

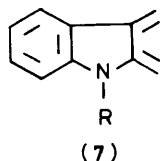
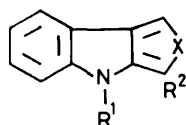
# Intramolecular 1,3-Dipolar Cycloaddition of Alkyl Azidoalkyldenemalonate and 1,3-Dipolar Cycloreversion of the Triazoline Intermediate: Synthesis and Reactions of an *N*-Sulphonyl-2,4-dihydropyrrolo[3,4-*b*]indole

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The 2,4-dihydropyrrolo[3,4-*b*]indole (**5**) was prepared by the intramolecular 1,3-dipolar cycloaddition of the azidoalkyldenemalonate (**11**), followed by 1,3-dipolar cycloreversion of the triazoline intermediates (**12**). Diels–Alder reaction of 2,4-dihydropyrrolo[3,4-*b*]indole derivative (**6**) with reactive dienophiles, such as *N*-phenylmaleimide, benzyne, and dimethyl acetylenedicarboxylate, gave the corresponding cycloadducts (**15**) and (**16**), (**17**), and (**20**) respectively. Arenimine (**17**) could be treated with lithium–ammonia to afford the dihydrobenzocarbazole (**18**), which was dehydrogenated by DDQ to give the benzocarbazole (**19**).

The novel heterocyclic ring system 2,4-dihydropyrrolo[3,4-*b*]indole present in compound (**1**), was first prepared by Welch during the lithium aluminium hydride reduction of 2-benzyl-4-phenyl-4*H*-pyrrolo[3,4-*b*]indol-3(2*H*)-one.<sup>1</sup> Closely related ring systems such as 4*H*-furo[3,4-*b*]indole (**2**),<sup>2</sup> 4*H*-thieno[3,4-*b*]indole (**3**),<sup>3</sup> and 4*H*-selenolo[3,4-*b*]indole (**4**)<sup>3</sup> have also been synthesized recently. These ring systems are of current interest mainly because they are of pharmaceutical importance,<sup>3</sup> but additionally they are stable cyclic analogues of indole-2,3-quinodimethane (**7**).<sup>4</sup> However, some of the cyclic analogues do not show marked diene character.<sup>1–4</sup> In particular the 2,4-dihydropyrrolo[3,4-*b*]indole derivative (**1**), the only compound prepared by Welch containing this ring system, was not found to undergo Diels–Alder reactions.<sup>1</sup>



- (1) X = NCH<sub>2</sub>Ph, R<sup>1</sup> = Ph, R<sup>2</sup> = H
- (2) X = O, R<sup>1</sup> = S(O)<sub>2</sub>Ph, R<sup>2</sup> = H
- (3) X = S, R<sup>1</sup> = C(=O)Ph, R<sup>2</sup> = Ph
- (4) X = Se, R<sup>1</sup> = C(=O)Ph, R<sup>2</sup> = Ph
- (5) X = NH, R<sup>1</sup> = S(O)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OMe-*P*, R<sup>2</sup> = H
- (6) X = NCO<sub>2</sub>Me, R<sup>1</sup> = S(O)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OMe-*P*, R<sup>2</sup> = H

As described earlier in a preliminary communication,<sup>5</sup> we have synthesized the new compounds (**5**) and (**6**), which contain the 2,4-dihydropyrrolo[3,4-*b*]indole ring system, by intramolecular 1,3-dipolar cycloaddition<sup>6</sup> of the azide (**11**)<sup>7</sup> followed by 1,3-dipolar cycloreversion<sup>8</sup> of the triazoline (**12**). We have also found that compound (**6**) reacted as a good diene system in Diels–Alder reactions with highly reactive dienophiles such as *N*-phenylmaleimide, benzyne, and dimethyl acetylenedicarboxylate (DMAD). Recently, we discovered that the deamination<sup>9</sup> of arenimine (**17**) could be accomplished by lithium–ammonia reduction, followed by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) dehydrogenation to give the benzocarbazole (**19**). Herein, we give our detailed study of, and experimental procedures for, this reaction.

## Results and Discussion

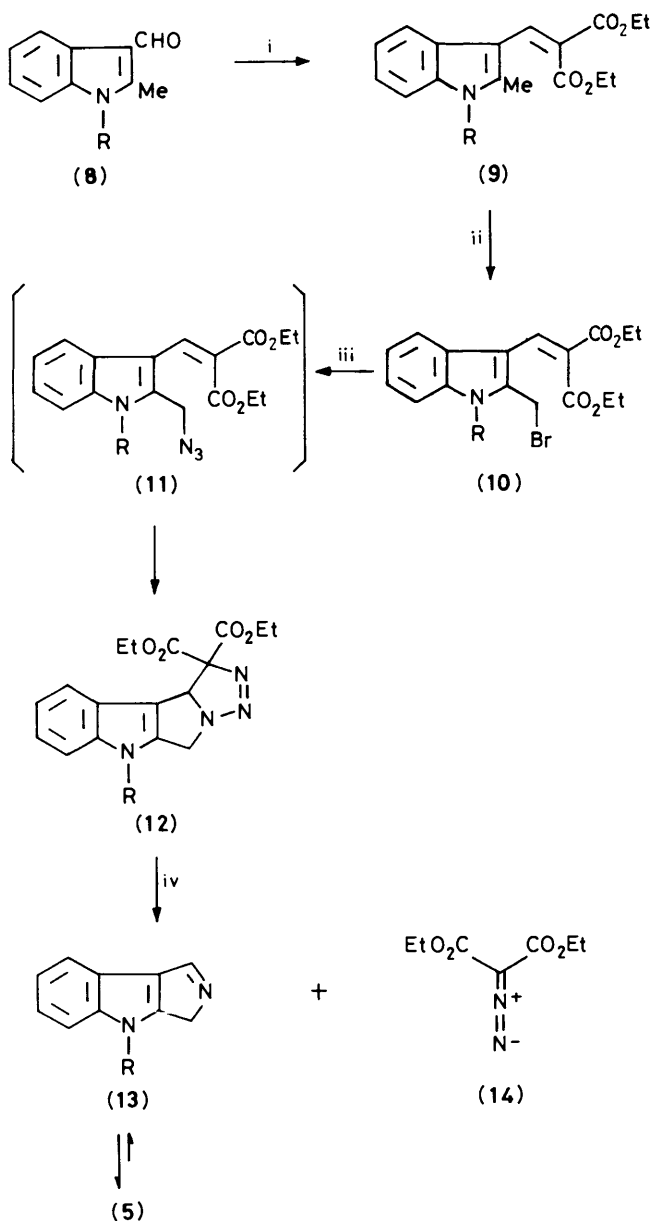
Knoevenagel condensation of the readily available formylindole (**8**) with diethyl malonate in benzene with piperidine afforded

compound (**9**). Bromination (allylic) of compound (**9**) with *N*-bromosuccinimide (NBS)–dibenzoyl peroxide in carbon tetrachloride gave bromide (**10**), which reacted with sodium azide in aqueous tetrahydrofuran (THF) to give the triazoline (**12**) directly. Presumably, displacement of bromide anion from compound (**10**) by azido anion produced the azide (**11**), which immediately underwent easy intramolecular 1,3-dipolar cycloaddition reaction to give the triazoline (**12**). Treatment of the triazoline (**12**) with a catalytic amount of toluene-*p*-sulphonic acid (PTSA) in THF at room temperature gave diethyl diazomalonate (**14**) and a more polar product, which was characterized spectroscopically as the 2,4-dihydropyrrolo[3,4-*b*]indole (**5**). We reasoned that acid-catalysed 1,3-dipolar cycloreversion of the triazoline (**12**) would give diethyl diazomalonate (**14**) and compound (**13**), which would tautomerize to give the more stable system (**5**), Scheme 1.

