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Supporting Information

69451 Weinheim, Germany

Synthesis and New Reactions of Highly Strained 2,3-Bridged 2*H*-Azirines

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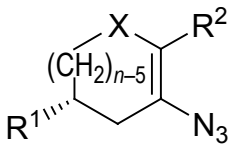
Table S1: Methods for the synthesis of cyclic vinyl azides **2**.



2

Cyclic vinyl azide **2**	*n*	R^1	R^2	X	Method for the synthesis of **2**	Reference
2a	5	H	H	CH_2	Zbiral's sequence[a]	[11b]
2b	6	H	H	CH_2	Zbiral's sequence[a]	[11b]
2c	7	H	H	CH_2	Hassner's method[b,c] (Zbiral's sequence is also possible)	this work (see also [11b])
2d	8	H	H	CH_2	Hassner's method[b]	[4]
2e[d]	12	H	H	CH_2	Hassner's method[b,c]	this work
2f	6	$CMe=CH_2$	Me	CH_2	Epoxid + NaN_3 followed by dehydration[e]	this work
2g	5	H	Me	CH_2	Radical addition of IN_3 followed by dehydrohalogenation[f]	this work
2h	6	H	Me	CH_2	Radical addition of IN_3 followed by dehydrohalogenation[f]	this work
2i	6	H	H	C=O	Nucleophilic substitution[g]	[6g]
2j	6	H	Me	C=O	Nucleophilic substitution[g]	[6g]
2k	5	H	Me	C=O	Nucleophilic substitution[g]	[6g]

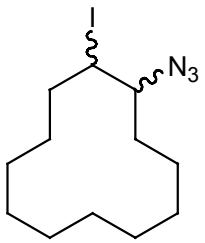
[a] The corresponding cyclic *trans*-1,2-halohydrins resulting from epoxides are treated with HN_3 under Mitsunobu conditions to give *cis*-1-azido-2-halocycloalkanes, which lead to **2** on base-induced dehydrohalogenation. [b] Generation of iodine azide in situ followed by electrophilic addition of this reagent at cycloalkenes and base-induced elimination of hydrogen iodide. [c] See also footnote [9]. [d] Mixture with (*Z*)-**2e** : (*E*)-**2e** = 2.5:1. [e] See also the upper part of Scheme 2. [f] See also the lower part of Scheme 2. [g] The corresponding chloro compounds are treated with NaN_3.

Selected physical data of compounds

E-**2e**, *Z*-**2e**, **2f**, **2g**, **2h**, **3e**, **3f**, **3h**, **3i**, **3j**, *cis*-**9a**, *trans*-**9g**, *cis*-**9h**, *trans*-**9h**, **10g**, **10h**, **11g**, **15k**, **16k**, **17b**, **17c**, **18b**, **18c**, **18h**, **18l**, **19b**, **19c**, **19j**, **20c**, **20j**, **21c**, **21d**
as well as **I**, **II**, **III**, **IV**.

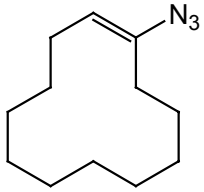
Only new compounds are listed in this supporting information. **Caution** should be exercised during isolation of azides, which may be explosive. Therefore, combustion analyses were not performed in the case of azides.

1-Azido-2-iodocyclododecane (**I**): Light-yellow liquid. – **IR** ($CDCl_3$): $\tilde{\nu}$ = 2103 cm^{-1} (N_3). – **^{1}H NMR** ($CDCl_3$): δ = 1.20 – 2.15 (m, 20 H), 3.29 (m, 1 H, CHN_3), 4.32 (m, 1 H, CHI). – **^{13}C NMR** ($CDCl_3$): δ = 20.98 (t), 22.82 (t), 23.19 (t), 23.38 (t), 23.62 (t), 24.13 (t), 24.16 (t), 24.29 (t), 30.68 (t), 35.66 (t), 36.68 (d, CHI), 62.97 (d, CHN_3).

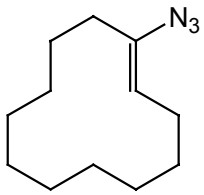


I

E-/*Z*-1-Azidocyclododecene (**2e**): Yellow liquid. – **IR** ($CDCl_3$): $\tilde{\nu}$ = 2110 cm^{-1} (N_3). – **^{1}H NMR** ($CDCl_3$): δ = 1.21 – 1.60 (m, 32 H), 2.08 (m, 4 H, 3-H or 12-H *E*-**2e** and *Z*-**2e**), 2.17 (m, 2 H, 3-H or 12-H, *E*-**2e**), 2.33 (m, 2 H, 3-H or 12-H, *Z*-**2e**), 4.79 (t, ^3J = 7.4 Hz, 1 H, =CH, *Z*-**2e**), 5.06 (t, ^3J = 8.0 Hz, 1 H, =CH, *E*-**2e**). – **^{13}C NMR** ($CDCl_3$): δ = 22.12 (t, *E*-**2e**), 22.36 (t, *E*-**2e**), 23.92 (t, *E*-**2e**), 24.09 (t, *Z*-**2e**), 24.12 (t, *E*-**2e**), 24.42 (t, *E*-**2e**), 24.44 (t, C-3 or C-12, *E*-**2e**), 24.47 (t, *Z*-**2e**), 24.68 (t, *E*-**2e**), 24.91 (t, *E*-**2e**), 24.98 (t, 2 C, *Z*-**2e**), 25.16 (t, *Z*-**2e**), 25.21 (t, C-3 or C-12, *E*-**2e**), 25.49 (t, *Z*-**2e**), 25.92 (t, *Z*-**2e**), 26.01 (t, C-3 or C-12, *Z*-**2e**), 26.14 (t, *Z*-**2e**), 27.19 (t, *E*-**2e**), 32.50 (t, C-3 or C-12, *Z*-**2e**), 116.41 (d, =CH, *E*-**2e**), 120.00 (d, =CH, *Z*-**2e**), 133.53 (s, *Z*-**2e**), 137.45 (s, *E*-**2e**).



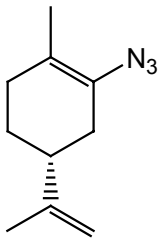
E-**2e**



Z-**2e**

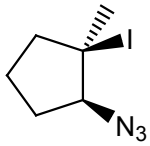
The assignment of the ^{13}C NMR signals was performed with the help of ^{13}C,^{1}H shift correlation and ^{13}C NMR spectra, for which the signals could be integrated. The γ effect of ^{13}C NMR spectroscopy was used to assign *E*- and *Z*-isomers.

(4*R*)-2-Azido-4-isopropenyl-1-methylcyclohexene (2f): Yellow liquid. – **IR** ($CDCl_3$): $\tilde{\nu}$ = 2099 cm^{-1} (N_3). – **^{1}H NMR** ($CDCl_3$): δ = 1.43 (m, 1 H), 1.61 (s, 3 H, CH_3), 1.75 (s, 3 H, CH_3), 1.76 (m, 1 H), 1.99 – 2.21 (m, 3 H), 2.24 – 2.34 (m, 2 H), 4.75 (m, 1 H, =CH_2), 4.77 (m, 1 H, =CH_2). – **^{13}C NMR** ($CDCl_3$): δ = 17.21 (q), 20.62 (q), 27.31 (t), 30.02 (t), 30.93 (t), 41.55 (d), 109.49 (t), 120.33 (s), 125.37 (s), 148.40 (s).



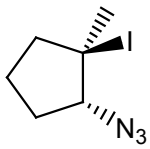
2f

cis-2-Azido-1-iodo-1-methylcyclopentane (*cis*-**9g**): Light-yellow liquid. – **IR** ($CDCl_3$): $\tilde{\nu}$ = 2106 cm^{-1} (N_3). – **^{1}H NMR** ($CDCl_3$): δ = 1.46 – 2.18 (m, 7 H), therein 2.02 (s, 3 H, CH_3), 2.32 – 2.47 (m, 2 H), 4.26 (m, 1 H, CHN_3). – **^{13}C NMR** ($CDCl_3$): δ = 19.70 (t), 28.85 (t), 33.27 (q), 44.50 (t), 60.04 (s), 72.38 (d, CHN_3).



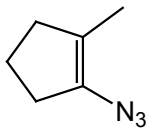
cis-**9g**

trans-2-Azido-1-iodo-1-methylcyclopentane (*trans*-**9g**): Light-yellow liquid. – **IR** ($CDCl_3$): $\tilde{\nu}$ = 2110 cm^{-1} (N_3). – **^{1}H NMR** ($CDCl_3$): δ = 1.72 – 2.00 (m, 4 H), 2.08 (s, 3 H, CH_3), 2.25 (m, 1 H), 2.40 (m, 1 H), 4.26 (m, 1 H, CHN_3). – **^{13}C NMR** ($CDCl_3$): δ = 21.97 (t), 29.37 (t), 30.40 (q), 44.48 (t), 54.64 (s), 75.33 (d, CHN_3).



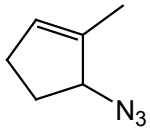
trans-**9g**

1-Azido-2-methylcyclopentene (**2g**): Yellow liquid. – **IR** ($CDCl_3$): $\tilde{\nu}$ = 2107 cm^{-1} (N_3). – **^{1}H NMR** ($CDCl_3$): δ = 1.57 (m, 3 H), 1.90 (m, 2 H), 2.30 (m, 2 H), 2.53 (m, 2 H). – **^{13}C NMR** ($CDCl_3$): δ = 12.50 (q), 20.18 (t), 30.64 (t), 35.95 (t), 123.42 (s), 129.46 (s).



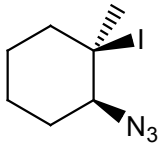
2g

5-Azido-1-methylcyclopentene (**10g**): Colorless liquid. – **IR** ($CDCl_3$): $\tilde{\nu}$ = 2105 cm^{-1} (N_3). – **^{1}H NMR** ($CDCl_3$): δ = 1.78 (m, 3 H), 1.96 (m, 1 H), 2.30 (m, 2 H), 2.41 (m, 1 H), 4.09 (br. s, 1 H, CHN_3), 5.63 (br. s, 1 H, =CH). – **^{13}C NMR** ($CDCl_3$): δ = 14.19 (q), 30.61 (t), 30.71 (t), 70.49 (d, CHN_3), 129.79 (d, =CH), 137.92 (s).



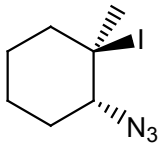
10g

cis-2-Azido-1-iodo-1-methylcyclohexane (*cis*-**9h**): Light-yellow liquid. – **IR** ($CDCl_3$): $\tilde{\nu}$ = 2104 cm^{-1} (N_3). – **^{1}H NMR** ($CDCl_3$): δ = 1.10 – 2.24 (m, 11 H), therein 2.07 (s, 3 H, CH_3), 3.96 (m, 1 H, CHN_3). – **^{13}C NMR** ($CDCl_3$): δ = 24.02 (t), 24.34 (t), 30.08 (t), 35.75 (q), 44.22 (t), 60.16 (s), 69.52 (d, CHN_3).



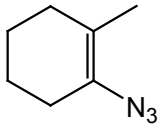
cis-**9h**

trans-2-Azido-1-iodo-1-methylcyclohexane (*trans*-**9h**): Light-yellow liquid. – **IR** ($CDCl_3$): $\tilde{\nu}$ = 2103 cm^{-1} (N_3). – **^{1}H NMR** ($CDCl_3$): δ = 1.37 – 2.25 (m, 11 H), therein 2.01 (s, 3 H, CH_3), 3.96 (m, 1 H, CHN_3). – **^{13}C NMR** ($CDCl_3$): δ = 22.19 (t), 23.74 (t), 28.14 (t), 30.77 (q), 43.66 (t), 54.35 (s), 70.95 (d, CHN_3).



