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SUPPLEMENTARY MATERIAL TO

Substituted proline derivatives as organocatalysts in the Michael reaction

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SPECTROSCOPIC DATA FOR THE CYCLOADDITION PRODUCTS **18**–**31**

*(2*S*,4*S*,5*R*)-4-[(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl]-2-methyl 5-(2--chlorophenyl)pyrrolidine-2,4-dicarboxylate (**18**)*. Yield: 24 %; Colourless oil; IR (KBr, cm^{-1}): 2953, 1739, 1198, 1169; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm) 7.52 (1H, *m*, phenyl-H), 7.33 (1H, *m*, phenyl-H), 7.25–7.17 (2H, *m*, phenyl-H), 4.74 (1H, *d*, *J* = 7.5 Hz, 5-H), 4.31–4.26 (1H, *m*, OCH), 3.95 (1H, *t*, *J* = 8.5 Hz, 2-H), 3.82 (3H, *s*, OCH_3), 3.55 (1H, *m*, 4-H), 2.85 (1H, *bs*, NH), 2.52–2.40 (2H, *m*, 3-H), 1.70 (1H, *m*, menthyl-H), 1.53 (2H, *m*, menthyl-H), 1.14 (3H, *m*, menthyl-H), 0.91 (2H, *m*, menthyl-H), 0.82 (3H, *d*, *J* = 7 Hz, CH_3), 0.68 and 0.65 (2×3H, 2×*d*, *J* = 6.5 Hz, $CH(C\mathbf{H}_3)_2$), 0.03 (1H, *m*, menthyl-H); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm) 173.39, 172.72, 136.20, 133.69, 129.18, 128.53, 127.77, 126.80, 74.09, 62.78, 59.34, 52.21, 46.47, 46.32, 39.31, 33.94, 33.89, 30.91, 26.15, 23.29, 21.70, 20.65, 16.32; HRMS (ESI, *m*/*z*): Calcd. for $C_{23}H_{32}ClNO_4$ $(M+H)^+$: 422.20926. Found: 422.20957; specific rotation $[\alpha]_D$ ($CHCl_3$, *c* = 5.0 mg/mL): +39.

*(2*S*,4*S*,5*R*)-4-[(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl]-2-methyl 5-(2-fluorophenyl)pyrrolidine-2,4-dicarboxylate (**19**)*. Yield 32 %; White solid; m.p.: 82–83 °C; IR (KBr, cm^{-1}): 2954, 1740, 1199, 1169; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm) 7.43 (1H, *m*, phenyl-H), 7.23 (1H, *m*, phenyl-H), 7.10 (1H, *m*, phenyl--H), 7.00 (1H, *m*, phenyl-H), 4.65 (1H, *d*, *J* = 7.5 Hz, 5-H), 4.35–4.29 (1H, *m*, OCH), 3.96 (1H, *t*, *J* = 8.5 Hz, 2-H), 3.82 (3H, *s*, OCH_3), 3.40 (1H, *m*, 4-H), 2.83 (1H, *bs*, NH), 2.49 (1H, *m*, 3-H), 2.39 (1H, *m*, 3-H), 1.67 (1H, *m*, menthyl-H),

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1.54 (2H, *m*, menthyl-H), 1.16 (3H, *m*, menthyl-H), 0.88 (2H, *m*, menthyl-H), 0.82 (3H, *d*, *J* = 7 Hz, CH_3), 0.69 and 0.63 (2×3H, 2×*d*, *J* = 6.5 Hz, $CH(CH_3)_2$), 0.08 (1H, *q*, *J* = 11.5 Hz, menthyl-H); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 173.40, 172.76, 161.47, 159.51, 128.90, 127.54, 125.82, 124.07, 74.13, 59.79, 59.76, 52.23, 47.65, 46.44, 39.41, 34.24, 33.95, 30.93, 26.07, 23.22, 21.69, 20.66, 16.21. HRMS (ESI, *m*/*z*): Calcd. for $C_{23}H_{32}FNO_4$ $(M+H)^+$: 406.23881. Found: 406.24055; specific rotation $[\alpha]_D$ ($CHCl_3$, *c* = 8.8 mg/mL): –1.8.

