Decarboxylative Claisen rearrangement reactions of allylic tosylmalonate esters

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General experimental:

Dichloromethane (CH_2Cl_2) was distilled from calcium hydride and all reactions were carried out with dry, freshly distilled solvents, under anhydrous conditions (N_2 atmosphere).

All reactions were monitored by thin-layer chromatography using precoated aluminium-backed plates (Merck Kieselgel 60 F254) and are visualised by UV light and/or vaporisation of a solution of KMnO_4 . Merck Kieselgel silica gel (230-400 mesh) was used for flash chromatography.

Infra-red spectra were recorded on a Perkin 881 spectrophotometer. NMR spectra were recorded in CDCl_3 on Jeol GX-270a spectrometer and calibrated using residual isotopic solvent as an internal reference. The following abbreviations are used to indicate the multiplicities: s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet. Mass spectra were recorded using a micromass Platform II instrument operating in chemical ionisation (ammonia) mode. Elemental analysis were performed at the analytical laboratories of the University of North London.

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Preparation of methyl malonate:¹ A mixture of Meldrum's acid and methanol (1 equiv.) was heated at 80°C for 20h. Evaporation of the residual acetone gave methyl malonate (quantitative yield) which was used directly in the next step without further purification.

General procedure for the preparation of allylic malonate esters 3a-j: To a solution of methyl malonate and the allylic alcohol (1 equiv.) in CH₂Cl₂, were added at 0 °C, 1,3-dicyclohexylcarbodiimide (1 equiv.) and 4-(dimethylamino)pyridine (0.1 equiv.). After 18 h of stirring at rt, the mixture was filtered through Celite and the residue washed with brine. The combined filtrate and washings were dried (MgSO₄) and concentrated under reduced pressure. Chromatography on silica gel (25→50% ethyl acetate–petroleum ether) of the residue gave allylic malonate esters **3a-j**.

General procedure for the preparation of allylic methyl (toluene-4-sulfonyl)malonates 4a-j: To a solution of allylic methyl malonates **3a-j** (4.5 equiv.) in DMSO ($c \geq 2 \text{ mol L}^{-1}$) was added very slowly, at rt and under N₂, potassium *tert*-butoxide (4 equiv. of a 1.0 M solution in THF²). The reaction was then stirred for 15 min before the addition of the tosyl fluoride (1 equiv.). After 20 h of stirring at rt, the mixture was poured into aqueous HCl (10%), extracted twice with ether and the combined organic layers were washed with brine, dried (MgSO₄) and concentrated under reduced pressure. Chromatography on silica gel (25→50% ethyl acetate–petroleum ether) of the residual mixture gave recovered excess allylic methyl malonates **3a-j**, followed by the desired allylic methyl (toluene-4-sulfonyl)malonates **4a-j**. Yields cited for **4** are based on tosyl fluoride; yields cited for recovered **3** are calculated from the total recoverable amount based on the yield of **4** and the amount of **3** used (4.5 equiv.). For example, a 70 % yield of **4** means the total recoverable amount of **3** is $(4.5 - 0.7) = 3.8$ equiv; 74% recovery means that $(0.74 \times 3.8 = 2.81 \text{ equiv.})$ of **3** was recovered

¹ Brooks, D. W.; Castro de Lee, N.; Peevey, R. *Tetrahedron Lett.* **1984**, 25, 4623–4626.

² Purchased from Aldrich Chemical Company.

(E)-Methyl (3-phenyl-2-propenyl) (toluene-4-sulfonyl)malonate (4a)

According to the general procedure, malonate **3a** (5.98 g, 25.5 mmol, 4.5 equiv.) was tosylated with *t*BuOK (2.55g, 22.7 mmol, 4 equiv.) and tosyl fluoride (988 mg, 5.67 mmol, 1 equiv.) in DMSO (6 mL). Chromatography (25→50% ethyl acetate–petroleum ether) yielded excess malonate **3a** (3.72 g, 74% recovery) and then (*E*)-methyl (3-phenyl-2-propenyl) (toluene-4-sulfonyl)malonate **4a** (1.55 g, 70%) as a pale yellow oil; R_f 0.37 (25% ethyl acetate–petroleum ether); IR (film) ν_{CO} 1739 cm^{-1} ; ^1H NMR δ 7.83 (2H, d, J 8.5 Hz, 2H-*ortho* Ts), 7.30 (7H, m, 2H-*meta* Ts, 5H Ph), 6.63 (1H, d, J 16.0 Hz, CH=CH-Ph), 6.16 (1H, td, J 6.5, 16.0 Hz, OCH₂-CH=CH), 5.00 (1H, s, CH-Ts), 4.80 (2H, td, J 6.5, 16.0 Hz, OCH₂), 3.79 (3H, s, OCH₃), 2.37 (3H, s, CH₃ Ts); ^{13}C NMR δ 161.5, 160.9, 146.2, 135.9, 135.7, 134.2, 130.2, 129.6, 128.8, 128.5, 126.8, 121.3, 74.5, 67.5, 53.8, 21.8; MS (CI) m/z : 406 [M+NH₄]⁺, 334, 117, 52; HMRS (CI) m/z calcd for [C₂₀H₂₀O₆S+NH₄]⁺: 406.1324, found: 406, 1324; Anal. calcd for C₂₀H₂₀O₆S: C, 61.84; H, 5.19; found: C, 61.77; H, 5.14.

Methyl (2-propenyl) (toluene-4-sulfonyl)malonate (4b)

According to the general procedure, malonate **3b** (2.17 g, 13.7 mmol, 4.5 equiv.) was tosylated with *t*BuOK (1.37 g, 12.2 mmol, 4 equiv.) and tosyl fluoride (531 mg, 3.05 mmol, 1 equiv.) in DMSO (6 mL). Chromatography (25→50% ethyl acetate–petroleum ether) yielded excess **3b** (1.45 g, 79% recovery) and then methyl (2-propenyl) (toluene-4-sulfonyl)malonate **4b** (640 mg, 67%) as a colorless oil; R_f 0.44 (25% ethyl acetate–petroleum ether); IR (film) ν_{CO} 1743 cm^{-1} ; ^1H NMR δ 7.83 (2H, d, J 8.0 Hz, 2H-*ortho* Ts), 7.34 (2H, d, J 8.0 Hz, 2H-*meta* Ts), 5.86 (1H, m, CH=CH₂), 5.30 (1H, d, J 18.0 Hz, CH=CH_aH_b), 5.25 (1H, d, J 10.5 Hz, CH=CH_aH_b), 4.98 (1H, s, CH-Ts), 4.63 (2H, d, J 6.0 Hz, OCH₂), 3.76 (3H, s, OCH₃), 2.43 (3H, s, CH₃ Ts); ^{13}C NMR δ 161.4, 160.6, 146.0, 134.0, 130.3, 130.0, 129.4, 119.4, 74.2, 67.2, 53.5, 21.5; MS (CI) m/z : 330 [M+NH₄]⁺, 176, 139, 108; HRMS (CI) m/z calcd for

[C₁₄H₁₆O₆S+NH₄]⁺: 330.1011, found: 330.1010; Anal. calcd for C₁₄H₁₆O₆S: C, 53.84; H, 5.04; found: C, 53.71; H, 5.04.

