Modification of the Gewald methodology for the synthesis of 3-amino-2-(1*H*-1,2,3-benzotriazol-1-yl) substituted benzofurans, benzothiophenes and 1*H*-indoles

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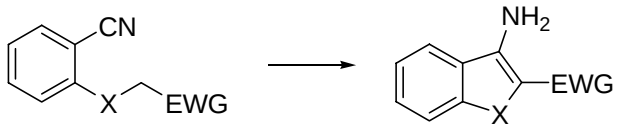
Abstract

Treatment of 1-chloromethylbenzotriazole (**4**) with salicylonitrile (**5a**), thiosalicylonitrile (**5b**), ethyl *N*-(2-cyanophenyl)carbamate (**5c**), and *N*-(2-cyanophenyl)methane-sulfonamide (**5d**) provided the corresponding intermediates **3**. Cyclization of compounds **3a-3c** with LDA gave 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)benzofuran-3-amine (**2a**), 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)benzo[*b*]thiophen-3-amine (**2b**), and ethyl 3-amino-2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1H-indole-1-carboxylate (**2c**), respectively. Attempts to accomplish elimination of the benzotriazole nitrogen under both thermal and photolytic conditions failed.

Keywords: Gewald methodology, benzofurans, benzothiophenes, indoles, benzotriazole

Introduction

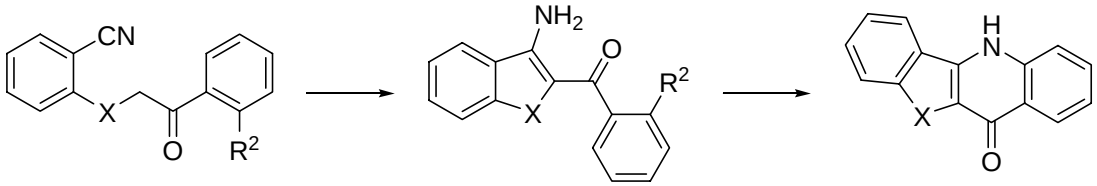
The Gewald reaction is a well known method of preparation of 2-aminothiophene derivatives.[1] Its modifications have been used for the synthesis of 3-amino-2-EWG substituted benzofurans,[2a,2b,3a,3b] benzothiophenes,[3a,3b,4] and 1*H*-indoles.[3a] The EWG groups includes esters,[2a,2b,4a,4b,4c,4d] nitriles,[2a,4a,4c] nitro,[4a,] and acyl groups[2a,2b,3a,3b,4a,4c,5] (Scheme 1).



X = O, S, N-R

Scheme 1

We have utilized this methodology as a key step of the synthesis of tetracyclic benzofuro[3,2-*b*]quinolines, benzothieno[3,2-*b*]quinolines and indolo[3,2-*b*]quinolines[6] (Scheme 2).



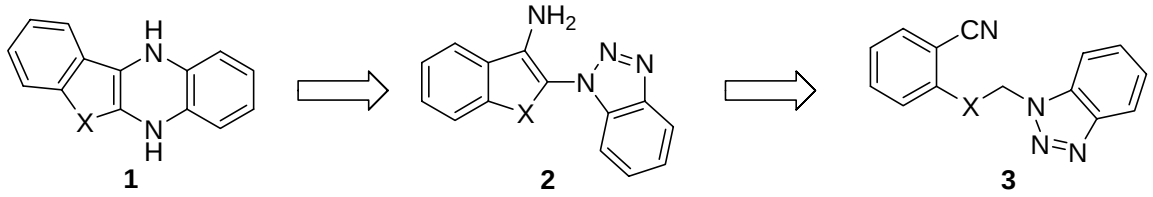
X = O, S, N-R^1; R^1 = SO_2Me. $SO_2C_6H_4Me(4)$, CO_2Et; R^2 = F, NO_2

Scheme 2

As a continuation of our work we were also interested in the synthesis of some azaanalogs of tetracyclic benzofuro[3,2-*b*]quinolines, benzothieno[3,2-*b*]quinolines and indolo[3,2-*b*]quinolines. We believed that the corresponding 3-amino-2-(1*H*-1,2,3-benzotriazol-1-yl) substituted benzofurans, benzothiophenes, and 1*H*-indoles **2** could serve as suitable precursors in the synthesis of the corresponding 11-oxa-, 11-thia, and 5,10,11-triaza-benzo[*b*]fluorenes **1**, respectively.

