Synthesis and dynamic NMR studies of novel hydantoin and thiohydantoin derivatives. Crystal structure of diethyl 2-(4,4-diaryl-2,5-dioxoimidazolidin-1-yl) fumarate and diethyl 2-(4,4-diaryl-2-mercapto-5-oxo-4,5-dihydro-1*H*-imidazol-1-yl)fumarate

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The reaction of stoichiometric amounts of dialkyl acetylenedicarboxylates with triphenylphosphine in the presence of hydantoins or thiohydantoins afforded stable crystalline phosphorus ylides. These compounds undergo smooth elimination of PPh_3 to produce dialkyl 2-(4,4-diaryl-2,5-dioxoimidazolidin-1-yl)fumarate, **4** or dialkyl 2-(4,4-diaryl-2-mercapto-5-oxo-4,5-dihydro-1*H*-imidazol-1-yl)fumarate, **7**. Single crystal X-ray diffraction study on **4b** and **7b** proved the structures unambiguously with C=O and SH functionality at the 2-position of the imidazole ring, respectively. Dynamic effects were observed in the NMR spectra of these compounds and were attributed to restricted rotation around the carbon-nitrogen single bonds. Rotational energy barrier ($\Delta G^{\#}$) for their interconversion process of rotational isomers equals to (53.6 and 17.2) ± 2 kcal mol^{-1}.

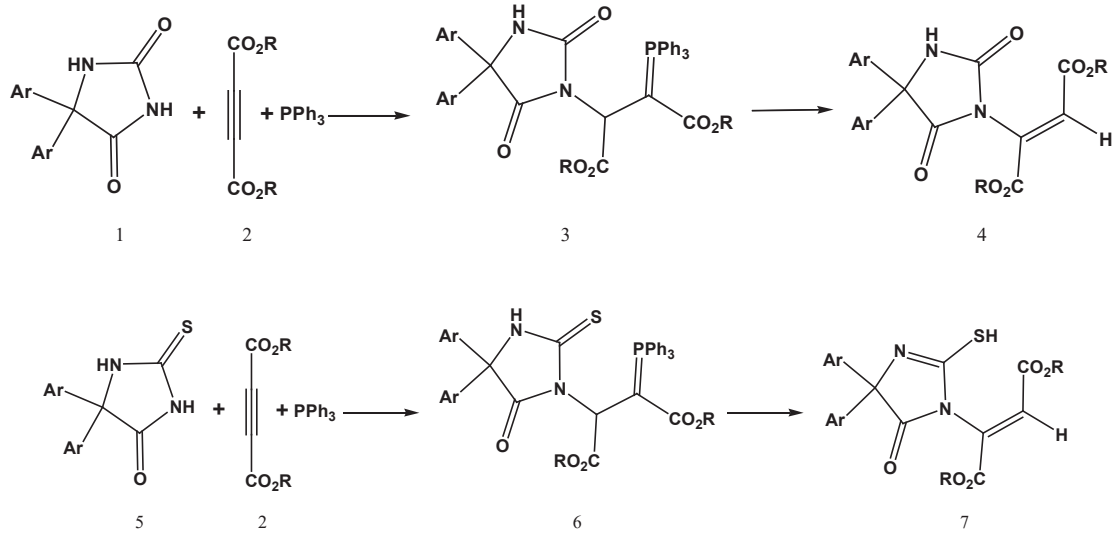
Keywords: dynamic ^{1}H NMR, hydantoin, thiohydantoin, phosphorus ylides, X-ray diffraction

The imidazole nucleus is found in a wide variety of natural products and also in pharmacologically active compounds such as antibiotics, antiarthritics, antihypercholesteremics, sodium channel modulators, glucagon receptors and as cholesterol acyltransferase and blood platelet aggregation inhibitors.[1–4] Different substituted imidazoles show various biological activities such as antimicrobial, anti-inflammatory, antibacterial, anti-allergic activity, inhibitors of p38 MAP kinase, fungicides, herbicides, plant growth regulators.[5–7] More recently, interest in imidazoles has augmented due to their role as green solvents by means of ionic liquids and in organometallic chemistry as *N*-heterocyclic carbenes. As part of our study on the heterocyclic and carbocyclic systems,[8–10] we report the synthesis, X-ray structural characterisation, and conformational behavior of functionalised hydantoins and thiohydantoins in the present paper. Thus, the reaction of hydantoins and activated acetylenes in the presence of triphenylphosphine (Ph_3P) leads to phosphoranes **3** and **6**,[10,11] which undergo elimination reactions in boiling toluene to produce **4** and **7**, respectively, in good yields. Syntheses of **3** and **6** have been reported previously. Some of these compounds exhibited dynamic ^{1}H NMR effect that affords good information regarding the interchangeable process of rotational isomers that provide important kinetic data (Scheme 1).