Subsequently, we studied the Diels–Alder reactions of the 2,4-dihydropyrrolo[3,4-*b*]indole (**5**). Attempted reaction of compound (**5**) by prolonged heating with either *N*-phenylmaleimide or benzyne in toluene led only to unchanged (**5**). On the basis of the reactivity of pyrrole derivatives as diene systems,<sup>10</sup> we concluded that the *N*-substituted derivatives of compound (**5**) should undergo Diels–Alder reaction. Thus, compound (**5**) was treated with potassium hydride and methyl chloroformate in THF to give the methoxycarbonyl derivative (**6**) (95%). Compound (**6**) was then heated with *N*-phenylmaleimide in refluxing THF, and the Diels–Alder reaction proceeded smoothly to give the *endo*-adduct (**15**) (57%) and the *exo*-adduct (**16**) (19%), Scheme 2. The Diels–Alder reaction of compound (**6**) with benzyne, generated from benzenediazonium-2-carboxylate, in refluxing THF (1 h) gave the adduct (**17**) (75%). Similarly, compound (**6**) was treated with DMAD in refluxing THF (10 h) to give the adduct (**20**) (52%). The difference between compounds (**5**) and (**6**) in their reactivity as dienes is in good accord with the reactivity of *N*-substituted pyrrole derivatives.<sup>10</sup>

Subsequently, we attempted the extrusion of the nitrogen atom at the imine bridge. All the known methods<sup>9</sup> when applied to arenimine (**17**) either gave low yields or involved too many steps. Finally, we found that lithium–ammonia reduction of arenimine (**17**) removed the imine bridge and the protecting group [–S(O)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OMe-*p*] in one step to give 6,11-dihydro-5*H*-benzo[*b*]carbazole (**18**) cleanly (95%). Compound (**18**) was then dehydrogenated by DDQ to give the benzocarbazole (**19**) (80%), Scheme 2.

Other applications of this 1,3-dipolar cycloaddition and cycloreversion reaction to prepare isocondensed pyrrolo-heterocycles, such as substituted isoindoles, pyrrolo[3,4-*b*]pyri-

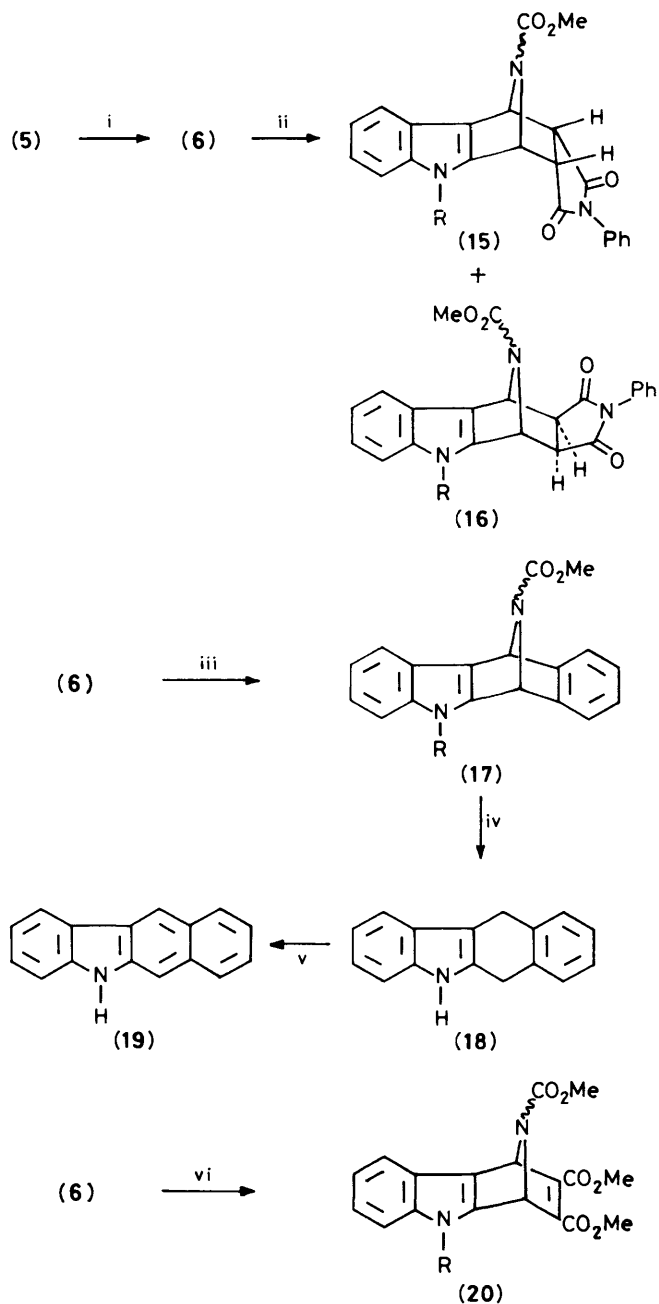


**Scheme 1.** R = S(O)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OMe-*p*. Reagents: i, CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub>, piperidine, benzene; ii, NBS, (PhCO<sub>2</sub>)<sub>2</sub>, CCl<sub>4</sub>; iii, NaN<sub>3</sub>, THF; iv, PTSA (cat.), THF

