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A CONVENIENT ONE-POT THREE COMPONENT APPROACH TO SYNTHESIS OF HIGHLY SUBSTITUTED IMINOTHIAZOLINES

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Abstract – An efficient one-pot three component method was developed for the synthesis of highly substituted 2-iminothizolines by the reaction of isothiocyanates, primary amines and α-bromoketones in ambient temperature. The reaction produced the desired products in a completely regioselective manner in excellent yields (78-94%).

INTRODUCTION

Iminothiazolines are significant group of organic compounds which have attracted a great deal of attention in organic synthesis due to their diverse biological activities such as bactericidal,[1] analgesicidal,[2] fungicidal,[3] insecticidal,[4] anti HIV,[5] anti-inflammatory,[6] vasodilator and antihypertensive,[7] anticonvulsant,[8] anthelmintic,[9] plant growth regulatory and antifungal activities,[10] pifithrin (Pft-α), skin whitening agent (KHG22394)[11] and fungitoxicity against rice blast.[12]

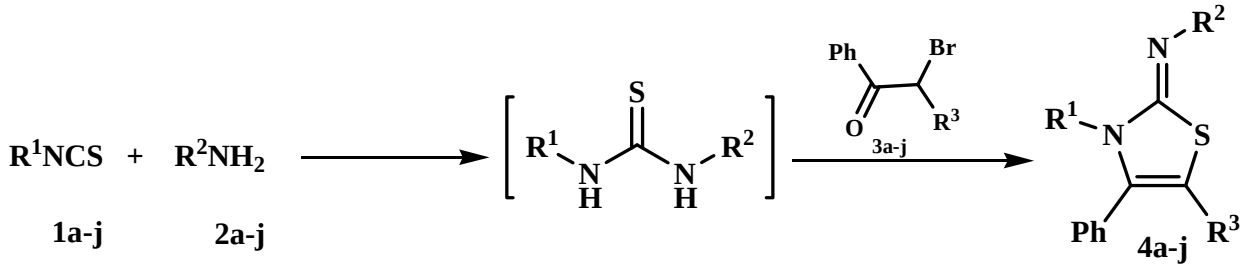
Several methods have been developed for the synthesis of iminothiazoline moity which include, *N*-alkylation of aminothiazoles,[13] solid- phase strategy,[14] the condensation of carbonyl compounds with thioureas and 1,3-disubstituted thioureas using 1,1′-(ethan-1,2-diyl)dipyridinium bistribromide (EDPBT),[15] reaction of *N*-monoalkylated thiaoureas with 3-bromomethyl-2-cyanocinnmonitrile, microwave-assisted reaction,[16] cycloaddition reaction,[17] by ring transformation of 2-(thiocyanomethyl)-aziridines,[18] the reaction of benzoyl-3-phenylthioureas with bromine and enolizable ketones in the presence of triethylamine,[19] reaction of *N*-propargylaniline with acylisothiocyannates, reaction of α-haloketones with *N*-benzoyl-*N*′-arylthioureas or *N,N*′-disubstituted thioureas.[20] The main disadvantages with most of these procedures are harsh reaction conditions, difficult workup, low yields, high reaction time and in the case of using unsymmetrical disubstituted thioureas low regioselectivity.

In spite of synthesis of numerous substituted 2-iminothiazolines and evaluation of their biological activities, only a few fully substituted iminothiazolines have been synthesized and examined for their biological properties.

These observations prompted us to synthesize a series of new, highly substituted aryl- and alkylimino-thiazolines via a convenient one-pot three component reaction under ambient temperature.

RESULTS AND DISCUSSION

As a continuation of our research devoted to the development of new methodologies in the synthesis of heterocyclic compounds,[21] in a search for a suitable protocol for the synthesis of 2-iminothiazoline ring system, as potential drug candidates possessing interesting biological activities, at mild reaction conditions using readily accessible reagents, we employed a simple one-pot three component pathway (Scheme 1). In this approach, the reaction of isothiocyanates (**1a-j**) and primary amines (**2a-j**) in ethanol, followed by the addition of α-bromoketones **(3a-j)** at ambient temperature, produced the desired 2-iminothiazoline (**4a-j**) as sole products in excellent yields (78-94%) (Table 1).



Scheme 1

In this approach the condensation of dissymmetric thioureas (via in situ formation from isothiocyanate and amine), and *α*-bromo ketone produced only one regio-isomer of iminothiazolines (**4a-j**) (Table 1).

Table 1. One-pot three component synthesis of iminothiazolines **4a-j**

Entry	R^1	R^2	R^3	Time (h)	Yield (%)[a]	mp (ºC)
a	Et	Et	Ph	7	81	146-148
b	Me	$PhCH_2CH_2$	Me	9	93	140-142
c	Me	$PhCH_2CH_2$	H	8	78	121-122
d	Me	$PhCH_2CH_2$	Ph	9	87	106-107
e	Et	4-Me-C_6H_4-	Me	9	92	105-107
f	Et	4-Me-C_6H_4-	Ph	9	91	88-90
g	Et	Bn	Me	8	94	198-200
h	Bn	Ph	Me	8	89	146-148
i	Bn	Ph	Ph	8	92	138-139
j	Bn	Ph	H	9	88	122-124

a. Isolated yield

Since the spectral data (e.g., NMR, IR, and elemental analysis) for the structural assignment of iminothiazolines with dissymmetrically substituted nitrogens were not conclusive, X-ray crystallographic analysis [22] was conducted on the hydrobromide salt of **4b** to verify product structure. As shown in the ORTEP plots of **4b** (Figure 1), the bulky phenethyl group resides on imino nitrogen. The result of X-ray analysis clearly confirms the stereoelectronic controlling nature of the reaction.

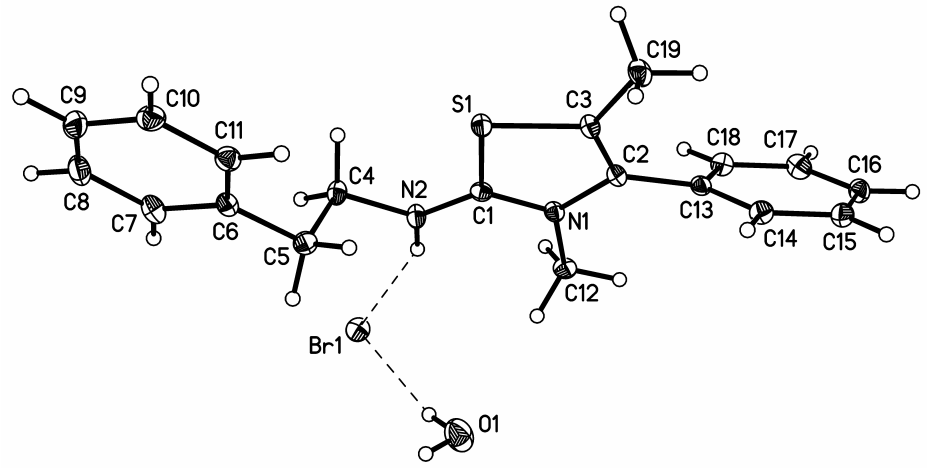
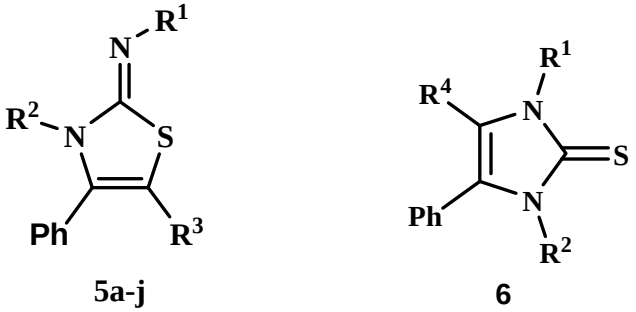


Figure 1. ORTEP plots of **4b**

In this reaction, under kinetic control sulfur from thiourea (formed in situ), attacks the carbon bearing Br (**3a-j**), then cyclization takes place by nucleophilic addition of N to the carbonyl group and finally dehydration of the intermediate thus formed, furnishes the desired 2-imino-thiazolines (**4a-j**). In this approach formation of two regio-isomers (**4a-j**, **5a-j**) is possible but under the reaction condition used only one regio-isomer is formed (**4a-j**). In all the reactions carried out for the synthesis of 2-iminothiozolines no trace of imidazole-2-thione (**6**) (Figure 2), which could have been the result of initial attack of nitrogen from in situ formed thioureas to the carbon bearing Br (**3a-j**), was detected.



