A Novel and Efficient 2,4,6-Trisubstituted Pyridine Ring Synthesis via α-Benzotriazolyl Ketones

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Abstract: Reaction of α-benzotriazolyl ketones with α,β-unsaturated ketones resulted in 2,4,6-triarylpyridines, 2,4-diaryl-5*H*-indeno[1,2-*b*]pyridines and 2,4-diaryl-5,6-dihydrobenzo[*h*]quinolines in good yields.

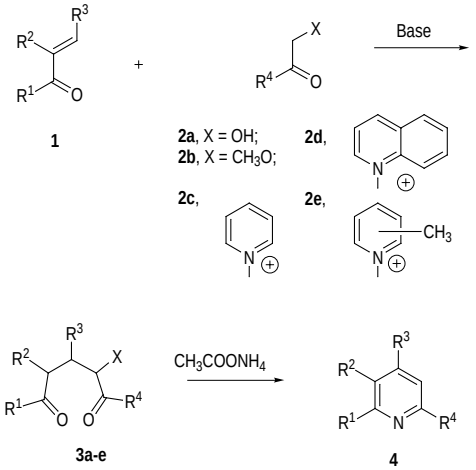
Key words: α-benzotriazolyl ketones, synthesis, 2,4,6-triarylpyridines, 2,4-diaryl-5*H*-indeno[1,2-*b*]pyridines, 2,4-diaryl-5,6-dihydrobenzo[*h*]quinolines

2,4,6-Trisubstituted pyridines are important because of their biological activity[1] and optical[2,3] (fluorescence and scintillation) properties. Their quaternary salts have synthetic applications.[4,5] The enormous number of preparative approaches proposed for 2,4,6-triarylpyridines includes (i) [5+1] type ring annulations from a nitrogen derivative and a five-carbon fragment, usually a 1,5-diketone,[6] (ii) [2+2+2] type reactions of substituted acetylenes and nitriles,[7] (iii) [3+3] cyclizations of chalcones and iminophosphoranes,[8] (iv) [4+2] reactions of unsaturated imines with enolates,[9] (v) [2+2+1+1] Hantzsch synthesis of polysubstituted, usually 4-aryl-3,5-alkoxycarbonylpyridines,[10,11] (vi) [3+2+1] approaches (see below).

Methods (i) and (v) are analogous in that they require the oxidation of dihydro intermediates.[6] Route (ii) is based on the cobalt(I) catalyzed cyclization of alkyl(aryl)alkynes and nitriles, and can give mixtures of 4- and 5-substituted products as well as trisubstituted benzenes as byproducts.[7] Methods (iii) and (iv) require the preparation of imine starting materials. The well-known synthesis from chalcones via pyrylium salts[12,13] is used especially for symmetrical 2,6-substituted pyridines, but yields are moderate and limited by reversal of the aldol reaction step.[14] Among approaches (i–vi), type (vi) is that most frequently employed.

The many [3+2+1] annulation reactions which produce 2,4,6-trisubstituted pyridines include the base-promoted Michael addition of α,β-unsaturated compounds **1** to ketones or their α-substituted derivatives **2** with the formation of five-carbon intermediates **3** (Scheme 1). The efficiency of such pyridine ring closures depends on the nature of α-substituent X in the ketone moiety, which performs as a leaving group in the aromatization process. Thus, the standard acetic acid/ammonium acetate treatment of a 4-hydroxy-substituted intermediate **3a** yields a mixture 2,4,6-triphenylpyridine (**4**) and its 3-amino derivative, with the latter as the major product,[15] while the utilization of α-methoxyacetophenone (**2b**) results in **3b** in 61% yield and the corresponding **4** in 60% yield.[16]

