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A novel synthesis of 4,5-diaryl-6-arylamino-2,3-benzo-1,3a,6a-triazapentalenes☆

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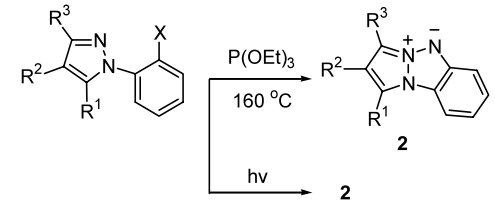
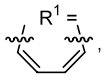
Abstract—Treatment of *N*-alkyl- and *N*-aryl-imines of 2,3-diaryl- and 2-alkyl-3-aryl-3-(benzotriazol-1-yl)propenals with trifluoroacetic anhydride in THF at room temperature gave 5-alkyl-4-aryl-6-[*N*-alkyl (and aryl)-*N*-trifluoroacetyl]amino-2,3-benzo-1,3a,6a-triazapentalenes in moderate to good yields. On heating triazapentalenes having R^2 = aryl in MeOH at reflux, detrifluoroacetylation of triazapentalene occurred to give title compounds in good yields. However, the same treatment of triazapentalenes having R^2 = alkyl did not give the corresponding detrifluoroacetylation product. The title compounds and 5-alkyl-4-aryl-6-(*N*-alkyl-*N*-trifluoroacetyl)amino-2,3-benzo-1,3a,6a-triazapentalenes were found to be good precursors for the synthesis of 1-(*o*-aminophenyl)-3-arylamino-4-alkyl (and aryl)-5-arylpyrazoles and 1-(*o*-aminophenyl)-3-(*N*-alkyl-*N*-trifluoroacetyl)amino-4-alkyl (and aryl)-5-arylpyrazoles, respectively.

Heteropentalene mesomeric betaines of type B have been the subject of extensive investigation, mainly because of their electronic structure and potential synthetic utility.[1] Among representatives of four of these types, i.e. pyrazolo[1,2-*a*]pyrazoles, pyrazolo[1,2-*a*]-1,2,3-triazoles, 1,2,3-triazolo[1,2-*b*]-1,2,3-triazoles, and 1,2,3-triazolo[1,2-*a*]-1,2,3-triazoles, pyrazolo[1,2-*a*]-1,2,3-triazoles **2** have been basically synthesized by two different methods involving the reactions of 1-(*o*-nitroaryl)pyrazoles **1a**[2] or indazoles **1b**[3] with triethylphosphite (Scheme 1) and photolysis of 1-(*o*-azidoaryl)indazoles **1c**.[3a] In these reactions, free nitrenes or nitrenoid-like species may be involved as intermediates. Conversion of 2-(*o*-benzoylphenyl)-2*H*-benzotriazole **3** into triazapentalene **2c** ($R^1 = R^2 = H$, R^3 = PhCO) on heating in triethylphosphite at 180–200°C[4] may be an analogous method to the reaction depicted in Scheme 1 but a carbene is involved as an intermediate.

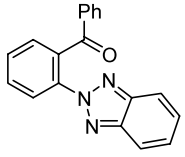


1a, $R^1 = R^2 = R^3 = H$, $X = NO_2$

1b, R^2 =  , $R^3 = H$, $X = NO_2$

1c, $R^1 = R^2 = R^3 = H$, $X = N_3$

Scheme 1.



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Very recently, we reported the synthesis of 4,5-diaryl-6-phenylsulfanyl-2,3-benzo-1,3a,6a-triazapentalenes **6** through Pummerer-type reactions of γ-(benzotriazol-1-yl)allylic sulfoxides **5** with trifluoroacetic anhydride (TFAA) in THF[5] (Scheme 2). This was the first example of the involvement of N-2 of benzotriazole for the intramolecular cyclization leading to **6**. In continuing to explore new benzo-1,3a,6a-triazapentalenes analogous to **6**, we intended to introduce various substituents instead of arylsulfanyl groups at position 6 by employ-

Keywords: betaines; pentalenes; pyrazoles.

