NOVEL HETEROCYCLIC ANALOGS OF TRITYL RADICALS: SYNTHESIS AND DIMERIZATION OF DIARYLMETHYL-1*H*-1,2,4-TRIAZOLES AND DIARYLMETHYL-2*H*-PHENANTHRO[9,10-*d*]-1,2,3-TRIAZOLES*

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Abstract — Diarylmethanes (**1a-h**, **9a-i** and **12**) containing a heterocyclic group attached to the central carbon atom have been synthesized. Lithiation of these substrates followed by the addition of iodine gave dimers (**2a,b,d,e** and **10**) *via* α, *para*-dimerization of novel heterocyclic diarylmethyl radical intermediates.

In continuation of our investigation into the stability and properties of trityl radical analogues in which one of the aryl groups has been replaced by a *N*-linked heterocyclic moiety, we have prepared further representatives. These comprise (i) diarylmethyl-1*H*-1,2,4-triazoles (**1a-h**), in which the 1,2,4-triazol-1-yl group bears similarities to the benzotriazolyl group,[1,2] (ii) diarylmethyl-2*H*-phenanthro[9,10-*d*]-1,2,3-triazoles (**9a-i**) containing the large conjugated and symmetrical phenanthrotriazol-2-yl moiety, and (iii) 2-diphenylmethyl-5-phenyl-2*H*-1,2,3,4-tetrazole (**12**).

Preparation of Diarylmethyl Heterocycles. The diarylmethyl-1*H*-1,2,4-triazoles (**1a-h**) were prepared in good to excellent yields by adaptations of known procedures,[3] either by heating 1,2,4-triazole with diarylmethanols under reflux in toluene, in the presence of a catalytic amount of *p*-toluenesulfonic acid (*Method A*) or by reacting the sodium 1,2,4-triazolate salt with diarylmethyl halides in toluene under reflux conditions (*Method B*) (Scheme 1, Table 1).

Diarylmethyl-2*H*-phenanthro[9,10-*d*]-1,2,3-triazoles (**9a-i**) were synthesized from phenanthrotriazole (**8**) which was itself obtained from 3-hydroxyphenanthrotriazine (**7**).[4] The conversion of **7** to **8** was effected by

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using *N*-chlorosuccinimide instead of chloramine[5] and gave phenanthrotriazole (**8**) in a yield of 84% (Scheme 2). Compounds (**9a-i**) were prepared in good to excellent yields (Table 1) from phenanthrotriazole (**8**) and either the corresponding diarylmethanol according to *Method A* or the diarylmethyl halide according to *Method C* (Scheme 2, Table 1). All these reactions generated exclusively 2-diarylmethyl-2*H*-phenanthro[9,10-*d*]-1,2,3-triazoles except in the instance of **9a** where the desired product was accompanied by a small amount of 1-diphenylmethyl-1*H*-phenanthro[9,10-*d*]-1,2,3-triazole (5%). The novel 2-diarylmethyl-2*H*-phenanthro[9,10-*d*]-1,2,3-triazole structures were supported by ^{1}H and ^{13}C NMR spectra and elemental analysis (Table 1). The ^{1}H NMR spectra displayed two groups of signals at 8.80-8.70 ppm and 8.50-8.20 ppm, indicating that **9a-i** were all generated in the symmetrical phenanthrotriazol-2-yl form. The characteristic singlet of the methine group is present in the range 7.8-7.6 ppm. In the ^{13}C NMR spectra, seven phenanthrotriazol-2-yl carbon signals were observed between 145 and 120 ppm, and the methine carbon resonates between 73 and 69 ppm. Both proton and carbon signals for the methine group appeared at abnormally low field due to the deshielding effect of the aryl and phenanthrotriazol-2-yl groups present.

