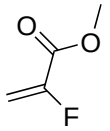
13.07.2016 Denksport Dima

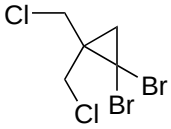
I.



1) $LiAlH_4$-$AlCl_3$
2) MsCl; NEt_3

→ **1.1** (73%) → **a**, *t*-BuOK → **1.2** (25%) → 1) UV 2) H_2SO_4 then "Amberlite" → **1.3** (55%)

II.



1) MeLi (2.4 eq.)
2) CF_3I, pentane rt, 20 h

→ **2.1** (64%) → 1) *t*-BuLi, Et_2O, -78C 2) HCO_2Me (excess) -78C - rt, 3 h → **2.2** (formally **2.2**xMeOH) →

1) **b**, DCM, rt
2) TMSCN (3 eq.)
3) chromatographic separation

→ **2.3** (80%) → 1) $Pb(OAc)_4$, DCM, 0C 2) 20% HCl, reflux, 3 h 3) chromatography on Dowex-50 → **2.4** (70%)

III.

Kemp's triacid

1) 190C, 0.01mmHg
2) 25% NH_3, DMAP, Δ, 24 h
3) $SOCl_2$, Δ, then MeOH
4) $LiAlH_4$, Et_2O, reflux

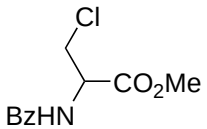
→ **3.1** (81%) → Jones reagent → **3.2** (67%)

→ Ac_2O, MeOH, 8 h → **3.3** (82%) →

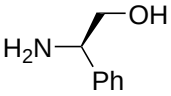
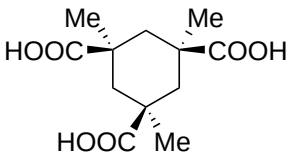
1) CrO_3x2Py, DCM
2) $KMnO_4$, acetone/H_2O
3) 1.5M HCl, reflux then pH to 7.45

→ **3.4** (63%) → 80C, 0.01 mmHg sublimation → **3.5** (100%) → just water → identical to 3.4

a:



b: (*R*)-α-phenylglycinol



Kemp's triacid: