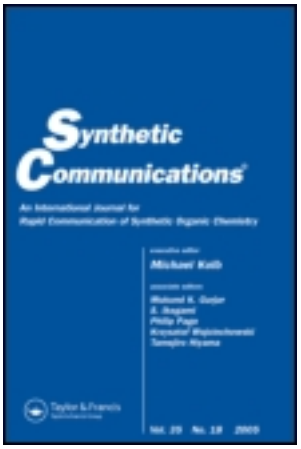


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Regio- and Stereoselective Synthesis of New Substituted Tetrahydrocarbazoles and Carbazoles Using Diels-Alder Reactions

Dattatray G. Hingane [a], Shailesh K. Goswami [a], Vedavati Puranik [b] & Radhika S. Kusurkar [a]

[a] Department of Chemistry, University of Pune, Pune, India

[b] Centre for Material Characterization, National Chemical Laboratory, Pune, India

Accepted author version posted online: 17 Nov 2011.Published online: 27 Feb 2012.

To cite this article: Dattatray G. Hingane , Shailesh K. Goswami , Vedavati Puranik & Radhika S. Kusurkar (2012): Regio- and Stereoselective Synthesis of New Substituted Tetrahydrocarbazoles and Carbazoles Using Diels-Alder Reactions, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 42:12, 1786-1795

To link to this article: http://dx.doi.org/10.1080/00397911.2010.544440

Synthetic Communications®, 42: 1786–1795, 2012

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2010.544440

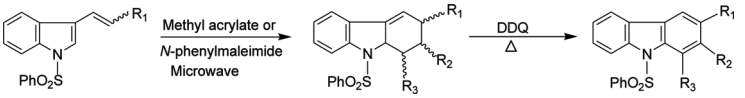
Taylor & Francis
Taylor & Francis Group

REGIO- AND STEREOSELECTIVE SYNTHESIS OF NEW SUBSTITUTED TETRAHYDROCARBAZOLES AND CARBAZOLES USING DIELS–ALDER REACTIONS

Dattatray G. Hingane,[1] Shailesh K. Goswami,[1] Vedavati Puranik,[2] and Radhika S. Kusurkar[1]

[1]*Department of Chemistry, University of Pune, Pune, India*
[2]*Centre for Material Characterization, National Chemical Laboratory, Pune, India*

GRAPHICAL ABSTRACT



Abstract *Diels–Alder reactions of 3-vinylindoles were carried out with methyl acrylate and N-phenylmaleimide as dienophiles under microwave conditions to furnish unreported tetrahydrocarbazoles regio- and stereoselectively in good yields. Further dehydrogenation resulted in new substituted carbazoles.*

Keywords Carbazoles; regio- and stereoselective Diels–Alder reactions; tetrahydrocarbazoles

INTRODUCTION

Carbazole and tetrahydrocarbazole ring systems are major artifacts of many naturally occurring biologically active compounds.[1] There has been strong interest in carbazole alkaloids from chemists and biologists because of the intriguing structural features and promising biological activities. In the literature,[1–7] various methods are available for the synthesis of carbazole alkaloids, including classical methods such as Fischer–Borsche synthesis and Graebe–Ullmann synthesis as well as methods based on transition metal–mediated and catalyzed coupling.[1] Electrocyclization and Diels–Alder reactions of vinylindoles have been extensively used[1,8,9] for the synthesis of tetrahydrocarbazoles and carbazoles. Recently, microwave irradiation, a green technique, has been shown[10] to be the most preferred method for many organic reactions because the reactions are fast, high-yielding, and stereoselective. We herein report the regio- and stereoselective synthesis of

Received July 5, 2010.
Address correspondence to Radhika S. Kusurkar, Department of Chemistry, University of Pune, Pune 411 007, India. E-mail: rsk@chem.unipune.ac.in

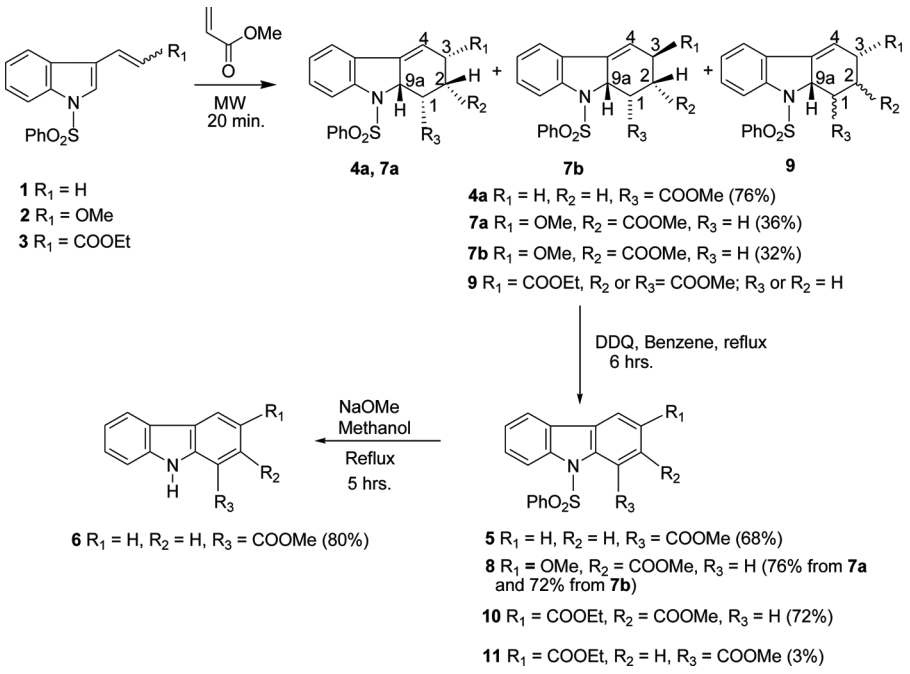
new substituted tetrahydrocarbazoles and carbazoles using Diels–Alder reactions with methyl acrylate and *N*-phenylmaleimide as dienophiles.

RESULTS AND DISCUSSION

Three different 3-vinylindoles **1**–**3** were used for the presented Diels–Alder reactions. Indole was first formylated, and the indole-3-aldehyde[11] formed was protected at the indole nitrogen with a phenylsulfonyl group.[12] Further reactions with appropriate Wittig reagents furnished dienes **1**–**3**.[13,14] According to ^{1}H NMR data, diene **2** was obtained as a mixture of *E* and *Z* isomers in the ratio of 1:1, while diene **3** was isolated as pure *E* isomer.

Reactions of Dienes 1–3 with Methyl Acrylate

Treatment of 1-phenylsulfonyl-3-vinylindole **1** with methyl acrylate at reflux temperature using microwave irradiation furnished a solid. After chromatography, compound **4a** (76%) was isolated as a major product (Scheme 1). The product was shown to be an *endo* adduct, and the structure was confirmed by the presence of a singlet for –COOMe at 3.6 δ and a narrow multiplet of an olefinic proton at 5.86 δ in ^{1}H NMR. A small amount of the other isomer was also isolated. Further dehydrogenation of the cycloadduct **4a**, using 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), furnished product **5** (68%). The ^{1}H NMR data of **5** differed from its



Scheme 1. Reactions of dienes **1**–**3** with methyl acrylate.

reported[15] regioisomer. Thus, the reported *N*-benzenesulfonyl-2-carbomethoxycarbazole showed a singlet at 8.88 δ for C_1H (meta coupling not seen) and a singlet at 3.95 δ for –OMe, whereas in *N*-benzenesulfonyl-1-carbomethoxy carbazole **5** no singlet was observed for aromatic protons, and –OMe was seen at 4.03 as a singlet. This data confirmed the position of the –COOMe group at C-1 also in the cycloadduct **4a**.

Finally, deprotection of the indole nitrogen in compound **5** using sodium methoxide furnished 1-carbomethoxy carbazole **6** in 80% yield (Scheme 1).

Treatment of diene **2** ($E + Z$) with methyl acrylate furnished two cycloadducts, **7a** and **7b**, in 68% yield in the ratio 1:1. The isomers were separated by column chromatography. The structure and stereochemistry of **7a** and **7b** was determined by ^{1}H NMR spectroscopy. Dehydrogenation carried out with **7a** and **7b** using DDQ in both cases gave **8**, indicating that **7a** and **7b** are diastereomers (Scheme 1). The structure of unreported carbazole **8** was confirmed by the presence of two singlets at 7.7 and 8.72 δ for C_4H and C_1H respectively. The formation of two diastereomers **7a** and **7b** can be explained by the *cis* addition in the Diels–Alder reaction on *E* and *Z* isomers respectively. Thus, diene **2** furnished cycloadducts **7a** and **7b** regio- and stereoselectively.

In the Diels–Alder reaction of diene **3** with methyl acrylate, an inseparable mixture of cycloadducts **9** was obtained. After dehydrogenation with DDQ, two new products, **10** and **11**, in the ratio of 1:0.04, were produced. Compound **10** showed two singlets at 8.29 and 8.66 δ for C_1H and C_4H in ^{1}H NMR indicating the position of –COOMe at C_2. This was further supported by x-ray analysis[16] (Fig. 1). Compound **11** exhibited two meta-coupled ($J = 1.65$ Hz) doublets at 8.49 and 8.58 δ for C_2H and C_4H respectively, indicating the position of –COOMe at C_1.

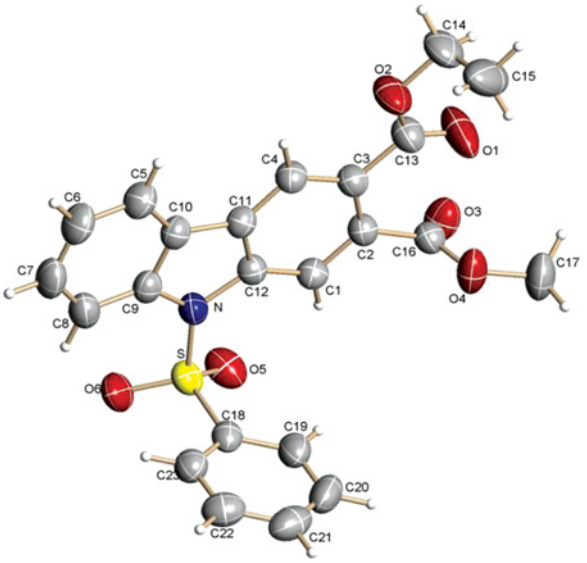


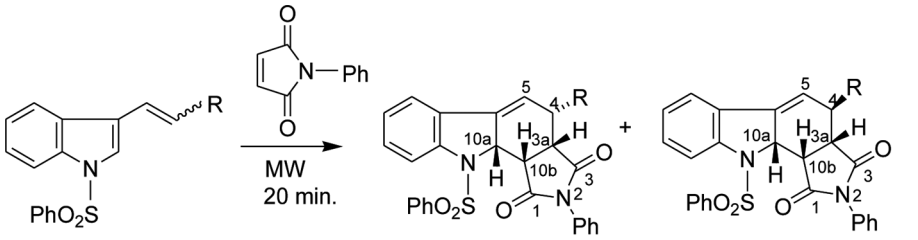
Figure 1. ORTEP diagram of the compound **10**. Ellipsoids are drawn at 50% probability. (Figure is provided in color online.)

These results showed that the dienes **1, 2**, and **3** furnished ortho adducts as major products. Formation of these adducts can be explained using frontier molecular orbital (FMO) theory. Diene **1** has an electron-withdrawing $-N\mathrm{SO_2Ph}$ at C_1 of the diene unit, giving **4a** as ortho adduct to the sulfonamido group. The electron-donating methoxy group is controlling the formation of the regiochemistry of the products **7a** and **7b**. Diene **3** has two electron-withdrawing groups at 1 and 4 positions. The formation of ortho adduct to –COOEt indicated its stronger controlling effect.

Reactions of Dienes 1–3 with *N*-Phenylmaleimide

1-Phenylsulfonyl-3-vinylindole (**1**) and *N*-phenylmaleimide (NPMI) were adsorbed on silica gel and exposed to microwave for 20 min to furnish selectively one cycloadduct[17,18] **12** (Scheme 2). The same result was observed by carrying out the reaction in the microwave oven using toluene as a solvent. The ^{1}H NMR of compound **12** was in agreement with reported data.[18] However, use of microwave heating improved the yield and minimized the reaction time (74%, 20 min) compared to the earlier report (60%, 7 h).

Diene **2** ($E/Z = 1{:}1$) and NPMI were adsorbed on silica gel and irradiated in a microwave oven for 20 min to furnish two cycloadducts, **13a** and **13b**. The major isomer was shown to be **13a**, which was identical with the reported[14] cycloadduct obtained in a similar reaction carried out by the conventional method. In contrast to that report, the other isomer **13b** was also isolated successfully and was characterized by spectral data. From ^{1}H NMR, **13a** and **13b** were shown to be the diastereomers of each other. The isomers **13a** and **13b** were obtained from the *E* and *Z* isomers of the diene **2** respectively according to *cis* addition rule in [4 + 2] cycloaddition reaction. In an observation, when the irradiation was carried out in toluene, product **13a** precipitated out after 15 min, which indicated that the *E* isomer was reacting faster than the *Z*. When starting diene was used in the ratio $E/Z = 1{:}1$, the product ratio of **13a/13b** was 9:1. The change in the ratios of the isomers of starting and product could be attributed to the conversion of *Z* to *E* isomer during the reaction. This was confirmed experimentally by irradiating the mixture of E/Z



1 R = H
2 R = OMe
3 R = COOEt

12 R = H (74%)
13a R = OMe (72%)
14 R = COOEt (72%)

13b R = OMe (8%)

Scheme 2. Reactions of dienes **1**–**3** with *N*-phenylmaleimide.

isomers in the ratio of 1:1 for 15 min in a microwave oven to get the conversion as $E/Z = 2{:}1$.

Thus, as compared to the earlier report[14] (15 h, 5% of **13a**, absence of **13b**), the reaction under microwave irradiation was rapid, and high yielding (20 min, 72% of **13a** and 8% of **13b**) and furnished unreported diastereomer **13b**. It should be noted that the dimer obtained in the earlier report was not formed in this reaction.

1-Phenylsulfonyl-3-(β-carbethoxyvinyl) indole **3** on reaction with NPMI using microwave-irradiation furnished cycloadduct **14** with 72% yield. When the microwave irradiation reaction was carried out in toluene, cycloadduct **14** was precipitated out after 20 min. By comparing the ^{1}H NMR spectrum and by using the analogy with **13a**, the structure of the product **14** was confirmed as a single unreported diastereomer, which is expected from the starting *E* isomer of **3**.

Surprisingly, in contrast to the dehydrogenation of cycloadducts **4a, 7a, 7b**, and **9**, attempts to dehydrogenate the cycloadducts **12**, **13a**, **13b**, and **14** using DDQ, chloranil, or Pd/C (10%) in different solvents failed to give aromatic products. This could be attributed to the presence of the fused NPMI ring at C_1 and C_2 positions.

CONCLUSION

The microwave-assisted Diels–Alder reaction of 3-vinylindoles was shown to be faster and furnished new cycloadducts stereoselectively and regioselectively in good yields. The cycloadducts obtained by using methyl acrylate were further dehydrogenated to new substituted carbazoles. Reactions using NPMI furnished new cycloadducts. The formation of major adducts was explained using FMO theory and the *cis* addition rule.

EXPERIMENTAL

The Diels–Alder reactions were carried out at reflux temperature of methyl acrylate at 700 W in a Raga microwave synthesizer. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz respectively on a Varian Mercury instrument as δ values in $CDCl_3$ with reference to tetramethylsilane (TMS) as an internal standard. Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu 8400 instrument. Mass spectra were recorded on a Shimadzu QP 5050 device. Elemental analysis was recorded on a Flash E. A. 1112 Thermo instrument.

General Procedure for the Cycloaddition Reaction of Vinylindoles 1–3 with Methyl Acrylate in Microwave Oven

Vinylindole (**1–3**, 1 mmol) was dissolved in methyl acrylate (5 ml) in a round-bottomed flask, equipped with a reflux condenser, and exposed to microwave irradiation. The reaction was monitored by thin-layer chromatography (TLC) after every 2 min. After completion of the reaction, methyl acrylate was removed using a rotary evaporator, and the reaction mixture was chromatographed using silica gel with hexane/ethyl acetate (90:10) as an eluent to furnish the products.

General Procedure for Dehydrogenation of Cycloadducts

Tetrahydrocarbazoles (**4a**, **7a**, **7b**, and **9**, 1 mmol) were dissolved in 10 ml dry benzene. To the well-stirred and ice-cooled solution, DDQ (2.5 mmol) was added in 3–4 lots. Addition of DDQ gave a green color to the solution, which vanished immediately. After complete addition of DDQ, the green color persisted. The reaction mixture was refluxed for 6 h, and the reaction was monitored by TLC. After completion of reaction, the reaction mixture was filtered and washed with benzene, and the solvent was removed using a rotary evaporator. The oily mixture obtained was chromatographed using silica gel with hexane/ethyl acetate (95:5) as an eluent to get the product.

Procedure for Deprotection of Carbazole 5

To a freshly prepared sodium methoxide solution (0.1 g sodium in 10 ml dry methanol), compound **5** (0.2 g) was added, and the reaction mixture was refluxed for 5 h. The reaction was monitored by TLC. After completion of reaction, it was neutralized with dilute HCl and extracted with dichloromethane (DCM). The solvent was removed using a rotary evaporator. The solid product was chromatographed using silica gel with hexane/ethyl acetate (95:5) as an eluent to furnish carbazole **6**.

General Procedure for the Cycloaddition Reaction of Vinylindoles with NPMI in Microwave Oven

Vinylindole (**1–3**, 1 mmol) and NPMI (1.1 mmol) were adsorbed on silica gel. The mixture was exposed to microwave radiation. The reaction was monitored by TLC every 2 min. The reaction was complete in 20 min of microwave irradiation. The reaction mixture was purified by column chromatography using silica gel with hexane/ethyl acetate (90:10) as an eluent to furnish the products.

Selected Data

Compound 4a. Yield: 76%; mp 115–116 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.05 (m, 1H, C_2H_α), 2.30 (m, 3H, C_3H_2 & C_2H_β), 3.60 (s, 3H, $-OCH_3$), 3.81 (nm, 1H, $J = 3.6$ Hz, C_1H_β), 4.39 (t, 1H, $J = 3.3$ Hz, $C_{9a}H_\beta$), 5.86 (d, 1H, $J = 3.3$ Hz, C_4H), 6.99 (t, 1H, $J = 3$ Hz, ArH), 7.18–7.26 (m, 2H, ArH), 7.41–7.56 (m, 3H, ArH), 7.72–7.80 (m, 3H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.58, 23.92, 41.65, 51.60, 63.68, 115.28, 116.42, 120.22, 123.94, 127.46, 128.94, 129.19, 133.26, 133.87, 135.34, 136.05, 143.04, 171.44; IR (Nujol): ν 1730, 1640 cm^{-1}; MS: m/z 369 (M^+). Anal. calcd. for $C_{20}H_{19}NO_4S$: C, 65.05; H, 5.14; N, 3.79%. Found: C, 65.22; H, 5.10; N, 3.68%.

Compound 5. Yield: 68%; mp 124–126 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.03 (s, 3H, $-COOCH_3$), 7.08 (t, $J = 8.3$ Hz, 2H, C_3H & C_6H), 7.20 (dd, $J = 8.5$, 1.2 Hz, 2H, ArH), 7.29 (m, 2H, ArH), 7.43 (m, 2H ArH), 7.7 (d, $J = 7.6$ Hz, 1H, ArH), 7.83 (dd, $J = 7.6$, 0.9 Hz, 1H, C_2H), 7.90 (d, $J = 7.9$ Hz, 1H, C_5H), 8.12 (d, $J = 8.2$ Hz, 1H, C_4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.4, 118.04, 119.8, 122.7, 124.54, 125.26, 126.27, 126.57, 127.63, 128.13, 128.56, 129.01, 130.09, 133.43,

135.15, 136.85, 140.16, 169.46; IR: ν 1738 cm^{-1}; MS: m/z 365 (M^+). Anal. calcd. for $C_{20}H_{15}NO_4S$: C, 65.75; H, 4.10; N, 3.84%. Found: C, 65.68; H, 4.12; N, 3.72%.

Compound 6. Yield: 80%, mp 143–144 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.01 (s, 3H $COOCH_3$), 7.22–7.54 (dd, $J = 8$, 1.3 Hz, 4H, ArH), 8.07–8.34, m, 3H, ArH), 9.89 (bs, 1H > N-H exchangeable with D_2O); ^{13}C NMR (75 MHz, $CDCl_3$): δ 51.06, 110.69, 117.25, 118.75, 119.15, 121.15, 123.55, 124.31, 125.42, 126.39, 138.57, 139.02, 140.20, 166.32; IR (Nujol): ν 1738 cm^{-1}; MS: m/z 225 (M^+). Anal. calcd. for $C_{14}H_{11}NO_2$: C, 74.76; H, 4.88; N, 6.22%. Found: C, 74.65; H, 4.70; N, 6.34%.

Compound 7a. Yield: 36%; mp 122–124 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.06 (dd, $J = 12.8$, 12.37 Hz, 1H, C_1H), 2.78 (dd, $J = 12.8$, 2.4 Hz, 1H, C_1H), 2.98 (dd, $J = 12.37$, 2.4 Hz, 1H, C_2H_β), 3.38 (s, 3H, $-OCH_3$), 3.78 (s, 3H, $-COOCH_3$), 4.10 (d, $J = 9.7$, 1H, $C_{9a}H_\beta$), 4.2 (bs, 1H, C_3H_β), 6.06 (d, $J = 2.8$ Hz, 1H, C_4H), 7.00 (t, $J = 7$ Hz, 1H, ArH), 7.28 (m, 4H, ArH), 7.42 (t, $J = 7$ Hz, 1H, ArH), 7.78 (m, 3H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.49, 44.56, 51.95, 57.70, 63.98, 73.46, 114.42, 115.38, 120.92, 124.05, 126.29, 127.51, 129.00, 130.24, 133.39, 136.11, 138.98, 144.39, 171.69; IR (Nujol): ν 1738 cm^{-1}; MS: m/z 399 (M^+). Anal. calcd. for $C_{21}H_{21}NO_5S$: C, 63.16; H, 5.26; N, 3.50%. Found: C, 63.24; H, 5.43; N, 3.72%.

