Electronic Supporting Information

for

Rediscovering copper-based catalysts for the intramolecular carbon-hydrogen bond functionalization by carbene insertion

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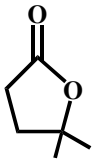
General Methods. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Ethyl diazoacetate and *tert*-butyl diazoacetate were purchased and employed without further purification. The complexes $[Tp^{X}Cu]$[1a-d] and diazocompounds[2] were prepared according to literature procedures. Reagents and solvents were dried and degassed before use. NMR spectra were recorded on a 400 MHz spectrometer (^{13}C NMR at 100MHz) using $CDCl_3$ as the solvent.

General Catalytic Procedure for the diazocompounds descomposition. A solution of the corresponding diazocompounds (1mmol) in 20mL of CH_2Cl_2 was added in one portion or with the aid of a syringe pump over the desired time to a solution of $Tp^{x}Cu$ (0.0125mmol) in 20mL of CH_2Cl_2. After addition, the consumption of the diazocompound (diazoacetates or diazoacetamides) was monitored by IR. When no diazo was observed, volatiles were removed under vacuum and the reaction crude was analyzed by ^{1}H NMR spectroscopy. All the products have been previously described and their identification came straight forward from comparison with data reported.[3-6] Conversion were determined by ^{1}H NMR spectroscopy using 1,4-dimethoxybenzene as an internal standard. Isolated yield of representative examples were obtained upon purification of products by column chromatography with neutral silica gel or basic alumina following previously describes reported.[6.]

Spectroscopic data for compounds 5-11

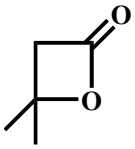
Data of Compounds:



5,5-dimethyl-dihydrofuran-2-one (5)

IR (NaCl) 1761 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.6 (t, *J* = 8.3 Hz, 2H), 2.0 (t, *J* = 8.3, Hz, 2H), 1.4 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.7 , 29.3, 35.6, 84.5, 176.7; MS 115 (M+1) 97(30), 69(8).

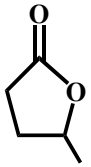
Data are in agreement with those reported in the literature.[3]



4,4-dimethyloxetan-2-one (6)

IR (NaCl) 1682 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.18 (s, 2H), 1.52 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.8 , 48.9, 76.8, 168.2; MS 101 (M+1) 85(31), 73(61).

Data are in agreement with those reported in the literature [4]

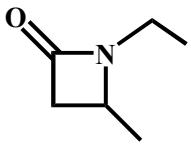


5-methyl-dihydrofuran-2-one (7)

IR (NaCl) 1770 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.6 (tq, *J* = 7.8, 6.2 Hz, 1H), 2.6-2.5 (m, 2H), 2.5-2.3 (m, 1H), 1.9-1.7 (m, 1H), 1.4 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 29.1, 29.8, 78.5, 178.5; MS 101 (M+1) 83(30), 56(8).

Data are in agreement with those reported in the literature [3]

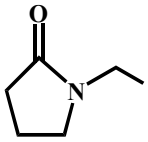
1-ethyl-4-methylazetidin-2-one (8)



IR (NaCl): 1760 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56 (m, 1H), 3.33 (m, *J* = 2H), 2.95 (m, 1H), 2.88 (dd, *J* = 14.3, 4.8 Hz, 1H), 2.35 (dd, *J* = 14.3, 2.1 Hz, 1H), 1.23 (d, *J* = 6.1 Hz, 3H), 1.1 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 19.1, 35.1, 44.0, 46.9, 166.2; MS 114 (M+1), 100(20), 86(5).

Data are in agreement with those reported in the literature.[5]

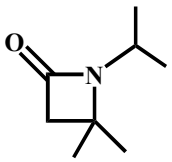
1-ethylpyrrolidin-2-one (9)



IR (NaCl): 1688 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.32 (m, 2H), 3.25 (q, *J* = 7.6 Hz, 2H), 2.31 (t, *J* = 8.2 Hz, 2H), 1.95 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.4, 17.8, 31.1, 37.0, 46.5, 174.7; MS 114 (M+1) 98(35), 70(30).

