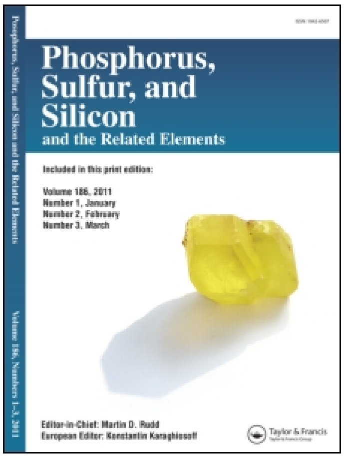

**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# SYNTHESIS AND SPECTRAL CHARACTERIZATION OF DIETHYL 2-[ARYL(4-ARYL-1,2,3-SELENADIAZOL-5-YL)METHYL]MALONATE

Sivaperuman Saravanan[a]; Shanmugam Muthusubramanian[a]
[a] Department of Organic Chemistry, Madurai Kamaraj University, Madurai, India

**To cite this Article** Saravanan, Sivaperuman and Muthusubramanian, Shanmugam(2004) 'SYNTHESIS AND SPECTRAL CHARACTERIZATION OF DIETHYL 2-[ARYL(4-ARYL-1,2,3-SELENADIAZOL-5-YL)METHYL]MALONATE', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 12, 2411 — 2421

**To link to this Article: DOI:** 10.1080/10426500490485255

**URL:** http://dx.doi.org/10.1080/10426500490485255

*Phosphorus, Sulfur, and Silicon*, 179:2411–2421, 2004
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490485255

# SYNTHESIS AND SPECTRAL CHARACTERIZATION OF DIETHYL 2-[ARYL(4-ARYL-1,2,3-SELENADIAZOL-5-YL)METHYL]MALONATE

*Sivaperuman Saravanan and Shanmugam Muthusubramanian*
*Department of Organic Chemistry, Madurai Kamaraj University, Madurai, India*

(Received February 25, 2004; accepted April 28, 2004)

*Synthesis and characterization of several diethyl 2-[aryl(4-aryl-1,2,3-selenadiazol-5-yl)methyl]malonates are reported.*

*Keywords:* 1,2,3-Selenadiazoles; 2D NMR; $^{13}$C NMR; diethyl 2-[aryl(4-aryl-1,2,3-selenadiazol-5-yl)methyl]malonate; $^{1}$H NMR; selenium dioxide

## INTRODUCTION

Much attention has been paid to the synthesis of various derivatives of 1,2,3-selenadiazoles and 1,2,3-thiadiazoles due to their pharmacological properties. Compounds with a 1,2,3-selena/thiadiazole moiety have been found to exhibit antifungal[1,2] and antibacterial[3–5] activities. 4,5-Bis(p-methoxyphenyl)-1,2,3-thiadiazole possesses platelet aggregation inhibitory activity in humans,[6] and some 1,2,3-thiadiazole derivatives are useful for the therapeutic and prophylactic treatment of viral, bacterial, fungal, and parasitic infections in humans and animals.[7] This article reports the synthesis of novel substituted 1,2,3-selenadiazoles with functional groups, which can be modified to give additional heterocyclic rings.

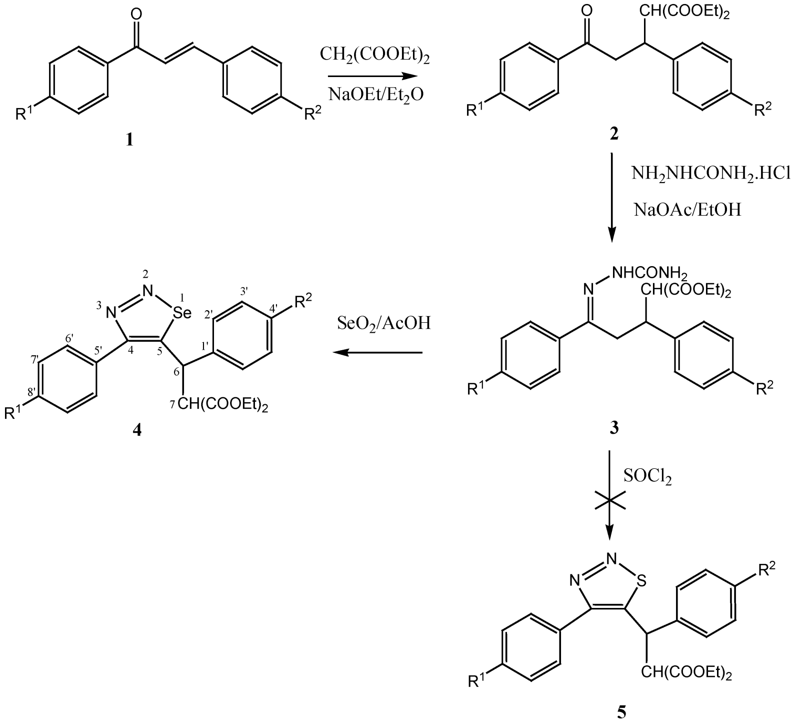
The authors thank DST, New Delhi for assistance under the IRHPA program for the NMR facility. S. Saravanan is grateful to CSIR, New Delhi for a Junior Research Fellowship.

