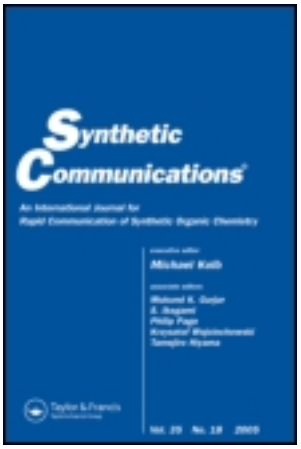

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Aqueous Synthesis of N-Phenyl/alkyl-2-quinolinone-3-carboxylic Acids from Coumarin-3-carboxylic Acids

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AQUEOUS SYNTHESIS OF *N*-PHENYL/ALKYL-2-QUINOLINONE-3-CARBOXYLIC ACIDS FROM COUMARIN-3-CARBOXYLIC ACIDS

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An efficient, ecofriendly aqueous synthesis of aromaticlaliphatic amines with coumarin-3-carboxylic acid in a one pot reaction in a sealed tube or $InCl_3$l H_2O in open vessel to afford N-phenyllalkyl-2-quinolinones is achieved. This method provides high yield of products in shorter time, making it a useful process for the synthesis of structurally diversified 2-quinolinones from corresponding coumarins.

Keywords: Coumarin-3-carboxylic acid; *N*-phenyl/alkyl-2-quinolinones; one pot

INTRODUCTION

Quinoline derivatives are widely known in medicinal chemistry because they are present in a wide range of natural products[1] and drugs.[2] Substituted *N*-phenyl/alkyl-2-quinolinones represent the structural basis of many biologically active compounds, such as protein kinase inhibitors, immune modulators, anti-ulcer agents, hypoglycemics, farnesyl transferase inhibitors, and antiviral agents.[3a–f] Only a few practical procedures are known for the synthesis of *N*-substituted-2-quinolinones that involve the coupling of *nor*-quinolinones with aryl halides,[4] boronic acids,[5] or organolead reagents.[6] In addition to these, some examples were also given in which coumarins were directly aminolyzed upon treatment with aminobenzimidazoles.[7] On the other hand, ammonia and primary amines are known to react with 2-pyrones to afford the corresponding 2-pyridones.[8]

In spite of these syntheses, there is still a wide scope for simple, convenient, and ecofriendly synthesis. Moreover, the conversions of coumarins into various *N*-substituted quinolones with the reaction of aliphatic/aromatic amines have not been explored extensively. Hence, in the present study, we report the preliminary results of a simple synthesis of *N*-substituted quinolone using water.

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Table 1. Screening of the effect of solvent for the synthesis of *N*-phenyl/alkyl-2-quinolinone-3-carboxylic acids at reflux temperature

Entry	Solvent	Conditions	Time (h)	Yield (%)[a]
1	EtOH	Sealed tube	1	20–30
2	EtOH	Open vessel	16	10
3	DMSO	Sealed tube	1	–
4	DMSO	Open vessel	1	–
5	Water	Sealed tube	1	95
6	Water	Open vessel	18	60
7	H_2O/10% (NaOH)	Sealed tube	1	6
8	H_2O/10% (NaOH)	Open vessel	16	3

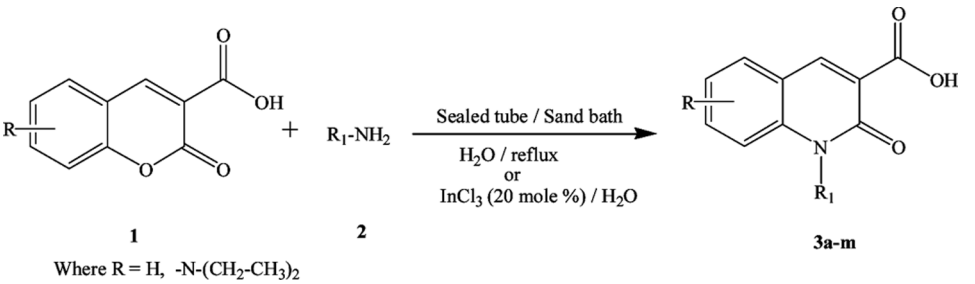
[a]Isolated yields.

