Expeditious Synthesis of New 1,2,3-Thiadiazoles and 1,2,3-Selenadiazoles from 1,2-Diaza-1,3-Butadienes *via* Hurd-Mori Type Reactions

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Table for compounds 3a-m. Yields and reaction times of α -substituted hydrazones.

								Yield	Time
1	R ¹	R ²	2	R ³	R ⁴	R ⁵	3	(%) ^a	(h)
1a	Me	<i>Ot</i> -Bu	2a	H	Me	CO ₂ Me	3a^b	92	0.1
1b	Et	<i>Ot</i> -Bu	2a	H	Me	CO ₂ Me	3b^b	89	0.1
1c	Et	NH ₂	2a	H	Me	CO ₂ Me	3c^b	93	0.1
1b	Et	<i>Ot</i> -Bu	2b	H	Bn	CO ₂ Bn	3d^b	76	0.1
1a	Me	<i>Ot</i> -Bu	2c	Ph	Et	CO ₂ Et	3e^b	69	0.1
1d	Me	NH ₂	2c	Ph	Et	CO ₂ Et	3f^b	89	0.1
1a	Me	<i>Ot</i> -Bu	2d	Me	Et	CO ₂ Et	3g^b	62	0.1
1a	Me	<i>Ot</i> -Bu	2e	CO ₂ Et	Et	CO ₂ Et	3h^b	79	0.1
1d	Me	NH ₂	2e	CO ₂ Et	Et	CO ₂ Et	3i^b	91	0.2
1b	Et	<i>Ot</i> -Bu	2f	H	Et	<i>p</i> NO ₂ Ph	3j^{b, d}	82	0.1
1b	Et	<i>Ot</i> -Bu	2g	<i>i</i> -Pr			3k^c	73	24.0
1a	Me	<i>Ot</i> -Bu	2h	Ph			3l^c	63	20.0
1d	Me	NH ₂	2h	Ph			3m^c	93	0.1

^aYield of pure isolated products. ^bMeONa was used. ^cNaH was used. ^d*Syn/anti* mixture in ratio 50:50.

Table for compounds 4a-i. Yields and reaction times of 1,2,3-thiadiazoles.

							Yield	Time
3	R ¹	R ²	R ³	R ⁴	R ⁵	4	(%) ^a	(h)
3a	Me	<i>Ot</i> -Bu	H	Me	CO ₂ Me	4a	82	4.5
3b	Et	<i>Ot</i> -Bu	H	Me	CO ₂ Me	4b	81	5.0
3d	Et	<i>Ot</i> -Bu	H	Bn	CO ₂ Bn	4c	75	12.0

3e	Me	<i>Ot</i> -Bu	Ph	Et	CO ₂ Et	4d	87	3.0
3g	Me	<i>Ot</i> -Bu	Me	Et	CO ₂ Et	4e	82	2.5
3h	Me	<i>Ot</i> -Bu	CO ₂ Et	Et	CO ₂ Et	4f	82	3.5
3j	Et	<i>Ot</i> -Bu	H	Et	<i>p</i> NO ₂ Ph	4g^b	83	1.0
3k	Et	<i>Ot</i> -Bu	<i>i</i> -Pr			4h	72	1.5
3l	Me	<i>Ot</i> -Bu	Ph			4i	80	1.0

^aYield of pure isolated products. ^b*Syn/anti* mixture in ratio 50:50.

Figure 1: Crystal structures of the two polymorphs of **12a**. Ellipsoid enclosed 50% of probability. For **12a2**, the atoms C(22) and C(23) having site occupation factor of 0.55(6) are reported.

Table 7. Selected torsion angles (°) for **12a1** and **12a2**.

	12a1	12a2
N(2)-C(3)-C(5)-C(6)	-140.91(17)	-124.8(7)
N(2)-C(3)-C(5)-C(8)	92.4(2)	105.2(7)
C(3)-C(5)-C(6)-O(6)	-89.9(2)	-99.6(7)
C(3)-C(5)-C(8)-C(11)	-168.11(14)	-160.8(5)
C(4)-C(3)-C(5)-C(6)	39.2(3)	54.3(10)
C(5)-C(8)-C(9)-O(9)	-59.9(2)	-64.1(8)
C(5)-C(8)-C(11)-O(11)	-22.2(2)	156.7(6)
C(5)-C(8)-C(11)-O(12)	159.84(14)	-24.6(7)
C(6)-C(5)-C(8)-C(11)	66.73(18)	73.0(6)
C(8)-C(13)-C(14)-O(14)	134.1(2)	-32.4(11)
C(8)-C(13)-C(14)-O(15)	-48.7(2)	150.4(6)
C(9)-C(8)-C(11)-O(11)	97.1(2)	-82.4(8)
C(9)-C(8)-C(11)-O(12)	-80.87(18)	96.3(6)
C(10)-O(10)-C(9)-O(9)	-0.2(3)	-4.8(11)
C(11)-C(8)-C(13)-C(16)	61.10(19)	65.6(7)
C(12)-O(12)-C(11)-O(11)	6.7(3)	-1.6(9)
C(13)-C(8)-C(11)-O(11)	-141.83(17)	34.2(8)
C(13)-C(8)-C(11)-O(12)	40.2(2)	-147.1(5)
C(16)-C(13)-C(14)-O(14)	6.0(3)	-163.2(8)

C(16)-C(13)-C(14)-O(15)	-176.81(15)	19.6(9)
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Trimethyl 3-[2-(*tert*-butoxycarbonyl)hydrazono]butane-1,1,2-tricarboxylate (3a): m.p. 133-135 °C. IR: $\nu_{\max}$ 3236, 3160, 1754, 1742, 1727, 1700 cm^{-1} . ^1H NMR: δ 1.41 (s, 9 H, *Ot*-Bu), 1.84 (s, 3 H, CH_3), 3.60 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 3.64 (s, 3 H, OCH_3), 3.86 (d, 1 H, $J = 10.8$ Hz, CH), 4.07 (d, 1 H, $J = 10.8$ Hz, CH), 9.67 (s, 1 H, NH). ^{13}C NMR: δ 16.61 (q), 28.71 (q), 51.87 (d), 53.22 (q), 53.33 (q), 53.41 (d), 53.46 (q), 80.04 (s), 153.42 (s), 167.99 (s), 168.54 (s), 170.51 (s). MS: m/z (%) 360 (6) [M^+], 358 (22), 304 (17), 287 (18), 273 (36), 241 (100). Anal. Calcd for $\text{C}_{15}\text{H}_{24}\text{N}_2\text{O}_8$: C, 50.00; H, 6.71; N, 7.77. Found: C, 49.89; H, 6.59; N, 7.85.

2-Ethyl 1,1-dimethyl 3-[2-(*tert*-butoxycarbonyl)hydrazono]butane-1,1,2-tricarboxylate (3b): m.p. 90-93 °C. IR: $\nu_{\max}$ 3230, 3150, 1745, 1730, 1720, 1690, 1640 cm^{-1} . ^1H NMR: δ 1.15 (t, 3 H, $J = 7.0$ Hz, OCH_2CH_3), 1.43 (s, 9 H, *Ot*-Bu), 1.86 (s, 3 H, CH_3), 3.61 (s, 3 H, OCH_3), 3.66 (s, 3 H, OCH_3), 3.84 (d, 1 H, $J = 10.8$ Hz, CH), 4.05-4.11 (m, 3 H, CH and OCH_2CH_3), 9.71 (s, 1 H, NH). ^{13}C NMR: δ 14.72 (q), 16.79 (q), 51.94 (d), 53.36 (q), 53.46 (d), 53.57 (q), 61.98 (t), 80.02 (s), 153.28 (s), 167.86 (s), 168.35 (s), 169.71 (s). MS: m/z (%) 374 (3) [M^+], 318 (4), 287 (6), 273 (8), 255 (11), 241 (36), 228 (27), 218 (63), 210 (34), 196 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{N}_2\text{O}_8$: C, 51.33; H, 7.00; N, 7.48. Found: C, 51.21; H, 7.17; N, 7.39.

2-Ethyl 1,1-dimethyl 3-[2-(aminocarbonyl)hydrazono]butane-1,1,2-tricarboxylate (3c): m.p. 119-122 °C. IR: $\nu_{\max}$ 3530, 3400, 3200, 1750, 1730, 1690, 1640

cm⁻¹. ¹H NMR: δ 1.16 (t, 3 H, J = 7.0 Hz, OCH₂CH₃), 1.86 (s, 3 H, CH₃), 3.61 (s, 3 H, OCH₃), 3.65 (s, 3 H, OCH₃), 3.88 (d, 1 H, J = 10.8 Hz, CH), 4.10 (q, 2 H, J = 7.0 Hz, OCH₂CH₃), 4.21 (d, 1 H, J = 10.8 Hz, CH), 6.20 (brs, 2 H, NH₂), 9.32 (s, 1 H, NH). ¹³C NMR: δ 14.82 (q), 16.72 (q), 51.98 (d), 53.29 (q), 53.42 (d), 53.59 (q), 62.01 (t), 142.59 (s), 157.49 (s), 168.22 (s), 168.46 (s), 170.34 (s). MS: m/z (%) 317 (4) [M⁺], 271 (3), 240 (29), 228 (25), 196 (74), 169 (100). Anal. calcd for C₁₂H₁₉N₃O₇: C, 45.42; H, 6.21; N, 13.16. Found: C, 45.35; H, 6.21; N, 13.16.

