Table S1. Rotational constants for isotopic species of 1,4-difluorobutadiene.

	B0(obs)/MHz	0.5*Alpha Sum /MHz	Be/MHz	Ie/(u*Å2)
d0				
A	12988.33270	122.97968	13111.31240	38.54526
B	1467.87909	5.48204	1473.36113	343.01095
C	1318.58451	5.97540	1324.55991	381.54484
Δ				-0.01137
1-13C1				
A	12936.89609	121.51124	13058.40733	38.70143
B	1455.98099	5.41105	1461.39204	345.82028
C	1308.45531	5.88963	1314.34494	384.51018
Δ				-0.01153
2-13C1				
A	12987.23619	123.38993	13110.62612	38.54728
B	1467.15800	5.42136	1472.57936	343.19305
C	1317.99830	5.92139	1323.91969	381.72935
Δ				-0.01098
3-13C1				
A	12742.05516	119.80044	12861.85560	39.29285
B	1465.88139	5.40982	1471.29121	343.49353
C	1314.38217	5.92093	1320.30310	382.77499
Δ				-0.01139
4-13C1				
A	12912.11123	120.79519	13032.90642	38.77715
B	1451.54352	5.44774	1456.99126	346.86482
C	1304.61373	5.91313	1310.52686	385.63041
Δ				-0.01156
1-d1				
A	12352.45909	104.89861	12457.35770	40.56872
B	1450.79041	5.78206	1456.57247	346.96455
C	1298.12749	6.00847	1304.13596	387.52018
Δ				-0.01308
2-d1				
A	12573.61281	134.90998	12708.52279	39.76614
B	1468.36340	4.72683	1473.09023	343.06715
C	1314.63960	5.46424	1320.10384	382.82509
Δ				-0.00820
3-d1				
A	11858.85620	99.01598	11957.87218	42.26329
B	1466.29319	5.92718	1472.22037	343.27674
C	1304.67801	6.19960	1310.87761	385.52722
Δ				-0.01280
4-d1				
A	12581.52829	112.09323	12693.62152	39.81282
B	1434.08720	5.82083	1439.90803	350.97302
C	1287.14603	6.10773	1293.25376	390.77317
Δ				-0.01267
1,4-d2				
A	11976.98271	96.01463	12072.99734	41.85944
B	1417.51048	6.09456	1423.60504	354.99233
C	1267.35823	6.13134	1273.48957	396.83785
Δ				-0.01391

[a] Inertial defect, $\Delta = I_c - I_a - I_c$.

Table S2. C–H bond lengths (Å)

Molecule	MP2/VTZ	r_e	e-c	Ref.
CH_2=C=CH_2	1.0808	1.0808	0.0000	a
CH_2=C=O	1.0758	1.0758	0.0000	b
CH_2=CHCl *gem*	1.0789	1.0783	-0.0006	c
CH_2=CHCl *cis*	1.0789	1.0794	0.0005	
CH_2=CHCl *trans*	1.0795	1.0796	0.0001	
CH_2=CHBr *gem*	1.0788	1.0780	-0.0008	d
CH_2=CHBr *cis*	1.0791	1.0794	0.0003	
CH_2=CHBr *trans*	1.0805	1.0804	-0.0001	
CH_2=CHF *gem*	1.0798	1.0796	-0.0002	e
CH_2=CHF *cis*	1.0780	1.0789	0.0009	
CH_2=CHF *trans*	1.0769	1.0774	0.0005	
CH_2=CHI *gem*	1.0795	1.0787	-0.0008	e
CH_2=CHI *cis*	1.0795	1.0799	0.0004	
CH_2=CHI *trans*	1.0818	1.0823	0.0005	
CH_2=CHOH *gem*	1.0801	1.0796	-0.0005	f
CH_2=CHOH *cis*	1.0810	1.0815	0.0005	
CH_2=CHOH *trans*	1.0768	1.0772	0.0004	
CH_2=CHCN *gem*	1.0806	1.0802	-0.0004	g
CH_2=CHCN *cis*	1.0798	1.0798	0.0000	
CH_2=CHCN *trans*	1.0792	1.0793	0.0001	
CH_2=$CHCH_3$ *gem*	1.0843	1.0845	0.0002	h
CH_2=$CHCH_3$ *cis*	1.0819	1.0825	0.0006	
CH_2=$CHCH_3$ *trans*	1.0800	1.0804	0.0004	
c-C_3H_2	1.0753	1.0753	0.0000	i
c-C_3H_6	1.0785	1.0788	0.0003	j
mediane			0.0001	
mean			0.0001	

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Table S3. C=C bond lengths (Å).

Molecule	MP2/VTZ	r_e	e-c	Ref.
$H_2C=C=O$	1.3161	1.3122	-0.0039	a
$CH_2=CH_2$	1.3319	1.3307	-0.0012	b
$H_2C=C=C$:	1.3316	1.3283	-0.0033	c
$H_2C=C=CH_2$	1.3082	1.3074	-0.0008	d
$CH_2=CHCl$	1.3289	1.3262	-0.0027	e
$CH_2=CHBr$	1.3289	1.3256	-0.0033	f
$CH_2=CHF$	1.3240	1.3210	-0.0030	g
$CH_2=CHI$	1.3306	1.3276	-0.0030	g
$CH_2=CHOH$	1.3334	1.3303	-0.0031	h
$CH_2=CHCN$	1.3374	1.3352	-0.0022	i
$CH_2=CHCH_3$	1.3338	1.3310	-0.0028	j
hexene diyne	1.3522	1.3480	-0.0042	k
mediane			-0.0030	
mean			-0.0028	

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Table S4. C–C bond lengths (Å).

Molecule	MP2/VTZ	r_e	e-c	Ref.
CH_3CN	1.4575	1.4586	0.0011	a
CH3CH3	1.5234	1.5221	-0.0013	b
H-C≡C-C≡N	1.3717	1.3760	0.0043	c
CH_3-C≡CH	1.4583	1.4580	-0.0003	d
$CH_3CH=CH_2$	1.4952	1.4956	0.0004	e
NC-CN	1.3774	1.3840	0.0066	f
$HCOCH_2OH$	1.5020	1.5016	-0.0004	g
CH_3CH_2OH	1.5101	1.5089	-0.0012	g
CH_3CH_2CN	1.4610	1.4639	0.0029	h
CH_3CH_2CN	1.5286	1.5276	-0.0010	h
$CH_2=CHCN$	1.4291	1.4332	0.0041	i
CHO-CHO	1.5142	1.5145	0.0003	j
HC≡C-C≡CH	1.3687	1.3727	0.0040	k
hexene diyne	1.4172	1.4190	0.0018	l

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Table S5. Cartesian coordinates for the semi-experimental equilibrium structure of *cis,trans*-1.4-difluorobutadiene (Å).

	a	b	c
C1	-1.6823	-0.3975	0.0
C2	-0.4278	0.0434	0.0
C3	0.6955	-0.8686	0.0
C4	1.9694	-0.4855	0.0
H1	-1.9844	-1.4351	0.0
H2	-0.2472	1.1082	0.0
H3	0.5149	-1.9338	0.0
H4	2.8240	-1.1436	0.0
F1	-2.7208	0.4470	0.0
F4	2.3117	0.8126	0.0