(E)-Methyl (2-pentenyl) (toluene-4-sulfonyl)malonate (4c)

According to the general procedure, malonate **3c** (2.03 g, 10.9 mmol, 4.5 equiv.) was tosylated with *t*BuOK (1.16 g, 10.4 mmol, 4 equiv.) and tosyl fluoride (453 mg, 2.60 mmol, 1 equiv.) in DMSO (5.5 mL). Chromatography (25→50% ethyl acetate–petroleum ether), yielded the excess malonate **3c** (1.04 g, 65% recovery) and then (*E*)-methyl (2-pentenyl) (toluene-4-sulfonyl)malonate **4c** (531 mg, 60%) as a colorless oil; *R*_f 0.55 (25% ethyl acetate–petroleum ether); IR (film) ν_{CO} 1745 cm⁻¹; ¹H NMR δ 7.84 (2H, d, *J* 8.0 Hz, 2H-*ortho* Ts), 7.34 (2H, d, *J* 8.0 Hz, 2H-*meta* Ts), 5.81 (1H, td, *J* 6.5, 15.0 Hz, OCH₂-CH=CH), 5.47 (1H, ttd, *J* 1.5, 6.5, 15.0 Hz, CH=CH-CH₂), 4.96 (1H, s, CH-Ts), 4.58 (2H, d, *J* 6.5 Hz, OCH₂), 3.77 (3H, s, OCH₃), 2.44 (3H, s, CH₃ Ts), 2.05 (2H, quint, *J* 7.5 Hz, CH₂-CH₃), 0.98 (3H, t, *J* 7.5 Hz, CH₂-CH₃); ¹³C NMR δ 161.5, 160.7, 146.0, 139.4, 134.3, 130.1, 129.5, 121.3, 74.4, 67.6, 53.6, 25.2, 21.7, 12.9; MS (CI) *m/z* : 358 [M+NH₄]⁺, 246, 204, 136, 52; HRMS (CI) *m/z* calcd for [C₁₆H₂₀O₆S+NH₄]⁺: 358.1324, found: 358.1320.; Anal. calcd for C₁₆H₂₀O₆S: C, 56.46; H, 5.92; found: C, 56.29; H, 6.01.

(Z)-Methyl (2-pentenyl) (toluene-4-sulfonyl)malonate (4d)

According to the general procedure, malonate **3d** (1.34 g, 7.20 mmol, 4.5 equiv.) was tosylated with *t*BuOK (718 mg, 6.40 mmol, 4 equiv.) and tosyl fluoride (279 mg, 1.60 mmol, 1 equiv.) in DMSO (3.5 mL). Chromatography (25→50% ethyl acetate–petroleum ether), yielded the excess malonate **3d** (921 mg, 89% recovery) and then (*Z*)-methyl (2-pentenyl) (toluene-4-sulfonyl)malonate **4d** (409 mg, 75%) as a colorless oil; *R*_f 0.50 (25% ethyl acetate–petroleum ether); IR (film) ν_{CO} 1741 cm⁻¹; ¹H NMR δ 7.81 (2H, d, *J* 8.0 Hz, 2H-*ortho* Ts),

7.32 (2H, d, J 8.0 Hz, 2H-*meta* Ts), 5.65 (1H, m, CH=CH), 5.38 (1H, m, CH=CH), 4.94 (1H, s, CH-Ts), 4.66 (2H, d, J 7.0 Hz, OCH₂), 3.74 (3H, s, OCH₃), 2.42 (3H, s, CH₃ Ts), 2.05 (2H, quint, J 7.0 Hz, CH₂-CH₃), 0.93 (3H, t, J 7.0 Hz, CH₂-CH₃); ¹³C NMR δ 161.5, 160.9, 146.1, 138.6, 134.2, 130.2, 129.6, 121.1, 74.5, 62.7, 53.7, 21.8, 20.9, 14.0; MS (CI) m/z : 358 [M+NH₄]⁺; HRMS (CI) m/z calcd for [C₁₆H₂₀O₆S+NH₄]⁺: 358.1324, found: 358.1331.; Anal. calcd for C₁₆H₂₀O₆S: C, 56.46; H, 5.92; found: C, 56.37; H, 5.95.

Methyl (3-methyl-2-butenyl) (toluene-4-sulfonyl)malonate (**4e**)

According to the general procedure, malonate **3e** (1.94 g, 10.4 mmol, 4.5 equiv.) was tosylated with *t*BuOK (1.04 g, 9.24 mmol, 4 equiv.) and tosyl fluoride (403 mg, 2.31 mmol, 1 equiv.) in DMSO (5 mL). Chromatography (25→50% ethyl acetate–petroleum ether), yielded the excess malonate **3e** (1.37 g, 91% recovery) and then *methyl (3-methyl-2-butenyl) (toluene-4-sulfonyl)malonate 4e* (707 mg, 90%) as a colorless oil; R_f 0.46 (25% ethyl acetate–petroleum ether); IR (film) ν_{CO} 1744 cm⁻¹; ¹H NMR δ 7.83 (2H, d, J 8.5 Hz, 2H-*ortho* Ts), 7.33 (2H, d, J 8.5 Hz, 2H-*meta* Ts), 5.25 (1H, m, CH=C(CH₃)₂), 4.94 (1H, s, CH-Ts), 4.63 (2H, d, J 7.5 Hz, OCH₂), 3.77 (3H, s, OCH₃), 2.44 (3H, s, CH₃ Ts), 1.74 (3H, s, CH₃), 1.67 (3H, s, CH₃); ¹³C NMR δ 161.5, 160.9, 146.0, 140.8, 134.3, 130.1, 129.5, 117.2, 74.4, 63.8, 53.6, 25.8, 21.8, 18.0; MS (CI) m/z : 358 [M+NH₄]⁺, 290, 246, 204, 174, 136, 86; HRMS (CI) m/z calcd for [C₁₆H₂₀O₆S+NH₄]⁺: 358.1324, found: 358.1331. Anal. calcd for C₁₆H₂₀O₆S: C, 56.46; H, 5.92; found: C, 56.36; H, 5.87.

(*E*)-Methyl (2-methyl-3-phenyl-2-propenyl) (toluene-4-sulfonyl)malonate (**4f**)

According to the general procedure, malonate **3f** (1.88 g, 7.57 mmol, 4.5 equiv.) was tosylated with *t*BuOK (754 mg, 6.72 mmol, 4 equiv.) and tosyl fluoride (293 mg, 1.68 mmol, 1 equiv.) in DMSO (3.5 mL). Chromatography (25→50% ethyl acetate–petroleum ether), yielded the excess malonate **3f** (1.45 g, 99% recovery) and then (*E*)-*methyl (2-methyl-3-phenyl-2-*

propenyl) (*toluene-4-sulfonyl*)malonate **4f** (380 mg, 56%) as a colorless oil; R_f 0.37 (25% ethyl acetate–petroleum ether); IR (film) ν_{CO} 1744 cm^{-1} ; 1H NMR δ 7.85 (2H, d, J 8.0 Hz, 2H-*ortho* Ts), 7.27 (7H, m, 2H-*meta* Ts, 5H Ph), 6.49 (1H, s, C=CH-Ph), 5.05 (1H, s, CH-Ts), 4.71 (2H, s, OCH₂), 3.77 (3H, s, OCH₃), 2.37 (3H, s, CH₃ Ts), 2.05 (2H, quint, J 7.5 Hz, CH₂-CH₃), 0.98 (3H, t, J 7.5 Hz, CH₂-CH₃), 1.82 (3H, s, CH₃); ^{13}C NMR δ 161.6, 160.8, 146.2, 136.7, 134.2, 131.3, 130.2, 129.8, 129.7, 129.0, 128.3, 127.1, 74.5, 72.7, 53.8, 21.8, 15.5; MS (CI) m/z : 420 [M+NH₄]⁺, 304, 289, 246, 174, 148, 131; HRMS (CI) m/z calcd for [C₂₁H₂₂O₆S+NH₄]⁺: 420.1481, found: 420.1475; Anal. calcd for C₂₁H₂₂O₆S: C, 62.67; H, 5.51; found: C, 62.55; H, 5.63.

(S)-(4-Isopropenyl-1-cyclohexenylmethyl) methyl (toluene-4-sulfonyl)malonate (4g)

According to the general procedure, malonate **3g** (1.83 g, 7.25 mmol, 4.5 equiv.) was tosylated with *t*BuOK (724 mg, 6.45 mmol, 4 equiv.) and tosyl fluoride (280 mg, 1.61 mmol, 1 equiv.) in DMSO (3.5 mL). Chromatography (25→50% ethyl acetate–petroleum ether), yielded the excess malonate **3g** (1.53 g, 100% recovery) and then (*S*)-(4-isopropenyl-1-cyclohexenylmethyl) methyl (toluene-4-sulfonyl)malonate **4g** (530 mg, 81%) as a colorless oil; R_f 0.48 (25% ethyl acetate–petroleum ether); IR (film) ν_{CO} 1744 cm^{-1} ; 1H NMR δ 7.84 (2H, d, J 8.0 Hz, 2H-*ortho* Ts), 7.34 (2H, d, J 8.0 Hz, 2H-*meta* Ts), 5.75 (1H, bs, CH=C), 4.97 (1H, s, CH-Ts), 4.70 (2H, d, J 4.5 Hz, CH₂=C), 4.53 (2H, s, OCH₂), 3.77 (3H, s, OCH₃), 2.44 (3H, s, CH₃ Ts), 2.20-1.72 (6H, m), 1.71 (3H, s, CH₃), 1.41 (1H, m, CH); ^{13}C NMR δ 161.6, 160.9, 149.4, 146.1, 134.3, 131.4, 130.2, 130.0, 129.6, 127.6, 108.9, 74.5, 71.0, 53.7, 40.7, 30.5, 27.3, 26.2, 21.9, 20.8; MS (CI) m/z : 424 [M+NH₄]⁺, 366, 270, 152, 135; HRMS (CI) m/z calcd for [C₂₁H₂₆O₆S +NH₄]⁺: 424.1794, found: 424.1778; Anal. calcd for C₂₁H₂₆O₆S: C, 62.05; H, 6.45; found: C, 62.13; H, 6.39.

(1'R, 5'R)-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl) methyl (toluene-4-sulfonyl)malonate (4h)

According to the general procedure, malonate **3h** (1.95 g, 7.75 mmol, 4.5 equiv.) was tosylated with *t*BuOK (811 mg, 7.22 mmol, 4 equiv.) and tosyl fluoride (300 mg, 1.72 mmol, 1 equiv.) in DMSO (3.8 mL). Chromatography (25→50% ethyl acetate–petroleum ether), yielded the excess malonate **3h** (1.50 g, 99% recovery) and then (*1'R, 5'R*)-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl) methyl (toluene-4-sulfonyl)malonate **4h** (549 mg, 78%) as a colorless oil; R_f 0.64 (25% ethyl acetate–petroleum ether); IR (film) ν_{CO} 1745 cm^{-1} ; 1H NMR δ 7.84 (2H, d, J 8.0 Hz, 2H-*ortho* Ts), 7.34 (2H, d, J 8.0 Hz, 2H-*meta* Ts), 5.55 (1H, s, C=CH-CH₂), 4.95 (1H, s, CH-Ts), 4.50 (2H, s, OCH₂), 3.76 (3H, s, OCH₃), 2.44 (3H, s, CH₃ Ts), 2.36 (1H, m, CH), 2.24 (2H, d, J 8.0 Hz, CH-CH₂-CH), 2.05 (2H, m, CH₂), 1.25 (3H, s, CH₃), 1.10 (1H, m, CH), 0.75 (3H, d, J 1.0 Hz, CH₃); ^{13}C NMR δ 161.5, 160.9 146.0, 141.6, 134.4, 134.3, 130.1, 129.6, 123.2, 74.4, 69.5, 53.6, 43.4, 40.5, 38.0, 31.4, 31.3, 26.1, 21.8, 20.9; MS (CI) m/z : 424 [M+NH₄]⁺, 304, 246, 174, 152, 135; HRMS (CI) m/z calcd for [C₂₁H₂₆O₆S+NH₄]⁺: 424.1794, found: 424.1785; Anal. calcd for C₂₁H₂₆O₆S: C, 62.05; H, 6.45; found: C, 62.13; H, 6.45.

(±)-(E)-Methyl (3-penten-2-yl) (toluene-4-sulfonyl)malonate (4i)

According to the general procedure, malonate **3i** (2.33 g, 12.5 mmol, 4.5 equiv.) was tosylated with *t*BuOK (1.25 g, 11.1 mmol, 4 equiv.) and tosyl fluoride (484 mg, 2.78 mmol, 1 equiv.) in DMSO (6 mL). Chromatography (25→50% ethyl acetate–petroleum ether), yielded the excess malonate **3i** (1.50 g, 83% recovery) and then (±)-(E)-methyl (3-penten-2-yl) (toluene-4-sulfonyl)malonate **4i** (750 mg, 79%) as a colorless oil; R_f 0.50 (25% ethyl acetate–petroleum ether); IR (film) ν_{CO} 1742 cm^{-1} ; 1H NMR δ 7.83 (2H, d, J 8.0 Hz, 2H-*ortho* Ts), 7.33 (2H, d,

J 8.0 Hz, 2H-*meta* Ts), 7.68 (1H, m, CH=C), 5.32 (2H, m, CH=C, OCH), 4.92 (1H, s, CH-Ts), 3.76 (3H, s, OCH₃), 2.43 (3H, s, CH₃ Ts), 1.66 (3H, t, *J* 6.0 Hz, CH₃-CH-O), 1.26 (3H, dd, *J* 2.5, 6.0 Hz, CH₃-CH=CH); ¹³C NMR δ 161.8, 160.2, 146.0, 130.2, 129.9, 129.8, 129.5, 129.3, 74.8, 74.7, 53.6, 21.8, 20.0, 17.8; MS (CI) *m/z*: 698, 358 [M+NH₄]⁺; HRMS (CI) *m/z* calcd for [C₁₆H₂₀O₆S+NH₄]⁺: 358.1324, found: 358.1335; Anal. calcd for C₁₆H₂₀O₆S: C, 56.46; H, 5.92; found: C, 56.29; H, 5.79.

(1'*R*, 5'*R*)-(5-Isopropenyl-2-methyl-cyclohex-2-enyl) methyl (toluene-4-sulfonyl)-malonate (4j)

According to the general procedure, malonate **3j** (3.16 g, 12.52 mmol, 4.5 equiv.) was tosylated with *t*BuOK (1.25 g, 11.13 mmol, 4 equiv.) and tosyl fluoride (485 mg, 2.78 mmol, 1 equiv.) in DMSO (6.2 mL). Chromatography (25→50% ethyl acetate–petroleum ether), yielded the excess malonate **3j** (1.63 g, 66% recovery) and then (*1'**R*, *5'**R*)-(5-isopropenyl-2-methylcyclohex-2-enyl) methyl (toluene-4-sulfonyl)malonate **4j** (838 mg, 74%) as a colorless oil; *R*_f 0.50 (25% ethyl acetate–petroleum ether); IR (film) ν_{CO} 1743 cm⁻¹; ¹H NMR δ 7.86 (2H, dd, *J* 2.0 8.0 Hz, 2H-*ortho* Ts), 7.34 (2H, d, *J* 8.0 Hz, 2H-*meta* Ts), 5.59 (1H, bs, CH=C), 5.46 (1H, bs, CH-OCO), 4.97 (1H, s, CH-Ts), 4.69 (2H, d, *J* 12.0 Hz, CH₂=C), 3.78 and 3.76 (3H, 2s, OCH₃), 2.43 (3H, s, CH₃ Ts), 2.30-1.80 (4H, m), 1.68 (3H, s, CH₃), 1.56 (3H, d, *J* 10.5 Hz, CH₃), 1.43 (1H, m); ¹³C NMR δ 161.5, 160.8, 147.9, 146.1, 131.7, 130.2, 129.6, 127.0, 109.7, 76.9 and 76.8, 74.7 and 74.5, 53.7, 40.2, 33.4 and 33.3, 30.7, 21.8, 20.5, 18.7 and 18.6; MS (CI) *m/z*: 558, 424 [M+NH₄]⁺, 304, 246, 152, 135; HRMS (CI) *m/z* calcd for [C₂₁H₂₆O₆S+NH₄]⁺: 424.1794, found: 424.1786; Anal. calcd for C₂₁H₂₆O₆S: C, 62.05; H, 6.45; found: C, 61.99; H, 6.47.

General procedure for decarboxylative Claisen rearrangement reactions:

Using BSA–KOAc (Method A): To solutions of tosylmalonates **4a–k** in CH₂Cl₂ were added, at rt and under N₂, BSA (1 equiv.) and KOAc (0.1 equiv.). After stirring for the periods indicated, the reaction mixtures were concentrated under reduced pressure. Chromatography on silica gel afforded the decarboxylated rearranged products **5a–k**.

Using TBDMSOTf–DBU (Method B): To solutions of tosylmalonates **4a–k** in CH₂Cl₂ were added simultaneously, at rt and under N₂, TBDMSOTf (2.1 equiv.) and DBU (2.1 equiv.). After 15–30 min of stirring, the reaction mixtures were concentrated under reduced pressure. Chromatography on silica gel afforded the decarboxylated rearranged products **5a–k**

Methyl 3-phenyl-(toluene-4-sulfonyl)pent-4-enoate (5a)³

Method A: According to the general procedure, a mixture of tosylmalonate **4a** (168 mg, 0.43 mmol), BSA (105 μ L, 0.43 mmol, 1 equiv.) and KOAc (4 mg, 0.04 mmol, 0.1 equiv.) in CH₂Cl₂ (5 mL) was stirred for 4 h at rt. Evaporation of solvent and chromatography of the residue (25% ethyl acetate–petroleum ether) yielded *methyl 3-phenyl-(toluene-4-sulfonyl)pent-4-enoate* **5a** (120 mg, 81%) as a colorless solid.

Method B: According to the general procedure, a mixture of tosylmalonate **4a** (112 mg, 0.29 mmol), TBDMSOTf (139 μ L, 0.61 mmol, 2.1 equiv.) and DBU (90 μ L, 0.61 mmol, 2.1 equiv.) in CH₂Cl₂ (1 mL) was stirred for 15 min. Evaporation of solvent and chromatography of the residue (25% ethyl acetate–petroleum ether) yielded **5a** (80 mg, 81%) as a colorless solid.

R_f 0.58 (25% ethyl acetate–petroleum ether); ¹H NMR δ 7.78 (2H, d, *J* 8.0 Hz, 2H-*ortho* Ts), 7.33 (2H, d, *J* 8.0 Hz, 2H-*meta* Ts), 7.15 (5H, m, 5H Ph), 6.12 (ddd, *J* 2.0, 8.0, 10.5 Hz, CH=CH₂ minor isomer), 5.85 (ddd, *J* 1.5, 9.0, 10.0 Hz, CH=CH₂ major isomer), 5.16 (1H, d, *J* 9.0 Hz, CH=CH*a*H*b*), 5.08 (d, *J* 17.0 Hz, CH=CH*a*H*b* one isomer), 5.03 (d, *J* 17.0 Hz, CH=CH*a*H*b* other isomer), 4.50 (d, *J* 8.5 Hz, CH-Ts minor isomer), 4.45 (d, *J* 8.5 Hz, CH-Ts major isomer), 4.16 (dd, *J* 8.5, 9.5 Hz, CH-Ph major isomer), 4.05 (dd, *J* 8.5, 9.5 Hz, CH-Ph

³ Masuyama, Y.; Mitsunaga, Y.; Kurusu, Y.; Segawa, K. I. *Bull. Chem. Soc. Japan* **1987**, 60, 3431–3432.

minor isomer), 3.72 (s, OCH₃ major isomer), 3.24 (s, OCH₃ minor isomer), 2.44 (s, CH₃ Ts minor isomer), 2.34 (s, CH₃ Ts major isomer).

Methyl (toluene-4-sulfonyl)pent-4-enoate (**5b**)⁴

Method A: According to the general procedure, a mixture of tosylmalonate **4b** (151 mg, 0.48 mmol) BSA (117 μ L, 0.48 mmol, 1 equiv.) and KOAc (5 mg, 0.05 mmol, 0.1 equiv.) in CH₂Cl₂ (4 mL) was stirred for 24 h. Chromatography (35% ethyl acetate–petroleum ether) yielded *methyl (toluene-4-sulfonyl)pent-4-enoate* **5b** (80 mg, 62%) as a colorless oil.

Method B: According to the general procedure, a mixture of tosylmalonate **4b** (130 mg, 0.42 mmol), TBDMSOTf (200 μ L, 0.87 mmol, 2.1 equiv.) and DBU (131 μ L, 0.87 mmol, 2.1 equiv.) in CH₂Cl₂ (1 mL) was stirred for 15 min. Chromatography (25% ethyl acetate–petroleum ether) yielded **5b** (82 mg, 73%) as a colorless oil.

R_f 0.61 (25% ethyl acetate–petroleum ether); ¹H NMR δ 7.73 (2H, d, *J* 8.0 Hz, 2H-*ortho* Ts), 7.35 (2H, d, *J* 8.0 Hz, 2H-*meta* Ts), 5.63 (1H, m, CH=CH₂), 5.09 (1H, d, *J* 18.0 Hz, CH=CH*a*H*b*), 5.07 (1H, d, *J* 9.5 Hz, CH=CH*a*H*b*), 3.98 (1H, dd, *J* 4.0, 11.0 Hz, CH-Ts), 3.65 (3H, s, OCH₃), 2.70 (2H, m, CH₂-CH=CH₂), 2.45 (3H, s, CH₃ Ts).

Methyl 3-ethyl-(toluene-4-sulfonyl)pent-4-enoate (**5c**)

From (*E*)-methyl (2-pentenyl) (toluene-4-sulfonyl)malonate **4c**

Method A: According to the general procedure, a mixture of tosylmalonate **4c** (56 mg, 0.16 mmol), BSA (24 μ L, 0.16 mmol, 1 equiv.) and KOAc (2 mg, 0.02 mmol, 0.1 equiv.) in

⁴ Ono, N.; Yoshimira, T.; Saito, T.; Tamura, R.; Tanikaga, R.; Kaji, A. *Bull. Chem. Soc. Japan* **1979**, 52, 1716–1719.

CH₂Cl₂ (2 mL) was stirred for 24 h. Chromatography (35% ethyl acetate–petroleum ether) yielded *methyl 3-ethyl-(toluene-4-sulfonyl)pent-4-enoate* **5c** (36 mg, 74%) as a colorless oil.

Method B: According to the general procedure, a mixture of tosylmalonate **4c** (103 mg, 0.31 mmol), TBDMSOTf (146 μ L, 0.64 mmol, 2.1 equiv.) and DBU (95 μ L, 0.64 mmol, 2.1 equiv.) in CH₂Cl₂ (1 mL) was stirred for 30 min. Chromatography (35% ethyl acetate–petroleum ether) yielded **5c** (55 mg, 61%) as a colorless oil.

From (Z)-methyl (2-pentenyl) (toluene-4-sulfonyl)malonate 4d

Method B: According to the general procedure, a mixture of tosylmalonate **4d** (98 mg, 0.29 mmol), TBDMSOTf (139 μ L, 0.61 mmol, 2.1 equiv.) and DBU (90 μ L, 0.61 mmol, 2.1 equiv.) in CH₂Cl₂ (1 mL) was stirred for 15 min. Chromatography (25% ethyl acetate–petroleum ether) yielded **5c** (15 mg, 18%) as a colorless oil.

R_f 0.74 (25% ethyl acetate–petroleum ether); IR (film) ν_{CO} 1742 cm⁻¹; ¹H NMR δ 7.76 (d, *J* 8.0 Hz, 2H-*ortho* Ts major isomer), 7.75 (d, *J* 8.0 Hz, 2H-*ortho* Ts minor isomer), 7.33 (d, *J* 8.0 Hz, 2H-*meta* Ts major isomer), 7.31 (d, *J* 8.0 Hz, 2H-*meta* Ts minor isomer), 5.55 (1H, m, CH=CH₂), 5.10 (2H, m, CH=CH₂), 3.99 (d, *J* 10.0 Hz, CH-Ts minor isomer), 3.98 (d, *J* 9.0 Hz, CH-Ts major isomer), 3.63 (s, OCH₃ minor isomer), 3.49 (s, OCH₃ major isomer), 2.77 (qd, *J* 3.0, 9.0 Hz, CH-CH=CH₂ major isomer), 2.67 (qd, 3.0, 10.0 Hz, CH-CH=CH₂ minor isomer), 2.43 (3H, s, CH₃ Ts), 1.45 (m, CH₂-CH₃ major isomer), 1.25 (m, CH₂-CH₃ minor isomer), 0.87 (t, *J* 7.5 Hz, CH₂-CH₃ major isomer), 0.81 (t, *J* 7.5 Hz, CH₂-CH₃ minor isomer); ¹³C NMR δ 166.4 and 166.1, 145.3, 136.4 and 136.1, 129.6, 129.4, 129.3, 128.9, 128.4, 118.8 and 118.6, 75.2 and 74.6, 52.7 and 52.5, 44.7 and 44.6, 25.2 and 25.1, 21.7, 11.2 and 11.0; MS (CI) *m/z*: 314 [M+NH₄]⁺; HRMS (CI) *m/z* calcd for [C₁₅H₂₀O₄S+NH₄]⁺: 314.1426, found: 314.1415; Anal. calcd for C₁₅H₂₀O₄S: C, 60.79; H, 6.80; found: C, 60.87; H, 7.00.

