Stereoselective approach to hydroxyalkyl-1,2,3-triazoles containing cyclooctane core and their use for CuAAC catalysis

Olga V. Ryzhikova, Kseniya N. Sedenkova, Sergey V. Kositov, Victor A. Tafeenko, Yuri K. Grishin and Elena B. Averina *

Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory 1-3, 119991 Moscow, Russia
*Correspondence: elaver@med.chem.msu.ru

Supplementary materials

1. X-Ray diffraction analysis of compound **16**…….. 2

2. Copies of NMR spectra of products.……..... 4

3. Copies of NMR spectra of reaction mixtures of CuAAC reactions in the presence of various ligands…….....…….…..... 36

1. X-Ray diffraction analysis of compound 16

Table S1. Crystal data and structure refinement for compound **16**.

Identification code	**16**	
Empirical formula	C34 H46 Cl2 Cu N6 O2	
Formula weight	705.21	
Temperature	295(2) K	
Wavelength	1.54186 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 9.7102(2) Å	α= 90°.
	b = 27.8811(8) Å	β= 104.481(2)°.
	c = 13.3168(3) Å	γ = 90°.
Volume	3490.73(15) $Å^3$	
Z	4	
Density (calculated)	1.342 Mg/m^3	
Absorption coefficient	2.599 mm^{-1}	
F(000)	1484	
Theta range for data collection	3.170 to 67.041°.	
Index ranges	-8<=h<=11, -33<=k<=31, -15<=l<=9	
Reflections collected	25179	
Independent reflections	6161 [R(int) = 0.1005]	
Completeness to theta = 67.041°	98.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6161 / 0 / 415	
Goodness-of-fit on F^2	0.823	
Final R indices [I>2sigma(I)]	R1 = 0.0511, wR2 = 0.1121	
R indices (all data)	R1 = 0.1040, wR2 = 0.1372	
Extinction coefficient	0.00235(14)	
Largest diff. peak and hole	0.796 and -0.611 e. $Å^{-3}$	

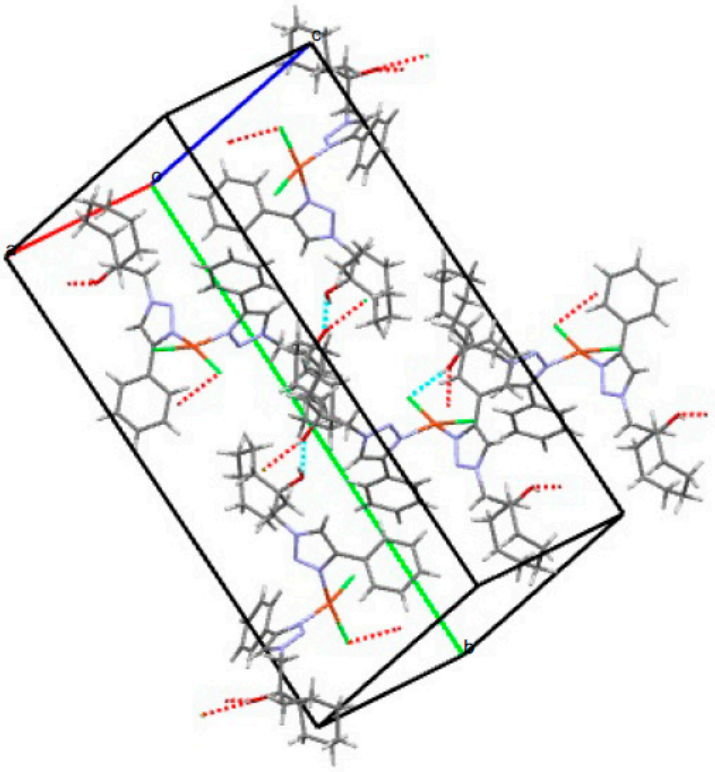


Figure S1. Cell unit for compound **16**.

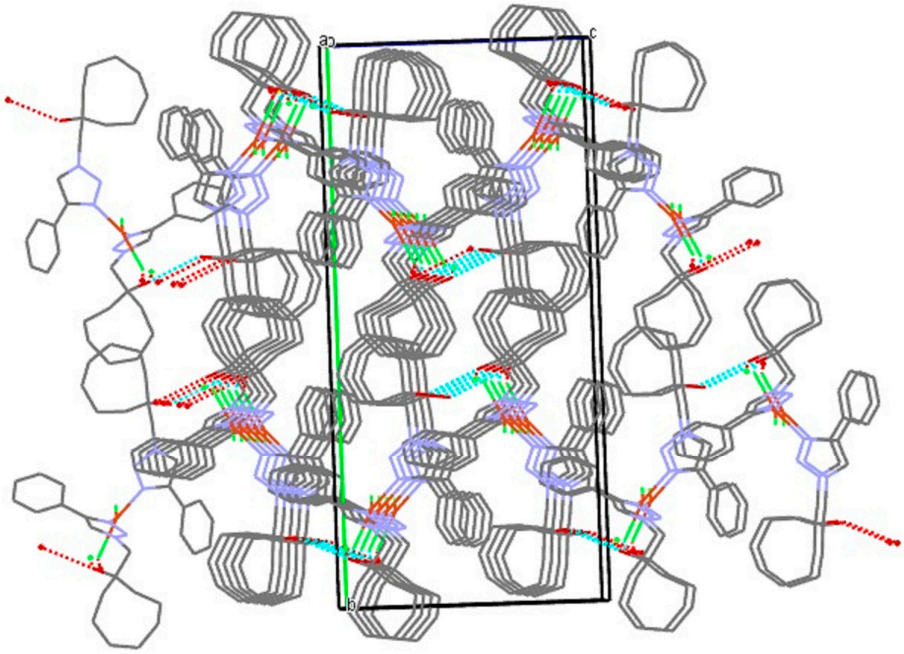
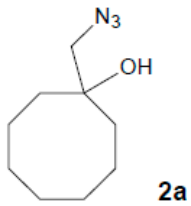


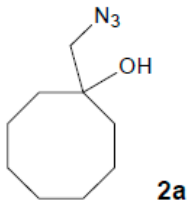
Figure S2. Molecular layers and hydrogen bonds in the crystal of **16**.

^{1}H NMR ($CDCl_3$) spectrum of compound **2a**



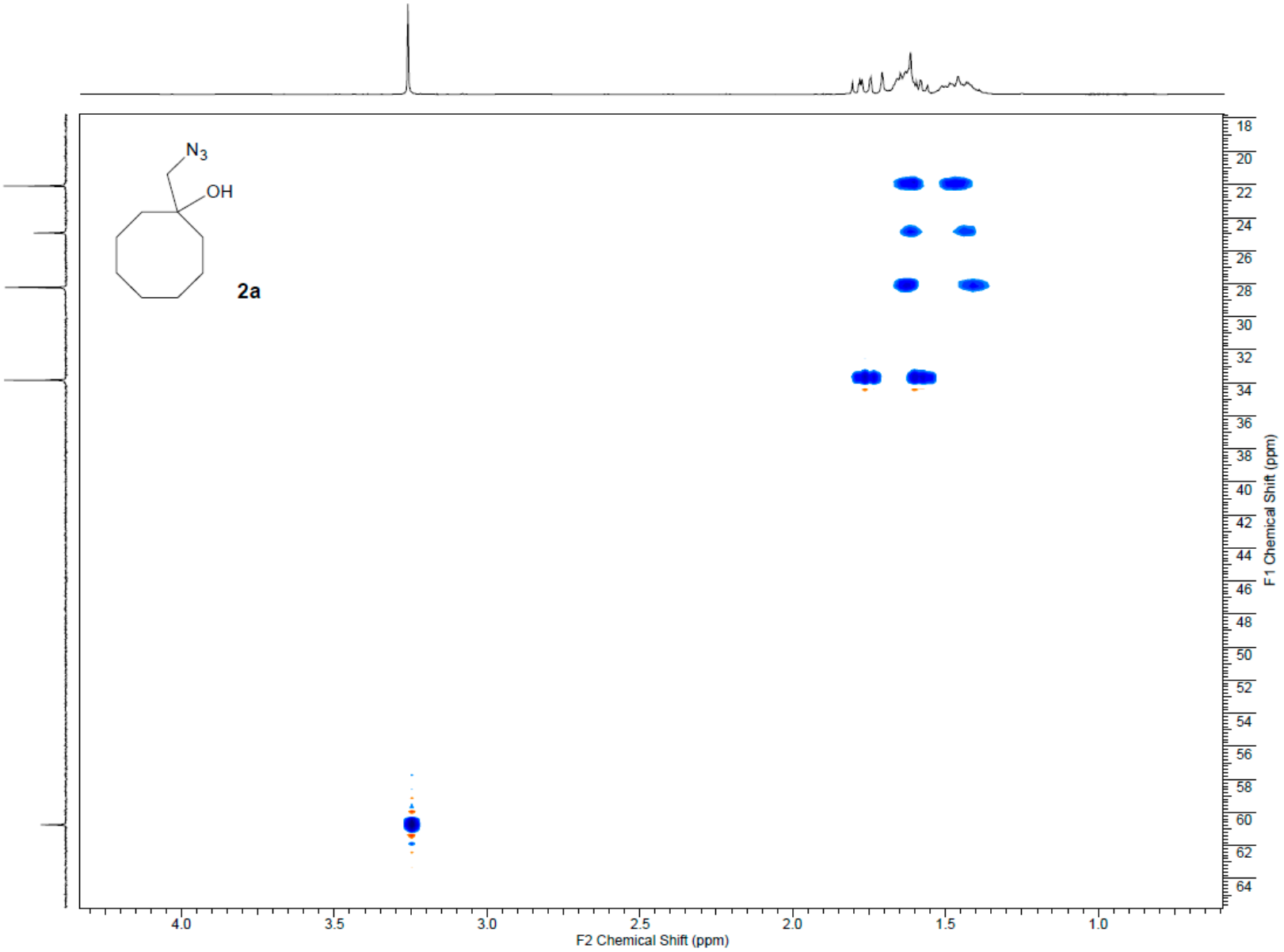
2a

^{13}C NMR ($CDCl_3$) spectrum of compound **2a**

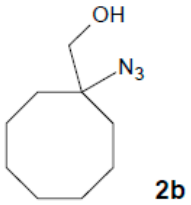


2a

HSQC NMR ($CDCl_3$) spectrum of compound **2a**

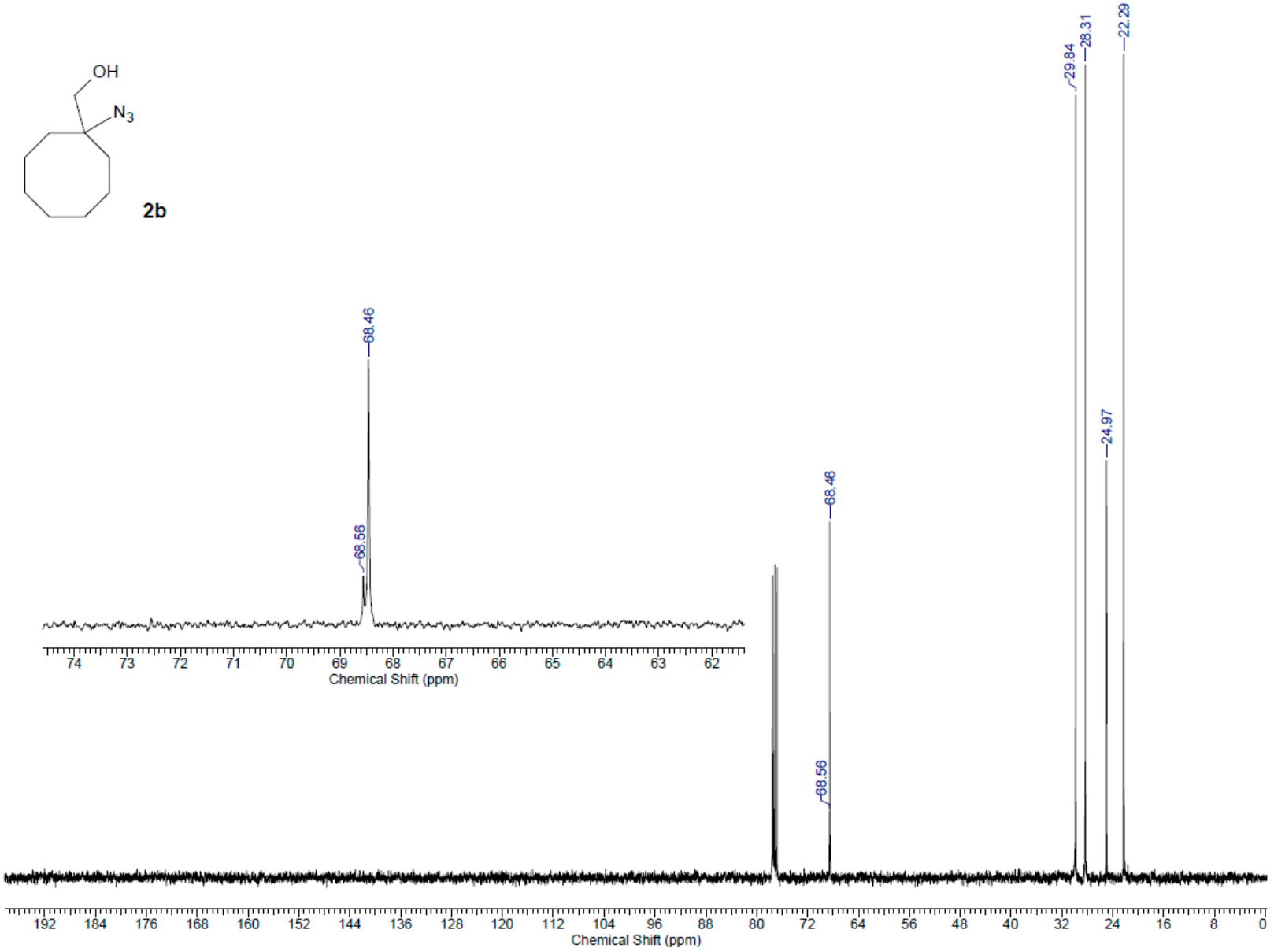


^{1}H NMR ($CDCl_3$) spectrum of compound **2b**

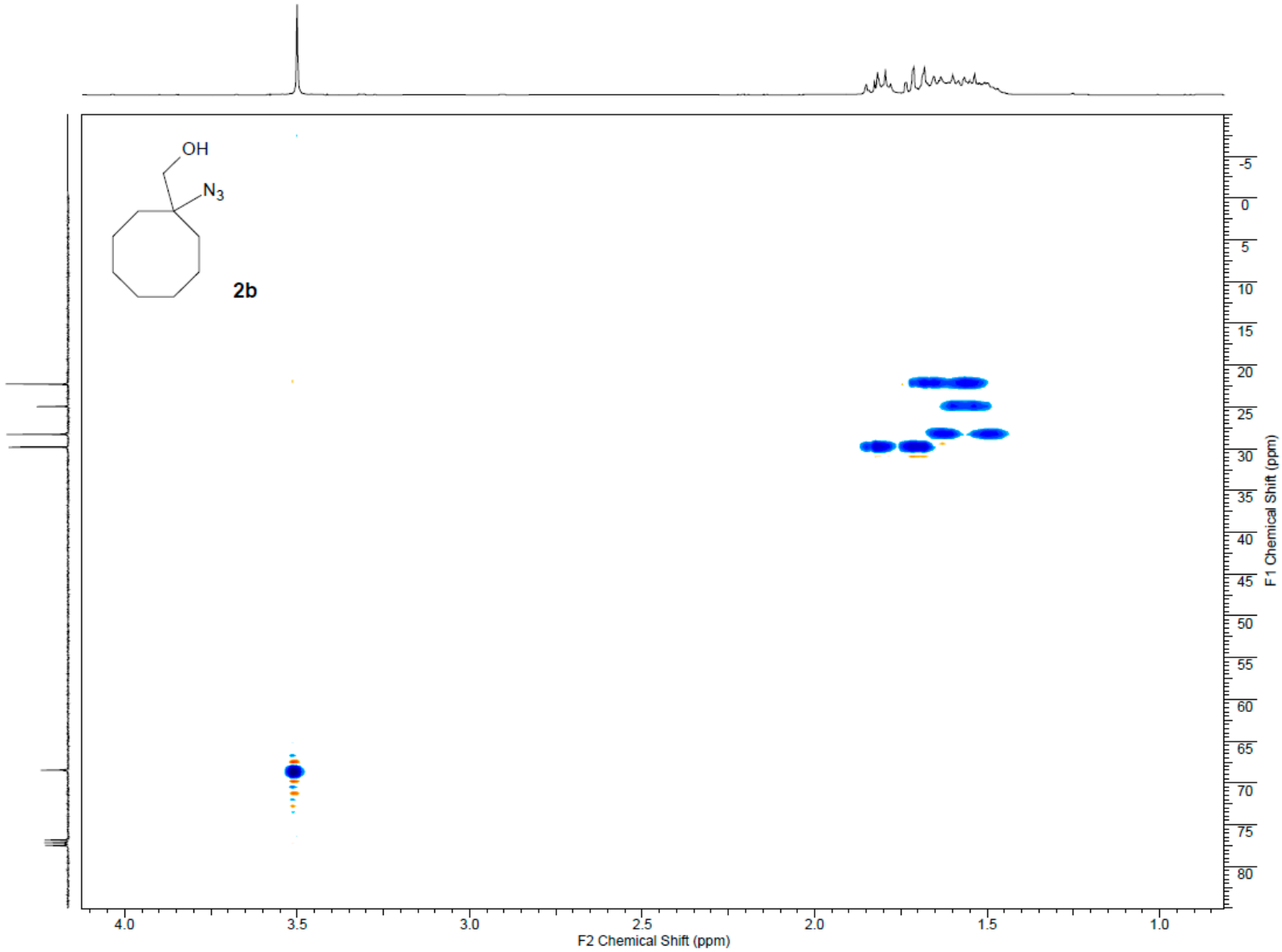


2b

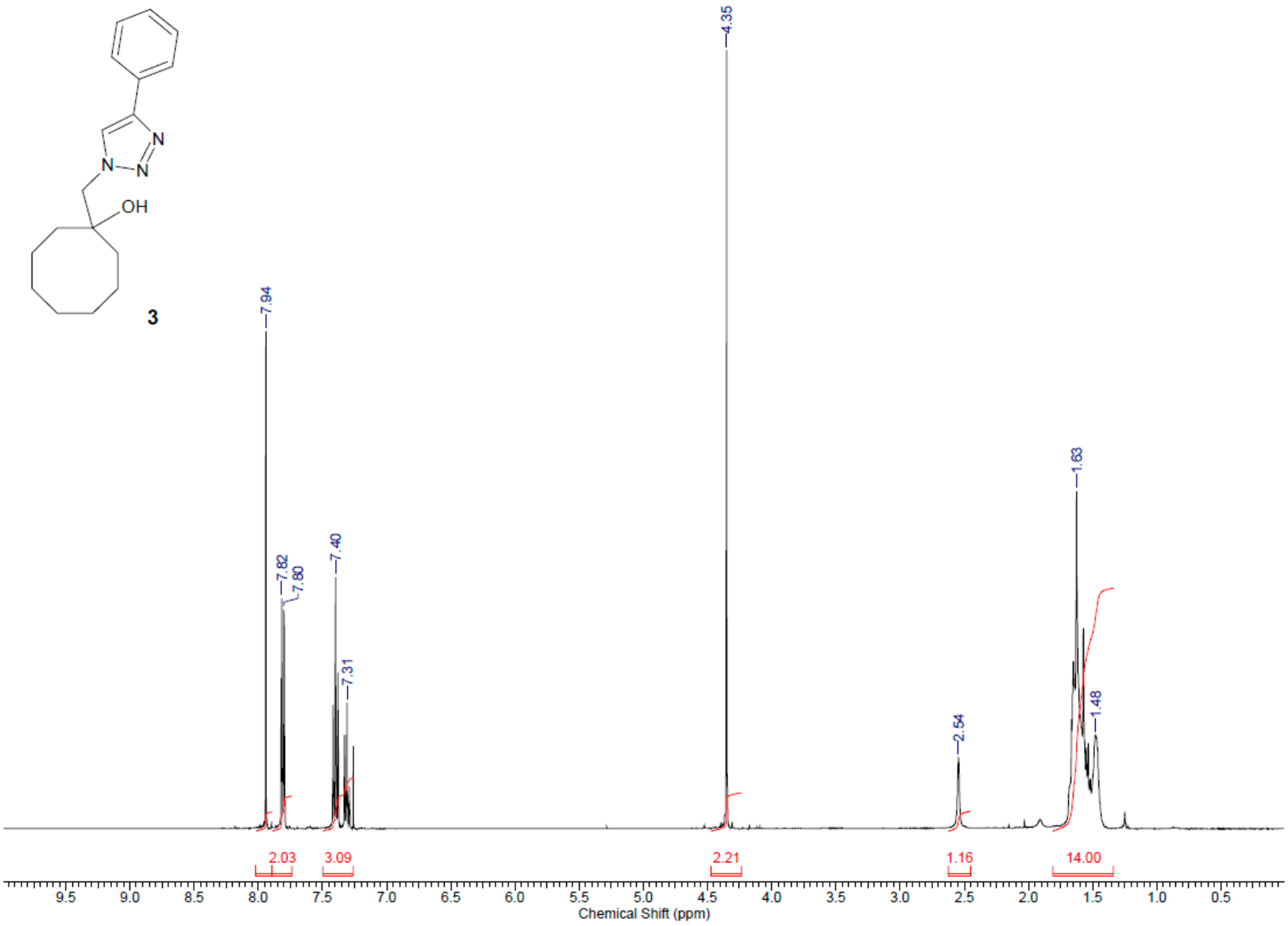
^{13}C NMR ($CDCl_3$) spectrum of compound **2b**