*(2*S*,4*S*,5*R*)-4-[(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl]-2-methyl 5-o--tolylpyrrolidine-2,4-dicarboxylate (**20**)*. Yield: 31 %; White solid; m.p.: 66–67 °C; IR (KBr, cm^{-1}): 2953, 1739, 1199, 1167; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / / ppm): 7.40 (1H, *m*, phenyl-H), 7.16–7.08 (3H, *m*, phenyl-H), 4.57 (1H, *d*, *J* = = 7.5 Hz, 5-H), 4.28–4.23 (1H, *m*, OCH), 3.91 (1H, *t*, *J* = 8.5 Hz, 2-H), 3.81 (3H, *s*, OCH_3), 3.35 (1H, *m*, 4-H), 2.86 (1H, *bs*, NH), 2.46–2.42 (2H, *m*, 3-H), 2.36 (3H, *s*, Phe-CH_3), 1.67 (1H, *m*, menthyl-H), 1.52 (2H, *m*, menthyl-H), 1.09 (3H, *m*, menthyl-H), 0.88 (2H, *m*, menthyl-H), 0.82 (3H, *d*, *J* = 7.5 Hz, CH_3), 0.67 and 0.63 (2×3H, 2×*d*, *J* = 6.5 Hz, $CH(CH_3)_2$), 0.07 (1H, *q*, *J* = 11.0 Hz, menthyl-H); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 173.34, 172.53, 136.48, 135.84, 129.98, 127.18, 125.93, 125.58, 73.97, 62.66, 59.49, 52.06, 46.76, 46.51, 38.98, 34.16, 33.89, 30.80, 26.08, 23.24, 21.57, 20.57, 19.60, 16.26; HRMS (ESI, *m*/*z*): Calcd. for $C_{24}H_{35}NO_4$ $(M+H)^+$: 402.26389. Found: 402.26458; specific rotation $[\alpha]_D$ ($CHCl_3$, *c* = 1.0 mg/mL): +22.

*(2*S*,4*S*,5*R*)-4-[(1*R*,2*S*,5*R*)-2-Isopropy-5-methylcyclohexyl]-2-methyl 5-(1--benzyl-1*H*-imidazol-2-yl)pyrrolidine-2,4-dicarboxylate (**22**)*. Yield: 29 %; Yellow oil; IR (KBr, cm^{-1}): 2952, 1723, 1203, 1168; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 7.35–7.30 (3H, *m*), 7.15 (2H, *m*), 6.96 (1H, *m*), 6.79 (1H, *m*), 5.19 (2H, *s*), 4.51 (1H, *m*, OCH), 4.43 (1H, *d*, *J* = 7.5 Hz, 5-H), 3.87 (1H, *m*, 2-H), 3.75 (3H, *s*, OCH_3), 3.19 (1H, *m*, 4-H), 2.63 (1H, *m*, 3-H), 2.41 (1H, *m*, 3-H), 1.73––1.59 (4H, *m*, menthyl-H), 1.38–1.17 (2H, *m*, menthyl-H), 0.97 (1H, *m*, menthyl--H), 0.86 and 0.82 (2×3H, 2×*d*, *J* = 6.5 Hz, $CH(CH_3)_2$, 0.76 (1H, *m*, menthyl-H), 0.67 (3H, *d*, *J* = 7 Hz, CH_3), 0.43 (1H, *q*, *J* = 11.0 Hz, menthyl-H); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 173.29, 171.42, 145.52, 136.23, 128.90, 127.97, 127.77, 126.91, 120.29, 74.27, 59.58, 57.26, 52.19, 49.56, 48.26, 46.81, 40.29, 34.13, 33.19, 31.07, 25.98, 23.27, 21.85, 20.74, 16.24; HRMS (ESI, *m*/*z*): Calcd. for $C_{27}H_{37}N_3O_4$ $(M+H)^+$: 468.28568. Found: 468.28442; specific rotation $[\alpha]_D$ ($CHCl_3$, *c* = 4.0 mg/mL): –18.

*(2*S*,4*S*,5*R*)-4-[(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl]-2-methyl 5-(pyridin-2-yl)pyrrolidine-2,4-dicarboxylate (**23**)*. Yield: 38 %; White solid; m.p.: 104––105 °C; IR (KBr, cm^{-1}): 2955, 1727, 1707, 1195, 1168; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm) 8.59 (1H, *m*, Py-H), 8.49 (1H, *m*, Py-H), 7.75 (1H, *m*, Py-H), 7.25 (1H, *m*, Py-H), 4.54 (1H, *d*, *J* = 8.0 Hz, 5-H), 4.37–4.32 (1H, *m*, OCH), 3.99 (1H, *t*, *J* = 8.5 Hz, 2-H), 3.82 (3H, *s*, OCH_3), 3.37 (1H, *m*, 4-H), 2.52–2.38 (2H,