1,1-Dibenzyl 2-ethyl 3-[2-(*tert*-butoxycarbonyl)hydrazono]butane-1,1,2-tricarboxylate (3d): m.p. 93-95 °C. IR: $\nu_{\max}$ 3095, 3037, 1736, 1718 cm⁻¹. ¹H NMR: δ 1.08 (t, 3 H, J = 7.0 Hz, OCH₂CH₃), 1.42 (s, 9 H, *Or*-Bu), 1.84 (s, 3 H, CH₃), 3.88 (d, 1 H, J = 11.0 Hz, CH), 4.01 (q, 2 H, J = 7.0 Hz, OCH₂CH₃), 4.22 (d, 1 H, J = 11.0 Hz, CH), 5.02-5.16 (m, 4 H, 2 OCH₂Ar), 7.27-7.32 (m, 10 H, 2 OCH₂Ar), 9.71 (s, 1 H, NH). ¹³C NMR: δ = 14.44 (q), 16.64 (q), 28.75 (q), 52.22 (d), 53.51 (d), 61.91 (t), 67.55 (t), 80.06 (s), 127.08 (s), 128.44 (d), 128.57 (d), 128.70 (d), 128.75 (d), 128.88 (d), 129.03 (d), 129.10 (d), 136.02 (s), 167.32 (s), 167.76 (s), 169.81 (s). MS : m/z (%) 526 (1) [M⁺], 470 (18), 453 (18), 426 (47), 370 (100). Anal. calcd for C₂₈H₃₄N₂O₈: C, 63.87; H, 6.51; N, 5.32. Found: C, 63.79; H, 6.59; N, 5.15.

1,1-Diethyl 2-methyl 3-[2-(*tert*-butoxycarbonyl)hydrazono]-1-phenylbutane-1,1,2-tricarboxylate (3e): m.p. 92-95 °C. IR: $\nu_{\max}$ 3247, 1780, 1735, 1695 cm⁻¹. ¹H NMR: δ 1.09-1.14 (m, 6 H, 2 OCH₂CH₃), 1.39 (s, 9 H, *Or*-Bu), 1.61 (s, 3 H, CH₃), 3.55 (s, 3 H, OCH₃), 4.09-4.18 (m, 4 H, 2 OCH₂CH₃), 4.47 (s, 1 H, CH), 7.25-7.27 (m, 5 H, Ar), 9.40 (s, 1 H, NH). ¹³C NMR: δ 14.45 (q), 14.51 (q), 17.86 (q), 28.91 (q), 52.76 (q), 58.85 (d), 62.14 (t), 62.38 (t), 64.97 (s), 79.89 (s), 127.90 (d), 129.70 (d), 136.20 (s), 147.23 (s), 153.20 (s), 168.52 (s), 169.40 (s), 170.48 (s). MS: m/z (%) 464 (1) [M⁺], 418 (6), 364 (28), 318 (32),

289 (50), 245 (100). Anal. calcd for $C_{23}H_{32}N_2O_8$: C, 59.47; H, 6.94; N, 6.03. Found: C, 59.59; H, 6.79; N, 6.18.

1,1-Diethyl 2-methyl 3-[2-(aminocarbonyl)hydrazono]-1-phenylbutane-1,1,2-tricarboxylate (3f): m.p. 153-160 °C. IR: $\nu_{\max}$ 3440, 3290, 3170, 1735, 1705, 1695, 1590 cm^{-1} . ^1H NMR: δ 1.10-1.22 (m, 6 H, 2 OCH_2CH_3), 1.96 (s, 3 H, CH_3), 3.67 (s, 3 H, OCH_3), 4.08-4.18 (m, 4 H, 2 OCH_2CH_3), 4.69 (s, 1 H, CH), 5.43 and 6.25 (2 brs, NH_2), 7.28-7.33 (m, 5 H, Ar), 9.21 (s, 1 H, NH). ^{13}C NMR: δ 14.21 (q), 14.64 (q), 18.6 (q), 52.34 (q), 58.06 (d), 62.07 (t), 62.29 (t), 65.17 (s), 124.44 (d), 126.80 (d), 128.13 (d), 134.92 (s), 151.61 (s), 154.94 (s), 168.73 (s), 169.57 (s), 170.44 (s). - MS: m/z (%) 407 (1) [M^+], 363 (9), 348 (25), 318 (37), 289 (51), 245 (100). Anal. calcd for $C_{19}H_{25}N_3O_7$: C, 56.01; H, 6.18; N, 10.31. Found: C, 56.15; H, 6.18; N, 10.31.

2,2-Diethyl 3-methyl 4-[2-(*tert*-butoxycarbonyl)hydrazono]pentane-2,2,3-tricarboxylate (3g): m.p. 70-74 °C. IR: $\nu_{\max}$ 3248, 1760, 1725, 1690, 1640 cm^{-1} . ^1H NMR: δ 1.07 (t, 6 H, $J = 7.0$ Hz, 2 OCH_2CH_3), 1.41 (s, 9 H, *Ot*-Bu), 1.46 (s, 3 H, CH_3), 1.95 (s, 3 H, CH_3), 3.64 (s, 3 H, OCH_3), 4.02-4.14 (m, 5 H, 2 OCH_2CH_3 and CH), 9.81 (s, 1 H, NH). ^{13}C NMR: δ 12.17 (q), 14.75 (q), 14.80 (q), 20.11 (q), 52.04 (d), 54.88 (q), 62.13 (t), 82.04 (s), 108.71 (s), 154.63 (s), 155.78 (s), 163.26 (s), 167.82 (s), 173.69 (s). MS: m/z (%) 402 (1) [M^+], 371 (16), 326 (25), 281 (51), 271 (100). Anal. calcd for $C_{18}H_{30}N_2O_8$: C, 53.72; H, 7.51; N, 6.96. Found: C, 53.65; H, 7.71; N, 6.88.

1,1,1-Triethyl 2-methyl 3-[2-(*tert*-butoxycarbonyl)hydrazono]butane-1,1,1,2-tetracarboxylate (3h): IR: $\nu_{\max}$ 3328, 3257, 1775, 1765, 1744, 1703 cm^{-1} . ^1H NMR: δ 1.14 (t, 9 H, $J = 7.0$ Hz, 3 OCH_2CH_3), 1.41 (s, 9 H, *Ot*-Bu), 1.84 (s, 3 H, CH_3), 3.59 (s, 3 H, OCH_3), 4.09 (s, 1 H, CH), 4.15 (q, 6 H, $J = 7.0$ Hz, 3 OCH_2CH_3), 9.52 (s, 1 H, NH). ^{13}C

NMR: δ 14.21 (q), 17.76 (q), 28.76 (q), 52.88 (q), 55.93 (d), 62.63 (t), 79.79 (s), 147.72 (s), 153.34 (s), 165.59 (s), 169.83 (s). MS: m/z (%) 460 (1) [M^+], 401 (7), 360 (22), 327 (50), 304 (52), 282 (54), 268 (27), 255 (40), 241 (100). Anal. calcd for $C_{20}H_{32}N_2O_{10}$: C, 52.17; H, 7.00; N, 6.08. Found: C, 52.35; H, 7.17; N, 6.87.

1,1,1-Triethyl 2-methyl 3-[2-(aminocarbonyl)hydrazono]butane-1,1,1,2-tetracarboxylate (3i): m.p. 100-101 °C. IR: $\nu_{\max}$ 3499, 3387, 1757, 1747, 1731 cm^{-1} . ^1H NMR: δ 1.28 (t, 9 H, $J = 7.2$ Hz, 3 OCH_2CH_3), 2.03 (s, 3 H, CH_3), 3.74 (s, 3 H, OCH_3), 4.19-4.33 (m, 7 H, 3 OCH_2CH_3 and CH), 5.82 (brs, 2 H, NH_2), 9.00 (s, 1 H, NH). ^{13}C NMR: δ 13.72 (q), 17.01 (q), 52.44 (q), 55.41 (d), 62.53 (t), 67.01 (s), 143.92 (s), 158.24 (s), 165.59 (s), 169.21 (s). MS: m/z (%) 403 (2) [M^+], 326 (9), 255 (11), 183 (100). Anal. calcd for $C_{16}H_{25}N_3O_9$: C, 47.64; H, 6.25; N, 10.42. Found: C, 47.81; H, 6.35; N, 10.37.

