**Supporting information**

# Efficient Synthesis and Environmentally Friendly Reactions of PEG-supported 1,2-Diaza-1,3-butadiene.

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**1. General.**

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. Solvents were purchased and used without purification with the exception of THF which was distilled over sodium hydroxide. Melting points were determined on in open capillary tubes and are uncorrected. IR-FT spectra were obtained as Nujol mulls. Mass spectra EI were made at an ionizing voltage of 70 eV. $^{1}$H-NMR and $^{13}$C-NMR spectra were recorded at 400, 100, MHz, respectively. All NMR spectra were recorded in DMSO-$d_6$. Chemical shifts ($\delta_H$) are reported in parts per million (ppm), relative to TMS as internal standard. All coupling constants (*J*) values are given in Hz. Chemical shifts ($\delta_C$) are reported in parts per million (ppm), relative to DMSO-$d_6$, as internal standard in a broad band decoupled mode; the multiplicities were obtained using 135° and 90° DEPT experiments to aid in assignment (q = methyl, t = methylene, d = methine, s = quaternary). The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet; br, broad. All the NH and $NH_2$ groups exchanged with $D_2O$. Precoated silica gel plates (0.25 mm) were employed for analytical thin layer chromatography and silica gel 35-70 μ for column chromatography. The nomenclature was generated using ACD/IUPAC Name (version 3.50, 5 Apr. 1998), Advanced Chemistry Development Inc., Toronto, ON (Canada).

**2. Procedure for the Synthesis of PEG-supported 1-Aminocarbonyl 1,2-diaza-1,3-butadiene 5.** Poly-(ethylene glycol)methyl ether (average MW 5000) **1** (5.00 g) in toluene (40 mL) was refluxed for 3 h in the presence of *tert*-butyl acetoacetate (10 equiv.). After completion of the reaction, diethyl ether (60 mL) was added to the mixture to allow the precipitation of the PEG-bound β-ketoester **2**, which was collected by filtration and washed three times with diethyl ether (20 mL). This latter compound **2** was treated with semicarbazide hydrochloride (5 equiv.) and sodium carbonate (5 equiv.) in methanol (50 mL). The reaction mixture was allowed to stand at room temperature for 5 h to obtain PEG

supported hydrazone **3**. The reaction solvent was evaporated under reduced pressure. The crude was dissolved in dichloromethane (180 mL) and washed with water. The organic layer was dried on sodium sulphate and PTAB was added portionwise under magnetic stirring in 1.5 h to obtain polymer-bound α–bromohydrazone **4**. Then the mixture was treated twice with an aqueous saturated solution of sodium carbonate (30 mL) and the organic layer was dried on sodium sulphate. Dichloromethane was evaporated under reduced pressure and the final 1-aminocarbonyl 1,2-diaza-1,3-butadiene **5** was precipitated with diethyl ether (40 mL), filtered and washed three times with diethyl ether (20 mL).

**3. General Procedure for the Synthesis of 2-Thiazolin-4-ones 8a-j.**

To a stirred solution of PEG-supported 1-aminocarbonyl-1,2-diaza-1,3-butadiene (5.00 g) in dichloromethane:methanol (1:4) (8 mL) was added a solution of thioamides (3.00 equiv.) in methanol (2 mL). After 1.0-4.5 h the typical red colour of 1,2-diaza-1,3-butadiene disappeared and a precipitate appeared. The TLC check revealed the presence of a spot corresponding to the final 2-thiazolin-4-ones **8a-j** that were collected by filtration in satisfactory purity.

**4. Characterization data of compounds 8a-j.**

**2-[1-(4-Oxo-2-phenyl-4,5-dihydro-1,3-thiazol-5-yliden)ethyl]-1-hydrazinecarboxamide (8a):**[7a] yellow solid; mp 173-174 °C; IR (nujol) $\nu_{max}$ 3300, 3150, 1700, 1680,1650, 1610, 1560 $cm^{-1}$; $^{1}H$ NMR (400 MHz, DMSO-$d_6$) $\delta_H$ 2.27 (s, 3H), 6.27 (br s, 2H), 7.47-7.50 (m, 3H), 7.86-7.90 (br s, 2H), 9.30 (br s, 1H), 11.68 (br s, 1H); $^{13}C$ NMR (100 MHz, DMSO-$d_6$) $\delta_C$ 14.4 (q), 107.3 (s), 125.4 (d), 129.2 (d), 130.6 (d), 132.7 (s), 143.5 (s), 156.7 (s), 161.7 (s), 162.9 (s); MS (EI) *m/z* 276 [M+] (9), 259 (9), 173 (21), 130 (100).

