Pergamon

Tetrahedron 55 (1999) 6109–6118

TETRAHEDRON

Free Radical Reaction of ω-Allylsulfonylalkyl Substituted Aromatic Derivatives

Sheow-Fong Wang, Che-Ping Chuang*, and Wan-Hua Lee

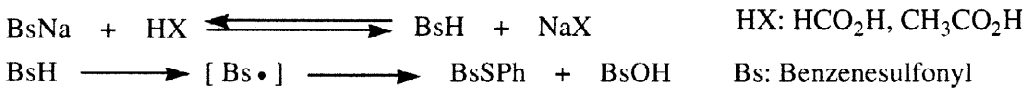
Department of Chemistry, National Cheng Kung University, Tainan, Taiwan, 70101, R.O.C.

Received 1 December 1998; revised 4 March 1999; accepted 18 March 1999

Abstract: Benzenesulfonyl radical can be generated from sodium benzenesulfinate in aqueous acetic acid or formic acid. A benzenesulfonyl radical induced radical reaction of ω-allylsulfonylalkyl substituted aromatic and heteroaromatic derivatives is described. Alkyl radicals can be generated efficiently from allylsulfones. This sulfonyl radical induced reaction provides a synthetically useful method for the synthesis of polycyclic aromatic and heteroaromatic derivatives.

INTRODUCTION

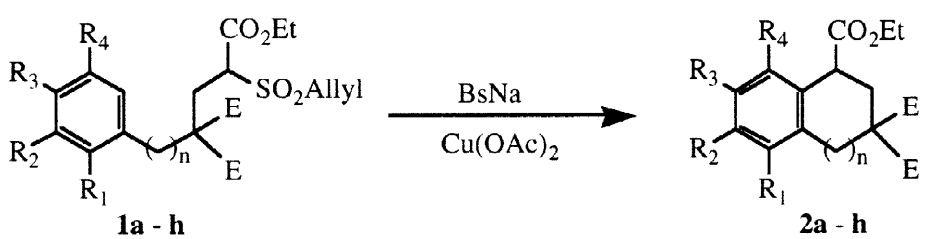
Free radical reactions mediated by sulfonyl radicals have been noted by several groups.[1,2] The α-scission of most alkanesulfonyl radicals to generate alkyl radicals is an unfavorable process, but if the alkyl group represents a stabilized radical, the extrusion of sulfur dioxide occurs readily.[3] The alkyl radicals generated from alkanesulfonyl radicals presumably can undergo free radical cyclization reaction. Benzenesulfonyl radical can be generated from sodium benzenesulfinate in aqueous acetic acid (Scheme 1).[4] This report describes the results of free radical reaction of ω-allylsulfonylalkyl substituted aromatic and heteroaromatic derivatives with sodium benzenesulfinate/copper(II) acetate.



Scheme 1

RESULTS AND DISCUSSION

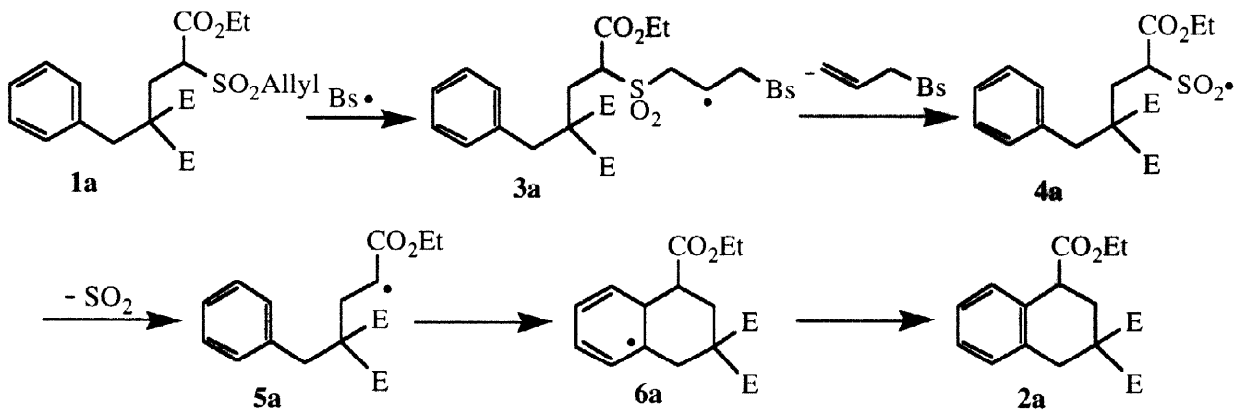
We began our studies by examining the reaction behaviour of **1a** (Eq. 1). Thus, treatment of **1a** with sodium benzenesulfinate (10 eq) and copper(II) acetate (2 eq) in 80% aqueous acetic acid at 90 °C gave **2a** in 89% yield. This free radical addition-cyclization reaction most likely proceeded *via* the mechanism shown in Scheme 2. Initiation occurs by benzenesulfonyl radical addition to **1a**, followed by the elimination of allylsulfonylbenzene to give sulfonyl radical **4a**, which is converted into **5a** by the extrusion of sulfur dioxide.



1a - h **2a - h** (Eq. 1)

PII: S0040-4020(99)00261-6

5a undergoes $Ar_2$6 cyclization and subsequent oxidation of radical intermediate **6a** to give tetrahydronaphthalene **2a**. The scope of this reaction is illustrated in Table 1. No product derived from $Ar_1$5 cyclization can be detected. Similar preference for $Ar_2$6 cyclization has been reported previously.[5,6,7] We also performed this reaction in 80% aqueous formic acid. In formic acid, this reaction proceeded much faster. This can be rationalized by the higher acidity of formic acid and therefore a higher concentration of benzenesulfinic acid is present in the reaction mixture by shifting the equilibration of Scheme 1 to the right. The tetrahydronaphthalene derivatives can be formed effectively by this sulfonyl radical induced reaction. We also studied the possibilities of $Ar_2$5 cyclizations with **1h**. When **1h** was treated with sodium benzenesulfinate and copper(II) acetate, reduction product **7** was obtained in 28% yield, which derived from the hydrogen atom abstraction of radical intermediate **5h**. No $Ar_2$5 cyclization product **2h** was observed. These results show that the $Ar_2$6 cyclizations are easier than those of $Ar_2$5 processes. Similar results have been reported by Citterio.[7]

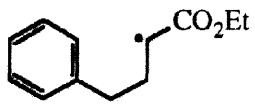


Scheme 2

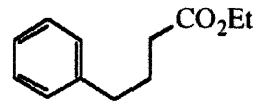
Table 1: Free Radical Reactions of ω-Allylsulfonylalkyl Substituted Aromatic Derivatives

Entry		Substrate						Solvent	Time	Product (Yield)
		E	R_1	R_2	R_3	R_4	n			
a	**1a**	CO_2Pr^i	H	H	H	H	1	acetic acid	24h	**2a** (89%)
								formic acid	4h	**2a** (92%)
b	**1b**	CO_2Pr^i	H	H	Me	H	1	acetic acid	24h	**2b** (90%)
								formic acid	4h	**2b** (94%)
c	**1c**	CO_2Pr^i	H	H	Cl	H	1	acetic acid	24h	**2c** (93%)
								formic acid	4h	**2c** (90%)
d	**1d**	CO_2Pr^i	H	H	Br	H	1	acetic acid	24h	**2d** (90%)
								formic acid	4h	**2d** (90%)
e	**1e**	CO_2Me	H	H	OMe	H	1	formic acid	24h	**2e** (81%)
								formic acid	4h	**2e** (85%)
f	**1f**	CO_2Me	OMe	H	H	OMe	1	formic acid	4h	**2f** (59%)
g	**1g**	CO_2Me	OMe	Me	Me	OMe	1	formic acid	4h	**2g** (60%)
h	**1h**	H	H	H	H	H	0	formic acid	4h	**7** (28%)

