A Tandem Reduction–Oxidation Protocol for the Conversion of 1-Keto-1,2,3,4-tetrahydrocarbazoles to Carbazoles via Tosylhydrazones through Microwave Assistance: Efficient Synthesis of Glycozoline, Clausenalene, Glycozolicine, and Deoxycarbazomycin B and the Total Synthesis of Murrayafoline A

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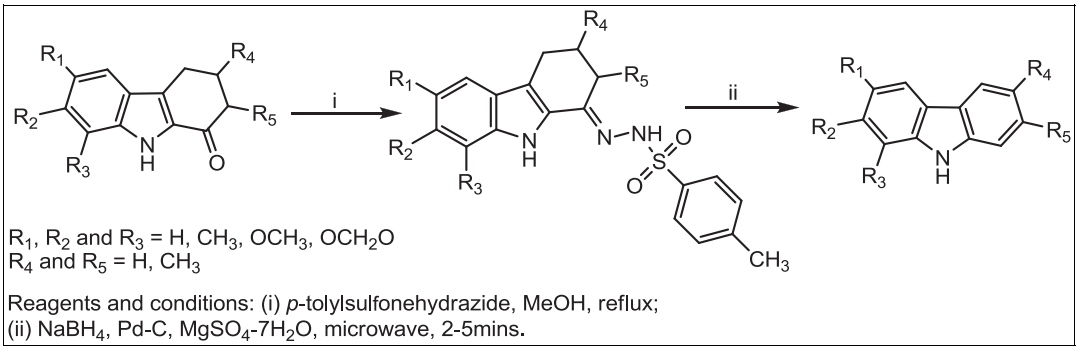

A novel and efficient methodology for the synthesis of carbazoles from 1-keto-1,2,3,4-tetrahydrocarbazoles via the corresponding tosylsulfonhydrazones by a one-pot tandem reduction–oxidation protocol using a combination of $NaBH_4$ and Pd–C on $MgSO_4{\cdot}7H_2O$, a solid support, under microwave is developed. The reaction is successfully extended toward the synthesis of several naturally occurring carbazole alkaloids, namely 3-methylcarbazole, glycozoline, clausenalene, glycozolicine, murrayafoline A, and deoxycarbazomycin B, a carbazole derivative that is known to have a promising antimicrobial activity.

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INTRODUCTION

In continuation [1] of our synthetic studies on biologically active [2] carbazole alkaloids exploiting the keto-functionality of easily available 1-keto-1,2,3,4-tetrahydrocarbazoles (**1**), prepared through Fischer indole cyclization of substituted cyclohexane-1,2-dione-1-phenylhydrazones obtained by Japp–Klingemann procedure [3] from diazonium salts and 1,3-dicarbonyl compounds, we became interested to develop a new methodology that would allow the ready conversion of **1** to 1,2,3,4-tetrahydrocarbazoles, toward a facile entry into carbazole nucleus. To date, the main approach for the above conversion is the Wolff–Kishner reduction of **1** to the corresponding 1,2,3,4-tetrahrdocarbazoles followed by aromatization [3] on refluxing with Pd–C in decalin. Unfortunately, there is no such report for the isolation and characterization of the intermediate 1,2,3,4-tetrahydrocarbazoles from **1**. In pursuance of such studies, we have developed here, an efficient method for the conversion of **1** to carbazoles (**3**) via the corresponding tosylhydrazones (**2**) followed by a one-pot tandem reduction–oxidation protocol using a combination of $NaBH_4$ and Pd–C on $MgSO_4{\cdot}7H_2O$, a solid support, through microwave assistance (Scheme 1).

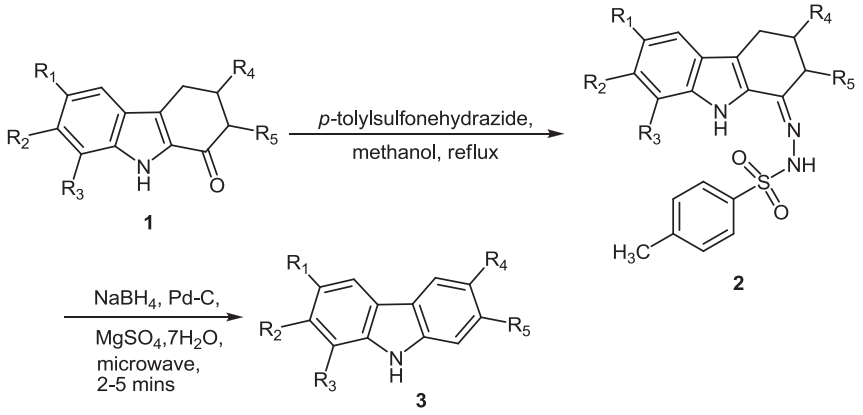
This protocol is efficiently extended toward the synthesis of several naturally occurring biologically active carbazole alkaloids, such as 3-methylcarbazole [4], glycozoline [5], clausenalene [6], glycozolicine [7], murrayafoline A [8], and deoxycarbazomycin B [3], a carbazole derivative that is known to have promising antimicrobial activity against both Gram-positive and Gram-negative bacteria (Figure 1).

RESULTS AND DISCUSSION

A mild and selective alternative to standard Wolff–Kishner deoxygenation [9] is the reduction of corresponding tosylhydrazones to hydrocarbons with sodium cyanoborohydride [10] or sodium borohydride [11] or with catecholborane [12]. This prompted us to obtain tosylhydrazones of **1**. Tosylhydrazones required for our purpose was obtained easily from the corresponding **1** by reaction [13] with tosylhydrazide in refluxing methanol (*vide* expt.). Physical characteristics of all the new tosylhydrazones (**2**) related to our exploitation are tabulated in Table 1.

We then attempted reductions on **2a** by using sodium borohydride under diverse conditions [11,13]. In our hands, however, all these attempts were proved to be unsuccessful in the transformation of **2a** to **4a**. Now in search of a proper reduction protocol involving tosylhydrazones (**2**) to the desired tetrahydrocarbazoles, recently reported

Scheme 1. Conversion of 1-keto-1,2,3,4-tetrahydrocarbazoles **1** to carbazoles **3**.