Address correspondence to Shanmugam Muthusubramanian, Department of Organic Chemistry, Madurai Kamaraj University, Madurai 625021, India. E-mail: muthumanian2001@yahoo.com

## RESULTS AND DISCUSSION

The adducts, diethyl 2-(3-oxo-1,3-diarylpropyl)malonates (**2a–j**) have all been synthesized by reported methods.[8] The semicarbazone derivatives of diethyl 2-(3-oxo-1,3-diarylpropyl)malonates **2** (**3a–j**) were prepared by refluxing aqueous ethanolic solutions of **2**, semicarbazide hydrochloride, and anhydrous sodium acetate. Selenium dioxide oxidation of the semicarbazones in glacial acetic acid gave the desired selenadiazoles **4** (Scheme 1). The yields of 1,2,3-selenadiazoles from semicarbazones are moderate (around 50%). However, the treatment of thionyl chloride with the semicarbazones (**3**) did not lead to the expected product but yielded the parent ketones (**2**) instead of thiadiazoles (**5**). Hydrolysis probably occurred, leading to the formation of the parent ketone (Scheme 1). Conversion of the parent ketones (**2**) to tosylhydrazones and subjecting the latter to thionyl chloride treatment also did not prove to be a useful method of preparing these thiadiazoles. The compounds **4** have been well characterized by $^{1}$H and $^{13}$C NMR.

The yields, melting points, and elemental analyses of the semicarbazones and the selenadiazoles are given in Table I, while the proton and carbon NMR of **3** and **4** are presented in Table II. The IR (KBr) spectrum of semicarbazone **3g** exhibits characteristic absorption bands in the regions 3511.74, 3397.96, 3191.61, 3089.40, 1679.69, and 1565.92 cm$^{-1}$. The formation of selenadiazoles is evident from the absence of the characteristic NH and $NH_2$ bands in the IR spectrum of the selenadiazole **4g**. The IR (KBr) spectrum of this selenadiazole shows absorption bands at 1751.05 cm$^{-1}$ for carbonyl stretching of the ester moiety and a weak band at 1513.85 cm$^{-1}$ for $\nu_{N=N}$. The complete assignment of proton and carbon NMR signals for a representative compound **4g** (numbered as shown in Scheme 1 for easy reference) is described here. The proton NMR spectrum of diethyl 2-{[4-(4-chlorophenyl)-1,2,3-selenadiazol-5-yl](4-methylphenyl)methyl} malonate (**4g**) exhibits two triplets, each accounting for three hydrogens at 0.97 ppm and 1.12 ppm with a coupling constant of 7.2 Hz. There are two quartets, each accounting for two hydrogens with the same coupling constant at 3.94 and 4.07 ppm. The diastereotopic characteristic of both methyl and methylene hydrogens of the esters is evident from the above sets of signals. Mutually coupled one-hydrogen doublets with a coupling constant of 10.8 Hz appear at 4.06 ppm and 5.25 ppm. There is a three-hydrogen singlet at 2.28 ppm (Ar—Me). Two pairs of AB pseudoquartets, one centered at 6.97 ppm and 7.07 ppm, another centered at 7.51 ppm and 7.60 ppm, are found. The former pair is due to the *p*-methylphenyl ring, while the latter is due to *p*-chlorophenyl ring.



|  | $R^1$ | $R^2$ |
|---|---|---|
| a | H | H |
| b | H | $CH_3$ |
| c | H | $OCH_3$ |
| d | H | Cl |
| e | H | $NO_2$ |
| f | Cl | H |
| g | Cl | $CH_3$ |
| h | Cl | $OCH_3$ |
| i | Cl | Cl |
| j | Cl | $NO_2$ |