The free radical cyclization reactions of carbon centered radicals onto heterocyclic rings have been studied by several groups.[8] In order to extend this study to the formation of heteroaromatic derivatives, we also studied this benzenesulfonyl radical initiated with **8a** (Eq. 2). The reaction of **8a** with sodium benzenesulfinate (10 eq) and copper(II) acetate (2 eq) in 80% aqueous acetic acid at 90 °C gave **9a** in 73% yield. This reaction proceeded

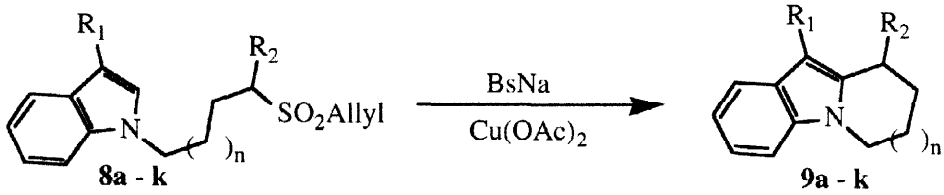


5h



7

much faster in formic acid. This free radical addition-cyclization reaction most likely proceeded *via* the radical intermediate **10a**. The scope of this reaction is illustrated in Table 2 (entries a - g). With R_2=CO_2Et or SO_2Ph, this reaction proceeded in good yields (entries a - e). On the other hand, with R_2=H, the reaction yields are rather poor (entries f and g). These results presumably can be ascribed to the stability of the radical intermediate **10**. With radical stabilizing groups, *i.e.* R_2=CO_2Et and SO_2Ph, radical intermediate **10** can be generated much more efficiently. We then studied the possibilities of Ar_25 and Ar_27 cyclizations. When **8h** (n=0) was treated with sodium benzenesulfinate and copper(II) acetate, the five-membered ring product **9h** derived from the Ar_25



8a - k **9a - k** (Eq. 2)

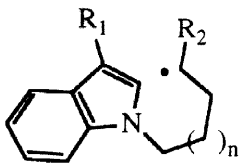
Table 2: Free Radical Reactions of ω-Allylsulfonylalkyl Substituted Heteroaromatic Derivatives

Entry		Substrate			Solvent	Time	Product (Yield)		
a	**8a**	R_1=COMe	R_2=CO_2Et	n=1	acetic acid	24h	**9a** (73%)		
					formic acid	3h	**9a** (94%)		
b	**8b**	R_1=COMe	R_2=SO_2Ph	n=1	acetic acid	24h	**9b** (80%)		
					formic acid	3h	**9b** (79%)		
c	**8c**	R_1=CN	R_2=CO_2Et	n=1	formic acid	3h	**9c** (84%)		
d	**8d**	R_1=CN	R_2=SO_2Ph	n=1	acetic acid	24h	**9d** (77%)		
					formic acid	3h	**9d** (86%)		
e	**8e**	R_1=CO_2Me	R_2=CO_2Et	n=1	acetic acid	39h[a]	**9e** (87%)		
					formic acid	3h	**9e** (87%)		
f	**8f**	R_1=CO_2Me	R_2=H	n=1	acetic acid	48h[a]	**9f** (50%)		
					formic acid	5h[b]	**9f** (33%)		
g	**8g**	R_1=COMe	R_2=H	n=1	acetic acid	33h[a]	**9g** (45%)		
					formic acid	4h	**9g** (25%)		
h	**8h**	R_1=CO_2Me	R_2=CO_2Et	n=0	formic acid	3h	**9h** (52%)		
i	**8i**	R_1=CO_2Me	R_2=CO_2Et	n=2	formic acid	4h	**9i** (42%)	**11a**	(17%)
j	**8j**	R_1=COMe	R_2=CO_2Et	n=2	formic acid	3h	**9j** (43%)	**11b**	(18%)
k	**8k**	R_1=CN	R_2=CO_2Et	n=2	formic acid	2h	**9k** (40%)	**11c**	(15%)
l	**12a**	R=CO_2Et			formic acid	6h[b]	**15a** (71%)		
m	**12b**	R=SO_2Ph			formic acid	4h	**15b** (64%)		
n	**13a**	R=CO_2Et			formic acid	2h	**16a** (66%)		
o	**13b**	R=SO_2Ph			formic acid	2h	**16b** (79%)		
p	**14**	R=CO_2Et	E=CO_2Me		formic acid	2h	**17** (88%)		

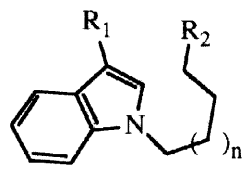
a. After heating for 24 h, another 10 eq of sodium benzenesulfinate and 2 eq of copper(II) acetate were added.

b. After heating for 4 h, another 10 eq of sodium benzenesulfinate and 2 eq of copper(II) acetate were added.

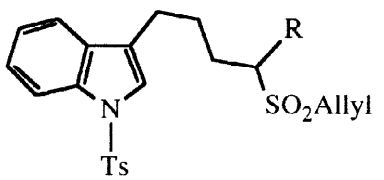
cyclization of radical intermediate **10h** was obtained in poorer yield (entry h) than the corresponding six-membered ring product **9e** (entry e). With n=2, the seven-membered ring product **9** derived from the Ar_27 cyclization of radical intermediate **10** was isolated along with the reduction product **11** (entries i - k). This demonstrates that the Ar_26 cyclizations of indole derivatives are easier than the Ar_25 cyclizations and these, in turn, are easier than the Ar_27 cyclizations. With **12**, under similar reaction conditions, tetrahydrocarbazoles **15** can also be formed (entries l and m). This radical cyclization reaction is also effective for pyrrole and thiophene derivatives. With **13a**, **13b** and **14**, the corresponding cyclization products **16a**, **16b** and **17** were produced in good yields (entries n - p).



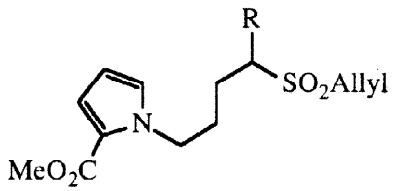
10a - k



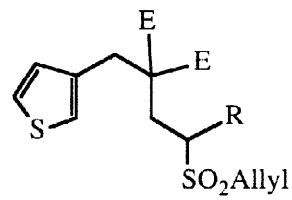
11a - c



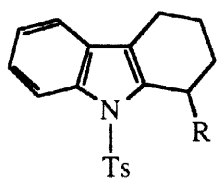
12a - b



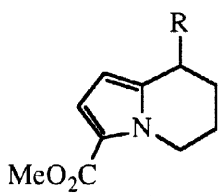
13a - b



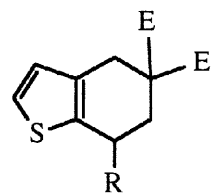
14



15a - b



16a - b



17

CONCLUSION

Alkyl radicals can be generated efficiently from allylsulfones. This sodium benzenesulfinate/copper(II) acetate reaction provides a synthetically useful method for the synthesis of polycyclic aromatic and heteroaromatic derivatives. The Ar_26 cyclizations are more facile than those of the Ar_25 and Ar_27 processes. This reaction proceeded much faster in aqueous formic acid than in aqueous acetic acid.