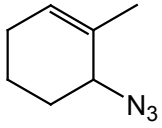
trans-**9h**

1-Azido-2-methylcyclohexene (**2h**): Yellow liquid. – **IR** ($CDCl_3$): $\tilde{\nu}$ = 2099 cm^{-1} (N_3). – **^{1}H NMR** ($CDCl_3$): δ = 1.56 (m, 2 H), 1.60 (s, 3 H), 1.72 (m, 2 H), 1.97 (m, 2 H), 2.22 (m, 2 H). – **^{13}C NMR** ($CDCl_3$): δ = 17.52 (q), 22.39 (t), 22.86 (t), 24.83 (t), 30.82 (t), 120.76 (s), 125.92 (s).



2h

6-Azido-1-methylcyclohexene (**10h**): Colorless liquid. – **IR** ($CDCl_3$): $\tilde{\nu}$ = 2107 cm^{-1} (N_3). – **^{1}H NMR** ($CDCl_3$): δ = 1.47 – 2.10 (m, 9 H), therein 1.75 (m, 3 H, CH_3), 3.65 (br. s, 1 H, CHN_3), 5.68 (br. s, 1 H, =CH). – **^{13}C NMR** ($CDCl_3$): δ = 18.31 (t), 21.46 (q), 24.98 (t), 29.19 (t), 60.25 (d, CHN_3), 127.46 (d, =CH), 130.96 (s).



10h

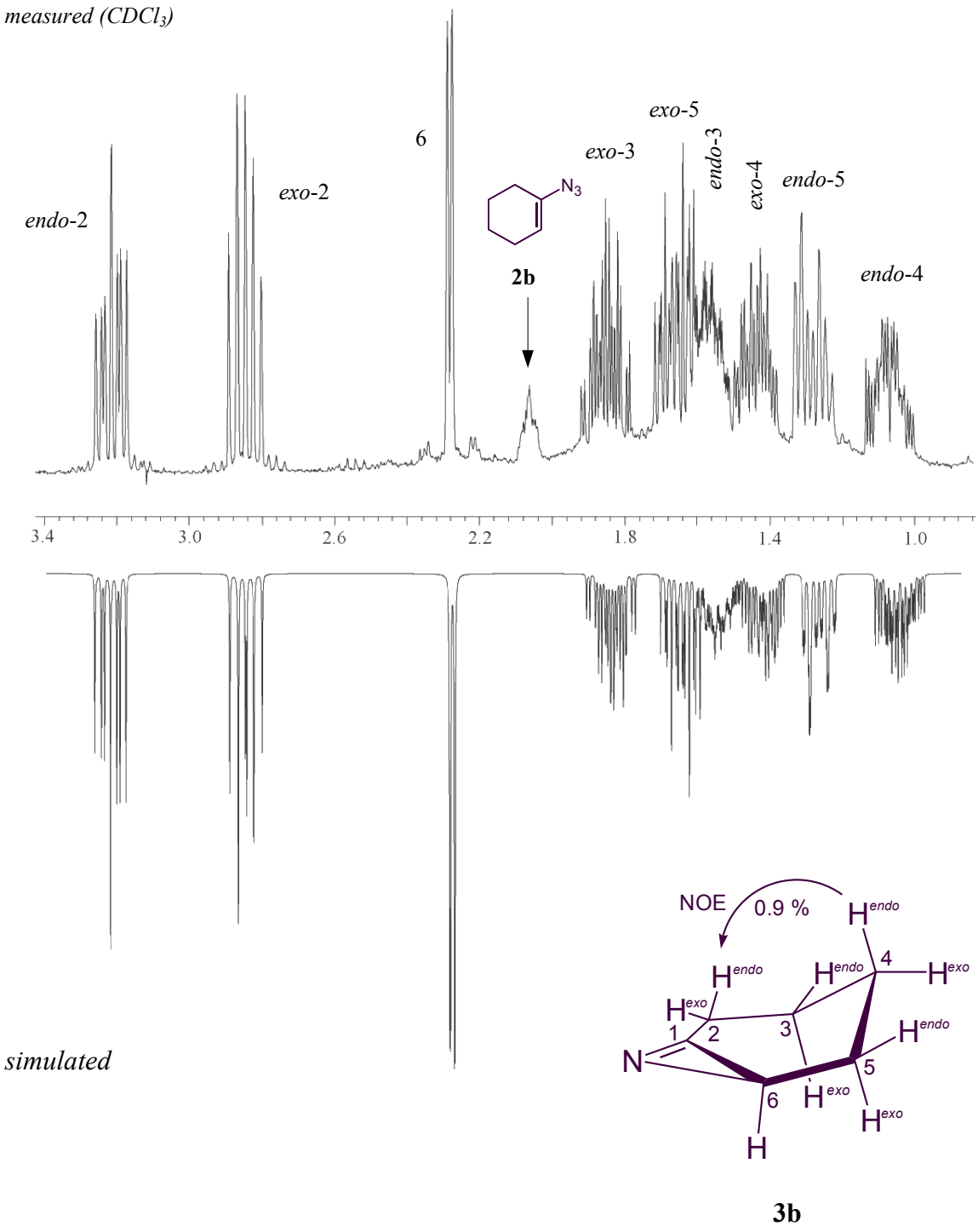
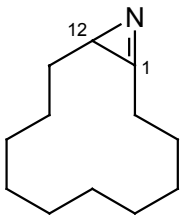


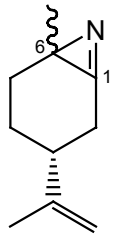
Figure 1. Measured and simulated ^{1}H NMR spectra of **3b** (δ scale).

13-Azabicyclo[10.1.0]tridec-1(13)-ene (**3e**): Colorless liquid; IR ($CDCl_3$): $\tilde{\nu}$ = 1748 cm^{-1} (C=N); ^1H NMR ($CDCl_3$): δ = 1.09 (m, 1 H), 1.19 – 1.55 (m, 14 H), 1.67 – 1.89 (m, 3 H), 2.02 (m, 1 H), 2.72 – 2.89 (m, 2 H, 2-H); ^{13}C NMR ($CDCl_3$): δ = 23.36 (t), 24.23 (t), 24.72 (t), 25.13 (t), 25.33 (t), 25.67 (t), 26.17 (t), 26.26 (t), 27.00 (t), 31.07 (t), 31.24 (d, $^1J_{(C,H)}$ = 175 Hz, C-12), 176.76 (s, C-1); HR-MS (ESI): m/z (%): 180.1740 (100) [M + H^+; ber. 180.1747], 359.3441 (63) [2M + H^+; ber. 359.3421].



