OXIDATIVE FREE RADICAL REACTION OF 2-PHENYLTHIO-1,4-NAPHTHOQUINONES INITIATED BY MANGANESE(III) ACETATE

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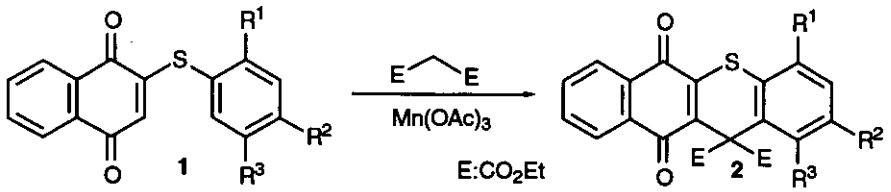
Abstract - A free radical reaction between 2-phenylthio-1,4-naphothoquinines and diethyl malonate initiated by manganese(III) acetate is described. This free radical reaction provides a new method for the synthesis of 6,11-dihydro-6,11-dioxo-12*H*-5-thianaphthacenes. This reaction was performed in various solvents, the best results were obtained in DMSO. With meta substituent on phenylthio ring, this reaction shows unusual high regioselectivity.

The addition of carbon-centered radicals to unsaturated substrates is an important process in free radical chemistry. Recently, such reactions have acquired remarkable importance in organic synthesis as a valuable method for C-C bond formation.[1] Electrophilic radicals produced from the manganese(III) acetate oxidation of β-dicarbonyl compounds undergo efficient addition to a C-C double bond.[2,3] The free radical addition of a carbon center radical to quinones has been reported.[4] Benzo[*b*]fluorene and related ring systems have been found in natural compounds (e.g. stealthin A, kinafluorenone, and prekinamycin)[5] and synthetic approach to such systems has recently been reported.[6] These ring systems can presumably be obtained by the desulfurization of thianaphthacenes (**2**).[7] 2-Phenylthio-1,4-naphthoquinones are readily available from 1,4-naphthoquinone and thiophenols.[8] We report here a new method for the synthesis of **2** from 2-phenylthio-1,4-naphthoquinones and diethyl malonate *via* manganese(III) initiated oxidative free radical reaction.

We began our studies with the reaction shown in Scheme 1. Treatment of **1a** with diethyl malonate and manganese(III) acetate in glacial acetic acid at 80°C for 2 h gave **2a** in 18% yield. An unidentified product was also obtained. To improve the reaction result, we also performed this reaction with **1a** in different solvents and the results were shown in Table 1 (Entry a). In DMSO, the yield is increased significantly to 90%, however, it proceeds in a much slower reaction rate (24 h) than that performed in acetic acid. In acetonitrile, the yield is 66% (42 h). In ethanol, after heated for 54 h, the yield is 67% based on 93% conversion. In DME, the reaction rate is even slower. After heated for 54 h, the yield is 35% based on 49% conversion. The generalities for this reaction by using DMSO and acetonitrile as solvents are also shown in Table 1. Best results were obtained in DMSO. This free radical reaction presumably occurs *via* the addition of malonyl radical generated from the oxidation of malonate by manganese(III) acetate to quinone ring and



Scheme 1

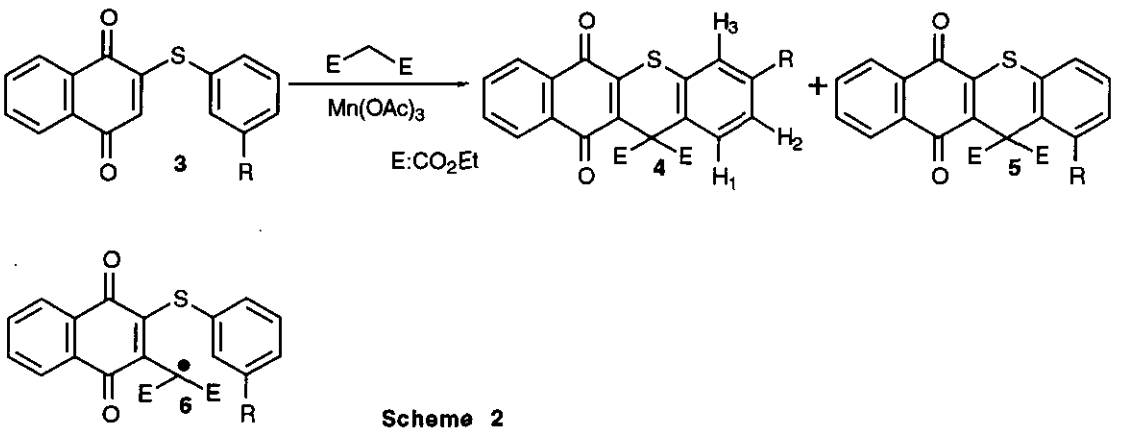
Table 1: The Free Radical Reaction between 2-Phenylthio-1,4-naphthoquinones (**1**) and Diethyl Malonate