**SCHEME 1**

**TABLE I** Physical Data of Compounds **3** and **4**

| Compound | Yield (%) | m.p. (°C) | Molecular formula | C% Calcd. | C% Found | H% Calcd. | H% Found |
|---|---|---|---|---|---|---|---|
| **3a** | 78 | 137 | $C_{23}H_{27}N_3O_5$ | 64.93 | 64.87 | 6.40 | 6.47 |
| **3b** | 80 | 119 | $C_{24}H_{29}N_3O_5$ | 65.59 | 65.70 | 6.65 | 6.56 |
| **3c** | 73 | 89 | $C_{24}H_{29}N_3O_6$ | 63.28 | 63.19 | 6.42 | 6.48 |
| **3d** | 68 | 139 | $C_{23}H_{26}ClN_3O_5$ | 60.06 | 59.92 | 5.70 | 5.62 |
| **3e** | 76 | 166 | $C_{23}H_{26}N_4O_7$ | 58.72 | 58.86 | 5.57 | 5.68 |
| **3f** | 87 | 156 | $C_{23}H_{26}ClN_3O_5$ | 60.06 | 59.90 | 5.70 | 5.87 |
| **3g** | 77 | 167 | $C_{24}H_{28}ClN_3O_5$ | 60.82 | 60.98 | 5.95 | 5.87 |
| **3h** | 75 | 159 | $C_{24}H_{28}ClN_3O_6$ | 58.83 | 58.58 | 5.76 | 5.59 |
| **3i** | 64 | 132 | $C_{23}H_{25}Cl_2N_3O_5$ | 55.88 | 56.09 | 5.10 | 4.95 |
| **3j** | 72 | 151 | $C_{23}H_{25}ClN_4O_7$ | 54.71 | 54.88 | 4.99 | 5.16 |
| **4a** | 47 | Oil | $C_{22}H_{22}N_2O_4Se$ | 57.77 | 57.58 | 4.85 | 4.69 |
| **4b** | 55 | 73–74 | $C_{23}H_{24}N_2O_4Se$ | 58.60 | 58.82 | 5.13 | 5.26 |
| **4c** | 44 | 82 | $C_{23}H_{24}N_2O_5Se$ | 56.68 | 56.59 | 4.96 | 4.83 |
| **4d** | 48 | 98 | $C_{22}H_{21}ClN_2O_4Se$ | 53.73 | 53.90 | 4.30 | 4.44 |
| **4e** | 52 | 136 | $C_{22}H_{21}N_3O_6Se$ | 52.60 | 52.55 | 4.21 | 4.34 |
| **4f** | 45 | 104 | $C_{22}H_{21}ClN_2O_4Se$ | 53.73 | 53.94 | 4.30 | 4.43 |
| **4g** | 56 | 91 | $C_{23}H_{23}ClN_2O_4Se$ | 54.61 | 54.53 | 4.58 | 4.63 |
| **4h** | 47 | 128 | $C_{23}H_{23}ClN_2O_5Se$ | 52.94 | 53.09 | 4.44 | 4.56 |
| **4i** | 40 | 102 | $C_{22}H_{20}Cl_2N_2O_4Se$ | 50.21 | 50.18 | 3.83 | 3.69 |
| **4j** | 37 | 78 | $C_{22}H_{20}ClN_3O_6Se$ | 49.22 | 49.40 | 3.76 | 3.68 |

The methyl singlet at 2.28 ppm shows HMBC contours with the signals at 129.73 and 137.75 ppm. The former signal is assigned to the C-3′ and the latter to the C-4′, as the former makes a C, H-COSY cross peak with the signal at 7.07 ppm, which is due to H-3′. As the signal at 6.97 ppm makes an H, H-COSY contour with H-3′, it is assigned to H-2′. This signal has a C, H-COSY contour with a signal at 127.84 ppm, and hence the latter is C-2′. The H-2′ proton makes an HMBC contour with the signal at 45.37 ppm, which is now assigned to C-6, and this correlates with 5.25 ppm (H-6) in C, H-COSY. The atoms C-7 and H-7 are assigned to signals at 61.59 ppm and 4.06 ppm, respectively, which is confirmed from H, H-COSY and C, H-COSY spectra. The signal at 159.20 ppm has to be assigned either to C-4 or C-5. This signal has an HMBC contour with aromatic hydrogen at 7.60 ppm. This shows that the carbon is C-4 and the hydrogen is H-6′. From H, H-COSY and C, H-COSY experiments it is very easy to assign signals at 7.51 ppm, 131.26 ppm, and 129.08 ppm to H-7′, C-6′, and C-7′. The other deshielded carbon signal at 161.82 ppm can be comfortably assigned to C-5. The H-7′ makes a strong HMBC contour with the signal at 130.38 ppm and a weak one with the signal at 134.92/135.08 ppm, suggesting the former to be due to C-5′ and the latter to C-8′. The final signal at 135.08/134.92 ppm is assigned to C-1′.

