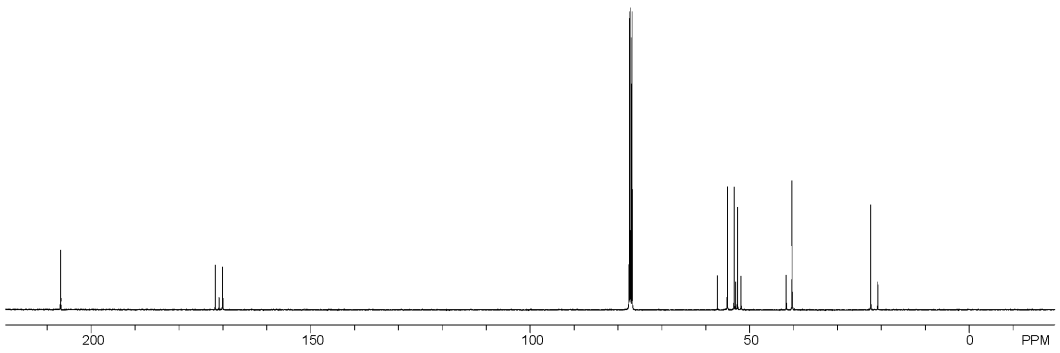
Table S1 Atomic coordinates of AcKepOMe in its minimal energy conformations

cis distal				**trans distal**			
C	1.05948000	2.04061100	0.04800900	C	–1.19044800	1.98304600	–0.00057800
C	1.75269500	0.80758800	–0.50659100	C	–1.79090800	0.65615700	0.45772200
N	1.07358900	–0.30411600	0.14693600	N	–1.01730100	–0.34512800	–0.26161000
C	–0.19996300	0.08411700	0.74123300	C	0.23676500	0.18567100	–0.79494100
C	–0.02521600	1.59012100	1.02413900	C	–0.04305100	1.68960400	–0.96002700
C	1.56092300	–1.57948400	0.02185500	C	–1.20298500	–1.70298000	–0.21893700
C	0.76293300	–2.69258500	0.67163200	C	–2.46848200	–2.19320300	0.45014300
O	2.60363900	–1.79093900	–0.57445400	O	–0.38361200	–2.46125800	–0.71309500
C	–1.38430700	–0.15023100	–0.20399000	C	1.39286400	–0.05030800	0.17914700
O	–1.29879700	–0.3326490	–1.38974400	O	1.26761600	–0.16192900	1.37225700
O	–2.54094700	–0.09588300	0.47816300	O	2.56600400	–0.05761200	–0.46815900
C	–3.74289100	–0.24169900	–0.30796000	C	3.73642100	–0.23910100	0.35491100
O	1.32263700	3.17986300	–0.22916600	O	–1.57410800	3.06871800	0.34035100
H	2.81960100	0.81507700	–0.27684900	H	–2.85435200	0.62769000	0.21040000
H	1.64895300	0.77796700	–1.59614800	H	–1.68448300	0.58095300	1.54561000
H	–0.39169300	–0.46862900	1.65975500	H	0.47683000	–0.30577800	–1.73458700
H	–0.93275200	2.18080200	0.91152300	H	0.80970300	2.33629800	–0.75784600
H	0.35099700	1.74681900	2.03890700	H	–0.39066600	1.90766500	–1.97386200
H	1.30020300	–3.62369200	0.51142400	H	–2.52011200	–3.27253700	0.33263900
H	–0.23232900	–2.77675400	0.22887600	H	–3.35867500	–1.73648700	0.01133700
H	0.64353000	–2.52970400	1.74560600	H	–2.45984400	–1.94868600	1.51544200
H	–3.74893900	–1.20845300	–0.80942100	H	3.68365000	–1.19666600	0.87092100
H	–4.56260300	–0.16988600	0.40136200	H	4.57844300	–0.21729800	–0.33131800
H	–3.80426900	0.55149800	–1.05193500	H	3.81234400	0.56408400	1.08706300
cis proximal				**trans proximal**			
C	–0.09285700	2.19898900	0.13509500	C	–1.15275600	1.94714500	0.15267700
C	0.94276000	1.40976900	–0.64956900	C	–1.60054000	0.57095900	0.64267500
N	1.02465100	0.13485700	0.05115000	N	–0.92226100	–0.35787800	–0.24759000
C	–0.07559900	–0.07152900	0.99997800	C	0.15596000	0.26718400	–1.01582600
C	–0.53836000	1.35923500	1.32965200	C	–0.22888400	1.75725400	–1.04210400
C	2.02253800	–0.75731100	–0.24603500	C	–1.05727100	–1.72162700	–0.25844100
C	2.04338800	–2.06049200	0.52831100	C	–2.15351100	–2.30117900	0.60998400
O	2.86226100	–0.48789000	–1.08979800	O	–0.32703700	–2.41703700	–0.94636500
C	–1.22622400	–0.90626300	0.42937800	C	1.55649400	0.07591200	–0.42861900
O	–1.72805100	–1.84054700	1.00079600	O	2.55931400	0.22574800	–1.07642100
O	–1.61748200	–0.44884100	–0.77002000	O	1.53536100	–0.21021800	0.88364400
C	–2.71601500	–1.14989900	–1.39072700	C	2.82732500	–0.39139100	1.49943900
O	–0.48601600	3.30146600	–0.13527500	O	–1.48878600	2.99240100	0.63974000
H	1.90695900	1.92237300	–0.65588600	H	–2.68903200	0.49723300	0.58321200
H	0.62166800	1.30088000	–1.68965000	H	–1.30634800	0.45706300	1.69206100
H	0.26900000	–0.60070700	1.88507100	H	0.19772400	–0.16999400	–2.01085900
H	–1.60694300	1.46343400	1.51081500	H	0.61634600	2.44278300	–1.00493100
H	–0.01057300	1.73099700	2.21288800	H	–0.80139200	1.98912200	–1.94507300
H	2.83899100	–2.67711700	0.11832100	H	–2.17961100	–3.37635400	0.45270800
H	1.09568600	–2.59820000	0.45874000	H	–3.12864300	–1.87490400	0.36258800
H	2.24500000	–1.88241500	1.58786800	H	–1.96144100	–2.09739400	1.66662500
H	–3.60087000	–1.09689200	–0.75790000	H	3.42716400	0.51129100	1.39134400
H	–2.88556700	–0.64186900	–2.33572100	H	2.62349200	–0.59733300	2.54666300
H	–2.44939200	–2.19298200	–1.55472600	H	3.34584300	–1.22907200	1.03530300

