Electronic Supplementary Material (ESI) for Polymer Chemistry.

Synthesis of fluorinated alkoxyamines and alkoxyamine-initiated nitroxide-mediated precipitation polymerizations of styrene in supercritical carbon dioxide

Christopher Magee, Aruna Earla, Jennifer Petraitis, Chad Higa, Rebecca Braslau, Per B. Zetterlund and Fawaz Aldabbagh

Electronic Supplementary Information (ESI)

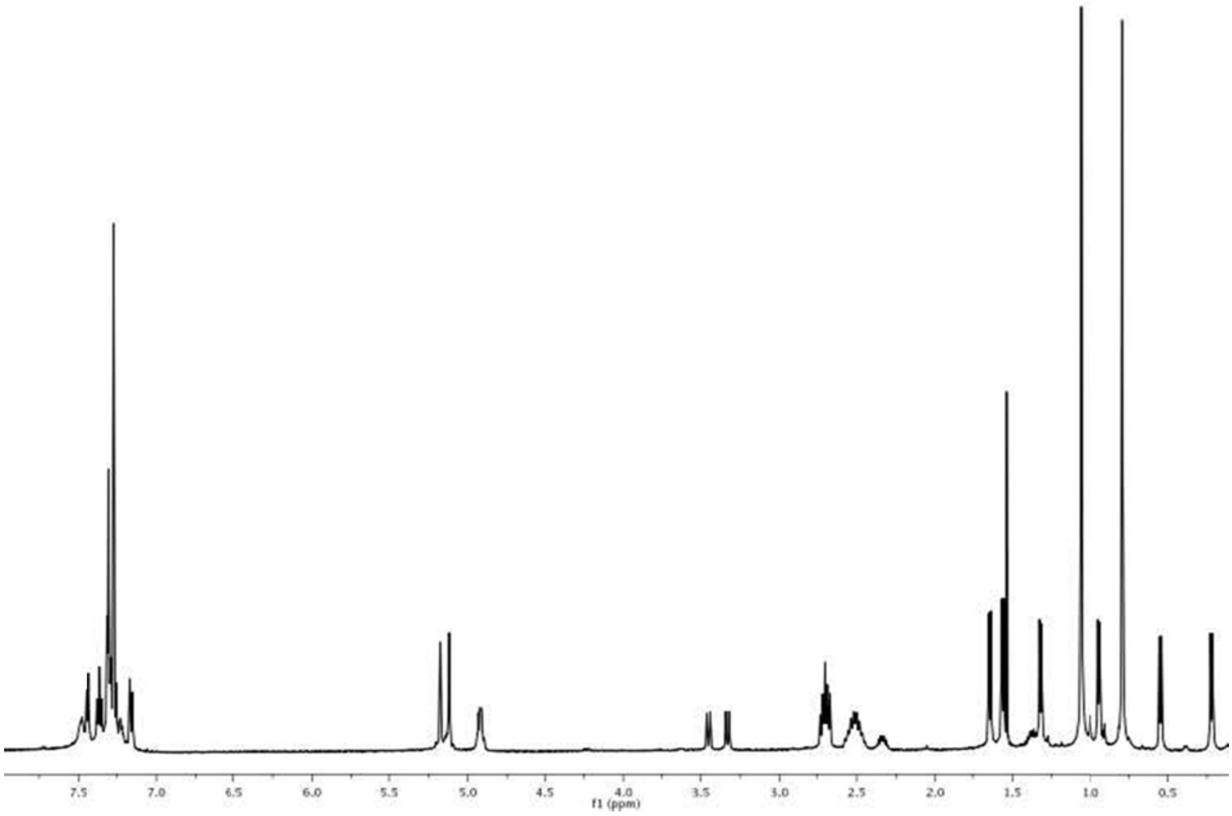

Figure S1. ^{1}H NMR spectrum of F-TIPNO alkoxyamine **1b**

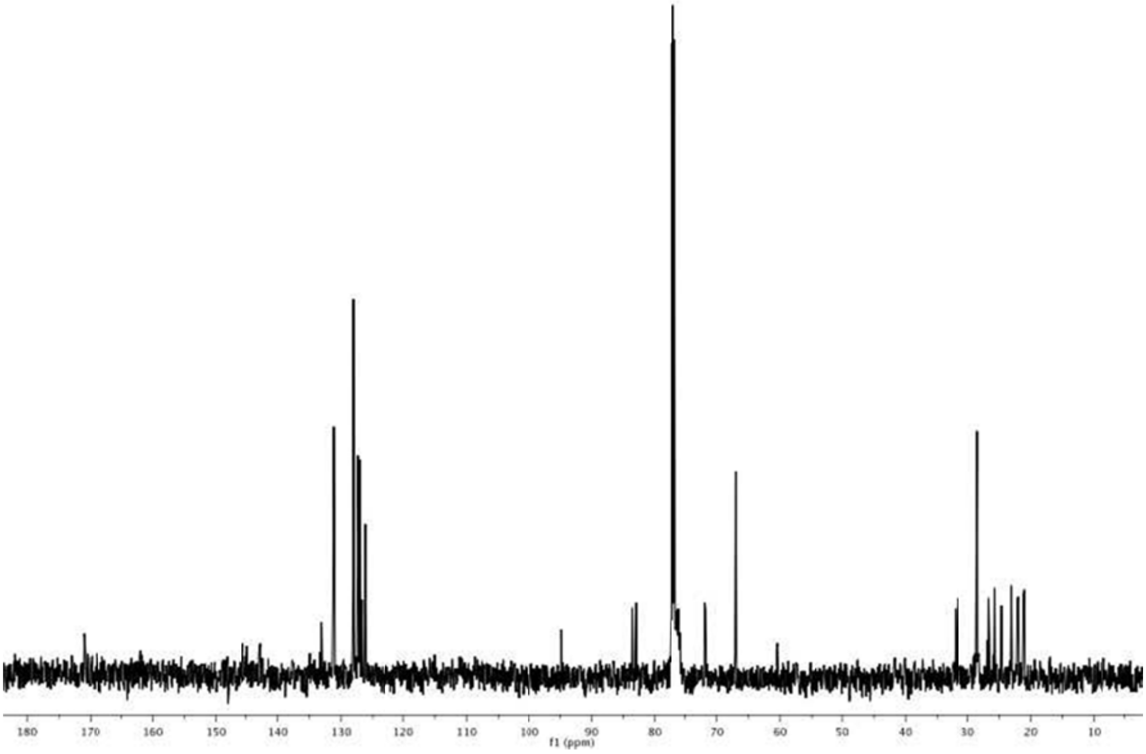

Figure S2. ^{13}C NMR spectrum of F-TIPNO alkoxyamine **1b**

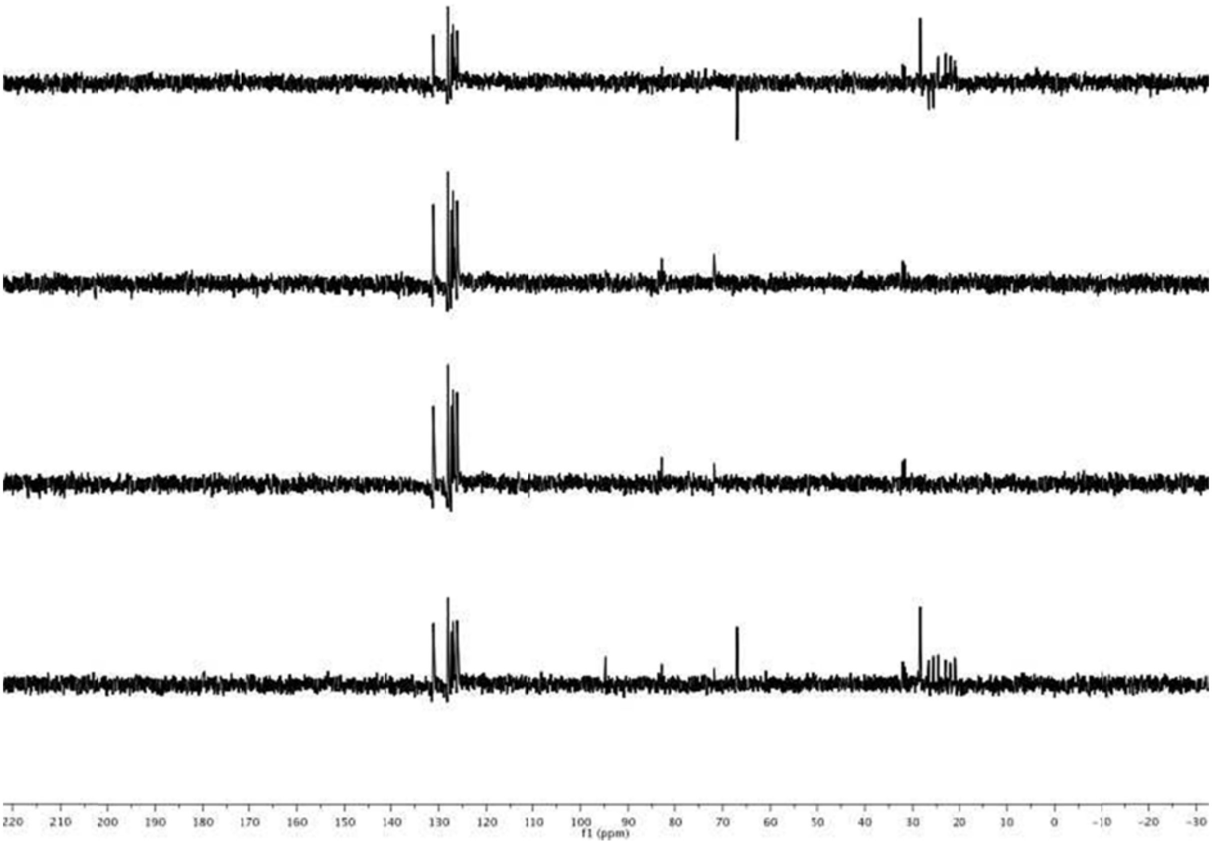

Figure S3. DEPT of F-TIPNO alkoxyamine **1b**

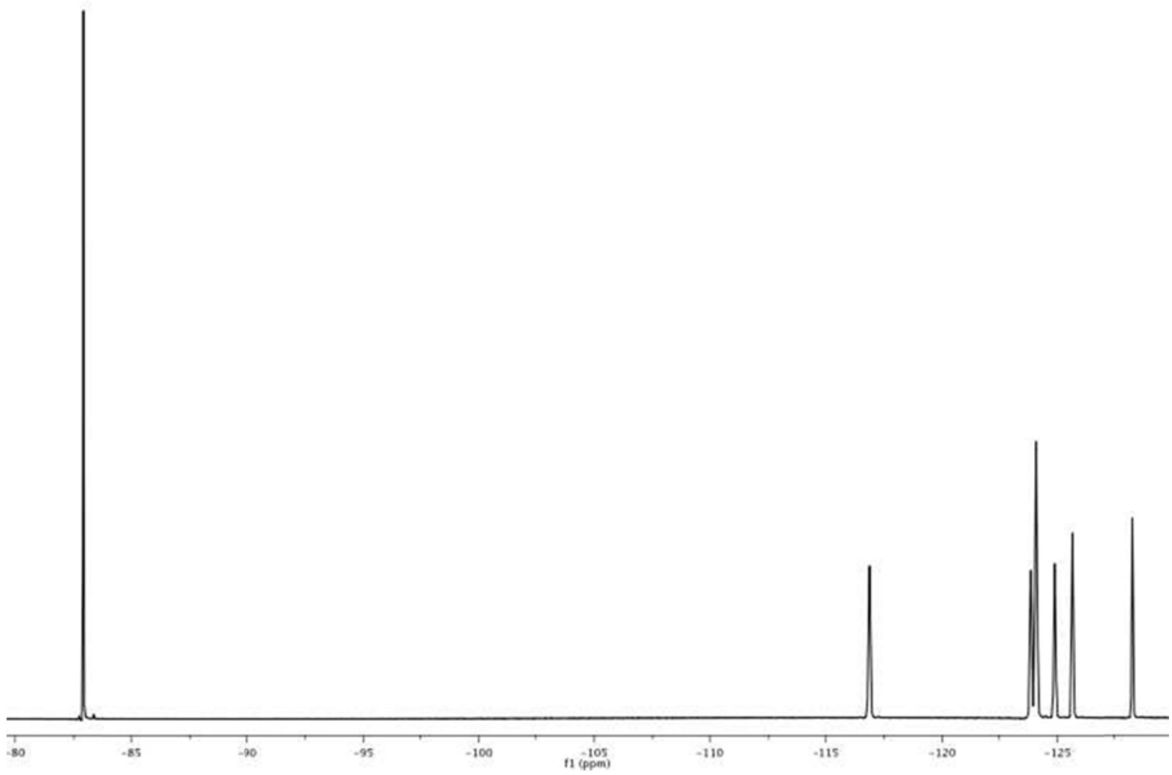

Figure S4. ^{19}F NMR of F-TIPNO alkoxyamine **1b**

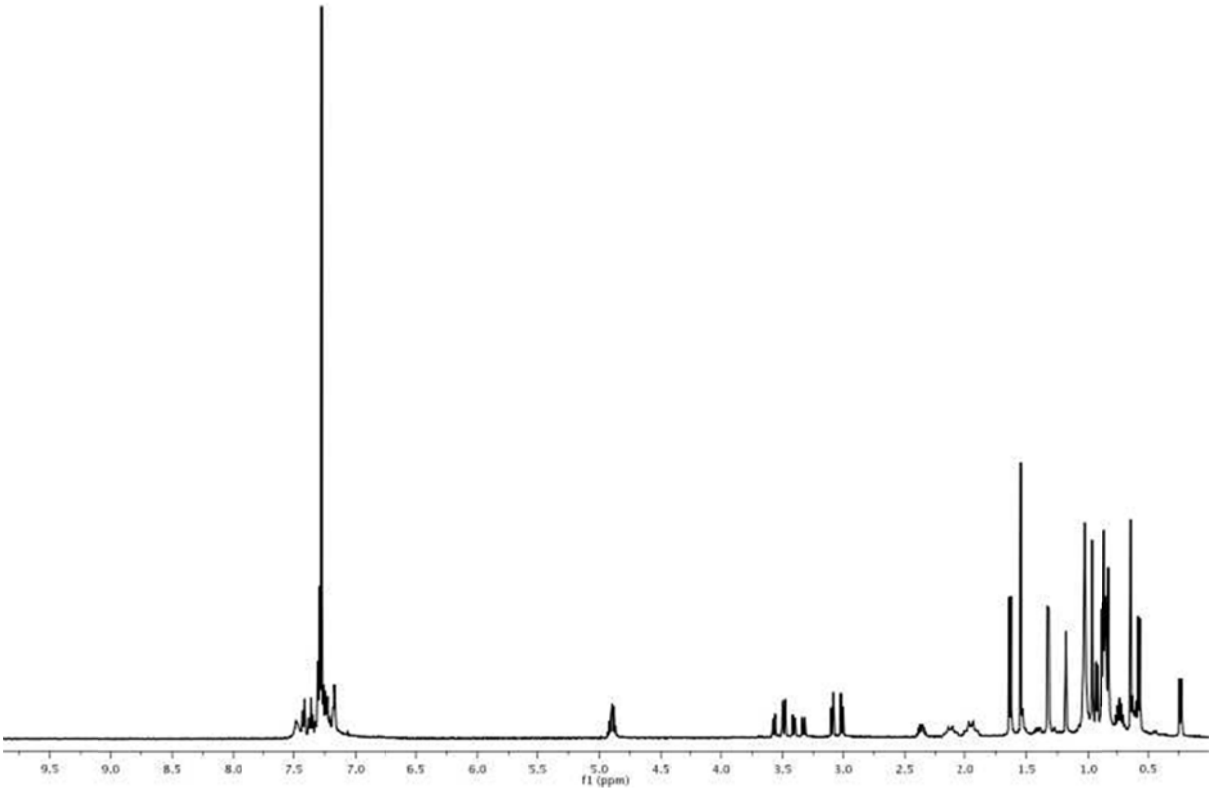

