Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

A comparison of verdazyl radicals modified at the 3-position as mediators in the living radical polymerisation of styrene and *n*-butyl acrylate

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Experimental

Materials

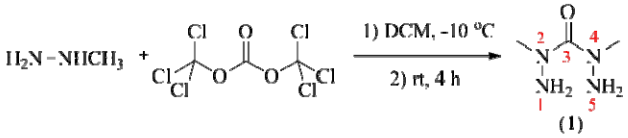
All chemicals were purchased from Sigma Aldrich and used as received unless otherwise stated. Inhibitors were removed from all monomers by passing through a short basic alumina column. *n*-Butyl acrylate was stabilised by adding 1 mg of the appropriate radical for initiator to 40 mL of monomer where stated. Mesitylene, where added, was used as an internal standard for determining conversion. Otherwise conversion was determined by measuring the disappearance of the monomer vinyl peaks with the appearance of polymer.

Characterisation techniques

Melting points were recorded using a Stuart Scientific SMP3 melting point apparatus at a rate of 3 ˚C/minute. Infra-red spectra were recorded using a Bruker Vector 22 FTIR spectrometer fitted with a Golden Gate attenuated total reflection cell. IR transmissions are reported as wavenumbers (cm^{-1}). The following abbreviations have been used; br = broad, w = weak, m = medium, s = strong, Ar = aromatic, adj = adjacent, def = deformation, sym = symmetrical and asym = asymmetrical. NMR spectra were recorded using Bruker DPX-300, DPX-400, DRX-500 and AV III-600 instruments as solutions in deuterated NMR solvents. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS). The following abbreviations are used to abbreviate multiplicities; s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. Mesitylene, where added, was used as an internal standard for determining conversion by NMR. Otherwise conversion was determined by measuring the disappearance of the monomer vinyl peaks with the appearance of polymer in NMR spectra. Microanalyses were performed in duplicate where possible by Warwick Analytical Service. High resolution mass spectrometry were performed by the Mass Spectroscopy Facility at Warwick. UV-visible spectra were recorded on a Perkin Elmer Lambdas 25 spectrophotometer using a quartz crystal cuvette. EPR spectra were recorded on Bruker EMX-E, EMX and ECS 080 spectrometers, using either an ER 041X or 041XG X-band microwave bridge and an EIP model 545A microwave frequency counter. The cavity for the ambient temperature measurements were recorded using a Bruker 4103TM/9106 cavity. High temperature measurements were recorded using the EX-102 high temperature cavity and Eurotherm B-V2 2000 control unit Gel permeation chromatography samples were run on an Agilent 390-LC system equipped with a PL-AS RT autosampler, a 100µL injection loop, a 5µm PLgel guard column (50 mm x 7.5 mm), 2 5µm PLgel Mixed D columns (50mm x 300 mm) and a differential refractive index (DRI) detector. The system was eluted with chloroform at a rate of 1 mL/minute and the detector was calibrated with PL narrow polystyrene (162–371,100 g/mol) and poly methyl methacrylate (200–467,400 g/mol) standard easy vials. Crystallographic data was obtained by Dr Guy Clarkson and theoretical calculations were carried out by Professor Rob Deeth both at the University of Warwick.

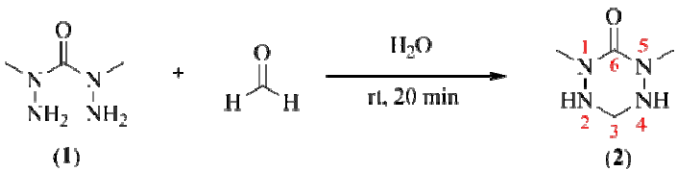
Synthetic procedures

2,4-dimethylcarbonohydrazide (1)



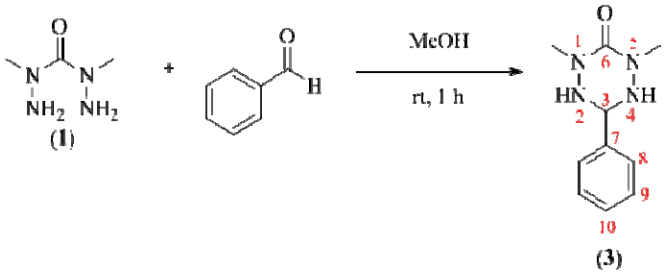
To a stirring solution of methyl hydrazine (54 mL, 1.04 mmol) in dichloromethane (400 mL), cooled to -10 ˚C, was added a solution of triphosgene (25.16 g, 84.25 mmol) in dichloromethane (300 mL) dropwise over 1.5 hours. Following the addition, the reaction was allowed to rise to ambient temperature and stirred for a further 4 hours. The reaction mixture was filtered and the solvent removed *in vacuo*. The resulting yellow oil was dried on a high vacuum line to give **1** a**s** a pale yellow solid (26.89 g, 89.5%). The compound is hygroscopic and requires storage under nitrogen in the fridge. Melting point: 49–51 ˚C. IR (neat): $\widetilde{\nu}$ = 3308, 3199 (br s, >N-H), 3020, 2920, 2839 (br m, CH stretch), 1583 (br m, C=O), 1385 (br m, CH_3 sym def) cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$, 298 K) δ = 3.01 (s, 6H, H2,4); 4.11 (br s, 4H, H1,5). ^{13}C NMR (75.48 MHz, $CDCl_3$, 298 K) δ = 42.10 (C2, 4); 164.58 (C3). Mass Spectrometry (+ESI-MS) *m/z*: 119.09 $[M + H]^+$, 141.07 $[M + Na]^+$.

1,5-dimethyl-tetrazinan-6-one (2)



To a solution of **1** (6.00 g, 50.81 mmol) in water (15 mL) stirring at ambient temperature was added dropwise a solution of 37% aqueous formaldehyde (3.80 mL, 43.19 mol) in water (15 mL). The resulting yellow solution was left stirring for 20 minutes. The water was removed on a high vacuum line to give off-white solid. The solid was dissolved in ethanol and the solvent removed *in vacuo*. This was repeated twice more with ethanol resulting in an off white solid which was recrystallised from ethyl acetate to give **2** (2.90 g, 51.5%) as an off white crystalline powder. Melting point: 107–109 ˚C. IR (neat): $\widetilde{\nu}$ = 3244 (br m, >N-H), 2932, 2873 (br w, CH stretch), 1601 (br m, C=O), 1532 (br w, >N-H), 1433 (br m, CH def), 1387 (m, CH_3 sym def) cm^{-1}. ^1H NMR (300.13 MHz, DMSO, 298 K) δ = 2.89 (s, 6H, H1, 5); 3.69 (t, *J* = 7.5 Hz, 2H, H3); 5.29 (t, *J* = 7.5 Hz, 2H, H2, 4). ^{13}C NMR (75.48 MHz, DMSO, 298 K) δ = 37.36 (C1, 5); 58.57 (C3); 163.26 (C6). Anal. Calcd. for $C_4H_{10}N_4O$: C, 36.91; H, 7.74; N, 43.05. Found: C, 36.43; H, 7.73; N, 42.64. Mass Spectrometry (+ESI-MS) *m/z*: 131.09 $[M+H]^+$.

