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Microwave Assisted Synthesis of *N*-Substituted-7-hydroxy-4-methyl-2-oxoquinolines as Anticonvulsant Agents

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Abstract: The reaction of resorcinol with ethylacetoacetate yielded the 7-hydroxy-4-methyl coumarin (**1**), which on treatment with benzidine gives 1-(4'-amino-biphenyl-4-yl)-7-hydroxy-4-methyl-1*H*-quinolin-2-one (**2**). 1-{4'-[(Substituted benzylidene)-amino]-biphenyl-4-yl}-7-hydroxy-4-methyl-1*H*-quinolin-2-one (**3a-j**) were obtained by reacting 1-(4'-amino-biphenyl-4-yl)-7-hydroxy-4-methyl-1*H*-quinolin-2-one (**2**) with different substituted aromatic aldehydes in presence of glacial acetic acid by microwave irradiation. The compound 1-{4'-[(substituted benzylidene)-amino]-biphenyl-4-yl}-7-hydroxy-4-methyl-1*H*-quinolin-2-one (**3a-j**) on cyclization with chloro acetyl chloride in presence of triethylamine as catalyst under microwave irradiation furnished 1-{4'-[3-chloro-2-(substituted phenyl)-4-oxo-azetidin-1-yl]-biphenyl-4-yl}-7-hydroxy-4-methyl-1*H*-quinolin-2-one (**4a-j**). Purity of synthesized compounds was checked by TLC and the structures were elucidated by their IR, ^{1}H NMR, Mass and elemental analysis data. The synthesized compounds were screened for anticonvulsant activity.

Keywords: Quinolinones, Microwave synthesis, Anticonvulsant activity.

Introduction

The derivatives of quinolinone have been known to possess various biological activities such as antitumour, antimalarial, antiplatelet, antidepressant, anticonvulsant, antiulcer, neuroleptic, cardiac stimulant, antiviral, antiasthmatic and anti-inflammatory activities[1]. Schiff base, a versatile lead molecule for potential bioactive agents and its derivatives have been reported to possess antibacterial, antifungal, antitumour, antimycobacterial and herbicidal activity[2,3]. Azetidinone derivatives are also reported to have powerful antimicrobial, anti-inflammatory, anticonvulsant, carbonic anhydrase inhibitor, local anaesthetic, anthelmentic, hypoglycemic antitubercular activity, antiviral and hypolipidemic

activity[4,5]. On consideration of the above observations, it was worthwhile to synthesize some new 1-{4'-[(substituted benzylidene)-amino]-biphenyl-4-yl}-7-hydroxy-4-methyl-1*H*-quinolin-2-one **(3a-j)** and 1-{4'-[3-chloro-2-(substituted phenyl)-4-oxo-azetidin-1-yl]-biphenyl-4-yl}-7-hydroxy-4-methyl-1*H*-quinolin-2-one **(4a-j)** by using microwave and to screen them for their anticonvulsant activity.

Experimental

The melting points of synthesized compounds were determined by open capillary tubes using paraffin bath and are uncorrected. The purity was checked by TLC on silica gel G plates using benzene-methanol as developer detected by iodine vapors. The IR spectra were recorded on a JASCO FT-IR 4100 spectrophotometer, using KBr powder technique. ^{1}H NMR spectra were recorded on a Varian-NMR-mercury 300 MHz spectrophotometer in DMSO using TMS as an internal standard. Mass spectra were recorded on LC-MS/MS, API-4000 using Electrospray ionization (ESI) as a source. Microwave irradiations were carried out on CATA's Scientific Microwave Synthesis System-700 W, 2450 MHz domestic microwave oven. All solvents were dried, deoxygenated and redistilled before use.

7-Hydroxy-4-methyl coumarin **(1)** was synthesized according to reported procedure[6]. Yield: 81.96%, m.p. 184-186 °C.