Scheme 1

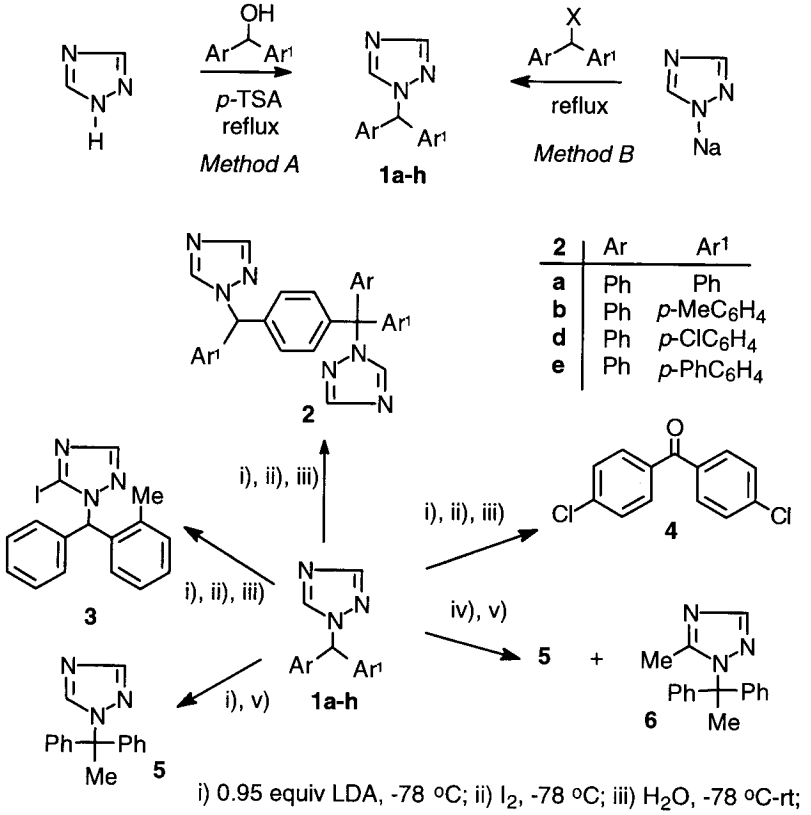
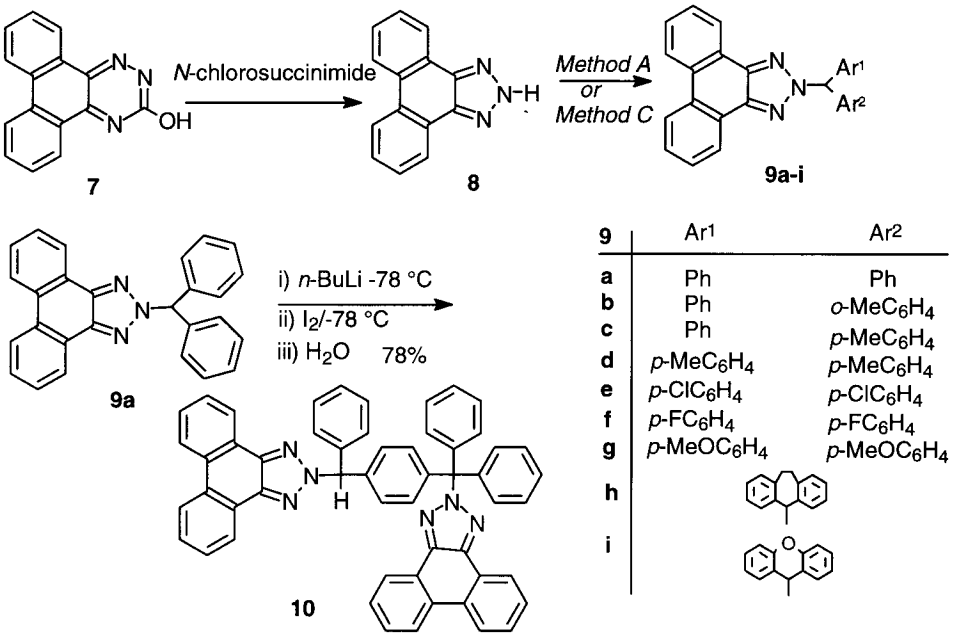


Table 1. Preparation of substrates (1, 9 and 12)

Compd	Ar	Ar^1	yield, %	mp, °C	CHN found (required)		
					C	H	N
1a[a]	Ph	Ph	80	100-102	76.87	5.59	17.87
					(76.51	5.57	17.86)
1b[a]	Ph	*p*-MeC_6H_4	78	89-90	77.22	6.14	16.74
					(77.08	6.06	16.84)
1c[a]	Ph	*o*-MeC_6H_4	68	93-94	77.00	6.07	16.75
					(77.08	6.06	16.84)
1d[b]	Ph	*p*-ClC_6H_4	85	75-77	66.65	4.56	15.48
					(66.79	4.48	15.58)
1e[d]	Ph	*p*-PhC_6H_4	85	167-169	81.31	5.50	13.48
					(81.00	5.50	13.49)
1f[d]	*p*-ClC_6H_4	*p*-ClC_6H_4	82	116-117	59.27	3.62	13.81
					(59.23	3.65	13.81)
1g[b]	suberanyl		80	146-148	78.03	5.84	16.19
					(78.13	5.79	16.08)
1h[b]	9-fluorenyl		22	162-164	77.56	4.78	18.02
					(77.22	4.76	18.02)
9a[c]	Ph	Ph	67	189-191	84.13	4.97	10.87
					(84.17	4.93	10.90)
9b[e]	Ph	*o*-MeC_6H_4	75	168-169	84.09	5.32	10.49
					(84.18	5.30	10.52)
9c[e]	Ph	*p*-MeC_6H_4	85	157-159	84.42	5.35	10.43
					(84.18	5.30	10.52)
9d[e]	*p*-MeC_6H_4	*p*-MeC_6H_4	75	205-207	84.22	5.21	10.27
					(84.22	5.61	10.17)
9e[e]	*p*-ClC_6H_4	*p*-ClC_6H_4	91	168-169	71.21	3.80	9.11
					(71.51	3.78	9.27)
9f[e]	*p*-FC_6H_4	*p*-FC_6H_4	63	162-164	76.79	4.07	9.91
					(76.95	4.07	9.97)
9g[c]	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	71	148-149	78.53	5.31	9.15
					(78.18	5.20	9.43)
9h[c]	suberanyl		63	272-273	84.29	5.15	10.29
					(84.64	5.14	10.21)
9i[f]	9-xanthenyl		68	278-279	81.22	4.19	10.42
					(81.22	4.26	10.52)
12[a]	Ph	Ph	95	113-114	76.52	5.09	17.78
					(76.90	5.16	17.94)

