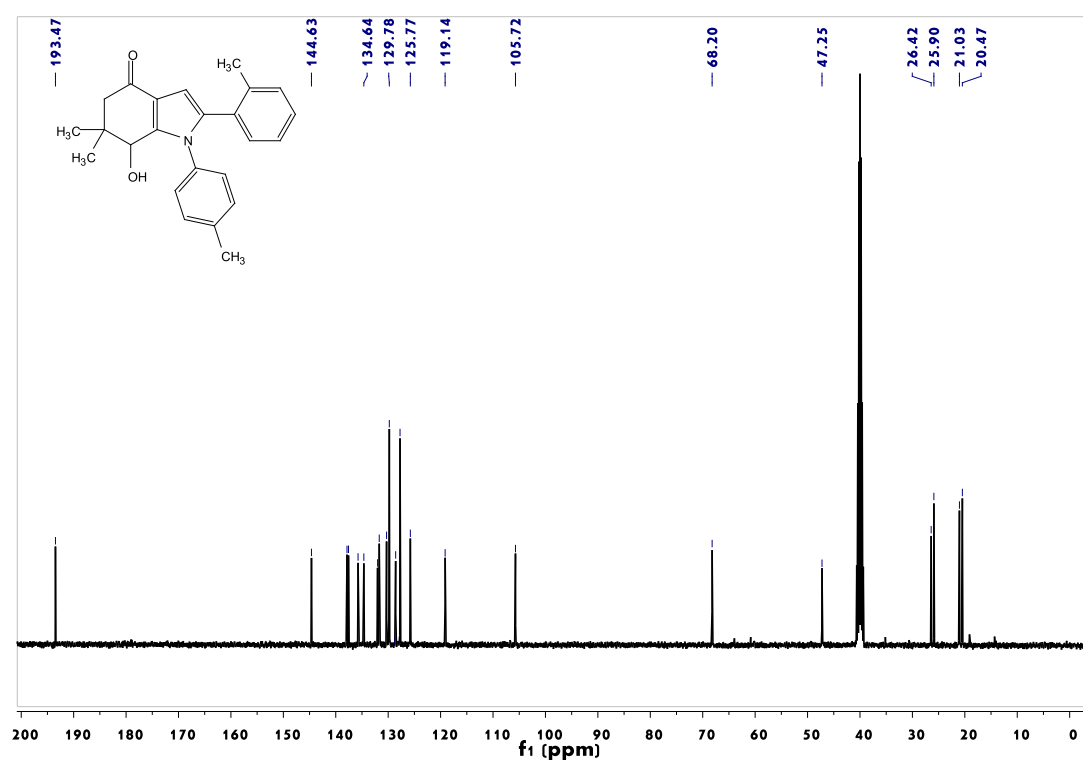
^1H NMR (400 MHz, DMSO) for **3I**



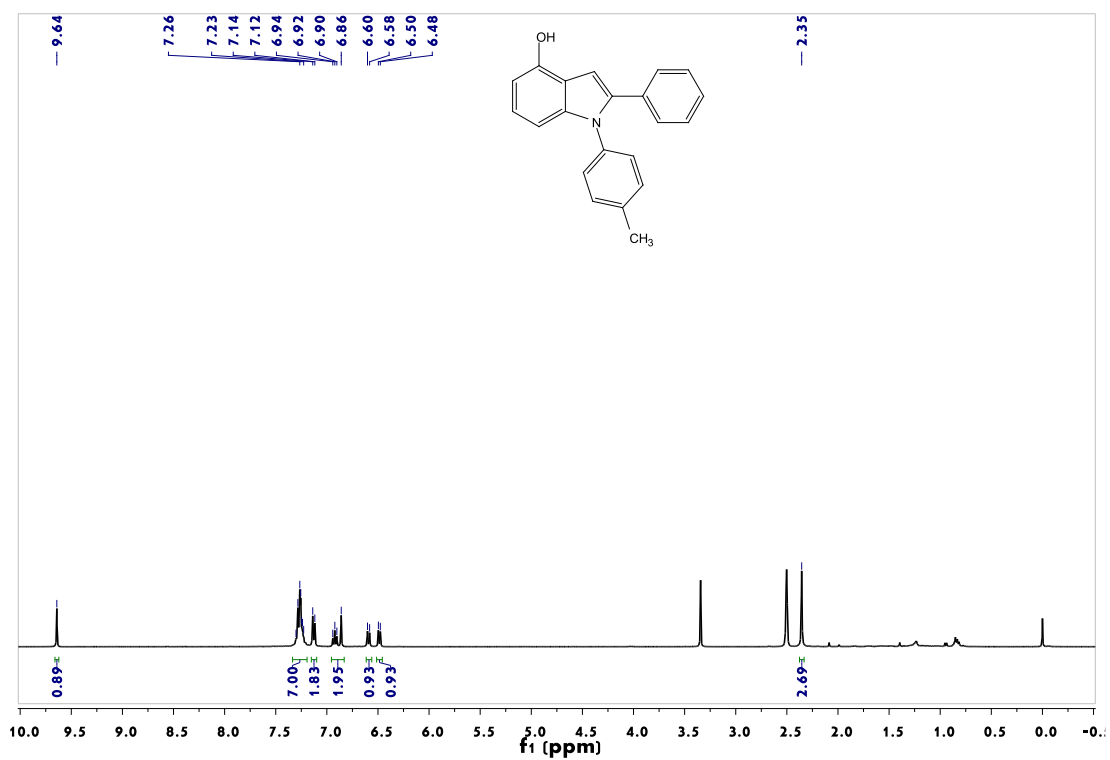
^{13}C NMR (400 MHz, DMSO) for **3I**