1,2-Diethyl 1-(4-nitrophenyl) 3-[2-(*tert*-butoxycarbonyl)hydrazono]butane-1,2-dicarboxylate (3j): m.p. 99-101 °C. IR: $\nu_{\max}$ 3320, 3243, 1737, 1732, 1701 cm^{-1} . ^1H NMR: δ 0.87, 1.08 and 1.15 (t, m and t, 6 H, $J = 6.8$ Hz, 2 OCH_2CH_3), 1.38 and 1.44 (2 s, 9 H, *Ot*-Bu), 1.64 and 1.87 (2 s, 3 H, CH_3), 3.82-4.14 (m, 5 H, 2 OCH_2CH_3 and CH), 4.40 and 4.50 (2 d, 1 H, $J = 12.0$ Hz, CH), 7.58 and 7.61 (2 d, 2 H, $J = 8.8$ Hz, Ar), 8.13 and 8.18 (2 d, 2 H, $J = 8.8$ Hz, Ar), 9.43 and 9.71 (2 s, 1 H, NH). ^{13}C NMR: δ 14.51 (q), 14.67 (q), 14.78 (q), 14.93 (q), 16.31 (q), 16.79 (q), 28.87 (q), 50.77 (d), 50.98 (d), 56.82 (d), 57.52 (d), 61.62 (t), 61.74 (t), 61.88 (t), 61.92 (t), 80.10 (s), 124.16 (d), 124.30 (d), 130.48 (d), 130.64 (d), 144.01 (s), 144.32 (s), 147.45 (s), 147.63 (s), 153.22 (s), 153.29 (s), 169.40 (s), 170.59 (s), 170.88 (s), 171.67 (s). MS: m/z (%) 451 (1) [M^+], 378 (10), 351 (50), 305 (100). Anal. calcd for $C_{21}H_{29}N_3O_8$: C, 55.87; H, 6.47; N, 9.31. Found: C, 55.71; H, 6.38; N, 9.50.

4-Ethyl 2-methyl 3-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)-5-[2-(*tert*-butoxycarbonyl)hydrazono]hexane-4-carboxylate (3k): m.p. 162-165 °C. IR: $\nu_{\max}$ 3234, 3160, 3121, 1772, 1737, 1698 cm^{-1} . ^1H NMR: δ 0.95 (d, 3 H, $J = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.02 (d, 3 H, $J = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.14 (t, 3 H, $J = 7.0$ Hz, OCH_2CH_3), 1.42 (s, 9 H, *Ot*-Bu), 1.70 (s, 3 H, CH_3), 1.78 (s, 3 H, CH_3), 1.82 (s, 3 H, CH_3), 2.27 (ept, 1 H, $J = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 4.06-4.19 (m, 2 H, OCH_2CH_3), 4.30 (s, 1 H, CH), 9.72 (s, 1 H, NH). ^{13}C NMR: δ 14.48 (q), 17.81 (q), 18.74 (q), 19.75 (q), 28.72 (q), 29.16 (q), 35.59 (d), 56.89 (d), 59.01 (s), 62.68 (t), 80.13 (s), 107.65 (s), 153.09 (s), 166.69 (s), 167.19 (s), 171.86 (s). MS: m/z (%) 428 (1) [M^+], 326 (23), 297 (9), 281 (10), 270 (20), 253 (24), 226 (100). Anal. calcd for $\text{C}_{20}\text{H}_{32}\text{N}_2\text{O}_8$: C, 56.06; H, 7.53; N, 6.54. Found: C, 56.25; H, 7.38; N, 6.37.

2-Methyl 1-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)-1-phenyl-3-[2-(*tert*-butoxycarbonyl)hydrazono]butane-2-carboxylate (3l): m.p. 183-184 °C. IR: $\nu_{\max}$ 3323, 1780, 1749 cm^{-1} . ^1H NMR: δ 1.10 (s, 3 H, CH_3), 1.42 (s, 9 H, *Ot*-Bu), 1.78 (s, 3 H, CH_3), 1.80 (s, 3 H, CH_3), 3.34 (s, 3 H, OCH_3), 4.42 (s, 1 H, CH), 7.31-7.45 (m, 5 H, Ar), 9.62 (s, 1 H, NH). ^{13}C NMR: δ 18.15 (q), 28.03 (q), 28.76 (q), 52.38 (q), 59.91 (d), 61.07 (s), 79.91 (s), 106.81 (s), 128.41 (d), 129.67 (d), 129.76 (d), 133.35 (s), 153.09 (s), 164.76 (s), 166.33 (s), 169.28 (s). MS: m/z (%) 448 (1) [M^+], 346 (9), 334 (15), 290 (41), 246 (85), 231 (49), 187 (100). Anal. calcd for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_8$: C, 58.92; H, 6.29; N, 6.25. Found: C, 58.78; H, 6.15; N, 6.34.

2-Methyl (2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)-1-phenyl-3-[2-(aminocarbonyl)hydrazono]butane-2-carboxylate (3m): m.p. 194-196 °C. IR: $\nu_{\max}$ 3440, 3280, 3200, 1766, 1736, 1720, 1700, 1590 cm^{-1} . ^1H NMR: δ 1.18 (s, 3 H, CH_3), 1.72 (s, 3 H, CH_3), 1.78 (s, 3 H, CH_3), 3.51 (s, 3 H, OCH_3), 4.57 (s, 1 H, CH), 6.01 (s, 2 H, NH_2), 7.31-7.48 (m, 5 H, Ar), 9.23 (s, 1 H, NH). ^{13}C NMR: δ 17.81 (q), 28.04 (q), 28.31 (q), 53.11

(q), 58.82 (d), 60.83 (s), 106.94 (s), 120.10 (d), 129.37 (d), 129.56 (d), 134.45 (s), 154.98 (s), 159.21 (s), 167.30 (s), 170.82 (s). MS: m/z (%) 391 (1) $[M^+]$, 348 (7), 316 (11), 171 (100). Anal. calcd for $C_{18}H_{21}N_3O_7$: C, 55.24; H, 5.41; N, 10.74. Found: C, 55.38; H, 5.70; N, 10.58.

Trimethyl 2-(1,2,3-thiadiazol-4-yl)ethane-1,1,2-tricarboxylate (4a): m.p. 119-121 °C. IR: $\nu_{\max}$ 3099, 1740, 1731 cm^{-1} . ^1H NMR: δ 3.48 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 3.71 (s, 3 H, OCH_3), 4.45 (d, 1 H, $J = 10.5$ Hz, CH), 5.03 (d, 1 H, $J = 10.5$ Hz, CH), 9.24 (s, 1 H, CH). ^{13}C NMR: δ 44.01 (d), 52.71 (q), 52.77 (q), 52.91 (q), 53.23 (d), 136.41 (d), 156.11 (s), 166.49 (s), 167.14 (s), 169.40 (s). MS: m/z (%) 228 (1) $[M^+]$, 257 (24), 225 (100). Anal. calcd for $C_{10}H_{12}N_2O_6S$: C, 41.67; H, 4.20; N, 9.72. Found: C, 41.85; H, 4.41; N, 9.78.

2-Ethyl 1,1-dimethyl 2-(1,2,3-thiadiazol-4-yl)ethane-1,1,2-tricarboxylate (4b): m.p. 162-165 °C. IR: $\nu_{\max}$ 3090, 1754, 1736 cm^{-1} . ^1H NMR: δ 1.08 (t, 3 H, $J = 7.0$ Hz, OCH_2CH_3), 1.43 (s, 9 H, *Ot*-Bu), 3.48 (s, 3 H, OCH_3), 3.71 (s, 3 H, OCH_3), 4.08 (q, 2 H, $J = 7.0$ Hz, OCH_2CH_3), 4.45 (d, 1 H, $J = 10.5$ Hz, CH), 4.99 (d, 1 H, $J = 10.5$ Hz, CH), 9.23 (s, 1 H, CH). ^{13}C NMR: δ 13.76 (q), 43.97 (d), 52.79 (q), 52.98 (q), 53.17 (d), 61.57 (t), 137.65 (d), 156.52 (s), 166.88 (s), 167.52 (s), 169.15 (s). MS: m/z (%) 302 (1) $[M^+]$, 271 (28), 211 (100). Anal. calcd for $C_{11}H_{14}N_2O_6S$: C, 43.70; H, 4.67; N, 9.27. Found: C, 43.61; H, 4.57; N, 9.39.

1,1-Dibenzyl 2-ethyl 2-(1,2,3-thiadiazol-4-yl)ethane-1,1,2-tricarboxylate (4c): m.p. 61-63 °C. IR: $\nu_{\max}$ 3090, 1745, 1730 cm^{-1} . ^1H NMR (CDCl_3): δ 1.14 (t, 3 H, $J = 7.0$ Hz, OCH_2CH_3), 4.00-4.19 (m, 2 H, OCH_2CH_3), 4.63 (d, 1 H, $J = 10.2$ Hz, CH), 4.99-5.19 (m, 5 H, 2 OCH_2Ar and CH), 7.05-7.20 (m, 2 H, 2 OCH_2Ar), 7.24-7.39 (m, 8 H, 2 OCH_2Ar),

8.38 (s, 1 H, CH). ^{13}C NMR (CDCl_3): δ 14.29 (q), 44.90 (d), 54.26 (d), 62.47 (t), 69.93 (t), 68.13 (t), 128.42 (d), 128.49 (d), 128.65 (d), 128.74 (d), 134.88 (s), 135.05 (s), 135.3 (d), 156.93 (s), 166.71 (s), 167.15 (s), 169.40 (s). MS: m/z (%) 454 (1) $[\text{M}^+]$, 409 (2), 361 (8), 348 (40), 317 (18), 291 (15), 257 (100). Anal. Calcd for $\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_6\text{S}$: C, 60.78; H, 4.88; N, 6.16. Found: C, 60.71; H, 4.71; N, 6.61.

