One-Pot Three-Component Mild Synthesis of 2-Aryl-3-(9-alkylcarbazol-3-yl)thiazolidin-4-ones

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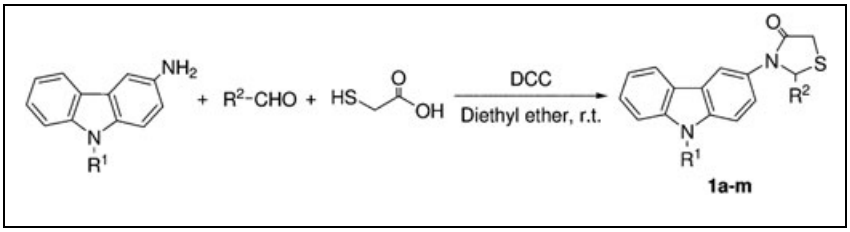

A series of novel 2-aryl-3-(9-alkylcarbazol-3-yl)thiazolidin-4-ones were synthesized by one-pot three-component reactions of 3-amino-9-alkylcarbazoles, aromatic aldehydes, and 2-mercaptoacetic acid by using dicyclohexylcarbodiimide (DCC) as a cyclizing agent in dry diethyl ether at room temperature. This protocol has advantages of mild condition, short reaction time, high yield, and simple work-up procedure.

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INTRODUCTION

Thiazolidinones are important heterocyclic compounds with a wide range of pharmaceutical and biological activities, such as anticancer [1], antibacterial [2], antiparasitic [3], anti-HIV [4], anti-toxoplasma gondii [5], antitubercular [6], antioxidant [7], and anti-inflammatory [8] activities. In addition, carbazole-involved compounds have received increasing interest because of their unique optical properties and strong hole-transporting ability in opto-electronic devices [9], and some important biological activities, such as antitumor [10], antibacterial, and antifungal [11], anti-mycobacterium tuberculosis [12], anti-HIV [13], and anti-proliferative [14] activities. Therefore, the compounds bearing both carbazole and thiazolidinone moieties may be good candidates for optical materials or biologically active chemicals.

The common synthetic routes to thiazolidinones include the reactions of α-chloroamide derivatives with thiocyanates or isothiocyanates [15], the reactions of thioureas with trichloromethylcarbinols [16], the reactions of 1,3,4-thiadiazoles, substituted benzaldehydes and mercaptoacetic acid [17], and the reactions of Schiff bases or imines with mercaptoacetic acid [18]. However, some methods often require long reaction time and high temperature, and the reagents used in the reactions are usually corrosive and environmentally unfriendly.

In this article, we report a one-pot three-component synthetic method for novel carbazole-based thiazolidinones by using dicyclohexylcarbodiimide (DCC) as a cyclizing agent in dry diethyl ether at room temperature.

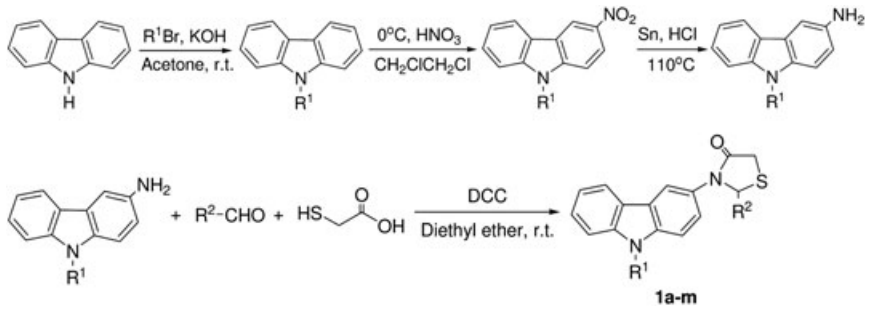
RESULTS AND DISCUSSION

The required 3-amino-9-alkylcarbazoles were prepared according to literature methods [19], [20] (Scheme 1). The reactions of carbazole with bromoalkanes in acetone in the presence of potassium hydroxide first gave 9-alkylcarbazoles in high yield. 9-Alkylcarbazoles on treatment with nitric acid in the solution of 1,2-dichloroethane at 0°C afforded 3-nitro-9-alkylcarbazols in high selectivity (no 3,6-dinitrocarbazoles by-product were observed). 3-Nitro-9-alkylcarbazols were further reduced with tin and hydrochloric acid to give 3-amino-9-alkylcarbazoles.

In order to explore the one-pot three-component reactions of 3-amino-9-alkylcarbazoles, aromatic aldehydes and 2-mercaptoacetic acid, and mild synthesis of carbazole-based thiazolidinones, 3-amino-9-ethylcarbazole, benzaldehyde and 2-mercaptoacetic acid were selected as substrates to conduct the reaction (Scheme 1). It was found that the optimal yield for the reaction was obtained by using 1 mmol of 3-amino-9-ethylcarbazole reacting with 1.2 mmol of benzaldehyde and 1.2 mmol of 2-mercaptoacetic acid. DCC was found to be an important promoting agent for the reaction, which was converted into insoluble solid, *N*,*N*′-dicyclohexylurea (DCU), after the reaction and could be easily removed from the reaction system only by filtration. In addition, the solvent played an important role in the reaction. Many aprotic solvents could be utilized in three-component reaction, among them diethyl ether gave the best result (Table 1).

To explore the generality and scope of the one-pot three-component reactions, and synthesis of a series of novel

Scheme 1



2-aryl-3-(9-alkylcarbazol-3-yl)thiazolidin-4-ones (**1a–m**), different 3-aminocabazoles and different aromatic aldehydes as substrates were examined under optimal conditions (Table 2). It was found that 9-ethyl and 9-butyl substituted 3-aminocarbazoles both were efficient for the reactions. Various aromatic aldehydes including nitro-, methoxy-, hydroxyl-, and dimethylamino- substituted benzaldehydes and heterocyclic aldehyde, furanaldehyde, were all suitable to the reactions. The electron-withdrawing and electron-donating groups on aromatic rings had no obvious effect on the yield of reactions. However, 4-(dimethylamino)benzaldehyde and furanaldehyde showed the slightly weaker activities for the reactions, and gave the corresponding products in slightly lower yield.

The resulting compounds **1a–m** are highly soluble in common organic solvents including $CHC1_3$, CH_2C1_2, DMSO, DMF, and EtOH. The structures of compounds **1a–m** were identified by IR, ^{1}H-NMR, ^{13}C-NMR, and elemental analyses. The ^{1}H-NMR spectra of compounds **1a–m** in $CDCl_3$ show CH group single proton peaks of thiazolidin-4-one at δ 6.08–6.13 ppm and CH_2 group two double proton peaks of thiazolidin-4-one at δ 3.92–4.11 ppm. The IR spectra of compounds **1a–m** show characteristic absorptions at 1680–1688 cm^{-1}, attributable to the carbonyl groups.

A possible mechanism for the synthesis of 2-aryl-3-(9-alkylcarbazol-3-yl)thiazolidin-4-ones is shown in Scheme 2. Presumably, condensation of 3-amino-9-alkylcarbazoles with aldehydes in the presence of DCC by releasing DCU first generates Schiff base intermediates **A**. The Schiff base **A** subsequently reacts with 2-mercaptoacetic acid by addition reaction to form intermediate **B**. Subsequently, the intermediate **B** in the presence of DCC undergoes the intramolecular dehydration by eliminating DCU to give five-membered heterocyclic compounds, 2-aryl-3-(9-alkylcarbazol-3-yl)thiazolidin-4-ones.

In conclusion, we have developed a highly efficient one-pot three-component method for the synthesis of a series of new carbazole-based thiazolidinones at room temperature in diethyl ether. This protocol has advantages of mild condition, short reaction time, high yield, and simple work-up procedure.

Table 1

The effect of solvents on the yield of the reaction product.[a]

Entry	Solvent	Yield (%)[b]
1	CH_2Cl_2	87
2	Et_2O	92
3	THF	90
4	PhMe	88
5	Free	60

[a]Reaction condition: 1 mmol of 3-amino-9-ethylcarbazole, 1.2 mmol of benzaldehyde, 1.2 mmol of 2-mercaptoacetic acid, and 2 mmol of DCC in 20 mL of solvent or no solvent.
[b]Yields refer to the isolated products.

EXPERIMENTAL

IR spectra were recorded using KBr pellets on a Digilab FTS 3000 FTIR spectrophotometer and ^{1}H-NMR and ^{13}C-NMR spectra on a Mercury Plus-400 instrument using $CDCl_3$ as solvent and Me_4Si as internal standard. Elemental analyses were performed on a Vario E1 elemental analysis instrument. Melting points were observed in an electrothermal melting point apparatus.

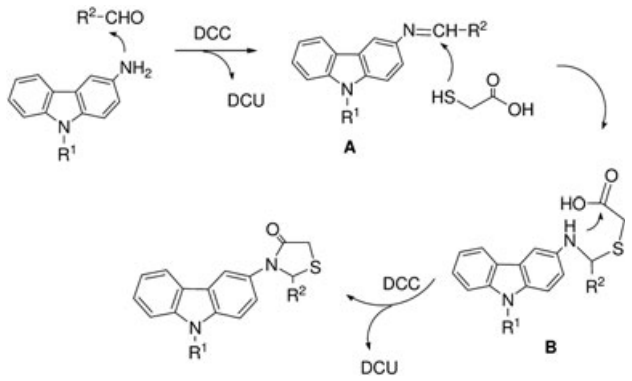
Table 2

Synthesis of 2-aryl-3-(9-alkylcarbazol-3-yl)thiazolidin-4-ones.

Compd.	R^1	R^2	Yield (%)[a]	m.p. (°C)
1a	Et	C_6H_5-	92	186–188
1b	Et	4-$NO_2C_6H_4$-	90	146–148
1c	Et	3-$NO_2C_6H_4$-	96	150–152
1d	Et	4-OHC_6H_4-	90	168–170
1e	Et	3-CH_3O-4-OHC_6H_3-	95	74–76
1f	Et	Furan-2-	81	144–146
1g	*n*-Bu	C_6H_5-	95	122–124
1h	*n*-Bu	4-$CH_3OC_6H_4$-	90	70–72
1i	*n*-Bu	4-OHC_6H_4-	88	172–174
1j	*n*-Bu	4-$NO_2C_6H_4$-	94	100–102
1k	*n*-Bu	4-$(CH_3)_2NC_6H_4$-	80	110–112
1l	*n*-Bu	3-CH_3O-4-OHC_6H_3-	94	60–62
1m	*n*-Bu	Furan-2-	82	124–126

[a]Yields refer to the isolated products.

Scheme 2



9-Ethylcarbazole, 9-butylcarbazole [19], 3-nitro-9-ethylcarbazole, 3-nitro-9-butylcarbazole, 3-amino-9-ethylcarbazole, and 3-amino-9-butylcarbazole [20] were prepared according to literature procedures.

Synthesis of 2-aryl-3-(9-alkylcarbazol-3-yl)thiazolidin-4-ones. The mixture of 3-amino-9-alkylcarbazoles (1 mmol) and aromatic aldehydes (1.2 mmol) in 20 mL of dry diethyl ether was stirred for 20 min, then 2-mercaptoacetic acid (1.2 mmol) and DCC (2 mmol) were added, and the reaction system was stirred for another 2 h at room temperature. The completion of the reactions was monitored by TLC. Then the solid was removed by filtration, and the liquor was washed with saturated sodium carbonate and water, and dried with anhydrous magnesium sulfate. After the solvent was evaporated off, the residue was recrystallized from ethanol to give products. Analytical data for compounds **1a–m** are given below.

1a. This compound was obtained as white solid (EtOH). IR (potassium bromide): 1684 (C═O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.15–7.96 (m, 12H, Ph-H), 6.12 (s, 1H, CH), 4.27–4.29 (q, *J* = 6.8 Hz, 2H, CH_2), 4.06–4.10 (d, *J* = 16 Hz, 1H, CH), 3.94–3.98 (d, *J* = 16 Hz, 1H, CH), 1.37 (t, *J* = 6.8 Hz, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.3, 140.3, 139.8, 138.7, 128.8, 128.7, 128.6, 127.3, 126.0, 124.3, 123.2, 122.5, 120.5, 119.0, 118.8, 108.8, 108.6, 66.6, 37.6, 33.5, 13.7. Analysis calculated for $C_{23}H_{20}N_2OS$: C, 74.16; H, 5.41; N, 7.52. Found: C, 74.19; H, 5.40; N, 7.49.