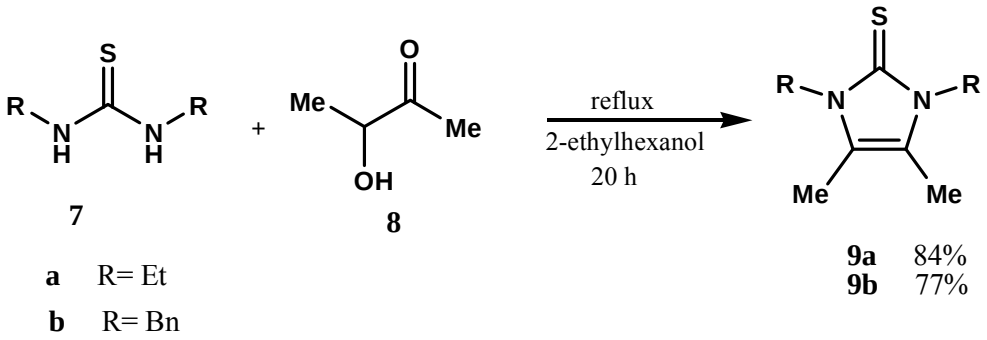
5a-j **6**

Figure 2

According to the literature report this type of products are formed by the reaction of *N,N′*-dialkylthioureas with 3-hydroxy-2-butanone in boiling 1-hexanol (bp 157 ^{o}C).[23] We examined this reaction by reacting *N,N′*-dialkylthioureas in boiling 2-ethylhexanol(bp 185 ^{o}C) (Scheme 2). The reaction cleanly produced

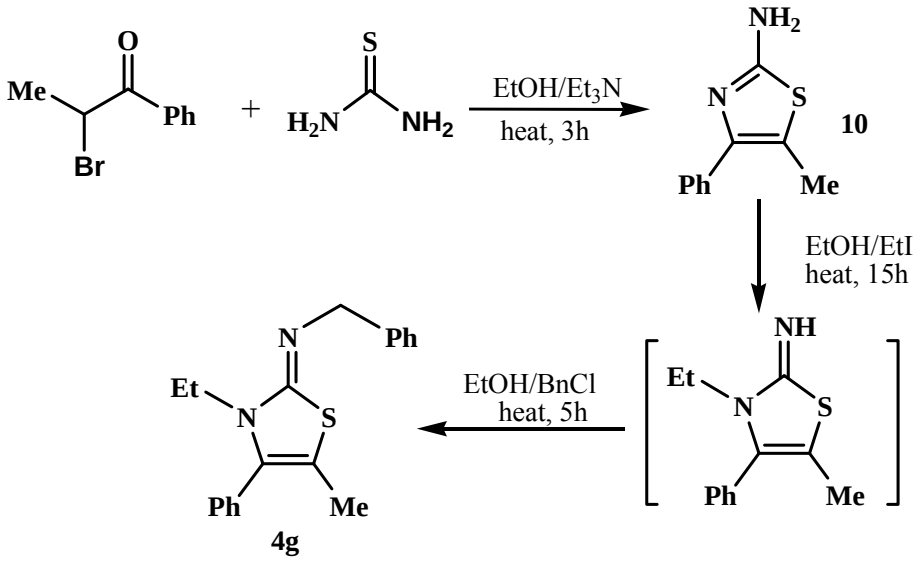
the related imidazole-2-thiones (**9a**, **9b**) in 20 h as sole products in high yields. These results also revealed that replacement of Br as better leaving group with OH in the α-haloketone, completely changes the reaction pathway.

