Supporting Information (Supporting File 1)

Article title: Auditing Spectral Evidence Cited by Large Language Models in Pyrazolone Glycoside Assignment

Author: Heba Ahmed Aboukhousa*

Affiliation: Mohamed Bin Zayed University for Humanities, Abu Dhabi, United Arab Emirates

*Corresponding author. Email: heba.aboukhousa@mbzuh.ac.ae

Contents: S1 prompts as sent; S2 stimulus images, label and order mapping, source figures; S3 the 90 API responses (72 on the four glycosides, analysed in the article, and 18 of the supplementary benzoyl task; coded record, verbatim justification fields, anomeric-carbon arguments, pilot, timing, benzoyl task); S4 value tables and coding (original script-based codes; separate coding of agreement, infrared feature, anomeric-carbon citation and field check; the coding rule as a script; tolerance check); S5 probe for retrievable thesis-specific facts; S6 the reaction records (audit, models, sensitivity); S7 specifications of controls and measurements not performed; S8 spectroscopic record of the four glycosides; S9 outline of a classroom exercise; S10 manifest of the deposited archive; S11 literature values as printed in their sources; S12 reading of the *Reasoning* field of the 36 NMR-added responses; S13 properties of the stimulus images as supplied; S14 second coding; S15 the text and figures of the source re-examined; S16 original spectrometer data reprocessed, and records of the 2-deoxy pair found afterwards; S17 re-examination of the source record, in full (reaction records; ribose pair; 2-deoxyribose pair); S18 the signal near 104 ppm and the answers of the second coders, in full; S19 comparison with published evaluations (Table S37), and status of verification of the main claims (Table S38); references.

Conventions. “The article” is the main text; “the source” is the author’s doctoral thesis (Aboukhousa 2017); “the deposit” is the Zenodo archive (Aboukhousa 2026); “source label” is the assignment made in the source, against which answers are compared. References are listed at the end of this file. Atom numbering follows Figure 1 of the article: pyrazole atoms unprimed, aryl carbons single-primed, sugar atoms double-primed. Quoted model responses keep their own notation. In condition names, `paired_*` is the paired presentation with the infrared spectrum only, `singleIR_*` the single-case presentation with the infrared spectrum only, `binary_*` the single-case presentation with NMR spectra added, and `pairedfull_*` the paired presentation with NMR spectra added; r1–r3 are the three replicates. Figure, table and section numbers of the source are those of the deposited version (Aboukhousa 2017).

S1 Frozen prompts (verbatim)

Nine prompt files were used. Each was sent as the text part of a request, with the images listed in `results_api.csv` attached in the order given there. The files form two families.

The five single-case files (`binary_HSQC`, `binary_gHMBC`, `binary_none`, `single_IR`, `single_IR_benzoyl`) share their task text, rules and response fields and differ only in the last sentence, which lists the attached images, and, for the benzoyl pair, in "the sugar" being replaced by "the benzoyl group". The four paired files (`paired`, `paired_benzoyl`, `paired_full_deoxy`, `paired_full_ribose`) differ from the single-case files in the task text, in the rules and in the response fields: they contain no instruction to explain ambiguity and no *Limitations* field, their prohibition reads "Do not invent peaks or experimental details" without the word "correlations", and they ask for two classification lines. The two `paired_full_*` files speak of "compounds" where `paired` speaks of "spectra". These differences mean that presentation is not the only thing that distinguishes a single-case from a paired item.

binary_HSQC.txt (SHA-256 2d295090e6c299212799702536208bc32e2e90649b5f6e67bf3801863cc26035)

```
TASK: Regiochemical assignment between two known candidates
A single compound was isolated. Its two possible structures are shown in the
candidate image: Candidate A and Candidate B. They are constitutional isomers
with the same molecular formula and the same nominal mass, and they differ
only
in the atom through which the sugar is attached.

Decide which candidate the attached spectroscopic evidence supports.

Rules:
1. Use only the evidence supplied for this case.
2. Do not infer the identity from filenames, source history, or external
lookup.
3. State the classification: A, B, or UNDETERMINED if the evidence supplied
   cannot decide between them.
4. Identify the decisive spectral feature.
5. Explain any ambiguity or insufficiency.
6. Report confidence from 0 to 100.
7. Do not invent peaks, correlations, or experimental details.
Answer in plain text only. Do not generate an image.

RESPONSE FORMAT:
Classification: [A / B / UNDETERMINED]
Confidence: [0-100]
Decisive evidence: [brief]
Reasoning: [brief]
Limitations: [brief]

Several images are attached: the two candidate structures, and the IR, 1H
NMR,
13C NMR and HSQC spectra of the compound.
```

binary_gHMBC.txt (SHA-256 182c6aa5d0877dd4d39c4e5de97402caeb86c9bebf1cb37d84f71c7ff05b2c19)

```
TASK: Regiochemical assignment between two known candidates
A single compound was isolated. Its two possible structures are shown in the
candidate image: Candidate A and Candidate B. They are constitutional isomers
with the same molecular formula and the same nominal mass, and they differ
only
in the atom through which the sugar is attached.

Decide which candidate the attached spectroscopic evidence supports.

Rules:
1. Use only the evidence supplied for this case.
2. Do not infer the identity from filenames, source history, or external
lookup.
3. State the classification: A, B, or UNDETERMINED if the evidence supplied
   cannot decide between them.
4. Identify the decisive spectral feature.
5. Explain any ambiguity or insufficiency.
6. Report confidence from 0 to 100.
7. Do not invent peaks, correlations, or experimental details.
Answer in plain text only. Do not generate an image.

RESPONSE FORMAT:
Classification: [A / B / UNDETERMINED]
Confidence: [0-100]
Decisive evidence: [brief]
Reasoning: [brief]
Limitations: [brief]

Several images are attached: the two candidate structures, and the IR, 1H
NMR,
13C NMR and gHMBC spectra of the compound.
```

binary_none.txt (SHA-256 ab29c1cac7841bb6a93093d011aee4546af30cadbb3ccb10ca8bbdafa3a5573d)

```
TASK: Regiochemical assignment between two known candidates
A single compound was isolated. Its two possible structures are shown in the
candidate image: Candidate A and Candidate B. They are constitutional isomers
with the same molecular formula and the same nominal mass, and they differ
only
in the atom through which the sugar is attached.

Decide which candidate the attached spectroscopic evidence supports.

Rules:
1. Use only the evidence supplied for this case.
2. Do not infer the identity from filenames, source history, or external
lookup.
3. State the classification: A, B, or UNDETERMINED if the evidence supplied
   cannot decide between them.
```

```
4. Identify the decisive spectral feature.
5. Explain any ambiguity or insufficiency.
6. Report confidence from 0 to 100.
7. Do not invent peaks, correlations, or experimental details.
Answer in plain text only. Do not generate an image.

RESPONSE FORMAT:
Classification: [A / B / UNDETERMINED]
Confidence: [0-100]
Decisive evidence: [brief]
Reasoning: [brief]
Limitations: [brief]

Several images are attached: the two candidate structures, and the IR, 1H NMR
and 13C NMR spectra of the compound.
```

paired.txt (SHA-256 2cd3caec9c4f2952a3d85f412597055b11afe0ea9d3fbe8cca4785ad67ecb020)

```
TASK: Match two spectra to two candidate structures
Two constitutional isomers are shown in the candidate image: Candidate A and
Candidate B. They have the same molecular formula and the same nominal mass
and
differ only in the atom through which the sugar is attached.

Two IR spectra are attached, labelled Spectrum 1 and Spectrum 2. One belongs
to
Candidate A and the other to Candidate B.

Decide which spectrum belongs to which candidate.

Rules:
1. Use only the evidence supplied.
2. Do not infer the identity from filenames, source history, or external
lookup.
3. State the assignment, or UNDETERMINED if the evidence cannot decide.
4. Identify the decisive spectral feature.
5. Report confidence from 0 to 100.
6. Do not invent peaks or experimental details.
Answer in plain text only. Do not generate an image.

RESPONSE FORMAT:
Spectrum 1 belongs to: [A / B / UNDETERMINED]
Spectrum 2 belongs to: [A / B / UNDETERMINED]
Confidence: [0-100]
Decisive evidence: [brief]
Reasoning: [brief]

Three images are attached: the two candidate structures, Spectrum 1 and
Spectrum 2.
```

paired_benzoyl.txt (SHA-256 391d787565d76b9f0d72c7cbd2467398cfb95b7d81dc6c20bbd6b6e523e19545)

```
TASK: Match two spectra to two candidate structures
Two constitutional isomers are shown in the candidate image: Candidate A and
Candidate B. They have the same molecular formula and the same nominal mass
and
differ only in the atom through which the benzoyl group is attached.

Two IR spectra are attached, labelled Spectrum 1 and Spectrum 2. One belongs
to
Candidate A and the other to Candidate B.

Decide which spectrum belongs to which candidate.

Rules:
1. Use only the evidence supplied.
2. Do not infer the identity from filenames, source history, or external
lookup.
3. State the assignment, or UNDETERMINED if the evidence cannot decide.
4. Identify the decisive spectral feature.
5. Report confidence from 0 to 100.
6. Do not invent peaks or experimental details.
Answer in plain text only. Do not generate an image.

RESPONSE FORMAT:
Spectrum 1 belongs to: [A / B / UNDETERMINED]
Spectrum 2 belongs to: [A / B / UNDETERMINED]
Confidence: [0-100]
Decisive evidence: [brief]
Reasoning: [brief]

Three images are attached: the two candidate structures, Spectrum 1 and
Spectrum 2.
```

paired_full_deoxy.txt (SHA-256 9eac82abebe3ca0630b7457fe4eb6f90fd7d5c8696c19331d39cb7b4d34bcee3)

```
TASK: Match two compounds to two candidate structures
Two constitutional isomers are shown in the candidate image: Candidate A and
Candidate B. They have the same molecular formula and the same nominal mass
and
differ only in the atom through which the sugar is attached.

Spectra of two compounds are attached, and each image is labelled Compound 1
or
Compound 2. One compound is Candidate A and the other is Candidate B.

Decide which compound is which candidate.
```

```
Rules:
1. Use only the evidence supplied.
2. Do not infer the identity from filenames, source history, or external
lookup.
3. State the assignment, or UNDETERMINED if the evidence cannot decide.
4. Identify the decisive spectral feature.
5. Report confidence from 0 to 100.
6. Do not invent peaks or experimental details.
Answer in plain text only. Do not generate an image.

RESPONSE FORMAT:
Compound 1 is: [A / B / UNDETERMINED]
Compound 2 is: [A / B / UNDETERMINED]
Confidence: [0-100]
Decisive evidence: [brief]
Reasoning: [brief]

Eight images are attached: the two candidate structures; the IR, 1H NMR and
13C NMR spectra of Compound 1 and of Compound 2; and the HSQC spectrum of
Compound 1.
```

paired_full_ribose.txt (SHA-256 a4e7865afd7d41135bc34f090e25f8632b942937c7f8988d48850e19848f00b4)

```
TASK: Match two compounds to two candidate structures
Two constitutional isomers are shown in the candidate image: Candidate A and
Candidate B. They have the same molecular formula and the same nominal mass
and
differ only in the atom through which the sugar is attached.

Spectra of two compounds are attached, and each image is labelled Compound 1
or
Compound 2. One compound is Candidate A and the other is Candidate B.

Decide which compound is which candidate.

Rules:
1. Use only the evidence supplied.
2. Do not infer the identity from filenames, source history, or external
lookup.
3. State the assignment, or UNDETERMINED if the evidence cannot decide.
4. Identify the decisive spectral feature.
5. Report confidence from 0 to 100.
6. Do not invent peaks or experimental details.
Answer in plain text only. Do not generate an image.

RESPONSE FORMAT:
Compound 1 is: [A / B / UNDETERMINED]
Compound 2 is: [A / B / UNDETERMINED]
Confidence: [0-100]
```

```
Decisive evidence: [brief]
Reasoning: [brief]

Nine images are attached: the two candidate structures, and the IR, 1H NMR,
13C NMR and gHMBC spectra of Compound 1 and of Compound 2.
```

single_IR.txt (SHA-256 136b4b4f9717a6a7c216e4ad59f853d5913799f07e363c704730ee646389ad80)

```
TASK: Regiochemical assignment between two known candidates
A single compound was isolated. Its two possible structures are shown in the
candidate image: Candidate A and Candidate B. They are constitutional isomers
with the same molecular formula and the same nominal mass, and they differ
only
in the atom through which the sugar is attached.

Decide which candidate the attached spectroscopic evidence supports.

Rules:
1. Use only the evidence supplied for this case.
2. Do not infer the identity from filenames, source history, or external
lookup.
3. State the classification: A, B, or UNDETERMINED if the evidence supplied
   cannot decide between them.
4. Identify the decisive spectral feature.
5. Explain any ambiguity or insufficiency.
6. Report confidence from 0 to 100.
7. Do not invent peaks, correlations, or experimental details.
Answer in plain text only. Do not generate an image.

RESPONSE FORMAT:
Classification: [A / B / UNDETERMINED]
Confidence: [0-100]
Decisive evidence: [brief]
Reasoning: [brief]
Limitations: [brief]

Two images are attached: the two candidate structures, and the IR spectrum of
the compound.
```

single_IR_benzoyl.txt (SHA-256 6a745192b357c9eca94ed93f500f002217dddd51cb62c4534f73b049c3c39c44)

```
TASK: Regiochemical assignment between two known candidates
A single compound was isolated. Its two possible structures are shown in the
candidate image: Candidate A and Candidate B. They are constitutional isomers
with the same molecular formula and the same nominal mass, and they differ
only
in the atom through which the benzoyl group is attached.
```

```
Decide which candidate the attached spectroscopic evidence supports.

Rules:
1. Use only the evidence supplied for this case.
2. Do not infer the identity from filenames, source history, or external
lookup.
3. State the classification: A, B, or UNDETERMINED if the evidence supplied
   cannot decide between them.
4. Identify the decisive spectral feature.
5. Explain any ambiguity or insufficiency.
6. Report confidence from 0 to 100.
7. Do not invent peaks, correlations, or experimental details.
Answer in plain text only. Do not generate an image.

RESPONSE FORMAT:
Classification: [A / B / UNDETERMINED]
Confidence: [0-100]
Decisive evidence: [brief]
Reasoning: [brief]
Limitations: [brief]

Two images are attached: the two candidate structures, and the IR spectrum of
the compound.
```

Pilot prompt versions v0.3/v0.4 are reproduced in the Legend sheet of the deposited pilot workbook.

S2 Stimulus images, label and order mapping, and source figures

All 41 images are deposited under `images/` exactly as sent (PNG) and are listed in Table S1; the mapping of letters and order is given in Table S2. Structure drawings, panel letters and embedded data-file names were masked. An identifier band was added above every NMR panel: the file stem in the single-case items (for example `PX-A01_13C`) and, in the paired NMR-added items, the compound number and kind of spectrum (for example "Compound 1 · ^{13}C NMR"), also above their infrared images. The paired infrared-only images are headed "Spectrum 1" or "Spectrum 2"; the single-case infrared images and the candidate drawings carry no identifier. The sugar-carbon annotations printed on the gHMBC panels of the source (C-1″ to C-5″) were not masked. The infrared crops cover about 1950–1030 cm^{-1}; the prompts state no range. What each image displays, as established by inspection of the deposited files, is described in Section S13. How each provider rescales or tiles an image before inference is not disclosed by the providers and was not controlled. The `PX-*` images are shared by the infrared-only and NMR-added single-case items; the `full_*_C1/C2` NMR images are the same panels, pixel for pixel, under a different identifier band, and the infrared trace of a compound is the same image in every presentation.

A single-case infrared-only request carried two images (candidate drawings, infrared spectrum) and a paired infrared-only request three. A single-case NMR-added request

carried five images for PX-A01, PX-A02 and PX-B01 (candidates, IR, ^{1}H, ^{13}C and one two-dimensional panel) and four for PX-B02, for which the source has no two-dimensional spectrum. The paired NMR-added request carried nine images for the ribose pair and eight for the 2-deoxy pair, the HSQC panel being available for Compound 1 (122a) only. “NMR added” is therefore not one uniform package across items.

Table S1. Stimulus images with pixel dimensions and SHA-256 checksums.

File	Pixels (w × h)	SHA-256
PX-A01_13C.png	935 × 632	a002ae28c07452961ff991836572b56c9b2952fbeac43d6eda6faef0e8f47a75
PX-A01_1H.png	935 × 622	72d53cfa73fa480b137b0a58826a3bbec0c6198b01baecb0266e784f2b76639b
PX-A01_HMBC.png	570 × 612	4e66b21ecfbb80890aa666ccf6c89b56defd5aa6ddbe2293c35174e905ddfd9c
PX-A01_IR.png	924 × 896	e0eb29760e6345f459e7eae5a6756a08e2bd209a4d3a1f9f17a4822ffd050fef
PX-A02_13C.png	935 × 702	f07149cd175e9927806381910432e9d3f278322d38eadd55ba11480c31fb1403
PX-A02_1H.png	935 × 662	6c85701fc6052b952fcb4287f587e9e0c4728690bf7986bbaaf779007fe74412
PX-A02_HMBC.png	565 × 682	a5b627d494b82dd510a80e7c88534e8a994fdbeff61bb0a553430d2b04782712
PX-A02_IR.png	924 × 880	654c10ab54477948ae8e82a9fd5f9d5ebeb417dea376282d2e0c251ce17ac723
PX-B01_13C.png	935 × 557	21b23b99001ac554b38f14efc96dc7e834f2fba35f892506ac610e8c3abe1436
PX-B01_1H.png	935 × 602	5145583f531a079e0c7da4342aac8343a743666847ce9e592407d01f63afbea4
PX-B01_HSQC.png	545 × 422	b5239566718f42b644473e4ebb5827a2f69ccb771a7602c216272535665088e4
PX-B01_IR.png	924 × 880	9fad14a66b3b53dd149cc79ab2147d28732c42908293e69cf206ecd11b6e1e11
PX-B02_13C.png	935 × 547	d6fd260cf30e2bf77a1f3399051479684b63ed633d03280fbae2f94d950c3afe
PX-B02_1H.png	935 × 622	5b7716e4fcdd2c911af9a3164fb04a4bb8aa53fbfc3ef88d5b1c8130fa1db980
PX-B02_IR.png	924 × 897	d0f157495ac81a1dd38cb9c99614c07205089709c3be6bb955a3bdbd71760d08
PX-C01_IR.png	924 × 943	e0f687d270a5eb9d89330b8317a8fbb699a136200e8a58149457ab519110ccf8
PX-C02_IR.png	924 × 943	984e1522f58ee7cbb9f6cf2a0d5bc0a612afa1c2e34b0cc6f716c946cea77cca
benzoyl_spectrum1.png	924 × 1011	e5c87cc5d49e9c8b5cbdecc121a184b7fae457eaf1e13e488bc60e68e10548fa
benzoyl_spectrum2.png	924 × 1011	ea1dc1cf96e9a2103578492add2c29ebb44d6954ac424e28998616f716b19f86
candidates_benzoyl.png	1500 × 560	37e5beaf632826a57e59b92b785b6f84bc17d9203bb3d97afc799704cdad8b0d
candidates_deoxy.png	1500 × 560	c2e5c9b273b736aa878c66599f289e50c87d7011b0a7f973b7eb8379b89d58ad
candidates_ribose.png	1500 × 560	564646879324cf2d9dbe602344ee966d4bbfa2788b65f1d26fd7e1fd8fe16781
deoxy_spectrum1.png	924 × 950	04340667475839a37c40f6131e84cffe1f839d824ca291ffcea0486096d727de
deoxy_spectrum2.png	924 × 967	66fabbb26f409775f4908a948834aad2b49a41bd567ea6393967fc842a593411
full_deoxy_C1_13C.png	935 × 557	7edff7997571feb1437d9dcb13dc28c8418e683084292ee8507e11443451568f
full_deoxy_C1_1H.png	935 × 602	c89e97ede7bc2677d0a33eb0fa2e9a2d489379c929dd8ec0be86c12848b93562
full_deoxy_C1_HSQC.png	545 × 422	813116e7da504532b3f9b5af29a0e652d8aceff32c04467044c4eabe59907e07
full_deoxy_C1_IR.png	924 × 934	c87f84b3c3b884b1254f228cd30a5719a15553acabef26e3e5244b708d77b398
full_deoxy_C2_13C.png	935 × 547	25e3425db639fdfb1e7a9b30fc8ecc015c06f0de8b4213947fbdfa576314dc29
full_deoxy_C2_1H.png	935 × 622	31a838ce2ab01015c47742876bf4fe8096770816b151c4427c329518ea445889
full_deoxy_C2_IR.png	924 × 951	a460dcb6d6e46d6907d79e633de8fbd9c7bbc9ed1adafda33df71599c2d4b6b5
full_ribose_C1_13C.png	935 × 702	6c5538b6f26f8bfab79e48a12a36b92f98854ec2f6a04ab87ee54103789a9952
full_ribose_C1_1H.png	935 × 662	9b8ae313e2d6fa36769c42f9f020748d34d838f37f17874610275daf53677433
full_ribose_C1_HMBC.png	565 × 682	ecebeda8cd1947178dbc98c3d13c8a5df7889329529de41ef243879717bd541c
full_ribose_C1_IR.png	924 × 934	7da852639b7cbd08171f3649aa40fe0235705921b15040b0c964343d0dff7995
full_ribose_C2_13C.png	935 × 632	04a93d25f8cad294bec772002e9ba9c70a16a7aa36dca716e7ad6e5fe4601a50
full_ribose_C2_1H.png	935 × 622	5e6894276d01542b681526bca75fd164a3518f53cc1ea1b6325bcfcc8a978b1e

File	Pixels (w × h)	SHA-256
full_ribose_C2_HMBC.png	570 × 612	7f110303100bb5e9c8ec1e7248f66db557c9fdc9f67dce3b3628b63ab574110a
full_ribose_C2_IR.png	924 × 950	37b7f42d224471a616b2467bba902aa6a1605d1e32926f61dad1e83089edc197
ribose_spectrum1.png	924 × 950	d0861a5868d385d5722b58d74e689bb5163231feae848dc5498333139e8ee7bf
ribose_spectrum2.png	924 × 966	7213172c089a65e559b88b6d5dfad5ae5840e94021680fc7130c7bd4a014cdb8

Table S2. Mapping of candidate letters and of spectrum or compound order to the compounds, as fixed for each pair. The last two columns give the source label expressed as the candidate letter.

Pair	Candidate A (drawing)	Candidate B (drawing)	Spectrum / Compound 1	Spectrum / Compound 2	Source label, single-case items	Source label, paired items (1 / 2)
Ribose	N-riboside	O-riboside	116a (PX-A02)	117a (PX-A01)	PX-A01 → A; PX-A02 → B	B / A
2-Deoxyribose	O-deoxyriboside	N-deoxyriboside	122a (PX-B01)	123a (PX-B02)	PX-B01 → A; PX-B02 → B	A / B
Benzoyl	N-benzoyl	O-benzoyl	127c (PX-C01)	124f (PX-C02)	PX-C01 → A; PX-C02 → B	A / B

The mapping was not counterbalanced and no item was run with reversed labels or reversed order. Three consequences follow. (i) In every single-case item the source label is A for the compound with suffix 01 and B for the compound with suffix 02, so a rule keyed to the suffix would reproduce the label. The suffix was visible in the identifier band of the NMR panels of the single-case NMR-added items and in no other item; no file name was sent with the images. The prompts forbid inferring identity from file names, and the answers do not follow the suffix: 8 of the 24 single-case NMR-added responses agree with the source label. (ii) A constant answer agrees with the source label in half of the single-case items of each pair. (iii) In both glycoside pairs the first spectrum or compound is the one the source assigns as the O-isomer. For the ribose pair a default that answers “A / B” gives the inverted assignment and for the 2-deoxy pair it gives the source assignment; all twelve paired NMR-added responses were “A / B” (Table S3), so in that condition a positional default and the anomeric-shift argument of Section 3.2 of the article predict the same answers and cannot be told apart.

Source figures. Every panel is a crop of a figure in the source, which is openly accessible in the repository of United Arab Emirates University: IR Figures 23 (116a/117a), 44 (122a/123a) and 53 (124f/127c); ^{13}C Figures 19 (116a), 25 (117a), 40 (122a) and 46 (123a); ^{1}H Figures 18 (116a), 24 (117a), 39 (122a) and 45 (123a); gHMBC Figures 20 (116a) and 29 (117a); HSQC Figure 42 (122a). The infrared figures of the source for the two glycoside pairs themselves show only the range from about 2000 to 1000 cm^{-1}, with a structure drawing placed over each trace; full-range traces of the four glycosides are not printed in it. The source also contains COSY and HSQC figures of 117a and a COSY figure of 122a, which were not supplied; they and the complete HSQC figure of 122a are examined in Section S15.

S3 API responses

S3.1 Coded record and verbatim justification fields

Table S3 lists all 90 API responses, the 72 on the four glycosides that the article analyses and the 18 of the supplementary task on the benzoyl pair (Section S3.5), with the model identifier returned by the service, the UTC timestamp, the answer, the stated confidence and the output of the original script-based coding (Section S4.2). Table S4 reproduces the *Decisive evidence* field of every response verbatim. The complete responses are in `raw/` of the deposit and in the `response` column of `results_api.csv`.

Column legend for Table S3. *Answer*: candidate letter, or for paired items the letters given to Spectrum/Compound 1 and 2; UNDET., UNDETERMINED. *Agrees*: yes, the answer matches the source label of Table S2; no; abst., abstained. The source labels of 116a and 122a are open, and the 2-deoxy pair is treated as open as a whole (Sections S17.2 and S17.3). *Code*: output of `code_responses.py` (J1–J3, abstain; Section S4.2). *Run*: replicate number (1–3, corresponding to r1–r3 of Table S4). *Orig. cited*: the category "agrees and coded J1" of the original coding, which is not used in the article (Section S4.3). *Conf.*: stated confidence. *No labelled value*: a cited value with no labelled value within tolerance; "C13:88.5" is the midpoint of a cited range of 88–89 ppm.

Table S3. Coded record of the 90 API responses.

Run	Condition	System	Model identifier returned	Timestamp (UTC)	Answer	Agrees	Code	Orig. cited	Conf.	No labelled value
1	paired_ribose	gpt-5	gpt-5-2025-08-07	2026-09-27T12:19:02Z	B / A	yes	J1	yes	90	
2	paired_ribose	gpt-5	gpt-5-2025-08-07	2026-09-27T12:19:37Z	B / A	yes	J1	yes	80	
3	paired_ribose	gpt-5	gpt-5-2025-08-07	2026-09-27T12:20:17Z	A / B	no	J2		70	
1	paired_deoxy	gpt-5	gpt-5-2025-08-07	2026-09-27T12:20:45Z	A / B	yes	J1	yes	75	
2	paired_deoxy	gpt-5	gpt-5-2025-08-07	2026-09-27T12:21:21Z	A / B	yes	J1	yes	80	
3	paired_deoxy	gpt-5	gpt-5-2025-08-07	2026-09-27T12:21:52Z	A / B	yes	J1	yes	70	
1	binary_PX-A01	gpt-5	gpt-5-2025-08-07	2026-09-27T12:23:00Z	B	no	J2		70	
2	binary_PX-A01	gpt-5	gpt-5-2025-08-07	2026-09-27T12:23:59Z	B	no	J2		80	
3	binary_PX-A01	gpt-5	gpt-5-2025-08-07	2026-09-27T12:24:42Z	B	no	J2		70	
1	binary_PX-A02	gpt-5	gpt-5-2025-08-07	2026-09-27T12:25:28Z	A	no	J1		80	
2	binary_PX-A02	gpt-5	gpt-5-2025-08-07	2026-09-27T12:26:33Z	UNDET.	abst.	abstain		20	
3	binary_PX-A02	gpt-5	gpt-5-2025-08-07	2026-09-27T12:27:03Z	A	no	J1		80	
1	binary_PX-B01	gpt-5	gpt-5-2025-08-07	2026-09-27T12:28:49Z	B	no	J2		70	
2	binary_PX-B01	gpt-5	gpt-5-2025-08-07	2026-09-27T12:29:28Z	B	no	J2		80	
3	binary_PX-B01	gpt-5	gpt-5-2025-08-07	2026-09-27T12:30:13Z	B	no	J3		78	C13:88.5
1	binary_PX-B02	gpt-5	gpt-5-2025-08-07	2026-09-27T12:30:52Z	A	no	J2		90	
2	binary_PX-B02	gpt-5	gpt-5-2025-08-07	2026-09-27T12:31:42Z	A	no	J2		85	
3	binary_PX-B02	gpt-5	gpt-5-2025-08-07	2026-09-27T12:32:27Z	A	no	J2		88	

Run	Condition	System	Model identifier returned	Timestamp (UTC)	Answer	Agrees	Code	Orig. cited	Conf.	No labelled value
1	paired_ribose	Gemini	gemini-3.1-pro-preview	2026-09-27T20:29:31Z	B / A	yes	J1	yes	95	
2	paired_ribose	Gemini	gemini-3.1-pro-preview	2026-09-27T20:30:29Z	B / A	yes	J1	yes	95	
3	paired_ribose	Gemini	gemini-3.1-pro-preview	2026-09-27T20:32:32Z	B / A	yes	J1	yes	95	
1	paired_deoxy	Gemini	gemini-3.1-pro-preview	2026-09-27T20:33:28Z	A / B	yes	J1	yes	95	
2	paired_deoxy	Gemini	gemini-3.1-pro-preview	2026-09-27T20:34:44Z	A / B	yes	J1	yes	95	
3	paired_deoxy	Gemini	gemini-3.1-pro-preview	2026-09-27T20:35:51Z	A / B	yes	J1	yes	95	
1	binary_PX-A01	Gemini	gemini-3.1-pro-preview	2026-09-27T20:38:49Z	A	yes	J1	yes	95	
2	binary_PX-A01	Gemini	gemini-3.1-pro-preview	2026-09-27T20:40:08Z	A	yes	J1	yes	99	
3	binary_PX-A01	Gemini	gemini-3.1-pro-preview	2026-09-27T20:42:39Z	A	yes	J1	yes	99	
1	binary_PX-A02	Gemini	gemini-3.1-pro-preview	2026-09-27T20:44:23Z	A	no	J1		95	
2	binary_PX-A02	Gemini	gemini-3.1-pro-preview	2026-09-27T20:46:31Z	A	no	J1		95	
3	binary_PX-A02	Gemini	gemini-3.1-pro-preview	2026-09-27T20:48:02Z	A	no	J1		95	
1	binary_PX-B01	Gemini	gemini-3.1-pro-preview	2026-09-27T20:50:20Z	A	yes	J2		95	
2	binary_PX-B01	Gemini	gemini-3.1-pro-preview	2026-09-27T20:52:16Z	A	yes	J2		95	
3	binary_PX-B01	Gemini	gemini-3.1-pro-preview	2026-09-27T20:54:34Z	A	yes	J2		95	
1	binary_PX-B02	Gemini	gemini-3.1-pro-preview	2026-09-27T20:56:55Z	B	yes	J1	yes	95	
2	binary_PX-B02	Gemini	gemini-3.1-pro-preview	2026-09-27T20:58:09Z	A	no	J2		95	
3	binary_PX-B02	Gemini	gemini-3.1-pro-preview	2026-09-27T20:59:41Z	B	yes	J1	yes	95	
1	singleIR_PX-A01	gpt-5	gpt-5-2025-08-07	2026-09-27T22:20:47Z	B	no	J1		75	
2	singleIR_PX-A01	gpt-5	gpt-5-2025-08-07	2026-09-27T22:21:19Z	UNDET.	abst.	abstain		30	
3	singleIR_PX-A01	gpt-5	gpt-5-2025-08-07	2026-09-27T22:21:57Z	UNDET.	abst.	abstain		85	
1	singleIR_PX-A02	gpt-5	gpt-5-2025-08-07	2026-09-27T22:22:32Z	B	yes	J1	yes	65	
2	singleIR_PX-A02	gpt-5	gpt-5-2025-08-07	2026-09-27T22:23:21Z	B	yes	J1	yes	60	
3	singleIR_PX-A02	gpt-5	gpt-5-2025-08-07	2026-09-27T22:23:42Z	B	yes	J1	yes	75	
1	singleIR_PX-B01	gpt-5	gpt-5-2025-08-07	2026-09-27T22:24:02Z	B	no	J2		80	
2	singleIR_PX-B01	gpt-5	gpt-5-2025-08-07	2026-09-27T22:24:35Z	UNDET.	abst.	abstain		25	
3	singleIR_PX-B01	gpt-5	gpt-5-2025-08-07	2026-09-27T22:25:02Z	B	no	J2		80	
1	singleIR_PX-B02	gpt-5	gpt-5-2025-08-07	2026-09-27T22:25:22Z	B	yes	J1	yes	80	
2	singleIR_PX-B02	gpt-5	gpt-5-2025-08-07	2026-09-27T22:26:11Z	A	no	J1		65	
3	singleIR_PX-B02	gpt-5	gpt-5-2025-08-07	2026-09-27T22:26:32Z	B	yes	J1	yes	88	
1	pairedfull_ribose	gpt-5	gpt-5-2025-08-07	2026-09-27T22:26:51Z	A / B	no	J2		90	
2	pairedfull_ribose	gpt-5	gpt-5-2025-08-07	2026-09-27T22:27:18Z	A / B	no	J2		90	
3	pairedfull_ribose	gpt-5	gpt-5-2025-08-07	2026-09-27T22:27:57Z	A / B	no	J2		80	
1	pairedfull_deoxy	gpt-5	gpt-5-2025-08-07	2026-09-27T22:29:07Z	A / B	yes	J1	yes	60	
2	pairedfull_deoxy	gpt-5	gpt-5-2025-08-07	2026-09-27T22:30:16Z	A / B	yes	J1	yes	60	
3	pairedfull_deoxy	gpt-5	gpt-5-2025-08-07	2026-09-27T22:31:15Z	A / B	yes	J3		80	C13:168.5

Run	Condition	System	Model identifier returned	Timestamp (UTC)	Answer	Agrees	Code	Orig. cited	Conf.	No labelled value
1	paired_benzoyl	gpt-5	gpt-5-2025-08-07	2026-09-27T22:31:46Z	A / B	yes	J1	yes	85	
2	paired_benzoyl	gpt-5	gpt-5-2025-08-07	2026-09-27T22:32:14Z	A / B	yes	J1	yes	90	
3	paired_benzoyl	gpt-5	gpt-5-2025-08-07	2026-09-27T22:32:43Z	A / B	yes	J1	yes	80	
1	singleIR_PX-C01	gpt-5	gpt-5-2025-08-07	2026-09-27T22:33:11Z	A	yes	J1	yes	85	
2	singleIR_PX-C01	gpt-5	gpt-5-2025-08-07	2026-09-27T22:33:34Z	B	no	J2		90	
3	singleIR_PX-C01	gpt-5	gpt-5-2025-08-07	2026-09-27T22:34:05Z	A	yes	J1	yes	80	
1	singleIR_PX-C02	gpt-5	gpt-5-2025-08-07	2026-09-27T22:34:31Z	B	yes	J1	yes	88	
2	singleIR_PX-C02	gpt-5	gpt-5-2025-08-07	2026-09-27T22:34:59Z	B	yes	J2		80	
3	singleIR_PX-C02	gpt-5	gpt-5-2025-08-07	2026-09-27T22:35:22Z	B	yes	J1	yes	88	
1	singleIR_PX-A01	Gemini	gemini-3.1-pro-preview	2026-09-27T22:42:41Z	A	yes	J1	yes	95	
2	singleIR_PX-A01	Gemini	gemini-3.1-pro-preview	2026-09-27T22:43:47Z	A	yes	J1	yes	95	
3	singleIR_PX-A01	Gemini	gemini-3.1-pro-preview	2026-09-27T22:45:46Z	A	yes	J1	yes	95	
1	singleIR_PX-A02	Gemini	gemini-3.1-pro-preview	2026-09-27T22:46:40Z	B	yes	J1	yes	95	
2	singleIR_PX-A02	Gemini	gemini-3.1-pro-preview	2026-09-27T22:47:57Z	B	yes	J1	yes	90	
3	singleIR_PX-A02	Gemini	gemini-3.1-pro-preview	2026-09-27T22:48:46Z	B	yes	J1	yes	95	
1	singleIR_PX-B01	Gemini	gemini-3.1-pro-preview	2026-09-27T22:50:29Z	A	yes	J1	yes	85	
2	singleIR_PX-B01	Gemini	gemini-3.1-pro-preview	2026-09-27T22:52:34Z	B	no	J2		85	
3	singleIR_PX-B01	Gemini	gemini-3.1-pro-preview	2026-09-27T22:54:36Z	B	no	J2		90	
1	singleIR_PX-B02	Gemini	gemini-3.1-pro-preview	2026-09-28T04:16:00Z	B	yes	J1	yes	95	
2	singleIR_PX-B02	Gemini	gemini-3.1-pro-preview	2026-09-28T04:17:14Z	B	yes	J1	yes	95	
3	singleIR_PX-B02	Gemini	gemini-3.1-pro-preview	2026-09-28T04:17:50Z	B	yes	J1	yes	95	
1	pairedfull_ribose	Gemini	gemini-3.1-pro-preview	2026-09-28T04:20:44Z	A / B	no	J2		95	
2	pairedfull_ribose	Gemini	gemini-3.1-pro-preview	2026-09-28T04:23:35Z	A / B	no	J2		95	
3	pairedfull_ribose	Gemini	gemini-3.1-pro-preview	2026-09-28T04:25:51Z	A / B	no	J2		95	
1	pairedfull_deoxy	Gemini	gemini-3.1-pro-preview	2026-09-28T04:52:12Z	A / B	yes	J1	yes	99	
2	pairedfull_deoxy	Gemini	gemini-3.1-pro-preview	2026-09-28T04:54:13Z	A / B	yes	J1	yes	95	
3	pairedfull_deoxy	Gemini	gemini-3.1-pro-preview	2026-09-28T04:56:41Z	A / B	yes	J1	yes	100	
1	paired_benzoyl	Gemini	gemini-3.1-pro-preview	2026-09-28T04:58:12Z	A / B	yes	J1	yes	95	
2	paired_benzoyl	Gemini	gemini-3.1-pro-preview	2026-09-28T04:59:05Z	A / B	yes	J1	yes	95	
3	paired_benzoyl	Gemini	gemini-3.1-pro-preview	2026-09-28T05:01:28Z	A / B	yes	J1	yes	95	
1	singleIR_PX-C01	Gemini	gemini-3.1-pro-preview	2026-09-28T05:02:18Z	A	yes	J1	yes	95	
2	singleIR_PX-C01	Gemini	gemini-3.1-pro-preview	2026-09-28T05:04:15Z	A	yes	J1	yes	95	
3	singleIR_PX-C01	Gemini	gemini-3.1-pro-preview	2026-09-28T05:04:46Z	A	yes	J1	yes	95	
1	singleIR_PX-C02	Gemini	gemini-3.1-pro-preview	2026-09-28T05:06:17Z	B	yes	J1	yes	95	
2	singleIR_PX-C02	Gemini	gemini-3.1-pro-preview	2026-09-28T05:07:37Z	B	yes	J1	yes	95	
3	singleIR_PX-C02	Gemini	gemini-3.1-pro-preview	2026-09-28T05:09:10Z	B	yes	J1	yes	95	

Table S4. *Decisive evidence* field of each API response, verbatim.