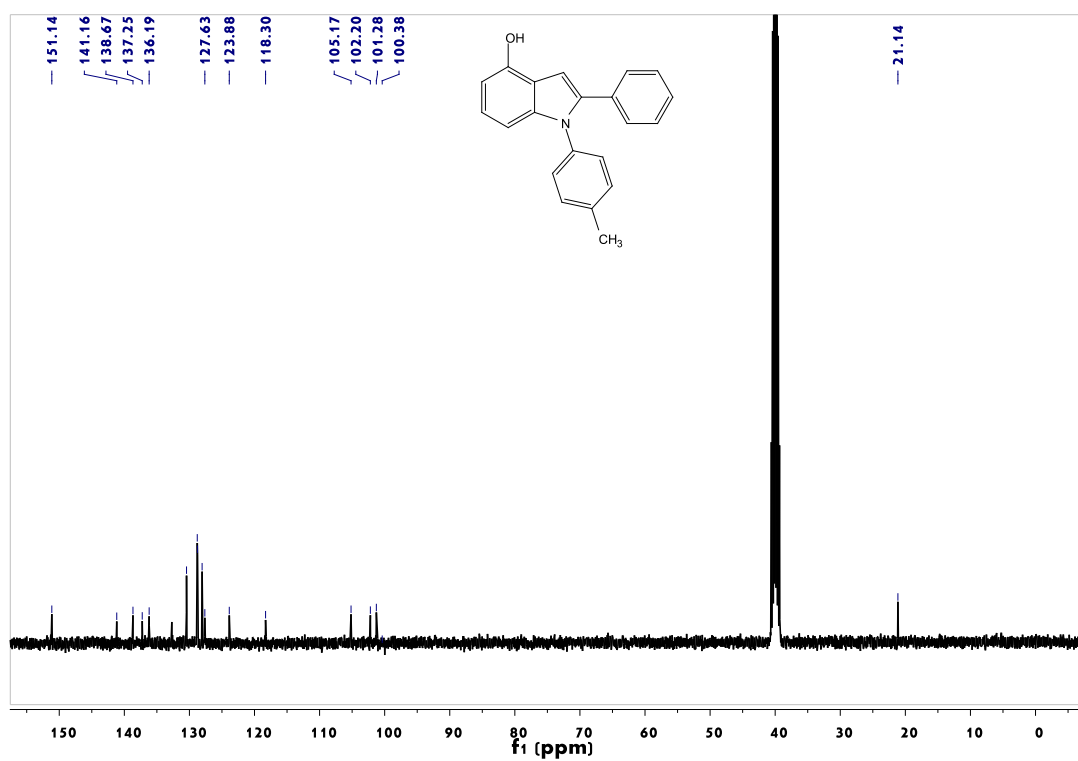
¹H NMR (400 MHz, DMSO) for 3m



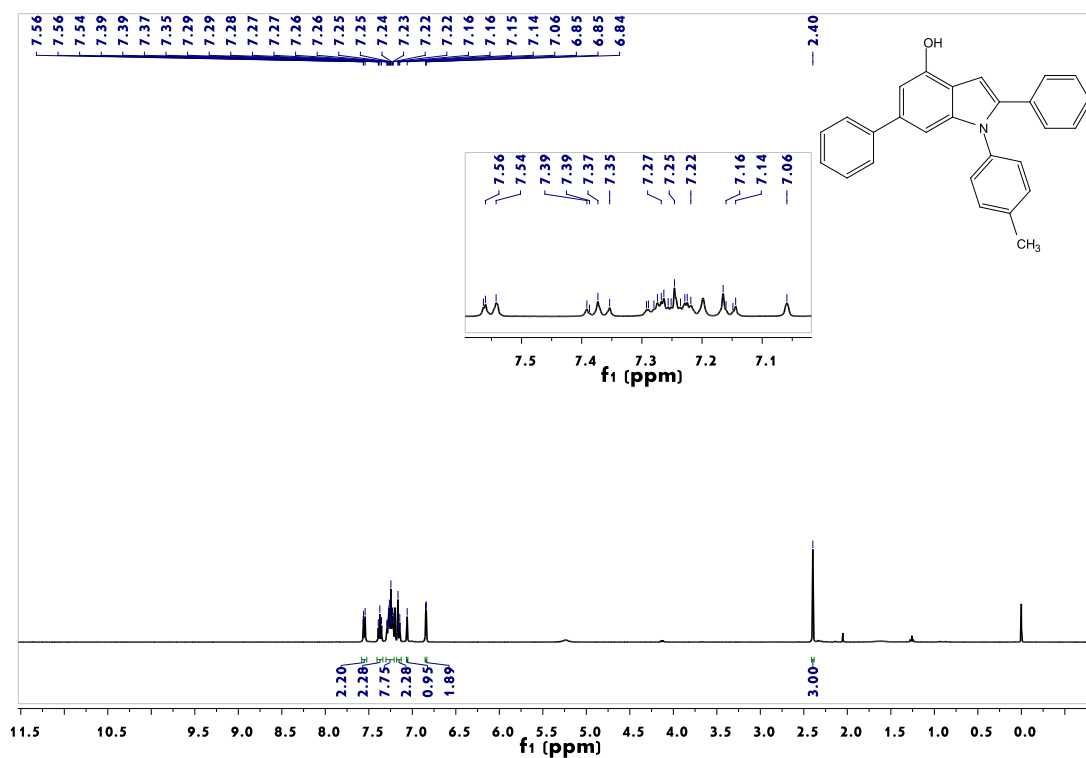
¹³C NMR (400 MHz, DMSO) for 3m