m, 3-H), 1.56 (3H, *m*, menthyl-H), 1.20 (2H, *m*, menthyl-H), 1.01 (1H, *m*, menthyl-H), 0.89 (2H, *m*, menthyl-H), 0.81 (3H, *d*, *J* = 7 Hz, CH_3) 0.74 and 0.59 (2×3H, 2×*d*, *J* = 6.5 Hz, CH(C**H**$_3$)$_2$), 0.25 (1H, *q*, *J* = 11.0 Hz, menthyl-H); ^{13}C--NMR (125 MHz, $CDCl_3$, *δ* / ppm): 173.38, 171.92, 149.21, 148.72, 134.93, 134.50, 123.22, 74.53, 63.05, 59.69, 52.28, 48.93, 46.43, 39.76, 33.85, 33.78, 30.98, 26.03, 23.14, 21.69, 20.63, 16.07; HRMS (ESI, *m*/*z*): Calcd. for $C_{22}H_{32}N_2O_4$ $(M+H)^+$: 389.24348. Found: 389.24347; specific rotation $[\alpha]_D$ ($CHCl_3$, *c* = 1.2 mg/mL): –16.

*(2*S*,4*S*,5*S*)-4-[(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl]-2-methyl 5-cyclohexylpyrrolidine-2,4-dicarboxylate (**24**)*. Yield: 33 %; White solid; m.p.: 106––107 °C; IR (KBr, cm^{-1}): 2917, 1737, 1719, 1158; ^{1}H-NMR (500 MHz, $CDCl_3$, *δ* / ppm) 4.68 (1H, *m*, OCH), 3.84 (1H, *m*, 2-H), 3.76 (3H, *s*, OCH_3), 2.90 (1H, *m*, 4-H), 2.79 (1H, *m*, 5-H), 2.37–2.30 (2H, *m*, 3-H), 2.17 (1H, *m*), 2.09 (1H, *m*), 1.95–1.83 (3H, *m*), 1.75–1.65 (5H, *m*), 1.46 (1H, *m*), 1.37 (2H, *m*), 1.23–1.16 (4H, *m*), 1.07–0.96 (3H, *m*), 0.91 and 0.89 (2×3H, 2×*d*, *J* = 3.5 Hz, CH(C**H**$_3$)$_2$), 0.75 (3H, *d*, *J* = 7 Hz, CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$, *δ* / ppm): 174.20, 173.63, 74.22, 70.16, 59.72, 52.07, 46.72, 45.79, 40.95, 39.48, 35.11, 34.15, 31.72, 31.29, 30.98, 26.31, 26.26, 25.89, 25.67, 23.26, 21.96, 20.72, 16.17; HRMS (ESI, *m*/*z*): Calcd. for $C_{23}H_{39}NO_4$ $(M+H)^+$: 394.29519. Found: 394.29437; specific rotation $[\alpha]_D$ ($CHCl_3$, *c* = 3.5 mg/mL): –4.5.

*(2*S*,4*S*,5*S*)-4-[(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl]-2-methyl 5-isopropylpyrrolidine-2,4-dicarboxylate (**25**)*. Yield: 20 %; White amorphous solid; m.p.: 51–53 °C; IR (KBr, cm^{-1}): 2955, 2928, 1738, 1205, 1167; ^{1}H-NMR (500 MHz, $CDCl_3$. *δ* / ppm): 4.68 (1H, *m*, OCH), 3.89 (1H, *m*, 2-H), 3.77 (3H, *s*, OCH_3), 3.00 (1H, *bs*, NH), 2.90 (1H, *m*, 4-H), 2.77 (1H, *m*, 5-H), 2.37 (1H, *m*, 3-H), 2.20 (1H, *m*, 3-H), 1.96 (1H, *m*), 1.85 (1H, *m*), 1.67 (3H, *m*), 1.49–1.34 (3H, *m*), 1.10 and 1.02 (2×3H, 2×*d*, *J* = 6.5 Hz, CH(C**H**$_3$)$_2$), 0.99–0.92 (2H, *m*), 0.90 and 0.89 (2×3H, 2×*d*, *J* = 2 Hz, CH(C**H**$_3$)$_2$-menthyl), 0.73 (3H, *d*, *J* = 7 Hz, CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$, *δ* / ppm) 174.09, 173.54, 74.48, 71.42, 59.66, 52.17, 46.80, 45.97, 40.70, 35.17, 34.18, 31.35, 30.09, 26.32, 23.31, 21.99, 21.60, 21.01, 20.71, 16.13; HRMS (ESI, *m*/*z*): Calcd. for $C_{20}H_{35}NO_4$ $(M+H)^+$: 354.26389. Found: 354.26240; specific rotation $[\alpha]_D$ ($CHCl_3$, *c* = 2.0 mg/mL): –44.

