Electronic Supplementary Material (ESI) for Dalton Transactions.

$MoCl_5$ as an Effective Chlorinating Agent Towards α-Aminoacids: Synthesis of α-Ammonium-Acylchloride Salts and α-Amino-Acylchloride Complexes

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Supporting Information

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Figure S1. DFT-calculated structures of pyrrolidinium-2-carbonylchloride salts, with implicit solvation (C-PCM, CH_2Cl_2).

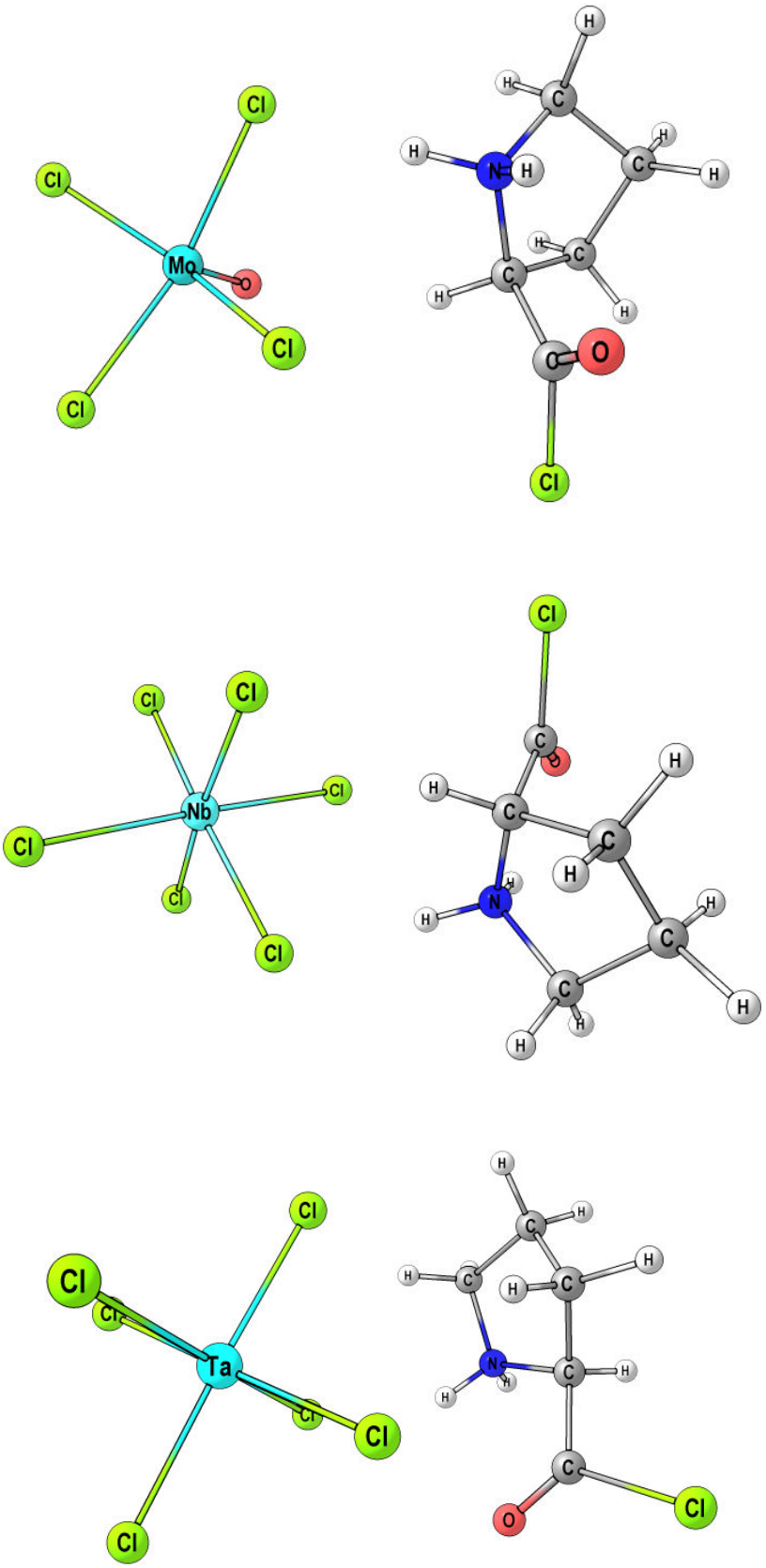
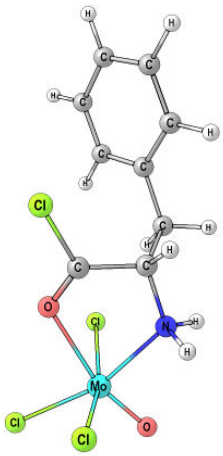


Table S1. Selected computed bond distances (Å) for pyrrolidinium-2-carbonylchloride salts (M06/C-PCM).

