

Supporting Information
for
Characterization of Free Radicals in Clathrate Hydrates of
Furan, 2,3-Dihydrofuran and 2,5-Dihydrofuran
by Muon Spin Spectroscopy

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Contents

The full reference for the Gaussian 09 software package.

Internal coordinates of optimized geometries for radicals **1–5**, computed with both B3LYP/6-31G(d) and B3LYP/EPR-II.

Alternative versions of Tables 3 and 6 with hyperfine constants calculated using the EPR-II basis set instead of 6-31G(d).

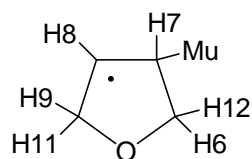
Gaussian 09

Gaussian 09, Revisions C.01, D.01, E.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2013-2016.

Internal coordinates of optimized geometries for radical 1

atom numbering

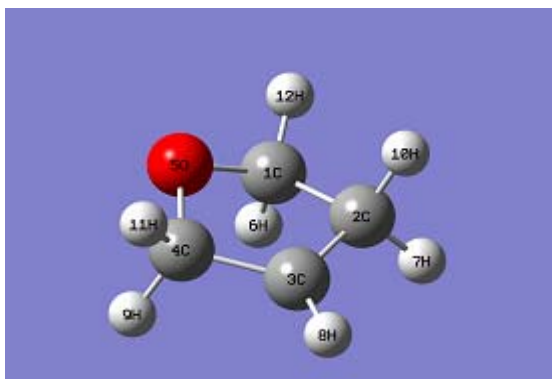
C1	H6	H12
C2	H7	H10 (Mu)
C3	H8	
C4	H9	H11
O5		



Optimized Parameters (Å and °)

Name	Definition	6-31G(d)	EPR-II
R1	R(1,2)	1.5425	1.5464
R2	R(1,5)	1.4268	1.4319
R3	R(1,6)	1.1028	1.1014
R4	R(1,12)	1.0936	1.0928
R5	R(2,3)	1.4948	1.5034
R6	R(2,7)	1.0981	1.0964
R7	R(2,10)	1.1037	1.1013
R8	R(3,4)	1.4956	1.5033
R9	R(3,8)	1.0833	1.0835
R10	R(4,5)	1.4292	1.4337
R11	R(4,9)	1.1086	1.1066
R12	R(4,11)	1.1004	1.0984
A1	A(2,1,5)	105.6811	105.6507
A2	A(2,1,6)	110.2107	110.2399
A3	A(2,1,12)	114.2188	113.9387
A4	A(5,1,6)	110.5816	110.2884
A5	A(5,1,12)	107.5267	107.6264
A6	A(6,1,12)	108.5591	109.0042
A7	A(1,2,3)	100.8831	101.0084
A8	A(1,2,7)	112.7245	112.6267
A9	A(1,2,10)	110.8374	110.7248
A10	A(3,2,7)	113.8109	113.5574
A11	A(3,2,10)	111.8674	111.5246
A12	A(7,2,10)	106.7835	107.4033
A13	A(2,3,4)	109.0473	108.8274
A14	A(2,3,8)	126.0527	126.1316
A15	A(4,3,8)	124.8704	124.9898
A16	A(3,4,5)	105.4043	105.3272
A17	A(3,4,9)	111.9963	111.7882
A18	A(3,4,11)	114.2030	113.8467
A19	A(5,4,9)	110.6335	110.3195
A20	A(5,4,11)	107.7945	107.9950