RESULTS AND DISCUSSION

The reaction was performed with molar equivalents of coumarin-3-carboxylic acid **1** (100 mg, 5 mmol) and aniline **2** (53 mg, 5 mmol) in absolute alcohol at reflux temperature. When the reaction was monitored by thin-layer chromatography (TLC), it shows less conversion of products and incomplete reaction even at longer reaction time. However, the effort to obtain *N*-phenyl-2-quinolinones **3a** was unsuccessful in various solvents (Table 1) under the same reaction condition. Hence, while searching an alternative method, we carried out this reaction in water (Scheme 1) (entries 6 and 7, Table 1).

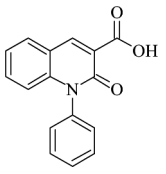
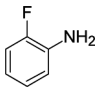
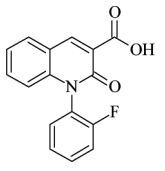
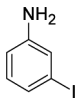
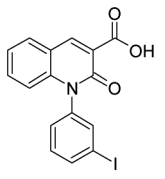
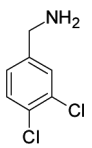
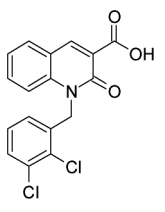
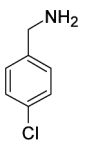
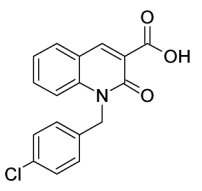
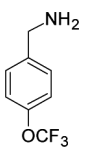
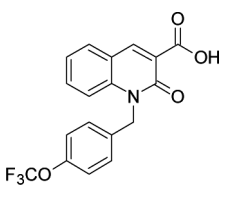
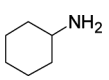
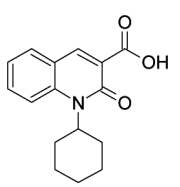
Thus, the reaction of molar equivalents of coumarin-3-carboxylic acid **1** (100 mg, 5 mmol) and aniline **2a** (53 mg, 5 mmol) was refluxed in water (5 ml). Interestingly, the reaction occurred smoothly in water at reflux temperature in 10 h. Further, it was noticed that the reaction time and yield of the products were significantly increased when the reaction was performed in a sealed tube refluxing in a sand bath (Table 1).

Similarly, we also observed that the rate of aminolysis of coumarin-3-carboxylic acids with aryl amines was slow in our series and usually required longer reaction time when compared to aliphatic amines. However, yields of the products were not much affected. For these reasons, we intended to seek an alternative route that would tolerate a variety of amines, providing good yields and reduction in the reaction time. Further, we thought to use a Lewis acid catalyst to increase the



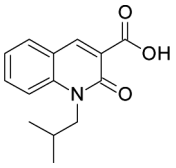
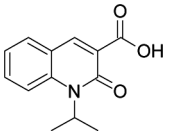
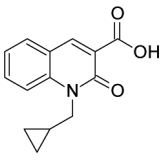
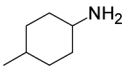
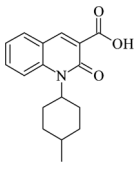
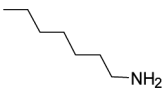
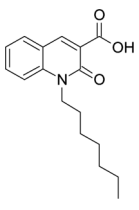
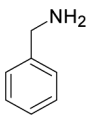
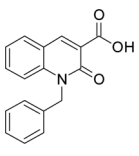
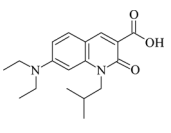
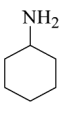
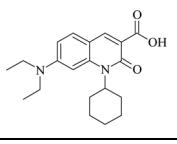
Scheme 1. Synthesis of *N*-phenyl/alkyl-2-quinolinones.