**2-(1-{4-Oxo-2-[4-(trifluoromethyl)phenyl]-4,5-dihydro-1,3-thiazol-5-yliden}ethyl)-1-hydrazinecarboxamide (8b)**: yellow solid; mp 184-185°C; IR (nujol) $\nu_{max}$ 3318, 3174, 1718, 1662, 1571 $cm^{-1}$; $^{1}H$ NMR (400 MHz, DMSO-$d_6$) $\delta_H$ 2.28 (s, 3H), 6.26 (br s, 2H), 7.85 (d, 2H, *J*=7.8 Hz),

8.03 (d, 2H, *J*=7.8 Hz), 9.36 (s, 1H), 11.73 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta_C$ 14.2 (q), 109.6 (s), 123.9 (s, $^1J_{CF}$=270 Hz), 126.1 (d, $^3J_{CF}$=16 Hz), 130.0 (d, $^2J_{CF}$=32 Hz), 136.2 (d), 142.2 (s), 143.9 (s), 156.6 (s), 160.0 (s), 161.1 (s); MS (EI) *m/z* 344 [M+] (11), 327 (21), 171 (100).

**2-{1-[2-(4-Methoxyphenyl)-4-oxo-4,5-dihydro-1,3-thiazol-5-yliden]ethyl}-1-hydrazinecarboxamide (8c)**: yellow solid; mp 179-181°C; IR (nujol) $\nu_{max}$ 3389, 3236, 1742, 1689, 1638 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta_H$ 2.24 (s, 3H), 3.79 (s, 3H), 6.21 (br s, 2H), 6.96 (d, 2H, *J*=7.6 Hz), 7.17 (d, 2H, *J*=7.6 Hz), 9.11 (s, 1H), 11.69 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta_C$ 14.7 (q), 55.0 (q), 105.8 (s), 128.8 (d), 131.3 (d), 133.4 (s), 138.5 (s), 143.9 (s), 154.0 (s), 161.7 (s), 162.9 (s); MS (EI) *m/z* 306 [M+] (2), 289 (11), 256 (6), 191 (8), 156 (11), 130 (100).

**2-{1-[2-(4-Chlorophenyl)-4-oxo-4,5-dihydro-1,3-thiazol-5-yliden]ethyl}-1-hydrazinecarboxamide (8d)**: Yellow solid, mp: 200-201°C; IR (nujol) $\nu_{max}$ 3313, 3147, 1712, 1661 cm-1; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta_H$ 2.27 (s, 3H), 6.22 (brs, 2H), 7.55 (d, 2H, *J*=7.6 Hz), 7.88 (d, 2H, *J*=7.6 Hz), 9.27 (s, 1H), 11.65 (brs, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta_C$ 15.1 (q), 108.8 (s), 127.9 (d), 130.0 (d), 132.3 (s), 135.8 (s), 143.8 (s) , 157.4 (s) , 161.2 (s) , 162.3 (s). MS (EI) *m/z* 312 [M$^+$+2] (1), 310 [M$^+$] (4), 295 (3), 293 (10), 156 (13), 139 (30), 137 (100).

**2-{1-[2-(2,4-Difluorophenyl)-4-oxo-4,5-dihydro-1,3-thiazol-5-yliden]ethyl}-1-hydrazinecarboxamide (8e)**: **)**: yellow solid; mp 196-198°C; IR (nujol) $\nu_{max}$ 3327, 3163, 1704, 1658, 1622, 1563 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta_H$ 2.27 (s, 3H), 6.21 (br s, 2H), 7.26 (dt, 1H, $^3J_{HF}$=8.0 Hz, *J*=2.4 Hz), 7.48 (ddd, 1H, $^3J_{HF}$=11.8 Hz, *J*=9.2 Hz, *J*=2.8 Hz), 8.14 (dt, 1H, *J*=8.8 Hz, $^4J_{HF}$=6.8 Hz), 9.30 (s, 1H), 11.66 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta_C$ 15.0 (q), 105.8 (d, $^2J_{CF}$=26 Hz), 109.2 (s), 113.5 (d, $^3J_{CF}$=19 Hz), 118.2 (s), 130.3 (d), 143.3 (s), 154.9 (s, $^3J_{CF}$=6 Hz), 157.3 (s), 160.5 (s, $^1J_{CF}$=252 Hz, $^3J_{CF}$=12 Hz), 161.2 (s), 163.6 (s, $^1J_{CF}$=250 Hz, $^3J_{CF}$=13 Hz); MS (EI) *m/z* 312 [M+] (21), 295 (35), 173 (26), 130 (100).

**2-{1-[4-Oxo-2-(4-pyridyl)-4,5-dihydro-1,3-thiazol-5-yliden]ethyl}-1-hydrazinecarboxamide (8f)**: yellow solid; mp 168-170°C; IR (nujol) $\nu_{max}$ 3636, 3501, 3436, 3301, 1696, 1660, 1560 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta_H$ 2.28 (s, 3H), 6.26 (br s, 2H), 7.78 (br s, 2H), 8.69 (br s, 2H), 9.39 (s, 1H), 11.81 (s, 1H); $^{13}C$ NMR (100 MHz, DMSO-$d_6$) $\delta_C$ 14.2 (q), 110.6 (s), 119.1 (d), 139.3 (d), 141.7 (s), 150.8 (d), 156.6 (s), 159.0 (s), 160.9 (s); MS (EI) *m/z* 277 [M+] (12), 260 (13), 173 (33), 156 (61), 130 (100).