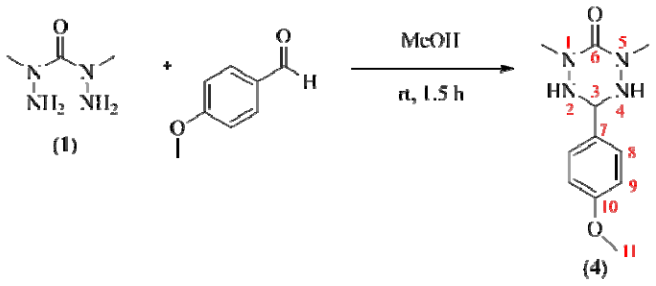
1,5-dimethyl-3-phenyl-tetrazinan-6-one (3)



(1) (3)

To a solution of **1** (5.00 g, 42.34 mmol) in methanol (53 mL) stirring at ambient temperature was added dropwise a solution of benzaldehyde (4.3 mL, 42.34 mmol) in methanol (42 mL). The resulting solution was left stirring for 1 hour. The solvent was removed *in vacuo* giving a pale orange solid which was recrystallised from methanol to give **3** (2.57 g, 29.4%) as white crystalline needles. Melting point: 124-125 ˚C. IR (neat): $\widetilde{\nu}$ = 3252, 3220 (w, >N-H), 3017 (w, Ar), 2964, 2912, 2868 (w, CH stretch), 1656 (m, C=O), 1596, 1569, 1478 (m, Ar), 1448 (m, CH def), 1400 (m, CH_3 sym def), 1234 (m, C-N stretch), 745, 628 (s, 5 adj H) cm^{-1}. ^1H NMR (300.13 MHz, DMSO, 298 K) δ = 2.95 (s, 6H, H1, 5); 4.90 (t, *J* = 8.0 Hz, 1H, H3); 5.70 (d, *J* = 8.0 Hz, 2H, H2,4); 7.31-7.41 (m, 3H, H9,10), 7.55 (br d, *J* = 7.3 Hz, 2H, H8). ^{13}C NMR (100.60 MHz, DMSO, 298 K) δ = 37.64 (C1, 5); 68.56 (C3); 127.01 (C9); 127.88 (C10); 128.19 (C8); 136.71 (C7); 154.47 (C6). Anal. Calcd. for $C_{10}H_{14}N_4O$: C, 58.24; H, 6.84; N, 27.17. Found: C, 58.02; H, 6.86; N, 27.10. Mass Spectrometry (+ESI-MS) *m/z*: 207.12 $[M+H]^+$.

1,5-dimethyl-3-(4-methoxyphenyl)tetrazinan-6-one (4)

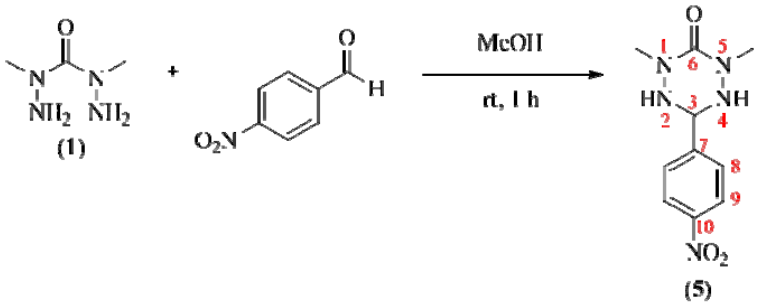


(1) (4)

To a solution of **1** (2.36 g, 20.00 mmol) in methanol (25 mL) stirring at ambient temperature was added dropwise a solution of 4-methoxybenzaldehyde (2.72 g, 20.00 mmol) in methanol (5 mL). The resulting solution was left stirring for 1.5 hours. The solvent was removed *in vacuo* to give a white solid with yellow staining which was recrystallised from methanol to give **4** (2.81 g, 59.5%) as white crystalline needles. Melting point: 146–147 ˚C. IR (neat): $\widetilde{\nu}$ = 3246 (s, >N-H), 3038 (w, Ar), 2965, 2920, 2871 (m, CH stretch), 2841 (m, C-OCH_3), 1591 (s, C=O), 1436 (s, CH def), 1404 (s, CH_3 sym def), 1242 (s, C-O stretch), 1170 (m, C-N), 1108 (C-O stretch), 877 (2 adj H) cm^{-1}. ^1H NMR (400.03 MHz, DMSO, 298 K) δ = 2.94 (s, 6H, H1, 5); 3.74 (s, 3H,

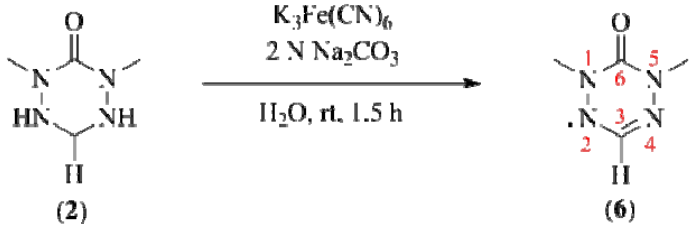
H11); 4.83 (t, *J* = 8.0 Hz, 1H, H3); 5.61 (d, *J* = 9.0 Hz, 2H, H2,4); 6.92 (d, *J* = 8.0 Hz, 2H, H8); 7.42 (d, *J* = 8.0 Hz, 2H, H9). ^{13}C NMR (100.60 MHz, DMSO, 298 K) δ = 37.71 (C1, 5); 55.04 (C11); 68.27 (C3); 113.60 (C8); 128.21 (C9); 128.66 (C7); 154.54 (C10); 158.96 (C6). Anal. Calcd. for $C_{11}H_{16}N_4O_2$: C, 55.92; H, 6.83; N, 23.71. Found: C, 55.94; H, 6.87; N, 23.65. Mass Spectrometry (+ESI-MS) *m/z*: 259.11 $[M+Na]^+$.

1,5-dimethyl-3-(4-nitrophenyl)tetrazinan-6-one (5)



To a solution of **1** (1.01 g, 8.55 mmol) in methanol (20 mL) stirring at ambient temperature was added dropwise a solution of 4-nitrobenzaldehyde (0.92 g, 6.09 mmol) in methanol (50 mL). The methanol required gentle heating in order to get the aldehyde to dissolve. The resulting solution was stirred for 1 hour. During this time a yellow precipitate formed and was collected by suction filtration. The resulting yellow powder was recrystallised from methanol to give **5** (0.25 g, 16.6%) as pale yellow needles. Melting point: 172–175 °C. IR (neat): $\tilde{\nu}$ = 3268, 3227 (s, >N-H), 3073 (w, Ar), 2952, 2910, 2865 (br w, CH stretch), 1628, 1607 (NO_2), 1606 (m, Ar), 1517 (s, C=O), 1490 (m, CH_3 sym def), 1432 (m, CH def), 1345 (s, C-NO_2), 1201 (m, C-N), 858 (s, C-OCH_3) cm^{-1}. ^{1}H NMR (400.03 MHz, DMSO, 298 K) δ = 2.94 (s, 6H, H1, 5); 5.12 (t, *J* = 6.0 Hz, 1H, H3); 5.91 (d, *J* = 6.0 Hz, 2H, H2, 4); 7.82 (d, *J* = 9.0 Hz, 2H, H8); 8.25 (d, *J* = 9.0 Hz, 2H, H9). ^{13}C NMR (100.60 MHz, DMSO, 298 K) δ = 37.50 (C1, 5); 67.69 (C3); 123.34 (C8); 128.70 (C9); 144.95 (C10); 147.11 (C7); 154.18 (C6). Anal. Calcd. for $C_{10}H_{13}N_5O_3$: C, 47.81; H, 5.22; N, 27.87. Found: C, 47.78; H, 5.01; N, 27.96. Mass Spectrometry (+ESI-MS) *m/z*: 247.09 $[M+Na]^+$.

