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Copper(I) Complexes of Mono- and Bis-ferrocenyl-vinyl 2,2′-Bipyridine-Ligands: Synthesis and Electrochemical Properties

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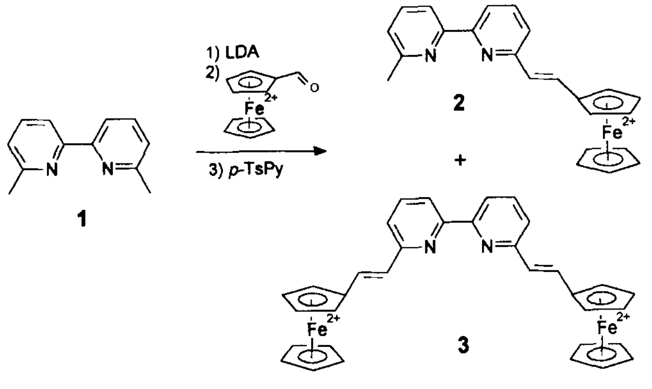
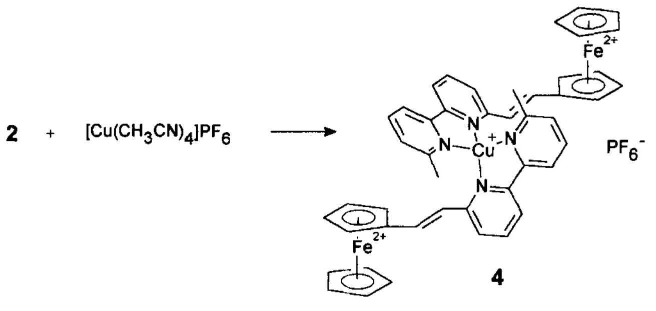
Abstract. New 2,2'-bipyridine ligands with one or two vinyl-ferrocenyl moieties (**2**, **3**) have been synthezised. The coordination of the bipyridine by copper(I) ions allows the assembly of up to four ferrocenes in a defined arrangement. Although the ferrocene moieties are in close proximity, they are electronically independent, as is shown by UV-spectroscopy and cyclic voltammetry.

Many important biological and catalytic processes [1] depend on molecular structures that contain different metal ions for energy or electron transfer. The distance between the metal centers and their orientation are essential for the degree of electronic interactions, i.e. the function of these molecules [2]. Electronic interactions of redox centers have been studied at various bimetallic model compounds [3], whereby ferrocenes [4] are frequently employed due to their good synthetic availability and well-known redox chemistry. Especially ferrocenyl-vinyl-2,2'-bipyridines allow the facile assembly of ferrocene units in defined geometries. Metal complexes of 4,4'-bis-ferrocenyl-vinyl-2,2'-bipyridines have been reported and it has been shown that their ferrocene moieties are electronically independent [5]. However, in this case, the ferrocene moieties are rather distant to each other, resulting in reduced ability to interact. In order to place the ferrocene moieties in closer proximity in copper(I)complexes the new ligands 6-ferrocenyl-vinyl- (**2**) and 6,6'-bis-ferrocenyl-vinyl-2,2'-bipyridine (**3**) were synthesized corresponding to a procedure by *Beer* [5].

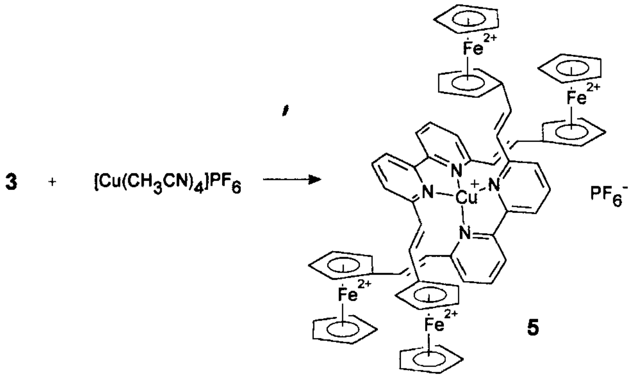


Complex **4** [6] was obtained in high yield upon mixing **2** and $[Cu(CH_3CN)_4]PF_6$ in stoichiometric amounts in acetonitrile, while the analogous procedure using **3** gave **5** in 93% yield. The tetrahedral coordination geometry of copper(I) bis-bipyridine complexes leads to a defined assembly of the ferrocene moieties in **5**. The copper(I) complex **7** of 4-ferrocenyl-vinyl-4-methyl-2,2'-bipyridine (**6**) [5] was synthesized for comparison.