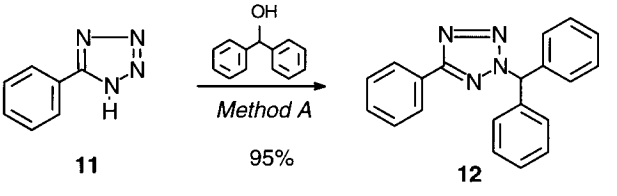
[a]Prepared according to *Method A*, heated under reflux for 12 h. [b]Prepared according to *Method B*, heated under reflux for 12 h. [c]Prepared according to *Method C*, heated under reflux for 48 h. [d]Prepared according to *Method A*, heated under reflux for 20 h. [e]Prepared according to *Method A*, heated under reflux for 24 h. [f]Prepared according to *Method A*, heated under reflux for 48 h.

Scheme 2



2-Diphenylmethyl-5-phenyl-2*H*-1,2,3,4-tetrazole (**12**) was prepared by reaction of 5-phenyltetrazole (**11**) and benzhydrol according to *Method A* in a yield of 95% (Scheme 3, Table 1).

Scheme 3



Dimerization of Diarylmethyl-1*H*-1,2,4-triazoles (1a-h). According to the protocol previously described,[1,2] treatment of **1a** with LDA at -78 °C, followed by addition of a solution of iodine in dry THF at -78 °C gave rise to the corresponding diphenyl(1,2,4-triazol-1-yl)methyl radical. It is well established that triarylmethyl radicals in solution are in equilibrium with their dimers[6,7] and our previous results showed that this also applies to diaryl(*N*-benzotriazolyl)methanes.[1,2] Indeed quenching the reaction mixtures from **1a, 1b, 1d,** and **1e** with water gave dimers (**2a**, **2b**, **2d**, **2e**) respectively, which were isolated in high yields (Scheme 1, Table 2). Arylmethyl radicals generally dimerize by attachment of the central carbon atom of one radical to a phenyl ring *para*-carbon atom of one other radical but symmetrical ethane

products (resulting from α,α-dimerization) are occasionally obtained.[8] Therefore, the structure of such dimers needs to be established in every case. The structures of dimers (**2a**, **2b**, **2d** and **2e**) were supported by NMR evidence. Thus the ^{1}H NMR spectrum of dimer (**2a**) displays four singlets each representing one proton at 8.07, 8.03, 8.02 and 7.97 ppm, indicating two non-equivalent 1,2,4-triazolyl groups. The singlet at 6.79 ppm is due to the central CH *alpha* to the 1,2,4-triazolyl group. The ^{13}C NMR spectrum also exhibits two sets of 1,2,4-triazolyl signals (152.3ppm, 145.6 ppm and 151.8 ppm, 143.5 ppm) and two signals at 77.5 ppm and 67.3 ppm for the quaternary and the tertiary carbon, respectively. Dimers (**2a**, **2b**, **2d** and **2e**) were further characterized by CHN analysis (Table 2).

Table 2. Characterization of dimers (2) and (10)

Compd	Ar	Ar^1	yield, %	mp, °C	CHN found (required)		
					C	H	N
2a	Ph	Ph	85	233-235	76.86	5.26	17.56
					(76.90	5.16	17.94)
2b	Ph	*p*-MeC_6H_5	60	135-137	77.73	5.79	16.97
					(77.39	5.68	16.92)
2d	Ph	*p*-ClC_6H_5	70	183-185	67.38	4.30	15.38
					(67.04	4.13	15.64)
2e	Ph	*p*-PhC_6H_5	72	118.5-120.5	81.42	5.32	13.26
					(81.27	5.20	13.54)
10	Ph	Ph	78	309-311	84.65	4.88	10.86
					(84.35	4.72	10.93)

