Electronic Supplementary Information (ESI):

Fine and hyperfine coupling constants of the cis-β-cyanovinyl radical, HCCHCN

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Table S-1 Observed line frequencies of the *cis*-β-cyanovinyl radical and their assignments.[a]

N'	K_a'	K_c'	J'	F_1'	F_2'	F'	N''	K_a''	K_c''	J''	F_1''	F_2''	F''	Obs.[b]	o.−c.[c]
1	0	1	1.5	1	1.5	0.5	0	0	0	0.5	1	1.5	1.5	10194.894	−2
			(0.5	1	1.5	0.5)									
			1.5	1	1.5	1.5				0.5	1	1.5	2.5	10195.354	−5
			(1.5	2	2.5	1.5)									
			1.5	2	1.5	1.5				0.5	0	0.5	1.5	10195.521	2
			(1.5	1	1.5	1.5)									
			1.5	1	1.5	1.5				0.5	1	1.5	0.5	10195.700	2
			(1.5	2	2.5	1.5)									
			1.5	2	2.5	2.5				0.5	1	1.5	2.5	10195.719	−4
			1.5	2	1.5	1.5				0.5	0	0.5	0.5	10195.837[d]	0
			(1.5	1	1.5	1.5)									
			1.5	1	0.5	0.5				0.5	1	0.5	0.5	10195.837[d]	−2
			0.5	1	1.5	1.5				0.5	1	0.5	1.5	10195.862[d]	−3
			(1.5	2	1.5	1.5)									
			1.5	2	1.5	0.5				0.5	0	0.5	0.5	10195.862[d]	−10
			(0.5	1	0.5	0.5)									
			1.5	2	2.5	2.5				0.5	1	1.5	1.5	10195.933	−1
			1.5	1	1.5	2.5				0.5	1	1.5	2.5	10196.396	2
			(0.5	1	1.5	2.5)									
			1.5	2	1.5	2.5				0.5	0	0.5	1.5	10196.478	3
			(1.5	1	1.5	2.5)									
			1.5	1	1.5	2.5				0.5	1	1.5	1.5	10196.609	4
			(0.5	1	1.5	2.5)									
			1.5	2	2.5	3.5				0.5	1	1.5	2.5	10196.638	2
			1.5	1	0.5	1.5				0.5	1	0.5	0.5	10196.844	1
			0.5	1	1.5	2.5				0.5	1	0.5	1.5	10197.112	0
			(1.5	2	1.5	2.5)									
			1.5	2	2.5	1.5				0.5	1	1.5	1.5	10197.763	−2
			(0.5	1	1.5	1.5)									
			0.5	0	0.5	1.5				0.5	0	0.5	0.5	10198.108	−2
			(0.5	1	0.5	1.5)									
			0.5	0	0.5	0.5				0.5	0	0.5	1.5	10198.617	0
			(1.5	1	1.5	0.5)									
			0.5	1	1.5	0.5				0.5	1	0.5	0.5	10198.644	−4
			(1.5	2	1.5	0.5)									
			0.5	1	1.5	0.5				0.5	1	0.5	1.5	10198.711	−2
			(1.5	2	1.5	0.5)									

Table S-I (*continue*)

N'	K'_a	K'_c	J'	F'_1	F'_2	F'	N''	K''_a	K''_c	J''	F''_1	F''_2	F''	Obs.[b]	o.−c.[c]
1	0	1	0.5	1	0.5	0.5	0	0	0	0.5	1	1.5	1.5	10199.084	−6
			(0.5	0	0.5	0.5)									
			0.5	1	0.5	0.5				0.5	1	1.5	0.5	10199.224	7
			(0.5	0	0.5	0.5)									
			0.5	1	0.5	1.5				0.5	1	1.5	2.5	10199.309	−2
			(0.5	0	0.5	1.5)									
			0.5	1	0.5	1.5				0.5	1	1.5	0.5	10199.647	−2
			(0.5	0	0.5	1.5)									
2	1	2	2.5	2	2.5	3.5	1	1	1	1.5	1	1.5	2.5	19859.356	2
			(1.5	2	2.5	3.5)				(0.5	1	1.5	2.5)		
			2.5	3	3.5	3.5				1.5	2	2.5	2.5	19859.948	1
			2.5	3	3.5	4.5				1.5	2	2.5	3.5	19860.552	4
			2.5	3	3.5	2.5				1.5	2	2.5	1.5	19861.398[d]	8
			1.5	2	2.5	3.5				0.5	1	1.5	2.5	19861.398[d]	4
			(2.5	2	2.5	3.5)				(1.5	1	1.5	2.5)		
			2.5	3	2.5	2.5				1.5	2	1.5	1.5	19861.732	−2
			2.5	3	2.5	3.5				1.5	2	1.5	2.5	19862.665	0
2	0	2	2.5	3	3.5	2.5	1	0	1	0.5	1	0.5	1.5	20386.637	−1
										(0.5	0	0.5	1.5)		
			2.5	2	2.5	1.5				1.5	2	2.5	1.5	20386.883[d]	4
			(1.5	2	2.5	1.5)				(0.5	1	1.5	1.5)		
			1.5	2	1.5	0.5				0.5	1	0.5	0.5	20386.883[d]	0
			(1.5	1	1.5	0.5)				(0.5	0	0.5	0.5)		
			2.5	3	2.5	1.5				0.5	0	0.5	1.5	20387.021	−1
			(2.5	2	2.5	1.5)				(0.5	1	0.5	1.5)		
			2.5	3	2.5	2.5				1.5	2	1.5	2.5	20387.315	−2
			(2.5	2	2.5	2.5)				(1.5	1	1.5	2.5)		
			2.5	3	3.5	3.5				1.5	2	2.5	3.5	20387.375	−5
			1.5	2	1.5	1.5				0.5	1	0.5	1.5	20387.487	−2
			(1.5	1	1.5	1.5)				(0.5	0	0.5	1.5)		
			1.5	2	1.5	2.5				0.5	1	0.5	1.5	20387.618	3
			(1.5	1	1.5	2.5)				(0.5	0	0.5	1.5)		
			2.5	2	1.5	0.5				0.5	1	1.5	0.5	20387.668[d]	3
										(1.5	2	1.5	0.5)		
			1.5	2	2.5	2.5				0.5	1	1.5	2.5	20387.668[d]	−4
			(2.5	3	2.5	2.5)				(1.5	2	1.5	2.5)		
			1.5	1	1.5	1.5				0.5	0	0.5	0.5	20387.935	6
			(1.5	2	1.5	1.5)				(1.5	1	1.5	0.5)		

Table S-I (*continue*)

N'	K'_a	K'_c	J'	F'_1	F'_2	F'	N''	K''_a	K''_c	J''	F''_1	F''_2	F''	Obs.[b]	o.−c.[c]
2	0	2	1.5	2	2.5	1.5	1	0	1	0.5	1	1.5	0.5	20387.982	−3
			(2.5	3	2.5	1.5)				(1.5	2	1.5	0.5)		
			2.5	3	2.5	2.5				1.5	2	1.5	1.5	20388.277	4
			(2.5	2	2.5	2.5)				(1.5	1	1.5	1.5)		
			2.5	3	3.5	3.5				1.5	2	2.5	2.5	20388.294	1
			2.5	3	3.5	4.5				1.5	2	2.5	3.5	20388.380	1
			2.5	3	2.5	3.5				1.5	2	1.5	2.5	20388.395[d]	4
			(2.5	2	2.5	3.5)				(1.5	1	1.5	2.5)		
			2.5	3	3.5	2.5				1.5	2	2.5	1.5	20388.395[d]	0
										(0.5	1	1.5	1.5)		
			2.5	2	2.5	2.5				1.5	1	1.5	1.5	20388.571	0
			(1.5	2	2.5	2.5)				(1.5	2	2.5	1.5)		
			2.5	2	1.5	1.5				1.5	1	0.5	0.5	20388.616	2
			2.5	2	1.5	1.5				0.5	1	1.5	1.5	20388.651	−2
										(1.5	2	1.5	1.5)		
			2.5	2	2.5	3.5				1.5	2	2.5	3.5	20388.651	−3
			(1.5	2	2.5	3.5)									
			1.5	1	1.5	0.5				0.5	0	0.5	0.5	20388.782[d]	8
			(1.5	2	1.5	0.5)				(1.5	1	1.5	0.5)		
			2.5	2	1.5	2.5				1.5	1	0.5	1.5	20388.782[d]	2
			2.5	2	2.5	3.5				1.5	1	1.5	2.5	20388.897	1
			(1.5	2	2.5	3.5)				(0.5	1	1.5	2.5)		
			1.5	2	2.5	2.5				0.5	1	1.5	1.5	20388.921	1
			(2.5	3	2.5	2.5)				(1.5	2	1.5	1.5)		
			1.5	2	2.5	3.5				0.5	1	1.5	2.5	20388.986	0
			(2.5	3	2.5	3.5)				(1.5	2	1.5	2.5)		
			2.5	3	2.5	1.5				1.5	2	1.5	0.5	20389.260	−1
			(2.5	2	2.5	1.5)				(0.5	1	0.5	0.5)		
			1.5	1	1.5	2.5				0.5	0	0.5	1.5	20389.451	1
			(1.5	2	1.5	2.5)				(0.5	1	0.5	1.5)		
			1.5	1	0.5	1.5				0.5	1	0.5	0.5	20389.516	−2
										(0.5	0	0.5	0.5)		
			2.5	2	2.5	1.5				1.5	1	1.5	0.5	20389.748	0
			(1.5	2	2.5	1.5)				(0.5	1	1.5	0.5)		
			2.5	3	3.5	2.5				1.5	2	2.5	2.5	20390.225	−1
			1.5	2	1.5	2.5				1.5	1	1.5	2.5	20390.529	−3
			(1.5	1	1.5	2.5)				(0.5	1	1.5	2.5)		

Table S-I (*continue*)

N'	K'_a	K'_c	J'	F'_1	F'_2	F'	N''	K''_a	K''_c	J''	F''_1	F''_2	F''	Obs.[b]	o.−c.[c]
2	0	2	1.5	2	2.5	1.5	1	0	1	0.5	1	1.5	1.5	20390.830[d]	−2
			(2.5	3	2.5	1.5)				(1.5	2	1.5	1.5)		
			1.5	1	0.5	1.5				1.5	2	2.5	1.5	20390.830[d]	−12
										(0.5	1	1.5	1.5)		
			1.5	1	1.5	1.5				1.5	2	1.5	1.5	20391.025	−1
			(1.5	2	1.5	1.5)				(1.5	1	1.5	1.5)		
			1.5	2	1.5	0.5				1.5	1	1.5	0.5	20391.077[d]	1
			(1.5	1	1.5	0.5)				(0.5	1	1.5	0.5)		
			1.5	2	1.5	1.5				1.5	2	2.5	2.5	20391.077[d]	0
			(1.5	1	1.5	1.5)									
			1.5	2	1.5	1.5				1.5	1	1.5	1.5	20391.439	−2
			(1.5	1	1.5	1.5)				(1.5	2	2.5	1.5)		
3	0	3	3.5	4	3.5	2.5	2	0	2	1.5	1	1.5	1.5	30569.247	2
			(3.5	3	3.5	2.5)				(1.5	2	1.5	1.5)		
			3.5	4	4.5	4.5				2.5	3	3.5	4.5	30569.498	−7
			3.5	4	3.5	3.5				2.5	3	2.5	3.5	30569.534	−3
			(3.5	3	3.5	3.5)				(2.5	2	2.5	3.5)		
			2.5	3	3.5	3.5				1.5	2	2.5	3.5	30569.911	−5
										(2.5	3	2.5	3.5)		
			3.5	4	4.5	4.5				2.5	3	3.5	3.5	30570.506	3
			3.5	4	4.5	5.5				2.5	3	3.5	4.5	30570.566	3
			3.5	4	4.5	3.5				2.5	3	3.5	2.5	30570.571	0
			3.5	4	3.5	3.5				2.5	3	2.5	2.5	30570.612	1
			(3.5	3	3.5	3.5)				(2.5	2	2.5	2.5)		
			3.5	4	3.5	4.5				2.5	3	2.5	3.5	30570.663	3
			(3.5	3	3.5	4.5)				(2.5	2	2.5	3.5)		
			3.5	3	2.5	1.5				2.5	2	1.5	0.5	30570.826	−1
			2.5	3	2.5	2.5				1.5	2	1.5	1.5	30570.873	5
			(2.5	2	2.5	2.5)				(1.5	1	1.5	1.5)		
			3.5	4	3.5	2.5				2.5	3	2.5	1.5	30570.974	−2
			(3.5	3	3.5	2.5)				(2.5	2	2.5	1.5)		
			3.5	3	2.5	2.5				2.5	2	1.5	1.5	30570.994	1
			3.5	3	3.5	3.5				2.5	2	2.5	2.5	30571.011	4
			(3.5	4	3.5	3.5)				(1.5	2	2.5	2.5)		
			2.5	3	3.5	2.5				1.5	2	2.5	1.5	30571.055	−5
										(2.5	3	2.5	1.5)		
			3.5	3	2.5	3.5				2.5	2	1.5	2.5	30571.073	1

