Selective One-Pot Synthesis of Trithiocarbonates, Xanthates and Dithiocarbamates for use in RAFT/MADIX Living Radical Polymerizations

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Supporting information

*Characterisation data for **8***.Yield =81%**.** δ_H (400MHz, $CDCl_3$) δ 4.62 (s, 4H, Ph*CH_2*), 7.29 (m, 10H, *Ph*CH_2), ^{13}C-NMR (100MHz) δ 222.8, 134.9, 129.1, 128.7, 127.8, 45.2, TOF-MS (ES^+) *m/z*= 291.034 (MH^+)

*Characterisation data for **9**. Yield* =64%**.** δ_H (400MHz, $CDCl_3$) δ 1.26-1.28 (t, *J*= 7.2 Hz, 3H, OCH_3*CH_3*), 1.59-1.61 (d, *J*= 7.4 Hz , 3H, SCH*CH_3*), 4.19-4.23 (q, *J*= 3.7 Hz, 2H, O*CH_2*CH_3), 4.59-4.62 (s, 2H, Ph*CH_2*), 4.78-4.83 (q, *J*= 7.4 Hz, 1H, S*CH*CH_3), 7.25 (m, 5H, *Ph*CH_2) ^{13}C-NMR (100MHz) δ 220.2, 170.4, 134.7, 128.1, 127.5, 127.3, 60.3, 48.6, 40.4, 16.2, 13.1, TOF-MS (ES^+) *m/z*= 269.067 (M^+-S)+H^+.[21]

*Characterisation data for **10***. Yield = 68%**.** δ_H (400MHz, $CDCl_3$) δ 1.37 (s, 6H, *CH_3*CH*CH_3*), 4.32 (s, 2H, Ph*CH_2*S), 5.71-5.81 (m, 1H, CH_3*CH*CH_3), 7.25-7.35 (m, 5H, *Ph*CH_2S), ^{13}C-NMR (100MHz) δ 213.15, 135.8, 129.4, 128.7, 127.5, 43.2, 40.3, 21.5, TOF-MS (ES^+) m/z= 227.056 (MH^+)

*Characterisation data for **11**.* Yield = 63%**.** δ_H (400MHz, $CDCl_3$) δ 1.67-1.69 (d, *J*= 7.3 Hz, 3H, SCH*CH_3*), 4.17-4.23 (q, *J*= 4.6 Hz, 1H, S*CH*CH_3), 5.05-5.17 (q, *J*= 14 Hz, 2H, Ph*CH_2*), 7.29-7.33 (m, 3H, *Ph*CH_2), 7.39-7.41 (d, *J*= 6.1 Hz, 2H, CH_2*Ph*), ^{13}C-NMR (100MHz) δ 200.3, 177.2, 134.8, 128.7, 128.5, 128.4, 47.9, 47.8, 47.6, 18.3, TOF-MS (ES^+) *m/z*= 238.036 (M^+-O)[21]

[21]As carbonyls and thiocarbonyls are particularly susceptible to fragmentation, the major peak in the MS analyses is assigned to the molecular ion, minus the carbonyl oxygen (sulfur). The nominal MS data show peaks with a lower intensity that do represent the expected molecular ion, but these peaks

could not be analyzed with high resolution MS because of too much interferences from other fragments. The data is still correct and consistent with what could be expected from high resolution MS.