*(2*S*,4*S*,5*R*)-2-Isopropyl-4-[(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl] 5-phenylpyrrolidine-2,4-dicarboxylate (**28**)*. Yield: 24 %; White solid: m.p.: 124––126 °C; IR (KBr, cm^{-1}): 2951, 2929, 1725, 1211, 1167; ^{1}H-NMR (500 MHz, $CDCl_3$, *δ* / ppm): 7.35 (2H, *m*, phenyl-H), 7.29 (2H, *m*, phenyl-H), 7.22 (1H, *m*, phenyl-H), 5.15 (1H, *m*, OC**H**$(CH_3)_2$), 4.49 (1H, *d*, *J* = 7.5 Hz, 5-H), 4.36 (1H, *m*, OCH), 3.92 (1H, *t*, *J* = 8.5 Hz, 2-H), 3.27 (1H, *m*, 4-H), 2.95 (1H, *bs*, NH), 2.47 (1H, *m*, 3-H), 2.32 (1H, *m*, 3-H), 1.55–1.46 (3H, *m*, menthyl-H), 1.30 and 1.29 (2×3H, 2×*d*, *J* = 2.5 Hz, OCH(C**H**$_3$)$_2$), 1.22–1.07 (3H, *m*, menthyl-H), 0.86

(1H, *m*, menthyl-H), 0.78 and 0.73 (2×3H, 2×*d*, *J* = 6.5 Hz, CH(C**H**$_3$)$_2$), 0.68 (1H, *m*, menthyl-H), 0.55 (3H, *d*, *J* = 7.0 Hz, CH_3), 0.29 (1H, *q*, *J* = 11.0 Hz, menthyl-H); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 172.70, 172.47, 139.13, 128.24, 127.38, 127.10, 74.05, 68.59, 65.83, 60.16, 49.32, 46.54, 39.75, 34.53, 33.99, 31.02, 25.87, 23.11, 21.77, 21.74, 20.72, 16.00; HRMS (ESI, *m*/*z*): Calcd. for $C_{25}H_{37}NO_4$ $(M+H)^+$: 416.27954. Found 416.27938; specific rotation $[\alpha]_D$ ($CHCl_3$, *c* = 1.5 mg/mL) = –26.

*(2*S*,4*S*,5*R*)-2-Cyclohexyl-4-[(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl] 5--phenylpyrrolidine-2,4-dicarboxylate (**29**)*. Yield: 54 %; White solid; m.p.: 126––127 °C; IR (KBr, cm^{-1}): 2940, 2864, 1735, 1711, 1199, 1168; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm) 7.35 (2H, *m*, phenyl-H), 7.30 (2H, *m*, phenyl-H), 7.23 (1H, *m*, phenyl-H), 4.91 (1H, *m*, OCH), 4.50 (1H, *d*, *J* = 7.5 Hz, 5-H), 4.36 (1H, *m*, OCH), 3.94 (1H, *t*, *J* = 8.5 Hz, 2-H), 3.33 (1H, *m*, 4-H), 2.92 (1H, *bs*, NH), 2.49 (1H, *m*, 3-H), 2.32 (1H, *m*, 3-H), 1.93–1.86 (2H, *m*), 1.78–1.69 (3H, *m*), 1.55–1.05 (12H, *m*), 086 (1H, *m*), 0.78 and 0.73 (2×3H, 2×*d*, *J* = 6.5 Hz CH(C**H**$_3$)$_2$, 0.55 (3H, *d*, *J* = 7.0 Hz, CH_3), 0.29 (1H, *q*, *J* = 11.0 Hz, menthyl-H); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 172.70, 172.47, 139.21, 128.27, 127.41, 127.13, 74.07, 73.41, 65.85, 60.23, 49.38, 46.56, 39.78, 34.63, 34.01, 31.51, 31.04, 25.89, 25.34, 23.62, 23.13, 21.77, 20.75, 16.02; HRMS (ESI, *m*/*z*): Calcd. for $C_{28}H_{41}NO_4$ $(M+H)^+$: 456.31084. Found: 456.31067; specific rotation $[\alpha]_D$ ($CHCl_3$, *c* = 1.6 mg/mL): –26.

