Supporting Information for:

Spectroscopic and Electrochemical Sensing of Lanthanides with π-Extended Chromophores Incorporating Ferrocenes and a Coordinative End

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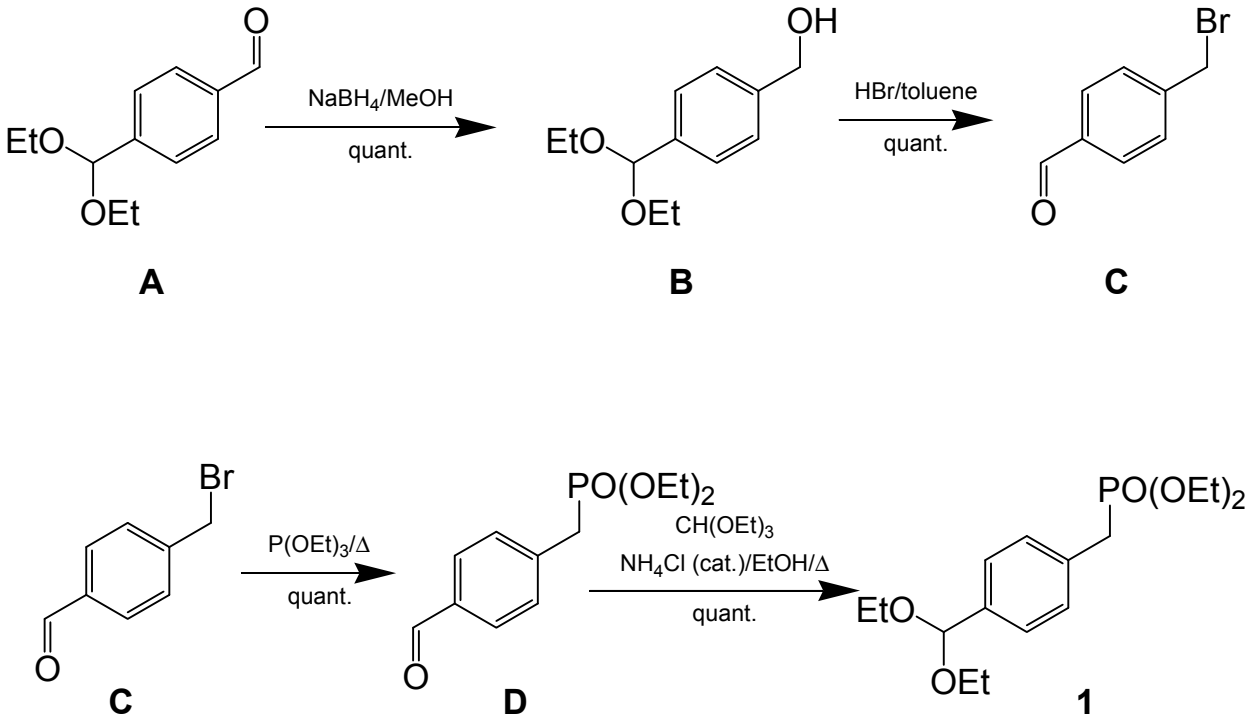
Contents:

Compound 1. This compound was prepared following the synthetic steps reported in Scheme S1. We substantially modified previous procedures[S1].

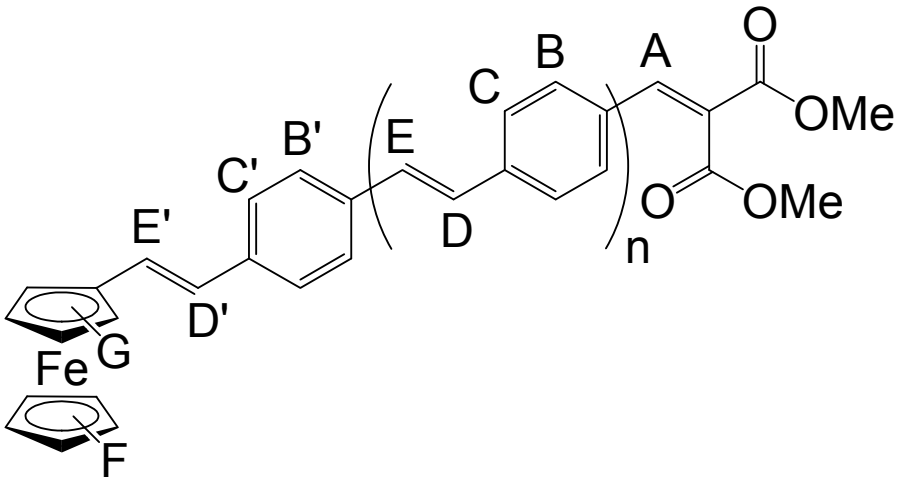


Scheme S1.

4-(diethoxymethyl)benzylalcohol B. $NaBH_4$ (625 mg, 16.4 mmol) was added to a solution of 4-(diethoxymethyl)benzaldehyde (1 ml, 1.043 g, 5 mmol) in MeOH (42 mL) at 0°C. After stirring at room temperature for 15 h, the solvent was removed in vacuo and the solution was treated with H_2O, extracted with CH_2Cl_2 and dried (Na_2SO_4) to give the title compound, which was used without further purification, in quantitative yield (1.057 g). **4-bromomethylbenzaldehyde C**. HBr (10 L, 13.2M in H_2O) were added to a solution of compound B (1.183 g) in toluene (20 mL). The reaction was stirred at reflux for 4h. After cooling at room temperature, the mixture was poured into a mixture of water/ice, extracted with CH_2Cl_2 and dried (Na_2SO_4) to yield the title compound, which was used without further purification, in quantitative yield (1.518 g).[S2] **4-(diethoxyphosphorylmethyl)benzaldehyde D**. A solution of compound C (1.3 g, 7 mmol) in 3 mL of triethylphosphite was stirred at 120°C for 15 h. The crude reaction mixture was purified by column chromatography (SiO_2; 1/1 hexane/ethyl acetate), to give the title compound as a

colorless oil in quantitative yield. [S3]. **4-(diethoxyphosphorylmethyl)benzyl bromide 1**. A catalytic amount of NH_4Cl was added to a solution of 4-(diethoxyphosphorylmethyl)benzaldehyde (1.8 g, 7 mmol) and triethylortoformiate (3.5 mL) in MeOH (3.2 mL). The homogeneous mixture was stirred at reflux for 15 h. After cooling at room temperature, an acqueous solution of $NaHCO_3$ was added. The mixture solution was extracted with Et_2O and the organic phase was separated and dried (Na_2SO_4), to yield the title compound (1.5 g, 69%) as a colorless oil. The ^1H NMR spectrum matched the one previously reported in the literature.[S1a]

Table S1. Selected ^{1}H NMR chemical shifts for molecular modules **6-8** (300 MHz, $CDCl_3$).[a]



Entry	Compound	A	B,B',C,C'	D,E,D',E'(*J*)	F, G	COOMe
1	**6**	7.65	b	b	4.47,4.22	3.91, 3.82
2	**7**	7.77	7.45, 7.41	7.00, 6.70 (16 Hz)	4.42,4.16	3.90, 3.87
3	**8**	7.78	7.56-7.43	7.20 (D), 7.10 (E), 6.94 (D'), 6.72 (E') (16 Hz)	4.41,4.16	3.90, 3.88

a) Concentrations were in the range 5-10 mM (300 MHz). b) Not applicable.

Figure S1. Modeled curves for 1:1 complexes between ligands **6-8** and $Sc(OTf)_3$ or $Eu(OTf)_3$

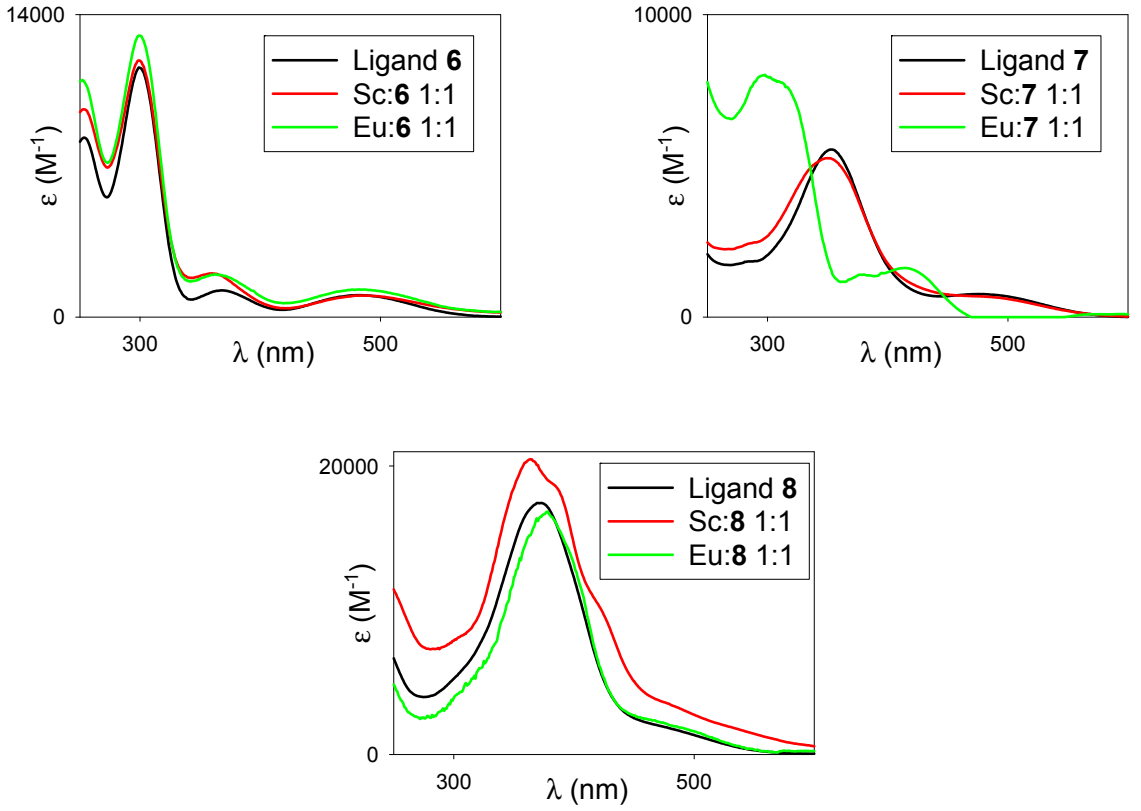
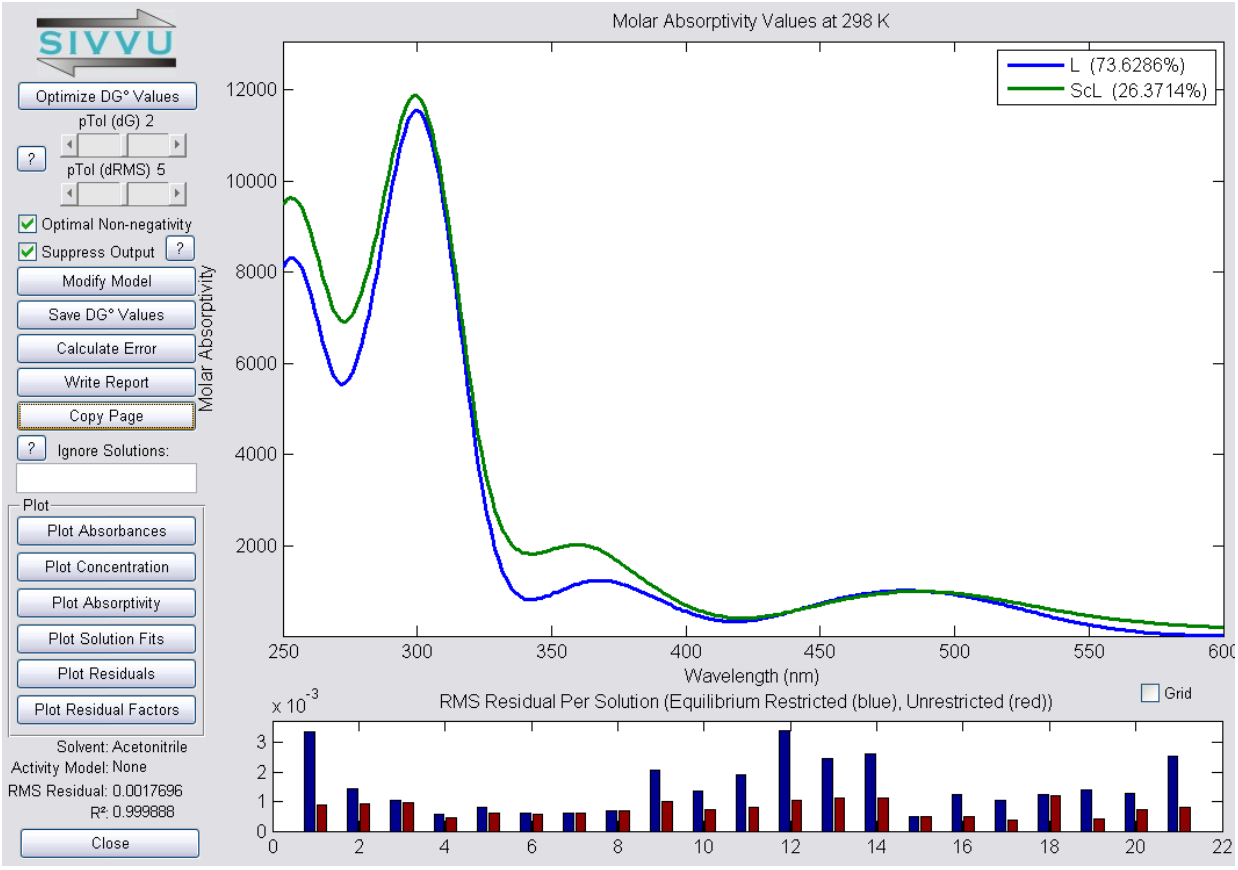


Figure S2. Compound **6** (0.000052 M in MeCN) is titrated with 0–12.4 equivalents of $Sc(OTf)_3$; 21 solutions analyzed.



Optimization Summary:
Data at 298 K
Non-negativity was enforced with optimization (not truncation).
Activity Coefficients Model: None.
Species with Fixed Molar Absorptivity Curves: None.
Solutions ignored: None.
Optimized Values (kJ/mol): $\Delta G_1° = -18$ (unrefined)
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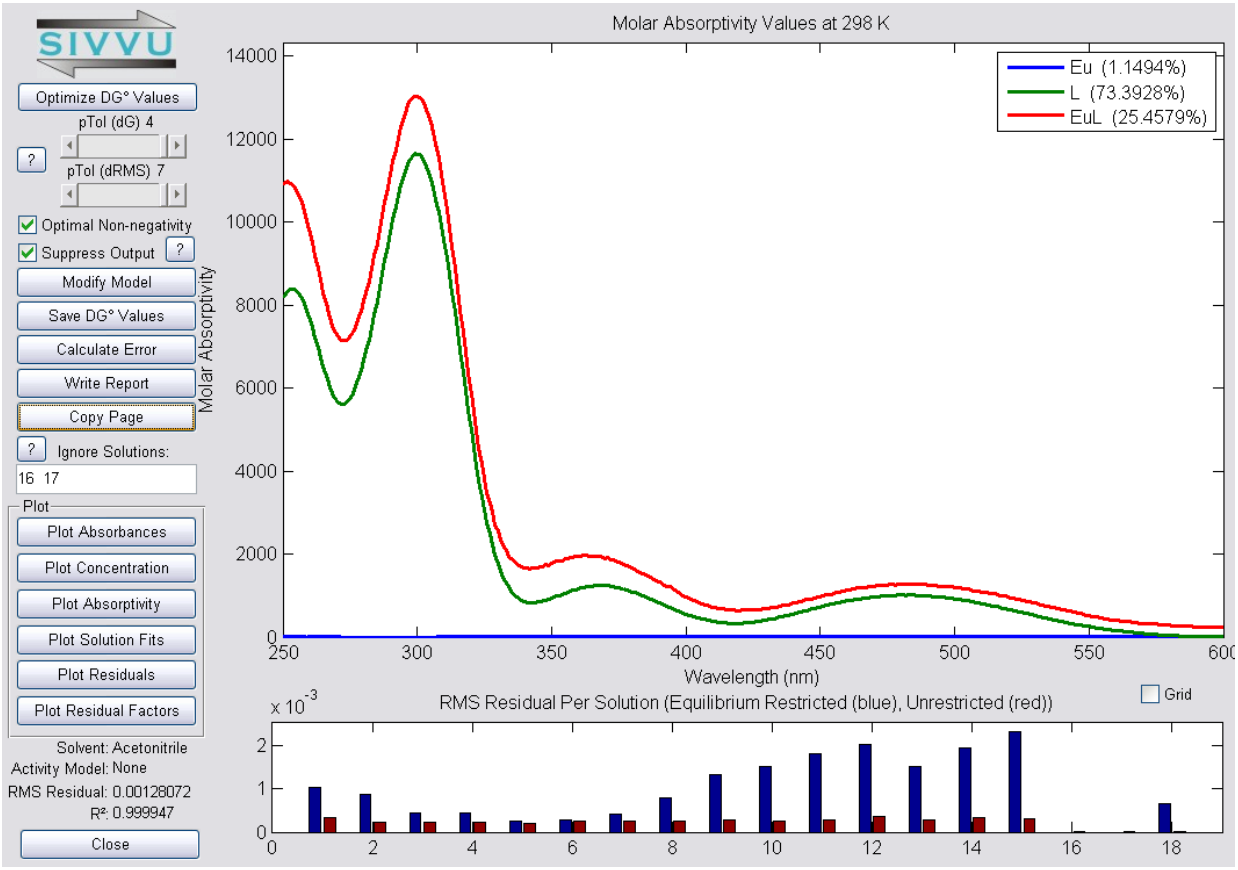
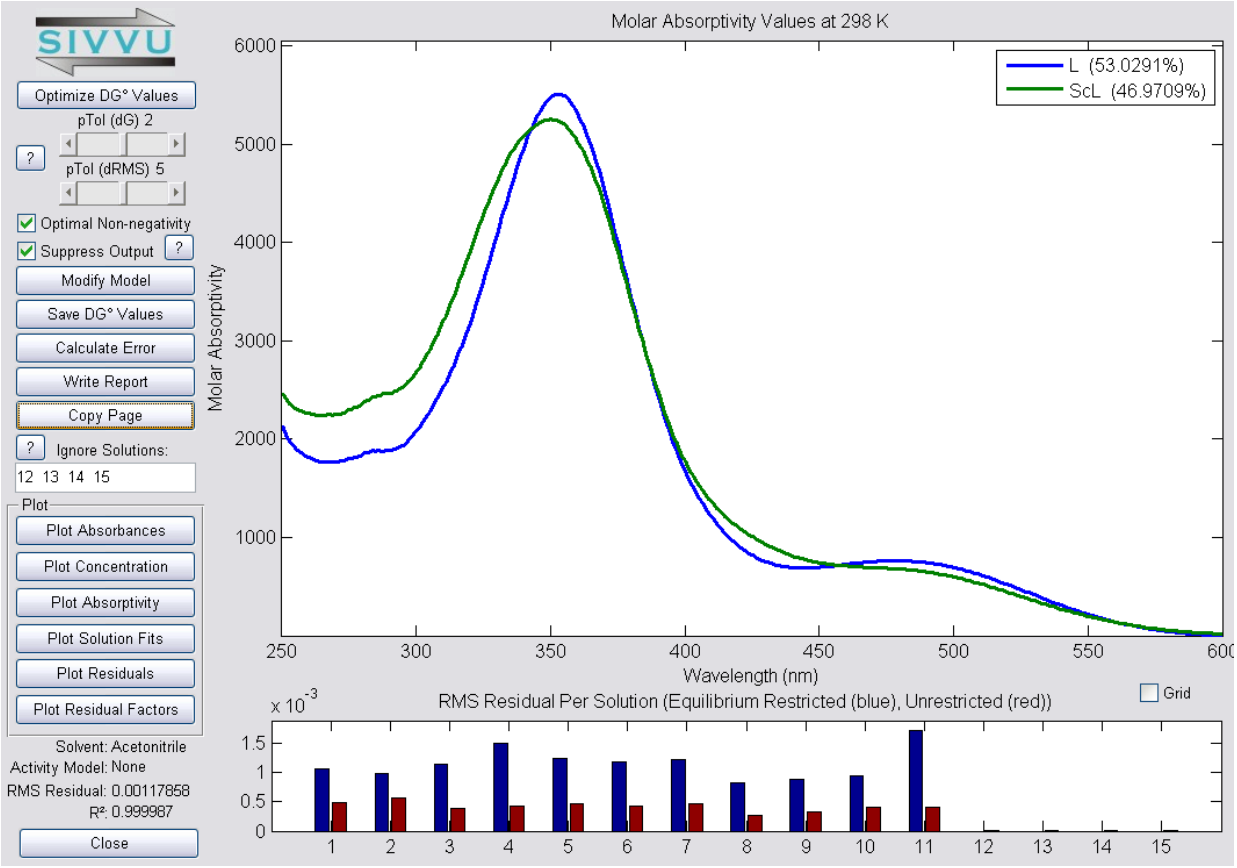
Unrestricted RMS Residual (2 mathematical factors): 0.00080047
Restricted Data Reconstruction (2 chemical factors): 99.0099%
Unrestricted Data Reconstruction (2 mathematical factors): 99.0268%
Remaining Error Imbedded in Absorbance Values: 0.00057414
R^2: 99.9888%

Figure S3. Compound **6** (0.000052 M in MeCN) is titrated with 0–11.2 equivalents of $Eu(OTf)_3$; 15 + 1 solutions analyzed. Error analysis performed by re-optimizing the data 40 times with a random subset of half the wavelengths ignored.



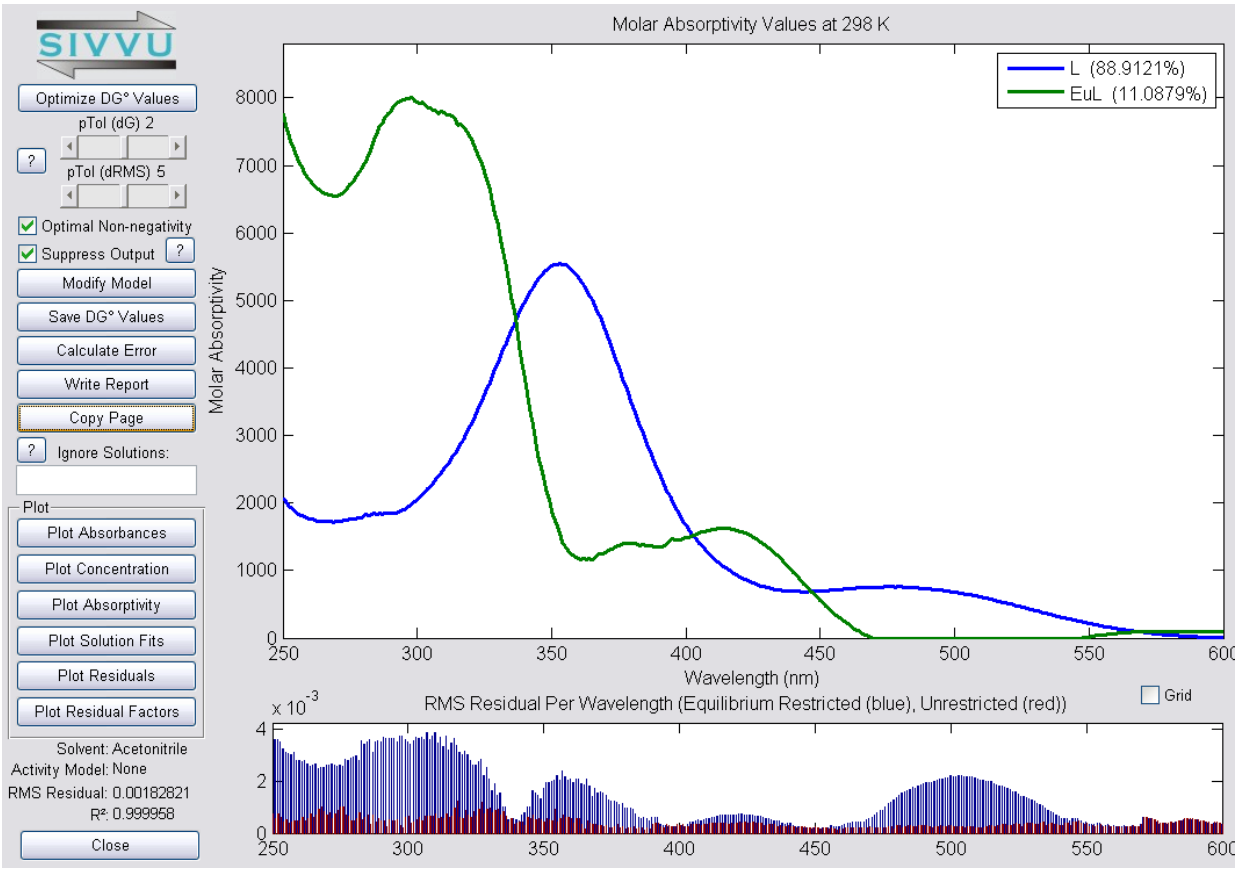
Optimization Summary:
Data at 298 K
Non-negativity was enforced with optimization (not truncation).
Activity Coefficients Model: None.
Species with Fixed Molar Absorptivity Curves: None.
Solutions ignored: 16 17
Optimized Values (kJ/mol): $\Delta G_1° = -16.95(2)$
Equilibrium Restricted RMS Residual (3 chemical factors): 0.0012807
Unrestricted RMS Residual (3 mathematical factors): 0.00026994
Restricted Data Reconstruction (3 chemical factors): 99.5656%
Unrestricted Data Reconstruction (3 mathematical factors): 99.5784%
Remaining Error Imbedded in Absorbance Values: 0.00061524
R^2: 99.9944%

Figure S4. Compound **7** (0.00018 M in MeCN) is titrated with 0–6.1 equivalents of $Sc(OTf)_3$; 11 solutions analyzed. Error analysis performed by re-optimizing the data 40 times with a random subset of half the wavelengths ignored.



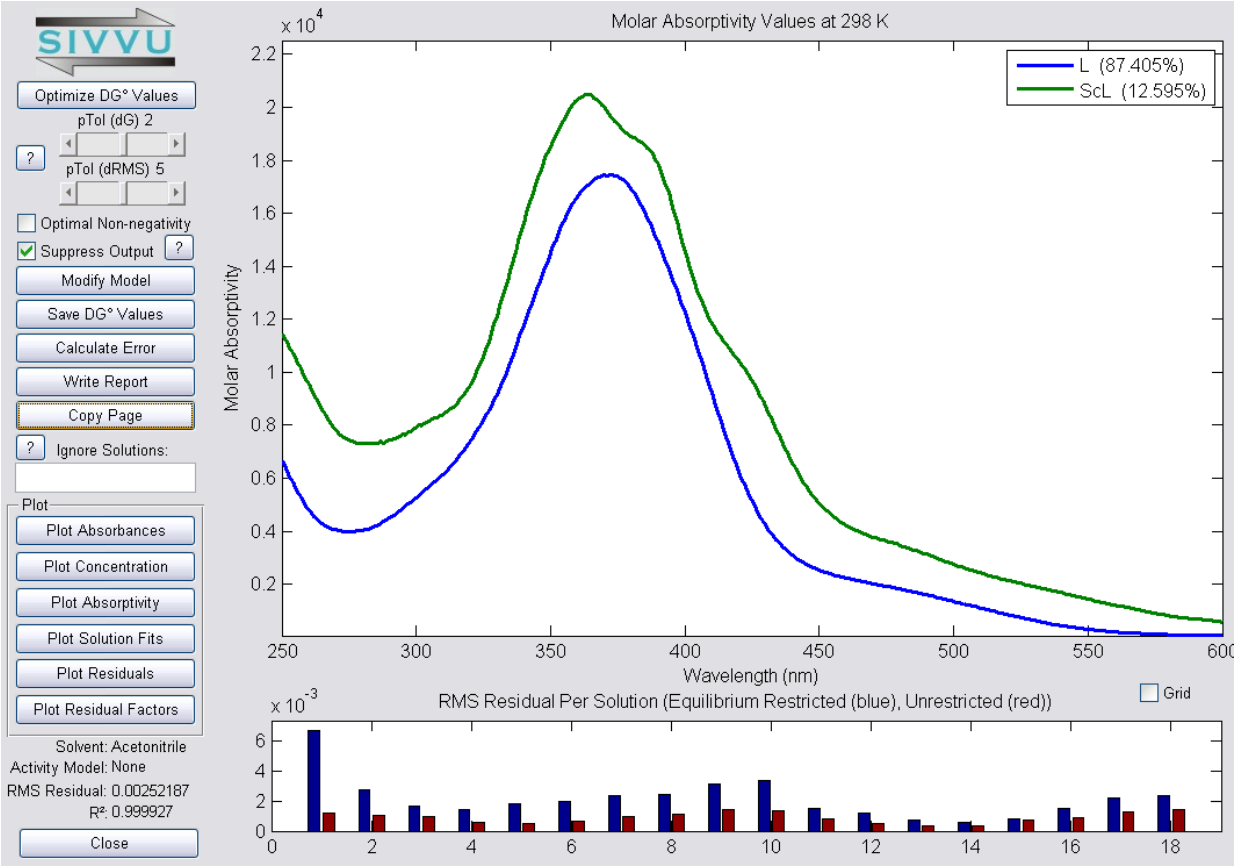
Optimization Summary:
Data at 298 K
Non-negativity was enforced with optimization (not truncation).
Activity Coefficients Model: None.
Species with Fixed Molar Absorptivity Curves: None.
Solutions ignored: 12 13 14 15
Optimized Values (kJ/mol): $\Delta G_1° = -18.36(1)$
Equilibrium Restricted RMS Residual (2 chemical factors): 0.0011786
Unrestricted RMS Residual (2 mathematical factors): 0.00042713
Restricted Data Reconstruction (2 chemical factors): 99.725%
Unrestricted Data Reconstruction (2 mathematical factors): 99.7332%
Remaining Error Imbedded in Absorbance Values: 0.00055559
R^2: 99.9983%

Figure S5. Compound **7** (0.00018 M in MeCN) is titrated with 0–4.4 equivalents of $Eu(OTf)_3$; 9 solutions analyzed. Error analysis performed by re-optimizing the data 40 times with a random subset of half the wavelengths ignored.



Optimization Summary:
Data at 298 K
Non-negativity was enforced with optimization (not truncation).
Activity Coefficients Model: None.
Species with Fixed Molar Absorptivity Curves: None.
Solutions ignored: None.
Optimized Values (kJ/mol): $\Delta G_1° = -13.47(3)$
Equilibrium Restricted RMS Residual (2 chemical factors): 0.0018282
Unrestricted RMS Residual (2 mathematical factors): 0.00044817
Restricted Data Reconstruction (2 chemical factors): 99.7223%
Unrestricted Data Reconstruction (2 mathematical factors): 99.7575%
Remaining Error Imbedded in Absorbance Values: 0.00097722
R^2: 99.9958%

Figure S6. Compound **8** (0.00055 M in MeCN) is titrated with 0–13.1 equivalents of $Sc(OTf)_3$; 18 solutions analyzed. Error analysis performed by re-optimizing the data 40 times with a random subset of half the wavelengths ignored.



Optimization Summary:
Data at 298 K
Non-negativity was enforced with truncation (not optimization).
Activity Coefficients Model: None.
Species with Fixed Molar Absorptivity Curves: None.
Solutions ignored: None.
Optimized Values (kJ/mol): $\Delta G_1° = -14.4(3)$
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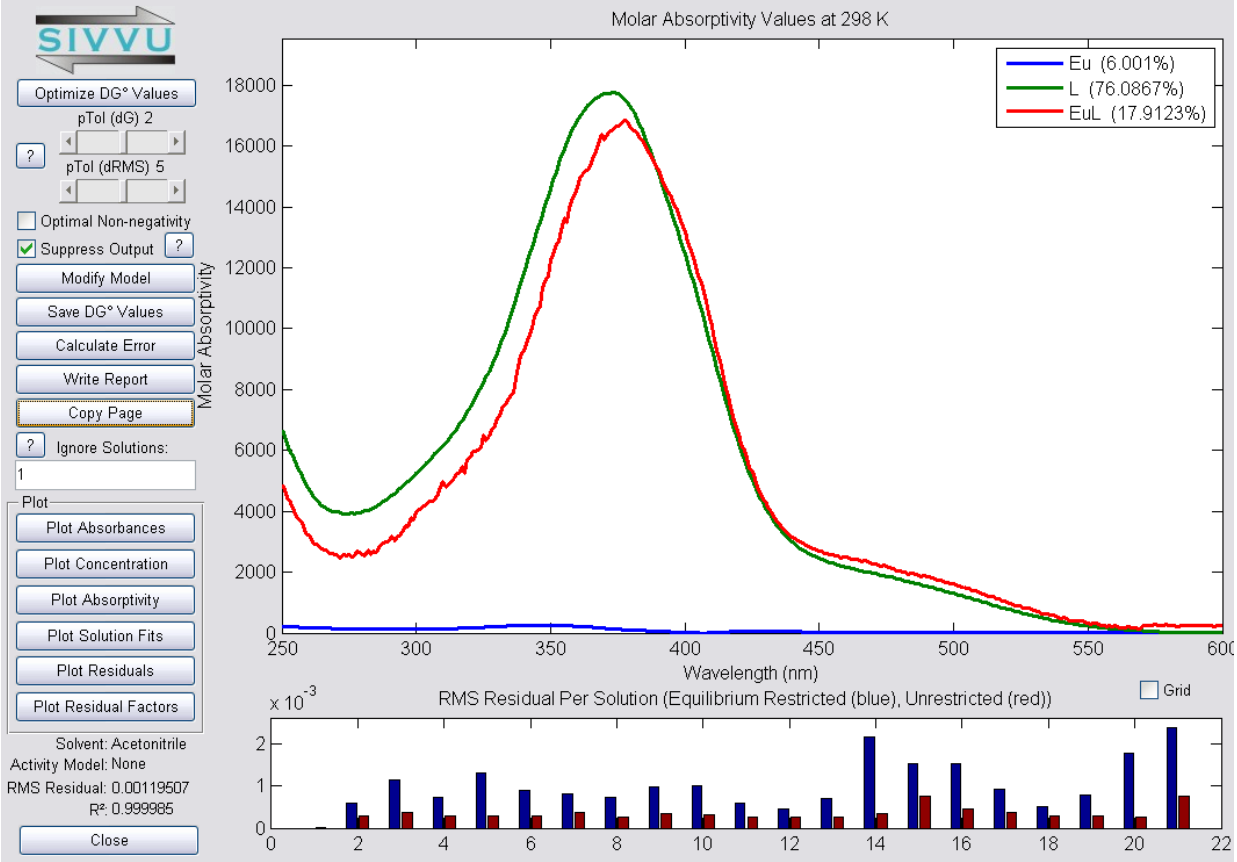
Restricted Data Reconstruction (2 chemical factors): 99.3987%
Unrestricted Data Reconstruction (2 mathematical factors): 99.4798%
Remaining Error Imbedded in Absorbance Values: 0.00089162
R^2: 99.9927%

Figure S7. Compound **8** (0.000054 M in MeCN) is titrated with 0.35–10.8 equivalents of $Eu(OTf)_3$; 20 solutions analyzed. Error analysis performed by re-optimizing the data 40 times with a random subset of half the wavelengths ignored.



Optimization Summary:
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Non-negativity was enforced with truncation (not optimization).
Activity Coefficients Model: None.
Species with Fixed Molar Absorptivity Curves: None.
Solutions ignored: 1
Optimized Values (kJ/mol): $\Delta G_1° = -17.70(2)$
Equilibrium Restricted RMS Residual (3 chemical factors): 0.0011951
Unrestricted RMS Residual (3 mathematical factors): 0.00038278
Restricted Data Reconstruction (3 chemical factors): 99.6488%
Unrestricted Data Reconstruction (3 mathematical factors): 99.6994%
Remaining Error Imbedded in Absorbance Values: 0.00050203
R^2: 99.9985%

Figure S8. Titration of compound **6** (0.0105 M in CD_3CN) with $Sc(OTf)_3$: A) 0 equivalents; B) 0.6 equivalents; C) 0.8 equivalents. As in Figure 3 but with complete NMR spectra

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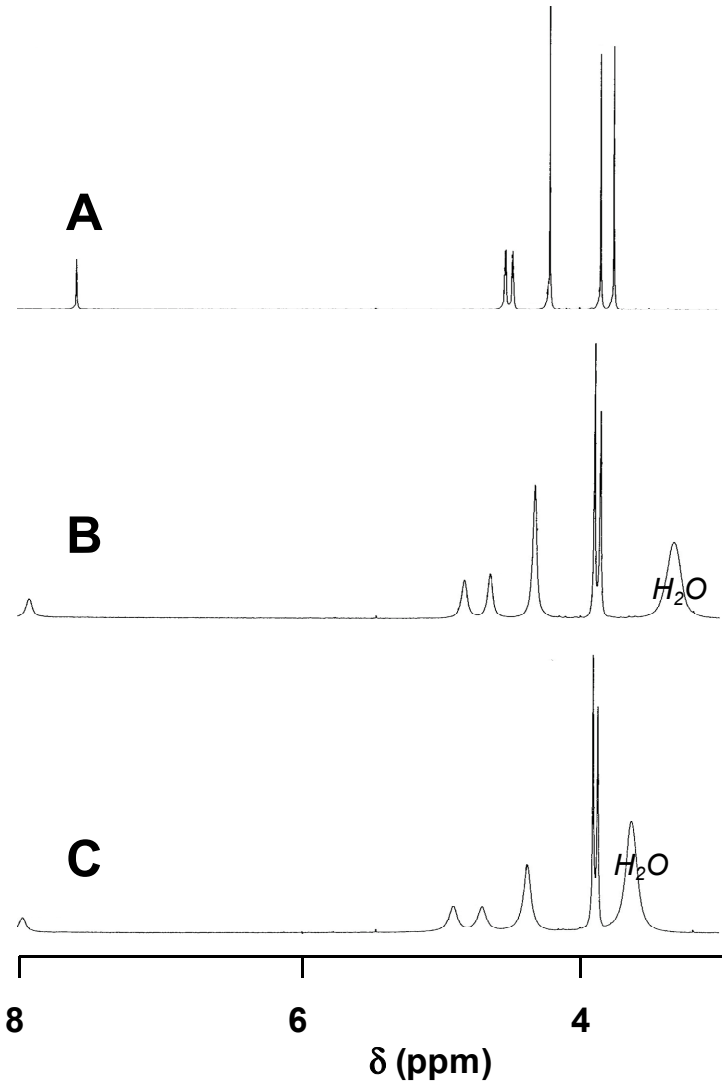
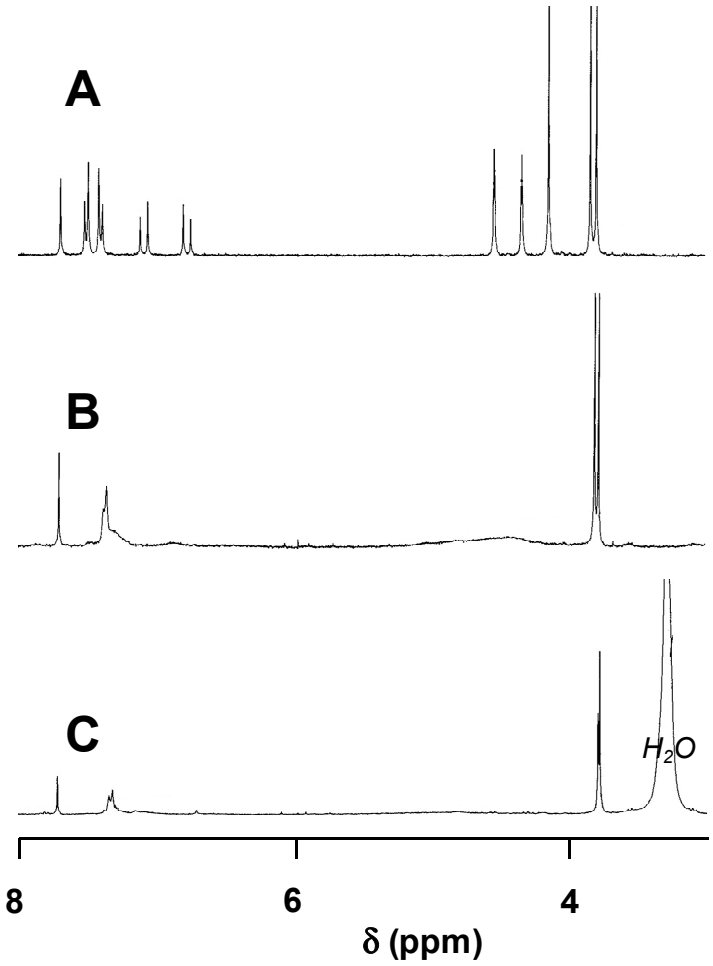
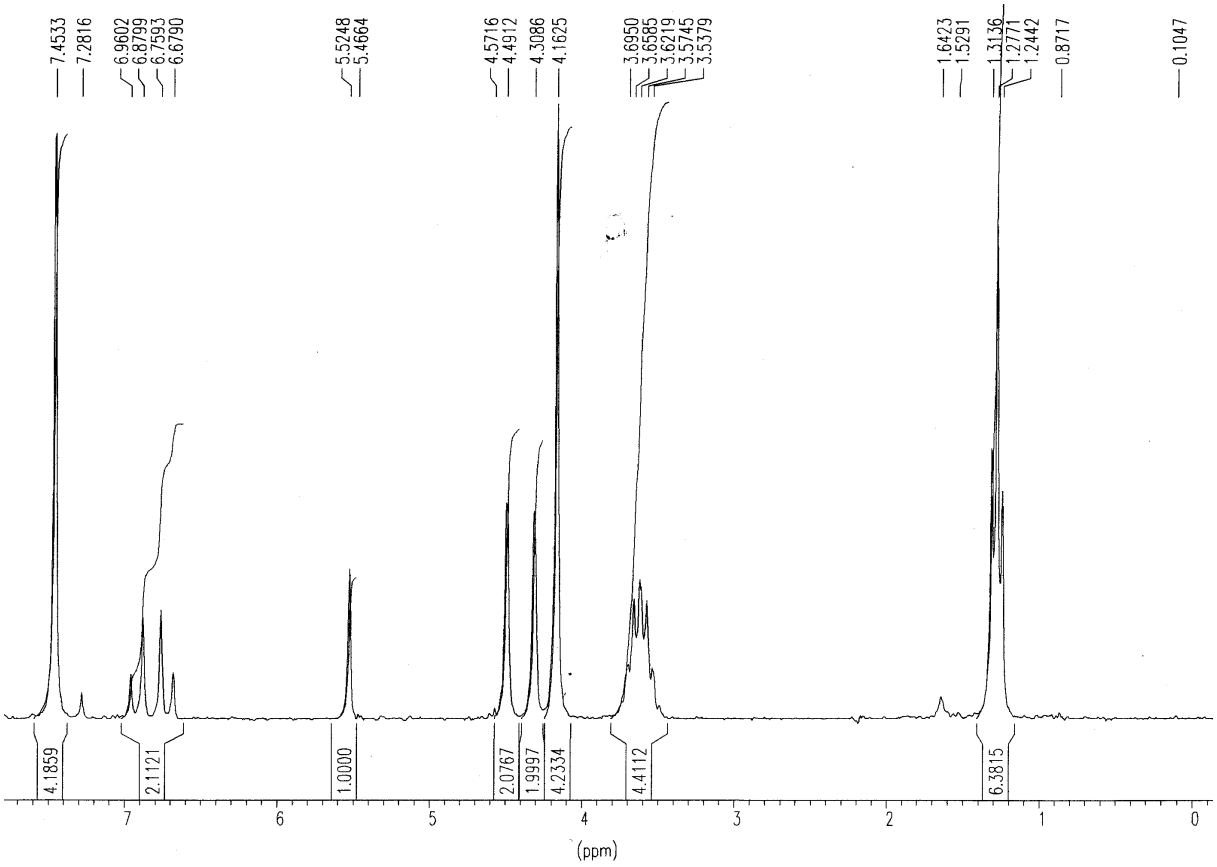


Figure S9. Titration of ligand **7** (2.5 x 10^{-3} M in CD_3CN) with $Sc(OTf)_3$: A) 0 equivalents; B) 0.3 equivalents; C) 1.5 equivalents. As in Figure 4 but with complete NMR spectra.

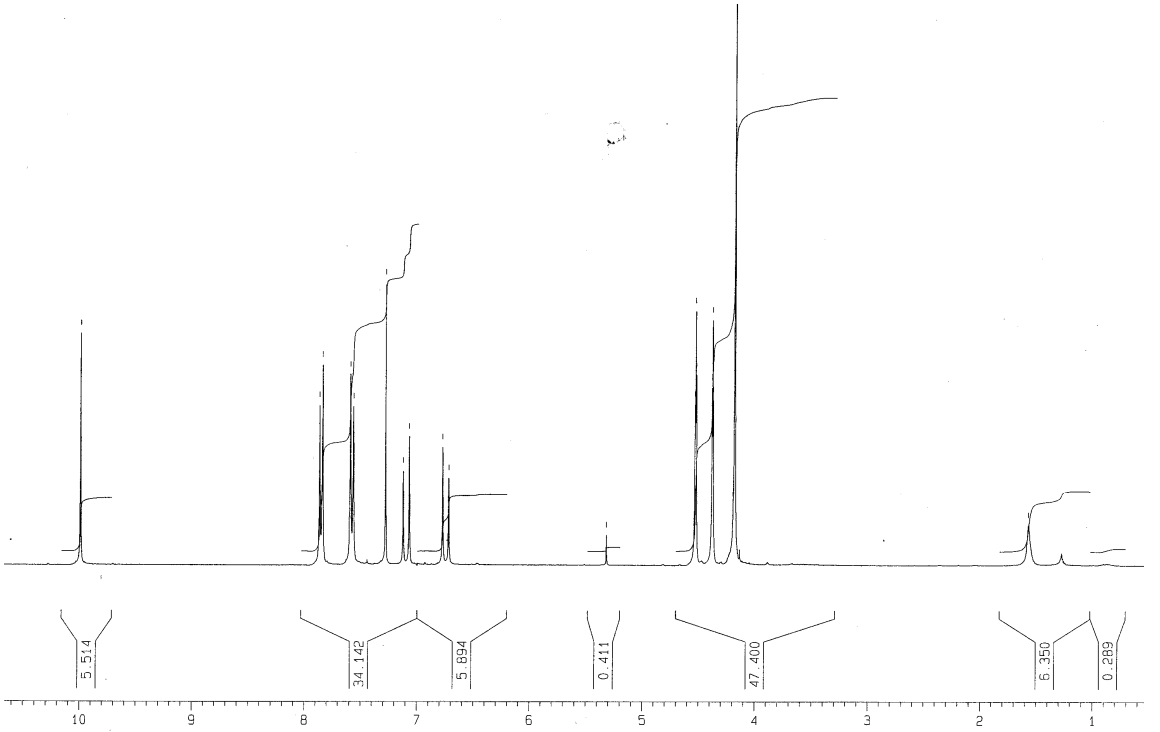


Copies of NMR and mass spectra.

Compound **2**.



Compound **4**.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7
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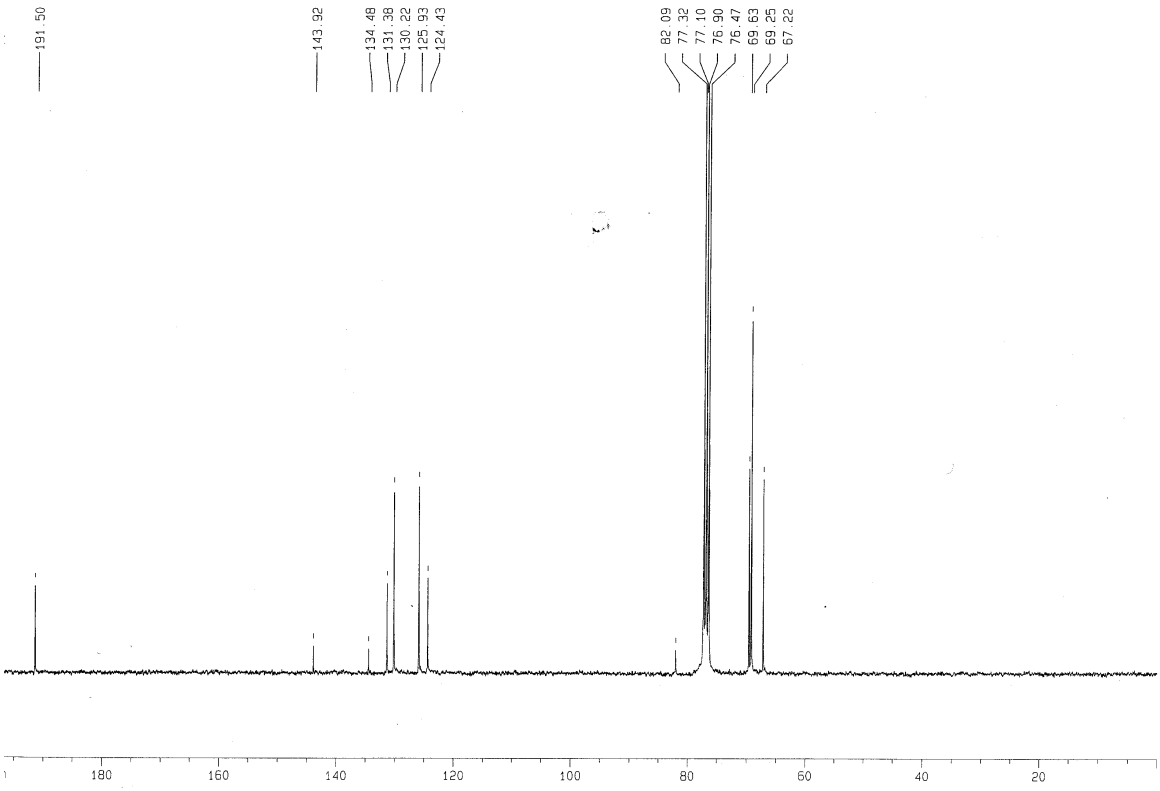
5
4
3
2
1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69.25
67.22
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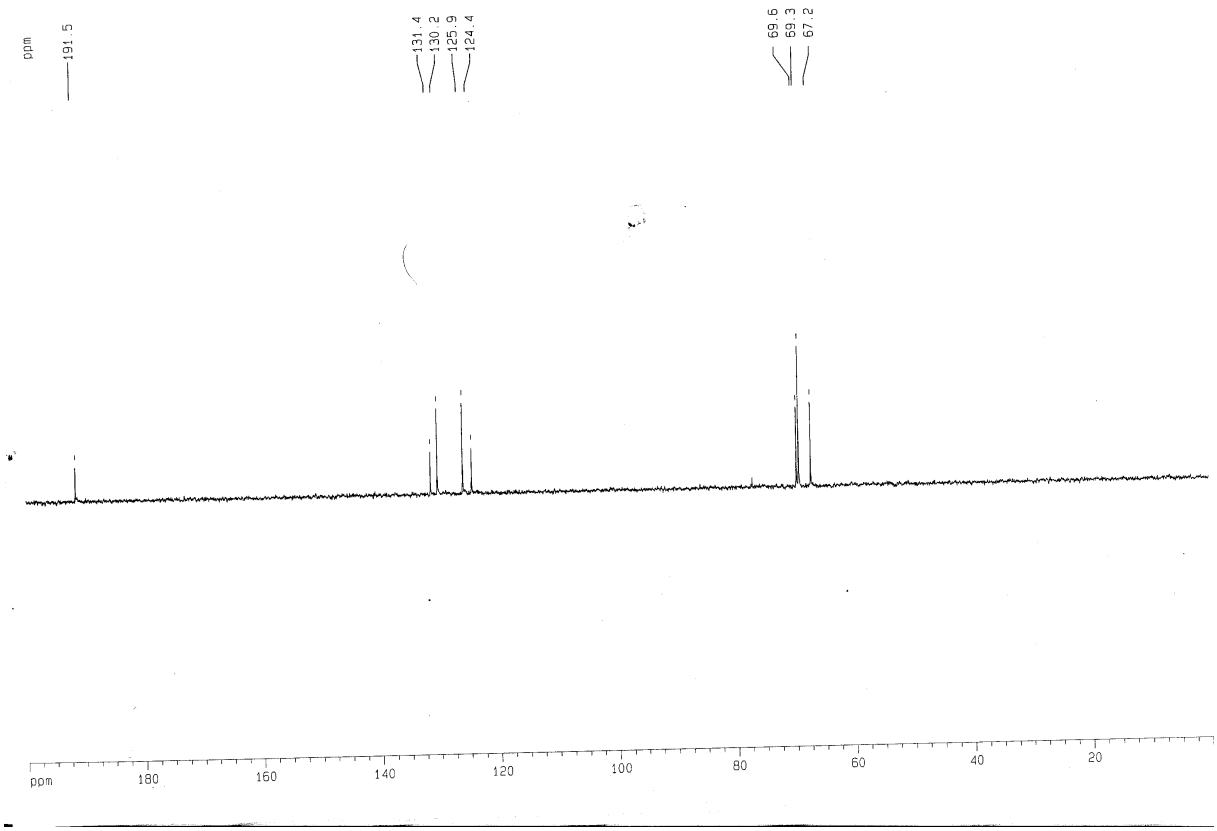
140
120
100
80
60
40
20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ppm
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160
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120
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80
60
40
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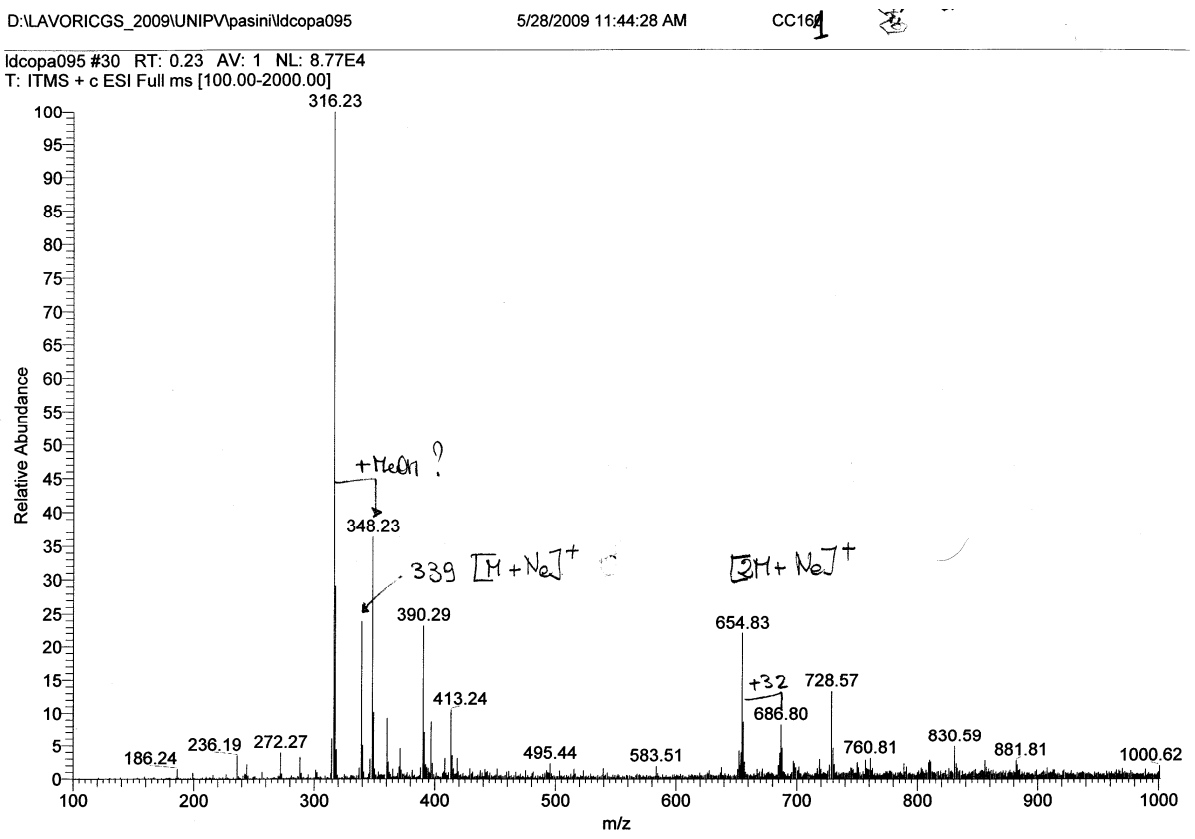
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[2M+Na]+
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413.24
654.83
+32
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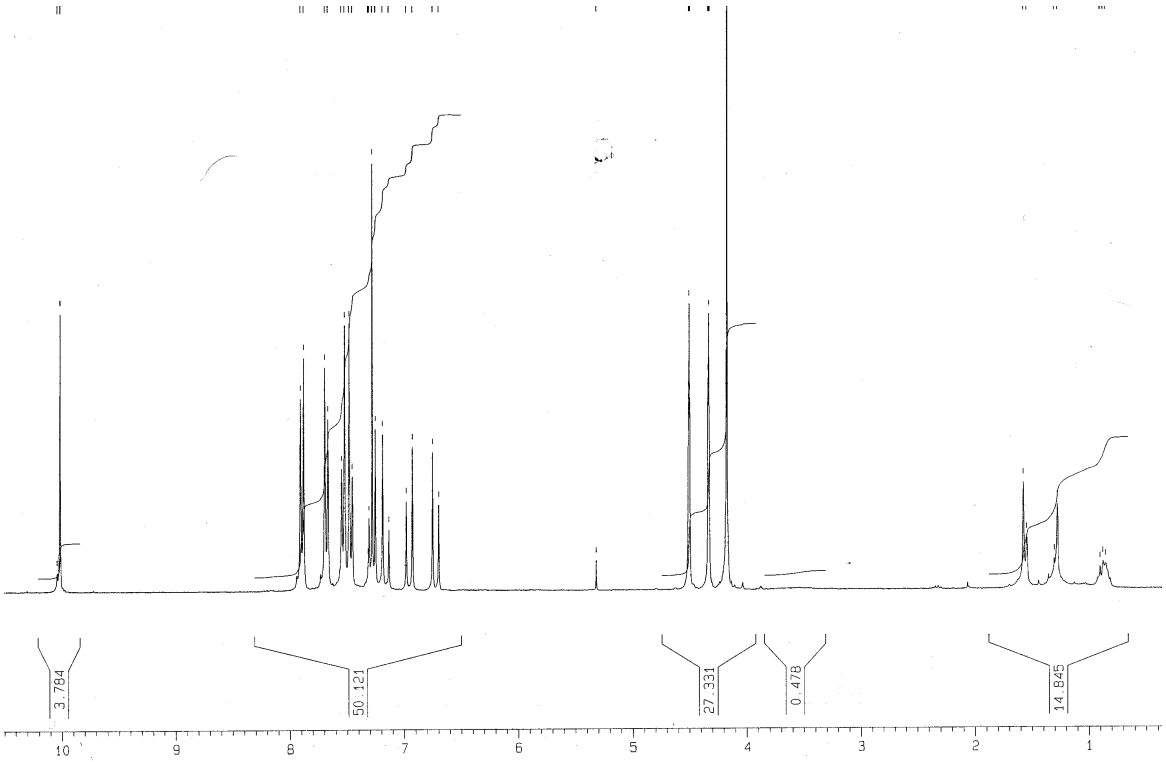
830.59
881.81
1000.62

Compound **5**.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4
3
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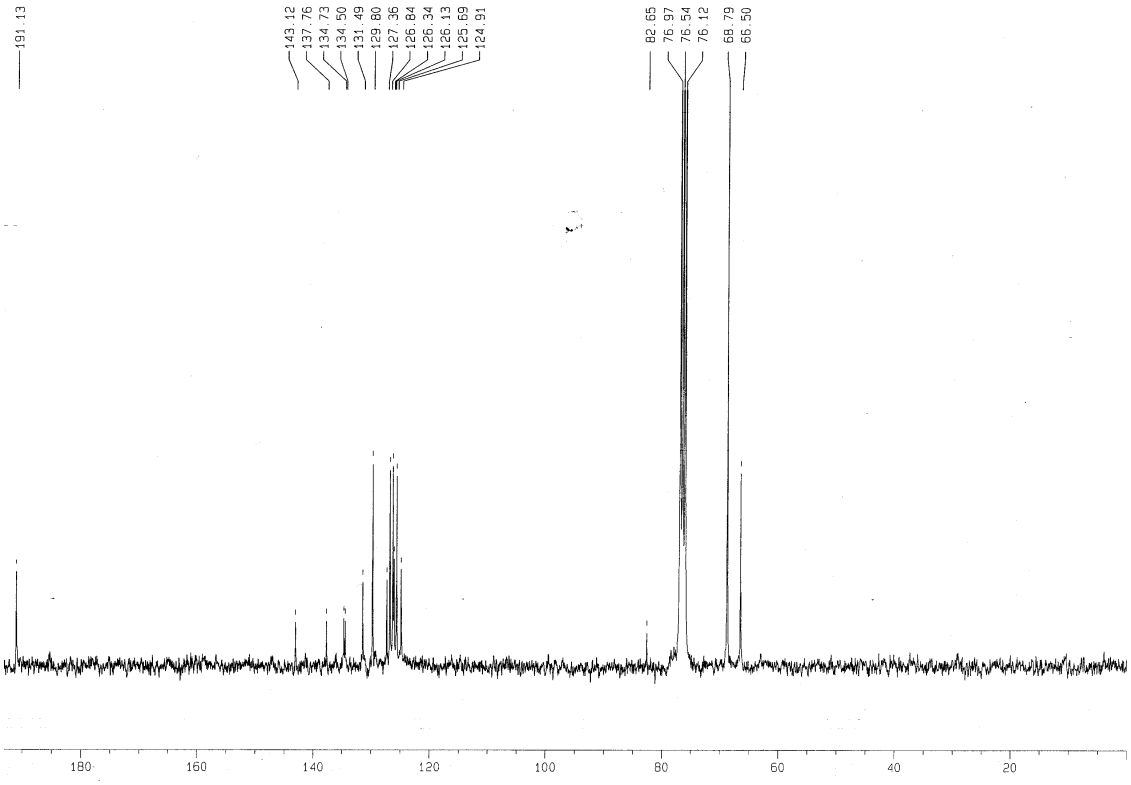
1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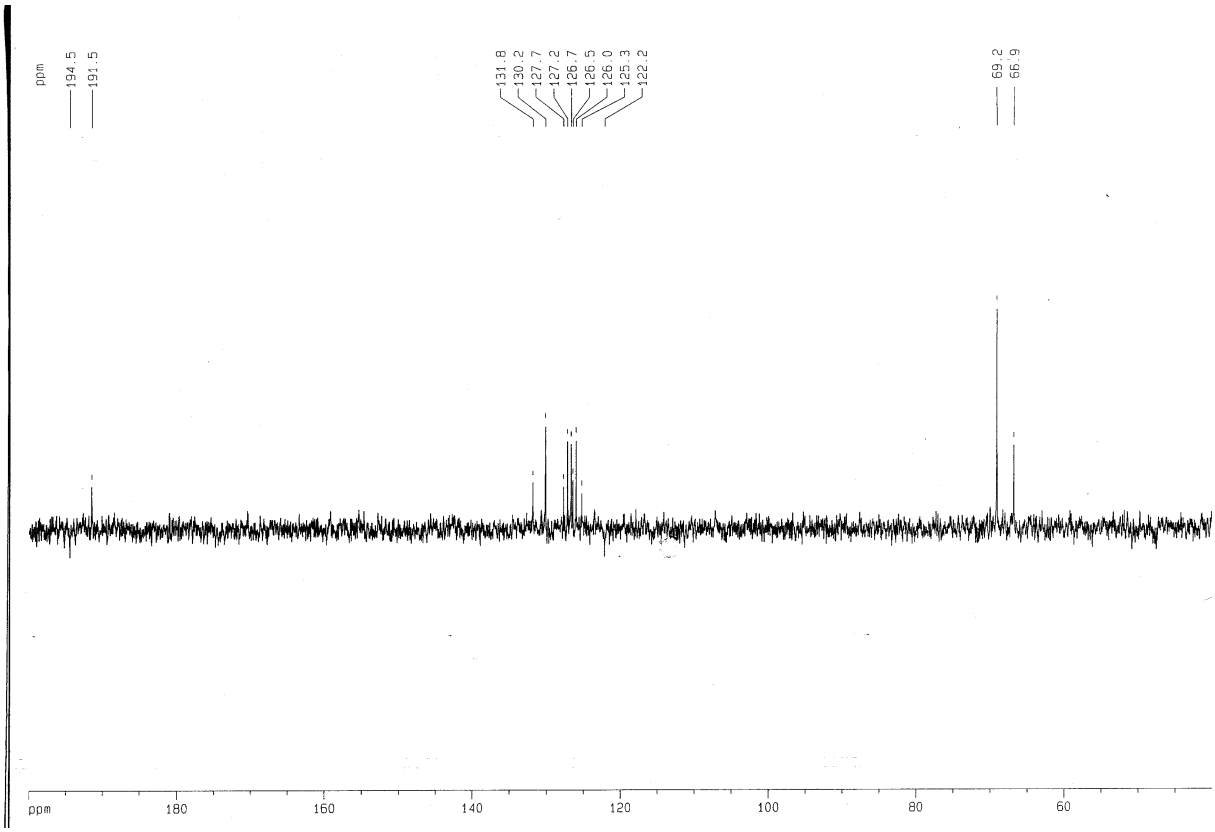
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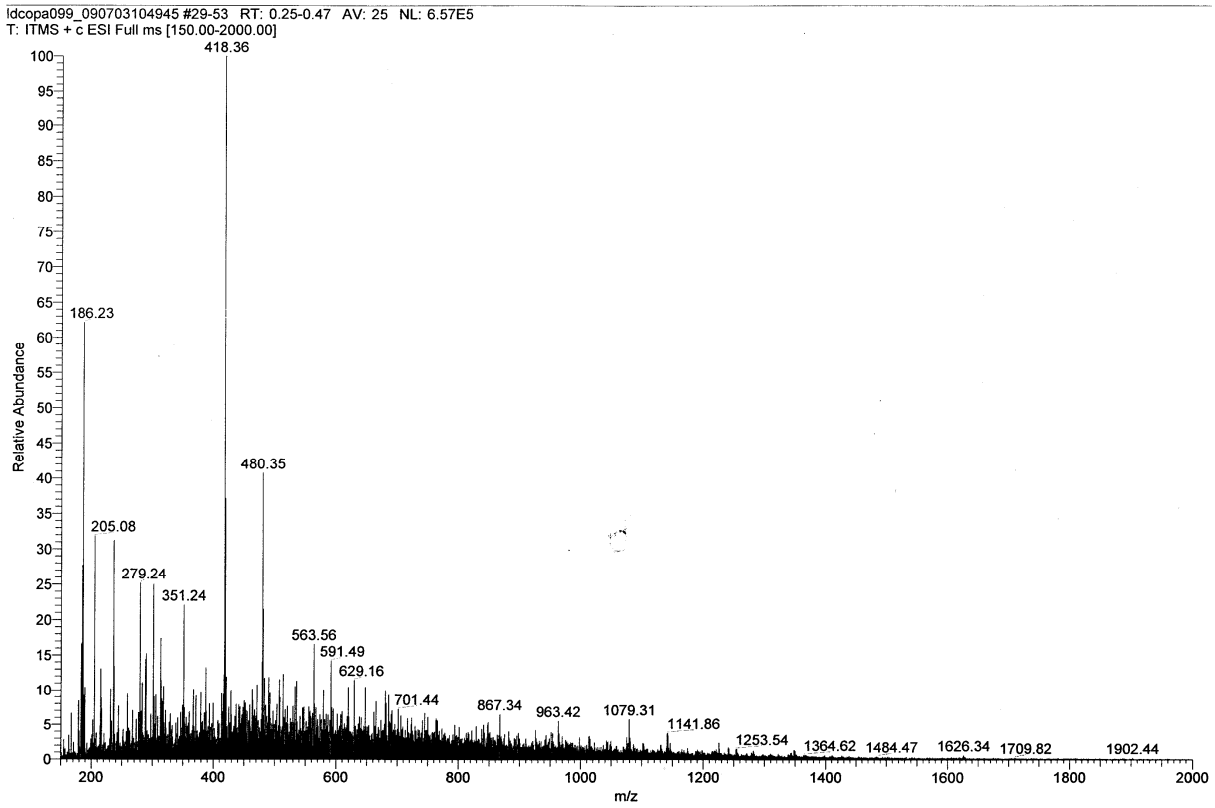
80
60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351.24
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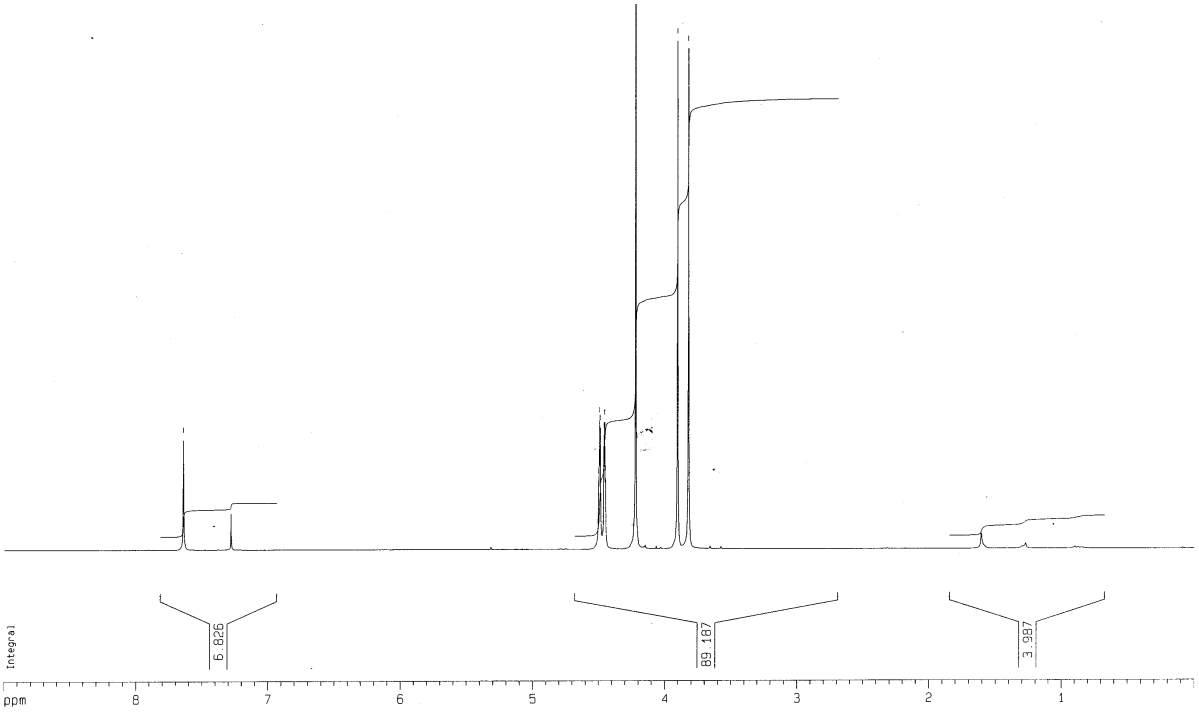
Compound **6**.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6
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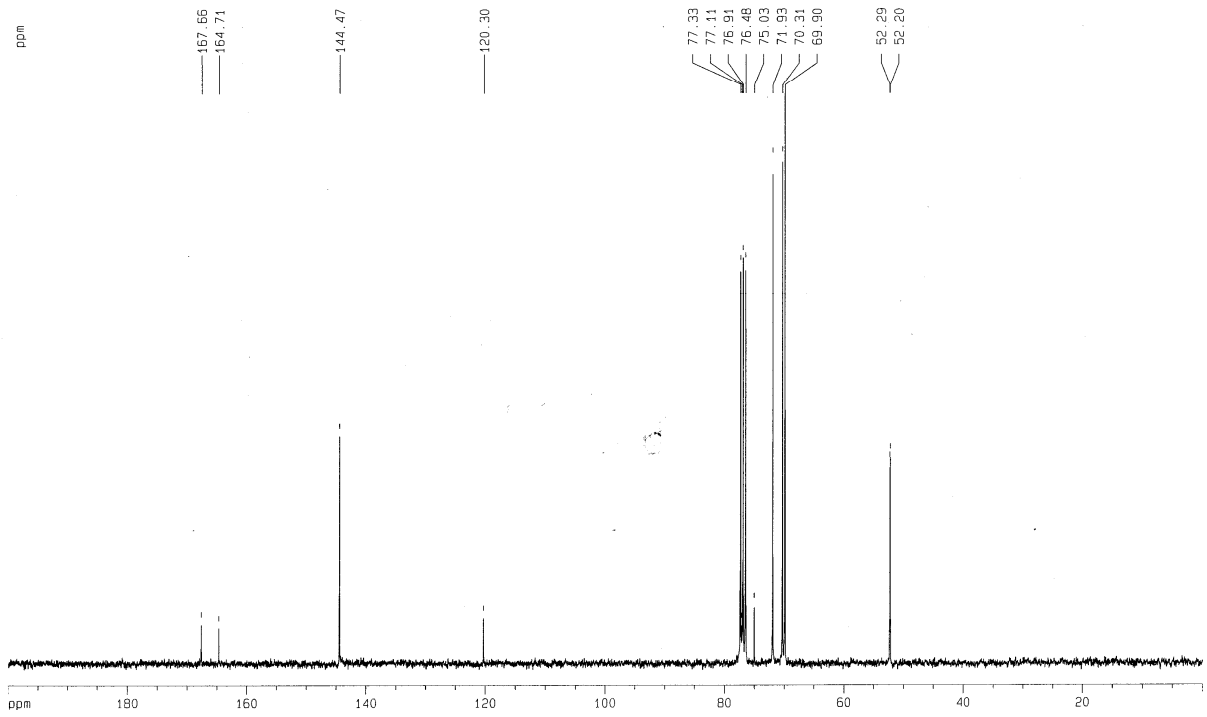
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ppm
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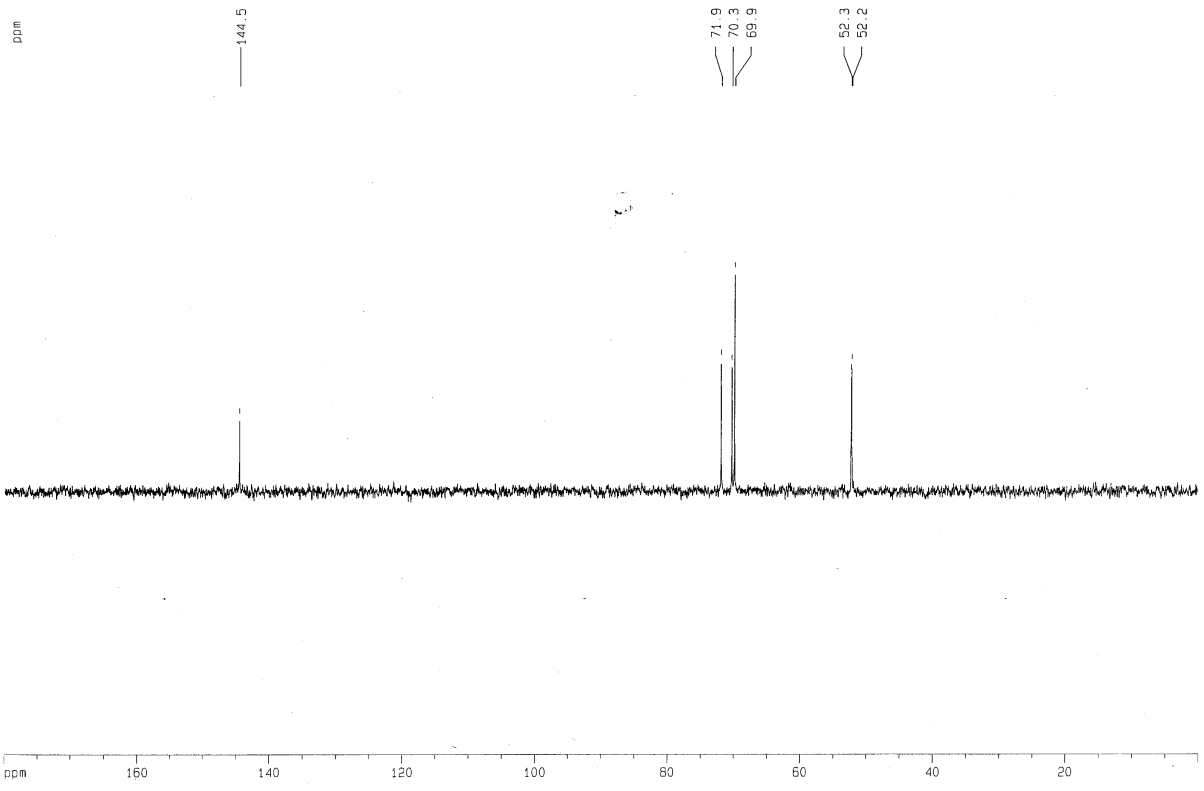
160
140
120
100
80
60
40
20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100
80
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40
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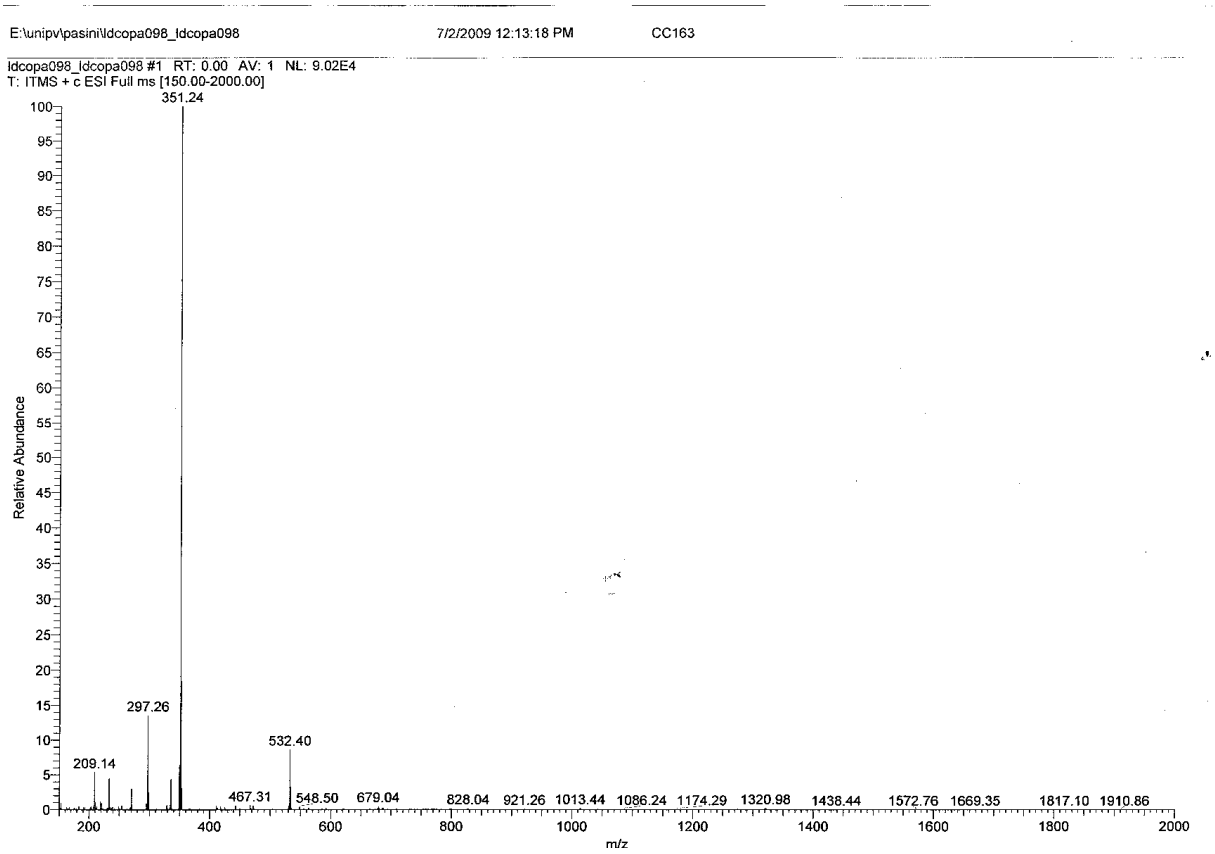
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467.31
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921.26
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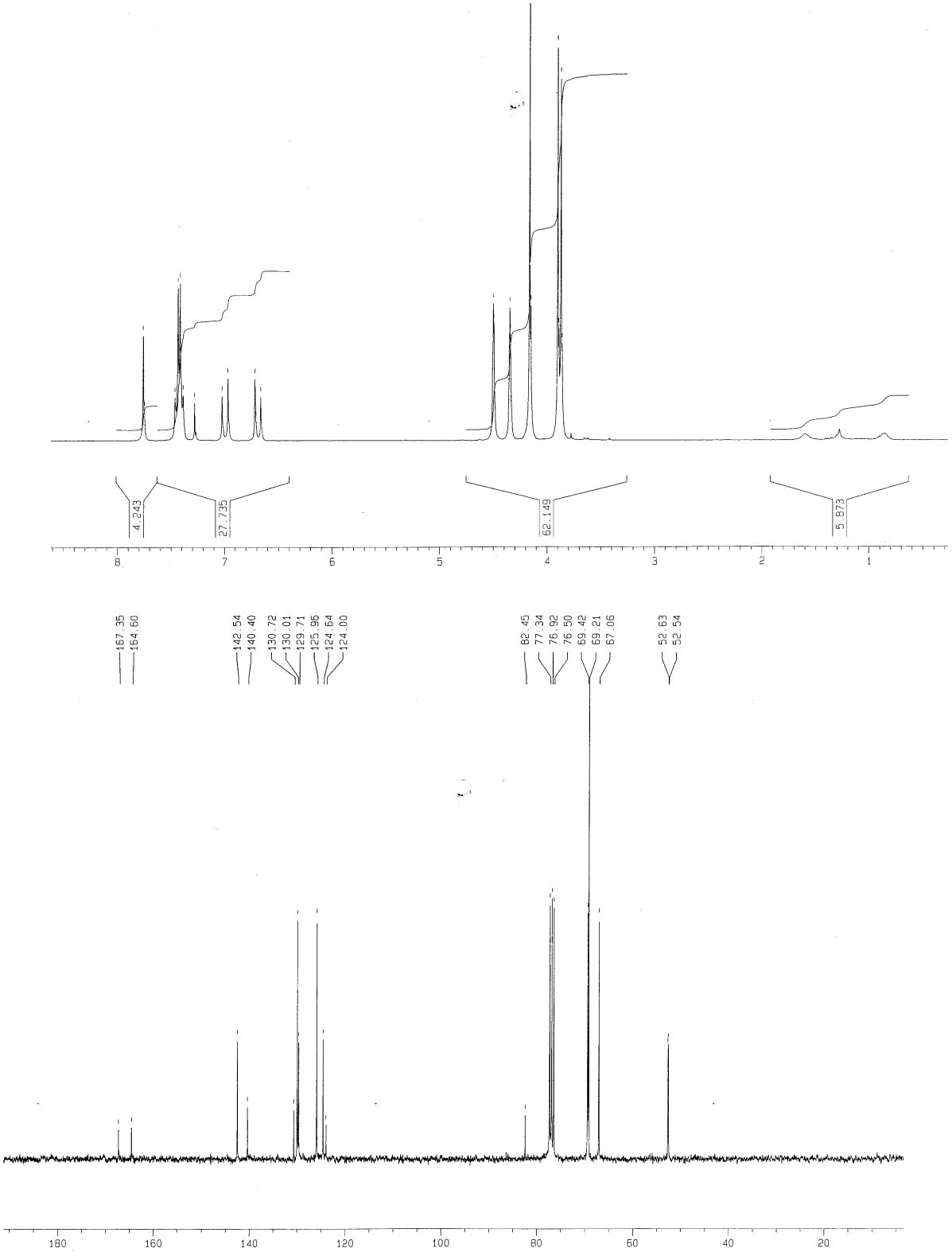
1817.10
1910.86

Compound **7**.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5.873
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7
6
5
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3
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142.54
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120
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80
60
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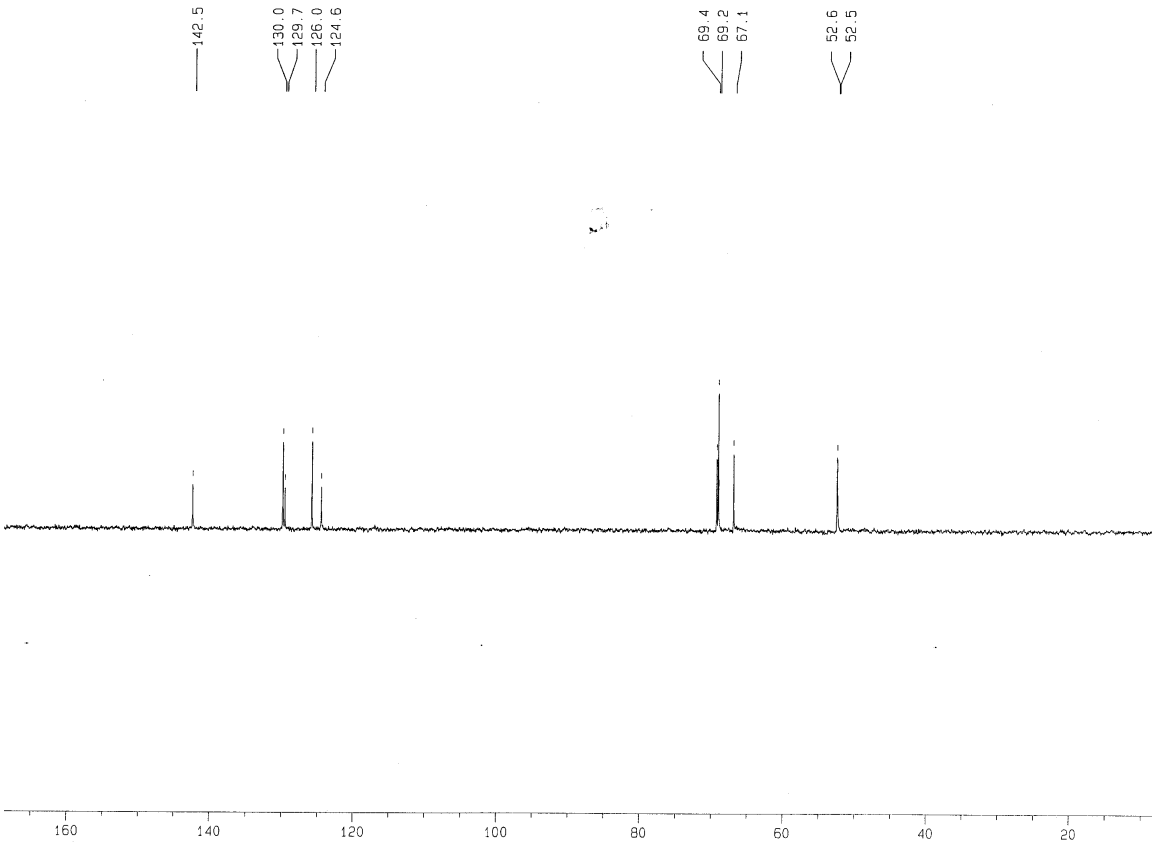
20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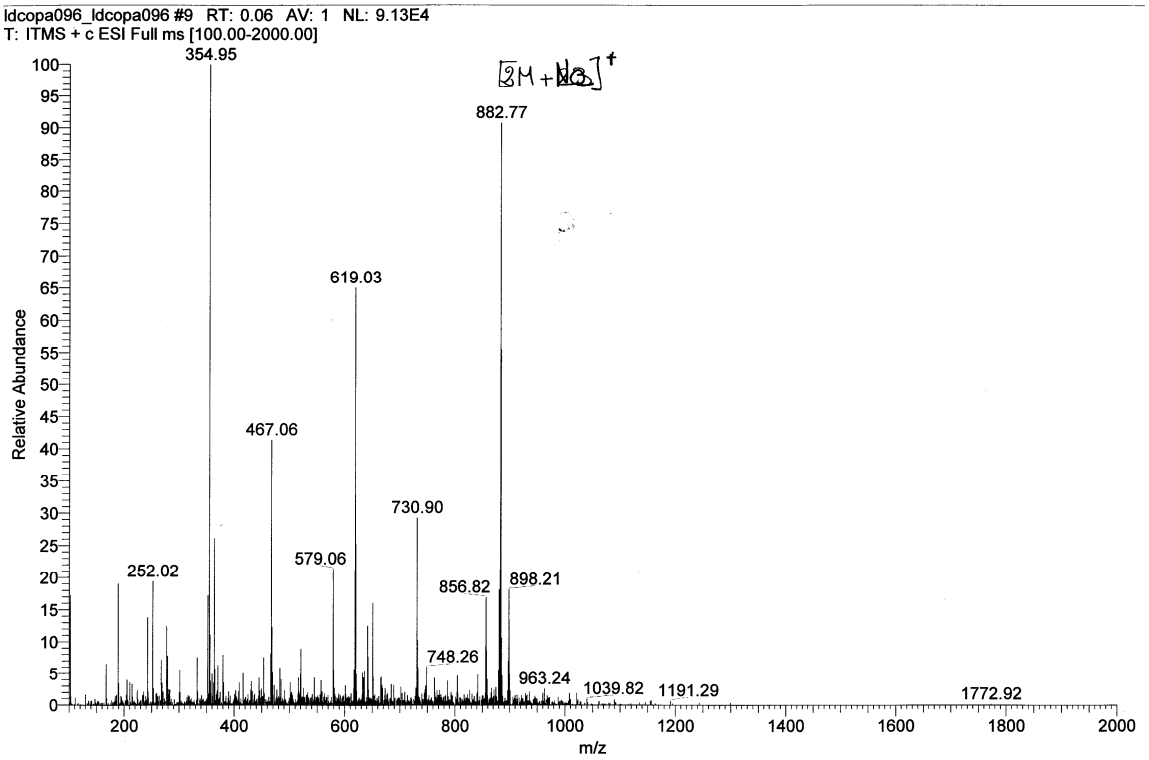
100
80
60
40
20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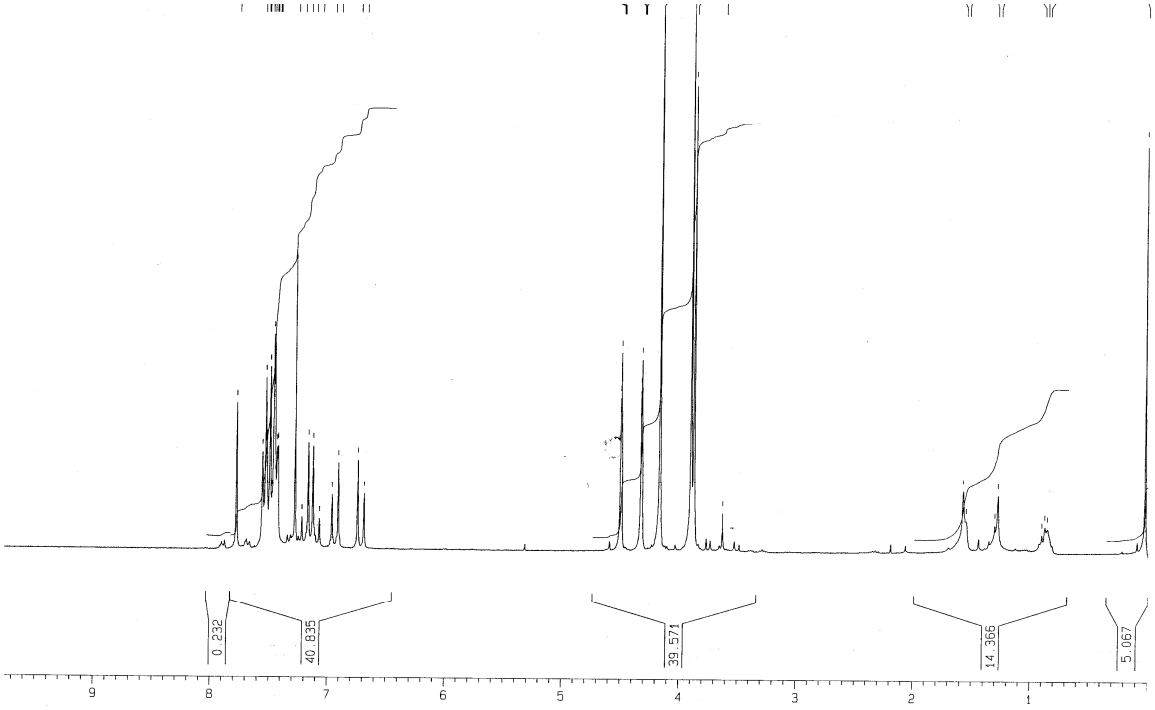
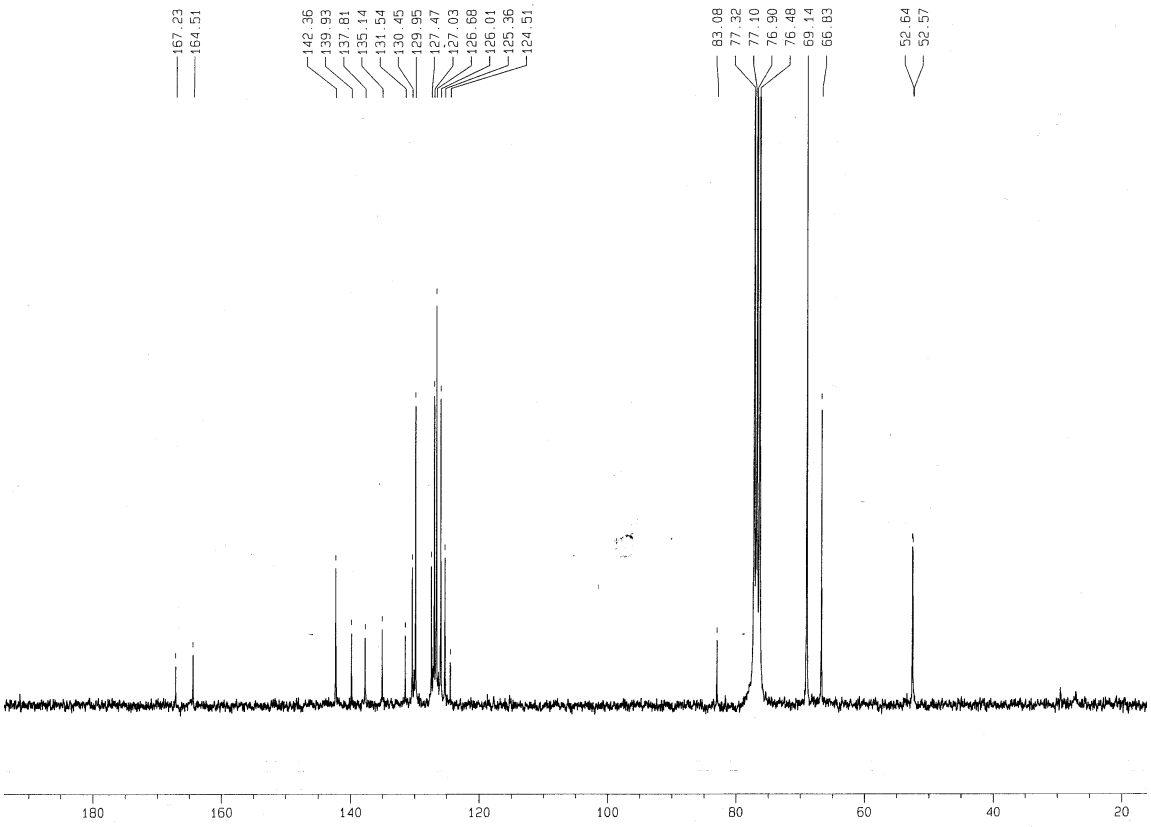
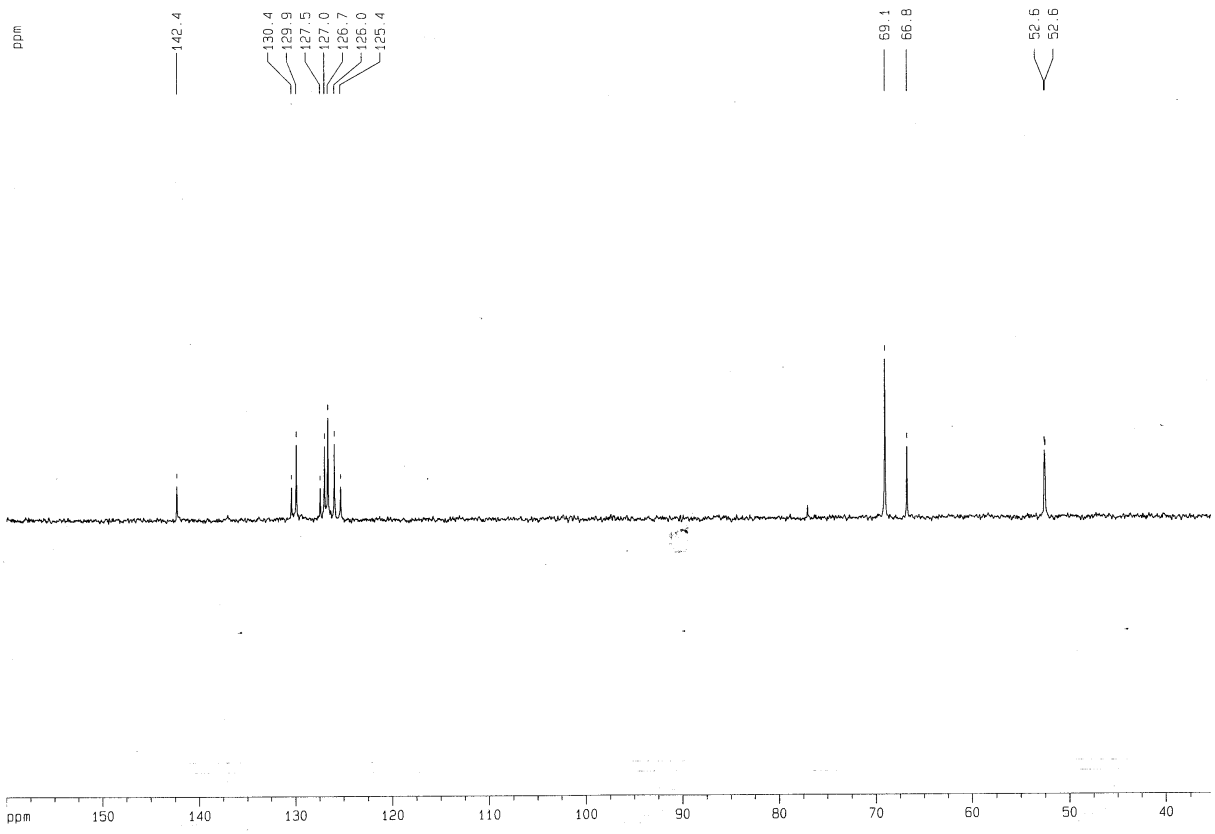
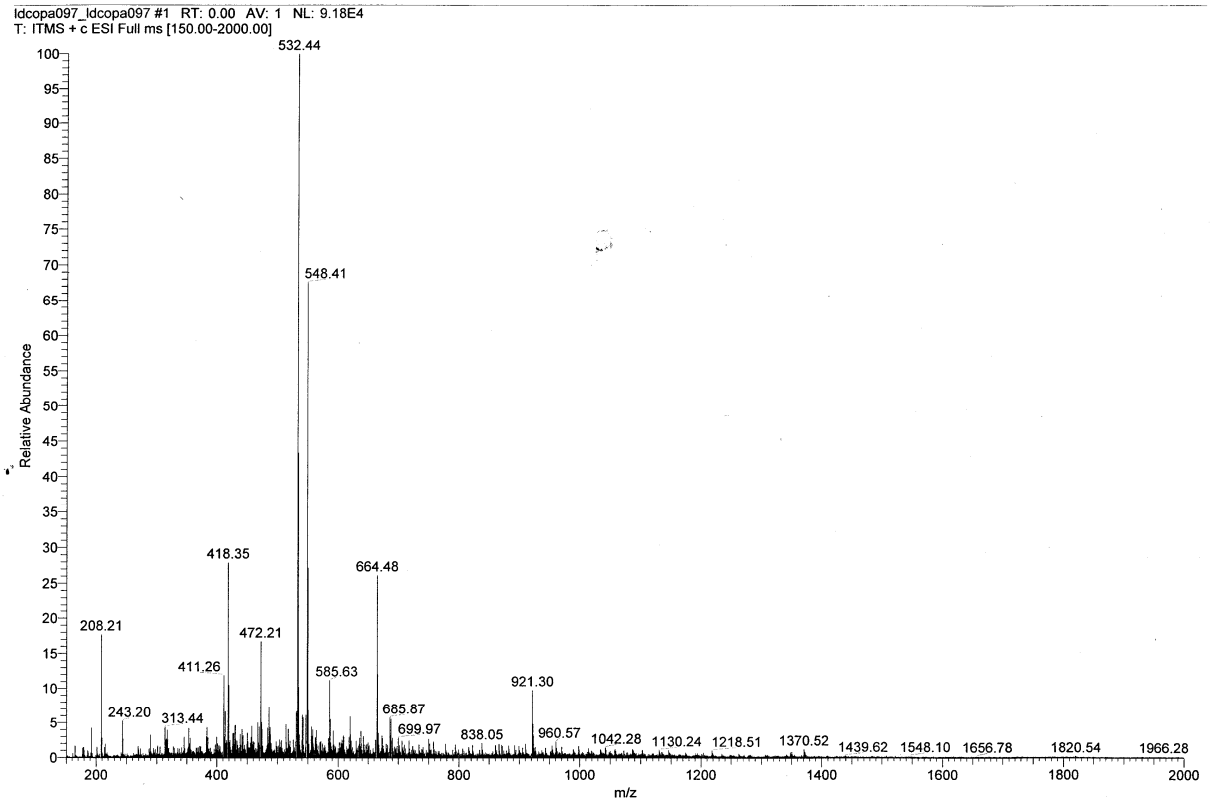
467.06
730.90
579.06
252.02
856.82
898.21
748.26
963.24
1039.82
1191.29
1772.92
Relative Abundance
m/z

Compound **8**.


0.232
40.835
39.571
14.366
5.067
9
8
7
6
5
4
3
2
1


167.23
164.51
142.36
139.93
137.81
135.14
131.54
130.45
129.95
127.47
127.03
126.68
126.01
125.36
124.51
83.08
77.32
77.10
76.90
76.48
69.14
66.83
52.64
52.57
180
160
140
120
100
80
60
40
20


ppm
142.4
130.4
129.9
127.5
127.0
126.7
126.0
125.4
69.1
66.8
52.6
52.6
ppm
150
140
130
120
110
100
90
80
70
60
50
40


ldcopa097_ldcopa097 #1 RT: 0.00 AV: 1 NL: 9.18E4
T: ITMS + c ESI Full ms [150.00-2000.00]
Relative Abundance
m/z
532.44
548.41
418.35
664.48
208.21
472.21
411.26
585.63
921.30
243.20
313.44
685.87
699.97
838.05
960.57
1042.28
1130.24
1218.51
1370.52
1439.62
1548.10
1656.78
1820.54
1966.28

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[S3] C. R. Mayer, M. Hervé, H. Lavanant, F. Sécheresse, *Tetrahedron Lett.* **2004**, 45, 7805-7807.