

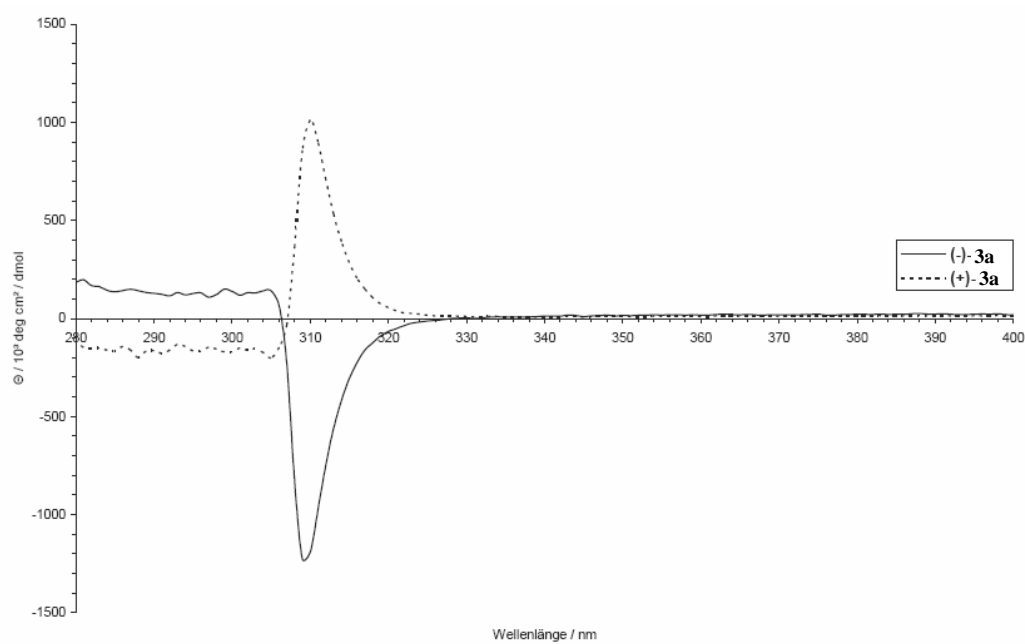
SUPPORTING INFORMATION

Title: Synthesis and Complexation Properties of Allenic Bipyridines, a New Class of Axially Chiral Ligands for Transition Metal Catalysis

Author(s): Sandra Löhr, Jan Aeverbeck, Markus Schürmann, Norbert Krause*

Ref. No.: I200701049

CD-Spectra of Enantiomerically Pure Bipyridine **3a** in *n*-Pentane:



Optical Rotations:

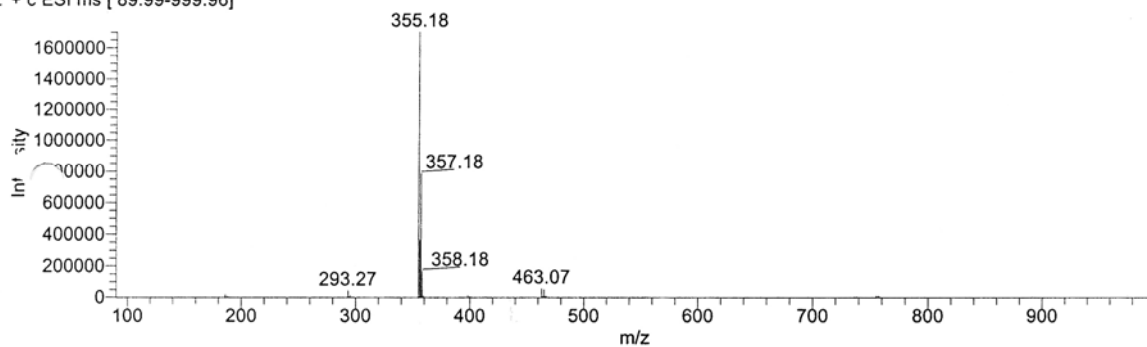
(-)-**3a** (>99% *ee*): $[\alpha]_{\text{D}}^{20} = -167$ ($c = 0.52$, *n*-pentane);

(+)-**3a** (99% *ee*): $[\alpha]_{\text{D}}^{20} = +164$ ($c = 0.64$, *n*-pentane).