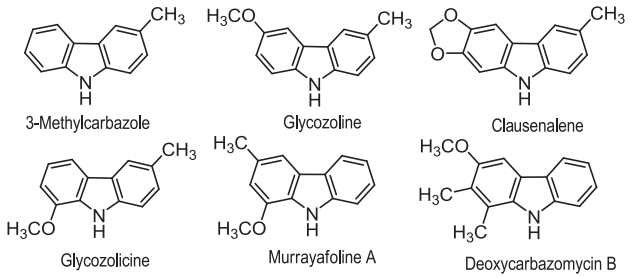


Figure 1. Representative carbazoles.

reduction [14] of α,β-unsaturated carbonyl compounds in solvent free condition using $NaBH_4$ supported over $MgSO_4{\cdot}7H_2O$ under microwave attracted our attention. Thus, **2a** was subjected to similar treatment. However, inconsistent yields were observed probably because of the decomposition of the product, under the reaction condition. In the course of such studies, a reduction [15] of an aromatic nitro-compound with $NaBH_4$ in the presence of Pd–C was noted. This led us to utilize $NaBH_4$ together with Pd–C on a solid support knowing fully well the fact that Pd–C is a reagent of choice for dehydrogenation [3] of tetrahydrocarbazoles to carbazoles. Accordingly, tosylhydrazone (**2a**) was treated with a combination of $NaBH_4$ and Pd–C on $MgSO_4{\cdot}7H_2O$ support, and the mixture was then subjected to microwave irradiation (100 W, 100°C, 50 psi) for 2 min. Then, usual work up led to the isolation of carbazole (**3a**) in excellent yield. As envisaged, to effect such tandem reduction–oxidation in solid phase under microwave (100 W, 100°C, 50 psi), several solid supports were tried, but satisfactory result was obtained only with $MgSO_4{\cdot}7H_2O$ (Table 2).

This method was found to be generalized by taking various tosylhydrazones (**2**) of appropriate 1-keto-tetrahydrocarbazoles (**1**), and the results are summarized in Table 3. The yields of carbazoles (**3**) almost in all cases are excellent.

The success of this protocol lies in the reduction of tosylhydrazone (**2a**) by $NaBH_4$ followed by aromatization of the intermediate (**4a**) to carbazole (**3a**) with Pd–C under microwave in a tandem manner (Scheme 2).

Evidently, this protocol prevents the decomposition of the intermediate 1,2,3,4-terahydrocarbazole (**4a**), as it undergoes dehydrogenation to carbazole (**3a**) through microwave acceleration. The rationale was supported by the fact that attempted dehydrogenation of 1,2,3,4-tetrahydrocarbazoles (**4**), prepared by an unambiguous method [16], was carried out by Pd–C supported on $MgSO_4{\cdot}7H_2O$ under microwave that afforded the desired carbazoles (**3**) (Scheme 3).

The protocol was successfully applied for the synthesis of several naturally occurring carbazole alkaloids such as 3-methylcarbazole (**3b**), glycozoline (**3m**), clausenalene (**3w**), glycozolicine (**3r**), and a carbazole derivative, deoxycarbazomycin B (**3y**). However, attempt to synthesize 3-nitrocarbazole from the corresponding tosylhydrazone (**2a′**) was unsuccessful as the nitro group does not survive under the reaction condition.

A total synthesis of murrayafoline A (**3x**) was then accomplished by taking 2-amino-5-methylanisole (**8**) as the key compound [8], obtained in a stepwise procedure from *m*-cresol (**5**) (Scheme 4). Diazotization of **8** followed by coupling with 2-hydroxymethylenecyclohexanone under Japp–Klingemann condition [3] furnished 2-(2-methoxy-4-methyphenyl)-hydrazonecyclohexanone (**9**). Acid catalyzed cyclization [3] of **9** afforded 8-methoxy-6-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-1-one (**10**), which was subsequently converted into the desired tosylhydrazone (**2x**) by treatment with tosylhydrazide. Finally, the target molecule **3x** was obtained using our newly developed protocol, tandem reduction–oxidation sequence under microwave, in very good yield (Scheme 4).

CONCLUSION

In summary, we have developed an efficient approach toward the synthesis of carbazoles from 1-keto-1,2,3,4-tetrahydrocarbazoles in two step route involving the

Table 1

Tosylhydrazones **2** from 1-keto-1,2,3,4-tetrahydrocarbazoles **1**.

Entry	1-Keto-1,2,3,4-tetrahydrocarbazoles **1**	Refluxing time (h)	Tosylhydrazones **2** (% yield)	Mp (°C)
1	**1a** $R_1=R_2=R_3=R_4=R_5=H$	4	**2a**[a] (92)	224
2	**1b** $R_1=R_2=R_3=R_5=H$, $R_4=CH_3$	4	**2b** (90)	251
3	**1c** $R_1=R_2=R_3=R_4=H$, $R_5=CH_3$	8	**2c** (74)	228
4	**1d** $R_2=R_3=R_4=R_5=H$, $R_1=CH_3$	5	**2d** (85)	238
5	**1e** $R_2=R_3=R_5=H$, $R_1=R_4=CH_3$	5	**2e**[a] (88)	215
6	**1f** $R_2=R_3=R_4=H$, $R_1=R_5=CH_3$	8	**2f** (74)	231
7	**1g** $R_1=R_2=R_4=R_5=H$, $R_3=CH_3$	4	**2g** (90)	239
8	**1h** $R_1=R_2=R_5=H$, $R_3=R_4=CH_3$	5	**2h** (88)	248
9	**1i** $R_1=R_2=R_4=H$, $R_3=R_5=CH_3$	10	**2i** (84)	184
10	**1j** $R_2=R_4=R_5=H$, $R_1=R_3=CH_3$	5	**2j** (85)	242
11	**1k** $R_2=R_5=H$, $R_1=R_3=R_4=CH_3$	5	**2k** (88)	235
12	**1l** $R_2=R_3=R_4=R_5=H$, $R_1=OCH_3$	4	**2l** (92)	241
13	**1m** $R_2=R_3=R_5=H$, $R_1=OCH_3$, $R_4=CH_3$	4	**2m**[a] (90)	245
14	**1n** $R_2=R_3=R_4=H$, $R_1=OCH_3$, $R_5=CH_3$	8	**2n** (72)	218
15	**1o** $R_1=R_3=R_4=R_5=H$, $R_2=OCH_3$	4	**2o**[a] (90)	213
16	**1p** $R_1=R_3=R_5=H$, $R_2=OCH_3$, $R_4=CH_3$	5	**2p** (88)	235
17	**1q** $R_1=R_2=R_4=R_5=H$, $R_3=OCH_3$	10	**2q** (86)	223
18	**1r** $R_1=R_2=R_5=H$, $R_3=OCH_3$, $R_4=CH_3$	5	**2r** (85)	221
19	**1s** $R_1=R_2=R_4=H$, $R_3=OCH_3$, $R_5=CH_3$	18	**2s** (67)	187
20	**1t** $R_3=R_4=R_5=H$, $R_1=R_2=OCH_3$	4	**2t**[a] (92)	240
21	**1u** $R_3=R_5=H$, $R_1=R_2=OCH_3$, $R_4=CH_3$	5	**2u** (90)	238
22	**1v** $R_3=R_4=R_5=H$, $R_1=R_2=OCH_2O$	5	**2v**[a] (84)	241
23	**1w** $R_3=R_5=H$, $R_1=R_2=OCH_2O$, $R_4=CH_3$	6	**2w** (90)	223
24	**1x** $R_2=R_4=R_5=H$, $R_3=OCH_3$, $R_1=CH_3$	5	**2x**[a] (88)	238
25	**1y** $R_4=R_5=H$, $R_1=OCH_3$, $R_2=R_3=CH_3$	5	**2y** (85)	258
26	**1z** $R_5=H$, $R_1=OCH_3$, $R_2=R_3=R_4=CH_3$	5	**2z**[a] (88)	254
27	**1a′** $R_2=R_3=R_4=R_5=H$, $R_1=NO_2$	5	**2a′** (85)	249

[a]Representative tosylhydrazones characterized by their spectral data in the experimental section.