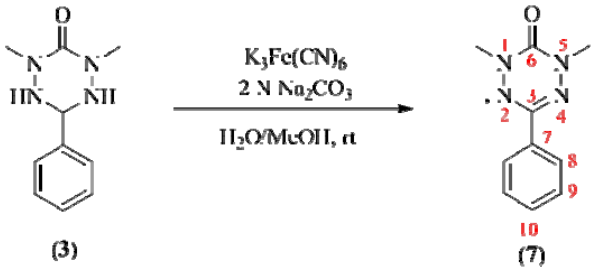
1,5-dimethyl oxoverdazyl (6)



To a solution of **2** (3.30 g, 25.6 mmol) in water (26 mL) stirring at ambient temperature was added dropwise a solution potassium ferricyanide (25.30 g, 76.8 mmol) dissolved in water (128 mL) and 2 N sodium carbonate

solution (38.5 mL). The resulting solution was stirred for 1.5 hours and then extracted eight times with diethyl ether (60 mL). The combined extracts were dried using magnesium sulphate and the solvent removed *in vacuo* to give a dark red solid. The compound was purified by neutral alumina column chromatography using 1:1 dichloromethane/petroleum ether 40-60 to give **6** (2.67 g, 82.1%) as a dark red crystalline solid, which can be recrystallised from petroleum ether but the crystals are not stable at ambient temperature and require storage in the freezer. Melting point: 36–38 ˚C. IR (neat): $\widetilde{\nu}$ = 3072 (br w, Ar), 2942 (br w, CH stretch), 1672 (br s, C=O), 1452 (br m, CH def), 1347 (br m, CH_3 sym def), 1262 (br m, C-O) cm^{-1}. EPR (9.77 GHz, toluene, 298K): $a(N_{2,4})$ = 6.50 G; $a(N_{1,5})$ = 5.19 G; $a(H_{CH_3})$ = 5.45 G (6H); $a(H_{CH})$ = 0.78 G; g = 2.0045. UV-vis (1,4-dioxane): λ_{max} (lg ε) = 254 nm (3.08), 378 nm (2.84), 416 nm, (2.75), 430 nm (2.79), 446 nm (2.69). Anal. Calcd. for $C_{24}H_{31}NO_3$: C, 37.79; H, 5.55; N, 44.07. Found: C, 36.37; H, 5.25; N, 41.25. Mass Spectrometry (+ESI-MS) *m/z*: 127.06 $[M]^+$.

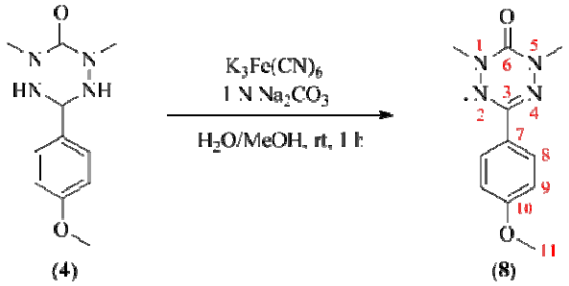
1,5-dimethyl-3-phenyl-6-oxoverdazyl (7)



(3) (7)

To a solution of **3** (1.00 g, 4.85 mmol) dissolved in water (23 mL) and methanol (15 mL) stirring at ambient temperature was added dropwise a solution of potassium ferricyanide (5.24 g, 15.9 mmol) in water (30 mL) and 2 N sodium carbonate solution (7 mL). The addition of an excess of water precipitated **7** (0.88 g, 89.3%) as an orange powder which was collected by suction filtration, washed thoroughly with water and dried in a vacuum oven. Melting point: 63–65 ˚C. IR (neat): $\widetilde{\nu}$ = 3034 (w, Ar), 2945 (w, CH stretch), 1670 (s, C=O), 1456 (m, CH def), 1375 (m, CH_3 sym def), 1248 (s, C-O), 1162 (w, C-O), 776 (s, 5 adj H) cm^{-1}. EPR (9.77 GHz, toluene, 298K): $a(N_{2,4})$ = 6.50 G; $a(N_{1,5})$ = 5.10 G; $a(H_{CH_3})$ = 5.45 G (6H); g = 2.0045. UV-vis (1,4-dioxane): λ_{max} (lg ε) = 248 nm (4.43), 389 nm (2.91), 400 nm (3.03), 440 nm, (3.17), 492 nm (2.48), 526 nm (2.34), 552 nm (1.29). Anal. Calcd. for $C_{24}H_{31}NO_3$: C, 59.10; H, 5.46; N, 27.57. Found: C, 57.50; H, 5.25; N, 26.61. Mass Spectrometry (+ESI-MS) *m/z*: 203.09 $[M]^+$.

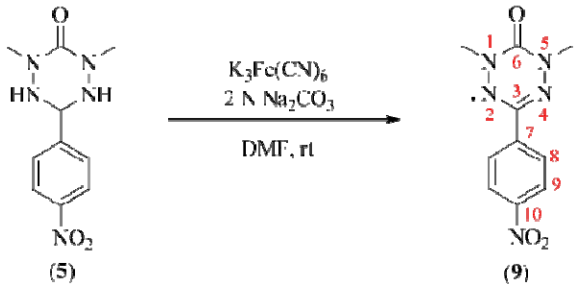
1,5-dimethyl-3-(4-methoxyphenyl)-6-oxoverdazyl (8)



(4) (8)

To a solution of **4** (1.50 g, 6.40 mmol) in methanol (77 mL) and water (52 mL) stirring at ambient temperature was added dropwise a solution of potassium ferricyanide (6.32 g, 19.2 mmol) in 1 N sodium carbonate solution (19 mL). The resulting solution was stirred for 1 hour. During which time a mixture of red and cream solids precipitated and was collected by suction filtration and washed thoroughly with water to give **8** (1.20 g, 80.5%) as a red powder which was recrystallised from methanol to give a dark red crystalline solid. Melting point: 86–88 ˚C. IR (neat): $\widetilde{\nu}$ = 3028 (w, Ar), 2941, 2912 (m, CH stretch), 2833 (m, C-OCH_3), 1678 (s, C=O), 1606, 1517 (m, Ar), 1469 (m, CH_3 sym def), 1433 (m, CH def), 1298 (s, C-N), 1244, 1110 (m, C-O), 840 (s, 2 adj H) cm^{-1}. EPR (9.81 GHz, toluene, 298K): $a(N_{2,4})$ = 6.53 G; $a(N_{1,5})$ = 5.37 G; $a(H_{CH_3})$ = 5.15 G (6H); g =2.0100. UV-vis (1,4-dioxane): λ_{max} (lg ε) = 263 nm (4.46), 318 nm (2.17), 394 nm (2.82), 407 nm (2.79), 417 nm (2.88), 499 nm (2.57), 523 nm (2.61), 557 nm (2.30). Anal. Calcd. for $C_{11}H_{13}N_4O_2$: C, 56.64; H, 5.62; N, 24.02. Found: C, 56.41; H, 5.35; N, 23.85. Mass Spectrometry (+ESI-MS) *m/z*: 240.10 $[M]^+$.

1,5-dimethyl-3-(4-nitrophenyl)-6-oxoverdazyl (9)



(5) (9)

To a solution of **5** in dimethylformamide (40 mL) stirring at ambient temperature was added dropwise a solution of potassium ferricyanide (1.74 g, 5.28 mmol) in water (20 mL) and 2 N sodium carbonate solution (2.64 mL). The solution got warm during the addition and a cream precipitate formed. On cooling a brown precipitate formed. The solids were collected by suction filtration and washed thoroughly with water to give **9** (0.26 g, 65.5%) as a *fluffy* brown solid which was recrystallised from methanol to give fine brown needles. Melting point: 144–146 ˚C. IR (neat): $\widetilde{\nu}$ = 3087 (w, Ar), 2947 (w, CH stretch), 1688 (s, NO_2), 1604 (m, NO_2), 1595 (m, Ar), 1520 (s, C=O), 1413 (m, CH def), 1402 (m, CH_3 sym def), 1341 (s, C-NO_2), 1292 (s, C-N stretch), 1248, 1107 (m, C-O), 854 (s, 2 adj H) cm^{-1}. EPR (9.81 GHz, toluene, 298K): $a(N_{2,4})$ = 6.45 G; $a(N_{1,5})$ = 5.35 G;

$a(H_{CH_3})$ = 5.48 G (6H); g = 2.0101. UV-vis (1,4-dioxane): λ_{max} (lg ε) = 293 nm (4.27), 408 nm (3.17), 424 nm (3.33), 487 nm (2.43). Anal. Calcd. for $C_{10}H_{10}N_5O_3$: C, 48.39; H, 4.06; N, 28.21. Found: C, 48.03; H, 3.82; N, 27.95. Mass Spectrometry (+ESI-MS) *m/z*: 271.07 $[M+Na]^+$.

