A Practical Synthesis of α-Substituted *tert*-Butyl Acrylates from Meldrum's Acid and Aldehydes

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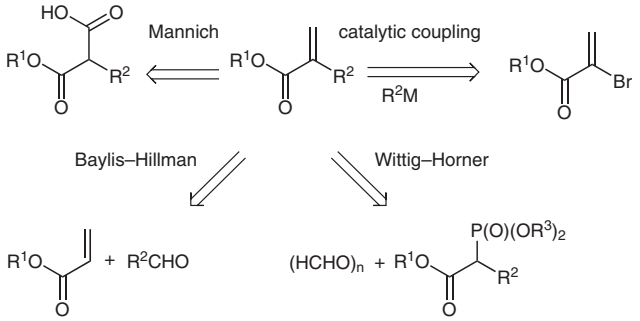
Abstract: An expeditious synthesis of α-substituted *tert*-butyl acrylates from commercially available aldehydes and Meldrum's acid has been established. The method benefits from a telescoped condensation–reduction sequence to afford 5-monosubstituted Meldrum's acid derivatives followed by a Mannich-type reaction triggered by a rapid cycloreversion of the dioxinone ring on heating with *tert*-butyl alcohol.

Key words: alkenes, Mannich bases, acrylate derivatives, tandem reactions, aldehydes

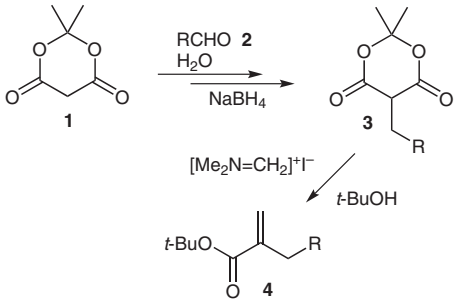
Functionalised α-substituted acrylic acid esters are of increasing importance in the design and synthesis of new polymer-based materials for a wide variety of applications in different areas of chemistry, biotechnology, nanotechnology, and material science.[1] Furthermore, they are valuable intermediates for the 1,4-addition reaction of nucleophiles in both biological systems and for organic synthesis.[2] Consequently, a number of methods have been developed to allow access to structurally diverse α-substituted acrylates, and some of the reported approaches are illustrated in Scheme 1.



Scheme 1

The classical method for acrylate synthesis involves a Mannich reaction of α-monosubstituted malonic half esters (Scheme 1).[3] This route can be problematic, with difficulties in the selective formation of the monosubstituted malonate diester. Furthermore, it is not possible to obtain the α-substituted *tert*-butyl acrylate by this method, due to difficulties with the hydrolysis of the corresponding diester. The α-functionalisation of acrylates employing the Baylis–Hillman reaction (Scheme 1) or aza variant is well documented, but limited to α-hydroxy- or α-amino-substituted products.[4] The methylenation of functionalised phosphonates via a Wittig–Horner reaction using paraformaldehyde (Scheme 1) allows convenient access to α-methylene adipate derivatives, although, surprisingly, this route is rarely utilised.[5] Palladium and nickel complexes have been studied in the catalytic synthesis of α-aryl-α,β-unsaturated carbonyl compounds by the cross-coupling of α-organometallics with aryl halides or the complementary combination of an α-halocarbonyl compound and an sp^2-carbon-derived organometallic compound (Scheme 1).[6] However, in the context of preparing α-substituted acrylates, there are few reported examples, and mixtures of products are often isolated.[7]

Herein, we report a practical and scalable synthesis of a wide range of α-substituted *tert*-butyl acrylates **4** from commercially available aldehydes **2** and Meldrum's acid (**1**) (Scheme 2); this approach is complementary to established routes from carboxylic acids.[8] The method entails a telescoped condensation–reduction sequence to afford 5-monosubstituted Meldrum's acid derivatives **3**, followed by a Mannich-type reaction triggered by a rapid cycloreversion of the dioxinone ring on heating (Scheme 2).[9]



Scheme 2

A number of methods for the synthesis of α,β-unsaturated Meldrum's acid derivatives has been reported, including the use of strong base and *N*,*N*-dimethylformamide as a solvent,[10] neat aldehyde,[11] zinc dust,[12] and, more recently, pyridinium acetate.[13] A remarkably expedient method is the uncatalysed Knoevenagel condensation of aldehydes and **1** in water, reported by Bigi et al.[14] This protocol of-

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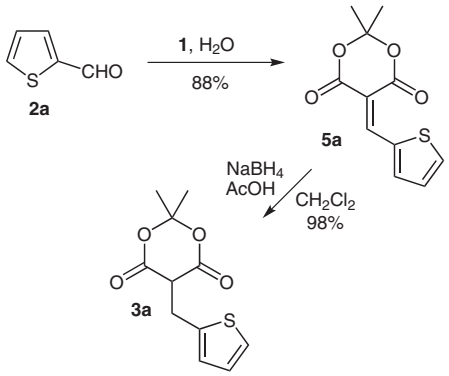
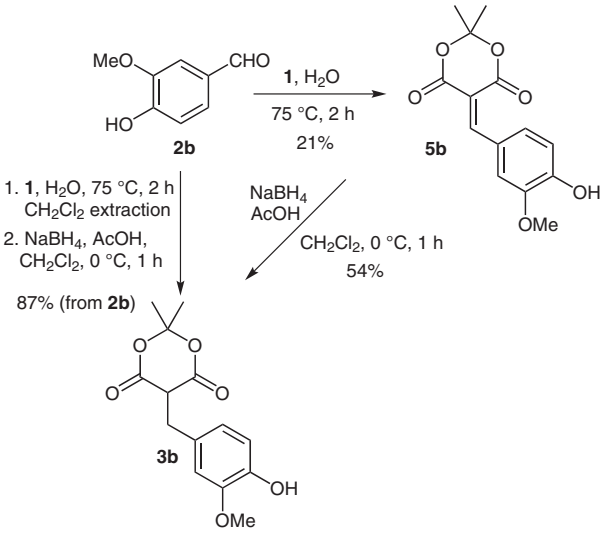
fers significant advantages over existing methods for the preparation of α-substituted *tert*-butyl acrylates, as it circumvents the use of expensive coupling reagents and the generation of side products. Thus, the Knoevenagel condensation of thiophene-2-carbaldehyde (**2a**) and **1** in water afforded a bright-yellow, solid condensation product after two hours at 75 °C (Scheme 3). The compound was isolated by simple filtration, and washed with water and hexane to give the desired α,β-unsaturated Meldrum's acid derivative **5a**. The crude product could be used in the next step without further purification. Consequently, **5a** was cooled to 0 °C and dissolved in dichloromethane, and acetic acid was introduced. After the reaction mixture had stirred for 15 minutes, sodium borohydride was added in small portions over one hour. A rapid colour change occurred in 15 minutes, corresponding to the loss in conjugation and completion of the reaction. After a simple aqueous workup, the 5-monosubstituted Meldrum's acid derivative **3a** was obtained in high yield (Scheme 3).



Scheme 3

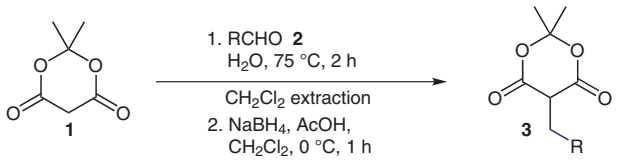
This two-step route proved to be effective for a range of aldehydes, notably those that are liquids at room temperature.[15] However, problems arose when solid aldehydes with poor solubility in water were used or when the intermediate α,β-unsaturated Meldrum's acid derivatives were not easily isolated as crystalline solids. This was rectified by telescoping the two operations by a simple extraction with dichloromethane. The improved procedure is illustrated for vanillin (**2b**) (Scheme 4). In this case, separation of the Knoevenagel condensation product **5b** from the starting aldehyde proved difficult and resulted in low yields of isolated product.

