Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Mechanistic Insights for the Transprotection of Tertiary Amines with Boc_2O *via* Charged Carbamates: Access to Both Enantiomers of 2-Azanorbornane-3-*exo*-carboxylic Acids

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Electronic Supplementary Information

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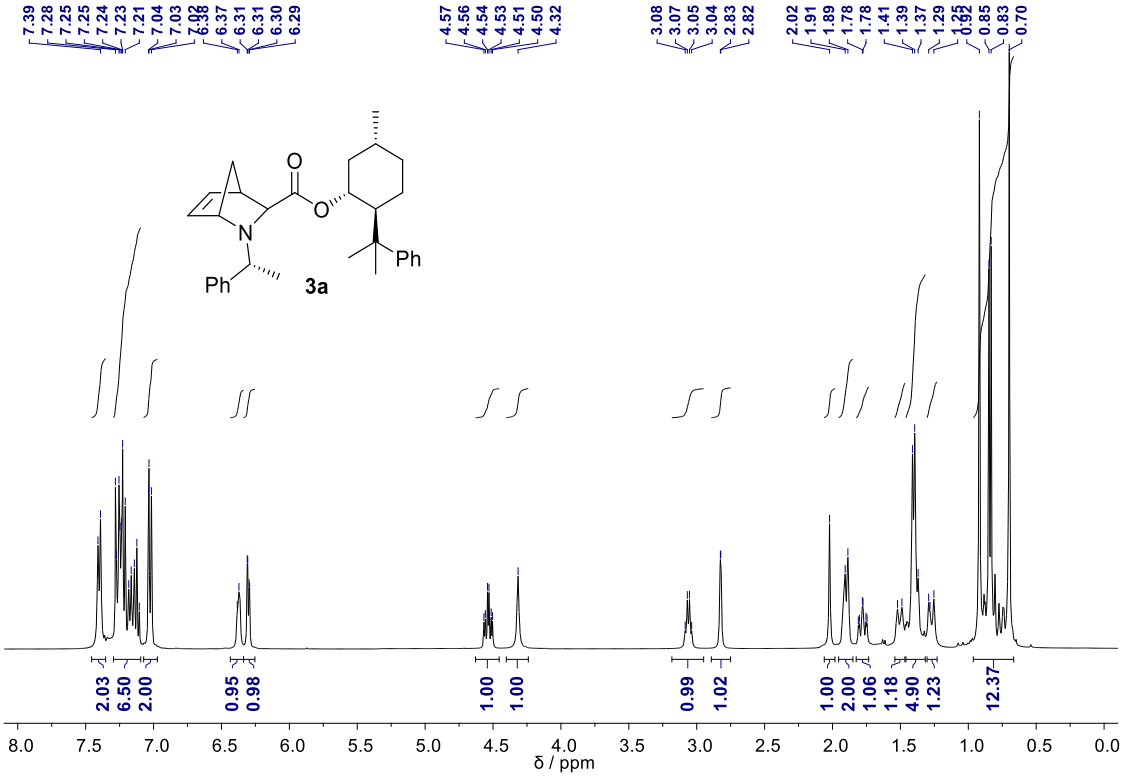

Figure S1. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of compound **3a**.

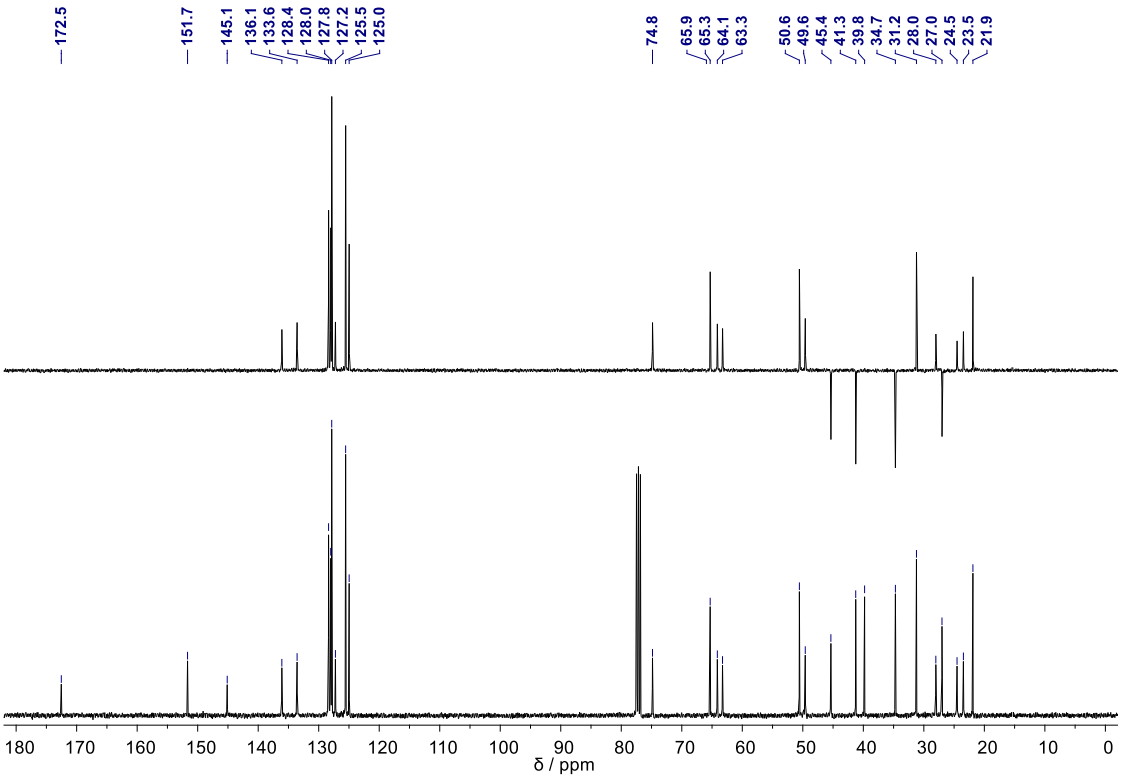

Figure S2. DEPT-135 (upper) and ^{13}C-NMR (lower) spectra ($CDCl_3$, 100 MHz) of compound **3a**.

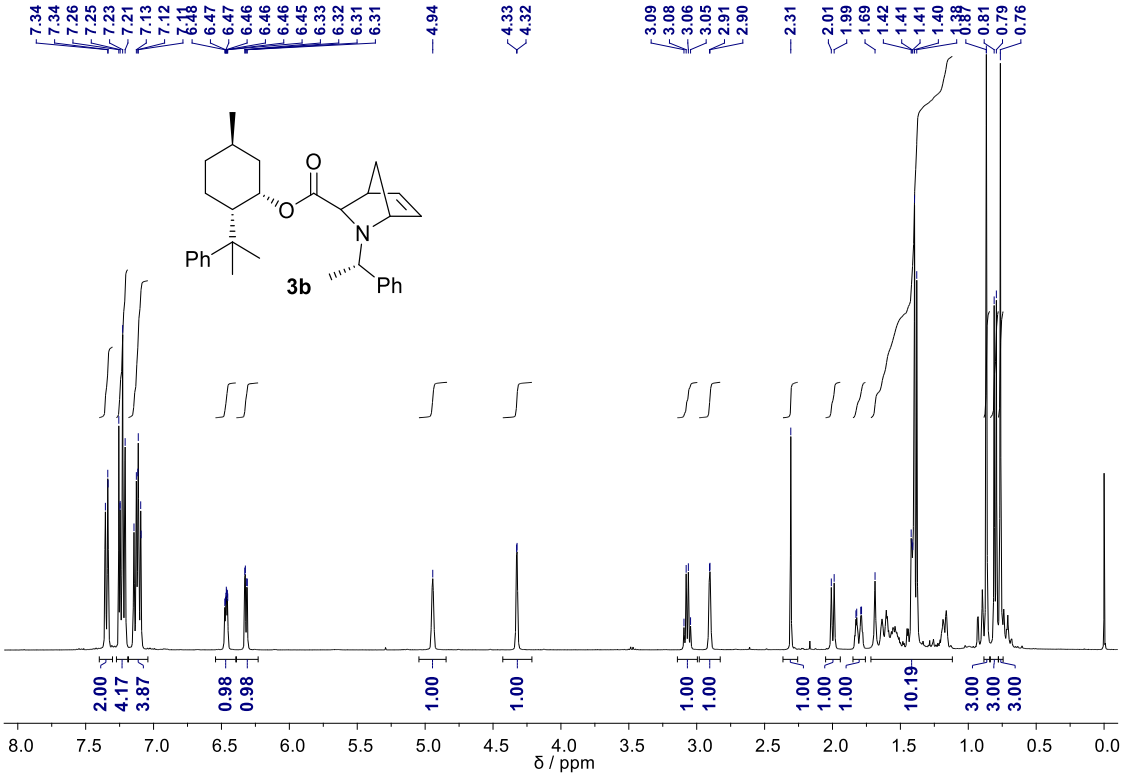

Figure S3. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of compound **3b**.

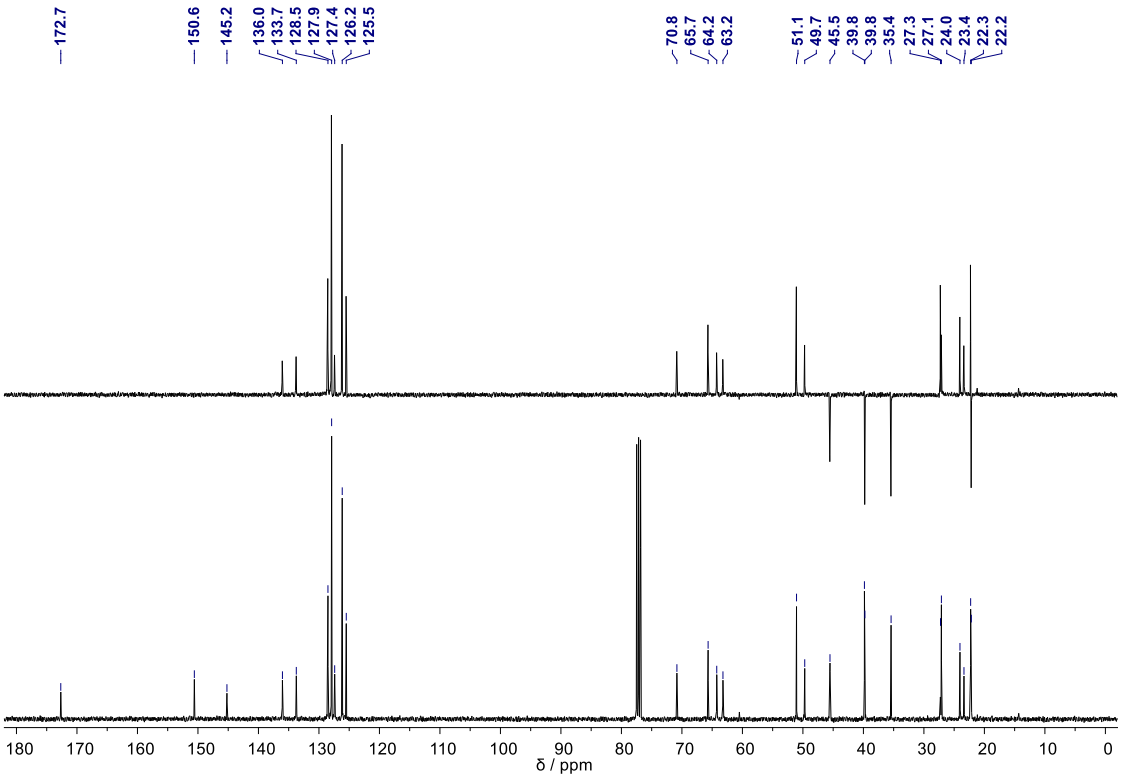

Figure S4. DEPT-135 (upper) and ^{13}C-NMR (lower) spectra ($CDCl_3$, 100 MHz) of compound **3b**.

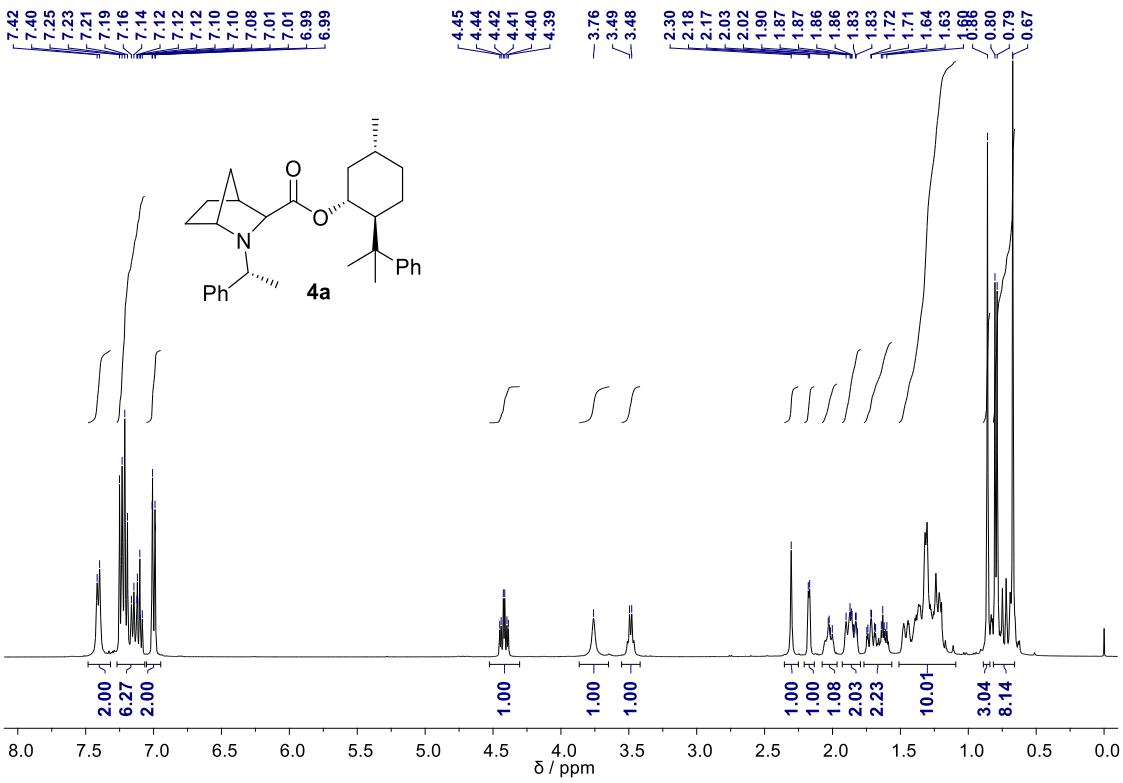

Figure S5. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of compound **4a**.