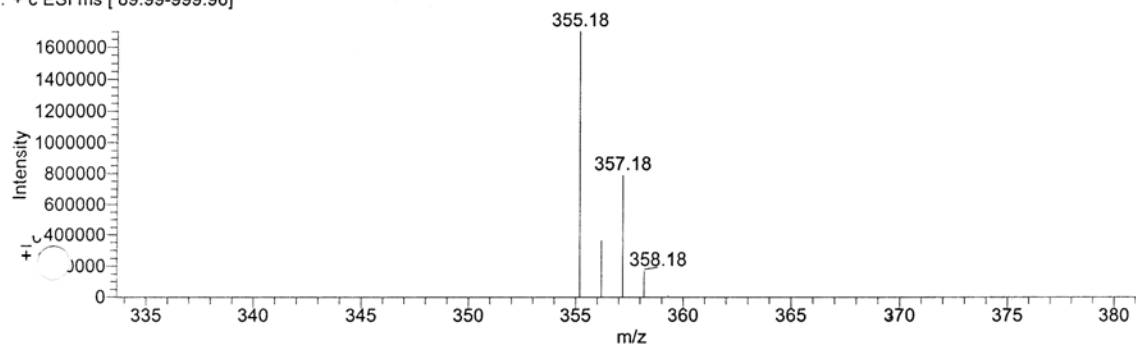
ESI Mass Spectra of Copper or Silver Complexes of Allenic Bipyridines 3:

3a·Cu⁺:

sla_031105141422 #191-198 RT: 2.04-2.11 AV: 8 SB: 22 0.04-0.23, 3.44-3.65 NL: 1.71E6
Γ: + c ESI ms [89.99-999.96]

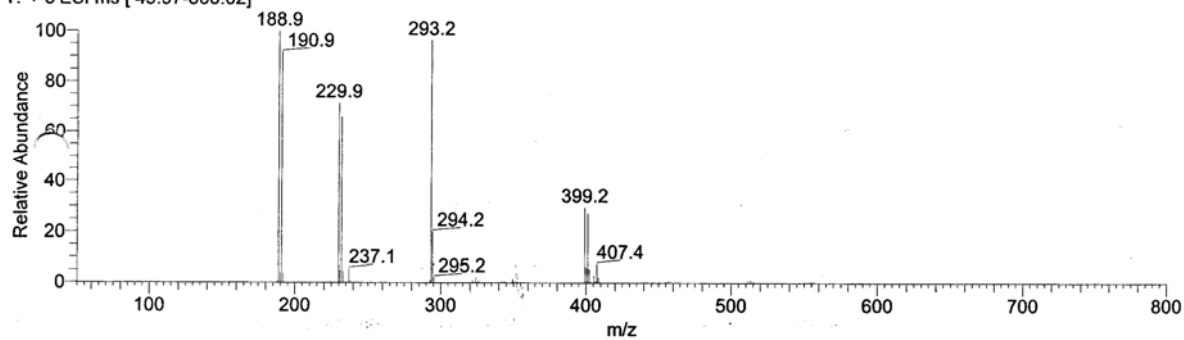


sla_031105141422 #191-198 RT: 2.04-2.11 AV: 8 SB: 22 0.04-0.23, 3.44-3.65 NL: 1.71E6
Γ: + c ESI ms [89.99-999.96]

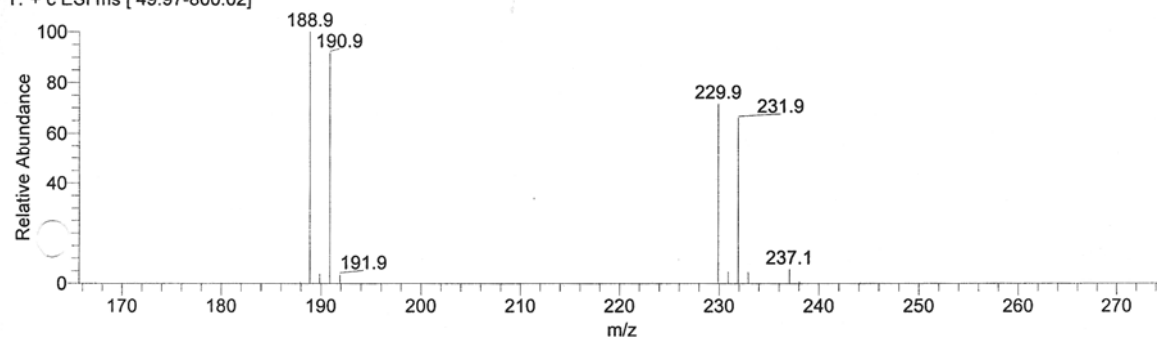


3a·Ag⁺:

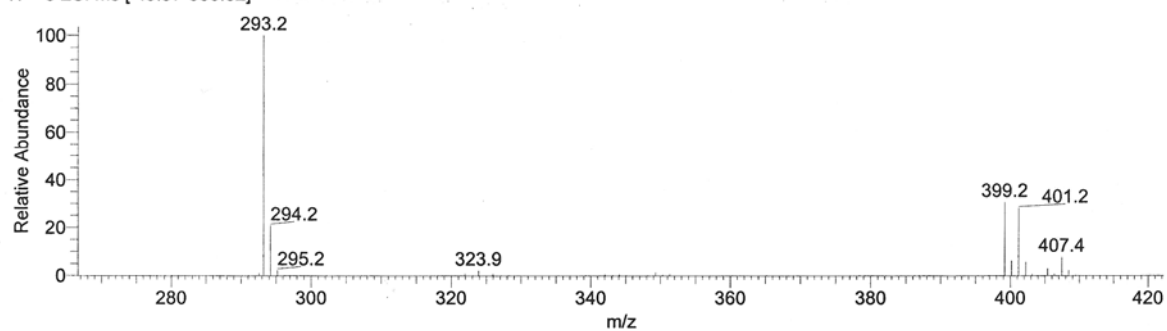
av040406b #115-144 RT: 1.29-1.62 AV: 30 SB: 23 0.64-0.89 NL: 2.46E5
T: + c ESI ms [49.97-800.02]