The telescoped procedure involved taking the dichloromethane extracts from the Knoevenagel condensation and drying them over magnesium sulfate before they were cooled to 0 °C for the conjugate reduction step (Scheme 4). This afforded product **3b** in 87% yield after a single recrystallisation from hot ethyl acetate. Using this telescoped method, 20 compounds were synthesised in good to excellent yields (Table 1). The products isolated were air and moisture stable, making them suitable for large-scale synthesis. The method was not suitable for certain heteroaromatic aldehydes such as furan and pyr-



Scheme 4

Table 1 Synthesis of 5-Substituted Derivatives of Meldrum's Acid



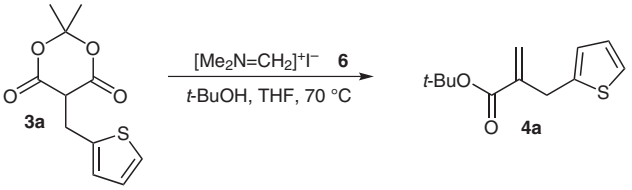
Product	R	Yield[a] (%)
3a	2-thienyl	88
3b	3-MeO-4-HOC_6H_3	87
3c	3-thienyl	88
3d	3-methyl-2-thienyl	91
3e	PMP	87
3f	2-$MeOC_6H_4$	94
3g	1,3-benzodioxol-4-yl	73
3h	1,3-benzodioxol-5-yl	76
3i	2,3,4-$(MeO)_3C_6H_2$	64
3j	2-F-4-$MeOC_6H_3$	82
3k	3-Cl-4-$MeOC_6H_3$	63
3l	4-FC_6H_4	61
3m	2,6-$F_2C_6H_3$	98
3n	4-$MeSC_6H_4$	89
3o	Tol	95
3p	2,6-$Me_2C_6H_3$	92
3q	1-naphthyl	97
3r	*i*-Pr	92

[a] Isolated yield.

role, due to sensitivity to acid and light, respectively. Other problematic aldehydes are straight-chain aliphatics, which tended to react with a second equivalent of Meldrum's acid to afford an insoluble solid.

With the 5-monosubstituted Meldrum's acid derivatives **3a–r** in hand, the Mannich-type reaction with *N*,*N*-dimethylmethyleneiminium iodide (**6**) to install the *exo*-methylene could be explored.[16] Initially, the reaction of **3a** with *tert*-butyl alcohol and **6** was optimised as shown in Table 2. The reaction proceeds by rapid cycloreversion of the dioxinone ring to establish the *tert*-butyl ester and trigger the Mannich-type reaction. A significant advantage of this method is that the reaction byproducts (acetone, carbon dioxide, and dimethylamine) are volatile, resulting in clean conversion to product. Using neat *tert*-butyl alcohol as a solvent led to incomplete dissolution of **6** and lower yields (Table 2, entries 1 and 2). The quantity of **6** was also critical, with 1.1 equivalents giving poor yields, while the use of an excess, 2.6–3.5 equivalents, afforded excellent yields of product **4a** (Table 2, entries 3–6).

Table 2 Optimisation of the Reaction of **3a** with *tert*-Butyl Alcohol and **6**

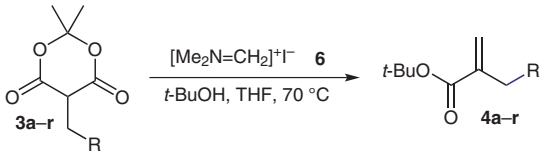


Entry	**6** (equiv)	Ratio *t*-BuOH/THF	Temp (°C)	Yield[a] (%) of **4a**
1	1.1	1:0	65	28
2	2.0	1:0	65	73
3	2.6	1:0	70	81
4	2.6	1:1	70	89
5	2.6	1:1	reflux	68
6	3.5	1:1	70	91

[a] Isolated yield.

The scope of the method was investigated with 5-monosubstituted Meldrum's acid derivatives **3a–r** (Table 3). When substrate **3** and reagent **6** were dissolved in a mixture of anhydrous tetrahydrofuran and *tert*-butyl alcohol for optimum solubility, and the mixture was heated to 70 °C overnight, the desired product was obtained in >95% purity after aqueous workup. Simple purification by short flash column chromatography afforded analytically pure materials. Pleasingly, α-substituted *tert*-butyl acrylates **4a–r** were all formed in good to excellent yields (Table 3), and all products were stable to air and moisture with no isomerisation to the *tert*-butyl 2-methyl-3-phenylacrylate species.

Table 3 Synthesis of α-Substituted *tert*-Butyl Acrylates **4** from 5-Substituted Derivatives **3** of Meldrum's Acid



Product	R	Yield[a] (%)
4a	2-thienyl	92
4b	3-MeO-4-HOC_6H_3	57
4c	3-thienyl	82
4d	3-methyl-2-thienyl	78
4e	PMP	95
4f	2-MeOC_6H_4	94
4g	1,3-benzodioxol-4-yl	90
4h	1,3-benzodioxol-5-yl	87
4i	2,3,4-$(MeO)_3C_6H_2$	88
4j	2-F-4-MeOC_6H_3	83
4k	3-Cl-4-MeOC_6H_3	91
4l	4-FC_6H_4	84
4m	2,6-$F_2C_6H_3$	84
4n	4-MeSC_6H_4	98
4o	Tol	82
4p	2,6-$Me_2C_6H_3$	85
4q	1-naphthyl	92
4r	*i*-Pr	98

[a] Isolated yield.

In conclusion, a practical synthesis of α-substituted *tert*-butyl acrylates from commercially available aldehydes and Meldrum's acid is presented. The reaction conditions are mild and tolerate many functional groups commonly used in organic synthesis. The method complements existing routes to α-substituted acrylates and is anticipated to be of particular utility for applications that require the *tert*-butyl ester.

Commercially available solvents and reagents were obtained from Sigma-Aldrich Company Ltd, Lancaster Synthesis Ltd and Fisher Scientific Ltd and were used without further purification, with the exception of Meldrum's acid which was recrystallised from EtOH. CH_2Cl_2 and THF were dried and degassed under an argon atmosphere over activated alumina columns using an Innovative Technology Solvent Purification System (SPS). Melting points were determined on a Buchi 235 melting point apparatus. IR spectra were recorded on a Nicolet Nexus FTIR spectrometer, over the range 4000–200 cm^{-1} and averaged over 32 scans, using KBr discs or NaCl plates. ^1H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) spectroscopic measurements were carried out on Bruker AV300 or

AVANCE 400 spectrometers. MS determinations were obtained on Fisons VG autospec Finnigan MAT 8340 (EI/CI MS) and Bruker micrOTOF-Q (CI-HRMS) instruments. Elemental analyses were carried out at the University of Bath using an Exeter Analytical CE 440 elemental analyser.

5-Monosubstituted Meldrum's Acid Derivatives 3a–r; General Procedure

2,2-Dimethyl-1,3-dioxane-4,6-dione (**1**; 1.5 g, 10.5 mmol) was added portionwise to a stirred suspension of aldehyde **2** (10.0 mmol) in H_2O (25 mL) at 23 °C. A reflux condenser was attached and the mixture was stirred at 75 °C for 2 h. After cooling of the mixture to r.t., the precipitated solid was dissolved in CH_2Cl_2 (100 mL), and the soln was passed through a hydrophobic frit into a second round-bottomed flask. The crude arylidene **5** was subsequently cooled to 0 °C (NaCl/ice), and AcOH (5 mL) was added with stirring of the mixture for 5 min under N_2. $NaBH_4$ (4 equiv) was added portionwise over 1 h or until the soln turned colourless. The reaction mixture was quenched with H_2O (50 mL) and extracted with CH_2Cl_2 (50 mL). The combined organic extracts were washed with brine (2×75 mL) and H_2O (2×75 mL) and dried ($MgSO_4$), yielding the title compound, which could be used without further purification. Recrystallisation from hot EtOAc–hexanes afforded analytically pure compounds.

2,2-Dimethyl-5-(2-thienylmethyl)-1,3-dioxane-4,6-dione (3a)

Cream solid; yield: 98%; mp 128 °C (EtOAc).

IR (KBr): 3100, 3014, 2936 (C–H), 1778, 1744 (C=O), 1298 (C–S) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.03 (dd, *J* = 5.0, 1.3 Hz, 1 H, C*H* Ar), 7.10–7.02 (m, 1 H, C*H* Ar), 6.94–6.90 (m, 1 H, C*H* Ar), 3.76 (t, *J* = 4.6 Hz, 1 H, C*H*), 3.72 (d, *J* = 4.6 Hz, 2 H, CH_2), 1.76 (s, 3 H, CCH_3), 1.59 (s, 3 H, CCH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 164.9, 138.1, 127.9, 126.8, 125.0, 105.3, 48.2, 28.3, 27.1, 26.4.