Results and discussion

Synthesis of 3-hyantoin and 3-thiohydantoin fumarates

The reaction of hydantoin **1** or thiohydantoin **5** with diethyl acetylenedicarboxylate in the presence of triphenylphosphine proceeded at room temperature in CH_2Cl_2, and was complete within a few hours. ^{1}H and ^{13}C NMR spectra of the crude products clearly indicated the formation of stable phosphorus ylides **3** and **6**.[10,11] No other products than **3** or **6** were detected. These compounds, when under reflux conditions, produce dialkyl 2-(4,4-diaryl-2,5-dioxoimidazolidin-1-yl)fumarate **4** and dialkyl 2-(2-mercapto-4,4-diaryl-5-oxo-4,5-dihydro-1*H*-imidazol-1-yl)fumarate **7** (Table 1). The structures of



1 2 3 4

5 2 6 7

Scheme 1

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Table 1 The 3-hyantoin and 3-thiohydantoin fumarates

Entry	Ar	R	Products
1	C_6H_5	Me	**4a**
2	C_6H_5	Et	**4b**
3	4-MeC_6H_4	Me	**4c**
4	4-MeC_6H_4	Et	**4d**
5	4-$MeOC_6H_4$	Me	**4e**
6	4-ClC_6H_4	Et	**4f**
7	C_6H_5	Me	**7a**
8	C_6H_5	Et	**7b**
9	4-MeC_6H_4	Me	**7c**
10	4-MeC_6H_4	Et	**7d**

compounds **4** and **7** were deduced from their elemental analyses and ^{1}H, ^{13}C, ^{1}H–^{1}H COSY, ^{1}H–^{13}C HSQC and HMBC spectra. The structures of compounds **4b** and **7b** were further verified by single crystal X-ray diffraction measurement.

The mass spectra of the compounds isolated from the **4b** and **7b** were determined using electrospray ionisation (ESI) mass spectrometry. The compound derived from **4b** showed molecular ions at 445.1 ([M + Na]$^+$, 100). Similarly the compound derived from **7b** showed molecular ions at 461.1 ([M + Na]$^+$, 100). The ^{1}H NMR spectrum of **4b** displayed two triplets at δ 1.22 and 1.34 corresponding to the two methyls, two quartets at δ 4.20 and 4.38 correspond to the two methylene groups, a singlet peak at δ 7.17 is assigned to the CH and a singlet at δ 8.16 corresponds to the NH. In the ^{1}H NMR spectrum of **7b**, the two triplets are at δ 0.99 and 1.19 for the two methyl groups and the methylene groups are displayed as a multiplet at δ 3.88–4.02 and a quartet at δ 4.21, a singlet at δ 7.11 corresponds to the CH and a singlet at δ 10.92 corresponding to the SH. Further evidence of the structure was obtained from the ^{13}C NMR spectra.

Although we have not yet established experimental proof for the mechanism of the formation of compounds **6** and **7**, a plausible mechanism was proposed as shown in Scheme 2. It is reasonable to assume that phosphorus ylide **6** results from the initial addition of Ph_3P to the acetylenic ester and subsequent protonation of the 1:1 adduct **8**, followed by attack of the anionic nitrogen of **10**, formed by deprotonation of the acidic N–H hydrogen of compound **2**, at the vinylphosphonium cation **9** to form the phosphoranes **6**. Ylides **6** with a proton shift and then tautomerisation produce the intermediates **11**, which apparently undergo an elimination reaction to produce the final products **7** (Scheme 2).

X-ray crystallographic study of **4b**

Weakly diffracting single crystals of **4b** were grown by evaporative crystallisation from a mixture of diethyl ether and acetone solution, however, suitable crystals were not obtained for **4a**, **4c** and **4d**. The light atom structure and the applied Mo radiation resulted in low ratio of measured reflections with high intensities. However, the structure is in agreement with the expected structure. An ORTEP plot of the crystal structure of **4b** is shown in Fig. 1.