1b. This compound was obtained as white solid (EtOH). IR (potassium bromide): 1688 (C═O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.17–8.07 (m, 11H, Ph-H), 6.10 (s, 1H, CH), 4.24–4.28 (q, *J* = 6.4 Hz, 2H, CH_2), 4.07–4.11 (d, *J* = 16 Hz, 1H, CH), 3.95–3.99 (d, *J* = 16 Hz, 1H, CH), 1.36 (t, *J* = 6.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.2, 146.3, 145.3, 138.2, 127.8, 127.7, 127.6, 127.3, 126.0, 124.3, 123.5, 122.8, 120.6, 119.5, 118.5, 108.4, 108.1, 66.7, 37.8, 33.4, 13.7. Analysis calculated for $C_{23}H_{19}N_3O_3S$: C, 66.17; H, 4.59; N, 10.07. Found: C, 66.12; H, 4.57; N, 10.03.

1c. This compound was obtained as white solid (EtOH). IR (potassium bromide): 1680 (C═O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.19–8.08 (m, 11H, Ph-H), 6.09 (s, 1H, CH), 4.22–4.26 (q, *J* = 6.8 Hz, 2H, CH_2), 4.08–4.12 (d, *J* = 16 Hz, 2H, CH), 3.96–4.00 (d, *J* = 16 Hz, 2H, CH), 1.34 (t, *J* = 6.8 Hz, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.2, 146.6, 140.8, 139.5, 138.3, 127.5, 127.2, 127.1, 127.0, 126.5, 124.5, 124.0, 123.2, 122.3, 120.1, 119.2, 118.4, 108.5, 108.5, 66.3, 37.3, 33.2, 13.9. Analysis calculated for $C_{23}H_{19}N_3O_3S$: C, 66.17; H, 4.59; N, 10.07. Found: C, 66.21; H, 4.58; N, 10.04.

1d. This compound was obtained as white solid (EtOH). IR (potassium bromide): 1683 (C═O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.43 (br, 1H, OH), 7.23–7.83 (m, 9H, Ph-H), 6.65–6.68 (m, 2H, Ph-H), 6.13 (s, 1H, CH), 4.24–4.28 (q, *J* = 6.8 Hz, 2H, CH_2), 4.05–4.09 (d, *J* = 16 Hz, 2H, CH), 3.93–3.97 (d, *J* = 16 Hz, 2H, CH), 1.37 (t, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.1, 156.9, 134.0, 131.8, 130.1, 127.5, 127.2, 127.1, 127.0, 126.4, 124.2, 123.2, 122.3, 120.3, 119.3, 118.1, 108.2, 108.1, 66.8, 37.7, 33.3, 13.8. Analysis calculated for $C_{23}H_{20}N_2O_2S$: C, 71.11; H, 5.19; N, 7.21. Found: C, 71.05; H, 5.21; N, 7.16.

1e. This compound was obtained as white solid (EtOH). IR (potassium bromide): 1688 (C═O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.83 (br, 1H, OH), 7.18–7.89 (m, 9H, Ph-H), 6.73–6.76 (m, 1H, Ph-H), 6.09 (s, 1H, CH), 4.21–4.26 (q, *J* = 6.4 Hz, 2H, CH_2), 4.02–4.06 (d, *J* = 16 Hz, 1H, CH), 3.92–3.96 (d, *J* = 16 Hz, 1H, CH), 3.70 (s, 3H, OCH_3), 1.39 (t, *J* = 6.4 Hz, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.0, 152.4, 147.1, 134.0, 131.8, 126.5, 126.2, 126.1, 125.5, 123.5, 123.2, 122.3, 120.1, 119.2, 118.4, 116.5, 114.3, 108.9, 108.8, 66.7, 56.9, 37.6, 33.5, 13.5. Analysis calculated for $C_{24}H_{22}N_2O_3S$: C, 68.88; H, 5.30; N, 6.69. Found: C, 68.94; H, 5.31; N, 6.65.

