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A NOVEL SYNTHESIS OF 2,3-DIALKYLPYRIDINE DERIVATIVES FROM DIALKYL-*N*-SILYLIMINES AND 1,3-DIARYL-2-PROPEN-1-ONE OR (*E*)-1,1,1-TRIFLUORO-4-PHENYL-3-BUTEN-2-ONE

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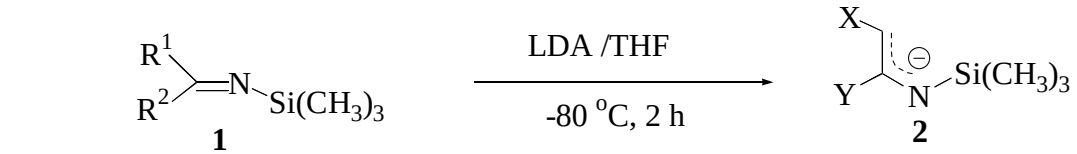
Abstract - A series of 2,3-dialkylpyridine derivatives (**4a-h)** have been prepared by the reaction of dialky-*N*-silylimines (**1a-c)** with 1,3-diaryl-2-propen-1-one (**3a-c**) or (*E*)-1,1,1-trifluoro-4-phenyl-3-buten-2-one (**3d**). Dialkyl-*N*-trimethylsilylimines (**1a-c)**, generated from alkylcyanides and MeLi or *n*-BuLi and trimethylchloro-silane, reacted with a slight excess amount of 1,3-diaryl-2-propen-1-one (**3a-c**) or (*E*)-1,1,1-trifluoro-4-phenyl-3-buten-2-one (**3d**) in the presence of LDA in dry tetrahydrofuran to afford the corresponding 2,3-dialkylpyridine derivatives (**4a-h)** in 62-86 % yields, respectively.

The pyridine nucleus is a major component of a variety of natural products and drugs.[1] Up to now, numerous synthetic sources of the pyridines ring have been reviewed. [2-4] On the other hand, the ability of *N*-trimethylsilylimines to undergo nucleophilic addition reactions is now well established and has been used in the synthesis of nitrogen-containing molecules such as β-lactams, imidazoles and aziridines.[5, 6] Recently we have developed an efficient method for the synthesis of 2,3,4,6-tetrasubstituted pyridine derivatives from *N*-silyl-1-azaallyl anions[7-9] with 1,3-diphenyl-2-propen-1-one, [10] trifluoroacetylketene diethyl ketal or (*E*)-1,1,1-trifluoro-4-phenyl-3-buten-2-one.[11] The *N*-silyl-1-azaallyl anion is an ambident nucleophile possessing nitrogen and carbon atoms as a reaction center, and can be utilized as a versatile building block for the synthesis of *N*-heterocyclic compounds.[12-14] Up to now, it was the major limitation of this approach that only the aromatic group can be introduced to the 2-position of the prepared

pyridine derivatives. Therefore, we propose now a convenient method for synthesizing 2,3-dialkyl-pyridine derivatives by the reaction of dialkyl-*N*-trimethylsilylimines (**1a-c**) with 1,3-diaryl-2-propen-1-one (**3a-c**) or (*E*)-1,1,1-trifluoro-4-phenyl-3-buten-2-one **(3d**).

N-Trimethylsilyl-2-heptanimine (**1a**), *N*-trimethylsilyl-4-octanimine **(1b**) and *N*-trimethylsilyl-5-nonan-imine (**1c**) were prepared by the literature methods.[15] A mixture of 2-pentyl-*N*-trimethylsilyl-1-azaallyl anion (**2a**) and 3-butyl-2-methyl-*N*-trimethylsilyl-1-azaallyl anion (**2b**) was generated at -80 ^{o}C by adding THF solution of **1a** to a slight excess of lithium diisopropylamide (LDA). This mixture was treated with a slight excess of 1,3-diphenyl-2-propen-1-one (**3a**) to give a mixture of 2-pentyl-4,6-diphenylpyridine (**4a**) and 3-butyl-2-methyl-4,6-diphenylpyridine (**4b**) in 44, 18% yields under the optimized reaction conditions, as shown in Scheme 1 and EXPERIMENTAL. Similarly, the reaction of **1b** with **3a** also afforded a mixture of 2-butyl-3-ethyl-4,6-diphenylpyridine (**4c**) and 4,6-diphenyl-2,3-dipropylpyridine (**4d**) in 48, 35% yields, respectively. However, *N*-silylimine (**1c**) reacted with **3a-c** to give the corresponding pyridine derivatives (**4e-g**) in 82, 80, 76% yields as single products, respectively. The

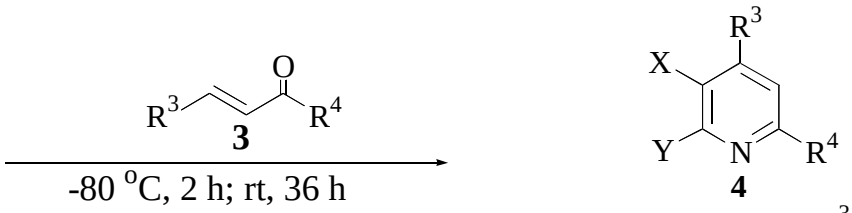


1

a, $R^1 = CH_3$, $R^2 = n\text{-}C_5H_{11}$
b, $R^1 = n\text{-}C_3H_7$, $R^2 = n\text{-}C_4H_9$
c, $R^1 = n\text{-}C_4H_9$, $R^2 = n\text{-}C_4H_9$

2

a, X = H, Y = n-C_5H_{11}
b, X = n-C_4H_9, Y = CH_3
c, X = C_2H_5, Y = n-C_4H_9
d, X = n-C_3H_7, Y = n-C_3H_7
e, X = n-C_3H_7, Y = n-C_4H_9



3

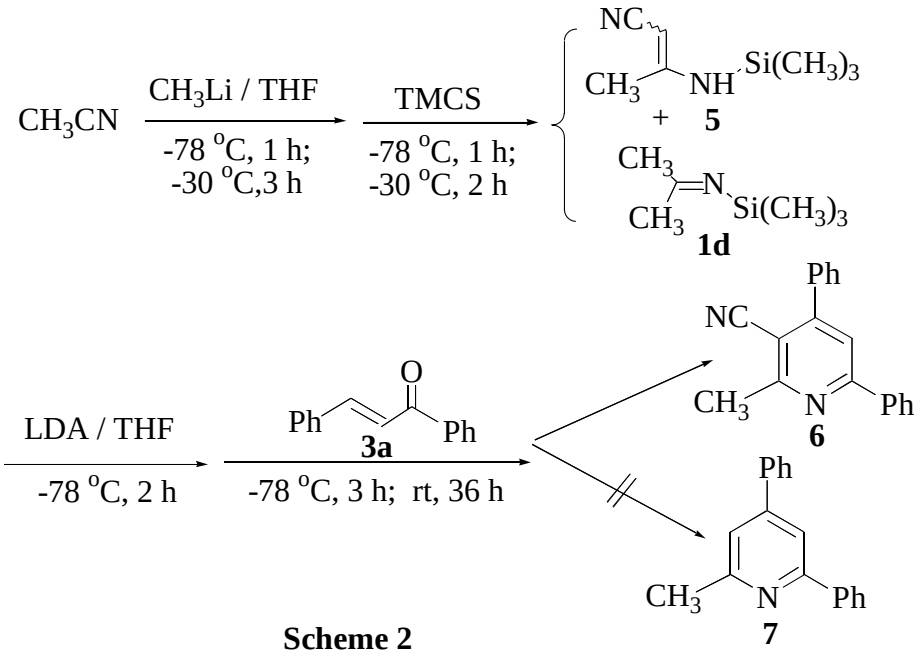
a, $R^3 = C_6H_5$, $R^4 = C_6H_5$
b, R^3 = 2-CH_3-C_6H_4, $R^4 = C_6H_5$
c, $R^3 = C_6H_5$, R^4 = 2-CH_3-C_6H_4
d, $R^3 = C_6H_5$, $R^4 = CF_3$

4

a, X = H, Y = n-C_5H_{11}, $R^3 = C_6H_5$, $R^4 = C_6H_5$
b, X = n-C_4H_9, Y = CH_3, $R^3 = C_6H_5$, $R^4 = C_6H_5$
c, X = C_2H_5, Y = n-C_4H_9, $R^3 = C_6H_5$, $R^4 = C_6H_5$
d, X = n-C_3H_7, Y = n-C_3H_7, $R^3 = C_6H_5$, $R^4 = C_6H_5$
e, X = n-C_3H_7, Y = n-C_4H_9, $R^3 = C_6H_5$, $R^4 = C_6H_5$
f, X = n-C_3H_7, Y = n-C_4H_9, R^3 = 2-CH_3-C_6H_4, $R^4 = C_6H_5$
g, X = n-C_3H_7, Y = n-C_4H_9, $R^3 = C_6H_5$, R^4 = 2-CH_3-C_6H_4
h, X = n-C_3H_7, Y = n-C_4H_9, $R^3 = C_6H_5$, $R^4 = CF_3$