Run	Condition	System	Decisive evidence field (verbatim)
r1	paired_ribose	gpt-5	Spectrum 2 shows a strong additional carbonyl band at ~1680 cm^{-1} (amide/lactam), which is present only in Candidate A; Spectrum 1 lacks this band beyond the ester C=O at ~1750 cm^{-1}, matching Candidate B which has no extra C=O.
r2	paired_ribose	gpt-5	Spectrum 2 shows an additional strong C=O band at ~1680 cm^{-1} (amide/carbamate N–C=O), while Spectrum 1 lacks this and shows only ester-type C=O near ~1750 cm^{-1}.
r3	paired_ribose	gpt-5	Spectrum 2 shows a very strong band at ~1278 cm^{-1} (with another at ~1230 cm^{-1}), characteristic of an aryl–O (C–O) stretch expected for an O-glycosidic linkage; Spectrum 1 lacks this strong 1275 cm^{-1} feature and instead shows stronger bands in the 1330–1400 cm^{-1} region consistent with C–N stretching of an N-glycosidic linkage.
r1	paired_deoxy	gpt-5	Spectrum 2 shows a strong band at ~1679 cm−1 (with a companion band near 1531 cm−1), consistent with an amide C=O/amide II pair. Candidate B contains an amide carbonyl; Candidate A does not (only esters and C=N).
r2	paired_deoxy	gpt-5	Spectrum 2 shows a distinct second carbonyl band at ~1679 cm^{-1} (amide/lactam C=O) in addition to the ester C=O at ~1742 cm^{-1}. Candidate B uniquely contains this extra amide carbonyl, while Candidate A does not.
r3	paired_deoxy	gpt-5	Spectrum 2 shows a distinct amide I band near 1680 cm^{-1} (with a companion amide II band near 1531 cm^{-1}), which fits Candidate B's amide carbonyl. Spectrum 1 lacks a clear amide I; its band around 1646 cm^{-1} is consistent with C=N/aryl C=C of Candidate A.
r1	binary_PX-A01	gpt-5	13C NMR shows the anomeric carbon at 104.09 ppm, which is characteristic of an O-glycosidic acetal; an N-glycoside would place C-1′ much further upfield (≈85–92 ppm).
r2	binary_PX-A01	gpt-5	The 13C NMR shows a single anomeric carbon at 104.09 ppm, which is characteristic of an O-acetal (O-glycosidic) C-1'. An N-glycosidic C-1' (Candidate A) would be expected around 86–92 ppm and is not observed.
r3	binary_PX-A01	gpt-5	13C NMR shows a single deshielded anomeric carbon at ~104.1 ppm, characteristic of an O-glycosidic acetal (C-1′ around 100–105 ppm). An N-glycoside would place C-1′ much further upfield (~85–90 ppm).
r1	binary_PX-A02	gpt-5	13C NMR shows the anomeric carbon at ~90.2 ppm, which is characteristic of an N-glycosidic C1′; an O-glycosidic acetal C1′ would appear much further downfield (~100–105 ppm).
r2	binary_PX-A02	gpt-5	No unambiguous HMBC connectivity to identify which heteroatom of the base is glycosylated.
r3	binary_PX-A02	gpt-5	13C NMR shows the anomeric carbon at ~90.2 ppm, characteristic of an N-glycosidic C1′. An O-glycosidic anomeric carbon would appear near 100–105 ppm.
r1	binary_PX-B01	gpt-5	Presence of an extra amide/lactam carbonyl band and carbonyl carbon
r2	binary_PX-B01	gpt-5	A very downfield, exchangeable proton at ~13.6 ppm in the 1H NMR indicates a strongly H-bonded heteroaromatic OH that would be absent in the O-glycoside (Candidate A) but retained when the sugar is attached through nitrogen (Candidate B). Supporting sign: the 13C spectrum shows an anomeric carbon at ~78.5 ppm, consistent with a C–N glycosidic center (O-glycosides typically appear >95 ppm).
r3	binary_PX-B01	gpt-5	HSQC shows the anomeric proton (~6.0 ppm) correlating to a 13C resonance at ~88–89 ppm, consistent with an N-glycosidic (O–C–N) anomeric carbon, not an O,O-acetal.
r1	binary_PX-B02	gpt-5	13C NMR shows a distinct resonance at ~103.9 ppm, diagnostic for an anomeric carbon bonded to two oxygens (O,O-acetal). That requires an O-glycosidic linkage as in Candidate A; an N-glycoside (Candidate B) would shift C1′ to ~85–90 ppm.
r2	binary_PX-B02	gpt-5	13C NMR shows the anomeric carbon at ~103.8 ppm, characteristic of an O,O-acetal (O-glycoside).
r3	binary_PX-B02	gpt-5	The anomeric carbon appears at 103.8 ppm in the 13C NMR, diagnostic of an acetal C–O–O linkage. Candidate B (C–O–N/N-glycoside) would place C1′ far upfield, typically ~88–95 ppm, which is not observed. The anomeric 1H at ~5.5 ppm also matches an O,O-acetal better than an N-glycoside.
r1	paired_ribose	Gemini	The presence of a prominent peak at ~1680 cm^{-1} in Spectrum 2, which is absent in

Run	Condition	System	Decisive evidence field (verbatim)
			Spectrum 1.
r2	paired_ribose	Gemini	The absorption peak at 1680 cm-1 in Spectrum 2.
r3	paired_ribose	Gemini	The absorption band at 1680.47 cm-1 in Spectrum 2.
r1	paired_deoxy	Gemini	The strong absorption peak at 1679.91 cm^-1 in Spectrum 2, corresponding to the pyrazolone ring carbonyl, which is absent in Spectrum 1.
r2	paired_deoxy	Gemini	The absorption peak at ~1680 cm-1 in Spectrum 2.
r3	paired_deoxy	Gemini	The distinct absorption peak at 1679.91 cm^{-1} in Spectrum 2, which is absent in Spectrum 1.
r1	binary_PX-A01	Gemini	13C NMR chemical shift of the anomeric carbon (C1'') at 84.39 ppm; IR peak at 1680 cm-1.
r2	binary_PX-A01	Gemini	13C chemical shift of the anomeric carbon at 84.39 ppm.
r3	binary_PX-A01	Gemini	The HMBC spectrum assigns the anomeric carbon (C-1'') to a chemical shift of 84.39 ppm.
r1	binary_PX-A02	Gemini	13C NMR chemical shift of the anomeric carbon (C-1') at 90.2 ppm.
r2	binary_PX-A02	Gemini	The 13C NMR chemical shift of the anomeric carbon (C1') at 90.2 ppm.
r3	binary_PX-A02	Gemini	13C NMR chemical shift of the anomeric carbon at 90.2 ppm.
r1	binary_PX-B01	Gemini	13C NMR signal at 103.80 ppm.
r2	binary_PX-B01	Gemini	The 13C NMR signal at 103.80 ppm.
r3	binary_PX-B01	Gemini	13C NMR peak at 103.80 ppm.
r1	binary_PX-B02	Gemini	The presence of a strong IR band at ~1680 cm^{-1} (ring C=O) and the absence of an unaccounted 13C NMR signal >100 ppm for an O-glycosyl anomeric carbon.
r2	binary_PX-B02	Gemini	The 13C NMR chemical shift of the anomeric carbon (C1').
r3	binary_PX-B02	Gemini	1H NMR NH signal at 13.5 ppm and IR band at 1679 cm-1.
r1	singleIR_PX-A01	gpt-5	Only one non-ester C=O stretch at ~1680 cm^{-1} (besides the strong ester C=O at 1749 cm^{-1}).
r2	singleIR_PX-A01	gpt-5	None—the IR shows only features (~1749 cm^{-1} ester C=O; ~1680 cm^{-1} amide/lactam C=O; 1600–1500 cm^{-1} ring bands; 1280–1140 cm^{-1} C–O/C–N stretches) that are expected for both candidates.
r3	singleIR_PX-A01	gpt-5	None – the IR features are consistent with both candidates.
r1	singleIR_PX-A02	gpt-5	IR shows a single very strong carbonyl band at ~1751 cm^{-1} (plus typical C–O bands at ~1234 and 1071 cm^{-1}), consistent with only ester/carbonate C=O groups and no separate amide/carbamate C=O around 1690–1715 cm^{-1}.
r2	singleIR_PX-A02	gpt-5	IR shows one strong ester νC=O at ~1751 cm^{-1} and one amide νC=O at ~1639 cm^{-1}, with no additional carbonyl band in the 1710–1730 cm^{-1} region.
r3	singleIR_PX-A02	gpt-5	IR shows a single strong carbonyl band at ~1751 cm−1 (ester). No additional strong band in the 1650–1700 cm−1 region expected for an amide/lactam carbonyl.
r1	singleIR_PX-B01	gpt-5	Strong IR band at 1646 cm^{-1} (with a companion near 1561 cm^{-1}) indicating an amide carbonyl (amide I) and amide II band in addition to the ester C=O at 1741 cm^{-1}.
r2	singleIR_PX-B01	gpt-5	None – the IR shows an ester C=O at ~1741 cm^{-1} and a band near 1646 cm^{-1} (amide/C=N), plus C–O/C–N bands in the 1250–1100 cm^{-1} region, all consistent with both candidates.
r3	singleIR_PX-B01	gpt-5	IR shows two distinct carbonyl regions: a very strong ester C=O at 1741 cm−1 and an additional strong band at 1646 cm−1 with a companion band at 1561 cm−1 (amide I and II).
r1	singleIR_PX-B02	gpt-5	IR shows an additional strong C=O band at ~1680 cm^{-1} (with amide-II bands near 1560–1530 cm^{-1}), indicating an amide carbonyl.
r2	singleIR_PX-B02	gpt-5	Only one non-ester carbonyl band at ~1679 cm^{-1} (besides the strong ester band at ~1742 cm^{-1}).
r3	singleIR_PX-B02	gpt-5	IR has two strong C=O absorptions: a strong ester band at ~1742 cm^{-1} and a second strong carbonyl at ~1680 cm^{-1} (amide).
r1	pairedfull_ribose	gpt-5	13C NMR position of the anomeric carbon. Compound 1 has C-1′ around 90 ppm (typical

Run	Condition	System	Decisive evidence field (verbatim)
			for N-glycosides), while Compound 2 shows C-1′ at ~104 ppm (typical acetal carbon for O-glycosides).
r2	pairedfull_ribose	gpt-5	13C NMR anomeric carbon shift — Compound 1 has C-1′ at ~90.2 ppm (typical for N-glycosides), while Compound 2 has C-1′ at ~104.1 ppm (typical for O-glycosidic acetals).
r3	pairedfull_ribose	gpt-5	13C NMR chemical shift of the anomeric carbon. Compound 1 shows C-1′ ≈ 90 ppm (typical for N-glycosides), while Compound 2 shows C-1′ ≈ 104 ppm (typical for O-glycosides).
r1	pairedfull_deoxy	gpt-5	Position of the heterocycle carbonyl in the IR. Compound 2 shows a strong C=O band at ~1679 cm−1 (amide/urea carbonyl attached to N), while Compound 1 has it lower at ~1646 cm−1 (O-alkylated variant).
r2	pairedfull_deoxy	gpt-5	The anomeric carbon signal. In Compound 1 the 13C NMR shows a C-1′ at ~103.8 ppm (HSQC shows it is a CH), which is characteristic of an O-acetal (O-glycoside). N-glycosides place C-1′ much farther upfield (~88–92 ppm). Compound 2 lacks a protonated carbon at ~104 ppm and instead shows the remaining sugar carbons below 90 ppm (window cropped), and its amide C=O IR band is shifted higher (1679 cm−1 vs ~1646 cm−1), consistent with N-linkage.
r3	pairedfull_deoxy	gpt-5	Compound 2 shows an extra strong carbonyl absorption at 1679 cm^{-1} in the IR and an additional carbonyl signal at ~168.5 ppm in the 13C NMR, consistent with the amide/carbamate C=O of Candidate B. Compound 1 lacks this extra carbonyl feature, matching Candidate A where the sugar is linked directly via oxygen without an intervening amide.
r1	paired_benzoyl	gpt-5	Spectrum 1 shows two intense C=O stretches (~1733 and ~1685 cm^{-1}), while Spectrum 2 shows only one strong C=O band (~1726 cm^{-1}).
r2	paired_benzoyl	gpt-5	Spectrum 1 shows strong additional bands at 1685 and 1633 cm^{-1} (amide I region), absent in Spectrum 2, indicating an amide carbonyl. Spectrum 2 shows only a strong carbonyl near 1726 cm^{-1}, consistent with an ester.
r3	paired_benzoyl	gpt-5	Spectrum 1 shows two strong carbonyl bands at ~1733 and 1685/1633 cm^{-1} (amide/imide-type), while Spectrum 2 shows a single strong C=O near 1726 cm^{-1} with prominent C–O stretches around 1267–1239–1191 cm^{-1} typical of an ester.
r1	singleIR_PX-C01	gpt-5	Strong carbonyl band at 1685 cm^{-1} (amide I), together with another C=O at 1733 cm^{-1}.
r2	singleIR_PX-C01	gpt-5	Strong ester carbonyl at ~1733 cm^{-1} together with paired strong C–O stretches at ~1247 and ~1142 cm^{-1}.
r3	singleIR_PX-C01	gpt-5	IR shows two C=O bands at 1733 and 1685 cm^{-1}; the 1685 cm^{-1} band is characteristic of an amide carbonyl (amide I), which exists only in Candidate A.
r1	singleIR_PX-C02	gpt-5	Strong C=O stretch at 1726 cm^{-1} with accompanying strong C–O bands at ~1267 and 1191 cm^{-1} indicates an aryl ester; no amide C=O band near 1640–1680 cm^{-1} is observed.
r2	singleIR_PX-C02	gpt-5	Strong C=O stretch at 1726 cm^{-1}, characteristic of an ester (O–C(=O)–Ar) and inconsistent with an N-benzoyl amide, which would show the amide-I band near ~1650 cm^{-1}.
r3	singleIR_PX-C02	gpt-5	Strong C=O stretch at 1726 cm^{-1} with intense C–O stretches at ~1267 and ~1239 cm^{-1} – pattern diagnostic for an aryl ester; no amide I band near 1650–1690 cm^{-1}.
r1	singleIR_PX-A01	Gemini	The absorption peak at 1680.47 cm^-1.
r2	singleIR_PX-A01	Gemini	The distinct absorption band at 1680.47 cm-1.
r3	singleIR_PX-A01	Gemini	The strong absorption band at 1680.47 cm^{-1}.
r1	singleIR_PX-A02	Gemini	Absence of an additional carbonyl stretching band in the 1650-1700 cm^{-1} region.
r2	singleIR_PX-A02	Gemini	Absence of a ring carbonyl (lactam) stretching band in the 1650-1700 cm^{-1} region.
r3	singleIR_PX-A02	Gemini	The absence of a second strong carbonyl stretching band in the 1650-1700 cm^{-1} region. The spectrum is dominated by a single carbonyl peak at 1751 cm^{-1}.
r1	singleIR_PX-B01	Gemini	The presence of only one distinct carbonyl absorption region (the strong peak at 1741.47 cm-1) and the absence of a distinct cyclic lactam/ketone carbonyl band.
r2	singleIR_PX-B01	Gemini	The moderately strong peak at 1646 cm^{-1}.
r3	singleIR_PX-B01	Gemini	The absorption band at 1646 cm^{-1}.

Run	Condition	System	Decisive evidence field (verbatim)
r1	singleIR_PX-B02	Gemini	The strong absorption peak at 1679.91 cm-1.
r2	singleIR_PX-B02	Gemini	The prominent IR absorption band at 1679.91 cm-1.
r3	singleIR_PX-B02	Gemini	The absorption peak at 1679.91 cm^{-1}.
r1	pairedfull_ribose	Gemini	13C NMR chemical shift of the anomeric carbon (C-1')
r2	pairedfull_ribose	Gemini	13C NMR chemical shift of the anomeric carbon (C-1').
r3	pairedfull_ribose	Gemini	13C NMR chemical shift of the anomeric carbon (C-1').
r1	pairedfull_deoxy	Gemini	IR carbonyl peak at ~1680 cm-1 in Compound 2 and 13C NMR anomeric carbon chemical shifts.
r2	pairedfull_deoxy	Gemini	The presence of a strong IR absorption band at 1679.91 cm-1 in Compound 2, which is absent in Compound 1.
r3	pairedfull_deoxy	Gemini	The presence of an IR peak at ~1680 cm-1 in Compound 2 and the chemical shift of the anomeric proton (5.84 ppm in Cpd 1 vs. 6.96 ppm in Cpd 2).
r1	paired_benzoyl	Gemini	The number of distinct carbonyl (C=O) stretching bands >1650 cm^{-1}.
r2	paired_benzoyl	Gemini	The number of strong carbonyl (C=O) stretching bands between 1650 and 1750 cm^{-1}.
r3	paired_benzoyl	Gemini	The number of carbonyl (C=O) stretching peaks in the 1650-1750 cm-1 region.
r1	singleIR_PX-C01	Gemini	Two strong absorption bands in the carbonyl region at approximately 1733 cm-1 and 1685 cm-1.
r2	singleIR_PX-C01	Gemini	The presence of two strong absorption bands in the carbonyl region at 1733 cm^{-1} and 1685 cm^{-1}.
r3	singleIR_PX-C01	Gemini	Presence of two distinct carbonyl stretching bands at 1733 cm^{-1} and 1685 cm^{-1}.
r1	singleIR_PX-C02	Gemini	The presence of a single carbonyl (C=O) stretching peak at 1725.76 cm^{-1} and the complete absence of any absorption bands in the 1600-1700 cm^{-1} region.
r2	singleIR_PX-C02	Gemini	The presence of a single, sharp carbonyl stretching peak at ~1726 cm-1.
r3	singleIR_PX-C02	Gemini	The presence of only a single strong carbonyl (C=O) stretching peak at 1726 cm^{-1}.

S3.2 Anomeric-carbon arguments in the NMR-added responses

Of the 36 NMR-added responses on the two glycoside pairs, 35 committed to an answer and 30 of these argued from the ^{13}C shift of the anomeric carbon (29 from a signal described as that carbon and one, Gemini `binary_PX-B02` r1, from the absence of such a signal above 100 ppm), in the *Decisive evidence* field or in the *Reasoning* field (17 of 17 on the ribose pair, 13 of 18 on the 2-deoxy pair). Table S5 lists them; rows group replicates that gave the same argument. Entries marked † are not in the *Decisive evidence* field and were taken from the *Reasoning* field of the deposited response. The five committed responses that did not argue from an anomeric carbon are gpt-5 `binary_PX-B01` r1, Gemini `binary_PX-B02` r3 (which states that the ^{13}C spectrum supplied is incomplete and that the anomeric carbon cannot be observed), gpt-5 `pairedfull_deoxy` r1 and r3, and Gemini `pairedfull_deoxy` r2; four of them are entered in Table S24 as discussing no anomeric carbon and one (Gemini `binary_PX-B02` r3) as "no", because it refers to the anomeric carbon only to say that it cannot be observed. The decision recorded for each of the 36 responses, with the sentence on which it rests, is given in Section S12 (Table S24).

In each row that states a range, the answer returned is the one that the range implies for the signal taken as the anomeric carbon. This correspondence was established after the fact and does not show that the range produced the answer.

Table S5. Anomeric-carbon arguments in the committed NMR-added responses. "Carbon assigned C-1″" is the carbon so listed in the source. For the 2-deoxy pair it is the value listed for the compound under whose number the ^{13}C panel was supplied: 78.54 ppm for 122a, and for 123a 77.21 ppm, which no correlation spectrum confirms. By the original records the panel supplied for 123a shows the spectrum of the compound whose ^{1}H spectrum is printed for 122a, and the panel supplied for 122a is attributed to the other compound; the anomeric carbon of the compound whose ^{1}H spectrum is printed for 122a is the line at 76.50 ppm of the spectrum printed for 123a (Sections S8, S15 and S16.3).

Condition, system, replicates	Signal taken as anomeric carbon (ppm)	What the signal is	Carbon assigned C-1″ (ppm)	Range stated	Answer implied	Answer returned	Source label
Single, PX-A01 (117a), gpt-5, r1–r3	104.09	aryl C-2′	84.39	N ≈ 85–92 (r2: 86–92; r3: 85–90); O ≈ 100–105 stated by r3 only	O (B)	B, B, B	A
Single, PX-A02 (116a), gpt-5, r1, r3	90.2	C-1″	90.22	N at about 90; O ≈ 100–105	N (A)	A, A	B
Single, PX-A01 (117a), Gemini, r1–r3	84.39	C-1″	84.39	O > 95 (r1–r3); N "typically 75–90" (r2 only)†	N (A)	A, A, A	A
Single, PX-A02 (116a), Gemini, r1–r3	90.2	C-1″	90.22	N ≈ 85–90 (r1), 80–95 (r2) or 85–95 (r3); O > 95†	N (A)	A, A, A	B
Paired, ribose, gpt-5, r1–r3	Cpd 1: 90–90.2; Cpd 2: 104–104.1	C-1″ of 116a; aryl C-2′ of 117a	90.22; 84.39	N ≈ 90; O ≈ 104	1 = A, 2 = B	A / B	B / A
Paired, ribose, Gemini, r1–r3	no value in the field; 90.2 and 104.09†	C-1″ of 116a; aryl C-2′ of 117a	90.22; 84.39	N ≈ 85–95 (r1, r2) or 80–95 (r3); O ≈ 95–110 (r1) or > 100 (r2, r3)†	1 = A, 2 = B	A / B	B / A
Single, PX-B01 (122a), gpt-5, r2	78.5, as support; main argument the proton at 13.6 ppm	the carbon listed as C-1″	78.54	O > 95	N (B)	B	A (source)
Single, PX-B01 (122a), gpt-5, r3	88–89, attributed by the response to the HSQC panel; no labelled value	—	78.54	below an O,O-acetal	N (B)	B	A (source)
Single, PX-B02 (123a), gpt-5, r1–r3	103.8–103.9	aryl C-2′	77.21 (listed; not confirmed)	O,O-acetal ≈ 104; N ≈ 85–90 or 88–95	O (A)	A, A, A	B (source)
Single, PX-B01 (122a), Gemini, r1–r3	103.80 (field gives the value only)	aryl C-2′	78.54	N ≈ 85–90 (r1) or 80–95 (r2, r3); O > 100 stated by r2†	O (A)	A, A, A	A (source)
Single, PX-B02 (123a), Gemini, r1	none: "absence of an unaccounted ^{13}C NMR signal >100 ppm", with the IR band	—	77.21 (listed; not confirmed)	O > 100	N (B)	B	B (source)
Single, PX-B02 (123a), Gemini, r2	no value in the field; 103.8†, with "a completely flat baseline in the 80–95 ppm region"†, a region that the supplied panel does not display	aryl C-2′	77.21 (listed; not confirmed)	N ≈ 80–95; O > 100 ("usually 103–108")†	O (A)	A	B (source)
Paired, 2-deoxy, gpt-5, r2	Cpd 1: 103.8, with the IR band as support	aryl C-2′ of 122a	78.54	O-acetal ≈ 104; N ≈ 88–92	1 = A	A / B	A / B (source)
Paired, 2-deoxy, Gemini, r1	no value in the field; Cpd 1: 103.80, "confirmed by HSQC"†; Cpd 2: 76.499†; with the IR band	aryl C-2′ of 122a; for 123a the line listed as C-3″ (76.50 ppm), beside the solvent	78.54; 77.21 (listed; not confirmed)	none stated ("characteristic of an O-glycoside"; "typical for an N-glycoside")†	1 = A, 2 = B	A / B	A / B (source)

Condition, system, replicates	Signal taken as anomeric carbon (ppm)	What the signal is	Carbon assigned C-1″ (ppm)	Range stated	Answer implied	Answer returned	Source label
Paired, 2-deoxy, Gemini, r3	the field cites anomeric protons (5.84 and 6.96 ppm); Cpd 1: 103.8, “The HSQC of Compound 1 also confirms”†; with the IR band	aryl C-2′ of 122a signal	78.54	none stated†	1 = A	A / B	A / B (source)

An aryl carbon near 104 ppm was given as the anomeric carbon in nine of the 17 ribose responses (three single-case gpt-5 responses on 117a and the six paired responses; six of the nine in the field and three in the *Reasoning* field) and in ten of the 18 2-deoxy responses: the three single-case gpt-5 responses on 123a and one paired gpt-5 response in the field; and, in the *Reasoning* field, the three single-case Gemini responses on 122a, whose fields cite 103.80 ppm alone, one single-case Gemini response on 123a and two paired Gemini responses. Over both pairs this is 19 of the 35 committed NMR-added responses: ten in the field, all from gpt-5 (10 of 17), and nine in the *Reasoning* field, all from Gemini (9 of 18). By item the figures are 3 of 6 (`binary_PX-A01`), 0 of 5 (`binary_PX-A02`), 6 of 6 (`pairedfull_ribose`), 3 of 6 (`binary_PX-B01`), 4 of 6 (`binary_PX-B02`) and 3 of 6 (`pairedfull_deoxy`). Of the other 16 committed responses, twelve do not give the aryl signal as the anomeric carbon and four discuss no anomeric carbon. The *Reasoning* field of all 36 NMR-added responses was read for this question (Section S12); the status of every response is given in the column `aryl_C2_given_as_anomeric` of Supporting File 2, with the sentence on which it rests in the column `aryl_C2_basis_sentence`.

S3.3 Pilot

The pilot was run through the consumer chat interfaces (ChatGPT and Gemini) on 22–26 September 2026, one case per temporary session, and produced 75 responses. It exposed an image-indexing problem, in which responses referred to the attached images by position, that was removed by adding an identifier band or heading to the spectrum images. The chat interfaces do not expose the model version, so differences between pilot and API results are reported as observed and are not attributed to a cause. The pilot workbook (`pilot-results-v0_36.xlsx`, deposited) contains all 75 responses, a key sheet, the excluded and exploratory runs with reasons, and the probe of Section S5. No pilot response enters any count in the article; 32 pilot responses enter the agreement check of Section S4.5.

Single-case presentation with NMR spectra added (ChatGPT, chat interface): 12 responses, of which seven committed (three agreeing with the source label, four not) and five abstained at stated confidences of 94–97. The four disagreeing responses comprised an aromatic CH near 104 ppm taken as the anomeric carbon (B003, B014); a long-range correlation from H-1″ to an aglycone carbon that no supplied panel shows (B006; the same unsupported correlation accompanied agreeing answers in B002 and B004); and a carbonyl-count argument applied to a misread label (157.54 read as 167.54) and to the band at 1646 cm^{-1} (B011).

The paired infrared-only pilot results are given in Table S6, and three of the sessions are shown in Figure S1.

Table S6. Pilot, paired presentation with infrared spectra only (three responses per row). The last column is the category of the original script coding (Section S4.3); the pilot fields were not recoded by the rule of Section S4.6.

System, pair	Agrees	Abstains	Disagrees	Agrees and coded J1 (original coding)
Gemini, ribose	3	0	0	3
Gemini, 2-deoxyribose	3	0	0	3
ChatGPT, 2-deoxyribose	3	0	0	3
ChatGPT, ribose	0	1	2	0

For the same conditions through the API (gpt-5-2025-08-07): paired infrared-only ribose 2 of 3 agreeing against 0 of 3 through the chat interface; paired infrared-only 2-deoxyribose 3 of 3 on both routes; single-case NMR-added 0 of 12 agreeing with one abstention through the API against 3 of 12 with five abstentions through the chat interface.

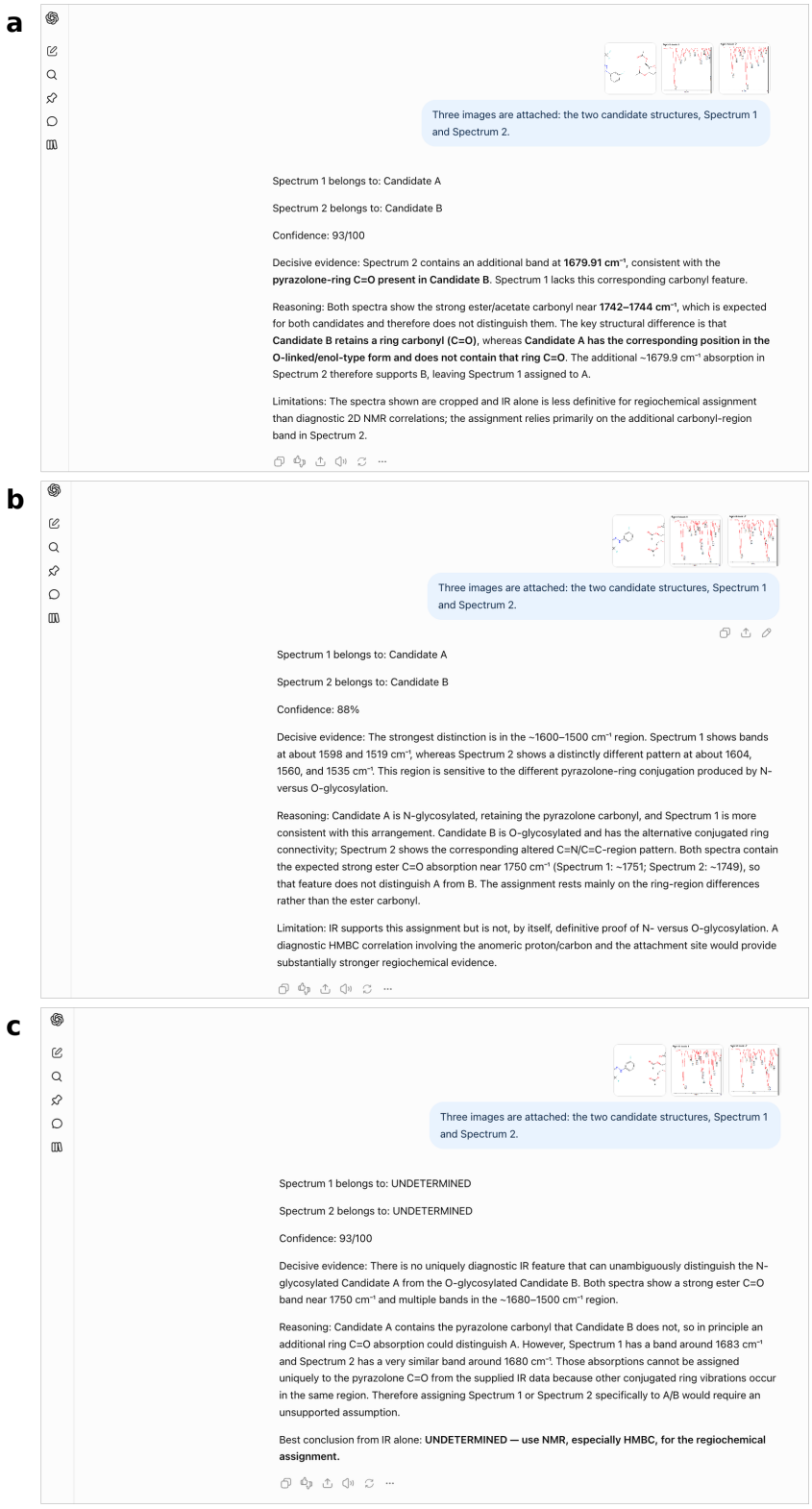


Figure S1. Three sessions of the paired infrared-only item in the pilot (ChatGPT chat interface, 26 September 2026; model version not exposed), reproduced from the deposited screenshots without editing. (a) A response on the 2-deoxy pair naming the band at

1679.91 cm^{-1} (P020, stated confidence 93). (b) A response on the ribose pair that rests on the 1600–1500 cm^{-1} region and does not mention the band at 1680.47 cm^{-1} (P022, stated confidence 88). (c) An abstention on the ribose pair (P023, stated confidence 93). In each screenshot the visible user message consists of the three images and the closing sentence of the prompt; how the preceding task text was supplied in these sessions is not visible in the screenshots. Transcriptions in Section S4.4.

Two further deposited screenshots of the same series (18:09 and 18:11 local time) show a message consisting of that closing sentence and the three images alone, to which the reply asks what the task is; these exchanges produced no classification. The deposit contains no screenshot of the sessions P019 and P021, so their transcriptions in Section S4.4 cannot be compared with an image here.

S3.4 Timing, batches and request settings

The first and last request of each condition group are listed in Table S7.

Table S7. First and last request of each condition group. The infrared-only groups include the benzoyl conditions (three paired and six single-case responses per system).

System	Condition group	n	First request (UTC)	Last request (UTC)	Model identifier returned
Gemini	paired, infrared only	9	2026-09-27T20:29:31Z	2026-09-28T05:01:28Z	gemini-3.1-pro-preview
Gemini	paired, NMR added	6	2026-09-28T04:20:44Z	2026-09-28T04:56:41Z	gemini-3.1-pro-preview
Gemini	single case, infrared only	18	2026-09-27T22:42:41Z	2026-09-28T05:09:10Z	gemini-3.1-pro-preview
Gemini	single case, NMR added	12	2026-09-27T20:38:49Z	2026-09-27T20:59:41Z	gemini-3.1-pro-preview
gpt-5	paired, infrared only	9	2026-09-27T12:19:02Z	2026-09-27T22:32:43Z	gpt-5-2025-08-07
gpt-5	paired, NMR added	6	2026-09-27T22:26:51Z	2026-09-27T22:31:15Z	gpt-5-2025-08-07
gpt-5	single case, infrared only	18	2026-09-27T22:20:47Z	2026-09-27T22:35:22Z	gpt-5-2025-08-07
gpt-5	single case, NMR added	12	2026-09-27T12:23:00Z	2026-09-27T12:32:27Z	gpt-5-2025-08-07

The responses were collected in two batches. Batch 1 comprised the paired infrared-only and the single-case NMR-added conditions; batch 2, added afterwards, comprised the single-case infrared-only, the paired NMR-added and the benzoyl conditions. For gpt-5 batch 1 ran at 12:19–12:32 UTC and batch 2 at 22:20–22:35 UTC on 27 September 2026. For Gemini batch 1 ran at 20:29–21:00 UTC on 27 September; batch 2 began at 22:42 UTC, was interrupted by a billing limit after the `singleIR_PX-B01` requests (last response 22:54 UTC) and resumed on 28 September at 04:16 UTC with `singleIR_PX-B02`, ending at 05:09 UTC. Within the Gemini `pairedfull` group there is a further interval of 26 minutes between the last ribose response (04:25:51 UTC) and the first 2-deoxy response (04:52:12 UTC); whether a request failed and was repeated in this interval is not recorded in the run log. No prompt file or image was changed between batches. The model identifier returned by the service was `gemini-3.1-pro-preview` for every Gemini response, before and after the interruption, and `gpt-5-2025-08-07` for every gpt-5 response. For Gemini the identifier is a preview name without a dated snapshot, and the returned identifier does not by itself show that the model was unchanged between 27 and 28 September.

Within each presentation the level of evidence coincides with the batch: infrared-only paired items and NMR-added single-case items are batch 1, and the other two cells are

batch 2. Batch 2 was designed after batch 1 had been collected. Replicates of a condition were requested consecutively, in the order of Table S3.

Request settings, as read from `run_api.py` of the deposit. Each request is a single user message. For gpt-5 it is sent with the `chat.completions.create` method of the OpenAI Python library, the message content being the images in the order of the `images` column of the run log, each as a base64 PNG data URL, followed by the prompt text. For Gemini it is sent with the `models.generate_content` method of the `google-genai` library, the contents being the images as PNG bytes in the same order, followed by the prompt text. No system message, no file name, no temperature and no reasoning, output-length or tool parameter is sent; the run log records the literal value `default` as the sampling setting of all 90 requests. The provider defaults in force and the versions of the two libraries were not recorded. The model identifier logged is the one returned in the response, and the timestamp is written after the response has been received. A request that raises an error is written by the script as a row whose response begins `__ERROR__`, and a row already present is skipped when the script is run again; the deposited file contains 90 rows and no such row, so any error rows written at the interruption described above were removed before the run was resumed and are not part of the deposit.

S3.5 Supplementary task on the benzoyl pair

The derivatives 124f (PX-C02, assigned O-benzoyl) and 127c (PX-C01, assigned N-benzoyl) differ in the printed infrared spectra in the number of carbonyl bands: one at 1725.76 cm^{-1} against two at 1732.96 and 1685.07 cm^{-1}. Because the source characterisation of this pair is inconsistent (audit item A5), the task tests only whether the number of carbonyl bands visible in an image is mapped to the candidate drawing with the corresponding number of carbonyl groups; agreement with the source labels does not show that the structure of either sample was read correctly. In the two infrared-only conditions (paired and single-case, three replicates per system), 17 of 18 responses agreed with the source labels. The exception (gpt-5 `singleIR_PX-C01` r2) described the 1733 cm^{-1} band as an ester carbonyl and did not use the band at 1685 cm^{-1}. The spectrum of 127c also carries a labelled band at 1633.45 cm^{-1}, which two gpt-5 responses included in their description of the amide region; the item is therefore not free of additional bands. The pair is not part of the glycoside analysis.

S4 Value tables and coding

S4.1 Labelled values of the source figures (`panels.json`)

The values below are those against which cited values were checked. Infrared and ^{13}C values are the peak labels printed on the source figures (IR Figures 23, 44 and 53; ^{13}C Figures 19, 25, 40 and 46); ^{1}H values are those listed in the experimental section of the source, not peak labels of the panels. The two-dimensional panels have no value table, so statements about cross-peaks could not be checked against values as supplied; the complete HSQC figure of the source is read in Section S15. For 122a and 123a the ^{13}C values are the labels of the figure printed for each compound, from which its panel was cut; by the

original records neither figure is the spectrum of the compound whose ^{1}H spectrum is printed with it (Section S16.3), and the tables are kept as the record of what was supplied. Labelled $CDCl_3$ lines (^{13}C 77.32, 77.0, 76.68; ^{1}H 7.26) are included. The two values near 164 and 162 ppm in each ^{13}C list are the two lines of the ^{1}J(C,F) doublet of C-3′, not two carbons (Table S19). Tolerances: IR 5 cm^{-1}, ^{13}C 0.6 ppm, ^{1}H 0.1 ppm (Section S4.7).

PX-A01 (117a). IR (cm^{-1}): 1749.46, 1680.47, 1604.67, 1560.39, 1534.91, 1492.07, 1372.87, 1278.44, 1229.85, 1190.74, 1140.65. ^{13}C (ppm): 170.65, 170.63, 169.59, 169.45, 164.81, 162.34, 157.77, 141.76, 138.7, 131.19, 123.28, 114.26, 112.73, 104.09, 84.39, 79.7, 72.53, 70.74, 62.91, 20.59, 20.55, 20.49, 77.32, 77.0, 76.68. ^{1}H (ppm): 2.09, 2.1, 2.11, 4.51, 4.33, 4.44, 5.53, 5.7, 5.99, 6.98, 7.18, 7.27, 7.39, 13.48, 7.26.

PX-A02 (116a). IR (cm^{-1}): 1750.99, 1639.05, 1598.15, 1518.91, 1474.87, 1452.71, 1400.14, 1384.11, 1332.7, 1234.33, 1181.74, 1138.44, 1070.86. ^{13}C (ppm): 170.677, 169.479, 169.293, 164.508, 162.037, 153.785, 152.252, 132.853, 130.688, 123.604, 120.427, 118.626, 107.672, 90.223, 80.892, 73.979, 71.025, 62.966, 20.762, 20.522, 20.447, 77.32, 77.0, 76.687. ^{1}H (ppm): 2.12, 2.13, 2.16, 3.71, 4.19, 4.44, 5.71, 5.9, 6.01, 7.23, 7.46, 7.63, 9.85, 7.26.

PX-B01 (122a). IR (cm^{-1}): 1741.47, 1646.32, 1560.81, 1463.35, 1373.04, 1252.27, 1191.59, 1139.93, 1091.73. ^{13}C (ppm): 170.59, 170.04, 164.31, 162.33, 157.54, 141.72, 138.23, 131.21, 123.49, 114.45, 112.68, 103.8, 78.54, 68.56, 67.09, 66.13, 29.69, 21.09, 20.86, 77.32, 77.0, 76.68. ^{1}H (ppm): 2.05, 2.1, 2.15, 2.67, 3.94, 5.11, 5.66, 5.83, 6.98, 7.18, 7.28, 7.4, 13.56, 7.26.

PX-B02 (123a). IR (cm^{-1}): 1742.37, 1679.91, 1605.18, 1561.43, 1530.79, 1462.33, 1375.66, 1247.0, 1189.43, 1141.13, 1095.64. ^{13}C (ppm): 169.894, 164.861, 162.387, 157.871, 141.811, 138.433, 131.23, 123.42, 114.487, 112.673, 103.831, 77.319, 77.205, 77.0, 76.689, 76.499, 66.609, 63.535, 31.278, 21.024, 20.789. ^{1}H (ppm): 2.04, 2.05, 2.2, 2.87, 3.83, 4.13, 5.15, 5.21, 5.5, 6.98, 7.18, 7.28, 7.4, 13.54, 7.26.

PX-C01 (127c). IR (cm^{-1}): 1732.96, 1685.07, 1633.45, 1531.76, 1466.41, 1352.69, 1247.12, 1202.07, 1141.9. ^{13}C (ppm): not supplied. ^{1}H (ppm): not supplied.

PX-C02 (124f). IR (cm^{-1}): 1725.76, 1595.61, 1543.85, 1466.69, 1452.94, 1426.83, 1348.69, 1285.62, 1267.06, 1238.96, 1190.95, 1145.69, 1118.21, 1079.92. ^{13}C (ppm): not supplied. ^{1}H (ppm): not supplied.

S4.2 Original script-based coding (codes J1–J4)

The original coding of the responses was done by a script, `code_responses.py` (deposited). It reads the *Decisive evidence* field, extracts every numerical observation, discards values stated as expectations ("typically", "would", "expected", ranges of the form a–b), checks each remaining value against the labelled values of the item's panels within tolerance, flags a claimed long-range correlation from the anomeric position to the aglycone, and assigns in order: abstain (the classification is UNDETERMINED); J3 (a cited value has no labelled value within tolerance); J1 (the field cites the observation designated in the key); J2 (other observations); J4 (no checkable observation). For an N-item the J1 test is a cited value

within 5 cm^{-1} of the 1680 cm^{-1} band or within 0.6 ppm of the carbon assigned C-1″; for an O-item it is a pattern match on a statement of absence in the 1660–1699 cm^{-1} region, on the phrase “ring carbonyl”, or on a statement that the spectrum shows a single or no additional carbonyl band, or a cited value within 0.6 ppm of the carbon assigned C-1″; for paired items it is the 1680 cm^{-1} band of the N-isomer, a carbonyl-count statement, or both anomeric carbons.

Properties of this coding that led to its replacement for the counts of the article:

(i) J1 accepts either the infrared feature or an anomeric-carbon value. Eight glycoside responses are J1 without naming the infrared feature (Table S9), among them the five NMR-added responses that cite 90.2 ppm for 116a and disagree with the source label.

(ii) J3 takes precedence over J1, so a response that names the infrared band and also cites a value with no labelled counterpart is J3 (gpt-5 `pairedfull_deoxy` r3).

(iii) The pattern window for O-items, 1660–1699 cm^{-1}, is wider than the 1670–1690 cm^{-1} criterion of the article, and the absence pattern is easier to satisfy than the numerical test for N-items. One response (gpt-5 `singleIR_PX-A02` r2) was coded J1 on the phrase “no additional carbonyl band” although it places that absence at 1710–1730 cm^{-1} and describes the band at 1639 cm^{-1} as an amide carbonyl.

(iv) J4 was assigned to no response, although five fields contain no checkable value (gpt-5 `binary_PX-B01` r1; Gemini `binary_PX-B02` r2; Gemini `pairedfull_ribose` r1–r3); they were coded J2. J2 is therefore a residual category.

(v) The rule that discards ranges was not applied to “~88–89 ppm” (gpt-5 `binary_PX-B01` r3), which was coded J3 at its midpoint.

(vi) The check establishes that a value is among the labelled values, not that it is attributed to the right signal.

The original codes are retained in Table S3 and in the deposit as a record of what was done.

S4.3 Output of the original table script

`make_tables.py` (deposited) reads `coded_all.csv` and prints, for the original coding, the number of responses that agree with the source label and are coded J1:

```
| Pair | System | IR only | Full evidence |
| Ribose (116a/117a) | gpt-5 | 5 / 9 | 0 / 9 |
| Ribose (116a/117a) | Gemini | 9 / 9 | 3 / 9 |
| Ribose (116a/117a), both systems | | 14 / 18 | 3 / 18 |
| 2-Deoxyribose (122a/123a) | gpt-5 | 5 / 9 | 2 / 9 |
| 2-Deoxyribose (122a/123a) | Gemini | 7 / 9 | 5 / 9 |
| 2-Deoxyribose (122a/123a), both systems | | 12 / 18 | 7 / 18 |
| Both pairs --- agreement with thesis assignments only; not an accuracy on
four confirmed keys; not used in the main text | | 26 / 36 | 10 / 36 |
```

In this verbatim output "Full evidence" is the NMR-added condition and "thesis assignments" are the source labels. On the ribose pair this category coincides in every cell with agreement alone (14 of 18 and 3 of 18), so on that pair it carried no information beyond the label. Over all 90 responses it contains 52 (17 ribose, 19 2-deoxy, 16 benzoyl). It is not used in the article.

S4.4 Screenshot transcriptions

Decisive evidence fields transcribed verbatim from the screenshots taken by H.A.A. of the pilot chat sessions of 26 September 2026 (times as recorded in the deposited transcription file: P019 18:11, P020 18:14, P021 18:15 local time, UTC+4; P022 and P023 the same day). The deposited screenshots show P020, P022 and P023 (Figure S1); none shows P019 or P021, and the screenshot taken at 18:11 shows an exchange without a classification (Section S3.3), so the time recorded for P019 does not correspond to a deposited image:

- **P019:** "Spectrum 2 contains a distinct additional absorption at 1679.91 cm^{-1}, consistent with the pyrazolone ring C=O present in Candidate B. Candidate A does not contain this ring carbonyl because the corresponding position is involved in the O-glycosidic/enol-type structure."
- **P020:** "Spectrum 2 contains an additional band at 1679.91 cm^{-1}, consistent with the pyrazolone-ring C=O present in Candidate B. Spectrum 1 lacks this corresponding carbonyl feature."
- **P021:** "The clearest distinction is in the heterocyclic carbonyl/conjugated-region pattern. Spectrum 2 shows a distinct band at ~1679 cm^{-1} in addition to the ester C=O at ~1742 cm^{-1}, whereas Spectrum 1 is dominated by the ~1741 cm^{-1} ester carbonyl and has a different pattern around ~1646–1561 cm^{-1}."
- **P022:** "The strongest distinction is in the ~1600–1500 cm^{-1} region. Spectrum 1 shows bands at about 1598 and 1519 cm^{-1}, whereas Spectrum 2 shows a distinctly different pattern at about 1604, 1560, and 1535 cm^{-1}. This region is sensitive to the different pyrazolone-ring conjugation produced by N- versus O-glycosylation."
- **P023:** "There is no uniquely diagnostic IR feature that can unambiguously distinguish the N-glycosylated Candidate A from the O-glycosylated Candidate B. Both spectra show a strong ester C=O band near 1750 cm^{-1} and multiple bands in the ~1680–1500 cm^{-1} region."

S4.5 Agreement between the contemporaneous codes of H.A.A. and the original script

Of the 144 responses coded by the script (90 API, 54 pilot), 68 carry a code assigned by H.A.A. during data collection, before the script was written: the 36 API responses of batch 1 and 32 pilot responses. None of the 54 API responses of batch 2 has such a code. Agreement was 62 of 68 (Cohen's $\kappa = 0.86$; observed agreement 0.912, chance agreement 0.346; Cohen 1960, Educ Psychol Meas 20:37–46). Marginals — H.A.A.: J1 30, J2 24, abstain 10, J3 4; script: J1 35, J2 18, abstain 10, J3 5. On the 36 API responses alone, agreement was 31 of 36 ($\kappa = 0.75$), and all five disagreements run the same way.

The six disagreements are listed in Table S8.

Table S8. The six disagreements.

Response	Item	H.A.A.	Script	Reason
gpt-5, `binary_PX-A02`, r1	single, NMR added	J2	J1	cites 90.2 ppm and reads it as an N-glycoside
gpt-5, `binary_PX-A02`, r3	single, NMR added	J2	J1	as above
Gemini, `binary_PX-A02`, r1	single, NMR added	J2	J1	as above
Gemini, `binary_PX-A02`, r2	single, NMR added	J2	J1	as above
Gemini, `binary_PX-A02`, r3	single, NMR added	J2	J1	as above
B011 (pilot)	single, NMR added, PX-B01	J2	J3	157.54 ppm read as 167.54 ppm

This compares one coder with a script written by the same coder after reading the same responses; it is a consistency check and not inter-rater reliability.

S4.6 Separate coding of agreement, infrared feature and anomeric-carbon citation, and the field check

For the article the 72 glycoside responses were coded again from the verbatim fields of Table S4 (the first coding; Section 2.4 of the article), with four records kept apart. The coding is also supplied in machine-readable form as Supporting File 2 (`ir_feature_coding.csv`, one row per response, with the verbatim field; for the 36 NMR-added responses the columns `aryl_C2_given_as_anomeric`, `aryl_C2_basis_sentence` and `aryl_C2_basis_where` record the reading of Section S12).

Agreement is taken from Table S3.

Infrared feature. The field names the designated feature if it (P) cites a band within 5 cm^{-1} of 1680.47 or 1679.91 cm^{-1} as present in the spectrum of the compound that shows it; or (A) states that carbonyl absorption is absent from a range that includes 1670–1690 cm^{-1}, or that the compound has no ring or lactam carbonyl band; or (C) states that the spectrum has a single, ester-only carbonyl absorption. In Table S9 these appear as “band cited”, “absence stated” and “single-carbonyl count”. A statement that asserts a second, non-ester carbonyl elsewhere (for example at 1639 or 1646 cm^{-1}) does not count as A or C.