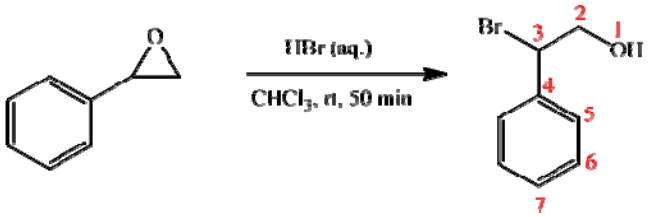
Sample preparation of verdazyl radicals 6-9 for EPR

To an oven dried Schlenk tube was added the verdazyl radical and toluene to make up the desired concentration. The solution was degassed using three freeze-pump-thaw cycles and kept under nitrogen. Using a gas tight syringe, 0.5 mL of solution was introduced to a degassed EPR tube which was then capped and sealed with parafilm. The EPR parameters used varied for each radical. This enabled the best spectrum to be obtained to determine the hyperfine couplings constants.

Table 1 Quantities of sample for the EPR of verdazyl radicals

Radical	R	Solution concentration	Radical		Toluene
		mM	mg	mmol	mL
6	H	1	0.3	0.0024	2
7	Ph	0.2	0.2	0.0010	5
8	PhOMe	0.05	0.6	0.0008	17
9	$PhNO_2$	0.05	0.9	0.0036	72

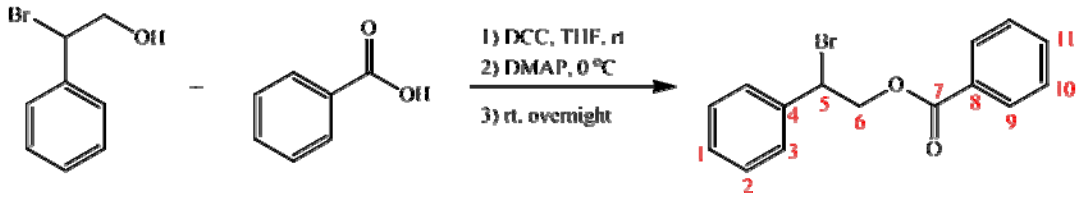
2-bromo-2-phenyl ethanol



To a stirring solution of styrene oxide (3.8 mL, 33.33 mmol) in chloroform (350 mL) at ambient temperature was added dropwise 48% aqueous hydrobromic acid (100 mL, 184 mmol). The resulting orange mixture was stirred for 50 minutes before being washed twice with water (100 mL), and twice with saturated sodium hydrogen carbonate solution (200 mL). The resulting organic solution was dried with magnesium sulphate and the solvent removed *in vacuo* to give 2-bromo-2-phenylethanol (6.1 g, 91%) as a pale orange oil. IR (neat): $\tilde{\nu}$ = 3349 (w, OH), 3030, 1492 (w, Ar), 1453 (m, CH def), 1060, 1021 (s, C-O), 694 (s, C-Br) cm^{-1}. ^1H NMR (300.13

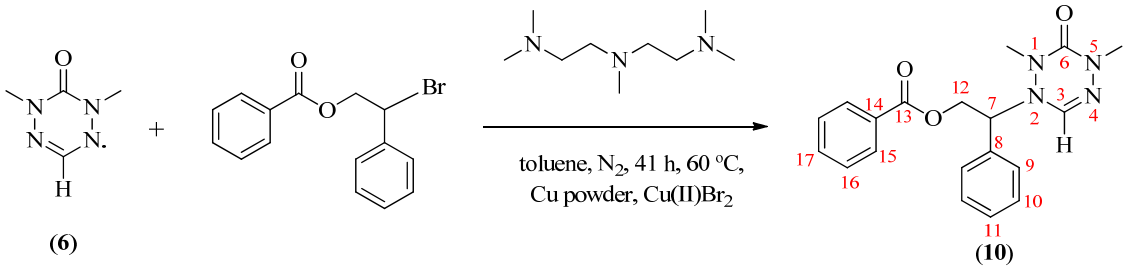
MHz, $CDCl_3$, 298 K) δ = 1.98 (br s, 1H, H1); 3.93-4.11 (m, 2H, H2); 5.06 (dd, *J* = 6.0, 2.0 Hz, 1H, H3); 7.31-7.44 (m, 5H, H5-7). ^{13}C NMR (75.47 MHz, $CDCl_3$, 298 K) δ = 56.40 (C3); 66.94 (C2); 127.32-128.40 (C5-7); 137.58 (C4). Anal. Calcd. for C_8H_9BrO: C, 47.79; H, 4.51. Found: C, 47.97; H, 4.56. Mass Spectrometry (+ESI-MS) *m/z*: 224.97 $[M+Na]^+$; 183.98 $[M-OH]^+$.

2-bromo-2-phenylethyl benzoate



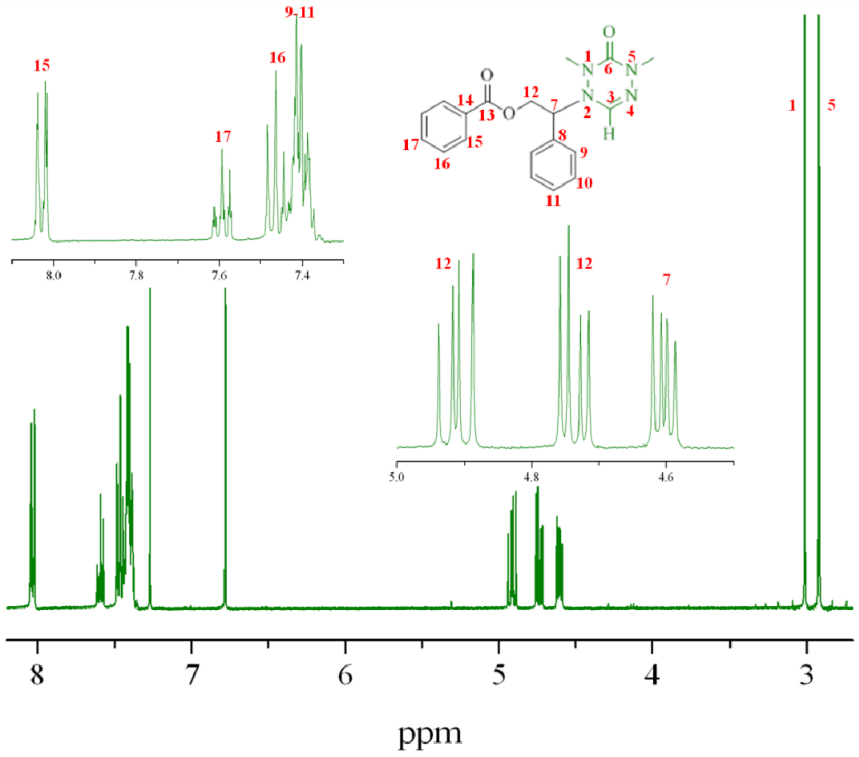
2-Bromo-2-phenylethylbenzoate was synthesised using a slightly modified procedure to that described in the literature. To a solution of 2-bromo-2-phenylethanol (5.01 g, 24.92 mmol) in tetrahydrofuran (100 mL) stirring at ambient temperature was added benzoic acid (3.35 g, 27.41 mmol). Once dissolved, the solution was cooled to 0 ˚C, and *N,N*'dicyclohexylcarbodiimide (5.99 g, 24.93 mmol) added followed by 4-(dimethylamino)pyridine (0.27 g, 2.27 mmol) once dissolved. The solution was left stirring overnight at ambient temperature. The solvent was removed *in vacuo* to give an off white solid. The solid was dissolved in diethyl ether and filtered before washing twice with water. The resulting solution was dried with magnesium sulphate and the solvent removed *in vacuo* to give a yellow oil and white solid. The oil was dissolved in 3:1 petroleum ether 40-60/dichloromethane and the white solid removed by suction filtration before purification of the filtrate by silica gel column chromatography using 3:1 petroleum ether 40-60/dichloromethane. The solvent was removed *in vacuo* to give 2-bromo-2-phenylethylbenzoate (3.82 g, 50.4%) as a pale blue oil which solidified overnight during storage in the fridge. Melting point: 36–38 ˚C. IR (neat): $\tilde{\nu}$ = 3031 (w, Ar), 2955, 2876 (w, CH stretch), 1600 (w, Ar), 1710 (br s, (C=O), 1109 (s, C-O stretch), 761, 707 (5 adj H), 692 (s, C-Br) cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$, 298 K) δ = 4.74 (dd, *J* = 6.0, 12 Hz, 1H, H6), 4.84 (dd, *J* = 7.0, 12 Hz, 1H, H6); 5.27 (dd, *J* = 8.0, 10.0 Hz, 1H, H5); 7.12 – 7.32 (m, 7H, H1-3, 10), 7.38 (tt, *J* = 1.0, 7.0 Hz, H11), 7.81 (dd, *J* = 1.0, 10.0 Hz, H9). ^{13}C NMR (75.48 MHz, $CDCl_3$, 298 K) δ = 50.00 (C5); 67.89 (C6), 127.80 – 129.61 (C1-3, 9, 10), 129.50 (C8), 133.25 (C11), 138.05 (C4), 165.84 (C7). Anal. Calcd. for $C_{15}H_{13}BrO_2$: C, 59.04; H, 4.29. Found: C, 59.02; H, 4.33. Mass Spectrometry (+ESI-MS) *m/z*: 326.99 $[M + Na]^+$.

2-phenyl-2-(1,5-dimethyl-6-oxoverdazyl) ethyl benzoate unimer (10)

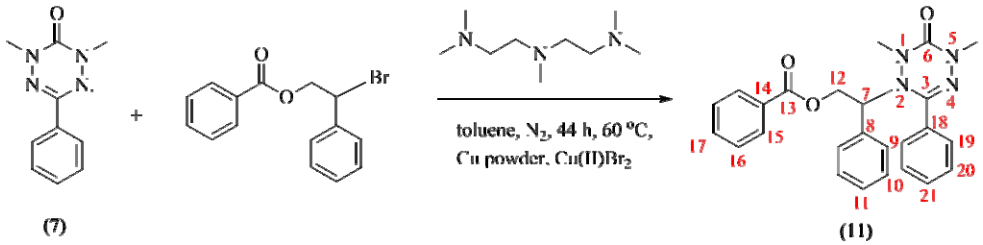


(6) (10)

Compound **10** was synthesised using a slightly modified procedure to that described in the literature.[53] A solution of **6** (0.52 g, 3.90 mmol), 2-bromo-2-phenylethylbenzoate (1.00 g, 3.50 mmol) and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, 0.15 mL, 0.7 mmol) in toluene (15 mL) was degassed by five freeze-pump-thaw cycles and cannulated into a nitrogen filled round bottom flask containing Cu powder (0.22 g, 3.50 mmol) and Cu(II)Br_2 (16 mg, 0.072 mmol). The reaction mixture was stirred at 60 ˚C under nitrogen for 41 hours. The reaction mixture was filtered and the solvent removed. The resulting pale yellow oil was dissolved in the minimum amount of dichloromethane and washed with water (3 x 15 mL). The resulting solution was dried using magnesium sulphate and the solvent removed to yield an off white solid. The compound was purified by silica gel column chromatography using 5:4:1 dichloromethane/petroleum ether 40-60/diethyl ether to give **10** (0.39 g, 31.6%) as white powder which was recrystallised from 9:1 petroleum ether 40-60/isopropanol to give a white crystalline solid. Melting point: 110–111 ˚C. IR (neat): $\widetilde{\nu}$ = 3034 (w, Ar), 2925, 2873, 2853 (w, CH stretch), 1717, 1657 (s, C=O), 1619 (m, Ar), 1452 (m, CH def), 1371 (s, CH_3 sym def), 1282 (br s, C-O stretch), 1178 (m, C-N stretch), 1116 (m, C-O stretch), 761, 707 (s, 5 adj H) cm^{-1}. ^{1}H NMR (400.03 MHz, $CDCl_3$, 298 K) δ = 2.91(s, 3H, H5); 3.00 (s, 3H, H1); 4.59 (dd, *J* = 5.0, 8.0 Hz, 1H, H7); 4.72 (dd, *J* = 5.0, 12.0 Hz, 1H, H14); 4.89 (dd, *J* = 9.0, 12.0 Hz, 1H, H14); 6.77 (s, 1H, H3); 7.34 – 7.42 (m, 5H, H9-11); 7.45 (br tt, *J* = 8.0 Hz, 2H, 16), 7.58 (tt, *J* = 1.0, 7.0 Hz, 1H, H17); 8.02 (dd, *J* = 1.0, 7.0 Hz, 2H, H15). ^{13}C NMR (100.60 MHz, $CDCl_3$, 298 K) δ = 36.33 (C5); 38.60 (C1); 62.95 (C12); 64.95 (C7); 128.14 – 128.96 (phenyl C); 129.59 (C8); 129.83 (C15); 133.47 (C17); 134.97 (C14); 137.84 (C3); 157.06 (C6); 166.26 (C13). Anal. Calcd. for $C_{19}H_{20}N_4O_3$: C, 64.76; H, 5.72; N, 15.90. Found: C, 64.78; H, 5.75; N, 15.47. Mass Spectrometry (+ESI-MS) *m/z*: 375.14 $[M+Na]^+$.

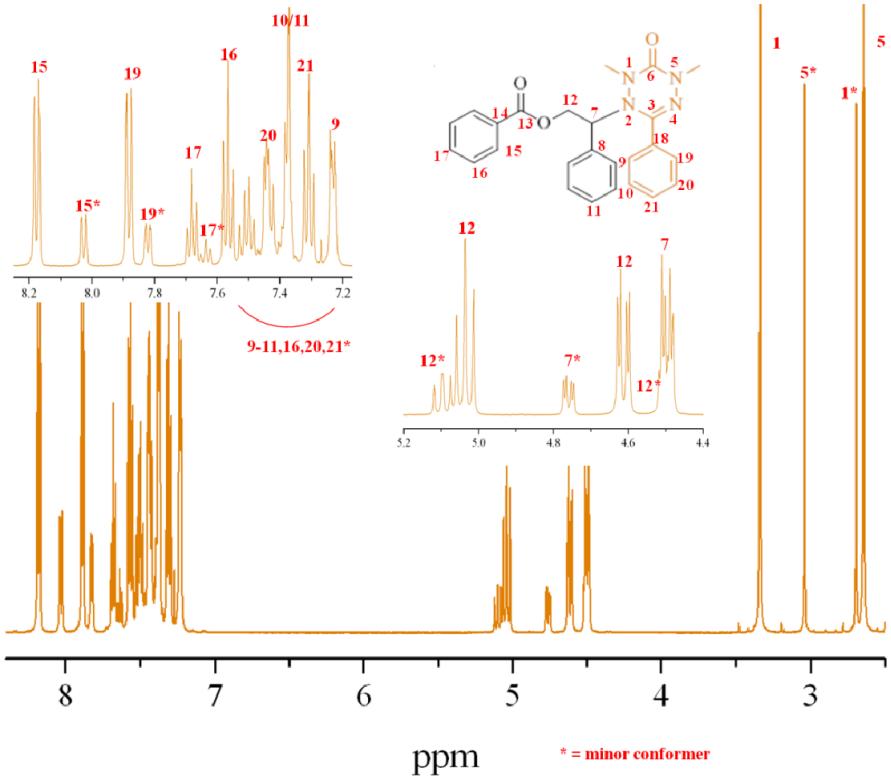


Synthesis of 2-phenyl-2-(1,5-dimethyl-3-Phenyl-6-oxoverdazyl)ethyl benzoate (11)

