Supporting Information

Reaction of Indole Carboxylic Acid/Amide with Propargyl Alcohols: [4+3]-Annulation, Unexpected 3- to 2- Carboxylate/Amide Migration and Decarboxylative Cyclization

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(1). General Methods: All reactions were carried out in air, unless otherwise specified. All required chemicals were procured from Aldrich or local manufacturers and used as purchased without further purification, unless noted. Melting points were determined using a hot stage apparatus and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded using 5 mm tubes on a 400 and 500 MHz NMR spectrometer [field strengths: 400/100 or 500/125 MHz respectively] in $CDCl_3$ solution (unless specified otherwise) with shifts referenced to TMS (^{1}H, ^{13}C: = 0). All *J* values are in Hz. Infrared spectra were recorded using ATR technique on a FT-IR spectrophotometer. Mass spectra were recorded using HRMS (ESI-TOF analyzer) equipment. Crystallographic data were collected at 293 K on an X-ray diffractometer system using Mo-K_α radiation (λ = 0.71073 Å) or Cu-K_α (λ = 1.54184 Å) radiation. Structures were solved and refined using standard methods. Thin-layer chromatography was performed on silica/alumina plates and components were visualized by observation under iodine/UV light at 254 nm. Column chromatography was performed on silica gel (100-200 mesh)/neutral alumina, for column elution process hexane-EtOAc mixture was used as the eluent unless otherwise stated.

(2). Synthesis of indole-2-carboxylic acids (1), indole-2-carboxamides (2), indole-3-carboxamides (4) and propargyl alcohols (5)

Substituted indole-2-carboxylic acids **1a-1g**,[1a] and **1h**,[1b] indole-2-carboxamides **2a-2c**,[1c] indole-3-carboxamides **4a-4c**,[1d] and propargyl alcohols **5a-5x**[1e] were prepared using literature methods.

Reference:

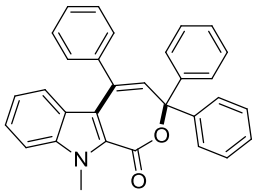
1. (a) Jiang, X.; Zhang, F.; Yang, J.; Yu, P.; Yi, P.; Sun, Y.; Wang, Y. *Adv. Synth. Catal.* **2016**, *358*, 3938. (b) Ren, L.; Nan, G.; Wang, Y.; Xiao, Z. *J. Org. Chem.* **2018**, *83*, 14472. (c) William, H. M.; Kenneth, A. N; Mark, A. S.; Irene, N. U.; PCT Int. Appl., 2001026652, **19 Apr 2001**. (d) Gary, M. K.; Peter Seongwoo, H.; James, J. T.; Hongyu, R.; Richard Gerald, W.; Anthony A. T.; Alexander A.; Guangming, C.; Jeffrey, A. C. U.S. Pat. Appl. Publ., 20070299069, **27 Dec 2007**. (e) Engel, D. A.; Dudley, G. B. *Org. Lett.* **2006**, *8*, 4027.

(3). Table S1. Optimization of reaction conditions[a]

entry	catalyst (10 mol %)	solvent	T (°C)	time (h)	yield (%)[b]	
					6aa	7aa
1	$Sc(OTf)_3$	DCM	rt	12	74	10
2	$Zn(OTf)_2$	DCM	rt	12	70	5
3	$In(OTf)_3$	DCM	rt	12	60	16
4	$Bi(OTf)_3$	DCM	rt	12	65	15
5	AgOTf	DCM	rt	12	72	10
6	NaOTf	DCM	rt	12	63	7
7	$FeCl_3$	DCM	rt	12	83	9
8	$Yb(OTf)_3$	DCM	rt	12	85	--
9	$Fe(OTf)_3$	DCM	rt	12	88	--
10	**$Cu(OTf)_2$**	**DCM**	**rt**	**6**	**93**	--
11	$Cu(OTf)_2$	DCM	rt	12	93	--
12	$Cu(OTf)_2$	DCM	0	6	70	--
13	$Cu(OTf)_2$	DCM	40	6	75	--
14	$Cu(OTf)_2$	DCE	rt	6	87	--
15	$Cu(OTf)_2$	$CHCl_3$	rt	6	78	--
16	$Cu(OTf)_2$	Dioxane	rt	6	76	--
17	$Cu(OTf)_2$	CH_3CN	rt	6	46	--
18	$Cu(OTf)_2$	THF	rt	6	40	--
19	$Cu(OTf)_2$	Toluene	rt	6	43	--
20	$Cu(OTf)_2$	DMSO	rt	6	44	--
21	no catalyst	DCM	rt	6	nr[c]	--
22	$Cu(OTf)_2$	DCM	rt	6	93[d]	--
23	$Cu(OTf)_2$	DCM	rt	6	93[e]	--

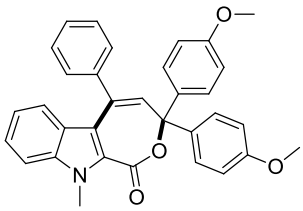
[a]Quantities used: **1a** (0.100 g, 0.57 mmol), **5a** (0.178 g, 0.62 mmol), solvent (5 mL). [b]Yield after isolation is based on **1a**. [c]nr = no reaction. [d]15 mol % $Cu(OTf)_2$ was used. [e]20 mol % $Cu(OTf)_2$ was used.

(4). General procedure (GP-I) for the synthesis of ε-lactones 6aa-6ga. An oven dried 25 mL round-bottomed flask was charged with 1-methylindole-2-carboxylic acid **1a** (0.100 g, 0.57 mmol), propargyl alcohol **5a** (0.178 g, 0.62 mmol) and $Cu(OTf)_2$ (0.020 g, 0.057 mmol (10 mol %)) in dichloromethane (10 mL). The mixture was stirred at rt (25 ^oC) in open air for 6 h and monitored by TLC for the disappearance of starting materials. After the appropriate period, the reaction mixture was treated with dichloromethane (10 mL) and water (15 mL). The organic phase was separated and the aqueous layer washed with dichloromethane (10 mL) and brine solution (10 mL). The combined organic part was dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to afford the crude product. Purification by column chromatography (ethyl acetate: hexane 1:9) afforded the desired product **6aa** as a white solid. Compounds **6ab-6ga** were prepared from appropriate indole-2-carboxylic acids and propargyl alcohols by using the same procedure and same molar quantities.



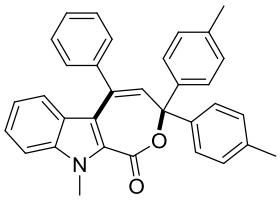
10-Methyl-3,3,5-triphenyl-3,10-dihydro-1*H*-oxepino[3,4-*b*]indol-1-one (6aa)

White solid, yield 0.235 g (93%), mp. 168-170 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54-7.39 (m, 9H), 7.26-7.10 (m, 8H), 6.89-6.85 (m, 1H), 6.65 (d, J = 8.4 Hz, 1H), 6.47 (s, 1H), 3.76 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.5, 142.0, 140.0, 138.7, 131.8, 131.2, 128.7, 128.5, 128.2, 127.5, 126.1, 125.2, 123.9, 122.9, 120.7, 118.3, 110.0, 85.9, 31.7; IR (neat): ν_{max} 3027, 1691, 1513, 1470, 1448, 1274, 1235, 1161, 1032, 986, 967, 799, 747, 696 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{24}NO_2$ (M^++H): *m/z* 442.1807. Found: 442.1808.



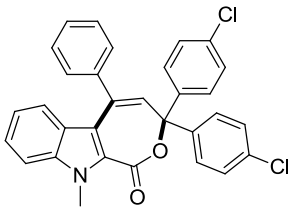
3,3-Bis(4-methoxyphenyl)-10-methyl-5-phenyl-3,10-dihydro-1*H*-oxepino[3,4-*b*]indol-1-one (6ab)

White solid, yield 0.259 g (91%), mp. 160-162 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.49 (m, 2H), 7.46-7.40 (m, 3H), 7.32 (d, *J* = 9.0 Hz, 4H), 7.26-7.22 (m, 2H), 6.88- 6.85 (m, 1H), 6.72 (d, *J* = 8.0 Hz, 4H), 6.60 (d, *J* = 7.0 Hz, 1H), 6.40 (s, 1H), 3.80 (s, 3H), 3.72 (s, 6H); ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$) δ 162.6, 158.8, 141.7, 140.2, 138.7, 132.3, 131.1, 128.5_4, 128.4_6, 127.5, 125.1, 124.0, 122.9, 120.5, 118.1, 113.5, 110.1, 85.9, 55.1, 31.7; IR (neat): ν_{max} 2934, 2835, 1689, 1605, 1506, 1464, 1405, 1382, 1233, 1175, 1122, 1030, 829, 738, 698 cm^{-1}; HRMS (ESI): Calcd. for $C_{33}H_{28}NO_4$ (M^++H): *m/z* 502.2018. Found: 502.2019.



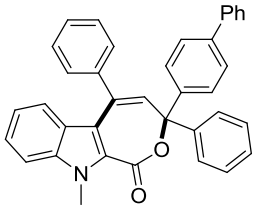
10-Methyl-5-phenyl-3,3-di-p-tolyl-3,10-dihydro-1*H*-oxepino[3,4-*b*]indol-1-one (6ac)

White solid, yield 0.252 g (94%), mp. 170-172 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.50 (m, 2H), 7.44-7.39 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 4H), 7.26-7.21 (m, 2H), 6.99 (d, *J* = 7.5 Hz, 4H), 6.89-6.86 (m, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.42 (s, 1H), 3.78 (s, 3H), 2.29 (s, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.6, 141.7, 140.2, 138.7, 137.1, 132.3, 131.2, 128.9, 128.6, 128.5, 126.0, 125.1, 124.0, 123.0, 120.5, 118.2, 110.0, 85.9, 31.8, 21.0; IR (neat): ν_{max} 3055, 2946, 1692, 1522, 1509, 1407, 1274, 1233, 1122, 1090, 822, 785, 770, 737, 672 cm^{-1}; HRMS (ESI): Calcd. for $C_{33}H_{28}NO_2$ (M^++H): *m/z* 470.2120. Found: 470.2121.



3,3-Bis(4-chlorophenyl)-10-methyl-5-phenyl-3,10-dihydro-1*H*-oxepino[3,4-*b*]indol-1-one (6ad)

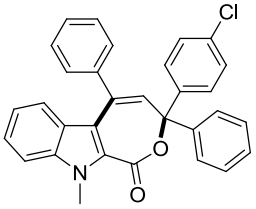
White solid, yield 0.234 g (80%), mp. 172-174 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.40 (m, 5H), 7.36 (d, *J* = 8.5 Hz, 4H), 7.30-7.25 (m, 2H), 7.18 (d, *J* = 7.5 Hz, 4H), 6.91-6.88 (m, 1H), 6.62 (d, *J* = 8.5 Hz, 1H), 6.32 (s, 1H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.9, 142.7, 139.7, 138.8, 133.6, 130.5, 130.3, 128.9, 128.6_2, 128.5_6, 128.5, 127.4, 125.7, 123.8, 122.9, 121.0, 118.3, 110.3, 84.8, 31.9; IR (neat): ν_{max} 3057, 2948, 1697, 1534, 1486, 1384, 1232, 1121, 1087, 1015, 989, 836, 818, 787, 755, 743, 697 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{22}Cl_2NO_2$ (M^++H), (M^++H+2), (M^++H+4),: *m/z* 510.1028, 512.0998, 514.0968. Found: 510.1023, 512.0998, 514.0986.



3-([1,1'-Biphenyl]-4-yl)-10-methyl-3,5-diphenyl-3,10-dihydro-1*H*-oxepino[3,4-*b*]indol-1-one (6ae)

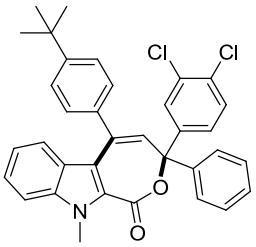
White solid, yield 0.198 g (67%), mp. 140-143 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.39 (m, 15H), 7.35-7.31 (m, 1H), 7.26-7.13 (m, 5H), 6.90-6.86 (m, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.49 (s, 1H), 3.78 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.5, 142.1, 140.3, 140.2, 140.0, 138.7, 131.6, 131.1, 128.8, 128.7, 128.6, 128.5, 128.2, 127.6, 127.4, 127.0, 126.9, 126.6, 126.1, 125.2, 123.9, 122.9, 120.7, 118.3, 110.1, 85.8, 31.7; IR (neat): ν_{max} 3021, 2919,

1605, 1507, 1460, 1334, 1237, 1185, 1115, 1071, 1019, 911, 817, 740, 722, 696 cm^{-1}; HRMS (ESI): Calcd. for $C_{37}H_{28}NO_2$ (M^++H): *m/z* 518.2120. Found: 518.2120.



3-(4-Chlorophenyl)-10-methyl-3,5-diphenyl-3,10-dihydro-1*H*-oxepino[3,4-*b*]indol-1-one (6af)

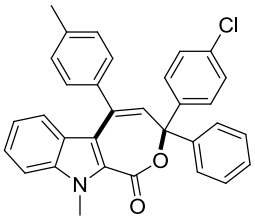
White solid, yield 0.235 g (87%), mp. 155-157 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.39 (m, 9H), 7.26-7.12 (m, 7H), 6.91-6.87 (m, 1H), 6.63 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.39 (s, 1H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.2, 142.4, 139.8, 138.7, 133.4, 131.0, 130.9, 128.8, 128.6, 128.5, 128.4, 128.3, 127.7, 127.5, 126.0, 125.4, 123.9, 122.9, 120.8, 118.3, 110.1, 85.3, 31.7; IR (neat): ν_{max} 3053, 1695, 1518, 1445, 1402, 1273, 1229, 1086, 1034, 982, 896, 765, 742, 718, 696 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{23}ClNO_2$ (M^++H), (M^++H+2): *m/z* 476.1417, 478.1387. Found: 476.1419, 478.1393.



5-(4-(*tert*-Butyl)phenyl)-3-(3,4-dichlorophenyl)-10-methyl-3-phenyl-3,10-dihydro-1*H*-oxepino[3,4-*b*]indol-1-one (6ag)

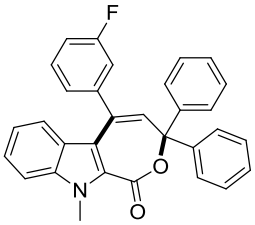
White solid, yield 0.253 g (78%), mp. 171-173 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.43-7.40 (m, 6H), 7.29- 7.13 (m, 7H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 8.4 Hz, 1H), 6.34 (d, *J* = 0.8 Hz, 1H), 3.79 (s, 3H), 1.39 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.0, 152.2, 142.5, 138.7, 136.6, 132.6, 131.6, 130.7, 130.2, 129.8, 128.4, 128.2, 127.9,

126.0, 125.5, 123.9, 123.0, 120.8, 118.5, 110.1, 84.9, 34.8, 31.7, 31.4; IR (neat): ν_{max} 2966, 1705, 1599, 1561, 1525, 1468, 1449, 1273, 1224, 1123, 1084, 1026, 997, 849, 783, 768, 744, 671 cm^{-1}; HRMS (ESI): Calcd. for $C_{35}H_{30}Cl_2NO_2$ (M^++H), (M^++H+2), (M^++H+2): *m/z* 566.1654, 568.1624, 570.1594. Found: 566.1654, 568.1610, 570.1594.



3-(4-Chlorophenyl)-10-methyl-3-phenyl-5-(p-tolyl)-3,10-dihydro-1*H*-oxepino[3,4-*b*]indol-1-one (6ah)

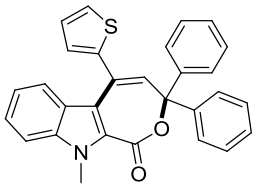
White solid, yield 0.236 g (84%), mp. 164-166 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.39 (m, 6H), 7.26-7.13 (m, 9H), 6.92-6.89 (m, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.37 (s, 1H), 3.78 (s, 3H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.3, 142.3, 138.8, 138.7, 136.9, 133.3, 130.9, 130.4, 129.3, 128.4, 128.3, 127.7, 127.6, 126.0, 125.4, 123.9, 123.1, 120.7, 118.5, 110.1, 85.4, 31.8, 21.4; IR (neat): ν_{max} 3024, 1704, 1688, 1488, 1446, 1401, 1275, 1228, 1086, 807, 781, 743, 710, 698 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{25}ClNO_2$ (M^++H), (M^++H+2): *m/z* 490.1574, 492.1544. Found: 490.1572, 492.1540.



5-(3-Fluorophenyl)-10-methyl-3,3-diphenyl-3,10-dihydro-1*H*-oxepino[3,4-*b*]indol-1-one (6ai)

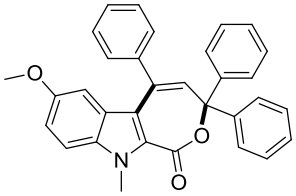
White solid, yield 0.203 g (77%), mp. 162-164 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.36 (m, 5H), 7.30-7.13 (m, 11H), 6.92-6.89 (m, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.47 (s, 1H), 3.76 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 163.8 (d, *J* = 245.1 Hz), 162.3, 142.2 (d, *J* = 7.5

Hz), 141.0, 138.6, 132.5, 131.2, 130.1 (d, *J* = 8.1 Hz), 128.3, 127.6, 126.0, 125.3, 124.4 (d, *J* = 2.4 Hz), 123.7, 122.6, 120.9, 117.6, 115.7 (d, *J* = 20.9 Hz), 115.5 (d, *J* = 21.8 Hz), 110.1, 85.8, 31.7; IR (neat): ν_{max} 3059, 1692, 1608, 1470, 1448, 1266, 1238, 1094, 1033, 976, 886, 781, 737, 698 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{23}FNO_2$ (M^++H): *m/z* 460.1713. Found: 460.1714.



10-Methyl-3,3-diphenyl-5-(thiophen-2-yl)-3,10-dihydro-1*H*-oxepino[3,4-*b*]indol-1-one (6aj)

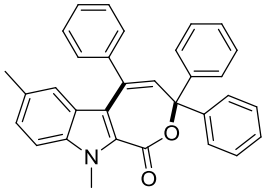
White solid, yield 0.193 g (75%), mp. 185-187 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.5 Hz, 4H), 7.38 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.29-7.07 (m, 10H), 7.02-6.96 (m, 2H), 6.59 (s, 1H), 3.74 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.4, 141.9, 138.4, 135.0, 131.2, 131.0, 128.2, 127.9, 127.5_2, 127.4_6, 126.0, 125.3, 123.8, 122.8, 120.7, 117.7, 110.0, 86.0, 31.6; IR (neat): ν_{max} 3052, 1690, 1600, 1528, 1487, 1468, 1342, 1227, 1081, 955, 697, 660, 632 cm^{-1}; HRMS (ESI): Calcd. for $C_{29}H_{22}NO_2S$ (M^++H): *m/z* 448.1371. Found: 448.1370.



7-Methoxy-10-methyl-3,3,5-triphenyl-3,10-dihydro-1*H*-oxepino[3,4-*b*]indol-1-one (6ba)

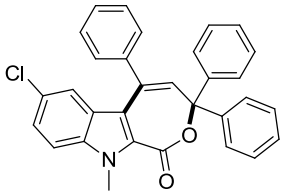
White solid, yield 0.206 g (90%), mp. 158-160 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.52 (m, 2H), 7.47-7.42 (m, 7H), 7.22-7.12 (m, 6H), 7.09 (d, *J* = 9.0 Hz, 1H), 6.89 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.42 (s, 1H), 5.94 (d, *J* = 2.5 Hz, 1H), 3.74 (s, 3H), 3.43 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.4, 154.2, 142.1, 140.0, 134.2, 131.1, 131.0,128.7, 128.5, 128.5, 128.2,

127.4, 126.1, 124.2, 117.8, 116.6, 110.9, 103.2, 85.8, 55.1, 31.8; IR (neat): ν_{max} 3032, 2940, 1699, 1515, 1485, 1290, 1201, 1121, 1094, 1069, 967, 794, 782, 697 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{26}NO_3$ (M^++H): *m/z* 472.1912. Found: 472.1914.



7,10-Dimethyl-3,3,5-triphenyl-3,10-dihydro-1*H*-oxepino[3,4-*b*]indol-1-one (6ca)

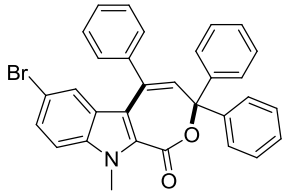
White solid, yield 0.213 g (88%), mp. 169-171 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.50 (m, 2H), 7.47-7.40 (m, 7H), 7.23-7.04 (m, 8H), 6.43 (s, 1H), 6.36 (d, *J* = 0.4 Hz, 1H), 3.73 (s, 3H), 2.18 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.6, 142.2, 140.0, 137.3, 131.4, 131.1, 129.9, 128.6_4, 128.5_7, 128.5, 128.2, 127.4, 127.2, 126.1, 124.1, 122.3, 117.8, 109.7, 85.8, 31.7, 21.5; IR (neat): ν_{max} 3029, 2934, 1703, 1485, 1446, 1424, 1293, 1228, 1072, 981, 874, 744, 696 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{26}NO_2$ (M^++H): *m/z* 456.1963. Found: 456.1964.



7-Chloro-10-methyl-3,3,5-triphenyl-3,10-dihydro-1*H*-oxepino[3,4-*b*]indol-1-one (6da)

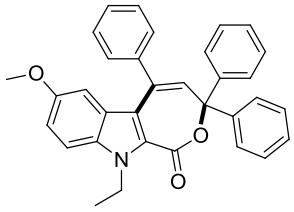
White solid, yield 0.189 g (86%), mp. 166-168 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.41 (m, 9H), 7.23-7.11 (m, 8H), 6.57 (d, *J* = 1.6 Hz, 1H), 6.47 (s, 1H), 3.73 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.2, 141.6, 139.3, 136.9, 132.2_0, 132.1_6, 129.1, 128.7, 128.4, 128.3, 127.6, 126.3, 126.1, 125.8, 124.7, 122.1, 117.6, 111.3, 86.0, 31.9; IR (neat): ν_{max} 3030, 1703, 1601, 1523, 1470, 1545, 1470, 1233, 1096, 1063, 977, 959, 791, 770, 694 cm^{-1}; LC-

MS: m/z 476 $[M+1]^+$; Anal. Calcd. for $C_{31}H_{22}ClNO_2$: C, 78.23; H, 4.66; N, 2.94. Found: C, 78.15; H, 4.62; N, 2.98.



7-Bromo-10-methyl-3,3,5-triphenyl-3,10-dihydro-1*H*-oxepino[3,4-*b*]indol-1-one (6ea)

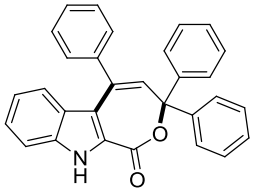
White solid, yield 0.170 g (84%), mp. 169-171 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.42 (m, 9H), 7.31 (dd, *J* = 8.8 Hz, 1.6 Hz, 1H), 7.23-7.12 (m, 6H), 6.08 (d, *J* = 8.8 Hz, 1H), 6.72 (d, *J* = 2.0 Hz, 1H), 6.48 (s, 1H), 3.73 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.2, 141.5, 139.3, 137.1, 132.2, 132.0, 129.0, 128.7, 128.4, 128.3, 127.6, 126.1, 125.3, 125.2, 117.5, 113.9, 111.6, 86.0, 31.8; IR (neat): ν_{max} 3030, 1701, 1601, 1523, 1468, 1444, 1407, 1233, 1095, 1052, 975, 958, 896, 789, 757, 744, 694 cm^{-1}; LC-MS: m/z 519 $[M-1]^+$; Anal. Calcd. for $C_{31}H_{22}BrNO_2$: C, 71.55; H, 4.26; N, 2.69. Found: C, 71.45; H, 4.29; N, 2.63.



10-Ethyl-7-methoxy-3,3,5-triphenyl-3,10-dihydro-1*H*-oxepino[3,4-*b*]indol-1-one (6fa)

White solid, yield 0.199 g (76%), mp. 159-161 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53-7.51 (m, 2H), 7.47-7.42 (m, 7H), 7.22-7.19 (m, 4H), 7.15-7.11 (m, 3H), 6.89 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.37 (s, 1H), 5.93 (d, *J* = 2.0 Hz, 1H), 4.37 (d, *J* = 6.0 Hz, 2H), 3.42 (s, 3H), 1.04 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.1, 154.1, 142.0, 140.2, 133.2, 130.9, 129.8, 128.7, 128.4, 128.2, 127.4, 126.2, 124.5, 118.3, 116.7, 111.0, 103.4, 85.6, 55.0, 39.7, 15.0; IR (neat): ν_{max} 2929, 1701, 1513, 1483, 1446, 1290, 1200, 1167, 1097, 1074, 795, 747,

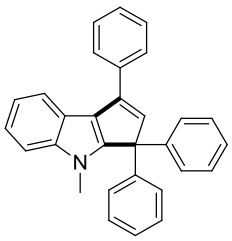
695 cm^{-1}; LC-MS: m/z 486 $[M+1]^+$; Anal. Calcd. for $C_{33}H_{27}NO_3$: C, 81.63; H, 5.60; N, 2.88. Found: C, 81.52; H, 5.65; N, 2.84.



3,3,5-Triphenyl-3,10-dihydro-1*H*-oxepino[3,4-*b*]indol-1-one (6ga)

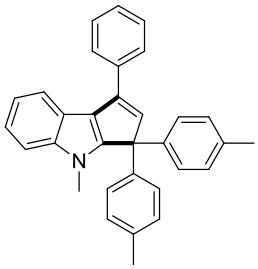
White solid, yield 0.260 g (71%), mp. 179-181 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.52-7.41 (m, 9H), 7.29-7.28 (m, 1H), 7.25-7.22 (m, 5H), 7.19-7.16 (m, 2H), 6.89-6.86 (m, 1H), 6.62 (dd, *J* = 8.0, 0.5 Hz, 1H), 6.36 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 163.4, 143.9, 141.7, 140.1, 136.3, 131.3, 128.8, 128.7_2, 128.6_7, 128.5, 128.4, 127.7, 126.3, 125.8, 124.9, 123.2, 120.8, 118.8, 112.1, 86.6; IR (neat): ν_{max} 3308, 3053, 1660, 1613, 1528, 1457, 1381, 1331, 1243, 1180, 1099, 958, 745, 696 cm^{-1}; LC-MS: m/z 428 $[M+1]^+$; Anal. Calcd. for $C_{30}H_{21}NO_2$: C, 84.29; H, 4.95; N, 3.28. Found: C, 84.19; H, 4.91; N, 3.25.

(5). General procedure (GP-II) for the synthesis of 3,4-dihydrocyclopenta[*b*]indoles 7aa-7al, 7as and 7ax by using 1-methylindole-2-carboxylic acid. An oven dried 25 mL round-bottomed flask was charged with 1-methylindole-2-carboxylic acid **1a** (0.100 g, 0.57 mmol), propargyl alcohol **5a** (0.178 g, 0.62 mmol) and $BF_3.OEt_2$ [0.008 g (0.1 mL), 0.057 mmol] (10 mol %) in dichloromethane (10 mL). The mixture was stirred at rt (25 ^{o}C) in open air for 12 h and monitored by TLC. Work up was similar to that given above in GP-I. Purification by column chromatography (ethyl acetate: hexane 1:9) afforded the desired product **7aa** as a white solid. Compounds **7ac-7al, 7as** and **7ax** were prepared from appropriate 1-methylindole-2-carboxylic acid and propargyl alcohols by using the same procedure and same molar quantities.



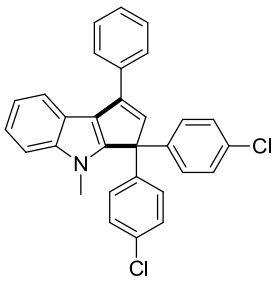
4-Methyl-1,3,3-triphenyl-3,4-dihydrocyclopenta[*b*]indole (7aa)

White solid, yield 0.184 g (81%), mp. 180-182 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.89 (m, 2H), 7.87-7.85 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.43-7.40 (m, 1H), 7.39-7.36 (m, 5H), 7.36-7.29 (m, 6H), 7.28-7.19 (m, 2H), 6.50 (s, 1H), 3.61 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 154.9, 141.3, 141.0, 139.9, 136.3, 136.0, 128.6$_4$, 128.6$_0$, 128.4, 127.9, 127.5, 127.2, 121.8, 120.7, 120.2, 120.1, 118.9, 110.1, 62.1, 31.4; IR (neat): ν_{max} 3019, 2922, 2851, 1747, 1596, 1511, 1490, 1475, 1459, 1441, 753, 739, 694 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{24}N$ (M^++H): *m/z* 398.1909. Found: 398.1906.



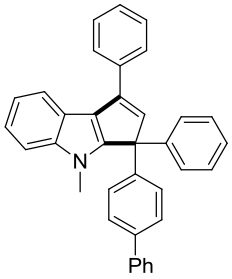
4-Methyl-1-phenyl-3,3-di-*p*-tolyl-3,4-dihydrocyclopenta[*b*]indole (7ac)

White solid, yield 0.196 g (81%), mp. 170-172 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90-7.88 (m, 2H), 7.87-7.85 (m, 1H), 7.52-7.49 (m, 2H), 7.42-7.37 (m, 2H), 7.28-7.25 (m, 5H), 7.23-7.19 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 4H), 6.46 (s, 1H), 3.62 (s, 3H), 2.38 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.2, 141.3, 140.7, 136.9, 136.7, 136.5, 136.2, 129.2, 128.6, 128.3, 127.8, 127.5, 121.8, 120.6, 120.1, 120.0, 118.7, 110.0, 61.4, 31.4, 21.2; IR (neat): ν_{max} 3022, 2920, 1905, 1737, 1604, 1507, 1460, 1020, 816, 782, 722 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{28}N$ (M^++H): *m/z* 426.2222. Found: 426.2222.



3,3-Bis(4-chlorophenyl)-4-methyl-1-phenyl-3,4-dihydrocyclopenta[*b*]indole (7ad)

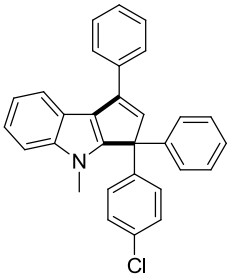
White solid, yield 0.228 g (86%), mp. 185-187 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85-7.82 (m, 3H), 7.51-7.48 (m, 2H), 7.42-7.39 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.29-7.24 (m, 9H), 7.20 (td, *J* = 8.0, 1.0 Hz, 1H), 6.36 (s, 1H), 3.57 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 153.8, 141.6, 141.3, 138.0, 135.8, 135.0, 133.1, 129.5, 128.8, 128.6, 128.1, 127.4, 121.5, 121.1, 120.3, 120.2, 119.0, 110.1, 60.8, 31.4; IR (neat): ν_{max} 3058, 2947, 1507, 1478, 1396, 1335, 1234, 1089, 1012, 909, 828, 809, 738, 707, 692 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{22}Cl_2N$ (M^++H), (M^++H+2), (M^++H+4): *m/z* 466.1129, 468.1099, 470.1069. Found: 466.1126, 468.1100, 470.1089.



3-([1,1'-Biphenyl]-4-yl)-4-methyl-1,3-diphenyl-3,4-dihydrocyclopenta[*b*]indole (7ae)

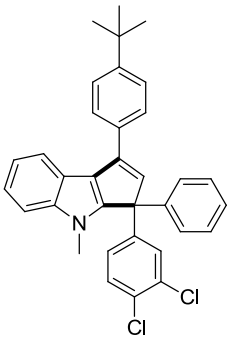
White solid, yield 0.216 g (80%), mp. 117-119 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90-7.88 (m, 2H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.61-7.59 (m, 2H), 7.54-7.30 (m, 16H), 7.26-7.23 (m, 1H), 7.21-7.18 (m, 1H), 6.50 (s, 1H), 3.62 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 154.8, 141.2, 141.0, 140.7, 139.9, 139.7, 138.9, 136.2, 135.7, 128.8, 128.7, 128.5, 128.3, 127.8, 127.4, 127.3, 127.2, 127.1, 127.0, 121.6, 120.6, 120.1, 120.0, 118.8, 110.0, 61.7, 31.4; IR

(neat): ν_{max} 3026, 1598, 1508, 1483, 1461, 1333, 1235, 1157, 1115, 1006, 914, 839, 739, 694 cm^{-1}; HRMS (ESI): Calcd. for $C_{36}H_{28}N$ (M^++H): *m/z* 474.2222. Found: 474.2222.



3-(4-Chlorophenyl)-4-methyl-1,3-diphenyl-3,4-dihydrocyclopenta[*b*]indole (7af)

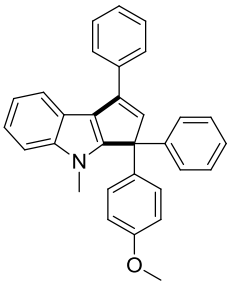
White solid, yield 0.207 g (84%), mp. 145-147 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.86 (m, 3H), 7.54-7.51 (m, 2H), 7.45-7.21 (m, 13H), 6.46 (s, 1H), 3.61 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 154.3, 141.3$_1$, 141.2$_8$, 139.3, 138.6, 136.0, 135.5, 132.9, 129.7, 128.6$_5$, 128.6$_0$, 128.2, 127.9, 127.4, 127.3, 121.6, 120.9, 120.2, 120.1, 119.0, 110.0, 61.4, 31.3; IR (neat): ν_{max} 3051, 2924, 1596, 1506, 1477, 1455, 1335, 1089, 1013, 972, 829, 796, 739 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{23}ClN$ (M^++H), (M^++H+2): *m/z* 432.1519, 434.1489. Found: 432.1518, 434.1497.



1-(4-(*tert*-Butyl)phenyl)-3-(3,4-dichlorophenyl)-4-methyl-3-phenyl-3,4-dihydrocyclopenta[*b*]indole (7ag)

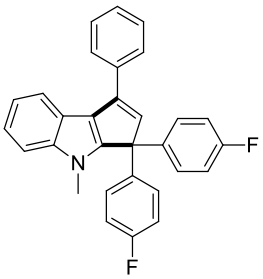
White solid, yield 0.246 g (83%), mp. 182-184 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.89 (m, 1H), 7.84-7.82 (m, 2H), 7.56-7.54 (m, 2H), 7.46-7.45 (m, 1H), 7.40-7.17 (m, 10H), 6.38 (s, 1H), 3.61 (s, 3H), 1.42 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 153.8, 151.3, 141.5,

141.4, 140.9, 138.9, 134.5, 132.9, 132.7, 131.2, 130.4, 130.1, 128.8, 128.2, 127.9, 127.5, 127.2, 125.6, 121.7, 121.1, 120.4, 120.3, 119.3, 110.1, 61.1, 34.8, 31.5_0, 31.4_7; IR (neat): ν_{max} 2964, 1737, 1592, 1512, 1463, 1375, 1268, 1204, 1115, 1026, 925, 882, 831, 792, 764, 742, 699 cm^{-1}; HRMS (ESI): Calcd. for $C_{34}H_{30}Cl_2N$ (M^++H), (M^++H+2), (M^++H+4): *m/z* 522.1755, 524.1725, 526.1695. Found: 522.1754, 524.1726, 526.1694.



3-(4-Methoxyphenyl)-4-methyl-1,3-diphenyl-3,4-dihydrocyclopenta[*b*]indole (7ak)

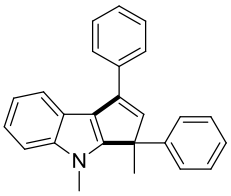
White solid, yield 0.195 g (80%), mp. 184-186 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.87 (m, 2H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.51-7.47 (m, 2H), 7.41-7.17 (m, 11H), 6.87-6.83 (m, 2H), 6.46 (s, 1H), 3.82 (s, 3H), 3.60 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 158.6, 155.0, 141.2, 140.6, 140.1, 136.3, 136.1, 131.6, 129.4, 128.5_0, 128.4_6, 128.2, 127.7, 127.4, 127.0, 121.7, 120.5, 120.0, 119.9, 118.6, 113.8, 109.9, 61.3, 55.3, 31.3; IR (neat): ν_{max} 3058, 2837, 1743, 1606, 1505, 1458, 1246, 1176, 1025, 830, 742, 698 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{26}NO$ (M^++H): *m/z* 428.2014. Found: 428.2016.



3,3-Bis(4-fluorophenyl)-4-methyl-1-phenyl-3,4-dihydrocyclopenta[*b*]indole (7al)

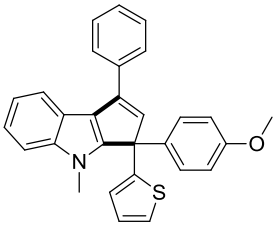
White solid, yield 0.213 g (86%), mp. 162-164 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.83 (m, 3H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.43-7.37 (m, 2H), 7.33-7.19 (m, 6H), 7.04-6.99 (m, 4H),

6.41 (s, 1H), 3.59 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 162.0 (d, *J* = 244.8 Hz), 154.4, 141.3, 141.1, 136.0, 135.6, 135.4 (d, *J* = 3.3 Hz), 129.8 (d, *J* = 7.9 Hz), 128.6, 128.0, 127.4, 121.6, 121.0, 120.2 (d, *J* = 11.6 Hz), 118.9, 115.4 (d, *J* = 21.1 Hz), 110.0, 60.7, 31.3; IR (neat): ν_{max} 3069, 2924, 1898, 1598, 1500, 1475, 1459, 1411, 1338, 1219, 1155, 1014, 911, 835, 739, 722, 692, 591 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{22}F_2N$ (M^++H): *m/z* 434.1720. Found: 434.1723.



3,4-Dimethyl-1,3-diphenyl-3,4-dihydrocyclopenta[*b*]indole (7as)

White solid, yield 0.143 g (75%), mp. 155-157 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86-7.82 (m, 3H), 7.51-7.48 (m, 2H), 7.41-7.35 (m, 2H), 7.32-7.27 (m, 4H), 7.26-7.17 (m, 3H), 6.16 (s, 1H), 3.63 (s, 3H), 1.98 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 156.4, 141.1, 140.5, 140.1, 136.6, 128.7, 128.5, 127.6, 127.3, 126.8, 126.2, 121.7, 120.4, 119.9, 118.7, 109.8, 51.7, 30.8, 19.8; IR (neat): ν_{max} 3049, 2931, 1598, 1509, 1489, 1476, 1460, 1335, 1236, 1176, 1016, 918, 737, 717, 696 cm^{-1}; LC-MS: m/z 336 $[M+1]^+$; Anal. Calcd. for $C_{25}H_{21}N$: C, 89.51; H, 6.31; N, 4.18. Found: C, 89.42; H, 6.34; N, 4.21.

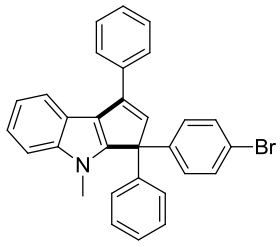


3-(4-Methoxyphenyl)-4-methyl-1-phenyl-3-(thiophen-2-yl)-3,4-dihydrocyclopenta[*b*]indole (7ax)

White solid, yield 0.196 g (79%), mp. 170-172 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.51-7.48 (m, 2H), 7.42-7.40 (m, 1H), 7.38 (d, *J*

= 8.0 Hz, 1H), 7.32-7.29 (m, 2H), 7.24 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.21-7.17 (m, 2H), 7.04 (dd, *J* = 3.5, 1.0 Hz, 1H), 6.99 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.85-6.82 (m, 2H), 6.42 (s, 1H), 3.81 (s, 3H), 3.70 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 158.9, 154.2, 144.2, 141.3, 140.4, 136.1, 135.8, 131.7, 128.6, 128.5, 127.8, 127.4, 126.5_4, 126.4_7, 124.2, 121.6, 120.6, 120.1, 120.0, 118.6, 113.9, 110.0, 57.7, 55.3, 31.4; IR (neat): ν_{max} 3064, 3000, 2929, 1606, 1506, 1458, 1299, 1247, 1176, 1114, 1025, 919, 838, 826, 742, 695 cm^{-1}; LC-MS: m/z 434 $[M+1]^+$; Anal. Calcd. for $C_{29}H_{23}NOS$: C, 80.34; H, 5.35; N, 3.23. Found: C, 80.41; H, 5.31; N, 3.26.

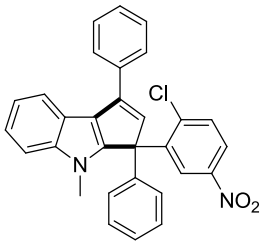
(6). General procedure (GP-III) for the synthesis of 3,4-dihydrocyclopenta[*b*]indoles 7aa, 7ac-7ad, and 7ak-7ap by using 1-methylindole-3-carbxylic acid. An oven dried 25 mL round-bottomed flask was charged with 1-methylindole-3-carboxylic acid **3a** (0.100 g, 0.57 mmol), propargyl alcohol **5a** (0.178 g, 0.62 mmol) and *p*-TSA (0.010 g, 0.057 mmol (10 mol %)) in dichloromethane (10 mL). The mixture was stirred at rt (25 ^{o}C) in open air for 12 h and monitored by TLC. Work up was similar to that given above in GP-I. Purification by column chromatography (ethyl acetate: hexane 1:9) afforded the desired product **7aa** as a white solid. Compounds **7ac-7ad** and **7ak-7ap** were prepared from appropriate 1-methylindole-3-carboxylic acid and propargyl alcohols by using the same procedure and same molar quantities.



3-(4-Bromophenyl)-4-methyl-1,3-diphenyl-3,4-dihydrocyclopenta[*b*]indole (7am)

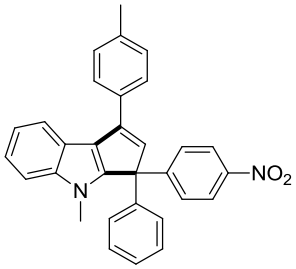
White solid, yield 0.224 g (83%), mp. 173-175 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.82 (m, 3H), 7.51-7.47 (m, 2H), 7.43-7.40 (m, 3H), 7.38-7.29 (m, 6H), 7.27-7.18 (m, 4H), 6.41

(s, 1H), 3.58 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 154.3, 141.3, 141.2_6, 139.2_0, 139.1_6, 136.0, 135.4, 131.6, 130.0, 128.6_3, 128.6_0, 128.2, 127.9, 127.4, 127.3, 121.6, 121.0, 120.8, 120.1, 118.9, 110.0, 61.5, 31.4; IR (neat): ν_{max} 3055, 1883, 1737, 1594, 1508, 1482, 1465, 1444, 1048, 1007, 910, 827, 743, 696 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{23}BrN$ (M^++H), (M^++H+2): *m/z* 476.1014, 478.0994. Found: 476.1015, 478.1004.



3-(2-Chloro-5-nitrophenyl)-4-methyl-1,3-diphenyl-3,4-dihydrocyclopenta[*b*]indole (7an)

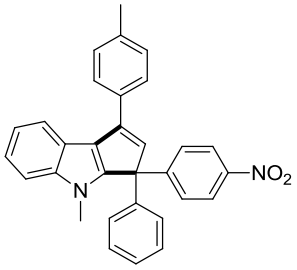
Red solid, yield 0.239 g (88%), mp. 220-222 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 2.8 Hz, 1H), 8.19 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.92-7.90 (m, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.55-7.51 (m, 2H), 7.46-7.39 (m, 2H), 7.31-7.19 (m, 7H), 6.98 (s, 1H), 3.61 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 152.6, 146.8, 144.3, 134.0, 141.7, 139.2, 137.0, 135.7, 132.4, 129.5, 128.8, 128.7, 128.3, 127.4, 127.3, 136.7, 123.6, 123.5, 121.5, 121.4, 120.5, 120.3, 119.1, 110.3, 62.2, 31.4; IR (neat): ν_{max} 3060, 1570, 1517, 1462, 1344, 1289, 1259, 1156, 1112, 1049, 924, 904, 856, 743, 699, 630 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{22}ClN_2O_2$ (M^++H), (M^++H+2): *m/z* 477.1370, 479.1340. Found: 477.1370, 479.1348.



4-Methyl-3-(4-nitrophenyl)-3-phenyl-1-(*p*-tolyl)-3,4-dihydrocyclopenta[*b*]indole (7ao)

Red solid, yield 0.224 g (86%), mp. 146-148 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.14 (m, 2H), 7.86-7.84 (m, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.52-7.48 (m, 2H), 7.38-7.20 (m, 10H),

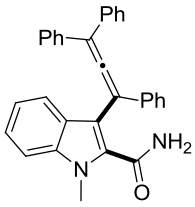
6.38 (s, 1H), 3.58 (s, 3H), 2.45 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 153.5, 148.5, 146.9, 142.0, 141.3, 138.4, 138.1, 134.0, 132.7, 129.3, 129.0, 128.8, 128.1, 127.6, 127.3, 123.7, 121.5, 121.2, 120.3_1, 120.2_5, 119.5, 110.1, 61.7, 31.4, 21.4; IR (neat): ν_{max} 2922, 1593, 1510, 1463, 1343, 1243, 1180, 1110, 1044, 911, 852, 825, 722, 700 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{25}N_2O_2$ (M^++H): *m/z* 457.1925. Found: 457.1917.