MS (EI/CI): *m*/*z* (%) = 258 (45) [M + NH_4^+], 240 (5) [M + H^+], 173 (50) [$C_8H_{10}OS + NH_4^+$].

HRMS (CI): *m*/*z* [M + NH_4^+] calcd for $C_{11}H_{16}O_4NS$: 258.0795; found: 258.0791.

Anal. Calcd for $C_{11}H_{12}O_4S$: C, 55.0; H, 5.03. Found: C, 54.2; H, 4.96.

5-(4-Hydroxy-3-methoxybenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3b)

Cream solid; yield: 66%; mp 133 °C (EtOAc).

IR (KBr): 3400 (O–H), 2831 (C–O–CH_3), 1778, 1754 (C=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.85 (br s, 1 H, C*H* Ar), 6.81–6.79 (m, 2 H, C*H* Ar), 5.56 (s, 1 H, O*H*), 3.82 (s, 3 H, OCH_3), 3.72 (t, *J* = 4.9 Hz, 1 H, C*H*), 3.42 (d, *J* = 4.9 Hz, 2 H, CH_2), 1.72 (s, 3 H, CCH_3), 1.47 (s, 3 H, CCH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 165.5, 146.2, 144.7, 128.8, 122.5, 114.3, 112.6, 105.2, 55.9, 48.3, 31.9, 28.4, 27.3.

ESI-HRMS: *m*/*z* [M + Na^+] calcd for $C_{14}H_{16}Na_1O_6$: 303.0845; found: 303.0822.

Anal. Calcd for $C_{14}H_{16}O_6$: C, 60.0; H, 5.75. Found: C, 60.8; H, 5.81.

2,2-Dimethyl-5-(3-thienylmethyl)-1,3-dioxane-4,6-dione (3c)

Cream solid; yield: 91%; mp 81–83 °C (EtOAc).

IR (KBr): 3102, 3014, 2936 (C–H), 1774, 1744 (C=O), 1298 (C–S) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.22 (dd, *J* = 4.9, 3.0 Hz, 1 H, C*H* Ar), 7.18–7.72 (m, 1 H, C*H* Ar), 7.02 (dd, *J* = 4.90, 1.13 Hz, 1 H, C*H* Ar), 3.74 (t, *J* = 4.6 Hz, 1 H, C*H*), 3.50 (d, *J* = 4.6 Hz, 2 H, CH_2), 1.73 (s, 3 H, CCH_3), 1.51 (s, 3 H, CCH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 165.2, 136.7, 129.2, 125.4, 123.9, 105.1, 47.5, 28.2, 27.1, 26.5.

MS (EI/CI): *m*/*z* (%) = 258 (55) [M + NH_4^+], 240 (5) [MH^+], 173 (45) [$C_8H_{10}OS + NH_4^+$].

HRMS (CI): *m*/*z* [M + NH_4^+] calcd for $C_{11}H_{16}O_4NS$: 258.0795; found: 258.0789.

Anal. Calcd for $C_{11}H_{12}O_4S$: C, 55.0; H, 5.03. Found: C, 54.4; H, 4.98.

2,2-Dimethyl-5-[(3-methyl-2-thienyl)methyl]-1,3-dioxane-4,6-dione (3d)

Cream solid; yield: 83%; mp 78–80 °C (EtOAc).

IR (KBr): 3108, 3007, 2987 (C–H), 1785, 1741 (C=O), 1298 (C–S) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.98 (d, *J* = 4.9 Hz, 1 H, Ar), 6.64 (d, *J* = 4.9 Hz, 1 H, Ar), 3.78 (t, *J* = 4.6 Hz, 1 H, C*H*), 3.53 (d, *J* = 4.6 Hz, 2 H, CH_2), 2.18 (s, 3 H, CH_3), 1.69 (s, 3 H, CCH_3), 1.54 (s, 3 H, CCH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 165.5, 136.2, 132.8, 130.6, 123.5, 105.7, 48.6, 48.5, 28.8, 27.5, 25.0, 16.0.

HRMS (CI): *m*/*z* [M + NH_4^+] calcd for $C_{12}H_{18}O_4NS$: 272.0957; found: 272.0924

Anal. Calcd for $C_{12}H_{14}O_4S$: C, 56.7; H, 5.55. Found: C, 56.2; H, 5.49.

5-(4-Methoxybenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3e)[17]

White solid; yield: 98%; mp 82–85 °C (EtOAc) (Lit.[17] 85–86 °C).

IR (KBr): 3006, 2961, 2915 (C–H), 1787, 1746 (C=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.24 (d, *J* = 8.7 Hz, 2 H, C*H* Ar), 6.81 (d, *J* = 8.7 Hz, 2 H, C*H* Ar), 3.77 (s, 3 H, OCH_3), 3.72 (t, *J* = 4.9 Hz, 1 H, C*H*), 3.44 (d, *J* = 4.9 Hz, 2 H, CH_2), 1.72 (s, 3 H, CCH_3), 1.48 (s, 3 H, CCH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 165.3, 158.6, 130.8, 129.0, 113.8, 105.1, 55.1, 48.1, 31.3, 28.3, 27.1.

MS (EI/CI): *m*/*z* (%) = 282 (45) [M + NH_4^+], 265 (5) [M + H^+], 198 (50) ($C_{10}H_{12}O_3 + NH_4$).

HRMS (CI): *m*/*z* [M + NH_4^+] calcd for $C_{14}H_{20}NO_5$: 282.3118; found: 282.3114.

Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.6; H, 6.10. Found: C, 63.1; H, 6.06.

5-(2-Methoxybenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3f)

Cream solid; yield: 92%; mp 97–100 °C (EtOAc).

IR (KBr): 3000, 2940, 2886 (C–H), 1772, 1751 (C=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.36 (dd, *J* = 7.5, 1.9 Hz, 1 H, C*H* Ar), 7.25 (td, *J* = 7.9, 1.9 Hz, 1 H, C*H* Ar), 6.93 (td, *J* = 7.5, 1.1 Hz, 1 H, C*H* Ar), 6.85 (d, *J* = 7.9 Hz, 1 H, C*H* Ar), 4.03 (t, *J* = 6.0 Hz, 1 H, C*H*), 3.83 (s, 3 H, OCH_3), 3.40 (d, *J* = 6.0 Hz, 2 H, CH_2), 1.77 (s, 3 H, CCH_3), 1.73 (s, 3 H, CCH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.4, 164.9, 156.7, 131.1, 127.8, 125.3, 120.0, 110.0, 104.4, 59.8, 54.7, 45.5, 28.0, 27.3, 25.8, 20.4, 13.7.

MS (EI/CI): *m*/*z* (%) = 282 (40) [M + NH_4^+], 265 (10) [M + H^+], 198 (50) ($C_{10}H_{12}O_3 + NH_4$).

HRMS (CI): *m*/*z* [M + NH_4^+] calcd for $C_{14}H_{20}NO_5$: 282.3118; found: 282.3112.

Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.6; H, 6.10. Found: C, 62.8; H, 6.01.

5-(1,3-Benzodioxol-4-ylmethyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3g)
Cream solid; yield: 73%; mp 127–128 °C (EtOAc).

IR (KBr): 1755, 1725 (C=O), 1276 (O–C–O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.81 (d, *J* = 2.3 Hz, 1 H, Ar), 6.77 (d, *J* = 6.8 Hz, 1 H, Ar), 6.72 (dd, *J* = 6.8 Hz, 1 H, 2.3 Hz, Ar), 5.93 (s, 2 H, OCH_2O), 3.99 (t, *J* = 5.7 Hz, 1 H, C*H*), 3.42 (d, *J* = 5.7 Hz, 2 H, CH_2), 1.80 (s, 3 H, CCH_3), 1.72 (s, 3 H, CCH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 147.5, 145.6, 123.6, 122.2, 119.4, 107.8, 105.4, 101.0, 46.4, 29.0, 27.0, 26.7.