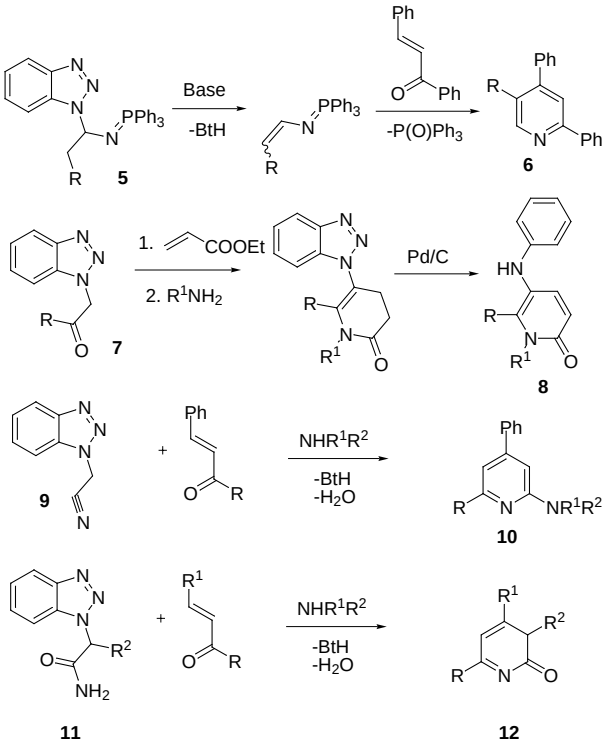
Usually, Kröhnke synthesis via α,β-unsaturated ketones and *N*-phenacyl-pyridinium,[17] -quinolinium[18] and -picolinium[19] salts (**2c–e**) gives 40–92% yields of a variety of polysubstituted pyridines. However, in the case of 4-aryl-2-oxobut-3-enoic acids (R^1 = COOH, R^3 = Ar) the yields were 40–77%, and 1,2,3-triphenylprop-2-en-1-one (R^2 = Ph) afforded the corresponding tetrasubstituted pyridine in 25% yield.[17] Moreover, while this reaction sequence works well for phenacetyl derivatives, it could not be extended to α-substituted ketones in general.[17] The instability of *N*-phenacylpyridinium salts in strongly basic media does not allow modification of such reagents with electrophiles and limits the method to compounds with an $ArCOCH_2$ unit as the principal building block.



Scheme 1

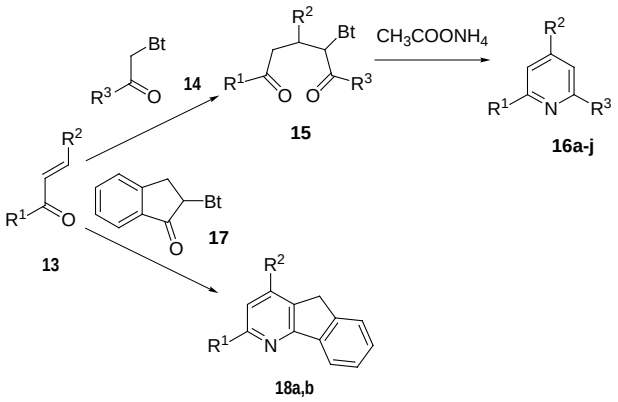
We previously reported 1-[α-(phosphoranylideneamino)alkyl]benzotriazole **5** mediated [3+3][20] and α-benzotriazolyl ketone **7** [3+2+1][21] pyridine ring annulations (Scheme 2), which lead to products **6** and **8**. Our recent study of [3+3] pyridine ring formation via α-benzotriazolylacetonitrile **9** and α-benzotriazolylacylamides **11** and α,β-unsaturated ketones[22] afforded the previously difficult to attain 3-unsubstituted 2-(dialkylamino)pyridines **10** and 2-pyridones **12**. We now report the reaction of α-benzotriazolyl ketones with α,β-unsaturated ketones as a

versatile [3+2+1] synthesis of 2,4,6-trisubstituted pyridines (Scheme 3).

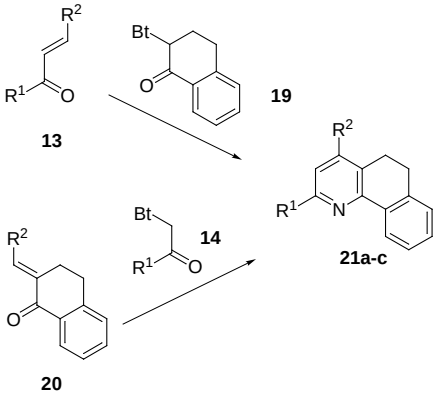


Scheme 2

α-Benzotriazolyl ketones **14**, **17**, and **19** were readily synthesized starting from *N*-chlorobenzotriazole and trimethylsilyl derivatives of corresponding ketones according to a procedure recently elaborated in our group.[23] Subsequent reaction with commercially available chalcones and ammonium acetate in acetic acid under reflux afforded corresponding 2,4,6-trisubstituted pyridines **16a–h** in high yields (Table). Although in the case of unsubstituted triphenylpyridine **16a** the isolated yield was lower, our approach gave us improved yields of previously synthesized products **16c,d,g** and provided novel pyridines **16e,f,h–j** in high yields.