Figure S5. ^{1}H NMR of F-Si-TIPNO alkoxyamine **1c**

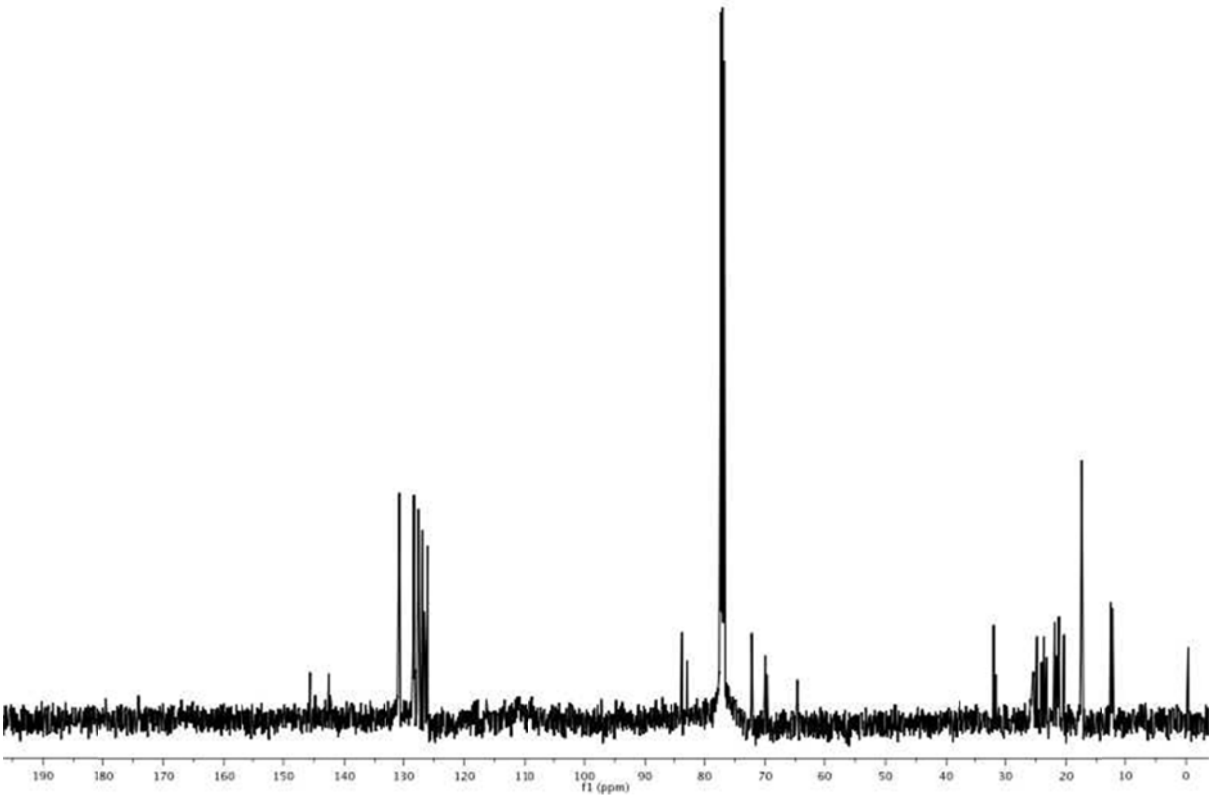

Figure S6. ^{13}C NMR of F-Si-TIPNO alkoxyamine **1c**

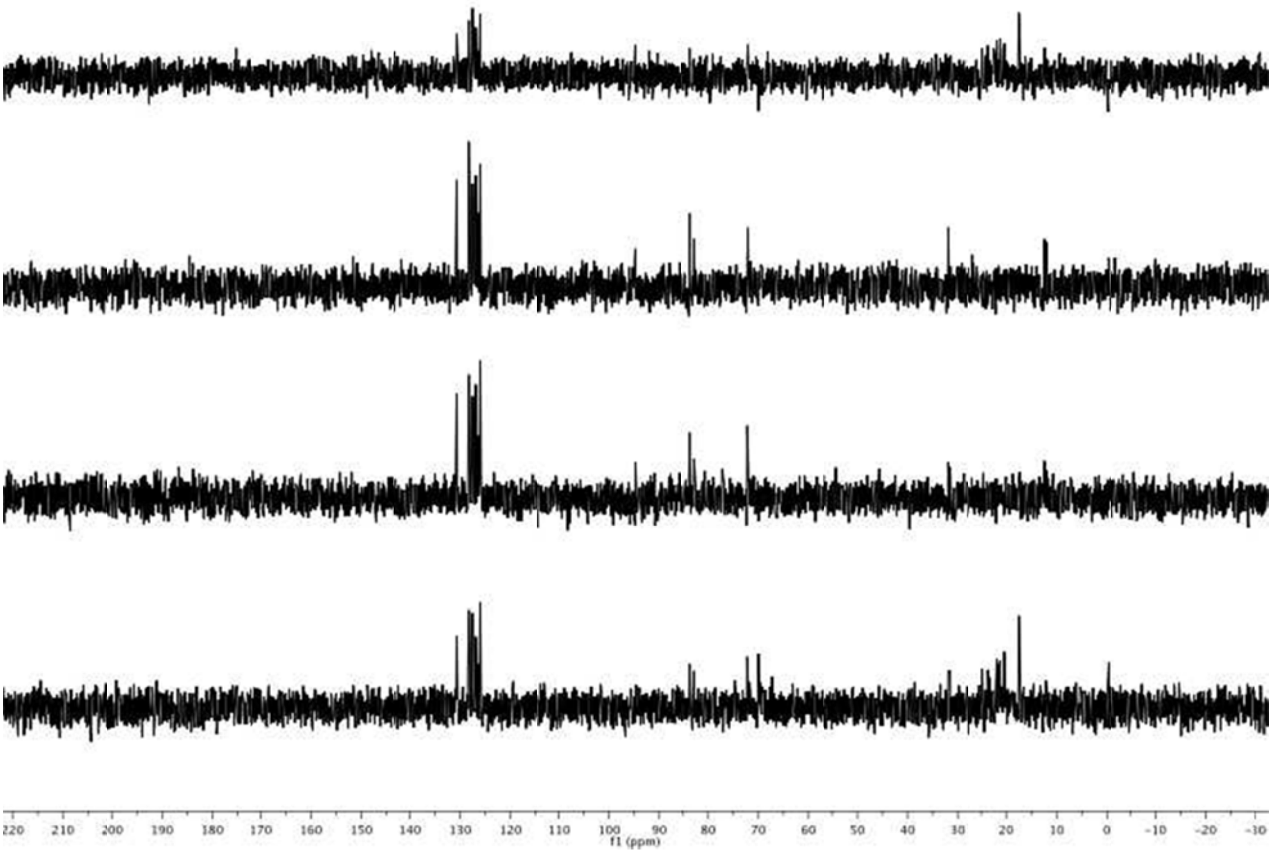

Figure S7. DEPT of F-Si-TIPNO alkoxyamine **1c**

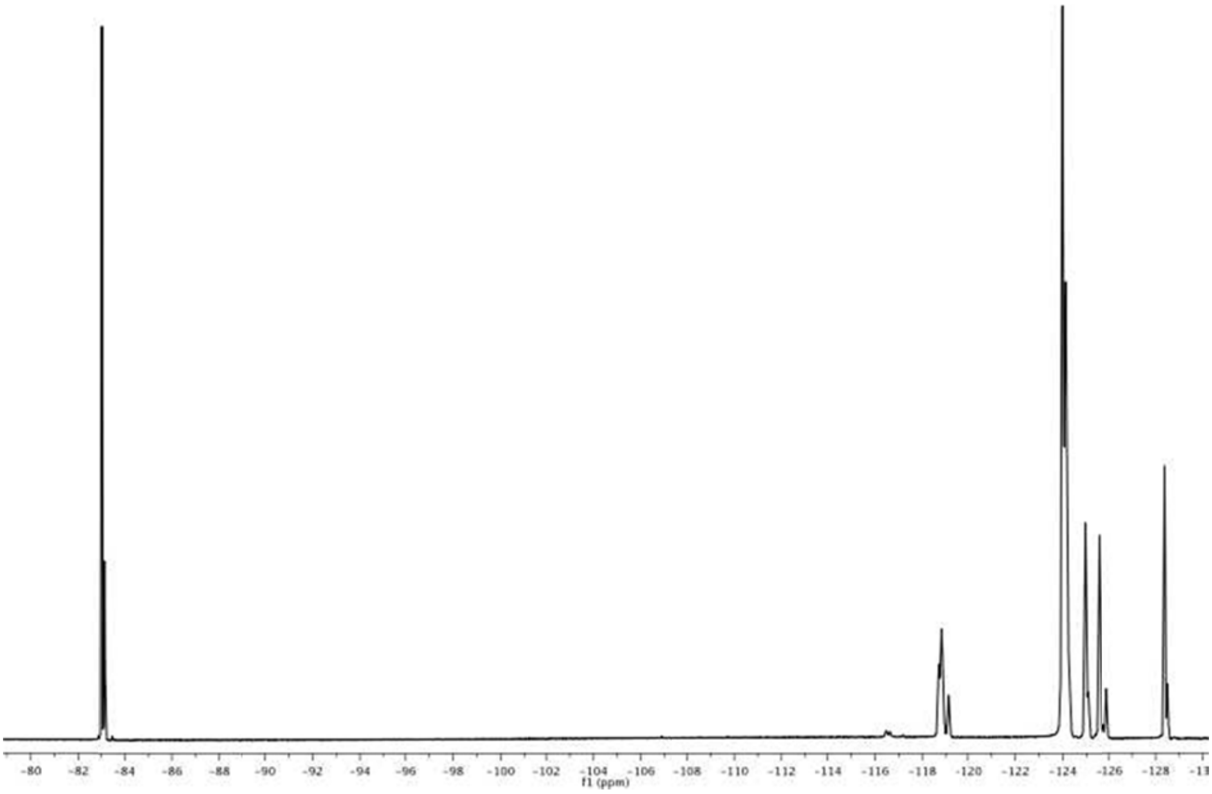

Figure S8. ^{19}F NMR of F-Si-TIPNO alkoxyamine **1c**

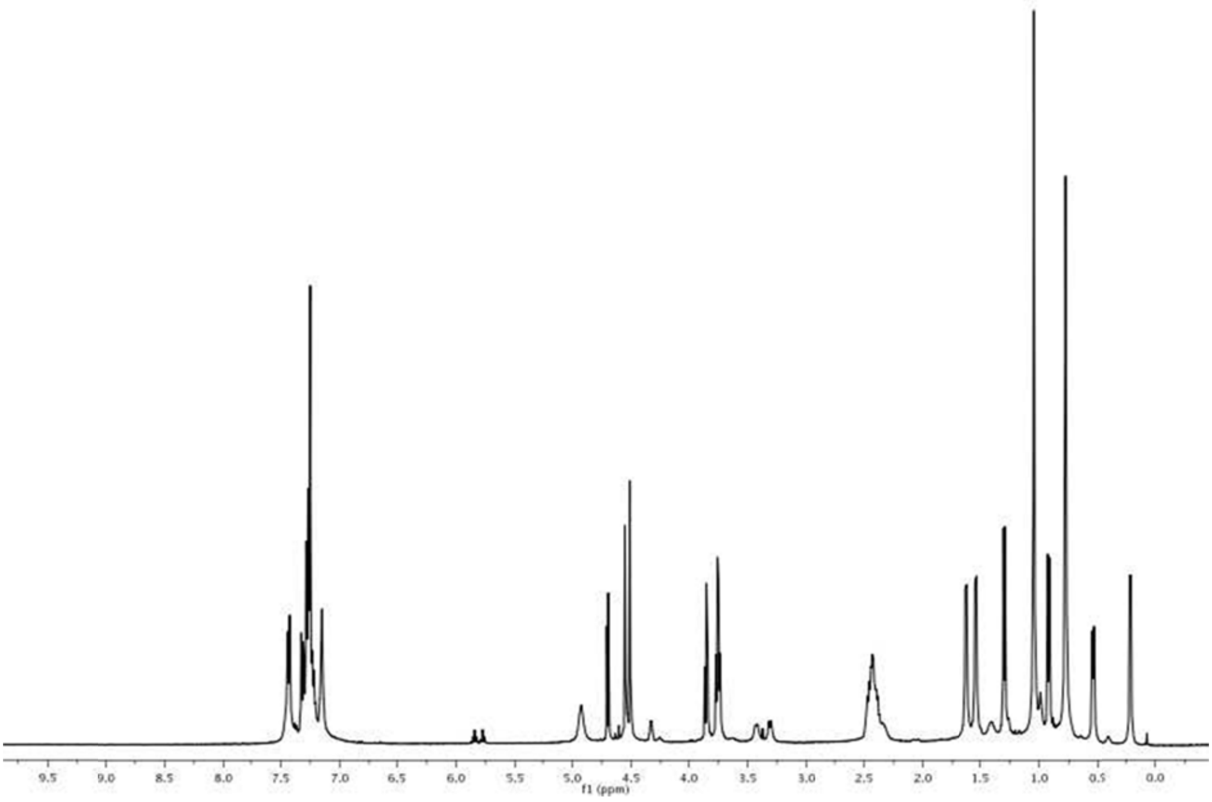