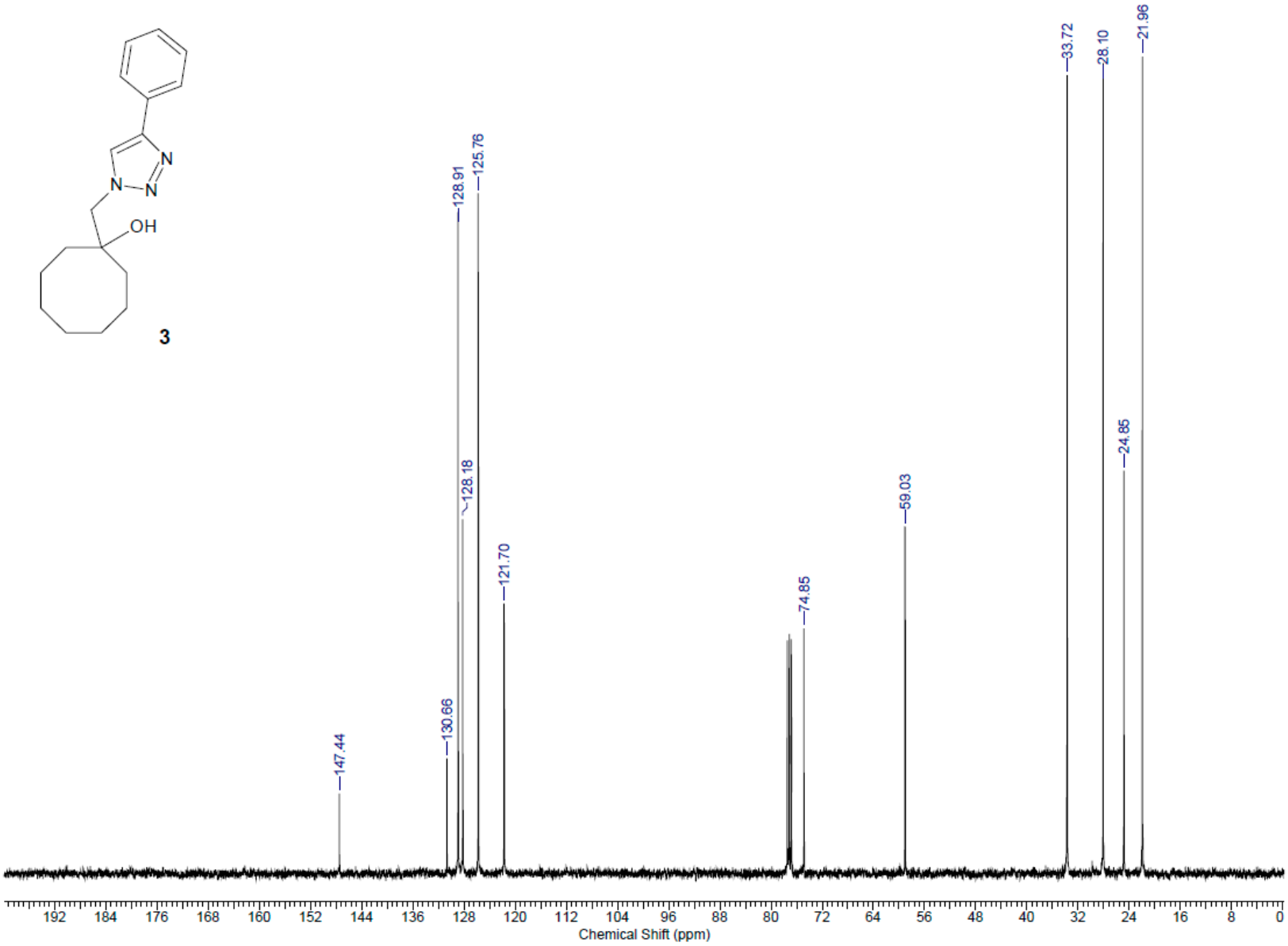
HSQC ($CDCl_3$) spectrum of compound **2b**



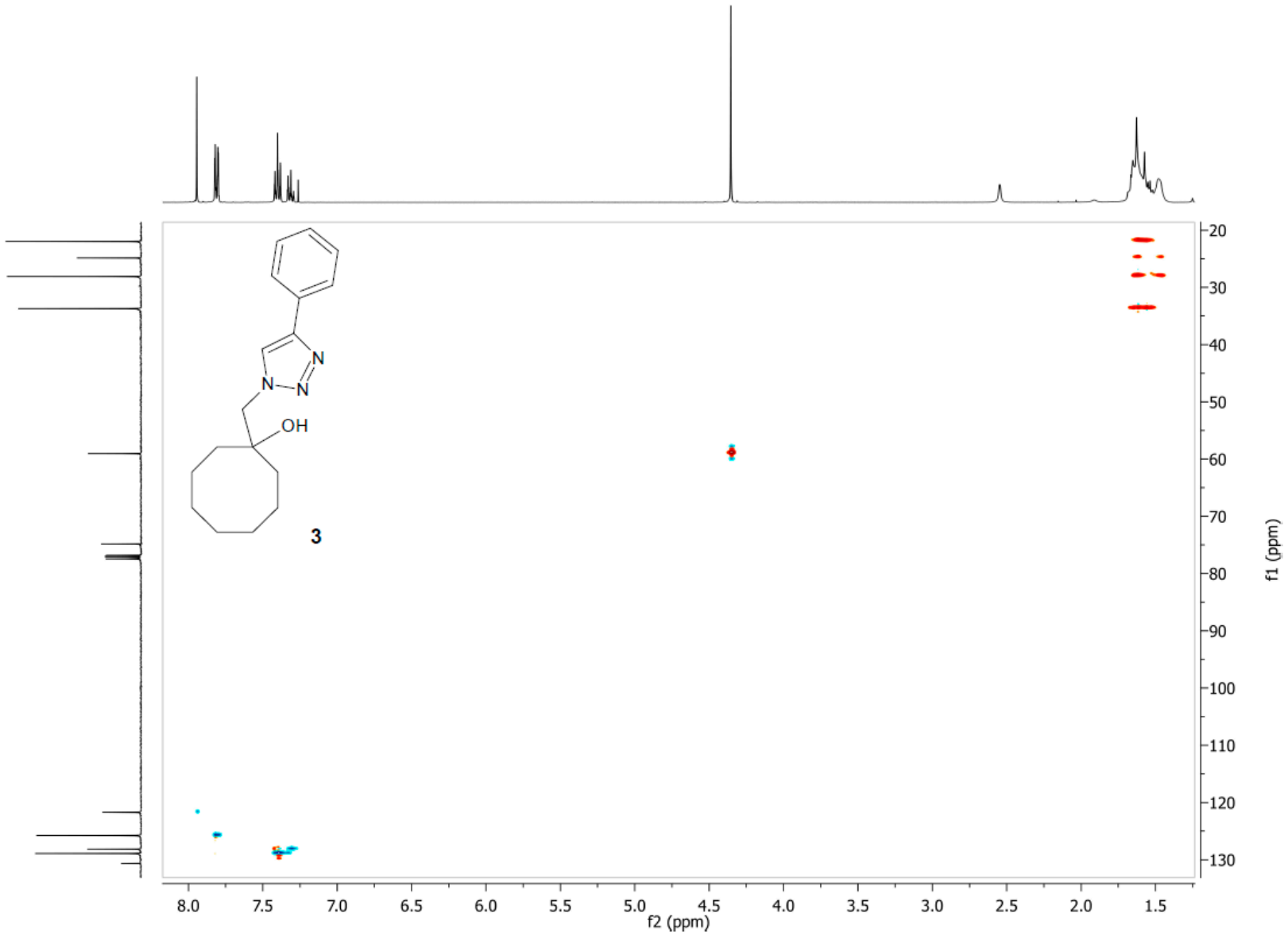
^{1}H NMR ($CDCl_3$) spectrum of compound **3**



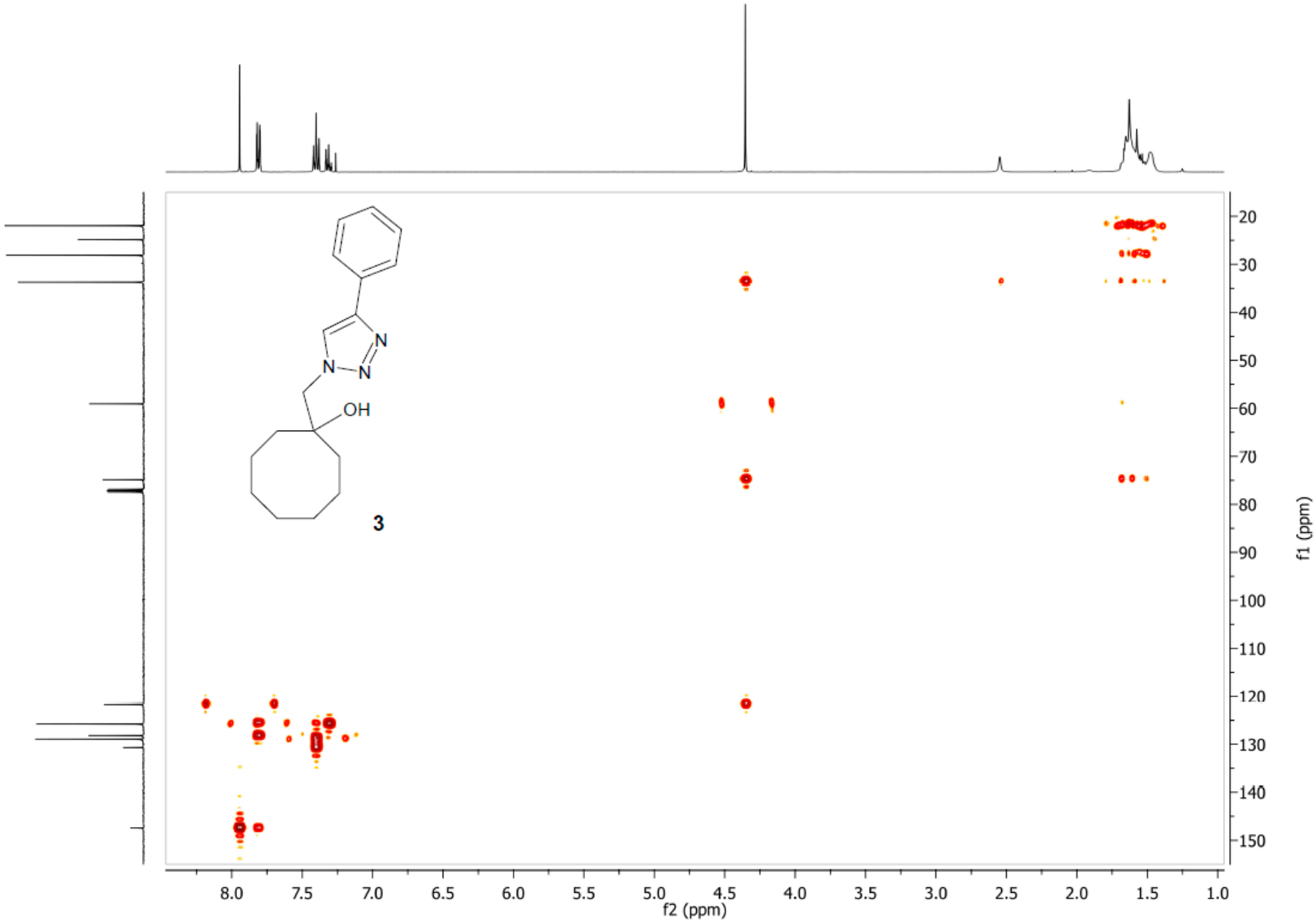
^{13}C NMR ($CDCl_3$) spectrum of compound **3**



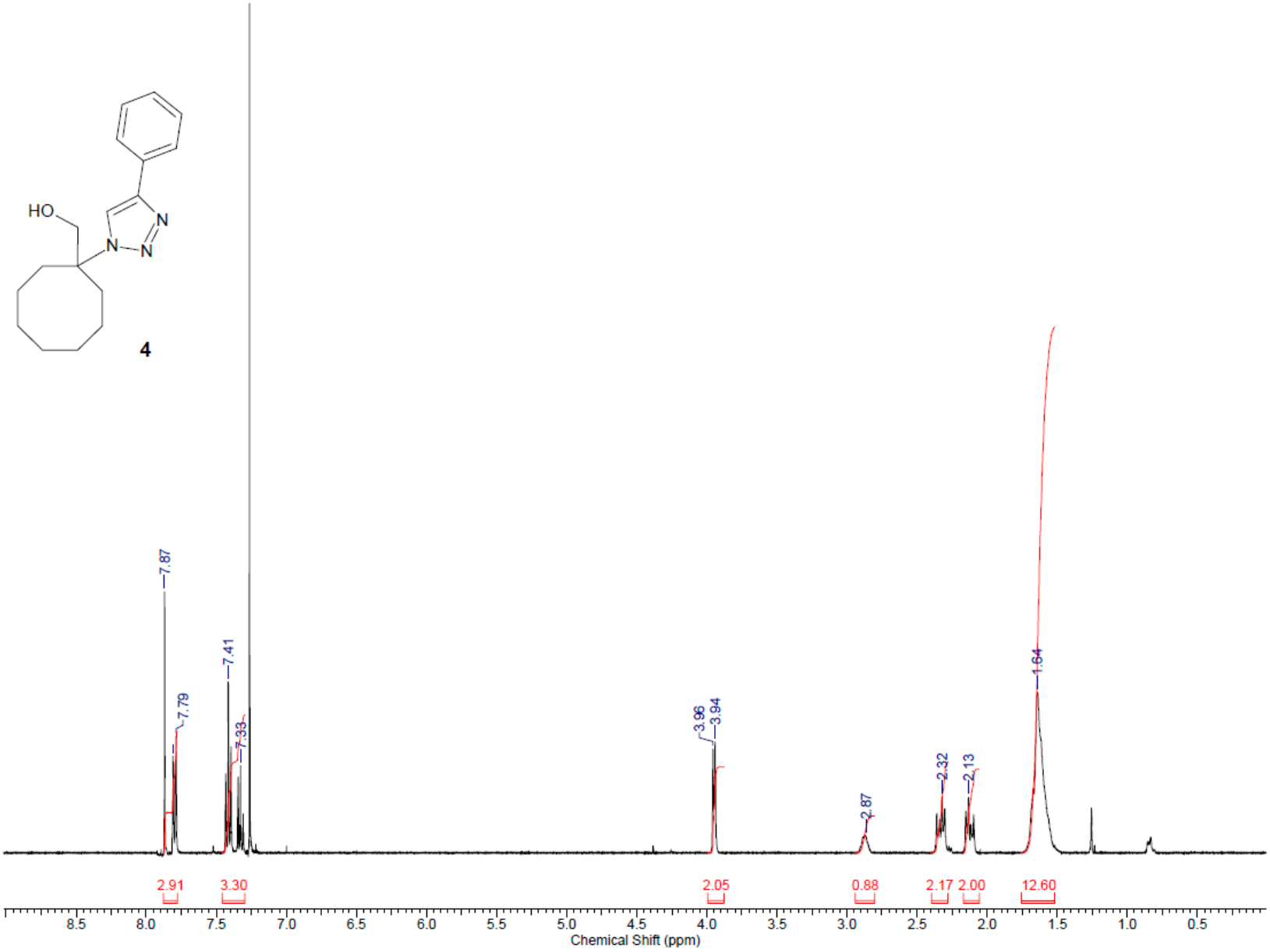
HSQC NMR ($CDCl_3$) spectrum of compound **3**



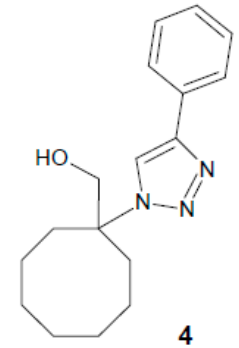
HMBC NMR ($CDCl_3$) spectrum of compound **3**



