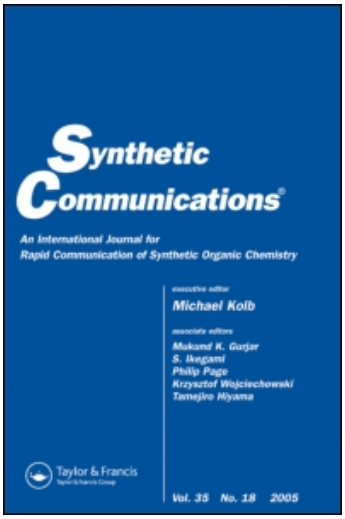

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Syntheses of 5,5'-Disubstituted 2,2'-Bipyridines

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SYNTHESES OF 5,5'-DISUBSTITUTED 2,2'-BIPYRIDINES

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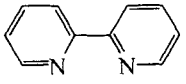
Abstract: New and improved syntheses of 5,5'-donor-functionalized 2,2'-bipyridines are reported with the 5,5'-donors being -NH_2 (**4**), -NMe_2 (**5**), -CN (**6**), and -NCS (**7**). A new route for **4** and **5** is based on the coupling of 2-chloro-5-amino-pyridine in the presence of $NiCl_2 \cdot 6\ H_2O/PPh_3/Zn$ in DMF (NiCRA). **6** was obtained by a dehydration treatment of 5,5'-dicarboxamide-2,2'-bipyridine with $(F_3CCO)_2O$ and P_4O_{10}. The new ligand **7** is prepared from **4** and $SCCl_2$.

Keywords biaryls, coupling reactions, pyridines, cyano compounds, isothiocyanates

Introduction

Bipyridines are highly important ligands for the coordination of transition metals. Metal complexes of 2,2'-bipyridines (**1**) and of secondary amines (**2**) are constantly investigated as building blocks for supramolecular complexes and for the construction of porous metal frameworks [1,2] that exhibit reversible guest exchange and selective catalytic activity.[1,3]



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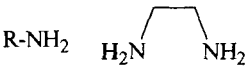

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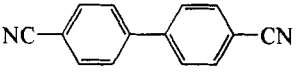
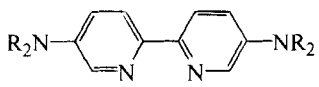


3

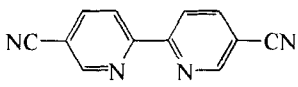
*To whom correspondence should be addressed.

Ligands containing CN-donors such as 4,4'-biphenyldicarbonitrile **3** and others also are excellent bridging ligands to synthesize porous coordination polymers.[4]

Because of the importance of bipyridines in many areas of chemistry the synthesis of substituted derivatives thereof is the subject of a steady interest. We are currently engaging into a program to study the coordination behavior of modified 2,2'-bipyridine ligands such as ambidentate 5,5'-diamino-2,2'-bipyridine (**4**),[5] 5,5'-bis-(N,N-dimethylamino)-2,2'-bipyridine (**5**), 5,5'-dicyano-2,2'-bipyridine (**6**) [6] or 5,5'-diisothiocyanato-2,2'-bipyridine (**7**). This is a continuation of our earlier investigations on modified and ambidentate tris(pyrazolyl)borate ligands.[7]



4 R = H
5 R = Me



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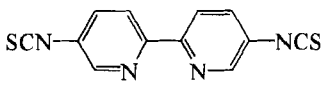
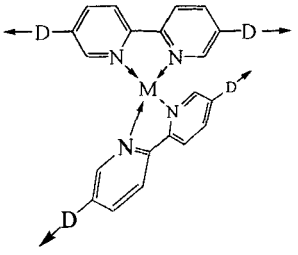


7

The ligand **4** can be thought of combining the ligating properties of the bipyridine and amine ligands **1** and **2**. The ligand **6** should incorporate the ligating properties of the chelating bipyridine **1** and the bridging 4,4'-biphenyldicarbonitrile ligand **3**. The synthesis of the ambidentate ligand **7** was based on the notion that it combines hard nitrogen and soft sulfur donor atoms within one molecule. Therefore, a controlled chelating or bridging mode should be possible through the selection of hard and soft metal ions. The idea behind the use of such functionalized bridging/chelating 2,2'-bipyridine ligands is to have cross-connecting blocks for coordination polymers based on the *endo*-chelation of two (or three) ligands with an appropriate metal center (**8**) or to supply functional donor atoms within the inner walls of a porous coordination polymer as is schematically depicted in **9**.[8]



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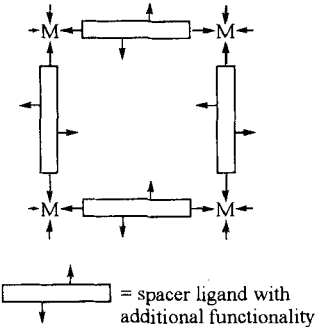


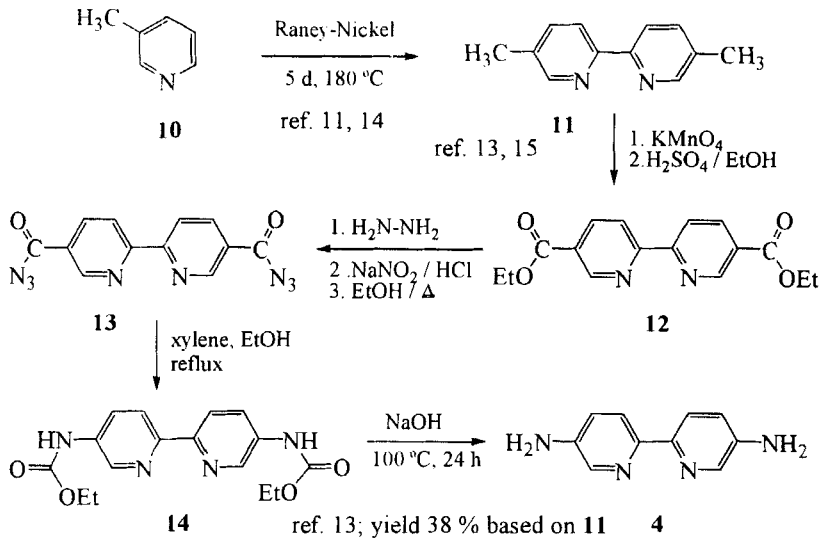
9

Results and Discussion

The synthesis of substituted 2,2'-bipyridines has been pioneered by Ullmann through the use of copper powder for the coupling of the 2-halo-pyridine precursors.[9] This route requires, however, drastic reaction conditions (temperature mostly >200 °C) and is limited to the iodo and bromo derivatives. Oae et al. developed a coupling of heteroarylsulfoxides with Grignard reagents and lithium organyls, but this limits the possible functional groups on the nitrogen heterocycle.[10] The action of Raney-nickel on substituted pyridines led to the formation of 2,2'-bipyridines in low yields.[11] Halopyridines could also be reductively coupled with formic acid and its salt in the presence of palladium on charcoal as catalyst and an additional surfactant.[12]

Our attempt to couple 5-amino-2-chloropyridine (**15**) with sodium formate over palladium charcoal gave only less than 20% yield of **4**. Instead, the product of the reductive dehalogenation, 3-amino-pyridine (**18**) was obtained in more than 50% yield. The synthesis of **4** could be achieved according to a route by Whittle as outlined in Scheme 1.[11,13,14,15]

In order to shorten the synthesis of **4** and to improve the yield, we tried a new coupling of 2-chloro-5-amino-pyridine (**15**) with $NiCl_2 \cdot 6\ H_2O$/L/reducing agent (eq. 1). Such *ni*ckel-containing *c*omplex *r*educing *a*gents are generally abbreviated as NiCRAL's, L being PPh_3 or 2,2'-bipyridine. Reducing agents can be Zn [16] or a

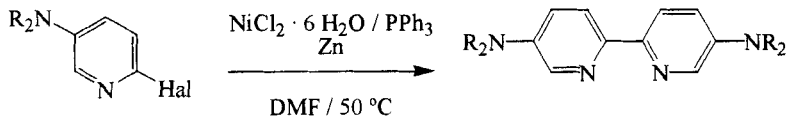


Scheme 1

mixture of NaH and NaO^{t}Bu.[17,18] Zerovalent nickel complexes for the coupling of aryl halides were first introduced by Semmelhack et al.[19,20]