dines, pyrrolo[3,4-*c*]pyridines, and thieno[3,4-*c*]pyrroles are under investigation, and will be reported in due course.

### Experimental

**General.**—I.r. spectra were recorded on a Perkin-Elmer 710B, 580, or 781 i.r. spectrometer. <sup>1</sup>H N.m.r. spectra were recorded at 90 MHz on a Varian EM-390 spectrometer, 100 MHz on a JEOL FX-100 FT spectrometer, and 400 MHz on a Bruker AM-400 spectrometer. <sup>13</sup>C N.m.r. spectra were recorded on a JEOL FX-100 FT spectrometer at 25.02 MHz. Mass spectra were recorded on a JEOL-D-100 mass spectrometer. Mass spectral data refer to the electron-impact mass spectrum unless otherwise noted. M.p.s were determined with a Fisher-Johns melting point block and are uncorrected. Chromatography was



**Scheme 2.** Reagents and conditions: i, ClCO<sub>2</sub>Me, KH; ii, *N*-phenylmaleimide, THF, heat; iii, C<sub>6</sub>H<sub>4</sub>(N<sub>2</sub><sup>+</sup>)CO<sub>2</sub><sup>-</sup>-1,2, THF, reflux; iv, Li, NH<sub>3</sub>(0); v, DDQ, benzene, reflux; vi, DMAD, THF, reflux

placed in a sintered glass funnel packed dry. Solvent was flushed through the silica gel under water-aspirator vacuum. The compound was deposited with a minimal amount of solvent and then eluted with solvent, with the water aspirator as the vacuum source. Diethyl ether and THF were distilled from potassium and sodium metal under nitrogen atmosphere with the corresponding benzophenone ketyl as the indicator. All reactions involving organometallic reagents were conducted under nitrogen atmosphere. Elemental analyses were carried out by the analytical chemistry laboratory at the Chung-Shan Institute of Science and Technology, Lungtan, Taiwan. 'Dry ice' refers to solid CO<sub>2</sub>.

*Diethyl*[2-*Methyl*-1-(*p*-methoxyphenylsulphonyl)indol-3-*yl*]-*methylenemalonate* (9).—To a solution of compound (8) (500 mg, 1.52 mmol) in dry benzene (25 ml) were added diethyl malonate (275 mg, 1.71 mmol) and piperidine (0.5 ml). The mixture was heated to reflux for 36 h with separation of water by a Dean–Stark tube. Benzene was then removed by simple distillation. The residue was chromatographed on silica gel (hexanes–ethyl acetate; 6:1) to give the title product (9) (551 mg, 77%),  $\nu_{\max}$  (CHCl<sub>3</sub>) 1 720 and 1 600 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (100 MHz; CDCl<sub>3</sub>) 0.83 (3 H, t, *J* 8 Hz, CH<sub>2</sub>Me), 1.32 (3 H, t, *J* 8 Hz, CH<sub>2</sub>Me), 2.60 (3 H, s, Me), 3.78 (3 H, s, OMe), 3.94 (2 H, q, *J* 8 Hz, CH<sub>2</sub>Me), 4.29 (2 H, q, *J* 8 Hz, CH<sub>2</sub>Me), 6.83 (2 H, d, *J*<sub>AB</sub> 9 Hz, ArH), 7.04–7.40 (3 H, m, ArH), 7.70 (2 H, d, *J*<sub>AB</sub> 9 Hz, ArH), 7.81 (1 H, s, CH=), and 8.00–8.20 (1 H, m, ArH); *m/z* 471 (*M*<sup>+</sup>, 36%), 226 (50), and 171 (100).