av040406b #115-144 RT: 1.29-1.62 AV: 30 SB: 23 0.64-0.89 NL: 2.46E5
T: + c ESI ms [49.97-800.02]

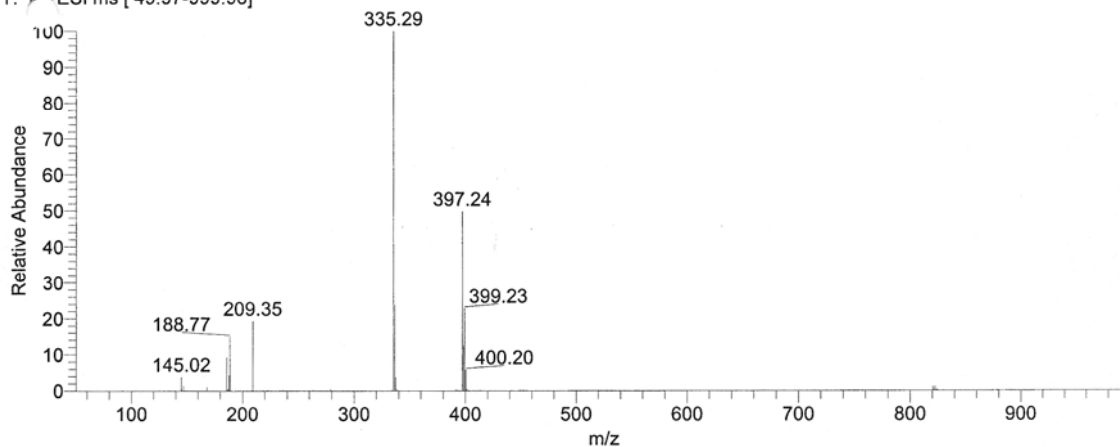


av040406b #115-144 RT: 1.29-1.62 AV: 30 SB: 23 0.64-0.89 NL: 2.37E5
T: + c ESI ms [49.97-800.02]

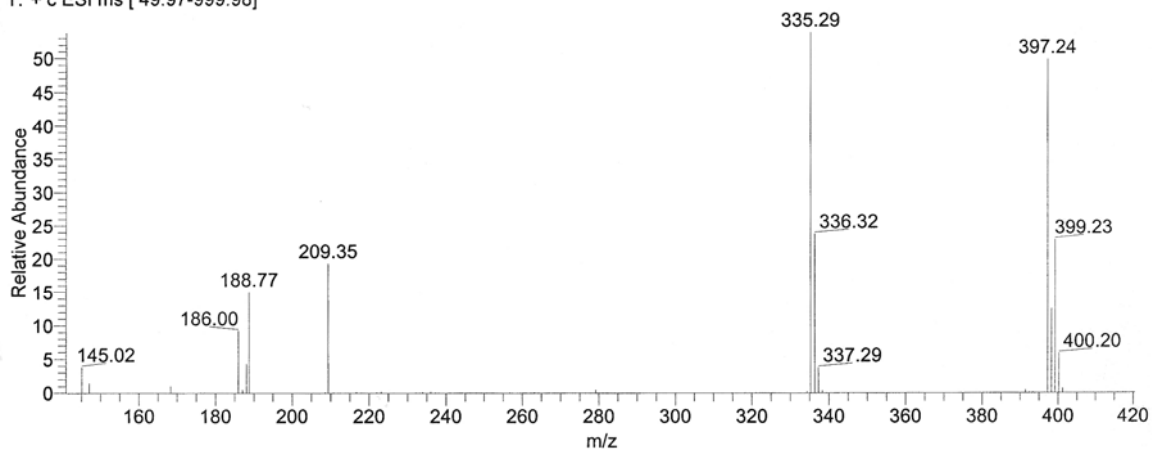


3b·Cu⁺:

av504b #200-203 RT: 2.14-2.18 AV: 4 SB: 18 1.63-1.81 NL: 3.00E6
T: + ESI ms [49.97-999.98]