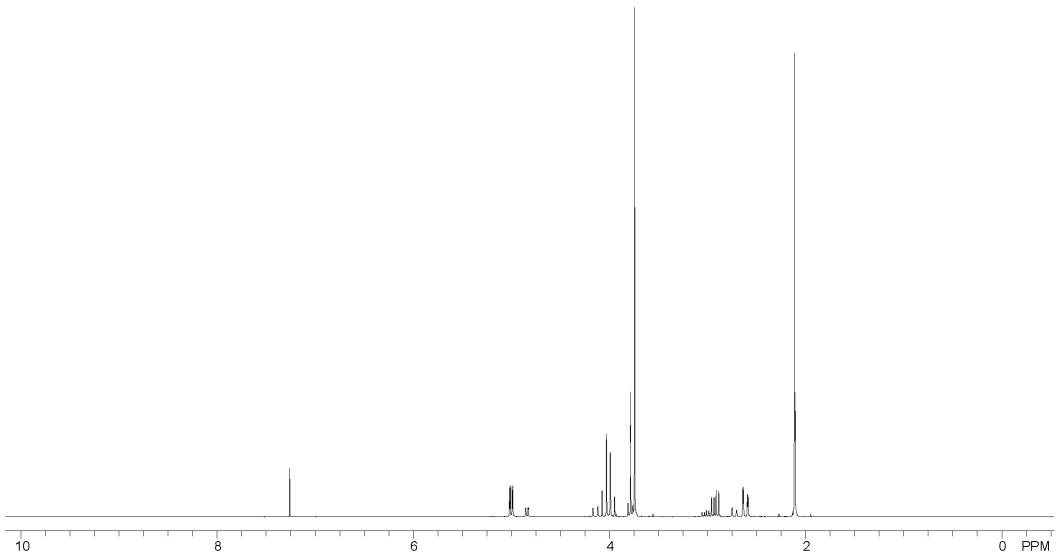
Table S2 SCF energies of AcKepOMe (atomic units; au)

Conformations	Energy (au)	ZPE correction (au)	Energy (ZPE–corrected)
Cis distal	–667.3481857	0.188879	–667.1593067
Cis proximal	–667.3479247	0.189073	–667.1588517
Trans distal	–667.3507856	0.189128	–667.1616576
Trans proximal	–667.3490935	0.189051	–667.1600425

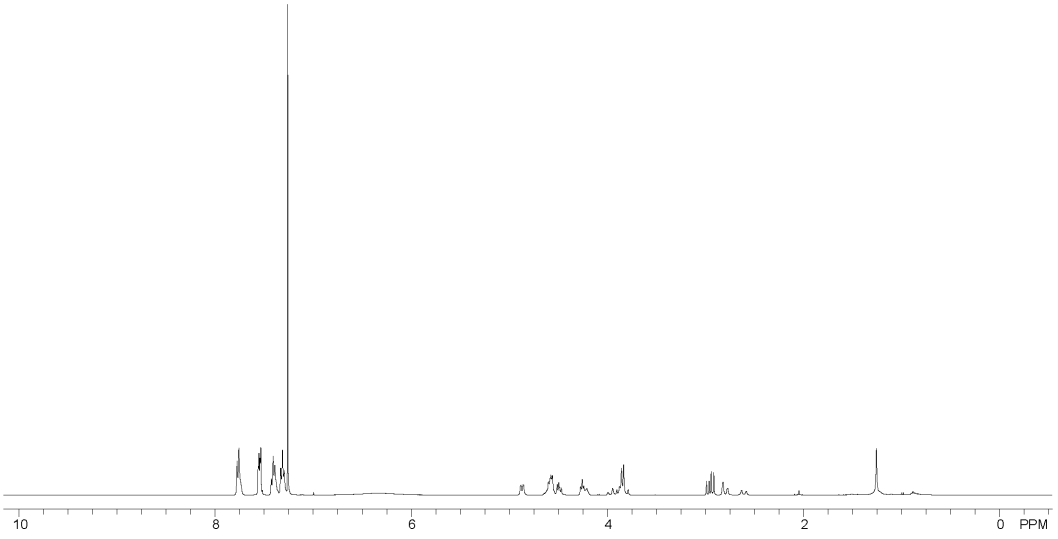
^{1}H NMR spectrum of AcKepOMe



^{13}C NMR spectrum of AcKepOMe



^{1}H NMR spectrum of FmocKepOH



^{13}C NMR spectrum of FmocKepOH