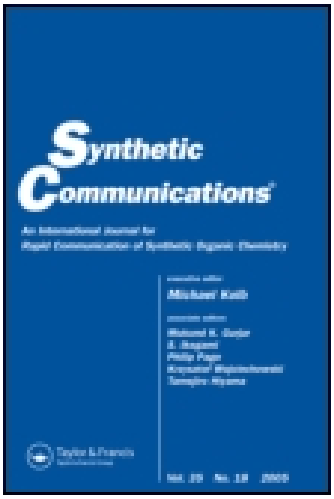

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Thio- and Selenocyanation Reactions of Quinone Imines—Derivatives of Pyrido[1,2-a]benzimidazole

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Accepted author version posted online: 27 Dec 2011.Published online: 14 May 2012.

To cite this article: Oleg Y. Slabko , Andrey V. Kachanov & Vladimir A. Kaminskii (2012) Thio- and Selenocyanation Reactions of Quinone Imines—Derivatives of Pyrido[1,2-a]benzimidazole, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 42:16, 2464-2470, DOI: 10.1080/00397911.2011.560743

To link to this article: http://dx.doi.org/10.1080/00397911.2011.560743

Synthetic Communications®, 42: 2464–2470, 2012

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2011.560743

THIO- AND SELENOCYANATION REACTIONS OF QUINONE IMINES—DERIVATIVES OF PYRIDO[1,2-*a*]BENZIMIDAZOLE

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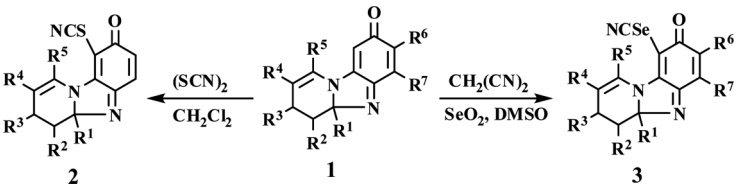
GRAPHICAL ABSTRACT



Abstract *The thio- and selenocyanation of quinone monoimines of pyrido[1,2-a]benzimidazole series with the participation of dithiocyanogen and triselenodicyanide in mild reaction conditions results in formation of 9- or 6-thiocyano- and 9-selenocyano- derivatives in good yields.*

Keywords Quinone imine; selenocyanate; thiocyanate; triselenodicyanide

INTRODUCTION

Organic thiocyanates are used as intermediate products in the synthesis of dyes, antiseptic agents, and bactericidal remedies, as insecticides and fungicides, and as stabilizers of chlorinated hydrocarbons, lubricants, and emulsifying agents. Organic selenocyanates play an important part as valuable reagents and intermediate products for synthesis of other selenorganic compounds; many of them are of great significance as anti-inflammatory and antineoplastic drugs because of their capability to inhibit the activity of protein kinase C for development of cancer.[1]

Thiocyanation and selenocyanation of quinoid compounds by hydrogen electrophilic substitution in a quinoid kernel have not been described yet. There are some examples of obtaining thiocyano-(benzo)naphthoquinones[2] and also quinone

Received November 18, 2010.
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monoimines[3] for nucleophilic substitution of atoms of chlorine in a quinoid kernel at interaction with potassium and ammonium thiocyanates. Analogous reaction with *N*-arylsulfonyl(aroyl)-1,4-benzoquinone imines[4] and *N*,*N*′-bis(methylsulfonyl)-1,4-benzoquinone diimine[5] leads to nucleophilic addition of the thiocyanate ion with intramolecular cyclization. Dithiocyanogen is a well-known agent for thiocyanation used in reactions of electrophilic attachment with alkenes and dienes[6] and in reactions of electrophilic substitution with arenes, amines, and thiols.[7] There are no examples of interaction of quinones with dithiocyanogen. Selenocyanoquinones have not been studied. The only example is 2-selenocyanoquinone, received by oxidation of 2,5-dimethyloxi-selenocyanobenzene with the help of cerium ammonium nitrate applied on silica gel.[8] Recently, we developed a new, simple, and convenient method of one pot selenocyanation of aromatic amines, indoles, and methyleneactive compounds with the help of triselenodicyanide, obtained by oxidative coupling of malononitrile and SeO_2.[9] Earlier, triselenodicyanide was used as a selenocyanation reagent (in reaction with aniline and *N*,*N*-dimethylaniline[10] and also polystyrene[11]) and cyanation reagent (in synthesis of cyano *N*-heterocycles[12]).

RESULTS AND DISCUSSION

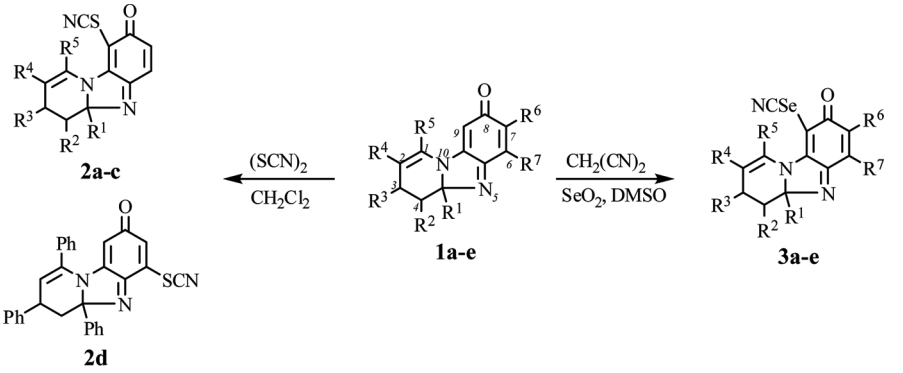
In the present work, we have investigated the behavior of the quinone monoimines of pyrido[1,2-a]benzimidazole series in the reactions with dithyocyanogen and triselenodicyanide.

Quinone imines **1a–c** easily interact with dithyocyanogen solution, yielding the 9-thiocyano-substituted products **2a–c**. In the case of quinone imine **1d**, the 6-thiocyano-substituted product **2d** was received unexpectedly.

The thiocyanation direction in position 6 in the case of a quinone imine **1d** is assumed to be caused by insufficient nucleophilic properties of position 9 in quinoid system, due to the least degree of a coplanarity vinylamine fragment to a quinoid kernel in comparison with quinone imines **1a–c** (because of the least rigidity of structure) and, hence, due to the least degree of charge transfer from atom N^{10} to atom of oxygen of quinoid carbonyl; this dependence was shown earlier.[13]

Similarly, quinone imines **1a–e** react with triselenodicyanide at ambient temperature in one pot selenocyanation reaction in a quinoid kernel.[9] Reaction is accompanied by selective formation of 9-selenocyanoquinone imines **3a–e** of the specified series. The reaction is supposed to have an electrophilic character because the selenocyanation of arylamines is accelerated by the electron-donating substituents. There is electron-donating powerful substituent in the *ortho*-position to the atom C^9 of the quinoid kernel of pyridobenzimidazole system.

The infrared (IR) spectra of the obtained thiocyanates **2a–d** and selenocyanates **3a–e** contain rather low-level absorption bands of vibrations of SCN (2150–2169 cm^{-1}) and SeCN (2150–2156 cm^{-1}) groups and absorption bands of vibrations of bands in the enaminoquinoid system. A relative displacement toward the big wave numbers of a strip of SCN (14–17 cm^{-1}) group in the spectrum of compound **2d** to the spectra of compounds **2a–c** may be explained by the absence of a donor influence of vinylamine fragment on the thiocyanate group in position 6 of the quinoid system. In electronic spectra, there is a gypsochromic strip displacement in the visible part of a spectrum of thiocyanates **2a–c** (23–35 nm) and selenocyanates



Scheme 1. Synthesis of thio- and selenocyanates of quinone imines. R^1, $R^2 = R^4$, $R^5 = (CH_2)_4$, $R^3 = R^6 = R^7 = H$ (**a**); R^1, $R^2 = (CH_2)_4$, $R^3 = Ph$, R^4, $R^5 = 1,2$-(3,4-dihydronaphtho), $R^6 = R^7 = H$ (**b**); R^1, $R^2 = (CH_2)_4$, $R^3 = R^5 = Ph$, $R^4 = R^6 = R^7 = H$ (**c**); $R^1 = R^3 = R^5 = Ph$, $R^2 = R^4 = R^6 = R^7 = H$ (**d**); R^1, $R^2 = (CH_2)_4$, $R^3 = Ph$, R^4, $R^5 = 1,2$-(3,4-dihydronaphtho), R^6, $R^7 =$ benzo (**e**).