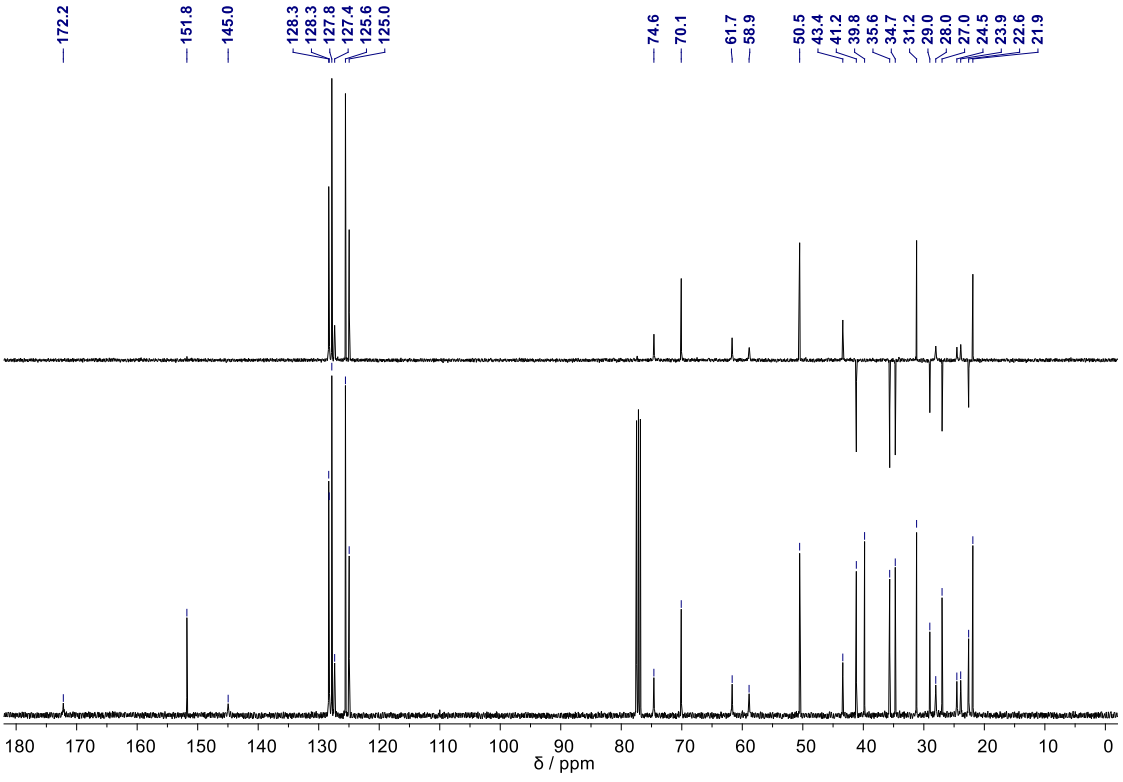

Figure S6. DEPT-135 (upper) and ^{13}C-NMR (lower) spectra ($CDCl_3$, 100 MHz) of compound **4a**.

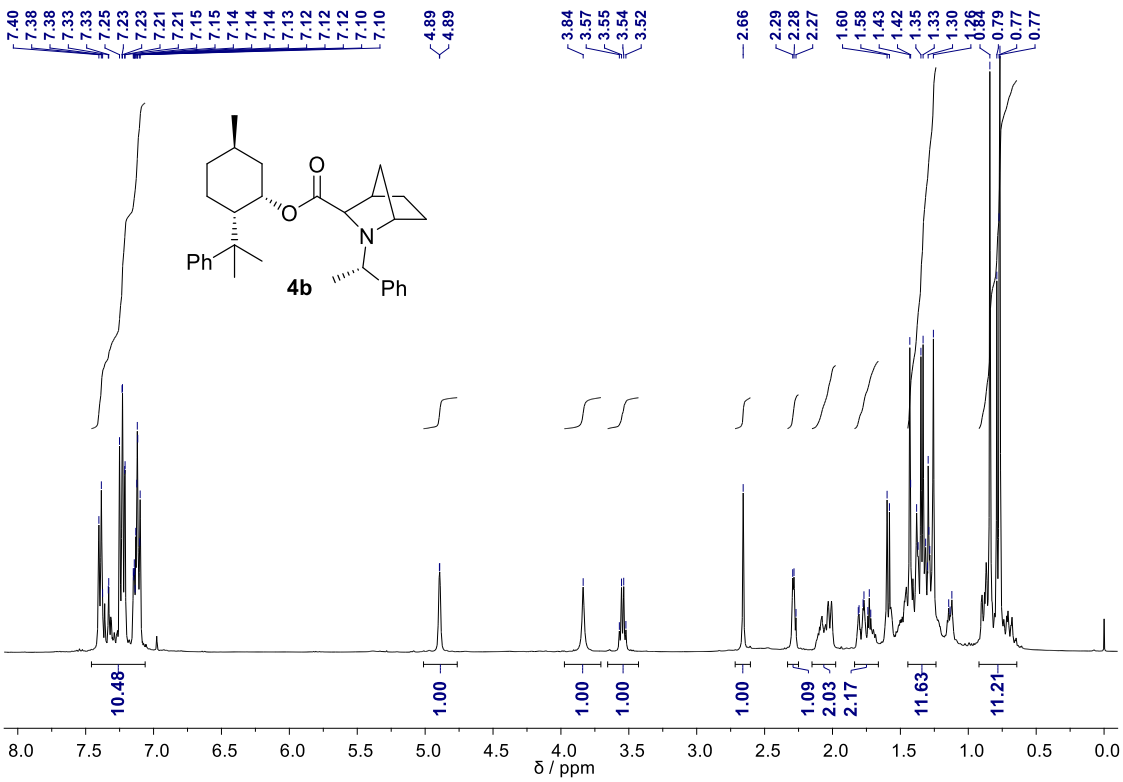

Figure S7. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of compound **4b**.

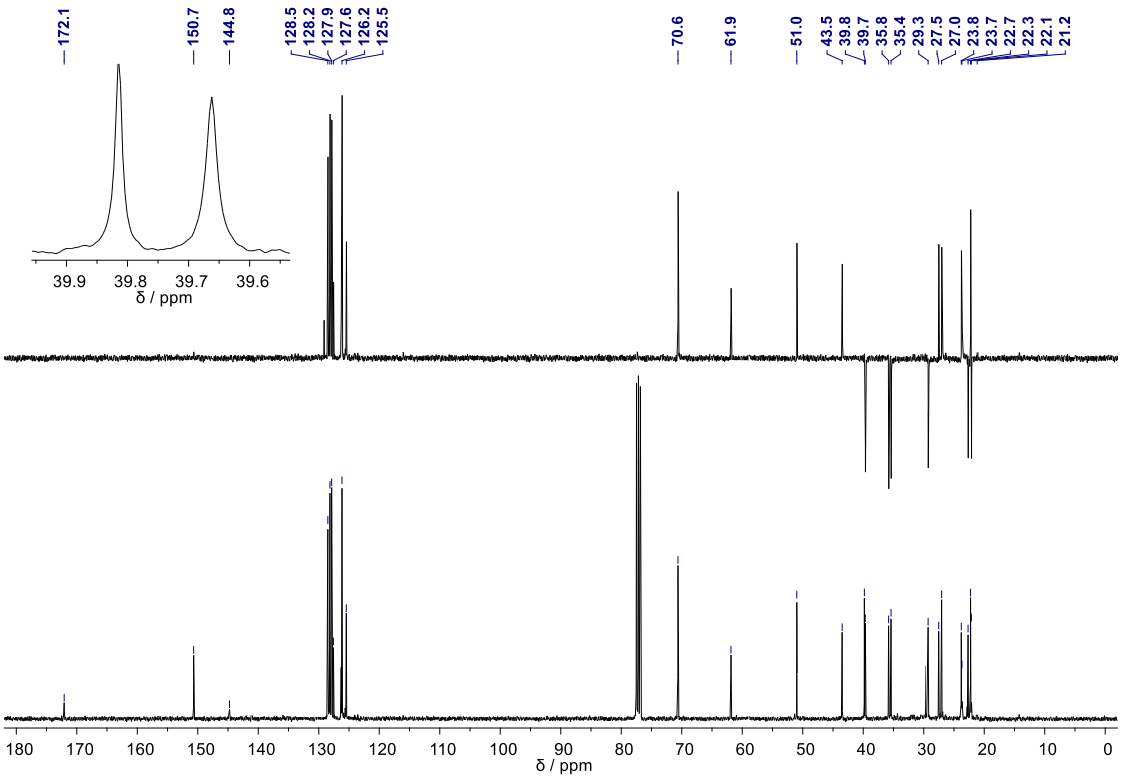

Figure S8. DEPT-135 (upper) and ^{13}C-NMR (lower) spectra ($CDCl_3$, 100 MHz) of compound **4b**.

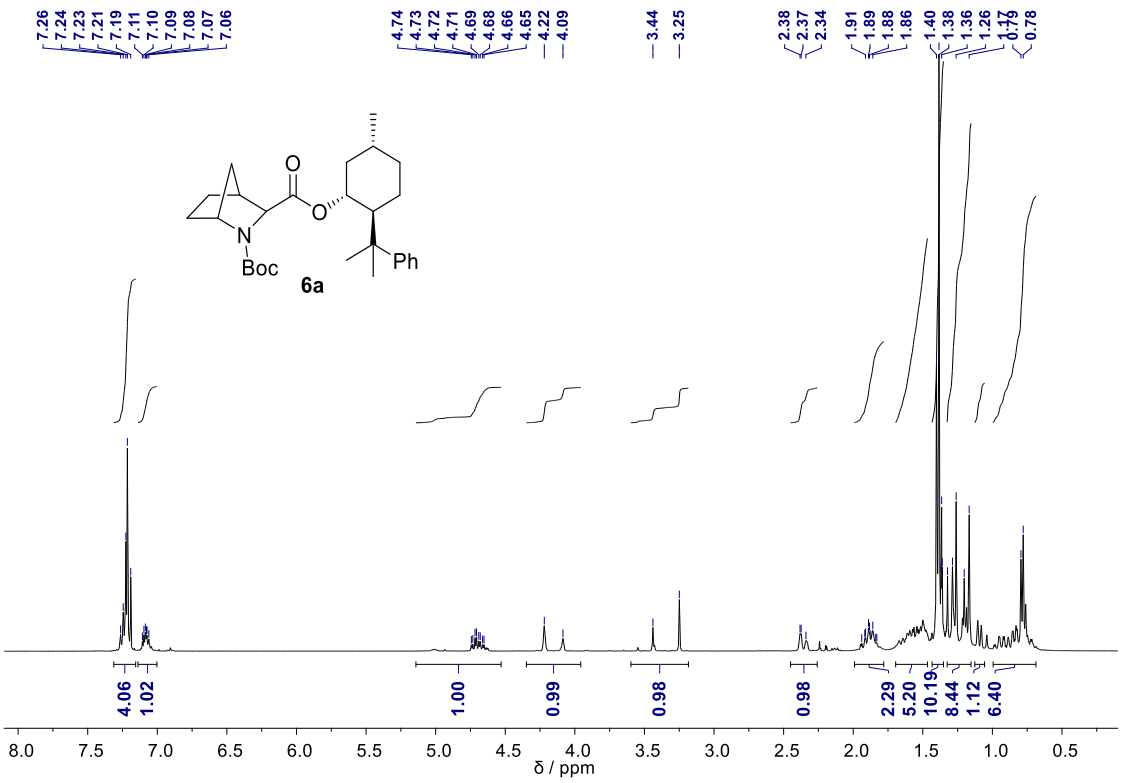

Figure S9. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of compound **6a**.

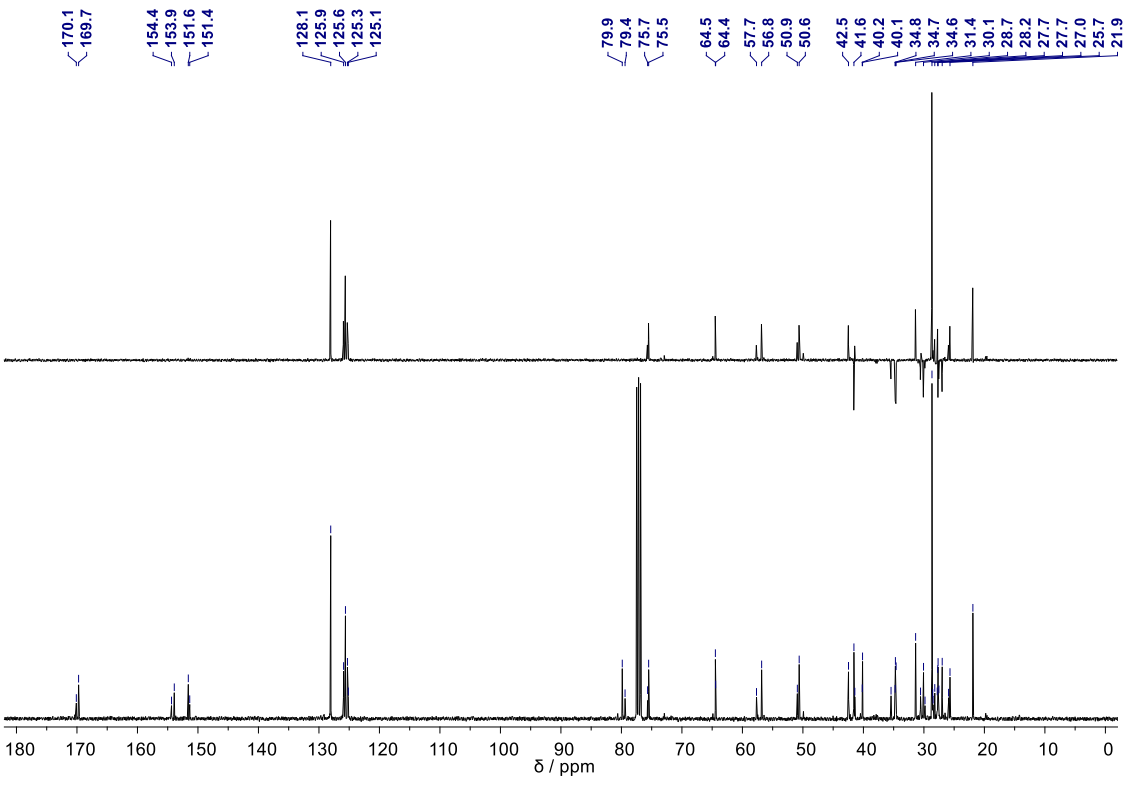

Figure S10. DEPT-135 (upper) and ^{13}C-NMR (lower) spectra ($CDCl_3$, 100 MHz) of compound **6a**.

