Table IV. ^{13}C Chemical Shifts of NBG in Me_2SO[a]

Anomer (rel signal inten)	C_1	C_2	C_3	C_4	C_5	C_6	C=O
α (90)	91.3	46.2	71.9	71.0	72.9	62.1	167.4
β (10)	96.3	58.6	75.0	[b]	77.7	62.1	167.4

[a] In parts per million from external Me_4Si. [b] This signal must coincide with another reported.

the gauche form. The relief of this gauche interaction accounts for the smaller $\Delta\delta$ values between the α-aminomannoses and their epimeric gluco brethren. That is, the shielding effect associated with the change in the bonding relationship of the C-2 amino group with respect to the ring is partially cancelled by a concomitant (but opposing) effect resulting from the relief of the gauche interaction with the 1-OH substituent.

To observe both anomers of NBG in dimethyl sulfoxide solution, the original sample was maintained at room temperature for a period of 2 months, at which time the α-D anomer was preponderant. The ^{13}C NMR spectrum confirmed the ^{15}N NMR results which indicated that both anomers were present in an α:β ratio of 90:10. The ^{15}N chemical-shift difference between anomers of NBG is 0.4 ppm, compared with values of 1.6 and 0.7 ppm, respectively, for anomers of GA·HCl and NAG; thus $\Delta\delta_{-NH_3^+} > \Delta\delta_{-NHAc} > \Delta\delta_{-NHCOPh}$.

The shielding differences in these 2-amino-2-deoxy-D-hexoses could well be a function of the orientation of the nitrogen about the N–C-2 bond and, because the shielding differences are often larger than 1 ppm, they could be a source of stereochemical information.

Experimental Section

All the 2-amino-2-deoxy-D-hexose derivatives were purchased from Sigma Chemical Co., Inc., and were used without further purification. The ^{15}N NMR spectra were recorded in 25-mm sample tubes at temperatures of ca. 30–40 °C on a Bruker WH-180 spectrometer equipped with a Nicolet B-NC 12 computer with 24K memory (16K for spectrum accumulation), operating at 18.25 MHz in a pulsed Fourier transform mode with complete broad-band, proton noise decoupling. The computer allowed acquisition of 8192 data points for a spectrum having a sweep width of 10 000 Hz. A typical experiment required 1–2 h of data acquisition, using a pulse width of 20 μs (20° flip angle) at pulse intervals of 2.0 s. Chemical shifts are reported in parts per million (ppm) upfield from external nitric acid (1 M 98% ^{15}N-enriched nitric acid in deuterium oxide) capillary in which deuterium oxide was used to produce the field lock signal. Spectra of 25% solutions of the 2-acetamido-2-deoxy-D-hexoses and the 2-amino-2-deoxy-D-hexose hydrochlorides in water were recorded after reaching their mutarotational equilibria. A 20% solution of *N*-benzoyl-2-amino-2-deoxy-α-D-glucose in dimethyl sulfoxide mutarotated to ca. 10% of the β anomer after standing at room temperature for 2 months.

The ^{13}C NMR spectrum of NBG was recorded for the same sample used for the ^{15}N spectrum with the Bruker WH-180 spectrometer operating at 45.28 MHz. The chemical shifts of the skeletal carbons of the pyranose ring and the carbonyl carbon in both anomers are reported in Table IV.

References and Notes

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(2) R. W. Jeanloz and E. A. Balazs, "The Amino Sugars", Vol. IA, IB, IIA, and IIB, Academic Press, New York, N.Y., 1969.
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(13) Two fundamental types of hydrogen bonding are possible, >N:···H–X and >N–H···:X. Such interactions are known to influence nitrogen resonance-line positions in opposite directions: R. O. Duthaler and J. D. Roberts, unpublished results.
(14) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Interscience, New York, N.Y., 1965, p 421.
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(16) G. L. Anderson and L. M. Stock, *J. Am. Chem. Soc.*, **90**, 212 (1968).
(17) In derivatives of β-mannosamine, the axial amino function has a cis-bonding relationship to both the C-1 and C-3 hydroxyl groups; therefore, a shift value must be estimated for a system in which an equatorial amino function retains the same bonding relationships to these hydroxyl groups. In the latter case, the C-1 and C-3 hydroxyl groups have an axial-bonding relationship with respect to the pyranose ring. A value of −1.6 (−0.7) ppm can be derived from the structural change 1-OH_e → 1-OH_a from the chemical shifts of the α and β forms of 2-amino-2-deoxyglucose. If an analogous change in the bonding of the 3-OH results in a similar shift difference, an additional factor of −1.6 (−0.7) ppm should be introduced into the shielding values of the α-aminoglucose derivatives. Thus, $\Delta\delta = \delta_{\beta\text{-MA·HCl}} - (\delta_{\alpha\text{-GA·HCl}} - 1.6) = +12.9$ ppm; $\Delta\delta = \delta_{\beta\text{-NAM}} - (\delta_{\alpha\text{-NAG}} - 0.7) = +10.6$ ppm.

