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Supporting Information

Experimental observation and quantum-chemical investigation of thallium(I) (*Z*)-methanediazotate: synthesis of a long sought and highly reactive species

Neeraj Singh, Benjamin Fiedler*, Joachim Friedrich and Klaus Banert*

Chemnitz University of Technology, Organic Chemistry, Strasse der Nationen 62, 09111 Chemnitz, Germany

Email: benjamin.fiedler@chemie.tu-chemnitz.de; klaus.banert@chemie.tu-chemnitz.de

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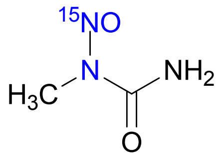
[1] General Information

NMR spectra were measured on *a UNITY INOVA 400* FT spectrometer from VARIAN. ^{1}H NMR spectra were measured at 400 MHz, ^{13}C NMR at 100 MHz and ^{15}N NMR at 40.5 MHz, respectively. NMR signals were referenced to TMS (δ = 0) or solvent signals and recalculated relative to TMS. ^{15}N NMR were referenced to external $MeNO_2$ (δ = 0). DEPT 135 and 2D NMR methods, such as $^{15}N,^{1}H$ gHMBCAD, etc. were used for assignment of signals, when necessary. Multiplicities of the signals are reported using the standard notations: s = singlet, d = doublet, t = triplet, q = quartet, m = sext. = sextet, br. s = broad singlet, etc.

***Note**: N-methyl-N-nitrosourea is a highly potent carcinogen, therefore, great precautions should be taken while handling it. Thallium(I) propoxide is a toxic compound and should be handled in accordance with safety protocols. Thallium (E)-diazotate can also lead to spontaneous explosions, therefore great care must be exercised while handling the highly reactive (Z)-diazotate.*

[2] Experimental procedures

[2a] Synthesis of ^{15}N labelled *N*-methyl-*N*-nitrosourea (7):



7

^{15}N labelled *N*-nitrosourea **7** was synthesised analogous to a literature known procedure.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 3.15 (d, 3H, $^{3}J(^{15}N,^{1}H)$ = 0.8 Hz, CH_3), 5.68 (br. s, 1H, NH), 6.90 (br. s, 1H, NH).

^{13}C NMR (100 MHz, CD_2Cl_2): δ = 26.50 (q, CH_3, $^{2}J(^{15}N,^{13}C)$ = 0.9 Hz), 154.53 (s, CO).

^{15}N NMR (40.5 MHz, CD_2Cl_2): δ = 182.56 (^{15}NO).

[2b] Synthesis of thallium(I) *n*-propoxide (TlOPr):

TlOPr was synthesised from thallium(I) ethoxide (TlOEt) utilising a known procedure, by an exchange reaction in ethanol.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.91 (t, 3H, ^{3}J = 7.2 Hz, CH_3), 1.66 (sext., 2H, ^{3}J = 7.2 Hz, $CH_3CH_2CH_2OTl$), 3.99 (t, 2H, ^{3}J = 7.2 Hz, $CH_3CH_2CH_2OTl$).

^{13}C NMR (100 MHz, CD_2Cl_2): δ = 10.99 (q, CH_3), 29.75 (t, $CH_3CH_2CH_2OTl$), 66.24 (t, $CH_3CH_2CH_2OTl$).

[2c] Reaction of ^{15}N labelled *N*-nitrosourea 7 with TlOEt:

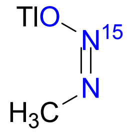
To a mixture of ^{15}N labelled *N*-methyl-*N*-nitrosourea (**7**) (0.096 mmol, 10 mg) in CD_2Cl_2 (0.76 mL) maintained at −40 °C, was added TlOEt (1.1 eq) and the reaction mixture was stirred for 5 min, and subsequently, transferred to a pre-cooled NMR tube maintained at the above mentioned temperature. Low-temperature NMR spectral analysis revealed the formation of $CH_2N^{15}N$ (21%) as the sole product.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 3.32 (d, $^{3}J(^{15}N,^{1}H)$ = 0.8 Hz).

^{15}N NMR (40.5 MHz, CD_2Cl_2): δ = 14.86 ($CH_2N^{15}N$).

The assignment was further confirmed by ^{15}N,^{1}H gHMBCAD 2D NMR technique.

[2d] Synthesis of thallium(I) (*Z*)-methanediazotate (3):



(*Z*)-diazotate **3**

To a mixture of ^{15}N labelled *N*-methyl-*N*-nitrosourea (**7**) (0.096 mmol, 10 mg) in CD_2Cl_2 (0.76 mL) maintained at −60 °C, was added TlOPr (1.1 eq) and the reaction mixture was stirred for 1 h. Subsequently, the reaction mixture was transferred to a pre-cooled NMR tube maintained at −60 °C and NMR spectra were recorded at the same temperature. The reaction was completed in an additional 30 min, as observed by NMR spectroscopy. NMR yields of (*Z*)-diazotate **3** and $CH_2N^{15}N$ are 14% and 31%, respectively. Diazotate **3** was stable for only for 2 h at −60 °C, and decomposed to $CH_2N^{15}N$ above −10 °C. Any attempt to isolate **3** led to the isolation of only $CH_2N^{15}N$, even at very low temperatures.

For (*Z*)-diazotate 3:

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 3.17 (d, $^3J(^{15}N,^1H)$ = 4.0 Hz).

^{15}N NMR (40.5 MHz, CD_2Cl_2): δ = 104.46 (^{15}NOTl).

Note: *^{13}C NMR data acquisition was not possible owing to the low concentration and very low stability of the diazotate **3**.*

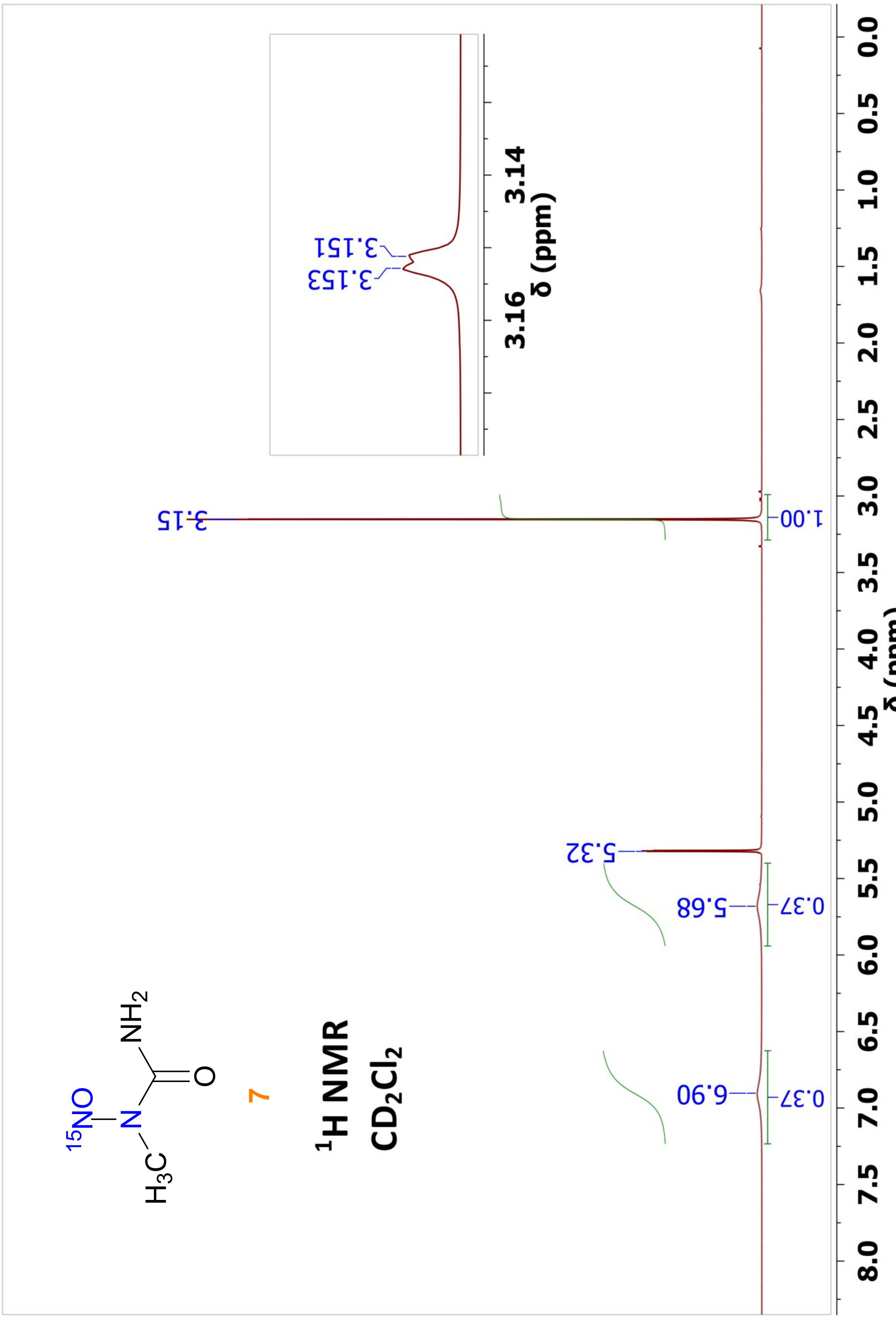
For $CH_2N^{15}N$:

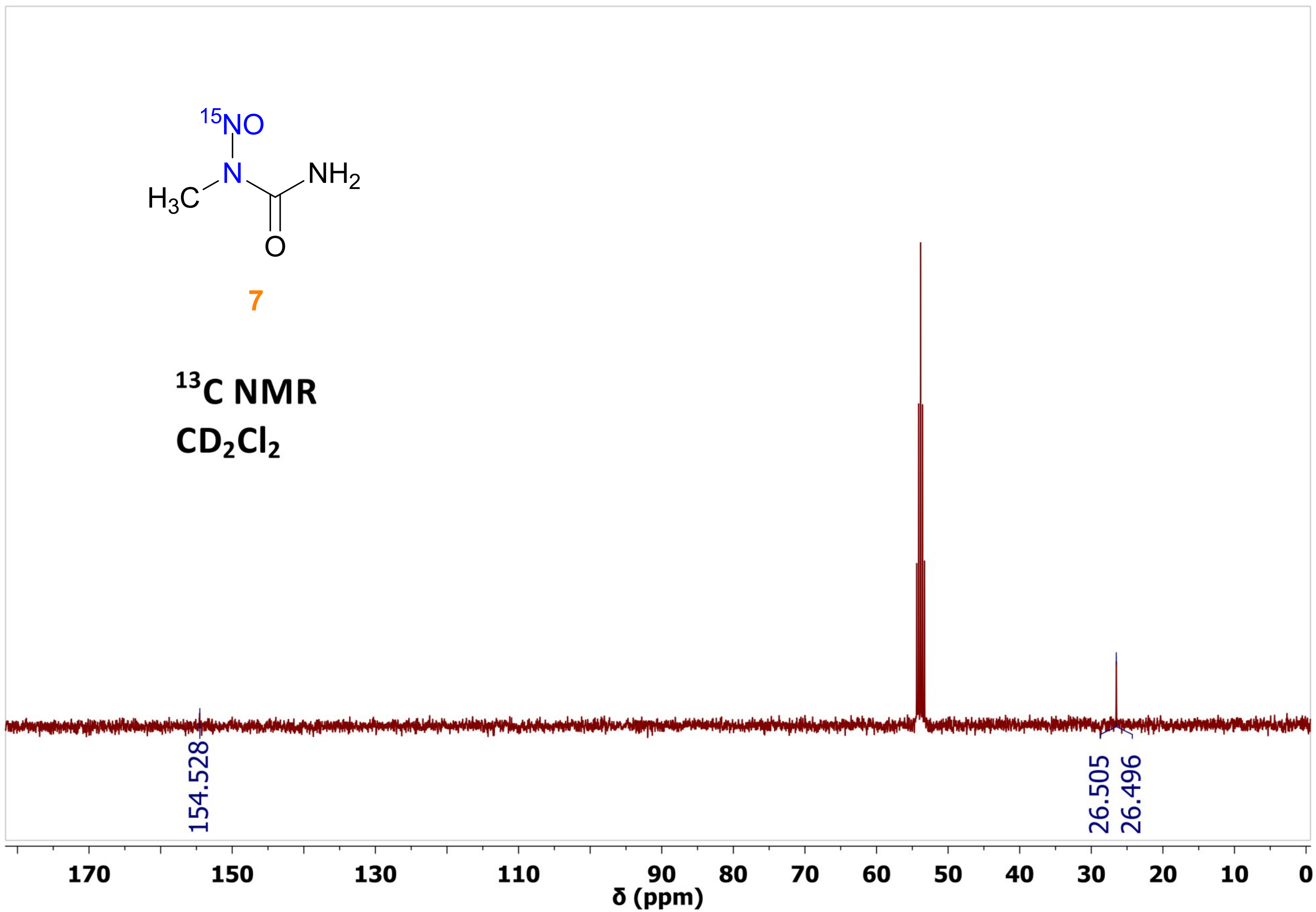
^{1}H NMR (400 MHz, CD_2Cl_2): δ = 3.33 (d, $^3J(^{15}N,^1H)$ = 1.2 Hz).

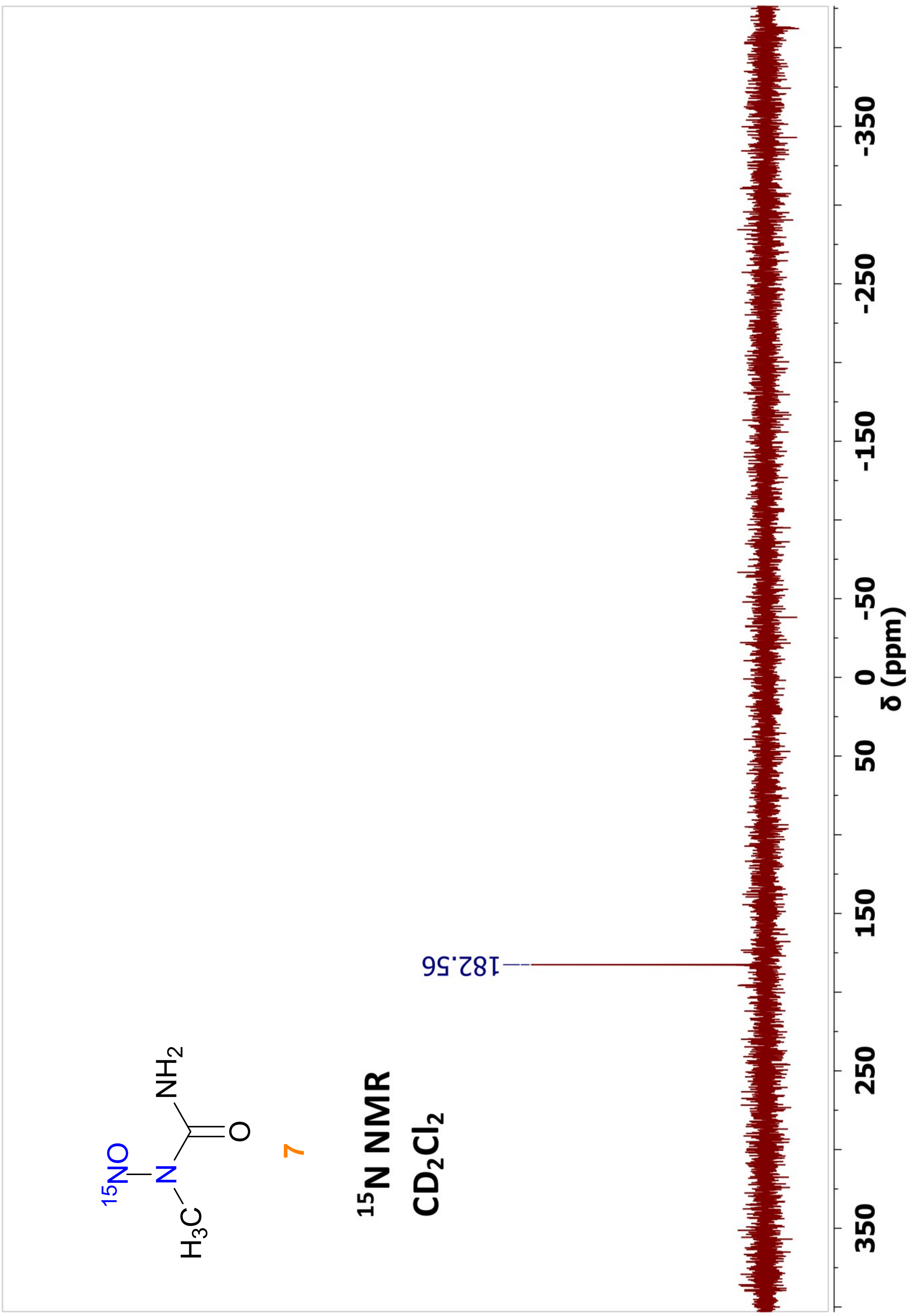
^{15}N NMR (40.5 MHz, CD_2Cl_2): δ = 14.57 ($CH_2N^{15}N$).

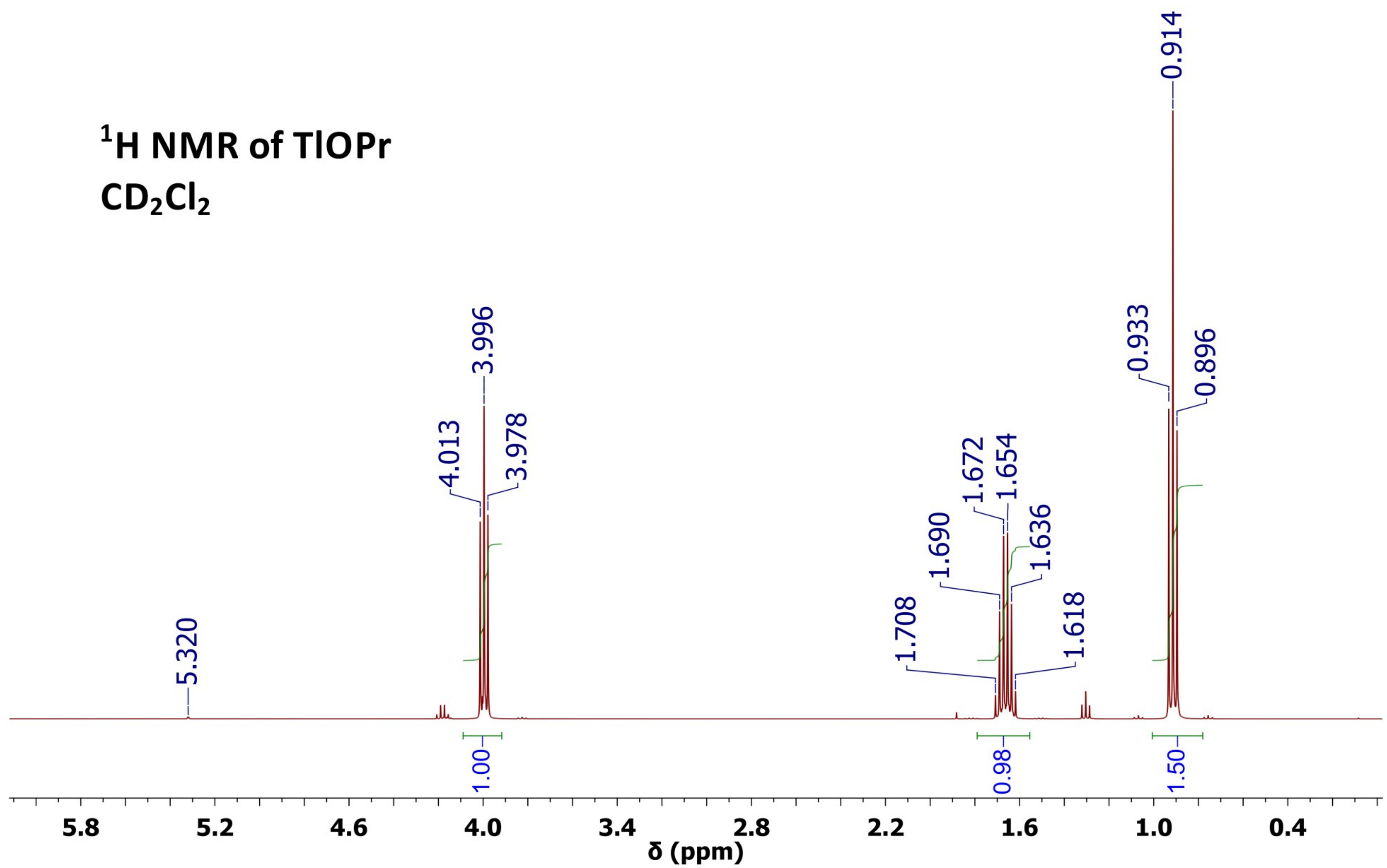
The assignments, in both the cases, were confirmed by $^{15}N,^1H$ gHMBCAD 2D NMR technique.

[3] NMR Spectra

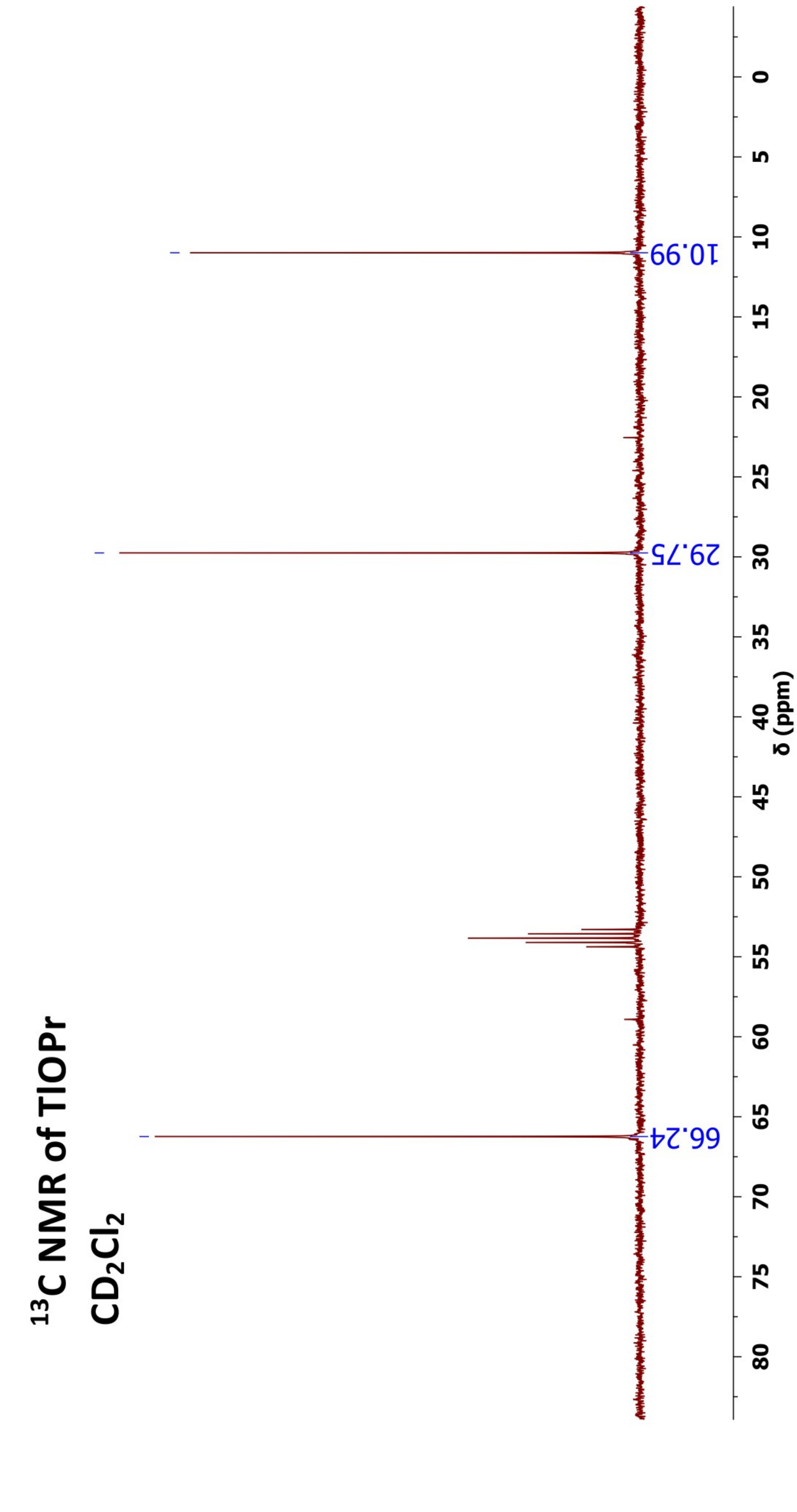



15NO
N
H3C
NH2
O
7
13C NMR
CD2Cl2
154.528
26.505
26.496
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)

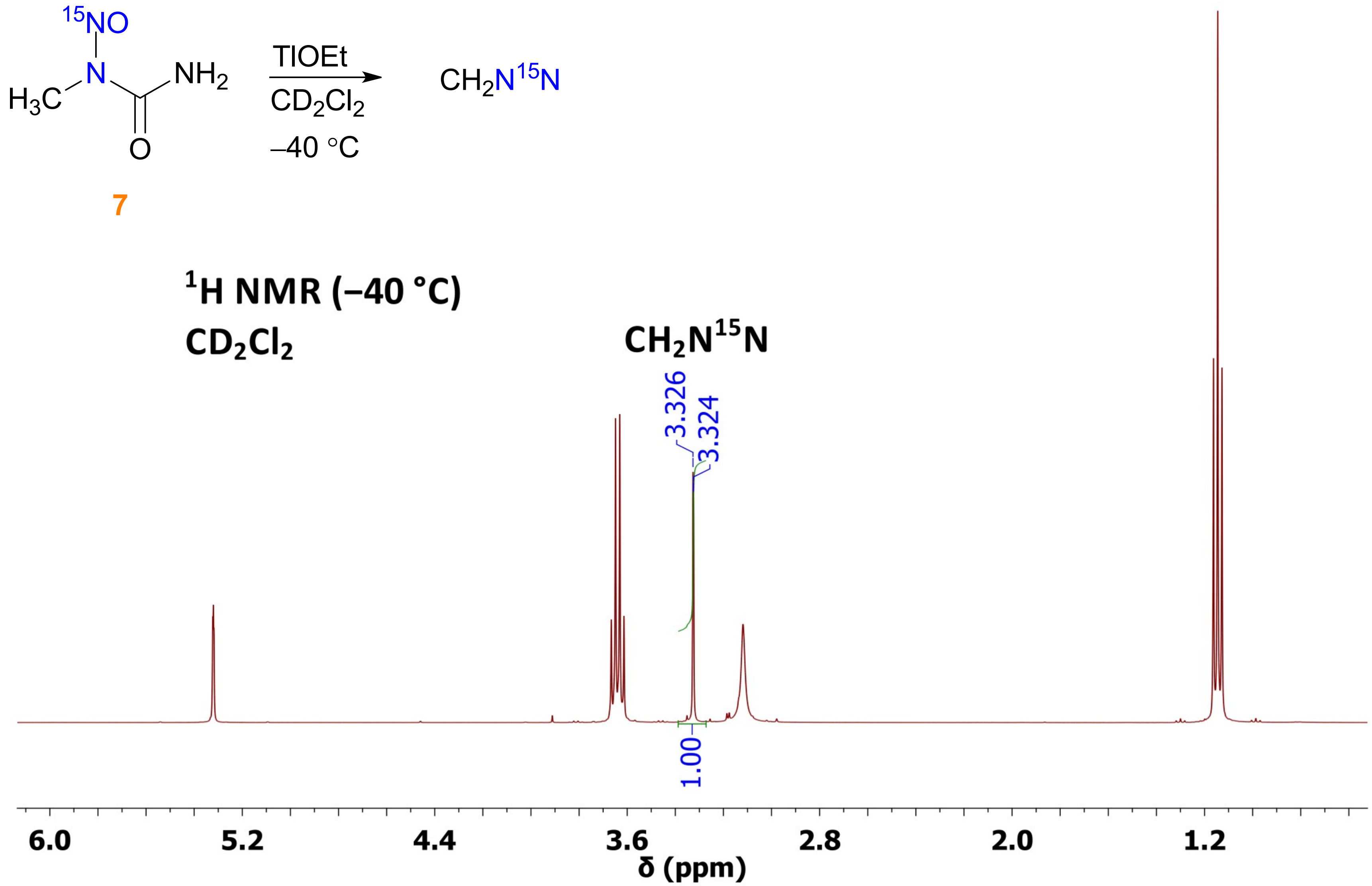

7
15N NMR
CD2Cl2
182.56
δ (ppm)



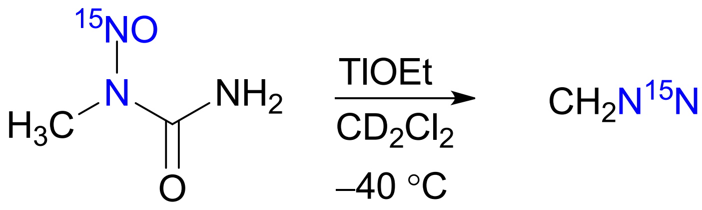
1H NMR of TlOPr
CD2Cl2
5.320
4.013
3.996
3.978
1.708
1.690
1.672
1.654
1.636
1.618
0.933
0.914
0.896
1.00
0.98
1.50
5.8
5.2
4.6
4.0
3.4
2.8
2.2
1.6
1.0
0.4
δ (ppm)



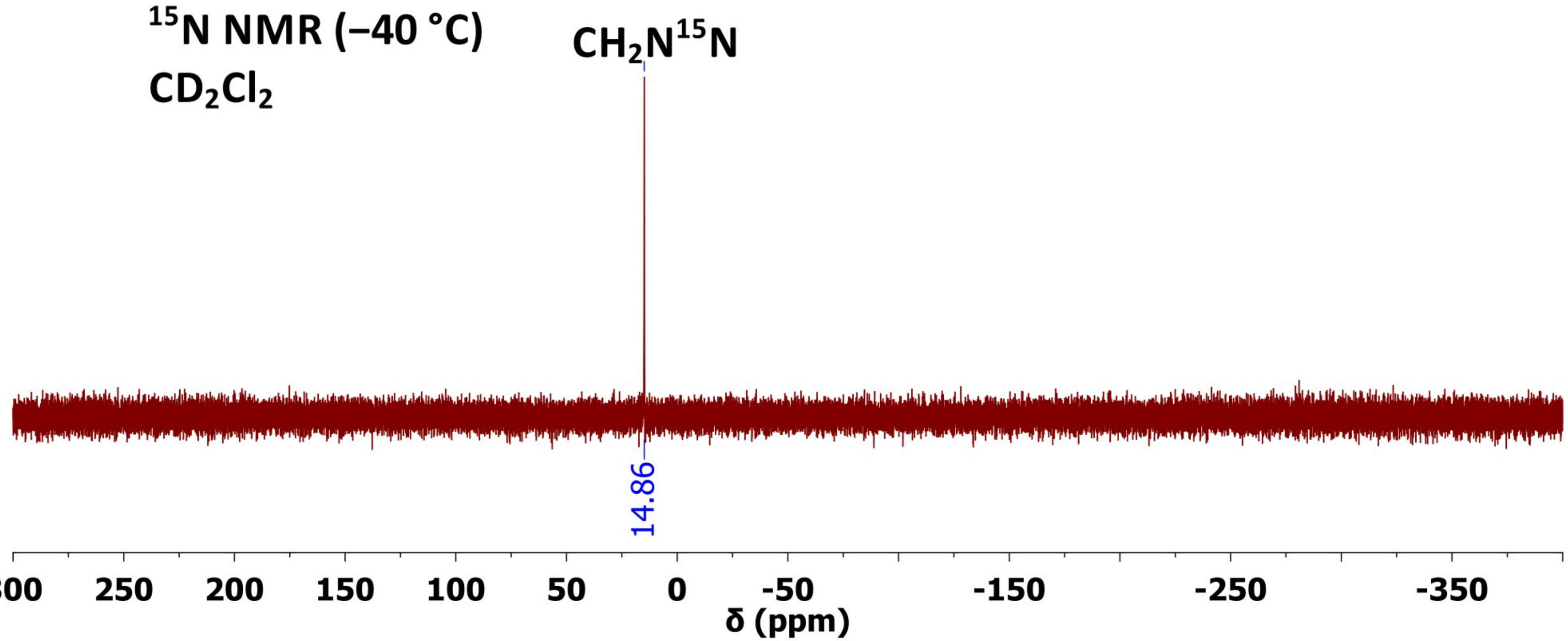
13C NMR of TIOPr
CD2Cl2
10.99
29.75
66.24
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
δ (ppm)

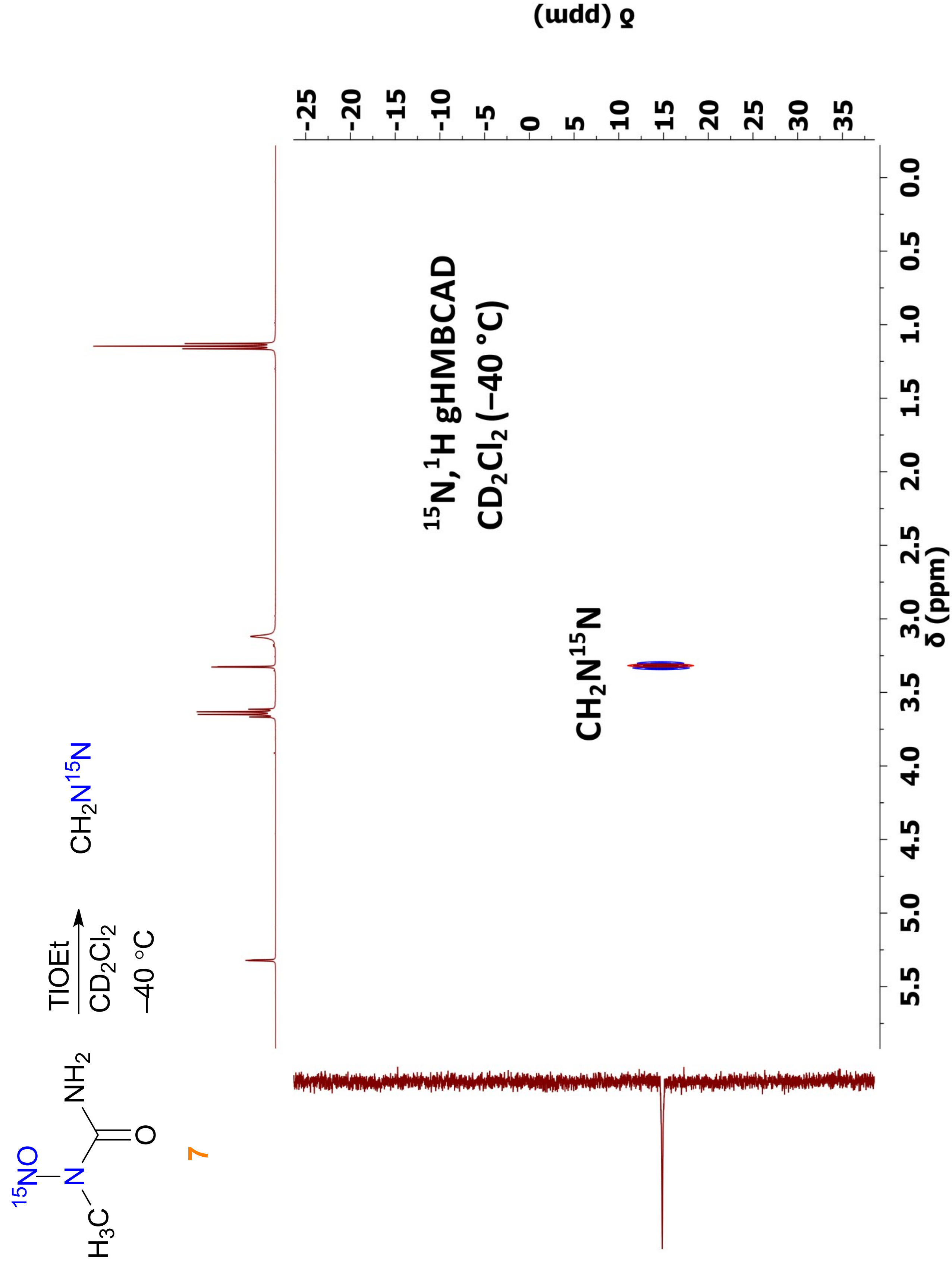


15NO
N
H3C
NH2
O
7
TlOEt
CD2Cl2
–40 °C
CH2N15N
1H NMR (–40 °C)
CD2Cl2
CH2N15N
3.326
3.324
1.00
6.0
5.2
4.4
3.6
2.8
2.0
1.2
δ (ppm)

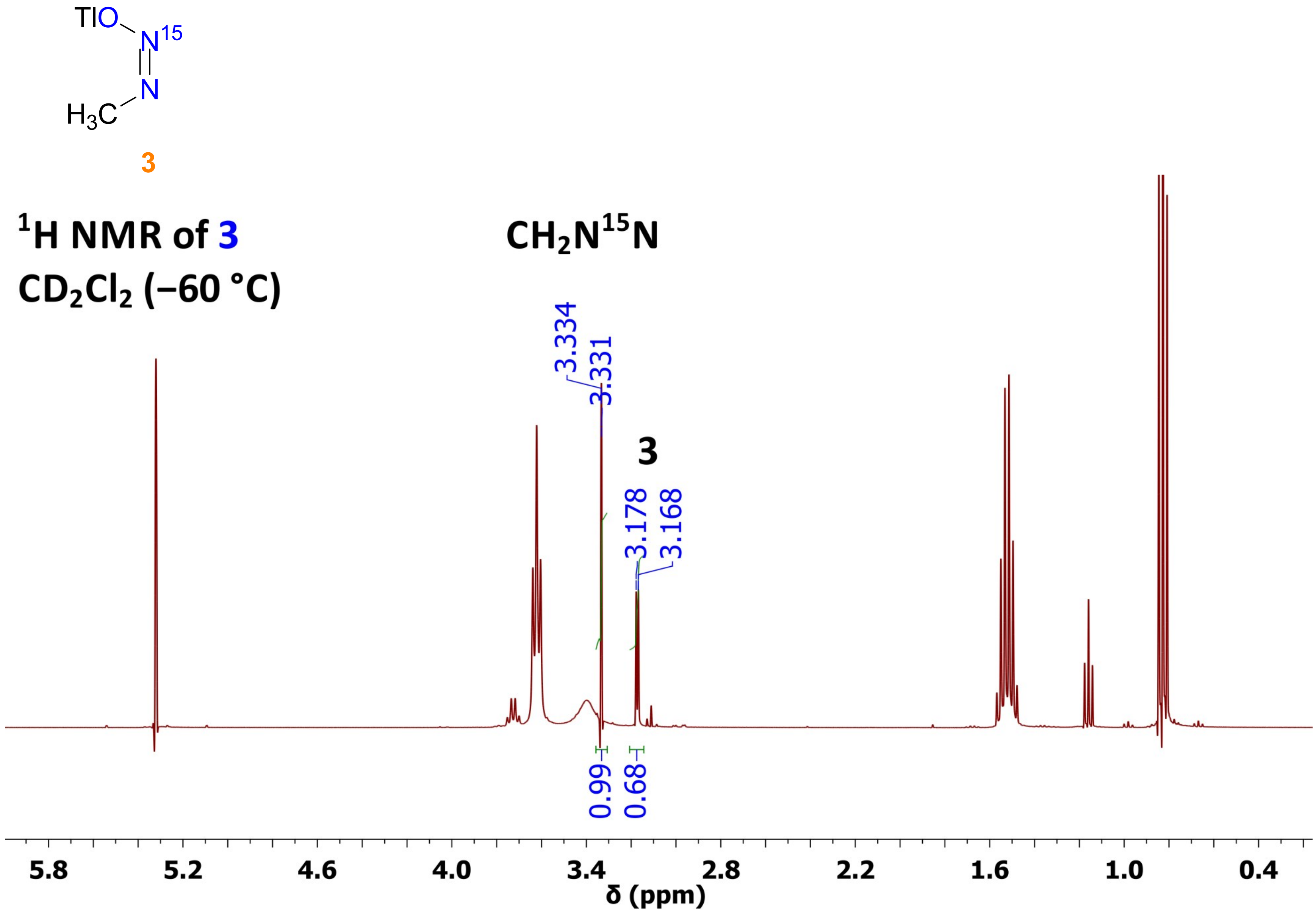

^{15}NO
H_3C
N
NH_2
O
TlOEt
CD_2Cl_2
–40 °C
$CH_2N^{15}N$

7

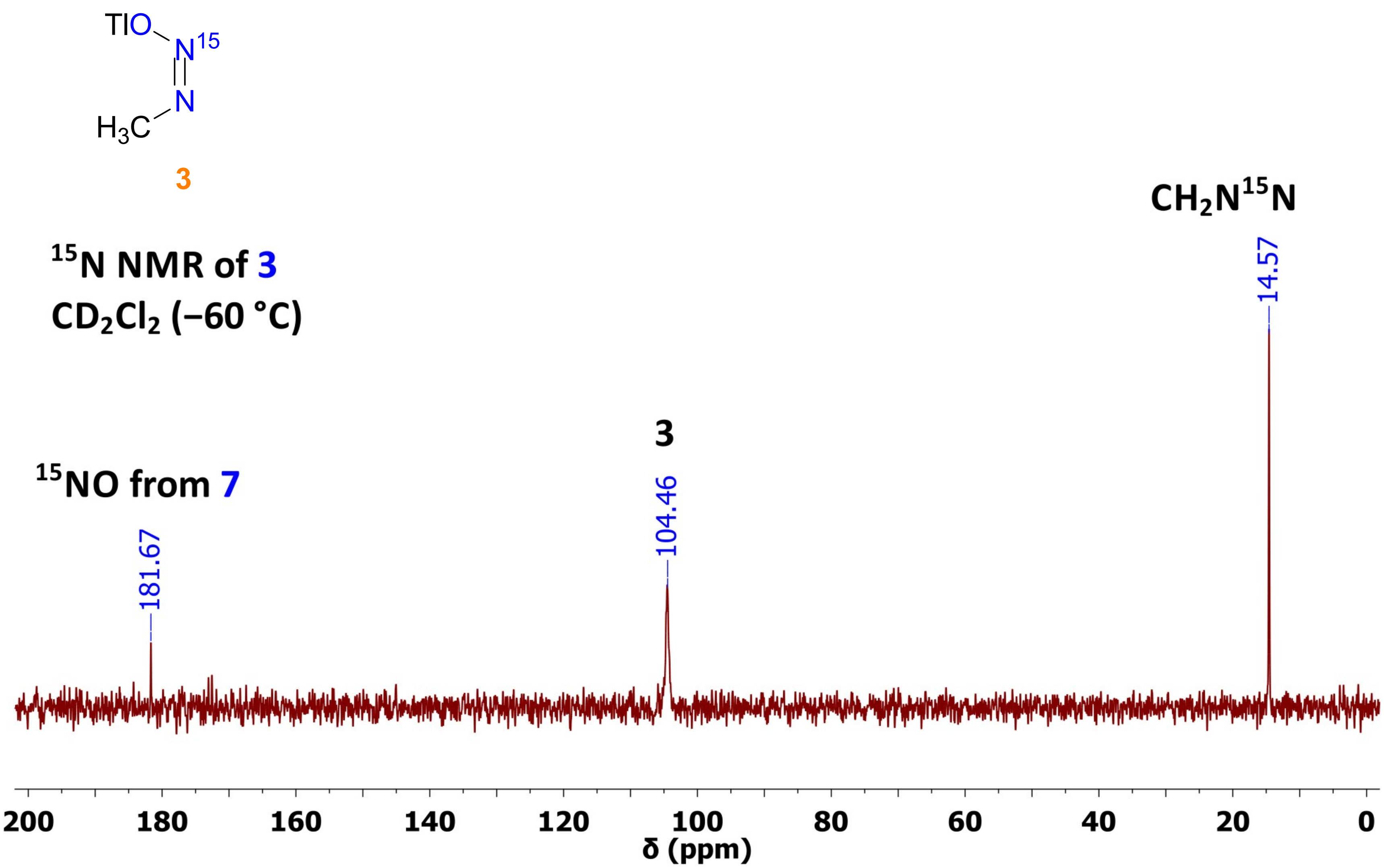

^{15}N NMR (–40 °C)
CD_2Cl_2
$CH_2N^{15}N$
14.86
300 250 200 150 100 50 0 -50 -150 -250 -350
δ (ppm)

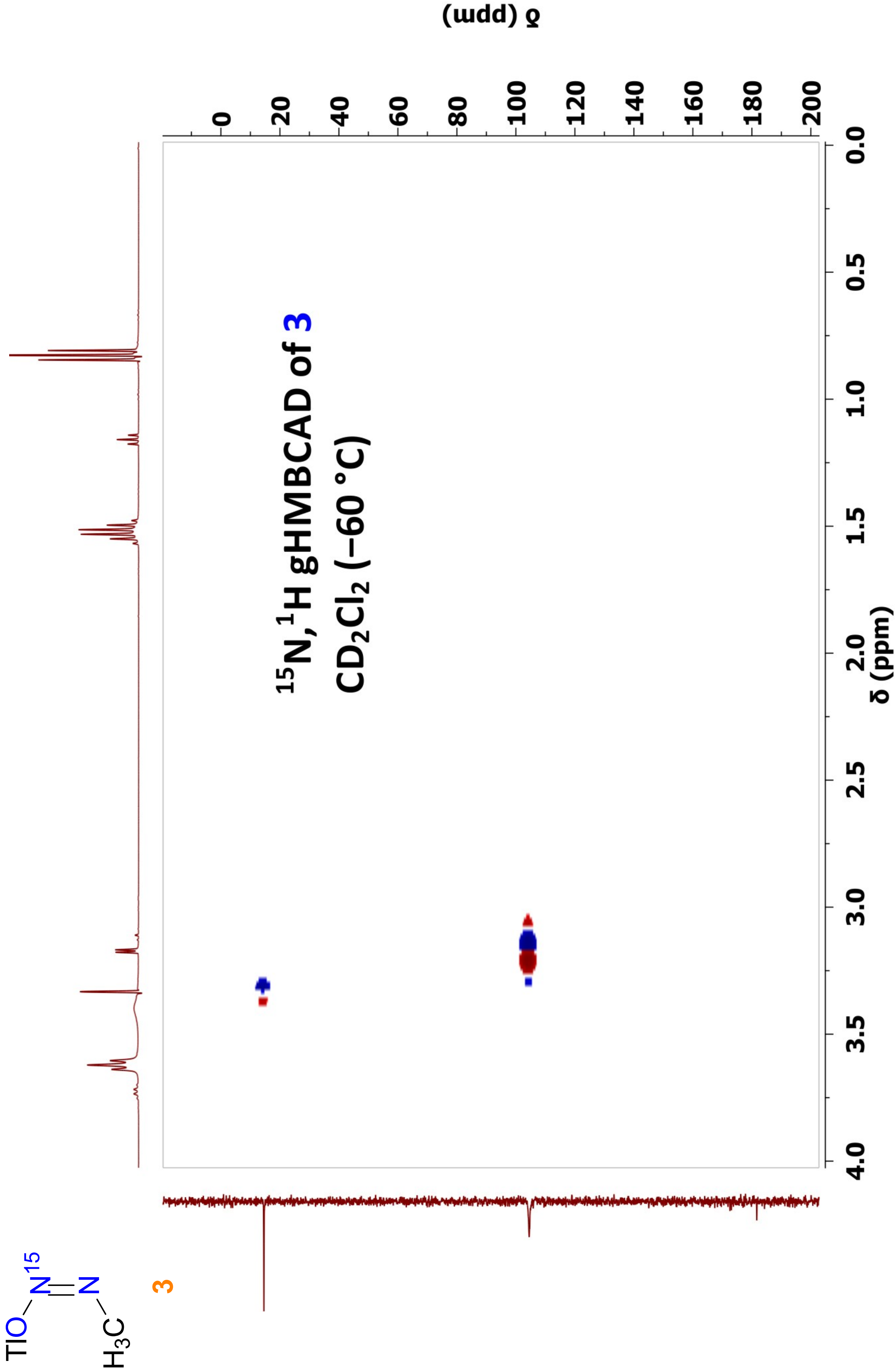


^{15}NO
H$_3$C
N
O
NH$_2$
7
TlOEt
CD$_2$Cl$_2$
−40 °C
CH$_2$N^{15}N
^{15}N,^{1}H gHMBCAD
CD$_2$Cl$_2$ (−40 °C)
CH$_2$N^{15}N
δ (ppm)
δ (ppm)



TlO
N15
N
H3C
3
1H NMR of 3
CD2Cl2 (−60 °C)
CH2N15N
3.334
3.331
3
3.178
3.168
0.99
0.68
5.8
5.2
4.6
4.0
3.4
2.8
2.2
1.6
1.0
0.4
δ (ppm)


TlO
N15
N
H3C
3
15N NMR of 3
CD2Cl2 (−60 °C)
15NO from 7
181.67
3
104.46
CH2N15N
14.57
200
180
160
140
120
100
80
60
40
20
0
δ (ppm)



$^{15}N,^{1}H$ gHMBCAD of 3
CD_2Cl_2 (−60 °C)
δ (ppm)
δ (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
0
20
40
60
80
100
120
140
160
180
200
TlO
N
15
N
H_3C
3

[4] Coordinates of Optimised Geometries

All coordinates are given in Å. The structures were optimised with PW6B95-D3/(def2-)TZVPP, using the COSMO model with ε = 8.9.

anti-**7**

N	-0.6127738	1.0431081	-0.2162466
N	0.6866870	1.1772793	-0.0334681
C	1.4531809	-0.0123174	0.1080782
N	0.7553940	-1.1459142	0.0478683
H	-0.2346590	-1.1477638	-0.0988224
H	1.2541830	-2.0094801	0.1325220
O	2.6514443	0.0677294	0.2716037
C	1.2992703	2.4871829	0.0200096
H	2.3573847	2.3503647	0.1789625
H	1.1159727	3.0091211	-0.9127111
H	0.8596594	3.0569593	0.8312030
O	-1.2230089	2.0816574	-0.3307703

syn-**7**

N	-0.0525209	0.2923150	-0.3303187
N	0.7383803	-0.5275242	-1.0054375
C	1.0732502	-1.8962566	-0.7401842
N	0.5302578	-2.4653256	0.3311873
H	-0.0925527	-1.9573320	0.9304880
H	0.7680551	-3.4218063	0.5134693
O	1.8320433	-2.4410462	-1.5149152
C	1.3496808	0.0651298	-2.1844809
H	1.0516017	-0.4816359	-3.0703096
H	1.0046150	1.0880174	-2.2397092
H	2.4285294	0.0357486	-2.0962309
O	-0.5992466	-0.1299344	0.6664837

3 *(Z)*

N	-2.3104582	0.9426749	0.5583372
N	-1.2625233	0.4075503	0.1658271
O	-2.3830793	1.3824559	1.7949834
C	-0.1867305	0.3169057	1.1442240
H	0.6594359	-0.1598508	0.6655630
H	0.0980121	1.3034975	1.5061289
H	-0.4964921	-0.2620968	2.0127478
Tl	-4.6247138	2.0523242	1.1655271

1 *(E)*

N	-2.3786410	0.4865301	0.1021794
N	-1.1397967	0.4881507	-0.0576665
O	-3.0525835	0.4851094	-0.9964676
C	-0.3818614	0.4878655	1.1744561
H	0.2604977	1.3644215	1.2072629
H	-1.0386398	0.4894827	2.0412439
H	0.2573176	-0.3910264	1.2084516
Tl	-1.2287061	0.4896909	-2.6966712

TS(*anti***-7→***syn***-7)**

N	-1.3799145	-0.2077805	-0.4858957
N	-0.2435314	0.4167522	0.2564041
C	0.9755997	-0.1801230	-0.0679708
N	0.9051733	-1.5199728	-0.2415117
H	0.1653134	-2.0507559	0.1764723
H	1.7790873	-1.9981472	-0.3552006
O	2.0024479	0.4630637	-0.1746723
C	-0.3198199	1.8579761	0.0591624
H	0.5421632	2.3002491	0.5409509
H	-0.3106580	2.1274159	-0.9951807
H	-1.2222491	2.2294853	0.5287109
O	-2.1594493	-0.6896340	0.2345367

TS(3→1)

N	1.6741022	0.0467306	-0.1616112
N	2.8903932	-0.1074936	-0.2420630
O	1.2159149	1.1791743	0.3109628
C	4.0049944	-0.6153150	0.4661369
H	4.8929451	-0.4750427	-0.1419314
H	4.1760142	-0.0915157	1.4117813
H	3.9164217	-1.6874494	0.6744311
Tl	-0.9035688	0.1266619	-0.4037864

Ed, *(Z)*

N	0.0266187	0.1030325	-0.5256345
N	1.1284205	-0.4651139	-0.9343232
C	1.0173528	-1.7011765	-1.6524379
N	-0.2086445	-2.1798421	-1.7963853
H	-1.0898985	-1.7653428	-1.4361563
H	-0.2635854	-3.0393455	-2.3091715
O	2.0408921	-2.2100545	-2.0684766
C	2.4153648	0.1416700	-0.6666014
H	3.1728264	-0.4899257	-1.1026744
H	2.4430012	1.1342352	-1.1024810
H	2.5553147	0.2290811	0.4052029
O	0.1742534	1.1487831	0.0823119
O	-2.6970881	-1.4165600	-1.0293859
C	-3.4840173	-2.5628881	-1.0531030
H	-4.4547706	-2.3744542	-1.5308888
H	-2.9986522	-3.3380697	-1.6641240
C	-3.7390535	-3.1483995	0.3272565
H	-4.2516558	-2.3991505	0.9339036
H	-2.7762101	-3.3299052	0.8031437
C	-4.5616813	-4.4225670	0.2803842
H	-4.7382251	-4.8232884	1.2745252
H	-5.5302299	-4.2434192	-0.1821882
H	-4.0558358	-5.1895035	-0.3023005
Tl	-2.9870726	0.4369806	0.2245960

TS(Ed-IM), *(Z)*

H	1.0223848	-0.3586137	-1.4132324
N	1.1419860	1.0684299	0.7155322
N	2.4032324	1.0031857	0.4390705
O	0.8543325	1.0504212	1.9094967
C	2.8074958	0.9946875	-0.9643484
C	3.3828864	0.9373157	1.5007697
N	1.9115816	0.4747297	-1.7672015
O	3.9174010	1.4534363	-1.2010762
H	4.3598682	0.9248027	1.0434105
H	3.2791740	1.7946969	2.1567543
H	3.2122642	0.0361785	2.0832197
O	0.1458548	-1.1203778	-1.0861406
H	2.2179858	0.5051233	-2.7264058
C	0.6110493	-2.3827151	-0.6789042
H	-0.2280284	-2.9683050	-0.2947626
H	1.0025860	-2.9312381	-1.5413239
C	1.6895698	-2.3064184	0.3865022
H	1.3113241	-1.7253213	1.2279559

Ed, *(E)*

N	0.2396524	0.3660172	-0.1014943
N	0.8318235	-0.4595191	-0.9099734
C	1.3174461	-1.7861036	-0.5187190
N	0.3573249	-2.6008021	-0.1416105
H	-0.6388800	-2.2772834	-0.0594489
H	0.6313707	-3.5138128	0.1722352
O	2.5049373	-2.0085261	-0.6307756
C	1.2273262	0.0517482	-2.2053402
H	0.8256870	-0.5804728	-2.9893216
H	0.8305275	1.0539615	-2.2980791
H	2.3090541	0.0708251	-2.2735693
O	0.0517563	-0.0285128	1.0440508
O	-2.1539221	-1.7192780	0.0052707
C	-3.0449869	-2.5573689	-0.6615038
H	-3.9453644	-2.0147150	-0.9786987
H	-2.5829919	-2.9313619	-1.5851672
C	-3.4776488	-3.7541396	0.1700390
H	-3.9631461	-3.3902333	1.0768063
H	-2.5854761	-4.2912355	0.4906989
C	-4.4094502	-4.6822927	-0.5869711
H	-4.7074254	-5.5339375	0.0180608
H	-5.3133037	-4.1605956	-0.8949291
H	-3.9288413	-5.0645451	-1.4851339
Tl	-2.6737127	-0.3488424	1.7440064

TS(Ed-IM), *(E)*

N	2.3272920	0.8540743	-1.0872972
N	2.9730956	-0.1221333	-0.5605331
O	1.4613631	1.3897626	-0.3840699
C	2.7964193	-0.5652835	0.8467479
C	4.0732795	-0.6850229	-1.3116177
N	1.6936890	-1.2391601	1.0177472
O	3.7070842	-0.2891173	1.6098366
H	3.9089006	-1.7469240	-1.4608729
H	4.1232490	-0.1791512	-2.2667398
H	4.9951700	-0.5367511	-0.7600238
O	-0.0924984	-1.2302576	-0.6800597
H	1.5589684	-1.5541039	1.9655768
C	-0.7419582	-2.4492609	-0.9187398
H	-1.5094871	-2.3093131	-1.6843376
H	-0.0290828	-3.1752575	-1.3238893
C	-1.3855220	-3.0359777	0.3257479
H	-2.0964313	-2.3118860	0.7261333
H	-0.6185329	-3.1744616	1.0866734

H	2.5411034	-1.7618965	-0.0166667	C	-2.0861520	-4.3511161	0.0418307
C	2.1267278	-3.6840418	0.8499663	H	-2.5431981	-4.7620394	0.9371283
H	2.9115210	-3.6213587	1.5981432	H	-2.8686979	-4.2204013	-0.7025754
H	1.2939089	-4.2321096	1.2853087	H	-1.3847172	-5.0883339	-0.3423656
H	2.5087841	-4.2707259	0.0172702	H	0.8118354	-1.3116914	0.1540388
Tl	-1.5021100	0.2299132	-0.0006660	Tl	-1.1099860	0.7829827	0.1277473

IM, *(Z)*				**IM,** *(E)*			
H	0.7016463	-0.8940281	-1.4608119	N	2.4985547	0.1207069	-1.2802731
N	1.0978628	0.8175431	1.0505793	N	2.7257612	-0.8047467	-0.4188849
N	1.8861635	1.4757373	0.2567694	O	1.8730719	1.1187597	-0.9006532
O	1.5006805	0.6433176	2.1887334	C	2.3842364	-0.7716298	1.0318205
C	1.4398554	1.7398798	-1.1131519	C	3.5445477	-1.9136648	-0.8655757
C	3.1598929	1.9545339	0.7449188	N	1.0984053	-0.7214749	1.2593943
N	0.3584870	1.0825382	-1.4652498	O	3.3494776	-0.8736349	1.7782696
O	2.1399601	2.5227377	-1.7465687	H	3.0053001	-2.8446524	-0.7237453
H	3.6507155	2.4607361	-0.0709072	H	3.7617115	-1.7683141	-1.9150495
H	3.0035961	2.6295152	1.5800750	H	4.4608848	-1.9394295	-0.2880819
H	3.7503038	1.1126771	1.0938783	O	-0.5500212	-1.2940936	-0.9127273
O	0.3217026	-1.7401961	-1.1785048	H	0.9456606	-0.7928101	2.2589084
H	0.1114752	1.3648302	-2.4039166	C	-1.5183650	-2.3267113	-1.0175899
C	1.3478620	-2.6797726	-0.8936490	H	-2.2306322	-2.0036314	-1.7723994
H	0.8452336	-3.5839428	-0.5602486	H	-1.0440409	-3.2386596	-1.3854569
H	1.8884549	-2.9233148	-1.8100068	C	-2.2324310	-2.6140449	0.2848289
C	2.3134740	-2.1996042	0.1657691	H	-2.7166566	-1.7032356	0.6350224
H	1.7570773	-1.9677994	1.0711073	H	-1.4952928	-2.8918877	1.0376749
H	2.7726635	-1.2694851	-0.1703089	C	-3.2527527	-3.7275933	0.1230045
C	3.3882089	-3.2320480	0.4550578	H	-3.7536207	-3.9452255	1.0613439
H	4.0778882	-2.8777000	1.2150383	H	-4.0125466	-3.4568909	-0.6063549
H	2.9488227	-4.1609018	0.8112180	H	-2.7765434	-4.6432272	-0.2202169
H	3.9644713	-3.4583654	-0.4390497	H	0.0378501	-1.4613315	-0.1548492
Tl	-1.4059842	0.0666543	0.0544992	Tl	-0.4794676	1.1522836	0.3615347