3a–e (15–30 nm) with simultaneous decreasing of a molar extinction in comparison with spectra of the initial quinone imines **1a–e**. This is likely to be explained by lowering the degree of intramolecular transfer from donor–vinylamine fragment to a carbonyl group of the quinoid kernel caused by the inductive electron-accepting influence of the thiocyanate and selenocyanate groups. In an electronic spectrum of thiocyanate **2d**, there is bathochromic displacement of a strip in a visible part of a spectrum (28 nm) toward the strip in the spectrum of initial compound **1d**. Possibly this is an effect of increasing planarization of the conjugated enaminoquinoid system in the case of 6-substitution.

Data of ^{1}H NMR spectra of compounds **2a–c** and **3a–e** unequivocally testify to substitution in position 9 because the signal of proton H^9 disappears, and a signal of proton H^7 becomes a doublet and undergoes a small shift (0.2–0.3 ppm), whereas in the spectra of initial quinoneimines **1a–e** the signal of proton H^7 is doublet-doublet. It may be interpreted as electron-accepting influence of SCN and SeCN groups. In contrast, there is disappearance of a signal of proton H^6, with preservation of doublet signals of protons H^7 and H^9 with ^4J (1.5 Hz) in the thiocyanate **2d** spectrum. Multiplicity and position of signals of other protons of pyridobenzimidazole system are similar to the spectral data of initial quinone imines **1a–e**. Values of pseudomolecular ions in mass spectra of compounds **2a–d** and **3a–e** correspond to the calculated ones.

CONCLUSION

In summary, we offer a new, simple, and efficient method for the synthesis of thio- and selenocyanates of heterocyclic quinone imines using dithiocyanogen and triselenodicyanide, respectively, by means of general electrophilic substitution of hydrogen in quinoid structure. The mild reaction conditions, simple procedure, and good yields are the main advantages of this method, which make it a valid contribution to the existing methodologies.

EXPERIMENTAL

IR spectra and electronic absorption spectra were recorded on a Fourier transform (FT)–IR spectrophotometer Spectrum BX-II in KBr and Ultraviolet–Visible spectrophotometer Cintra-5 in ethanol (visible region), respectively. NMR ^{1}H spectra were received on a Bruker AC-250 spectrometer (250 MHz) with tetramethylsilane (TMS) as the internal standard and $CDCl_3$ as solvent. Elemental analysis was obtained on a Flash EA 1112 CHN/MAS200 elemental analyzer. High-performance liquid chromatography (HPLC) analysis carried out on a HP 1100 LC/MSD instrument with column Hypersil ODS (4 × 125 mm), a mobile phase 2-propanole/water (60:40), rate of flow of 0.3 mL/min, temperature 55 °C, and diode matrix. Conditions of shooting of the mass spectrum were API-ES source and positive polarity. Melting points were obtained on a Büchi B-540 and Boëtius instruments and are uncorrected. Reactions and purity of products were monitored by thin-layer chromatography (TLC) using Silufol UV-254 and Sorbfil plates. Preparative chromatography was performed using silica gel (60-120 mesh) as sorbent.

All received compounds were synthesized by typical experimental procedures, but isolation and purification methods were different. Compounds **1a–e,** dithiocyanogen and triselenodicyanide, were prepared by reported procedures.[14,15,9]

Thiocyanates 2a–d: Typical Experimental Procedure

Freshly made solution of dithiocyanogene in dry CH_2Cl_2 was added to a stirred solution of compounds **1a–d** (0.5 mmol) in dry CH_2Cl_2 (8 mL) by drops over a period of 1 h under ice-cold/NaCl conditions until the spot of starting compound **1** on TLC had disappeared. After completion of the reaction, the mixture was evaporated up to 5 mL of volume and was purified by preparative TLC in petroleum ether/EtOAc 1:1 (**2a**) and 2:1 (**2b–d**) as eluent.