Compound 7b. Yield: 32%; mp 126–128 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.04 (m, 1H, C_1H), 3.02 (bs, 1H, C_2H_β), 3.06 (dd, $J = 16.8$, 2.75 Hz, 1H, C_1H), 3.42 (s, 3H $-OCH_3$) 3.78 (s, 3H $-COOCH_3$), 4.16 (t, $J = 2.5$ Hz, 1H, $C_{9a}H_\beta$), 4.2 (bs, 1H, C_3H_α), 5.92 (d, $J = 2.5$ Hz, 1H, C_4H), 6.98 (t, $J = 7.4$ Hz, 1H, ArH), 7.26 (m, 2H, ArH), 7.45 (m, 3H, ArH), 7.80 (m, 3H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.48, 41.91, 52.25, 57.23, 60.52, 74.50, 115.26, 115.46, 120.96, 124.18, 126.30, 127.65, 128.90, 130.12, 133.44, 135.39, 138.45, 144.31, 173.68; IR (Nujol): ν 1730 cm^{-1}; MS: 399 (M^+). Anal. calcd. for $C_{21}H_{21}NO_5S$: C, 63.16; H, 5.26; N, 3.50%. Found: C, 63.31; H, 5.10; N, 3.34%.

Compound 8. Yield 76% from **7a** and 72% from **7b**, mp 158–160 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.96 (s, 6H $-OCH_3$ and $-COOCH_3$), 7.2–7.4 (m, 5H, ArH), 7.5 (t, $J = 7.8$ Hz, 1H, ArH), 7.7 (s, 1H, C_4H), 7.74 (d, $J = 7.7$ Hz, 1H, ArH), 7.85 (d, $J = 7.7$ Hz, 1H, ArH), 8.28 (d, $J = 8.2$ Hz, 1H, C_5H), 8.72 (s, 1H, C_1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.36, 56.44, 102.39, 115.39, 118.26, 119.60, 120.46, 124.06, 125.58, 126.31, 128.50, 128.92, 130.44, 131.34, 133.74, 137.11, 139.58, 156.24, 166.24; MS: 395 (M^+). Anal. calcd. for $C_{21}H_{17}NO_5S$: C, 63.80; H, 4.30; N, 3.54%. Found: C, 63.62; H, 4.41; N, 3.42%.

Compound 10. Yield: 72%; mp 135–137 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40 (t, $J = 7.2$ Hz, 3H, $-COOCH_2C\underline{H}_3$), 3.99 (s, 3H, $-COOCH_3$), 4.42 (q, 7.2 Hz, 2H, $-COOC\underline{H}_2CH_3$), 7.30 (m, 3H, ArH), 7.43 (t, $J = 8$ Hz, 1H, ArH), 7.56 (t, $J = 7.7$ Hz, 1H, ArH), 7.81 (d, $J = 8$ Hz, 2H, ArH), 7.92 (d, $J = 7.7$ Hz, 1H, ArH), 8.29 (s, 1H, C_1H), 8.30 (d, $J = 6.3$ Hz, 1H, C_5H), 8.66 (s, 1H, C_4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.12, 52.77, 61.72, 114.79, 115.20, 120.57, 121.12, 124.32, 124.63, 126.18, 127.42, 127.62, 128.67, 129.08, 131.10, 134.06, 137.09, 138.73, 138.96, 166.94, 167.86; IR (Nujol): ν 1738 cm^{-1}; MS: m/z 437 (M^+). Anal. calcd. for $C_{23}H_{19}NO_6S$: C, 63.16; H, 4.35; N, 3.20%. Found: C, 63.28; H, 4.16; N, 3.32%.

Compound 11. Yield 3%; mp 140–142 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.45 (t, $J = 7.2$ Hz, 3H, $-COOCH_2C\underline{H}_3$), 4.03 (s, 3H, $-COOCH_3$), 4.46 (q, $J = 7.2$ Hz, 2H, $-COOC\underline{H}_2CH_3$), 7.12 (t, $J = 8.2$ Hz, 1H, ArH), 7.27 (m, 5H, ArH), 7.45 (t, $J = 7.4$ Hz, 1H, ArH), 7.8 (d, $J = 7.4$ Hz, 1H, ArH), 8.1 (d, $J = 7.9$ Hz, 1H, C_5H), 8.49 (d, $J = 1.65$ Hz, 1H, C_2H), 8.58 (d, $J = 1.65$ Hz, 1H, C_4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.46, 52.78, 61.62, 117.90, 120.22, 124.04, 124.28, 125.51, 126.63, 127.02, 127.47, 128.24, 128.40, 129.66, 130.20, 133.70, 135.50, 139.53, 140.52, 165.35, 167.75; MS: 437 (M^+). Anal. calcd. for $C_{23}H_{19}NO_6S$: C, 63.16; H, 4.35; N, 3.20%. Found: C, 63.35; H, 4.18; N, 3.42%.