Scheme 3



Scheme 4

2-(1*H*-1,2,3-Benzotriazol-1-yl)indan-1-one **17** gave good yields of the corresponding 2,4-diphenyl-5*H*-indeno[1,2-*b*]pyridines **18a,b**. 2,4-Diphenyl-5,6-dihydroben-

Table 2,4,6-Triarylpyridines **16**, 2,4-Diphenyl-5*H*-indeno[1,2-*b*]pyridines **18**, and 2,4-Diphenyl-5,6-dihydrobenzo[*h*]quinolines **21**

	R^1	R^2	R^3	Yield (%)	Lit. Yield (%)
16a	Ph	Ph	Ph	81	92[17]
16b	Ph	Ph	*p*-MeC_6H_4	78	70[24]
16c	Ph	Ph	*p*-$MeOC_6H_4$	71	55[25]
16d	Ph	Ph	*p*-BrC_6H_4	84	55[18]
16e	Ph	*p*-ClC_6H_4	*p*-MeC_6H_4	75	-
16f	*p*-BrC_6H_4	*p*-MeC_6H_4	*p*-$MeOC_6H_4$	85	-
16g	Ph	*p*-ClC_6H_4	*p*-ClC_6H_4	80	60[19]
16h	*p*-BrC_6H_4	3,4-$(OCH_2O)C_6H_4$	*p*-MeC_6H_4	83	-
16i	2-naphthyl	3,4-$(OCH_2O)C_6H_4$	*p*-MeC_6H_4	87	-
16j	2-naphthyl	*p*-$NO_2C_6H_4$	Ph	62	-
18a	Ph	Ph	-	77	88[27]
18b	*p*-BrC_6H_4	*p*-$MeOC_6H_4$	-	72	-
21a	Ph	Ph	-	55	60[17]
21b	*p*-BrC_6H_4	*p*-MeC_6H_4	-	77	-
21c	Ph	*p*-ClC_6H_4	-	57	-

zo[*h*]quinolines **21a–c** were synthesized using two synthetic approaches (Scheme 4). Both of them, i.e. starting from α-benzotriazolylacetophenones **14** and 2-(1*H*-1,2,3-benzotriazol-1-yl)-3,4-dihydronaphthalen-1(2*H*)-one **19**, led to desired products **21a–c** in good yields (Table). Thus, the extension of α-phenacetyl mediated methodology[17] to α-substituted ketones in general was achieved. We believe that the reaction mechanism involves initial formation of intermediate 2-benzotriazolyl 1,5-diketone **15**, further reaction with ammonia and elimination of the benzotriazole moiety to result in the desired annulation product. Thus, in a separate experiment under mild conditions (THF, –78 °C, BuLi) in the absence of an ammonia precursor, the intermediate 2-(benzotriazol-1-yl)-1,3,5-triphenylpentane-1,5-dione (**15**, $R^1 = R^2 = R^3$ = Ph) was isolated in 74% yield.

Mps were measured with a Kofler hot stage apparatus without correction. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini (300 MHz) spectrometer in $CDCl_3$ with TMS as the internal standard. Elemental analyses were performed using a Carlo Erba 1106 elemental analyzer.

