Electronic supplementary information

Iron hexamesityl-5,15-diazaporphyrin: Synthesis, structure and catalytic use for direct oxidation of sp^3 C–H bonds

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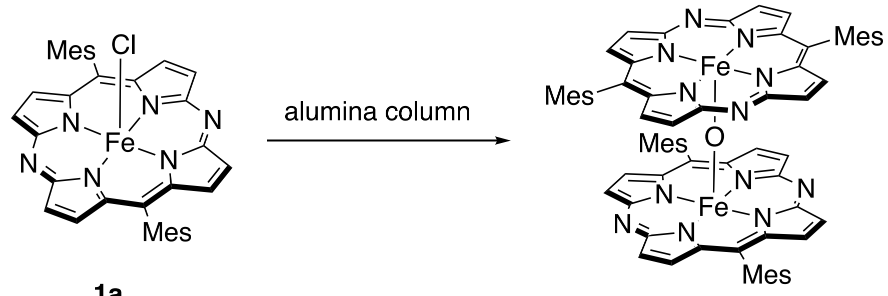
Instrumentation and Materials

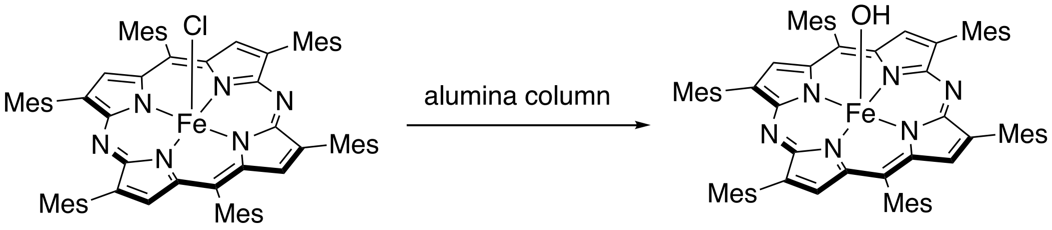
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were recorded on a Bruker AVANCE III HD spectrometer, and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ (δ 7.26 ppm) for ^{1}H NMR and $CHCl_3$ (δ 77.16 ppm) for ^{13}C NMR. UV/vis absorption spectra were recorded on a Shimadzu UV-2550. Mass spectra were recorded on a Bruker microTOF using positive mode ESI-TOF method for 2-propanol solutions and positive mode APCI-TOF method. X-ray data were taken on a Rigaku CCD diffractometer (Saturn 724 with MicroMax-007) with Varimax Mo optics using graphite monochromated Mo-Kα radiation (λ = 0.71075 Å) or a Bruker D8 QUEST X-ray diffractometer equipped with PHOTON 100 CMOS active pixel sensor detector and IμS micro focus source using Mo-Kα radiation (λ = 0.71073 Å). Elemental analysis were recorded on a ParkinElmer 2400II. Redox potentials were measured by cyclic voltammetry method on an ALS electrochemical analyzer model 612C. Time profile analyses were performed by Shimadzu-GC-2025 instrument with FID detector and CBP10 capillary column (25 m × 0.22 mm). Benzene, dichloromethane, and toluene were dried by the general methods, and degassed before use. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Reactions of 1a and 1b with alumina column.



1a **6**

The solution of **1a** (12.7 mg, 20.0 μmol) in $CHCl_3$ was passed through a short column chromatography (Al_2O_3, eluent: $CHCl_3$) and then evaporated to give *μ*-oxo dimer **6** (10.7 mg, 8.77 μmol, 88%). ^{1}H NMR ($CDCl_3$): *δ* 14.50, 14.37, 7.62, 7.10, 2.60, 2.16, 0.900. HRMS (ESI): Calcd. for $C_{72}H_{60}N_{12}Fe_2O$ $[M+H]^+$: 1221.3785. Found: 1221.3826.



1b **7**

The solution of **1b** (22.2 mg, 20.0 μmol) in $CHCl_3$ was passed through a short column chromatography (Al_2O_3, eluent: $CHCl_3$) and then evaporated to give **7** (20.1 mg, 18.4 μmol, 92%). ^{1}H NMR ($CDCl_3$): *δ* 86.71, 11.94, 11.66, 11.06, 10.15, 7.15, 5.82, 5.77, 4.26, 3.37, 2.55. HR MS (APCI): Calcd. for $C_{72}H_{71}N_6OFe$ $[M^+]$: 1091.5033. Found: 1091.4993.

Catalytic oxidations of 8 catalyzed by 1

A typical experimental procedure for the catalytic oxidation of alkanes is described below. In a 20 mL Schlenk tube were placed **1b** (2.22 mg, 2.00 μmol) under N_2, and then a dry benzene (5.0 mL), cyclooctane (673 μL, 5.00 mmol) and iodosylbenzene (220.1 mg, 1.00 mmol) was added. After the mixture was stirred for 3 h at room temperature, remained iodosylbenzene was removed by the filtration through Celite pad, and then the solvent was removed in *vacuo*. Yield was determined by ^{1}H NMR measurement (1,1,2,2-tetrachloroethane was used as an internal standard).

Time profile of oxidation of cyclooctane.

In a 20 mL Schlenk tube were placed **1b** (2.22 mg, 2.00 μmol) and biphenyl as an internal standard under N_2, and then a dry benzene (5.0 mL), cyclooctane (673 μL, 5.00 mmol) and iodosylbenzene (220.0 mg, 1.00 mmol) was added. the oxidation reaction was monitored over time at 15 °C by GC analysis.

Oxidation of cyclooctane by sequential addition of PhIO

A typical experimental procedure for the catalytic oxidation is described below. In a 20 mL Schlenk tube were placed **1b** (2.22 mg, 2.00 μmol) under N_2, and then a dry benzene (5.0 mL), cyclooctane (1.34 mL, 10.0 mmol). Iodosylbenzene (220.1 mg, 1.00 mmol, 220.0 mg, 1.00 mmol, 220.0 mg, 1.00 mmol) was added in a stepwise per 1 h. After the addition of PhIO of 3.0 mmol, the reaction mixture is stirred for 24 h in total at room temperature. Yield was determined by GC analysis.

X-Ray Diffraction Analysis

A crystal suitable for X-ray analysis of **2b**, **6•C_6H_{14}** and **7•C_8H_{18}** were obtained by recrystallization from dichloromethane/methanol and hot octane. X-ray diffraction data for **2b**, **6•C_6H_{14}** and **7•C_8H_{18}** were taken on a Bruker D8 QUEST X-ray diffractometer equipped with PHOTON 100 CMOS active pixel sensor detector and IμS micro focus source using Mo-Kα radiation (λ = 0.71073 Å) or a Rigaku CCD diffractometer (Saturn 724 with MicroMax-007) with Varimax Mo optics using graphite monochromated Mo-Kα radiation (λ = 0.71075 Å). All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed in idealized positions and refined as rigid atoms with the relative isotropic displacement parameters. Crystallographic data for the structures of **2b**, **6•C_6H_{14}** and **7•C_8H_{18}** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2071242 (**2b**), CCDC-2071243 (**6•C_6H_{14}**) and CCDC-2071244 (**7•C_8H_{18}**). This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data of **2b**, **6•C_6H_{14}** and **7•C_8H_{18}**

compound	**2b**	**6•C_6H_{14}**	**7•C_8H_{18}**
Formula	$C_{72}H_{72}N_6$	$C_{78}H_{74}Fe_2N_{12}O$	$C_{80}H_{89}FeN_6O$
Formula weight	1021.35	1307.19	1206.42
Crystal system	monoclinic	Triclinic	monoclinic
Space group	*C* 2/*c*	*P*−1	*C* 2/*c*
Crystal color	black	purple	black
Crystal description	prism	prism	block
a [Å]	30.8193(16)	11.8870(8)	21.0219(6)
b [Å]	12.6917(7)	13.2939(10)	26.3677(6)
c [Å]	16.8411(9)	23.5461(16)	13.5664(4)
α [°]	90	78.373(2)	90
β [°]	116.726(2)	89.739(2)	95.128(2)
γ [°]	90	65.489(2)	90
V [Å^3]	5883.6(6)	3303.0(4)	7489.7(4)
Z	4	2	4
d_{calcd} [g cm^{-3}]	1.153	1.314	1.070
$R1$ ($F^2 < 2\sigma < (F^2)$)	0.0453	0.0402	0.0761
*R*w (all data)	0.1164	0.1029	0.2350
GOF	1.055	1.054	1.088
Temperature [K]	93	98	93
Structure solution	SHELXT[S1]	SHELXT[S1]	SHELXT[S1]
Structure refinement	SHELXL[S1]	SHELXL[S1]	SHELXL[S1]