*(2*S*,4*S*,5*R*)-2-*tert*-Butyl-4-[(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl] 5--phenylpyrrolidine-2,4-dicarboxylate (**30**)*. Yield: 24 %; White solid; m.p.: 134––135 °C; IR (KBr, cm^{-1}): 2961, 2929, 1732, 1190, 1156l; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm) 7.35 (2H, *m*, phenyl-H), 7.28 (2H, *m*, phenyl-H), 7.22 (1H, *m*, phenyl-H), 4.48 (1H, *d*, *J* = 7.5 Hz, 5-H), 4.36 (1H, *m*, OCH), 3.86 (1H, *t*, *J* = 8.5 Hz, 2-H), 3.32 (1H, *m*, 4-H), 2.46 (1H, *m*, 3-H), 2.26 (1H, *m*, 3-H), 1.51 (3×3H, s, C(CH_3)$_3$), 1.45 (3H, *m*, menthyl-H), 1.26–1.08 (3H, *m*, menthyl-H), 0.86 (1H, *m*, menthyl-H), 0.78 and 0.73 (2×3H, 2×*d*, *J* = 6.5 Hz CH(C**H**$_3$)$_2$), 0.68 (1H, *m*, menthyl-H), 0.55 (3H, *d*, *J* = 7.0 Hz, CH_3), 0.32 (1H, *q*, *J* = 11.0 Hz, menthyl-H); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm): 172.49, 172.31, 139.30, 128.25, 127.35, 127.11, 81.44, 74.02, 65.73, 60.65, 49.39, 46.57, 39.80, 34.75, 34.02, 31.05, 28.09, 25.85, 23.11, 21.77, 20.76, 16.00; HRMS (ESI, *m*/*z*): Calcd. for $C_{26}H_{39}NO_4$ $(M+H)^+$: 430.29519. Found 430.29574; specific rotation $[\alpha]_D$ ($CHCl_3$, *c* = 2.0 mg/mL): –29.5.

*(2*R*,3*S*,5*S*)-[(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl] 5-(*N*,*N*-diethyl-carbamoyl)-2-phenylpyrrolidine-3-carboxylate (**31**)*. Yield: 29 %; Yellow amorphous solid; m.p.: 103–104 °C; IR (KBr, cm^{-1}): 2961, 2933, 1720, 1632, 1418, 1161; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm) 7.39 (2H, *m*, phenyl-H), 7.29 (2H, *m*, phenyl-H), 7.22 (1H, *m*, phenyl-H), 4.55 (1H, *d*, *J* = 8.5 Hz, 5-H), 4.35 (1H, *m*, OCH), 4.06 (1H, *m*, 2-H), 3.51 (1H, *m*, 4-H), 3.46–3.32 (4H, *m*, N(CH_2)$_2$),

2.40 (1H, *m*, 3-H), 2.21 (1H, *m*, 3-H), 1.52 (2H, *m*, menthyl-H), 1.44 (1H, *m*, menthyl-H), 1.23–1.16 (2×3H, 2×*t*, *J* = 7.5 Hz, $N(CH_2C\mathbf{H}_3)_2$), 1.20 (2H, *m*, menthyl-H), 1.05 (1H, *m*, menthyl-H), 0.88 (1H, *m*, menthyl-H), 0.78 and 0.73 (2×3H, 2×*d*, *J* = 6.5 Hz, $CH(C\mathbf{H}_3)_2$), 0.68 (1H, *m*, menthyl-H), 0.54 (3H, *d*, *J* = = 7.0 Hz, CH_3), 0.36 (1H, *q*, *J* = 11.0 Hz, menthyl-H); ^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm) 172.01, 170.72, 139.61, 128.30, 127.46, 127.07, 74.18, 65.07, 58.18, 50.46, 46.43, 41.13, 40.28, 39.67, 34.97, 33.95, 31.01, 25.77, 23.07, 21.74, 20.74, 16.00, 14.45, 12.90; HRMS (ESI, *m*/*z*): Calcd. for $C_{26}H_{40}N_2O_3$ $(M+H)^+$: 429.31117. Found: 429.31006. specific rotation $[\alpha]_D$ ($CHCl_3$, *c* =1.2 mg/mL): –38.3.