1,1-Diethyl 2-methyl 2-(1,2,3-thiadiazol-4-yl)-1-phenylethane-1,1,2-tricarboxylate (4d): m.p. 90-92 °C. IR: ν_{max} 3130, 1745, 1714 cm^{-1} . ^1H NMR: δ 1.10-1.18 (m, 6 H, 2 OCH_2CH_3), 3.61 (s, 3 H, OCH_3), 4.13-4.26 (m, 4 H, 2 OCH_2CH_3), 5.52 (s, 1 H, CH), 7.00-7.03 (m, 2 H, Ar), 7.14-7.18 (m, 3 H, Ar), 8.51 (s, 1 H, CH). ^{13}C NMR: δ 14.48 (q), 14.50 (q), 51.07 (d), 53.31 (q), 62.58 (t), 62.94 (t), 65.88 (s), 128.33 (d), 128.39 (d), 129.15 (d), 135.12 (s), 138.59 (d), 156.58 (s), 168.49 (s), 169.62 (s), 170.49 (s). MS: m/z (%) 392 (11) $[\text{M}^+]$, 361 (8), 347 (15), 332 (100). Anal. calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_6\text{S}$: C, 55.09; H, 5.14; N, 7.14. Found: C, 55.29; H, 5.27; N, 7.01.

2,2-Diethyl 1-methyl 1-(1,2,3-thiadiazol-4-yl)propane-1,1,2-tricarboxylate (4e): IR: ν_{max} 3126, 1736, 1740 cm^{-1} . ^1H NMR (CDCl_3): δ 1.20-1.27 (m, 6 H, 2 OCH_2CH_3), 1.49 (s, 3 H, CH_3), 3.69 (s, 3 H, OCH_3), 4.15-4.23 (m, 4 H, 2 OCH_2CH_3), 5.28 (1 H, s, CH), 8.52 (s, 1 H, CH). ^{13}C NMR (CDCl_3): δ 14.34 (q), 18.77 (q), 49.23 (d), 52.98 (q), 57.50 (s), 62.41 (t), 62.49 (t), 136.24 (d), 156.94 (s), 170.26 (s), 170.34 (s). MS: m/z (%) 331 (2) $[\text{M}^+]$, 299 (38), 285 (100). Anal. calcd for $\text{C}_{13}\text{H}_{18}\text{N}_2\text{O}_6\text{S}$: C, 47.27; H, 5.49; N, 8.48. Found: C, 47.35; H, 5.61; N, 8.28.

1,1,1-Triethyl 2-methyl 2-(1,2,3-thiadiazol-4-yl)ethane-1,1,1,2-tetracarboxylate (4f): IR: ν_{max} 3130, 1740, 1731 cm^{-1} . ^1H NMR (CDCl_3): δ 1.20 (t, 9 H, J = 7.0 Hz, 3 OCH_2CH_3), 3.72 (s, 3 H, OCH_3), 4.22 (q, 6 H, J = 7.0 Hz, 3 OCH_2CH_3), 5.49 (s, 1 H, CH),

8.66 (s, 1 H, CH). ^{13}C NMR (CDCl_3): δ 14.16 (q), 48.05 (d), 53.39 (q), 63.15 (t), 67.87 (s), 136.40 (d), 156.43 (s), 165.43 (s), 169.70 (s). MS: m/z (%) 388 (1) $[\text{M}^+]$, 357 (14), 343 (49), 328 (27), 314 (8), 300 (53), 286 (20), 272 (100). Anal. calcd for $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_8\text{S}$: C, 46.39; H, 5.19; N, 7.21. Found: C, 46.31; H, 5.21; N, 7.37.

1,2-Diethyl 1-(4-nitrophenyl)-2-(1,2,3-thiadiazol-4-yl)ethane-1,2-dicarboxylate (4g): m.p. 78-80 °C. IR: ν_{max} 3104, 1727 cm^{-1} . ^1H NMR (CDCl_3): δ 0.94-1.04 and 1.17-1.22 (2 m, 6 H, 2 OCH_2CH_3), 3.93-4.00 and 4.06-4.18 (2 m, 4 H, 2 OCH_2CH_3), 4.87-4.93, 5.00 and 5.08 (m and 2 d, 2 H, $J = 10.2$ Hz, 2 CH), 7.29, 7.62, 7.99 and 8.19 (4 d, 4 H, $J = 6.4$ Hz, Ar), 8.82 (s, 1 H, CH). ^{13}C NMR (CDCl_3): δ 14.32 (q), 14.49 (q), 48.80 (d), 49.21 (d), 53.65 (d), 54.20 (d), 62.58 (t), 62.63 (t), 62.76 (t), 62.92 (t), 124.92 (d), 130.40 (d), 130.72 (d), 135.98 (d), 143.67 (s), 144.01 (s), 148.50 (s), 148.81 (s), 158.05 (s), 158.94 (s), 170.26 (s), 171.19 (s), 171.42 (s), 172.59 (s). MS: m/z (%) 379 (11) $[\text{M}^+]$, 350 (5), 334 (50), 305 (100). Anal. calcd for $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_6\text{S}$: C, 50.65; H, 4.52; N, 11.08. Found: C, 50.78; H, 4.39; N, 11.30.

1-Ethyl 2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)-3-methyl -(1,2,3-thiadiazol-4-yl)butane-1-carboxylate (4h): m.p. 110-112 °C. IR: ν_{max} 3144, 1767, 1736 cm^{-1} . ^1H NMR (CDCl_3): δ 1.01 (d, 6 H, $J = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.09 (t, 3 H, $J = 7.0$ Hz, OCH_2CH_3), 1.80 (s, 3 H, CH_3), 1.86 (ept, 1 H, $J = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.99 (s, 3 H, CH_3), 4.11 (q, 2 H, $J = 7.0$ Hz, OCH_2CH_3), 5.91 (s, 1 H, CH), 8.97 (s, 1 H, CH). ^{13}C NMR (CDCl_3): δ = 14.29 (q), 18.48 (q), 19.97 (q), 29.30 (q), 36.02 (d), 49.29 (d), 58.96 (s), 63.03 (t), 107.75 (s), 138.23 (d), 156.55 (s), 166.24 (s), 168.59 (s), 171.59 (s). MS: m/z (%) 356 (1) $[\text{M}^+]$, 341 (7), 299 (57), 270 (100). Anal. calcd for $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_6\text{S}$: C, 50.55; H, 5.66; N, 7.86. Found: C, 50.64; H, 5.48; N, 7.59.

1-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)-2-methyl-1-phenyl-2-(1,2,3-thiadiazol-4-yl)ethane-2-carboxylate (4i): m.p. 138-140 °C. IR: $\nu_{\max}$ 3130, 1767, 1736 cm^{-1} . ^1H NMR: δ = 1.15 (s, 3 H, CH_3), 1.75 (s, 3 H, CH_3), 3.67 (s, 3 H, OCH_3), 5.90 (s, 1 H, CH), 7.04-7.07 (m, 2 H, Ar), 7.31-7.33 (m, 3 H, Ar), 8.81 (s, 1 H, CH). ^{13}C NMR: δ 26.67 (q), 28.75 (q), 52.29 (d), 60.05 (q), 116.52 (s), 126.93 (d), 129.61 (d), 129.73 (d), 130.42 (s), 139.51 (d), 155.07 (s), 165.02 (s), 165.83 (s), 170.65 (s). MS: m/z (%) 376 (4) [M^+], 345 (1), 317 (100). Anal. calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_6\text{S}$: C, 54.25; H, 4.28; N, 7.44. Found: C, 54.38; H, 4.15; N, 7.31.

2-Ethyl-1,1-dimethyl-2-[2-(*tert*-butoxycarbonyl)-2,3-dihydro-1,2,3-selenadiazol-4-yl]ethane,1,1,2-tricarboxylate (5a): IR: $\nu_{\max}$ 3105, 1745, 1725 cm^{-1} . ^1H NMR (CDCl_3): δ 1.19 (t, 3 H, J = 7.2 Hz, OCH_2CH_3), 1.56 (s, 9 H, *Ot*-Bu), 3.66 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 4.03-4.17 (m, 3 H, OCH_2CH_3 and CH), 4.36 (d, 1 H, J = 7.2 Hz, CH), 9.40 (s, 1 H, CH), 9.63 (brs, 1 H, NH). ^{13}C NMR (CDCl_3): δ = 14.11 (q), 28.34 (q), 40.87 (d), 50.22 (d), 53.63 (q), 53.81 (q), 62.86 (q), 83.84 (s), 143.02 (s), 151.59 (s), 167.84 (s), 168.15 (s), 168.34 (s), 190.95 (s). MS: m/z (%) 454 (1) [M^{+3}], 452 (3) [M^{+1}], 450 (2), 449 (1), 448 (1), 423 (4), 421 (18), 419 (8), 418 (3), 364 (23), 362 (100). Anal. calcd for $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_8\text{Se}$: C, 42.58; H, 5.36; N, 6.21. Found: C, 42.71; H, 5.49; N, 6.15.