Entry		Substrate R^1	R^2	R^3	Solvent	Product (Yield)
a	**1a**	H	Me	H	acetic acid	**2a**(18%)
					DMSO	**2a**(90%)
					acetonitrile	**2a**(66%)
					ethanol	**2a**(67%)
					DME	**2a**(35%)
b	**1b**	H	H	H	DMSO	**2b**(92%)
					acetonitrile	**2b**(75%)
c	**1c**	Me	H	Me	DMSO	**2c**(85%)
					acetonitrile	**2c**(63%)
d	**1d**	H	F	H	DMSO	**2d**(91%)
					acetonitrile	**2d**(69%)
e	**1e**	Cl	H	H	DMSO	**2e**(95%)
					acetonitrile	**2e**(74%)
f	**1f**	Br	H	H	acetonitrile	**2f**(80%)
g	**1g**	H	Br	H	DMSO	**2g**(93%)
					acetonitrile	**2g**(79%)
h	**1h**	H	OMe	H	DMSO	**2h**(83%)
					acetonitrile	**2h**(49%)
i	**1i**	CO_2Et	H	H	DMSO	**2i**(89%)
					acetonitrile	**2i**(75%)

phenylthio ring consecutively.

With meta substituent on phenylthio ring, the regioselectivity of this reaction was also examined. Presumably, two possible products (**4**) and (**5**) could be obtained (Scheme 2). When **3a** was treated with diethyl malonate and manganese(III) acetate in DMSO surprisingly only **4a** was isolated in 90% yield and no trace of **5a** could be found. The structure of **4a** was determined by the proton nmr analysis. The proton nmr spectrum clearly shows three signals at δ 7.15 (dd, J=8.2, 1.3 Hz), δ 7.20 (d, J=1.3 Hz) and δ 7.50 (d, J=8.2 Hz) corresponding to the aromatic protons on benzothiopyran ring. Other examples are

summarized in Table 2. In all cases, only one product was obtained. The nmr spectral data for protons on benzothiopyran ring are listed in Table 3. This high regioselectivity can be ascribed to the steric effect between tertiary malonyl radical (**6**) and substituent R.



Scheme 2

Table 2: The Regioselective Free Radical Reaction between 1,4-Naphthoquinones (**3**) and Diethyl Malonate

Entry	Substrate R	Solvent	Product (Yield)
a	**3a** Me	DMSO acetonitrile	**4a**(90%) **4a**(59%)
b	**3b** CF_3	DMSO acetonitrile	**4b**(87%) **4b**(78%)
c	**3c** Cl	DMSO acetonitrile	**4c**(92%) **4c**(80%)
d	**3d** Br	DMSO acetonitrile	**4d**(96%) **4d**(76%)

Table 3: The Proton Nmr Spectral Data for 1,4-Naphthoquinones (**4**)

Entry	Substrate	H_1	H_2	H_3
a	**4a**	7.50(d)	7.15(dd)	7.20(d)
b[1]	**4b**	7.72(d)	7.57(dd)	7.67(d)
c	**4c**	7.54(d)	7.30(dd)	7.40(d)
d	**4d**	7.55(d)	7.42-7.48(m)	

1. The ^{19}F was decoupled.

In conclusion, this oxidative free radical reaction provides a novel method for the synthesis of 6,11-dihydro-6,11-dioxo-12*H*-5-thianaphthacenes from readily available 2-phenylthio-1,4-naphthoquinones and diethyl malonate.