As expected from our previous results,[1,2] dimers (**2a**, **2b**, **2d** and **2e**) result from α, *para*-dimerization and no products of α,α- or α, *ortho*-dimerization were observed. The α, *para*-process occurred even when one *para*-position was substituted (dimers **2b**, **2d**, **2e**). However substrate (**1c**), where both *para*-positions were unsubstituted but a methyl group was present in *ortho*-position of one of the phenyl rings, under these conditions, gave 5-iodo-1-[(2-methylphenyl)(phenyl)methyl]-1*H*-1,2,4-triazole (**3**) in a yield of 40% along with traces of the desired dimer and some starting material, although the corresponding benzotriazol-2-yl substrate dimerized as expected.[2] The formation of **3** (as the main product) could be ascribed to the known acidity of the hydrogen atom at the 5-position (H-5) on the triazolyl.[9] To determine the relative acidity of the hydrogens attached to the 1,2,4-triazol-1-yl ring, compound (**1a**) was reacted with 0.95 equiv of LDA at -78 °C followed by addition of methyl iodide (Scheme 1). Compound **5** was the only product obtained, along with a small amount of starting material (**1a**). When **1a** was treated with 1.5 equiv of LDA in the same conditions, compound (**6**)was obtained along with **5**. These reactions show that

H-5 is the most acidic hydrogen after the one attached to the central carbon atom and could explain the isolation of **3** when dimerization of **1c** was attempted. Considerable steric hindrance at the central carbon (reinforced by the presence of a methyl group at the *ortho*-position of one of the phenyl rings) evidently renders H-5 more prone to nucleophilic attack.

When the respective *para*-positions of each aryl group was substituted as in compound (**1f**), no α,α- or α,*ortho*-dimerization occurred. The corresponding diaryl ketone (**4**) was obtained after the reaction mixture was quenched with water. This result is in agreement with previous reports.[1,7] Attempted dimerization of substrates (**1g**) and (**1h**) failed.

Dimerization of 2-Diphenylmethyl-2*H*-phenanthro[9,10-*d*]-1,2,3-triazole (9a). Attempted dimerizations of diarylmethyl-2*H*-phenanthro[9,10-*d*]-1,2,3-triazoles (**9a-i**) were carried out according to the protocol above by using *n*-BuLi. Substrate (**9a**) afforded the corresponding dimer (**10**) *via* α, *para*-dimerization in a good yield (78%) (Scheme 2, Table 2). The structure of the dimer (**10**) was supported by NMR and elemental analysis. The ^{1}H NMR spectrum displays signals at 8.72, 8.41 and 8.26 ppm accounting for 8 protons, indicating two non-equivalent phenanthrotriazol-2-yl groups. The ^{13}C NMR spectrum also shows two sets of phenanthrotriazol-2-yl signals and two signals at 82.8 and 71.7 ppm for the quaternary and the tertiary central carbon atoms respectively. Lithiation with *n*-BuLi and treatment of substrates (**9b**) and (**9c**) (with one *ortho* and one *para* position substituted respectively) with iodine failed to produce the corresponding dimers, even under forceful conditions (heating under reflux in THF for several hours). The lithiation of **9b** and **9c** took place successfully as evidenced by the resulting dark blue solution upon treatment with *n*-BuLi. However, the starting materials were recovered along with small amounts of the corresponding ketones. These results constitute a noteworthy departure from the trend observed with diarylmethyl benzotriazol-2-yl radicals.[2] The unsuccessful formation of the dimers is presumably due to the more stable and therefore less reactive nature of these radicals. When substrates (**9d-g**) (with both *para* positions substituted) were subjected to the conditions of dimerization, the corresponding ketones (hydrolysis/oxidation products) were isolated as previously observed. As reported in the case of substrates (**1g**) and (**1h**), the attempted dimerization of substrates (**9h**) and (**9i**) was not fruitful. Attempted dimerization of 2-(diphenylmethyl)-5-phenyl-1,2,3,4-tetrazole (**12**) was also unsuccessful.

EXPERIMENTAL SECTION

General Comments. Melting points were determined with a Kofler hot stage apparatus without correction. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer in $CDCl_3$ with

tetramethylsilane or solvent as the internal reference. Microanalyses were performed on a Carlo Erba 1106 elemental analyzer. THF was distilled from sodium/benzophenone prior to use. Lithiation reactions were carried out under an inert atmosphere of dry nitrogen. All glassware was oven-dried. All moisture-sensitive reagents were transferred by means of pre-dried syringes.