1-(4'-Amino-biphenyl-4-yl)-7-hydroxy-4-methyl-1H-quinolin-2-one **(2)**

A mixture of 7-hydroxy-4-methyl coumarin **(1)** (1.76 g, 0.01 mole) and benzidine (1.84 g, 0.01 mole) in anhydrous pyridine (50 mL) was heated under reflux for five hours under anhydrous conditions. Subsequently, the reaction mixture was poured into ice (90 mL H_2O + 10 mL HCL). A solid separated out which was filtered off and washed successively with water and purified by recrystallization from methanol.

Yield: 70%, m.p. 165-168 °C, Anal. Calc. for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18%; Found: C, 77.19; H, 5.33; N, 8.15%. IR (KBr): 1359.57 (C-N), 1641.13 (C=O), 1677.77 (aromatic C=C stretching), 2924.52 (aromatic C-H stretching), 3326.61 (O-H stretching) and 3386.39 cm^{-1} (Ar-NH_2).

General procedure

1-{4'-[(Substitutedbenzylidene)-amino]-biphenyl-4-yl}-7-hydroxy-4-methyl-1H-quinolin-2-one (3a-j)

To a mixture of 1-(4'-amino-biphenyl-4-yl)-7-hydroxy-4-methyl-1*H*-quinolin-2-one **(2)**, (0.01 mole) in methanol (20 mL), substituted aromatic aldehydes (0.015 mole), glacial acetic acid (1 mL) were added and the reaction mixture was irradiated with microwaves at power level 8 (490 W) for about 5-10 minutes inside the microwave oven. Reaction was monitored by TLC after completion the reaction mixture was allowed to cool and poured over crushed ice. The precipitated solid thus obtained was filtered, washed with ice-cold water and recrystallised from methanol.

3a: Yield: 78.4%, m.p. 178-180 °C, Anal. Calc. for $C_{29}H_{22}N_2O_2$: C, 80.91; H, 5.15; N, 6.51%; Found: C, 80.80; H, 5.11; N, 6.56%. IR (KBr): 1197.58 (C-N), 1605.45 cm^{-1} (N=C stretching), 1653.66 (C=O), 1677.77 (aromatic C=C stretching), 2852.2 (aromatic C-H stretching) and 3349.75 cm^{-1} (O-H stretching).

3b: Yield: 75.77%, m.p. 188-190 °C, Anal. Calc. for $C_{29}H_{21}N_2O_2Cl$: C, 74.92; H, 4.55; N, 6.02%; Found: C, 74.85; H, 4.46; N, 6.12%. IR (KBr): 754.031 (C-Cl bending), 1113.69 (C-N), 1617.02 (N=C stretching), 1641.13 (C=O), 1671.02 (aromatic C=C stretching),

2924.52 (aromatic C-H stretching) and 3319.86 cm^{-1} (O-H stretching); ^1H NMR: δ 2.359 (s,3H,CH_3); 7.603-6-702 (m,15H,Ar-H); 6.124 (s,1H,N=CH) and 3.349 ppm (s,1H,Ar-OH); MS: *m/z* 465.5 (M^+, 100% base peak), 464.3 (11.12%), 451.1 (66.67%), 441.1 (54.45%), 439.2 (55.56%), 425.5 (54.45%), 417.5 (76.67%) and 409.2 (55.56%).

3c: Yield: 77.17%, m.p. 176-178 °C, Anal. Calc. for $C_{29}H_{21}N_3O_4$: C, 73.25; H, 4.45; N, 8.84%; Found: C, 73.33; H, 4.48; N, 8.97%. IR (KBr): 1179.26 (C-N), 1545.67 (N=O stretching), 1611.23 (N=C stretching), 1665.23 (C=O), 1767.44 (aromatic C=C stretching), 3338.18 (O-H stretching) and 2924.52 cm^{-1} (aromatic C-H stretching).