Methyl 3,3-dimethyl-(toluene-4-sulfonyl)pent-4-enoate (5e)

Method A: According to the general procedure, a mixture of tosylmalonate **4e** (114 mg, 0.34 mmol), BSA (81 μ L, 0.34 mmol, 1 equiv.) and KOAc (3 mg, 0.03 mmol, 0.1 equiv.) in CH₂Cl₂ (2 mL) was stirred for 18 h. Chromatography (25% ethyl acetate–petroleum ether)

yielded *methyl 3,3-dimethyl-(toluene-4-sulfonyl)pent-4-enoate* **5e** (83 mg, 80%) as a colorless oil.

Method B: According to the general procedure, a mixture of tosylmalonate **4e** (121 mg, 0.36 mmol), TBDMSOTf (172 μ L, 0.55 mmol, 2.1 equiv.) and DBU (112 μ L, 0.75 mmol, 2.1 equiv.) in CH_2Cl_2 (1 mL) was stirred for 15 min. Chromatography (25% ethyl acetate–petroleum ether) yielded **5e** (75 mg, 71%) as a colorless oil.

R_f 0.63 (25% ethyl acetate–petroleum ether); IR (film) ν_{CO} 1743 cm^{-1} ; ^1H NMR δ 7.72 (2H, d, J 8.0 Hz, 2H-*ortho* Ts), 7.30 (2H, d, J 8.0 Hz, 2H-*meta* Ts), 6.01 (1H, dd, J 10.5, 17.5 Hz, $\text{CH}=\text{CH}_2$), 5.01 (1H, d, J 17.5 Hz, $\text{CH}=\text{CHaHb}$), 4.99 (1H, dd, J 1.0, 17.5 Hz, $\text{CH}=\text{CHaHb}$), 3.96 (1H, s, CH-Ts), 3.46 (3H, s, OCH_3), 2.41 (3H, s, CH_3 Ts), 1.37 (3H, s, CH_3), 1.35 (3H, s, CH_3); ^{13}C NMR δ 166.0, 145.1, 143.6, 136.9, 129.6, 129.1, 113.1, 78.7, 52.5, 41.0, 26.1, 25.1, 21.8; MS (CI) m/z : 426, 315, 314 $[\text{M}+\text{NH}_4]^+$, 297 $[\text{M}+\text{H}]^+$, 174; HRMS (CI) m/z calcd for $[\text{C}_{15}\text{H}_{20}\text{O}_4\text{S}+\text{NH}_4]^+$: 297.1161, found: 297.1158; Anal. calcd for $\text{C}_{15}\text{H}_{20}\text{O}_4\text{S}$: C, 60.79; H, 6.80; found: C, 61.00; H, 6.96.

Methyl 4-methyl-3-phenyl-(toluene-4-sulfonyl)pent-4-enoate (**5f**)

Method A: According to the general procedure, a mixture of tosylmalonate **4f** (61 mg, 0.15 mmol), BSA (37 μ L, 0.15 mmol, 1 equiv.) and KOAc (1.5 mg, 0.015 mmol, 0.1 equiv.) in CH_2Cl_2 (2 mL) was stirred for 24 h. Chromatography (35% ethyl acetate–petroleum ether) yielded *methyl 4-methyl-3-phenyl-(toluene-4-sulfonyl)pent-4-enoate* **5f** (30 mg, 55%) as a colorless solid.

Method B: According to the general procedure, a mixture of tosylmalonate **4f** (106 mg, 0.26 mmol), TBDMSOTf (146 μ L, 0.55 mmol, 2.1 equiv.) and DBU (83 μ L, 0.55 mmol, 2.1 equiv.) in CH_2Cl_2 (1 mL) was stirred for 15 min. Chromatography (25% ethyl acetate–petroleum ether) yielded **5f** (55 mg, 59%) as a colorless solid.

R_f 0.59 (25% ethyl acetate–petroleum ether); IR (film) ν_{CO} 1743 cm^{-1} ; ^1H NMR δ 7.80 (2H, d, J 8.5 Hz, 2H-*ortho* Ts), 7.32–7.00 (7H, m, 2H-*meta* Ts, 5H Ph), 5.09 (s, $\text{C}=\text{CHaHb}$ minor isomer), 4.90 (s, $\text{C}=\text{CHaHb}$ major isomer), 4.87 (s, $\text{C}=\text{CHaHb}$ minor isomer), 4.77 (d, J 12.0

Hz, *CH*-Ts minor isomer), 4.75 (s, *C=CHaHb* major isomer), 4.74 (d, *J* 12.0 Hz, *CH*-Ts major isomer), 4.10 (d, *J* 12.0 Hz, *CH*-Ph minor isomer), 4.08 (d, *J* 12.0 Hz, *CH*-Ph major isomer), 3.71 (s, OCH₃ major isomer), 3.29 (s, OCH₃ minor isomer), 2.44 (s, CH₃ Ts minor isomer), 2.34 (s, CH₃ Ts major isomer), 1.60 (s, CH₃ major isomer), 1.57 (s, CH₃ minor isomer); ¹³C NMR δ 166.0 and 165.7, 145.8 and 145.4, 144.5, 142.6, 138.8, 136.9, 136.2, 135.0, 129.7, 129.5, 129.4, 129.1, 128.5, 128.3, 127.9, 127.4, 114.8, 111.4, 74.5 and 12.8, 53.2 and 52.7, 52.2 and 51.6, 21.9 and 19.5, 21.8 and 21.7; MS (CI) *m/z*: 734, 735, 377, 376 [M+NH₄]⁺, 359 [M+H]⁺, 203; HRMS (CI) *m/z* calcd for [C₂₀H₂₂O₄S+NH₄]⁺: 376.1583, found: 376.1596; Anal. calcd for C₂₀H₂₂O₄S: C, 67.01; H, 6.19; found: C, 66.89; H, 6.22.