*Diethyl* [2-*Bromomethyl*-1-(*p*-methoxyphenylsulphonyl)indol-3-*yl*]-*methylenemalonate* (10).—To a solution of compound (9) (551 mg, 1.27 mmol) in carbon tetrachloride (10 ml) were added NBS (229 mg, 1.28 mmol) and dibenzoyl peroxide (8 mg). The reaction mixture was heated to reflux for 4 h, diluted with methylene dichloride (10 ml), and washed with water (2 × 10 ml). The organic layer was dried with anhydrous magnesium sulphate and concentrated. Silica gel chromatography (hexanes–ethyl acetate; 10:1) gave the bromide (10) (593 mg, 92%),  $\nu_{\max}$  (CHCl<sub>3</sub>) 1 725 and 1 600 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (100 MHz; CDCl<sub>3</sub>) 0.66 (3 H, t, *J* 8 Hz, CH<sub>2</sub>Me), 1.36 (3 H, t, *J* 8 Hz, CH<sub>2</sub>Me), 3.79 (3 H, s, OMe), 3.86 (2 H, q, *J* 8 Hz, CH<sub>2</sub>Me), 4.32 (2 H, q, *J* 8 Hz, CH<sub>2</sub>Me), 5.04 (2 H, s, CH<sub>2</sub>Br), 6.82 (2 H, d, *J*<sub>AB</sub> 9 Hz, ArH), 7.04–7.46 (3 H, m, ArH), 7.83 (1 H, s, CH=), 7.82 (2 H, d, *J*<sub>AB</sub> 9 Hz, ArH), and 7.92–8.12 (1 H, m, ArH); *m/z* 551 (*M*<sup>+</sup> + 2, 3%), 549 (*M*<sup>+</sup>, 3), 470 (56), 225 (50), and 171 (100).

*Diethyl* 8-(*p*-Methoxyphenylsulphonyl)-3a,9-dihydro-3H,8H-[1',2',3']triazolo[1',5':1,5]pyrrolo[3,4-*b*]indole-3,3-dicarboxylate (12).—To a solution of compound (10) (253 mg, 0.46 mmol) in a mixture of THF (2 ml) and water (2 ml) was added sodium azide (90 mg, 1.38 mmol). The reaction mixture was stirred at room temperature for 36 h, and THF was removed on a rotary evaporator. The aqueous residue was extracted with methylene dichloride (3 × 5 ml). The organic layers were combined, and dried with anhydrous magnesium sulphate. Concentration and silica gel chromatography (hexanes–ethyl acetate; 12:1) gave the tetracycle (12) (206 mg, 87%),  $\nu_{\max}$  (CHCl<sub>3</sub>) 1 745 and 1 600 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (100 MHz; CDCl<sub>3</sub>) 0.68 (3 H, t, *J* 8 Hz, CH<sub>2</sub>Me), 1.34 (3 H, t, *J* 8 Hz, CH<sub>2</sub>Me), 3.76 (3 H, s, OMe), 3.88 (2 H, q, *J* 8 Hz, CH<sub>2</sub>Me), 4.04–4.60 (2 H, m, CH<sub>2</sub>Me), 4.69, 4.72, 4.86, and 4.89 (1 H, dd, *J*<sub>AB</sub> 1.7, *J*<sub>AC</sub> 3 Hz, CHHN), 5.40, 5.42, 5.77, and 5.79 (1 H, dd, *J*<sub>AB</sub> 17, *J*<sub>AC</sub>, 3 Hz, CHHN), 5.71 (1 H, brs, NCH), 6.82 (2 H, d, *J*<sub>AB</sub> 9 Hz, ArH), 7.00–7.36 (3 H, m, ArH), 7.62 (2 H, d, *J*<sub>AB</sub> 9 Hz, ArH), and 7.80–7.94 (1 H, m, ArH);  $\delta_{\text{C}}$  (25.02 MHz; CDCl<sub>3</sub>) 13.07 (q, CH<sub>2</sub>CH<sub>3</sub>), 13.87 (q, CH<sub>2</sub>CH<sub>3</sub>), 51.86 (t, CH<sub>2</sub>N), 55.49 (q, OCH<sub>3</sub>), 62.58 (t, CH<sub>2</sub>Me), 63.11 (t, CH<sub>2</sub>Me), 65.39 (d, CHN), 92.05 (s), 113.91 (d), 114.37 (d), 119.47 (d), 120.41 (s), 123.34 (d), 124.22 (s), 124.39 (d), 128.44 (s), 128.61 (d), 138.81 (s), 139.86 (s), 163.71 (s), 164.17 (s), and 165.00 (s); *m/z* 484 (*M*<sup>+</sup> - 28, 3%), 326 (24), 155 (68), and 83 (100).