^{1}H NMR ($CDCl_3$) spectrum of compound **4**

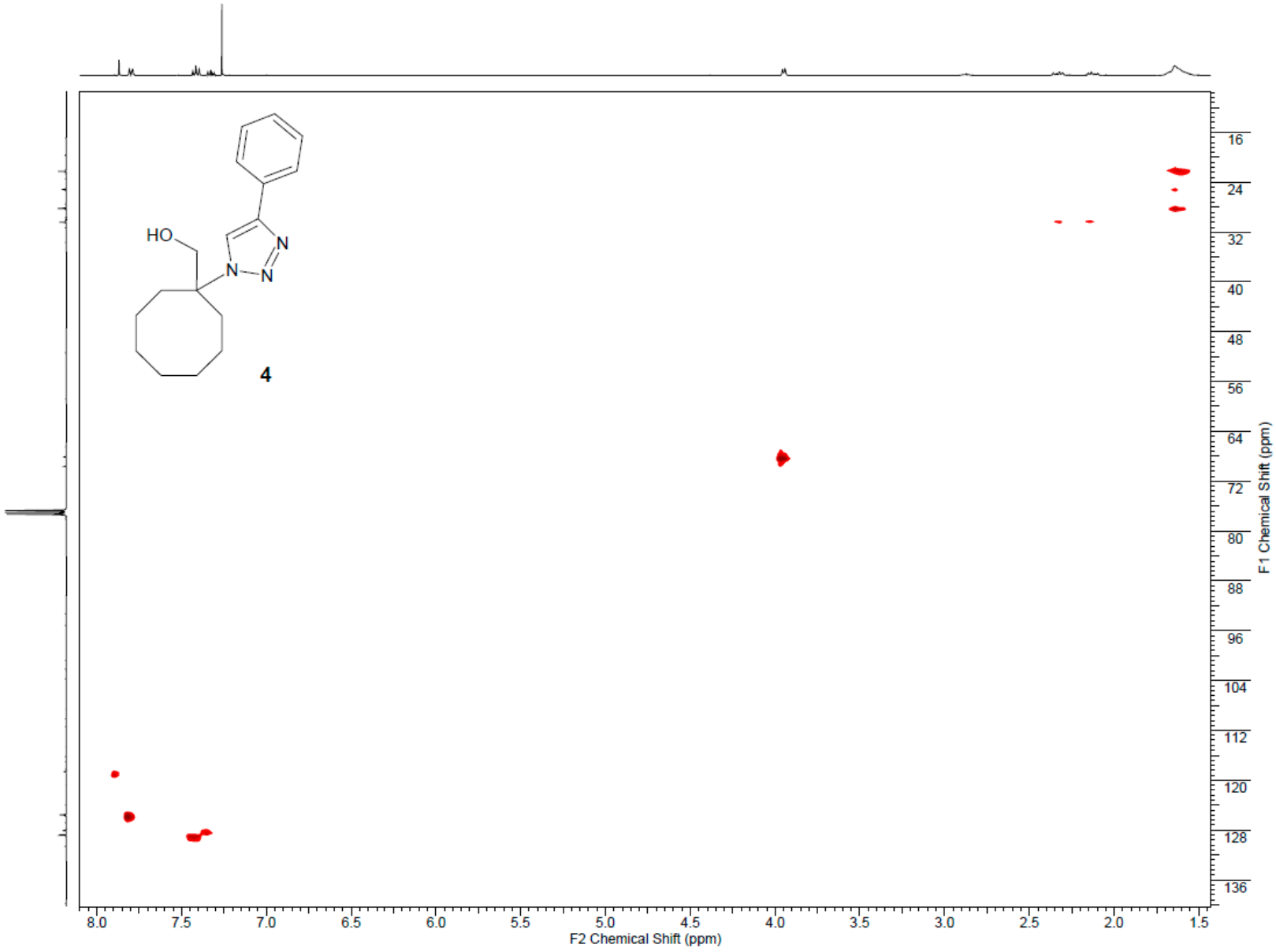


^{13}C NMR ($CDCl_3$) spectrum of compound **4**

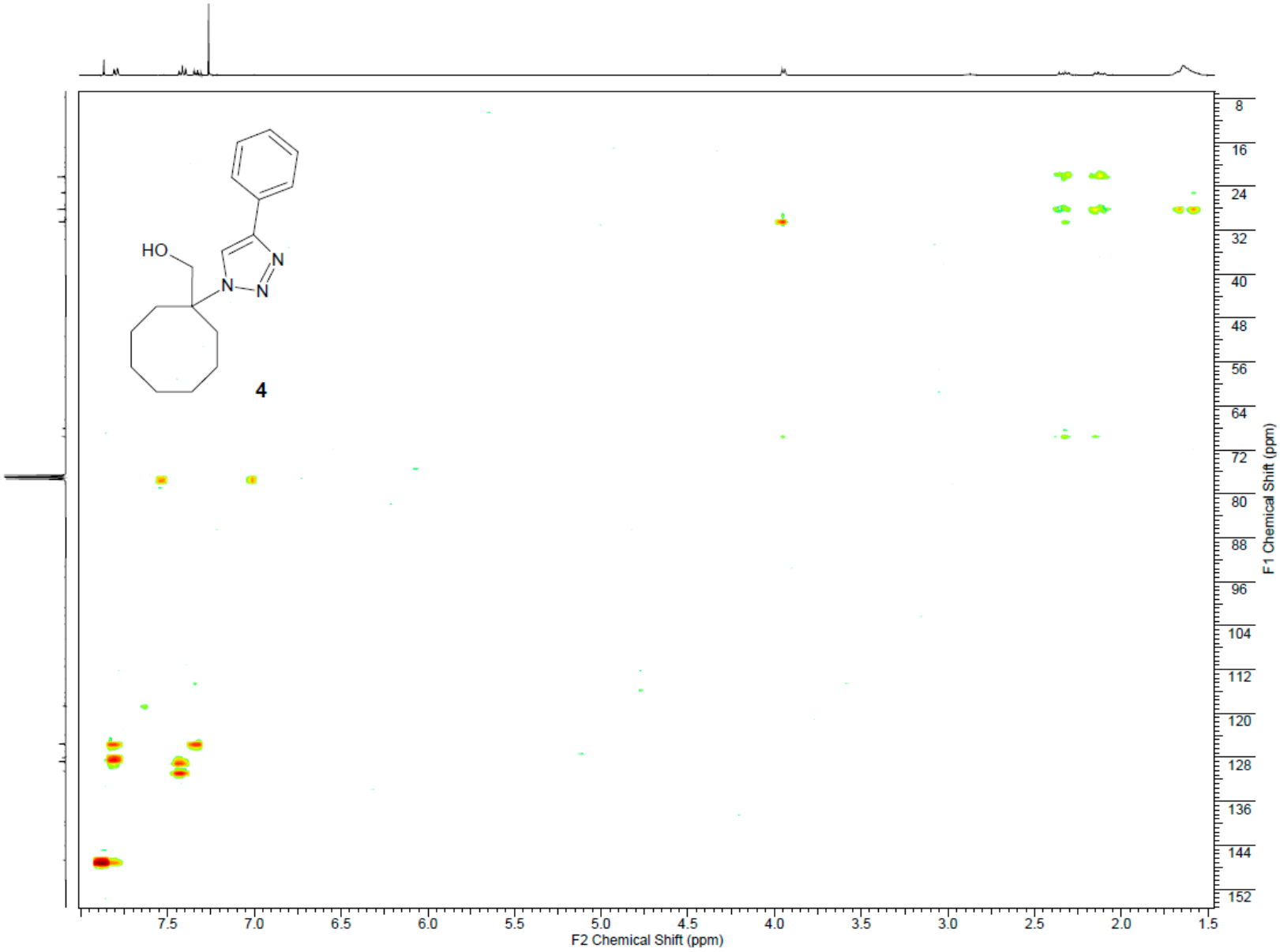


4

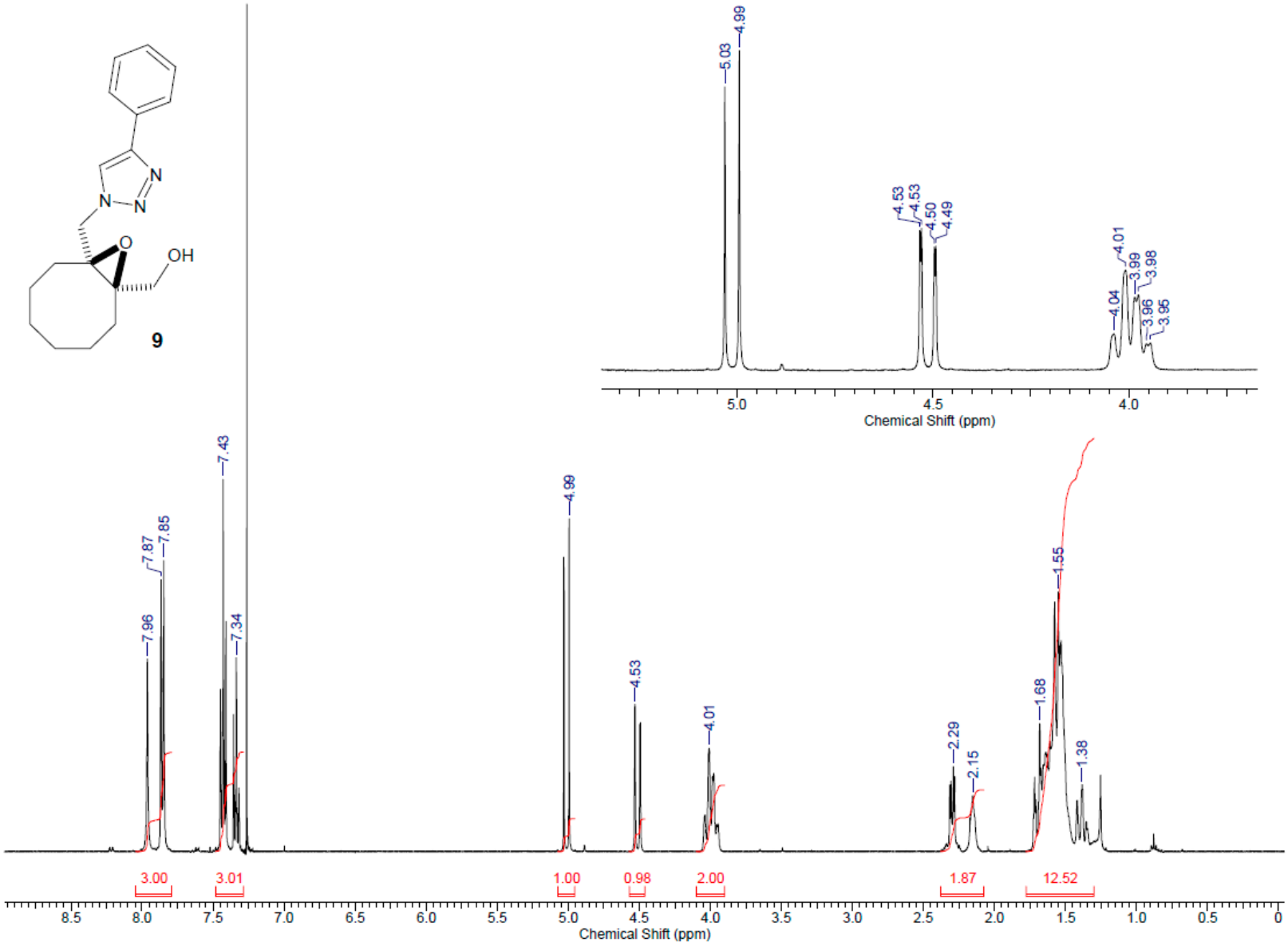
HSQC NMR ($CDCl_3$) spectrum of compound **4**



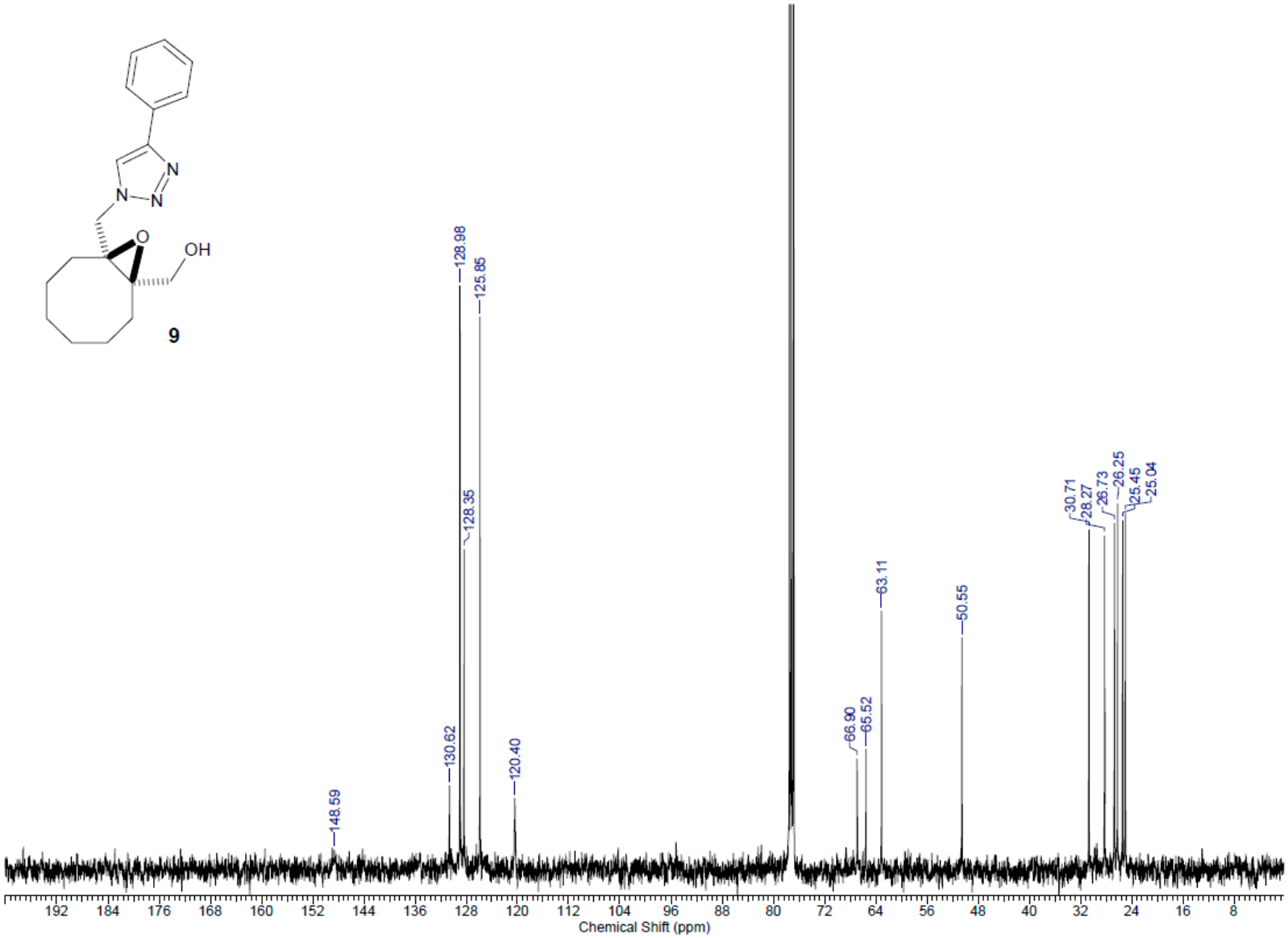
HMBC NMR ($CDCl_3$) spectrum of compound **4**



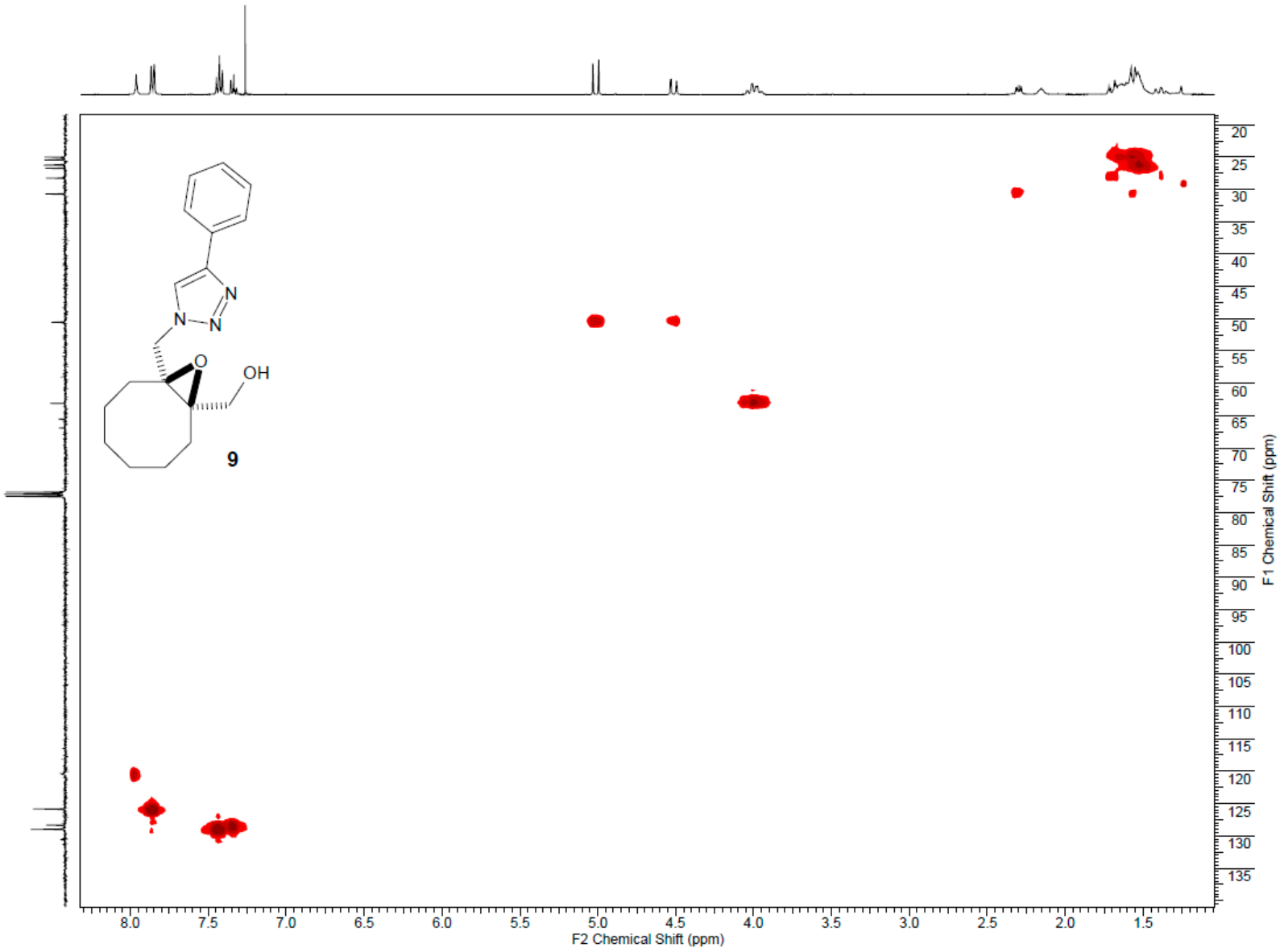
^{1}H NMR ($CDCl_3$) spectrum of compound **9**



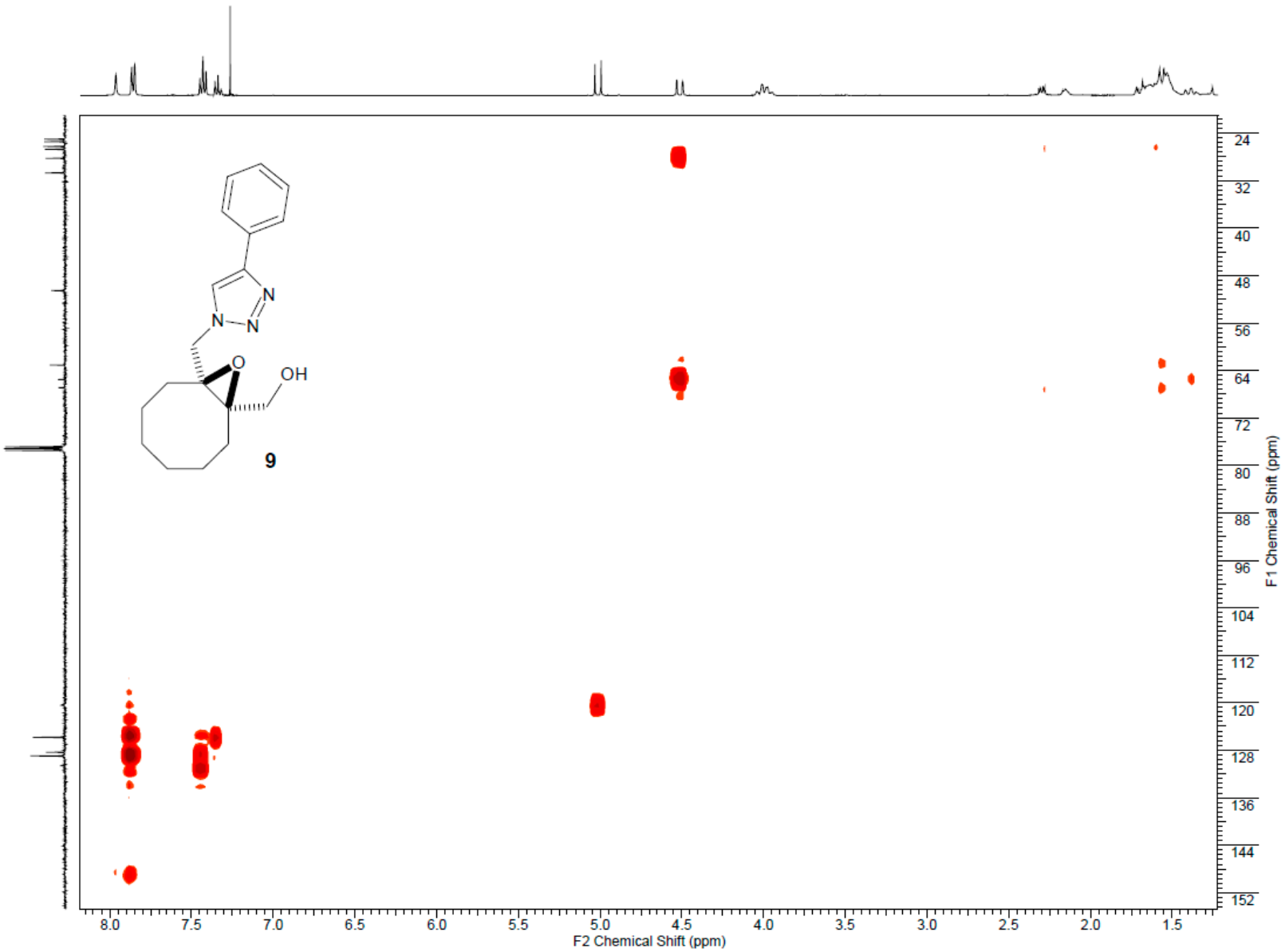
^{13}C NMR ($CDCl_3$) spectrum of compound **9**



