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A direct phosphine-mediated synthesis of polyfunctionalized 1-aminopyrroles from arylglyoxals, phenylhydrazine and acetylene diesters

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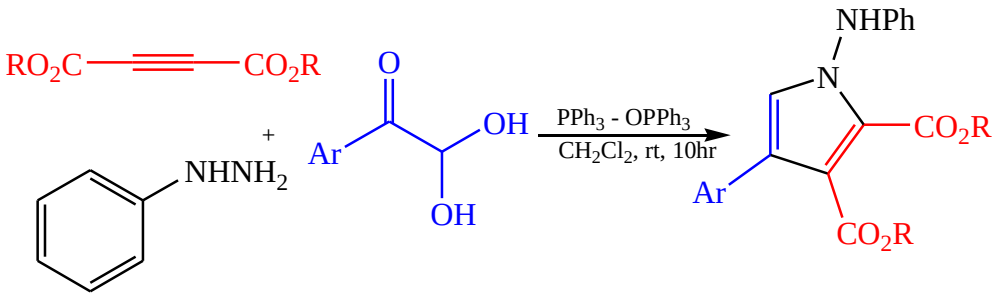
Abstract

A new and efficient one-pot synthesis of 1-Aminopyrrole derivatives by three-component reaction of dialkyl acetylenedicarboxylates, phenylhydrazine and arylglyoxals in the presence of triphenylphosphine is described. The reactions were performed in dichloromethane at room temperature and neutral conditions and afforded good yields of products.



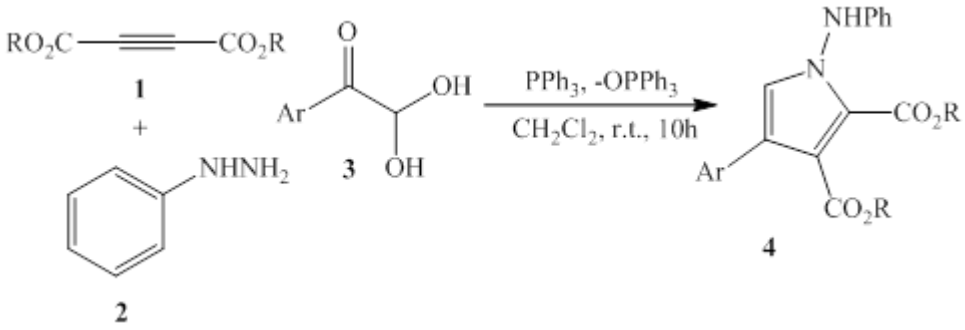
Ar: 4-ClC_6H_4, 4-BrC_6H_4, 4-$O_2NC_6H_4$, C_6H_5, 2-Naphthyl, 4-MeC_6H_4 12 examples
R: Me, Et, t-Bu Yield: 70 - 87%

Keywords: Phenylhydrazine, arylglyoxals, dialkyl acetylenedicarboxylates, 1-Aminopyrrole, triphenylphosphine

Introduction

Pyrrole moieties are common subunits in numerous natural products[1,2] and biological and medicinal important compounds[3] and some are the building blocks for porphirine synthesis.[3] 1-aminopyrroles are important substructures as precursors for the synthesis of biologically active compounds.[4-7] Despite the wide application of 1-aminopyrroles, only a few methods are available for their preparation.[8] Direct synthetic routs to these compounds are relative few and the reported methods suffer from severe reaction conditions, formation of by-products and tedious workup procedures.[9-16]

Multicomponent reactions (MCRs), especially three-component reactions, offer significant advantages over conventional linear-type syntheses because the combination of the reaction components to generate new products in a single step is easy and economic.[17,18] Multi-component reactions of arylglyoxals have been recently attracted many attention for synthesis of a wide range of heterocyclic compounds.[19-21] In continuation of our previous studies on the application of arrylglyoxals for the synthesis of heterocyclic compounds[22-25] here we wish to report a facile route to the synthesis of 1-aminopyrrole derivatives by a triphenylphosphine mediated three-component reaction between arylglyoxal derivatives, dialkyl acetylenedicarboxylates (DAADs) and phenylhydrazine (Scheme 1).



Scheme 1. Reaction between triphenylphosphine, arylglyoxals, phenylhydrazine and triphenylphosphine.