3d: Yield: 76.81%, m.p. 229-232 °C, Anal. Calc. for $C_{31}H_{27}N_3O_2$: C, 78.62; H, 5.75; N, 8.87%; Found: C, 78.58; H, 5.79; N, 8.88%. IR (KBr): 1197.58 (C-N), 1623.77 (N=C stretching), 1653.66 (C=O), 1677.77 (aromatic C=C stretching), 2924.52 (aromatic C-H stretching) and 3349.75 cm^{-1} (O-H stretching).

3e: Yield: 71.05%, m.p. 164-166 °C, Anal. Calc. for $C_{32}H_{28}N_2O_5$: C, 73.83; H, 5.42; N, 5.38%; Found: C, 73.88; H, 5.49; N, 5.42%. IR (KBr): 1197.58 (C-N), 1233.25 (Ph-O-C stretching), 1617.02 (N=C stretching), 1646.91 (C=O), 1700.91 (aromatic C=C stretching), 2924.52 (aromatic C-H stretching) and 3343.96 cm^{-1} (O-H stretching).

3f: Yield: 89.55%, m.p. 238-240 °C, Anal. Calc. for $C_{30}H_{24}N_2O_3$: C, 78.24; H, 5.25; N, 6.08%; Found: C, 78.27; H, 5.28; N, 6.12%. IR (KBr): 1233.25 (Ph-O-C stretching), 1317.14 (C-N), 1623.77 (N=C stretching), 1646.91 (C=O), 1677.77 (aromatic C=C stretching), 2924.52 (aromatic C-H stretching) and 3338.18 cm^{-1} (O-H stretching).

3g: Yield: 92.3%, m.p. 219-222 °C, Anal. Calc. for $C_{29}H_{22}N_2O_3$: C, 78.01; H, 4.97; N, 6.27%; Found: C, 78.07; H, 4.89; N, 6.30%. IR (KBr): 1323.89 (C-N), 1617.02 (N=C stretching), 1646.91 (C=O), 1671.02 (aromatic C=C stretching), 2924.52 (aromatic C-H stretching) and 3373.85 cm^{-1} (O-H stretching).

3h: Yield: 66.67%, m.p. 166-170 °C, Anal. Calc. for $C_{29}H_{21}N_3O_4$: C, 73.25; H, 4.45; N, 8.84%; Found: C, 73.29; H, 4.48; N, 8.79%. IR (KBr): 1227.47 (C-N), 1545.67 (N=O stretching), 1605.45 (N=C stretching), 1641.13 (C=O), 1677.77 (aromatic C=C stretching), 2924.52 (aromatic C-H stretching) and 3319.86 cm^{-1}(O-H stretching).

3i: Yield: 66.92%, m.p. 198-202 °C, Anal. Calc. for $C_{29}H_{22}N_2O_3$: C, 78.01; H, 4.97; N, 6.27%; Found: C, 78.09; H, 4.99; N, 6.30%. IR (KBr): 1186.01 (C-N), 1605.45 (N=C stretching), 1646.91 (C=O), 1677.77 (aromatic C=C stretching), 2924.52 (aromatic C-H stretching) and 3379.64 cm^{-1} (O-H stretching).

3j: Yield: 85%, m.p. 190-192 °C, Anal. Calc. for $C_{27}H_{20}N_2O_3$: C, 77.13; H, 4.79; N, 6.66%; Found: C, 77.18; H, 4.82; N, 6.65%. IR (KBr): 1035.59 (C-O stretching), 1083.8 (C-N), 1611.23 (N=C stretching), 1641.13 (C=O), 1671.02 (aromatic C=C stretching), 2918.73 (aromatic C-H stretching) and 3356.5 cm^{-1} (O-H stretching).