For the coupling of **15** the use of NaH as a reducing agent failed. The necessary excess of NaH apparently deprotonates the amino function, which then coordinates to nickel so that the reaction is slowed down considerably. After 5 d at reaction conditions, the educt is still present and only traces of **4** were found. This is remarkable, since under the same conditions 2-amino-3-chloropyridine is coupled to the 2,2'-diamino-3,3'-bipyridine in 44% yield in 17 hours.[17,18]

The use of zinc powder as a reducing agent for the NiCRAL was eventually succesful: A solution of $NiCl_2 \cdot 6\ H_2O$ and PPh_3 in DMF was reduced with Zn and was subsequently reacted with a stoichiometric amount of 5-amino substituted 2-halopyridine. No pyridine educt could be detected anymore after 2 to 2.5 h and workup yielded the coupling product **4** and the tetramethyl derivative **5** in over 60% yield (eq. 1).

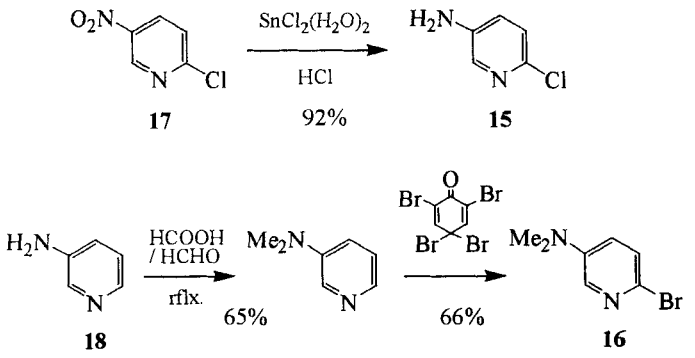


15 R = H, Hal = Cl
16 R = Me, Hal = Br

4 R = H
5 R = Me

(eq. 1)

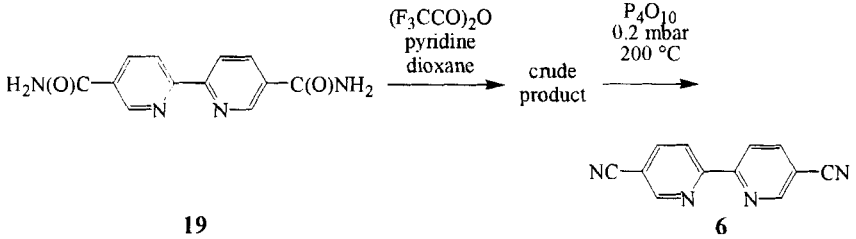
The amino substituted 2-halopyridines **15** and **16** were obtained from the commercially available starting materials 2-chloro-5-nitropyridine (**17**)[21] and 3-amino-pyridine (**18**),[22] respectively (Scheme 2).



Scheme 2

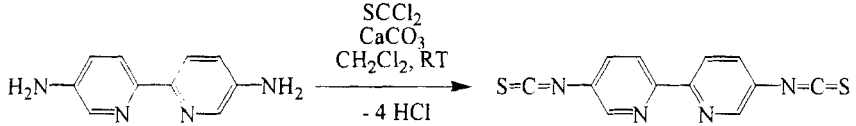
The synthesis of 5,5'-dicyano-2,2'-bipyridine (**6**) as reported in the literature is the reaction of 5,5'-dicarboxamide-2,2'-bipyridine (**19**) with $POCl_3$ in $CHCl_3$ under sonication (50KHz) to give the product in 86% yield.[23] Another method is the sublimation of the mixture of **19** and P_4O_{10} under vacuum at a temperature of 300 °C.[13] However, a two-fold dehydration treatment and a two-fold sublimation of the crude (sublimed) product was found necessary to obtain **6** in satisfactory purity. This finally gave the dicyano-bipyridine in a low yield of only 29%. Furthermore, if more than 0.5 g of the dicarboxamide was used in the dehydration reaction with P_2O_5, this resulted in a further decrease of the yield of the product. Thus, we report

here a modified method which is based on a two-times dehydration treatment of **19**, first with a trifluoroacetic anhydride-pyridine system and then with P_4O_{10} (eq. 2). The initial dehydrated crude product is obtained in high yield. This crude product was then again dehydrated with P_4O_{10} at 0.2 mbar/180 °C to give the final product in 43% yield. This method has the advantage of a higher yield (compared to the literature)[13], the possibility of starting with an increased amount of the dicarboxamide, and the use of a lower sublimation temperature.