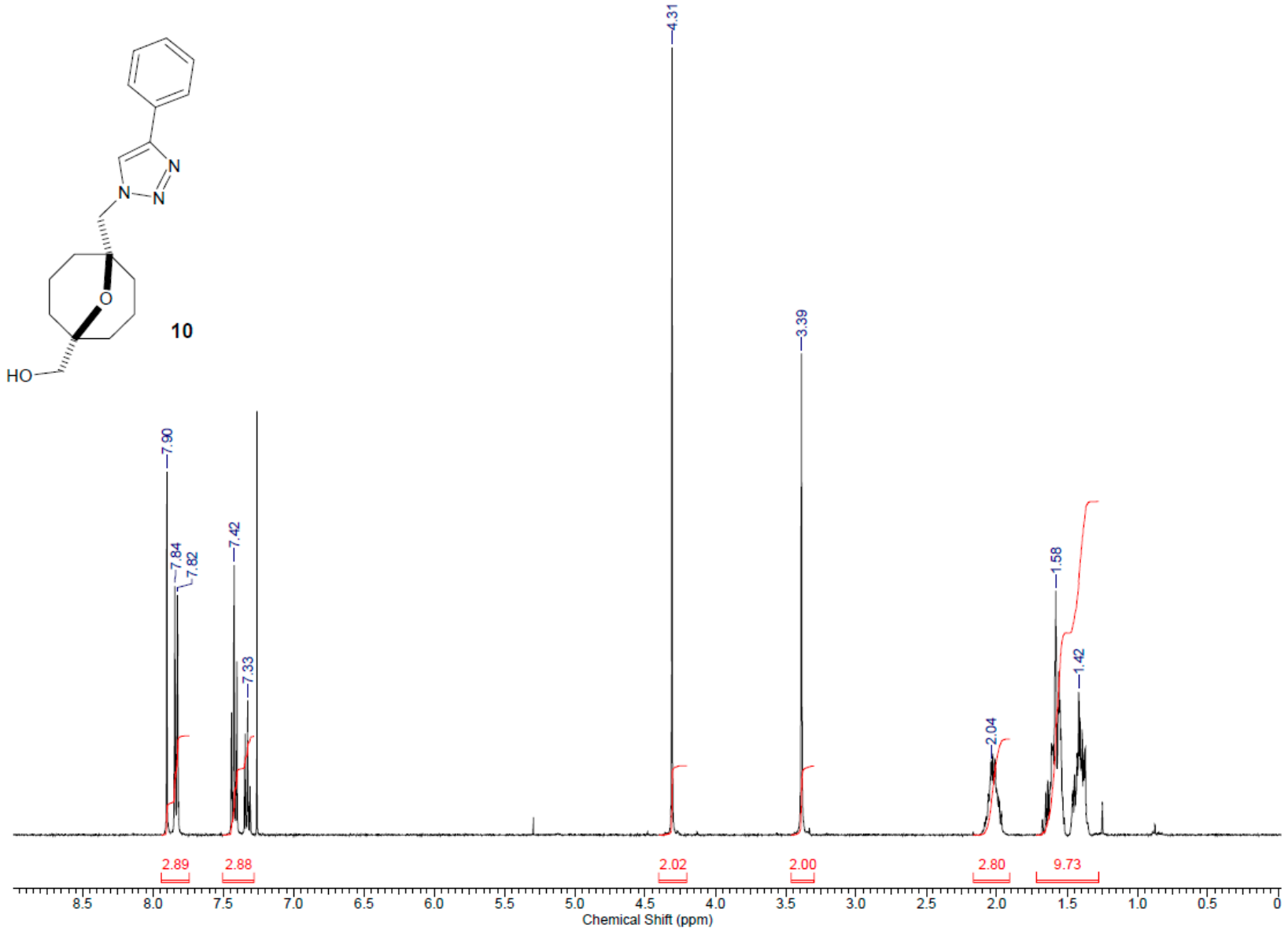
HSQC NMR ($CDCl_3$) spectrum of compound **9**



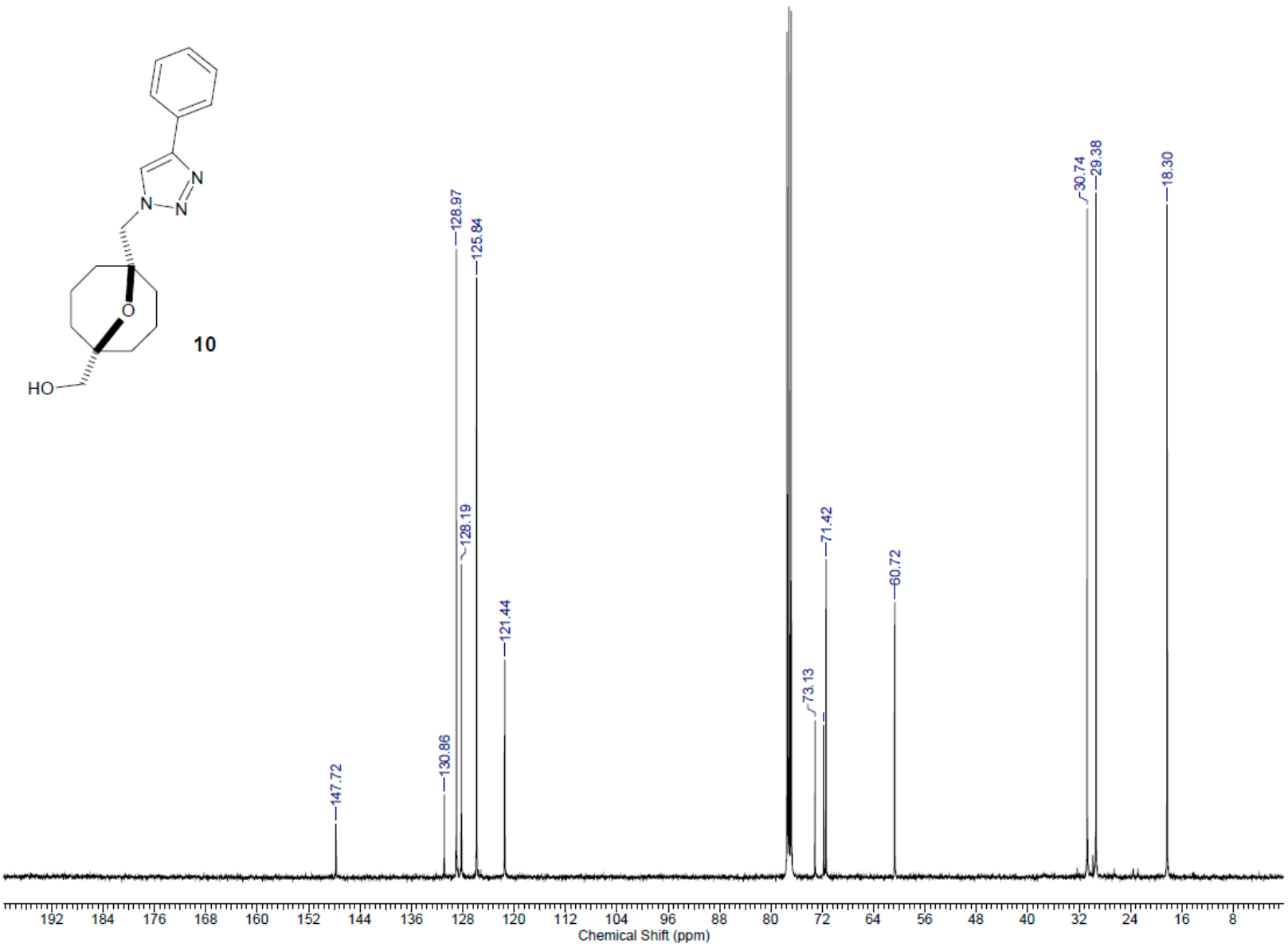
HMBC NMR ($CDCl_3$) spectrum of compound **9**



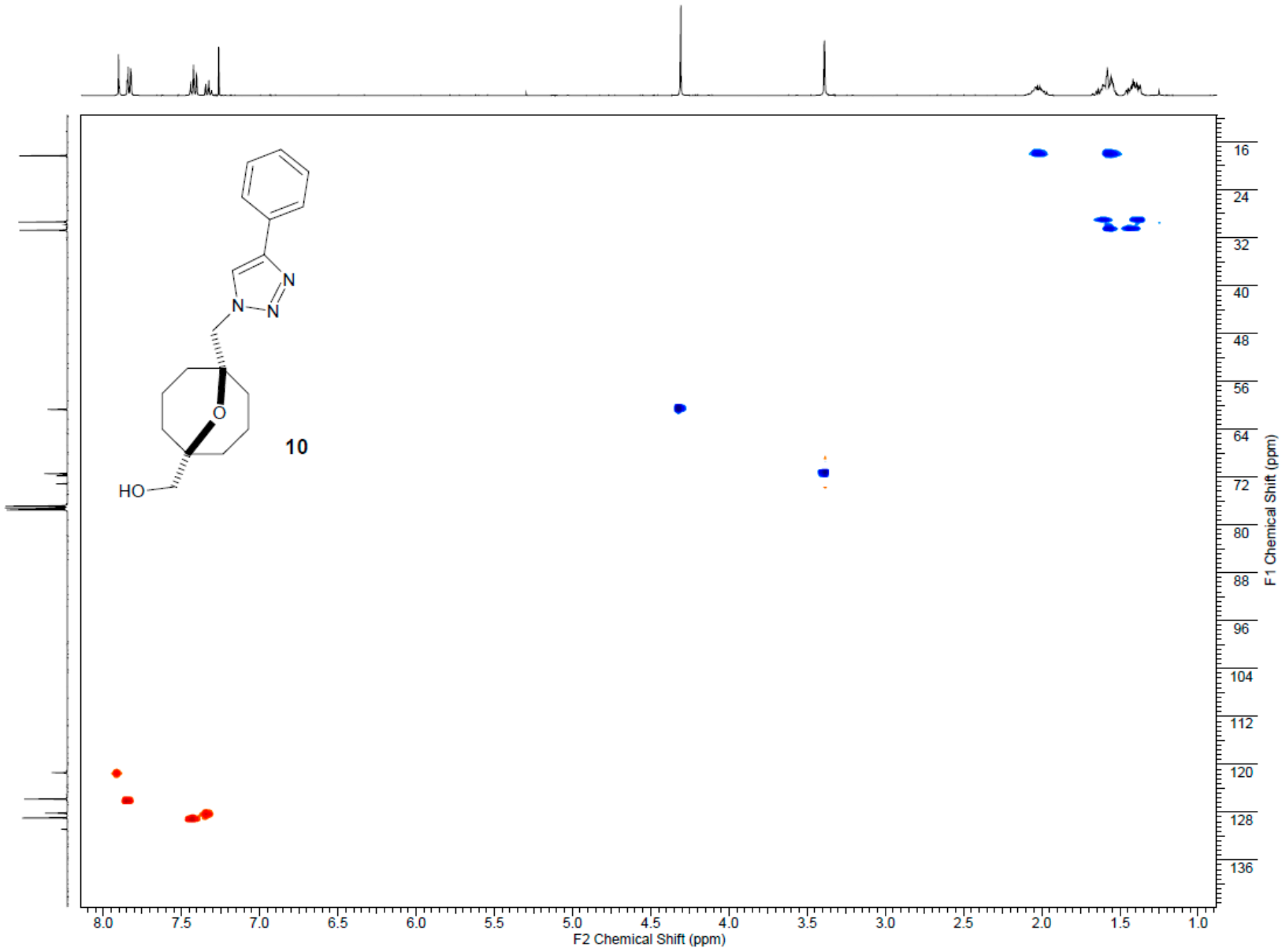
^{1}H NMR ($CDCl_3$) spectrum of compound **10**



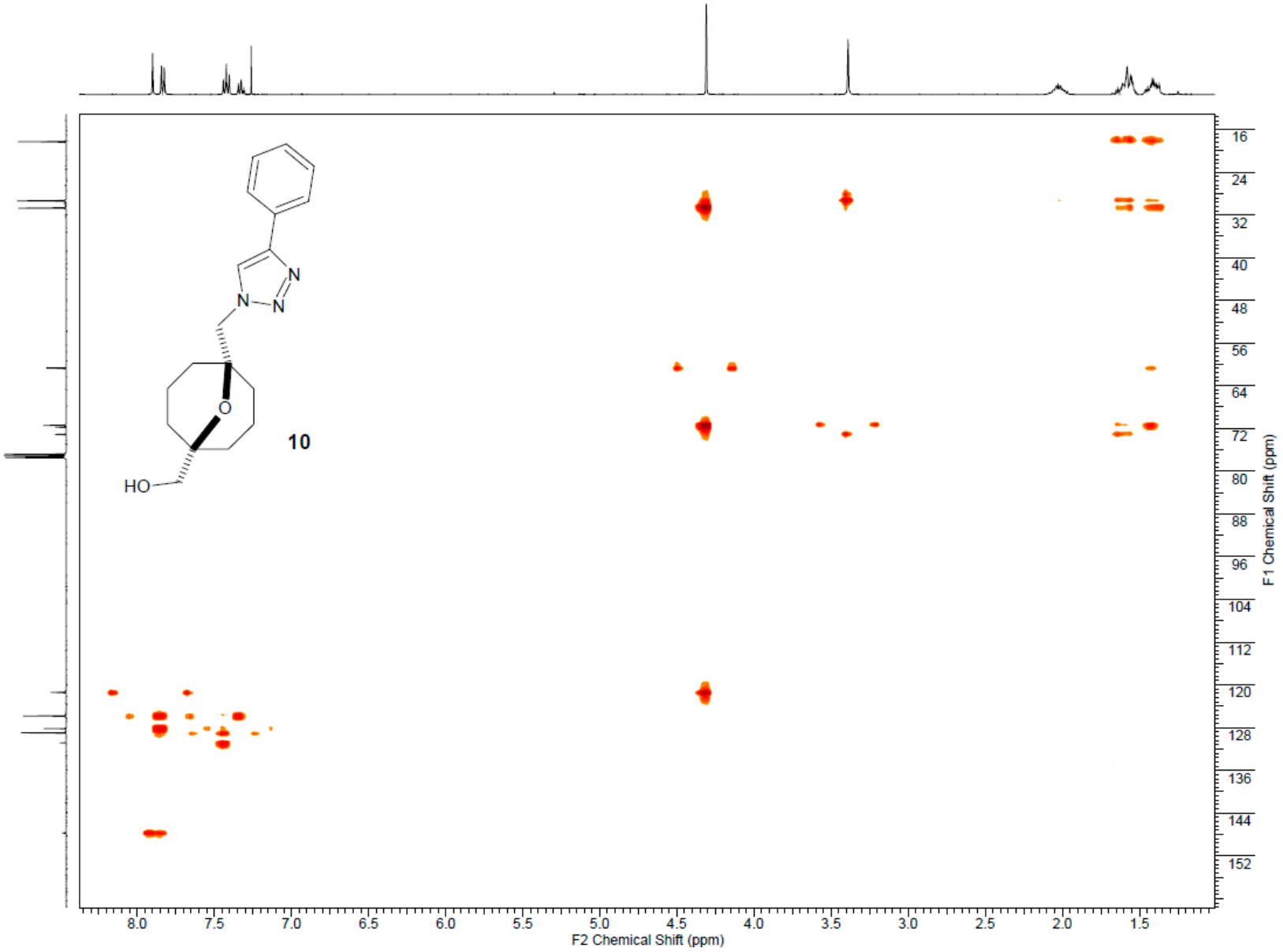
^{13}C NMR ($CDCl_3$) spectrum of compound **10**



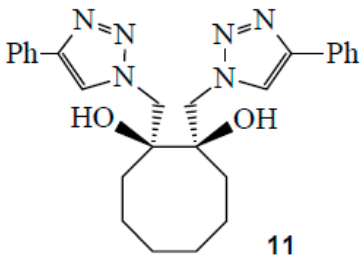
HSQC NMR ($CDCl_3$) spectrum of compound **10**