☆ Supplementary data associated with this article can be found at doi:10.1016/j.tetlet.2003.08.012

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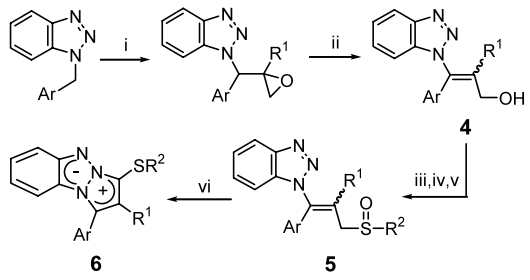
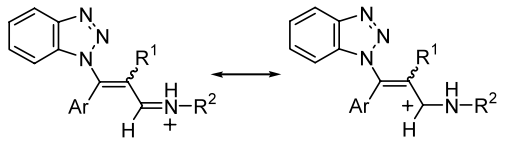
doi:10.1016/j.tetlet.2003.08.012



Scheme 2. *Reagents and conditions*: (i) (a) *n*-BuLi, THF, −78°C, (b) 1-aryl-2-chloroethanones; (ii) (a) *n*-BuLi, THF, −78°C, (b) H_3O^+; (iii) $SOCl_2$, THF, rt; (iv) R^2SH, NaOEt, THF, rt; (v) *m*-CPBA (1 equiv.); (vi) TFAA (5 equiv.), THF, rt.

ing our methodology. The key point of the methodology leading to **6** is to generate an electron-deficient center at the carbon atom α to the double bond of **5**.

Since an allylic cation **9** having an amino group, which is a resonance form of protonated imine **8** was envisaged to be a precursor of triazapentalenes **11** bearing an alkyl- and arylamino group instead of an R^2S group at position **6**, the imine **8** was prepared from compound **4** via an aldehyde **7** (Scheme 3).



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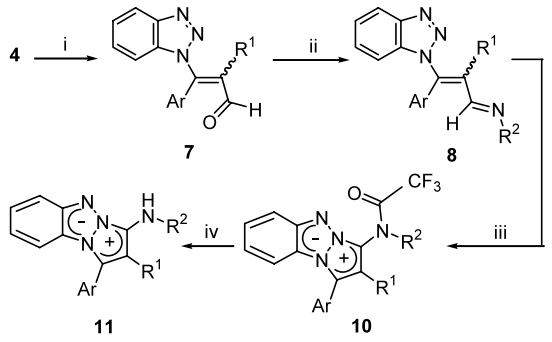
The stereochemistry of compound **4** was found to be maintained through Swern oxidation reaction[6] in view of the ^1H NMR spectroscopic data.[7]

Treatment of **7** with primary arylamines in absolute EtOH at room temperature gave α,β-unsaturated imines **8** in good yields.[8] Since the imines **8a–i** and **8l–o** undergo hydrolysis during the chromatographic purification and recrystallization from EtOH, the solid imines obtained after stripping off the solvent from the reaction mixture were used for the subsequent reaction and recording of spectroscopic data. The stereochemistry around the C=C double bond of **8** was retained. The NOE study[9] on the compound **8m** revealed that the C=N double bond had an (*E*)-configuration.

In the meantime, the reactions of **7e** (Ar = 4-ClC_6H_4, R^1 = 4-BrC_6H_4) with diethylamine in CH_2Cl_2 at room and reflux temperatures did not occur. Only reactant **7e** was quantitatively recovered.

Treatment of α,β-unsaturated aldimines **8a–i** and **8l–o** with Lewis acids such as CF_3CO_2H, CF_3SO_3H, *p*-TsOH, and BF_3·OEt in dried CH_2Cl_2 at room temperature quantitatively led to the corresponding compounds **7**. However, when compounds **8** were treated with TFAA in THF at room temperature, triazapentalenes



Scheme 3. *Reagents and conditions*: (i) (a) DMSO, $(COCl)_2$, CH_2Cl_2, −78°C, N_2, 15 min, (b) TEA, −78°C, N_2, 2 h; (ii) R^2NH_2, absolute EtOH, 12 h, rt; (iii) TFAA (1.2 equiv.), THF, rt; (iv) MeOH, reflux.