EXPERIMENTAL

Melting points are uncorrected. Nmr spectra were recorded on Bruker Ac-200 or Bruker AMX-400 spectrometer. Elemental analyses were performed with a Heraeus CHN-Rapid Analyzer. All reactions were carried out under a nitrogen atmosphere. Analytical thin layer chromatography was performed by precoated silica gel 60 F-254 plates (0.25 mm thick) of EM Laboratories and visualized either by uv or by spraying with 5% phosphomolybdic acid in ethanol following by heating. The reaction mixture was purified by column chromatography over EM Laboratories silica gel (230-400 Mesh).

Typical experimental procedure: A solution of 145 mg (0.52 mmol) of **1a**, 333 mg (2.08 mmol) of diethyl malonate and 840 mg (3.13 mmol) of manganese(III) acetate in 10 ml of DMSO was heated in an 80°C oil bath for 24 h. The reaction mixture was diluted with 100 ml of dichloromethane, washed with 50 ml of saturated aqueous sodium bisulfite, 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 dichloromethane-hexane, 3:1) followed by recrystallization (chloroform-hexane) to give 203 mg (90%) of **2a** .

2-Methyl-6,11-dihydro-6,11-dioxo-12*H*-5-thianaphthacene-12,12-dicarboxylic acid diethyl ester (2a): mp 180°C; ir ($CHCl_3$) 2990, 1735, 1670, 1595, 1325, 1290, 1230, 1045 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$) δ 1.17 (t, J=7.1 Hz, 6H, CH_3), 2.37 (s, 3H, CH_3), 4.16-4.29 (m, 4H, OCH_2), 7.16 (dm, J=8.0 Hz, 1H, ArH), 7.29 (d, J=8.0 Hz, 1H, ArH), 7.41-7.45 (m, 1H, ArH), 7.74 (td, J=7.5, 1.5 Hz, 1H, ArH), 7.78 (td, J=7.5, 1.5 Hz, 1H, ArH), 8.15 (dd, J=7.5, 1.5 Hz, 2H, ArH); ^{13}C nmr (100.6 MHz, $CDCl_3$) δ 13.7(q), 21.2(q), 60.1(s), 62.3(t), 123.9(s), 126.4(d), 126.5(d), 127.2(d), 128.1(s), 129.6(d), 130.2(d), 131.1(s), 132.0(s), 133.4(d), 133.9(s), 134.6(d), 138.0(s), 145.9(s), 167.8(s), 179.4(s), 180.9(s); Anal. Calcd for $C_{24}H_{20}O_6S$: C, 66.04; H, 4.62. Found: C, 66.00; H, 4.63.

6,11-Dihydro-6,11-dioxo-12*H*-5-thianaphthacene-12,12-dicarboxylic acid diethyl ester (2b): mp 203°C; ir ($CHCl_3$) 2990, 1730, 1670, 1595, 1290, 1245 cm^{-1}; ^1H nmr (200 MHz, $CDCl_3$) δ 1.18 (t, J=6.9 Hz, 6H, CH_3), 4.23 (q, J=6.9 Hz, 4H, OCH_2), 7.28-7.49 (m, 3H, ArH), 7.57-7.69 (m, 1H, ArH), 7.69-7.88 (m, 2H, ArH), 8.10-8.20 (m, 2H, ArH); ^{13}C nmr (50.3 MHz, $CDCl_3$) δ 13.7(q), 60.2(s), 62.4(t), 126.6(d), 127.3(d), 127.9(d), 128.4(s), 128.6(d), 129.9(d), 131.0(s), 132.0(s), 133.5(d), 134.1(s), 134.7(d), 145.7(s), 167.8(s), 179.4(s), 180.9(s); Anal. Calcd for $C_{23}H_{18}O_6S$: C, 65.39; H, 4.29. Found: C, 65.25; H, 4.26.