There are several thermal and photochemical reactions of benzotriazole-containing compounds accompanied with the loss of nitrogen. Probably the best known example is the Graebe-Ullmann synthesis of carbazole derivatives from the corresponding 1-aryl-1*H*-benzotriazoles.[7] Similar flash-vacuum pyrolysis (FVP) of β-substituted 1-vinyl-1*H*-benzotriazoles provided the corresponding indole derivatives, probably *via* the corresponding *N*-phenylketeneimines.[8] Recently, heating of 1-(1,2,3-thiadiazol-5-yl)-1*H*-benzotriazoles in DMF leading to the corresponding 4*H*-1,2,3-thiadiazolo[3,4-*a*]-3,1-benzimidazol-9-ium has been reported.[9] Analogous elimination of nitrogen under photolytic conditions has been described for 1-(4,5-dihydro-1*H*-imidazol-2-yl)benzotriazole[10a] and acyclic 1-imidoyl-1*H*-benzotriazoles.[10b]

The intended intermediates **2** should be formed by the modified Gewald methodology from easily available benzonitriles **3.** Nitrogen-assisted deprotonation of α-methylene groups on benzotriazole moiety is well known, widely used and thoroughly reviewed.[7] The mentioned compounds **3** should be formed by nucleophilic displacement reactions of 1-chloromethylbenzotriazole and the respective salicylonitrile, thiosalicylonitrile or activated anthranilonitrile. Retrosynthetic analysis is outlined in Scheme 3.



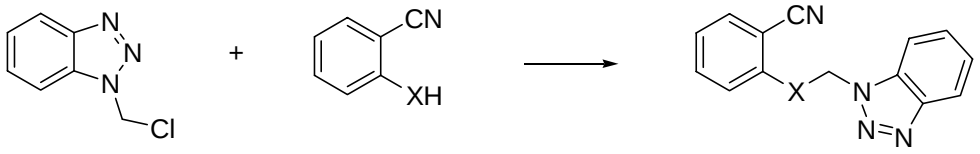
1 **2** **3**

X = O, S, N-R; R = SO_2Me, $SO_2C_6H_4Me(4)$, CO_2Et, etc.

Scheme 3

Results and Discussion

Easily available 1-chloromethyl-1*H*-benzotriazole **4** treated with the corresponding 2-substituted benzonitriles **5** provided good yields of compounds **3a-d** (Scheme 4). Starting benzonitriles **5** were either commercially available (salicylonitrile) or were prepared by known methods.

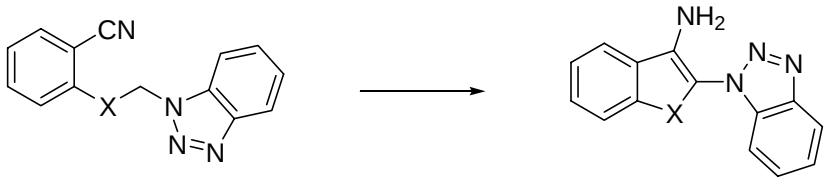


4 **5** **3**

3, 5	X
a	O
b	S
c	N-CO_2Et
d	N-SO_2Me

Scheme 4

Transformation of nitriles **3** into amino derivatives **2** under mild conditions was unsuccessful. On the other hand, acceptable to good yields (55-80 %) of compounds **2a-c** were obtained using LDA in THF (Scheme 5). However, compound **3d** under the same conditions gave a rather complex mixture. The formed compounds **2a-c** are yellow light-sensitive solids which darken on light.



3 **2**

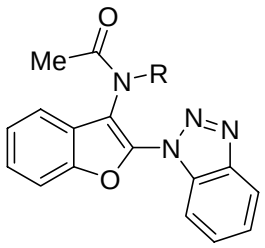
2,3	X
a	O
b	S
c	N-CO_2Et

Scheme 5

We have studied both thermal and photochemical behavior of these compounds. Heating of these compounds in boiling DMF or in various high-boiling solvents (quinoline, diphenylether, xylenes) at 200 °C, as well as in orthophosphoric or polyphosphoric acid led to complex mixtures. Similar results were obtained by photochemical treatment in various solvents (acetonitrile, methanol).