10 were formed along with a small amount of the corresponding *N*-aryltrifluoroacetamides.[10] It is envisaged that the latter compounds may be formed by the reaction of TFAA with aniline derivatives formed by hydrolysis of **8** during the course of the reactions. On the other hand, *N*-alkylimines were sticky liquids, which underwent rapidly hydrolysis to give **7**. Consequently, compounds **10j**,**k** and **10p** were prepared by treatment of **7h** and **7o** with the corresponding alkylamines in dried Et_2O (10 mL) for 24 h at room temperature, followed by immediate addition of TFAA with a stirring for 1 h.

The structures of **10** were determined based on the spectroscopic (^1H, ^{13}C, and ^{19}F NMR, IR) and analytical data.[10] The X-ray single-crystal structure of **10p**[11] clearly shows that a trifluoroacetyl group is bonded to the amino nitrogen instead of the benzotriazol moiety (Fig. 1). Compounds **10** were stable under dry conditions, but decomposed slowly in the air. On heating in methanol at reflux, compounds **10a–c**, **10e**, **10g–i**, and **10l–o** underwent deacylation to give the desired compounds **11**,[11] which slowly decomposed in the air.

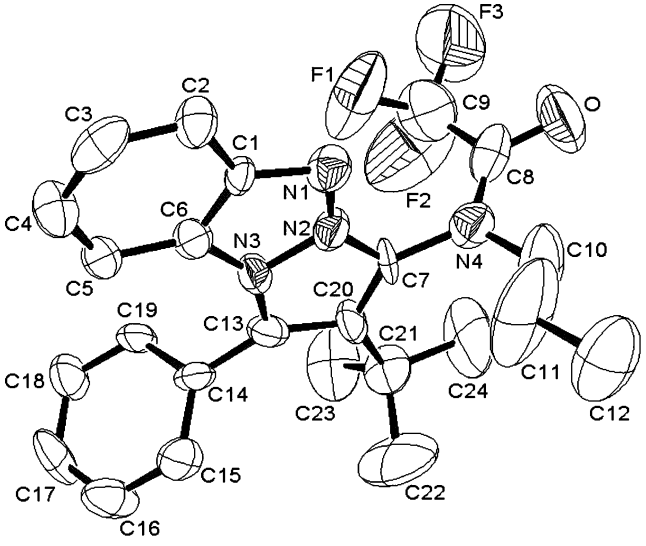


Figure 1.

Table 1. Yields of compounds **7**–**11**

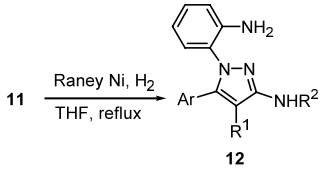
Product	Ar	R^1	R^2	**7**	Yield[a] (%)		
					8	**10**	**11**
a	4-$MeOC_6H_4$	4-MeC_6H_4	4-ClC_6H_4	69[b]	79	66	87
b	4-$MeOC_6H_4$	4-MeC_6H_4	4-MeC_6H_4		83	89	78
c	3-MeC_6H_4	4-MeC_6H_4	Ph	90[c]	85[d]	89	87
d	3-MeC_6H_4	4-MeC_6H_4	C_6H_4Ph		78	85	0
e	4-ClC_6H_4	4-BrC_6H_4	4-$MeOC_6H_4$	88[e]	90	55	82
f	4-ClC_6H_4	4-BrC_6H_4	2-Me-4-$MeOC_6H_4$		76	0	0
g	4-ClC_6H_4	4-BrC_6H_4	4-MeC_6H_4		88[f]	89	75
h	4-FC_6H_4	4-BrC_6H_4	Ph	91[g]	85	79	80
i	4-FC_6H_4	4-BrC_6H_4	4-ClC_6H_4		84[h]	76	83
j	4-FC_6H_4	4-BrC_6H_4	*n*-Pr			35	
k	4-FC_6H_4	4-BrC_6H_4	Allyl			38	
l	Ph	Me	Ph	80[i]	90[j]	67	83
m	4-FC_6H_4	*tert*-Bu	Ph	52[k]	77[l]	88	85
n	4-FC_6H_4	*tert*-Bu	4-MeC_6H_4		72[m]	84	80
o	Ph	*tert*-Bu	Ph	64[n]	73[o]	75	81
p	Ph	*tert*-Bu	*n*-Pr			42	