HMBC NMR ($CDCl_3$) spectrum of compound **10**

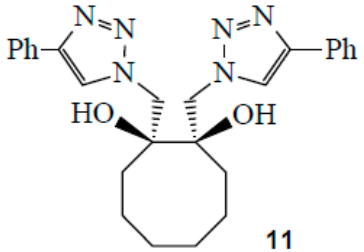


^{1}H NMR (d6-DMSO) spectrum of compound **11**



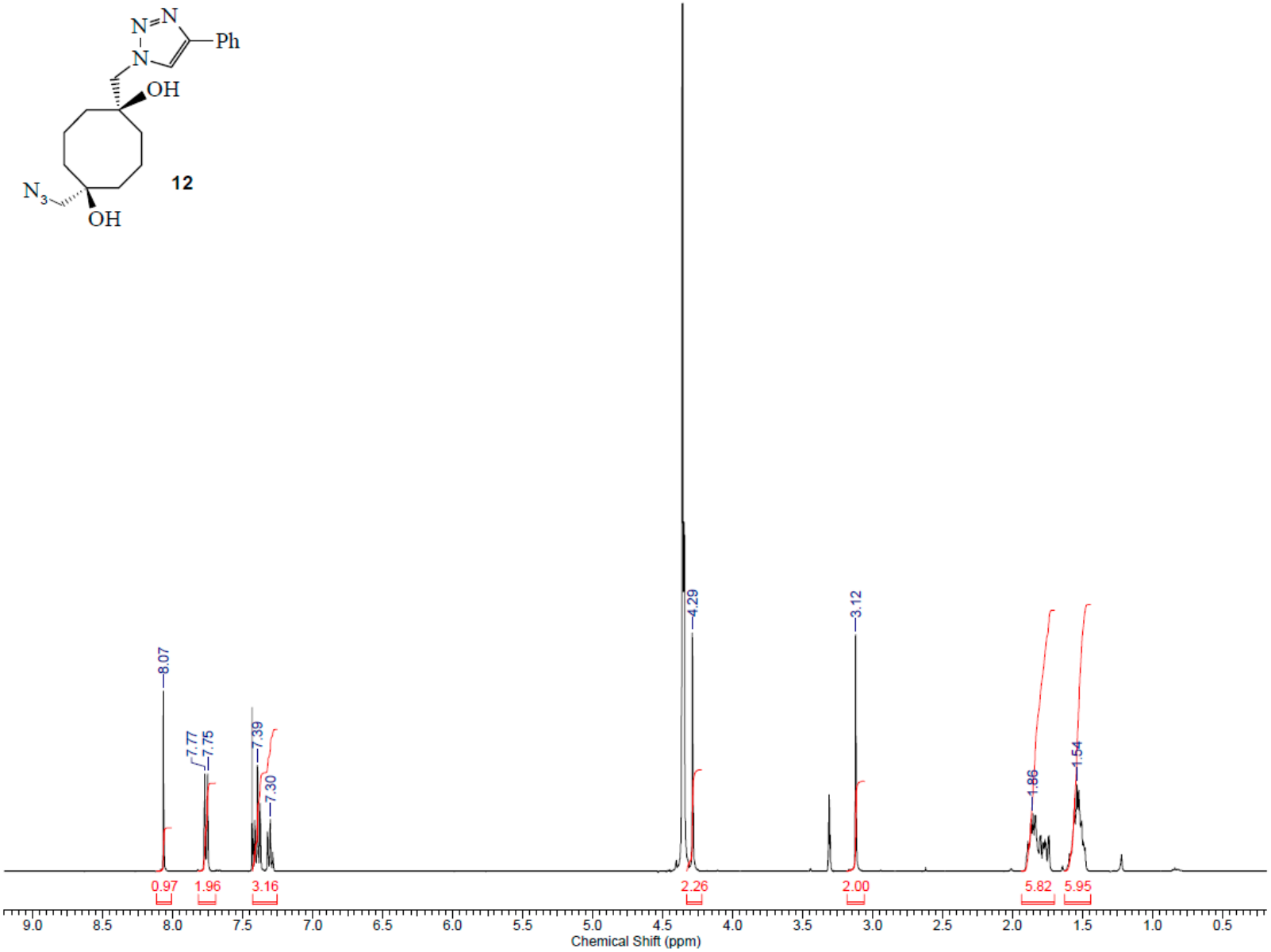
11

^{13}C NMR ($CDCl_3$+CD_3OD) spectrum of compound **11**

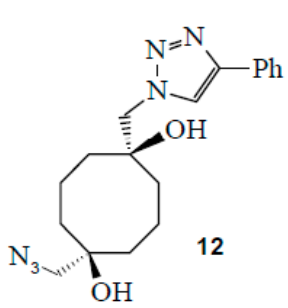


11

^{1}H NMR ($CDCl_3$+CD_3OD) spectrum of compound **12**

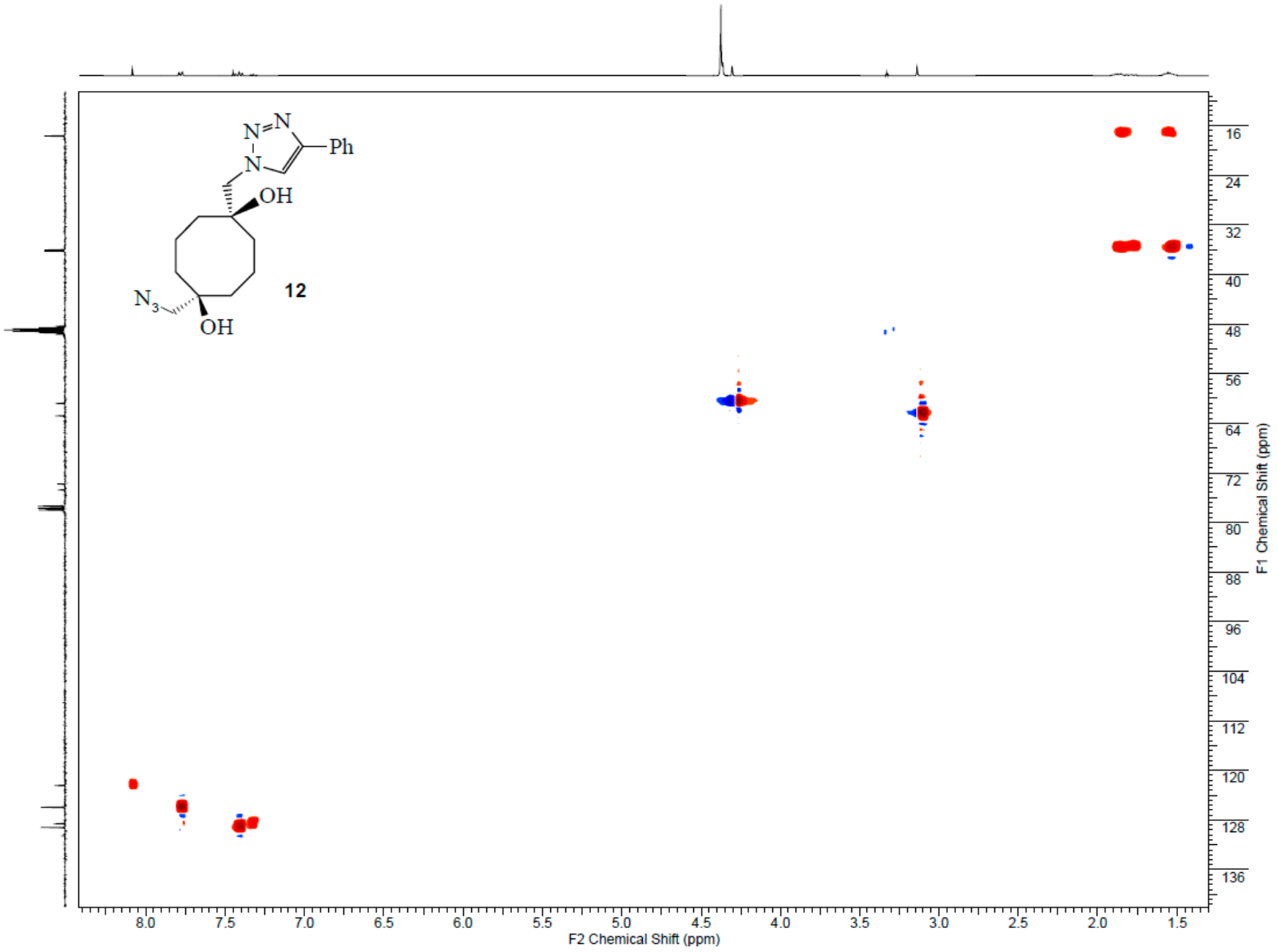


^{13}C NMR ($CDCl_3$+CD_3OD) spectrum of compound **12**

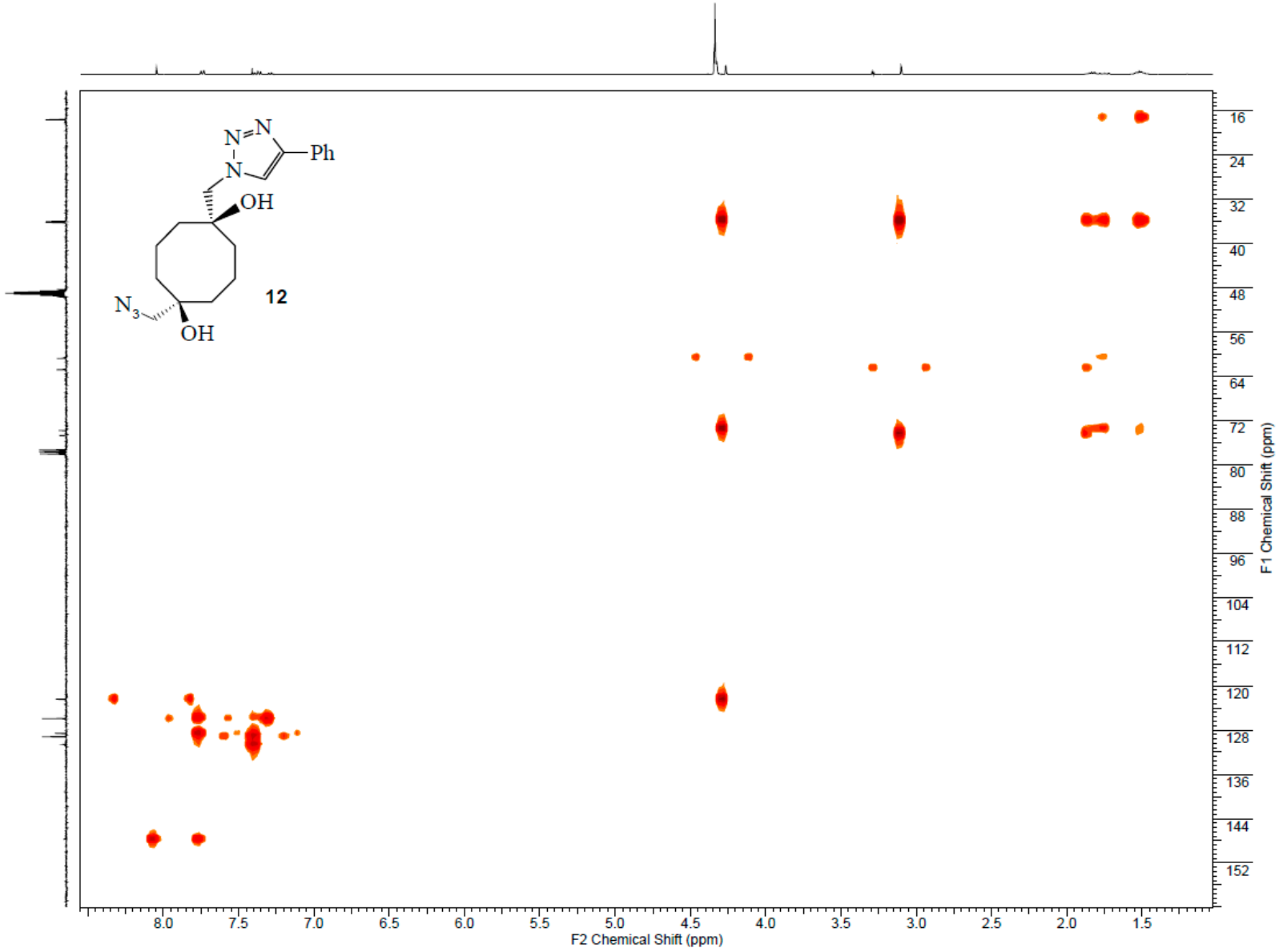


12

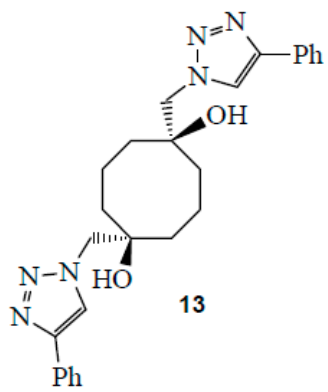
HSQC NMR ($CDCl_3$+CD_3OD) spectrum of compound **12**