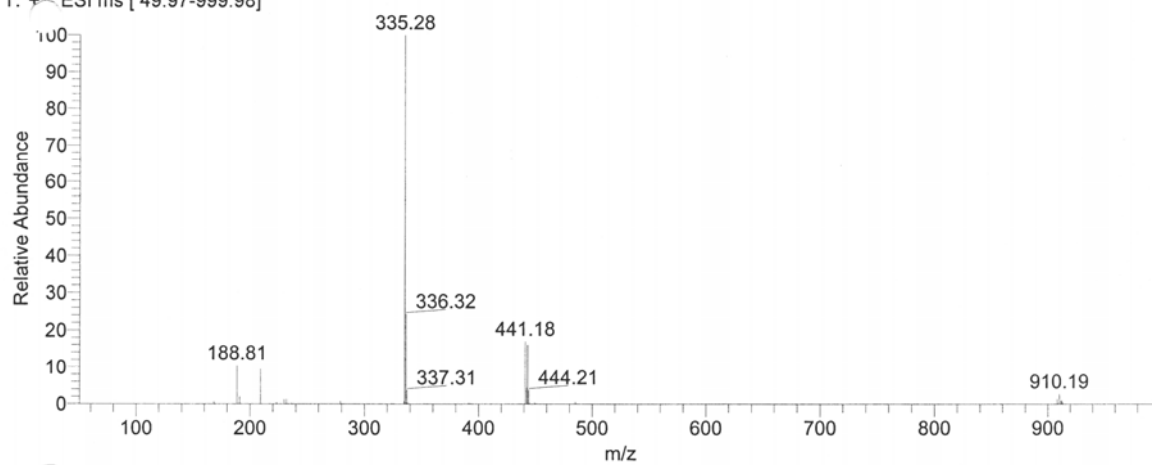


av5 #200-203 RT: 2.14-2.18 AV: 4 SB: 18 1.63-1.81 NL: 3.00E6
T: + c ESI ms [49.97-999.98]

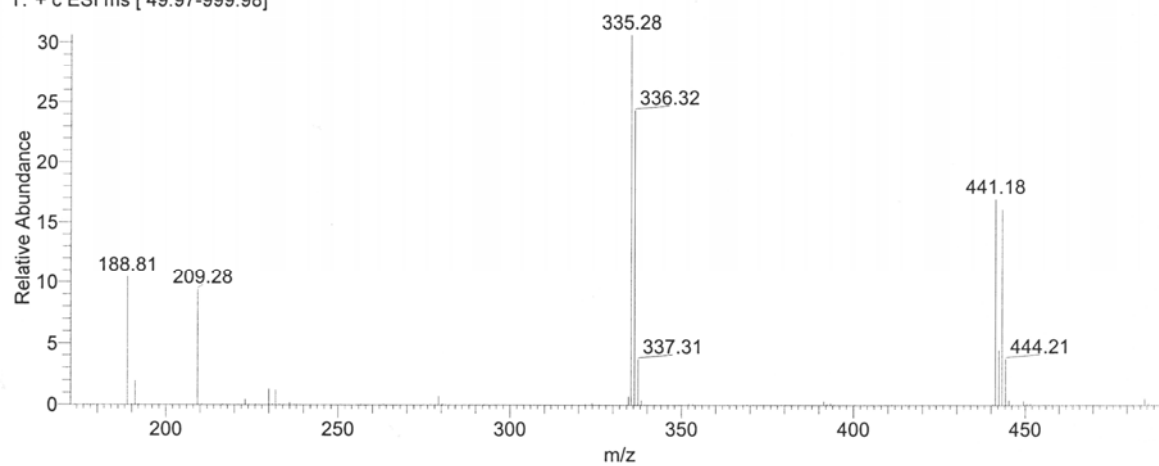


3b·Ag⁺

av504a #196-200 RT: 2.09-2.13 AV: 5 SB: 17 1.59-1.75 NL: 3.54E6
T: + c ESI ms [49.97-999.98]