Table 2. Synthesis of various *N*-phenyl/alkyl-2-quinolinones in $InCl_3/H_2O$

Comp.	Amine (R_1)	Product	Time (h)	Yield (%)[a]	Mp (°C)
3a			0.5	94	160–162
3b			1.5	95	129–131
3c			2.0	93	179–180
3d			4.0	94	178–180
3e			3.0	95	201–202
3f			2.5	90	145–146
3g			1.0	90	169–170

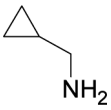
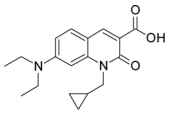
(*Continued*)

Table 2. Continued

Comp.	Amine (R_1)	Product	Time (h)	Yield (%)[a]	Mp (°C)
3h			0.5	95	184–185
3i			1.0	93	178–180
3j			1.0	95	147–148
3k			1.0	90	194–195
3l			1.0	90	200–202
3m			1.0	96	190–191
3n			1.5	95	185–188
3o			1.5	94	200–202

(*Continued*)

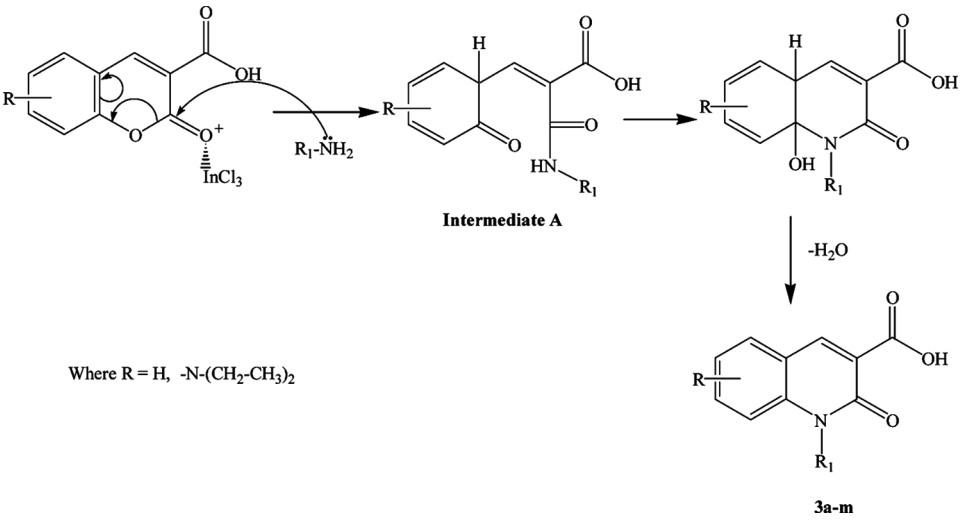
Table 2. Continued

Comp.	Amine (R_1)	Product	Time (h)	Yield (%)[a]	Mp (°C)
3p			2.0	97	165–167

[a]Isolated yield.

efficiency of this reaction. Through a literature survey, we came to know that indium trichloride was an effective catalyst in the Diels–Alder reactions in water media[9] and was also known to facilitate imino Diels–Alder reaction in the synthesis of tetrahydrofuro/pyrano quinolines[10] in water. In continuation of our work,[11] and in view of developing an environmentally benign synthesis, here we trace out the possibility of using indium trichloride in water in our synthesis.

When we did this reaction in the presence of indium trichloride (20 mol%) in water, the reaction went smoothly to give good yield and a reduction in the reaction time (Table 2). The formation of the products *N*-phenyl/alkyl-2-quinolinone-3-carboxylic acids **3a–m** is postulated through nucleophilic addition of the amine group to the pyran ring system and subsequent cyclization of intermediate A, affording 2-quinolinone-3-carboxylic acids **3a–m**, as illustrated in Scheme 2. The results of preliminary investigations during these reactions are presented in this article. To the best of our knowledge, this is the first report in which the coumarin nucleus can be directly converted into quinoline-2-ones with a wide variety of aromatic and aliphatic amines. Further exploration of this reaction with various substituted coumarins is under way in this laboratory.



Scheme 2. Mechanism of synthesis of *N*-phenyl/alkyl-2-quinolinones.

In conclusion, various *N*-phenyl/alkyl-2-quinolinone-3-carboxylic acids could be synthesized without catalyst in a sealed tube by refluxing on a sand bath using water as media. Thus, efficient, ecofriendly, water-mediated cyclization of aromatic/aliphatic amines and coumarin-3-carboxylic acid in a one pot reaction to afford *N*-phenyl/alkyl-2-quinolinones is achieved. This method provides excellent yield of products in less time, making it a useful process for the synthesis of structurally diversified 2-quinolinones from corresponding coumarins.

EXPERIMENTAL

Products were identified by their physical and spectroscopic data, all the melting points were recorded in open capillaries. The purity of the compounds were checked by thin-layer chromatography (TLC) on silica gel. ^{1}H NMR spectra were recorded on a Bruker 400-Hz spectrometer using CD_3OD as a solvent. Mass spectra were recorded on a Jeol SX102 = DA-6000 (10 kV) fast atomic bombardment mass spectrometer. Solvents, chemicals, and reagents were purchased from Merck Chemical Company in high-grade quality.

General Procedure for the Synthesis of *N*-Phenyl-2-quinolinones (3a)

Method A. Coumarin-3-carbaxylic acid (100 mg, 5 mmol) was taken in a sealed tube containing 5 ml of water and aniline (53 mg, 5 mmol). The mixture was heated on a sand bath for 1 h. After the completion of the reaction as indicated by liquid chromatography–mass spectrometry (LC-MS), the compound was extracted with ethyl acetate (50 mL × 2), dried with anhydrous sodium sulfate, concentrated in vacuum, and purified by column chromatography. Further, the compound was analyzed by ultra performance liquid chromatography (UPLC)-mass, ^{1}H NMR, and ^{13}C NMR. Melting points were recorded in an open capillary. Other quinolinones were prepared similarly.

Method B. A mixture of coumarin-3-carbaxylic acid (100 mg, 5 mmol), aniline (53 mg, 5 mmol), and indium trichloride (20 mol%) were taken in 20 ml of water. Then the mixture was heated on a water bath for the appropriate time. After the completion of the reaction as indicated by LC-MS analysis, the compound was extracted with ethyl acetate (50 mL × 2), dried with sodium sulfate, concentrated in vacuo, and purified by column chromatography. Further, the compound was analyzed by UPLC-mass, ^{1}H NMR, and ^{13}C NMR. Melting points were recorded in an open capillary. Other quinolinones were prepared similarly.

Selected Data

Compound 3a. IR (KBr, cm^{-1}): 3600, 1733.9, 1606.8. ^{1}H NMR (300 MHz, CD_3OD) δ: 8.72 (s, 1H), 7.80 (m, 2H), 7.42 (m, 2H), 7.14 (m, 2H), 6.80 (m, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ: 166.1, 160.8, 156.2, 150.2, 146.6, 135.6, 131.2, 131.5, 130.1, 126.3, 126.3, 120.5, 119.7, 119.3, 117.5, 117.49. MS: $m/z = 266.3$ (M + 1).

Compound 3b. IR (KBr, cm^{-1}): 3626, 1700, 1598. ^{1}H NMR (300 MHz, CD_3OD) δ: 8.10 (s, 1H), 7.84 (d, $J = 1.48$ Hz, 1H), 7.76 (t, $J = 1.2$ Hz, 1H), 7.44

(m, 2H), 6.87 (m, 3H), 6.64 (m, $J = 1.84$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.5, 161, 156.8, 150.6, 155, 147, 140, 131.5, 130.1, 126.6, 126.6, 120.58, 120.5, 120.5, 116.4, 116.4. MS: $m/z = 284.2$ (M + 1), 285.3 (M + 2).

Compound 3c. IR (KBr, cm^{-1}): 3625.2, 1739.6, 1609.^{1}H NMR (300 MHz, CD_3OD) δ: 8.79 (s, 1H), 7.83 (m, 2H), 7.44 (m, 2H), 7.12 (t, $J = 2.52$ Hz, 1H), 6.96 (m, 1H), 6.82 (t, $J = 10.4$ Hz, 1H), 6.66 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.5, 161, 156.8, 127.8, 155, 147, 140, 148, 135.14, 126.9, 126.8, 121.0, 121.0, 120.8, 100.3, 116.4. MS: $m/z = 392.1$ (M + 1).

Compound 3d. IR (KBr, cm^{-1}): 3243.6, 1715.6, 1599.4. ^{1}H NMR (300 MHz, CD_3OD) δ: 8.29 (s, 1H), 7.08 (m, 2H), 7.39 (m, 2H), 7.23 (s, 1H), 7.08 (m, 1H), 6.83 (m, 1H), 4.11 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.7, 163.8, 155.8, 126.8, 146.5, 146.5, 140, 147, 135.14, 126.9, 126.8, 121.0, 121.0, 120.8, 135, 128.4, 55.8. MS: $m/z = 348.2$ (M + 2).

