Supporting Information for

Enhancing NMR Prediction for Organic Compounds Using Molecular Dynamics

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I. References

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II. Animations of Quasiclassical Trajectories

Two animations are provided as MPEG files: lysergic_acid_methyl_ester.mp4 (B3LYP/MIDI! surface) and annulene.mp4 (M06-2X/cc-pVDZ surface). Both depict 250 fs quasiclassical trajectories with 1 fs timesteps. Each proton and carbon is shaded by its shielding (B3LYP/cc-pVDZ/GIAO). Red indicates the maximum shielding over the course of the trajectory and blue indicates the minimum shielding. Colors are independent by atom. Oxygens and nitrogens are fixed in color. Each frame was ray-traced in Pymol and the movie assembled with FFMPEG.

III. Method Optimization

1. Detailed Benchmark of Dynamics Methods based on CCSD Dynamics

To identify suitable potential energy surfaces for dynamics, a core set of 11 small molecules was selected: methane, ethane, ethylene, acetylene, methyl fluoride, methanol, methyl amine, hydrogen cyanide, carbon monoxide, carbon dioxide, and formaldehyde. Raw dynamic corrections were calculated for each molecule (298 K, 25 trajectories each, 1000 points per trajectory, NMR every 4 points at B3LYP/cc-pVTZ). The corrections were compared to those calculated using CCSD/cc-pVTZ trajectories, and the error was evaluated as an indicator of the similarity of a given dynamics surface to the CCSD/cc-pVTZ standard. A summary of the calculated errors is provided below, followed by a complete table of the raw corrections. All values in ppm.

(dz = cc-pVDZ, tz = cc-pVTZ, MPW = mPW1PW91, bh&h=BHandHLYP, RMSE = root-mean-square error)

Table S1. Similarity of dynamic corrections to CCSD/tz corrections for core set.

	RMSE vs. CCSD/tz		**Mean error vs. CCSD/tz**	
	Carbon	*Hydrogen*	*Carbon*	*Hydrogen*
MP2/dz	0.38	0.11	–0.13	–0.02
B3LYP/dz	0.19	0.03	0.07	0.00
B3LYP/tz	0.28	0.04	0.17	–0.02
PBE0/dz	0.24	0.02	0.11	0.01
PBE0/tz	0.36	0.02	0.22	–0.01
M062X/dz	0.35	0.03	0.16	0.02
M062X/tz	0.47	0.02	0.33	0.00
B97D/dz	0.20	0.08	–0.12	–0.04
B97D/tz	0.35	0.08	0.14	–0.04
MPW/dz	0.44	0.09	–0.03	–0.03
MPW/tz	0.37	0.08	0.02	–0.03
ωB97/dz	0.43	0.03	0.21	0.00
ωB97/tz	0.49	0.03	0.32	0.00
b2plyp/dz	0.36	0.08	0.03	–0.02
b2plyp/tz	0.37	0.07	0.18	–0.03
b3pw91/dz	0.40	0.04	0.13	–0.01
b3pw91/tz	0.30	0.03	0.15	–0.01
bh&h/dz	0.52	0.03	0.41	0.01
bh&h/tz	0.47	0.03	0.33	0.01
bmk/dz	0.44	0.07	0.3	0.06
bmk/tz	0.39	0.04	0.25	0.01
cam-b3lyp/dz	0.47	0.03	0.36	0.00
cam-b3lyp/tz	0.57	0.02	0.41	0.01
hf/dz	0.74	0.08	0.66	0.05
hf/tz	0.52	0.08	0.44	0.04
lc-ωpbe/dz	0.48	0.03	0.29	0.01
lc-ωpbe/tz	0.40	0.04	0.22	0.01
tpssh/dz	0.42	0.06	0.16	–0.03
tpssh/tz	0.27	0.06	0.05	–0.01
CCSD/dz	0.29	0.05	–0.03	0.00

Table S2. Raw dynamic corrections for core set.

molecule	atom	mp2 /dz	b3lyp /dz	b3lyp /tz	pbe0 /dz	pbe0 /tz	m062x /dz	m062x /tz	b97d /dz	b97d /tz	mpw /dz	mpw /tz	CCSD /tz
methane	C	–3.67	–3.47	–3.39	–3.53	–3.30	–3.12	–3.04	–3.96	–3.44	–2.74	–3.07	–3.90
	H	–0.63	–0.64	–0.68	–0.61	–0.65	–0.64	–0.64	–0.65	–0.66	–0.68	–0.64	–0.65
	H	–0.63	–0.63	–0.66	–0.63	–0.64	–0.66	–0.61	–0.66	–0.65	–0.68	–0.64	–0.64
	H	–0.65	–0.64	–0.64	–0.63	–0.64	–0.65	–0.66	–0.68	–0.64	–0.67	–0.64	–0.63
	H	–0.63	–0.64	–0.68	–0.63	–0.66	–0.62	–0.66	–0.66	–0.67	–0.65	–0.66	–0.62
ethane	C	–4.84	–4.64	–4.44	–4.69	–4.51	–5.00	–4.51	–5.89	–3.92	–4.80	–5.21	–4.79
	H	–0.78	–0.73	–0.77	–0.74	–0.74	–0.73	–0.78	–0.82	–0.68	–0.80	–0.92	–0.79
	H	–0.75	–0.74	–0.75	–0.74	–0.76	–0.70	–0.81	–0.82	–0.75	–0.75	–0.81	–0.76
	H	–0.75	–0.71	–0.76	–0.67	–0.78	–0.75	–0.75	–0.83	–0.71	–0.73	–0.83	–0.77
	C	–4.95	–4.61	–4.71	–5.01	–4.68	–5.18	–4.52	–4.29	–4.24	–5.18	–4.98	–4.56
	H	–0.76	–0.76	–0.77	–0.76	–0.82	–0.79	–0.71	–0.73	–0.85	–0.76	–0.74	–0.81
	H	–0.77	–0.72	–0.87	–0.78	–0.80	–0.77	–0.75	–0.75	–0.83	–0.79	–0.76	–0.73
	H	–0.71	–0.79	–0.79	–0.78	–0.77	–0.80	–0.77	–0.75	–0.83	–0.79	–0.72	–0.74
ethylene	C	–6.16	–5.86	–6.27	–5.28	–5.51	–6.07	–5.43	–5.88	–6.19	–6.19	–6.06	–6.02
	C	–6.33	–5.22	–5.07	–5.59	–5.73	–5.36	–5.73	–6.04	–4.99	–5.88	–5.58	–5.52
	H	–0.56	–0.58	–0.61	–0.55	–0.56	–0.58	–0.57	–0.57	–0.61	–0.58	–0.58	–0.56
	H	–0.57	–0.58	–0.62	–0.56	–0.57	–0.58	–0.56	–0.57	–0.59	–0.60	–0.58	–0.56
	H	–0.58	–0.57	–0.56	–0.57	–0.58	–0.55	–0.58	–0.57	–0.54	–0.57	–0.58	–0.58
	H	–0.57	–0.55	–0.55	–0.59	–0.58	–0.55	–0.57	–0.59	–0.53	–0.57	–0.57	–0.57
acetylene	C	–5.76	–5.25	–4.96	–4.92	–5.09	–4.77	–4.88	–5.49	–5.38	–5.70	–5.71	–5.36
	C	–5.70	–5.23	–5.00	–4.97	–5.10	–4.75	–4.91	–5.43	–5.42	–5.65	–5.80	–5.45
	H	–0.73	–0.75	–0.76	–0.73	–0.74	–0.71	–0.74	–0.78	–0.76	–0.78	–0.79	–0.75
	H	–0.73	–0.75	–0.77	–0.73	–0.74	–0.72	–0.73	–0.76	–0.77	–0.76	–0.78	–0.79
CH_3F	C	–4.53	–4.62	–4.49	–4.67	–4.45	–4.38	–4.37	–4.66	–4.52	–4.87	–4.55	–4.42
	H	–0.67	–0.69	–0.70	–0.66	–0.67	–0.64	–0.66	–0.68	–0.71	–0.67	–0.74	–0.71
	H	–0.68	–0.62	–0.73	–0.66	–0.70	–0.64	–0.67	–0.70	–0.72	–0.73	–0.69	–0.69
	H	–0.64	–0.67	–0.68	–0.67	–0.71	–0.70	–0.67	–0.67	–0.70	–0.65	–0.70	–0.68
CH_3OH	C	–4.57	–4.77	–4.57	–4.46	–4.34	–4.62	–4.02	–4.69	–4.64	–4.87	–4.68	–4.70
	H	–0.74	–0.77	–0.80	–0.77	–0.81	–0.73	–0.79	–0.80	–0.81	–0.74	–0.83	–0.76
	H	–0.67	–0.71	–0.72	–0.72	–0.73	–0.70	–0.74	–0.73	–0.77	–0.78	–0.77	–0.71
	H	–0.72	–0.69	–0.79	–0.68	–0.67	–0.70	–0.70	–0.73	–0.73	–0.77	–0.76	–0.78
	(OH)	–0.83	–0.78	–0.82	–0.82	–0.83	–0.83	–0.82	–0.88	–0.86	–0.81	–0.83	–0.82
CH_3NH_2	C	–4.16	–4.80	–4.52	–4.70	–4.02	–4.63	–3.94	–4.69	–4.11	–4.50	–4.38	–4.89
	(NH)	–0.80	–0.81	–0.84	–0.80	–0.82	–0.80	–0.85	–0.82	–0.86	–0.84	–0.81	–0.77
	H	–0.70	–0.75	–0.75	–0.75	–0.75	–0.75	–0.73	–0.74	–0.67	–0.72	–0.73	–0.71
	(NH)	–0.78	–0.84	–0.87	–0.80	–0.88	–0.79	–0.86	–0.84	–0.90	–0.86	–0.80	–0.86
	H	–0.80	–0.78	–0.83	–0.78	–0.79	–0.80	–0.81	–0.87	–0.86	–0.81	–0.80	–0.76
	H	–0.79	–0.79	–0.83	–0.78	–0.81	–0.79	–0.80	–0.86	–0.88	–0.85	–0.79	–0.77
CO	C	–2.60	–2.32	–2.33	–2.24	–2.29	–2.22	–2.23	–2.48	–2.51	–2.53	–2.51	–2.24
CO_2	C	–1.74	–1.69	–1.77	–1.66	–1.73	–1.65	–1.68	–1.87	–1.79	–1.86	–1.82	–1.66
HCN	C	–2.98	–2.43	–2.33	–2.35	–2.20	–2.20	–2.19	–2.50	–2.43	–2.45	–2.50	–2.38
	H	–0.74	–0.73	–0.77	–0.71	–0.73	–0.69	–0.76	–0.76	–0.74	–0.72	–0.76	–0.74
CH_2O	C	–5.26	–4.68	–4.44	–4.55	–4.68	–4.88	–4.90	–4.93	–4.98	–4.84	–4.63	–4.94
	H	–0.59	–0.60	–0.57	–0.60	–0.57	–0.60	–0.62	–0.59	–0.61	–0.59	–0.59	–0.60
	H	–0.60	–0.60	–0.58	–0.60	–0.59	–0.60	–0.62	–0.59	–0.60	–0.58	–0.59	–0.64

molecule	atom	ωb97 /dz	ωb97 /tz	b2plyp /dz	b2plyp /tz	b3pw91 /dz	b3pw91 /tz	bh&h /dz	bh&h /tz	bmk /dz	bmk /tz	CCSD /tz
methane	C	–3.23	–2.65	–3.49	–3.37	–3.02	–3.78	–3.44	–3.41	–3.2	–2.89	–3.90
	H	–0.63	–0.65	–0.65	–0.66	–0.64	–0.69	–0.65	–0.64	–0.6	–0.59	–0.65
	H	–0.65	–0.62	–0.65	–0.66	–0.63	–0.67	–0.66	–0.7	–0.6	–0.61	–0.64
	H	–0.6	–0.62	–0.64	–0.66	–0.61	–0.67	–0.68	–0.65	–0.6	–0.6	–0.63
	H	–0.64	–0.64	–0.64	–0.64	–0.64	–0.64	–0.64	–0.64	–0.64	–0.64	–0.62
ethane	C	–4.74	–4.29	–4.95	–4.04	–4.67	–4.67	–4.04	–5.16	–4.4	–5.12	–4.79
	H	–0.79	–0.74	–0.82	–0.72	–0.74	–0.78	–0.75	–0.74	–0.7	–0.77	–0.79
	H	–0.74	–0.77	–0.77	–0.75	–0.72	–0.79	–0.84	–0.76	–0.7	–0.79	–0.76
	H	–0.73	–0.81	–0.76	–0.78	–0.72	–0.83	–0.76	–0.72	–0.7	–0.75	–0.77
	C	–4.7	–4.41	–4.69	–4.55	–5.54	–4.72	–4.05	–4.51	–4.5	–4.35	–4.56
	H	–0.78	–0.78	–0.75	–0.81	–0.82	–0.77	–0.75	–0.8	–0.7	–0.79	–0.81
	H	–0.77	–0.84	–0.73	–0.8	–0.82	–0.82	–0.78	–0.76	–0.8	–0.73	–0.73
	H	–0.82	–0.75	–0.75	–0.79	–0.82	–0.77	–0.81	–0.73	–0.7	–0.72	–0.74
ethylene	C	–5.72	–5.35	–5.93	–5.73	–5.79	–5.27	–5.02	–5.79	–5.6	–5.84	–6.02
	C	–5.64	–5.78	–6.04	–5.68	–5.54	–5.4	–4.79	–6.06	–5.4	–5.28	–5.52
	H	–0.57	–0.56	–0.58	–0.6	–0.59	–0.55	–0.56	–0.57	–0.5	–0.57	–0.56
	H	–0.56	–0.56	–0.56	–0.61	–0.58	–0.54	–0.57	–0.57	–0.5	–0.58	–0.56
	H	–0.56	–0.58	–0.58	–0.58	–0.57	–0.55	–0.54	–0.58	–0.5	–0.53	–0.58
	H	–0.55	–0.6	–0.56	–0.6	–0.56	–0.56	–0.59	–0.57	–0.5	–0.53	–0.57
acetylene	C	–5.01	–5.03	–5.64	–5.4	–5.38	–5.14	–4.78	–4.68	–5.3	–5.23	–5.36
	C	–5.03	–4.97	–5.67	–5.42	–5.47	–5.2	–4.86	–4.53	–5.4	–5.35	–5.45
	H	–0.72	–0.73	–0.76	–0.74	–0.75	–0.77	–0.73	–0.73	–0.7	–0.78	–0.75
	H	–0.73	–0.73	–0.76	–0.76	–0.76	–0.77	–0.71	–0.72	–0.7	–0.76	–0.79
CH_3F	C	–4.64	–4.5	–4.45	–4.43	–4.57	–4.61	–4.35	–3.91	–4.3	–4.21	–4.42
	H	–0.68	–0.69	–0.68	–0.71	–0.66	–0.7	–0.67	–0.68	–0.6	–0.7	–0.71
	H	–0.69	–0.68	–0.7	–0.73	–0.7	–0.71	–0.69	–0.74	–0.7	–0.71	–0.69
	H	–0.67	–0.71	–0.65	–0.69	–0.67	–0.7	–0.68	–0.7	–0.6	–0.69	–0.68
CH_3OH	C	–4.74	–4.4	–4.76	–4.44	–4.75	–4.83	–4.63	–4.23	–4.7	–4.28	–4.70
	H	–0.77	–0.82	–0.77	–0.8	–0.78	–0.8	–0.74	–0.81	–0.7	–0.78	–0.76
	H	–0.68	–0.69	–0.71	–0.74	–0.7	–0.75	–0.73	–0.69	–0.7	–0.76	–0.71
	H	–0.75	–0.71	–0.74	–0.75	–0.7	–0.72	–0.73	–0.74	–0.7	–0.72	–0.78
	(OH)	–0.86	–0.85	–0.83	–0.84	–0.86	–0.84	–0.8	–0.84	–0.8	–0.83	–0.82
CH_3NH_2	C	–3.81	–4.25	–4.17	–4.16	–4.33	–4.34	–3.86	–4.02	–4	–4.71	–4.89
	(NH)	–0.8	–0.81	–0.9	–0.84	–0.84	–0.83	–0.89	–0.86	–0.8	–0.79	–0.77
	H	–0.71	–0.76	–0.72	–0.72	–0.75	–0.73	–0.67	–0.71	–0.7	–0.75	–0.71
	(NH)	–0.89	–0.85	–0.81	–0.84	–0.86	–0.8	–0.86	–0.79	–0.8	–0.84	–0.86
	H	–0.8	–0.82	–0.81	–0.82	–0.81	–0.82	–0.8	–0.78	–0.7	–0.81	–0.76
	H	–0.82	–0.8	–0.81	–0.82	–0.81	–0.82	–0.8	–0.76	–0.7	–0.81	–0.77
CO	C	–2.29	–2.28	–2.51	–2.47	–2.35	–2.32	–2.18	–2.16	–2.2	–2.11	–2.24
CO_2	C	–1.78	–1.74	–1.89	–1.86	–1.79	–1.71	–1.65	–1.57	–1.7	–1.77	–1.66
HCN	C	–2.23	–2.19	–2.57	–2.48	–2.29	–2.24	–2.11	–2.16	–2.2	–2.21	–2.38
	H	–0.71	–0.75	–0.7	–0.73	–0.72	–0.71	–0.73	–0.73	–0.6	–0.73	–0.74
CH_2O	C	–4.56	–4.53	–4.89	–4.64	–4.3	–4.33	–4.53	–4.52	–4.1	–4.45	–4.94
	H	–0.59	–0.56	–0.6	–0.6	–0.59	–0.59	–0.6	–0.58	–0.5	–0.57	–0.60
	H	–0.6	–0.56	–0.59	–0.58	–0.58	–0.59	–0.61	–0.57	–0.5	–0.58	–0.64

molecule	atom	cam–b3lyp /dz	cam–b3lyp /tz	hf /dz	hf /tz	lc-ωpbe /dz	lc-ωpbe /tz	tpssh /dz	tpssh /tz	CCSD /dz	CCSD /tz
methane	C	–3.22	–3.72	–3.00	–3.20	–2.79	–3.54	–3.55	–3.47	–3.47	–3.90
	H	–0.65	–0.67	–0.63	–0.62	–0.63	–0.61	–0.63	–0.64	–0.64	–0.65
	H	–0.65	–0.67	–0.62	–0.67	–0.65	–0.62	–0.67	–0.64	–0.64	–0.64
	H	–0.64	–0.65	–0.61	–0.64	–0.68	–0.65	–0.65	–0.63	–0.63	–0.63
	H	–0.64	–0.64	–0.64	–0.64	–0.64	–0.64	–0.64	–0.64	–0.64	–0.62
ethane	C	–4.22	–4.17	–3.47	–4.11	–5.33	–4.80	–4.35	–5.45	–5.45	–4.79
	H	–0.83	–0.76	–0.68	–0.73	–0.81	–0.78	–0.78	–0.80	–0.80	–0.79
	H	–0.77	–0.74	–0.71	–0.73	–0.75	–0.76	–0.75	–0.81	–0.81	–0.76
	H	–0.79	–0.74	–0.71	–0.75	–0.81	–0.76	–0.84	–0.78	–0.78	–0.77
	C	–4.25	–4.12	–4.03	–5.26	–4.12	–5.11	–4.19	–4.33	–4.33	–4.56
	H	–0.75	–0.78	–0.81	–0.77	–0.75	–0.79	–0.83	–0.70	–0.70	–0.81
	H	–0.77	–0.72	–0.75	–0.78	–0.74	–0.80	–0.77	–0.72	–0.72	–0.73
	H	–0.76	–0.70	–0.79	–0.75	–0.74	–0.78	–0.73	–0.72	–0.72	–0.74
ethylene	C	–5.15	–5.32	–4.98	–5.22	–5.33	–5.60	–5.46	–5.74	–5.74	–6.02
	C	–5.44	–5.05	–4.78	–5.58	–5.73	–6.07	–5.58	–6.37	–6.37	–5.52
	H	–0.56	–0.55	–0.55	–0.54	–0.58	–0.56	–0.57	–0.55	–0.55	–0.56
	H	–0.55	–0.56	–0.55	–0.55	–0.55	–0.56	–0.54	–0.56	–0.56	–0.56
	H	–0.56	–0.54	–0.55	–0.56	–0.59	–0.60	–0.58	–0.60	–0.60	–0.58
	H	–0.55	–0.53	–0.54	–0.56	–0.58	–0.58	–0.58	–0.60	–0.60	–0.57
acetylene	C	–4.88	–4.96	–4.40	–4.35	–4.98	–4.32	–5.48	–5.46	–5.72	–5.36
	C	–4.90	–4.86	–4.39	–4.39	–4.90	–4.60	–5.43	–5.42	–5.68	–5.45
	H	–0.72	–0.75	–0.68	–0.70	–0.73	–0.72	–0.75	–0.76	–0.75	–0.75
	H	–0.71	–0.75	–0.67	–0.68	–0.73	–0.69	–0.75	–0.76	–0.75	–0.79
CH_3F	C	–4.34	–4.49	–3.88	–3.89	–4.44	–4.54	–4.60	–4.52	–4.63	–4.42
	H	–0.68	–0.68	–0.68	–0.68	–0.67	–0.68	–0.69	–0.68	–0.66	–0.71
	H	–0.70	–0.70	–0.64	–0.70	–0.63	–0.67	–0.69	–0.70	–0.67	–0.69
	H	–0.69	–0.70	–0.69	–0.65	–0.68	–0.66	–0.68	–0.73	–0.68	–0.68
CH_3OH	C	–4.51	–4.19	–4.28	–3.93	–4.84	–4.34	–4.62	–4.60	–4.86	–4.70
	H	–0.79	–0.80	–0.73	–0.78	–0.75	–0.76	–0.79	–0.83	–0.73	–0.76
	H	–0.71	–0.69	–0.70	–0.70	–0.71	–0.73	–0.70	–0.73	–0.73	–0.71
	H	–0.71	–0.78	–0.70	–0.70	–0.72	–0.71	–0.74	–0.72	–0.73	–0.78
	(OH)	–0.82	–0.81	–0.75	–0.79	–0.81	–0.78	–0.85	–0.82	–0.81	–0.82
CH_3NH_2	C	–3.99	–3.66	–3.63	–4.57	–4.03	–4.31	–3.69	–4.67	–4.67	–4.89
	(NH)	–0.86	–0.77	–0.81	–0.83	–0.89	–0.88	–0.84	–0.82	–0.82	–0.77
	H	–0.72	–0.73	–0.70	–0.70	–0.71	–0.75	–0.74	–0.73	–0.73	–0.71
	(NH)	–0.88	–0.78	–0.79	–0.78	–0.84	–0.85	–0.88	–0.79	–0.79	–0.86
	H	–0.80	–0.79	–0.80	–0.80	–0.80	–0.82	–0.81	–0.80	–0.80	–0.76
	H	–0.80	–0.78	–0.78	–0.79	–0.78	–0.80	–0.83	–0.82	–0.82	–0.77
CO	C	–2.31	–2.26	–2.01	–2.01	–2.24	–2.19	–2.44	–2.42	–2.39	–2.24
CO_2	C	–1.74	–1.67	–1.52	–1.52	–1.67	–1.63	–1.87	–1.80	–1.77	–1.66
HCN	C	–2.20	–2.17	–1.96	–1.93	–2.12	–2.10	–2.46	–2.23	–2.50	–2.38
	H	–0.71	–0.72	–0.66	–0.68	–0.68	–0.72	–0.75	–0.72	–0.73	–0.74
CH_2O	C	–4.30	–4.05	–3.88	–4.38	–4.47	–4.67	–4.77	–4.35	–4.35	–4.94
	H	–0.58	–0.57	–0.57	–0.58	–0.57	–0.57	–0.61	–0.54	–0.54	–0.60
	H	–0.58	–0.57	–0.56	–0.57	–0.57	–0.57	–0.62	–0.54	–0.54	–0.64

2. Refinement of Dynamics and NMR Methods based on Experimental Training Set

For each of three candidate dynamics methods (B3LYP/cc-pVDZ, PBE0/cc-pVDZ, TPSSh/cc-pVDZ), a variety of NMR methods were evaluated by calculating raw corrections for the molecules considered in the previous section (excluding formaldehyde, 298 K, 200 trajectories each, 250 points per trajectory, NMR evaluated every 8 points using the indicated method). Evaluation of the methods was performed by comparison of the predicted absolute shielding of these molecules to experiment. Predicted shielding is calculated by adding the dynamic correction to a high-level stationary shift, then subtracting the intercept for the set. Both experimental and stationary shieldings were obtained from reference 5 in the manuscript. A summary of the calculated errors is provided below. All values in ppm.

(dz = cc-pVDZ, tz = cc-pVTZ, RMSE = root-mean-square error)

Table S3. RMSE of predicted shifts from experiment.

NMR method	B3LYP /dz	B3LYP /tz	B97D /dz	B97D /tz	BLYP /dz	BLYP /tz	BMK /dz	BMK /tz	M062X /dz	M062X /tz
b3lyp /dz dyn	0.48	0.46	0.50	0.45	0.50	0.45	0.56	0.63	0.60	0.72
pbe0 /dz dyn	0.50	0.49	0.50	0.47	0.51	0.46	0.60	0.67	0.64	0.76
tpssh /dz dyn	0.52	0.50	0.54	0.50	0.55	0.49	0.59	0.64	0.63	0.75

NMR method	MPW /dz	MPW /tz	PBE0 /dz	PBE0 /tz	VSXC /dz	VSXC /tz	ωB97XD /dz	ωB97XD /tz
b3lyp /dz dyn	0.48	0.48	0.48	0.48	0.53	0.49	0.48	0.50
pbe0 /dz dyn	0.51	0.51	0.51	0.52	0.53	0.50	0.52	0.54
tpssh /dz dyn	0.52	0.51	0.52	0.51	0.58	0.53	0.53	0.53

3. Effect of Trajectory Length and Replication

Because our procedure is inherently statistical in nature, it was important to evaluate the effect of trajectory length and replication. Trajectories that are too short will be unable to sample a meaningful portion of the energy surface. In the limit of initialization-only sampling, only the harmonic region near the stationary point would be sampled. Conversely, trajectories that are too long are not useful because each trajectory can only examine a small part of the phase space of the system. In very long trajectories, unphysical intramolecular vibrational redistribution is also expected to occur. We simultaneously considered the effect of replication on the dynamical procedure: more trajectories cost more time, but give greater precision. Ideally, the procedure would use the minimum number of points per trajectory to allow the greatest number of trajectories to be sampled.

Acetylene was chosen as a test molecule to investigate the above parameters because it is small enough to allow the collection of a very large number of trajectory points. Additionally, its carbon shift has a pronounced sensitivity to C–C bond length. (In general, proton shifts statistically converge well before carbon ones, so they were ignored for this analysis.) 500 quasiclassical trajectories (298 K) of 1000 points were obtained using a time step of 1.0 fs.

We considered three datasets. Using all the points from each trajectory (500 forward and 500 backward) constituted the "long" set. Selection of the middle 500 points (250 forward and 250 backward) formed the "medium" set, while selection of the middle 250 points created the "short" set. In order to evaluate the effect of trajectory length and replication, bootstrap resampling was performed on each of these three sets. For each set, random selection with replacement of n = 5, 10, 25, 50, 75, 100 trajectories was repeated 500 times and average carbon dynamical correction was evaluated using B3LYP/cc-pVDZ. The sampling distribution is shown by the histogram below using data for the medium set (x-axis: mean carbon correction in ppm, y-axis: count):

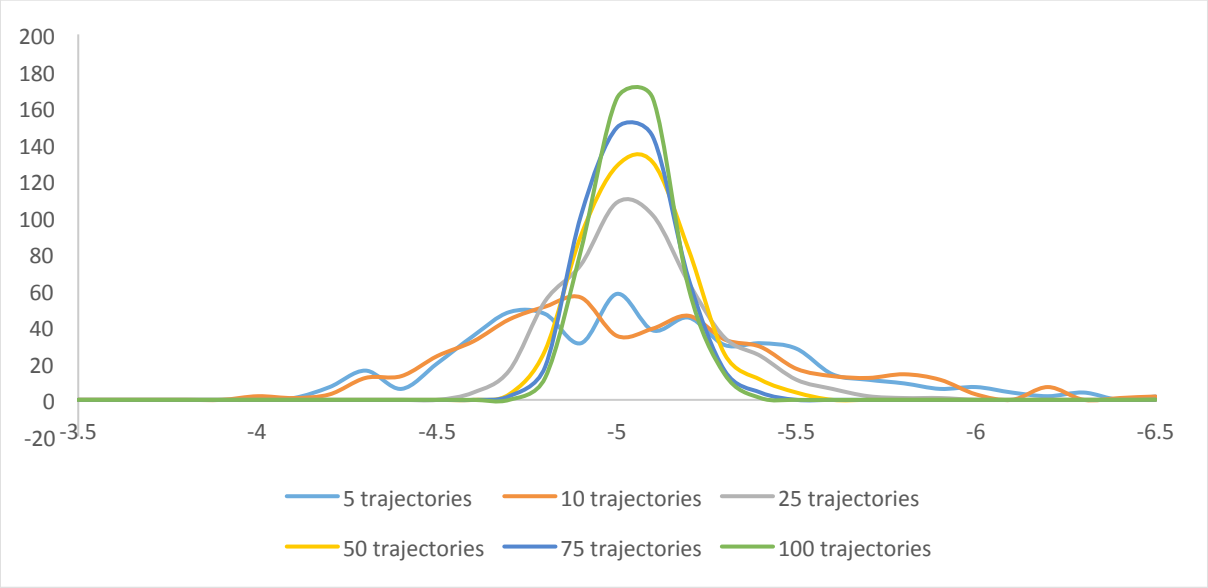


Figure S1. Histogram of bootstrap resampling experiment.

Some selected results are displayed below. Error between samples measures the standard deviation of sample mean corrections across all the samples selected; intrinsic sample error refers to the standard error of trajectory mean corrections within each sample. These measures agree closely. As expected, the variance of the sampling distribution declines as the square root of the number of observations, with 25 trajectories as the minimum number of required observations. Notably, the length of the simulations does not affect the mean or sampling error significantly.

Table S4. Effect of replication with varying trajectory lengths.

	Sample size	Mean	Error between samples	Intrinsic sample error
Short (250 pts)	5	-5.164	0.489	0.434
	10	-5.145	0.340	0.322
	25	-5.125	0.211	0.205
	50	-5.130	0.154	0.147
	75	-5.136	0.127	0.121
	100	-5.134	0.109	0.105
Medium (500 pts)	5	-5.133	0.463	0.409
	10	-5.098	0.322	0.301
	25	-5.094	0.211	0.198
	50	-5.096	0.140	0.142
	75	-5.101	0.125	0.116
	100	-5.098	0.102	0.100
Long (1000 pts)	5	-5.134	0.466	0.430
	10	-5.142	0.345	0.322
	25	-5.140	0.219	0.207
	50	-5.137	0.136	0.147
	75	-5.137	0.124	0.120
	100	-5.126	0.106	0.104

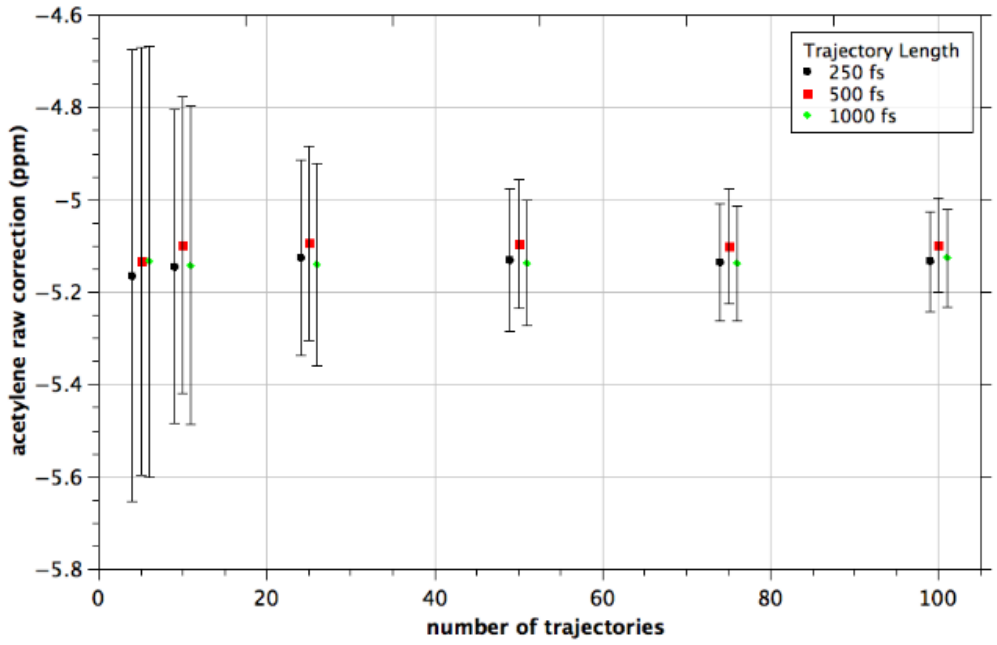


Figure S2. Graphical representation of correction distribution with variation of trajectory length and replication.