Therefore we decided to evaluate the influence of the free amino group on this behavior. For this purpose, we prepared acetyl derivative **6a** and diacetyl derivative **6b**. Treatment of amino derivative **2a** with acetic anhydride provided good yields of **6b**. Compound **6a** was prepared by acylation of **2a** with one equivalent of acetyl chloride in the presence of triethylamine. However, the compounds were either resistant to any reaction or provided also inseparable mixtures.

Benzotriazole chemistry advanced by the Katritzky group[7] has proved its wide scope and further applications could be expected in the future. In spite of the failed cyclization, we believe that the heteroaryl substituted benzotriazoles **2** or similar compounds available by this methodology could be useful in some other transformations. Therefore the present paper could be of interest for the methodology of the synthesis of this type of compounds.



6a, R = H
6b, R = MeCO

Experimental Section

General Procedures. Melting points were measured on a Kofler block and are uncorrected. NMR spectra were measured on a Bruker 250 DPX spectrometer (250.13 MHz for ^{1}H, 62.89 MHz for ^{13}C). Reference for ^{1}H $\delta_{(TMS)}$= 0.00*ppm*, for ^{13}C $\delta_{(CDCl3)}$= 77.0*ppm*. Chemical shifts are given in *ppm* (δ-scale), coupling constants (*J*) in Hz. IR spectra (KBr) were recorded on a Unicam SP 2006 and Perkin-Elmer FT-IR System Spectrum BX spectrometers, wavenumbers are given in cm^{-1}. UV spectra were measured on a Shimadzu UV-260 spectrometer in ethanol and wavelengths are given in nm. Flash chromatography was done on silica gel 60 (230-400 mesh) and preparative TLC on pre-coated PLC plates (silica gel 60) from EM Science.
Spectroquality acetonitrile or methanol (Merck) was used without further purification in all photochemical experiments. A Hanovia merury lamp was used as the light source in a photochemical reactor with double-walled quartz immersion well.
The following starting compounds were prepared by the previously published methods: thiosalicylonitrile (**5b**),[3a] ethyl *N*-(2-cyanophenyl)carbamate (**5c**),[11] and *N*-(2-cyanophenyl)methanesulfonamide (**5d**).[12]

2-((1*H*-Benzo[*d*][1,2,3]triazol-1-yl)methoxy)benzonitrile (3a). A mixture of salicylonitrile (**5a;** 1.68 g, 10 mmol), anhydrous potassium carbonate (2 g) and 2-butanone (10 ml) was stirred at ambient temperature for 1h. Then 1-chloromethyl benzotriazole (**4;** 1.2 g, 10 mmol) was added and the mixture was refluxed for 2 h. Insoluble portion was filtered off, washed with hot 2-butanone, the filtrate was evaporated and crystallized from ethanol to give 2.4 g (96 %) of colorless crystals; m.p. 131-132 °C. For $C_{14}H_{10}N_4O$ (250.26) calculated: C, 67.19; H, 4.03; N, 22.39; found: C, 67.33; H, 3.89; N, 22.63. ^{1}H NMR spectrum ($CDCl_3$; 30 °C) : δ 6.70 s, 2H (O-CH_2); 7.06 m, 1H (arom. H); 7.42 ddd, *J* = 8.3, *J* = 7.0, *J* = 1.0, 1H (arom. H); 7.50 m, 3H (arom. H); 7.57 ddd, *J* = 8.3, *J* = 7.0, *J* = 1.0, 1H (arom. H); 7.82 dt, *J* = 8.3, *J* = 1.0, 1H (arom. H); 8.05 dt, *J* = 8.3, *J* = 1.0, 1H (arom. H). ^{13}C NMR spectrum ($CDCl_3$; 30 °C): δ 74.2; 103.2; 109.7; 114.5; 115.4; 120.0; 123.0; 124.7; 128.6; 132.5; 133.8; 134.3; 146.2; 157.3. IR spectrum (KBr): 2231 (CN). UV spectrum λ_{max} (log ε): 207.6 (4.47), 232.4 (4.00), 253.2 (3.81), 285.2 (3.72).
2-((1*H*-Benzo[*d*][1,2,3]triazol-1-yl)methylthio)benzonitrile (3b). A mixture of 1-chloromethylbenzotriazole (**4**; 6.4 g, 38 mmol), thiosalicylonitrile (**5b**; 5.15 g, 38 mmol), anhydrous potassium carbonate (5.5 g) and 2-butanone (50 ml) was stirred under nitrogen at ambient temperature for 22h. The reaction mixture was diluted with 2-butanone (25 ml) and the stirring continued for 3 days. The mixture was evaporated, the residue was triturated with water, the insoluble portion was filtered off and washed with water. The crude product was crystallized twice from ethanol using charcoal to give 2.9 g (29 %) of colorless crystals; m.p. 140-141 °C. For $C_{14}H_{10}N_4S$ (266.32) calculated: C, 63.14; H, 3.78; N, 21.04; S, 12.04; found: C, 62.97; H, 3.44; N, 21.40; S, 12.35. ^{1}H NMR spectrum ($CDCl_3$; 30 °C) : δ 6.06 s, 2H (S-CH_2); 7.36 m, 2H (arom. H); 7.42 m, 2H (arom. H); 7.53 td, *J* = 6.5, *J* = 1.1, 1H (arom. H); 6.00 ddd, *J* = 7.9, *J* = 1.4, *J* = 1.0, 1H (arom. H); 7.66 ddd, *J* = 6.4, *J* = 2.9, *J* = 0.7, 1H (arom. H); 8.05 dt, *J* = 8.3, *J* =