[a] Isolated yields.
[b] (*E*)/(*Z*) = 4.85:1.
[c] (*E*)/(*Z*) = 2.03:1.
[d] (*E*)/(*Z*) = 1.89:1.
[e] (*E*)/(*Z*) = 1:1.02.
[f] (*E*)-Isomer only.
[g] (*E*)/(*Z*) = 2.46:1.
[h] (*E*)/(*Z*) = 1.37:1.
[i] (*E*)/(*Z*) = 3.14:1.
[j] (*E*)/(*Z*) = 2.04:1.
[k] (*E*)-Isomer only.
[l] (*E*)-Isomer only.
[m] (*E*)-Isomer only.
[n] (*E*)-Isomer only.
[o] (*E*)-Isomer only. *d, f, h, j, l, m, o*The compounds **8** with the specified (*E*)/(*Z*)-ratios were used to prepare **10**.

However, compounds **10j**,**k** and **10p** did not give deacylation products **11** under the same foregoing conditions. Presumably this may be due to lack of the stabilization of the amide ions to be formed.

Preparation of single crystals of both **10** and **11** for X-ray structural determinations was unsuccessful. Yields of compounds **7**–**11** are summarized in Table 1.

Interestingly it has been found that compounds **11** can be utilized for the synthesis of 1-(*o*-aminophenyl)-5-aryl-4-aryl (or alkyl)-3-arylaminopyrazoles **12**[12] (Scheme 4). Similar treatment of **10j** and **10p** with Raney Ni under the same conditions gave pyrazoles **13** having a [*N*-(*n*-propyl)-*N*-trifluoroacetyl]amino group at C-3. Yields of **12** are summarized in Table 2.

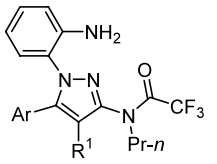


Scheme 4.

Table 2. Yields of pyrazole derivatives **12**

Compound	Ar	R^1	R^2	Product	Yield[a] (%)
11b	4-$MeOC_6H_4$	4-MeC_6H_4	4-MeC_6H_4	**12b**	88
11c	3-MeC_6H_4	4-MeC_6H_4	Ph	**12c**	95
11e	4-ClC_6H_4	4-BrC_6H_4	4-$MeOC_6H_4$	**12e**	92
11h	4-FC_6H_4	4-BrC_6H_4	Ph	**12h**	80
11l	Ph	Me	Ph	**12l**	86
11o	Ph	*tert*-Bu	Ph	**12o**	76

[a] Isolated yields.



13a, Ar = 4-FC_6H_4, R^1 = 4-BrC_6H_4, 85%

13b, Ar = Ph, R^1 = *tert*-Bu, 74 %

In summary, we have explored a novel synthesis of 2,3-benzo-1,3a,6a-triazapentalenes bearing an arylamino group at position 6 starting from 2,3-diaryl- and 2-alkyl-3-aryl-2-(benzotriazol-1-yl)propenals in three steps. The key step leading to the desired products is the generation of iminium ions from α,β-unsaturated imines using trifluoroacetic anhydride. Title compounds are found to be good precursors for the synthesis of 1-(*o*-aminophenyl)-3-arylamino-4-alkyl (and aryl)-5-arylpyrazoles, which have been biologically important.[13] The scope of the reaction is in progress.