ESI-HRMS: *m*/*z* [M + Na^+] calcd for $C_{14}H_{14}O_6Na_1$: 301.0688; found: 301.0671.

Anal. Calcd for $C_{14}H_{12}O_6$: C, 60.9; H, 4.40. Found: C, 59.9; H, 4.30.

5-(1,3-Benzodioxol-5-ylmethyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3h)
Cream solid; yield: 76%; mp 114–116 °C (EtOAc).

IR (KBr): 1772, 1751 (C=O), 1256 (O–C–O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.31 (s, 1 H, C*H* Ar), 8.06 (d, *J* = 1.9 Hz, 1 H, C*H* Ar), 7.54 (dd, *J* = 8.3, 1.9 Hz, 1 H, C*H* Ar), 6.09 (s, 2 H, OCH_2O), 4.12 (t, *J* = 6.1 Hz, 1 H, C*H*), 3.40 (d, *J* = 6.1 Hz, 2 H, CH_2), 1.76 (s, 3 H, CCH_3), 1.71 (s, 3 H, CCH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 164.3, 160.7, 153.6, 148.7, 134.6, 126.8, 111.7, 108.9, 104.7, 102.8, 54.1, 32.7.

HRMS (EI/CI): *m*/*z* [M + Na^+] calcd for $C_{14}H_{12}O_6Na_1$: 301.0688; found: 301.0692.

Anal. Calcd for $C_{14}H_{12}O_6$: C, 60.9; H, 4.40. Found: C, 60.2; H, 4.37.

2,2-Dimethyl-5-(2,3,4-trimethoxybenzyl)-1,3-dioxane-4,6-dione (3i)
Cream solid; yield: 79%; mp 91–94 °C (EtOAc).

IR (KBr): 2895, 2845, 2828 (C–O–CH_3), 1775, 1742 (C=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.02 (d, *J* = 8.7 Hz, 1 H, C*H* Ar), 6.61 (d, *J* = 8.7 Hz, 1 H, C*H* Ar), 4.03 (t, *J* = 5.7 Hz, 1 H, C*H*), 3.91 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 3.31 (d, *J* = 5.7 Hz, 2 H, CCH_2), 1.77 (s, 3 H, CH_3), 1.71 (s, 3 H, CCH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 165.2, 152.9, 151.6, 141.8, 125.4, 123.4, 107.0, 104.8, 60.7, 60.6, 55.8, 47.0, 28.5, 27.2, 26.4.

HRMS (EI): *m*/*z* [M + Na^+] calcd for $C_{16}H_{20}O_7Na$: 347.1107; found: 347.1100.

Anal. Calcd for $C_{16}H_{20}O_7$: C, 59.3; H, 6.22. Found: C, 58.8; H, 6.17.

5-(2-Fluoro-4-methoxybenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3j)
Cream solid; yield: 82%; mp 128–130 °C (EtOAc).

IR (KBr): 2840 (C–O–CH_3), 1786, 1744 (C=O), 1514 (C–F) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.23 (t, *J* = 8.67 Hz, 1 H, C*H* Ar), 6.59 (dd, *J* = 8.67, 2.64 Hz, 1 H, C*H* Ar), 6.53 (dd, *J* = 12.1, 2.64 Hz, 1 H, C*H* Ar), 3.72 (t, *J* = 6.03 Hz, 1 H, C*H*), 3.71 (s, 3 H, OCH_3), 3.32 (d, *J* = 6.03 Hz, 2 H, CH_2), 1.72 (s, 3 H, CCH_3), 1.64 (s, 3 H, CCH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 164.9, 163.1, 160.1, 159.9, 159.8, 132.3, 132.2, 116.2, 109.8, 109.8, 105.1, 101.7, 101.4, 55.5, 46.9, 46.9, 28.6, 26.6, 25.2, 25.2.

ESI-HRMS: *m*/*z* [M + Na^+] calcd for $C_{14}H_{15}O_5F_1Na_1$: 305.0801; found: 305.0810.

Anal. Calcd for $C_{16}H_{20}O_7$: C, 59.6; H, 5.36. Found: C, 59.1; H, 5.32.

5-(3-Chloro-4-methoxybenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3k)
Cream solid; yield: 63%; mp 142 °C (EtOAc).

IR (KBr): 2837 (C–O–CH_3), 1784, 1741 (C=O), 7584 (C–Cl) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.35 (s, 1 H, C*H* Ar), 7.21 (d, *J* = 8.3 Hz, 1 H, C*H* Ar), 6.84 (d, *J* = 8.3 Hz, 1 H, C*H* Ar), 3.87 (s, 3 H, OCH_3), 3.71 (t, *J* = 4.9 Hz, 1 H, C*H*), 3.40 (d, *J* = 4.9 Hz, 2 H, CH_2), 1.75 (s, 3 H, CCH_3), 1.58 (s, 3 H, CCH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 165.0, 154.1, 131.5, 130.1, 129.3, 122.2, 111.9, 105.2, 56.1, 48.1, 30.8, 28.4, 27.1.

ESI-HRMS: *m*/*z* [M + Na^+] calcd for $C_{14}H_{15}Cl_1O_5Na_1$: 321.0506; found: 321.0503.

Anal. Calcd for $C_{14}H_{15}Cl_1O_5$: C, 56.3; H, 5.06. Found: C, 56.0; H, 4.94.

5-(4-Fluorobenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3l)[18]
White solid; yield: 97%; mp 107–110 °C (EtOAc).

IR (KBr): 3014, 2954, 2893 (C–H), 1786, 1744 (C=O), 1514 (C–F) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.27 (m, 2 H, C*H* Ar), 6.97 (t, *J* = 8.7 Hz, 2 H, C*H* Ar), 3.73 (t, *J* = 4.9 Hz, 1 H, C*H*), 3.46 (d, *J* = 4.9 Hz, 2 H, CH_2), 1.79 (s, 3 H, CCH_3), 1.74 (s, 3 H, CCH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 173.9, 165.1, 163.5, 160.3, 132.6, 132.6, 131.5, 131.4, 130.2, 115.4, 115.3, 115.1, 105.2, 48.0, 31.1, 28.3, 27.1.

ESI-HRMS: *m*/*z* [M + Na^+] calcd for $C_{13}H_{13}F_1O_6$ Na_1: 275.0696; found: 275.0690

Anal. Calcd for $C_{13}H_{13}F_1O_4$: C, 61.9; H, 5.19; found: C, 61.8; H, 5.16.

5-(2,6-Difluorobenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3m)
White solid; yield: 98%; mp 125–127 °C (EtOAc).

IR (KBr): 3004, 2954, 2909 (C–H), 1782, 1748 (C=O), 1625, 1593 (C–F) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.26–7.14 (m, 1 H, Ar), 6.97 (t, *J* = 8.3 Hz, 2 H, C*H* Ar), 3.98 (t, *J* = 6.9 Hz, 1 H, C*H*), 3.43 (d, *J* = 6.9 Hz, 2 H, CH_2), 1.81 (s, 3 H, CCH_3), 1.77 (s, 3 H, CCH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 164.4, 163.0, 159.7, 128.5, 113.4, 111.4, 111.1, 105.1, 45,1, 28.5, 26.4, 19.8.

HRMS (EI/CI): *m*/*z* [M + NH_4^+] calcd for $C_{13}H_{16}F_2O_4N$: 288.1047; found: 288.1042.

Anal. Calcd for $C_{13}H_{12}F_2O_4$: C, 57.8; H, 4.48; found: C, 57.9; H, 4.45.

5-[4-(Methylsulfanyl)benzyl]-2,2-dimethyl-1,3-dioxane-4,6-dione (3n)
Cream solid; yield: 89%; mp 96–98 °C (EtOAc).

IR (KBr): 2996, 2945, 2897, 2875 (C–H), 1789, 1747 (C=O), 1498 (S–CH_3) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 6.4 Hz, 2 H, C*H* Ar), 7.17 (d, *J* = 6.4 Hz, 2 H, C*H* Ar), 3.73 (t, *J* = 4.9 Hz, 1 H, C*H*), 3.44 (s, 3 H, SCH_3), 3.44 (d, *J* = 4.9 Hz, 2 H, CH_2), 1.73 (s, 3 H, CCH_3), 1.54 (s, 3 H, CCH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 165.1, 137.3, 133.8, 130.3, 126.7, 105.1, 48.1, 31.5, 28.4, 27.2, 15.8.