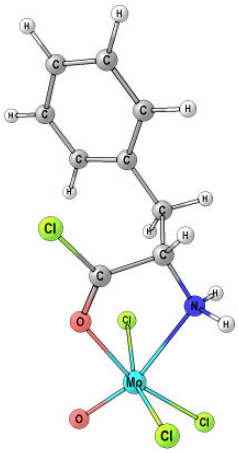
	1	**[PRO][$NbCl_6$] ***	**[PRO][$TaCl_6$] ***
C=O	1.193	1.193	1.190
C–Cl	1.763	1.763	1.770
ClC–C	1.512	1.510	1.506
N–CH_2	1.510	1.513	1.525
N–CH	1.508	1.510	1.507
CH–CH_2	1.540	1.537	1.527
$CHCH_2$–CH_2	1.524	1.525	1.523
NCH_2–CH_2	1.514	1.513	1.521
N–H	1.030	1.030	1.022
	1.039	1.032	1.036
CO···N	2.688	2.605	2.724
Mo=O	1.638		
Metal–Cl	2.359	2.330	2.329
	2.373	2.338	2.340
	2.399	2.348	2.343
	2.432	2.386	2.369
		2.414	2.374
		2.456	2.422
MCl···HN(*shortest*)	2.195	2.322	2.350

* PRO = $[\overline{NH_2(CH_2)_3CH}C(O)Cl]$

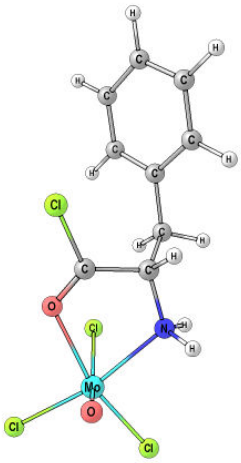
Figure S2. DFT-calculated structures with implicit solvation (C-PCM, CH_2Cl_2) of $MoOCl_3[O=C(Cl)CH(CH_2Ph)NH_2]$, **2a**, and relative energy values (Kcal mol^{-1}).



