

Searches for bridged bicyclic molecules in Space—Norbornadiene and its cyano derivatives

Electronic Supplementary Information

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1 Supplementary Figures

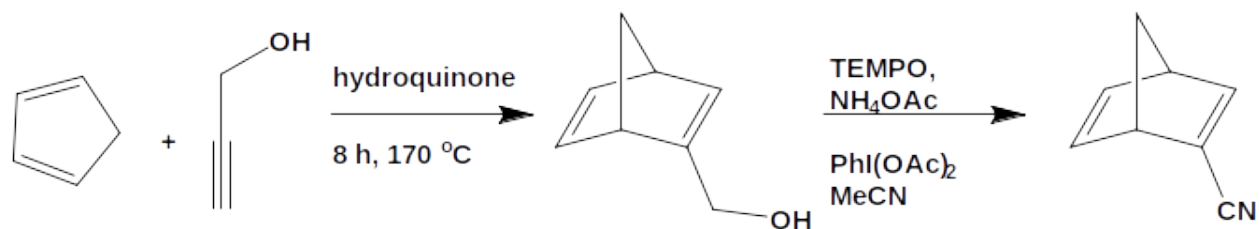


Figure S1: Synthesis of CN-NBD

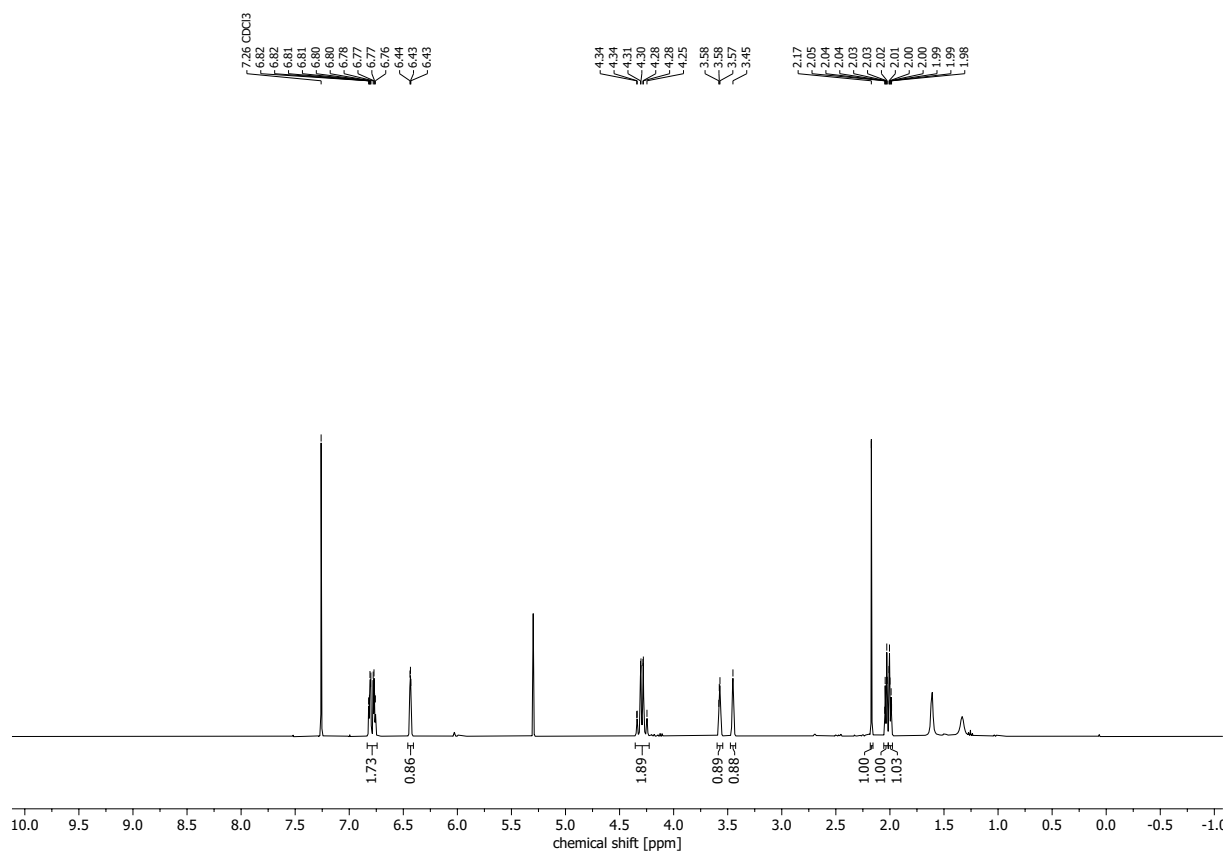


Figure S2: ¹H NMR (400 MHz) of (±)-2-hydroxymethylbicyclo[2.2.1]hepta-2,5-diene in CDCl₃ at room temperature, with dichloromethane (5.2 ppm) and water residues (1.6 ppm); $\delta = 6.82 - 6.76$ (m, 2H), 6.44 – 6.43 (m, 1H), 4.34 – 4.25 (m, 2H), 3.58 – 3.57 (m, 1H), 3.45 (m, 1H), 2.17 (s, 1H), 2.03 (d, 1H, $J = 4$ Hz), 2.00 (d, 1H, $J = 4$ Hz).

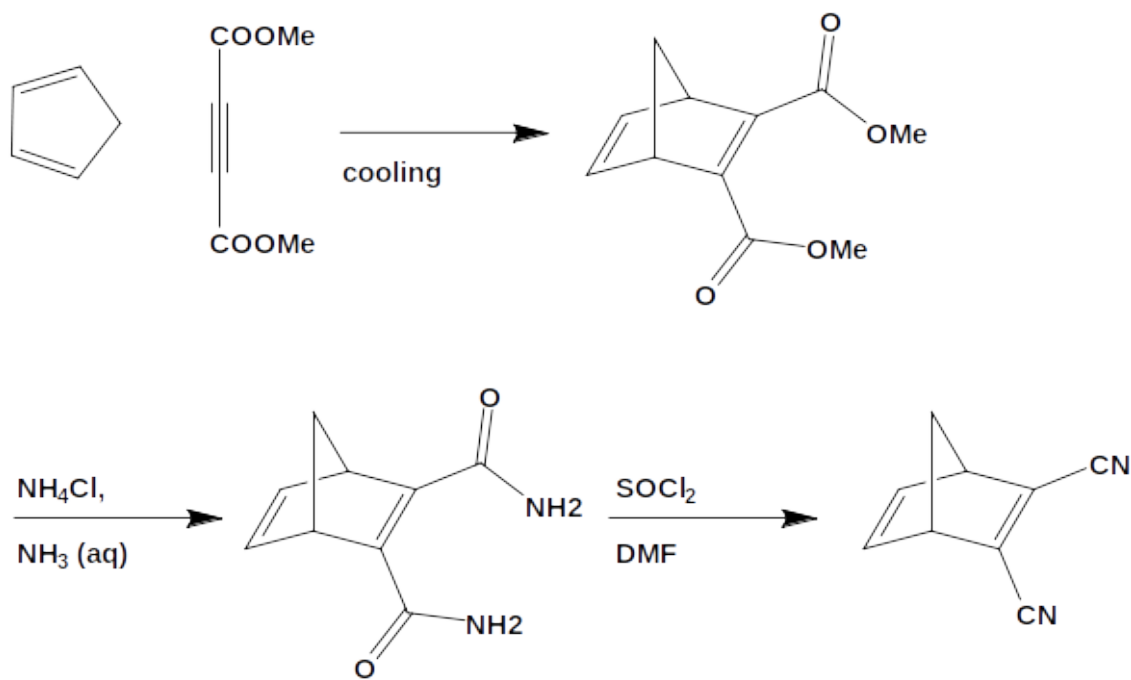


Figure S3: Synthesis of DCN-NBD

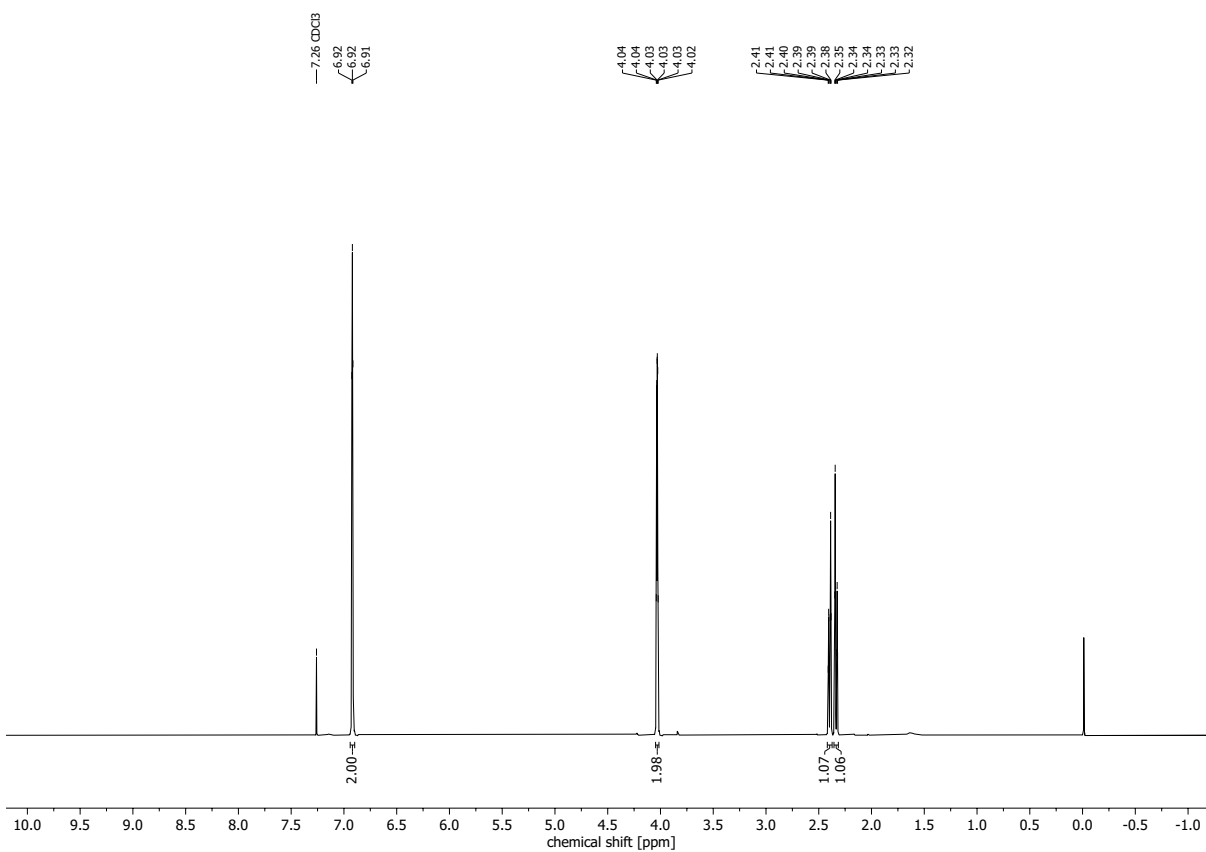


Figure S4: ^1H NMR (400 MHz) of DCN-NBD in CDCl_3 at room temperature; $\delta = 6.925\text{--}6.915$ (m, 2H), 4.04 – 4.02 (m, 2H), 2.40 (dt, $J = 7.5, 1.7$ Hz, 1H), 2.33 (dt, $J = 7.4, 1.6$ Hz, 1H).