EXPERIMENTAL

Melting points were taken on a Thomas Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were taken with a Hitachi 260-30 spectrometer. Nuclear magnetic resonance spectra were recorded on a Bruker AC-200 or AMX-400 spectrometer. Elemental analyses were performed with a Heraeus CHN-Rapid Analyzer. Mass spectra were recorded with a Jeol JMS-SX/SX 102A mass spectrometer. All reactions were carried out under an atmosphere of nitrogen. Analytical thin-layer chromatography was performed on precoated silica gel 60 F-254 plates (0.25 mm thick) of EM Laboratories. Column chromatography was performed over EM Laboratories silica gel (70-230 mesh) using ethyl acetate-hexane mixture as eluent.

Typical experimental procedure for sulfonyl radical reaction: A solution of 151 mg (0.31 mmol) of **1a**, 520 mg (3.17 mmol) of sodium benzenesulfinate and 106 mg (0.66 mmol) of copper(II) acetate in 10 ml of 80% aqueous formic acid was heated in a 90 °C oil bath for 4 h. The reaction mixture was diluted with 50 ml of

ethyl acetate, washed with three 50-mL portions of aqueous saturated sodium bicarbonate, three 25-mL portions of water, dried (Na_2SO_4) and concentrated in vacuo. The residue was chromatographed over 20 g of silica gel (eluted with ethyl acetate-hexane, 1:3) to give 109 mg (92%) of **2a** as a single product.

2,4-Dihydro-3,3-diisopropoxycarbonyl-1-ethoxycarbonyl-1*H*-naphthalene 2a: white crystals; mp 44-45 °C; IR ($CHCl_3$) 2985, 1730, 1375, 1305, 1270, 1240, 1180, 1105 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.05 (d, *J*= 6.3 Hz, 3H, CH_3), 1.17 (d, *J*= 6.3 Hz, 3H, CH_3), 1.25 (d, *J*= 6.3 Hz, 6H, CH_3), 1.28 (t, *J*= 7.2 Hz, 3H, CH_3), 2.40 (dd, *J*= 13.6, 10.6 Hz, 1H, CH), 2.75 (ddd, *J*= 13.6, 6.8, 2.3 Hz, 1H, CH), 3.19 (d, *J*= 16.0 Hz, 1H, CH), 3.34 (dd, *J*= 16.0, 2.3 Hz, 1H, CH), 4.00 (dd, *J*= 10.6, 6.8 Hz, 1H, CH), 4.14-4.27 (m, 2H, OCH_2), 4.92 (septet, *J*= 6.3 Hz, 1H, OCH), 5.08 (septet, *J*= 6.3 Hz, 1H, OCH), 7.10-7.20 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.1(q), 21.3(q), 21.4(q), 21.5(q), 31.3(t), 34.8(t), 43.3(d), 53.3(s), 61.0(t), 68.8(d), 69.2(d), 126.5(d), 127.0(d), 127.7(d), 129.1(d), 131.9(s), 133.8(s), 169.6(s), 170.7(s), 174.1(s); Anal. Calcd for $C_{21}H_{28}O_6$: C, 67.00; H, 7.50. Found: C, 67.05; H, 7.58.

2,4-Dihydro-3,3-diisopropoxycarbonyl-1-ethoxycarbonyl-7-methyl-1*H*-naphthalene 2b: white crystals; mp 56-57 °C; IR ($CHCl_3$) 2985, 1730, 1375, 1305, 1270, 1240, 1180, 1105 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.06 (d, *J*= 6.3 Hz, 3H, CH_3), 1.18 (d, *J*= 6.3 Hz, 3H, CH_3), 1.25 (d, *J*= 6.3 Hz, 6H, CH_3), 1.29 (t, *J*= 6.3 Hz, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.37 (dd, *J*= 13.5, 10.7 Hz, 1H, CH), 2.73 (ddd, *J*= 13.5, 6.8, 2.3 Hz, 1H, CH), 3.14 (d, *J*= 15.9 Hz, 1H, CH), 3.30 (dd, *J*= 15.9, 2.3 Hz, 1H, CH), 3.96 (dd, *J*= 10.7, 6.8 Hz, 1H, CH), 4.15-4.29 (m, 2H, CH_2), 4.92 (septet, *J*= 6.3 Hz, 1H, CH), 5.07 (septet, *J*= 6.3 Hz, 1H, CH), 6.95-7.02 (m, 3H, ArH); ^{13}C NMR ($CDC1_3$, 50.3 MHz) δ 14.2(q), 21.1(q), 21.35(q), 21.43(q), 21.5(q), 31.4(t), 34.5(t), 43.4(d), 53.4(s), 61.0(t), 68.7(d), 69.2(d), 128.0(d), 128.2(d), 129.0(d), 130.8(s), 131.7(s) 136.0(s), 169.7(s), 170.9(s), 174.2(s); Anal. Calcd for $C_{22}H_{30}O_6$: C, 67.67; H, 7.74. Found: C, 67.73; H, 7.72.

7-Chloro-2,4-dihydro-3,3-diisopropoxycarbonyl-1-ethoxycarbonyl-1*H*-naphthalene 2c: white crystals; mp 86-87 °C; IR ($CHCl_3$) 3015, 2985, 1730, 1375, 1305, 1265, 1240, 1180, 1105, 1080 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.06 (d, *J*= 6.3 Hz, 3H, CH_3), 1.18 (d, *J*= 6.3 Hz, 3H, CH_3), 1.250 (d, *J*= 6.3 Hz, 3H, CH_3), 1.251 (d, *J*= 6.3 Hz, 3H, CH_3), 1.30 (t, *J*= 7.1 Hz, 3H, CH_3), 2.37 (dd, *J*= 13.7, 10.4 Hz, 1H, CH), 2.74 (ddd, *J*= 13.7, 7.0, 2.2 Hz, 1H, CH), 3.13 (d, *J*= 16.1 Hz, 1H, CH), 3.30 (dd, *J*= 16.1, 2.2 Hz, 1H, CH), 3.96 (dd, *J*= 10.4, 7.0 Hz, 1H, CH), 4.14-4.30 (m, 2H,OCH_2), 4.92 (septet, *J*= 6.3 Hz, 1H, OCH), 5.07 (septet, *J*= 6.3 Hz, 1H, OCH), 7.06 (d, *J*= 8.2 Hz, 1H, ArH), 7.14 (dd, *J*= 8.2, 1.9 Hz, 1H, ArH), 7.20 (d, *J*= 1.9 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.1(q), 21.3(q), 21.4(q), 21.5(q), 31.0(t), 34.3(t), 43.1(d), 53.2(s), 61.3(t), 69.0(d), 69.4(d), 127.3(d), 127.9(d), 130.4(d), 132.1(s), 132.5(s), 133.7(s), 169.4(s), 170.5(s), 173.4(s); Anal. Calcd for $C_{21}H_{27}ClO_6$: C, 61.39; H, 6.62. Found: C, 61.37; H, 6.72.