Table 2

Screening of solid support.

Entry	Solid support	Microwave heating time (min)[a]	Yield (%)
1	$ZnSO_4·7H_2O$	5	50
2	$Na_2SO_4·10H_2O$	5	66
3	Na_2SO_4 (anhy.)	5	70
4	$MgSO_4$ (anhy.)	5	65
5	$MgSO_4·7H_2O$	5	90
6	None	5	45

[a]Tosylhydrazone **2** (1 mmol), $NaBH_4$ (20 mmol), Pd–C (10%, 100 mg), and 15 g solid support mixed thoroughly.

formation of corresponding tosylhydrazones followed by hither to unreported one-pot tandem reduction–oxidation sequence on the intermediate tosylhydrazones by using a combination of $NaBH_4$ and Pd–C on $MgSO_4·7H_2O$ support under microwave irradiation. The protocol was successfully extended toward the synthesis of several naturally occurring biologically active carbazole alkaloids as well. In addition, a new methodology for the dehydrogenation of 1,2,3,4-tetrahydrocarbazoles to carbazoles comes into the picture where the reagent is Pd–C on $MgSO_4·7H_2O$, a solid support through microwave assistance. The present study thus not only expands the application of two renowned reagents, $NaBH_4$ and Pd-C, in synthetically useful transformations but also unlocked a novel course to synthesize carbazoles in appreciable yields.

EXPERIMENTAL

General methods and materials. Melting points were determined in open capillaries and are uncorrected. Reagent-grade chemicals were purchased from a commercial source and used without further purification. Microwave reactions were carried out by using DISCOVER-Microwave Reactor CEM. Chemglass heavy wall cylindrical pressure vessels (15 mL) with a Teflon bushing as a pressure seal were used for the sealed tube studies. IR spectra were recorded in KBr disks on Shimadzu FTIR-8300, and NMR spectra were recorded on Bruker AV 300 and 500. Results of DEPT–^{13}C NMR experiments are shown in parentheses where "+" denotes CH_3 or CH and "–" denotes CH_2 or C. HRMS were performed on Qtof Micro YA263.

General experimental procedure for the preparation of tosylhydrazones of 1-keto-1,2,3,4-tetrahydrocarbazoles (2). A mixture of 1-keto-1,2,3,4-tetrahydrocarbazole derivative (**1**, 15 mmol) and tosylhydrazide (20 mmol) was taken in methanol (100–120 mL) and heated under reflux for 4–6 h. The resulting solution was then cooled to give **2**, a light yellow solid. It was washed with cold methanol, dried, and used in the next step without further purification.

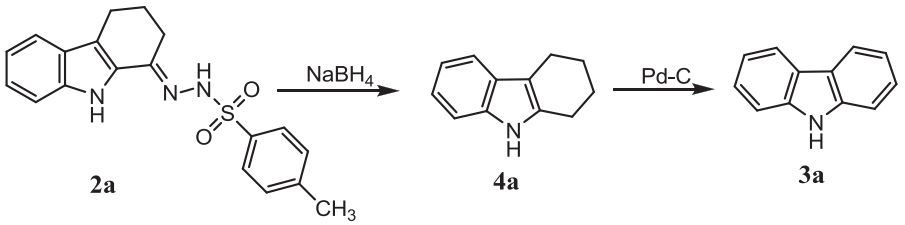
Table 3

Synthesis of carbazoles **3** from tosylhydrazones **2** through microwave assistance.

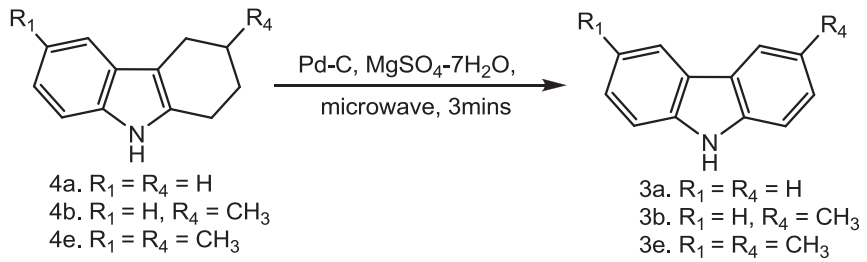
Entry	Tosylhydrazones **2**	Carbazoles **3**	Time[a] (min)	Yield (%)	Mp (lit. mp)[b] of carbazole (°C)
1	**2a**	**1a** $R_1=R_2=R_3=R_4=R_5=H$	2	90	246 (245–246) [8]
2[d]	**2b**	**1b** $R_1=R_2=R_3=R_5=H$, $R_4=CH_3$	3	86[c]	208 (207–208) [17]
3	**2c**	**1c** $R_1=R_2=R_3=R_4=H$, $R_5=CH_3$	4	88	264 (264–266) [17]
4[d]	**2d**	**1d** $R_2=R_3=R_4=R_5=H$, $R_1=CH_3$	5	87	208 (207–208) [17]
5	**2e**	**1e** $R_2=R_3=R_5=H$, $R_1=R_4=CH_3$	5	94	222 (217–218) [17]
6	**2f**	**1f** $R_2=R_3=R_4=H$, $R_1=R_5=CH_3$	3	84	224 (224–225.5) [16]
7	**2g**	**1g** $R_1=R_2=R_4=R_5=H$, $R_3=CH_3$	3	81	118 (121–121.7) [17]
8	**2h**	**1h** $R_1=R_2=R_5=H$, $R_3=R_4=CH_3$	4	80	173 (174–175.5) [17]
9	**2i**	**1i** $R_1=R_2=R_4=H$, $R_3=R_5=CH_3$	4	78	167 (166–168) [17]
10	**2j**	**1j** $R_2=R_4=R_5=H$, $R_1=R_3=CH_3$	4	90	97 (91–93) [17]
11	**2k**	**1k** $R_2=R_5=H$, $R_1=R_3=R_4=CH_3$	5	86[c]	125 (126) [18]
12	**2l**	**1l** $R_2=R_3=R_4=R_5=H$, $R_1=OCH_3$	5	72	153 (148–149) [8]
13[d]	**2m**	**1m** $R_2=R_3=R_5=H$, $R_1=OCH_3$, $R_4=CH_3$	5	75[c]	179 (178–179) [5]
14	**2n**	**1n** $R_2=R_3=R_4=H$, $R_1=OCH_3$, $R_5=CH_3$	5	73	123 (125–126) [8]
15	**2o**	**1o** $R_1=R_3=R_4=R_5=H$, $R_2=OCH_3$	5	75	236 (238–239) [8]
16	**2p**	**1p** $R_1=R_3=R_5=H$, $R_2=OCH_3$, $R_4=CH_3$	3	74	231 (228–229) [8]
17	**2q**	**1q** $R_1=R_2=R_4=R_5=H$, $R_3=OCH_3$	3	72	65 (65–67) [19,20]
18[d]	**2r**	**1r** $R_1=R_2=R_5=H$, $R_3=OCH_3$, $R_4=CH_3$	3	69[c]	149 (150) [7,21]
19	**2s**	**1s** $R_1=R_2=R_4=H$, $R_3=OCH_3$, $R_5=CH_3$	3	70	172 (172–174) [22,23]
20	**2t**	**1t** $R_3=R_4=R_5=H$, $R_1=R_2=OCH_3$	4	72	184 (184–186) [19]
21	**2u**	**1u** $R_3=R_5=H$, $R_1=R_2=OCH_3$, $R_4=CH_3$	5	71[c]	184 (185) [24]
22	**2v**	**1v** $R_3=R_4=R_5=H$, $R_1=R_2=OCH_2O$	5	72[c]	120
23[d]	**2w**	**1w** $R_3=R_5=H$, $R_1=R_2=OCH_2O$, $R_4=CH_3$	4	70[c]	223 (224–225) [6]
24[d]	**2x**	**1x** $R_2=R_4=R_5=H$, $R_3=OCH_3$, $R_1=CH_3$	4	65[c]	51 (51–53) [8]
25	**2y**	**1y** $R_4=R_5=H$, $R_1=OCH_3$, $R_2=R_3=CH_3$	3	75[c]	126 (128–129) [3]
26	**2z**	**1z** $R_5=H$, $R_1=OCH_3$, $R_2=R_3=R_4=CH_3$	3	73[c]	196

