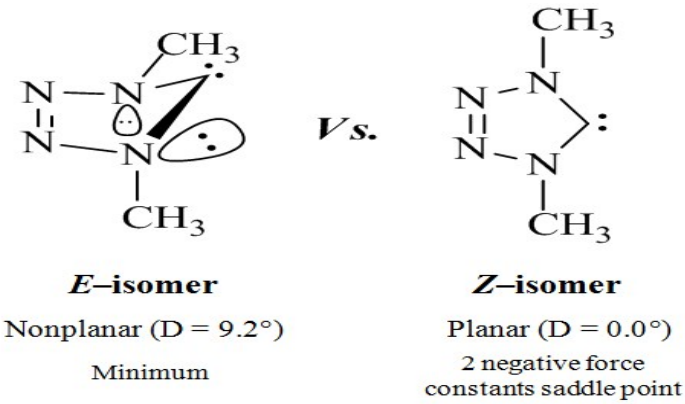
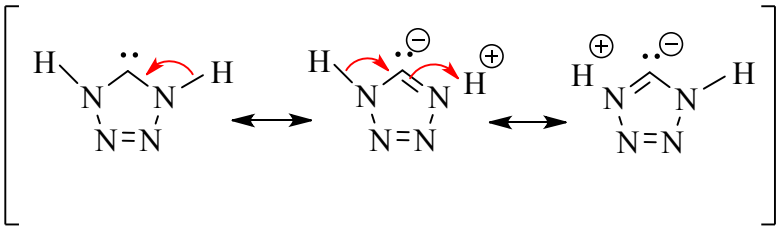
Supplementary

Table 1 Hammett substituent constants, σ_m and σ_p for the substituents employed in this study

substituent	σ_m	σ_p
H	0.00	0.00
methyl	-0.07	-0.17
ethyl	-0.07	-0.15
***i*-propyl**	-0.07	-0.15
***t*-butyl**	-0.10	-0.20



Scheme 1 Possible structures for $\mathbf{1}_{methyl}$ including nonplanar **(*E*)** minimum with 9.2 degrees of puckering *vs.* planar *Z* saddle point with 0.0 dihedral angle



Scheme 2 Possible canonical forms for normal carbene $\mathbf{1}_H$, displaying double bond character for $C_{carbene}$—N bonds