HRMS (CI): *m*/*z* [M + Na^+] calcd for $C_{14}H_{16}O_4Na_1S$: 303.0662; found: 303.0651.

Anal. Calcd for $C_{14}H_{16}O_4S$: C, 59.9; H, 5.75; found: C, 59.9; H, 5.72%

2,2-Dimethyl-5-(4-methylbenzyl)-1,3-dioxane-4,6-dione (3o)[19]
White solid; yield: 95%; mp 110–112 °C (EtOAc) (Lit.[19] 112–113 °C).

IR (KBr): 3004, 2942, 2896 (C–H), 1786, 1751 (C=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.19 (d, *J* = 7.9 Hz, 2 H, C*H* Ar), 7.08 (d, *J* = 7.9 Hz, 2 H, C*H* Ar), 3.78 (t, *J* = 4.9 Hz, 1 H, C*H*), 3.60 (d, *J* = 4.9 Hz, 2 H, CH_2), 2.29 (s, 3 H, CH_3), 1.72 (s, 3 H, CCH_3), 1.50 (s, 3 H, CCH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 165.2, 162.8, 136.5, 134.0, 129.4, 129.0, 106.0, 105.0, 47.9, 35.9, 31.4, 28.2, 27.3, 26.9, 20.8.

5-(2,6-Dimethylbenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3p)
White solid; yield: 92%; mp 112–115 °C (EtOAc).

IR (KBr): 3000, 2960, 2867 (C–H), 1776, 1739 (C=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.13–7.01 (m, 3 H, C*H* Ar), 3.70 (t, *J* = 6.0 Hz, 1 H, C*H*), 3.50 (d, *J* = 6.0 Hz, 2 H, CH_2), 2.42 (s, 6 H, CH_3), 1.79 (s, 3 H, CCH_3), 1.77 (s, 3 H, CCH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 165.0, 137.0, 134.9, 128.6, 126.8, 104.9, 47.0, 28.7, 26.6, 26.4, 20.2.

HRMS (CI): *m*/*z* [M + Na^+] calcd for $C_{15}H_{18}O_4Na_1$: 285.1097; found: 285.1091.

Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.6; H, 6.92; found: C, 68.4; H, 6.88%

2,2-Dimethyl-5-(1-naphthylmethyl)-1,3-dioxane-4,6-dione (3q)[20]
Cream solid; yield: 97%; mp 135–137 °C (EtOAc).

IR (KBr): 3057, 3000, 2869 (C–H), 1781, 1750 (C=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 8.3 Hz, 1 H, C*H* Ar), 7.90 (d, *J* = 8.3 Hz, 1 H, C*H* Ar), 7.79 (d, *J* = 8.3 Hz, 1 H, C*H* Ar), 7.65 (d, *J* = 7.2 Hz, 1 H, C*H* Ar), 7.61–7.47 (m, 2 H, C*H* Ar), 7.44 (t, *J* = 7.2 Hz, 1 H, C*H* Ar), 3.93 (d, *J* = 5.3 Hz, 2 H, CH_2), 3.81 (t, *J* = 5.3 Hz, 1 H, C*H*), 1.70 (s, 3 H, CCH_3), 1.69 (s, 3 H, CCH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 165.3, 134.0, 133.9, 131.2, 129.2, 128.4, 127.8, 126.7, 125.7, 125.5, 122.7, 105.1, 47.7, 28.7, 28.6, 26.4.

5-Isobutyl-2,2-dimethyl-1,3-dioxane-4,6-dione (3r)[20]
White solid; yield: 92%; mp 119–120 °C (EtOAc) (Lit.[20] 120 °C).

IR (KBr): 3003, 2893, 2861 (C–H), 1797, 1748 (C=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.43 (t, *J* = 5.7 Hz, 1 H, C*H*), 1.8–2.15 [m, 3 H, $CH(CH_3)_2$, CH_2 overlap], 1.77 (s, 3 H, CH_3), 1.72 (s, 3 H, CH_3), 0.85 [d, *J* = 6.0 Hz, 6 H, $CH(CH_3)_2$].

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = δ 165.9, 104.8, 44.1, 35.2, 28.5, 26.7, 25.8, 22.0.

α-Substituted *tert*-Butyl Acrylates 4a–r from 5-Monosubstituted Meldrum's Acid Derivatives 3a–r; General Procedure
An oven-dried 50-mL round-bottomed flask was charged under N_2 with the appropriate **3** (2.08 mmol) and **6** (1.00 g, 5.41 mmol). The solids were dissolved in THF (12 mL) and anhyd *t*-BuOH (12 mL). The reaction mixture was then heated to 70 °C and stirred at that temperature for 18 h. Upon cooling of the mixture to r.t., the solvent was removed in vacuo, and the yellow residue was taken up in Et_2O (25 mL), extracted with a sat. $NaHCO_3$ soln (20 mL), 10% aq $KHSO_4$ (20 mL), and a sat. NaCl soln (20 mL), and dried ($MgSO_4$). The solvent was removed in vacuo and the resulting oils were purified by flash column chromatography [silica gel, petrol (40–60) CH_2Cl_2, 2:1]; this gave the corresponding product **4**.

***tert*-Butyl 2-(2-Thienylmethyl)acrylate (4a)**
Acrylate **4a** was prepared by the general procedure described above, from Meldrum's acid derivative **3a** (0.50 g, 2.08 mmol) and **6** (1.24 g, 6.69 mmol).

Colourless oil; yield: 0.43 g (92%); R_f = 0.55 (petrol–CH_2Cl_2, 2:1).

IR (neat): 2979, 2931 (C=CH_2), 1711 (C=O), 1368 (C–S) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.0 (dd, *J* = 5.3, 1.1 Hz, 1 H, Ar), 7.0 (dd, *J* = 3.4, 5.3 Hz, 1 H, Ar), 6.82 (dd, *J* = 3.4, 1.1 Hz, 1 H, Ar), 6.16 (s, 1 H, C*H*H), 5.50 (s, 1 H, CH*H*), 3.79 (s, 2 H, CH_2), 1.47 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 165.8, 141.6, 141.1, 126.8, 125.5, 126.8, 123.8, 80.9, 32.3, 28.8, 28.0.

MS (EI/CI): *m*/*z* (%) = 242 (25) [M + NH_4^+], 225 (25) [M + H^+], 186 (50) [$C_8H_7O_2S$ + NH_4^+].

HRMS (CI): *m*/*z* [M + H^+] calcd for $C_{12}H_{17}O_2S$: 225.0944; found: 225.0943.

***tert*-Butyl 2-2-(4-Hydroxy-3-methoxybenzyl)acrylate (4b)**
Acrylate **4b** was prepared by the general procedure described above, from Meldrum's acid derivative **3b** (0.50 g, 1.79 mmol) and **6** (0.875 g, 4.73 mmol).

White semisolid; yield: 0.27 g (57%); R_f = 0.20 (petrol–CH_2Cl_2, 2:1); mp 41–43 °C (hexanes).

IR (neat): 2979 (C=CH_2), 1711 (C=O), 1493 (O–CH_3) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.84 (dd, *J* = 7.2, 1.1 Hz, 1 H, C*H* Ar), 6.70 (s, 1 H, C*H* Ar), 6.68 (dd, *J* = 7.2, 1.9 Hz, 1 H, C*H* Ar), 6.12 (dd, *J* = 1.5, 0.75 Hz, 1 H, C=CH_2), 5.37 (dd, *J* = 3.0, 1.5 Hz, 1 H, C=CH_2), 3.85 (s, 3 H, OCH_3), 3.53 (s, 2 H, CH_2), 1.46 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 166.2, 146.3, 143.9, 142.0, 130.8, 124.7, 121.6, 114.1, 111.4, 80.6, 55.7, 37.7, 27.9.

MS (EI/CI): *m*/*z* (%) = 282 (35) [M + NH_4^+], 264 (15) [M + H^+], 208 (50) [$C_{11}H_{12}O_4$ + NH_4^+].