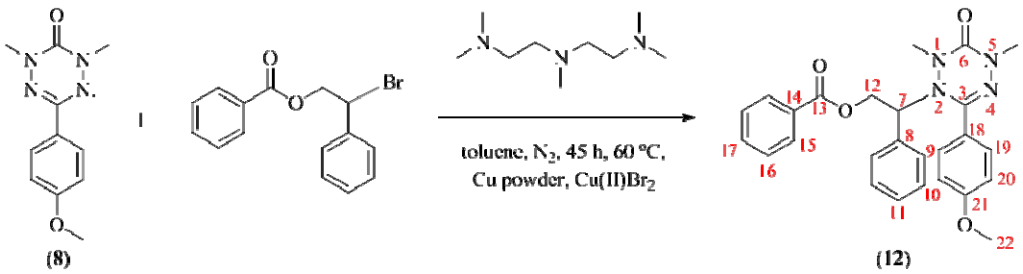


Compound **11** was synthesised using the same procedure as described for **10** to give **11** (0.94 g, 62.7%) as a white solid which was recrystallised from isopropanol to give a white crystalline solid. Melting point: 102-104 °C. IR (neat): $\widetilde{\nu}$ = 3063 (w, Ar), 2964, 2941, 2895, 2869 (w, CH stretch), 1721, 1617 (s, C=O), 1447 (m, CH def), 1360 (s, CH_3 sym def), 1276 (s, C-O stretch), 1254 (m, C-N stretch), 1118 (s, C-O), 769, 705 (s, 5 adj H) cm^{-1}. ^1H NMR (500.13 MHz, $CDCl_3$, 253 K) major conformer (78%) δ = 2.63 (s, 3H, H5); 3.33 (s, 3H, H1); 4.48 (dd, *J* = 4.0 Hz, 1H, H7); 4.60 (dd, *J* = 4.0, 12.0 Hz, 1H, H12); 5.02 (t, *J* = 12.0 Hz, 1H, H12); 7.21-7.26 (m, 2H, H9); 7.28 (t, *J* = 8Hz, 2H, H21); 7.34-7.40 (m, 3 H, H10, 11); 7.43-7.53 (m, 2H, H20); 7.50 (t, J = 8Hz, 2H, H16); 7.67 (br t, J = 7.0 Hz, 1H, H17); 7.88 (br d, *J* = 7.0 Hz, 2H, H19), 8.12 (br d, *J* = 7.0 Hz, 2H, H15); minor conformer (22%) δ = 2.68 (s, 3H, H1); 3.02 (s, 3H, H5); 4.49 (m, 1H, H12); 4.75 (br dd, *J* = 4.0, 10.0 Hz, 1H, H7); 5.08 (br dd, *J* = 10.0, 12.0 Hz, 1H, H12); 7.20 – 7.53 (m, 10 H, H9-11, 16, 20, 21); 7.63 (br t, J = 7.0 Hz, H17); 7.81 (br d, *J* = 7.0 Hz, 2H, H19); 8.02 (br d, *J* = 7.0 Hz, 2H, H15). ^{13}C NMR (125.77 MHz, $CDCl_3$,

253 K) δ = major conformer (78%) δ = 35.74 (C5); 40.59 (C1); 62.32 (C12); 64.43 (C7); 127.00 – 129.84 (C9-11, 16, 19-21); 129.53 (C8); 130.58 (C18); 130.93 (C15); 133.76 (C17); 134.35 (C14); 147.43 (C3); 157.38 (C6); 166.31 (C13); minor conformer (22%) δ = 36.89 (C5); 40.26 (C1); 63.41 (C12); 63.98 (C7); 127.00 – 129.84 (C9-11, 16, 19-21); 129.37 (C8); 130.85 (C18); 131.08 (C15); 133.61 (C17); 135.38 (C14); 149.47 (C3); 159.63 (C6); 166.20 (C13). Anal. Calcd. for $C_{25}H_{24}N_4O_3$: C, 70.08; H, 5.65; N, 13.08. Found: C, 69.86; H, 5.66; N, 12.99. Mass Spectrometry (+ESI-MS) *m/z*: 451.17 $[M+Na]^+$.

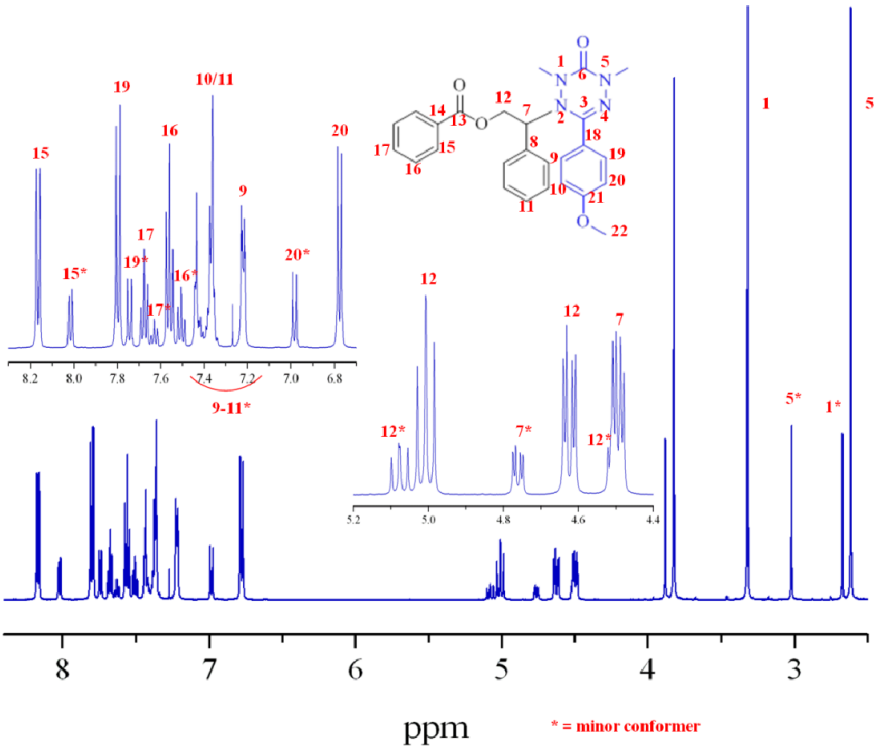


Synthesis of 2-phenyl-2-(1,5-dimethyl-3-methoxyphenyl-6-oxoverdazyl)ethyl benzoate (12)

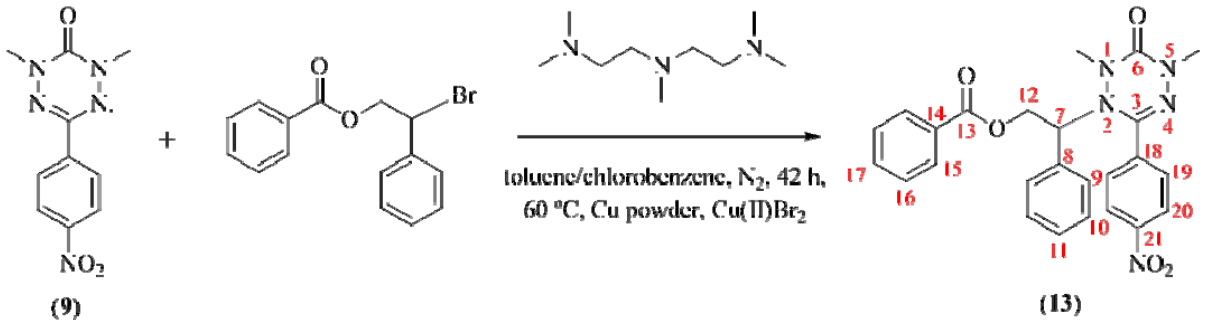


Compound **12** was synthesised using the same procedure as described for **10** to give **12** (0.44 g, 36.1%) as an off white solid which was recrystallised from isopropanol to give a white crystalline solid. Melting point: 101-102 °C. IR (neat): $\widetilde{\nu}$ = 3032 (w, Ar), 3005, 2935, 2911 (w, CH stretch), 2838 (w, C-OCH_3), 1719, 1670 (s, C=O),