Data are in agreement with those reported in the literature.[6]

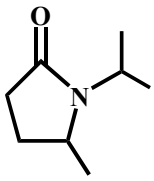
1-isopropyl-4,4-dimethylazetidin-2-one (10)



IR (NaCl): 1745 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.58 (hept, *J* = 6.4 Hz, 1H), 2.66 (s, 2H), 1.41 (s, 6H), 1.31 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 26.3, 44.5, 50.3, 56.1, 166.0; MS 142 (M+1) 126(12), 84(55).

Data are in agreement with those reported in the literature.[7]

1-isopropyl-5-methylpyrrolidin-2-one (11)



IR (NaCl): 1680 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22-4.10 (m, 1H), 4.09-4.00 (m, 1H), 2.52-2.35 (m, 2H), 2.15-2.03 (m 2H), 1.26-1.15 (9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.7, 21.8, 22.5, 27.3, 30.5, 44.3, 53.2, 174.8; MS 142 (M+1)126(62), 84(15).

Data are in agreement with those reported in the literature [7]

References

1. (a) $Tp^{X}Cu$ = Tp*Cu: C. Mealli, C. S. Arcus, J. L. Wilkinson, T. J. Marks and J.A. Ibers, *J. Am. Chem. Soc.,* 1976, **98**, 711-718. (b) $Tp^{Ms}Cu$: M. C. Schneider, S. M. Carrier, C. E. Ruggiero, V. G. Young and W. B. Tolman, *J. Am. Chem. Soc.,* 1998, **120**, 11408-11418. (c) $Tp^{Br3}Cu$: A. Caballero, M. M. Diaz-Requejo, T. R. Belderrain, M. C. Nicasio and P. J. Pérez; *J. Am. Chem. Soc.,* 2003, **125** , 1446. d) $Tp^{Cy,4Br}Cu$: M. A. Mairena, J. Urbano, J. Carbajo, J. J. Maraver, E. Alvarez, M. M. Diaz-Requejo and P. J. Pérez, *Inorg. Chem.*. **2007**, *46* , 7428-7435.
2. Diazoacetates and diazoacetamides were prepared as described in: T. Toma, J. Shimokawa and T. Fukuyama, *Org. Lett*. 2007, **9**, 3195-3197.
3. L. Coulombel and E. Duñach, *Synth. Commun.,* 2005, **35**, 153-160.
4. J. K. Crandall, W. H. Machleder and S. A. Sojka, *J. Org. Chem.,* 1973, **38**, 1149-1154.
5. R. R. Rando, *J. Am. Chem. Soc.,* 1970, **92**, 6706-6797.
6. G. Markus, S. Buck, L. Schäffler and G. Maas, *Adv. Synth. Catal.,* 2006, **348**, 2203-2211.
7. M. P. Doyle, S. M. Oon, F. R. Heide and C. B. Brown, *Bioorg. Med. Chem. Lett*. 1993, **3**, 2409-2414.

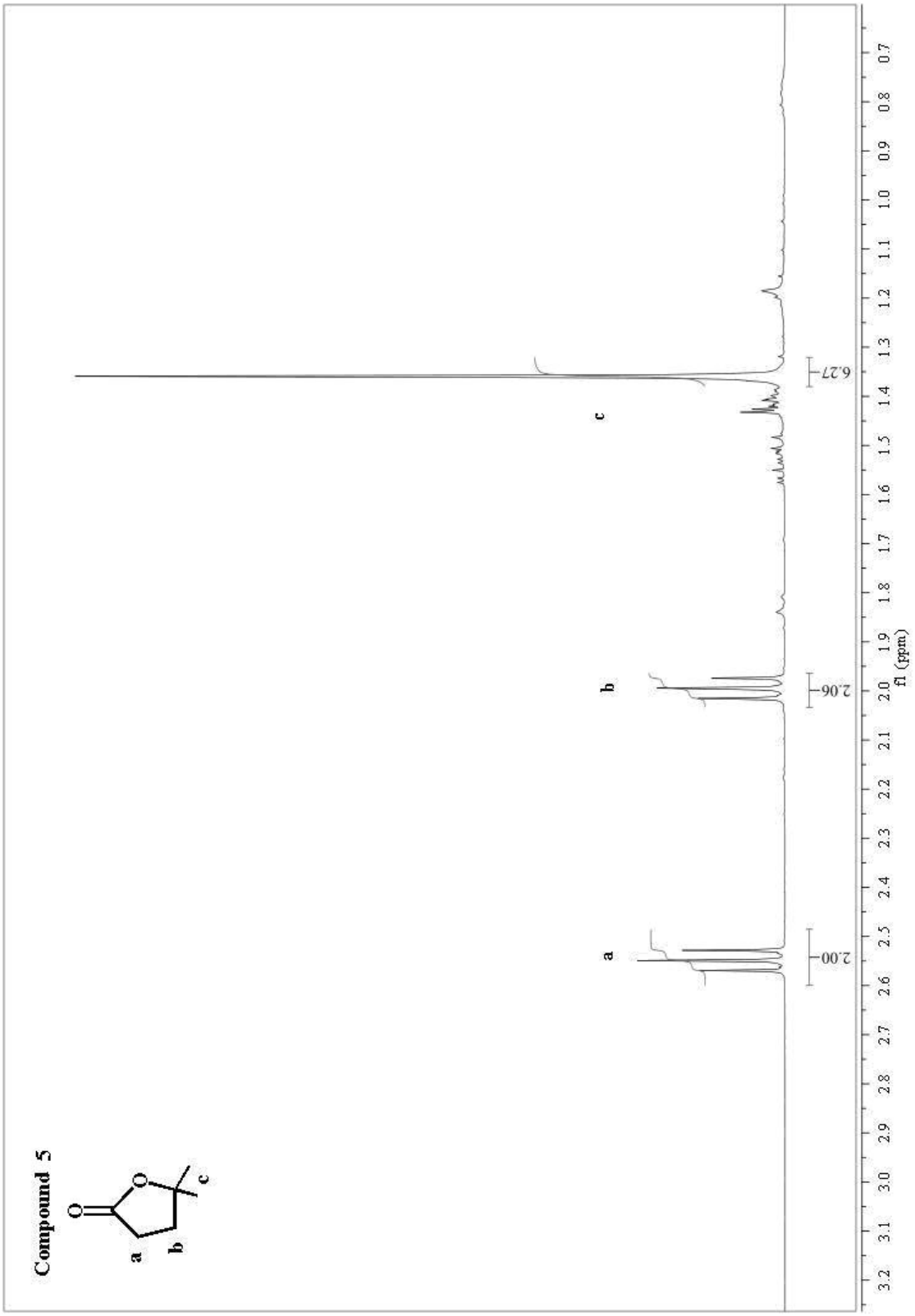


Figure 1.- ^{1}H NMR spectrum of product obtained from the decomposition of *tert*-Butyl diazoacetate in the presence of $Tp^{Ms}Cu$ as catalyst.

