Electronic Supplementary Material (ESI) for ChemComm.

Supporting information of

"Tuning the Thermodynamic Onset Potential of O_2 Reduction Reaction by Synthetic Iron-Porphyrin Complex"

Sk Amanullah, Pradip Kumar Das, Subhra Samanta and Abhishek Dey*

Table of Contents

1. Experimental Details

1.1. Materials:

All reagents were of the highest grade commercially available. Iodine, Trifluoroacetic acid (TFA), 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), Ethanol, aqueous Ammonia solution, Ceric ammonium nitrate (CAN) were purchased from Spectrochem Ltd. Diethyl ether, THF, Acetonitrile were purchased from RANKEM Ltd. Cobalt acetate was purchased from AVRA pvt. Ltd, anhydrous Ferrous bromide ($FeBr_2$), 2,4,6-Collidine, Tetrabutylammonium perchlorate (TBAP), Potassium hexafluorophosphate (KPF_6) and all buffers were purchased from Sigma-Aldrich chemical company. Dichloromethane, Na_2SO_4 were from MERCK and used without any further purification. Unless otherwise mentioned all reactions were performed at room temperature and the column chromatography were performed on silica gel (60-100 mesh) and neutral Alumina.

1.2. Instrumentation:

All electrochemical experiments were performed using a CH Instruments (model CHI710D Electrochemical Analyzer). Biopotentiostat, reference electrodes, Teflon plate material evaluating cell (ALS Japan) were purchased from CH Instruments. The RDE and RRDE set up from Pine Research Instrumentation (E6 series ChangeDisk tips with AFE6M rotor) was used to obtain the RDE and RRDE data. Resonance Raman data were collected using a Trivista 555 spectrograph (Princeton Instruments) and using 413.1 nm excitation from a Kr+ laser (Coherent, Sabre Innova SBRC-DBWK). Edge Plane Graphite (EPG) discs were purchased from Pine Instruments. The absorption spectra are measured in the SHIMDZU spectrograph (UV-2100). The FT-IR data are measured on the Shimadzu FTIR 8400S instrument. All the NMR spectra were recorded on the Bruker DPX-400 or DPX-500 spectrometer at room temperature. The mass spectra are recorded by QTOF Micro YA263 instrument. X-ray single crystal data was collected at 120 K using radiation on a SMART APEX diffractometer equipped with CCD area detector. Data collection, data reduction, structure solution refinement were carried out using the software package of APEX II. The structure was solved by direct method and refined in a routine manner. The non-hydrogen atoms were treated anisotropically. All the hydrogen atoms were located on a difference Fourier map and refined.

1.3. Electrochemical Measurements:

1.3.1. Construction of the Electrodes: Physiadsorption of the Catalysts on EPG: A 50 μL portion of catalyst from a 1 mM solution of the respective catalysts in chloroform ($CHCl_3$) is deposited on a freshly cleaned EPG electrode mounted on a RDE setup. After the evaporation of the solvent, the surface is thoroughly dried with N_2 gas and sonicated in ethanol. Finally before using it for electrochemical experiments, the modified electrodes are washed with triple distilled water.

1.3.2. Cyclic Voltammetry (CV) Experiments: All CV experiments are done in pH 7 buffer (unless otherwise mentioned) containing 100 mM $Na_2HPO_4{\cdot}2H_2O$ and 100 mM KPF_6 (supporting electrolyte) using Pt wire as the counter electrode and Ag/AgCl as the reference electrode.

1.3.3. Rotating Disc Voltammetry: The RDE measurements were performed on a CHI 710D bi-potentiostat with a Pine Instruments. Modulated speed rotor fitted with an E6 series Changedisc tip. The graphite surface was cleaned by polishing it uniformly on a Silicon carbide grinding paper. The complex was physiadsorbed on the disc as described above. The Koutecky-Levich experiment was done at different rotations 200 rpm, 300 rpm, 400 rpm, 500 rpm, 600 rpm.

1.3.4. Partially Reduced Oxygen Species (PROS): The platinum ring was polished by alumina powder (grit sizes: 1 μ, 0.3 μ, and 0.05 μ) and electrochemically cleaned and inserted into the RRDE tip which is then mounted on the rotor and immersed into a cylindrical glass cell equipped with Ag/AgCl reference and Pt counter electrodes. The collection efficiency (CE) of the RRDE setup is measured in a 2 mM $K_3Fe(CN)_6$ and 0.1 M KNO_3 solution at 10 mV/S scan rate and 300 rpm rotation speed. A 20 ± 2% CE is generally recorded during these experiments. The potential at which the ring is held during the collection experiments at pH 7 for detecting H_2O_2 has been obtained from the literature.

2. Synthetic procedures:

2.1. diethyl 2,3-diacetylsuccinate: Sodium metal (1.76g, 76.84mmol) was dissolved in 100ml dry EtOH and stirred for 10min under Ar-atmosphere. Ethyl acetoacetate (9.8ml, 76.84mmol) was added and stirred for 1h at room temperature. EtOH was evacuated off and 120ml dry diethyl ether was added. I_2 (9.75g, 38.42 mmol) was dissolved in 40ml dry THF and added drop wise to ethereal solution. Finally color change from yellow to violet indicates the completion of the reaction. The solvents were evaporated out and worked up with EtOAc. The organic layer was dried over Na_2SO_4 and evaporated through a rotary-evaporator and purified by column chromatography on silica gel with 5% EtOAc-Hexane mixture as the eluent. Yield: 50-55% (10-11g).

^{1}H NMR ($CDCl_3$): δ 1.20 (t, 6H), 2.31 (s, 6H), 4.10 (q, 4H), 4.38 (s, 2H), *1 (THF, -CH_2). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ(ppm) 14.0, 29.9, 57.7, 61.9, 167.0, 200.9. ESI-MS (positive-ion mode, CH_3CN): m/z 281 (100%; $[M+Na]^+$). Anal. Calcd. for $C_{12}H_{18}O_6$: C, 55.81; H, 7.02. Found: C, 54.06; H, 7.69 ($C_{12}H_{18}O_6$, 0.5 H_2O).

2.2. Diethyl 2,5-dimethyl-pyrrole-3,4-dicarboxylate: Diethyl 2,3-diacetylsuccinate (10g, 38.72 mmol) was added to 150ml freshly prepared methanolic NH_3 solution and stirred for 2h at room temperature. The solvents were evaporated out and worked up with EtOAc. The organic layer was dried over Na_2SO_4 and evaporated through a rotary-evaporator and purified by column chromatography on silica gel with 30% EtOAc-Hexane mixture as the eluent. Yield: 95-97% (8.7-8.9g).

^{1}H NMR ($CDCl_3$): δ 1.26 (t, 6H), 2.27 (s, 6H), 4.22 (q, 4H), 9.40 (br s, 1H), *1 (EtOAc, -$COCH_3$), *2 (MeOH, -OCH_2). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ(ppm) 14.3, 60.2, 111.8, 133.0, 166.0. ESI-MS (positive-ion mode, CH_3CN): m/z 261 (100%; $[M+Na]^+$). Anal. Calcd. for $C_{12}H_{17}NO_4$: C, 60.24; H, 7.16; N, 5.85. Found: C, 59.01; H, 7.99; N, 5.12 ($C_{12}H_{17}NO_4$, 0.25 H_2O).

2.3. Diethyl 2,5-diformyl-pyrrole-3,4-dicarboxylate: Diethyl 2,5-dimethyl-1H-pyrrole-3,4-dicarboxylate (2g, 8.36 mmol) was dissolved in acetonitrile-water (210ml-35ml). CAN (41.24g, 75.24 mmol) was added and refluxed for 5h. Colour change from red to yellow indicates the completion of the reaction. The solvents were evaporated out and worked up with EtOAc. The organic layer was dried over Na_2SO_4 and evaporated through a rotary-evaporator and purified by column chromatography on silica gel with 50% EtOAc-Hexane mixture as the eluent.Yield:40-45% (0.9-1g).

^1H NMR ($CDCl_3$): δ 1.38 (t, 6H), 4.42 (q, 4H), 10.11 (s, 2H), 10.49 (br s, 1H), *1 (EtOAc, -$COCH_3$), *2 (CH_3CN). $^{13}C\ \{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ(ppm) 13.9, 61.9, 123.1, 133.4, 162.2, 182.0. ESI-MS (positive-ion mode, CH_3CN): m/z 308 (100%; $[M+K]^+$). FT-IR (CH_2Cl_2): ῡ, (cm^{-1}): 3224 (br), 2984, 1718, 1687, 1502, 1285, 1228,1103. Anal. Calcd. for $C_{12}H_{13}NO_6$: C, 53.93; H, 4.90; N, 5.24. Found: C, 49.73; H, 4.73; N, 5.09 ($C_{12}H_{13}NO_6$, 1.25 H_2O).

2.4. 6,12-Diphenyltripyrrane: Freshly distilled and degassed benzaldehyde (4.8 ml, 47.12 mmol) was added to freshly distilled and degassed pyrrole (16.3ml, 235.58 mmol) and the mixture was degassed for 10min. TFA (0.36ml, 4.71mmol) was added keeping the reaction vessel at 0^0C. It was then stirred for 20min at room temperature. Reaction was quenched by 50 ml 0.1M NaOH solution and worked up with dichloromethane. The organic layer was dried over Na_2SO_4 and evaporated through a rotary-evaporator and purified by column chromatography on neutral alumina with 5% EtOAc-Hexane mixture as the eluent. Yield: 10-12% (1.9-2g).

^1H NMR ($CDCl_3$): δ 5.37 (s, 2H), 5.82 (s, 2H), 5.93 (m,2H), 6.18 (m, 2H), 6.68 (m, 2H), 7.22-7.38 (m, 10H), 7.80 (br s, 2H), *1 (EtOAc, -$COCH_3$), *2 (EtOAc, -OCH_2). ESI-MS (positive-ion mode, CH_3CN): m/z 376 (100%; $[M]^+$). Anal. Calcd. for $C_{26}H_{23}N_3$: C, 82.73; H, 6.14; N, 11.13. Found: C, 79.40; H, 6.14; N, 10.30 ($C_{26}H_{23}N_3$, 1.0 H_2O).

2.5. 10,15-Diphenyl-22,24-dihydro-porphine-3,4-dicarboxylic Acid Diethyl Ester (PP-diester): To a vigorously stirred solution of TFA (14.34 mL, 187 mmol) in dry degassed chloroform (200 mL), solutions of 6,12-diphenyltripyrrane

(0.705g, 1.87 mmol) in dry degassed chloroform (20 mL) and Diethyl 2,5-diformyl-pyrrole-3,4-dicarboxylate (0.5g, 1.87 mmol) in dry degassed chloroform (20 mL), were added simultaneously during 15 min. Then the reaction was stirred for 10 min. A solution of DDQ (0.42g, 1.87 mmol) in dry toluene (6 mL) was added keeping the reaction vessel in ice-bath. After an additional 10 min of stirring at room temperature, the reaction mixture was quenched using triethanoloamine (24.82ml, 187 mmol). The reaction mixture was then cooled for 20 min in the refrigerator and filtered. Black crystals of salt (triethanoloammonium trifluoroacetate) were washed with ethyl acetate until they became pale green and solvent was evaporated through a rotary-evaporator and purified by column chromatography on silica gel with 80% DCM-Hexane mixture as the eluent. Yield: 11-15% (0.13-0.15g).

λ_{max} (DCM)/nm: 418, 517, 550, 591, 658. FT-IR : $\bar{\upsilon}$ (cm^{-1}): 1708.81, 1726.17 (CO_2Et group). ^1H NMR ($CDCl_3$): δ -3.15 (br s, 2H), 1.73 (t, 6H), 4.93 (q, 4H), 7.76-8.21 (m, 10H), 8.80 (s, 2H), 9.06 (d, 2H), 9.48 (d, 2H), 10.78 (t, 2H), *1 (EtOAc, -$COCH_3$). ^{13}C {^1H} NMR ($CDCl_{3,}$ 100 MHz): δ(ppm) 14.2, 62.1, 105.5, 114.2, 116.0, 120.2, 123.6, 126.9, 128.0, 134.7, 139.4, 141.7, 166.5. ESI-MS (positive-ion mode, CH_3CN): m/z 607 (100%; $[M]^+$). Anal. Calcd. for $C_{38}H_{30}N_4O_4$: C, 75.23; H, 4.98; N, 9.24. Found: C, 73.99; H, 5.31; N, 8.75 ($C_{38}H_{30}N_4O_4$, 0.50 H_2O).

2.6. Fe-PP-diester: To a solution of the PP-diester (50 mg, 0.082 mmol) in 20 ml dry degassed THF, 2,4,6-collidine (21 µl, 0.164 mmol) was added and stirred for 10min in glove box. $FeBr_2$ (70 mg, 0.328 mmol) was added and stirred overnight. The reaction mixture was quenched by acidic water followed by the addition of DCM. The organic layer was washed with brine solution and collected. It was dried over anhydrous Na_2SO_4 and purified by column chromatography with silica gel using 1% MeOH-DCM mixture as eluent. Yield: 90-92% (45-50mg).

λ_{max} (DCM)/nm: 412, 575, 612. ESI-MS (positive-ion mode, MeOH): m/z 659 (45%; [M]+). Anal. Calcd for $C_{38}H_{28}FeN_4O_4$: C, 69.10; H, 4.27; N, 8.48. Found: C, 68.93; H, 4.44; N, 8.02.

2.7. Co-PP-diester: To a solution of the PP-diester (50 mg, 0.082 mmol) in 20 ml dry THF, 2,4,6-collidine (21 μl, 0.164 mmol) was added and stirred for 10 min. $Co(OAc)_2$ (81 mg, 0.328 mmol) was added to the solution and refluxed overnight. The reaction mixture was quenched by acidic water followed by the addition of DCM. The organic layer was washed with brine solution and collected. It was dried over anhydrous Na_2SO_4 and purified by column chromatography with silica gel using 1% MeOH-DCM mixture as eluent. Yield: 90-95% (45-50mg).

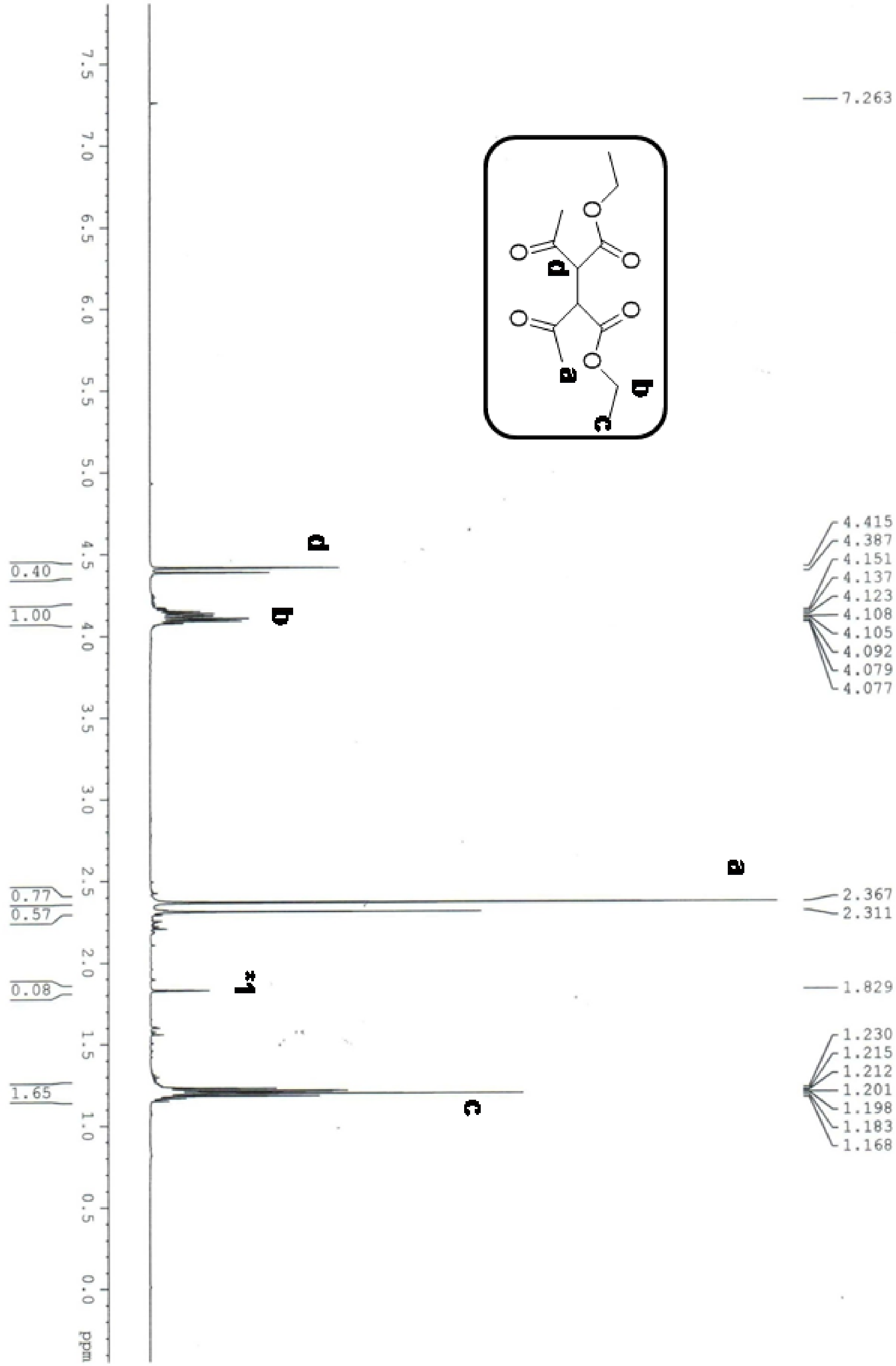
ESI-MS (positive-ion mode, MeOH): m/z 663 (100%; [M]+). Anal. Calcd for $C_{38}H_{28}CoN_4O_4$: C, 68.78; H, 4.25; N, 8.44. Found: C, 68.20; H, 4.61; N, 8.23.

3. Crystal data:

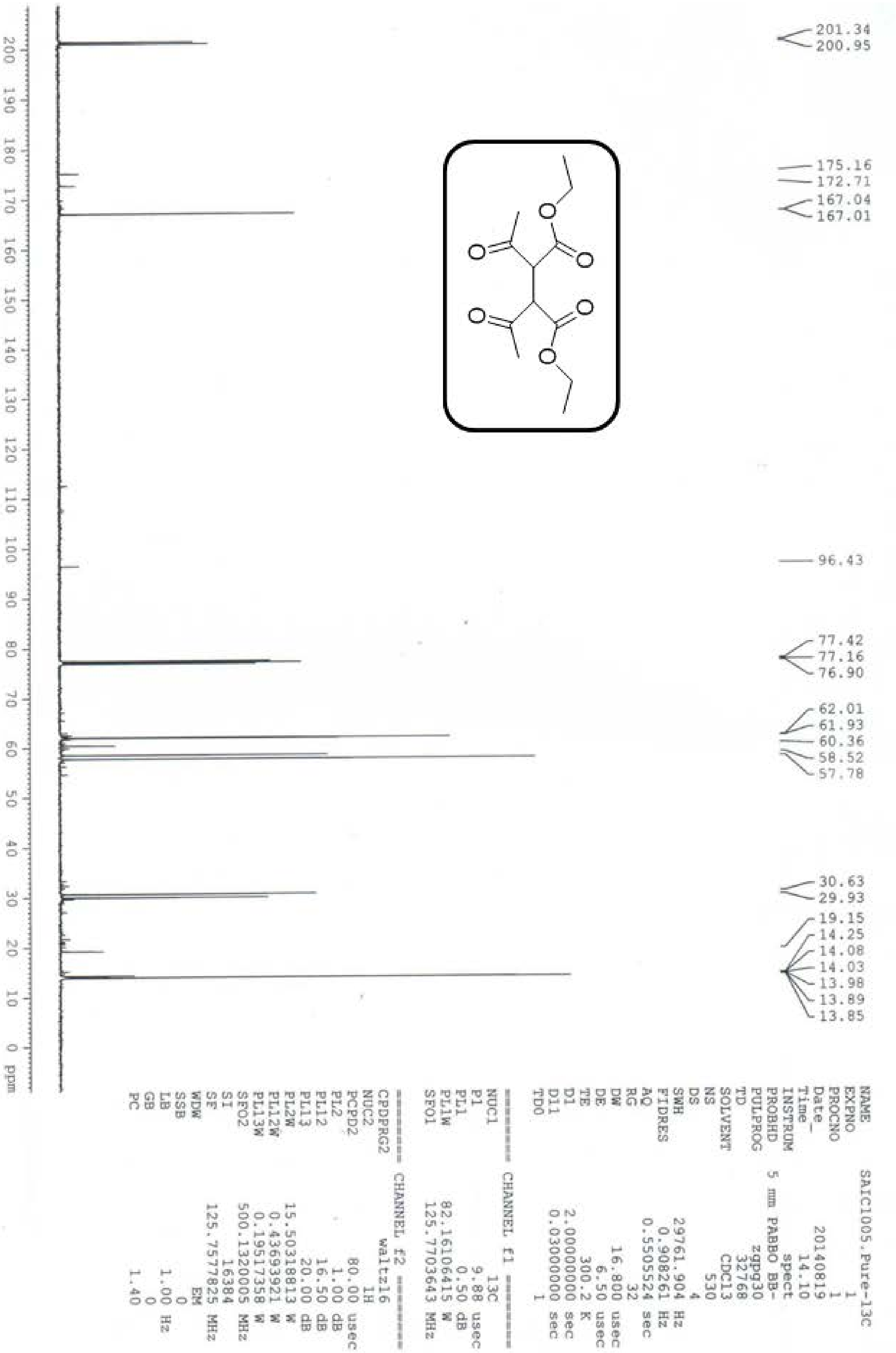
We have tried several times to get the angle of diffraction greater than 50^0. But we did not able to achieve that. The best possible data is deposited to Cambridge Crystallographic Data Centre. **CCDC Number: 1051391**

4. Spectral data:

4.1.1. ^{1}H NMR ($CDCl_3$, 500 MHz) of diethyl 2,3-diacetylsuccinate



4.1.2. ^{13}C {1H}(NMR CDCl$_3$, 100 MHz) of diethyl 2,3-diacetylsuccinate



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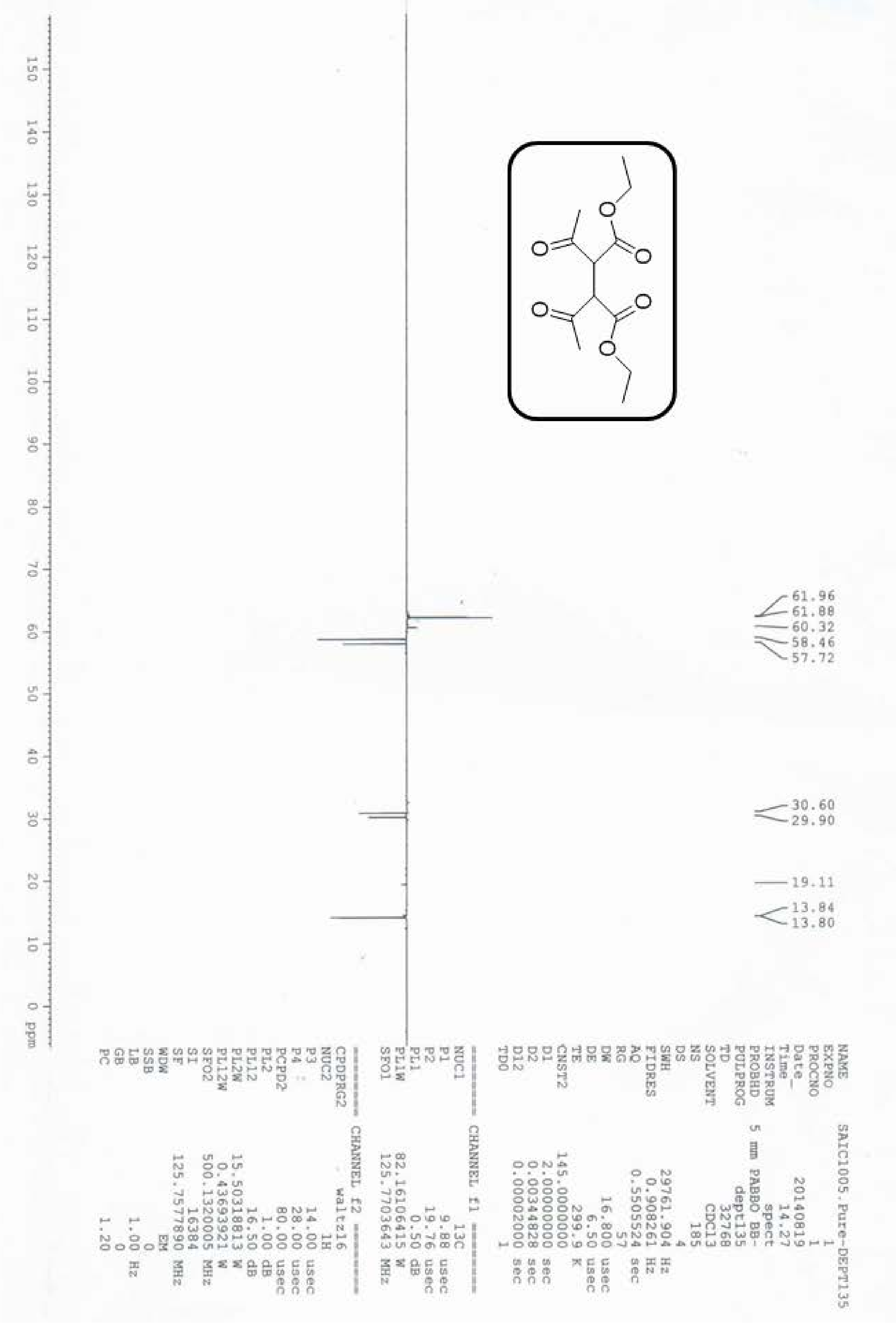
4.1.3. DEPT-135 NMR ($CDCl_3$) of diethyl 2,3-diacetylsuccinate



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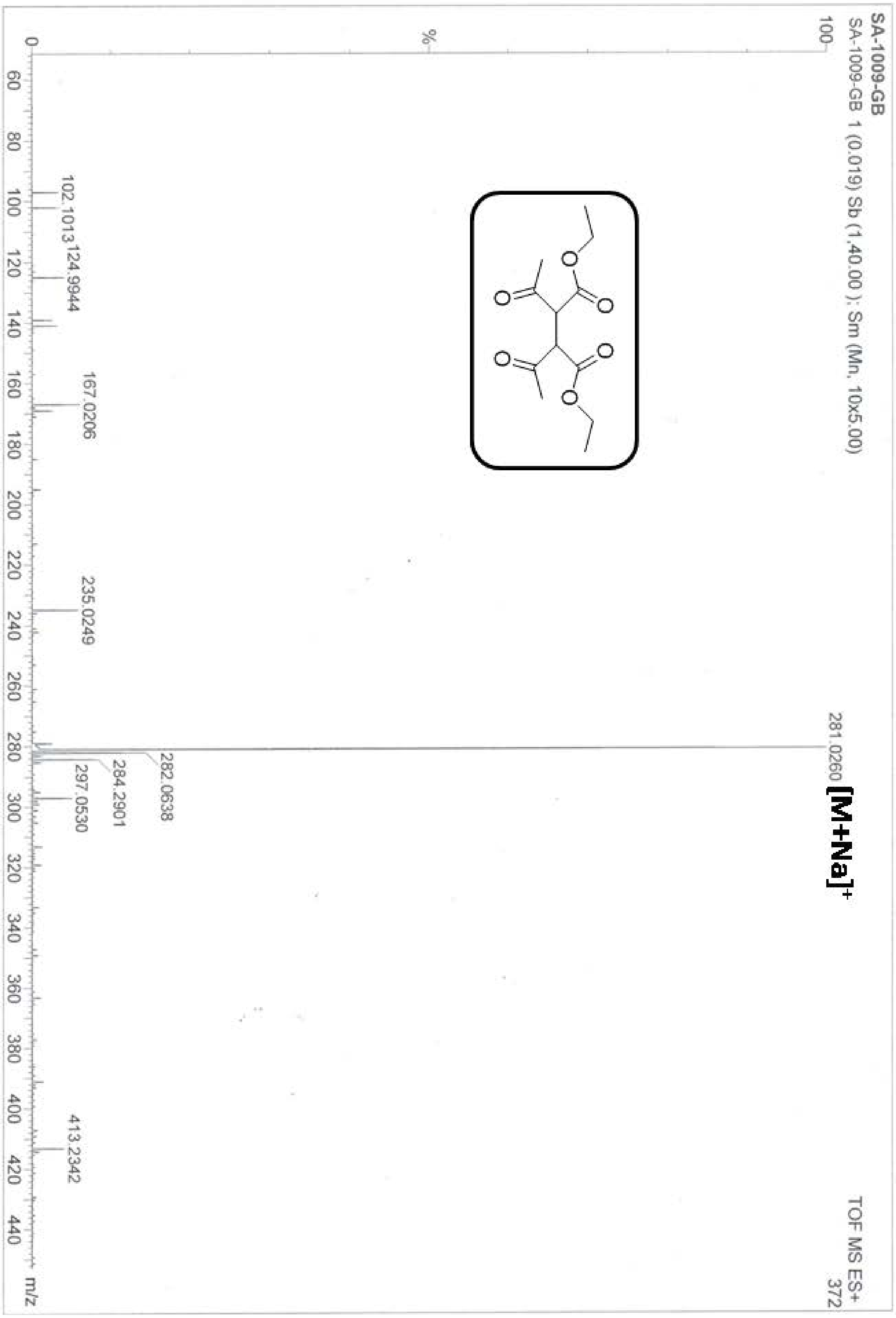
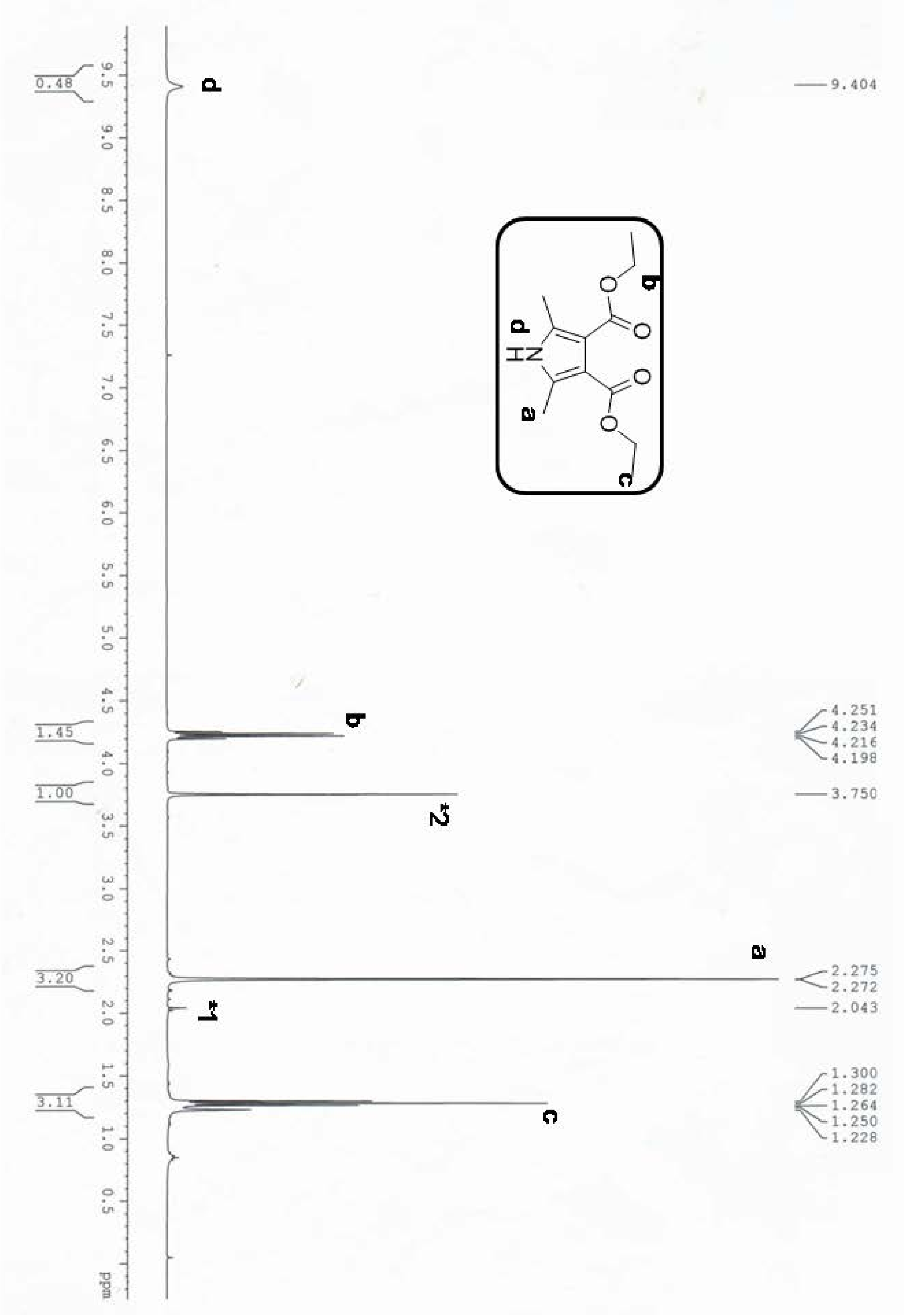
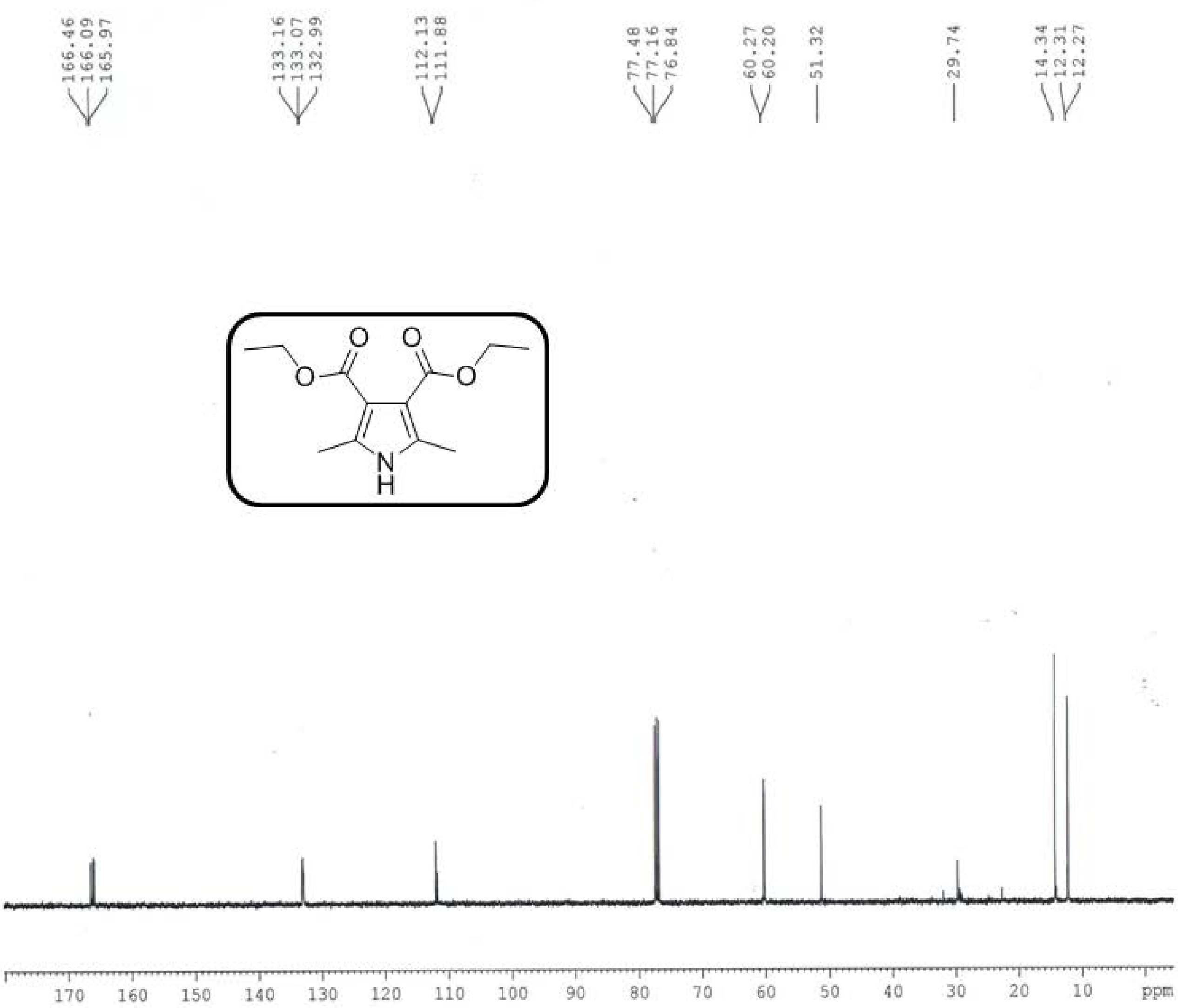
4.1.4. ESI-MS of diethyl 2,3-diacetylsuccinate



4.2.1. ^{1}H NMR ($CDCl_3$, 500 MHz) of Diethyl 2,5-dimethyl-pyrrole-3,4-dicarboxylate



4.2.2. ^{13}C {1H}(NMR CDCl$_3$, 100 MHz) of Diethyl 2,5-dimethyl-pyrrole-3,4-dicarboxylate