1,4-Dimethyl-6,11-dihydro-6,11-dioxo-12*H*-5-thianaphthacene-12,12-dicarboxylic acid diethyl ester (2c): mp 155°C (decomp.); ir ($CHCl_3$) 2985, 1730, 1670, 1595, 1570, 1285, 1240 cm^{-1}; ^1H nmr (200 MHz, $CDCl_3$) δ 1.26 (t, J=7.1 Hz, 6H, CH_3), 2.46 (s, 3H, CH_3), 2.51 (s, 3H, CH_3), 4.18-4.41 (m, 4H, OCH_2), 7.08 (s, 2H, ArH), 7.68 (td, J=7.2, 1.7 Hz, 1H, ArH), 7.75 (td, J=7.2, 1.7 Hz, 1H, ArH), 8.09 (dd, J=7.2, 1.7 Hz, 1H, ArH), 8.12 (dd, J=7.2, 1.7 Hz, 1H, ArH); ^{13}C nmr (50.3 MHz, $CDCl_3$) δ 13.6(q), 20.9(q), 22.2(q), 61.6(s), 62.3(t), 126.1(d), 127.3(d), 127.5(s), 129.7(d),

130.6(s), 132.5(d), 132.7(s), 133.1(d), 134.6(d), 137.7(s), 145.8(s), 168.7(s), 179.6(s), 180.9(s); Anal. Calcd for $C_{25}H_{22}O_6S$: C, 66.65; H, 4.92. Found: C, 66.64; H, 4.86.

2-Fluoro-6,11-dihydro-6,11-dioxo-12*H*-5-thianaphthacene-12,12-dicarboxylic acid diethyl ester (2d): mp 205°C; ir ($CHCl_3$) 3030, 2990, 1740, 1670, 1595, 1485, 1290, 1230 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$) δ 1.20 (t, J=8.0 Hz, 6H, CH_3), 4.25-4.35 (m, 4H, OCH_2), 7.10 (ddd, J=8.8, 7.6, 2.5 Hz, 1H, ArH), 7.35 (dd, J=10.2, 2.5 Hz, 1H, ArH), 7.39 (dd, J=8.8, 5.6 Hz, 1H, ArH), 7.75 (td, J=7.4, 1.6 Hz, 1H, ArH), 7.80 (td, J=7.4, 1.6 Hz, 1H, ArH), 8.12-8.18 (m, 2H, ArH); ^{13}C nmr (100.6 MHz, $CDCl_3$) δ 13.8(q), 60.6(s), 62.8(t), 116.7(dd, J_{C-F}=22.1 Hz), 117.1(dd, J_{C-F}=25.1 Hz), 122.9(d, J_{C-F}=3.0 Hz), 126.7(d), 127.4(d), 128.1(dd, J_{C-F}=7.0 Hz), 130.5(d, J_{C-F}=8.0 Hz), 131.1(s), 132.0(s), 133.3(s), 133.6(d), 134.8(d), 145.7(s), 162.1(d, J_{C-F}=248.5 Hz), 167.5(s), 179.4(s), 180.8(s); Anal. Calcd for $C_{23}H_{17}O_6FS$: C, 62.72; H, 3.89. Found: C, 62.71; H, 3.93.

4-Chloro-6,11-dihydro-6,11-dioxo-12*H*-5-thianaphthacene-12,12-dicarboxylic acid diethyl ester (2e): mp 238°C; ir ($CHCl_3$) 2990, 1740, 1670, 1600, 1290, 1260, 1195 cm^{-1}; ^1H nmr (200 MHz, $CDCl_3$) δ 1.18 (t, J=7.0 Hz, 6H, CH_3), 4.22 (q, J=7.0 Hz, 4H, OCH_2), 7.28 (t, J=8.0 Hz, 1H, ArH), 7.44 (dd, J=8.0, 1.3 Hz, 1H, ArH), 7.54 (dd, J=8.0, 1.3 Hz, 1H, ArH), 7.70-7.85 (m, 2H, ArH), 8.10-8.22 (m, 2H, ArH); ^{13}C nmr (50.3 MHz, $CDCl_3$) δ 13.8(q), 61.0(s), 62.7(t), 126.7(d), 127.4(d), 127.7(s), 128.0(d), 128.3(d), 129.5(d), 130.2(s), 131.1(s), 131.6(s), 131.9(s), 133.7(d), 134.0(s), 134.8(d), 144.7(s), 167.6(s), 179.7(s), 180.9(s); Anal. Calcd for $C_{23}H_{17}O_6ClS$: C, 60.46; H, 3.75. Found: C, 60.51; H, 3.57.

