

Article

Atom Exchange Radical Cyclization: A Sustainable Synthetic Approach towards New Functionalized Targets

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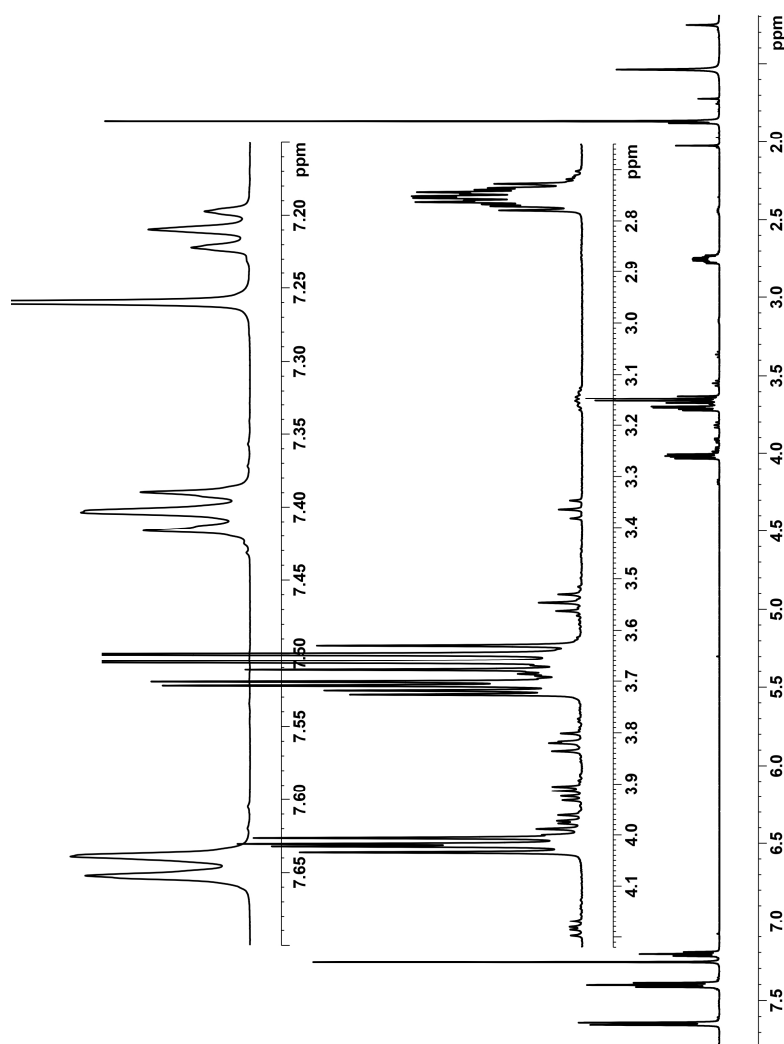
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Supplementary Information



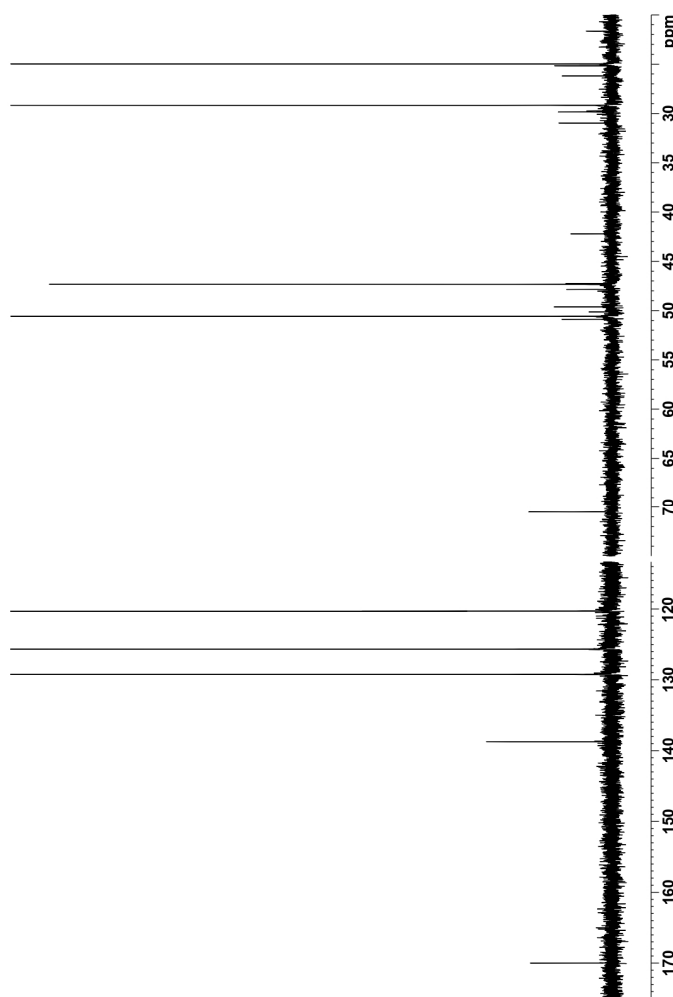
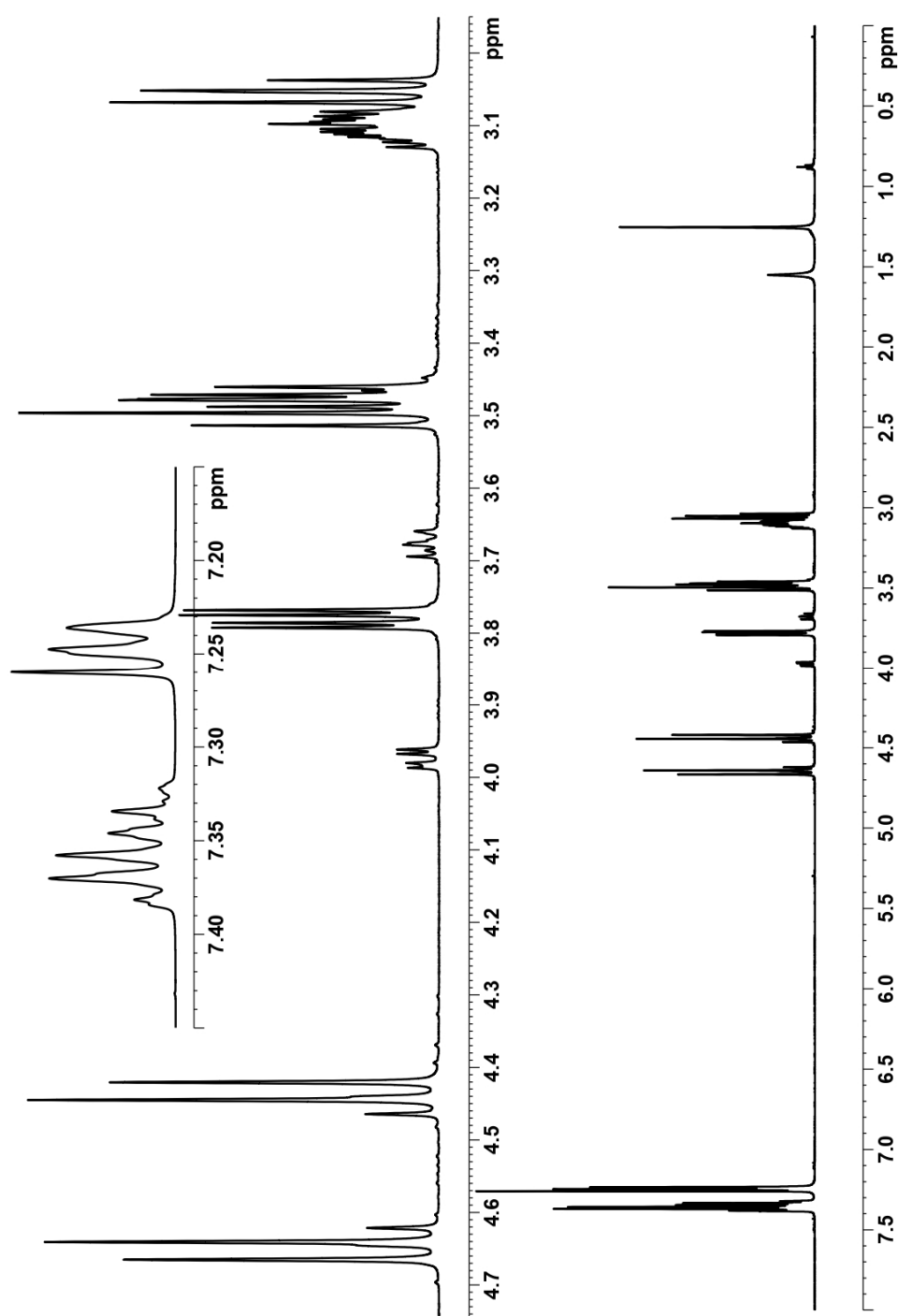


Figure S1. ^1H and ^{13}C NMR of **3** (raw reaction mixture, after extraction), featuring small amounts of byproducts: dibromolactam **3b** (6%) and ATRC dichlorolactam **2** (6%).

Main product **3**: (**3-cis**, 85 %): ^1H NMR (600 MHz, CDCl_3): δ = 1.86 (s, 3 H, CH_3), 2.75 (m, 1 H, CH), 3.65 (pq, J = 9.4 Hz, 2 H, CHHBr , CHHNCO), 3.71 (pdd, J = 4.74, 10.4 Hz, 1 H, CHHBr), 4.02 (pdd, J = 6.9, 9.9 Hz, 1 H, CHHNCO), 7.21 (pt, J = 7.4 Hz, 1 H, $p\text{-ArH}$), 7.40 (pt, J = 7.6 Hz, 2 H, $m\text{-ArH}$), 7.65 (pd, J = 8.1 Hz, 2H, $o\text{-ArH}$) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 25.0 (CH_3), 29.2 (CH_2Br), 47.3 (CH), 50.6 (CH_2NCO), 120.3 ($o\text{-ArC}$), 125.7 ($p\text{-ArC}$), 129.2 ($m\text{-ArC}$), 138.7 (N-ArC), 170.0 (NCO) ppm. (**3-trans**, 3 %): ^1H NMR (600 MHz, CDCl_3): δ = 1.72 (s, 3 H, CH_3), 3.15 (m, 1 H, CH), 3.36 (t, J = 10.4 Hz, 1 H, CHHBr), 3.69 (m, 1 H, CHHNCO), 4.04 (m, 1 H, CHHBr), 4.18 (pdd, J = 6.8, 10.1 Hz, 1 H, CHHNCO), 7.21 (pt, J = 7.4 Hz, 1 H, $p\text{-ArH}$), 7.40 (pt, J = 7.6 Hz, 2 H, $m\text{-ArH}$), 7.65 (pd, J = 8.1 Hz, 2H, $o\text{-ArH}$) ppm.

Dibromolactam by-product (**3b**, 6 %): ^1H NMR (600 MHz, CDCl_3): δ = 2.02 (s, 3 H, CH_3), 2.45 (m, 1 H, CH), 3.55 (t, J = 9.6 Hz, 1 H, CHHBr), 3.82 (m, 1 H, CHHNCO), 3.92 (pdd, J = 5.1, 11.2 Hz, 1 H, CHHNCO), 3.98 (m, 1 H, CHHBr), 7.21 (pt, J = 7.4 Hz, 1 H, $p\text{-ArH}$), 7.40 (pt, J = 7.6 Hz, 2 H, $m\text{-ArH}$), 7.65 (pd, J = 8.1 Hz, 2H, $o\text{-ArH}$) ppm.

Dichlorolactam by-product (**2**, 6 %): ^1H NMR (600 MHz, CDCl_3): δ = 1.88 (s, 3 H, CH_3), 2.72 (m, 1 H, CH), 3.65 (m, 2 H, CHHCl + CHHNCO), 3.71 (m, 1 H, CHHCl), 4.03 (m, 1 H, CHHNCO), 7.21 (pt, J = 7.4 Hz, 1 H, $p\text{-ArH}$), 7.40 (pt, J = 7.6 Hz, 2 H, $m\text{-ArH}$), 7.65 (pd, J = 8.1 Hz, 2H, $o\text{-ArH}$) ppm.



