

Supplementary Materials

Table S1. Calculated nuclear magnetic shieldings (ppm) on atoms in **2a**.

	MC_B3LYP		B3LYP//MC_B3LYP		B3LYP
	H	D	H	D	Conv
C1	83.89	83.93	83.53	83.48	83.38
C2	60.48	60.45	60.01	59.97	59.90
C3	87.33	87.29	86.86	86.82	86.79
C4	24.23	24.45	23.88	24.07	24.55
C5	84.45	84.56	83.98	84.04	84.15
C6	24.83	25.54	24.66	25.29	26.74
C7	-2.39	-2.34	-2.74	-2.67	-2.31
C8	167.32	167.13	166.93	166.73	166.33
C9	-6.00	-6.00	-6.26	-6.28	-6.26
C10	158.82	158.80	158.49	158.46	158.37
O1	170.04	175.24	168.62	174.02	185.54
O2	-99.37	-109.21	-103.97	-112.57	-131.02
O3	174.77	175.49	174.39	175.06	176.87
O4	-143.19	-144.31	-143.41	-144.46	-147.36
H1	11.90	13.03	13.30	14.03	15.84
H2	15.85	15.87	15.82	15.87	16.03
H3	24.23	24.23	24.24	24.23	24.21
H4	25.51	25.50	25.50	25.49	24.47
H5	29.81	29.81	29.82	29.82	29.83
H6	29.19	29.19	29.19	29.19	29.19
H7	29.19	29.19	29.19	29.19	29.19
H8	29.65	29.65	29.65	29.64	29.64
H9	28.82	28.82	28.81	28.82	28.82
H10	28.82	28.82	28.81	28.82	28.82

Table S2. Calculated nuclear magnetic shieldings (ppm) on atoms in **2b**.

	MC_B3LYP		B3LYP//MC_B3LYP		B3LYP
	H	D	H	D	Conv
C1	84.49	84.32	83.83	83.67	83.38
C2	59.98	60.09	59.55	59.64	59.90
C3	86.54	86.75	86.44	86.54	86.79
C4	23.03	23.60	22.81	23.32	24.55
C5	84.92	84.89	84.53	84.41	84.15
C6	26.82	26.94	26.41	26.50	26.74
C7	-1.81	-1.88	-2.41	-2.21	-2.31
C8	166.74	166.73	166.37	166.35	166.33
C9	-6.86	-6.64	-7.12	-6.90	-6.26
C10	159.38	159.18	159.00	158.80	158.37
O1	184.47	184.90	184.05	184.44	185.54
O2	-126.97	-128.06	-127.26	-128.25	-131.02
O3	160.93	166.21	160.34	165.57	176.87
O4	-118.39	-127.33	-123.03	-130.72	-147.36

Table S2. Cont.

	MC_B3LYP		B3LYP//MC_B3LYP		B3LYP
	H	D	H	D	Conv
H1	15.64	15.69	15.65	15.69	15.84
H2	12.21	13.30	13.65	14.33	16.03
H3	24.22	24.21	24.22	24.21	24.21
H4	25.48	25.48	25.48	25.48	24.47
H5	29.83	29.83	29.83	29.83	29.83
H6	29.20	29.20	29.20	29.20	29.19
H7	29.20	29.20	29.20	29.20	29.19
H8	29.62	29.63	29.63	29.63	29.64
H9	28.80	28.81	28.82	28.82	28.82
H10	28.80	28.81	28.82	28.82	28.82

Table S3. Calculated nuclear magnetic shieldings (ppm) on atoms in 3.

	MC_B3LYP		B3LYP//MC_B3LYP		B3LYP
	H	D	H	D	Conv
C1	89.94	90.04	89.78	89.78	89.60
C2	21.35	21.48	20.94	21.06	21.35
C3	90.61	90.54	89.80	89.73	89.77
C4	21.09	21.28	20.77	20.93	21.34
C5	89.70	89.87	89.18	89.31	89.63
C6	19.68	20.28	19.40	19.95	21.38
C7	−5.68	−5.63	−6.07	−6.01	−5.58
C8	160.09	159.83	159.75	159.47	158.82
C9	−5.22	−5.26	−5.52	−5.56	−5.63
C10	159.30	159.27	158.98	158.95	158.83
C11	−5.35	−5.34	−5.61	−5.60	−5.60
C12	159.33	159.31	158.94	159.91	158.88
O1	139.56	146.82	138.70	146.07	162.30
O2	−73.53	−84.78	−77.04	−87.55	−111.25
O3	161.05	161.51	160.63	161.06	162.27
O4	−107.31	−108.25	−107.62	−108.52	−111.18
O5	160.38	160.97	160.01	160.58	162.26
O6	−106.76	−107.90	−107.05	−108.15	−111.22
H1	9.68	10.72	11.07	11.72	13.55
H2	13.37	13.42	13.36	13.40	13.55
H3	13.36	13.40	13.36	13.40	13.54
H4	29.66	29.66	29.67	29.67	29.67
H5	28.85	28.85	28.86	28.86	28.86
H6	28.85	28.85	29.68	28.86	28.86
H7	29.68	29.68	29.68	29.68	29.67
H8	28.87	28.87	28.86	28.86	28.86
H9	28.87	28.87	28.86	28.86	28.86
H10	29.69	29.69	29.68	29.67	29.68
H11	28.86	28.86	28.85	28.85	28.86
H12	28.86	28.86	28.85	28.85	28.86