(eq. 2)

The ligand 5,5'-diisothiocyanato-2,2'-bipyridine (**7**) was prepared in high yield from the reaction of **4** with thiophosgene ($SCCl_2$) in methylene chloride in the presence of acid-binding calcium carbonate in water (eq. 3).



(eq. 3)

Experimental part

Solvents were dried according to standard procedures over potassium metal (diethyl ether, tetrahydrofuran [THF]), CaH_2 (dimethyl formamide [DMF]) and distilled and stored under argon. $CHCl_3$, CH_2Cl_2 and toluene were bought with a residual water content of less than 0.05% and used as such. All aniline educts were purified by vacuum distillation under argon prior to use. Commercial nickel(II) acetate tetrahydrate was dried 12 h in vacuum at 100 °C and stored under argon. Commercial PPh_3 was dried for 24 h in vacuum at 50 °C.

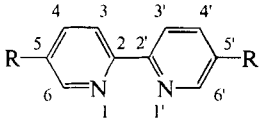
NMR spectra were collected on a Bruker ARX200 (200.1 MHz for ^1H, 50.3 MHz for ^{13}C) or a Varian O-300 instrument (300.0 MHz for ^1H, 75.4 MHz for

^{13}C) and calibrated against the solvent signal (DMSO-d_6 ^1H-NMR 2.53 ppm, ^{13}C-NMR 39.5 ppm; $CDCl_3$ ^1H-NMR 7.26 ppm, ^{13}C-NMR 77.0 ppm; C_6D_6 ^1H-NMR 7.19 ppm, ^{13}C-NMR 128.0 ppm). IR-spectra were measured on a Perkin-Elmer 783 Infrared Spectrophotometer as KBr disks or nujol mulls. Mass spectra were obtained on a GC/MS Finnigan MAT in solid-probe EI mode at an ionization energy of 70 eV. Elemental analyses were carried out with a Perkin-Elmer Elemental Analyzer E 240.

Synthesis of ***4*** *by coupling of 5-amino-2-chloro-pyridine (**15**)* (eq. 1): In a 250 ml three-necked flask were placed 2.37 g (10 mmol) of nickel dichloride hexahydrate and 10.5 g (40 mmol) of triphenyl phosphine. The flask was evacuated and refilled with argon for three times. 100 ml of dried DMF was added under inert gas and the solution rapidly turned blue. After PPh_3 and $NiCl_2 \cdot 6\ H_2O$ had completely dissolved in DMF, 0.7 g (11 mmol) of zinc powder was added to the solution under inert gas at 50 °C and the solution slowly turned brown-red. After stirring this mixture for 1 h, 10 ml of a DMF solution with 1.28 g (10 mmol) of 5-amino-2-chloro-pyridine (**15**) was added dropwise into the mixture. Stirring was continued for 4 h at 50 °C at which time the starting material could not be detected anymore by thin-layer chromatography (eluent ethyl acetate). The reaction mixture was then narrowed in vacuum to half of its volume. After adding 250 ml of water the mixture was carefully poured into 150 ml of conc. ammonia and stirred for 18 h. The solution turned blue because of the formation of hexaammin-nickel(II) complexes. The PPh_3 precipate was removed by filtration and the filtrate was extracted three times with 50 ml of CH_2Cl_2 each. The combined organic phases were treated with 50 ml of half-concentrated HCl for three times each to separate the diamino-bipyridine from PPh_3. During this procedure strongly colored diamino-dihydro-dichlorides formed. The combined acidic aqueous phases were carefully neutralized with a 10 % Na_2CO_3 solution. The product **4** separated as a yellowish solid and was sublimed as described above to give a colorless powder (yield 1.11 g, 60 %). M.p. 205 °C (Lit.: 205-206 °C [13]). — ^1H-NMR (DMSO-d_6): 7.92 (d, 2H, J = 2.8 Hz, H6,H6'), 7.84 (d, 2H, J = 8.6 Hz, H3,H3'), 6.95 (dd, 2H, J_1 = 8.6 Hz, J_2 = 2.5 Hz, H4,H4'), 5.30 (s (br), 4H, $-NH_2$). — ^{13}C-NMR ($CDCl_3$): 144.7