**TABLE II** $^1$H and $^{13}$C NMR Spectral Data of Compounds **3** and **4**

| Compound | $^1$H NMR (ppm) | $^{13}$C NMR Aliphatic carbons (ppm) | $^{13}$C NMR Aromatic carbons (ppm) | $^{13}$C NMR Ester carbonyl (ppm) |
|---|---|---|---|---|
| **3a** | 0.89 (t, $J = 7.2$ Hz, 3H), 1.32 (t, $J = 7.2$ Hz, 3H), 2.99 (dd, $J = 13.95$, 11.1 Hz, 1H), 3.14 (dd, $J = 13.95$, 3.0 Hz, 1H), 3.70 (dt, $J = 11.1$, 3.0 Hz, 1H), 3.88 (d, $J = 11.1$ Hz, 1H), 3.89 (m, 2H), 4.36 (m, 2H), 5.41 (br s, 1H, NH), 6.12 (br s, 1H, NH), 7.07–7.22 (m, 8H-Ar), 7.29 (dd, $J = 7.8$, 1.8 Hz, 2H-Ar), 9.10 (br s, 1H, NH) | 13.63, 14.10, 33.21, 41.80, 50.88, 61.57, 62.50 | 126.20, 127.71, 128.05, 128.07, 128.54, 128.63, 137.40, 138.73, 146.43, 157.40 | 167.20, 169.23 |
| **3b** | 0.92 (t, $J = 7.2$ Hz, 3H), 1.31 (t, $J = 7.2$ Hz, 3H), 2.21 (s, 3H), 2.97 (dd, $J = 13.95$, 11.1 Hz, 1H), 3.12 (dd, $J = 14.1$, 3.3 Hz, 1H), 3.66 (dt, $J = 10.65$, 3.3 Hz, 1H), 3.85 (d, $J = 10.5$ Hz, 1H), 3.90 (m, 2H), 4.35 (m, 2H), 5.22 (br s, 1H, NH), 6.15 (br s, 1H, NH), 6.97 (s, 4H-Ar), 7.19–7.24 (m, 3H-Ar), 7.32 (dd, $J = 7.8$, 1.8 Hz, 2H-Ar), 9.08 (br s, 1H, NH) | 13.67, 14.10, 20.98, 33.16, 41.43, 56.99, 61.51, 62.38 | 126.26, 127.86, 128.03, 128.57, 129.16, 135.62, 137.29, 137.41, 146.59, 157.50 | 167.28, 169.23 |
| **3c** | 0.94 (t, $J = 7.2$ Hz, 3H), 1.34 (t, $J = 7.2$ Hz, 3H), 2.94 (dd, $J = 13.8$, 11.4 Hz, 1H), 3.11 (dd, $J = 13.8$, 3.0 Hz, 1H), 3.64 (dt, $J = 10.8$, 3.0 Hz, 1H), 3.70 (s, 3H), 3.81 (d, $J = 10.5$ Hz, 1H), 3.91 (m, 2H), 4.35 (m, 2H), 4.94 (br s, 1H, NH), 6.18 (br s, 1H, NH), 6.69 (d, $J = 8.7$ Hz, 2H-Ar), 7.00 (d, $J = 8.7$ Hz, 2H-Ar), 7.18–7.22 (m, 3H-Ar), 7.30 (dd, $J = 7.65$, 2.1 Hz, 2H-Ar), 9.06 (br s, 1H, NH) | 13.70, 14.10, 32.90, 41.23, 55.20, 57.21, 61.48, 62.33 | 113.81, 126.32, 128.10, 128.62, 129.17, 130.67, 137.43, 146.77, 157.85, 158.86 | 167.38, 169.17 |

*(Continued on next page)*

**TABLE II** $^1$H and $^{13}$C NMR Spectral Data of Compounds **3** and **4** *(Continued)*

| Compound | $^1$H NMR (ppm) | $^{13}$C NMR<br>Aliphatic carbons (ppm) | <br>Aromatic carbons (ppm) | <br>Ester carbonyl (ppm) |
|---|---|---|---|---|
| **3d** | 0.94 (t, $J = 7.2$ Hz, 3H), 1.32 (t, $J = 7.2$ Hz, 3H), 3.04 (dd, $J = 14.1$, 11.1 Hz, 1H), 3.14 (dd, $J = 13.95$, 3.6 Hz, 1H), 3.68 (dt, $J = 10.5$, 3.6 Hz, 1H), 3.84 (d, $J = 10.5$ Hz, 1H), 3.91 (q, $J = 7.2$ Hz, 2H), 4.35 (m, 2H), 5.14 (br s, 1H, NH), 6.18 (br s, 1H, NH), 7.01 (d, $J = 8.4$ Hz, 2H-Ar), 7.11 (d, $J = 8.7$ Hz, 2H-Ar), 7.21–7.26 (m, 3H-Ar), 7.31 (dd, $J = 7.8$, 1.8 Hz, 2H-Ar), 9.36 (br s, 1H, NH) | 13.70, 14.09, 32.57, 41.31, 56.83, 61.69, 62.55 | 126.17, 128.18, 128.51, 128.78, 129.55, 133.35, 137.20, 146.26, 157.53 | 167.09, 168.93 |
| **3e** | 0.94 (t, $J = 7.2$ Hz, 3H), 1.33 (t, $J = 7.2$ Hz, 3H), 3.20 (m, 2H), 3.75–3.96 (m, 4H), 4.31–4.42 (m, 2H), 5.12 (br s, 1H, NH), 6.17 (br s, 1H, NH), 7.23–7.35 (m, 7H-Ar), 7.98 (d, $J = 8.7$ Hz, 2H-Ar), 9.59 (br s, 1H, NH) | 13.70, 14.06, 31.79, 41.83, 56.47, 61.82, 62.67 | 123.34, 126.09, 128.32, 129.03, 129.28, 136.87, 145.84, 146.35, 147.06, 157.58 | 166.83, 168.42 |
| **3f** | 0.89 (t, $J = 7.2$ Hz, 3H), 1.32 (t, $J = 7.2$ Hz, 3H), 2.97 (dd, $J = 13.8$, 11.4 Hz, 1H), 3.12 (dd, $J = 13.95$, 3.0 Hz, 1H), 3.66 (dt, $J = 10.95$, 3.0 Hz, 1H), 3.89 (d, $J = 10.5$ Hz, 1H), 3.89 (m, 2H), 4.39 (m, 2H), 5.28 (br s, 1H, NH), 6.09 (br s, 1H, NH), 7.07–7.17 (m, 7H-Ar), 7.23 (d, $J = 9.0$ Hz, 2H-Ar), 9.25 (br s, 1H, NH) | 13.63, 14.10, 33.11, 41.81, 56.79, 61.58, 62.53 | 127.47, 127.82, 128.05, 128.21, 128.60, 134.53, 135.88, 138.63, 145.24, 157.34 | 167.14, 169.25 |
| **3g** | 0.92 (t, $J = 7.2$ Hz, 3H), 1.31 (t, $J = 7.2$ Hz, 3H), 2.22 (s, 3H), 2.97 (dd, $J = 14.1$, 11.4 Hz, 1H), 3.10 (dd, $J = 14.1$, 3.3 Hz, 1H), 3.62 (dt, $J = 10.95$, 3.3 Hz, 1H), 3.87 (d, $J = 10.8$ Hz, 1H), 3.89 (q, $J = 7.2$ Hz, 2H), 4.34 (m, 2H), 5.55 (br s, 1H, NH), 6.07 (br s, 1H, NH), 6.96 (s, 4H-Ar), 7.16 (d, $J = 8.7$ Hz, 2H-Ar), 7.26 (d, $J = 8.4$ Hz, 2H-Ar), 9.25 (br s, 1H, NH) | 13.69, 14.09, 20.99, 32.99, 41.51, 56.95, 61.52, 62.40 | 127.58, 127.89, 128.19, 129.19, 134.47, 135.53, 135.96, 137.41, 145.46, 157.53 | 167.23, 169.25 |

| | | | | |
|---|---|---|---|---|
| **3h** | 0.94 (t, $J=7.2$ Hz, 3H), 1.31 (t, $J=7.2$ Hz, 3H), 2.94 (dd, $J=14.1$, 11.4 Hz, 1H), 3.09 (dd, $J=13.95$, 3.0 Hz, 1H), 3.61 (dt, $J=10.95$, 3.0 Hz, 1H), 3.71 (s, 3H), 3.83 (d, $J=10.8$ Hz, 1H), 3.90 (m, 2H), 4.35 (m, 2H), 5.28 (br s, 1H, NH), 6.10 (br s, 1H, NH), 6.69 (d, $J=8.7$ Hz, 2H-Ar), 6.99 (d, $J=8.7$ Hz, 2H-Ar), 7.16 (d, $J=8.7$ Hz, 2H-Ar), 7.25 (d, $J=8.7$ Hz, 2H-Ar), 9.24 (br s, 1H, NH) | 13.73, 14.10, 33.18, 41.06, 55.26, 57.05, 61.56, 62.46 | 113.95, 127.54, 128.22, 129.11, 130.54, 134.50, 135.95, 145.49, 157.33, 159.02 | 167.22, 169.27 |
| **3i** | 0.94 (t, $J=7.2$ Hz, 3H), 1.32 (t, $J=7.2$ Hz, 3H), 2.99 (dd, $J=13.95$, 11.4 Hz, 1H), 3.12 (dd, $J=14.25$, 3.3 Hz, 1H), 3.65 (dt, $J=10.8$, 3.0 Hz, 1H), 3.84 (d, $J=10.5$ Hz, 1H), 3.91 (q, $J=7.2$ Hz, 2H), 4.35 (m, 2H), 5.19 (br s, 1H, NH), 6.16 (br s, 1H, NH), 7.01 (d, $J=8.4$ Hz, 2H-Ar), 7.13 (d, $J=8.4$ Hz, 2H-Ar), 7.19 (d, $J=8.7$ Hz, 2H-Ar), 7.25 (d, $J=8.7$ Hz, 2H-Ar), 9.40 (br s, 1H, NH) | 13.70, 14.08, 32.55, 41.26, 56.73, 61.76, 62.63 | 127.43, 128.38, 128.65, 129.48, 133.58, 134.81, 135.65, 137.09, 145.15, 157.40 | 167.02, 168.99 |
| **3j** | 0.93 (t, $J=7.2$ Hz, 3H), 1.33 (t, $J=7.2$ Hz, 3H), 3.18 (dd, $J=14.4$, 4.5 Hz, 1H), 3.27 (dd, $J=14.4$, 10.8 Hz, 1H), 3.79 (dt, $J=10.65$, 4.5 Hz, 1H), 3.89 (m, 2H), 3.98 (d, $J=10.8$ Hz, 1H), 4.35 (m, 2H), 5.32 (br s, 1H, NH), 6.12 (br s, 1H, NH), 7.26–7.30 (m, 4H-Ar), 7.39 (d, $J=8.7$ Hz, 2H-Ar), 8.01 (d, $J=8.7$ Hz, 2H-Ar), 9.84 (br s, 1H, NH) | 13.73, 14.09, 31.30, 42.05, 56.57, 61.84, 62.92 | 123.39, 127.51, 128.67, 129.34, 135.13, 135.31, 144.98, 146.31, 147.17, 157.81 | 166.88, 168.33 |
| **4a** | 0.93 (t, $J=7.2$ Hz, 3H), 1.11 (t, $J=7.2$ Hz, 3H), 3.92 (m, 2H), 4.07 (m, 2H), 4.09 (d, $J=10.8$ Hz, 1H), 5.35 (d, $J=10.8$ Hz, 1H), 7.10 (dd, $J=7.8$, 1.8 Hz, 2H-Ar), 7.20–7.29 (m, 3H-Ar), 7.49–7.56 (m, 3H-Ar), 7.63 (dd, $J=7.8$, 1.8 Hz, 2H-Ar) | 13.64, 13.84, 45.72, 61.59, 61.89, 62.10 | 127.80, 128.07, 128.81, 128.96, 128.99, 129.90, 131.85, 138.24, 160.52, 161.07 | 166.27, 166.97 |

(Continued on next page)