1.1, 1H (arom. H). ^{13}C NMR spectrum ($CDCl_3$; 30 °C): δ 51.3; 109.8; 116.6; 117.0; 120.2; 124.4; 127.8; 129.1; 131.9; 133.2; 133.9; 134.2; 135.3; 146.3. IR spectrum (KBr): 2225 (CN). UV spectrum λ_{max} (log ε): 204.6 (4.52), 257.0 (3.99), 286.8 (3.77).

Ethyl *N*-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)methyl-*N*-(2-cyanophenyl)carbamate (3c). A mixture of ethyl 2-cyanophenylcarbamate (**5c;** 9.5 g, 50 mmol), anhydrous potassium carbonate (10 g) and 2-butanone (100 ml) was stirred at ambient temperature for 1h. Then 1-chloromethylbenzotriazole (**4;** 8.4 g, 50 mmol) was added and the mixture was refluxed for 15 h. Insoluble portion was filtered off, washed with hot 2-butanone, the filtrate was evaporated to give dark brown solid. Flash chromatography (dichloromethane) followed by crystallization from ethanol provided 13.8 g (86 %) of colorless crystals; m.p. 97-100 °C. For $C_{17}H_{15}N_5O_2$ (321.33) calculated: C, 63.54; H, 4.71; N, 21.79; found: C, 63.27; H, 4.52; N, 22.12. ^{1}H NMR spectrum ($CDCl_3$; 60 °C) : δ 1.19 t, *J* = 7.0, 3H ($COOCH_2C\underline{H}_3$); 4.23 q, *J* = 7.1, 2H ($COOC\underline{H}_2CH_3$); 6.48 bs, 2H, ($N\text{-}CH_2$); 7.03 d, *J* = 7.9, 1H (arom. H); 7.38 m, 2H (arom. H); 7.51 m, 2H (arom. H); 7.61 dd, *J* = 7.6, *J* = 1.5, 1H (arom. H); 7.92 bd, *J* = 8.1, 1H (arom. H); 8.01 dt, *J* = 8.3, *J* = 0.9, 1H (arom. H). ^{13}C NMR spectrum ($CDCl_3$; 30 °C): δ 13.9; 60.2; 63.1; 110.7; 112.8; 115.3; 119.4; 124.1; 127.8; 128.5; 129.0; 132.3; 133.1; 133.8; 141.5; 145.9; 154.4. IR spectrum (KBr): 2232 (CN). UV spectrum λ_{max} (log ε): 206.0 (4.59), 254.4 (3.84), 281.4 (3.77); $\lambda_{infl.}$ = 269.2.