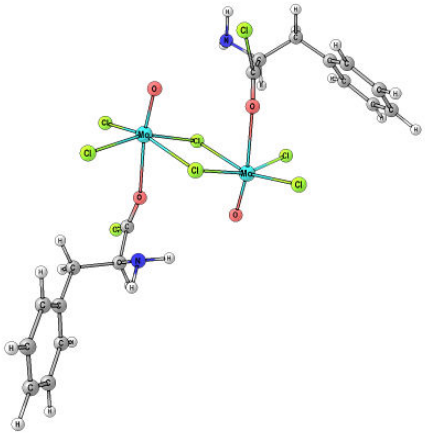
is1



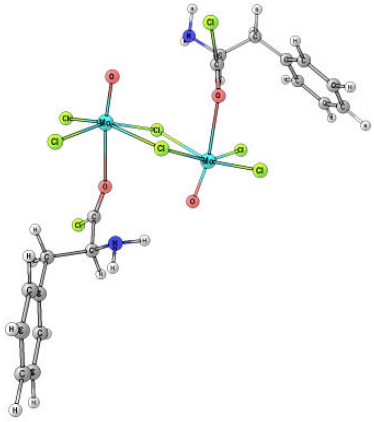
is2



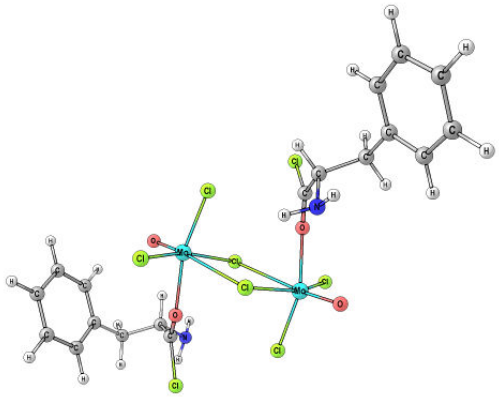
is3



is4-triplet



is4-singlet



is5-triplet

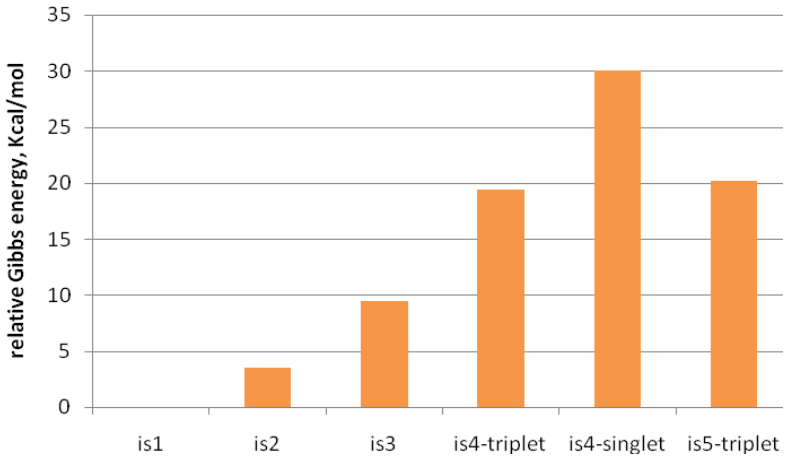
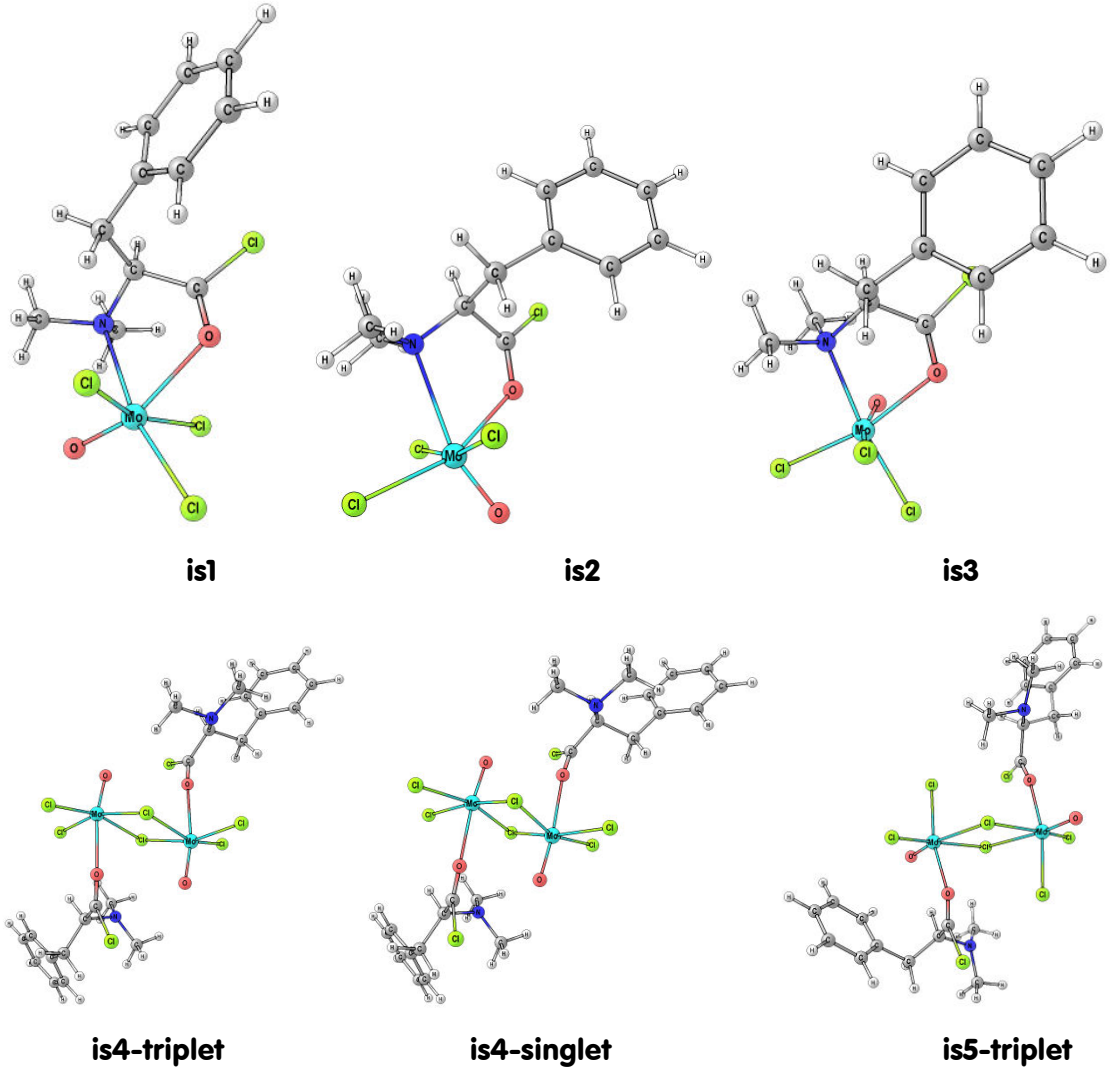


Table S2. Selected computed bond distances (Å) and angles (°) for the most stable isomer (*is1 in Figure S2*) of $MoOCl_3[\kappa(O):\kappa(N)\text{-}O{=}C(Cl)CH(CH_2Ph)NH_2]$, **2a** (M06/C-PCM calculations).