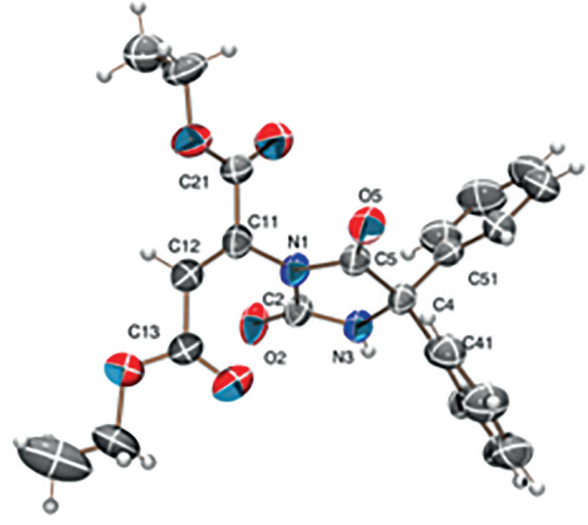
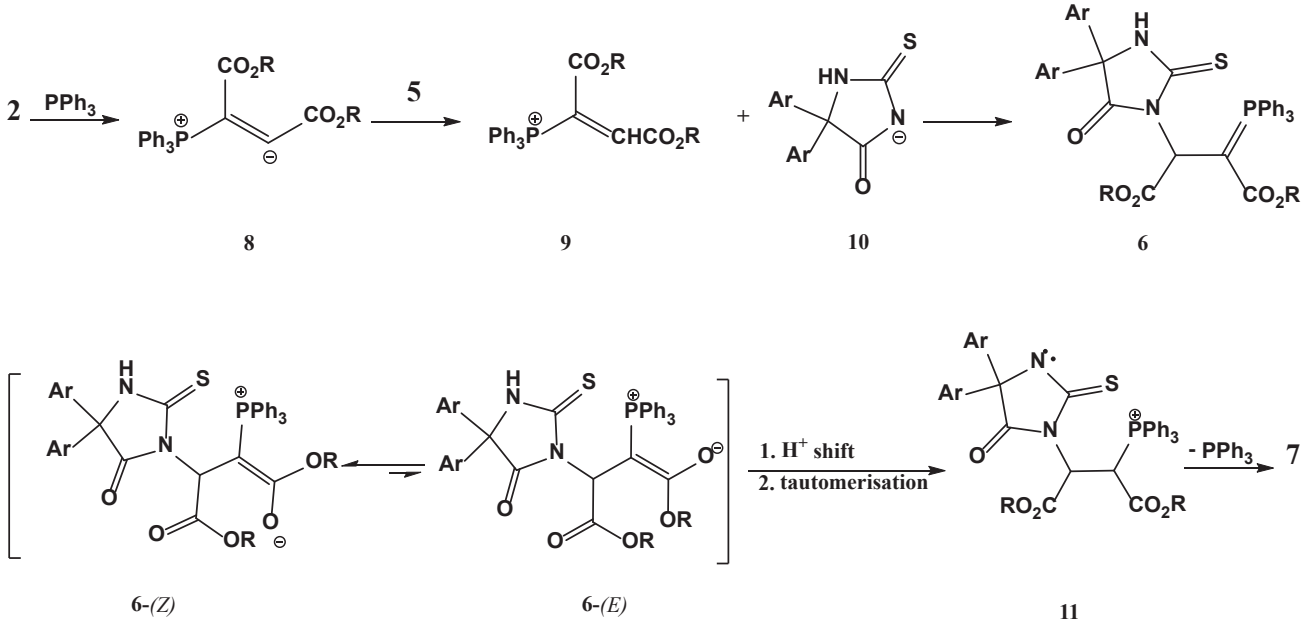


Fig. 1 ORTEP view of **4b** at 50% probability level with partial numbering. Selected bond lengths (Å) and angles (°): C(5)–O(5) 1.200(5), C(2)–O(2) 1.203(5), N(3)–C(4) 1.447(5), N(1)–C(11) 1.411(5), C(11)–C(12) 1.301(6), C(12)–C(13) 1.482(7), C(11)–C(21) 1.487(6) ; C(11)–C(12)–C(13) 124.2(3), C(5)–N(1)–C(11) 122.8(4), N(3)–C(2)–N(1) 105.9(3).



Scheme 2 Proposed mechanism to produce **7**.

X-ray crystallographic study of **7b**

Weakly diffracting single crystals of **7b** as DMSO solvate were grown by evaporative crystallisation from a mixture of chloroform and dimethylsulfoxide, however, suitable crystals were not obtained for **7a**, **7c** and **7d**. An ORTEP plot of the crystal structure of **7b** is shown in Fig. 2. The S–H group can rotate around the C–S bond but as the distance of the sulfur atom from the nearest oxygen atom is 3.69 Å presence of intramolecular S–H···O bond can be excluded. (Table 2).

Table 2 The crystallography data for **4b** and **7b**

Compound	4b	7b
Formula	$C_{23}H_{22}N_2O_6$	$C_{23}H_{22}N_2O_5S{\cdot}C_2H_6OS$
Formula weight	422.43	516.61
Crystal system	Monoclinic	Triclinic
Space group	P21/n	P-1
a (Å)	9.37(2)	8.343(1)
b (Å)	14.36(4)	10.820(1)
c (Å)	15.70(4)	16.090(1)
α (˚)	90.00	80.00(1)
β (˚)	90.47(9)	75.32(1)
γ (˚)	90.00	89.58(1)
V (Å^3)	2112(9)	1382.7(2)
Z	4	2
D_c (g cm^{-3})	1.329	1.241
F(000)	888	544
μ (mm^{-1})	0.10	0.23
Reflections collected	4189	5837
Unique reflections with I > 2σ(I)	1907	1840
Parameters refined	285	321
GOF on F^2	1.03	0.89
R[$F^2 > 2\sigma(F^2)$]	0.075	0.097
R_{int}	0.047	0.070
wR(F^2)	0.226	0.225
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.28	0.59, −0.35