4-Bromo-6,11-dihydro-6,11-dioxo-12*H*-5-thianaphthacene-12,12-dicarboxylic acid diethyl ester (2f): mp 234°C; ir ($CHCl_3$) 3015, 2990, 1735, 1670, 1600, 1290, 1260, 1220 cm^{-1}; ^1H nmr (200 MHz, $CDCl_3$) δ 1.18 (t, J=7.1 Hz, 6H, CH_3), 4.22 (q, J=7.1 Hz, 4H, OCH_2), 7.21 (t, J=7.9 Hz, 1H, ArH), 7.57 (dd, J=7.9, 1.4 Hz, 1H, ArH), 7.61 (dd, J=7.9, 1.4 Hz, 1H, ArH), 7.71-7.86 (m, 2H, ArH), 8.10-8.22 (m, 2H, ArH); ^{13}C nmr (50.3 MHz, $CDCl_3$) δ 13.8(q), 61.4(s), 62.7(t), 121.5(s), 126.7(d), 127.4(d), 128.3(d), 128.9(d), 129.4(s), 130.3(s), 131.1(s), 131.9(s), 132.9(d), 133.7(d), 134.1(s), 134.8(d), 145.2(s), 167.6(s), 179.7(s), 180.9(s); Anal. Calcd for $C_{23}H_{17}O_6BrS$: C, 55.10; H, 3.42. Found: C, 55.10; H, 3.39.

2-Bromo-6,11-dihydro-6,11-dioxo-12*H*-5-thianaphthacene-12,12-dicarboxylic acid diethyl ester (2g): mp 237°C; ir ($CHCl_3$) 2990, 1740, 1670, 1595, 1470, 1320, 1285, 1230 cm^{-1}; ^1H nmr (200 MHz, $CDCl_3$) δ 1.20 (t, J=7.1 Hz, 6H, CH_3), 4.25 (q, J=7.1 Hz, 4H, OCH_2), 7.27 (d, J=8.4 Hz, 1H, ArH), 7.47 (dd, J=8.4, 2.0 Hz, 1H, ArH), 7.70-7.87 (m, 3H, ArH), 8.10-8.20 (m, 2H, ArH); ^{13}C nmr (50.3 MHz, $CDCl_3$) δ 13.8(q), 60.2(s), 62.8(t), 121.6(s), 126.7(d), 127.5(d), 127.9(d), 130.3(s), 131.0(s), 131.87(d), 131.9(s), 132.8(d), 133.7(d), 133.9(s), 134.9(d), 145.3(s), 167.5(s), 179.4(s), 180.7(s); Anal. Calcd for $C_{23}H_{17}O_6BrS$: C, 55.10; H, 3.42. Found: C, 54.95; H, 3.35.

2-Methoxy-6,11-dihydro-6,11-dioxo-12*H*-5-thianaphthacene-12,12-dicarboxylic acid diethyl ester (2h): mp 194°C; ir ($CHCl_3$) 2985, 1740, 1670, 1600, 1320, 1290, 1245 cm^{-1}; ^1H nmr (200 MHz, $CDCl_3$) δ 1.19 (t, J=7.0 Hz, 6H, CH_3), 3.82 (s, 3H, OCH_3), 4.23 (q, J=7.0 Hz, 4H, OCH_2), 6.93 (dd, J=8.7, 2.5 Hz, 1H, ArH), 7.19 (d, J=2.5 Hz, 1H, ArH), 7.31 (d, J=8.7 Hz, 1H, ArH), 7.73 (td, J=7.4, 1.8 Hz, 1H, ArH), 7.79 (td, J=7.4, 1.8 Hz, 1H, ArH), 8.06-8.20 (m, 2H, ArH); ^{13}C nmr (50.3 MHz, $CDCl_3$) δ 13.8(q), 55.5(q), 60.4(s), 62.5(t), 114.9(d), 115.7(d), 118.4(s),