Table S4. Calculated nuclear magnetic shieldings (ppm) on atoms in **4**.

	MC_B3LYP		B3LYP//MC_B3LYP		B3LYP
	H	D	H	D	Conv
C1	82.61	82.60	83.23	82.14	81.98
C2	61.19	61.22	60.74	60.75	60.74
C3	82.63	82.62	82.00	81.98	81.98
C4	27.45	27.51	27.02	27.07	27.25
C5	91.43	91.48	91.27	91.22	91.13
C6	26.01	26.51	25.79	26.22	27.25
C7	−2.91	−2.66	−3.13	−2.89	−2.25
C8	167.34	167.22	166.96	166.84	166.60
C9	−1.91	−1.95	−2.21	−2.24	−2.25
C10	166.98	166.97	166.60	166.60	166.60
O1	178.79	182.49	177.39	181.27	189.71
O2	−142.69	−149.84	−147.59	−153.28	−165.38
O3	−164.94	−164.93	−164.75	−164.75	−165.38
O4	189.55	189.68	188.97	189.11	189.71
H1	14.49	15.55	15.95	16.60	18.12
H2	18.07	18.07	18.07	18.06	18.12
H3	23.88	23.89	23.89	23.89	23.88
H4	25.53	25.53	25.53	25.52	25.50
H5	29.78	29.79	29.80	29.80	29.80
H6	29.15	29.16	29.17	29.17	29.17
H7	29.15	29.16	29.17	29.17	29.17
H8	29.81	29.81	29.80	29.81	29.80
H9	29.18	29.18	29.17	29.17	29.17
H10	29.18	29.18	29.17	29.17	29.17

Table S5. Calculated nuclear magnetic shieldings (ppm) on atoms in **5**.

	MC_B3LYP		B3LYP//MC_B3LYP		B3LYP
	H	D	H	D	Conv
C1	74.97	74.85	74.47	74.29	73.99
C2	80.22	80.15	79.73	79.66	79.56
C3	80.62	80.42	80.15	79.97	79.56
C4	74.59	74.59	73.88	73.87	73.99
C5	38.52	38.69	38.27	38.38	38.67
C6	36.69	37.43	36.66	37.28	38.67
C7	−5.98	−5.77	−6.21	−6.00	−5.44
C8	166.10	165.96	165.63	165.49	165.30
C9	−5.25	−5.23	−5.46	−5.45	−5.44
C10	165.64	165.65	165.28	165.29	165.30
O1	199.93	203.79	198.59	202.59	211.07
O2	−158.82	−167.00	−164.21	−170.79	−184.48
O3	210.30	210.62	210.20	210.41	211.07
O4	−183.45	−183.65	−183.36	−183.53	−184.07

Table S5. Cont.

	MC_B3LYP		B3LYP//MC_B3LYP		B3LYP
	H	D	H	D	Conv
H1	14.57	15.68	16.03	16.71	18.31
H2	18.19	18.21	18.19	18.20	18.31
H3	24.84	24.84	24.83	24.83	24.82
H4	24.87	24.86	24.86	24.85	24.82
H5	29.73	29.74	29.76	29.74	29.75
H6	29.09	29.10	29.09	29.09	29.11
H7	29.09	29.10	29.09	29.09	29.11
H8	29.75	29.75	29.75	29.75	29.75
H9	29.11	29.11	29.10	29.10	29.11
H10	29.11	29.11	29.10	29.10	29.11

Table S6. Calculated nuclear magnetic shieldings (ppm) on atoms in **6**.