In order to assign the right structure of the regio-isomers obtained, the synthesis of **4g** was conducted using the method reported by De Kimpe and co-workers[13] (Scheme 3). Spectral properties of the product



Scheme 2

(**4g**) from this reaction was identical the one obtained from our approach. With respect to the spectral data from **4a, 4b** and **4g** (Figure 3) and the results of X-ray analysis, full structural assignments of all the



Scheme 3

synthesized regio-isomers were possible (Table 1). It is quite evident from the ^{1}H NMR data (Figure 3) that CH_2 protons attached to the ring nitrogen compared with those on imino nitrogen are observed in relatively downfields. This may also be explained by the result of X-ray analysis of hydrobromide salt of **4b** (Figure 1) which confirms the more basic nature of exocyclic imino nitrogen.

CONCLUSION

In summary this research work describes an efficient and facile synthesis of highly substituted 2-iminothiazolines by one-pot three component reaction in a completely regio-selective reaction in ambient temperature with excellent yields (78-94%). The research in this respect for the synthesis of fused ring iminothiazolines is under way.

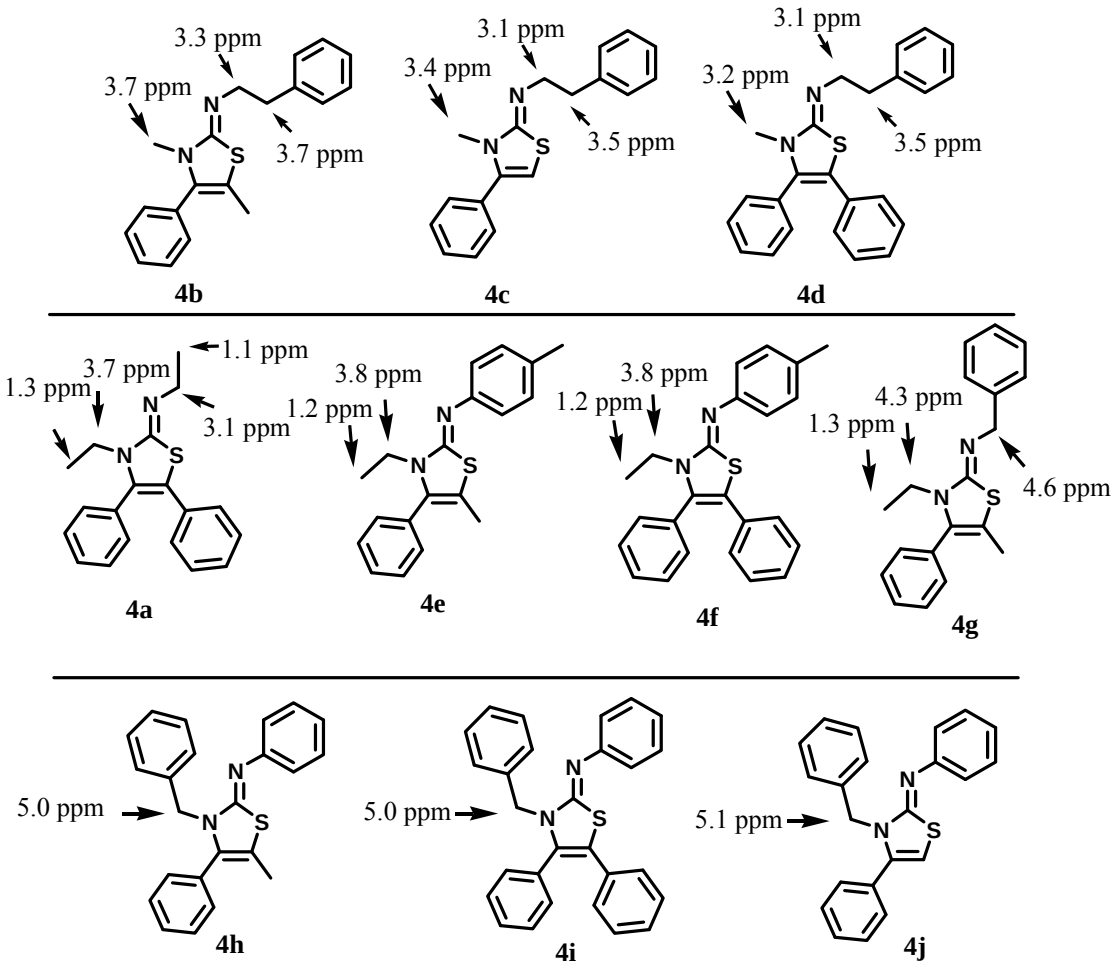


Figure 3. ^{1}H NMR chemical shifts of various alkyl groups attached to N

EXPERIMENTAL

^{1}H NMR spectra were obtained on a Bruker DRX-500 and those of ^{13}C NMR spectra on a Bruker DRX-125 Avance spectrometer. FT-IR spectra were recorded on a Shimadzu FT-IR-8400S spectrometer. Chemical shifts of ^{1}H and ^{13}C NMR spectra were expressed in ppm in downfield from tetramethylsilane. Melting points were measured on a Buchi melting point B-540 instrument and are uncorrected. Elemental analyses were made by a Carlo-Erba EA1110CNNO-S analyzer and agreed with the calculated values. All the chemicals were purchased from Merck and used without further purification.

General procedure for synthesis of iminothiazoles via three component reaction