1605, 1511 (m, Ar), 1452 (m, CH def), 1350 (m, CH_3 sym def), 1267 (s, C-O stretch), 1250 (s, C-N stretch), 1170 (m, C-O stretch), 837 (s, 2 adj H), 752, 709 (s, 5 adj H) cm^{-1}. ^1H NMR (500.13 MHz, $CDCl_3$, 253 K) major conformer (76%) δ = 2.63 (s, 3H, H5); 3.34 (s, 3H, H1); 3.84 (s, H22); 4.51 (dd, *J* = 4.0, 11.0 Hz, 1H, H7); 4.63 (dd, *J* = 4.0, 12.0 Hz, 1H, H12); 5.03 (t, *J* = 11.0 Hz, 1H, H12); 6.77 (d, *J* = 9.0 Hz, 2H, H20); 7.23 – 7.25 (m, 2 H, H9), 7.36 – 7.50 (m, 3H, H10-11); 7.58 (t, *J* = 8 Hz, 2H, H16); 7.70 (t, *J* = 8 Hz, 1H, H17); 7.81 (d, *J* = 9 Hz, 2H, H19); 8.18 (d, *J* = 7 Hz, 2H, H15); minor conformer (24%) δ = 2.69 (s, 3H, H1); 3.04 (s, 3H, H5); 3.90 (s, 3H, H22); 4.51 (m, 1H, H12); 4.77 (dd, *J* = 4.0, 10.0 Hz, 1H, H7); 5.10 (br dd, *J* = 10.0, 12.0 Hz, 1H, 12); 7.00 (d, *J* = 9.0 Hz, 2H, H20); 7.23 – 7.46 (m, 5 H, H9-11), 7.52 (t, *J* = 8 Hz, 2H, H16); 7.65 (t, *J* = 8 Hz, 1H, H17); 7.76 (d, *J* = 9 Hz, 2H, H19); 8.03 (d, *J* = 7 Hz, 2H, H15). ^{13}C NMR (125.77 MHz, $CDCl_3$, 253 K) δ = major conformer (76%) δ = 35.48 (C5); 40.45 (C1); 55.54 (C22); 62.27 (C12); 64.26 (C7); 114.10 (C20); 122.65 (18); 127.00 – 129.80 (C8-11, 15, 16, 19); 133.61 (C17); 134.20 (C14); 147.58 (C3); 157.41 (C6); 161.41 (C21); 166.17 (C23); minor conformer (24%) δ = 36.65 (C5); 40.13 (C1); 55.52 (C22); 63.31 (C12); 63.84 (C7); 114.25 (C20); 122.83 (C18); 127.00 – 129.80 (C8-11, 15, 16, 19); 133.46 (C17); 135.36 (C14); 149.56 (C3); 159.74 (C6); 161.55 (C21); 166.07 (C13). Anal. Calcd. for $C_{26}H_{26}N_4O_4$: C, 68.11; H, 5.72; N, 12.22. Found: C, 67.43; H, 5.55; N, 11.90. Mass Spectrometry (+ESI-MS) *m/z*: 459.20 $[M+H]^+$, 451.17 $[M+Na]^+$.

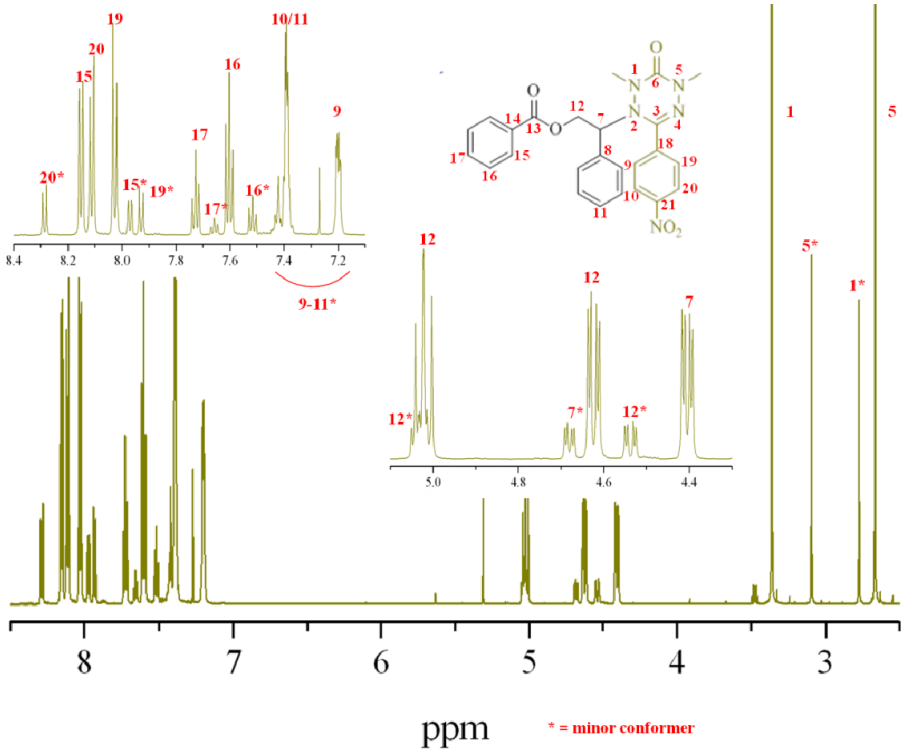


Synthesis of 2-phenyl-2-(1,5-dimethyl-3-nitrophenyl-6-oxoverdazyl)ethyl benzoate (18)

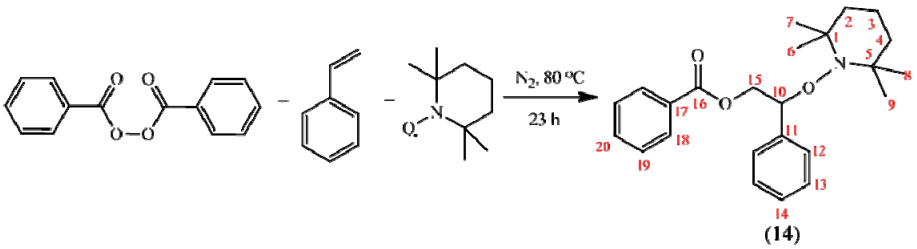


(9) (13)

Compound **13** was synthesised using the same procedure as described for **10** except toluene and chlorobenzene (2:1) were used as the reaction solvent to give **13** (0.39 g, 48.5%) as a yellow solid. Melting point: 158-159 ˚C. IR (neat): $\widetilde{\nu}$ = 3064 (w, Ar), 2939, 2877 (w, CH stretch), 1723, 1714 (s, NO_2), 1684 (s, C=O), 1454 (m, CH def), 1342 (s, CH_3 sym def), 1272 (s, C-N stretch), 1103 (m, C-O stretch), 853 (m, 5 adj H), 749, 703 (s,2 adj H) cm^{-1}. ^{1}H NMR (600.13 MHz, $CDCl_3$, 253 K) major conformer (81%) δ = 2.65 (s, 3H, H5); 3.35 (s, 3H, H1); 4.41 (dd, *J* = 4.0, 7.0 Hz, 1H, H7); 4.61 (dd, *J* = 4.0, 8.0 Hz, 1H, H12); 5.01 (t, *J* = 11.0 Hz, 1H, H12); 7.10 – 7.22 (m, 2H, H9); 7.35 - 7.40 (m, 3H, H10, 11), 7.58 (t, *J* = 8 Hz, 2H, H16); 7.71 (t, *J* = 7 Hz, 1H, H17); 8.01 (d, *J* = 9 Hz, 2H, H19); 8.11 (d, *J* = 9 Hz, 2H, H20); 8.14 (d, *J* = 7 Hz, 2H, H15); minor conformer (19%) δ = 2.76 (s, 3H, H1); 3.08 (s, 3H, H5); 4.52 (dd, *J* = 4.0 , 8.0 Hz, 1H, H12); 4.67 (dd, *J* = 4.0, 6.0 Hz, 1H, H7); 4.99 – 5.04 (m, 1H, 12); 7.10 – 7.45 (m, 5H, H9-11); 7.51 (t, *J* = 8 Hz, 2H, H16); 7.64 (t, *J* = 8 Hz, 1H, H17); 7.91 (d, *J* = 8 Hz, 2H, H19); 7.95 (d, *J* = 8 Hz, 2H, H15); 8.27 (d, *J* = 8 Hz, 2H, H20). ^{13}C NMR (150.92 MHz, $CDCl_3$, 253 K) δ = major conformer (81%) δ = 35.93 (C5); 37.05 (C1); 62.17 (C12); 62.27 (C7); 124.27 (C20); 127.70 – 130.00 (C9-11, 15, 16, 19); 133.71 (C18); 134.07 (C17); 137.14 (C14); 148.53 (C3); 156.48 (C6); 166.22 (C13); minor conformer (19%) δ = 37.13 (C5); 39.78 (C1); 63.43 (C12); 64.75 (C7); 127.70 – 130.00 (C9-11, 15, 16, 19, 20); 133.81 (C17); 134.66 (C18); 146.25 (C21); 148.60 (C3); 158.37 (C6); 166.06 (C13). Anal. Calcd. for $C_{25}H_{23}N_5O_5$: C, 63.42; H, 4.90; N, 14.79. Found: C, 63.05 H, 4.70; N, 14.61. Mass Spectrometry (+ESI-MS) *m/z*: 496.16 $[M+Na]^+$.