The UV spectra of the ligands **2** and **3** show strong absorptions of the ferrocene chromophores at 462 nm (lg ε 3.188) resp. 472 nm (lg ε 3.453).



Only small changes to 462 nm (lg ε 3.626) (**4**) resp. 470 nm (lg ε 3.922) (**5**) were observed upon copper(I) complexation [7]. This indicates a similar electronic structure of the ground state of the ligands and their copper(I) coordination compounds. All complexes give intense molecular ions in FAB- or electrospray mass spectra. The isotope patterns are in full compliance with theory.



The electrochemical properties of the ligands and their copper(I) complexes were investigated by cyclic voltammetry. If restricted to the ferrocene potential range compounds **2**, **4**, **5** and **7** [8] each exhibit quasi-reversible redox waves (table 1), with the number of electrons being confirmed by coulometry [9]. The change in redox potential of the ferrocene moities by copper ion coordination to the 2,2'-bipyridine is comparable to the previous investigated Ruthenium complexes [5]. The single-step redox processes of **4**, **5** and **7** indicate that the respective two or four ferrocene moieties do not electrochemically interact with one another either through bond or through space. By expanding the potential range to –0.6 V *vs*. Fc/Fc$^+$ the redox wave for irreversible Cu$^+$/Cu^{2+} oxidation is observed for **7**. The similarity of the cyclovoltammogram of **7** and an equimolar mixture of ferrocene and Cu(I)-bis-2,2'-bipyridine indicates the independent redox chemistry of both metal centers.

Electrochemical polymerisation of vinyl-2,2'-bipyridine metal complexes has been previously described [5]. Consecutive scans over a broader potential range (–1 to +2.5 V *vs*. SCE) lead, as expected, to irreversible deposition processes.

In summary we have shown that even with a close molecular arrangement of ferrocene moieties as in **5** no significant electronic interaction between the redox centers is observed.

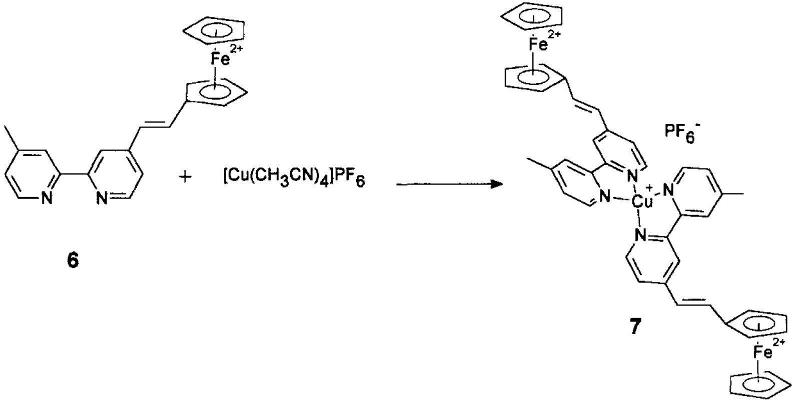


Table 1 Electrochemical data for the ferrocene redox waves of **2**, **4**, **5** and **7** $^{a)}$

	E^f [mV *vs*. Fc]	$\Delta E_p^{a,c}$ [mV]
2	+50	120
4	+10	70
5	+75	100
6 [5]	+40	100
7	+110	110

$^{a)}$ Values quoted were (+/– 10) at 50 mV s^{-1} in 3 x 10^{-3} mol dm^{-3} solutions of the compounds in 0.05 mol dm^{-3} NBu_4PF_6 CH_3CN. $E_{p,c}$ = Cathodic peak potential, $E_{p,a}$ = anodic peak potential. Formal potential $E^f = 1/2(E_{p,c} + E_{p,a})$. Separation of peak potential $\Delta E_p = |E_{p,c} - E_{p,a}|$. Reference electrode: Ag/AgCl.

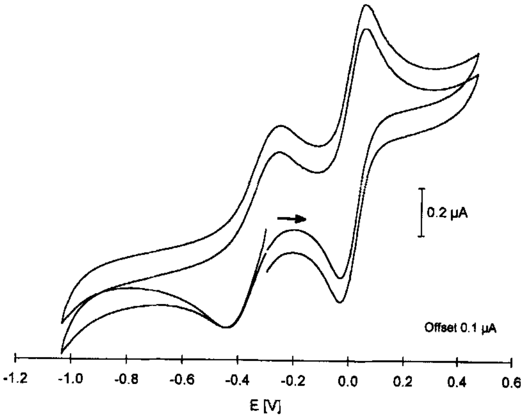


Fig. 1 Cyclic voltammogram of **7** (lower curve) and a mixture of Cu(I)(bipy)$_2$PF$_6$ and ferrocene (upper curve). For conditions see table 1.

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Experimental

^{1}H NMR: Bruker AM 400; δ = 0 for tetramethylsilane as internal standard, δ = 7.26 for chloroform. – ^{13}C NMR: AM

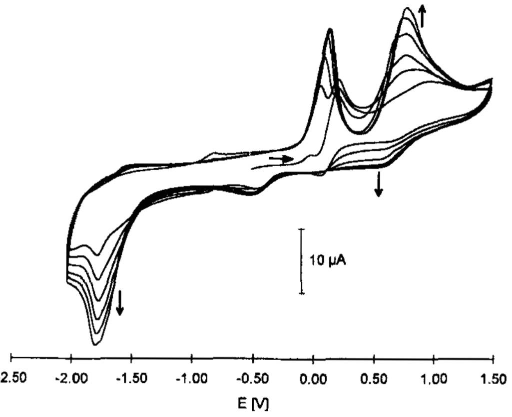

Fig. 2 Cyclic voltammograms of consecutive scans of a solution of **7**. For conditions see table 1.

400; δ = 77.0 for deuteriochloroform; the multiplicity of the C-NMR signals was determined by the DEPT technique (distortionless enhancement by polarization transfer) and quoted as (+) for CH_3 and CH groups, (–) for CH_2- and (C_{quart}) for quarternary carbons. – IR: Nicolet 320 FT-IR. – MS: Finnigan MAT 8430. – UV/VIS: Hewlett Packard 8452A. – Melting points were measured with a hot-plate microscope apparatus and are not corrected. – Column chromatography (CC): Merck silica gel 60, mesh 70–230; PE (60/70) means petroleum ether with a boiling range of 60– 70 °C. – TLC was carried out on silica gel (Macherey-Nagel; Sil G/UV_{254}). – Electrochemical measurements: Autolab PSTAT20, eco Chemie; all measurements were performed in dry CH_3CN, 0.05 M tetrabutylammonium hexafluorophosphate under nitrogen at room temp. with a scan rate of 0.05 V/s.

6-[2-(Ferrocenyl)-2-hydroxyethyl]-6'-methyl-2,2'-bipyridine and *6,6'-Bis[2-ferrocenyl)-2-hydroxyethyl]-2,2'-bipyridine*