***N*-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)methyl-*N*-(2-cyanophenyl)methanesulfonamide (3d).** Sodium hydride (0.25 g, 50 % dispersion) was added to a solution of **3d** (1 g, 5 mmol) in DMF (20 ml) and the mixture was stirred under nitrogen at ambient temperature for 2 h. Then a solution of **4** (0.85 g, 5 mmol) in DMF (10 ml) was added and the mixture was stirred overnight (15 h). The mixture was poured into water (150 ml), the formed precipitate was filtered off, washed with water and the dry product was crystalized from ethanol to give 1.1 g of colorless crystals (59 %); m.p 148-150 °C (ethanol). For $C_{15}H_{13}N_5O_2S$ (327.36) calculated: C, 55.03; H, 4.00; N, 21.39; S, 9.79; found: C, 54.77; H, 4.12; N, 21.09; S, 9.94. ^{1}H NMR spectrum ($CDCl_3$; 30 °C) : δ 3.16 s, 3H (CH_3); 6.54 s, 2H (NCH_2); 6.96 m, 1H (arom. H); 7.43 ddd, *J* = 8.4, *J*=7.0, *J*=1.0, 1H (arom. H); 7.48-7.60 m, 3H (arom. H); 7.77 m, 1H (arom. H); 7.86 dt, *J* = 8.4, *J* = 1.0 (arom. H); 8.06 dt, *J* = 8.3, *J* = 1.0, 1H (arom. H).

2-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)benzofuran-3-amine (2a). A solution of LDA (12 ml, 2M solution in THF) was added to a solution of **3a** (5 g, 20 mmol) in THF (75 ml) at –78 °C under argon and the mixture was stirred at this temperature for 6 h. The mixture was then poured into a saturated solution of ammonium chloride (200 ml) and the mixture was extracted with ether and dried with magnesium sulfate. Dark red-brown solid obtained after evaporation was purified by flash chromatography (hexane-acetone. 9 : 1) followed by crystallization from cyclohexane to give 2.95 g (59 %) of yellow crystals; m.p. 110-114 °C. The product is light-sensitive. For $C_{14}H_{10}N_4O$ (250.26) calculated: C, 67.19; H, 4.03; N, 22.39; found:C, 67.03; H, 3.88; N, 22.62 . ^{1}H NMR spectrum ($CDCl_3$; 30 °C) : δ 4.06 bs, 2H (NH_2); 7.35 m, 2H (arom. H); 7.48 m, 2H (arom. H); 7.58 m, 2H (arom. H); 7.99 d, *J* = 8.3, 1H (arom. H); 8.13 dt, J = 8.3, *J* = 1.0, 1H (arom. H). ^{13}C NMR spectrum ($CDCl_3$; 30 °C): 111.6; 111.7; 118.0; 118.6; 120.1; 123.0; 123.9;

125.0; 125.5; 128.7; 129.3; 132.0; 145.2; 150.7. UV spectrum λ_{max} (log ε): 205.2 (4.60), 243.6 (4.15), 357.4 (3.77); $\lambda_{infl.}$ = 270.

2-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)benzo[*b*]thiophen-3-amine (2b). Using the procedure described for **2a**, 78 % of **2b** was obtained as light-sensitive yellowish crystals; m.p 126-130 °C (ethanol, charcoal). For $C_{14}H_{10}N_4S$ (266.32) calculated: C, 63.14; H, 3.78; N, 21.04; S, 12.04; found: C, 62.90; H, 3.83; N, 21.37; S, 12.17. ^{1}H NMR spectrum ($CDCl_3$; 30 °C) : δ 4.45 bs, 2H (NH_2); 7.42-7.50 m, 3H (arom. H); 7.56 m, 1H (arom. H); 7.69 m, 1H (arom. H); 7.75-7.81 m, 2H (arom. H); 8.14 dt, *J* = 8.3, *J* = 1.0, 1H (arom. H). ^{13}C NMR spectrum ($CDCl_3$; 30 °C): 108.5; 110.7; 120.3; 120.6; 123.0; 124.6; 124.7; 126.2; 128.5; 131.8; 133.6; 135.6; 145.5. UV spectrum λ_{max} (log ε): 205.8 (4.52), 258.4 (4.21), 313.2 (3.67).

Ethyl 3-amino-2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1*H*-indole-1-carboxylate (2c). Using the procedure described for **2a**, 70 % of **2c** was obtained as brownish crystals; m.p 182-185 °C (ethanol, charcoal). For $C_{17}H_{15}N_5O_2$ (321.33) calculated: C, 63.54; H, 4.71; N, 21.79; found: C, 63.37; H, 4.55; N, 22.03. ^{1}H NMR spectrum ($CDCl_3$; 30 °C) : δ 0.55 t, *J* = 7.1, 3H ($COOCH_2C\underline{H}_3$); 1.26 s, 2H (NH_2); 3.90 q, *J* = 7.2, 2H ($COOC\underline{H}_2CH_3$); 7.33-7.57 m, 5H (arom. H); 7.59 ddd, *J* = 7.8, *J* = 1.3, *J* = 0.8, 1H (arom. H); 8.15 m, 1H (arom. H); 8.33 dt, *J* = 8.4, *J* = 0.9, 1H (arom. H). ^{13}C NMR spectrum ($CDCl_3$; 30 °C): 13.1; 62.6; 108.8; 110.1; 116.1; 118.1; 120.1; 122.0; 123.2; 124.4; 127.3; 128.0; 128.6; 134.3; 135.7; 145.4; 150.4. IR spectrum (KBr): 1714 (COO). UV spectrum λ_{max} (log ε): 204.4 (4.68), 253.0 (4.34), 283.4 (4.31).

***N*-(2-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)benzofuran-3-yl)acetamide (6a).** Acetyl chloride (0.4 g, 5 mmol) was added dropwise to a stirred mixture of amino derivative **2a** (1 g, 4 mmol), triethylamine (0.5 g) and dichloromethane (20 ml) at 0°C and the mixture was stirred at this temperature for 1h. The mixture was washed consecutively with 0.2M hydrochloric acid and water, dried with magnesium sulfate and evaporated. The obtained dark residue (0.7 g) was crystallized from ethanol (charcoal) to give 0.4 g (34 %) of off-white crystals; m.p. 205-207 °C. For $C_{16}H_{12}N_4O_2$ (292.29) calculated: C, 65.75; H, 4.14; N, 19.17; found: C, 65.44; H, 4.29; N, 19.13. ^{1}H NMR spectrum ($CDCl_3$; 30 °C) : δ 2.23 s, 3H ($COCH_3$); 7.35 m, 2H (arom. H); 7.48 m, 2H (arom. H); 7.63 ddd, *J* = 8.1, *J* = 7.1, *J* = 1.1, 1H (arom. H); 7.80 dd, *J* = 7.1, *J* = 1.8, 1H (arom. H); 7.98 d, *J* = 8.4, 1H (arom. H); 8.11 d, *J* = 8.4, 1H (arom. H); 8.43 bs, 1H (NH). ^{13}C NMR spectrum ($CDCl_3$; 30 °C): 23.5; 110.1; 111.4; 111.6; 120.2; 122.9; 123.9; 124.4; 125.5; 125.8; 129.5; 131.8; 136.1; 145.2; 150.9; 168.8. IR spectrum (KBr): 1671 (CONH). UV spectrum λ_{max} (log ε): 208.4 (4.68), 260.6 (4.36).

***N*-Acetyl-*N*-(2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)benzofuran-3-yl)acetamide (6b).** A mixture of amino derivative **2a** (0,5 g, 2 mmol) and acetic anhydride (20 ml) was stirred at ambient temperature for 2 days (TLC monitoring showed only one product formation). The mixture was evaporated and crystallized from ethanol to give 0.47 g (70 %) of white crystals; m.p. 150-153 °C. For $C_{18}H_{14}N_4O_3$ (334.33) calculated: C, 64.66; H, 4.22; N, 16.76; found: C, 64.49; H, 4.02; N, 16.89. ^{1}H NMR spectrum ($CDCl_3$; 30 °C) : δ 2.45 s, 6H ($COCH_3$); 7.40-7.54 m, 4H (arom. H); 7.62-7.70 m, 2H (arom. H); 8.02 dt, *J* = 8.3, *J*=0.9, 1H, (arom. H); 8.15 dt, *J*=8.3, *J*=1.0, 1H (arom. H). ^{13}C NMR spectrum ($CDCl_3$; 30 °C): 26.1; 110.2; 111.4; 112.2; 118.7;

120.4; 125.0; 125.5; 125.7; 126.3; 129.7; 132.1; 141.9; 145.3; 150.9; 172.3. IR spectrum (KBr): 1659 (CON). UV spectrum λ_{max} (log ε): 206.2 (4.78), 257.6 (4.14), 315.2 (3.86).

Acknowledgements

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