4-Methyl-3-phenyl-1,3-di-*p*-tolyl-3,4-dihydrocyclopenta[*b*]indole (7ap)

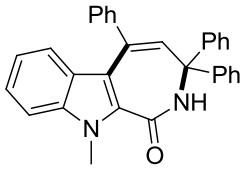
White solid, yield 0.193 g (79%), mp. 182-184 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.84 (m, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.37-7.17 (m, 12H), 7.13-7.11 (m, 2H), 6.42 (s, 1H), 3.60 (s, 3H), 2.45 (s, 3H), 2.36 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 155.0, 141.2, 140.6, 140.2, 137.5, 136.8, 136.7, 135.4, 133.5, 129.2, 128.5, 128.3_2, 128.2_6, 127.3, 127.0, 121.7, 120.5, 120.1, 119.9, 118.9, 109.9, 61.6, 31.4, 21.4, 21.1; IR (neat): ν_{max} 2939, 1738, 1594, 1509, 1463, 1335, 1234, 1179, 1158, 1112, 1034, 1017, 817, 765, 724 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{28}N$ (M^++H): *m/z* 426.2222 Found: 426.2219.

(7). Synthesis of 1-methyl-3-(1,3,3-triphenylpropa-1,2-dien-1-yl)-*1H*-indole-2-carboxamide (8aa). An oven dried 25 mL round-bottomed flask was charged with 1-methylindole-2-carboxamide **2a** (0.100 g, 0.57 mmol), propargyl alcohol **5a** (0.178 g, 0.62 mmol) and $Cu(OTf)_2$ (0.020 g, 0.057 mmol (10 mol %)) in dichloromethane (10 mL). The mixture was stirred at rt (25 ^{o}C) in open air for 6 h and monitored by TLC. Work up was similar to that given above in GP-I. Purification by column chromatography (ethyl acetate: hexane 1:4) afforded the desired product **8aa**.



White solid, yield 0.224 g (89%), mp. 192-194 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.46 (m, 2H), 7.45-7.25 (m, 17H), 7.11 (td, *J* = 7.6, 0.8 Hz, 1H), 6.27 (s, 1H), 5.10 (s, 1H), 4.14 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 208.3, 163.8, 138.4, 135.9, 135.3, 129.0, 128.8, 128.7, 128.6, 128.1, 128.0, 126.8, 126.7, 124.9, 121.4, 120.8, 113.1, 112.7, 110.3, 104.1, 32.3; IR (neat): ν_{max} 3446, 3027, 1883, 1665, 1611, 1520, 1487, 1468, 1440, 1321, 1072, 1026, 758, 738, 693 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{24}N_2NaO$ (M^++Na): *m/z* 463.1786. Found: 463.1787.

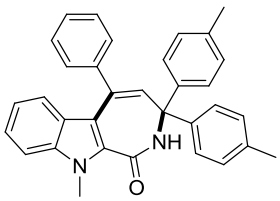
(8). Synthesis of 10-methyl-3,3,5-triphenyl-2,3-dihydroazepino[3,4-*b*]indol-1(10*H*)-one (9aa). An oven dried 25 mL round-bottomed flask was charged with compound **8aa** (0.100 g, 0.16 mmol) in DCM (10 mL). The mixture was stirred at reflux temperature with ice-cold water circulation using a condenser for 6 h and monitored by TLC. Work up was similar to that given in GP-I above. Purification by column chromatography (ethyl acetate: hexane 1:4) afforded the desired product **9aa**.



White solid, yield 0.085 g (85%), mp. > 220 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.44 (m, 2H), 7.42-7.39 (m, 3H), 7.37-7.34 (m, 4H), 7.24-7.16 (m, 8H), 6.88 (s, 1H), 6.81-6.77 (m, 1H), 6.60 (s, 1H), 6.49 (d, *J* = 8.4 Hz, 1H), 3.93 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.4, 145.3, 141.2, 139.5, 138.3, 135.3, 132.3, 128.7, 128.4, 128.2, 127.7, 127.1, 124.4, 124.2, 122.7, 119.9, 117.2, 109.7, 64.5, 31.7; IR (neat): ν_{max} 3166, 3029, 1629, 1521, 1473,

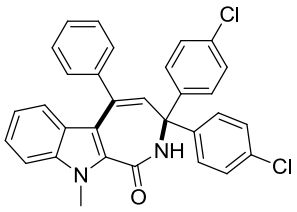
1444, 1315, 1236, 1137, 894, 790, 741, 697, 663 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{25}N_2O$ (M^++H): *m/z* 441.1967. Found: 441.1966.

(9). General procedure (GP-IV) for the synthesis of ε-lactams 9aa, 9ac-9ai, and 9ba-9ca by using indole-2-carboxamides. An oven dried 25 mL round-bottomed flask was charged with indole-2-carboxamides **3** (0.100 g, 0.57 mmol), one of the propargyl alcohols **5** (0.62 mmol) and $Cu(OTf)_2$ (0.020 g, 0.057 mmol (10 mol %)) in dichloromethane (10 mL). The mixture was stirred at reflux temperature with ice-cold water circulation using a condenser for 6 h and monitored by TLC. Work-up was similar to that given in GP-I above. Purification by column chromatography (ethyl acetate: hexane 1:4) afforded the desired products **9aa, 9ac-9ai, 9ba-9ca**.



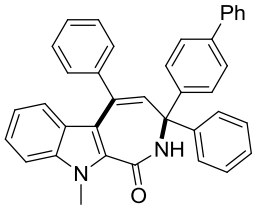
10-Methyl-5-phenyl-3,3-di-p-tolyl-2,3-dihydroazepino[3,4-*b*]indol-1(10*H*)-one (9ac)

White solid, yield 0.226 g (85%), mp. > 220 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.36 (m, 5H), 7.25-7.16 (m, 6H), 7.00 (d, *J* = 8.0 Hz, 4H), 6.81-6.77 (m, 2H), 6.57 (s, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 3.95 (s, 3H), 2.26 (s, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 163.3, 142.5, 141.4, 139.2, 138.3, 137.3, 135.6, 132.2, 128.8, 128.7, 128.3, 128.0, 127.0, 124.5, 124.1, 122.9, 119.8, 117.2, 109.8, 64.0, 31.8, 21.0; IR (neat): ν_{max} 3376, 3025, 2916, 1915, 1640, 1509, 1468, 1438, 1311, 1187, 1019, 819, 736, 702 cm^{-1}; HRMS (ESI): Calcd. for $C_{33}H_{29}N_2O$ (M^++H): *m/z* 469.2280. Found: 469.2281.



3,3-bis(4-Chlorophenyl)-10-methyl-5-phenyl-2,3-dihydroazepino[3,4-*b*]indol-1(10*H*)-one (9ad)

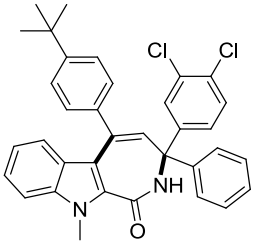
White solid, yield 0.238 g (82%), mp. 170-172 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.38 (m, 5H), 7.28-7.26 (m, 5H), 7.23-7.20 (m, 5H), 7.03 (s, 1H), 6.83-6.80 (m, 1H), 6.48 (d, *J* = 8.0 Hz, 1H), 6.47 (s, 1H), 3.94 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 163.1, 143.5, 140.9, 140.2, 138.4, 133.8_3, 133.8_0, 131.8, 128.6, 128.5, 128.4_6, 128.4_0, 128.3_7, 124.6, 124.3, 122.7, 120.2, 117.2, 110.0, 63.7, 31.8; IR (neat): ν_{max} 3374, 3050, 1644, 1513, 1486, 1469, 1314, 1093, 1012, 819, 737, 695 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{23}Cl_2N_2O$ (M^++ H), (M^++H+2), (M^++H+4): *m/z* 509.1187, 511.1157, 513.1127. Found: 509.1187, 511.1162, 513.1146.



3-([1,1'-Biphenyl]-4-yl)-10-methyl-3,5-diphenyl-3,10-dihydroazepino[3,4-*b*]indol-1(2*H*)one (9ae)

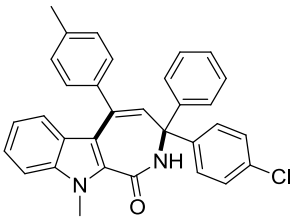
White solid, yield 0.259 g (88%), mp. > 220 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.43 (m, 6H), 7.41-7.35 (m, 9H), 7.36-7.28 (m, 1H), 7.26-7.15 (m, 5H), 6.93 (s, 1H), 6.81-6.77 (m, 1H), 6.63 (s, 1H), 6.51 (d, *J* = 8.4 Hz, 1H), 3.94 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.5, 145.3, 144.5, 141.3, 140.4, 140.2, 139.6, 138.3, 135.2, 132.3, 128.8_4, 128.7_5, 128.5, 128.2_3, 128.2_0, 127.7_3, 127.6_9, 127.5, 127.2, 127.0, 126.8, 124.4, 124.3, 122.8, 120.0, 117.3, 109.8, 64.4, 31.8; IR (neat): ν_{max} 3160, 3026, 2161, 2001, 1627, 1517, 1474, 1442, 1313, 832,

767, 695 cm^{-1}; HRMS (ESI): Calcd. for $C_{37}H_{29}N_2O$ (M^+ + H): *m/z* 517.2280. Found: 517.2283.



5-(4-(*tert*-Butyl)phenyl)-3-(3,4-dichlorophenyl)-10-methyl-3-phenyl-2,3-dihydroazepino[3,4-*b*]indol-1(10*H*)-one (9ag)

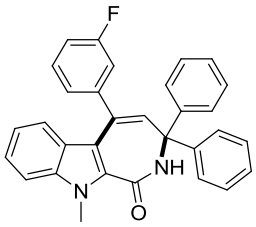
White solid, yield 0.253 g (79%), mp. 177-179 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.42-7.36 (m, 4H), 7.29-7.20 (m, 9H), 6.99 (s, 1H), 6.84-6.81 (m, 1H), 6.55-6.53 (m, 2H), 3.94 (s, 3H), 1.39 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 163.4, 151.6, 145.3, 139.9, 138.3, 137.8, 133.6, 132.3, 132.1, 131.6, 129.9, 129.3, 128.6, 128.3, 128.1, 127.1, 126.5, 125.3, 124.5, 124.4, 122.9, 120.1, 117.4, 109.9, 64.0, 34.7, 31.7, 31.4; IR (neat): ν_{max} 3179, 3031, 2958, 1636, 1519, 1469, 1444, 1378, 1316, 1028, 820, 737, 701 cm^{-1}; HRMS (ESI): Calcd. for $C_{35}H_{30}Cl_2N_2NaO$ (M^++Na), (M^++Na+2), (M^++Na+4): *m/z* 587.1633, 589.1603, 591.1573. Found: 587.1632, 589.1607, 591.1592.



3-(4-Chlorophenyl)-10-methyl-3-phenyl-5-(*p*-tolyl)-3,10-dihydroazepino[3,4-*b*]indol-1(2*H*)-one (9ah)

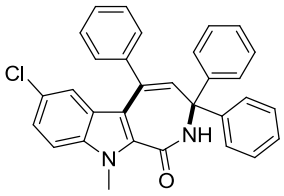
White solid, yield 0.231 g (83%), mp. 190-192 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.15 (m, 15H), 6.86-6.80 (m, 2H), 6.55 (d, *J* = 8.4 Hz, 1H), 6.51 (s, 1H), 3.93 (s, 3H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.3, 145.5, 143.5, 139.7, 138.3, 138.2, 138.1, 134.1,

133.4, 132.0, 129.1, 128.5, 128.4, 128.2, 127.9, 127.1, 124.4, 122.9, 120.0, 117.4, 109.9, 64.1, 31.7, 21.3; IR (neat): ν_{max} 3171, 3031, 2001, 1877, 1801, 1630, 1520, 1486, 1469, 1443, 1383, 1319, 1093, 1014, 739, 697 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{26}ClN_2O$ (M^++H), (M^++H+2) : *m/z* 489.1734, 491.1704. Found: 489.1734, 491.1698.



5-(3-Fluorophenyl)-10-methyl-3,3-diphenyl-2,3-dihydroazepino[3,4-*b*]indol-1(10*H*)-one (9ai)

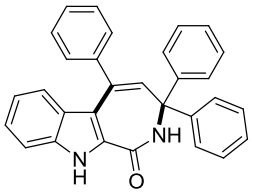
White solid, yield 0.216 g (83%), mp. above 220 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.33 (m, 5H), 7.24-7.17 (m, 10H), 7.14-7.09 (m, 1H), 7.06 (s, 1H), 6.85-6.81 (m, 1H), 6.63 (s, 1H), 6.54 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 163.8 (d, *J* = 244.6 Hz), 163.3, 145.1, 143.4 (d, *J* = 7.5 Hz), 138.5, 138.2, 136.0, 132.4, 129.9 (d, *J* = 8.3 Hz), 128.2, 127.8, 127.1, 124.5 (d, *J* = 2.4 Hz), 124.3, 124.2, 122.5, 120.1, 116.5, 115.5 (d, *J* = 21.6 Hz), 115.0 (d, *J* = 20.9 Hz), 109.9, 64.5, 31.7; IR (neat): ν_{max} 3163, 3027, 2886, 2236, 1629, 1612, 1579, 1523, 1470, 1444, 1325, 1182, 914, 878, 726, 700 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{24}FN_2O$ (M^++H): *m/z* 459.1873. Found: 459.1874.



7-Chloro-10-methyl-3,3,5-triphenyl-2,3-dihydroazepino[3,4-*b*]indol-1(10*H*)-one (9ba)

White solid, yield 0.178 g (80%), mp. > 220 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.39 (m, 5H), 7.34-7.32 (m, 4H), 7.24-7.17 (m, 6H), 7.14-7.10 (m, 2H), 6.94 (s, 1H), 6.63 (s, 1H), 6.43-6.42 (m, 1H), 3.89 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.0, 140.5, 139.1,

136.5, 135.7, 133.3, 128.5$_4$, 128.4$_5$, 128.2, 127.7, 127.0, 125.5, 125.2, 124.7, 121.9, 116.6, 110.9, 64.5, 31.8; IR (neat): ν_{max} 3182, 3025, 2986, 1737, 1625, 1523, 1470, 1443, 1323, 1235, 1069, 836, 743, 696 cm^{-1}; LC-MS: m/z 475 $[M+1]^+$; Anal. Calcd. for $C_{31}H_{23}ClN_2O$: C, 78.39; H, 4.88; N, 5.90. Found: C, 78.31; H, 4.92; N, 5.85.

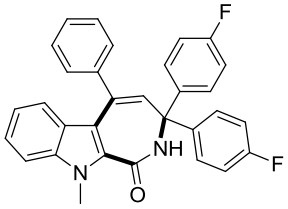


3,3,5-Triphenyl-2,3-dihydroazepino[3,4-*b*]indol-1(10*H*)-one (9ca)

White solid, yield 0.207 g (78%), mp. > 220 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.48 (s, 1H), 7.45-7.38 (m, 5H), 7.36-7.34 (m, 4H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.26-7.19 (m, 6H), 7.17-7.14 (m, 1H), 6.85 (s, 1H), 6.81-6.78 (m, 1H), 6.49 (d, *J* = 8.5 Hz, 1H), 6.44 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.8, 145.6, 141.3, 139.2, 135.8, 133.9, 130.4, 128.9, 128.3, 128.1, 127.8, 127.3, 125.6, 124.8, 123.1, 120.1, 117.1, 111.8, 64.8; IR (neat): ν_{max} 3382, 3254, 1623, 1524, 1490, 1467, 1445, 1400, 1334, 1286, 1013, 776, 744, 698 cm^{-1}; LC-MS: m/z 427 $[M+1]^+$; Anal. Calcd. for $C_{30}H_{22}N_2O$: C, 84.48; H, 5.20; N, 6.57. Found: C, 84.39; H, 5.16; N, 6.63.

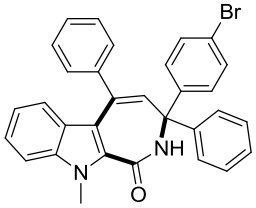
(10). General procedure (GP-V) for the synthesis of ε-lactam 9aa, 9al-9ar, and 9bs by using 1-methylindole-3-carbxamide. An oven dried 25 mL round-bottomed flask was charged with 1-methylindole-3-carboxamide **4a** (0.100 g, 0.57 mmol), propargyl alcohol **5a** (0.178 g, 0.62 mmol) and *p*-TSA (0.010 g, 0.057 mmol (10 mol %)) in dichloromethane (10 mL). The mixture was stirred at rt (25 ^{o}C) in open air for 12 h and monitored by TLC. Work-up was similar to that in GP-I given above. Purification by column chromatography (ethyl acetate: hexane 1:4) afforded the desired product **9aa** as a white solid. Compounds **9am-9aq**

and **9bs** were prepared from appropriate indole-3-carboxamide and propargyl alcohol by using the same procedure and same molar quantities.



3,3-Bis(4-fluorophenyl)-10-methyl-5-phenyl-2,3-dihydroazepino[3,4-*b*]indol-1(10*H*)-one (9al)

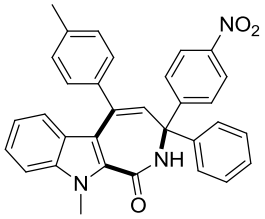
White solid, yield 0.105 g (38%), mp. > 220 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.37 (m, 5H), 7.34-7.30 (m, 4H), 7.27-7.19 (m, 2H), 7.05 (s, 1H), 6.94-6.91 (m, 4H), 6.83-6.79 (m, 1H), 6.52 (s, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 3.92 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 163.5, 162.0 (d, *J* = 245.8 Hz), 141.0, 139.9, 138.3, 134.7, 132.1, 128.9 (d, *J* = 8.0 Hz), 128.7, 128.5, 128.3, 124.5, 124.3, 122.7, 120.2, 117.2, 115.2 (d, *J* = 21.3 Hz), 109.9, 63.7, 31.7; IR (neat): ν_{max} 3161, 3033, 1632, 1600, 1503, 1470, 1443, 1323, 1220, 1163, 833, 739, 700 cm^{-1}; LC-MS: m/z 475 $[M-1]^{+}$; Anal. Calcd. for $C_{31}H_{22}F_2N_2O$: C, 78.14; H, 4.65; N, 5.88. Found: C, 78.07; H, 4.63; N, 5.82.



3-(4-Bromophenyl)-10-methyl-3,5-diphenyl-2,3-dihydroazepino[3,4-*b*]indol-1(10*H*)-one (9am)

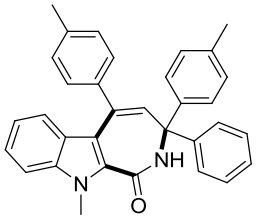
White solid, yield 0.116 g (39%), mp. > 220 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.37 (m, 5H), 7.34-7.18 (m, 11H), 6.95 (s, 1H), 6.50-6.48 (m, 1H), 6.54 (s, 1H), 6.50-6.48 (m, 1H), 3.93 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 163.5, 141.1, 139.8, 138.3, 134.6, 132.1, 131.2, 128.9, 128.7, 128.4_3, 128.3_9, 128.3, 127.9, 127.1, 124.4_3, 124.3_5, 122.8, 121.7, 120.1,

117.2, 109.9, 64.2, 31.7; IR (neat): ν_{max} 3162, 3027, 1634, 1520, 1470, 1441, 1317, 1261, 1072, 1007, 818, 738, 698 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{24}BrN_2O$ (M^++H), (M^++H+2): *m/z* 519.1072, 521.1052. Found: 519.1073, 521.1056.



10-Methyl-3-(4-nitrophenyl)-3-phenyl-5-(*p*-tolyl)-2,3-dihydroazepino[3,4-*b*]indol-1(10*H*)-one (9ao)

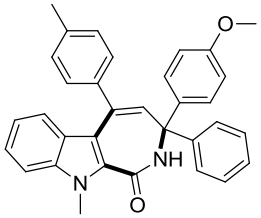
White solid, yield 0.115 g (40%), mp. 139-141 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.35-7.20 (m, 11H), 6.95 (s, 1H), 6.85-6.81 (m, 1H), 6.57 (s, 1H), 6.58 (d, *J* = 10.4 Hz, 1H), 3.94 (s, 3H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.2, 152.1, 147.1, 145.3, 140.3, 138.4, 138.3, 137.7, 133.0, 131.8, 129.2, 128.9, 128.5, 128.4, 127.8, 126.9, 124.8, 124.3, 123.1, 122.8, 120.3, 117.5, 109.9, 64.3, 31.8, 21.3; IR (neat): ν_{max} 3173, 3028, 1634, 1516, 1470, 1443, 1343, 1315, 1237, 1110, 905, 876, 849, 814, 735, 700 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{26}N_3O_3$ (M^++H): *m/z* 500.1974. Found: 500.1974.



10-Methyl-3-phenyl-3,5-di-*p*-tolyl-2,3-dihydroazepino[3,4-*b*]indol-1(10*H*)-one (9ap)

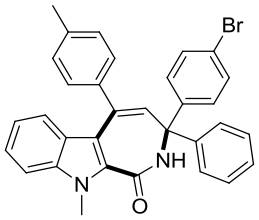
White solid, yield 0.097 g (36%), mp. > 220 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 4H), 7.28-7.14 (m, 9H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.90 (s, 1H), 6.82-6.79 (m, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 6.56 (s, 1H), 3.92 (s, 3H), 2.43 (s, 3H), 2.27 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 163.3, 139.2, 138.4, 138.3, 137.9, 137.3, 134.9, 132.2, 129.0, 128.9,

128.5, 128.0, 127.5, 127.1, 127.0, 124.5, 124.1, 122.9, 119.8, 117.4, 109.7, 64.3, 31.7, 21.3, 20.9; IR (neat): ν_{max} 3173, 3029, 1633, 1518, 1476, 1468, 1448, 1381, 1320, 1095, 1014, 730, 699 cm^{-1}; HRMS (ESI): Calcd. for $C_{33}H_{29}N_2O$ (M^++H): *m/z* 469.2280. Found: 469.2280.



3-(4-Methoxyphenyl)-10-methyl-3-phenyl-5-(*p*-tolyl)-2,3-dihydroazepino[3,4-*b*]indol-1(10*H*)-one (9aq)

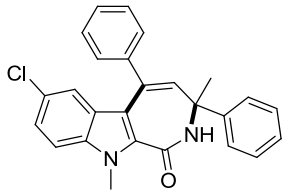
White solid, yield 0.103 g (37%), mp. > 220 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.5 Hz, 4H), 7.24-7.14 (m, 9H), 6.88 (s, 1H), 6.80 (t, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 8.5 Hz, 2H), 6.56-6.55 (m, 2H), 3.92 (s, 3H), 3.74 (s, 3H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 163.3, 158.8, 139.3, 138.4, 138.3, 137.9, 134.9, 132.2, 129.0, 128.5, 128.3, 128.0, 127.5, 127.0, 124.5, 124.1, 122.9, 119.8, 117.4, 113.5, 109.7, 64.1, 55.2, 31.7, 21.3; IR (neat): ν_{max} 3159, 3018, 1626, 1604, 1508, 1473, 1442, 1315, 1254, 1182, 1032, 815, 757, 701, 671 cm^{-1}; HRMS (ESI): Calcd. for $C_{33}H_{29}N_2O_2$ (M^++H): *m/z* 485.2229. Found: 485.2232.



3-(4-Bromophenyl)-10-methyl-3-phenyl-5-(*p*-tolyl)-2,3-dihydroazepino[3,4-*b*]indol-1(10*H*)-one (9ar)

White solid, yield 0.119 g (39%), mp. >170-172 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.19 (m, 15H), 6.98 (s, 1H), 6.84-6.80 (m, 1H), 6.56 (d, *J* = 8.4 Hz, 1H), 6.50 (s, 1H), 3.92 (s, 3H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 163.3, 139.7, 138.3, 138.1$_4$, 138.1$_1$, 134.0,

132.0, 131.2. 129.1, 128.9, 128.5, 128.4, 127.9, 127.0, 124.4, 122.9, 121.6, 112.0, 117.4, 109.9, 64.2, 31.8, 21.3; IR (neat): ν_{max} 3161, 3024, 1632, 1509, 1472, 1443, 1315, 1237, 1074, 1008, 874, 814, 782, 702 cm^{-1}; LC-MS: m/z 533 $[M-1]^+$; Anal. Calcd. for $C_{32}H_{25}BrN_2O$: C, 72.05; H, 4.72; N, 5.25. Found: C, 72.15; H, 4.68; N, 5.28.



7-Chloro-3,10-dimethyl-3,5-diphenyl-2,3-dihydroazepino[3,4-*b*]indol-1(10*H*)-one (9bs)

White solid, yield 0.065 g (34%), mp. > 220 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.42 (m, 5H), 7.39-7.37 (m, 2H), 7.11-7.10 (m, 2H), 7.07-7.03 (m, 2H), 6.99-6.95 (m, 1H), 6.86 (s, 1H), 6.45-6.44 (m, 1H), 6.31 (s, 1H), 3.88 (s, 3H), 1.78 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.5, 145.8, 140.3, 139.0, 136.5, 134.2, 133.4, 128.5, 128.4_4, 128.4_1, 127.8, 126.8, 125.1, 124.7, 121.8, 116.9, 110.8, 57.1, 34.3, 31.7; IR (neat): ν_{max} 3175, 3040, 2971, 1640, 1521, 1468, 1441, 1321, 1067, 1025, 819, 794, 743, 723, 696 cm^{-1}; LC-MS: m/z 413 $[M+1]^+$; Anal. Calcd. for $C_{26}H_{21}ClN_2O$: C, 75.63; H, 5.13; N, 6.78. Found: C, 75.52; H, 5.16; N, 6.73.

(11). X-ray data collection, solution, refinement and the ORTEPs/crystal data: Single crystal X-ray data for crystals of compounds **6aa, 6aj, 7al, 9ac, 7an, 9aa, 9ap** and **4a** (order in which they appear in the main manuscript) were collected on an X-ray diffractometer using Mo-K_α (λ = 0.71073 Å) radiation after mounting on glass fibers inside a brass pin in open air. The structures were solved by direct methods and refined by full-matrix least squares method using standard procedures; absorption corrections were done using SADABS program, where applicable [(a) Sheldrick, G. M. *SADABS, Siemens Area Detector Absorption Correction*, University of Gottingen, Germany, **1996**. (b) Sheldrick, G. M. SHELX-97-*A program for crystal structure solution and refinement*, University of Gottingen, **1997**. (c) Sheldrick, G. M.

SHELXTL NT Crystal Structure Analysis Package, Bruker AXS, Analytical X-ray System, WI, USA, **1999**, version 5.10]. In general, all non-hydrogen atoms were refined anisotropically; hydrogen atoms were fixed by geometry or located by a Difference Fourier map and refined isotropically. CCDC numbers are 1915530-1915537.

ORTEPs and crystal data of 6aa, 6aj, 7al, 9ac, 7an, 9aa, 9ap and 4a (Figures S1-S8)

Note: Figure numbers are in the order in which they appear in the main manuscript

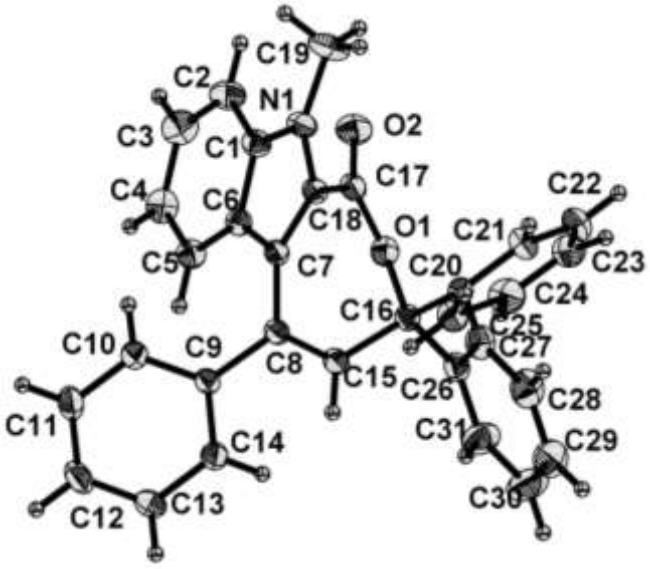


Figure S1. ORTEP view of ε-lactone **6aa** with 30% probability of ellipsoids: ***Crystal data***: $C_{31}H_{23}NO$, M = 441.50, Monoclinic, Space group *P21/n*, a = 9.5504(9), b = 17.3600(19), c = 14.7835(16) Å, V = 2365.9(4) $Å^3$, β = 105.148(3)°, Z = 4, μ = 0.077 mm^{-1}, data/restraints/parameters: 5396/0/307, R indices (I> 2σ\(I)): R1 = 0.0466, *w*R2 (all data) = 0.1377. CCDC No: 1915530.

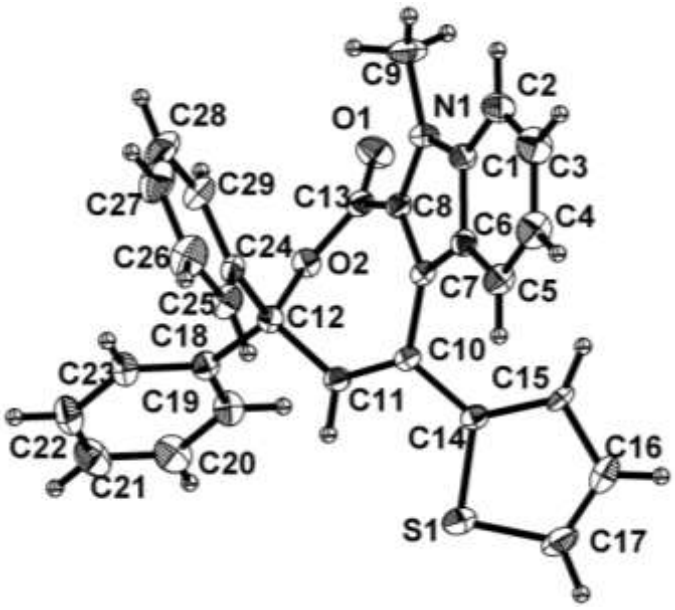


Figure S2. ORTEP view of ε-lactone **6aj** with 30% probability of ellipsoids. ***Crystal data***: $C_{29}H_{21}NO_2S$, M = 447.53, Monoclinic, Space group *P2(1)/n*, a = 11.9339(13), b = 10.8446(12), c = 17.9980(17) Å, V = 2262.9(4) Å^3, β = 103.711(3)^o, Z = 4, μ = 0.170 mm^{-1}, data/restraints/parameters: 3983/0/299, R indices (I> 2σ\(I)): R1 = 0.0519, *w*R2 (all data) = 0.1642. CCDC No: 1915531.

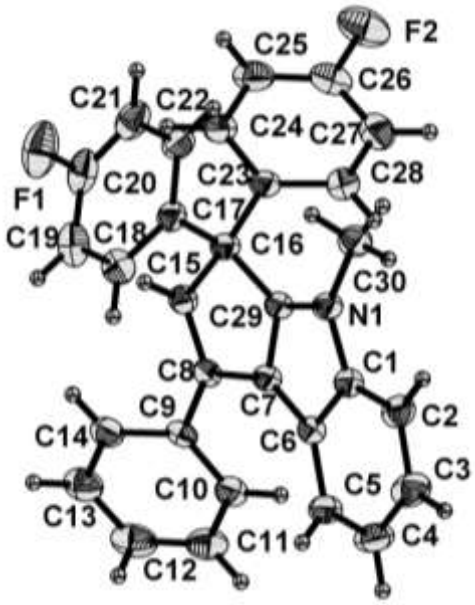


Figure S3. ORTEP view of 3,4-dihydrocyclopenta[*b*]indole **7al** with 30% probability of ellipsoids. ***Crystal data***: $C_{30}H_{21}F_2N$, M = 433.48, Orthorhombic, Space group *Pna21*, a = 9.0702(4), b = 20.8446(8), c = 12.0332(4) Å, V = 2275.05(15) $Å^3$, Z = 4, μ = 0.085 mm^{-1}, data/restraints/parameters: 4474/1/298, R indices (I> 2σ\(I)): R1 = 0.0394, *w*R2 (all data) = 0.1031. CCDC No: 1915532

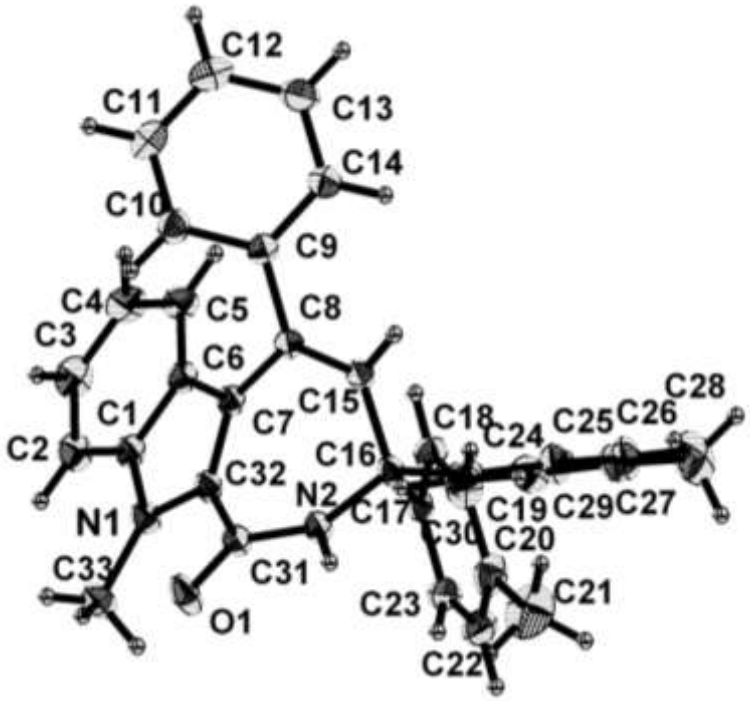


Figure S4. ORTEP view of ε-lactam **9ac** with 30% probability of ellipsoids. ***Crystal data***: $C_{33}H_{27}N_2O$, M = 468.57, Triclinic, Space group *P-1*, a = 10.7428(4), b = 11.5805(4), c = 11.8540(5) Å, V = 1292.89(9) $Å^3$, α = 102.3017(15)°, β = 103.6326(16)°, γ = 108.3261(14)°, Z = 2, μ = 0.072 mm^{-1}, data/restraints/parameters: 4553/0/332, R indices (I> 2σ\(I)): R1 = 0.0429, *w*R2 (all data) = 0.1202. CCDC No: 1915533.

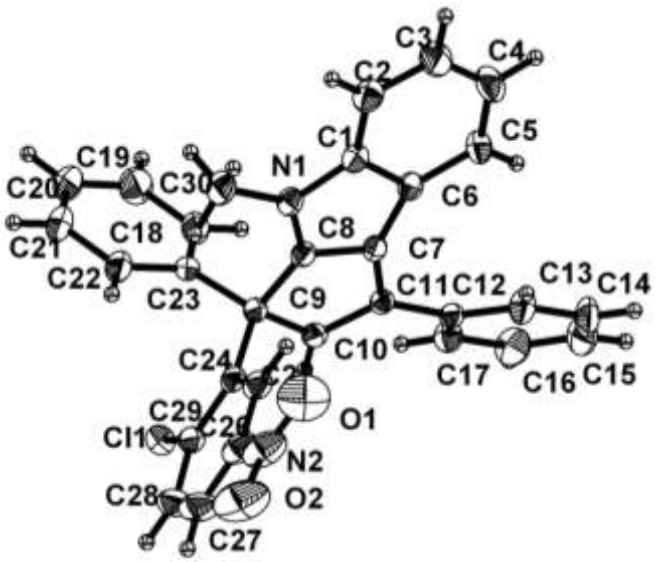


Figure S5. ORTEP view of 3,4-dihydrocyclopenta[*b*]indole **7an** with 30% probability of ellipsoids. ***Crystal data***: $C_{30}H_{21}ClN_2O_2$, M = 476.94, Orthorhombic, Space group *Pbca*, a = 13.8267(8), b = 17.2618(13), c = 20.2956(15) Å, V = 4844.0(6) $Å^3$, α = β = γ = 90^o, Z = 8, μ = 0.188 mm^{-1}, data/restraints/parameters: 4245/0/317, R indices (I> 2σ\(I)): R1 = 0.0425, *w*R2 (all data) = 0.1167. CCDC No: 1915534.

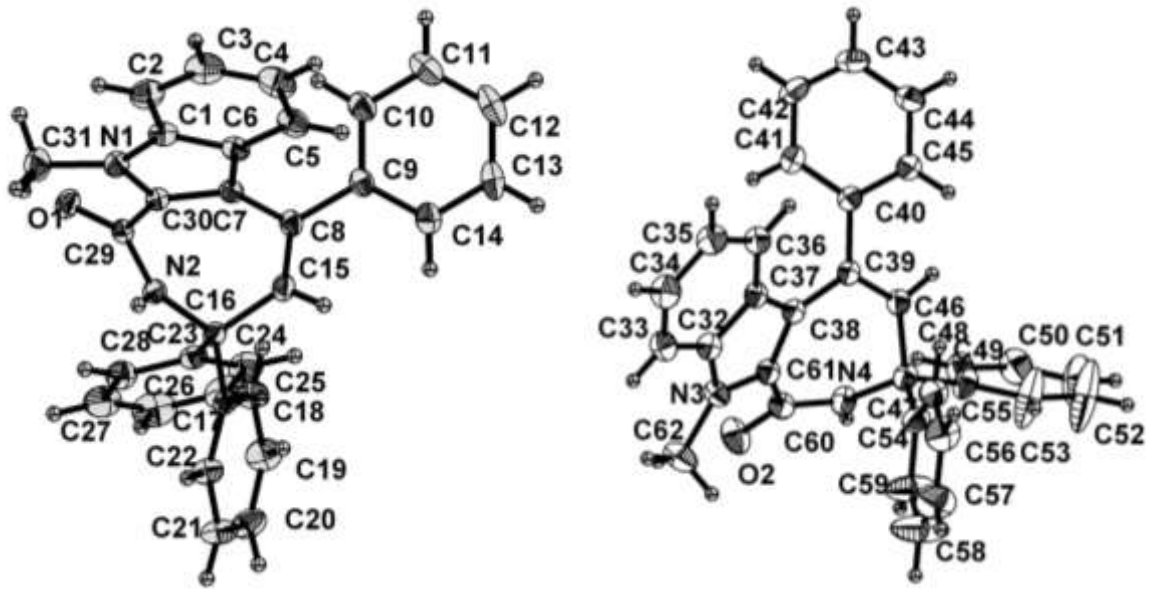


Figure S6. ORTEP view of ε-lactam **9aa** with 30% probability of ellipsoids. Two molecules are present in asymmetric unit. ***Crystal data***: $C_{31}H_{24}N_2O$, *M* = 440.52, Triclinic, Space group *P-1*, *a* = 10.1870(4), *b* = 12.0867(4), *c* = 20.2712(7) Å, *V* = 2373.07(15) $Å^3$, α = 76.231(2)°, β = 78.228(2)°, γ = 86.594(2)°, *Z* = 4, μ = 0.075 mm^{-1}, data/restraints/parameters: 9771/0/621, R indices (I> 2\s(I)): R1 = 0.0625, *w*R2 (all data) = 0.1462. CCDC No: 1915535.

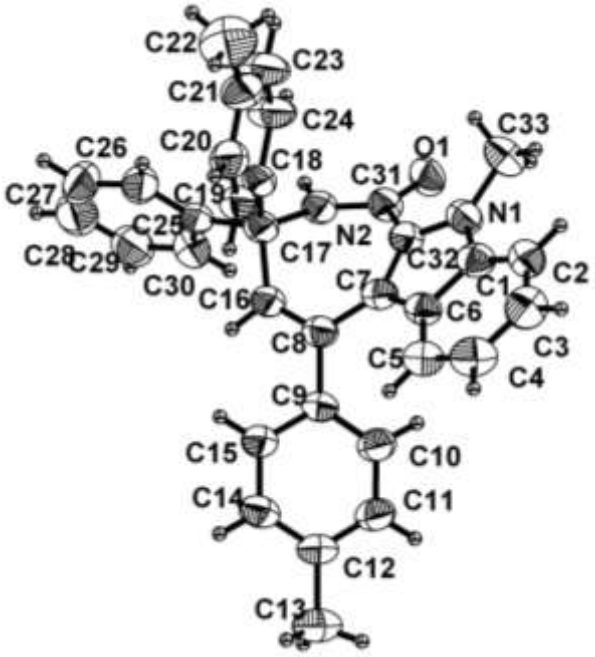


Figure S7. ORTEP view of ε-lactone **9ap** with 30% probability of ellipsoids. ***Crystal data***: $C_{23}H_{28}N_2O$, *M* = 468.57, Monoclinic, Space group *C12/c1*, *a* = 23.3055(12), *b* = 12.5430(4), *c* = 19.5823(12) Å, *V* = 5225.0(5) $Å^3$, β = 114.108(7)°, *Z* = 8, μ = 0.072 mm^{-1}, data/restraints/parameters: 4598/1/332, R indices (I> 2σ\(I)): R1 = 0.0938, *w*R2 (all data) = 0.3380. CCDC No: 1915536.

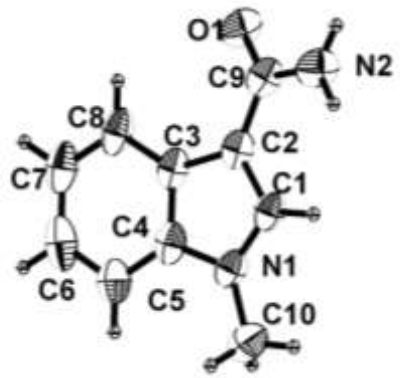


Figure S8. ORTEP view of ε-lactone **4a** with 30% probability of ellipsoids. ***Crystal data***: $C_{10}H_{10}N_2O$, *M* = 174.20, Monoclinic, Space group *C2/c*, *a* = 20.717(2), *b* = 11.7670(11), *c* = 9.8845(8) Å, *V* = 2364.2(4) $Å^3$, β = 101.146(3)°, *Z* = 8, μ = 0.065 mm^{-1}, data/restraints/parameters: 2074/0/120, R indices (I> 2σ\(I)): R1 = 0.0850, *w*R2 (all data) = 0.2753. Squeeze option was used in refinement. CCDC No: 1915537.