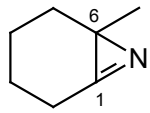
3e

(3*R*,6*S*)-/(3*R*,6*R*)-3-Isopropenyl-6-methyl-7-azabicyclo[4.1.0]hept-1(7)-ene (**3f**, 1:1 mixture of diastereomers): IR ($CDCl_3$): $\tilde{\nu}$ = 1728 cm^{-1} (C=N); ^1H NMR ($CDCl_3$): δ = 0.75 – 0.95 (m, 2 H), 1.26 – 1.82 (m, 18 H), therein 1.45 (s, 3 H, CH_3) and 1.46 (s, 3 H, CH_3) and 1.69 (s, 3 H, CH_3) and 1.73 (s, 3 H, CH_3), 2.00 (m, 1 H), 2.38 (m, 1 H), 2.72 (m, 1 H, 2-H), 2.92 (m, 2 x 1 H, 2-H), 3.47 (m, 1 H, 2-H), 4.72 (m, 1 H, =CH_2), 4.73 (m, 1 H, =CH_2), 4.77 (m, 1 H, =CH_2), 4.81 (m, 1 H, =CH_2); ^{13}C NMR ($CDCl_3$): δ = 20.46 (q), 20.61 (q), 21.80 (q), 22.18 (q), 27.25 (t), 27.69 (t), 29.97 (t), 32.41 (s, C-6), 33.02 (t), 33.37 (s, C-6), 34.92 (t), 34.97 (t), 41.89 (d), 46.28 (d), 110.35 (t, =CH_2), 110.65 (t, =CH_2), 147.16 (s), 147.91 (s), 184.23 (s, C-1), 184.60 (s, C-1).



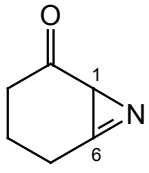
3f

6-Methyl-7-azabicyclo[4.1.0]hept-1(7)-ene (**3h**): IR ($CDCl_3$): $\tilde{\nu}$ = 1720 cm^{-1} (C=N); ^1H NMR ($CDCl_3$): δ = 0.95 (m, 1 H), 1.35 – 1.61 (m, 7 H), therein 1.45 (s, 3 H, CH_3), 1.74 (m, 1 H), 2.78 (ddd, ^2J = 12.9 Hz, ^3J = 6.8 Hz, ^3J = 6.7 Hz, 1 H, 2-H_{exo}), 3.20 (ddd, ^2J = 12.9 Hz, ^3J = 8.0 Hz, ^3J = 4.4 Hz, 1 H, 2-H_{endo}); ^{13}C NMR ($CDCl_3$): δ = 21.97 (t), 22.12 (q), 24.07 (t), 27.75 (t), 33.08 (s), 33.97 (t), 185.39 (s, C-1).



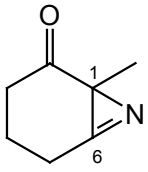
3h

7-Azabicyclo[4.1.0]hept-6-en-2-one (**3i**): ^1H NMR ($CDCl_3$, –50°C): δ = 1.79 – 2.30 (m, 4 H), 2.89 (s, 1 H), 3.30 (m, 1 H, 5-H), 3.47 (m, 1 H, 5-H).

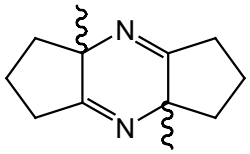


3i

1-Methyl-7-azabicyclo[4.1.0]hept-6-en-2-one (**3j**): IR ($CDCl_3$): $\tilde{\nu}$ = 1763 cm^{-1} (C=N), 1696 (C=O); ^1H NMR ($CDCl_3$): δ = 1.53 (s, 3 H), 1.58 – 2.65 (m, 4 H), 3.15 (m, 1 H, 5-H), 3.36 (m, 1 H, 5-H); ^{13}C NMR ($CDCl_3$): δ = 13.73 (q), 18.77 (t), 26.91 (t), 39.89 (t), 41.28 (s, C-1), 174.25 (s, C-6), 207.38 (s, C=O).

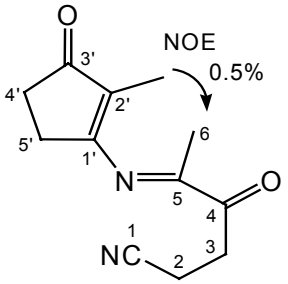


3j



11g

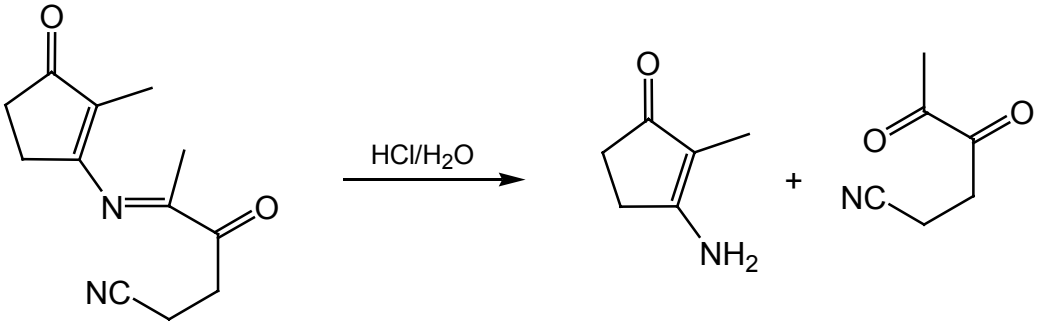
cis-/*trans*-3a,7a-Dimethyl-1,2,3,3a,5,6,7,7a-octahydro-4,8-diaza-*s*-indacene **11g**: Orange oil.– **IR** ($CDCl_3$): $\tilde{\nu}$ = 1658 cm^{-1} (C=N). – **^{1}H NMR** ($CDCl_3$): δ = 0.73 – 2.68 (m, 2 x 18 H), therein 1.21 (s, 6 H, CH_3) and 1.27 (s, 6 H, CH_3). – **^{13}C NMR** ($CDCl_3$): δ = 15.16 (t), 18.42 (t), 25.01 (q), 27.94 (q), 29.54 (t), 29.97 (t), 35.19 (t), 39.45 (t), 61.17 (s), 62.29 (s), 176.92 (s), 180.33 (s). **– HR-MS** (ESI): m/z: 191.1543 [M + H^+; calc. 191.1543].