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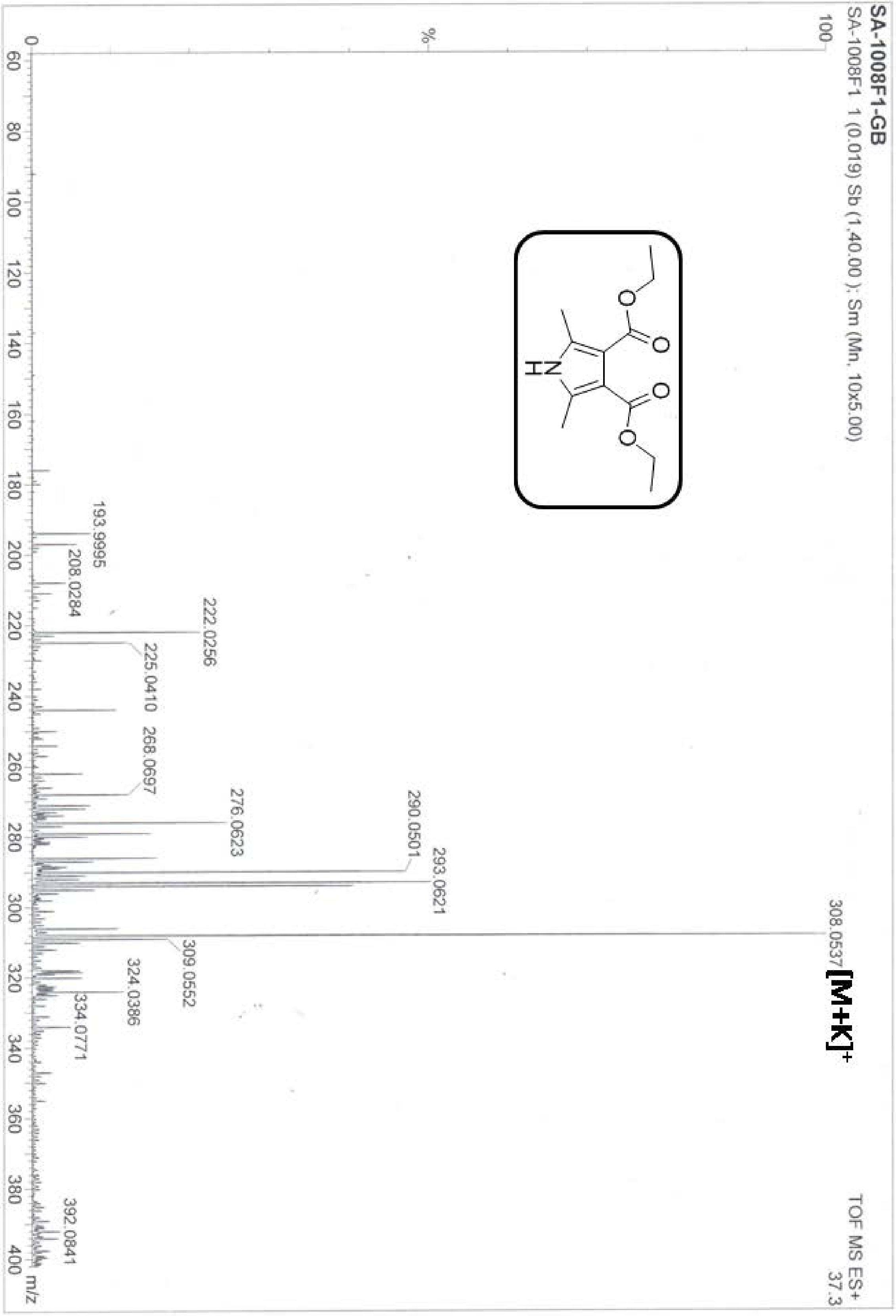
4.2.3. ESI-MS of Diethyl 2,5-dimethyl-pyrrole-3,4-dicarboxylate



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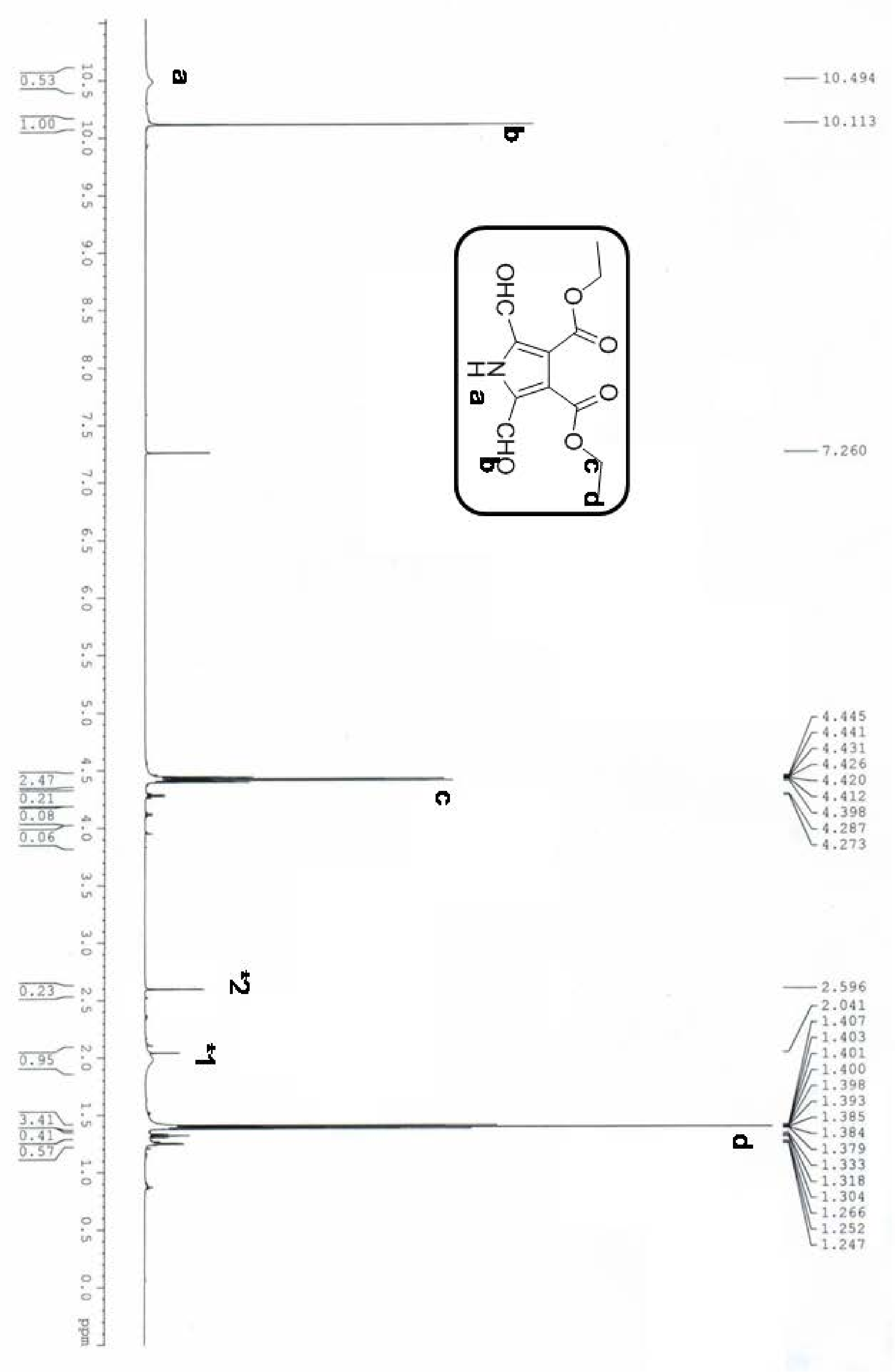
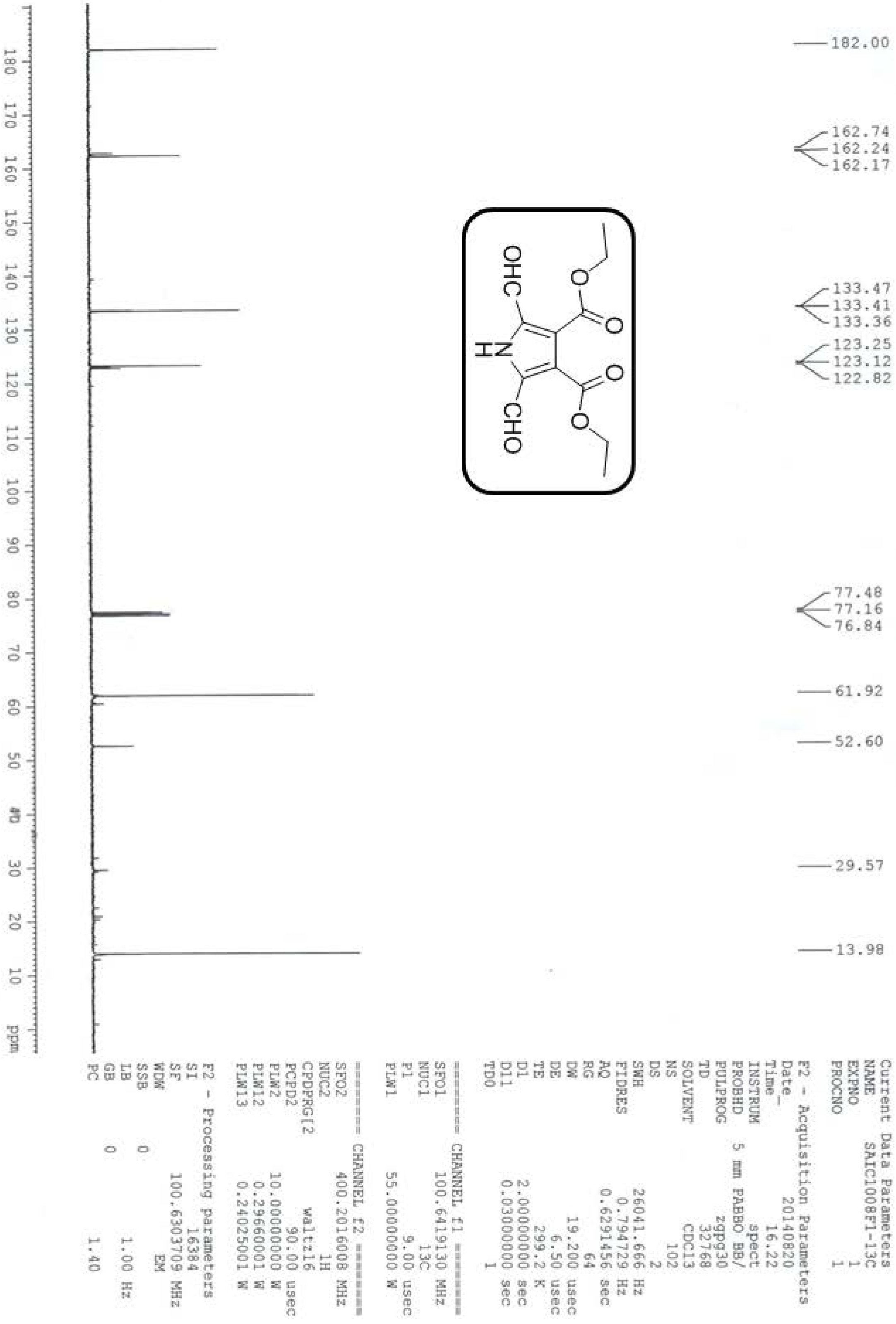


4.3.2. ^{13}C {1H}(NMR $CDCl_3$, 100 MHz) of Diethyl 2,5-diformyl-pyrrole-3,4-dicarboxylate



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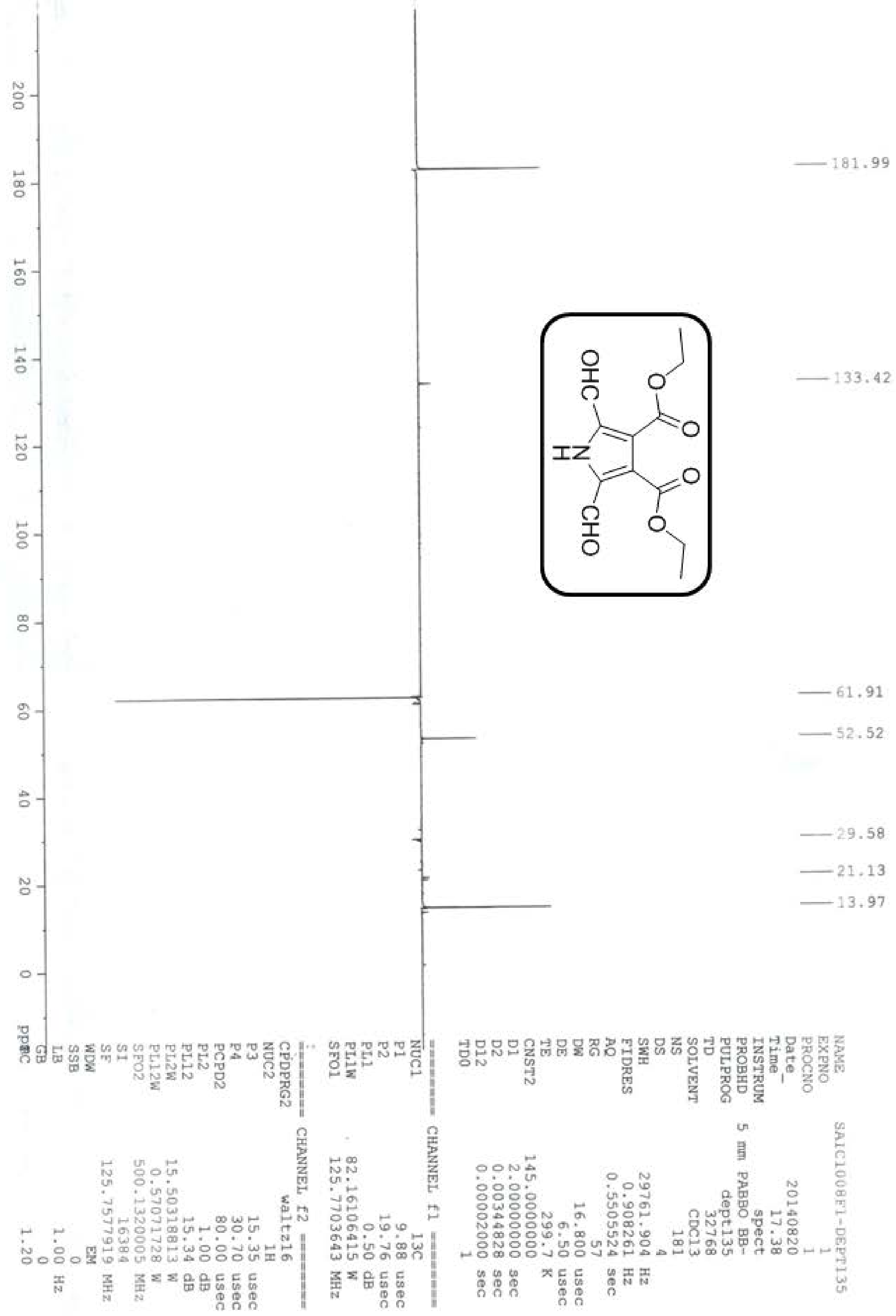
4.3.3. DEPT-135 NMR ($CDCl_3$) of Diethyl 2,5-diformyl-pyrrole-3,4-dicarboxylate