*1-{4'-[3-chloro-2-(substituted phenyl)-4-oxo-azetidin-1-yl]-biphenyl-4-yl}-7-hydroxy-4-methyl-1H-quinolin-2-one (**4a-j**)*

A mixture of 1-{4'-[(substituted benzylidene)-amino]-biphenyl-4-yl}-7-hydroxy-4-methyl-1*H*-quinolin-2-one **(3a-j)** (0.01 mole) in DMF and chloroacetyl chloride (0.01 mole) with a catalytic amount of triethylamine (1 mL) were put in flask and irradiated under microwave for 5-25 minutes at power level 8 (490 W). Reaction was monitored by TLC after completion of reaction; it was then diluted with ice-cold water. The separated solid was filtered, dried and recrystallized from DMSO.

4a: Yield: 76.46%, m.p. 140-150 °C, Anal. Calc. for $C_{31}H_{23}N_2O_3Cl$: C, 73.44; H, 4.57; N, 5.53%; Found: C, 73.41; H, 4.59; N, 5.49%. IR (KBr): 748.245 (C-Cl bending), 1299.79 (C-N), 1641.13 (C=O), 1689.34 (C=O stretching *β*-lactam) and 1719.23 cm^{-1} (aromatic C=C stretching).

4b: Yield: 78.99%, m.p. 174-176 °C, Anal. Calc. for $C_{31}H_{22}N_2O_3Cl_2$: C, 68.77; H, 4.10; N, 5.17%; Found: C, 68.72; H, 4.13; N, 5.19%. IR (KBr): 783.922 (C-Cl bending), 1281.47 (C-N), 1646.91 (C=O), 1677.77 (aromatic C=C stretching), 1700.91 (C=O stretching β-lactam) and 3349.75 cm^{-1} (O-H stretching); ^1H NMR: δ 2.436 (s,3H,CH_3); 4.282 (s,1H,Ar-OH); 4.937 (s,1H,CH-N of *β*- lactam); 6.817 (d,1H,C-C_6H_5 of *β*- lactam) and 8.708-7.331 ppm (m,15H,Ar-H); and MS: *m/z* 545.3 (17.72%), 542.9 (43.03%), 535.3 (M^+, 100% base peak), 529.3 (43.03%), 523.1 (56.96%), 521.3 (74.68%), 508.7 (55.69%) and 507.4 (68.35%).

4c: Yield: 76.72%, m.p. 168-170 °C, Anal. Calc. for $C_{31}H_{22}N_3O_5Cl$: C, 67.46; H, 4.02; N, 7.61%; Found: C, 67.44; H, 4.05; N, 7.59%. IR (KBr): 789.707 (C-Cl bending), 1348 (C-N), 1521.56 (N=O stretching), 1659.45 (C=O), 1689.34 (C=O stretching *β*-lactam), 1737.55 (aromatic C=C stretching), 3140.51 (aromatic C-H stretching) and 3218.61 cm^{-1} (O-H stretching).

4d: Yield: 75%, m.p. 100-104 °C, Anal. Calc. for $C_{33}H_{28}N_3O_3Cl$: C, 72.06; H, 5.13; N, 7.64%; Found: C, 72.09; H, 5.14; N, 7.63%. IR (KBr): 783.922 (C-Cl bending), 1275.68 (C-N), 1611.23 (aromatic C=C stretching), 1646.91 (C=O), 1671.02 (C=O stretching *β*-lactam) and 2978.52 cm^{-1} (aromatic C-H stretching).

4e: Yield: 72.36%, m.p. 148-150 °C, Anal. Calc. for $C_{34}H_{29}N_2O_6Cl$: C, 68.40; H, 4.90; N, 4.69%; Found: C, 68.38; H, 4.92; N, 4.72%. IR (KBr): 765.601 (C-Cl bending), 1245.79 (Ph-O-C stretching), 1359.57 (C-N), 1641.13 (C=O), 1671.02 (C=O stretching *β*-lactam) and 3373.85 cm^{-1} (O-H stretching).

4f: Yield: 78.35%, m.p. 112-115 °C, Anal. Calc. for $C_{32}H_{25}N_2O_4Cl$: C, 71.57; H, 4.69; N, 5.22%; Found: C, 71.55; H, 4.67; N, 5.27%. IR (KBr): 782.958 (C-Cl bending), 1143.58 (C-N), 1244.83 (Ph-O-C stretching), 1641.13 (C=O), 1676.8 (C=O stretching *β*-lactam), 2878.24 (aromatic C-H stretching) and 3375.78 cm^{-1} (O-H stretching).

4g: Yield: 74.23%, m.p. 141-145 °C, Anal. Calc. for $C_{31}H_{23}N_2O_4Cl$: C, 71.20; H, 4.43; N, 5.36%; Found: C, 71.18; H, 4.44; N, 5.32%. IR (KBr): 771.387 (C-Cl bending), 1280.5 (C-N), 1676.8 (C=O stretching *β*-lactam), 1641.13 (C=O) and 3375.78 cm^{-1} (O-H stretching).

4h: Yield: 68.26%, m.p. 139-142 °C, Anal. Calc. for $C_{31}H_{22}N_3O_5Cl$: C, 67.46; H, 4.02; N, 7.61%; Found: C, 67.48; H, 4.05; N, 7.59%. IR (KBr): 788.743 (C-Cl bending), 1267.97 (C-N), 1558.2 (N=O stretching), 1646.91 (C=O), 1682.59 (C=O stretching *β*-lactam) and 3162.69 cm^{-1} (O-H stretching).

4i: Yield: 59.39%, m.p. 138-140 °C, Anal. Calc. for $C_{31}H_{23}N_2O_4Cl$: C, 71.20; H, 4.43; N, 5.36%; Found: C, 71.23; H, 4.45; N, 5.38%. IR (KBr): 756.601 (C-Cl bending), 1280.5 (C-N), 1611.23 (aromatic C=C stretching), 1646.91 (C=O), 1671.02 (C=O stretching *β*-lactam) and 3381.57 cm^{-1} (O-H stretching).

4j: Yield: 77.96%, m.p. 150-155 °C, Anal. Calc. for $C_{29}H_{21}N_2O_4Cl$: C, 70.09; H, 4.26; N, 5.64%; Found: C, 70.06; H, 4.28; N, 5.66%. IR (KBr): 765.601 (C-Cl bending), 1065.48 (C-O), 1371.14 (C-N), 1641.13 (C=O) and 1677.77 cm^{-1} (C=O stretching *β*-lactam).

Anticonvulsant activity

The experimental protocol was approved by the Institutional Animal Ethical Committee (IAEC) and was conducted according to the guidelines for use and care of experimental

animals. Adult, healthy, overnight fasted, male albino mice, weighing between 20-25 g were used. They were housed under standard environmental conditions of temperature (24±2 °C), relative humidity of 30-70% and 12 h light/dark cycle as per CPCSEA guidelines. All animals had free access to water and standard pelletized laboratory animal diet *ad libitum*.

The animals were divided into different groups with each group consisting of six animals. After 30 minutes of oral administration of test compounds, animals were stimulated through corneal electrodes with 50 mA current at a pulse of 60 Hz alternating current for 0.2 sec. The abolition of hind limb tonic extensor spasm was recorded as a measure of anticonvulsant activity. The above procedure was repeated after 60, 90 and 120 minutes of administration.

Statistical analysis

Data obtained from pharmacological experiments are expressed as mean ± S.E.M. At the end of experiment, test groups were compared with control and were tested for its significance using ANOVA followed by Dunnett's test. Values of $P < 0.05$ or lower were regarded as significant. The result of anticonvulsant activity of all the synthesized compounds is presented below.

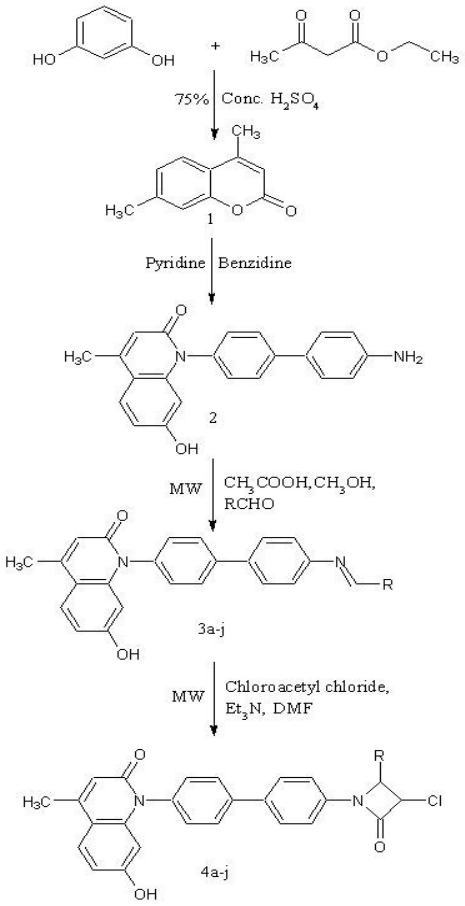
Results and Discussion

After 30 minutes, compound **3b, 3c, 3j** and **4h** showed better activity, at 60 minutes interval compound **3a, 3c** and **4a** were found to show better activity, at 90 minutes, compound **3j, 4a** and **4c** exhibited better activity, whereas at 120 minutes, compound **3j, 4a** and **4d** displayed better activity. Thus, amongst all the synthesized compounds, compound **3j** and **4a** were found to be the most active candidates, compound **3c** also exhibited good activity at 30 and 60 minutes, whereas the remaining compounds exhibited moderate activity.

Table 1. Duration of hind limb extensor of the synthesized compounds

Group	Treatment	Dose, mg/kg	Duration of hind limb extensor in seconds (mean±S.E.M)			
			30 minutes	60 minutes	90 minutes	120 minutes
I	Control	0.1 mL/10 gm	71±0.577	74±2.082	71±1.155	72.33±1.202
II	Standard (Diazepam)	5 mg/kg, i.p.	25±2.646	19.66±0.882	11.66±1.202	8.66±1.202
III	**3a**	27	44±0.577	25.66±1.856	39.66±1.453	41.33±1.764
IV	**3b**	27	40±0.577	26±1.155	29.66±1.202	37.66±1.202
V	**3c**	27	35±0.577	25±2.082	28±1.155	$65.66±1.453^{ns}$
VI	**3d**	27	48.66±0.882	28±0.577	30.66±1.202	40.33±1.202
VII	**3e**	27	43.66±2.028	30±1.155	34±1.528	39.33±0.882
VIII	**3f**	27	46±0.577	28±0.577	32.33±1.202	40±1.732
IX	**3g**	27	42±1.528	29.33±1.202	30.66±1.453	$64±1.528^{ns}$
X	**3h**	27	$55.33±0.882^{ns}$	29±0.577	31±1.155	45±0.577
XI	**3i**	27	49±1.155	28.66±1.453	32±0.577	37±0.577
XII	**3j**	27	36±1.528	26.33±0.882	26.33±1.764	30±0.577
XIII	**4a**	27	$65.66±1.856^{ns}$	25.66±0.882	27±2.082	32±1.155
XIV	**4b**	27	49±0.577	29±0.577	32±1.732	38±2.082
XV	**4c**	27	45±2.309	27.66±1.453	27±0.577	39±1.528
XVI	**4d**	27	42.33±1.202	28±1.000	33.66±1.202	35±1.732
XVII	**4e**	27	$57±1.528^{ns}$	28.66±1.764	34.66±1.453	36.66±2.404
XVIII	**4f**	27	46.33±2.186	26.66±0.882	28.66±1.453	39.66±1.202
XIX	**4g**	27	42±0.577	26±1.528	29±2.082	42.66±0.882
XX	**4h**	27	40±1.155	29.33±0.882	35.66±0.882	53.33±2.404
XXI	**4i**	27	48.33±0.333	25.66±1.202	27.66±1.453	39±1.528
XXII	**4j**	27	$59±1.528^{ns}$	30±1.528	29.33±1.856	37.33±1.453