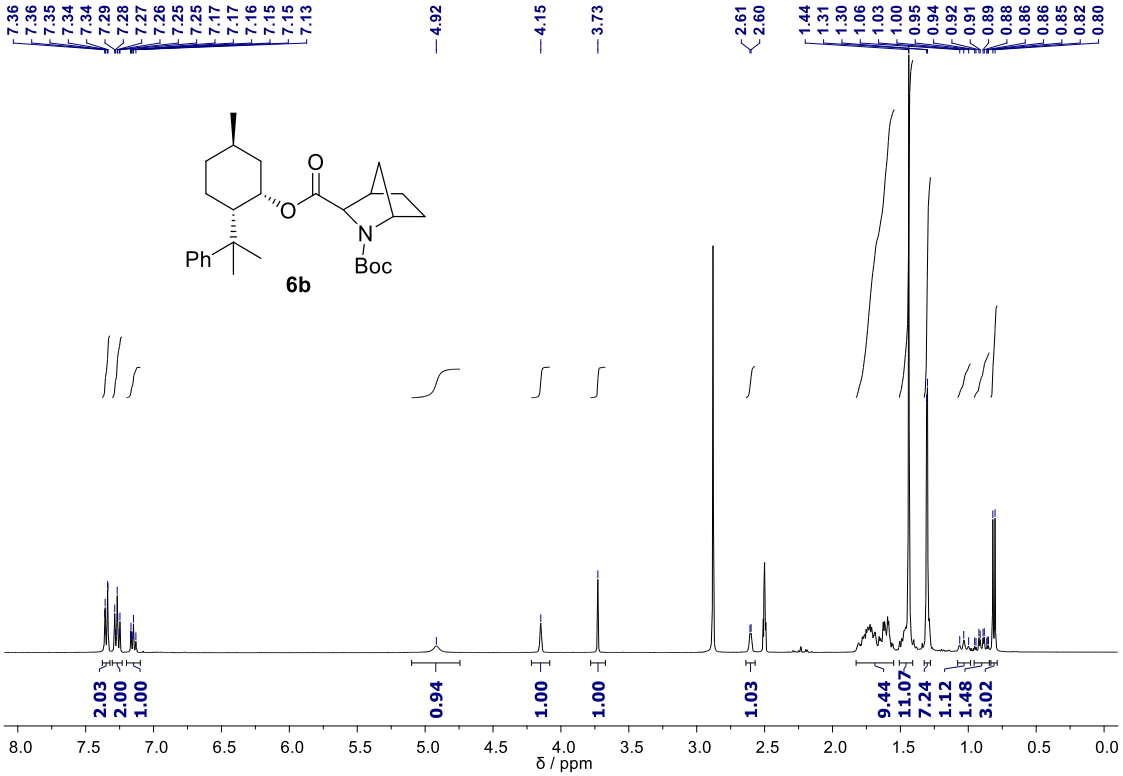

Figure S11. ^{1}H-NMR spectrum (DMSO-d_6, 115 ºC, 400 MHz) of compound **6b**.

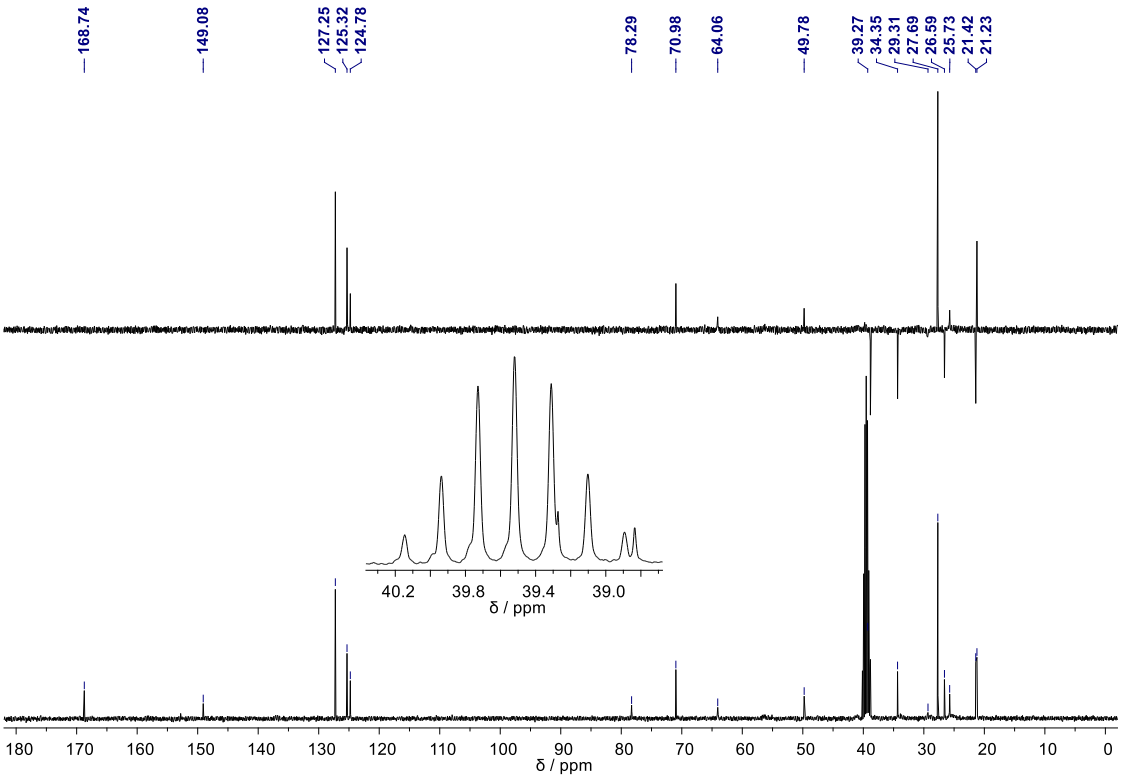

Figure S12. DEPT-135 (upper) and ^{13}C-NMR (lower) spectra (DMSO-d_6, 115 ºC, 100 MHz) of compound **6b**.

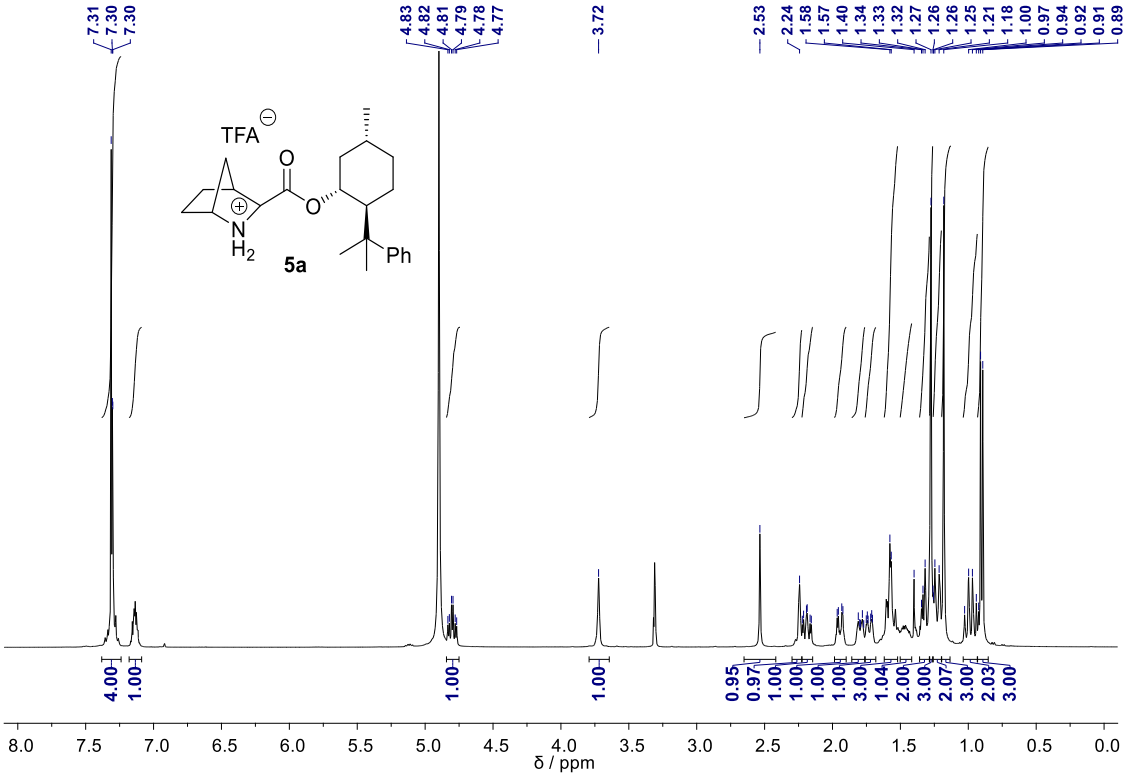

Figure S13. ^{1}H-NMR spectrum (MeOD, 400 MHz) of compound **5a**.

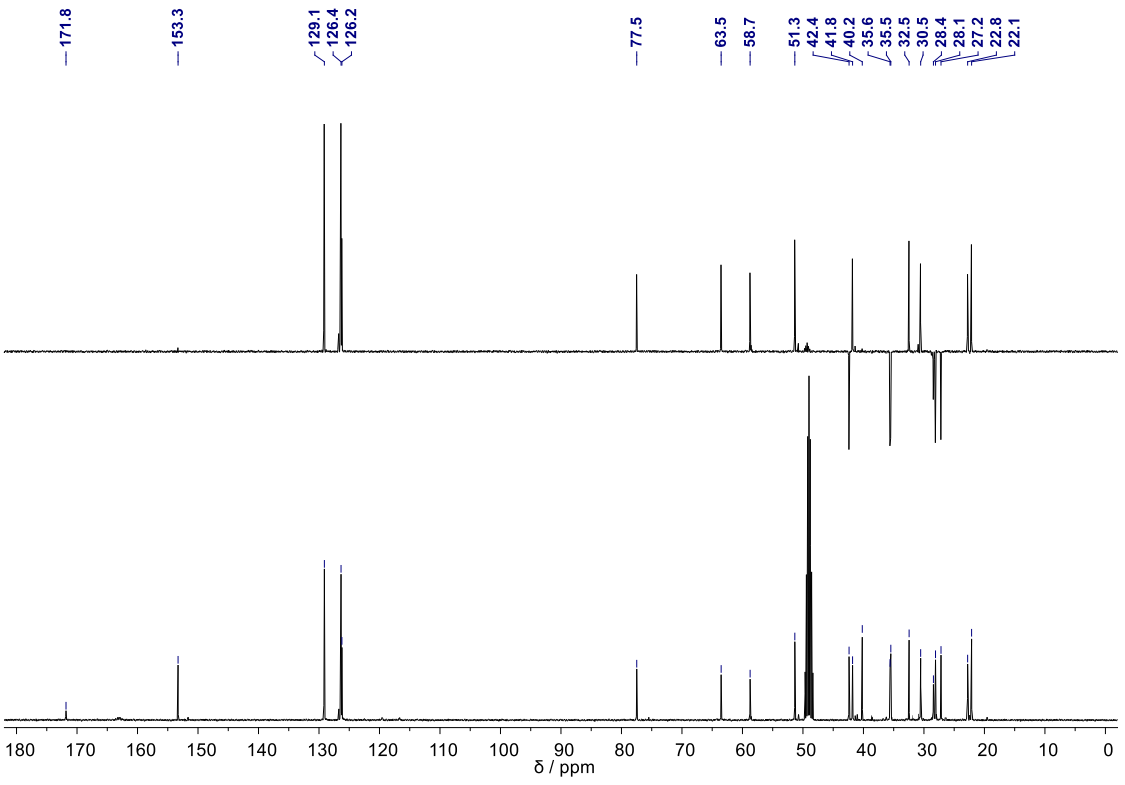

Figure S14. DEPT-135 (upper) and ^{13}C-NMR (lower) spectra (MeOD, 100 MHz) of compound **5a**.

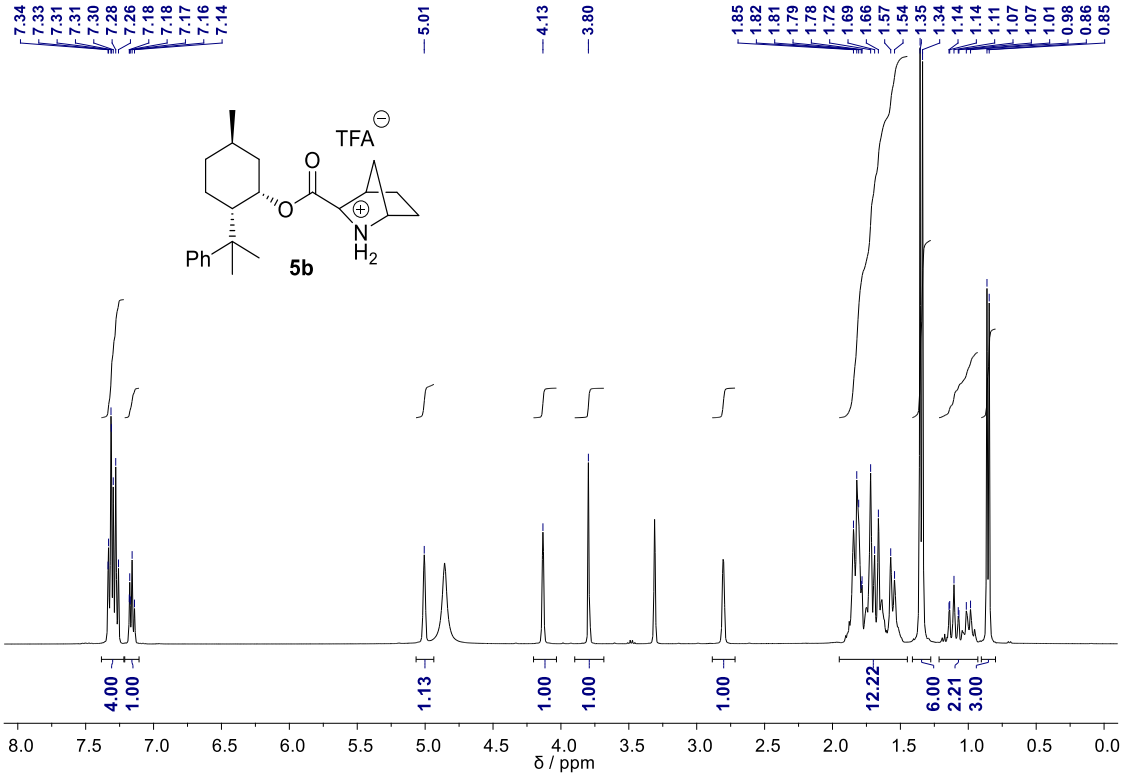

Figure S15. ^{1}H-NMR spectrum (MeOD, 400 MHz) of compound **5b**.

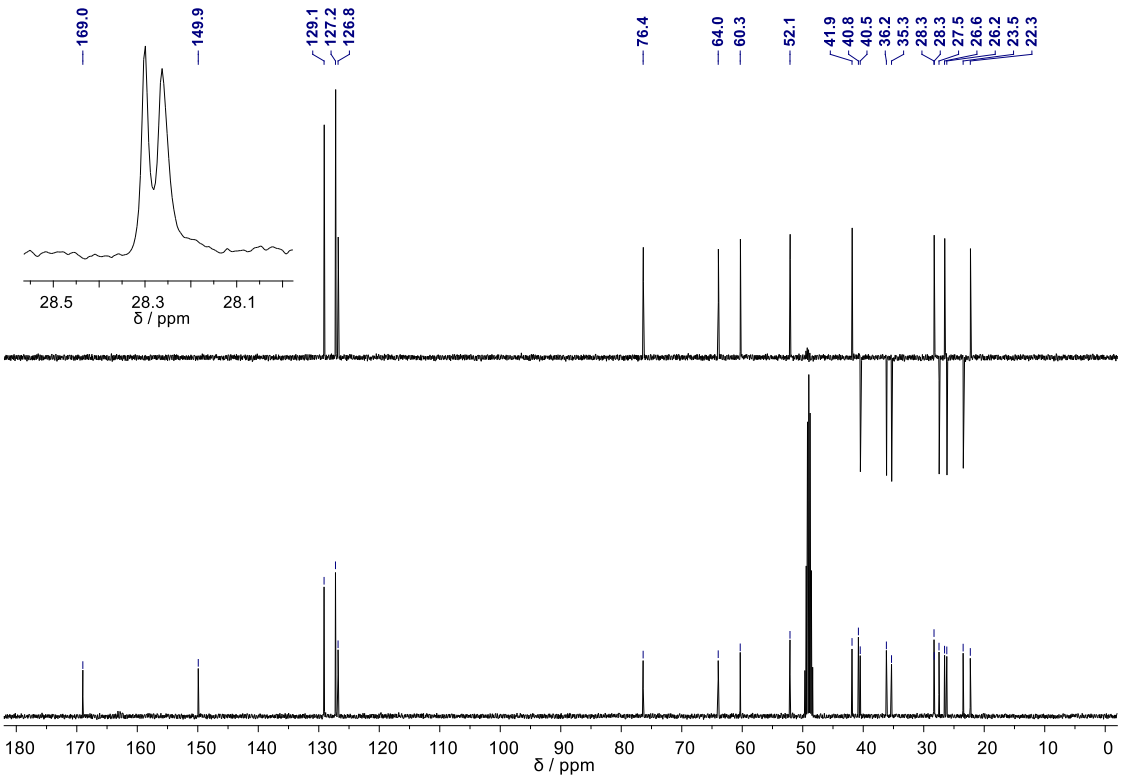

Figure S16. DEPT-135 (upper) and ^{13}C-NMR (lower) spectra (MeOD, 100 MHz) of compound **5b**.

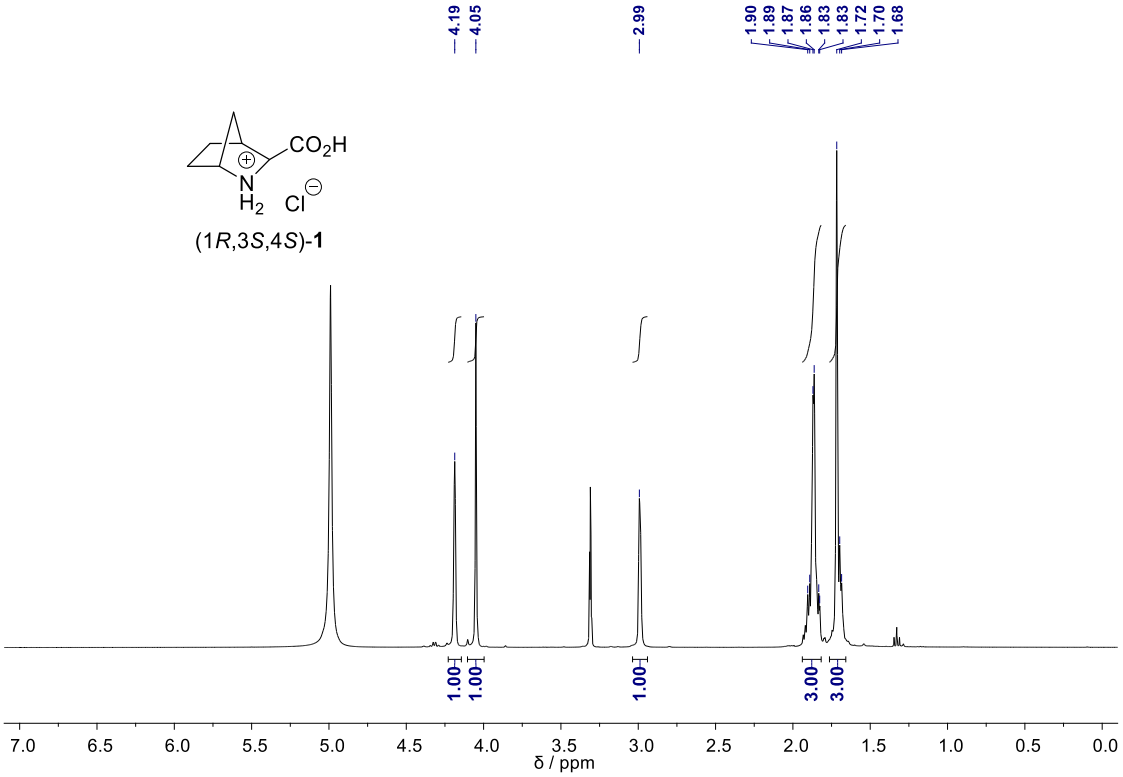

Figure S17. ^{1}H-NMR spectrum (MeOD, 400 MHz) of compound (1*R*,3*S*,4*S*)-**1**. Spectroscopic data is the same for (1*S*,3*R*,4*R*)-**1**.

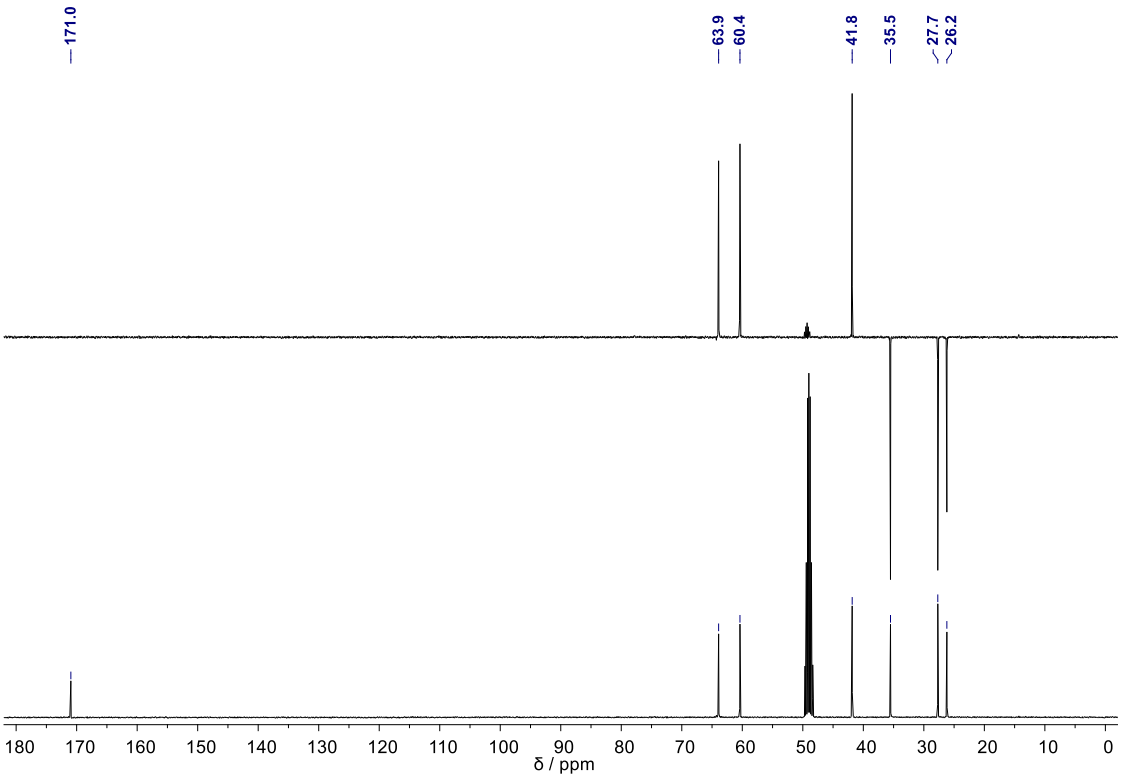

Figure S18. DEPT-135 (upper) and ^{13}C-NMR (lower) spectra (MeOD, 100 MHz) of compound (1*R*,3*S*,4*S*)-**1**. Spectroscopic data are the same for (1*S*,3*R*,4*R*)-**1**.

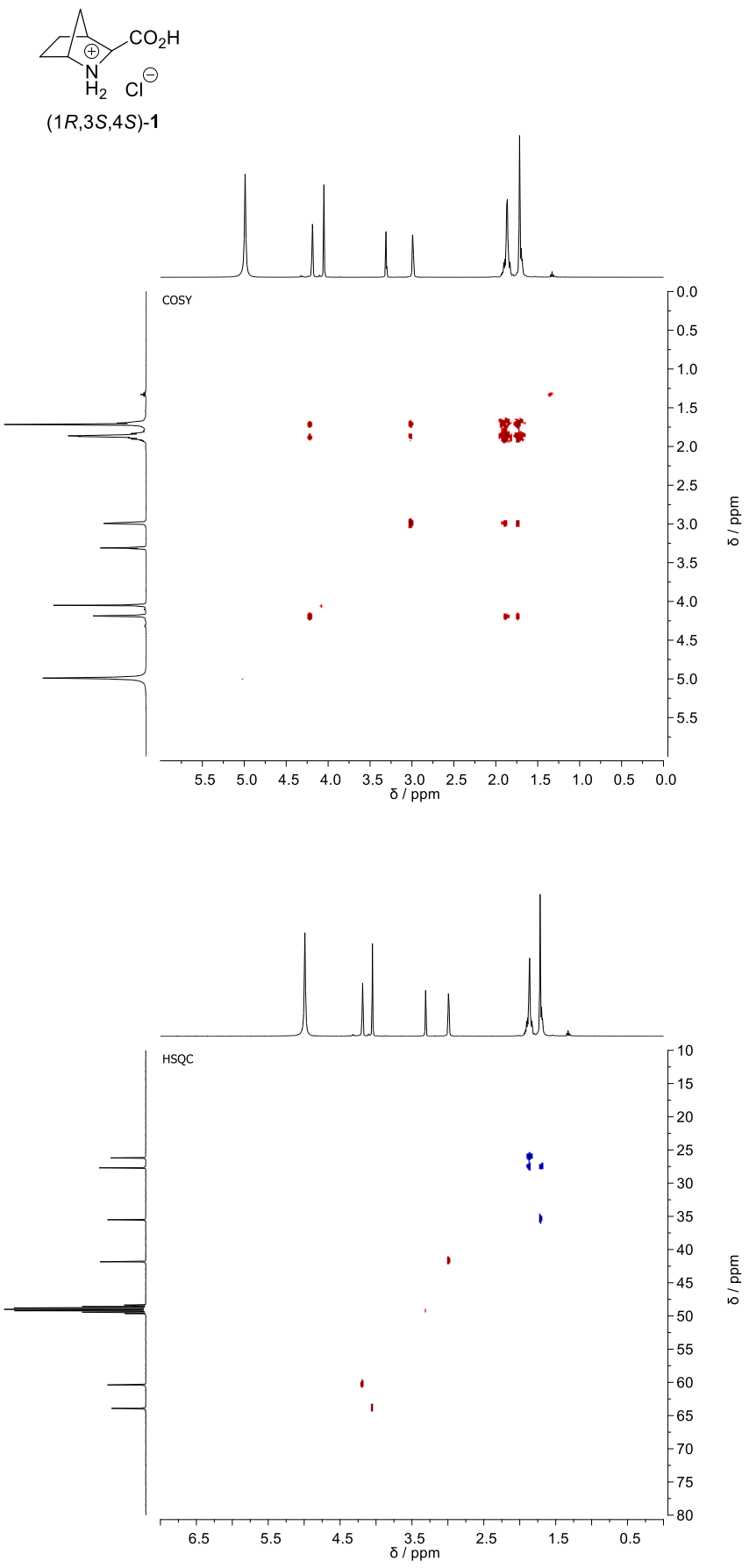

Figure S19. COSY (upper) and HSQC (lower) spectra (MeOD) of compound (1*R*,3*S*,4*S*)-**1**. Spectroscopic data are identical for (1*S*,3*R*,4*R*)-**1**.

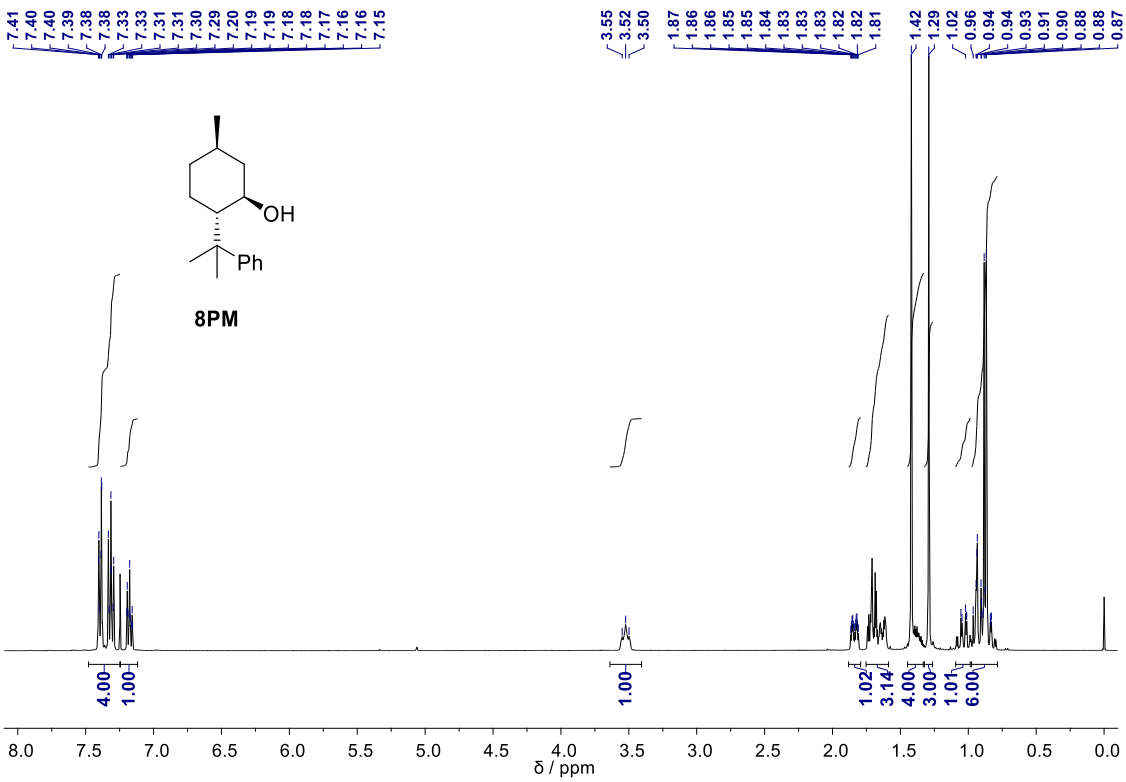

Figure S20. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **8PM**.

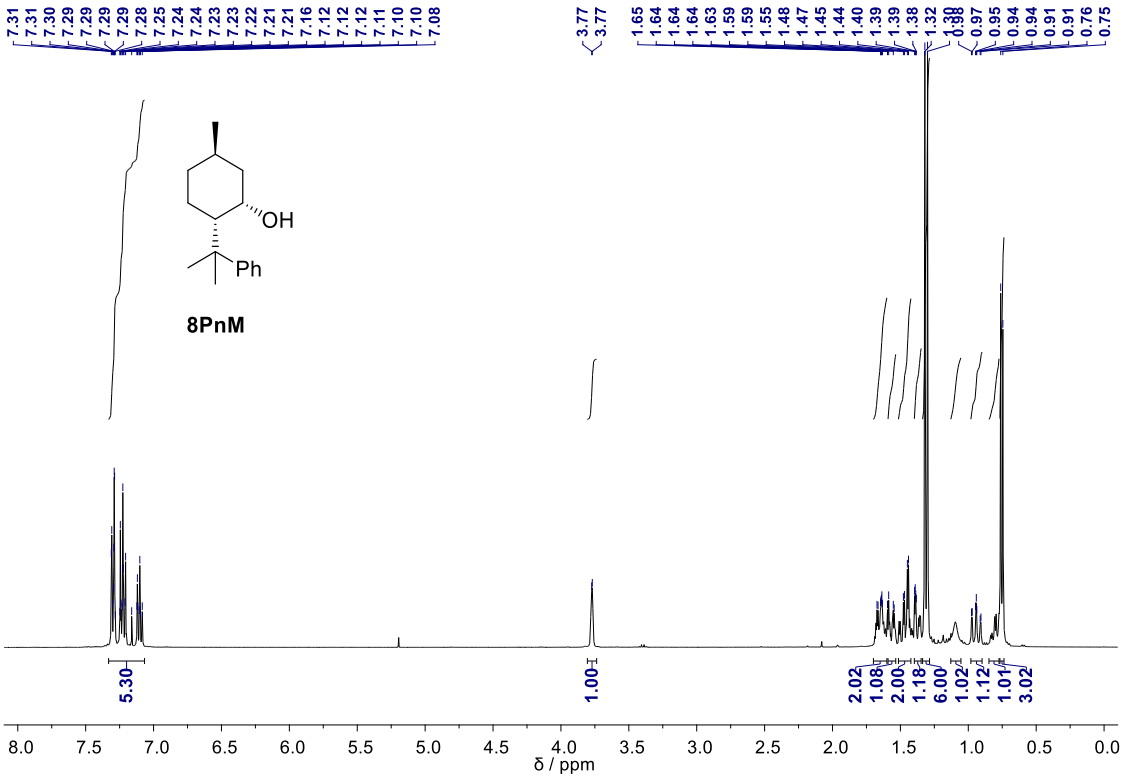

Figure S21. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **8PnM**.

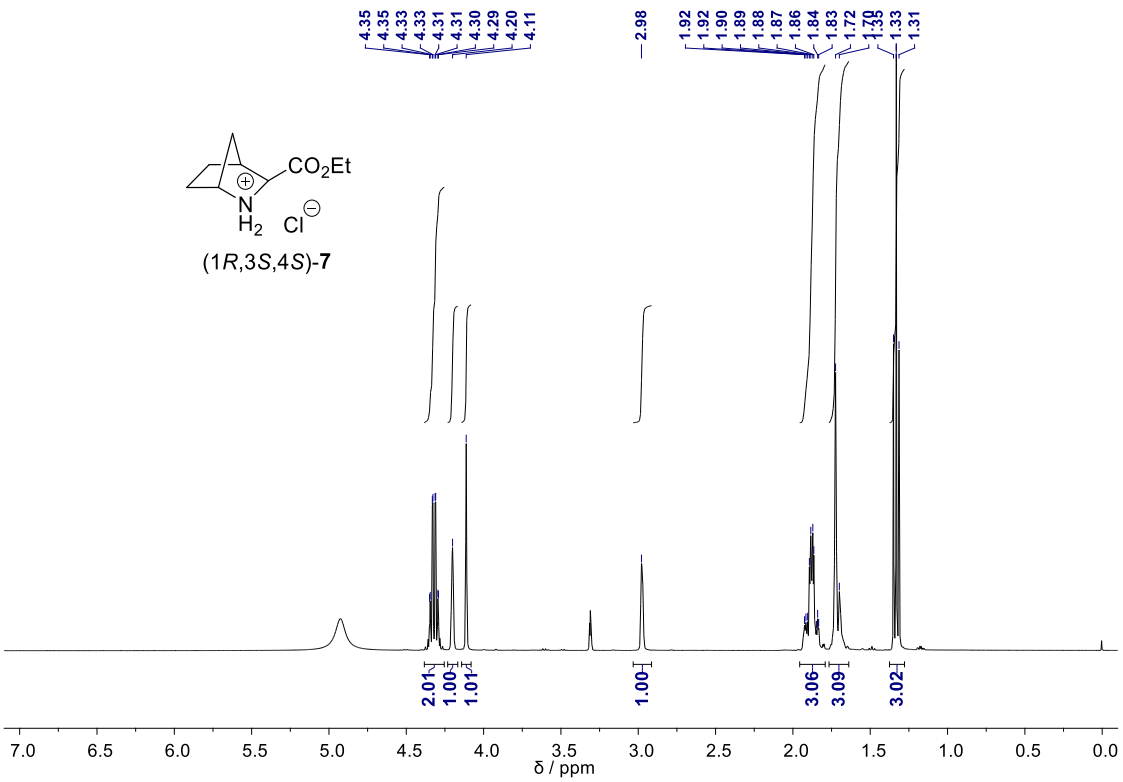

Figure S22. ^{1}H-NMR spectrum (MeOD, 400 MHz) of compound (1*R*,3*S*,4*S*)-**7**. Spectroscopic data is the same for (1*S*,3*R*,4*R*)-**7**.

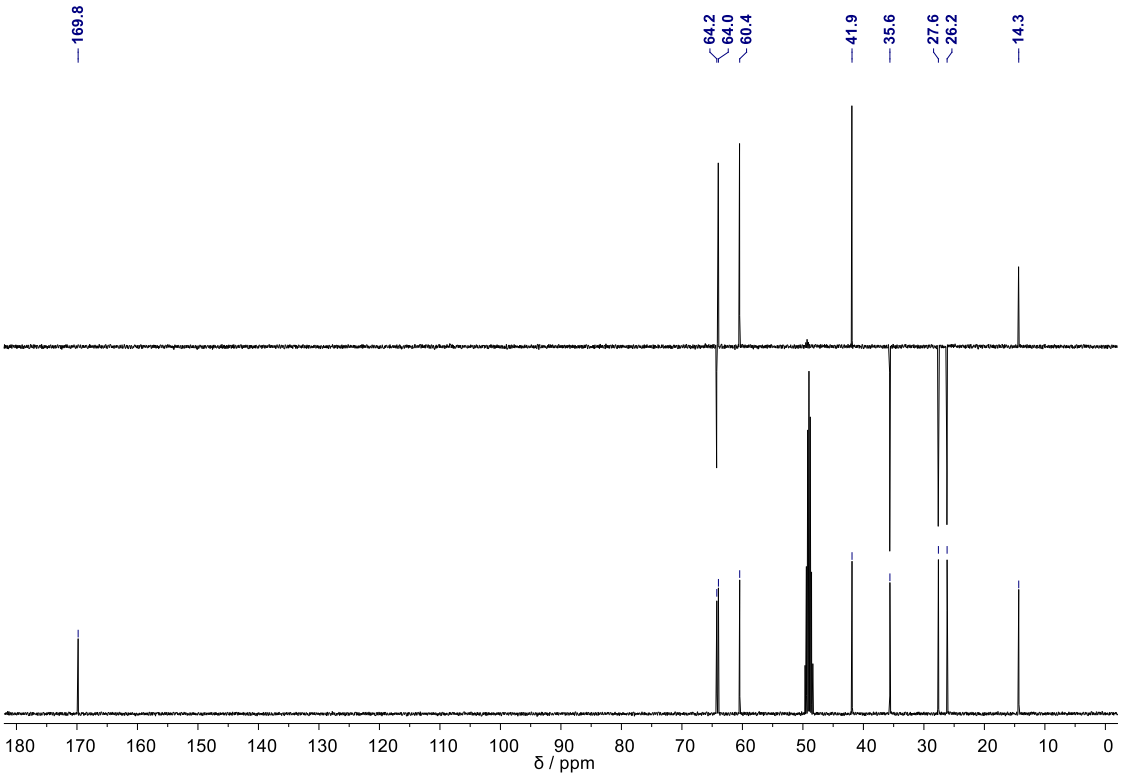

Figure S23. DEPT-135 (upper) and ^{13}C-NMR (lower) spectra (MeOD, 100 MHz) of compound (1*R*,3*S*,4*S*)-**7**. Spectroscopic data are the same for (1*S*,3*R*,4*R*)-**7**.

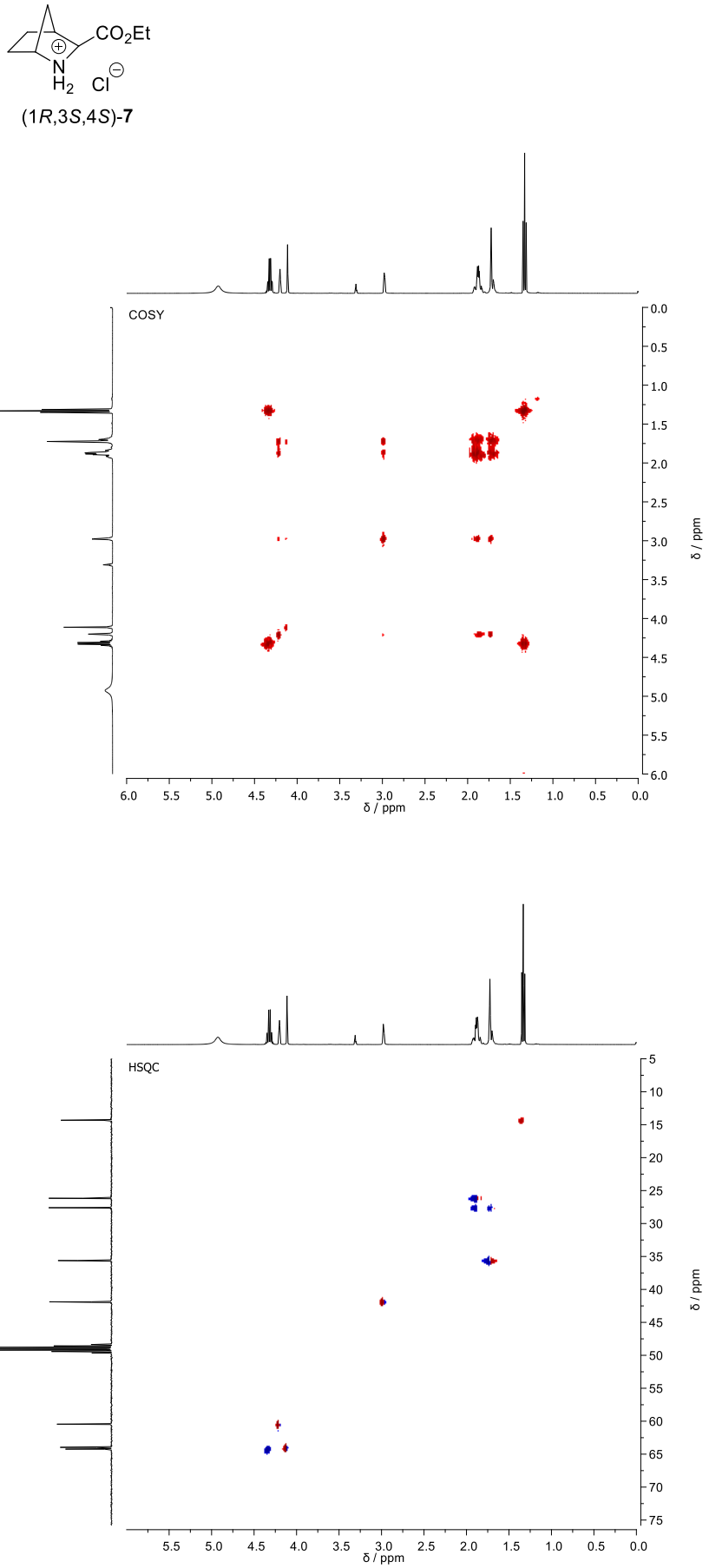

Figure S24. COSY (upper) and HSQC (lower) spectra (MeOD) of compound (1*R*,3*S*,4*S*)-**7**. Spectroscopic data are the same for (1*S*,3*R*,4*R*)-**7**.

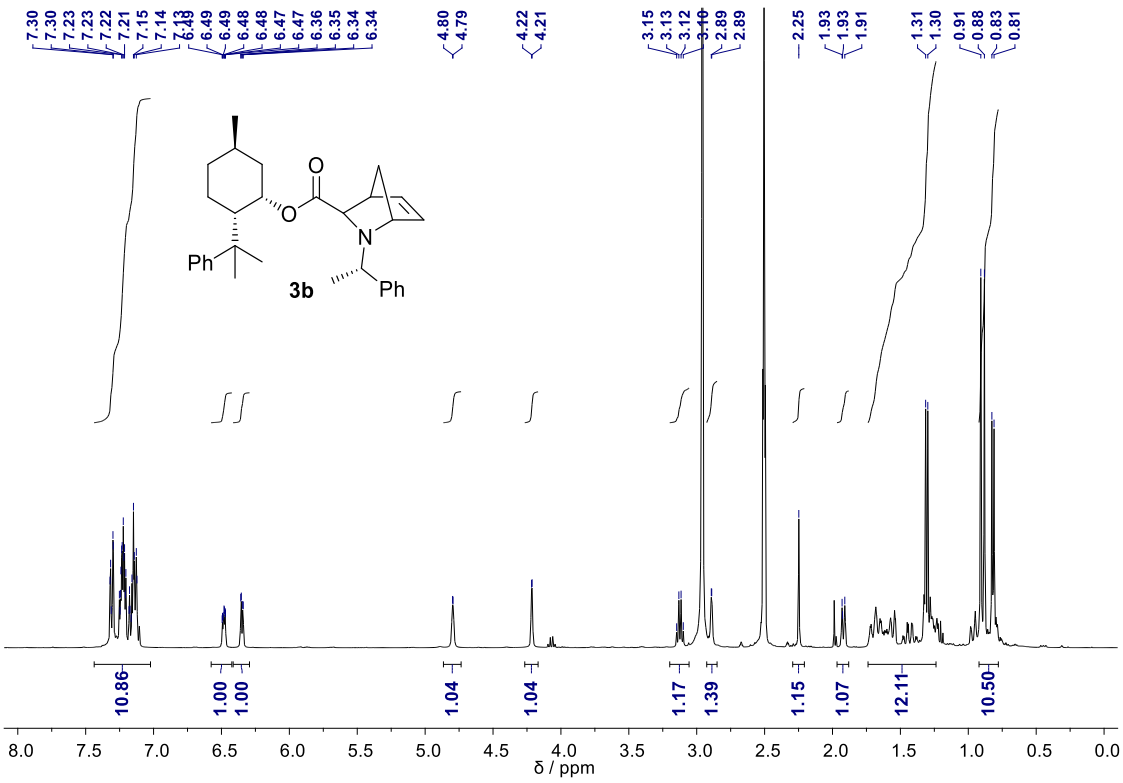

Figure S25. ^{1}H-NMR spectrum (DMSO-d_6, 100 MHz, 100 ºC) of **3b**.

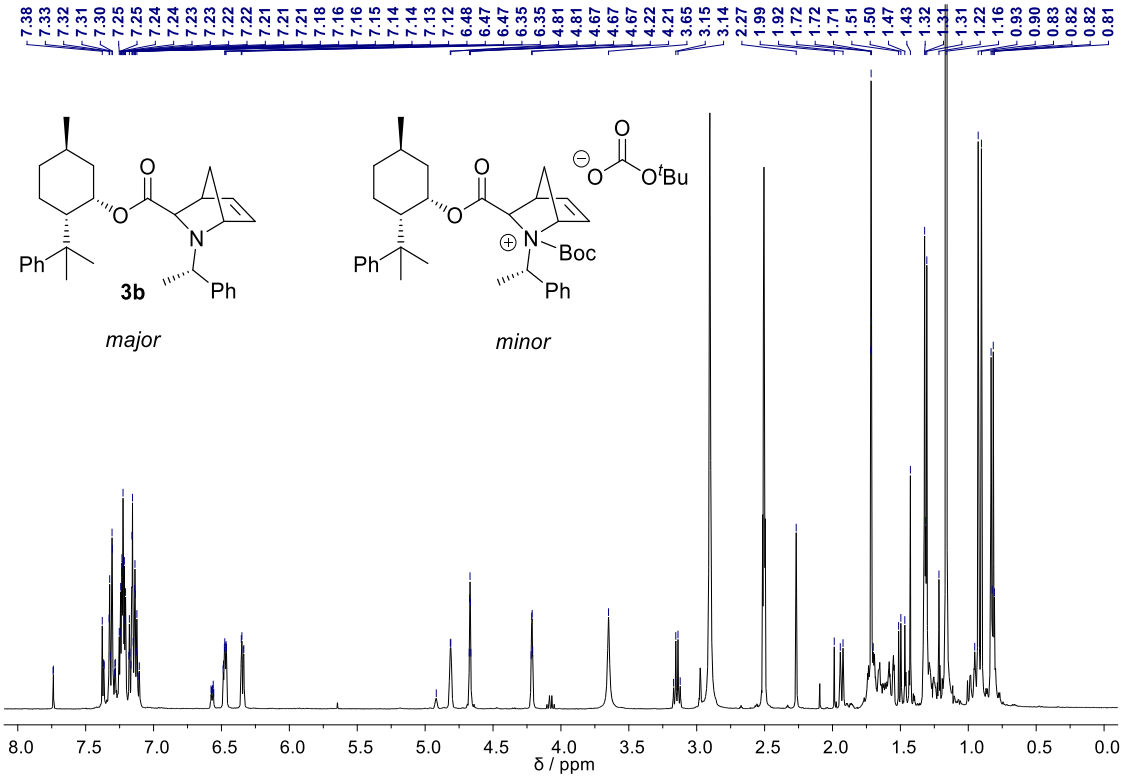

Figure S26. ^{1}H-NMR spectrum (DMSO-d_6, 100 MHz, 100 ºC) of **3b** in presence of equimolar amounts of Boc_2O.

Table S1. Cartesian coordinates of species **3a**, at the M06-2X level of theory, with zero imaginary frequencies and a total energy of -1409.392275 hartree.

Atom	x	y	z	Atom	x	y	z
C	-4.54033	2.68966	0.41254	H	3.11644	3.21808	-2.71094
C	-5.00130	1.43462	0.40585	H	4.49138	4.18180	-2.18118
C	-3.16343	2.65855	1.05095	H	2.84714	4.80570	-1.98576
C	-2.27250	1.91115	0.01700	H	3.19336	0.93660	1.98434
C	-3.91555	0.56910	1.04212	H	2.20134	-0.28510	2.78441
N	-2.71493	0.51472	0.15622	H	1.43750	1.14264	2.08359
C	-3.36704	1.53999	2.09806	H	-0.13719	-0.22581	1.03111
H	-4.99346	3.56401	-0.04031	H	0.58903	-1.77367	1.46748
H	-5.91772	1.07174	-0.04497	H	0.26250	-1.39601	-0.22642
H	-2.74274	3.60277	1.39373	C	-2.74052	-0.29478	-1.05990
C	-0.78838	2.01337	0.34154	C	-2.84251	-1.77800	-0.70523
H	-2.42754	2.30267	-0.99808	C	-3.32435	-2.71098	-1.62836
H	-4.20306	-0.43218	1.36232	C	-3.37263	-4.06804	-1.31924
H	-2.43661	1.19303	2.55197	C	-2.94494	-4.52055	-0.07554
H	-4.10369	1.81552	2.85390	C	-2.46793	-3.60182	0.85509
O	-0.35243	2.34466	1.41840	C	-2.41786	-2.24688	0.54294
O	-0.06319	1.66724	-0.72810	H	-1.74726	-0.14094	-1.50717
C	1.37633	1.81666	-0.82330	C	-3.78645	0.12675	-2.10534
C	1.96377	3.00520	-0.05876	H	-3.66915	-2.38451	-2.60357
C	3.40305	3.28586	-0.53053	H	-3.75132	-4.77155	-2.05428
C	4.24494	2.00411	-0.43016	H	-2.98530	-5.57761	0.16708
C	3.59194	0.81214	-1.13735	H	-2.13227	-3.93918	1.83092
C	2.14610	0.48787	-0.67990	H	-2.04741	-1.53202	1.26983
H	1.47489	2.06265	-1.88737	H	-4.78763	-0.21036	-1.82194
H	1.95975	2.83005	1.01496	H	-3.54981	-0.29714	-3.08443
H	1.33311	3.88380	-0.24035	H	-3.81096	1.21322	-2.21538
H	3.82477	4.02489	0.16148	C	2.82638	-2.52160	-0.45216
C	3.46331	3.90295	-1.93148	C	3.73224	-3.56530	-0.60445
H	4.41766	1.76307	0.62368	C	4.15496	-1.61602	1.32049
H	5.23433	2.18086	-0.86865	C	5.06511	-2.66155	1.17333
H	4.22176	-0.07391	-1.03327	C	4.85966	-3.64143	0.20991
H	3.55165	1.02720	-2.21313	H	1.95358	-2.48783	-1.09794
C	2.01775	-0.36339	0.63440	H	3.55499	-4.32412	-1.36046
H	1.73030	-0.16767	-1.45805	H	4.34501	-0.86571	2.07963
C	2.23591	0.41368	1.94170	H	5.93824	-2.70462	1.81721
C	0.60064	-0.97019	0.72340	H	5.56760	-4.45564	0.09372
C	3.01800	-1.52329	0.51347				

Table S2. Cartesian coordinates of species **3b**, at the M06-2X level of theory, with zero imaginary frequencies and a total energy of -1409.411792 hartree.

Atom	x	y	z	Atom	x	y	z
C	-3.42962	-2.13012	-0.49675	C	3.92070	0.06806	2.67979
C	-3.16013	-1.87983	-1.78102	H	3.69181	0.91714	3.32973
C	-2.08935	-2.06027	0.24265	H	4.91131	0.23178	2.24626
C	-1.66387	-1.68919	-1.90311	H	3.97134	-0.82760	3.30570
C	-1.31555	-0.34891	-1.17360	C	3.16739	-1.37120	0.79313
N	-1.56818	-0.65855	0.23850	C	2.25202	-2.41195	0.62679
C	-2.27691	0.30594	1.09345	C	4.41761	-1.49966	0.17173
C	-3.77419	0.46321	0.84509	C	2.56781	-3.53885	-0.13237
C	-4.68035	-0.15784	1.70644	C	3.81029	-3.64832	-0.74364
C	-6.05338	-0.07729	1.48988	C	4.73665	-2.61939	-0.58729
C	-6.54248	0.63507	0.39920	C	1.97762	4.63057	-1.87882
C	-5.65122	1.28215	-0.45389	H	0.74575	3.29729	-0.72765
C	-4.28112	1.20577	-0.22567	H	1.60035	5.54586	-1.41278
C	-1.57451	1.66091	1.08946	H	1.44106	4.48139	-2.82057
H	-2.10623	2.35266	1.74741	H	3.03547	4.78841	-2.11855
H	-1.54735	2.10122	0.08746	H	-4.30003	-0.72605	2.55299
H	-0.54603	1.54679	1.42832	H	-6.73976	-0.56899	2.17242
C	0.14158	0.00877	-1.48673	H	-3.60423	1.73629	-0.88939
O	0.64712	-0.23101	-2.55868	H	-7.61125	0.69810	0.22159
O	0.78804	0.61930	-0.48497	H	-6.02550	1.85470	-1.29698
C	2.18640	0.91736	-0.72173	H	1.27438	-2.34949	1.09259
C	2.31736	2.14838	-1.61790	H	1.83181	-4.32964	-0.24526
C	1.81501	3.43037	-0.95206	H	5.15548	-0.70835	0.27424
H	1.79382	1.95692	-2.55920	H	5.71218	-2.68978	-1.05857
H	3.38196	2.26854	-1.86486	H	4.05724	-4.52300	-1.33635
C	2.54801	3.63223	0.37473	C	-1.17034	-2.67478	-0.82216
C	2.37142	2.42425	1.29452	H	-1.22139	-1.75228	-2.89464
H	2.18462	4.53915	0.87193	H	-1.42103	-3.70981	-1.05760
H	3.61709	3.79100	0.16781	H	-0.10750	-2.57146	-0.59088
C	2.86569	1.12612	0.63855	H	-2.05456	-2.47325	1.25329
H	1.30767	2.32749	1.53613	H	-1.94104	0.46690	-1.56083
H	2.89669	2.59333	2.23997	H	-2.17778	-0.10794	2.10688
C	2.83546	-0.11116	1.59770	H	2.61520	0.05242	-1.23448
C	1.48989	-0.24892	2.32810	H	3.92524	1.28400	0.37975
H	1.52128	-1.11621	2.99629	H	-4.40571	-2.23592	-0.04016
H	0.64481	-0.36201	1.64275	H	-3.87127	-1.73557	-2.58588
H	1.31269	0.63070	2.95404				

Table S3. Cartesian coordinates of species **5a**, at the M06-2X level of theory, with zero imaginary frequencies and a total energy of -1101.080286 hartree.

Atom	x	y	z	Atom	x	y	z
C	-5.70827	-0.17651	-0.15704	H	3.52861	0.73147	-0.69139
C	-5.48720	-1.61425	-0.71949	H	2.67602	1.83731	-1.74106
C	-4.39807	0.10466	0.60555	C	1.38345	-0.62631	0.40734
C	-3.28503	0.24247	-0.44133	H	1.26970	0.02556	-1.60597
C	-4.08040	-1.95864	-0.19194	C	1.25104	-0.18771	1.87288
N	-3.05832	-1.15634	-0.88613	C	0.21899	-1.60755	0.14053
C	-4.07823	-1.28523	1.18365	C	2.69368	-1.39468	0.17357
H	-6.55883	-0.15006	0.52956	H	1.58198	3.84268	-1.86957
H	-5.52412	-1.65340	-1.81264	H	2.46890	5.02847	-0.91775
H	-4.43468	0.93223	1.31377	H	0.69948	5.03789	-0.91521
C	-1.98334	0.78286	0.14028	H	2.00697	0.53658	2.18322
H	-3.57899	0.89877	-1.27030	H	1.34569	-1.06489	2.52233
H	-3.82338	-3.01959	-0.21686	H	0.26427	0.24508	2.04422
H	-3.10935	-1.33286	1.68448	H	-0.72645	-1.23001	0.52947
H	-4.86529	-1.66036	1.84336	H	0.42530	-2.56032	0.63814
O	-1.79441	0.97157	1.31949	H	0.07004	-1.80364	-0.92455
O	-1.09618	0.97677	-0.83777	C	2.88567	-2.09034	-1.02836
C	0.20877	1.57272	-0.64126	C	4.06576	-2.77600	-1.28982
C	0.28702	2.64887	0.44425	C	3.73421	-1.41791	1.10541
C	1.58570	3.46231	0.29793	C	4.91959	-2.10647	0.84924
C	2.79203	2.51121	0.29446	C	5.09290	-2.78791	-0.34910
C	2.65683	1.38766	-0.73955	H	2.09714	-2.09873	-1.77556
C	1.35835	0.54412	-0.64160	H	4.18253	-3.30488	-2.23088
H	0.32951	2.09694	-1.59699	H	3.63039	-0.89285	2.04855
H	0.24068	2.21308	1.44051	H	5.70934	-2.10633	1.59455
H	-0.58252	3.30983	0.34647	H	6.01537	-3.32335	-0.54928
H	1.65999	4.10367	1.18473	H	-5.89625	0.56188	-0.94197
C	1.58093	4.38930	-0.92194	H	-6.23730	-2.31527	-0.34066
H	2.91951	2.08568	1.29470	H	-3.12438	-1.24130	-1.89471
H	3.70683	3.07838	0.08461				

Table S4. Cartesian coordinates of species **5b**, at the M06-2X level of theory, with zero imaginary frequencies and a total energy of -1101.101507 hartree.