7-Bromo-2,4-dihydro-3,3-diisopropoxycarbonyl-1-ethoxycarbonyl-1*H*-naphthalene 2d: white crystals; mp 77-78 °C; IR ($CHCl_3$) 2985, 1730, 1375, 1300, 1270, 1240, 1195, 1105 cm^{-1}; ^1H NMR ($CDC1_3$, 400 MHz) δ 1.07 (d, *J*= 6.3 Hz, 3H, CH_3), 1.18 (d, *J*= 6.3 Hz, 3H, CH_3), 1.251 (d, *J*= 6.3 Hz, 3H, CH_3), 1.252 (d, *J*= 6.3 Hz, 3H, CH_3), 1.30 (t, *J*= 7.1 Hz, 3H, CH_3), 2.37 (dd, *J*= 13.5, 10.7 Hz, 1H, CH), 2.74 (ddd, *J*= 13.7, 6.9, 2.3 Hz, 1H, CH), 3.11 (d, *J*= 16.2 Hz, 1H, CH), 3.29 (dd, *J*= 16.2, 2.3 Hz, 1H, CH), 3.96 (dd, *J*= 10.4, 6.9 Hz, 1H, CH), 4.16-4.30 (m, 2H, OCH_2), 4.93 (septet, *J*= 6.3 Hz, 1H, OCH), 5.07 (septet, *J*= 6.3 Hz, 1H, OCH), 7.01 (d, *J*= 8.2 Hz, 1H, ArH), 7.29 (ddm, *J*= 8.2, 1.8 Hz, 1H, ArH), 7.33-7.36 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.1(q), 21.3(q), 21.35(q), 21.43(q), 31.0(t), 34.4(t), 43.0(d), 53.1(s), 61.3(t), 68.9(d), 69.3(d), 120.1(d), 130.2(d), 130.6(d), 130.8(s), 133.0(s) 134.1(s), 169.4(s), 170.4(s), 173.3(s); Anal. Calcd for $C_{21}H_{27}BrO_6$: C, 55.39; H, 5.98. Found: C, 55.35; H, 6.02.

2,4-Dihydro-3,3-dimethoxycarbonyl-1-ethoxycarbonyl-7-methoxy-1*H*-naphthalene 2e: white crystals; mp 86-87 °C; IR ($CHCl_3$) 3005, 2955, 1730, 1615, 1435, 1270, 1235, 1085, 1040 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.30 (t, J= 7.1 Hz, 3H, CH_3), 2.45 (dd, J= 13.6, 10.4 Hz, 1H, CH), 2.75 (ddd, J= 13.6, 6.7, 2.1 Hz, 1H, CH), 3.18 (d, J= 15.9 Hz, 1H, CH), 3.32 (dd, J= 15.9, 2.1 Hz, 1H, CH), 3.64 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 3.96 (dd, J= 10.4, 6.7 Hz, 1H, CH), 4.15-4.29 (m, 2H, OCH_2), 6.72-6.77 (m, 2H, ArH), 7.04 (d, J= 8.1 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.2(q), 31.2(t), 34.1(t), 43.4(d), 52.8(q), 52.9(q), 53.4(s), 55.2(q), 61.2(t), 112.6(d), 113.6(d), 125.5(s), 130.1(d), 132.6(s), 158.2(s), 170.8(s), 171.6(s), 173.7(s); Anal. Calcd for $C_{18}H_{22}O_7$: C, 61.71; H, 6.33. Found: C, 61.66; H, 6.37.

2,4-Dihydro-5,8-dimethoxy-3,3-dimethoxycarbonyl-1-ethoxycarbonyl-1*H*-naphthalene 2f: white crystals; mp 103-104 °C; IR ($CHCl_3$) 3005, 2955, 1730, 1480, 1465, 1435, 1295, 1260, 1180, 1110, 1090, 1075 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.25 (t, *J*= 7.1 Hz, 3H, CH_3), 2.30 (dd, *J*= 13.4, 9.9 Hz, 1H, CH), 2.76 (ddd, *J*= 13.4, 6.9, 1.6 Hz, 1H, CH), 2.99 (d, *J*= 17.1 Hz, 1H, CH), 3.45 (d, *J*= 17.1 Hz, 1H, CH), 3.68 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 3.78-3.85 (m, 1H, CH), 4.16 (q, *J*= 7.1 Hz, 2H, OCH_2), 6.63 (d, *J*= 8.8 Hz, 1H, ArH), 6.71 (d, *J*= 8.8 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.2(q), 28.8(t), 31.2(t), 39.6(d), 52.3(s), 52.79(q), 52.83(q), 55.5(q), 55.7(q), 60.6(t), 107.8(d), 108.8(d), 122.4(s), 124.3(s), 151.0(s), 151.1(s), 170.7(s), 171.5(s), 174.7(s); Anal. Calcd for $C_{19}H_{24}O_8$: C, 59.99; H, 6.36. Found: C, 59.90; H, 6.34.

2,4-Dihydro-5,8-dimethoxy-3,3-dimethoxycarbonyl-6,7-dimethyl-1-ethoxycarbonyl-1*H*-naphthalene 2g: white crystals; mp 73-74 °C; IR ($CHCl_3$) 3025, 2955, 1730, 1455, 1300, 1245, 1210, 1200, 1180, 1085 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.28 (t, *J*= 7.1 Hz, 3H, CH_3), 2.13 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.26 (dd, *J*= 13.4, 10.0 Hz, 1H, CH), 2.78 (ddd, *J*= 13.4, 6.9, 1.7 Hz, 1H, CH), 3.01 (d, *J*= 16.7 Hz, 1H, CH), 3.53 (dd, *J*= 16.7, 1.7 Hz, 1H, CH), 3.58 (s, 3H, OCH3), 3.68 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.87 (dd, *J*= 10.0, 6.9 Hz,1H, CH), 4.11-4.27 (m, 2H, OCH_2); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 12.66(q), 12.74(q), 14.2(q), 29.1(t), 31.7(t), 39.7(d), 52.71 (q), 52.75(d), 52.9 (q), 59.7 (q), 60.0 (q), 60.7(t), 123.9(s), 125.3(s), 128.6(s), 130.0(s), 151.9(s), 152.3(s), 170.7(s), 171.6(s), 174.7(s); Anal. Calcd for $C_{21}H_{28}O_8$: C, 61.75; H, 6.91. Found: C, 61.65; H, 6.80.

10-Acetyl-9-ethoxylcarbonyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole 9a: white crystals; mp 81-83 °C; IR ($CHCl_3$) 3005, 1730, 1635, 1510, 1460, 1435, 1320, 1180, 1155 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.29 (t, *J*= 7.1 Hz, 3H, CH_3), 2.07-2.22 (m, 3H, CH and CH_2), 2.30-2.38 (m, 1H, CH), 2.69 (s, 3H, CH_3), 3.93-4.03 (m, 1H, CH), 4.21 (q, *J*= 7.1 Hz, 2H, OCH_2), 4.29 (dt, *J*= 12.4, 4.2 Hz, 1H, NCH), 4.55-4.61 (m, 1H, NCH), 7.27-7.34 (m, 2H, ArH), 7.37 (dm, *J*= 7.0 Hz, 1H, ArH), 7.91 (dm, *J*= 7.0 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.2(q), 19.5(t), 24.1(t), 30.9(q), 41.6(d), 42.3(t), 61.0(t), 109.8(d), 113.7(s), 120.4(d), 122.0(d), 122.4(d), 125.8(s), 136.1(s), 141.9(s), 172.3(s), 193.8(s); Anal. Calcd for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.55; H, 6.69; N, 4.99.