ESI-HRMS: *m*/*z* [M + Na^+] calcd for $C_{15}H_{20}O_4Na_1$: 287.1259; found: 287.1258

***tert*-Butyl 2-(3-Thienylmethyl)acrylate (4c)**
Acrylate **4c** was prepared by the general procedure described above, from Meldrum's acid derivative **3c** (0.50 g, 2.08 mmol) and **6** (1.24 g, 6.69 mmol).

Colourless oil; yield: 0.41 g (82%); R_f = 0.55 (petrol–CH_2Cl_2, 2:1).

IR (neat): 2976, 2934 (C=CH_2), 1709 (C=O), 1366 (C–S) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.23 (dd, *J* = 5.0, 3.0 Hz, 1 H, Ar), 6.97 (s, 1 H, Ar), 6.91 (dd, *J* = 5.0, 1.1 Hz, 1 H, Ar), 6.12 (s, 1 H, C*H*H), 5.39 (s, 1 H, CH*H*), 3.60 (s, 2 H, CH_2), 1.44 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 166.1, 141.2, 139.3, 128.4, 125.2, 124.7, 121.4, 80.6, 65.7, 32.6, 15.2, 27.9.

MS (EI/CI): *m*/*z* (%) = 242 (20) [M + NH_4^+], 225 (20) [M + H^+], 186 (60) [$C_8H_7O_2S$ + NH_4^+].

HRMS (CI): *m*/*z* [M + H^+] calcd for $C_{12}H_{17}O_2S$: 225.0944; found: 225.0943.

***tert*-Butyl 2-[(3-Methyl-2-thienyl)methyl]acrylate (4d)**
Acrylate **4d** was prepared by the general procedure described above, from Meldrum's acid derivative **3d** (0.50 g, 1.97 mmol) and **6** (1.05 g, 5.91 mmol).

Colourless oil; yield: 0.38 g (78%); R_f = 0.5 (petrol–CH_2Cl_2, 2:1).

IR (neat): 2977, 2929 (C=CH_2), 1712 (C=O), 1392 (C–S) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.06 (d, *J* = 4.9 Hz, 1 H, Ar), 6.81 (d, *J* = 4.9 Hz, 1 H, Ar), 6.15 (s, 1 H, CH*H*), 5.33 (s, 1 H, C*H*H), 3.69 (s, 3 H, CH_2), 2.14 (s, 3 H, CH_3), 1.50 [s, 9 H, C(CH_3)$_3$].

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 165.8, 140.4, 134.1, 133.9, 129.9, 124.8, 122.0, 80.8, 29.8, 27.9, 13.5, 53.3.

MS (EI/CI): *m*/*z* (%) = 256 (10) [M + NH_4^+], 239 (20) [M + H^+], 200 (80) [$C_9H_{10}O_2S$ + NH_4^+].

HRMS (CI): *m*/*z* [M + H^+] calcd for $C_{13}H_{18}O_2S$: 239.1100; found: 239.1099

***tert*-Butyl 2-(4-Methoxybenzyl)acrylate (4e)**

Acrylate **4e** was prepared by the general procedure described above, from Meldrum's acid derivative **3e** (0.50 g, 1.89 mmol) and **6** (1.05 g, 5.68 mmol).

Colourless oil; yield: 0.45 g (95%); R_f = 0.35 (petrol–CH_2Cl_2, 2:1).

IR (neat): 2979 (C=CH_2), 1710 (C=O), 1512 (O–CH_3) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.10 (d, *J* = 6.8 Hz, 2 H, C*H* Ar), 6.82 (d, *J* = 6.8 Hz, 2 H, C*H* Ar), 6.11 (dd, *J* = 1.5, 0.75 Hz, 1 H, C=CH_2), 5.40 (dd, *J* = 3.4, 1.5 Hz, 1 H, C=CH_2), 3.79 (s, 3 H, OCH_3), 3.53 (s, 2 H, CH_2), 1.44 [s, 9 H, C(CH_3)$_3$].

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 158.0, 142.1, 131.1, 129.9, 124.8, 113.7, 80.6, 55.2, 37.3, 28.0.

MS (EI/CI): *m*/*z* (%) = 282 (30) [M + NH_4^+], 266 (80) [M + H^+], 210 (50) [$C_{11}H_{12}O_3$ + NH_4^+].

HRMS (CI): *m*/*z* [M + NH_4^+] calcd for $C_{15}H_{24}O_3N$: 266.1751; found: 266.1750.

***tert*-Butyl 2-(2-Methoxybenzyl)acrylate (4f)**

Acrylate **4f** was prepared by the general procedure described above, from Meldrum's acid derivative **3f** (0.50 g, 1.89 mmol) and **6** (0.875 g, 4.73 mmol).

Colourless oil; yield: 0.43 g (94%); R_f = 0.35 (petrol–CH_2Cl_2, 2:1).

IR (neat): 2979 (C=CH_2), 1711 (C=O), 1493 (O–CH_3) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (td, *J* = 7.9, 1.5 Hz, 1 H, C*H* Ar), 7.12 (dd, *J* = 7.5, 1.5 Hz, 1 H, C*H* Ar), 6.89 (td, *J* = 7.5, 1.1 Hz, 1 H, C*H* Ar), 6.86 (d, *J* = 7.9 Hz, 1 H, C*H* Ar), 6.10 (dd, *J* = 2.6, 1.1 Hz, 1 H, C=CH_2), 5.26 (dd, *J* = 3.4, 1.5 Hz, 1 H, C=CH_2), 3.80 (s, 3 H, OCH_3), 3.59 (s, 2 H, CH_2), 1.47 [s, 9 H, C(CH_3)$_3$].

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 208.5, 192.0, 181.5, 178.6, 175.6, 171.4, 161.4, 131.5, 106.4, 82.9, 79.0.

MS (EI/CI): *m*/*z* (%) = 282 (10) [M + NH_4^+], 266 (80) [M + H^+], 210 (50) [$C_{11}H_{12}O_3$ + NH_4^+].

HRMS (CI): *m*/*z* [M + NH_4^+] calcd for $C_{15}H_{24}O_3N$: 266.1751; found: 266.1749.

***tert*-Butyl 2-(1,3-Benzodioxol-4-ylmethyl)acrylate (4g)**

Acrylate **4g** was prepared by the general procedure described above, from Meldrum's acid derivative **3g** (0.51 g, 1.83 mmol) and **6** (0.961 g, 5.20 mmol).

Colourless oil; yield: 0.43 g (90%); R_f = 0.35 (petrol–CH_2Cl_2, 1:1).

IR (neat): 1712 (C=O), 1247 (O–C–O) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.81 (s, 1 H, C*H* Ar), 6.72 (dd, *J* = 7.5, 1.9 Hz, 1 H, C*H* Ar), 6.61 (dd, *J* = 8.3, 1.9 Hz, 1 H, C*H* Ar), 6.19 (dd, *J* = 2.6, 1.1 Hz, 1 H, C=CH_2), 5.87 (s, 2 H, OCH_2O), 5.43 (dd, *J* = 2.6, 1.1 Hz, 1 H, C=CH_2), 3.54 (s, 2 H, CH_2), 1.45 [s, 9 H, C(CH_3)$_3$].

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 165.9, 148.7, 145.8, 139.8, 130.8 125.0, 122.4, 120.4, 115.2, 114.1 106.7, 100.4, 80.5, 31.4, 27.9.

MS (EI/CI): *m*/*z* (%) = 280 (15) [M + NH_4^+], 262 (25) [M + H^+], 224 (60) [$C_{11}H_{10}O_4$ + NH_4^+].

ESI-HRMS: *m*/*z* [M + Na^+] calcd for $C_{15}H_{18}O_4Na_1$: 285.1103; found: 285.1101

***tert*-Butyl 2-(1,3-Benzodioxol-5-ylmethyl)acrylate (4h)**

Acrylate **4h** was prepared by the general procedure described above, from Meldrum's acid derivative **3h** (0.51 g, 1.83 mmol) and **6** (0.961 g, 5.20 mmol).

Colourless oil; yield: 0.41 g (87%); R_f = 0.35 (petrol–CH_2Cl_2, 1:1).