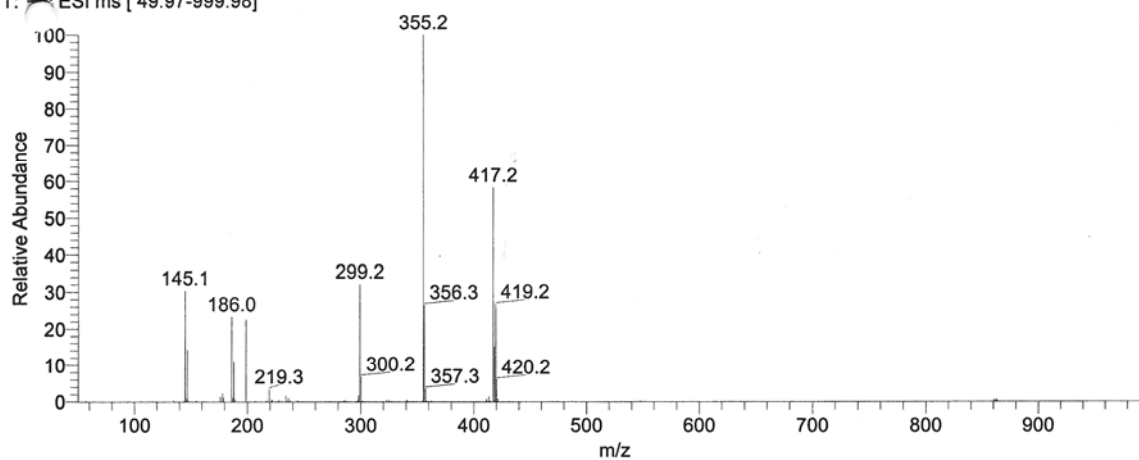


av5 #196-200 RT: 2.09-2.13 AV: 5 SB: 17 1.59-1.75 NL: 3.54E6
T: + c ESI ms [49.97-999.98]

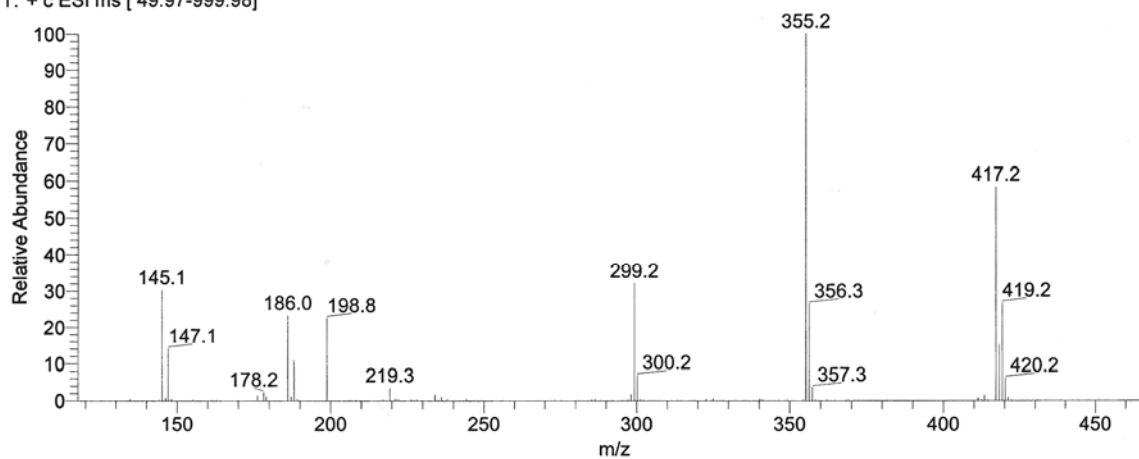


$3e\text{-Cu}^+$

av624_050726132821 #226-361 RT: 3.01-4.83 AV: 136 SB: 58 2.01-2.77 NL: 3.87E4
T: + c ESI ms [49.97-999.98]

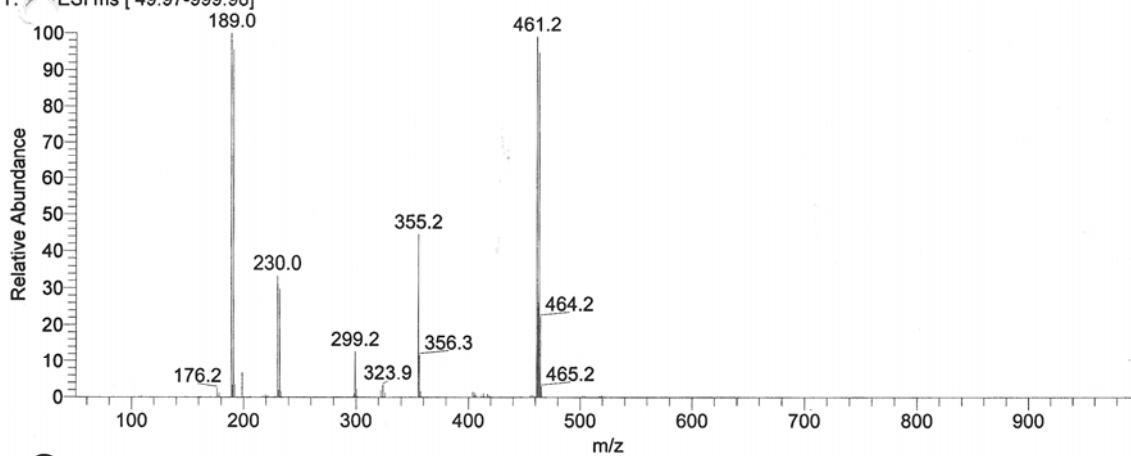


av624_050726132821 #226-361 RT: 3.01-4.83 AV: 136 SB: 58 2.01-2.77 NL: 3.87E4
T: + c ESI ms [49.97-999.98]