10-Acetyl-9-benzenesulfonyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole 9b: white crystals; mp 149-150 °C; IR ($CHCl_3$) 3005, 1645, 1510, 1450, 1425, 1375, 1345, 1310, 1145, 1080 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.01-2.13 (m, 1H, CH), 2.13-2.28 (m, 1H, CH), 2.90-3.04 (m, 2H, CH_2), 4.06 (ddd, *J*= 12.6, 8.6, 6.0 Hz, 1H, NCH), 4.42-4.51 (m, 1H, NCH), 5.95-6.01 (m, 1H, CH), 7.31 (td, *J*= 7.3, 1.3 Hz, 1H, ArH), 7.35 (td, *J*= 7.3, 1.3 Hz, 1H, ArH), 7.45 (t, *J*= 7.7 Hz, 2H, ArH), 7.48 (dm, *J*= 7.3 Hz, 1H, ArH), 7.61 (t, *J*= 7.7 Hz, 1H, ArH), 7.73 (d, *J*= 7.7 Hz, 2H, ArH), 7.83 (dm, *J*= 7.3 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 18.7(t), 19.9(t), 31.1(q), 41.5(t), 57.9(d), 110.3(d), 115.7(s), 120.7(d), 122.5(d), 123.0(d), 125.5(s), 128.6(d), 129.4(d), 133.6(d), 133.9(s), 137.0(s), 137.7(s), 193.8(s); Anal. Calcd for $C_{20}H_{19}NO_3S$: C, 67.97; H, 5.42; N, 3.96. Found: C, 67.90; H, 5.44; N, 3.86.

10-Cyano-9-ethoxycarbonyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole 9c: pale yellow liquid; IR ($CHCl_3$) 3005, 2965, 2215, 1730, 1480, 1455, 1435, 1360, 1320, 1265, 1250, 1180 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.31 (t, *J*= 7.1 Hz, 3H, CH_3), 2.03-2.16 (m, 2H, CH_2), 2.19-2.33 (m, 1H, CH), 2.35-2.44 (m, 1H, CH), 3.91-4.00 (m, 1H, CH), 4.16-4.31 (m, 4H, NCH_2 and OCH_2), 7.23-7.36 (m, 3H, ArH), 7.66-7.71 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 13.9(q), 19.7(t), 23.5(t), 39.7(d), 42.2(t), 61.8(t), 84.6(s), 109.8(d), 115.6(s), 118.9(d), 122.3(d), 123.0(d), 127.2(s), 135.1(s), 141.2(s), 170.6(s); mass spectrum, m/e (relative intensity) 268(M^+, 23), 239(1), 211(1), 195(100), 140(9); exact mass calcd for $C_{16}H_{16}N_2O_2$: m/e 268.1212, found m/e 268.1207.

9-Benzenesulfonyl-10-cyano-6,7,8,9-tetrahydropyrido[1,2-*a*]indole 9d: white crystals; mp 205-206 °C; IR ($CHCl_3$) 3010, 2960, 2220, 1480, 1450, 1430, 1360, 1320, 1310, 1290, 1150 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.10-2.28 (m, 2H, CH_2), 2.87-3.13 (m, 2H, CH_2), 3.95-4.08 (m, 1H, CH), 4.41-4.54 (m, 1H, NCH), 4.75-4.86 (m, 1H, NCH), 7.30 (t, *J*= 7.6 Hz, 1H, ArH), 7.37 (t, *J*= 7.6 Hz, 1H, ArH), 7.42 (d, *J*= 7.6 Hz, 1H, ArH), 7.60 (t, *J*= 7.6 Hz, 2H, ArH), 7.65 (d, *J*= 7.6 Hz, 1H, ArH), 7.76 (t, *J*= 7.6 Hz, 1H, ArH), 7.80 (d, *J*= 7.6 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 18.4(t), 20.5(t), 42.0(t), 58.9(d), 87.7(s), 110.4(d), 113.9(s), 119.6(d), 122.8(d), 124.3(d), 127.0(s), 129.3(d), 129.8(d), 134.8(d), 136.4(s), 136.6(s); Anal. Calcd for $C_{19}H_{16}N_2O_2S$: C, 67.84; H, 4.79; N, 8.33. Found: C, 67.87; H, 4.84; N, 8.34.

9-Ethoxycarbonyl-10-methoxycarbonyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole 9e: white crystals; mp 114-115 °C; IR ($CHCl_3$) 3005, 2950, 1730, 1670, 1480, 1460, 1440, 1280, 1185, 1155, 1120 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.25 (t, *J*= 7.1 Hz, 3H, CH_3), 2.09-2.30 (m, 3H, CH and CH_2), 2.34-2.44 (m, 1H, CH), 3.90 (s, 3H, OCH_3), 3.88-4.07 (m, 1H, CH), 4.15-4.35 (m, 3H, NCH and OCH_2), 4.60-4.68 (m, 1H, NCH), 7.22-7.37 (m, 3H, ArH), 8.12-8.20 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.1(q), 19.6(t), 24.2(t), 40.8(d), 42.2(t), 50.6(q), 61.0(t), 104.0(s), 109.1(d), 121.3(d), 122.09(d), 122.13(d), 126.3(s), 135.8(s), 141.1(s), 165.6(s), 172.4(s); Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.76; H, 6.35; N, 4.65. Found: C, 67.76; H, 6.44; N, 4.67.

10-Methoxycarbonyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole 9f: white crystals; mp 105-106 °C; IR ($CHCl_3$) 3010, 2950, 1690, 1530, 1460, 1445, 1155, 1145, 1115 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.91-1.99 (m, 2H, CH_2), 2.06-2.15 (m, 2H, CH_2), 3.34 (t, *J*= 6.4 Hz, 2H, CH_2), 3.91 (s, 3H, OCH_3), 4.09 (t, *J*= 6.1 Hz, 2H, NCH_2), 7.19-7.31 (m, 3H, ArH), 8.09-8.13 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 20.0(t), 22.5(t), 24.5(t), 42.4(t), 50.6(q), 102.3(s), 108.8(d), 121.1(d), 121.6(d), 121.9(d), 126.5(s), 135.9(s), 145.9(s), 166.3(s); Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.44; H, 6.58; N, 6.03.

10-Acetyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole 9g: white crystals; mp 135-136 °C; IR ($CHCl_3$) 3005, 2955, 2870, 1630, 1505, 1490, 1460, 1440, 1420, 1320, 1150 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.94-2.00 (m, 2H, CH_2), 2.07-2.16 (m, 2H, CH_2), 2.70 (s, 3H, CH_3), 3.35 (t, *J*= 6.4 Hz, 2H, CH_2), 4.10 (t, *J*= 6.1 Hz, 2H, NCH_2), 7.22-7.36 (m, 3H, ArH), 7.97-8.03 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 19.9(t), 22.2(t), 25.6(t), 31.0(q), 42.5(t), 109.3(d), 112.9(s), 120.6(d), 121.8(d), 122.4(d), 126.3(s), 136.2(s), 146.6(s), 193.9(s); Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.81; H, 7.00; N, 6.53.