126.6(d), 127.3(d), 127.6(d), 129.5(s), 131.2(s), 132.1(s), 133.1(s), 133.4(d), 134.7(d), 146.1(s), 159.5(s), 167.7(s), 179.5(s), 181.1(s); Anal. Calcd for $C_{24}H_{20}O_7S$: C, 63.71; H, 4.46. Found: C, 63.73; H, 4.34.

6,11-Dihydro-6,11-dioxo-12*H*-5-thianaphthacene-4,12,12-tricarboxylic acid triethyl ester (2i): mp 144°C(decomp.); ir ($CHCl_3$) 2990, 1735, 1670, 1600, 1285, 1235, 1160 cm^{-1}; ^1H nmr (200 MHz, $CDCl_3$) δ 1.20 (t, J=7.1 Hz, 6H, CH_3), 1.45 (t, J=7.1 Hz, 3H, CH_3), 4.26 (q, J=7.1 Hz, 4H, OCH_2), 4.47 (q, J=7.1 Hz, 2H, OCH_2), 7.43 (t, J=7.9 Hz, 1H, ArH), 7.69-7.85 (m, 3H, ArH), 8.05-8.20 (m, 3H, ArH); ^{13}C nmr (50.3 MHz, $CDCl_3$) δ 13.6(q), 14.1(q), 60.5(s), 61.7(t), 62.5(t), 126.4(d), 126.5(d), 127.0(d), 127.5(s), 130.2(s), 130.9(s), 131.1(s), 131.3(d), 131.8(s), 133.5(d), 133.6(s), 133.8(d), 134.5(d), 145.2(s), 165.6(s), 167.9(s),179.4(s), 180.9(s); Anal. Calcd for $C_{26}H_{22}O_8S$: C, 63.15; H, 4.48. Found: C, 63.09; H, 4.47.

3-Methyl-6,11-dihydro-6,11-dioxo-12*H*-5-thianaphthacene-12,12-dicarboxylic acid diethyl ester (4a): mp 183°C; ir ($CHCl_3$) 2990, 2940, 1745, 1670, 1600, 1320, 1290, 1245 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$) δ 1.18 (t, J=7.1 Hz, 6H, CH_3), 2.35 (s, 3H, CH_3), 4.15-4.28 (m, 4H, OCH_2), 7.15 (dd, J=8.2, 1.3 Hz, 1H, ArH), 7.20 (d, J=1.3 Hz, 1H, ArH), 7.50 (d, J=8.2 Hz, 1H, ArH), 7.73 (td, J=7.4, 1.5 Hz, 1H, ArH), 7.78 (td, J=7.4, 1.5 Hz, 1H, ArH), 8.11-8.18 (m, 2H, ArH); ^{13}C nmr (50.3 MHz, $CDCl_3$) δ 13.7(q), 20.7(q), 59.8(s), 62.3(t), 125.3(s), 126.5(d), 126.7(d), 127.0(s), 127.2(d), 129.0(d), 129.6(d), 131.1(s), 131.9(s), 133.4(d), 134.1(s), 134.6(d), 138.8(s), 145.7(s), 167.9(s), 179.4(s), 180.9(s); Anal. Calcd for $C_{24}H_{20}O_6S$: C, 66.04; H, 4.62. Found: C, 66.06; H, 4.56.