Preparation of 2*H*-Phenanthro[9,10-*d*]-1,2,3-triazole (8). A mixture of 3-hydroxyphenanthrotriazine (4.8 g, 18.6 mmol) and *N*-chlorosuccinimide (2.67 g, 20 mmol) in CH_2Cl_2 (50 mL) was stirred overnight at 30-35 °C. After cooling, the solution was filtered and the solid washed with CH_2Cl_2 (2 x 20 mL), hexane (2 x 20 mL) and dried *in vacuo* to give **8** (3.4 g, 84%) (mp 314-316 °C, lit.,[5] mp 322-325 °C).

General Procedure for the Preparation of Substrates (1a-h, 9a-i and 12).

Method A. A solution of starting material (1,2,4-triazole or compounds **8** or **11**) (11 mmol), diarylmethanol (10 mmol) and a catalytic amount of *p*-toluenesulfonic acid in toluene (100 mL) was placed in a flask equipped with a Dean-Stark trap and heated under reflux for several hours (see Table 1). The reaction, monitored by TLC, was continued until no starting material remained. After cooling down and removal of the solvent under reduced pressure, the reaction mixture was washed with 2N aqueous NaOH, extracted with EtOAc and dried over Na_2SO_4. Removal of the solvent under reduced pressure gave a residue which was purified by column chromatography (silica gel, hexane/EtOAc) and compounds (**1**) were isolated.

Method B. To a solution of starting material (1,2,4-triazole or compounds **8** or **11**) (30 mmol) in dry toluene (100 mL), was added sodium hydride (35 mmol) under a dry atmosphere of N_2. The mixture was heated under reflux for 2 h before diarylmethyl chloride or bromide (10 mmol) was added and heating under reflux was continued for 12 h. After cooling down and removal of the solvent under reduced pressure, the reaction mixture was washed with water, extracted with EtOAc and the organic layer dried over Na_2SO_4. Removal of the solvent under vacuum gave a residue which was purified by column chromatography.

Method C. A solution of phenanthrotriazole (**8**) (1.1 g, 5 mmol), diaryl bromide (5 mmol), triethylamine (15 mmol) in toluene (100 mL) was heated under reflux for several hours (see Table 1). After cooling down and removal of the solvent under reduced pressure, the reaction mixture was washed with 2 N aqueous NaOH, extracted with EtOAc and dried over Na_2SO_4. Removal of the solvent under reduced pressure gave a residue which was purified by column chromatography (silica gel, hexane/EtOAc) and compounds (**9**) were isolated.

1-[Di(phenyl)methyl]-1*H*-1,2,4-triazole (1a): ^{1}H NMR ($CDCl_3$) δ 8.02 (s, 1H), 7.93 (s, 1H), 7.30-7.40 (m, 6H), 7.12-7.15 (m, 4H), 6.77 (s, 1H); ^{13}C NMR δ 152.1, 143.4, 137.8, 128.7, 128.4, 128.0, 67.6.

1-[(4-Methylphenyl)(phenyl)methyl]-1*H*-1,2,4-triazole (1b): ^{1}H NMR ($CDCl_3$) δ 8.03 (s, 1H), 7.92 (s, 1H), 7.33-7.40 (m, 3H),), 7.18 (d, J = 8.0 Hz, 2H), 7.10-7.14 (m, 2H), 7-04 (d, J = 8.0 Hz, 2H), 6.74 (s, 1H), 2.36 (s, 3H); ^{13}C NMR δ 152.1, 143.5, 138.6, 138.1, 134.9, 129.7, 128.9, 128.5, 128.1, 127.9, 67.7, 21.1.

1-[(2-Methylphenyl)(phenyl)methyl]-1*H*-1,2,4-triazole (1c): ^{1}H NMR ($CDCl_3$) δ 8.03 (s, 1H), 7.80 (s, 1H), 7.34-7.39 (m, 3H), 7.14 -7.29 (m, 3H), 7.05-7.10 (m, 2H), 6.93 (s, 1H), 6.71 (d, J = 7.7 Hz, 1H), 2.20 (s, 3 H); ^{13}C NMR δ 152.2, 143.7, 136.2, 136.1, 131.0, 128.9, 128.5, 128.1, 127.5, 126.4, 65.0, 19.1.

1-[(4-Chlorophenyl)(phenyl)methyl]-1*H*-1,2,4-triazole (1d): ^{1}H NMR ($CDCl_3$) δ 8.00 (s, 1H), 7.92 (s, 1H), 7.26-7.42 (m, 5H), 7.03-7.21 (m, 4H), 6.72 (s, 1H); ^{13}C NMR δ 152.3, 143.4, 137.4, 136.6, 134.5, 129.4, 129.1, 129.0, 128.8, 128.1, 67.1.

1-[(Diphenyl-4-yl)(phenyl)methyl]-1*H*-1,2,4-triazole (1e): ^{1}H NMR ($CDCl_3$) δ 8.07 (s, 1H), 8.00 (s, 1H), 7.57-7.63 (m, 4H), 7.34-7.49 (m, 6H), 7.18-7.24 (m, 4H), 6.82 (s, 1H); ^{13}C NMR δ 152.3, 143.5, 141.5, 140.2, 137.9, 136.8, 128.9, 128.8, 128.6, 128.5, 128.1, 127.6, 127.0, 67.6.