[a]MW 100 W, 100°C, 50 psi (max).
[b]References of carbazoles.
[c]Carbazoles characterized by their spectral data.
[d]Natural products.

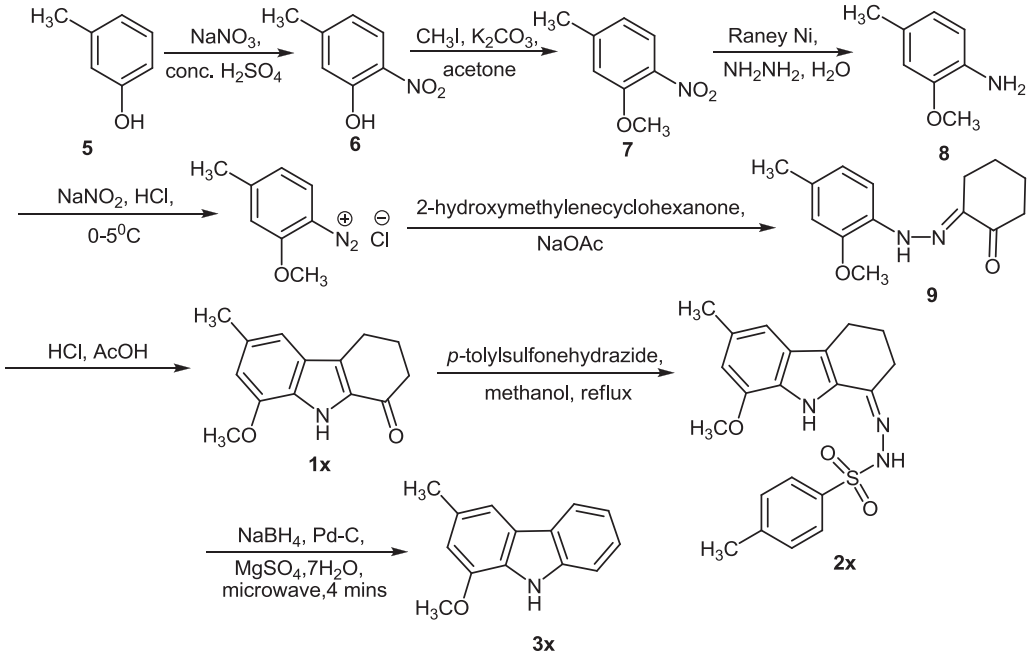
Scheme 2. Tandem reduction–oxidation of tosylhydrazone of 1-keto-1,2,3,4-tetrahydrocarbazole.



Scheme 3. Conversion of 1,2,3,4-tetrahydrocarbazoles **4** to carbazoles **3** through microwave.



Scheme 4. Total synthesis of murrayafoline A.



Representative spectral data of the tosylhydrazones.

Tosylhydrazone of 1-keto-1,2,3,4-tetrahydrocarbazole (2a). UV (MeOH): 314 nm. ^{1}H-NMR (DMSO-d_6, 500 MHz): δ 1.900 (quintet, 2H, C_3-H), 2.358 (s, 3H, Ar-CH_3), 2.549 (t, 2H, C_2-H), 2.731 (t, 2H, C_4-H), 6.975 (m, 1H, C_7-H), 7.149 (t, 1H, C_6-H), 7.392 (d, J = 10.50 Hz, 2H, *ortho*-Ar-CH_3), 7.414 (m, 1H, C_8-H), 7.470 (d, J = 8.00 Hz, 1H, C_5-H), 7.970 (d, J = 8.50 Hz, 2H, *ortho*-Ar-SO_2NH-), 10.347 (s, 1H, -$NHSO_2$-), 10.856 (s, 1H, N-H). ^{13}C-NMR (DMSO-d_6, 125 MHz): δ 20.66 (−), 21.45 (+), 23.29 (−), 25.87(−), 112.41 (+), 119.35 (+), 119.58 (+), 124.05 (+), 126.60 (−), 128.33 × 2 (+), 129.84 × 2 (+), 130.39 × 2 (−), 136.92 (−), 137.80 (−), 143.67 (−), 149.23 (−).