^{15}N Nuclear Magnetic Resonance Spectroscopy. Natural-Abundance ^{15}N Nuclear Magnetic Resonance Spectra of Enamines[1]

Philip W. Westerman and John D. Roberts*

Contribution No. 5471 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91125

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The ^{15}N chemical shifts of 18 cyclic enamines have been determined at the natural-abundance level of ^{15}N using the Fourier transform technique. The shifts depend on the size of both the cycloalkene and nitrogen-containing rings. Methyl substituents on the cycloalkene ring also influence the chemical shifts of enamines. Tertiary amines formed on hydrogenation of cyclic enamines are found to have ^{15}N chemical shifts 3.9–19.7 ppm upfield of the shift for the corresponding unsaturated compound. A carbonyl group in conjugation with an enamine group results in a large downfield shift of approximately 30–40 ppm for the nitrogen resonance of the enamine.

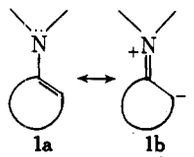
The nitrogen lone-pair electrons of an enamine can interact with the π electrons of the enamine double bond, enhancing the electron density of the β-alkenic carbon and making this position available for introduction of a substituent by a wide variety of electrophilic reagents.[2] The reactivities of enamines formed from cyclic ketones depend on the ring size and substitution pattern of both the ketone and amine parts.[3-7]

Table I. ^{15}N Chemical Shifts of Cyclic Enamines[a]

R	2	3	4	5	6	7
a —N⟨	304.1	300.7	299.3	301.2	317.6	302.9
b —N⟨	304.0	301.1	298.6		319.9	307.4
c —N⟨	306.5	305.7				
d —N⟨O	308.8	305.4	303.2			
e —N(Et)$_2$	304.5	304.0				

[a] Upfield with respect to external 1.0 M $D^{15}NO_3$ for 20 mol % solutions in cyclohexane.

The conformation and the degree of p–π overlap in cyclic enamines have been studied by ^1H and ^{13}C NMR spectroscopy.[5-9] It has been postulated[5,7,9] that the chemical shifts of the alkenic proton and β-alkenic carbon reflect the degree of p–π overlap in these molecules, i.e., the relative contributions of resonance forms **1a** and **1b** to the structure.



1a **1b**

In principle, an indication of the relative contributions of these canonical forms should also be available through consideration of ^{15}N chemical shifts for these compounds. For this reason, we have studied the natural-abundance ^{15}N NMR spectra of 18 cyclic enamines and a number of closely related compounds. We have also obtained ^{15}N NMR spectra of the 16 tertiary amines formed on hydrogenation of the above enamines, to ascertain how the removal of p–π overlap influences the ^{15}N chemical shifts.

Experimental Section

The cyclic enamines were synthesized and purified by the method of Stork and co-workers.[10] Physical properties and ^1H NMR spectral parameters were consistent with reported data.[5,8,10,11] *N,N*-Diethylenamines were prepared as described by Blanchard.[12]

Cyclic enamines were hydrogenated in ethanol at room temperature and 50 psi pressure of hydrogen, over 5% palladium on charcoal. Uptake of hydrogen was complete after 20 min, at which time shaking was discontinued and the catalyst removed by filtration. The solvent was evaporated and the residue distilled under reduced pressure. Physical and spectral properties for each tertiary amine were consistent with reported values.[4,13]

Cyclic enamino ketones were prepared by the method of Panouse and Sannié.[14] All other compounds used were commercial materials.

Proton noise-decoupled ^{15}N NMR spectra were recorded at the natural-abundance level with a Bruker WH-180 NMR spectrometer operating at 18.25 MHz. Measurements were made on large sample volumes (25-mm o.d. tubes, using 15–22-mL samples) with quadrature detection and Fourier-transform mode operation. Each spectrum was obtained with a repetition rate of 4.5 s, an acquisition time of 0.819 s, and a total accumulation of 2000 transients. The pulse angle was 20° (20-μs pulse width) at a decoupling power of 4 W. The chemical shifts are reported in parts per million upfield from external 1.0 M $H^{15}NO_3$ in D_2O (5-mm o.d. NMR tube).

Results and Discussion

The ^{15}N chemical shifts of cyclic enamines for cyclohexane solutions are reported in Table I. The results show that the ^{15}N shifts for cyclic enamines occur in the range 298.6–319.6 ppm upfield of $D^{15}NO_3$. If the compounds with a methyl ring substituent are excluded from consideration the range is much smaller (10.2 ppm).

That the alkenic proton and β-alkenic carbon-13 chemical shifts in pyrrolidine enamines are upfield by approximately 0.3 and 4–6 ppm, respectively, of the corresponding shifts in piperidine enamines has been attributed to a greater contribution of canonical form **1b** in the resonance hybrid of the structure of pyrrolidine enamines compared with piperidine enamines. This explanation is consistent with the greater reactivity of the pyrrolidine enamines in electrophilic substitution at their β-alkenic carbons. Comparison of the ^{15}N chemical shifts in pyrrolidine enamines with the shifts in the corresponding piperidine enamines reveals no systematic trends. For compounds **2a** and **2b** as well as **3a** and **3b** there are no significant chemical-shift differences while for **4a** and **4b** a small downfield shift is observed. Of **6a** and **6b**, and **7a** and **7b**, the piperidine enamines have shifts at higher field.

The relative degree of nitrogen lone-pair overlap with the alkene group has been estimated for ketone enamines corresponding to **a–e** by the ^{13}C carbonyl chemical shifts,[9] but the values so obtained do not correlate with the ^{15}N chemical shifts for the analogous compounds of either series **2** or **3**.

Table I shows that there is an upfield shift of about 3 ppm for enamines of cyclopentanone compared with the corresponding enamine of cyclohexanone. Because a double bond exo to a five-membered ring is more stable than the related double bond which is exo to a six-membered ring, we might have predicted that the dipolar resonance form **1b** of the enamines would have a greater contribution in the cyclopentanones compared to the cyclohexanones examined. The upfield shifts of both the β-alkenic carbon[9] and alkenic proton[7] signals in the former series are in agreement with this notion, but the upfield shift of the ^{15}N signals is not.

For ^{15}N chemical shifts, a decrease in electron density at a particular atom does not necessarily result in a downfield shift as is generally the case for ^1H and ^{13}C chemical shifts. Upfield shifts in the resonances of sp^2-hybridized nitrogens and downfield shifts for sp^3-hybridized nitrogens are well established for protonation of nitrogen atoms in organic molecules.[15] Apparently with sp^2-hybridized nitrogens carrying a lone pair, the second-order paramagnetic effect which is associated with the energy of the $n \rightarrow \pi^*$ transition is an important influence on the shift and will usually dominate simple electron density effects.

The data of Table I show that the shifts in cycloheptanone enamines are generally downfield by 1.4–2.5 ppm of the shifts in related cyclohexanone enamines. Again the relative order of the alkenic proton chemical shifts[7] corresponds to that of nitrogen shifts. It has been argued[7] that the maximum conformational hindrance to form **1b** in five- to seven-membered cycloalkanone enamines is offered by the seven-membered ring and consequently the cycloheptanone enamine should have the lowest field signal for the alkenic proton. If the resonances of sp^3-hybridized nitrogens move downfield with decreasing electron density, then the observed order of nitrogen shifts in Table I is not consistent with this reasoning.

The nitrogen resonances of 1-(pyrrolidino)cyclooctene is upfield of the corresponding cycloheptene derivative by 1.9 ppm. The relative alkenic proton shifts are the same for these two compounds.

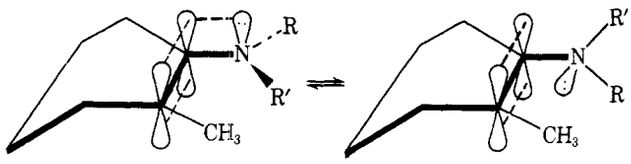
The ^{15}N shifts in morpholine enamines are upfield of the shifts in related piperidine enamines by about 4 ppm. The oxygen in the morpholine ring probably should not greatly affect the degree of interaction of the nitrogen with the double bond in the enamine and the ^1H and ^{13}C NMR data support this assertion.[7,9] If so, then the observed upfield shifts must have a different origin. The same shift difference is in fact displayed by morpholine (342.7 ppm) and piperidine (336.2

ppm), both measured in cyclohexane under comparable conditions (20 mol %). A similar upfield shift is observed[16] in butylamine on replacement of the γ-methylene group with an oxygen atom. It is possible that the observed shift difference for these enamines is a consequence of the inductive effect of the substituted 3-oxapentamethylene group [(-CH_2CH_2)$_2$O, σ^* = +0.67] compared with the pentamethylene group [-$(CH_2)_5$, σ^* = −0.18], although again the relative order is the opposite of that anticipated on the basis of simple electron-density considerations. Irrespective of its origin, there is a counterpart in the upfield ^{13}C shift which occurs through replacement of a γ-methylene or methyl group with a γ-oxygen or nitrogen of the same spatial disposition (Chart I of ref 17).

$CH_3OCH_2CH_2NH_2$ 361.7 ppm $CH_3CH_2CH_2CH_2NH_2$ 352.3 ppm

In Table II we have summarized methyl-substituent parameters for 1-(cycloalkylamino)-6-methylcyclohexenes and 1-(cycloalkylamino)-2-methylcyclohexenes. The assignment of resonances in the two isomeric 1-(pyrrolidino)methylcyclohexenes was made on the basis of the relative signal intensities and the reported isomer ratios.[5,9] The two piperidine isomers are present in approximately equal amounts,[5,9] so by analogy with the relative order of the signal in the pyrrolidine case, it was assumed that the upfield signal resulted from 1-(piperidino)-2-methylcyclohexene.

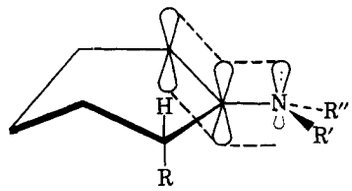
The data in Table II show that a 2- or 6-methyl substituent on the cyclohexene ring causes an upfield shift in the ^{15}N resonance of 1-(cycloalkylamino)cyclohexenes. The greater shifts are found for piperidine than pyrrolidine compounds, and much larger for a 2-methyl than a 6-methyl substituent. The steric and electronic factors which influence the isomer ratio of these four compounds have been discussed on the basis of ^{13}C and ^{1}H NMR data.[5,9] It has been argued[5] that in 2-methyl substituted 1-(*N,N*-dialkylamino)cyclohexenes **8**, the large steric interactions between R and R′ and the methyl substituent precludes their coplanarity and any substantial high degree of p–π overlap in the molecule. Consequently, the



8 **9**

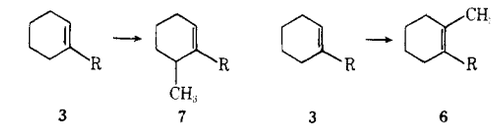
replacement of the alkenic proton by a 2-methyl group should result in an increase in steric interactions and a twisting of the R and R′ groups out of plane, thus increasing the proportion of conformations such as **9**. Because the nitrogen atom in **9** is more like an ordinary tertiary amine nitrogen (cf. Table III), the observed upfield shift caused by a 2-methyl substituent is expected. The larger shift changes for piperidine derivatives compared to pyrrolidine derivatives on 2-methyl substitution results from greater steric interactions in structures such as **8** with six-membered rings.

The methyl group of the 6-methyl derivatives of Table II is pseudoaxial[5,9] and relatively free from the steric interactions described above, so a large degree of overlap can be maintained on changing R = H to R = CH_3 in structure **10**. Con-



10

Table II. Methyl Effects on ^{15}N Chemical Shifts in Cyclic Enamines



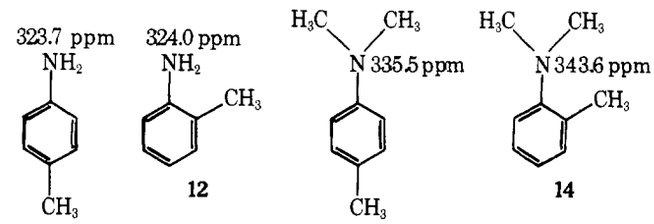
3 7 3 6

R	$\Delta\delta_{^{15}N}$[a]	$\Delta\delta_{^{15}N}$[a]
a —N⟨	2.2	16.9
b —N⟨	6.3	18.5

[a] $\Delta\delta_{^{15}N}$ = [δ(6 or 7) − δ(3)].

sequently, a smaller change in ^{15}N chemical shifts takes place when a 6-methyl is introduced.

This analysis of enamine shifts is supported by the ^{15}N spectra of several aniline derivatives (**11–14**). The effect of introducing two *N*-methyl substituents on the shift of *p*-toluidine (that is, **11** → **13**) is a *diamagnetic* shift of 11.8 ppm.

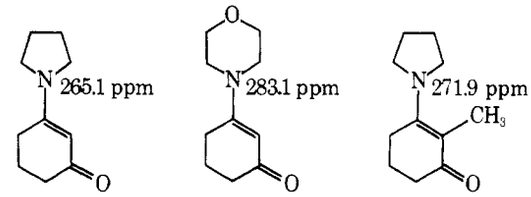


323.7 ppm 324.0 ppm 335.5 ppm 343.6 ppm

11 **12** **13** **14**

The same substitutions change the ^{15}N shift of *o*-toluidine (**12** → **14**) upfield by 19.6 ppm. This larger upfield shift results from steric interactions preventing nonplanarity of the $N(CH_3)_2$ group with the benzene ring in **14**. It is unlikely that there is any corresponding steric inhibition of resonance in either **11** or **13**. Comparison of the shifts in **11** and **12** show the equality of *o*- and *p*-methyl substituent effects in the ^{15}N shift of aniline. The ^{13}C shifts of *o*-toluidine and *N,N*-dimethyl-*o*-toluidine also support these conclusions.[9]

The ^{15}N shifts of enamino ketones **15** and **16** occur at 265.1 and 283.1 ppm, respectively, in agreement with earlier ^{14}N

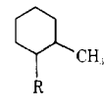
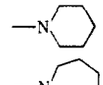
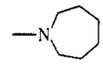
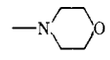


265.1 ppm 283.1 ppm 271.9 ppm

15 **16** **17**

measurements of compounds containing the same functional group.[18] Thus, a carbonyl group in conjugation with the double bond of an enamine induces a large downfield shift in the ^{15}N resonance of an enamine (compare $\delta_{^{15}N}$ in **3a** and **3b** with $\delta_{^{15}N}$ in **15** and **16**, respectively). The observed shift can be associated either with (1) increased electron withdrawal of the nitrogen lone-pair electrons by the strongly electron-withdrawing carbonyl group or (2) the expected decrease in the n → π* transition energy associated with introduction of the carbonyl group thus increasing the second-order paramagnetic effect at the nitrogen, and (3) a possible change in geometry of the nitrogen from pyramidal in enamines to planar in enamino ketones. Whatever the relative importance of each factor, there are corresponding ^{1}H and ^{13}C chemical shift differences between enamines and enamino ketones.[6,9] The ^{15}N shift of **17** shows that the effect of a 2-methyl substituent on the shift of **15** is smaller than the effect of a 2-methyl group on the shift of the enamine **3a**. The upfield shift

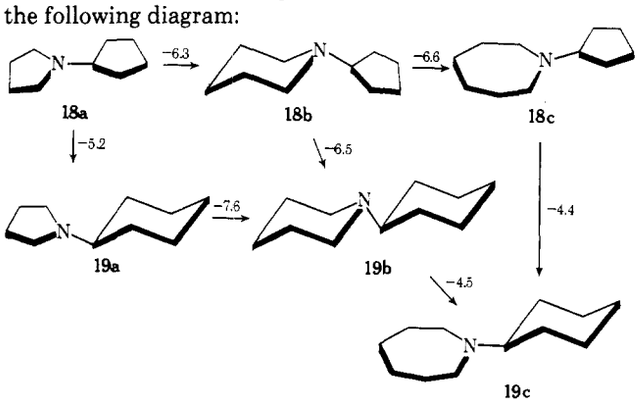
Table III. ^{15}N Chemical Shifts of Cyclic Tertiary Amines[a]

	R	 18	 19	 20	 21	 22
a		308.0 (3.9)	313.2 (12.5)	313.3 (14.0)	311.5 (10.3)	312.9 (−4.7)
b		314.3 (10.3)	320.8 (19.7)	317.9 (19.3)		319.6 (−0.3)
c		320.9 (14.4)	325.3 (19.6)			
d		318.5 (9.7)	323.9 (18.5)	322.5 (19.3)		
e	—N(Et)$_2$	321.1 (16.6)	321.0 (17.0)			

[a] See corresponding footnote in Table I. Numbers in parentheses are the shift differences between tertiary amines and the related enamines. $\Delta\delta = \delta(\text{amine}) - \delta(\text{enamine})$.

produced by a 2-methyl group in **15** could result from both torsional distortion about the C (alkene)–N bond, smaller than that postulated in the corresponding enamine, or a change in the nitrogen configuration from planar to pyramidal.

The ^{15}N chemical shifts for tertiary amines resulting from hydrogenation of cyclic enamines are summarized in Table III. This table shows that chemical shifts for compounds **18–21** occur in the range 308.0–325.3 ppm or 3.9–19.6 ppm upfield of shifts in the corresponding enamines. The increased shielding, although not large, is in the direction expected for an increase in electron density in the nitrogen atom as a result of the removal of p–π overlap of the nitrogen lone pair with the double bond. For two cases, **22a** and **22b**, the resonance of the tertiary amine is downfield of the shift in the corresponding enamine. Comparisons of shifts for **22a,b** and **19a,b** show that the 2-methyl substituent has little influence on the shifts for **19a** and **19b**. The downfield shift changes thus result from the unusually high-field resonances of enamines **6a** and **6b** and hydrogenation removes the factors responsible for these high-field shifts. It is evident from Table III that the cycloalkyl group and the heterocyclic ring size influence the ^{15}N chemical shifts of compounds **18–21**, as can be seen from the following diagram:



Introducing a γ-methylene group into either ring of 1-cyclopentylpyrrolidine (**18a**) produces an upfield shift of 5–6 ppm. The effect is additive so that a γ-methylene group in each ring causes an approximately double upfield shift (12.8 ppm). Two adjacent methylene groups added to the five-membered ring of pyrrolidine in either **18a** or **19a** move the nitrogen shift upfield by 12.9 and 12.1 ppm, respectively.

The ^{15}N shifts in the tertiary amines of Table III which are morpholine derivatives are upfield of the shifts in their piperidine analogues by 3–4 ppm.

One difference between tertiary amines and enamines is the large shift difference between diethylamine derivatives and the related pyrrolidine compounds. Conversion of an *N,N*-diethylamino group to a five-membered ring causes 13.1 and 7.8 ppm downfield shifts in the ^{15}N signals of compounds **18e** and **19e**, respectively, but no change in the corresponding enamine compounds. The explanation for this observation and others noted above awaits further clarification of the conformations of compounds **18–21**, as well as increased understanding of the other factors which might influence ^{15}N chemical shifts.

Registry No.—**2a**, 7148-07-4; **2b**, 1614-92-2; **2c**, 7374-91-6; **2d**, 936-52-7; **2e**, 34969-48-7; **3a**, 1125-99-1; **3b**, 2981-10-4; **3c**, 23430-63-9; **3d**, 670-80-4; **3e**, 10468-24-3; **4a**, 14092-11-6; **4b**, 19353-04-9; **4d**, 7182-08-3; **5a**, 942-81-4; **6a**, 5049-40-1; **6b**, 6128-00-3; **7a**, 5049-51-4; **7b**, 6127-99-7; **18a**, 18707-33-0; **18b**, 7335-04-8; **18c**, 5024-91-9; **18d**, 39198-78-2; **18e**, 34969-56-7; **19a**, 7731-02-4; **19b**, 3319-01-5; **19c**, 19797-11-6; **19d**, 6425-41-8; **19e**, 91-65-6; **20a**, 18707-34-1; **20b**, 62059-30-7; **20d**, 39198-79-3; **21a**, 18707-36-3; **22a**, 18707-25-0; **22b**, 55905-10-7.

References and Notes

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