SPECTRAL DATA FOR THE ADDITION PRODUCTS **6**–**13**

*(*R*)-2-[2,2-Bis(phenylsulphonyl)ethyl]heptanal*[1] ***(6)***. Yield: 97 %; White amorphous solid; m.p.: 86–87 °C; IR (KBr, cm^{-1}): 2925, 1728, 1449, 1312, 1152; ^{1}H-NMR (200 MHz, $CDCl_3$; δ / ppm): 9.53 (1H, *s*), 7.96–7.87 (4H, *m*), 7.74–7.66 (2H, *m*), 7.60–7.52 (4H, *m*), 4.76–4.70 (1H, *m*), 3.00–2.89 (1H, *m*), 2.56–2.42 (1H, *m*), 2.24–2.10 (1H, *m*), 1.73–1.39 (2H, *m*), 1.34–1.14 (6H, *m*), 0.88 (3H, *t*, *J* = 6.4 Hz); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 203.48, 137.70, 134.72, 134.57, 129.64, 129.35, 129.15, 80.53, 48.85, 31.59, 29.26, 26.06, 24.31, 22.25, 13.84; HRMS (ESI, *m*/*z*): Calcd. for $C_{21}H_{26}O_5S_2$ $(M+H)^+$: 423.12944. Found: 423.13019; specific rotation $[\alpha]_D$ ($CHCl_3$, *c* = 1.5 mg/mL): +16.

*(*R*)-2-[2,2-Bis(phenylsulphonyl)ethyl]hexanal*[1] ***(7)***. Yield: 99 %; White amorphous solid; m.p.: 60–62 °C; IR (KBr, cm^{-1}): 2924, 1723, 1447, 1332, 1308, 1163; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 9.53 (1H, *s*), 7.96–7.87 (4H, m), 7.73–7.66 (2H, *m*), 7.60–7.52 (4H, *m*), 4.76–4.70 (1H, m), 2.99–2.89 (1H, *m*), 2.56–2.42 (1H, *m*), 2.24–2.10 (1H, *m*), 1.73–1.43 (2H, *m*), 1.33–1.19 (4H, *m*), 0.88 (3H, *t*, *J* = 6.8 Hz); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 203.46, 137.70, 134.72, 134.57, 129.64, 129.35, 129.15, 80.53, 48.81, 28.99, 28.48, 24.31, 22.52, 13.68; HRMS (ESI, *m*/*z*): Calcd. for $C_{20}H_{24}O_5S_2$ $(M+H)^+$: 409.11379. Found: 409.11308; specific rotation $[\alpha]_D$ ($CHCl_3$, *c* = 4.0 mg/mL): +6.

*(*R*)-2-[2,2-Bis(phenylsulphonyl)ethyl]dodecanal* ***(8)***. Yield: 70 %; Colourless oil; IR (KBr, cm^{-1}): 2923, 1723, 1447, 1311, 1150; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 9.54 (1H, *s*), 7.96–7.87 (4H, *m*), 7.71–7.65 (2H, *m*), 7.60–7.52 (4H, *m*), 4.76–4.70 (1H, *m*), 3.00–2.89 (1H, *m*), 2.56–2.42 (1H, *m*), 2.24–2.10 (1H, *m*), 1.73–1.40 (2H, *m*), 1.34–1.14 (16H, *m*), 0.88 (3H, *t*, *J* = 6.4 Hz); ^{13}C--NMR (50 MHz, $CDCl_3$, δ / ppm): 203.47, 137.67, 134.70, 134.55, 129.65, 129.36, 129.15, 129.11, 80.53, 48.85, 31.79, 29.46, 29.31, 29.22, 26.40, 24.33, 22.58, 14.02; HRMS (ESI, *m*/*z*): Calcd. for $C_{26}H_{36}O_5S_2$ $(M+NH_4)^+$: 510.23424. Found: 510.23410; specific rotation $[\alpha]_D$ ($CHCl_3$, *c* = 5.0 mg/mL): +4.8.

*(*R*)-2-Benzyl-4,4-bis(phenylsulphonyl)butanal*[1] ***(9)***. Yield: 99 %; White amorphous solid; m.p.: 80–81 °C); IR (KBr, cm^{-1}): 1722, 1327, 1311, 1150; ^{1}H-NMR

(200 MHz, $CDCl_3$, δ / ppm): 9.66 (1H, *s*), 7.87–7.84 (2H, *m*), 7.71–7.59 (4H, *m*), 7.58–7.26 (7H, *m*), 7.22–7.15 (2H, *m*), 4.73–4.67 (1H, *m*), 3.48–3.34 (1H, *m*), 3.20–3.10 (1H, *m*), 2.67–2.45 (2H, *m*), 2.13–1.99 (1H, *m*); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 202.59, 137.94, 137.03, 136.61, 134.57, 134.48, 129.87, 129.22, 129.13, 129.09, 128.94, 127.01, 80.28, 50.27, 35.63, 24.13; HRMS (ESI, *m*/*z*): Calcd. for $C_{23}H_{22}O_5S_2$ $(M+H)^+$: 443.09814. Found: 443.09792; specific rotation $[\alpha]_D$ ($CHCl_3$, *c* = 5.0 mg/mL): +5.4.