1-Ethoxycarbonyl-8-methoxycarbonyl-2,3-dihydro-1*H*-3a-azacyclopenta[*a*]indene 9h: white crystals; mp 108-109 °C; IR ($CHCl_3$) 3005, 2950, 1735, 1695, 1560, 1450, 1440, 1380, 1300, 1265, 1180, 1155, 1130, 1110 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.25 (t, *J*= 7.1 Hz, 3H, CH_3), 2.75-2.85 (m, 1H, CH), 2.92-3.03 (m, 1H, CH), 3.86 (s, 3H, OCH_3), 4.10-4.15 (m, 1H, NCH), 4.19 (q, *J*= 7.1 Hz, 2H, OCH_2), 4.24-4.32 (m, 1H, NCH), 4.40 (dd, *J*= 9.2, 4.5 Hz, 1H, CH), 7.21-7.32 (m, 3H, ArH), 8.02-8.08 (m, 1H,

ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.1(q), 32.4(t), 43.9(t), 44.3(d), 50.7(q), 61.3(t), 100.3(s), 110.1(d), 121.8(d), 121.9(d), 122.3(d), 136.0(s), 132.6(s), 148.3(s), 165.0(s), 171.7(s); Anal. Calcd for $C_{16}H_{17}NO$: C, 66.89; H, 5.96; N, 4.88. Found: C, 66.86; H, 6.01; N, 4.90.

10-Ethoxycarbonyl-11-methoxycarbonyl-7,8,9,10-tetrahydro-6*H*-azepino[1,2-*a*]indole 9i: white crystals; mp 100-101 °C; IR ($CHCl_3$) 3005, 2935, 1730, 1685, 1535, 1460, 1440, 1420, 1370, 1280, 1225, 1185, 1160, 1140, 1120, 1100, 1020 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.25 (t, *J*= 7.1 Hz, 3H, CH_3),1.40-1.53 (m, 1H, CH), 1.62-1.85 (m, 2H, CH), 1.93-2.10 (m, 2H, CH), 2.58-2.66 (m, 1H, CH), 3.92 (s, 3H, OCH_3), 3.92 (dd, *J*= 14.6, 11.8 Hz, 1H, NCH), 4.20 (q, *J*= 7.1 Hz, 2H, OCH_2), 4.53 (dd, *J*= 14.6, 5.4 Hz, 1H, NCH), 5.88 (dd, *J*= 5.7, 2.9 Hz, 1H, CH), 7.22 (td, *J*= 7.3, 1.4 Hz, 1H, ArH), 7.26 (td, *J*= 7.3, 1.4 Hz,1H, ArH), 7.34 (dm, *J*= 7.3 Hz, 1H, ArH), 8.12 (dm, *J*= 7.3 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.2(q), 26.4(t), 28.0(t), 29.1(t), 41.2(d), 45.0(t), 50.8(q), 61.1(t), 104.6(s), 109.3(d), 121.5(d), 122.0(d), 122.4(d), 126.0(s), 136.2(s), 146.3(s), 166.6(s), 171.4(s); Anal. Calcd for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.61; H, 6.70; N, 4.22.

11-Acetyl-10-ethoxycarbonyl-7,8,9,10-tetrahydro-6*H*-azepino[1,2-*a*]indole 9j: white crystals; mp 78-79 °C; IR ($CHCl_3$) 3010, 2935, 1725, 1640, 1510, 1460, 1445, 1420, 1375, 1345, 1205, 1165, 1120, 1020 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.26 (t, *J*= 7.1 Hz, 3H, CH_3) 1.42-1.55 (m, 1H, CH),1.61-1.71 (m, 1H, CH), 1.73-1.86 (m, 1H, CH), 1.95-2.13 (m, 2H, CH), 2.56-2.65 (m, 1H, CH), 2.73 (s, 3H, CH_3), 3.94 (dd, *J*= 14.6, 11.9 Hz, 1H, NCH), 4.21 (q, *J*= 7.1 Hz, 2H, OCH_2), 4.55 (dd, *J*= 14.6, 5.5 Hz, 1H, NCH), 6.02 (dd, *J*= 5.7, 3.0 Hz, 1H, CH), 7.23-7.31 (m, 2H, ArH), 7.36-7.42 (m, 1H, ArH), 7.87-7.93 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.3(q), 26.4(t), 27.8(t), 28.8(t), 32.1(q), 41.3(d), 44.9(t), 61.1(t), 109.9(d), 114.3(s), 120.9(d), 121.7(d), 122.3(d), 125.9(s), 136.4(s), 146.1(s), 171.7(s) 195.6(s); Anal. Calcd for $C_{18}H_{21}NO_3$: C, 72.22; H, 7.07; N, 4.68. Found: C, 72.24; H, 7.12; N, 4.73.

11-Cyano-10-ethoxycarbonyl-7,8,9,10-tetrahydro-6*H*-azepino[1,2-*a*]indole 9k: white crystals; mp 108-109 °C; IR ($CHCl_3$) 3010, 2935, 2215, 1730, 1475, 1460, 1425, 1365, 1190, 1165 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.29 (t, *J*= 7.1 Hz, 3H, CH_3) 1.45-1.61 (m, 1H, CH), 1.71-1.84 (m, 2H, CH), 1.98-2.14 (m, 2H, CH), 2.53-2.66 (m, H, CH), 4.04 (ddd, *J*= 14.7, 11.9, 0.8 Hz, 1H, NCH), 4.24 (q, *J*= 7.1 Hz, 2H, OCH_2), 4.50-4.59 (m, 2H, CH and NH), 7.23-7.28 (m, 1H, ArH), 7.29-7.34 (m, 1H, ArH), 7.38 (dm, *J*= 7.9 1H, ArH), 7.70 (dm, *J*= 7.9 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.2(q), 26.4(t), 28.2(t), 29.6(t), 43.7(d), 45.5(t), 61.7(t), 86.6(s), 110.0(d), 116.2(s), 119.5(d), 121.9(d), 123.5(d), 126.8(s), 136.4(s), 146.6(s), 170.2(s); Anal. Calcd for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.29; H, 6.51; N, 9.90.

1-(5-Ethoxycarbonyl)pentyl-3-methoxycarbonylindole 11a: white crystals; mp 42-43 °C; IR ($CHCl_3$) 3010, 2950, 1695, 1530, 1470, 1380, 1270, 1220, 1155, 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.23 (t, *J*= 7.1 Hz, 3H, CH_3), 1.30-1.40 (m, 2H, CH_2), 1.66 (quintet, *J*= 7.5 Hz, 2H, CH_2), 1.89 (quintet, *J*= 7.3 Hz, 2H, CH_2), 2.28 (t, *J*= 7.5 Hz, 2H, CH_2), 3.91 (s, 3H, OCH_3), 4.11 (q, *J*= 7.1 Hz, 2H, CH_2), 4.15 (t, *J*= 7.3 Hz, 2H, NCH_2), 7.24-7.32 (m, 2H, ArH), 7.33-7.39 (m, 1H, ArH), 7.81 (s, 1H, ArH), 8.15-8.21 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.2(q), 24.4(t), 26.3(t), 29.5(t), 34.0(t), 46.7(t), 51.0(q), 60.3(t), 106.9(s), 109.9(d), 121.75(d), 121.80(d), 122.7(d), 126.7(s), 134.2(d), 136.4(s), 165.5(s), 173.4(s); Anal. Calcd for $C_{18}H_{23}NO_4$: C, 68.12; H, 7.30; N, 4.41. Found: C, 68.16; H, 7.41; N, 4.30.