(12). ^{1}H and ^{13}C NMR spectra of all new compounds

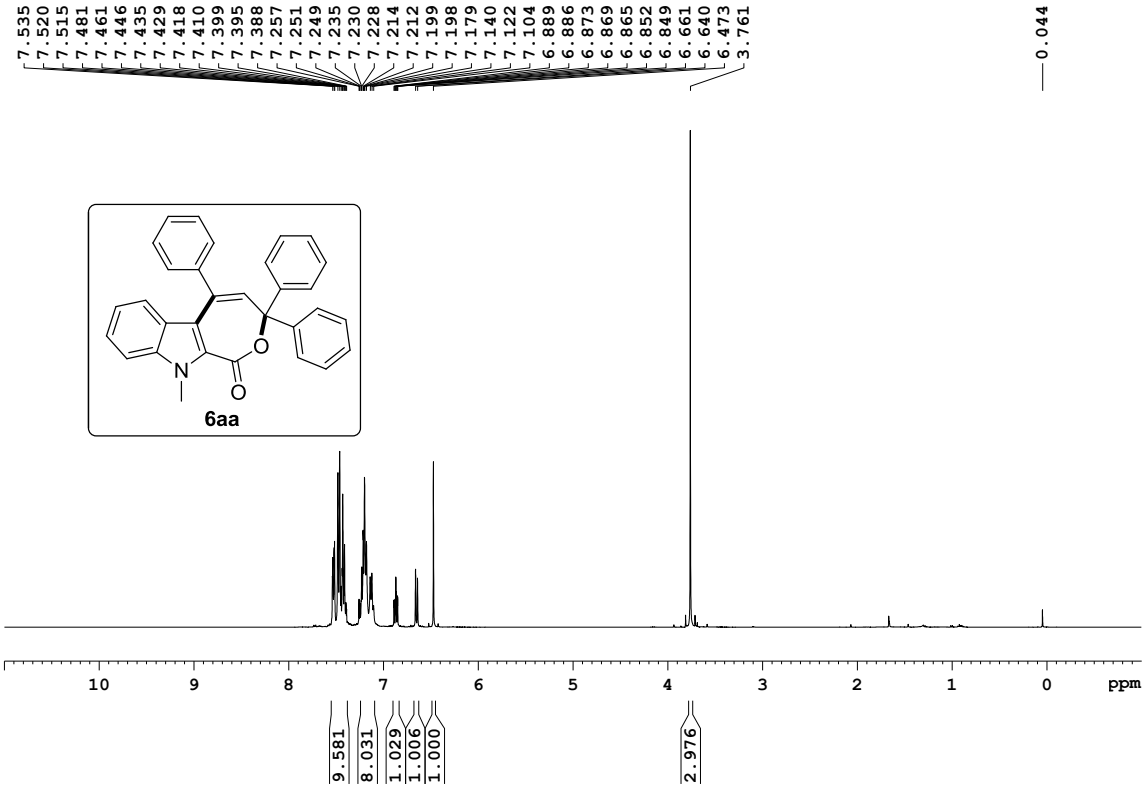


Figure S9. ^{1}H NMR spectrum of compound **6aa**

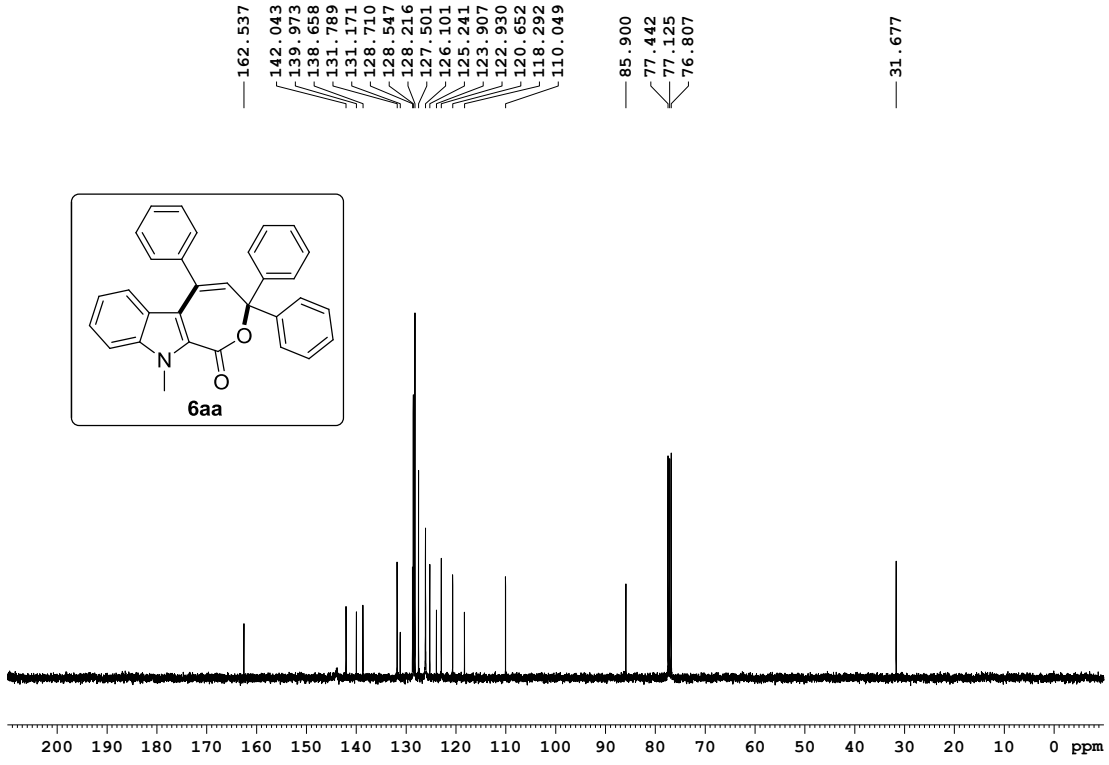


Figure S10. ^{13}C NMR spectrum of compound **6aa**

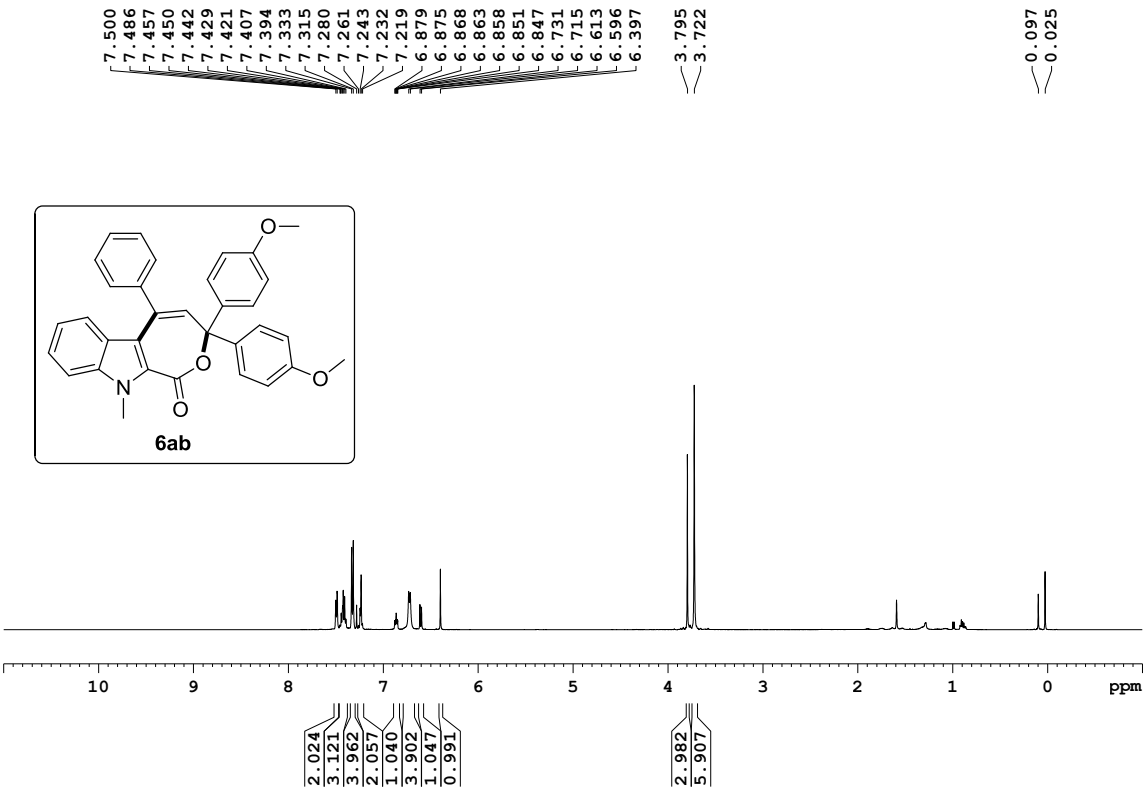


Figure S11. ^{1}H NMR spectrum of compound **6ab**

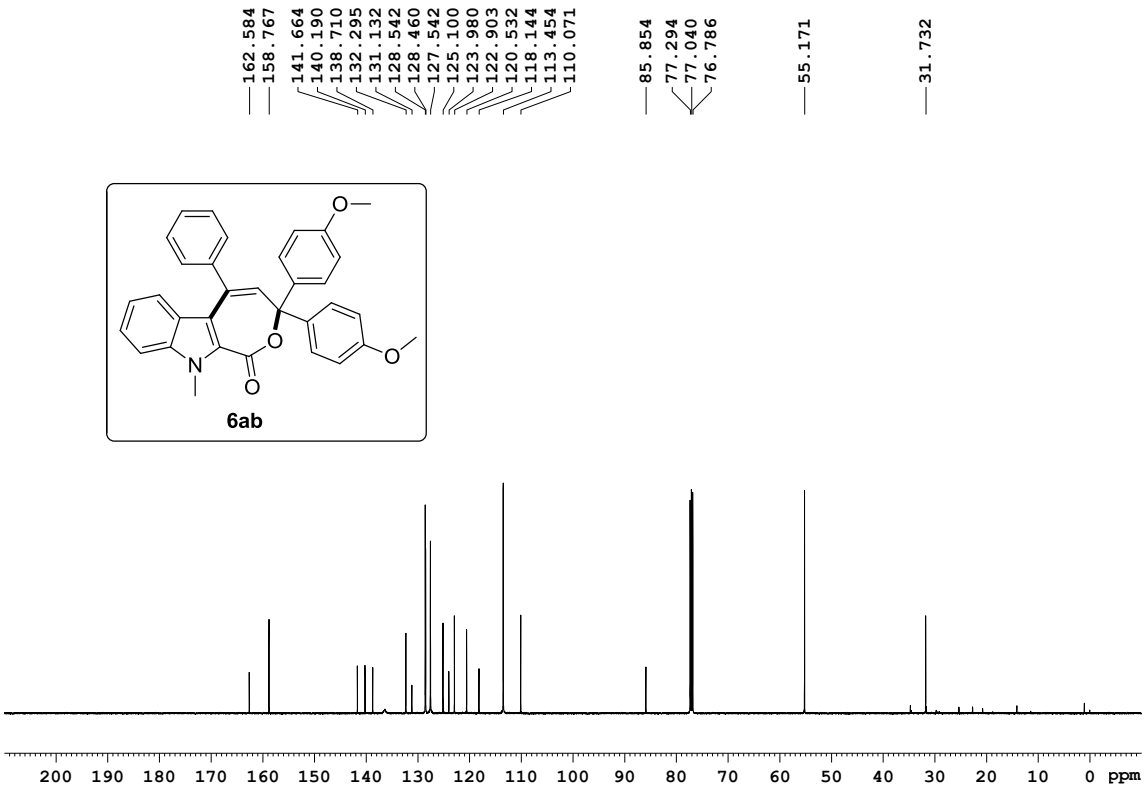


Figure S12. ^{13}C NMR spectrum of compound **6ab**

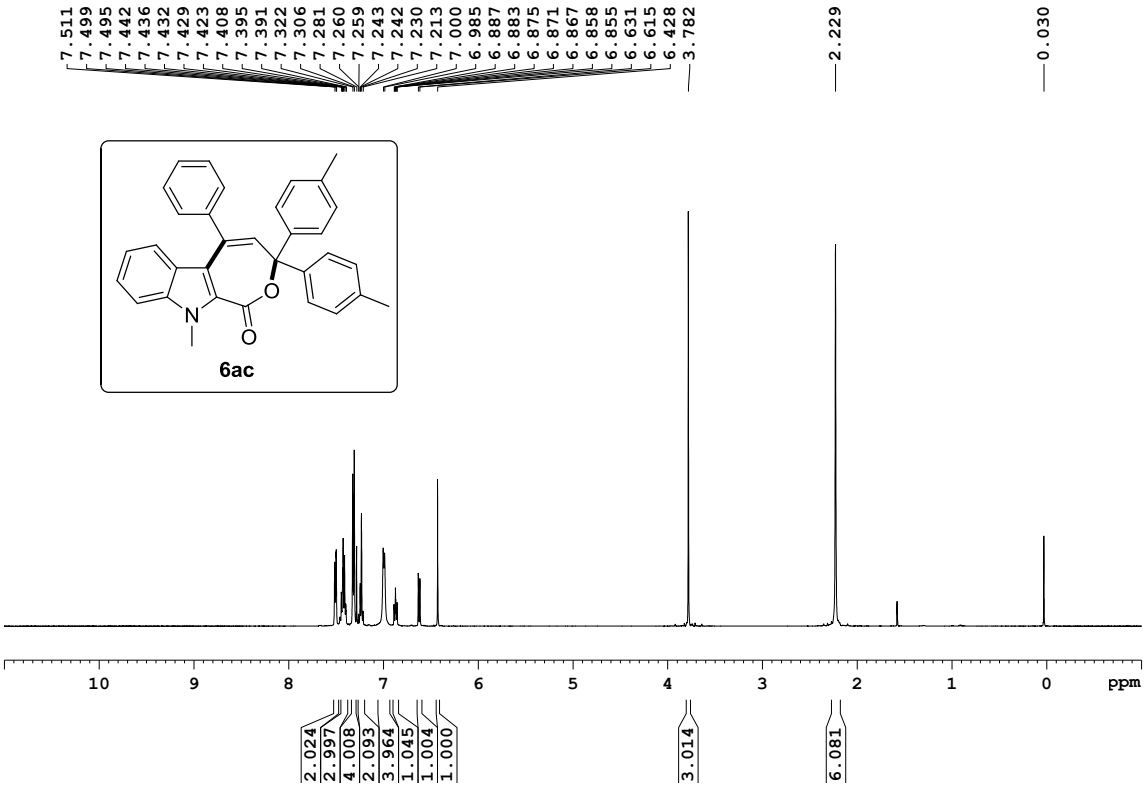


Figure S13. ^{1}H NMR spectrum of compound **6ac**

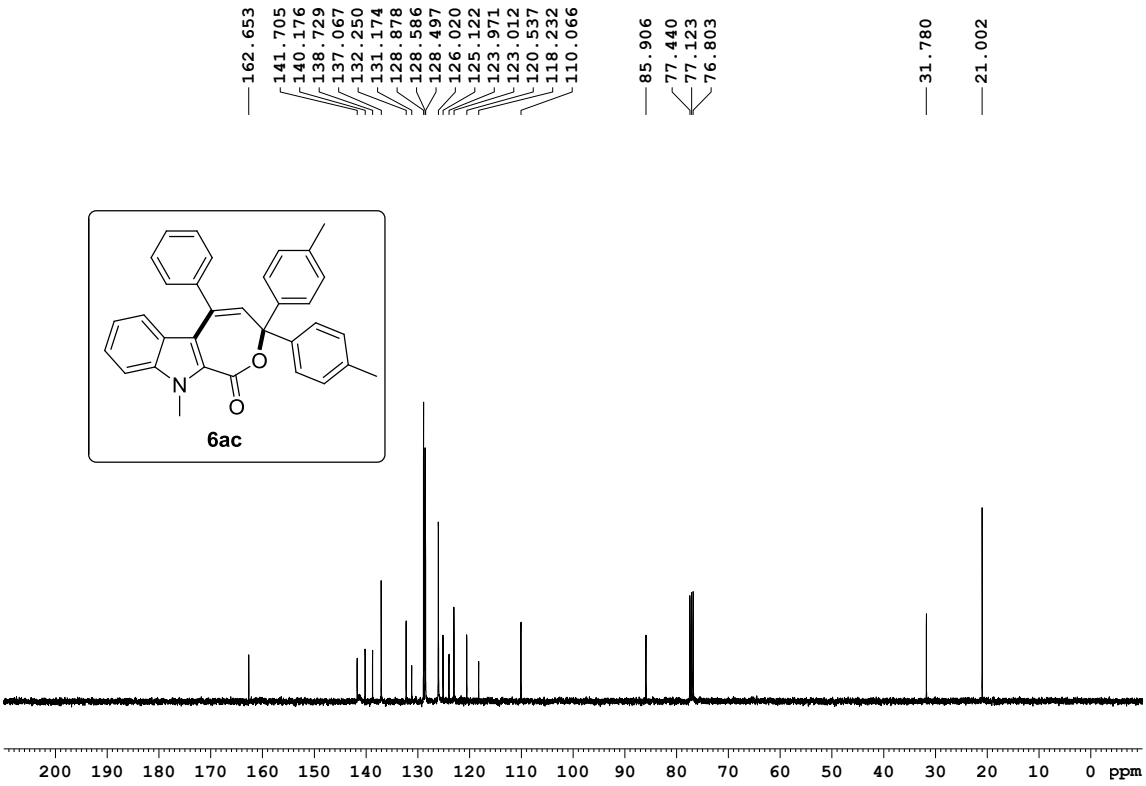


Figure S14. ^{13}C NMR spectrum of compound **6ac**

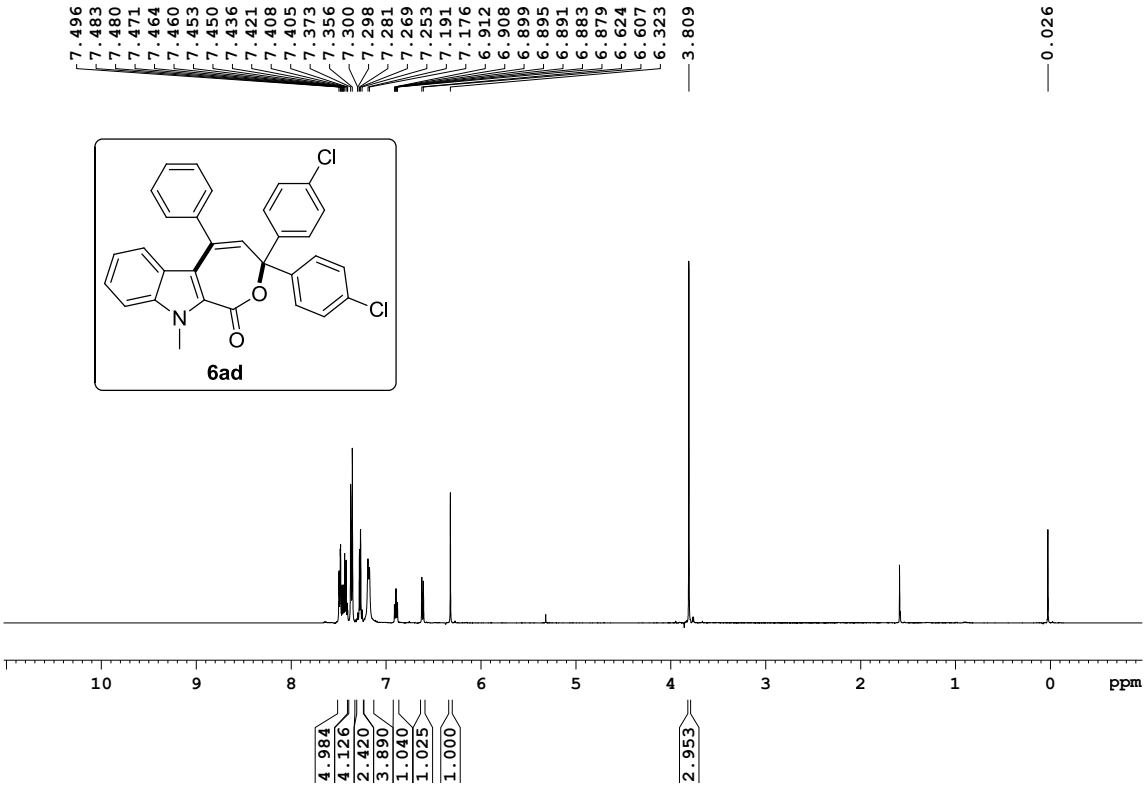


Figure S15. ^{1}H NMR spectrum of compound **6ad**

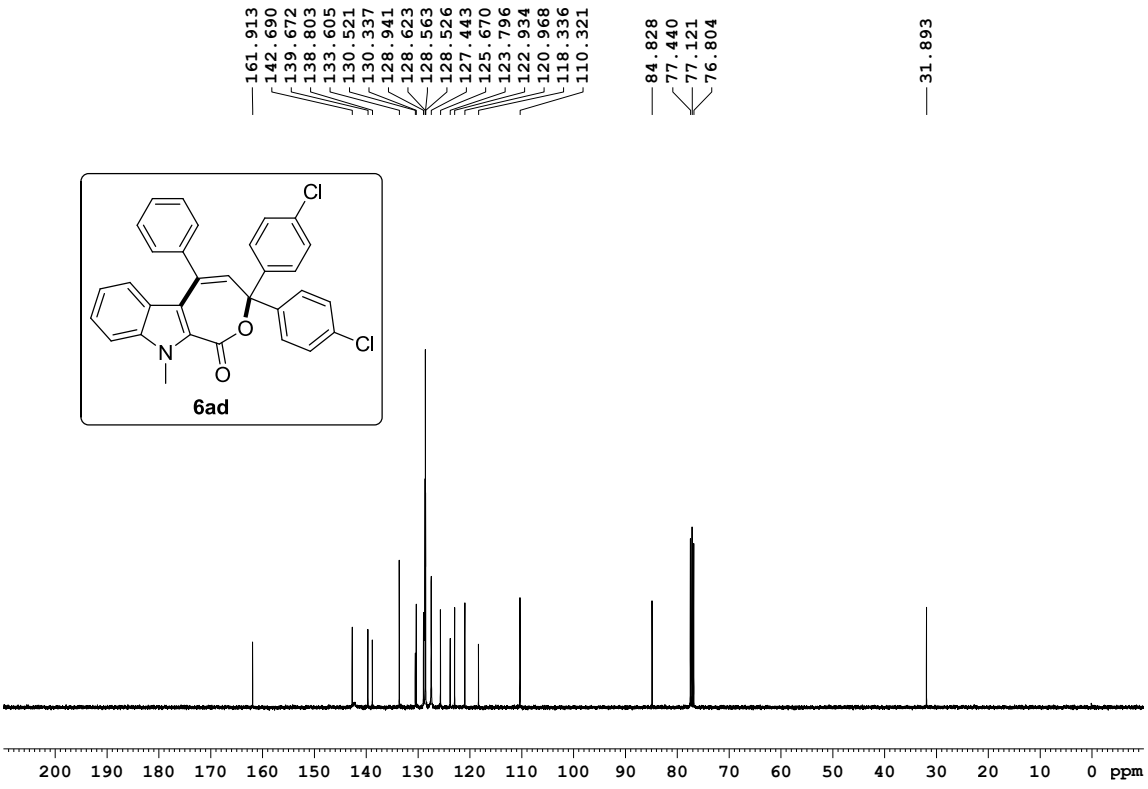


Figure S16. ^{13}C NMR spectrum of compound **6ad**

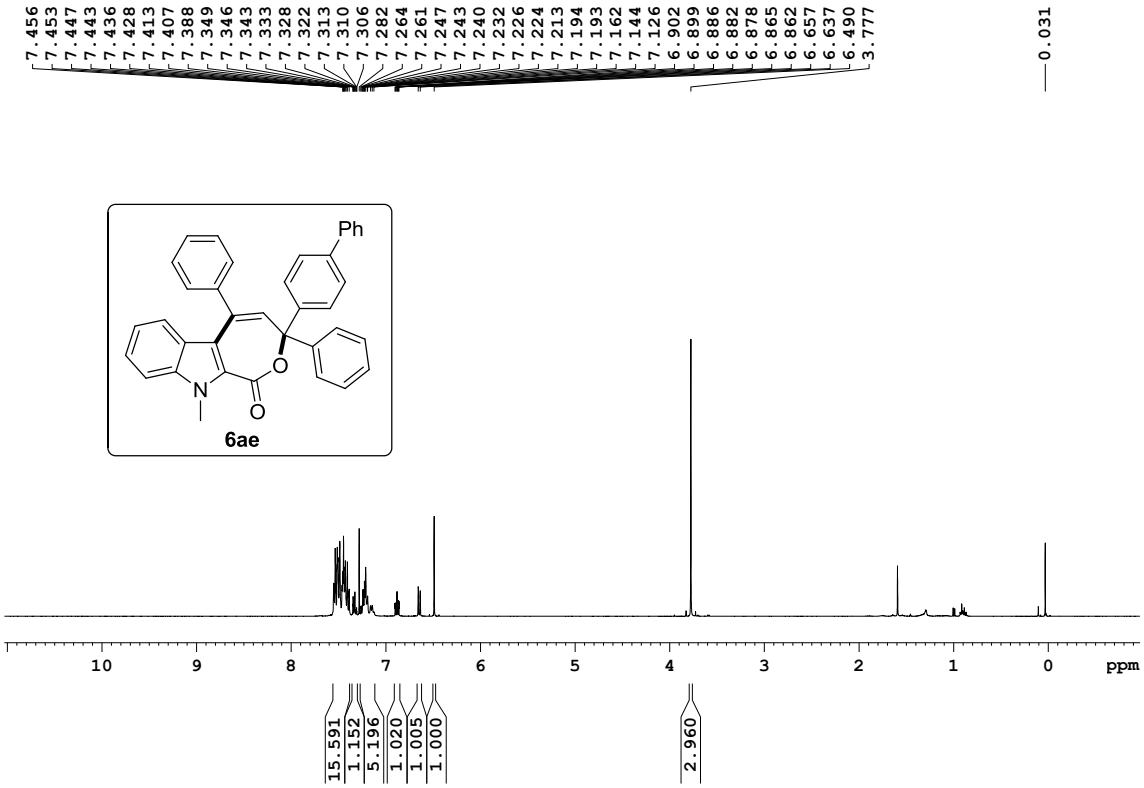


Figure S17. ^{1}H NMR spectrum of compound **6ae**

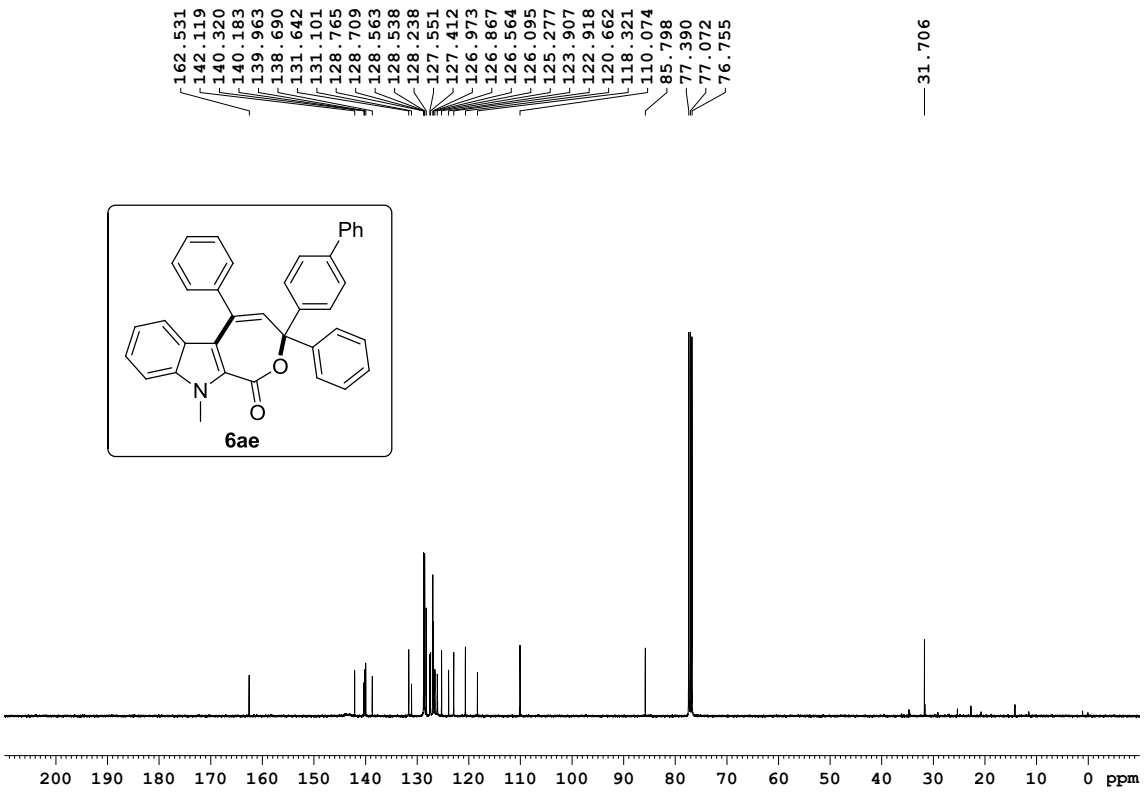


Figure S18. ^{13}C NMR spectrum of compound **6ae**

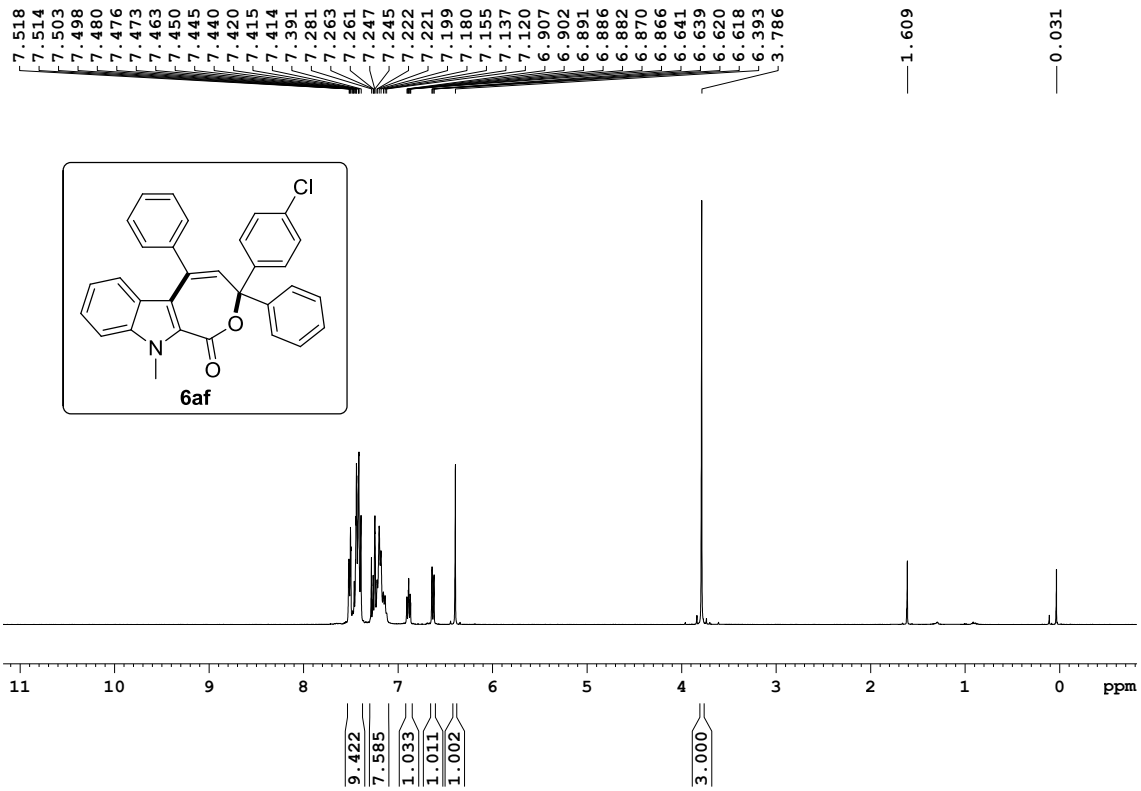


Figure S19. ^{1}H NMR spectrum of compound **6af**

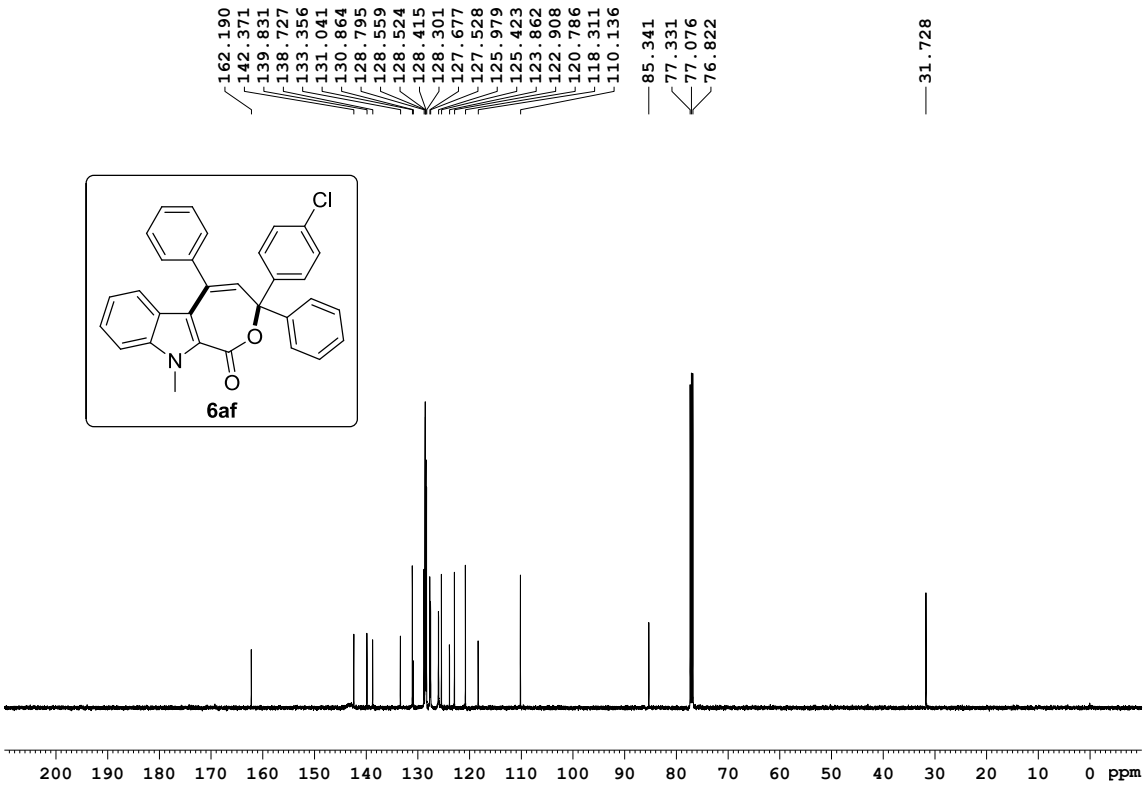


Figure S20. ^{13}C NMR spectrum of compound **6af**

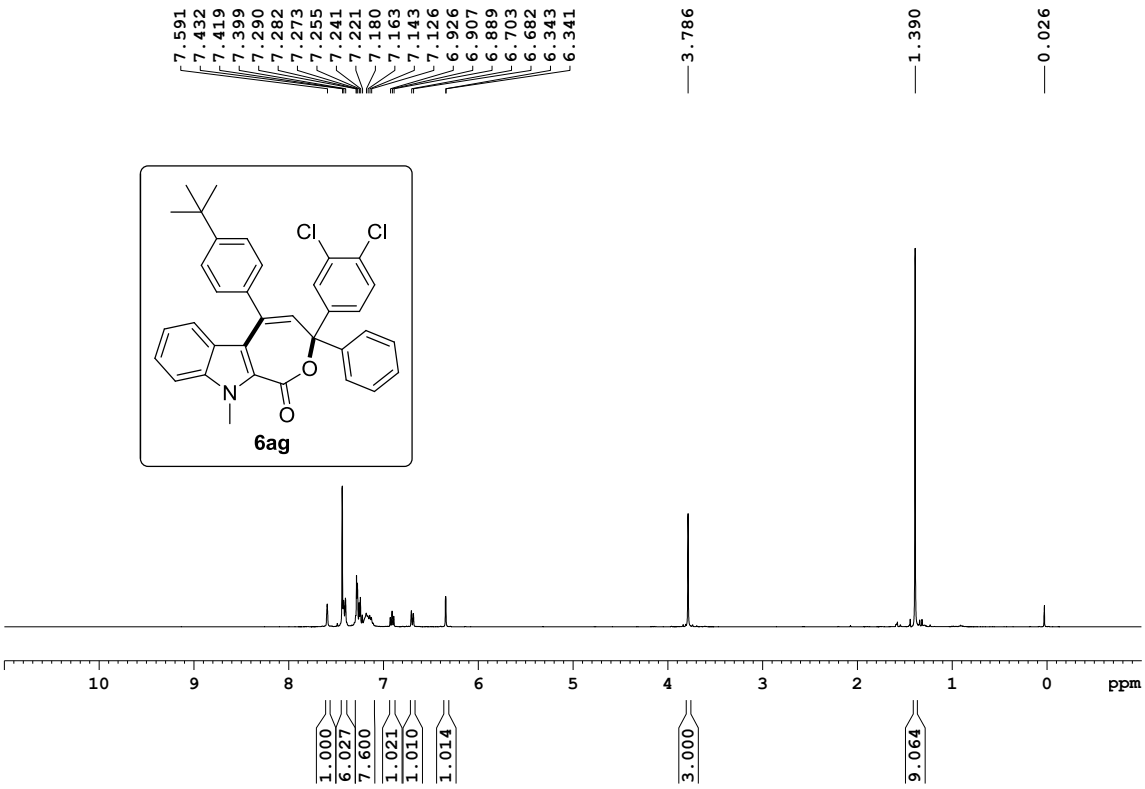


Figure S21. ^{1}H NMR spectrum of compound **6ag**

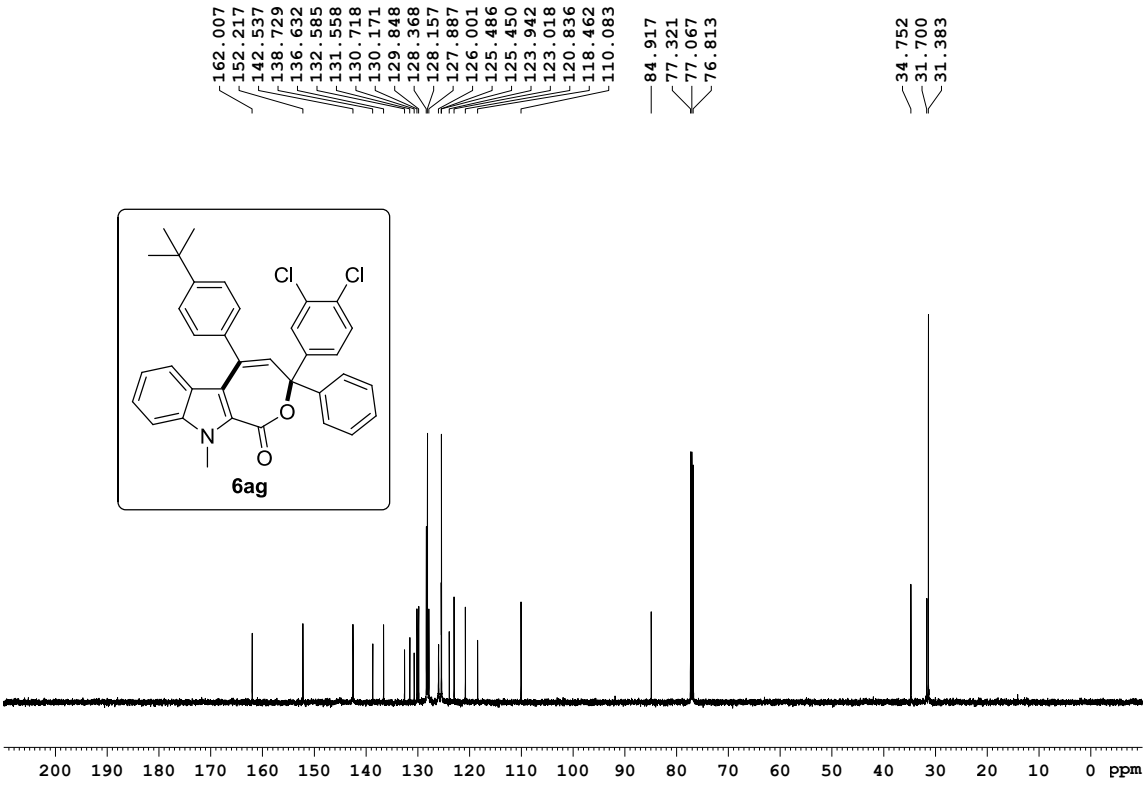


Figure S22. ^{13}C NMR spectrum of compound **6ag**

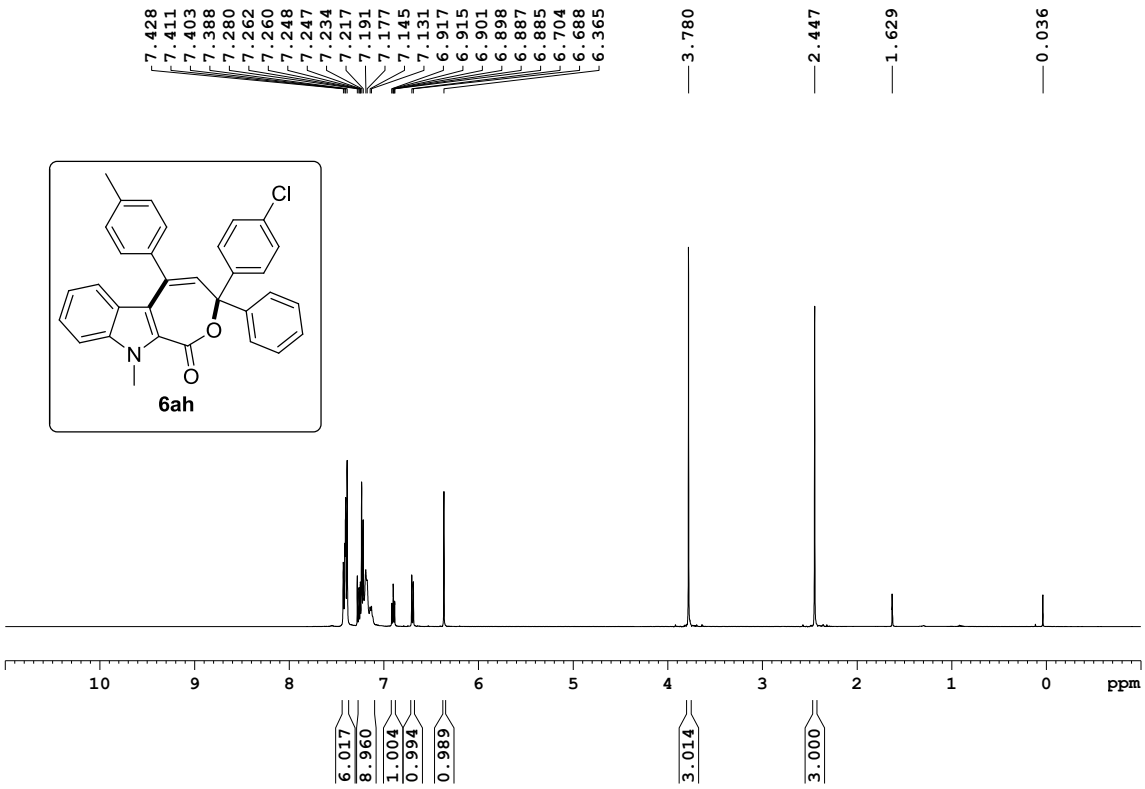


Figure S23. ^{1}H NMR spectrum of compound **6ah**