(1'*R*, 5'*S*)-Methyl (5-isopropenyl-2-methylenecyclohexyl)(toluene-4-sulfonyl)acetate and (1'*S*, 5'*S*)-methyl (5-isopropenyl-2-methylenecyclohexyl)(toluene-4-sulfonyl)acetate (5g**)**

Method A: According to the general procedure, a mixture of tosylmalonate **4g** (55 mg, 0.14 mmol), BSA (33 μL, 0.14 mmol, 1 equiv.) and KOAc (1 mg, 0.014 mmol, 0.1 equiv.) in CH₂Cl₂ (4 mL) was stirred for 20 h. Chromatography (35% ethyl acetate–petroleum ether) yielded an inseparable mixture of (1'*R*, 5'*S*)-methyl (5-isopropenyl-2-methylenecyclohexyl)(toluene-4-sulfonyl)acetate and (1'*S*, 5'*S*)-methyl (5-isopropenyl-2-methylenecyclohexyl)(toluene-4-sulfonyl)acetate **5g** (22 mg, 45%) as a colorless solid.

*R*_f 0.50 (25% ethyl acetate–petroleum ether); IR (film) ν_{CO} 1743 cm⁻¹; ¹H NMR δ 7.81–7.74 (2H, m, 2H-ortho Ts), 7.35–7.26 (2H, m, 2H-meta Ts), 4.95–4.60 (4H, m, 2 C=CH₂), 4.51 (d, *J* 11.5 Hz, CH-Ts minor (1'*R*, 5'*S*) compound), 4.47 (d, *J* 12.0 Hz, CH-Ts major (1'*R*, 5'*S*) compound), 4.19 (d, *J* 11.5 Hz, CH-Ts (1'*S*, 5'*S*) compound), 3.44–2.90 (m, 1H), 2.72–2.45 (m, 1H), 2.43 (3H, s, CH₃ Ts), 2.40–1.72 (m, 4H), 1.71 (s, CH₃ major (1'*R*, 5'*S*) compound), 1.60 (s, CH₃ minor (1'*R*, 5'*S*) compound), 1.59–1.10 (m, 2H); ¹³C NMR δ 166.3 and 166.2, 148.9 and 148.5, 135.4, 129.7, 129.6, 129.3, 113.7, 112.4, 109.5 and 109.2, 53.0 and 52.7 and 52.6, 42.9 and 42.3, 40.0 and 39.5, 38.7, 37.2, 37.1, 37.0, 33.9, 33.0, 32.6, 31.1, 30.6, 21.8

and 21.1 and 20.5; MS (CI) m/z : 380 $[M+NH_4]^+$, 134; HRMS (CI) m/z calcd for $[C_{20}H_{26}O_4S+NH_4]^+$: 380.1896, found: 380.1888; Anal. calcd for $C_{20}H_{26}O_4S$: C, 66.27; H, 7.23; found: C, 66.39; H, 7.20.

(1'R, 3'S, 5'R)-Methyl (6,6-dimethyl-2-methylenebicyclo[3.1.1]hept-3-yl)(toluene-4-sulfonyl)acetate (5h)

Method A: According to the general procedure, a mixture of tosylmalonate **4h** (82 mg, 0.20 mmol), BSA (49 μ L, 0.20 mmol, 1 equiv.) and KOAc (2 mg, 0.02 mmol, 0.1 equiv.) in CH_2Cl_2 (2 mL) was stirred for 18 h. Chromatography (25% ethyl acetate–petroleum ether) yielded (1'R, 3'S, 5'R)-methyl (6,6-dimethyl-2-methylenebicyclo[3.1.1]hept-3-yl)(toluene-4-sulfonyl)acetate **5h** (53 mg, 72%) as a colorless oil.

Method B: According to the general procedure, a mixture of tosylmalonate **4h** (72 mg, 0.18 mmol), TBDMSOTf (85 μ L, 0.37 mmol, 2.1 equiv.) and DBU (56 μ L, 0.37 mmol, 2.1 equiv.) in CH_2Cl_2 (1 mL) was stirred for 15 min. Chromatography (25% ethyl acetate–petroleum ether) yielded **5h** (49 mg, 76%) as a colorless oil.

R_f 0.76 (25% ethyl acetate–petroleum ether); IR (film) ν_{CO} 1742 cm^{-1} ; 1H NMR δ 7.81 (d, J 8.0 Hz, 2H-*ortho* Ts one isomer), 7.80 (d, J 8.5 Hz, 2H-*ortho* Ts other isomer), 7.35 (d, J 8.5 Hz, 2H-*meta* Ts one isomer), 7.34 (d, J 8.0 Hz, 2H-*meta* Ts other isomer), 4.79 (dd, J 2.0, 10.0 Hz, $C=CH_2$ major isomer), 4.63 (s, $C=CH_2$ minor isomer), 4.35 (d, J 3.5 Hz, CH -Ts major isomer), 4.25 (d, J 11.0 Hz, CH -Ts minor isomer), 3.60 (m, CH -CH-Ts), 3.58 (s, OCH_3 major isomer), 3.46 (s, OCH_3 minor isomer), 3.21 (m, CH -CH-Ts), 2.60-1.90 (5H, m), 2.44 (3H, s, CH_3 Ts), 1.41 (d, J 10.5 Hz, CH one isomer), 1.22 (s, CH_3 one isomer), 1.21 (s, CH_3

other isomer), 0.82 (d, *J* 10.0 Hz, CH other isomer), 0.78 (s, CH₃ one isomer), 0.78 (s, CH₃ one isomer), 0.64 (s, CH₃ other isomer); ¹³C NMR δ 166.7 and 166.0, 151.7, 149.3, 145.3, 135.5 and 134.8, 129.8, 129.7, 129.5, 129.3, 112.7 and 109.9, 80.1 and 75.6, 52.6, 52.3, 52.2, 52.0, 41.0, 40.7, 40.6, 40.0, 34.1 and 32.7, 28.9, 27.6, 26.9, 26.1, 26.0, 25.7, 21.9, 21.8, 21.7; MS (CI) *m/z*: 380 [M+NH₄]⁺, 363 [M+H]⁺, 209; HRMS (CI) *m/z* calcd for [C₂₀H₂₆O₄S+NH₄]⁺: 380.1896, found: 380.1907; Anal. calcd for C₂₀H₂₆O₄S: C, 66.27; H, 7.23; found: C, 66.08; H, 7.15.