Compound 3e. IR (KBr, cm^{-1}): 3620, 1738, 1615. ^{1}H NMR (300 MHz, CD_3OD) δ: 8.18 (s, 1H), 7.69 (m, 1H), 7.62 (m, 1H), 7.44 (s, 4H), 7.36 (t, $J =$ 6.8 Hz, 2H), 4.10 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.5, 163.2, 155.3, 126.1, 146.2, 146, 139, 146, 133.1, 121.9, 124.8, 120.8, 120.0, 119.8, 134, 126.4, 56.3. MS: $m/z = 314.3$ (M + 1), 314.3 (M + 2).

Compound 3f. IR (KBr, cm^{-1}): 3638, 1749, 1632. ^{1}H NMR (400 MHz, CD_3OD) δ: 8.24 (s, 1H), 7.69 (d, $J = 7.64$ Hz, 1H), 7.63 (t, $J = 11.2$ Hz, 3H), 7.34 (t, $J = 7.72$ Hz, 4H), 4.17 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.5, 163.2, 161.8 155.3, 126.1, 146.2, 146, 139, 146, 133.1, 128.9, 124.0, 120.0, 126.8, 134, 113.6, 113.6, 56.3. MS: m/z, 363.2 (M + 1).

Compound 3g. IR (KBr, cm^{-1}): 3708, 3616, 1629. ^{1}H NMR (300 MHz, CD_3OD) δ: 8.22 (s, 1H), 7.69 (d, $J = 10.28$ Hz, 1H), 7.63 (t, $J = 9.4$ Hz, 1H), 7.36 (m, 2H), 3.12 (s, 1H), 2.10 (s, 2H), 1.84 (s, 2H), 1.70 (d, $J = 12.56$ Hz, 1H), 1.34 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.5, 163.2, 155.3, 126.1, 146.2, 146, 139, 146, 133.1, 128.9, 50.2, 31.2, 31.2, 23.1, 23.1, 27.8. MS : $m/z = 271.3$ (M + 1).

Compound 3h. IR (KBr, cm^{-1}): 3592, 1698, 1612. ^{1}H NMR (400 MHz, CD_3OD) δ: 8.18 (s, 1H), 7.69 (m, 1H), 7.68 (m, 1H), 7.36 (m, 2H), 2.74 (d, $J = 7.12$ Hz, 2H), 1.94 (m, 1H), 1.09 (d, $J = 10.72$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.3, 163.5, 155.3, 126.1, 146.2, 146, 139, 146, 133.14, 128.9, 60.1, 28, 20.3, 20.3. MS: m/z, 246.2 (M + 1), 247.2 (M + 2).

Compound 3i. IR (KBr, cm^{-1}): 3584, 1690, 1608. ^{1}H NMR (300 MHz, CD_3OD) δ: 8.27 (s, 1H), 7.71 (m, 1H), 7.64 (m, 1H), 7.37 (m, 2H), 3.45 (m, 1H), 1.30 (d, $J = 8.72$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.3, 162.5, 154.3, 126.1, 146.2, 146, 139, 146, 133.14, 128.9, 47, 22.3, 22.3. MS: m/z, 232.2 (M + 1).

Compound 3j. IR (KBr, cm^{-1}): 3621, 1770, 1622.8 ^{1}H NMR (400 MHz, CD_3OD) δ: =8.42 (s, 1H), 7.74 (m, 1H), 7.39 (t, $J = 7.2$ Hz, 3H), 2.84 (d, $J = 7.6$ Hz, 2H), 1.12 (m, 1H), 0.69 (m, 2H), 0.38 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.3, 162.8, 154.3, 126.1, 146.2, 146, 139, 146, 133.1, 128.9, 59.9, 8, 2.1, 2.1. MS: m/z, 243.3 (M + 1).