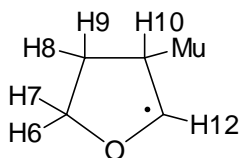
A21	A(9,4,11)	106.7655	107.4975
A22	A(1,5,4)	107.6030	107.4723
D1	D(5,1,2,3)	29.4400	29.2275
D2	D(5,1,2,7)	151.1914	150.7070
D3	D(5,1,2,10)	-89.1803	-89.0175
D4	D(6,1,2,3)	-90.0609	-89.9224
D5	D(6,1,2,7)	31.6905	31.5572
D6	D(6,1,2,10)	151.3188	151.8327
D7	D(12,1,2,3)	147.4260	147.1606
D8	D(12,1,2,7)	-90.8226	-91.3599
D9	D(12,1,2,10)	28.8057	28.9156
D10	D(2,1,5,4)	-35.0962	-35.7563
D11	D(6,1,5,4)	84.1597	83.3614
D12	D(12,1,5,4)	-157.4728	-157.8397
D13	D(1,2,3,4)	-14.1534	-13.1812
D14	D(1,2,3,8)	167.7558	169.3261
D15	D(7,2,3,4)	-135.1385	-134.0042
D16	D(7,2,3,8)	46.7707	48.5031
D17	D(10,2,3,4)	103.7174	104.4814
D18	D(10,2,3,8)	-74.3734	-73.0112
D19	D(2,3,4,5)	-5.6849	-7.0840
D20	D(2,3,4,9)	114.6806	112.7388
D21	D(2,3,4,11)	-123.8091	-125.2077
D22	D(8,3,4,5)	172.4338	170.4441
D23	D(8,3,4,9)	-67.2007	-69.7330
D24	D(8,3,4,11)	54.3096	52.3204
D25	D(3,4,5,1)	25.3961	26.6324
D26	D(9,4,5,1)	-95.8610	-94.1578
D27	D(11,4,5,1)	147.7432	148.6236



Internal coordinates of optimized geometries for radical 2

atom numbering

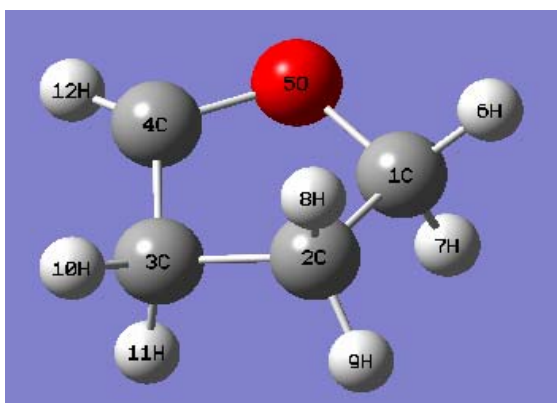
C1	H6	H7
C2	H8	H9
C3	H10	H11 (Mu)
C4	H12	
O5		



Optimized Parameters (Å and °)

Name	Definition	6-31G(d)	EPR-II
R1	R(1,2)	1.5344	1.5394
R2	R(1,5)	1.4408	1.4460
R3	R(1,6)	1.0939	1.0931
R4	R(1,7)	1.0989	1.0977
R5	R(2,3)	1.5436	1.5481
R6	R(2,8)	1.0953	1.0938
R7	R(2,9)	1.0939	1.0928
R8	R(3,4)	1.4978	1.5060
R9	R(3,10)	1.0961	1.0940
R10	R(3,11)	1.1054	1.1032
R11	R(4,5)	1.3775	1.3799
R12	R(4,12)	1.0853	1.0856
A1	A(2,1,5)	105.9675	106.0793
A2	A(2,1,6)	114.0962	113.7626
A3	A(2,1,7)	111.6547	111.5786
A4	A(5,1,6)	108.1730	108.1567
A5	A(5,1,7)	108.1765	108.0080
A6	A(6,1,7)	108.5451	109.0160
A7	A(1,2,3)	102.0391	102.0695
A8	A(1,2,8)	110.2344	110.2674
A9	A(1,2,9)	112.4973	112.2810
A10	A(3,2,8)	110.0921	110.0041
A11	A(3,2,9)	113.5664	113.3389
A12	A(8,2,9)	108.3130	108.7496
A13	A(2,3,4)	100.8611	100.8915
A14	A(2,3,10)	112.9188	112.9257
A15	A(2,3,11)	110.4521	110.4931
A16	A(4,3,10)	113.1622	112.9256
A17	A(4,3,11)	112.6669	112.0366
A18	A(10,3,11)	106.8498	107.5661
A19	A(3,4,5)	111.1154	110.9677
A20	A(3,4,12)	126.2475	126.1630
A21	A(5,4,12)	113.8633	114.1925

