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Unusual C-alkylation of pyrazolines with 2-(het)arylcyclopropane-1,1-dicarboxylates in the presence of $GaCl_3$

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Compound (5*R**,1′*R**)-**6ba**. Thick colourless oil. HRMS calculated for $C_{28}H_{34}N_2O_{10}S_2$: $[M+Na]^+$, 645.1547. Found: *m/z* 645.1552. ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 0.99 (s, 3H, CH_3), 2.31 (d, 1H, H_a(4), ^2J=16.8 Hz), 2.39 (ddd, 1H, H_a(2′), ^2J=13.9 Hz, ^3J=8.7 and 5.1 Hz), 2.55 (ddd, 1H, H_a(2′′), ^2J=14.8 Hz, ^3J=7.9 and 7.3 Hz), 2.70 (ddd, 1H, H_b(2′), ^2J=13.9 Hz, ^3J=10.0 and 5.3 Hz), 2.74 (ddd, 1H, H_b(2′′), ^2J=14.8 Hz, ^3J=7.9 and 7.5 Hz), 3.13 (d, 1H, H_b(4), ^2J=16.8 Hz), 3.51 (dd, 1H, H(3′′), ^3J=7.5 and 7.3 Hz), 3.74 (dd, 1H, H(3′), ^3J=8.7 and 5.3 Hz), 3.71, 3.730, 3.733, 3.76 and 3.77 (all s, 5×3H, 5OCH_3), 3.99 (t, 1H, H(1′′), ^3J=7.9 Hz), 4.75 (dd, 1H, H(1′), ^3J=10.0 and 5.1 Hz), 6.88 (dd, 1H, $H_{thi(a)}$(4), ^3J=5.0 and 3.5 Hz), 6.89 (br.d, 1H, $H_{thi(a)}$(3), ^3J=3.5 Hz), 6.94 (dd, 1H, $H_{thi(b)}$(4), ^3J=5.0 and 3.5 Hz), 6.95 (br.d, 1H, $H_{thi(b)}$(3), ^3J=3.5 Hz), 7.16 (dd, 1H, $H_{thi(a)}$(5), ^3J=5.0 Hz, ^4J=0.5 Hz), 7.19 (dd, 1H, $H_{thi(b)}$(5), ^3J=5.0 Hz, ^4J=0.8 Hz). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 20.9 (CH_3), 33.4 (C(2′′)), 38.1 (C(2′)), 39.9 (C(1′′)), 45.6 (C(4)), 49.1 (C(3′)), 49.3 (C(3′′)), 52.4, 52.5, 52.62, 52.64 and 52.66 (5OCH_3), 56.5 (C(1′)), 71.6 (C(5)), 124.8, 125.0, 125.1, 125.3, 125.9 and 127.0 (2C_{thi}(3), 2C_{thi}(4) and 2C_{thi}(5)), 143.4 and 146.0 (2C_{thi}(2)), 149.1 (C(3)), 169.6, 169.7, 169.9 and 170.1 (4COO), 173.3 (COO at C(5)).

Compound (5*R**,1′*R**)-**6bb**. Thick colourless oil. HRMS calculated for $C_{28}H_{34}N_2O_{10}S_2$: $[M+H]^+$, 623.1728; $[M+Na]^+$, 645.1547; $[M+K]^+$, 661.1286. Found: *m/z* 623.1721, 645.1550, 661.1301. ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 0.94 (s, 3H, CH_3), 2.30 (d, 1H, H_a(4), ^2J=16.8 Hz), 2.38 (ddd, 1H, H_a(2′), ^2J=13.7 Hz, ^3J=8.8 and 4.7 Hz), 2.52 (ddd, 1H, H_a(2′′), ^2J=14.5 Hz, ^3J=7.6 and 7.4 Hz), 2.73 (ddd, 1H, H_b(2′), ^2J=13.7 Hz, ^3J=10.3 and 5.2 Hz), 2.80 (ddd, 1H, H_b(2′′), ^2J=14.5 Hz, ^3J=8.0 and 7.4 Hz), 3.11 (d, 1H, H_b(4), ^2J=16.8 Hz), 3.58 (t, 1H, H(3′′), ^3J=7.4 Hz), 3.70 (s, 3H, OCH_3), 3.73 (dd, 1H, H(3′), ^3J=8.8 and 5.2 Hz), 3.75 (s, 9H, 3OCH_3), 3.76 (s, 3H, OCH_3), 3.92 (dd, 1H, H(1′′), ^3J=8.0 and 7.6 Hz), 4.75 (dd, 1H, H(1′), ^3J=10.3 and 4.4 Hz), 6.86 (br.d, 1H, $H_{thi(a)}$(3), ^3J=3.8 Hz), 6.90 (dd, 1H, $H_{thi(a)}$(4), ^3J=5.1 and 3.2 Hz), 6.91 (dd, 1H, $H_{thi(b)}$(4), ^3J=4.9 and 3.8 Hz), 6.97 (br.d, 1H, $H_{thi(b)}$(3), ^3J=3.2 Hz), 7.17 (br.d, 1H, $H_{thi(a)}$(5), ^3J=5.1 Hz), 7.20 (br.d, 1H, $H_{thi(b)}$(5), ^3J=4.9 Hz). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 20.8 (CH_3), 33.4 (C(2′′)), 37.8 (C(2′)), 40.0 (C(1′′)), 45.7 (C(4)), 49.1 (C(3′)), 49.3 (C(3′′)), 52.4, 52.5, 52.63, 52.65 and 52.67 (5OCH_3), 56.6 (C(1′)), 71.9 (C(5)), 124.9, 125.3, 125.5,

125.8, 125.9 and 127.0 ($2C_{thi}$(3), $2C_{thi}$(4) and $2C_{thi}$(5)), 143.8 and 146.0 ($2C_{thi}$(2)), 149.3 (C(3)), 169.6, 169.7, 169.9 and 170.1 (4COO), 173.4 (COO at C(5)).