Tosylhydrazone of 3,6-dimethyl-1-keto-1,2,3,4-tetrahydrocarbazole (2e). UV (MeOH): 316 nm. ^{1}H-NMR (DMSO-d_6, 300 MHz): δ 1.102 (d, J = 4.35 Hz, 3H, C_3-CH_3), 2.022 (d, J = 10.15 Hz, 2H, C_2-H), 2.371 (s, 6H, Ar-CH_3), 2.487 (m, 1H, C_3-H), 2.825 (d, J = 10.77 Hz, 2H, C_4-H), 6.542 (d, J = 7.29 Hz, 1H, C_7-H), 6.806 (d, J = 8.32 Hz, 1H, C_8-H), 7.021 (s, 1H, C_5-H), 7.335 (d, J = 8.71 Hz, 2H, *ortho*-Ar-CH_3), 8.024 (d, J = 7.94 Hz, 2H, *ortho*-Ar-SO_2NH-), 10.294 (s, 1H, -$NHSO_2$-), 10.583 (s, 1H, N-H). ^{13}C-NMR (DMSO-d_6, 75 MHz): δ 21.44 (+), 21.61 (+), 21.72 (+), 29.07 (−), 30.90 (+), 33.82 (−), 102.72 (+), 113.45 (+), 114.56 (+), 119.05 (−), 126.74 (−), 128.41 × 2 (+), 129.84 × 2 (+), 130.69 (−), 133.32 (−), 136.79 (−), 143.67 (−), 146.27 (−), 149.75 (−).

Tosylhydrazone of 6-methoxy-3-methyl-1-keto-1,2,3, 4-tetrahydrocarbazole (2m). UV (MeOH): 320 nm. ^{1}H-NMR (DMSO-d_6, 300 MHz): δ 1.095 (d, J = 4.38 Hz, 3H, C_3-CH_3), 2.032 (d, J = 10.17 Hz, 2H, C_2-H), 2.26 (s, 3H, Ar-CH_3), 2.264–2.487 (m, 1H, C_3-H), 2.858 (d, J = 11.97 Hz, 2H, C_4-H), 3.73 (s, 3H, Ar-OCH_3), 6.79 (d, J = 7.23 Hz, 1H, C_7-H), 6.938 (s, 1H, C_5-H), 7.285 (d, J = 8.76 Hz, 2H, *ortho*-Ar-CH_3), 7.366 (d, J = 7.86 Hz, 2H, *ortho*-Ar-SO_2NH-), 7.944 (d, J = 7.95 Hz, 1H, C_8-H), 10.305 (s, 1H, -$NHSO_2$-), 10.683 (s, 1H, N-H). ^{13}C-NMR (DMSO-d_6, 75 MHz): δ 21.50 (+), 21.76 (+), 29.05 (−), 30.81(+), 33.90 (−), 55.79 (+), 100.79 (+), 113.18 (+), 114.56 (+), 118.64 (−), 126.69 (−), 128.32 × 2 (+), 129.82 × 2 (+), 130.72 (−), 133.15 (−), 136.88 (+), 143.64 (−), 149.27 (−), 153.75 (−).

Tosylhydrazone of 7-methoxy-1-keto-1,2,3,4-tetrahydrocarbazole (2o). UV (MeOH): 317 nm. ^{1}H-NMR (DMSO-d_6, 500 MHz): δ 1.891 (quintet, 2H, C_3-H), 2.347 (s, 3H, Ar-CH_3), 2.543 (t, 2H, C_2-H), 2.728 (t, 2H, C_4-H), 3.781 (s, 3H, Ar-OCH_3), 6.588 (s, 1H, C_8-H), 6.795 (d, J = 8.52 Hz, 1H, C_6-H), 7.257 (d, J = 8.54 Hz, 1H, C_5-H), 7.389 (d, J = 8.12 Hz, 2H, *ortho*-Ar-CH_3), 8.011 (d, J = 8.50 Hz, 2H, *ortho*-Ar-SO_2NH-), 10.342 (s, 1H, -$NHSO_2$-), 10.847 (s, 1H, N-H). ^{13}C-NMR (DMSO-d_6, 125 MHz): δ 20.57 (−), 21.54 (+), 23.35 (−), 29.47 (−), 55.82 (+), 110.31 (+), 113.35 (+), 124.55 (+), 126.67 (−), 128.34 × 2 (+), 129.85 × 2 (+), 130.39 (−), 131.49 (−), 135.82 (−), 137.47 (−), 141.67 (−), 148.23 (−), 151.75(−).

Tosylhydrazone of 6,7-dimethoxy-1-keto-1,2,3,4-tetrahydrocarbazole (2t). UV (MeOH): 321 nm. ^{1}H-NMR (DMSO-d_6, 500 MHz): δ 1.901 (quintet, 2H, C_3-2H), 2.332 (s, 3H, Ar-CH_3), 2.454 (t, 2H, C_2-H), 2.544 (t, 2H, C_4-H), 3.832 (s, 6H, Ar-OCH_3), 6.524 (s, 1H, C_8-H), 6.802 (s, 1H, C_5-H), 7.306 (d, J = 8.00 Hz, 2H, *ortho*-Ar-CH_3), 8.021 (d, J = 7.50 Hz, 2H, *ortho*-Ar-SO_2NH-), 10.320 (s, 1H, -$NHSO_2$-), 10.480 (s, 1H, N-H). ^{13}C-NMR (DMSO-d_6, 125 MHz): δ 21.97 (−), 21.57 (+), 25.45 (−), 26.23 (−), 55.71 (+), 56.50 (+), 110.68 (+), 114.47 (+), 119.86 (−), 126.33 (−), 128.75 (−), 128.54 × 2 (+), 129.53 (−), 129.81 × 2 (+), 133.34 (−), 137.57 (−), 141.55 (−), 148.14 (−), 149.67 (−).

Tosylhydrazone of 6,7-methylenedioxo-1-keto-1,2,3, 4-tetrahydrocarbazole (2v). UV (MeOH): 314 nm. ^{1}H-NMR (DMSO-d_6, 500 MHz): δ 2.10 (quintet, 2H, C_3-H), 2.312 (s, 3H, Ar-CH_3), 2.49 (t, 2H, C_2-H), 2.86 (t, 2H, C_4-H), 6.023 (s, 2H, Ar-OCH_2O-), 6.82 (s, 1H, C_8-H), 7.08 (s, 1H, C_5-H), 7.462 (d, J = 8.50 Hz, 2H, *ortho*-Ar-CH_3), 7.925 (d, J = 7.32 Hz, 2H, *ortho*-Ar-SO_2NH-), 10.570 (s, 1H, -$NHSO_2$-), 11.480 (s, 1H, N-H). ^{13}C-NMR (DMSO-d_6, 125 MHz): δ 21.44 (−), 21.57 (+), 25.16 (−), 38.29 (−), 92.67 (+), 98.85 (+), 101.04 (−), 119.66 (−), 128.91 (−), 130.98 (−), 128.54 × 2 (+), 129.53 (−), 129.81 × 2 (+), 135.54 (−), 138.87 (−), 141.55 (−), 143.14 (−), 148.67 (−).