IR (neat): 1708 (C=O), 1251 (O–C–O) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.74 (dd, *J* = 15.1, 7.5 Hz, 1 H, C*H* Ar), 6.70 (dd, *J* = 7.5, 1.5 Hz, 1 H, C*H* Ar), 6.66 (dd, *J* = 7.5, 1.5 Hz, 1 H, C*H* Ar), 6.16 (dd, *J* = 2.6, 1.1 Hz, 1 H, C=CH_2), 5.91 (s, 2 H, OCH_2O), 5.39 (dd, *J* = 2.6, 1.1 Hz, 1 H, C=CH_2), 3.56 (s, 2 H, CH_2), 1.46 [s, 9 H, C(CH_3)$_3$].

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 165.9, 147.0, 145.5, 139.8, 125.0, 122.8, 121.2, 120.4, 106.7, 100.4, 80.5, 31.4, 27.9.

MS (EI/CI): *m*/*z* (%) = 280 (15) [M + NH_4^+], 262 (25) [M + H^+], 224 (60) [$C_{11}H_{10}O_4$ + NH_4^+].

ESI-HRMS: *m*/*z* [M + Na^+] calcd for $C_{15}H_{18}O_4Na_1$: 285.1103; found: 285.1091

***tert*-Butyl 2-(2,3,4-Trimethoxybenzyl)acrylate (4i)**

Acrylate **4i** was prepared by the general procedure described above, from Meldrum's acid derivative **3i** (0.50 g, 1.54 mmol) and **6** (0.856 g, 4.62 mmol).

Yellow oil; yield: 0.42 g (88%); R_f = 0.3 (CH_2Cl_2).

IR (neat): 2976, 2937 (C=CH_2), 1712 (C=O) 1627, 1618 (O–CH_3) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.80 (d, *J* = 8.7 Hz, 1 H, C*H* Ar), 6.60 (H, d, *J* = 8.7 Hz, C*H* Ar), 6.14 (dd, *J* = 2.6, 1.1 Hz, 1 H, C=CH_2), 5.38 (dd, *J* = 3.4, 1.5 Hz, 1 H, C=CH_2), 3.86 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 3.53 (s, 2 H, CH_2), 1.46 [s, 9 H, C(CH_3)$_3$].

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 166.3, 152.3, 151.9, 142.2, 141.6, 125.0, 124.5, 124.4, 107.0, 80.5, 60.8, 60.6, 55.9, 31.6, 28.7, 28.0.

MS (EI/CI): *m*/*z* (%) = 326 (10) [M + NH_4^+], 309 (10) [M + H^+], 210 (80) [$C_{13}H_{16}O_5$ + NH_4^+].

HRMS (CI): *m*/*z* [M + H^+] calcd for $C_{17}H_{25}O_3N$: 309.1697; found: 309.1698.

***tert*-Butyl 2-(2-Fluoro-4-methoxybenzyl)acrylate (4j)**

Acrylate **4j** was prepared by the general procedure described above, from Meldrum's acid derivative **3j** (0.50 g, 1.77 mmol) and **6** (0.875 g, 4.73 mmol).

Pale yellow oil; yield: 0.39 g (83%); R_f = 0.35 (petrol–CH_2Cl_2, 2:1).

IR (neat): 2978 (C=CH_2), 1708 (C=O), 1627 (O–CH_3), 1509 (C–F) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.06 (t, *J* = 8.7 Hz, 1 H, C*H* Ar), 6.60 (dd, *J* = 8.7, 2.6 Hz, 1 H, C*H* Ar), 6.51 (s, 1 H, C*H* Ar), 6.12 (dd, *J* = 2.6, 1.1 Hz, 1 H, C=CH_2), 5.32 (dd, *J* = 1.5, 0.74 Hz, 1 H, C=CH_2), 3.76 (s, 3 H, OCH_3), 3.53 (s, 2 H, CH_2), 1.45 [s, 9 H, C(CH_3)$_3$].

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 165.9, 163.0, 159.5, 159.4, 140.4, 131.3, 131.2, 124.8, 117.5, 109.5, 101.5, 80.6, 55.3, 30.3, 27.9.

MS (EI/CI): *m*/*z* (%) = 284 (10) [M + NH_4^+], 266 (20) [M + H^+], 228 (70) [$C_{11}H_{11}F_1O_3$ + NH_4^+].

ESI-HRMS: *m*/*z* [M + Na^+] calcd for $C_{15}H_{19}O_3F_1Na_1$: 289.1216; found: 289.1204

***tert*-Butyl 2-(3-Chloro-4-methoxybenzyl)acrylate (4k)**
Acrylate **4k** was prepared by the general procedure described above, from Meldrum's acid derivative **3k** (0.50 g, 1.67 mmol) and **6** (0.875 g, 4.73 mmol).

Yellow oil; yield: 0.43 g (91%); R_f = 0.30 (petrol–CH_2Cl_2, 2:1).

IR (neat): 2979 (C=CH_2), 1711 (C=O), 1590 (O–CH_3) 756 (C–Cl) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.17 (d, *J* = 2.3 Hz, 1 H, C*H* Ar), 7.02 (dd, *J* = 8.3, 2.3 Hz, 1 H, C*H* Ar), 6.82 (d, *J* = 8.3 Hz, 1 H, C*H* Ar), 6.12 (dd, *J* = 1.5, 0.75 Hz, 1 H, C=CH_2), 5.37 (dd, *J* = 3.0, 1.5 Hz, 1 H, C=CH_2), 3.84 (s, 3 H, OCH_3), 3.48 (s, 2 H, CH_2), 1.42 [s, 9 H, C(CH_3)$_3$].

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 165.8, 153.3, 141.3, 132.1, 130.5, 128.0, 125.1, 121.9, 111.8, 80.6, 55.9, 37.0, 27.8.

MS (EI/CI): *m*/*z* (%) = 300 (10) [M + NH_4^+], 282 (10) [M + H^+], 244 (80) [$C_{11}H_{11}Cl_1O_3$ + NH_4^+].

ESI-HRMS: *m*/*z* [M + Na^+] calcd for $C_{15}H_{19}Cl_1O_3Na_1$: 305.0920; found: 305.0919

***tert*-Butyl 2-(4-Fluorobenzyl)acrylate (4l)**
Acrylate **4l** was prepared by the general procedure described above, from Meldrum's acid derivative **3l** (0.52 g, 2.20 mmol) and **6** (0.925 g, 5.00 mmol).

Colourless oil; yield: 0.46 g (84%); R_f = 0.55 (petrol–CH_2Cl_2, 2:1).

IR (neat): 2983, 3052 (C=CH_2), 1712 (C=O), 1510 (C–F) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.14 (dd, *J* = 8.7, 5.7 Hz, 2 H, C*H* Ar), 6.97 (t, *J* = 8.7 Hz, 2 H, C*H* Ar), 6.14 (dd, *J* = 1.5, 0.75 Hz, 1 H, C=CH_2), 5.37 (dd, *J* = 3.0, 1.5 Hz, 1 H, C=CH_2), 3.56 (s, 2 H, CH_2), 1.35 [s, 9 H, C(CH_3)$_3$].

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 165.9, 163.0, 159.8, 141.5, 134.6, 130.3, 130.2, 125.2, 115.1, 114.9, 80.7, 37.4, 27.9.

MS (EI/CI): *m*/*z* (%) = 254 (34) [M + NH_4^+], 237 (15) [M + H^+], 198 (50) [$C_{10}H_9F_1O_2$ + NH_4^+].

HRMS (CI): *m*/*z* [M + NH_4^+] calcd for $C_{14}H_{21}O_2F_1N$: 254.1551; found: 254.1551

***tert*-Butyl 2-(2,6-Difluorobenzyl)acrylate (4m)**
Acrylate **4m** was prepared by the general procedure described above, from Meldrum's acid derivative **3m** (0.52 g, 2.20 mmol) and **6** (0.925 g, 5.00 mmol).

Colourless oil; yield: 0.46 g (84%); R_f = 0.6 (petrol–CH_2Cl_2, 2:1).