4-(*p*-Methoxyphenylsulphonyl)-2,4-dihydropyrrolo[3,4-*b*]indole (5).—To a solution of compound (12) (432 mg, 0.84 mmol) in THF (10 ml) was added PTSA (10 mg). The solution was stirred at room temperature for 5 min, and then diluted with methylene dichloride (30 ml). The solution was washed successively with water (2 × 10 ml) and brine (10 ml), and dried with anhydrous magnesium sulphate. Concentration and silica gel chromatography (hexanes–ethyl acetate; 5:1) gave the title compound (5) (227 mg, 82%) (Found: C, 62.5; H, 4.3; N, 8.4; S, 9.9. C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>S requires C, 62.56; H, 4.32; N, 8.58; S, 9.82%);

$\nu_{\max}$  (CHCl<sub>3</sub>) 1 590 and 1 500 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (100 MHz; CDCl<sub>3</sub>) 3.68 (3 H, s, OMe), 6.65 (2 H, d, *J*<sub>AB</sub> 9 Hz, ArH), 6.83–6.88 (1 H, m, ArH), 6.96–7.01 (1 H, m, ArH), 7.11–7.24 (2 H, m, ArH), 7.44–7.56 (1 H, m, ArH), 7.67 (2 H, d, *J*<sub>AB</sub> 9 Hz, ArH), 7.92–8.04 (1 H, m, ArH), and 8.34 (1 H, br s, NH);  $\delta_{\text{C}}$  [25.02 MHz; CDCl<sub>3</sub> + (CD<sub>3</sub>)<sub>2</sub>SO; 2:1] 54.20 (q, OMe), 98.85 (d), 104.94 (d), 112.67 (d), 113.67 (d), 115.49 (s), 119.12 (d), 122.52 (d), 123.10 (d), 124.10 (s), 127.15 (s), 127.44 (d), 129.78 (s), 141.03 (s), and 162.07 (s); *m/z* 326 (*M*<sup>+</sup>, 37%), 155 (100), and 128 (28).

*Methyl* 4-(*p*-Methoxyphenylsulphonyl)-2,4-dihydropyrrolo-[3,4-*b*]indole-2-carboxylate (6).—To a suspension of potassium hydride (12.5 mg, 0.31 mmol) in THF (1 ml) was added dropwise a solution of compound (5) (48 mg, 0.15 mmol) in THF (1 ml) at 0 °C. The reaction mixture was warmed up to room temperature and stirred for 1 h, and then cooled to 0 °C. Methyl chloroformate (37.8 mg, 0.4 mmol) was added. The reaction mixture was warmed up to room temperature and stirred for 1 h. Water (3 ml) was then added. After removal of THF on a rotary evaporator, the aqueous residue was extracted with methylene dichloride (3 × 3 ml). The combined extracts were dried with anhydrous magnesium sulphate and concentrated. Silica gel chromatography (hexanes–ethyl acetate; 5:1) gave the title carbamate (6) (54 mg, 95%), m.p. 145–147 °C (Found: C, 59.4; H, 4.1; N, 7.1; S, 8.5. C<sub>19</sub>H<sub>16</sub>N<sub>1</sub>O<sub>5</sub>S requires C, 59.37; H, 4.20; N, 7.29; S, 8.34%);  $\nu_{\max}$  (CHCl<sub>3</sub>) 1 745 and 1 600 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (100 MHz; CDCl<sub>3</sub>) 3.67 (3 H, s, ArOMe), 4.01 (3 H, s, CO<sub>2</sub>Me), 6.70 (2 H, d, *J*<sub>AB</sub> 9 Hz, ArH), 7.04–7.59 (5 H, m, ArH), 7.70 (2 H, d, *J*<sub>AB</sub> 9 Hz, ArH), and 7.89–8.01 (1 H, m, ArH);  $\delta_{\text{C}}$  (25.02 MHz; CDCl<sub>3</sub>) 54.26 (q, OCH<sub>3</sub>), 55.31 (q, OCH<sub>3</sub>), 101.31 (d), 107.70 (d), 113.91 (d), 114.78 (d), 121.05 (s), 121.64 (d), 123.05 (s), 123.81 (d), 126.68 (d), 128.49 (s), 128.67 (d), 133.24 (s), 143.61 (s), 150.99 (s), and 163.47 (s); *m/z* 384 (*M*<sup>+</sup>, 11%), 220 (100), and 205 (55).