1-[Di(4-chlorophenyl)methyl]-1*H*-1,2,4-triazole (1f): ^{1}H NMR ($CDCl_3$) δ 8.05 (s, 1H), 7.99 (s, 1H), 7.38 (d, J = 8.5 Hz, 4 H), 7.09 (d, J = 8.5 Hz, 4 H), 6.72 (s, 1H); ^{13}C NMR δ 152.5, 143.4, 136.0, 134.8, 129.4, 129.2, 66.4.

1-[10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)-1*H*-1,2,4-triazole (1g): ^{1}H NMR ($CDCl_3$) δ 7.93 (s, 1H), 7.66 (s, 1H), 7.44-7.48 (m, 2H), 7.20-7.38 (m, 6H), 6.21 (s, 1H), 2.80-3.02 (m, 4H); ^{13}C NMR δ 152.2, 143.1, 140.2, 134.3, 131.6, 131.2, 129.7, 126.9, 71.1, 31.9.

1-[9*H*-9-Fluorenyl]-1*H*-1,2,4-triazole (1h): ^{1}H NMR ($CDCl_3$) δ 8.04 (s, 1H), 7.85 (s, 1H), 7.76-7.85 (m, 2H), 7.45-7.52 (m, 4H), 7.30-7.36 (m, 2H), 6.45 (s, 1H); ^{13}C NMR δ 152.2, 141.5, 140.7, 140.6, 129.8, 128.2, 125.3, 120.5, 64.1.

2-(Diphenylmethyl)-2*H*-phenanthro[9,10-*d*]-1,2,3-triazole (9a): ^{1}H NMR (DMSO-d_6) δ 8.78-8.81 (m, 2H), 8.41-8.44 (m, 2H), 7.69-7.76 (m, 5H), 7.37-7.45 (m, 2H); ^{13}C NMR δ 140.2, 138.7, 129.8, 128.6, 128.2, 128.1, 128.0, 124.3, 123.6, 123.2, 72.1.

2-[(2-Methylphenyl)(phenyl)methyl]-2*H*-phenanthro[9,10-*d*]-1,2,3-triazole (9b): ^{1}H NMR (DMSO-d_6) δ 8.79-8.82 (m, 2H), 8.38-8-41 (m, 2H), 7.68-7.79(m, 5H), 7.38-7.46 (m, 5H), 7.19-7.33 (m, 3H), 6.95 (d, J = 7.7 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR δ 140.2, 137.9, 137.1, 136.3, 130.6, 129.8, 128.6, 128.4, 128.2, 128.0, 127.7, 126.1, 124.2, 123.6, 123.2, 69.8, 18.9.

2-[(4-Methylphenyl)(phenyl)methyl]-2*H*-phenanthro[9,10-*d*]-1,2,3-triazole (9c): ^{1}H NMR (DMSO-d_6) δ 8.78-8.81 (m, 2H), 8.40-8.43 (m, 2H), 7.68-7.83 (m, 4H), 7.63 (s, 1H), 7.37-7.46 (m, 5H), 7.30 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR δ 140.2, 139.0, 137.5, 135.8, 129.8, 129.1, 128.5, 128.2, 128.1, 128.05, 128.02, 127.5, 124.3, 123.7, 123.1, 72.0, 20.6.

2-[Di(4-methylphenyl)methyl]-2*H*-phenanthro[9,10-*d*]-1,2,3-triazole (9d): ^{1}H NMR (DMSO-d_6) 8.78-8.80 (m, 2H), 8.42-8.44 (m, 2H), 7.72-7.74 (m, 4H), 7.57 (s, 1H), 7.31 (d, J = 8.0 Hz, 4H), 7.22 (d, J = 8.0 Hz, 4H), 2.31 (s, 6H, CH_3); ^{13}C NMR δ 140.1, 137.4, 136.0, 129.8, 129.0, 128.1, 124.2, 123.7, 123.1, 71.9, 20.6.

2-[Di(4-chlorophenyl)methyl]-2*H*-phenanthro[9,10-*d*]-1,2,3-triazole (9e): ^{1}H NMR (DMSO-d_6) δ 8.81 (d, J = 8.5 Hz, 2H), 8.41-8.44 (m, 2H), 7.80 (s, 1H), 7.71-7.77 (m, 4H), 7.52 (d, J = 8.7 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H); ^{13}C NMR δ 140.4, 137.4, 133.1, 130.0, 129.9, 128.7, 128.3, 128.1, 124.3, 123.5, 123.2, 70.4.