Table 1. The scope of the reaction between triphenylphosphine, arylglyoxals, phenylhydrazine and DAADs

4	R	Ar	Yield%*
a	Me	4-ClC_6H_4	87
b	Me	4-BrC_6H_4	83
c	Me	4-$O_2NC_6H_4$	82
d	Me	C_6H_5	80
e	*t*-Bu	4-BrC_6H_4	75
f	*t*-Bu	4-ClC_6H_4	70
g	Et	4-BrC_6H_4	86
h	Et	4-ClC_6H_4	85
i	Et	2-Naphthyl	80
j	*t*-Bu	4-MeC_6H_4	79
k	Me	4-MeC_6H_4	83
l	Me	2-NaphC_6H_4	75

*Isolated yields. Coditions: CH_2Cl_2, room temperature, 10 hs

Initially, to investigate the reaction between triphenylphosphine, DAADs, phenylhydrazine and arylglyoxals, dimethyl acetylenedicarboxylate (DMAD) was added to a mixture of phenylhydrazine and triphenyphosphine in CH_2Cl_2 as solvent at room temperature. Then 4-chlorophenylglyoxal monohydrate was added and the progress of the reaction was monitored by TLC. After 10 h, the TLC of the mixture of the reaction showed only the presence of pyrrole derivative **4a** and triphenylphosphine oxide. Silica-gel chromatography afforded the product 1-Aminopyrrole **4a** in 87% yield. To investigate the scope of the reaction, diferrent DAADs were treated with triphenylphosphine, phenylhydrazine and different arylglyoxals and the corresponding 1-aminopyrroles **4b-i** were obtained in good yields (Table 1).

Results and Discussion

The structures of compounds **4a–i** were deduced from their elemental analyses and their infrared (IR), ^{1}H NMR, and ^{13}CNMR spectral data. 500-MH_Z ^{1}H NMR spectrum of **4a** exhibited three sharp signals at δ 3.75, 3.85, and 6.60 ppm for two methoxy groups protons and the proton of pyrrole ring, respectively. Aromatic protons resonated between 7.00 and 7.38 ppm. The NH proton resonated at 7.80 ppm as a broad signal. The ^{13}C NMR spectrum of compound **4a** showed 15 distinct resonances in agreement with the proposed structure. The structural assignments made on the basis of the NMR spectra of compound **4a** were supported by its IR spectrum. The ester carbonyl groups exhibited strong absorption bands at about 1731 and 1713 cm^{-1}. Finally, the structure of **4a** was unambiguously confirmed by its X-Ray crystal structure (Figure 1).

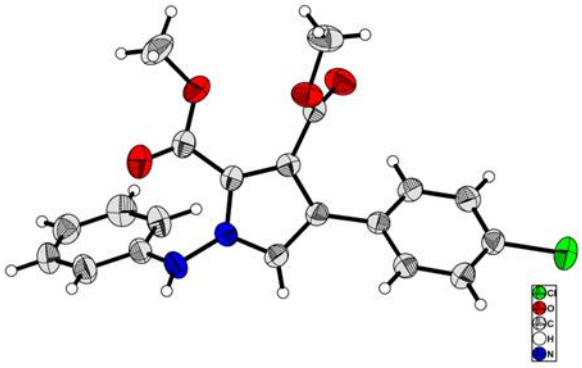
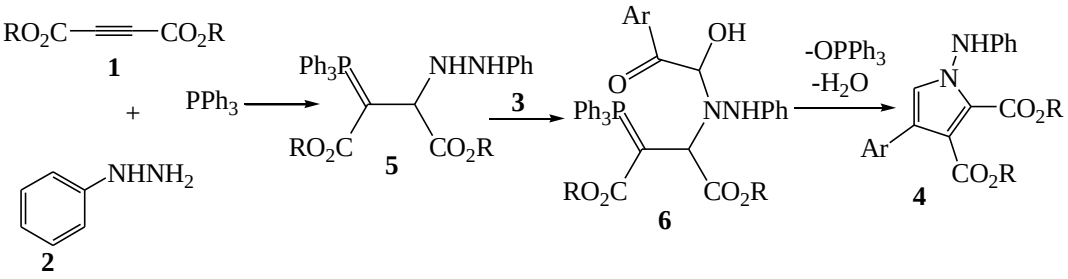


Figure 1. ORTEP diagram of **4a** with atom numbering scheme. Thermal ellipsoids are shown at 50% probability (CCDC number 1508905).