HMBC NMR ($CDCl_3$+CD_3OD) spectrum of compound **12**

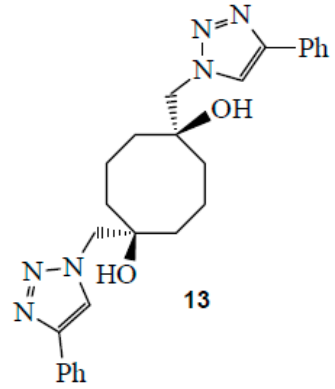


^{1}H NMR (d6-DMSO) spectrum of compound **13**



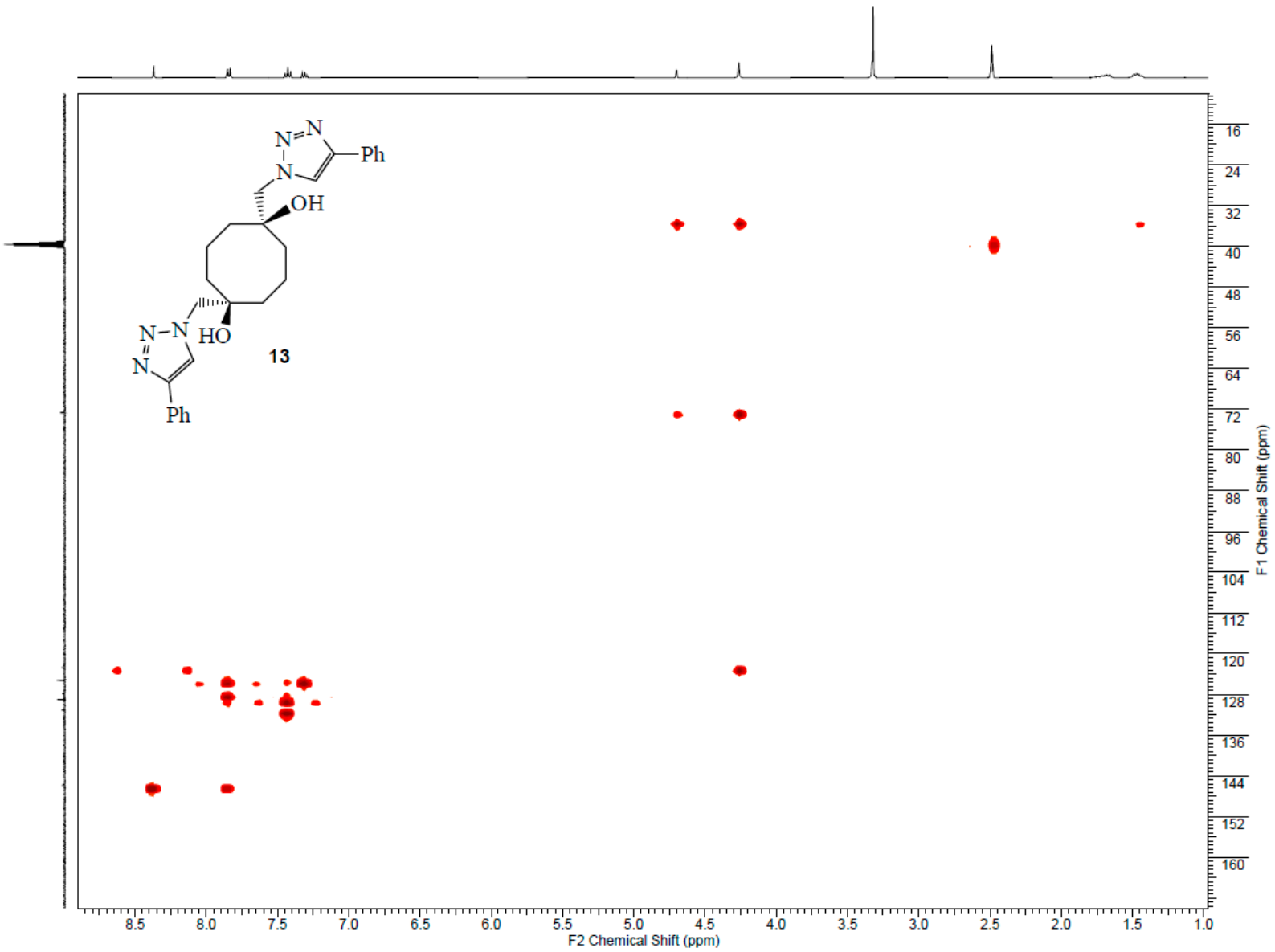
13

^{13}C NMR (d6-DMSO) spectrum of compound **13**

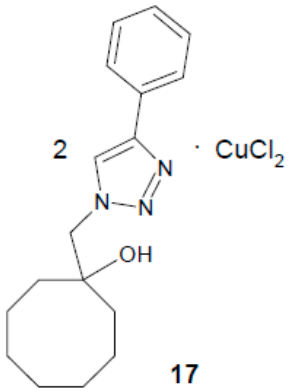


13

HMBC NMR (d6-DMSO) spectrum of compound **13**

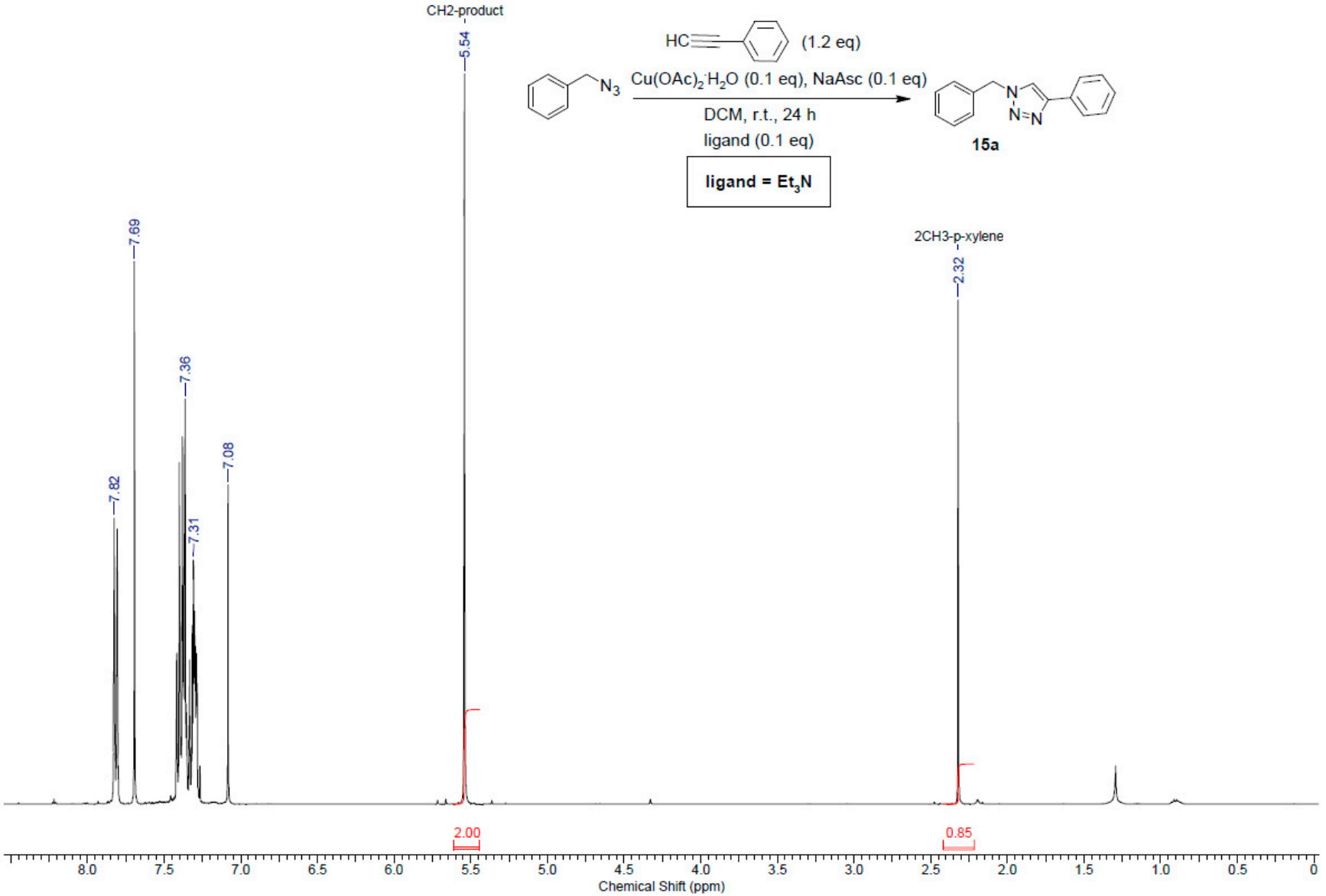


^{1}H NMR (CD_3OD) spectrum of compound **16**

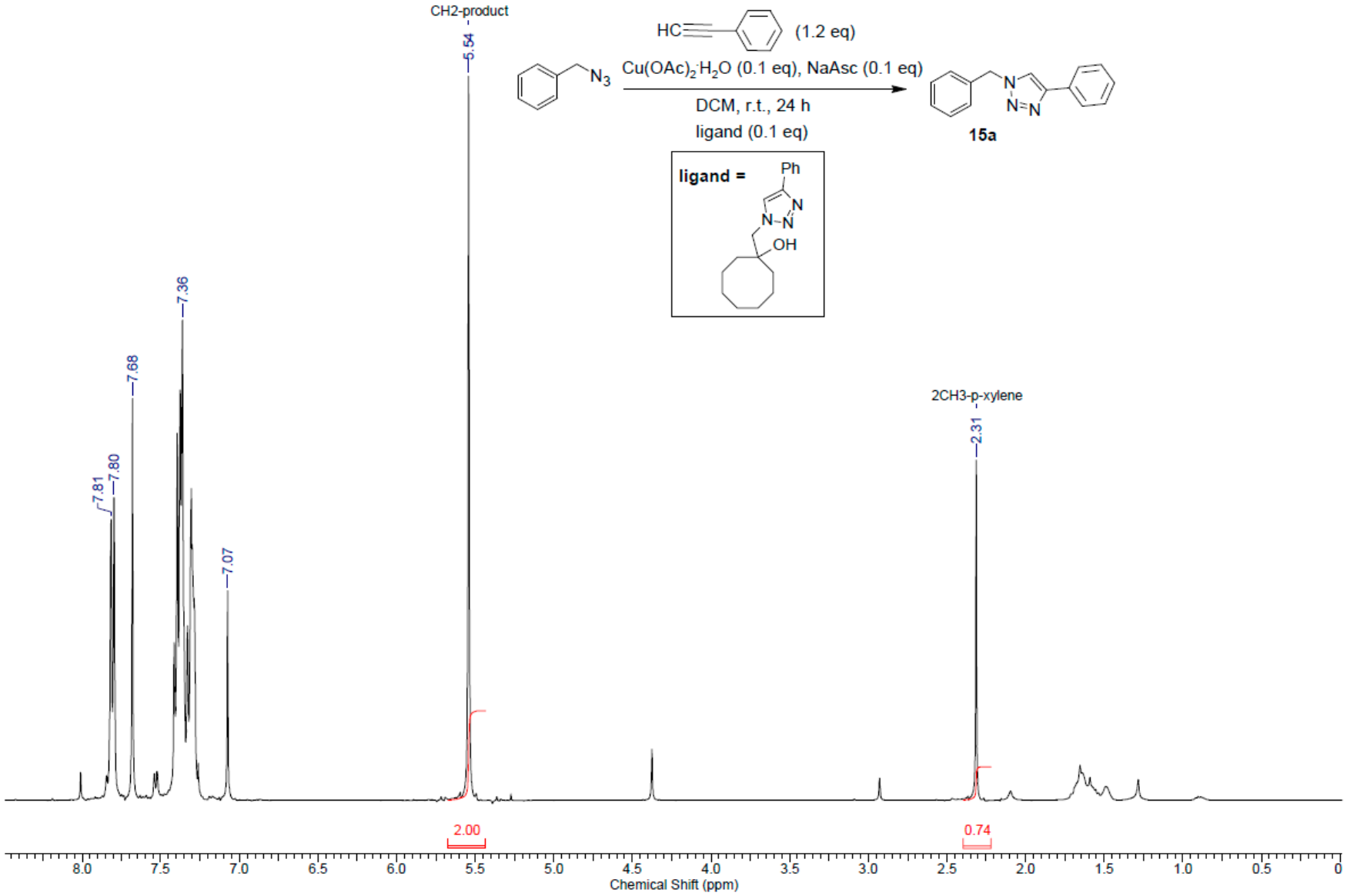


17

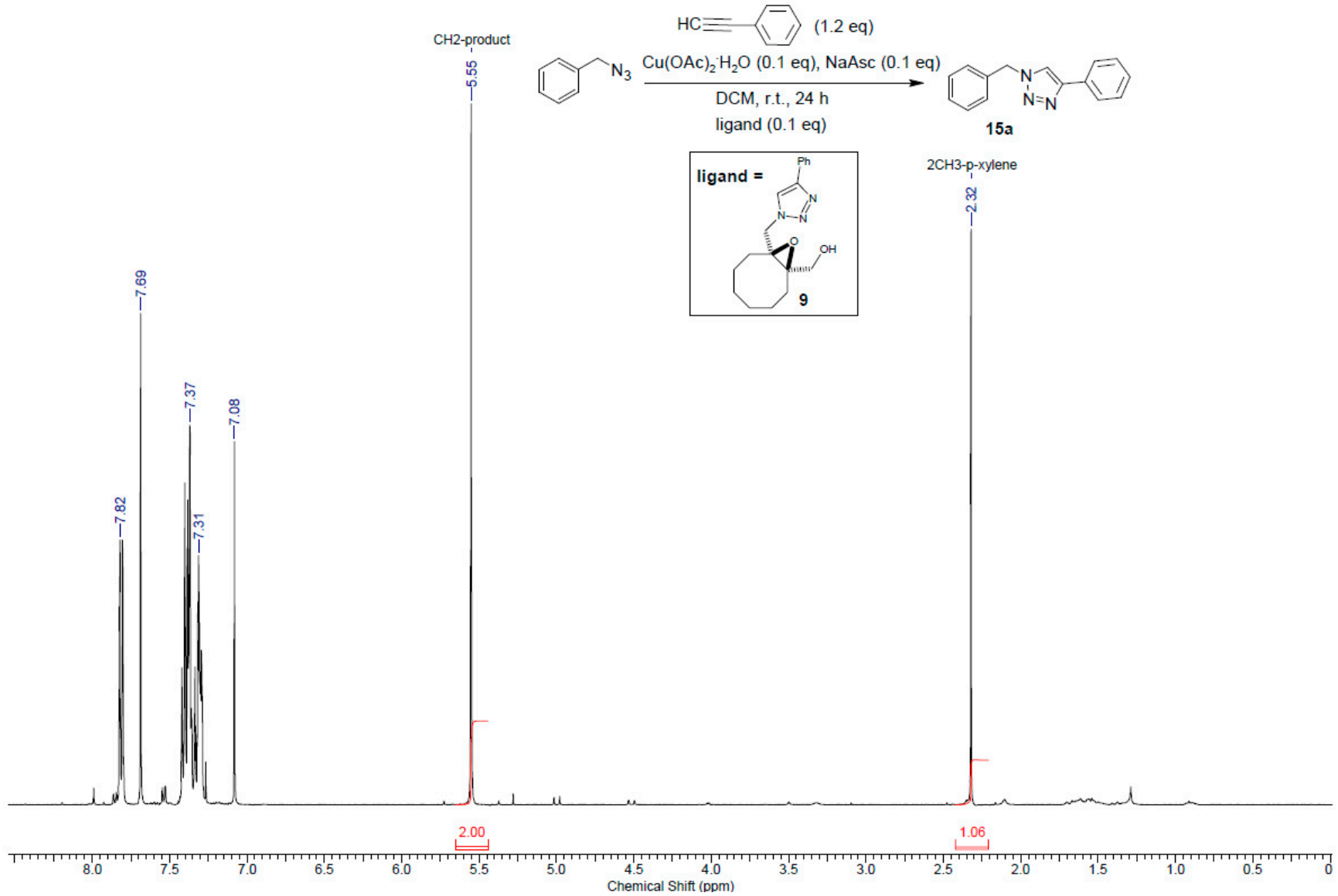
^{1}H NMR ($CDCl_3$) spectrum of reaction mixture

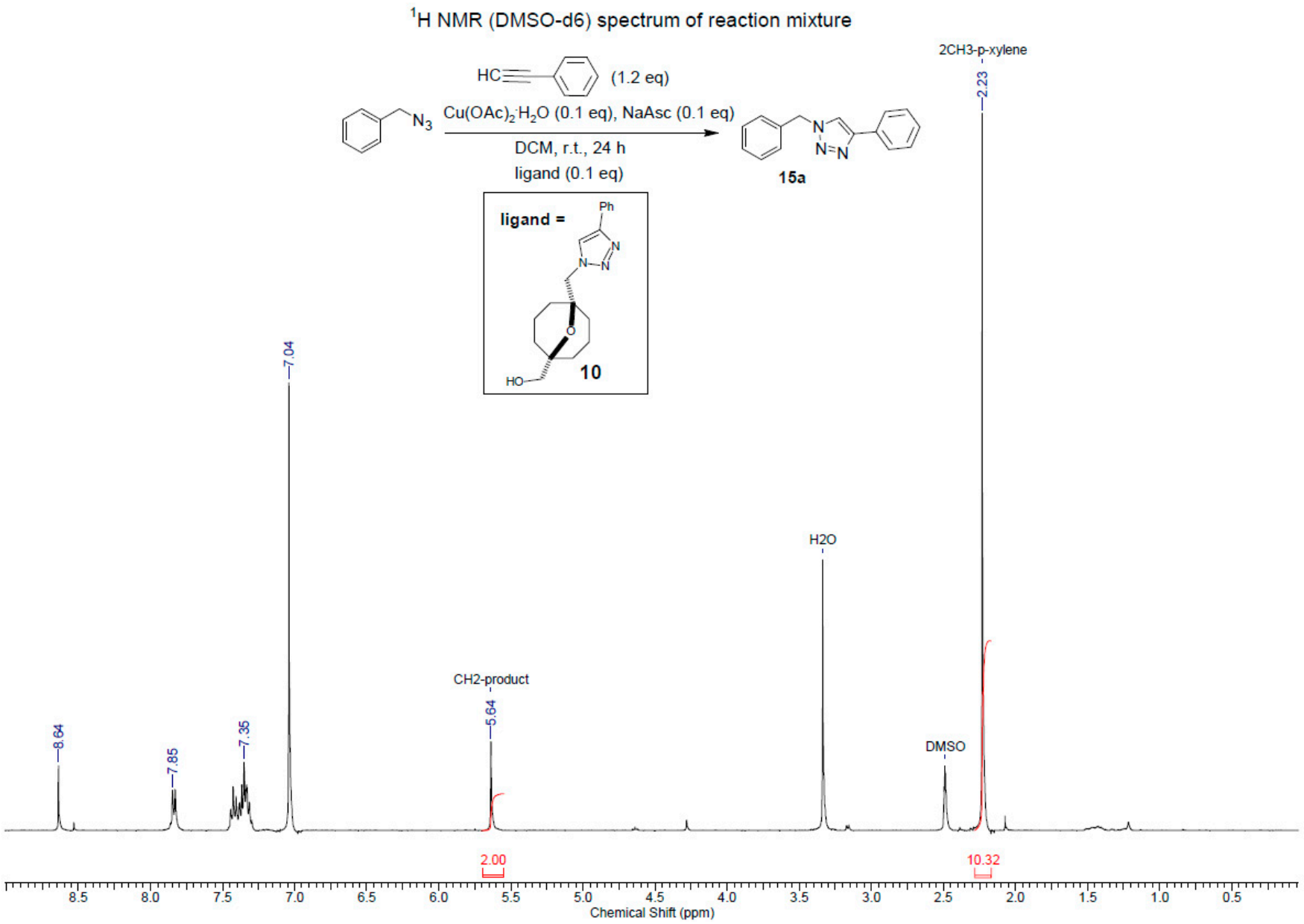


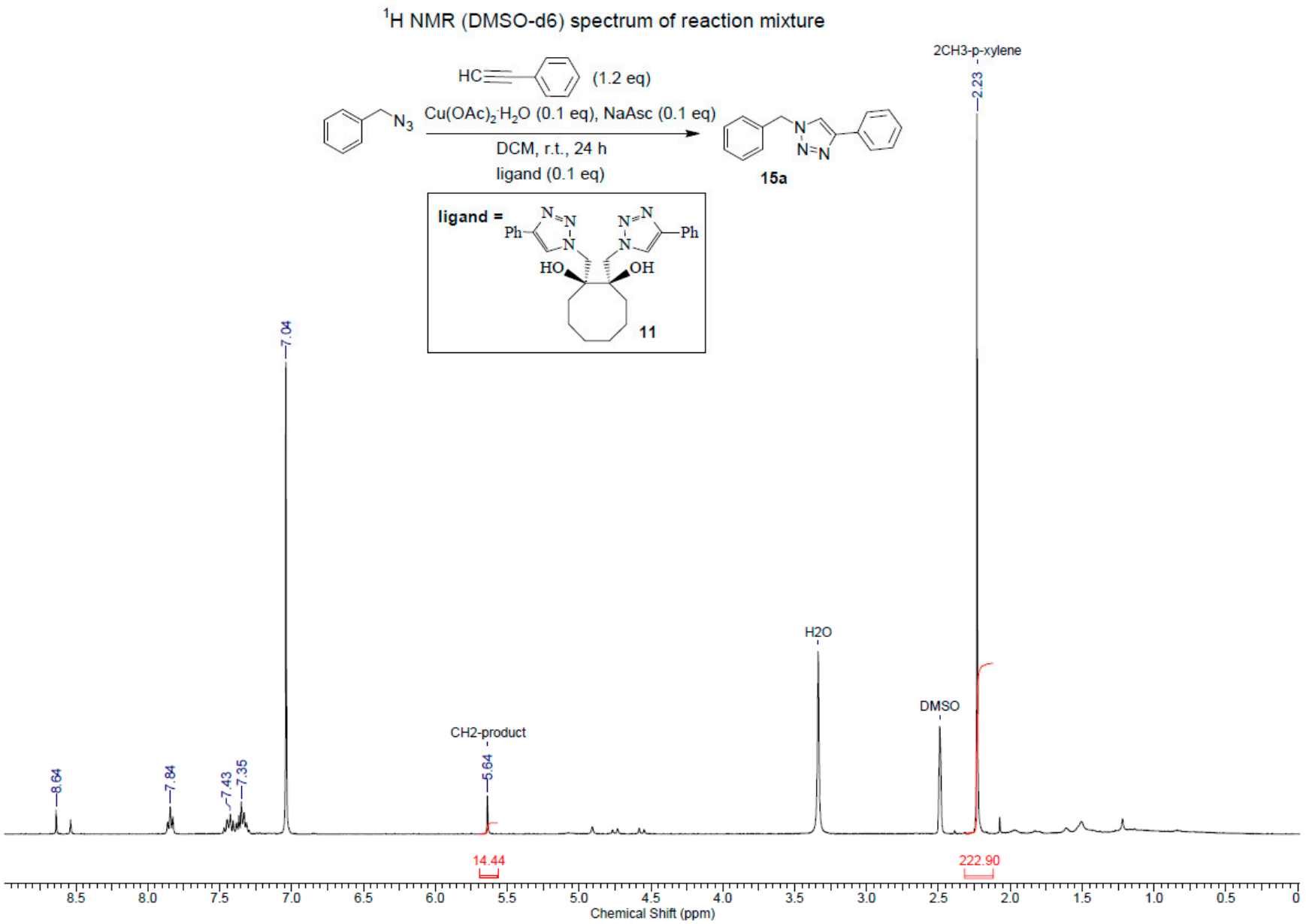
^{1}H NMR ($CDCl_3$) spectrum of reaction mixture



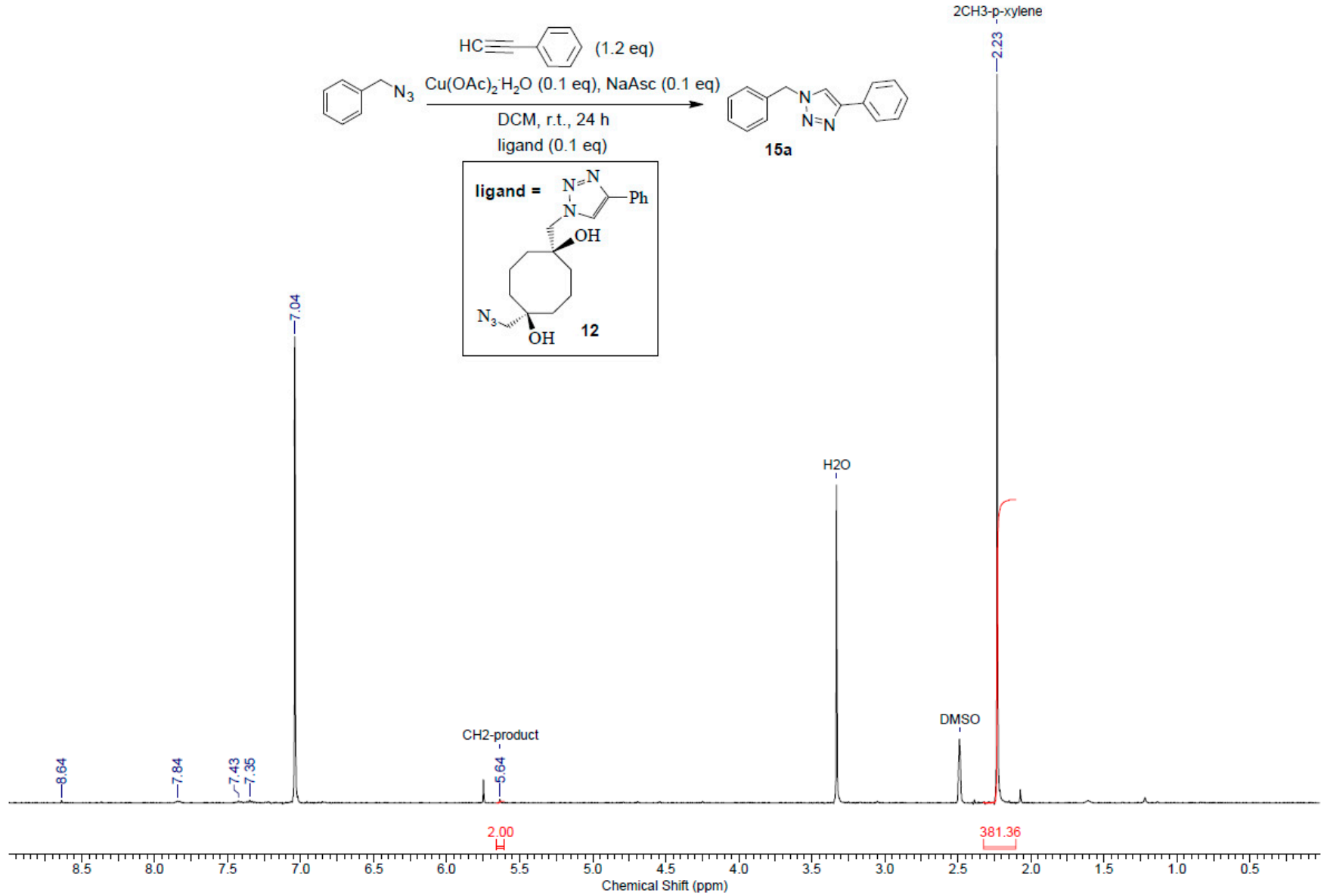
^{1}H NMR ($CDCl_3$) spectrum of reaction mixture



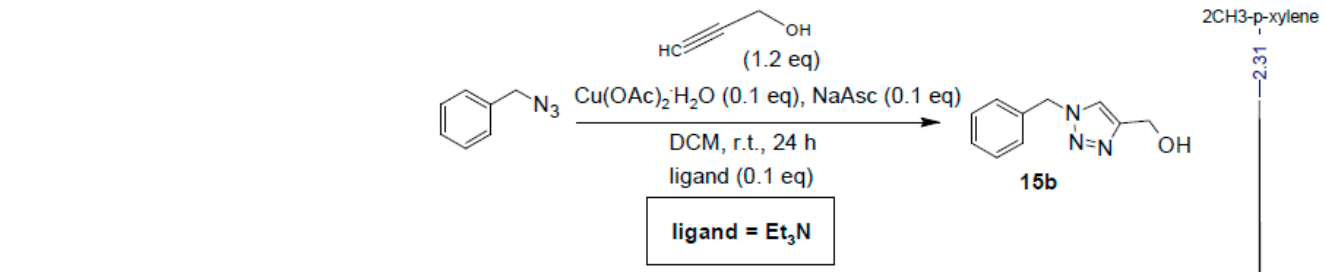

^{1}H NMR (DMSO-d6) spectrum of reaction mixture
HC≡ (1.2 eq)
N3
Cu(OAc)2·H2O (0.1 eq), NaAsc (0.1 eq)
DCM, r.t., 24 h
ligand (0.1 eq)
15a
ligand =
Ph
HO
10
2CH3-p-xylene
2.23
7.04
H2O
CH2-product
5.64
DMSO
8.64
7.85
7.35
2.00
10.32
Chemical Shift (ppm)


^{1}H NMR (DMSO-d6) spectrum of reaction mixture
HC≡ (1.2 eq)
$Cu(OAc)_2 \cdot H_2O$ (0.1 eq), NaAsc (0.1 eq)
DCM, r.t., 24 h
ligand (0.1 eq)
15a
ligand =
11
2CH3-p-xylene
2.23
7.04
H2O
DMSO
CH2-product
5.64
8.64
7.84
7.43
7.35
14.44
222.90
Chemical Shift (ppm)

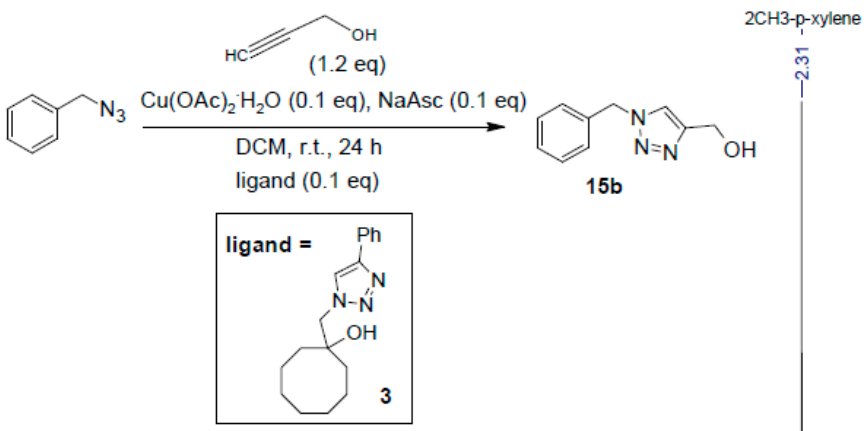
^{1}H NMR (DMSO-d6) spectrum of reaction mixture