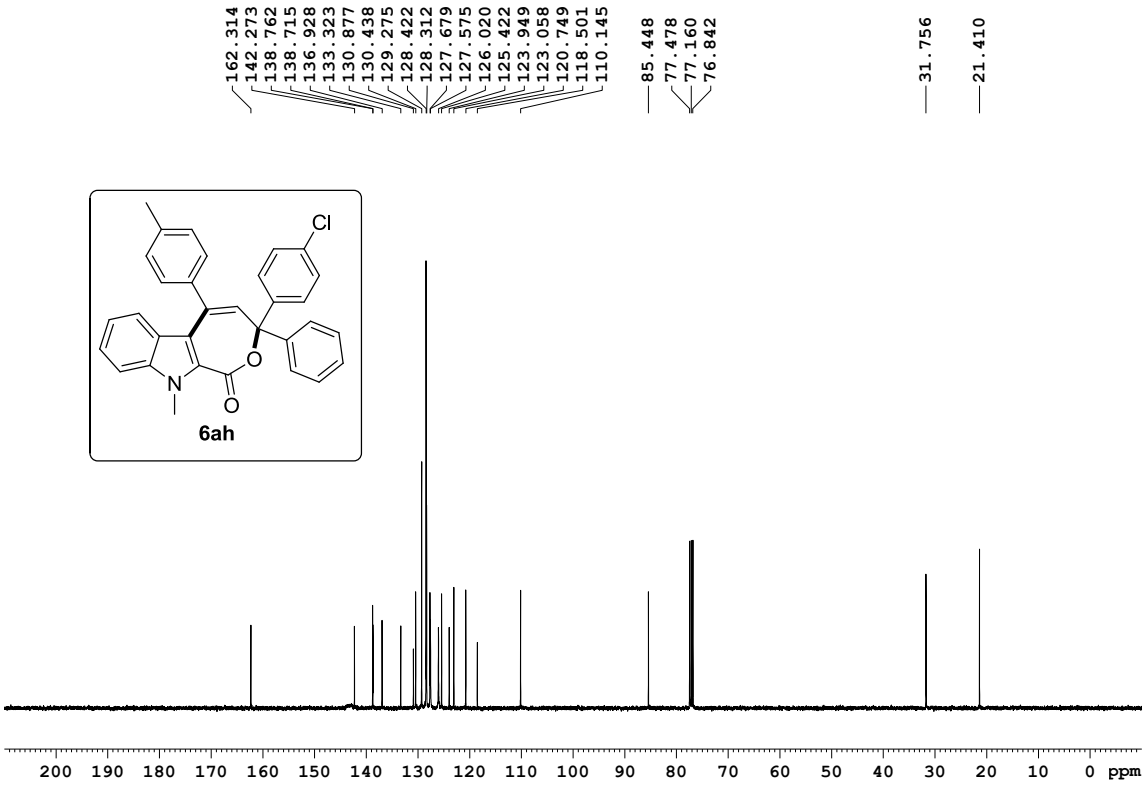


Figure S24. ^{13}C NMR spectrum of compound **6ah**

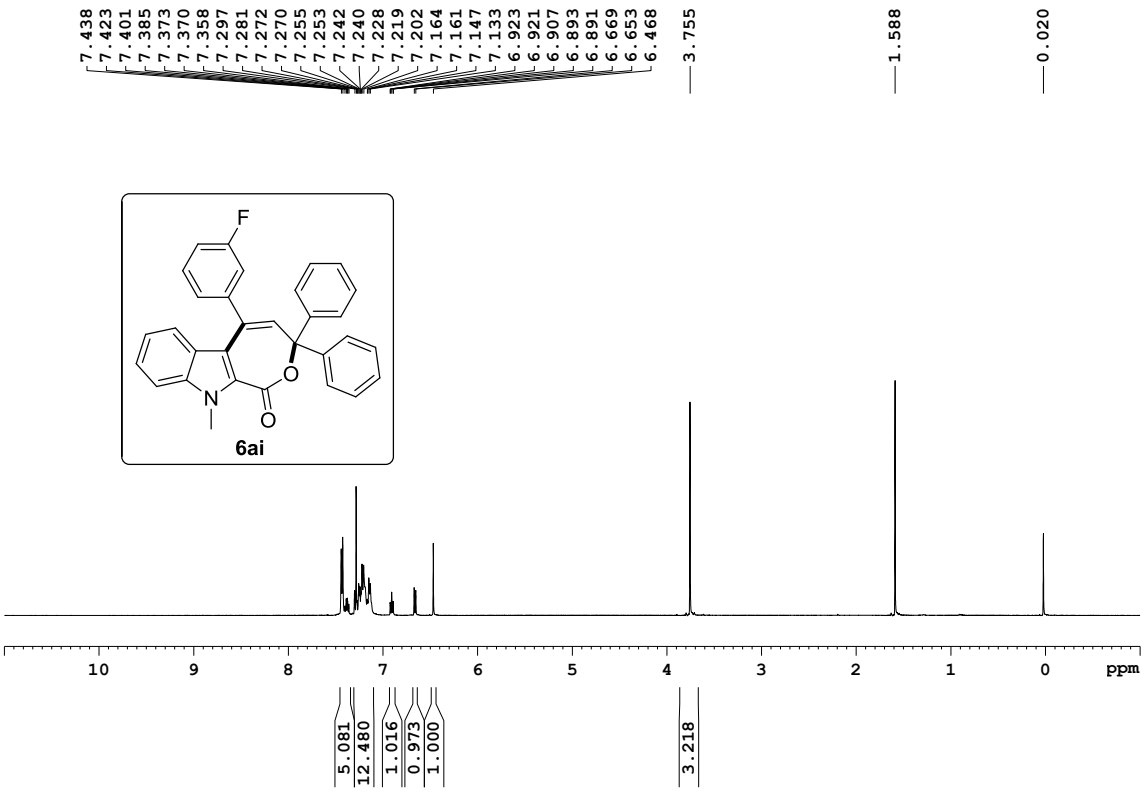


Figure S25. ^{1}H NMR spectrum of compound **6ai**

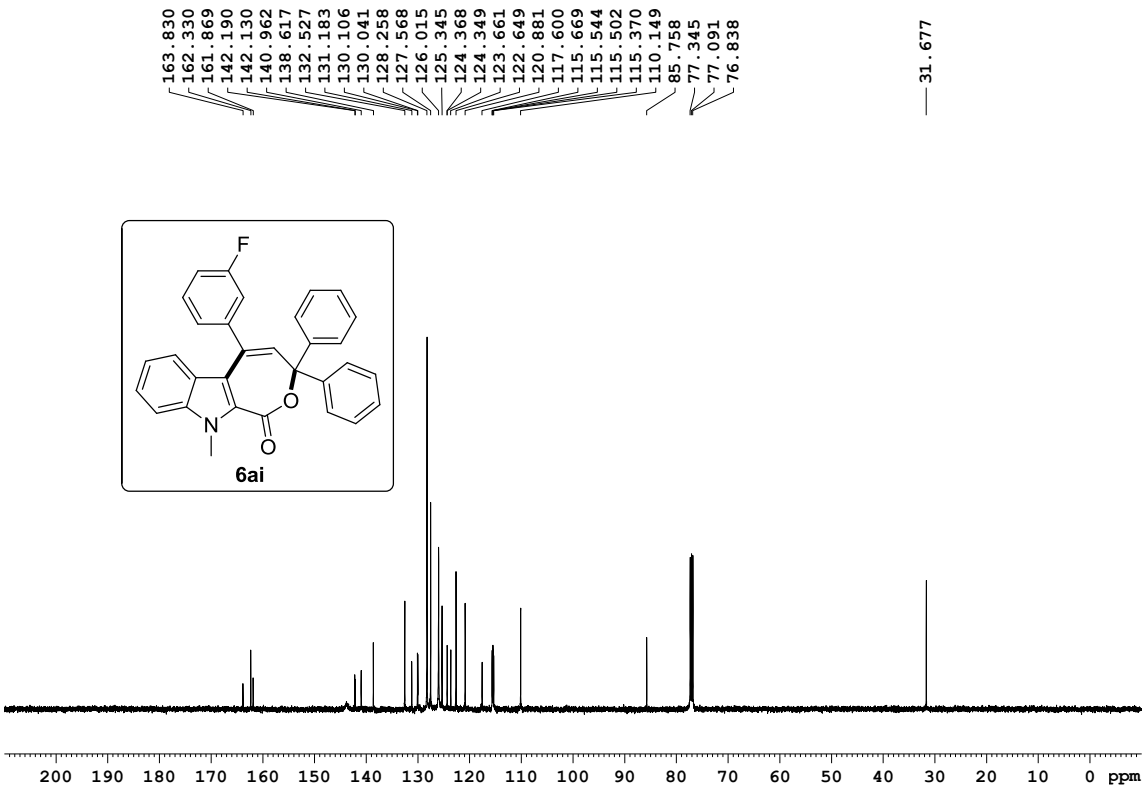


Figure S26. ^{13}C NMR spectrum of compound **6ai**

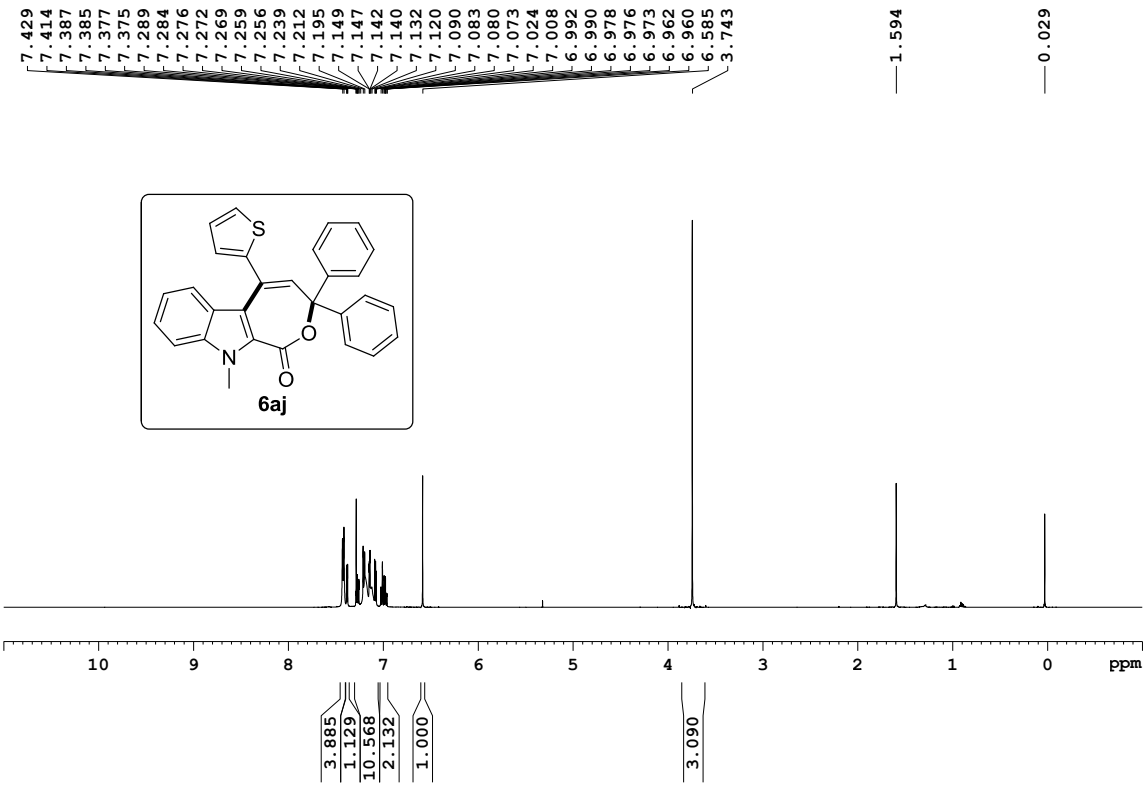


Figure S27. ^{1}H NMR spectrum of compound **6aj**

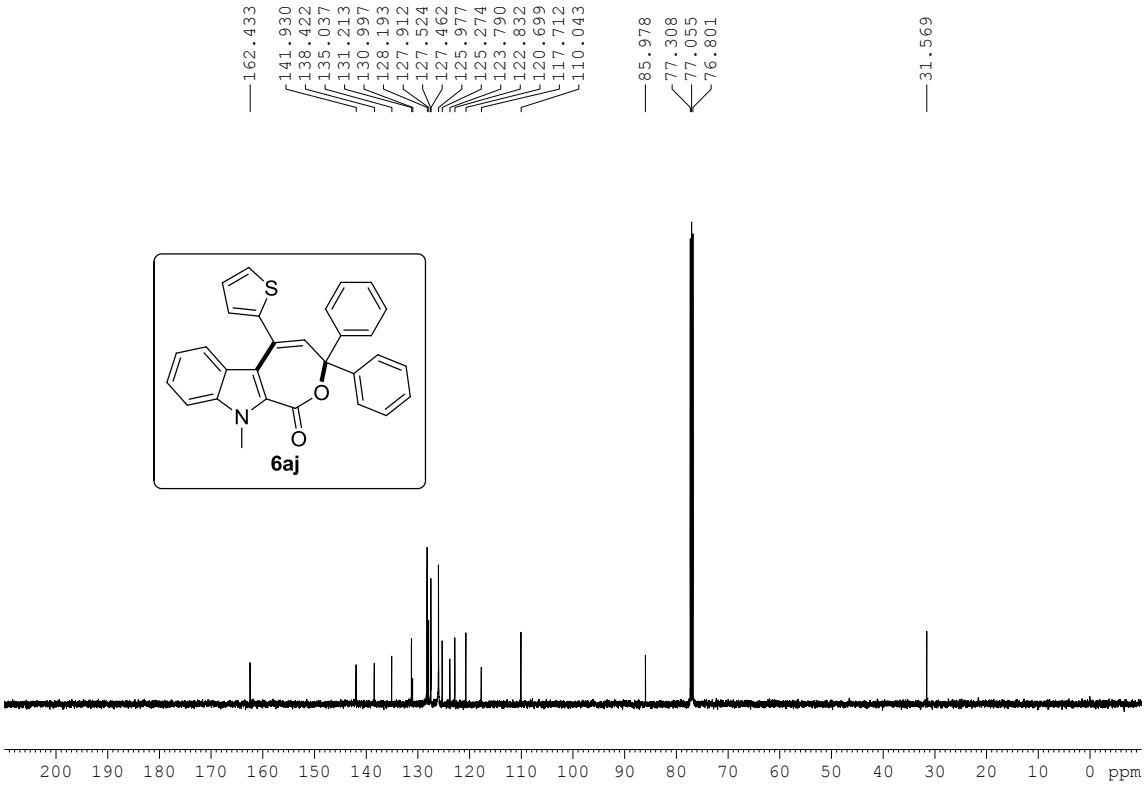


Figure S28. ^{13}C NMR spectrum of compound **6aj**

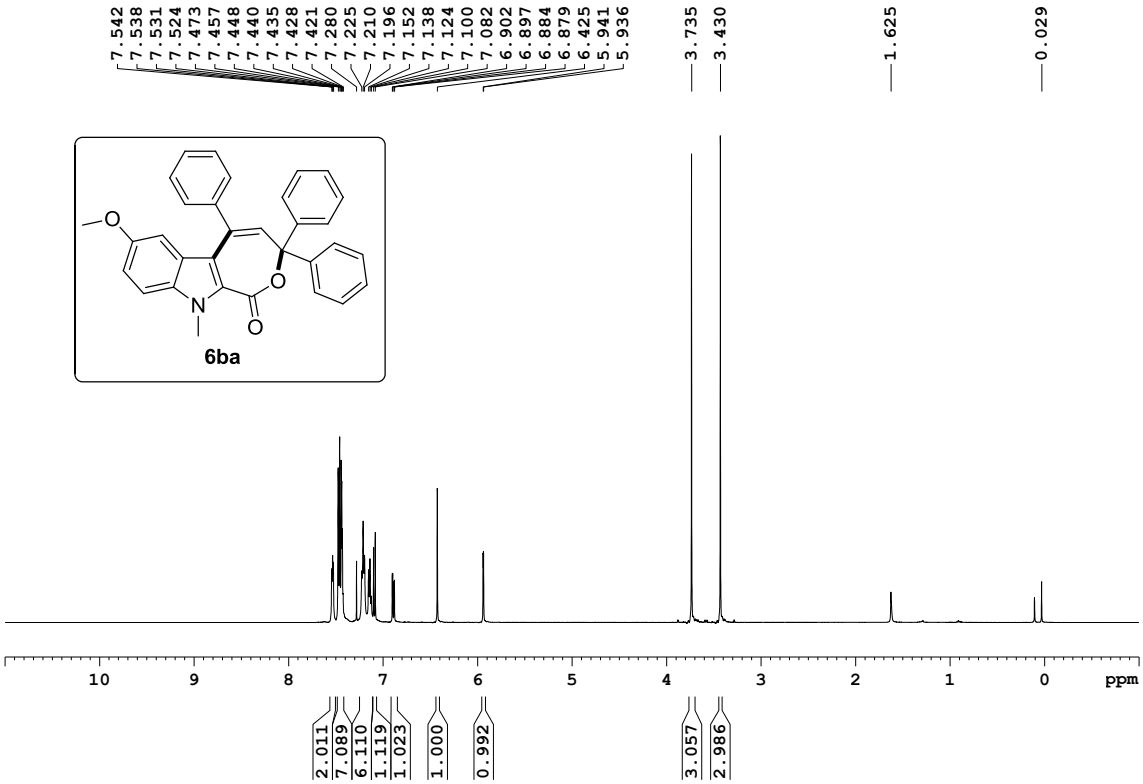


Figure S29. ^{1}H NMR spectrum of compound **6ba**

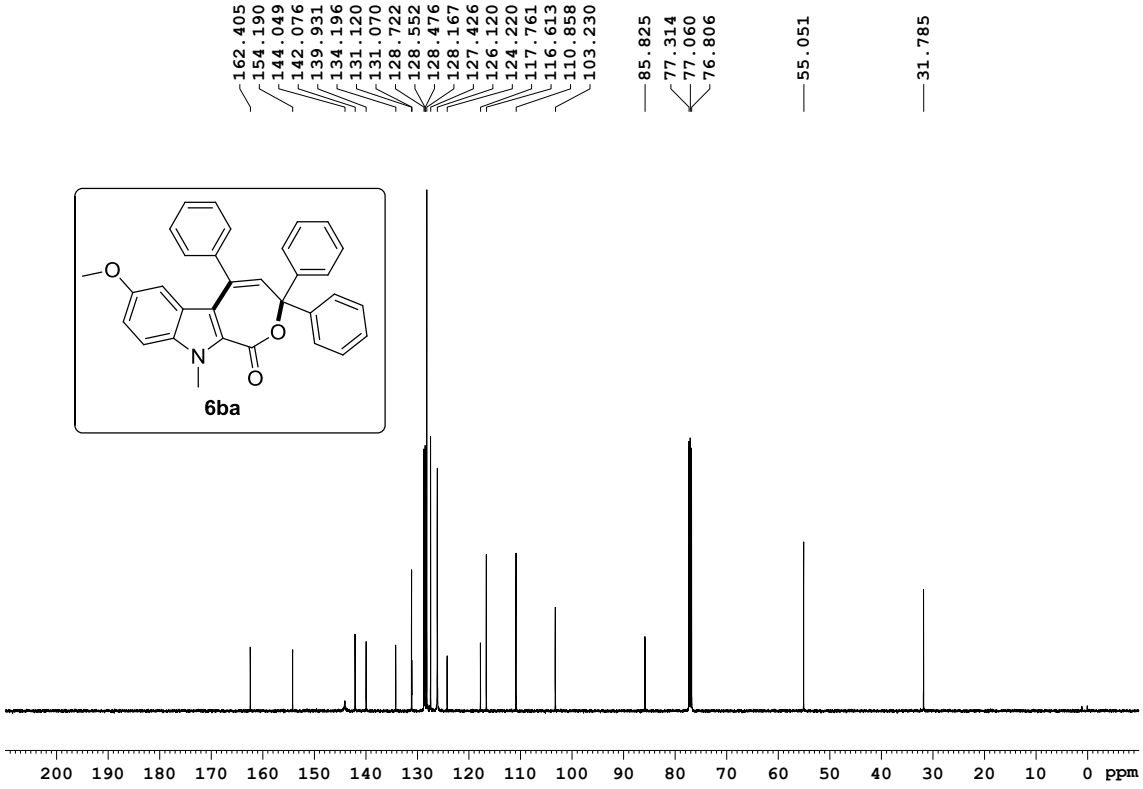


Figure S30. ^{13}C NMR spectrum of compound **6ba**

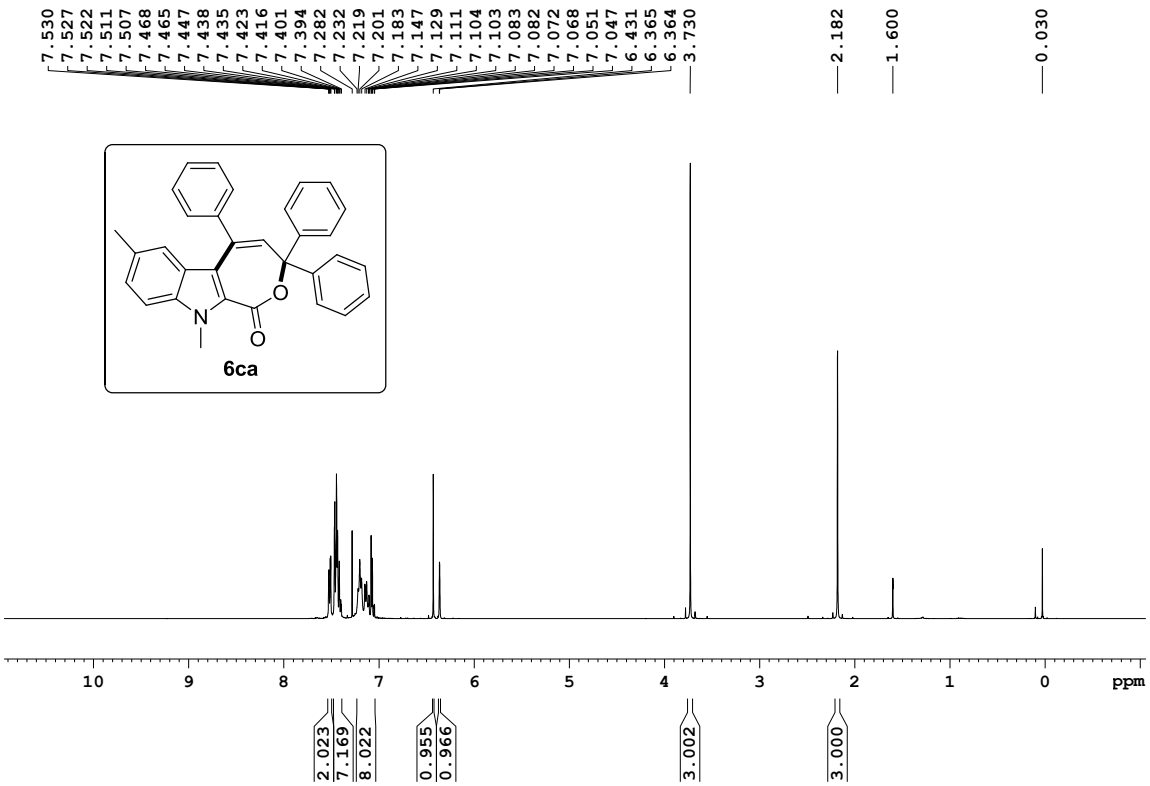


Figure S31. ^{1}H NMR spectrum of compound **6ca**

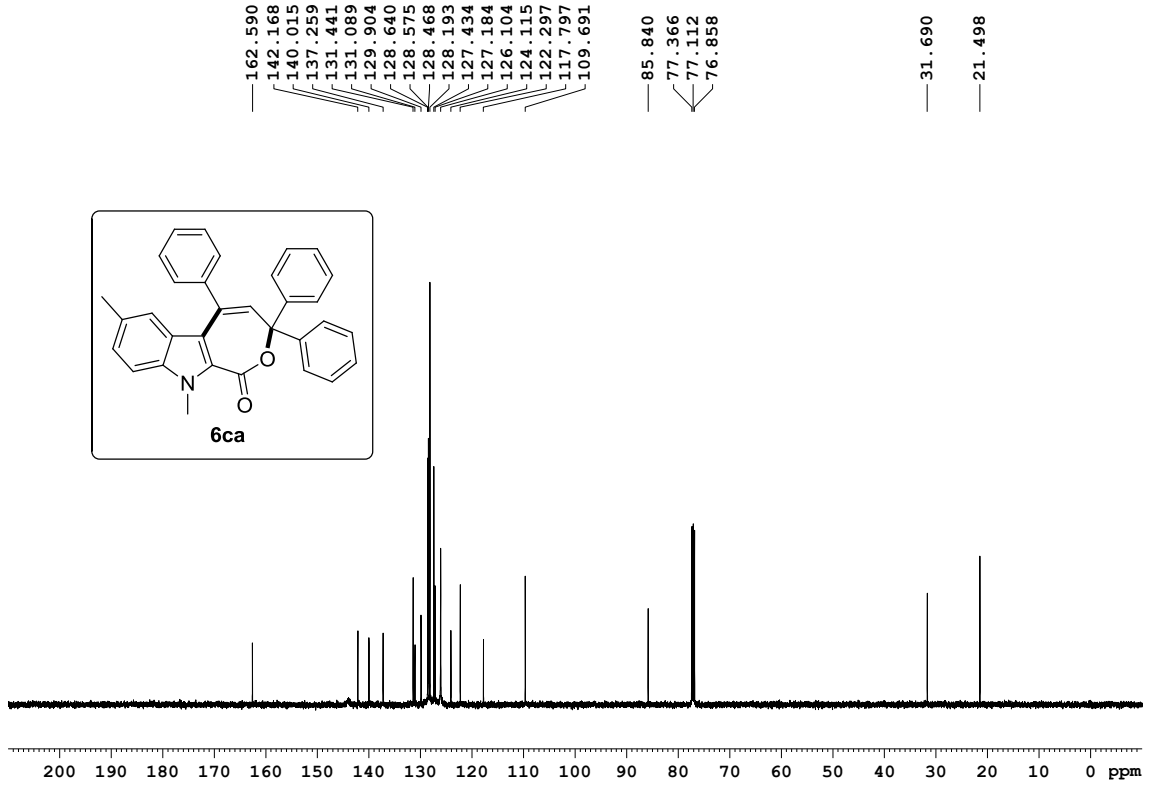


Figure S32. ^{13}C NMR spectrum of compound **6ca**

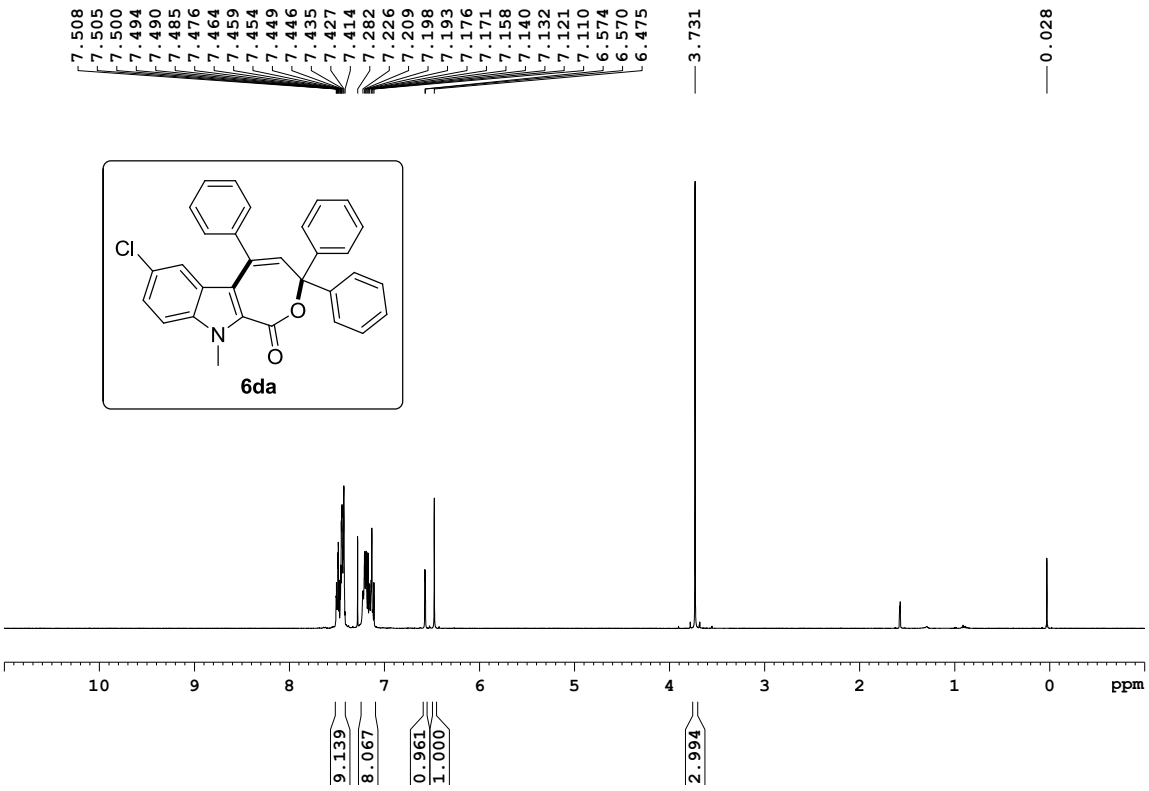


Figure S33. ^{1}H NMR spectrum of compound **6da**

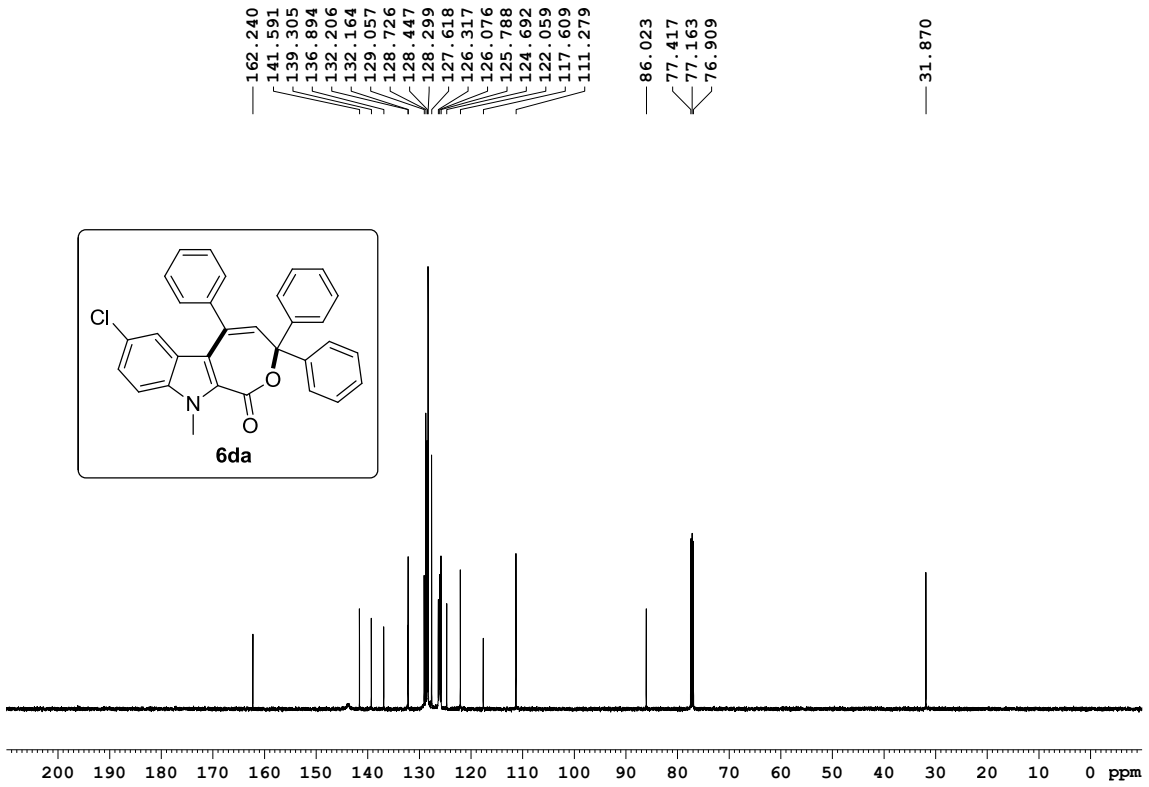


Figure S34. ^{13}C NMR spectrum of compound **6da**

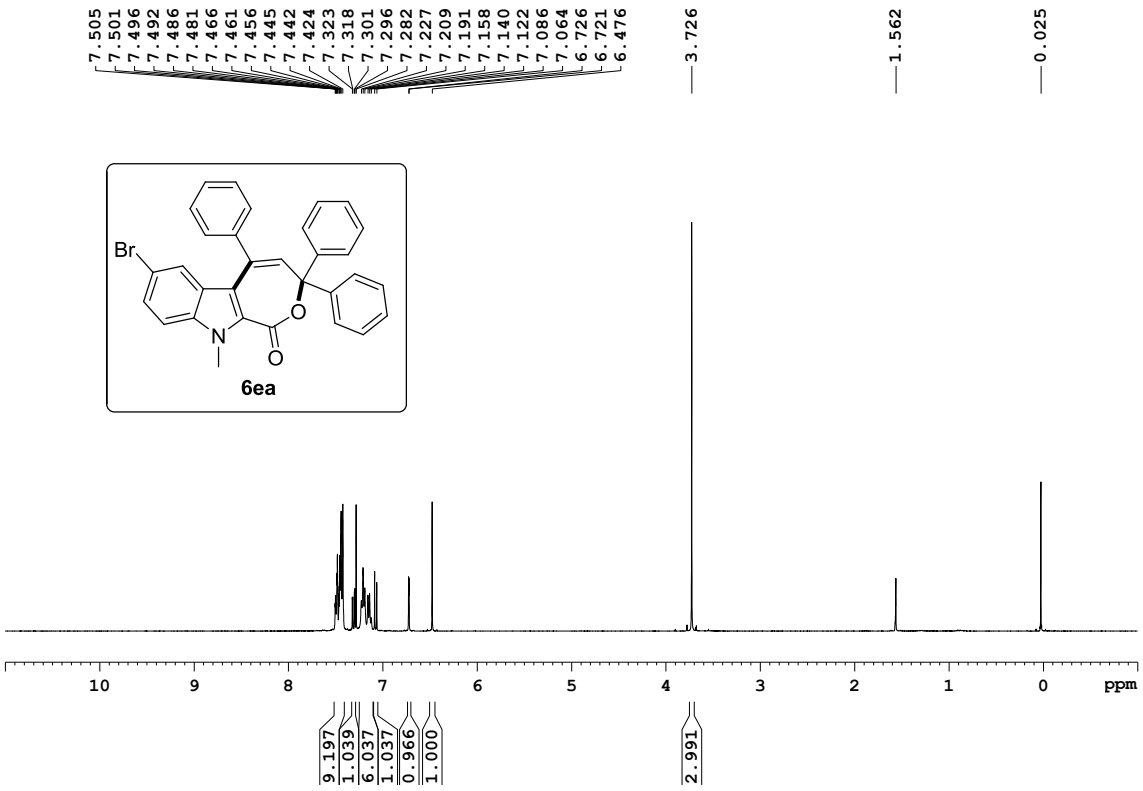


Figure S35. ^{1}H NMR spectrum of compound **6ea**

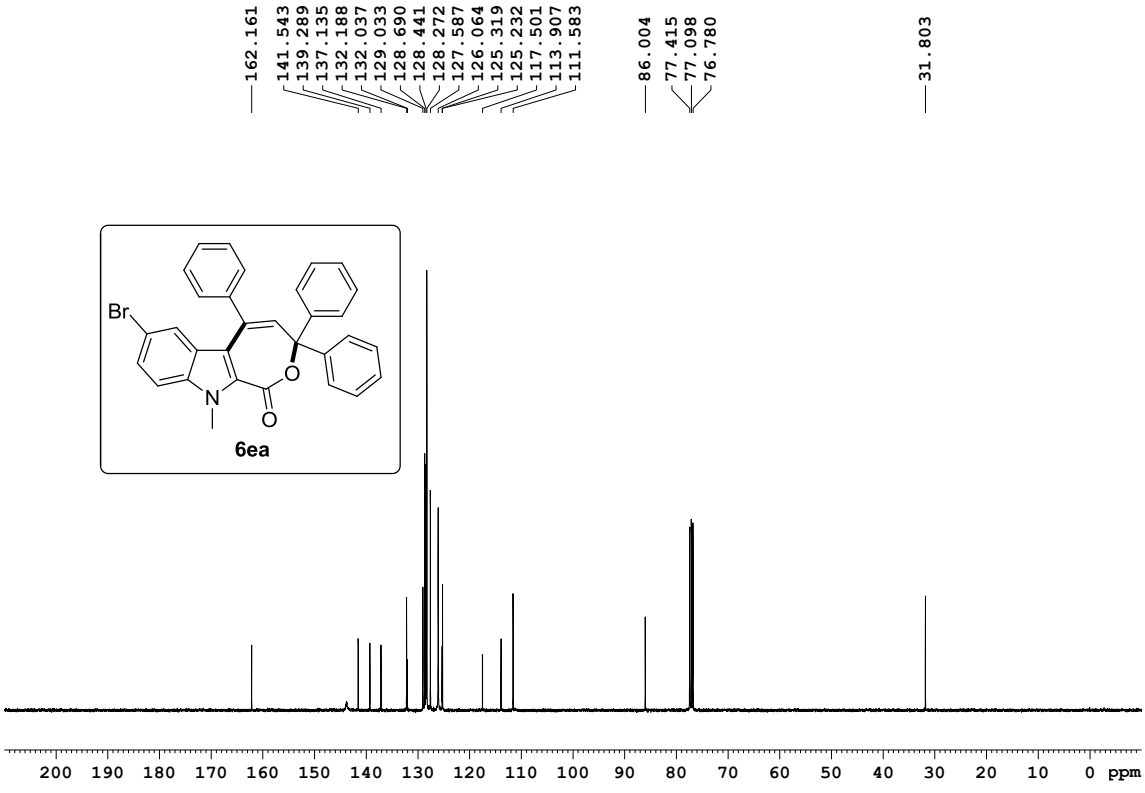


Figure S36. ^{13}C NMR spectrum of compound **6ea**

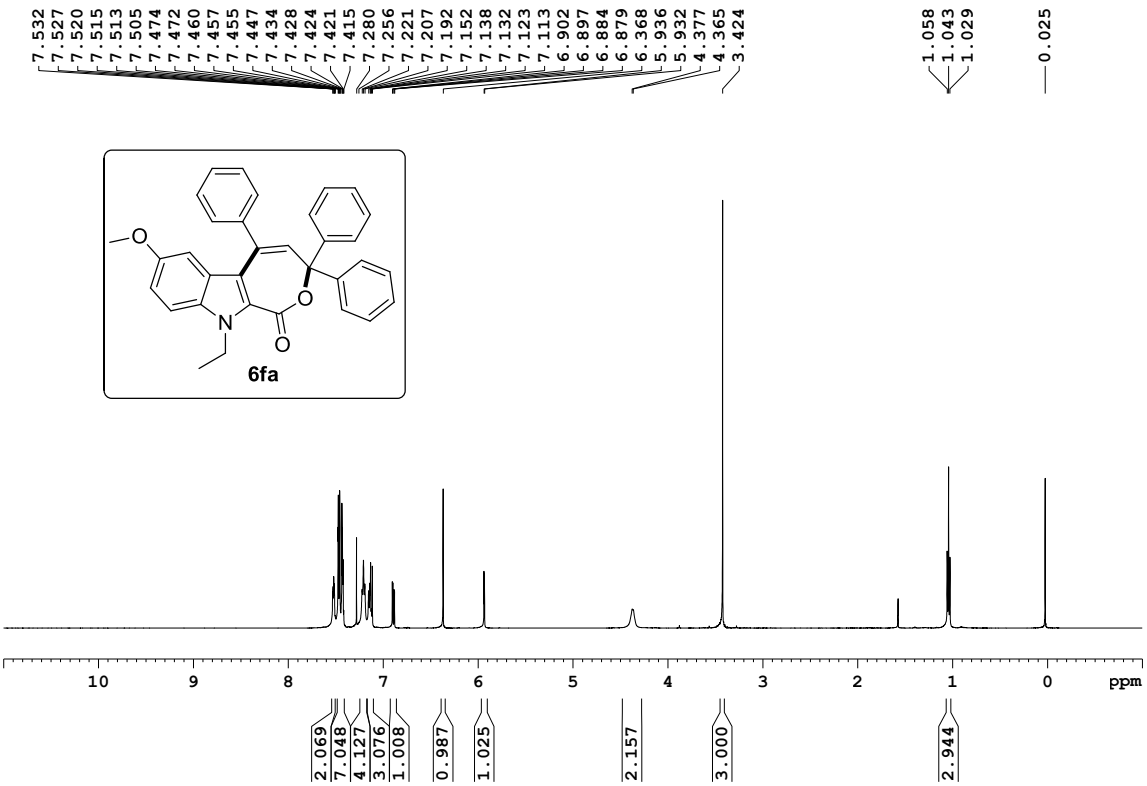


Figure S37. ^{1}H NMR spectrum of compound **6fa**

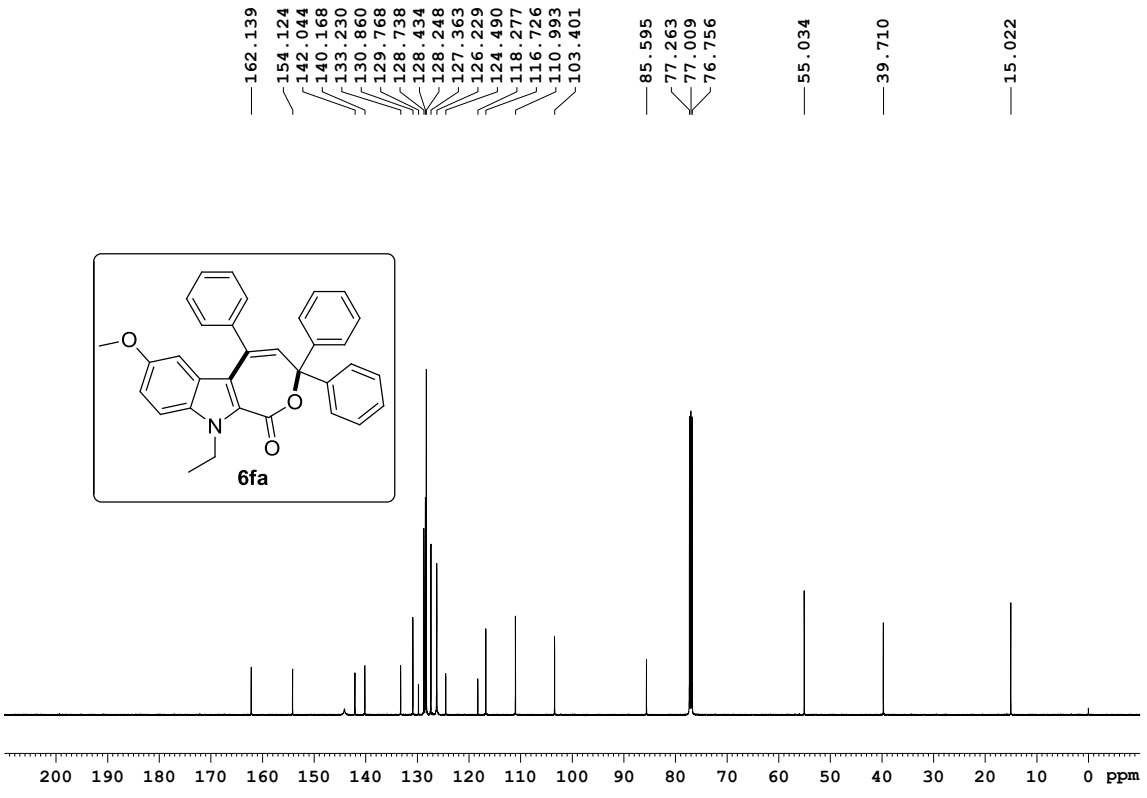


Figure S38. ^{13}C NMR spectrum of compound **6fa**

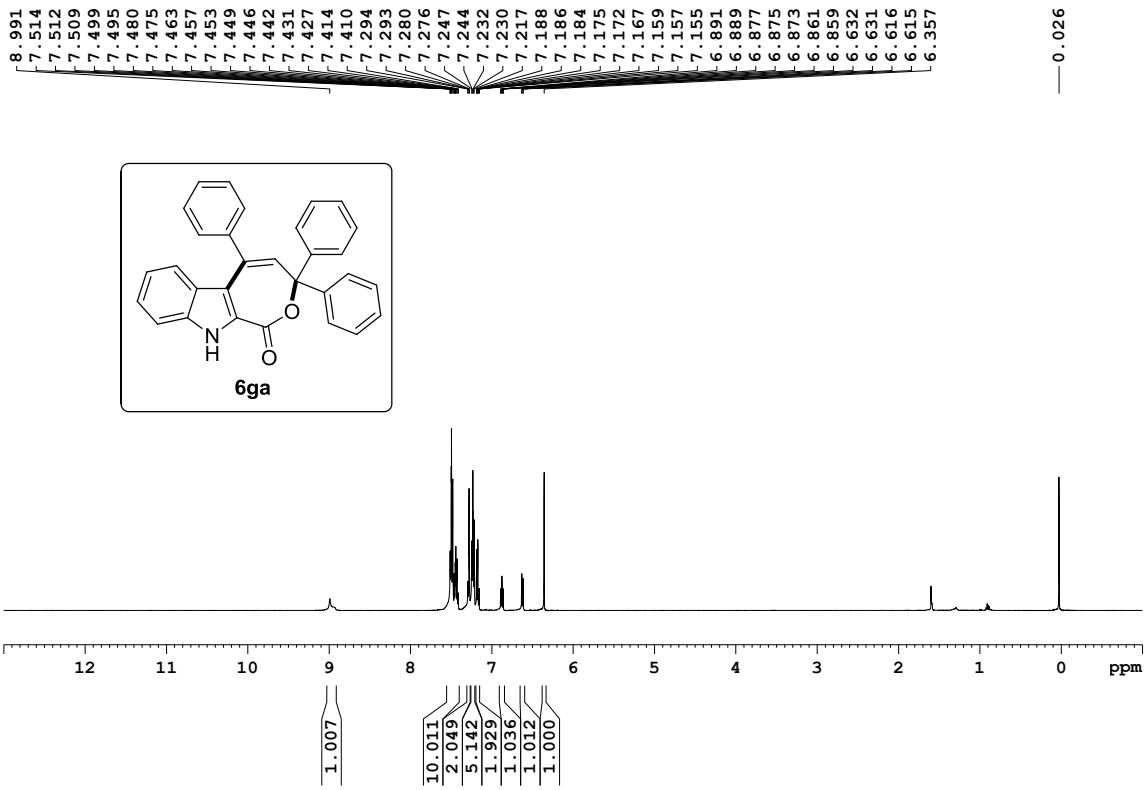


Figure S39. ^{1}H NMR spectrum of compound **6ga**