A mixture of diastereomers **(**5*R**,1′*S**)-**6bc** and **(**5*R**,1′*S**)-**6bd.** Thick colourless oil. HRMS calculated for $C_{28}H_{34}N_2O_{10}S_2$: $[M+H]^+$, 623.1728; $[M+Na]^+$, 645.1547; $[M+K]^+$, 661.1286. Found: *m/z* 623.1720, 645.1549, 661.1304.

Compound **(**5*R**,1′*S**)-**6bc**: ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 1.42 (s, 3H, CH_3), 2.39 (ddd, 1H, H_a(2′), ^2J=14.3 Hz, ^3J=8.7 and 5.6 Hz), 2.46 (d, 1H, H_a(4), ^2J=16.8 Hz), 2.56 (ddd, 1H, H_a(2′′), ^2J=14.2 Hz, ^3J=7.8 and 7.3 Hz), 2.66 (ddd, 1H, H_b(2′), ^2J=14.3 Hz, ^3J=10.0 and 5.0 Hz), 2.72 (ddd, 1H, H_b(2′′), ^2J=14.2 Hz, ^3J=7.7 and 7.5 Hz), 2.93 (s, 3H, OCH_3 at C(5)), 3.00 (d, 1H, H_b(4), ^2J=16.8 Hz), 3.58 (dd, 1H, H(3′′), ^3J=7.5 and 7.3 Hz), 3.64 (dd, 1H, H(3′), ^3J=8.7 and 5.0 Hz), 3.71, 3.744, 3.747 and 3.78 (all s, 4×3H, 4OCH_3), 4.04 (dd, 1H, H(1′′), ^3J=7.8 and 7.7 Hz), 4.45 (dd, 1H, H(1′), ^3J=10.0 and 5.6 Hz), 6.81 (dd, 1H, $H_{thi(a)}$(3), ^3J=3.5 Hz, ^4J=1.0 Hz), 6.87 (dd, 1H, $H_{thi(a)}$(4), ^3J=5.0 and 3.5 Hz), 6.89 (br.d, 1H, $H_{thi(b)}$(3), ^3J=3.5 Hz), 6.94 (dd, 1H, $H_{thi(b)}$(4), ^3J=5.0 and 3.5 Hz), 7.19 (br.d, 2H, $H_{thi(a)}$(5) and $H_{thi(b)}$(5), ^3J=5.0 Hz). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 22.1 (CH_3), 32.9 (C(2′′)), 37.9 (C(2′)), 39.8 (C(1′′)), 44.6 (C(4)), 49.0 (C(3′)), 49.5 (C(3′′)), 51.2 (OCH_3 at C(5)), 52.4, 52.5, 52.6 and 52.7 (4OCH_3), 55.3 (C(1′)), 68.8 (C(5)), 124.5, 125.3, 125.4, 125.5, 126.4 and 126.9 ($2C_{thi}$(3), $2C_{thi}$(4) and $2C_{thi}$(5)), 142.6 and 143.3 ($2C_{thi}$(2)), 150.7 (C(3)), 169.74, 169.79, 169.81 and 169.84 (4COO), 171.8 (COO at C(5)).

Compound **(**5*R**,1′*S**)-**6bd**: ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 1.40 (s, 3H, CH_3), 2.39 (m, 1H, H_a(2′)), 2.52 (d, 1H, H_a(4), ^2J=16.8 Hz), 2.55 (m, 1H, H_a(2′′)), 2.70 (m, 1H, H_b(2′′)), 2.72 (m, 1H, H_b(2′)), 2.96 (d, 1H, H_b(4), ^2J=16.8 Hz), 3.01 (s, 3H, OCH_3 at C(5)), 3.57 (m, 1H, H(3′′)), 3.73 (m, 1H, H(3′)), 3.73, 3.74, 3.77 and 3.78 (all s, 4×3H, 4OCH_3), 3.94 (dd, 1H, H(1′′), ^3J=8.2 and 7.4 Hz), 4.48 (dd, 1H, H(1′), ^3J=9.8 and 5.9 Hz), 6.84–6.96 (m, 4H, $2H_{thi}$(3) and $2H_{thi}$(4)), 7.14–7.21 (m, 2H, $2H_{thi}$(5)). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 21.7 (CH_3), 32.9 (C(2′′)), 37.9 (C(2′)), 39.9 (C(1′′)), 46.0 (C(4)), 49.1 (C(3′)), 49.7 (C(3′′)), 51.4 (OCH_3 at C(5)), 52.4, 52.5, 52.6 and 52.7 (4OCH_3), 55.3 (C(1′)), 69.1 (C(5)), 124.7, 125.29, 125.33, 126.39, 126.43 and 126.9 ($2C_{thi}$(3), $2C_{thi}$(4) and $2C_{thi}$(5)), 142.7 and 143.6 ($2C_{thi}$(2)), 150.9 (C(3)), 169.69, 169.71, 169.74 and 169.8 (4COO), 172.0 (COO at C(5)).