**2-{1-[4-Oxo-2-(3-pyridyl)-4,5-dihydro-1,3-thiazol-5-yliden]ethyl}-1-hydrazinecarboxamide (8g):**[7a] yellow solid; mp 170-172 °C; IR (nujol) ν 3480, 3300, 3180, 1690, 1680,1570 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta_H$ 2.27 (s, 3H), 6.26 (s, 2H), 7.50-7.56 (m, 1H), 8.16-8.23 (m, 1H), 8.65 (d, 1H, *J*=4.6 Hz), 9.06 (s, 1H), 9.34 (s, 1H), 11.77 (s, 1H); $^{13}C$ NMR (100 MHz, DMSO-$d_6$) $\delta_C$ 15.0 (q), 109.4 (s), 124.9 (d), 129.4 (d), 133.6 (s), 143.4 (s), 147.0 (d), 151.7 (d), 157.4 (s), 160.2 (s), 162.1 (s); MS (EI) *m/z* 277 [M+] (11), 260 (17), 234 (7), 173 (31), 156 (47), 130 (100).

**2-{1-[4-Oxo-2-(2-thienyl)-4,5-dihydro-1,3-thiazol-5-yliden]ethyl}-1-hydrazinecarboxamide (8h)**: brown solid; mp 178-179 °C; IR (nujol) ν 3291, 3239, 3148, 1709, 1644,1609 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta_H$ 2.25 (s, 3H), 6.22 (s, 2H), 7.17 (dd, 1H, *J*=4.8 Hz, *J*=4.0 Hz), 7.65 (dd, 1H, *J*=4.0 Hz, *J*=0.8 Hz), 7.75 (dd, 1H, *J*=5.2 Hz, *J*=0.8 Hz), 9.19 (s, 1H), 11.64 (s, 1H); $^{13}C$ NMR (100 MHz, DMSO-$d_6$) $\delta_C$ 14.4 (q), 106.1 (s), 127.4 (d), 128.6 (d), 129.7 (d), 136.6 (s), 143.7 (s), 156.8 (s), 157.6 (s), 161.9 (s); MS (EI) *m/z* 282 [M+] (1), 265 (7), 207 (11), 130 (100).

**2-{1-[2-(2-Methyl-1,3-thiazol-4-yl)-4-oxo-4,5-dihydro-1,3-thiazol-5-yliden]ethyl}-1-hydrazinecarboxamide (8i)**: yellow solid; mp 176-177 °C; IR (nujol) ν 3457, 3291, 3147, 1707, 1653, 1576 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta_H$ 2.26 (s, 3H), 2.70 (s, 3H), 6.23 (s, 2H), 7.97 (s, 1H), 9.20 (s, 1H), 11.63 (s, 1H); $^{13}C$ NMR (100 MHz, DMSO-$d_6$) $\delta_C$ 14.6 (q), 18.6 (q), 108.7 (s), 117.4 (d), 122.3 (s), 144.2 (s), 147.6 (s), 156.7 (s), 158.0 (s), 167.1 (s); MS (EI) *m/z* 297 [M+] (4), 280 (13), 254 (6), 247 (7), 156 (6), 130 (89), 124 (100).

**2-(1-{-2-[3-(Methylsulfanyl)-1-phenyl-1*H*-4-pyrazolyl]-4-oxo-4,5-dihydro-1,3-thiazol-5-yliden}ethyl)-1-hydrazinecarboxamide (8j)**: yellow solid; mp 188-190 °C; IR (nujol) ν 3407, 3267, 3162, 1710, 1674, 1609 $cm^{-1}$; $^{1}H$ NMR (400 MHz, DMSO-$d_6$) $\delta_H$ 2.26 (s, 3H), 2.64 (s, 3H), 6.20 (s, 2H), 7.36 (t, 1H, *J*=7.6 Hz), 7.53 (t, 2H, *J*=8.0 Hz), 7.91 (d, 2H, *J*=7.6 Hz), 9.09 (s, 1H), 9.11 (s, 1H), 11.52 (s, 1H); $^{13}C$ NMR (100 MHz, DMSO-$d_6$) $\delta_C$ 14.2 (q), 15.4 (q), 100.1 (s), 116.8 (s), 118.4 (d), 121.4 (d), 126.8 (s), 128.8 (d), 129.5 (d), 138.7 (s) 147.4 (s), 156.8 (s), 158.8 (s), 165.6 (s); MS (EI) *m/z* 388 [M+] (1), 371 (19), 234 (11), 215 (75), 182 (100).