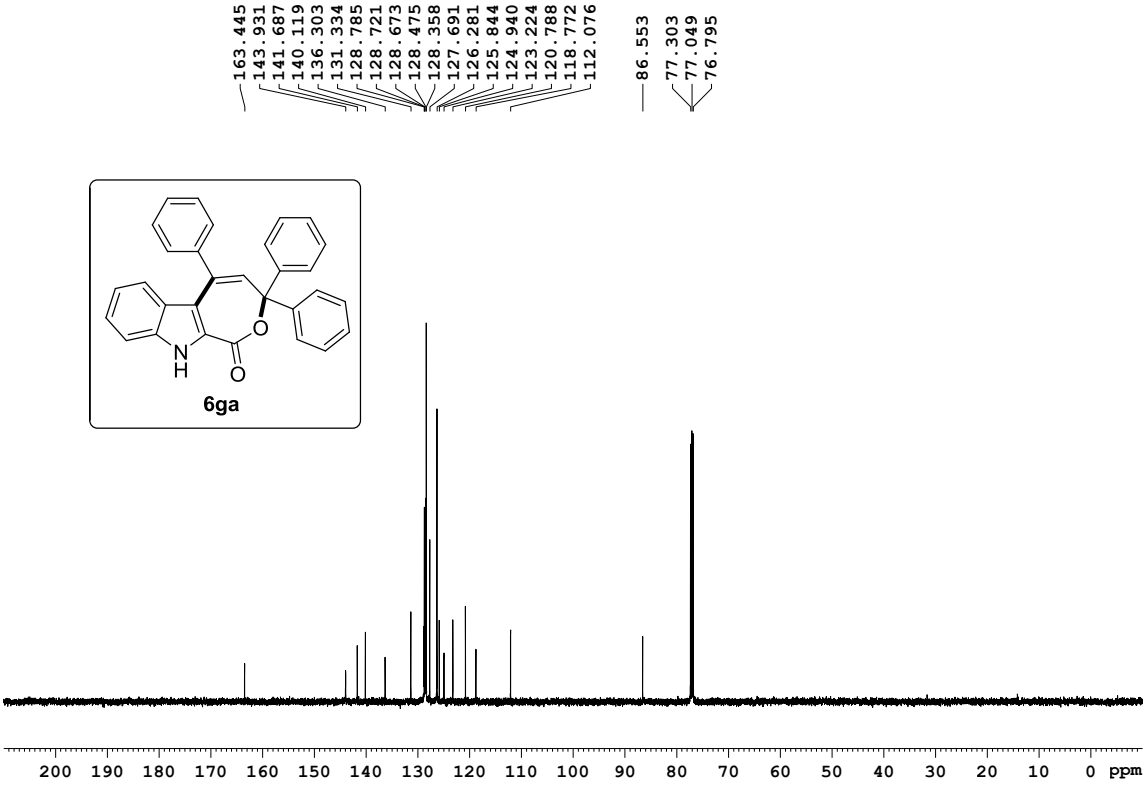


Figure S40. ^{13}C NMR spectrum of compound **6ga**

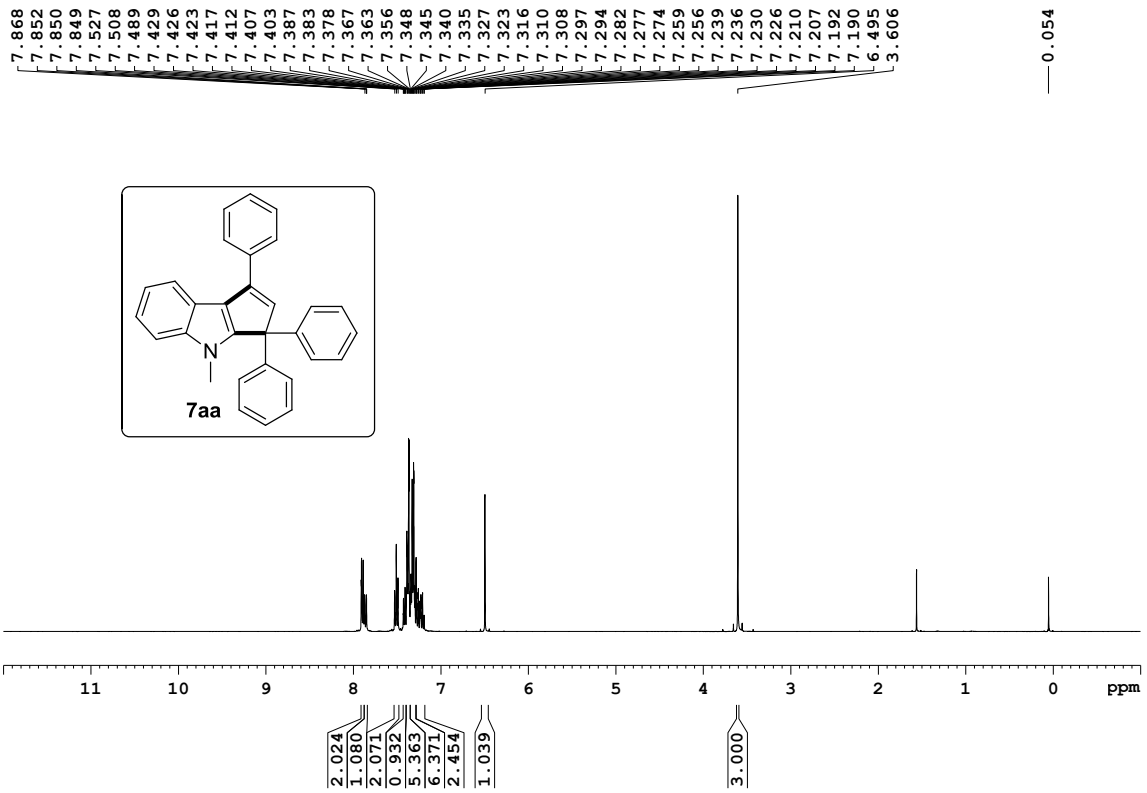


Figure S41. ^{1}H NMR spectrum of compound **7aa**

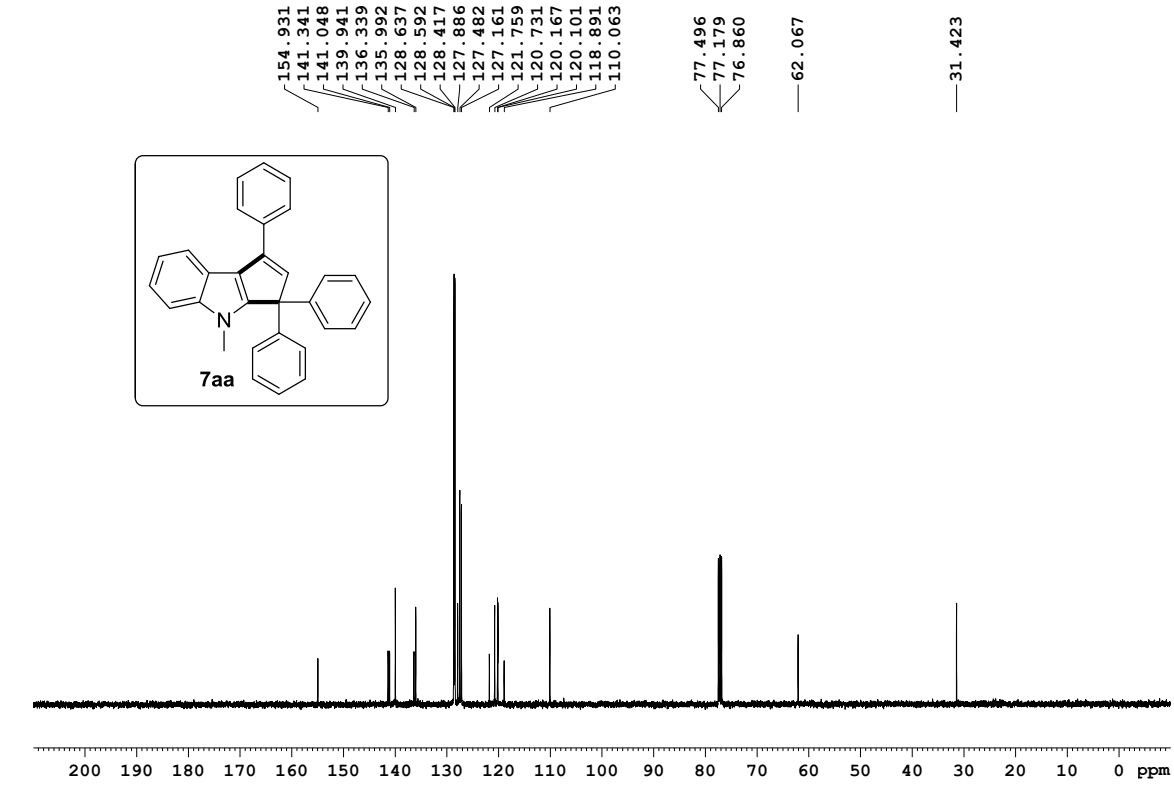


Figure S42. ^{13}C NMR spectrum of compound **7aa**

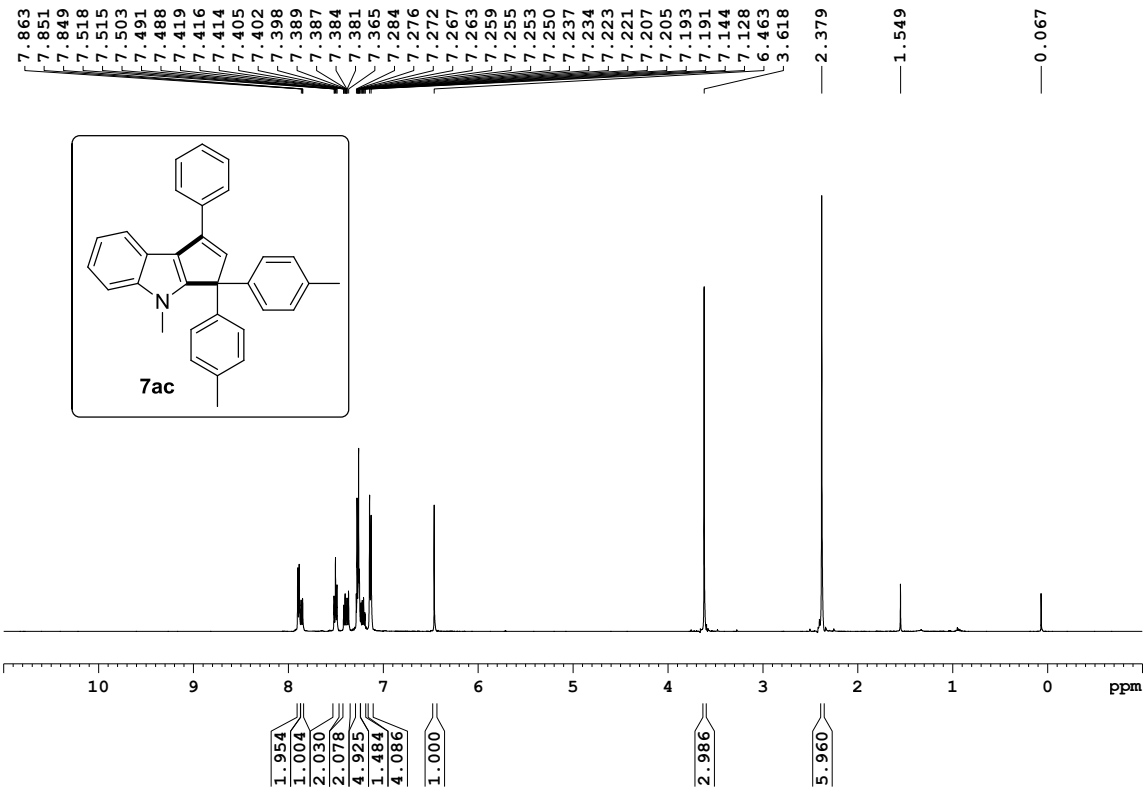


Figure S43. ^{1}H NMR spectrum of compound **7ac**

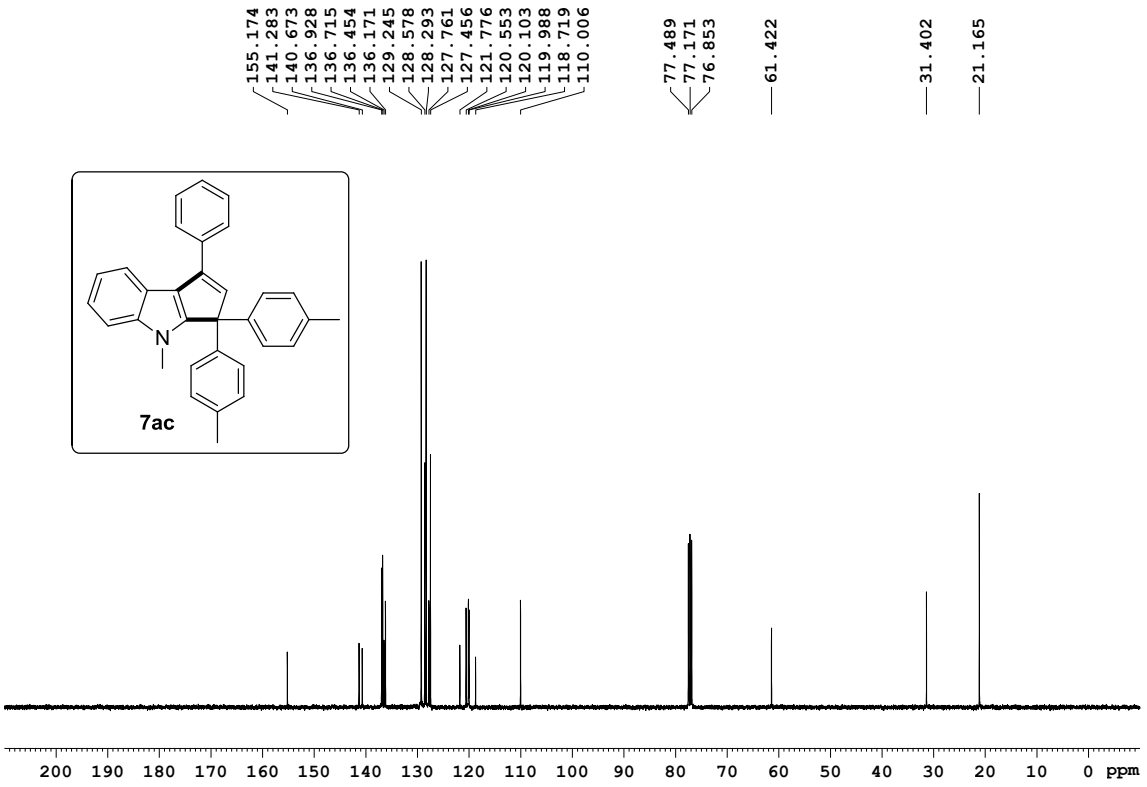


Figure S44. ^{13}C NMR spectrum of compound **7ac**

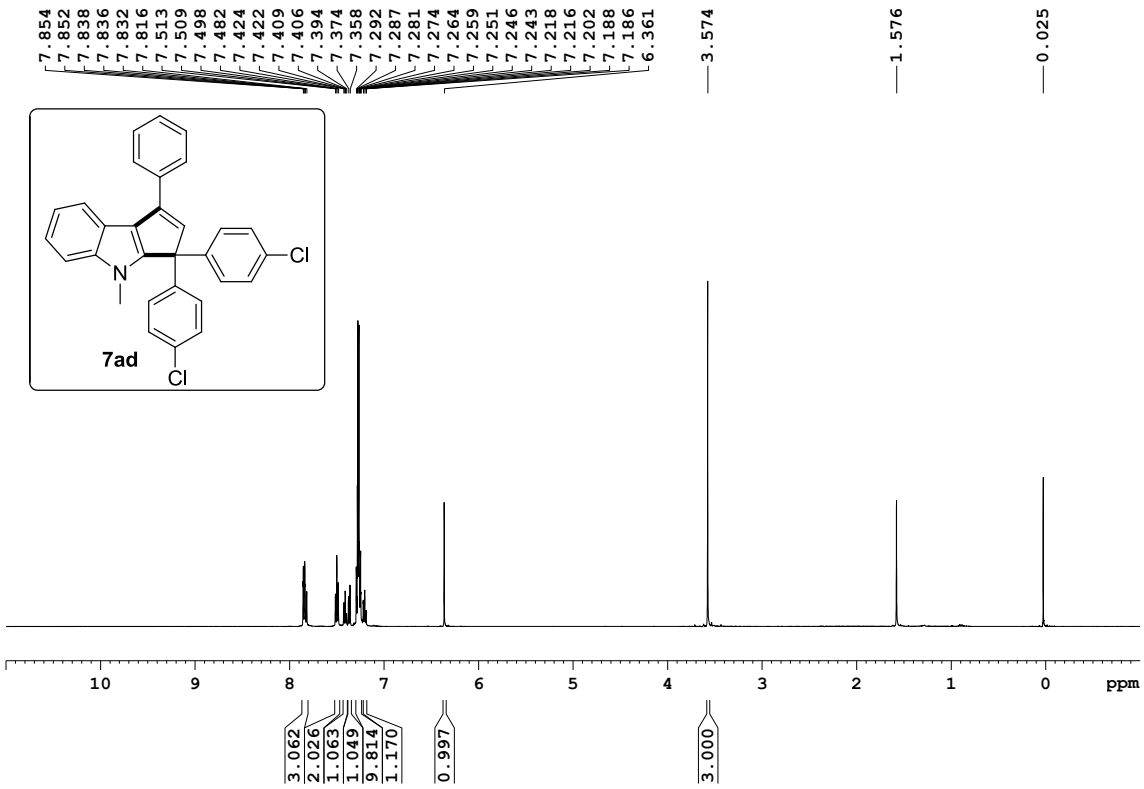


Figure S45. ^{1}H NMR spectrum of compound **7ad**

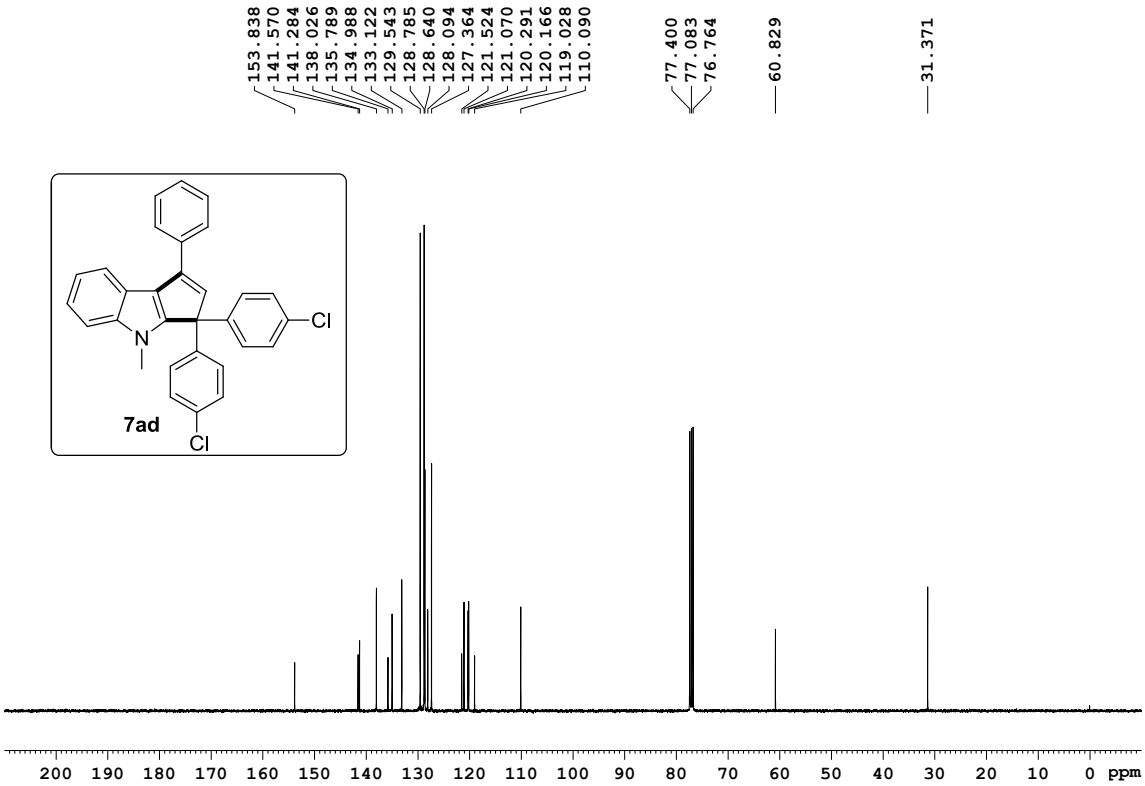


Figure S46. ^{13}C NMR spectrum of compound **7ad**

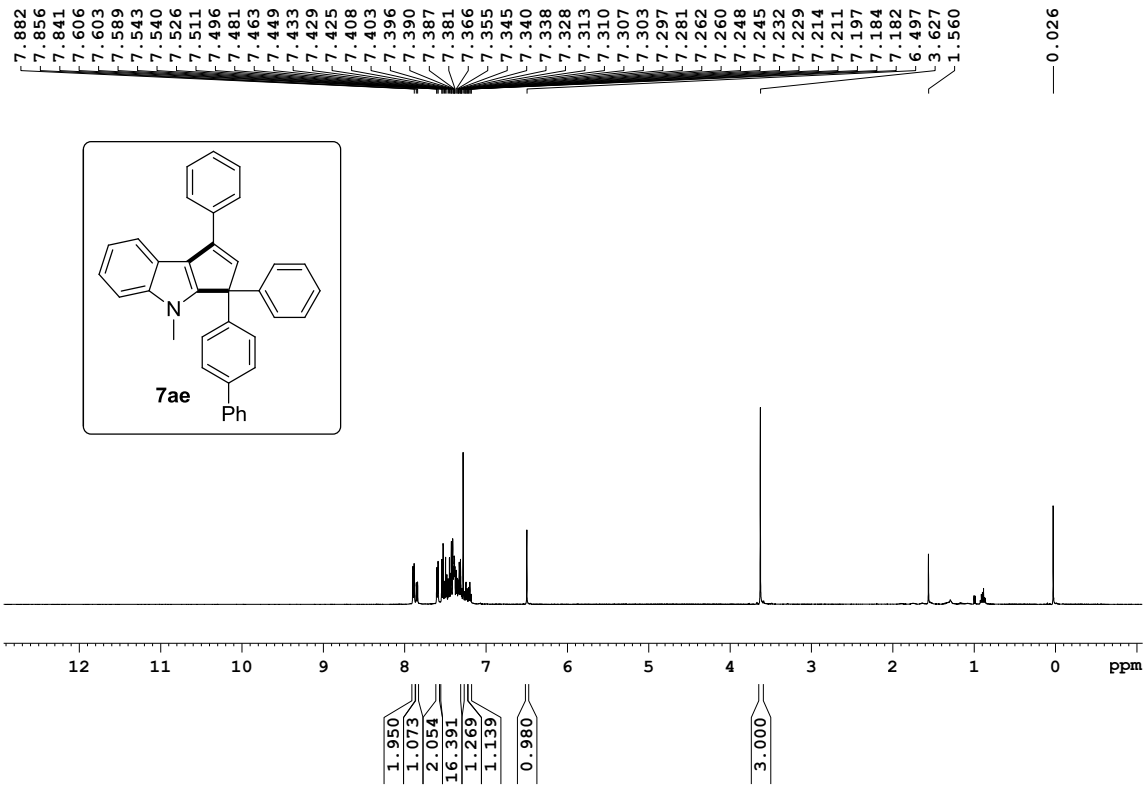


Figure S47. ^{1}H NMR spectrum of compound **7ae**

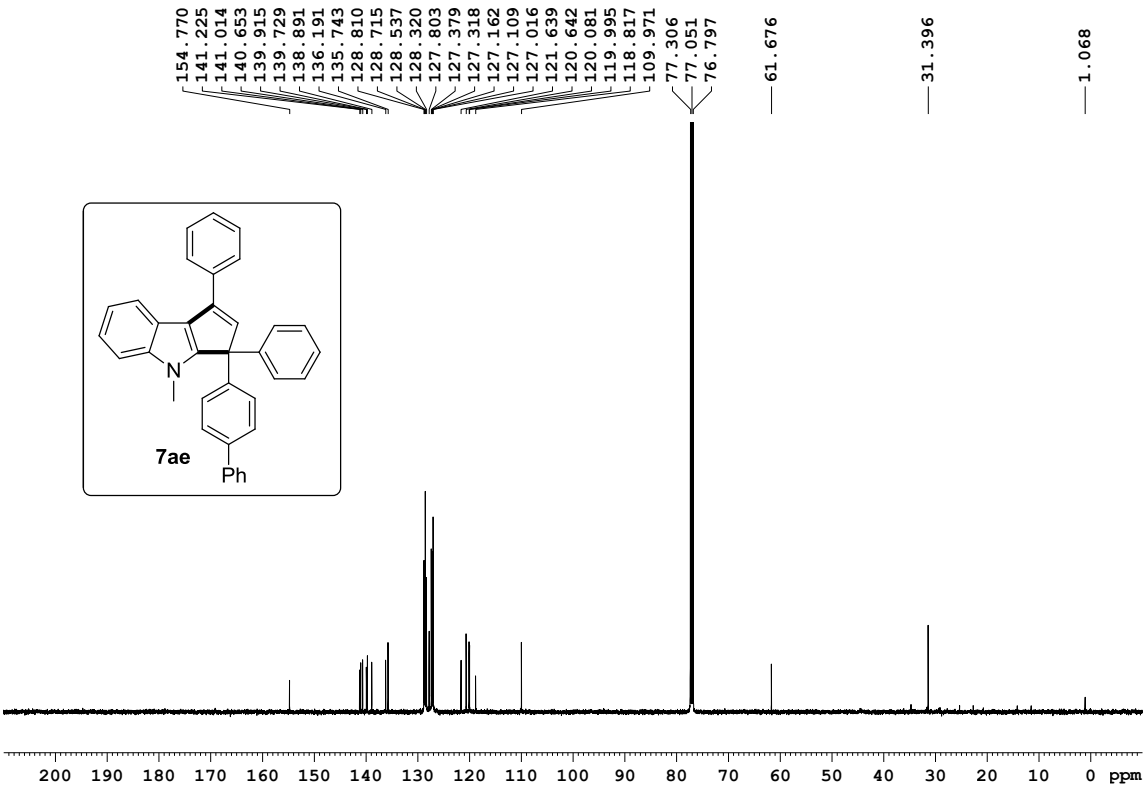


Figure S48. ^{13}C NMR spectrum of compound **7ae**

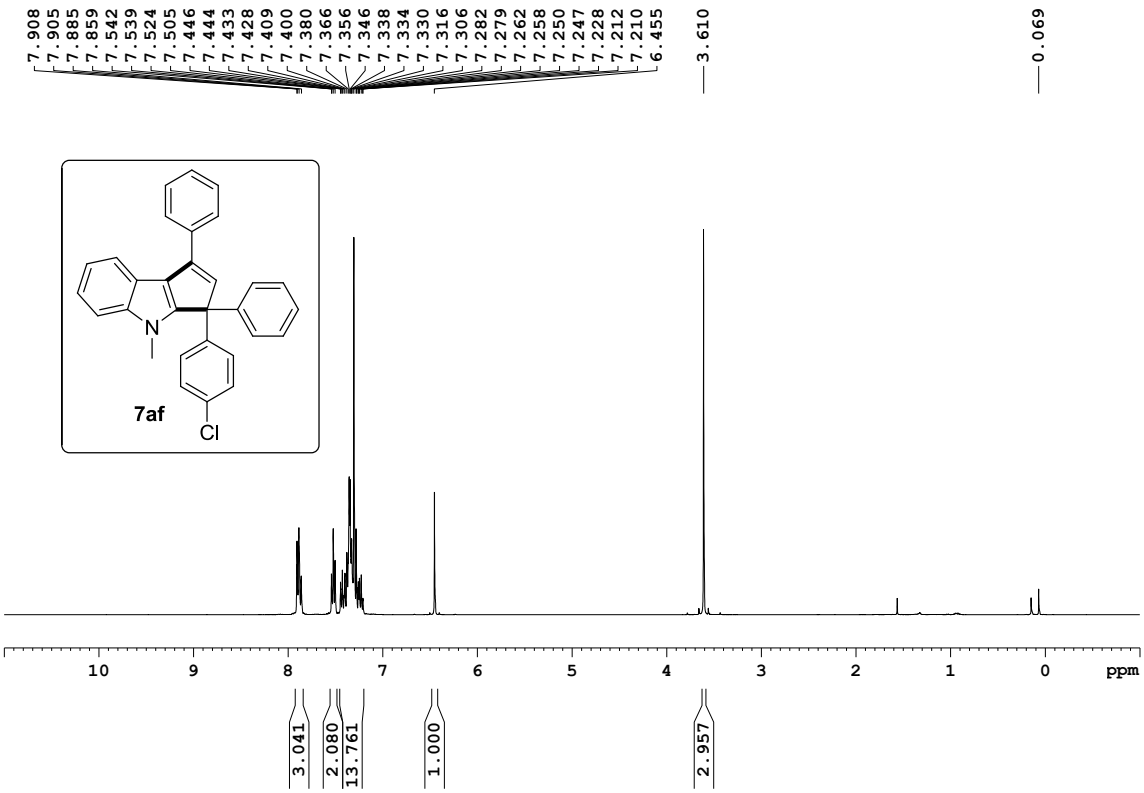


Figure S49. ^{1}H NMR spectrum of compound **7af**

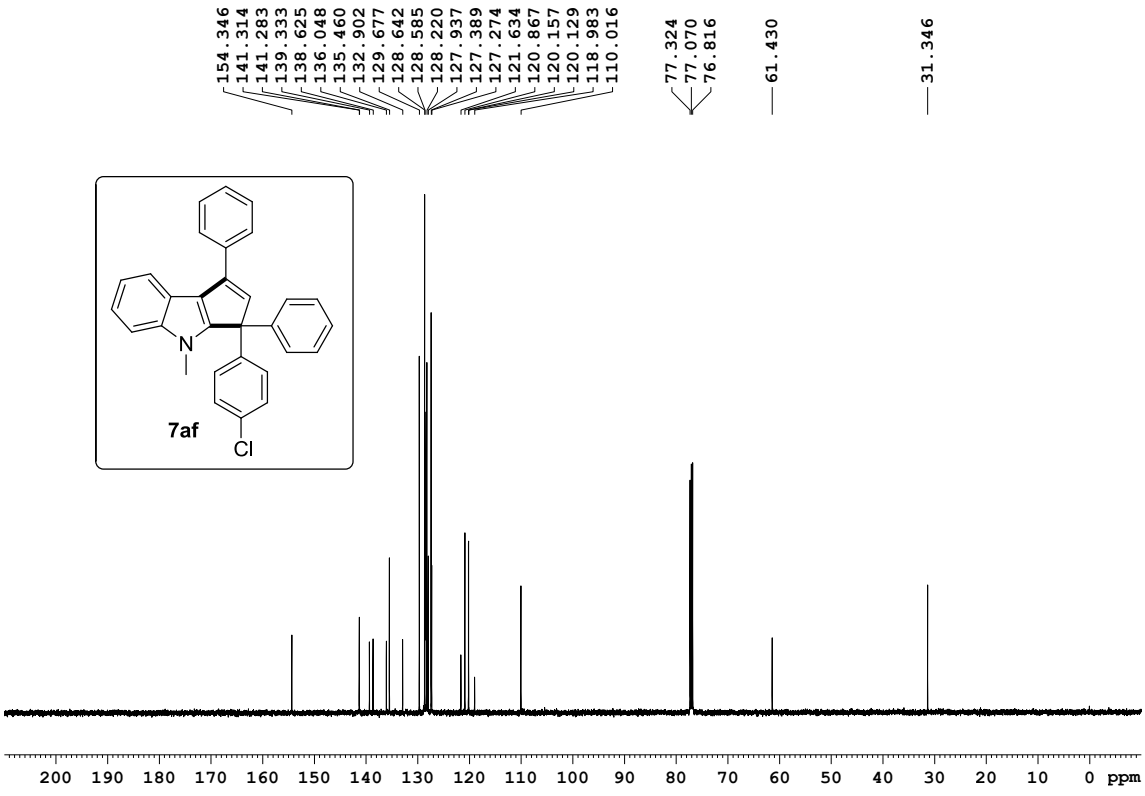


Figure S50. ^{13}C NMR spectrum of compound **7af**

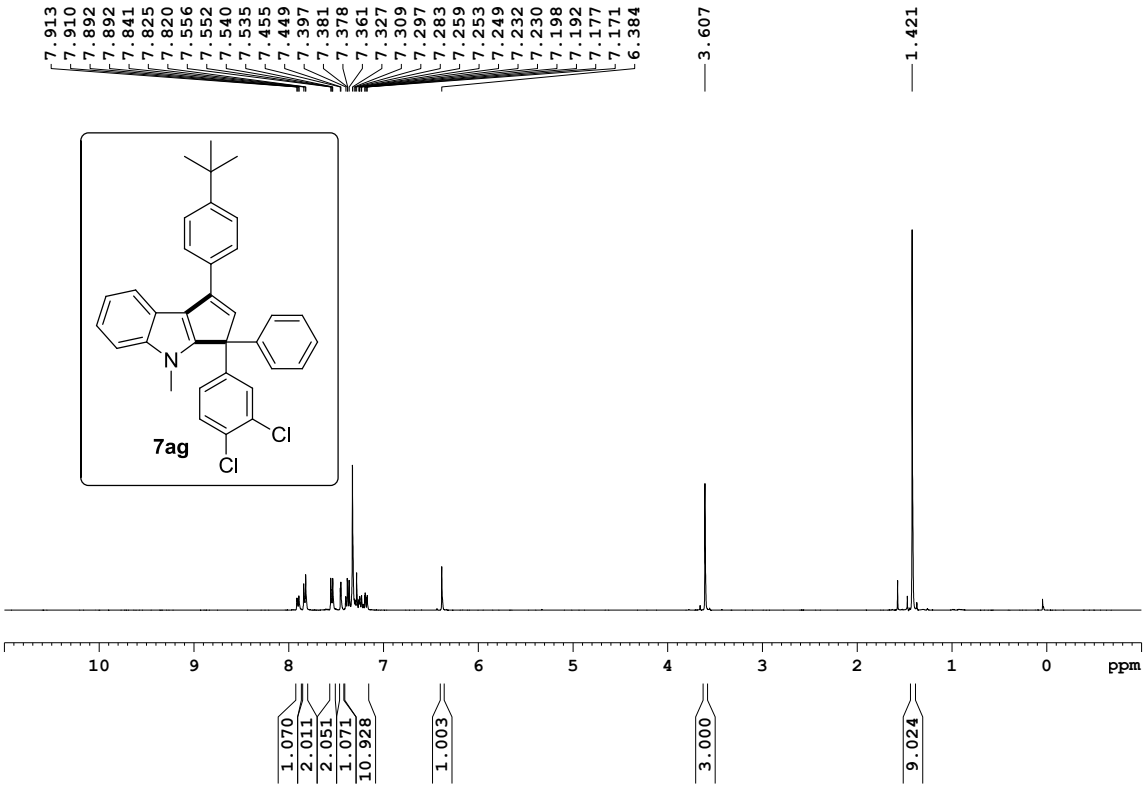


Figure S51. ^{1}H NMR spectrum of compound **7ag**

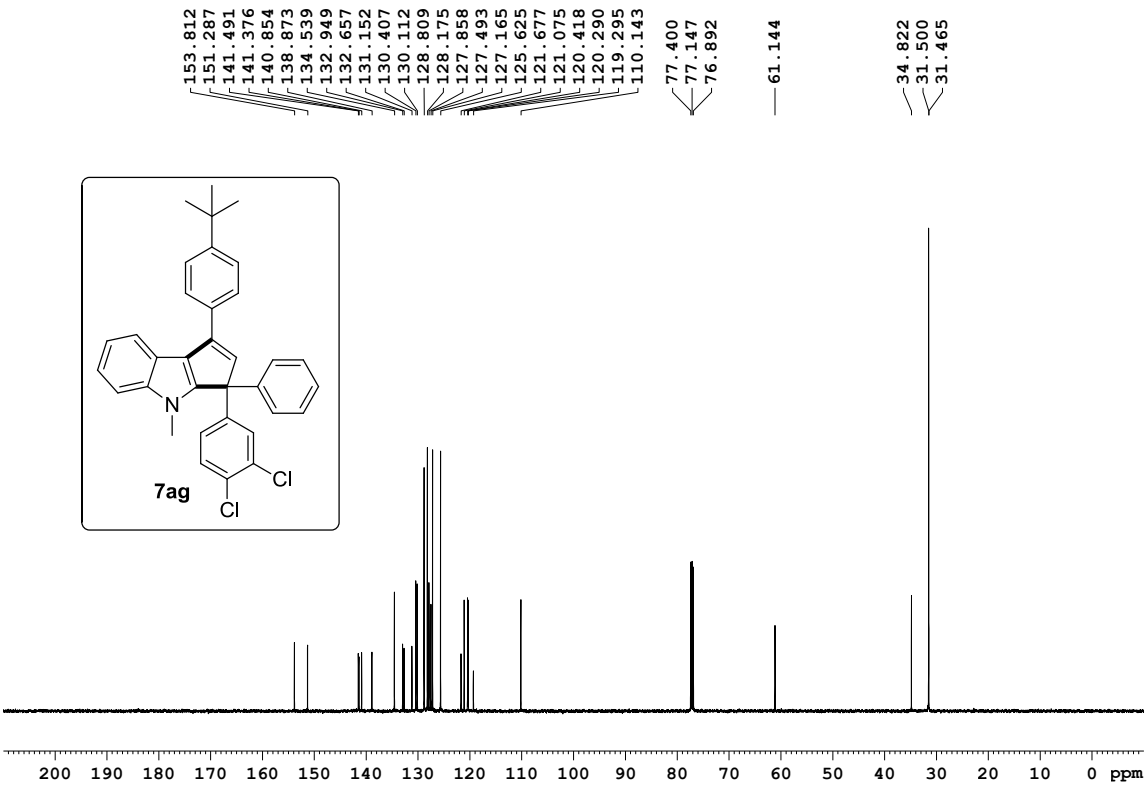


Figure S52. ^{13}C NMR spectrum of compound **7ag**

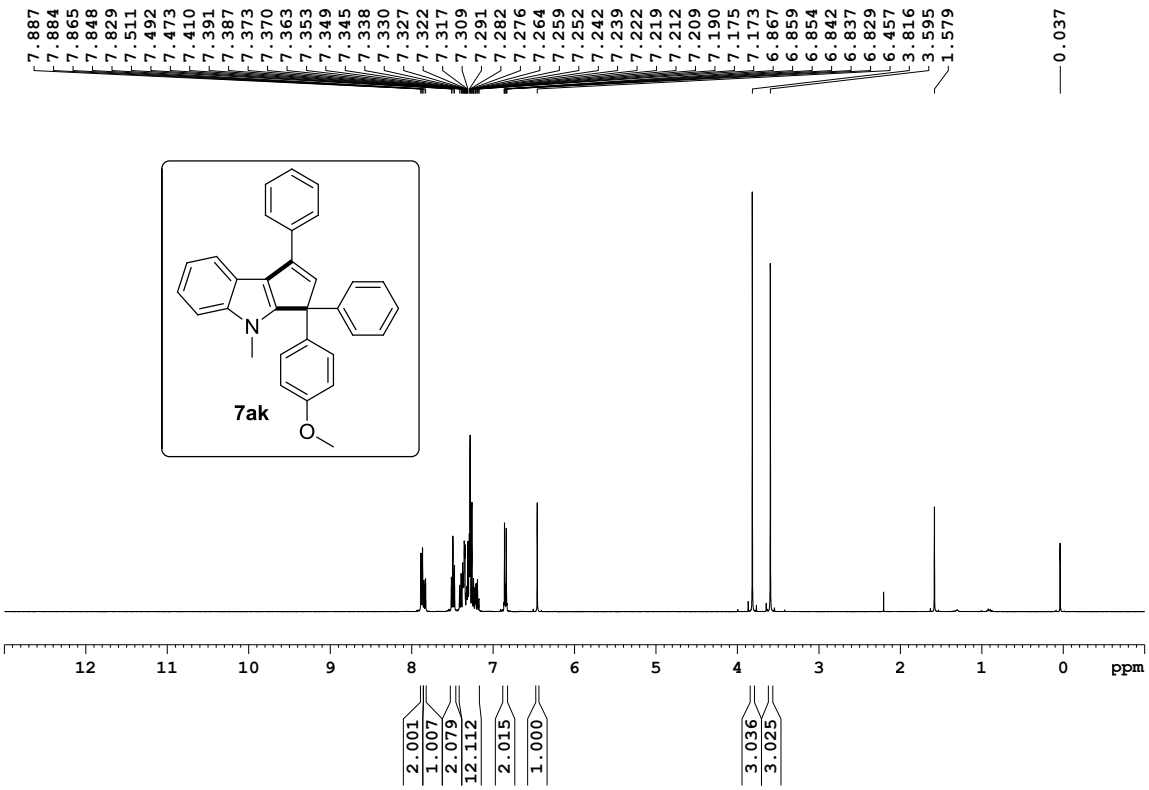


Figure S53. ^{1}H NMR spectrum of compound **7ak**

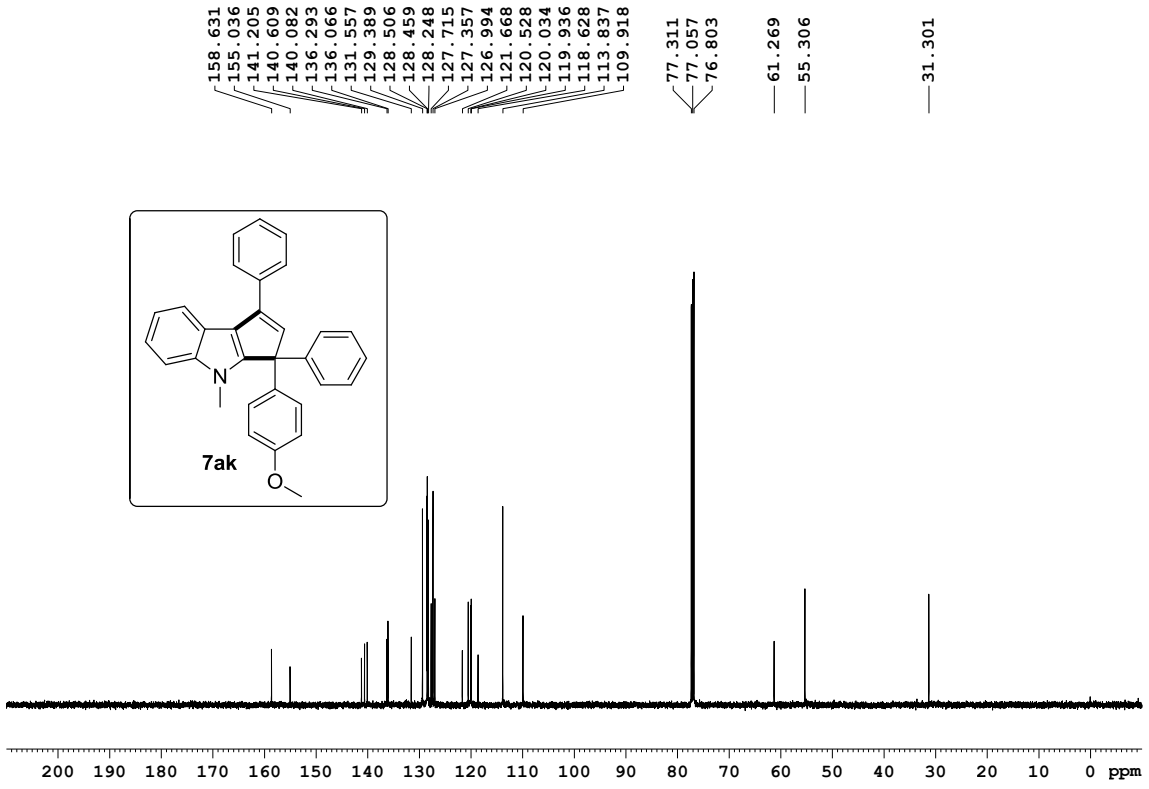


Figure S54. ^{13}C NMR spectrum of compound **7ak**

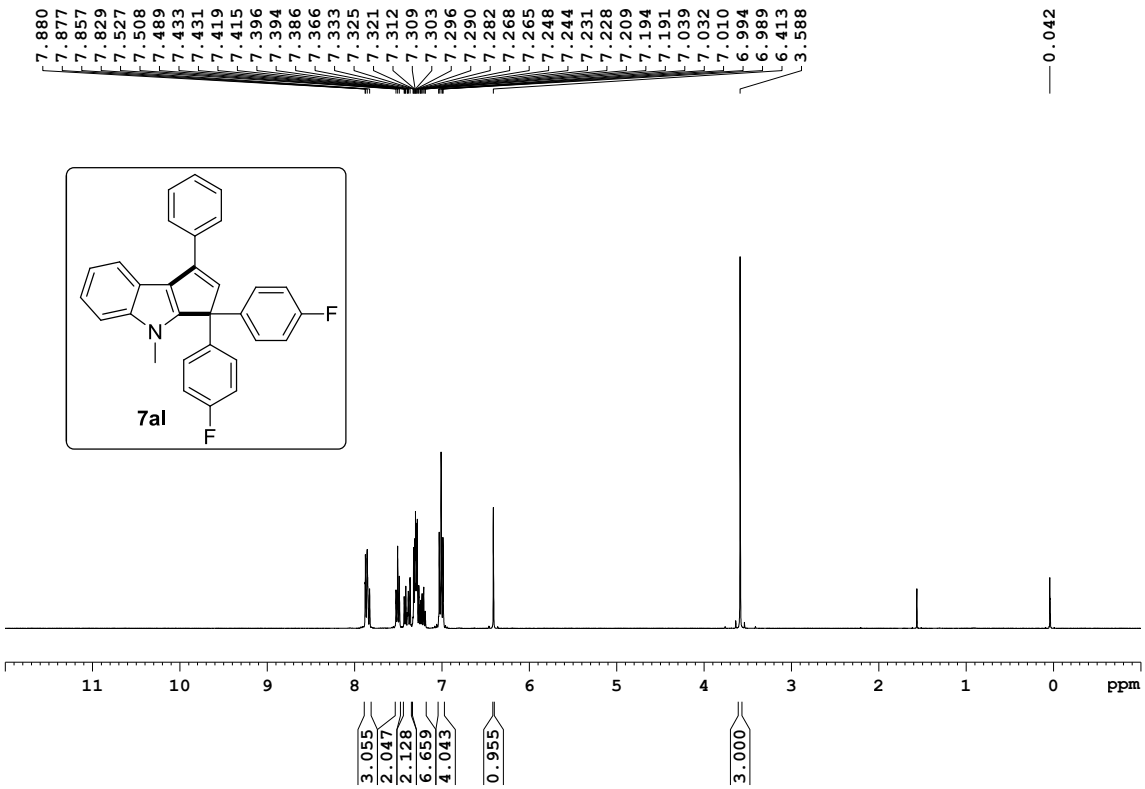