To a solution of alkyl or arylamine (1 mmol) in EtOH (10 mL), isothiocyanate (1 mmol) was added and the reaction mixture was stirred at rt for 3 h. To the resulting reaction mixture 2-bromoketone **(3)** (1mmol) was added and stirring was continued for 3-6 h. The mixture was concentrated with evaporation under reduced pressure, washed with aqueous Na_2CO_3 (10%) and extracted with CH_2Cl_2 (3x10 mL). The organic phase was evaporated and the residue dissolved in EtOH, addition of water gave 2-iminothiazolines (**4**) as white precipitate with 78-94% yields. Pure products of **4b**, **4d**, **4e** and **4g** were obtained by recrystalization from mixed H_2O/EtOH/DMSO (10:3:3).

General procedure for synthesis of thiazol-2-thione (9a and 9b)

To a solution of *N,N′*-diethyl(or dibenzyl)thiourea (2 mmol) in 2-ethylhexanol (7 mL), 3-hydroxy-2-butanone (0.17 g, 2 mmol) was added. The reaction was heated under reflux for 20 h. Purification of the mixture by column chromatography (silica gel, EtOAc-hexane: 1/4) provided thiazol-2-thione **9a** (mp 120-122 °C) and **9b** (mp 114-116 °C) in 84 and 77 % yields, respectively.

4a. Yield 81%, white solid, mp 146-148 °C, ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 1.1 (s, 3H), 1.3 (s, 3H), 3.1 (s, 2H), 3.7 (s, 2H), 7.0-8.1 (m, 10H); ^{13}C-NMR ($CDCl_3$, 125 MHz): 13.0, 17.5, 24.6, 49.0, 110.3, 121.1, 127.7, 128.6, 128.9, 129.3, 130.8, 130.9, 138.1, 152.3, 158.5; IR (KBr, cm^{-1}): 3035, 2960, 1610, 1590, 1450, 1375, 750, 700. Anal. Calcd for $C_{19}H_{20}N_2S$ (308.44): C, 73.99; H, 6.54; N, 9.08. Found: C, 73.69; H, 6.82; N, 9.15.

4b. Yield 93%, white solid, mp 140-142 °C, ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 2.15 (s, 3H), 3.29 (t, 2H, *J* = 7.3 Hz), 3.70 (s, 3H), 3.70 (t, 2H, *J* = 7.3 Hz), 7.26-7.28 (m, 3H), 7.32-7.37 (m, 4H), 7.54-7.59 (m, 3H); ^{13}C-NMR ($CDCl_3$, 125 MHz): 12.6, 34.9, 38.0, 50.8, 115.2, 127.2, 127.3, 127.8, 129.2, 129.5, 130.0, 131.2, 138.1, 138.5, 167.0; IR (KBr, cm^{-1}): 3030, 2950, 1620, 1590, 1435, 1377, 780, 757, 700, 500. Anal. Calcd for $C_{19}H_20N_2S$ (308.44): C, 73.99; H, 6.54; N, 9.08. Found: C, 74.10; H, 6.44; N, 9.15.