Atom	x	y	z	Atom	x	y	z
C	-4.93003	-0.25084	1.04755	C	3.00960	-0.84828	2.32582
C	-4.96338	-0.26203	-0.51114	H	2.95997	-0.11745	3.13767
C	-3.43163	-0.43278	1.33485	H	3.96538	-0.71734	1.81052
H	-5.51534	-1.07517	1.46588	H	3.00340	-1.84654	2.77299
H	-5.29098	0.68681	1.47297	C	1.88879	-1.82613	0.33180
C	-3.49150	-0.52145	-0.89143	C	0.85578	-2.74462	0.13366
H	-5.33082	0.67893	-0.92979	C	3.02977	-1.94810	-0.47407
H	-5.60160	-1.06465	-0.89101	C	0.95171	-3.74113	-0.83796
C	-2.68387	0.74915	-0.54565	C	2.08621	-3.84145	-1.63246
N	-2.77702	0.82955	0.92330	C	3.12982	-2.93760	-1.44366
C	-1.27248	0.63975	-1.11129	C	1.63850	4.62192	-1.26353
O	-1.04130	0.39543	-2.27022	H	0.19721	3.44907	-0.18856
O	-0.32395	0.86191	-0.18688	H	1.52302	5.51589	-0.64330
C	1.05413	0.82748	-0.62978	H	1.02229	4.74676	-2.15890
C	1.37847	2.11931	-1.37893	H	2.68570	4.56802	-1.58255
C	1.24955	3.36278	-0.49534	H	-0.03798	-2.69897	0.74601
H	0.72998	2.19221	-2.25752	H	0.13100	-4.43933	-0.96991
H	2.41052	2.04107	-1.74864	H	3.85489	-1.25212	-0.34852
C	2.09277	3.19210	0.77175	H	4.02503	-3.00296	-2.05427
C	1.74263	1.90471	1.52117	H	2.16069	-4.61407	-2.39069
H	1.95898	4.05932	1.42868	C	-3.02847	-1.44386	0.24798
H	3.15577	3.17151	0.48783	H	-3.32029	-0.85749	-1.91409
C	1.92900	0.67436	0.62083	H	-3.58634	-2.38373	0.29339
H	0.69881	1.95944	1.85283	H	-1.95417	-1.65543	0.21868
H	2.36070	1.81849	2.42029	H	-3.18824	-0.68104	2.36971
C	1.81232	-0.69712	1.36479	H	-3.12726	1.63330	-1.02358
C	0.53958	-0.78762	2.21778	H	1.16210	-0.02843	-1.30141
H	0.51103	-1.74198	2.75335	H	2.95886	0.71671	0.23450
H	-0.37043	-0.69721	1.62122	H	-1.84905	0.91123	1.32607
H	0.53462	0.00833	2.96754				

Table S5. Cartesian coordinates of species **6a**, at the M06-2X level of theory, with zero imaginary frequencies and a total energy of -1446.792819 hartree.

Atom	x	y	z	Atom	x	y	z
C	-3.63981	-2.57038	2.19732	H	3.46115	-4.11902	0.02528
C	-4.80324	-1.81982	1.47782	H	4.29850	-4.58067	-1.45287
C	-2.52884	-2.63235	1.12399	H	2.57124	-4.91954	-1.27271
C	-1.95134	-1.20613	0.95627	H	2.61834	0.57366	-2.11925
C	-4.17149	-1.49343	0.11377	H	1.80554	2.04698	-1.58153
N	-3.08858	-0.53348	0.36010	H	0.93909	0.51281	-1.55932
C	-3.35209	-2.75855	-0.17322	H	0.22334	0.99989	0.60383
H	-3.93973	-3.58094	2.48700	H	1.20556	2.42306	0.89019
H	-5.11042	-0.90907	1.99612	H	1.31086	1.04727	1.99709
H	-1.75765	-3.38254	1.30331	C	4.01574	1.76346	1.71600
C	-0.74121	-1.19973	0.02492	C	5.17812	2.45549	2.03580
H	-1.65394	-0.75860	1.91079	C	4.43117	2.11932	-0.61326
H	-4.84734	-1.13397	-0.65914	C	5.59723	2.81601	-0.29804
H	-2.75506	-2.67462	-1.08384	C	5.97793	2.98720	1.02717
H	-3.96539	-3.66312	-0.19871	H	3.40832	1.35882	2.52041
O	-0.79454	-0.93777	-1.15055	H	5.45812	2.58291	3.07711
O	0.33749	-1.57501	0.71701	H	4.16279	1.99971	-1.65708
C	1.64040	-1.82977	0.13566	H	6.20764	3.22574	-1.09712
C	1.64167	-2.29942	-1.32163	H	6.88449	3.53038	1.27370
C	3.03057	-2.83748	-1.71138	H	-3.30148	-2.05447	3.09991
C	4.10086	-1.77801	-1.40724	H	-5.68271	-2.45945	1.35776
C	4.03389	-1.27916	0.03891	C	-3.06078	0.80014	0.12435
C	2.65620	-0.72058	0.47607	O	-2.10101	1.50002	0.39704
H	1.96686	-2.68863	0.73482	O	-4.21684	1.21937	-0.42402
H	1.36214	-1.49389	-1.99719	C	-4.36400	2.61230	-0.81976
H	0.88719	-3.08641	-1.43895	C	-4.27653	3.51885	0.40480
H	3.01267	-3.00255	-2.79563	C	-5.76753	2.64589	-1.41335
C	3.35583	-4.18634	-1.06168	C	-3.32491	2.96965	-1.87854
H	3.98408	-0.93467	-2.09574	H	-3.27446	3.49658	0.83281
H	5.09668	-2.19549	-1.59798	H	-4.99840	3.19476	1.16044
H	4.81019	-0.53134	0.21243	H	-4.52130	4.54469	0.11428
H	4.27123	-2.11810	0.70606	H	-6.00817	3.65850	-1.74717
C	2.34969	0.76921	0.07093	H	-6.50398	2.33780	-0.66633
H	2.68671	-0.68929	1.57400	H	-5.83438	1.96906	-2.26931
C	1.91303	0.97437	-1.38782	H	-2.31899	2.95132	-1.45971
C	1.20453	1.33019	0.94574	H	-3.53389	3.97049	-2.26774
C	3.61713	1.57815	0.38502	H	-3.37956	2.25883	-2.70801

Table S6. Cartesian coordinates of species **6b**, at the M06-2X level of theory, with zero imaginary frequencies and a total energy of -1446.816157 hartree.

Atom	x	y	z	Atom	x	y	z
C	1.96596	4.00309	0.46948	C	-4.47583	1.97656	-0.08772
C	1.69843	4.09958	-1.06481	C	-5.40447	1.27564	-0.84537
C	0.96489	2.91503	0.89413	C	-5.36837	-0.11757	-0.84380
H	1.75480	4.94864	0.97756	C	1.27644	-4.01345	-1.98313
H	2.98856	3.70852	0.71597	H	1.35955	-2.17378	-0.86896
C	0.52262	3.12246	-1.29462	H	2.15545	-4.46220	-1.50816
H	2.57328	3.82678	-1.66146	H	1.59208	-3.57173	-2.93365
H	1.40762	5.11292	-1.35327	H	0.56989	-4.82100	-2.20682
C	1.06182	1.68545	-1.15276	H	-2.81214	1.86867	1.25150
N	1.40290	1.65982	0.26391	H	-4.49256	3.06208	-0.07207
C	0.00762	0.65426	-1.54827	H	-4.39915	-1.87796	-0.11456
O	-0.51714	0.65287	-2.63574	H	-6.08925	-0.68182	-1.42732
O	-0.25561	-0.21249	-0.56894	H	-6.15066	1.80473	-1.42898
C	-1.21780	-1.25674	-0.84314	C	-0.25503	3.24948	0.02805
C	-0.57615	-2.31372	-1.74214	H	-0.03504	3.26640	-2.21977
C	0.63178	-2.97274	-1.07441	H	-0.63354	4.25865	0.20915
H	-0.29613	-1.84988	-2.69277	H	-1.06788	2.52401	0.12006
H	-1.33560	-3.07610	-1.96600	H	0.82167	2.78045	1.96531
C	0.21268	-3.56875	0.27037	H	1.93684	1.50816	-1.78719
C	-0.40383	-2.50011	1.17378	H	-2.06770	-0.79717	-1.35448
H	1.07700	-4.02919	0.76480	H	-2.32543	-2.66088	0.25523
H	-0.51411	-4.37617	0.09480	C	2.36830	0.88603	0.82885
C	-1.62857	-1.84805	0.51251	O	2.74730	1.01686	1.97730
H	0.35175	-1.72863	1.36942	O	2.83111	-0.02364	-0.05781
H	-0.67912	-2.93458	2.14012	C	3.97634	-0.85266	0.29519
C	-2.41168	-0.88311	1.46635	C	5.16684	0.01706	0.69622
C	-1.46160	0.04684	2.23630	C	4.28804	-1.58783	-1.00397
H	-2.03178	0.70623	2.89827	C	3.58283	-1.83115	1.39600
H	-0.84023	0.65203	1.57104	H	4.99442	0.51265	1.65037
H	-0.79276	-0.54101	2.86988	H	5.35009	0.77281	-0.07398
C	-3.16923	-1.72980	2.51066	H	6.05803	-0.61237	0.77340
H	-2.47645	-2.29716	3.13896	H	4.52522	-0.87330	-1.79685
H	-3.85615	-2.43656	2.03611	H	3.43682	-2.19363	-1.32410
H	-3.75744	-1.07779	3.16303	H	5.14792	-2.24706	-0.85864
C	-3.45642	-0.10030	0.66512	H	3.31841	-1.29500	2.30812
C	-3.51550	1.29431	0.65979	H	4.41997	-2.50366	1.60588
C	-4.41037	-0.79097	-0.09658	H	2.72974	-2.43575	1.07157

Table S7. Cartesian coordinates of species **Ia**, at the M06-2X level of theory, with zero imaginary frequencies and a total energy of -1756.713532 hartree.

Atom	x	y	z	Atom	x	y	z
C	2.50457	-3.04486	-1.87866	C	2.12528	0.17431	1.17682
C	3.70524	-2.0937	-1.61719	C	3.42883	0.59593	1.81812
C	1.71473	-2.93302	-0.56721	C	4.01247	1.84849	1.61027
C	1.07398	-1.53267	-0.50525	C	5.16883	2.2112	2.29249
C	3.47149	-1.59698	-0.1809	C	5.75765	1.32856	3.19512
N	2.28539	-0.6064	-0.19186	C	5.17602	0.08549	3.42557
C	2.82633	-2.80989	0.48564	C	4.01492	-0.2706	2.74764
H	2.83866	-4.07208	-2.03798	H	1.6854	-0.58054	1.82451
H	3.79118	-1.28939	-2.3503	C	1.12304	1.3039	0.969
H	0.97768	-3.71902	-0.39916	H	3.56298	2.55224	0.9178
C	-0.05662	-1.5266	0.5276	H	5.60614	3.19073	2.12777
H	0.66483	-1.2	-1.45601	H	6.6568	1.61624	3.72937
H	4.31951	-1.11317	0.29593	H	5.61329	-0.59969	4.14358
H	2.44823	-2.64003	1.49436	H	3.54851	-1.23033	2.95571
H	3.50403	-3.6666	0.48572	H	1.5213	2.10081	0.33429
O	0.06027	-1.95213	1.65451	H	0.89829	1.7366	1.94572
O	-1.17094	-1.08174	-0.0207	H	0.18856	0.95468	0.52205
C	-2.40029	-1.16834	0.78364	C	-4.82222	2.55759	-0.18539
C	-2.89953	-2.61303	0.73922	C	-5.66728	3.39623	-0.9016
C	-3.45972	-3.0616	-0.61824	C	-6.67471	1.14573	0.37042
C	-4.49134	-2.03728	-1.11205	C	-7.52718	1.98561	-0.34576
C	-3.92113	-0.61803	-1.15341	C	-7.02896	3.11412	-0.98399
C	-3.3348	-0.10914	0.18028	H	-3.76328	2.79768	-0.14294
H	-2.11031	-0.91245	1.80675	H	-5.26219	4.27422	-1.39474
H	-3.68605	-2.7081	1.49276	H	-7.09599	0.27134	0.85384
H	-2.08586	-3.27066	1.06662	H	-8.58536	1.75098	-0.40094
H	-3.978	-4.01205	-0.44399	H	-7.69155	3.76792	-1.54117
C	-2.37077	-3.33584	-1.66152	H	1.91133	-2.74834	-2.74675
H	-5.37657	-2.06955	-0.46711	H	4.6579	-2.62836	-1.63013
H	-4.8352	-2.3155	-2.11438	C	2.45531	0.41307	-1.29822
H	-4.67952	0.08165	-1.51123	O	1.58647	0.61341	-2.09272
H	-3.11178	-0.58871	-1.89328	O	3.63244	0.95455	-1.1762
C	-4.33819	0.5013	1.2244	C	4.0929	1.98919	-2.15997
H	-2.67968	0.73325	-0.07965	C	4.13586	1.36232	-3.54618
C	-5.09037	-0.54819	2.05517	C	5.48838	2.32049	-1.65833
C	-3.5448	1.3618	2.2311	C	3.16373	3.19178	-2.08777
C	-5.3084	1.41726	0.46815	H	3.14321	1.07394	-3.89492
H	-1.85182	-2.42411	-1.96988	H	4.80015	0.49363	-3.55587
H	-2.80614	-3.79024	-2.55594	H	4.54172	2.09762	-4.2454
H	-1.6249	-4.03494	-1.26539	H	5.93932	3.06274	-2.32092
H	-5.6394	-1.27098	1.44804	H	6.11939	1.4286	-1.65443
H	-5.80617	-0.05074	2.71589	H	5.4544	2.72906	-0.64604
H	-4.39577	-1.09901	2.6956	H	2.15616	2.94903	-2.42777
H	-2.88288	0.74796	2.85058	H	3.56382	3.97614	-2.73535
H	-4.23571	1.87886	2.90251	H	3.12261	3.5933	-1.07085
H	-2.93437	2.11997	1.73285				

Table S8. Cartesian coordinates of species **IIa**, at the M06-2X level of theory, with zero imaginary frequencies and a total energy of -1411.034738 hartree.

Atom	x	y	z	Atom	x	y	z
C	-5.16288	-0.78599	-1.32413	H	0.15625	-2.02798	4.05147
C	-4.87393	0.73541	-1.174	H	-0.9598	-2.79586	2.91151
C	-3.77364	-1.37043	-1.6354	H	4.32078	-2.16858	0.14788
C	-2.92889	-1.3181	-0.35378	H	4.59726	-2.20038	-1.59944
C	-3.35764	0.8281	-1.37223	H	3.26634	-3.12405	-0.90743
N	-2.60766	0.16356	-0.21951	H	1.94478	-2.08703	-2.68665
C	-3.11956	-0.23805	-2.45066	H	3.06423	-0.82142	-3.17858
H	-5.5996	-1.2237	-0.42222	H	1.46121	-0.38241	-2.58236
H	-5.23311	1.16274	-0.24216	C	-2.59831	0.74059	1.20078
H	-3.76294	-2.36651	-2.07592	C	-1.80674	2.02836	1.13013
C	-1.63908	-2.13447	-0.48137	C	-2.39661	3.27698	0.92519
H	-3.47024	-1.64888	0.53755	C	-1.59558	4.40837	0.78687
H	-2.9465	1.82639	-1.5219	C	-0.20769	4.30058	0.84315
H	-2.06327	-0.4059	-2.68747	C	0.3881	3.05722	1.04373
H	-3.65787	-0.00844	-3.37184	C	-0.41388	1.93019	1.18824
O	-1.61906	-3.20433	-1.02541	H	-1.98944	-0.0031	1.72754
O	-0.59833	-1.49628	0.05416	C	-3.95464	0.8161	1.88223
C	0.73243	-2.12965	-0.0986	H	-3.47657	3.38258	0.87568
C	0.8552	-3.30141	0.87028	H	-2.05833	5.37789	0.63682
C	1.13438	-2.90357	2.3202	H	0.40804	5.18769	0.73807
C	2.41159	-2.06006	2.34249	H	1.46862	2.95972	1.08989
C	2.27522	-0.78784	1.49923	H	0.04123	0.95723	1.35939
C	1.74789	-0.97612	0.05255	H	-4.54502	1.67762	1.57473
H	0.73331	-2.52017	-1.11833	H	-3.773	0.91281	2.95462
H	1.69008	-3.91526	0.51151	H	-4.54742	-0.09008	1.72793
H	-0.03945	-3.92568	0.78403	C	2.93229	1.54591	-1.13569
H	1.32225	-3.82864	2.87736	C	3.56719	2.7803	-1.06574
C	-0.04655	-2.19595	2.9902	C	4.99484	0.43954	-0.6355
H	3.24054	-2.67733	1.97799	C	5.63678	1.67611	-0.56355
H	2.66345	-1.77648	3.36995	C	4.92822	2.85173	-0.77636
H	3.23808	-0.27008	1.45557	H	1.87101	1.52285	-1.37339
H	1.60924	-0.10348	2.03758	H	2.99928	3.68835	-1.24745
C	2.8862	-0.99179	-1.02247	H	5.57941	-0.4578	-0.4658
H	1.16921	-0.07884	-0.19681	H	6.69802	1.71322	-0.34013
C	3.82404	-2.18568	-0.82557	H	5.42902	3.81248	-0.7223
C	2.2957	-1.07962	-2.4458	H	-5.33706	1.30665	-1.98235
C	3.63084	0.34926	-0.92038	H	-5.85345	-0.9786	-2.14707
H	-0.24466	-1.22031	2.53315	H	-1.61302	0.24259	-0.46824

Table S9. Cartesian coordinates of species **Ib**, at the M06-2X level of theory, with zero imaginary frequencies and a total energy of -1756.708610 hartree.

Atom	x	y	z	Atom	x	y	z
C	-2.09948	-2.97933	1.23784	C	3.64084	-2.68067	-0.60230
C	-0.95629	-3.34691	0.25326	C	4.99252	-0.91102	-1.47817
C	-1.71033	-1.57179	1.71060	C	3.70969	-3.33953	-1.83122
H	-2.09710	-3.62376	2.12056	C	4.41464	-2.78075	-2.88874
H	-3.09498	-3.05431	0.80276	C	5.06102	-1.55945	-2.70444
C	-0.00853	-2.13849	0.37362	C	1.98999	4.77376	0.36825
H	-1.31832	-3.48498	-0.76810	H	1.18927	2.94775	1.14005
H	-0.44899	-4.26434	0.55761	H	1.79101	5.35954	1.26978
C	-0.61533	-0.93940	-0.37103	H	1.16851	4.94665	-0.33481
N	-1.84528	-0.57329	0.52027	H	2.90841	5.15865	-0.08751
C	-2.04987	0.89213	1.05716	H	-4.41268	1.66605	0.02105
C	-2.27511	1.86647	-0.07750	H	-4.84769	3.25525	-1.82337
C	-3.58225	2.14196	-0.49090	H	-0.21064	2.43043	-0.30927
C	-3.82745	3.04685	-1.51803	H	-2.95050	4.40103	-2.94206
C	-2.76389	3.69701	-2.13829	H	-0.63018	3.98656	-2.16398
C	-1.46221	3.46403	-1.70308	H	3.10943	-3.16037	0.21340
C	-1.22281	2.56663	-0.66863	H	3.21836	-4.29998	-1.95257
C	-0.99116	1.32728	2.05962	H	5.50919	0.03826	-1.35797
H	-1.23648	2.35569	2.33606	H	5.62437	-1.11332	-3.51766
H	0.01863	1.31767	1.65316	H	4.47048	-3.29180	-3.84390
H	-1.01653	0.72547	2.96940	C	-0.19423	-1.70908	1.83477
C	0.47279	0.07864	-0.77193	H	1.01477	-2.32518	0.04490
O	0.55010	0.42723	-1.92014	H	0.06678	-2.49589	2.54733
O	1.38359	0.35060	0.16935	H	0.33767	-0.79574	2.09175
C	2.62115	0.98672	-0.32151	H	-2.28465	-1.17614	2.54770
C	2.40144	2.47705	-0.57585	H	-1.03770	-1.21426	-1.33360
C	2.13445	3.29075	0.69468	H	-2.99189	0.78596	1.59603
H	1.60965	2.61050	-1.32025	H	2.85538	0.48662	-1.26335
H	3.32067	2.85396	-1.04449	H	4.58594	1.30004	0.25338
C	3.23300	3.02794	1.72671	C	-3.12608	-0.94961	-0.24976
C	3.39682	1.53132	1.99944	O	-3.07732	-1.40904	-1.34760
H	3.00461	3.56147	2.65566	O	-4.15186	-0.74952	0.52925
H	4.18201	3.43743	1.35249	C	-5.53815	-1.14254	0.09081
C	3.73496	0.77062	0.70828	C	-5.60189	-2.66149	0.04683
H	2.46252	1.13562	2.42277	C	-5.88480	-0.51741	-1.25343
H	4.17440	1.37149	2.75197	C	-6.39355	-0.57389	1.21050
C	4.23217	-0.69804	0.93173	H	-4.92579	-3.06895	-0.70884
C	3.38064	-1.43081	1.97277	H	-6.61911	-2.95966	-0.21898
H	3.78211	-2.43078	2.16039	H	-5.37209	-3.09061	1.02586
H	2.34316	-1.52703	1.64876	H	-5.27991	-0.92163	-2.06434
H	3.39444	-0.89386	2.92426	H	-5.77696	0.56852	-1.23125
C	5.67426	-0.64119	1.47768	H	-6.93454	-0.74313	-1.45910
H	5.71543	-0.12672	2.44214	H	-6.09199	-0.98411	2.17717
H	6.34528	-0.12445	0.78630	H	-7.43888	-0.83652	1.03325
H	6.05875	-1.65466	1.62038	H	-6.31588	0.51622	1.24672
C	4.27188	-1.45039	-0.40247				

Table S10. Cartesian coordinates of species **IIb**, at the M06-2X level of theory, with zero imaginary frequencies and a total energy of -1411.047989 hartree.

Atom	x	y	z	Atom	x	y	z
C	-2.59165	-3.36383	0.86450	H	2.70589	-1.05267	2.78817
C	-2.42339	-3.47584	-0.67826	H	1.29827	-0.78493	1.75642
C	-1.32717	-2.61409	1.30040	H	1.76869	0.42511	2.97124
H	-2.59531	-4.34326	1.34774	C	4.27094	0.95988	2.00044
H	-3.51468	-2.86060	1.15758	H	3.95908	1.63713	2.80032
C	-1.09316	-2.74421	-0.92636	H	4.95632	1.50059	1.34215
H	-3.25387	-3.01853	-1.22184	H	4.82650	0.13546	2.45528
H	-2.35113	-4.51835	-0.99391	C	3.59886	-0.57756	0.17429
C	-1.32981	-1.24555	-0.67328	C	3.34284	-1.94957	0.22552
N	-1.44498	-1.16224	0.84483	C	4.41652	-0.11023	-0.86479
C	-2.58289	-0.35081	1.50553	C	3.85673	-2.82030	-0.73705
C	-3.59599	0.17383	0.51779	C	4.64536	-2.33481	-1.77113
C	-4.87929	-0.37067	0.47875	C	4.92879	-0.97126	-1.82716
C	-5.82976	0.12756	-0.41131	C	-0.31558	4.69644	-1.15329
C	-5.49813	1.16896	-1.27112	H	-0.69334	2.93339	0.00601
C	-4.21611	1.71724	-1.23975	H	-0.84848	5.36977	-0.47651
C	-3.27208	1.22647	-0.34644	H	-0.99009	4.43263	-1.97374
C	-1.93013	0.74366	2.34259	H	0.52796	5.24888	-1.58075
H	-2.70084	1.28762	2.89068	H	-5.15048	-1.17290	1.16091
H	-1.39454	1.45356	1.70628	H	-6.82796	-0.29637	-0.42728
H	-1.22599	0.32057	3.06770	H	-2.27061	1.65149	-0.33642
C	-0.19035	-0.37620	-1.19436	H	-6.23640	1.55747	-1.96423
O	0.14681	-0.43232	-2.34454	H	-3.95416	2.53133	-1.90716
O	0.34469	0.40943	-0.25073	H	2.76415	-2.36687	1.04302
C	1.46344	1.25906	-0.69574	H	3.64701	-3.88308	-0.66475
C	0.89090	2.49749	-1.37824	H	4.65942	0.94765	-0.92805
C	0.17921	3.45472	-0.41899	H	5.55630	-0.57813	-2.62032
H	0.22933	2.18308	-2.19320	H	5.04660	-3.00952	-2.51952
H	1.73028	3.02588	-1.85005	C	-0.27264	-3.12520	0.31612
C	1.10351	3.80398	0.74822	H	-0.63158	-2.91136	-1.89889
C	1.58839	2.54432	1.46681	H	-0.11596	-4.20144	0.41492
H	0.58474	4.46430	1.45149	H	0.69098	-2.61050	0.38163
H	1.96719	4.36607	0.36543	H	-1.09776	-2.62479	2.36744
C	2.33958	1.60706	0.51031	H	-2.25554	-0.89532	-1.12960
H	0.72041	2.02124	1.88844	H	-3.07622	-1.06395	2.16968
H	2.22804	2.81673	2.31109	H	2.01969	0.66137	-1.41958
C	3.06045	0.40819	1.21724	H	3.14125	2.21029	0.05845
C	2.14954	-0.28911	2.23747	H	-0.58173	-0.68798	1.13998

Table S11. Crystal data and structure refinement for **5b** trifluoroacetate.

Identification code	**5b** · **TFA**	
Empirical formula	C25 H35 F3 N O4.25	
Formula weight	477.53	
Temperature	446(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 20.6626(8) Å	α = 90°.
	b = 10.3356(4) Å	β = 123.325(2)°.
	c = 13.6724(5) Å	γ = 90°.
Volume	2439.76(16) $Å^3$	
Z	4	
Density (calculated)	1.300 Mg/m^3	
Absorption coefficient	0.103 mm^{-1}	
F(000)	1016	
Crystal size	0.34 x 0.21 x 0.11 mm^3	
Theta range for data collection	1.78 to 26.41°.	
Index ranges	-25<=h<=25, -12<=k<=12, -17<=l<=17	
Reflections collected	40491	
Independent reflections	5001 [R(int) = 0.0340]	
Completeness to theta = 26.41°	99.8 %	
Max. and min. transmission	0.9892 and 0.9663	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5001 / 7 / 304	
Goodness-of-fit on F^2	1.083	
Final R indices [I>2sigma(I)]	R1 = 0.0410, wR2 = 0.1123	
R indices (all data)	R1 = 0.0434, wR2 = 0.1181	
Absolute structure parameter	0.4(11)	
Largest diff. peak and hole	0.611 and -0.346 $e.Å^{-3}$	

The crystallographic data for the structure **5b** · **TFA** salt have been deposited at the Cambridge Crystallographic Data Center as supplementary publication number CCDC 1830953.

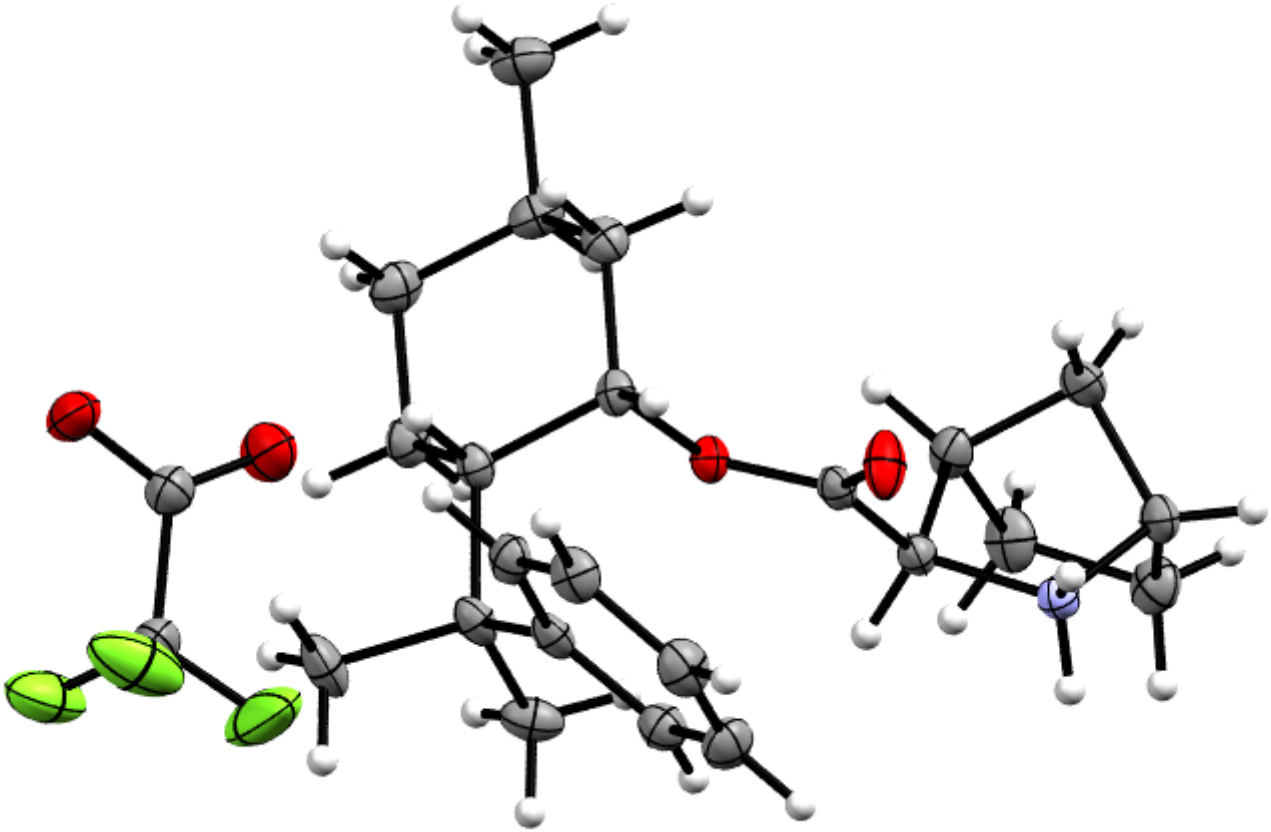

Figure S27. ORTEP diagram for **5b** trifluoracetate salt (displacement ellipsoids are drawn at the 30% probability level). Suitable crystals were obtained by recrystallization in Hexane / EtOAc (1: 1) affording colorless sugar-like crystals.
Color Key: Blue - Nitrogen; Grey - Carbon; Red - Oxygen; Green - Fluorine; White - Hydrogen.