Figure S55. ^{1}H NMR spectrum of compound **7al**

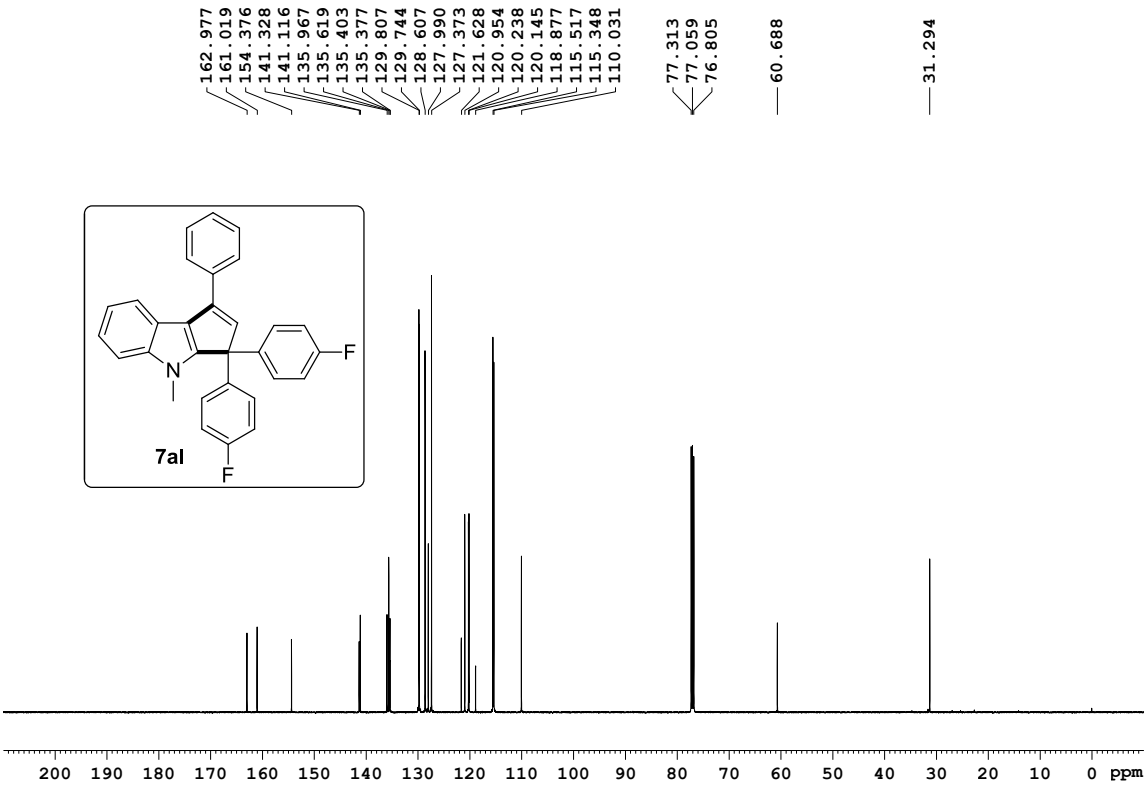


Figure S56. ^{13}C NMR spectrum of compound **7al**

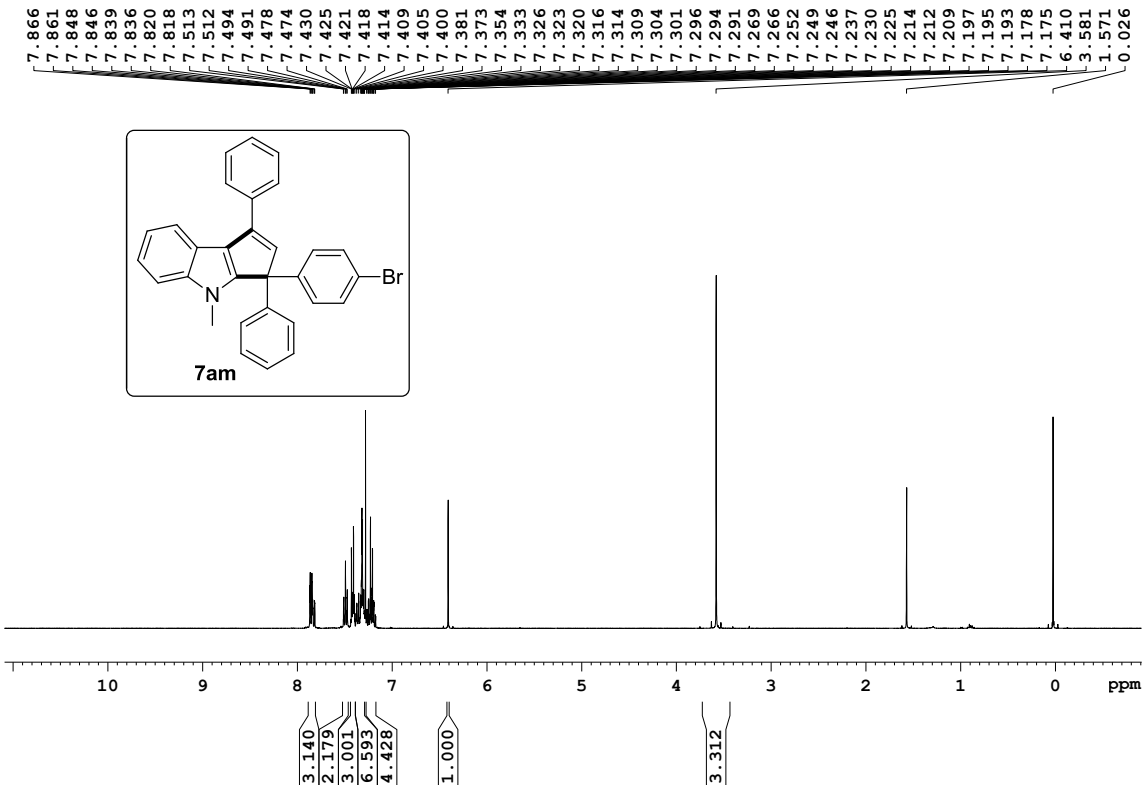


Figure S57. ^{1}H NMR spectrum of compound **7am**

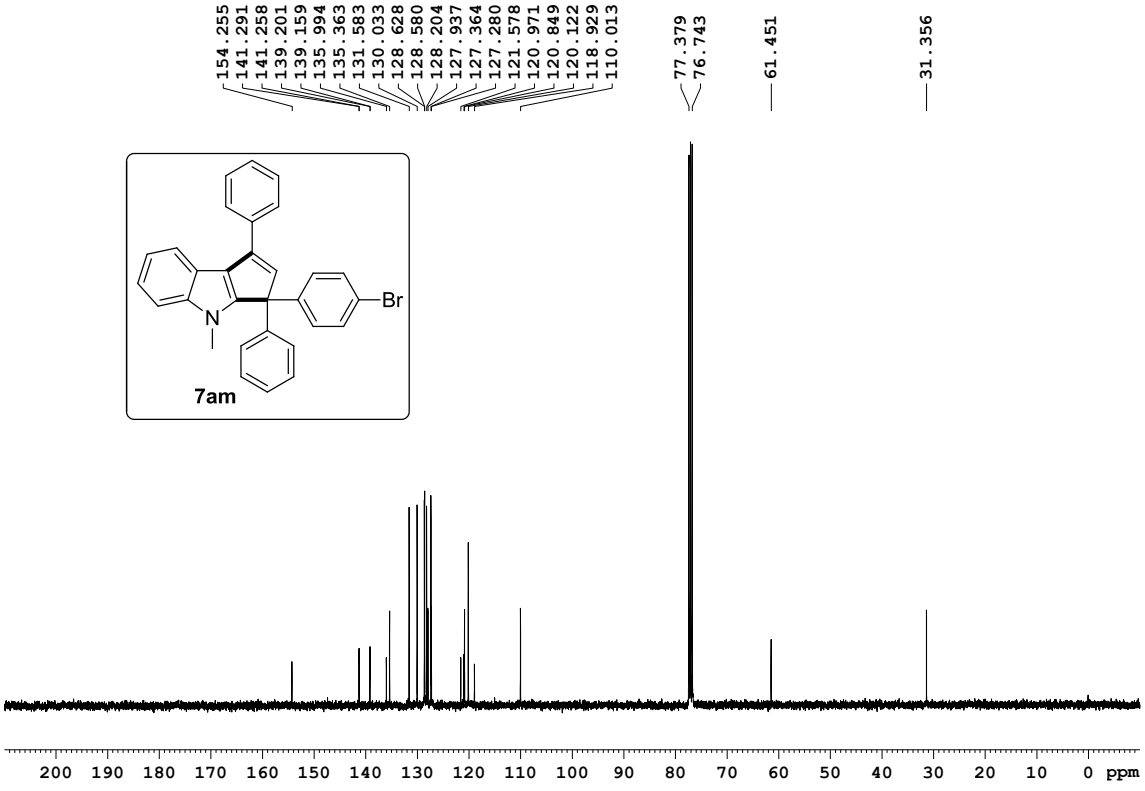


Figure S58. ^{13}C NMR spectrum of compound **7am**

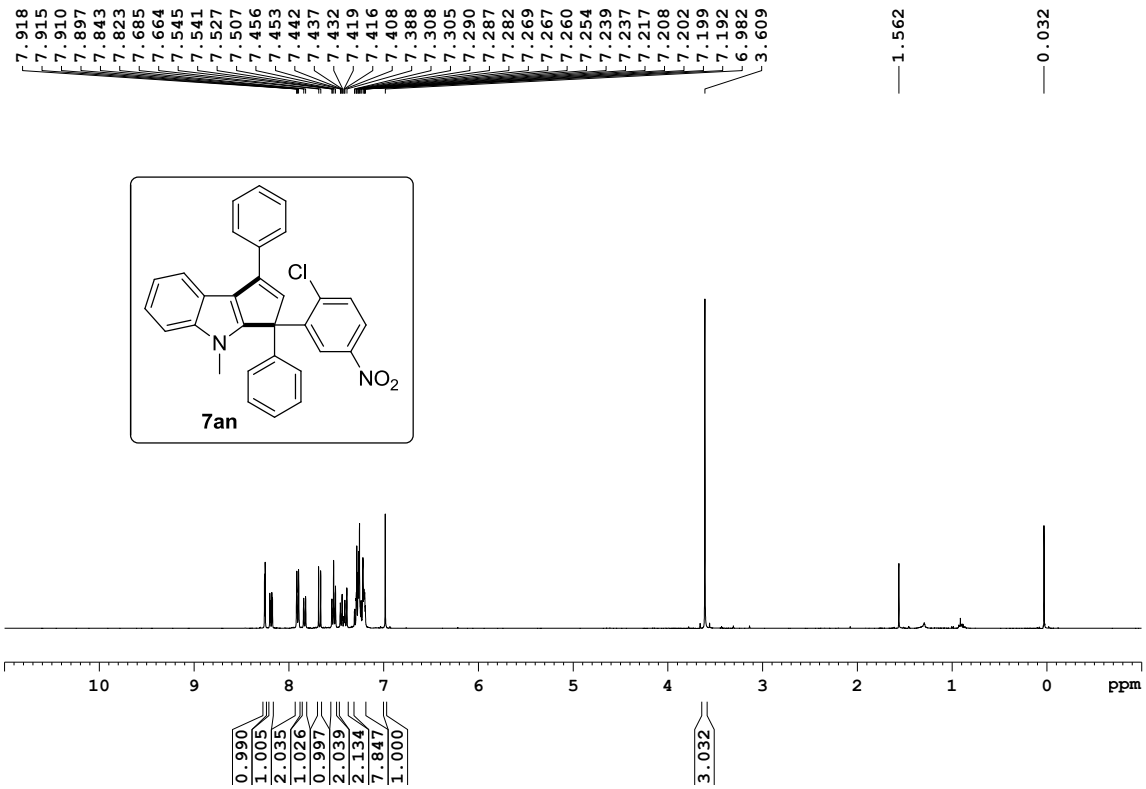


Figure S59. ^{1}H NMR spectrum of compound **7an**

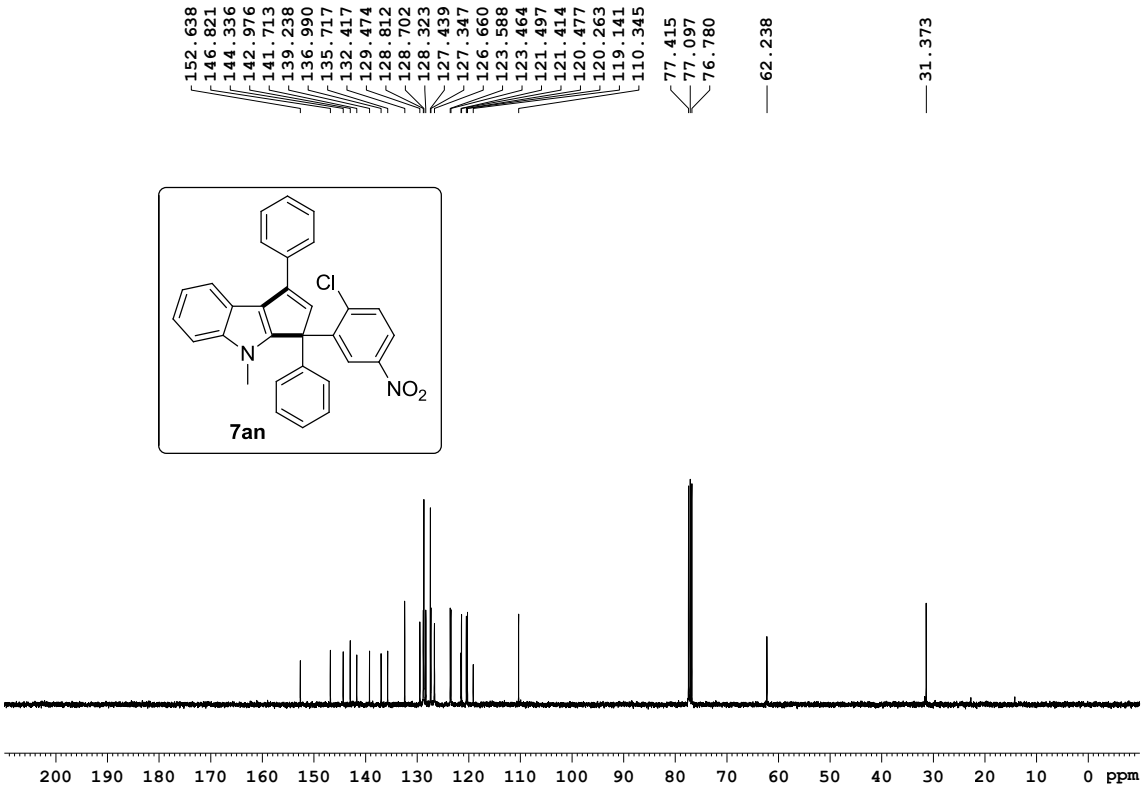


Figure S60. ^{13}C NMR spectrum of compound **7an**

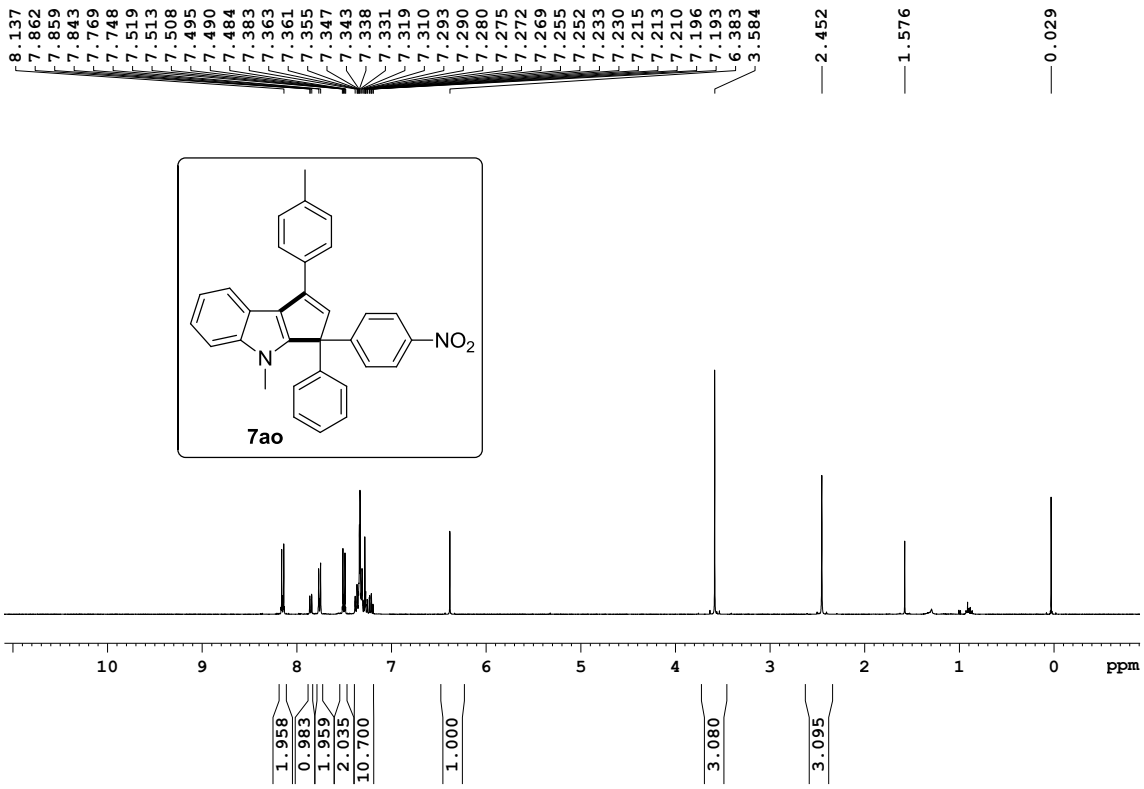


Figure S61. ^{1}H NMR spectrum of compound **7ao**

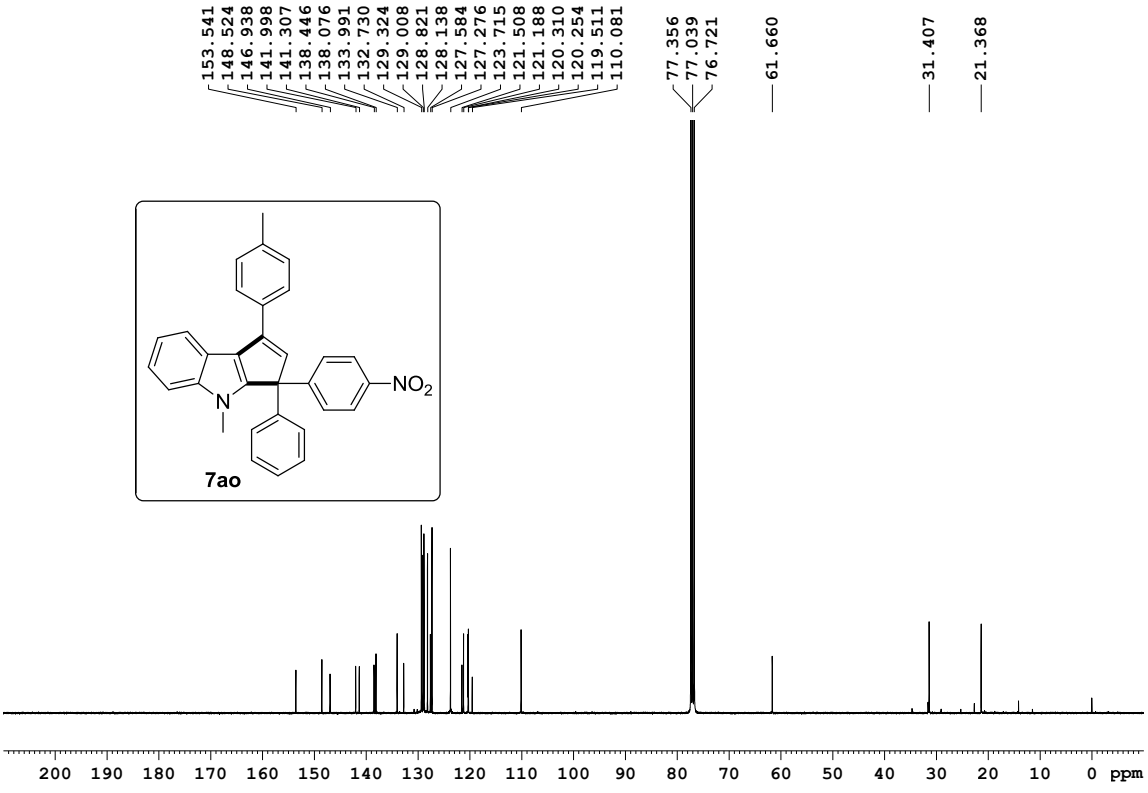


Figure S62. ^{13}C NMR spectrum of compound **7ao**

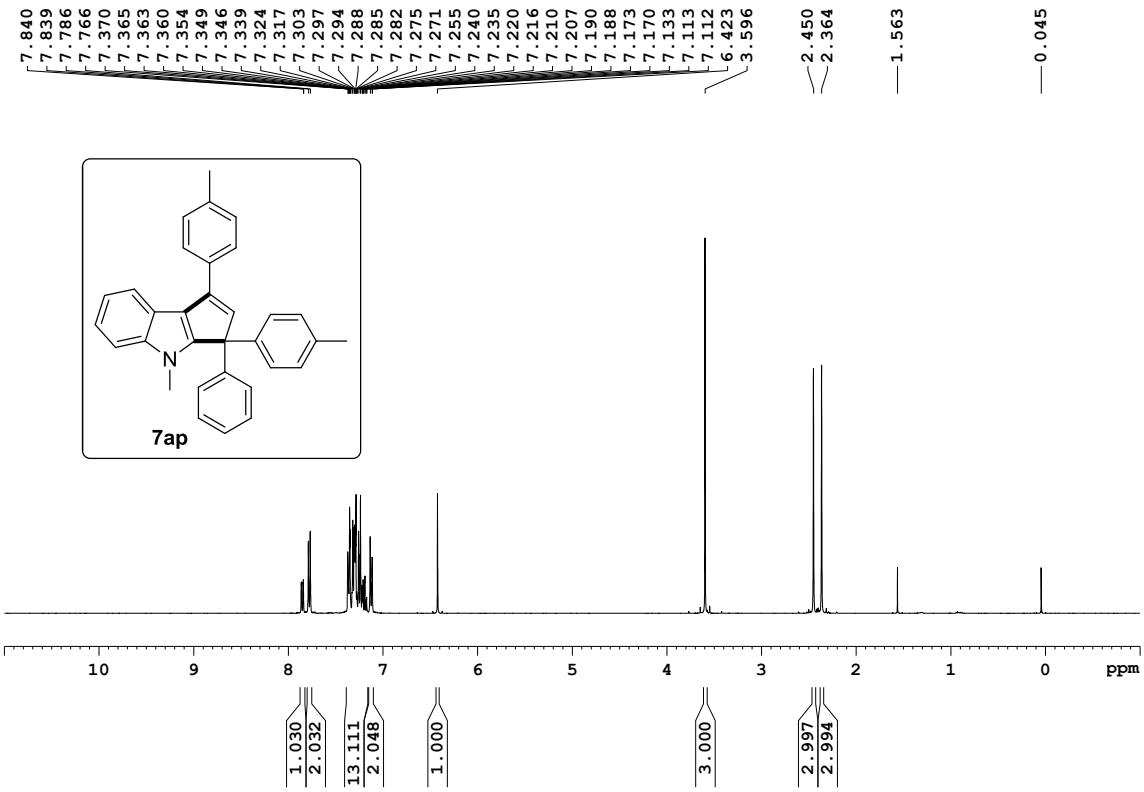


Figure S63. ^{1}H NMR spectrum of compound **7ap**

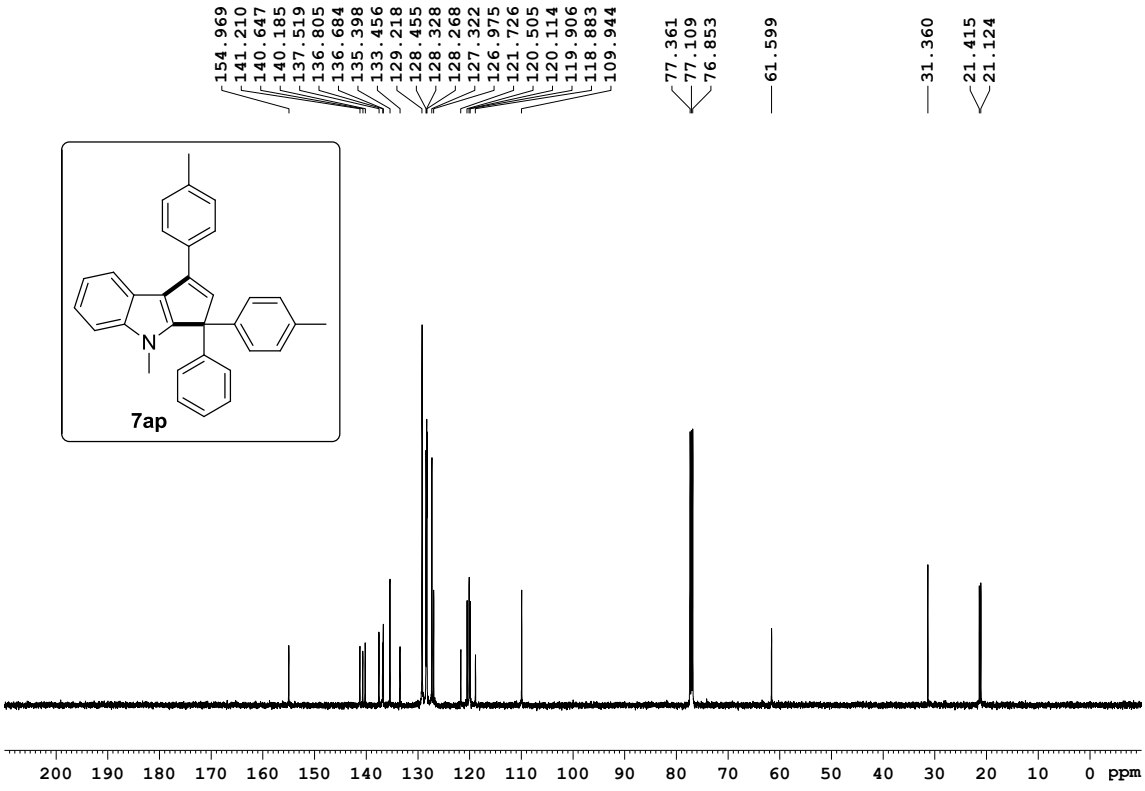


Figure S64. ^{13}C NMR spectrum of compound **7ap**

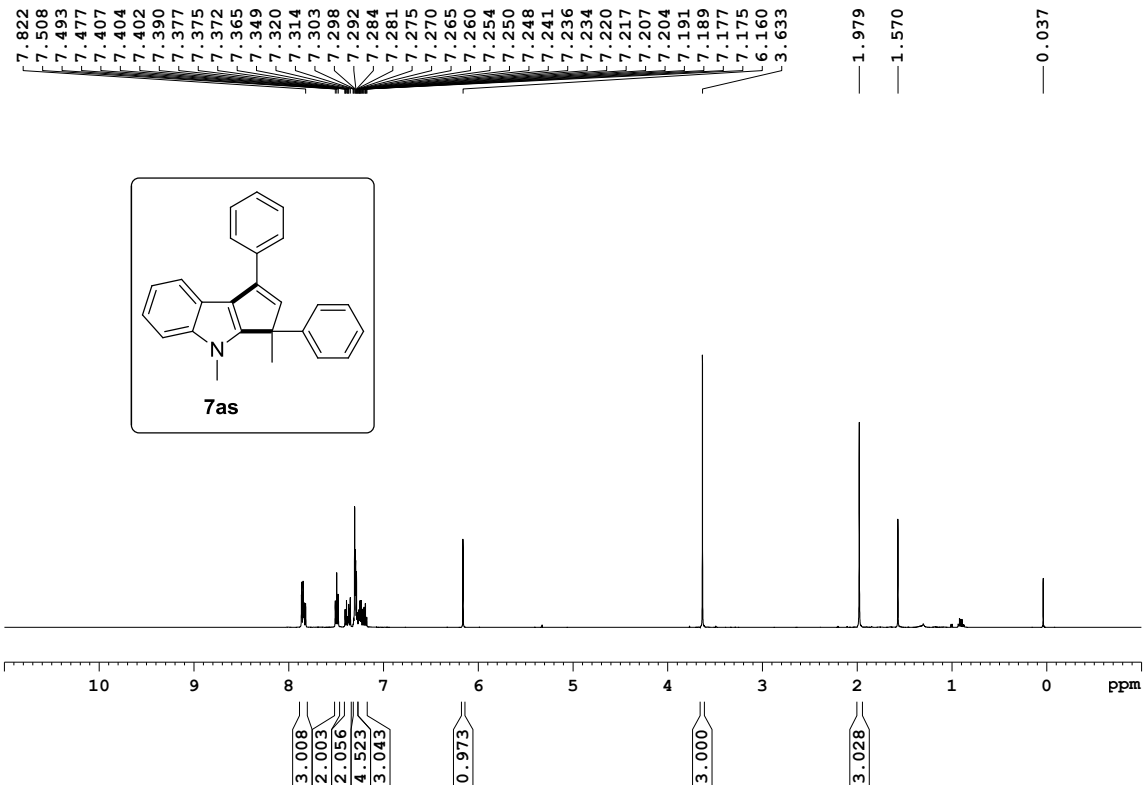


Figure S65. ^{1}H NMR spectrum of compound **7as**

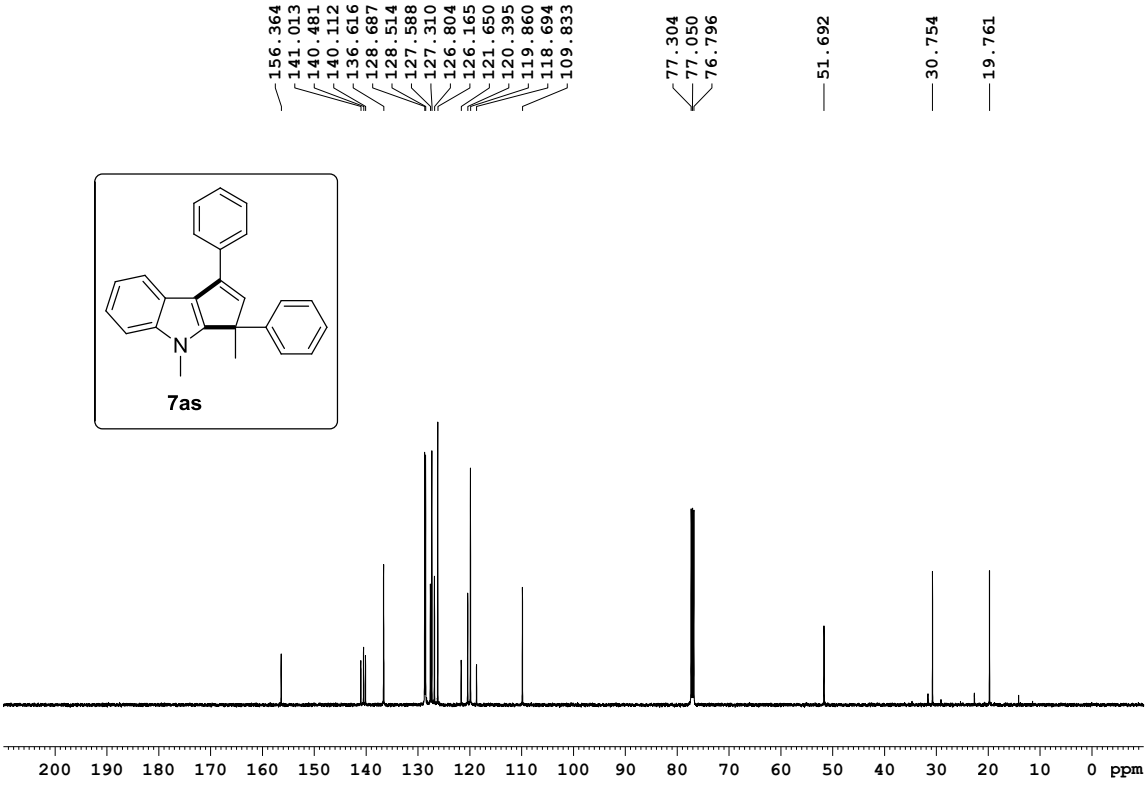


Figure S66. ^{13}C NMR spectrum of compound **7as**

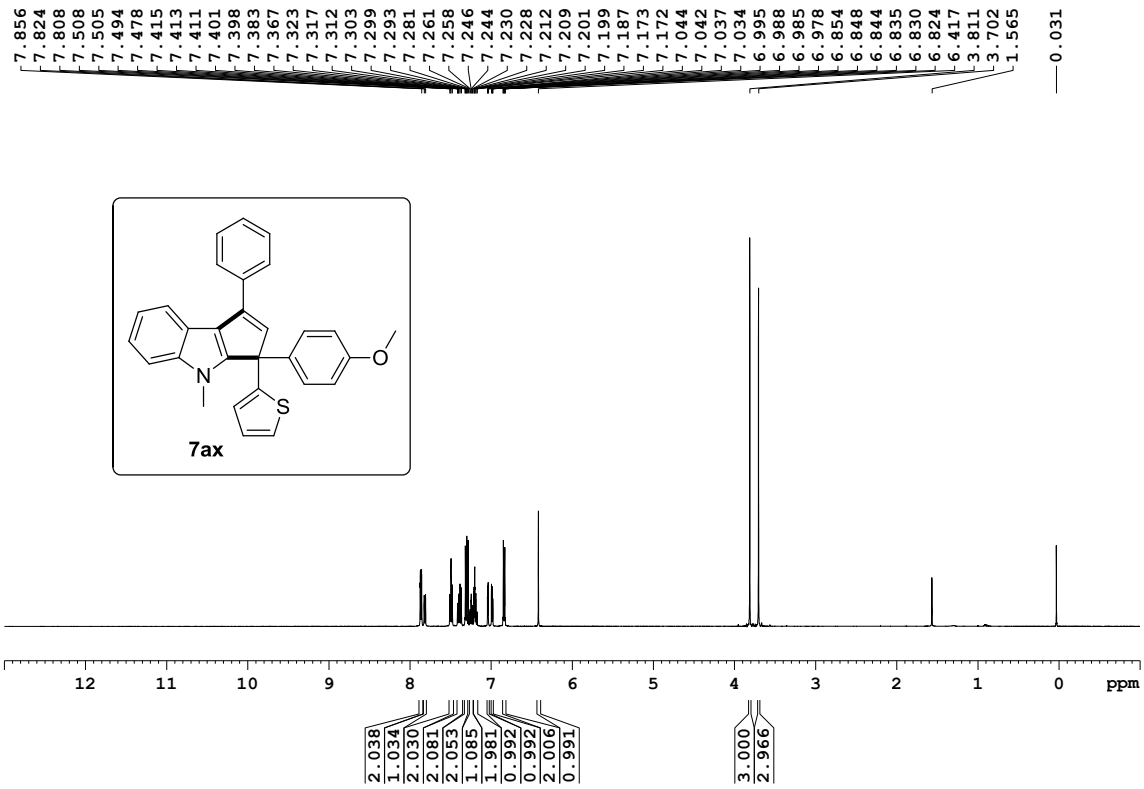


Figure S67. ^{1}H NMR spectrum of compound **7ax**

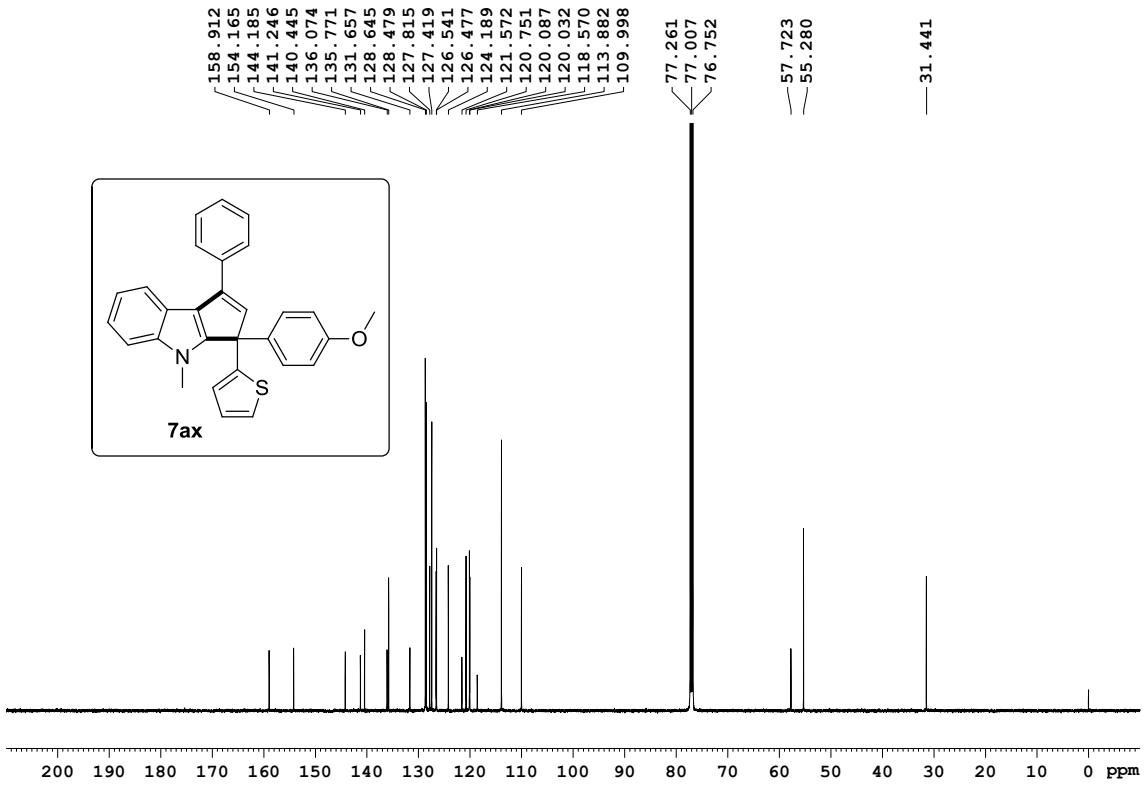


Figure S68. ^{13}C NMR spectrum of compound **7ax**

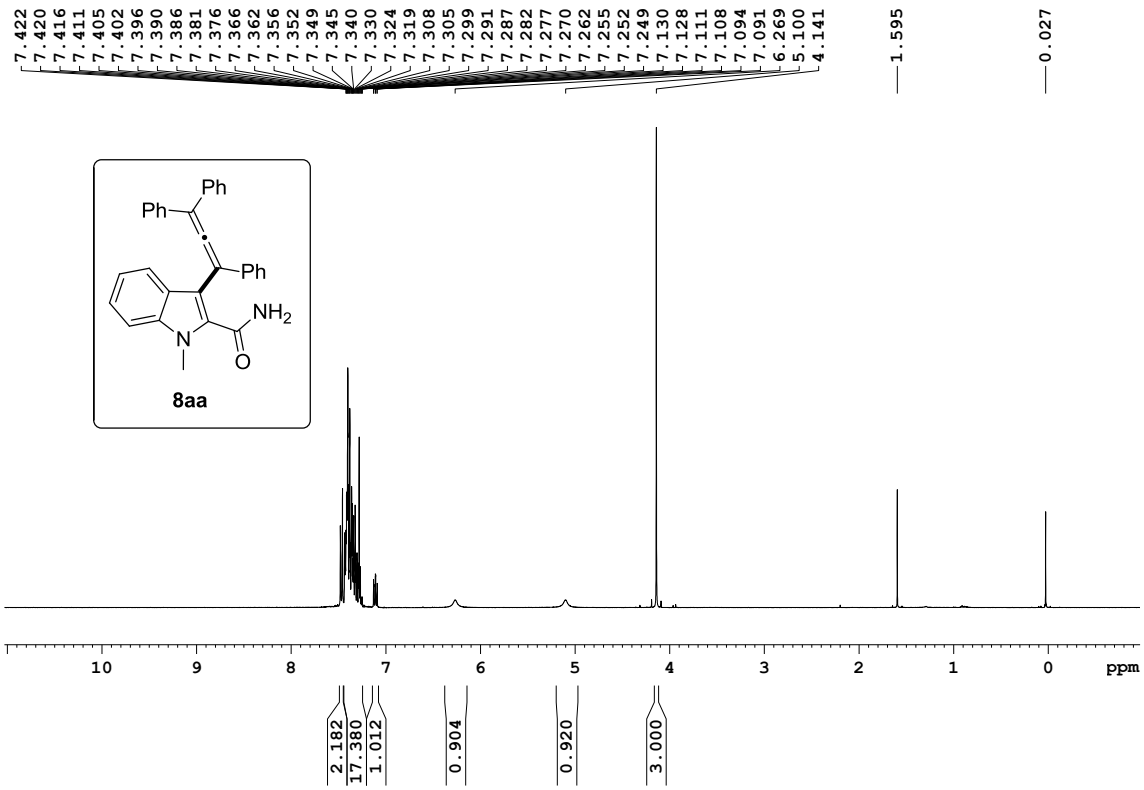


Figure S69. ^{1}H NMR spectrum of compound **8aa**

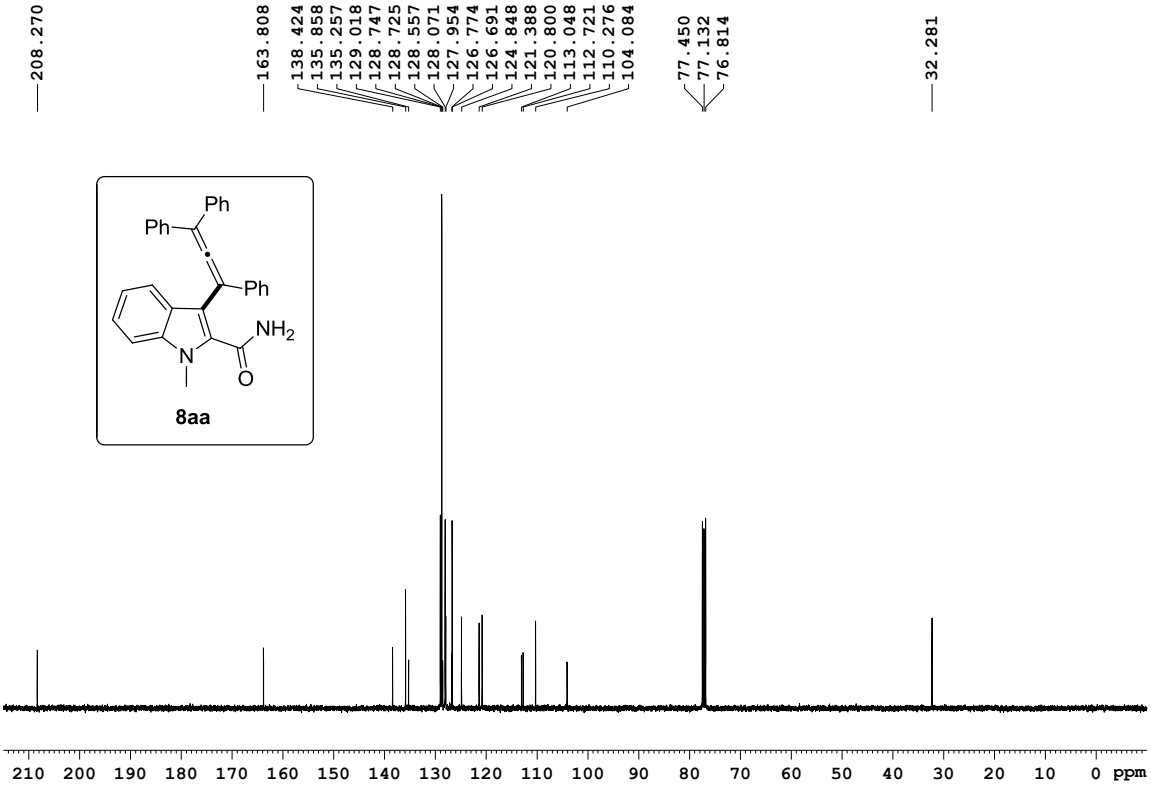


Figure S70. ^{13}C NMR spectrum of compound **8aa**

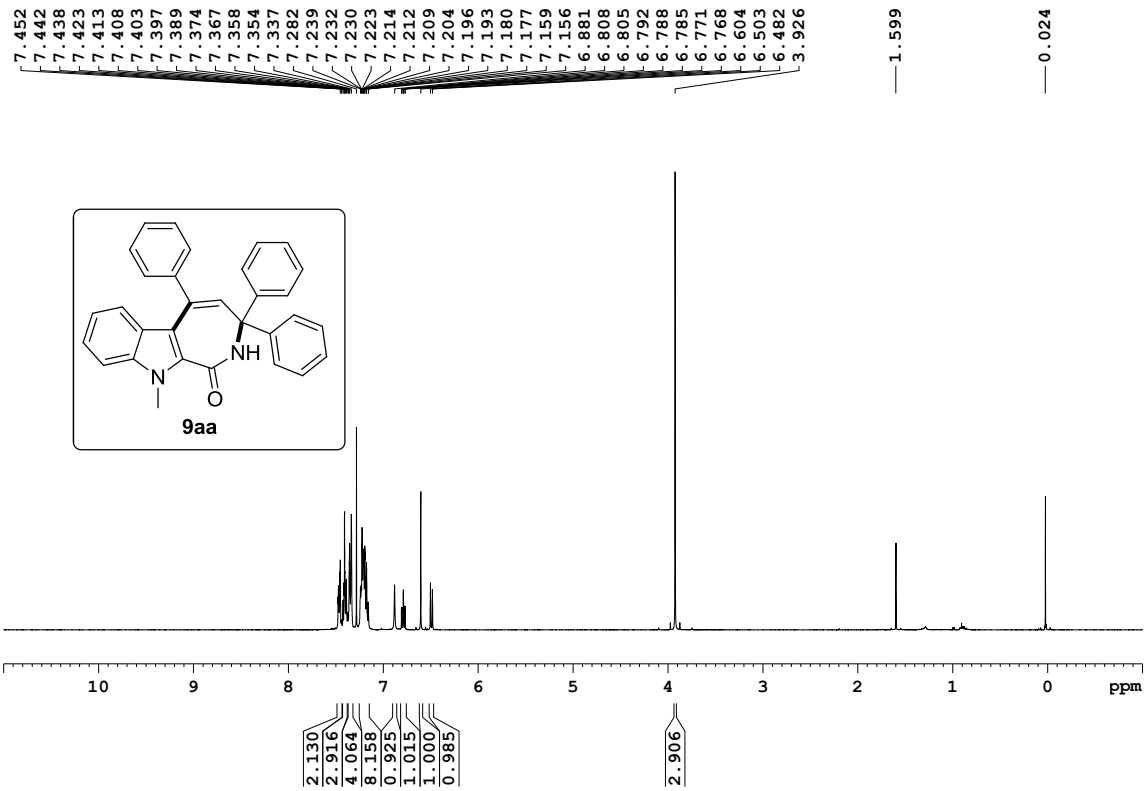