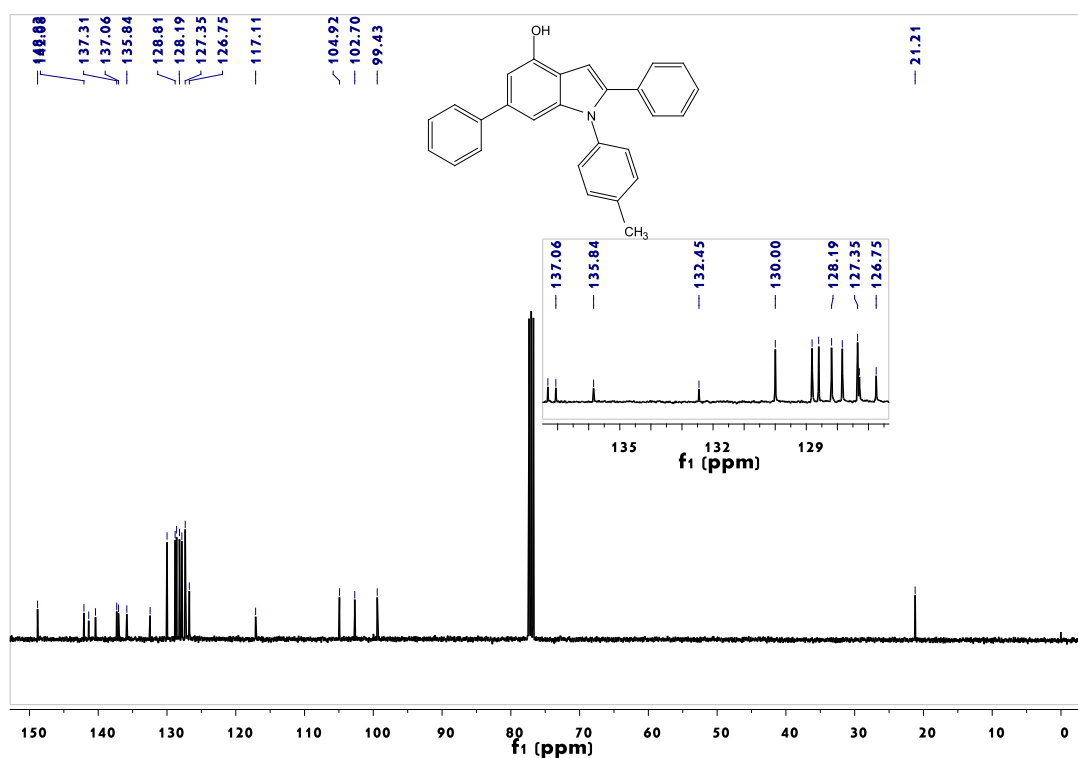
¹H NMR (400 MHz, DMSO) for 5a



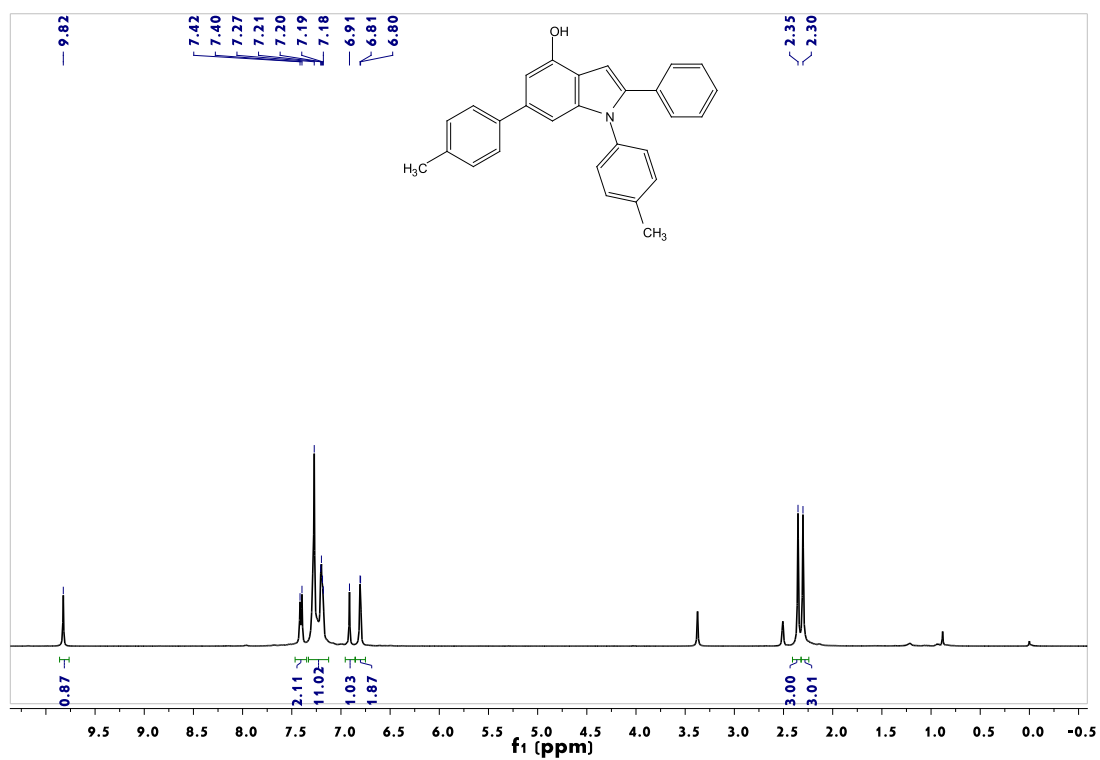
¹³C NMR (400 MHz, DMSO) for 5a



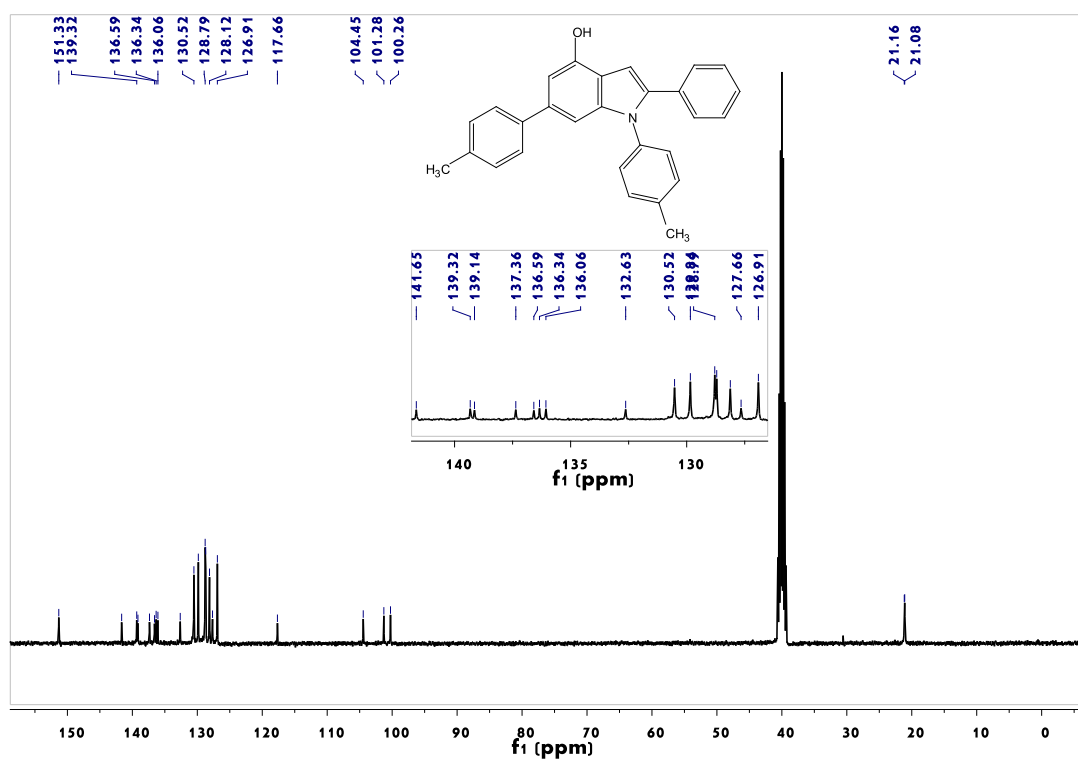
¹H NMR (400 MHz, CDCl₃) for 5b



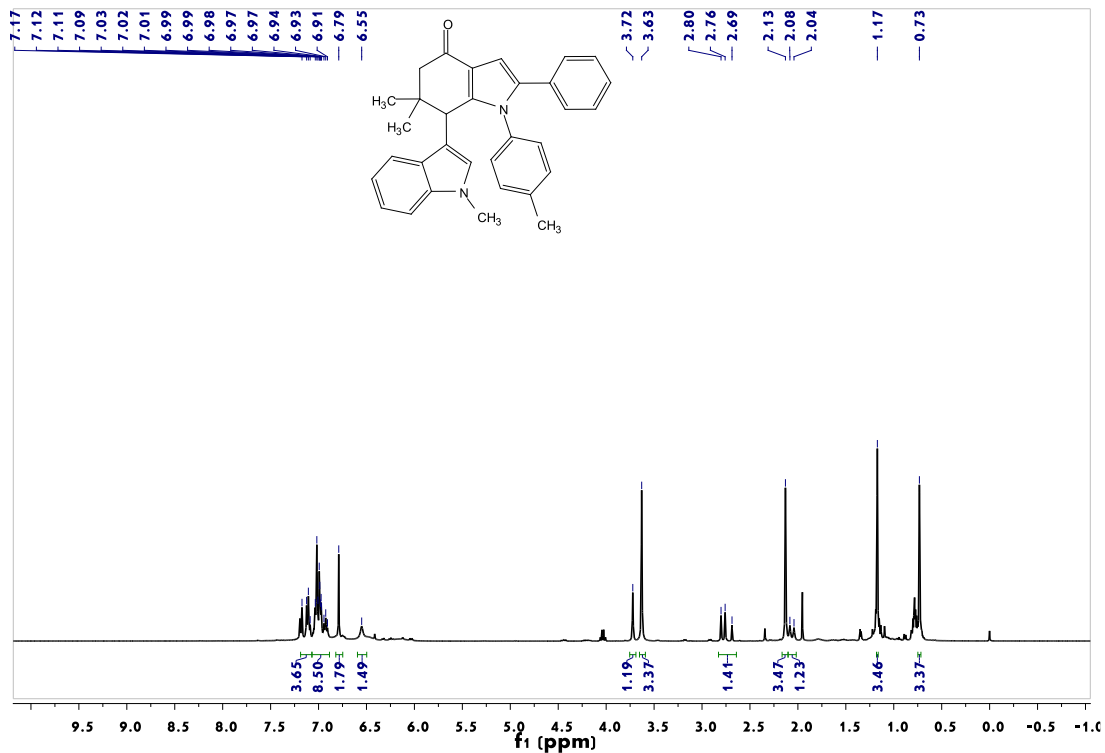
¹³C NMR (400 MHz, CDCl₃) for 5b