(C2,C2'),143.6 (C5,C5'), 134.9 (C6,C6'), 120.5 (C3,C3'), 119.0 (C4,C4'); (DMSO-d_6): 147.1, 145.5, 136.6, 123.5, 122.2. — IR (KBr): 3424 w, 3338 m, 3310 m, 3207 m, 3062 w, 3057 w, 3005 w, 1632 w, 1600 m, 1568 m, 1478 s, 1412 m, 1289 m, 1248 w, 1137 w, 1108 w, 1088 w, 1060 w, 1024 w, 920 w, 897 w, 846 m, 832 m, 737 w, 656 m, 552 m, 517 m, 509 w, 418 w.

The numbering scheme for the NMR notation for **4** and **5** is as follows:



5,5'-Bis(dimethylamino)-2,2'-bipyridine (**5**): The same procedure as described for **4** was used, starting from 4.0 g (17 mmol) of $NiCl_2 \cdot 6\ H_2O$, 17.8 g (68 mmol) of PPh_3, 1.2 g (19 mmol) of Zn powder and 3.5 g (17 mmol) of 2-bromo-5-*N,N*-dimethylamino-pyridine (**16**). The product **5** separated as a yellowish solid and purified by sublimation at 150 °C/0.2 mbar to give 2.6 g (64%) of dendritic crystals. M.p. 234 °C. — ^{1}H-NMR (DMSO-d_6):: 8.03 (d, 2H, J = 2.6 Hz, H6,H6'), 7.99 (d, 2H, J = 8.6 Hz, H3,H3'), 7.14 (dd, 2H, J_1 = 8.6 Hz, J_2 = 2.6 Hz, H4,H4'), 2.92 (s, 12H, -N(CH_3)$_2$). — ^{13}C-NMR (DMSO-d_6): 145.1 (C5,C5'), 144.5 (C2,C2'), 133.4 (C6,C6'), 119.2 (C3,C3'), 118.9 (C4,C4'), 43.9 (methyl-C). — IR (nujol): 1695 w, 1596 s, 1540 m, 1518 m, 1498 m, 1492 s, 1428 w, 1420 w, 1370 w, 1358 m, 1292 m, 1280 w, 1268 w, 1220 w, 1175 s,1152 w, 1130 w, 1073 w, 1060 w, 1047 w, 1004 w, 946 m, 870 w, 842 m, 760 m, 735 m, 660 w. — $C_{14}H_{18}N_4$: calc. C 69.40, H 7.40, N 23.10; found C 69.56, H 7.07, N 23.33%.

5,5'-Dicarboxamide-2,2'-bipyridine (**19**): A mixture of 3.0 g of 5,5'-bis(ethylcarboxylate)-2,2'-bipyridine (**12**), 100 ml of ethanol and 100 ml of ethylene glycol was saturated with ammonia and heated in a sealed round bottom flask in an oil bath at 95 °C for 48 h. The precipitate formed was collected and washed with hot ethanol and ethylene glycol. 1.9 g of 5,5'-dicarboxamide-2,2'-bipyridine was obtained in the yield of 79%. M.p. >280 °C (Lit. >310 °C [13]). IR: 3375s, 3170s, 1660s, 1634s, 1599s, 1548m, 1480w, 1410s, 1370m, 1285w, 1252m, 1165w,

1132m, 1118w, 1055w, 1028m, 955w, 860m, 810w, 790m, 760w, 720m, 665m, 659m, 638m, 600w, 535w.

5,5'-Dicyano-2,2'-bipyridine (**6**): This compound was prepared by two methods.

Literature method:[13] 0.2 g (0.8 mmol) of 5,5'-dicarboxamide-2,2'-bipyridine (**19**) and 0.5 g (1.7 mmol) of P_4O_{10} were placed into a sublimator and kept at 0.2 mbar/300 °C until the sublimation had ceased. The crude product which easily absorbs water from the air was resublimed to obtain 0.1 g of a colorless solid. This amount was repurified with 0.2 g of P_4O_{10} in a sublimator at 0.2 mbar/300 °C followed by resublimation to give 0.05 g of **5** (29% yield). M.p. 275.9-276.6 °C (Lit. 269-271 °C [13], 284-285 °C [23]). IR: 3420 w, 3070 w, 2240 s, 1985 w, 1898 w, 1796 w, 1720 s, 1597 s, 1540 m, 1468 s, 1373 s,1292 m, 1240 s, 1170w, 1130 w, 1053 w, 1030 s, 948 w, 850 s, 795 w, 776 w, 751 m, 726 m, 652 m, 554 m.

Modified method: Trifluoroacetic anhydride (2.5 ml, 18.4 mmol) was added dropwise to a stirred ice-cooled suspension of 5,5'-dicarboxamide-2,2'-bipyridine, **19**, (2.0 g, 8.4 mmol) in anhydrous dioxane (150 ml) and anhydrous pyridine (1.5 ml, 18.4 mmol). Over the period of the addition the temperature was kept below 5 °C. The reaction mixture was then allowed to warm to room temperature and stirred for another 10 h. Then 100 ml of distilled water were added into the reaction mixture, the solid product was removed by filtration and washed with water to obtain 1.5 g of crude product. From this amount, 0.2 g of the crude product were heated together with 0.5 g of P_4O_{10} in a sublimator at 0.2 mbar/180 °C until sublimation had ceased. The solid was purified by resublimation to obtain 0.12 g of a colorless solid (**6**) (43% yield). M.p. 275.4-276.2 °C (Lit. 269-271 °C [13], 284-285 °C [23]). The IR spectrum of this product was identical to the above sample from the literature method. - ^{1}H NMR (d_8-THF): 8.34 (dd, 2H, H4,H4', J = 8.3, 2.1 Hz), 8.57 (dd, 2H, H3,H3', J = 8.2, 0.8 Hz), 8.9 (br, 2H, H6,H6'). - ^{13}C NMR (d_8-THF): 111.63 (C5,C5'), 117.49 (CN), 122.38 (C3,C3'), 142.33 (C4,C4'), 153.40 (C6,C6'), 157.75 (C2,C2').

5,5'-Diisothiocyanato-2,2'-bipyridine (7): 1.10 g (5.9 mmol) of 5,5'-diamino-2,2'-bipyridine (**4**) and 3.0 g (30 mmol) of $CaCO_3$ were suspended in a mixture of 50 ml of CH_2Cl_2 and 30 ml of H_2O. After addition of 1.5 ml (2.3 g, 19.2 mmol) of $SCCl_2$ the reaction mixture was stirred for 24 h at room temperature. Excess $CaCO_3$ was removed by filtration and the filter cake was washed with hot toluene several times. The combined organic phases were narrowed carefully (because of excess thiophosgene) to dryness by distillation. The resulting solid was washed with water to remove $CaCl_2$ and the crude product was recrystallized from toluene or THF to yield 1.36 g (84%) pale yellow needle-shaped crystals. Compound 7 is soluble in CH_2Cl_2 but poorly so in THF. M.p. 231 °C. - ^{1}H-NMR (C_6D_6): 6.63 (dd, 2H, J = 2.5, 8.7 Hz, H4, H4'), 8.04 (d, 2H, J = 2.5 Hz, H6, H6'), 8.17 (d, 2H, J = 8.7 Hz, H3, H3'). - ^{13}C-NMR (C_6D_6): 121.5 (NCS), 128.8 (C3, C3'), 133.0 (C4, C4'), 146.1 (C6, C6'), 153.0 (C2, C2'), 163.5 (C5, C5'). - IR (KBr): 3060 w, 2208 m, 2118 s, 1585 w, 1547 w, 1465 w, 1378 w, 1355 w, 1280 w, 1272 w, 1232 w, 1124 w, 1058 w, 1047 w, 1022 w, 972 w, 943 m, 840 s, 732 w, 708 w, 650 w, 458 w, br, 407 w, 396 w, 378 w. - MS (m/e): 270 (100%, $[M]^+$), 226 (6%, $[M - CS]^+$), 212 (5%, $[M - NCS]^+$), 199 (15%, $[M - CS - HCN]^+$), 185 (16%, $[M - NCS - HCN]^+$), 135 (8%, $[M/2]^+$).

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