TS(IM-Pr), *(Z)*				**TS(IM-Pr),** *(E)*			
H	4.2797514	-3.0813730	-0.7698899	H	-3.7874021	-3.9238813	0.1268911
C	3.4309895	-3.2014047	-0.1006150	C	-3.9415171	-2.8710907	0.3511365
C	2.5150009	-1.9930052	-0.1586476	C	-2.6286512	-2.1101350	0.3125643
H	3.8160791	-3.3525872	0.9028622	H	-4.4065666	-2.8034759	1.3298341
H	2.9010888	-4.1044626	-0.3950991	H	-4.6423230	-2.4749498	-0.3799037
C	1.9836191	-1.7653430	-1.5550891	C	-1.9651993	-2.2092070	-1.0439404
H	1.6775466	-2.1258475	0.5254770	H	-2.7985560	-1.0608827	0.5509804
H	3.0415577	-1.0997843	0.1751714	H	-1.9463490	-2.4990577	1.0676435
O	1.0743306	-0.6716855	-1.6284518	O	-0.7314930	-1.5058642	-1.1144845
H	1.4296427	-2.6358012	-1.8964909	H	-2.6035075	-1.7764615	-1.8096901
H	2.8086046	-1.6046243	-2.2503779	H	-1.8057201	-3.2572926	-1.3025646

H	1.4843845	0.1034509	-1.2258885
N	-0.4987173	1.9155990	-0.9750959
C	0.5110904	2.6315339	-0.9344143
H	-1.2100773	2.2978030	-1.5877831
O	1.2687663	3.4982071	-1.1225658
N	1.6819714	1.4486196	0.4641340
N	1.0641455	0.6380803	1.2135017
C	2.9415272	1.9669534	0.9481885
O	1.5616062	0.2826344	2.3061865
H	3.3050207	2.6845047	0.2227130
H	2.8225463	2.4451125	1.9191284
H	3.6674521	1.1637567	1.0747819
Tl	-1.0581890	-0.5223281	0.1634317

H	-0.1755773	-1.7734506	-0.3713710
N	0.6051448	-1.1930657	1.4701502
C	1.8480857	-1.2596704	1.5011999
H	0.2087234	-1.2761931	2.4007934
O	2.9298390	-1.3614508	1.9293611
N	2.2984887	-1.2361471	-0.5962253
N	2.3129789	-0.2957519	-1.4117621
C	3.0199292	-2.4108102	-1.0354520
O	1.7151644	0.7855645	-1.0483943
H	2.3396678	-3.2578034	-1.0832787
H	3.4700406	-2.2526557	-2.0112886
H	3.7933427	-2.6435708	-0.3084828
Tl	-0.4681171	1.0521101	0.0019575

Pr, *(Z)*

N	1.1620805	-2.2829478	-0.1369651
N	2.0326936	-2.9865999	0.3990956
O	1.4926501	-1.1324648	-0.6475075
C	3.3798898	-2.4416994	0.4064282
H	4.0274454	-3.1571847	0.8966322
H	3.7295088	-2.2558576	-0.6078031
H	3.4111489	-1.4889609	0.9323257
O	-2.1597006	-0.7747441	-1.7687842
C	-3.3338081	-0.1514768	-1.2576020
H	-2.0376063	-1.6294419	-1.3250190
H	-3.4552151	0.7717351	-1.8185412
H	-4.2002371	-0.7790828	-1.4671081
C	-3.2444586	0.1394469	0.2241242
H	-2.3826717	0.7809433	0.4087322
H	-3.0619908	-0.7923567	0.7568334
C	-4.5083289	0.8003037	0.7430791
H	-4.4363695	1.0025475	1.8071208
H	-4.6932013	1.7439614	0.2349349
H	-5.3735057	0.1614632	0.5827459
C	-1.9015556	-4.1443294	-0.0975757
N	-1.3734734	-3.1023749	-0.3578791
O	-2.4945282	-5.1250489	0.1280895
H	-0.3381794	-2.8105825	-0.2345510
Tl	0.1608171	0.6053383	-1.7061739

Pr, *(E)*

H	-3.3495060	-3.6723466	-1.6306583
C	-3.1615451	-3.9809703	-0.6047247
C	-1.8778687	-3.3665905	-0.0756227
H	-3.1149736	-5.0653923	-0.5868319
H	-4.0154104	-3.6739483	-0.0050360
C	-1.9334433	-1.8558819	-0.0958303
H	-1.6880448	-3.6946031	0.9441908
H	-1.0290726	-3.6949740	-0.6757652
O	-0.7506173	-1.2711863	0.4334524
H	-2.7574626	-1.5001268	0.5178204
H	-2.1073371	-1.5030803	-1.1147666
H	0.0121201	-1.5063676	-0.1450297
N	2.2015573	-0.7110844	1.8126706
C	1.8879582	-1.8481299	2.0334773
H	2.1550445	-0.2548974	0.8857891
O	1.6159231	-2.9330497	2.3615800
N	1.3721747	-1.5662849	-1.3066270
N	2.0533644	-0.5480351	-1.5042985
C	1.6578587	-2.6368521	-2.2397575
O	1.8345963	0.4307164	-0.6613946
H	0.7589955	-2.8687675	-2.8057047
H	2.4602635	-2.3705149	-2.9222799
H	1.9320920	-3.5275896	-1.6807766
Tl	-0.3266651	1.3172804	0.3007954

TS(IM,*(Z)***→IM,***(E)***)**

H	0.6849802	-0.8364805	-1.6532276
N	1.2135054	1.1351723	1.3945549
N	2.0301390	1.4553359	0.2294848
O	0.5086503	2.0202222	1.7218902

C	1.3068402	1.7245193	-0.9599494
C	3.1057185	2.3522006	0.6057032
N	0.1715730	1.0372425	-1.0846917
O	1.8169913	2.4860735	-1.7839051
H	3.7158145	2.5150050	-0.2719773
H	2.7335961	3.3110345	0.9656111
H	3.7062770	1.8832705	1.3789175
O	0.4515658	-1.7779093	-1.6537206
H	-0.2524271	1.2951225	-1.9665387
C	1.5714752	-2.5325101	-1.2040408
H	1.3268806	-3.5770786	-1.3760189
H	2.4455471	-2.2942053	-1.8111434
C	1.8753333	-2.2932707	0.2588657
H	1.0139969	-2.6019572	0.8512672
H	2.0067734	-1.2233867	0.4121046
C	3.1158510	-3.0364195	0.7193626
H	3.3134951	-2.8544430	1.7713807
H	3.0043705	-4.1092783	0.5813280
H	3.9896101	-2.7171283	0.1563445
Tl	-1.2997216	-0.5138298	0.2086310

[5] Energies

All energies are given in Hartree and represent electronic energies, except for $G_{-60°C}$, which includes the zero-point vibrational energy as well as additional temperature-dependent (T = 213.15 K) enthalpic and entropic terms. Furthermore, foT/TZ refers to the focal-point method according to Eq. (3) in the paper and CBS(34) refers to two-point CBS extrapolations, using cc-pVTZ / cc-pVQZ basis sets. For Tl we had to use the aug-cc-pwCVTZ-PP basis set instead of cc-pVTZ-F12. The energies were calculated for the geometries, provided above, which were optimised with PW6B95-D3 / (def2-) TZVPP and COSMO (ε = 8.9).

	PW6B95-D3/ (def2-)TZVPP COSMO	$G_{-60°C}$ (freeh)	PW6B95-D3/ (def2-)TZVPP no COSMO	CCSD(T)/ foT/TZ	CCSD(T)/ CBS(34)	CCSD(T)(F12) /cc-pVTZ-F12
anti-**7**	-394.5203	0.0693	-394.5066	-393.4995	-393.4843	-393.4563
TS(*anti***-7→***syn***-7)**	-394.4794	0.0677	-394.4659	-393.4639	-393.4480	-393.4202
syn-**7**	-394.5127	0.0696	-394.5000	-393.4937	-393.4783	-393.4503
3	-397.5717	0.0281	-397.5513	-396.4825	-396.1899	-396.3968
TS(3→1)	-397.5018	0.0254	-397.4832	-396.4089	-396.1159	-396.3226
1	-397.5784	0.0280	-397.5620	-396.4918	-396.2002	-396.4065
Ed, *(Z)*	-761.2394	0.1575	-761.2226	-759.1930	-	-
TS(Ed-IM), *(Z)*	-761.2352	0.1554	-761.2139	-759.1843	-	-
IM, *(Z)*	-761.2476	0.1581	-761.2295	-759.1997	-	-
TS(IM-Pr), *(Z)*	-761.2175	0.1552	-761.1984	-759.1647	-	-
Pr, *(Z)*	-761.2302	0.1514	-761.2118	-759.1818	-	-
Ed, *(E)*	-761.2296	0.1571	-761.2123	-759.1830	-	-
TS(Ed-IM), *(E)*	-761.2256	0.1538	-761.2042	-759.1751	-	-
IM, *(E)*	-761.2361	0.1569	-761.2151	-759.1864	-	-
TS(IM-Pr), *(E)*	-761.2131	0.1528	-761.1928	-759.1609	-	-
Pr, *(E)*	-761.2363	0.1527	-761.2165	-759.1865	-	-
TS(IM,*(Z)***→IM,***(E)***)**	-761.1939	0.1562	-761.1728	-759.1469	-	-