3-Acetyl-1-(5-ethoxycarbonyl)pentylindole 11b: pale yellow liquid; IR ($CHCl_3$) 3005, 2940, 1725, 1640, 1615, 1525, 1465, 1390, 1185, 1155 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.23 (t, *J*= 7.2 Hz, 3H, CH_3) 1.33-1.43 (m, 2H, CH_2), 1.68 (quintet, *J*= 7.5 Hz, 2H, CH_2), 1.91 (quintet, *J*= 7.3 Hz, 2H, CH_2), 2.29 (t, *J*= 7.5 Hz, 2H, CH_2), 2.53 (s, 3H, CH_3), 4.11 (q, *J*= 7.2 Hz, 2H, OCH_2), 4.16 (t, *J*= 7.3 Hz, 2H, NCH_2), 7.25-

7.38 (m, 3H, ArH), 7.75 (s, 1H, ArH), 8.34-8.41 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.2(q), 24.3(t), 26.2(t), 27.6(q), 29.5(t), 33.9(t), 46.8(t), 60.3(t), 109.7(d), 116.9(s), 122.5(d), 122.6(d), 123.2(d), 126.3(s), 134.8(d), 136.7(s), 173.3(s), 193.0(s); mass spectrum, m/e (relative intensity) 301(M^+, 81), 286(100), 256(19), 172(27), 130(17); exact mass calcd for $C_{18}H_{23}NO_3$ m/e 301.1678, found m/e 301.1686.

3-Cyano-1-(5-ethoxycarbonyl)pentylindole 11c: pale yellow liquid; IR ($CHCl_3$) 2940, 2220, 1725, 1530, 1465, 1390, 1375, 1335, 1230, 1180, 1025 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.23 (t, *J*= 7.1 Hz, 3H, CH_3), 1.31-1.41 (m, 2H, CH_2), 1.67 (quintet, *J*= 7.5 Hz, 2H, CH_2), 1.89 (quintet, *J*= 7.3 Hz, 2H, CH_2), 2.29 (t, *J*= 7.5 Hz, 2H, CH_2), 4.11 (q, *J*= 7.1 Hz, 2H, OCH_2), 4.17 (t, *J*= 7.3 Hz, 2H, NCH_2), 7.29 (tm, *J*= 7.6 Hz, 1H, ArH), 7.34 (td, *J*= 7.6, 1.1 Hz, 1H, ArH), 7.40 (dm, *J*= 7.6 Hz, 1H, ArH), 7.60 (s, 1H, ArH), 7.76 (dm, *J*= 7.6 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.2(q), 24.3(t), 26.2(t), 29.5(t), 33.9(t), 47.0(t), 60.4(t), 85.6(s), 110.4(d), 115.9(s), 120.0(d), 122.1(d), 123.7(d), 127.9(s), 134.6(d), 135.2(s), 173.3(s); mass spectrum, m/e (relative intensity) 284(M^+, 100), 239(23), 210(10), 155(74), 142(15); exact mass calcd for $C_{17}H_{20}N_2O_2$ m/e 284.1525, found m/e 284.1530.

1-Ethoxycarbonyl-9-(*p*-toluenesulfonyl)-2,3,4,9-tetrahydrocarbazole 15a: white crystals; mp 131-132 °C; IR ($CHCl_3$) 3010, 2940, 1730, 1455, 1370, 1295, 1265, 1170, 1140, 1090 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.28 (t, *J*= 7.1 Hz, 3H, CH_3), 1.76-1.94 (m, 2H, CH_2), 1.97-2.09 (m, 1H, CH), 2.24-2.35 (m, 1H, CH), 2.32 (s, 3H, CH_3), 2.51-2.62 (m, 1H, CH), 2.73-2.83 (m, 1H, CH), 4.13-4.27 (m, 2H, OCH_2), 4.27-4.33 (m, 1H, CH), 7.17 (d, *J*= 8.3 Hz, 2H, ArH), 7.15-7.28 (m, 2H, ArH), 7.39 (dm, *J*= 7.6 Hz, 1H, ArH), 7.68 (d, *J*= 8.3 Hz, 2H, ArH), 7.94 (dm, *J*= 7.6 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.2(q), 19.1(t), 21.1(t), 21.5(q), 28.1(t), 41.1(d), 61.0(t), 114.3(d), 118.6(d), 120.6(s), 123.1(d), 124.5(d), 126.7(d), 129.7(d), 132.2(s), 136.1(s), 136.2(s), 144.5(s), 173.3(s); Anal. Calcd for $C_{22}H_{23}NO_4S$: C, 66.48; H, 5.83; N, 3.52. Found: C, 66.42; H, 5.87; N, 3.59.

1-Benzenesulfonyl-9-(*p*-toluenesulfonyl)-2,3,4,9-tetrahydrocarbazole 15b: white crystals; mp 137-138 °C; IR ($CHCl_3$) 3030, 2950, 1600, 1450, 1370, 1310, 1170, 1140, 1080 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.86-1.98 (m, 1H, CH), 1.98-2.10 (m, 1H, CH), 2.24 (s, 3H, CH_3), 2.53-2.70 (m, 2H, CH_2), 2.78-2.97 (m, 2H, CH_2), 5.33-5.40 (m, 1H, CH), 7.03 (d, *J*= 8.3 Hz, 2H, ArH), 7.23 (tm, *J*= 8.0 Hz, 1H, ArH), 7.28-7.34 (m, 1H, ArH), 7.32 (d, *J*= 8.3 Hz, 2H, ArH), 7.36 (dm, *J*= 8.0 Hz, 1H, ArH), 7.55 (t, *J*= 7.8 Hz, 2H, ArH), 7.68 (tm, *J*= 7.8 Hz, 1H, ArH), 7.91 (dm, *J*= 7.8 Hz, 2H, ArH), 7.94 (dm, *J*= 8.0 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 16.9(t), 19.9(t), 21.5(q), 24.5(t), 59.7(d), 116.2(d), 119.2(d), 124.2(d), 125.7(d), 126.3(d), 126.8(s), 127.9(s), 128.8(d), 129.3(d), 129.5(d), 130.6(s), 133.7(d), 134.0(s), 137.9(s), 139.1(s), 144.5(s); Anal. Calcd for $C_{25}H_{23}NO_4S_2$: C, 64.49; H, 4.98; N, 3.01. Found: C, 64.30; H, 5.02; N, 3.02.