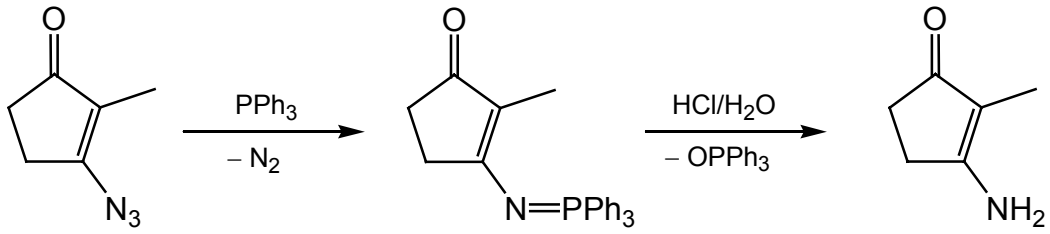
15k

E-5-(2-Methyl-3-oxocyclopent-1-enylimino)-4-oxohexanenitrile **15k**: Yellow oil. – **IR** ($CDCl_3$): $\tilde{\nu}$ = 1700 cm^{-1} (C=O). – **^{1}H NMR** ($CDCl_3$): δ = 1.49 (t, ^5J = 1.7 Hz, 3 H, 2′-Me), 1.99 (s, 3 H, 6-H), 2.55 (m, 2 H, 4′-H or 5′-H), 2.62 (m, 2 H, 4′-H or 5′-H), 2.66 (t, ^3J = 7.1 Hz, 2 H, 2-H), 3.33 (t, ^3J = 7.1 Hz, 2 H, 3-H). – **^{13}C NMR** ($CDCl_3$): δ = 7.17 (q), 11.61 (t, C-2), 15.38 (q), 27.61 (t), 32.71 (t), 33.57 (t), 118.74 (s), 120.79 (s), 162.26 (s), 172.67 (s), 196.00 (s, C=O), 205.47 (s, C=O). **– GC** (1 min 50°C, 10°C/min, 220°C): t_R = 19.4 min. – **GC-MS**: m/z (%): 218 (5) [M^+], 136 (56), 95 (77), 67 (100), 53 (32), 41 (69), 39 (49). – **HR-MS** (ESI): m/z: 219.1098 [M + H^+; calc. 219.1128].

The structure of **15k** is proved not only by its spectroscopic data but also by hydrolysis to yield the products **II** and **III**. Moreover, **II** was prepared from **2k** via **IV** in a control experiment.

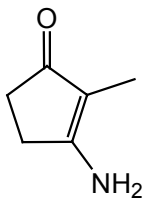


15k **II** 11% **III** 55%



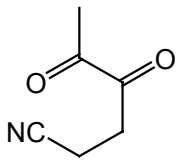
2k **IV** 100% **II** 19%

3-Amino-2-methylcyclopent-2-enone **II**: Colorless solid, m.p. 131 – 135°C ($CHCl_3$/hexane). – **IR** ($CDCl_3$): $\tilde{\nu}$ = 3521, 3419 cm^{-1} (NH_2), 1601 (C=O). – **^{1}H NMR** ($CDCl_3$): δ = 1.57 (t, ^5J = 1.4 Hz, 3 H), 2.37 (m, 2 H), 2.49 (m, 2 H), 5.05 (br. s, NH_2). – **^{13}C NMR** ($CDCl_3$): δ = 5.98 (q), 26.47 (t), 33.19 (t), 109.24 (s, C-2), 171.90 (s, C-3), 203.98 (s, C=O). – **C_6H_9NO** (111.14): calc. C 64.84, H 8.16, N 12.60; found C 64.42, H 7.97, N 12.51.



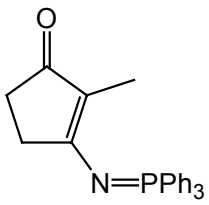
II

4,5-Dioxohexanenitrile **III**: Yellow oil. – **IR** (CCl_4): $\tilde{\nu}$ = 1721 cm^{-1} (C=O). – **^{1}H NMR** ($CDCl_3$): δ = 2.36 (s, 3 H), 2.60 (t, ^3J = 7.1 Hz, 2 H), 3.14 (t, ^3J = 7.1 Hz, 2 H). – **^{13}C NMR** ($CDCl_3$): δ = 10.97 (t, C-2), 23.47 (q, C-6), 31.92 (t, C-3), 118.39 (s, C≡N), 194.53 (s, C=O), 195.87 (s, C=O). – **$C_6H_7NO_2$** (125.13): calc. C 57.59, H 5.64, N 11.19; found C 57.55, H 5.75, N 11.07.



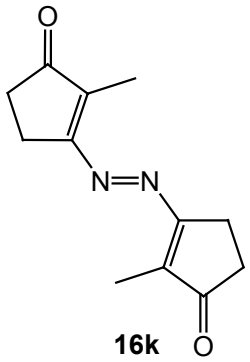
III

N-(2-Methyl-3-oxocyclopent-1-enyl)-triphenyl-iminophosphorane **IV**: Colorless solid, m.p. 195 – 199°C ($CHCl_3$/diethylether). – **IR** ($CDCl_3$): $\tilde{\nu}$ = 1555 cm^{-1} (C=O), 1419 (N=P). – **^{1}H NMR** ($CDCl_3$): δ = 1.86 (s, 3 H), 1.94 (m, 2 H), 2.20 (m, 2 H), 7.45 – 7.79 (m, 15 H, Ph). – **^{13}C NMR** ($CDCl_3$): δ = 7.41 (q), 31.37 (t and d, $^3J_{(P,C)}$ = 9 Hz, C-5), 33.82 (t, C-4), 119.79 (s and d, $^3J_{(P,C)}$ = 22 Hz, C-2), 128.73 (d and d, $^3J_{(P,C)}$ = 13 Hz, *m*-Ph), 129.54 (s and d, $^1J_{(P,C)}$ = 100 Hz, *i*-Ph), 132.23 (d and d, $^2J_{(P,C)}$ = 10 Hz, *o*-Ph), 132.29 (d and d, $^4J_{(P,C)}$ = 2 Hz, *p*-Ph), 180.94 (s, C-1), 205.22 (s, C=O). – **$C_{24}H_{22}NOP$** (371.41): calc. C 77.61, H 5.97, N 3.77; found C 77.68, H 6.16, N 3.66.