Tosylhydrazone of 6-methoxy-3,7,8-trimethyl-1-keto-1,2,3, 4-tetrahydrocarbazole (2z). UV (MeOH): 314 nm. ^{1}H-NMR (DMSO-d_6, 500 MHz): δ 1.21 (d, J = 6.20 Hz, 3H, C_3-CH_3), 2.230 (s, 3H, Ar-CH_3), 2.245 (s, 3H, Ar-CH_3), 2.27 (s, 3H, Ar-CH_3), 2.49–2.65 (m, 3H, C_2-H and C_3-H), 3.10 (d, J = 12.90 Hz, 2H, C_4-H), 3.86 (s, 3H, Ar-OCH_3), 6.82 (s, 1H, C_5-H), 7.489 (d, J = 8.55 Hz, 2H, *ortho*-Ar-CH_3), 8.021 (d, J = 7.25 Hz, 2H, *ortho*-Ar-SO_2NH-), 10.380 (s, 1H, -NHSO_2-), 11.4042 (s, 1H, N-H). ^{13}C-NMR (DMSO-d_6, 125 MHz): δ 12.46 (+), 13.58 (+), 21.47 (+), 21.76 (+), 33.05 (+), 46.41 (−), 55.79 (+), 97.36 (+), 110.68 (−), 114.47 (−), 120.60 (−), 122.84 (−), 126.92 (−), 128.54 × 2 (+), 129.53 (−), 129.81 × 2 (+), 135.54 (−), 138.87 (−), 141.55 (−), 143.14 (−), 153.27 (−).

General experimental procedure for tandem reduction–oxidation of tosylhydrazone (2) using the combination of $NaBH_4$ and Pd–C on $MgSO_4 \cdot 7H_2O$ support under microwave irradiation. A solution of tosylhydrazone (**2**) (1 mmol) in dichloromethane–methanol mixture (2:1, 20 mL) was poured in $MgSO_4 \cdot 7H_2O$ (1.5 g) in a porcelain basin. Solvent was then evaporated at room temperature to obtain a dry mass, which was further dried in vacuum. To this mixture Pd–C (10%, 100 mg) was added and mixed intimately. After that, $NaBH_4$ (20 mmol) was added, mixed thoroughly, and dried in vacuum. This reaction mixture in four equal parts was then irradiated under microwave at 100 W power, 100°C, and 50 psi (max) for 2–5 min. During the reaction, pressure inside the reaction tube raised up to 30 psi. After completion, the whole reaction mixture was extracted with dry dichloromethane, the solvent was then evaporated to dryness, and the residue so obtained was chromatographed over silica gel (15 g) column using a mixture of *n*-hexane and dichloromethane as eluent to afford **3** as colorless solid. It was crystallized from *n*-hexane–dichloromethane mixture. In the case of methoxy carbazoles, particularly for the entry nos. **16**, **17**, **18**, **19**, **23**, and **24**, often isolation and purification was carried out through vacuum (0.5 mm of Hg) sublimation.

Spectral data of the unknown carbazoles and natural carbazole alkaloids.

3-Methyl-9H-carbazole (3b). IR (KBr): 3307 cm^{-1} (-NH). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 2.453 (s, 3H, C_3-CH_3), 7.181 (dd, J_1 = 8.17 Hz, J_2 = 0.78 Hz, 1 H, C_6-H), 7.281 (dd, J_1 = 8.07 Hz, J_2 = 0.67 Hz, 1H, C_2-H), 7.314 (m, 2H, C_1-H and C_7-H), 7.521 (d, J = 8.18 Hz, 1H, C_8-H), 7.862 (s, 1H, C_4-H), 8.100 (d, J = 8.00 Hz, 1H, C_4-H), 10.01 (br s, 1H, NH). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 21.46 (+), 100.04 (−), 111.41 (+) x 2C, 119.02 (+), 119.65 (+), 120.07 (+), 123.09 (−), 124.45 (+), 126.35 (+), 128.24 (−), 129.25 (−), 145.51 (−). HRMS: *m/z* calcd for $C_{13}H_{11}NNa$ $[M+Na]^+$ 204.0788; found 204.0785.

1,3,6-Trimethyl-9H-carbazole (3k). IR (KBr): 3310 cm^{-1} (-NH). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 2.493 (s, 3H, C_1-CH_3), 2.516 (s, 6H, C_3-CH_3 and C_6-CH_3), 7.194 (s, 1H, C_2-H), 7.210 (d, J = 7.19 Hz, 1H, C_7-H), 7.323 (d, J = 8.18 Hz, 1H, C_8-H), 7.684 (s, 1H, C_4-H), 7.817 (s, 1H, C_5-H), 10.10 (br s, 1H, NH). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 16.83 (+), 21.38 (+), 21.46 (+), 110.35 (+), 117.73 (+), 119.35 (−), 120.35 (+), 122.97 (−), 123.97 (−), 126.86 (+), 127.79 (+), 128.55 (−), 128.68 (−), 137.49 (−), 138.05 (−). HRMS: *m/z* calcd for $C_{15}H_{15}NNa$ $[M+Na]^+$ 232.1101; found 232.1100.

3-Methoxy-6-methyl-9H-carbazole (3m), glycozoline. IR (KBr): 3435 cm^{-1} (-NH). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 2.432 (s, 3H, C_6-CH_3), 3.843 (s, 3H, C_3-OCH_3), 7.171 (dd, J_1 = 8.10 Hz, J_2 = 0.76 Hz, 1H, C_2-H), 7.281 (dd, J_1 = 8.15 Hz, J_2 = 0.77 Hz, 1H, C_7-H), 7.414 (m, 2H, C_1 and C_8-H), 7.662 (s, 1H, C_4-H), 7.900 (s, 1H, C_5-H), 10.12 (br s, 1H, NH). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 21.36 (+), 55.32 (+), 99.04 (−), 110.41 (+), 112.51 (+) × 2C, 119.67 (+), 119.77 (−), 123.89 (+), 124.48 (−), 127.35 (+), 128.24 (−), 133.59 (−), 150.51 (−). HRMS: *m/z* calcd for $C_{14}H_{13}NONa$ $[M+Na]^+$ 234.0894; found 234.0890.

1-Methoxy-6-methyl-9H-carbazole (3r), glycozolicine. IR (KBr): 3485 cm^{-1} (–NH). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 2.422 (s, 3H, C_6-CH_3), 3.852 (s, 3H, C_1-OCH_3), 7.201 (m, 2H, C_2 and C_3-H), 7.271 (dd, J_1 = 8.15 Hz, J_2 = 0.77 Hz, 1H, C_7-H), 7.484 (d, J = 8.18 Hz, 1H, C_8-H), 7.662 (d, J = 8.12 Hz, 1H, C_4-H), 7.941 (s, 1H, C_5-H), 10.01 (br s, 1H, NH). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 21.30 (+), 55.36 (+), 99.15 (−), 110.38 (+), 112.48 (+) × 2C, 119.47 (+), 119.87 (−), 123.78 (+), 124.58 (−), 127.40 (+), 128.32 (−), 135.49 (−), 149.81 (−). HRMS: *m/z* calcd for $C_{14}H_{13}NONa$ $[M+Na]^+$ 234.0894; found 234.0892.