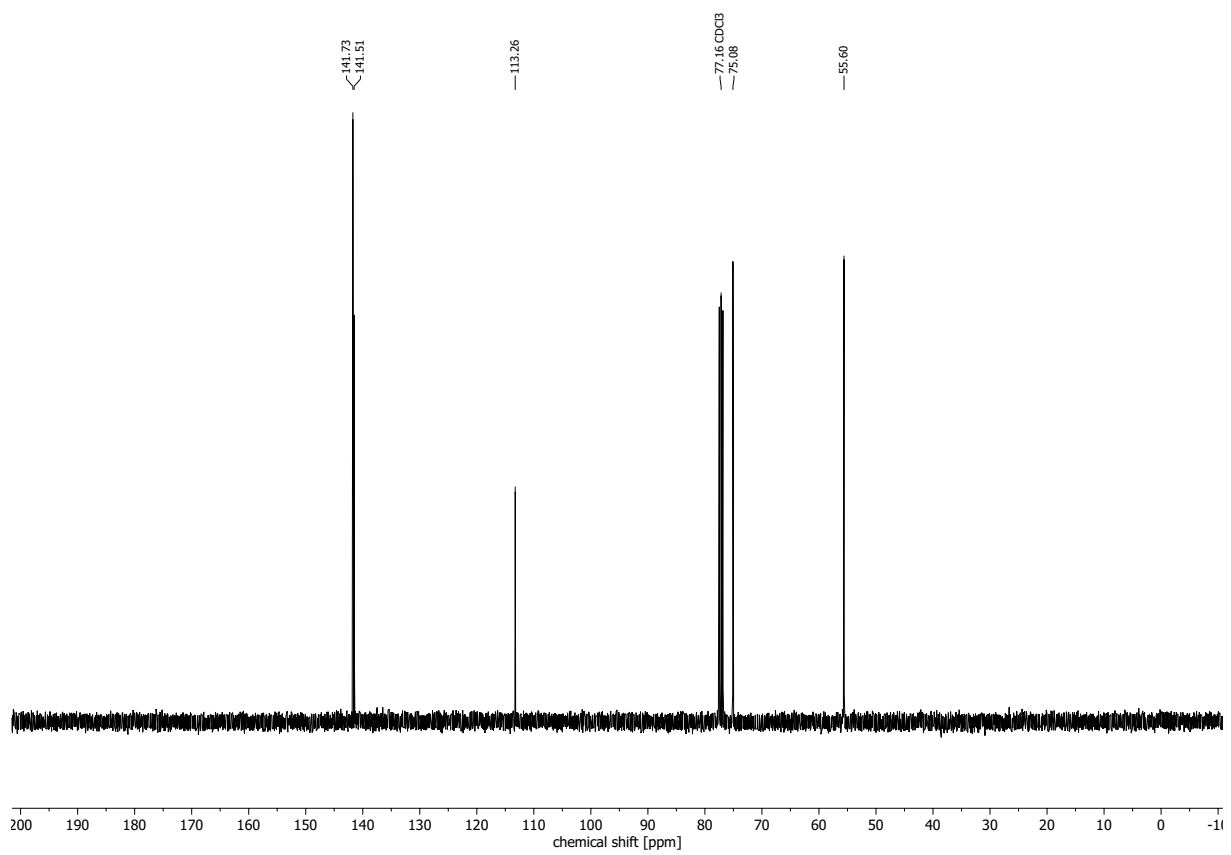


Figure S5: ¹³C NMR (101 MHz) of **DCN-NBD** in CDCl₃ at room temperature; $\delta = 141.7, 141.5, 113.3, 75.1, 55.6$.

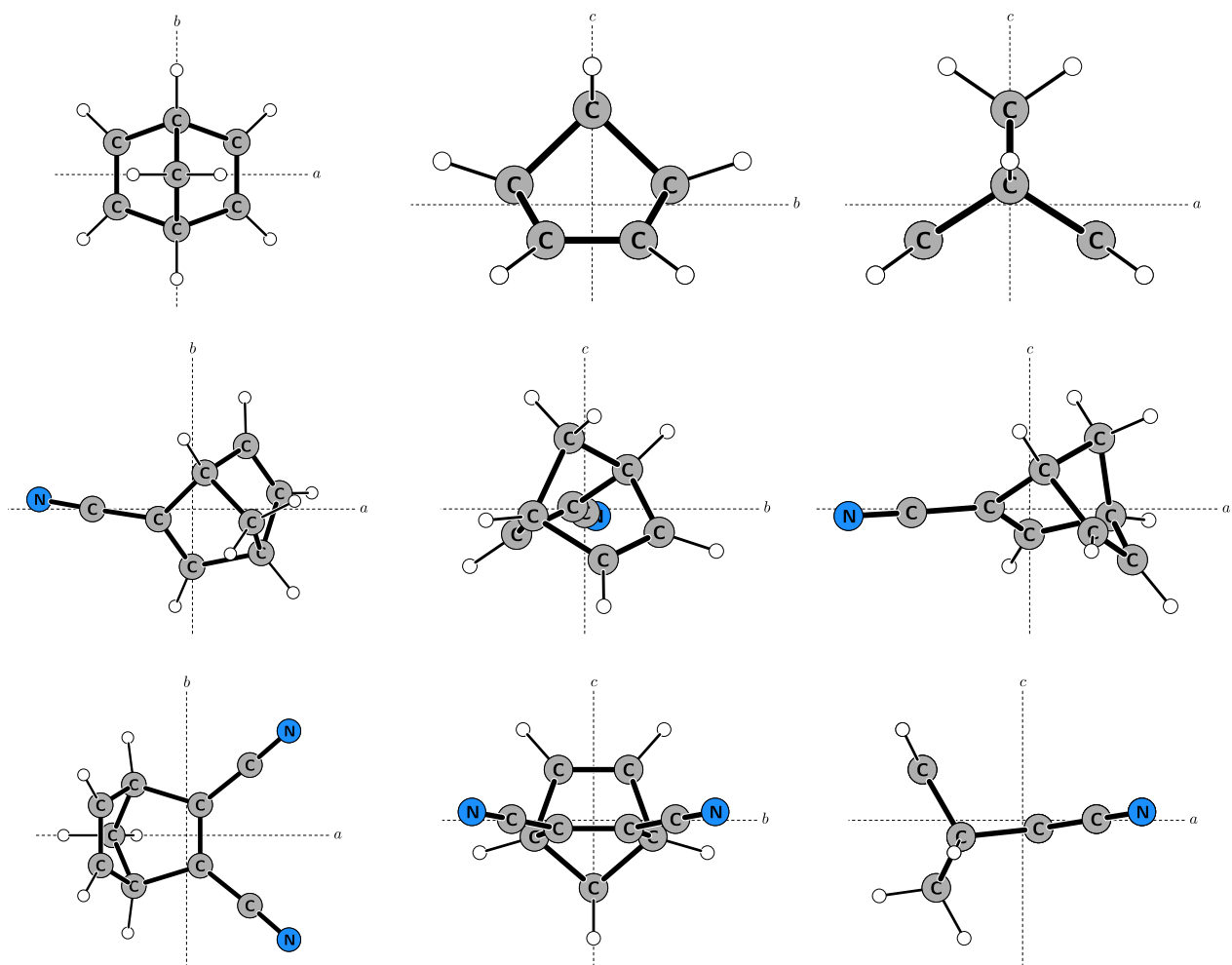


Figure S6: Structural projections of **NBD**, **CN-NBD**, and **DCN-NBD** (from top to bottom) along the ab , bc , and ac planes (from left to right). Projections performed using the PMIFST software [Kisiel, 2001].

2 Supplementary Tables

Table S1: Equilibrium structure of **NBD** optimised at the ω B97X-D/cc-pVQZ level of theory

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	1.234587	0.662534	-0.506805
2	6	0.000000	1.115107	0.284273
3	6	-0.000000	-1.115107	0.284273
4	6	1.234587	-0.662534	-0.506805
5	1	1.921016	1.327440	-1.006736
6	1	1.921016	-1.327440	-1.006736
7	6	-0.000000	0.000000	1.360071
8	1	-0.896713	0.000000	1.977776
9	1	0.896713	-0.000000	1.977776
10	6	-1.234587	0.662534	-0.506805
11	6	-1.234587	-0.662534	-0.506805
12	1	0.000000	2.146246	0.622713
13	1	-0.000000	-2.146246	0.622713
14	1	-1.921016	-1.327440	-1.006736
15	1	-1.921016	1.327440	-1.006736

Table S2: Equilibrium structure of **CN-NBD** optimised at the ω B97X-D/cc-pVQZ level of theory

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	1.135855	1.337063	-0.419208
2	6	0.263004	0.767406	0.703669
3	6	1.455698	-0.928441	-0.125094
4	6	1.843471	0.331709	-0.912139
5	1	1.108016	2.361093	-0.754656
6	1	2.527090	0.343161	-1.745666
7	6	1.254320	-0.278097	1.267717
8	1	0.803211	-0.949008	1.996844
9	1	2.164215	0.168280	1.662762
10	6	-0.723205	-0.213291	0.041377
11	6	-0.007463	-1.220436	-0.453923
12	1	-0.179385	1.480841	1.389593
13	1	2.133626	-1.771241	-0.202342
14	6	-2.118980	0.001145	-0.063983
15	7	-3.248271	0.204618	-0.127906
16	1	-0.367473	-2.059766	-1.026778

Table S3: Equilibrium structure of **DCN-NBD** optimised at the ω B97X-D/cc-pVQZ level of theory

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-1.890363	0.662127	0.957296
2	6	-1.160793	1.116595	-0.311532
3	6	-1.160793	-1.116595	-0.311532
4	6	-1.890363	-0.662127	0.957296
5	1	-2.267117	1.331146	1.713516
6	1	-2.267117	-1.331146	1.713516
7	6	-1.630029	0.000000	-1.274722
8	1	-1.103390	0.000000	-2.227379
9	1	-2.706257	0.000000	-1.427021
10	6	0.300584	0.668929	-0.155806
11	6	0.300584	-0.668929	-0.155806
12	1	-1.293665	2.149487	-0.610975
13	1	-1.293665	-2.149487	-0.610975
14	6	1.394734	1.546991	0.022035
15	7	2.253691	2.296969	0.159589
16	6	1.394734	-1.546991	0.022035
17	7	2.253691	-2.296969	0.159589

Table S4: Equilibrium rotational constants of **DCN-NBD**, **DCN-NBD**, and **DCN-NBD** (in MHz) derived from the structure optimised at the ω B97X-D/cc-pVQZ level of theory

Constant	DCN-NBD	DCN-NBD	DCN-NBD
A_e	4337.3177	3881.0223	1540.2270
B_e	3639.0411	1326.8412	1196.7806
C_e	3219.7849	1252.3365	798.7702

Table S5: Partitions functions of **NBD**, **CN-NBD**, and **DCN-NBD** as a function of the temperature calculated using the SPCAT program

NBD

TEMPERATURE	Q(SPIN-ROT.)	log Q(SPIN-ROT.)
300.000	2000043.0864	6.3010
225.000	1299167.5476	6.1137
150.000	707147.2317	5.8495
75.000	250047.4339	5.3980
37.500	88449.2918	4.9467
18.750	31306.4805	4.4956
9.375	11093.9073	4.0451

CN-NBD

TEMPERATURE	Q(SPIN-ROT.)	log Q(SPIN-ROT.)
300.000	350337.5958	5.5445
225.000	227576.9790	5.3571
150.000	123851.3301	5.0929
75.000	43780.4448	4.6413
37.500	15480.2707	4.1898
18.750	5475.4236	3.7384
10.000	2134.4195	3.3293
9.375	1937.7144	3.2873

DCN-NBD

TEMPERATURE	Q(SPIN-ROT.)	log Q(SPIN-ROT.)
300.000	713498.2663	5.8534
225.000	470975.6689	5.6730
150.000	258541.8459	5.4125
75.000	91530.2785	4.9616
37.500	32358.6627	4.5100
18.750	11442.9034	4.0585
10.000	4459.2338	3.6493
9.375	4048.0995	3.6073

References

- Z. Kisiel. Assignment and Analysis of Complex Rotational Spectra. In J. Demaison, K. Sarka, and E. A. Cohen, editors, *Spectroscopy from Space*, pages 91–106. Springer Netherlands, Dordrecht, 2001. ISBN 978-0-7923-6993-6 978-94-010-0832-7. doi:[10.1007/978-94-010-0832-7_6](https://doi.org/10.1007/978-94-010-0832-7_6).