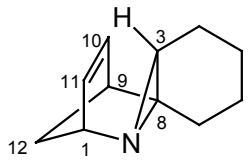
IV

E-Bis(2-methyl-3-oxocyclopent-1-enyl)-diazene **16k**: Red-brown crystals, m.p. 157 – 165°C (diethylether/CH_2Cl_2). – **IR** ($CDCl_3$): $\tilde{\nu}$ = 1686 cm^{-1} (C=O). – **^{1}H NMR** ($CDCl_3$): δ = 2.22 (t, ^5J = 1.9 Hz, 3 H), 2.60 (m, 2 H), 2.79 (m, 2 H). – **^{13}C NMR** ($CDCl_3$): δ = 8.27 (q), 22.98 (t), 33.95 (t), 146.19 (s), 173.33 (s), 208.47 (s, C=O). **– GC** (1 min 50°C, 10°C/min, 220°C): t_R = 23.4 min. – **GC-MS**: m/z (%): 218 (43) [M^+], 55 (64), 54 (92), 53 (88), 52 (85), 41 (93), 39 (100). – **HR-MS** (ESI): m/z: 219.1103 [M + H^+; calc. 219.1128].



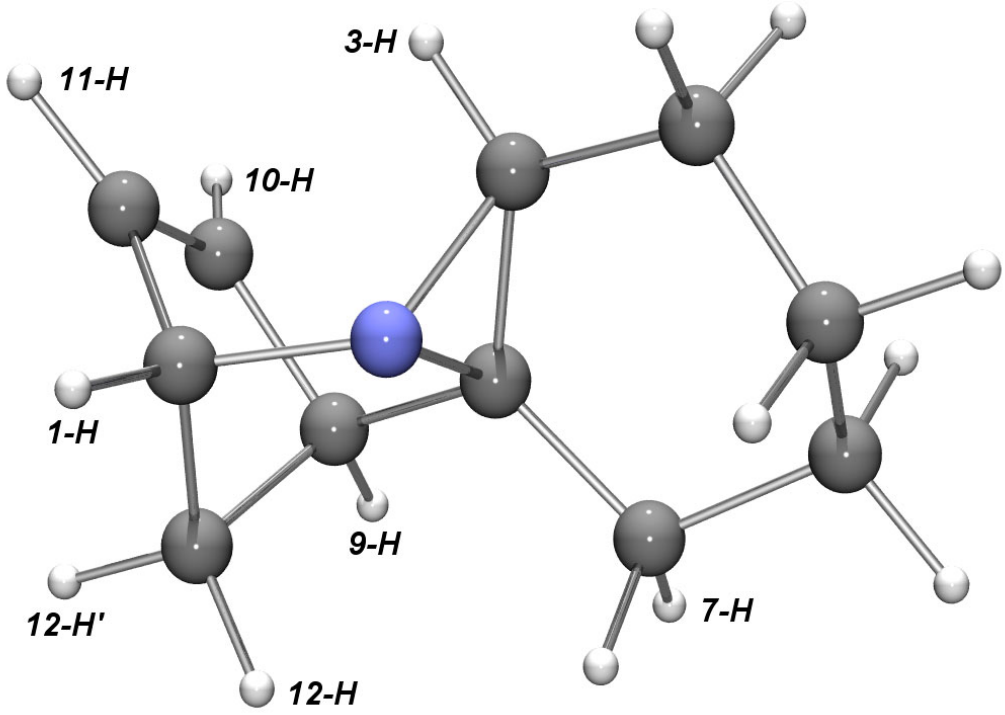
16k

2-Azatetracyclo[7.2.1.$0^{2,8}$.$0^{3,8}$]dodec-10-ene **17b**: Light-yellow oil. –**^{1}H NMR** ($CDCl_3$): δ = 1.05 – 2.03 (m, 10 H), therein 1.45 (dd, J = 6.0 Hz, J = 1.6 Hz , 1 H, 3-H) and 1.59 (br. d, ^2J = 7.7 Hz, 1 H, 12-H′), 2.07 (dt, ^2J = 7.7 Hz, J = 1.6 Hz, 1 H, 12-H), 2.66 (m, 1 H, 9-H), 3.98 (s, 1 H, 1-H), 5.56 (m, 1 H, 11-H), 5.98 (m, 1 H, 10-H). – **^{13}C NMR** ($CDCl_3$): δ = 21.03 (t), 21.81 (t), 25.51 (t), 28.66 (t), 41.86 (s, C-8), 46.15 (d, C-3), 50.42 (d, C-9), 57.91 (t, C-12), 66.05 (d, C-1), 126.54 (d, C-11), 131.77 (d, C-10). **– HR-MS** (ESI): m/z: 162.1263 [M + H^+; calc. 162.1277].



17b

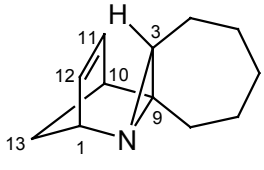
The assignment of NMR signals was performed with the help of ^{13}C,^{1}H correlation and ^{1}H-NMR NOE difference spectra (see Figure 2).



Irradiated at the signal	NOE effect (%)							
	1-H	*3-H*	*7-H*	*9-H*	*10-H*	*11-H*	*12-H*	*12-H′*
1-H	–	–	–	–	–	2.2	0.9	1.2
3-H	0.3	–	–	–	1.0	1.1	–	–
7-H	–	–	–	–	–	–	–	–
9-H	–	–	2.1	–	1.7	–	1.2	1.3
10-H	–	1.3	–	1.4	–	1.6	–	–
11-H	2.3	1.9	–	–	2.1	–	–	–
12-H	0.7	–	–	0.8	–	–	–	8.7
12-H′	0.4	–	–	0.5	0.05	0.03	4.9	–

Figure 2: NOE effects based on ^{1}H NMR experiments with **17b**. The structure of shown molecule of **17b** is resulting from MOPAC minimizing of energy with CS Chem3D 7.0.