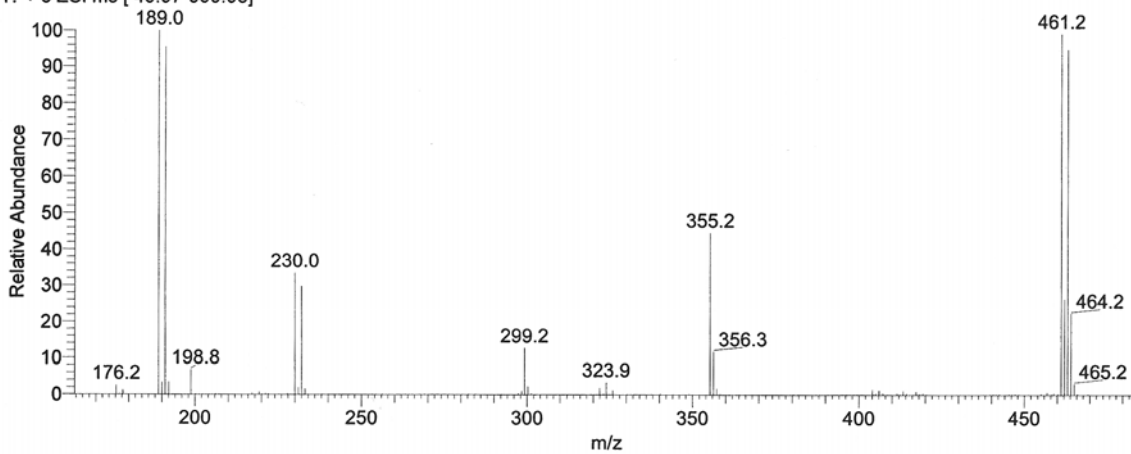


$3c \cdot Ag^+$

av626 #246-278 RT: 3.31-3.74 AV: 33 SB: 41 1.80-2.34 NL: 9.11E4
T: ESI ms [49.97-999.98]

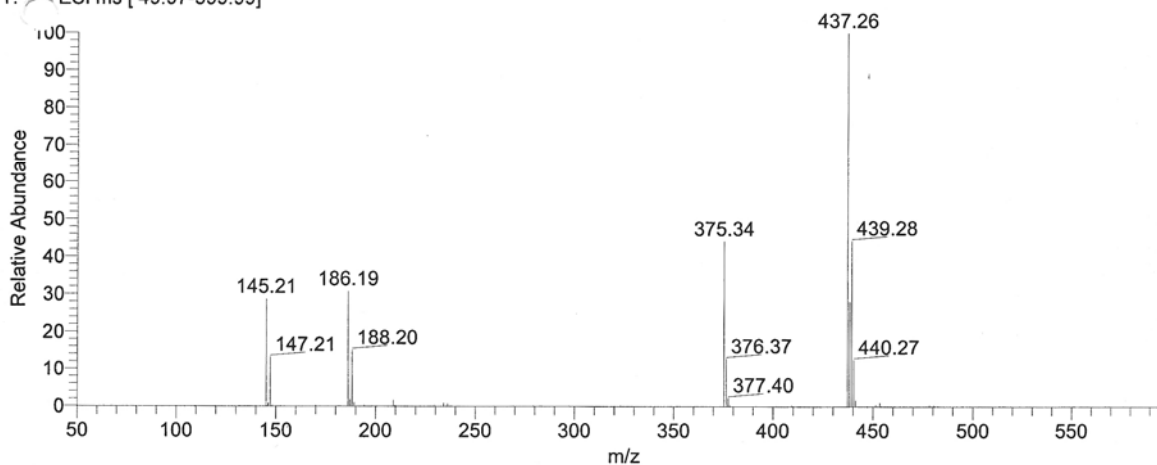


av626 #246-278 RT: 3.31-3.74 AV: 33 SB: 41 1.80-2.34 NL: 9.11E4
T: + c ESI ms [49.97-999.98]

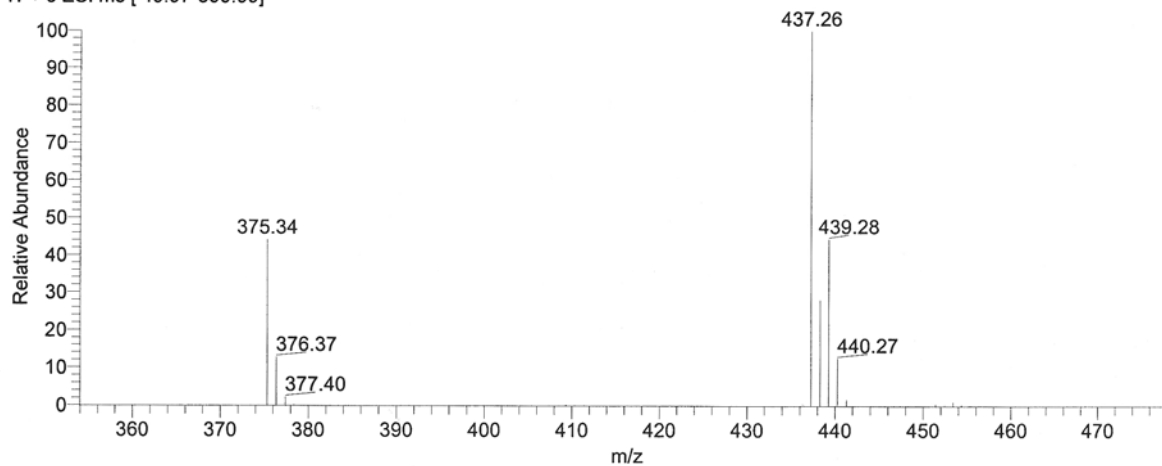


3d·Cu⁺

av525 #237-276 RT: 2.31-2.70 AV: 40 SB: 33 1.44-1.76 NL: 1.15E5
T: + c ESI ms [49.97-599.99]

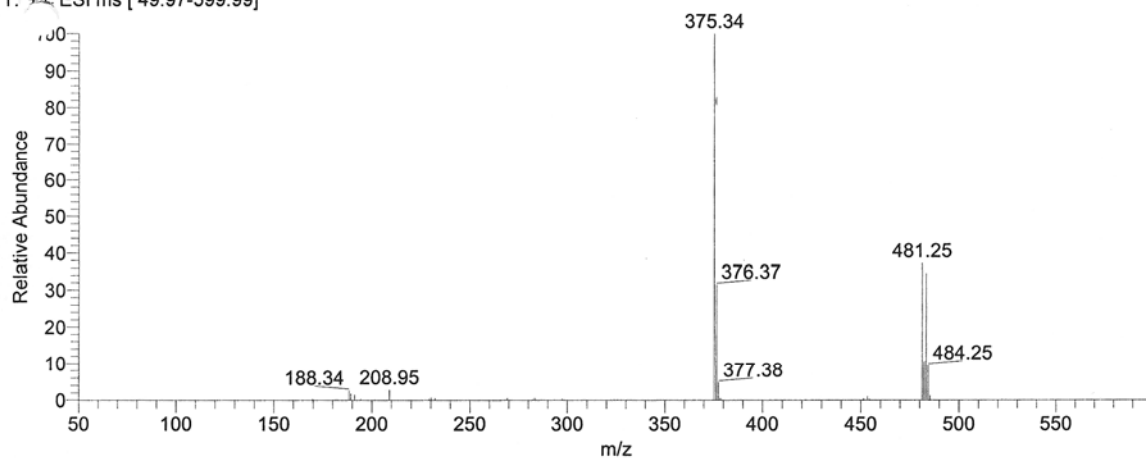


av: #237-276 RT: 2.31-2.70 AV: 40 SB: 33 1.44-1.76 NL: 1.15E5
T: + c ESI ms [49.97-599.99]