The suggested mechanism for formation of 1-aminopyrroles by the reaction between triphenylphosphine, arylglyoxal derivatives, DAADs and phenylhydrazine is showed in Scheme 2. Three component reaction between triphenylphosphine, DAAD and phenylhydrazine afforded phosphorane **5**. The addition of intermediate **5** to arylgyoxal derivative lead to intermediate **6** which converted to the 1-amininopyrrle derivative by an intramolecular Wittig reaction and elimination of a molecule of water.

In conclusion, here we report a three-component reaction between dialkyl acetylenedicarboxylates, phenylhydrazine and arylglyoxals promoted by triphenylphosphine to produce functionalized 1-aminopyrrole derivatives in good yields. The reaction performed under neutral conditions, and the substances can be mixed without any activation or modification to afford high yields of products.



Scheme 2. Suggested mechanism for formation of 1-aminopyrrole derivatives **4a-i**.

Experimental Section

General. All the utilized arylglyoxals were prepared by the SeO_2-oxidation of the related aryl methylketones on the basis of the reported procedure and used as their monohydrates.1 Elemental analyses were performed using a Heraeus CHN-O-Rapidanalyzer. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ^{26}H, and ^{13}C NMRspectra were recorded on Bruker DRX-400 Avance spectrometer at 400 and 100 MHz, respectively. The chemicals used in this work purchased from Merck and were used without further purification.

General procedure of dimethyl 5-(4-chlorophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (4a). A mixture of dimethyl acetylenedicarboxylate (142 mg, 1 mmol) in CH_2Cl_2 (3 mL) was added drop wise to a magnetically stirred solution of triphenylphosphine (262 mg, 1 mmol) and phenylhydrazine (108 mg, 1 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was then stirred for 1 min. 4-Chlorophenylglyoxal monohydrate (186 mg, 1 mmol) was added, and the reaction mixture was stirred for more 10 hr at room temperature. The solvent was evaporated, and the residue was purified by column chromatography on silica gel using ethyl acetate–hexane mixture (4:1 ratio) as eluent to give the product (308 mg, 80%) as a white solid.

Dimethyl 5-(4-chlorophenyl)-1-(phenylamino)-1*H*-pyrrole-2,3-dicarboxylate (4a). Yield: (308 mg, 80%); white solid; mp 134-136˚C. IR (KBr) ($\bar{\upsilon}$max, cm-1): 3333 (NH), 1731, 1713 (C=O). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.85(3 H, s), 3.75(3 H, s), 6.60 (2 H, t $^3J_{HH}$ 8 HZ), 7.00 (1 H, t, $^3J_{HH}$ 8 Hz), 7.19 (1 H, S, Pyr-H), 7.26 (2 H, t, $^3J_{HH}$ 8 Hz), 7.38 (4 H, m), 7.80(1 H, s, NH PhNH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 51.6, 52.0 (aliphathic carbon), 113.0, 119.0, 120.0, 120.1, 122.1, 125.5, 126.3, 126.4, 128.3, 128.4, 130.8, 132.7, 147.2 (aromatic carbons), 165.5, 169.6 (C=O). Calcd. for ($C_{20}H_{17}ClN_2O_4$): C, 62.42; H, 4.45; N, 7.28%. Found: C, 62.33; H, 4.52; N, 7.35%.

Dimethyl 5-(4-bromophenyl)-1-(phenylamino)-1*H*-pyrrole-2,3-dicarboxylate (**4b**). Yield: (356 mg, 83%); white solid; mp 150-153˚C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3335 (NH), 1715 (C=O). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.75 (3 H, s), 3.84 (3 H, s), 6.60 (2 H, d, $^3J_{HH}$ 8 Hz), 7.00 (1 H, t $^3J_{HH}$ 8 Hz), 7.19 (1 H, S, Pyr-H), 7.26 (1 H, t, $^3J_{HH}$ 8 Hz), 7.33 (2 H, d, $^3J_{HH}$ 8 Hz), 7.52(2 H, d, t $^3J_{HH}$ 8 Hz), 7.79 (1 H, s, NH PhNH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 52.1, 52.5 (aliphathic carbon), 113.7, 120.7, 121.3, 122.6, 123.1, 125.9, 127.5, 128.8, 129.2, 129.4, 131.1, 147.1 (aromatic carbons), 160.1, 166.1 (C=O). Calcd. for ($C_{20}H_{17}BrN_2O_4$): C, 55.96; H, 3.99; N, 6.53%. Found: C, 55.85; H, 4.01; N, 6.60%.

Dimethyl 5-(4-nitrophenyl)-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (**4c**). Yield: (323 mg, 82%); white solid; mp 165-167˚C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3321 (NH), 1717 (C=O).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.77 (3 H, s), 3.87 (3 H, s), 6.61 (2 H, d, $^3J_{HH}$ 8 Hz), 7.01 (1 H, t $^3J_{HH}$ 8 Hz), 7.25 (1 H, S, Pyr-H), 7.28 (1 H, t, $^3J_{HH}$ 8 Hz), 7.61 (2 H, d, $^3J_{HH}$ 8 Hz), 7.81 (1 H, s, NH PhNH), 8.26 (2 H, d, t $^3J_{HH}$ 8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 52.2, 52.6 (aliphathic carbon), 113.8, 119.6, 120.5, 121.0, 122.8, 124.9, 126.6, 128.1,

129.5, 139.6, 146.7, 147.4 (aromatic carbons), 159.9, 165.6 (C=O).Calcd. for ($C_{20}H_{17}N_3O_6$): C, 60.76; H, 4.33; N, 10.63%. Found: C, 60.83; H, 4.21; N, 10.52%

Dimethyl 4-phenyl-1-(phenylamino)-1H-pyrrole-2,3-dicarboxylate (**4d**). Yield: (304 mg, 87%); white solid; mp 153-155˚C. IR (KBr) ($\bar{\upsilon}_{max}$, cm-1): 3263 (NH), 1716 (C=O). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 3.76(3 H, s), 3.85(3 H, s), 6.61 (2 H, t $^3J_{HH}$ 8 Hz), 6.99 (1 H, t $^3J_{HH}$ 8 Hz), 7.28 (1 H, S, Pyr-H), 7.31 (1 H, t $^3J_{HH}$ 8 Hz), 7.41 (2 H, t, $^3J_{HH}$ 8 Hz), 7.47(2 H, d, t $^3J_{HH}$ 8 Hz), 7.47(2 H, d $^3J_{HH}$ 8 Hz), 7.80(1 H, s, NH PhNH). ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* =21.08, 29.7, 52.0, 52.5 (aliphathic carbon), 113.7, 119.7, 120.8, 121.7, 122.5, 123.1, 126.1, 127.2, 127.5, 128.9, 129.4, 132.8, 147.9 (aromatic carbons), 160.1, 166.3 (C=O). Calcd. for ($C_{20}H_{18}N_2O_4$): C, 68.56; H, 5.18; N, 8.00%.Found: C, 68.64; H, 5.06; N, 8.19%.

Di-*t*-butyl 5-(4-bromophenyl)-1-(phenylamino)-1*H*-pyrrole-2,3-dicarboxylate (**4e**). Yield: (309 mg, 75%); White solid; mp 90-93˚C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3380 (NH), 1720, 1699 (C=O). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.39 (9 H, s), 1.45 (9 H, s), 6.67 (2 H, d, $^3J_{HH}$ 8 Hz), 6.98 (1 H, t $^3J_{HH}$ 8 Hz), 7.25 (2H, t, $^3J_{HH}$ 8 Hz), 7.28 (1 H, S, Pyr-H), 7.32 (2 H, d, $^3J_{HH}$ 8 Hz), 7.51 (2 H, t, $^3J_{HH}$ 8 Hz), 7.70 (1 H, s, NH PhNH, t $^3J_{HH}$ 8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 27.4, 81.2, 82.1 (aliphathic carbon), 131.3, 113.3, 120.3, 120.4, 120.6, 121.9, 124.0, 128.8, 129.6, 130.7, 147.9 (aromatic carbons), 158.7, 163.3 (C=O). Calcd. for ($C_{26}H_{29}BrN_2O_4$): C, 60.82; H, 5.69; N, 5.46%. Found: C, 60.71; H, 5.81; N, 5.58%.

Di-*t*-butyl 5-(4-chlorophenyl)-1-(phenylamino)-1*H*-pyrrole-2,3-dicarboxylate (**4f**). Yield: (257 mg, 70%); White solid; mp 111-113˚C; mp IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3280 (NH), 1720, 1699 (C=O). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 1.39 (9 H, s,), 1.45 (9 H, s), 6.59 (2 H, d, $^3J_{HH}$ 8 Hz), 6.59 (2 H, d, $^3J_{HH}$ 8 Hz), 6.98 (1 H, t, $^3J_{HH}$ 8 Hz), 7.25 (1 H, d, $^3J_{HH}$ 8 Hz), 7.28 (1 H, s, Pyr-H), 7.36 (3 H, d, t $^3J_{HH}$ 8 Hz), 7.70 (1 H, s, NH PhNH). ^{13}C NMR ($CDCl_3$, 100 MHZ): *δ* 27.4, 81.2, 82.1 (aliphathic carbon), 131.3, 113.3, 120.3, 120.4, 120.6, 121.9, 124.0, 128.8, 129.6, 130.7, 147.9 (aromatic carbons), 158.7, 163.3 (C=O). Calcd. for ($C_{26}H_{29}ClN_2O_4$): C, 60.82; H, 5.69; N, 5.46%. Found: C, 60.94; H, 5.53; N, 5.32%.

Diethyl 5-(4-bromophenyl)-1-(phenylamino)-1*H*-pyrrole-2,3-dicarboxylate (**4g**). Yield: (393 mg, 86%); white solid; mp 153-155˚C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3328 (NH), 1709 (C=O). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 1.21 (3 H, t, $^3J_{HH}$ 8 Hz), 1.31 (3 H, t, $^3J_{HH}$ 8 Hz), 4.22 (2 H, q, $^3J_{HH}$ 8 Hz), 4.32 (2 H, q, $^3J_{HH}$ 8 Hz), 6.62 (2 H, d, $^3J_{HH}$ 8 Hz, arom), 7.00 (1 H, t, $^3J_{HH}$ 8 Hz, arom), 7.18 (1 H, S, Pyr-H)), 7.27(1 H, t, $^3J_{HH}$ 8 Hz, arom), 7.39(4 H, m, arom), 7.81(1 H, s, NH PhNH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.9, 14.0, 61.1, 61.6 (aliphathic carbon), 113.8, 120.2, 120.5, 120.8, 121.2, 122.6, 125.7, 129.3, 129.4, 131.96, 147.8 (aromatic carbons), 159.7, 165.6 (C=O). Calcd. for ($C_{22}H_{21}BrN_2O_4$): C, 57.78; H, 4.63; N, 6.13%. Found: C, 57.62; H, 4.77; N, 6.26%.

Diethyl 5-(4-chlorophenyl)-1-(phenylamino)-1*H*-pyrrole-2,3-dicarboxylate (**4h**). Yield: (351 ng, 85%); white solid; mp 153-155˚C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3328 (NH), 1709 (C=O).

^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 1.23 (3 H, t, $^3J_{HH}$ 8 Hz), 1.31 (3 H, t, $^3J_{HH}$ 8 Hz), 4.22 (2 H, q $^3J_{HH}$ 8 Hz), 4.32 (2 H, q $^3J_{HH}$ 8 Hz), 6.62 (2 H, d, $^3J_{HH}$ 8 Hz, arom), 7.00 (1 H, t, $^3J_{HH}$ 8 Hz, arom), 7.18 (1 H, S, Pyr-H)), 7.27(1 H, t, $^3J_{HH}$ 8 Hz, arom), 7.39(4 H, m, arom), 7.81(1 H, s, NH PhNH). ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 13.9, 14.2, 61.3, 61.8 (aliphatic carbon), 114.0, 120.2, 120.5, 120.9, 121.2, 122.6, 126.1, 129.7, 129.9, 131.96, 147.8 (aromatic carbons), 159.7, 165.6 (C=O). Calcd. for ($C_{22}H_{21}ClN_2O_4$): C, 57.78; H, 4.63; N, 6.13%. Found: C, 57.67; H, 4.76; N, 6.27%.

Diethyl 4-(naphthalen-2-yl)-1-(phenylamino)-1*H*-pyrrole-2,3-dicarboxylate (4i). Yield: (342 mg, 80%); white solid; mp 97-99˚C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3304 (NH), 1720 (C=O). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 1.25 (3 H, t, $^3J_{HH}$ 8 Hz), 1.31 (3 H, t, $^3J_{HH}$ 8 Hz), 4.24 (2 H, q $^3J_{HH}$ 8 Hz), 4.35 (2 H, q $^3J_{HH}$ 8 Hz), 6.67 (2 H, d, $^3J_{HH}$ 8 Hz, arom), 7.01 (1 H, t, $^3J_{HH}$ 8 Hz, arom), 7.29 (2 H, t, $^3J_{HH}$ 8 Hz, arom)), 7.48-7.54(2 H, m), 7.60-7.63(1 H, m, arom), 7.85-7.89 (3H, m, naph, py), 7.95(1 H, s, NH PhNH). ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 13.9, 14.1, 61.0 (aliphatic carbon), 113.8,

119.9, 121.3, 121.5, 125.9, 126.0, 126.1, 126.3, 127.6, 127.9, 128.2, 129.4, 130.4, 132.4, 133.5, 148.0(aromatic carbons), 165.9(C=O). Calcd. for ($C_{26}H_{24}N_2O_4$): C, 72.88; H, 5.65; N, 6.54%.Found: C, 73.02; H, 5.51; N, 6.43%

Di-*t*-butyl 1-(phenylamino)-4-(*p*-tolyl)-1*H*-pyrrole-2,3-dicarboxylate (4j). Yield: (260 mg, 75%); White solid; mp 142-144˚C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3320 (NH), 1725, 1705 (C=O).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.40 (9 H, s), 1.45 (9 H, s),2.40 (1H, s, CH_3), 6.61 (2 H, d, $^3J_{HH}$ 8 H_Z), 6.98 (1 H, t $^3J_{HH}$ 8 $_{HZ}$), 7.02 (1 H, S, Pyr-H), 7.20 (2H, d, $^3J_{HH}$ 8 H_Z), 7.26 (2H, m), 7.35 (2 H, d, $^3J_{HH}$ 8 H_Z), 7.73 (1 H, s, NH PhNH). ^{13}C NMR ($CDCl_3$, 100 MH_Z): δ 27.4 (aliphathic carbon), 81.2, 82.1, 131.3, 113.3, 120.3, 120.4, 120.6, 121.9, 124.0, 128.8, 129.6, 130.7, 147.9 (aromatic carbons), 159.4, 164.2 (C=O). Calcd. for ($C_{27}H_{32}N_2O_4$): C, 72.30; H, 7.19; N, 6.25;%. Found: C, 72.15; H, 7.33; N, 6.38;%.
Dimethyl 1-(phenylamino)-4-(*p*-tolyl)-1*H*-pyrrole-2,3-dicarboxylate (4k). Yield: (316 mg, 83%); white solid; mp 105˚C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3310 (NH), 1717 (C=O). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.40 (3 H, s), 3.67 (3 H, s), 3.88 (3H, s), 6.62 (2 H, d, $^3J_{HH}$ 8 H_Z), 7.00 (1 H, t $^3J_{HH}$ 8 H_Z), 7.20 (1 H, S, Pyr-H), 7.21-7.24 (2 H, m), 7.26-7.28 (2 H, m), 7.35(2 H, d, t $^3J_{HH}$ 8 H_Z), 7.81 (1 H, s, NH PhNH). ^{13}C NMR ($CDCl_3$, 100 MH_Z): δ 21.2, 52.0, 52.5 (aliphathic carbon), 113.7, 119.5, 120.7, 121.7, 122.5, 126.0, 127.4, 129.4, 129.8, 137.0, 147.9 (aromatic carbons), 160.2, 166.4(C=O). Calcd. for ($C_{21}H_{20}N_2O_4$): C, 69.22; H, 5.53; N, 7.69%. Found: C, 69.37; H, 5.40; N, 7.56%.
Dimethyl 4-(naphthalen-2-yl)-1-(phenylamino)-1*H*-pyrrole-2,3-dicarboxylate (4l) Yield: (300 mg, 75%); white solid; mp 119˚C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3286 (NH), 1723 (C=O). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.79 (3 H, s), 3.87 (3 H, s), 3.88, 6.66 (2 H, d, $^3J_{HH}$ 8 H_Z), 7.00 (1 H, t $^3J_{HH}$ 8 H_Z), 7.29 (3 H, t $^3J_{HH}$ 8 H_Z), 7.48-7.55 (2 H, m), 7.56-7.61 (1 H, m), 7.86-7.90 (4 H, m, arom, Pyr-H)), 7.94 (1 H, s, NH PhNH). ^{13}C NMR ($CDCl_3$, 100 MH_Z): δ 52.1, 52.5 (aliphathic carbon), 113.8, 119.8, 121.0, 121.7, 122.6, 125.9, 126.0, 126.3, 126.4, 127.6, 128.0, 128.3, 129.4, 130.3, 132.5, 133.5, 147.9 (aromatic carbons), 160.2, 166.4(C=O). Calcd. for ($C_{24}H_{20}N_2O_4$): C, 71.99; H, 5.03; N, 7.00%. Found: C, 71.85; H, 5.17; N, 7.13%.

Supplementary Material

The experimental procedures and IR, ^{1}H NMR and ^{13}C NMR spectra associated with this article are available as supplementary data.

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