	MC_B3LYP		B3LYP//MC_B3LYP		B3LYP
	H	D	H	D	Conv
C1	71.89	71.80	71.48	71.32	71.20
C2	77.52	77.40	76.92	76.80	76.49
C3	40.31	42.53	42.11	41.96	41.80
C4	71.08	71.25	70.60	70.73	71.20
C5	76.62	76.79	76.43	76.48	76.49
C6	40.31	40.90	40.17	40.65	41.80
C7	−6.83	−6.57	−7.03	−6.79	−6.08
C8	165.98	165.88	165.73	165.63	165.35
C9	−6.12	−6.07	−6.35	−6.31	−6.08
C10	165.63	165.64	165.41	165.42	165.35
O1	215.66	218.22	213.60	216.52	223.06
O2	−180.50	−187.09	−185.77	−190.71	−201.89
O3	224.32	223.98	223.53	223.25	223.06
O4	−202.49	−201.99	−201.87	−201.45	−201.89
H1	16.11	17.13	17.58	18.18	19.63
H2	19.56	19.54	19.56	19.54	19.63
H3	24.64	24.64	24.63	24.62	24.64
H4	24.62	24.63	24.62	24.62	24.64
H5	29.73	29.74	29.74	29.74	29.75
H6	29.01	29.02	29.02	29.02	29.03
H7	29.01	29.02	29.02	29.02	29.03
H8	29.75	29.75	29.75	29.75	29.75
H9	29.02	29.03	29.02	29.02	29.03
H10	29.02	29.03	29.02	29.02	29.03

Table S7. Differences between the GIAO-calculated nuclear magnetic shieldings (ppm) obtained with the MC_B3LYP and B3LYP/MC_B3LYP methods on atoms in each molecule.

	1		2a		2b		3		4		5		6	
	H	D	H	D	H	D	H	D	H	D	H	D	H	D
C1	0.39	0.47	0.36	0.45	0.66	0.65	0.16	0.26	−0.62	0.46	0.50	0.56	0.41	0.48
C2	0.46	0.47	0.47	0.48	0.43	0.45	0.41	0.42	0.45	0.47	0.49	0.49	0.60	0.60
C3	0.49	0.48	0.47	0.47	0.10	0.21	0.81	0.81	0.63	0.64	0.47	0.45	−1.80	0.57
C4	0.33	0.37	0.35	0.38	0.22	0.28	0.32	0.35	0.43	0.44	0.71	0.72	0.48	0.52
C5	0.05	0.17	0.47	0.52	0.39	0.48	0.52	0.56	0.16	0.26	0.25	0.31	0.19	0.31
C6	0.18	0.27	0.17	0.25	0.41	0.44	0.28	0.33	0.22	0.29	0.03	0.15	0.14	0.25
C7	0.23	0.24	0.35	0.33	0.33	0.33	0.39	0.38	0.22	0.23	0.23	0.23	0.20	0.22
C8	0.39	0.39	0.39	0.40	0.37	0.38	0.34	0.36	0.38	0.38	0.47	0.47	0.25	0.25
C9			0.26	0.28	0.26	0.26	0.30	0.30	0.30	0.29	0.21	0.22	0.23	0.24
C10			0.33	0.34	0.38	0.38	0.32	0.32	0.38	0.37	0.36	0.36	0.22	0.22
C11							0.26	0.26						
C12							0.39	−0.60						
O1	1.76	1.50	1.42	1.22	0.42	0.46	0.86	0.75	1.40	1.22	1.34	1.20	2.06	1.70
O2	5.18	3.61	4.60	3.36	0.29	0.19	3.51	2.77	4.90	3.44	5.39	3.79	5.27	3.62
O3			0.38	0.43	0.59	0.64	0.42	0.45	−0.19	−0.18	0.10	0.21	0.79	0.73
O4			0.22	0.15	4.64	3.39	0.31	0.27	0.58	0.57	−0.09	−0.12	−0.62	−0.54
O5							0.37	0.39						
O6							0.29	0.25						
H1	−1.45	−1.04	−1.4	−1.00	−0.01	0.00	−1.39	−1.00	−1.46	−1.05	−1.46	−1.03	−1.47	−1.05
H2	0.00	0.01	0.00	0.00	−1.44	−1.03	0.01	0.02	0.00	0.01	0.00	0.01	0.00	0.00
H3	0.01	0.01	−0.01	0.00	0.00	0.00	0.00	0.00	−0.01	0.00	0.01	0.01	0.01	0.02
H4	0.01	0.01	0.01	0.01	0.00	0.00	−0.01	−0.01	0.00	0.01	0.01	0.01	0.00	0.01
H5	0.00	0.01	0.00	0.00	0.00	0.00	−0.01	−0.01	−0.02	−0.01	−0.01	0.00	−0.01	0.00
H6	−0.01	−0.01	0.00	0.00	0.00	0.00	−0.01	−0.01	−0.02	−0.01	0.00	0.01	−0.01	0.00
H7	−0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−0.02	−0.01	0.00	0.01	−0.01	0.00
H8	−0.01	0.00	0.00	0.01	−0.01	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00
H9			0.01	0.00	−0.02	−0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01
H10			0.01	0.00	−0.02	−0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.00	0.01
H11							0.01	0.01						
H12							0.01	0.01						

Table S8. Differences between the calculated nuclear magnetic shieldings $\Delta\sigma$ (ppm) induced by H/D isotope effect on atoms in compounds **2–6**.

	2a		2b		3		4		5		6	
	B3LYP//		B3LYP//		B3LYP//		B3LYP//		B3LYP//		B3LYP//	
	MC B3LYP ^a	MC B3LYP ^a	MC B3LYP ^a	MC B3LYP ^a	MC B3LYP ^a	MC B3LYP ^a	MC B3LYP ^a	MC B3LYP ^a	MC B3LYP ^a	MC B3LYP ^a	MC B3LYP ^a	MC B3LYP ^a
C1	0.04	−0.05	−0.17	−0.16	0.10	0.00	−0.01	−1.09	−0.12	−0.18	−0.09	−0.16
C2	−0.03	−0.04	0.11	0.09	0.13	0.12	0.03	0.01	−0.07	−0.07	−0.12	−0.12
C3	−0.04	−0.04	0.21	0.10	−0.07	−0.07	−0.01	−0.02	−0.20	−0.18	2.22	−0.15
C4	0.22	0.19	0.57	0.51	0.19	0.16	0.06	0.05	0.00	−0.01	0.17	0.13
C5	0.11	0.06	−0.03	−0.12	0.17	0.13	0.05	−0.05	0.17	0.11	0.17	0.05
C6	0.71	0.63	0.12	0.09	0.60	0.55	0.50	0.43	0.74	0.62	0.59	0.48
C7	0.05	0.07	−0.07	−0.07	0.05	0.06	0.25	0.24	0.21	0.21	0.26	0.24
C8	−0.19	−0.20	−0.01	−0.02	−0.26	−0.28	−0.12	−0.12	−0.14	−0.14	−0.10	−0.10
C9	0.00	−0.02	0.22	0.22	−0.04	−0.04	−0.04	−0.03	0.02	0.01	0.05	0.04
C10	−0.02	−0.03	−0.20	−0.20	−0.03	−0.03	−0.01	0.00	0.01	0.01	0.01	0.01
C11					0.01	0.01						
C12					−0.02	0.97						
O1	5.20	5.40	0.43	0.39	7.26	7.37	3.70	3.88	3.86	4.00	2.56	2.92
O2	−9.84	−8.60	−1.09	−0.99	−11.25	−10.51	−7.15	−5.69	−8.18	−6.58	−6.59	−4.94
O3	0.72	0.67	5.28	5.23	0.46	0.43	0.01	0.00	0.32	0.21	−0.34	−0.28
O4	−1.12	−1.05	−8.94	−7.69	−0.94	−0.90	0.13	0.14	−0.20	−0.17	0.50	0.42
O5					0.59	0.57						
O6					−1.14	−1.10						
H1	1.13	0.73	0.05	0.04	1.04	0.65	1.06	0.65	1.11	0.68	1.02	0.60
H2	0.05	0.05	1.09	0.68	0.05	0.04	0.00	−0.01	0.02	0.01	−0.02	−0.02
H3	0.00	−0.01	−0.01	−0.01	0.04	0.04	0.01	0.00	0.00	0.00	0.00	−0.01
H4	−0.01	−0.01	0.00	0.00	0.00	0.00	0.00	−0.01	−0.01	−0.01	0.01	0.00
H5	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.00
H6	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.00
H7	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.00
H8	0.00	−0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.00
H9	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
H10	0.00	0.01	0.01	0.00	0.00	−0.01	0.00	0.00	0.00	0.00	0.01	0.00
H11					0.00	0.00						
H12					0.00	0.00						

^a The calculated H/D isotope effect on nuclear shieldings using the conventional B3LYP-GIAO/MC_B3LYP method and using the MC_B3LYP-GIAO method are defined as $\Delta\sigma(\text{B3LYP//MC_B3LYP}) = \sigma(\text{B3LYP//MC_B3LYP-D}) - \sigma(\text{B3LYP//MC_B3LYP-H})$ and $\Delta\sigma(\text{MC_B3LYP}) = \sigma(\text{MC_B3LYP-D}) - \sigma(\text{MC_B3LYP-H})$, respectively.