2-(Benzotriazol-1-yl)-1,3,5-triphenylpentane-1,5-dione (15, $R^1 = R^2 = R^3$ = Ph)

Under a N_2 atmosphere, 1.6 M BuLi in hexane (1.63 mL, 2.6 mmol) was added to a solution of 2-benzotriazol-1-ylacetophenone (0.47 g, 2 mmol) in dry THF at –78 °C. Benzalacetophenone (0.41 g, 2 mmol) was added dropwise and the mixture was stirred for 12 h while the temperature was allowed to rise to r.t. The mixture was quenched with water (50 mL) and extracted with CH_2Cl_2 (2 × 30 mL). The combined organics were dried ($MgSO_4$). The solvent was removed under reduced pressure to give crude product, which was recrystallized from MeOH to give **15** as microcrystals; yield: 0.66 g (74%); mp 177–179 °C.

^{1}H NMR: δ = 8.13 (d, 2H, *J* = 7.6 Hz), 7.93 (d, 1H, *J* = 7.5 Hz), 7.86 (d, 2H, *J* = 8.5 Hz), 7.59–7.00 (m, 15H), 4.92–4.85 (m, 1H), 3.62 (d, 2H, *J* = 6.5 Hz).

^{13}C NMR: δ = 197.5, 192.6, 146.0, 138.2, 136.7, 135.0, 134.2, 133.2, 132.2, 128.9, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 128.0, 127.8, 127.5, 127.3, 123.8, 119.8, 111.0, 66.4, 41.7, 41.2.

$C_{29}H_{23}N_3O_2$	calcd	N	9.43
(445.52)	found		9.42

Synthesis of 2,4,6-Triarylpyridines 16, 2,4-Diaryl-5*H*-indeno[1,2-*b*]pyridines 18, and 2,4-Diaryl-5,6-dihydrobenzo[*h*]quinolines 21; General Procedure

A solution of corresponding α-(benzotriazol-1-yl) ketone **14**, **17**, or **19** (3 mmol), corresponding chalcone (3 mmol) and ammonium acetate (3 g) in glacial HOAc (4 mL) was refluxed for 30 h. After addition of ice water (50 mL), the precipitate was separated and purified by column chromatography (silica gel, $CHCl_3$/hexanes 2:1) or by recrystallization from hexanes to give products **16a–j**, **18a,b** and **21a–c**.

2,4,6-Triphenylpyridine (16a)

Needles; yield: 0.75 g (81%); mp 129–131 °C (Lit.[17] mp 137–138 °C).

^{1}H NMR: δ = 8.25 (d, 4H, *J* = 8.5 Hz), 7.92 (s, 2H), 7.89–7.76 (m, 2H), 7.58–7.45 (m, 9H).

^{13}C NMR: δ = 157.5, 150.2, 139.6, 139.1, 129.1, 129.0, 128.7, 127.1, 117.1.

$C_{23}H_{17}N_1$	calcd	N	4.56
(307.14)	found		4.56

2-(4-Methylphenyl)-4,6-diphenylpyridine (16b)

Needles; yield: 0.75 g (78%); mp 133–135 °C (Lit.[24] mp 124–125 °C).

^{1}H NMR: δ = 8.22 (d, 2H, *J* = 7.1 Hz), 8.13 (d, 2H, *J* = 8.0 Hz), 7.89 (s, 2H), 7.75 (d, 2H, *J* = 6.9 Hz), 7.55–7.43 (m, 6H), 7.33 (d, 2H, *J* = 8.0 Hz), 2.44 (s, 3H).

^{13}C NMR: δ = 157.4, 150.1, 139.7, 139.0, 129.4, 129.1, 129.0, 128.9, 128.7, 127.2, 127.1, 127.0, 117.1, 116.8, 21.3.

$C_{24}H_{19}N$	calcd	C	89.68	H	5.96	N	4.36
(321.41)	found		89.91		6.12		4.46

2-(4-Methoxyphenyl)-4,6-diphenylpyridine (16c)

Needles; yield: 0.72 g (71%); mp 99–101 °C (Lit.[25] mp 105–107 °C).

^{1}H NMR: δ = 8.21 (d, 2H, *J* = 7.4 Hz), 8.19 (d, 2H, *J* = 8.8 Hz), 7.84 (s, 2H), 7.75 (d, 2H, *J* = 7.1 Hz), 7.55–7.45 (m, 6H), 7.05 (d, 2H, *J* = 8.7 Hz), 3.89 (s, 3H).