**TABLE II** $^{1}$H and $^{13}$C NMR Spectral Data of Compounds **3** and **4** *(Continued)*

| Compound | $^{1}$H NMR (ppm) | $^{13}$C NMR Aliphatic carbons (ppm) | $^{13}$C NMR Aromatic carbons (ppm) | $^{13}$C NMR Ester carbonyl (ppm) |
|---|---|---|---|---|
| **4b** | 0.96 (t, $J = 7.2$ Hz, 3H), 1.11 (t, $J = 7.2$ Hz, 3H), 2.28 (s, 3H), 3.93 (m, 2H), 4.07 (m, 2H), 4.07 (d, $J =$ 10.8 Hz, 1H), 5.31 (d, $J = 10.8$ Hz, 1H), 6.98 (d, $J = 8.1$ Hz, 2H-Ar), 7.06 (d, $J = 8.1$ Hz, 2H-Ar), 7.51–7.57 (m, 3H-Ar), 7.64 (dd, $J = 7.8$, 1.8 Hz, 2H-Ar) | 13.63, 13.84, 21.02, 45.31, 61.61, 61.86, 62.07 | 127.85, 128.79, 128.95, 129.64, 129.90, 131.87, 135.26, 137.57, 160.39, 161.39 | 166.30, 167.02 |
| **4c** | 0.97 (t, $J = 7.2$ Hz, 3H), 1.12 (t, $J = 7.2$ Hz, 3H), 3.75 (s, 3H), 3.94 (m, 2H), 4.04 (d, $J = 10.8$ Hz, 1H), 4.07 (q, $J = 7.2$ Hz, 2H), 5.30 (d, $J = 10.8$ Hz, 1H), 6.78 (d, $J = 8.7$ Hz, 2H-Ar), 7.01 (d, $J = 8.7$ Hz, 2H-Ar), 7.51–7.56 (m, 3H-Ar), 7.63 (dd, $J = 7.8$, 1.8 Hz, 2H-Ar) | 13.72, 13.86, 44.99, 55.24, 61.81, 61.88, 62.08 | 114.27, 128.80, 128.96, 129.21, 129.89, 130.14, 131.87, 158.90, 160.31, 161.53 | 166.33, 167.03 |
| **4d** | 0.98 (t, $J = 7.2$ Hz, 3H), 1.13 (t, $J = 7.2$ Hz, 3H), 3.95 (m, 2H), 4.05 (d, $J = 10.8$ Hz, 1H), 4.09 (q, $J =$ 7.2 Hz, 2H), 5.33 (d, $J = 10.5$ Hz, 1H), 7.01 (d, $J = 8.7$ Hz, 2H-Ar), 7.23 (d, $J = 8.4$ Hz, 2H-Ar), 7.51–7.62 (m, 5H-Ar) | 13.66, 13.82, 44.98, 61.23, 62.03, 62.22 | 128.86, 129.09, 129.39, 129.77, 131.63, 133.69, 136.69, 160.31, 160.56 | 166.07, 166.79 |
| **4e** | 1.00 (t, $J = 7.2$ Hz, 3H), 1.16 (t, $J = 7.2$ Hz, 3H), 3.97 (m, 2H), 4.10–4.16 (m, 3H), 5.49 (d, $J = 10.5$ Hz, 1H), 7.23 (d, $J = 8.4$ Hz, 2H-Ar), 7.56 (m, 5H-Ar), 8.11 (d, $J = 8.4$ Hz, 2H-Ar) | 13.74, 13.88, 45.13, 60.64, 62.32, 62.53 | 124.12, 129.06, 129.08, 129.38, 129.73, 131.42, 145.43, 147.19, 158.94, 160.90 | 165.86, 166.61 |

| | | | | |
|---|---|---|---|---|
| **4f** | 0.94 (t, $J = 7.2$ Hz, 3H), 1.13 (t, $J = 7.2$ Hz, 3H), 3.93 (m, 2H), 4.08 (d, $J = 10.5$ Hz, 1H), 4.08 (q, $J = 7.2$ Hz, 2H), 5.28 (d, $J = 10.8$ Hz, 1H), 7.09 (dd, $J = 7.8$, 1.5 Hz, 2H-Ar), 7.20–7.30 (m, 3H-Ar), 7.51 (d, $J = 8.7$ Hz, 2H-Ar), 7.59 (d, $J = 8.7$ Hz, 2H-Ar) | 13.66, 13.87, 45.75, 61.56, 61.99, 62.19 | 127.96, 128.03, 129.08, 129.10, 130.33, 131.25, 135.15, 137.89, 159.34, 161.49 | 166.17, 167.01 |
| **4g** | 0.97 (t, $J = 7.2$ Hz, 3H), 1.12 (t, $J = 7.2$ Hz, 3H), 2.28 (s, 3H), 3.94 (m, 2H), 4.06 (d, $J = 10.8$ Hz, 1H), 4.07 (q, $J = 7.2$ Hz, 2H), 5.25 (d, $J = 10.8$ Hz, 1H), 6.97 (d, $J = 8.1$ Hz, 2H-Ar), 7.07 (d, $J = 8.1$ Hz, 2H-Ar), 7.51 (d, $J = 8.4$ Hz, 2H-Ar), 7.60 (d, $J = 8.4$ Hz, 2H-Ar) | 13.68, 13.87, 21.02, 45.37, 61.59, 61.95, 62.13 | 127.84, 129.07, 129.73, 130.39, 131.23, 134.92, 135.08, 137.75, 159.20, 161.83 | 166.19, 167.06 |
| **4h** | 0.98 (t, $J = 7.2$ Hz, 3H), 1.13 (t, $J = 7.2$ Hz, 3H), 3.75 (s, 3H), 3.95 (q, $J = 7.2$ Hz, 2H), 4.03 (d, $J = 10.8$ Hz, 1H), 4.08 (q, $J = 7.2$ Hz,2H), 5.23 (d, $J = 10.5$ Hz, 1H), 6.79 (d, $J = 8.7$ Hz, 2H-Ar), 7.00 (d, $J = 8.7$ Hz, 2H-Ar), 7.51 (d, $J = 8.4$ Hz, 2H-Ar), 7.59 (d, $J = 8.4$ Hz, 2H-Ar) | 13.74, 13.88, 45.06, 55.26, 61.80, 61.95, 62.13 | 114.38, 129.08, 129.20, 129.83, 130.42, 131.26, 135.11, 159.03, 159.11, 161.99 | 166.22, 167.07 |
| **4i** | 0.99 (t, $J = 7.2$ Hz, 3H), 1.14 (t, $J = 7.2$ Hz, 3H), 3.96 (q, $J = 7.2$ Hz, 2H), 4.04 (d, $J = 10.8$ Hz, 1H), 4.10 (q, $J = 7.2$ Hz, 2H), 5.27 (d, $J = 10.5$ Hz, 1H), 7.01 (d, $J = 8.4$ Hz, 2H-Ar), 7.24 (d, $J = 8.4$ Hz, 2H-Ar), 7.52 (d, $J = 8.4$ Hz, 2H-Ar), 7.57 (d, $J = 8.4$ Hz, 2H-Ar) | 13.72, 13.88, 45.06, 61.23, 62.16, 62.33 | 129.20, 129.24, 129.39, 130.16, 131.17, 133.91, 135.30, 136.42, 159.40, 160.78 | 166.00, 166.87 |
| **4j** | 1.01 (t, $J = 7.2$ Hz, 3H), 1.17 (t, $J = 7.2$ Hz, 3H), 3.96–4.00 (m, 2H), 4.10–4.17 (m, 3H), 5.43 (d, $J = 10.5$ Hz, 1H), 7.24 (d, $J = 9.0$ Hz, 2H-Ar), 7.55 (s, 4H-Ar), 8.13 (d, $J = 8.7$ Hz, 2H-Ar) | 13.76, 13.90, 45.15, 60.61, 62.42, 62.60 | 124.24, 129.02, 129.39, 129.89, 131.10, 135.60, 145.13, 147.28, 159.35, 159.71 | 165.75, 166.65 |