Table S-I (*continue*)

N'	K'_a	K'_c	J'	F'_1	F'_2	F'	N''	K''_a	K''_c	J''	F''_1	F''_2	F''	Obs.[b]	o.−c.[c]
3	0	3	3.5	3	3.5	4.5	2	0	2	2.5	2	2.5	3.5	30571.214	1
			(3.5	4	3.5	4.5)				(1.5	2	2.5	3.5)		
			2.5	3	3.5	3.5				1.5	2	2.5	2.5	30571.231	1
										(2.5	3	2.5	2.5)		
			2.5	3	2.5	3.5				1.5	2	1.5	2.5	30571.277[d]	8
			(2.5	2	2.5	3.5)				(1.5	1	1.5	2.5)		
			2.5	3	3.5	4.5				1.5	2	2.5	3.5	30571.277[d]	−1
										(2.5	3	2.5	3.5)		
			3.5	3	3.5	2.5				2.5	2	2.5	1.5	30571.442	2
			(3.5	4	3.5	2.5)				(1.5	2	2.5	1.5)		
			3.5	3	3.5	4.5				2.5	3	3.5	4.5	30571.482	−4
			(3.5	4	3.5	4.5)									
			2.5	2	1.5	2.5				1.5	1	0.5	1.5	30571.548[d]	1
			2.5	2	2.5	1.5				1.5	1	1.5	0.5	30571.548[d]	−12
			(2.5	3	2.5	1.5)				(1.5	2	1.5	0.5)		
			2.5	2	2.5	3.5				1.5	1	1.5	2.5	30571.736	2
			(2.5	3	2.5	3.5)				(1.5	2	1.5	2.5)		
			2.5	2	1.5	1.5				1.5	2	1.5	1.5	30572.424	3
										(1.5	1	1.5	1.5)		
			3.5	4	4.5	3.5				2.5	3	3.5	3.5	30572.501	−2
			3.5	3	2.5	1.5				2.5	2	1.5	1.5	30572.686	−2
			2.5	3	2.5	3.5				2.5	2	2.5	3.5	30572.906	0
			(2.5	2	2.5	3.5)				(1.5	2	2.5	3.5)		
			2.5	3	3.5	2.5				1.5	2	2.5	2.5	30572.968[d]	−6
										(2.5	3	2.5	2.5)		
			2.5	2	2.5	2.5				2.5	3	2.5	1.5	30572.968[d]	−12
			(2.5	3	2.5	2.5)				(2.5	2	2.5	1.5)		
			2.5	2	1.5	2.5				1.5	2	1.5	2.5	30573.022	3
										(1.5	1	1.5	2.5)		
			2.5	3	2.5	2.5				2.5	2	2.5	2.5	30573.739	2
			(2.5	2	2.5	2.5)				(1.5	2	2.5	2.5)		
			2.5	2	2.5	2.5				2.5	3	2.5	2.5	30574.000	−2
			(2.5	3	2.5	2.5)				(2.5	2	2.5	2.5)		
			2.5	2	2.5	3.5				2.5	3	2.5	3.5	30574.121	11
			(2.5	3	2.5	3.5				2.5	2	2.5	3.5)		
1	1	0	1.5	1	1.5	2.5	1	0	1	1.5	2	2.5	3.5	44915.255[e]	0
			(0.5	1	1.5	2.5)									