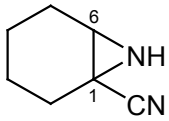
2-Azatetracyclo[8.2.1.0^{2,9}.0^{3,9}]tridec-11-ene **17c**: Light-yellow oil. –**^{1}H NMR** ($CDCl_3$): δ = 1.12 – 1.99 (m, 13 H), 2.66 (m, 1 H, 10-H), 3.92 (s, 1 H, 1-H), 5.54 (m, 1 H, 12-H), 5.97 (m, 1 H, 11-H). – **^{13}C NMR** ($CDCl_3$): δ = 26.64 (t), 27.09 (t), 30.21 (t), 32.01 (t), 34.49 (t), 46.77 (s, C-9), 49.91 (d), 50.85 (d), 58.50 (t, C-13), 65.92 (d, C-1), 126.80 (d, C-12), 132.14 (d, C-11). **– HR-MS** (ESI): m/z: 176.1421 [M + H^{+}; calc. 176.1434].



17c

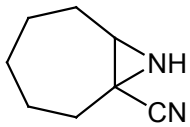
The assignment of NMR signals is based on comparison with the data of **17b**.

7-Azabicyclo[4.1.0]heptane-1-carbonitrile **18b**: Colorless oil. – **IR** (CCl_4): $\tilde{\nu}$ = 3317 cm^{-1} (NH), 2234 (C≡N). – **^{1}H NMR** (C_6D_6): δ = 0.50 (br. s, 1 H, NH), 0.65 (m, 2 H), 0.97 (m, 2 H), 1.14 (m, 1 H), 1.28 (m, 1 H), 1.53 (m, 1 H), 1.70 (m, 1 H), 1.87 (m, 1 H). – **^{1}H NMR** ($CDCl_3$): δ = 1.18 – 1.41 (m, 5 H, 2 x CH_2 and NH), 1.79 (m, 1 H), 1.88 (m, 1 H), 2.05 (m, 2 H), 2.74 (br. s, 1 H, 6-H). – **^{13}C NMR** ($CDCl_3$): δ = 18.43 (t), 19.11 (t), 23.41 (t), 24.95 (s), 26.98 (t), 37.47 (d), 122.38 (s, C≡N). – **$C_7H_{10}N_2$** (122.17): calc. C 68.82, H 8.25, N 22.93; found C 68.52, H 8.24, N 22.79. If D_2O is added to the NMR solution (C_6D_6), the NH signal at δ = 0.50 is lost. The assignment of the signal of 6-H is based on ^{13}C,^{1}H shift correlation.



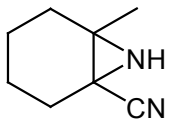
18b

8-Azabicyclo[5.1.0]octane-1-carbonitrile **18c**: Colorless solid, m.p. 49°C (diethylether/hexane). – **IR** (CCl_4): $\tilde{\nu}$ = 3317 cm^{-1} (NH), 2232 (C≡N). – **^{1}H NMR** (C_6D_6): δ = 0.53 (br. s, 1 H, NH), 0.86 – 1.08 (m, 4 H), 1.14 – 1.32 (m, 4 H), 1.45 (m, 1 H), 1.80 (m, 1 H), 1.88 (m, 1 H). – **^{1}H NMR** ($CDCl_3$): δ = 1.29 – 1.73 (m, 9 H, 4 x CH_2 and NH), 2.16 (m, 1 H), 2.32 (m, 1 H), 2.69 (m, 1 H). – **^{13}C NMR** ($CDCl_3$): δ = 25.22 (t), 25.35 (t), 29.83 (t), 30.23 (s), 31.29 (t), 32.44 (t), 42.06 (d), 122.79 (s, C≡N). – **$C_8H_{12}N_2$** (136.19): calc. C 70.55, H 8.88, N 20.57; found C 70.16, H 8.86, N 20.27. If D_2O is added to the NMR solution (C_6D_6), the NH signal at δ = 0.53 is lost.



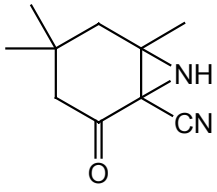
18c

6-Methyl-7-Azabicyclo[4.1.0]heptane-1-carbonitrile **18h**: Colorless solid,m.p. 48 – 52°C (diethylether/hexane). – **IR** (CCl_4): $\tilde{\nu}$ = 3302 cm^{-1} (NH), 2230 (C≡N). – **^{1}H NMR** (C_6D_6): δ = 0.29 (br. s, 1 H, NH), 0.68 (m, 1 H), 0.81 (m, 1 H), 0.99 – 1.18 (m, 6 H), therein 1.01 (s, 3 H, CH_3), 1.41 (m, 1 H), 1.68 (m, 1 H), 1.75 (m, 1 H). – **^{13}C NMR** ($CDCl_3$): δ = 19.40 (t), 19.74 (t), 24.55 (q), 27.81 (t), 29.78 (t), 31.56 (s), 42.18 (s), 121.35 (s, C≡N). – **HR-MS** (ESI): m/z: 137.1094 [M + H^+; calc. 137.1073]. If D_2O is added to the NMR solution (C_6D_6), the signal at δ = 0.29 is lost.