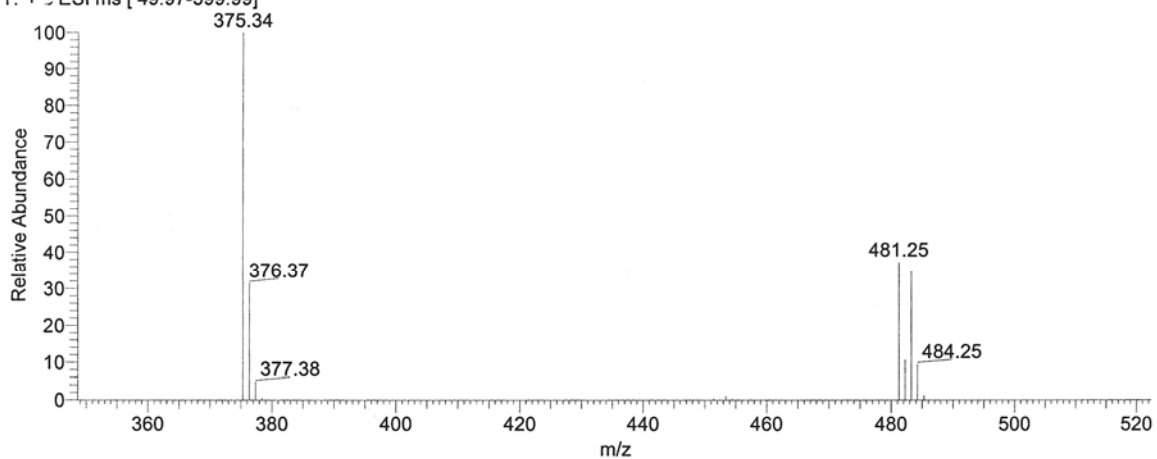


3d·Ag⁺

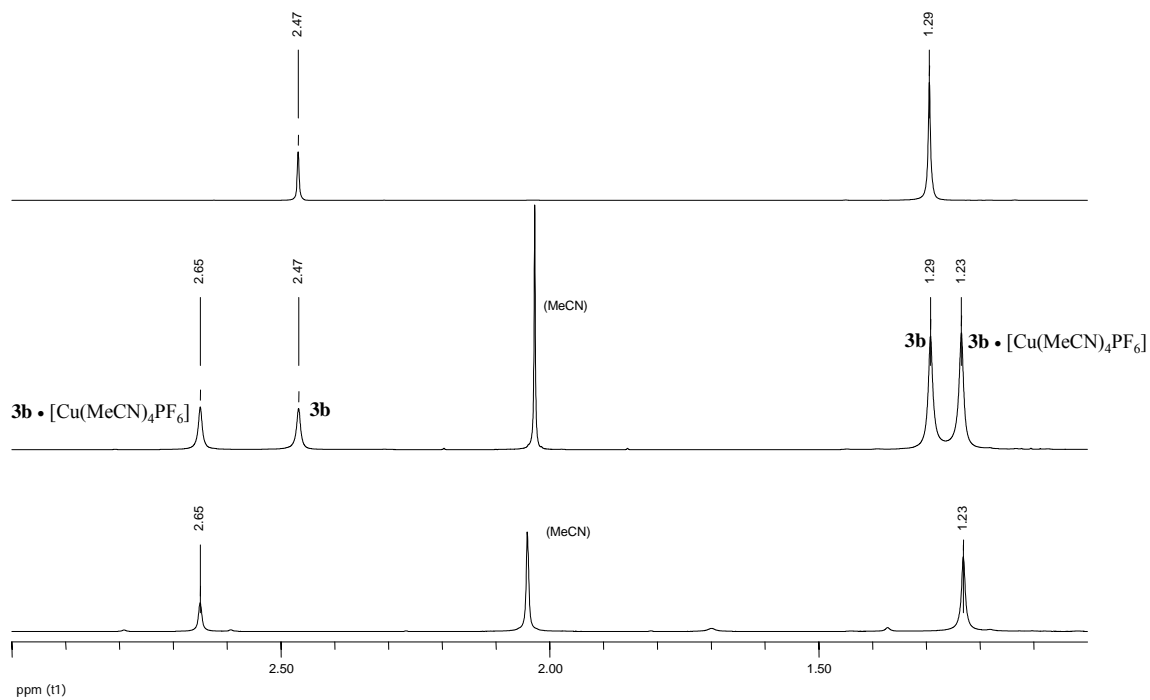
av528 #186-226 RT: 1.83-2.22 AV: 41 SB: 35 0.13-0.46 NL: 1.16E5
T: +c ESI ms [49.97-599.99]



av528 #186-226 RT: 1.83-2.22 AV: 41 SB: 35 0.13-0.46 NL: 1.16E5
T: +c ESI ms [49.97-599.99]



^1H -NMR-Spectra of free Ligand **3b (top), a 2:1-Mixture of **3b** and $[\text{Cu}(\text{MeCN})_4\text{PF}_6]$ (middle), and a 1:1-Mixture of **3b** and $[\text{Cu}(\text{MeCN})_4\text{PF}_6]$ (bottom; CD_2Cl_2 , 236 K):**



Estimation of the Free Activation Enthalpy for Ligand Exchange in the 1:1-Complex prepared from Allenic Bipyridine **3b and [Cu(MeCN)₄PF₆]:**

Approximation for the rate constant k_c at the coalescence temperature:^[18]

$$k_c = \pi\Delta\nu/\sqrt{2} = 2.22 \Delta\nu \quad (\Delta\nu = \text{resonance frequency difference at slow exchange})$$

Approximation for the free activation energy at the coalescence temperature T_c :^[18]

$$\Delta G^\ddagger = 19.13 T_c (9.97 + \lg T_c/\Delta\nu) \text{ [J mol}^{-1}\text{]}$$

For the ligand exchange in the complex prepared from allenic bipyridine **3b** and [Cu(MeCN)₄PF₆], the following data were obtained from the temperature-dependent ¹H-NMR spectra (Scheme 4):

tert-Butyl groups: $\Delta\nu = 23 \text{ Hz}$, $T_c = 271 \text{ K} \rightarrow k_c = 51 \text{ s}^{-1}$, $\Delta G^\ddagger = 55 \text{ kJ mol}^{-1}$

Pyridine-methyl groups: $\Delta\nu = 74 \text{ Hz}$, $T_c = 293 \text{ K} \rightarrow k_c = 164 \text{ s}^{-1}$, $\Delta G^\ddagger = 57 \text{ kJ mol}^{-1}$

Solid State Structure of the 2:2-Complex of Allenic Bipyrindine 3b and Silver Triflate:

