Carbocation Forming Reactions in Dimethyl Sulfoxide

Supporting Information

Xavier Creary,* Elizabeth A. Burtch, and Ziqi Jiang
Department of Chemistry and Biochemistry
University of Notre Dame
Notre Dame, Indiana 46556

Experimental Procedures for Reactions in DMSO-d₆

Reaction of Chloride **22 in DMSO-d₆.** A solution of 3.9 mg of chloride **22** in 1.0 mL of DMSO-d₆ was placed in an NMR tube and heated at 50.0 °C for 45 min. Analysis by 600 MHz ¹H NMR showed 49% unreacted chloride **22**. In a similar fashion, a solution of 3.9 mg of **15** in 1.0 mL DMSO-d₆ containing 10.4 mg of tetramethylammonium chloride was heated at 50.0 °C for 45 min. ¹H NMR analysis of this mixture now showed 88% unreacted chloride **22**.

In a separate run, 0.01 M solutions of **22** in DMSO-d₆ were heated at 50.0 °C. The time required for 50% of **22** to react at 50 °C was determined to be 32 min.

In a third run, 3.6 mg of chloride **22** in 1 mL of DMSO-d₆ was heated at 50.0 °C for 9 h. ¹H NMR analysis showed indole **23** and alcohol **24** (which were identified by spectral comparison with authentic samples) in an 83:17 ratio.

Reaction of Chloride **28 in DMSO-d₆.** A solution was prepared by stirring 9.0 mg of chloride **28** in 2.38 g of DMSO-d₆. A portion of this solution was placed in an NMR tube. A 0.9 mL portion of the remaining solution was added to 9.9 mg of tetramethylammonium chloride and the mixture was stirred until the chloride dissolved. This second solution was also placed in an NMR tube and both tubes were placed in a bath at 70.0 °C. After 5 h, analysis of the first tube by 600 MHz ¹H NMR showed 27% of **29** and 73% of unreacted **28**. The tube containing the tetramethylammonium chloride showed 3% of **29** and 97% of unreacted **28**. The product **23** was identified by NMR spectral comparison with an authentic sample in DMSO-d₆.

In a separate run, 0.01 M solutions of **28** in DMSO-d₆ were heated at various temperatures for approximately 30 min. The time required for 50% reaction was determined. At 112 °C, a total of 33.5 min was required for **28** to be 50% reacted.

Reaction of Trifluoroacetate **30 in DMSO- d_6 .** A solution of 10 mg of *exo*-2-phenyl-*endo*-bicyclo[2.2.1]heptyl trifluoroacetate, **30**,³³ in 1 mL of DMSO- d_6 was prepared and a portion of the solution was placed in an NMR tube. The tube was immediately placed in the probe of a 600 Mhz NMR spectrometer at 25.0 °C and the signals due to unreacted **30** at δ 3.04 and the product **32** at δ 2.97 were monitored as a function of time. The rate constant given in Table 1 was determined from these integrals. After 1.5 h, the NMR showed alkene **32** as the sole product, with the vinylic hydrogen of **32** appearing at δ 6.38.

The reaction of *endo*-deuterated **30** was monitored in an identical fashion. At the end of the reaction, the ^1H NMR spectrum showed no trace of the vinylic signal at δ 6.38.

Reaction of Trifluoroacetate **31 in DMSO- d_6 .** A solution of 11 mg of *exo*-2-(*p*-trifluoromethylphenyl)-*endo*-bicyclo[2.2.1]heptyl trifluoroacetate, **31**,³³ in 1 mL of DMSO- d_6 was prepared and a portion of the solution was placed in an NMR tube. The solution was periodically analyzed by 600 MHz NMR at 25.0 °C. Between analyses, the tube was kept in a constant temperature bath at 25.0 °C. The appearance of the olefinic signal of **33** at δ 6.60 was monitored as a function of time. The rate constant given in Table 1 was determined from these integrals. After 3 days at 25 C and 10 h at 50 °C, the NMR showed alkene **33** as the sole product, with the vinylic hydrogen of **33** appearing at δ 6.60.

The reaction of *endo*-deuterated **31** was monitored in a similar fashion. At the end of the reaction, the ^1H NMR spectrum showed no trace of the vinylic signal at δ 6.60.

Reaction of Trifluoroacetate **35 in DMSO- d_6 .** A solution of 11 mg of 2-methyl-2-adamantyl trifluoroacetate, **35**, and 7 mg of 2,6-lutidine in 1.0 mL of DMSO- d_6 was prepared and a portion of the solution was placed in an NMR tube. The NMR tube was immersed in a constant temperature bath at the appropriate temperature (50.0 or 70.0 °C) and the tube was periodically cooled to room temperature and

analyzed by ^1H NMR spectroscopy. The shift of the methyl group of the 2,6-lutidine was measured as a function of time and this was used to determine the rate constant.³⁴ After an additional 6 h at 70 °C the NMR spectrum showed 2-methyleneadamantane, **36**,³⁵ as the only product. The reaction of **35-d₃** was monitored in a completely analogous fashion.

Reaction of Trifluoroacetate 37 in DMSO-d₆. A solution of 10 mg of 9-methyl-9-fluorenyl trifluoroacetate, **37**, and 6 mg of 2,6-lutidine in 1.0 mL of DMSO-d₆ was prepared and a portion of the solution was placed in an NMR tube. The tube was immediately placed in the probe of an NMR spectrometer at 25.0 °C and the shift of the methyl group of the 2,6-lutidine was measured as a function of time. The rate constant was determined as previously described.³⁴ After 3 h, the NMR showed 9-methylenefluorene, **38**,³⁶ as the only product.

Reaction of Chloride 39 in DMSO-d₆. A solution of 4 mg of chloride **39**^{16a} in 1 mL of DMSO-d₆ was prepared and a portion of the solution was sealed in an NMR tube. The solution was periodically analyzed by 600 MHz NMR at 25.0 °C. The disappearing downfield singlet at δ 7.92 due to **39** was monitored along with the developing signal at δ 8.11 due to the product **40**. The rate constant given in Table 1 was determined from these integrals. After 30 h the NMR spectrum showed only alkene **40** as the sole product. ^1H NMR of **40** (CDCl_3) δ 7.98 (d, J = 0.6 Hz, 1 H), 7.47 (d, J = 6 Hz, 2 H), 7.39-7.28 (m, 3 H), 5.62 (d, J = 1.1 Hz, 1 H), 5.54, (d of d, J = 1.1, 0.6 Hz, 1 H), 3.88 (s, 3 H). ^{13}C NMR of **40** (CDCl_3) δ 150.13, 142.52, 137.35, 128.26, 128.12, 128.07, 122.30, 61.94. Exact mass (EI) calcd for $\text{C}_{10}\text{H}_{11}\text{NO}$ 161.0841, found 161.0814. The alkene **40**, which is stable in solution, readily dimerizes on attempted isolation as a pure substance.

Reaction of Mesylate 41 in DMSO-d₆. A solution of 7.1 mg of the mesylate derivative of methyl mandelate, **41**,²⁴ in 1 mL of DMSO-d₆ was prepared and a portion of the solution was sealed in an NMR

tube. The tube was immersed in a bath at 70.0 °C and periodically analyzed by 600 MHz NMR. The mesylate **41** reacted with a half-life of 152 min (Method 2) at this temperature. After 50 min at 70.0 °C, the spectrum showed signals in the methoxy region at δ 3.70, 3.94, and 3.59, corresponding to starting mesylate **41** (80%), products **43** (6%) and **44** (1.5%), which were identified by spectral comparisons with authentic samples. Also present were signals at δ 6.30 and 3.77 that were assigned to the oxosulfonium intermediate **42** (13.5%). The amount of intermediate **42** builds up to a maximum of 16.5 % under these conditions. After 14 h at 70 °C, the ratio of products **43:44** was 83:17.

Reaction of Benzyl Mesylate, 45, in DMSO-d₆. A solution of 4.4 mg of benzyl mesylate, **45**, in 1.607 g of DMSO-d₆ was prepared and a portion was sealed in an NMR tube. The tube was immediately placed in the probe of a 600 MHz NMR spectrometer at 25.0 °C and the progress on the reaction was monitored over 22 h. The amount of benzyl mesylate was determined from the area of the signal at δ 5.245 and the amount of the intermediate **46** was determined from the signal at δ 5.298. The amount of the final product **47** was determined from the signal at δ 5.425. Figure 5 summarizes the data. The first order rate constant calculated from the data over the first 3 h was $6.21 \times 10^{-5} \text{ s}^{-1}$ ($r = 0.9998$). After 4 h, the ¹³C NMR spectrum showed unreacted **45** as well as **46**. ¹³C NMR of **46** (DMSO-d₆) δ 134.04, 129.73, 129.53, 128.85, 76.76. The CD₃ signal of **46** was not visible under the spectral conditions. After 22 h at 25 °C, the sample was heated for 3 h at 70 °C. ¹H and ¹³C NMR spectra now showed the sulfonium salt **47**. ¹³C NMR of **47** (DMSO-d₆) δ 131.86 (d, $J = 162 \text{ Hz}$), 130.41 (d, $J = 162 \text{ Hz}$), 129.45 (d, $J = 162 \text{ Hz}$), 123.55 (s), 56.65 (t, $J = 145 \text{ Hz}$), 39.77 (q, $J = 133 \text{ Hz}$, OMs⁻).

In a separate experiment, 9.8 mg of benzyl mesylate, **45**, was dissolved in 2.60 g of DMSO-d₆ containing 0.04% H₂O. A portion of this solution was sealed in an NMR tube. Water was added to a second portion such that the second solution contained 1.0% H₂O. Water was added to a third portion such that the third solution contained 2.0% H₂O. The three samples were kept at 25 °C for 25 h and then heated at 50 °C for 7 h. They were then analyzed by 600 MHz ¹H NMR spectroscopy. The first sample

(0.04% H₂O) contained 83% of sulfonium salt **47**, 14% of the oxosulfonium intermediate **46**, and 3% of unreacted benzyl mesylate, **45**. Only a trace (~1%) of benzyl alcohol was present. The second sample (1.0% H₂O) contained 65% of sulfonium salt **47**, 6% of the oxosulfonium intermediate **46**, and 29% of benzyl alcohol, **49**. The third sample (2.0% H₂O) gave 52% of **47**, 2.4% of **46**, and 45.6% of benzyl alcohol, **49**.

Reaction of 1-Adamantyl Mesylate, 50, in DMSO-d₆. A solution of 7 mg of 1-adamantyl mesylate^{27,37} (prepared by reaction of 1-adamantyl bromide with silver mesylate) in 1.1 mL of DMSO-d₆ was sealed in an NMR tube and the tube was heated at 80 °C for 4.5 h. Analysis by 600 MHz NMR showed the oxosulfonium salt **51**. ¹H NMR of **51** (DMSO-d₆) δ 2.29 (s, 3 H, OMs⁻), 2.24 (br s, 3 H), 1.95 (d, *J* = 3 Hz, 6 H), 1.62 (d, *J* = 13 Hz, 3 H), 1.58 (d, *J* = 13 Hz, 3 H). ¹³C NMR of **51** (DMSO-d₆) δ 89.0 (s), 41.3 (t, *J* = 133 Hz), 39.78 (q, *J* = 133 Hz, OMs⁻), 34.6 (t, *J* = 127 Hz), 30.9 (d, *J* = 135 Hz). The CD₃ signal of **51** was not visible under the spectral conditions.

Kinetic Studies. Rates of reaction of 1-adamantyl mesylate, **50**, were determined by Method 2 previously described. The CH₃ signal at δ 3.09 due to covalent **50** and the signal at δ 2.29 due to ionic OMs⁻ were monitored as a function of time.

Reaction of Triflate 54 in DMSO-d₆. A solution of 4.1 mg of the triflate derivative of pivaloin, **54**,^{12,28} in 0.7 mL of DMSO-d₆ was placed in an NMR tube and the tube was immediately placed in the probe of a 600 MHz NMR spectrometer at 25.0 °C. Rates of reaction were determined after allowing 3 min for the temperature to equilibrate. The amount of unreacted triflate **54** was determined from the signal at δ 5.71 and the amounts of products **55**¹⁰ and **56** were determined from the signals that appeared at δ 3.78 and 3.43 respectively. On completion of the reaction, **55** and **56** were present in a 63:37 ratio. ¹H NMR of **55** (DMSO-d₆) δ 4.79 (m, 1 H), 4.73 (m, 1 H), 3.78 (q, *J* = 6.8 Hz, 1 H), 1.67 (m, 3 H), 1.08

(s, 9 H), 1.046 (d, $J = 6.8$ Hz, 3 H). ^1H NMR of **55** (DMSO- d_6) δ 3.43 (q, $J = 7.0$ Hz, 1 H), 1.53 (s, 3 H), 1.47 (s, 3 H), 1.11 (s, 9 H), 1.050 (d, $J = 7.0$ Hz, 3 H).

References and Notes for Supporting Information

- (33) Creary, X.; Casingal, V. P.; Leahy, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 1734.
- (34) Creary, X.; Z. Jiang, Z. *J. Org. Chem.* **1994**, *59*, 5106.
- (35) Fort, Jr., R. C.; Schleyer, P. v. R. *J. Org. Chem.* **1965**, *30*, 789.
- (36) Greenhow, E. J.; McNeil, D.; White, E. N. *J. Chem. Soc.* **1952**, 986.
- (37) Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195.

B3LYP/6-31G* Optimized Structure and Energy of **40-H₆**

E(RB+HF-LYP) = -823.916086 au

Zero Point Correction = 0.201572 au

No Imaginary Frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	-0.325653	0.358233	0.889377
2	16	0	-0.964095	0.515306	2.382792
3	6	0	0.384914	1.356408	3.251476
4	6	0	-2.136089	1.871563	2.119997
5	6	0	-0.345855	-1.041376	0.293397
6	1	0	0.216868	-1.685638	0.972993
7	6	0	0.282139	-0.919520	-1.048510
8	1	0	-1.391584	-1.354677	0.250165
9	1	0	-1.633953	2.687809	1.595579
10	1	0	-2.507065	2.193667	3.097580
11	1	0	-2.960735	1.475361	1.523554
12	1	0	0.725998	2.205739	2.655063
13	1	0	1.187479	0.627831	3.384996
14	1	0	0.010869	1.678847	4.227780
15	6	0	1.466964	-0.654830	-3.564572
16	6	0	1.669045	-1.074325	-1.195004
17	6	0	-0.506152	-0.629498	-2.172517
18	6	0	0.085030	-0.498726	-3.426685
19	6	0	2.258897	-0.943233	-2.449756
20	1	0	2.282959	-1.307509	-0.328260
21	1	0	-1.582427	-0.517006	-2.065326
22	1	0	-0.528737	-0.282977	-4.295787
23	1	0	3.331061	-1.072223	-2.561214
24	1	0	1.926658	-0.558759	-4.543777

B3LYP/6-31G* Optimized Structure and Energy of **53**

E(RB+HF-LYP) = -900.345095 au

Zero Point Correction = 0.225557 au

No Imaginary Frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	-0.475782	0.533309	0.575733
2	16	0	-1.091832	0.679929	2.078919
3	6	0	0.252684	1.529888	2.940663
4	8	0	1.230525	-1.480858	2.787470
5	6	0	-2.270768	2.030729	1.815664
6	6	0	-0.500921	-0.861165	-0.018389
7	1	0	0.054678	-1.501261	0.668482
8	6	0	0.129848	-0.739921	-1.362248
9	1	0	-1.548848	-1.167270	-0.073085
10	1	0	-1.773081	2.854584	1.299107
11	1	0	-2.650305	2.346810	2.791800
12	1	0	-3.089809	1.634914	1.211403
13	1	0	0.632574	2.333968	2.306137
14	1	0	1.006639	0.763990	3.134384
15	1	0	-0.146494	1.921942	3.880961
16	1	0	0.992042	-2.178343	3.418817
17	1	0	2.153496	-1.673860	2.558399
18	6	0	1.323416	-0.482411	-3.877885
19	6	0	1.517497	-0.885900	-1.504904
20	6	0	-0.654002	-0.461183	-2.491177
21	6	0	-0.059514	-0.334624	-3.744865
22	6	0	2.112324	-0.758457	-2.757931
23	1	0	2.128033	-1.106915	-0.632659
24	1	0	-1.731230	-0.353340	-2.388395
25	1	0	-0.672010	-0.127115	-4.617003
26	1	0	3.186072	-0.879758	-2.864349
27	1	0	1.786224	-0.388548	-4.855884

B3LYP/6-31G* Optimized Structure and Energy of 12-H₆

E(RB+HF-LYP) = -1392.970790 au

Zero Point Correction = 0.260390 au

No Imaginary Frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	1	0	-0.829225	3.106447	-3.261161
2	6	0	-0.989767	2.691995	-2.270331
3	6	0	-1.388881	1.640709	0.294386
4	6	0	-0.089902	1.764827	-1.752155
5	6	0	-2.088915	3.100179	-1.506669
6	6	0	-2.284609	2.576174	-0.229299
7	6	0	-0.284989	1.229539	-0.464720
8	1	0	0.772459	1.461012	-2.341604
9	1	0	-2.785868	3.830019	-1.907782
10	1	0	-3.134598	2.894435	0.366541
11	6	0	0.714057	0.233888	0.052762
12	1	0	-1.547908	1.233787	1.287075
13	6	0	2.190448	0.696383	0.255690
14	8	0	0.739580	-0.989276	-0.792522
15	16	0	-0.250748	-1.009408	2.528104
16	1	0	2.377493	1.757755	0.071276
17	1	0	2.937302	0.074065	-0.247977
18	7	0	2.000393	0.346729	1.672979
19	6	0	0.762887	-0.159561	1.542828
20	6	0	2.909982	0.403440	2.798431
21	1	0	3.220753	1.437383	2.980070
22	1	0	3.797321	-0.208369	2.600739
23	1	0	2.388824	0.017024	3.676258
24	16	0	-0.692557	-1.806525	-0.849114
25	6	0	-0.149501	-3.463775	-0.360486
26	6	0	-0.836025	-1.994505	-2.647971
27	1	0	0.043573	-3.421784	0.712948
28	1	0	0.746820	-3.737884	-0.921038
29	1	0	-0.973378	-4.153345	-0.568987
30	1	0	0.102976	-2.371951	-3.058936
31	1	0	-1.071052	-1.006846	-3.049822
32	1	0	-1.660711	-2.685472	-2.846912

B3LYP/6-31G* Optimized Structure and Energy of 55

$E(\text{RB+HF-LYP}) = -1469.395895 \text{ au}$

Zero Point Correction = 0.284602 au

No Imaginary Frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	1	0	-0.444981	3.365941	-3.520270
2	6	0	-0.717696	2.981967	-2.541744
3	6	0	-1.406682	2.006759	-0.009633
4	6	0	0.060217	1.995291	-1.942751
5	6	0	-1.840100	3.487166	-1.875878
6	6	0	-2.180413	3.000661	-0.614302
7	6	0	-0.280441	1.498470	-0.670805
8	1	0	0.938455	1.612566	-2.457787
9	1	0	-2.442111	4.262342	-2.340680
10	1	0	-3.048289	3.393749	-0.093588
11	6	0	0.584062	0.432438	-0.063735
12	1	0	-1.677280	1.631262	0.971255
13	6	0	2.086044	0.733121	0.234797
14	8	0	0.579010	-0.800112	-0.893557
15	16	0	-0.671479	-0.622082	2.390077
16	1	0	2.397146	1.770210	0.083372
17	1	0	2.787132	0.036424	-0.234242
18	7	0	1.774417	0.398911	1.634188
19	6	0	0.495046	0.062366	1.434376
20	6	0	2.635103	0.244717	2.789545
21	1	0	3.408917	1.015680	2.771271
22	1	0	3.096016	-0.750015	2.776586
23	1	0	2.030607	0.352269	3.692942
24	8	0	1.594517	-2.987087	2.015345
25	6	0	-0.251309	-3.290125	-0.594225
26	6	0	-1.097009	-1.678459	-2.739247
27	1	0	0.265810	-3.254787	0.375492
28	1	0	0.434882	-3.602974	-1.384346
29	1	0	-1.126749	-3.945252	-0.549415
30	1	0	-0.174561	-2.001786	-3.226814
31	1	0	-1.377819	-0.672875	-3.058918
32	1	0	-1.914175	-2.378260	-2.939201
33	16	0	-0.852298	-1.618593	-0.942559
34	1	0	1.925548	-3.765201	2.491440
35	1	0	0.971837	-2.559514	2.630620

B3LYP/6-31G* Optimized Structure and Energy of **56**

E(RB+HF-LYP) = -1131.394786 au

Zero Point Correction = 0.311790 au

No Imaginary Frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.870633	0.712521	-1.791076
2	6	0	-0.344776	0.116131	-0.462413
3	8	0	0.391465	-1.144622	-0.861854
4	8	0	-1.699768	-1.194311	1.088894
5	6	0	0.561914	0.968281	0.390315
6	1	0	-2.697764	0.203054	-2.928918
7	1	0	-0.108436	0.774232	-2.570227
8	6	0	-1.556608	2.061768	-1.453411
9	6	0	-2.836841	1.631763	-0.668162
10	1	0	-1.817938	2.566192	-2.388004
11	1	0	-0.914967	2.738163	-0.885322
12	1	0	-3.749862	1.984304	-1.155665
13	1	0	-2.852468	2.010866	0.357933
14	6	0	-2.797877	0.074569	-0.722197
15	6	0	-1.677727	-0.399970	0.169142
16	6	0	-2.103396	-0.176117	-2.092595
17	1	0	-3.743871	-0.429251	-0.523161
18	1	0	-1.861701	-1.226168	-2.281410
19	6	0	2.300516	2.565801	1.906713
20	6	0	0.279133	1.244834	1.735970
21	6	0	1.731915	1.497997	-0.186546
22	6	0	2.595499	2.288023	0.567915
23	6	0	1.144250	2.044893	2.486309
24	1	0	-0.608109	0.834393	2.205941
25	1	0	1.957502	1.300012	-1.231326
26	1	0	3.491442	2.697363	0.110525
27	1	0	0.911428	2.256753	3.525466
28	1	0	2.970148	3.188635	2.492279
29	16	0	0.979171	-2.040672	0.383661
30	6	0	2.620229	-2.404111	-0.294596
31	6	0	0.135885	-3.623871	0.125677
32	1	0	0.630875	-4.366945	0.758388
33	1	0	0.191814	-3.905327	-0.928217
34	1	0	-0.895726	-3.484562	0.451987
35	1	0	3.088996	-3.157308	0.345667
36	1	0	3.191723	-1.474618	-0.254894
37	1	0	2.527700	-2.762637	-1.322216

B3LYP/6-31G* Optimized Structure and Energy of **58**

$E(\text{RB+HF-LYP}) = -1207.823452 \text{ au}$

Zero Point Correction = 0.335435 au

No Imaginary Frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.136048	0.107752	-1.012427
2	6	0	-3.206920	1.601788	-0.563264
3	1	0	-2.719512	2.280931	-1.269195
4	6	0	-2.513009	1.600655	0.832615
5	1	0	-4.239660	1.942671	-0.449065
6	1	0	-2.677578	-0.019669	-1.995114
7	1	0	-4.133792	-0.338213	-1.057061
8	6	0	-2.333739	-0.573054	0.126586
9	6	0	-0.872484	-0.064340	0.040077
10	1	0	-2.409403	-1.661952	0.147808
11	6	0	-2.877726	0.184521	1.363347
12	1	0	-2.381102	-0.078832	2.301693
13	6	0	-1.035806	1.378897	0.618218
14	1	0	-2.727998	2.461595	1.465947
15	1	0	-3.957180	0.059329	1.489010
16	8	0	-0.133414	-0.822699	1.107747
17	6	0	-0.151470	-0.221067	-1.277919
18	8	0	-0.092374	2.057856	0.972787
19	6	0	1.164794	-0.601636	-3.728188
20	6	0	0.423082	0.866299	-1.951467
21	6	0	-0.054405	-1.505161	-1.846059
22	6	0	0.601842	-1.693574	-3.059880
23	6	0	1.072983	0.674132	-3.173226
24	1	0	0.373970	1.862528	-1.525368
25	1	0	-0.503889	-2.355760	-1.340067
26	1	0	0.664173	-2.688400	-3.491210
27	1	0	1.507554	1.525649	-3.688317
28	1	0	1.668661	-0.747526	-4.679067
29	16	0	1.455869	-0.411272	1.302305
30	1	0	2.510531	0.245450	3.306160
31	6	0	2.141045	-2.084170	1.400811
32	6	0	1.461872	0.100792	3.038805
33	1	0	3.199538	-1.972412	1.642038
34	1	0	2.022652	-2.524773	0.408823
35	1	0	1.602428	-2.665582	2.151960
36	1	0	0.977515	-0.661441	3.652562
37	1	0	0.926385	1.050418	3.081387
38	8	0	4.363781	0.183876	1.763001
39	1	0	4.625439	0.881134	1.141640
40	1	0	5.169340	0.001936	2.272099

22 ^1H NMR in CDCl_3

22¹³C NMR in CDCl₃

24¹H NMR in CDCl₃

24¹³C NMR in CDCl₃

^1H NMR in CDCl_3

^{13}C NMR in CDCl_3

35

 ^1H NMR in CDCl_3

35 ^{13}C NMR in CDCl_3