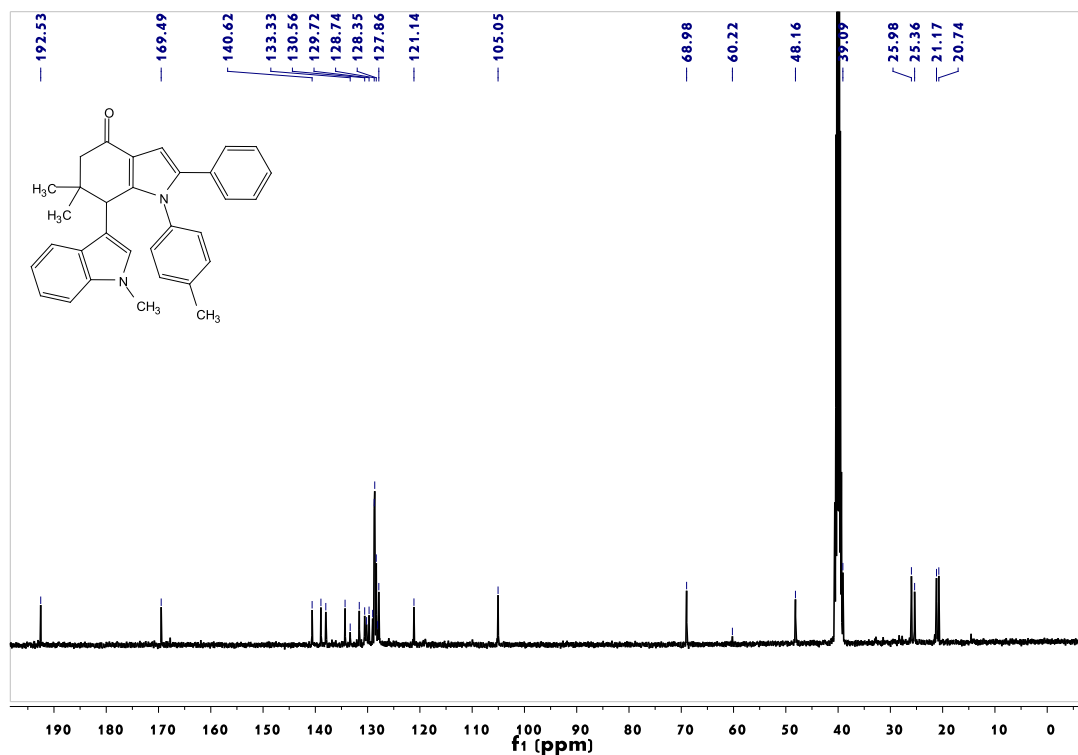
¹H NMR (400 MHz, DMSO) for 5c



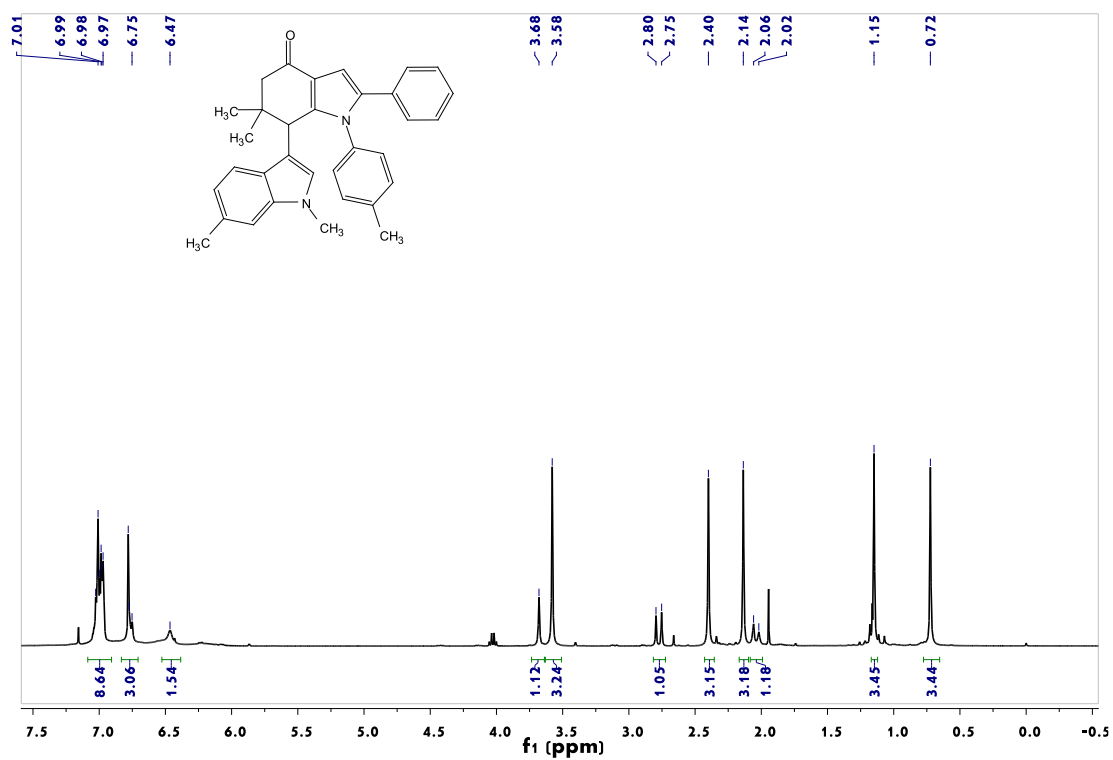
¹³C NMR (400 MHz, DMSO) for 5c