IR (neat): 2980, 2934 (C=CH_2), 1712 (C=O), 1594, 1470 (C–F) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.26–7.14 (m, 1 H, Ar), 6.97 (t, *J* = 7.6 Hz, 2 H, C*H* Ar), 6.12 (d, *J* = 1.1 Hz, 1 H, C=CH_2), 5.19 (d, *J* = 0.75 Hz, 1 H, C=CH_2), 3.64 (s, 2 H, CH_2), 1.49 [s, 9 H, C(CH_3)$_3$].

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 165.7, 163.2, 159.9, 138.8, 128.3, 124.3, 114.8, 111.0, 80.9, 27.9, 24.5.

MS (EI/CI): *m*/*z* (%) = 272 (30) [M + NH_4^+], 255 (10) [M + H^+], 216 (60) [$C_{10}H_8F_2O_2$ + NH_4^+].

HRMS (CI): *m*/*z* calcd for $C_{14}H_{20}O_2F_2N$ [M + NH_4^+]: 272.1457; found: 272.1459.

***tert*-Butyl 2-[4-(Methylsulfanyl)benzyl]acrylate (4n)**
Acrylate **4n** was prepared by the general procedure described above, from Meldrum's acid derivative **3n** (0.50 g, 1.78 mmol) and **6** (1.01 g, 5.35 mmol).

Yellow oil; yield: 0.46 g (98%); R_f = 0.4 (petrol–CH_2Cl_2, 2:1).

IR (neat): 2978, 2934 (C=CH_2), 1712 (C=O), 1137 (C–S) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.20 (d, *J* = 8.3 Hz, 2 H, C*H* Ar), 6.11 (d, *J* = 8.3 Hz, 2 H, C*H* Ar), 6.14 (d, *J* = 1.5, 0.75 Hz, 1 H, C=CH_2), 5.38 (dd, *J* = 3.0, 1.5 Hz, 1 H, C=CH_2), 3.53 (s, 2 H, CH_2), 2.46 (s, 3 H, SCH_3), 1.42 [s, 9 H, C(CH_3)$_3$].

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 141.5, 135.8, 129.4, 126.9, 125.1, 80.6, 53.3, 37.6, 27.9, 16.1.

MS (EI/CI): *m*/*z* (%) = 282 (10) [M + NH_4^+], 265 (80) [M + H^+], 226 (50) [$C_{11}H_{12}O_2S$ + NH_4^+].

HRMS (EI/CI): *m*/*z* [M + H^+] calcd for $C_{15}H_{20}O_2S$: 265.1257; found: 265.1255

***tert*-Butyl 2-(4-Methylbenzyl)acrylate (4o)**
Acrylate **4o** was prepared by the general procedure described above, from Meldrum's acid derivative **3o** (0.50 g, 2.01 mmol) and **6** (1.08 g, 6.04 mmol).

Colourless oil; yield: 0.38 g (82%); R_f = 0.65 (petrol–CH_2Cl_2, 2:1).

IR (neat): 2971, 2964 (C=CH_2), 1704.1 (C=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.15–7.06 (m, 4 H, Ar), 6.13 (dd, *J* = 1.5, 0.75 Hz, 1 H, C=CH_2), 5.36 (dd, *J* = 3.0, 1.5 Hz, 1 H, C=CH_2), 3.56 (s, 2 H, CH_2), 2.33 (s, 3 H, CH_3), 1.45 [s, 9 H, C(CH_3)$_3$].

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 166.2, 141.9, 135.9, 135.5, 128.9, 128.8, 124.9, 80.5, 37.6, 27.9, 20.9.

MS (EI/CI): *m*/*z* (%) = 250 (32) [M + NH_4^+], 233 (8) [M + H^+], 194 (60) [$C_{11}H_{16}O_2$ + NH_4^+].

HRMS (CI): *m*/*z* [M + NH_4^+] calcd for $C_{15}H_{24}O_2N$: 250.1807; found: 250.1802.

***tert*-Butyl 2-(2,6-Dimethylbenzyl)acrylate (4p)**
Acrylate **4p** was prepared by the general procedure described above, from Meldrum's acid derivative **3p** (0.50 g, 1.91 mmol) and **6** (1.06 g, 5.72 mmol).

Colourless oil; yield: 0.40 g (85%); R_f = 0.5 (petrol–CH_2Cl_2, 3:1).

IR (neat): 2978, 2964 (C=CH_2), 1708 (C=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ =7.12–7.00 (m, 3 H, Ar), 6.02 (dd, *J* = 3.4, 1.9 Hz, 1 H, C=CH_2), 4.85 (dd, *J* = 3.8, 1.9 Hz, 1 H, C=CH_2), 3.59 (s, 2 H, CH_2), 2.33 (s, 6 H, CH_3), 1.56 [s, 9 H, C(CH_3)$_3$].

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 166.5, 139.3, 137.0, 135.4, 127.9, 126.3, 123.0, 80.7, 31.1, 28.0, 19.7.

MS (EI/CI): *m*/*z* (%) = 264 (25) [M + NH_4^+], 247 (5) [M + H^+], 208 (70) [$C_{12}H_{14}O_2$ + NH_4^+].

HRMS (CI): *m*/*z* [M + NH_4^+] calcd for $C_{16}H_{26}O_2N$: 264.1958; found: 264.1959.

***tert*-Butyl 2-(1-Naphthylmethyl)acrylate (4q)**
Acrylate **4q** was prepared by the general procedure described above, from Meldrum's acid derivative **3q** (0.50 g, 1.76 mmol) and **6** (0.875 g, 4.73 mmol).

Orange oil; yield: 0.43 g (92%); R_f = 0.55 (petrol–CH_2Cl_2, 3:1).

IR (neat): 2978 (C=CH_2), 1711 (C=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.96–7.89 (m, 1 H, C*H* Ar), 7.89–7.83 (m, 1 H, C*H* Ar), 7.77 (d, *J* = 8.3 Hz, 1 H, C*H* Ar), 7.53–7.44 (m, 2 H, C*H* Ar), 7.42 (d, *J* = 8.3 Hz, 1 H, C*H* Ar), 7.34 (d, *J* = 7.2 Hz, 1 H, C*H* Ar), 6.14 (dd, *J* = 2.6, 1.5 Hz, 1 H, C=CH_2), 5.10 (dd, *J* = 3.0, 1.5 Hz, 1 H, C=CH_2), 4.06 (s, 2 H, CH_2), 1.51 [s, 9 H, C(CH_3)$_3$].

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 166.4, 140.9, 135.0, 133.8, 131.9, 129.1, 128.6, 127.3, 127.2, 125.8, 125.5, 125.4, 125.2, 124.2, 124.2, 80.8, 34.7, 28.0.

MS (EI/CI): *m/z* (%) = 286 (12) [M + NH_4^+], 269 (3) [M + H^+], 230 (75) [$C_{14}H_{12}O_2$ + NH_4^+].

HRMS (CI): *m/z* calcd for $C_{18}H_{21}O_2$ [M + H^+]: 269.1536; found: 269.1538.

***tert*-Butyl 4-Methyl-2-methylenepentanoate (4r)**

Acrylate **4r** was prepared by the general procedure described above from Meldrum's acid derivative **3r** (0.50 g, 1.91 mmol) and **6** (1.06 g, 5.72 mmol).

Colourless oil; yield: 0.348 g (98%); R_f = 0.55 (petrol–CH_2Cl_2, 4:1).

IR (neat): 2959 (C=CH_2), 1710 (C=O) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.05 (d, *J* = 1.9 Hz, 1 H, C=CH_2), 5.39 (dd, *J* = 1.9, 1.1 Hz, 1 H, C=CH_2), 2.13 (dd, *J* = 6.8, 1.1 Hz, 2 H, CH_2), 1.77 [tsept, *J* = 6.8, 3.4 Hz, 1 H, $CH(CH_3)_2$], 1.48 [s, 9 H, $C(CH_3)_3$], 0.88 [d, *J* = 6.4 Hz, 6 H, $CH(CH_3)_2$].

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 167.2, 141.8, 125.0, 80.7, 41.8, 28.5, 27.8, 22.7.

MS (EI/CI): *m/z* (%) = 202 (45) [M + NH_4^+], 184 (5) [M + H^+], 146 (50) [$C_7H_{12}O_2$ + NH_4^+].

HRMS (CI): *m/z* [M + NH_4^+] calcd for $C_{11}H_{24}O_2N$: 202.1802; found: 202.1803.

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