Bond	
Mo=O	1.643
Mo–O	2.401
Mo–N	2.287
Mo–Cl (*trans* to N)	2.336
Mo–Cl (*cis* to N)	2.377
	2.379
C=O	1.208
C–Cl	1.732

Angle	
O–Mo=O	163.1
O–Mo–N	69.7
N–Mo–Cl (*trans*)	159.7
N–Mo–Cl (*cis*)	83.4
	88.0

Figure S3. DFT-calculated structures with implicit solvation (C-PCM, CH_2Cl_2) of $MoOCl_3[O=C(Cl)CH(CH_2Ph)NMe_2]$, **2d**, and relative energy values (Kcal mol^{-1}).



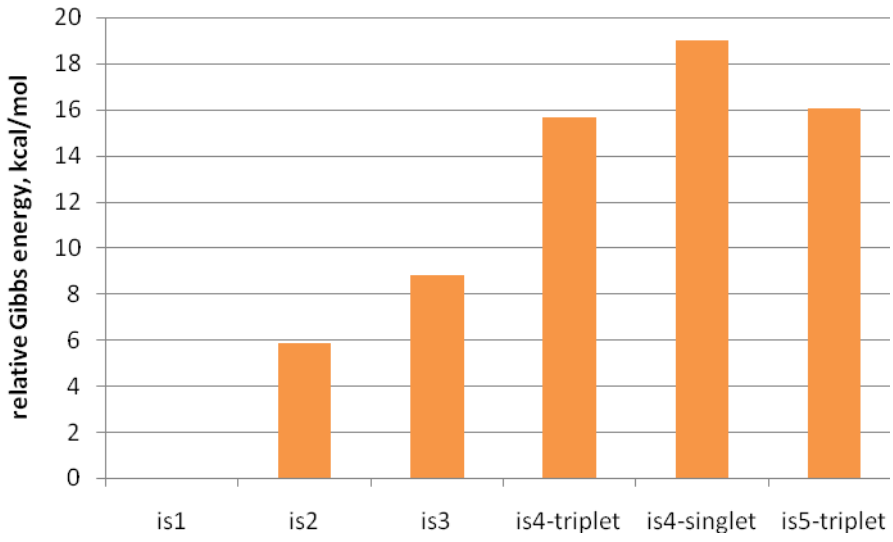


Table S3. Selected computed bond distances (Å) and angles (°) for the most stable isomer (*is1 in Figure S3*) of $MoOCl_3[\kappa(O):\kappa(N)\text{-}O{=}C(Cl)CH(CH_2Ph)NMe_2]$, **2d** (M06/C-PCM calculations).

Bond	
Mo=O	1.643
Mo–O	2.367
Mo–N	2.399
Mo–Cl (*trans* to N)	2.345
Mo–Cl (*cis* to N)	2.377
	2.378
C=O	1.211
C–Cl	1.728

Angle	
O–Mo=O	158.1
O–Mo–N	69.9
N–Mo–Cl (*trans*)	165.1
N–Mo–Cl (*cis*)	89.0
	90.6

Table S4. Selected computed bond distances (Å) and angles (°) for $MoCl_5[O_2CCH(CH_2Ph)NH_3]$, **4** (M06/C-PCM calculations).

Bond	
Mo–O	1.944
Mo–Cl (*cis* to O)	2.321
	2.338
	2.370
	2.455
Mo–Cl (*trans* to O)	2.282
C–O	1.331
C=O	1.202

Angle	
O–Mo–Cl (*trans* to O)	172.9
O–Mo–Cl (*cis* to O)	84.8
	86.7
	88.0
	92.7

Table S5. Selected computed bond distances (Å) and angles (°) for $MoCl_4$[κ(*O*):κ(*N*)-OC(Cl)(OH)CH(CH_2Ph)NH_2], **5** (M06/C-PCM calculations).

Bond	
Mo–O	1.860
Mo–N	2.292
Mo–Cl (*trans* to O)	2.308
Mo–Cl (*trans* to N)	2.306
Mo–Cl (*trans* to Cl)	2.362
	2.355
C–O	1.389
C–OH	1.358
C–Cl	1.829

Angle	
O–Mo–N	72.8
O–Mo–Cl (*trans*)	154.0
N–Mo–Cl (*trans*)	172.5
Cl–Mo–Cl (*trans*)	174.5

Table S6. Selected computed bond distances (Å) and angles (°) for $[NH_3CH(CH_2Ph)C(O)Cl][MoOCl_4]$, **3** (M06/C-PCM calculations).

Bond	
Mo–Cl	2.367
	2.371
	2.413
	2.435
Mo=O	1.636
C=O	1.190
C–Cl	1.768
NH---Cl (*shortest*)	2.377

Angle	
O–Mo–Cl	102.3
	101.2
	103.0
	102.9