2,3-Dimethoxy-6-methyl-9H-carbazole (3u). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 2.511 (s, 3H, C_6-CH_3), 3.952 (s, 3H, Ar-OCH_3), 3.990 (s, 3H, Ar-OCH_3), 6.813 (s, 1H, C_1-H), 6.901(d, J = 7.88 Hz, 1H, C_7-H), 7.149 (d, J = 7.90 Hz, 1H, C_8-H), 7.495 (s, 1H, C_4-H), 7.74 (s, 1H, C_5-H), 10.18 (br s, 1H, NH). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 21.44 (+), 56.42 (+), 56.47 (+), 94.34 (+), 102.74 (+), 109.47 (−), 110.18 (+), 119.24 (+), 120.59 (−), 125.54 (+), 128.58 (−), 134.65 (−), 137.70 (−), 144.32 (−), 149.35 (−). HRMS: *m/z* calcd for $C_{15}H_{15}NO_2Na$ $[M+Na]^+$ 264.1000; found 264.1000.

5H-[1,3]-dioxolo[4,5-b]carbazole (3v). IR (KBr): 3402 cm^{-1} (-NH). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 6.008 (s, 2H, O-CH_2-O), 6.898 (s, 1H, C_1-H), 7.180 (m, 1H, C_6-H), 7.312 (m, 1H, C_7-H), 7.372 (d, J = 8.07 Hz, C_8-H), 7.437 (s, 1H, C_4-H), 7.909 (d, J = 7.81 Hz, 1H, C_5-H), 10.28 (1H, NH). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 92.08 (+), 99.52 (+), 102.56 (−), 110.55 (+), 116.54 (−), 119.29 (+), 119.33 (+), 123.69 (−), 124.28 (+), 134.90 (−), 139.47 (−), 142.52 (−), 147.34 (−). HRMS: *m/z* calcd for $C_{13}H_9NO_2Na$ $[M+Na]^+$ 234.0530; found 234.0527.

8-Methyl-5H-[1,3]-dioxolo[4,5-b]carbazole (3w), clausenalene. IR (KBr): 3410 cm^{-1} (-NH). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 2.410 (s, 3H, Ar-CH_3), 6.102 (s, 2H, O-CH_2-O), 6.902 (s, 1H, C_1-H), 7.282 (m, 1H, C_7-H), 7.363 (d, J = 8.07 Hz, C_8-H), 7.434 (s, 1H, C_4-H), 7.912 (s, 1H, C_5-H), 10.26 (br s, 1H, NH). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 21.28 (+), 92.13 (+), 99.57 (+), 102.59 (−), 110.61 (+), 117.64 (−), 119.22 (+), 119.87 (+), 124.20 (−), 125.47(−), 135.12 (−), 139.87 (−), 143.32 (−), 147.87 (−). HRMS: *m/z* calcd for $C_{14}H_{11}NO_2Na$ $[M+Na]^+$ 248.0687; found 248.0683.

3-Methoxy-1,2-dimethyl-9H-carbazole (3y), deoxycarbazomycin B. IR (KBr): 3428 cm^{-1} (-NH). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 2.343 (s, 3H, C_2-CH_3), 2.423 (s, 3H, C_1-CH_3), 3.947 (s, 3H, C_3-OCH_3), 7.181–7.582 (m, 1H, C_6-H, C_7-H and C_8-H), 7.358 (s, 1H, C_4-H), 7.904 (s, 1H, C_5-H). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 12.17 (+), 14.01 (+), 57.12 (+), 99.04 (+), 110.41 (+), 119.02(+), 119.87 (+), 120.07 (−), 124.09 (−), 124.38 (−), 126.35 (+), 128.24 (−), 134.59 (−), 137.96 (−), 152.51 (−). HRMS: *m/z* calcd for $C_{15}H_{15}NONa$ $[M+Na]^+$ 248.1051; found 248.1053.

3-Methoxy-1,2,6-trimethyl-9H-carbazole (3z). IR (KBr): 3425 cm^{-1} (-NH). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 2.343 (s, 3H, C_2-CH_3), 2.453 (s, 3H, C_6-CH_3), 2.523 (s, 3H, C_1-CH_3), 3.943 (s, 3H, C_3-OCH_3), 7.181 (dd, J_1 = 8.17 Hz, J_2 = 0.78 Hz, 1H, C_7-H), 7.314 (d, J = 8.18 Hz, 1H, C_8-H), 7.362 (s, 1H, C_4-H), 7.800 (s, 1H, C_5-H). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 12.27 (+), 13.88 (+), 21.46 (+), 56.32 (+), 99.04 (+), 110.41 (+), 119.02 (−), 119.87 (+), 120.07 (−), 124.09 (−), 124.38 (−), 126.35 (+), 128.24 (−), 134.59 (−),

137.96 (−), 152.51 (−). HRMS: *m/z* calcd for $C_{16}H_{17}NONa$ $[M+Na]^+$ 262.1207; found 262.1201.

General experimental procedure for aromatization of 1,2,3, 4-tetrahydrocarbazole (4) using Pd–C on $MgSO_4 \cdot 7H_2O$ support under microwave irradiation. A solution of **4** (1 mmol) in dichloromethane was poured in $MgSO_4 \cdot 7H_2O$ (1.5 g) in a porcelain basin. Solvent was then evaporated at room temperature to obtain a dry mass that was further dried under vacuum. To this, mixture Pd–C (10%, 100 mg) was added and mixed intimately. This reaction mixture in three equal parts was then irradiated under microwave at 100 W power, 120°C and 50 psi (max) for 2 min. During the reaction, pressure inside the reaction tube raised up to 20 psi. After cooling, the whole reaction mixture was extracted with dry dichloromethane, the solvent was then evaporated to dryness, and the residue so obtained was chromatographed over silica gel (15 g) column using a mixture of *n*-hexane and dichloromethane as eluent to afford **3** as colorless solid. It was crystallized from *n*-hexane–dichloromethane mixture.

Total synthesis of 1-methoxy-3-methylcarbazole 3x (murrayafoline A).

5-Methyl-2-nitrophenol (6). Concentrated sulfuric acid (13.6 mL) was added in thin stream to 40 mL of cold water, and then sodium nitrate (15 g, 175 mmol) was dissolved in diluted acid [25]. The reaction mixture was then cooled in ice–salt bath to 0°C. To this reaction, mixture *m*-cresol (10.8 mL, 100 mmol) was added dropwise with vigorous stirring maintaining the reaction temperature around 10°C. This stirring was continued for a further period of 2 h after complete addition of *m*-cresol. Sticky resinous mass thus obtained was poured in water, and the mixture was steam distilled. Distillate was extracted with ether (~5 × 100 mL), and after drying the ether extract over anhydrous Na_2SO_4, the light yellow colored product **6**, mp 54–55°C (Lit. [26] 55°C), was obtained in 30 % yield.

5-Methyl-2-nitroanisole (7). A mixture of **6** (1.53 g, 10 mmol), anhydrous potassium carbonate (1.38 g, 100 mmol), and iodomethane (1.56 g, 11 mmol) were taken in 10 mL anhydrous acetone and refluxed for 5 h. The mixture was poured in cold water, and the resulting solution was extracted with dichloromethane (2 × 50 mL). After washing the organic layer with 5% KOH solution (20 mL) followed by brine solution (20 mL), it was dried over anhydrous sodium sulfate. On evaporation of the solvent, a light yellow colored compound **7** thus obtained was crystallized from dichloromethane–hexane mixture, mp 58–59°C (Lit [27] 58–60°C), in 94% yield.

2-Methoxy-4-methylaniline (8). **7** (1.67 g, 10 mmol) was dissolved in methanol (50 mL), and to this, solution Raney nickel (~3 g) was added. The mixture was heated under reflux on a steam bath for 1 h during which methanolic solution of hydrazine hydrate (3 mL 60% hydrazine hydrate in 7 mL methanol) was added in dropwise. Heating was continued for a further period of 2 h, and the mixture was allowed to attain room temperature and filtered. Solvent was then removed to obtain a brown mass that was dissolved in 10% HCl solution (20 mL), filtrated, and basified with aq. ammonia. The resulting solution was then extracted with dichloromethane (100 mL), and the organic layer was dried over anhydrous sodium sulfate. After removal of solvent, the required amine [8] (**8**, 1.20 g, 87.5 % yield) was obtained and considered to be pure enough for the next step.

2-(2-Methoxy-4-methylphenyl)hydrazonocyclohexanone (9). To aqueous solution of sodium acetate (8.5 g, in 35 mL of water), 2-hydroxymethylenecyclohexanone [28] (5.40 g, 40 mmol) in methanol (50 mL) was added. The solution of 2-methoxy-4-methylphenyldiazonium chloride (prepared from 6.0 g, 40 mmol 2-methoxy-4-methylaniline) was added to the previous solution during 1 h with stirring, when red crystals of **9** were obtained. It was filtered, and the crude product (6.0 g) was utilized in the next step without further purification.

8-Methoxy-6-methyl-2,3,4,9-tetrahydro-1H-carbazol-1-one (1x). A mixture of **9** (6.0 g) was boiled with glacial acetic acid (40 mL) and conc. hydrochloric acid (10 mL) for 5 min and poured in ice–water (300 mL). The semisolid mass thus obtained was collected by filtration, washed with water, dried, and then chromatographed over silica gel (80 g) column. The eluent from hexane–dichloromethane (3:2) furnished a colorless solid that on crystallization from dichloromethane–hexane furnished colorless crystals of **1x** (3.2 g), mp 130–131°C. IR (KBr): ν = 3255, 2997, 2829, 1648 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 2.195–2.277 (quintet, 2H, C_3-2H), 2.442 (s, 3H, Ar-CH_3), 2.628 (t, 2H, C_4-2H), 2.949 (t, 2H, C_2-2H), 3.935 (s, 3H, Ar-OCH_3), 6.596 (s, 1H, C_6-H), 7.005 (s, 1H, C_5-H), 8.854 (br, 1H, N-H, exch). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 21.59 (−), 22.07 (+), 25.15 (−), 38.36 (−), 55.43 (+), 107.94 (+), 112.69 (+), 127.14 (−), 127.60 (−), 129.20 (−), 130.70 (−), 131.12 (−), 146.60 (−), 191.21 (−). HRMS: *m/z* calcd for $C_{14}H_{15}NO_2Na$ $[M+Na]^+$ 252.1000; found 252.1003.

Tosylhydrazone of 8-methoxy-6-methyl-2,3,4,9-tetrahydro-1H-carbazol-1-one (2x). The general procedure for the preparation of tosylhydrazones of 1-keto-1,2,3,4-tetrahydrocarbazoles (**2**) was employed to obtain the tosylhydrazone of 8-methoxy-6-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-1-one (**2x**), mp 238°C. UV (MeOH): 316 nm ^{1}H-NMR (DMSO-d_6, 500 MHz): δ 1.837 (quintet, 2H, C_3-2H), 2.327 (s, 6H, Ar-CH_3), 2.496 (t, 2H, C_2-2H), 2.644 (t, 2H, C_4-2H), 3.866 (s, 3H, Ar-OCH_3), 6.546 (s, 1H, C_7-H), 6.826 (s, 1H, C_5-H), 7.336 (d, J = 8.50 Hz, 2H, *ortho*-Ar-CH_3), 8.018 (d, J = 6.00 Hz, 2H, *ortho*-Ar-SO_2NH-), 10.205 (s, 1H, -$NHSO_2$-), 10.490 (s, 1H, N-H). ^{13}C-NMR (DMSO-d_6, 125 MHz): δ 20.97 (−), 21.57 (+), 22.11 (+), 23.35 (−), 26.02 (−), 55.71 (+), 106.68 (+), 111.67 (+), 119.76 (−), 126.27 (−), 128.25 (−), 128.58 × 2 (+), 129.13 (−), 129.81 × 2 (+), 130.32 (−), 137.07 (−), 143.57 (−), 146.44 (−), 149.33 (−).

1-Methoxy-3-methylcarbazole (3x), murrayafoline A. The general procedure for tandem reduction–oxidation of tosylhydrazone of 1-keto-1,2,3,4-tetrahydrocarbazole derivative using the combination of $NaBH_4$ and Pd–C on $MgSO_4 \cdot 7H_2O$ support under microwave irradiation was followed to synthesize Murrayafoline A (**3x**) from **2x**. The compound was isolated from the reaction mixture as a pale yellow liquid through vacuum (0.5 mm of Hg) sublimation. Yellow crystal, mp 51°C. IR (KBr): 3485 cm^{-1} (-NH). ^{1}H-NMR ($CDCl_3$, 500 MHz): 2.422 (s, 3H, C_3-CH_3), 3.852 (s, 3H, C_1-OCH_3), 6.832 (s, 1H, C_2-H), 7.282–7.355 (m, 1H, C_6-H), 7.482-7.501 (m, 2H, C_7 and C_8-H), 7.683 (s, 1H, C_4-H), 8.124 (d, J = 7.8 Hz, 1H, C_5-H), 10.11 (br s, 1H, NH). ^{13}C-NMR ($CDCl_3$, 125 MHz): 21.30 (+), 55.36 (+), 99.15 (−), 105.38 (+), 116.48 (+), 119.47 (+), 119.87 (−), 123.78 (+), 124.58 (−), 127.40 (+), 129.32 (+), 129.49 (−), 129.94 (−), 149.81 (−). HRMS; *m/z* calcd for $C_{14}H_{13}NONa$ $[M+Na]^+$ 234.0894; found 234.0893.

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