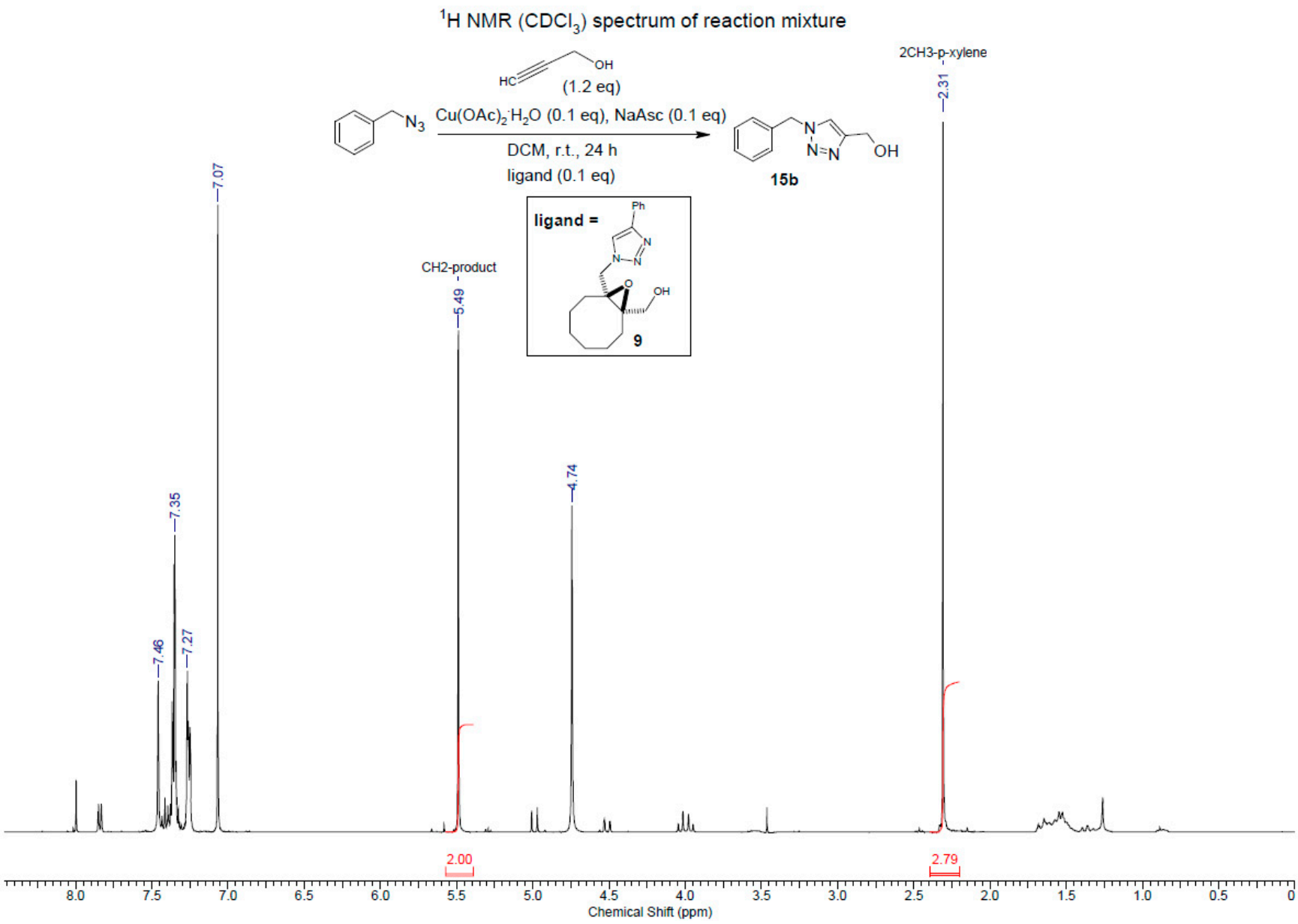


^{1}H NMR ($CDCl_3$) spectrum of reaction mixture

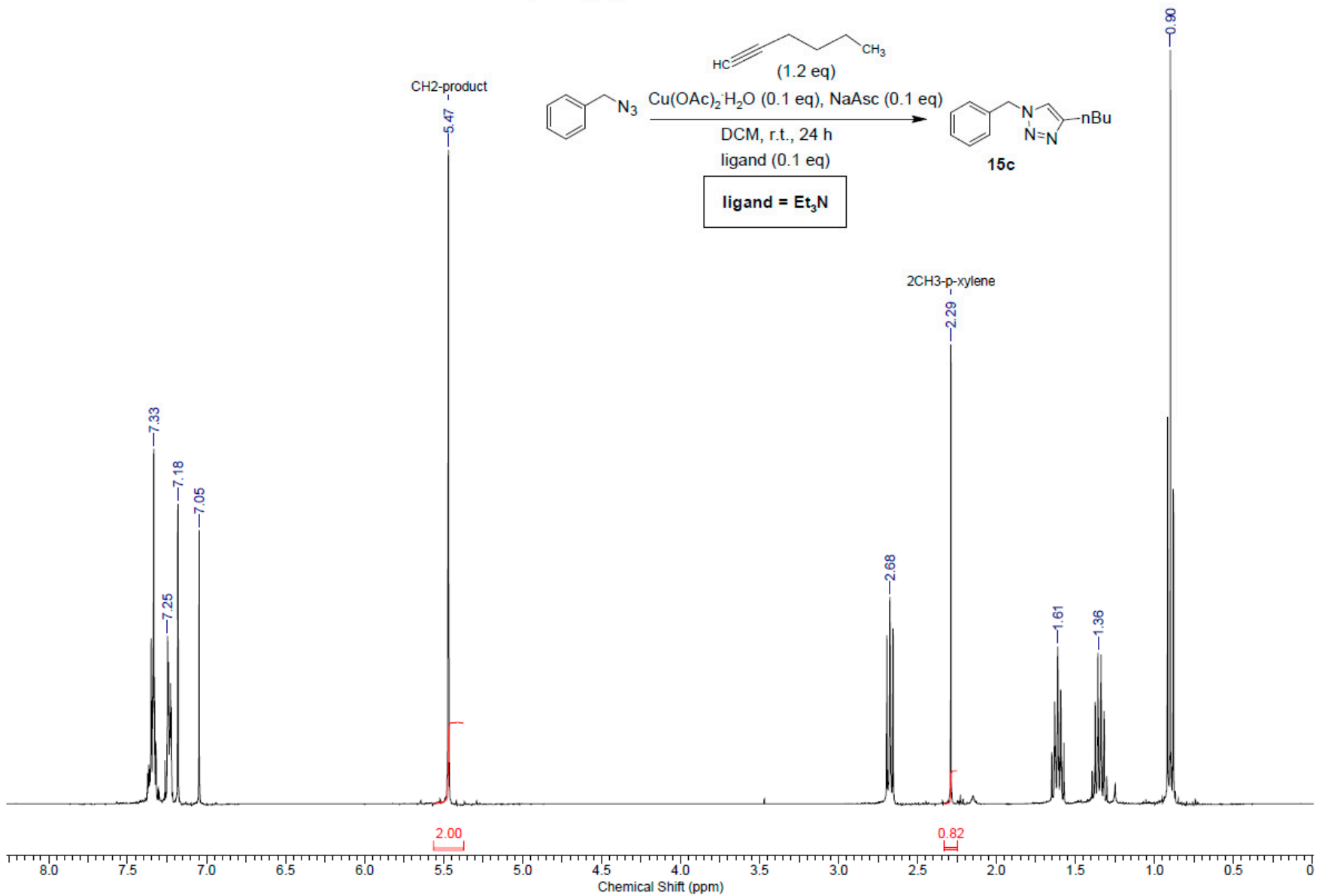


^{1}H NMR ($CDCl_3$) spectrum of reaction mixture

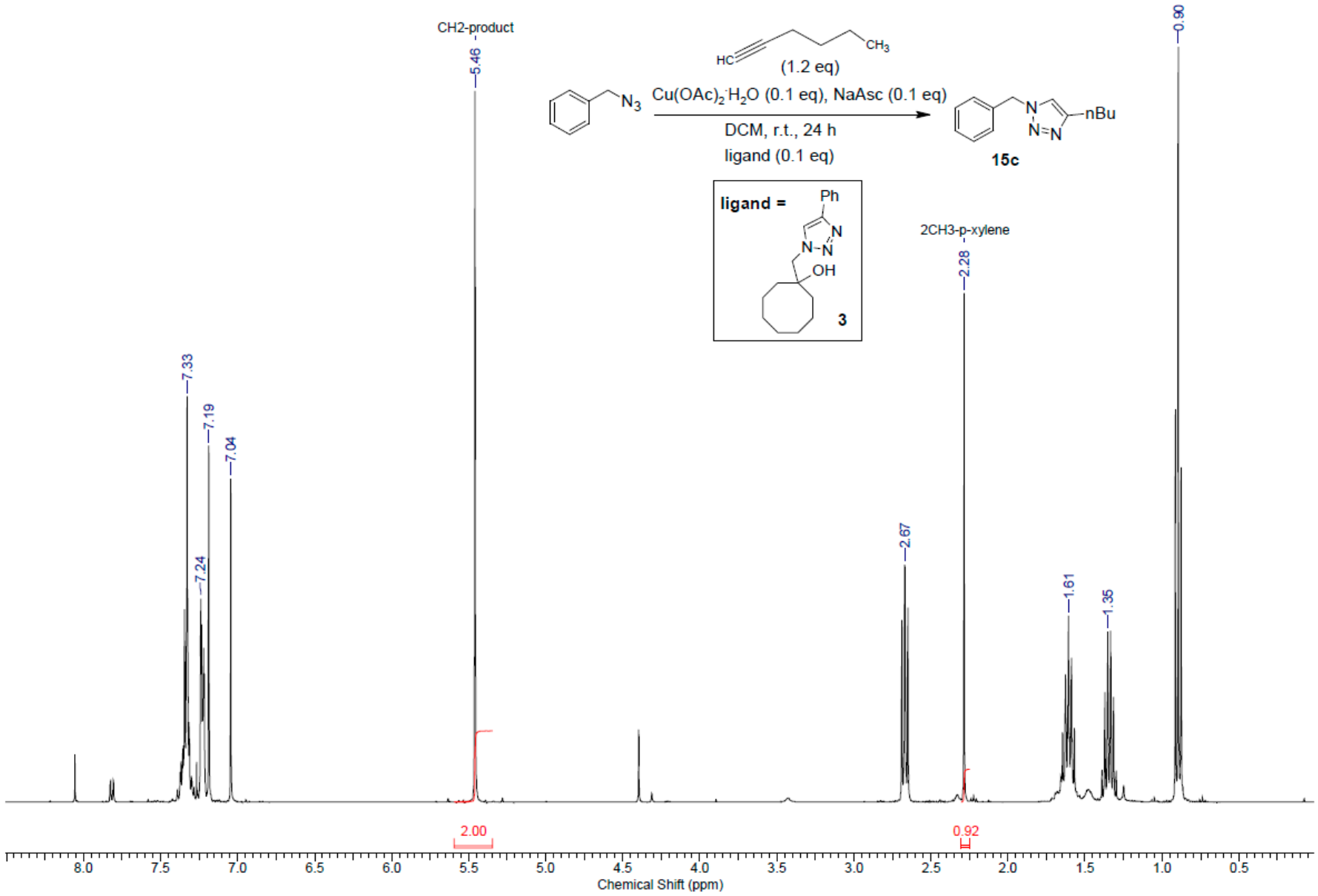


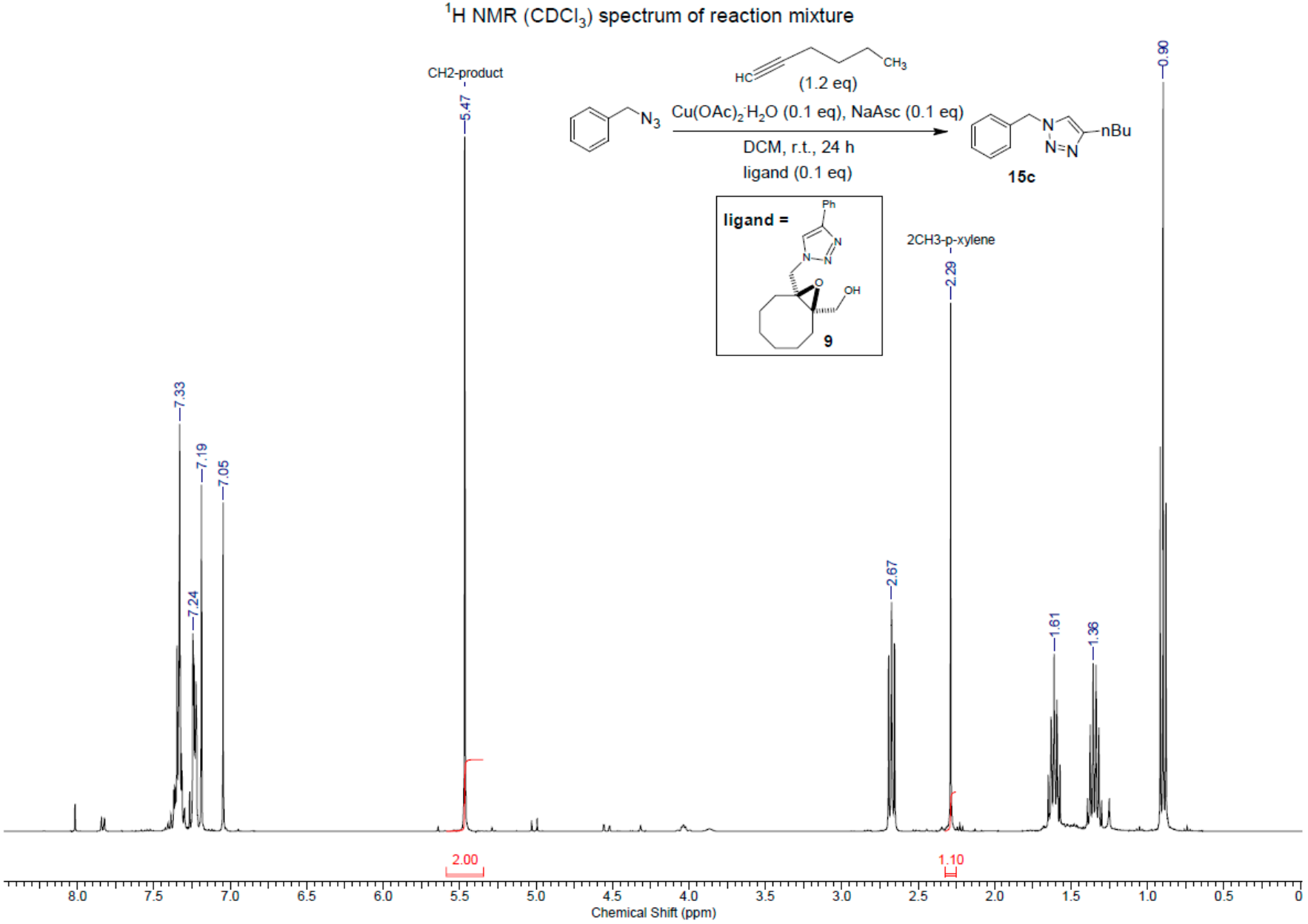

^{1}H NMR ($CDCl_3$) spectrum of reaction mixture
(1.2 eq)
$Cu(OAc)_2 \cdot H_2O$ (0.1 eq), NaAsc (0.1 eq)
DCM, r.t., 24 h
ligand (0.1 eq)
15b
ligand =
9
2CH3-p-xylene
2.31
CH2-product
5.49
4.74
7.07
7.35
7.46
7.27
2.00
2.79
Chemical Shift (ppm)

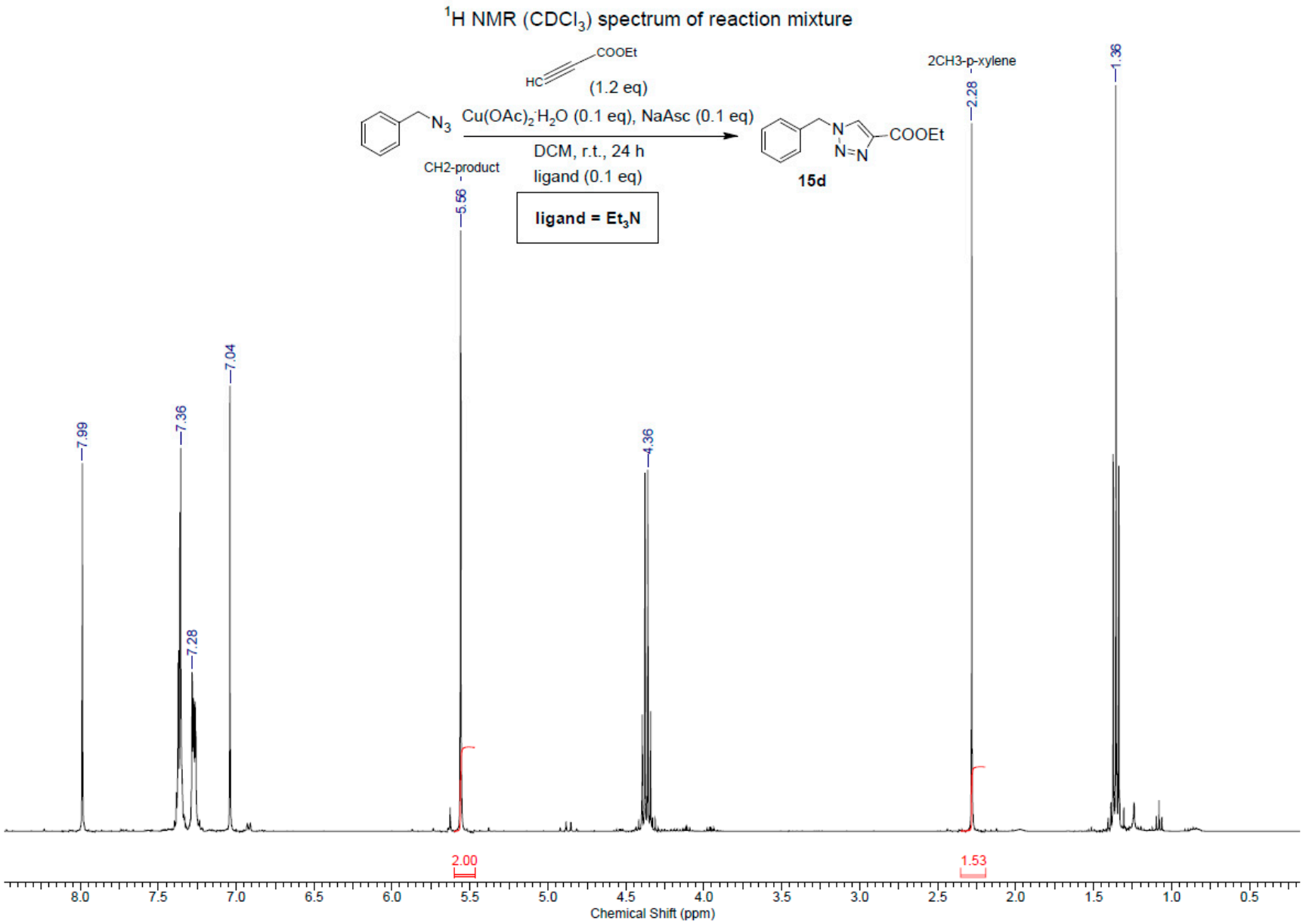
^{1}H NMR ($CDCl_3$) spectrum of reaction mixture