Figure S9. ^{1}H NMR of TIPNO alkoxyamine F-Foot **2**

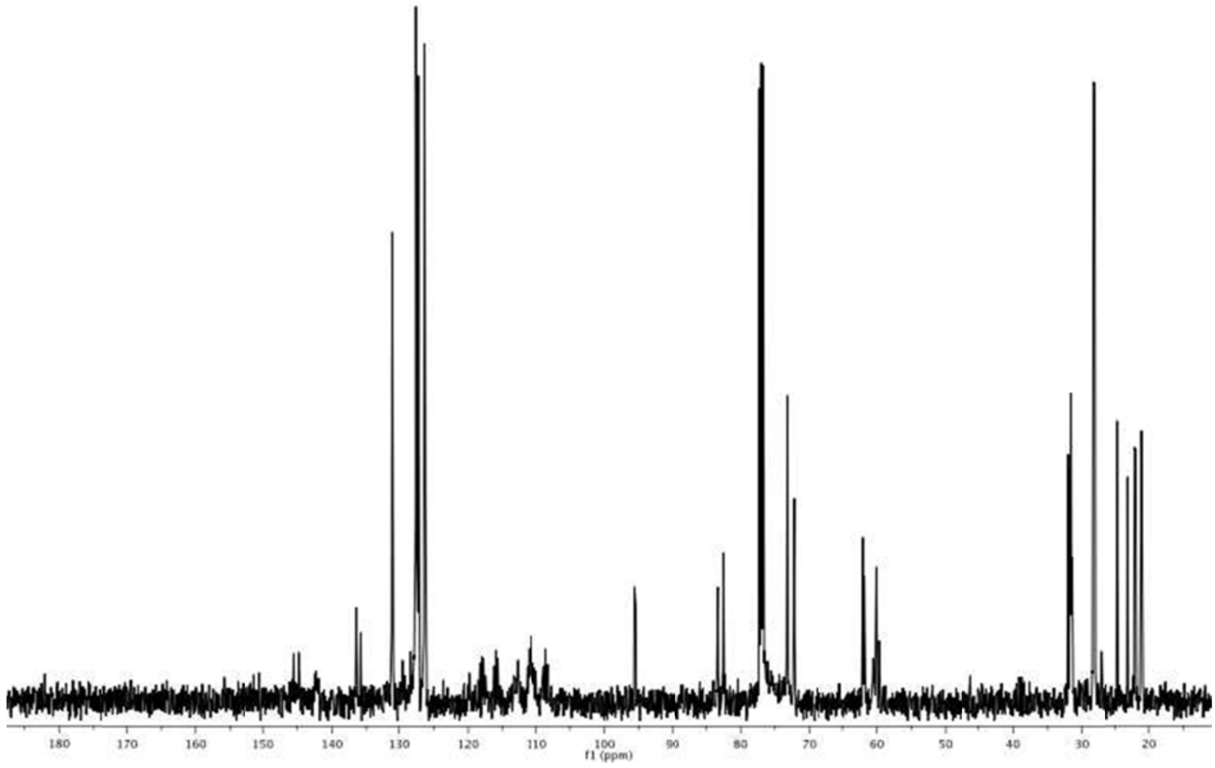

Figure S10: ^{13}C NMR of TIPNO alkoxyamine F-Foot **2**

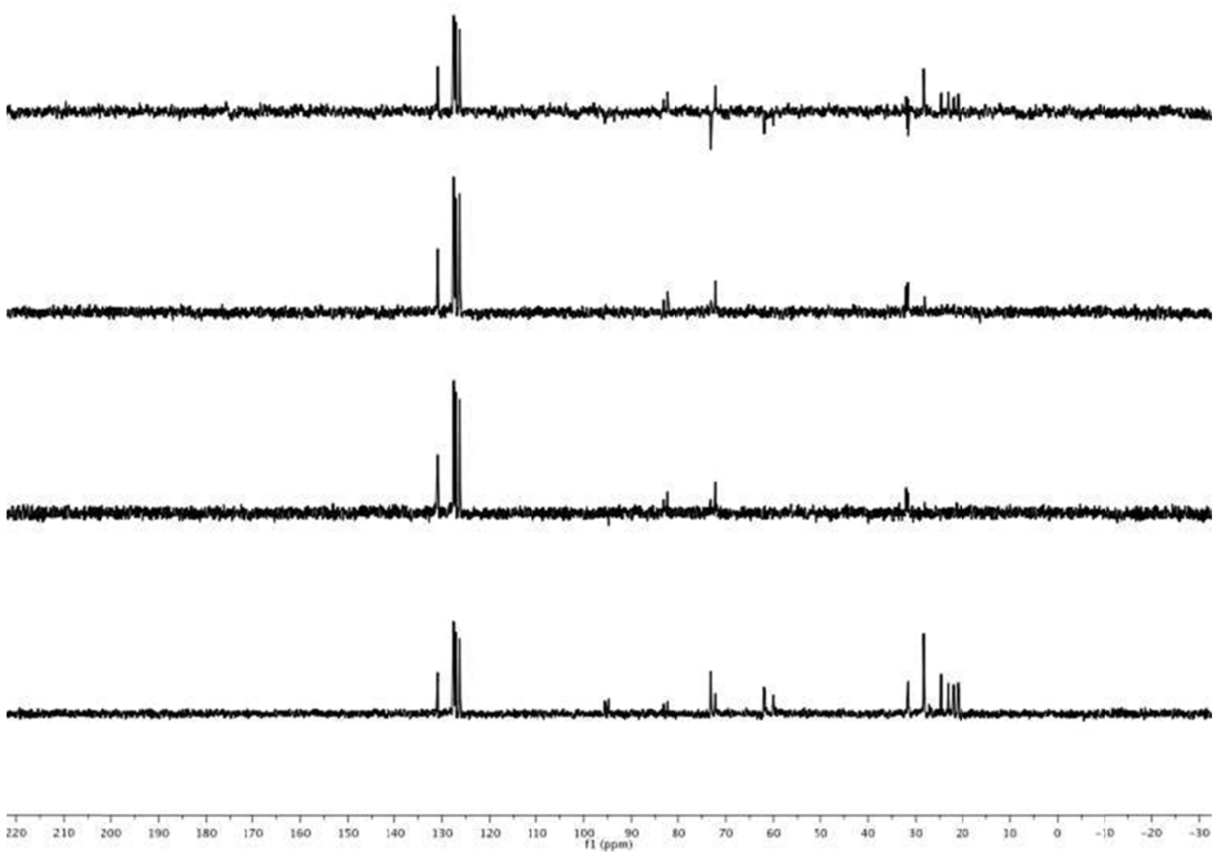

Figure S11: DEPT of TIPNO alkoxyamine F-Foot **2**

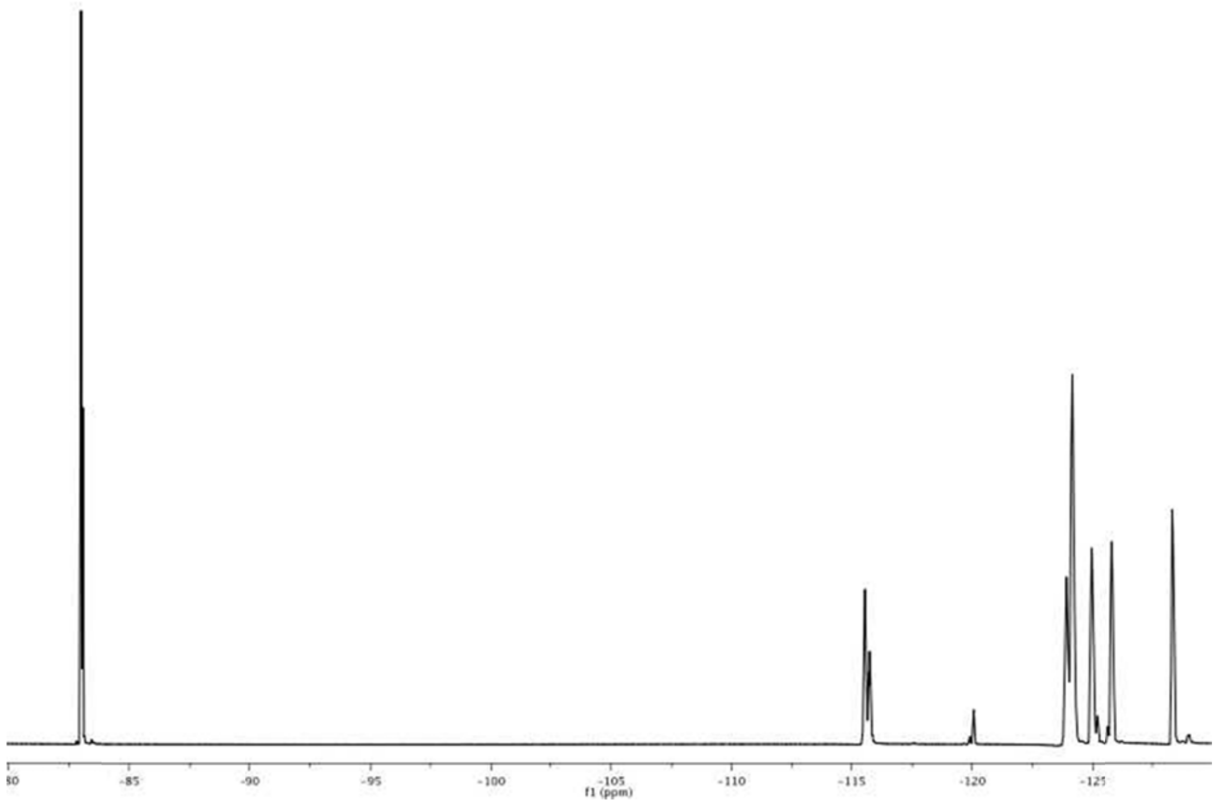

Figure S12: ^{19}F NMR of TIPNO alkoxyamine F-Foot **2**

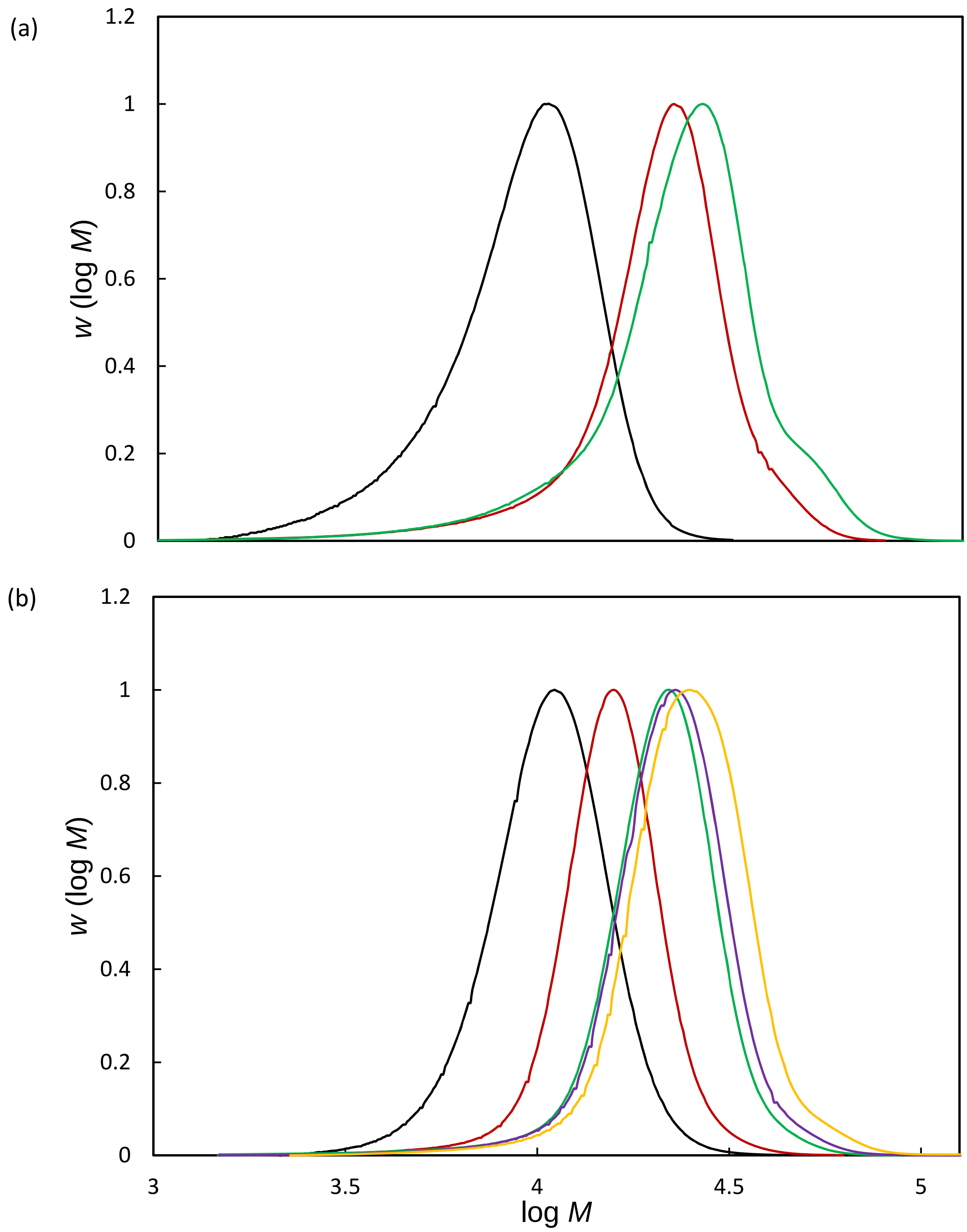