Selenocyanates 3a–e: Typical Experimental Procedure

SeO_2 (2.0 mmol) was added to a solution of propanedinitrile (1.0 mmol) in DMSO (1 mL); the mixture was exposed for 10–15 min to the beginning of exothermic reaction, cooled, and filtered. The solution received triselenodicyanide and added to a solution of compounds **1a–e** (0.5 mmol) in DMSO (3 mL). A reaction mixture was stirred at an ambient temperature for 20−30 h (controlled by TLC), and diluted with 3 volumes of water. Saturated solution NaCl (3 mL) was added; the dropped precipitate was filtered off, washed with water (3 × 3 mL), and dried. In the case of compounds **3c** and **d**, a precipitate represented practically chromatographically pure products (recrystallized from hexane/acetone mixture); in other cases, a precipitates was purified by preparative TLC in petroleum ether/EtOAc 1:1 (**3a**) and 2:1 (**3b**, **e**) as eluent.

Data

1,2;4,4a-Di (tetramethylene)-8-oxo-3,4,4a,8-tetrahydropyrido[1,2-*a*] benzimidazole-9-yl thiocyanate (2a). Red powder, 69% yield, mp 158–160 °C. ^{1}H NMR (250 MHz, $CDCl_3$), δ, ppm: 1.25–2.45 (m, 17H), 2.93 (m, 2H, CH_2),

6.82 (d, 1H, H^7, $^3J = 9.8$ Hz), 7.20 (d, 1H, H^6, $^3J = 9.8$ Hz). IR (KBr) ν, cm^{-1}: 2150 (SCN), 1678 ($C^1{=}C^2$), 1624, 1607 (C=O, C=N), 1588, 1564 ($C{=}C_{quin.}$). UV (EtOH) λ_{max}, nm: 455. $C_{20}H_{21}N_3OS$ (351.47): calcd. C, 68.18; H, 5.86; N, 12.07. Found: C, 68.35; H, 6.02; N, 11.96. MS (ESI): 352 ($M + H^+$).

1,2-(3,4-Dihydronaphtho)-4,4a-tetramethylene-8-oxo-3,4,4a,8-tetrahydropyrido[1,2-*a*]benzimidazole-9-yl thiocyanate (2b). Brown powder, 78% yield, mp 234–236 °C. ^{1}H NMR (250 MHz, $CDCl_3$), δ, ppm: 1.25–2.45 (m, 11H), 2.75 (m, 2H, CH_2), 3.50 (d, 1H, H^3, $^3J = 9.0$ Hz), 6.72 (d, 1H, ArH, $^3J = 7.0$ Hz), 6.91 (d, 1H, H^7, $^3J = 10.0$ Hz), 7.10–7.40 (m, 9H, H^6, ArH). IR (KBr) ν, cm^{-1}: 2154 (SCN), 1625 ($C^1{=}C^2$), 1619, 1606 (C=O, C=N), 1579, 1558 ($C{=}C_{quin.}$). UV (EtOH) λ_{max}, nm: 460. $C_{30}H_{25}N_3OS$ (475.61): calcd. C, 75.69; H, 5.23; N, 8.97. Found: C, 75.76; H, 5.30; N, 8.84. MS (ESI): 476 ($M + H^+$).

4,4a-Tetramethylene-8-oxo-1,3-diphenyl-3,4,4a,8-tetrahydropyrido[1,2-*a*]benzimidazole-9-yl thiocyanate (2c). Orange powder, 72% yield, mp 218–220 °C. ^{1}H NMR (250 MHz, $CDCl_3$), δ, ppm: 1.20–2.20 (m, 9H), 3.83 (dd, 1H, H^3, $^3J =$ 9.0 Hz, $^3J = 4.5$ Hz), 6.15 (d, 1H, H^2, $^3J = 4.5$ Hz), 6.88 (d, 1H, H^7, $^3J = 9.8$ Hz), 7.20–7.40 (m, 11H, H^6, ArH). IR (KBr) ν, cm^{-1}: 2155 (SCN), 1642 ($C^1{=}C^2$), 1626, 1605 (C=O, C=N), 1581, 1557 ($C{=}C_{quin.}$). UV (EtOH) λ_{max}, nm: 440. $C_{28}H_{23}N_3OS$. (449.57): calcd. C, 74.60; H, 5.02; N, 9.43. Found: C, 74.81; H, 5.16; N, 9.35. MS (ESI): 450 ($M + H^+$).

