Tetrahedron Letters 52 (2011) 2642–2644

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

A convenient Fischer indole synthesis of 2,3′-biindoles

Philip E. Alford, Liangfeng Fu, Joseph K. Kubert, Lingshan Wang, Gordon W. Gribble *

Department of Chemistry, Dartmouth College, Hanover, NH 03755, USA

ARTICLE INFO

Article history:
Received 25 February 2011
Accepted 9 March 2011

ABSTRACT

Both symmetrical and unsymmetrical 2,3′-biindoles are efficiently synthesized in good to excellent yields by Fischer indole synthesis. The scope of the method was evaluated by examining substituent effects with *para*-substituted hydrazines and 3-acylindoles.

The Fischer indole synthesis, first described by Emil Fischer in 1883, has prevailed as the flagship indolization method for more than a century.[1] Given our recent interest in the synthesis of bipyrroles and biindole natural products, we were surprised to find that the present method has apparently not been investigated as a general approach to 2,3′-biindoles.[2] Biindole natural products are ubiquitous and have a strong history of medicinal value.[3] The vast majority of these compounds exhibit a 2,2′-linkage, notably the numerous naturally occurring indolocarbazoles and related derivatives.[4] In contrast, 2,3′-biindoles, inaccessible from typical bioorganic building blocks, are relatively underrepresented in nature.[5]

Indirubin (**1**), isolated from *Isatis indigotin*, is the biologically active component of the traditional Chinese preparation *Danggui Longhui Wan*.[6] It has been noted that indolocarbazoles bearing a 2,3′-biindole are angular equivalents to medicinally active 2,2′-linked structures and members of the remarkably bioactive [*b*]-annulated carbazole family.[7] Ancorinazole (**2**), isolated in 2002, is the first naturally occurring indolocarbazole to contain a 2,3′-biindole (Fig. 1).[8] In supramolecular chemistry progress with anion sensing molecular devices has celebrated biindoles as some of the few structures that have found success in this application.[9]

Few general synthetic methods have been described for 2,3′-biindoles.[10] Acid-catalyzed dimerization of indole is a well known source of the indole dimer **4** which may be dehydrogenated to furnish the parent 2,3′-biindole **5** (Scheme 1).[11] Though limited to the preparation of symmetrical biindoles, this method has been widely used.[12] A related method uses 3-bromoindole to produce **5** in one step.[13] While this improved process (Scheme 2) allows the preparation of asymmetric 2,3′-biindoles **8** in good to excellent yields, a tendency for 3-bromoindole to self-condense and the competitive production of several types of indole oligomers can result in problematic reaction conditions.[14]

Young et al. described a route to 5,6-dialkoxy-2,3′-biindoles **10** via *ortho*-nitration of a 3-(phenylacetyl)indole **9** followed by reductive cyclization (Scheme 3).[15] Unfortunately, this specialized route relies on the presence of both alkoxy-substituents.

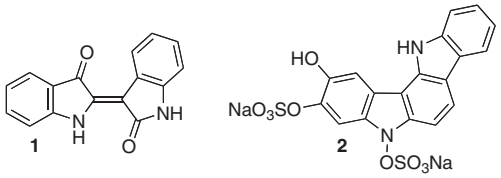
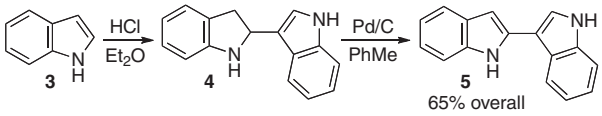
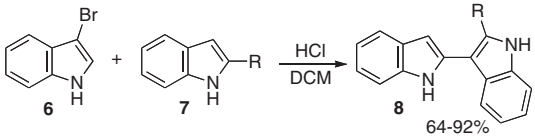


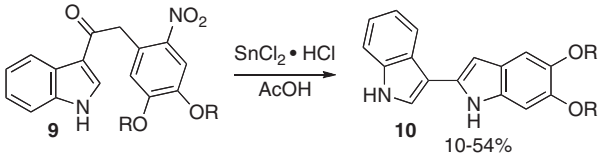
Figure 1. Biindole natural products.



Scheme 1. Preparation of **5** via the indole dimer.



Scheme 2. One-step indole dimerization to asymmetric **8**.



Scheme 3. Reductive-cyclization to 5,6-disubstituted **10**.

* Corresponding author. Tel.: +1 603 646 3118; fax: +1 603 646 3946.
E-mail address: ggribble@dartmouth.edu (G.W. Gribble).

0040-4039/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2011.03.049

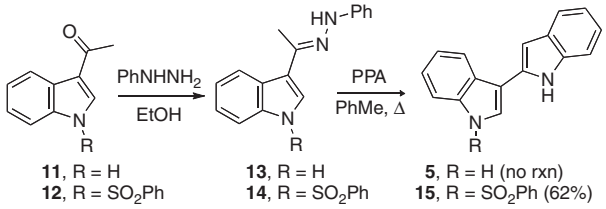
Palladium-catalyzed cross-coupling has also been used to produce 2,3′-biindoles.[16]

Intrigued by the absence of a general Fischer method, we examined the indolization of readily available 3-acetylindole **11** and 3-acetyl-1-(phenylsulfonyl)indole **12**.

In the event, acid-catalyzed generation of the desired hydrazones was complete by TLC and NMR, and these hydrazones were used directly in the next step (Scheme 4). Since the neighboring indole moiety seems to facilitate hydrolysis of the resulting hydrazone, anhydrous conditions were necessary. From the protected hydrazone **14**, neat PPA cleanly generated the corresponding 2,3′-biindole **15** in good yield, which was deprotected with aqueous hydroxide to the parent compound **5**, spectroscopically identical to a sample prepared via indole dimerization (Scheme 1). Direct conversion of the unprotected hydrazone **13** to the parent 2,3′-biindole was not successful under these conditions.[17]

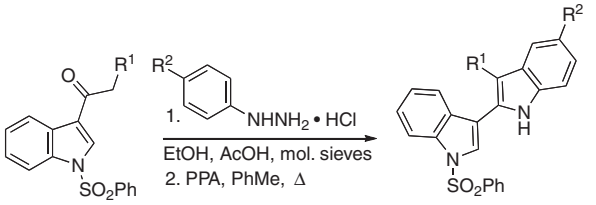
To explore the generality of this method, we investigated the effect of substituents at the *para*-position of the hydrazine and the α-position of the starting ketone. Hydrazone formation was performed over molecular sieves and indolizations were conducted with PPA in toluene in the usual manner to produce 2,3′-biindoles (Table 1).[18–33]

In each case where *para*-nitrophenylhydrazine was used, the resulting hydrazones **23**–**25** (not shown) resisted indolization. These stable nitro-substituted hydrazones are deactivated toward the protonation that precedes both hydrolysis and tautomerization, thus allowing them to survive chromatography. The stability of these compounds highlights the importance of hydrazone tautomerization to the corresponding ene-hydrazine for indolization.



Scheme 4. A Fischer indole approach to 2,3′-biindole.

Table 1
Synthesis of substituted 2,3′-biindoles **15**–**22**



Entry	R^1	R^2	Product	Yield[a]
1	H	H	**15**	62
2	H	F	**16**	68
3	H	NO_2	**23**	0/78[b]
4	Me	H	**17**	83
5	Me	F	**18**	76
6	Me	NO_2	**24**	0/58[b]
7	Ph	H	**19**	86
8	Ph	F	**20**	91
9	Ph	NO_2	**25**	0/77[b]
10	Ph	Me	**21**	91
11	Ph	MeO	**22**	92

[a] Yields after column chromatography.
[b] Yield of recovered hydrazone.

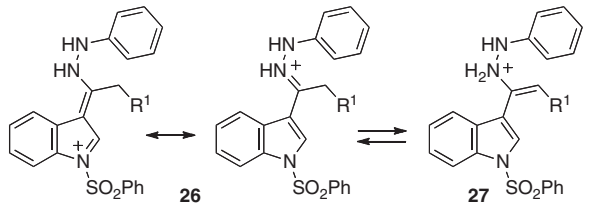


Figure 2. Stabilization and tautomerization of hydrazone **26**.

It might be noted that the intermediate hydrazone (e.g., **26**) can be considered a vinylogous amidrazone in which the positive charge resulting from protonation is resonance stabilized by the indole double bond. Although this stabilized species is still capable of hydrolysis, indolization requires tautomerization to the ene-hydrazine **27**—a tautomer that lacks the advantage of a delocalized cation (Fig. 2). We suspect that this effect is amplified in the case of the unprotected hydrazone **13**.

Since many Fischer indole syntheses are known to be rate limiting at tautomerization,[1] we suggest that substrates favoring formation of the ene-hydrazine will show improved indolization. An α-phenyl substituent provides a major driving force for this tautomerization via conjugative stabilization of the ene-hydrazine—an effect that results in substantially improved yields. While hydrazines with electron-donating substituents were problematic with the acetyl and propionyl substrates, phenylacetyl-substituted hydrazines (entries 10 and 11) give excellent results.

In conclusion, a convenient Fischer indole synthesis employing 3-acylindoles and phenylhydrazines affords 2,3′-biindoles in good to excellent yields.

Acknowledgments

This work was supported by the Donors of the Petroleum Research Fund (PRF), administered by the American Chemical Society, and by Wyeth.

References and notes

1. Robinson, B. *The Fischer Indole Synthesis*; Wiley: New York, 1982.
2. Fu, L.; Gribble, G. W. *Tetrahedron Lett.* **2008**, *49*, 7352–7354; Fu, L.; Gribble, G. W. *Org. Prep. Proced. Int.* **2008**, *40*, 561–566; Fu, L.; Gribble, G. W. *Tetrahedron Lett.* **2008**, *49*, 3545–3548; Gribble, G. W.; Berthel, S. J. *Tetrahedron* **1992**, *48*, 8869–8880; Roy, S.; Eastman, A.; Gribble, G. W. *Synth. Commun.* **2005**, *35*, 595–601.
3. Hibino, S.; Choshi, T. *Nat. Prod. Rev.* **2001**, *18*, 66–87; Sánchez, C.; Méndez, C.; Salas, J. A. *Nat. Prod. Rev.* **2006**, *23*, 1007–1045.
4. Cordell, G. A. *The Alkaloids, Chemistry and Biology*; Academic Press: Amsterdam, The Netherlands, 2008. Vol. 65; Gribble, G. W.; Berthel, S. J. *Studies in Natural Products Chemistry, Vol. 12*; Elsevier: Amsterdam, The Netherlands, 1993. 365.
5. Ryan, K. S.; Drennan, C. L. *Chem. Biol.* **2009**, *16*, 351–364.
6. Hoessel, R.; Leclerc, S.; Endicott, J. A.; Nobel, M. E. M.; Lawrie, A.; Tunnah, P.; Leost, M.; Damiens, E.; Marie, D.; Marko, D.; Niederberger, E.; Tang, W.; Eisenbrand, G.; Meijer, L. *Nat. Cell Biol.* **1999**, *1*, 60–67; Leclerc, S.; Garnier, M.; Hoessel, R.; Marko, D.; Bibb, J. A.; Snyder, G. L.; Greengard, P.; Biernat, J.; Wu, Y.-Z.; Mandelkow, E.-M.; Eisenbrand, G.; Meijer, L. *J. Biol. Chem.* **2001**, *276*, 251–260; Eisenbrand, G.; Hippe, F.; Jakobs, S.; Muehlbeyer, S. *J. Cancer Res. Clin. Oncol.* **2004**, *130*, 627–635.
7. Bergman, J.; Desarbre, E.; Koch, E. *Tetrahedron* **1996**, *55*, 2363–2370; Janosik, T.; Bergman, J. *Tetrahedron* **1999**, *55*, 2371–2380; Tsuchimoto, T.; Matsubayashi, H.; Kaneko, M.; Nagase, Y.; Miyamura, T.; Shirakawa, E. *J. Am. Chem. Soc.* **2008**, *130*, 15823–15835.
8. Meragelman, K. M.; West, L. M.; Northcote, P. T.; Pannel, L. K.; McKee, T. C.; Boyd, M. R. *J. Org. Chem.* **2002**, *67*, 6671–6677.
9. Gale, P. A. *Chem. Commun.* **2008**, 4525–4540.
10. Bocchi, V.; Palla, G. *J. Chem. Soc., Chem. Commun.* **1983**, 1074–1075; Bergman, J. *J. Heterocycl. Chem.* **1973**, *10*, 121–122.
11. Smith, G. F. *Adv. Heterocycl. Chem.* **1963**, *2*, 287–309.
12. Scmitz-Dumont, O.; Nicolojannis, B. *Chem. Ber.* **1930**, *63*, 323–328; Wahlström, N.; Slätt, J.; Stensland, B.; Ertan, A.; Bergman, J.; Janosik, T. *J. Org. Chem.* **2007**, *72*, 5886–5889.
13. Bocchi, V.; Palla, G. *Tetrahedron* **1984**, *40*, 3251–3256; Bocchi, V.; Palla, G. *J. Chem. Soc., Chem. Commun.* **1983**, 1074–1075.