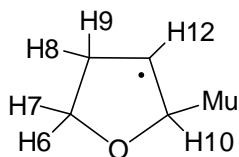
A22	A(1,5,4)	109.0032	109.1312
D1	D(5,1,2,3)	29.3682	28.7902
D2	D(5,1,2,8)	-87.5664	-88.0733
D3	D(5,1,2,9)	151.4280	150.4872
D4	D(6,1,2,3)	148.2721	147.5573
D5	D(6,1,2,8)	31.3374	30.6939
D6	D(6,1,2,9)	-89.6682	-90.7457
D7	D(7,1,2,3)	-88.1936	-88.5959
D8	D(7,1,2,8)	154.8718	154.5406
D9	D(7,1,2,9)	33.8662	33.1011
D10	D(2,1,5,4)	-14.6413	-13.8000
D11	D(6,1,5,4)	-137.3845	-136.2021
D12	D(7,1,5,4)	105.2214	105.9467
D13	D(1,2,3,4)	-31.7441	-31.5936
D14	D(1,2,3,10)	-152.8057	-152.3962
D15	D(1,2,3,11)	87.6197	87.0794
D16	D(8,2,3,4)	85.2931	85.4597
D17	D(8,2,3,10)	-35.7684	-35.3429
D18	D(8,2,3,11)	-155.3430	-155.8673
D19	D(9,2,3,4)	-153.0678	-152.5597
D20	D(9,2,3,10)	85.8707	86.6377
D21	D(9,2,3,11)	-33.7039	-33.8868
D22	D(2,3,4,5)	25.2541	25.6244
D23	D(2,3,4,12)	170.4266	171.0796
D24	D(10,3,4,5)	146.1431	146.4271
D25	D(10,3,4,12)	-68.6844	-68.1176
D26	D(11,3,4,5)	-92.5020	-91.9241
D27	D(11,3,4,12)	52.6705	53.5311
D28	D(3,4,5,1)	-7.1417	-7.9035
D29	D(12,4,5,1)	-156.9009	-157.7790



Internal coordinates of optimized geometries for radical 3

atom numbering

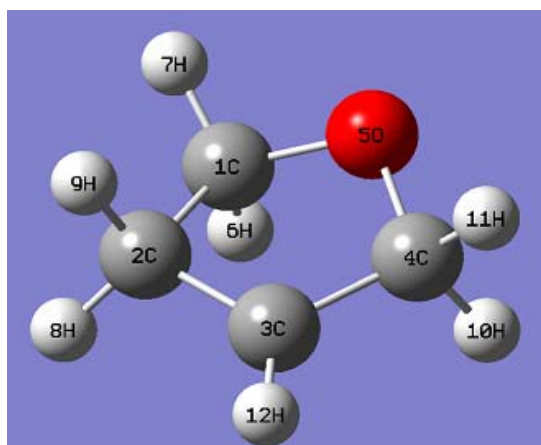
C1	H6	H7
C2	H8	H9
C3	H12	
C4	H10	H11 (Mu)
O5		



Optimized Parameters (Å and °)

Name	Definition	6-31G(d)	EPR-II
R1	R(1,2)	1.5425	1.5465
R2	R(1,5)	1.4266	1.4318
R3	R(1,6)	1.1028	1.1014
R4	R(1,7)	1.0936	1.0928
R5	R(2,3)	1.4948	1.5035
R6	R(2,8)	1.0981	1.0964
R7	R(2,9)	1.1037	1.1013
R8	R(3,4)	1.4956	1.5033
R9	R(3,12)	1.0833	1.0835
R10	R(4,5)	1.4292	1.4337
R11	R(4,10)	1.1087	1.1066
R12	R(4,11)	1.1004	1.0984
A1	A(2,1,5)	105.6925	105.6432
A2	A(2,1,6)	110.1992	110.2228
A3	A(2,1,7)	114.2229	113.9350
A4	A(5,1,6)	110.5891	110.2968
A5	A(5,1,7)	107.5345	107.6325
A6	A(6,1,7)	108.5417	109.0183
A7	A(1,2,3)	100.8837	101.0001
A8	A(1,2,8)	112.7099	112.6437
A9	A(1,2,9)	110.8674	110.7104
A10	A(3,2,8)	113.8075	113.5698
A11	A(3,2,9)	111.8748	111.5177
A12	A(8,2,9)	106.7662	107.4024
A13	A(2,3,4)	109.0513	108.8237
A14	A(2,3,12)	126.0604	126.1471
A15	A(4,3,12)	124.8673	124.9803
A16	A(3,4,5)	105.3984	105.3211
A17	A(3,4,10)	111.9910	111.7769
A18	A(3,4,11)	114.2155	113.8598
A19	A(5,4,10)	110.6350	110.3192
A20	A(5,4,11)	107.7951	107.9975
A21	A(10,4,11)	106.7623	107.4997