^{13}C NMR: δ = 160.5, 157.3, 157.1, 150.1, 139.7, 139.2, 132.2, 129.0, 128.9, 128.6, 128.4, 127.1, 116.4, 116.3, 114.0, 55.3.

$C_{24}H_{19}NO$	calcd	C	85.43	H	5.68	N	4.15
(337.15)	found		85.16		5.76		4.20

2-(4-Bromophenyl)-4,6-diphenylpyridine (16d)

Needles; yield: 0.97 g (84%); mp 150–152 °C (Lit.[18] mp 152–153 °C).

^{1}H NMR: δ = 8.19 (d, 2H, *J* = 7.1 Hz), 8.08 (d, 2H, *J* = 8.5 Hz), 7.89 (s, 1H), 7.84 (s, 1H), 7.73 (d, 2H, *J* = 6.8 Hz), 7.64 (d, 2H, *J* = 8.5 Hz), 7.56–7.46 (m, 6H).

^{13}C NMR: δ = 157.6, 156.2, 150.3, 139.4, 138.8, 138.4, 131.8, 129.1, 129.0, 128.7, 127.1, 123.5, 117.4, 116.8.

$C_{23}H_{16}BrN$	calcd	C	71.50	H	4.17	N	3.63
(386.29)	found		71.34		4.23		3.63

4-(4-Chlorophenyl)-2-(4-methylphenyl)-6-phenylpyridine (16e)

Needles; yield: 0.80 g (75%); mp 120–122 °C.

^{1}H NMR: δ = 8.18 (d, 2H, *J* = 7.1 Hz), 8.08 (d, 2H, *J* = 8.2 Hz), 7.79 (s, 1H), 7.78 (s, 1H), 7.64 (d, 2H, *J* = 8.5 Hz), 7.53–7.42 (m, 5H), 7.31 (d, 2H, *J* = 8.0 Hz), 2.43 (s, 3H).

^{13}C NMR: δ = 157.6, 148.8, 139.5, 139.2, 137.6, 136.6, 135.1, 129.5, 129.3, 129.2, 129.1, 128.7, 128.5, 128.4, 127.1, 127.0, 116.8, 116.4, 21.3.

$C_{24}H_{18}ClN$	calcd	C	81.10	H	5.11	N	3.94
(355.11)	found		81.10		5.24		3.99

2-(4-Bromophenyl)-6-(4-methoxyphenyl)-4-(4-methylphenyl)pyridine (16f)

Plates; yield: 1.1 g (85%); mp 167–169 °C.

^{1}H NMR: δ = 8.13 (d, 2H, *J* = 8.3 Hz), 8.06 (d, 2H, *J* = 8.2 Hz), 7.81 (s, 1H), 7.76 (s, 1H), 7.62 (d, 4H, *J* = 8.0 Hz), 7.32 (d, 2H, *J* = 7.7 Hz), 7.03 (d, 2H, *J* = 8.3 Hz), 3.88 (s, 3H), 2.44 (s, 3H).

^{13}C NMR: δ = 160.6, 157.1, 156.0, 150.0, 139.1, 138.6, 136.0, 132.0, 131.7, 129.8, 128.6, 128.3, 126.9, 123.3, 116.3, 115.9, 114.0, 55.4, 21.3.

$C_{25}H_{20}BrNO$	calcd	C	69.77	H	4.68	N	3.25
(430.35)	found		69.58		4.47		3.26

2,4-Bis(4-chlorophenyl)-6-phenylpyridine (16g)

Plates; yield: 0.90 g (80%); mp 140–142 °C (Lit.[19] mp 136–137 °C).

^{1}H NMR: δ = 8.13 (dd, 4H, *J* = 7.9, 8.5 Hz), 7.80 (s, 1H), 7.74 (s, 1H), 7.62 (d, 2H, *J* = 8.2 Hz), 7.52–7.44 (m, 7H).

^{13}C NMR: δ = 157.7, 156.3, 149.0, 139.1, 137.7, 137.2, 135.3, 135.3, 129.3, 129.2, 128.9, 128.8, 128.4, 128.3, 127.1, 117.0, 116.4.