Figure S71. ^{1}H NMR spectrum of compound **9aa**

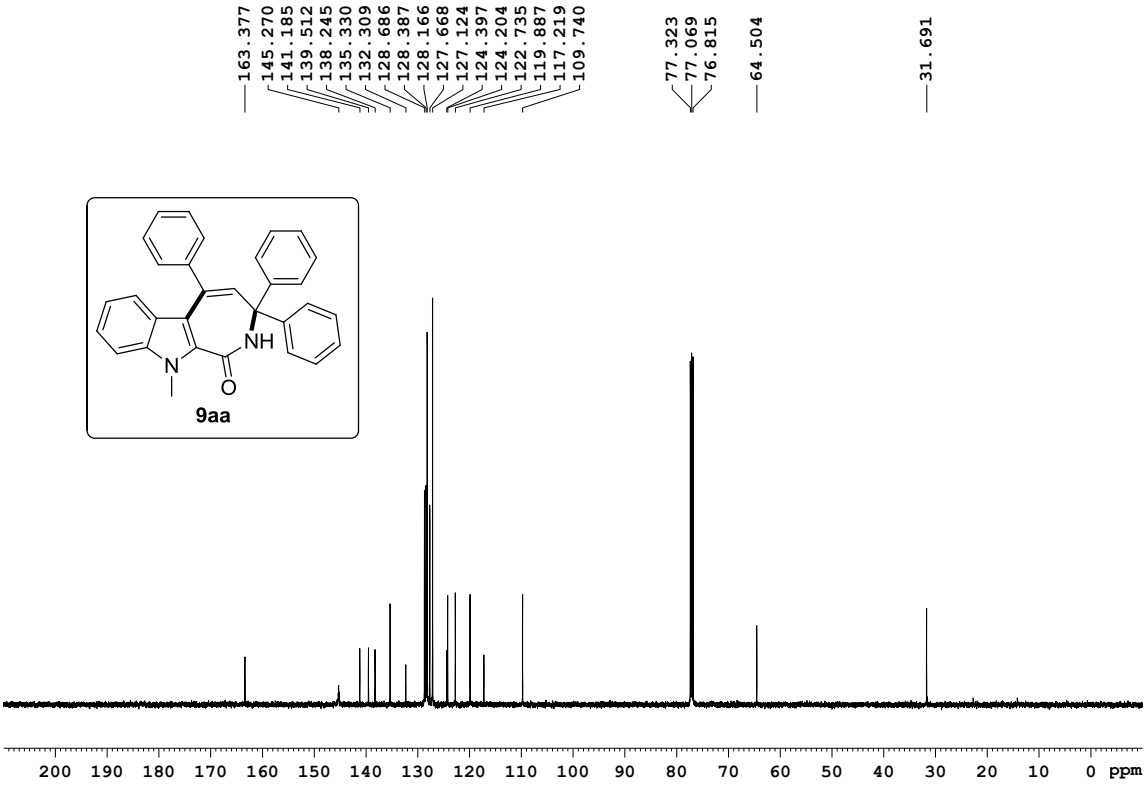


Figure S72. ^{13}C NMR spectrum of compound **9aa**

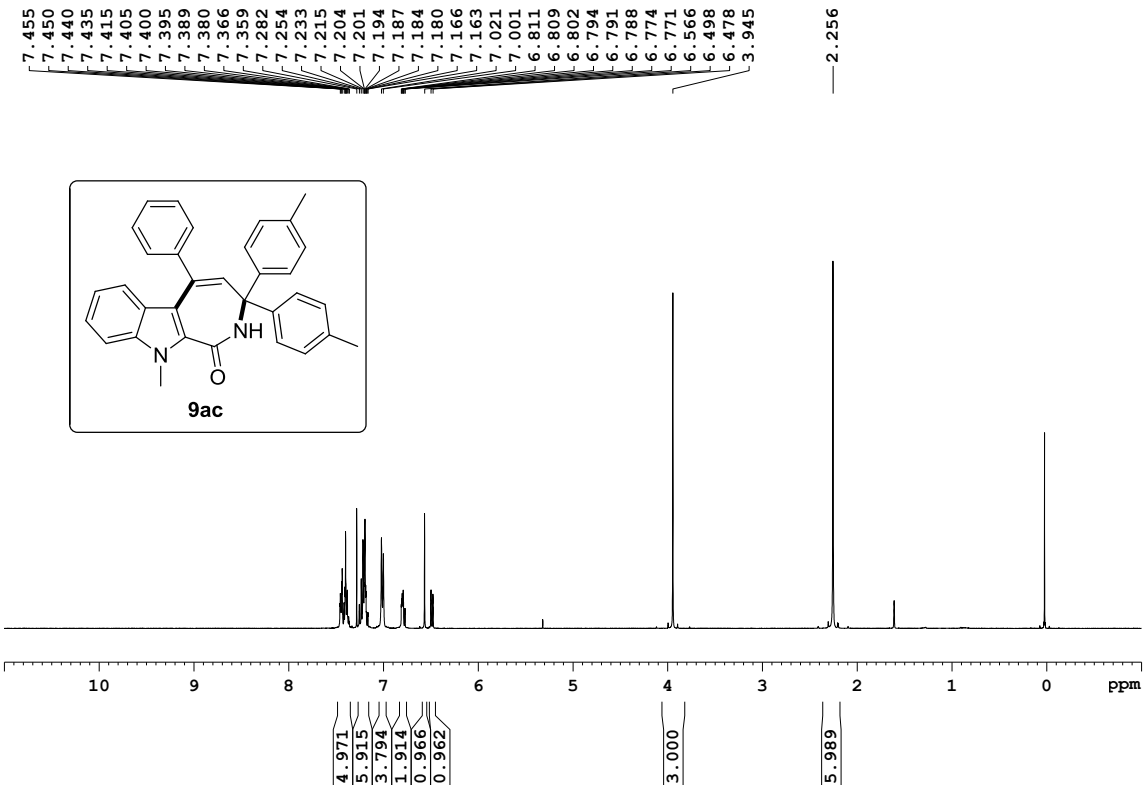


Figure S73. ^{1}H NMR spectrum of compound **9ac**

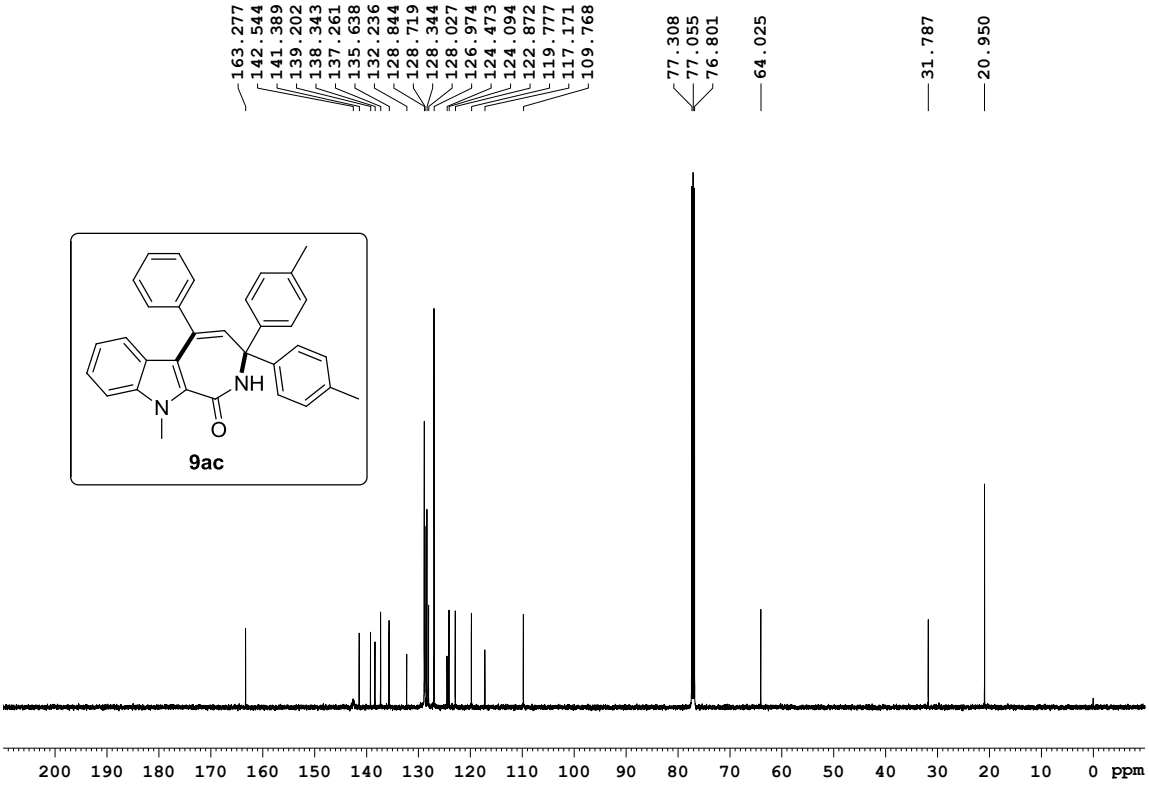


Figure S74. ^{13}C NMR spectrum of compound **9ac**

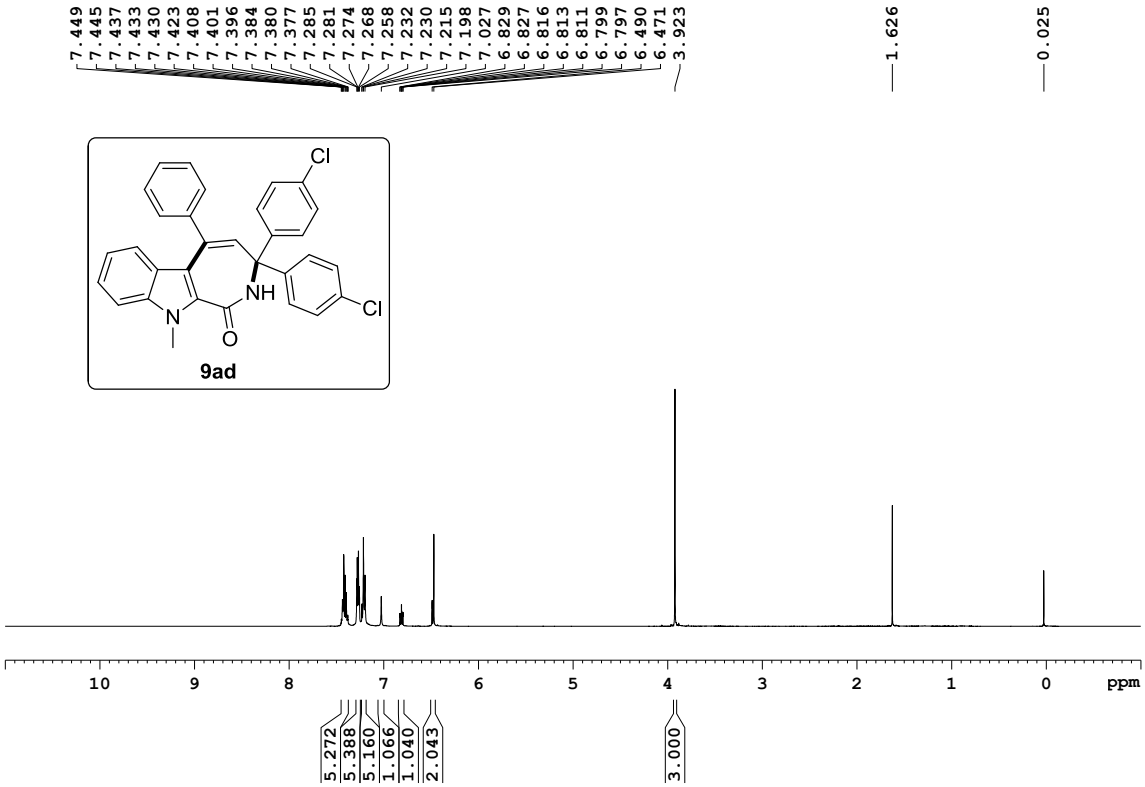


Figure S75. ^{1}H NMR spectrum of compound **9ad**

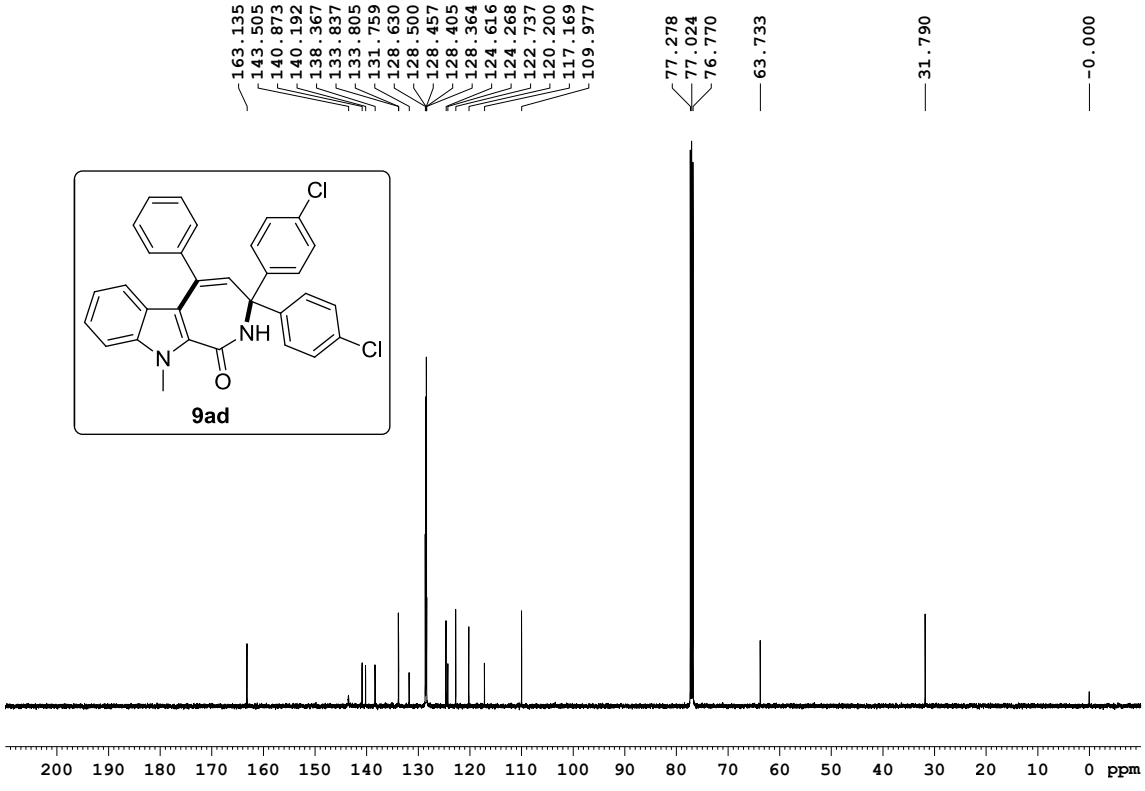


Figure S76. ^{13}C NMR spectrum of compound **9ad**

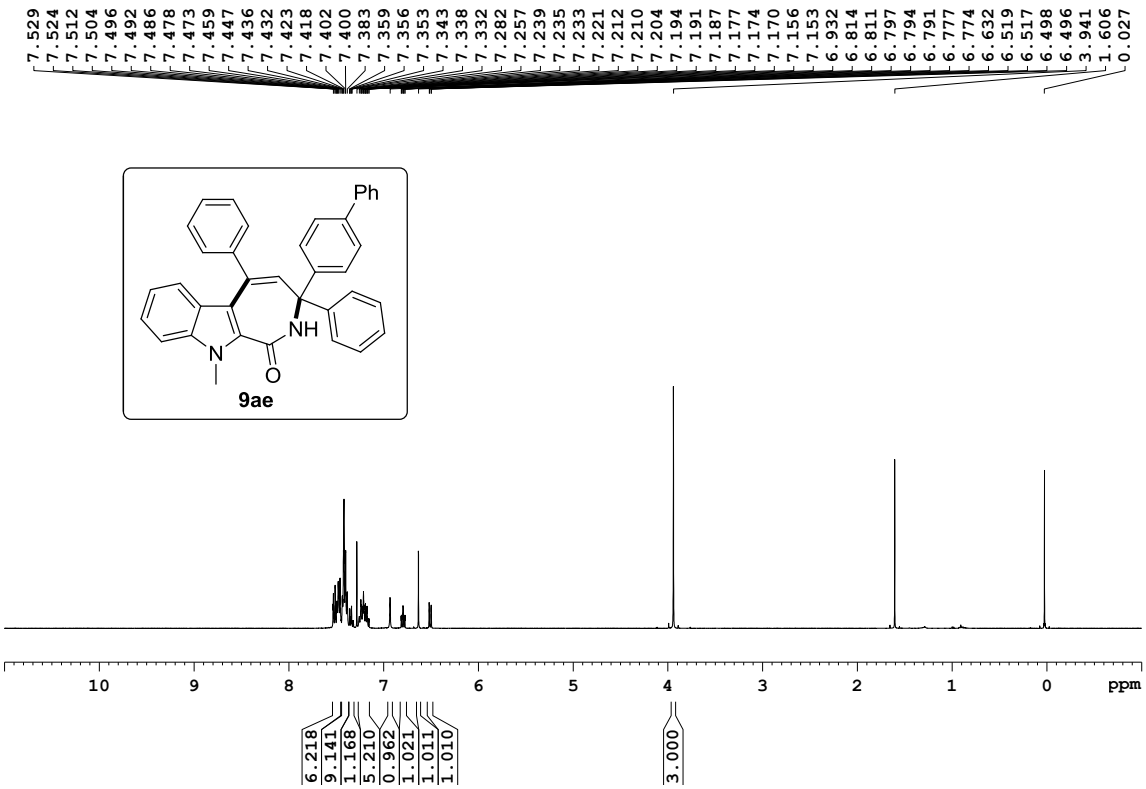


Figure S77. ^{1}H NMR spectrum of compound **9ae**

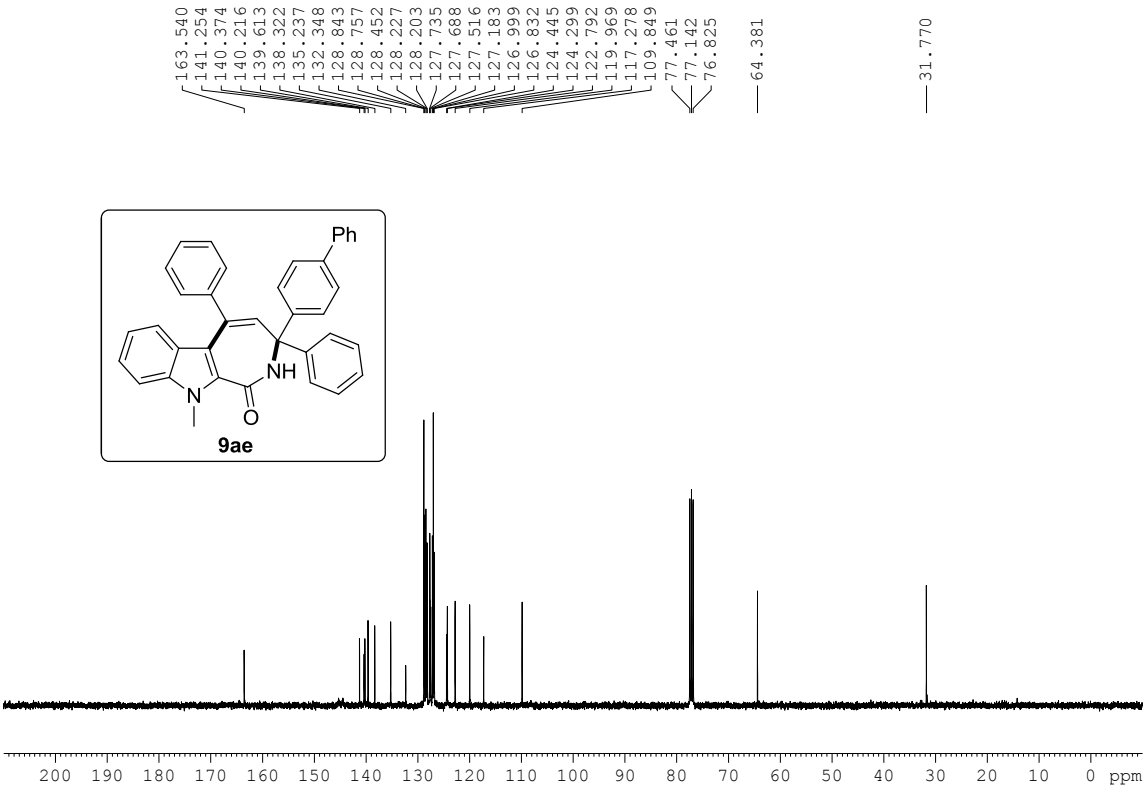


Figure S78. ^{13}C NMR spectrum of compound **9ae**

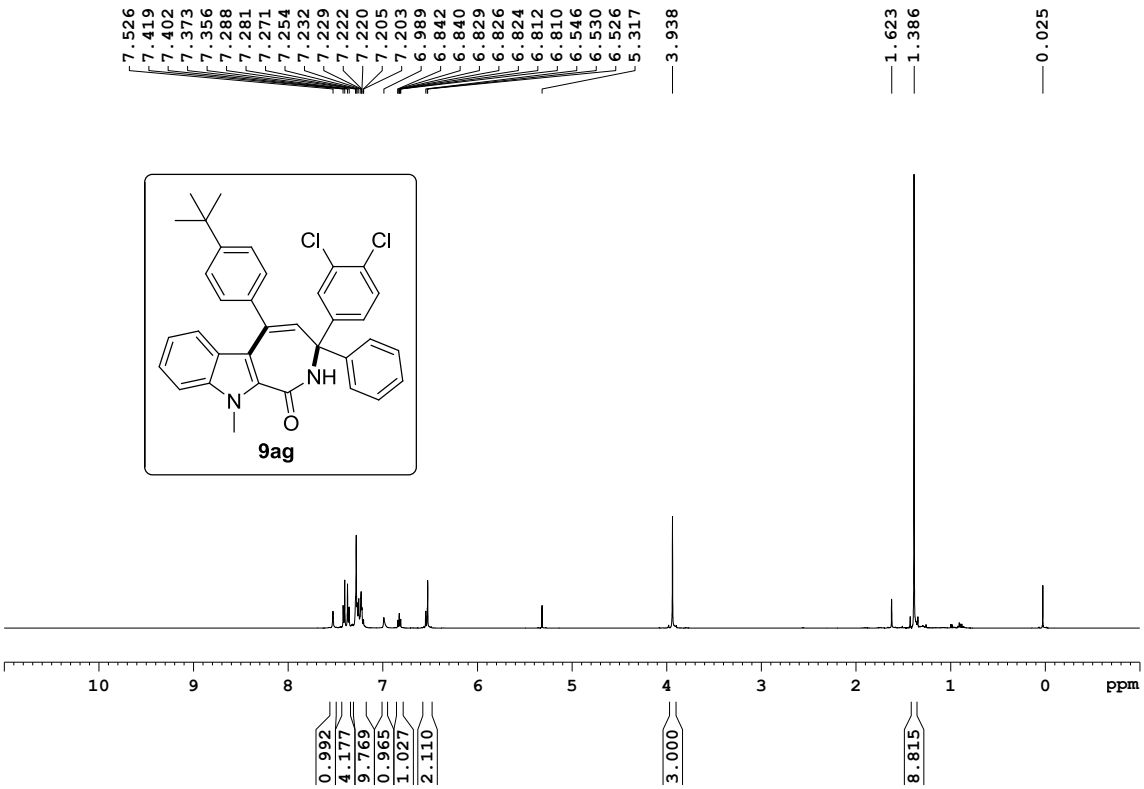


Figure S79. ^{1}H NMR spectrum of compound **9ag**

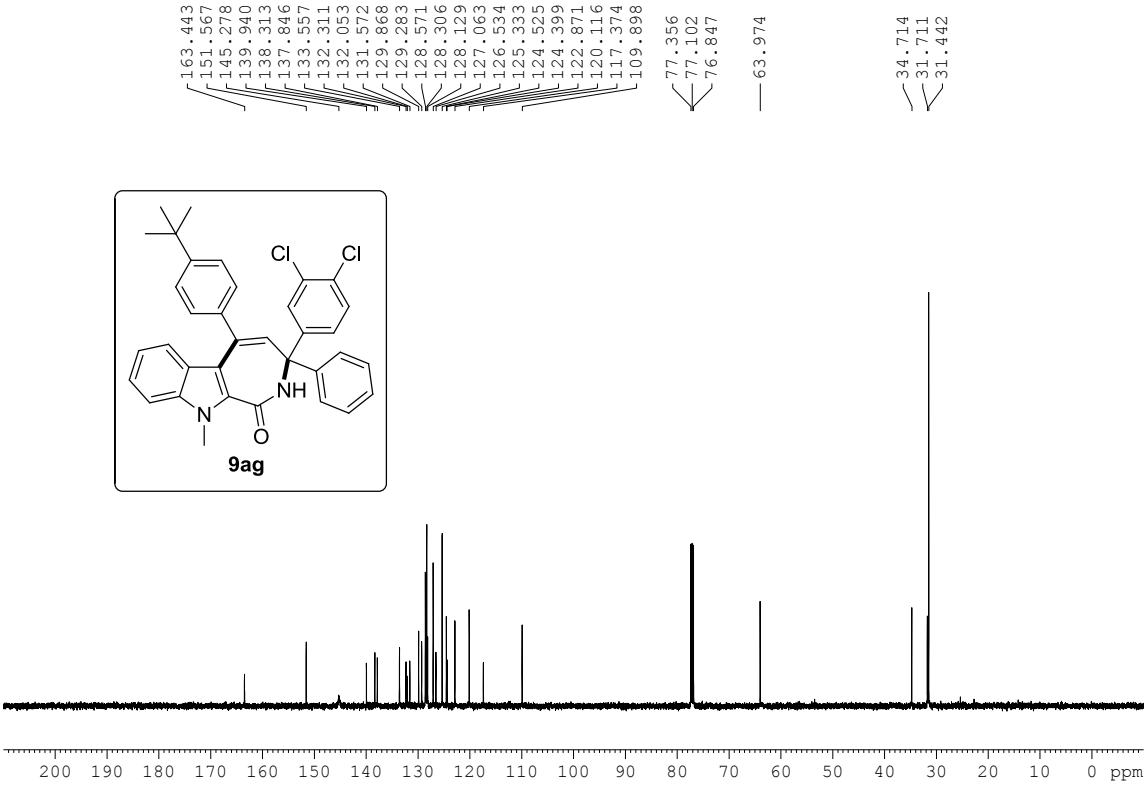


Figure S80. ^{13}C NMR spectrum of compound **9ag**

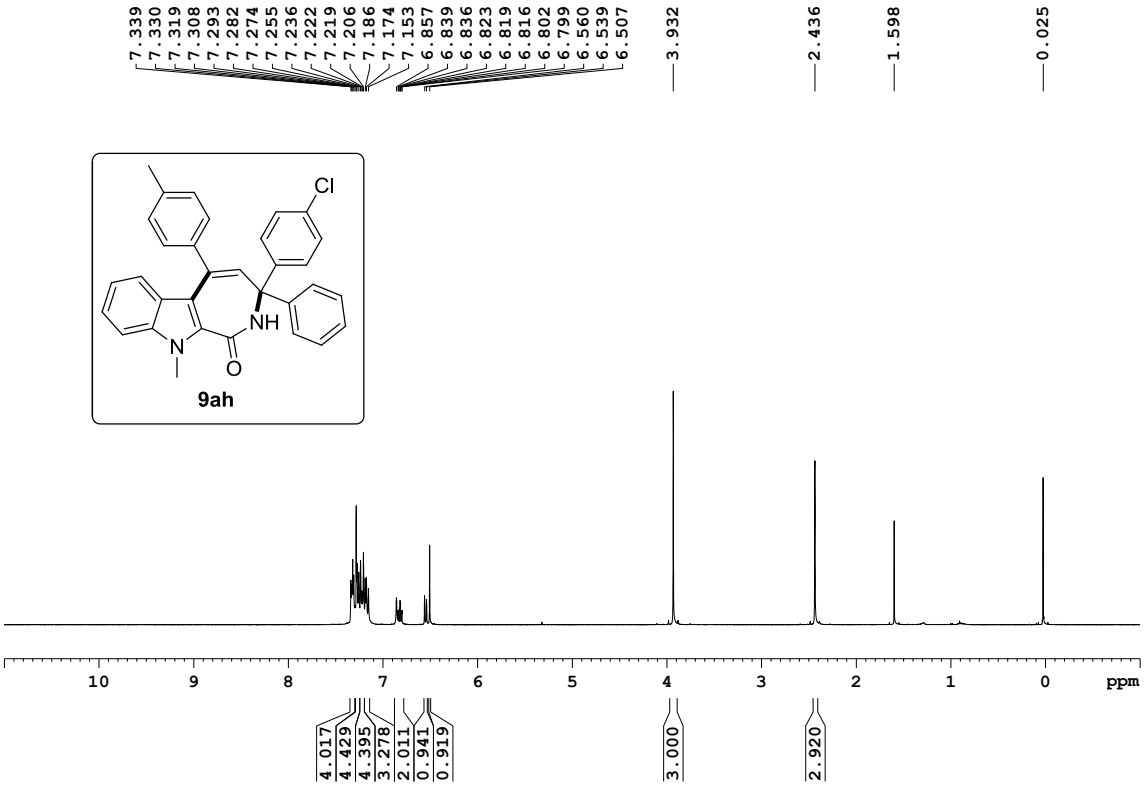


Figure S81. ^{1}H NMR spectrum of compound **9ah**

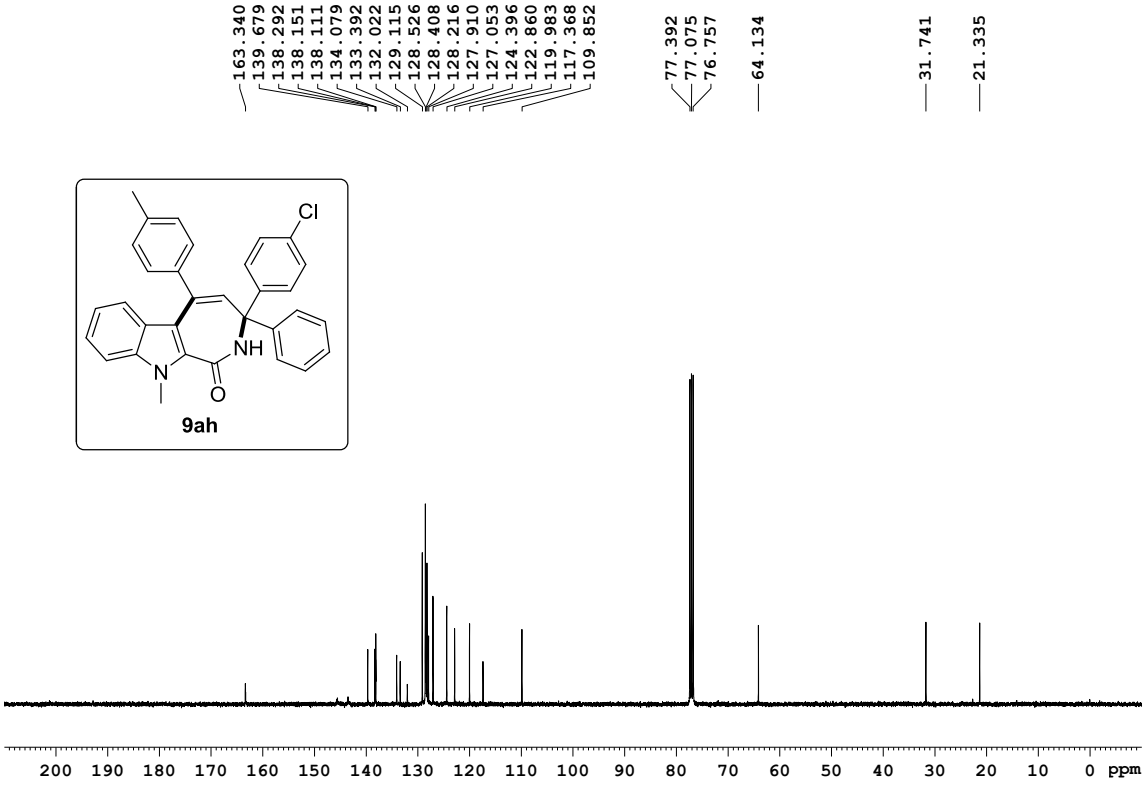


Figure S82. ^{13}C NMR spectrum of compound **9ah**

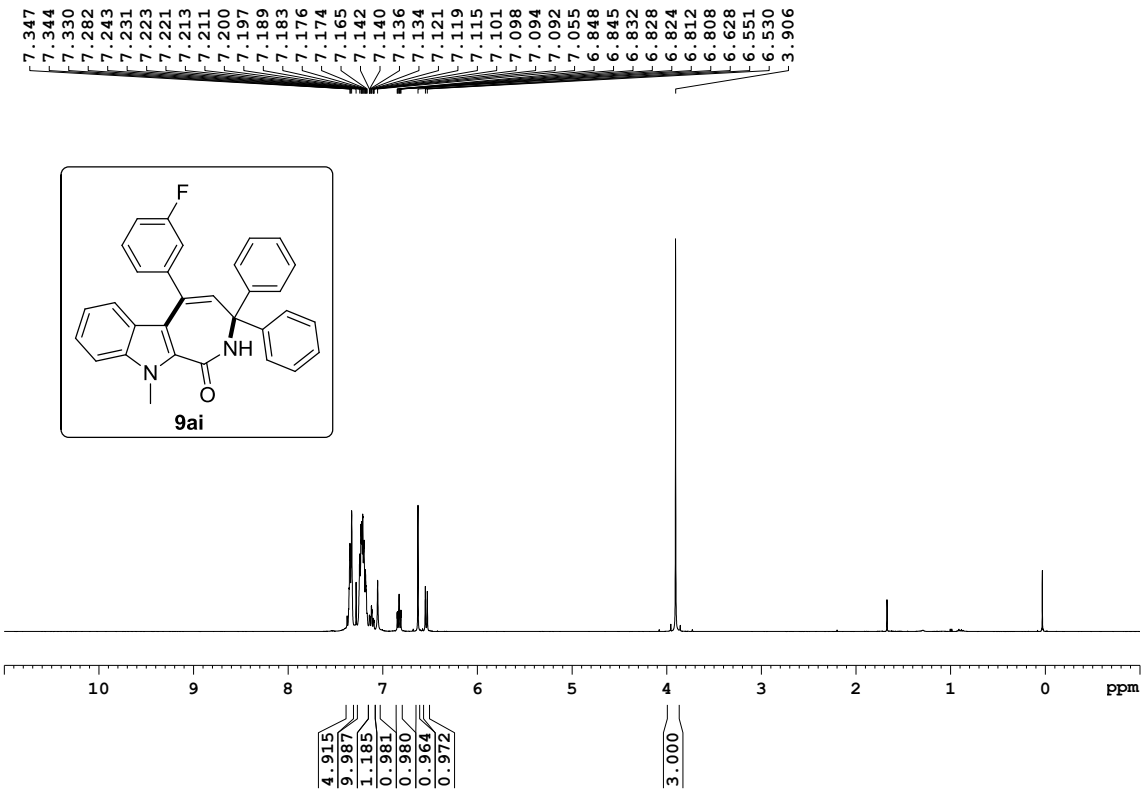


Figure S83. ^{1}H NMR spectrum of compound **9ai**

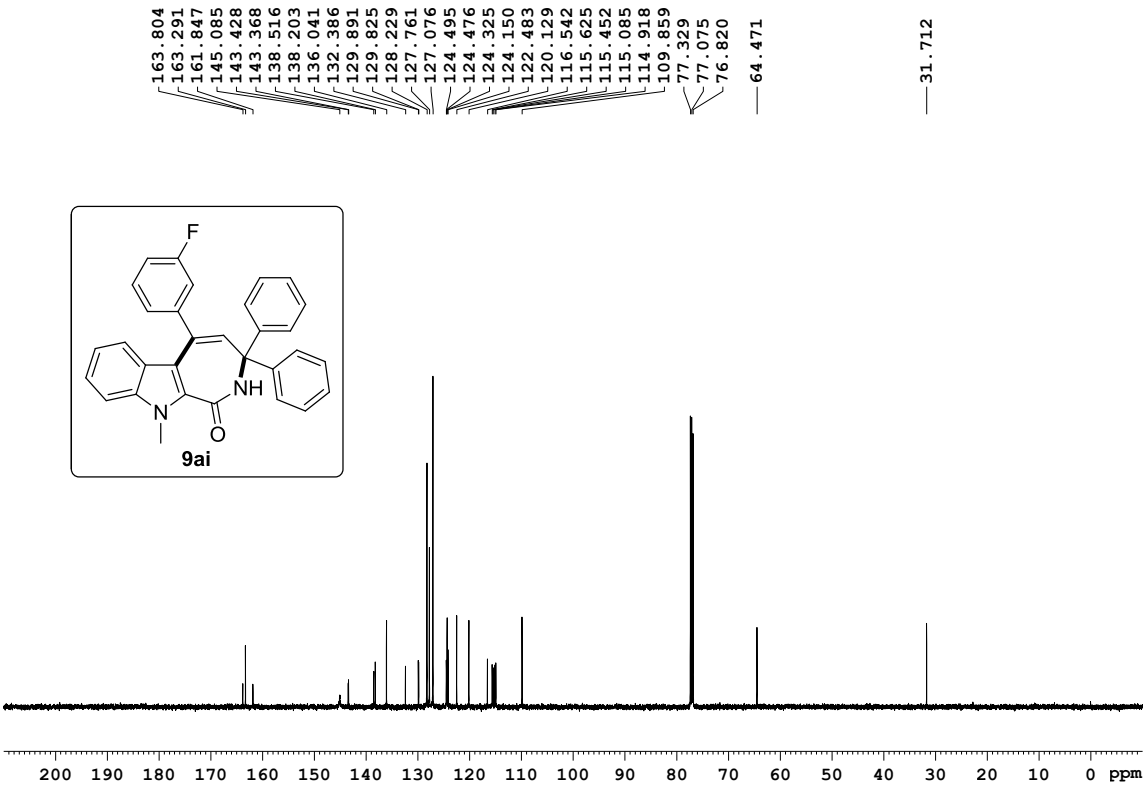


Figure S84. ^{13}C NMR spectrum of compound **9ai**

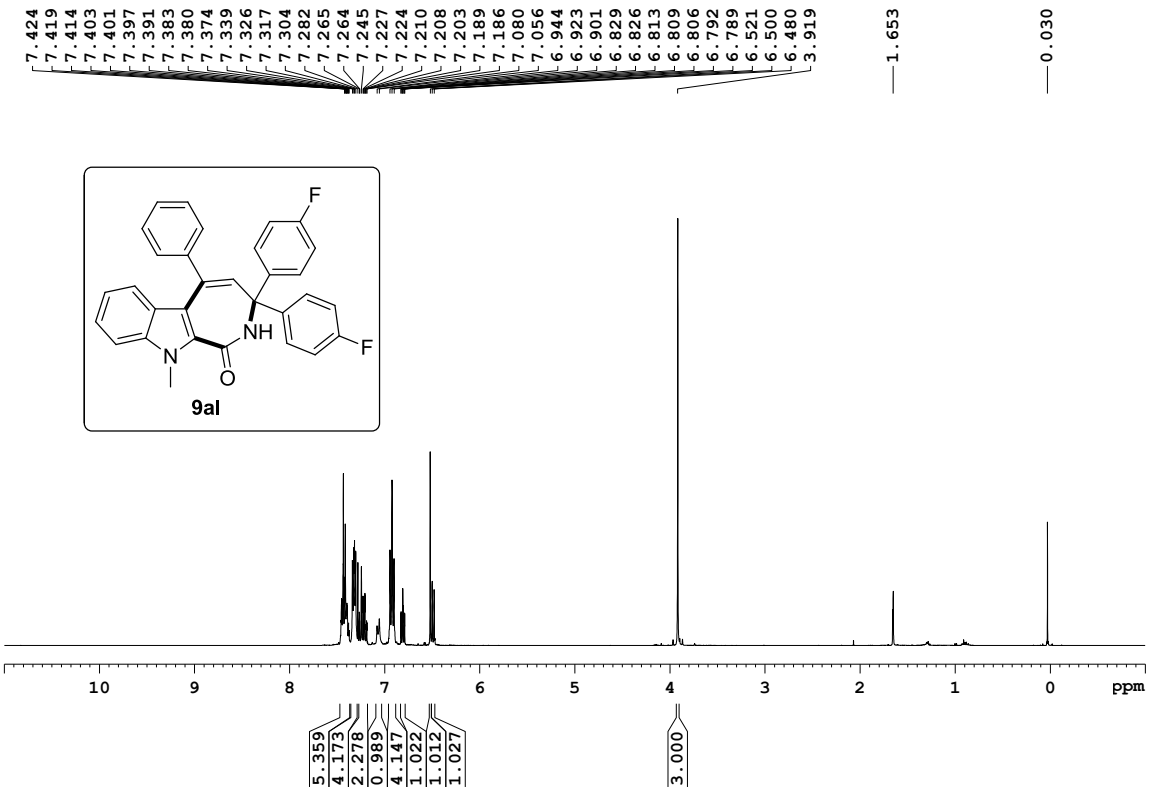


Figure S85. ^{1}H NMR spectrum of compound **9al**

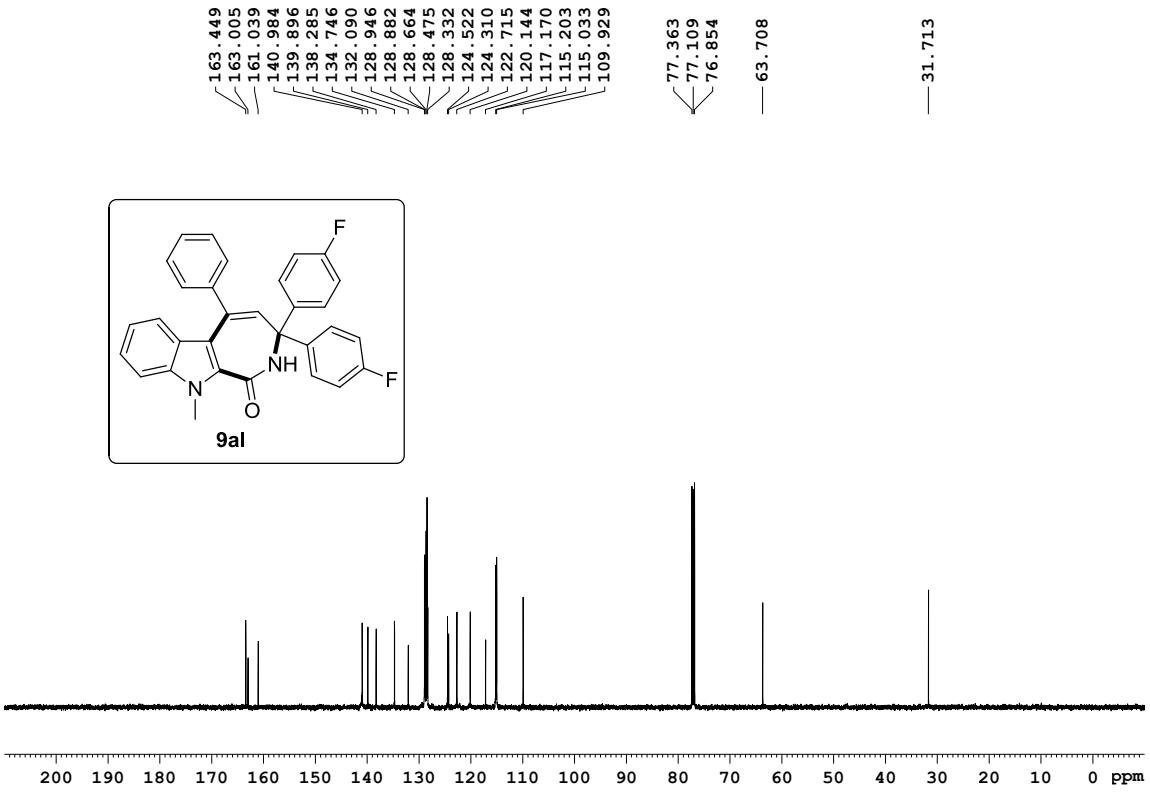


Figure S86. ^{13}C NMR spectrum of compound **9al**

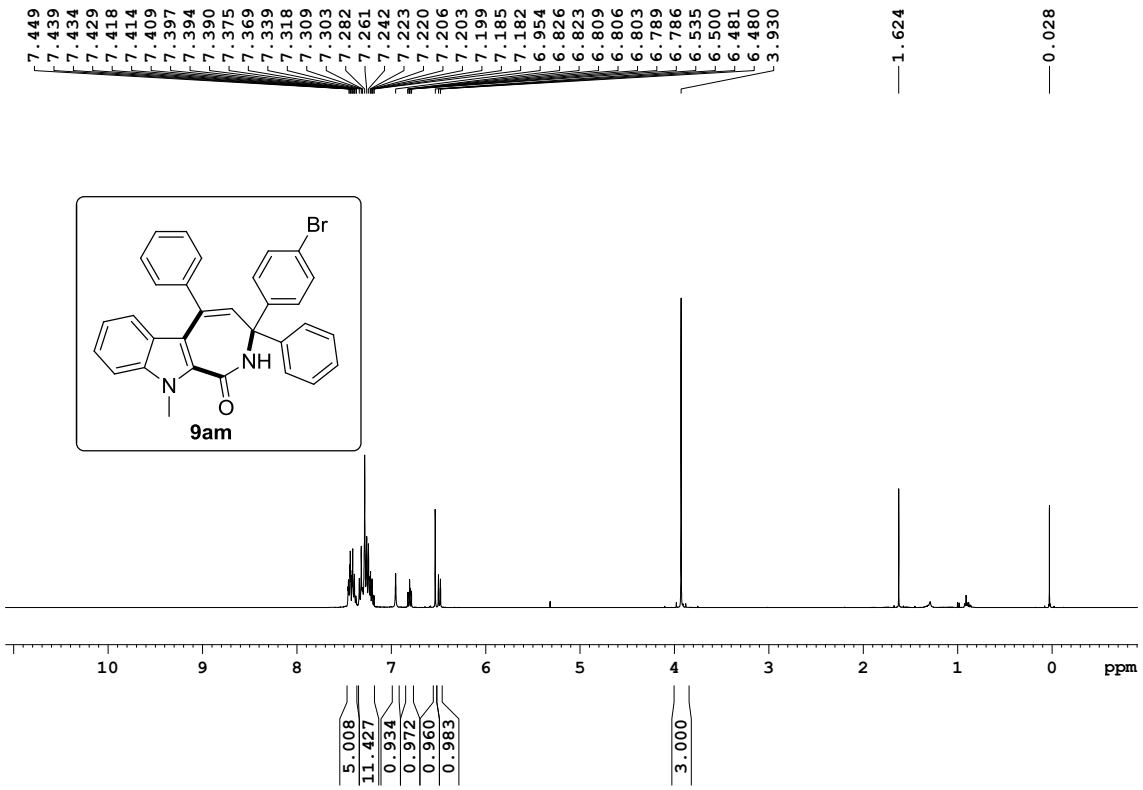