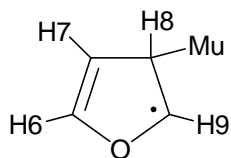
A22	A(1,5,4)	107.5950	107.4628
D1	D(5,1,2,3)	-29.3837	-29.2509
D2	D(5,1,2,8)	-151.1244	-150.7484
D3	D(5,1,2,9)	89.2583	88.9757
D4	D(6,1,2,3)	90.1266	89.8956
D5	D(6,1,2,8)	-31.6141	-31.6019
D6	D(6,1,2,9)	-151.2314	-151.8778
D7	D(7,1,2,3)	-147.3891	-147.1846
D8	D(7,1,2,8)	90.8702	91.3179
D9	D(7,1,2,9)	-28.7471	-28.9580
D10	D(2,1,5,4)	35.1092	35.8118
D11	D(6,1,5,4)	-84.1436	-83.2856
D12	D(7,1,5,4)	157.5010	157.8901
D13	D(1,2,3,4)	14.0471	13.1663
D14	D(1,2,3,12)	-167.5575	-169.2850
D15	D(8,2,3,4)	135.0135	134.0105
D16	D(8,2,3,12)	-46.5911	-48.4407
D17	D(9,2,3,4)	-103.8620	-104.4723
D18	D(9,2,3,12)	74.5334	73.0764
D19	D(2,3,4,5)	5.8000	7.1298
D20	D(2,3,4,10)	-114.5607	-112.6827
D21	D(2,3,4,11)	123.9280	125.2598
D22	D(12,3,4,5)	-172.6190	-170.4544
D23	D(12,3,4,10)	67.0203	69.7330
D24	D(12,3,4,11)	-54.4910	-52.3244
D25	D(3,4,5,1)	-25.4733	-26.6956
D26	D(10,4,5,1)	95.7747	94.0772
D27	D(11,4,5,1)	-147.8322	-148.7002



Internal coordinates of optimized geometries for radical 4

atom numbering

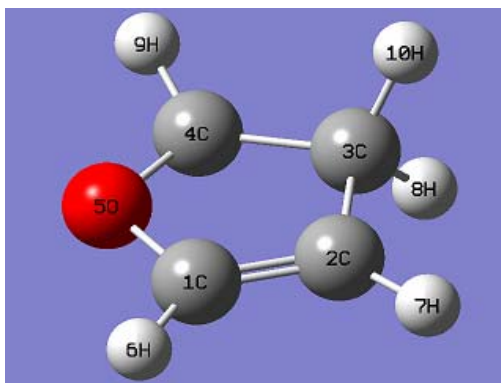
C1 H6
 C2 H7
 C3 H8
 C4 H9
 O5 H10 (Mu)



Optimized Parameters (Å and °)