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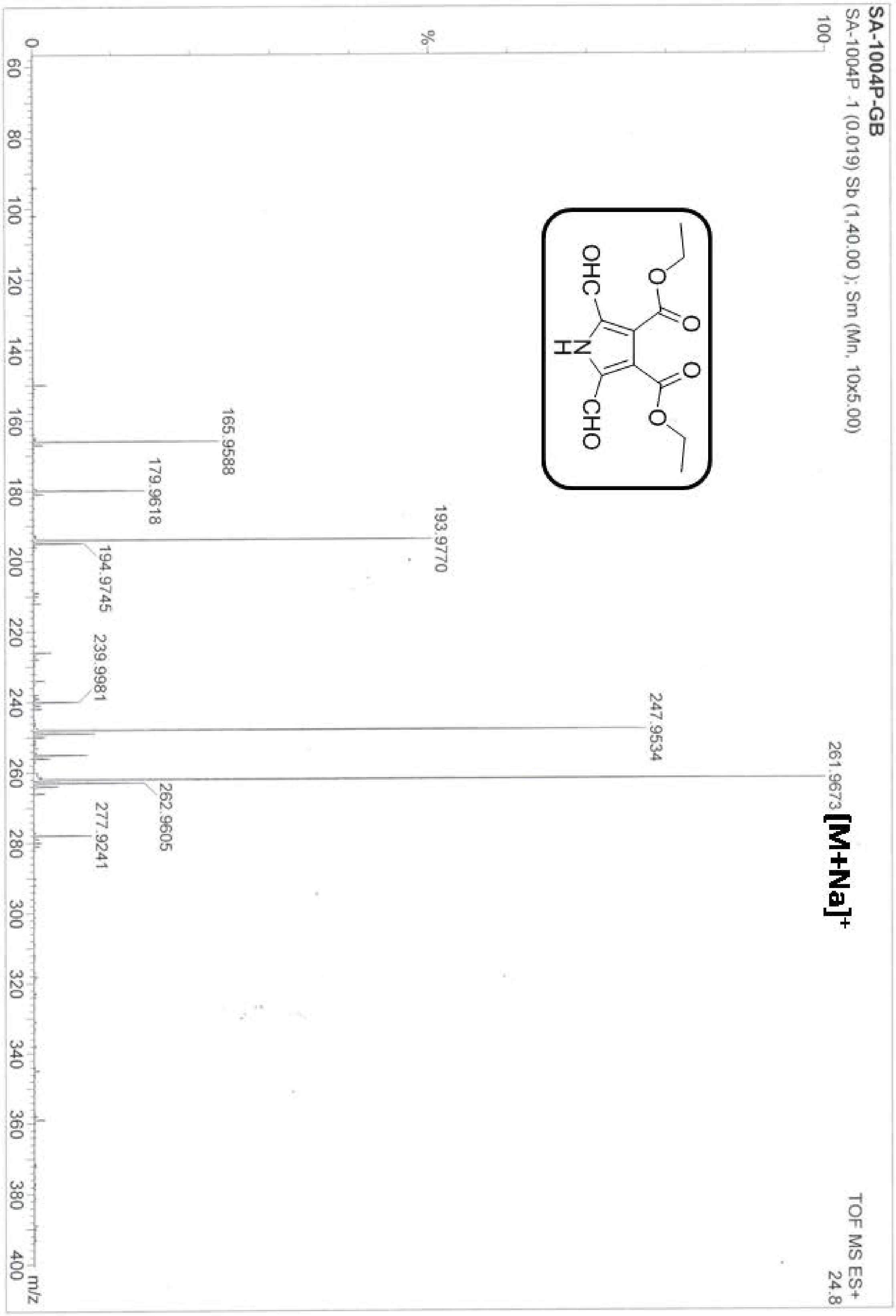
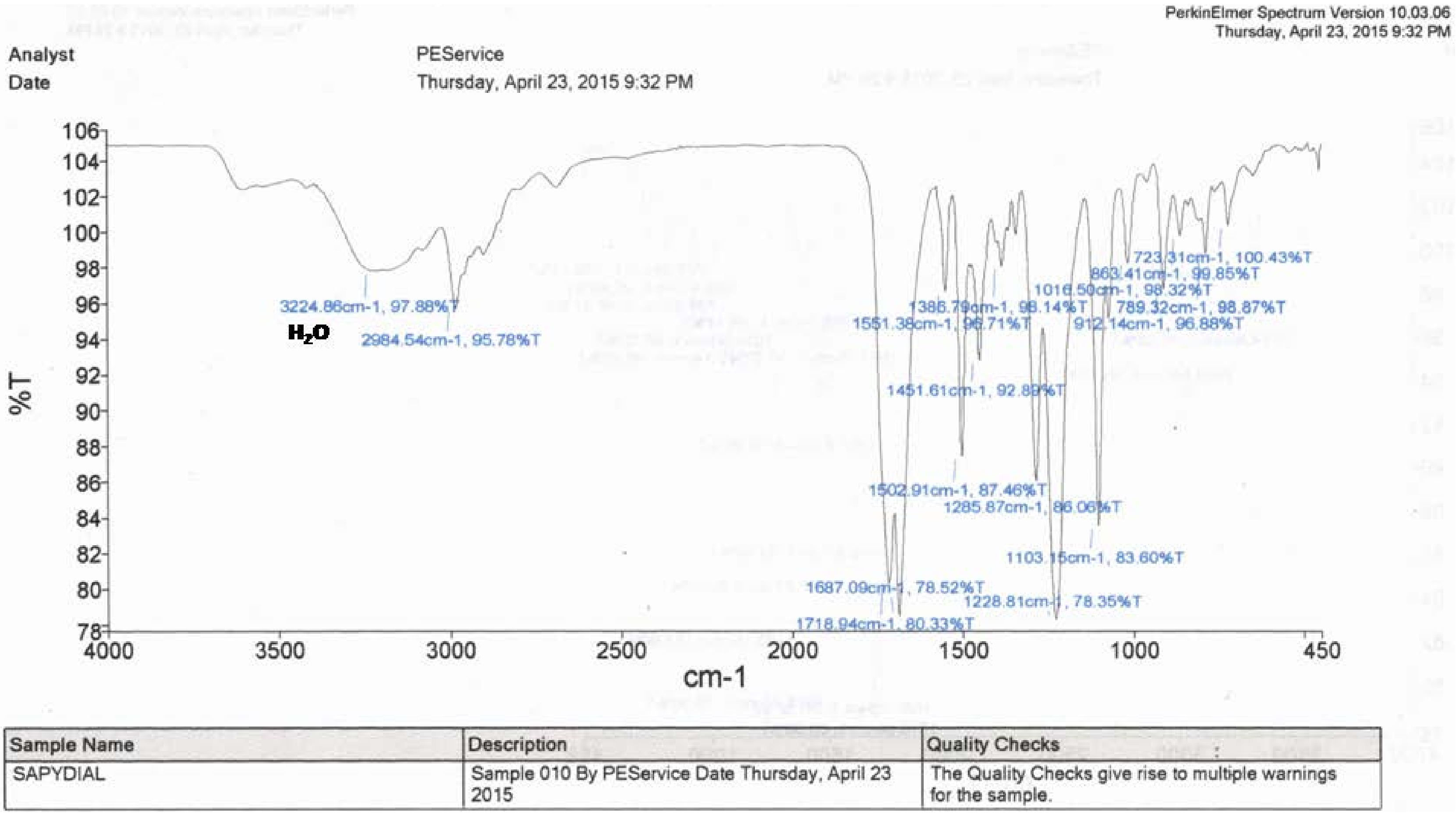


4.3.5. IR spectrum of Diethyl 2,5-diformyl- pyrrole-3,4-dicarboxylate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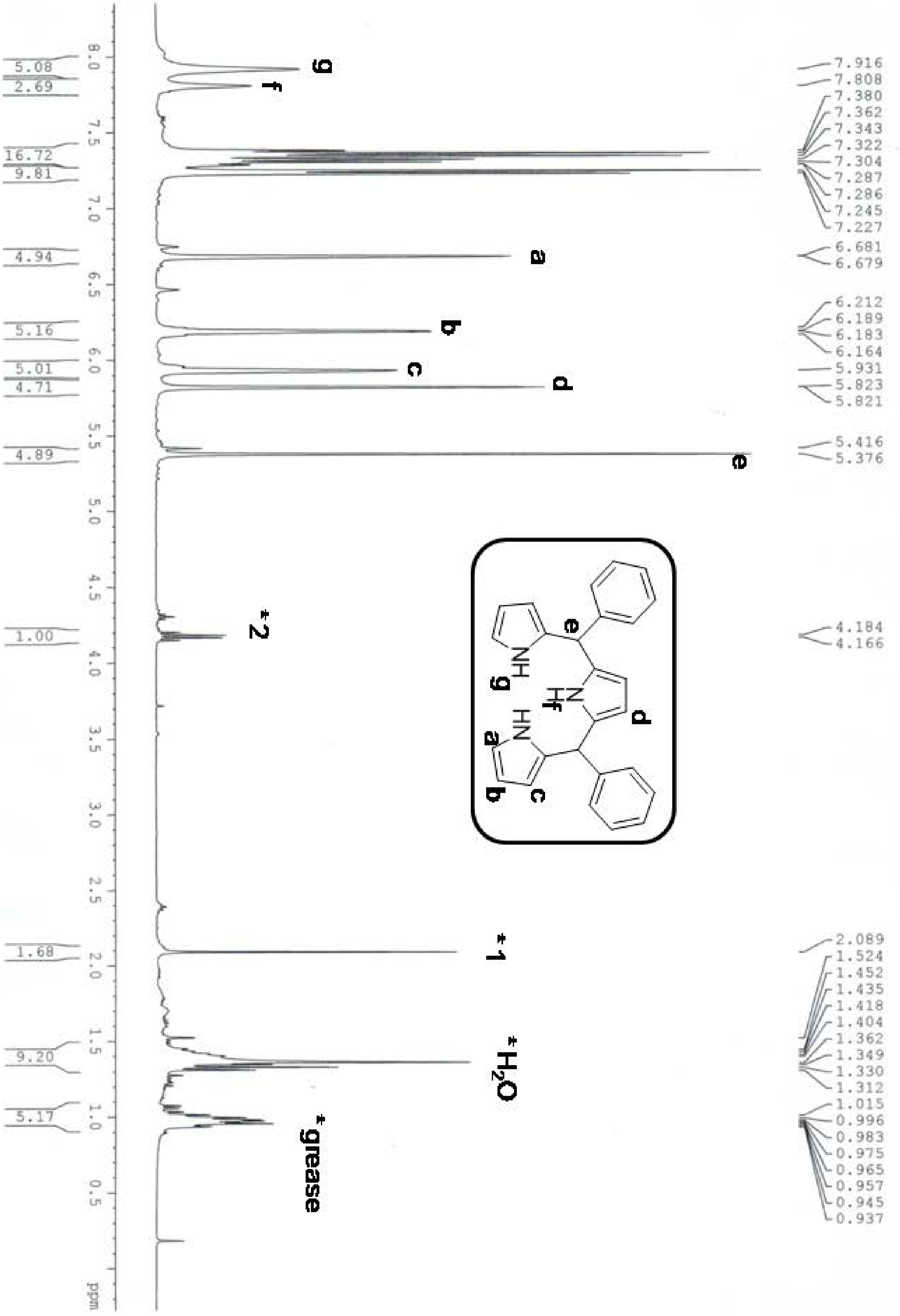
Thursday, April 23, 2015 9:32 PM