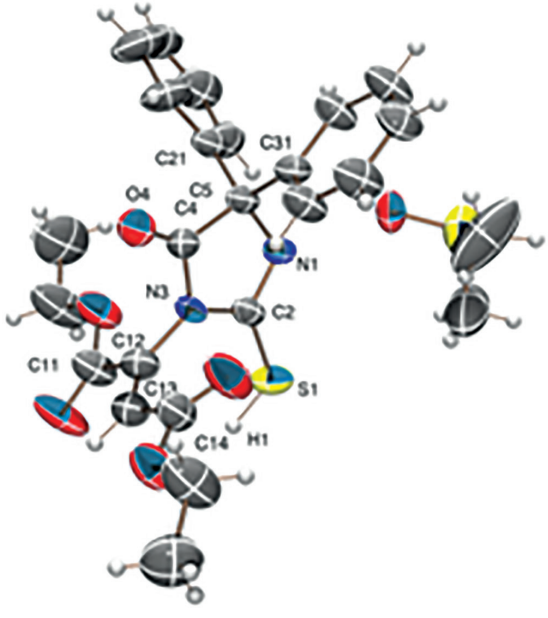


Fig. 2 ORTEP view of **7b** at 40% probability level with partial numbering. Selected bond lengths (Å) and angles (°): C(4)–O(4) 1.196(6), C(2)–S(1) 1.663(6), N(3)–C(4) 1.397(7), N(3)–C(12) 1.439(7), C(12)–C(13) 1.266(8), C(12)–C(11) 1.529(5), C(13)–C(14) 1.514(9), C(11)–C(12)–C(13) 119.7(7), C(5)–N(1)–C(2) 110.9(5), N(1)–C(2)–S(1) 126.3(5).

Dynamic NMR spectroscopic study

The analysis in relation to the dynamic NMR effect observed for **4b** and **7b** in the present work, the variable temperature spectra are sufficient to calculate the free energy barrier as well as enthalpy and entropy of activation for the restricted C–N bond rotation. From the coalescence of the methine protons and using the expression $k = \pi\Delta\nu/1.42$, the first-order rate constants (k) were calculated. Application of the absolute rate theory with a transmission coefficient of **4b** gives a free energy of activation ($\Delta G^{\neq}$) of 53.6 ± 2 kcal mol^{-1} (Fig. 3). For **7b** gives a free energy of activation ($\Delta G^{\neq}$) of 17.2 ± 2 kcal mol^{-1}, where all known sources of errors are estimated and included (Fig. 4).[12]

Conclusions

In summary, dialkyl 2-(4,4-diaryl-2,5-dioxoimidazolidin-1-yl)fumarate and dialkyl 2-(4,4-diaryl-2-mercapto-5-oxo-4,5-dihydro-1*H*-imidazol-1-yl)fumarate were synthesised *via* stable

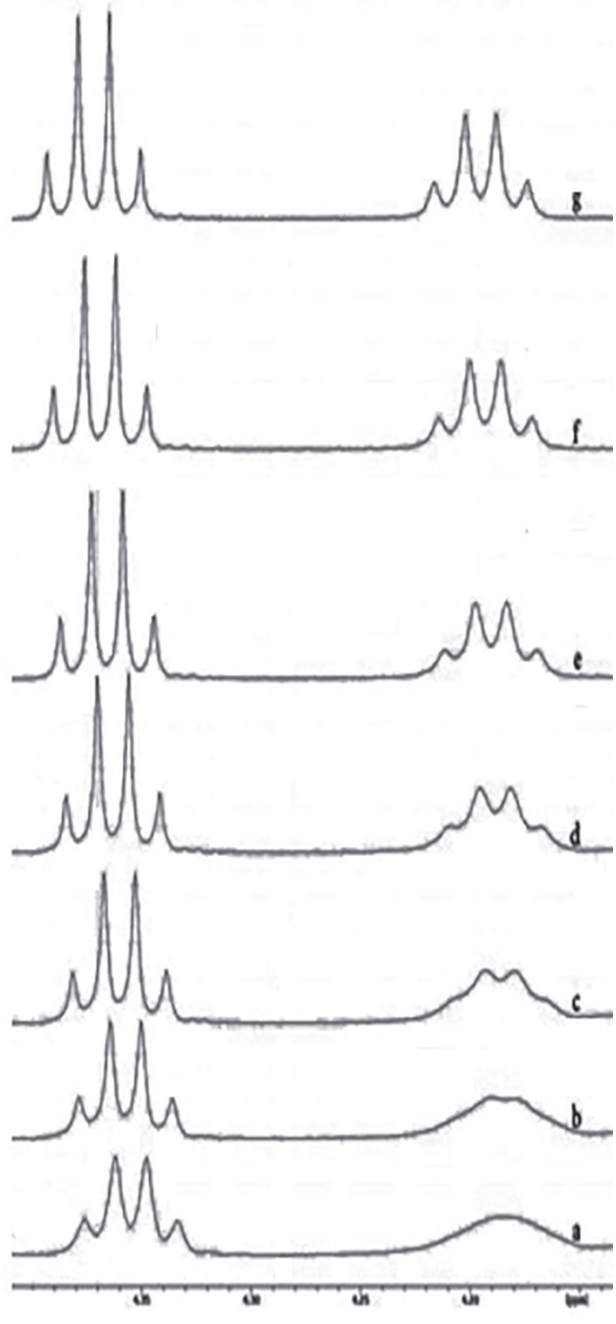


Fig. 3 The variable temperature ^{1}H NMR spectra of **4b** in acetone-d_6. (a) 260 K; (b) 265 K; (c) 270 K; (d) 275 K; (e) 280 K; (f) 258 K and (g) 290 K.