18h

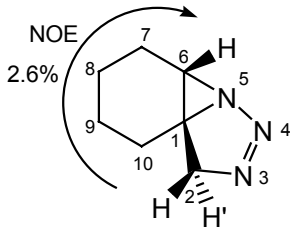
4,4,6-Trimethyl-2-oxo-7-azabicyclo[4.1.0]heptane-1-carbonitrile **18l**: Orange oil. –**IR** (CCl_4): $\tilde{\nu}$ = 3299 cm^{-1} (NH), 2244 (C≡N), 1725 (C=O). – **^{1}H NMR** (C_6D_6): δ = 0.43 (s, 6 H, 2 x CH_3), 0.88 (br. d, ^2J = 13.9 Hz, 1 H), 0.94 (s, 3



18l

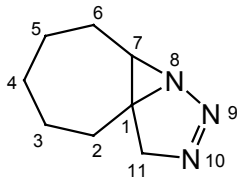
H, CH_3), 0.99 (br. s, 1 H, NH), 1.28 (br. d, ^2J = 13.9 Hz, 1 H), 1.57 (br. d, ^2J = 13.9 Hz, 1 H), 2.22 (br. d, ^2J = 13.6 Hz, 1 H). – **^{13}C NMR** ($CDCl_3$): δ = 25.49 (q), 27.22 (q), 30.60 (q), 35.79 (s), 41.18 (s), 43.39 (t), 46.77 (t), 50.51 (s), 115.62 (s, C≡N), 200.79 (s, C=O). **– HR-MS** (ESI): m/z: 179.1153 [M + H^+; calc. 179.1179]. If D_2O is added to the NMR solution (C_6D_6), the signal at δ = 0.99 is lost.

3,4,5-Triazatricyclo[4.4.0.0^{1,5}]dec-3-ene **19b**: **^{1}H NMR** ($CDCl_3$, –50°C): δ = 1.33 (m, 4 H), 1.68 (s, 1 H, 6-H), 1.78 (m, 2 H), 2.04 (m, 2 H), 4.36 (d, ^2J = 18.6 Hz, 1 H, 2-H′), 4.78 (d, ^2J = 18.6 Hz, 1 H, 2-H). – **^{13}C NMR** ($CDCl_3$, –50°C): δ = 19.56 (t), 20.70 (t), 23.42 (t), 24.02 (t), 45.13 (s, C-1), 49.39 (d, C-6), 79.52 (t, C-2).



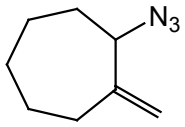
19b

8,9,10-Triazatricyclo[6.3.0.0^{1,7}]undec-9-ene **19c**: **^{1}H NMR** ($CDCl_3$, –50°C): δ = 1.24 – 2.18 (m, 11 H), 4.36 (d, ^2J = 18.7 Hz, 1 H, 11-H), 4.78 (d, ^2J = 18.7 Hz, 1 H, 11-H). – **^{13}C NMR** ($CDCl_3$, –50°C): δ = 25.26 (t), 27.12 (t), 28.75 (t), 30.93 (t), 31.54 (t), 49.62 (s, C-1), 53.48 (d, C-7), 81.01 (t, C-11).

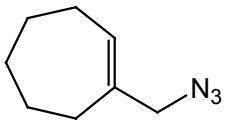


19c

1-Azidomethylcycloheptene **20c** and 1-Azido-2-methylenecycloheptane **21c**: Colorless liquid. – **IR** ($CDCl_3$): $\tilde{\nu}$ = 2099 cm^{-1} (N_3). – **^{1}H NMR** ($CDCl_3$): δ = 1.19 – 2.33 (m, 2 x 10 H), 3.63 (s, 2 H, CH_2N_3, **20c**), 4.07 (m, 1 H, CHN_3, **21c**), 4.95 (br. s, 1 H, =CH_2, **21c**), 5.05 (br. s, 1 H, =CH_2, **21c**), 5.85 (t, ^3J = 6.5 Hz, 1 H, =CH, **20c**). – **^{13}C NMR** ($CDCl_3$): δ = 24.07 (t), 26.47 (t), 26.95 (t), 28.25 (t), 29.82 (t), 30.04 (t), 31.23 (t), 32.22 (t), 32.23 (t), 33.18 (t), 59.73 (t, CH_2N_3, **20c**), 67.27 (d, CHN_3, **21c**), 115.79 (t, =CH_2, **21c**), 132.33 (d, =CH, **20c**), 138.39 (s, **20c**), 148.23 (s, **21c**).

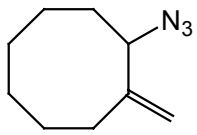


21c



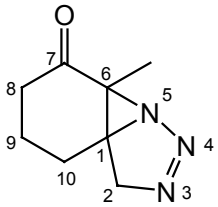
20c

1-Azido-2-methylenecyclooctane **21d**: **^{1}H NMR** ($CDCl_3$): δ = 1.31 – 2.31 (m, 12 H), 3.95 (m, 1 H, CHN_3), 5.05 (br. s, 1 H, $=CH_2$), 5.09 (br. s, 1 H, $=CH_2$). – **^{13}C NMR** ($CDCl_3$): δ = 24.08 (t), 25.23 (t), 25.35 (t), 29.57 (t), 30.33 (t), 30.52 (t), 68.25 (d, CHN_3), 116.14 (t, $=CH_2$), 147.90 (s).



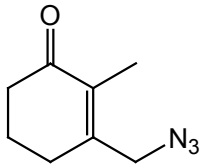
21d

6-Methyl-3,4,5-triazatricyclo[4.4.0.0^{1,5}]dec-3-en-7-one **19j**: **^{1}H NMR** ($CDCl_3$, –50°C): δ = 0.90 (s, 3 H), 1.55 – 2.70 (m, 6 H), 4.61 (d, ^2J = 20.1 Hz, 1 H, 2-H), 4.70 (d, ^2J = 20.1 Hz, 1 H, 2-H). – **^{13}C NMR** ($CDCl_3$, –50°C): δ = 6.87 (q), 20.45 (t), 24.38 (t), 36.39 (t), 53.43 (s), 53.61 (s), 78.56 (t, C-2), 203.55 (s, C-7).



19j

3-Azidomethyl-2-methylcyclohex-2-enone **20j**: Yellow liquid. – **IR** ($CDCl_3$): $\tilde{\nu}$ = 2103 cm^{-1} (N_3), 1668 (C=O). – **^{1}H NMR** ($CDCl_3$): δ = 1.79 (s, 3 H), 1.97 (m, 2 H), 2.41 (m, 4 H), 4.02 (s, 2 H). – **^{13}C NMR** ($CDCl_3$): δ = 10.74 (q), 22.02 (t), 28.96 (t), 37.55 (t), 53.00 (t, CH_2N_3), 133.45 (s), 149.67 (s), 199.03 (s, C-1).



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