1,1-Diethyl-2-methy-2-[2-(*tert*-butoxycarbonyl)-2,3-dihydro-1,2,3-selenadiazol-4-yl]-1-phenylethane,1,1,2-tricarboxylate (5b): IR: $\nu_{\max}$ 3130, 1759, 1732 cm^{-1} . ^1H NMR (CDCl_3): δ 1.23-1.29 (m, 6 H, 2 OCH_2CH_3), 1.42 (s, 9 H, *Ot*-Bu), 3.72 (s, 3 H, OCH_3), 4.24-4.36 (m, 4 H, 2 OCH_2CH_3), 4.76 (s, 1 H, CH), 7.21-7.30 (m, 5 H, Ar), 9.00 (s, 1 H, CH), 12.21 (brs, 1 H, NH). ^{13}C NMR (CDCl_3): δ 14.12 (q), 28.29 (q), 53.04 (q), 56.16 (d), 62.76 (t), 62.87 (t), 66.18 (s), 82.42 (s), 128.48 (d), 128.66 (s), 128.95 (d), 134.81 (s),

135.18 (d), 151.82 (s), 169.38 (s), 169.76 (s), 170.75 (s), 188.81 (s). MS: m/z (%) 541 (1) $[M^+]$, 497 (3), 495 (1), 443 (3), 441 (17), 439 (9), 438 (2), 437 (1), 424 (6), 422 (57), 420 (25), 418 (16), 417 (9), 395 (23), 393 (100). Anal; calcd for $C_{23}H_{29}N_2O_8Se$: C, 51.12; H, 5.41; N, 5.18. Found: C, 51.38; H, 5.27; N, 5.29.

1,1-Diethyl 2-methyl 2-(1,2,3-selenadiazol-4-yl)-1-phenylethane-1,1,2-tricarboxylate (6a): IR: ν_{max} 3077, 1762, 1749, 1736, 1469, 1460 cm^{-1} . 1H NMR ($CDCl_3$): δ 1.22-1.34 (m, 6 H, 2 OCH_2CH_3), 3.73 (s, 3 H, OCH_3), 4.28-4.38 (m, 4 H, 2 OCH_2CH_3), 5.70 (s, 1 H, CH), 7.07-7.20 (m, 5 H, Ar), 8.94 (s, 1 H, CH). ^{13}C NMR ($CDCl_3$): δ 13.73 (q), 13.88 (q), 52.06 (d), 52.65 (q), 62.19 (t), 62.43 (t), 65.97 (s), 127.68 (d), 128.70 (d), 134.57 (s), 143.32 (d), 155.63 (s), 166.72 (s), 169.72 (s), 170.54 (s). MS: m/z (%) 442 (1) $[M^{++2}]$, 440 (10) $[M^+]$ 438 (4), 437 (1), 436 (1), 413 (1), 411 (13), 409 (5), 407 (1), 397 (5), 395 (27), 393 (15), 391 (4), 354 (13), 352 (100). Anal. calcd for $C_{18}H_{20}N_2O_6Se$: C, 49.09; H, 4.58; N, 6.36. Found: C, 49.15; H, 4.61; N, 6.31.

1,1,1-Triethyl 2-methyl 2-(1,2,3-selenadiazol-4-yl)ethane-1,1,1,2-tetracarboxylate (6b): IR: ν_{max} 3059, 1759, 1728, 1721 cm^{-1} . 1H NMR ($CDCl_3$): δ 1.22 (t, 9 H, $J = 7.2$ Hz, 3 OCH_2CH_3), 2.03 (s, 3 H, CH_3), 3.76 (s, 3 H, OCH_3), 4.25 (q, 6 H, $J = 7.2$ Hz, 3 OCH_2CH_3), 5.54 (s, 1 H, CH), 9.39 (s, 1 H, CH). - ^{13}C NMR ($CDCl_3$): δ 14.02 (q), 48.71 (d), 53.24 (q), 63.01 (t), 68.03 (s), 143.71 (d), 155.82 (s), 165.74 (s), 170.09 (s). MS: m/z (%) 436 (3) $[M^{++1}]$, 434 (1), 409 (5), 407 (29), 405 (13), 404 (3), 403 (4), 393 (14), 391 (100). Anal. calcd for $C_{15}H_{20}N_2O_8Se$: C, 41.28; H, 4.62; N, 6.42. Found: C, 41.32; H, 4.75; N, 6.37.

1-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)-2-methyl 1-phenyl-2-(1,2,3-selenadiazol-4-yl)ethane-2-carboxylate (6c): IR: ν_{max} 3117, 1780, 1740, 1727, 1468,

1460 cm^{-1} . ^1H NMR (CDCl_3): δ 1.16 (s, 3 H, CH_3), 1.76 (s, 3 H, CH_3), 3.69 (s, 3 H, OCH_3), 5.39 (s, 1 H, CH), 7.06-7.36 (m, 5 H, Ar), 9.26 (s, 1 H, CH). - ^{13}C NMR (CDCl_3): δ 27.02 (q), 28.49 (q), 52.01 (q), 60.38 (q), 106.48 (s), 126.95 (d), 129.68 (d), 129.81 (d), 130.45 (d), 145.21 (d), 155.29 (s), 165.82 (s), 165.99 (s), 170.21 (s). MS: m/z (%) 424 (3) [M^{++1}], 411 (3), 409 (15), 407 (9), 406 (3), 395 (1), 393 (5), 391 (2), 389 (1), 367 (14), 365 (100). Anal. calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_6\text{Se}$: C, 48.24; H, 3.81; N, 6.62. Found: C, 48.36; H, 3.89; N, 6.58.

2-Ethyl 1,1-dimethyl 2-(1,2,3-selenadiazol-4yl)ethane-1,1,2 tricarboxylate (6d): IR: ν_{max} 1778, 1764, 1721, 1716 cm^{-1} . ^1H NMR (CDCl_3): δ 1.20 (t, 3 H, $J = 7.2$ Hz, OCH_2CH_3), 3.57 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 4.19 (q, 2 H, $J = 7.2$ Hz, OCH_2CH_3), 4.55 (d, 1 H, $J = 10.4$ Hz, CH), 5.04 (d, 1 H, $J = 10.4$ Hz, CH), 9.25 (s, 1 H, CH). ^{13}C NMR (CDCl_3): δ 14.22 (q), 45.92 (d), 53.22 (q), 53.45 (d), 54.12 (d), 62.31 (t), 142.51 (d), 156.69 (s), 167.72 (s), 168.16 (s), 169.94 (s). MS: m/z (%) 320 (1) [M^+], 318 (17), 316 (10), 315 (2), 264 (13), 262 (100). Anal. calcd for $\text{C}_{11}\text{H}_{13}\text{N}_2\text{O}_6\text{Se}$: C, 37.94; H, 3.76; N, 8.05. Found: C, 38.03; H, 3.51; N, 8.11.

2-Ethyl 1,1-dimethyl 2-(1,2,3-selenadiazol-4yl)ethylene-1,1,2 tricarboxylate (7a): IR: ν_{max} 3071, 1742, 1729, 1700 cm^{-1} . ^1H NMR (CDCl_3): δ 1.39 (t, 3 H, $J = 7.2$ Hz, OCH_2CH_3), 3.86 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 4.45 (q, 2 H, $J = 7.2$ Hz, OCH_2CH_3), 9.44 (s, 1 H, CH). ^{13}C NMR (CDCl_3): δ 14.22 (q), 53.21 (d), 53.52 (q), 63.01 (t), 127.58 (s), 136.07 (s), 146.31 (d), 163.31 (s), 165.24 (s), 166.01 (s), 169.29 (s). MS: m/z (%) 348 (1) [M^+], 319 (1), 317 (20), 315 (12), 314 (2), 313 (2), 262 (17), 260 (100). Anal. calcd for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_6\text{Se}$: C, 37.93; H, 3.48; N, 8.05. Found: C, 37.81; H, 3.52; N, 8.19.