$C_{23}H_{15}Cl_2N$	calcd	C	73.35	H	3.97	N	3.72
(376.29)	found		72.94		3.88		3.69

4-(1,3-Benzodioxol-5-yl)-2-(4-bromophenyl)-6-(4-methylphenyl)pyridine (16h)
Plates ; yield: 1.1 g (83%); mp 160–162 °C (Lit.[26] mp 178–181 °C).

^{1}H NMR: δ = 8.06–8.02 (dd, 4H, *J* = 2.8, 3.2 Hz), 7.75 (s, 1H), 7.69 (s, 1H), 7.60 (d, 2H, *J* = 8.2 Hz), 7.30 (d, 2H, *J* = 8.0 Hz), 7.20–7.16 (m, 2H), 6.92 (d, 1H), 6.02 (s, 2H), 2.42 (s, 3H).

^{13}C NMR: δ = 157.5, 156.0, 149.7, 148.5, 139.1, 138.5, 136.5, 133.0, 131.7, 129.4, 129.3, 128.6, 126.9, 123.4, 121.0, 116.6, 116.0, 108.8, 107.4, 101.5, 21.3.

$C_{25}H_{18}BrNO_2$	calcd	C	67.58	H	4.08	N	3.15
(444.33)	found		67.66		4.01		3.14

4-(1,3-Benzodioxol-5-yl)-2-(2-naphthyl)-6-(4-methylphenyl)pyridine (16i)
Plates; yield: 1.08 g (87%); mp 161–163 °C.

^{1}H NMR: δ = 8.62 (s, 1H), 8.34 (d, 1H, *J* = 8.6 Hz), 8.11 (d, 2H, *J* = 8.0 Hz), 7.99–7.94 (m, 2H), 7.90–7.86 (m, 2H), 7.78 (s, 1H), 7.50 (t, 2H, *J* = 4.6 Hz), 7.32 (d, 2H, *J* = 8.0 Hz), 7.23 (s, 1H), 7.23 (s, 1H), 6.94 (d, 1H, *J* = 7.8 Hz), 6.02 (s, 2H), 2.43 (s, 3H).

^{13}C NMR: δ = 157.6, 157.2, 149.6, 148.5, 148.4, 139.0, 137.0, 136.8, 133.7, 133.5, 133.2, 129.4, 128.7, 128.3, 127.7, 127.0, 126.4, 126.2, 124.9, 121.1, 116.7, 116.5, 108.8, 107.5, 101.5, 21.3.

$C_{29}H_{21}NO_2$	calcd	C	83.83	H	5.09	N	3.37
(415.50)	found		83.56		5.11		3.35

2-(2-Naphthyl)-4-(4-nitrophenyl)-6-phenylpyridine (16j)
Plates; yield: 0.75 g (62%); mp 183–184 °C.

^{1}H NMR: δ = 8.66 (s, 1H), 8.38 (t, 3H, *J* = 8.8 Hz), 8.24 (d, 2H, *J* = 7.1 Hz), 8.01 (s, 2H), 7.99 (d, 1H, *J* = 9.9 Hz), 7.94–7.89 (m, 4H), 7.59–7.47 (m, 5H), 7.26 (s, 1H).

^{13}C NMR: δ = 156.9, 156.7, 147.9, 147.4, 144.2, 138.6, 135.9, 133.5, 133.1, 129.5, 128.9, 128.9, 128.7, 128.3, 127.7, 127.1, 126.9, 126.6, 126.5, 124.7, 124.1, 117.3, 117.1.

$C_{27}H_{18}N_2O_2$	calcd	N	6.96
(402.46)	found		6.97

2,4-Diphenyl-5*H*-indeno[1,2-*b*]pyridine (18a)
Microcrystals; yield: 0.74 g (77%); mp 157–159 °C (Lit.[27] mp 156 °C).

^{1}H NMR: δ = 8.29 (d, 1H, *J* = 7.4 Hz), 8.21 (d, 2H, *J* = 7.2 Hz), 7.90–7.42 (m, 12H), 4.01 (s, 2H).

^{13}C NMR: δ = 161.1, 157.1, 146.3, 144.1, 141.2, 139.9, 138.9, 132.8, 128.8, 128.7, 128.5, 128.2, 127.1, 124.9, 121.4, 118.1, 34.4.