Data were analyzed by one-way ANOVA followed by Dennett's test.
Values are expressed as mean±S.E.M; P<0.01 when compared to control; ns- non significant



Scheme 1

Table 2. Physical data of synthesized compounds

No	R	Molecular Formula	Mol. Wt	Melting Point, °C	*R_f value	% yield	Reaction time minutes
3a	C_6H_5-	$C_{29}H_{22}N_2O_2$	430.51	178-180	0.8	78.4	8
3b	4-Cl C_6H_4-	$C_{29}H_{21}N_2O_2Cl$	464.96	188-190	0.59	75.77	5
3c	4-NO_2 C_6H_4-	$C_{29}H_{21}N_3O_4$	475.51	176-178	0.7	77.17	7
3d	4-$(CH3)_2N$ C_6H_4-	$C_{31}H_{27}N_3O_2$	473.58	229-232	0.75	76.81	7
3e	3,4,5-$(OCH3)_3C_6H_2$-	$C_{32}H_{28}N_2O_5$	520.59	164-166	0.73	71.05	5
3f	4-OCH3 C_6H_4-	$C_{30}H_{24}N_2O_3$	460.54	238-240	0.54	89.55	6
3g	2-OH C_6H_4-	$C_{29}H_{22}N_2O_3$	446.51	219-222	0.63	92.3	6
3h	3-NO_2 C_6H_4-	$C_{29}H_{21}N_3O_4$	475.51	166-170	0.58	66.67	8
3i	4-OH C_6H_4-	$C_{29}H_{22}N_2O_3$	446.51	198-202	0.53	66.92	9
3j	C_4H_3O-	$C_{27}H_{20}N_2O_3$	420.47	190-192	0.74	85	5
4a	C_6H_5-	$C_{31}H_{23}N_2O_3Cl$	506.99	140-150	0.55	76.46	15
4b	4-Cl C_6H_4-	$C_{31}H_{22}N_2O_3Cl_2$	541.44	174-176	0.65	78.99	12

Contd…

4c	4-NO_2 C_6H_4-	$C_{31}H_{22}N_3O_5Cl$	551.99	168-170	0.46	76.72	17
4d	4-$(CH3)_2N$ C_6H_4-	$C_{33}H_{28}N_3O_3Cl$	550.06	100-104	0.73	75	14
4e	3,4,5-$(OCH3)_3C_6H_2$-	$C_{34}H_{29}N_2O_6Cl$	597.07	148-150	0.6	72.36	18
4f	4-OCH3 C_6H_4-	$C_{32}H_{25}N_2O_4Cl$	537.02	112-115	0.51	78.35	22
4g	2-OH C_6H_4-	$C_{31}H_{23}N_2O_4Cl$	522.99	141-145	0.75	74.23	22
4h	3-NO_2 C_6H_4-	$C_{31}H_{22}N_3O_5Cl$	551.99	139-142	0.55	68.26	16
4i	4-OH C_6H_4-	$C_{31}H_{23}N_2O_4Cl$	522.99	138-140	0.63	59.39	11
4j	C_4H_3O-	$C_{29}H_{21}N_2O_4Cl$	496.95	150-155	0.44	77.96	8

[*] *benzene: methanol*

Conclusion

From the anticonvulsant data of the synthesized compounds, we can conclude that the compounds **3j** and **4a** have exhibited excellent anticonvulsant activity in MES model and hold promise as anticonvulsant agents after further development.

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