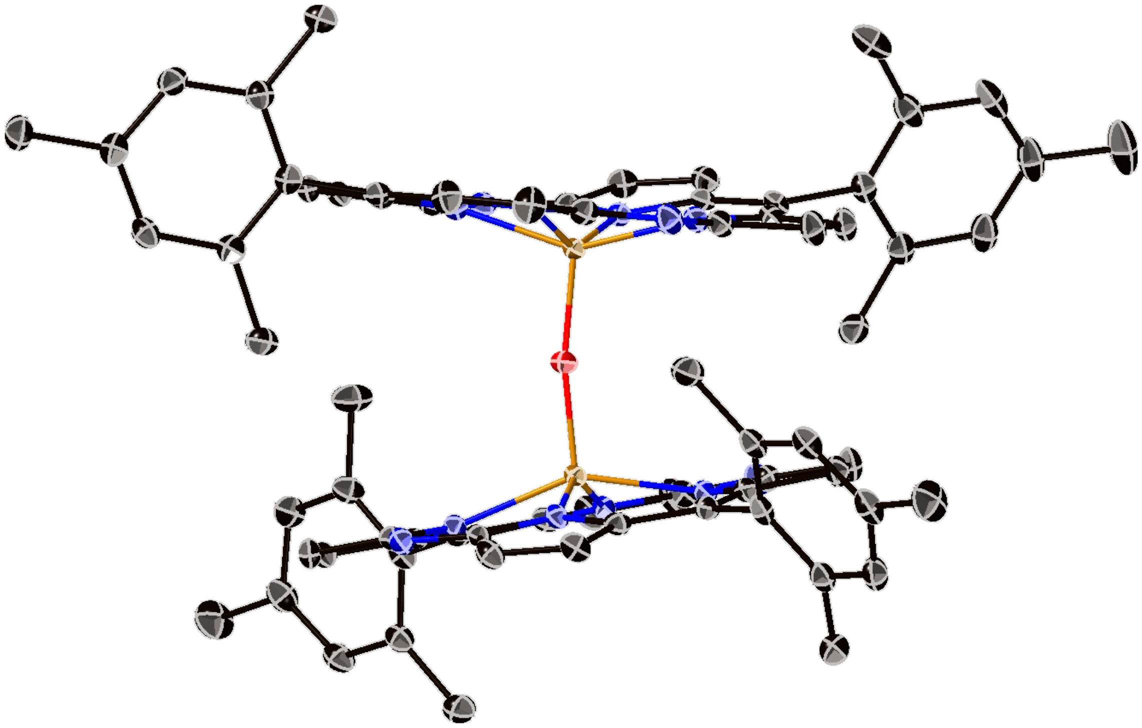


Fig. S1. Molecular structure of **6** in the crystalline state. All hydrogen atoms and solvents are omitted for clarity and thermal ellipsoids are shown at 50% probability.

Electrochemical Measurement

Electrochemical measurements were recorded on ALS electrochemical analyser 612C. Measurements of the iron complexes (0.1 mM) were performed in chlorobenzene with $n\text{Bu}_4\text{NPF}_6$ as an electrolyte (0.1M). A platinum electrode, a platinum wire and Ag/AgNO_3 were used as working, counter, and reference electrodes, respectively. The scan rate was 100 mVs^{-1}. The measurement was performed after bubbling of nitrogen gas. All potentials are referenced to the potential of ferrocene/ferrocenium cation couple.

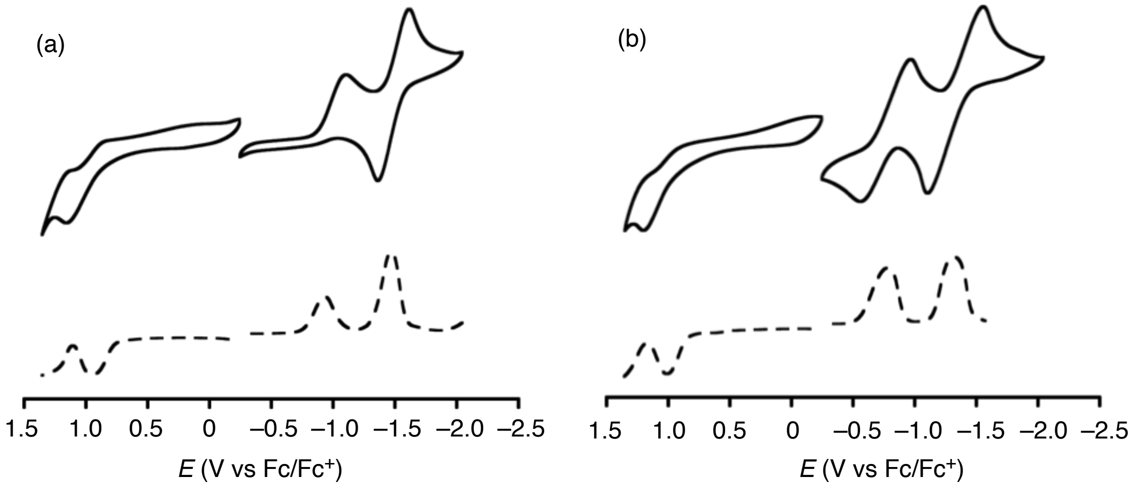


Fig. S2. Cyclic Voltammograms of iron complexes. (a): **1b**, (b): **1a**. (solid line: cyclic voltammetry, dashed line differential pulse voltammetry)

Reference

(S1) Crystal structure refinement with SHELXL, G. M. Sheldrick, *Acta Cryst*. 2015, **C71**, 3-8.