3-Trifluoromethyl-6,11-dihydro-6,11-dioxo-12*H*-5-thianaphthacene-12,12-dicarboxylic acid diethyl ester (4b): mp 165°C; ir ($CHCl_3$) 2990, 1740, 1670, 1330, 1280, 1245, 1180, 1135 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$) δ 1.20 (t, J=7.1 Hz, 6H, CH_3), 4.17-4.31 (m, 4H, OCH_2), 7.57 (dm, J=8.4 Hz, 1H, ArH), 7.66-7.68 (m, 1H, ArH), 7.72 (d, J=8.4 Hz, 1H, ArH), 7.77 (td, J=7.4, 1.5 Hz, 1H, ArH), 7.82 (td, J=7.4, 1.5 Hz, 1H, ArH), 8.14-8.20 (m, 2H, ArH); ^{13}C nmr (100.6 MHz, $CDCl_3$) δ 13.6(q), 60.3(s), 62.8(t), 123.1(q, J_{C-F}=272.6 Hz), 123.5(qd, J_{C-F}=3.0 Hz), 124.2(qd, J_{C-F}=3.0 Hz), 126.6(d), 127.4(d), 128.9(s), 130.6(d), 130.85(s), 130.9(q, J_{C-F}=33.5 Hz), 131.8(s), 132.1(s), 133.7(d), 133.9(s), 134.8(d), 144.9(s), 167.3(s), 179.3(s), 180.4(s); Anal. Calcd for $C_{24}H_{17}O_6F_3S$: C, 58.78; H, 3.49. Found: C, 58.83; H, 3.43.

3-Chloro-6,11-dihydro-6,11-dioxo-12*H*-5-thianaphthacene-12,12-dicarboxylic acid diethyl ester (4c): mp 207°C; ir ($CHCl_3$) 2990, 1740, 1670, 1595, 1480, 1290, 1245 cm^{-1}; ^1H nmr (200 MHz, $CDCl_3$) δ 1.19 (t, J=7.1 Hz, 6H, CH_3), 4.23 (q, J=7.1 Hz, 4H, OCH_2), 7.30 (dd, J=8.6, 2.1 Hz, 1H, ArH), 7.40 (d, J=2.1 Hz, 1H, ArH), 7.54 (d, J=8.6 Hz, 1H, ArH), 7.75 (td, J=7.4, 1.8 Hz, 1H, ArH), 7.81 (td, J=7.4, 1.8 Hz, 1H, ArH), 8.10-8.22 (m, 2H, ArH); ^{13}C nmr (100.6 MHz, $CDCl_3$) δ 13.8(q), 59.9(s), 62.7(t), 126.1(d), 126.7(d), 126.9(s), 127.4(d), 128.1(d), 129.3(s), 131.0(s), 131.2(d), 131.9(s), 133.7(d), 134.2(s), 134.77(s), 134.84(d), 145.0(s), 167.6(s), 179.4(s), 180.7(s); Anal. Calcd for $C_{23}H_{17}O_6ClS$: C, 60.46; H, 3.75. Found: C, 60.34; H, 3.71.

3-Bromo-6,11-dihydro-6,11-dioxo-12*H*-5-thianaphthacene-12,12-dicarboxylic acid diethyl ester (4d): mp 221°C; ir ($CHCl_3$) 2990, 1740, 1670, 1595, 1580, 1475, 1290, 1245 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$) δ 1.19 (t, J=7.1 Hz, 6H, CH_3), 4.17-4.28 (m, 4H, OCH_2), 7.42-7.48 (m, 2H,

ArH), 7.55 (d, J=1.8 Hz, 1H, ArH), 7.76 (td, J=7.4, 1.5 Hz, 1H, ArH), 7.80 (td, J=7.4, 1.5 Hz, 1H, ArH), 8.13-8.17 (m, 2H, ArH); ^{13}C nmr (100.6 MHz, $CDCl_3$) δ 13.8(q), 60.0(s), 62.7(t), 122.8(s), 126.7(d), 127.38(s), 127.44(d), 128.9(d), 129.7(s), 130.9(d), 131.0(s), 131.4(d), 131.9(s), 133.7(d), 134.1(s), 134.9(d), 145.0(s), 167.5(s), 179.4(s), 180.7(s); Anal. Calcd for $C_{23}H_{17}O_6BrS$: C, 55.10; H, 3.42. Found: C, 55.18; H, 3.39.

ACKNOWLEDGMENT

The authors wish to thank the National Science Council, R.O.C. for financial support. (NSC-85-2113-M-006-006)

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Received, 17th June, 1996