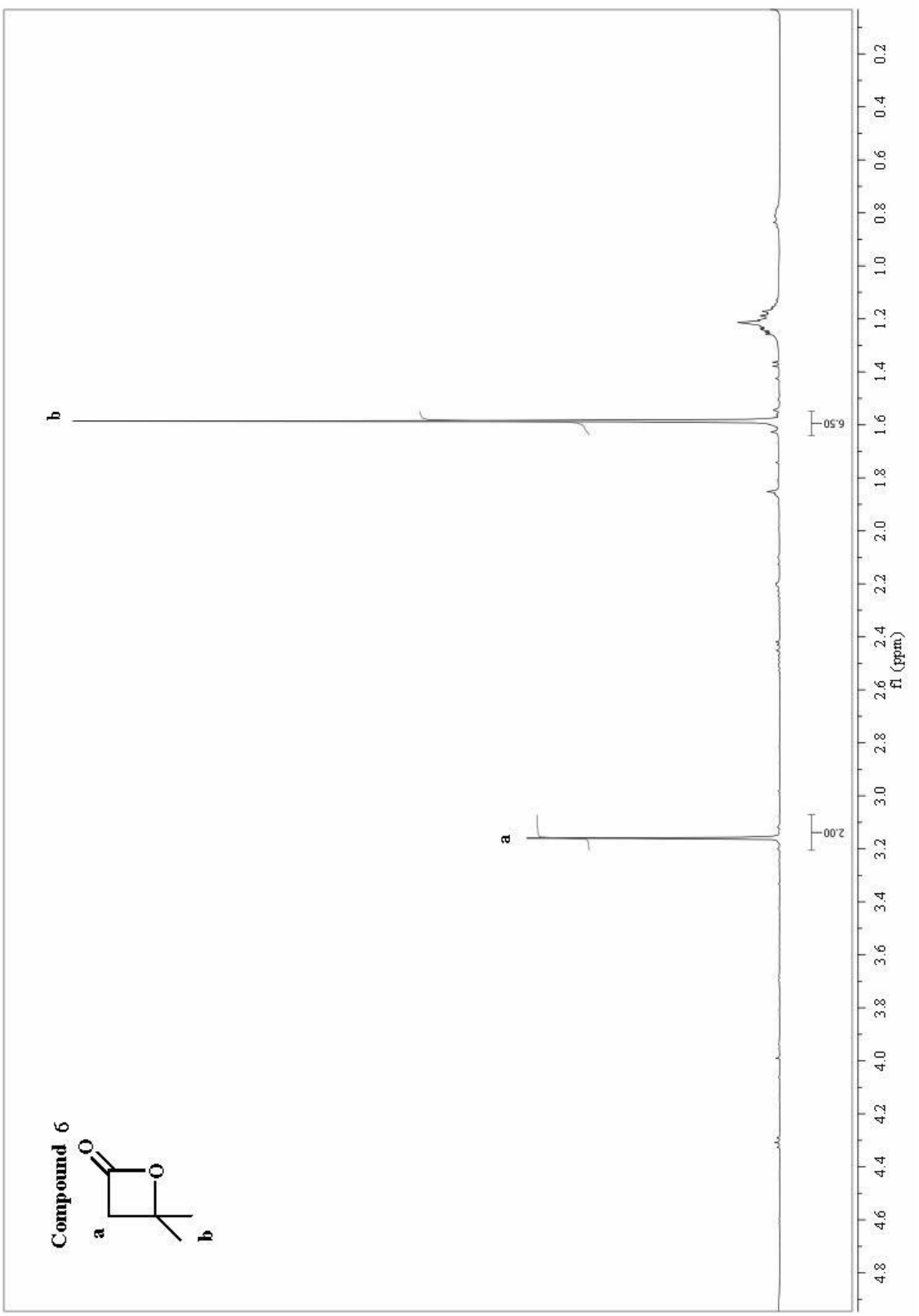


Figure 2.- ^{1}H NMR spectrum of the major product obtained from the decomposition of isopropyl diazoacetate in the presence of $Tp^{Ms}Cu$ as catalyst.

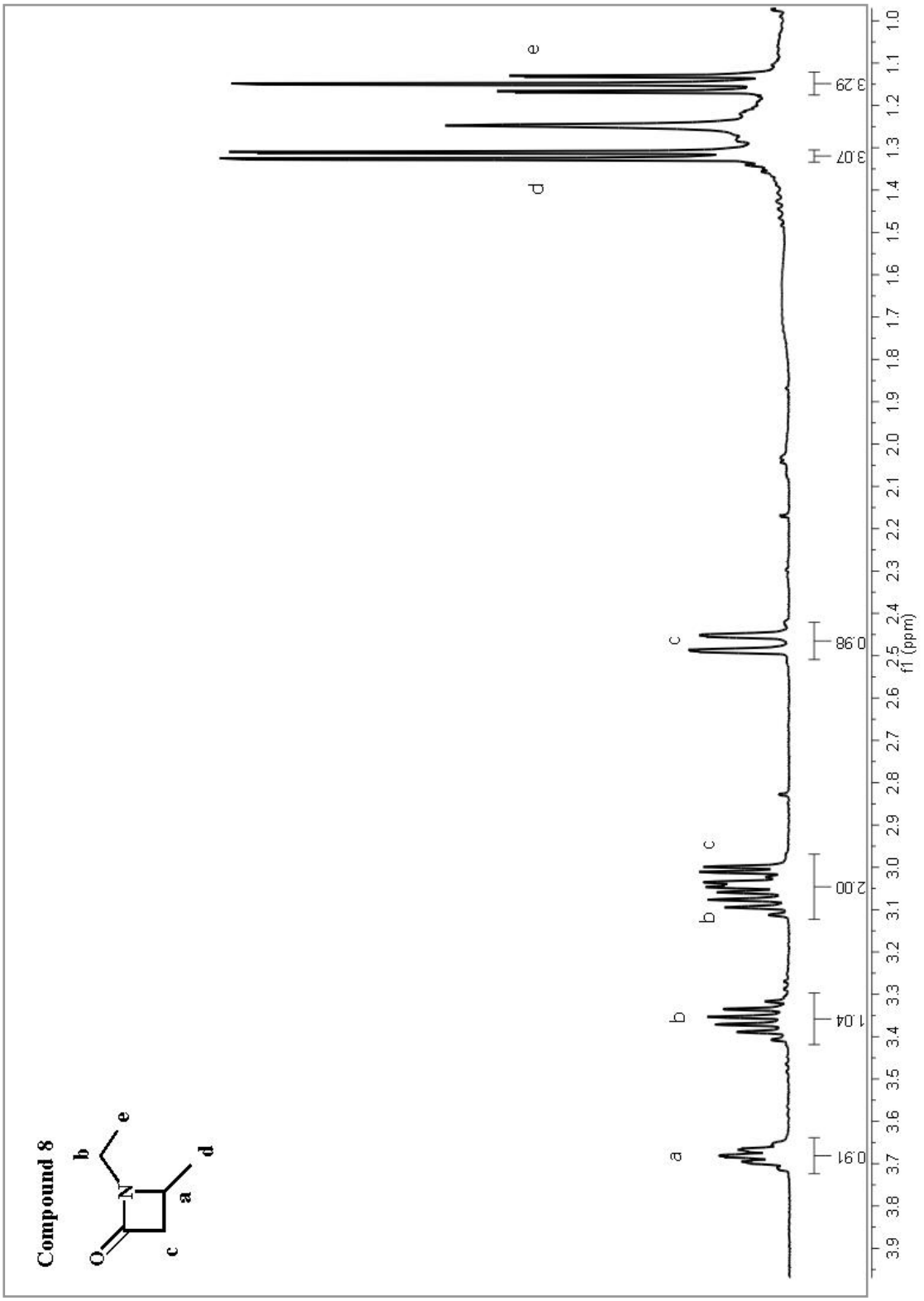


Figure 3.- ^{1}H NMR spectrum of major products obtained from the decomposition of the diethyl diazocetamides in the presence of $Tp^{Br3}Cu$ as catalyst.

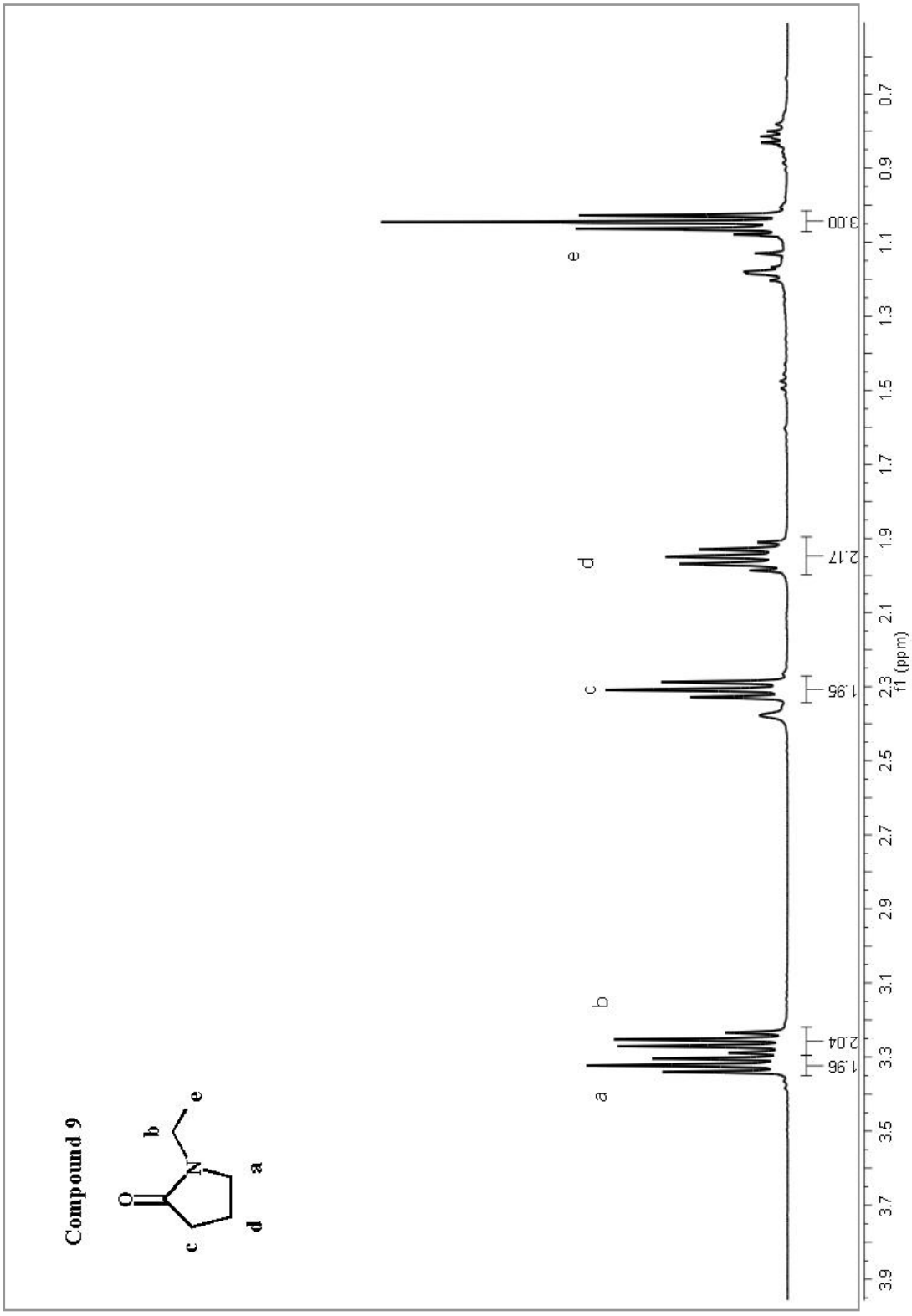


Figure 4.- ^{1}H NMR spectrum of minor product obtained from the decomposition of the diisopropyl diazocetamides in the presence of $Tp^{Br}Cu$ as catalyst.