Anomeric carbon. T, the field cites the carbon assigned C-1″ in the source as the anomeric carbon; F, it cites the aryl carbon near 104 ppm as the anomeric carbon; f, it cites 103.80 ppm without calling it anomeric in the field; U, it names the anomeric carbon without a value; X, the value cited has no labelled value within tolerance. In Table S9 these appear as “C-1″ value”, “aryl ∼104 as anomeric”, “103.80 cited, not called anomeric”, “named, no value” and “no labelled value”; a paired response may carry one entry for each compound.

Note and field check. For every response the note records what the field cites, and the column *Check* records the result of comparing every value cited in the field with the value table of the compound concerned (Section S4.1: peak labels of the infrared and ^{13}C panels and the ^{1}H list of the source; tolerances 5 cm^{-1}, 0.6 ppm, 0.1 ppm; the two-dimensional panels have no value table). The entries are: “ok”, every value cited has a counterpart and the anomeric carbon or proton, where one is given with a value, is the signal so assigned;

"no value", the field cites no numerical value; "flag: signal", the value given for the anomeric carbon or the anomeric proton belongs to another signal; "flag: no labelled value", a cited value has no counterpart within tolerance. The anomeric carbon is the one assigned C-1″ in the source; the signal near 104 ppm is assigned to the aryl ring here (Table S15). The identity of other signals is not checked: for the infrared bands and the low-field proton the recorded data do not establish one. Two further entries are consistency notes and not value flags; the values of these fields all have counterparts: "note: contradiction", the field contains a statement that contradicts another statement of the field or the answer given; "note: range", the absent carbonyl band is placed in a range that does not contain 1670–1690 cm^{-1} (the statement itself is true of the spectrum). The check was applied to all 72 responses, whether or not they agree with the source label; it is of the field only and is not a judgement of the validity of the reasoning. The three single-case Gemini responses on 122a cite 103.80 ppm without saying what the signal is; they are entered as "ok" here, and the reading of that value as the anomeric carbon, which is in their *Reasoning* field, is recorded in Tables S5 and S24. The value table is that of the source figure: for 123a it contains sugar-carbon labels (66.61 and 63.54 ppm) that the supplied crop does not display (Section S13), and no field cites them.

Of the 72 fields, 7 cite no value, 52 pass the value check and 13 are flagged: 11 for a value given for the anomeric carbon or proton that belongs to another signal, and 2 for a value with no counterpart. Three of the flagged fields belong to responses that agree with the source label (all on the 2-deoxy pair) and ten to responses that do not. Five of the fields that pass the value check carry a consistency note (4 contradiction, 1 range); three of them belong to agreeing responses. By pair and evidence (18 responses each; passing, no value, flagged): ribose pair, infrared only: 17, 1, 0; ribose pair, NMR added: 8, 4, 6; 2-deoxy pair, infrared only: 18, 0, 0; 2-deoxy pair, NMR added: 9, 2, 7. Ten of the fields flagged for the anomeric signal give the aryl carbon near 104 ppm as the anomeric carbon; the eleventh (Gemini `pairedfull_deoxy` r3) gives 6.96 ppm, an aromatic proton, as the anomeric proton of 123a.

The first coding was done by H.A.A. from the verbatim fields, starting from a first-pass classification prepared with an AI assistant (Section 2.6 of the article). A second coding was requested for two of its judgements, the naming of the infrared feature and the question of Section S12. It was obtained for the second of them, from one coder, and not for the first (Section S14); the field check was not part of it. The rule for the infrared feature is given in executable form at the end of this section. Its differences from the original coding are these. Eight responses are J1 without naming the infrared feature: gpt-5 `binary_PX-A02` r1 and r3, Gemini `binary_PX-A02` r1–r3, Gemini `binary_PX-A01` r2 and r3, and gpt-5 `singleIR_PX-A02` r2. Two responses name the infrared feature without being J1: gpt-5 `singleIR_PX-A01` r2 (an abstention) and gpt-5 `pairedfull_deoxy` r3 (J3).

Table S9. Classification of the 72 glycoside responses. Verbatim fields in Table S4.

Condition	System	Rep.	Answer	Agreement	Infrared feature	Anomeric carbon	Orig. code	Check	Note
paired_ribose	gpt-5	r1	B / A	agrees	band cited; absence stated	—	J1	ok	1680 band in Spectrum 2, absent in Spectrum 1
paired_ribose	gpt-5	r2	B / A	agrees	band cited; absence stated	—	J1	ok	1680 band in Spectrum 2, absent in Spectrum 1

Condition	System	Rep.	Answer	Agreement	Infrared feature	Anomeric carbon	Orig. code	Check	Note
paired_ribose	gpt-5	r3	A / B	disagrees	—	—	J2	ok	cites 1278 and 1230 (bands of 117a) as aryl–O stretches of an O-glycoside; 1680 not mentioned
paired_deoxy	gpt-5	r1	A / B	agrees	band cited	—	J1	ok	1679 band in Spectrum 2
paired_deoxy	gpt-5	r2	A / B	agrees	band cited	—	J1	ok	second C=O at 1679 in Spectrum 2
paired_deoxy	gpt-5	r3	A / B	agrees	band cited; absence stated	—	J1	ok	1680 band in Spectrum 2; Spectrum 1 lacks it, 1646 read as C=N/C=C
binary_PX-A01	gpt-5	r1	B	disagrees	—	aryl ~104 as anomeric	J2	flag: signal	104.09 (aryl C-2′) taken as the anomeric carbon
binary_PX-A01	gpt-5	r2	B	disagrees	—	aryl ~104 as anomeric	J2	flag: signal	104.09 (aryl C-2′) taken as the anomeric carbon; 84.39 not mentioned
binary_PX-A01	gpt-5	r3	B	disagrees	—	aryl ~104 as anomeric	J2	flag: signal	104.09 (aryl C-2′) taken as the anomeric carbon
binary_PX-A02	gpt-5	r1	A	disagrees	—	C-1″ value	J1	ok	90.2 (C-1″) read as N-glycosidic
binary_PX-A02	gpt-5	r2	UNDET.	abstains	—	—	abstain	no value	abstains: no HMBC connectivity to the aglycone
binary_PX-A02	gpt-5	r3	A	disagrees	—	C-1″ value	J1	ok	90.2 (C-1″) read as N-glycosidic
binary_PX-B01	gpt-5	r1	B	disagrees	—	—	J2	no value	asserts an extra lactam carbonyl band and carbonyl carbon; no value
binary_PX-B01	gpt-5	r2	B	disagrees	—	C-1″ value	J2	ok	13.6 ppm proton called a heteroaromatic OH; 78.5 (listed as C-1″) as support
binary_PX-B01	gpt-5	r3	B	disagrees	—	no labelled value	J3	flag: no labelled value	88–89 ppm, attributed to the HSQC panel, has no labelled value; ^{1}H ~6.0 also outside tolerance (nearest 5.83)
binary_PX-B02	gpt-5	r1	A	disagrees	—	aryl ~104 as anomeric	J2	flag: signal	103.9 (aryl C-2′) taken as the anomeric carbon
binary_PX-B02	gpt-5	r2	A	disagrees	—	aryl ~104 as anomeric	J2	flag: signal	103.8 (aryl C-2′) taken as the anomeric carbon
binary_PX-B02	gpt-5	r3	A	disagrees	—	aryl ~104 as anomeric	J2	flag: signal	103.8 (aryl C-2′) taken as the anomeric carbon; H-1″ 5.5
paired_ribose	Gemini	r1	B / A	agrees	band cited; absence stated	—	J1	ok	1680 band in Spectrum 2, absent in Spectrum 1
paired_ribose	Gemini	r2	B / A	agrees	band cited	—	J1	ok	1680 band in Spectrum 2
paired_ribose	Gemini	r3	B / A	agrees	band cited	—	J1	ok	1680.47 band in Spectrum 2
paired_deoxy	Gemini	r1	A / B	agrees	band cited; absence stated	—	J1	ok	1679.91 band in Spectrum 2, absent in Spectrum 1
paired_deoxy	Gemini	r2	A / B	agrees	band cited	—	J1	ok	1680 band in Spectrum 2
paired_deoxy	Gemini	r3	A / B	agrees	band cited; absence stated	—	J1	ok	1679.91 band in Spectrum 2, absent in Spectrum 1
binary_PX-A01	Gemini	r1	A	agrees	band cited	C-1″ value	J1	ok	84.39 (C-1″) and the 1680 band
binary_PX-A01	Gemini	r2	A	agrees	—	C-1″ value	J1	ok	84.39 (C-1″) only
binary_PX-A01	Gemini	r3	A	agrees	—	C-1″ value	J1	ok	84.39 (C-1″), read from the annotated gHMBC panel
binary_PX-A02	Gemini	r1	A	disagrees	—	C-1″ value	J1	ok	90.2 (C-1″); value only in the field
binary_PX-A02	Gemini	r2	A	disagrees	—	C-1″ value	J1	ok	90.2 (C-1″); value only in the field
binary_PX-A02	Gemini	r3	A	disagrees	—	C-1″ value	J1	ok	90.2 (C-1″); value only in the field
binary_PX-B01	Gemini	r1	A	agrees	—	103.80 cited, not called anomeric	J2	ok	103.80 (aryl C-2′) cited alone; read as the anomeric carbon in the Reasoning field
binary_PX-B01	Gemini	r2	A	agrees	—	103.80 cited, not called anomeric	J2	ok	103.80 (aryl C-2′) cited alone; read as the anomeric carbon in the Reasoning field
binary_PX-B01	Gemini	r3	A	agrees	—	103.80 cited, not called anomeric	J2	ok	103.80 (aryl C-2′) cited alone; read as the anomeric carbon in the Reasoning field
binary_PX-B02	Gemini	r1	B	agrees	band cited	named, no value	J1	ok	1680 band as ring C=O; no ^{13}C signal above 100 ppm for an O-glycosidic anomeric carbon
binary_PX-B02	Gemini	r2	A	disagrees	—	named, no value	J2	no value	anomeric-carbon shift named, no value
binary_PX-B02	Gemini	r3	B	agrees	band cited	—	J1	ok	N–H at 13.5 ppm and the 1679 band
singleIR_PX-A01	gpt-5	r1	B	disagrees	band cited	—	J1	note:	1680 band cited as the only non-ester

Condition	System	Rep.	Answer	Agreement	Infrared feature	Anomeric carbon	Orig. code	Check	Note
								contradiction	C=O; candidate without ring carbonyl chosen
singleIR_PX-A01	gpt-5	r2	UNDET.	abstains	band cited	—	abstain	ok	abstains; 1680 band named but said to be expected for both candidates
singleIR_PX-A01	gpt-5	r3	UNDET.	abstains	—	—	abstain	no value	abstains; no feature named
singleIR_PX-A02	gpt-5	r1	B	agrees	single-carbonyl count	—	J1	note: range	single C=O at 1751; absent second band placed at 1690–1715
singleIR_PX-A02	gpt-5	r2	B	agrees	—	—	J1	note: contradiction	1639 band called an amide C=O; absence placed at 1710–1730; answer B contradicts the stated carbonyl
singleIR_PX-A02	gpt-5	r3	B	agrees	single-carbonyl count; absence stated	—	J1	ok	single C=O; none at 1650–1700
singleIR_PX-B01	gpt-5	r1	B	disagrees	—	—	J2	ok	1646 band read as amide C=O, 1561 as amide II
singleIR_PX-B01	gpt-5	r2	UNDET.	abstains	—	—	abstain	ok	abstains; 1646 band “amide/C=N”
singleIR_PX-B01	gpt-5	r3	B	disagrees	—	—	J2	ok	two carbonyl regions, 1741 and 1646
singleIR_PX-B02	gpt-5	r1	B	agrees	band cited	—	J1	ok	1680 band as second C=O
singleIR_PX-B02	gpt-5	r2	A	disagrees	band cited	—	J1	note: contradiction	1679 band cited as the only non-ester C=O; candidate without ring carbonyl chosen
singleIR_PX-B02	gpt-5	r3	B	agrees	band cited	—	J1	ok	1680 band as second C=O
pairedfull_ribose	gpt-5	r1	A / B	disagrees	—	C-1″ value (Cpd 1) and aryl ~104 (Cpd 2)	J2	flag: signal	Cpd 1: ~90 (C-1″ of 116a) read as N; Cpd 2: ~104 (aryl C-2′ of 117a) read as O
pairedfull_ribose	gpt-5	r2	A / B	disagrees	—	C-1″ value (Cpd 1) and aryl ~104 (Cpd 2)	J2	flag: signal	Cpd 1: 90.2 (C-1″ of 116a) read as N; Cpd 2: 104.1 (aryl C-2′ of 117a) read as O
pairedfull_ribose	gpt-5	r3	A / B	disagrees	—	C-1″ value (Cpd 1) and aryl ~104 (Cpd 2)	J2	flag: signal	Cpd 1: ~90 (C-1″ of 116a) read as N; Cpd 2: ~104 (aryl C-2′ of 117a) read as O
pairedfull_deoxy	gpt-5	r1	A / B	agrees	band cited	—	J1	note: contradiction	1679 band in Cpd 2; a ring C=O also asserted for Cpd 1 at 1646
pairedfull_deoxy	gpt-5	r2	A / B	agrees	band cited	aryl ~104 as anomeric	J1	flag: signal	103.8 (aryl C-2′ of 122a) taken as C-1″; says Cpd 2 lacks a carbon near 104 although 103.83 is labelled; 1679 band as support
pairedfull_deoxy	gpt-5	r3	A / B	agrees	band cited; absence stated	—	J3	flag: no labelled value	1679 band in Cpd 2, absent in Cpd 1; 168.5 ppm has no labelled value (nearest 169.89, acetate)
singleIR_PX-A01	Gemini	r1	A	agrees	band cited	—	J1	ok	1680.47 band
singleIR_PX-A01	Gemini	r2	A	agrees	band cited	—	J1	ok	1680.47 band
singleIR_PX-A01	Gemini	r3	A	agrees	band cited	—	J1	ok	1680.47 band
singleIR_PX-A02	Gemini	r1	B	agrees	absence stated	—	J1	ok	no carbonyl band at 1650–1700
singleIR_PX-A02	Gemini	r2	B	agrees	absence stated	—	J1	ok	no ring (lactam) carbonyl band at 1650–1700
singleIR_PX-A02	Gemini	r3	B	agrees	absence stated; single-carbonyl count	—	J1	ok	no second carbonyl band at 1650–1700; single band at 1751
singleIR_PX-B01	Gemini	r1	A	agrees	single-carbonyl count; absence stated	—	J1	ok	one carbonyl region (1741); no lactam/ketone band
singleIR_PX-B01	Gemini	r2	B	disagrees	—	—	J2	ok	1646 band cited
singleIR_PX-B01	Gemini	r3	B	disagrees	—	—	J2	ok	1646 band cited
singleIR_PX-B02	Gemini	r1	B	agrees	band cited	—	J1	ok	1679.91 band
singleIR_PX-B02	Gemini	r2	B	agrees	band cited	—	J1	ok	1679.91 band
singleIR_PX-B02	Gemini	r3	B	agrees	band cited	—	J1	ok	1679.91 band
pairedfull_ribose	Gemini	r1	A / B	disagrees	—	named, no value	J2	no value	anomeric-carbon shift named, no value
pairedfull_ribose	Gemini	r2	A / B	disagrees	—	named, no value	J2	no value	anomeric-carbon shift named, no value
pairedfull_ribose	Gemini	r3	A / B	disagrees	—	named, no value	J2	no value	anomeric-carbon shift named, no value
pairedfull_deoxy	Gemini	r1	A / B	agrees	band cited	named, no value	J1	ok	1680 band in Cpd 2 and anomeric-

Condition	System	Rep.	Answer	Agreement	Infrared feature	Anomeric carbon	Orig. code	Check	Note
									carbon shifts, no value
pairedfull_deoxy	Gemini	r2	A / B	agrees	band cited; absence stated	—	J1	ok	1679.91 band in Cpd 2, absent in Cpd 1
pairedfull_deoxy	Gemini	r3	A / B	agrees	band cited	—	J1	flag: signal	1680 band in Cpd 2; 6.96 ppm (an aromatic proton; labelled 6.98) called the anomeric proton

Table S10. Counts from Table S9 by pair, evidence, presentation and system: responses naming the infrared feature, with the number of those that also agree with the source label in brackets. The last two columns give the number of responses that name the feature, agree, and are entered as "ok" in the *Check* column. One of the single-case infrared-only gpt-5 responses counted as naming the feature on the ribose pair is an abstention whose field begins "None" and cites the band as expected for both candidates; without it the ribose infrared-only counts are 3/6 for gpt-5 single-case and 9/12 and 14/18 overall.

Pair	Evidence	Paired, gpt-5	Paired, Gemini	Single case, gpt-5	Single case, Gemini	Paired, both	Single case, both	Agreeing, paired	Agreeing, single case	Named, agreeing, check "ok": paired	Named, agreeing, check "ok": single case
Ribose	Infrared only	2/3 [2]	3/3 [3]	4/6 [2]	6/6 [6]	5/6 [5]	10/12 [8]	5/6	9/12	5/6	7/12
Ribose	NMR added	0/3 [0]	0/3 [0]	0/6 [0]	1/6 [1]	0/6 [0]	1/12 [1]	0/6	3/12	0/6	1/12
2-Deoxyribose	Infrared only	3/3 [3]	3/3 [3]	3/6 [2]	4/6 [4]	6/6 [6]	7/12 [6]	6/6	6/12	6/6	6/12
2-Deoxyribose	NMR added	3/3 [3]	3/3 [3]	0/6 [0]	2/6 [2]	6/6 [6]	2/12 [2]	6/6	5/12	2/6	2/12

Among the ribose responses that agree with the source label: of the 14 infrared-only responses, 13 name the infrared feature; the fourteenth (gpt-5 `singleIR_PX-A02` r2) describes the 1639 cm^{-1} band as an amide carbonyl and answers B; and one of the 13 (gpt-5 `singleIR_PX-A02` r1) states a single carbonyl band but places the absent second band at 1690–1715 cm^{-1}. The three NMR-added responses that agree (Gemini `binary_PX-A01` r1–r3) cite 84.39 ppm, the carbon assigned C-1″; r1 also names the 1680 cm^{-1} band, and r1 and r3 state that the gHMBC panel assigns this signal to C-1″.

The rule for the infrared feature as a script. The listing below is the function that assigns the codes P, A and C to a *Decisive evidence* field. Applied to the 72 fields of Table S4 it returns "named" or "not named" as in Table S9 for all 72. Only this binary outcome is reproduced: the sub-codes returned by the function differ from the entries of Table S9 in six fields. The function was written after the first coding and adjusted until it reproduced that coding, so it documents the rule and lets any reader re-apply it, and it is not an independent validation. It is supplied as Supporting File 3 (`code_ir_feature.py`). The function implements the rule for the infrared feature and nothing else: it does not check the flags of the field check, the identity of the aryl carbon, the counts of Table 3 of the article or any chemical argument. The counts of the article and of Table S10 are recomputed from the coding file by a second script, Supporting File 4 (`summarise_coding.py`), which tabulates the codes and does not derive them. It marks two fields for reading (a range that does not contain 1670–1690 cm^{-1}; a band cited but not used to discriminate), which are the fields of gpt-5 `singleIR_PX-A02` r1 and `singleIR_PX-A01` r2 discussed above.

```
import re

def numbers(s):
    """All numbers of the text except those followed by Hz or MHz."""
    return [float(x) for x in
re.findall(r"(?<![\d.])(\d{2,4}(?:\.\d+)?)(?![\d.]*\s*(?:Hz|MHz))", s)]

def ir_named(field):
    """Return (code, note). code is '0' (not named) or a '+'-joined set of
       P  a band within 5 cm-1 of 1680.47 / 1679.91 cm-1 is cited (not as a
range limit)
       A  carbonyl absorption is stated to be absent from a range that
includes
          1670-1690 cm-1, or the compound is said to have no ring/lactam
carbonyl
       C  a single (ester-only) carbonyl absorption is stated
    A and C are withdrawn if the field asserts another carbonyl at 1620-1659
cm-1."""
    s = field.replace("−", "-").replace("–", "-").replace("⁻¹", "-1")
    low = s.lower()
    codes, note = [], ""
    ranges = [(float(a), float(b)) for a, b in
              re.findall(r"(1[5-7]\d\d(?:\.\d+)?)\s*(?:-|to)\s*(1[5-
7]\d\d(?:\.\d+)?)", s)]
    range_limits = {v for r in ranges for v in r}
    band = [v for v in numbers(s) if 1674.9 <= v <= 1685.5 and v not in
range_limits]
    if band:
        codes.append("P")
    no_ranges = re.sub(r"1[5-7]\d\d(?:\.\d+)?\s*(?:-|to)\s*1[5-
7]\d\d(?:\.\d+)?", " RANGE ", low)
    other_carbonyl = re.search(r"(16[2-
5]\d)[^.;]{0,40}(amide|carbonyl|c=o|lactam)|"
                               r"(amide|carbonyl|c=o|lactam)[^.;]{0,40}(16[2-
5]\d)", no_ranges)
    if re.search(r"\b(no|not|absen\w*|lack\w*|without|missing)\b", low):
        if any(a <= 1670 and b >= 1690 for a, b in ranges) and
re.search(r"carbonyl|c=o|band|absorption|amide|lactam", low):
            codes.append("A")
        elif re.search(r"(no|absence
of|lacks?|without)[^.;]{0,60}(ring|lactam|cyclic|pyrazolone)[^.;]{0,30}(carbo
nyl|c=o)", low):
            codes.append("A")
        elif
re.search(r"(absent|lack\w*|missing)[^.;]{0,25}(in|from)\s+(spectrum|compound
|cpd)", low) and band:
            codes.append("A")
    if re.search(r"(single|only one|one distinct|only a
single)[^.;]{0,40}(carbonyl|c=o)", low):
        codes.append("C")
```

```
    if other_carbonyl and not band:
        if codes:
            note = "asserts a carbonyl near 1620-1659: read the field"
        codes = [c for c in codes if c == "P"]
    if ranges and not any(a <= 1670 and b >= 1690 for a, b in ranges) and
("C" in codes or "A" in codes):
        note = "a range is stated that does not contain 1670-1690: read the
field"
    if band and re.search(r"expected for both|both candidates|consistent with
both", low):
        note = "band cited but not used to discriminate: read the field"
    return ("+".join(dict.fromkeys(codes)) if codes else "0"), note
```

S4.7 Effect of the tolerances

The counts of Table S10 do not depend on the infrared tolerance between 1 and 25 cm^{-1}: every band cited as the feature lies within 1 cm^{-1} of 1680.47 or 1679.91 cm^{-1} (cited as 1679, 1679.91, 1680 or 1680.47), and no other labelled band of the four glycosides lies within 25 cm^{-1} of them (the nearest are at 1646.32 and 1741.47 cm^{-1}). The anomeric-carbon classification of Table S5 is unchanged for ^{13}C tolerances between 0.25 and 1.0 ppm: cited values are 84.39, 90.2, "~90", 104.09–104.1, "~104", 103.8–103.9 and 78.5 ppm against labelled values of 84.39, 90.22, 104.09, 103.80, 103.83 and 78.54 ppm, and the nearest other labelled lines are more than 1.1 ppm away, with one exception: a cited "77.2" could not be distinguished from the $CDCl_3$ line at 77.32 ppm at any of these tolerances, and no response cited it. At the ^{1}H tolerance of 0.1 ppm the value "~6.0 ppm" given for the anomeric proton of PX-B01 by gpt-5 `binary_PX-B01` r3 has no labelled counterpart (nearest 5.83 ppm); that response is already recorded as citing a ^{13}C value with no labelled counterpart. A recomputation of the field check gives the same 13 flags at tolerances between 3.5 and 25 cm^{-1} and between 0.25 and 1.0 ppm; below 3.5 cm^{-1} one further field is flagged (gpt-5 `paired_ribose` r3, which gives "1275 cm^{-1}" for the band labelled at 1278.44 cm^{-1}). The sensitivity analyses of the article name their rows as follows: the 16 flags obtained when the reading of the *Reasoning* field is applied add the three fields of Gemini `binary_PX-B01` r1–r3; the stricter reading of the infrared naming removes gpt-5 `pairedfull_deoxy` r1 and r2; and the count of 19 of 30 leaves out the four responses that discuss no anomeric carbon and Gemini `binary_PX-B02` r3, which states that the anomeric carbon cannot be observed.

S5 Probe for retrievable thesis-specific facts

Three questions were put to each service in a fresh temporary chat with no uploaded material on 27 September 2026 at 14:37–14:41 local time (UTC+4; 10:37–10:41 UTC), that is, after the chat-interface pilot and before the API runs, which began at 12:19 UTC the same day. The times are those shown on the screenshots. Each question was asked first with the interface's default behaviour (for ChatGPT, web retrieval on) and then with the appended instruction "Answer only from what you already know. Do not search the web. If you do not know, say so." Screenshots are deposited under `screenshots/method4/`

(ChatGPT, six sessions; Gemini with the memory-only instruction, three sessions). Nine of the twelve responses are retained and transcribed below; citation chips are marked [source chip: …]. The three Gemini default-mode responses were not retained. A note made by H.A.A. at the time records that Gemini returned, for question 1, a table of yields and isomer ratios with no source; that note cannot be verified from the retained material and is not used.

Q1. In the glycosylation of 4-arylhydrazono-5-(trifluoromethyl)-2,4-dihydro-3H-pyrazol-3-one with protected ribofuranose donors, what regiochemical outcomes are reported for TMSOTf versus SnCl4 catalysis? Name any specific compounds, yields or isomer ratios you are aware of.

Q2. Has anyone reported both the O-riboside and the N-riboside regioisomers of a 4-(3-fluorophenylhydrazono)-5-(trifluoromethyl)pyrazol-3-one? If so, give the source, the compound numbering used, and the isolated yields.

Q3. What is the molecular ion and the anomeric carbon chemical shift reported for 2,3,5-tri-O-acetyl-beta-D-ribofuranosyl derivatives of trifluoromethyl pyrazolones?

S5.1 ChatGPT, default mode (web retrieval on)

Q1 (screenshot 2.37.10 PM). The literature I can verify reports a strong **N2-regioselectivity under $SnCl_4$-promoted Vorbrüggen conditions**. For silylated 4-(arylhydrazono)-5-(trifluoromethyl)pyrazol-3-ones **4–7** reacted with 1-O-acetyl-2,3,5-tri-O-benzoyl-β-D-ribofuranose **17**, $SnCl_4/CH_2Cl_2$ gives the corresponding **N2-linked β-D-ribofuranosides 18–21**. The N2 assignment was supported by the unusually downfield H-1′ signals at δ 6.24–6.28 and later HMBC data. [source chip: ResearchGate +1] Specific examples include **19 (70%)**, **20 (72%)**, and **21 (75%)**; after debenzoylation, the free N2 nucleosides **8–11** were obtained in roughly **89–90%** yield. With the protected 5′-deoxyribose donor **22**, the same regiochemistry was reported: protected N2 products **23–26**, including **23, 78%; 24, 72%; 25, 92%; 26, 73%**. [source chip: ResearchGate] I **cannot substantiate a corresponding TMSOTf experiment on this exact 4-arylhydrazono/CF_3-pyrazolone series** from the primary/review literature I located. In particular, the 2019 paper uses $SnCl_4$ for these ribosylations, not TMSOTf. So I would be cautious about the sometimes-repeated claim that "TMSOTf gives the alternative N1 isomer whereas $SnCl_4$ gives N2": I haven't found a primary source supporting that comparison for this exact substrate class. The earlier 2004 work likewise used $SnCl_4$ and obtained N2 glycosides—for example the protected β-D-glucoside **3a in 78%**. [source chip: PubMed Central +1] If you have a particular paper, scheme, thesis, or compound number in mind for the **TMSOTf case**, send it over; I can reconcile its N1/N2 assignment with the $SnCl_4$ series.

Q2 (2.37.26 PM). Yes. The reported parent scaffold is **4-(3′-fluorophenylhydrazono)-5-trifluoromethyl-2,4-dihydropyrazol-3-one**, designated **2c**, but the literature I could verify reports its **N-glycoside with glucose**, not both O- and N-riboside regioisomers. The 2004 paper by Abdou, Saleh, and Zohdi gives 2c in 78% yield and its protected β-D-glucopyranosyl **N-glycoside 3c** in **68% isolated yield**. [source chip: PubMed Central +1] I **could not verify a publication reporting both the O-riboside and N-riboside of the 3-**

fluorophenyl compound. The closest ribose paper I found is Ahmed *et al.*, *Nucleosides, Nucleotides & Nucleic Acids* **2019**, 38, 590–603, DOI 10.1080/15257770.2019.1591445, which prepares ribofuranosides of related 4-arylhydrazono-5-trifluoromethylpyrazolones, but its reported aryl series is nitrophenyl, trifluoromethylphenyl, and p-tolyl rather than 3-fluorophenyl. [source chip: PubMed +1] So, based on the searchable primary literature: **no confirmed report of both O- and N-riboside regioisomers for that exact 3-fluorophenyl scaffold**. If you have a structure/database hit suggesting otherwise, send me the CAS, SMILES, or reference and I can trace the specific O/N pair.

Q3 (2.37.21 PM). For the reported 2-(2′,3′,5′-tri-O-acetyl-β-D-ribofuranosyl) trifluoromethyl pyrazolone derivative—specifically the p-tolylazo compound—the characterization data are: **Molecular ion (MS): m/z 528**. **Anomeric carbon C-1′ (^{13}C NMR, $CDCl_3$): δ 84.4 ppm**. For context, the corresponding anomeric proton H-1′ appears at **δ 6.03 ppm** (d, J = 4.2 Hz). [source chip: ResearchGate] A related **3-nitrophenylazo derivative** reports essentially the same anomeric-carbon position, **C-1′ = δ 84.44 ppm**. [source chip: ResearchGate] So, if you're looking for the characteristic values for these **tri-O-acetyl β-D-ribofuranosyl trifluoromethyl pyrazolones**, the concise answer is **M^+ = m/z 528 and C-1′ ≈ δ 84.4 ppm** for the p-tolylazo derivative.

S5.2 ChatGPT, memory-only instruction

Q1 (2.40.53 PM). I don't know the specific literature result well enough to answer reliably from memory. In particular, I can't confidently state the **N1/N2 (or possible O-) glycosylation regiochemistry under TMSOTf versus $SnCl_4$**, nor give trustworthy compound numbers, isolated yields, or isomer ratios for protected ribofuranose donors. I'd rather not invent those details.

Q2 (2.41.00 PM). I do not know. I can't reliably identify from memory a source reporting both the **O-riboside** and **N-riboside** regioisomers of 4-(3-fluorophenylhydrazono)-5-(trifluoromethyl)pyrazol-3-one, including their compound numbers and isolated yields, without searching the literature.

Q3 (2.41.06 PM). I don't know the specific reported molecular ion (m/z) and anomeric carbon (^{13}C NMR) chemical shift for those 2,3,5-tri-O-acetyl-β-D-ribofuranosyl trifluoromethyl pyrazolone derivatives from memory.

S5.3 Gemini, memory-only instruction

Q1 (2.37.47 PM). I do not have specific, reliable data in my knowledge base regarding the exact regiochemical outcomes, yields, or isomer ratios for TMSOTf versus $SnCl_4$ catalysis in the glycosylation of 4-arylhydrazono-5-(trifluoromethyl)-2,4-dihydro-3H-pyrazol-3-one with protected ribofuranose donors.

Q2 (2.37.42 PM). I do not know the answer to this specific literature question from my current internal knowledge.

Q3 (2.37.36 PM). I do not have access to specific NMR and mass spectrometry experimental data for those particular 2,3,5-tri-O-acetyl-β-D-ribofuranosyl derivatives of trifluoromethyl pyrazolones in my knowledge base.

S5.4 Reading

With retrieval, ChatGPT returned published analogues (Ahmed et al. 2019; Haikal et al. 2003; Abdou et al. 2004) and stated that it could not verify a report of both O- and N-ribosides of the 3-fluorophenyl compound; the anomeric carbon it retrieved for the *p*-tolyl analogue (84.4 ppm) coincides with that of 117a in this study. With the memory-only instruction all six retained responses stated that the model did not know. No thesis-specific information (compound numbering, the conditions or yields of the eleven experiments, or the riboside pair itself) was elicited in any retained response. This does not show that the thesis was absent from training data, or that the information could not be elicited by other questions; and the probe used the chat interfaces, which need not serve the model versions evaluated through the APIs.

S6 The reaction records of the source

S6.1 Audit of the source values (reaction records and spectra)

The points are listed in Table S11.

Table S11. Points noted on digitisation and re-examination, and their treatment.

#	Observation	Treatment
A1	Entries 2–10 of the source table report O and N values summing to exactly 100, whereas entries 1 and 11 sum to 67 and 80; the footnote calls all values isolated yields.	Nine consecutive pairs of values summing to exactly 100% are implausible as isolated yields; entries 2–10 are treated as product composition. N/(O + N) is the same for either reading but does not make the two kinds of record comparable.
A2	Entry 5: narrative 38% N, table 39% N.	Tabulated value used; sensitivity in Section S6.4.
A3	Entry 1 (N) and entry 11 (O) recorded as not detected.	Encoded as zero; both entries are flagged wherever they carry a result.
A4	Compound 122c: anomeric carbon recorded at 91.8 ppm against 78.5 and 78.6 ppm for the other compounds assigned as O-deoxyribosides. Its other listed sugar carbons (76.5, 66.5, 63.5 and 31.2 ppm) lie within 0.3 ppm of the cross-peak positions read from the HSQC figure printed for 122a (76.3, 66.5 and 66.7, 63.3 and 31.1 ppm; Section S15), whereas 122b is listed with 78.6, 68.6, 67.1, 66.2 and 29.7 ppm.	Not used in the evaluation; noted as the only recorded value of this series in the range of 116a.
A5	127c: the list gives IR 1725 and 1660 cm^{-1}; the two-panel figure from which the stimulus was cut is labelled 1732.96 and 1685.07 cm^{-1}, and a second, full-range spectrum printed for 127c is labelled 1725.92 and 1660.40 cm^{-1}, so two different spectra are printed for this compound; the labels of the full-range spectrum otherwise nearly reproduce those of the panel of 124f (1725.76, 1595.61, 1543.85, 1426.83, 1348.69 cm^{-1}). 124f: stated formula $C_{17}H_{12}F_3N_5O_4$ (*m/z* 407) does not match the formula required for a benzoyl derivative of a nitrophenylhydrazono base, $C_{17}H_{10}F_3N_5O_4$ (exact mass	Used only for the supplementary task of Section S3.5.

#	Observation	Treatment
	405.068; the stated formula gives 407.084). The formula contains a fifth nitrogen and no aryl fluorine; according to the figure captions of the source both 124f and 127c are 3-nitrophenyl compounds, although their compound letters differ.	
A6	122a and 123a: aglycone ^{13}C, aromatic ^{1}H and the low-field ^{1}H signal coincide; see Section S17.3 and Section S8.	Agreement with the labels of this pair is tabulated as agreement with the source labels and is not interpreted as chemical accuracy. Infrared naming and the signal-identity check do not depend on the assignment and are reported for both pairs.
A7	122a: the two lines of the C–F doublet are labelled 164.31 and 162.33 ppm (spacing 1.98 ppm) against 2.47 ppm in the other three compounds (Table S19). One-bond C–F couplings of aryl fluorides are close to 245 Hz (Weigert and Roberts 1971), so a spacing that differs by 0.5 ppm from that of the three analogues casts doubt on one of the two labels.	Compared, in the reading of Section S15, with Figure 40 of the source, which carries the labels 164.31 and 162.33 ppm (162.34 ppm on the full trace): the digitisation is faithful and the anomaly belongs to the source figure. No *Decisive evidence* field cites the value; one *Reasoning* field cites 164.3 ppm as a carbonyl signal (Section 3.2 of the article).
A8	No CF_3 quartet and no quartet structure of C-5 is among the labelled values of any of the four compounds, so one aglycone carbon is unlabelled in each; 117a has four labelled acetate C=O values for three acetyl groups (170.65 and 170.63 ppm are 0.02 ppm apart); 123a has one for two.	Noted under Table S15; carbon counts are not used as evidence.
A9	123a: two labelled lines that are not part of the $CDCl_3$ triplet (77.205 and 76.499 ppm) lie within or beside the solvent signal; the source has no correlation spectrum of 123a. Its list gives 77.2 ppm as C-1″ and 76.5 ppm as C-3″. The cross-peak of the anomeric proton in the HSQC figure printed for 122a lies near 76.3 ppm, within 0.3 ppm of the line labelled 76.50 ppm (A12). By the original records the spectrum printed for 123a is that of the compound whose ^{1}H spectrum is printed for 122a, and the line at 76.50 ppm is the anomeric carbon of that compound (Section S16.3).	The anomeric carbon of the compound whose ^{1}H spectrum is printed for 123a is treated as not established; the value listed in the source for 123a (77.2 ppm) is given in Table 3 of the article.
A10	The source states the infrared criterion as the absence of absorption at 1640–1690 cm^{-1} (for 116a, for 122a and for the benzoyl pair). The labelled band of 122a at 1646.32 cm^{-1} lies inside this range and that of 116a at 1639.05 cm^{-1} lies 0.95 cm^{-1} below it. Neither band appears in the infrared lists of the source, which give 3475 and 1750 cm^{-1} for 116a and 3414, 2922, 1741, 1463 and 1373 cm^{-1} for 122a.	The article uses an operational criterion, a labelled band at 1670–1690 cm^{-1}, for the four spectra of this study.
A11	The ^{1}H value tables of the deposit hold shifts only. The lists of the source also give multiplicities, proton counts, couplings and assignments, which were read for this article (Table S33). 116a lists three aromatic values for four protons (7.23, one proton; 7.46, two; 7.63, one) and assigns the signal at 3.71 ppm to H-5″b; 122a and 123a each list three values at 2.04–2.20 ppm, one of which the source assigns to H-2″b.	Noted. The aromatic values of 116a are used in Section S17.2 and the sugar values of 122a and 123a in Section S17.3, where the printed integrals of the ^{1}H panels are used beside the lists (Section S13).
A12	The HSQC figure printed for 122a (Figure 42 of the source): the cross-peaks of the sugar protons lie at about 76.3, 66.5, 66.7, 63.3 and 31.1 ppm, which coincide within 0.3 ppm with four labelled lines of the ^{13}C spectrum printed for 123a (76.50, 66.61, 63.54 and 31.28 ppm; its line at 77.21 ppm has no cross-peak) and not with the sugar lines of the spectrum printed for 122a (Section S15, Table S31, Figure S3). The account of this spectrum in the text of the source gives the labelled values of 122a. Original records found afterwards show the cause: the ^{13}C spectrum printed for 123a is that of the compound whose ^{1}H, COSY and HSQC spectra are printed	The ^{13}C figures of the pair are treated as printed with the wrong compound: the spectrum printed for 123a is attributed to the compound of the ^{1}H spectrum printed for 122a on the evidence of the records, and the spectrum printed for 122a to the other compound by elimination. The value tables used for the field check are those of the supplied panels and were not changed; C-1″ of 122a in Table 3 of the article is the value assigned in the source, with a note. No code of Table S9 changes.

#	Observation	Treatment
	for 122a (Section S16.3).	
A13	Lists of the source that differ from the labels of its figures, or from its own text, at values used here. 123a: C-2″ listed at 29.7 ppm, labelled 31.28 ppm (the figure has an unlabelled line near 29.7 ppm); five aromatic protons listed for four. 116a: H-1″ listed as a doublet of 4 Hz, whereas the two labelled lines (6.009 and 6.002 ppm) are 2.8 Hz apart. 122a: H-1″ listed as a doublet of doublets of 2.8 and 2.8 Hz, whereas the four labelled lines (5.840, 5.833, 5.818, 5.810 ppm) give about 9 and 3 Hz. 117a: H-5″b is 4.51 ppm in the ^{1}H value table of the deposit, which was taken from an earlier file of the thesis; the final version lists 4.15 ppm, in agreement with its figure (labelled lines at 4.13–4.17 ppm) and with its accounts of the COSY and HSQC spectra; the account of the HSQC spectrum gives 123.3 ppm for the carbon of the proton at 7.39 ppm, whereas the cross-peak in the figure lies near 131 ppm. 116a: aromatic protons listed at 7.23–7.63 ppm and described in the text as 6.98–7.39 ppm.	The labels of the figures are used for ^{13}C and infrared values and the lists for ^{1}H shifts (Section 2.1 of the article). H-5″b of 117a is given in Table S18 as in the final version of the source; the value table of the deposit is left as it was used, and no coded field cites a ^{1}H value between 4.0 and 4.6 ppm for 117a.
A14	The donor 121 is named 1,3,5-tri-O-acetyl-2-deoxy-D-ribofuranose. For its preparation the source cites a paper whose title compound is 1,3,4-tri-O-acetyl-2-deoxy-β-D-*erythro*-pentopyranose (Chen et al. 2009), and it lists for 121 the ^{13}C values 91.5 (C-1), 66.9, 65.0, 62.7 and 29.4 ppm, with no carbon between 67 and 91 ppm. Its procedure describes two crystalline fractions (13%, named as the furanose, and 67%) and does not say which was used.	The ring size of the donor and of the 2-deoxy products is treated as unconfirmed (Section S17.3). The cited paper was consulted as a bibliographic record only (Table S23).

S6.2 Time trend and matched comparisons

The eleven records are given in Table S36 and plotted in Figure S8 (both in Section S17.1). They are single, unreplicated experiments with no stated uncertainty. Over all eleven, N-selectivity and time give Pearson $r = 0.828$ ($r^2 = 0.685$) and Spearman $\rho = 0.892$. Excluding entries 1 and 11, $r = 0.925$ and $\rho = 0.858$ ($n = 9$); the rank correlation therefore falls slightly when the Pearson coefficient rises. Leave-one-out values of r lie between 0.785 and 0.853. N-selectivity rises with time in three of the four catalyst–solvent series; in $SnCl_4/CH_2Cl_2$ it falls from 0.40 to 0.39 between 4 and 8 h before rising to 0.57 at 10 h. The series have different time points (only $SnCl_4/CH_2Cl_2$ has a 10 h record and no 18 h record; TMSOTf/MeCN has two records).

The source infers from entries 8 and 10, which differ in both solvent and time, that acetonitrile favours the N-isomer. At matched catalyst and time, N-selectivity is lower in acetonitrile in each of the four available comparisons: 0.36 against 0.40 and 0.38 against 0.39 ($SnCl_4$, 4 and 8 h), 0.00 against 0.34 and 0.62 against 1.00 (TMSOTf, 4 and 18 h). The first two differences are four and one percentage points; whether they exceed experimental variation cannot be assessed without replicates. The last two both involve entries 1 and 11 (audit items A1 and A3). No solvent effect is claimed in either direction.

S6.3 Regression models (descriptive)

The linear model is given in Table S12. The p values below are conditional on the assumptions of each model (independent records, correct functional form, homoscedastic

or robustly estimated errors), which eleven unbalanced and unreplicated records cannot test. They are reported for completeness and are not used for inference in the article.

Table S12. Linear model of N-selectivity on time, solvent and catalyst (n = 11; R^2 = 0.843, adjusted R^2 = 0.776; residual degrees of freedom 7).

Term	β	SE	t	p
Intercept	0.2195	0.0785	2.80	0.027
Time (per hour)	0.0388	0.0065	5.93	< 0.001
Solvent = MeCN (vs CH_2Cl_2)	−0.1885	0.0731	−2.58	0.036
Catalyst = TMSOTf (vs $SnCl_4$)	−0.0718	0.0731	−0.98	0.359

Entries 11, 1 and 2 have the largest influence on this fit (Cook's distance 0.72, 0.49 and 0.46). Without entries 1 and 11 (n = 9; R^2 = 0.895) the coefficients are: time 0.0235 per hour (p = 0.002), solvent −0.0445 (p = 0.32), catalyst −0.0404 (p = 0.33). The solvent term of Table S12 is therefore carried by the two records in which one isomer was not detected.

A fractional-response specification is given in Table S13.

Table S13. Fractional-response model (binomial GLM, logit link, heteroskedasticity-robust HC0 standard errors; n = 11).

Term	β (logit)	SE	z	p
Intercept	−1.263	0.330	−3.82	< 0.001
Time (per hour)	0.179	0.042	4.25	< 0.001
Solvent = MeCN (vs CH_2Cl_2)	−0.948	0.450	−2.11	0.035
Catalyst = TMSOTf (vs $SnCl_4$)	−0.345	0.308	−1.12	0.26

The pattern is that of the linear model.

S6.4 Sensitivity to audit item A2

Substituting the narrative value for entry 5 (N 38%, O 61%) changes its N-selectivity from 0.390 to 0.384. The linear model then gives time 0.0388 (p < 0.001), solvent −0.1873 (p = 0.039), catalyst −0.0706 (p = 0.37), R^2 = 0.841; Pearson r = 0.828 and Spearman ρ = 0.892. No summary changes.

S7 Specifications for work not performed

S7.1 Electronic-structure calculations bearing on the time trend

The proposal of the source, that the first-formed isomer is converted into the second, makes two computable predictions: (a) the N2-glycoside is lower in free energy than the isomer assigned as O; (b) the barrier for glycosylation at the site of the first isomer is lower than at N2. A calculation intended to test them would need: the candidate structures of the first isomer (O- and N1-glycoside), each in its lowest tautomer, with conformer searches over sugar pucker, acetate orientation and rotation about the N–N and glycosidic bonds; geometry optimisation and frequencies at a stated density-functional level with dispersion

correction, single-point energies with a larger basis set, and a stated implicit-solvent model for acetonitrile and dichloromethane; a stated form of the silylated base; and transition states for attack at O, N1 and N2 on the electrophile appropriate to each donor (the 1,2-acyloxonium ion for the ribose donor, which has a participating 2-O-acetyl group; an oxocarbenium ion for the 2-deoxy donor, which has none), confirmed by intrinsic-reaction-coordinate calculations. Implicit solvation does not represent coordination of acetonitrile to the Lewis acid or nitrilium-ion formation, so the solvent question of Section S17.1 is outside what such calculations can address. Parallel pathways and selective loss of one isomer are not tested by them either and require resubjection and cross-over experiments.

Computed NMR shifts could provide additional discrimination among candidate structures (Section S7.3). A probability computed from the agreement of calculated and experimental shifts is defined only for the levels of theory for which it was parameterised, is distributed over the candidates supplied, and is sensitive to missing candidates, tautomers and conformers; it ranks candidates and does not establish a structure.

S7.2 Controls for the evidence manipulation

(i) Transcribed-text arm: the NMR-added items with every NMR spectrum replaced by a verified peak list, the infrared spectrum still as an image. (ii) Input-load control: the infrared-only items with the same number of additional images as the NMR-added items, the added images being uninformative. (iii) Intervention items: the NMR-added single-case items with the anomeric ^{13}C label removed, edited to fall in the other stated range, or exchanged between the isomers, everything else fixed. (iv) Label and order: every item repeated with the candidate letters exchanged and with the order of the two spectra or compounds reversed. (v) Interleaved collection: all conditions requested in one randomised sequence, so that condition is not aliased with batch. (vi) Sequential instruction: an item that asks for the infrared spectrum to be interpreted first and the NMR spectra to be integrated afterwards. (vii) Coding of the complete response, including the *Reasoning* field, and of the two-dimensional panels against a value table. (viii) A second coding of the infrared naming, which was requested and not obtained (Section S14), on a sheet that puts the question in the heading of the answer column and begins with worked examples; and a second coding of the field check, which the second coding of Section S14 did not cover: every response coded by a spectroscopist who has not seen the existing codes, in three separate columns: is the cited value present in the panel of the right compound; is it attributed to the right signal; does it support the answer given. Disagreements to be adjudicated and published. (ix) The same items put to a spectroscopist without access to the source, as a human reference; the questions of Task 1 of the second coding (Section S14, Table S27) are a first step, in which two chemists answered closed questions on the panels without the ^{1}H spectra and were not asked to assign the compounds. (x) A check of every stimulus image before any request is sent: that each two-dimensional panel contains its contours, that each ^{13}C panel displays the sugar region with untruncated labels, that no groups overlap in a candidate drawing, and that no identifier carries the item suffix (Section S13). (xi) Candidates balanced for tautomer and connectivity: the O-glycoside drawn in the arylazo as well as in the hydrazone form, an N1-glycoside added as a third

candidate, pyranosyl candidates for the 2-deoxy pair, and a check from original records that the spectra of each item come from one compound (Section S16.3).

S7.3 Measurements that would discriminate the candidate structures

Coupling pathways from the anomeric proton, traced on the structures of Figure 1 of the article. The ring is N1–N2–C-3–C-4–C-5–N1, with oxygen on C-3 and CF_3 on C-5. For attachment at O, H-1″ is three bonds from C-3 and four or more from every other ring atom. For attachment at N2, H-1″ is three bonds from C-3 and from N1, two from N2, and four from C-4 and C-5. For attachment at N1, H-1″ is three bonds from C-5 and from N2, two from N1, and four from C-3 and C-4. A $^{1}H–^{13}C$ HMBC correlation from H-1″ to C-3 is therefore common to O- and N2-attachment; a correlation to C-5, which is identifiable by its ^{2}J(C,F) quartet, would support N1 within an analysis of all the long-range correlations. A single correlation does not count bonds: correlations over four bonds are observed in HMBC spectra, and the absence of a cross-peak does not show that a proton is more than three bonds away (Saurí et al. 2016a, b). The pathways therefore give expectations and not exclusions.

The measurements are listed in Table S14.

Table S14. Measurements and what each could show.

Measurement	Bears on	Positive result and its meaning	Limits
$^{1}H–^{13}C$ HMBC optimised for small couplings, with the ^{13}C range extended to 175 ppm (116a, 117a, 122a, 123a)	attachment at N1 against O or N2; ring size	H-1″ → C-5 (quartet): supports N1. H-1″ → C-3: O or N2, not distinguished. H-1″ → C-4″ or C-5″ of the sugar: supports a furanose or a pyranose ring respectively. Sugar protons → acetate C=O: two ring CH protons correlating and the CH_2 protons not, 3,4-di-O-acetylpyranosyl; the CH_2 protons correlating, 5-O-acetylfuranosyl	a missing cross-peak is inconclusive; the H-1″ → C-4″/C-5″ correlation depends on the dihedral angle
$^{1}H–^{19}F$ HOESY (Dewis et al. 2019); ^{19}F NMR of 116a, 122a and 123a (recorded in the source for 117a only)	N1 against O or N2	a through-space contact between H-1″ and the CF_3 fluorines, or resolved coupling of the CF_3 fluorines to H-1″ or C-1″: consistent with the sugar next to CF_3 (N1)	the ^{19}F shift alone does not discriminate, because 116a and 117a differ in tautomeric type and their CF_3 shifts will differ whether the sugar is on O or N1; a contact requires a suitable conformation, and its absence is not evidence
$^{1}H–^{15}N$ HMBC at natural abundance	N2 or N1 against O	H-1″ → N over two bonds (usually also to the neighbouring nitrogen over three): supports an N-glycoside; which nitrogen is suggested by the ^{13}C HMBC partner (C-3 or C-5)	for an O-glycoside H-1″ is four bonds from N2, so the experiment is expected to give no correlation, which is not evidence; ^{15}N shifts alone may not separate N1 from N2; sensitivity-limited
D_2O exchange and $^{1}H–^{15}N$ HSQC of the low-field proton	identity of the low-field proton	a one-bond N–H correlation: ring or hydrazone N–H; none: O–H, or fast exchange	does not by itself give the attachment site
Full analysis of the ^{1}H coupling constants of	anomeric configuration and ring conformation of	coupling and contact patterns of the two compounds that differ as two	reports the sugar only; the aglycone has no protons

Measurement	Bears on	Positive result and its meaning	Limits
the sugar protons, and NOESY/ROESY, on spectra recorded again (122a, 123a)	the 2-deoxy compounds	anomers of one ring form would	near the attachment site
^{1}H, ^{13}C and HSQC spectra of both 2-deoxy compounds recorded again on characterised samples	the attribution of the ^{13}C spectrum printed for 122a to the compound whose ^{1}H spectrum is printed for 123a, which rests on elimination (Section S16.3), and the anomeric carbon of that compound	the HSQC cross-peaks of each compound coinciding with the ^{13}C lines attributed to it	requires the compounds to be prepared again
Single-crystal X-ray structure	everything for the crystal examined	attachment atom, tautomer, ring size and anomeric configuration directly	one compound per structure; the solid-state tautomer need not be the solution one
Computed ^{13}C/^{1}H shifts for a complete candidate set (O, N1, N2; both anomers; furanose and pyranose for the 2-deoxy compounds; relevant tautomers)	additional discrimination among candidates	one candidate reproducing the experimental shifts clearly better than the others	probabilistic; depends on the completeness of the candidate set and of the experimental list (the CF_3 carbon is unlabelled, the multiplet structure of C-5 is not recorded, and C-1″ of 123a is not confirmed)
Infrared spectra of 122a and 123a in solution	whether the 1646/1680 cm^{-1} difference is a solid-state effect	the two compounds showing the same carbonyl band in solution	concentration- and solvent-dependent; if the two still differ, the difference is structural
UV–visible spectra in $CHCl_3$	hydrazone against arylazo chromophore	absorption maxima of 116a differing from those of 117a, 122a and 123a as an arylazo group differs from a hydrazone	qualitative; the absorption spectra in a later chapter of the source concern other compounds

S8 Spectroscopic record of the four glycosides

Structures used for Table 1 of the article (SMILES; RDKit 2026.03.6). N2-riboside, hydrazone–lactam form: `CC(=O)OC[C@H]1O[C@@H](N2N=C(C(F)(F)F)C(=NNc3cccc(F)c3)C2=O)[C@H](OC(C)=O)[C@@H]1OC(C)=O`. O-riboside, hydrazone (4*H*-pyrazole) form: `CC(=O)OC[C@H]1O[C@@H](OC2=NN=C(C(F)(F)F)C2=NNc2cccc(F)c2)[C@H](OC(C)=O)[C@@H]1OC(C)=O`. O-riboside, arylazo (1*H*-pyrazole) form: `CC(=O)OC[C@H]1O[C@@H](Oc2n[nH]c(C(F)(F)F)c2N=Nc2cccc(F)c2)[C@H](OC(C)=O)[C@@H]1OC(C)=O`. The sugar is drawn β-D as assigned in the source; the anomeric configuration is not established by the data used here. Fingerprints were generated as 2048-bit hashed bit vectors with chirality not included (Morgan radius 2 and 3; atom pair; topological torsion) and as MACCS keys; similarity is the Tanimoto coefficient. All three structures have the formula $C_{21}H_{20}F_4N_4O_8$, neutral monoisotopic mass 532.1217 Da and calculated *m/z* 533.1290 for $[M+H]^+$. The 2-deoxy compounds are $C_{19}H_{18}F_4N_4O_6$, 474.1162 Da, for either ring size.

The values in Tables S15, S18 and S19 are the labelled values of Section S4.1. For 122a and 123a the ^{13}C entries of Tables S15, S16, S18 and S19 are those of the spectrum printed

under each number. By the original records the spectrum printed for 123a is that of the compound whose ^{1}H spectrum is printed for 122a, and the spectrum printed for 122a is attributed to the other compound (Section S16.3), so that for this pair the ^{1}H and the ^{13}C entries of a column belong to different compounds. The assignments in Table S15 marked as proposed are made here from shift position and from the comparison with published values in Table S16; they are tentative and, apart from the CH/CH_2 distinction of the HSQC figures, have not been checked against multiplicities or DEPT data. The aryl CH assignments are supported by the two-dimensional figures of the source: the row of the signal at 104.09 ppm of 117a in the supplied gHMBC panel has cross-peaks to aromatic protons only (Section S13), and in the HSQC figures the cross-peaks near 104, 112.7, 114.3 and 131.2 ppm lie in the columns of the aromatic protons near 7.27, 7.18, 6.98 and 7.40 ppm (Section S15). The lists of the source assign several aglycone carbons differently. For 117a they give 104.1 ppm as C-2′, 112.7 as C-6′, 114.3 as C-4′, 123.3 as C-5′, 131.2 as C-4, 138.7 as CF_3, 141.8 as C-1′, 157.8 as C-5, 162.3 as C-3 and 164.8 as C-3′; they agree with Table S15 for C-1′, C-2′, C-4′ and C-6′ and differ from it for the others, and they take the two lines read here as the C–F doublet for two carbons.

Table S15. Aglycone and low-field proton signals (ppm; IR in cm^{-1}), with proposed assignments.

Signal (proposed)	116a	117a	122a	123a
C-3′ (C–F), centre of the ^{1}J(C,F) doublet	163.27	163.58	163.32 as labelled (A7)	163.62
C-3	152.25 or 153.79	157.77	157.54	157.87
C-1′ (aryl carbon on N)	153.79 or 152.25	141.76	141.72	141.81
C-5 (carries CF_3)	132.85	138.70 (one line of the quartet centred at 138.90; Section S16.1)	138.23	138.43
C-5′ (aryl CH)	130.69	131.19	131.21	131.23
C-4	123.60	123.28	123.49	123.42
C-4′ and C-6′ (aryl CH; told apart in 117a by their C–F couplings, Section S16.1)	120.43, 118.63 (not told apart; by analogy with the diazene of Table S16, C-6′ and C-4′)	114.26, 112.73	114.45, 112.68	114.49, 112.67
C-2′ (aryl CH between C-1′ and C-3′)	107.67	104.09	103.80	103.83
CF_3	not labelled	not labelled	not labelled	not labelled
Aromatic ^{1}H	7.23, 7.46, 7.63	6.98, 7.18, 7.27, 7.39	6.98, 7.18, 7.28, 7.40	6.98, 7.18, 7.28, 7.40
Low-field ^{1}H	9.85	13.48	13.56	13.54
IR, labelled bands at 1630–1700	1639.05	1680.47	1646.32	1679.91

In each list one aglycone carbon is unlabelled: no CF_3 quartet (expected near 118–122 ppm with a line spacing of about 2.7 ppm) is among the labelled values, and C-5 is labelled as a single line without its quartet structure (audit item A8). In a 2-phenyl analogue the carbon bearing CF_3 is printed at 138.21 ppm (q, J = 32.2 Hz, smaller than the 39.5 Hz measured for C-5 of 117a in the original data, Table S34), the CF_3 carbon at 119.62 ppm (q, J = 271.1 Hz) and the most deshielded carbon, read here as the ring carbonyl, at 157.18 ppm (compound 5f of Burgart et al. 2023; Table S23). The signal at 123.3–123.6 ppm is common to the three

hydrazone-type compounds and to 116a, although C-4 differs in kind between them; its assignment in 116a is the least secure in Table S15.

Table S16. Aryl ^{13}C shifts (ppm) of the four glycosides ($CDCl_3$) compared with published values for a 3-fluorophenyl ring on a hydrazone nitrogen (the parent aglycone 2c and its N-glucoside 3c; Abdou et al. 2004, values as printed, unassigned in that paper) and on an azo group (1-(1-azidopentan-2-yl)-2-(3-fluorophenyl)diazene; Shen et al. 2021, with the reported C–F couplings). The assignment of the literature values to ring positions is made here. The solvent of the data for 2c and 3c is not part of the quotations in Table S23.

Aryl carbon	117a	122a	123a	2c (hydrazone)	3c (hydrazone)	116a	3-Fluorophenyl diazene (azo)
C-1′	141.76	141.72	141.81	141.0	141.6	153.79 (or 152.25)	153.24 (d, 6.8 Hz)
C-2′	104.09	103.80	103.83	103.8, 104.1	103.7, 104.2	107.67	108.04 (d, 23.1 Hz)
C-3′ (C–F)	163.58	163.32 (A7)	163.62	162.0 (not assignable: one line of the C–F doublet, or C-3)	not listed	163.27	163.17 (d, 247.9 Hz)
C-4′ and C-6′	114.26, 112.73	114.45, 112.68	114.49, 112.67	114.1, 114.3; 112.6, 112.7	114.2, 114.6; 112.7	120.43, 118.63	119.85 (d, 3.0 Hz, C-6); 117.65 (d, 22.1 Hz, C-4)
C-5′	131.19	131.21	131.23	131.2, 131.3	131.2	130.69	130.25 (d, 8.3 Hz)

The explanations left open for the 2-deoxy pair are set out in Table S17. At C-1′, C-2′, C-4′, C-5′ and C-6′ the values of 117a, 122a and 123a coincide within 0.9 ppm with those printed for the parent aglycone and its N-glucoside, which are hydrazone-type compounds (N–H at 13.56 ppm and a carbonyl band at 1670 cm^{-1} for 2c; a carbonyl band at 1682 cm^{-1} for 3c; Table S23). Those of 116a lie within 1.0 ppm of the 3-fluorophenyl ring of an aryl diazene and 3.6 to 12 ppm from those of 117a at C-1′, C-2′, C-4′ and C-6′. For comparison, C-1 of azobenzene is at 152.7 ppm (Singh et al. 2015). The pairs of values printed for 2c and 3c near 104, 114 and 131 ppm may be the two lines of C–F doublets; the paper does not state at which frequency its ^{13}C spectra were recorded, so the pairing cannot be checked from the spacings, and the argument of the article does not depend on it. C-4′ and C-6′ of the hydrazone-type compounds are not distinguished in the printed lists (in 117a and on the printout of 2016 their couplings tell them apart; Sections S16.1 and S16.3); their two-bond and four-bond C–F couplings (21.0 and 3.3 Hz in fluorobenzene, Weigert and Roberts 1971; 22.1 and 3.0 Hz in the diazene of this table) would distinguish them. In the original ^{13}C data of 117a the couplings were measured (Section S16.1, Table S34): 21.7 Hz at 114.4 ppm and 2.7–3.0 Hz at 112.7 ppm, so that C-4′ is the carbon at 114.4 ppm and C-6′ that at 112.7 ppm in 117a, as the source lists them.

Table S17. The 2-deoxy pair: explanations not excluded by the available records, with the recorded evidence for and against each.

Explanation	Supporting	Contrary or unexplained
(i) Source assignment: 122a O-glycoside, 123a N-glycoside	infrared: no labelled band at 1670–1690 cm^{-1} in 122a (its trace has an unlabelled shoulder there; Section S13), band at 1679.91 cm^{-1} in 123a (which infrared spectrum belongs to which compound is not settled by the original records and rests on the statement of H.A.A.; Section S16.3)	Both ^{13}C spectra of the pair show, at the eight labelled aglycone positions compared (C-3′, audit item A7, and the unlabelled CF_3 carbon excepted), the carbons of the hydrazone–lactam type and the aryl pattern of a hydrazone, so that 122a does so whichever spectrum is its own (Section S16.3), and its ^{1}H spectrum has a low-field proton at 13.56 ppm. Its anomeric carbon

Explanation	Supporting	Contrary or unexplained
		lies at 76.5 ppm (HSQC cross-peak near 76.3 ppm; 76.499 ppm on the original printout), and the line listed as its C-1″, 78.54 ppm, belongs to the spectrum attributed to the other compound (Sections S15 and S16.3); both lie below the anomeric carbons of the N-ribosides compared in Table S23 (84.4 to 90.5 ppm; ribofuranosides, not 2-deoxy sugars, and of a different ring size if the ring of 122a is pyranosyl); it lies 15 ppm below the acetal carbon C-1 of the donor 121 as listed in the source (91.5 ppm), a carbon that bears two oxygen atoms, as C-1″ of an O-glycoside would, whereas C-1″ of an N-glycoside bears one oxygen and one nitrogen and is expected at higher field. Every original infrared printout of the two samples, including one of the sample with the ^{1}H spectrum printed for 122a whose printed name is not altered, labels a band between 1677 and 1680 cm^{-1} (read from the scans with the assistant and compared by H.A.A. with the printouts; Section S16.3). An O-glycoside in its 4-hydrazono-4*H*-pyrazole form would share the aryl pattern but is not expected to reproduce C-3, C-4, C-5 and the chelated N–H of the lactam
(ii) Two N2-glycosides differing in the sugar (most simply anomers of one ring form; Section S17.3)	coincident aglycone ^{13}C and ^{1}H; different sugar ^{13}C and ^{1}H; a coupling of H-1″ of 9–11 Hz in both compounds (of axial–axial size; not decisive by itself, Section S17.3); a 2-deoxy donor has no participating group at C-2; the record of the donor (A14); for the compound whose ^{1}H spectrum is printed for 122a, its anomeric carbon (76.5 ppm) and the original infrared printouts (1677–1680 cm^{-1}; Section S16.3)	requires the lactam carbonyl of 122a to absorb at 1646 cm^{-1} in the solid, or to be the unlabelled shoulder at about 1665–1680 cm^{-1} (Section S13), where the original printouts label a band (Section S16.3), and that of 123a to absorb at 1680 cm^{-1}; both compounds show a large H-1″ coupling (about 9 and 11 Hz), so as anomers of one pyranosyl ring they would adopt opposite chair forms
(iii) Glycosylation at the two different ring nitrogens	—	no uncharged hydrazone–lactam structure can be written for an N1-glycoside (N1 cannot form the C-5=N1 double bond and C-5 bears no hydrogen), yet both compounds show its fingerprint
(iv) An error in the record (a peak list or figure associated with the wrong compound; a transcription error)	established for the ^{13}C figures: by the original records the spectrum printed for 123a is that of the compound whose ^{1}H, COSY and HSQC spectra are printed for 122a, and the spectrum printed for 122a is attributed to the other compound (A12; Sections S15 and S16.3); further, near-identical aglycone lists; the label anomaly of audit item A7; differences between lists and figures (A13)	the misplacement of the ^{13}C figures concerns which spectra belong together and explains no structural feature: both ^{13}C spectra show the same aglycone fingerprint and different sugar lines, and the misplacement does not by itself explain the infrared difference; which infrared spectrum belongs to which compound is not settled by the records and rests on the statement of H.A.A. (Section S16.3)
(v) The infrared and NMR spectra do not describe the same species (solid against $CDCl_3$ solution; isomerisation of an acid-labile glycoside in solution; a mixture)	the infrared and NMR evidence on 122a point in different directions	not testable from the values used here; the age of the solution and the purity of the sample are not known to this study

Table S18. Sugar signals (ppm). The ^{13}C values in the columns of 122a and 123a are the labels of the figure printed under each number; by the original records the figure printed for 123a is the spectrum of the compound whose ^{1}H signals are in the column of 122a, and the figure printed for 122a is attributed to the compound whose ^{1}H signals are in the column of 123a (Sections S15 and S16.3).

Signal	116a	117a	122a	123a
C-1″	90.22	84.39	78.54 as listed in the source, in the spectrum printed for 122a; the anomeric carbon of the compound of this ^{1}H spectrum is the line at 76.50 of the spectrum printed for 123a (HSQC cross-peak of H-1″ near 76.3; 76.499 on the printout of 2016)	77.21 as listed in the source, without a correlation spectrum; 76.50 is listed as C-3″ (both within or beside the $CDCl_3$ triplet); the anomeric carbon of the compound of this ^{1}H spectrum is not established
Other oxygenated sugar carbons	80.89, 73.98, 71.03, 62.97	79.70, 72.53, 70.74, 62.91	68.56, 67.09, 66.13	66.61, 63.54 (76.50: see the row above)
C-2″ (2-deoxy), as labelled under the assignment of the source	—	—	29.69	31.28 (label of the figure; the list gives 29.7, A13)
H-1″	6.01 (d; listed 4 Hz, labelled lines 2.8 Hz apart)	5.99 (d; listed 4 Hz, labelled lines 4.4 Hz apart)	5.83 (dd; listed 2.8 and 2.8 Hz, labelled lines about 9 and 3 Hz)	5.50 (listed as d, 10.8 Hz; the small coupling of H-1″ is not resolved in the list)
Other sugar ^{1}H, as listed	5.90, 5.71, 4.44, 4.19, 3.71	5.70, 5.53, 4.44, 4.33, 4.15 (4.51 in the value table of the deposit; audit item A13)	5.66, 5.11, 3.94, 2.67	5.21, 5.15, 4.13, 3.83, 2.87
^{1}H at 2.0–2.2 (acetyl CH_3 and, for the 2-deoxy compounds, H-2″)	2.12, 2.13, 2.16	2.09, 2.10, 2.11	2.05, 2.10, 2.15	2.04, 2.05, 2.20
Acetate C=O	170.68, 169.48, 169.29	170.65, 170.63, 169.59, 169.45	170.59, 170.04	169.89
Acetate CH_3	20.76, 20.52, 20.45	20.59, 20.55, 20.49	21.09, 20.86	21.02, 20.79

The ^{13}C list printed for 3′,5′-di-O-acetylthymidine, a 3,5-di-O-acetyl-2-deoxy-β-D-ribofuranosyl N-nucleoside, in $CDCl_3$ contains 85.0, 82.2, 74.7, 64.1 and 36.8 ppm, read here as its sugar carbons (the list is unassigned in its source), and in its assigned ^{1}H list one sugar proton besides H-1′ lies above 5 ppm (H-3′, 5.22 ppm), with H-4′ at 4.24 and H-5′ at 4.37 ppm (Bdour et al. 2006; Table S23). Neither ^{13}C spectrum of the pair has a labelled carbon between 79 and 103 ppm (the line at 78.54 ppm of the spectrum printed for 122a is the one listed as C-1″; were it C-4″ of a furanose ring, that spectrum would have no anomeric carbon), and each has two signals above 5 ppm besides H-1″ and signals between 3.8 and 4.2 ppm. Two acyloxy-substituted methine protons and a ring O–CH_2 group would be the pattern of a 3,4-di-O-acetyl-2-deoxy-D-*erythro*-pentopyranosyl ring (ring closure

through O-5; acetyl groups on O-3 and O-4), which has the same formula; a pyranose triacetate of 2-deoxy-D-ribose, 1,3,4-tri-O-acetyl-2-deoxy-β-D-*erythro*-pentopyranose, is a known crystalline compound (Chen et al. 2009), and the source cites that paper for the preparation of its donor 121 (audit item A14). The three oxygenated carbons at 66–69 ppm of the spectrum printed for 122a fit this ring, and so do the lines at 66.61 and 63.54 ppm of the spectrum printed for 123a (in the HSQC figure printed for 122a two cross-peaks lie near 66.6 ppm; Section S15); the line at 77.21 ppm of that spectrum is not accounted for. For comparison with the sugar carbons of the ribose pair: those of 117a (84.39, 79.70, 72.53, 70.74, 62.91 ppm) lie within 0.2 ppm of the values assigned to C-1′, C-4′, C-2′, C-3′ and C-5′ of the *p*-tolyl N2-riboside (84.4, 79.7, 72.7, 70.84, 63.0 ppm; Haikal et al. 2003), and those of 116a (90.22, 80.89, 73.98, 71.03, 62.97 ppm) within 0.5 ppm of the five sugar carbons printed for a 1-(2,3,5-tri-O-acetyl-β-D-ribofuranosyl)-1,2,3-triazole (90.0, 80.9, 74.4, 70.8, 62.9 ppm; compound 10 of Beghennou et al. 2024, unassigned there; a second such triazole has its most deshielded sugar carbon at 90.5 ppm). Reading the most deshielded sugar carbon of those lists as the anomeric carbon is done here (Table S23). The ^{1}H lists of the source give proton counts and couplings (Table S33), and the ^{1}H panels carry printed integrals (Section S13): in 122a the signals at 5.66 and 5.11 ppm carry printed integrals of 1.03 and 1.04 and the signal at 3.94 ppm one of 2.04; in 123a the signals near 5.21 and 5.15 ppm carry 1.03 and 1.04, and those near 4.13 and 3.83 ppm carry 0.99 and 1.02 and are each labelled as two lines 0.033–0.035 ppm apart (about 13–14 Hz at 400 MHz). Two one-proton acyloxy-methine signals and a CH_2 group near 3.8–4.1 ppm are the pattern of the pyranosyl ring and not of a 3,5-di-O-acetyl furanoside, which has one such methine proton and three protons near 4.2–4.4 ppm; a 2-deoxypentofuranoside has hydroxy groups at C-3 and C-5 only, so no acetylation pattern of a furanoside gives two acylated methine protons. A splitting of about 13–14 Hz in each of the signals near 4.13 and 3.83 ppm is of geminal size and suggests that they are the two protons of one CH_2 group; no COSY spectrum of this compound is available to confirm it, and the splitting does not distinguish a ring O–CH_2 from an exocyclic CH_2OAc group, whereas the shifts favour the ring O–CH_2. Taken with the shifts, the integrals therefore favour the pyranosyl ring; they are read from an image, the other multiplets are not analysed, and the ring size is not established. The anomeric configuration of none of the four compounds is established by the values used here.

Table S19. The two labelled lines of the aryl C–F doublet.

Compound	Lines (ppm)	Spacing (ppm)	Centre (ppm)
116a	164.508, 162.037	2.471	163.27
117a	164.81, 162.34	2.47	163.58
122a	164.31, 162.33	1.98	163.32
123a	164.861, 162.387	2.474	163.62

The labelled $CDCl_3$ lines are 0.32 ppm apart, which for the 32 Hz carbon–deuterium coupling of the solvent corresponds to a ^{13}C frequency of about 100 MHz, in agreement with the 400 MHz spectrometer stated in the source; at that frequency a spacing of 2.47 ppm is a one-bond C–F coupling of about 248 Hz (248.4 Hz in the original data of 117a; Table S34), as expected for an aryl fluoride (245 Hz in fluorobenzene; Weigert and Roberts 1971). The spacing of 1.98 ppm in 122a is the anomaly of audit item A7. Smaller C–F

couplings (for example that of C-2′, 26.7 Hz or 0.27 ppm in the original data of 117a; Table S34) are not resolved into separate labels in any of the four lists.

The carbonyl region of the four infrared spectra is shown on a common wavenumber scale in Figure S2.

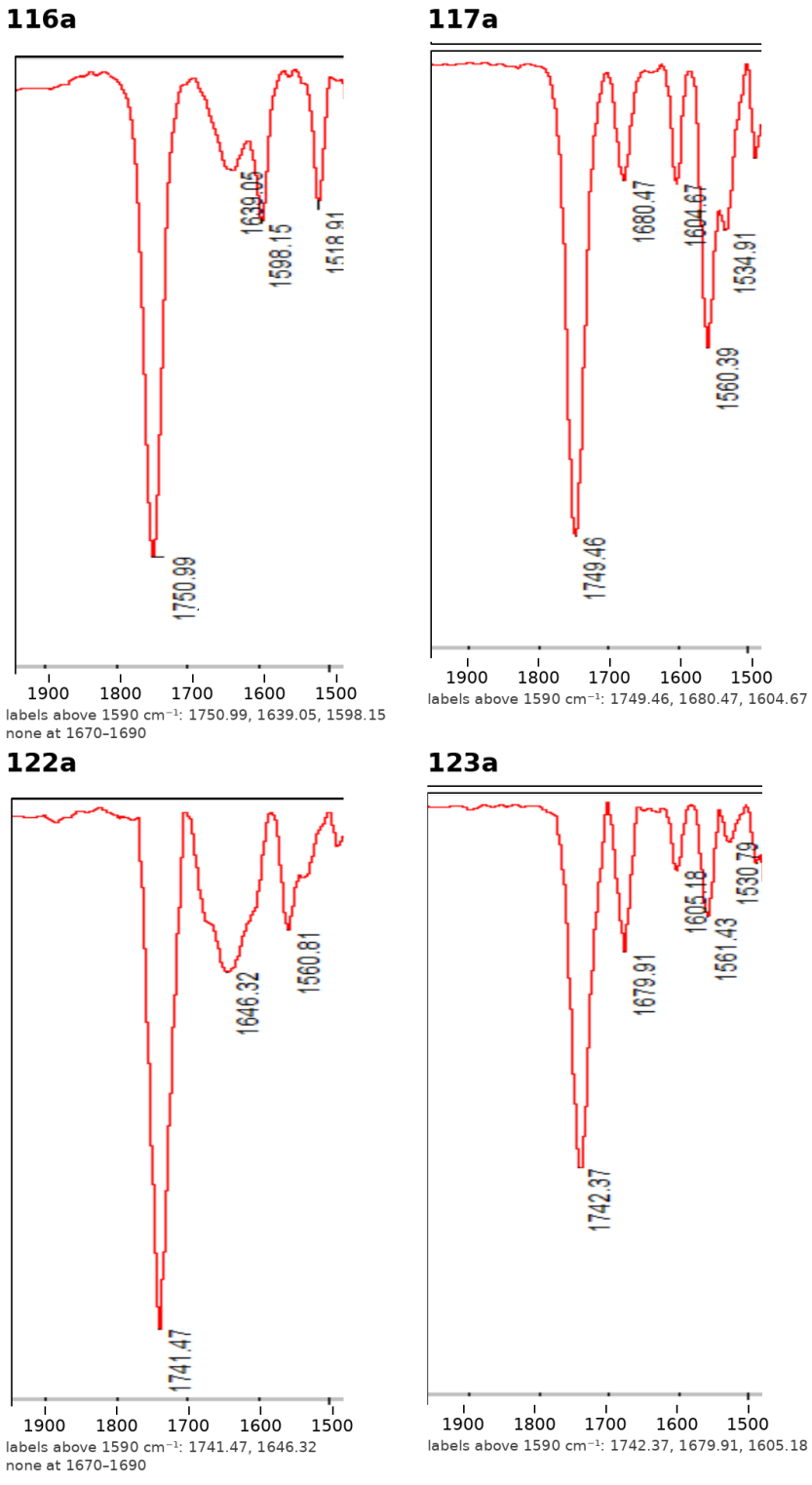


Figure S2. Carbonyl region (1950–1480 cm^{-1}) of the four infrared spectra, cut from the stimulus images without redrawing. The wavenumber scale beneath each panel is not part of the image: it was computed from the tick marks of that image (100 cm^{-1} apart; the tick printed 1500 as the reference). The lines of text beneath each panel are the present reading

and are not annotations of the source figure. In the trace of 122a the band labelled 1646.32 cm^{-1} has an unlabelled shoulder whose level part lies at about 1665–1675 cm^{-1} on this scale, which places the labelled bands up to 6 cm^{-1} below their printed values.

S9 Outline of a classroom exercise

This section outlines how the materials could be used in an upper-level organic or spectroscopy course. It has not been trialled. Its purpose is to have students audit a justification against the spectra, asking of every cited value whether it is present, which signal it belongs to and whether it supports the answer; the field check of the article covers the presence of each cited value and the identity of NMR signals, and not whether the value supports the answer.

Session 1: the ribose pair. (a) Given the two candidate drawings and the infrared spectrum of one compound, students state which observation should differ between the candidates before reading the spectrum, then assign the compound and record the observation with its value. (b) They repeat the assignment with the NMR spectra added. (c) They audit three responses from Table S4 value by value: Gemini `singleIR_PX-A01` r1 (names the 1680 cm^{-1} band), gpt-5 `binary_PX-A01` r1 (takes 104.09 ppm as the anomeric carbon) and Gemini `binary_PX-A02` r1 (reads 90.2 ppm as an N-glycosidic anomeric carbon). (d) They audit their own answers in the same way. Points for discussion: whether 104.09 ppm can be an anomeric carbon, given the aryl pattern of Table S16; what can and cannot be inferred from the anomeric carbon of 116a at 90.2 ppm without a comparison value for an O-riboside; and what the data do and do not establish about 116a (Section S17.2).

Session 2: a case with an open assignment. Students receive the data of 122a and 123a (the ^{13}C spectra as printed in the source, with the attribution of Section S16.3), the source assignment and its stated reason, and two responses that disagree with each other: gpt-5 `binary_PX-B01` r2 and Gemini `binary_PX-B01` r1. They list the observations that differ between the compounds and those that coincide, sort them as supporting or contradicting each explanation of Table S17, state what cannot be decided from the records, and propose measurements, naming for each the sample, the result that would count as positive evidence and its limit (Table S14). They then judge each response on whether its evidence is present, correctly identified and relevant. The exercise can be extended with the HSQC figure of the source (Figure S3): students check whether its cross-peaks agree with the ^{13}C labels of the spectrum printed for the same compound, and find that they do not (Section S15).

The status of each source label is summarised in Table S20 and a rubric is given in Table S21.

Table S20. Status of the source label for each item, for the instructor.

Item	Source label	What the recorded data show	Not established
117a (PX-	candidate A (N2-	infrared band at 1680 cm^{-1}; a carbon at 157.8 ppm; low-field proton at 13.48 ppm, as expected for a chelated	anomeric configuration

Item	Source label	What the recorded data show	Not established
A01)	glycoside)	hydrazone N–H; hydrazone aryl pattern; C-1″ at 84.39 ppm	
116a (PX-A02)	candidate B (O-glycoside)	an arylazo form is favoured: no band at 1680 cm^{-1}, arylazo aryl pattern, low-field proton at 9.85 ppm; N2-attachment disfavoured, not excluded	site of attachment (O or N1); anomeric configuration; why C-1″ is at 90.2 ppm
122a, 123a	open; source: 122a O, 123a N	source assignment supported by the infrared figure printed for 122a only; the corrected record of the compound whose ^{1}H spectrum is printed for 122a favours an N-glycoside (Table S17); the ^{13}C spectra of the pair are printed in the source with the wrong compound (Sections S15 and S16.3)	attachment in 122a, ring size, anomeric configuration; which infrared spectrum belongs to which compound rests on the statement of H.A.A. (Section S16.3)

Table S21. Rubric for the Session 2 argument sheet (20 points).

Criterion	4	2	0
Observations listed (differences and coincidences)	complete and attributed to the right signals	partial, or one misattribution	major omissions or misattributions
Evidence sorted by explanation	supporting and contrary evidence placed correctly for each explanation of Table S17	one explanation incomplete	evidence assigned to one explanation only
Statement of what cannot be decided	explicit, with the reason	stated without reason	absent, or the case is declared decided
Proposed measurements	a set that addresses attachment site and sugar ring, with the positive result and the limit of each; no argument from an absent cross-peak	one measurement, or no limits stated	irrelevant or absent
Evaluation of the two responses	each judged on presence, identification and relevance of its evidence; “better argued” kept apart from “agrees with the source”	judged by agreement with the source or with the student’s own view	no evaluation

No marks are awarded or withheld for agreeing or disagreeing with the source assignment. If student work is collected for research, institutional ethics approval and consent are required.

S10 Manifest of the deposited archive

The responses, images, prompts and scripts are those of data version v1.0.1 (archive `deposit-v1.0.1.zip`, MD5 17c4f877e1691da28142e367c9915098; version DOI of v1.0.1 https://doi.org/10.5281/zenodo.23015879; concept DOI for all versions https://doi.org/10.5281/zenodo.23014095). Version v1.0.1 differs from the first published version (DOI 10.5281/zenodo.23014096) only in the names of nine pilot screenshots, in which the Arabic digit U+0662 was replaced by the ASCII digit 2 so that `SHA256SUMS.txt` verifies on every platform. No response, image or prompt has changed since the first deposit. Licence: CC BY 4.0 (data), MIT (code). The coding used in the article (Table S9) is given in full in this file and is not part of version v1.0.1. The title of the Zenodo record was changed on 30 September 2026 to the title cited here; no file was changed. Version 1.1.0 of the deposit (version DOI https://doi.org/10.5281/zenodo.23440612) changes no file of version 1.0.1, in particular neither the stimulus images nor the value table `panels.json`, which stay exactly as they were used in the evaluation; it adds one archive (MD5 2641a7f46858b075250230e4c1b6237c), which holds the coding of Table S9 and the files of the later analyses (Sections S12–S16) and is Supporting File 6 of the article.

The files are listed in Table S22.

Table S22. Files of version v1.0.1.

File	SHA-256	Size (bytes)
README.md	5b549854a3ff2bbedf3762c532f1617dc141c52106f4457842f650c40d7aac90	2109
code_responses.py	9308654916075d6fc778f77af5106e9eac966db80de67082a3e8dfff5f111eed	12997
coded_all.csv	6bdd8e05e7cd341f9d656db241c28166bcc8a5fdffcba0863a7e182006a1990c	43391
make_tables.py	e488364d37934152a31316934a82b2b18bf6a652154dcb0b872e3fa3a5311e3c	3247
panels.json	034299a09383410999c6ec9973a9c54df44300d0a4c4aebe29ce56187a3f4f46	3993
pilot-results-v0_36.xlsx	aa904dbfc4de8f2c479c46691e8e1999001ea13a578de6fdb1a590c8916be917	79663
prompts/binary_HSQC.txt	2d295090e6c299212799702536208bc32e2e90649b5f6e67bf3801863cc26035	1163
prompts/binary_gHMBC.txt	182c6aa5d0877dd4d39c4e5de97402caeb86c9bebf1cb37d84f71c7ff05b2c19	1164
prompts/binary_none.txt	ab29c1cac7841bb6a93093d011aee4546af30cadbb3ccb10ca8bbdafa3a5573d	1157
prompts/paired.txt	2cd3caec9c4f2952a3d85f412597055b11afe0ea9d3fbe8cca4785ad67ecb020	1081
prompts/paired_benzoyl.txt	391d787565d76b9f0d72c7cbd2467398cfb95b7d81dc6c20bbd6b6e523e19545	1089
prompts/paired_full_deoxy.txt	9eac82abebe3ca0630b7457fe4eb6f90fd7d5c8696c19331d39cb7b4d34bcee3	1165
prompts/paired_full_ribose.txt	a4e7865afd7d41135bc34f090e25f8632b942937c7f8988d48850e19848f00b4	1138
prompts/single_IR.txt	136b4b4f9717a6a7c216e4ad59f853d5913799f07e363c704730ee646389ad80	1134
prompts/single_IR_benzoyl.txt	6a745192b357c9eca94ed93f500f002217dddd51cb62c4534f73b049c3c39c44	1142
results_api.csv	0b63d10659b73b776eb377010b078c6cb35e7fb63e9648154b5a9f94318fe821	104153
results_api_coded.csv	8f3a01d4cffc851c3cecb6d462e81ea851b6a27df5674ea3155342a6cecfc442	9132
run_api.py	97e56196cef462b6a5b6848d0dc75595e800ee39fb9536482a3904d04e71c907	11350
screenshot_transcriptions.json	ab0b677f82eb6554d746bf28a1646eea22b5074b1adbb07cfab2f9947224f9f8	1656
tables_output.txt	a919df066d1d6ee687e0f2c5d3b561aaa27eea83e3becfe337051595467a1ba0	1462
raw/ (90 files)	individual hashes in SHA256SUMS.txt	—
images/ (41 files)	individual hashes in Table S1 and SHA256SUMS.txt	—
screenshots/ (pilot and probe sessions)	individual hashes in SHA256SUMS.txt	—

Notes. (i) The deposited pilot workbook is version 0.36; `code_responses.py` reads it under that name. (ii) `coded_all.csv` holds the original script codes of all 144 coded responses (90 API, 54 pilot) and `results_api_coded.csv` covers the 36 batch 1 API responses. (iii) The source labels are given in Table 2 of the article, in Table S2, in `panels.json` and in the key sheet of the pilot workbook; a separate answer-key document prepared for classroom use is not part of the deposit. (iv) `run_api.py` reads API keys from environment variables; no credential is stored. (v) Individual checksums of the files under `raw/`, `images/` and `screenshots/` are in `SHA256SUMS.txt`, which is part of the archive. (vi) The files of version 1.1.0 (Supporting File 6), among them the copy of Supporting File 5, were not changed after they were published, so that their checksums stay those of the deposit. They refer to the article by its working title (“Artificial intelligence in structure elucidation: auditing the spectral evidence cited by large language models in pyrazolone glycoside assignment”) and to its sections by the numbering of the drafts in which they were written; the copy of the plan of 9 October 2026 keeps its blank date field (Section S14). The README of that version describes its files as supplied with the manuscript submitted to the Journal of Chemical Information and Modeling, which they are with this submission; it does not state

its own DOI, which is the version DOI of version 1.1.0 given above; and it describes the script of Section S13 as measuring the infrared trace of 116a, whereas the script measures the traces of 116a and 122a.

S11 Literature values as printed in their sources

Table S23 gives every literature value used in the article and in this file as it is printed in its source, with the compound, the place in the source, whether the source assigns the value, and the reading made here. Quotations keep the punctuation and any misprints of the source. They were retrieved, with the AI assistant of Section 2.6 of the article, from the publishers' pages and supporting-information files on 30 September 2026. H.A.A. did not check the quotations against the papers, except the values that the article compares for compounds 2c and 3c of Abdou et al. (2004), C-1′ and the carbonyl band of Haikal et al. (2003) and compounds 10 and 6 of Beghennou et al. (2024), which she compared with the papers (check sheet of 18 October 2026). Where only the bibliographic record of a source was consulted, this is stated, and the statement made from it is limited accordingly.

Table S23. Literature values used, as printed.

Source; compound; place	As printed	Assigned in the source?	Used here for
Abdou et al. 2004; 2c, the 4-(3-fluorophenylhydrazono) parent pyrazolone; Experimental	IR: "3450 (NH), 3060 (aromatic C–H), 2995 (aliphatic C–H), 1670 (C=O), 1560 (C=C),1550 (C=N), 1528 cm-1(N–N)". ^{1}H: "δ 6.90 (t, 1H), 7.17-7.29 (m, 2H), 7.36-7.40 (m, 1H), 7.80 (s, exchangeable with D2O), 13.56 (bs, exchangeable with D2O)". ^{13}C: "δ 103.8, 104.1, 112.6, 112.7, 114.1, 114.3, 131.2, 131.3, 141.0, 162.0"	IR bands yes; ^{13}C no	Table S16; the signal near 104 ppm in a compound without sugar (article, Section 3.2); carbonyl band at 1670 cm^{-1}; N–H at 13.56 ppm. The pairing of lines into C–F doublets and their ring positions are readings made here
Abdou et al. 2004; 3c, the N-glucoside of 2c (tetra-O-acetyl); Experimental	IR: "3070 (aromatic C–H), 2996 (C–H), 1750 (acetyl C=O), 1682 (C=O), 1604 (C=C), 1558 (C=N), 1528 (N–N), 1026 cm-1(C–O–C)". ^{13}C: "δ 20.4, 20.5, 20.6, 20.8, 76.6, 68.3, 69.7, 73.5, 74.3, 80.3, 103.7, 104.2, 112.7, 114.2, 114.6, 122.9, 128.3, 131.2, 141.6, 158.1, 168.6, 169.3, 170.2, 170.6"	IR bands yes; ^{13}C no	Table S16; carbonyl band at 1682 cm^{-1}. The list also contains 158.1 and 122.9 ppm, close to 157.77 and 123.28 ppm of 117a
Haikal et al. 2003; the title compound, 2-(2′,3′,5′-tri-O-acetyl-β-D-ribofuranosyl)-4-(p-tolylazo)-5-trifluoromethyl-2,4-dihydropyrazol-3-one; single-compound report	"IR (KBr, cm-1): 1747 (CO ester), 1674 (CO Pyrazolone)." ^{13}C (75 MHz, CDCl3): "21.9 (CH3); 48.5 (CH); 63.0 (C-5`), 70.84 (C-3`); 72.7 (C-2`); 79.7 (C-4`); 84.4 (C-1`); 116.9 (2 aromatic carbons), 121.1, 122.0 (2 aromatic carbons), 130.5, 144.1 (2 quaternary aromatic carbons); 137.5 (q, CF3); 149.2 (C=N); 169.5, 169.8, 170.7, 173.0 (4 CO)." ^{1}H includes "2.42 (s, 1H, CH)" and	yes, including C-1′ at 84.4 ppm	sugar carbons of an N2-riboside, compared with 117a; pyrazolone carbonyl band at 1674 cm^{-1}, quoted with this caveat. The aglycone is described there as the 4-arylazo-4*H* tautomer (a ^{13}C value at 48.5 ppm and a ^{1}H singlet at 2.42 ppm assigned to CH), unlike the hydrazone form indicated for 117a; that description is not evaluated

Source; compound; place	As printed	Assigned in the source?	Used here for
	"6.03 (d, 1H, H-1`, J1`,2`=4.2 Hz)"		here, and the aglycone ^{13}C values are not compared
Burgart et al. 2023; compounds 5–9 (2-substituted 4-arylhydrazinylidene-5-polyfluoroalkylpyrazol-3-ones); Results	"The NMR spectra of heterocycles 5–9 recorded in CDCl3 and DMSO-d6 contained one set of signals, which also corresponds to the Z-isomeric form of the HA tautomer, since the 1H NMR spectra contain downfield proton signals at δ 13–14 ppm of the NNH group that can participate in the IHB formation." The crystal structures are described as "existing in a Z-hydrazone amide (HA) tautomeric form in crystals"	—	hydrazone tautomer of N-substituted analogues in solution and in the crystal; N–H at 13–14 ppm
Burgart et al. 2023; 5f, (4Z)-4-[2-(4-methylphenyl)hydrazinylidene]-2-phenyl-5-(trifluoromethyl)-2,4-dihydro-3H-pyrazol-3-one; Experimental	IR: "ν 1658 (C=O)". ^{1}H (CDCl3): "14.06 (1H, br. s, NNH)". ^{13}C (CDCl3, 125 MHz): "δ 21.15, 116.84, 119.36, 119.62 (q, J = 271.1 Hz, CF3), 122.75, 123.26, 126.34, 129.08, 130.47, 137.42, 137.99, 138.21 (q, J = 32.2 Hz, C–CF3), 157.18"	CF_3 and C–CF_3 yes; 157.18 no	carbonyl band at 1658 cm^{-1}; CF_3 and C–CF_3 quartets (Section S8, audit item A8); 157.18 ppm read here as the ring carbonyl
Deneva et al. 2019; abstract	"5-methyl-2-phenyl-4-(2-phenylhydrazono)-2,4-dihydro-3H-pyrazol-3-ones exist as hydrazone tautomers" (in solution; UV–Vis, NMR and calculations)	—	hydrazone tautomer of 2-substituted 4-arylhydrazono-pyrazol-3-ones in solution
Shen et al. 2021; 4y, 1-(1-azidopentan-2-yl)-2-(3-fluorophenyl)diazene; Supporting Information, p. 10	"13C NMR (126 MHz, CDCl3) δ 163.17 (d, J = 247.9 Hz), 153.24 (d, J = 6.8 Hz), 130.25 (d, J = 8.3 Hz), 119.85 (d, J = 3.0 Hz), 117.65 (d, J = 22.1 Hz), 108.04 (d, J = 23.1 Hz), 53.50, 32.95, 19.05, 13.91". Aromatic ^{1}H: "7.56 (d, J = 7.9 Hz, 1H), 7.45 (td, J = 8.1, 5.8 Hz, 1H), 7.38 (dt, J = 9.6, 2.2 Hz, 1H), 7.16 (td, J = 8.4, 2.2 Hz, 1H)"	no (couplings given)	Table S16: a 3-fluorophenyl ring on an azo group. Ring positions are assigned here from the C–F couplings
Singh et al. 2015; 2b, 1,2-diphenyldiazene; Supporting Information, p. S3	"13C NMR (100 MHz, CDCl3) δC 122.9, 129.1, 131.0, 152.7"	no	C-1 of azobenzene, read here as the most deshielded value
Beghennou et al. 2024; 10, a 1-(2,3,5-tri-O-acetyl-β-D-ribofuranosyl)-1,2,3-triazole, printed as "(2R,3R,4R,5R)-2-(acetoxymethyl)-5-(4-(2-chloro-3-(dimethoxymethyl)pyridin-4-yl)-1H-1,2,3-triazol-1-yl)tetrahydrofuran-3,4-diyl Diacetate"; Experimental	"13C NMR (100 MHz, Chloroform-d) δ 170.4, 169.4, 169.2, 151.7, 149.5, 143.2, 140.3 126.6, 123.9, 104.8, 90.0, 80.9, 77.2, 74.4, 70.8, 62.9, 56.1, 56.0, 20.6, 20.4, 20.4." ^{1}H includes "6.18 (d, J = 3.6 Hz, 1H)"	no	sugar carbons of an N-ribosylazole, compared with 116a. Read here: 90.0, 80.9, 74.4, 70.8 and 62.9 ppm as the five sugar carbons and 90.0 ppm as C-1′; 104.8 ppm as the acetal carbon of the dimethoxymethyl group; 77.2 ppm coincides with the solvent signal and is not counted
Beghennou et al. 2024; 6, a second 1-(tri-O-acetyl-β-D-ribofuranosyl)-1,2,3-triazole, printed as "(2R,3R,4R,5R)-2-(4-	^{13}C: "170.7, 169.8, 169.7, 153.6, 150.7, 147.8, 136.1, 135.3, 131.5, 130.5, 129.3, 126.8, 123.5, 119.4,	no	90.5 ppm read here as C-1′, and 101.2 ppm as the acetal carbon of the dioxolane ring;

Source; compound; place	As printed	Assigned in the source?	Used here for
(4-((3-(1,3-dioxolan-2-yl)pyridin-2-yl)(cyano)methyl)phenyl)-1H-1,2,3-triazol-1-yl)-5-(acetoxymethyl)tetrahydrofuran-3,4-diyl Diacetate"; Experimental	101.2, 90.5, 81.4, 74.7, 71.17, 65.8, 65.7, 63.2, 60.8, 47.7, 21.1, 20.9, 20.8, 14.6."		the other sugar carbons are not separated from further oxygenated carbons of the molecule and are not used
Bdour et al. 2006; 4, [3-^{15}N]-3′,5′-di-O-acetylthymidine; Experimental	"1H NMR (300 MHz, CDCl3) δ 1.94(s, 3H, C5CH3), 2.12(s, 3H, OCOCH3), 2.14(s, 3H, OCOCH3), 2.18(m, 1H, H2′), 2.47(m, 1H, H2″), 4.24(m, 1H, H4′). 4.37(m, 2H, H5′ and H5″), 5.22(m, 1H, H3′), 6.33(t, J=7.1 Hz, 1H, H1′), 7.28(s, 1H, ArH), 8.95(d, J = 90.6 Hz, 1H, 15NH)". "13C NMR (75.4 MHz, CDCl3) δ 12.0, 20.3, 20.4, 36.8, 64.1, 74.7, 82.2, 85.0, 110.8, 135.8, 150.9, 164.0, 170.4"	^{1}H yes; ^{13}C no	reference pattern of a 3,5-di-O-acetyl-2-deoxy-β-D-ribofuranosyl N-nucleoside. Read here: 85.0, 82.2, 74.7, 64.1 and 36.8 ppm as the sugar carbons
Weigert and Roberts 1971; abstract	the carbon–fluorine coupling constants of fluorobenzene are given as −245.3 Hz (one bond), +21.0 Hz (two bonds), +7.7 Hz (three bonds) and +3.3 Hz (four bonds); values transcribed, the coupling symbols of the abstract are not reproduced	yes	one-bond, two-bond and four-bond C–F couplings of an aryl fluoride (audit item A7; Tables S16 and S19)
Ahmed et al. 2019; abstract	"A series of 4-arylhydrazono-5-trifluoromethyl-pyrazolones, their ribofuranosyl, and 5'-deoxyribofuranosyl nucleosides were synthesized"	—	precedent for ribofuranosyl nucleosides of the scaffold (article, Section 1). No spectroscopic value is taken from this source
Khalil 2009; title	"… novel 4-arylhydrazono-5-trifluoromethyl-2,4-dihydropyrazol-3-ones, their N- and N,O-bis-β-D-glucosides"	—	precedent for O-glycosylation within N,O-bis-glucosides (article, Section 1). Only the bibliographic record was consulted; no value is taken from this source
Chen et al. 2009; title	"X-ray structure of 1,3,4-tri-O-acetyl-2-deoxy-β-D-erythro-pentopyranose"	—	existence of the crystalline pyranose triacetate of 2-deoxy-D-ribose. Only the bibliographic record was consulted; no statement about product ratios on acetylation is made from it

S12 Reading of the *Reasoning* field of the 36 NMR-added responses

One question was put to the complete text of each of the 36 NMR-added responses (`response` column of `results_api.csv` in the deposit): does the response give the aryl carbon near 104 ppm (104.09 ppm in 117a, 103.80 ppm in 122a, 103.83 ppm in 123a) as the anomeric carbon? For a committed response the decision is "yes, in the field" if the *Decisive evidence* field does so; "yes, in the Reasoning field" if the field does not and another part of the response does; "no" if the response gives another signal as the anomeric carbon,

assigns the signal near 104 ppm to the aglycone, or states that the anomeric carbon cannot be observed; and "no anomeric carbon discussed" if the response argues without reference to an anomeric carbon. The one abstention is entered as "abstained"; it discusses no anomeric carbon. Table S24 gives the decision for every response with the sentence on which it rests, quoted verbatim, and the part of the response in which the sentence stands. A first reading was prepared with the AI assistant of Section 2.6 of the article; every quoted sentence was verified by script to occur verbatim in the deposited response. The assistant then repeated the reading twice (1 October 2026), in two separate sessions. Each session received only the 36 complete responses, under random identifiers and in a random order, with the rule above written out as four categories, and was instructed to open no other file; it was given neither the first decisions nor the names of the systems. Each returned a category for every response, with a sentence of the response quoted verbatim. Both repetitions returned the category of the first reading for all 36 responses, including the place of the statement. One session marked gpt-5 `binary_PX-B02` r1 as open to another category (its field gives "~103.9 ppm"; the statement is in the field or elsewhere, a yes in either case), and both marked Gemini `binary_PX-B02` r3 (the anomeric carbon is mentioned only in its *Limitations* field, as not observable; "no" or "no anomeric carbon discussed", not a yes in either case). Neither bears on the count of 19. The repetitions were made by the same assistant; they are a check of consistency and neither a human check nor an independent coding. The file of the two repetitions (`reasoning_rereadings_ai.csv`) and the blind packet are in version 1.1.0 of the deposit and in Supporting File 6. H.A.A. checked every decision against the response. Each decision was put to her with the complete response and with the sentence on which it rests, so her check is a confirmation of the recorded decisions and not an independent coding; she declares that she made it without having looked at the codings returned by the second coders (Section S14). She agreed with 35 of the 36 decisions as recorded. For the abstention (gpt-5 `binary_PX-A02` r2), for which the four categories of a committed response were offered to her, she entered "no anomeric carbon discussed", which is what the entry says of that response. The entry "abstained" records that the response gives no classification; the coding file was left as it is, and no count changes. The judgement was coded a second time by coder A, who had not seen this reading (Section S14). The reading answers this one question and is not a coding of the *Reasoning* field in any other respect; the statements about two-dimensional spectra reported in Section 3.4 of the article were found by searching the responses concerned for "HSQC" and "HMBC" and reading the sentences found. In two decisions the quoted sentence does not itself contain the word anomeric and the reading rests on an earlier sentence of the same passage, which introduces the anomeric carbon (Gemini `binary_PX-B01` r2 and `binary_PX-B02` r2); these are two of the five responses on which coder A decided otherwise (Table S30). For the three single-case Gemini responses on 122a the value 103.80 ppm stands alone in the field and is called the anomeric carbon in the *Reasoning* field.

Table S24. Does the response give the aryl carbon near 104 ppm as the anomeric carbon? Decision for each of the 36 NMR-added responses, with the sentence on which it rests.

Condition	System	Rep.	Decision	Where	Sentence on which the decision rests (verbatim)
binary_PX-A01	gpt-5	r1	yes, in the field	Decisive evidence	"13C NMR shows the anomeric carbon at 104.09 ppm"

Condition	System	Rep.	Decision	Where	Sentence on which the decision rests (verbatim)
binary_PX-A01	gpt-5	r2	yes, in the field	Decisive evidence; Limitations mention 84.4 ppm as possibly misassigned	"The 13C NMR shows a single anomeric carbon at 104.09 ppm"
binary_PX-A01	gpt-5	r3	yes, in the field	Decisive evidence; Reasoning lists 104.1 and 84.4 among the sugar carbons	"13C NMR shows a single deshielded anomeric carbon at ~104.1 ppm"
binary_PX-A02	gpt-5	r1	no	Reasoning	"The most downfield sugar carbon at 90.2 ppm must be C1′"
binary_PX-A02	gpt-5	r2	abstained	Decisive evidence (abstention; no anomeric-carbon value anywhere in the response)	"No unambiguous HMBC connectivity to identify which heteroatom of the base is glycosylated"
binary_PX-A02	gpt-5	r3	no	Decisive evidence	"13C NMR shows the anomeric carbon at ~90.2 ppm"
binary_PX-B01	gpt-5	r1	no anomeric carbon discussed	Reasoning argues from carbonyl counting; no anomeric carbon	"an additional carbonyl-type signal at 164.3 ppm"
binary_PX-B01	gpt-5	r2	no	Decisive evidence	"the 13C spectrum shows an anomeric carbon at ~78.5 ppm"
binary_PX-B01	gpt-5	r3	no	Reasoning; the anomeric carbon is placed at ~88.6 ppm, a value with no counterpart	"no HSQC correlation appears near 103–105 ppm"
binary_PX-B02	gpt-5	r1	yes, in the field	Decisive evidence	"13C NMR shows a distinct resonance at ~103.9 ppm, diagnostic for an anomeric carbon bonded to two oxygens"
binary_PX-B02	gpt-5	r2	yes, in the field	Decisive evidence	"13C NMR shows the anomeric carbon at ~103.8 ppm"
binary_PX-B02	gpt-5	r3	yes, in the field	Decisive evidence	"The anomeric carbon appears at 103.8 ppm in the 13C NMR"
binary_PX-A01	Gemini	r1	no	Reasoning: 104.09 assigned to the aryl ring; 84.39 given as C-1″	"The peak observed at 104.09 ppm is perfectly consistent with the C2 aromatic carbon of the 3-fluorophenyl ring"
binary_PX-A01	Gemini	r2	no	Reasoning	"the anomeric carbon (C-1″) appears at 84.39 ppm"
binary_PX-A01	Gemini	r3	no	Limitations: the peak above 100 ppm is explicitly not taken as C-1″	"it unambiguously falls within the 60-85 ppm cluster rather than the isolated peak at >100 ppm"
binary_PX-A02	Gemini	r1	no	Reasoning	"The provided 13C NMR spectrum shows the anomeric carbon at 90.2 ppm"
binary_PX-A02	Gemini	r2	no	Reasoning: the aryl signal of 116a (107.7) is explicitly excluded	"corresponds to this 90.2 ppm peak, not the further downfield peak at 107.7 ppm"
binary_PX-A02	Gemini	r3	no	Reasoning	"The chemical shift of 90.2 ppm for C1' is highly characteristic of an N-glycosidic linkage"
binary_PX-B01	Gemini	r1	yes, in the Reasoning field	Reasoning (the field cites 103.80 alone)	"The chemical shift at 103.80 ppm is characteristic of an anomeric carbon in an O-glycoside"
binary_PX-B01	Gemini	r2	yes, in the Reasoning field	Reasoning, in a passage on the anomeric carbon (C1') (the field cites 103.80 alone)	"The observed peak at 103.80 ppm is strongly indicative of an O-glycosidic linkage"
binary_PX-B01	Gemini	r3	yes, in the Reasoning field	Reasoning (the field cites 103.80 alone)	"The 13C NMR chemical shift at 103.80 ppm is highly characteristic of an acetal anomeric carbon (O-C-O)"
binary_PX-B02	Gemini	r1	no	Reasoning	"all peaks above 100 ppm can be neatly assigned to the aromatic ring"
binary_PX-B02	Gemini	r2	yes, in the Reasoning field	Reasoning, in a passage on the C1' signal (the field names the anomeric carbon without a value)	"The provided 13C NMR spectrum shows a distinct peak at 103.8 ppm and a completely flat baseline in the 80–95 ppm region, clearly indicating an O-glycosidic linkage"
binary_PX-B02	Gemini	r3	no	Limitations: no value given for the anomeric carbon	"A complete 13C NMR spectrum is not provided, which prevents the explicit observation of the anomeric carbon"
pairedfull_ribose	gpt-5	r1	yes, in the field	Decisive evidence	"Compound 2 shows C-1′ at ~104 ppm"

Condition	System	Rep.	Decision	Where	Sentence on which the decision rests (verbatim)
pairedfull_ribose	gpt-5	r2	yes, in the field	Decisive evidence	“Compound 2 has C-1′ at ~104.1 ppm”
pairedfull_ribose	gpt-5	r3	yes, in the field	Decisive evidence	“Compound 2 shows C-1′ ≈ 104 ppm”
pairedfull_deoxy	gpt-5	r1	no anomeric carbon discussed	Reasoning mentions anomeric protons only	“the anomeric H in Compound 2 appears slightly more downfield (~5.5 ppm) than in Compound 1 (~5.1 ppm)”
pairedfull_deoxy	gpt-5	r2	yes, in the field	Decisive evidence	“In Compound 1 the 13C NMR shows a C-1′ at ~103.8 ppm (HSQC shows it is a CH)”
pairedfull_deoxy	gpt-5	r3	no anomeric carbon discussed	Reasoning (carbonyl argument only)	“Only Compound 2 exhibits the extra amide carbonyl”
pairedfull_ribose	Gemini	r1	yes, in the Reasoning field	Reasoning (no value in the field)	“Compound 2 exhibits its anomeric carbon at 104.1 ppm”
pairedfull_ribose	Gemini	r2	yes, in the Reasoning field	Reasoning (no value in the field)	“Compound 2 has a C-1’ signal at 104.09 ppm”
pairedfull_ribose	Gemini	r3	yes, in the Reasoning field	Reasoning (no value in the field)	“The 13C NMR of Compound 2 shows it at 104.1 ppm”
pairedfull_deoxy	Gemini	r1	yes, in the Reasoning field	Reasoning (the field names anomeric-carbon shifts without values)	“Compound 1 has an anomeric 13C NMR signal at 103.80 ppm (confirmed by HSQC)”
pairedfull_deoxy	Gemini	r2	no anomeric carbon discussed	Reasoning (infrared argument only)	“only Compound 2 shows the additional C=O stretch at ~1680 cm-1”
pairedfull_deoxy	Gemini	r3	yes, in the Reasoning field	Reasoning (the field gives anomeric protons only)	“The HSQC of Compound 1 also confirms an O-glycosidic anomeric carbon at 103.8 ppm”

Counts: 19 of the 35 committed responses give the aryl carbon as the anomeric carbon: 10 in the field (gpt-5 10, Gemini 0) and 9 in the *Reasoning* field (gpt-5 0, Gemini 9); 12 do not, and 4 discuss no anomeric carbon; one response abstains. By system: gpt-5 10 of 17, Gemini 9 of 18.

S13 Properties of the stimulus images as supplied

The 41 deposited images were inspected for this article on 30 September 2026, after the responses had been collected and coded. The inspection was made with the AI assistant of Section 2.6 of the article, by viewing the images and by measuring pixel positions in them. H.A.A. checked eight statements of this description against the images, which were shown to her as embedded in a review file. The statements, as put to her: (1) HSQC panel of 122a: “The panel shows the ^{1}H projection, with the proton labels 3″ and 4″ legible, and an empty contour region; no cross-peak is visible.”; (2) ^{13}C panel of 123a: “The panel shows 96–172 ppm and an inset of the solvent signal only; most labels are cut off at the upper edge, those of 112.673 and 103.831 ppm are complete; the inset carries the labels 77.205 and 76.499 ppm; no other sugar carbon is displayed.”; (3) ^{13}C panel of 122a: “The labels 78.54, 68.56, 67.09 and 66.13 ppm are displayed; the expansion ends near 35 ppm, so the line at 29.69 ppm is not displayed.”; (4) Candidate drawings of the ribose pair: “Candidate A (N2-riboside) is drawn in the hydrazone–lactam form, with the 2″-O-acetyl group drawn over the ring carbonyl group; candidate B (O-riboside) is drawn as the 4-hydrazono-4H-pyrazole tautomer, so both drawings show a hydrazone N–H.”; (5) Candidate drawings of the 2-deoxy pair: “Both candidates are drawn with a furanosyl (five-membered) sugar ring.”; (6) Infrared panel of 122a: “The band labelled 1646.32 cm^{-1} has an unlabelled

shoulder on its high-wavenumber side, at about 1665–1680 cm^{-1}; no band is labelled between 1670 and 1690 cm^{-1}."; (7) Infrared panel of 116a: "No band is labelled between 1670 and 1690 cm^{-1}. The trace falls from about 1690 cm^{-1} to the band labelled 1639.05 cm^{-1} without a level part, but the upper part of this flank (about 1673–1686 cm^{-1}) is less steep than the part below it."; (8) gHMBC panel of 117a: "The first row of cross-peaks below the row annotated C-1″ has two cross-peaks; both lie in the columns of aromatic protons, and none lies in the columns of the sugar protons." She confirmed seven as written. On statement 2 she wrote: "The inset shows the solvent region, including the solvent triplet and the additional labelled lines at 77.205 and 76.499 ppm, rather than the solvent signal only." The description was reworded accordingly (Section 2.3 of the article; Table S25). Statement 7 was put to her with the information that both second coders had reported a shoulder there. She did not check the other entries of Table S25 or the measurements reported after it, except the row of cross-peaks below the row annotated C-1″ in the gHMBC figure of 117a (two cross-peaks in the columns near 7.18 and 6.98 ppm, none near 7.39 or 7.27 ppm or in the columns of the sugar protons, the row of C-1″ in the column of a sugar proton, and the row at about 104 ppm on the printed axis of the complete figure), which she compared with the figure of the source and found as stated (check sheet of 18 October 2026). The two second coders answered six questions on what the spectra of each compound display without having seen this description (Section S14, Table S27); where both differ from it, this is stated below. Table S25 summarises what each group of images displays; the observations that bear on the results follow.

Table S25. What the stimulus images display.

Images	Identifier in the image	Displayed
`candidates_ribose.png`, `candidates_deoxy.png`, `candidates_benzoyl.png`	the captions "Candidate A" and "Candidate B"	two structure drawings. In the two glycoside files the N2-glycoside is drawn in the hydrazone–lactam form and the O-glycoside as the 4-hydrazono-4*H*-pyrazole tautomer (exocyclic C=N–NH–aryl). In `candidates_ribose.png` the 2″-O-acetyl group of candidate A is drawn over the ring carbonyl group
`PX-*_IR.png` (single case)	none	infrared trace with the peak labels of the source; about 1950–1030 cm^{-1} for the four glycosides; axis ticks without labels except 1500
`ribose_spectrum1/2.png`, `deoxy_spectrum1/2.png`, `benzoyl_spectrum1/2.png`	heading "Spectrum 1" or "Spectrum 2"	the same infrared images under the heading
`full_*_IR.png`	band "Compound 1 · IR" or "Compound 2 · IR"	the same infrared images under the band
`PX-*_1H.png`; `full_*_1H.png`	band with the file stem; band "Compound n · ^{1}H NMR"	^{1}H spectrum with peak labels and printed integrals, an expansion of part of the spectrum (for 117a 6.1–4.3 ppm; for the other three the aromatic and sugar region), and an inset of the low-field proton
`PX-A01_13C.png` (117a), `PX-A02_13C.png` (116a), `PX-B01_13C.png` (122a); `full_*` counterparts	as above	^{13}C spectrum or expansion from about 172 ppm to below 40 ppm with peak labels, including the oxygenated sugar carbons (for 116a the labels are displayed and the lower part of the trace is cut off; for 122a the expansion ends near 35 ppm, so C-

Images	Identifier in the image	Displayed
		2″ at 29.69 ppm is not displayed)
`PX-B02_13C.png` (123a); `full_deoxy_C2_13C.png`	as above	expansion from 172 to 96 ppm and an inset of the solvent region with the labels 77.319, 77.000 and 76.689 (the solvent triplet) and 77.205 and 76.499 (two further lines). Most peak labels of the expansion are cut off at the upper edge: “16” and part of a third digit for 169.89, then “164.8”, “162.3”, “157.8”, “141.8”, “138.4”, “131.”, “123.4” and “114.4”; “112.673” and “103.831” are complete. No sugar carbon other than the two further lines of the inset is displayed
`PX-A01_HMBC.png`, `PX-A02_HMBC.png`; `full_ribose_C1/C2_HMBC.png`	as above	gHMBC contour plot with the ^{1}H projection, the proton labels 1″, 2″ and 3″ (116a) or 2″ and 3″ (117a), and the carbon labels C-1″ to C-5″ with their guide lines; no axis has a printed scale
`PX-B01_HSQC.png`; `full_deoxy_C1_HSQC.png`	as above	the ^{1}H projection with the proton labels of the source, of which 3″ and 4″ are legible (over the signals at 5.66 and 5.11 ppm), and the frame of the contour region. The contour region contains no contour

Identifier bands. The band is a dark blue strip 53 px high (single-case items) or 54 px high (paired NMR-added items) above the panel. Below the band, each `full_*` NMR image is identical, pixel for pixel, to the corresponding `PX-*` image, and each infrared image is identical in all presentations.

Infrared crops. In the four glycoside images the axis ticks are 90–95 px apart (mean 92–94 px per 100 cm^{-1}) and the tick printed 1500 lies 447–456 px from the left edge of a 924 px image, which places the left edge of the plot near 1950 cm^{-1} and the right edge near 1030 cm^{-1}; a truncated second axis label is visible at the right edge. On the tick scale the minima of labelled bands fall 1–6 cm^{-1} below their printed values (in 122a, 1741.47 at about 1737, 1646.32 at about 1645 and 1560.81 at about 1556 cm^{-1}), so the scale is good to about 5 cm^{-1} and reads low. In the trace of 122a the transmission falls steeply from about 1700 cm^{-1}, is nearly level over 10–12 px, and then falls to the minimum of the band labelled 1646.32 cm^{-1}. The level part lies at about 1665–1675 cm^{-1} on the tick scale and at 1670–1680 cm^{-1} on a scale fixed by the labelled bands of the same trace at 1741.47 and 1560.81 cm^{-1}. It is an unlabelled shoulder that cannot be placed outside the window of 1670–1690 cm^{-1}, within about 10 cm^{-1} of the band labelled 1679.91 cm^{-1} in 123a. The trace of 116a falls to its band at 1639 cm^{-1} without a level part, and the inspection of 30 September recorded no shoulder in it. Both second coders, however, answered that it has an unlabelled shoulder or band between 1655 and 1695 cm^{-1} (Table S27), and the trace was measured again after their returns (`measure_ir_flank.py`). From its maximum near 1689 cm^{-1} on the tick scale the transmission falls by 5 px for every 3 px of abscissa between about 1680 and 1673 cm^{-1} (1686–1679 cm^{-1} on a scale fixed at the labelled minimum of the band) and by 8–12 px for every 3 px from 1670 cm^{-1} down to about 1648 cm^{-1}. The flank is thus about half as steep in its upper part as below it; this change of slope is presumably the feature that the coders report, and the first inspection had not recorded it. Whether it is a separate absorption cannot be decided from the image. No response mentions either shoulder.

gHMBC panel of 117a. The annotated row of C-5″ (62.91 ppm) and that of C-1″ (84.39 ppm) are 62–66 px apart, which gives 2.9–3.1 px per ppm. The first row of cross-peaks below the

row of C-1″ lies 59–60 px below it, that is at 103.5–105.2 ppm on this linear scale; the only labelled carbon between 84.39 and 112.73 ppm is 104.09 ppm. The row has two cross-peaks, in the columns of the aromatic multiplets near 7.18 and 6.98 ppm, and none in the columns of the multiplets near 7.39 and 7.27 ppm or of H-1″, H-2″ and H-3″. The rows below it, at about 112–115, 130–134 and 140–145 ppm on the same scale, correspond to the labelled carbons at 112.73 and 114.26, 131.19 and 141.76 ppm and likewise have cross-peaks in the aromatic columns only. The row annotated C-1″ has its cross-peak in the column labelled 3″. The scale is a two-point linear calibration of an axis without printed values and is no more accurate than the range given. In the complete figure of the source the carbon axis carries printed values from 20 to 160 ppm and extends to about 172 ppm, and the row lies at about 104 ppm on it.

HSQC panel of 122a. The image measures 545 × 422 px. Below the ^{1}H projection, the framed contour region contains no pixel that differs from white (about 69 000 px examined in each of the two files). Figure 42 of the source, from which the panel was cropped, contains cross-peaks; the crop covers its upper left corner, and every cross-peak of the figure lies outside it (Section S15).

^{1}H panels: printed integrals. 122a: 1.02 (5.83 ppm, H-1″), 1.03 (5.66 ppm), 1.04 (5.11 ppm), 2.04 (3.94 ppm). 123a: 1.01 (5.519 and 5.491 ppm, H-1″), 1.03 (5.211 ppm), 1.04 (5.166 and 5.135 ppm), 0.99 (4.156 and 4.123 ppm), 1.02 (3.848 and 3.813 ppm), 0.99 (2.91–2.83 ppm). 117a: 1.01 (6.003 and 5.992 ppm, H-1″), 1.04 (5.70 ppm), 1.00 (5.53 ppm). 116a: 1.01 (6.009 and 6.002 ppm, H-1″), 1.07 (5.90 ppm), 1.06 (5.71 ppm).

Candidate drawings. Because the O-glycoside is drawn as the hydrazone tautomer, both candidates show an N–H on the hydrazone nitrogen; the presence of a low-field N–H proton therefore does not separate the two drawings; its shift bears on them, because an N–H at 13–14 ppm is reported for hydrazones chelated to the ring carbonyl of 2-substituted pyrazol-3-ones (Burgart et al. 2023; Table S23), an acceptor that the O-glycoside drawing lacks. The overlap in the drawing of candidate A of the ribose pair is recorded in a deposited, undated screenshot of a chat-interface probe (`screenshots/promt.png`), in which that drawing is described as containing a “cyclic carbonate/ester bridge”. Both drawings of the 2-deoxy pair show a furanosyl ring. Two gpt-5 responses to `singleIR_PX-A02` (r1 and r2) describe candidate A as containing a carbamate that links the sugar to the base; similar wording occurs in gpt-5 responses on the 2-deoxy pair, whose drawing has no overlap, so it cannot be attributed to the drawing.

Consequences for the record. (i) For 123a no response could cite a displayed sugar carbon other than the two further lines of the inset; one response (Gemini `pairedfull_deoxy` r1) gives 76.499 ppm as its anomeric carbon (by the original records the panel shows the spectrum of the compound whose ^{1}H spectrum is printed for 122a, and this line is the anomeric carbon of that compound; Section S16.3), and one (Gemini `binary_PX-B02` r2) reports “a completely flat baseline in the 80–95 ppm region”, a region that the panel does not display. (ii) Four responses report HSQC correlations of 122a (gpt-5 `binary_PX-B01` r3 and `pairedfull_deoxy` r2 in the field; Gemini `pairedfull_deoxy` r1 and r3 in the *Reasoning* field); the panel contains none; and the abstaining response gpt-5 `binary_PX-A02` r2 reports gHMBC correlations “from the anomeric region to several heteroaryl

carbons", whereas the panel of 116a has cross-peaks on the rows of C-5″, C-2″ and C-1″ only. (iii) The value "~168.5 ppm" flagged in gpt-5 `pairedfull_deoxy` r3 corresponds to a truncated label. (iv) For 122a the operational infrared feature is the absence of a labelled band; the trace has an unlabelled shoulder in the window, and that of 116a a change of slope there, which is presumably what both second coders reported. (v) The ^{13}C panels of 122a and 123a are crops of figures that the source prints with the wrong compound: by the original records the figure printed for 123a is the spectrum of the compound whose ^{1}H and HSQC spectra are printed for 122a, and the figure printed for 122a is attributed to the other compound (Sections S15 and S16.3). In the NMR-added items of this pair the ^{1}H and ^{13}C panels presented for a compound therefore do not come from one compound; this could not be seen in the panels supplied. None of these observations changes a code of Table S9.

S14 Second coding

Two chemists of the Department of Chemistry of United Arab Emirates University each received the same workbook (`Second-coder-workbook.xlsx`, built from the deposit by `build_simple_workbook.py` with seed 20261001; SHA-256 1ed9155335b1d220…), which H.A.A. sent by e-mail to both under the same invitation, within one day. The workbook and the script that builds it were prepared with the AI assistant of Section 2.6 of the article. They are called coder A and coder B here and in the article; whether the letters of the working files were kept or exchanged was settled by lot on 10 October 2026. At the request of one of them the returns are not attributed by name, and the sheet of the workbook that carries personal details is not deposited. Both had been invited as co-authors; after reading the manuscript both declined authorship, and they are thanked in the acknowledgments of the article, one of them, at his request, without his name. Neither had taken part in the design of the study, in the collection of the responses or in the first coding. Both are thanked, among the staff of the department, in the acknowledgments of the source; neither was a member of its advisory or examining committee. The workbook contains: the infrared and ^{13}C panels of the four compounds, the two-dimensional panel of three of them and the candidate drawings, as supplied to the systems (the ^{1}H panels were not included); the 72 *Decisive evidence* fields and the 36 complete NMR-added responses, under random identifiers and without the names of the systems; and the two coding rules, which restate those of Sections S4.6 and S12 in the wording of the workbook. The first coding, the counts and the text of the article were withheld. The workbook sets three tasks: six questions on what the spectra of each compound display (Task 1), the naming of the infrared feature in the 72 fields (Task 2), and the question on the signal near 104 ppm in the 36 NMR-added responses (Task 3). In the workbook each coder declared that he did the three tasks himself without an AI tool, had not seen the manuscript, its results or the first coding, had not discussed individual rows with the first coder, and had not seen the spectra or the compounds before. All returns are reported here as received. The answers, comments and declarations of every return are given as tables in Supporting File 5 (`task1_answers.csv`, `task2_three_returns.csv`, `task3_three_codings.csv`, `declarations.csv`), with the workbook as sent; the returned workbooks themselves carry personal details and are kept by the corresponding author. The returns were read, compared with the workbook as sent and with the first coding, and tabulated by a script (`s14_real.py`, Supporting File 5)

prepared and run with the AI assistant of Section 2.6 of the article; the figures were recomputed from the returned workbooks by a second script written separately and without sight of the first (`recompute_second_coding.py`, Supporting File 5), with the same results, and that recomputation corrected one check of Task 3 (below): a response first counted as not containing the value of the signal contains it as 107.7 ppm, so that 15 responses with 14 answers "yes" became 14 with 13. A third script recomputes the figures from the deposited tables (`recompute_from_tables.py`). The sheet with personal details also holds each coder's wish as to naming and, from one coder, a request to check whether the relation of the study to the supervisors of the thesis is a conflict of interest; that request is answered in the Notes of the Author Information of the article.

Table S26. The returns of the second coding.

Return	Date completed in the file	Received	SHA-256 (first 16 characters)	Cells left unanswered	Changes against the previous return
Coder A, first return	2026-10-05	2026-10-08	1b2fee0cef453fd4	Task 2: R014; Task 1: PX-B02, question 4	—
Coder A, second return	2026-10-05 (not changed)	2026-10-08	6e8662dd9e46532f	Task 1: PX-B02, question 4	Task 2: R014: unanswered → yes; R024: no → yes; R070: no → yes. Task 1, PX-B02, question 5: "cannot tell" → "anomeric (sugar) carbon". Task 3 and all comments unchanged. Affiliation added
Coder B	2026-10-09	2026-10-10	a6d6372578d037d1	Task 2: R037	—

No cell of the material as sent was altered in any return (cell-by-cell comparison with the workbook as sent). After the first return of coder A, H.A.A. sent him a message (8 October 2026) with three requests: to fill the two unanswered cells, one of which is the question on the anomeric carbon of PX-B02; to add his affiliation; and, on Task 2, the following (single quotation marks replace the double ones of the message): "Task 2. The check suggests that column D may have been answered as 'is what the AI system says correct?'. The question is narrower, and I see now that the sheet did not make this clear enough. It asks only whether the text in column C mentions the infrared band near 1680 cm^{-1} in one of the three ways (a) to (c) written at the top of the sheet, whether or not the statement is right, strong or well supported. A text that speaks only of NMR signals, or only of another band such as 1646 cm^{-1}, is 'no'. Could you go through column D of Task 2 once more on that basis, change only what needs changing, and leave your comments as they are? If you had already answered it in that sense, please tell me and change nothing." The message gave no code of the first coding and no result of a comparison; it did tell him, as quoted, how the pattern of his answers to Task 2 had appeared. H.A.A. had not opened the returned file; the completeness of the return and the pattern of the answers to Task 2 had been reported to her by the AI assistant, and the message says so. Coder B was sent no restatement and no other clarification before he returned his workbook.

A plan for the use of two second coders was written down on 9 October 2026, after the two returns of coder A and before the return of coder B was received. It had been drafted by the AI assistant and had not been formally adopted by H.A.A. when that return was opened. Its check for Task 2 (below) was applied as written. Its provision for Task 3, that every return is used and that the final entry is that of the majority of the three codings, did not foresee a

return that does not discriminate between the responses; both analyses are given below. It also provided that H.A.A. would record her own check of the 36 decisions before any row-by-row comparison of Task 3 was shown to her. The comparison was made by the AI assistant; H.A.A. declares that she made her check (Section S12) without having looked at the codings returned by the two coders. A copy of the plan, with one name removed and one wrong description replaced (both marked) and with a dated list of the points on which it was not followed, is in Supporting File 5. It is reproduced as written on 9 October 2026: its blank date field ("exact date to be entered by the author") and its references to sections of the article are those of the draft of that day (the section that it numbers 3.4 is Section 3.2 of the article, and the answers concerned are given in full in Section S18.2).

Task 1: what the supplied spectra display

The workbook asked each coder to answer, before coding, six questions on the panels of each compound (Table S27); neither coder had seen the description of the images given in Section S13. Of the 23 questions put (one cell is pre-filled), coder A answered 22 and 12 of his answers coincide with the statements of the article; coder B answered 23 and 18 coincide. In 5 of the 23 questions neither answer coincides with the article. One concerns the infrared trace of 116a: both coders report an unlabelled shoulder or band between 1655 and 1695 cm^{-1}, where the inspection of Section S13 had recorded none; the trace was measured again after the returns, and Section S13 gives the result. The other four concern the anomeric carbon. For 122a both coders marked the signal at 103.80 ppm as the anomeric carbon, and, asked which labelled value is the anomeric carbon, coder A typed 103.8 and coder B 103. For 123a coder B marked the signal at 103.83 ppm as the anomeric carbon (and answered "cannot tell" when asked for the value, as the article does); coder A answered "cannot tell" in his first return, with the comment "need more data to confirm", and "anomeric (sugar) carbon" in his second, which followed the request to complete the unanswered question on the anomeric carbon of this compound; he left that question unanswered in both returns. For 116a coder A named 107.672 ppm and coder B answered "cannot tell", where the article has 90.22 ppm. On the two ribosides the coders differ from each other: coder B named 84.39 ppm for 117a and marked the signals at 104.09 and 107.67 ppm as aromatic; coder A named 104.09 ppm for 117a and marked both signals as anomeric carbons. The article assigns all four signals to the aryl carbon C-2′, on the evidence given in its Section 3.2 (Tables S15 and S16); that evidence was not in the workbook. Besides these, coder A differs from the article in two answers on 123a: he answered that its infrared trace has no labelled band between 1670 and 1690 cm^{-1}, where the label 1679.91 is printed (coder B: yes), and he answered "yes" to the question whether labelled sugar carbons are displayed, with a comment that names the two inset lines; that comment agrees in substance with Section S13, and the answer is counted as not coinciding because the rule of comparison had been fixed beforehand. Three conditions limit what these answers show. The question on the signal named it and offered "aromatic (aglycone) carbon", "anomeric (sugar) carbon" and "cannot tell". The workbook asked for Task 1 to be done first, but the order in which the coders worked was not recorded, and the same file contained the 36 responses, 19 of which make the identification. The ^{1}H panels were not in the workbook.

Table S27. What the supplied spectra display: answers of the two second coders beside the statements of the article (Sections 2.3, 3.1 and 3.2 of the article; Sections S13, S17.2 and S17.3). Answers of coder A are those of his second return; the one answer that differs from his first return is marked. For question 4 on PX-B01 (122a) the value 78.54 ppm is the one listed as C-1″ in the source and labelled in the panel, and no supplied panel identifies it as the anomeric carbon, so that 78.54 and "cannot tell" both coincide with the article.

Compound	Question	Coder A	Coder B	Article	Coincides: coder A / coder B
PX-A01 (117a)	Infrared: is there a LABELLED band between 1670 and 1690 cm-1?	yes	yes	yes	yes / yes
PX-A01 (117a)	Infrared: besides the labelled bands, do you see an unlabelled shoulder or band between 1655 and 1695 cm-1?	no	no	no	yes / yes
PX-A01 (117a)	13C: are labelled sugar carbons between 60 and 95 ppm displayed in the panel?	yes	yes	yes	yes / yes
PX-A01 (117a)	13C: which labelled value is the anomeric carbon (C-1 of the sugar)? Type the value in ppm, or: cannot tell	104.09	84.39	84.39	no / yes
PX-A01 (117a)	13C: the labelled signal at 104.09 ppm is …	anomeric (sugar) carbon	aromatic (aglycone) carbon	aromatic (aglycone) carbon	no / yes
PX-A01 (117a)	gHMBC panel: does it show cross-peaks (contours)?	yes	yes	yes	yes / yes
PX-A02 (116a)	Infrared: is there a LABELLED band between 1670 and 1690 cm-1?	no	no	no	yes / yes
PX-A02 (116a)	Infrared: besides the labelled bands, do you see an unlabelled shoulder or band between 1655 and 1695 cm-1?	yes	yes	no	no / no
PX-A02 (116a)	13C: are labelled sugar carbons between 60 and 95 ppm displayed in the panel?	yes	yes	yes	yes / yes
PX-A02 (116a)	13C: which labelled value is the anomeric carbon (C-1 of the sugar)? Type the value in ppm, or: cannot tell	107.672 ppm	cannot tell	90.22	no / no
PX-A02 (116a)	13C: the labelled signal at 107.67 ppm is …	anomeric (sugar) carbon	aromatic (aglycone) carbon	aromatic (aglycone) carbon	no / yes
PX-A02 (116a)	gHMBC panel: does it show cross-peaks (contours)?	yes	yes	yes	yes / yes
PX-B01 (122a)	Infrared: is there a LABELLED band between 1670 and 1690 cm-1?	no	no	no	yes / yes
PX-B01 (122a)	Infrared: besides the labelled bands, do you see an unlabelled shoulder or	yes	yes	yes	yes / yes

Compound	Question	Coder A	Coder B	Article	Coincides: coder A / coder B
	band between 1655 and 1695 cm-1?				
PX-B01 (122a)	13C: are labelled sugar carbons between 60 and 95 ppm displayed in the panel?	yes; comment: "The range is between 60 and 80 pmm to be more precise"	yes	yes	yes / yes
PX-B01 (122a)	13C: which labelled value is the anomeric carbon (C-1 of the sugar)? Type the value in ppm, or: cannot tell	103.8	103	78.54 is the value listed as C-1″ in the source and labelled in the panel; no supplied panel identifies this signal as the anomeric carbon	no / no
PX-B01 (122a)	13C: the labelled signal at 103.80 ppm is …	anomeric (sugar) carbon	anomeric (sugar) carbon	aromatic (aglycone) carbon	no / no
PX-B01 (122a)	HSQC panel: does it show cross-peaks (contours)?	no; comment: "The HSQC is not clear. 13C peaks are too weak and indiscernable"	no	no	yes / yes
PX-B02 (123a)	Infrared: is there a LABELLED band between 1670 and 1690 cm-1?	no	yes	yes	no / yes
PX-B02 (123a)	Infrared: besides the labelled bands, do you see an unlabelled shoulder or band between 1655 and 1695 cm-1?	no	no	no	yes / yes
PX-B02 (123a)	13C: are labelled sugar carbons between 60 and 95 ppm displayed in the panel?	yes; comment: "there are only two peaks corresponding to the sugar carbon at 76.499 and 77.205. A complete 13C would be useful (0 to 220 ppm)"	no	no	no / yes
PX-B02 (123a)	13C: which labelled value is the anomeric carbon (C-1 of the sugar)? Type the value in ppm, or: cannot tell	not answered	cannot tell	cannot tell	not answered / yes
PX-B02 (123a)	13C: the labelled signal at 103.83 ppm is …	anomeric (sugar) carbon (first return: cannot tell); comment: "need more data to confirm."	anomeric (sugar) carbon	aromatic (aglycone) carbon	no / no
PX-B02 (123a)	Two-dimensional panel	(pre-filled: no panel supplied)	(pre-filled: no panel supplied)	no panel supplied	—

Task 2: naming of the infrared feature

One check, which does not use the first coding, decides whether a return is a coding of the rule. Twenty-six of the 72 fields contain no reference of any kind to the infrared spectrum (none of: IR, infrared, cm^{-1}, absorption, band, carbonyl, C=O, lactam, amide I, "Spectrum 1" or "Spectrum 2"); under the written rule each of them is "no". A return counts as a coding of the rule if at most two of the 26 are answered "yes". None of the three returns meets this condition (Table S28).

Table S28. Task 2 in the three returns. The last four columns compare each return with the first coding and are given for the record; they are not measures of the reliability of the rule.

Return	Fields answered	Answered "yes"	Of the 26 fields without any reference to the infrared spectrum: yes / no / unanswered	Agrees with the first coding	Cohen's κ	First yes, return yes / first yes, return no	First no, return yes / first no, return no
Coder A, first return	71	63	21 / 4 / 1	37 of 71	0.01	33 / 4	30 / 4
Coder A, second return	72	66	23 / 3 / 0	37 of 72	0.00	34 / 3	32 / 3
Coder B	71	70	25 / 0 / 1	36 of 71	−0.03	36 / 1	34 / 0

In the first coding the feature is named in 37 of the 72 fields. The comments entered by coder A judge the statements of the systems and not what they name: "The conclusion is fine." (`singleIR_PX-B02`, gpt-5 r3); "What is the question here?" on the field "13C NMR signal at 103.80 ppm." (`binary_PX-B01`, Gemini r1); and "it is not strong" on the field "The strong absorption band at 1680.47 cm^{-1}.", answered "no" in the first return and "yes" in the second. Coder B answered "yes" to all but one of the 71 fields he answered (the exception is the field "1H NMR NH signal at 13.5 ppm and IR band at 1679 cm-1.", with the comment "I don't see 1H NMR spectrum"). Neither coder's answers can be read as an application of the written rule. The layout of the sheet, a short column heading under a rule set in one long line, may have contributed; the restatement sent to coder A did not change the pattern of his answers, and the reason was not established. This is reported as a failure of the second coding of this task, and not as a measure of the rule or of the coders. No second coding of the naming of the infrared feature was therefore obtained. The counts of Section 3.3 of the article rest on the first coding and on the rule published as a script (Supporting File 3), which returns the outcome of the first coding for all 72 fields.

Task 3: the signal near 104 ppm given as the anomeric carbon

The coding of coder A agrees with the first coding in 31 of the 36 responses on yes or no (Cohen's κ = 0.72) and in 28 of 36 when the place of the statement is included (κ = 0.64; Table S29a). In his coding the signal is given as the anomeric carbon in 16 of the 35 committed responses, against 19 in the first coding. On yes or no the two codings agree on 15 responses with yes and 16 with no; the first coding alone answers yes for 4 responses and coder A alone for 1, so that the proportions of positive and of negative agreement are both 0.86. In the 14 responses in which no value of the signal occurs (next paragraph) both codings answer no; on the other 22 they agree on 17 (κ = 0.32), so that the κ of 0.72 owes much to the responses in which no value of the signal occurs. Resampling the twelve system–item cells with replacement (10 000 samples drawn with `random.choices` of the Python standard library, seed 1, the twelve cells in their order of first appearance in `task3_three_codings.csv`; percentile intervals) gives 95% intervals of 0.50–0.89 for κ on yes or no over all 36 responses and of −0.13 to 0.73 for κ over the 22 responses in which a value of the signal occurs. These figures were computed with the assistant from `task3_three_codings.csv` (Supporting File 5).

The return of coder B gives "yes, in the field" for 34 of the 36 responses and "no" for 2; the middle category is not used (Table S29b). A check that does not use the first coding was introduced on 10 October 2026, after this return had been seen: in 14 of the 36 responses no value of the signal (104.09, 103.80, 103.83 or 107.67 ppm, in any rounding) occurs anywhere in the text; these responses give another signal as the anomeric carbon, assign

the signals above 100 ppm to the aglycone, or discuss no anomeric carbon. Coder B answered “yes” for 13 of these 14; coder A and the first coding for none. The return of coder B does not discriminate between the responses and cannot be read as a coding of the written question (agreement with the first coding on yes or no: 19 of 36, κ = 0.01; with coder A: 16 of 36, κ = −0.01; Fleiss’ κ for the three codings: 0.16). Why the question was not conveyed to this coder is not known.

Table S29. Task 3, first coding against the second coders. (a) Coder A. (b) Coder B.

a

First coding ↓ / second coding →	yes, in the field	yes, elsewhere in the response	no
yes, in the field	8	1	1
yes, elsewhere in the response	2	4	3
no	0	1	16

b

First coding ↓ / second coding →	yes, in the field	yes, elsewhere in the response	no
yes, in the field	10	0	0
yes, elsewhere in the response	8	0	1
no	16	0	1

The two analyses. By the majority of the three codings, as the plan of 9 October provided, the signal is given as the anomeric carbon in 20 of the 35 committed responses, and the final entry differs from the first coding in 1 response; because coder B answered “yes” almost throughout, this majority is in effect the rule “yes wherever the first coding and coder A differ”. Without the return of coder B, which is the analysis adopted in the article after that return had been seen, the two codings stand side by side: 19 of 35 in the first coding and 16 of 35 in that of coder A. They differ on yes or no in 5 responses and on the place only in 3 (Table S30). Of the 5, in three the response states the matter in so many words (two give the signal as the anomeric carbon, one assigns it to the aryl ring), and in two the response makes the identification by implication, the quoted sentence not containing the word anomeric and an earlier sentence of the same passage introducing the anomeric carbon. These two are the decisions noted in Section S12 as resting on an earlier sentence of the same passage; without them the first coding gives 17 of 35. The differences were not discussed with coder A, and no entry of the first coding was changed: the counts of the article are those of the first coding.

Table S30. Task 3: the responses on which the first coding and the coding of coder A differ, with the sentence of the response on which the first coding rests (verbatim). The last column is the reading of the first coding.

Condition	System	Rep.	First coding	Coder A	Coder B	Sentence of the response	How the response puts it
`pairedfull_ribose`	Gemini	r1	yes, elsewhere in the response	no	yes, in the field	“Compound 2 exhibits its anomeric carbon at 104.1 ppm”	stated in so many words
`binary_PX-B02`	Gemini	r2	yes, elsewhere in	no	yes, in the	“The provided 13C NMR spectrum shows a distinct peak at 103.8 ppm and	by implication: the sentence before

Condition	System	Rep.	First coding	Coder A	Coder B	Sentence of the response	How the response puts it
			the response		field	a completely flat baseline in the 80–95 ppm region, clearly indicating an O-glycosidic linkage"	speaks of the C1′ signal
binary_PX-A01	Gemini	r1	no	yes, elsewhere in the response	yes, in the field	"The peak observed at 104.09 ppm is perfectly consistent with the C2 aromatic carbon of the 3-fluorophenyl ring"	the response assigns the signal to the aryl ring in so many words
pairedfull_ribose	gpt-5	r2	yes, in the field	no	yes, in the field	"Compound 2 has C-1′ at ∼104.1 ppm"	stated in so many words, in the field
binary_PX-B01	Gemini	r2	yes, elsewhere in the response	no	yes, in the field	"The observed peak at 103.80 ppm is strongly indicative of an O-glycosidic linkage"	by implication: the sentence before speaks of the anomeric carbon
binary_PX-B01	Gemini	r1	yes, elsewhere in the response	yes, in the field	yes, in the field	"The chemical shift at 103.80 ppm is characteristic of an anomeric carbon in an O-glycoside"	both codings: yes; they differ on the place only
pairedfull_ribose	gpt-5	r1	yes, in the field	yes, elsewhere in the response	yes, in the field	"Compound 2 shows C-1′ at ∼104 ppm"	both codings: yes; they differ on the place only
binary_PX-B01	Gemini	r3	yes, elsewhere in the response	yes, in the field	yes, in the field	"The 13C NMR chemical shift at 103.80 ppm is highly characteristic of an acetal anomeric carbon (O-C-O)"	both codings: yes; they differ on the place only

Remarks entered by the coders in Tasks 2 and 3 (verbatim, with the identifier of the row). Coder A, Task 2: "The conclusion is fine." (R001: singleIR_PX-B02, gpt-5 r3); "What is the question here?" (R003: binary_PX-B01, Gemini r1); "it is assigned to 3" according to the label on the HSQC" (R004: binary_PX-A01, Gemini r3); "There is a distinct peak at 103.9 ppm however it is not clear if it is the anonomeric carbon. A complete 13C spectrum should be provided." (R005: binary_PX-B02, gpt-5 r1); "I would qualify it as broad and weak." (R006: singleIR_PX-B01, Gemini r2); "Note IR alone should be used to distinguish between O and N glucoside." (R009: paired_ribose, gpt-5 r1); "it is clear" (R010: binary_PX-A02, gpt-5 r2); "although made I and amide II bands assignment look plausible, it cannot be used with certainty." (R013: singleIR_PX-B01, gpt-5 r1); "not clear. The full 13C NMR is required." (R015: binary_PX-B02, Gemini r2); "but there are other peaks 1600 cm-1 and less" (R016: singleIR_PX-B02, gpt-5 r2); "The first two sentences are correct." (R017: pairedfull_deoxy, gpt-5 r2); "although there is a shoulder in IR spectrum 1 which could correspond to 1679 cm-1" (R018: paired_deoxy, Gemini r3); "ir band is not strong but well defined" (R021: binary_PX-B02, Gemini r1); "it is not strong" (R024: singleIR_PX-A01, Gemini r3); "there is a shoulder which could be considered" (R025: singleIR_PX-A02, Gemini r1); "anomeric carbon is debatable" (R031: binary_PX-B02, gpt-5 r2); "but not strong" (R032: singleIR_PX-B02, Gemini r1); "1H nmr is not provided and cannot discern from the HSQC" (R035: pairedfull_deoxy, Gemini r3); "shoulder is present in compoound 1" (R039: pairedfull_deoxy, Gemini r2); "band at 1646 is not strong" (R040: singleIR_PX-B01, gpt-5 r3); "no 1h nmr provided" (R056: binary_PX-B02, Gemini r3); "no spectrum available in the 88-95 ppm" (R070: binary_PX-B02, gpt-5 r3); "hsqc does not display any data" (R072: binary_PX-B01, gpt-5 r3). Coder A, Task 3: "does not state exact ppm but approximate" (R050: pairedfull_ribose, gpt-5 r3). Coder B: "I don't see 1H NMR spectrum" (R056: binary_PX-B02, Gemini r3). Several remarks of coder A describe the supplied panels and agree with Section S13, which he had not seen: that the HSQC panel

displays no data, that a complete ^{13}C spectrum of 123a was not supplied, and that an infrared trace without the labelled band has a shoulder near it.

The check of every cited value against the value table (the 13 flagged fields of Section 3.2 of the article) and the consistency notes were not coded a second time. Ten of the 13 flags are the misidentification of the signal near 104 ppm in the *Decisive evidence* field, which Task 3 covers; the other three flags, the five consistency notes and the value table itself (Section S4.1) rest on the first coding alone.

S15 The text and figures of the source re-examined

After the evaluation the chemical part of the source (its Sections 2.2 and 2.3) and the figures of those sections were read again in full for this article (30 September 2026), including the spectra that had not been supplied to the models: the COSY and HSQC figures of 117a, the COSY figure and the complete HSQC figure of 122a, and the spectra of the sugar donor 121. The reading was made with the AI assistant of Section 2.6 of the article, which also repeated the reading of the cross-peak positions in separate passes; that repetition is not an independent check. H.A.A. compared four statements on the HSQC figure printed for 122a (Figure S3) with that figure in the source and found each as stated: (1) “The cross-peaks of the sugar protons lie at about 76.3, 66.5, 66.7, 63.3 and 31.1 ppm on the carbon axis. They agree within 0.3 ppm with lines labelled in the ^{13}C spectrum printed for 123a (76.50, 66.61, 63.54 and 31.28 ppm), and they do not agree with the sugar lines labelled in the ^{13}C spectrum printed for 122a (78.54, 68.56, 67.09, 66.13 and 29.69 ppm).”; (2) “The cross-peak of the proton at 5.83 ppm (H-1″) lies near 76.3 ppm, and not at 78.54 ppm, the value that the thesis lists as C-1″.”; (3) “The protons at 5.66 and 5.11 ppm have their cross-peaks near 66.6 ppm; the two protons at 3.94 ppm have theirs at 63.3 ppm; no cross-peak lies between 77 and 103 ppm.”; (4) “The cross-peak at 103.9 ppm lies in the column of an aromatic proton (7.27 ppm), not of a sugar proton.” The other positions of Table S31, the control of Table S32 and the statements of Table S33, except the one that she confirmed in the deposited file (below), were not checked by her; the statements of Table S33 were compared by script with the text of the final file of the thesis. Table S31 and Figure S3 give the positions of the cross-peaks in the HSQC figure printed for 122a, Table S32 a control on the HSQC figure of 117a, and Table S33 the statements of the source that the article uses, with their place in the source.

Files read. The text of the source was read in two files of the author: a PDF of 22 March 2017 and the final Word file of 13 May 2017. They agree in every passage used here except one value (H-5″b of 117a; audit item A13), and their HSQC images are identical, pixel for pixel, in the region they share. Figure and table numbers are those of the lists of figures and tables of the deposited PDF, whose captions are numbered one higher than in these two files from Figure 14 on; the body of the deposited PDF could not be read by the means used here. H.A.A. looked up three places of the deposited PDF and confirmed that its Figure 42 is the HSQC image of 122a shown in Figure S3, that its ^{1}H list of 117a gives H-5″b at 4.15 ppm, and that the “General” paragraph of its Section 2.2 names the KBr disc method for the infrared spectra and a Varian 400 MHz spectrometer for the NMR spectra. She also noted that a reference numbered 105, cited in the section of the deposited PDF on the synthesis of

the sugar, is missing from its reference list; which citation this is was not established here, and what this file says the source cites for the donor 121 (Table S33; audit item A14) is taken from the two files named above. On 10 October 2026 H.A.A. supplied screenshots of Figures 40, 42 and 46 of the deposited PDF (the ^{13}C and HSQC figures printed for 122a and the ^{13}C figure printed for 123a); read with the AI assistant, they carry the file names and peak labels of the corresponding figures in the two files named above, and the eleven cross-peaks of the HSQC figure lie at the same positions in the screenshot and in the figure of those files once the two images are brought to the same height and width (the figure is about 1.2 times taller relative to its width in the deposited file). The original spectrometer data that H.A.A. holds were supplied later and are described in Section S16; they do not include the HSQC spectrum of 122a or the ^{13}C spectra of 122a and 123a. Scans of spectrometer printouts of 2016 and processed files of 2014, found afterwards in her files, hold ^{1}H records of both samples of this pair and ^{13}C records of one of them (Section S16.3).

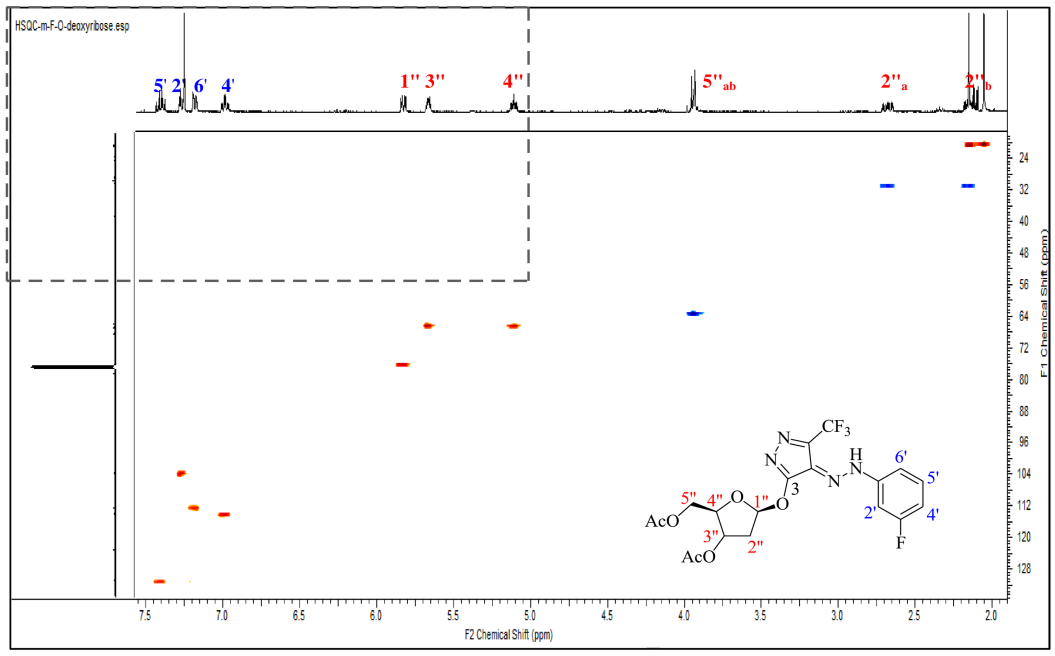
Method. Each HSQC spectrum was taken as the image embedded in the thesis file (1347 × 504 px for 122a in the PDF, which is the 1356 × 505 px image of the Word file less a margin; 781 × 536 px for 117a). For 122a this image is the spectrum alone, the structure drawing and the atom labels being separate objects on the page; for 117a it includes the drawing, the labels and the annotation lines. The axes were calibrated on two printed tick marks each (carbon axis: the ticks printed 24 and 128 ppm; proton axis: the ticks printed 7.5 and 2.0 ppm for 122a, and 7.0 and 2.0 ppm for 117a). Coloured contours were located as connected groups of red or blue pixels, and the position of a cross-peak is the centre of its bounding box. One pixel is 0.32 ppm (122a) or 0.30 ppm (117a) on the carbon axis and 0.005 or 0.009 ppm on the proton axis; with the width of the contours, a carbon position is good to about 0.5 ppm. The script used (`measure_hsqc.py`) and the scripts that draw Figures S3 and S4 (`make_2d_figures.py` and `locate_supplied.py`; `make_figS3.py` drew an earlier form of Figure S3) are in version 1.1.0 of the deposit and in Supporting File 6.

Table S31. Cross-peaks of the HSQC figure printed for 122a (Figure 42 of the source), read from the image, beside the carbon that the account of this spectrum in the source gives for each proton (which is the labelled line of the ^{13}C spectrum printed for 122a) and the nearest labelled line of the ^{13}C spectrum printed for 123a. Differences are measured minus labelled values.

^{1}H (ppm)	Proton, as labelled in the figure	^{13}C read (ppm)	Colour	Carbon in the account of the source; line of 122a (difference)	Nearest labelled line of 123a (difference)
7.41	5′	131.2	red	131.2; 131.21 (0.0)	131.23 (0.0)
7.27	2′	103.9	red	103.8; 103.80 (+0.1)	103.83 (+0.1)
7.19	6′	112.6	red	112.7; 112.68 (−0.1)	112.67 (−0.1)
6.99	4′	114.2	red	114.5; 114.45 (−0.3)	114.49 (−0.3)
5.83	1″	76.3	red	78.5; 78.54 (−2.2)	76.50 (−0.2)
5.66	3″	66.5	red	68.6; 68.56 (−2.1)	66.61 (−0.1)
5.12	4″	66.7	red	67.1; 67.09 (−0.4)	66.61 (+0.1)
3.93	5″a,b	63.3	blue	66.1; 66.13 (−2.8)	63.54 (−0.2)
2.68	2″a	31.1	blue	29.7; 29.69 (+1.4)	31.28 (−0.2)
2.16 (listed 2.10; the list has an acetyl singlet at 2.15)	2″b	31.1	blue	29.7; 29.69 (+1.4)	31.28 (−0.2)
2.12 and 2.04	acetyl CH_3	20.6	red	not given; 20.86 and 21.09 (−0.3, −0.5)	20.79 and 21.02 (−0.2, −0.4)

The aromatic and acetyl cross-peaks lie within 0.5 ppm of labelled lines, which the two spectra share at these positions. The six sugar cross-peaks (five carbons) lie 0.4 to 2.8 ppm from the carbons that the source gives for them, at four of the five carbons by 1.4 ppm or more, and all lie within 0.3 ppm of labelled lines of the spectrum printed for 123a. The result does not depend on the pairing: whichever labelled line of the spectrum printed for 122a is compared, the cross-peaks of H-1″, of the two H-5″ protons and of the H-2″ protons have none within 1.3 ppm, and the lines at 78.54 and 68.56 ppm have no cross-peak. On the positions as read, a single linear error of the carbon scale would not produce these deviations, which differ in sign and size while the aromatic cross-peaks fit; an error confined to the sugar region is not excluded by the figure. The carbon projection drawn at the left of the figure has small peaks at the labelled values of 122a (78.6, 68.6, 67.0, 66.1 and 29.8 ppm on the same calibration) and none near 63.5 ppm, and the sugar cross-peaks do not line up with them (Figure S3). The ^{13}C figure printed for 122a has no line, labelled or unlabelled, near 63.5 or 31.3 ppm.

a 122a, as printed



b sugar region enlarged; lines added

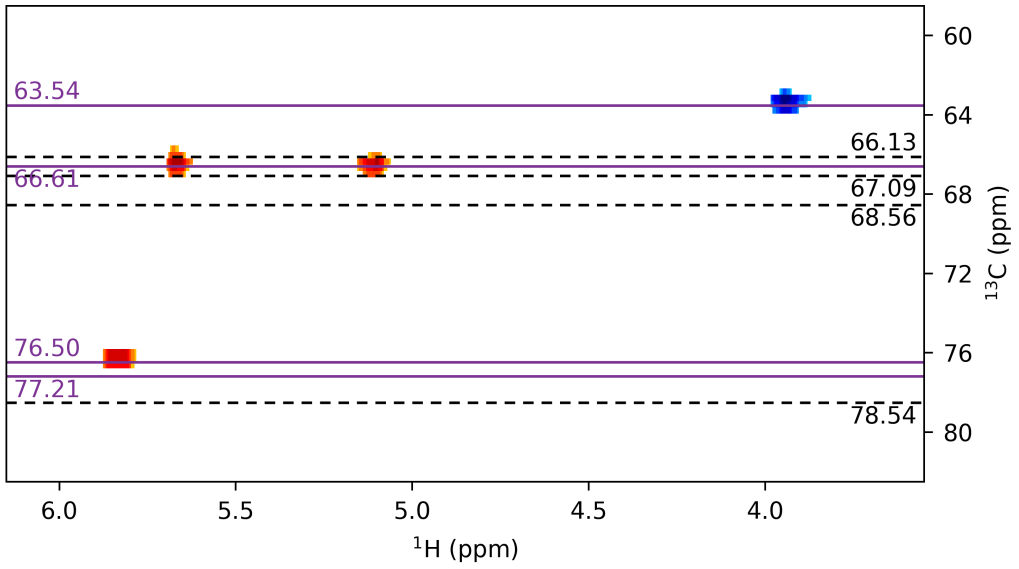


Figure S3. The HSQC spectrum printed for 122a in the source (its Figure 42). (a) The figure reproduced complete from the page of the thesis file, with the atom labels and the structure drawing of the source; the broken grey frame, added here, marks the part that was supplied to the models, which contains no cross-peak. (b) The region of the oxygenated sugar carbons, enlarged from the image embedded in the thesis file without redrawing, with axes computed from the printed tick marks. The lines of panel b are added here: broken black lines at the sugar lines labelled in the ^{13}C spectrum printed for 122a (78.54, 68.56, 67.09 and 66.13 ppm; its line at 29.69 ppm lies outside the region), continuous violet

lines at those labelled in the ^{13}C spectrum printed for 123a (77.21, 76.50, 66.61 and 63.54 ppm; its line at 31.28 ppm lies outside the region); the cross-peaks of H-1″ (5.83 ppm), H-3″ (5.66 ppm), H-4″ (5.12 ppm) and the two H-5″ protons (3.93 ppm) lie on the lines of the spectrum printed for 123a.

Table S32. Control: cross-peaks of the HSQC figure of 117a that its annotation lines leave uncovered, read in the same way.

^{1}H (ppm)	^{13}C read (ppm)	Labelled line of 117a (difference)	Annotation of the row in the source
7.28	104.0	104.09 (−0.1)	C-2′
7.20	112.8	112.73 (+0.1)	C-6′
7.00	114.3	114.26 (0.0)	C-4′
4.35	79.3	79.70 (−0.4)	C-4″

In that figure the source annotates the rows of C-1″ to C-5″ and of C-2′, C-4′, C-5′ and C-6′; the row annotated C-2′ is the row at 104.0 ppm, with its cross-peak in the column of the proton labelled 2′, and the row annotated C-5′ lies near 131 ppm (Figure S4).

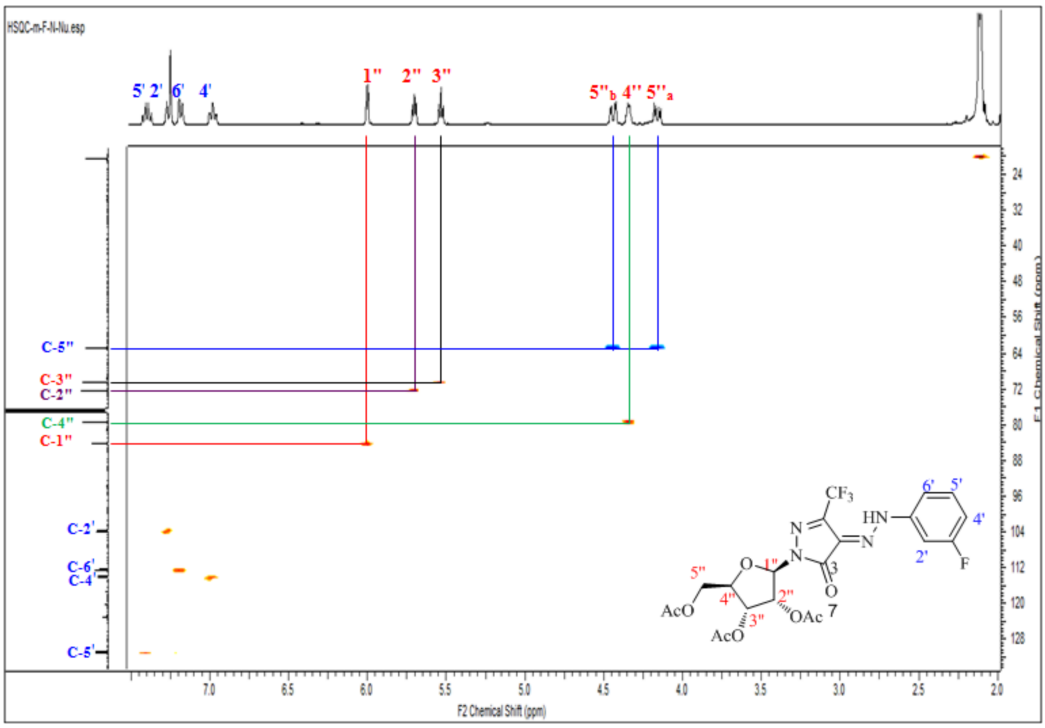


Figure S4. The HSQC spectrum printed for 117a in the source (its Figure 28), reproduced complete from the page of the thesis file, with the atom labels, guide lines and structure drawing of the source. This figure was not supplied to the models. The row that the source annotates C-2′ lies at 104 ppm and has its cross-peak in the column of the proton labelled 2′ (Table S32).

Colours. In the figure of 122a the cross-peaks of the acetyl methyl, aromatic and sugar methine signals are red, and those of the two H-2″ protons and of the two-proton signal at 3.93 ppm are blue. In the figure of 117a the cross-peaks of the two H-5″ protons are blue

and the others red. This is the pattern of a multiplicity-edited experiment in which methylene groups have the opposite sign; the source does not describe the experiment.

What follows. (i) In the figure the proton positions are those of the ^{1}H spectrum printed for 122a, and the sugar cross-peaks lie within 0.3 ppm of lines labelled in the ^{13}C spectrum printed for 123a: a red cross-peak near 76.3 ppm (proton listed at 5.83 ppm; labelled line at 76.50 ppm), two red ones near 66.6 ppm (5.66 and 5.11 ppm; 66.61 ppm), a blue one near 63.3 ppm (3.94 ppm, two protons; 63.54 ppm) and blue ones near 31.1 ppm (2.67 and about 2.1 ppm; 31.28 ppm). The spectrum printed for 123a has one labelled line at 66.61 ppm, where two cross-peaks fall. (ii) The cause was established afterwards from original records in the files of H.A.A. (Section S16.3): the ^{13}C spectrum printed for 123a is the spectrum of the compound whose ^{1}H, COSY and HSQC spectra are printed for 122a. The spectrum printed for 122a (78.54, 68.56, 67.09, 66.13 and 29.69 ppm) is not a spectrum of that compound and is attributed, by elimination, to the compound whose ^{1}H spectrum is printed for 123a. An error of the carbon scale of the HSQC figure is thereby excluded as the cause. (iii) The data-file names embedded in the figures of the source are `H1-m-F-O-deoxy-2017.esp`, `C13-m-F-dN-B-O-9-1.esp` and `HSQC-m-F-O-deoxyribose.esp` for 122a, and `H1-m-F-N-deoxy-Nucleoside.esp` and `C13-m-F-N-deoxy-2-2017.esp` for 123a. They contain O or N as the captions do (the ^{13}C name of 122a contains both), but such names are not reliable in the source: the ^{1}H figure of 117a, the N-riboside, is named `H1-m-F-O-Nucleoside.esp`. H.A.A. states that she recorded all the spectra of 122a herself and on the same sample tube. The original records are in keeping with this: they hold a ^{1}H and a ^{13}C spectrum under one sample designation and one date (Section S16.3). They do not show at which stage the ^{13}C figures came to be printed with the wrong compound. (iv) The account of the HSQC spectrum in the text of the source gives the carbons as 78.5, 68.6, 67.1, 66.1 and 29.7 ppm, which are the labelled values of the one-dimensional spectrum and not the positions of the cross-peaks. (v) No cross-peak lies between 77 and 103 ppm, and the cross-peaks of the protons listed at 5.66 and 5.11 ppm lie near 66.6 ppm; no cross-peak of a furanose ring carbon C-4″, expected near 80–85 ppm, is seen at the contour level plotted (Section S17.3). (vi) A cross-peak lies at 103.9 ppm in the column of the proton at 7.27 ppm, labelled 2′ in the figure, as in the figure of 117a; in both figures the cross-peak near 104 ppm lies in the column of an aromatic proton. (vii) The lists of the analogues carry both sets of sugar carbons under one ^{1}H pattern. 122c is listed with the ^{1}H pattern of 122a and with the sugar carbons 76.5, 66.5, 63.5 and 31.2 ppm (and 91.8 ppm as C-1″; audit item A4), which lie within 0.3 ppm of the positions of the HSQC cross-peaks; 122b is listed with the same ^{1}H pattern and with 78.6, 68.6, 67.1, 66.2 and 29.7 ppm.

The other figures read. The account of the COSY spectrum of 122a in the source couples H-1″ (5.83 ppm) with H-2″a (2.67 ppm), H-2″b (2.10 ppm) with H-3″ (5.66 ppm), and H-4″ (5.11 ppm) with the two H-5″ protons (3.94 ppm); the aromatic proton at 7.28 ppm shows no coupling, and those at 6.98 and 7.18 ppm couple with the one at 7.40 ppm. The ^{13}C figure of the donor 121 is labelled 91.49, 66.88, 64.98, 62.73 and 29.37 ppm, in agreement with its list. The gHMBC figures of 116a and 117a have a carbon axis with printed values from 20 to 160 ppm that extends to about 172 ppm; cross-peaks of sugar protons with the acetyl carbonyl carbons are visible near 170 ppm, and none is visible in the column of H-1″ below the row of C-1″.

Table S33. Statements of the source used in the article, with their place in the source. Section numbers are those of the source; quotation marks enclose its wording.

Statement	Place in the source	Used in
Infrared spectra recorded "using KBr disk method" on a Shimadzu FT-IR-8400 instrument; ^{1}H and ^{13}C NMR spectra "recorded on Varian NMR 400 MHz spectrometer", shifts referred to the solvent peak	Section 2.2, General	article, Section 2.1; Section S17.2; Table S19
113a (sugar-free aglycone, DMSO-d_6): ^{13}C 104.1 ppm listed as C-2′; infrared 1633 cm^{-1} listed as C=C, and in the discussion 1635 cm^{-1} as C=C and 1558 cm^{-1} as C=N	Section 2.2.2, entry 113a; Section 2.3.1	Section S17.2; article, Section 3.2
116a: infrared 3475 and 1750 cm^{-1}; ^{1}H 6.01 (d, 4 Hz, H-1″), 5.90 (H-2″), 5.71 (H-3″), 4.44 (H-5″a), 4.19 (H-4″), 3.71 (H-5″b), 7.23, 7.46, 7.63 (aromatic), 9.85 (NH); ^{13}C 90.2 (C-1″), 107.7 (C-2′). "no signals observed at ν = 1640-1690 cm-1"	Section 2.2.3; Section 2.3.2	Section S17.2; Tables S15, S18
gHMBC of 116a: H-1″ with C-2″; H-3″ with C-1″, C-2″ and C-5″; H-5″a with C-2″; H-4″ with C-3″; H-3″ and H-4″ weakly with acetyl carbonyl carbons	Section 2.3.2	Section S17.2
Eleven condensations (table with footnotes: molar ratio 1:1:1; "isolated yield of O- and N-isomers by column chromatography"; ND, not detected), whereas the procedures of Sections 2.2.3 and 2.2.4 give 1.1 mmol of catalyst for 3.0 mmol of base; entry 5 given as 38% N in the text; the conclusion that "the time is the most significant effect" (entries 3, 7 and 11); the inference from entries 8 and 10 that acetonitrile favours the N-isomer	Section 2.3.3 and its Table 3	Section S17.1; Table S11
117a: infrared 1749 and 1680 cm^{-1}; ^{13}C 84.4 (C-1″), 104.1 (C-2′), 157.8 (C-5), 162.3 (C-3), 164.8 (C-3′); ^{19}F −64.5 and −109.5 ppm	Section 2.2.4; Section 2.3.4	Section S17.2; Table S15
HSQC of 117a: H-2′ (7.27 ppm) with C-2′ (104.1 ppm), H-4′ (6.98) with C-4′ (114.3), H-6′ (7.18) with C-6′ (112.7). gHMBC of 117a: H-1″ with C-2″; H-2″ with C-4″; H-3″ with C-1″ and C-5″; H-5″a,b with C-3″	Section 2.3.4	Section S17.2; article, Section 3.2
Donor 121 named 1,3,5-tri-O-acetyl-2-deoxy-D-ribofuranose, "synthesized using a well-developed methodology" with a reference to Chen et al. 2009 (a second reference, to a synthesis of 2-deoxy-D-ribose, is cited in the preceding sentence for "the method described in literature"); ^{13}C 91.5 (C-1), 29.4, 62.7, 65.0, 66.9 ppm (C-2, C-5, C-4, C-3); ^{1}H 6.25 (t, 4.0 Hz, H-1), 5.30, 5.20, 4.00, 3.85, 2.26, 1.90 ppm	Section 2.2.6; Section 2.3.6	Section S17.3; Table S11 (A14)
122a: infrared 3414, 2922, 1741, 1463, 1373 cm^{-1}; ^{1}H 5.83 (dd, 2.8 and 2.8 Hz, H-1″), 5.66 (m, H-3″), 5.11 (m, H-4″), 3.94 (m, 2H, H-5″a,b), 2.67 and 2.10 (H-2″), 13.56 (NH); ^{13}C 78.5 (C-1″), 68.6 (C-3″), 67.1 (C-4″), 66.1 (C-5″), 29.7 (C-2″). HSQC account: H-1″ with 78.5 ppm, H-3″ with 68.6, H-4″ with 67.1, H-5″ with 66.1, H-2″ with 29.7; aromatic protons at 6.98, 7.18, 7.28 and 7.40 ppm with carbons at 114.5, 112.7, 103.8 and 131.2 ppm	Section 2.2.7; Section 2.3.7	Section S17.3; article, Section 3.2; Tables S18, S31
123a: infrared 1742 and 1679 cm^{-1}; ^{1}H 5.50 (d, 10.8 Hz, H-1″), 5.21 (s, H-3″), 5.15 (m, H-4″), 4.13 (dd, H-5″a), 3.83 (d, 13.2 Hz, H-5″b), 2.87 and 2.04 (H-2″), 13.54 (NH); ^{13}C 77.2 (C-1″), 76.5 (C-3″), 66.6 (C-4″), 63.5 (C-5″), 29.7 (C-2″). "the anomeric carbon in 123a observed at δ 77.2 ppm"	Section 2.2.7; Section 2.3.7	Section S17.3; Table S18
Infrared criterion for the 2-deoxy pair and the benzoyl pair: "disappearance of the amid carbonyl at 1640-1690 cm-1" in the O-isomer	Sections 2.3.7 and 2.3.8	Section S17.2; Table S11 (A10)

S16 Original spectrometer data reprocessed, and records of the 2-deoxy pair found afterwards

After the other sections of this file had been written, H.A.A. supplied the original spectrometer data of the thesis work that she holds (10 October 2026). The archive contains 56 Varian data sets, of which 47 are different free induction decays (30 ^{1}H and 17 ^{13}C, one of the latter without a completed transient) and nine are copies under another

name. All are one-dimensional (pulse sequences `s2pul` and `PRESAT`), recorded in $CDCl_3$ or DMSO-d_6 between 18 January and 11 February 2016 at 399.73 MHz (^{1}H) and 100.52 MHz (^{13}C). The archive contains no two-dimensional spectrum and no data set of 2017. The ^{13}C figures printed in the source for 116a, 122a and 123a and the ^{1}H figure printed for 122a carry file names with "2017" or "9-1" (`C13-m-F-Nucleoside-O-2017`, `C13-m-F-dN-B-O-9-1`, `C13-m-F-N-deoxy-2-2017`, `H1-m-F-O-deoxy-2017`), and no data set of these names is in the archive. None of its 17 different ^{13}C data sets has the lines printed for 116a or the sugar lines printed for 122a. Five show the lines of 117a (three acquisitions and two earlier states, Section S16.1), and only these five have the two doublets of the 3-fluorophenyl ring near 104 and 114 ppm (`scan_signatures.py`); the archive thus holds no ^{13}C data of 116a, 122a or 123a. Six ^{1}H data sets carry names of the 3-fluorophenyl glycosides, and none shows the pattern listed for 116a or for 123a (`survey1h.py`). Three show the signals of 117a; at the two positions that distinguish 116a from it (5.90 and 3.71 ppm) they have at most 22 times the noise, against 240 to 1700 times the noise at the six sugar signals listed for 117a. Three show the signals of the spectrum printed for 122a, one of them weakly (15 to 44 times the noise); the weak one was not analysed. One ^{13}C data set is stored under a ^{1}H name of a 3-fluorophenyl glycoside (folder `H1-m-F-N-Nucleoside-3-2016`, 26–27 January 2016, 25600 transients), whereas its parameter file gives the sample name `C13-p-Cl-Nucleosides-free-2016`. It has a solvent septet, that is, it was recorded in DMSO-d_6 although the parameter file names $CDCl_3$, and apart from the solvent it has five lines of 9 to 14 times the noise (84.5, 72.4, 71.0, 62.7 and 8.8 ppm; `survey13c.py`); it was not used. The HSQC and gHMBC data are not in the archive either. The inconsistency of Section S15 could therefore not be examined on the original data of the spectra concerned; it was resolved from records found afterwards (Section S16.3).

Method. The data sets were catalogued from their parameter files, and those bearing on the four glycosides were reprocessed, with the AI assistant of Section 2.6 of the article, by scripts that are in version 1.1.0 of the data deposit and in Supporting File 6, with the data sets used (`catalog.py`, `proc1d.py`, `scan_signatures.py`, `survey1h.py`, `survey13c.py`, `c13_117a.py`, `c13_line_shapes.py`, `h1_117a.py`, `h1_deoxy.py`, `make_fid_figures.py`; nmrglue 0.12). Processing: exponential line broadening of 1.0 Hz (^{13}C) or 0.5 Hz (^{1}H), zero-filling to 131072 (^{13}C) or 65536 (^{1}H) complex points, Fourier transformation, phase correction, and a shift axis computed from the acquisition parameters and then set on the solvent (centre line of the $CDCl_3$ triplet at 77.00 ppm; $CHCl_3$ at 7.26 ppm). The phase of the ^{1}H spectra was corrected automatically. For the ^{13}C spectra the zero-order correction stored with each data set was used, because the automatic routine added a first-order term that left the lines far from the solvent out of phase. The two survey scripts and the scan of the ^{13}C data sets use half as many points, and the ^{1}H survey a line broadening of 0.3 Hz. A line is a local maximum of the real spectrum refined by three-point interpolation, and a coupling is the distance of two lines. No line fitting was made, and no baseline correction beyond an offset; heights are given in units of the noise of a signal-free region. For data sets A to E the line positions and couplings were also computed with separately written code (the second computation, which is deposited with the scripts). Where it reports the same quantity, it gave the same positions within 0.01 ppm and the same couplings within about 0.2 Hz; where it differs in what it resolves, this is stated below. The values for data sets F, G and H and the survey values were computed once. H.A.A. supplied the data; she has not

checked the processing or the other readings of Sections S16.1 and S16.2 (what she checked of the records of Section S16.3 is stated there).

S16.1 The ^{13}C spectrum of 117a

Three acquisitions with the signals of 117a are in the archive. A (`C13-m-F-N-Nucleoside-1#`, 40000 transients, 4–5 February 2016) bears the file name that is printed on the ^{13}C figure of 117a in the source. B (`C13-m-F-O-Nu-2-Heba`, 25152 transients, 31 January–1 February 2016) and C (`C13-m-F-N-Nucleoside-3-2016`, 14208 transients, 3 February 2016) are further acquisitions; earlier states of A and of C, saved after 1216 and 5312 transients, are also present. The three give the same lines within 0.03 ppm (Table S34), although one of the file names contains O and two contain N: a further instance of file names that do not follow the assignment (Section S15). Data set A has a line within 0.01 ppm of every label printed on the figure of the source, with three exceptions: the labels 20.55 and 20.49 ppm lie 0.013 and 0.014 ppm from the acetyl methyl lines found, and the label 170.63 ppm has no line of its own at a line broadening of 1.0 Hz; it corresponds to the second maximum of the carbonyl line at 170.65 ppm (170.634 ppm at a line broadening of 0.3 Hz; see below).

Table S34. ^{13}C lines of 117a in three original data sets (ppm; $CDCl_3$ at 77.00 ppm), beside the labels printed on the figure of the source. For a doublet both lines are given; for a quartet, the lines found above five times the noise. The coupling is the distance of the lines of a doublet, or one third of the distance of the outer lines of a quartet (in C, where only two adjacent lines of each quartet are found, their distance). Assignments as in Table S15; the aryl carbons are assigned by their couplings as described in the text.

Carbon	Label printed on the figure of 117a in the source	Lines in A	Lines in B	Lines in C	Coupling to fluorine in A; B; C (Hz)
acetyl C=O	170.65, 170.63	170.65	170.66	170.67	—
acetyl C=O	169.59	169.59	169.60	169.61	—
acetyl C=O	169.45	169.45	169.46	169.47	—
C-3′ (C–F), d	164.81, 162.34	164.82, 162.34	164.83, 162.36	164.83, 162.36	248.4; 248.4; 248.4
C-3	157.77	157.78	157.79	157.80	—
C-1′, d	141.76	141.76, 141.66	141.77, 141.67	141.77, 141.67	10.0; 9.9; 10.1
C-5 (carries CF_3), q	138.70	139.49, 139.10, 138.70, 138.31	139.51, 139.11, 138.72, 138.33	139.12, 138.73	39.5; 39.5; 39.5
C-5′, d	131.19	131.29, 131.20	131.29, 131.20	131.30, 131.21	9.1; 9.1; 9.2
C-4	123.28	123.28	123.29	123.29	—
CF_3, q	none	123.09, 120.39, 117.69, 114.99	123.10, 120.40, 117.70, 115.00	120.40, 117.70	271.4; 271.4; 271.4
C-4′, d	114.26	114.47, 114.26	114.49, 114.27	114.50, 114.29	21.7; 21.7; 21.6
C-6′, d	112.73	112.73, 112.70	112.73, 112.70	112.74, 112.71	2.7; 2.9; 3.0
C-2′, d	104.09	104.09, 103.83	104.11, 103.84	104.11, 103.85	26.7; 26.7; 26.7
C-1″	84.39	84.39	84.41	84.41	—
C-4″	79.70	79.70	79.71	79.71	—

Carbon	Label printed on the figure of 117a in the source	Lines in A	Lines in B	Lines in C	Coupling to fluorine in A; B; C (Hz)
sugar CH	72.53	72.52	72.53	72.54	—
sugar CH	70.74	70.73	70.75	70.75	—
C-5″	62.91	62.91	62.92	62.93	—
acetyl CH_3 (three lines)	20.59, 20.55, 20.49	20.59, 20.54, 20.48	20.59, 20.55, 20.48	20.61, 20.56, 20.49	—

The aryl carbons are identified by their couplings to fluorine (Figure S5a). The carbon bearing fluorine is a doublet of 248.4 Hz centred at 163.58 ppm; the source labels its two lines (164.81 and 162.34 ppm) and lists them as two carbons (Table S33). The two carbons ortho to fluorine are doublets of 26.7 Hz (104.09 and 103.83 ppm) and 21.7 Hz (114.47 and 114.26 ppm), the two meta carbons doublets of 10.0 Hz (141.76 and 141.66 ppm) and 9.1 Hz (131.29 and 131.20 ppm), and the para carbon a doublet of 2.7 Hz (112.73 and 112.70 ppm; 2.9 and 3.0 Hz in B and C). These are one- to four-bond carbon–fluorine couplings of a fluorophenyl ring; the larger of the two two-bond couplings and both three-bond couplings exceed those of fluorobenzene itself (245.3, 21.0, 7.7 and 3.3 Hz; Weigert and Roberts 1971; Table S23). With the HSQC figure of 117a, in which the row at 104 ppm correlates with the proton labelled 2′ and the row at 114.3 ppm with the proton labelled 4′ (Figure S4, Table S32), the ortho carbons are C-2′ (104 ppm) and C-4′ (114.4 ppm), the para carbon is C-6′ (112.7 ppm), and the meta carbons are C-1′ and C-5′. C-4′ and C-6′, which Table S15 left undistinguished, are thereby distinguished for 117a. The trifluoromethyl carbon, which the source does not label, is a quartet of 271.4 Hz centred at 119.04 ppm, and C-5 a quartet of 39.5 Hz centred at 138.90 ppm, of which the source labels one line (138.70 ppm).

The signal near 104 ppm is therefore a doublet with the coupling of an aryl carbon ortho to fluorine. The label 104.09 ppm of the source is its low-field line. The signal of C-1″ at 84.39 ppm has no splitting of that size (Figure S5b). It is not a single line in every acquisition. With a line broadening of 0.3 Hz it has, in the two longer acquisitions, a second maximum 3.0 Hz to low field, of 0.60 (A) and 0.88 (B) of the height of the main one; in C it is a single line of 51 times the noise (`c13_line_shapes.py`). The three acetyl carbonyl lines likewise have second maxima in A and B, 1.6–1.9 Hz away, and are single in C, whereas the two lines of the doublet at 104 ppm and the other four sugar lines are single in all three. The two lines of the doublet at 104 ppm are of nearly the same height in each acquisition (144 and 142, 101 and 103, and 26 and 27 times the noise in A, B and C at a line broadening of 0.3 Hz; `c13_line_shapes.py`), as the two lines of a carbon split by one fluorine nucleus are expected to be. H.A.A. opened data set A in her own NMR program and found the two lines near 104 ppm, of nearly the same height, and no splitting of about 27 Hz in the line at 84.39 ppm, as given here. A coupling to fluorine would appear in every acquisition of the compound, so the second maximum is not read as one. What causes it in A and B was not examined; a second component with nearly the same shifts is one possibility. The labels printed near 104 and 114 ppm for the two 2-deoxy compounds (103.80 and 114.45 ppm for 122a; 103.83 and 114.49 ppm for 123a) lie within 0.03 ppm of the high-field line of the first doublet and of the low-field line of the second as measured here for 117a. On this reading the difference between “104.09 ppm” in 117a and “103.8 ppm” in the 2-deoxy compounds is one of label placement on a doublet and not of chemical shift. The archive holds no ^{13}C data of the 2-deoxy compounds; the printout of 2016 of the compound whose

^{1}H spectrum is printed for 122a labels both lines of each doublet (104.098 and 103.833 ppm; 114.490 and 114.277 ppm), and the measurement of 2014 has them at 104.10 and 103.84 ppm and at 114.48 and 114.26 ppm (Section S16.3).

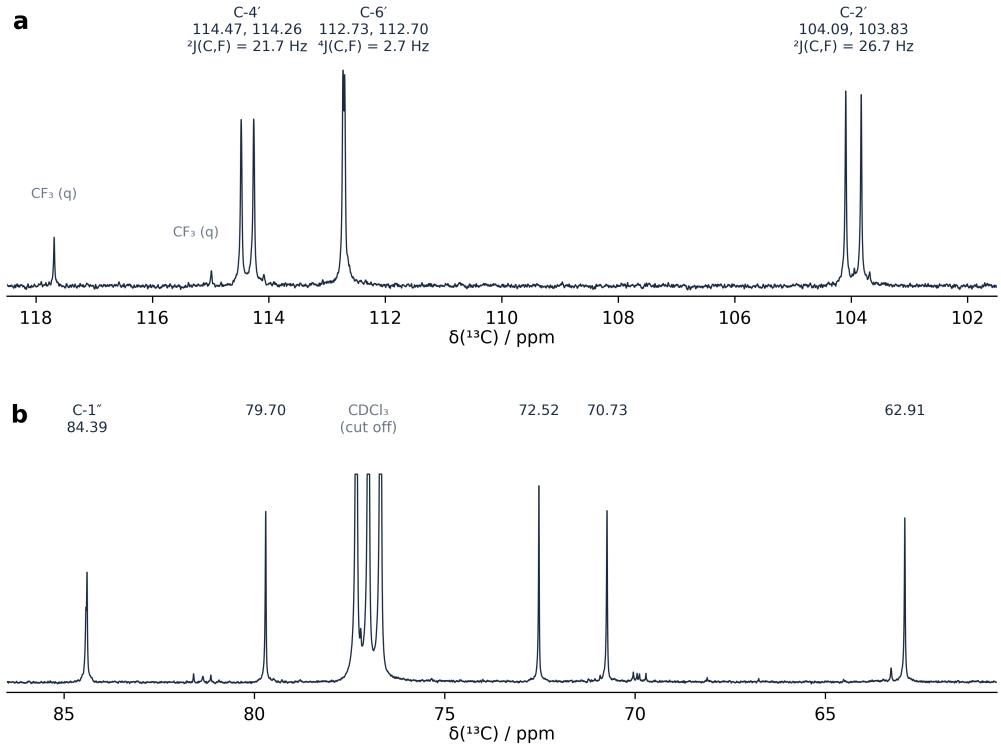


Figure S5. ^{13}C spectrum of 117a reprocessed from the original data (data set A, the file named on the figure of the source; 40000 transients, line broadening 1.0 Hz). (a) 118.5–101.5 ppm: the doublets of the two carbons ortho to fluorine (C-2′ and C-4′) and of the para carbon (C-6′), with two lines of the trifluoromethyl quartet. (b) 86.5–60.5 ppm: the sugar carbons; the signal of C-1″ at 84.39 ppm has no splitting of the size found at 104 ppm (its second maximum, 3 Hz away, is discussed in the text). The captions are added here.

In the three ^{1}H data sets with the signals of 117a (F, `H1-m-F-Nucleoside-1-2016`; G, `H1-m-F-O-Nucleoside-2-2016`; H, `H1-m-F-N-Nucleoside-3`; 26 January and 4 February 2016), H-1″ is a doublet of 3.9–4.1 Hz (4.09, 3.92 and 4.11 Hz; `h1_117a.py`); the two labelled lines of the figure of the source are 4.4 Hz apart.

S16.2 Original data bearing on the 2-deoxy pair

^{1}H data with the signals printed for 122a. Two ^{1}H data sets, D (`H1-m-F-a-Deoxy-Nucleoside-2016`, 26 January 2016) and E (`H1-m-F-a-Nuc-2016-2`, 4 February 2016), of eight transients each, show the signals of the ^{1}H spectrum printed for 122a: a broad signal near 13.6 ppm, aromatic multiplets at 7.41, 7.20 and 6.99 ppm, and sugar signals at 5.84, 5.67, 5.12, 3.95 and 2.68 ppm in D, with $CHCl_3$ at 7.26 ppm (centres of gravity; the aromatic and sugar signals lie within 0.01 ppm of these in E; 5.83, 5.66, 5.11, 3.94 and 2.67 ppm in

the list of the source). Relative to the first, the areas of the other four sugar signals are 1.0, 1.1, 2.1 and 1.2 in D and 1.0, 1.1, 2.3 and 1.4 in E without baseline correction; the last two depend on the baseline, and the second computation gives 2.0–2.2 and 0.9–1.1 for them in both data sets (Figure S6). In both, H-1″ has four lines 2.6–2.8, 6.2–6.4 and 2.7–2.9 Hz apart, a doublet of doublets of about 9.0 and 2.8 Hz (9.1 and 2.7–3.1 Hz in the second computation); the source lists it as a doublet of doublets of 2.8 and 2.8 Hz (audit item A13). The signal listed at 2.67 ppm (H-2″a) has seven resolved lines over 26.5 Hz with spacings of 3.0–3.1, 6.1, 4.2–4.8, 3.3–3.7, 6.1–6.5 and 2.9–3.1 Hz, which fit couplings of about 14.4, 9.1 and 3.0 Hz with the two central lines unresolved (14.2–14.4, 9.2–9.3 and 3.1–3.2 Hz in the second computation). The signal listed at 5.66 ppm is a multiplet 18–19 Hz wide at one tenth of its height; at a line broadening of 0.5 Hz no line is resolved in it, and at 0.3 Hz the second computation finds maxima 2–3 Hz apart. That listed at 5.11 ppm is 24–26 Hz wide, with maxima about 8 Hz apart (two in E here; three in D in the second computation). H-2″a thus has one large vicinal coupling, to H-1″, and a small one besides its geminal coupling, which does not bear on the ring size, and the proton listed at 5.66 ppm, which the source assigns as H-3″, has small couplings only. This fits the pattern of a six-membered ring in a chair form with axial H-1″ and H-2″a and an equatorial H-3″, and it agrees with the 2-deoxypentopyranosyl ring that the shifts, the integrals and the HSQC figure favour (Section S15; Table S18). Couplings alone do not exclude a furanosyl ring, and no authentic compound was compared.

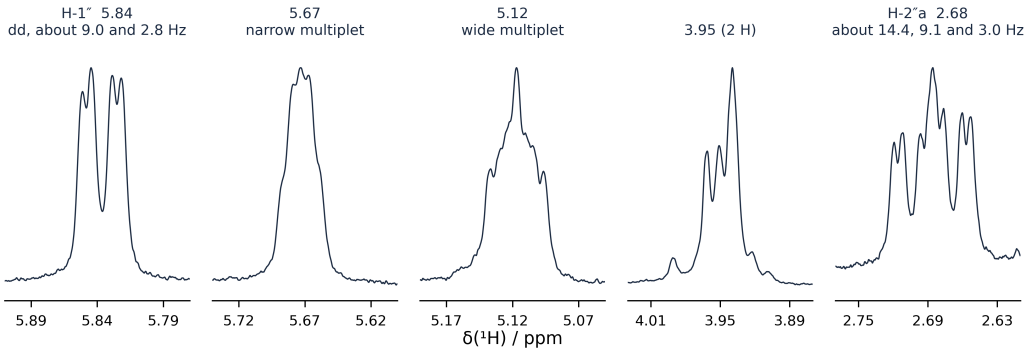


Figure S6. The sugar multiplets of data set D (^{1}H data with the signals of the spectrum printed for 122a; line broadening 0.5 Hz). The captions are added here.

S16.3 Records of the 2-deoxy pair found afterwards: spectrometer printouts of 2016 and a measurement of 2014

After Sections S15 to S16.2 had been written, H.A.A. made the folder of her thesis work available (10 October 2026). It does not contain the data files named on the figures printed in the source for 122a and 123a, and it holds no spectrometer data of 2017 and no two-dimensional data set. It does contain two older records of the two 3-fluorophenyl 2-deoxy compounds, which explain the inconsistency of Section S15. They were read with the AI assistant of Section 2.6 of the article. H.A.A. compared the sample names, the dates, the 32 labels of Table S35 and the ^{1}H labels and integrals given below with the two printouts of

Figure S7 and found them as given; the low-field signal, which is on another plot, was not part of her comparison. She states that the two printouts are of measurements that she made herself and that they are of the same sample.

Printouts of 2016. A folder named "Orginal spectra" holds scans of printouts of the spectrometer software (PDF files dated 21 January 2017); each printout carries the sample name, the pulse sequence and the date of collection. Its part on the 2-deoxy compounds has 15 files with 108 pages. Two of the printouts carry one sample designation, m-F-a-deoxy-un4, and one date of collection, 29 February 2016: a ^{1}H spectrum (sample name `H1-m-F-a-deoxy-un4`) and a ^{13}C spectrum (sample name `C13-m-F-a-deoxy-un4-29-2-2016`, with the printed title "m-F-a-deoxy- un4-after drying-no aromatic imp. 29-2-2016"; Figure S7).

The ^{1}H printout has the sugar signals labelled at 5.841–5.810 (four lines), 5.668–5.647, 5.127–5.084, 3.951–3.926 and 2.708–2.642 ppm, with printed integrals of 5.57, 6.23, 6.52, 11.86 and 6.96, and on its full-range plot a low-field signal at 13.515 ppm. These are the signals of the ^{1}H spectrum printed in the source for 122a (listed there at 5.83, 5.66, 5.11, 3.94 for two protons, 2.67 and 13.56 ppm); the four lines of H-1″ labelled on that figure (5.840, 5.833, 5.818 and 5.810 ppm) are those of the printout within 0.001 ppm.

The ^{13}C printout carries 32 labels (Table S35). A second printout of the spectrum with the same sample name and date, plotted over a narrower range, carries the same labels 0.002–0.003 ppm lower and four further ones (120.477, 117.782, 29.435 and 29.238 ppm); the values used here are those of the printout reproduced in Figure S7. Twenty of the 21 labels of the ^{13}C spectrum printed in the source for 123a have a label of the printout within 0.008 ppm; the exception is 138.43 ppm, where the printout has no label. The differences run from −0.008 ppm at 164.9 ppm to +0.005 ppm at 20.8 ppm and are zero at 169.894 and 66.609 ppm and at the five labels between 76.5 and 77.3 ppm; whether the figure of the source was made from this data set or from another recording of the same sample was not established. The sugar lines of the printout, at 76.499, 66.654, 66.609, 63.534 and 31.275 ppm, lie at the positions of the sugar cross-peaks of the HSQC figure printed for 122a (76.3, 66.7, 66.5, 63.3 and 31.1 ppm; Table S31), with two lines near 66.6 ppm, where that figure has two cross-peaks and the spectrum printed for 123a one label. Of the 19 labels of the ^{13}C spectrum printed for 122a (Figure 40 of the source), apart from the solvent, nine have no label of the printout within 0.10 ppm: 170.59 and 170.04 ppm (the printout has one carbonyl label), 164.31, 157.54, 138.23, 78.54, 68.56, 67.09 and 66.13 ppm. These include four of the five labels that the source lists as its sugar carbons; the fifth, 29.69 ppm, coincides with one of several aliphatic labels of the printout (14.127–31.920 ppm) that are not assigned here.

Table S35. The labels of the ^{13}C printout of 29 February 2016 (sample name `C13-m-F-a-deoxy-un4-29-2-2016`), read from the scan, beside the labels of the two ^{13}C spectra printed in the source for the 2-deoxy pair and the cross-peaks of the HSQC figure printed for 122a. Each label of a figure is entered once, in the row of the label of the printout nearest to it, if it lies within 0.02 ppm (spectrum printed for 123a) or 0.10 ppm (spectrum printed for 122a); differences are label of the figure minus label of the printout; "solvent" marks the three lines of $CDCl_3$, which have no cross-peak.

Label on the printout (ppm)	Label of the spectrum printed for 123a (difference)	Label of the spectrum printed for 122a (difference)	Cross-peak of the HSQC figure printed for 122a (ppm; Table S31)
169.894	169.894 (0.000)	—	—
164.869	164.861 (−0.008)	—	—
162.394	162.387 (−0.007)	162.33 (−0.06)	—
157.878	157.871 (−0.007)	—	—
141.816	141.811 (−0.005)	—	—
141.717	—	141.72 (0.00)	—
131.326	—	—	—
131.235	131.230 (−0.005)	131.21 (−0.03)	131.2 (H-5′)
123.424	123.420 (−0.004)	123.49 (+0.07)	—
114.490	114.487 (−0.003)	114.45 (−0.04)	114.2 (H-4′)
114.277	—	—	—
112.706	—	—	—
112.676	112.673 (−0.003)	112.68 (0.00)	112.6 (H-6′)
104.098	—	—	—
103.833	103.831 (−0.002)	103.80 (−0.03)	103.9 (H-2′)
77.319	77.319 (0.000)	77.32 (0.00)	solvent
77.205	77.205 (0.000)	—	—
77.000	77.000 (0.000)	77.00 (0.00)	solvent
76.689	76.689 (0.000)	76.68 (−0.01)	solvent
76.499	76.499 (0.000)	—	76.3 (H-1″)
66.654	—	—	66.5 and 66.7 (H-3″ and H-4″; not told apart)
66.609	66.609 (0.000)	—	66.5 and 66.7 (H-3″ and H-4″; not told apart)
63.534	63.535 (+0.001)	—	63.3 (H-5″a,b)
31.920	—	—	—
31.275	31.278 (+0.003)	—	31.1 (H-2″a,b)
30.030	—	—	—
29.696	—	29.69 (−0.01)	—
29.362	—	—	—
22.690	—	—	—
21.020	21.024 (+0.004)	21.09 (+0.07)	20.6 (acetyl CH_3)
20.784	20.789 (+0.005)	20.86 (+0.08)	20.6 (acetyl CH_3)
14.127	—	—	—

Both lines of six aryl signals are labelled on the printout (Table S35). At 100.52 MHz their spacings are 248.8 Hz (164.869 and 162.394 ppm), 26.6 Hz (104.098 and 103.833 ppm), 21.4 Hz (114.490 and 114.277 ppm), 10.0 Hz (141.816 and 141.717 ppm), 9.1 Hz (131.326 and 131.235 ppm) and 3.0 Hz (112.706 and 112.676 ppm): the one-bond coupling of C-3′, the two-bond couplings of the two carbons ortho to fluorine, the three-bond couplings of the two meta carbons and the four-bond coupling of the para carbon of a 3-fluorophenyl ring, within 0.4 Hz of the couplings measured in the original data of 117a (Table S34). The line pair near 104 ppm is therefore one of the two carbons ortho to fluorine; a doublet requires coupling to a single fluorine nucleus, the aryl fluorine (coupling to the CF_3 group

would give a quartet), and in each attachment isomer every sugar carbon is at least nine bonds from that fluorine. C-2′ and C-4′ are told apart by their shifts and HSQC cross-peaks (Table S31), and C-4′ and C-6′ also by the size of their couplings; C-1′ and C-5′ are told apart by their shifts and the HSQC cross-peak of C-5′, not by their couplings, which differ by less than 1 Hz. None of the six pairs coincides with a line of the CF_3 quartet or of the C-5 quartet (centred at 138.90 ppm in 117a), which this printout does not label. The spacings are differences of printed labels at a digital resolution that is not known, so the smallest of them is approximate. The two further labels of the second printout, 120.477 and 117.782 ppm, are 271 Hz apart and are presumably the inner lines of the CF_3 quartet; that printout was not part of the comparison made by H.A.A.

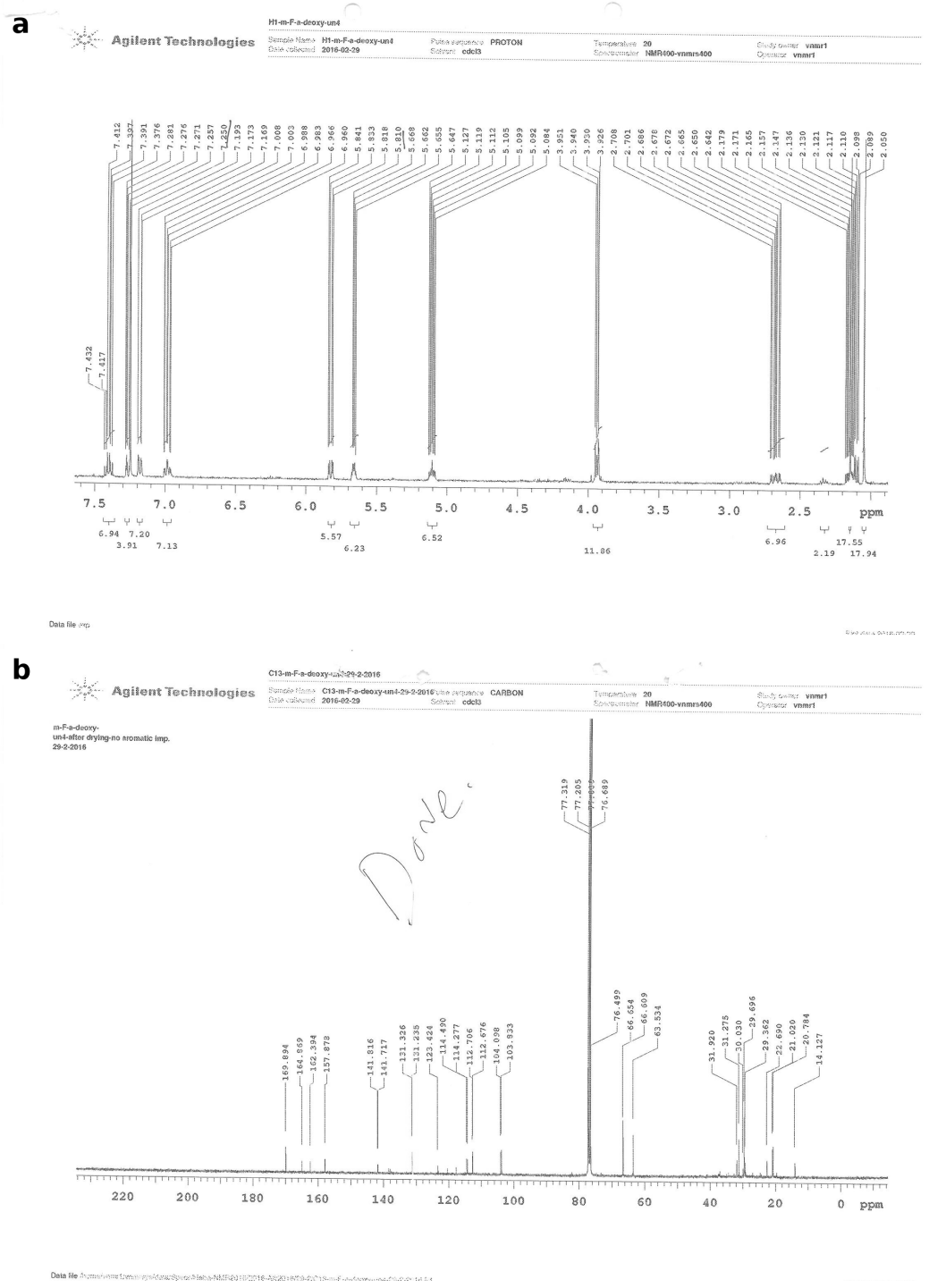


Figure S7. The two printouts of 29 February 2016 that carry one sample designation, reproduced from the scans without redrawing; the panel letters are added here, and the word written by hand on panel b is on the original. (a) ^{1}H spectrum, sample name `H1-m-F-a-deoxy-un4`: the signals of the ^{1}H spectrum printed in the source for 122a. (b) ^{13}C spectrum, sample name `C13-m-F-a-deoxy-un4-29-2-2016`: the labels of the ^{13}C spectrum printed in the source for 123a (Table S35).

The other sample of 2016. Printouts of a ^{1}H spectrum with the sample name `H1-m-F-B-deoxy-Nucleoside` (collected 22 February 2016) are labelled at 5.518 and 5.491, 5.211, 5.166 and 5.135, 4.156 and 4.123, 3.847 and 3.813, and 2.884 and 2.852 ppm; these are the signals of the ^{1}H spectrum printed in the source for 123a (5.50, 5.21, 5.15, 4.13, 3.83 and 2.87 ppm). No ^{13}C printout of this sample is among the scans. Four further ^{1}H spectra whose sample name or printed title contains the letter a (collected 26 January, 22 February, 6 March and 17 April 2016; eleven printed pages) have the signals of the spectrum printed for 122a; the first is data set D of Section S16.2. Three ^{1}H printouts collected on 28 February 2016 (sample name `H1-m-F-Deoxy-Un4`), which have the same signals, carry the printed title "m-F-Deoxy-Nucleoside / Unknow a ro B ? / un-4 / after drying".

A measurement of 2014. Files of the program ACD/Labs, saved in 2015, hold measurements of July and August 2014 of two samples named a and B. Each file contains the spectrum as saved, the list of the peaks picked in the program and the free induction decay as read from the spectrometer file. The layout of these files is not documented; it was established by inspection and agrees with the parameters printed by the program itself for the same files (number of points, spectral width, number of transients, sample name). In the saved ^{1}H spectra the sugar signals of sample a (26 July 2014) lie at 5.826, 5.663, 5.107, 3.938 (area 2.1 relative to the first) and 2.675 ppm, and those of sample B at 5.500, 5.177 (area 2.0), 4.133, 3.826 and 2.866 ppm (centres of gravity; $CHCl_3$ at 7.250 ppm in the files); the first set is that of the ^{1}H spectrum printed for 122a and the second that of the spectrum printed for 123a. The ^{13}C spectrum computed from the free induction decay of sample a (1 August 2014, 23744 transients; line broadening 1.0 Hz, $CDCl_3$ at 77.00 ppm) has, apart from the solvent, lines at 169.86, 164.88, 157.88, 131.32, 131.23, 114.48, 114.26, 112.67, 104.10, 103.84, 66.67, 66.62, 63.56, 31.29, 29.70, 21.01 and 20.78 ppm, each within 0.035 ppm of a label of the printout of 2016. The three pairs near 104, 114 and 131 ppm are 26.6, 21.8 and 8.8 Hz apart at the frequency stored in the file (100.52 MHz), against 26.6, 21.4 and 9.1 Hz between the labels of the printout of 2016 and 26.7, 21.7 and 9.1 Hz in 117a (Table S34); the two lines near 104 ppm are of nearly the same height (9.5 and 9.8 times the noise; `doublets_2014.py`). Between 78 and 103.5 ppm the computed spectrum has no maximum that meets the criterion of this list (a maximum higher than six times the noise that stands out from its surroundings by five times the noise), whereas the sugar lines found are 19 to 24 times the noise, so that no sugar carbon of the main component of the sample lies there (not checked by H.A.A.). Maxima between 72.5 and 77.5 ppm, on the foot of the solvent signal, are left out of this list, and the line that the printout labels at 76.499 ppm is not resolved there. At the labels of the printout at 162.39, 141.82, 141.72 and 123.42 ppm the spectrum rises to 3–6 times the noise, and no line is entered. At the sugar labels 78.54, 68.56, 67.09 and 66.13 ppm of Figure 40 no point within 0.15 ppm rises above 2.0 times the noise. The files hold no ^{13}C measurement of sample B: the file stored under that name contains the free induction decay of sample a. In the saved ^{1}H spectrum of sample B, whose signals are those of the spectrum printed for 123a, the two maxima of the signal at 5.500 ppm (H-1″ in the source) are 11.0 Hz apart, the signal at 2.866 ppm has four maxima 12.1 Hz apart, as a geminal and two vicinal couplings of about 12 Hz would give, and each of the signals at 4.133 and 3.826 ppm has two maxima 13.3 Hz apart (`H1-m-F-B-Deoxy-Nucleoside-f4_h1_signals.csv`). Vicinal couplings of 11–12 Hz are those of axial protons

on adjacent carbons of a six-membered ring in a chair form and are larger than the vicinal couplings usually found in furanose rings; on a 2-deoxy-D-*erythro*-pentopyranosyl ring this pattern would fit the α-anomer in the $^{1}C_{4}$ chair (and the narrow signal at 5.21 ppm, listed as H-3″ in the source, would then be H-4″), as that of sample a (Section S16.2) would fit the β-anomer in the $^{4}C_{1}$ chair, each with the aglycone equatorial. These maxima were read with the assistant from the saved spectrum and were not checked by H.A.A.; they are distances between maxima and not fitted couplings, no NOE or long-range correlation is available, and the ring size and the anomeric configurations remain unestablished.

What follows. (i) The ^{1}H spectrum printed in the source for 122a and the ^{13}C spectrum printed for 123a are spectra of one compound. Spectra with these signals and these labels were recorded under one sample designation on one day in 2016 (Figure S7), a pair of the same kind exists from 2014, and the HSQC figure printed for 122a connects the protons of the one with the carbons of the other (Section S15). (ii) The ^{13}C spectrum printed for 122a is not a spectrum of that compound. It is attributed here, by elimination, to the compound whose ^{1}H spectrum is printed for 123a. This half of the attribution is not documented, because no ^{13}C record of a sample with that ^{1}H spectrum was found. (iii) On this attribution the source prints, for each compound of the pair, the proton spectra of one compound with the carbon spectrum of the other. The ^{13}C panels supplied to the models were cut from these figures (Section S2), so in every NMR-added item of this pair the ^{13}C panel presented for a compound is not the spectrum of the compound whose ^{1}H panel it accompanies; this holds for both panels whether or not the attribution of (ii) is right. The value tables (Section S4.1), the coding and the counts are those of the panels as supplied and are unchanged. (iv) The anomeric carbon of the compound whose ^{1}H spectrum is printed for 122a is the line at 76.50 ppm (the cross-peak of H-1″ in the HSQC figure; 76.499 ppm on the printout), and not 78.54 ppm, the value listed in the source. For the other compound no correlation spectrum exists, and, on the attribution of (ii), which line of Figure 40 is its anomeric carbon is not established. (v) H.A.A. states that she recorded all the spectra of 122a herself and on the same sample tube (Section S15). The records are in keeping with this: they hold a ^{1}H and a ^{13}C spectrum under one sample designation. They do not show at which stage the ^{13}C figures came to be printed with the wrong compound. The data-file names printed on the figures of the source put O on the ^{1}H, COSY and HSQC figures printed for 122a and N on the ^{13}C figure printed for 123a, which are spectra of one compound, and both B and O on the ^{13}C figure printed for 122a (Section S15); the printouts of 2016 name the samples a and B. H.A.A. states that these letters stand for the two products separated from the 2-deoxy glycosylation.

Infrared printouts. The same scans contain three infrared printouts of samples of these compounds. One, with the printed name `m-F-a-deoxy`, is labelled 1740.03 and 1677.40 cm^{-1} among others. One, with the printed name `m-F-a-deoxy-Nucleoside-7-2016-2`, is labelled 1744.54, 1679.77, 1605.47, 1561.04, 1462.26, 1375.91 and 1245.92 cm^{-1} among others, each within 2.2 cm^{-1} of a label of the infrared figure printed in the source for 123a. One, with the printed name `m-F-B-deoxy-Nucleoside-7-2016`, is labelled 1741.28, 1679.34, 1649.73, 1562.35 and 1252.34 cm^{-1} among others; apart from 1679.34 cm^{-1}, each lies within 3.5 cm^{-1} of a label of the figure printed for 122a, whose trace has an unlabelled shoulder near the place of the label 1679.34 cm^{-1} of this printout (Section S13). On the

second and the third of these printouts a pen stroke crosses the letter a or B of the printed name: on the second (`m-F-a-deoxy-Nucleoside-7-2016-2`) a capital B, with an arrow to a letter O, is written beside the struck a, and on the third (`m-F-B-deoxy-Nucleoside-7-2016`) a handwritten mark that was not read with certainty stands beside the B. Taken as printed, the names attach to sample a, whose ^{1}H spectrum has the signals printed for 122a, the pattern of the infrared figure printed for 123a, and to sample B the pattern of the figure printed for 122a; the pen strokes put the printed names in doubt, and these records do not settle which infrared spectrum belongs to which compound. H.A.A. states that the handwritten corrections on these two printouts are the right ones. On her statement the pattern of the infrared figure printed for 123a is that of sample B and the pattern of the figure printed for 122a that of sample a, so that the source prints each infrared spectrum under the number under which it prints the ^{1}H spectrum of the same sample. The first printout, whose printed name is not altered, was not put to her. H.A.A. later compared the wavenumbers given in this paragraph with the three printouts and found them as given. The infrared spectra are used in this article as printed in the source.

Limits. The printouts and files are records of 2014 and 2016; the spectra printed in the source carry other file names, two of them with the year 2017 (Section S15), and the data of those files were not found. That the ^{1}H and ^{13}C printouts of 29 February 2016 are of one sample rests on the sample name and the date printed on them and on the statement of H.A.A., and for the measurement of 2014 on the sample name. The readings are those of the AI assistant from the scans, made twice in separate passes with the same result for every value given here, which is not a check by a person; the check by H.A.A. covers the two printouts of Figure S7 and the wavenumbers of the three infrared printouts and no other reading of this section; the handwritten notes on the printouts were not used as evidence for the attribution of the NMR spectra. The records bear on which spectra belong together, and not on the structures: the site of attachment, the ring size and the anomeric configuration of the two compounds remain open (Section S17.3). The two pages of Figure S7, the values read from the ACD/Labs files of the two samples of 2014 (spectra as saved, peak tables and free induction decays, exported without the text blocks of the files, which hold folder paths of the computer on which they were saved) and the scripts used (`esp_export.py`, `esp_read.py`, `esp_fid.py`, `esp_c13_fid.py`, `esp_h1.py`, `esp_fid_compare.py`, `doublets_2014.py`, `records_2deoxy.py`) are in version 1.1.0 of the data deposit and in Supporting File 6; the files themselves are kept by the corresponding author.

S17 Re-examination of the source record

This section gives in full the re-examination that Section 3.1 of the article summarises. Section S17.1 concerns the reaction records of the source and does not bear on the evaluation of the models. Sections S17.2 and S17.3 examine the spectroscopic support for the assignments of the two pairs. The infrared spectra and the gHMBC spectra referred to below are reproduced in Figures 2 and 3 of the article.

S17.1 Association between reaction time and the reported O/N composition

Table 3 of the source reports eleven condensations of the silylated base with the protected ribose donor, giving the ribosides 116a and 117a, at room temperature and at a stated molar ratio of sugar, base and catalyst of 1:1:1 (the experimental procedures give 1.1 mmol of catalyst for 3.0 mmol of base), in which the catalyst (trimethylsilyl trifluoromethanesulfonate, TMSOTf, or $SnCl_4$), the solvent (acetonitrile, MeCN, or dichloromethane) and the reaction time (4–18 h) were varied (Table S36). The outcome is expressed as N-selectivity, N/(O + N). This ratio is the same whether the percentages are isolated yields or normalised product distributions, but it does not make the two kinds of record comparable (audit item A1). The labels O and N are the source assignments, which Section S17.2 qualifies; N-selectivity means selectivity for the isomer assigned as the N-glycoside.

Table S36. Digitised condition–composition data for the eleven glycosylations of the source (Aboukhousa 2017). N-selectivity = N/(O + N). n.d., not detected (encoded as zero; audit item A3). Entries 1 and 11 are the only records whose percentages do not sum to 100 (audit item A1). O and N are the source assignments (Section S17.2).

Entry	Catalyst	Solvent	Time (h)	O (%)	N (%)	N-selectivity
1	TMSOTf	MeCN	4	67	n.d.	0.00
2	$SnCl_4$	MeCN	4	64	36	0.36
3	TMSOTf	CH_2Cl_2	4	66	34	0.34
4	$SnCl_4$	CH_2Cl_2	4	60	40	0.40
5	$SnCl_4$	CH_2Cl_2	8	61	39	0.39
6	$SnCl_4$	MeCN	8	62	38	0.38
7	TMSOTf	CH_2Cl_2	8	58	42	0.42
8	$SnCl_4$	CH_2Cl_2	10	43	57	0.57
9	TMSOTf	MeCN	18	38	62	0.62
10	$SnCl_4$	MeCN	18	33	67	0.67
11	TMSOTf	CH_2Cl_2	18	n.d.	80	1.00

N-selectivity rises with reaction time in three of the four catalyst–solvent series (Table S36, Figure S8); in the $SnCl_4/CH_2Cl_2$ series it falls slightly between 4 and 8 h before rising at 10 h. No series passes from exclusive formation of one isomer to exclusive formation of the other: the record with no N-isomer detected (entry 1) and the record with no O-isomer detected (entry 11) were obtained in different solvents. Over the eleven records the association with time is strong (Pearson $r = 0.83$; Spearman $\rho = 0.89$). Entries 1 and 11 are the most influential records; without them $r = 0.93$ and $\rho = 0.86$ ($n = 9$). With unreplicated, unbalanced records, no mass balance and no kinetic measurements, these figures describe an association in the recorded data and do not show that reaction time determines the composition.

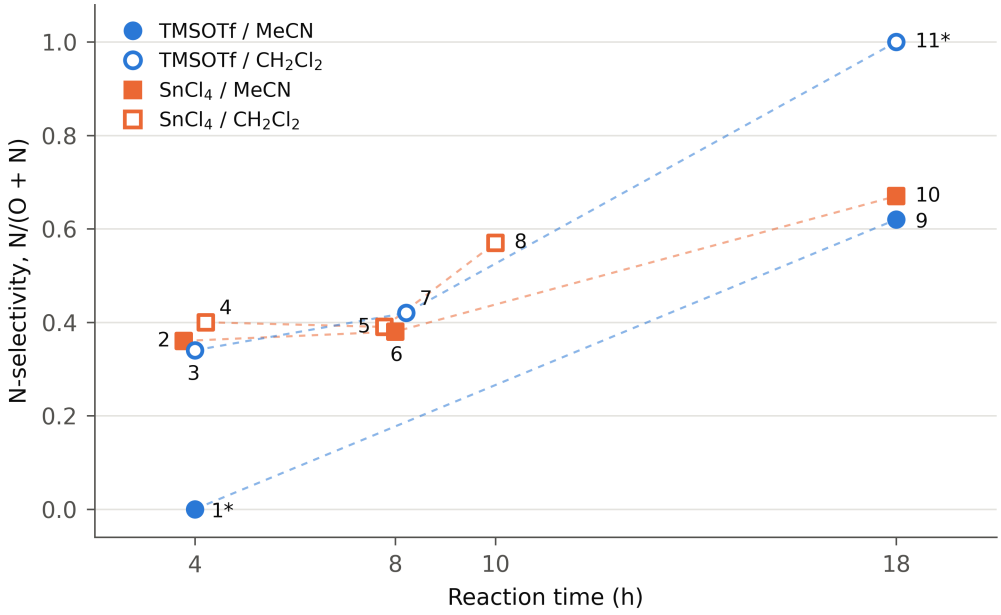


Figure S8. N-selectivity against reaction time for the eleven condensations; entry numbers as in Table S36. Symbols are the recorded experiments; points recorded at the same time are displaced horizontally by up to 0.22 h for legibility. The dashed lines join the records of one catalyst–solvent series to guide the eye and do not represent measurements between the points. Asterisks mark the two records in which one isomer was not detected.

The source concludes from entries 3, 7 and 11 that reaction time has the most significant effect, a conclusion that the association above supports as far as it goes. It also infers from entries 8 and 10 that acetonitrile shifts the reaction towards the N-isomer. Those two experiments share a catalyst but differ in both solvent and reaction time (10 h against 18 h), so the comparison is confounded by time. In the four pairs of records matched in catalyst and time, N-selectivity is lower in acetonitrile (Section S6.2); two of the differences are four and one percentage points, and the other two involve entries 1 and 11, the records that differ in kind from the other nine. When N-selectivity is regressed on time, solvent and catalyst the solvent coefficient is −0.19 with all eleven records and −0.04 without those two (Section S6.3). The recorded data therefore do not support the solvent effect claimed in the source, and they do not establish an effect in the opposite direction either.

A shift from the isomer assigned as O at short times to the isomer assigned as N at long times is compatible with conversion of the first-formed isomer into the second, which is the pathway proposed in the source, with formation of the two isomers by different species or steps of different kinetic order, and with preferential loss of the first isomer during longer reactions or work-up. The source reports no resubjection or cross-over experiment, and no mechanism is claimed here.

S17.2 The ribose pair: what the recorded data support and what they leave open

Infrared. The infrared spectra of the four glycosides are reproduced in Figure 2 of the article. The ester carbonyl absorption appears in all four, between 1741 and 1751 cm^{-1}. 117a and 123a each show a further labelled band, at 1680.47 and 1679.91 cm^{-1}; 116a and 122a show no labelled band between 1670 and 1690 cm^{-1} and instead a band at 1639.05 and 1646.32 cm^{-1}. In the trace of 122a the band at 1646 cm^{-1} has an unlabelled shoulder on its high-wavenumber side. Its level part lies at about 1665–1675 cm^{-1} on a scale computed from the tick marks of the image and at about 1670–1680 cm^{-1} on a scale fixed by the labelled bands of the same trace (Section S13 and Figure S2). It therefore cannot be placed outside the window of 1670–1690 cm^{-1}, and it lies within about 10 cm^{-1} of the band labelled 1679.91 cm^{-1} in 123a. Whether it is a separate absorption cannot be decided from the image, and no response mentions it. For 122a the operational feature is thus the absence of a labelled band and not the absence of absorption. The same caution applies to 116a. The inspection made for this article had recorded no shoulder in its trace, but both second coders, asked about each trace in the workbook of the second coding, reported an unlabelled shoulder or band between 1655 and 1695 cm^{-1} in it (Section 2.4 of the article; Table S27). Measured again after their returns, the trace has no level part, but at about 1673–1680 cm^{-1} on the tick scale of the image (1679–1686 cm^{-1} on a scale fixed at the labelled band) it falls about half as steeply as over the next 20 cm^{-1} below it (Section S13). The criterion used in this study, a labelled band at 1670–1690 cm^{-1}, is an operational description of these four spectra and not a validated diagnostic range for pyrazolone glycosides. The source states its own criterion as the absence of absorption at 1640–1690 cm^{-1}; the labelled band of 122a lies inside this range and that of 116a 1 cm^{-1} below it, and neither band is listed or discussed in the source. The origin of the 1639–1646 cm^{-1} band is not established. The source assigns a band at 1633–1635 cm^{-1} of the sugar-free aglycone to C=C stretching and does not assign the band of the glycosides. A conjugated, hydrogen-bonded lactam carbonyl absorbing below 1650 cm^{-1} cannot be excluded from the infrared data alone. The carbonyl band of the related hydrazone-type pyrazolones compared here is, however, reported at 1658 cm^{-1} for a 2-phenyl compound (Burgart et al. 2023) and at 1670 and 1682 cm^{-1} for the parent aglycone and its N-glucoside (Abdou et al. 2004), that is, about 12 to 36 cm^{-1} above the band of 122a; the N2-riboside of Haikal et al. (2003), whose aglycone is described there as an arylazo tautomer, has its pyrazolone carbonyl band at 1674 cm^{-1} (Table S23). The unlabelled shoulder of 122a lies within the range of these values. These bands extend below the window of 1670–1690 cm^{-1} used here, so the window would not capture every compound of this type. The spectra were recorded as KBr discs (Section 2.1 of the article), so the bending band of adsorbed water near 1630–1640 cm^{-1} may also contribute. Wavenumbers are quoted as printed on the figures. The infrared spectra refer to the solid and the NMR spectra to a $CDCl_3$ solution, and the tautomeric form need not be the same in both.

117a. Five recorded observations are consistent with the source assignment, the N2-glycoside in its hydrazone–lactam form (Figure 1a of the article): the band at 1680 cm^{-1}; a ^{13}C signal at 157.8 ppm; a low-field signal at 13.48 ppm, listed as one proton; five signals at 141.8, 131.2, 114.3, 112.7 and 104.1 ppm, assigned here to aryl carbons (Table S15); and

an anomeric carbon at 84.39 ppm. Each has a counterpart in the literature; the values are quoted as printed, with their location in each source, in Table S23. The carbon assignments used here differ in several places from the lists of the source, which give 157.8 ppm as C-5, the two lines read here as the aryl C–F doublet (164.8 and 162.3 ppm) as C-3′ and C-3, and 138.7 ppm as the CF_3 carbon (Table S15); the comparisons below do not depend on the lists of the source. 2-Substituted 4-arylhydrazinylidene-5-(polyfluoroalkyl)pyrazol-3-ones are reported as the Z-hydrazone tautomer in $CDCl_3$ and in the crystal, with the NNH proton at 13–14 ppm; for the 2-phenyl 5-(trifluoromethyl) compound the NNH proton is at 14.06 ppm and the most deshielded carbon, read here as the ring carbonyl, at 157.18 ppm (Burgart et al. 2023). 5-Methyl-2-phenyl analogues are likewise reported as hydrazone tautomers in solution (Deneva et al. 2019). The parent aglycone of the present compounds and its N-glucoside are printed with unassigned signals at the positions assigned here to the aryl carbons and with carbonyl bands at 1670 and 1682 cm^{-1} (Table S16; Abdou et al. 2004). The five sugar carbons of 117a (84.39, 79.70, 72.53, 70.74 and 62.91 ppm) lie within 0.2 ppm of those assigned for the *p*-tolyl analogue described as the N2-riboside (84.4, 79.7, 72.7, 70.84 and 63.0 ppm, with 84.4 ppm assigned to C-1′; Haikal et al. 2003); the aglycone of that compound is described there as the 4-arylazo-4*H* tautomer, so only its sugar signals are compared. Haikal et al. (2003) and Abdou et al. (2004) share an author, and Abdou et al. (2004) comes from the research group in which the source was prepared; the connectivity assigned in them was not examined independently here. The comparisons therefore show only that the sugar carbons of 117a match those of the compound assigned in Haikal et al. (2003) as an N2-riboside and that its aglycone signals match those of the parent aglycone and its N-glucoside; they do not establish the connectivity independently. A ^{19}F spectrum is recorded for 117a only (−64.5 and −109.5 ppm, two fluorine environments).

116a. The isomer differs in each of these respects. It shows no labelled band at 1680 cm^{-1} and no signal near 157.8 ppm, and its low-field proton appears at 9.85 ppm. The signals assigned here to its aryl carbons (153.8 or 152.3, 130.7, 120.4, 118.6 and 107.7 ppm; Table S15) lie within 1 ppm of those printed for a 3-fluorophenyl ring on an azo group (153.24, 130.25, 119.85, 117.65 and 108.04 ppm in an alkyl 3-fluorophenyl diazene, the ring positions being assigned here from the printed C–F couplings (Shen et al. 2021); the most deshielded value of azobenzene, read here as C-1, is 152.7 ppm; Singh et al. 2015) and up to 12 ppm from those of 117a (Table S16), and its aromatic protons lie at lower field (7.23–7.63 against 6.98–7.39 ppm). The recorded data therefore favour an arylazo form for 116a in $CDCl_3$ and raise uncertainty about the source assignment; they do not by themselves identify the site of attachment. Three qualifications apply. First, an N2-glycoside would be expected to show the hydrazone–lactam pattern of 117a (Burgart et al. 2023), which 116a does not. This argues against attachment at N2, but it does not exclude it: the argument assumes that a second N2-glycoside, for example the other anomer or the E isomer about the C-4=N bond, would adopt the hydrazone–lactam form of 117a in $CDCl_3$ and so show its aryl pattern (C-1′ near 142 ppm); prototropic tautomers of one connectivity would interconvert in solution and could not be isolated as two compounds. It also assumes that the spectra are correctly attributed, and the tautomeric behaviour of these glycosides has not been studied. Second, the ^{13}C shift of C-3 does not by itself distinguish a lactam carbonyl from the oxygen-bearing carbon of a 3-alkoxy- or 3-hydroxypyrazole; 116a has signals at

152.3 and 153.8 ppm, one assigned here to C-1′ and the other to C-3. Third, the identity of the low-field proton (N–H or O–H) was not established, and its shift depends on hydrogen bonding, concentration and tautomer; the difference between 13.48 and 9.85 ppm is consistent with the presence and absence of a lactam carbonyl that accepts an intramolecular N–H···O hydrogen bond and is not direct evidence of the site of attachment.

O or N1. The source assigns 116a as the O-riboside (Figure 1b of the article). An alternative that it does not consider is the N1-riboside (Figure 1c of the article). An N1-riboside has no uncharged hydrazone–lactam form; its uncharged tautomers are the 3-hydroxy–arylazo form and the N2–H 3-oxo–arylazo form. Either would give the arylazo pattern of the aryl ring and no hydrazone-type lactam band at 1680 cm^{-1}; the oxo form has a lactam carbonyl further conjugated with the N1–C-5=C-4 enamine unit, expected at lower wavenumber, which the band of 116a at 1639 cm^{-1} does not exclude. The anomeric carbon of 116a, at 90.22 ppm, lies 5.8 ppm from that of 117a. For comparison, the unassigned ^{13}C list printed for a 1-(2,3,5-tri-O-acetyl-β-D-ribofuranosyl)-1,2,3-triazole contains 90.0, 80.9, 74.4, 70.8 and 62.9 ppm, which are read here as its five sugar carbons, with 90.0 ppm as C-1′ (a value at 104.8 ppm is read as the acetal carbon of a dimethoxymethyl substituent, and one at 77.2 ppm coincides with the solvent signal); the list of a second such triazole contains 90.5 ppm (Beghennou et al. 2024). The five values lie within 0.5 ppm of the sugar carbons of 116a (90.22, 80.89, 73.98, 71.03 and 62.97 ppm). No anomeric-carbon value for an O-ribofuranoside of a hydroxypyrazole was found in the sources consulted, and the N,O-bis-glucosides of Khalil (2009), which would give an O-glycosidic value on this scaffold, were consulted only as a bibliographic record (Table S23). The resemblance to an N-ribosylazole therefore raises the N1 alternative without deciding it. Whether the sugar of 116a is attached at O or at N1 remains open. The measurements that could decide it are specified in Section S7.3. Within a full analysis of the long-range correlations, a correlation from H-1″ to C-5, which is identified in the one-dimensional spectrum by its ^{2}J(C,F) quartet, would support attachment at N1; a ^{1}H–^{19}F heteronuclear Overhauser contact between H-1″ and the CF_3 group (Dewis et al. 2019) would point the same way; and a crystal structure would settle the question for the solid.

Two-dimensional spectra. In the gHMBC spectra of 116a and 117a (Figure 3 of the article) the annotated correlations connect sugar protons with sugar carbons, and the text of the source describes no others except weak correlations of H-3″ and H-4″ of 116a with acetyl carbonyl carbons. No correlation from H-1″ to a pyrazole carbon is annotated or described. In the complete figures of the source the carbon axis extends to about 172 ppm; cross-peaks of sugar protons with the acetyl carbonyl carbons are visible there, and none is visible in the column of H-1″ at the shifts of the pyrazole carbons at the contour level plotted. A correlation weaker than that level cannot be excluded, the long-range delay of the experiment is not stated, and no inference is drawn from the absence. A correlation from H-1″ to C-3 would in any case not separate O- from N2-attachment, since both place C-3 three bonds from H-1″. Nor does a single correlation count bonds: correlations over four bonds can appear in HMBC spectra, and the absence of a correlation does not place the proton more than three bonds away (Saurí et al. 2016a; Saurí et al. 2016b).

Consequence for the evaluation. The items offer two candidates, the N2-glycoside (A) and the O-glycoside (B). For 117a the source label, candidate A, is consistent with the

recorded data. For 116a the source label is candidate B; the recorded data favour it over candidate A, but they do not establish it, and if the compound is the N1-riboside the set of candidates offered is incomplete. Agreement with the source labels is therefore reported as a secondary, conditional result. What a response cites, and whether a value given for the anomeric carbon or proton is that signal, do not depend on the label of 116a. An abstention on 116a is defensible.

S17.3 The 2-deoxyribose pair: one aglycone fingerprint, two sugar patterns

The two 2-deoxy compounds do not show the differences that the ribose pair shows. The aglycone carbons of the ^{13}C spectra printed for 122a and 123a coincide within 0.35 ppm at eight positions (157.54/157.87, 141.72/141.81, 138.23/138.43, 131.21/131.23, 123.49/123.42, 114.45/114.49, 112.68/112.67 and 103.80/103.83 ppm), the four aromatic proton shifts are the same (6.98, 7.18, 7.28 and 7.40 ppm), and the low-field proton is at 13.56 and 13.54 ppm. Both compounds therefore show the aglycone signals of 117a, including the signal near 157.5 ppm, whichever of the two ^{13}C spectra belongs to which compound (below), and this includes 122a, which the source assigns as the O-glycoside on the strength of its infrared spectrum. One line of the aryl C–F doublet is labelled 164.31 ppm in the spectrum printed for 122a against 164.86 ppm in that printed for 123a; the resulting doublet spacing differs from that of the other three compounds, and the source figure carries the same labels, so the anomaly belongs to the source record (audit item A7).

In the solid state, too, 122a resembles the hydrazone-type compounds in one respect: a labelled band at 1560–1561 cm^{-1} is common to 117a, 122a and 123a and absent from 116a, although 122a has no labelled bands near 1605 and 1531–1535 cm^{-1}, which 117a and 123a share.

The sugar signals, by contrast, differ between the two compounds (Table S18). The ^{1}H spectrum printed for 122a has H-1″ at 5.83 ppm and that printed for 123a at 5.50 ppm. The ^{13}C spectrum printed for 122a has labelled sugar lines at 78.54, 68.56, 67.09, 66.13 and 29.69 ppm; that printed for 123a has them at 66.61, 63.54 and 31.28 ppm, with two further labelled lines, at 77.21 and 76.50 ppm, within or beside the $CDCl_3$ signal. The source lists 78.5 ppm as C-1″ of 122a, with reference to its HSQC spectrum, and 77.2 and 76.5 ppm as C-1″ and C-3″ of 123a, for which it contains no correlation spectrum; its list for 123a gives C-2″ at 29.7 ppm, whereas the label on its figure is 31.28 ppm (audit item A13).

The HSQC figure of the source (its Figure 42), of which only an empty corner reached the models (Section 2.3 of the article), was examined for this article after the evaluation. It does not agree with the ^{13}C spectrum printed for the same compound (Section S15, Table S31 and Figure S3). Its proton axis carries the signals of the ^{1}H spectrum printed for 122a: the centres of the cross-peaks lie at 5.83, 5.66, 5.12, 3.93, 2.68 and 2.16 ppm, against listed values of 5.83, 5.66, 5.11, 3.94, 2.67 and 2.10 ppm (the list has an acetyl singlet at 2.15 ppm). Its aromatic and acetyl cross-peaks lie within 0.5 ppm of labelled ^{13}C values. The cross-peaks of the sugar protons, however, lie at about 76.3, 66.5, 66.7, 63.3 and 31.1 ppm on the carbon axis (one pixel of the image is 0.3 ppm, and the reading is good to about 0.5 ppm). They coincide within 0.3 ppm with lines labelled in the spectrum printed for 123a

(76.50, 66.61, 63.54 and 31.28 ppm, two cross-peaks falling on the line at 66.61 ppm). They do not coincide with the sugar lines labelled in the spectrum printed for 122a: whatever pairing is chosen, the cross-peaks of H-1″, of the two-proton signal and of the H-2″ protons have no labelled sugar line of that spectrum within 1.3 ppm, and its lines at 78.54 and 68.56 ppm have no cross-peak. Read in the same way, the cross-peaks of the HSQC figure of 117a that its annotation lines leave uncovered lie within 0.4 ppm of the labelled values of 117a (Table S32). The carbon projection drawn beside the map of 122a is the one-dimensional spectrum printed for that compound, and the sugar cross-peaks do not line up with its peaks.

What the figure shows directly is an inconsistency between two printed figures: the sugar cross-peaks of the HSQC figure printed for 122a do not lie at the labelled sugar-carbon positions of its printed ^{13}C spectrum, and they agree, within 0.3 ppm, with those printed for 123a. The positions were read, with the AI assistant (Section 2.6 of the article), from the figure as embedded in the author's files of the thesis; H.A.A. then compared the positions of the sugar cross-peaks and of the cross-peak at 103.9 ppm with the figure of the source and found them as given.

Original records found afterwards in the author's files explain the inconsistency (Section S16.3). Among scans of spectrometer printouts of 2016 are a ^{1}H and a ^{13}C spectrum recorded on 29 February 2016 under one sample designation. The ^{1}H printout has the signals of the ^{1}H spectrum printed for 122a; the four lines of H-1″ labelled on that figure are those of the printout within 0.001 ppm. The ^{13}C printout has the lines labelled in the spectrum printed for 123a (20 of its 21 labels within 0.008 ppm), among them 76.499, 66.609, 63.534 and 31.275 ppm; the printout has in addition a line at 66.654 ppm. These are the positions of the HSQC cross-peaks. A ^{13}C measurement of August 2014, of a sample whose ^{1}H spectrum likewise has the signals of that printed for 122a, has the sugar lines at 66.67, 66.62, 63.56 and 31.29 ppm and none of the four labelled at 78.54, 68.56, 67.09 and 66.13 ppm in the spectrum printed for 122a; the line at 76.50 ppm is not resolved from the solvent in it. The ^{13}C spectrum printed in the source for 123a is therefore the spectrum of the compound whose ^{1}H, COSY and HSQC spectra are printed for 122a, and the spectrum printed for 122a is not a spectrum of that compound. It is attributed here, by elimination, to the compound whose ^{1}H spectrum is printed for 123a; no original ^{13}C record of that compound was found, so this half of the attribution is not documented. On this attribution the source prints, for each compound of the pair, the proton spectra of one compound with the carbon spectrum of the other. H.A.A. compared the values read from the two printouts with the printouts and found them as given; on her statement both are measurements that she made herself on one sample. She states that she recorded all the spectra of 122a herself and on the same sample tube. The records are in keeping with this: they hold a ^{1}H and a ^{13}C spectrum under one sample designation. They do not show at which stage the ^{13}C figures came to be printed with the wrong compound. The data-file names embedded in the figures put O on the ^{1}H, COSY and HSQC figures printed for 122a and N on the ^{13}C figure printed for 123a, which are spectra of one compound, and such names are not reliable in the source: the ^{1}H figure of 117a, the N-riboside, carries a name with O. Which infrared spectrum belongs to which compound could not be verified in the same way from the records, because the letter that names the sample is crossed out by hand on two of the three

original infrared printouts. H.A.A. states that the handwritten corrections are the right ones; on her statement the source prints each infrared spectrum under the number under which it prints the ^{1}H spectrum of the same sample. The infrared spectra are used as printed.

The anomeric carbon of the compound whose ^{1}H spectrum is printed for 122a is thus the line at 76.50 ppm of the spectrum printed for 123a, where the HSQC figure has the cross-peak of the proton at 5.83 ppm, and not 78.54 ppm, the value that the list of the source gives for C-1″ with reference to that figure. All five sugar carbons of that compound appear in the spectrum printed for 123a (76.50 ppm, 66.61 ppm with a second line at 66.65 ppm on the printout, 63.54 and 31.28 ppm), and the line at 77.21 ppm, which the source lists as C-1″ of 123a, is not accounted for. On the attribution made above, the sugar carbons of the other compound, whose H-1″ is at 5.50 ppm, would be those labelled in the spectrum printed for 122a (78.54, 68.56, 67.09, 66.13 and 29.69 ppm); no correlation spectrum of that compound exists, and which of them is its anomeric carbon is not established. The lists of the analogues in the source carry both sets of sugar carbons under one ^{1}H pattern (Section S15). For the compound whose ^{1}H spectrum is printed for 122a the anomeric carbon is established in this way, at 76.50 ppm, 15 ppm below the acetal carbon C-1 of the donor 121 as listed in the source (91.5 ppm); C-1 of the donor, like C-1″ of an O-glycoside, bears two oxygen atoms, whereas C-1″ of an N-glycoside bears one oxygen and one nitrogen and is expected at higher field, so this value is more easily reconciled with an N-glycoside; no reference value for an O-glycoside of a 2-deoxypentose with a heteroaryl aglycone, and none for an N-glycoside of a 2-deoxypentopyranose, was compared. The anomeric carbons of the N-ribofuranosides compared (84.4–90.5 ppm) lie higher, but they are neither 2-deoxy sugars nor, if this ring is pyranosyl, of the same ring size; both differences move C-1 to higher field, so this comparison does not argue against an N-glycoside. The source lists no ^{13}C data of its ribose donor, a commercial tetra-O-acetylribofuranose, and no literature value for a 1-O-acylribofuranose was compared here; if C-1 of such a donor lies well above 90 ppm, the same reasoning would disfavour an O-glycoside for 116a as well, and the statement that its data do not distinguish O from N1 would have to be revised. For the other compound the anomeric carbon is not established and is not used.

The ring size of the series is also unconfirmed, and several observations are more easily reconciled with a pyranosyl ring than with the furanosyl ring that the source names. For comparison, the ^{13}C list printed for 3′,5′-di-O-acetylthymidine, a 3,5-di-O-acetyl-2-deoxy-β-D-ribofuranosyl N-nucleoside, in $CDCl_3$ contains 85.0, 82.2, 74.7, 64.1 and 36.8 ppm, which are read here as its sugar carbons (the list is unassigned in its source), and its assigned ^{1}H list has, besides H-1′, one sugar proton above 5 ppm (H-3′, 5.22 ppm), with H-4′ and H-5′ at 4.24–4.37 ppm (Bdour et al. 2006). The 2-deoxy compounds do not follow this pattern. For both, the ^{1}H lists of the source assign two one-proton signals above 5 ppm to H-3″ and H-4″ (5.66 and 5.11 ppm in 122a; 5.21 and 5.15 ppm in 123a). They assign the signals at 3.8–4.1 ppm to the two H-5″ protons (3.94 ppm, two protons, in 122a; 4.13 and 3.83 ppm in 123a, the latter listed as a doublet of 13.2 Hz). The integrals printed on the ^{1}H panels agree with these proton counts (1.03, 1.04 and 2.04 in 122a; 1.03, 1.04, 0.99 and 1.02 in 123a). In the HSQC figure the protons listed at 5.66 and 5.11 ppm have their cross-peaks at carbons near

66.6 ppm. The two-proton signal listed at 3.94 ppm has its cross-peak at 63.3 ppm, in the colour of the H-2″ methylene cross-peaks, as in a multiplicity-edited spectrum. No cross-peak lies between 77 and 103 ppm, and the account of the COSY spectrum in the source couples the proton at 5.11 ppm with the two-proton signal at 3.94 ppm. A furanoside acetylated at O-3 and O-5 has one acyloxy-substituted methine proton, a ring carbon C-4″ near 80–85 ppm, and its H-4″ and two H-5″ protons together near 4.2–4.4 ppm, as in the thymidine derivative. A 3,4-di-O-acetyl-2-deoxy-D-*erythro*-pentopyranosyl ring, which has the same formula, has two acyloxy-substituted methine groups, one of them next to a ring O–CH_2 group, which is the pattern found. A furanoside with a different acetylation pattern would not account for the data: a 2-deoxypentofuranoside has hydroxy groups at C-3 and C-5 only, so acetyl migration cannot produce a second acylated methine proton.

The couplings of H-1″ do not decide the ring size by themselves. The source lists H-1″ of 123a as a doublet of 10.8 Hz (the two lines labelled on the figure are 0.028 ppm, about 11 Hz, apart) and H-1″ of 122a as a doublet of doublets of 2.8 and 2.8 Hz, although the four lines labelled on its figure (5.840, 5.833, 5.818 and 5.810 ppm) correspond to couplings of about 9 and 3 Hz; it reads both patterns as evidence of the β configuration of a furanoside. A coupling of 9–11 Hz is of the size of an axial–axial coupling in a pyranose chair, but H-1′ of the furanosyl thymidine derivative is a triplet of 7.1 Hz (Bdour et al. 2006), and a difference of this size does not discriminate without an analysis of the other multiplets. Two original ^{1}H data sets of 2016 that show the signals printed for 122a allow one (Section S16.2): H-1″ is a doublet of doublets of about 9.0 and 2.8 Hz, H-2″a (listed at 2.67 ppm) has couplings of about 14.4, 9.1 and 3.0 Hz, the signal at 5.66 ppm is narrow and that at 5.11 ppm wide. A large vicinal coupling between H-1″ and H-2″a and only small ones at the proton at 5.66 ppm are the pattern of a chair with axial H-1″ and an equatorial H-3″, although couplings alone do not exclude a furanosyl ring. For comparison, H-1″ of the ribofuranoside 117a is a doublet of about 4 Hz (the labelled lines, at 6.003 and 5.992 ppm, are 4.4 Hz apart; 3.9–4.1 Hz in the original ^{1}H data, Section S16.1); 4.2 Hz is reported for the ribofuranosyl analogue of Haikal et al. (2003).

The record of the donor agrees with a pyranosyl ring. The source names the donor 121 as 1,3,5-tri-O-acetyl-2-deoxy-D-ribofuranose. Of the two papers it cites for the preparation of 121, however, the one given for the method of acetylation is Chen et al. (2009), whose title compound is the pyranose triacetate 1,3,4-tri-O-acetyl-2-deoxy-β-D-*erythro*-pentopyranose (consulted here as a bibliographic record only). The ^{13}C values listed for 121 (91.5, 66.9, 65.0, 62.7 and 29.4 ppm) include no carbon between 67 and 91 ppm, whereas C-4 of a furanose ring is expected near 80–85 ppm (79.7 and 80.9 ppm in the two ribofuranosides of this study; 82.2 ppm in the thymidine derivative). Its ^{1}H list has the pattern of the products (5.30 and 5.20 ppm; 4.00 and 3.85 ppm).

Taken together, these observations favour a pyranosyl ring for 122a, as far as its printed ^{1}H spectrum and HSQC figure go, and, with less support, for 123a and for the donor; for 123a the support comes from its ^{1}H list and integrals and from the maxima in the ^{1}H data of sample B of 2014, read with the assistant and not checked by H.A.A. (Section S16.3). They do not establish it: the shifts, integrals and line positions of the printed spectra are read from images, the multiplets were analysed in two original ^{1}H data sets only, the original HSQC data and the data files of the ^{13}C spectra printed in the source are not available, and

no authentic 2-deoxypentopyranosyl or 2-deoxyribofuranosyl derivative of this aglycone was available for comparison.

The available records do not exclude several explanations, which are not equally supported (Table S17). (i) The source assignment, an O- and an N-glycoside, requires the O-glycoside to reproduce the eight aglycone carbons of the hydrazone–lactam type compared and the proton at 13.56 ppm; it is supported only by the infrared figure printed for 122a, which shows no labelled band between 1670 and 1690 cm^{-1}, whereas every original infrared printout of the two samples, including one of the sample with the ^{1}H spectrum printed for 122a whose printed name is not altered, labels a band between 1677 and 1680 cm^{-1} (read from the scans with the assistant and compared by H.A.A. with the printouts; Section S16.3), and the anomeric carbon of the compound whose ^{1}H spectrum is printed for 122a argues against an O-glycoside (above). (ii) Two N2-glycosides that differ in the sugar, most simply as anomers of one pyranosyl ring form, account for the common aglycone fingerprint and the different sugar signals, and are compatible with the record of the donor; the anomeric carbon and the original infrared printout favour this reading for the compound whose ^{1}H spectrum is printed for 122a, and since both compounds show a large coupling of H-1″ (about 9 and 11 Hz), as anomers of one pyranosyl ring they would adopt opposite chair forms; this reading requires the lactam carbonyl of 122a to absorb at 1646 cm^{-1} in the solid, or to be the unlabelled shoulder at about 1665–1680 cm^{-1}, neither of which the infrared data exclude (Section S17.2). (iii) Attachment at the two different ring nitrogens is not supported, since an N1-glycoside has no hydrazone–lactam form (Figure 1c of the article) and both compounds show the signals of that form. (iv) An error in the record is established for the ^{13}C figures, which are printed with the wrong compound (above). It concerns which spectra belong together and leaves the structural question as it was: both ^{13}C spectra show the same aglycone carbons, which could be checked against original data for one of them only (Section S16.3), and the structural reading rests on the other observations of this section. (v) The infrared and NMR spectra may not describe the same species (Section S17.2): an acid-labile O-glycoside could isomerise in $CDCl_3$, and neither the age of the solution nor the purity of the sample is recorded in the source; an admixture of 123a in the solid sample of 122a would also give a shoulder near 1680 cm^{-1} and is equally untested. The original HSQC data are not among the records that H.A.A. holds, which infrared spectrum belongs to which compound is not settled by them and rests on her statement (Section S16.3), and the measurements that would decide the question of structure are specified in Section S7.3.

Because an assignment that is itself unresolved cannot be used to score an answer as chemically wrong, agreement with the labels of this pair is tabulated as agreement with the source labels and is not interpreted as chemical accuracy (Section 2.2 of the article). Infrared naming and the identification of the signal near 104 ppm do not depend on the assignment and are reported for both pairs. If reading (ii) holds, the premise of the items, that one compound is candidate A and the other candidate B, is not met for this pair. One consequence bears on the infrared criterion of Section S17.2: if reading (ii) is right, 122a is a lactam without a labelled band at 1680 cm^{-1}, and the criterion fails for it. A further consequence bears on the candidates: both drawings of this pair show a furanosyl ring, so if the ring is pyranosyl neither drawing depicts the compound, and the premise that one of

the two candidates is the compound does not hold. The last consequence bears on the items themselves: every NMR-added item of this pair contains the ^{13}C panel of 122a or that of 123a, and neither panel shows the spectrum of the compound whose ^{1}H panel it accompanies. The premise that the spectra of an item describe one compound is therefore not met for these items: the ^{1}H panel (and, for 122a, the HSQC panel) and the ^{13}C panel presented for a compound come from different compounds, and in the paired item, on the attribution made above, the two ^{13}C panels stand under each other's number. None of the 18 responses to these items remarks on an inconsistency between the panels, and the panels as supplied gave little means of detecting one, since the HSQC panel was empty and the sugar region of one ^{13}C panel was not displayed.

S18 The signal near 104 ppm and the answers of the second coders, in full

Section 3.2 of the article summarises the four observations that place the signal near 104 ppm in the aryl ring, and the answers that the two second coders gave to the questions on the anomeric carbon. Both are given here in full.

S18.1 The four observations

Four observations place the signal near 104 ppm in the aryl ring and not in the sugar. First, signals at 103.8 and 104.1 ppm are printed for the parent aglycone, which carries no sugar, and at 103.7 and 104.2 ppm for its N-glucoside (Abdou et al. 2004); the signal recurs in all three hydrazone-type compounds here (Table S16). Second, the gHMBC panel of 117a supplied to the models has a row of cross-peaks directly below the row annotated C-1″, that is, at the next higher carbon shift. Its two cross-peaks lie in the columns of the aromatic multiplets near 7.18 and 6.98 ppm; it has none near 7.39 and 7.27 ppm or in the columns of the sugar protons. The row annotated C-1″, by contrast, has its cross-peak in the column of a sugar proton (Figure 3b of the article). The carbon axis of the panel has no printed scale. On a linear scale fixed by the annotated rows of C-5″ and C-1″ and extrapolated over about 20 ppm, the row lies at about 103.5–105 ppm; on the printed carbon axis of the complete source figure it lies at about 104 ppm. The only labelled carbon between 84.39 and 112.73 ppm is 104.09 ppm, and the rows beyond it fall at the positions of the labelled aromatic carbons (Section S13). H-4′ and H-6′ are the protons three bonds from C-2′, and the source assigns the multiplets at 6.98 and 7.18 ppm to those protons, so the pattern is the one expected for C-2′. Third, the source itself assigns this signal to C-2′. Its ^{13}C lists give 104.1 ppm as C-2′ for the sugar-free aglycone and for 117a, its account of the HSQC spectrum of 117a connects this carbon with the aromatic proton at 7.27 ppm, and in its HSQC figure of 122a the cross-peak at 103.9 ppm lies in the column of the aromatic proton at 7.27 ppm (listed at 7.28 ppm; Section S15). Neither HSQC spectrum was displayed to the models. Fourth, the original ^{13}C printout of 29 February 2016 of the 2-deoxy compound whose ^{1}H spectrum is printed for 122a, whose labels H.A.A. compared with the original (Section S16.3), labels both lines of all six aryl signals. At 100.52 MHz their spacings are about 249 Hz, 26.6 Hz (104.098 and 103.833 ppm), 21.4 Hz, 10.0 and 9.1 Hz, and 3.0 Hz: the one-bond coupling of C-3′, the two-bond couplings of the two carbons ortho to fluorine, the three-

bond couplings of the two meta carbons and the four-bond coupling of the para carbon of a 3-fluorophenyl ring. The signal near 104 ppm is therefore one of the two carbons ortho to fluorine. A doublet requires coupling to a single fluorine nucleus, that is, to the aryl fluorine on C-3′ (coupling to the CF_3 group would give a quartet), and in each of the three attachment isomers of Figure 1 of the article every sugar carbon is at least nine bonds from that fluorine. The reprocessed original data of 117a give the same couplings within 0.4 Hz (26.7 Hz for the doublet at 104.09 and 103.83 ppm; Section S16.1), and the signal of C-1″ at 84.39 ppm shows no splitting of that size (a second maximum 3.0 Hz to low field in two of the three acquisitions is absent from the third, in which the line is 1.1 Hz wide at half height, and is not read as a coupling; Section S16.1). In each of the three acquisitions of 117a the two lines of this doublet are of nearly the same height (144 and 142, 101 and 103, and 26 and 27 times the noise at a line broadening of 0.3 Hz), as the two lines of a carbon split by one fluorine nucleus should be, and a ^{13}C measurement of August 2014 of a sample whose ^{1}H spectrum has the signals of the one printed for 122a has the doublet with the same spacing (26.6 Hz) and with lines of nearly the same height (9.5 and 9.8 times the noise at a line broadening of 1.0 Hz; Sections S16.1 and S16.3). The pair thus recurs at the same shifts within about 0.02 ppm, and with the same spacing (26.6–26.7 Hz), in compounds that carry a ribose and a 2-deoxyribose unit and whose anomeric carbons lie 8 ppm apart (84.39 and 76.50 ppm). The labels 103.80 and 103.83 ppm of the spectra printed for 122a and 123a lie at the high-field line of this doublet. Of the four observations, the third rests on the source itself, including a cross-peak position that H.A.A. checked, and the fourth on a printout whose labels she checked, on the original data of 117a, in which she found the doublet near 104 ppm, and no splitting of that size in the line of C-1″, herself, and on the processing, by the assistant, of the files of 2014, which she did not check; the first rests on published lists, whose values she compared with the papers, and the second on a reading of the gHMBC image made with the assistant, which she compared with the figure of the source (Section 2.6 of the article). For the panel supplied for 122a, which by the original records is not a spectrum of the compound whose HSQC figure is printed for 122a, the assignment rests on the first observation and on the coincidence of 103.80 ppm with the aryl signal of the other spectra (Table S16). The signal is accordingly assigned, in the source and here, to C-2′, the aryl CH between C-1′ and C-3′. Whatever its exact position within the aryl ring, it belongs to the aglycone and is not an anomeric carbon, so this finding does not depend on whether the compounds are N- or O-glycosides or on which sugar carbon is C-1″; besides the reading of the responses (Section 2.4 of the article), it depends on the assignment of the 104 ppm signal to the aryl ring. The answer that accompanied it differs between the compounds: on 117a and 123a it disagrees with the source label, and on 122a it agrees. The source labels one line of the doublet in each spectrum, and the splitting (0.27 ppm) is not resolved in the supplied image, so no claim is made that the multiplicity was available to the models.

S18.2 The answers of the two second coders

The answers of the two second coders show what the panels allowed a chemist to read. The workbook of the second coding asked the two coders to answer, before coding, questions on the infrared, ^{13}C and two-dimensional panels of each compound; they did not have the ^{1}H panels, the source or the article (Section 2.4 of the article; Table S27). One question

asked which labelled value is the anomeric carbon, and the next named the signal near 104 ppm and offered the answers “aromatic (aglycone) carbon”, “anomeric (sugar) carbon” and “cannot tell”. For 122a both coders gave the signal at 103.80 ppm in answer to the first question (typed as 103.8 and as 103) and marked it as the anomeric carbon in the second. For 123a, whose panel does not display the sugar region, coder B answered “cannot tell” to the first question and marked the signal at 103.83 ppm as the anomeric carbon in the second. Coder A left the first question unanswered and answered “cannot tell” to the second, with the comment “need more data to confirm”. In his second return, made after he had been asked to complete the unanswered cell, the first question is still unanswered and the second answer is “anomeric (sugar) carbon”; his remarks on two responses to this compound call the identification “not clear” and “debatable”. On the ribose pair the coders differ. Coder B named 84.39 ppm as the anomeric carbon of 117a, answered “cannot tell” for 116a and marked the signals at 104.09 and 107.67 ppm as aromatic. Coder A named 104.09 and 107.67 ppm as the anomeric carbons of 117a and 116a; on 116a all eleven committed responses, by contrast, cited the carbon assigned C-1″, at 90.2 ppm. By the assignment adopted here, an answer that gives one of these signals as the anomeric carbon is the misidentification counted in Table 3 of the article, whoever gives it.

Three conditions limit the comparison. One question named the signal and offered “anomeric (sugar) carbon” among its answers. The same workbook contained the 36 responses, 19 of which make the identification, and the order in which the coders worked was not recorded. The coders did not have the ^{1}H panels. The answers of coder B to these questions are reported, although his coding of the responses was not used (Section 2.4 of the article); the reservation about that coding may apply to them as well. Within these limits, the answers show that for 122a two chemists who had the supplied carbon panel and no reference data read the signal as the systems did. They are not a human baseline: they are the answers of two chemists to a few questions under the conditions just stated, and they are not compared statistically with the responses. The four observations above rest on data that the panels of the 2-deoxy pair do not display: the spectrum of the sugar-free aglycone, the one-bond and long-range correlations, and the original data. The count of 19 is to be read accordingly. The ten responses on 122a and 123a made an identification for which the supplied panels gave no direct evidence, only counts of the labelled carbons: for 123a the count between 100 and 165 ppm, and for 122a, besides that count with its anomalously spaced pair near 163 ppm, its four oxygenated sugar carbons, which leave no place for a fifth. The nine on 117a made it against a ^{13}C panel that labels the carbon assigned C-1″ and a gHMBC panel that marks its row, and there one of the two chemists made it as well.

S19 Comparison with published evaluations, and status of verification

S19.1 Published evaluations of language models on spectra

Table S37 compares the present audit with the seven evaluations cited in Section 1 of the article, as far as the texts consulted describe them. The entries were prepared with the assistant from the texts that could be read, named in the last column: for NMR-Challenge

the abstract of the published paper and the full text of the preprint; for ChemIQ and MaCBench the preprints, because the published texts could not be retrieved (for ChemIQ the number of questions also from the published abstract); for NMRArena the description of its repository; for CheMM-Bench the abstract, the repository and the model card of the authors. They were not checked against the publications by H.A.A. "Not described" means that the text consulted does not describe such a step, not that the step was not taken.

Table S37. What published evaluations of language models on spectra score and check, as described in the texts consulted.

Evaluation	Input	What is scored	Spectral sub-tasks scored	Cited values compared with the spectra, signal by signal	Stimulus images inspected for what they display	Text consulted
MolPuzzle (Guo et al. 2024)	IR, MS, ^{1}H and ^{13}C spectra as images	molecule understanding, spectrum interpretation and molecule construction (exact match, Levenshtein distance, validity, fingerprint similarity); error analysis	yes: spectrum interpretation, F1 per type of spectrum	not described	not described	paper
NMRArena (OdanChem 2026)	experimental ^{1}H and ^{13}C peak lists as text; 105 molecules	a ranked list of candidate SMILES (top-1 and top-10 recovery after RDKit canonicalization; Tanimoto similarity)	no	not described	not applicable (text input)	description of the repository
NMR-Challenge for LLMs (Sharlin et al. 2026)	112 problems in plain text (115 in the preprint), the spectra given as peak lists after multiplet analysis	the structure returned (name or SMILES; a Tanimoto similarity above 0.99 counted as correct), against that of human solvers; types of error	no	not described	not applicable (text input)	abstract of the published paper; full text of the preprint
ChemIQ (Runcie et al. 2026)	816 short-answer questions; for structure elucidation, simulated ^{1}H and ^{13}C NMR data (with two-dimensional data for the larger molecules) and the formula as text	the SMILES string (canonical match) or name returned	no	not described; the preprint notes that reasoning traces may not describe the method by which an answer was produced	not applicable (text input)	preprint (arXiv, version 2); the number of questions also in the published abstract
MaCBench (Alampara et al. 2025)	1,155 questions with images, among them NMR and mass spectra, X-ray diffractograms and microscopy images	the answer to each question; numerical answers within a stated tolerance (1% by default)	spectral items as whole questions	not described	questions reviewed by scientists; what each image displays not described	preprint (arXiv, version 2)
Priessner et al. (2026)	HSQC peak-matching data (JSON), with ^{1}H, ^{13}C and COSY data in support, and candidate structures	top-1 accuracy of the ranked candidates (23 of 34 molecules in the best workflow); stated confidence	no	not described; the reasoning of the model quoted in case studies	not applicable (spectra given as text)	paper
CheMM-Bench (Huang et al. 2026)	spectral images (IR, ^{1}H and ^{13}C NMR, MS) and text; SpectraQA asks for the SMILES	exact and fuzzy matching of the answer and the SMILES, as stated in the authors' repository and model card	not described	not described	not described	abstract, repository and model card
This work	IR, ^{1}H, ^{13}C and two-	the observation named;	no	yes: every value in	yes (Section	—

Evaluation	Input	What is scored	Spectral sub-tasks scored	Cited values compared with the spectra, signal by signal	Stimulus images inspected for what they display	Text consulted
	dimensional spectra as image crops; two drawn candidates	each value cited, against the value table; the identity of the signal given as the anomeric carbon; agreement with the source label (secondary)		the justification field; for the anomeric carbon also the rest of the response	S13)	

S19.2 Status of verification of the main claims

Table S38 lists the main claims of the article with the record on which each rests, who made the reading, and whether H.A.A. checked it; Section 2.6 of the article states the same in prose. A claim that rests on a reading she did not check rests on the work of the AI assistant, and every such reading can be repeated from the deposited files named.

Table S38. Claims of the article, the record on which each rests, and its status.

Claim (section of the article)	Record	Reading made by	Checked by H.A.A.
13 of the 72 justification fields are flagged (3.2)	verbatim fields (Table S4); value tables of the source figures (`panels.json`)	first-pass classification by the assistant; coding by H.A.A.	yes: the classification against the verbatim fields, and the values of the source against the labelled values of its figures; not coded a second time
The aryl carbon is given as the anomeric carbon in 19 of 35 committed NMR-added responses (3.2)	complete responses (deposit); Table S24	first reading by the assistant, repeated twice by it (Section S12); coded independently by coder A (16 of 35)	yes: each of the 36 decisions against the response
Naming of the operational infrared feature (3.3)	verbatim fields; the rule of Section S4.6	first coding by H.A.A.; rule as a script (Supporting File 3)	coded once; the second coding did not succeed (Section S14)
Agreement figures of the second coding (2.4)	returned workbooks (Supporting File 5)	computed by the assistant	no; they can be recomputed from Supporting File 5
The signal near 104 ppm is printed for the sugar-free aglycone (3.2)	published lists (Table S23)	quotations retrieved with the assistant	yes, against the paper (check sheet of 18 October 2026)
The gHMBC row below C-1″ of 117a lies in the columns of aromatic protons (3.2)	supplied image; Figure 3 of the article	reading by the assistant (Section S13)	yes: the row, its two cross-peaks in the columns of the aromatic multiplets, the absence of cross-peaks in the other columns and its position near 104 ppm on the printed axis, against the figure of the source (check sheet of 18 October 2026)
The source assigns the signal to C-2′; its HSQC cross-peak at 103.9 ppm in the figure of 122a (3.2)	the thesis (Section S15)	reading by the assistant	the cross-peak position: yes; the other statements about the source: no
C–F couplings of the aryl ring (3.2; Sections S16.1, S16.3)	printout of 29 February 2016 (Table S35); original data of	read and processed by the assistant	the labels of the printout: yes; the doublet near 104 ppm and the absence of a 27 Hz splitting of C-1″ in the original data of 117a: yes; the second

Claim (section of the article)	Record	Reading made by	Checked by H.A.A.
	117a; processed files of 2014		maximum 3 Hz from C-1″, the other couplings of 117a and the files of 2014: no
The HSQC cross-peaks of the figure of 122a agree with the lines printed for 123a (3.1)	the thesis figure (Section S15; Table S31)	positions measured by the assistant with a script	the sugar cross-peaks and the one at 103.9 ppm: yes
The ^{13}C spectra of the 2-deoxy pair are printed with the wrong compound (3.1)	the two printouts of 2016 (Figure S7; Table S35); the files of 2014; the HSQC figure	read by the assistant	the printouts: yes; the files of 2014: no; the HSQC figure: as above
Every original infrared printout of the two 2-deoxy samples labels a band at 1677–1680 cm^{-1} (3.1)	scans of three printouts (Section S16.3)	read by the assistant	yes, against the printouts (check sheet of 18 October 2026)
The ^{1}H couplings of the 2-deoxy compounds fit a six-membered ring (3.1; Sections S16.2, S16.3)	original ^{1}H data of 2016 and 2014	processed and read by the assistant	no
One sample tube for the spectra of 122a; the handwritten corrections on two infrared printouts are right (3.1)	statements of H.A.A.	—	her statements; not verifiable from the records
Status of 117a and 116a (Table 2 of the article; 3.1; Section S17.2)	values of the source; literature values (Table S23)	comparisons prepared with the assistant	the values of the source against its figures: yes; the quotations: those of compounds 2c and 3c of Abdou et al. (the values the article compares), of C-1′ and the carbonyl band of Haikal et al. and of compounds 10 and 6 of Beghennou et al.: yes (check sheet of 18 October 2026); the other values of these papers and the other quotations (among them Burgart et al.): no
What each stimulus image displays (2.3)	deposited images (Section S13)	inspection by the assistant	eight statements, among them the empty HSQC panel and the panel of 123a without its sugar region: yes; the others: no
Four responses report HSQC correlations that the panel cannot show (3.4)	complete responses; HSQC panel	text search by the assistant	the emptiness of the panel: yes (statement 1 of Section S13); the statements of the responses: no
Comparison with published evaluations (Table S37)	the publications as retrieved	the assistant	no

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