Figure S87. ^{1}H NMR spectrum of compound **9am**

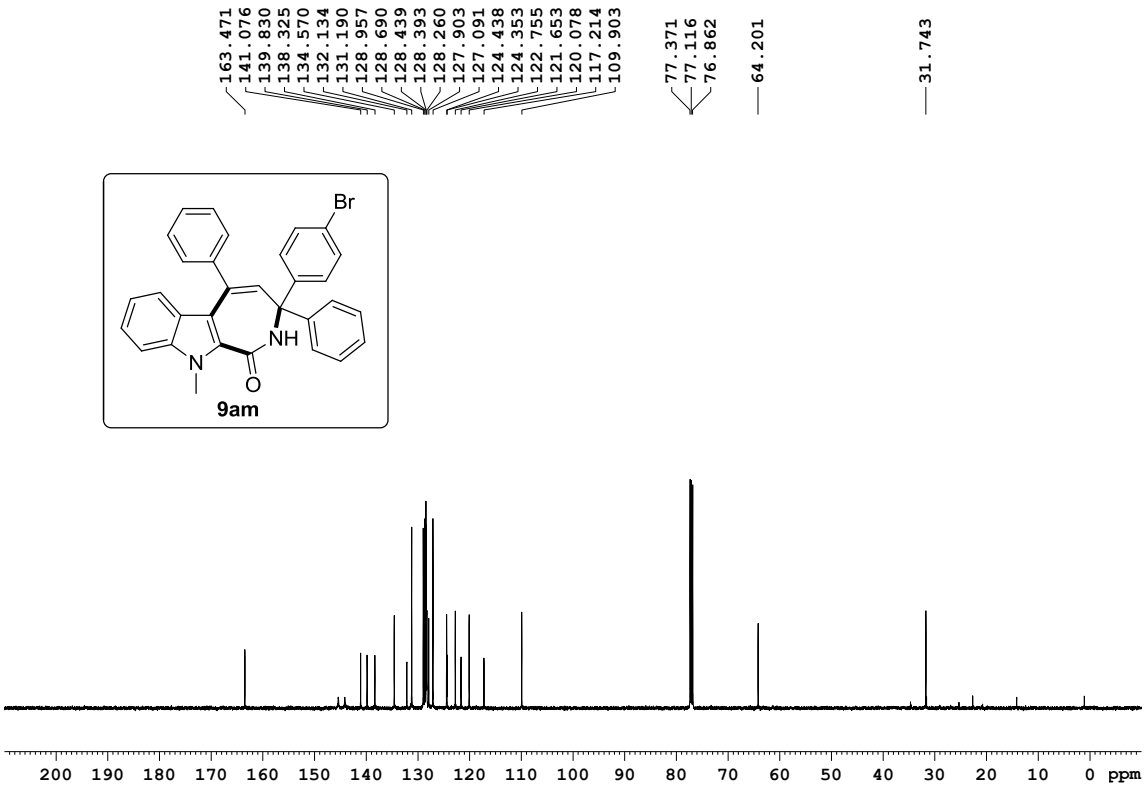


Figure S88. ^{13}C NMR spectrum of compound **9am**

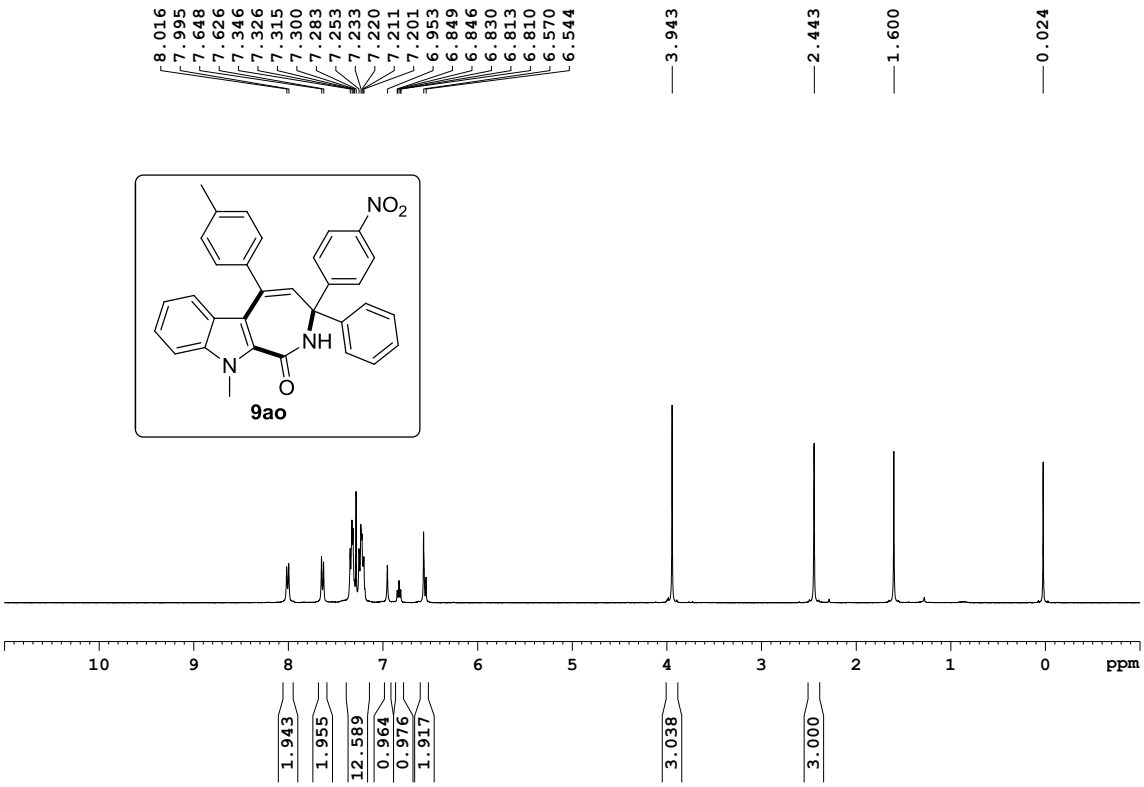


Figure S89. ^{1}H NMR spectrum of compound **9ao**

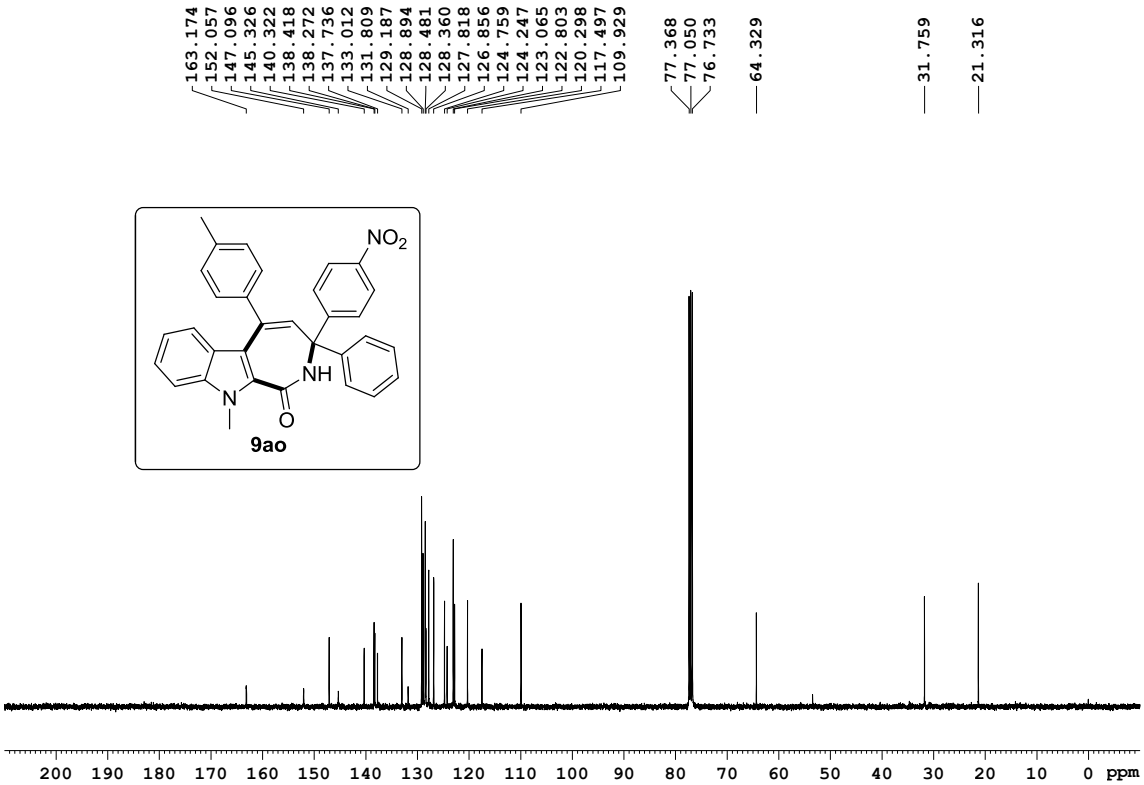


Figure S90. ^{13}C NMR spectrum of compound **9ao**

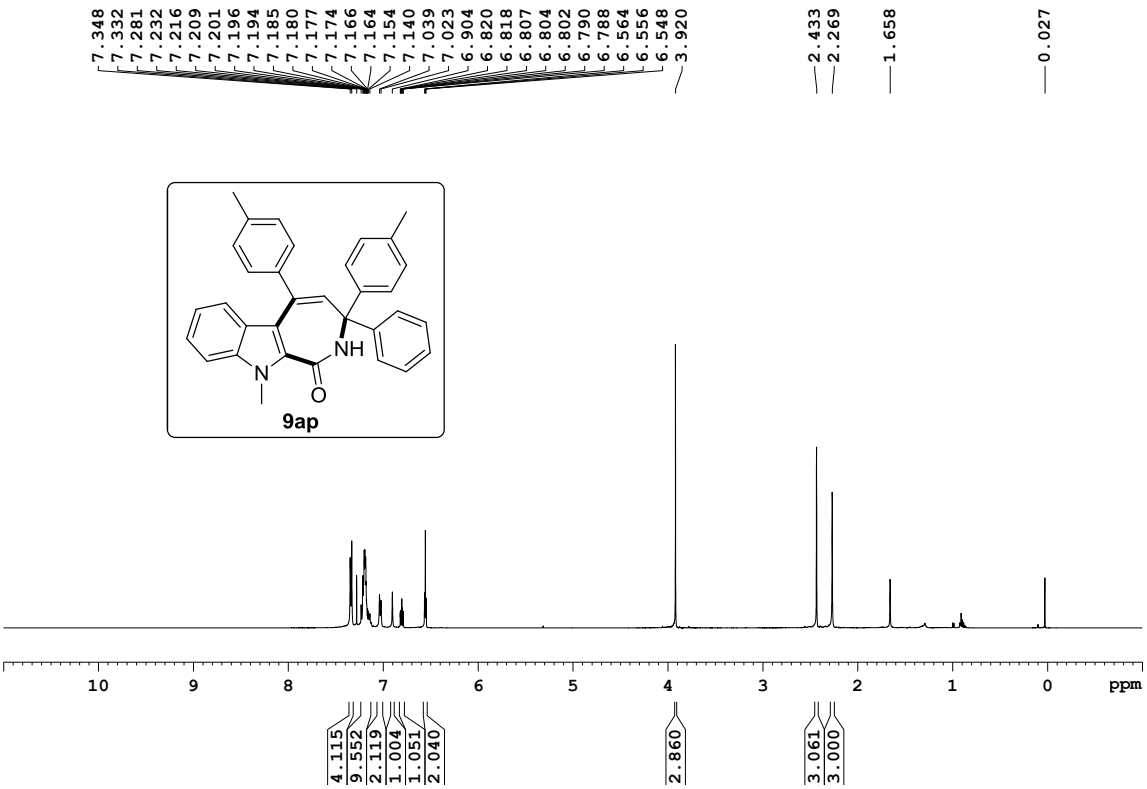


Figure S91. ^{1}H NMR spectrum of compound **9ap**

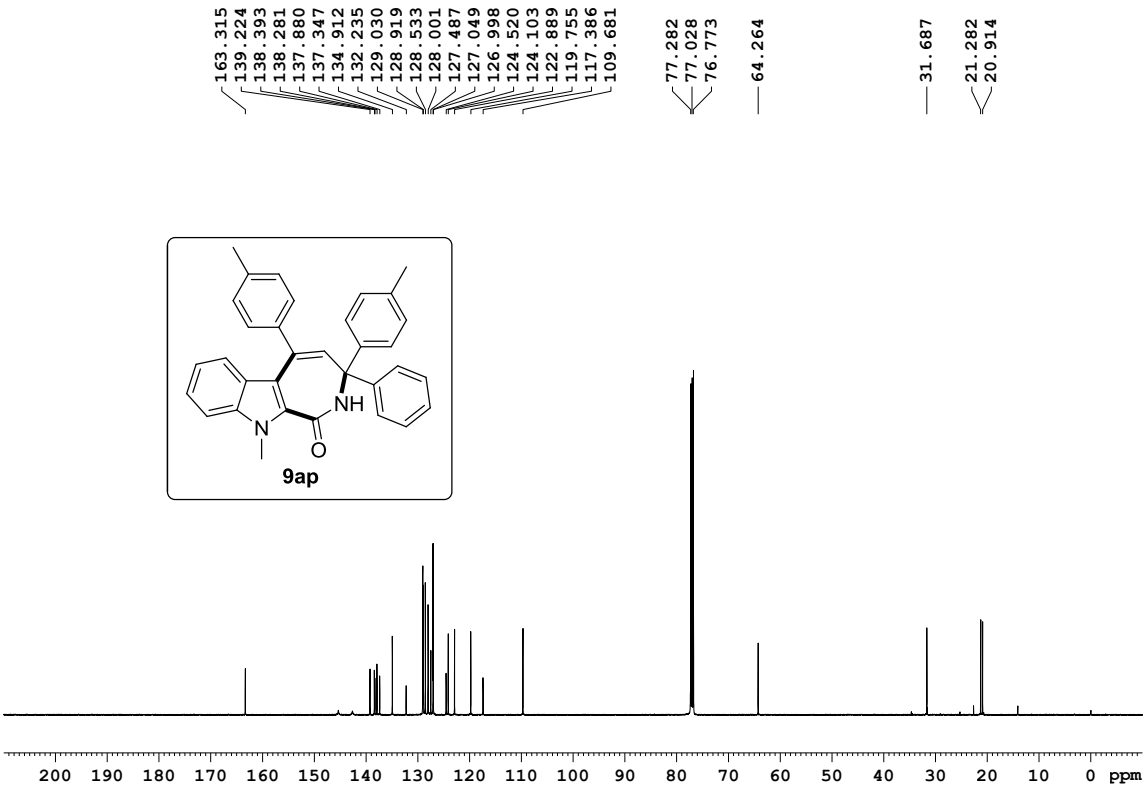


Figure S92. ^{13}C NMR spectrum of compound **9ap**

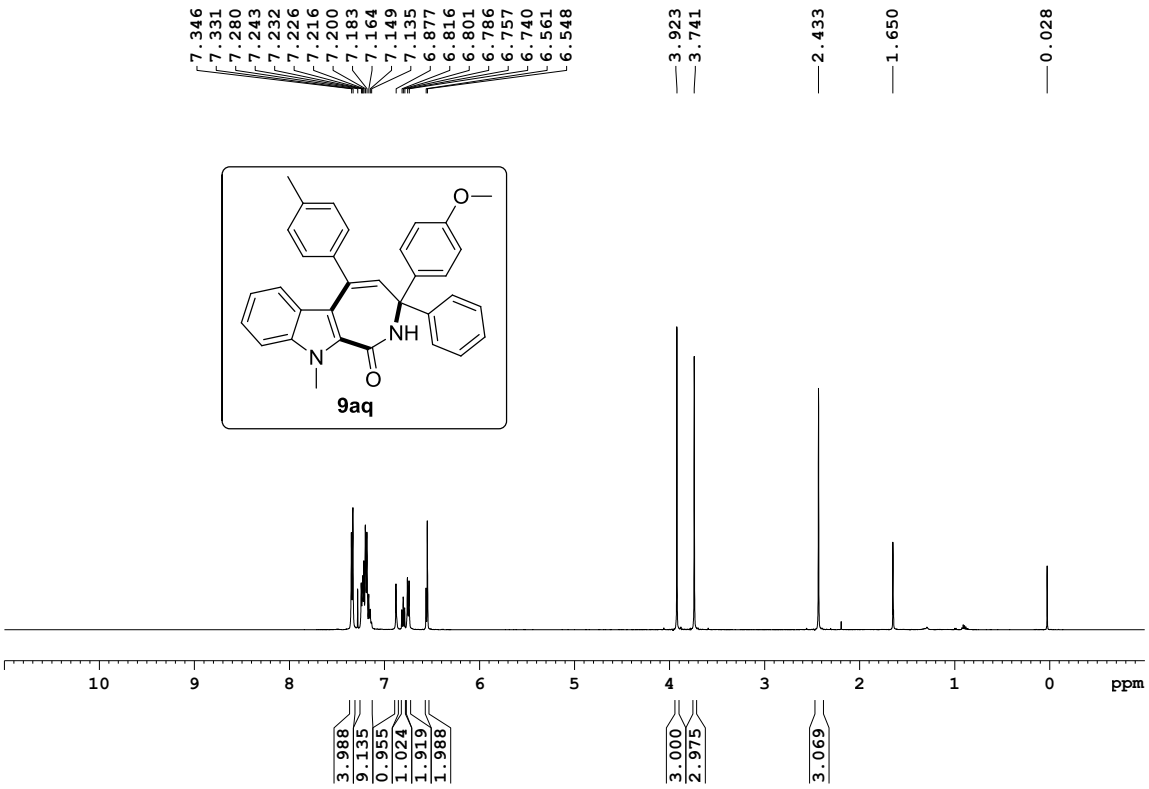


Figure S93. ^{1}H NMR spectrum of compound **9aq**

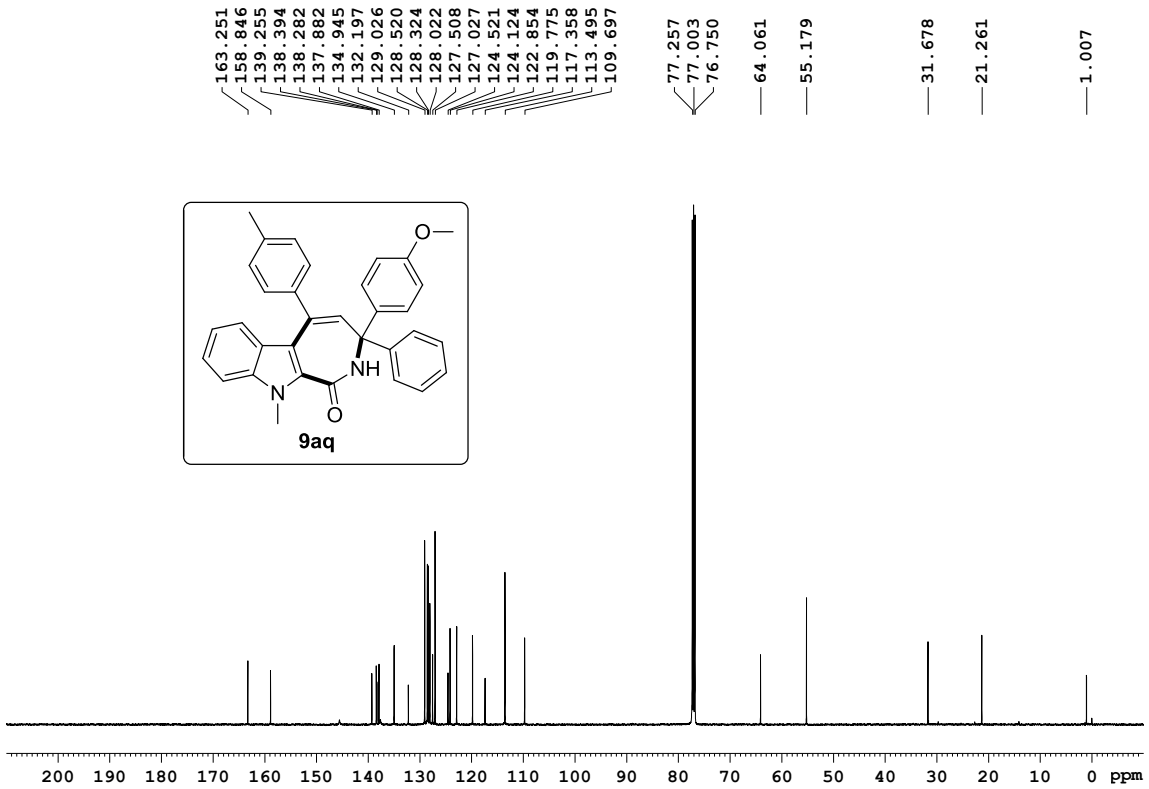


Figure S94. ^{13}C NMR spectrum of compound **9aq**

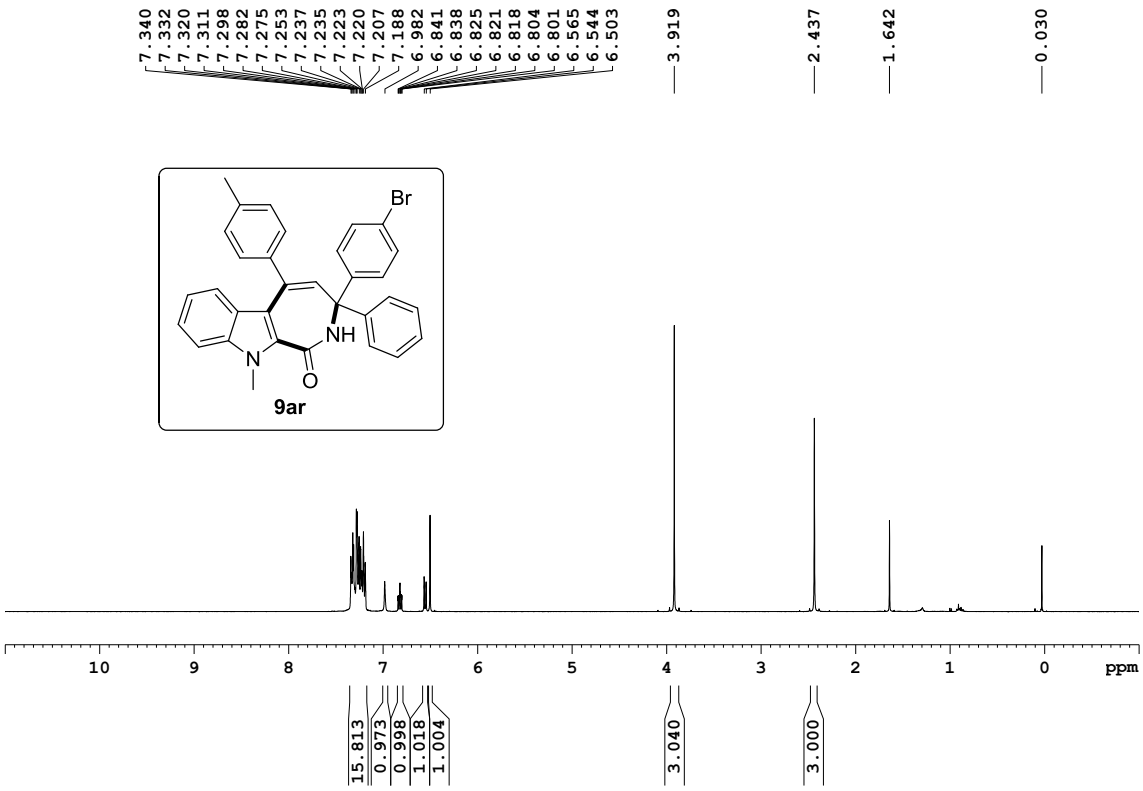


Figure S95. ^{1}H NMR spectrum of compound **9ar**

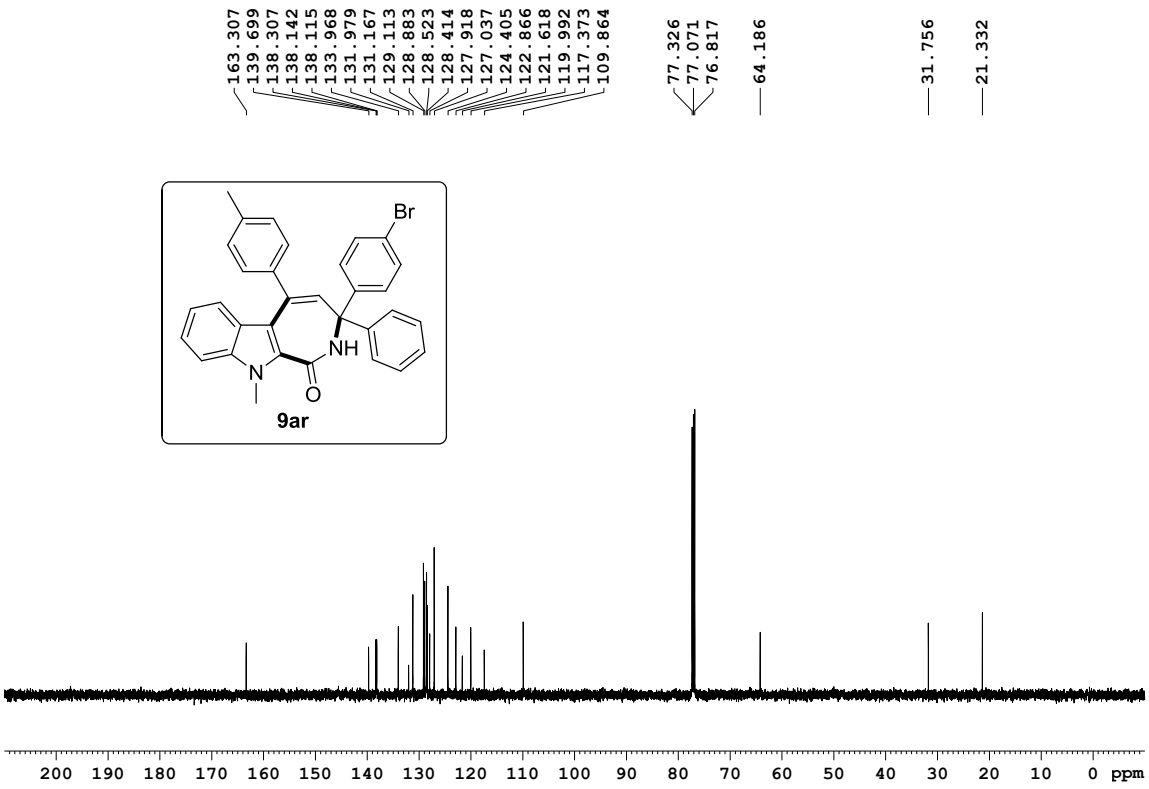


Figure S96. ^{13}C NMR spectrum of compound **9ar**

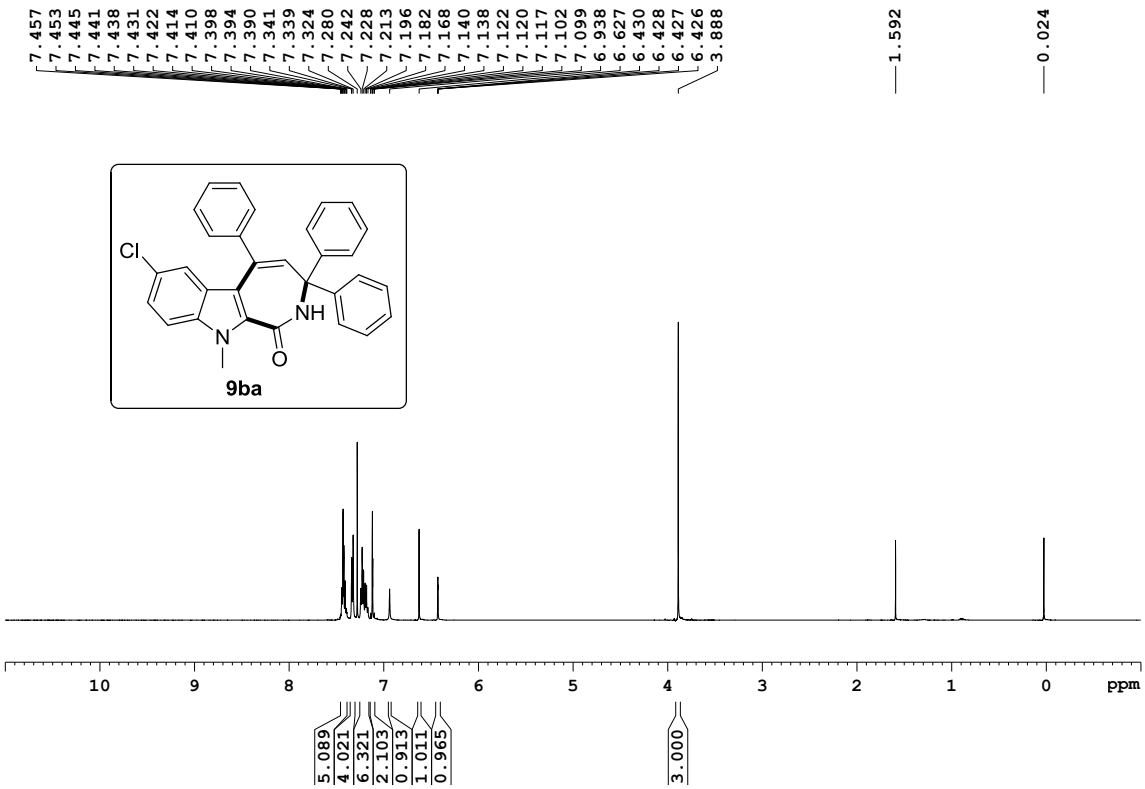


Figure S97. ^{1}H NMR spectrum of compound **9ba**

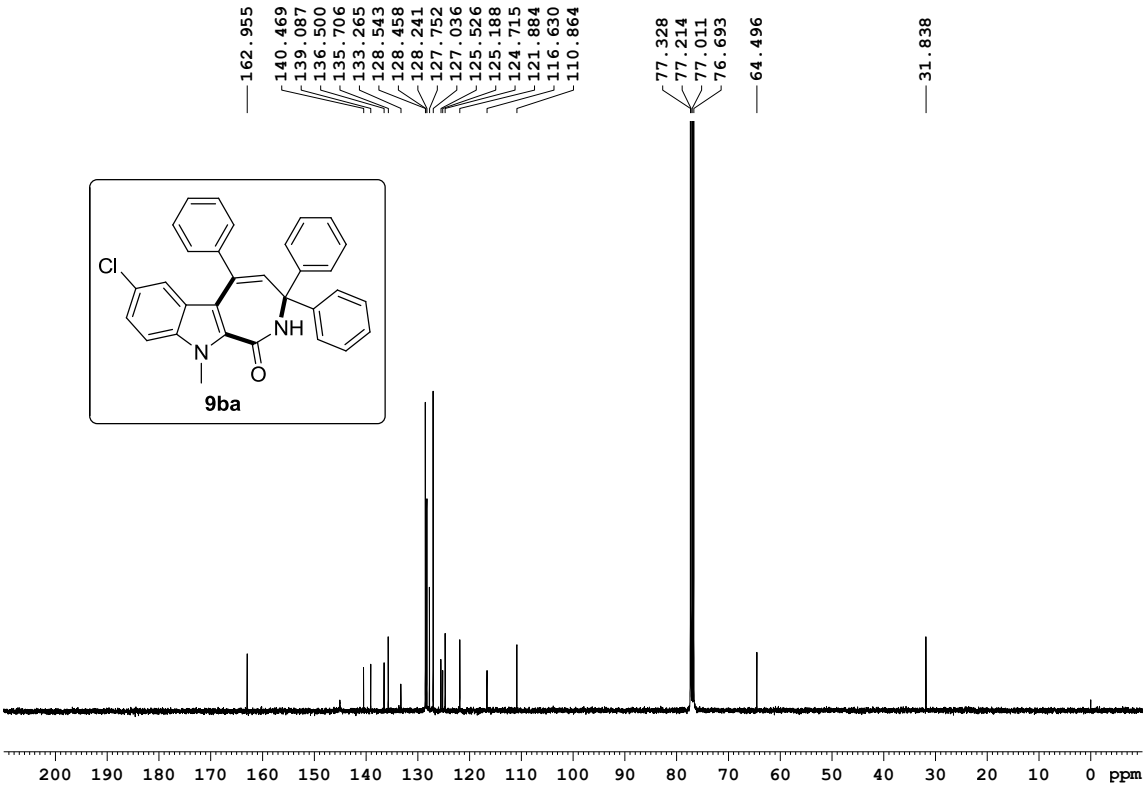


Figure S98. ^{13}C NMR spectrum of compound **9ba**

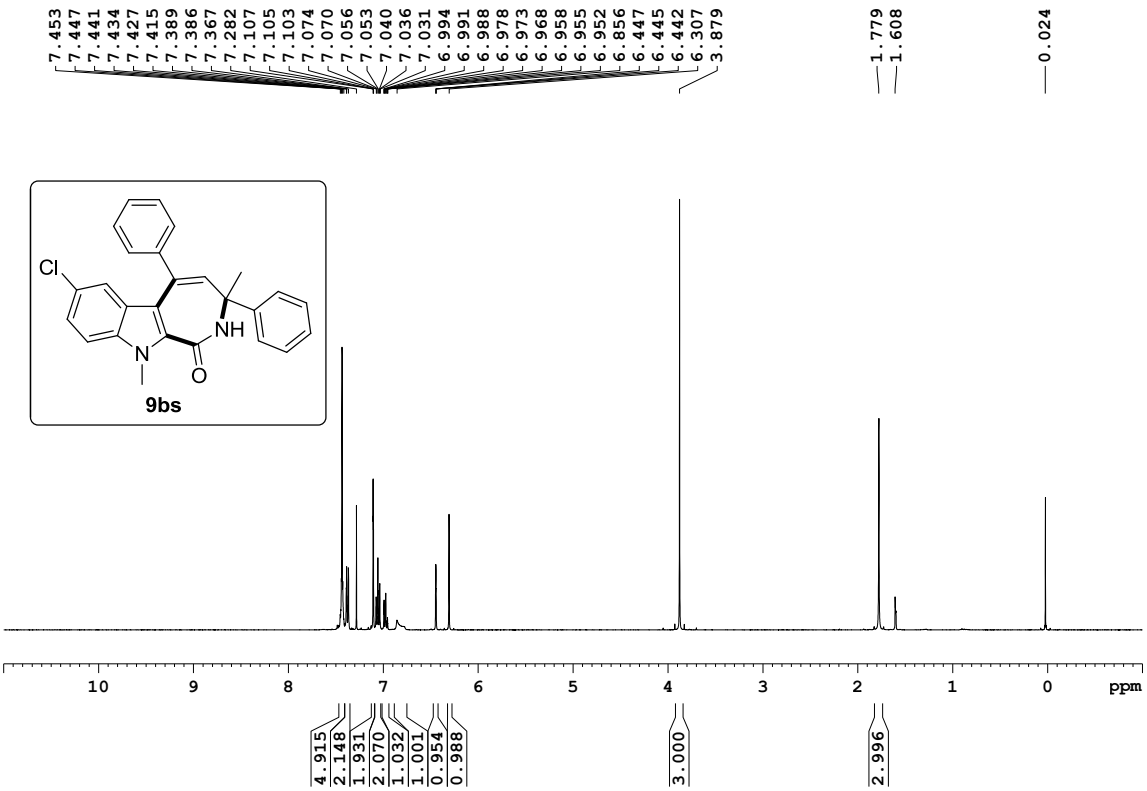


Figure S99. ^{1}H NMR spectrum of compound **9bs**

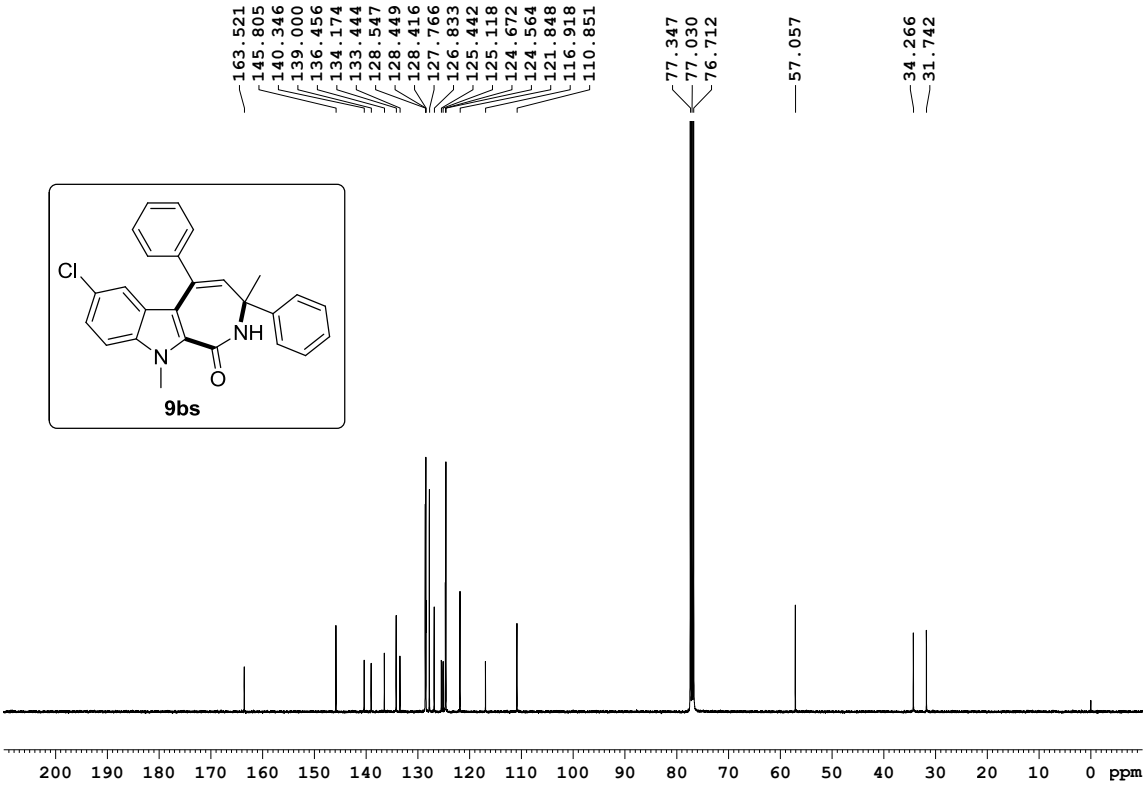


Figure S100. ^{13}C NMR spectrum of compound **9bs**

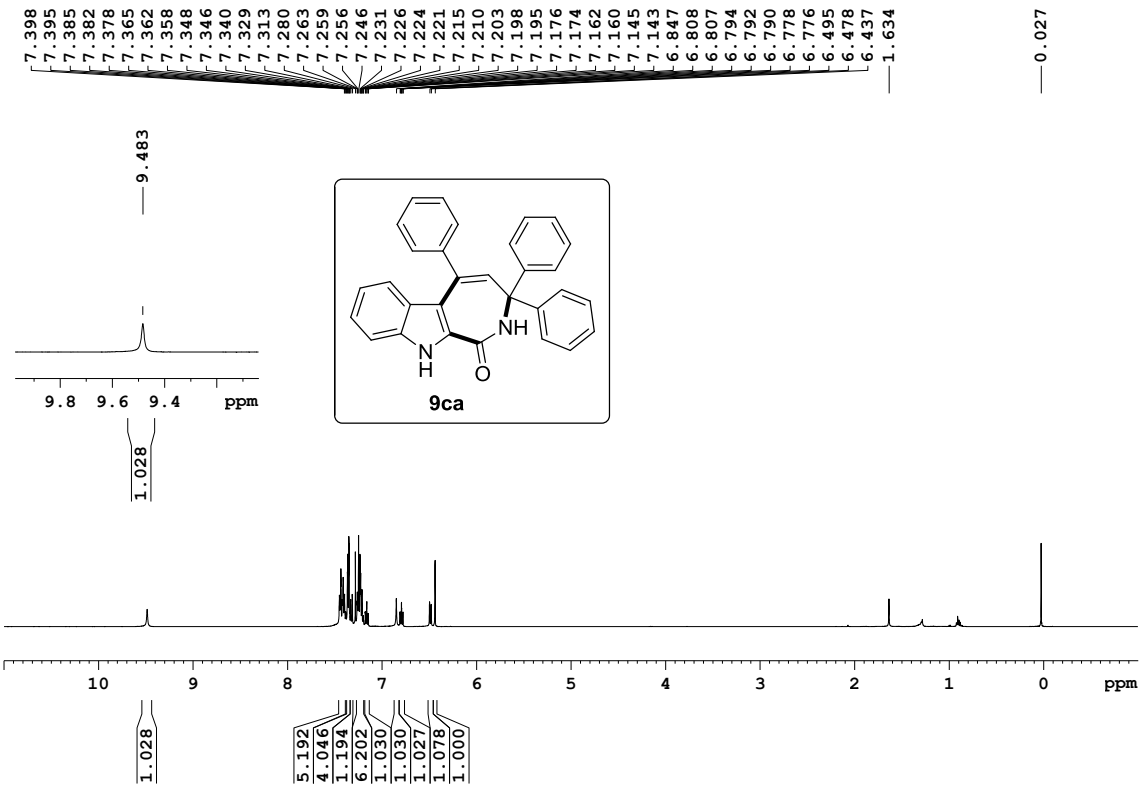


Figure S101. ^{1}H NMR spectrum of compound **9ca**

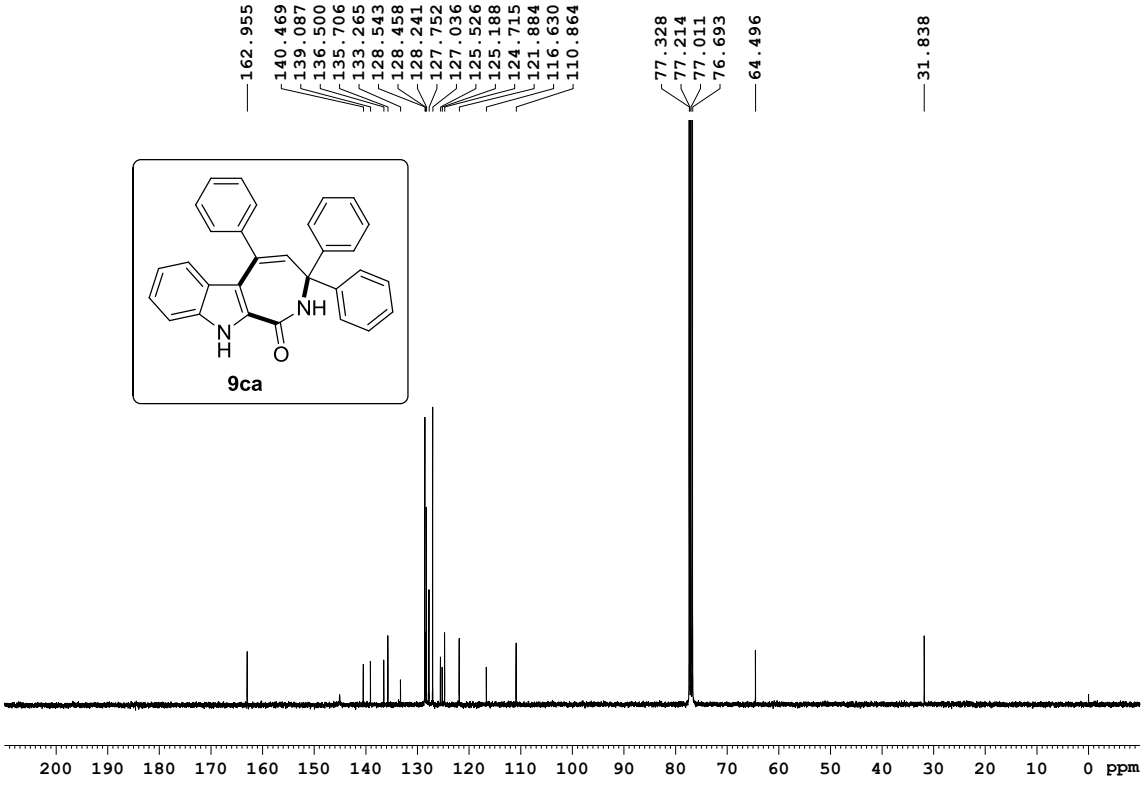


Figure S102. ^{13}C NMR spectrum of compound **9ca**