*Diels–Alder Reaction of Compound (6) with Benzyne*.—To a solution of compound (6) (64.5 mg, 0.17 mmol) in THF (8 ml) was added benzenediazonium-2-carboxylate (49.7 mg, 0.34 mmol). The solution was heated to reflux for 1 h. Concentration and silica gel chromatography (hexanes–ethyl acetate; 8:1) afforded the adduct (17) (57.7 mg, 75%), m.p. 180–181 °C (Found: C, 65.4; H, 4.35; N, 6.1; S, 6.8. C<sub>25</sub>H<sub>20</sub>N<sub>2</sub>O<sub>5</sub>S requires C, 65.21; H, 4.38; N, 6.08; S, 6.96%);  $\nu_{\max}$  (CHCl<sub>3</sub>) 1 730 and 1 600 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (100 MHz; CDCl<sub>3</sub>) 3.66 (3 H, br s, CO<sub>2</sub>Me), 3.72 (3 H, s, OMe), 6.01 (1 H, br s, CH), 6.29 (1 H, br s, CH), 6.77–6.90 (4 H, m, ArH), 7.08–7.22 (3 H, m, ArH), 7.32–7.48 (2 H, m, ArH), and 7.72–8.04 (3 H, m, ArH); *m/z* 460 (*M*<sup>+</sup>, 65%) and 289 (100).

*Diels–Alder Reaction of Compound (6) with N-Phenylmaleimide*.—To a solution of compound (6) (50.7 mg, 0.13 mmol) in THF (5 ml) was added *N*-phenylmaleimide (68.5 mg, 0.39 mmol). The solution was heated to reflux for 5 h. Concentration and silica gel chromatography (hexanes–ethyl acetate; 8:1) gave *endo*-adduct (15) (50 mg, 57%), m.p. 154–155 °C and *exo*-adduct (16) (14 mg, 19%), m.p. 126–127 °C.

Spectral data for *endo*-adduct (15):  $\nu_{\max}$  (CHCl<sub>3</sub>) 1 725 and 1 600 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 3.69 (3 H, s, OMe), 3.76 (3 H, s, OMe), 3.80–4.10 (2 H, m, 2 × CHC=O), 5.78 (1 H, d, *J* 4 Hz, bridgehead H), 5.90–6.08 (2 H, m, ArH), 6.13 (1 H, d, *J* 4 Hz, bridgehead H), 6.80 (2 H, d, *J*<sub>AB</sub> 9 Hz, ArH), 6.90–7.52 (6 H, m, ArH), and 7.68–7.92 (3 H, m, ArH); *m/z* 384 (20%) and 173 (100).

Spectral data for *exo*-adduct (16):  $\nu_{\max}$  (CHCl<sub>3</sub>) 1 725, 1 715, and 1 600 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 2.90 (1 H, d, *J* 6.7 Hz, CHC=O), 3.08 (1 H, d, *J* 6.7 Hz, CHC=O), 3.65 (3 H, br s, OMe), 3.80 (3 H, s, OMe), 5.73 (1 H, br s, bridgehead H), 6.04 (1 H, br s, bridgehead H), 6.90 (2 H, d, *J*<sub>AB</sub> 8.4 Hz, ArH), 7.27–7.54 (8 H,

m, ArH), 7.94 (1 H, br s, ArH), and 8.02 (2 H, d,  $J_{AB}$  8.4 Hz, ArH);  $m/z$  384 (17%) and 173 (100).