Figure S13. MWDs for alkoxyamine **1a** initiated NMP of styrene (50% w/v) at 110 °C using $[\text{Monomer}]_0/[\text{Alkoxyamine}]_0$ = 384: (a) Precipitation polymerizations in $scCO_2$ at 30 MPa; conversions are 23 (black), 42 (red) and 49% (green) and (b) solution polymerization in toluene; conversions are 27 (black), 40 (red), 55 (green), 63 (purple) and 72% (orange).

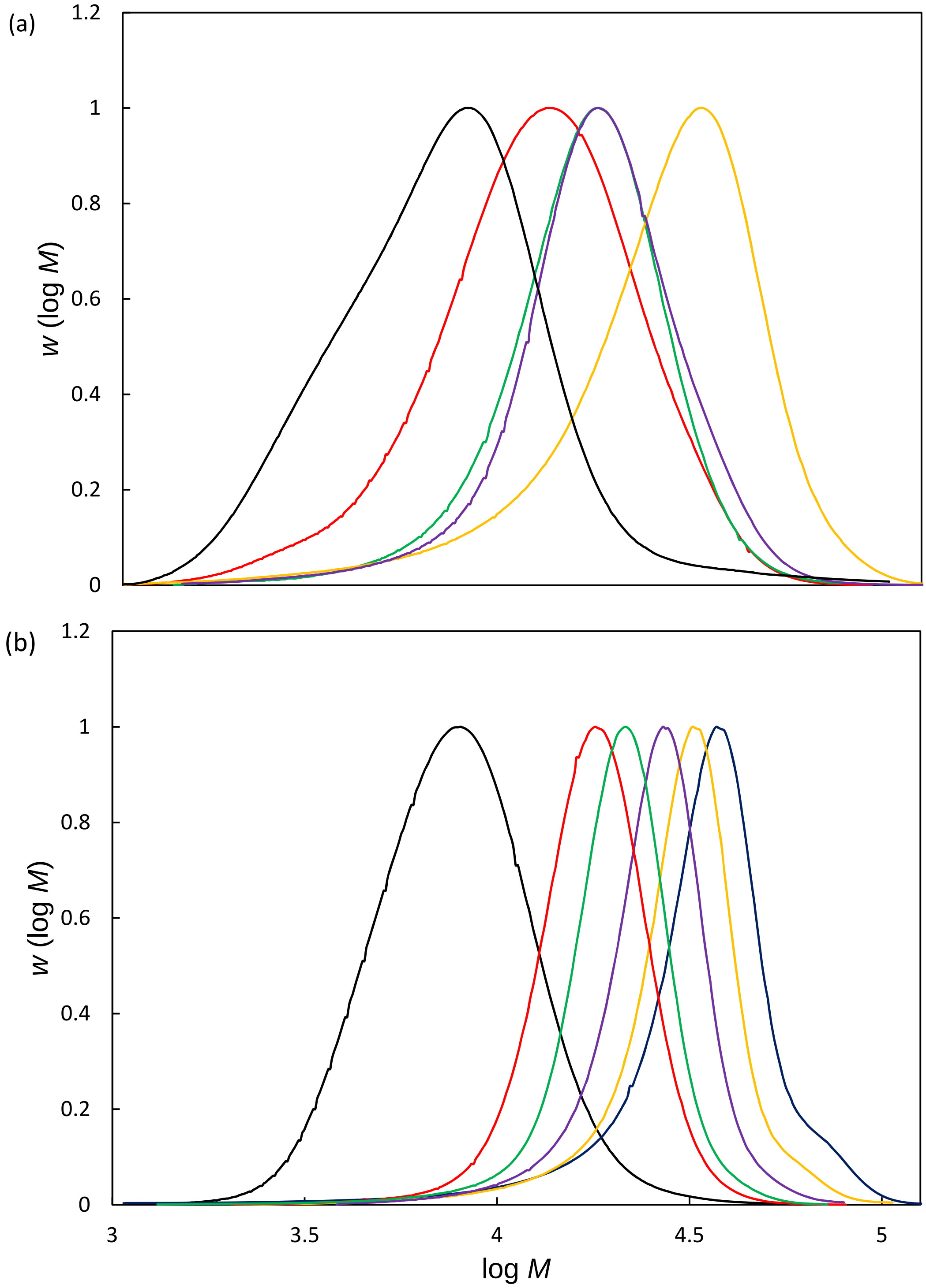

Figure S14. MWDs for alkoxyamine **1b** initiated NMP of styrene (50% w/v) at 110 °C using $[Monomer]_0/[Alkoxyamine]_0$ = 384: (a) Precipitation polymerizations in $scCO_2$ at 30 MPa; conversions are 8 (black), 17 (red), 21 (green), 35 (purple) and 43% (orange) and (b) solution polymerizations in toluene; conversions are 13 (black), 33 (red), 51 (green), 63 (purple), 74% (orange) and 80 % (blue).

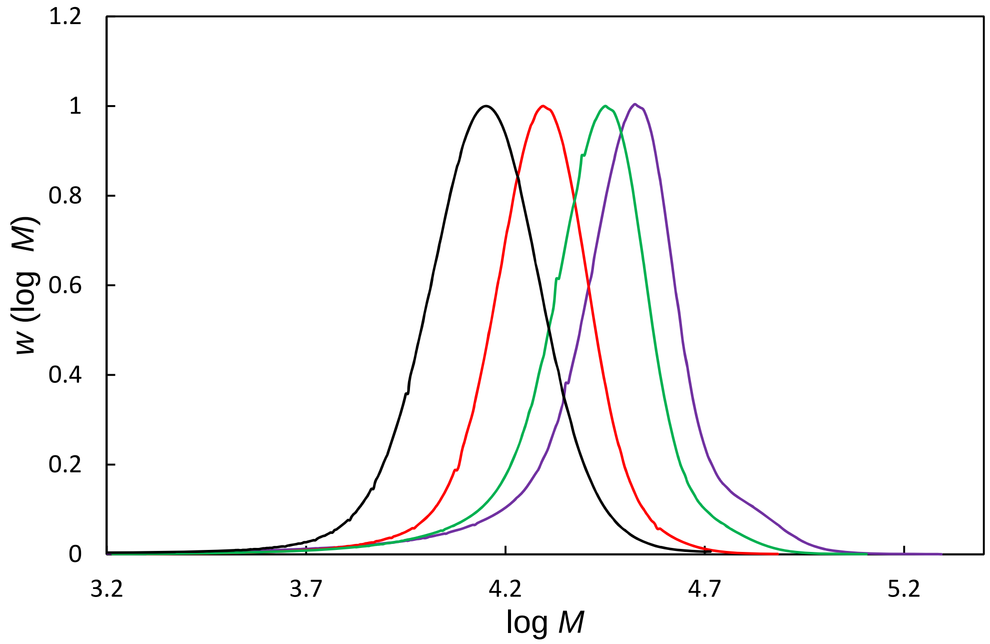

Figure S15. MWDs for alkoxyamine **1c** initiated solution NMP of styrene (50% w/v) at 110 °C in toluene using $[\text{Monomer}]_0/[\text{Alkoxyamine}]_0 = 384$: conversions are 24 (black), 44 (red), 65 (green) and 75% (purple).

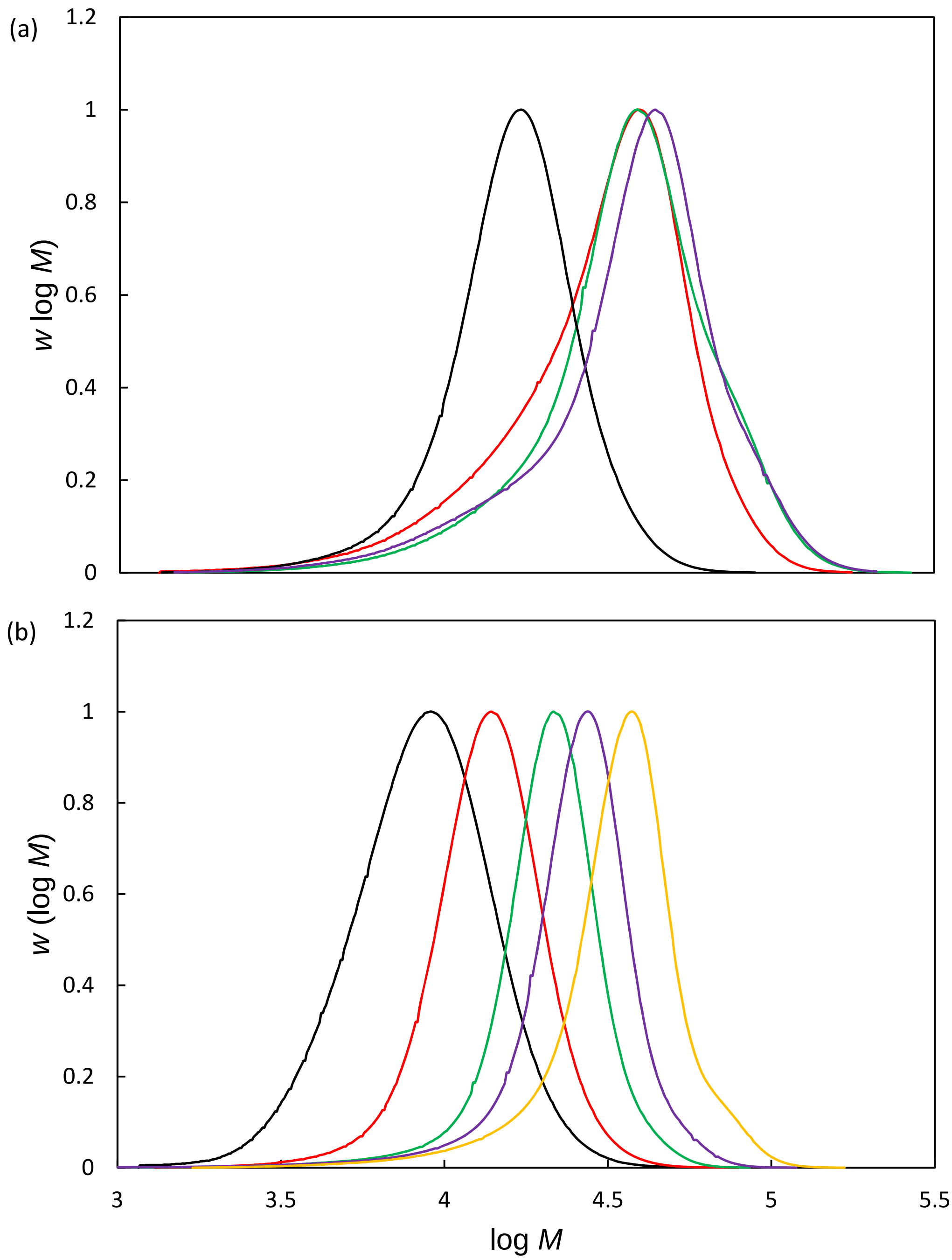

Figure S16. MWDs for the alkoxyamine **1d** initiated NMP of styrene (50% w/v) at 110 °C using $[Monomer]_0/[Alkoxyamine]_0$ = 384: (a) Precipitation polymerizations in $scCO_2$ at 30 MPa; conversions are 20 (black), 33 (red), 47 (green) and 62 (purple) and (b) solution polymerizations in toluene; conversions are 17 (black), 31 (red), 51 (green), 62 (purple) and 82% (orange).