*(*R*)-2-(4-Methoxybenzyl)-4,4-bis(phenylsulphonyl)butanal (**10**)*. Yield 98 %; White amorphous solid; m.p.: 95–96 °C; IR (KBr, cm^{-1}): 1721, 1511, 1447, 1327, 1311, 1151; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 9.65 (1H, *s*), 7.87–7.83 (2H, *m*), 7.71–7.65 (4H, *m*), 7.64–7.40 (4H, *m*), 7.10 (2H, *d*, *J* = 8.5 Hz), 6.90 (2H, *d*, *J* = 8.5 Hz), 4.74–4.67 (1H, *m*), 3.83 (3H, *s*), 3.44–3.30 (1H, *m*), 3.14––3.05 (1H, *m*), 2.63–2.43 (2H, *m*), 2.13–1.99 (1H, *m*); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 202.79, 158.62, 137.92, 136.65, 134.57, 134.48, 130.15, 129.91, 129.24, 129.09, 128.89, 114.31, 80.29, 55.26, 50.45, 34.74, 24.03; HRMS (ESI, *m*/*z*): Calcd. for $C_{24}H_{24}O_6S_2$ $(M+H)^+$: 473.10871. Found: 473.10822; specific rotation $[\alpha]_D$ ($CHCl_3$, *c* = 5.0 mg/mL): +1.2.

*(*R*)-2-[(Naphthalen-1-yl)methyl]-4,4-bis(phenylsulphonyl)butanal (**11**)*. Yield: 99 %; Yellow amorphous solid; m.p.: 120–121 °C; IR (KBr, cm^{-1}): 1721, 1447, 1328, 1310, 1150; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 9.73 (1H, *s*), 8.00–7.87 (2H, *m*), 7.83–7.75 (3H, *m*), 7.64–7.34 (9H, *m*), 7.27–7.21 (3H, *m*), 4.70–4.64 (1H, *m*), 3.70–3.40 (2H, *m*), 3.02–2.91 (1H, *m*), 2.76–2.62 (1H, *m*), 2.14–2.00 (1H, *m*); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 202.61, 137.99, 136.21, 134.41, 134.02, 132.75, 131.35, 129.56, 129.07, 129.04, 128.73, 127.94, 127.80, 126.67, 126.07, 125.50, 123.15, 80.19, 48.98, 33.07, 24.51; HRMS (ESI, *m*/*z*): Calcd. for $C_{27}H_{24}O_5S_2$ $(M+NH_4)^+$: 510.14034. Found: 510.13951. specific rotation $[\alpha]_D$ ($CHCl_3$, *c* = 6.4 mg/mL): –3.3.

*(*R*)-2-(3,4-Dichlorobenzyl)-4,4-bis(phenylsulphonyl)butanal (**12**)*. Yield: 98 %; Colourless oil; IR (KBr, cm^{-1}): 1723, 1447, 1328, 1311, 1150; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 9.64 (1H, *s*), 7.89–7.83 (2H, *m*), 7.75–7.64 (4H, *m*), 7.59–7.48 (4H, *m*), 7.41 (1H, *d*, *J* = 7.8 Hz), 7.25 (1H, *d*, *J* = 1.8 Hz), 7.03 (1H, *m*), 4.73–4.66 (1H, *m*), 3.43–3.29 (1H, *m*), 3.14–3.04 (1H, *m*), 2.67–2.42 (2H, *m*), 2.09–1.95 (1H, *m*); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm); 201.81, 137.65, 137.28, 136.65, 134.83, 134.66, 132.86, 131.26, 130.95, 130.84, 129.75, 129.24, 129.20, 129.02, 128.54, 80.17, 49.91, 34.54, 24.05; HRMS (ESI, *m*/*z*): Calcd. for $C_{23}H_{20}Cl_2O_5S_2$ $(M+H)^+$: 511.02020. Found 511.01930; specific rotation $[\alpha]_D$ ($CHCl_3$, *c* = 6.0 mg/mL): –4.