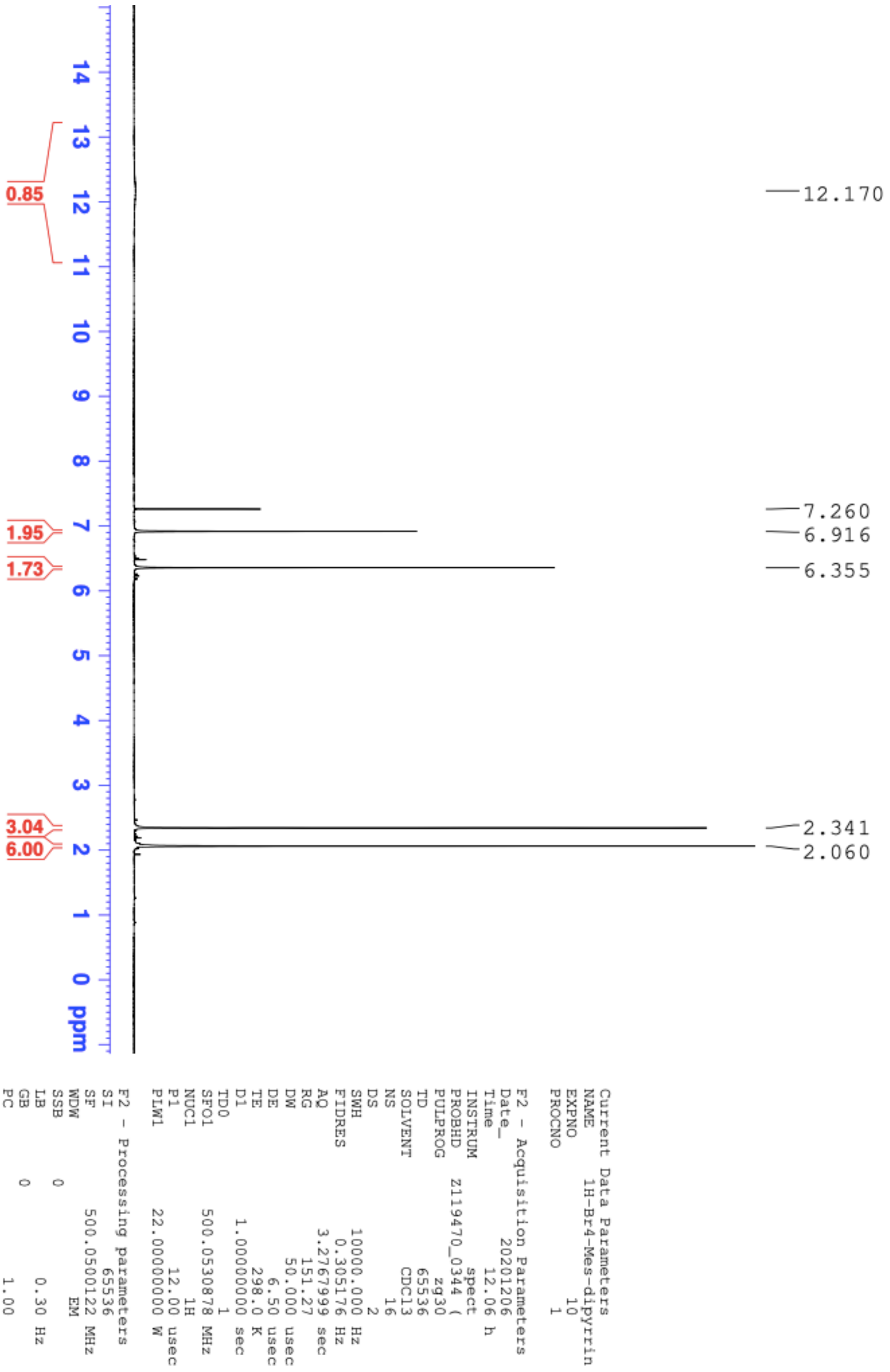
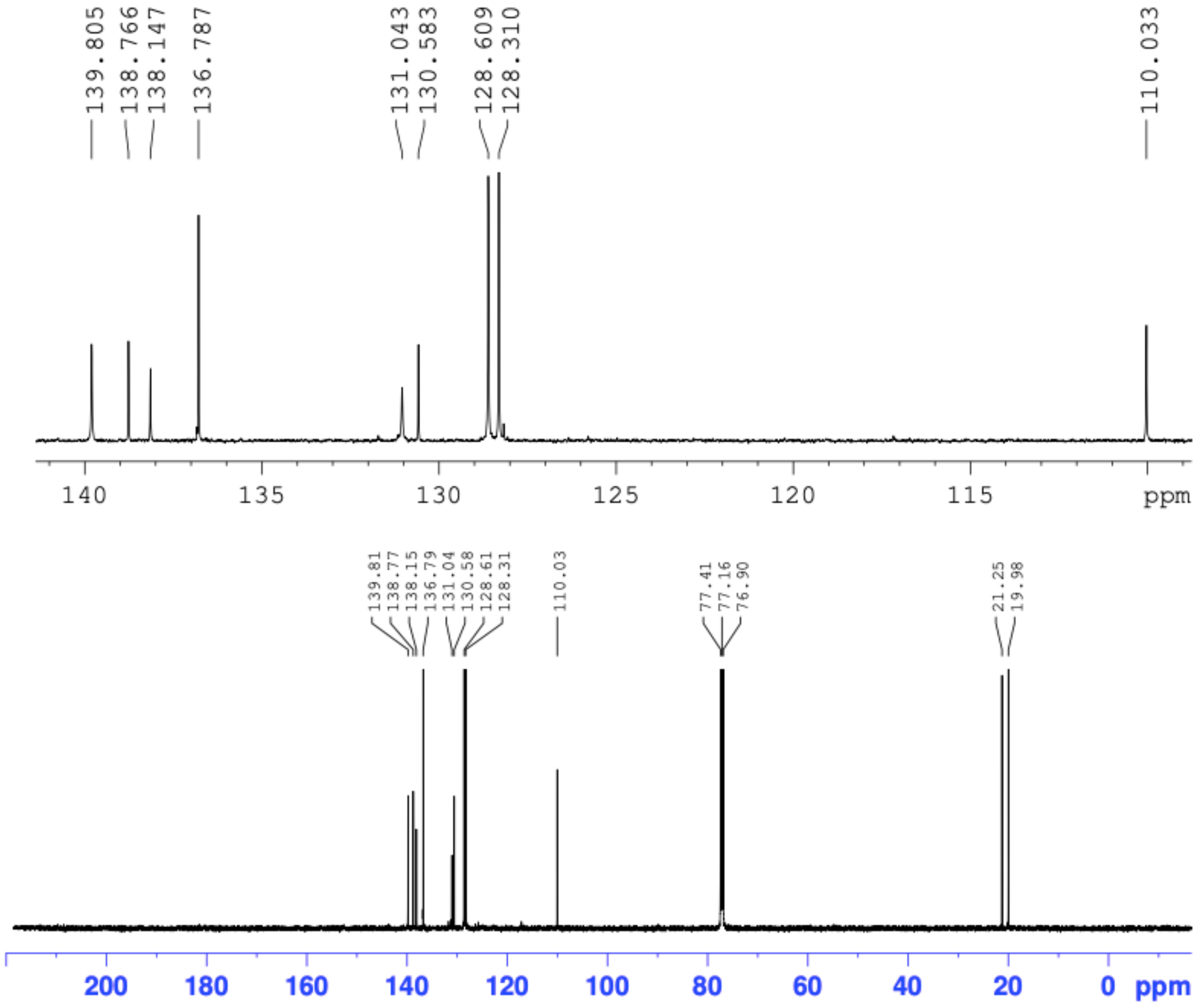


Fig. S3. ^{1}H NMR spectrum of **4** in $CDCl_3$



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PROCNO                       1

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PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    4000
DS                       4
SWH             29761.904 Hz
FIDRES           0.908261 Hz
AQ              1.1010048 sec
RG                  190.44
DW                  16.800 usec
DE                    6.50 usec
TE                   299.6 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1
SFO1         125.7502463 MHz
NUC1                   13C
P1                   10.00 usec
PLW1          83.00000000 W
SFO2         500.0520002 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2          22.00000000 W
PLW12          0.49500000 W
PLW13          0.24898000 W

F2 - Processing parameters
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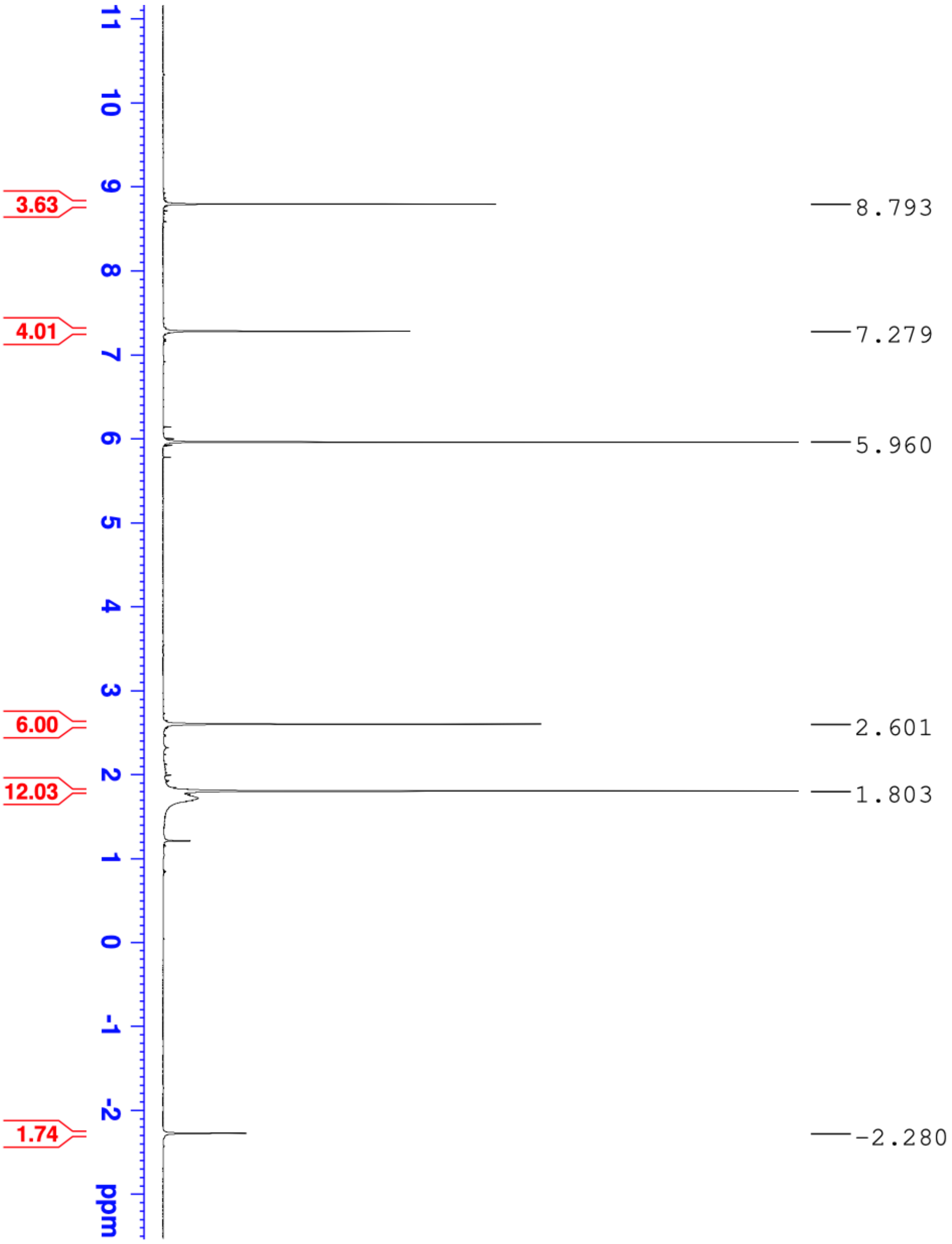
Fig. S4. ^{13}C NMR spectrum of **4** in $CDCl_3$



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PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     2
SWH            10000.000 Hz
FIDRES          0.305176 Hz
AQ             3.2767999 sec
RG                 135.3
DW                50.000 usec
DE                  6.50 usec
TE                 294.1 K
D1            1.00000000 sec
TD0                    1
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NUC1                  1H
P1                 13.80 usec
PLW1         13.00000000 W

F2 - Processing parameters
SI                 65536
SF           500.1106625 MHz
WDW                   EM
SSB      0
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PC                  1.00
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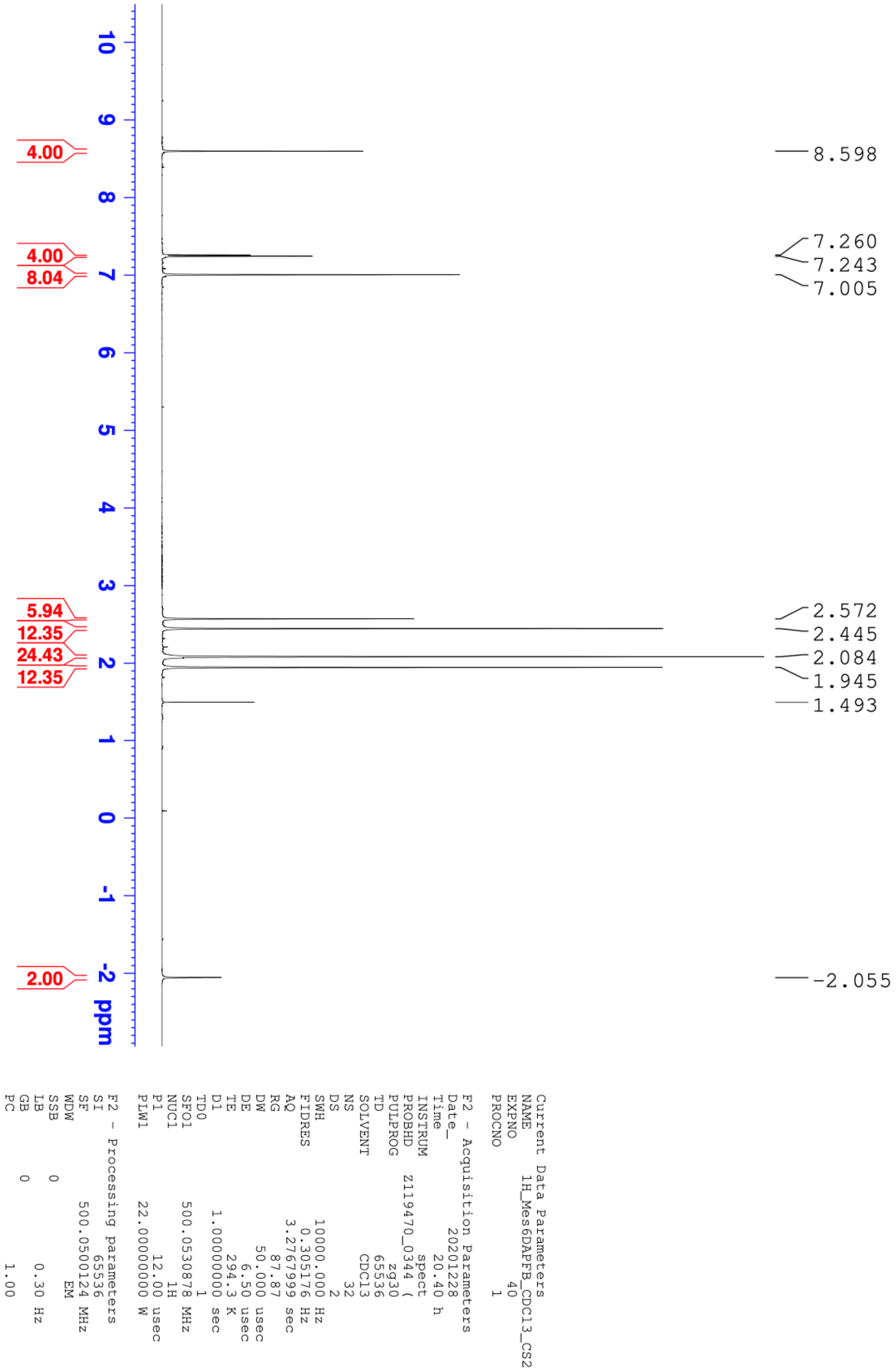
Fig. S5. ^{1}H NMR spectrum of **5** in 1,1,2,2-tetrachloroethane-d_2



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PROCNO                    1

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TD                    65536
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NS                       32
DS                        2
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FIDRES             0.305176 Hz
AQ                3.2767999 sec
RG                    87.87
DW                   50.000 usec
DE                     6.50 usec
TE                    294.3 K
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TD0                       1
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NUC1                     1H
P1                    12.00 usec
PLW1            22.00000000 W

F2 - Processing parameters
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SF              500.0500124 MHz
WDW                      EM
SSB      0
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GB       0
PC                     1.00
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Fig. S6. ^{1}H NMR spectrum of **2b** in $CDCl_3/CS_2$

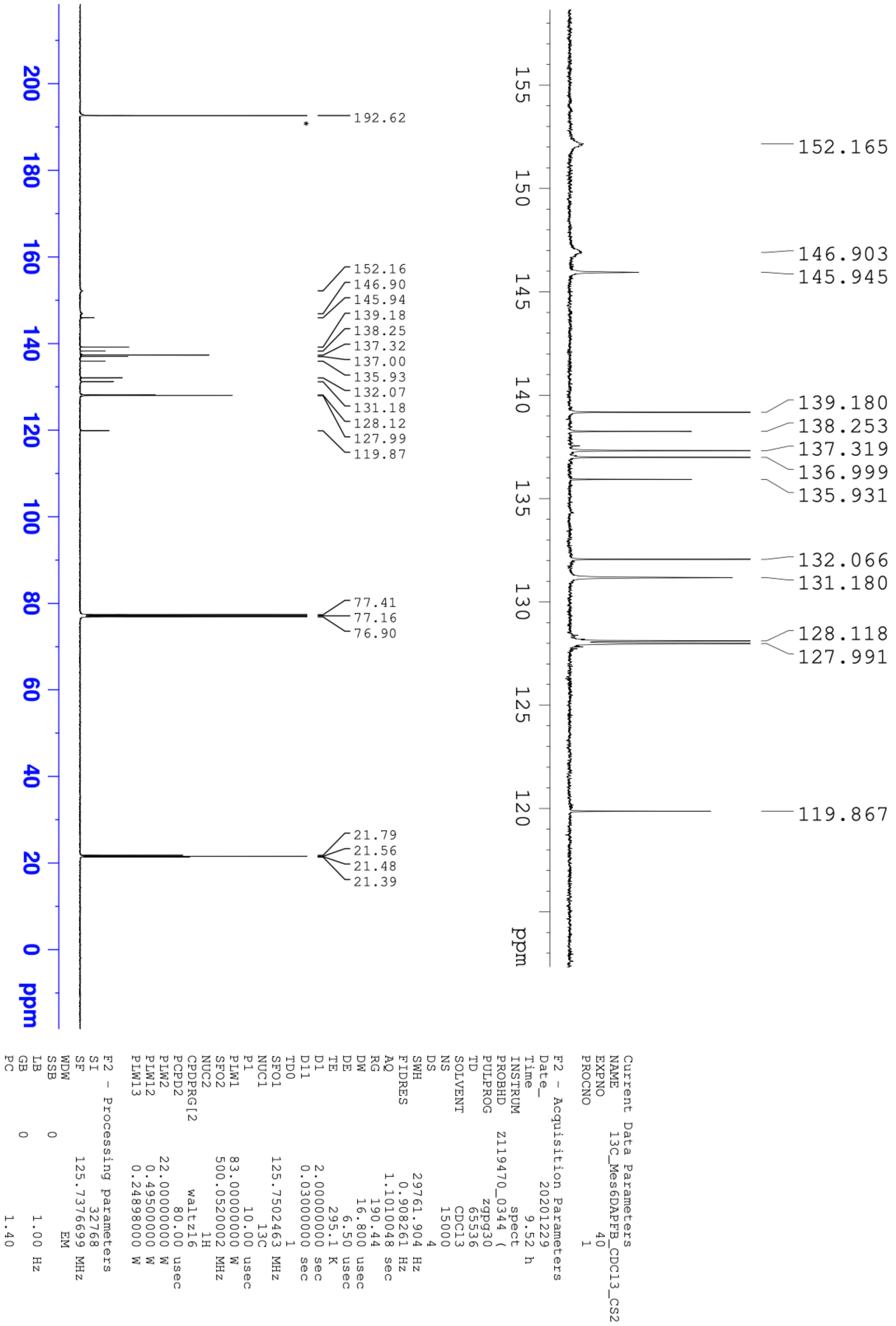


Fig. S7. ^{13}C NMR spectrum of **2b** in CDCl$_3$/CS$_2$

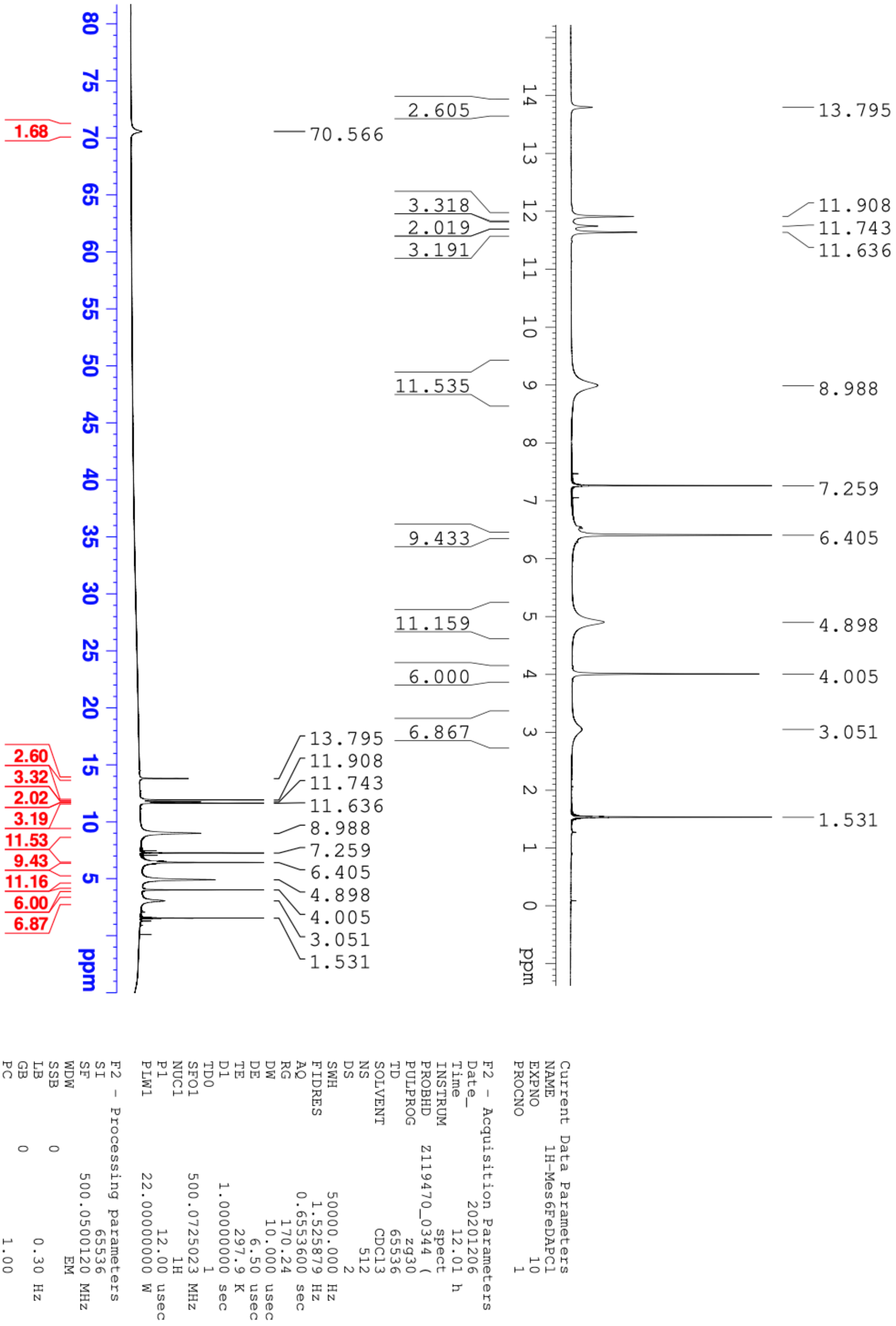
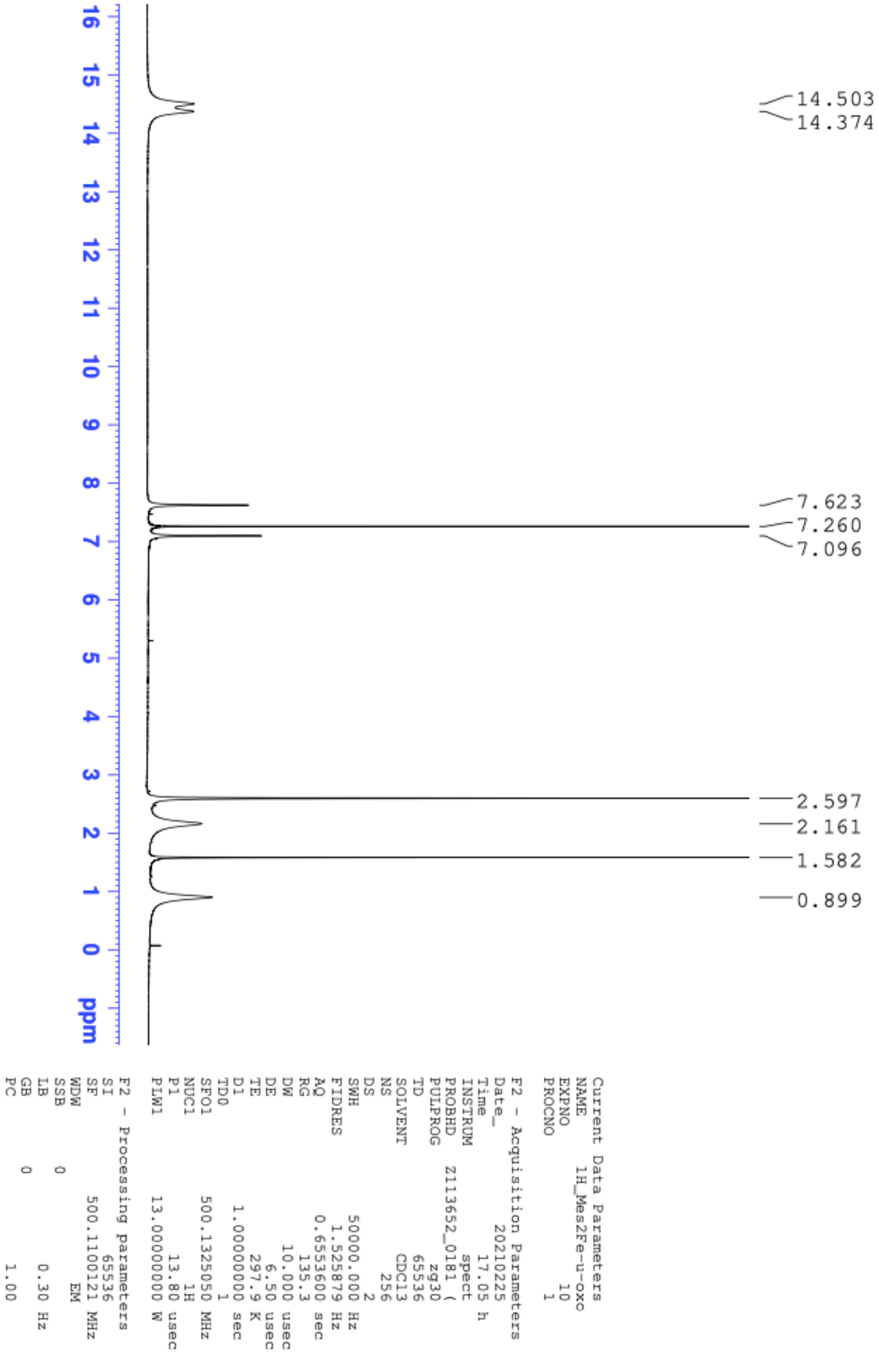


Fig. S8. ^{1}H NMR spectrum of **1b** in CDCl$_3$



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EXPNO                 10
PROCNO                 1

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PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     2
SWH            50000.000 Hz
FIDRES          1.525879 Hz
AQ             0.6553600 sec
RG                 135.3
DW                10.000 usec
DE                  6.50 usec
TE                 297.9 K
D1            1.00000000 sec
TD0                    1
SFO1         500.1325050 MHz
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P1                 13.80 usec
PLW1         13.00000000 W

F2 - Processing parameters
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SF           500.1100121 MHz
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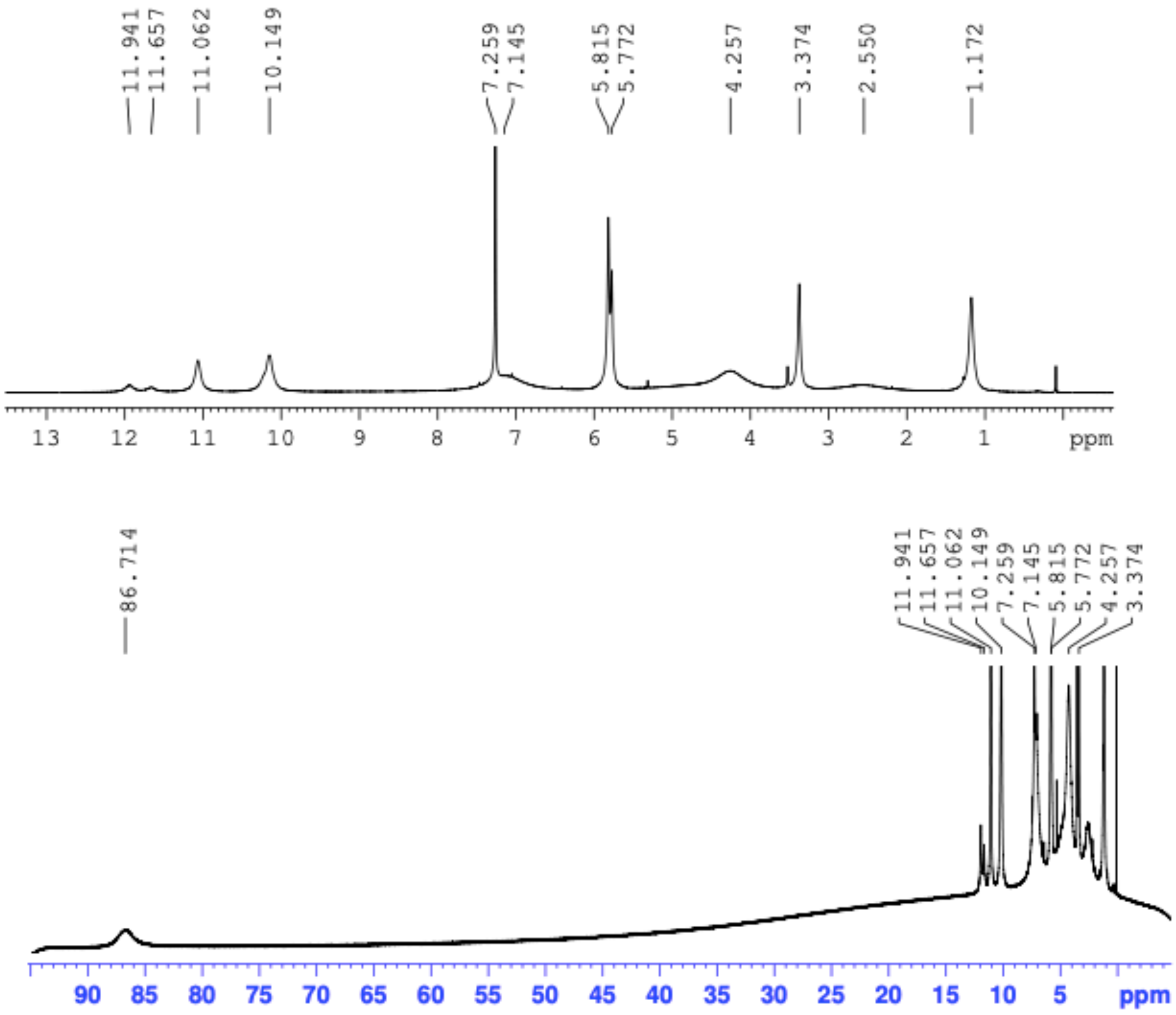
Fig. S9. ^{1}H NMR spectrum of **6** in CDCl$_3$



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PROCNO                  1

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PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                    512
DS                      2
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FIDRES           1.525879 Hz
AQ              0.6553600 sec
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DW                 10.000 usec
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TE                  297.8 K
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P1                  13.80 usec
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F2 - Processing parameters
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SF            500.1100120 MHz
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Fig. S10. ^{1}H NMR spectrum of **7** in $CDCl_3$

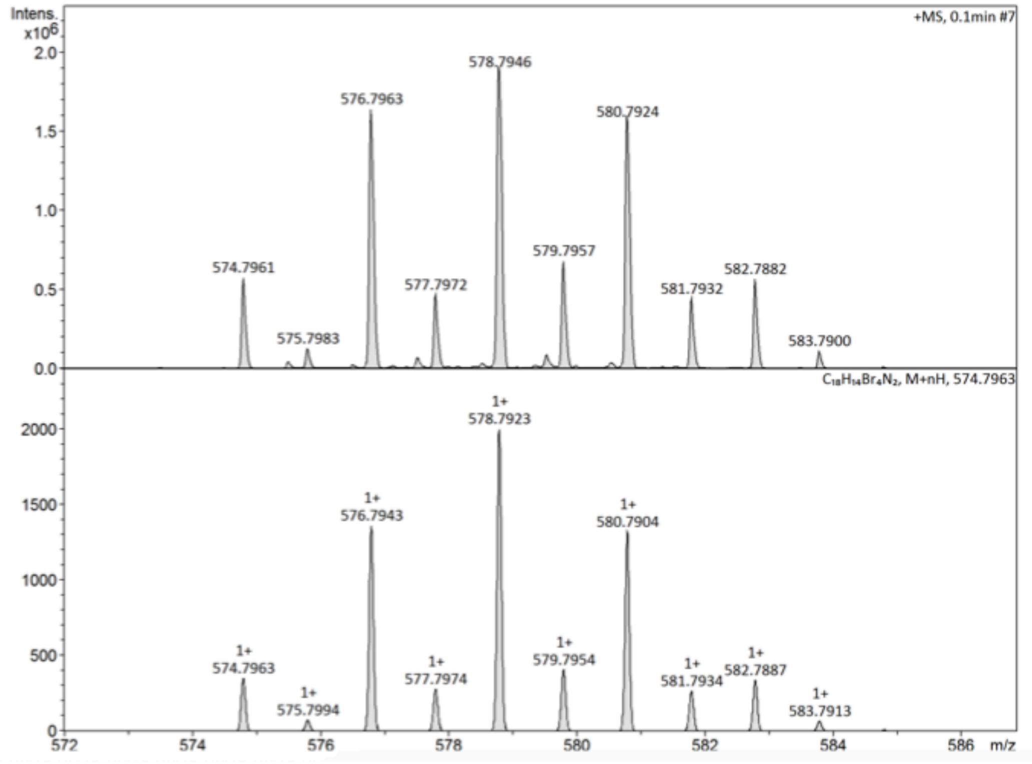

Fig. S11. APCI-MS spectrum of **4** (top: observed, bottom: simulated).

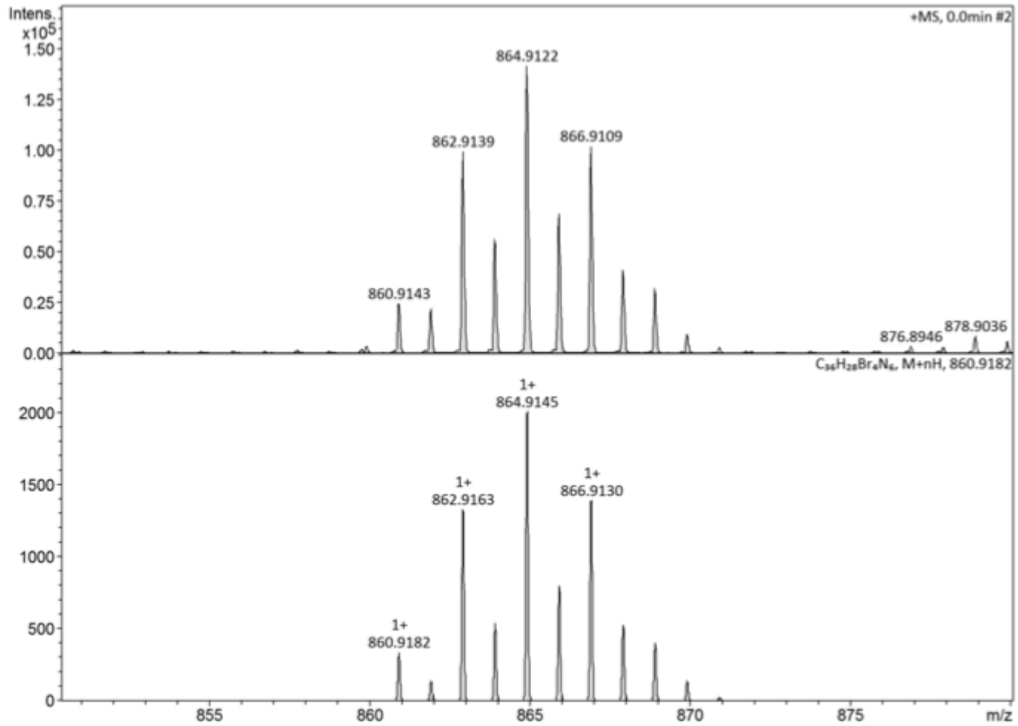

Fig. S12. APCI-MS spectrum of **5** (top: observed, bottom: simulated).

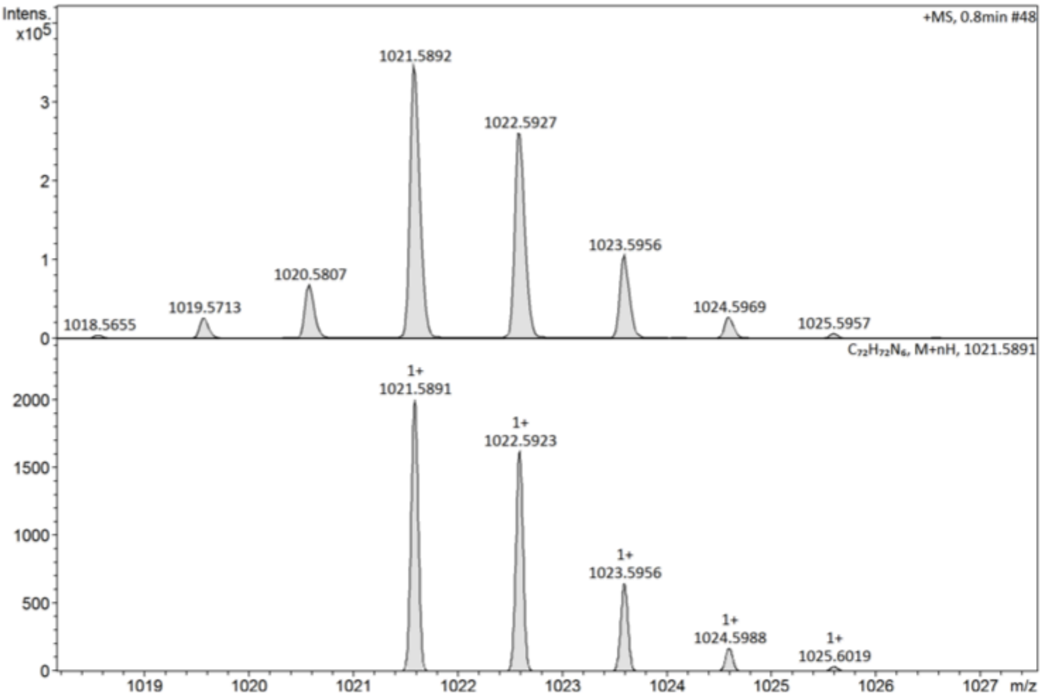

Fig. S13. APCI-MS spectrum of **2b** (top: observed, bottom: simulated).

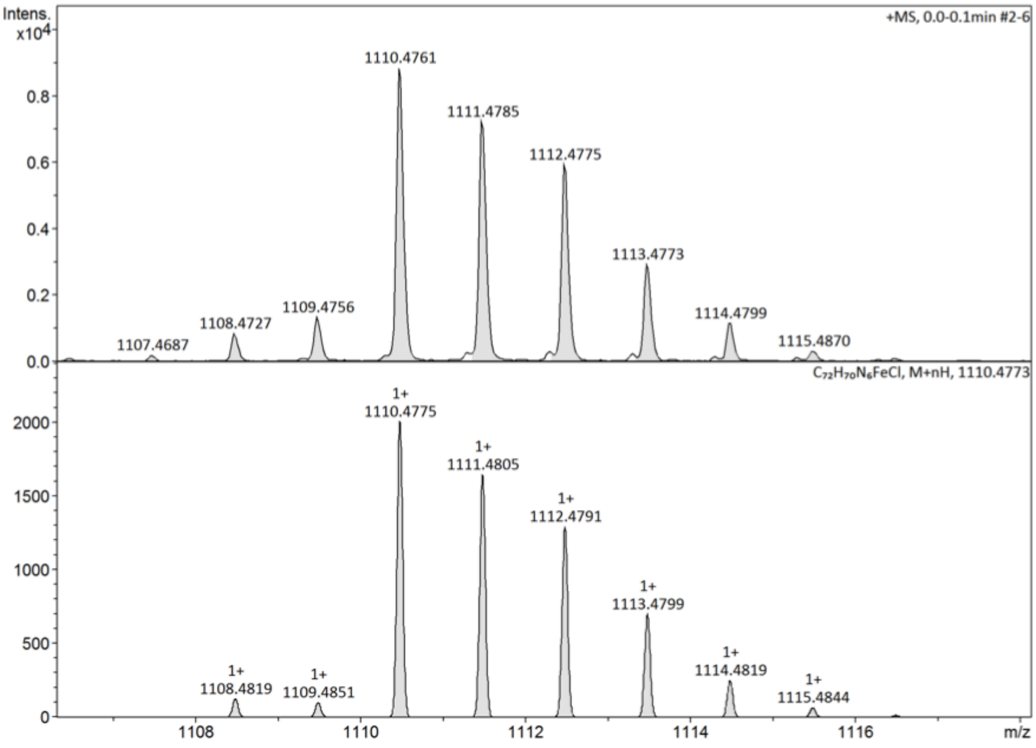

Fig. S14. APCI-MS spectrum of **1b** (top: observed, bottom: simulated).

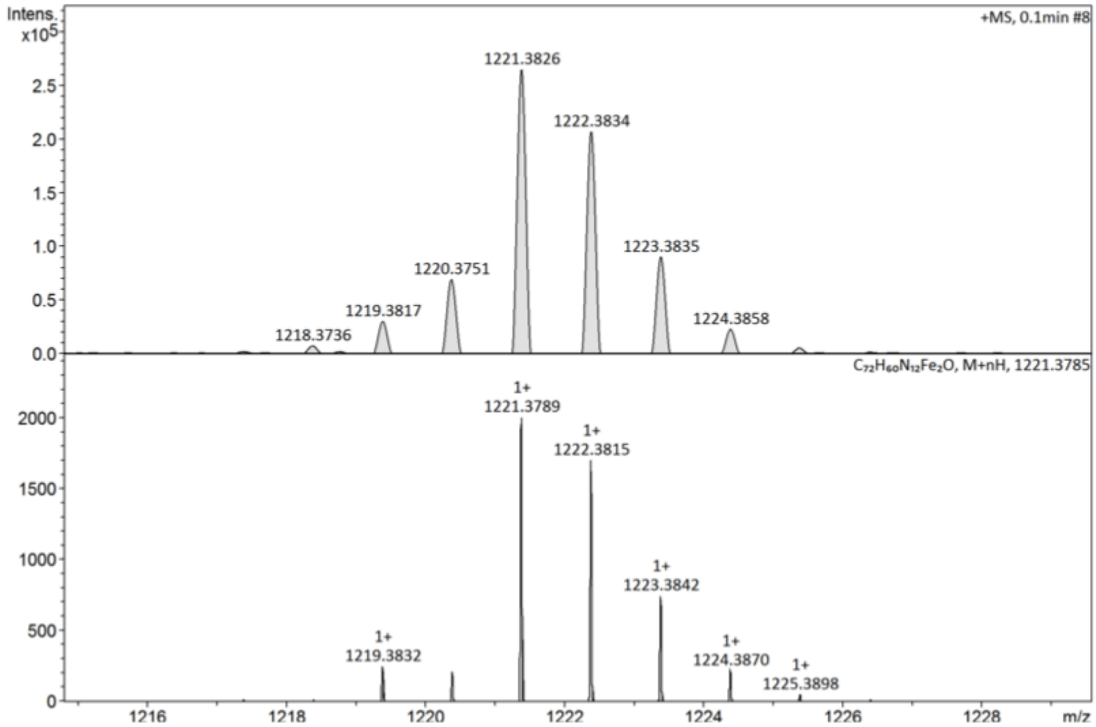

Fig. S15. ESI-MS (2-propanol) spectrum of **6** (top: observed, bottom: simulated).

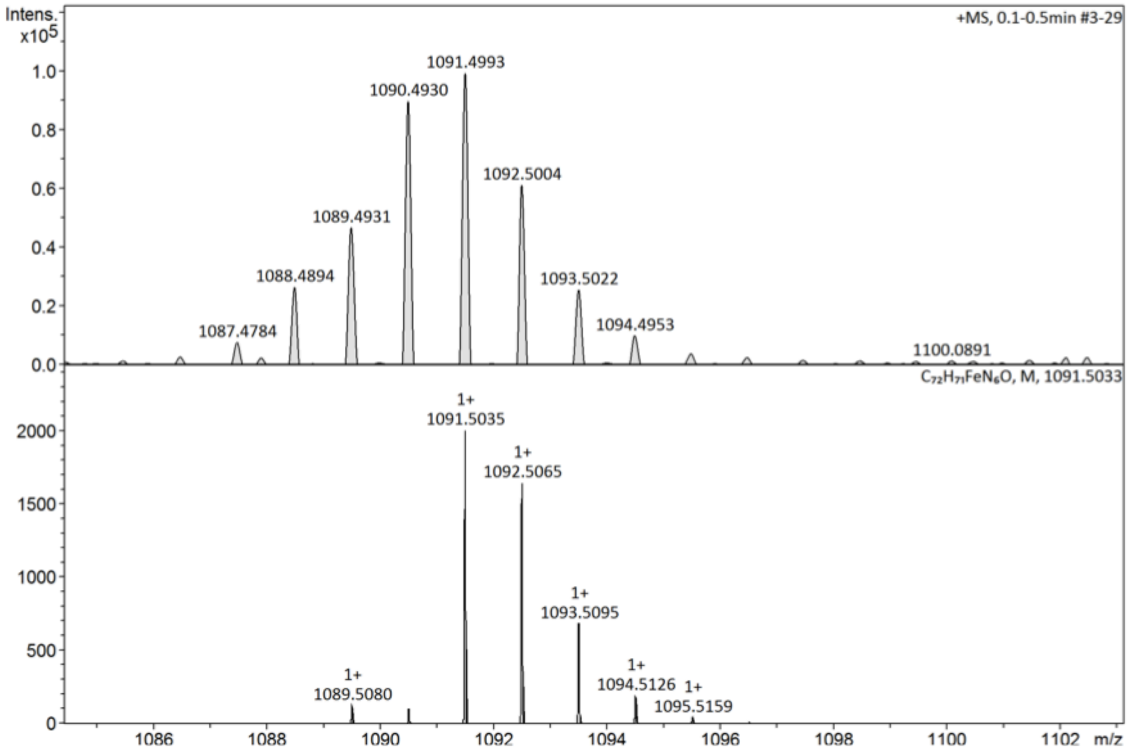

Fig. S16. APCI-MS spectrum of **7** (top: observed, bottom: simulated).