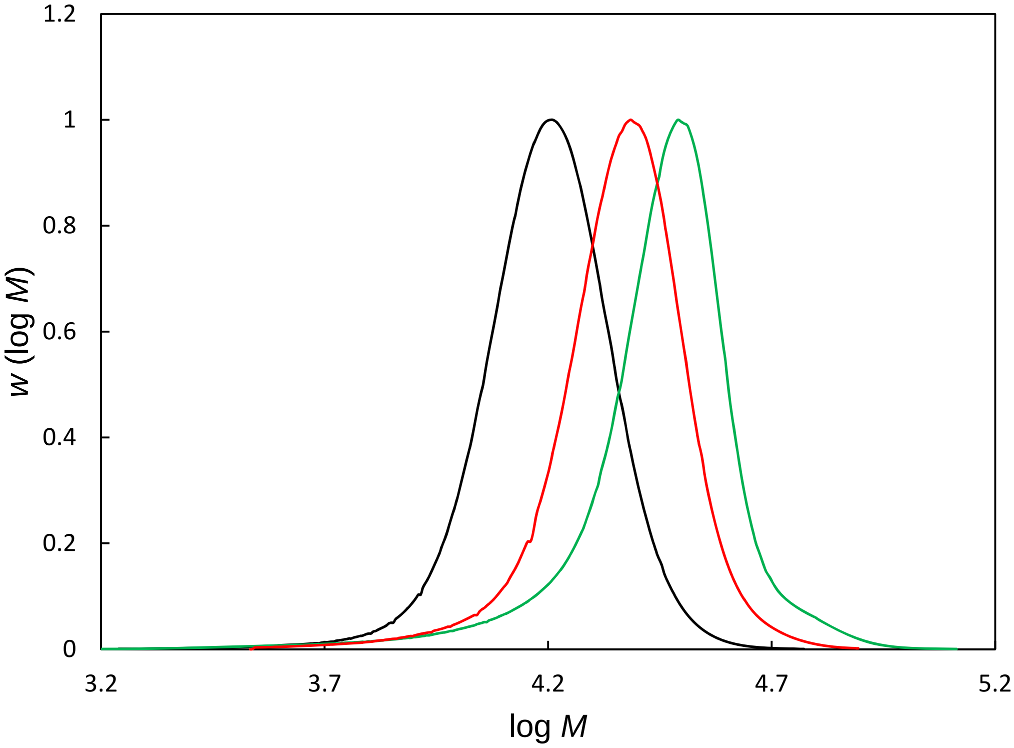

Figure S17. MWDs for alkoxyamine **2** initiated solution NMPs of styrene (50% w/v) at 110 °C in toluene using $[\text{Monomer}]_0/[\text{Alkoxyamine}]_0 = 384$: conversions are 38 (black), 61 (red) and 78% (green).

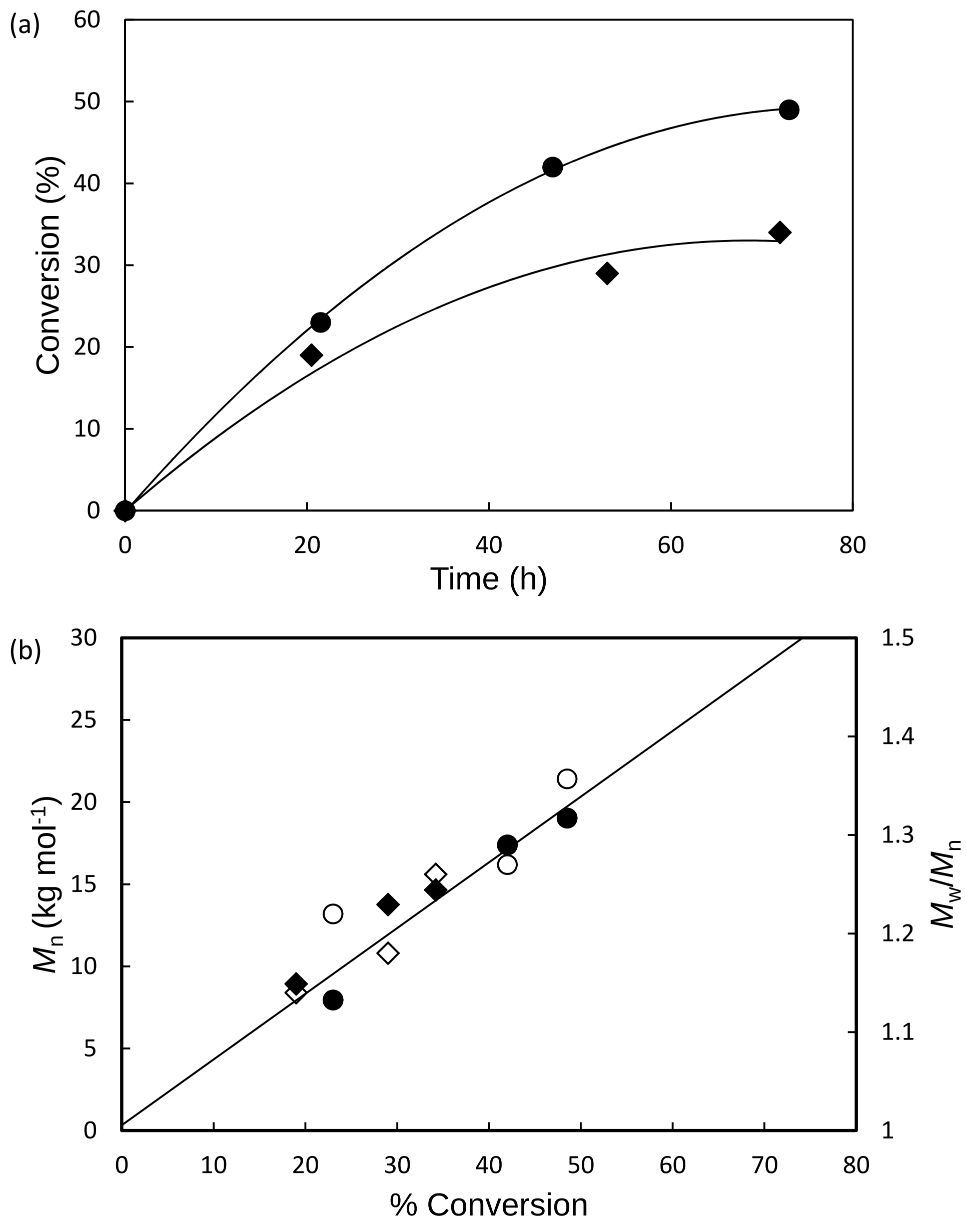

Figure S18 The effect of free TIPNO on NMP in $scCO_2$ at 110 °C. (a) Conversion versus time and (b) M_n (closed symbols) and M_w/M_n (open symbols) vs conversion plots for TIPNO-**1a** alkoxyamine initiated precipitation NMP of styrene (50% w/v) using $[Monomer]_0/[Alkoxyamine]_0 = 384$ with $[Free\ TIPNO]_0/[Alkoxyamine]_0 = 0.05$ (diamonds) and $[Free\ TIPNO]_0/[Alkoxyamine]_0 = 0$ (circles).

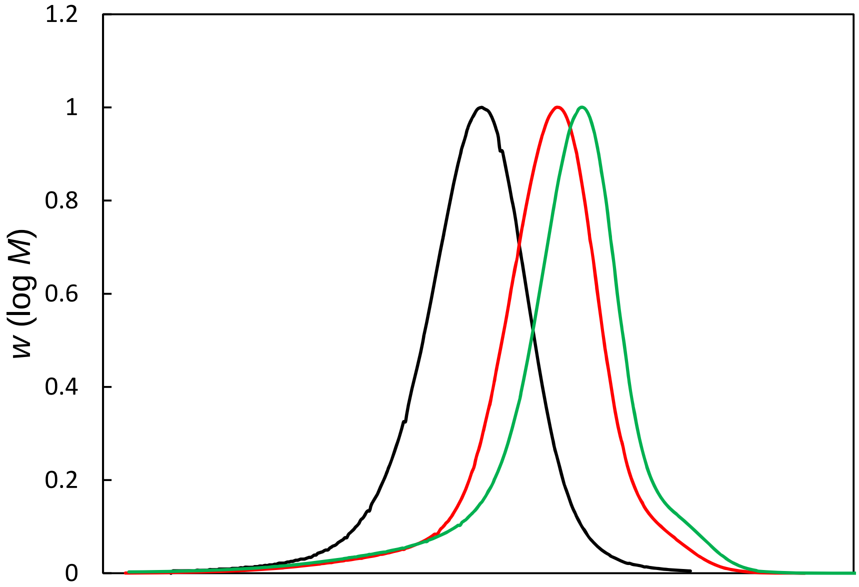

Figure S19 MWDs for alkoxyamine **TIPNO-1a** initiated precipitation NMP of styrene (50% w/v) at 110 °C in $scCO_2$ using $[Monomer]_0/[Alkoxyamine]_0$ = 384 with $[Free\ TIPNO]_0/[Alkoxyamine]_0$ = 0.05: conversions are 19 (black), 29 (red) and 34% (green).