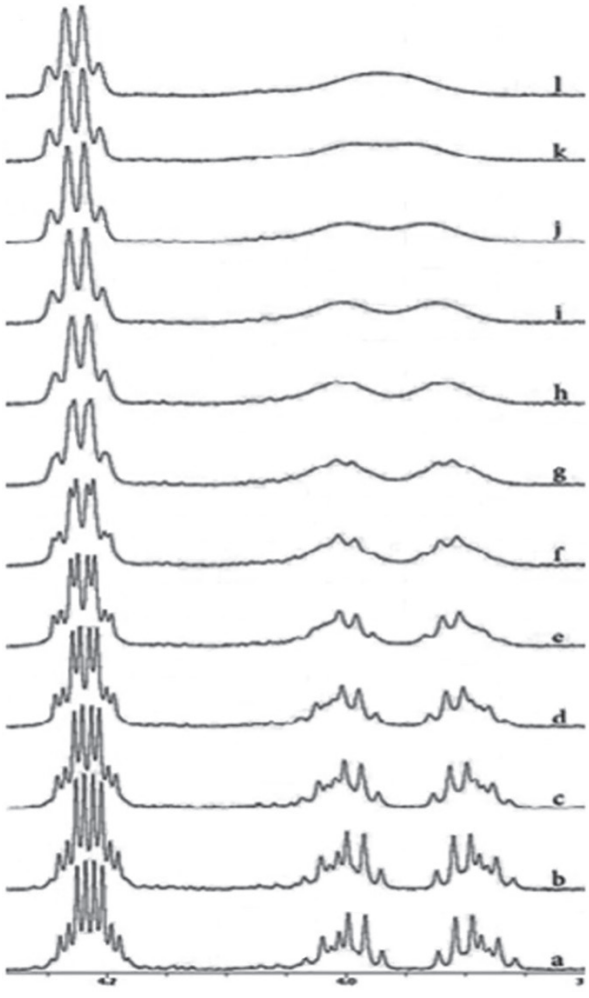


Fig. 4 The variable temperature ^{1}H NMR spectra of **7b** in DMSO-d_6: (a) 298 K; (b) 300 K; (c) 305 K; (d) 310 K;(e) 315 K; (f) 320 K; (g) 325 K; (h) 330 K; (i) 335 K; (j) 340 K; (k) 345 K and (l) 350 K.

phosphorus ylides with good yields and characterised by ^{1}H, ^{13}C, IR spectroscopy and elemental analysis. Based on acquired dynamic ^{1}H NMR spectra and X-ray crystallography, we were able to identify **4b** and **7b** structures unambiguously. The lack of H–bonding of SH group in the crystal structure - in contrast to the solution NMR structure, corroborated with extremely high 12.01 ppm shift - can be explained by the difference between the crystal and solution structure caused by solvation effects.

Experimental

Acetylenic esters and triphenylphosphine were obtained from Fluka and were used without further purification. 5,5-diarylhydantoin and 5,5-diarylthiohydantoin were prepared by known methods.[13] Melting points (uncorrected) were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H, N and S were performed using a Heraeus CHN–O-Rapid analyser. The experimental data were in good agreement with the calculated values. ^{1}H and ^{13}C NMR spectra ($CDCl_3$) were measured with a Bruker DRX-360 Avance and Avance II-500 spectrometer. IR spectra were recorded on a Shimadzu IR-460 spectrometer. Mass spectra were determined on a VG Micromass 7035 mass spectrometer at 70 eV with electron impact or on a Finnegan TSQ mass spectrometer with electrospraying ionisation. Relative intensities are given in parenthesis. Chromatography columns were prepared from Aldrich silica gel 70–230 mesh. X-ray quality crystal of **4b** or **7b** was mounted on top of a glass capillary using epoxy glue. Diffraction intensity data collection was carried out at 293(2) K on a Bruker-Nonius MACH3 diffractometer equipped with a point detector using graphite-monochromated Mo–$K\alpha$ radiation (λ = 0.71073 Å). The structures were solved by SIR-92 program and refined by full-matrix least-squares method on F^2, with all non-hydrogen atoms refined with anisotropic thermalparameters using the SHELXL-97 package,[14,15] publication material was prepared with the WINGX- suite.[16] Hydrogen atoms were located geometrically and refined in the rigid mode except N–H or S–H hydrogens which could be found at the difference electron density map. However in the final stage of refinement these hydrogen atoms were placed into geometric position, too. The solid state structure is stabilised by N–H···O hydrogen bond in case of **4b** and also by weak C–H···O hydrogen bonds. Other crystallographic and experimental details are summarised in Table 2.