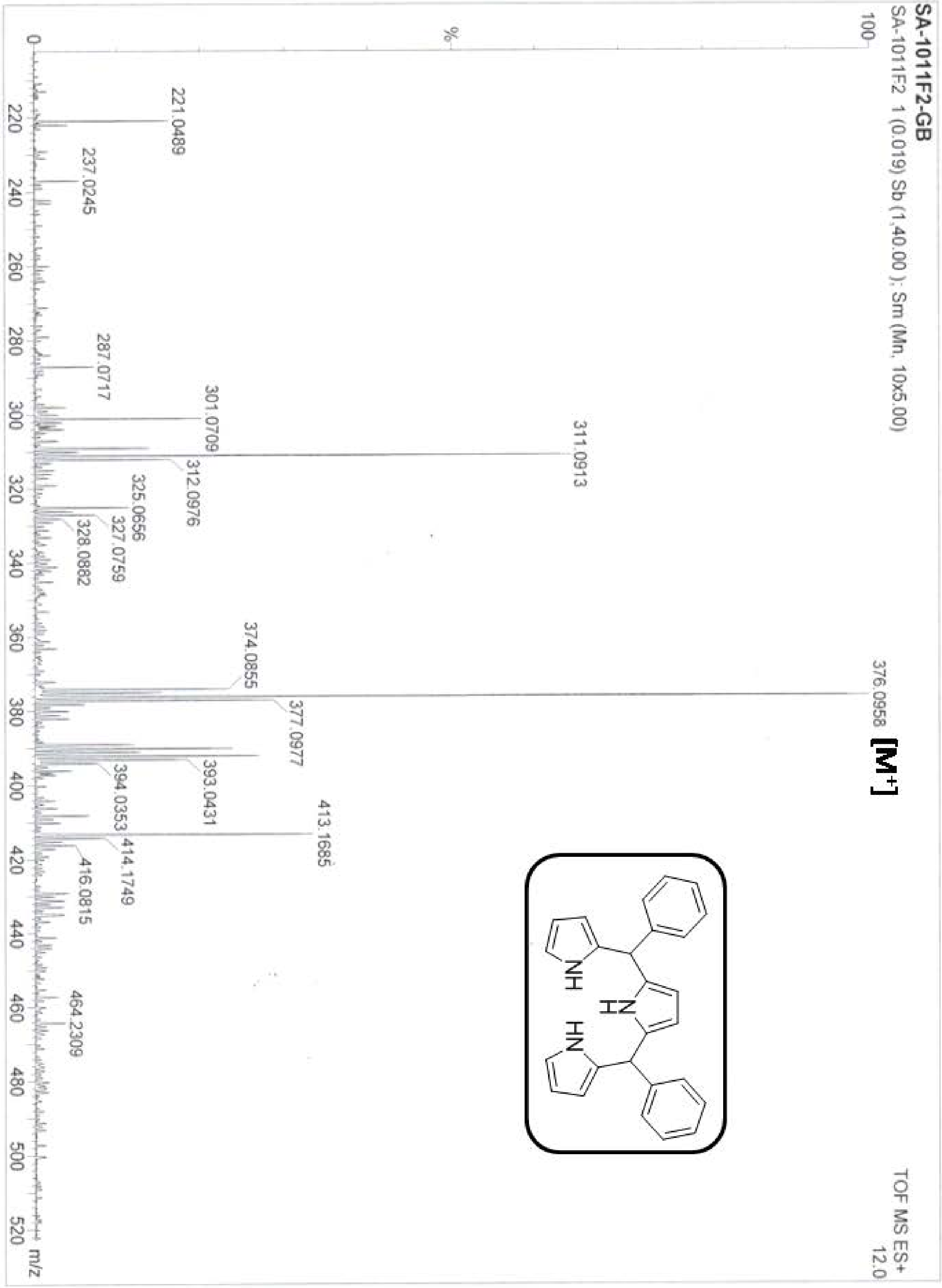
Analyst PEService
Date Thursday, April 23, 2015 9:32 PM

Sample Name	Description	Quality Checks
SAPYDIAL	Sample 010 By PEService Date Thursday, April 23 2015	The Quality Checks give rise to multiple warnings for the sample.

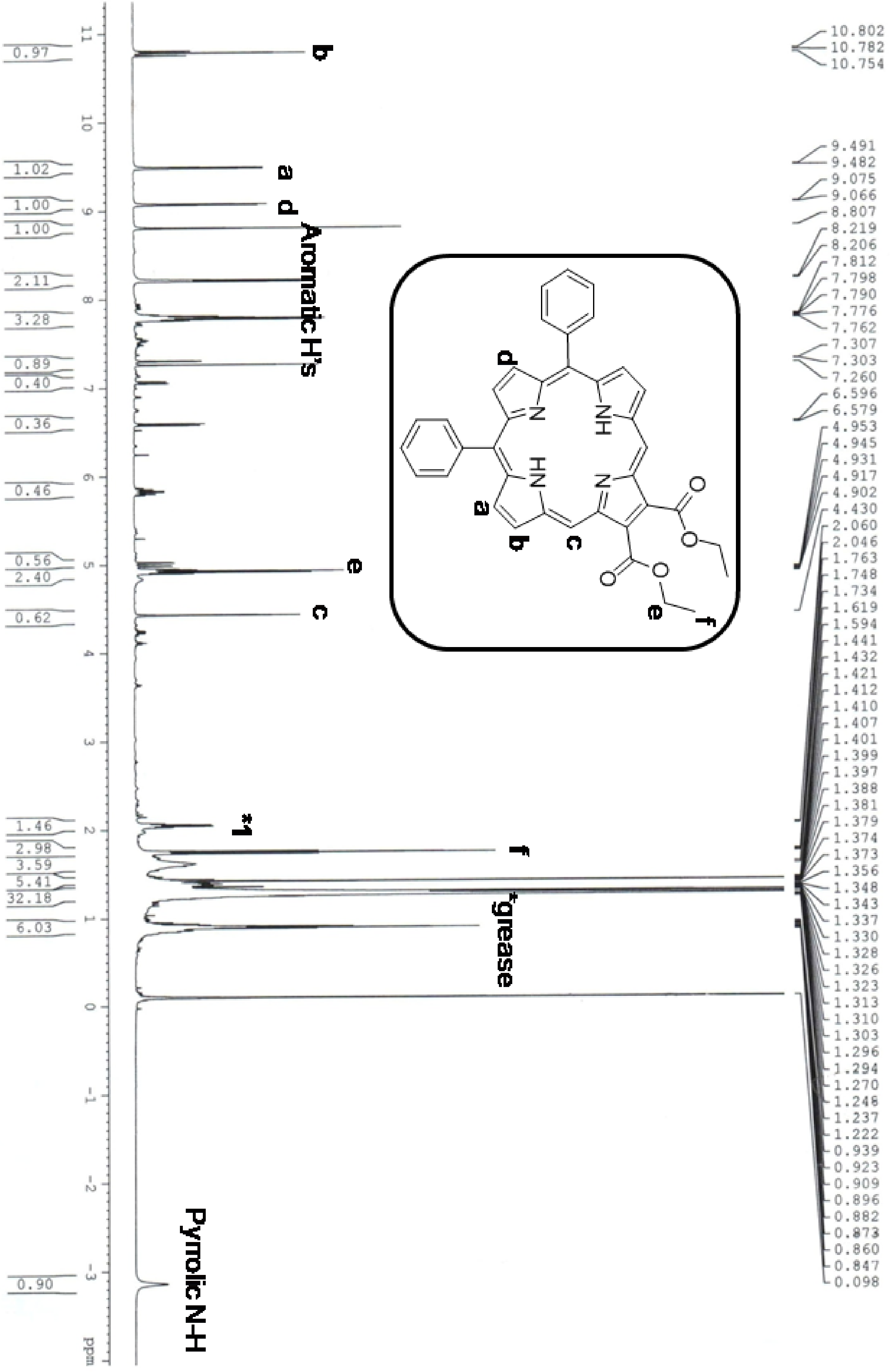
4.4.1. ^1H NMR ($CDCl_3$, 500 MHz) of 6,12-Diphenyltripyrrane



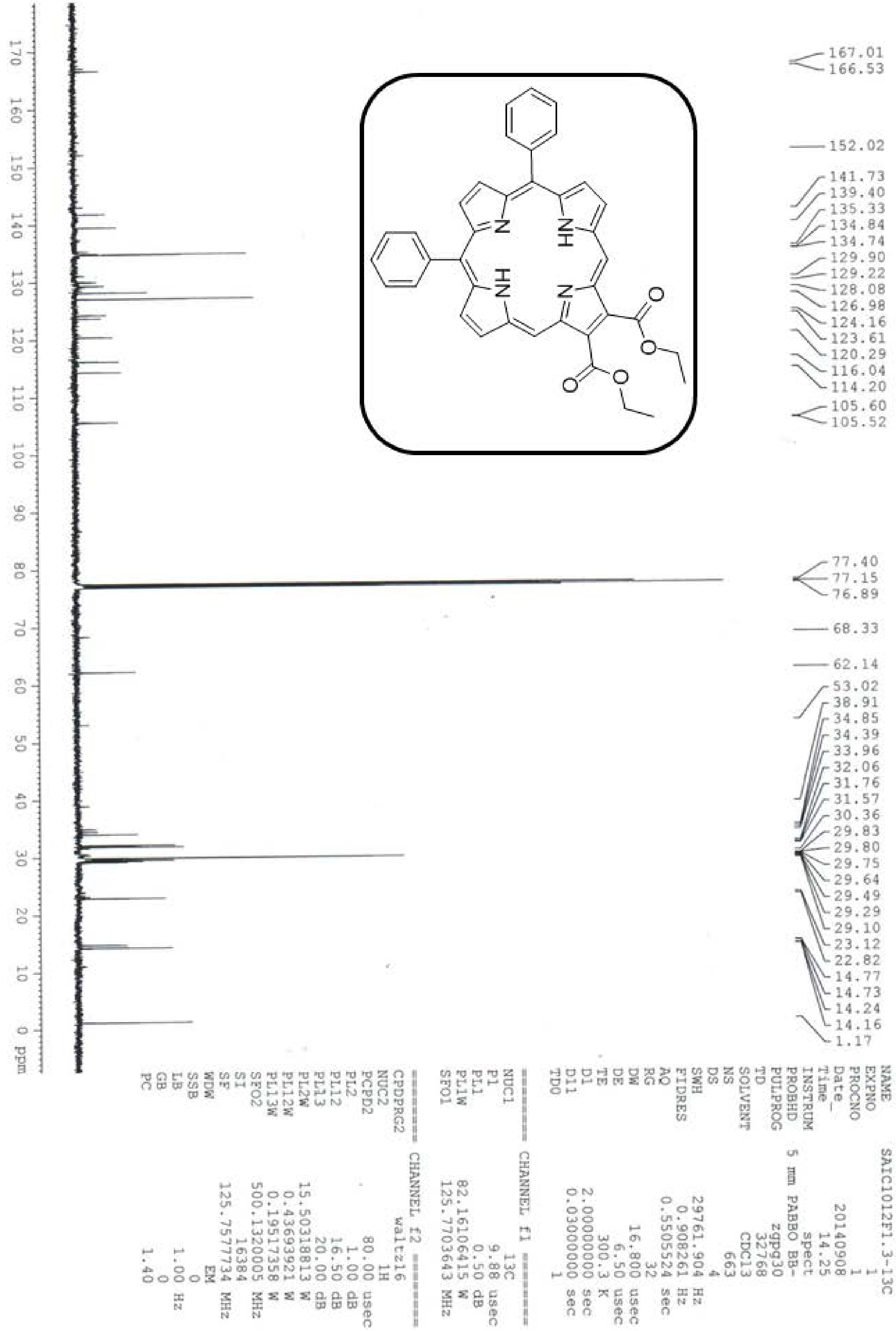
4.4.2. ESI-MS of 6,12-Diphenyltripyrrane