1,1-Dimethyl 2-ethyl 3-[2-(aminocarbonyl)hydrazono]but-1-ene-1,1,2-tricarboxylate (10a): m.p. 170-173 $^{\circ}\text{C}$. IR: ν_{max} 3476, 3234, 1742, 1729, 1698 cm^{-1} . ^1H

NMR: δ 1.24 (t, 3 H, $J = 7.0$ Hz, OCH_2CH_3), 1.86 (s, 3 H, CH_3), 3.71 (s, 3 H, OCH_3), 3.72 (s, 3 H, OCH_3), 4.25 (q, 2 H, $J = 7.0$ Hz, OCH_2CH_3), 6.01 and 6.52 (2 brs, 2 H, NH_2), 10.07 (s, 1 H, NH). ^{13}C NMR: $\delta = 19.51$ (q), 19.82 (q), 58.59 (q), 58.88 (q), 67.81 (t), 143.73 (s), 150.01 (s), 156.04 (s), 161.79 (s), 168.71 (s), 170.93 (s), 171.01 (s). MS: m/z (%) 315 (1) $[\text{M}^+]$, 213 (32), 181 (24), 167 (100). Anal. calcd for $\text{C}_{12}\text{H}_{17}\text{N}_3\text{O}_7$: C, 45.72; H, 5.43; N, 13.33. Found: C, 45.61; H, 5.51; N, 13.28.

Triethyl 3-[2-(*tert*-butoxycarbonyl)hydrazono]but-1-ene-1,1,2-tricarboxylate (10b): m.p. 115-117 °C. IR: ν_{max} 3315, 1740, 1730, 1700 cm^{-1} . ^1H NMR: (CDCl_3): δ 1.22-1.28 (m, 9 H, 3 OCH_2CH_3), 1.45 (s, 9 H, *Ot*-Bu), 1.88 (s, 3 H, CH_3), 4.20-4.26 (m, 6 H, 3 OCH_2CH_3), 8.16 (s, 1 H, NH). - ^{13}C NMR (CDCl_3) : δ 13.81 (q), 14.56 (q), 14.83 (q), 61.73 (t), 62.01 (t), 62.38 (t), 126.59 (s), 139.52 (s), 142.83 (s), 163.84 (s), 164.21 (s), 165.87 (s), 168.03 (s). MS: m/z (%) 400 (1) $[\text{M}^+]$, 355 (8), 312 (32), 255 (100). Anal. calcd for $\text{C}_{18}\text{H}_{28}\text{N}_2\text{O}_8$: C, 53.99; H, 7.05; N, 7.00. Found: C, 53.75; H, 6.95; N, 7.14.

1,1-Diethyl 2-methyl 3-[2-(aminocarbonyl)hydrazono]but-1-ene-1,1,2-tricarboxylate (10c): m.p. 146-148 °C. IR: ν_{max} 3415, 3287, 1741, 1728, 1703, 1639 cm^{-1} . ^1H NMR: δ 1.20 (t, 6 H, $J = 7.2$ Hz, 2 OCH_2CH_3), 1.87 (s, 3 H, CH_3), 3.79 (s, 3 H, OCH_3), 4.19 (q, 4 H, $J = 7.2$ Hz, 2 OCH_2CH_3), 5.84 and 6.62 (2 brs, 2 H, NH_2), 10.02 (s, 1 H, NH). ^{13}C NMR: δ 13.81 (q), 14.22 (q), 52.89 (q), 61.71 (t), 62.03 (t), 126.33 (s), 138.18 (s), 143.51 (s), 156.04 (s), 162.49 (s), 164.57 (s), 165.64 (s). MS: m/z (%) 329 (1) $[\text{M}^+]$, 256 (10), 241 (21), 213 (100). Anal. calcd for $\text{C}_{13}\text{H}_{19}\text{N}_3\text{O}_7$: C, 47.42; H, 5.82; N, 12.76. Found: C, 47.51; H, 5.95; N, 12.57.

1,1,2-Triethyl 2-(1,2,3-thiadiazol-4-yl)ethylene-1,1,2-tricarboxylate (11a): IR: ν_{max} 3108, 1740, 1725, 1640 cm^{-1} . ^1H NMR (CDCl_3): δ 1.22-1.39 (m, 9 H, 3 OCH_2CH_3), 4.28-4.48 (m, 6 H, 3 OCH_2CH_3), 8.65 (s, 1 H, CH). ^{13}C NMR (CDCl_3): δ 14.36 (q), 14.39

(q), 14.48 (q), 63.13 (t), 63.30 (t), 63.57 (t), 130.41 (s), 134.76 (s), 138.39 (d), 155.68 (s), 163.74 (s), 165.42 (s), 166.86 (s). MS: m/z (%) 328 (1) [M^+], 283 (25), 252 (12), 212 (100). Anal. Calcd for $C_{13}H_{16}N_2O_6S$: C, 47.56; H, 4.91; N, 8.53. Found: C, 47.45; H, 4.99; N, 8.65.

1,1-Diethyl 2-methyl 2-(1,2,3-thiadiazol-4-yl)ethylene-1,1,2-tricarboxylate (11b): IR: $\nu_{\max}$ 3107, 1745, 1720, 1643 cm^{-1} . ^1H NMR (CDCl_3): δ 1.28 (t, 3 H, $J = 7.0$ Hz, OCH_2CH_3), 1.33 (t, 3 H, $J = 7.0$ Hz, OCH_2CH_3), 3.95 (s, 3 H, OCH_3), 4.34 (q, 4 H, $J = 7.0$ Hz, 2 OCH_2CH_3), 8.65 (s, 1 H, CH). ^{13}C NMR (CDCl_3): δ 14.26 (q), 14.39 (q), 53.79 (q), 62.74 (t), 62.96 (t), 129.74 (s), 133.64 (s), 137.49 (d), 154.47 (s), 162.62 (s), 164.18 (s), 166.23 (s). MS: m/z (%) 314 (1) [M^+], 269 (37), 226 (18), 212 (100). Anal. Calcd for $C_{12}H_{14}N_2O_6S$: C, 45.85; H, 4.49; N, 8.92. Found: C, 45.78; H, 4.59; N, 8.76.

Tetramethyl (3RS, 5RS)-4-[2-(tert-butoxycarbonyl)hydrazono]-1-(1,2,3-thiadiazol-4-yl)pentane-1,2,2,3-tetracarboxylate (12a): m.p. 175-177 $^\circ\text{C}$. IR: $\nu_{\max}$ 3289, 3156, 1759, 1733 cm^{-1} . ^1H NMR: δ 1.47 (s, 9 H, $\text{O}t\text{-Bu}$), 1.60 (s, 3 H, CH_3), 3.16 (s, 1 H, CH), 3.55 (s, 3 H, OCH_3), 3.59 (s, 3 H, OCH_3), 3.67 (s, 3 H, OCH_3), 3.71 (s, 3 H, OCH_3), 5.48 (s, 1 H, CH), 8.95 (s, 1 H, CH), 9.68 (brs, 1 H, NH). ^{13}C NMR: δ 18.97 (q), 29.00 (q), 47.72 (d), 53.08 (q), 53.19 (q), 53.64 (q), 56.41 (d), 60.27 (s), 80.10 (s), 139.82 (d), 146.05 (s), 153.48 (s), 156.33 (s), 169.06 (s), 169.49 (s), 169.75 (s), 170.83 (s). MS: m/z (%) 516 (4) [M^+], 485 (4), 429 (18), 398 (100). Anal. Calcd for $C_{20}H_{28}N_4O_{10}S$: C, 46.51; H, 5.46; N, 10.85. Found: C, 46.65; H, 5.41; N, 10.77.

Table 8. Crystal data for the two polymorphs of **12a**.

	12a1	12a2
Formula	C ₂₀ H ₂₈ N ₄ O ₁₀ S	C ₂₀ H ₂₈ N ₄ O ₁₀ S
M	516.52	516.52
Crystal size/(mm)	0.5 × 0.4 × 0.4	0.5 × 0.2 × 0.2
Crystal System	Triclinic	Orthorhombic
Space Group	P-1 (no. 2)	Pbca (no. 61)
<i>a</i> /Å	9.577(1)	14.033(1)
<i>b</i> /Å	10.965(1)	9.166(5)
<i>c</i> /Å	13.773(2)	39.408(4)
<i>α</i> /°	69.91(1)	
<i>β</i> /°	88.28(1)	
<i>γ</i> /°	72.23(1)	
U/Å ³	1289.0(3)	5069(3)
Temperature /K	293	293
Z	2	8
F(000)	544	2176
D _c /g cm ⁻³	1.33	1.35
μ(Mo-K _α)/mm ⁻¹	0.184	0.187
Scan mode	ω/2θ	ω/2θ
Scan range/°	1 ≤ θ ≤ 25	1 ≤ θ ≤ 25
Scan width/°	0.98	1.34
Scan speed/° min ⁻¹	3.0	3.0
Independent reflections	4423 (R _{int} =0.01)	4461 (R _{int} =0.07)

Obs. reflections ($I > 2\sigma(I)$)	3552	1446
N. parameters refined	281	349
R_1 ($I > 2\sigma(I)$)	0.04	0.08
wR_2 ($I > 2\sigma(I)$)	0.09	0.13

3-Ethyl 1,2,2-methyl (3RS, 5RS)-4-[2-(*tert*-butoxycarbonyl)-hydrazono]-1-(1,2,3-thiadiazol-4-yl)pentane-1,2,2,3-tetracarboxylate (12b): m.p. 148-150 °C. IR: $\nu_{\max}$ 3304, 3114, 1748, 1722 cm^{-1} . ^1H NMR: δ 1.11 (t, 3 H, $J = 7.2$ Hz, OCH_2CH_3), 1.46 (s, 9 H, *Or*-Bu), 1.58 (s, 3 H, CH_3), 3.12 (s, 1 H, CH), 3.60 (s, 3 H, OCH_3), 3.64 (s, 3 H, OCH_3), 3.69 (s, 3 H, OCH_3), 3.92-4.05 (m, 2 H, OCH_2CH_3), 5.48 (s, 1 H, CH), 8.93 (s, 1 H, CH), 9.67 (brs, 1 H, NH). ^{13}C NMR: $\delta = 14.55$ (q), 19.03 (q), 29.00 (q), 47.81 (d), 53.13 (q), 53.49 (q), 56.41 (d), 60.21 (s), 61.68 (t), 80.10 (s), 139.81 (d), 146.11 (s), 153.52 (s), 156.33 (s), 169.07 (s), 169.15 (s), 169.47 (s), 170.84 (s). MS: m/z (%) 530 (5) [M^+], 515 (2), 485 (7), 443 (10), 429 (9), 414 (27), 400 (100). Anal. Calcd for $\text{C}_{21}\text{H}_{30}\text{N}_4\text{O}_{10}\text{S}$: C, 47.54; H, 5.70; N, 10.56. Found: C, 47.55; H, 5.51; N, 10.61.