8-Oxo-1,3,4a-triphenyl-3,4,4a,8-tetrahydropyrido[1,2-*a*]benzimidazole-6-yl thiocyanate (2d). Dark red powder, 84% yield, mp 237–239 °C. ^{1}H NMR (250 MHz, $CDCl_3$), δ, ppm: 1.70 (dd, 1H, $H^4{}_{ax.}$, $^3J = 12.5$ Hz, $^2J = -11.5$ Hz), 3.30 (dd, 1H, $H^4{}_{eq.}$, $^3J = 8.3$ Hz, $^2J =$ 11.5 Hz), 3.45 (kd, 1H, H^3, $^3J = 12.5$ Hz, $^3J = 8.3$ Hz, $^3J = 2.5$ Hz), 4.86 (d, 1H, H^9, $^4J = 1.5$ Hz), 5.64 (d, 1H, H^2, $^3J = 2.5$ Hz), 6.92 (d, 1H, H^7, $^4J = 1.5$ Hz), 7.20-7.70 (m, 15H, ArH). IR (KBr) ν, cm^{-1}: 2169 (SCN), 1644 ($C^1{=}C^2$), 1605 (C=O, C=N), 1589, 1563 ($C{=}C_{quin.}$). UV (EtOH) λ_{max}, nm: 485. $C_{30}H_{21}N_3OS$. (471.57): calcd. C, 76.35; H, 4.29; N, 9.08. Found: C, 76.41; H, 4.49; N, 8.91. MS (ESI): 472 ($M + H^+$).

1,2;4,4a-Di(tetramethylene)-8-oxo-3,4,4a,8-tetrahydropyrido[1,2-*a*]benzimidazole-9-yl selenocyanate (3a). Dark red powder, 66% yield, mp 146–148 °C. ^{1}H NMR (250 MHz, $CDCl_3$), δ, ppm: 1.25–2.45 (m, 17H), 2.95 (m, 2H, CH_2), 6.86 (d, 1H, H^7, $^3J = 9.8$ Hz), 7.22 (d, 1H, H^6, $^3J = 9.8$ Hz). IR (KBr, ν, cm^{-1}): 2153 (SeCN), 1672 ($C^1{=}C^2$), 1618, 1602 (C=O, C=N), 1582, 1555 ($C{=}C_{quin.}$). UV (visible region, EtOH, λ_{max}, nm): 460. $C_{20}H_{21}N_3OSe$ (398.36): calcd. C, 60.06; H, 5.22; N, 10.87. Found: C, 60.30; H, 5.31; N, 10.55. MS (ESI): 400 ($M + H^+$).

1,2-(3,4-Dihydronaphtho)-4,4a-tetramethylene-8-oxo-3,4,4a,8-tetrahydropyrido[1,2-*a*] benzimidazole-9-yl selenocyanate (3b). Red powder, 80% yield, mp 220–222 °C. ^{1}H NMR (250 MHz, $CDCl_3$), δ, ppm: 1.25–2.20 (m, 11H), 2.75 (m, 2H, CH_2), 3.50 (d, 1H, H^3, $^3J = 11.0$ Hz), 6.66 (d, 1H, ArH, $^3J = 8.5$ Hz), 6.93 (d, 1H, H^7, $^3J = 10.0$ Hz), 7.10–7.40 (m, 9H, H^6, ArH). IR (KBr) ν, cm^{-1}: 2154 (SeCN), 1648 ($C^1{=}C^2$), 1621, 1607 (C=O, C=N), 1578, 1562 ($C = C_{quin}$). UV (EtOH) λ_{max}, nm: 461. $C_{30}H_{25}N_3OSe$ (522.50): calcd. C, 68.53; H, 4.65; N, 8.16. Found: C, 68.96; H, 4.82; N, 8.04. MS (ESI): 524 ($M + H^+$).