4c. Yield 78%, white solid, mp 121-122 °C, ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.10 (t, 2H, *J* = 5.9 Hz), 3.35 (s, 3H), 3.64 (t, 2H, *J* = 5.9 Hz), 5.92 (s, 1H), 7.27 (m, 1H), 7.35 (d, 3H, *J* = 4.4 Hz), 7.39 (dd, 2H, *J* = 7.3, 2.3 Hz), 7.49 (dd, 2H, *J* = 4.6, 3.9 Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz): 34.4, 36.7, 51.2, 112.2, 127.5, 127.8, 128.8, 129.2, 129.7, 130.1, 131.7, 138.2, 138.2, 165.4; IR (KBr, cm^{-1}): 3050, 2965, 2920, 2880, 1634, 1580, 1500, 1450, 1381, 1251, 700. Anal. Calcd for $C_{19}H_{22}N_2S$ (310.46): C, 73.51; H, 7.14; N, 9.02. Found: C, 73.37; H, 7.05, N, 9.22.

4d. Yield 87%, white solid, mp 106-107 °C, ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 3.11 (t, 2H, *J* = 5.96 Hz), 3.19 (s, 3H), 3.52 (t, 2H, *J* = 5.96 Hz), 7.05 (dd, 2H, *J* = 5.9, 1 Hz), 7.13 (m, 3H), 7.30 (m, 1H), 7.34 (dd, 2H, *J* = 5.6, 2.1 Hz), 7.40 (d, 4H, *J* = 6.7 Hz), 7.48 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): 33.2, 37.8,

57.4, 126.4, 126.8, 128.1, 128.2, 128.7, 128.8, 129.1, 129.4, 129.6, 129.7, 130.8, 132.0, 133.2, 135.9, 141.1, 158.8; IR (KBr, cm^{-1}): 3100, 2990, 1620, 1400, 1350, 757, 690. Anal. Calcd for $C_{26}H_{30}N_2S$ (402.59): C, 77.57; H, 7.51; N, 6.96. Found: C, 77.50; H, 7.57; N, 6.87.

4e. Yield 92%, white solid, mp 105-107 °C, ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 1.73 (t, 3H, *J* = 7 Hz), 1.93 (s, 3H), 2.38 (s, 3H), 3.78 (q, 2H, *J* = 7 Hz), 7.03 (d, 2H, *J* = 6.4 Hz), 7.18 (d, 2H, *J* = 8.0 Hz), 7.36 (dd, 2H, *J* = 7.6, 1.3 Hz), 7.48-7.53 (m, 3H); ^{13}C-NMR ($CDCl_3$, 125 MHz): 13.0, 49.0, 106.3, 121.5, 128.7, 128.9, 130.0, 130.2, 131.0, 132.1, 134.3, 149.8, 158.6.; IR (KBr, cm^{-1}): 3057, 2968, 2918, 2862, 1634, 1580, 1502, 1439, 1381, 1251, 705. Anal. Calcd for $C_{19}H_{20}N_2S$ (308.44): C, 73.99; H, 6.54; N, 9.08. Found: C, 73.87; H, 6.64; N, 9.13.

4f. Yield 91%, white solid, mp 88-90 °C, ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 1.19 (t, 2H, *J* = 7 Hz), 2.34 (s, 3H), 3.80 (q, 2H, *J* = 7 Hz), 6.9 (m, 2H), 7.05 (m, 5H), 7.15 (s, 1H), 7.16 (s, 1H), 7.35 (m, 2H), 7.45 (m, 3H); ^{13}C-NMR ($CDCl_3$, 125 MHz): 11.6, 12.8, 36.0, 115.8, 121.0, 126.3, 127.1, 127.8, 128.1, 128.8, 129.1, 129.4, 129.9, 120.1, 130.4, 133.4, 137.0, 162.3; IR (KBr, cm^{-1}): 3050, 2980, 1620, 1580, 1500, 1420, 1380, 1320, 1200, 1080, 820, 750, 690, 500; Anal. Calcd for $C_{24}H_{22}N_2S$ (370.50): C, 77.80; H, 5.98; N, 7.56. Found: C, 77.75; H, 5.99; N, 7.60.