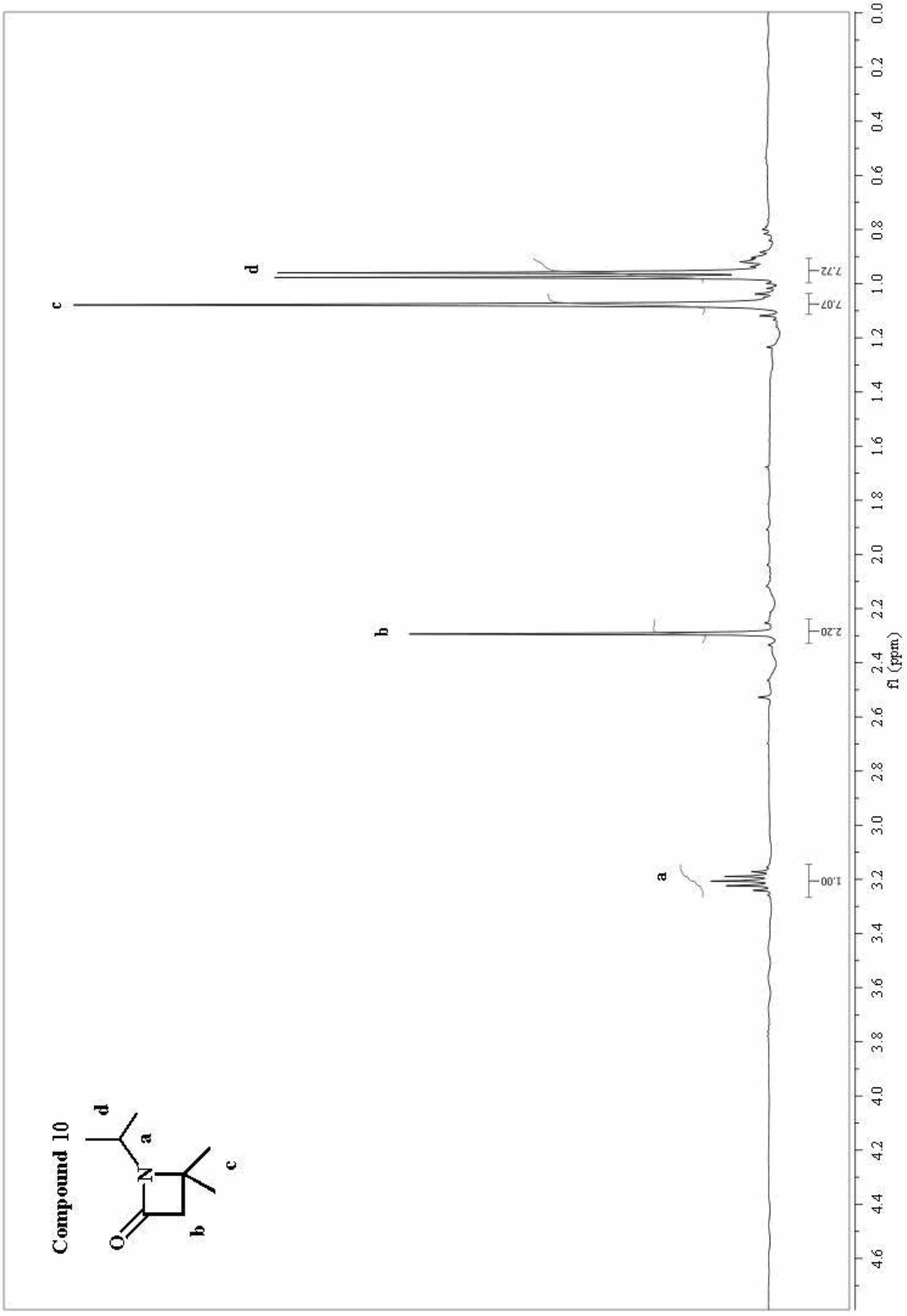


Figure 5.- ^{1}H NMR spectrum of major product obtained from the decomposition of the diisopropyl diazocetamides in the presence of $Tp^{Br}Cu$ as catalyst.