2-[Di(4-fluorophenyl)methyl]-2*H*-phenanthro[9,10-*d*]-1,2,3-triazole (9f): ^{1}H NMR ($CDCl_3$) δ 8.59-8.62 (m, 2H), 8.52-8.55 (m, 2H), 7.63-7.72 (m, 4H), 7.34-7.40 (m, 5H), 7.06-7.11 (m, 2H); ^{13}C NMR δ 141.3, 134.6, 134.5, 130.5, 130.2, 130.1, 127.8, 127.6, 124.5, 123.9, 123.6, 115.7, 115.4, 72.0.

2-[Di(4-methoxyphenyl)methyl]-2*H*-phenanthro[9,10-*d*]-1,2,3-triazole (9g): ^{1}H NMR (DMSO-d_6) δ 8.80 (d, J = 7.8 Hz, 2H), 8.40 (d, J = 7.8 Hz, 2H), 7.69-7.76 (m, 4H), 7.53 (s, 1H), 7.33 (d, J = 8.4 Hz, 4H), 6.96 (d, J = 8.4 Hz, 4H), 3.74 (s, 6H, OCH_3); ^{13}C NMR δ 158.9, 140.1, 131.1, 129.8, 129.4, 128.1,128.0, 124.3, 123.7, 123.1, 113.9, 71.3, 55.1.

2-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)-2*H*-phenanthro[9,10-*d*]-1,2,3-triazole (9h): ^{1}H NMR (DMSO-d_6) δ 8.76 (d, *J* = 7.4 Hz, 2H), 8.26 (d, *J* = 7.0 Hz, 2H), 7.64-7.71 (m, 5H), 7.27-7.37 (m, 8H), 3.15-3.29 (m, 2H), 2.80-2.95 (m, 2H); ^{13}C NMR δ 139.8, 135.8, 135.5, 131.5, 130.6, 129.6, 129.0, 128.0, 126.2, 124.2, 123.6, 123.0, 31.4.

2-(9*H*-9-Xanthenyl)-2*H*-phenanthro[9,10-*d*]-1,2,3-triazole (9i): ^{1}H NMR (DMSO-d_6) δ 8.75-8.78 (m, 2H), 8.31-8.34 (m, 2H), 7.65-7.72 (m, 5H), 7.37-7.50 (m, 6H), 7.12-7.17 (m, 2H); ^{13}C NMR δ 150.7, 130.5, 129.7, 129.4, 128.2, 128.0, 124.3, 123.8, 123.2, 118.1, 116.9, 105.9, 60.6.

2-(Diphenylmethyl)-5-phenyl-2*H*-1,2,3,4-tetrazole (12): ^{1}H NMR ($CDCl_3$) δ 8.13-8.20 (m, 2H), 7.38-7.45 (m, 3H), 7.26-7.37 (m, 11H); ^{13}C NMR δ 165.1, 137.1, 130.2, 128.7, 128.6, 128.3, 128.2, 127.3, 126.8, 71.1.

General Procedure for the Preparation of Dimers (2a, 2b, 2d, and 2e) and Compound (3). To a solution of diaryl(1,2,4-triazol-1-yl)methane (5 mmol) in dry THF (50 mL) at -78 °C under nitrogen was added LDA (4.7 mmol, 1.5 M in hexane, 3.1 mL). The reaction mixture was stirred for 2 h at -78 °C before addition of a solution of iodine (0.635 g, 2.5 mmol) in dry THF (10 mL). Stirring was continued for 4 h, water (2 mL) was added and the reaction mixture extracted with EtOAc (3 x 20 mL). The organic extracts were washed with water and dried over Na_2SO_4. Removal of the solvent under vacuum gave a residue which was purified by column chromatography to yield dimers (**2**) and compound (**3**).

1-(Diphenyl-{4-[phenyl(1*H*-1,2,4-triazol-1-yl)methyl]phenyl}methyl)-1*H*-1,2,4-triazole (2a): ^{1}H NMR ($CDCl_3$) δ 8.07 (s, 1H), 8.03 (s, 1H), 8.02 (s, 1H), 7.97 (s, 1H), 7.33-7.40 (m, 9H), 7.17-7.22 (m, 4H), 7.09-7.13 (m, 6H), 6.79 (s, 1H); ^{13}C NMR δ 152.3, 151.8, 145.6, 143.5, 142.2, 141.4, 138.0, 137.4, 130.4, 129.8, 129.0, 128.7, 128.4, 128.2, 128.1, 127.5, 77.5, 67.3.

1-((4-Methylphenyl)-{4-[(4-methylphenyl)(1*H*-1,2,4-triazol-1-yl)methyl]phenyl}phenylmethyl)-1*H*-1,2,4-triazole (2b): ^{1}H NMR ($CDCl_3$) δ 8.05 (s, 1H), 8.03 (s, 1H), 8.00 (s, 1H), 7.98 (s, 1H), 7.28-7.34 (m, 3H), 7.05-7.21 (m, 12H), 7.00 (d, *J* = 6.9 Hz, 2H), 6.76 (s, 1H), 2.33 (s, 3H), 2.32 (s, 3H); ^{13}C NMR δ 151.9, 151.5, 145.3, 143.2, 142.0, 141.4, 138.3, 138.0, 137.9, 134.3, 130.0, 129.5, 129.4, 129.3, 128.5, 128.0, 127.7, 127.1, 77.7, 66.7, 20.8, 20.7.

1-((4-Chlorophenyl)-{4-[(4-chlorophenyl)(1*H*-1,2,4-triazol-1-yl)methyl]phenyl}phenylmethyl)-1*H*-1,2,4-triazole (2d): ^{1}H NMR ($CDCl_3$) δ 8.07 (s, 1H), 8.03 (s, 1H), 8.01 (s, 1H), 8.00 (s, 1H), 7.30-7.40 (m, 8H), 7.06-7.19 (m, 10H), 6.77 (s, 1H); ^{13}C NMR δ 152.4, 151.9, 145.5, 143.4, 142.1, 140.8, 140.0, 137.8, 135.9, 134.8, 134.4, 131.1, 130.3, 129.6, 129.5, 129.1, 128.7, 128.3, 128.2, 127.6, 77.2, 66.4.

1-((Diphenyl-4-yl)-{4-[(diphenyl-4-yl)(1*H*-1,2,4-triazol-1-yl)methyl]phenyl}phenylmethyl)-1*H*-1,2,4-triazole (2e): ^{1}H NMR ($CDCl_3$) δ 8.10 (s, 1H), 8.08 (s, 1H), 8.07 (s, 1H), 8.03 (s, 1H), 7.55-7.64 (m, 8H), 7.41-7.48 (m, 4H), 7.34-7.41 (m, 5H), 7.24-7.30 (m, 4H), 7.14-7.22 (m, 6H), 6.84 (s, 1H); ^{13}C NMR δ 152.4, 152.0, 145.6, 143.5, 142.4, 141.8, 141.4, 141.2, 140.4, 140.1, 139.9, 138.1, 136.3, 130.5, 130.3, 129.8, 129.0, 128.8, 128.7, 128.5, 128.2, 127.7, 127.6, 127.1, 127.0, 126.7, 77.6, 67.1.

5-Iodo-1-[(2-methylphenyl)(phenyl)methyl]-1*H*-1,2,4-triazole (3): yield 40%, mp 184-186 °C; ^{1}H NMR ($CDCl_3$) δ 8.00 (s, 1H), 6.93-7.36 (m, 10H), 2.24 (s, 3H); ^{13}C NMR δ 154.5, 137.2, 136.1, 128.8, 128.7, 128.6, 128.4, 128.4, 126.5, 76.6, 65.2, 19.6. Anal. Calcd for $C_{16}H_{14}N_3I$: C, 51.22; H, 3.76; N, 11.20. Found: C, 51.11; H, 3.67; N, 10.80.

Preparation of 2-{[4-[2*H*-Phenanthro[9,10-*d*]-1,2,3-triazol-2-yl(phenyl)methyl]phenyl}(diphenyl)-methyl]-2*H*-phenanthro[9,10-*d*]-1,2,3-triazole (10). To a solution of diphenyl(phenanthrotriazol-2-yl)methane (0.385 g, 1 mmol) in dry THF (20 mL) at -78 °C was added *n*-BuLi (1.1 mmol, 0.55 ml of a 2 M hexane solution). The reaction mixture was stirred at -78 °C for l h before addition of a solution of iodine (0.254 g, 1 mmol) in dry THF (5 mL). The colour changed from dark blue to light red and the reaction mixture stirred at rt overnight. Water (2 mL) was added and the reaction mixture was extracted with EtOAc (3 x 20 mL). The organic extracts were washed with water and dried over Na_2SO_4. Removal of the solvent under vacuum gave a residue which was purified by column chromatography (10% EtOAc/hexane) to give dimer (**10**) (0.3 g, 78%). ^{1}H NMR (DMSO-d_6) δ 8.71-8.74 (m, 4H), 8.40-8.42 (m, 2H), 8.25-8.28 (m, 2H), 7.59-7.73 (m, 8H), 7.16-7.51 (m, 20H); ^{13}C NMR δ 142.1, 140.3, 139.7, 138.4, 138.3, 130.2, 129.9, 129.8, 128.5, 128.3, 128.1, 128.0, 127.8, 127.5, 127.3, 124.0, 123.7, 123.3, 123.2, 82.8, 71.7.

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