8-Ethoxycarbonyl-3-methoxycarbonyl-5,6,7,8-tetrahydroindolizine 16a: white crystals; mp 51-52 °C; IR ($CHCl_3$) 2990, 2955, 1730, 1695, 1490, 1470, 1435, 1355, 1240, 1180, 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.28 (t, *J*= 7.2 Hz, 3H, CH_3), 1.84-1.98 (m, 1H, CH), 1.98-2.21 (m, 3H, CH and CH_2), 3.78 (s, 3H, OCH_3), 3.86 (t, *J*= 6.6 Hz, 1H, CH), 4.12-4.26 (m, 2H, OCH_2), 4.27-4.43 (m, 2H, NCH_2), 6.07 (d, *J*= 4.0 Hz, 1H, ArH), 6.92 (d, *J*= 4.0 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.0(q), 21.1(t), 23.1(t), 40.6(d), 45.1(t), 50.7(q), 61.0(t), 107.4(d), 117.4(d), 121.2(s), 132.6(s), 161.4(s), 172.1(s); Anal. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.07; H, 6.77; N, 5.53.

8-Benzenesulfonyl-3-methoxycarbonyl-5,6,7,8-tetrahydroindolizine 16b: white crystals; mp 118-119 °C; IR ($CHCl_3$) 3010, 2950, 1700, 1485, 1470, 1450, 1435, 1355, 1310, 1290, 1240, 1145, 1085 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.76-1.87 (m, 1H, CH), 2.07-2.24 (m, 2H, CH_2), 2.35-2.47 (m, 1H, CH), 3.79 (s, 3H, OCH_3), 4.11-4.23 (m, 1H, NCH), 4.26-4.36 (m, 1H, NCH), 4.49-4.57 (m, 1H, CH), 6.05 (d,

J= 4.1 Hz, 1H, ArH), 6.89 (d, *J*= 4.1 Hz, 1H, ArH), 7.51 (t, *J*= 7.6 Hz, 2H, ArH), 7.66 (tm, *J*= 7.6 Hz, 1H, ArH), 7.73 (dm, *J*= 7.6 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 20.1(t), 21.0(t), 44.7(t), 51.1(q), 60.1(d), 111.2(d), 117.2(d), 123.1(s), 126.1(s), 129.0(d), 129.3(d), 134.0(s), 137.0(s), 161.3(s); Anal. Calcd for $C_{16}H_{17}NO_4S$: C, 60.17; H, 5.36; N, 4.39. Found: C, 60.15; H, 5.47; N, 4.42.

5,5-Dimethoxycarbonyl-7-ethoxycarbonyl-6,7-dihydro-4*H*-benzo[*b*]thiophene 17: colorless liquid; IR ($CHCl_3$) 3010, 2955, 1735, 1450, 1435, 1290, 1255, 1180 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.34 (t, *J*= 7.1 Hz, 3H, CH_3), 2.47 (dd, *J*= 13.6, 10.8 Hz, 1H, CH), 2.83 (ddd, *J*= 13.6, 6.0, 2.0 Hz, 1H, CH), 3.05 (dd, *J*= 16.2, 2.0 Hz, 1H, CH), 3.42 (d, *J*= 16.2 Hz, 1H, CH), 3.69 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.98-4.05 (m, 1H, CH), 4.18-4.32 (m, 2H, OCH_2), 6.17 (d, *J*= 5.1 Hz, 1H, ArH), 6.78 (d, *J*= 5.1 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.1(q), 31.2(t), 31.3(t), 40.1(d), 52.9(q), 53.0(q), 53.7(s), 61.5(t), 124.9(d), 126.9(d), 130.1(s), 133.6(s), 170.5(s), 171.4(s), 172.0(s); mass spectrum, m/e (relative intensity) 326(M^+, 11), 280(100), 267(14), 253(12), 235(9), 207(11), 193(63), 161(32), 135(55); exact mass calcd for $C_{15}H_{18}O_6S$ m/e 326.0824, found m/e 326.0829.

ACKNOWLEDGMENT

The authors wish to thank the National Science Council, R.O.C. for financial support (NSC 86-2113-M006-009).

REFERENCES

1. Cristol, S. J.; Reeder, J. A. *J. Org. Chem.* **1961**, *26*, 2182. Orochov, A.; Asscher, M.; Vofsi, D. *J. Chem. Soc. (B),* **1969**, 225. Sinnerich, J.; Asscher, M. *J. Chem. Soc. Perkin I,* **1972**,1543. Fang, J. -M.; Chen, M. -Y. *Tetrahedron Lett.*, **1987**, *28*, 2853.
2. De Riggi, I; Surzur, J. -M.; Bertrand, M. P. *Tetrahedron*, **1988**, *44*, 7119. Chuang, C. -P.; Ngoi, T. H. J. *Tetrahedron Lett.*, **1989**, *30*, 6369. Chuang,C. -P.; Wang, R. -Z. *J. Chinese Chem. Soc.*, **1990**, *37*, 89. De Riggi, I.; Surzur, J. -M.; Bertrand, M. P. *Tetrahedron*, **1990**, *46*, 5285. Chuang, C. -P. *Synlett.*, **1990**, 527. Chuang, C. -P. *Tetrahedron*, **1991**, *47*, 5425. Chuang, C. -P.; Hou, S. -S.; Wu, R. -R. *Synth. Commun.* **1992**, *22*, 467. Chuang, C. -P.; Wang, S. -F. *Synlett*, **1995**, 763.
3. Chatgiliaoglu, C.; Lunazzi, L.; Ingold, K. U. *J. Org. Chem.* **1983**, *48*, 3588. Kang, Y. -H.; Kice, J. L. *J. Org. Chem.* **1984**, *49*, 1507.
4. Kice, J. L.; Pawlowski, N. E. *J. Am. Chem. Soc.* **1964**, *86*, 4898. Smith, T. A. K.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* **1985**, 897. Smith, T. A. K.; Whitham, G. H. *J. Chem. Soc. Perkin Trans. I*, **1989**, 319. Padwa, A.; Bullock, W. H.; Dyszlewski, A. D. *J. Org. Chem.*, **1990**, *55*, 955.
5. Chottard, J. C.; Julia, M. *Tetrahedron*, **1972**, *28*, 5615. Narasimhan, N. S.; Aidhen, I. S. *Tetrahedron Lett.* **1988**, *29*, 2987. Rosa, A. M. ; Prabhakar, S.; Lobo, A. M. *Tetrahedron Lett.* **1990**, *31*, 1881. Chuang, C. -P. *Tetrahedron Lett.* **1992**, *33*, 6311.
6. Oumar-Mahamat, H.; Moustrou, C.; Surzur, J. -M.; Berstrand, M. P. *J. Org. Chem.* **1989**, *54*, 5684. Snider B. B.; Wan, B. Y. F.; Buckman, B. O.; Foxman, B. M. *J. Org. Chem.* **1991**, *56*, 328.
7. Citterio, A.; Fancelli, D.; Finzi, C.; Pesce, L. *J. Org. Chem.*, **1989**, *54*, 2713.
8. Ziegler, F. E.; Jeronic, L. O. *J. Org. Chem.* **1991**, *56*, 3479. Baciocchi, E.; Muraglia, E. *Tetrahedron Lett.* **1993**, *34*, 3799 and 5015. Artis, D. R.; Cho, I. -S.; Jaime-Figueroa, S.; Muchowski, J. M. *J. Org. Chem.* **1994**, *59*, 2456. Chuang, C. -P.; Wang, S. -F. *Tetrahedron Lett.* **1994**, *35*, 1283. Chuang, C. -P.; Wang, S. -F. *Heterocycles*, **1996**, *43*, 2215. Chuang, C. -P.; Wang, S. -F. *Heterocycles*, **1997**, *45*, 347.