5g. Yield 94%, white solid, mp 198-200 °C, ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 1.24 (t, 3H, *J* = 7 Hz), 2.04 (s, 3H), 4.27 (q, 2H, *J* = 7 Hz), 4.70 (s, 2H), 7.25 (m, 2H), 7.36 (m, 3H), 7.5-7.6 (m, 5H).; ^{13}C-NMR ($CDCl_3$, 125 MHz): 12.1, 13.7, 43.9, 50.1, 116.0, 127.3, 128.4, 128.7, 128.8, 129.5, 130.2, 130.8, 134.2, 137.6, 165.4; (KBr, cm^{-1}): 3020, 2985, 2985, 2820, 1580, 1490, 1440, 1350, 1330, 1240, 1010, 750, 690. Anal. Calcd for $C_{20}H_{23}N_2S$ (323.48): C, 74.26; H, 7.17; N, 8.66. Found: C, 74.30; H, 7.20, N, 8.76.

4h. Yield 89%, white solid, mp 146-148 °C, ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 1.97 (s, 3H), 5.00 (s, 2H), 7.06-7.10 (m, 3H), 7.11-7.15 (m, 4H), 7.22-7.25 (m, 3H), 7.36-7.42 (m, 5H); ^{13}C-NMR ($CDCl_3$, 125 MHz): 13.0, 49.0, 107.3, 122.1, 123.3, 127.4, 127.7, 128.6, 129.0, 129.3, 129.8, 130.8, 130.9, 134.9, 138.1, 152.3, 159.5; IR (KBr, cm^{-1}): 3067, 3024, 2921, 1626, 1604, 1578, 1489, 1380, 1321, 1147, 815, 694, 658. Anal. Calcd for $C_{23}H_{20}N_2S$ (356.48): C, 77.49; H, 5.65; N, 7.86. Found: C, 77.60; H, 5.66; N, 7.97.

4i. Yield 92%, white solid, mp 138-139 °C, ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 5.06 (s, 2H), 6.98 (d, *J* = 5.35 Hz, 2H), 7.11 (m, 6H), 7.17 (m, 5H), 7.27 (d, 1H, *J* = 7.2 Hz), 7.36 (t, 2H, *J* = 7.3 Hz), 7.43 (m, 4H); ^{13}C-NMR ($CDCl_3$, 125 MHz): 48.8, 122.0, 123.5, 127.1, 127.5, 127.6, 128.2, 128.7, 128.7, 129.3, 129.7, 129.9, 131.2, 131.5, 132.6, 135.2, 138.0, 152.1; IR (KBr, cm^{-1}): 3060, 2926, 2854, 1620, 1585, 1440, 1377, 1325, 1195, 1074, 757, 694. Anal. Calcd for $C_{28}H_{22}N_2S$ (418.55): C, 80.35; H, 5.30; N, 6.69. Found: C, 80.30; H, 5.35; N, 6.61.

4j. Yield 88%, white solid, mp 122-124 °C, ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 5.13 (s, 2H), 5.83 (s, 1H) 7.07-7.13 (m, 5H), 7.22-7.30 (m, 5H), 7.39 (t, 4H, *J* = 8.2 Hz), 7.40 (d, 1H, *J* = 7.3 Hz). ^{13}C-NMR ($CDCl_3$,

125 MHz): 48.5, 95.9, 121.5, 123.0, 127.1, 127.2, 128.3, 128.5, 129.0, 129.1, 129.4, 131.7, 137.5, 140.4; IR (KBr, cm^{-1}): 3096, 3056, 3025, 1588, 1563, 1490, 1445, 1385, 1234, 176, 765, 730, 707, 698. Anal. Calcd for $C_{23}H_{22}N_2S$ (358.5): C, 77.06; H, 6.19; N, 7.81. Found: C, 77.16; H, 6.09; N, 7.85.

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