Tetramethyl (3RS, 5RS)-4-[2-(aminocarbonyl)hydrazono]-1-(1,2,3-thiadiazol-4-yl)pentane-1,2,2,3-tetracarboxylate (12c): m.p. 173-177 °C. IR: $\nu_{\max}$ 3471, 3450, 3221, 1749, 1734, 1703, 1607 cm^{-1} . ^1H NMR: δ 1.65 (s, 3 H, CH_3), 3.23 (s, 1 H, CH), 3.56 (s, 3 H, OCH_3), 3.59 (s, 3 H, OCH_3), 3.64 (s, 3 H, OCH_3), 3.71 (s, 3 H, OCH_3), 5.32 (s, 1 H, CH), 6.27 and 6.58 (2 brs, 2 H, NH_2), 8.91 (s, 1 H, CH), 9.47 (s, 1 H, NH). ^{13}C NMR: $\delta = 18.80$ (q), 47.88 (d), 53.33 (q), 53.47 (q), 53.52 (q), 53.64 (q), 56.05 (d), 60.21 (s), 140.08 (d), 142.95 (s), 155.89 (s), 157.57 (s), 168.81 (s), 169.52 (s), 170.64 (s), 171.60 (s). MS: m/z (%) 459 (6) [M^+], 428 (8), 414 (31), 400 (61), 354 (28), 327 (63), 316 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{N}_5\text{O}_9\text{S}$: C, 41.83; H, 4.61; N, 15.24. Found: C, 41.68; H, 4.63; N, 15.17.

3-Ethyl 1,2,2-methyl (3RS, 5RS)-4-[2-(aminocarbonyl)hydrazono]-1-(1,2,3-thiadiazol-4-yl)pentane-1,2,2,3-tetracarboxylate (12d): m.p. 202-204 °C. IR: $\nu_{\max}$ 3462, 3306, 3230, 3216, 1747, 1724, 1700, 1596 cm^{-1} . ^1H NMR: δ 1.12 (t, 3 H, $J = 7.2$ Hz, OCH_2CH_3), 1.66 (s, 3 H, CH_3), 3.22 (s, 1 H, CH), 3.60 (s, 3 H, OCH_3), 3.65 (s, 3 H, OCH_3), 3.72 (s, 3 H, OCH_3), 3.75-4.07 (m, 2 H, OCH_2CH_3), 5.34 (s, 1 H, CH), 5.50 and 6.51 (2 brs, 2 H, NH_2), 8.92 (s, 1 H, CH), 9.47 (s, 1 H, NH). ^{13}C NMR: δ 14.58 (q), 18.87 (q), 47.93 (d), 53.24 (q), 53.46 (q), 53.58 (q), 56.01 (d), 60.18 (s), 61.90 (t), 139.94 (d), 143.08 (s), 155.92 (s), 157.83 (s), 168.80 (s), 168.92 (s), 170.63 (s), 171.62 (s). MS: m/z (%) 473 (5) [M^+], 428 (5), 414 (26), 400 (55), 354 (53), 327 (66), 316 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{N}_5\text{O}_9\text{S}$: C, 43.13; H, 4.90; N, 14.79. Found: C, 43.25; H, 4.78; N, 14.66.

Tetramethyl (1RS, 3RS)-1,3-di(1,2,3-thiadiazol-4-yl)propane-1,2,2,3-tetracarboxylate (13a): m.p. 153-155 °C. IR: $\nu_{\max}$ 3114, 3098, 1742 cm^{-1} . ^1H NMR: δ 3.52 (s, 6 H, 2 OCH_3), 3.77 (s, 6 H, 2 OCH_3), 4.73 (s, 2 H, 2 CH), 8.88 (s, 2 H, 2 CH). ^{13}C NMR: δ 47.79 (d), 52.65 (q), 53.12 (q), 60.28 (s), 139.63 (d), 154.69 (s), 168.69 (s), 169.13 (s). MS: m/z (%) = 412 (31) [M^+], 383 (100). Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{N}_4\text{O}_8\text{S}_2$: C, 40.54; H, 3.63; N, 12.61. Found: C, 40.66; H, 3.48; N, 12.78.

1-Ethyl 2,2,3-trimethyl (1RS, 3RS)-1,3-di(1,2,3-thiadiazol-4-yl)propane-1,2,2,3-tetracarboxylate (13b): m.p. 118-1220 °C. IR: $\nu_{\max}$ 3140, 3120, 3092, 1752, 1728 cm^{-1} . ^1H NMR: δ 1.05 (t, 3 H, $J = 7.2$ Hz, OCH_2CH_3), 3.51 (s, 3 H, OCH_3), 3.77 (s, 6 H, 2 OCH_3), 3.90-4.07 (m, 2 H, OCH_2CH_3), 4.70 (s, 1 H, CH), 4.73 (s, 1 H, CH), 8.87 (s, 1 H, CH). ^{13}C NMR: δ 14.55 (q), 48.69 (d), 53.41 (q), 53.78 (q), 53.82 (d), 61.06 (s), 62.07 (t), 140.30 (d), 140.37 (d), 155.52 (s), 155.61 (s), 169.30 (s), 169.46 (s), 169.90 (s). MS: m/z

(%) = 458 (1) [M⁺], 427 (20), 413 (16), 397 (100). Anal. Calcd for C₁₆H₁₈N₄O₈S₂: C, 41.92; H, 3.96; N, 12.22. Found: C, 42.00; H, 3.78; N, 12.41.

Dimethyl 1-[(aminocarbonyl)amino]-5-methyl-3-[methyl (1,2,3-thiadiazol-4-yl)methyl-1-carboxylate]-2-oxo-2,3-dihydro-1H-pyrrole-3,4-dicarboxylate (14a): m.p. 202-204 °C. IR: ν_{max} 3297, 3156, 1745, 1717, 1675, 1609 cm⁻¹. ¹H NMR: δ 1.97 and 2.12 (2 s, 3 H, CH₃), 3.29, 3.42, 3.57, 3.62, 3.64 and 3.69 (6 s, 9 H, 3 OCH₃), 5.59 and 5.62 (2 s, 1 H, CH), 5.88, 6.17 and 6.52 (3 brs, 2 H, NH₂), 8.99 and 9.03 (2 s, 1 H, CH), 9.08 and 9.24 (2 brs, 1 H, NH). ¹³C NMR: δ = 14.70 (q), 14.96 (q), 46.78 (d), 47.43 (d), 51.83 (q), 52.03 (q), 53.26 (q), 53.43 (q), 54.13 (s), 54.26 (q), 59.13 (s), 59.64 (s), 103.17 (s), 103.29 (s), 138.83 (d), 139.12 (d), 155.97 (s), 156.08 (s), 157.39 (s), 157.84 (s), 159.33 (s), 159.46 (s), 162.52 (s), 162.94 (s), 166.79 (s), 167.07 (s), 169.40 (s), 169.57 (s), 170.85 (s), 171.79 (s). MS: m/z (%) 427 (9) [M⁺], 411 (10), 383 (51), 368 (20), 353 (35), 338 (18), 278 (38), 251 (100). Anal. Calcd for C₁₅H₁₇N₅O₈S: C, 42.15; H, 4.01; N, 16.39. Found: C, 42.19; H, 4.13; N, 16.27.

