Reactivity and Selectivity in Catalytic Reactions of Enoldiazoacetamides. Assessment of Metal Carbenes as Intermediates.

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Supporting Information

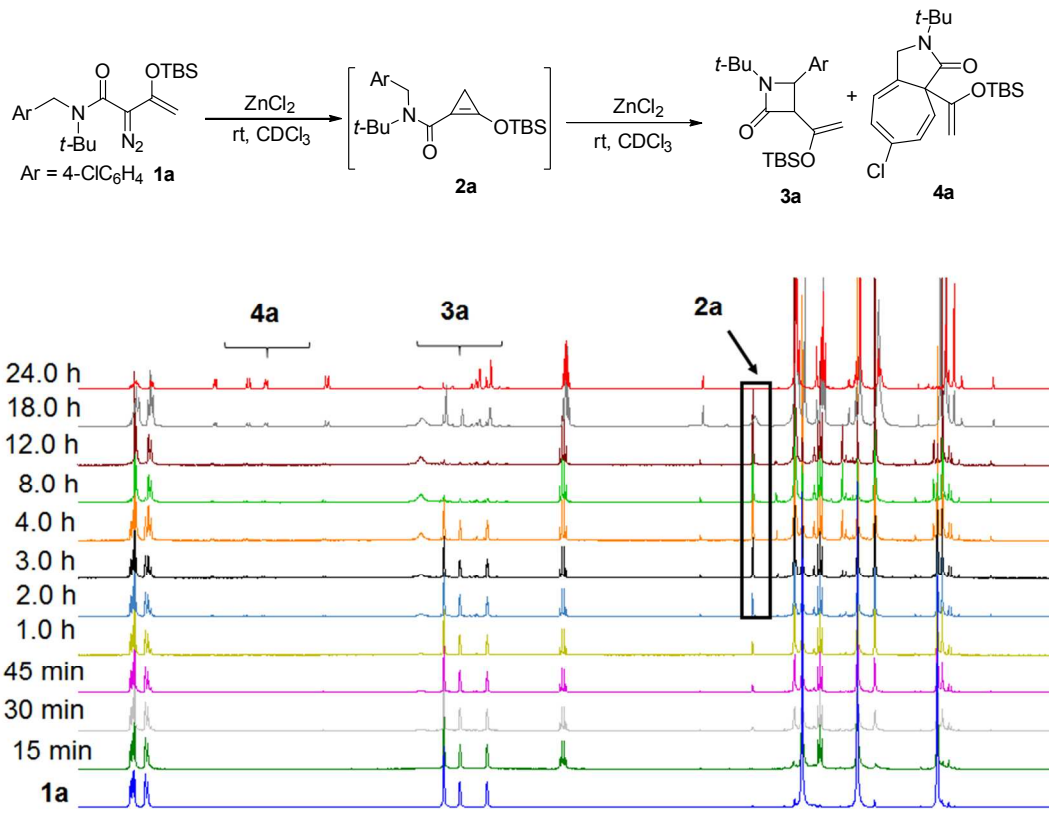


Figure S1. Intramolecular reaction of enoldiazoacetamide **1a** catalyzed by $ZnCl_2$ through its cyclopropene intermediate **2a** to form **3a** and **4a** monitored by ^{1}H NMR spectroscopy.

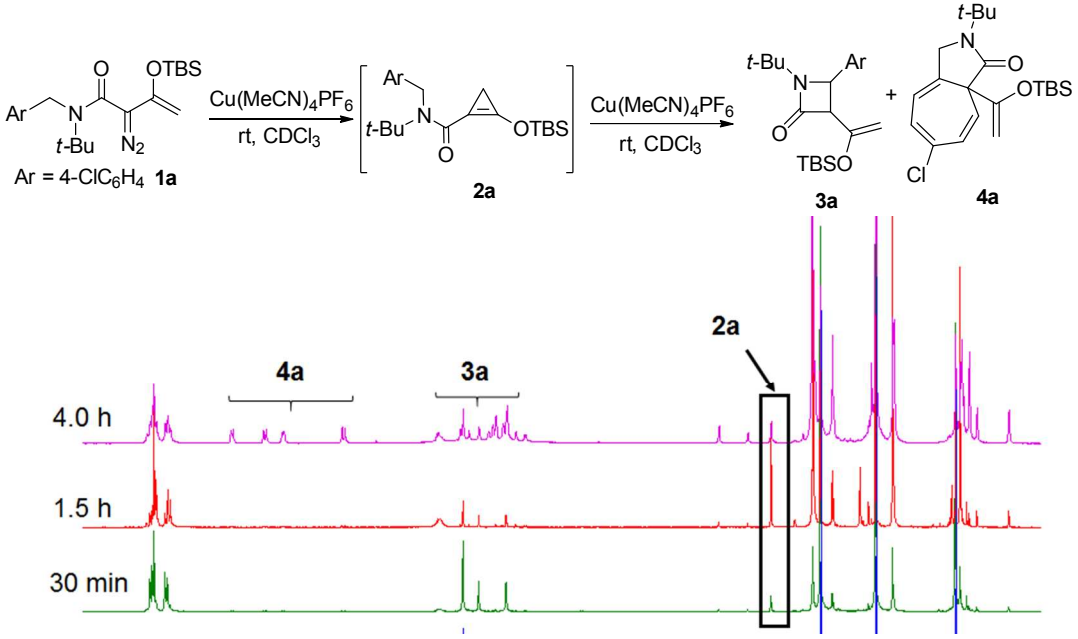


Figure S2. Intramolecular reaction of enoldiazoacetamide **1a** catalyzed by $Cu(MeCN)_4PF_6$ through its cyclopropene intermediate **2a** to form **3a** and **4a** monitored by ^{1}H NMR spectroscopy.

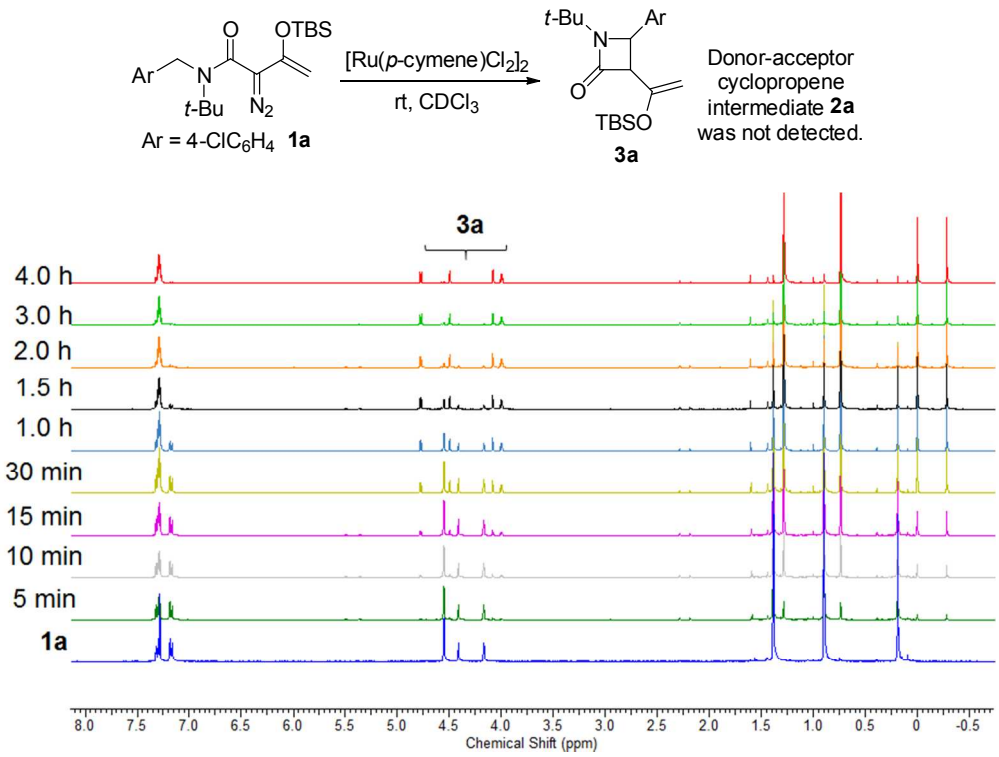


Figure S3. Intramolecular reaction of enoldiazoacetamide **1a** catalyzed by [Ru(*p*-cymene)Cl_2]$_2$ to form **3a** monitored by ^{1}H NMR spectroscopy.

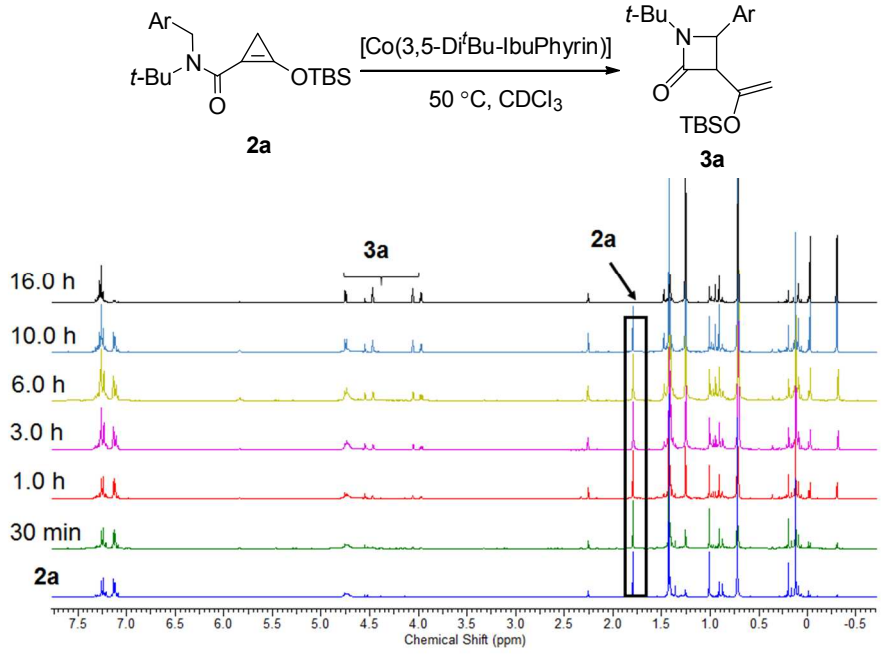


Figure S4. Intramolecular reaction of donor-acceptor cyclopropene **2a** catalyzed by [Co(3,5-Di^{t}Bu-IbuPhyrin)] to form **3a** monitored by ^{1}H NMR spectroscopy.

X-Ray Diffraction Analysis for Compound 6.

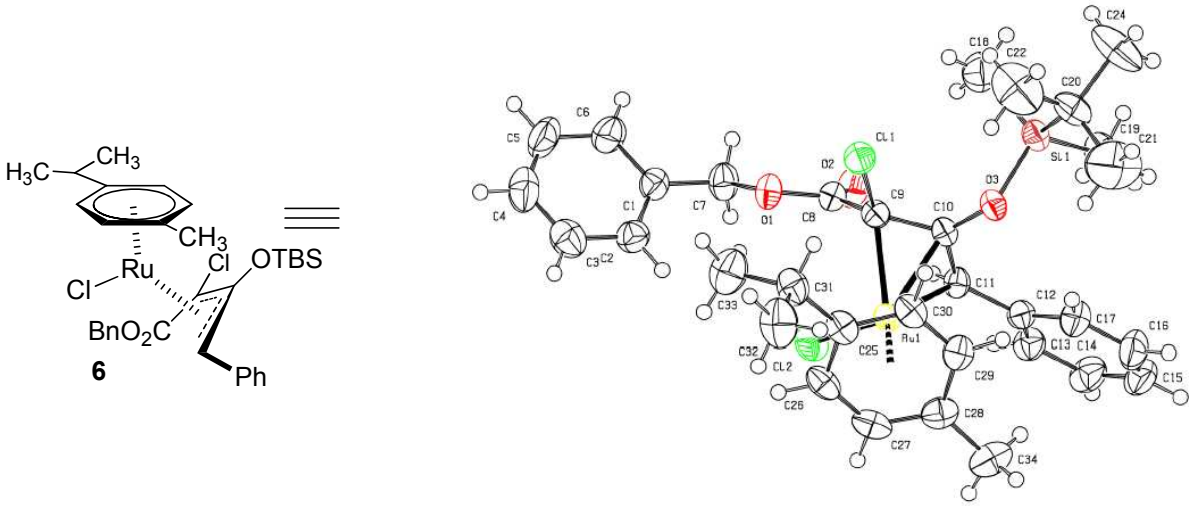


Figure S5. ORTEP view of 6. CCDC 1498257 contains supplementary crystallographic data for 6.

Single crystals of $C_{33}H_{42}Cl_2O_3RuSi$ **6** were prepared by slow evaporation of DCM. A suitable yellow plank-like crystal, with dimensions of 0.36 mm × 0.26 mm × 0.07 mm, was mounted, using Paratone oil, onto a nylon loop. The data were collected at 98(2) K using a Rigaku AFC12 / Saturn 724 CCD fitted with MoKα radiation (λ = 0.71075 Å). Data collection and unit cell refinement were performed using *CrystalClear* software.[1] The total number of data were measured in the range 4.6° < 2θ < 51.0° using ω scans. Data processing and absorption correction, giving minimum and maximum transmission factors (0.842, 1.000), were accomplished with *CrystalClear*[1] and *ABSCOR*[2], respectively. The structure, using Olex2[3], was solved with the ShelXT[4] structure solution program using direct methods and refined (on F^2) with the ShelXL[5] refinement package using full-matrix, least-squares techniques. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atom positions were determined by geometry and refined by a riding model.

[1] *CrystalClear User's Manual*, Rigaku/MSC Inc., Rigaku Corporation, the Woodlands, TX, **2011**.
[2] T. Higashi, *ABSCOR*, Rigaku Corporation, Tokyo, Japan, **1995**.
[3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339.
[4] G. M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3.
[5] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.

Table S1: Crystallographic data and structure refinement for CCDC 1498257.

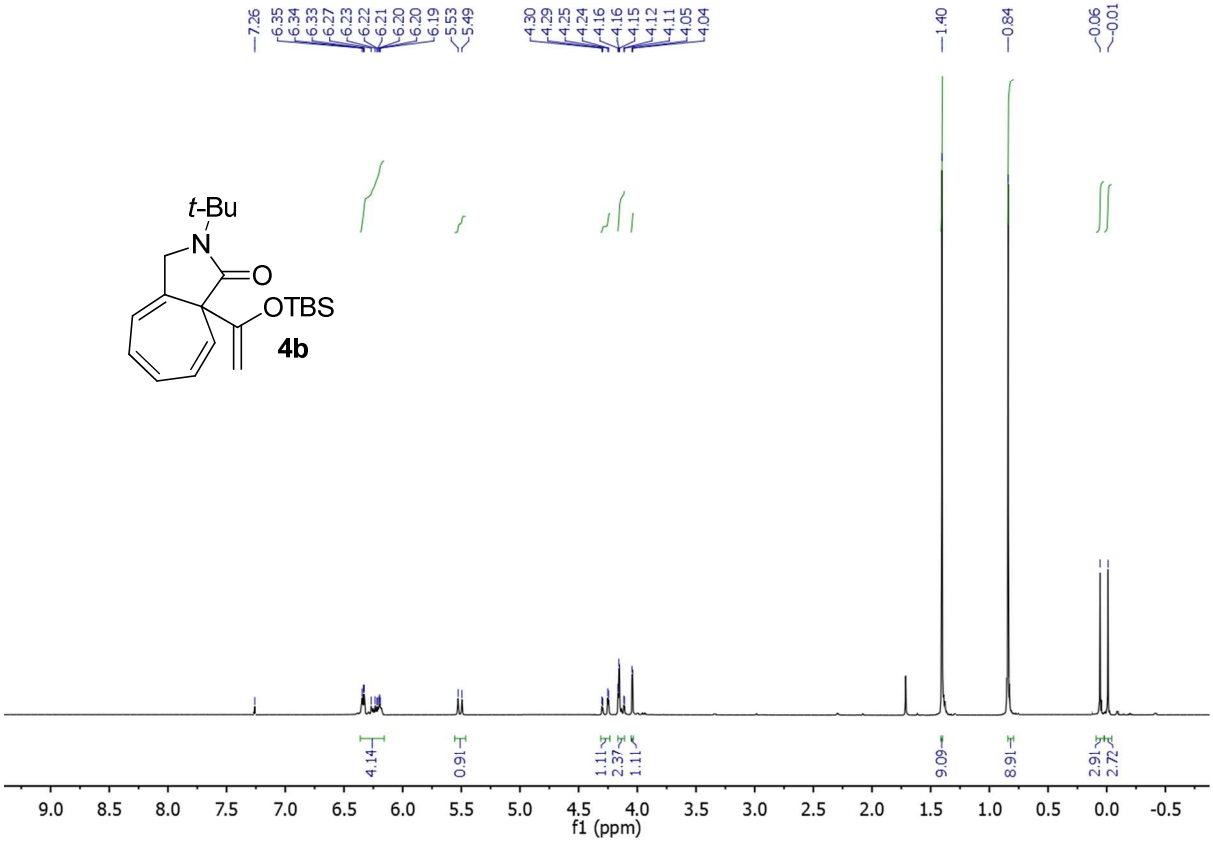
Identification code	CCDC 1498257
Empirical formula	$C_{33}H_{42}Cl_2O_3RuSi$
Formula weight	686.72
Crystal system	Monoclinic
Space group	*P* 1 2_1/n 1
a (Å)	10.1410(15)
b (Å)	15.406(2)
c (Å)	21.056(3)
α (°)	90
β (°)	95.288(3)
γ (°)	90
Volume (Å^3)	3275.6(8)
Z	4
ρ (calc.)	1.393
λ	0.71075
Temp. (K)	98(2)
F(000)	1424
μ (mm^{-1})	0.709
T_{min}, T_{max}	0.842, 1.000
$2\theta_{range}$ (°)	4.64 to 51.0
Reflections collected	21737
Independent reflections	6095 [R(int) = 0.0664]
Completeness	99.7%
Data / restraints / parameters	6095 / 0 / 369
Observed data	5512

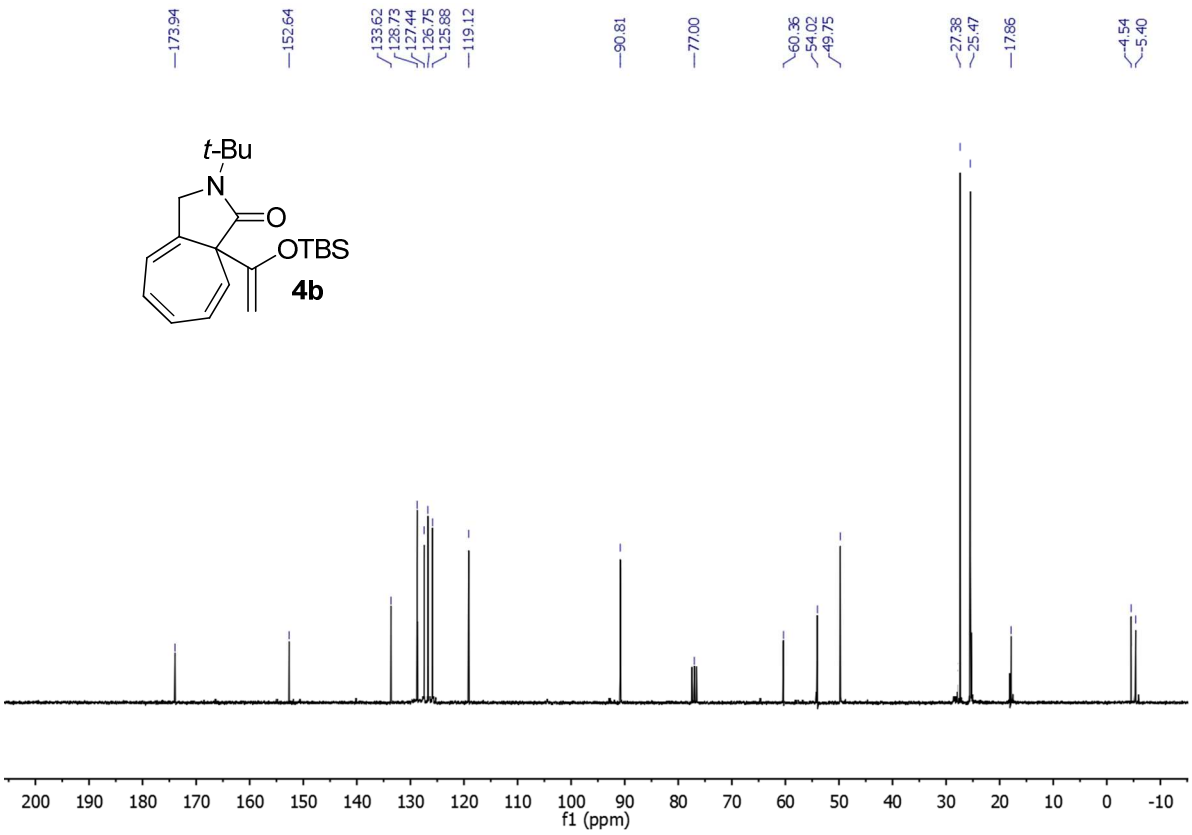
[I > 2σ(I)]	
$wR(F^2$ all data)	0.0973
$R(F$ obsd data)	0.0366
Goodness-of-fit on F^2	1.05
largest diff. peak and hole (e Å^{-3})	0.90 / -0.77

$$wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$$

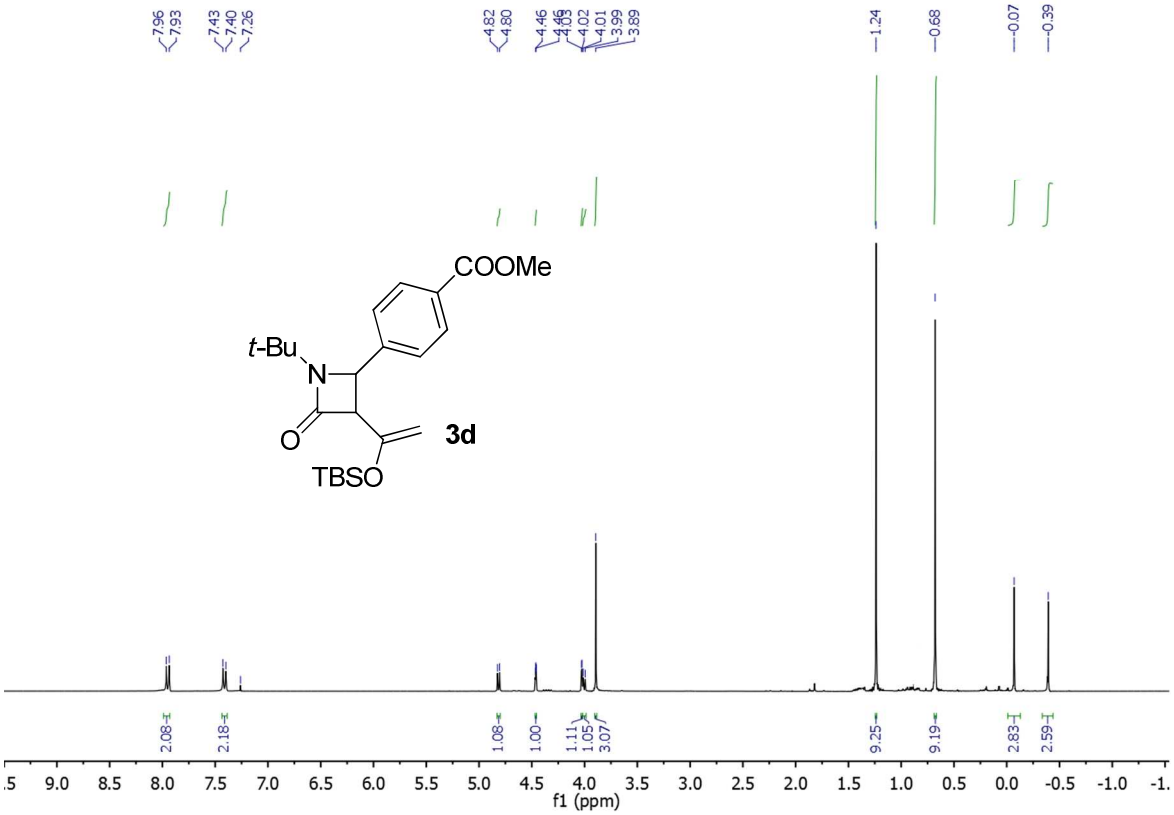
$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

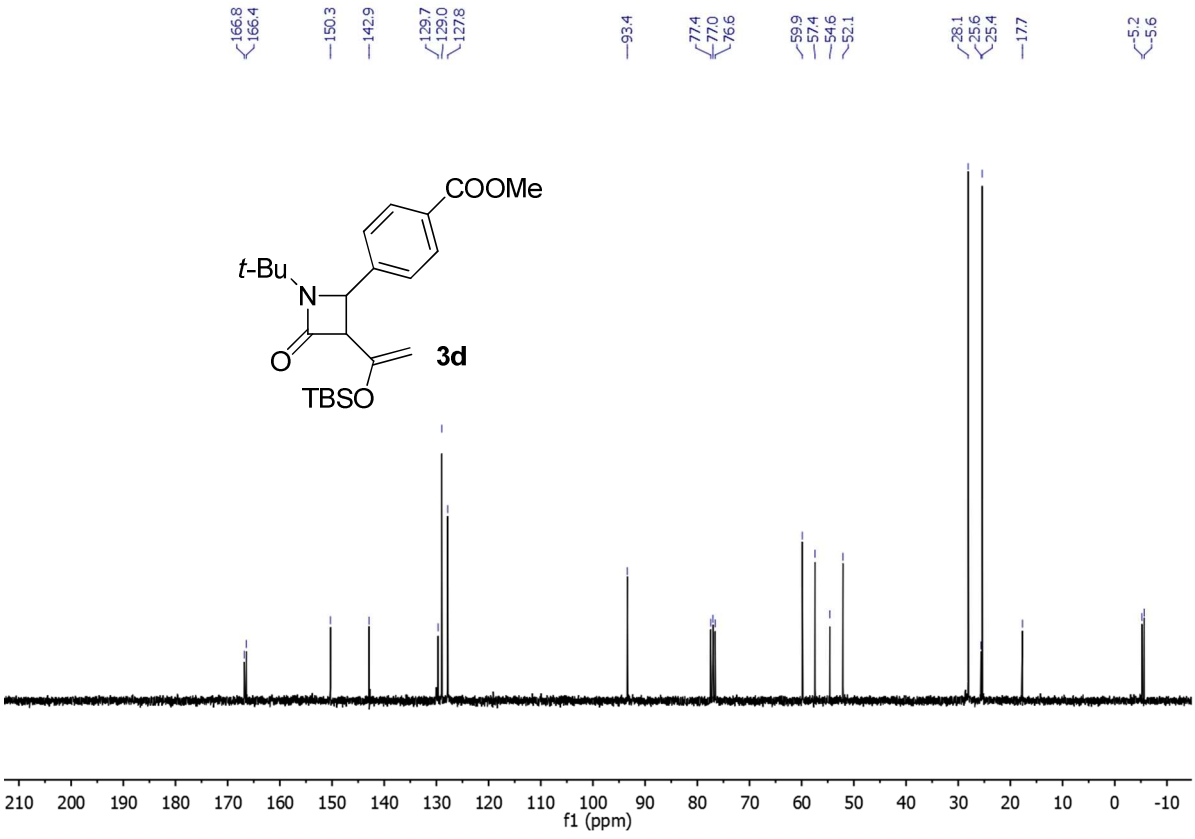
2-(*tert*-Butyl)-8a-[1-(tert-butyldimethylsilyloxy)vinyl]-2,3-dihydrocyclohepta[c]pyrrol-1(8a*H*)-one (**4b**).



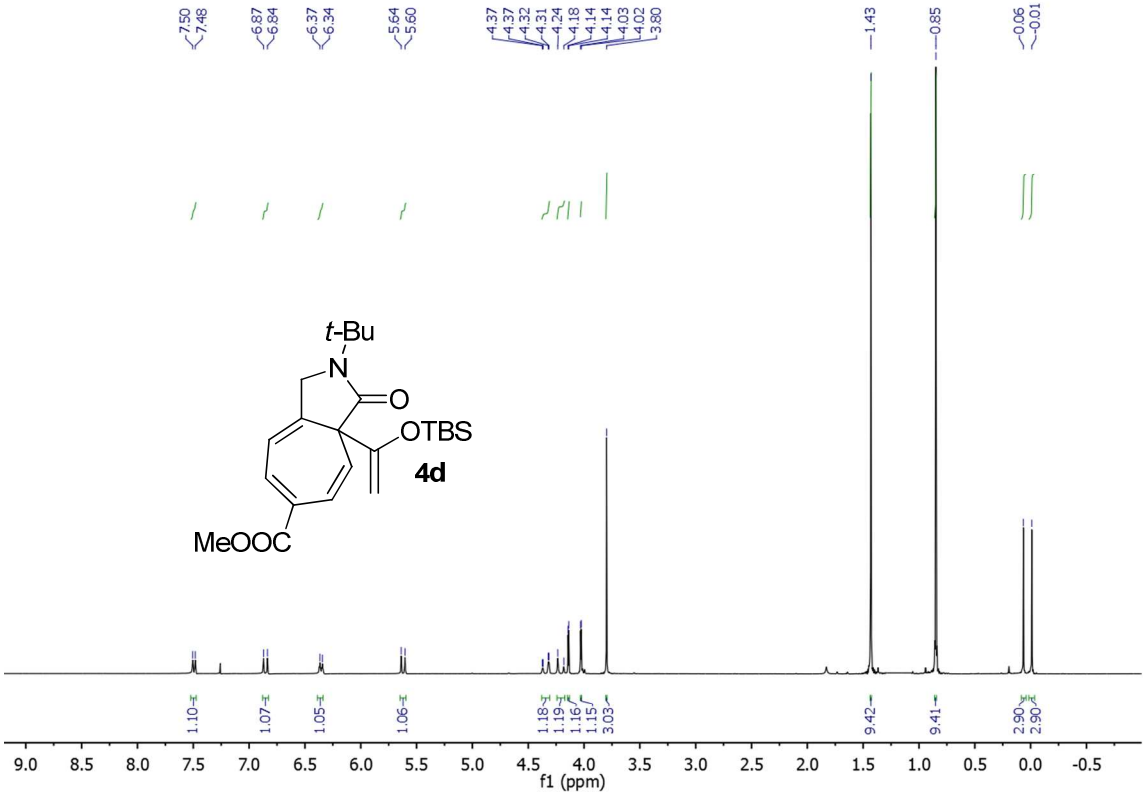


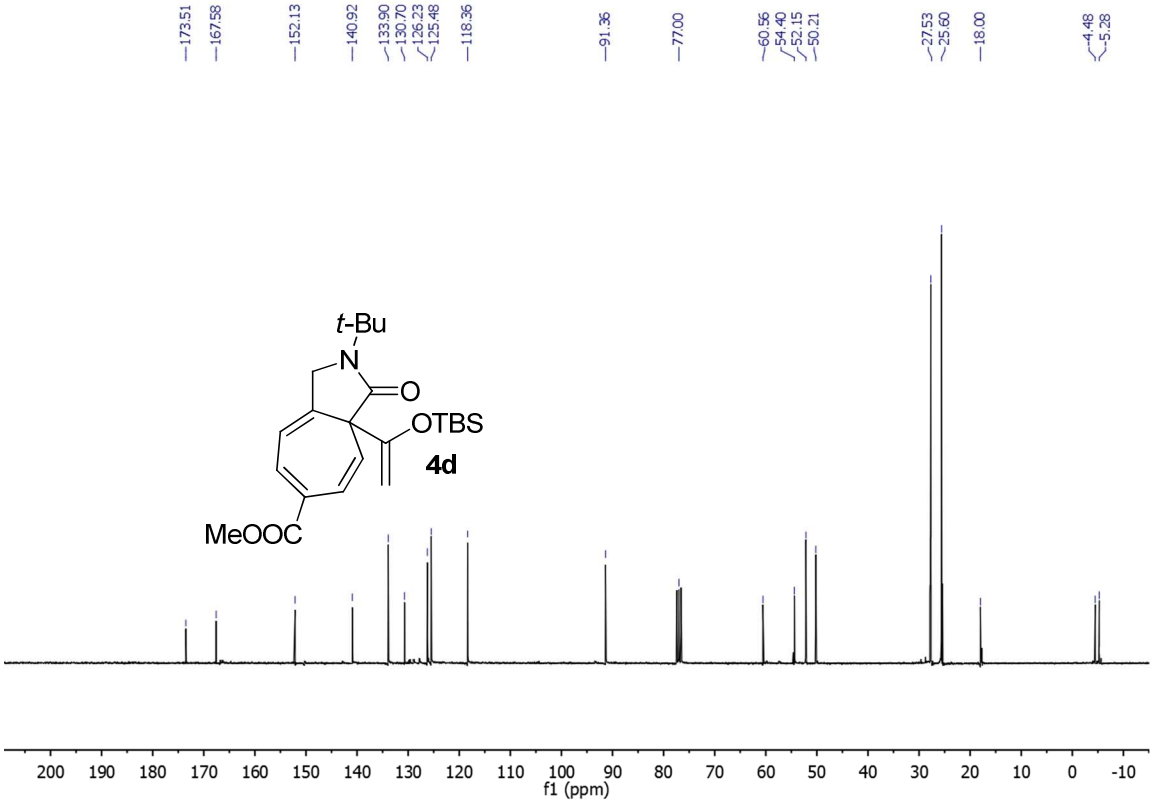
Methyl-4-1-(tert-butyl)-3-[1-(tert-butyldimethylsilyloxy)vinyl]-4-oxoazetidin-2-yl-benzoate (**3d**).





Methyl-2-(*tert*-butyl)-3a-[1-(*tert*-butyldimethylsilyloxy)vinyl]-3-oxo-1,2,3,3a-tetrahydrocyclo-hepta[c]pyrrole-6-carboxylate (**4d**)





η^3-Allyl ruthenium(II) complex **6**.