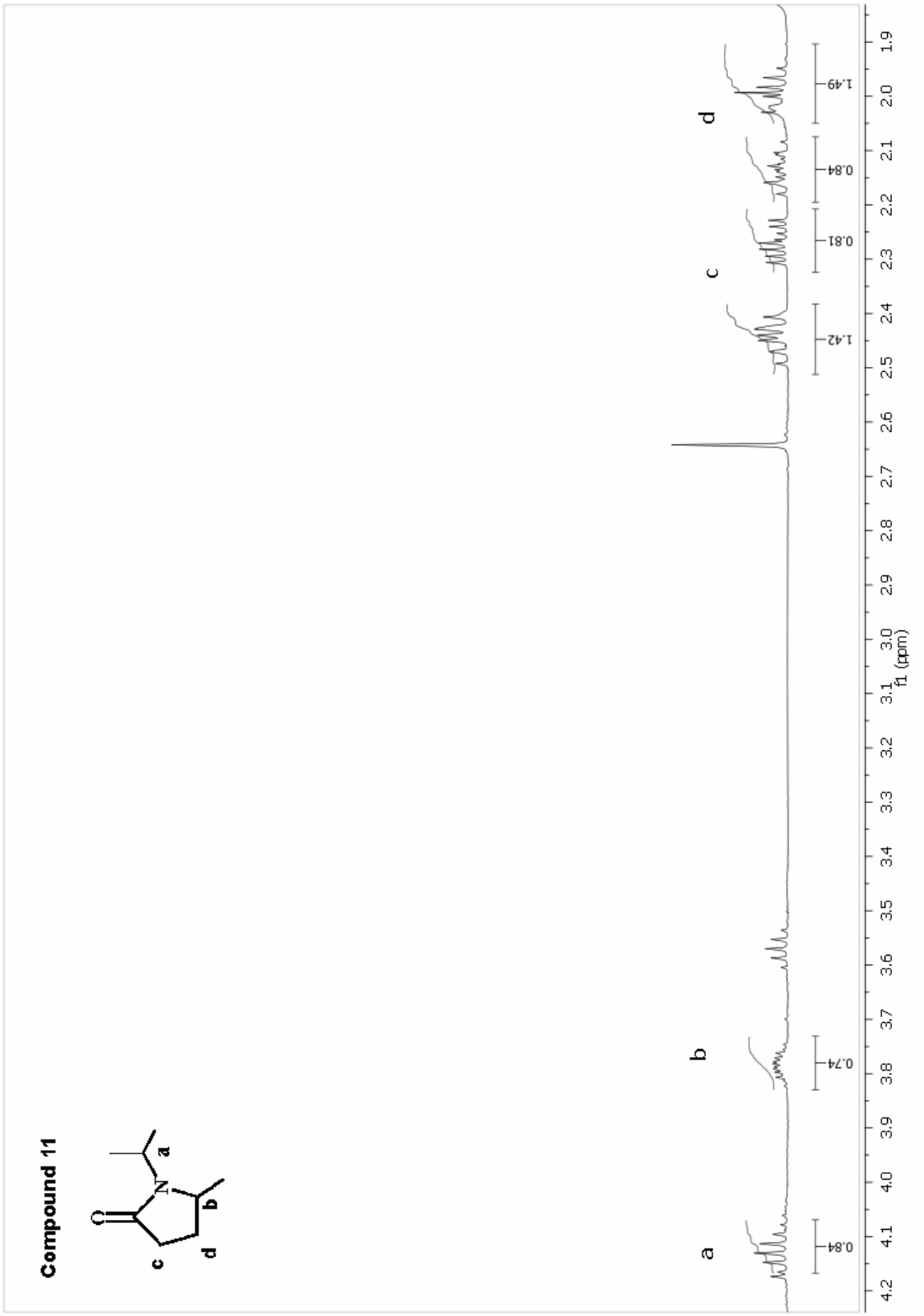


Figure 6.- ^{1}H NMR spectrum of the minor products obtained from the decomposition of the diisopropyl diazocetamides in the presence of $Tp^{Br}Cu$ as catalyst.