Synthesis of phosphorus ylides **3** *and* **6***; general procedure*

To a magnetically stirred solution of 0.504 g **1** (2 mmol) and 0.284 g dimethyl acetylene dicarboxylate (2 mmol) in 5 mL CH_2Cl_2 was added dropwise a solution of 0.524 g triphenylphosphine (2 mmol) in 2 mL CH_2Cl_2 at 5 °C over 10 min. After 6 h stirring at room temperature, the product was filtered and washed with cold CH_2Cl_2.

Synthesis of **4** *and* **7***; general procedure*

A mixture of 0.788 g **3a** (1.2 mmol) in toluene (30 mL) was refluxed for 48 h. The solvent was removed and the product residue was separated by silica column chromatography (Merck 230–400 mesh) using hexane–ethyl acetate as eluent.

Dimethyl 2-(2,5-dioxo-4,4-diphenyl imidazolidin-1-yl)fumarate (**4a**): White powder; yield 0.421 g, 89%; m.p. 147–148 °C; IR (ν_{max}, cm^{-1}): 3383 (NH), 1724 and 1631 (C=O); ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.66 (3H, s, MeO), 3.95 (3H, s, MeO), 7.20 (1H, s, CH), 7.32–7.80 (10H, m, CH); ^{13}C NMR (90 MHz, $CDCl_3$) δ 52.9 (MeO), 54.1 (MeO), 71.7 (C), 127.9 (2 × CH), 129.3 (CH), 129.4 (2 × CH), 129.5 (2 × CH), 129.6 (CH), 130.1 (CH), 131.2 (C), 131.5 (CH), 133.0 (CH), 139.3 (2 × C), 154.1 (C=O), 162.6 (OC=O), 163.4 (OC=O), 171.7 (C=O); Anal. calcd for $C_{21}H_{18}N_2O_6$: C, 63.96; H, 4.60; N, 7.10; found: C, 63.90; H, 4.65; N, 7.14%.

Diethyl 2-(2,5-dioxo-4,4-diphenylimidazolidin-1-yl)fumarate (**4b**): Colourless crystals; yield 0.441 g, 87%; m.p. 156–158 °C; IR (ν_{max}, cm^{-1}): 3390 (NH), 1725 and 1630 (C=O); ^{1}H NMR (500 MHz, Acetone-d_6) δ 1.21 (3H, t, J = 7.1 Hz, Me), 1.34 (3H, t, J = 7.1 Hz, Me), 4.20 (2H, q, J = 7.1 Hz, CH_2O), 4.38 (2H, q, J = 7.1 Hz, CH_2O), 7.17 (1H, s, CH), 7.41–7.57 (10H, m, CH), 8.16 (1H, s, NH); ^{13}C NMR (125 MHz, Acetone-d_6) δ 13.9 (Me), 14.0 (Me), 61.5 (CH_2O), 62.8 (CH_2O), 70.4 (C), 127.3 (2 × CH), 128.0 (2 × CH), 128.7 (2 × CH), 128.8 (2 × CH), 129.1 (CH), 129.2 (2 × CH), 130.5 (C), 139.5 (2 × C), 152.6 (C=O), 161.8 (OC=O), 162.7 (OC=O), 171.5 (C=O); MS (EI) *m/z* (%): 422.16 [M]$^+$ (100); Anal. calcd for $C_{23}H_{22}N_2O_6$: C, 65.39; H, 5.25; N, 6.63; found: C, 65.25; H, 5.20; N, 6.62%.

Dimethyl 2-(2,5-dioxo-4,4-di-p-*tolylimidazolidin-1-yl)fumarate* (**4c**): White powder; yield 0.400 g, 79%; m.p. 148–149 °C; IR (ν_{max}, cm^{-1}): 3406 (NH), 1709 and 1680 (C=O); ^{1}H NMR (360 MHz, $CDCl_3$:DMSO-d_6, 3:1) δ 2.32 (3 H, s, Me), 2.36 (3 H, s, Me), 3.42 (3 H, s, MeO), 3.88 (3 H, s, MeO), 7.16 (1 H, s, CH), 7.24–7.74 (8 H, m, CH), 9.34 (1 H, s, NH) ppm; ^{13}C NMR (90 MHz, $CDCl_3$) δ 24.0 (Me), 25.3 (Me), 53.5 (MeO), 53.9 (MeO), 72.9 (C), 127.2 (CH), 127.4 (CH), 127.6 (2 × CH), 128.0 (2 × CH), 128.7 (2 × CH), 130.3 (CH), 135.8 (C), 137.1 (C), 137.8 (C), 138.2 (2 × C), 157.4 (C=O), 166.0 (OC=O), 168.5 (OC=O), 177.0 (C=O); Anal. calcd for $C_{23}H_{22}N_2O_6$: C, 65.39; H, 5.25; N, 6.63; found: C, 65.33; H, 5.21; N, 6.65%.