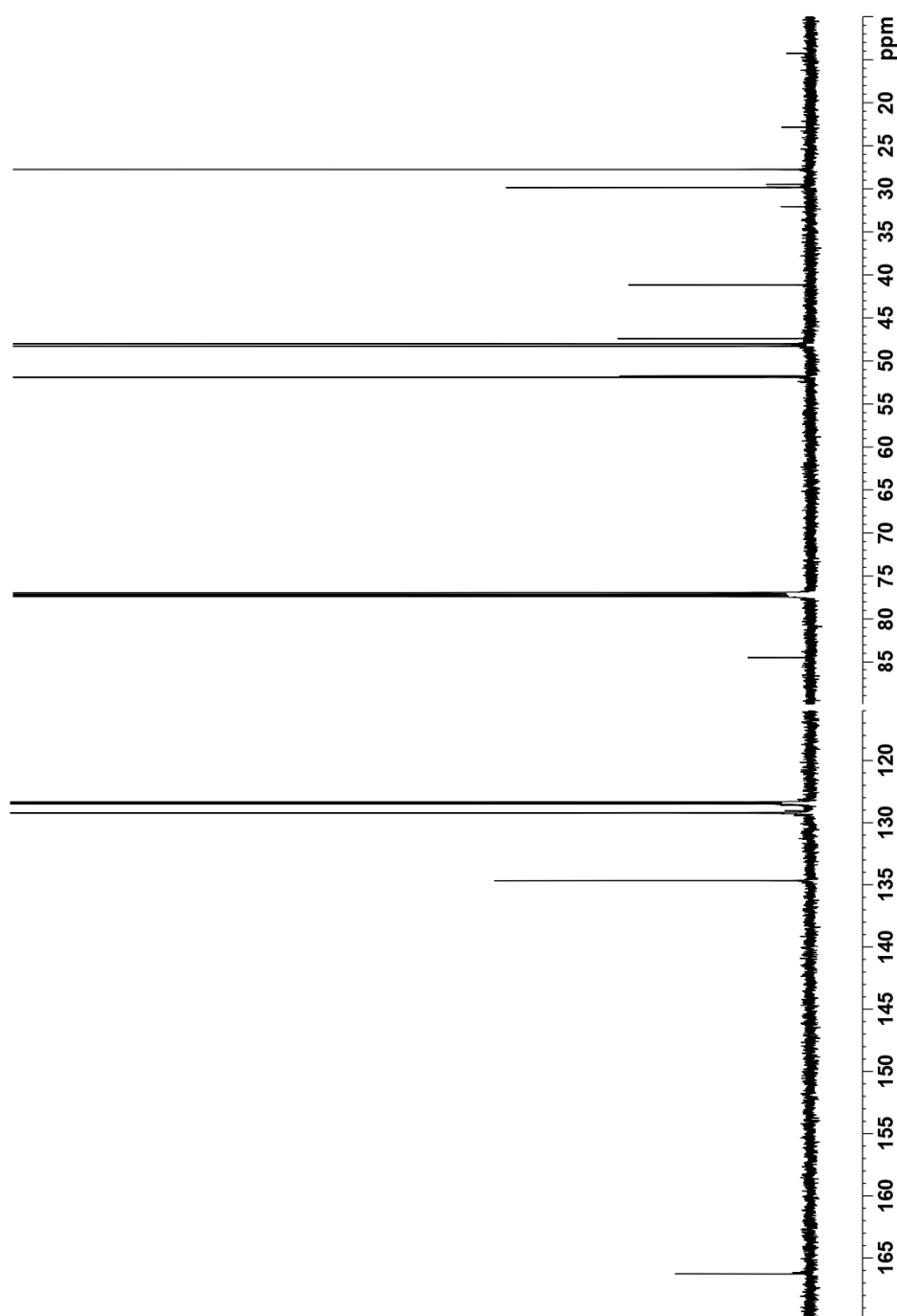


Figure S2. ^1H and ^{13}C NMR of **6** (raw reaction mixture, after extraction), contaminated by minor amounts of ATRC trichloro product **5** (15 %).

Main product (**6**, 85 %): ^1H NMR (600 MHz, CDCl_3): δ = 3.06 (q, J = 9.3 Hz, 1 H, CHHNCO), 3.10 (m, 1 H, CH), 3.43–3.53 (m, 2 H, CHHNCO , CHHBr), 3.78 (dd, J = 3.9, 10.4 Hz, 1 H, CHHBr), 4.43 (d, J = 14.6 Hz, 1 H, CHHPh), 4.65 (d, J = 14.6 Hz, 1 H, CHHPh), 7.24 (pd, J = 7.5 Hz, 2 H, *o*-ArH), 7.31–7.39 (m, 3 H, *m,p*-ArH) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 27.8 (CH_2Br), 48.0 (CH_2Ph), 48.3 (CH_2NCO), 51.9 (CH), 84.5 (CCl_2), 128.4 (*o*-ArC), 128.5 (*p*-ArC), 129.2 (*m*-ArC), 166.3 (NCO) ppm.

Trichlorolactam by-product (**5**, 15 %): ^1H NMR (600 MHz, CDCl_3): δ = 3.06 (m, 1 H, CHHNCO), 3.10 (m, 1 H, CH), 3.48 (m, 1 H, CHHNCO), 3.68 (m, 1 H, CHHCl), 3.97 (m, 1 H, CHHCl), 4.45 (d, J = 14.3 Hz, 1 H, CHHPh), 4.63 (d, J = 14.3 Hz, 1 H, CHHPh), 7.24 (pd,

$J = 7.5$ Hz, 2 H, *o*-ArH), 7.31–7.39 (m, 3 H, *m,p*-ArH) ppm. ^{13}C NMR (150 MHz, CDCl_3): $\delta =$ 41.2 (CH_2Cl), 47.4 (CH_2NCO), 48.1 (CH_2Ph), 51.7 (CH), 84.5 (CCl_2), 128.4 (*o*-ArC), 128.5 (*p*-ArC), 129.2 (*m*-ArC), 166.3 (NCO) ppm.