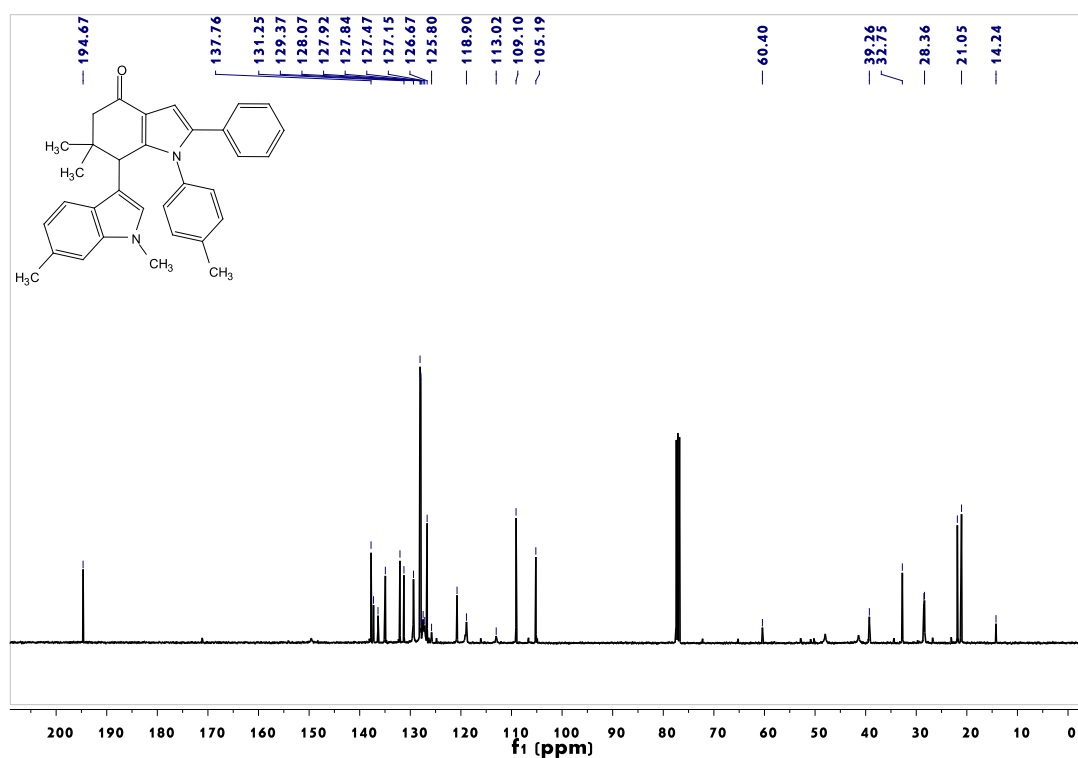
¹H NMR (400 MHz, CDCl₃) for **8a**



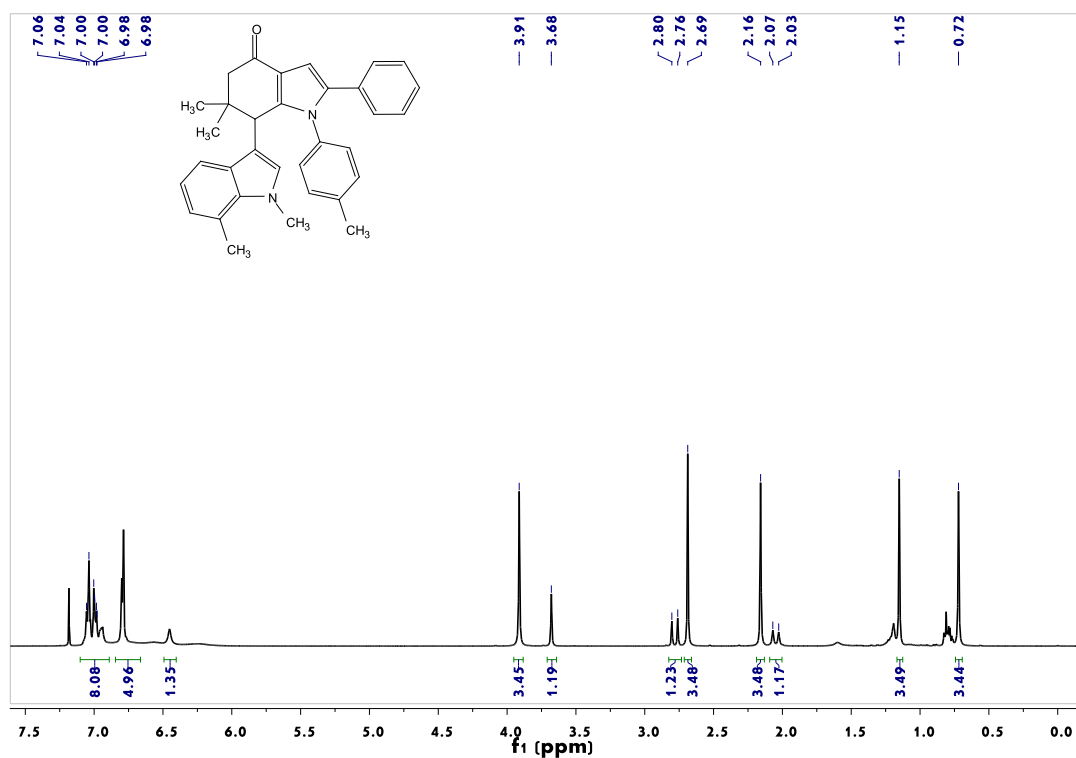
¹³C NMR (400 MHz, DMSO) for **8a**



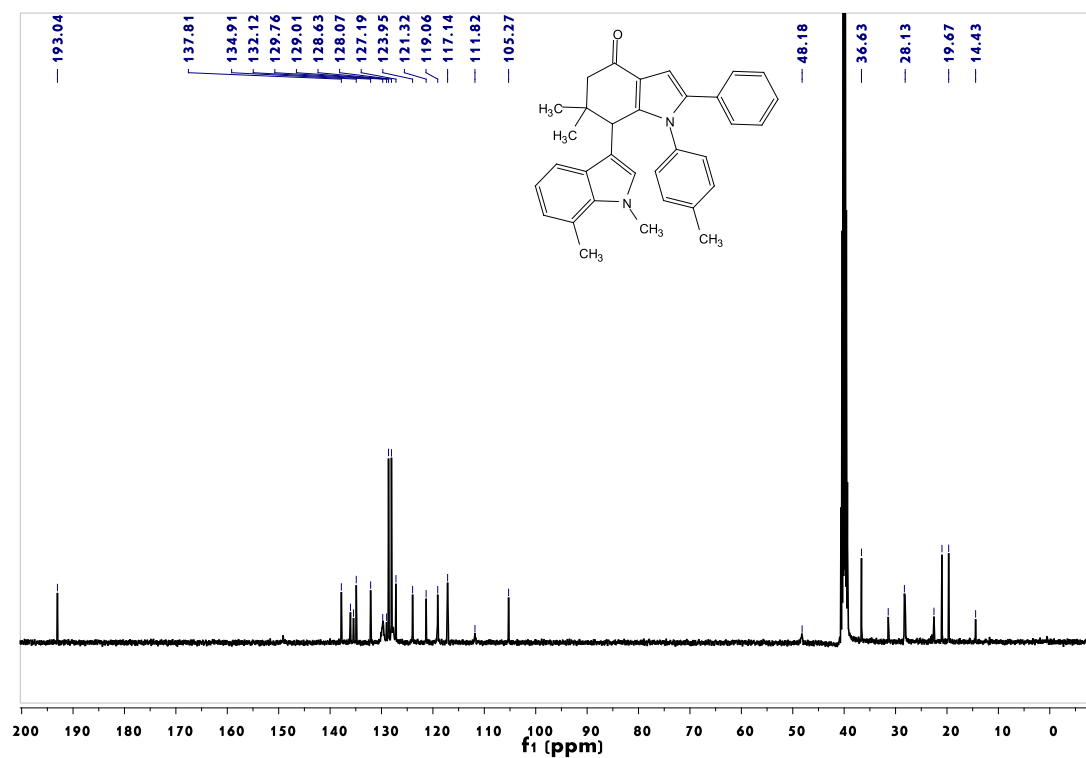
1H NMR (400 MHz, $CDCl_3$) for **8b**



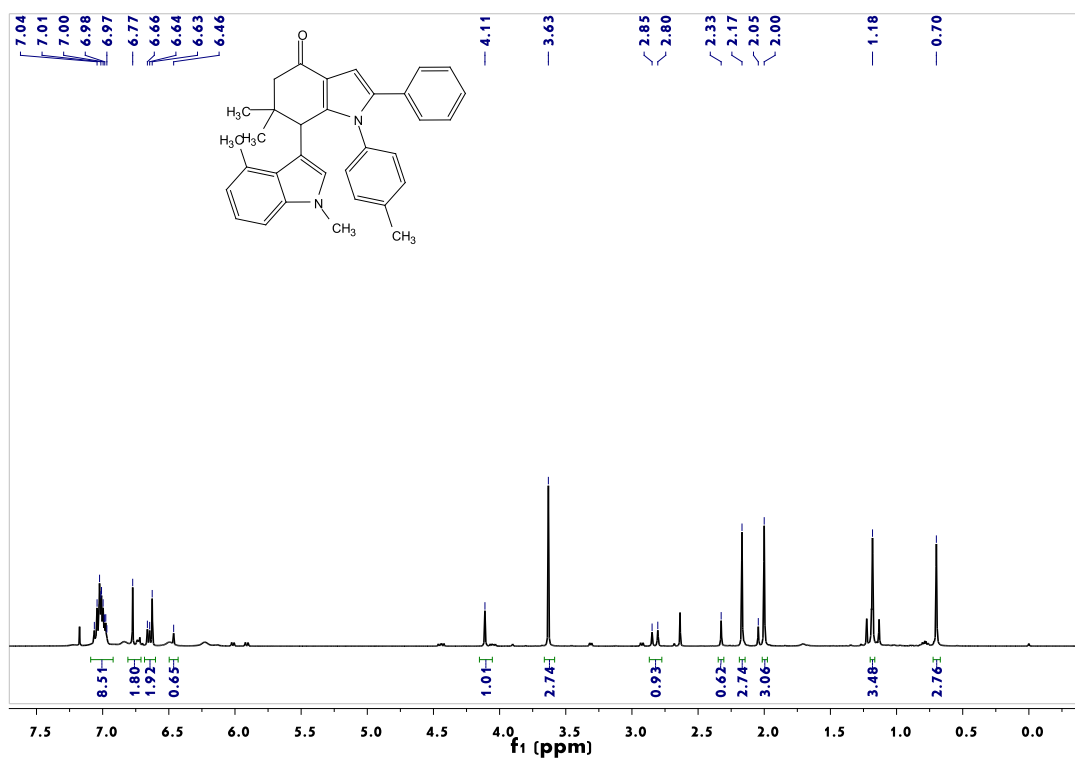
^{13}C NMR (400 MHz, $CDCl_3$) for **8b**