Diethyl 2-(2,5-dioxo-4,4-di-p-*tolylimidazolidin-1-yl)fumarate* (**4d**): White powder; yield 0.373 g, 69%; m.p. 153–155 °C; IR (ν_{max}, cm^{-1}): 3428 (NH), 1733 and 1653 (C=O); ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.08 (3H , t, J = 6.8 Hz, Me), 1.19 (3H , t, J = 6.84 Hz, Me), 2.33 (3 H, s, Me), 2.52 (3 H, s, Me), 4.03 (2H, q, J = 6.84 Hz, CH_2O), 4.23 (2H, q, J = 6.8 Hz, CH_2O), 7.01 (1H, s, CH), 7.19–7.62 (8H, m, CH), 9.96 (1H, s, NH); ^{13}C NMR (90 MHz, $CDCl_3$) δ 14.0 (Me), 14.1 (Me), 24.3 (Me), 24.6 (Me), 62.3 (CH_2O), 62.5 (CH_2O), 70.4 (C), 127.1 (2 × CH), 127.9 (2 × CH), 128.5 (2 × CH), 129.9 (2 × CH), 130.0 (CH), 130.5 (C), 132.0 (2 × C), 134.5 (2 × C), 156.2 (C=O), 161.5 (OC=O), 166.7 (OC=O), 169.5 (C=O); Anal. calcd for $C_{25}H_{26}N_2O_6$: C, 66.65; H, 5.82; N, 6.22; found: C, 66.71; H, 5.89; N, 6.18%.

Dimethyl 2-[4,4-bis(4-methoxyphenyl)-2,5-dioxoimidazolidin-1-yl] fumarate (**4e**): White powder; yield 0.480 g, 88%; m.p. 146–147 °C; IR (ν_{max}, cm^{-1}): 3416 (NH), 1720 and 1672 (C=O); ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.92 (3H, s, MeO), 4.23 (3H, s, MeO), 4.26 (3H, s, MeO), 4.29 (3H, s, MeO), 6.99 (1H, s, CH), 7.58–7.78 (8H, m, CH), 8.08 (1H, s, NH); ^{13}C NMR (90 MHz, $CDCl_3$) δ 51.8 (MeO), 52.5 (MeO), 53.8 (MeO), 55.3 (MeO), 74.5 (C), 118.3 (2 × CH), 127.0 (2 × CH), 127.9 (2 × CH), 128.5 (2 × CH), 129.9 (CH), 130.5 (C), 132.0 (2 × C), 150.9 (2 × C), 156.2 (C=O), 161.5 (OC=O), 166.7 (OC=O), 169.5 (C=O); Anal. calcd for $C_{23}H_{22}N_2O_8$: C, 60.79; H, 4.88; N, 6.16; found: C, 60.83; H, 4.86; N, 6.14%.

Diethyl 2-[4,4-bis(4-chlorophenyl)-2,5-dioxoimidazolidin-1-yl] fumarate (**4f**): White powder; yield 0.501 g, 85%; m.p. 121–123 °C; IR (ν_{max}, cm^{-1}): 3384 (NH), 1725 and 1669 (C=O) cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.23 (3H, t, *J* = 7.2 Hz, Me), 1.30 (3H, t, *J* = 7.2 Hz, Me), 4.17 (2H, q, *J* = 7.2 Hz, CH_2O), 4.49 (2H, q, *J* = 7.2 Hz, CH_2O), 7.18 (1H, s, CH), 7.32–7.66 (8H, m, CH), 8.69 (1 H, s, NH) ppm; ^{13}C NMR (90 MHz, $CDCl_3$) δ 13.9 (Me), 14.1 (Me), 62.5 (CH_2O), 62.7 (CH_2O), 70.4 (C), 123.7 (2 × CH), 125.6 (2 × CH), 127.1 (CH), 127.9 (CH), 128.5 (2 × CH), 129.9 (CH), 130.5 (C), 132.0 (C), 134.7 (C), 140.5 (2 × C), 157.8 (C=O), 165.4 (OC=O), 165.8 (OC=O), 171.2 (C=O); Anal. calcd for $C_{23}H_{20}Cl_2N_2O_6$: C, 56.23; H, 4.10; N, 5.70; found: C, 56.28; H, 4.06; N, 5.71%.

Dimethyl 2-(2-mercapto-5-oxo-4,4-diphenyl-4,5-dihydroimidazol-1-yl)fumarate (**7a**): White powder; yield 0.394 g, 80%; m.p. 165–167 °C; IR (ν_{max}, cm^{-1}): 2524 (SH), 1736 (C=O); ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.77 (3H, s, MeO), 4.07 (3H, s, MeO), 7.40 (1H, s, CH), 7.59–7.85 (10H, m, CH), 11.80 (1H, s, NH); ^{13}C NMR (90 MHz, DMSO-d_6) δ 53.4 (MeO), 55.0 (MeO), 72.3 (C), 126.0 (2 × CH), 127.1 (2 × CH), 128.5 (2 × CH), 129.5 (2 × CH), 129.9 (2 × CH), 131.5 (CH), 132.0 (C), 136.0 (C), 137.4 (C), 167.0 (OC=O), 168.5 (OC=O), 171.2 (C=O), 185.6 (C=N); Anal. calcd for $C_{21}H_{18}N_2O_5S$: C, 61.45; H, 4.42; N, 6.83; S, 7.81; found: C, 61.50; H, 4.36; N, 6.80; S, 7.85%.

