Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

A multifunctional use of bis(methylene)bis(5-bromo-2-hydroxyl salicyloylhydrazone): From metals sensing to ambient catalysing A3 coupling reaction.

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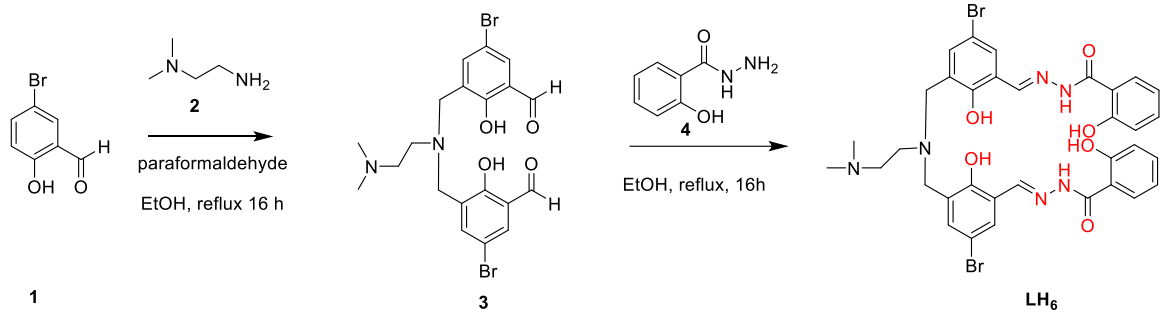
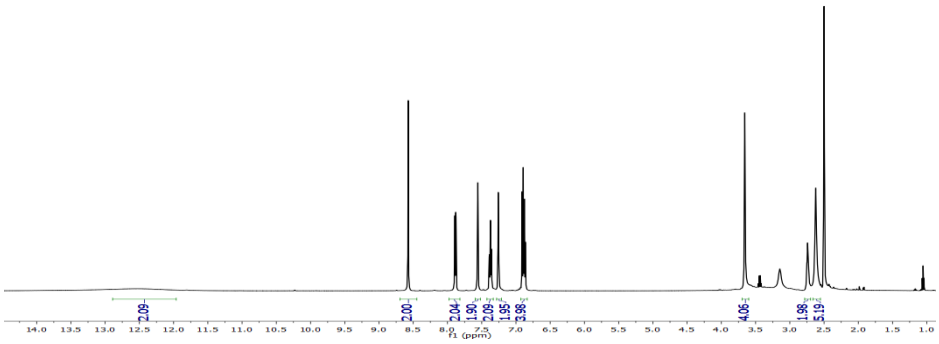
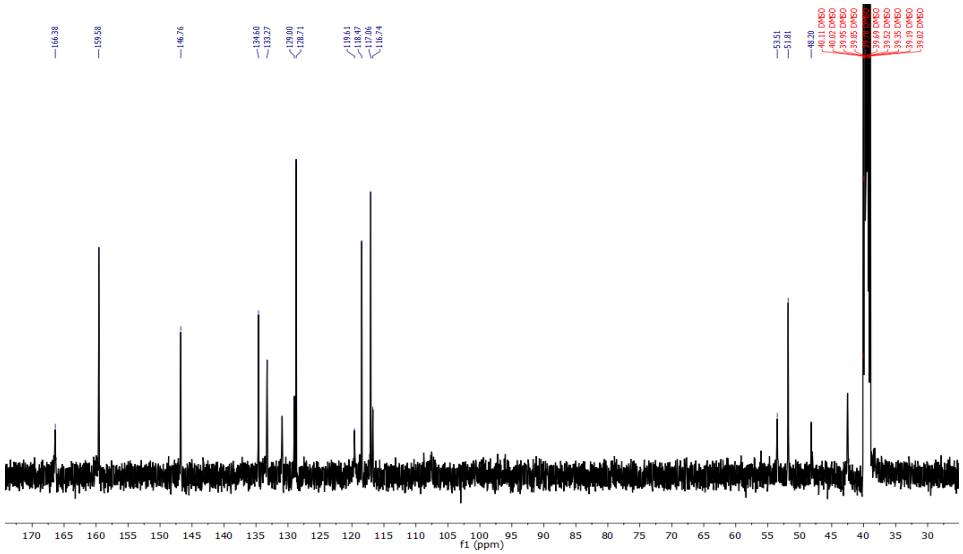
General considerations. All reagents and solvents were used as received from commercial supplies without further purification. IR spectra were obtained from Perkin Elmer Spectrum GX FT-IR System in the range of 400-4000 cm^{-1} in KBr pellets at room temperature. NMR spectra were collected on a Bruker Ultrashield plus 500 operating at 500 MHz. All chemical shifts are reported in parts per million and referenced to tetramethylsilane for ^{1}H. Single crystal X-ray diffraction (SCXD) data were collected at 180(2) K on a STADIVARI (Ga-Kα, λ = 1.34143 Å, detector: Dectris Eiger2 R 4M (detector type: HPC)) (STOE). Powder X-ray diffraction (PXRD) measurements were performed on a STOE STADI-P diffractometer with Cu-Kα radiation.

Preparation of ligand (LH_6)

5-bromosalicylaldehyde (**1**, 4.20 g, 20 mmol), *N*,*N*''-dimethylethylenediamine (**2**, 0.88 g, 10 mmol) and paraformaldehyde (1.2 g) refluxed in ethanol for 16 h. The corresponding intermediate (**3**) was obtained in 68 % yield after purification using column chromatography and it was further reacted with 2-hydroxybenzhydrazide (**4**, 3.48 g, 13.5 mmol) under reflux in ethanol for 16 h. The bis(methylene)bis(5-bromo-2-hydroxyl salicyloylhydrazone) (**H_6L**) was obtained as a yellow solid in 92 % yield after removal of ethanol and washed with Et_2O. ^{1}H NMR (500 MHz, DMSO-d_6) δ = 12.5 (brs, 2H), 8.57 (s, 2H), 7.89 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.56 (d, *J* = 2.6 Hz, 2H), 7.44 – 7.32 (m, 2H), 7.25 (d, *J* = 2.6 Hz, 2H), 6.99 – 6.81 (m, 4H), 3.65 (s, 4H), 3.14 (s, 2H), 2.73 (t, *J* = 6.0 Hz, 2H), 2.62 (s, 6H). ^{13}C NMR (126 MHz, DMSO-d6) δ = 166.8, 160.1, 147.2, 135.0, 133.7, 131.3, 129.4, 129.1, 120.0, 118.9, 117.5, 117.1, 108.2, 56.5, 54.0, 52.2, 48.6, 43.0, 19.0. IR (ATR): 3657-3239 (br), 3049 (w), 2844 (w), 1646 (m), 1602 (s), 1546 (s), 1460 (m), 1333 (s), 1240 (m), 1090 (m), 1045 (w), 1026 (w), 1007 (w), 936 (w), 896 (w), 753 (s). HRMS-TOF (m/z): mass cal. for $[C_{34}H_{34}Br_2N_6O_6+H]^+$ = 781.0979 m/z, mass found = 781.1063 m/z.


Br
OH
O
H
1
2
paraformaldehyde
EtOH, reflux 16 h
3
4
EtOH, reflux, 16h
LH6





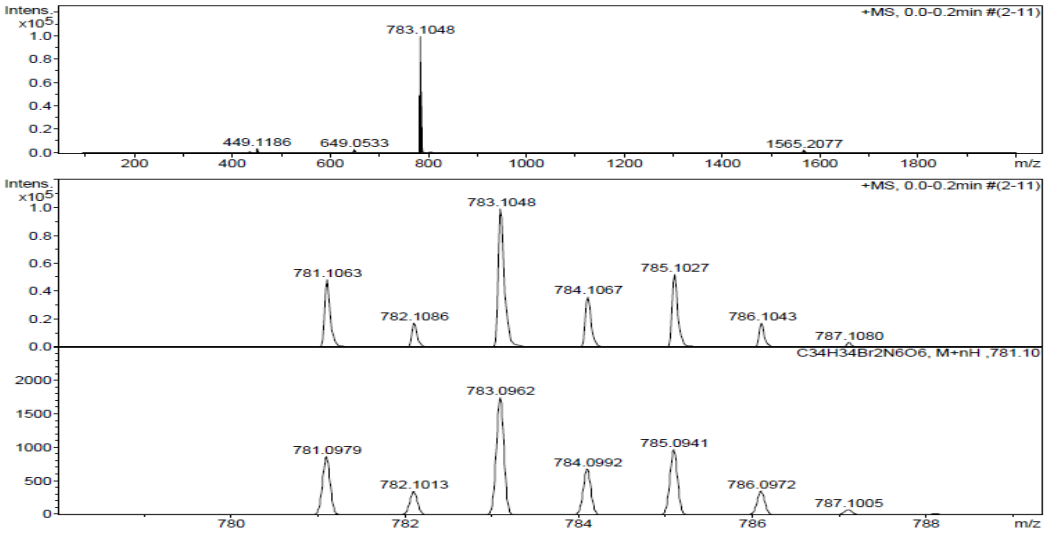
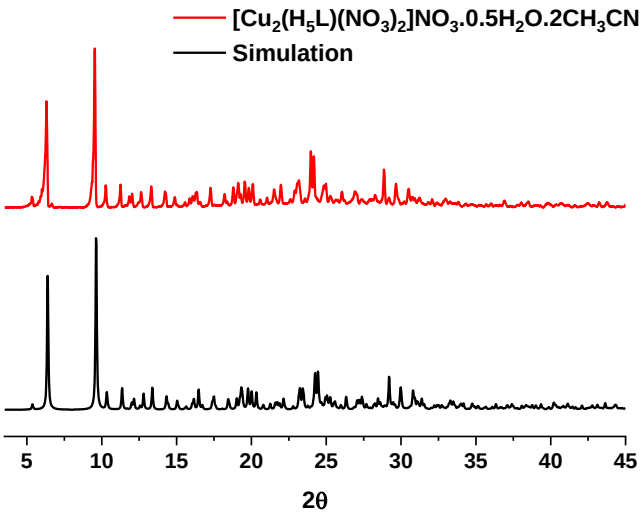


Figure S1. ^{1}H, ^{13}C NMR and mass spectra of **H_6L** (dissolved in *i*-PrOH).

Preparation of the copper(II)-complex; $[Cu_2(H_5L)(NO_3)_2]NO_3.0.5H_2O.2CH_3CN$

H_6L (78 mg, 0.1 mmol) was dissolved in 5 mL of a mixture of acetonitrile and methanol (1:1, %v/v) at room temperature. Then $Cu(NO_3)_2.2.5\ H_2O$ (56 mg, 2.0 mmol) was added to the solution and the reaction mixture was stirred at room temperature for 30 min. After standing for 7 days, crystals were collected by filtration (70 % yield). FT-IR (cm^{-1}) IR (ATR): 3601-2609 (br), 1613 (s), 1528 (s), 1488 (s), 1378 (s), 1280 (s), 1217 (s), 1157 (s), 1102 (m), 1039 (m), 912 (m), 754 (s).



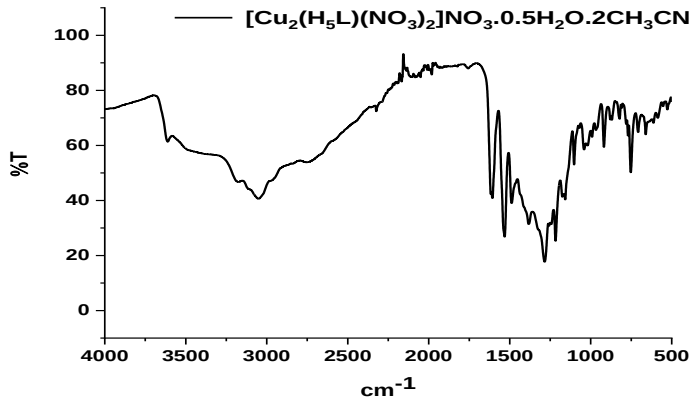


Figure S2. PXRD of $[Cu_2(H_5L)(NO_3)_2]NO_3.0.5H_2O.2CH_3CN$ comparison to the simulation pattern and IR spectrum.

Table S1. Crystal data and structure refinement for $[Cu_2(H_5L)(NO_3)_2]NO_3.0.5H_2O.2CH_3CN$

Compound	$[Cu_2(H_5L)(NO_3)_2]NO_3.0.5H_2O.2CH_3CN$
Empirical formula	$C_{38}H_{40}Br_2Cu_2N_{11}O_{11.5}$
Formula weight	1185.71
Temperature/K	180(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a [Å]	9.3905(4)
b [Å]	14.9547(6)
c [Å]	17.6271(6)
α [°]	109.496(3)
β [°]	94.616(3)
γ [°]	99.025(3)
Volume [Å^3]	2281.02(16)
Z	2
ρ_{calc}g [cm^3]	1.726
μ [mm^{-1}]	6.914
F(000)	1194
Crystal size [mm^3]	0.14 × 0.03 × 0.02
Radiation	GaKα (λ = 1.34143)
2Θ range for data collection [°]	8.38 to 116.208
Index ranges	-11 ≤ h ≤ 11, -6 ≤ k ≤ 18, -22 ≤ l ≤ 20
Reflections collected	23734
Independent reflections	9418 [R_{int} = 0.0343, R_{sigma} = 0.0427]
Data/restraints/parameters	9418/18/664

Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0426, wR_2 = 0.1056
Final R indexes [all data]	R_1 = 0.0662, wR_2 = 0.1150
Largest diff. peak/hole [e $Å^{-3}$]	0.82/-0.69

Bond Lengths						
Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
Br1	C13	1.901(4)		N6	C28	1.317(4)
Br2	C25	1.895(3)		C1	C2	1.395(6)
Cu1	O2	1.964(2)		C1	C6	1.407(5)
Cu1	O3	1.893(2)		C2	C3	1.374(7)
Cu1	O7	1.987(2)		C3	C4	1.380(7)
Cu1	O10A	2.339(4)		C4	C5	1.373(6)
Cu1	O11B	2.393(15)		C5	C6	1.396(6)
Cu1	N2	1.931(3)		C6	C7	1.473(5)
Cu2	O4	1.889(2)		C8	C9	1.448(5)
Cu2	O5	1.926(3)		C9	C10	1.426(5)
Cu2	O7	1.999(2)		C9	C14	1.393(5)
Cu2	O10A	2.595(4)		C10	C11	1.415(5)
Cu2	O10B	2.582(13)		C11	C12	1.376(5)
Cu2	N5	1.910(3)		C11	C15	1.507(4)
O1	C1	1.347(5)		C12	C13	1.396(5)
O2	C7	1.260(4)		C13	C14	1.357(5)
O3	C10	1.316(4)		C16	C17	1.512(5)
O4	C22	1.320(4)		C20	C21	1.499(5)
O5	C28	1.295(4)		C21	C22	1.420(5)
O6	C30	1.342(5)		C21	C26	1.373(5)
O7	N7	1.313(4)		C22	C23	1.425(5)
O8	N7	1.223(4)		C23	C24	1.402(5)
O9	N7	1.220(4)		C23	C27	1.436(5)
O10A	N8	1.243(5)		C24	C25	1.369(6)
O10B	N8	1.260(12)		C25	C26	1.397(5)
O11A	N8	1.311(5)		C28	C29	1.484(5)
O11B	N8	1.114(13)		C29	C30	1.411(5)
O12A	N8	1.192(5)		C29	C34	1.392(5)
O12B	N8	1.35(2)		C30	C31	1.392(6)
N1	N2	1.387(4)		C31	C32	1.375(6)
N1	C7	1.337(5)		C32	C33	1.387(6)

N2	C8	1.284(5)		C33	C34	1.378(6)
N3	C15	1.513(4)		O13	N9	1.268(5)
N3	C16	1.495(4)		O14	N9	1.234(4)
N3	C20	1.512(4)		O15	N9	1.217(5)
N4	C17	1.487(5)		N10	C35	1.129(5)
N4	C18	1.503(5)		C35	C36	1.457(6)
N4	C19	1.482(6)		N11	C37	1.162(9)
N5	N6	1.377(4)		C37	C38	1.447(10)
N5	C27	1.284(4)				

Bond Angles

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
O2	Cu1	O7	92.51(10)		O1	C1	C6	118.0(3)
O2	Cu1	O10A	90.37(12)		C2	C1	C6	119.7(4)
O2	Cu1	O11B	94.4(4)		C3	C2	C1	119.9(4)
O3	Cu1	O2	171.62(10)		C2	C3	C4	121.4(4)
O3	Cu1	O7	91.77(10)		C5	C4	C3	118.8(4)
O3	Cu1	O10A	97.77(12)		C4	C5	C6	122.0(4)
O3	Cu1	O11B	91.1(4)		C1	C6	C7	123.4(4)
O3	Cu1	N2	93.76(11)		C5	C6	C1	118.1(3)
O7	Cu1	O10A	73.06(11)		C5	C6	C7	118.4(3)
O7	Cu1	O11B	108.5(3)		O2	C7	N1	119.1(3)
N2	Cu1	O2	81.34(11)		O2	C7	C6	119.8(3)
N2	Cu1	O7	172.32(11)		N1	C7	C6	121.1(3)
N2	Cu1	O10A	111.38(12)		N2	C8	C9	122.6(3)
N2	Cu1	O11B	76.7(3)		C10	C9	C8	123.2(3)
O4	Cu2	O5	176.51(10)		C14	C9	C8	116.7(3)
O4	Cu2	O7	90.03(10)		C14	C9	C10	120.1(3)
O4	Cu2	O10A	92.30(11)		O3	C10	C9	125.7(3)
O4	Cu2	O10B	85.3(3)		O3	C10	C11	117.3(3)
O4	Cu2	N5	95.01(11)		C11	C10	C9	117.0(3)
O5	Cu2	O7	92.94(10)		C10	C11	C15	118.1(3)
O5	Cu2	O10A	90.55(11)		C12	C11	C10	121.5(3)
O5	Cu2	O10B	96.5(3)		C12	C11	C15	120.4(3)
O7	Cu2	O10A	67.20(11)		C11	C12	C13	119.8(3)
O7	Cu2	O10B	92.0(3)		C12	C13	Br1	120.0(3)
N5	Cu2	O5	82.00(11)		C14	C13	Br1	119.5(3)
N5	Cu2	O7	174.90(12)		C14	C13	C12	120.5(3)

N5	Cu2	O10A	113.30(12)		C13	C14	C9	121.0(3)
N5	Cu2	O10B	89.3(3)		C11	C15	N3	110.9(3)
C7	O2	Cu1	113.2(2)		N3	C16	C17	111.7(3)
C10	O3	Cu1	125.8(2)		N4	C17	C16	111.0(3)
C22	O4	Cu2	125.4(2)		C21	C20	N3	111.6(3)
C28	O5	Cu2	110.2(2)		C22	C21	C20	117.2(3)
Cu1	O7	Cu2	126.62(13)		C26	C21	C20	121.5(3)
N7	O7	Cu1	117.7(2)		C26	C21	C22	121.3(3)
N7	O7	Cu2	114.93(19)		O4	C22	C21	117.0(3)
Cu1	O10A	Cu2	92.27(12)		O4	C22	C23	124.7(3)
N8	O10A	Cu1	120.8(3)		C21	C22	C23	118.2(3)
N8	O10A	Cu2	139.0(3)		C22	C23	C27	123.8(3)
N8	O10B	Cu2	138.7(8)		C24	C23	C22	119.2(3)
N8	O11B	Cu1	124.6(11)		C24	C23	C27	117.0(3)
C7	N1	N2	114.9(3)		C25	C24	C23	120.7(3)
N1	N2	Cu1	111.4(2)		C24	C25	Br2	118.9(3)
C8	N2	Cu1	128.4(2)		C24	C25	C26	121.2(3)
C8	N2	N1	120.2(3)		C26	C25	Br2	119.9(3)
C16	N3	C15	112.0(3)		C21	C26	C25	119.4(3)
C16	N3	C20	112.0(2)		N5	C27	C23	123.5(3)
C20	N3	C15	110.5(3)		O5	C28	N6	123.2(3)
C17	N4	C18	110.9(3)		O5	C28	C29	119.5(3)
C19	N4	C17	112.7(3)		N6	C28	C29	117.3(3)
C19	N4	C18	110.8(4)		C30	C29	C28	121.6(3)
N6	N5	Cu2	114.0(2)		C34	C29	C28	119.3(3)
C27	N5	Cu2	127.2(3)		C34	C29	C30	119.0(4)
C27	N5	N6	118.7(3)		O6	C30	C29	123.2(3)
C28	N6	N5	110.5(3)		O6	C30	C31	117.2(4)
O8	N7	O7	116.9(3)		C31	C30	C29	119.6(4)
O9	N7	O7	117.0(3)		C32	C31	C30	119.9(4)
O9	N7	O8	126.1(4)		C31	C32	C33	121.2(4)
O10A	N8	O11A	113.7(4)		C34	C33	C32	119.3(4)
O10B	N8	O12B	109.2(9)		C33	C34	C29	121.0(4)
O11B	N8	O10B	129.3(10)		O14	N9	O13	117.6(4)
O11B	N8	O12B	121.4(10)		O15	N9	O13	119.7(4)
O12A	N8	O10A	127.4(5)		O15	N9	O14	122.6(4)

O12A	N8	O11A	118.7(5)		N10	C35	C36	178.9(5)
O1	C1	C2	122.2(4)		N11	C37	C38	179.0(8)

Hydrogen Bonds

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O1	H1	O11A[1]	0.83(3)	1.97(5)	2.618(5)	134(6)
O1	H1	O11B[1]	0.83(3)	2.11(4)	2.899(15)	158(6)
O6	H6	N6	0.87(3)	1.81(4)	2.579(4)	146(5)
N1	H1A	O1	0.78(3)	2.06(4)	2.596(4)	127(4)
N3	H3	O3	0.82(3)	2.29(3)	2.844(4)	125(3)
N3	H3	O4	0.82(3)	2.28(3)	2.847(4)	127(3)
N4	H4	O13	0.89(3)	1.88(3)	2.775(5)	176(4)
O16	H16C	O2	1.05(4)	2.31(4)	3.219(10)	144(7)
O16	H16D	O5	1.01(4)	2.02(4)	2.923(9)	148(8)

Table S2. SHAPE analysis of $[Cu_2(H_5L)(NO_3)_2]NO_3.0.5H_2O.2CH_3CN$ complex.

S H A P E v2.1 Continuous Shape Measures calculation
(c) 2013 Electronic Structure Group, Universitat de Barcelona
Contact: llunell@ub.edu
Ideal structures ML5: Cu(1)
PP-5 1 D5h Pentagon
vOC-5 2 C4v Vacant octahedron
TBPY-5 3 D3h Trigonal bipyramid
SPY-5 4 C4v Spherical square pyramid
JTBPY-5 5 D3h Johnson trigonal bipyramid J12

Structure 1 [Cu]
Cu 5.9243 0.8283 -2.6247
O 7.1472 -0.6364 -3.0913
O 4.6262 2.0583 -2.0047
O 5.3049 1.0261 -4.5019
O 7.3514 2.3676 -3.6544
N 6.5350 0.3822 -0.8478
PP-5 Ideal structure CShM = 25.02739

Cu	M	6.1482	1.0043	-2.7875
O	L1	7.5934	0.0834	-2.5579
O	L3	4.6650	1.4888	-2.0423
O	L4	5.2928	2.0099	-3.9040
O	L5	7.1026	1.1413	-4.2226
N	L2	6.0869	0.2982	-1.2104
vOC-5	Ideal structure	CShM =	2.52605	
Cu	M	5.9220	0.7700	-2.7124
O	L2	7.1929	-0.6537	-3.3277
O	L4	4.6511	2.1937	-2.0970
O	L3	5.1707	0.9009	-4.5669
O	L1	7.2789	2.1760	-3.1629
N	L5	6.6733	0.6391	-0.8579
TBPY-5	Ideal structure	CShM =	7.26322	
Cu	M	6.1482	1.0043	-2.7875
O	L2	6.5470	-0.8569	-3.0609
O	L3	4.4558	1.5249	-2.0372
O	L1	5.3951	1.1025	-4.5541
O	L4	7.4417	2.3450	-3.2643
N	L5	6.9012	0.9061	-1.0208
SPY-5	**Ideal structure**	**CShM =**	**2.46308**	
Cu	M	6.1482	1.0043	-2.7875
O	L2	7.0275	-0.6980	-3.2545
O	L4	4.6077	2.0146	-2.0833
O	L3	5.0804	0.7600	-4.4274
O	L1	7.4704	2.3886	-3.2617
N	L5	6.5548	0.5566	-0.9104
JTBPY-5	Ideal structure	CShM =	9.76926	
Cu	M	6.1482	1.0043	-2.7875
O	L1	6.4693	-0.5454	-3.0428
O	L2	4.7316	1.4392	-2.1756
O	L4	5.2953	1.1727	-4.8813
O	L3	7.2435	2.1192	-3.1440
N	L5	7.0010	0.8360	-0.6936

Ideal structures ML4: Cu(2)		
SP-4	1 D4h	Square
T-4	2 Td	Tetrahedron

SS-4	3	C2v	Seesaw	
vTBPY-4	4	C3v	Vacant trigonal bipyramid	
Structure	1	[Cu]		
Cu		5.9375	2.3798	-5.8301
O		5.3049	1.0261	-4.5019
O		4.7229	3.6419	-5.1239
O		7.1631	1.1434	-6.6555
N		6.6288	3.5475	-7.1744
SP-4	**Ideal structure**		**CShM =**	**0.24553**
Cu	M	5.9514	2.3477	-5.8572
O	L1	5.3358	1.0561	-4.5639
O	L2	4.7360	3.6562	-5.1290
O	L4	7.1669	1.0392	-6.5853
N	L3	6.5671	3.6393	-7.1504
T-4	Ideal structure		CShM =	32.99939
Cu	M	5.9514	2.3477	-5.8572
O	L1	6.1593	1.7087	-4.4265
O	L2	4.5122	2.9958	-5.9407
O	L3	6.0884	1.2246	-6.9608
N	L4	7.0459	3.4618	-6.1006
SS-4	Ideal structure		CShM =	18.43750
Cu	M	6.3214	2.4940	-5.5224
O	L1	5.7068	1.2618	-4.3046
O	L2	4.5932	3.0208	-5.8616
O	L3	6.1998	1.2357	-6.8570
N	L4	6.9360	3.7262	-6.7402
vTBPY-4	Ideal structure		CShM =	33.68517
Cu	M	5.9751	2.5661	-5.6208
O	L2	6.2470	1.3847	-4.5563
O	L3	4.4658	3.0521	-5.9186
O	L1	5.8566	1.4741	-6.8025
N	L4	7.2126	3.2616	-6.3876

The application of H_6L for M^{2+} sensing

The optical properties of the **H_6L + M^{2+}** were investigated. A stock solution of **H_6L** (100 µM) in DMSO was prepared and 25 µM and used as the working solution in this experiment. The absorption maximum at 310 nm was selected as an excitation wavelength for the fluorescence experiment.

1. Pb^{2+} sensing

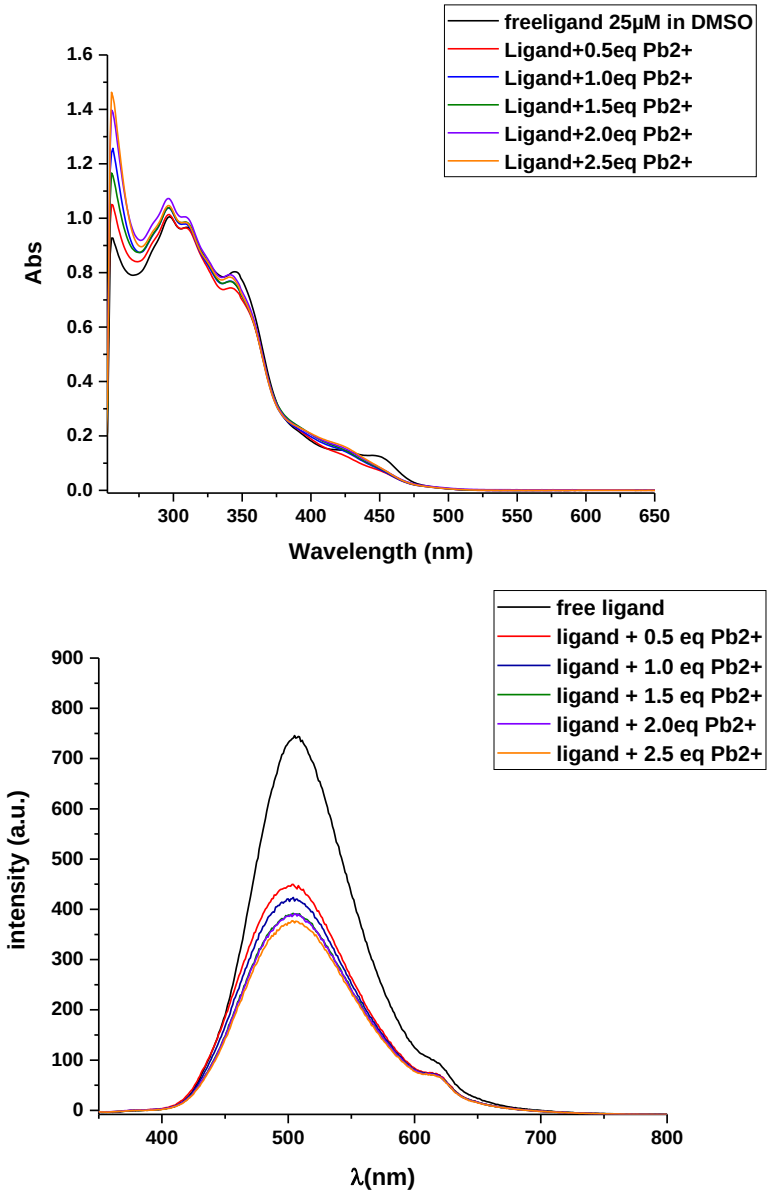


Figure S3. a) Uv-vis titration spectra, b) fluorescence titration spectra (λ_{ex} = 310 nm, slit; 10 nm/10 nm) of **H_6L** (25 µM) with increasing amount of Pb^{2+} in DMSO.

2. Cd^{2+} sensing

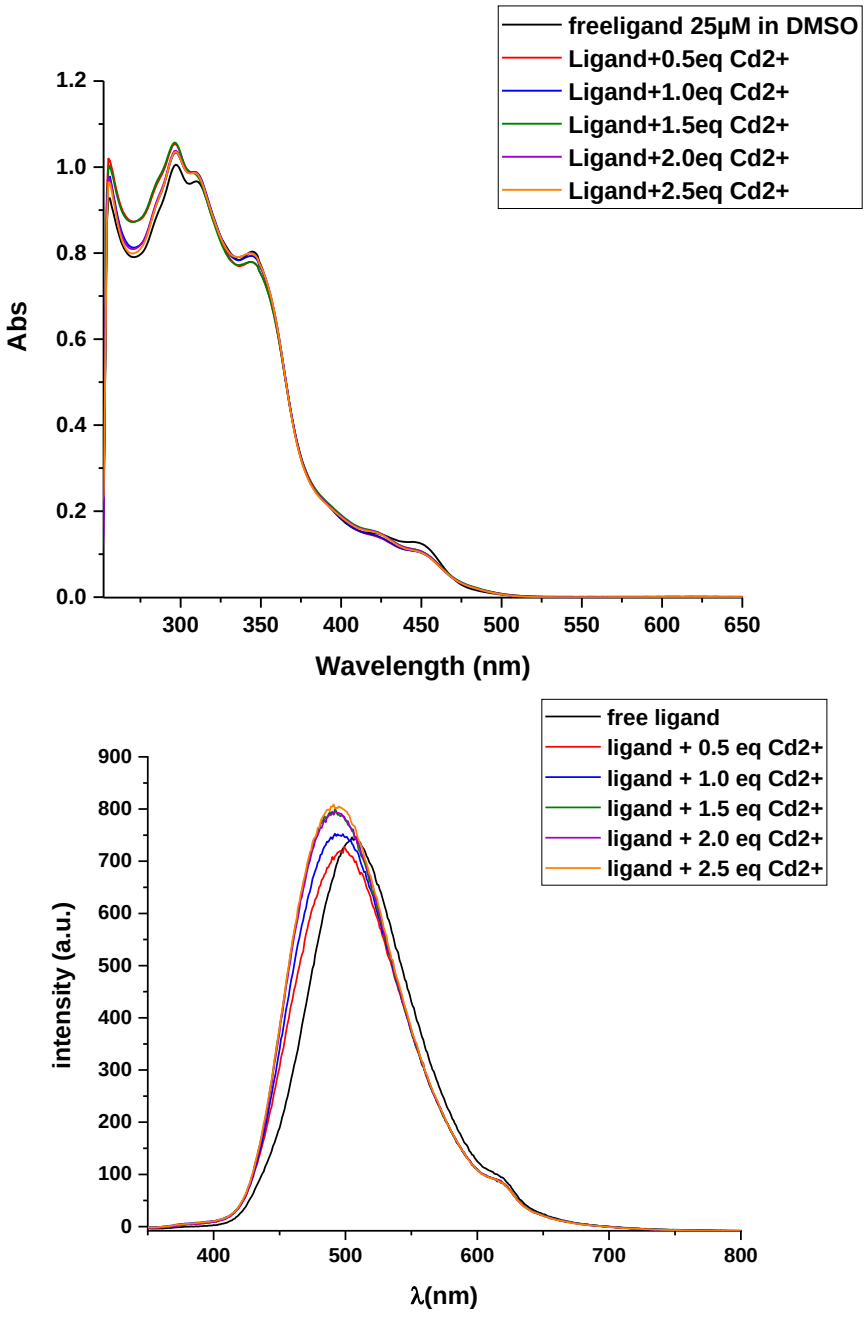


Figure S4. a) Uv-vis titration spectra, b) fluorescence titration spectra (λ_{ex} = 310 nm, slit; 10 nm/10 nm) of **H_6 L** (25 μM) with increasing amount of Cd^{2+} in DMSO.

3. Zn^{2+} sensing

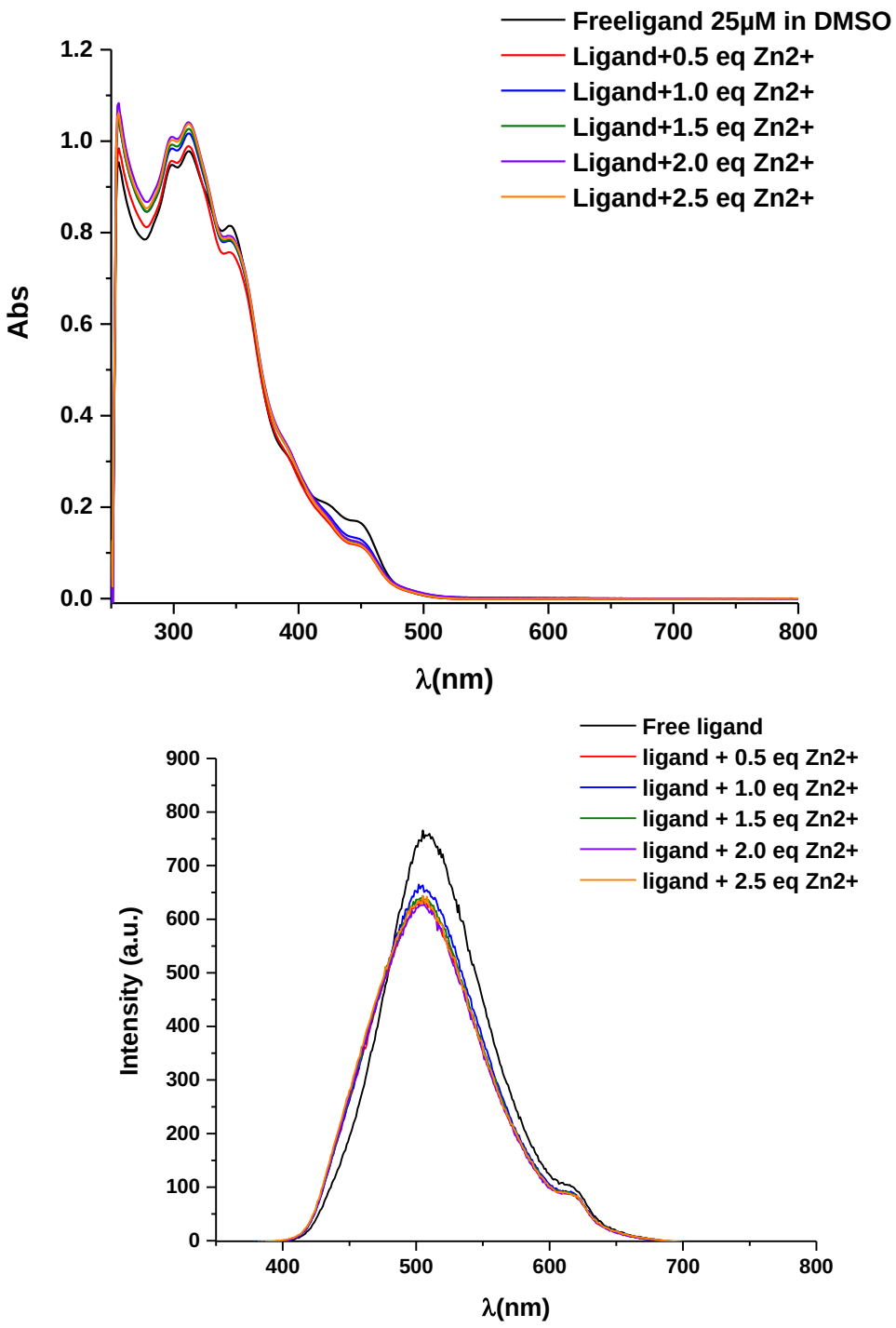


Figure S5. a) Uv-vis titration spectra, b) fluorescence titration spectra (λ_{ex} = 310 nm, slit; 10 nm/10 nm) of **H_6L** (25 μM) with increasing amount of Zn^{2+} in DMSO.

4. Ni^{2+} sensing

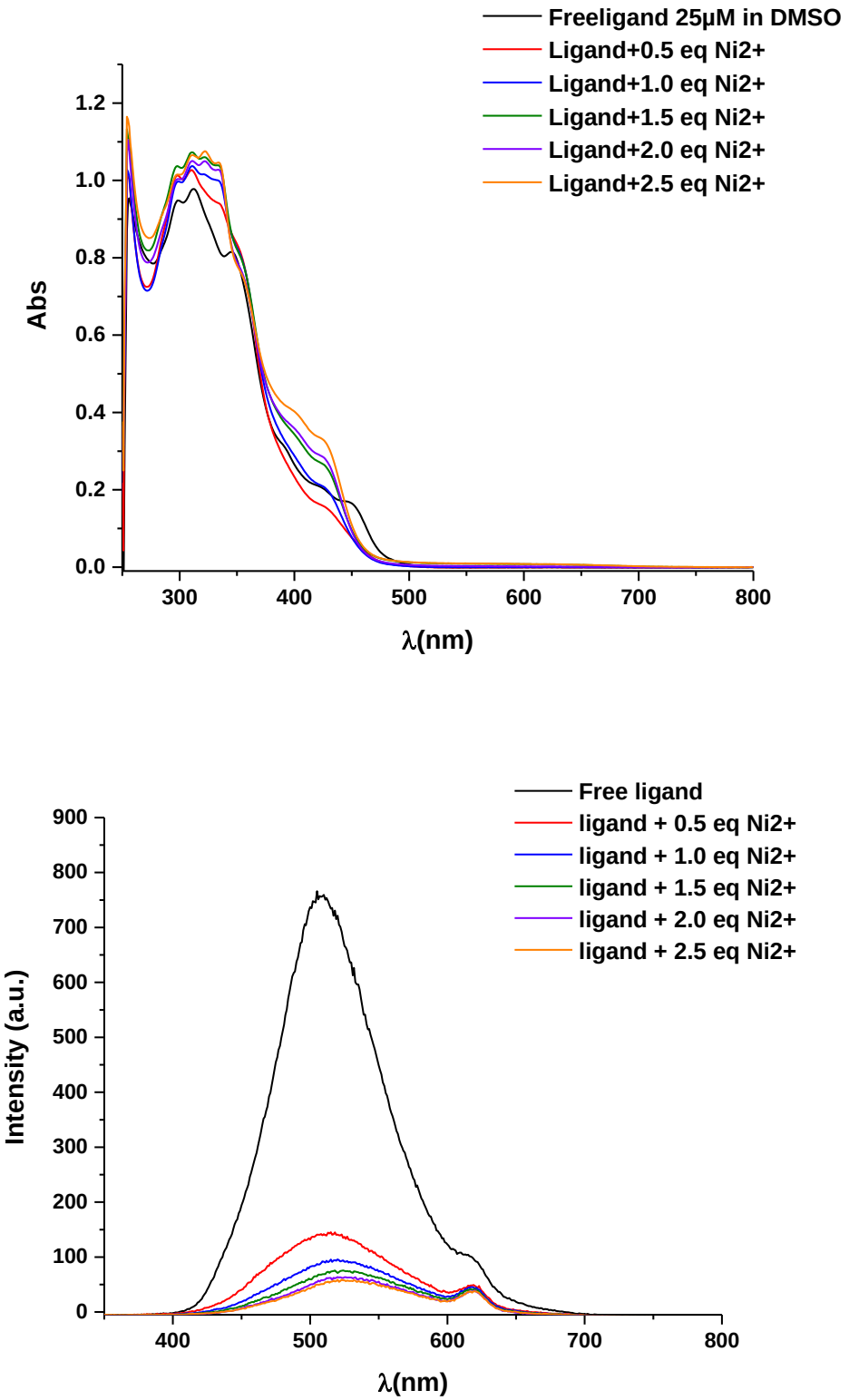


Figure S6. a) Uv-vis titration spectra, b) fluorescence titration spectra (λ_{ex} = 310 nm, slit; 10 nm/10 nm) of **H_6L** (25 μM) with increasing amount of Ni^{2+} in DMSO.

5. Co^{2+} sensing

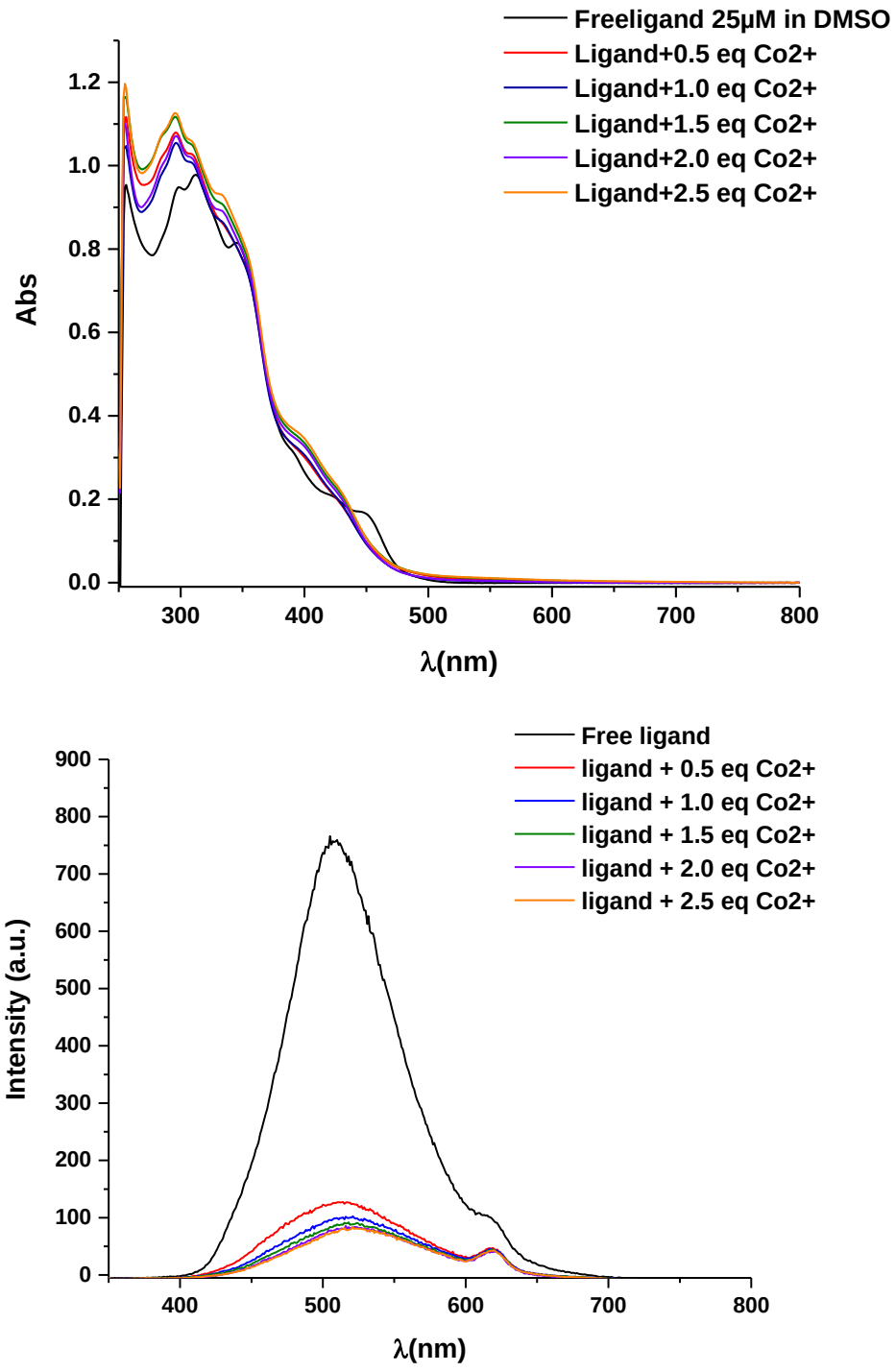


Figure S7. a) Uv-vis titration spectra, b) fluorescence titration spectra (λ_{ex} = 310 nm, slit; 10 nm/10 nm) of **H_6L** (25 μM) with increasing amount of Co^{2+} in DMSO.

6. Fe^{2+} sensing

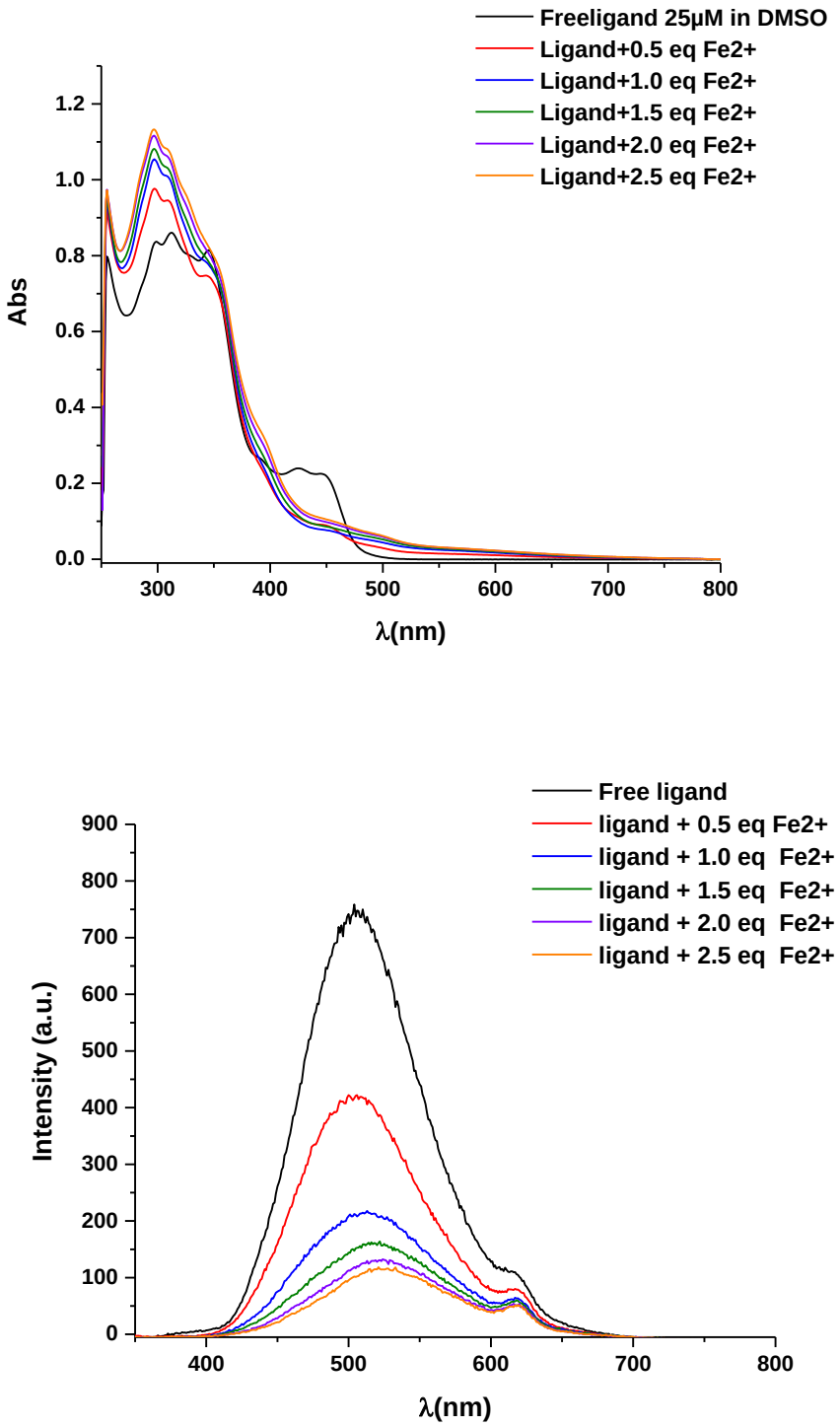


Figure S8. a) Uv-vis titration spectra, b) fluorescence titration spectra (λ_{ex} = 310 nm, slit; 10 nm/10 nm) of **H_6L** (25 μM) with increasing amount of Fe^{2+} in DMSO.

7. Sn^{2+} sensing

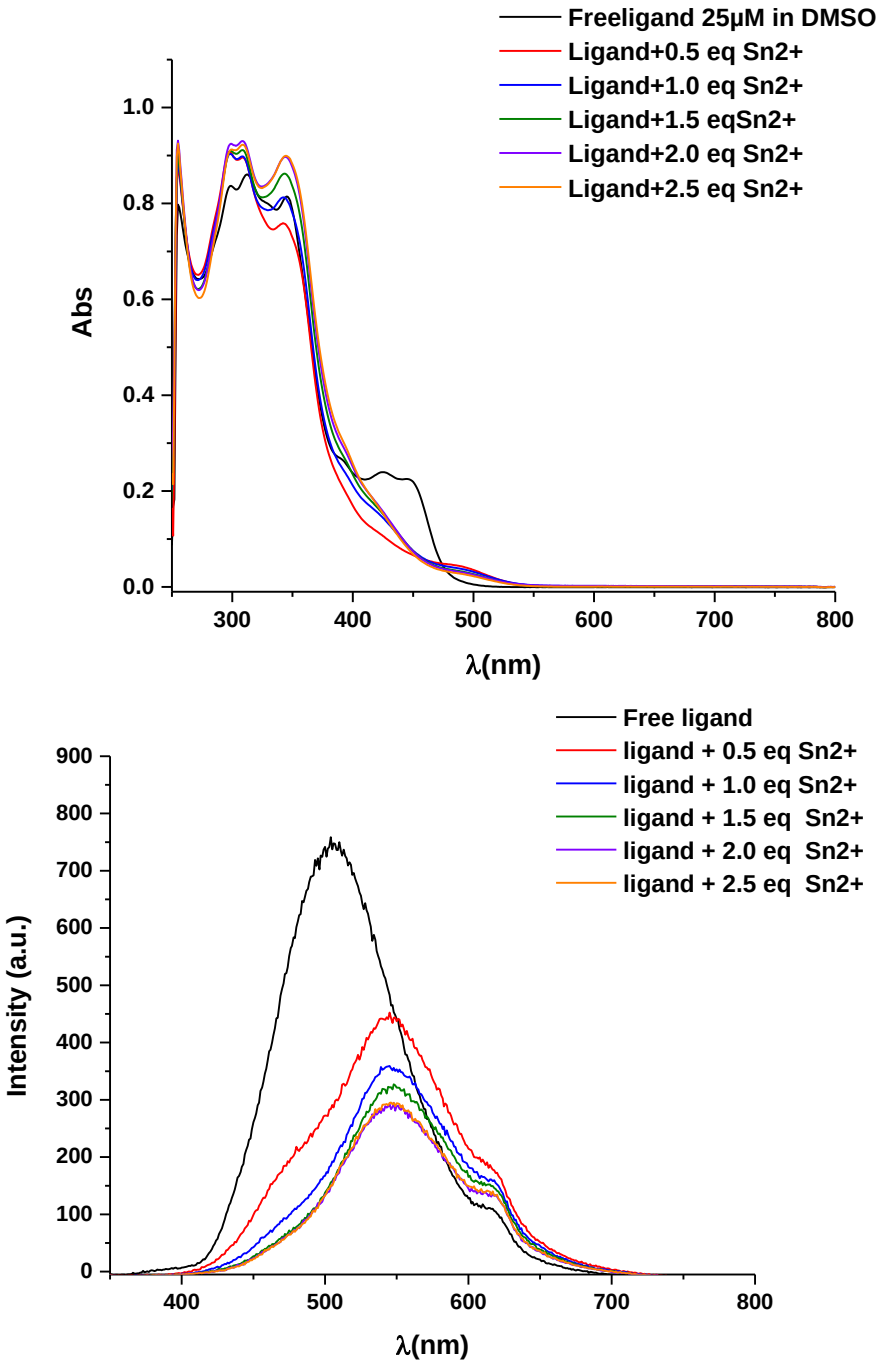


Figure S9. a) Uv-vis titration spectra, b) fluorescence titration spectra (λ_{ex} = 310 nm, slit; 10 nm/10 nm) of **H_6L** (25 μM) with increasing amount of Fe^{2+} in DMSO.

Catalytic study.

The investigation of the potential of the $[Cu_2(H_5L)(NO_3)_2]^+$ complex as a catalyst for the reaction of aldehyde, alkyne and amine (A3 coupling) was performed. Cyclopentane carboxaldehyde (**5**), piperidine (**6**) and phenylacetylene (**7**) were chosen as model reagents. The catalytic loading for the A3 coupling reaction was first investigated by varying the amount of catalyst from 0.1-5.0 mol % with the reaction performed in air at room temperature for 16 h (**Figure S10**). The efficiency of this catalytic system can be followed by a disappearance of the aldehyde proton signal at 9.60 ppm and the appearance of a new peak assigned to a quaternary proton of the propargylamine product at 3.50 ppm.

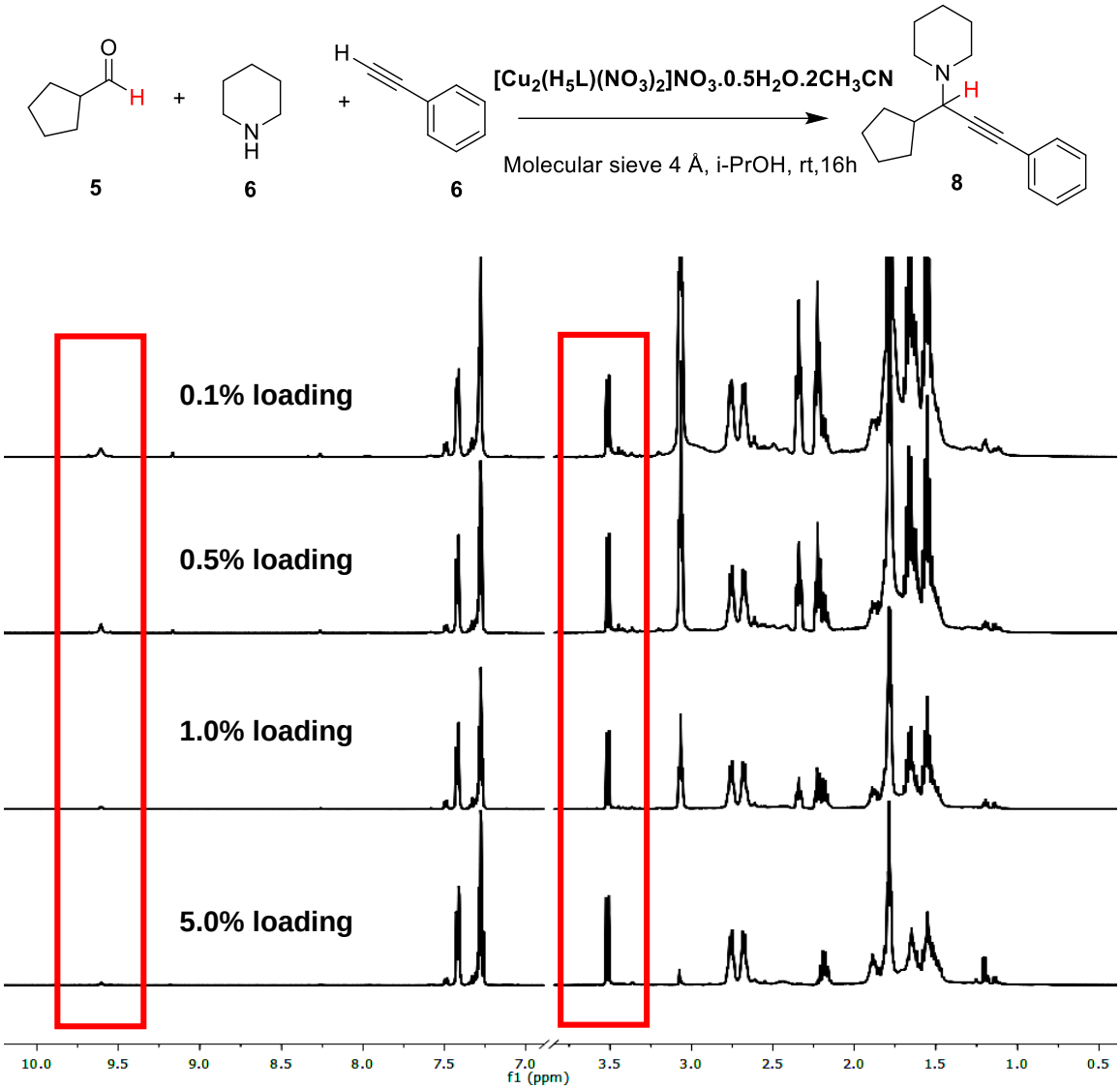
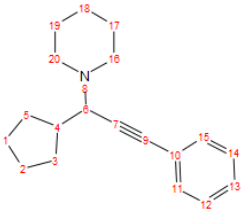
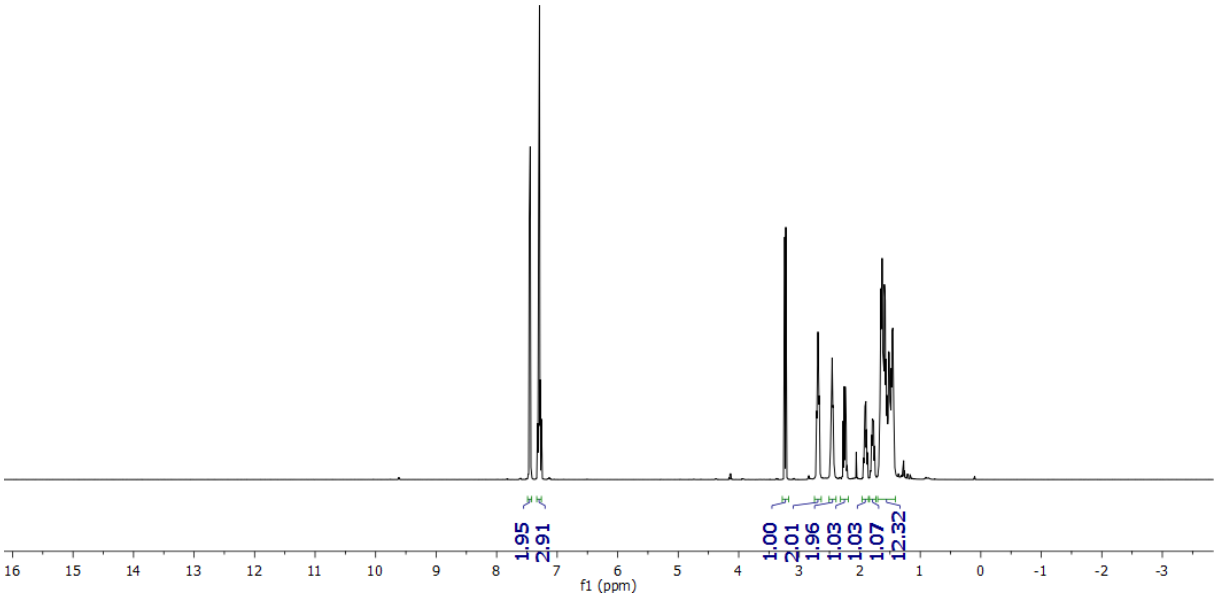


Figure S10. ^{1}H NMR spectra for optimisation reaction of A3 coupling reaction with various catalytic loading.

General procedure for the investigation of the efficiency of catalyst for A3 coupling reactions. To a solution of $[Cu_2(H_5L)(NO_3)_2]NO_3 \bullet 0.5H_2O \bullet 2CH_3CN$ (1 mol%) and 200 mg 4Å molecular sieve in *i*-PrOH (5 mL) were added aldehyde (215 µl, 2.0 mmol), amine (220 µl, 2.2 mmol) and alkyne (330 µl, 2.4 mmol). The mixture was stirred vigorously at room temperature for 24 h. The resulting solution was filtered through celite, washed with CH_2Cl_2. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (EtOAc-Hexane: 1:4, %v/v) to obtain oily product.

Compound 8: ^{1}H NMR (500 MHz, Chloroform-d) δ: 7.50 – 7.41 (m, 2H), 7.35 – 7.26 (m, 3H), 3.24 (d, *J* = 9.3 Hz, 1H), 2.75 – 2.65 (m, 2H), 2.53 – 2.40 (m, 2H), 2.25 (p, *J* = 8.4, 7.8 Hz, 1H), 1.98 – 1.86 (m, 2H), 1.83 – 1.74 (m, 1H), 1.71 – 1.40 (m, 13H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 131.6 (2×CH), 128.0 (2×CH), 127.5 (CH), 123.7 (C), 87.9 (C≡C), 85.4 (C≡C), 63.6 (CH), 50.7 (CH), 42.3 (2×CH_2), 30.8 (CH_2), 30.3 (CH_2), 26.2 (2×CH_2), 25.3 (CH_2), 25.1 (CH_2), 24.5 (CH_2).





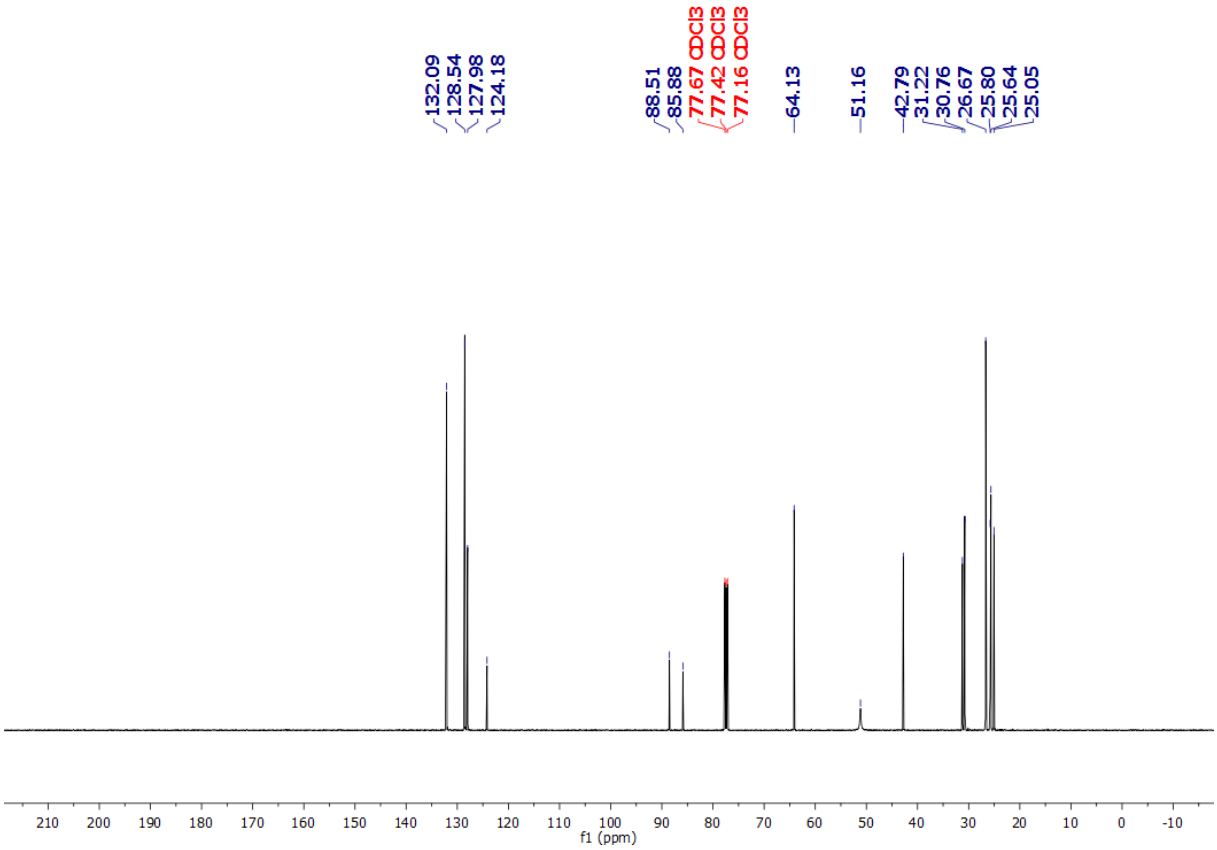


Figure S11. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 8.

Compound 9: ^{1}H NMR (500 MHz, Chloroform-d) δ:7.47 – 7.41 (m, 2H), 7.33 – 7.24 (m, 3H), 3.53 (d, *J* = 8.4 Hz, 1H), 2.78 (qd, *J* = 6.5, 6.1, 2.9 Hz, 2H), 2.69 (qd, *J* = 7.3, 6.6, 2.8 Hz, 2H), 2.20 (h, *J* = 8.3 Hz, 1H), 1.96 – 1.86 (m, 1H), 1.87 – 1.74 (m, 5H), 1.70 – 1.47 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ:132.1 (2×CH), 128.5 (2×CH), 128.0 (CH), 124.0 (C), 88.4 (C≡C), 85.6 (C≡C), 60.4 (CH), 50.3 (2×CH_2), 44.3 (CH_2), 30.9 (CH_2), 30.6 (CH_2), 25.9 (CH_2), 25.8 (CH_2), 23.9 (2×CH_2).

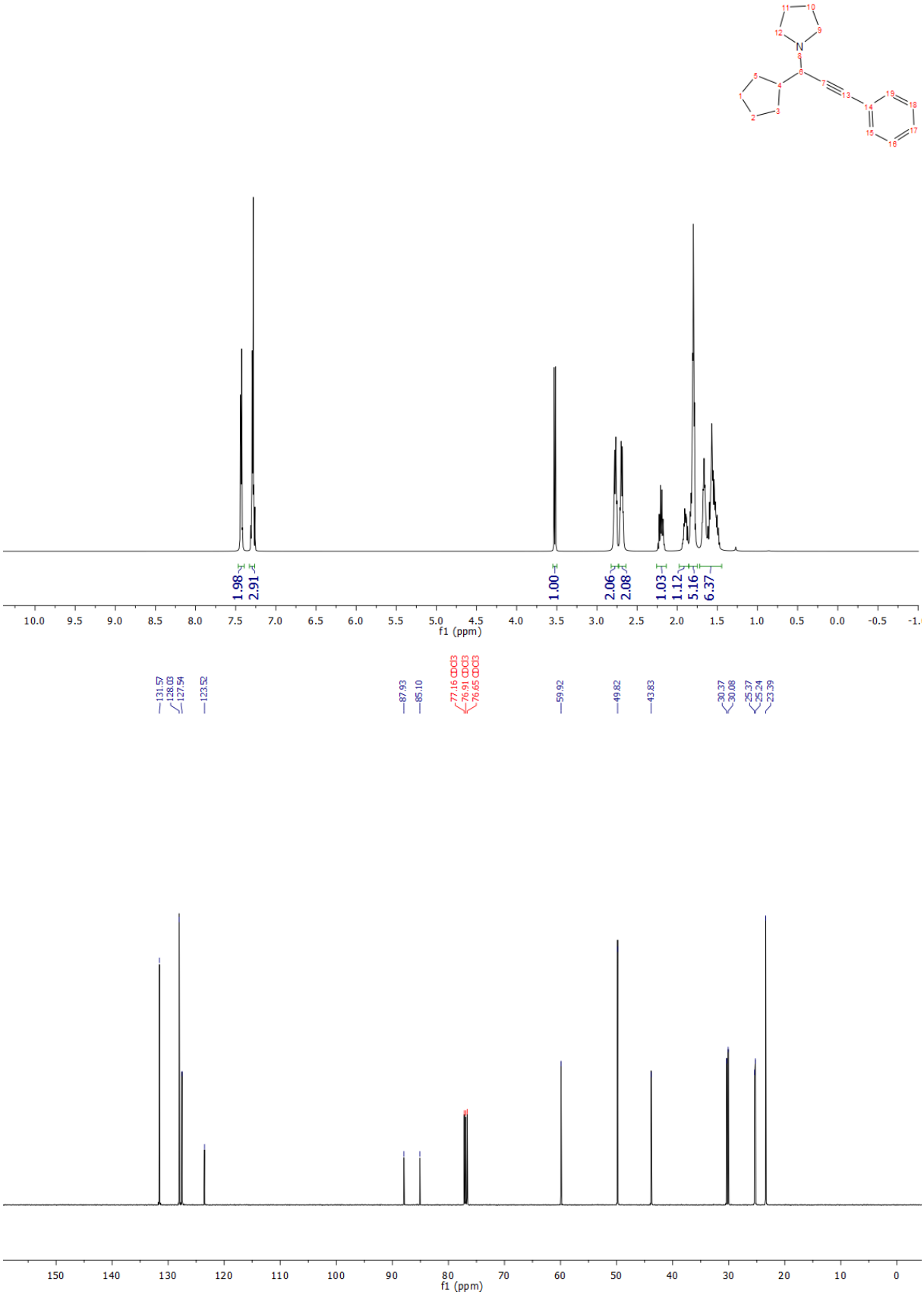
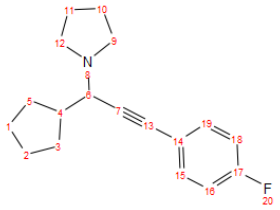
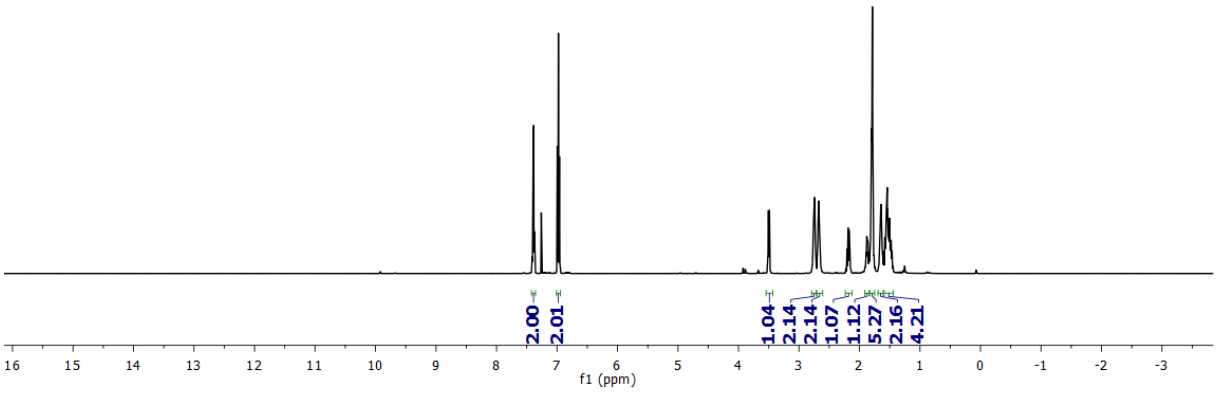


Figure S12. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 9.

Compound 10: ^{1}H NMR (500 MHz, Chloroform-d) δ: 7.42 – 7.36 (m, 2H), 7.01 – 6.95 (m, 2H), 3.50 (d, *J* = 8.3 Hz, 1H), 2.80 – 2.71 (m, 2H), 2.71 – 2.63 (m, 2H), 2.18 (h, *J* = 8.1 Hz, 1H), 1.92 – 1.84 (m, 1H), 1.84 – 1.75 (m, 5H), 1.71 – 1.58 (m, 2H), 1.60 – 1.44 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 162.1 (d, *J* = 248.7 Hz, C), 133.4 (d, *J* = 8.2 Hz, 2×CH), 119.6 (d, *J* = 3.5 Hz, CH), 115.3 (d, *J* = 21.9 Hz, 2×CH), 87.6 (C≡C), 84.1 (C≡C), 60.4 (CH), 50.3 (2×CH_2), 44.3 (CH_2), 30.9 (CH_2), 30.6 (CH_2), 25.9 (CH_2), 25.8 (CH_2), 23.9 (2×CH_2).





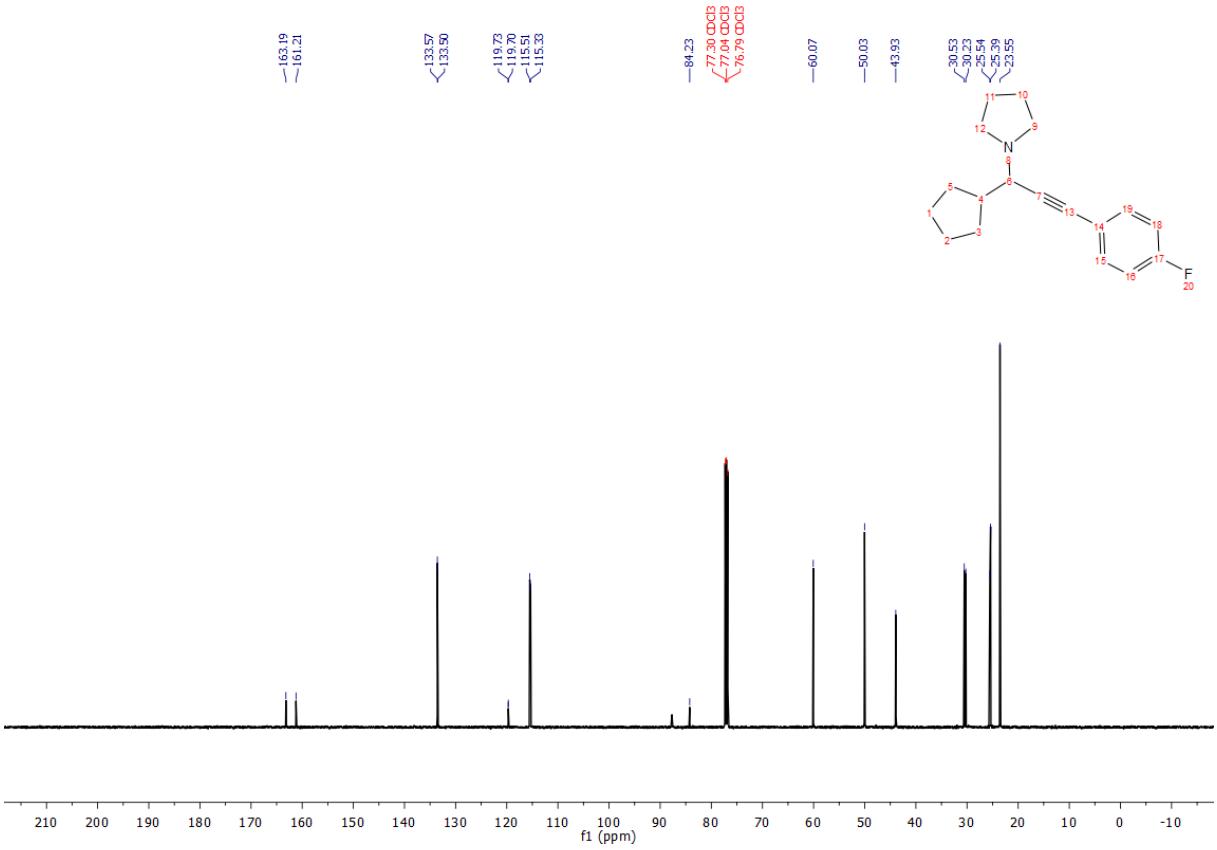


Figure S13. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 10.

Compound 11: ^{1}H NMR (500 MHz, Chloroform-d) δ: 7.69 – 7.65 (m, 2H), 7.58 – 7.52 (m, 2H), 7.41 – 7.29 (m, 6H), 4.83 (s, 1H), 2.59 (d, *J* = 6.4 Hz, 4H), 1.62 (tq, *J* = 12.9, 5.6 Hz, 4H), 1.54 – 1.41 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 138.7 (C), 131.9 (2×CH), 128.6 (2×CH), 128.3 (2×CH), 128.1 (2×CH), 127.5 (2×CH), 123.4 (C), 87.9 (C≡C), 86.1 (C≡C), 62.5 (CH), 50.8 (2×CH_2), 26.2 (2×CH_2), 24.5 (2×CH_2).

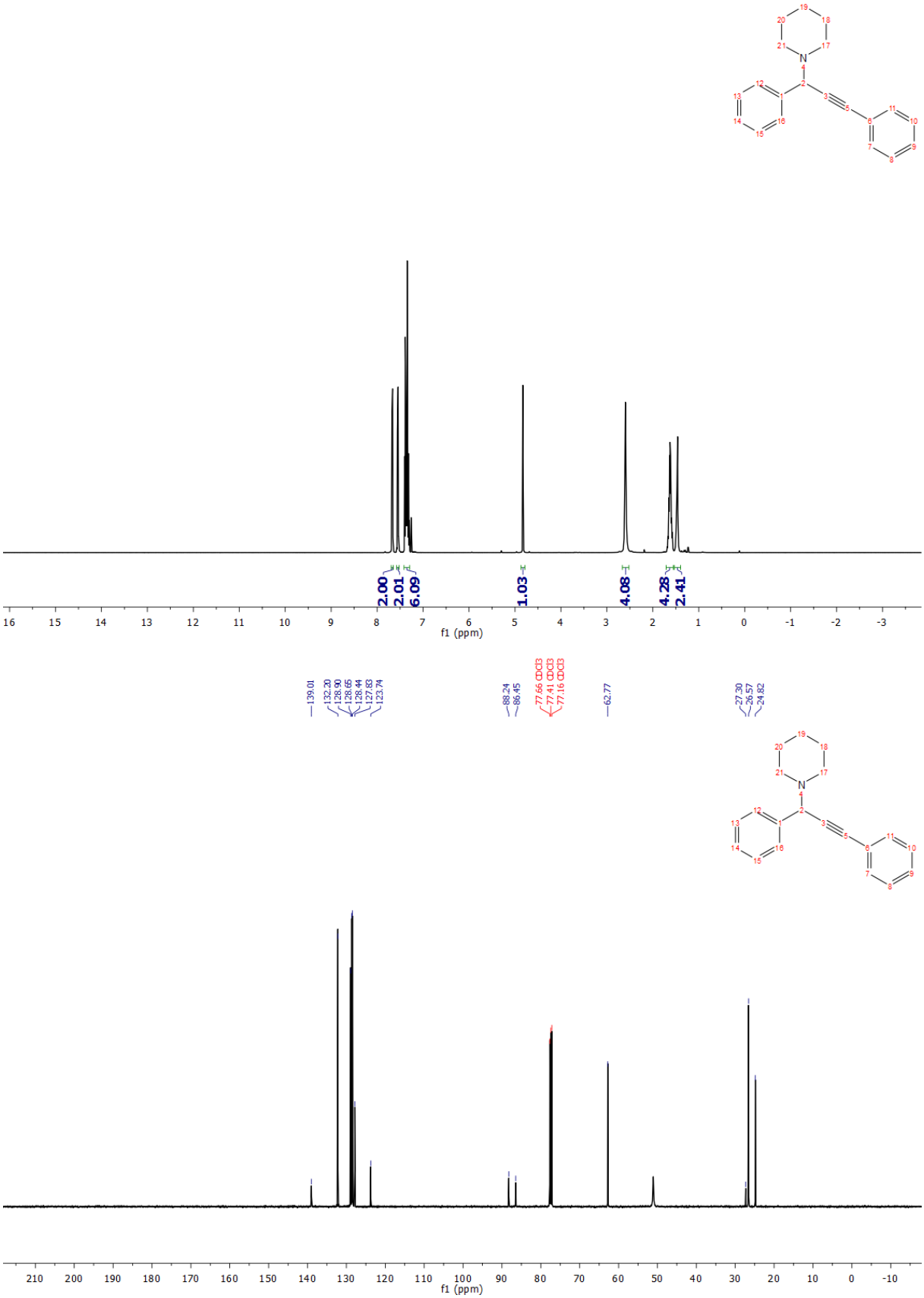
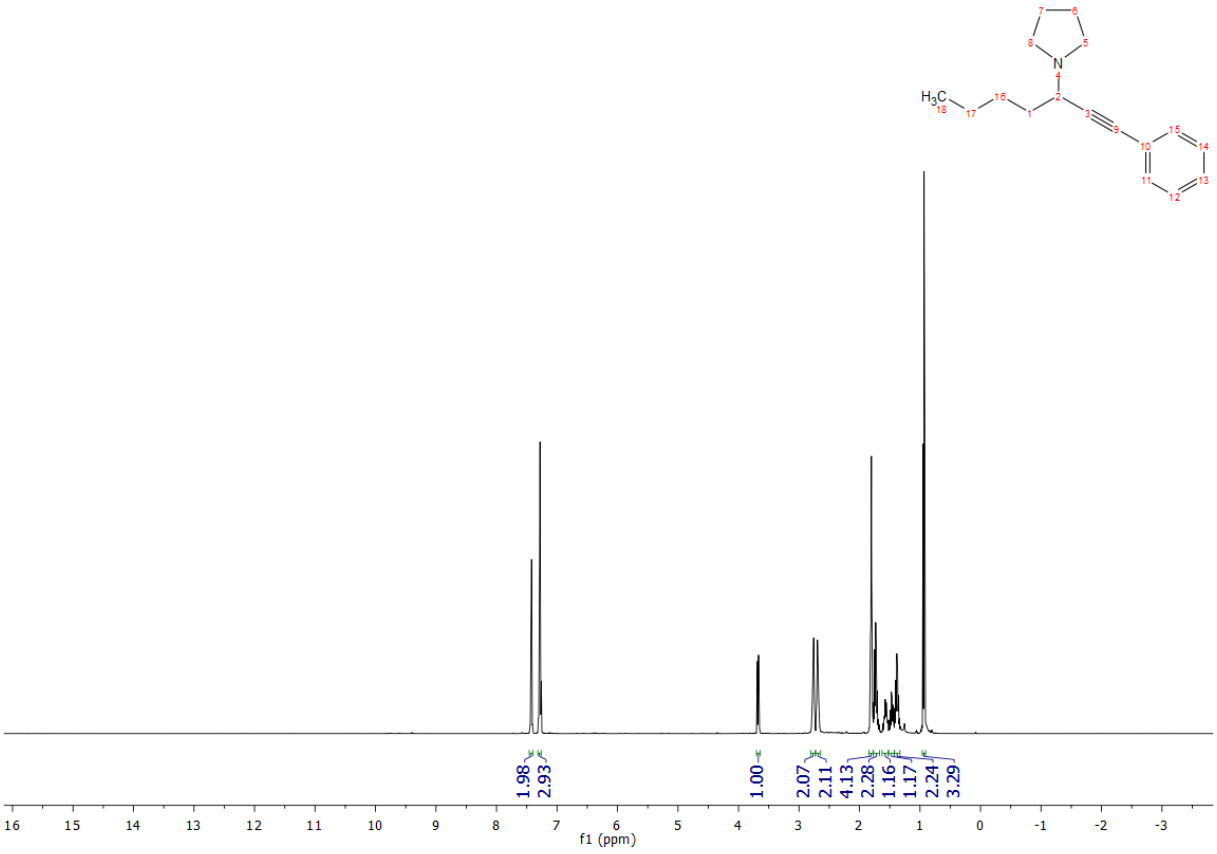


Figure S14. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 11.

Compound 12: ^{1}H NMR (500 MHz, Chloroform-d) δ: 7.46 – 7.40 (m, 2H), 7.32 – 7.27 (m, 3H), 3.68 (dd, *J* = 9.1, 5.7 Hz, 1H), 2.82 – 2.74 (m, 2H), 2.73 – 2.65 (m, 2H), 1.87 – 1.77 (m, 4H), 1.77 – 1.67 (m, 2H), 1.62 – 1.52 (m, 1H), 1.51 – 1.41 (m, 1H), 1.41 – 1.33 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 131.6 (2×CH), 128.1 (2×CH), 128.3 (CH), 123.4 (C), 88.2 (C≡C), 85.4 (C≡C), 55.0 (CH), 49.6 (2×CH_2), 34.7 (CH_2), 28.8 (CH_2), 23.4 (2× CH_2), 22.4 (CH_2), 19.9 (CH_3).



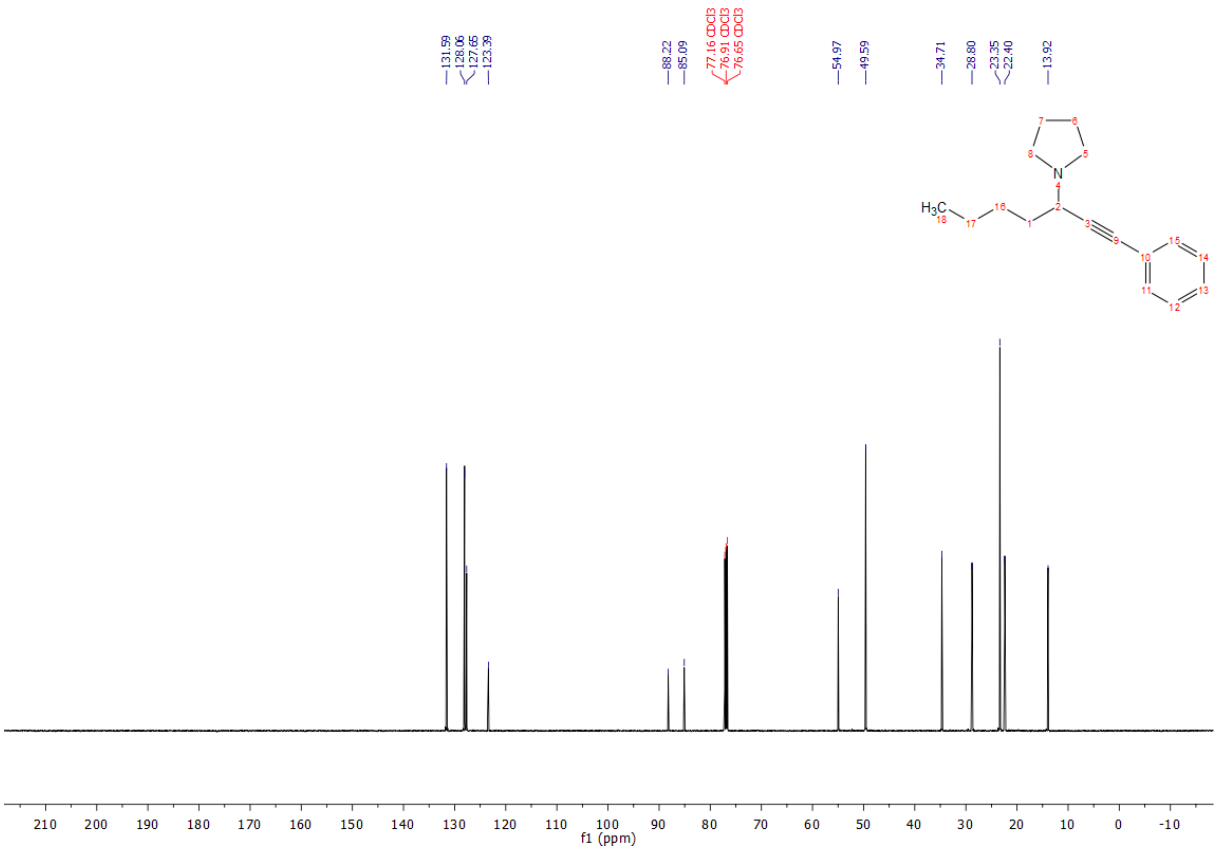


Figure S15. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 12.

Compound 13: ^{1}H NMR (500 MHz, Chloroform-d) δ: 7.45 – 7.33 (m, 2H), 7.04 – 6.92 (m, 2H), 3.64 (dd, *J* = 9.1, 5.7 Hz, 1H), 2.78 – 2.70 (m, 2H), 2.72 – 2.61 (m, 4H), 1.84 – 1.76 (m, 4H), 1.76 – 1.65 (m, 2H), 1.61 – 1.49 (m, 2H), 1.49 – 1.42 (m, 1H), 1.41 – 1.32 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 162.1 (d, *J* = 248.1 Hz, C), 133.4 (d, *J* = 8.3 Hz, 2×CH), 119.5 (C), 115.3 (d, *J* = 22.0 Hz, 2×CH), 88.9 (C≡C), 84.0 (C≡C), 54.9 (CH), 49.6 (2×CH_2), 34.7 (CH_2), 28.8 (CH_2), 23.4 (2× CH_2), 22.4 (CH_2), 19.9 (CH_3).

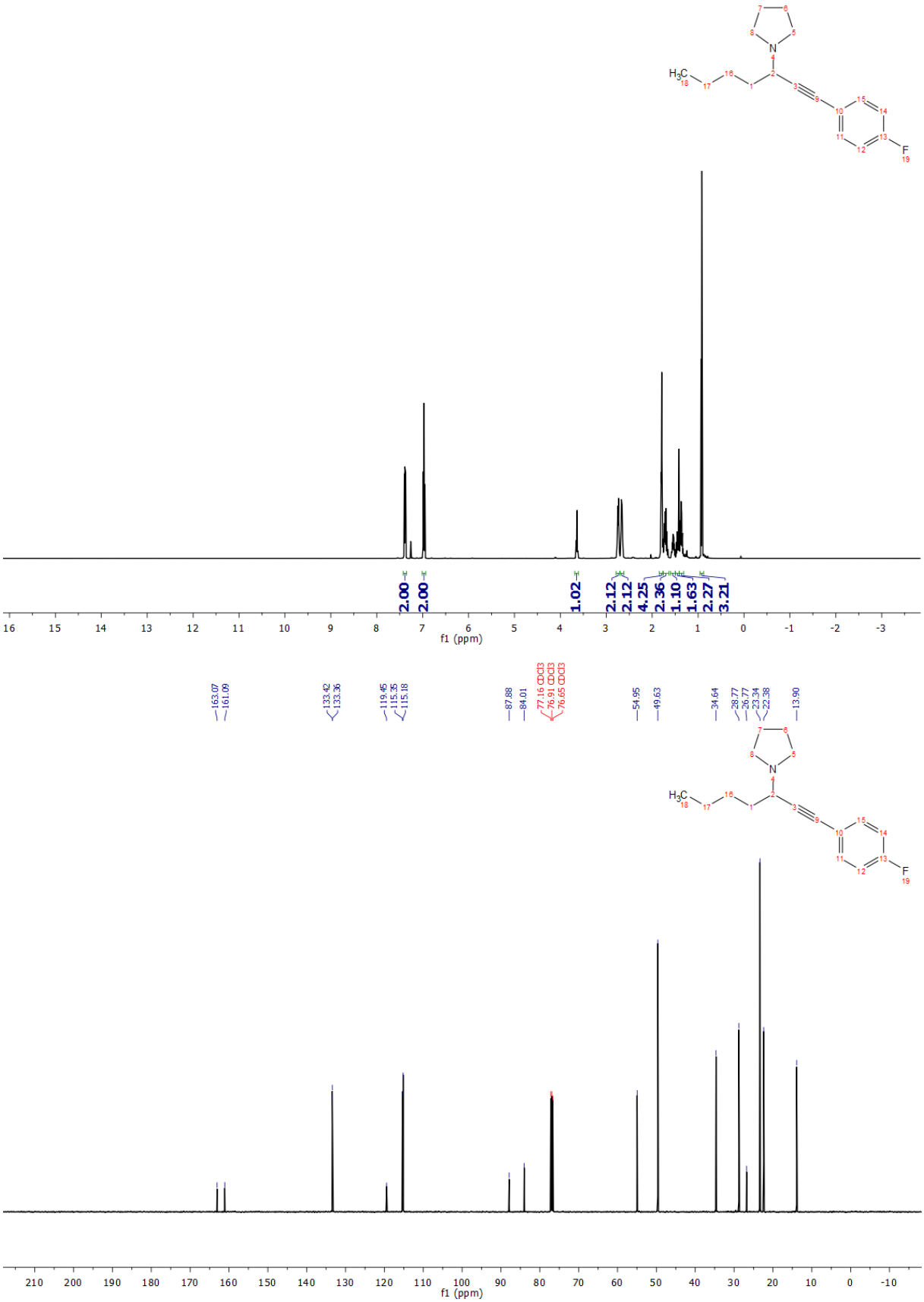
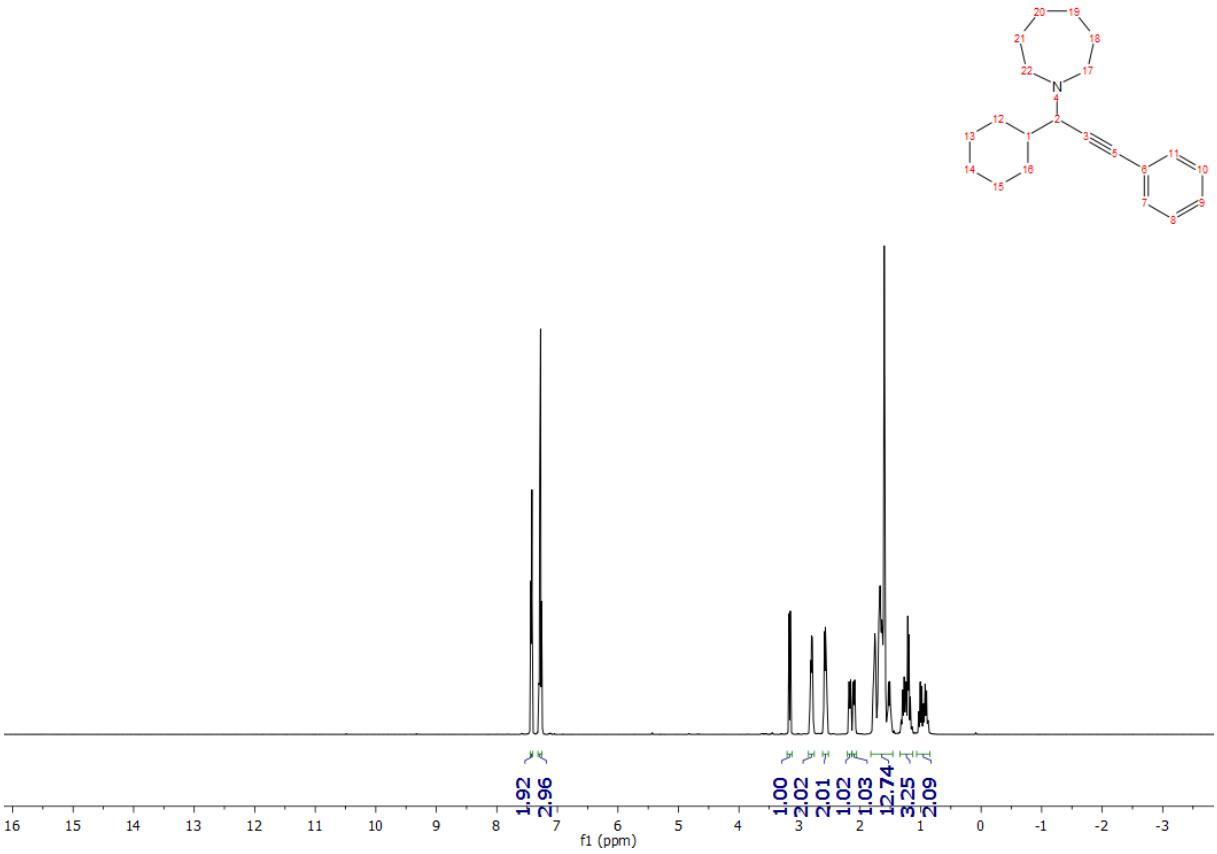


Figure S16. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 13.

Compound 14: ^{1}H NMR (500 MHz, Chloroform-d) δ: 7.43 (dd, *J* = 7.5, 2.2 Hz, 2H), 7.34 – 7.23 (m, 3H), 3.16 (d, *J* = 10.1 Hz, 1H), 2.80 (ddd, *J* = 12.2, 6.9, 3.5 Hz, 2H), 2.57 (dt, *J* = 12.7, 6.0 Hz, 2H), 2.23 – 2.05 (m, 2H), 1.82 – 1.60 (m, 10H), 1.58 – 1.46 (m, 1H), 1.37 – 1.11 (m, 4H), 0.96 (dqd, *J* = 39.3, 12.0, 3.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 131.7 (2×CH), 128.2 (2×CH), 127.6 (CH), 123.9 (C), 88.9 (C≡C), 84.9 (C≡C), 65.3 (CH), 52.7 (2×CH_2), 40.8 (2×CH_2), 31.2 (CH_2), 30.6 (CH_2), 29.3 (CH_2), 27.2 (2×CH_2), 26.9 (CH_2), 26.3 (CH_2), 26.19 (CH_2).



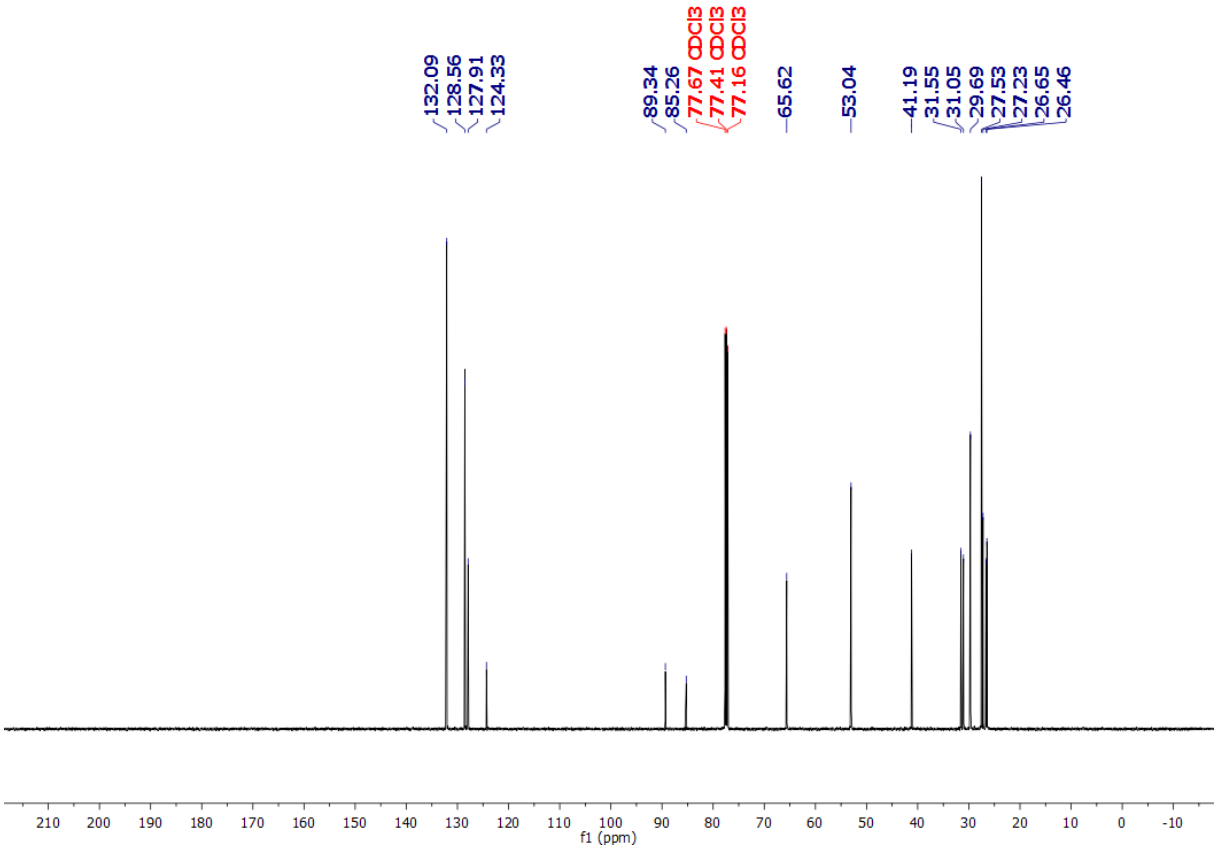


Figure S17. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 14.

Compound 15: ^{1}H NMR (500 MHz, Chloroform-d) δ: 7.52 – 7.43 (m, 2H), 7.38 – 7.26 (m, 3H), 3.13 (d, *J* = 9.9 Hz, 1H), 2.73 – 2.56 (m, 2H), 2.53 – 2.33 (m, 2H), 2.24 – 1.99 (m, 2H), 1.84 – 1.52 (m, 8H), 1.46 (p, *J* = 6.0 Hz, 2H), 1.38 – 1.14 (m, 3H), 1.00 (dqd, *J* = 46.1, 12.2, 3.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 132.1 (2×CH), 128.2 (2×CH), 127.9 (CH), 124.2 (C), 88.2 (C≡C), 86.5 (C≡C), 64.8 (CH), 51.1 (2×CH_2), 49.9 (CH_2), 31.7 (CH_2), 30.8 (CH_2), 27.2 (CH_2), 26.7 (CH_2), 26.6 (CH_2), 26.5 (CH_2), 25.1 (CH_2).

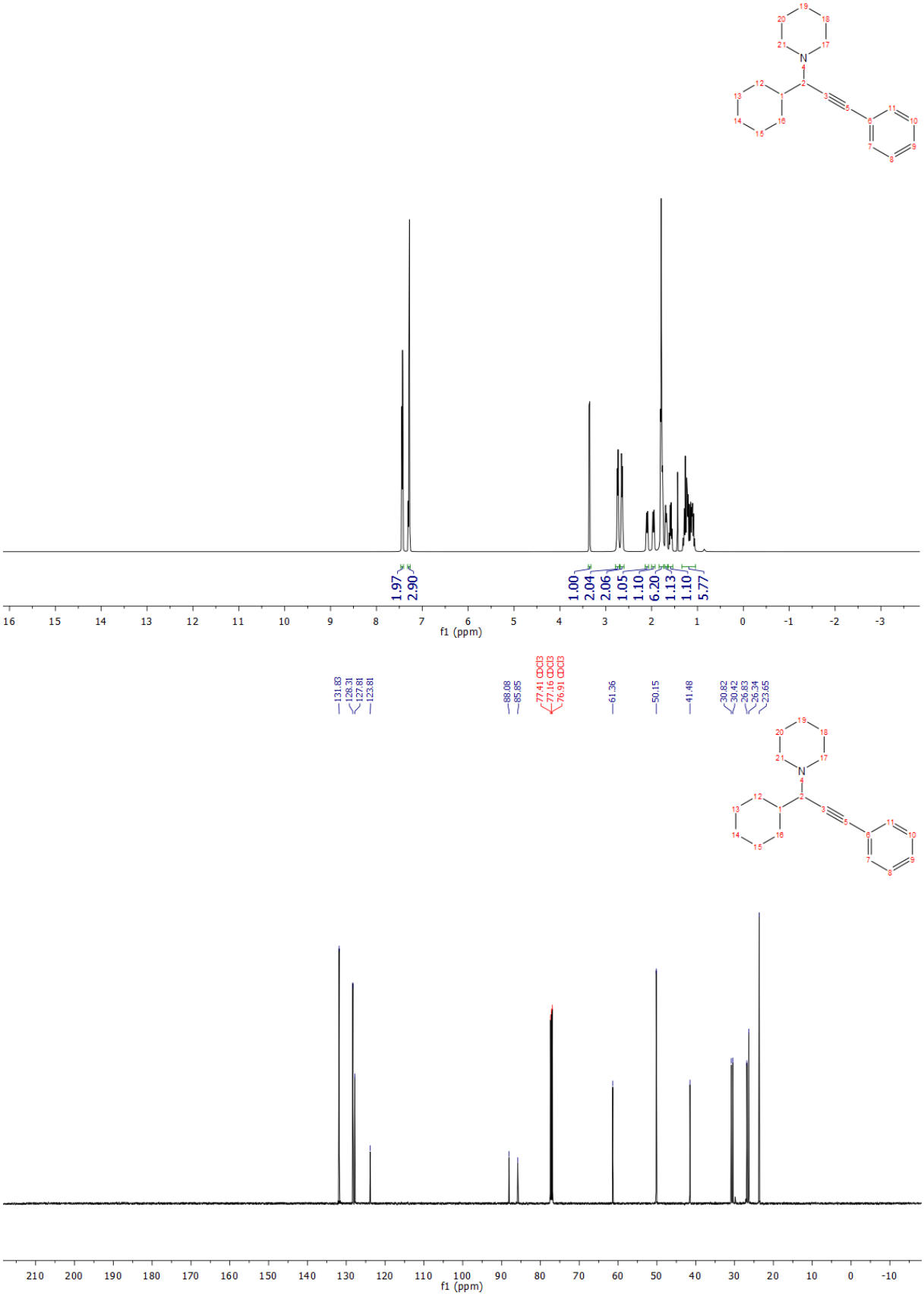
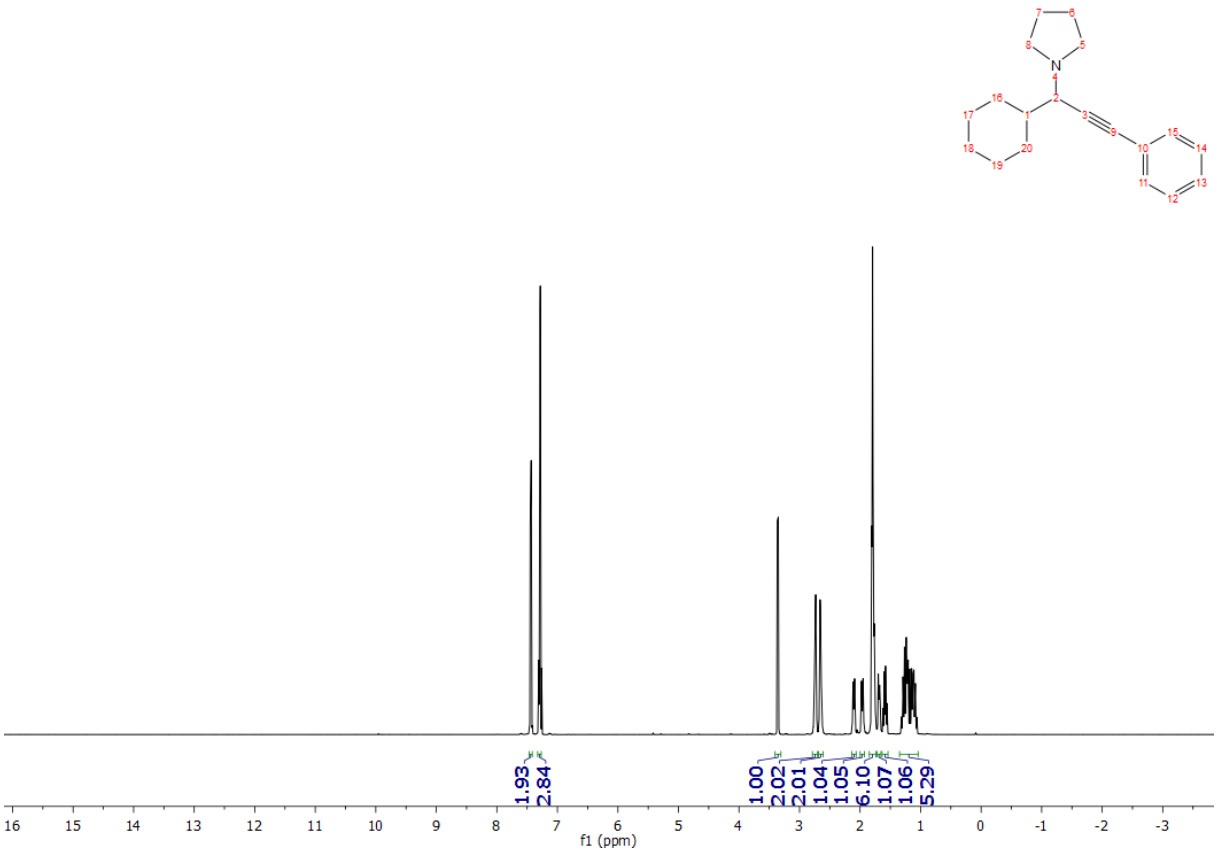


Figure S18. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 15.

Compound 16. ^{1}H NMR (500 MHz, Chloroform-d) δ: 7.50 – 7.37 (m, 2H), 7.37 – 7.22 (m, 4H), 3.37 (d, *J* = 8.4 Hz, 1H), 2.75 (tq, *J* = 6.5, 4.2, 3.5 Hz, 2H), 2.65 (qt, *J* = 7.6, 4.3 Hz, 2H), 2.10 (d, *J* = 13.3 Hz, 1H), 1.96 (d, *J* = 13.1 Hz, 1H), 1.85 – 1.73 (m, 6H), 1.73 – 1.64 (m, 1H), 1.66 – 1.53 (m, 1H), 1.35 – 1.02 (m, 5H).^{13}C NMR (126 MHz, $CDCl_3$) δ: 132.1 (2×CH), 128.6 (2×CH), 128.1 (CH), 124.0 (C), 88.2 (C≡C), 86.2 (C≡C), 61.6 (×CH), 50.4 (2×CH_2), 41.7 (CH_2), 31.1 (CH_2), 30.7 (CH_2), 27.1 (CH_2), 26.6 (CH_2), 23.9 (2×CH_2).



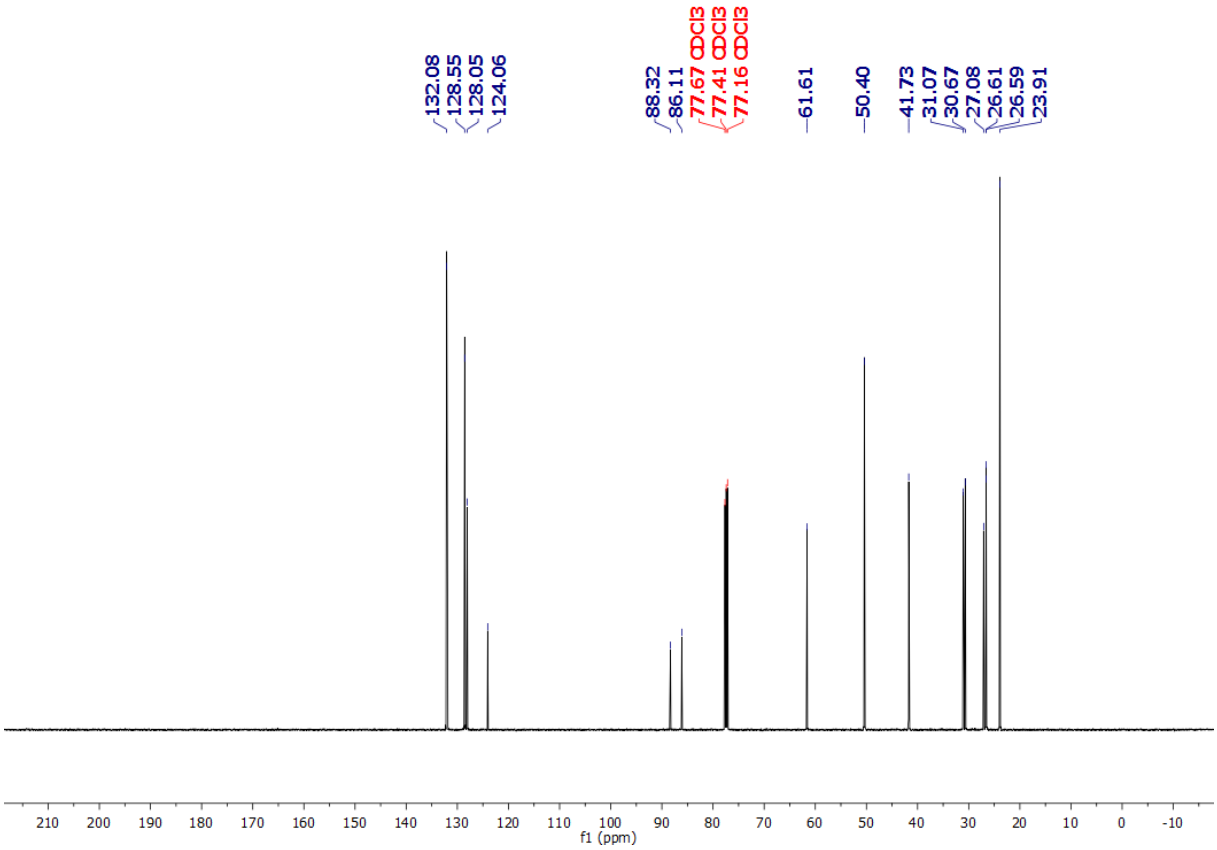


Figure S19. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 16.

Compound 17. ^{1}H NMR (500 MHz, Chloroform-d) δ: 7.47 – 7.40 (m, 2H), 7.34 – 7.25 (m, 3H), 3.82 – 3.68 (m, 4H), 3.13 (d, *J* = 9.8 Hz, 1H), 2.71 (ddd, *J* = 11.6, 6.2, 3.3 Hz, 2H), 2.52 (ddd, *J* = 11.3, 6.2, 3.3 Hz, 2H), 2.15 – 2.02 (m, 2H), 1.82 – 1.54 (m, 4H), 1.37 – 1.13 (m, 3H), 1.12 – 0.91 (m, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ: 131.8 (2×CH), 128.3 (2×CH), 127.9 (CH), 123.5 (C), 86.9 (C≡C), 86.7 (C≡C), 67.3 (2×CH2), 64.0 (CH), 49.9 (2×CH_2), 39.2 (2×CH_2), 31.1 (2×CH_2), 30.5 (2×CH_2), 26.8 (2×CH_2), 26.3 (2×CH_2), 26.1 (2×CH_2).

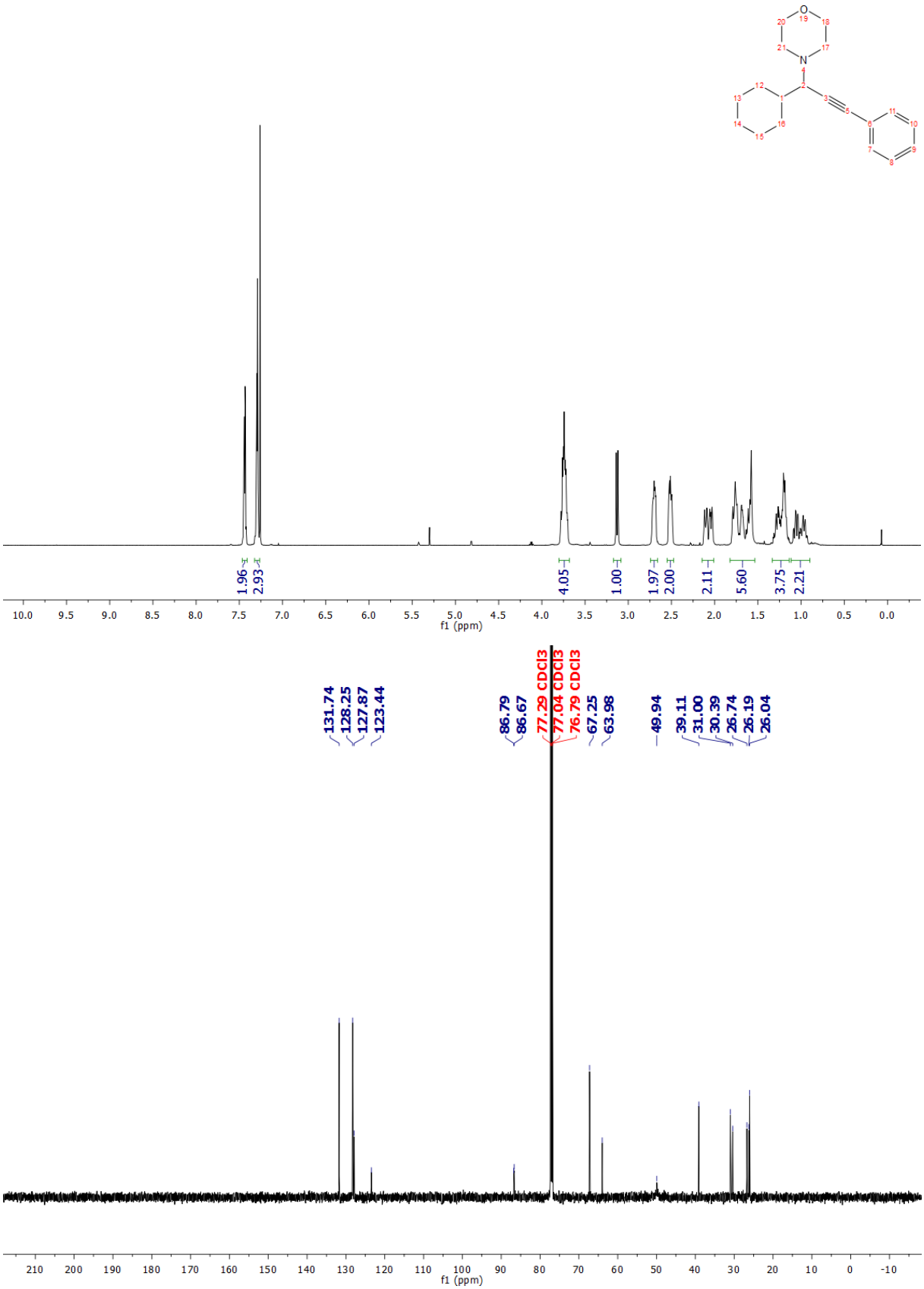
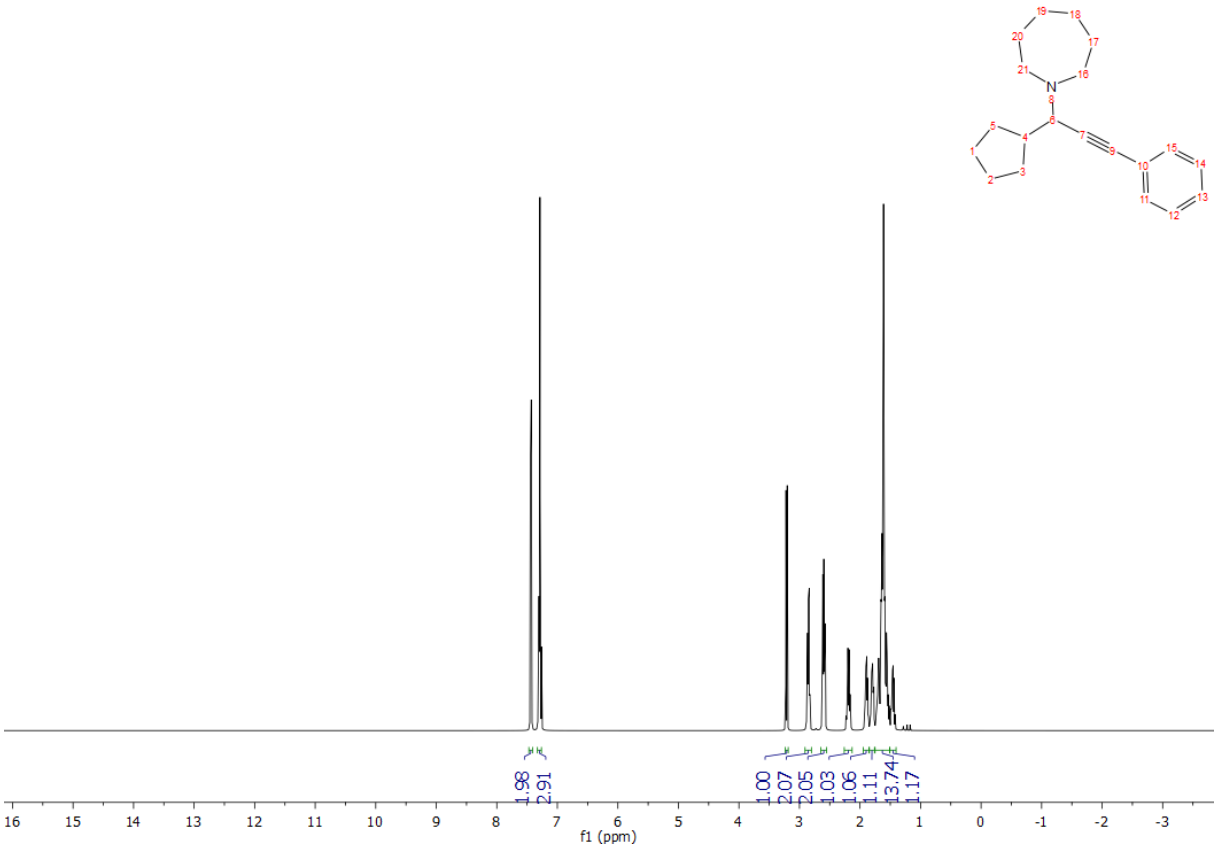


Figure S20. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 17.

Compound 18: ^{1}H NMR (500 MHz, Chloroform-d) δ: 7.48 –7.40 (m, 2H), 7.35 – 7.25 (m, 3H), 3.21 (d, *J* = 10.1 Hz, 1H), 2.85 (ddd, *J* = 10.8, 5.9, 2.9 Hz, 2H), 2.60 (ddd, *J* = 12.6, 7.7, 4.3 Hz, 2H), 2.19 (dp, *J* = 10.0, 7.6 Hz, 1H), 1.95 – 1.85 (m, 1H), 1.84 – 1.75 (m, 1H), 1.74 – 1.50 (m, 13H), 1.46 (dq, *J* = 12.7, 7.7Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 132.1 (2×CH), 128.5 (2×CH), 127.9 (CH), 124.3 (C), 89.9 (C≡C), 84.3 (C≡C), 64.7 (CH), 52.8 (2×CH_2), 43.9 (CH_2), 31.2 (CH_2), 30.8 (CH_2), 29.7(2×CH_2), 27.5 (2×CH_2), 25.9 (CH_2), 25.7 (CH_2).



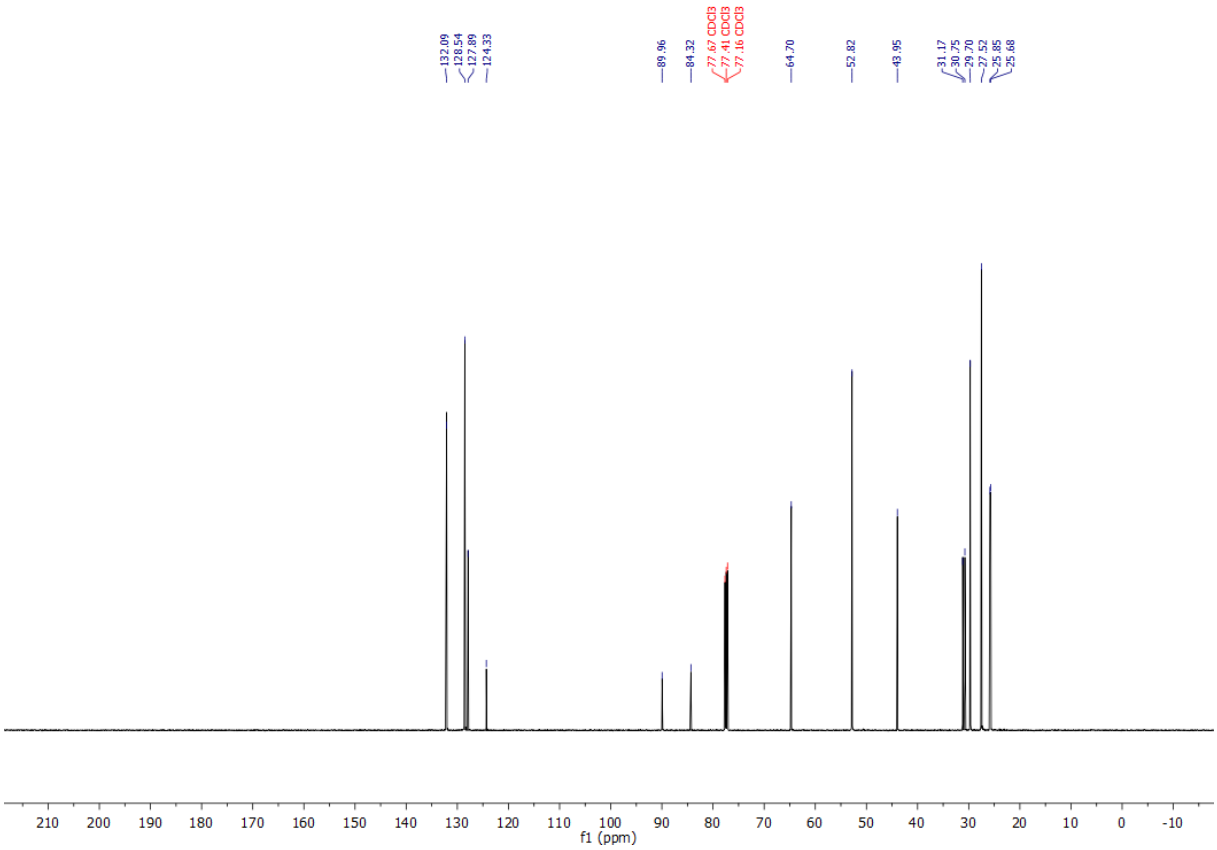


Figure S21. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 18.

Compound 19. ^{1}H NMR (500 MHz, Chloroform-d) δ: 7.41 – 7.32 (m, 2H), 6.85 – 6.77 (m, 2H), 3.80 (s, 3H), 3.32 (d, *J* = 8.4 Hz, 1H), 2.77-2.66 (m, 2H), 2.69-2.59 (m, 2H), 2.15-2.02 (m, 1H), 1.99-1.90 (m, 1H), 1.84 – 1.71 (m, 6H), 1.70 – 1.64 (m, 1H), 1.56(tdt, *J* = 11.6, 8.4, 3.4 Hz, 1H), 1.34 – 1.04 (m, 5H).^{13}C NMR (126 MHz, $CDCl_3$) δ: 159.5 (C), 133.4 (2×CH), 116.2 (CH), 114.2 (2×CH), 86.6 (C≡C), 85.8 (C≡C), 61.6 (CH), 55.6 (CH_2), 50.4 (CH_2), 41.7 (CH_2), 32.2 (CH_2), 31.9 (CH_2), 27.1 (CH_2), 26.6 (2×CH_2), 23.9 (2×CH_2).

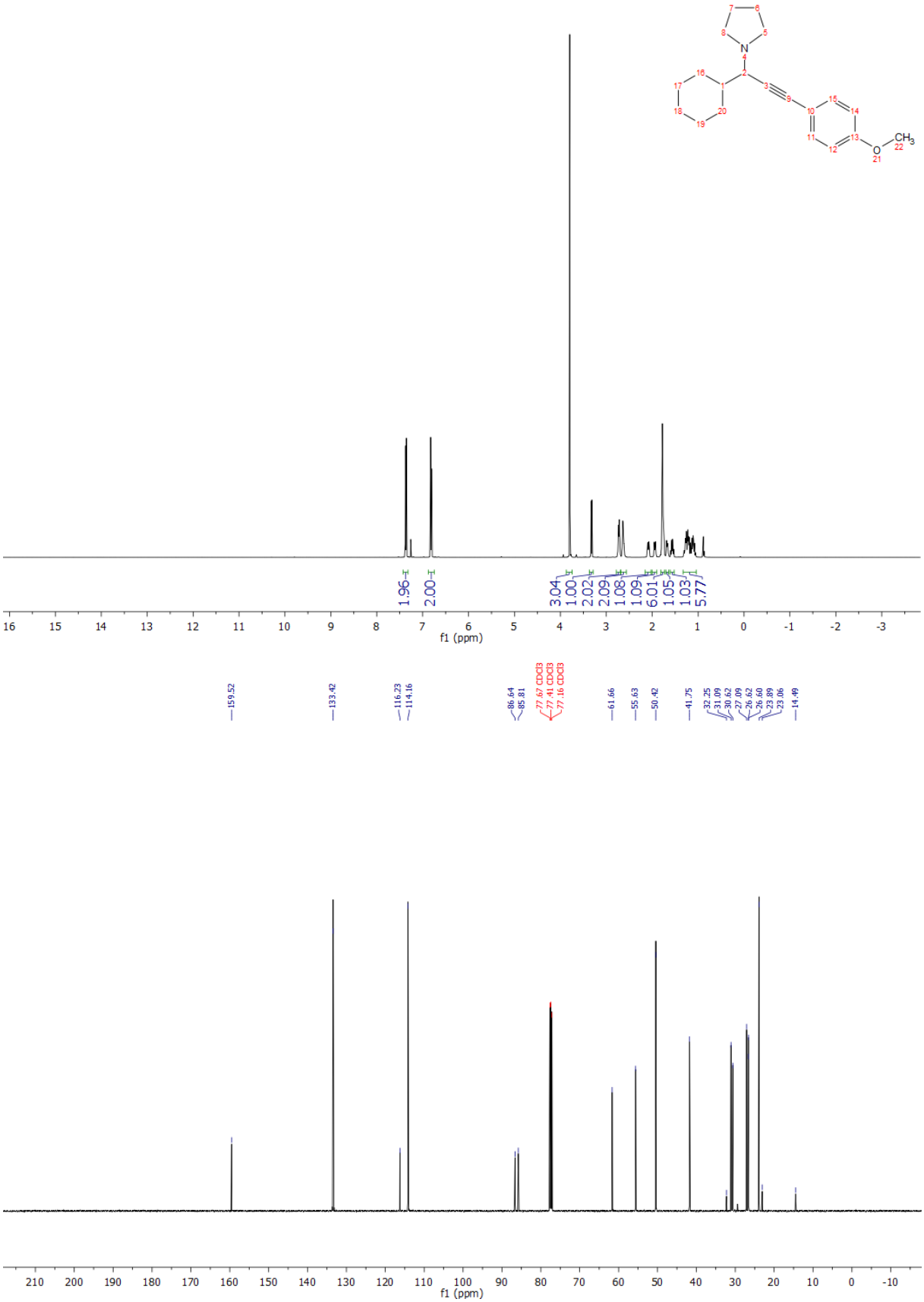
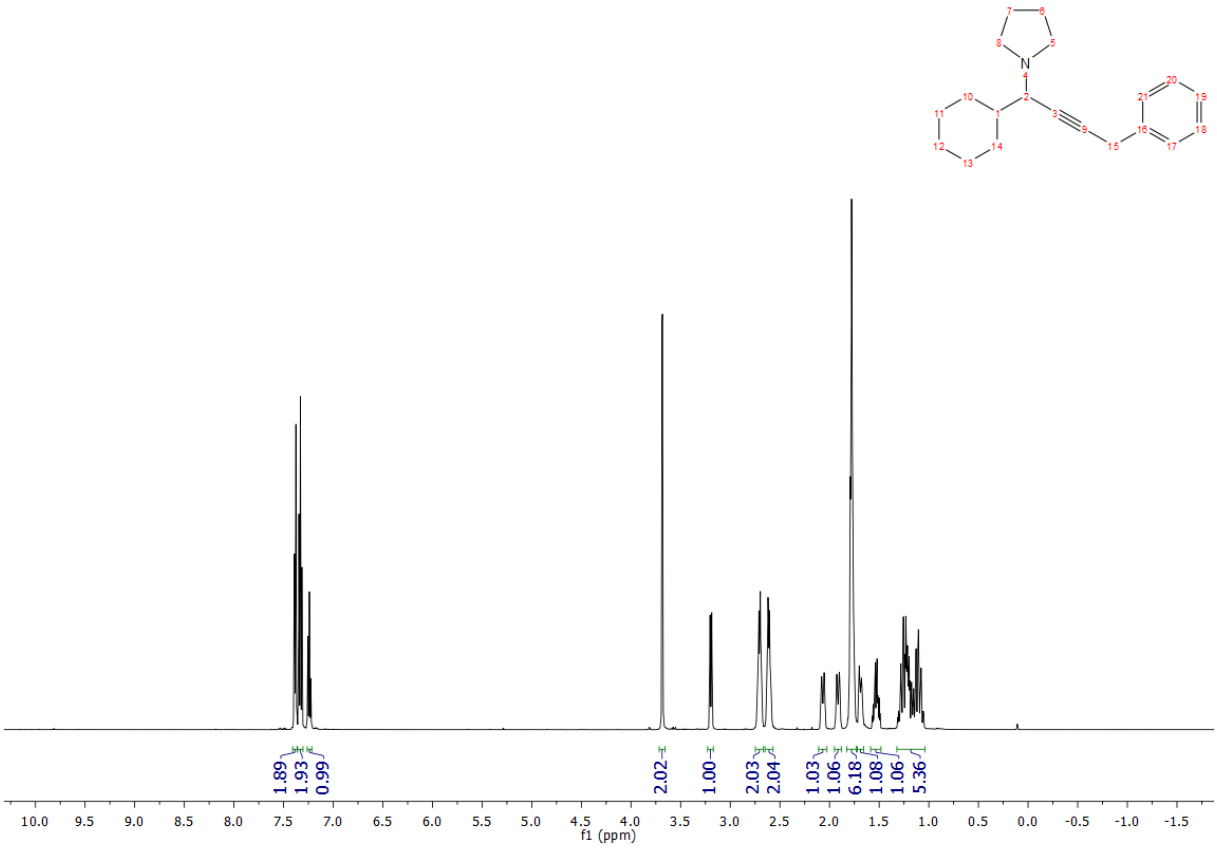


Figure S22. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 19.

Compound 20. ^{1}H NMR (500 MHz, Chloroform-d) δ: 7.38 (d, *J* = 7.2 Hz, 2H), 7.33 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.26 – 7.22 (m, 1H), 3.68 (d, *J* = 2.8 Hz, 2H), 2.11-2.02 (m, 1H), 1.95-1.88 (m, 1H), 1.83-1.72 (m, 4H), 1.72-1.65 (m, 1H), 1.53 (tdt, *J* = 11.5, 8.2, 3.5 Hz, 1H), 1.33 – 1.04 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 137.6 (C), 128.5 (2×CH), 127.9 (2×CH), 126.5 (CH), 82.8 (C≡C), 80.4 (C≡C), 61.1 (CH_2), 50.2 (2×CH_2), 41.4 (CH_2), 30.8 (CH_2), 30.2 (CH_2), 26.8 (CH_2), 26.4 (CH_2), 26.3 (CH_2), 25.2 (CH_2), 23.6 (2×CH_2).



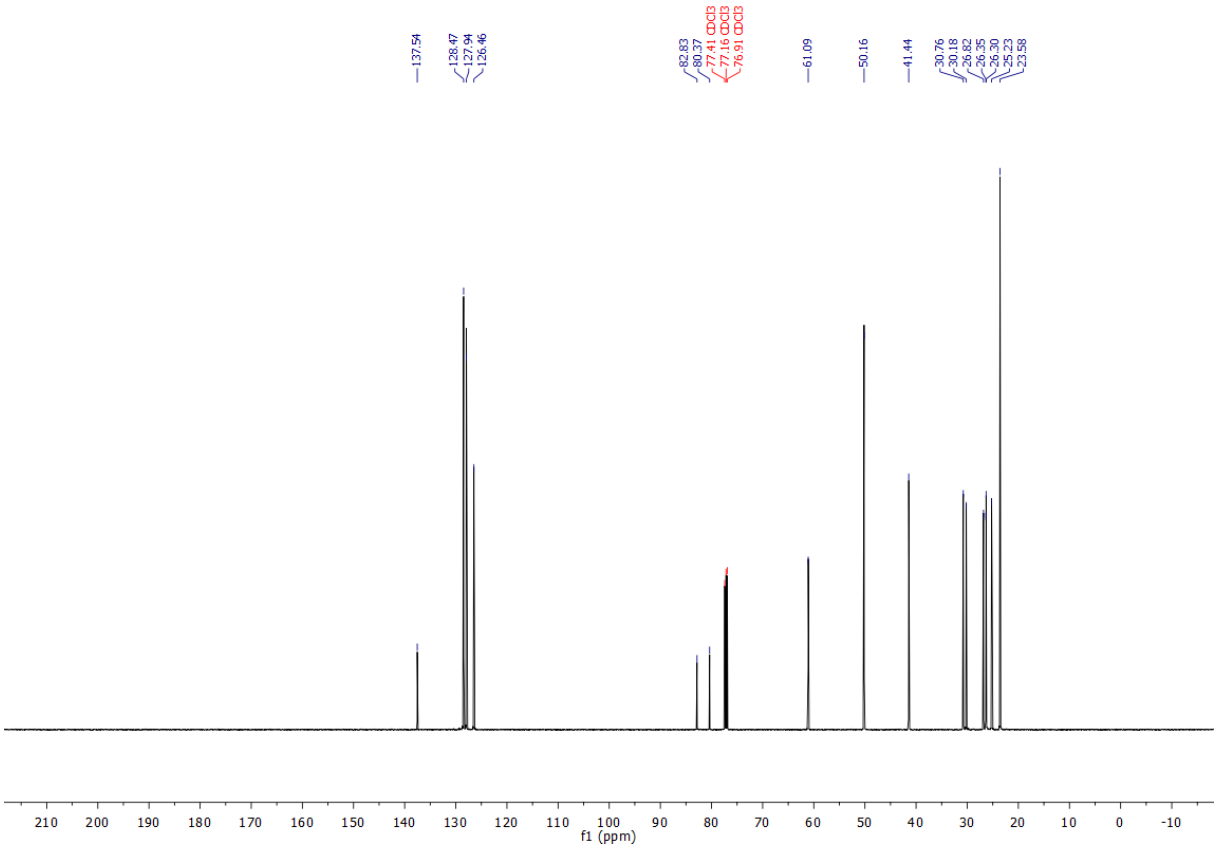


Figure S23. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 20.

Compound 21. ^{1}H NMR (500 MHz, Chloroform-d) δ: 3.03 (d, J = 7.9 Hz, 1H), 2.66-2.56 (m, 2H), 2.56-2.48 (m, 2H), 1.99-1.90 (m, 1H), 1.86-1.79 (m, 1H), 1.79 – 1.69 (m, 6H), 1.68 – 1.63 (m, 1H), 1.42 (tdt, J = 11.3, 7.9, 3.4 Hz, 1H), 1.21 (s, 9H), 1.23-1.44 (m, 2H), 1.09 – 0.97 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 94.6 (C≡C), 76.3 (C≡C), 61.3 (CH_2), 50.5 (2×CH_2), 41.7 (CH_2), 31.9 (3×CH_3), 31.1 (CH_2), 30.7 (CH_2), 27.9 (CH_2), 27.2 (CH_2), 26.7 (CH_2), 26.6 (CH_2), 23.8 (2×CH_2).

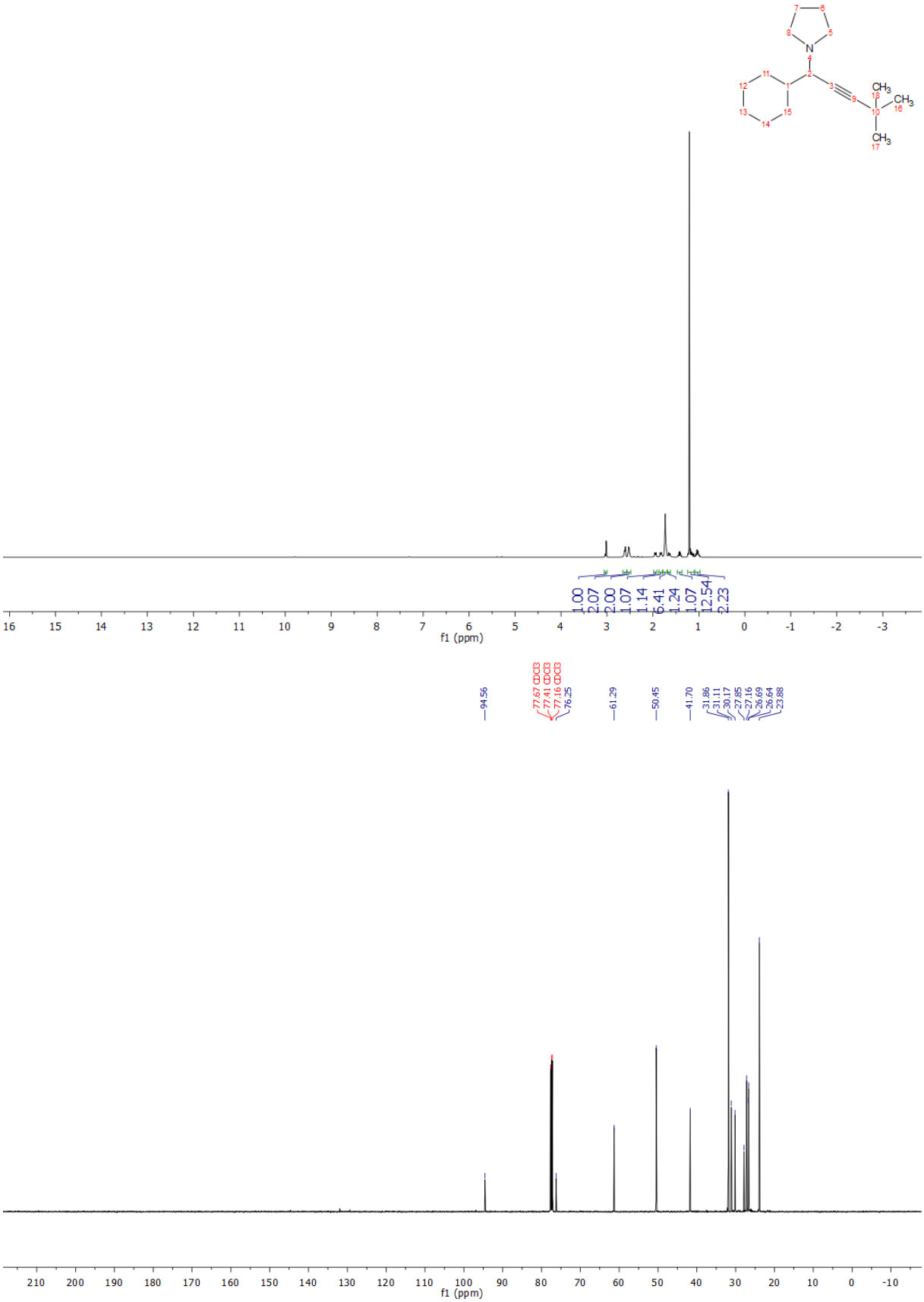
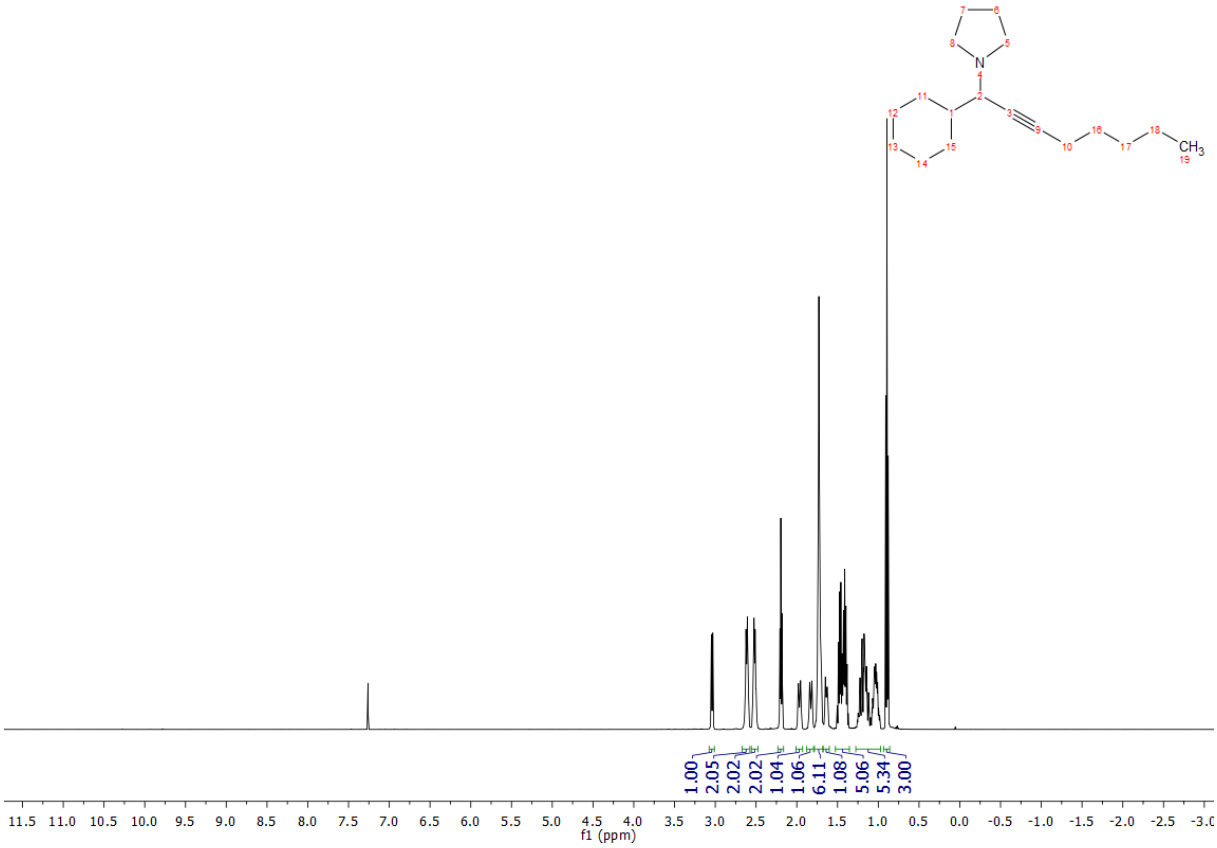


Figure S24. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 21.

Compound 22. ^{1}H NMR (500 MHz, Chloroform-d) δ: 3.04 (dt, *J* = 8.0, 2.1 Hz, 1H), 2.65-2.58 (m, 2H), 2.56-2.49 (m, 2H), 2.19 (td, *J* = 6.9, 2.1 Hz, 2H), 2.00-1.92 (m, 1H), 1.88-1.79 (m, 1H), 1.78 – 1.68 (m, 6H), 1.68 – 1.59 (m, 1H), 1.53 – 1.35 (m, 5H), 1.29 – 0.97 (m, 5H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 85.6 (C≡C), 77.8 (C≡C), 61.1 (CH_2), 50.2 (2×CH_2), 41.5 (CH_2), 31.4 (CH_2), 30.8 (CH_2), 30.0 (CH_2), 26.8 (CH_2), 26.4 (CH_2), 26.3 (CH_2), 23.6 (2×CH_2), 22.1 (CH_2), 18.5 (CH_2) 13.7 (CH_3).



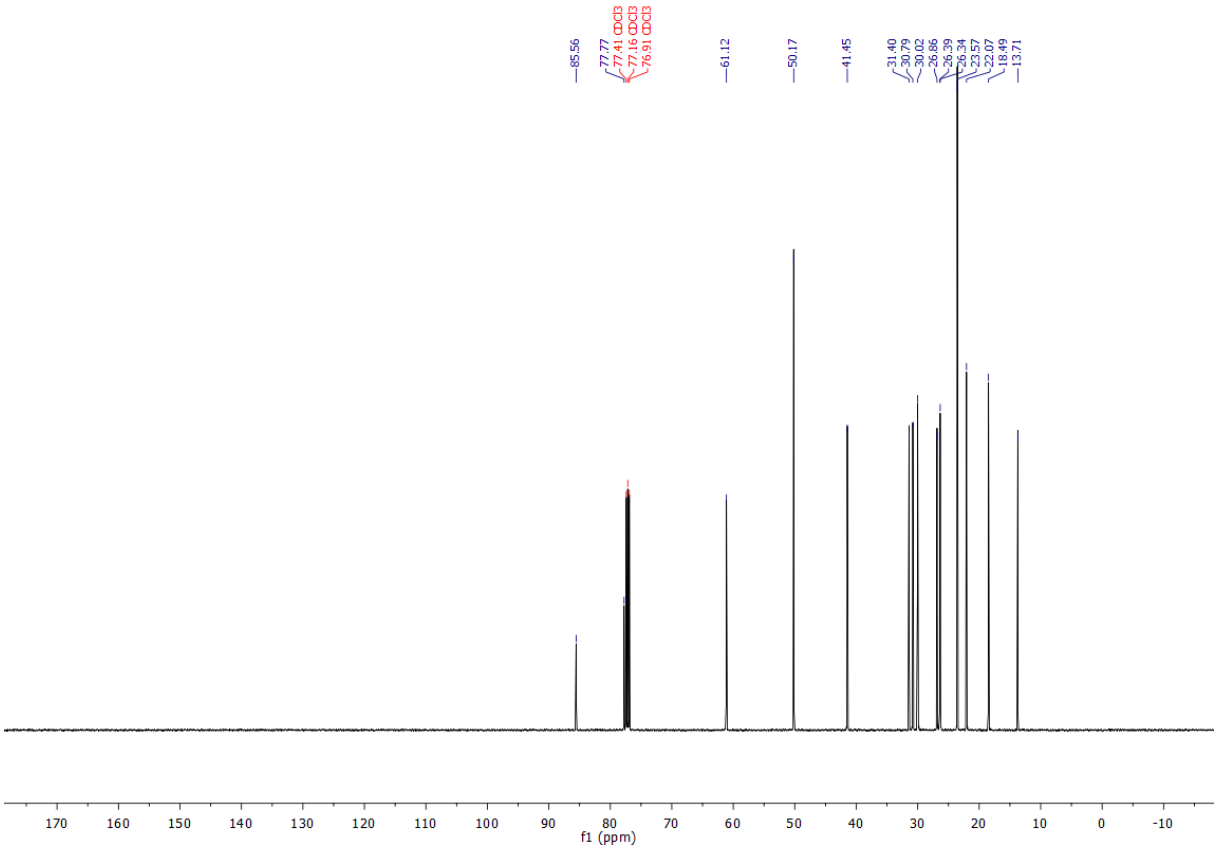


Figure S25. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 22.

Compound 23: ^{1}H NMR (500 MHz, Chloroform-d) δ: 7.63 – 7.61 (m, 2H), 7.52 – 7.49 (m, 2H), 7.39 – 7.29 (m, 6H), 4.95 (s, 1H), 2.74 – 267 (m, 4H), 1.85 – 1.76 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 139.6 (C), 131.8 (2×CH), 128.3 (4×CH), 128.1 (2×CH), 127.6 (2×CH), 123.3 (CH), 86.9 (C≡C), 86.7 (C≡C), 59.2 (CH), 50.3 (2× CH_2), 23.5 (2×CH_2).

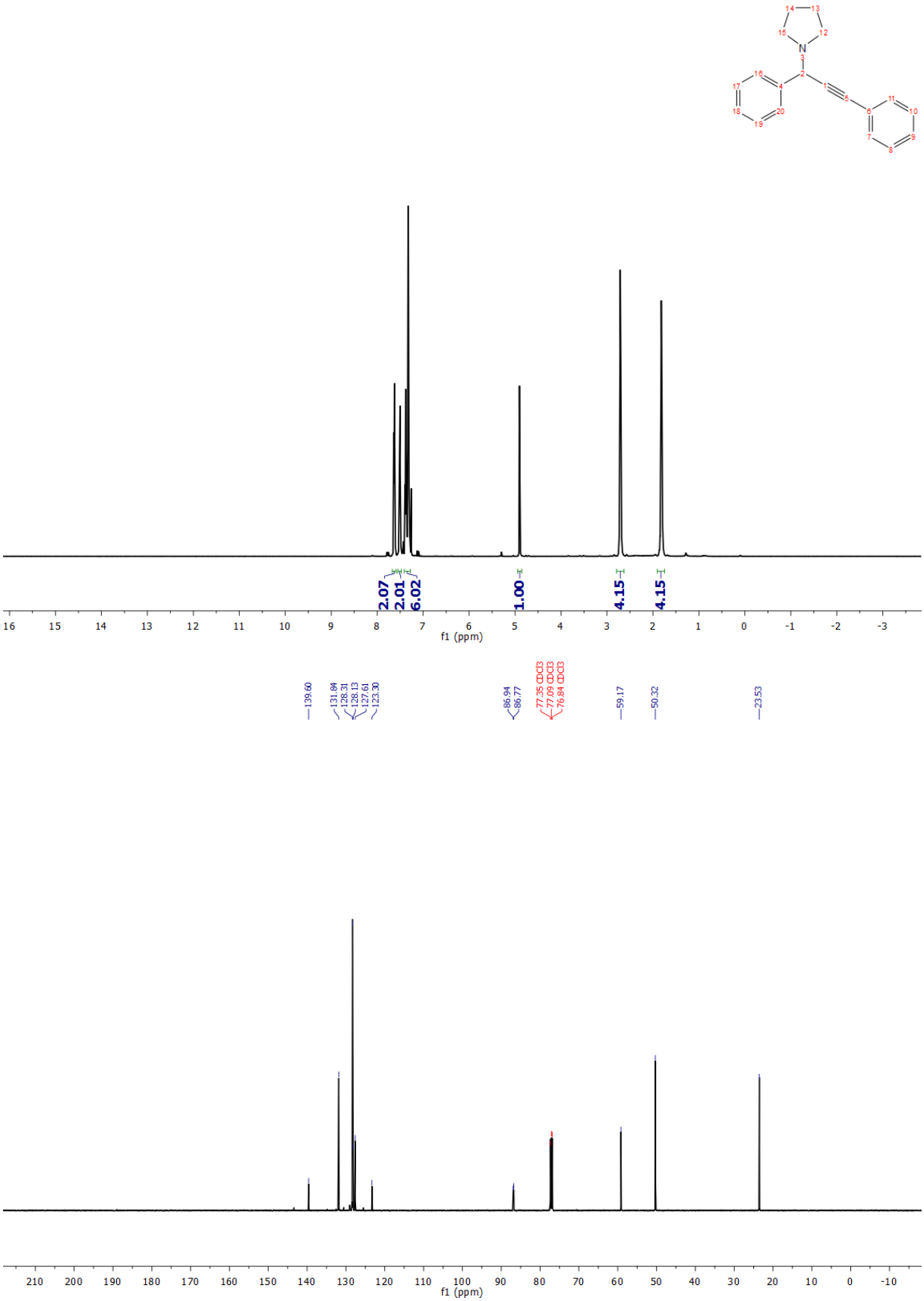
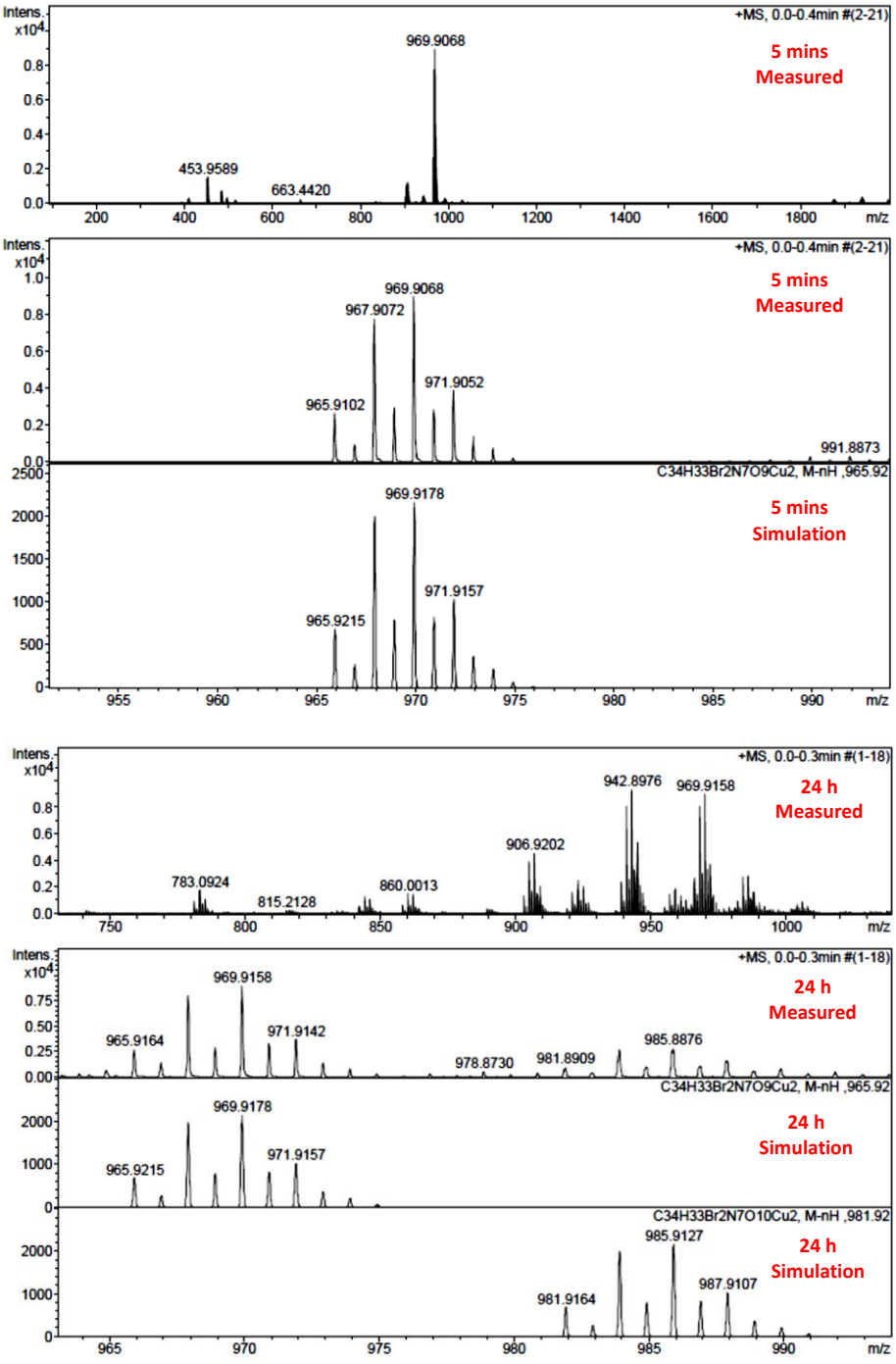


Figure S26. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 23.

Stability test of catalyst followed by mass spectrometry.



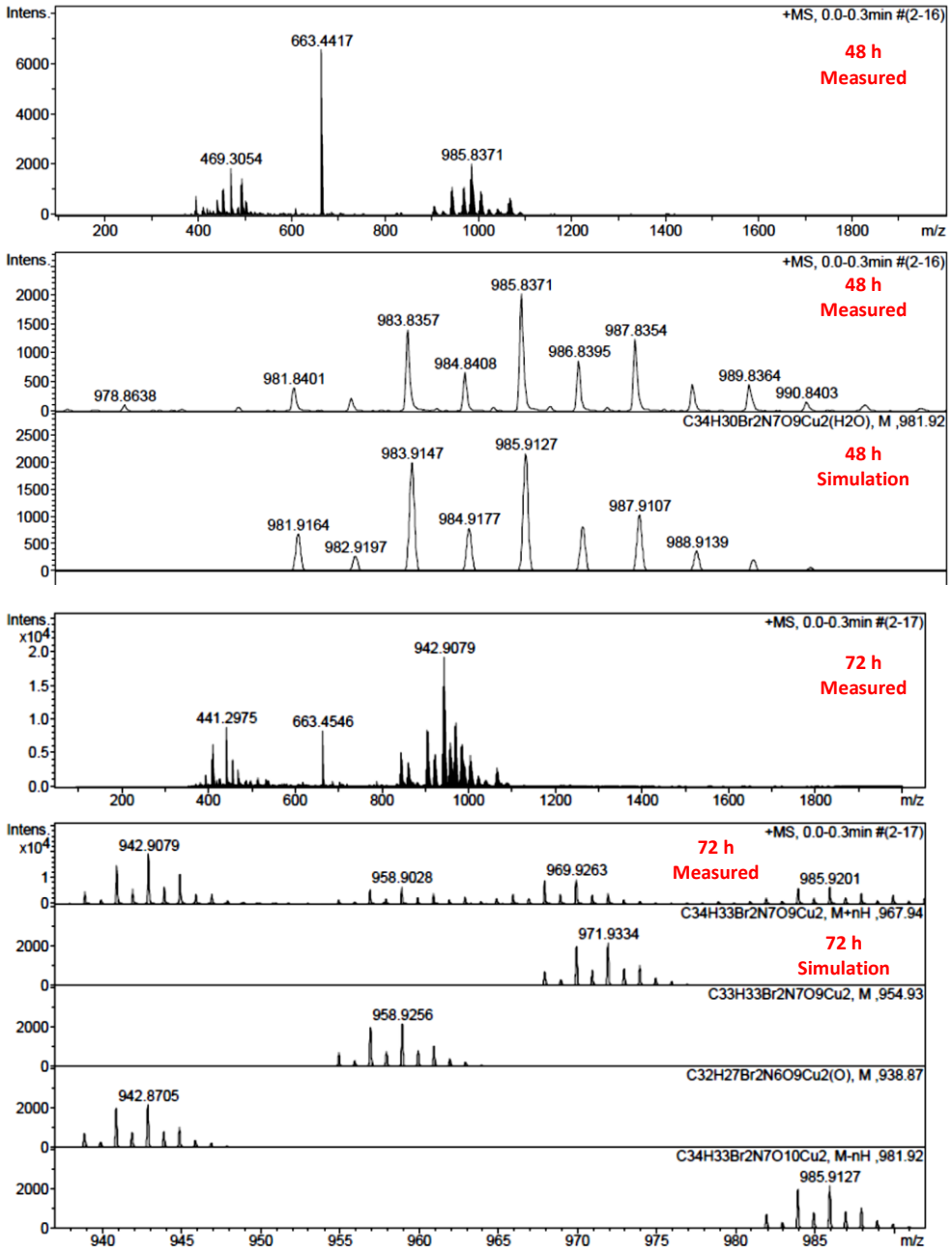


Figure S27. Mass spectra of Cu-catalyst dissolved in *i*-PrOH.