4. Effect of NMR Interval

To increase the efficiency of our method, we investigate the effect of increasing the interval between calculating NMR shieldings during trajectory studies. Quasiclassical dynamics (298 K, B3LYP/cc-pVDZ surface and NMR) on methane, ethane, and acetylene show that an 8.0 fs interval results in no loss of accuracy:

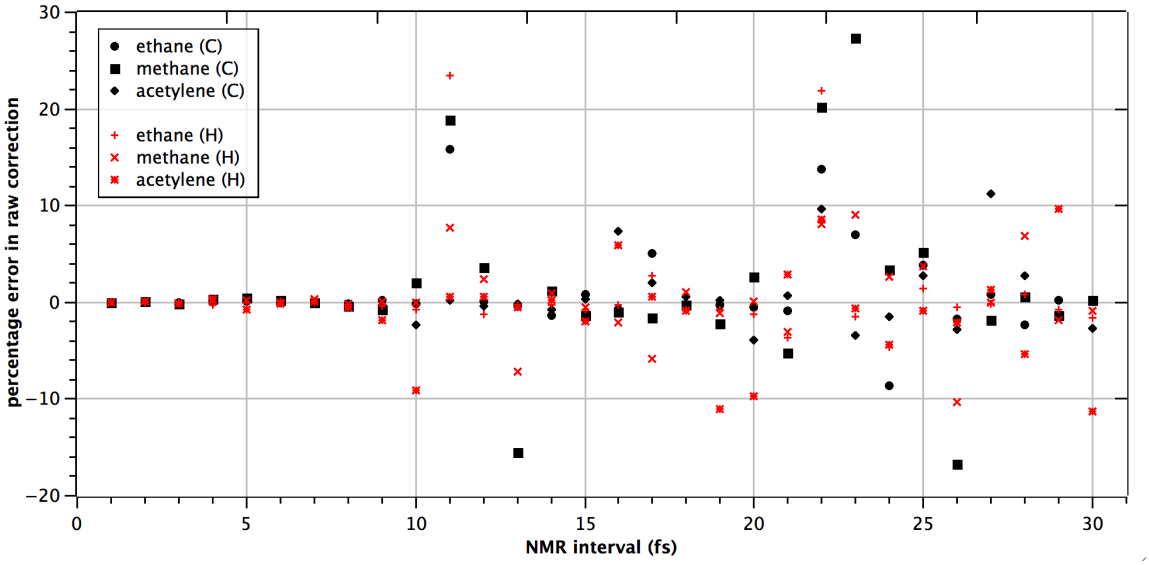


Figure S3. Effect of NMR Interval.

5. Comparison with Purely Classical Dynamics

To confirm our hypothesis that quasiclassical dynamics should reveal much larger vibrational corrections than a purely classical model, presumably due to consideration of the zero-point vibrational energy, we performed both classical and quasiclassical trajectory studies on a small set of molecules (298 K, without rotation, 25 trajectories each, 1000 points per trajectory, NMR every 4 points at B3LYP/6-31G(d)).

Classical initialization is identical to the standard initialization procedure used, except that the vibrational energy per mode is drawn from an equilibrium Boltzmann distribution and the displacements are made on a classical probability distribution for position. The raw corrections are summarized below, and they confirm that classical corrections are significantly smaller than quasi-classical ones.

Table S5. Comparison of classical and quasi-classical raw corrections (ppm).

molecule	atom	classical correction	quasi–classical correction	molecule	atom	classical correction	quasi–classical correction	molecule	atom	classical correction	quasi–classical correction
methane	C	–0.30	–3.51	CH_3NH_2	C	–0.60	–3.41	allene	C	–0.60	–2.61
	H	–0.11	–0.64		H	–0.15	–0.78		C	–1.20	–2.71
	H	–0.11	–0.62		H	–0.15	–0.82		H	–0.10	–0.43
	H	–0.11	–0.61		H	–0.14	–0.70		H	–0.10	–0.47
	H	–0.11	–0.63		H	–0.16	–0.72		C	–0.60	–2.61
ethane	C	–0.50	–3.85		H	–0.16	–0.72		H	–0.09	–0.40
	H	–0.14	–0.72	CH_3F	C	–0.80	–3.48		H	–0.09	–0.45
	H	–0.15	–0.67		H	–0.14	–0.66	acetylene	C	–2.30	–4.77
	H	–0.15	–0.64		H	–0.14	–0.68		C	–2.30	–4.77
	C	–0.50	–4.09		H	–0.14	–0.67		H	–0.24	–0.68

	H	–0.14	–0.78	CH_3CN	C	–0.80	–3.17		H	–0.24	–0.69
	H	–0.15	–0.76		H	–0.14	–0.65	acetone	C	–1.30	–4.38
	H	–0.15	–0.75		H	–0.15	–0.66		H	–0.12	–0.61
ethylene	C	–1.30	–4.80		H	–0.15	–0.60		H	–0.22	–0.79
	C	–1.30	–5.19		C	–0.60	–1.82		H	–0.11	–0.58
	H	–0.12	–0.55	CH_3CHO	C	–0.40	–4.11		C	–1.20	–4.17
	H	–0.12	–0.54		H	–0.18	–0.74		C	–1.20	–4.27
	H	–0.12	–0.51		H	–0.11	–0.57		H	–0.11	–0.57
	H	–0.12	–0.52		H	–0.11	–0.64		H	–0.11	–0.55
HCN	C	–0.70	–2.40		C	–1.30	–3.28		H	–0.21	–0.78
	H	–0.20	–0.69		H	–0.16	–0.52				
CH_3OH	C	–0.60	–3.96	CH_2O	C	–1.10	–4.34				
	H	–0.16	–0.71		H	–0.14	–0.59				
	H	–0.14	–0.70		H	–0.14	–0.60				
	H	–0.13	–0.71	CF_4	C	–0.70	–1.55				
	H	–0.23	–0.82								

6. Effect of Rotations

To examine the importance of rotations, several dynamics and NMR methods were evaluated by calculating raw corrections on a subset of the molecules used in SI-III.2 (298 K, 200 trajectories each, 250 points per trajectory, NMR evaluated every 8 points using the indicated method). Each set of trajectories was propagated with and without rotations, and the predicted carbon shieldings were compared by linear scaling to experimentally determined numbers. Although root-mean-square errors were unchanged by rotation, the intercept was improved in all cases. All values in ppm.

Table S6. Effect of Rotations on Carbon Intercept.

		NMR basis set (B3LYP)					
		MIDI!	6-31G(d)	cc-pVDZ	cc-pVTZ	pcS-2	pcS-3
Dynamics basis set (B3LYP)	MIDI!	–0.91	–0.69	–0.43	–0.34	–0.20	–0.20
	MIDI! with rotations	–0.83	–0.61	–0.34	–0.25	–0.11	–0.10
	6-31G(d)	–1.06	–0.85	–0.60	–0.51	–0.38	–0.38
	6-31G(d) with rotations	–1.02	–0.80	–0.56	–0.46	–0.32	–0.32
	cc-pVDZ	–1.00	–0.78	–0.53	–0.44	–0.30	–0.30
	cc-pVDZ with rotations	–0.89	–0.67	–0.41	–0.31	–0.17	–0.17

IV. Proton Shieldings

1. Summary of Stationary Point Geometry and Shielding Calculations

Molecule: acetylene
B3LYP/MIDI! energy (hartree): -76.87967268

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	0.00000000	0.00000000	0.60264000	127.4970
H	0.00000000	0.00000000	1.67029900	30.3000
C	0.00000000	0.00000000	-0.60264000	127.4970
H	0.00000000	0.00000000	-1.67029900	30.3000

CCSD(T)/cc-pVQZ/gas phase Energy (hartree): -0.77209316045D+02

CCSD(T)/cc-pVQZ Gas Phase Geometry (angstroms):

H	0.00000000	0.00000000	-2.26984000
C	0.00000000	0.00000000	-1.20647700
C	0.00000000	0.00000000	0.00000000
H	0.00000000	0.00000000	1.06336300

CCSD(T)/pcS-n energies (hartree):

acetylene_pcS-0	-76.822972730041
acetylene_pcS-1	-77.094363855241
acetylene_pcS-2	-77.185280746155
acetylene_pcS-3	-77.211153245459

CCSD(T)/pcS-n Shieldings (ppm):

Basis Set	H1	C2	C3	H4
acetylene_pcS-0	31.518	128.776	128.776	31.518
acetylene_pcS-1	30.159	126.353	126.353	30.159
acetylene_pcS-2	30.128	123.843	123.843	30.128
acetylene_pcS-3	30.033	124.035	124.035	30.033

Molecule: allene
B3LYP/MIDI! energy (hartree): -115.97856799

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	0.00000000	-0.00000100	-0.00000300	-16.7615
C	1.30619400	0.00000100	0.00000100	121.3132
H	1.88070900	-0.27669100	-0.88549700	26.8703
H	1.88070400	0.27668700	0.88550400	26.8699
C	-1.30619400	0.00000000	0.00000100	121.2997
H	-1.88070400	0.88550200	-0.27668700	26.8701
H	-1.88070600	-0.88550100	0.27669000	26.8698

CCSD(T)/cc-pVQZ/gas phase Energy (hartree): -0.11646678924D+03

CCSD(T)/cc-pVQZ Gas Phase Geometry (angstroms):

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.31049900
C	0.00000000	0.00000000	-1.31049900
H	0.00000000	0.92899400	1.86608500
H	0.00000000	-0.92899400	1.86608500
H	0.92899400	0.00000000	-1.86608500
H	-0.92899400	0.00000000	-1.86608500

CCSD(T)/pcS-n energies (hartree):

allene_pcS-0	-115.868536912929
allene_pcS-1	-116.286091832636
allene_pcS-2	-116.430117466884
allene_pcS-3	-116.469733543883

CCSD(T)/pcS-n Shieldings (ppm):

Basis Set	C1	C2	C3	H4	H5	H6	H7
allene_pcS-0	-10.389	124.730	124.730	28.382	28.382	28.382	28.382
allene_pcS-1	-18.029	121.454	121.454	27.032	27.032	27.032	27.032
allene_pcS-2	-24.123	119.485	119.485	26.864	26.864	26.864	26.864
allene_pcS-3	-23.083	119.685	119.685	26.751	26.751	26.751	26.751

Molecule: CH_3CN
B3LYP/MIDI! energy (hartree): -131.99933612

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	0.00000000	0.00000000	-1.18126100	190.8274
H	0.00000000	1.02889100	-1.56828900	29.7751
H	-0.89104500	-0.51444500	-1.56828900	29.7743
H	0.89104500	-0.51444500	-1.56828900	29.7743
C	0.00000000	0.00000000	0.28435300	86.0972
N	0.00000000	0.00000000	1.44090200	-5.1183

CCSD(T)/cc-pVQZ/gas phase Energy (hartree): -0.13256577975D+03

CCSD(T)/cc-pVQZ Gas Phase Geometry (angstroms):

C	0.00000000	0.00000000	-1.18303100
C	0.00000000	0.00000000	0.28041300
H	0.00000000	1.02367300	-1.55221000
H	0.88652700	-0.51183700	-1.55221000
H	-0.88652700	-0.51183700	-1.55221000
N	0.00000000	0.00000000	1.43890500

CCSD(T)/pcS-n energies (hartree):

CH3CN_pcS-0	-131.870857279842
CH3CN_pcS-1	-132.371556136135
CH3CN_pcS-2	-132.525148633087
CH3CN_pcS-3	-132.569751834419

CCSD(T)/pcS-n Shieldings (ppm):

Basis Set	C1	C2	H3	H4	H5	N6
CH3CN_pcS-0	199.528	77.093	31.353	31.353	31.353	-21.848
CH3CN_pcS-1	193.334	81.525	30.073	30.073	30.073	-1.945
CH3CN_pcS-2	192.059	76.787	29.967	29.967	29.967	-4.178
CH3CN_pcS-3	191.560	77.910	29.807	29.807	29.807	-2.240

Molecule: CH_3NH_2
B3LYP/MIDI! energy (hartree): -95.29880355

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	-0.71389000	-0.00000200	0.01808000	159.8386
H	-1.11688500	0.88751000	-0.49018000	29.0789
H	-1.09572200	-0.00029200	1.05840800	28.8022
H	-1.11695800	-0.88718700	-0.49069700	29.0787
N	0.76540600	-0.00000300	-0.13860100	238.1187
H	1.12752200	0.81319300	0.39210300	31.1950
H	1.12753900	-0.81319500	0.39209300	31.1952

CCSD(T)/cc-pVQZ/gas phase Energy (hartree): -0.95727787084D+02

CCSD(T)/cc-pVQZ Gas Phase Geometry (angstroms):

C	-0.02422900	0.70678900	0.00000000
H	0.98254800	1.12909100	0.00000000
H	-0.54495800	1.08407800	0.88228900
H	-0.54495800	1.08407800	-0.88228900
N	-0.08114400	-0.75735300	0.00000000
H	0.41037500	-1.11825500	0.80761000
H	0.41037500	-1.11825500	-0.80761000

CCSD(T)/pcS-n energies (hartree):

CH3NH2_pcS-0	-95.180246709763
CH3NH2_pcS-1	-95.566621470001
CH3NH2_pcS-2	-95.696072105869
CH3NH2_pcS-3	-95.731855168877

CCSD(T)/pcS-n Shieldings (ppm):

Basis Set	C1	H2	H3	H4	N5	H6	H7
CH3NH2_pcS-0	175.121	30.887	30.455	30.455	266.860	33.704	33.704
CH3NH2_pcS-1	165.786	29.421	29.346	29.346	261.737	31.811	31.811
CH3NH2_pcS-2	163.644	29.168	29.217	29.217	256.266	31.409	31.409
CH3NH2_pcS-3	163.413	29.013	29.131	29.131	255.581	31.210	31.210

Molecule: CH_3OH
B3LYP/MIDI! energy (hartree): -115.04813370

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	0.66983900	-0.01836700	0.00000100	140.5270
H	1.07812800	1.00079400	-0.00093900	28.0172
H	1.05324800	-0.54216500	-0.89621800	27.8788
H	1.05340800	-0.54057200	0.89709000	27.8784
O	-0.76140100	0.12424400	0.00000400	312.3693
H	-1.11261300	-0.80181200	0.00002500	31.7549

CCSD(T)/cc-pVQZ/gas phase Energy (hartree): -0.11558893259D+03

CCSD(T)/cc-pVQZ Gas Phase Geometry (angstroms):

H	-0.98487500	1.08100800	0.00000000
C	0.01979900	0.66421300	0.00000000
O	-0.12180300	-0.74788500	0.00000000
H	0.75507900	-1.13276500	0.00000000
H	0.54271400	1.02478000	0.88985100
H	0.54271400	1.02478000	-0.88985100

CCSD(T)/pcS-n energies (hartree):

CH3OH_pcS-0	-114.944742600581
CH3OH_pcS-1	-115.401811763479
CH3OH_pcS-2	-115.549685541209
CH3OH_pcS-3	-115.696420683738

CCSD(T)/pcS-n Shieldings (ppm):

Basis Set	H1	C2	O3	H4	H5	H6
CH3OH_pcS-0	29.331	156.509	350.683	33.879	29.714	29.714
CH3OH_pcS-1	28.304	145.393	349.003	32.185	28.343	28.343
CH3OH_pcS-2	28.257	142.255	344.112	31.802	28.172	28.172
CH3OH_pcS-3	28.135	141.067	343.200	31.592	28.002	28.002

Note: the hydroxyl proton in methanol has an unusually large error bar and was therefore ignored. A detailed coupled-cluster analysis of methanol has been performed: Auer, A.A. *Chem. Phys. Lett.* **467**, 230–232 (2009).

Molecule: dimethyl ether
B3LYP/MIDI! energy (hartree): -154.13404516

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

O	0.00000000	0.00000000	0.61163100	312.6369
C	0.00000000	1.17392100	-0.20395800	131.9721
H	0.00000000	2.03106700	0.48110700	27.9085
H	0.89697900	1.23120000	-0.85194000	28.4287
H	-0.89697900	1.23120000	-0.85194000	28.4287
C	0.00000000	-1.17392100	-0.20395800	131.9721
H	0.89697900	-1.23120000	-0.85194000	28.4287
H	0.00000000	-2.03106700	0.48110700	27.9085
H	-0.89697900	-1.23120000	-0.85194000	28.4287

CCSD(T)/cc-pVQZ/gas phase Energy (hartree): -0.15482570954D+03

CCSD(T)/cc-pVQZ Gas Phase Geometry (angstroms):

C	0.00000000	1.16123400	-0.19840500
O	0.00000000	0.00000000	0.59897000
C	0.00000000	-1.16123400	-0.19840500
H	0.00000000	2.01891800	0.47072900
H	0.88976700	1.20423900	-0.83809100
H	-0.88976700	1.20423900	-0.83809100
H	0.00000000	-2.01891800	0.47072900
H	-0.88976700	-1.20423900	-0.83809100
H	0.88976700	-1.20423900	-0.83809100

CCSD(T)/pcS-n energies (hartree):

dimethyl_ether_pcS-0	-153.979919407210
dimethyl_ether_pcS-1	-154.578040135866
dimethyl_ether_pcS-2	-154.773522193715
dimethyl_ether_pcS-3	-154.831826267198

CCSD(T)/pcS-n Shieldings (ppm):

Basis Set	C1	O2	C3	H4	H5	H6	H7	H8	H9
dimethyl_ether_pcS-0	146.884	353.076	146.884	29.342	30.288	30.288	29.342	30.288	30.288
dimethyl_ether_pcS-1	136.582	351.792	136.582	28.137	28.853	28.853	28.137	28.853	28.853
dimethyl_ether_pcS-2	132.865	348.570	132.865	27.996	28.576	28.576	27.996	28.576	28.576
dimethyl_ether_pcS-3	132.753	348.096	132.753	27.898	28.436	28.436	27.898	28.436	28.436

Molecule: **ethane**
B3LYP/MIDI! energy (hartree): -79.36287752

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	0.00000000	0.00000000	0.77213500	181.8097
H	0.00000000	1.02676100	1.16653100	30.4711
H	0.88920100	-0.51338100	1.16653100	30.4704
H	-0.88920100	-0.51338100	1.16653100	30.4704
C	0.00000000	0.00000000	-0.77213500	181.8097
H	0.88920100	0.51338100	-1.16653100	30.4704
H	0.00000000	-1.02676100	-1.16653100	30.4711
H	-0.88920100	0.51338100	-1.16653100	30.4704

CCSD(T)/cc-pVQZ/gas phase Energy (hartree): -0.79698716950D+02

CCSD(T)/cc-pVQZ Gas Phase Geometry (angstroms):

C	0.00000000	0.00000000	0.76324400
C	0.00000000	0.00000000	-0.76324400
H	0.00000000	1.01692500	1.15784300
H	-0.88068300	-0.50846200	1.15784300
H	0.88068300	-0.50846200	1.15784300
H	0.00000000	-1.01692500	-1.15784300
H	-0.88068300	0.50846200	-1.15784300
H	0.88068300	0.50846200	-1.15784300

CCSD(T)/pcS-n energies (hartree):

ethane_pcS-0	-79.247095407310
ethane_pcS-1	-79.560987165872
ethane_pcS-2	-79.671588687560
ethane_pcS-3	-79.701064098900

CCSD(T)/pcS-n Shieldings (ppm):

Basis Set	C1	C2	H3	H4	H5	H6	H7	H8
ethane_pcS-0	195.925	195.925	31.981	31.981	31.981	31.981	31.981	31.981
ethane_pcS-1	187.358	187.358	30.816	30.816	30.816	30.816	30.816	30.816
ethane_pcS-2	185.694	185.694	30.719	30.719	30.719	30.719	30.719	30.719
ethane_pcS-3	185.605	185.605	30.631	30.631	30.631	30.631	30.631	30.631

Molecule: ethylene
B3LYP/MIDI! energy (hartree): -78.13039452

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	0.00000000	0.66481100	0.00000000	72.3879
H	0.92477200	1.24204400	0.00000000	25.9183
H	-0.92474200	1.24207700	0.00000000	25.9182
C	0.00000000	-0.66481100	0.00000000	72.3879
H	-0.92477200	-1.24204400	0.00000000	25.9183
H	0.92474200	-1.24207700	0.00000000	25.9182

CCSD(T)/cc-pVQZ/gas phase Energy (hartree): -0.78461737034D+02

CCSD(T)/cc-pVQZ Gas Phase Geometry (angstroms):

C	0.00000000	0.00000000	0.66712400
C	0.00000000	0.00000000	-0.66712400
H	0.00000000	0.92343300	1.23166400
H	0.00000000	-0.92343300	1.23166400
H	0.00000000	0.92343300	-1.23166400
H	0.00000000	-0.92343300	-1.23166400

CCSD(T)/pcS-n energies (hartree):

ethylene_pcS-0	-78.041525248399
ethylene_pcS-1	-78.334871902859
ethylene_pcS-2	-78.435743319388
ethylene_pcS-3	-78.464041059656

CCSD(T)/pcS-n Shieldings (ppm):

Basis Set	C1	C2	H3	H4	H5	H6
ethylene_pcS-0	80.984	80.984	27.601	27.601	27.601	27.601
ethylene_pcS-1	76.053	76.053	26.398	26.398	26.398	26.398
ethylene_pcS-2	71.517	71.517	26.153	26.153	26.153	26.153
ethylene_pcS-3	71.536	71.536	26.036	26.036	26.036	26.036

Molecule: CH_3F
B3LYP/MIDI! energy (hartree): -138.93897997

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	0.00000000	0.00000000	-0.62962200	124.7747
H	0.00000000	1.03404500	-1.01253200	27.2146
H	-0.89550900	-0.51702200	-1.01253200	27.2141
H	0.89550900	-0.51702200	-1.01253200	27.2141
F	0.00000000	0.00000000	0.75725800	451.5024

CCSD(T)/cc-pVQZ/gas phase Energy (hartree): -0.13960341413D+03

CCSD(T)/cc-pVQZ Gas Phase Geometry (angstroms):

C	0.00000000	0.00000000	-0.63236900
F	0.00000000	0.00000000	0.74999400
H	0.00000000	1.03005900	-0.98524400
H	0.89205700	-0.51503000	-0.98524400
H	-0.89205700	-0.51503000	-0.98524400

CCSD(T)/pcS-n energies (hartree):

CH3F_pcS-0	-138.870194630664
CH3F_pcS-1	-139.390090921503
CH3F_pcS-2	-139.555830757978
CH3F_pcS-3	-139.607499335479

CCSD(T)/pcS-n Shieldings (ppm):

Basis Set	C1	F2	H3	H4	H5
CH3F_pcS-0	139.751	457.427	28.817	28.817	28.817
CH3F_pcS-1	126.930	472.405	27.549	27.549	27.549
CH3F_pcS-2	122.815	480.144	27.465	27.465	27.465
CH3F_pcS-3	122.503	480.810	27.307	27.307	27.307

Molecule: water
B3LYP/MIDI! energy (hartree): -75.96706387

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

O	0.00000000	0.00000000	0.12677900	324.1066
H	0.00000000	0.76184900	-0.50711600	30.9619
H	0.00000000	-0.76184900	-0.50711600	30.9619

CCSD(T)/cc-pVQZ/gas phase Energy (hartree): -0.76359797391D+02

CCSD(T)/cc-pVQZ Gas Phase Geometry (angstroms):

O	0.00000000	0.00000000	0.11779600
H	0.00000000	0.75541800	-0.47118300
H	0.00000000	-0.75541800	-0.47118300

CCSD(T)/pcS-n energies (hartree):

water_pcS-0	-75.915470184734
water_pcS-1	-76.233036912382
water_pcS-2	-76.333642594011
water_pcS-3	-76.364616876634

CCSD(T)/pcS-n Shieldings (ppm):

Basis Set	O1	H2	H3
water_pcS-0	354.912	32.340	32.340
water_pcS-1	347.947	31.056	31.056
water_pcS-2	339.167	30.890	30.890
water_pcS-3	337.647	30.694	30.694

Molecule: ammonia
B3LYP/MIDI! energy (hartree): -56.59201069

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

N	0.00000000	0.00000000	0.13510300	264.1257
H	0.00000000	0.93593600	-0.31524000	31.5293
H	-0.81054400	-0.46796800	-0.31524000	31.5294
H	0.81054400	-0.46796800	-0.31524000	31.5294

CCSD(T)/cc-pVQZ/gas phase Energy (hartree): -0.56493053020D+02

CCSD(T)/cc-pVQZ Gas Phase Geometry (angstroms):

N	0.00000000	0.00000000	0.11665900
H	0.00000000	0.93476600	-0.27220500
H	0.80953100	-0.46738300	-0.27220500
H	-0.80953100	-0.46738300	-0.27220500

CCSD(T)/pcS-n energies (hartree):

NH3_pcS-0	-56.151305151440
NH3_pcS-1	-56.393297725966
NH3_pcS-2	-56.474150464284
NH3_pcS-3	-56.496273189977
NH3_pcS-4	-56.500062254857

CCSD(T)/pcS-n Shieldings (ppm):

Basis Set	N1	H2	H3	H4
NH3_pcS-0	281.604	33.389	33.389	33.389
NH3_pcS-1	278.482	31.886	31.886	31.886
NH3_pcS-2	271.568	31.609	31.609	31.609
NH3_pcS-3	270.295	31.429	31.429	31.429
NH3_pcS-4	270.342	31.405	31.405	31.405

2. Performance of Optimally Scaled DFT Methods

Table S7. Linear scaling of DFT methods to experiment for proton set.

Method name					B3LYP	M06-2X	MPW1-PW91	PBE0	PBE0/PBE0	Tantillo E (gas)
Geometry method					B3LYP /cc-pVQZ	B3LYP /cc-pVQZ	B3LYP /cc-pVQZ	B3LYP/cc-pVQZ	PBE0 /cc-pVTZ	M06-2X /6-31+G(d,p)
NMR method					B3LYP /pcS-3	M06-2X /pcS-3	MPW1PW91 /pcS-3	PBE0 /pcS-3	PBE0 /cc-pVTZ	MPW1PW91 /6-311+G(2d,p)
Optimal scaling to experiment				**RMSE**	0.105	0.210	0.108	0.106	0.0952	0.1346
				MAE	0.0786	0.167	0.0883	0.085	0.0776	0.0992
				Slope	1.0411	1.0737	1.049	1.0559	1.0763	1.0965
				Intercept	-1.1468	-2.0816	-1.4253	-1.6702	-2.2204	-2.4463
	Molecule	*Desc.*	*Exp.*	*Dyn.corr.*			*Prediction*			
	acetylene		29.32	-0.72	29.57	29.57	29.51	29.51	29.49	29.25
	allene		26.28	-0.44	26.43	26.25	26.37	26.38	26.35	26.38
	MeCN		29.22	-0.64	29.15	29.23	29.14	29.15	29.06	29.06
	methyl amine	methyl	28.31	-0.76	28.29	28.45	28.35	28.34	28.26	28.22
		amino	30.47	-0.76	30.46	30.51	30.48	30.47	30.43	30.53
	methanol	methyl	27.35	-0.71	27.31	27.53	27.39	27.38	27.35	27.35
	dimethyl ether		27.54	-0.74	27.57	27.72	27.61	27.60	27.56	27.55
	ethane		29.89	-0.74	29.91	29.95	29.91	29.90	29.80	29.74
	methane		30.63	-0.64	30.50	30.44	30.48	30.48	30.55	30.49
	ethylene		25.46	-0.55	25.33	25.00	25.25	25.25	25.38	25.42
	methyl fluoride		26.64	-0.67	26.61	26.85	26.68	26.68	26.67	26.67
	water		30.10	-0.57	30.00	29.77	29.98	29.99	30.26	30.47
	ammonia		30.73	-0.70	30.79	30.67	30.78	30.78	30.77	30.79
							Raw prediction			
	acetylene				29.64	29.67	29.53	29.49	29.53	29.62
	allene				26.36	26.10	26.24	26.18	26.14	26.48
	MeCN				29.20	29.30	29.15	29.11	29.05	29.42
	methyl amine	methyl			28.31	28.46	28.32	28.26	28.20	28.50
		amino			30.57	30.68	30.55	30.51	30.53	31.03
	methanol	methyl			27.29	27.47	27.31	27.25	27.22	27.54
	dimethyl ether				27.55	27.68	27.53	27.48	27.45	27.76
	ethane				29.99	30.08	29.95	29.91	29.85	30.17
	methane				30.60	30.60	30.54	30.51	30.66	30.98
	ethylene				25.23	24.76	25.06	24.99	25.10	25.43
	methyl fluoride				26.56	26.74	26.56	26.50	26.48	26.80
	water				30.09	29.88	30.02	30.00	30.35	30.96
	ammonia				30.91	30.85	30.86	30.84	30.89	31.32

V. Carbon Shieldings

1. Complete Basis Set Extrapolation Procedure

CCSD(T) carbon stationary shieldings were taken from reference 5 in the manuscript. For shieldings that were not converged with respect to basis set, an ordinal extrapolation procedure was used (tzp=3, qz2p=4, etc.). The results are comparable to those obtained by Teale, A.M.; Lutnaes, O.B., Helgaker, T., Tozer, D.J., Gauss, J. "Benchmarking density-functional theory calculations of NMR shielding constants and spin-rotation constants using accurate coupled-cluster calculations." *J. Chem. Phys.* **138**, 024111 (2013).

Shieldings were assumed to fit a first-order exponential decay of the form $y = a + be^{-cx}$, where y is the shielding and x is the basis set ordinal. The parameters a, b, and c are to be estimated, where a is the shielding in the complete basis set limit. Observations of x and y are $(x_1, y_1),(x_2, y_2),\ldots,(x_n, y_n)$, where $x_1, x_2, \ldots, x_n$ are always positive.

Let $\hat{a}$, $\hat{b}$, and $\hat{c}$ be the fitted values of the three parameters. We assume the shieldings are variational by demanding that the fit satisfy $y_n = \hat{a} + \hat{b}e^{-\hat{c}x_n}$. That is, the best observation n is required to be fitted perfectly. For each of the remaining observations, the square deviation is

$$\left[y_i - \left(\hat{a} + \hat{b}e^{-\hat{c}x_i} \right) \right]^2,$$

for $i = 1,2,\ldots,n-1$. To minimize the sum of squared errors subject to the above constraint, the Lagrangian is

$$L = \sum_{i=1}^{n-1} \left[y_i - \left(\hat{a} + \hat{b}e^{-\hat{c}x_i} \right) \right]^2 - 2g \left[y_n - \left(\hat{a} + \hat{b}e^{-\hat{c}x_n} \right) \right],$$

where $2g$ is a Lagrange multiplier. (The use of $2g$ instead of g is for notational convenience later on.) From

$$\frac{\partial L}{\partial \hat{a}} = 0,\ \frac{\partial L}{\partial \hat{b}} = 0,\ \frac{\partial L}{\partial \hat{c}} = 0,\ \text{and}\ \frac{\partial L}{\partial g} = 0,$$

we have, respectively,

$$(n-1)\hat{a}+\left(\sum_{i=1}^{n-1}e^{-\hat{c}x_i}\right)\hat{b}+g=\sum_{i=1}^{n-1}y_i,$$

$$\left(\sum_{i=1}^{n-1}e^{-\hat{c}x_i}\right)\hat{a}+\left(\sum_{i=1}^{n-1}e^{-2\hat{c}x_i}\right)\hat{b}+\left(e^{-\hat{c}x_n}\right)g=\sum_{i=1}^{n-1}y_i e^{-\hat{c}x_i},$$

$$\left(\sum_{i=1}^{n-1}x_i e^{-\hat{c}x_i}\right)\hat{a}+\left(\sum_{i=1}^{n-1}x_i e^{-2\hat{c}x_i}\right)\hat{b}+\left(x_n e^{-\hat{c}x_n}\right)g=\sum_{i=1}^{n-1}x_i y_i e^{-\hat{c}x_i}, \text{ and}$$

$$\hat{a}+\left(e^{-\hat{c}x_n}\right)\hat{b}=y_n.$$

The first three of these four equations allow us to solve $\hat{a}$, $\hat{b}$, and g in terms of $\hat{c}$. There is a specific value of $\hat{c}$ that satisfies the fourth equation. In matrix notation, we can write

$$\begin{bmatrix} n-1 & \sum_{i=1}^{n-1}e^{-\hat{c}x_i} & 1 \\ \sum_{i=1}^{n-1}e^{-\hat{c}x_i} & \sum_{i=1}^{n-1}e^{-2\hat{c}x_i} & e^{-\hat{c}x_n} \\ \sum_{i=1}^{n-1}x_i e^{-\hat{c}x_i} & \sum_{i=1}^{n-1}x_i e^{-2\hat{c}x_i} & x_n e^{-\hat{c}x_n} \end{bmatrix}\begin{bmatrix} \hat{a} \\ \hat{b} \\ g \end{bmatrix}=\begin{bmatrix} \sum_{i=1}^{n-1}y_i \\ \sum_{i=1}^{n-1}y_i e^{-\hat{c}x_i} \\ \sum_{i=1}^{n-1}x_i y_i e^{-\hat{c}x_i} \end{bmatrix}$$

and then

$$\begin{bmatrix} \hat{a} \\ \hat{b} \\ g \end{bmatrix}=\begin{bmatrix} n-1 & \sum_{i=1}^{n-1}e^{-\hat{c}x_i} & 1 \\ \sum_{i=1}^{n-1}e^{-\hat{c}x_i} & \sum_{i=1}^{n-1}e^{-2\hat{c}x_i} & e^{-\hat{c}x_n} \\ \sum_{i=1}^{n-1}x_i e^{-\hat{c}x_i} & \sum_{i=1}^{n-1}x_i e^{-2\hat{c}x_i} & x_n e^{-\hat{c}x_n} \end{bmatrix}^{-1}\begin{bmatrix} \sum_{i=1}^{n-1}y_i \\ \sum_{i=1}^{n-1}y_i e^{-\hat{c}x_i} \\ \sum_{i=1}^{n-1}x_i y_i e^{-\hat{c}x_i} \end{bmatrix}.$$

A simple way to find $\hat{c}$ is to use *Microsoft Excel Solver* ^{TM}. We look for the value of $\hat{c}$ that makes

$$y_n-\left(\hat{a}+\hat{b}e^{-\hat{c}x_n}\right)$$

equal to zero. As $x_1, x_2, \ldots, x_n$ are always positive, we impose $\hat{c}\geq 0$ in each *Solver* search. Otherwise, erroneous results can be reached.

2. Summary of Stationary Point Geometry and Shielding Calculations

Molecule: methane
B3LYP/MIDI! energy (hartree): -40.28207750

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	0.00000000	0.00000000	0.00000000	196.9101
H	0.63390100	0.63390100	0.63390100	31.1067
H	-0.63390100	-0.63390100	0.63390100	31.1067

H -0.63390100 0.63390100 -0.63390100 31.1067
H 0.63390100 -0.63390100 -0.63390100 31.1067

Molecule: ethane
B3LYP/MIDI! energy (hartree): -79.36287752

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):
C 0.00000000 0.00000000 0.77213500 181.8097
H -1.02676100 0.00000000 1.16653100 30.4711
H 0.51338100 0.88920100 1.16653100 30.4704
H 0.51338000 -0.88920100 1.16653100 30.4704
C 0.00000000 0.00000000 -0.77213500 181.8097
H -0.51338000 0.88920100 -1.16653100 30.4704
H 1.02676100 0.00000000 -1.16653100 30.4711
H -0.51338100 -0.88920100 -1.16653100 30.4704

Molecule: ethylene
B3LYP/MIDI! energy (hartree): -78.13039452

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):
C 0.00000000 0.66481100 0.00000000 72.3879
H 0.92477200 1.24204400 0.00000000 25.9183
H -0.92474200 1.24207700 0.00000000 25.9182
C 0.00000000 -0.66481100 0.00000000 72.3879
H -0.92477200 -1.24204400 0.00000000 25.9183
H 0.92474200 -1.24207700 0.00000000 25.9182

Molecule: acetylene
B3LYP/MIDI! energy (hartree): -76.87967268

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):
C 0.00000000 0.00000000 0.60264000 127.4970
H 0.00000000 0.00000000 1.67029900 30.3000
C 0.00000000 0.00000000 -0.60264000 127.4970
H 0.00000000 0.00000000 -1.67029900 30.3000

Molecule: CH_3F
B3LYP/MIDI! energy (hartree): -138.93897997

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):
C 0.00000000 0.00000000 -0.62962200 124.7747
H 1.03404500 0.00000000 -1.01253200 27.2146
H -0.51702200 0.89550900 -1.01253200 27.2141
H -0.51702200 -0.89550900 -1.01253200 27.2141
F 0.00000000 0.00000000 0.75725800 451.5024

Molecule: CH_3OH
B3LYP/MIDI! energy (hartree): -115.04813370

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	0.66983900	-0.01836700	0.00000100	140.5270
H	1.07812800	1.00079400	-0.00093900	28.0172
H	1.05324800	-0.54216500	-0.89621800	27.8788
H	1.05340800	-0.54057200	0.89709000	27.8784
O	-0.76140100	0.12424400	0.00000400	312.3693
H	-1.11261300	-0.80181200	0.00002500	31.7549

Molecule: CH_3NH_2
B3LYP/MIDI! energy (hartree): -95.29880355

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	-0.71389000	-0.00000200	0.01808000	159.8386
H	-1.11688500	0.88751000	-0.49018000	29.0789
H	-1.09572200	-0.00029200	1.05840800	28.8022
H	-1.11695800	-0.88718700	-0.49069700	29.0787
N	0.76540600	-0.00000300	-0.13860100	238.1187
H	1.12752200	0.81319300	0.39210300	31.1950
H	1.12753900	-0.81319500	0.39209300	31.1952

Molecule: CH_3CN
B3LYP/MIDI! energy (hartree): -131.99933612

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	0.00000000	0.00000000	-1.18126100	190.8274
H	1.02889100	0.00000000	-1.56828900	29.7751
H	-0.51444500	0.89104600	-1.56828900	29.7743
H	-0.51444500	-0.89104600	-1.56828900	29.7743
C	0.00000000	0.00000000	0.28435300	86.0972
N	0.00000000	0.00000000	1.44090200	-5.1183

Molecule: acetaldehyde
B3LYP/MIDI! energy (hartree): -152.94231749

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	-1.17851200	-0.14896200	0.00000000	159.7592
H	-1.72857700	0.20586300	0.88671300	29.3571
H	-1.13214000	-1.24402700	0.00000400	29.6170
H	-1.72858100	0.20585600	-0.88671200	29.3571
C	0.23766600	0.40649100	0.00000000	-0.5281
H	0.29401500	1.52228400	-0.00000200	21.4429

Molecule: acetone
B3LYP/MIDI! energy (hartree): -192.03670539

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	0.00000000	0.19057300	-0.00000100	-8.7846
C	1.29706900	-0.62350500	0.00000000	161.9718
H	1.34886300	-1.27332700	-0.88783900	29.3296
H	2.14352600	0.07165700	0.00000000	29.7623
H	1.34886100	-1.27332300	0.88784100	29.3296

C	-1.29706700	-0.62350800	0.00000000	161.9719
H	-1.34886300	-1.27332500	-0.88784000	29.3297
H	-1.34885800	-1.27332400	0.88784200	29.3297
H	-2.14352700	0.07165200	0.00000300	29.7623
O	-0.00000200	1.41107900	0.00000000	-329.7446

Molecule: carbon monoxide
B3LYP/MIDI! energy (hartree): -112.67211576

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	0.00000000	0.00000000	-0.65283400	3.6094
O	0.00000000	0.00000000	0.48962500	-61.5547

Molecule: carbon dioxide
B3LYP/MIDI! energy (hartree): -187.52237300

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

O	0.00000000	0.00000000	-1.17193400	220.6515
C	0.00000000	0.00000000	-0.00000200	72.5595
O	0.00000000	0.00000000	1.17193500	220.6525

Molecule: HCN
B3LYP/MIDI! energy (hartree): -92.89933295

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	0.00000000	0.00000000	-0.50078000	94.6239
H	0.00000000	0.00000000	-1.57365000	29.1491
N	0.00000000	0.00000000	0.65404800	-14.6089

Molecule: allene
B3LYP/MIDI! energy (hartree): -115.97856799

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	0.00000300	0.00000100	0.00000000	-16.7615
C	-0.00845300	0.10456400	-1.30197400	121.3132
H	0.84822600	0.49680500	-1.85241100	26.8703
H	-0.87257300	-0.19568800	-1.89685100	26.8699
C	0.00845200	-0.10456600	1.30197500	121.2997
H	0.35907500	-1.00803500	1.80351000	26.8701
H	-0.33473700	0.70692000	1.94574900	26.8698

Molecule: CF_4
B3LYP/MIDI! energy (hartree): -435.04955604

B3LYP/MIDI!/gas phase Geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	0.00000000	0.00000000	0.00000000	66.6787
F	0.76906700	0.76906700	0.76906700	258.1983
F	-0.76906700	-0.76906700	0.76906700	258.1983
F	-0.76906700	0.76906700	-0.76906700	258.1983
F	0.76906700	-0.76906700	-0.76906700	258.1983

3. Performance of Optimally Scaled DFT Methods

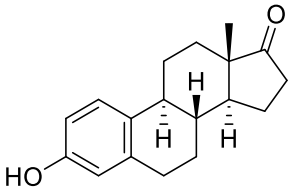
Table S8. Linear scaling of DFT methods to experiment for carbon set.

Method name (see Fig. 3)				**B3LYP /pcS-3**	**M06-2X /pcS-3**	**MPW1PW91 /pcS-3**	**PBE0 /pcS-3**	**PBE0 /cc-pVTZ**	**M06-2X /6-31+G(d,p)**
Geometry method				B3LYP /cc-pVQZ	B3LYP /cc-pVQZ	B3LYP /cc-pVQZ	B3LYP /cc-pVQZ	PBE0 /cc-pVTZ	M06-2X /6-31+G(d,p)
NMR method				B3LYP /pcS-3	M06-2X /pcS-3	MPW1PW91 /pcS-3	PBE0 /pcS-3	PBE0 /cc-pVTZ	MPW1PW91 /6-311+G(2d,p)
Optimal scaling to experiment			**RMSE**	2.8983	4.4207	2.4174	2.4429	2.9355	1.4632
			MAE	2.3358	3.4072	1.8143	1.8204	1.9974	1.1299
			Slope	1.0672	1.1771	1.0672	1.068	1.0562	1.0325
			Intercept	-24.7222	-38.5011	-20.968	-20.4058	-17.8441	-12.1363
	Molecule	*Desc.*	*Exp.*	*Dyn.corr.*			*Prediction*		
	methane		195	-4.13	193.7751	191.5382	193.2405	193.4947	194.2018	194.4575
	ethane		180.8	-5.08	178.8099	179.6085	179.5295	179.6731	178.9983	179.6561
	ethylene		64.4	-5.7	60.5141	57.2169	60.1174	59.9828	59.5151	61.6743
	acetylene		117.1	-5.29	116.8278	111.4699	115.1322	114.7332	114.5338	115.8298
	CH3F		116.7	-5.13	115.6125	121.8403	116.8265	116.797	116.7801	117.5588
	CH3OH		136.5	-5.01	134.9797	139.7938	136.3024	136.3219	135.9262	137.0562
	CH3NH2		158.2	-5.03	156.4426	159.3488	157.5645	157.6425	156.9735	157.831
	MeCN	methyl	187.6	-3.61	188.607	186.8101	188.1937	188.3628	188.1952	187.8971
	MeCN	nitrile	73.7	-1.86	76.7278	73.6998	75.4468	75.2889	73.3983	74.7029
	CH3CHO	methyl	157.1	-4.53	159.804	159.087	160.3482	160.2132	164.5244	156.2451
	CH3CHO	carbonyl	-6.8	-3.54	-10.3794	-10.1741	-10.0585	-10.1783	-0.9894	-8.0714
	acetone	methyl	157.9	-4.89	157.629	156.9424	157.8879	157.8243	157.3542	158.1578
	acetone	carbonyl	-13.2	-2.01	-14.9599	-13.8599	-13.6827	-13.4988	-14.7281	-12.3114
	CO		0.9	-2.46	2.4978	-4.4427	0.0192	0.0116	-2.4136	-1.0397
	CO2		58.7	-1.95	66.065	68.6111	65.2579	65.2278	63.5305	62.9199
	HCN		82	-2.35	85.7002	79.8989	83.3684	83.1061	81.6084	82.5671
	allene	CH2	115.1	-3.23	117.2331	113.4231	116.3755	116.5136	115.3349	115.9139
	allene	center	-29.4	-2.91	-28.7444	-27.5224	-27.0811	-26.7158	-29.4099	-30.0165
	CF4		64.4	-1.78	59.5581	73.4103	61.9117	61.8994	63.3662	65.6715
							Raw prediction			
	methane				186.1999	191.0889	189.3933	190.3829	191.4103	192.778
	ethane				171.1794	177.9964	175.7105	176.571	176.3017	178.4451
	ethylene				45.557	34.549	48.8909	49.3578	50.7184	57.2446
	acetylene				105.2436	98.0003	107.1941	107.423	108.4215	112.7521
	CH3F				103.7866	110.0473	108.8423	109.4672	110.6341	114.3774
	CH3OH				124.3349	131.0604	129.5074	130.2005	130.7371	134.3891
	CH3NH2				147.2595	154.0986	152.2189	152.9916	152.9881	155.8599
	MeCN	methyl			180.1646	185.0034	183.4872	184.3819	184.5458	185.4842
	MeCN	nitrile			59.0198	50.1111	61.4108	61.8652	61.5424	66.8571
	CH3CHO	methyl			150.3467	153.2905	154.6897	155.2372	160.4637	153.7224
	CH3CHO	carbonyl			-32.2589	-46.937	-28.1626	-27.7366	-15.3491	-16.9303
	acetone	methyl			148.3856	151.1261	152.4241	153.0458	153.2503	156.0573
	acetone	carbonyl			-38.6771	-52.8056	-33.5605	-32.813	-31.3905	-22.8382
	CO				-19.5966	-41.2706	-18.4875	-17.9334	-17.9334	-10.7498
	CO2				47.7308	44.2112	50.6269	51.2096	51.2096	54.7808
	HCN				69.085	57.898	70.3549	70.7043	70.7043	75.4672
	allene	CH2			103.6161	98.2394	106.4609	107.2646	107.2077	110.779
	allene	center			-52.4875	-67.9878	-46.9596	-46.0292	-45.9981	-40.2194
	CF4				40.6168	49.6903	46.8858	47.4848	50.8661	57.4519

VI. Natural Products

1. Summary of Stationary Point Calculations and Resonance Assignments

Natural Product: estrone

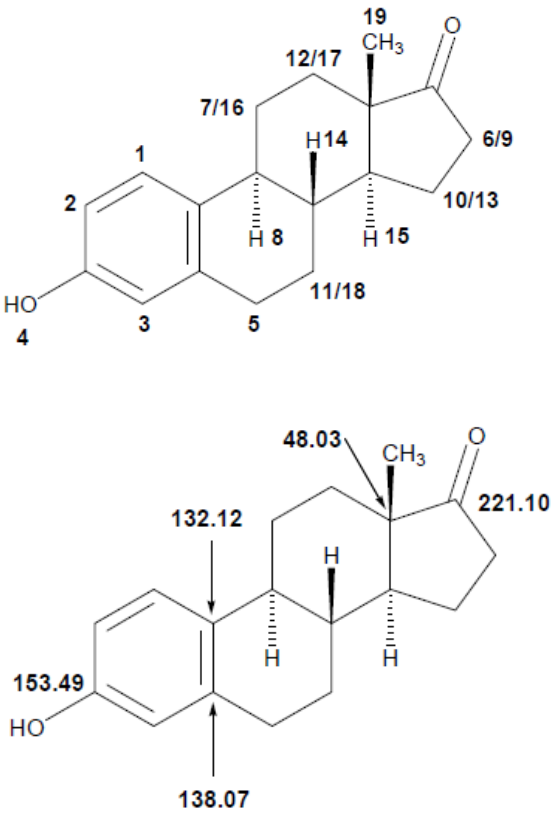


estrone

NMR data were obtained at 500 MHz in $CDCl_3$. Resonances were assigned by 2D NMR methods.

Table S9. NMR Assignments for Estrone.

#	δ ^{1}H	δ ^{13}C	Hs	Type	*J* (Hz)
1	7.15	126.55	1	d	8.3
2	6.64	122.83	1	dd	8.3, 2.4
3	6.59	115.28	1	d	2.4
4	4.74	---	1	OH	---
5	2.87	29.47	2	m	---
6	2.51	35.89	1	dd	18.8, 8.5
7	2.38	25.93	1	m	---
8	2.25	43.97	1	m	---
9	2.15	35.89	1	m	---
10	2.06	21.59	1	m	---
11	2.00	26.50	1	m	---
12	1.95	31.57	1	m	---
13	1.64	21.59	1	m	---
14	1.59	38.35	1	m	---
15	1.53	50.41	1	m	---
16	1.52	25.93	1	m	---
17	1.49	31.57	1	m	---
18	1.44	26.50	1	m	---
19	0.91	13.86	3	m	---
Quaternary carbons: 221.10, 153.49, 138.07, 132.12, 38.03					



B3LYP/MIDI!/gas phase energy (hartree): -844.68347498

B3LYP/MIDI!/gas phase geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

H	6.33247300	-0.99674500	0.22103500	27.8490
O	5.94136300	-0.09140200	0.31714100	211.9122
C	4.58377900	-0.23014200	0.11320200	37.8603
C	3.96855800	-1.45351900	-0.16612200	83.1735

C	3.79931000	0.92052700	0.18780200	78.7870
C	2.59123400	-1.50275900	-0.35806500	67.3840
H	4.56668700	-2.36185500	-0.23560900	25.4517
C	2.41790300	0.87199800	-0.00399600	55.0243
H	4.29479700	1.86659400	0.39711600	25.0567
C	1.78590500	-0.35873700	-0.27582500	61.8034
H	2.13991200	-2.46515300	-0.58361800	24.5277
C	1.63663100	2.17554000	0.10758100	157.8812
C	0.27727200	-0.44050600	-0.53191100	141.6195
C	0.21145300	2.07814900	-0.46963700	160.7215
H	1.56709400	2.45931200	1.17233100	28.6578
H	2.19685700	2.98009900	-0.39187100	28.7692
C	-0.46812900	0.80061700	0.05773400	148.5361
C	-0.36554700	-1.77495900	-0.04565300	161.5405
H	0.11679400	-0.39299500	-1.62628000	29.4037
H	-0.36265100	2.97082400	-0.18222300	29.6802
H	0.24358300	2.04589300	-1.57099700	30.1905
C	-1.94516300	0.68520000	-0.32442500	137.7690
H	-0.36902200	0.78976700	1.15529400	30.0856
C	-1.89672800	-1.83321400	-0.31336400	156.1145
H	-0.15661100	-1.90521300	1.02663700	30.1177
H	0.10169100	-2.62248900	-0.56433000	29.2819
C	-2.58848100	-0.59654000	0.26490000	138.1792
C	-2.95895600	1.81021000	0.02547200	166.7297
H	-1.98267000	0.57107100	-1.42540300	30.2671
H	-2.32720300	-2.75051800	0.11351900	29.5787
H	-2.07702900	-1.87008700	-1.39976600	30.1596
C	-4.05739100	-0.41778900	-0.16008600	-25.7342
C	-2.59912800	-0.63835200	1.81874600	176.2870
C	-4.33858100	1.11732300	-0.20879600	154.2854
H	-2.84663300	2.13089100	1.07026000	29.9288
H	-2.83176000	2.69320800	-0.61181400	29.5921
O	-4.84630100	-1.30538100	-0.42117800	-260.9447
H	-3.16914100	-1.52254300	2.14125900	30.9792
H	-1.58560300	-0.71308900	2.23098400	30.1748
H	-3.07731600	0.25113000	2.25164300	30.5737
H	-4.75696300	1.35591800	-1.19735100	29.5357
H	-5.10142400	1.38196400	0.53613800	29.1639

PBE0/cc-pVTZ/pcm=chloroform energy (hartree): -849.01507518

PBE0/cc-pVTZ/pcm=chloroform geometry (angstroms) and shieldings (ppm):

H	6.30418000	-0.95681300	0.23370200	26.9117
O	5.89075400	-0.09277100	0.30750500	216.0872
C	4.55207800	-0.22150400	0.11371100	19.5796
C	3.94441300	-1.44226100	-0.14884200	66.5906
C	3.77262800	0.92205400	0.18076100	62.3834
C	2.57313800	-1.49256300	-0.33511400	48.8777
H	4.53885200	-2.34817900	-0.20955300	24.7099
C	2.39547500	0.86986500	-0.00625600	34.8051

H	4.25669500	1.87182100	0.38110100	24.4724
C	1.76776000	-0.35655800	-0.26696100	43.7372
H	2.12689000	-2.45660200	-0.54375300	23.8706
C	1.61572300	2.15506800	0.10290800	150.7455
C	0.27286700	-0.43496700	-0.52156800	136.0097
C	0.20437600	2.05519800	-0.44565100	154.8482
H	1.56707300	2.43875800	1.16119700	28.4472
H	2.16884700	2.95629600	-0.39407700	28.4772
C	-0.46261800	0.78590000	0.05615600	142.6742
C	-0.36522400	-1.75541100	-0.07330000	155.7745
H	0.12816500	-0.37465900	-1.61196300	29.2056
H	-0.36673600	2.93875700	-0.15031000	29.4250
H	0.22235400	2.04141500	-1.54169500	30.1033
C	-1.92889300	0.67537600	-0.31036400	130.5056
H	-0.36497200	0.76851500	1.14986000	29.9138
C	-1.87009600	-1.81722600	-0.34499400	149.5465
H	-0.16465200	-1.90841100	0.99188600	30.0150
H	0.10590000	-2.59251800	-0.59144200	28.9965
C	-2.57195200	-0.60516000	0.24152800	131.8373
C	-2.92215500	1.78000900	0.05062100	160.6888
H	-1.96866500	0.57711500	-1.40714600	29.9601
H	-2.28760000	-2.74361800	0.05731200	29.5456
H	-2.04315400	-1.83845500	-1.42628700	30.0785
C	-4.02025300	-0.39020100	-0.15499800	-53.9985
C	-2.59859100	-0.67337800	1.77880800	170.3022
C	-4.27566900	1.11065000	-0.21604000	145.1192
H	-2.82347600	2.07097600	1.09906600	29.7727
H	-2.78398100	2.68009800	-0.54828400	29.3787
O	-4.83615300	-1.24824800	-0.38560900	-254.2880
H	-3.13257900	-1.57417500	2.08776100	31.1124
H	-1.59352900	-0.71726400	2.19704200	30.1330
H	-3.10537600	0.18282600	2.22709300	30.5156
H	-4.64903400	1.33626600	-1.21890100	29.2915
H	-5.07006200	1.38668100	0.47979800	28.9554

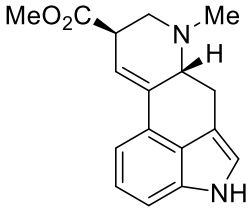
Proton Assignments (atom numbers followed by $CDCl_3$ shift in ppm):

7 6.64
9 6.59
11 7.15
15 16 2.87
19 2.25
20 2.00
21 1.44
23 1.59
25 1.52
26 2.38
29 1.53
30 1.95
31 1.49
35 1.64

36 2.06
38 39 40 0.91
41 2.15
42 2.51

Carbon Assignments (atom numbers followed by $CDCl_3$ shift in ppm):
3 153.49
4 112.83
5 115.28
6 126.55
8 138.07
10 132.12
12 29.47
13 43.97
14 26.50
17 38.35
18 26.22
22 50.41
24 31.57
27 48.03
28 21.59
32 221.10
33 13.86
34 35.89

Natural Product: lysergic acid methyl ester



lysergic acid methyl ester

Reference: Moldvai, I.; Gacs-Baitz, E.; Termesvari-Major, E.; Russo, L.; Papai, I.; Rissanen, K.; Szarics, E.; Kardos, J.; Szantay, C. Heterocycles 2007, 71, 1075-1094.

B3LYP/MIDI!/gas phase energy (hartree): -913.28287596

B3LYP/MIDI!/gas phase geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	3.65873500	-0.97098900	0.07338000	60.5481
C	1.21167700	-2.28775700	0.36541400	80.1323
C	2.43663100	-2.97864800	0.48424200	70.1926
C	3.67281100	-2.34580100	0.34627900	85.5486
N	4.63889700	-0.01354400	-0.13966300	128.9838
C	4.03746400	1.22955700	-0.39448600	76.5341
C	2.43036700	-0.29015500	-0.04978600	68.0261
C	2.67314400	1.07862600	-0.34970700	79.5949
C	1.19150600	-0.91964100	0.09073000	63.8633
C	0.00609400	-0.05169700	-0.05233100	53.2716
C	0.25209500	1.44264200	0.24626900	123.6069
C	1.49223600	1.98025400	-0.56358300	159.8491
N	-0.92836200	2.27841000	-0.08708900	200.8210
C	-0.83137900	3.60364200	0.55134400	146.3887
C	-2.18806200	1.63600700	0.33540400	133.9256
C	-2.41039200	0.37079600	-0.50437700	145.0640
C	-1.19309300	-0.51637500	-0.42227000	71.6134
C	-3.67048500	-0.35291000	-0.03263700	19.5467
O	-4.46147300	0.07446700	0.78952500	-84.0321
H	0.27941200	-2.82861300	0.51347300	24.5244
H	2.41568900	-4.04420500	0.70389000	24.4454
H	4.60109900	-2.90330200	0.44987400	24.6679
H	5.64461500	-0.17788300	-0.11500900	24.5284
H	4.64924100	2.10153400	-0.58971400	24.9119
H	1.18132300	2.00907900	-1.62022200	28.9569
H	1.71326100	3.00990500	-0.25652500	28.1859
H	0.50437100	1.52074000	1.32757400	28.6275
H	-3.01019600	2.34234600	0.16579600	28.6136
H	-2.20044300	1.36728300	1.41122300	28.9395
H	-2.57882500	0.66563100	-1.55506000	28.0523
H	-1.33090100	-1.56516400	-0.67759100	24.9684
H	-1.72061100	4.18837700	0.27796100	29.1355

H	-0.77380000	3.55143600	1.66055300	29.4191
H	0.05087300	4.14109900	0.18450300	28.4867
O	-3.81188200	-1.55368800	-0.67164000	145.6801
C	-4.99746200	-2.28908300	-0.25102400	139.7595
H	-4.97274500	-3.21887000	-0.82659400	27.9184
H	-4.96410900	-2.49463500	0.82642500	27.6409
H	-5.90648200	-1.71586100	-0.47355400	27.6345

PBE0/cc-pVTZ/pcm=chloroform energy (hartree): -917.85761903

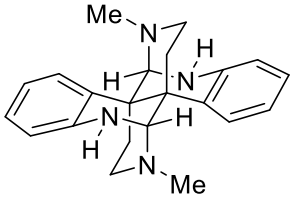
PBE0/cc-pVTZ/pcm=chloroform geometry (angstroms) and shieldings (ppm):

C	3.63770800	-0.97062200	0.07624100	52.4565
C	1.19901100	-2.28931000	0.29816300	73.2527
C	2.41889200	-2.97345800	0.41489600	62.0116
C	3.65188100	-2.34339600	0.31114800	76.5692
N	4.61047600	-0.02069400	-0.08726300	122.0344
C	4.02272800	1.21053200	-0.31081000	67.8331
C	2.41611300	-0.29440900	-0.04918700	58.5607
C	2.66341900	1.07422000	-0.30027200	74.0069
C	1.17876800	-0.92216700	0.05579000	55.8743
C	0.00636800	-0.04477100	-0.07676300	43.8160
C	0.25038700	1.43174800	0.21605200	123.1134
C	1.50012900	1.97880900	-0.51356500	158.8504
N	-0.91451900	2.24454300	-0.11346300	208.7695
C	-0.81505400	3.58599200	0.42481000	144.8054
C	-2.15602500	1.63045700	0.31678400	132.9626
C	-2.40795400	0.36158400	-0.46948200	143.2252
C	-1.19424200	-0.51092600	-0.42373900	63.7449
C	-3.63978000	-0.35923200	0.03093900	9.4787
O	-4.35219100	0.02006100	0.92588800	-70.0251
H	0.27435400	-2.84025300	0.42414800	24.0505
H	2.39667300	-4.03969300	0.60784300	24.0372
H	4.57303900	-2.90362400	0.41522300	24.0887
H	5.60026800	-0.18126900	-0.04944000	23.6215
H	4.64063300	2.08175900	-0.46362300	24.4748
H	1.25316700	2.05507500	-1.57838800	28.9706
H	1.71777900	2.98780100	-0.16353800	27.8376
H	0.46321000	1.49825400	1.30264500	28.5440
H	-2.96745500	2.34036500	0.15092200	28.5200
H	-2.15178400	1.39527100	1.39429000	28.9353
H	-2.62448300	0.61762700	-1.51597000	27.8175
H	-1.31762900	-1.55870200	-0.67211600	24.6089
H	-1.71805700	4.14229300	0.17023900	29.0853
H	-0.70711600	3.59584600	1.52334500	29.5594
H	0.03055900	4.12151000	-0.00388200	28.3526
O	-3.86526000	-1.47566000	-0.66476500	151.2394
C	-5.01580100	-2.22673300	-0.27691200	135.9598
H	-5.04290100	-3.08963000	-0.93660400	27.8500
H	-4.93214500	-2.54527200	0.76190500	27.7930
H	-5.91949900	-1.62941200	-0.39546000	27.7426

Proton Assignments (atom numbers followed by $CDCl_3$ shift in ppm):
32 33 34 2.59
25 2.68
29 2.69
27 3.17
28 3.26
26 3.50
30 3.71
37 38 39 3.77
31 6.59
24 6.87
20 21 22 7.19

Carbon Assignments (atom numbers followed by $CDCl_3$ shift in ppm):
12 27.4
16 42.4
14 43.9
36 52.2
15 55.1
11 63.1
2 109.9
8 111.0
4 112.7
17 118.2
6 118.5
3 123.5
7 126.5
9 128.3
1 134.2
10 136.4
18 173.0

Natural Product: meso-calycanthine



***meso*-calycanthine**

Reference: Link, J.T.; Overman, L.E. J. Am. Chem. Soc. 1996, 118, 8166-8167.

B3LYP/MIDI!/gas phase energy (hartree): -1066.78462184

B3LYP/MIDI!/gas phase geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	4.67047500	-0.23274200	-0.16861200	67.5754
H	5.74385300	-0.17675900	-0.33920900	24.5695
C	3.83263900	0.71666800	-0.73967400	82.3331
H	4.24362000	1.51075700	-1.36209000	25.1731
C	2.44190400	0.66673000	-0.53161900	48.2307
C	1.88924500	-0.36184400	0.26499600	66.9161
C	2.75533200	-1.30373400	0.82358500	66.7686
H	2.34835500	-2.10358100	1.43683900	24.5795
C	4.13328100	-1.25549500	0.61561200	76.2632
H	4.77998900	-2.00723400	1.06184200	24.9086
C	0.20634100	1.74455600	-0.77257600	116.6017
H	-0.29122400	2.26329900	-1.60234000	27.5472
N	-0.05641300	2.54849700	0.43837900	193.9504
C	0.29898800	3.96042800	0.25173100	148.5644
H	-0.22843000	4.35464400	-0.62967400	29.2785
H	-0.03283500	4.52847100	1.13260400	29.3141
H	1.38859500	4.14166100	0.12317900	29.0441
C	0.60717900	1.99780100	1.63945100	143.0057
H	1.71033800	2.08191800	1.58294500	29.2030
H	0.27867600	2.60316500	2.49749600	29.3305
C	0.19245100	0.53263800	1.87027700	154.1283
H	0.80050100	0.10748100	2.68276200	30.6160
H	-0.85845300	0.49537300	2.17235400	29.1253
N	1.60851200	1.58564000	-1.18356100	183.7566
H	2.07366400	2.45134700	-1.46922600	27.1139
C	-4.67054900	0.23262200	0.16841400	67.5751
H	-5.74393600	0.17659500	0.33893600	24.5695
C	-3.83271400	-0.71675900	0.73952400	82.3332
H	-4.24370600	-1.51086900	1.36190700	25.1731
C	-2.44196700	-0.66676400	0.53156300	48.2304
C	-1.88929200	0.36184300	-0.26499400	66.9182
C	-2.75537900	1.30369800	-0.82364200	66.7699
H	-2.34839200	2.10356500	-1.43686300	24.5794
C	-4.13334100	1.25540000	-0.61576800	76.2633
H	-4.78004800	2.00711500	-1.06204000	24.9086

C	-0.39773900	0.32810800	-0.58587000	148.0858
C	0.39771800	-0.32805400	0.58596700	148.0853
C	-0.20637200	-1.74450000	0.77267300	116.6010
H	0.29115900	-2.26323100	1.60246400	27.5472
N	0.05648200	-2.54843400	-0.43826200	193.9503
C	-0.29889600	-3.96037500	-0.25163800	148.5647
H	0.22847200	-4.35457800	0.62980200	29.2786
H	0.03300000	-4.52840900	-1.13248900	29.3142
H	-1.38850700	-4.14163400	-0.12316000	29.0441
C	-0.60704200	-1.99774900	-1.63937800	143.0059
H	-1.71020200	-2.08190300	-1.58295300	29.2030
H	-0.27845800	-2.60309600	-2.49740400	29.3305
C	-0.19235200	-0.53256600	-1.87016500	154.1267
H	-0.80035300	-0.10742200	-2.68269300	30.6161
H	0.85857900	-0.49525500	-2.17215300	29.1248
N	-1.60858000	-1.58563600	1.18356400	183.7584
H	-2.07371800	-2.45136100	1.46919500	27.1139

PBE0/cc-pVTZ/pcm=chloroform energy (hartree): -1072.10898224

PBE0/cc-pVTZ/pcm=chloroform geometry (angstroms) and shieldings (ppm):

C	4.63782700	0.24054600	0.17974100	57.5804
H	5.70503900	0.19053300	0.36256900	24.2254
C	3.80345400	-0.69846300	0.75367400	74.9684
H	4.21278700	-1.48158400	1.38359500	24.8010
C	2.42188300	-0.66085100	0.52947400	39.0158
C	1.87444800	0.35349900	-0.27430900	60.6427
C	2.74016700	1.28150600	-0.83975900	57.2399
H	2.33760500	2.06778200	-1.46695200	24.1740
C	4.10955000	1.24080100	-0.62647100	69.6538
H	4.75431700	1.98267600	-1.08082100	24.6259
C	0.20885100	-1.72879200	0.75843000	115.9810
H	-0.27942300	-2.24300500	1.58941000	27.2100
N	-0.03584300	-2.52705400	-0.43204500	201.7376
C	0.30294700	-3.91865300	-0.25262800	146.5472
H	-0.20738300	-4.31757500	0.62710200	29.2682
H	-0.02847100	-4.49011400	-1.12209200	29.3707
H	1.38558300	-4.09641000	-0.13398400	29.1645
C	0.58445400	-1.97734900	-1.62603700	141.6560
H	1.68278700	-2.06747700	-1.58350200	29.4048
H	0.25789600	-2.57828100	-2.47906300	29.3313
C	0.18130900	-0.53033000	-1.85007000	152.4688
H	0.77543000	-0.11259300	-2.66725400	30.5560
H	-0.86498100	-0.49394800	-2.15213800	29.3286
N	1.60095800	-1.58598600	1.13284600	182.5192
H	2.04900700	-2.38273800	1.54942800	26.5832
C	-4.63779200	-0.24060400	-0.17983300	57.5807
H	-5.70499900	-0.19061400	-0.36269700	24.2255
C	-3.80341900	0.69841900	-0.75374400	74.9683

H	-4.21274700	1.48152900	-1.38368200	24.8010
C	-2.42185400	0.66083500	-0.52950000	39.0158
C	-1.87442700	-0.35349900	0.27431100	60.6419
C	-2.74014500	-1.28152200	0.83973400	57.2394
H	-2.33758800	-2.06778800	1.46694300	24.1740
C	-4.10952200	-1.24084500	0.62640000	69.6538
H	-4.75428900	-1.98273200	1.08073100	24.6259
C	-0.38775400	-0.32446800	0.58507600	147.7346
C	0.38776400	0.32449500	-0.58503200	147.7351
C	-0.20883800	1.72881800	-0.75838500	115.9813
H	0.27945200	2.24303700	-1.58935200	27.2100
N	0.03581000	2.52708400	0.43209800	201.7375
C	-0.30299100	3.91867900	0.25267000	146.5470
H	0.20735900	4.31760600	-0.62704500	29.2682
H	0.02839400	4.49014500	1.12214400	29.3707
H	-1.38562600	4.09642300	0.13399400	29.1645
C	-0.58451500	1.97737500	1.62607300	141.6559
H	-1.68284900	2.06748500	1.58350300	29.4047
H	-0.25799400	2.57831500	2.47910800	29.3312
C	-0.18135200	0.53036500	1.85012200	152.4695
H	-0.77549200	0.11262100	2.66728800	30.5559
H	0.86492700	0.49400500	2.15222700	29.3288
N	-1.60092900	1.58598700	-1.13284600	182.5183
H	-2.04897800	2.38273000	-1.54944500	26.5831

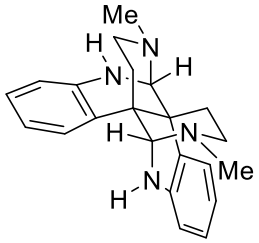
Proton Assignments (atom numbers followed by $CDCl_3$ shift in ppm):

22 49	1.14
19 46	2.11
23 50	2.11
42 43 44 15 16 17	2.27
20 47	2.33
12 39	4.25
4 29	6.54
10 35	6.63
2 27	6.97
8 33	6.97

Carbon Assignments (atom numbers followed by $CDCl_3$ shift in ppm):

21 48	34.4
36 37	37.2
14 41	42.2
18 45	46.3
11 38	71.1
3 28	112.3
34 9	117.4
32 7	126.9
1 26	126.7
31 6	124.9
30 5	145.1

Natural Product: minus-calycanthine



(–)-calycanthine

Reference: Movassaghi, M.; Schmidt, M.A. Angew. Chem. Int. Ed. 2007, 46, 3725-3728.

B3LYP/MIDI!/gas phase energy (hartree): -1066.78675301

B3LYP/MIDI!/gas phase geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	-2.71853700	2.76416000	-1.60197700	67.4267
H	-3.37514600	3.60802600	-1.80513400	24.7478
C	-2.71587200	2.18502600	-0.33963700	82.5146
H	-3.35988400	2.57670000	0.44680800	25.4771
C	-1.87676000	1.09332600	-0.04920500	48.0814
C	-1.02272400	0.58438900	-1.05615100	66.7988
C	-1.04501600	1.18787900	-2.31460500	68.5205
H	-0.39141300	0.80885200	-3.09648900	24.5976
C	-1.87768900	2.26926600	-2.60083800	77.1567
H	-1.86951300	2.72032100	-3.59023500	25.0794
C	1.15740400	-0.68922300	-1.53153900	117.0940
H	0.97218200	-0.71509000	-2.61384200	27.5803
C	-0.18900000	-0.66018100	-0.75764600	149.1695
N	1.86707800	-1.95466800	-1.22712000	195.2556
C	3.03330900	-2.14706700	-2.09947000	148.0891
H	2.71383000	-2.09281500	-3.15071500	29.2350
H	3.45171800	-3.14742400	-1.91806900	29.1343
H	3.84434200	-1.40501100	-1.93609400	29.0195
C	2.25841100	-2.05657100	0.19563800	143.0820
H	3.02504000	-1.30511100	0.46890400	29.0962
H	2.70955200	-3.04991300	0.33854400	29.0931
C	1.02773200	-1.92016500	1.10950300	156.1259
H	1.36381500	-1.83138900	2.15371800	30.5625
H	0.38616500	-2.80397100	1.04013100	28.2184
C	0.18885200	-0.66028000	0.75750200	149.1702
C	-1.15754000	-0.68938000	1.53140000	117.0967
H	-0.97231500	-0.71530900	2.61369900	27.5801
N	-1.86719200	-1.95481400	1.22687700	195.2567
C	-3.03338800	-2.14732900	2.09922300	148.0883
H	-2.71393600	-2.09297400	3.15047200	29.2352
H	-3.45167500	-3.14775300	1.91788900	29.1342
H	-3.84451300	-1.40538000	1.93579600	29.0195
C	-2.25854300	-2.05652700	-0.19587100	143.0833
H	-3.02515600	-1.30500200	-0.46902200	29.0961
H	-2.70972700	-3.04983100	-0.33890800	29.0931

C	-1.02789400	-1.92002200	-1.10977600	156.1254
H	-1.36402600	-1.83109900	-2.15396300	30.5621
H	-0.38632800	-2.80384000	-1.04054600	28.2185
C	1.87791900	2.26862900	2.60117500	77.1489
H	1.86978900	2.71953700	3.59064100	25.0790
C	1.04500600	1.18748300	2.31473300	68.5242
H	0.39130100	0.80847000	3.09653900	24.5977
C	1.02264200	0.58420600	1.05617000	66.7898
C	1.87679900	1.09315700	0.04935200	48.0739
C	2.71621300	2.18454100	0.34001500	82.5045
H	3.36037400	2.57617700	-0.44632600	25.4764
C	2.71897600	2.76346000	1.60245900	67.4270
H	3.37581400	3.60710000	1.80581000	24.7477
N	-1.86129500	0.55873700	1.24191900	183.8260
H	-2.69150800	0.75331700	1.80596600	27.3172
N	1.86107200	0.55899700	-1.24205500	183.8139
H	2.69177200	0.75298300	-1.80563700	27.3169

PBE0/cc-pVTZ/pcm=chloroform energy (hartree): -1072.10999241

PBE0/cc-pVTZ/pcm=chloroform geometry (angstroms) and shieldings (ppm):

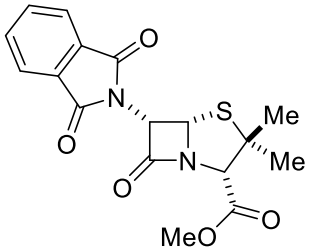
C	2.56575400	2.79834700	1.63491100	57.5752
H	3.18047900	3.66744000	1.83954400	24.4355
C	2.61422800	2.21088300	0.38608700	75.8249
H	3.26446300	2.61486000	-0.38298400	25.1725
C	1.83436500	1.08499700	0.09250300	38.9915
C	0.97501900	0.56169700	1.07662100	61.7688
C	0.95516500	1.17083400	2.32470000	59.4673
H	0.30640800	0.77372400	3.09655400	24.2156
C	1.73641600	2.27813800	2.62024900	71.1355
H	1.69426200	2.73036300	3.60318500	24.8227
C	-1.19221600	-0.70570000	1.47961800	115.6735
H	-1.04151600	-0.71250400	2.56162800	27.2006
C	0.16482900	-0.68291800	0.75604600	148.9506
N	-1.90173300	-1.93957000	1.16840100	203.6896
C	-3.06955700	-2.12704200	1.99797800	145.9201
H	-2.79185500	-2.06901500	3.05295300	29.2328
H	-3.49323800	-3.11654000	1.81453000	29.1986
H	-3.86259100	-1.38464000	1.80772400	29.1737
C	-2.23264000	-2.05446600	-0.24324700	141.2080
H	-2.98875000	-1.30585000	-0.53350000	29.3269
H	-2.68930400	-3.03498600	-0.40214900	29.0688
C	-0.99711100	-1.92386400	-1.11612900	154.7093
H	-1.30344300	-1.85093600	-2.16315600	30.4678
H	-0.37596200	-2.81382700	-1.02555300	28.3016
C	-0.16494800	-0.68289000	-0.75611000	148.9491
C	1.19209900	-0.70569700	-1.47968400	115.6726
H	1.04138300	-0.71252100	-2.56169500	27.2007
N	1.90161800	-1.93956200	-1.16846900	203.6897
C	3.06942100	-2.12709300	-1.99805800	145.9207

H	2.79173100	-2.06895100	-3.05302900	29.2325
H	3.49300100	-3.11664800	-1.81468700	29.1982
H	3.86255500	-1.38480500	-1.80775000	29.1737
C	2.23250100	-2.05453000	0.24317400	141.2085
H	2.98864100	-1.30596200	0.53347900	29.3267
H	2.68912400	-3.03507400	0.40204000	29.0686
C	0.99696100	-1.92392100	1.11603700	154.7095
H	1.30327500	-1.85103500	2.16307300	30.4680
H	0.37579600	-2.81386600	1.02542200	28.3015
C	-1.73619400	2.27847100	-2.62012500	71.1380
H	-1.69398300	2.73075600	-3.60303200	24.8228
C	-0.95515300	1.17099100	-2.32467900	59.4640
H	-0.30646600	0.77383000	-3.09656500	24.2154
C	-0.97507800	0.56177900	-1.07663900	61.7704
C	-1.83432500	1.08515100	-0.09247100	38.9915
C	-2.61393200	2.21124800	-0.38593200	75.8269
H	-3.26407400	2.61529500	0.38318300	25.1726
C	-2.56536200	2.79880300	-1.63470800	57.5754
H	-3.17988900	3.66805800	-1.83924800	24.4355
N	1.90604400	0.50390600	-1.14663400	182.5272
H	2.56158300	0.88128500	-1.80532900	26.9008
N	-1.90625600	0.50383100	1.14652800	182.5361
H	-2.56081800	0.88200600	1.80573000	26.9015

Proton Assignments (atom numbers followed by $CDCl_3$ shift in ppm):
46 4 6.27
48 2 6.82
40 10 6.55
42 8 7.01
24 38 3.13
23 37 1.29
20 35 2.27
21 34 2.62
30 31 32 16 17 18 2.42
52 50 4.58
12 27 4.32

Carbon Assignments (atom numbers followed by $CDCl_3$ shift in ppm):
44 5 145.56
47 1 126.72
22 36 31.90
19 33 46.72
25 13 36.13
15 29 42.78
45 3 112.18
39 9 116.51
11 26 71.20
41 7 124.61
43 6 125.21

Natural Product: penam1



isomer 1

Reference: Compound 1 (rrr, conf 6) in Wiitala, K.W.; Cramer, C.J.; Hoye, T.R. Magn. Reson. Chem. 2007, 45, 819-829.

B3LYP/MIDI!/gas phase energy (hartree): -1532.79238002

B3LYP/MIDI!/gas phase geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	-0.19196300	-1.06353400	-1.33429600	126.4982
N	0.94089500	-0.02884900	-1.76098000	91.0309
C	1.90696800	-0.82733000	-1.11478300	119.6602
C	0.93662400	-1.72257600	-0.45381600	118.9617
C	-1.38919600	-0.57009200	-0.72186000	114.3985
S	1.02851500	0.97728600	-2.41924400	412.8396
C	-2.61315000	-1.28249800	-0.84940200	27.0785
O	-3.62060400	-0.44977000	-0.13188200	-97.9420
N	-2.99318900	0.69630600	0.34742500	83.6866
C	-1.54715200	0.66391900	-0.03534000	165.1715
C	-4.96991900	-0.67590600	0.07300200	160.4352
O	-5.69054700	0.29194400	0.78612600	128.1059
C	-5.05975200	1.44557000	1.26771100	139.1712
C	-3.69189300	1.66119700	1.04922300	24.3527
O	-2.74033900	-2.33911000	-1.44465300	-80.5492
C	-0.68141200	1.49684600	0.15435300	62.7476
C	3.06450900	-0.37790400	-0.33062900	70.4444
C	2.88752100	-0.98378000	1.12939500	60.7692
C	1.04991100	-1.31389800	1.33168200	60.1292
C	3.19125200	1.15626800	-0.39849600	69.9669
C	3.33934300	-0.03253100	2.25274200	60.8362
H	3.66131300	-2.31801600	1.21075400	23.8478
H	4.14426600	1.74420700	-0.86789200	23.9829
H	2.08632500	1.73042900	0.13696000	23.9492
H	1.96146600	3.15677400	-0.14474800	23.7718
C	-0.50216400	-1.73282700	-2.14477500	26.2329
O	1.10401500	-2.78947100	-0.62875600	-104.9474
C	-5.44375800	-1.57620000	-0.31166900	26.7968
O	-6.75301500	0.14778500	0.96779100	-115.6262
H	-5.64055400	2.18251200	1.81748800	28.4640
H	-3.18548400	2.55210300	1.41363300	30.4458
H	3.99740300	-0.76529100	-0.75718000	29.3192
H	3.21239100	-0.52066700	3.22869100	29.9552
H	4.40434200	0.21799100	2.12874000	30.2304

H	2.74531900	0.88565000	2.22961100	29.2348
H	4.74315500	-2.13295600	1.11473900	26.1599
H	3.46999300	-2.80408300	2.17586100	26.6549
H	3.35807600	-3.00935700	0.41244000	28.0065
H	1.02680100	3.44521200	0.33891700	27.9073
H	2.81954600	3.70883900	0.25668300	27.3907
H	1.89358000	3.29812800	-1.22954900	27.5861

PBE0/cc-pVTZ/pcm=chloroform energy (hartree): -1540.28652729

PBE0/cc-pVTZ/pcm=chloroform geometry (angstroms) and shieldings (ppm):

C	0.29214000	-1.12319500	0.84609500	128.2285
N	-1.75225800	-0.71073700	0.77475100	92.8821
C	-0.69203300	-0.20535000	1.62499600	121.4514
C	-2.85192600	0.20582700	0.60632100	116.2863
C	-2.25171300	1.61455500	0.34476700	117.8385
S	-0.70050600	1.60069700	1.38618500	423.1079
C	-0.89284800	-1.32282100	-0.12727800	16.8550
O	-1.05781400	-1.83796400	-1.19195300	-81.5757
N	1.56036000	-0.67249600	0.38758800	85.2304
C	-1.89164300	1.85655900	-1.11316200	161.2991
C	-3.16692100	2.71192000	0.86572400	158.2467
O	-4.04336800	-1.57906500	-0.34929600	137.2221
C	-5.06719300	-2.11751800	-1.19022400	135.4702
C	-3.92253000	-0.26027600	-0.36415900	15.6748
O	-4.62855800	0.48258900	-0.99489600	-72.7986
C	3.84766700	-0.43046900	0.30227800	53.5454
C	5.20640000	-0.45757200	0.53829800	60.4550
C	6.02508400	0.19069100	-0.38173900	49.3418
C	5.48889300	0.83637800	-1.49263800	48.8507
C	4.11607900	0.85597800	-1.72174500	60.2409
C	3.31374700	0.21269900	-0.80320100	52.4188
H	5.61618600	-0.96341900	1.40308900	23.3319
H	7.09776900	0.19360900	-0.23365100	23.4077
H	6.15378900	1.33077500	-2.18988900	23.3873
H	3.69267900	1.35439500	-2.58428000	23.3087
C	2.73211600	-1.01881600	1.07447500	15.2351
O	2.76106400	-1.67289500	2.08578400	-94.5953
C	1.83909600	0.05892200	-0.77371900	16.0733
O	1.02826800	0.45128100	-1.56928800	-111.8069
H	-1.27341200	1.05831800	-1.51944300	29.0487
H	-1.32509200	2.78474000	-1.19995100	30.3664
H	-2.80030600	1.94978500	-1.70888700	29.6077
H	-2.68960700	3.68805000	0.76686200	29.9299
H	-3.41684500	2.55958600	1.91663400	30.2427
H	-4.08654900	2.72441000	0.27791800	29.4495
H	0.46868100	-2.03231400	1.42484600	25.8681
H	-0.79785900	-0.43805800	2.68352000	26.3678
H	-3.37095100	0.24950200	1.57268800	27.5894
H	-5.02206300	-3.19390100	-1.05377800	27.8582

H	-6.04274900	-1.73350100	-0.89405900	27.7163
H	-4.87551300	-1.85714800	-2.23028900	27.6758

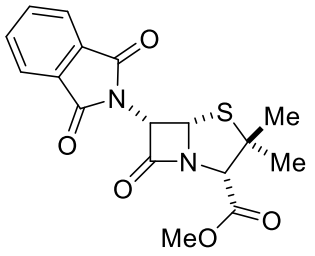
Proton Assignments (atom numbers followed by $CDCl_3$ shift in ppm):

30 31 32 1.73
33 34 35 1.71
39 40 41 3.9
38 4
36 5.63
37 5.29
23 24 7.77
22 25 7.89

Carbon Assignments (atom numbers followed by $CDCl_3$ shift in ppm):

10 27.4
11 30.4
13 52.8
1 59.1
3 63.6
5 65.1
4 73.1
17 20 124
16 21 131.7
18 19 134.7
7 165.3
14 165.7
26 28 166.8

Natural Product: penam2



isomer 2

Reference: Compound 2 (rrs, conf 2) in Wiitala, K.W.; Cramer, C.J.; Hoye, T.R. Magn. Reson. Chem. 2007, 45, 819-829.

B3LYP/MIDI!/gas phase energy (hartree): -1532.79658777

B3LYP/MIDI!/gas phase geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	0.35660200	-1.62148600	0.38667500	126.0538
N	-0.67035400	-1.51637800	-0.82388000	85.8629
C	-1.64592900	-0.92876400	0.01644500	113.9282
C	-0.76387300	-0.87751800	1.21534500	120.5813
C	1.59246900	-0.92572300	0.16309700	112.4452
S	-0.67878900	-1.78281900	-1.99715100	427.3871
C	2.81986100	-1.37864900	0.71813300	28.9000
O	3.84505400	-0.42364300	0.20358200	-80.3814
N	3.21784500	0.50530700	-0.62307700	82.6741
C	1.75666300	0.19941800	-0.68304500	158.7697
C	5.20786800	-0.38136200	0.43519300	162.6364
O	5.94320200	0.63480500	-0.19103300	135.1786
C	5.31282700	1.56859800	-1.02210000	139.8860
C	3.93043400	1.51126800	-1.24900200	21.5668
O	2.93692500	-2.35305400	1.44068100	-79.2030
C	0.87600100	0.75279900	-1.32162100	60.9263
C	-2.30901900	0.31905400	-0.36859900	70.1233
C	-2.19002500	1.31578500	0.84787300	60.2052
C	-0.53590600	0.89302600	1.62866700	60.6582
C	-3.77853700	0.16453100	-0.75496100	70.4645
C	-2.15493700	2.76751900	0.34487700	62.5097
H	-3.31758300	1.09343800	1.87712300	23.7720
H	-4.42713200	1.06283300	-1.26766500	23.9508
H	-4.27526600	-1.05092900	-0.41421400	23.9736
H	-5.68696200	-1.20032600	-0.75351300	23.8374
C	0.60196900	-2.62360400	0.75085300	25.9970
O	-1.14995500	-1.43857600	2.07081000	-112.0094
C	5.68144600	-1.11686000	1.08158300	26.7383
O	7.01695600	0.69964100	-0.03145200	-106.7598
H	5.90503100	2.34697900	-1.49752300	30.2385
H	3.42414500	2.22613000	-1.89358700	30.1591
H	-1.78101300	0.75186700	-1.22840500	28.0816
H	-2.12311000	3.47165900	1.18767000	30.0059
H	-1.26866200	2.92448700	-0.28412700	30.1042

H	-3.06007000	2.95193900	-0.25033200	29.8297
H	-4.27252100	1.46218600	1.47342300	26.1604
H	-3.42845700	0.02796800	2.11914300	25.8650
H	-3.08986300	1.64235100	2.79885100	27.2483
H	-5.93433000	-2.22876100	-0.47685300	27.5494
H	-6.29725600	-0.48483500	-0.18743600	27.7554
H	-5.84389000	-1.03239400	-1.82586600	27.9914

PBE0/cc-pVTZ/pcm=chloroform energy (hartree): -1540.29136707

PBE0/cc-pVTZ/pcm=chloroform geometry (angstroms) and shieldings (ppm):

C	-0.35883500	-1.33523800	0.41034600	127.7211
N	1.63784800	-0.76950900	0.62765100	87.0202
C	0.82636100	-1.01107600	-0.54847400	115.1770
C	2.71523600	0.16776200	0.50645700	118.0064
C	2.22470700	1.31028200	-0.45152900	114.5814
S	0.89233800	0.53369000	-1.49987600	442.5776
C	0.58729500	-0.81947400	1.52169200	16.9605
O	0.51557400	-0.59507800	2.69382000	-66.9481
N	-1.65035400	-0.76573300	0.23702000	85.0521
C	1.63954500	2.44566000	0.37727300	154.2004
C	3.30896200	1.84226800	-1.37809000	160.7046
O	5.05873400	0.03671300	0.46922600	138.5349
C	6.29562500	-0.51283400	0.00534700	135.8621
C	3.95842400	-0.53647000	-0.00720000	12.5164
O	3.94821900	-1.47808400	-0.75596800	-71.1642
C	-3.50505900	0.58817900	0.25892800	52.5826
C	-4.39998800	1.62667600	0.40636600	60.3121
C	-5.70517100	1.40905400	-0.02572300	48.9870
C	-6.08659500	0.19065600	-0.58108600	49.3565
C	-5.17578900	-0.85210400	-0.72326000	60.3616
C	-3.88498100	-0.62509600	-0.29341700	53.3241
H	-4.09687900	2.57083600	0.84039000	23.3073
H	-6.43872400	2.19979100	0.07106000	23.3850
H	-7.11024300	0.05421700	-0.90686600	23.3968
H	-5.46591000	-1.80244000	-1.15264000	23.3269
C	-2.06843800	0.51407100	0.61794300	15.8602
O	-1.38080400	1.35029300	1.14138900	-109.0003
C	-2.70377900	-1.51571300	-0.30384400	15.5051
O	-2.60633800	-2.65570700	-0.68004100	-95.9604
H	1.18612700	3.19394800	-0.27450800	30.1868
H	2.43526100	2.93110900	0.94973500	30.1443
H	0.87124100	2.09099600	1.06210100	28.6337
H	2.89390400	2.61221900	-2.02970900	29.9744
H	3.72711200	1.05823700	-2.01017200	30.2343
H	4.11198000	2.29786800	-0.79472900	30.0531
H	-0.49263500	-2.41661800	0.47900900	25.8497
H	1.15471100	-1.84195100	-1.16837100	25.7542
H	2.93205500	0.59234800	1.48664800	26.9196
H	6.36847200	-1.56429700	0.28008800	27.7209

H	6.36937300	-0.41715200	-1.07750900	27.8317
H	7.07609100	0.06381500	0.49298900	27.9033

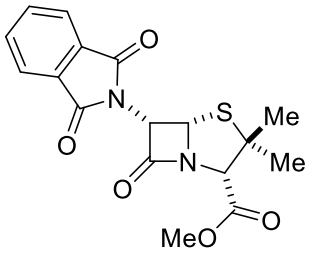
Proton Assignments (atom numbers followed by $CDCl_3$ shift in ppm):

30 31 32 1.83
33 34 35 1.51
39 40 41 3.81
38 4.68
36 5.61
37 5.68
23 24 7.77
22 25 7.89

Carbon Assignments (atom numbers followed by $CDCl_3$ shift in ppm):

10 31.1
11 28.2
13 52.7
1 58.6
3 67.1
5 71.1
4 66.2
17 20 124
16 21 131.7
18 19 134.7
7 168.6
14 168.6
26 28 166.8

Natural Product: penam3



isomer 3

Reference: Compound 3 (srr, conf 6) in Wiitala, K.W.; Cramer, C.J.; Hoye, T.R. Magn. Reson. Chem. 2007, 45, 819-829.

B3LYP/MIDI!/gas phase energy (hartree): -1532.79632973

B3LYP/MIDI!/gas phase geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	-0.23114100	0.23107400	0.38133700	126.5553
N	0.62191500	0.77267500	-0.84057700	91.2463
C	1.41430700	-0.38683800	-0.81557400	116.9436
C	0.70400900	-1.03329400	0.30613500	118.4479
C	-1.64686000	0.09095200	0.25521100	114.4212
S	0.67897200	1.77630400	-1.51014400	429.9297
C	-2.27719700	-0.51402800	-0.85553500	25.3770
O	-3.74079200	-0.36005600	-0.59282000	-97.6791
N	-3.91264000	0.31909600	0.61229600	81.5319
C	-2.56887100	0.63696300	1.18599900	166.1637
C	-4.82228700	-0.77732500	-1.34668900	159.8256
O	-6.10573200	-0.49431900	-0.85794800	141.2433
C	-6.27834400	0.18768700	0.35216100	139.2078
C	-5.17223900	0.60532900	1.10608800	21.5505
O	-1.68667100	-1.03679900	-1.78654700	-90.5673
C	-2.26414200	1.22819300	2.20689600	61.1861
C	2.87355900	-0.44768800	-0.86094900	70.1471
C	3.31503300	-1.41227700	0.31412100	60.5309
C	1.97571500	-1.25997400	1.61810000	60.5412
C	3.48885700	0.95995600	-0.77356900	70.5225
C	4.66144300	-1.01107600	0.94307300	61.7455
H	3.36549700	-2.86016600	-0.21717000	23.8220
H	4.33053900	1.38562400	-1.53726900	23.9756
H	2.97248300	1.63390000	0.29418200	23.9746
H	3.30418000	3.05696900	0.30241300	23.8260
C	-0.02836300	0.82321600	1.27955500	27.9943
O	0.20573100	-1.96862400	0.04296600	-106.0722
C	-4.66998500	-1.30408000	-2.28609200	25.5401
O	-6.97936100	-0.80654700	-1.42532900	-113.4646
H	-7.28389600	0.39609200	0.71000100	30.3571
H	-5.28825400	1.13739600	2.04764600	30.0888
H	3.23359400	-0.86509200	-1.80897000	29.8430
H	4.58151400	-0.02084000	1.40596300	30.0429
H	5.44808500	-0.99052200	0.17377700	29.3739

H	4.94759200	-1.73857500	1.71459400	30.0949
H	2.41499600	-3.14487800	-0.68868400	25.9549
H	3.56231400	-3.55554800	0.60868400	26.1003
H	4.16767300	-2.95955900	-0.96563500	27.7892
H	2.70017800	3.55981600	-0.46301100	27.4350
H	4.37003400	3.20481700	0.09871700	27.9823
H	3.03364000	3.40881600	1.30160700	27.7835

PBE0/cc-pVTZ/pcm=chloroform energy (hartree): -1540.29315649

PBE0/cc-pVTZ/pcm=chloroform geometry (angstroms) and shieldings (ppm):

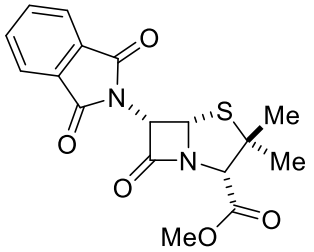
C	-0.33947300	-0.19202200	0.45385200	128.9265
N	1.35655900	0.01836900	-0.75730500	87.6896
C	0.58400400	0.97481000	0.02572300	116.9532
C	2.79219700	0.13784700	-0.77275800	118.3989
C	3.10082100	1.50551600	-0.07646700	114.7595
S	1.76624100	1.69076400	1.19054200	431.0552
C	0.53062800	-1.05301800	-0.48346400	18.5832
O	0.54358100	-2.19687000	-0.83446900	-69.1668
N	-1.74659500	-0.11914400	0.26722500	83.7227
C	4.44820800	1.54806900	0.62358900	164.2564
C	3.00862800	2.61951400	-1.11318400	155.9037
O	4.60519700	-1.34091000	-0.62725400	141.0775
C	5.34713600	-2.38802000	0.00472600	135.3879
C	3.44988400	-1.02763900	-0.04850200	13.7111
O	3.00522800	-1.56892300	0.92739600	-79.1618
C	-4.00491000	-0.17440400	0.67750600	53.1057
C	-5.26100300	-0.25183700	1.24097500	60.0713
C	-6.35224800	-0.12759300	0.38560600	49.0332
C	-6.17683700	0.06674900	-0.98150200	48.7425
C	-4.90419500	0.14413500	-1.54066900	60.4127
C	-3.82983200	0.01985000	-0.68532400	53.0789
H	-5.39037100	-0.40394700	2.30483800	23.3100
H	-7.35582400	-0.18330300	0.78850400	23.3937
H	-7.04696400	0.15839500	-1.61953800	23.3789
H	-4.76116900	0.29382300	-2.60315100	23.3234
C	-2.66852600	-0.26900800	1.31007300	16.5648
O	-2.37717400	-0.43760500	2.46568900	-94.4552
C	-2.37517300	0.05705000	-0.96594100	15.0010
O	-1.79771100	0.21082200	-2.01253700	-104.3165
H	4.51874900	0.80614300	1.41973400	30.3350
H	4.60413500	2.53394700	1.06340100	30.0804
H	5.25075600	1.37211300	-0.09541700	30.0445
H	3.11736900	3.59103600	-0.63126900	30.1205
H	2.05703300	2.60566600	-1.64640600	29.4883
H	3.80846800	2.50763200	-1.85034300	30.1332
H	-0.15189400	-0.48506700	1.48789300	25.9791
H	0.09242600	1.73833900	-0.57611900	26.0252
H	3.18763000	0.17717300	-1.78940700	27.7195
H	4.76499800	-3.30860400	0.01382700	27.6956

H 6.24824100 -2.51158200 -0.58882600 27.9088
H 5.59799200 -2.11067700 1.02816500 27.8207

Proton Assignments (atom numbers followed by $CDCl_3$ shift in ppm):
30 31 32 1.49
33 34 35 1.69
39 40 41 3.84
38 3.9
36 5.44
37 5.56
23 24 7.77
22 25 7.9

Carbon Assignments (atom numbers followed by $CDCl_3$ shift in ppm):
10 25
11 31.4
13 52.8
1 60.1
3 66.6
5 70.5
4 66
17 20 124.1
16 21 131.8
18 19 134.8
7 165.9
14 167.3
26 28 166.8

Natural Product: penam4



isomer 4

Reference: Compound 4 (srs conf 2) in Wiitala, K.W.; Cramer, C.J.; Hoye, T.R. Magn. Reson. Chem. 2007, 45, 819-829.

B3LYP/MIDI!/gas phase energy (hartree): -1532.79708328

B3LYP/MIDI!/gas phase geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	0.46871500	-0.92715400	0.54655600	120.5407
N	-0.47329600	-0.00310400	1.43548400	83.6129
C	-1.40784600	0.08075400	0.38758800	112.9846
C	-0.66779900	-0.80705400	-0.53540300	121.7870
C	1.79610900	-0.49381900	0.24131600	115.4704
S	-0.49942400	0.40346400	2.57023600	410.4469
C	2.93659100	-1.32485600	0.39815800	27.2789
O	4.09272600	-0.44587000	0.04372700	-70.1693
N	3.61400500	0.82277700	-0.27873600	81.0016
C	2.12461500	0.82512200	-0.14832500	157.3073
C	5.44429800	-0.73680700	0.01248200	165.1431
O	6.32392900	0.29081000	-0.35675800	137.5554
C	5.84314100	1.56505200	-0.68041600	139.9549
C	4.46986100	1.84562600	-0.64378500	23.1189
O	2.90811100	-2.49014800	0.75289000	-84.2037
C	1.31310200	1.71817500	-0.32528100	61.7070
C	-2.84030800	-0.13257800	0.54506500	70.3790
C	-3.27540600	-1.16368500	-0.57155600	60.3200
C	-1.77051400	-2.26941800	-0.75949100	60.5330
C	-3.69294200	1.13160500	0.42271200	70.1835
C	-4.48384200	-1.98810500	-0.10347400	61.4832
H	-3.56536800	-0.45458100	-1.91214400	23.8065
H	-4.87542700	1.16391700	0.72398100	23.9575
H	-2.99654300	2.16476100	-0.10868100	23.9697
H	-3.80138200	3.37233700	-0.26814600	23.8188
C	0.53895300	-1.94032300	0.95503100	26.5280
O	-0.38063100	-0.34660500	-1.48284300	-120.3859
C	5.80067300	-1.73188500	0.26905300	27.6610
O	7.39356700	0.09784800	-0.39156300	-102.5838
H	6.54535400	2.34610500	-0.96232000	29.7627
H	4.07921700	2.83050700	-0.88979100	29.9728
H	-3.04485200	-0.56201700	1.53591400	30.0540
H	-4.83352500	-2.65536200	-0.90291000	29.9520
H	-4.22177200	-2.59598000	0.77276400	30.2811

H	-5.29082700	-1.29353100	0.16935100	29.8526
H	-4.51261600	0.10158000	-1.84585700	26.3590
H	-2.76576700	0.25150800	-2.17154000	25.9974
H	-3.65214600	-1.20103000	-2.71086800	27.2485
H	-3.10804000	4.11933600	-0.66322800	27.9991
H	-4.62841000	3.19455800	-0.96753400	27.5307
H	-4.21257200	3.68886500	0.69805500	27.7682

PBE0/cc-pVTZ/pcm=chloroform energy (hartree): -1540.29610552

PBE0/cc-pVTZ/pcm=chloroform geometry (angstroms) and shieldings (ppm):

C	0.46021500	-0.79388200	0.33690900	122.3479
N	-1.36073100	0.22338600	0.51036100	85.4404
C	-0.66699100	-0.33849100	-0.63342300	114.2657
C	-2.78825400	0.10921700	0.55931300	119.3555
C	-3.12986100	-1.28245100	-0.07141800	117.9227
S	-1.81661800	-1.55112500	-1.35431900	433.3880
C	-0.40560800	-0.13853600	1.43377200	16.8394
O	-0.34963200	-0.02567400	2.62525800	-57.4085
N	1.80598100	-0.37799100	0.14596400	83.1575
C	-3.04001000	-2.35428000	1.00792800	152.7229
C	-4.48644200	-1.33430400	-0.75646100	162.7762
O	-4.61306100	1.57203700	0.37634900	140.2416
C	-5.34298200	2.62286900	-0.26368900	135.8429
C	-3.44053100	1.26826300	-0.17228700	13.4271
O	-2.96743100	1.82574100	-1.12661800	-74.8226
C	3.70455600	0.89661900	-0.05045700	52.9317
C	4.62816200	1.91709700	-0.13268800	60.2728
C	5.96054900	1.55788400	-0.31640800	49.1020
C	6.33975600	0.22197700	-0.41224700	49.1713
C	5.39949700	-0.80115800	-0.32816000	60.0989
C	4.08253900	-0.43509400	-0.14657300	52.4434
H	4.32669000	2.95386600	-0.05607900	23.3110
H	6.71704300	2.32962300	-0.38540700	23.3939
H	7.38487300	-0.02318000	-0.55434500	23.3892
H	5.68748000	-1.84203000	-0.40099900	23.3023
C	2.23663800	0.95049000	0.14414500	15.4512
O	1.51291000	1.90390400	0.27802100	-107.1860
C	2.86854300	-1.27427800	-0.01865600	16.6529
O	2.75870700	-2.47302400	-0.04093800	-92.0799
H	-2.09377100	-2.31197100	1.54871300	29.9556
H	-3.12666100	-3.34590900	0.56318800	29.9834
H	-3.85155600	-2.22818500	1.73012800	30.0614
H	-4.65194300	-2.32521400	-1.18164400	29.9666
H	-4.56234000	-0.60558500	-1.56389500	30.3869
H	-5.28092200	-1.14539300	-0.03164600	30.0391
H	0.46538600	-1.87803800	0.45726200	26.1290
H	-0.36950300	0.38650400	-1.38783000	25.8751
H	-3.11427300	0.12255100	1.59965700	26.9490
H	-6.26190700	2.73268400	0.30468800	27.9080

H	-4.76807900	3.54782200	-0.24369800	27.7213
H	-5.56198200	2.35716100	-1.29744100	27.8344

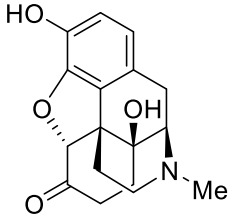
Proton Assignments (atom numbers followed by $CDCl_3$ shift in ppm):

30 31 32 1.66
33 34 35 1.49
39 40 41 3.8
38 4.64
36 5.41
37 5.58
23 24 7.79
22 25 7.88

Carbon Assignments (atom numbers followed by $CDCl_3$ shift in ppm):

10 34.7
11 25.6
13 52.6
1 64.5
3 69.2
5 69.4
4 64.3
17 20 124.1
16 21 131.7
18 19 134.9
7 167.4
14 167.8
26 28 166.6

Natural Product: oxymorphone



oxymorphone

Reference: Compound 2 in Caldwell, G.W.; Gauthier, A.D.; Mills, J.E.; Greco, M.N. Magn. Reson. Chem. 1993, 31, 309-317.

B3LYP/MIDI!/gas phase energy (hartree): -1009.01421655

B3LYP/MIDI!/gas phase geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	-1.12511500	-2.47744400	-1.25976700	75.6458
C	-2.42477800	-2.40540400	-0.74293200	78.5527
C	-2.83293400	-1.38544300	0.13654200	51.0538
C	-1.86550000	-0.44133900	0.49249700	46.4531
C	-0.86196900	1.51504300	1.00017500	96.0499
C	-1.23882000	2.42695500	-0.19561100	-15.7656
C	-0.04667600	2.97042200	-0.97575600	153.1857
C	0.75926800	1.76568000	-1.54548500	153.7544
C	2.13336700	-0.32039000	-0.79048900	121.4164
C	1.25149200	-1.44236500	-1.43756700	167.4663
C	-0.16012000	-1.53385300	-0.87802100	69.9259
C	-0.57102800	-0.56289300	0.01388800	62.7715
C	0.27556600	0.51309800	0.63230300	134.3938
C	1.35976200	0.98249000	-0.37289200	117.0360
C	0.99357900	-0.01633100	1.89917500	156.5794
C	1.98471100	-1.14248200	1.53511500	144.3627
C	3.97079500	-1.65067800	0.19734600	148.1932
N	2.88546400	-0.69147000	0.44481500	206.1445
O	-4.10427100	-1.25864000	0.64864700	223.4968
O	-2.03159500	0.67383400	1.30194100	198.5813
O	-2.40197000	2.61477400	-0.50204600	-315.5223
O	2.30735500	1.85569500	0.25667800	259.7911
H	-0.87714000	-3.26634900	-1.96811400	25.1405
H	-3.16415300	-3.14601800	-1.04770600	25.3905
H	-0.64703000	2.11550200	1.89247400	27.0677
H	-0.43372300	3.61688400	-1.77111900	29.6092
H	0.62960100	3.54163600	-0.32350100	28.3200
H	0.10431000	1.13049300	-2.15705600	29.8410
H	1.58471700	2.13296900	-2.16937600	29.7050
H	2.89963300	-0.01554500	-1.51748700	29.0362
H	1.19637100	-1.23806400	-2.51961000	29.0341
H	1.77565600	-2.40657500	-1.34278400	28.4500
H	1.53634800	0.82688000	2.34614500	28.9412
H	0.24819000	-0.38524100	2.61623500	30.0831
H	2.61522300	-1.37729900	2.40462300	29.3403
H	1.43427200	-2.06166700	1.26158500	29.3434

H	4.62307300	-1.25779400	-0.59488200	29.4052
H	3.61878400	-2.65751100	-0.10295300	29.0287
H	4.56333900	-1.75770200	1.11709100	29.1041
H	-4.63799600	-1.99368200	0.25279200	28.0524
H	2.96651600	1.18367300	0.61704400	25.7600

PBE0/cc-pVTZ/pcm=chloroform energy (hartree): -1014.09784381

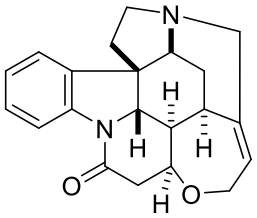
PBE0/cc-pVTZ/pcm=chloroform geometry (angstroms) and shieldings (ppm):

C	-1.06176300	-2.48349900	-1.25305100	66.4674
C	-2.35441200	-2.43415800	-0.74065000	69.8393
C	-2.78060400	-1.42833200	0.13199600	44.2046
C	-1.83472000	-0.47880600	0.48547000	39.8736
C	-0.88795000	1.47701300	0.97203000	95.2454
C	-1.25664700	2.41946300	-0.18316200	-30.7536
C	-0.11560600	2.89959100	-1.03163500	150.2274
C	0.69932100	1.71118900	-1.54487800	154.4283
C	2.12268700	-0.28655000	-0.76417600	121.2237
C	1.28025000	-1.39987300	-1.42418600	165.3011
C	-0.11349900	-1.53302900	-0.87422900	59.9484
C	-0.54295600	-0.57935000	0.01753000	53.1386
C	0.26878500	0.51696600	0.63275700	134.8364
C	1.33319800	0.98628300	-0.37501100	116.5631
C	0.97793300	-0.00499800	1.89048500	155.5092
C	1.98589200	-1.08946200	1.53898900	142.1049
C	3.93922700	-1.59153400	0.21682500	145.8355
N	2.85457500	-0.66554100	0.44925100	216.2423
O	-4.04208400	-1.33166800	0.61722800	235.7420
O	-2.01496100	0.62814900	1.26545000	212.3712
O	-2.40471300	2.72890500	-0.38429000	-297.4185
O	2.24833500	1.89063600	0.21732500	269.8433
H	-0.80636100	-3.26542500	-1.95931900	24.6963
H	-3.07664400	-3.18368800	-1.04965100	24.8142
H	-0.69063700	2.08652700	1.85753300	27.0110
H	-0.52280000	3.50303900	-1.84222200	29.4795
H	0.53792400	3.53167900	-0.42218100	28.3793
H	0.05798900	1.03613700	-2.11563900	29.9524
H	1.48945200	2.06226800	-2.21141900	29.8016
H	2.88532200	0.02298100	-1.48509900	28.8151
H	1.21559000	-1.18705900	-2.49638200	28.9975
H	1.82348200	-2.34700200	-1.35344900	28.2582
H	1.48282400	0.83195400	2.37923900	29.1013
H	0.24169000	-0.40274100	2.59206700	30.0775
H	2.61546600	-1.30075900	2.40645000	29.1922
H	1.46189200	-2.02677200	1.29426300	29.4280
H	4.58132500	-1.21603900	-0.58182200	29.3747
H	3.60240600	-2.60247500	-0.06021300	29.0979
H	4.53973000	-1.68193300	1.12412400	29.0430
H	-4.57595000	-2.04213400	0.25166500	27.3993
H	2.90783400	1.30656000	0.63097300	26.4327

Proton Assignments (atom numbers followed by $CDCl_3$ shift in ppm):
34 1.57
28 1.90
29 1.65
35 2.42
26 2.34
36 2.21
37 38 39 2.41
33 2.45
31 2.55
30 2.90
27 3.05
32 3.15
25 4.75
23 6.60
24 6.73

Carbon Assignments (atom numbers followed by $CDCl_3$ shift in ppm):
10 21.9
15 30.3
8 31.2
7 36.1
17 42.7
16 45.2
13 50.4
9 64.5
14 70.6
5 90.4
2 117.9
1 119.9
11 124.1
12 128.8
3 138.9
4 143.5
6 209.8

Natural Product: strychnine



strychnine

Reference: Martin, G.E.; Hadden, C.E.; Crouch, R.C.; Krishnamurthy, V.V. Magn. Reson. Chem. 1999, 37, 517-528. Erroneous assignments for the aromatic ring have been corrected.

B3LYP/MIDI!/gas phase energy (hartree): -1067.20200963

B3LYP/MIDI!/gas phase geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	4.27189700	-1.48017100	-0.47905900	70.6402
C	4.62357700	-0.13700400	-0.32358400	65.7257
C	3.67125700	0.82781900	0.01815700	76.2583
C	2.35126700	0.40842000	0.19389600	48.9132
C	1.98571100	-0.93700800	0.04297300	61.0836
C	2.94458300	-1.88457400	-0.28918100	72.9151
N	1.21140100	1.18798300	0.51061500	92.8937
C	1.13052600	2.55681800	0.28369700	25.3425
O	2.11694400	3.27888100	0.14813600	-102.2022
C	-0.30220800	3.11600400	0.24476000	145.7973
C	-1.39347400	2.22453500	-0.43547800	108.4885
O	-2.43299200	2.13239600	0.55506900	254.3494
C	-3.67114800	1.57187500	0.05382700	124.3559
C	-3.69130800	0.06439900	0.15610500	65.6231
C	-2.81543500	-0.73218400	-0.45990400	50.1925
C	-2.75146200	-2.22645300	-0.20219900	137.1094
C	-1.73803000	-0.21801100	-1.41663000	154.1548
C	-0.78960400	0.85255900	-0.82603600	139.1278
C	-0.82356200	-1.39842400	-1.83790600	160.9922
C	-0.29009700	-2.08074600	-0.56449100	127.1835
C	0.52270700	-1.12724300	0.36754600	133.6875
C	-0.01865000	0.34521600	0.41185400	127.1066
C	0.30964800	-1.81811600	1.74611000	145.4539
C	-1.17539200	-2.22810100	1.69500700	139.9208
N	-1.40792300	-2.63143800	0.27997100	203.3172
H	5.02981500	-2.21398200	-0.74356400	24.6007
H	5.65709300	0.16977400	-0.47074800	24.4024
H	3.91328600	1.87557000	0.13242700	23.1935
H	2.66954400	-2.93228800	-0.40102800	24.5448
H	-0.65205100	3.27161100	1.27652000	28.9047
H	-0.22140900	4.09941600	-0.22898200	28.6945
H	-1.78690500	2.72118100	-1.33994900	27.6180
H	-4.45672700	2.00365900	0.68579400	27.4626
H	-3.84365700	1.91451800	-0.98476400	27.5820
H	-4.43564700	-0.37547300	0.82281700	25.7209

H	-3.48653900	-2.52409600	0.55673200	29.1740
H	-2.98096200	-2.79853300	-1.11413800	27.8413
H	-2.22369100	0.20900600	-2.31010100	28.7640
H	-0.04592600	1.05756700	-1.61341800	30.7151
H	-1.36754700	-2.12558100	-2.45484500	29.3737
H	0.01946200	-1.03032400	-2.43900700	30.2435
H	0.37048300	-2.91371500	-0.85044600	27.8482
H	-0.65641600	0.50478500	1.28952000	27.6710
H	0.55062100	-1.15258900	2.58424400	29.7871
H	0.95829900	-2.70308300	1.80757400	29.7623
H	-1.39969400	-3.06741200	2.36858100	28.5465
H	-1.81220200	-1.37369700	1.99025600	28.6166

PBE0/cc-pVTZ/pcm=chloroform energy (hartree): -1072.55196007

PBE0/cc-pVTZ/pcm=chloroform geometry (angstroms) and shieldings (ppm):

C	4.27803700	-1.40011100	-0.51611100	61.7652
C	4.60582100	-0.06034400	-0.36013200	56.1811
C	3.64595400	0.88475000	-0.01437400	69.3366
C	2.34141100	0.44552100	0.16395400	40.5967
C	1.99999300	-0.89896800	0.02116300	49.3158
C	2.96777900	-1.82523400	-0.31815500	62.1535
N	1.19748500	1.19416300	0.47437500	88.0688
C	1.05836900	2.54293700	0.31677600	15.3913
O	2.00404500	3.30406700	0.19778600	-82.1133
C	-0.37211700	3.03353800	0.33490300	143.6563
C	-1.41627600	2.17653900	-0.40507200	108.6547
O	-2.52613800	2.11740200	0.46923000	270.1093
C	-3.69255900	1.50712000	-0.06194500	122.1069
C	-3.69436900	0.02083500	0.13015100	55.4901
C	-2.79293100	-0.77523600	-0.43743600	37.6209
C	-2.68628200	-2.24416400	-0.14400500	134.8115
C	-1.72310300	-0.25139000	-1.37418200	153.7462
C	-0.81108200	0.82294300	-0.78146400	138.0607
C	-0.80872300	-1.40032300	-1.79348600	159.6594
C	-0.25704100	-2.06136900	-0.54392900	125.1534
C	0.55370000	-1.11315900	0.36546800	133.1662
C	0.00254500	0.33477300	0.41398000	125.8843
C	0.37514900	-1.81347400	1.72179800	142.7642
C	-1.08252900	-2.23253400	1.69810400	137.4345
N	-1.34294500	-2.59672700	0.30557200	212.7170
H	5.04386300	-2.11708600	-0.78528400	24.1575
H	5.62943600	0.26213500	-0.50971300	23.9780
H	3.89471000	1.92766100	0.10473500	23.0523
H	2.71376100	-2.87376700	-0.42540500	24.0520
H	-0.68637600	3.06528400	1.38301400	28.9761
H	-0.36178500	4.06029300	-0.02375600	28.5508
H	-1.72666400	2.68420000	-1.32816500	27.3537
H	-4.53233100	1.95992600	0.46624500	27.4318
H	-3.79482000	1.76971900	-1.12489100	27.3847

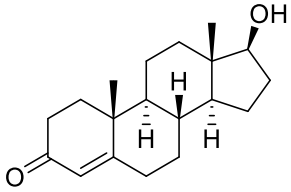
H	-4.43613800	-0.40223400	0.80129900	25.3121
H	-3.39871300	-2.53826300	0.62825600	28.9486
H	-2.93356000	-2.83218000	-1.03385900	27.8432
H	-2.21131600	0.17489200	-2.25882900	28.4668
H	-0.08840300	1.05039300	-1.57546600	30.5322
H	-1.34322000	-2.13525100	-2.39816700	29.2683
H	0.01469200	-1.02906500	-2.40792400	30.2403
H	0.40680100	-2.88370400	-0.83513200	27.6029
H	-0.59179000	0.47280300	1.32103800	27.7486
H	0.62587500	-1.16953900	2.56589200	29.7808
H	1.02904100	-2.68819600	1.75811300	29.6709
H	-1.28579500	-3.07098500	2.36974200	28.5202
H	-1.72276700	-1.39672200	2.01645600	28.6351

Proton Assignments (atom numbers followed by $CDCl_3$ shift in ppm):
29 7.145
26 7.076
27 7.230
28 8.085
30 2.657
31 3.105
32 4.266
33 4.047
34 4.127
35 5.881
37 3.691
36 2.712
47 2.861
46 3.185
44 1.870
45 1.869
43 3.846
39 1.252
38 3.126
40 2.338
41 1.430
42 3.924

Carbon Assignments (atom numbers followed by $CDCl_3$ shift in ppm):
6 122.8
1 124.4
2 128.8
3 116.3
4 142.2
5 132.9
8 170.3
10 42.7
11 77.6
13 64.8
14 127.9

15 140.0
16 52.9
24 50.3
23 42.8
21 52.3
20 60.1
19 26.9
17 31.7
18 48.2
22 60.1

Natural Product: testosterone



testosterone

Reference: Compound 1 in Hayamizu, K.; Ishii, T.; Yanagisawa, M. Magn. Reson. Chem. 1990, 28, 250-256.

B3LYP/MIDI!/gas phase energy (hartree): -886.14334580

B3LYP/MIDI!/gas phase geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	2.58545600	-1.52249000	-0.36803100	150.9769
C	1.77949500	-0.43618900	0.40676600	146.7298
C	-0.44323400	-1.74396000	0.00931400	167.2553
C	-1.87181800	-1.72305500	-0.60179700	151.4642
C	-2.68355300	-0.53835500	-0.05532900	142.3499
C	-1.90493000	0.76894300	-0.35410400	135.7028
C	-2.93721400	1.89598300	-0.06999800	163.7426
C	-4.00628700	-0.25669400	-0.81056800	106.2237
C	-3.00618800	-0.73521300	1.44308200	179.0374
C	1.78293500	-0.76752400	1.92752100	172.4681
C	4.11066400	-1.40698900	-0.17762700	155.8118
C	4.60920700	-0.01596000	-0.57773200	-1.3508
C	3.68102300	1.08891000	-0.27181600	68.4724
C	2.43373500	0.93668500	0.20984600	25.2102
C	1.62048800	2.14209300	0.62473200	155.2061
C	0.20943700	2.13190200	-0.00772800	155.2132
C	-0.52739200	0.81906900	0.32425800	151.5973
C	0.31405300	-0.39779200	-0.18117900	131.3263
H	2.25032500	-2.52056600	-0.05742800	29.5544
H	4.65395700	-2.14447900	-0.78185700	29.4778
H	4.10164500	2.08313300	-0.42549000	25.9266
H	2.15999400	3.06038700	0.35595600	29.4104
H	0.29601900	2.23308400	-1.10202900	30.4973
H	-0.65803600	0.75637200	1.41567100	29.9552
H	0.43485200	-0.24445500	-1.26936100	30.7081
H	-0.51340700	-1.98501000	1.07808100	29.9797
H	-1.79444500	-1.62840500	-1.69819100	30.4259
H	-1.71909100	0.77427100	-1.44506800	30.5485
H	-2.93479900	2.16872800	0.99446600	29.9674
H	-3.81851400	-0.37036400	-1.89402400	27.8527
H	-3.65381900	-1.61429700	1.55136100	30.2314
H	2.80634600	-0.71899600	2.32525000	30.2408
H	0.12564100	-2.55507800	-0.46427700	29.9812
H	-2.38711800	-2.67174300	-0.38965100	29.4615
H	1.50905300	2.14437100	1.72341400	29.0561
H	-0.36375300	2.99456100	0.36105900	29.7248
H	2.35915600	-1.42090400	-1.44179900	29.9379

H	4.38520200	-1.58197700	0.87611500	29.1668
H	-2.72224200	2.80398000	-0.64631400	29.8810
H	-2.10013900	-0.88862400	2.04206200	30.6161
H	1.39637300	-1.77988900	2.10583100	30.3457
H	-3.54428600	0.12656300	1.85932000	30.7566
H	1.16755400	-0.05914700	2.49759700	30.0401
O	5.71892400	0.17569500	-1.06798600	-292.7020
C	-4.31253700	1.25263000	-0.48182800	155.7139
H	-5.03588100	1.27006000	0.34328700	29.9532
H	-4.76045900	1.76819000	-1.34175600	29.6249
O	-5.02235100	-1.17207400	-0.37668100	271.1119
H	-5.81275100	-0.98068400	-0.94156300	30.8246

PBE0/cc-pVTZ/pcm=chloroform energy (hartree): -890.60327964

PBE0/cc-pVTZ/pcm=chloroform geometry (angstroms) and shieldings (ppm):

C	2.55419000	-1.50724500	-0.34845700	149.9186
C	1.76098300	-0.42696500	0.40216900	146.8784
C	-0.43597500	-1.72104900	0.01954900	166.0240
C	-1.84638100	-1.71069000	-0.57072500	149.6496
C	-2.66194200	-0.54386800	-0.03254000	143.6970
C	-1.89417800	0.74939000	-0.32792700	134.9646
C	-2.90997700	1.86109000	-0.05507800	162.9681
C	-3.95517800	-0.24294900	-0.79338100	104.1819
C	-2.97507800	-0.73710200	1.45204600	177.8495
C	1.78048000	-0.72148400	1.91216200	170.9178
C	4.05964900	-1.39155200	-0.18956200	152.3906
C	4.55720300	-0.02633400	-0.57402300	-15.1283
C	3.64503400	1.08050300	-0.30664700	60.4367
C	2.40257900	0.92961100	0.18259300	6.7567
C	1.60137600	2.12990500	0.57365400	152.3855
C	0.19743600	2.10712000	-0.01484100	154.1375
C	-0.52046500	0.80997800	0.31964800	150.5644
C	0.30787600	-0.39321700	-0.16617400	131.4565
H	2.23109400	-2.49601000	-0.01892800	29.4929
H	4.58790000	-2.13824800	-0.78388600	29.3948
H	4.05140000	2.07446700	-0.46713600	25.6161
H	2.13572600	3.03845400	0.29032300	29.2440
H	0.25562100	2.21417900	-1.10456000	30.6161
H	-0.64072400	0.75731400	1.40907900	29.9501
H	0.42544400	-0.24533400	-1.25051700	30.7612
H	-0.49578000	-1.96682300	1.08266900	30.0309
H	-1.78115000	-1.61951400	-1.66171900	30.5082
H	-1.71761100	0.74531600	-1.41479900	30.5555
H	-2.90402100	2.14041600	1.00183100	30.1214
H	-3.73360900	-0.32932700	-1.86636100	27.8252
H	-3.57988600	-1.63488200	1.58611000	30.7599
H	2.79906000	-0.67489300	2.30124500	30.4003
H	0.13023200	-2.53015900	-0.44587800	29.9887
H	-2.34171100	-2.66353600	-0.36222100	29.6095

H	1.51885000	2.14384200	1.66787400	28.9911
H	-0.36737700	2.96525400	0.35711200	29.6957
H	2.31027300	-1.43608100	-1.41396500	29.9515
H	4.35566200	-1.55427800	0.85337300	29.1352
H	-2.69242600	2.76687700	-0.62236400	29.9169
H	-2.07039300	-0.84884400	2.04944500	30.6386
H	1.39302500	-1.72046800	2.11631300	30.4456
H	-3.53937400	0.10011500	1.86533700	30.8648
H	1.18233400	-0.00671000	2.47774500	30.1229
O	5.67366400	0.15533200	-1.03042100	-252.3028
C	-4.26209700	1.22906500	-0.45216700	155.7204
H	-4.97684600	1.25590700	0.37286200	30.0595
H	-4.72741900	1.74335600	-1.29498700	29.6372
O	-4.98623300	-1.14995500	-0.45541300	287.6227
H	-5.74095000	-0.96863800	-1.01911300	30.7474

Proton Assignments (atom numbers followed by $CDCl_3$ shift in ppm):

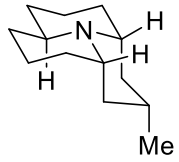
37 1.702
19 2.034
20 2.347
38 2.424
21 5.731
22 2.278
35 2.391
23 1.007
36 1.848
24 1.579
25 0.932
33 1.603
26 1.436
27 1.093
34 1.862
28 0.978
39 1.628
29 1.313
46 1.466
47 2.084
30 3.655
31 40 42 0.795
32 41 43 1.198

Carbon Assignments (atom numbers followed by $CDCl_3$ shift in ppm):

1 35.73
11 33.94
12 199.60
13 123.85
14 171.35
15 32.80
16 31.55
17 35.67

18 53.93
2 38.67
3 20.65
4 36.44
5 42.82
6 50.49
7 23.34
45 30.41
8 81.56
9 11.06
10 17.42

Natural Product: precoccinelline



precoccinelline

Reference: Compound 3 in Lebrun, B.; Braekman, J.C.; Daloze, D. Magn. Reson. Chem. 1999, 37, 60-64.

B3LYP/MIDI!/gas phase energy (hartree): -560.72173432

B3LYP/MIDI!/gas phase geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	-1.37417500	-2.55433700	-0.46445900	167.7961
C	-0.54552900	-2.48627000	0.83404000	156.8080
C	0.32388700	-1.21123400	0.88635300	128.5319
N	-0.52423300	0.00000000	0.71087700	183.6863
C	-1.30826200	0.00000000	-0.55114000	139.4280
C	-2.20141600	-1.26131500	-0.59572800	153.0788
C	0.32388700	1.21123400	0.88635300	128.5319
C	-0.54552900	2.48627000	0.83404000	156.8080
C	-1.37417500	2.55433700	-0.46445900	167.7962
C	-2.20141600	1.26131500	-0.59572800	153.0789
C	1.53335200	-1.26252100	-0.08944500	158.6678
C	2.41496300	0.00000000	0.05694600	153.1438
C	1.53335200	1.26252000	-0.08944500	158.6678
C	3.57605900	0.00000000	-0.95606000	167.2436
H	-0.71287500	-2.66658900	-1.33747800	29.9837
H	-2.03695400	-3.43188400	-0.44540900	30.0995
H	0.09946600	-3.37150800	0.93667300	30.0475
H	-1.23297700	-2.46802300	1.69331000	29.6885
H	0.73615800	-1.13208800	1.90619400	28.8104
H	-0.66839600	0.00000000	-1.45703400	28.7949
H	-2.91770100	-1.20214100	0.23888900	30.3962
H	-2.77324700	-1.25893100	-1.53586600	30.0722
H	0.73615800	1.13208800	1.90619400	28.8104
H	0.09946700	3.37150800	0.93667400	30.0475
H	-1.23297700	2.46802300	1.69331000	29.6885
H	-2.03695300	3.43188400	-0.44541000	30.0995
H	-0.71287500	2.66658900	-1.33747800	29.9838
H	-2.91770100	1.20214200	0.23888900	30.3962
H	-2.77324600	1.25893200	-1.53586600	30.0722
H	1.18684400	-1.34221300	-1.13094700	29.8420
H	2.13291100	-2.16142200	0.12542400	30.6433
H	2.83994600	0.00000000	1.07574500	30.0742
H	2.13291100	2.16142200	0.12542400	30.6433
H	1.18684400	1.34221200	-1.13094700	29.8420
H	4.20882200	0.89164600	-0.82867300	30.3929
H	3.18718400	0.00000000	-1.98670800	30.6775
H	4.20882200	-0.89164700	-0.82867200	30.3929

PBE0/cc-pVTZ/pcm=chloroform energy (hartree): -563.51719295

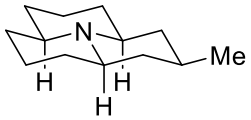
PBE0/cc-pVTZ/pcm=chloroform geometry (angstroms) and shieldings (ppm):

C	0.45200400	-1.37264300	2.52260900	166.4184
C	-0.81121100	-0.53049500	2.45832000	155.2745
C	-0.86483300	0.32400500	1.19901800	128.2199
N	-0.68780700	-0.50131200	0.00000000	190.0795
C	0.52753500	-1.31605300	0.00000000	139.4453
C	0.57533300	-2.18726700	1.24777900	151.5842
C	-0.86483300	0.32400500	-1.19901800	128.2199
C	-0.81121100	-0.53049500	-2.45832000	155.2745
C	0.45200400	-1.37264300	-2.52260900	166.4184
C	0.57533300	-2.18726700	-1.24777900	151.5842
C	0.08679700	1.52292100	1.24603900	156.6685
C	-0.04944200	2.39086100	0.00000000	152.3301
C	0.08679700	1.52292100	-1.24603900	156.6685
C	0.93744200	3.54585500	0.00000000	165.1396
H	1.33217800	-0.73181000	2.64015200	30.0331
H	0.42783400	-2.02842400	3.39696800	30.1575
H	-0.90007900	0.11610500	3.33560300	30.0872
H	-1.67961800	-1.19696700	2.45952400	29.8118
H	-1.88057400	0.73424000	1.12281100	28.7503
H	1.43661500	-0.68662400	0.00000000	28.8898
H	-0.25075400	-2.90578400	1.19471600	30.5754
H	1.50551100	-2.76257700	1.23805300	30.1089
H	-1.88057400	0.73424000	-1.12281100	28.7503
H	-0.90007900	0.11610500	-3.33560300	30.0872
H	-1.67961800	-1.19696700	-2.45952400	29.8118
H	0.42783400	-2.02842400	-3.39696800	30.1575
H	1.33217800	-0.73181000	-2.64015200	30.0331
H	-0.25075400	-2.90578400	-1.19471600	30.5754
H	1.50551100	-2.76257700	-1.23805300	30.1089
H	1.12553700	1.18680400	1.33821600	30.0398
H	-0.12791700	2.11701600	2.14055700	30.7344
H	-1.06602200	2.80868100	0.00000000	30.0689
H	-0.12791700	2.11701600	-2.14055700	30.7344
H	1.12553700	1.18680400	-1.33821600	30.0398
H	0.81131000	4.17617900	-0.88398600	30.5347
H	1.96690300	3.17534000	0.00000000	30.9015
H	0.81131000	4.17617900	0.88398600	30.5347

Proton Assignments (atom numbers followed by $CDCl_3$ shift in ppm):
31 33 1.02
30 34 1.50
32 1.62
19 23 2.95
17 24 1.50
18 25 1.88
16 26 1.50
15 27 1.50
22 29 1.56
21 28 1.18
20 2.74
35 36 37 0.94

Carbon Assignments (atom numbers followed by $CDCl_3$ shift in ppm):
11 13 31.2
12 32.6
3 7 58.1
2 8 31.1
1 9 19.8
6 10 34.6
5 48.3
14 22.7

Natural Product: myrrhine



myrrhine

Reference: Compound 1 in Lebrun, B.; Braekman, J.C.; Daloze, D. Magn. Reson. Chem. 1999, 37, 60-64.

B3LYP/MIDI!/gas phase energy (hartree): -560.72742036

B3LYP/MIDI!/gas phase geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	-1.81647400	2.54692500	0.21024900	163.8216
C	-0.33904900	2.49912000	-0.21025800	153.3928
C	0.35800900	1.22317200	0.31297600	125.7851
N	-0.33580000	-0.00000100	-0.18850200	156.6466
C	-1.76346800	-0.00000100	0.25139400	125.3910
C	-2.49620700	1.25583900	-0.27117500	153.3960
C	0.35801000	-1.22317100	0.31297600	125.7853
C	-0.33904900	-2.49912000	-0.21025800	153.3927
C	-1.81647400	-2.54692500	0.21024900	163.8217
C	-2.49620700	-1.25583900	-0.27117500	153.3961
C	1.83271400	1.23858400	-0.14520500	145.8344
C	2.60482800	-0.00000100	0.33746600	156.2257
C	1.83271300	-1.23858300	-0.14520500	145.8345
C	4.06051800	0.00000000	-0.16641600	167.6997
H	-2.31388900	3.43077000	-0.21406600	29.9449
H	-1.88960400	2.62000900	1.30753100	30.2345
H	0.20517900	3.37660800	0.16868300	30.0777
H	-0.26865500	2.50423900	-1.30910400	30.2442
H	0.33727300	1.24715200	1.42639200	29.7155
H	-1.82160900	-0.00000400	1.36382200	29.7580
H	-2.49086000	1.22540300	-1.37182600	30.2510
H	-3.54314500	1.21530300	0.06378300	30.0883
H	0.33727700	-1.24715000	1.42639200	29.7155
H	-0.26865300	-2.50423500	-1.30910400	30.2442
H	0.20517800	-3.37660900	0.16868100	30.0777
H	-2.31388900	-3.43076900	-0.21406700	29.9449
H	-1.88960400	-2.62001100	1.30753100	30.2345
H	-3.54314600	-1.21530100	0.06378100	30.0883
H	-2.49086400	-1.22540800	-1.37182600	30.2510
H	1.85326900	1.27116800	-1.24663900	30.5509
H	2.30807100	2.15785900	0.23021600	30.1067
H	2.61230200	-0.00000100	1.44020000	30.2299
H	1.85327100	-1.27116600	-1.24663900	30.5509
H	2.30806900	-2.15786000	0.23021400	30.1067
H	4.59925200	0.89112500	0.18961200	30.4658
H	4.08692500	-0.00001900	-1.26741100	30.8208
H	4.59926500	-0.89110300	0.18964500	30.4657

PBE0/cc-pVTZ/pcm=chloroform energy (hartree): -563.52503912

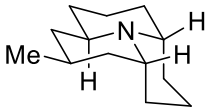
PBE0/cc-pVTZ/pcm=chloroform geometry (angstroms) and shieldings (ppm):

C	1.79527500	-2.51710100	0.20250900	162.2509
C	0.33590100	-2.47178100	-0.20109100	151.9567
C	-0.35384200	-1.20899000	0.29395200	125.5922
N	0.33306500	0.00000000	-0.17573400	160.4446
C	1.74327400	0.00000000	0.23387000	125.3980
C	2.46867400	-1.24239900	-0.26152700	152.1049
C	-0.35384200	1.20899000	0.29395200	125.5921
C	0.33590000	2.47178100	-0.20109100	151.9565
C	1.79527400	2.51710100	0.20250900	162.2509
C	2.46867400	1.24239900	-0.26152700	152.1050
C	-1.81160600	-1.22411900	-0.13925500	143.4485
C	-2.57658700	0.00000000	0.32576200	155.3318
C	-1.81160600	1.22411800	-0.13925500	143.4486
C	-4.01554100	0.00000000	-0.16092000	165.7583
H	2.29032800	-3.39665800	-0.21726300	29.9649
H	1.87341200	-2.59906000	1.29265800	30.2777
H	-0.20732300	-3.33771200	0.18710000	30.0772
H	0.25488600	-2.50380900	-1.29347600	30.3931
H	-0.32998300	-1.22576700	1.40346400	29.8525
H	1.79281900	0.00000000	1.34266500	29.8975
H	2.49056800	-1.21550400	-1.35677400	30.3971
H	3.50593000	-1.19718000	0.08168900	30.0901
H	-0.32998300	1.22576700	1.40346500	29.8525
H	0.25488500	2.50380800	-1.29347700	30.3930
H	-0.20732500	3.33771200	0.18710000	30.0772
H	2.29032600	3.39665800	-0.21726300	29.9649
H	1.87341100	2.59906100	1.29265800	30.2777
H	3.50592900	1.19718300	0.08168900	30.0901
H	2.49056800	1.21550500	-1.35677400	30.3971
H	-1.84831000	-1.27621700	-1.23432200	30.7658
H	-2.27874100	-2.13775000	0.24124400	30.1004
H	-2.58282600	-0.00000100	1.42385900	30.2126
H	-1.84831100	1.27621700	-1.23432100	30.7659
H	-2.27874100	2.13774900	0.24124500	30.1004
H	-4.55400600	-0.88351700	0.19095300	30.5867
H	-4.05464000	0.00000200	-1.25426200	31.0374
H	-4.55400800	0.88351200	0.19095900	30.5868

Proton Assignments (atom numbers followed by $CDCl_3$ shift in ppm):
31 34 1.54
30 33 1.04
32 1.47
19 23 1.85
17 25 1.56
18 24 1.38
15 26 1.65
16 27 1.34
22 28 1.56
21 29 1.38
20 1.82
35 36 37 0.86

Carbon Assignments (atom numbers followed by $CDCl_3$ shift in ppm):
11 13 42.6
12 30.3
3 7 62.2
2 8 34.0
1 9 24.3
6 10 34.0
5 62.2
14 22.0

Natural Product: hippodamine



hippodamine

Reference: Compound 5 in Lebrun, B.; Braekman, J.C.; Daloze, D. Magn. Reson. Chem. 1999, 37, 60-64.

B3LYP/MIDI!/gas phase energy (hartree): -560.72134925

B3LYP/MIDI!/gas phase geometry (angstroms) with B3LYP/cc-pVDZ shieldings (ppm):

C	2.31524400	-1.93311000	-0.34738400	167.8304
C	2.63534000	-0.91167200	0.76273400	156.6421
C	1.74532000	0.34491700	0.65171200	128.5629
N	0.30699200	-0.03973100	0.65529500	182.6467
C	-0.06161900	-0.99351100	-0.42115100	139.7238
C	0.81135200	-2.26384700	-0.29974200	153.0146
C	-0.52957100	1.18962100	0.67398700	127.9919
C	-2.02205600	0.81966100	0.80857600	148.8173
C	-2.48387900	-0.15447900	-0.29489500	160.2063
C	-1.55003700	-1.38003800	-0.26745100	145.1236
C	2.13433000	1.26143800	-0.54307800	166.6086
C	1.25177100	2.53122800	-0.55035400	161.1429
C	-0.24671200	2.14888500	-0.51833400	165.8463
C	-3.95658200	-0.56482900	-0.09808500	167.1732
H	2.57808100	-1.52289100	-1.33464500	29.9986
H	2.91238700	-2.84585200	-0.20617700	30.1109
H	3.69352200	-0.61257200	0.73009100	30.0692
H	2.44712900	-1.38011800	1.74079100	29.7443
H	1.89024500	0.93688800	1.57121900	28.7542
H	0.08123800	-0.57551100	-1.43871300	28.6616
H	0.57712500	-2.74929500	0.66081300	30.4038
H	0.54016000	-2.95957900	-1.10788000	30.0403
H	-0.23725200	1.72722400	1.59198600	28.7315
H	-2.62858900	1.73835400	0.79098900	30.0875
H	-2.17206500	0.33530700	1.78664400	30.0959
H	-2.38790300	0.33874900	-1.27493300	29.9767
H	-1.67307600	-1.90106800	0.69621700	30.7202
H	-1.81999300	-2.08283900	-1.07129000	30.0748
H	2.01412900	0.72369900	-1.49438100	29.4914
H	3.19599700	1.53884600	-0.45566700	30.7016
H	1.47271100	3.14825400	-1.43370400	29.6185
H	1.48807500	3.13898600	0.33947200	29.9983
H	-0.86580400	3.05255800	-0.41016300	30.6650
H	-0.52641800	1.67301500	-1.46924500	29.5568
H	-4.28202300	-1.25425900	-0.89193800	30.4295
H	-4.61655400	0.31585400	-0.11710400	30.4989
H	-4.08746800	-1.07122800	0.87134200	30.8245

PBE0/cc-pVTZ/pcm=chloroform energy (hartree): -563.51690608

PBE0/cc-pVTZ/pcm=chloroform geometry (angstroms) and shieldings (ppm):

C	2.27489400	-1.92860800	-0.33957700	166.6577
C	2.60435100	-0.90819500	0.73732700	155.2648
C	1.72911900	0.33347100	0.63559800	128.0819
N	0.30798900	-0.02882100	0.63078600	188.7404
C	-0.07043200	-0.99805600	-0.39671900	139.5216
C	0.79193300	-2.24805200	-0.28733300	151.5490
C	-0.51993800	1.17955500	0.65692000	127.6590
C	-1.99502200	0.82442400	0.78139500	146.5005
C	-2.45956800	-0.15446900	-0.28721000	160.1699
C	-1.54054600	-1.36436300	-0.25339600	142.8210
C	2.11714300	1.25037000	-0.52882300	165.3202
C	1.25045400	2.50200800	-0.53621100	159.6113
C	-0.22713600	2.13519900	-0.50516600	164.2770
C	-3.91613500	-0.54404700	-0.09770500	165.1129
H	2.53544400	-1.53661200	-1.32834600	30.0389
H	2.86916500	-2.83531600	-0.19909600	30.1738
H	3.65558800	-0.61067200	0.69154100	30.1132
H	2.44122100	-1.36602800	1.71826200	29.8769
H	1.87756100	0.91717500	1.55408300	28.6999
H	0.07122200	-0.58763100	-1.41387300	28.7225
H	0.56077100	-2.74290500	0.66314100	30.5909
H	0.51073800	-2.93822000	-1.08777700	30.0800
H	-0.23182700	1.71092500	1.57407000	28.6815
H	-2.59031800	1.74215600	0.74867100	30.1107
H	-2.16339100	0.36754500	1.76331500	30.2845
H	-2.35969400	0.32319300	-1.26964900	29.9467
H	-1.67604400	-1.88662400	0.70212700	30.9633
H	-1.80670600	-2.07006800	-1.04682800	30.1180
H	2.00990200	0.72237500	-1.48137300	29.6231
H	3.17412300	1.51808200	-0.43729800	30.7834
H	1.47682600	3.12467500	-1.40595900	29.6712
H	1.48711800	3.10412100	0.34961800	30.0489
H	-0.84181500	3.03347700	-0.39385700	30.7414
H	-0.51290000	1.67707200	-1.45726800	29.6731
H	-4.24569900	-1.24013400	-0.87313300	30.5593
H	-4.56987400	0.33112900	-0.13151100	30.6298
H	-4.06203500	-1.03139100	0.87103100	31.0634

Proton Assignments (atom numbers followed by $CDCl_3$ shift in ppm):

30 0.95
29 1.78
31 1.83
32 1.48
33 0.92
34 1.82
23 2.92
24 1.40

25 1.40
26 1.60
28 1.48
27 0.78
20 2.76
22 1.49
21 1.10
16 1.40
15 1.40
17 1.44
18 1.78
19 2.90
35 36 37 0.78

Carbon Assignments (atom numbers followed by $CDCl_3$ shift in ppm):
11 23.0
12 26.0
13 22.3
7 58.0
8 39.9
9 25.6
10 43.3
5 47.9
6 34.5
1 19.7
2 31.3
3 58.8
14 22.4

2. Summary of Dynamic Corrections

The natural product calculation results are summarized below. Experimental values are taken from the previous section. Raw corrections and stationary shieldings were calculated using the standard procedure described in the manuscript. The unscaled dynamic prediction is calculated relative to methanol, then adjusted to the conventional TMS scale using experimental methanol shifts of 3.40 and 50.41 for proton and carbon respectively. Additionally, dynamic corrections of methanol and TMS were calculated using the same method and applied (methanol raw corrections: C = –5.01, H = –0.61, TMS raw corrections: C = –6.46, H = –0.71). Scaled dynamic refers to the dynamic prediction after linear re-scaling of the entire set to experiment, which does not improve the error significantly (see manuscript). All values in ppm.

Table S10. Predictions for Natural Products Dataset

						Shift predictions		
Atom	Experiment	Raw corrections	Nucleus	Molecule	Shielding	Unscaled stationary	Scaled dynamic	Unscaled dynamic
7	6.64	-0.49	H	estrone	24.88	6.57	6.43	6.45
9	6.59	-0.49	H	estrone	24.66	6.79	6.65	6.67
11	7.15	-0.46	H	estrone	24.01	7.44	7.27	7.29
15 16	2.87	-0.75	H	estrone	28.59	2.86	2.98	3.00
19	2.25	-0.86	H	estrone	29.32	2.13	2.36	2.38
20	2.00	-0.82	H	estrone	29.56	1.89	2.08	2.10
21	1.44	-0.73	H	estrone	30.21	1.24	1.33	1.36
23	1.59	-0.83	H	estrone	30.02	1.43	1.63	1.65
25	1.52	-0.88	H	estrone	30.13	1.32	1.56	1.59
26	2.38	-0.81	H	estrone	29.12	2.33	2.51	2.53
29	1.53	-0.88	H	estrone	30.08	1.37	1.61	1.64
30	1.95	-0.77	H	estrone	29.66	1.79	1.93	1.95
31	1.49	-0.86	H	estrone	30.18	1.27	1.49	1.52
35	1.64	-0.68	H	estrone	29.91	1.54	1.59	1.61
36	2.06	-0.68	H	estrone	29.51	1.94	1.99	2.01
38 39 40	0.91	-0.79	H	estrone	30.70	0.75	0.90	0.93
41	2.15	-0.82	H	estrone	29.44	2.01	2.20	2.22
42	2.51	-0.77	H	estrone	29.11	2.34	2.47	2.50
3	153.49	-3.56	C	estrone	29.05	157.40	154.67	155.95
4	112.83	-5.26	C	estrone	75.12	111.33	110.61	111.58
5	115.28	-4.62	C	estrone	71.15	115.30	113.92	114.91
6	126.55	-3.94	C	estrone	57.66	128.79	126.64	127.72
8	138.07	-3.73	C	estrone	43.84	142.61	140.16	141.33
10	132.12	-4.14	C	estrone	52.41	134.04	132.05	133.17
12	29.47	-5.25	C	estrone	155.78	30.67	30.51	30.91
13	43.97	-5.86	C	estrone	141.66	44.79	45.14	45.64
14	26.50	-5.84	C	estrone	159.66	26.79	27.24	27.62
17	38.35	-6.12	C	estrone	148.44	38.01	38.67	39.12
18	26.22	-6.28	C	estrone	160.43	26.02	26.92	27.29
22	50.41	-6.37	C	estrone	135.87	50.58	51.39	51.94
24	31.57	-5.62	C	estrone	154.73	31.72	31.93	32.33
27	48.03	-5.16	C	estrone	137.83	48.62	48.24	48.77
28	21.59	-5.54	C	estrone	164.95	21.50	21.70	22.03
32	221.10	-1.45	C	estrone	-41.01	227.46	222.14	223.90
33	13.86	-6.06	C	estrone	174.78	11.67	12.45	12.72
34	35.89	-6.06	C	estrone	150.75	35.70	36.31	36.75
32 33 34	2.59	-0.73	H	lysergic ester	29.00	2.45	2.55	2.57
25	2.68	-0.71	H	lysergic ester	28.97	2.48	2.55	2.58
29	2.69	-0.79	H	lysergic ester	28.94	2.51	2.67	2.69
27	3.17	-0.74	H	lysergic ester	28.54	2.91	3.01	3.04
28	3.26	-0.78	H	lysergic ester	28.52	2.93	3.08	3.10
26	3.50	-0.67	H	lysergic ester	27.84	3.61	3.65	3.67
30	3.71	-0.77	H	lysergic ester	27.82	3.63	3.77	3.79
37 38 39	3.77	-0.79	H	lysergic ester	27.80	3.65	3.81	3.83
31	6.59	-0.49	H	lysergic ester	24.61	6.84	6.70	6.72

24	6.87	-0.46	H	lysergic ester	24.47	6.98	6.81	6.83
20 21 22	7.19	-0.41	H	lysergic ester	24.06	7.39	7.17	7.19
12	27.40	-5.02	C	lysergic ester	158.85	27.60	27.24	27.61
16	42.40	-5.91	C	lysergic ester	143.23	43.22	43.63	44.12
14	43.90	-4.87	C	lysergic ester	144.81	41.64	41.03	41.50
36	52.20	-3.94	C	lysergic ester	135.96	50.49	48.89	49.42
15	55.10	-5.49	C	lysergic ester	132.96	53.49	53.41	53.97
11	63.10	-5.51	C	lysergic ester	123.11	63.34	63.21	63.84
2	109.90	-4.38	C	lysergic ester	73.25	113.20	111.60	112.57
8	111.00	-5.19	C	lysergic ester	74.01	112.44	111.65	112.62
4	112.70	-5.08	C	lysergic ester	76.57	109.88	109.00	109.95
17	118.20	-3.46	C	lysergic ester	63.74	122.71	120.12	121.16
6	118.50	-5.80	C	lysergic ester	67.83	118.62	118.39	119.41
3	123.50	-4.50	C	lysergic ester	62.01	124.44	122.88	123.93
7	126.50	-3.41	C	lysergic ester	58.56	127.89	125.22	126.29
9	128.30	-3.04	C	lysergic ester	55.87	130.58	127.52	128.61
1	134.20	-5.42	C	lysergic ester	52.46	133.99	133.28	134.40
10	136.40	-3.27	C	lysergic ester	43.82	142.63	139.72	140.89
18	173.00	-2.06	C	lysergic ester	9.48	176.97	172.62	174.02
22 49	1.14	-0.84	H	meso_calycanthine	30.56	0.89	1.10	1.12
19 46	2.11	-0.81	H	meso_calycanthine	29.40	2.05	2.22	2.25
23 50	2.11	-0.77	H	meso_calycanthine	29.33	2.12	2.26	2.28
42 43 44 15 16 17	2.27	-0.74	H	meso_calycanthine	29.27	2.18	2.29	2.31
20 47	2.33	-0.72	H	meso_calycanthine	29.33	2.12	2.20	2.23
12 39	4.25	-0.67	H	meso_calycanthine	27.21	4.24	4.28	4.30
4 29	6.54	-0.45	H	meso_calycanthine	24.80	6.65	6.47	6.49
10 35	6.63	-0.45	H	meso_calycanthine	24.63	6.82	6.64	6.66
2 27	6.97	-0.42	H	meso_calycanthine	24.23	7.22	7.02	7.03
8 33	6.97	-0.50	H	meso_calycanthine	24.17	7.28	7.15	7.17
21 48	34.40	-5.98	C	meso_calycanthine	152.47	33.98	34.53	34.95
36 37	37.20	-4.56	C	meso_calycanthine	147.73	38.72	37.82	38.27
14 41	42.20	-5.14	C	meso_calycanthine	146.55	39.90	39.57	40.03
18 45	46.30	-5.39	C	meso_calycanthine	141.66	44.79	44.68	45.17
11 38	71.10	-5.17	C	meso_calycanthine	115.98	70.47	69.95	70.63
3 28	112.30	-4.69	C	meso_calycanthine	74.97	111.48	110.20	111.16
34 9	117.40	-4.61	C	meso_calycanthine	69.65	116.80	115.40	116.40
32 7	126.90	-4.21	C	meso_calycanthine	57.24	129.21	127.33	128.41
1 26	126.70	-4.30	C	meso_calycanthine	57.58	128.87	127.08	128.16
31 6	124.90	-3.84	C	meso_calycanthine	60.64	125.81	123.58	124.64
30 5	145.10	-3.19	C	meso_calycanthine	39.02	147.43	144.41	145.61
46 4	6.27	-0.48	H	minus_calycanthine	25.17	6.28	6.13	6.15
48 2	6.82	-0.46	H	minus_calycanthine	24.44	7.01	6.84	6.86
40 10	6.55	-0.48	H	minus_calycanthine	24.82	6.63	6.48	6.50
42 8	7.01	-0.46	H	minus_calycanthine	24.22	7.23	7.07	7.08
24 38	3.13	-0.79	H	minus_calycanthine	28.30	3.15	3.30	3.33
23 37	1.29	-0.82	H	minus_calycanthine	30.47	0.98	1.17	1.19
20 35	2.27	-0.82	H	minus_calycanthine	29.20	2.25	2.44	2.46
21 34	2.62	-0.80	H	minus_calycanthine	29.20	2.25	2.42	2.44
30 31 32 16 17 18	2.42	-0.72	H	minus_calycanthine	29.20	2.25	2.33	2.36
52 50	4.58	-0.45	H	minus_calycanthine	26.90	4.55	4.37	4.39
12 27	4.32	-0.73	H	minus_calycanthine	27.20	4.25	4.35	4.37
44 5	145.56	-3.75	C	minus_calycanthine	38.99	147.46	144.99	146.20
47 1	126.72	-4.61	C	minus_calycanthine	57.58	128.87	127.39	128.47
22 36	31.90	-6.30	C	minus_calycanthine	154.71	31.74	32.62	33.03
19 33	46.72	-5.84	C	minus_calycanthine	141.21	45.24	45.57	46.07
25 13	36.13	-4.22	C	minus_calycanthine	148.95	37.50	36.27	36.71
15 29	42.78	-5.11	C	minus_calycanthine	145.92	40.53	40.16	40.63
45 3	112.18	-5.50	C	minus_calycanthine	75.83	110.62	110.15	111.11
39 9	116.51	-5.10	C	minus_calycanthine	71.14	115.31	114.41	115.40
11 26	71.20	-5.70	C	minus_calycanthine	115.67	70.78	70.78	71.47
41 7	124.61	-3.39	C	minus_calycanthine	59.47	126.98	124.30	125.36
43 6	125.21	-4.50	C	minus_calycanthine	61.77	124.68	123.12	124.17
30 31 32	1.73	-0.66	H	penam1	29.67	1.78	1.80	1.83
33 34 35	1.71	-0.79	H	penam1	29.87	1.58	1.73	1.76

39 40 41	3.90	-0.82	H	penam1	27.75	3.70	3.89	3.91
38	4.00	-0.75	H	penam1	27.59	3.86	3.98	4.00
36	5.63	-0.56	H	penam1	25.87	5.58	5.51	5.53
37	5.29	-0.67	H	penam1	26.37	5.08	5.12	5.14
23 24	7.77	-0.47	H	penam1	23.40	8.05	7.89	7.91
22 25	7.89	-0.41	H	penam1	23.32	8.13	7.91	7.93
10	27.40	-5.90	C	penam1	161.30	25.15	25.68	26.04
11	30.40	-5.79	C	penam1	158.25	28.20	28.60	28.98
13	52.80	-3.94	C	penam1	135.47	50.98	49.38	49.91
1	59.10	-5.59	C	penam1	128.23	58.22	58.21	58.80
3	63.60	-5.09	C	penam1	121.45	65.00	64.44	65.08
5	65.10	-5.20	C	penam1	117.84	68.61	68.14	68.80
4	73.10	-6.09	C	penam1	116.29	70.16	70.56	71.24
17 20	124.00	-3.82	C	penam1	60.35	126.10	123.85	124.91
16 21	131.70	-3.45	C	penam1	52.98	133.47	130.80	131.91
18 19	134.70	-4.59	C	penam1	49.10	137.35	135.79	136.93
7	165.30	-2.46	C	penam1	16.86	169.60	165.69	167.05
14	165.70	-2.15	C	penam1	15.67	170.78	166.55	167.92
26 28	166.80	-2.18	C	penam1	15.65	170.80	166.61	167.97
30 31 32	1.83	-0.69	H	penam2	29.65	1.80	1.85	1.88
33 34 35	1.51	-0.74	H	penam2	30.09	1.36	1.47	1.49
39 40 41	3.81	-0.81	H	penam2	27.82	3.63	3.81	3.83
38	4.68	-0.67	H	penam2	26.92	4.53	4.57	4.59
36	5.61	-0.63	H	penam2	25.85	5.60	5.60	5.62
37	5.68	-0.67	H	penam2	25.75	5.70	5.73	5.76
23 24	7.77	-0.44	H	penam2	23.39	8.06	7.87	7.89
22 25	7.89	-0.40	H	penam2	23.32	8.13	7.90	7.92
10	31.10	-5.99	C	penam2	154.20	32.25	32.82	33.23
11	28.20	-5.01	C	penam2	160.70	25.75	25.38	25.75
13	52.70	-3.71	C	penam2	135.86	50.59	48.76	49.29
1	58.60	-5.40	C	penam2	127.72	58.73	58.52	59.12
3	67.10	-5.20	C	penam2	115.18	71.27	70.78	71.46
5	71.10	-6.40	C	penam2	114.58	71.87	72.56	73.26
4	66.20	-5.87	C	penam2	118.01	68.44	68.64	69.30
17 20	124.00	-3.89	C	penam2	60.34	126.11	123.93	124.99
16 21	131.70	-3.56	C	penam2	52.95	133.50	130.94	132.05
18 19	134.70	-4.43	C	penam2	49.17	137.28	135.56	136.70
7	168.60	-2.72	C	penam2	16.96	169.49	165.84	167.20
14	168.60	-2.14	C	penam2	12.52	173.93	169.68	171.06
26 28	166.80	-1.98	C	penam2	15.68	170.77	166.38	167.74
30 31 32	1.49	-0.75	H	penam3	30.15	1.30	1.41	1.44
33 34 35	1.69	-0.80	H	penam3	29.91	1.54	1.70	1.73
39 40 41	3.84	-0.81	H	penam3	27.81	3.64	3.82	3.84
38	3.90	-0.69	H	penam3	27.72	3.73	3.79	3.81
36	5.44	-0.60	H	penam3	25.98	5.47	5.44	5.46
37	5.56	-0.66	H	penam3	26.03	5.42	5.45	5.47
23 24	7.77	-0.44	H	penam3	23.39	8.06	7.88	7.89
22 25	7.90	-0.43	H	penam3	23.32	8.13	7.94	7.95
10	25.00	-4.62	C	penam3	164.26	22.19	21.47	21.80
11	31.40	-6.07	C	penam3	155.90	30.55	31.20	31.61
13	52.80	-3.97	C	penam3	135.39	51.06	49.49	50.02
1	60.10	-5.32	C	penam3	128.93	57.52	57.25	57.83
3	66.60	-4.88	C	penam3	116.95	69.50	68.70	69.37
5	70.50	-5.36	C	penam3	114.76	71.69	71.35	72.04
4	66.00	-5.50	C	penam3	118.40	68.05	67.88	68.54
17 20	124.10	-3.94	C	penam3	60.24	126.21	124.08	125.14
16 21	131.80	-3.51	C	penam3	53.09	133.36	130.75	131.86
18 19	134.80	-4.41	C	penam3	48.89	137.56	135.82	136.96
7	165.90	-2.52	C	penam3	18.58	167.87	164.03	165.38
14	167.30	-2.87	C	penam3	13.71	172.74	169.22	170.60
26 28	166.80	-2.21	C	penam3	15.78	170.67	166.51	167.87
30 31 32	1.66	-0.75	H	penam4	30.00	1.45	1.56	1.59
33 34 35	1.49	-0.74	H	penam4	30.13	1.32	1.42	1.45
39 40 41	3.80	-0.79	H	penam4	27.82	3.63	3.79	3.81

38	4.64	-0.66	H	penam4	26.95	4.50	4.53	4.55
36	5.41	-0.73	H	penam4	26.13	5.32	5.42	5.44
37	5.58	-0.69	H	penam4	25.88	5.57	5.63	5.65
23 24	7.79	-0.42	H	penam4	23.39	8.06	7.85	7.87
22 25	7.88	-0.43	H	penam4	23.31	8.14	7.95	7.96
10	34.70	-5.79	C	penam4	152.72	33.73	34.08	34.51
11	25.60	-4.98	C	penam4	162.78	23.67	23.30	23.64
13	52.60	-3.83	C	penam4	135.84	50.61	48.90	49.43
1	64.50	-5.97	C	penam4	122.35	64.10	64.42	65.06
3	69.20	-5.64	C	penam4	114.27	72.18	72.12	72.81
5	69.40	-5.84	C	penam4	117.92	68.53	68.69	69.36
4	64.30	-5.71	C	penam4	119.36	67.09	67.14	67.79
17 20	124.10	-3.95	C	penam4	60.19	126.26	124.14	125.20
16 21	131.70	-3.56	C	penam4	52.69	133.76	131.20	132.31
18 19	134.90	-4.23	C	penam4	49.14	137.31	135.39	136.53
7	167.40	-2.48	C	penam4	16.84	169.61	165.73	167.08
14	167.80	-2.30	C	penam4	13.43	173.02	168.94	170.31
26 28	166.60	-2.20	C	penam4	16.05	170.40	166.23	167.59
34	1.57	-0.74	H	oxymorphone	30.08	1.37	1.48	1.50
28	1.90	-0.86	H	oxymorphone	29.95	1.50	1.72	1.75
29	1.65	-0.75	H	oxymorphone	29.80	1.65	1.76	1.79
35	2.42	-0.79	H	oxymorphone	29.19	2.26	2.41	2.44
26	2.34	-0.73	H	oxymorphone	29.48	1.97	2.07	2.09
36	2.21	-0.80	H	oxymorphone	29.43	2.02	2.19	2.21
37 38 39	2.41	-0.81	H	oxymorphone	29.17	2.28	2.45	2.48
33	2.45	-0.73	H	oxymorphone	29.10	2.35	2.44	2.47
31	2.55	-0.75	H	oxymorphone	29.00	2.45	2.57	2.59
30	2.90	-0.67	H	oxymorphone	28.82	2.63	2.67	2.69
27	3.05	-0.64	H	oxymorphone	28.38	3.07	3.08	3.10
32	3.15	-0.70	H	oxymorphone	28.26	3.19	3.26	3.28
25	4.75	-0.64	H	oxymorphone	27.01	4.44	4.45	4.47
23	6.60	-0.46	H	oxymorphone	24.70	6.75	6.58	6.60
24	6.73	-0.53	H	oxymorphone	24.81	6.64	6.54	6.56
10	21.90	-6.08	C	oxymorphone	165.30	21.15	21.88	22.22
15	30.30	-5.93	C	oxymorphone	155.51	30.94	31.46	31.86
8	31.20	-5.75	C	oxymorphone	154.43	32.02	32.35	32.76
7	36.10	-5.19	C	oxymorphone	150.23	36.22	35.97	36.40
17	42.70	-5.48	C	oxymorphone	145.84	40.61	40.62	41.08
16	45.20	-5.75	C	oxymorphone	142.10	44.35	44.59	45.09
13	50.40	-4.47	C	oxymorphone	134.84	51.61	50.53	51.07
9	64.50	-5.62	C	oxymorphone	121.22	65.23	65.19	65.84
14	70.60	-4.41	C	oxymorphone	116.56	69.89	68.62	69.29
5	90.40	-4.58	C	oxymorphone	95.25	91.20	89.96	90.77
2	117.90	-5.91	C	oxymorphone	69.84	116.61	116.50	117.51
1	119.90	-4.29	C	oxymorphone	66.47	119.98	118.24	119.26
11	124.10	-4.57	C	oxymorphone	59.95	126.50	125.00	126.06
12	128.80	-3.04	C	oxymorphone	53.14	133.31	130.24	131.34
3	138.90	-3.25	C	oxymorphone	44.20	142.25	139.32	140.49
4	143.50	-3.67	C	oxymorphone	39.87	146.58	144.04	145.24
6	209.80	-1.69	C	oxymorphone	-30.75	217.20	212.20	213.88
29	7.15	-0.43	H	strychnine	24.05	7.40	7.20	7.22
26	7.08	-0.40	H	strychnine	24.16	7.29	7.06	7.08
27	7.23	-0.42	H	strychnine	23.98	7.47	7.26	7.28
28	8.09	-0.38	H	strychnine	23.05	8.40	8.15	8.17
30	2.66	-0.67	H	strychnine	28.98	2.47	2.51	2.53
31	3.11	-0.72	H	strychnine	28.55	2.90	2.99	3.01
32	4.27	-0.75	H	strychnine	27.35	4.10	4.21	4.24
33	4.05	-0.66	H	strychnine	27.43	4.02	4.05	4.07
34	4.13	-0.71	H	strychnine	27.38	4.07	4.14	4.17
35	5.88	-0.45	H	strychnine	25.31	6.14	5.96	5.98
37	3.69	-0.76	H	strychnine	27.84	3.61	3.73	3.76
36	2.71	-0.77	H	strychnine	28.95	2.50	2.64	2.66
47	2.86	-0.78	H	strychnine	28.64	2.81	2.96	2.98
46	3.19	-0.87	H	strychnine	28.52	2.93	3.17	3.19

44	1.87	-0.74	H	strychnine	29.78	1.67	1.77	1.80
45	1.87	-0.72	H	strychnine	29.67	1.78	1.86	1.89
43	3.85	-0.72	H	strychnine	27.75	3.70	3.79	3.81
39	1.25	-0.95	H	strychnine	30.53	0.92	1.23	1.26
38	3.13	-0.67	H	strychnine	28.47	2.98	3.02	3.04
40	2.34	-0.74	H	strychnine	29.27	2.18	2.29	2.31
41	1.43	-0.78	H	strychnine	30.24	1.21	1.35	1.38
42	3.92	-0.79	H	strychnine	27.60	3.85	4.00	4.03
6	122.80	-4.14	C	strychnine	62.15	124.30	122.38	123.43
1	124.40	-4.21	C	strychnine	61.77	124.68	122.83	123.88
2	128.80	-4.49	C	strychnine	56.18	130.27	128.66	129.75
3	116.30	-3.63	C	strychnine	69.34	117.11	114.74	115.73
4	142.20	-3.26	C	strychnine	40.60	145.85	142.91	144.10
5	132.90	-3.11	C	strychnine	49.32	137.13	134.10	135.23
8	170.30	-2.19	C	strychnine	15.39	171.06	166.88	168.24
10	42.70	-4.92	C	strychnine	143.66	42.79	42.22	42.70
11	77.60	-6.17	C	strychnine	108.65	77.80	78.22	78.96
13	64.80	-5.46	C	strychnine	122.11	64.34	64.16	64.79
14	127.90	-3.86	C	strychnine	55.49	130.96	128.72	129.81
15	140.00	-4.29	C	strychnine	37.62	148.83	146.89	148.11
16	52.90	-5.02	C	strychnine	134.81	51.64	51.11	51.65
24	50.30	-5.90	C	strychnine	137.43	49.02	49.37	49.91
23	42.80	-5.39	C	strychnine	142.76	43.69	43.58	44.07
21	52.30	-5.10	C	strychnine	133.17	53.28	52.82	53.37
20	60.10	-5.72	C	strychnine	125.15	61.30	61.39	62.01
19	26.90	-6.02	C	strychnine	159.66	26.79	27.43	27.80
17	31.70	-5.30	C	strychnine	153.75	32.70	32.58	32.99
18	48.20	-6.01	C	strychnine	138.06	48.39	48.86	49.39
22	60.10	-5.15	C	strychnine	125.88	60.57	60.10	60.71
37	1.70	-0.90	H	testosterone	29.95	1.50	1.76	1.79
19	2.03	-0.81	H	testosterone	29.49	1.96	2.13	2.16
20	2.35	-0.72	H	testosterone	29.39	2.06	2.14	2.17
38	2.42	-0.71	H	testosterone	29.14	2.31	2.39	2.41
21	5.73	-0.51	H	testosterone	25.62	5.83	5.71	5.73
22	2.28	-0.75	H	testosterone	29.24	2.21	2.32	2.35
35	2.39	-0.80	H	testosterone	28.99	2.46	2.62	2.65
23	1.01	-0.84	H	testosterone	30.62	0.83	1.04	1.06
36	1.85	-0.78	H	testosterone	29.70	1.75	1.90	1.92
24	1.58	-0.84	H	testosterone	29.95	1.50	1.70	1.73
25	0.93	-0.85	H	testosterone	30.76	0.69	0.90	0.93
33	1.60	-0.73	H	testosterone	29.99	1.46	1.56	1.58
26	1.44	-0.87	H	testosterone	30.03	1.42	1.65	1.68
27	1.09	-0.78	H	testosterone	30.51	0.94	1.09	1.11
34	1.86	-0.69	H	testosterone	29.61	1.84	1.90	1.92
28	0.98	-0.91	H	testosterone	30.56	0.89	1.17	1.19
39	1.63	-0.79	H	testosterone	29.92	1.53	1.69	1.71
29	1.31	-0.74	H	testosterone	30.12	1.33	1.43	1.46
46	1.47	-0.79	H	testosterone	30.06	1.39	1.54	1.57
47	2.08	-0.72	H	testosterone	29.64	1.81	1.90	1.92
30	3.66	-0.76	H	testosterone	27.83	3.62	3.75	3.77
31 40 42	0.80	-0.79	H	testosterone	30.75	0.70	0.85	0.88
32 41 43	1.20	-0.75	H	testosterone	30.32	1.13	1.24	1.27
1	35.73	-6.49	C	testosterone	149.92	36.53	37.56	38.01
11	33.94	-5.39	C	testosterone	152.39	34.06	34.02	34.44
12	199.60	-2.18	C	testosterone	-15.13	201.58	197.17	198.75
13	123.85	-3.56	C	testosterone	60.44	126.01	123.51	124.56
14	171.35	-3.17	C	testosterone	6.76	179.69	176.42	177.85
15	32.80	-5.34	C	testosterone	152.39	34.06	33.97	34.39
16	31.55	-5.54	C	testosterone	154.14	32.31	32.43	32.84
17	35.67	-6.52	C	testosterone	150.56	35.89	36.95	37.40
18	53.93	-6.17	C	testosterone	131.46	54.99	55.58	56.15
2	38.67	-5.97	C	testosterone	146.88	39.57	40.07	40.53
3	20.65	-6.18	C	testosterone	166.02	20.43	21.26	21.60
4	36.44	-5.84	C	testosterone	149.65	36.80	37.19	37.63

5	42.82	-6.04	C	testosterone	143.70	42.75	43.30	43.78
6	50.49	-5.69	C	testosterone	134.96	51.49	51.62	52.17
7	23.34	-6.00	C	testosterone	162.97	23.48	24.12	24.47
45	30.41	-5.99	C	testosterone	155.72	30.73	31.31	31.71
8	81.56	-5.22	C	testosterone	104.18	82.27	81.72	82.48
9	11.06	-5.55	C	testosterone	177.85	8.60	8.90	9.14
10	17.42	-5.59	C	testosterone	170.92	15.53	15.82	16.11
31 33	1.02	-0.84	H	precoccinelline	30.73	0.72	0.92	0.95
30 34	1.50	-0.87	H	precoccinelline	30.04	1.41	1.64	1.67
32	1.62	-0.91	H	precoccinelline	30.07	1.38	1.66	1.68
19 23	2.95	-0.91	H	precoccinelline	28.75	2.70	2.98	3.00
17 24	1.50	-0.77	H	precoccinelline	30.09	1.36	1.50	1.52
18 25	1.88	-0.83	H	precoccinelline	29.81	1.64	1.83	1.86
16 26	1.50	-0.82	H	precoccinelline	30.16	1.29	1.48	1.50
15 27	1.50	-0.82	H	precoccinelline	30.03	1.42	1.60	1.63
22 29	1.56	-0.73	H	precoccinelline	30.11	1.34	1.44	1.46
21 28	1.18	-0.83	H	precoccinelline	30.58	0.87	1.07	1.09
20	2.74	-0.83	H	precoccinelline	28.89	2.56	2.76	2.78
35 36 37	0.94	-0.74	H	precoccinelline	30.66	0.79	0.90	0.92
11 13	31.20	-7.26	C	precoccinelline	156.67	29.78	31.63	32.03
12	32.60	-6.86	C	precoccinelline	152.33	34.12	35.54	35.97
3 7	58.10	-5.74	C	precoccinelline	128.22	58.23	58.37	58.96
2 8	31.10	-6.15	C	precoccinelline	155.27	31.18	31.91	32.32
1 9	19.80	-6.49	C	precoccinelline	166.42	20.03	21.18	21.51
6 10	34.60	-6.03	C	precoccinelline	151.58	34.87	35.45	35.89
5	48.30	-5.86	C	precoccinelline	139.45	47.00	47.34	47.85
14	22.70	-5.62	C	precoccinelline	165.14	21.31	21.59	21.92
31 34	1.54	-0.80	H	myrrhine	30.10	1.35	1.51	1.54
30 33	1.04	-0.81	H	myrrhine	30.77	0.68	0.86	0.88
32	1.47	-0.99	H	myrrhine	30.21	1.24	1.59	1.62
19 23	1.85	-0.80	H	myrrhine	29.85	1.60	1.76	1.79
17 25	1.56	-0.79	H	myrrhine	30.08	1.37	1.53	1.55
18 24	1.38	-0.81	H	myrrhine	30.39	1.06	1.23	1.26
15 26	1.65	-0.86	H	myrrhine	29.96	1.49	1.71	1.74
16 27	1.34	-0.90	H	myrrhine	30.28	1.17	1.44	1.46
22 28	1.56	-0.77	H	myrrhine	30.09	1.36	1.49	1.52
21 29	1.38	-0.82	H	myrrhine	30.40	1.05	1.24	1.26
20	1.82	-0.94	H	myrrhine	29.90	1.55	1.86	1.88
35 36 37	0.86	-0.75	H	myrrhine	30.74	0.71	0.83	0.85
11 13	42.60	-6.35	C	myrrhine	143.45	43.00	43.85	44.34
12	30.30	-6.77	C	myrrhine	155.33	31.12	32.47	32.88
3 7	62.20	-6.00	C	myrrhine	125.59	60.86	61.23	61.85
2 8	34.00	-5.97	C	myrrhine	151.96	34.49	35.02	35.45
1 9	24.30	-6.59	C	myrrhine	162.25	24.20	25.42	25.78
6 10	34.00	-6.09	C	myrrhine	152.10	34.35	35.00	35.43
5	62.20	-6.42	C	myrrhine	125.40	61.05	61.84	62.46
14	22.00	-5.00	C	myrrhine	165.76	20.69	20.36	20.68
30	0.95	-0.74	H	hippodamine	30.78	0.67	0.77	0.80
29	1.78	-0.74	H	hippodamine	29.62	1.83	1.93	1.96
31	1.83	-0.83	H	hippodamine	29.67	1.78	1.97	2.00
32	1.48	-0.93	H	hippodamine	30.05	1.40	1.70	1.72
33	0.92	-0.85	H	hippodamine	30.74	0.71	0.92	0.95
34	1.82	-0.91	H	hippodamine	29.67	1.78	2.05	2.08
23	2.92	-0.79	H	hippodamine	28.68	2.77	2.92	2.95
24	1.40	-0.82	H	hippodamine	30.11	1.34	1.52	1.55
25	1.40	-0.81	H	hippodamine	30.28	1.17	1.34	1.37
26	1.60	-0.97	H	hippodamine	29.95	1.50	1.84	1.86
28	1.48	-0.78	H	hippodamine	30.12	1.33	1.48	1.50
27	0.78	-0.78	H	hippodamine	30.96	0.49	0.63	0.66
20	2.76	-0.84	H	hippodamine	28.72	2.73	2.93	2.96
22	1.49	-0.81	H	hippodamine	30.08	1.37	1.54	1.57
21	1.10	-0.87	H	hippodamine	30.59	0.86	1.09	1.12
16	1.40	-0.81	H	hippodamine	30.17	1.28	1.45	1.48
15	1.40	-0.84	H	hippodamine	30.04	1.41	1.62	1.64

17	1.44	-0.73	H	hippodamine	30.11	1.34	1.43	1.46
18	1.78	-0.82	H	hippodamine	29.88	1.57	1.76	1.78
19	2.90	-0.85	H	hippodamine	28.70	2.75	2.97	2.99
35 36 37	0.78	-0.84	H	hippodamine	30.75	0.70	0.90	0.93
11	23.00	-6.09	C	hippodamine	165.32	21.13	21.87	22.21
12	26.00	-6.80	C	hippodamine	159.61	26.84	28.25	28.63
13	22.30	-7.32	C	hippodamine	164.28	22.17	24.13	24.48
7	58.00	-5.51	C	hippodamine	127.66	58.79	58.69	59.29
8	39.90	-6.11	C	hippodamine	146.50	39.95	40.58	41.05
9	25.60	-6.30	C	hippodamine	160.17	26.28	27.20	27.57
10	43.30	-5.95	C	hippodamine	142.82	43.63	44.08	44.57
5	47.90	-6.23	C	hippodamine	139.52	46.93	47.63	48.15
6	34.50	-6.86	C	hippodamine	151.55	34.90	36.31	36.75
1	19.70	-6.33	C	hippodamine	166.66	19.79	20.78	21.11
2	31.30	-6.53	C	hippodamine	155.26	31.19	32.30	32.71
3	58.80	-5.99	C	hippodamine	128.08	58.37	58.75	59.35
14	22.40	-5.92	C	hippodamine	165.11	21.34	21.91	22.25

3. Literature Scaling Methods for Natural Products

DFT methods and linear scaling factors suggested in the literature were used to examine the natural products dataset. All methods were referenced to the indicated intercept unless otherwise stated.

Table S11. Effect of linear scaling for natural products dataset.

				Proton (left)/Carbon (right); values in ppm							
Method	**NMR // Geometry**	**Proton Slope/ Intercept**	**Carbon Slope/ Intercept**	**RMSE (lit. scaling)**		**RMSE (optimal scaling)**		**Slope**		**Intercept**	
quasicla. dynamics	PBE0/cc-pVTZ/PCM (unscaled)	n/a	n/a	0.1067	1.8413	0.1041	1.6334	0.9988	1.0071	0.0276	0.1813
TantilloA (ref. 2)	mPW1PW91/6-311+G(2d,p)/PCM // B3LYP/6-31+G(d,p)	-1.0936/ 31.8018	-1.0533/ 186.5242	0.1304	2.1168	0.0863	2.0887	0.9839	0.9912	-0.0430	0.7086
TantilloB (ref. 2)	mPW1PW91/6-311+G(2d,p)/PCM // B3LYP/6-311+G(2d,p)	-1.0933/ 31.9088	-1.0449/ 187.1018	0.1267	2.0454	0.0859	2.0152	0.9840	0.9921	-0.0384	0.7975
TantilloC (ref. 2)	PBE0/6-311+G(2d,p)/PCM // B3LYP/6-31+G(d,p)	-1.0958/ 31.7532	-1.0533/ 187.3123	0.1390	2.1186	0.0857	2.0776	0.9842	0.9899	-0.0563	0.8465
TantilloD (ref. 2)	PBE0/6-311+G(2d,p)/PCM // B3LYP/6-311+G(2d,p)	-1.0956/ 31.8603	-1.0450/ 187.8859	0.1235	2.0484	0.0855	2.0035	0.9842	0.9907	-0.0352	0.9354
TantilloE (ref. 2)	mPW1PW91/6-311+G(2d,p)/PCM // M06-2X/6-31+G(d,p)	-1.0938/ 31.8723	-1.0446/ 186.7246	0.1222	1.7522	0.0992	1.7374	0.9832	0.9942	-0.0124	0.5085
TantilloF (ref. 2)	mPW1PW91/6-311+G(2d,p)/PCM // M06-2X/6-311+G(2d,p)	-1.0951/ 31.9773	-1.0379/ 187.2065	0.1185	1.7536	0.0946	1.7358	0.9833	0.9947	-0.0127	0.5735
TantilloG (ref. 2)	B3LYP/6-31+G(d,p)/PCM // B3LYP/6-31G(d)	-1.0472/ 31.6874	-0.9600/ 190.0155	0.2937	3.4429	0.1243	2.8289	0.9970	0.9935	0.2756	2.4782
TantilloH (ref. 2)	WP04/aug-cc-pVDZ/PCM // B3LYP/6-31+G(d,p)	-1.0410/ 31.9173	n/a	0.1114	n/a	0.1111	n/a	1.0001	n/a	-0.0079	n/a
BallyA (ref. 17)	WP04/6-31g(d,p) // B3LYP/6-31G*	-1.0332/ 32.018	n/a	0.1928	n/a	0.1455	n/a	0.9514	n/a	0.0624	n/a
BallyB (ref. 17)	WP04/cc-pVDZ // B3LYP/6-31G*	-1.0205/ 31.844	n/a	0.1938	n/a	0.1126	n/a	0.9568	n/a	0.0004	n/a
BallyC (ref. 17)	WP04/cc-pVDZ/PCM // B3LYP/6-31G*	-1.0544/ 31.905	n/a	0.1491	n/a	0.1049	n/a	0.9825	n/a	-0.0505	n/a
BallyD (ref. 17)	B3LYP/6-31G(d,p)/PCM // B3LYP/6-31G*	-1.0552/ 31.840	n/a	0.1667	n/a	0.1243	n/a	0.9894	n/a	0.1434	n/a
Cramer (ref. 18)	WP04 and WC04/ 6-311+g(2d,p) // B3LYP/6-31G*	0.9587/ 0.1127	1.0032/ -0.9647	0.1694	3.2961	0.1069	3.1941	1.0580	1.0055	-0.2201	-1.1246

Notes:
Quasicla. dynamics: quasiclassical dynamics (B3LYP/MIDI! surface, B3LYP/cc-pVDZ NMR points, PBE0/cc-pVTZ geometry and NMR, 298 K) with no linear scaling applied.
TantilloE: Table 3, method 1.
TantilloG: Table 3, method 2.
TantilloH: estrone and *meso*-calycanthine were not included due to SCF convergence failures.
BallyB: Table 3, method 4.
BallyC: Table 3, method 3. Strychnine and *meso*-calycanthine were not included due to SCF convergence failures.
Cramer: Table 3, method 5. Referenced to tetramethylsilane.

VII. [18]-Annulene Calculations

1. Benchmark of Dynamics Surface

To assess the suitability of various DFT methods for quasiclassical dynamics on [18]-annulene, 75 blind initializations (298 K) of the low modes (<1300 cm^{-1}) of C_2, D_{3h}, and D_{6h} [18]-annulene were constructed from frequencies obtained at KMLYP/cc-pVTZ, BHandHLYP/cc-pVTZ, and B3LYP/cc-pVTZ. Using the correlation coefficient as the metric, M06-2X/cc-pVDZ was found to be optimal.

Table S12. Results of [18]-annulene benchmark.

Method	RMSE (kcal)	Slope	Intercept	R^2
C_2 annulene				
B3LYP/cc-pVDZ	3.89	0.92	-2.94	0.78
BHandHLYP/cc-pVDZ	1.38	0.97	0.06	0.91
BMK/cc-pVDZ	3.06	0.97	-2.67	0.92
KMLYP/cc-pVDZ	2.35	0.85	1.68	0.79
M06-2X/cc-pVDZ	**1.56**	**0.92**	**-1.01**	**0.97**
D_{3h} annulene				
B3LYP/cc-pVDZ	3.94	0.87	-3.34	0.72
BHandHLYP/cc-pVDZ	1.97	0.95	-1.47	0.89
BMK/cc-pVDZ	2.41	0.95	-1.93	0.87
KMLYP/cc-pVDZ	3.05	0.87	-2.17	0.72
M06-2X/cc-pVDZ	**1.81**	**0.91**	**-1.66**	**0.96**
D_{6h} annulene				
B3LYP/cc-pVDZ	1.38	0.90	0.33	0.92
BHandHLYP/cc-pVDZ	1.77	1.14	0.78	0.94
BMK/cc-pVDZ	1.64	0.86	-0.91	0.93
KMLYP/cc-pVDZ	3.00	1.20	1.47	0.85
M06-2X/cc-pVDZ	**0.89**	**0.94**	**-0.45**	**0.98**

2. Geometry Optimization of D_{6h} [18]-Annulene

To compute the stationary point NMR shifts for D_{6h} [18]-annulene, a high quality geometry is required. Traditional coupled cluster calculations are not feasible for molecules of this size, but approximate CCSD(T) calculations can be performed. In this case, we chose DLPNO-CCSD(T)/cc-pVTZ. Unfortunately, analytic gradients and frequencies are not available. Instead, we optimized the geometry numerically by using taking single point energies inside the six-dimensional D_{6h} subspace. The following is the corresponding Z-matrix:

```
0 1
X
C    1 CX
C    1 CX     2 SIXTY
C    1 CX     3 SIXTY    2 FLAT
C    1 CX     4 SIXTY    3 FLAT
C    1 CX     5 SIXTY    4 FLAT
C    1 CX     6 SIXTY    5 FLAT
C    2 CC     1 ACX      3 ZERO
C    2 CC     1 ACX      7 ZERO
C    3 CC     1 ACX      4 ZERO
C    3 CC     1 ACX      2 ZERO
C    4 CC     1 ACX      5 ZERO
C    4 CC     1 ACX      3 ZERO
C    5 CC     1 ACX      6 ZERO
C    5 CC     1 ACX      4 ZERO
C    6 CC     1 ACX      7 ZERO
```

```
C     6 CC      1 ACX      5 ZERO
C     7 CC      1 ACX      2 ZERO
C     7 CC      1 ACX      6 ZERO
X     2 RDUM    1 NINETY   3 NINETY
H     2 CH1    20 NINETY   1 ZERO
X     3 RDUM    1 NINETY   4 NINETY
H     3 CH1    22 NINETY   1 ZERO
X     4 RDUM    1 NINETY   5 NINETY
H     4 CH1    24 NINETY   1 ZERO
X     5 RDUM    1 NINETY   6 NINETY
H     5 CH1    26 NINETY   1 ZERO
X     6 RDUM    1 NINETY   7 NINETY
H     6 CH1    28 NINETY   1 ZERO
X     7 RDUM    1 NINETY   2 NINETY
H     7 CH1    30 NINETY   1 ZERO
H     8 CH2     2 ACH      1 FLAT
H     9 CH2     2 ACH      1 FLAT
H    10 CH2     3 ACH      1 FLAT
H    11 CH2     3 ACH      1 FLAT
H    12 CH2     4 ACH      1 FLAT
H    13 CH2     4 ACH      1 FLAT
H    14 CH2     5 ACH      1 FLAT
H    15 CH2     5 ACH      1 FLAT
H    16 CH2     6 ACH      1 FLAT
H    17 CH2     6 ACH      1 FLAT
H    18 CH2     7 ACH      1 FLAT
H    19 CH2     7 ACH      1 FLAT

CX         3.009118
CC         1.407290
CH1        1.092922
CH2        1.097890
ACX      115.745004
ACH      118.274203

RDUM=1.000000
ZERO=0.000000
SIXTY=60.000000
NINETY=90.000000
FLAT=180.000000
```

In the above, CX, CC, CH1, CH2, ACX, and ACH are the adjustable variables. After initial exploration at B3LYP/cc-pVTZ to define the useful bounds of the parameter space, a central composite design was created using JMP. After additional rounds of energy evaluation and design augmentation, the following points were gathered:

Table S13. Summary of [18]-annulene geometry optimization.

CX	CC	CH1	CH2	ACX	ACH	Y	Yadj	Weight
2.95	1.38	1.07	1.07	114	122	37.388	39.908	0.000627491
2.95	1.38	1.07	1.07	118	116	20.8017	23.3217	0.001835193
2.95	1.38	1.07	1.12	114	116	30.8549	33.3749	0.000896954
2.95	1.38	1.07	1.12	118	122	22.2537	24.7737	0.001626714
2.95	1.38	1.12	1.07	114	116	30.1457	32.6657	0.000936288
2.95	1.38	1.12	1.07	118	122	21.1144	23.6344	0.001787039
2.95	1.38	1.12	1.12	114	122	42.5972	45.1172	0.000491024
2.95	1.38	1.12	1.12	118	116	28.4447	30.9647	0.00104187
2.95	1.43	1.07	1.07	114	116	80.9636	83.4836	0.000143461
2.95	1.43	1.07	1.07	118	122	12.2032	14.7232	0.004591946
2.95	1.43	1.07	1.12	114	122	99.8857	102.4057	9.53477E-05
2.95	1.43	1.07	1.12	118	116	16.0378	18.5578	0.002895262
2.95	1.43	1.12	1.07	114	122	100.164	102.684	9.48316E-05
2.95	1.43	1.12	1.07	118	116	15.9218	18.4418	0.002931692
2.95	1.43	1.12	1.12	114	116	88.0084	90.5284	0.000122005

2.95	1.43	1.12	1.12	118	122	21.634	24.154	0.001711111
3.05	1.38	1.07	1.07	114	116	8.28045	10.80045	0.008499808
3.05	1.38	1.07	1.07	118	122	65.2117	67.7317	0.000217932
3.05	1.38	1.07	1.12	114	122	14.3627	16.8827	0.003496191
3.05	1.38	1.07	1.12	118	116	76.9852	79.5052	0.000158176
3.05	1.38	1.12	1.07	114	122	12.4544	14.9744	0.004439854
3.05	1.38	1.12	1.07	118	116	75.402	77.922	0.000164668
3.05	1.38	1.12	1.12	114	116	12.585	15.105	0.004363744
3.05	1.38	1.12	1.12	118	122	74.0568	76.5768	0.000170503
3.05	1.43	1.07	1.07	114	122	24.2251	26.7451	0.001396062
3.05	1.43	1.07	1.07	118	116	48.4046	50.9246	0.000385458
3.05	1.43	1.07	1.12	114	116	19.7412	22.2612	0.002013851
3.05	1.43	1.07	1.12	118	122	49.9742	52.4942	0.00036276
3.05	1.43	1.12	1.07	114	116	18.6609	21.1809	0.002224048
3.05	1.43	1.12	1.07	118	122	48.1026	50.6226	0.000390069
3.05	1.43	1.12	1.12	114	122	30.117	32.637	0.000937933
3.05	1.43	1.12	1.12	118	116	56.3603	58.8803	0.00028836
2.95	1.405	1.095	1.095	116	119	2.30218	4.82218	0.041231299
3.05	1.405	1.095	1.095	116	119	11.3891	13.9091	0.005142365
3	1.38	1.095	1.095	116	119	5.1226	7.6426	0.016832372
3	1.43	1.095	1.095	116	119	5.90871	8.42871	0.01388057
3	1.405	1.07	1.095	116	119	0.0202931	2.5402931	0.134172555
3	1.405	1.12	1.095	116	119	2.87949	5.39949	0.033162555
3	1.405	1.095	1.07	116	119	0.815982	3.335982	0.082448551
3	1.405	1.095	1.12	116	119	4.86629	7.38629	0.017999441
3	1.405	1.095	1.095	114	119	16.3342	18.8542	0.0028052
3	1.405	1.095	1.095	118	119	25.2367	27.7567	0.001296287
3	1.405	1.095	1.095	116	116	1.50064	4.02064	0.05825623
3	1.405	1.095	1.095	116	122	3.46208	5.98208	0.027184786
3	1.405	1.095	1.095	116	119	0	2.52	0.136047018
2.99	1.38	1.075	1.075	115	119	1.32	3.84	0.063509806
2.99	1.38	1.075	1.11	115	119	3.03	5.55	0.031444069
3.01	1.4	1.075	1.075	116	121	3	5.52	0.031775891
2.99	1.38	1.075	1.0925	117	117	15.56	18.08	0.003049837
2.99	1.38	1.11	1.11	116	121	7.64	10.16	0.009594572
3.01	1.38	1.075	1.0925	115	117	1.96	4.48	0.047459944
2.99	1.38	1.11	1.075	116	121	5.54	8.06	0.015159876
3.01	1.38	1.0925	1.075	117	121	21.65	24.17	0.00170885
3.01	1.38	1.0925	1.075	115	121	3.65	6.17	0.025595806
3.01	1.38	1.075	1.11	117	119	24.02	26.54	0.001417692
3	1.4	1.075	1.075	117	119	8.88	11.4	0.007635919
2.99	1.38	1.11	1.075	115	119	2.56	5.08	0.037304524
3.01	1.38	1.075	1.075	117	119	21.63	24.15	0.001711677
2.99	1.38	1.075	1.075	115	119	1.32	3.84	0.063509806
3.01	1.38	1.075	1.11	116	121	10.76	13.28	0.005638301
3	1.4	1.075	1.075	117	121	9.5	12.02	0.006873778
2.99	1.38	1.075	1.075	117	119	13.92	16.44	0.003686315
2.99	1.38	1.0925	1.075	117	117	15.94	18.46	0.002925931
2.99	1.38	1.0925	1.075	115	117	1.41	3.93	0.060809126

2.99	1.38	1.075	1.11	116	117	5.92	8.44	0.013843973
3.01	1.38	1.075	1.0925	117	117	23.57	26.09	0.001466947
2.99	1.38	1.11	1.0925	115	117	2.02	4.54	0.046271447
3.01	1.38	1.0925	1.075	115	121	3.65	6.17	0.025595806
3	1.4	1.075	1.075	116	117	0.71	3.23	0.087466872
2.99	1.38	1.0925	1.075	117	121	14.28	16.8	0.003530575
2.99	1.38	1.11	1.075	116	117	5.4	7.92	0.015692084
3.01	1.38	1.075	1.075	115	119	1.97	4.49	0.047258756
2.99	1.38	1.0925	1.075	115	121	3.4	5.92	0.027742021
2.99	1.4	1.075	1.075	116	121	0.71	3.23	0.087466872
3.01	1.38	1.11	1.075	117	119	23.21	25.73	0.001508221
3.01	1.38	1.0925	1.075	115	117	2.36	4.88	0.040299181
2.99	1.38	1.075	1.0925	116	121	3.69	6.21	0.025275439
2.99	1.38	1.075	1.0925	115	117	0.87	3.39	0.080050592
3.01	1.38	1.11	1.0925	117	117	25.07	27.59	0.001311978
2.99	1.38	1.0925	1.075	117	117	15.94	18.46	0.002925931
2.99	1.38	1.0925	1.11	115	121	5.2	7.72	0.016502086
3.01	1.38	1.075	1.0925	115	121	3.3	5.82	0.028675973
3	1.4	1.075	1.075	117	117	10.41	12.93	0.005945837
2.99	1.4	1.075	1.075	116	117	-0.47	2.05	0.192215281
3.01	1.4	1.075	1.075	116	117	2.44	4.96	0.039060059
3.01	1.38	1.11	1.11	116	117	12.42	14.94	0.004460232
2.99	1.38	1.11	1.11	117	119	17.9	20.42	0.00239248
3.01	1.38	1.075	1.11	115	119	3.76	6.28	0.02472897
3.01	1.38	1.11	1.11	116	121	12.18	14.7	0.004606384
3.01	1.38	1.11	1.0925	115	121	4.48	7	0.02
3.01	1.38	1.0925	1.11	117	121	24.12	26.64	0.001407084
2.99	1.38	1.075	1.11	117	119	16.25	18.77	0.002830352
3	1.4	1.075	1.075	116	121	1.6	4.12	0.05563468
3	1.4	1.075	1.11	117	117	13.05	15.57	0.004108043
3	1.4	1.075	1.075	115	117	0.76	3.28	0.085045584
3	1.4	1.075	1.11	115	121	3.11	5.63	0.030583939
2.99	1.38	1.0925	1.11	117	117	18.14	20.66	0.002337346
3.01	1.38	1.0925	1.075	117	117	23.9	26.42	0.001430582
3	1.4	1.075	1.075	115	121	3.26	5.78	0.029062671
3	1.4	1.11	1.075	115	117	2.47	4.99	0.03860989
3.01	1.38	1.075	1.0925	117	121	21.38	23.9	0.00174761
3.01	1.38	1.11	1.075	115	119	3.09	5.61	0.030795668
3.01	1.38	1.075	1.075	117	119	21.63	24.15	0.001711677
3.01	1.38	1.075	1.0925	115	117	1.96	4.48	0.047459944
3	1.4	1.11	1.075	117	121	11.37	13.89	0.005156444
2.99	1.38	1.075	1.0925	115	121	2.96	5.48	0.032226462
3.01	1.38	1.0925	1.11	115	117	3.95	6.47	0.023331288
3.01	1.38	1.11	1.075	116	117	10.47	12.99	0.00589136
2.99	1.38	1.075	1.0925	117	121	13.93	16.45	0.003681851
2.99	1.38	1.11	1.0925	117	121	15.66	18.18	0.003016478
2.969	1.396	1.08	1.087	116.14	118.44	-2.51	0.01	0.99990001
2.95	1.4	1.09	1.095	116.5	117	-1.21	1.31	0.368174957
2.95	1.4	1.09	1.075	116.5	120	-0.58	1.94	0.209925267

2.95	1.4	1.09	1.075	116.5	120	-0.58	1.94	0.209925267
2.95	1.39	1.07	1.075	116.5	117	-0.69	1.83	0.229943204
2.95	1.4	1.07	1.095	116.5	120	-0.63	1.89	0.218717876
2.95	1.39	1.09	1.095	115.5	117	2.8	5.32	0.034126897
2.95	1.39	1.07	1.075	115.5	117	3.16	5.68	0.030063976
2.99	1.4	1.07	1.075	115.5	117	-0.37	2.15	0.177856825
2.95	1.39	1.09	1.095	116.5	117	-1.08	1.44	0.325351379
2.95	1.39	1.07	1.095	116.5	120	-0.9	1.62	0.275907736
2.95	1.39	1.09	1.095	115.5	117	2.8	5.32	0.034126897
2.95	1.4	1.07	1.075	116.5	120	-0.55	1.97	0.204880247
2.95	1.39	1.09	1.095	115.5	117	2.8	5.32	0.034126897
2.95	1.39	1.07	1.095	116.5	120	-0.9	1.62	0.275907736
2.95	1.4	1.09	1.075	116.5	117	-0.98	1.54	0.296595088
2.95	1.39	1.09	1.075	116.5	120	-0.8	1.72	0.252627324
2.95	1.4	1.09	1.075	115.5	117	5.44	7.96	0.015537215
2.95	1.39	1.07	1.075	115.5	120	4.58	7.1	0.019451469
2.95	1.4	1.09	1.075	115.5	117	5.44	7.96	0.015537215
2.95	1.4	1.09	1.075	115.5	120	7.43	9.95	0.00999975
2.95	1.39	1.07	1.075	116.5	117	-0.69	1.83	0.229943204
2.95	1.39	1.09	1.095	115.5	120	4	6.52	0.022983011
2.95	1.4	1.07	1.095	115.5	120	7.24	9.76	0.01038879
2.95	1.39	1.07	1.075	115.5	120	4.58	7.1	0.019451469
2.95	1.39	1.07	1.075	115.5	117	3.16	5.68	0.030063976
2.95	1.4	1.07	1.095	115.5	117	5.23	7.75	0.016376663
2.99	1.4	1.07	1.075	116.5	117	2.52	5.04	0.037876492
2.99	1.4	1.07	1.095	116.5	117	2.37	4.89	0.040141136
2.99	1.4	1.07	1.075	115.5	120	0.33	2.85	0.109619074
2.95	1.4	1.07	1.095	115.5	120	7.24	9.76	0.01038879
2.95	1.4	1.07	1.095	115.5	117	5.23	7.75	0.016376663
2.95	1.4	1.07	1.095	116.5	120	-0.63	1.89	0.218717876
2.99	1.4	1.07	1.075	115.5	117	-0.37	2.15	0.177856825
2.95	1.4	1.09	1.095	116.5	117	-1.21	1.31	0.368174957
2.95	1.4	1.09	1.075	115.5	117	5.44	7.96	0.015537215
2.95	1.39	1.09	1.075	116.5	117	-0.83	1.69	0.259329374
2.95	1.4	1.09	1.075	115.5	120	7.43	9.95	0.00999975
2.95	1.39	1.07	1.095	116.5	117	-0.94	1.58	0.286008466
2.95	1.39	1.09	1.095	116.5	120	-0.99	1.53	0.299320542
2.95	1.4	1.07	1.095	116.5	120	-0.63	1.89	0.218717876
2.95	1.39	1.07	1.075	116.5	120	-0.71	1.81	0.233857955
2.95	1.39	1.07	1.075	116.5	117	-0.69	1.83	0.229943204
2.95	1.4	1.07	1.095	115.5	117	5.23	7.75	0.016376663
2.95	1.4	1.09	1.075	116.5	117	-0.98	1.54	0.296595088
2.99	1.4	1.07	1.095	115.5	117	-0.71	1.81	0.233857955
2.99	1.4	1.07	1.095	116.5	117	2.37	4.89	0.040141136
2.95	1.4	1.09	1.095	115.5	120	7.06	9.58	0.010778603
2.95	1.39	1.07	1.095	116.5	117	-0.94	1.58	0.286008466
2.95	1.39	1.07	1.075	115.5	120	4.58	7.1	0.019451469
2.95	1.39	1.07	1.075	115.5	120	4.58	7.1	0.019451469
2.964	1.396	1.082	1.086	116.28	118.36	-2.52	0	1

The Y column indicates relative energies in kcal/mol. Some entries have negative numbers because their parameters were derived from augmented points. Therefore, the Yadj column adjusts the energy values such that the best energy found is set to 0 kcal/mol. (Distances are in Å and angles are in degrees.) The values were then weighted by $1/(Yadj^2+1)$ to bias the response surface to the minimum energy region. The response surface was constructed from a second-order polynomial including all the possible cross-terms. The fit was very good (adjusted $R^2 = 0.99$) and the curvature in the response surface indicates a true minimum.
The best estimate of the minimum is:

CX = 2.963	CH1 = 1.082	ACX = 116.29
CC = 1.396	CH2 = 1.086	ACH = 118.40

The response surface indicates that this structure is within 0.1 kcal/mol of the minimum. The geometrical parameters compare well to those of the X-ray structure:

Table S14. Comparison of optimized geometry with x-ray structure.

Parameter	CCSD(T)/cc-pVTZ	X-ray average
External C-C	1.413 Å	1.405 Å
Internal C-C	1.395 Å	1.385 Å
External C-C-C	123.72°	124.04°
Inner C-C-C	127.44°	127.93°

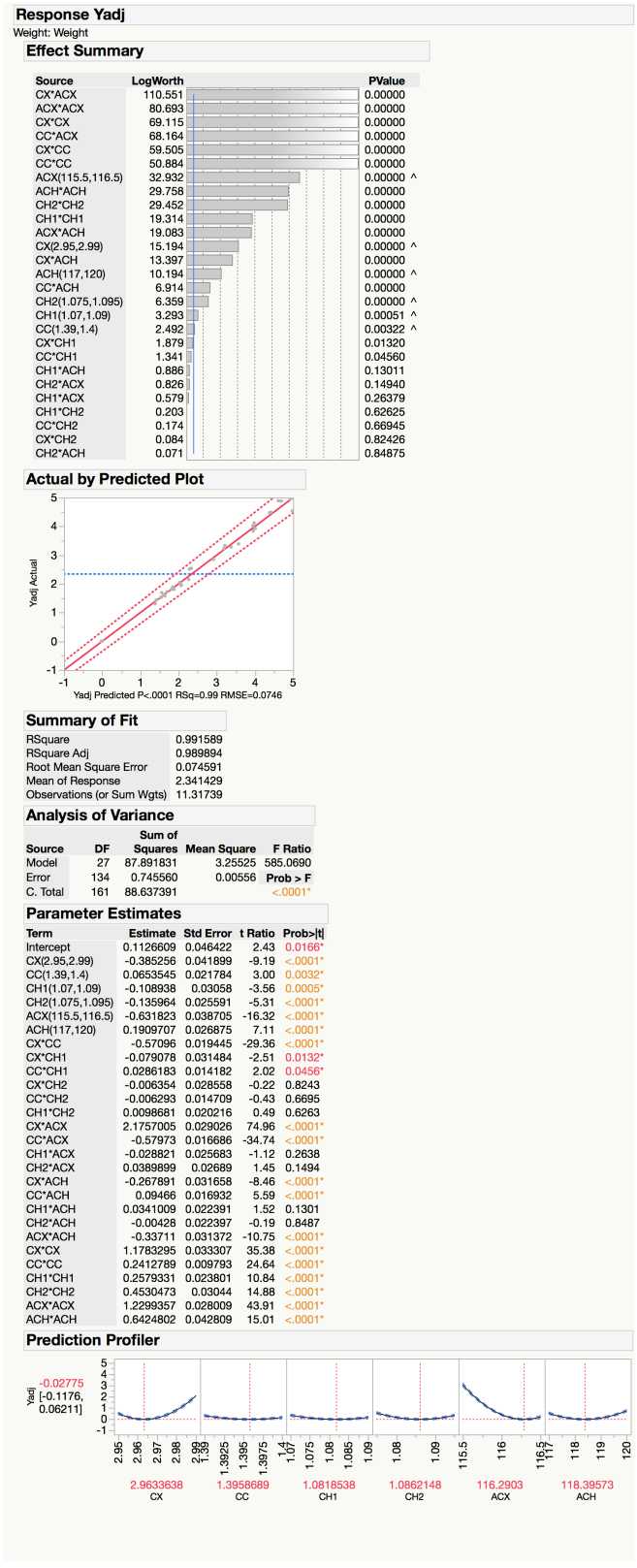


Figure S4. The most important effects in the model, some statistical metrics, and the curvature along each dimension in the neighborhood of the predicted minimum.

3. [18]-Annulene Stationary Predictions

Literature methods and linear scaling methods were used to determine the stationary point chemical shifts of D_{6h} [18]-annulene (values shown below). Methods and scaling factors were taken from Tantillo and co-workers (http://cheshirenmr.info/).

Table S15. Literature methods applied to D_{6h} [18]-annulene.

			Temperature (K)	203	203	213	213	333	393
Method (NMR//Geometry)	**Proton Slope/Intercept**	**Carbon Slope/Intercept**	**Resonance**	external carbons	internal carbons	external protons	internal protons	coalesced carbons	coalesced protons
Experiment	n/a	n/a		128	121	9.17	-2.96	126	5.45
mPW1PW91/6-311+G(2d,p)/PCM // B3LYP/6-31+G(d,p)	-1.0936/31.8018	-1.0533/186.5242		124.71	113.68	11.08	-10.09	121.03	4.02
mPW1PW91/6-311+G(2d,p)/PCM // B3LYP/6-311+G(2d,p)	-1.0933/31.9088	-1.0449/187.1018		125.09	113.7	11.11	-10.17	121.29	4.02
PBE0/6-311+G(2d,p)/PCM // B3LYP/6-31+G(d,p)	-1.0958/31.7532	-1.0533/187.3123		124.68	113.45	11.08	-10.05	120.94	4.04
PBE0/6-311+G(2d,p)/PCM // B3LYP/6-311+G(2d,p)	-1.0956/31.8603	-1.0450/187.8859		124.70	113.13	11.01	-10.22	120.84	3.93
mPW1PW91/6-311+G(2d,p)/PCM // M06-2X/6-31+G(d,p)	-1.0938/31.8723	-1.0446/186.7246		125.36	114.41	11.09	-9.95	121.71	4.08
mPW1PW91/6-311+G(2d,p)/PCM // M06-2X/6-311+G(2d,p)	-1.0951/31.9773	-1.0379/187.2065		125.71	114.47	11.11	-10.00	121.96	4.07
B3LYP/6-31+G(d,p)/PCM // B3LYP/6-31G(d)	-1.0472/31.6874	-0.9600/190.0155		124.58	113.44	11.11	-10.29	120.87	3.98

The literature optimization methods generally collapse to the D_{6h} symmetry, so no numbers are shown for the D_{3h} or C_2 alternatives. Methods involving augmented basis sets also suffer from serious SCF convergence problems.

4. Details of [18]-Annulene Predictions

Various stationary point geometries were evaluated using B3LYP/cc-pVDZ, B3LYP/cc-pVTZ and B3LYP/jul-cc-pVTZ NMR and dynamic corrections evaluated on the M06-2X/cc-pVDZ surface with B3LYP/cc-pVDZ NMR. Although D_{6h} was the clear best candidate at all levels of stationary NMR, the B3LYP/jul-cc-pVTZ results were closest to experimental. Use of even larger basis sets such as aug-cc-pVTZ were challenging because of SCF convergence issues. All values in ppm.

Table S16. Stationary NMR shieldings for various geometries of [18]-annulene.

Symmetry	Geometry Method (cc-pVTZ basis)	NMR Basis (B3LYP functional)	External C shielding	Internal C shielding	External H shielding	Internal H shielding	Benzene C shielding (CCSD(T)/cc-pVQZ geom)	Benzene C shielding (CCSD(T)/cc-pVQZ geom)
C_2	BH&HLYP	jul-cc-pVTZ	52.3508	60.8928	22.4115	34.3841	50.4942 (jul-cc-pVTZ)	23.9819
	BH&H	jul-cc-pVTZ	54.0273	63.3349	21.8172	36.3531		
	HF	jul-cc-pVTZ	49.5476	54.4845	24.329	27.8249		
	LC-ωPBE	jul-cc-pVTZ	49.468	54.8677	23.7332	29.1069		
	M05-2X	jul-cc-pVTZ	50.4758	57.4028	22.5686	33.2813		
	M06-2X	jul-cc-pVTZ	50.246	57.1379	22.567	33.0445		
	M06-HF	jul-cc-pVTZ	48.2408	52.93	23.9644	28.2471		
	VSXC	jul-cc-pVTZ	51.7729	61.2789	19.9732	41.8958		
	ωB97XD	jul-cc-pVTZ	50.2297	57.0106	22.8311	32.1651		
	ωB97X	jul-cc-pVTZ	49.2083	54.9086	23.4541	29.8995		
	KMLYP	jul-cc-pVTZ	53.4932	61.862	22.5946	34.0172		

	BH&HLYP	cc-pVDZ	70.1843	80.6589	22.189	36.984	67.5278	24.2644
	BH&H	cc-pVDZ	68.7868	78.3525	22.7665	35.0056	(cc-pVDZ)	
	HF	cc-pVDZ	66.1108	72.1158	24.632	28.3683		
	LC-ωPBE	cc-pVDZ	65.921	72.5668	24.0508	29.6825		
	M05-2X	cc-pVDZ	66.6048	75.2601	22.9093	33.8836		
	M06-2X	cc-pVDZ	66.3753	75.0123	22.9073	33.6435		
	M06-HF	cc-pVDZ	64.684	70.606	24.2724	28.8146		
	VSXC	cc-pVDZ	66.9413	78.8731	20.3353	42.504		
	ωB97XD	cc-pVDZ	66.4885	74.8211	23.1681	32.7614		
	ωB97X	cc-pVDZ	65.625	72.6687	23.7767	30.4818		
	KMLYP	cc-pVDZ	69.9105	79.1932	22.9491	34.6524		
	BH&HLYP	cc-pVTZ	52.9774	61.6288	22.4908	34.5935	51.0999	24.0451
	BH&H	cc-pVTZ	54.4861	64.0672	21.8948	36.5602	(cc-pVTZ)	
	HF	cc-pVTZ	49.9556	55.2626	24.4042	27.9876		
	LC-ωPBE	cc-pVTZ	49.8358	55.6905	23.8089	29.2824		
	M05-2X	cc-pVTZ	50.6993	58.35	22.645	33.4764		
	M06-2X	cc-pVTZ	50.4595	58.0969	22.6442	33.2394		
	M06-HF	cc-pVTZ	48.5469	53.694	24.0369	28.4159		
	VSXC	cc-pVTZ	51.3424	62.0203	20.038	42.1438		
	ωB97XD	cc-pVTZ	50.5363	57.9372	22.9088	32.3568		
	ωB97X	cc-pVTZ	49.5663	55.7695	23.5308	30.081		
	KMLYP	cc-pVTZ				34.2242		
			54.1396	62.5195	22.6688			
D_{3h}	CAM-B3LYP	jul-cc-pVTZ	53.9222	62.5676	21.8878	35.6288		
	M06-HF	jul-cc-pVTZ	52.58	59.4163	23.0076	31.3898		
	ωB97XD	jul-cc-pVTZ	53.4307	61.6975	22.0253	34.9619		
	ωB97X	jul-cc-pVTZ	53.0143	60.5118	22.5522	32.9432		
	BH&HLYP	jul-cc-pVTZ	54.9781	63.8655	21.8417	36.4125		
	BH&H	jul-cc-pVTZ	56.0363	65.5642	21.4072	37.8152		
	HF	jul-cc-pVTZ	53.9558	60.9618	23.3653	30.9516		
	LC-ωPBE	jul-cc-pVTZ	53.6133	61.0308	22.7671	32.3219		
	M05-2X	jul-cc-pVTZ	53.63	62.44	21.66	36.49		
	M06-2X	jul-cc-pVTZ				36.1056		
			53.2747	61.9588	21.6971			
D_{6h}	CCSD(T)	jul-cc-pVTZ	51.5325	63.3475	19.9778	42.3342		
	CCSD(T)	cc-pVDZ	67.404	79.761	20.2824	42.734		
	CCSD(T)	cc-pVTZ	51.7762	63.3148	19.9818	42.3555		

Table S17. Raw corrections for [18]-annulene.

Symmetry	Temperature (Kelvin)	External C raw correction	Internal C raw correction	External H raw correction	Internal H raw correction	Benzene C raw correction	Benzene H raw correction
C_2	203	-4.54	-5.19	-0.27	-1.26	-4.72	-0.44
D_{3h}		-5.42	-6.10	0.02	-2.27		
D_{6h}							
		-6.56	-9.88	1.69	-8.52		
C_2	213	-4.47	-4.96	-0.25	-1.32		
D_{3h}		-5.73	-6.91	0.20	-2.90		
D_{6h}							
		-6.65	-10.17	1.75	-8.62		
C_2	333	-4.86	-5.70	-0.09	-1.88		
D_{3h}		-5.81	-7.38	0.23	-3.00		
D_{6h}							
		-7.12	-11.24	1.92	-9.38		
C_2	393	-4.86	-5.70	-0.09	-1.88		
D_{3h}		-5.84	-7.01	0.14	-2.75		
D_{6h}							
		-7.24	-11.30	1.92	-9.39		

Note: the benzene shift was assumed to be temperature-independent, since the temperature dependence for normal organic molecules is several orders of magnitude smaller than for large annulenes.

Table S18. Summary of dynamically-corrected predicted shifts.

Symmetry	Geometry Method	NMR Method	External C (203 K)	Internal C (203 K)	External H (213 K)	Internal H (213 K)	Coalesced C (333 K)	Coalesced H (393 K)
experiment	n/a	n/a	128	121	9.17	–2.96	126	5.45
C_2	BH&HLYP	jul-cc-pVTZ	126.8	118.9	8.69	-2.22	124.6	5.14
	BH&H	jul-cc-pVTZ	125.1	116.5	9.28	-4.19	122.6	4.88
	HF	jul-cc-pVTZ	129.6	125.3	6.77	4.34	128.6	6.04
	LC-ωPBE	jul-cc-pVTZ	129.7	124.9	7.37	3.06	128.5	6.01
	M05-2X	jul-cc-pVTZ	128.7	122.4	8.53	-1.11	127.0	5.40
	M06-2X	jul-cc-pVTZ	128.9	122.7	8.53	-0.88	127.2	5.48
	M06-HF	jul-cc-pVTZ	130.9	126.9	7.14	3.92	130.0	6.15
	VSXC	jul-cc-pVTZ	127.4	118.5	11.13	-9.73	124.0	4.26
	ωB97XD	jul-cc-pVTZ	129.0	122.8	8.27	0.00	127.3	5.60
	ωB97X	jul-cc-pVTZ	130.0	124.9	7.65	2.27	128.7	5.94
	KMLYP	jul-cc-pVTZ	125.7	118.0	8.52	-1.90	123.5	5.14
	BH&HLYP	cc-pVDZ	126.0	116.2	9.19	-4.53	123.1	4.70
	BH&H	cc-pVDZ	127.4	118.5	8.62	-2.56	124.8	4.97
	HF	cc-pVDZ	130.1	124.8	6.75	4.08	128.7	5.94
	LC-ωPBE	cc-pVDZ	130.3	124.3	7.33	2.77	128.6	5.89
	M05-2X	cc-pVDZ	129.6	121.6	8.47	-1.43	127.3	5.25
	M06-2X	cc-pVDZ	129.8	121.8	8.48	-1.19	127.5	5.34
	M06-HF	cc-pVDZ	131.5	126.2	7.11	3.64	130.1	6.03
	VSXC	cc-pVDZ	129.2	118.0	11.05	-10.05	125.9	4.10
	ωB97XD	cc-pVDZ	129.7	122.0	8.22	-0.31	127.5	5.46
	ωB97X	cc-pVDZ	130.6	124.2	7.61	1.97	128.8	5.81
	KMLYP	cc-pVDZ	126.3	117.6	8.43	-2.20	123.8	4.97
	BH&HLYP	cc-pVTZ	126.8	118.8	8.67	-2.36	124.5	5.08
	BH&H	cc-pVTZ	127.3	121.0	7.27	2.98	126.0	5.98
	HF	cc-pVTZ	125.3	116.3	9.27	-4.33	122.7	4.82
	LC-ωPBE	cc-pVTZ	125.6	117.9	8.50	-1.99	123.4	5.08
	M05-2X	cc-pVTZ	129.9	124.7	7.36	2.95	128.6	5.97
	M06-2X	cc-pVTZ	129.1	122.1	8.52	-1.25	127.1	5.35
	M06-HF	cc-pVTZ	129.3	122.3	8.52	-1.01	127.4	5.43
	VSXC	cc-pVTZ	131.2	126.7	7.13	3.82	130.1	6.11
	ωB97XD	cc-pVTZ	129.2	122.5	8.26	-0.13	127.4	5.54
	ωB97X	cc-pVTZ	130.2	124.6	7.63	2.15	128.7	5.89
	KMLYP	cc-pVTZ	129.8	125.1	6.76	4.24	128.6	6.00
D_{3h}	CAM-B3LYP	jul-cc-pVTZ	126.1	118.2	8.76	-1.87	124.1	5.21
	M06-HF	jul-cc-pVTZ	127.5	121.3	7.64	2.37	126.1	5.87
	ωB97XD	jul-cc-pVTZ	126.6	119.0	8.63	-1.21	124.8	5.34
	ωB97X	jul-cc-pVTZ	127.0	120.2	8.10	0.81	125.4	5.66
	BH&HLYP	jul-cc-pVTZ	125.1	116.9	8.81	-2.66	123.0	4.98
	BH&H	jul-cc-pVTZ	124.0	125.2	9.25	-4.06	121.7	4.80
	HF	jul-cc-pVTZ	126.1	119.8	7.29	2.80	124.7	5.78
	LC-ωPBE	jul-cc-pVTZ	126.4	119.7	7.89	1.43	124.9	5.72
	M05-2X	jul-cc-pVTZ	126.4	118.3	9.00	-2.73	124.4	5.07
	M06-2X	jul-cc-pVTZ	126.8	118.8	8.96	-2.35	124.8	5.18
D_{6h}	CCSD(T)	jul-cc-pVTZ	129.6	121.1	9.13	-2.86	127.6	5.27
	CCSD(T)	cc-pVDZ	130.8	121.8	9.10	-2.98	128.6	5.22
	CCSD(T)	cc-pVTZ	130.0	121.8	9.18	-2.82	128.1	5.32

VIII. Miscellaneous

1. Analysis of Carbon Monoxide Shielding and Potential Energy Surface

To illustrate the interplay between the shielding surface and potential energy surface during the dynamical simulation, DFT energies were obtained at B3LYP/MIDI! for a series of geometries of CO with varying bond length. At each point, the carbon shielding was calculated at B3LYP/cc-pVDZ/GIAO.

Table S19. Examination of CO Shielding as a Function of Bond Length.

C-O bond length (A)	C shielding (ppm)	B3LYP/MIDI! energy (hartree)	
0.75	122.0569	-112.3845338	
0.8	116.4547	-112.7128432	
0.85	107.0715	-112.9414737	
0.9	94.6386	-113.0973556	
0.95	79.6813	-113.2003355	
1	62.5692	-113.2649272	
1.05	43.5384	-113.3017217	
1.1	22.7054	-113.3184654	
1.11	18.3252	-113.3199379	
1.115	16.1082	-113.3204724	
1.12	13.8732	-113.3208785	
1.125	11.6201	-113.3211605	
1.13	9.3488	-113.3213226	
1.135	7.0592	-113.3213689	
1.14	4.7513	-113.3213034	
1.142	3.8229	-113.3212468	stationary ground state
1.144	2.8916	-113.3211731	
1.146	1.9572	-113.3210826	dynamic average
1.148	1.0199	-113.3209756	
1.15	0.0796	-113.3208522	
1.155	-2.2843	-113.3204738	
1.16	-4.6672	-113.3199983	
1.165	-7.0691	-113.3194291	
1.17	-9.4904	-113.3187695	
1.175	-11.9311	-113.3180226	
1.18	-14.3914	-113.3171917	
1.185	-16.8715	-113.3162797	
1.19	-19.3717	-113.3152896	
1.195	-21.8921	-113.3142243	
1.2	-24.4329	-113.3130865	
1.25	-51.0229	-113.2982783	
1.3	-79.9779	-113.2787377	
1.35	-111.6799	-113.2561709	
1.4	-146.6079	-113.2318355	
1.45	-185.354	-113.2066491	
1.5	-228.6422	-113.1812676	
1.7	-468.9292	-113.0849869	
2	-1323.4557	-112.9685732	

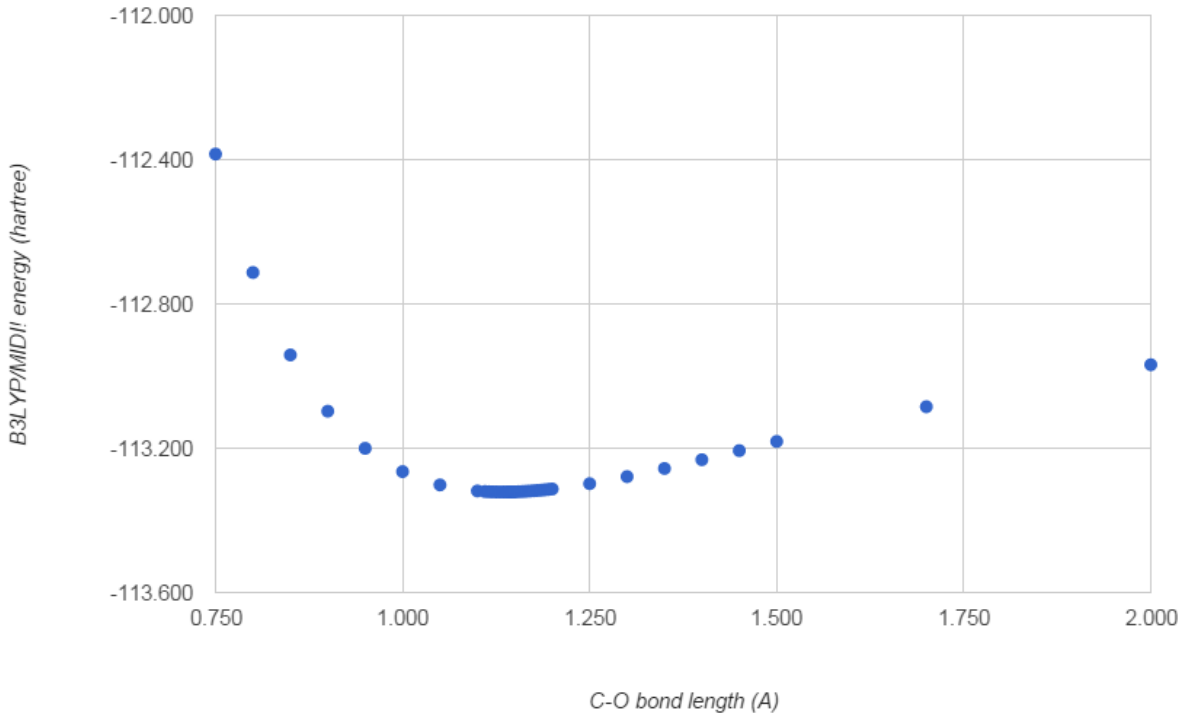


Figure S5. Calculated potential energy curve of CO.

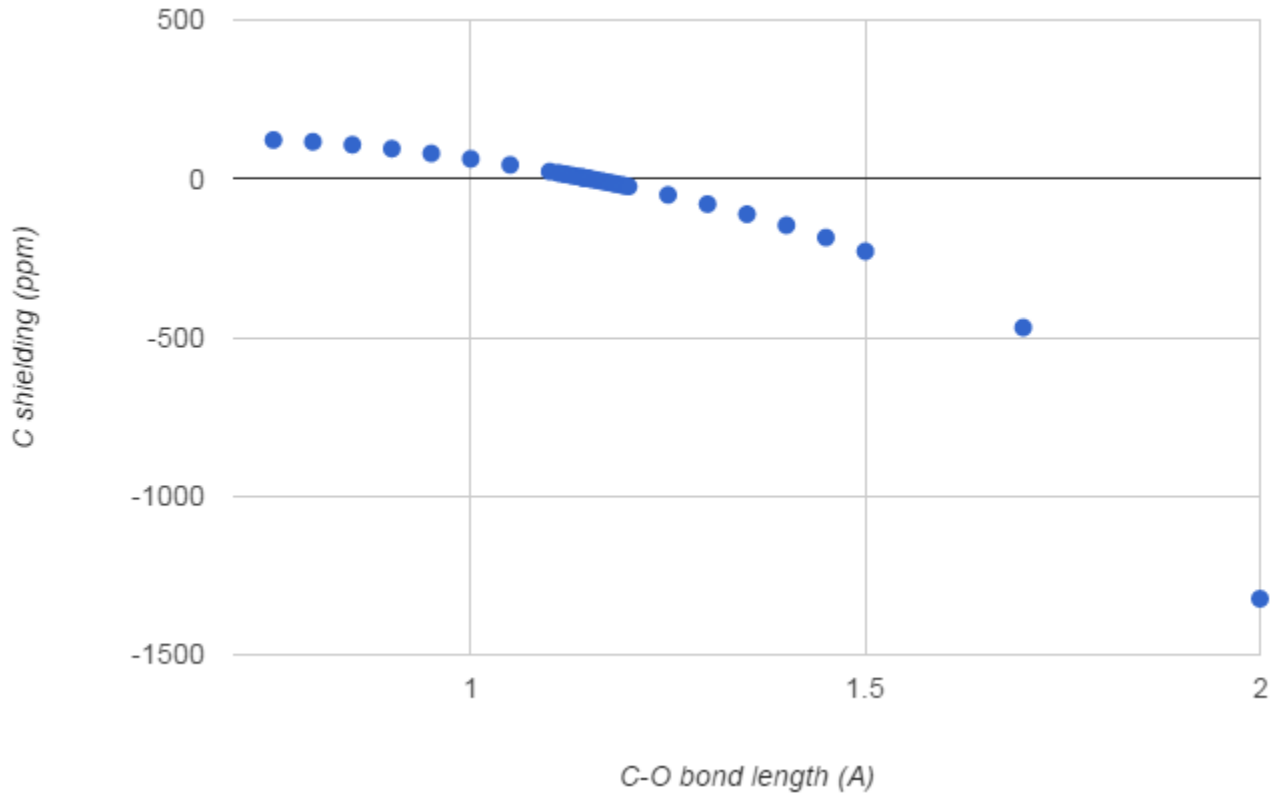


Figure S6. Calculated NMR shielding of the carbon atom in CO as a function of bond length.

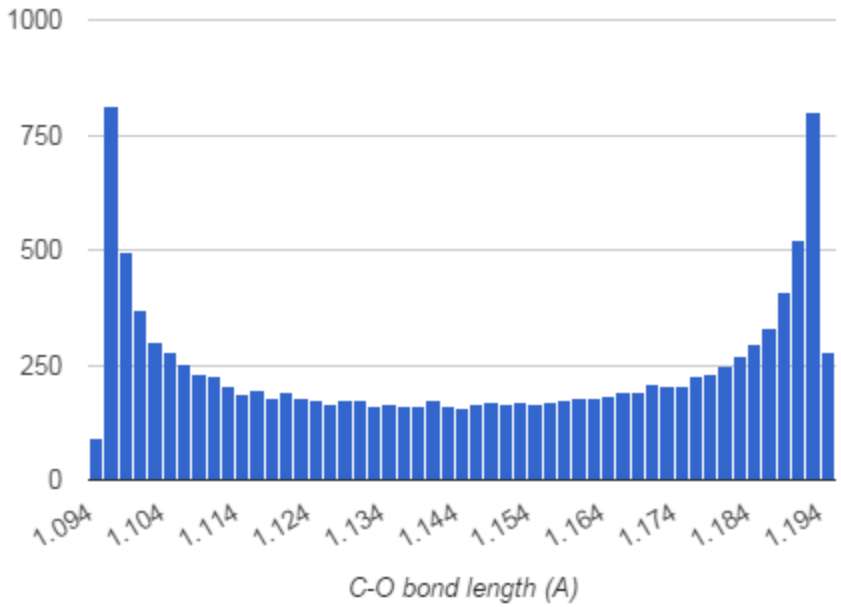


Figure S7. Histogram of C-O bond length over the simulation.

Since dynamical propagation is classical, we find that there is significant sampling of the bond length extrema during the vibration. Compared to the stationary bond length, the dynamical average is 0.004 angstroms longer. Unfortunately, attempting to approximate the dynamical behavior by adjusting the bond length to this dynamical average underestimates the magnitude of the vibrational correction. While the time-average dynamic correction is –2.46 ppm, an effective bond length adjustment only corresponds to a correction of –1.87 ppm. This is a consequence of both the anharmonicity of the potential energy surface and the convexity of the shielding response surface.

2. Tutorial for Performing Quasiclassical Calculations

Although many quantum chemistry software packages contain routines to carry out molecular dynamics simulations, the particulars of our method require a custom procedure. We are in the process of developing a user-friendly package for carrying out these calculations, which will be reported in due course. In the meantime, those who wish to reproduce our calculations can follow the procedure outlined below. This procedure assumes the use of Gaussian 09 to carry out quasiclassical NMR calculations on a natural product.

a) Optimize the molecule of interest using opt=b3lyp/midix. If there are multiple conformations, perform preliminary calculations to identify the lowest energy conformation, and use that for the rest of this procedure.

b) Carry out a frequency calculation using "freq=hpmodes b3lyp/midix". For each vibrational mode with a frequency above 50 cm^{-1}, select an energy level randomly from its corresponding quantum harmonic oscillator Boltzmann distribution. Make a random displacement according to the quantum harmonic oscillator eigenfunction that corresponds to the selected energy level. Initialize the molecular dynamics simulation, using the total energy from the harmonic oscillator approximation and the calculated potential energy to determine the kinetic energy. Additional classical rotational kinetic energy can be added if desired. For each principal axis, draw a random angular momentum from a Gaussian distribution, such that the average rotational energy in each axis is equal to the classical equipartition energy of 0.5kT. However, rotations are unlikely to affect the shieldings of typical natural products significantly because of their size.

c) The potential energy of the displaced initialization geometry should be calculated at b3lyp/midix and compared to the expected potential energy from the harmonic oscillator approximation. If the error is greater than 1 kcal/mol, the initialization step should be repeated.

d) Propagate the trajectory classically using the velocity Verlet algorithm in 1.0 fs steps. Proceed 125 steps in the forward and reverse directions. The required forces are calculated at each point with the "b3lyp/midix force" keywords. Every 8 points, calculate the NMR shieldings at b3lyp/cc-pVDZ using "b3lyp/cc-pvdz NMR".

e) Average the shieldings over the entire trajectory and apply symmetry-averaging. Compare the shieldings to those obtained with b3lyp/cc-pvdz at the b3lyp/midix geometry to compute the raw correction.

f) Optimize the molecule with "pbe1pbe/cc-pvtz scrf=(pcm,solvent=chloroform) opt" and compute the NMR shieldings at the same level with the NMR keyword. Use this as the high level shielding.

g) Use the equation given in Section 3.3 to calculate the final predicted shielding using methanol as the reference.