The vicinal coupling constant around 10.8 Hz between the H-6 and H-7 in both the semicarbazones and the selenadiazoles shows that these two hydrogens are *anti* to each other, and this locked conformation seems to be the predominant one. If other conformations also contribute, the coupling constant should be smaller than this value. The diastereotopic character due to the asymmetry at C-6 was noticed even at the terminal methyls of the ester groups. There are two methyl signals, two methylene signals, and two carbonyl signals for the ester groups noted in the $^1$H and $^{13}$C NMR spectra. The NOESY spectrum shows only the normal bonded relationship and no nonbonded relations.

## EXPERIMENTAL

The melting points are uncorrected. NMR spectra were recorded on a Bruker 300 MHz (UltraShield) NMR spectrometer at room temperature using $CDCl_3$ as solvent with tetramethylsilane (TMS) as internal standard. IR spectra were recorded on a JASCO FTIR instrument.

### General Procedure for the Preparation of Diethyl 2-(3-Oxo-1,3-diarylpropyl)malonates (2)

The adducts, diethyl 2-(3-oxo-1,3-diarylpropyl)malonates (**2**) have all been prepared by reported procedures.[8] Diethyl malonate (0.06 mole) was added to different chalcones **1** (0.06 mole) in ether solution in the presence of a small amount of sodium ethoxide (0.012 mole) in ethanol, and the reaction mixture was kept at room temperature for about 20 h to get **2**, which were recrystallised from ethanol.

### General Procedure for the Preparation of Diethyl 2-{3-[2-(Aminocarbonyl)hydrazono]-1,3-diarylpropyl}-malonates (3)

To a warm solution of 0.005 mole of the appropriate ketone (**2**) in 30 ml of ethanol, a solution of equimolar amount of semicarbazide hydrochloride (5.57 g, 0.05 mole) and anhydrous sodium acetate (4.1 g, 0.05 mole) in 20 ml of water was added and refluxed for 4 h. The solution was cooled and poured onto crushed ice. The precipitated semicarbazone was washed with water, dried, and recrystallised from ethanol.

## General Procedure for the Preparation of Diethyl 2-[aryl(4-Aryl-1,2,3-selenadiazol-5-yl)methyl]-malonates (4)

2.22 g (0.02 mole) of powdered selenium dioxide was dissolved in glacial acetic acid by gentle warming. To this warm solution, 0.002 mole of the appropriate semicarbazone (**3**) was added at once, and the mixture was gently heated in a water bath until gas evolution ceased. The selenium deposited on cooling was removed by filtration, and the filtrate was poured onto crushed ice, extracted with chloroform, and purified by column chromatography using silica gel (60–120 mesh).

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