Acknowledgements

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6. **Typical procedure**: A mixture of DMSO (634 mg, 3.12 mmol) and oxalyl chloride (618 mg, 4.87 mmol) in CH_2Cl_2 (30 mL) was stirred for 15 min at −78°C under a nitrogen atmosphere, followed by addition of 3-(benzotriazol-1-yl)-3-(4-methoxyphenyl)-2-(*p*-tolyl)propenol **4a** (603 mg, 1.62 mmol). The mixture was stirred for an additional 2 h, followed by the addition of triethylamine (1150 mg, 11.36 mmol). After stirring for 2 h at −78°C under a nitrogen atmosphere, water (100 mL) was added and the reaction mixture was extracted with dichloromethane (50 mL×4). The combined extract was dried over $MgSO_4$. After removal of the solvent under vacuo, the residue was chromatographed on a silica gel (70–230 mesh, 3×18 cm) using a mixture of *n*-hexane and EtOAc (7:1) to give a unknown compound (31 mg), and 3-(benzotriazol-1-yl)-3-(4-methoxyphenyl)-2-(*p*-tolyl)propenal **7a** (413 mg, 69%): IR (neat) 2928, 1721, 1667, 1600, 1507, 1443, 1382, 1251, 1174, 1024, 905, 825, 745, 668, 518 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.16 (s, 3H, CH_3), 3.87 (s, 3H, OCH_3), 6.71–7.29 (m, 1H, ArH), 8.00 (d, J=4.1 Hz, 1H, ArH), 9.92 (d, J=7.6 Hz, 1H, CHO). 2.33 (s, 3H, CH_3), 3.75 (s, 3H, OCH_3), 6.71–7.29 (m, 11H, ArH), 8.21 (d, J=4.1 Hz, 1H, ArH), 9.35 (d, J=7.6 Hz, 1H, CHO); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21, 55, 110, 111, 114, 120, 124, 125, 128, 129, 130, 131, 132, 133, 135, 138, 145, 149, 161, 162, 192. Anal. calcd for $C_{23}H_{19}N_3O_2$: C, 74.78; H, 5.18; N, 11.37. Found: C, 74.72; H, 5.16; N, 11.34.
7. The (*E*)/(*Z*)-ratios of **7** were determined on the basis of the ^1H NMR intensities of the CHO group.
8. **Typical procedure**: To a solution of 3-(benzotriazol-1-yl)-2-methyl-3-phenylpropenal **7l** (85 mg, 0.32 mmol) in absolute EtOH (10 mL) was added aniline (30 mg, 0.32 mmol). The mixture was stirred for 12 h at room temperature, followed by addition of water (50 mL). The aqueous solution was extracted with CH_2Cl_2 (30 mL×3). The combined extract was dried over $MgSO_4$ and removal of the solvent in vacuo gave a viscous residue (98 mg, 90%) which was a mixture of *N*-phenylimine of (*E*)- and (*Z*)-**7l** (2.84:1): IR (neat) 3056, 1590, 1478, 1440, 1372, 1273, 1222, 1152, 1056, 1020, 905, 841, 748, 694, and 528 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.15 (s, 3H, CH_3, *E*), 2.46 (s, 3H, CH_3, *Z*), 7.01–7.40 (m, 26H, ArH, *E* and *Z*), 7.84 (s, 1H, CH, *Z*), 8.10–8.12 (m, 2H, ArH, *E* and *Z*), 8.45 (s, 1H, CH, *E*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.0, 15.5, 110.6, 115.0, 120.1, 120.8, 120.9, 124.3, 126.3, 128.2, 128.3, 128.7, 128.8, 129.0, 129.1, 129.2, 130.1, 130.2, 133.2, 134.0, 134.1, 134.6, 141.7, 145.7, 151.6, 159.9, 160.0. Anal. calcd for $C_{22}H_{18}N_4$: C, 78.08; H, 5.36; N, 16.56. Found: C, 78.01; H, 5.32; N, 16.49.
9. Compound (*E*)-**8m** (Ar = 4-FC_6H_4, R^1 = *tert*-Bu, R^2 = Ph), with a singlet at δ = 8.25 (600 MHz, $CDCl_3$) assigned to the imine proton, displayed NOE effects between one *ortho* proton (δ = 6.88–6.89) of the 4-FC_6H_4 group and one *ortho* proton (δ = 7.23–7.26) of the Ph group.
10. **Typical procedure**: To a solution of **8b** (68 mg, 0.15 mmol) in THF (5 mL) was added trifluoroacetic anhydride (62 mg, 0.30 mmol). The mixture was stirred for 1 h at room temperature, followed by the addition of water (50 mL). The aqueous solution was extracted with CH_2Cl_2 (30 mL×3). The combined extract was dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was chromatographed on a silica gel (70–230 mesh, 3×10 cm) using a mixture of *n*-hexane and EtOAc (10:1) to give 4-(4-methoxyphenyl)-5-(*p*-tolyl)-6-[*N*-(*p*-tolyl)-*N*-trifluoroacetyl]amino-2,3-benzo-1,3a,6a-triazapentalene **10b** (73 mg, 89%): mp 198–200°C (*n*-hexane); IR (neat) 1715, 1600, 1507, 1456, 1379, 1209, 1116, 1030, 908, 825, 732, and 534 cm^{-1}; ^1H NMR (300 MHz,