4.5.1. ^{1}H NMR ($CDCl_3$, 500 MHz) of PP-diester



4.5.2. ^{13}C {1H}(NMR CDCl$_3$, 100 MHz) of PP-diester



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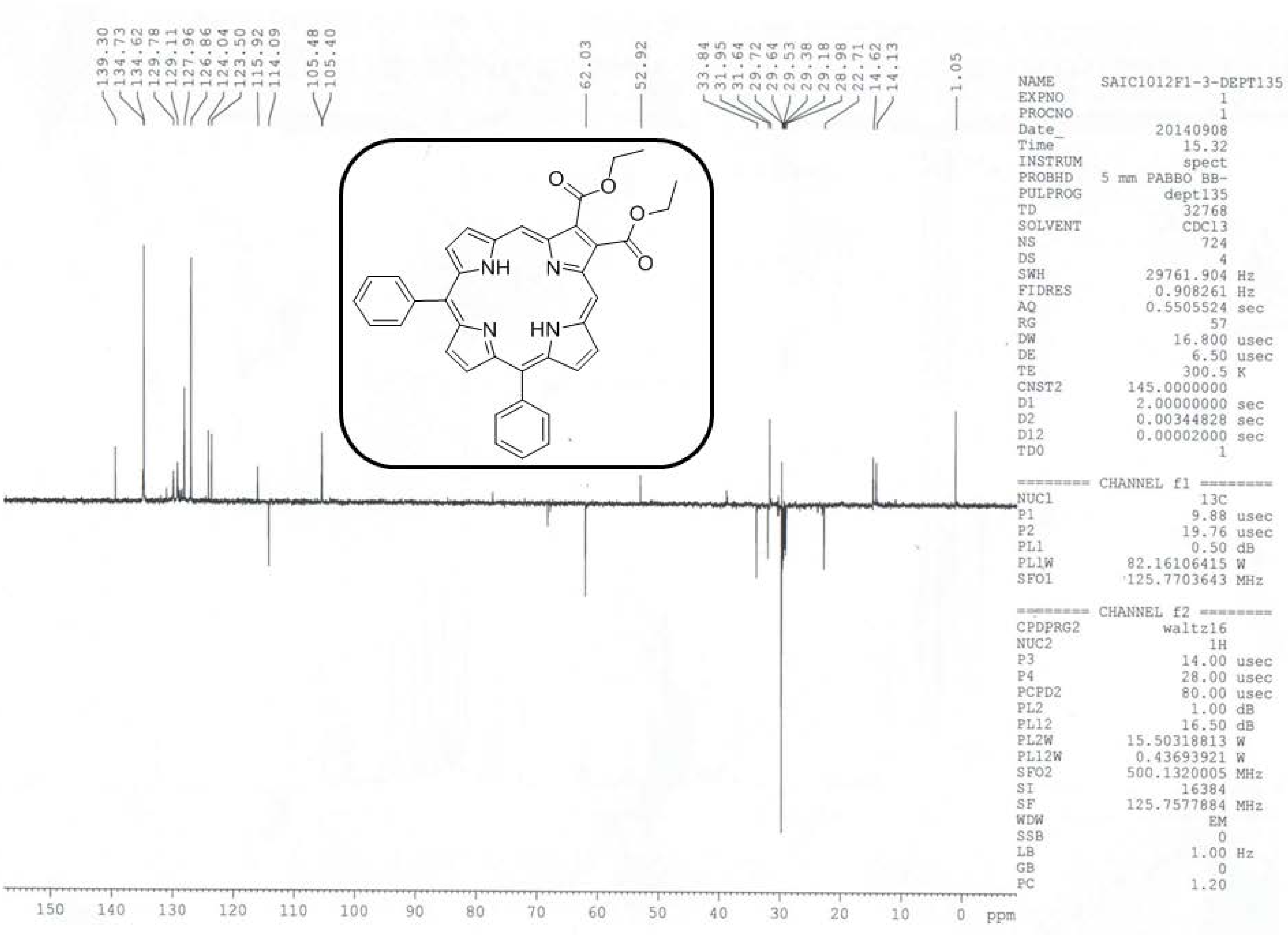
DW               16.800 usec
DE                 6.50 usec
TE                  300.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                 9.88 usec
PL1                 0.50 dB
PL1W          82.16106415 W
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2             80.00 usec
PL2                  1.00 dB
PL12                16.50 dB
PL13                20.00 dB
PL2W          15.50318813 W
PL12W          0.43693921 W
PL13W          0.19517358 W
SFO2         500.1320005 MHz
SI                    16384
SF           125.7577334 MHz
WDW                      EM
SSB                       0
LB                  1.00 Hz
GB                        0
PC                     1.40
```

4.5.3. DEPT-135 NMR ($CDCl_3$) of PP-diester



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NAME      SAIC1012F1-3-DEPT135
EXPNO                        1
PROCNO                       1
Date_                 20140908
Time                     15.32
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                dept135
TD                       32768
SOLVENT                  CDCl3
NS                         724
DS                           4
SWH                  29761.904 Hz
FIDRES                0.908261 Hz
AQ                   0.5505524 sec
RG                          57
DW                      16.800 usec
DE                        6.50 usec
TE                       300.5 K
CNST2              145.0000000
D1                  2.00000000 sec
D2                  0.00344828 sec
D12                 0.00002000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                        9.88 usec
P2                       19.76 usec
PL1                       0.50 dB
PL1W               82.16106415 W
SFO1              125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
P3                       14.00 usec
P4                       28.00 usec
PCPD2                    80.00 usec
PL2                       1.00 dB
PL12                     16.50 dB
PL2W               15.50318813 W
PL12W               0.43693921 W
SFO2              500.1320005 MHz
SI                       16384
SF                125.7577884 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.20
```
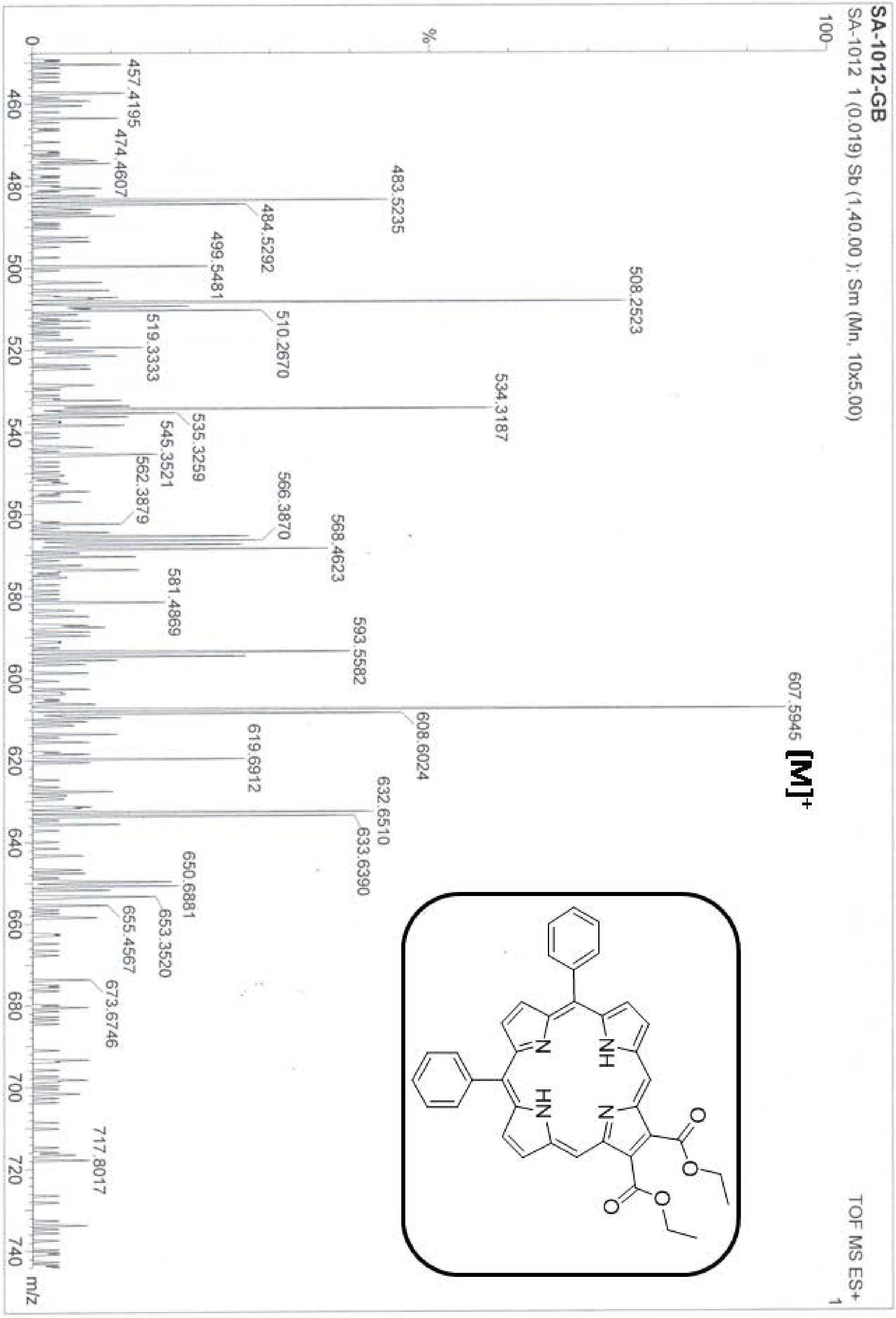
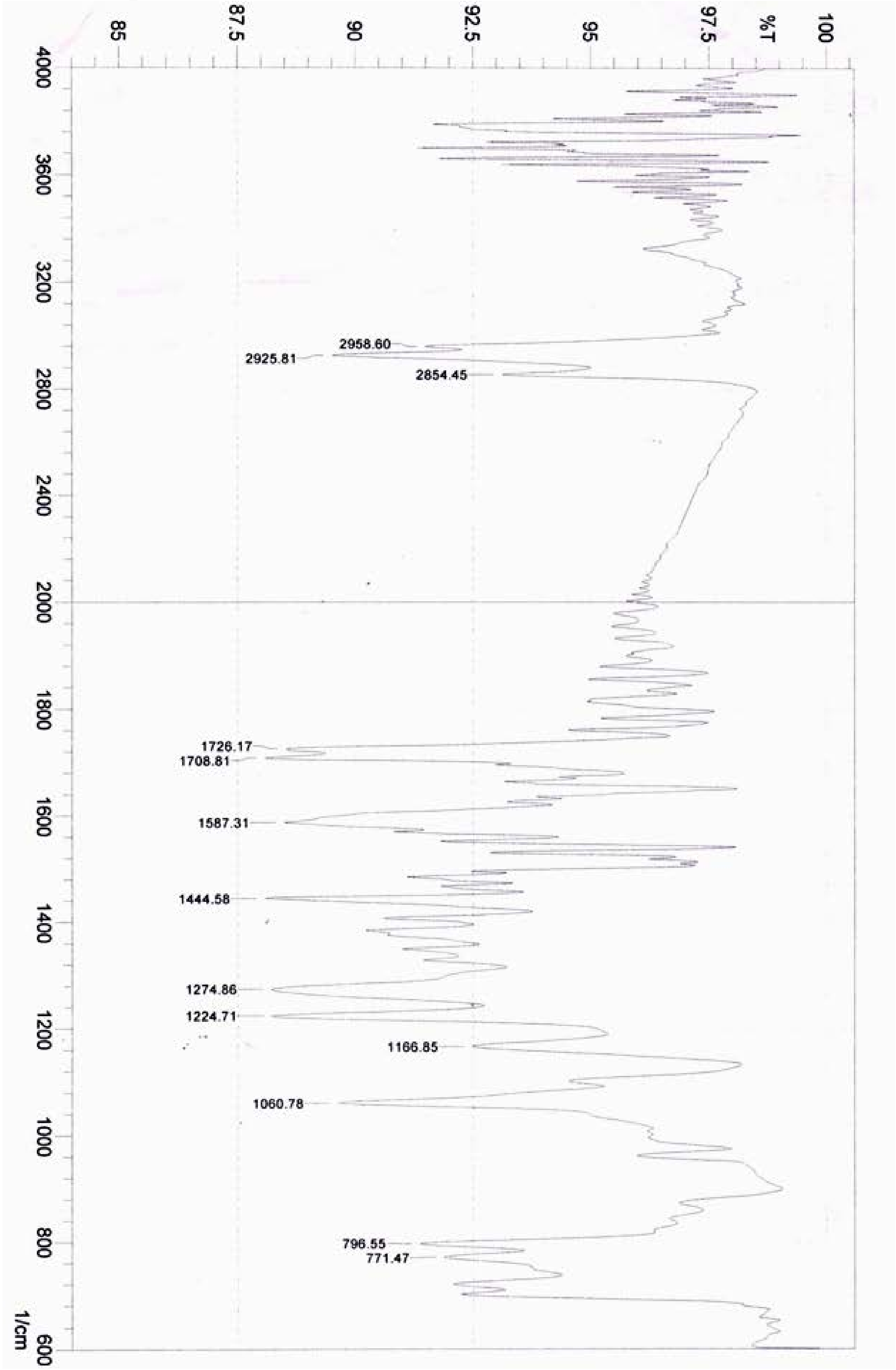
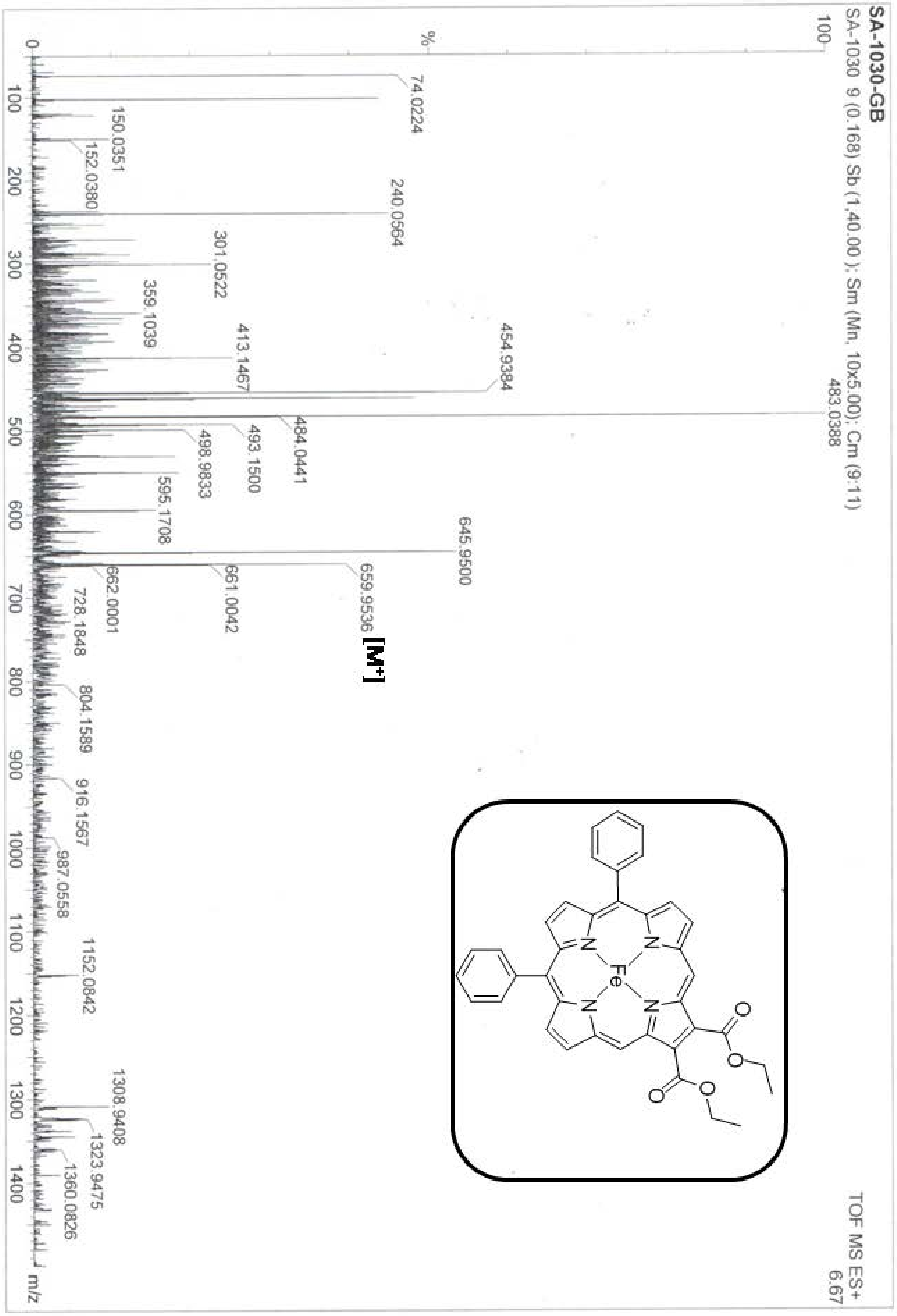