1f. This compound was obtained as white solid (EtOH). IR (potassium bromide): 1680 (C═O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.15–7.80 (m, 8H, Ph-H), 6.43–6.46 (m, 1H, Fu-H), 6.24–6.26 (m, 1H, Fu-H), 6.12 (s, 1H, CH), 4.21–4.24 (q, *J* = 6.4 Hz, 2H, CH_2), 4.02–4.04 (d, *J* = 16 Hz, 1H, CH), 3.90–3.94 (d, *J* = 16 Hz, 1H, CH), 1.33 (t, *J* = 6.4 Hz, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.3, 151.5, 142.1, 134.2, 134.0, 128.4, 126.2, 125.1, 121.7, 121.4, 119.8, 112.6, 110.6, 110.2, 109.9, 108.5, 107.0, 66.0, 37.5, 33.7, 13.3. Analysis calculated for $C_{21}H_{18}N_2O_2S$: C, 69.59; H, 5.01; N, 7.73. Found: C, 69.55; H, 5.03; N, 7.69.

1g. This compound was obtained as white solid (EtOH). IR (potassium bromide): 1683 (C═O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.15–7.80 (m, 12H, Ph-H), 6.11 (s, 1H, CH), 4.23–4.26 (t, *J* = 6.8 Hz, 2H, CH_2), 4.03–4.07 (d, *J* = 16 Hz, 1H, CH), 3.93–3.97 (d, *J* = 16 Hz, 1H, CH), 1.76–1.80 (m, 2H, CH_2), 1.35–1.38 (m, 2H, CH_2), 0.89–0.93 (t, *J* = 6.4 Hz, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.5, 140.1, 139.5, 138.2, 128.5, 128.4, 128.3, 127.1, 126.5, 124.8, 123.5, 122.8, 120.2, 119.3, 118.4, 108.5, 108.2, 66.0, 42.6, 33.2, 30.7, 20.2, 13.5. Analysis calculated for $C_{25}H_{24}N_2OS$: C, 74.97; H, 6.04; N, 6.99. Found: C, 74.89; H, 6.03; N, 6.93.

1h. This compound was obtained as white solid (EtOH). IR (potassium bromide): 1688 (C═O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.95–7.97 (m, 1H, Ph-H), 7.78 (s, 1H, Ph-H), 7.11–7.44 (m, 7H, Ph-H), 6.77–6.79 (m, 2H, Ph-H), 6.09 (s, 1H, CH), 4.20–4.23 (t, *J* = 6.8 Hz, 2H, CH_2), 4.04–4.08 (d, *J* = 16 Hz, 1H, CH), 3.94–3.98 (d, *J* = 16 Hz, 1H, CH), 3.72 (s, 3H, OCH_3), 1.77–1.81 (m, 2H, CH_2), 1.36–1.39 (m, 2H, CH_2), 0.90–0.94 (t, *J* = 6.4 Hz, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.2, 159.6, 140.5, 138.9, 131.2, 128.5, 128.3, 125.7, 124.1, 122.8, 122.1, 120.2, 118.6, 118.5, 113.7, 108.7, 108.5, 66.0, 54.9, 42.6, 33.3, 30.7, 20.2, 13.5. Analysis calculated for $C_{26}H_{26}N_2O_2S$: C, 72.53; H, 6.09; N, 6.51. Found: C, 72.58; H, 6.10; N, 6.54.

1i. This compound was obtained as white solid (EtOH). IR (potassium bromide): 1685 (C═O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.38 (br, 1H, OH), 7.23–7.83 (m, 9H, Ph-H), 6.63 (m, 2H, Ph-H), 6.11 (s, 1H, CH), 4.10–4.16 (t, *J* = 6.4 Hz, 2H, CH_2), 4.04–4.08 (d, *J* = 16 Hz, 1H, CH), 3.93–3.97 (d, *J* = 16

Hz, 1H, CH), 1.78–1.83 (m, 2H, CH_2), 1.35–1.37 (m, 2H, CH_2), 0.90–0.93 (t, J = 6.4 Hz, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.3, 156.5, 134.2, 131.2, 130.0, 127.8, 127.3, 127.1, 127.5, 126.2, 124.1, 123.2, 122.5, 120.5, 119.4, 118.7, 108.8, 108.1, 66.2, 42.5, 33.1, 30.4, 20.5, 13.4. Analysis calculated for $C_{25}H_{24}N_2O_2S$: C, 72.09; H, 5.81; N, 6.73. Found: C, 72.03; H, 5.82; N, 6.69.