Name	Definition	6-31G(d)	EPR-II
R1	R(1,2)	1.3351	1.3445
R2	R(1,5)	1.3790	1.3809
R3	R(1,6)	1.0817	1.0821
R4	R(2,3)	1.5138	1.5203
R5	R(2,7)	1.0816	1.0814
R6	R(3,4)	1.5019	1.5103
R7	R(3,8)	1.1038	1.1003
R8	R(3,10)	1.1070	1.1041
R9	R(4,5)	1.3856	1.3890
R10	R(4,9)	1.0823	1.0831
A1	A(2,1,5)	113.7019	113.6254
A2	A(2,1,6)	131.8107	131.4487
A3	A(5,1,6)	114.4874	114.9257
A4	A(1,2,3)	108.4004	108.2921
A5	A(1,2,7)	126.0736	125.8232
A6	A(3,2,7)	125.5251	125.8830
A7	A(2,3,4)	100.3506	100.3345
A8	A(2,3,8)	112.8065	112.6545
A9	A(2,3,10)	112.3964	112.1815
A10	A(4,3,8)	112.8724	112.6224
A11	A(4,3,10)	113.2847	112.8689
A12	A(8,3,10)	105.3850	106.3325
A13	A(3,4,5)	110.5131	110.4009
A14	A(3,4,9)	128.0419	127.9467
A15	A(5,4,9)	114.2330	114.4363
A16	A(1,5,4)	106.6291	106.9029
D1	D(5,1,2,3)	0.2466	0.3647
D2	D(5,1,2,7)	179.9222	179.9052
D3	D(6,1,2,3)	-179.8489	-179.8140
D4	D(6,1,2,7)	-0.1733	-0.2734
D5	D(2,1,5,4)	3.8197	3.9235
D6	D(6,1,5,4)	-176.1021	-175.9289
D7	D(1,2,3,4)	-3.7928	-4.0419

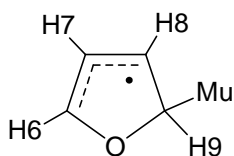
D8	D(1,2,3,8)	-124.1521	-124.0286
D9	D(1,2,3,10)	116.8636	116.0212
D10	D(7,2,3,4)	176.5293	176.4179
D11	D(7,2,3,8)	56.1700	56.4312
D12	D(7,2,3,10)	-62.8143	-63.5190
D13	D(2,3,4,5)	6.1723	6.4818
D14	D(2,3,4,9)	154.2973	154.6618
D15	D(8,3,4,5)	126.4842	126.4917
D16	D(8,3,4,9)	-85.3908	-85.3283
D17	D(10,3,4,5)	-113.8448	-113.0838
D18	D(10,3,4,9)	34.2802	35.0962
D19	D(3,4,5,1)	-6.3352	-6.6101
D20	D(9,4,5,1)	-159.2012	-159.4362



Internal coordinates of optimized geometries for radical 5

atom numbering

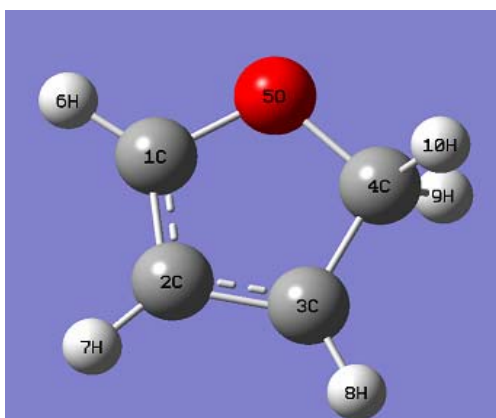
C1 H6
 C2 H7
 C3 H8
 C4 H9 H10 (Mu)
 O5



Optimized Parameters (Å and °)

Name	Definition	6-31G(d)	EPR-II
R1	R(1,2)	1.3854	1.3954
R2	R(1,5)	1.3658	1.3680
R3	R(1,6)	1.0805	1.0812
R4	R(2,3)	1.3881	1.3967
R5	R(2,7)	1.0827	1.0826
R6	R(3,4)	1.4998	1.5071
R7	R(3,8)	1.0815	1.0815
R8	R(4,5)	1.4506	1.4540
R9	R(4,9)	1.1022	1.1003
R10	R(4,10)	1.1022	1.1003
A1	A(2,1,5)	112.3307	112.2387
A2	A(2,1,6)	131.9891	131.7258
A3	A(5,1,6)	115.6802	116.0355
A4	A(1,2,3)	108.1692	108.0791
A5	A(1,2,7)	124.9118	124.9030
A6	A(3,2,7)	126.9190	127.0179
A7	A(2,3,4)	107.3316	107.1923
A8	A(2,3,8)	128.0597	128.0957
A9	A(4,3,8)	124.6087	124.7120
A10	A(3,4,5)	104.8061	104.8734
A11	A(3,4,9)	114.3687	113.9385
A12	A(3,4,10)	114.3715	113.9454
A13	A(5,4,9)	107.8776	107.8724
A14	A(5,4,10)	107.8776	107.8704
A15	A(9,4,10)	107.1879	107.9919
A16	A(1,5,4)	107.3623	107.6164
D1	D(5,1,2,3)	-0.0091	0.0126
D2	D(5,1,2,7)	179.9978	180.0103
D3	D(6,1,2,3)	-179.9888	-179.9665
D4	D(6,1,2,7)	0.0181	0.0313
D5	D(2,1,5,4)	0.0081	-0.0025
D6	D(6,1,5,4)	180.0087	179.9801
D7	D(1,2,3,4)	0.0061	-0.0168