*(R)-2-(4-Fluorobenzyl)-4,4-bis(phenylsulphonyl)butanal (**13**)*. Yield: 77 %; Colourless oil; IR (KBr, cm^{-1}): 1722, 1508, 1447, 1327, 1311, 1151; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 9.65 (1H, *s*), 7.87–7.83 (2H, *m*), 7.71–7.65 (4H, *m*), 7.62–7.42 (4H, *m*), 7.17–6.98 (4H, *m*), 4.74–4.67 (1H, *m*), 3.47–3.32 (1H, *m*),

3.16–3.06 (1H, *m*), 2.69–2.42 (2H, *m*), 2.11–1.97 (1H, *m*); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 202.43, 164.30, 159.41, 137.77, 136.65, 134.70, 134.55, 132.68, 132.62, 130.73, 130.57, 129.82, 129.22, 129.13, 128.94, 115.98, 115.54, 80.22, 50.27, 34.74, 24.02; HRMS (ESI, *m*/*z*): Calcd. for $C_{23}H_{21}FO_5S_2$ $(M+H)^+$: 461.08872. Found: 461.08804; specific rotation $[\alpha]_D$ ($CHCl_3$, *c* = 6.3 mg/mL): –1.3.

SPECTRAL DATA FOR THE ADDITION PRODUCTS **14**–**16**

*(*S*)-2-[2,2-Bis(phenylsulphonyl)ethyl]cyclohexanone*[2] ***(14)***. Yield: 42 %, White amorphous solid; m.p.: 149–151 °C; IR (KBr, cm^{-1}): 2940, 1702, 1448, 1310, 1144; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 7.97–7.87 (4H, *m*), 7.74–7.67 (2H, *m*), 7.61–7.56 (4H, *m*), 5.02–4.96 (1H, *q*), 3.16–3.01 (1H, *m*), 2.60–2.45 (1H, *m*), 2.35–2.29 (2H, *m*), 2.16–1.98 (3H, *m*), 1.87–1.56 (2H, *m*), 1.32–1.21 (2H, *m*); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 212.44, 137.92, 134.63, 134.44, 129.73, 129.25, 129.11, 129.04, 80.61, 47.29, 41.99, 34.76, 27.75, 26.44, 24.95; HRMS (ESI, *m*/*z*): Calcd. for $C_{20}H_{22}O_5S_2$ $(M+H)^+$: 407.09814. Found: 407.09747; specific rotation $[\alpha]_D$ ($CHCl_3$, *c* = 1.1 mg/mL): –5.5.

(S)-2-[2,2-Bis(phenylsulphonyl)ethyl]cyclopentanone ***(15)***. Yield: 56 %; White amorphous solid; m.p.: 110–112 °C; IR (KBr, cm^{-1}): 2916, 1731, 1447, 1327, 1310, 1140; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 7.97–7.90 (4H, *m*), 7.74–7.64 (2H, *m*), 7.61–7.48 (4H, *m*), 5.43–5.38 (1H, *q*), 2.80–2.63 (1H, *m*), 2.44–2.37 (1H, *m*), 2.34–2.21 (2H, *m*), 2.07–1.74 (3H, *m*), 1.58–1.43 (2H, *m*); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / pm): 220.04, 137.88, 137.54, 134.59, 134.53, 129.55, 129.11, 125.52, 79.60, 45.25, 38.02, 30.26, 25.96, 20.25; HRMS (ESI, *m*/*z*): Calcd. for $C_{19}H_{20}O_5S_2$ $(M+H)^+$: 393.08249. Found: 393.08133; specific rotation $[\alpha]_D$ ($CHCl_3$, *c* = 1.2 mg/mL): –10.8.

(S)-4-Methyl-6,6-bis(phenylsulphonyl)3-hexanone ***(16)***. Yield: 51 %; Colourless oil; IR (KBr, cm^{-1}): 2935, 1708, 1447, 1327, 1311, 1148; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 7.98–7.90 (4H, *m*), 7.75–7.65 (2H, *m*), 7.61–7.52 (4H, *m*), 4.67 (1H, *q*), 3.26–3.20 (1H, *m*), 2.58–2.51 (1H, *m*), 2.48–2.40 (2H, *m*), 2.12–2.06 (1H, *m*), 1.10 (3H, *d*, *J* = 7.5 Hz), 1.04 (3H, *t*, *J* = 7 Hz); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 213.57, 137.90, 137.77, 134.65, 134.49, 129.74, 129.29, 129.15, 129.07, 80.79, 42.98, 34.01, 28.19, 17.58, 7.63; HRMS (ESI, *m*/*z*): Calcd. for $C_{19}H_{22}O_5S_2$ $(M+H)^+$: 395.09814. Found: 395.09843; specific rotation $[\alpha]_D$ ($CHCl_3$, *c* = 1.0 mg/mL): –8.0.

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