To a solution of 6,6'-dimethyl-2,2'-bipyridine (**1**) (250 mg, 1.36 mmol) in 30 ml THF was added freshly prepared LDA (2.7 mmol) at 0 °C, and the blue reaction mixture was stirred for 2 h. 290 mg (1.36 mmol) of ferrocenecarbaldehyd was added, the mixture was stirred for an additional h, quenched with 10 ml sat. NH_4Cl_4 and extracted with ethyl acetate. The organic phase was dried with $MgSO_4$, evaporated *in vacuo* and CC of the residue (PE(50/70)/EE 1:1) yielded fraction I: 190 mg (35%) *6-[2-(Ferrocenyl)-2-hydroxyethyl]-6'-methyl-2,2'-bipyridine*, (R_f = 0.4). – ^1H NMR (400 MHz, $CDCl_3$): δ = 2.58 (s, 3 H), 3.14 (d, ^3J = 8.6 Hz, 1 H), 3.17 (d, ^3J = 3.3 Hz, 1 H), 4.13–4.16 (m, 9 H), 4.93 (dd, ^3J = 3.3 Hz, ^3J = 8.6 Hz, 1 H), 5.23 (s, 1 H), 7.11 (m, 2 H), 7.64 (dd, ^3J = 7.7 Hz, 1 H), 7.69 (dd, ^3J = 7.8 Hz, 1 H), 8.08 (d, ^3J = 7.8 Hz), 8.26 (d, ^3J = 7.8 Hz). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.62 (+), 44.94 (–), 66.15 (+), 66.31 (+), 67.59 (+), 67.62 (+), 68.51 (+), 69.52 (+), 92.11 (C_{quart}), 117.98 (+), 119.11 (+), 123.35 (+), 123.61 (+), 137.11 (+), 137.62 (+), 155.04 (C_{quart}), 155.47 (C_{quart}), 157.93 (C_{quart}), 159.11 (C_{quart}). – IR (CCl_4): ν = 3365 cm^{-1}, 3099, 2854, 1440, 1254, 1084. – UV/VIS (CH_3CN): λ_{max} (lg ε) = 200 nm (4.828), 238 (4.116), 290 (4.187). – MS (70 eV), *m/z* (%): 398 (8) [M^+], 380 (4) [$M^+ - H_2O$], 333 (36) [$M^+ - C_5H_5$], 315 (100) [$M^+ - H_2O - C_5H_5$]. – Fraction II: 60 mg (7%) *6,6'-Bis[2-ferrocenyl)-2-hydroxyethyl]-2,2'-bipyridine*, (R_f = 0.3); as a red solid, m. p. 153 °C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 3.15–3.28 (m, 4 H), 4.09–4.30 (m, 18 H), 4.99 (m, 2 H), 7.18 (d, ^3J = 7.6 Hz, 2 H), 7.76 (dd, ^3J = 7.7 Hz, 2 H), 8.23 (d, ^3J = 7.7 Hz, 2 H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.16 (+), 66.28 (+), 67.71 (+), 67.74 (+), 68.58 (+), 69.60 (+), 92.19 (C_{quart}), 119.09 (+), 124.03 (+), 137.84 (+), 154.85 (C_{quart}), 159.34 (C_{quart}). – IR (CCl_4): ν = 3370 cm^{-1}, 3098, 2952, 1441, 1256. – UV/VIS (CH_3CN): λ_{max} (lg ε) = 202 nm (5.015), 238 (4.246), 290 (4.268). – MS (70 eV), *m/z* (%): 612 (2) [M^+], 576 (4) [$M^+ - 2\ H_2O$], 529 (16), 315 (100).

6-Ferrocenylvinyl-6'-methyl-2,2'-bipyridine (**2**)

150 mg (0.38 mmol) of 6-[2-(ferrocenyl)-2-hydroxyethyl]-6'-methyl-2,2'-bipyridine and 38 mg (0.15 mmol) of pyridinium-4-tolylsulfonate were refluxed in 25 ml dry toluene for 1 h, 20 ml water were added, and the mixture was extracted with 3 portions of dichloromethane. The combined organic phase was dried with $MgSO_4$, evaporated *in vacuo* and the solid residue was recrystallized from *n*-heptane to give 112 mg (76%) of **2** (R_f = 0.35 PE/EE 2:1); as a red solid, m. p. 168 °C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 2.63 (s, 3 H), 4.16 (s, 5 H), 4.33 (m, 2 H), 4.54 (m, 2 H), 6.85 (d, ^3J = 15.9 Hz, 1 H), 7.17 (d, ^3J = 7.6, 1 H), 7.31 (d, ^3J = 7.8 Hz, 1 H), 7.49 (d, 1 H, ^3J = 15.9 Hz), 7.72 (dd, ^3J = 7.9 Hz, 1 H), 7.73 (dd, ^3J = 7.8 Hz, 1 H), 8.22 (d, ^3J = 7.9 Hz, 1 H), 8.32 (d, ^3J = 7.8 Hz, 1 H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.66 (+), 67.44 (+), 69.29 (+), 69.43 (+), 82.30 (C_{quart}), 118.23 (+), 118.73 (+), 120.72 (+), 123.14 (+), 125.94 (+), 131.6 (+), 136.94 (+), 137.15 (+), 155.39 (C_{quart}), 155.87 (C_{quart}), 156.02 (C_{quart}), 157.76 (C_{quart}). – IR (KBr): ν = 1635 cm^{-1}, 1459, 1105, 820, 484. – UV/VIS (CH_3CN): λ_{max} (lg ε) = 200 nm (4.689), 242 (4.278), 270 (4.210), 296 (4.284), 318 (4.302), 462 (3.188). – MS (70 eV), *m/z* (%): 380 (38) [M^+], 315 (100) [$M^+ - C_5H_5$]. – $C_{23}H_{20}FeN_2$: calcd. C 72.65, H 5.30, N 7.37, found C 72.73, H 5.67, N 7.01.

6,6'-Bis(ferrocenylvinyl)-2,2'-bipyridine (**3**)

60 mg (0.1 mmol) of 6,6'-bis[2-ferrocenyl-2-hydroxyethyl]-2,2'-bipyridine and 10 mg (0.04 mmol) of pyridinium-tolyl-4-sulfonate were refluxed in 20 ml toluene for 1 h and worked up as described for **2**. CC (CH_2Cl_2/PE(50/70) 9:1) of the crude product yielded 35 mg (60%) of **3** (R_f = 0.45) as a red solid, m. p. >320 °C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 4.17 (s, 10 H,), 4.33 (m, 4 H), 4.55 (m, 4 H), 6.86 (d, ^3J = 15.9 Hz, 2 H), 7.33 (d, ^3J = 7.8 Hz, 2 H), 7.51 (d, ^3J = 15.9 Hz, 2 H), 7.78 (dd, ^3J = 7.8 Hz, 2 H), 8.36 (d, ^3J = 7.8 Hz, 2 H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 67.44 (+), 69.29 (+), 69.42 (+), 82.31 (C_{quart}), 118.84 (+), 120.85 (+), 125.92 (+), 131.62 (+), 137.13 (+), 155.34 (C_{quart}), 155.99 (C_{quart}). – IR (KBr): ν = 1633 cm^{-1}, 1433, 1104, 463. – UV/VIS (CH_3CN): λ_{max} (lg ε) = 206 nm (4.741), 240 (4.363), 322 (4.485), 472 (3.453). – MS (70 eV), *m/z* (%): 576 (38) [M^+], 511 (100) [$M^+ - C_5H_5$]. – Calcd. for $C_{34}H_{28}N_2Fe_2$: 576.095; found: 576.095.

Bis[6-ferrocenylvinyl-6'-methyl-2,2'-bipyridine]copper (I) hexafluorophoshate (**4**)

2 (32 mg, 0.084 mmol) and 16 mg (0.042 mmol) of $[Cu(CH_3CN)_4]PF_6$ were mixed in 3 ml dry acetonitrile under dinitrogen, stirred for 30 min and evaporated *in vacuo*. CC (CH_2Cl_2/EE 6:1) of the solid residue gave 35 mg (86%) **4** (R_f = 0.4); as a red solid, m. p. >320 °C. – ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 2.22 (s, 6 H), 3.68 (m, 2 H), 3.78 (m, 10 H), 3.89 (m, 4 H) 4.22 (m, 4 H), 6.63 (d, ^3J = 16.3 Hz, 2 H), 7.46 (d, ^3J = 16.3 Hz, 2 H), 7.68 (d, ^3J = 7.7 Hz, 2 H), 8.13 (d, ^3J = 7.9 Hz, 2 H), 8.21 (dd, ^3J = 7.8 Hz, 2 H), 8.26 (dd, ^3J = 7.9 Hz, 2 H), 8.68 (m, 4 H). – ^{13}C NMR (100 MHz, [D$_6$]-DMSO): δ = 24.55 (+), 66.45 (+), 67.55 (+), 69.25 (+), 70.05 (+), 80.24 (C_{quart}), 120.0867 (+), 120.16 (+), 121.93 (+), 124.01 (+), 126.24 (+), 135.23 (+), 138.72 (+), 138.94 (+), 151.25 (C_{quart}), 151.41 (C_{quart}), 154.59 (C_{quart}), 156.92 (C_{quart}). – IR (KBr): ν = 1629 cm^{-1}, 1472. – UV/VIS (CH_3CN): λ_{max} (lg ε) = 200 nm (4.997), 242 (4.555), 322 (4.598), 462 (3.626). – MS (FAB; Matrix: NBA), *m/z* (%): 823 (100) [M$^+$], 758 (5) [M$^+$ – C_5H_5], 703 (5) [M$^+$ – C_5H_5Fe], 443 (58) [M$^+$ – $C_{23}H_{30}FeN_2$]. – $C_{46}H_{40}CuFe_2N_4PF_6$: calcd. C 57.01, H 4.16, N 5.78, found C 56.80, H 4.31, N 5.99.