(*E*)-Methyl 3-methyl-(toluene-4-sulfonyl)hex-4-enoate (5i)

Method A: According to the general procedure, a mixture of tosylmalonate **4i** (86 mg, 0.25 mmol), BSA (61 μL, 0.25 mmol, 1 equiv.) and KOAc (3 mg, 0.025 mmol, 0.1 equiv.) in CH₂Cl₂ (2 mL) was stirred for 15 h. Chromatography (25% ethyl acetate–petroleum ether) yielded (*E*)-methyl 3-methyl-(toluene-4-sulfonyl)hex-4-enoate **5i** (66 mg, 88%) as a colorless oil.

Method B: According to the general procedure, a mixture of tosylmalonate **4i** (139 mg, 0.41 mmol), TBDMSOTf (197 μL, 0.86 mmol, 2.1 equiv.) and DBU (128 μL, 0.86 mmol, 2.1 equiv.) in CH₂Cl₂ (1.5 mL) was stirred for 15 min. Chromatography (25% ethyl acetate–petroleum ether) yielded **5i** (100 mg, 83%) as a colorless oil.

*R*_f 0.67 (25% ethyl acetate–petroleum ether); IR (film) ν_{CO} 1743 cm⁻¹; ¹H NMR δ 7.74 (d, *J* 8.5 Hz, 2H-*ortho* Ts one isomer), 7.71 (d, *J* 8.5 Hz, 2H-*ortho* Ts other isomer), 7.31 (d, *J* 8.0 Hz, 2H-*meta* Ts one isomer), 7.30 (d, *J* 8.0 Hz, 2H-*meta* Ts other isomer), 5.49 (qd, *J* 2.0, 6.0 Hz, CH=CH-Me one isomer), 5.43 (qd, *J* 2.0, 6.5 Hz, CH=CH-Me other isomer), 5.24 (m, CH=CH-Me one isomer), 5.19 (m, CH=CH-Me other isomer), 3.86 (d, *J* 14.0 Hz, CH-Ts one isomer), 3.83 (d, *J* 15.5 Hz, CH-Ts other isomer), 3.64 (s, OCH₃ one isomer), 3.47 (s, OCH₃ other isomer), 2.93 (1H, m, CH-CH₃), 2.42 (3H, s, CH₃ Ts), 1.59 (dd, *J* 1.0, 6.0 Hz, CH-CH₃ one isomer), 1.55 (dd, *J* 1.5, 6.5 Hz, CH-CH₃ other isomer), 1.28 (d, *J* 6.5 Hz, CH=CH-CH₃ one isomer), 1.02 (d, *J* 6.5 Hz, CH=CH-CH₃ other isomer); ¹³C NMR δ 166.3, 145.3 and

145.2, 135.6 and 135.4, 131.5 and 130.8, 129.7, 129.5, 129.3, 127.9 and 127.3, 76.3 and 75.8, 52.8 and 52.5, 37.0 and 36.6, 21.8, 19.4, 19.1, 17.9; MS (CI) m/z : 314 $[M+NH_4]^+$, 297 $[M+H]^+$, 141; HRMS (CI) m/z calcd for $[C_{15}H_{20}O_4S+NH_4]^+$: 297.1161, found: 297.1159; Anal. calcd for $C_{15}H_{20}O_4S$: C, 60.79; H, 6.80; found: C, 60.84; H, 6.91.

(1'S, 5'S)-Methyl (5-isopropenyl-2-methyl-cyclohex-2-enyl)(toluene-4-sulfonyl)acetate (5j)

Method A: According to the general procedure, a mixture of tosylmalonate **4j** (60 mg, 0.15 mmol), BSA (36 μ L, 0.15 mmol, 1 equiv.) and KOAc (1.5 mg, 0.015 mmol, 0.1 equiv.) in CH_2Cl_2 (1.5 mL) was stirred for 15 h. Chromatography (25% ethyl acetate–petroleum ether) yielded (1'S, 5'S)-methyl (5-isopropenyl-2-methyl-cyclohex-2-enyl)(toluene-4-sulfonyl)acetate **5j** (10 mg, 19%) as a colorless oil.

Method B: According to the general procedure, a mixture of tosylmalonate **4j** (118 mg, 0.29 mmol), TBDMSOTf (140 μ L, 0.61 mmol, 2.1 equiv.) and DBU (91 μ L, 0.61 mmol, 2.1 equiv.) in CH_2Cl_2 (1.5 mL) was stirred for 15 min. Chromatography (25% ethyl acetate–petroleum ether) yielded **5j** (60 mg, 57%) as a colorless oil.

R_f 0.61 (25% ethyl acetate–petroleum ether); IR (film) ν_{CO} 1747 cm^{-1} ; 1H NMR δ 7.79 (2H, m, 2H-*ortho* Ts), 7.31 (2H, m, 2H-*meta* Ts), 5.58 (bs, CH=C major isomer), 5.51 (bs, CH=C minor isomer), 4.69 (2H, m, $CH_2=C$), 4.32 (d, J 3.0 Hz, CH-Ts major isomer), 4.25 (d, J 4.5 Hz, CH-Ts minor isomer), 3.60 (s, OCH_3 major isomer), 3.56 (s, OCH_3 minor isomer), 3.49–3.41 (1H, m), 3.15 (1H, bs), 2.43 (3H, s, CH_3 Ts), 2.40–1.40 (10H, m); ^{13}C NMR δ 166.8 and 165.3, 148.8, 145.3, 136.1, 131.8, 130.7, 129.8, 129.6, 129.1, 127.1, 126.3, 109.2, 71.8 and 70.6, 52.7 and 52.5, 42.0, 41.7, 41.2, 40.0, 31.7, 30.8, 30.5, 30.1, 25.8, 21.9, 21.8, 21.1, 20.8;

MS (CI) m/z: 380 $[M+NH_4]^+$, 226, 207, 174, 152, 135, 52; HRMS (CI) m/z calcd for $[C_{20}H_{26}O_4S+NH_4]^+$: 380.1896, found: 380.1877; Anal. calcd for $C_{20}H_{26}O_4S$: C, 66.27; H, 7.23; found: C, 66.41; H, 7.09.