Diethyl 2-(2-mercapto-5-oxo-4,4-diphenyl-4,5-dihydroimidazol-1-yl)fumarate (**7b**): Colourless crystals; yield 0.426 g, 81%; m.p. 169–170 °C; IR (ν_{max}, cm^{-1}): 2528 (SH), 1745 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.99 (3H, t, *J* = 7.5 Hz, Me), 1.19 (3H, t, *J* = 7.5 Hz, Me), 3.88–4.02 (2H, m, ABX_3 system, J_{AX} = 7.1, J_{BX} = 7.0, J_{AB} = 10.8 Hz, CH_2O), 4.21 (2H, q, *J* = 7.0 Hz, CH_2O), 7.11 (1H, s, CH), 7.29–7.51 (10H, m, CH), 10.92 (1H, s, SH); ^{13}C NMR (125 MHz, DMSO-d_6/$CDCl_3$) δ 13.7 (Me), 13.8 (Me), 61.5 (CH_2O), 62.6 (CH_2O), 73.7 (C), 126.7 (CH), 126.9 (CH), 127.0 (CH), 127.2 (CH), 127.4 (CH), 127.6 (CH), 128.2 (CH), 128.4 (CH), 128.5 (CH), 128.6 (CH), 130.3 (CH), 132.3 (C), 137.4 (C), 138.7 (C), 139.6 (C), 161.6 (OC=O), 162.3 (OC=O), 172.0 (C=O), 179.7 (C=N); MS (EI) *m/z* (%): 438.13 $[M]^+$ (100); Anal. calcd for $C_{23}H_{22}N_2O_5S$: C, 63.00; H, 5.06; N, 6.39; S, 7.31; found: C, 63.04; H, 5.09; N, 6.36; S, 7.35%.

Dimethyl 2-(2-mercapto-5-oxo-4,4-di-p-tolyl-4,5-dihydroimidazol-1-yl)fumarate (**7c**): White powder; yield: 0.405 g (77%); m.p. 160–162 °C; IR (ν_{max}, cm^{-1}): 2532 (SH), 1730, 1694 (C=O); ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.31 (3H, s, Me), 2.44 (3H, s, Me), 3.59 (3H, s, MeO), 3.94 (3H, s, MeO), 7.00 (1H, s, CH), 7.02–7.91 (8H, m, CH), 9.95 (1H, s, SH); ^{13}C NMR (90 MHz, $CDCl_3$) δ 22.7 (Me), 23.0 (Me), 55.4 (MeO), 55.5 (MeO), 68.2 (C), 128.8 (2 × CH), 129.2 (2 × CH), 130.0 (2 × CH), 130.8 (2 × CH), 131.5 (CH), 132.5 (C), 134.5 (C), 135.2 (C), 135.8 (C), 139.9 (C), 162.3 (OC=O), 162.9 (OC=O), 167.8 (C=O), 171.8 (C=N); Anal. calcd for $C_{23}H_{22}N_2O_5S$: C, 63.00; H, 5.06; N, 6.39; S, 7.31; found: C, 63.06; H, 5.08; N, 6.35; S, 7.28%.

*Diethyl 2-(2-mercapto-5-oxo-4,4-di-*p*-tolyl-4,5-dihydroimidazol-1-yl)fumarate* (**7d**): White powder; yield 0.397 g, 71%; m.p. 163–165 °C; IR (ν_{max}, cm^{-1}): 2530 (SH), 1735 (C=O); ^{1}H NMR (500 MHz, DMSO-d_6:$CDCl_3$, 3:1) δ 0.95 (3H, t, *J* = 7.1 Hz, Me), 1.18 (3H, t, *J* = 7.1 Hz, Me), 2.41 (3H, s, Me), 2.50 (3H, s, Me), 3.31–4.02 (2H, m, ABX_3 system, J_{AX} = 7.2, J_{BX} = 7.1, J_{AB} = 10.8 Hz, CH_2O), 4.21 (2H, q, *J* = 7.0 Hz, CH_2O), 7.17 (1H, s, CH), 7.29–7.35 (8H, m, CH), 12.17 (1H, s, SH); ^{13}C NMR (90 MHz, DMSO-d_6) δ 14.0 (Me), 14.1 (Me), 29.1 (Me), 29.5 (Me), 61.7 (CH_2O), 63.0 (CH_2O), 73.4 (C), 127.0 (CH), 127.3 (CH), 127.4 (CH), 127.5 (CH), 128.9 (CH), 129.0 (CH), 129.3 (CH), 130.8 (CH), 131.9 (C), 137.5 (2 × C), 138.8 (C), 138.9 (C), 161.7 (OC=O), 162.6 (OC=O), 172.0 (C=O), 179.3 (C=N). Anal. calcd for $C_{25}H_{26}N_2O_5S$: C, 64.36; H, 5.62; N, 6.00; S, 6.87; found: C, 64.43; H, 5.60; N, 6.01; S, 6.84%.

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