Bis[6,6'-bis(ferrocenylvinyl)-2,2'-bipyridine]copper (I)hexafluorophosphate (**5**)

16 mg (0.03 mmol) of **3** and 5 mg (0.014 mmol) of [Cu(CH_3CN)$_4$]PF_6 were stirred in 5 ml dry CH_3CN for 5 h. Evaporation of the solvent *in* vacuo and CC (CH_2Cl_2/CH_3OH 14:1) of the residue yielded 18 mg **5** (93%) as a purple-red solid, m. p. 303 °C (dec.). – ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 3.80 (s, 20 H), 3.84 (m, 8 H), 4.26 (m, 8 H), 6.72 (d, ^3J = 16.3 Hz, 4 H), 7.50 (d, ^3J = 16.3 Hz, 4 H), 8.21 (d, ^3J = 8.0 Hz, 4 H), 8.36 (dd, ^3J = 7.9 Hz, 4 H), 8.88 (d, ^3J = 7.9 Hz, 4 H). – ^{13}C NMR (100 MHz, [D$_6$]-DMSO): δ = 67.12 (+), 69.32 (+), 70.18 (+), 80.15 (C_{quart}), 120.29 (+), 122.16 (+), 123.96 (+), 135.62 (+), 151.41 (C_{quart}), 154.82(C_{quart}). – IR (KBr): ν = 1627 cm^{-1}, 1446. – UV/VIS (CH_3CN): λ_{max} (lg ε) = 206 nm (5.134), 318 (4.847), 470 (3.922). – MS (FAB; Matrix: NBA), *m/z* (%): 1214 (2.5) [M$^+$], 55 (100).

Bis[4-ferrocenylvinyl-4'-methyl-2,2'-bipyridine]copper(I) hexafluorophosphate (7)

*160 mg (0.42 mmol) of 4-ferr*ocenylvinyl-4'-methyl-2,2'-bipyridine (**6**) and 78 mg (0.21 mmol) of [Cu(CH_3CN)$_4$] PF_6 in 10 ml CH_3CN were stirred for 2 h, the reaction mixture was evaporated *in vacuo,* and the solid residue chromatographed (CH_2Cl_2/CH_3OH 95:5) to yield 200 mg (98%) **7** (R_f = 0.53) as a purple solid, m. p. > 320 °C. – ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 2.57 (s, 6 H), 4.20 (s, 10 H), 4.50 (m, 4 H), 4.66 (m, 4 H), 6.87 (d, ^3J = 16.0 Hz, 2 H), 7.22 (m, 2 H), 7.32 (2 H), 7.38 (2 H), 7.46 (2 H), 7.72 (d, ^3J = 15.6 Hz, 2 H), 8.85 (2 H), 8.91 (2 H). – ^{13}C NMR (100 MHz, [D$_6$]-DMSO): δ = 20.77 (+), 67.88 (+), 69.30 (+), 69.40 (+), 81.01 (C_{quart}) – IR (KBr): ν = 1602 cm^{-1}, 1490. – UV/VIS (CH_3CN): λ_{max} (lg ε) = 206 nm (4.841), 250 (4.471), 322 (4.483), 338 (4.517) 514 (3.791). – MS (FAB; Matrix: NBA), *m/z* (%): 823 (2) [M$^+$], 154 (100).

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