D8	D(1,2,3,8)	-179.9857	180.0118
D9	D(7,2,3,4)	179.9991	-180.0145
D10	D(7,2,3,8)	0.0073	0.0141
D11	D(2,3,4,5)	-0.0014	0.0151
D12	D(2,3,4,9)	-117.9262	-117.7161
D13	D(2,3,4,10)	117.9249	117.7476
D14	D(8,3,4,5)	-180.0093	-180.0122
D15	D(8,3,4,9)	62.0659	62.2565
D16	D(8,3,4,10)	-62.0830	-62.2797
D17	D(3,4,5,1)	-0.0039	-0.0077
D18	D(9,4,5,1)	122.2513	121.7783
D19	D(10,4,5,1)	-122.2624	-121.8007



Hyperfine constants calculated using the EPR-II basis set

Table S1. Computed^a Hyperfine Constants for Radicals **2** and **3** Compared with those Determined by μ LCR Spectroscopy on Liquid and Clathrate Hydrate Samples of 2,3-Dihydrofuran at $-10\text{ }^{\circ}\text{C}$

Nucleus	A(Mu-ax)	A(Mu-eq)	$A_{\text{calc.}}^b$	$A_{\text{exp}}(\text{liq})^c$	$A_{\text{exp}}(\text{hydr.})^d$
radical 2					
muon	405.4	167.1	314.6	(299.9) ^c	301.5
β -CHMu	49.1	114.2	73.9	74.9	72.5
α -CH	-32.4	-33.2	-32.7	-36.7	-36.4 ^a
radical 3					
muon	409.7	337.5	381.6	(371.2) ^c	374.1
β -CHMu	93.1	114.2	101.3	101.8	101.9
α -CH	-50.1	-49.6	-49.9	-58.8	-60.1 ^a
β -H axial	126.0	66.9	103.0	97.8	96.0
β -H equatorial	70.0	127.2	92.3	93.8	91.1

^a UBLYP/EPR-II. ^b Weighted average of two conformations. ^c Value obtained by TF- μ SR.

Table S2. Computed^a Hyperfine Constants for Radicals **4** and **5** Compared with those Determined by μ LCR Spectroscopy on a Clathrate Hydrate Sample of Furan at $-13\text{ }^{\circ}\text{C}$

Nucleus	A(Mu-ax)	A(Mu-eq)	$A_{\text{calc.}}^b$	$A_{\text{exp}}(\text{liq})^c$	$A_{\text{exp}}(\text{hydr.})^d$
radical 4					
muon	549.7	505.9	531.4	(497) ^e	500.1
β -CHMu	139.7	150.9	144.3	130	129.5
α -CH	-45.5	-47.9	-46.5		-40.8
radical 5					
muon	–	–	411.5	(378.8) ^e	382.2
β -CHMu	–	–	109.2	100.2	100.1
C(3)H	–	–	10.0		14.3
C(2)H	–	–	-37.9	-37.2	-37.7
C(4)H	–	–	-36.5	-36.4	-36.6

^a UBLYP/EPR-II. ^b Weighted average of two conformations. ^c Ref. 23, 25 $^{\circ}\text{C}$. ^d This work. ^e Value obtained by TF- μ SR.