1j. This compound was obtained as white solid (EtOH). IR (potassium bromide): 1688 (C═O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.19–8.08 (m, 11H, Ph-H), 6.08 (s, 1H, CH), 4.27–4.29 (t, J = 6.8 Hz, 2H, CH_2), 4.05–4.09 (d, J = 16 Hz, 2H, CH), 3.95–3.99 (d, J = 16 Hz, 2H, CH), 1.75–1.80 (m, 2H, CH_2), 1.35 (m, 2H, CH_2), 0.89–0.92 (t, J = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.2, 146.5, 145.8, 139.2, 138.1, 127.9, 127.8, 127.5, 126.5, 124.7, 123.9, 122.5, 120.3, 119.8, 118.9, 108.7, 108.5, 66.7, 42.9, 33.5, 30.8, 20.5, 13.6. Analysis calculated for $C_{25}H_{23}N_3O_3S$: C, 67.40; H, 5.20; N, 9.43. Found: C, 67.35; H, 5.19; N, 9.39.

1k. This compound was obtained as white solid (EtOH). IR (potassium bromide): 1687 (C═O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.64–7.90 (m, 11H, Ph-H), 6.10 (s, 1H, CH), 4.17–4.19 (t, J = 6.4 Hz, 2H, CH_2), 4.04–4.08 (d, J = 16 Hz, 2H, CH), 3.94–3.98 (d, J = 16 Hz, 2H, CH), 3.06 (s, 6H, NCH_3), 1.75–1.78 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), 0.87–0.90 (t, J = 6.4 Hz, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.2, 149.5, 139.8, 134.1, 128.7, 128.4, 127.8, 127.5, 125.1, 121.7, 121.5, 119.8, 112.8, 109.9, 109.6, 108.5, 103.3, 66.7, 42.9, 40.2, 33.5, 32.6, 20.5, 13.6. Analysis calculated for $C_{27}H_{29}N_3OS$: C, 73.10; H, 6.59; N, 9.47. Found: C, 73.18; H, 6.67; N, 9.44.

1l. This compound was obtained as white solid (EtOH). IR (potassium bromide): 1688 (C═O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.80 (br, 1H), 7.34–7.85 (m, 9H, Ph-H), 6.73 (m, 1H, Ph-H), 6.12 (s, 1H, CH), 4.22–4.25 (t, J = 6.8 Hz, 2H, CH_2), 4.05–4.09 (d, J = 16 Hz, 2H, CH), 3.95–3.99 (d, J = 16 Hz, 2H, CH), 3.70 (s, 3H, OCH_3), 1.74–1.75 (m, 2H, CH_2), 1.32–1.36 (m, 2H, CH_2), 0.89–0.90 (t, J = 6.8 Hz, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.0, 147.6, 147.0, 134.5, 131.2, 126.5, 126.3, 126.0, 125.2, 123.7, 123.6, 122.3, 120.4, 119.6, 118.8, 114.3, 112.5, 108.9, 108.4, 66.0, 54.3, 42.6, 33.5, 30.6, 20.4, 13.8. Analysis calculated for $C_{26}H_{26}N_2O_3S$: C, 69.93; H, 5.87; N, 6.27. Found: C, 69.85; H, 5.85; N, 6.30.

1m. This compound was obtained as white solid (EtOH). IR (potassium bromide): 1680 (C═O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.17–7.82 (m, 8H, Fu-H), 6.48 (m, 1H, Fu-H), 6.27 (m, 1H, Fu-H), 6.10 (s, 1H, CH), 4.26–4.29 (t, J = 6.4 Hz, 2H, CH_2), 4.02–4.06 (d, J = 16 Hz, 2H, CH), 3.92–3.96 (d, J = 16 Hz, 2H, CH), 1.74–1.78 (m, 2H, CH_2), 1.33–1.36 (m, 2H, CH_2), 0.87–0.90 (t, J = 6.4 Hz, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.3, 151.8, 141.8, 133.9, 128.2, 126.1, 125.7, 121.9, 121.6, 119.5, 112.9, 112.2, 110.5, 110.2, 109.7, 108.9, 107.0, 66.0, 42.8, 37.9, 33.6, 20.6, 13.7. Analysis calculated for $C_{23}H_{22}N_2O_2S$: C, 70.74; H, 5.68; N, 7.17. Found: C, 70.79; H, 5.70; N, 7.14.

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