14. Bocchi, V.; Palla, G. *Tetrahedron* **1986**, *42*, 5019–5024.
15. Young, T. E. *J. Org. Chem.* **1962**, *27*, 507–510; Young, T. E.; Mizianty, M. F. *J. Org. Chem.* **1964**, *29*, 2030–2031.
16. Liang, Z.; Zhao, J.; Zhang, Y. *J. Org. Chem.* **2010**, *75*, 170–171.
17. This transformation has previously been reported as successful, though the melting point and spectroscopic characteristics of the resulting compound did not closely match 2,3′-biindole Shukri, J.; Al-Azawe, S.; Al-Tai, A. S. *J. Indian Chem. Soc.* **1970**, *47*, 123–124; Al-Azawe, S.; Sarkis, G. Y. *J. Chem. Eng. Data* **1973**, *18*, 109–111.
18. *Representative procedure*: A solution of phenylhydrazine hydrochloride (75 mg, 0.52 mmol), 3-acetyl-1-(phenylsulfonyl)indole (150 mg, 0.5 mmol), and acetic acid (3 drops, 0.15 mL) in anhydrous ethanol (2 mL) over molecular sieves (3 Å) was brought to reflux for 2 h and monitored by TLC. When conversion to **14** was complete, after 8 h, the solvent was removed by rotary evaporation. Toluene (3 mL) and PPA (1 mL) was added without removing molecular sieves and the reaction mixture was brought to reflux and monitored by TLC. After 3 h, TLC showed complete conversion. The reaction mixture was neutralized using sat aq sodium bicarbonate solution, extracted with DCM, washed with brine, dried over sodium sulfate, and concentrated in vacuo. The resulting brown oil was purified by column chromatography over silica gel (1:1 hexanes/DCM) to produce product **15** as a solid (116 mg, 62%).
19. *3-(Phenylacetyl)-1-(phenylsulfonyl)indole*: white solid; mp 104–105 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, J = 7.0 Hz, 1H), 8.25 (s, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 6.6 Hz, 2H), 7.57–7.61 (m, 1H), 7.45–7.49 (m, 2H), 7.29–7.39 (m, 7H), 4.21 (s, 2H); ^{13}C NMR, (500 MHz, $CDCl_3$) δ 193.6, 137.6, 125.1, 134.9, 134.8, 132.6, 129.9, 129.6, 129.0, 128.1, 127.3, 127.3, 1276.2, 125.3, 123.5, 121.1, 113.3, 47.6; HRMS: m/z Calcd for $C_{22}H_{16}O_2N_2S$: 375.0929. Found: 375.0919.
20. *1′-(Phenylsulfonyl)-2,3′-biindole* (**15**), 62%: yellow solid; mp 165–166 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (br s, 1H), 8.09 (m, 1H), 7.94–7.97 (m, 3H), 7.86 (m, 1H), 7.67 (m, 1H), 7.54–7.58 (m, 1H), 7.35–7.48 (m, 5H), 7.22–7.26 (m, 1H), 7.15–7.19 (m, 1H), 6.88 (m, 1H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 138.1, 136.5, 135.7, 134.4, 130.5, 129.7, 129.2, 128.8, 127.1, 125.8, 124.3, 122.9, 122.3, 121.1, 120.8, 120.6, 116.4, 114.1, 111.1, 102.1; MS (EI): m/z (%) 372 ([M+]), 316, 292, 276, 248, 231 (100), 204, 176, 141, 129, 107, 77; HRMS: m/z Calcd for $C_{22}H_{16}O_2N_2S$: 372.0933. Found: 372.0931.
21. *5-Fluoro-1′-(phenylsulfonyl)-2,3′-biindole* (**16**), 68%: yellow solid, mp 190–192 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (br s, 1H), 8.08 (m, 1H), 7.91–7.97 (m, 3H), 7.87 (s, 1H), 7.54–7.59 (m, 1H), 7.28–7.49 (m, 6H), 6.95–7.00 (m, 1H), 6.83 (m, 1H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 160.0, 156.9, 138.1, 135.6, 134.4, 132.3, 129.7, 128.7, 127.1, 125.8, 124.3, 122.5, 116.1, 114.1, 111.5, 111.2, 110.9, 109.1, 105.7, 102.1; MS (EI): m/z (%) 390 ([M$^+$]), 365, 325, 316, 289, 276, 249 (100), 236, 222, 191, 177, 149, 125, 111, 97, 71. HRMS: m/z Calcd for $C_{22}H_{15}O_2N_2SF$: 390.0838. Found: 390.0837.
22. *3-(1-(2-(4-Nitrophenyl)hydrazono)ethyl)-1-(phenylsulfonyl)indole* (**23**), 78%: yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45–8.48 (m, 1H), 8.23 (m, 2H), 8.00–8.03 (m, 1H), 7.91–7.94 (m, 2H), 7.88 (br s, 1H), 7.81 (s, 1H), 7.56–7.60 (m, 1H), 7.46–7.50 (m, 2H), 7.40–7.43 (m, 2H), 7.17–7.20, (m, 2H), 2.36 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 171.5, 149.9, 142.1, 140.7, 138.1, 135.9, 134.4, 129.7, 127.1, 126.5, 126.0, 124.6, 123.9, 122.3, 113.6, 112.3, 13.6; MS (EI): m/z (%) 434 ([M$^+$]), 404, 293 (100), 278, 247, 232, 206, 117, 156, 143, 115, 103, 77; HRMS: m/z Calcd for $C_{22}H_{18}O_4N_4S$: 434.1049. Found: 434.1049.
23. *3-Methyl-1′-(phenylsulfonyl)-2,3′-biindole* (**17**), 83%: yellow–white solid, 85–87 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (br s, 1H), 7.99–8.01 (m, 1H), 7.84–7.87 (m, 2H), 7.63 (s, 1H), 7.57–7.60 (m, 1H), 7.52–7.55 (m, 1H), 7.43–7,47 (m, 1H), 7.33–7.37 (m, 2H), 7.27–7.30 (m, 2H), 7.19–7.23 (m, 1H), 7.11–7.15 (m, 1H), 7.06–7.10 (m, 1H), 2.29 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 138.2, 136.4, 135.3, 134.4, 129.9, 129.7, 129.6, 127.1, 126.7, 125.6, 124.6, 124.2, 122.7, 121.1, 119.9, 119.2, 115.9, 114.2, 111.1, 110.4, 10.0.
24. *5-Fluoro-3-methyl-1′-(phenylsulfonyl)-2,3′-biindole* (**18**), 76%: yellow solid, mp 78–79 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09–8.11 (d, J = 8.3 Hz, 1H), 8.06 (br s, 1H), 7.95–7.97 (d, J = 8.7 Hz, 2H), 7.73 (s, 1H), 7.68–7.69 (d, J = 8.5 Hz, 1H), 7.56–7.59 (m, 1H), 7.47–7.50 (m, 2H), 7.28–7.43 (m, 1H), 7.24–7.26 (m, 3H), 6.95–6.99 (m, 1H), 2.35 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 159.1, 138.2, 135.3, 134.4, 132.8, 129.7, 128.5, 127.1, 125.7, 124.7, 124.2, 120.9, 115.4, 114.2, 111.6, 111.5, 111.0, 110.8, 104.2, 104.0, 9.9; HRMS: m/z Calcd for $C_{23}H_{17}N_2O_2FS$: 404.0995. Found: 404.0980.
25. *3-(1-(2-(4-Nitrophenyl)hydrazono)propyl)-1-(phenylsulfonyl)indole* (**24**), 58%: orange solid, mp 167–168 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45–8.47 (m, 1H), 8.22–8.24 (d, J = 9.3 Hz, 2H), 8.01–8.03 (m, 1H), 7.98 (br s, 1H), 7.91–7.93 (m, 2H), 7.81 (s, 1H), 7.55–7.57 (m 1H), 7.45–7.49 (m, 2H), 7.40–7.42 (m, 2H), 7.17–7.19 (d, J = 9.3 Hz, 2H), 2.76 (q, J = 7.8 Hz, 2H), 1.33 (t, J = 7.8 Hz, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 149.9, 147.2, 138.0, 136.0, 134.4, 129.9, 129.7, 128.1, 127.1, 126.5, 126.0, 125.6, 124.6, 123.9, 121.1, 113.7, 112.3, 20.6, 11.1; HRMS: m/z Calcd for $C_{23}H_{20}N_4O_4S$: 448.1205. Found: 448.1220
26. *3-Phenyl-1′-(phenylsulfonyl)-2,3′-biindole* (**19**), 86%: white solid; mp 201–202 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (br s, 1H), 8.03–8.04 (d, J = 8.3 Hz, 1H), 7.81–7.83 (m, 2H), 7.75–7.77 (d, J = 7.8 Hz, 1H), 7.57–7.60 (m, 2H), 7.56 (s, 1H), 7.45–7.48 (m, 2H), 7.37–7.40 (m, 3H), 7.25–7.36 (m, 5H), 7.16-7.21 (m, 2H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 138.1, 136.3, 135.3, 135.0, 134.2, 129.9, 129.6, 129.5, 128.7, 128.3, 127.1, 126.7, 126.6, 125.5, 125.4, 124.0, 123.1, 121.1, 120.8, 119.9, 116.9, 115.5, 114.0, 111.2; HRMS: m/z Calcd for $C_{28}H_{20}N_2O_2S$: 448.1246. Found 448.1237
27. *5-Fluoro-3-phenyl-1′-(phenylsulfonyl)-2,3′-biindole* (**20**), 91%: white–yellow solid, 195–196 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (br s, 1H), 8.02–8.04 (d, J = 8.3 Hz, 1H), 7.80–7.81 (d, J = 8.8 Hz, 2H), 7.57–7.60 (m, 1H), 7.56 (s, 1H), 7.45–7.48 (m, 2H), 7.26–7.40 (m, 10H), 7.15–7.18 (m, 1H), 7.00–7.04 (m, 1H) ^{13}C NMR (500 MHz, $CDCl_3$) δ 159.7, 157.9, 138.1, 135.3, 134.6, 134.3, 132.8, 129.7, 129.6, 129.2, 128.9, 128.5, 127.1, 126.8, 125.6, 125.5, 124.1, 121.0, 115.2, 114.0, 111.9, 111.6, 111.3, 104.9, 104.7; HRMS: m/z Calcd for $C_{28}H_{19}N_2O_2SF$: 466.1151. Found 466.1145.
28. *5-Methoxy-3-phenyl-1′-(phenylsulfonyl)-2,3′-biindole* (**22**), 92%: white solid, mp 176–179 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (br s, 1H), 8.01–8.03 (d, J = 8.3 Hz, 1H), 7.78–7.82 (m, 2H), 7.54–7.57 (m, 1H), 7.52 (s, 1H), 7.26–7.47 (m, 9H), 7.15–7.19 (m, 2H), 6.92–6.96 (d, 1H), 3.84 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 155.1, 138.1, 135.3, 135.2, 134.2, 131.5, 129.9, 129.6, 129.4, 128.8, 128.8, 127.5, 127.1, 126.5, 125.5, 125.3, 124.0, 121.1, 116.7, 115.6, 114.0, 113.4, 112.1, 101.3, 56.2; HRMS: m/z Calcd for $C_{29}H_{22}N_2O_3S$: 478.1351. Found: 478.1359.