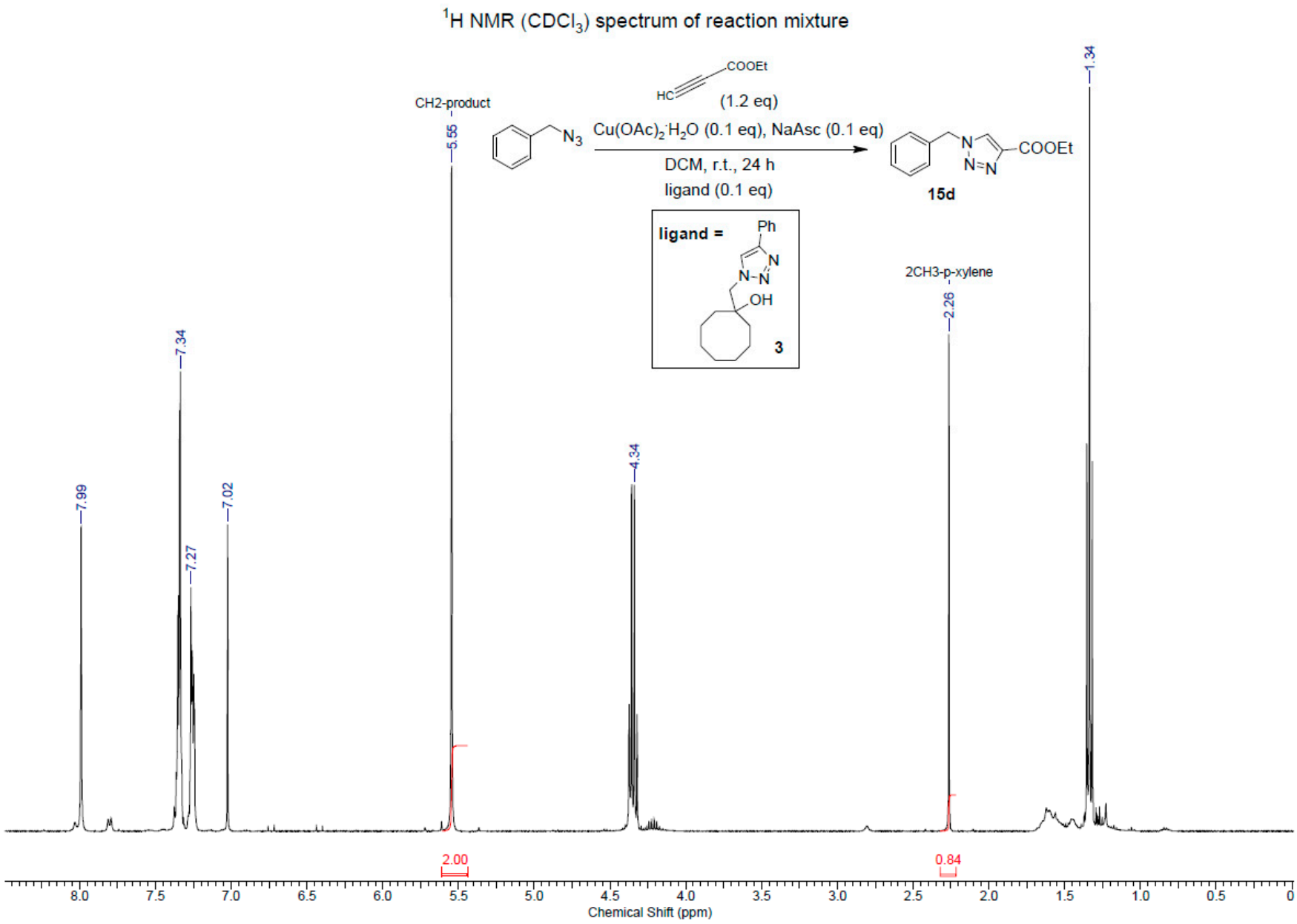


^{1}H NMR ($CDCl_3$) spectrum of reaction mixture

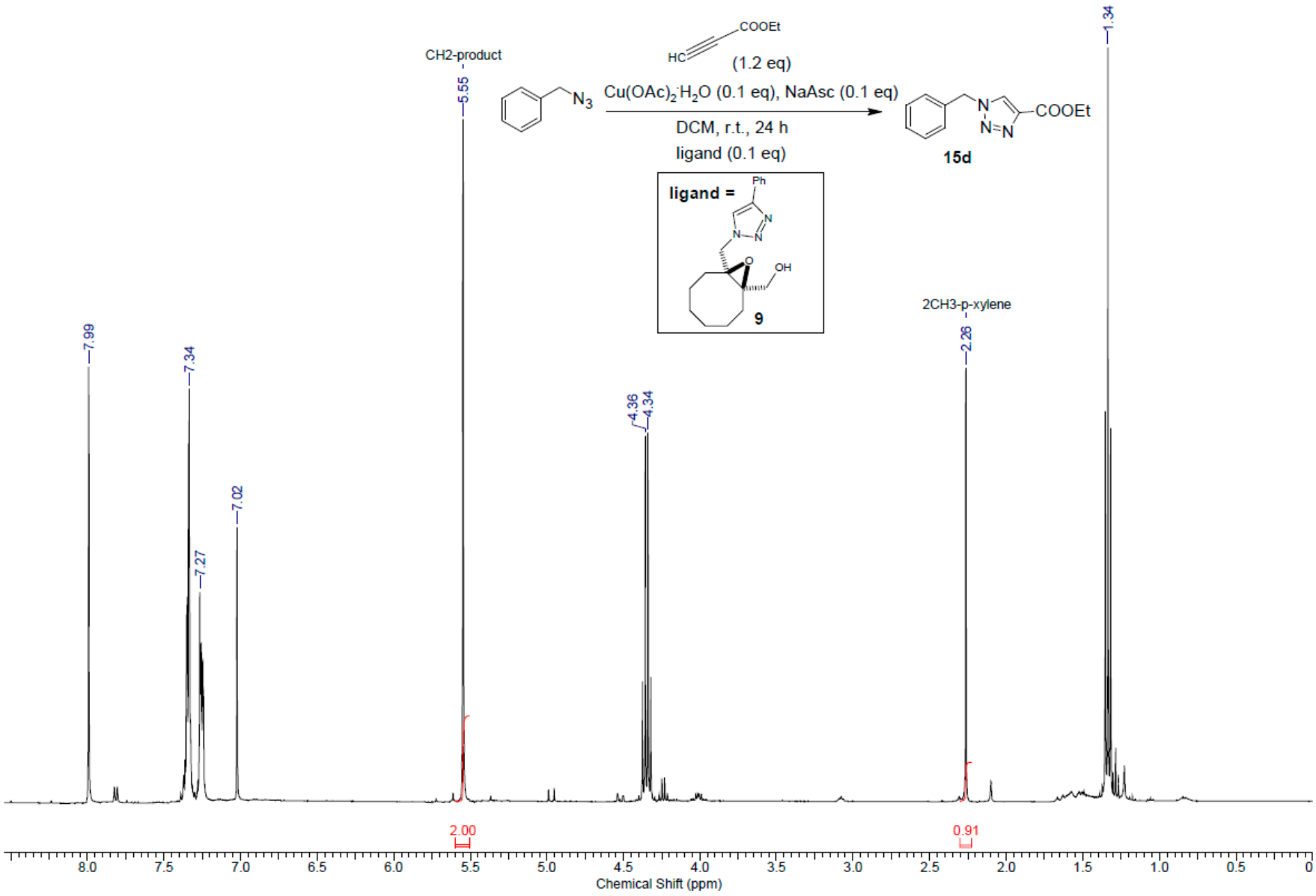



^{1}H NMR ($CDCl_3$) spectrum of reaction mixture
CH2-product
5.47
(1.2 eq)
$Cu(OAc)_2 \cdot H_2O$ (0.1 eq), NaAsc (0.1 eq)
DCM, r.t., 24 h
ligand (0.1 eq)
15c
ligand =
9
2CH3-p-xylene
2.29
0.90
7.33
7.19
7.24
7.05
2.67
1.61
1.36
2.00
1.10
Chemical Shift (ppm)

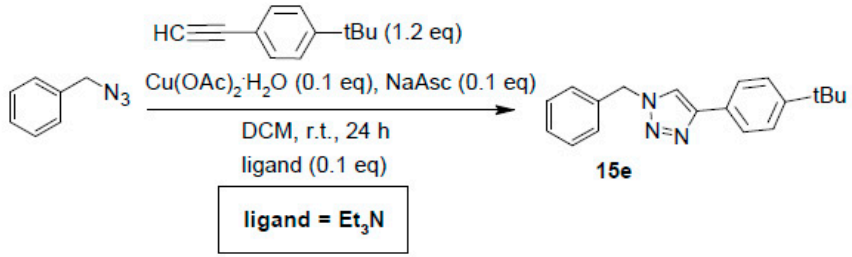

^{1}H NMR ($CDCl_3$) spectrum of reaction mixture
COOEt
HC
(1.2 eq)
N_3
$Cu(OAc)_2 \cdot H_2O$ (0.1 eq), NaAsc (0.1 eq)
DCM, r.t., 24 h
ligand (0.1 eq)
ligand = Et_3N
CH2-product
15d
2CH3-p-xylene
5.56
2.28
1.36
7.99
7.36
7.28
7.04
4.36
2.00
1.53
Chemical Shift (ppm)


^{1}H NMR ($CDCl_3$) spectrum of reaction mixture
COOEt
HC
(1.2 eq)
CH2-product
5.55
N_3
$Cu(OAc)_2 \cdot H_2O$ (0.1 eq), NaAsc (0.1 eq)
DCM, r.t., 24 h
ligand (0.1 eq)
COOEt
15d
1.34
ligand =
Ph
N
N-N
OH
3
2CH3-p-xylene
2.26
7.34
7.99
7.27
7.02
4.34
2.00
0.84
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

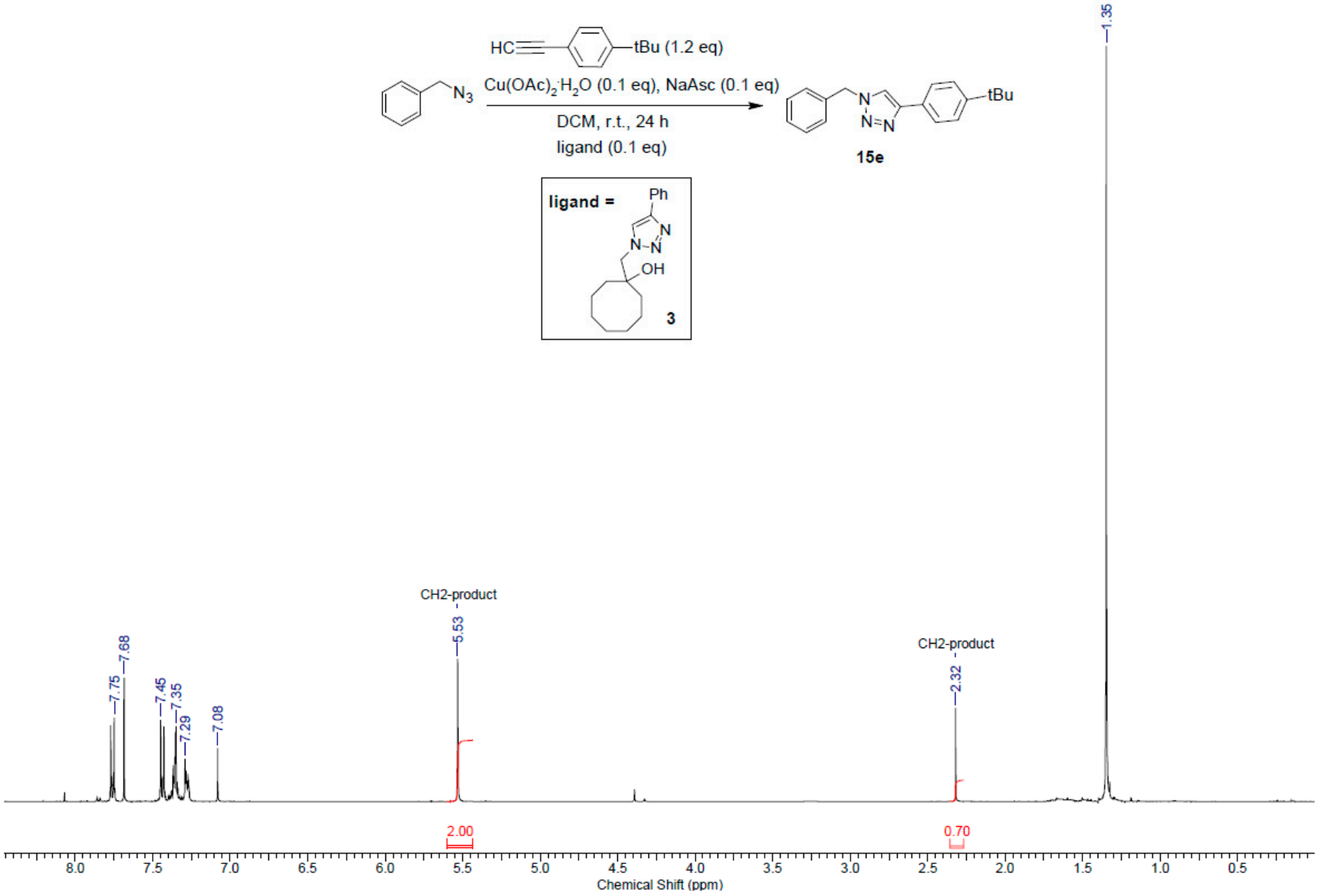
^{1}H NMR ($CDCl_3$) spectrum of reaction mixture



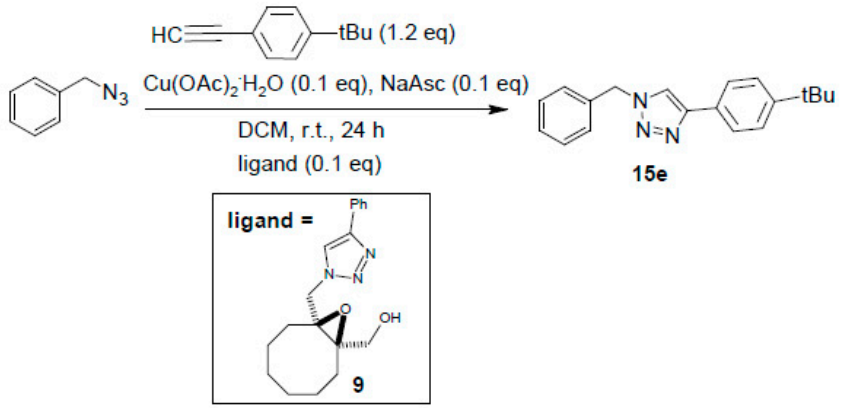
^{1}H NMR ($CDCl_3$) spectrum of reaction mixture



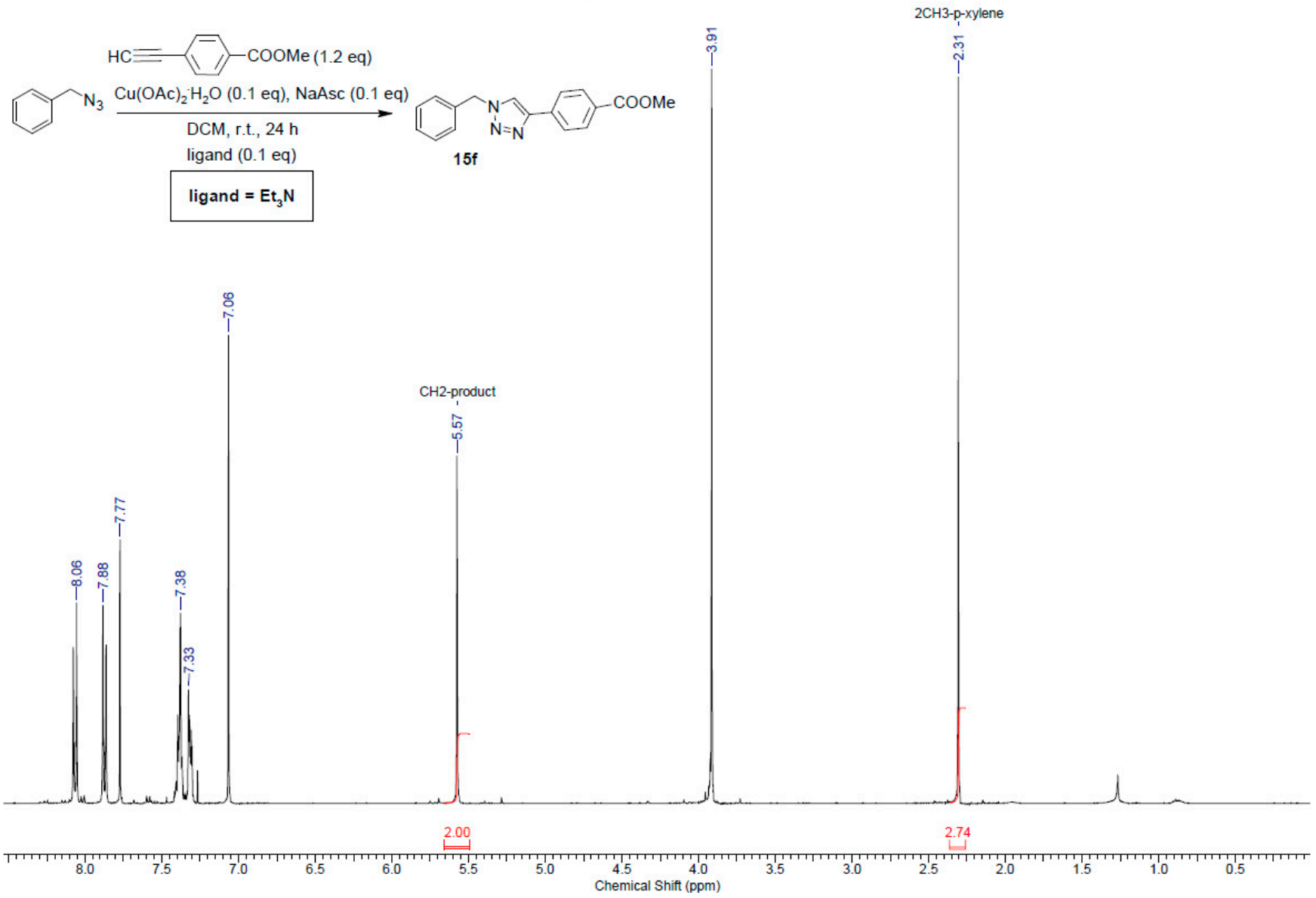
^{1}H NMR ($CDCl_3$) spectrum of reaction mixture



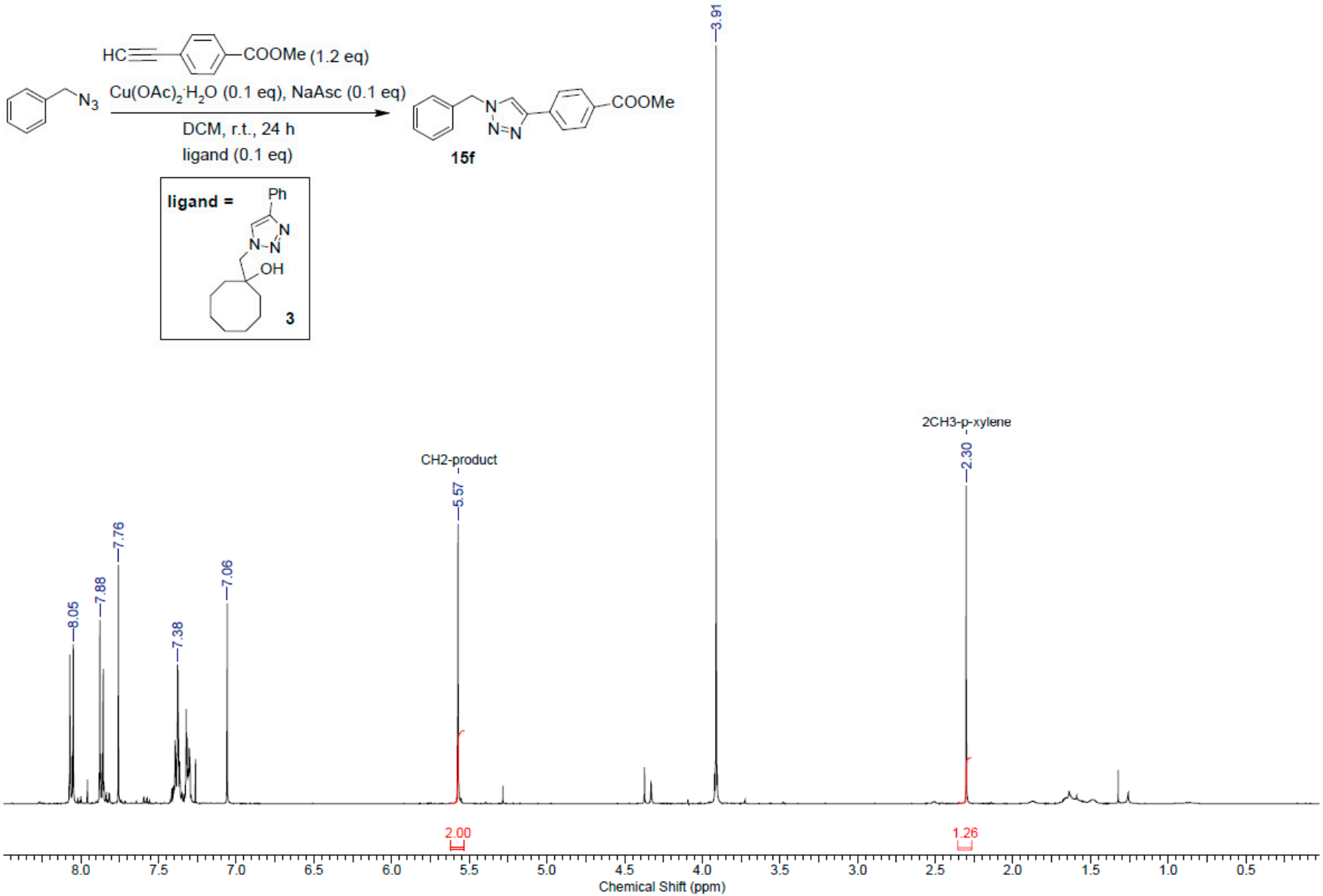
^{1}H NMR ($CDCl_3$) spectrum of reaction mixture



^{1}H NMR ($CDCl_3$) spectrum of reaction mixture



^{1}H NMR ($CDCl_3$) spectrum of reaction mixture



^{1}H NMR ($CDCl_3$) spectrum of reaction mixture