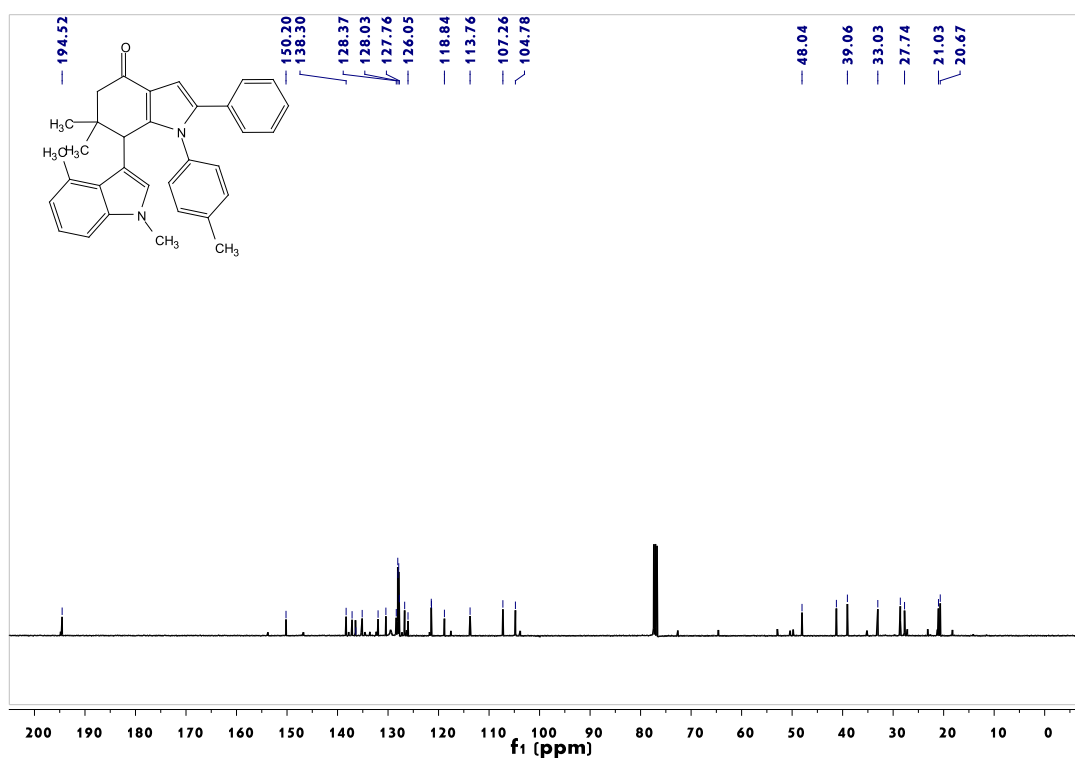
¹H NMR (400 MHz, CDCl₃) for 8c



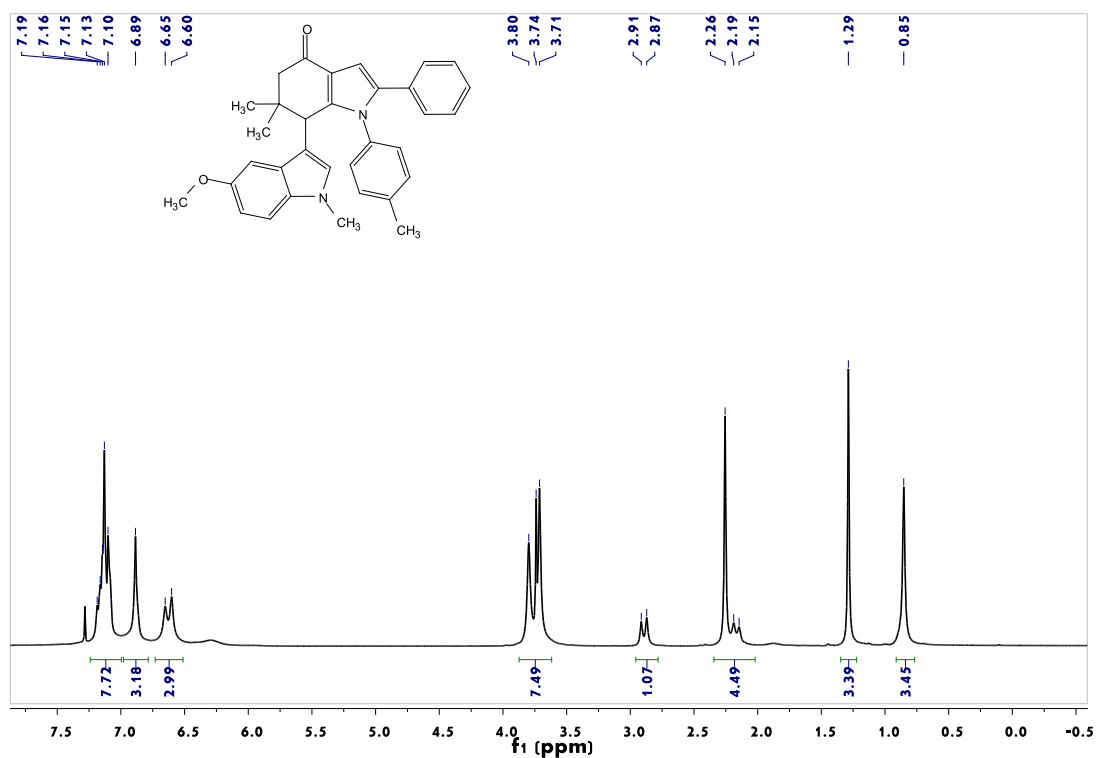
¹³C NMR (400 MHz, DMSO) for 8c



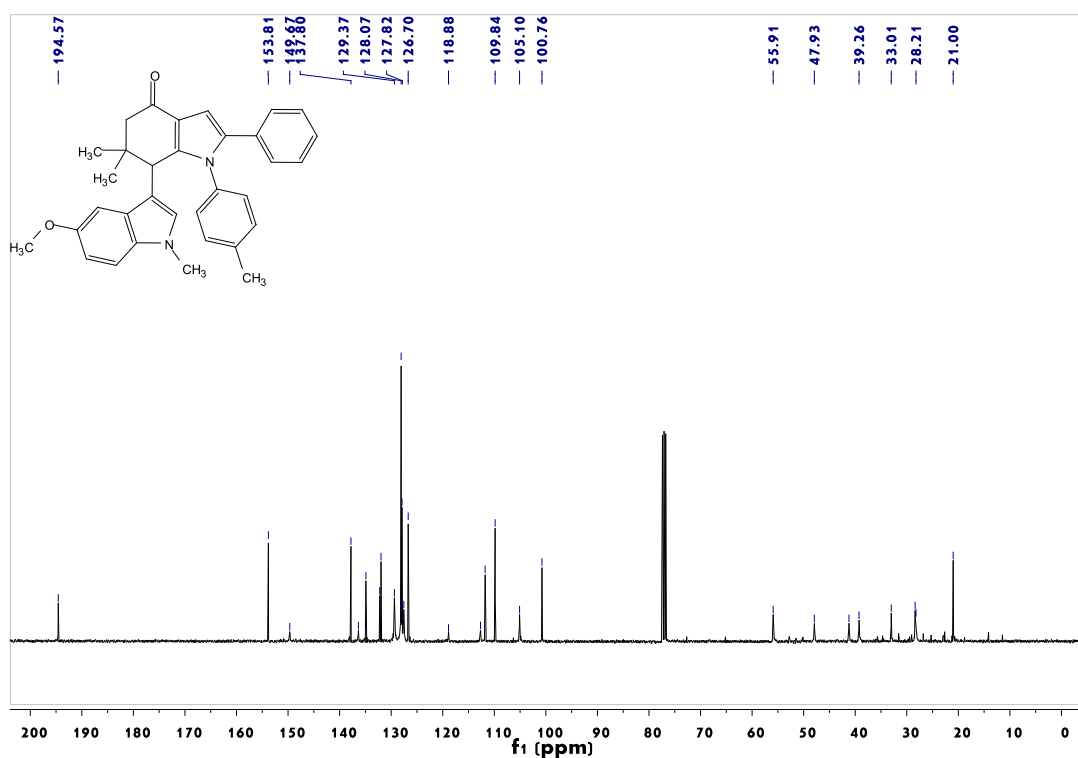
¹H NMR (400 MHz, CDCl₃) for **8d**



¹³C NMR (400 MHz, CDCl₃) for **8d**



¹H NMR (400 MHz, CDCl₃) for **8e**



¹³C NMR (400 MHz, CDCl₃) for **8e**

X-ray structure of compound **3a**