29. *3-(1-(2-(4-Nitrophenyl)hydrazono)-2-phenylethyl)-1-(phenylsulfonyl)indole* (**25**), 77%: bright orange solid, mp 198–200 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50–8.54 (m, 1H), 8.15–8.18 (d, J = 2H), 8.00–8.05 (m, 1H), 7.98 (s, 1H), 7.81–7.86 (m, 3H), 7.32–7.58 (m, 10H), 7.01–7.06 (d, J = 2H), 4.17 (s, 2H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 149.7, 143.9, 140.8, 137.9, 136.0, 134.5, 134.4, 129.9, 129.8, 129.7, 128.1, 127.9, 127.1, 126.4, 126.4, 126.0, 124.7, 123.9, 122.4, 113.8, 112.4, 34.3; HRMS: m/z Calcd for $C_{28}H_{22}N_4O_4S$: 510.1362. Found: 510.1373.
30. *5-Methyl-3-phenyl-1′-(phenylsulfonyl)-2,3′-biindole* (**21**), 91%: white solid, mp 135–136 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (br s, 1H), 8.03 (d, J = 8.3 Hz, 1H), 7.81 (d, J = 8.3 Hz, 2H), 7.53–7.59 (m, 3H), 7.44–7.47 (m, 2H), 7.28–7.40 (m, 8H), 7.15–7.18 (m, 1H), 7.1–7.12 (m, 1H), 2.47 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 138.1, 135.3, 135.2, 134.7, 134.2, 130.2, 130.0, 129.6, 128.7, 128.6, 127.1, 126.8, 126.5, 125.5, 125.3, 124.7, 124.0, 121.1, 119.4, 115.7, 114.0, 110.9, 21.8.
31. *2,3′-Biindole* (**5**): white solid, mp 197–198 °C (Lit.[13] mp 204–205 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.08 (br s, 1H), 8.86 (br s, 1H), 7.99 (m, Hz), 7.58 (m, 1H), 7.46 (m, 1H), 7.33 (m, 1H), 7.17–7.23 (m, 2H), 7.04–7.14 (m, 2H), 6.75 (m, 1H).
32. *3-(1-(2-Phenylhydrazono)ethyl)indole* (**13**): brown oil, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (br s, 1H), 7.69 (m, 2H), 7.43–7.47 (m, 1H), 7.11–7.19 (m, 2H), 6.78–6.83 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 149.8, 145.0, 140.2, 131.4, 129.7, 129.0, 126.7, 126.4, 120.0, 118.9, 118.6, 118.3, 115.5, 12.8; MS (EI): m/z (%) 249 ([M$^+$], 100), 233, 207, 180, 157, 132, 104, 91, 77; HRMS: m/z Calcd for $C_{16}H_{15}N_3$: 249.1266. Found: 249.1268.
33. *3-(1-(2-Phenylhydrazono)ethyl)-1-(phenylsulfonyl)indole* (**14**): brown oil, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58–8.60 (m, 1H), 8.02–8.03 (m, 1H), 7.91–7.92 (d, J = 7.5 Hz, 2H), 7.72 (s, 1H), 7.50–7.53, (m, 1H), 7.38–7.44 (m, 7H), 7.32–7.35 (m, 2H), 7.19–7.20 (m, 1H) 2.25 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 145.3, 138.1, 138.1, 136.0, 134.6, 129.6, 129.6, 128.4, 127.0, 125.7, 124.6, 124.4, 124.4, 123.3, 120.5, 113.5, 113.4, 13.3.