Compound 12. Yield 74%; mp 162–163 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.28 (ddd, $J = 15.6$, 7.42, 3.5 Hz, 1H, C_4H), 3.12 (dd, $J = 15.6$, 7.7 Hz, 1H, C_4H), 3.36 (dd, $J = 7.7$, 7.42 Hz, 1H, $C_{3a}H_\beta$), 4.22 (dd, $J = 8.8$, 6.8 Hz, 1H, $C_{10b}H_\beta$), 4.64 (dd, $J = 6.8$, 3.58 Hz, 1H, $C_{10a}H_\beta$), 6.14 (m, 1H, C_5H), 6.95–7.92 (m, 14 H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.84, 35.74, 42.09, 59.97, 112.30, 112.96, 119.35, 122.31, 124.75, 124.89, 125.43, 126.65, 127.07, 127.66, 128.15, 130.25, 132.10, 134.64, 134.86, 142.12, 171.90, 176.35. Anal. calcd. for $C_{26}H_{20}N_2O_4S$: C, 68.42; H, 4.38; N, 6.14%. Found: C, 68.28; H, 4.42; N, 6.32%.

Compound 13a. Yield: 72%; mp 230–232 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.66 (s, 3H, $-OCH_3$), 3.71 (dd, $J = 8.3$, 7.7 Hz, 1H, $C_{3a}H_\beta$), 4.12 (ddd, J = 7.7, 3, 1.9 Hz, 1H, C_4H_β), 4.17 (dd, $J = 8.5$, 6.1 Hz, 1H, $C_{10b}H_\beta$), 4.59 (m, 1H, $C_{10a}H_\beta$), 6.12 (dd, $J = 3$ Hz, 1H, C_5H), 6.99–7.92 (m, 14H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 37.72, 37.98, 41.75, 56.18, 59.48, 113.28, 115.38, 119.92, 122.59, 124.42, 125.12, 125.66, 126.80, 127.24, 127.84, 128.88, 130.44, 132.26, 133.32, 135.14, 143.18, 171.28, 171.46. MS: m/z 486 (M^+).

Compound 13b. Yield: 8%; mp 176–178 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.34 (s, 3H, $-OCH_3$), 3.67 (dd, $J = 8.5$, 2.2 Hz, 1H, $C_{3a}H_\beta$), 4.27 (dd, $J = 8.5$, 7.4 Hz, 1H, $C_{10b}H_\beta$), 4.66 (dd, $J = 5.7$, 2.2 Hz, 1H, C_4H_α), 5.22 (dd, $J = 7.4$, 3.3 Hz, 1H, $C_{10a}H_\beta$), 6.25 (dd, $J = 5.7$, 3.3 Hz, 1H, C_5H), 6.98–7.94 (m, 14 H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.70, 44.05, 56.66, 60.54, 73.76, 112.40, 115.49, 121.47, 123.91, 125.89, 126.09, 127.28, 128.39, 128.78, 129.04, 131.29, 131.46, 133.40, 136.82, 141.77, 144.96, 172.55, 174.80; MS: 486 (M+). Anal. calcd. for $C_{27}H_{22}N_2O_5S$: C, 66.66; H, 4.52; N, 5.76%. Found: C, 66.50; H, 4.62; N, 5.88%.

Compound 14. Yield: 72%; mp 205–207 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.35 (t, $J = 7.14$ Hz, 3H, $-COOCH_2C\underline{H}_3$), 3.22 (brs, 1H, $C_{3a}H_\beta$), 3.95 (dd, $J = 9$, 5.3 Hz, 1H, $C_{10b}H_\beta$), 4.27 (ddd, $J = 8.8$, 3.6, 2.6 Hz, 1H, C_4H_β), 4.34 (q, $J = 7.14$ Hz, 2H, $-COOC\underline{H}_2CH_3$), 4.6 (ddd, $J = 7.42$, 5.3, 2.6 Hz, 1H, $C_{10a}H_\beta$), 6.62 (dd, $J = 7.42$, 3.6 Hz, 1H, C_5H), 6.62–7.90 (m, 14 H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.16, 40.44, 41.88, 42.70, 61.66, 61.94, 112.18, 115.28, 121.20, 124.12, 125.64, 126.06, 127.12, 128.32 128.70, 129.14, 130.60, 131.14, 133.50, 136.48, 136.76, 144.48, 169.58, 171.86, 174.84; MS: m/z 528 (M+). Anal. calcd. for $C_{29}H_{24}N_2O_6S$: C, 65.90; H, 4.54; N, 5.30%. Found: C, 65.72; H, 4.70; N, 5.14%.

Crystallographic Data of Compound 10

Single crystals of the compound were grown by slow evaporation of the compound in methanol. A colorless crystal of approximate size $0.42 \times 0.28 \times 0.03$ mm, was used for data collection on *Bruker Smart Apex* CCD diffractometer using Mo K_α radiation C23 H19 N O6 S, $M = 437.45$. Crystals belong to monoclinic space group $P2_1/c$, $a = 11.8641(7)$, $b = 14.7655(9)$, $c = 13.0207(8)$ Å, $\beta = 115.425(1)^\circ$, $V = 2060.0(2)$ Å^3, $Z = 4$. SHELX-97 (ShelxTL)[19] was used for structure solution and full matrix least squares refinement on F^2. Hydrogen atoms were included in the refinement as per the riding model.