4,4a-Tetramethylene-8-oxo-1,3-diphenyl-3,4,4a,8-tetrahydropyrido[1,2-*a*] benzimidazole-9-yl selenocyanate (3c). Red powder, 87% yield, mp 242–244 °C. ^{1}H NMR (250 MHz, $CDCl_3$), δ, ppm: 1.45–2.20 (m, 9H), 3.83 (dd, 1H, H^3, $^3J = 9.0$ Hz, $^3J = 4.5$ Hz), 6.16 (d, 1H, H^2, $^3J = 4.5$ Hz), 6.91 (d, 1H, H^7, $^3J = 9.8$ Hz), 7.30 (d, 1H, H^6, *J*9.8 Hz), 7.15–7.45 (m, 10H, ArH). IR (KBr) ν, cm^{-1}: 2156 (SeCN), 1645 (C^1=C^2), 1620, 1608 (C=O, C=N), 1584, 1559 (C=$C_{quin.}$). UV (EtOH) λ_{max}, nm: 448. $C_{28}H_{23}N_3OSe$ (496.46): calcd. C, 67.50; H, 4.32; N, 8.58. Found: C, 67.74; H, 4.67; N, 8.46. MS (ESI): 498 ($M + H^+$).

8-Oxo-1,3,4a-triphenyl-3,4,4a,8-tetrahydropyrido[1,2-*a*]benzimidazole-9-yl thiocyanate (3d). Orange powde, 96% yield, mp 143–145 °C (dec.)$^{-1}$H NMR (250 MHz, $CDCl_3$), δ, ppm: 1.85 (dd, 1H, $H^4{}_{ax.}$, $^3J = 13.5$ Hz, $^2J = -13.2$ Hz), 3.55 (dd, 1H, $H^4{}_{eq.}$, $^3J = 6.6$ Hz, $^2J = -13.2$ Hz), 3.67 (kd, 1H, H^3, $^3J = 13.5$ Hz, $^3J = 6.6$ Hz, $^3J = 3.4$ Hz), 6.08 (d, 1H, H^2, $^3J = 3.4$ Hz), 6.88 (d, 1H, H^7, $^3J = 10.0$ Hz), 7.20–7.60 (m, 16H, H^6, ArH). IR (KBr) ν, cm^{-1}: 2150 (SeCN), 1642 (C^1=C^2), 1624, 1604 (C=O, C=N), 1586, 1561 (C = $C_{qiun.}$). UV (EtOH) λ_{max}, nm: 455. $C_{30}H_{21}N_3OSe$ (518.47): calcd. C, 69.41; H, 3.87; N, 8.23. Found: C, 69.50; H, 4.08; N, 8.10. MS (ESI): 520 ($M + H^+$).

6,7-Benzo-1,2-(3,4-dihydronaphtho)-4,4a-tetramethylene-8-oxo-3,4,4a,8-tetrahydropyrido[1,2-*a*]benzimidazole-9-yl selenocyanate (3e). Orange powder, 90% yield, mp 234–236 °C. ^{1}H NMR (250 MHz, $CDCl_3$), δ, ppm: 1.25–2.40 (m, 11H), 2.75 (m, 2H, CH_2), 3.51 (d, 1H, H^3, $^3J = 9.5$ Hz), 6.71 (d, 1H, ArH, $^3J = 7.3$ Hz), 7.10–7.40 (m, 3H, ArH), 7.68 (td, 1H, ArH, $^3J = 7.6$ Hz, $^3J = 7.3$ Hz, $^4J = 1.7$ Hz), 7.73 (td, 1H, ArH, $^3J = 7.8$ Hz, $^3J = 7.3$ Hz, $^4J = 1.7$ Hz), 8.34 (dd, 1H, ArH, $^3J = 7.6$ Hz, $^4J = 1.7$ Hz), 8.37 (dd, 1H, ArH, $^3J = 7.8$ Hz, $^4J = 1.7$ Hz). IR (KBr) ν, cm^{-1}: 2153 (SeCN), 1654 (C^1=C^2), 1624, 1605 (C=O, C=N), 1581, 1562 (C=$C_{quin.}$). UV (EtOH) λ_{max}, nm: 440. $C_{34}H_{27}N_3OSe$ (572.56): calcd. C, 71.48; H, 4.92; N, 7.28. Found: C, 71.32; H, 4.75; N, 7.34. MS (ESI): 574 ($M + H^+$).

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