**Diels–Alder Reaction of Compound (6) with Dimethyl Acetylenedicarboxylate.**—To a solution of compound (6) (94 mg, 0.24 mmol) in THF (10 ml) was added DMAD (116 mg, 0.81 mmol). The reaction mixture was heated to reflux for 10 h. Concentration and silica gel chromatography (hexanes–ethyl acetate, 2:1) gave the *adduct* (20) (67 mg, 53%), m.p. 201–202 °C (Found: C, 57.0; H, 4.3; N, 5.1; S, 6.05.  $C_{25}H_{22}N_2O_9S$  requires C, 57.03; H, 4.21; N, 5.32; S, 6.09%;  $\nu_{max}$ . (CHCl<sub>3</sub>) 1 725 and 1 595  $cm^{-1}$ ;  $\delta_H$  (90 MHz; CDCl<sub>3</sub>) 3.66 (3 H, s, OMe), 3.73 (3 H, s, OMe), 3.78 (3 H, s, OMe), 3.83 (3 H, s, OMe), 5.98 (1 H, s, bridgehead H), 6.26 (1 H, s, bridgehead H), and 6.75–8.05 (8 H, m, ArH);  $m/z$  526 ( $M^+$ , 40%), 384 (100), and 355 (64).

**6,11-Dihydro-5H-benzo[b]carbazole (18).**—Ammonia (10 ml) was distilled into a three-neck reaction flask equipped with a 'dry ice' condenser. The liquid ammonia was cooled to –78 °C with a 'dry ice'–acetone-bath. A solution of compound (17) (53.6 mg, 0.12 mmol) in THF (3 ml) was added, followed by lithium metal (21 mg, 3 mmol, cut in small pieces). The reaction mixture turned dark blue. The 'dry ice'–acetone-bath was removed. The reaction mixture was kept at reflux at –33 °C for 15 min, and was then cooled to –78 °C in the 'dry ice'–acetone-bath. Excess of solid ammonium chloride was added. The 'dry ice'–acetone-bath and condenser were removed. Ammonia was evaporated off in a fume hood. Water (20 ml) was added. The aqueous mixture was extracted with methylene dichloride (3 × 20 ml). The combined solution was dried with anhydrous magnesium sulphate and concentrated. Silica gel chromatography (hexanes–ethyl acetate; 5:1) gave the *title compound* (18) (26 mg, 95%) (Found: C, 87.8; H, 6.0; N, 6.4.  $C_{16}H_{13}N$  requires C, 87.64; H, 5.98; N, 6.39%;  $\nu_{max}$ . (CHCl<sub>3</sub>) 3 480 and 1 595  $cm^{-1}$ ;  $\delta_H$  (90 MHz; CDCl<sub>3</sub>) 4.15 (4 H, s, 2 × CH<sub>2</sub>), 7.00–7.80 (8 H, m, ArH), and 7.85 (1 H, br s, NH);  $m/z$  219 ( $M^+$ , 100%), 218 (44), and 217 (61).

**5H-Benzo[b]carbazole (19).**—To a solution of compound (18) (60 mg, 0.27 mmol) in benzene (10 ml) was added DDQ (85 mg, 0.37 mmol). The reaction mixture was heated to reflux for 14 h, cooled to room temperature, and diluted with methylene dichloride (10 ml). The solution was filtered through a short pad of silica gel and concentrated. The residue was chromatographed

on silica gel (hexanes–ethyl acetate; 5:1) to give the *title compound* (19) (48 mg, 80%). Compound (19) was recrystallized from benzene, m.p. 335–337 °C (Found: C, 88.7; H, 5.1; N, 6.3. Calc. for  $C_{16}H_{11}N$ : C, 88.45; H, 5.10; N, 6.45%;  $\nu_{max}$ . (KBr) 3 415, 1 645, and 1 615  $cm^{-1}$ ;  $\delta_H$  (400 MHz; CDCl<sub>3</sub>) 7.00–7.57 (5 H, m, ArH), 7.77 (1 H, s, ArH), 7.93 (1 H, d,  $J$  8.2 Hz, ArH), 7.98 (1 H, br s, NH), 8.05 (1 H, d,  $J$  8.2 Hz, ArH), 8.20 (1 H, d,  $J$  7.2 Hz, ArH), and 8.55 (1 H, s, ArH);  $m/z$  217 ( $M^+$ , 100%).

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