$CDCl_3$) δ 2.27 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 3.84 (s, 3H, OCH_3), 6.82–7.38 (m, 15H, ArH), 7.60 (d, $J=8.2$ Hz, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 21.3, 55, 111, 113, 114, 116, 119, 120, 126.4, 126.8, 127, 129.5, 129.7, 129.8, 131, 138, 159; ^{19}F NMR ($\delta=-72.6$). Anal. calcd for $C_{32}H_{25}F_3N_4O_2$: C, 69.31; H, 4.54; N, 10.10. Found: C, 69.12; H, 4.58; N, 10.09.

11. **Typical procedure**: A solution of **10b** (70 mg, 0.13 mmol) in MeOH (10 mL) was heated for 1 h at reflux and then cooled to room temperature. Water (50 mL) was added to the reaction mixture and then the aqueous solution was extracted with CH_2Cl_2 (30 mL×3). The combined extract was dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on a silica gel (70–230 mesh, 3×10 cm) using a mixture of EtOAc and *n*-hexane (1:5) to give 4-(4-methoxyphenyl)-6-(*p*-toluidino)-5-(*p*-tolyl)-2,3-benzo-1,3a,6a-triazapentalene **11b** (45 mg, 78%): mp 150–152°C (CH_2Cl_2–*n*-hexane); IR (neat) 3264, 3024, 1603, 1536, 1507, 1456, 1350, 1286, 1248, 1177, 1107, 1027, 905, 816, 726, 643, and 518 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.23 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 3.87 (s, 3H, OCH_3), 5.70 (s, 1H, NH), 6.55–6.75 (m, 3H, ArH), 6.96–7.47 (m, 13H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.5, 21.1, 55.2, 110.9, 112.9, 114.2, 114.3, 115.1, 115.4, 117.2, 118.8, 120.2, 120.4, 125.9, 127.6, 128.9, 129.2, 129.5, 129.8, 131.2, 137.1, 142.0, 147.2, 159.8. Anal. calcd for $C_{30}H_{26}N_4O$: C, 78.58; H, 5.72; N, 12.22. Found: C, 78.46; H, 5.68; N, 12.20.
12. **Typical procedure**: A solution of **11o** (60 mg, 0.16 mmol) and Raney-Ni (50 mg) in MeOH (10 mL) was heated for 1.5 h at reflux under hydrogen. Removal of the insoluble materials by filtration followed by evaporation of the solvent, gave a residue, which was chromatographed on a silica gel column (70–230 mesh, 2×10 cm) using a mixture of EtOAc and *n*-hexane (1:3) to give [1-(2-aminophenyl)-4-*tert*-butyl-5-phenyl-1*H*-pyrazol-3-yl]phenylamine **12o** (46 mg, 76%): mp 120–121°C (CH_2Cl_2-*n*-hexane); IR (neat) 3456, 3360, 2960, 1603, 1500, 1440, 1350, 1302, 1241, 1024, 963, 905, 742, and 544 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.23 (s, 9H, $C(CH_3)_3$), 4.01 (s, 1H, NH_2), 5.64 (s, 1H, NH), 5.70 (s, 1H, NH), 6.55–6.75 (m, 3H, ArH), 6.96–7.47 (m, 13H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.9, 31.8, 115.3, 116.2, 117.4, 119.0, 119.1, 125.8, 127.5, 128.3, 128.4, 128.7, 129.0, 131.0, 132.7, 141.4, 143.6, 144.8, 148.9. Anal. calcd for $C_{25}H_{26}N_4$: C, 78.50; H, 6.85; N, 14.65. Found: C, 78.59; H, 7.00; N, 14.85.
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