2-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-oxy)ethyl benzoate (14)



(14)

To styrene (320 mL, 279 mmol) was added benzoyl peroxide (8.04 g, 33.19 mmol) and 2,2,6,6-tetramethyl-piperidin-1-yloxy (TEMPO) (11.36 g, 72.7 mmol) producing a deep red solution. The solution was degassed by bubbling with nitrogen for 1 hour. The reaction mixture was kept under nitrogen and stirred at 80 ˚C for 23 hours. The solution was cooled to ambient temperature before removing the styrene on a high vacuum line to give a dark orange oil. The product was purified by repeated silica gel column chromatography with 1:1 dichloromethane/petroleum ether 40-60 changing to 9:1 dichloromethane/petroleum ether 40-60, 30:1 petroleum ether 40-60/diethyl ether changing to 20:1 petroleum ether 40-60/diethyl ether to give **14** (2.47 g, 19.5%) as white crystalline solid. Melting point: 73–74 ˚C. IR (neat): $\widetilde{\nu}$ = 3002 (w, Ar), 2967, 2923 (m, CH stretch), 1602 (w, Ar), 1712 (s, C=O), 1450 (m, CH def), 1364, 1311 (m, N-O asym stretch), 1295 (m, C-N stretch), 1264 (s, C-O stretch), 1132 (m, C-O stretch), 764 (m, 5 adj H) cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$, 298 K) δ = 0.75,

1.06, 1.20, 1.36 (br s, 12H, H6, 7, 8, 9); 1.50 (br s, 6H, H2, 3, 4); 4.52 (dd, *J* = 6.0, 11.0 Hz, 1H, H15); 4.82 (dd, *J* = 5.0, 11.0 Hz, 1H, H15); 5.05 (dd, *J* = 5.0, 6.0 Hz, 1H, H10); 7.23 – 7.28 (m, 7H, H12-14, 19); 7.38 (tt, *J* = 7.0, 1.0 Hz, 1H, H20); 7.92 (dd, *J* = 8.0, 1.0 Hz, 2H, H18). ^{13}C NMR (75.47 MHz, $CDCl_3$, 298 K) δ = 17.15 (C3); 20.40 (C7, 8); 34.00 (C6, 9); 40.41 (C2, 4); 60.11 (C1, 5); 66.78 (C15); 83.94 (C10); 127.61 – 129.57 (C12-15, 18, 19); 130.20 (C18); 132.83 (C20); 140.691 (C11); 166.50 (C16). Anal. Calcd. for $C_{24}H_{31}NO_3$: C, 75.56; H, 8.19; N, 3.67. Found: C, 75.59; H, 8.19; N, 3.64. Mass Spectrometry (+ESI-MS) *m/z*: 382.26 $[M+H]^+$, 404.22$[M+Na]^+$.

Polymerisation procedures

Polymerisation of styrene using initiators 10-14

To an oven dried Schlenk tube was added styrene (2 mL, 17.46 mmol), initiator (0.036 mmol) and mesitylene (1.2 mL). The solution was degassed using three freeze-pump-thaw cycles and stirred at 125 ˚C under nitrogen for 50 hours. The polymerisation was terminated by bubbling with air for 10 minutes followed by the addition of dichloromethane (2 mL). The crude polymer was precipitated twice into methanol using dichloromethane to dissolve the polymer.

Table 1 Final polymerisation data for the verdazyl mediated polymerisation of styrene

Initiator	R	Conversion (%)	M_n (g/mol)*	PDi*
10	H	77.0	20,300	1.29
11	Ph	60.6	7,500	1.63
12	PhOMe	63.6	9,609	1.71
13	$PhNO_2$	56.1	5,200	1.50
TEMPO	-	76.9	17,100	1.28

*precipitated polymer

Polymerisation of verdazyl stabilised *n*-butyl acrylate using initiators 10-14

To an oven dried Schlenk tube was added verdazyl stabilised (1 mg/ 40 mL) *n*-butyl acrylate (15 mL, 0.11 mol) and verdazyl initiator (0.23 mmol). The solution was degassed using three freeze-pump-thaw cycles and stirred at 130 ˚C under nitrogen for 70 hours except for with **13** which was stopped after 2 hours. The polymerisation

was terminated by bubbling with air for 10 minutes followed by the addition of dichloromethane (15 mL). The crude polymer was precipitated once into 80:20 methanol/ water using dichloromethane to dissolve the polymer.

Table 3 Final polymerisation data for the verdazyl mediated polymerisation of *n*-butyl acrylate

Initiator	R	Conversion (%)	M_n (g/mol)*	PDi*
10	H	23.3	11,200	1.17
11	Ph	42.4	21,200	1.23
12	PhOMe	50.4	41,400	4.41
13	$PhNO_2$	21.4	11,100	1.17
TEMPO	-	7.4	2,900	1.40

*precipitated polymer

Polymerisation of styrene at a lower temperature

Using the same procedure described for the polymerisation of styrene, verdazyl initiators **11** (R = Ph) and **12** (R = PhOMe, 0.036 mmol) were used to polymerise styrene at 100 ˚C under nitrogen for 44 hours. The polymerisation was terminated by bubbling with air for 10 minutes followed by the addition of dichloromethane (2 mL). The crude polymer was precipitated once into methanol using dichloromethane to dissolve the polymer.

Table 3 Final polymerisation data for the verdazyl mediated polymerisation of styrene by 11 (R = Ph) and 12 (R = PhOMe) at 100 ˚C

Initiator	R	Time (h)	Conversion (%)	M_n (g/mol)*	PDi*
11	Ph	44	28.3	4,900	1.45
12	PhOMe	47	41.8	13,200	1.30

*precipitated polymer

Block copolymer formation

Polystyrene or poly(n-butyl acrylate) (1 equivalent) was dissolved in n-butyl acrylate or styrene (4 equivalents) respectively. The solutions were degassed using three freeze-pump-thaw cycles and stirred at 125 ˚C under nitrogen for 18 hours. The polymerisation was terminated by bubbling with air for 10 minutes and precipitated into methanol using dichloromethane to dissolve the polymer.

Electronic Supplementary Material (ESI) for Polymer Chemistry

Crystallographic data

2-phenyl-2-(1,5-dimethyl-3-phenyl-6-oxoverdazyl)ethyl benzoate (11)

Table 4 Crystal data for 2-phenyl-2-(1,5-dimethyl-3-phenyl-6-oxoverdazyl)ethyl benzoate

Compound reference	2-phenyl-2-(1,5-dimethyl-3-phenyl-6-oxoverdazyl)ethyl benzoate
Chemical formula	$C_{25}H_{24}N_4O_3$
Formula Mass	428.48
Crystal system	Monoclinic
a/Å	8.56617(18)
b/Å	34.5561(6)
c/Å	7.35229(14)
α/°	90.00
β/°	95.2700(18)
γ/°	90.00
Unit cell volume/Å^3	2167.18(7)
Temperature/K	100(2)
Space group	*P2(1)/c*
No. of formula units per unit cell, *Z*	4
No. of reflections measured	10435
No. of independent reflections	4052
R_{int}	0.0183
Final R_1 values ($I > 2\sigma(I)$)	0.0380
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0982
Final R_1 values (all data)	0.0401
Final $wR(F^2)$ values (all data)	0.0998