Compound 3k. IR (KBr, cm^{-1}): 3606, 1701, 1620. ^1H NMR (400 MHz, CD_3OD) δ: 8.14 (s, 1H), 7.69 (dd, $J = 1.6$ Hz, 1H), 7.63 (m, 1H), 7.36 (d, $J = 8.2$ Hz, 2H), 1.82 (m, 6H), 1.42 (d, $J = 3.8$ Hz, 3H), 1.06 (d, $J = 3.1$ Hz, 1H), 1.05 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.2, 161.8, 154.3, 126.1, 146.2, 146, 139, 146, 133.14, 128.9, 50.5, 30, 30, 29.3, 29.2, 29.2, 20.4. MS: m/z, 286.3 (M + 1), 287.3 (M + 2).

Compound 3l. IR (KBr, cm^{-1}): 3583, 1682, 1604. ^1H NMR (400 MHz, CD_3OD) δ = 8.16 (s, 1H), 7.69 (m, 1H), 7.62 (m, 1H), 7.36 (m, 2H), 2.08 (m, 2H), 1.5 (m, 10H) 1.48 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.3, 162.8, 154.3, 126.1, 146.2, 146, 139, 146, 133.14, 128.9, 50.8, 35.3, 31.4, 31, 33.1, 24, 28.8, 28.4, 29.6, 29.6, 28.3, 28.3, 15.1. MS: m/z, 287.4 (M + 1).

Compound 3m. IR (KBr, cm^{-1}): 1708, 1604, 3221. ^1H NMR (400 MHz, CD_3OD) δ: 8.24 (s, 1H), 7.74 (d, $J = 7.44$ Hz, 1H), 7.63 (m, 4H), 7.35 (m, 4H), 4.16 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.3, 162.6, 154.2, 126.3, 146.2, 146.1, 143.4, 139, 146, 133.1, 128.9, 56.3, 128.9, 128.2, 127.3, 128.9, 56.1. MS: m/z, 280.3 (M + 1).

Compound 3n. IR (KBr, cm^{-1}): 1708, 1604, 3221. ^1H NMR (400 MHz, DMSO-d_6) δ: 8.698–8.8649 (m, 1H), 7.676 (d, $J = 9.2$ Hz, 1H), 6.799 (d, d, $J = 2.3$, 9.2, 1H), 6.612 (d, $J = 2$, 1H), 3.50–3.44 (m, 4H), 3.138 (t, $J = 9.6$, 2H), 1.826–1.175 (m, 1H), 1.130 (t, J = 6.8, 6H), 0.888 (d, $J = 6.8$, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.3, 161.6, 151.2, 140.3, 135.2, 126.5, 126.1, 111.2, 100.3, 53.6, 48.5, 26.1, 23.7, 19.6, 13.3,MS: m/z, 317.3 (M + 1).

Compound 3o. IR (KBr, cm^{-1}): 1708, 1604, 3221. ^1H NMR (400 MHz, DMSO-d_6) δ: 8.181 (s, 1H), 7.412 (d, $J = 9.6$ Hz, 1H), 6.715 (d, d, $J = 2.58$, 8.91, 1H), 6.485 (d, $J = 2.4$, 1H), 3.51–3.41 (m, 4H), 2.941 (d, $J = 9.9$, 1H), 1.956 (d, $J = 9.9$, 2H), 1.817–1.646 (m, 4H), 1.347 (d, $J = 12.6$, 4H), 1.244–1.161 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.3, 162.3, 150.2, 143.9, 136.2, 126.2, 116.3, 109.3, 49.3, 48.1, 30.5, 27.0, 22.1, 13.2. MS: m/z, 343.3 (M + 1).

Compound 3p. IR (KBr, cm^{-1}): 1708, 1604, 3221. ^1H NMR (400 MHz, DMSO-d_6) δ: 8.181 (s, 1H), 7.671 (d, $J = 9.3$ Hz, 1H), 6.79 (d, $J = 9.9$, 1H), 6.610 (s, 1H), 3.482 (t, $J = 10.7$, 2H), 1.171–0.911 (m, 11H), 0.4469 (d, $J = 7.5$, 2H), 0.203 (d, $J = 5.7$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.5, 162.0, 151.2, 143.3, 136.9, 126.9, 124.6, 108.4, 104.6, 59.1, 48.5, 13.2, MS: m/z, 315.2 (M + 1).

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