ACKNOWLEDGMENTS

We are grateful to M. S. Wadia for helpful discussions, A. P. Gadgil for IR spectra, J. P. Chaudhari for NMR spectra, and Mr. Shishupal for GC-MS. D. G. H. is thankful to the University Grants Commission for FIP.

REFERENCES

1. Knolker, H. J.; Reddy, K. R. Isolation and synthesis of biologically active carbazole alkaloids. *Chem. Rev.* **2002**, *102*, 4303–4427.
2. Saxton, J. E. Recent progress in the chemistry of the monoterpenoid indole alkaloids. *Nat. Prod. Rep.* **1997**, *14*, 559–590.
3. Bonjoch, J.; Sole, D. Synthesis of strychnine. *Chem. Rev.* **2000**, *100*, 3455–3482.
4. Abbiati, G.; Canevari, V.; Facoetti, D.; Rossi, E. Diels–Alder reactions of 2-vinylindoles with open-chain C=C dienophiles. *Eur. J. Org. Chem.* **2007**, 517–525.
5. Siripurapu, U.; Kolanos, R.; Dukat, M.; Roth, B. L.; Glennon, R. A. Binding of methoxy-substituted *N*1-benzenesulfonylindole analogs at human 5-HT6 serotonin receptors. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 3793–3796.
6. Fabio, R. D.; Giovannini, R.; Bertani, B.; Borriello, M.; Bozzoli, A.; Donati, D.; Falchi, A.; Ghirlanda, D.; Leslie, C. P.; Pecunioso, A.; Rumboldt, G.; Spada, S. Synthesis and SAR of substituted tetrahydrocarbazole derivatives as new NPY-1 antagonists. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 1749–1752.
7. Hesse, M. *Alkaloids, Nature Curse or Blessing?* Wiley-VCH: New York, 2002.
8. Pindur, U.; Pfeuffer, L. [4 + 2]-Cycloaddition to 4-demethoxycarbazomycin. *Heterocycles* **1987**, *26*, 325–327.
9. Kusurkar, R. S.; Patil, U. G. Synthesis of carbazoles via Diels–Alder reaction of 3-vinylindoles. *Indian J. Chem.* **1986**, *25B*, 1038–1041.
10. Caddick, S.; Fitzmaurice, R. Microwave enhanced synthesis. *Tetrahedron* **2009**, *65*, 3325–3355.
11. Smith, G. F. Indoles, part I: The formylation of indole and some reactions of 3-formylindole. *J. Chem. Soc.* **1954**, 3842–3846.
12. Hibino, S.; Sugino, E.; Yamochi, T.; Kuwata, M.; Hashimoto, H.; Sato, K.; Karasawa, Y. Syntheses and sleeping-time-prolonging effect of nitramarine and related compounds. *Chem. Pharm. Bull.* **1987**, *35*, 2261–2265.
13. Pindur, U.; Pfeuffer, L. Wittig-Olefinierung zu neuen donor-und akzeptor-substituierten 3 Vinyl indolen: Optimierte Syntheseverfahren. *Monatsh. Chem.* **1989**, *120*, 157–162.

14. Pfeuffer, L.; Pindur, U. Diels–Alder-Reaktionen von 2′-substituierten 3-Vinyl-1H-indolen zu neuen anellierten Indol-und Carbazol-Derivaten. *Helv. Chim. Acta* **1987**, *70*, 1419–1428.
15. Pindur, U.; Kim, M. H.; Rogge, M.; Massa, W.; Moliniert, M. New Diels–Alder reactions of (*E*/*Z*)-2′-methoxy-substituted 3-vinylindoles with carbo- and heterodienophiles: Regio- and stereoselective access to [*b*] annelated indoles and functionalized or [a] annelated carbazoles. *J. Org. Chem.* **1992**, *57*, 910–915.
16. Cambridge Crystallographic Data Centre, 758883.
17. Srinivasan, P. C.; Saroja, B. Synthesis and [4 + 2]-cycloadditions of *N*-phenylsulfonyl-3-vinylindole. *Synthesis* **1986**, *9*, 748–749.
18. Pindur, U.; Pfeuffer, L. New reactions of 3-vinyl- and 3-(2-propenyl) indoles with *N*-phenylmaleimide: [4 + 2] Cycloaddition, ene reaction, and dimerization. *Helv. Chim. Acta* **1988**, *71*, 467–471.
19. Sheldrick, G. M. *SHELX-97 Program for Crystal Structure Solution and Refinement*; University of Gottingen: Gottingen, Germany, 1997.