4-Ethyl 3-methyl 1-[(aminocarbonyl)amino]-5-methyl-3-[methyl(1,2,3-thiadiazol-4-yl)methyl-1-carboxylate]-2-oxo-2,3-dihydro-1H-pyrrole-3,4-dicarboxylate (14b): m.p. 168-170 °C. IR: ν_{max} 3301, 3159, 1741, 1720, 1675, 1611 cm⁻¹. ¹H NMR: δ 0.98 and 1.07 (2 t, 3 H, J = 7.2 Hz, OCH₂CH₃), 2.12 and 2.14 (2 s, 3 H, CH₃), 3.56, 3.59, 3.62 and 3.69 (4 s, 6 H, 2 OCH₃), 3.70-4.00 (m, 2 H, OCH₂CH₃), 5.58 and 5.60 (2 s, 1 H, CH), 5.93, 6.20 and 6.48 (3 brs, 2 H, NH₂), 8.94 and 9.03 (2 s, 1 H, CH), 9.07 and 9.27 (2 brs, 1 H, CH). ¹³C NMR: δ 12.38 (q), 12.43 (q), 14.68 (q), 14.96 (q), 46.82 (d), 47.50 (d), 53.32 (q), 53.50 (q), 54.10 (q), 54.19 (q), 59.22 (s), 60.14 (s), 60.48 (t), 60.68 (t), 103.44 (s), 104.15 (s), 138.82 (d), 139.93 (d), 156.01 (s), 156.11 (s), 157.44 (s), 157.91 (s), 158.82 (s), 159.26 (s), 162.04 (s), 162.48 (s), 166.73 (s), 167.14 (s), 168.92 (s), 169.61 (s),

170.85 (s), 171.87 (s). MS: m/z (%) 441 (11) [M^+], 424 (14), 398 (46), 383 (21), 352 (39), 338 (23), 278 (37), 250 (100). Anal. Calcd for $C_{16}H_{19}N_5O_8S$: C, 43.54; H, 4.34; N, 15.87. Found: C, 43.45; H, 4.48; N, 15.76.

Table 1S. Crystal data for the two polymorphs of **12a**

	12 a 1	12 a 2
Formula	$C_{20}H_{28}N_4O_{10}S$	$C_{20}H_{28}N_4O_{10}S$
M	516.52	516.52
Crystal size/(mm)	$0.5 \times 0.4 \times 0.4$	$0.5 \times 0.2 \times 0.2$
Crystal System	Triclinic	Orthorhombic
Space Group	P-1 (no. 2)	Pbca (no. 61)
$a/\text{\AA}$	9.577(1)	14.033(1)
$b/\text{\AA}$	10.965(1)	9.166(5)
$c/\text{\AA}$	13.773(2)	39.408(4)
$\alpha/^\circ$	69.91(1)	
$\beta/^\circ$	88.28(1)	
$\gamma/^\circ$	72.23(1)	
$U/\text{\AA}^3$	1289.0(3)	5069(3)
Temperature /K	293	293
Z	2	8
F(000)	544	2176
$D_c/\text{g cm}^{-3}$	1.33	1.35
$\mu(\text{Mo-K}_\alpha)/\text{mm}^{-1}$	0.184	0.187
Scan mode	$\omega/2\theta$	$\omega/2\theta$
Scan range/ $^\circ$	$1 \leq \theta \leq 25$	$1 \leq \theta \leq 25$
Scan width/ $^\circ$	0.98	1.34
Scan speed/ $^\circ \text{ min}^{-1}$	3.0	3.0
Independent reflections	4423 ($R_{\text{int}}=0.01$)	4461 ($R_{\text{int}}=0.07$)
Obs. reflections ($I > 2\sigma(I)$)	3552	1446

N. parameters refined	281	349
R_1 ($I > 2\sigma(I)$)	0.04	0.08
wR_2 ($I > 2\sigma(I)$)	0.09	0.13

Table 2S. Bond lengths (Å) for the two polymorphs of **12a**.^a

	12a1	12a2
S1-N1	1.6645(19)	1.661(7)
S1-C4	1.673(2)	1.667(7)
O6-C6	1.198(2)	1.204(7)
O7-C6	1.331(2)	1.317(8)
O7-C7	1.456(3)	1.445(7)
O10-C9	1.329(2)	1.340(7)
O10-C10	1.438(3)	1.438(7)
O9-C9	1.201(2)	1.205(7)
O11-C11	1.200(2)	1.210(7)
O12-C11	1.329(2)	1.343(8)
O12-C12	1.438(2)	1.446(7)
O14-C14	1.195(2)	1.182(9)
O15-C14	1.333(2)	1.319(8)
O15-C15	1.438(3)	1.523(9)
O19-C19	1.199(3)	1.189(8)
O20-C19	1.334(2)	1.339(8)
O20-C20	1.479(2)	1.459(8)
N1-N2	1.296(2)	1.296(7)
N2-C3	1.364(2)	1.362(7)
N17-C16	1.270(2)	1.267(8)
N17-N18	1.377(2)	1.369(7)
N18-C19	1.360(3)	1.353(8)
C3-C4	1.354(3)	1.341(8)
C3-C5	1.510(3)	1.509(8)
C5-C6	1.524(3)	1.526(8)
C5-C8	1.566(2)	1.554(7)
C8-C11	1.536(2)	1.541(8)
C8-C9	1.544(2)	1.547(8)
C8-C13	1.567(2)	1.564(8)
C13-C16	1.522(2)	1.510(8)
C13-C14	1.525(3)	1.544(10)

C16-C17	1.497(3)	1.493(9)
C20-C21	1.497(5)	1.474(11)
C20-C22	1.497(4)	
C20-C23	1.500(4)	
C20-C22A		1.44(3)
C20-C22B		1.60(3)
C20-C23A		1.56(4)
C20-C23B		1.41(4)

^a Site occupancy factor (s.o.f.) for C22A and C23A is equal to 0.55(6), while for C22B and C23B s.o.f. is 0.56(6)

Table 3S. Bond angles (°) for the two polymorphs of **12a**.^a

	12a1	12a2
N1-S1-C4	92.60(9)	93.5(3)
C6-O7-C7	115.3(2)	115.8(5)
C9-O10-C10	117.24(17)	115.5(6)
C11-O12-C12	116.43(16)	115.6(6)
C14-O15-C15	115.7(2)	105.6(7)
C19-O20-C20	120.53(17)	124.6(7)
N2-N1-S1	111.46(13)	109.9(5)
N1-N2-C3	113.87(16)	115.0(5)
C4-C3-N2	112.77(17)	112.5(6)
C16-N17-N18	119.17(15)	117.6(6)
C19-N18-N17	117.07(16)	120.1(7)
C4-C3-N2	112.77(17)	117.8(5)
C4-C3-C5	128.99(17)	129.6(6)
N2-C3-C5	118.24(16)	112.5(6)
C3-C4-S1	109.29(15)	109.1(6)
C3-C5-C6	109.37(14)	107.1(5)
C3-C5-C8	114.10(15)	116.4(5)
C6-C5-C8	112.28(15)	114.8(5)
O6-C6-O7	124.28(18)	124.9(7)
O6-C6-C5	125.13(18)	124.4(7)
O7-C6-C5	110.50(17)	110.7(6)
C11-C8-C9	110.10(14)	109.1(5)
C11-C8-C5	107.18(14)	111.3(5)
C9-C8-C5	109.72(14)	109.4(5)
C11-C8-C13	111.26(14)	109.0(5)
C9-C8-C13	109.08(14)	107.1(5)
C5-C8-C13	109.47(14)	110.8(5)
O9-C9-O10	125.09(18)	124.6(7)
O9-C9-C8	123.61(17)	122.9(7)
O10-C9-C8	111.30(15)	112.5(7)
O11-C11-O12	125.79(17)	124.8(6)

O11-C11-C8	123.67(17)	124.3(6)
O12-C11-C8	110.51(15)	110.9(6)
C16-C13-C14	107.55(15)	115.6(6)
C16-C13-C8	114.26(14)	113.4(5)
C14-C13-C8	114.50(15)	110.8(6)
O14-C14-O15	123.83(19)	125.7(9)
O14-C14-C13	124.44(19)	125.7(8)
O15-C14-C13	111.66(17)	108.5(8)
N17-C16-C17	127.26(17)	123.9(6)
N17-C16-C13	114.89(15)	118.4(6)
C17-C16-C13	117.75(16)	117.6(6)
O19-C19-O20	125.9(2)	125.2(7)
O19-C19-N18	125.5(2)	126.6(8)
O20-C19-N18	108.62(17)	108.1(7)
O20-C20-C21	110.4(2)	108.8(7)
O20-C20-C22	109.4(2)	
C21-C20-C22	111.9(3)	
O20-C20-C23	102.0(2)	
C21-C20-C23	113.1(4)	
C22-C20-C23	109.5(3)	
C23B-C20-C22A		84(2)
C23B-C20-O20		104.1(19)
C22A-C20-O20		103.6(16)
C23B-C20-C21		123(3)
C22A-C20-C21		129(3)
C23B-C20-C23A		28(3)
C22A-C20-C23A		110(2)
O20-C20-C23A		105.0(15)
C21-C20-C23A		97.7(15)
C23B-C20-C22B		114(3)
C22A-C20-C22B		38.7(19)
O20-C20-C22B		116.4(14)
C21-C20-C22B		92(3)
C23A-C20-C22B		132(2)

^a Site occupancy factor (s.o.f.) for C22A and C23A is equal to 0.55(6), while for C22B and C23B s.o.f. is 0.56(6)