Table S-I (*continue*)

N'	K'_a	K'_c	J'	F'_1	F'_2	F'	N''	K''_a	K''_c	J''	F''_1	F''_2	F''	Obs.[b]	o.−c.[c]
1	1	0	1.5	1	0.5	1.5	1	0	1	0.5	1	1.5	2.5	44921.480[f]	1
										(1.5	2	1.5	2.5)		
			0.5	1	1.5	2.5				0.5	1	1.5	2.5	44922.234[f]	−15
			(1.5	2	1.5	2.5)				(1.5	2	1.5	2.5)		
			0.5	1	1.5	1.5				0.5	1	1.5	2.5	44922.928[f]	−6
			(1.5	2	1.5	1.5)				(1.5	2	1.5	2.5)		
			1.5	2	2.5	3.5				1.5	2	2.5	3.5	44924.270[e]	−6
1	1	1	1.5	2	2.5	3.5	0	0	0	0.5	1	1.5	2.5	54582.164[g]	5
			1.5	2	2.5	2.5				0.5	1	1.5	2.5	54582.577[g]	2
			1.5	1	0.5	1.5				0.5	1	0.5	1.5	54585.924[h]	2
			1.5	1	0.5	0.5				0.5	1	0.5	1.5	54586.001[h]	8
			0.5	1	0.5	1.5				0.5	1	1.5	2.5	54586.238[g]	0
			1.5	2	1.5	2.5				0.5	1	0.5	1.5	54587.624[f]	−8
			1.5	2	1.5	1.5				0.5	1	0.5	1.5	54588.094[f]	8
			1.5	1	1.5	2.5				0.5	1	1.5	2.5	54599.455[g]	17
2	1	2	2.5	3	3.5	4.5	1	0	1	1.5	2	2.5	3.5	64246.102[e]	32
			2.5	3	3.5	3.5				1.5	2	2.5	2.5	64246.808[i]	9
			2.5	2	2.5	3.5				1.5	2	2.5	3.5	64262.136[e]	−19
			(1.5	2	2.5	3.5)									
3	1	3	3.5	4	4.5	5.5	2	0	2	2.5	3	3.5	4.5	73646.245[e]	−24
			3.5	4	4.5	4.5				2.5	3	3.5	3.5	73646.836[i]	−28

[a] Quantum numbers labeling each line are defined by the coupling scheme, $\mathbf{J} = \mathbf{N} + \mathbf{S}$, $\mathbf{F_1} = \mathbf{J} + \mathbf{I}(\mathrm{H}_\alpha)$, $\mathbf{F_2} = \mathbf{F_1} + \mathbf{I}(\mathrm{H}_\beta)$, and $\mathbf{F} = \mathbf{F_2} + \mathbf{I}(\mathrm{N})$. **N** and **S** denote the rotational and electron-spin angular momenta, respectively, **I** the nuclear spin angular momentum of each nucleus, and **F** the total angular momentum of the system. The quantum number label of eigenstate in the spfit/spcat program is given in parenthesis if the label is different from that in our fitting program.

[b] Observed line frequencies in MHz. Lines without superscript letter were observed by FTMW spectroscopy, and the weight of 1.0 is given in the least-squares analysis.

[c] The residuals in the least-squares fit in kHz.

[d] Observed by FTMW spectroscopy. The weight of 0.5 is given in the least-squares analysis, because of overlapping with other line.

[e] Observed by double-resonance spectroscopy with monitoring the 20388.380 MHz line. The weight of 0.1 is given in the least-squares analysis.

[f] Observed by double-resonance spectroscopy with monitoring the 10197.112 MHz line. The weight of 0.1 is given in the least-squares analysis.

[g] Observed by double-resonance spectroscopy with monitoring the 10196.638 MHz line. The weight

of 0.1 is given in the least-squares analysis.
[h] Observed by double-resonance spectroscopy with monitoring the 10197.112 MHz line. The weight of 0.05 is given in the least-squares analysis.
[i] Observed by double-resonance spectroscopy with monitoring the 20388.294 MHz line. The weight of 0.1is given in the least-squares analysis.