$C_{24}H_{17}N$	calcd	C	90.24	H	5.37	N	4.39
(319.40)	found		90.46		5.37		4.45

2-(4-Bromophenyl)-4-(4-methoxyphenyl)-5*H*-indeno[1,2-*b*]pyridine (18b)
Prisms; yield: 0.93 g (72%); mp 134–136 °C.

^{1}H NMR: δ = 8.20 (d, 1H, *J* = 7.3 Hz), 8.02 (d, 2H, *J* = 7.0 Hz), 7.61–7.37 (m, 8H), 7.03 (d, 2H, *J* = 6.9 Hz), 3.92 (s, 2H), 3.88 (s, 3H).

^{13}C NMR: δ = 161.1, 159.9, 155.6, 145.9, 144.0, 141.0, 138.7, 132.9, 131.7, 130.8, 129.4, 128.7, 128.6, 127.1, 124.9, 123.0, 121.2, 117.4, 114.2, 55.4, 34.5.

$C_{25}H_{18}BrNO$	calcd	C	70.10	H	4.24	N	3.27
(428.33)	found		70.05		4.16		3.24

2,4-Diphenyl-5,6-dihydrobenzo[*h*]quinoline (21a)
Prisms; yield: 0.55 g (55%); mp 121–123 °C.

^{1}H NMR: δ = 8.58 (d, 1H, *J* = 7.7 Hz), 8.18 (d, 2H, *J* = 8.1 Hz), 7.59 (s, 1H), 7.51–7.39 (m, 8H), 7.33 (t, 1H, *J* = 7.4 Hz), 7.23 (s, 1H), 7.21(t, 1H, *J* = 7.4 Hz), 2.96–2.92 (m, 2H), 2.88–2.82 (m, 2H).

^{13}C NMR: δ = 154.4, 152.6, 149.2, 139.6, 139.4, 138.2 135.2, 129.0, 128.8, 128.7, 128.6, 128.5, 128.0, 127.9, 127.6, 127.1, 126.8, 125.7, 119.9, 28.2, 25.3.

$C_{25}H_{19}N$	calcd	N	4.20
(333.44)	found		4.14

2-(4-Bromophenyl)-4-(4-methylphenyl)-5,6-dihydrobenzo-[*h*]quinoline (21b)
Prisms; yield: 0.98 g (77%); mp 170–172 °C.

^{1}H NMR: δ = 8.54 (d, 1H, *J* = 7.3 Hz), 8.05 (d, 2H, *J* = 8.4 Hz), 7.59 (d, 2H, *J* = 8.2 Hz), 7.54 (s, 1H), 7.43–7.21 (m, 7H), 2.93–2.91 (m, 2H), 2.86–2.84 (m, 2H), 2.44 (s, 3H).

^{13}C NMR: δ = 153.1, 152.6, 149.4, 138.5, 138.2, 138.0, 136.1, 135.0, 131.7, 129.2, 128.7, 128.6, 128.3, 127.5, 127.0, 125.6, 123.0, 119.6, 28.1, 25.3, 21.3.

$C_{25}H_{19}N$	calcd	N	3.29
(426.36)	found		3.25

4-(4-Chlorophenyl)-2-phenyl-5,6-dihydrobenzo[*h*]quinoline (21c)
Prisms; yield: 0.63 g (57%); mp 130–131 °C.

^{1}H NMR: δ = 8.57 (d, 1H, *J* = 7.5 Hz), 8.16 (d, 2H, *J* = 7.4 Hz), 7.53 (s, 1H), 7.50–7.38 (m, 7H), 7.33 (s, 1H), 7.32 (d, 1H, *J* = 8.3 Hz), 7.22 (s, 1H), 7.21 (d, 1H, *J* = 7.8 Hz), 2.90–2.79 (m, 4H).

^{13}C NMR: δ = 154.4, 152.6, 149.2, 139.6, 139.3, 138.2, 135.2, 129.0, 128.8, 128.7, 128.6, 128.5, 128.0, 127.9, 127.5, 127.1, 126.8, 125.7, 119.9, 28.2, 25.3.

$C_{25}H_{18}ClN$	calcd	C	81.62	H	4.93	N	3.81
	found		81.49		4.96		3.75

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