4.5.4. ESI-MS of PP-diester



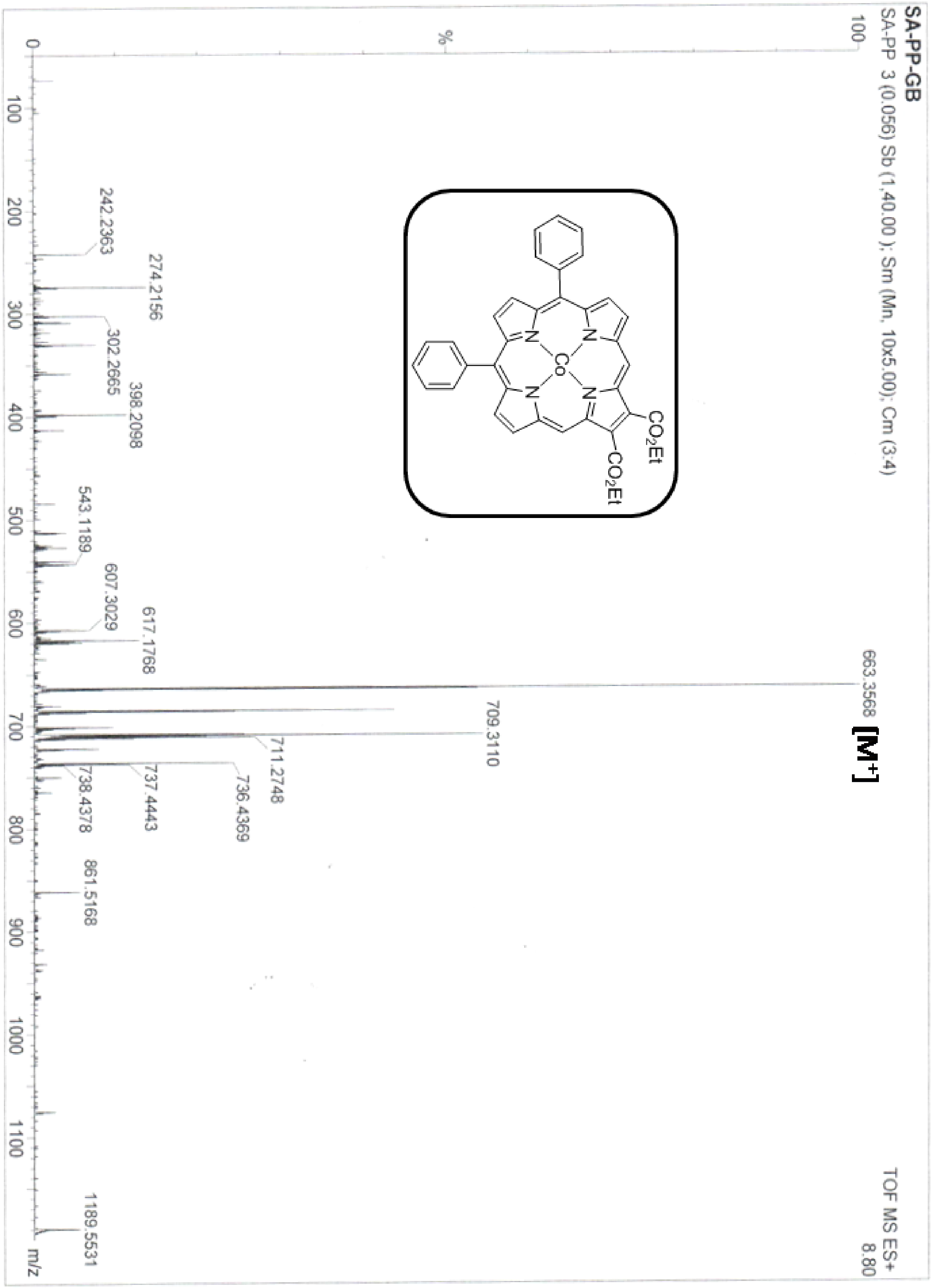
4.5.5. IR spectrum of PP-diester



4.6. ESI-MS of Fe-PP-diester



4.7. ESI-MS of Co-PP-diester



5. UV-Vis absorption spectra:

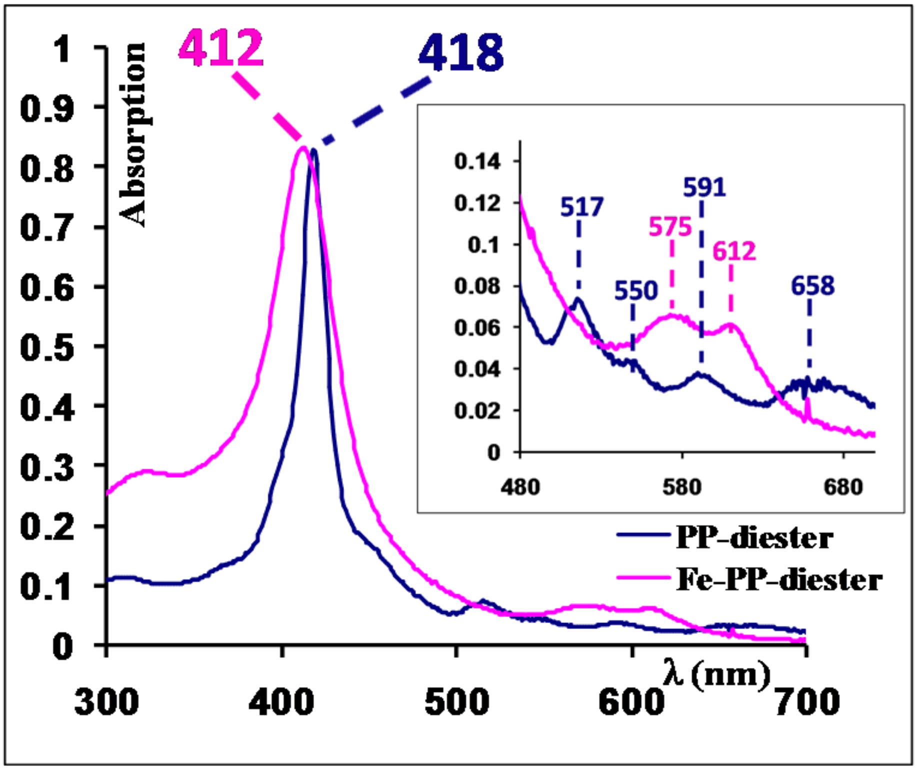


Figure S28: Absorption spectra in the UV-Visible region for the free ligand (blue) and the Fe(III) (pink) complex in CH_2Cl_2

6. Resonance-Raman spectra:

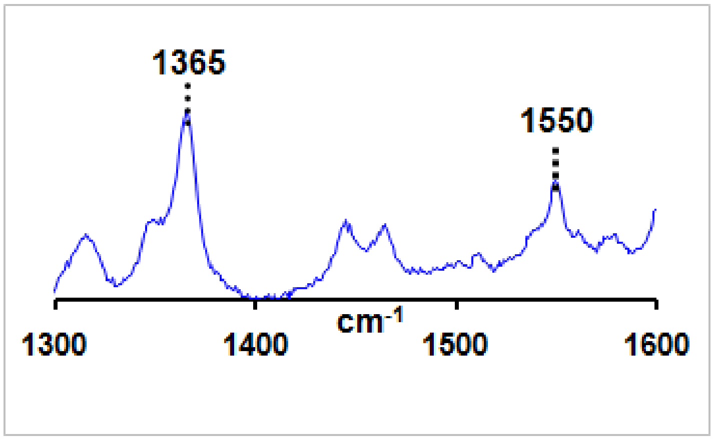


Figure S29: The ν_4 and ν_2 region of the resonance-Raman spectra of Fe-PP-diester complex is shown here in THF at room temperature (Power: 5 mW).

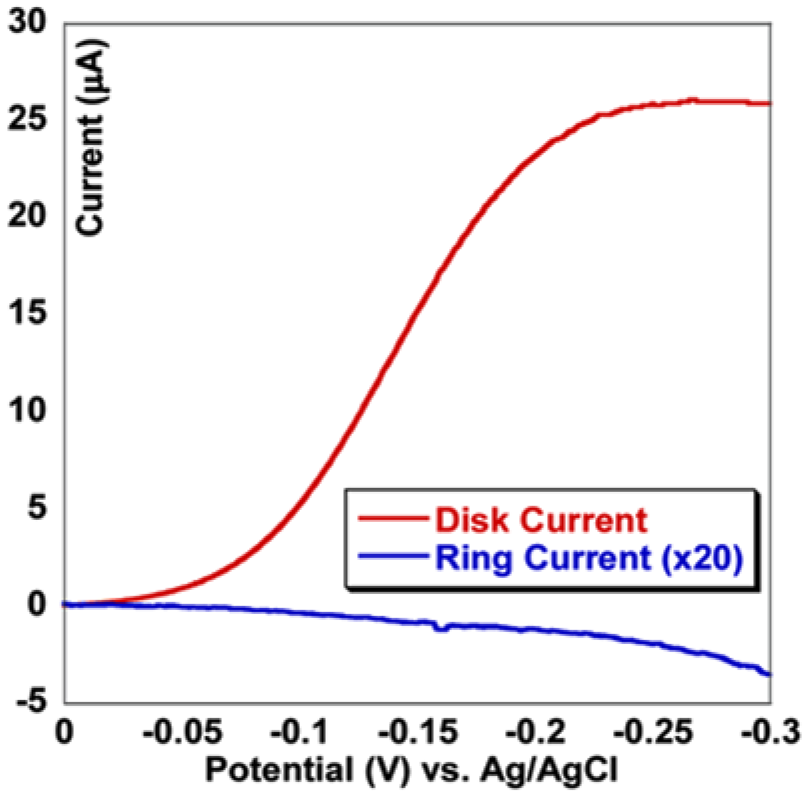


Figure S30: RRDE of the Fe-PP-diester, showing the disc (red) and Pt ring (blue) currents, physiabsorbed on EPG in air saturated pH 7 buffer at a scan rate of 10 mV/s using Ag/AgCl reference and Pt wire counter electrodes.