Scheme 1

reaction of **1c** and (*E*)-1,1,1-trifluoro-4-phenyl-3-buten-2-one (**3d**) [16] afforded 2-butyl-3-propyl-4-phenyl-6-(trifluoromethyl)pyridine (**4h**) in 86% yield. When *N*-trimethylsilyl-2-propanimine (**1d**) was tried to



Scheme 2

prepare from methyllithium and acetonitrile, all attempts to isolate **1d** failed. The reaction of this mixture with **3a**, gave not the expected pyridine derivative (**7**) but 3-cyano-2-methyl-4,6-diphenylpyridine (**6**) in 36% yield (Scheme 2). The pyridine (**6**) must have been formed from 1-cyano-2-(trimethylsilyl)amino-1-propene (**5**) or the corresponding desilylated enamine (1-cyano-2-amino-1-propene), which was generated by self-condensation of acetonitrile. In fact , The Michael addition of this enamine to **3a** gave pyridine derivative **6**. [17] In addition, even propionitrile causes the self-condensation reaction in the presense of LDA. [8] Butyronitrile, however, did not give the self-condensation product when **1b** was prepared in this solvent. It is considered that the self-condensation of butyronitrile is sterically hindered by the ethyl group of the carbanion.

The structures of **4** were established by their spectral analyses. For example, the MS of **4h** showed *m/z* 321 (M^+), and the IR spectrum suggested the presence of a C-F functional group (1400-1130 cm^{-1}), but no carbonyl group. In the ^1H NMR spectra, four triplet signals and two multiplet signals at δ 0.67, 0.84, 1.26, 1.66, 2.46, 2.76 are assignable to the propyl and butyl group; a singlet signal at δ 7.19 is assignable to 5-H of the pyridine nucleus; the multiplet signal at 7.11-7.31 is assignable to the phenyl group.

EXPERIMENTAL

IR spectra were recorded on a JOEL JIR-5300 spectrophotometer. ^1H and ^{13}C NMR spectra were

obtained on a Bruker DPX-300 or JEOL AL-300 spectrometer in $CDCl_3$ solution using tetramethylsilane (Me_4Si) as an internal standard, ^{19}F NMR spectra were obtained on the same apparatus using fluoro-trichloromethane ($CFCl_3$) as an internal standard. *J* values are given in Hz. MS were obtained with a Shimazu GC/MS-QP2000A mass spectrometer at 70 eV. High-resolution MS were obtained on a JOEL JMS-700 mass spectrometer by a FAB ionization mode.

(*E*)-1,1,1-Trifluoro-4-phenyl-3-buten-2-one[16] was prepared in a literature method. Acetonitrile, butyronitrile, valeronitrile, and capronitrile were used after distillation of commercial products, and tetrahydrofuran was distilled from Na-benzophenone ketyl before use.

Synthesis of Pyridines 4a-h; General procedure.

Synthesis of the pyridine (**4h)** is representative.

2-Butyl-3-propyl-4-phenyl-6-(trifluoromethyl)pyridine (4h):

To a stirred solution of diisopropylamine (0.225 g, 2.22 mmol) in THF (10 mL) was added a solution of butyllithium (0.944 g of 15 % hexane solution, 2.21 mmol) at -80 ^oC, the mixture was stirred in atmosphere of nitrogen for 30 min. To this solution, **1c** (0.435 g, 2.04 mmol) in THF (5 mL) was added slowly and the reaction mixture was stirred for additional 2 h at -80 ^oC to give **2e**. Then a THF solution (5 mL) of **3c** (0.442 g, 2.21 mmol) was added dropwise to the solution of **2e**, and the mixture was stirred for 2 h at -80 ^oC and then for 36 h at rt. The reaction mixture was treated with a solution of cupric acetate (1.01 g, 5.02 mmol) in acetic acid (5 mL) for 1 h at rt, and finally neutralized by $NaHCO_3$ after cooling to 0 ^oC, then extracted with ether. The combined extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, then was purified by column chromatography on silica gel with CH_2Cl_2/hexane elution to give **4h** (0.556 g, 86%) as colorless oil. IR υ_{max}(liq. film) 3060, 2954, 1587, 1542, 1429, 1346, 1270,1136, 760, 694 cm^{-1}; ^1H NMR (300.13 MHz; $CDCl_3$; Me_4Si) 0.67 [3H, t, *J* 7.2, $(CH_2)_3C\underline{H}_3$], 0.84 [3H, t, *J* 7.2, $(CH_2)_2C\underline{H}_3$], 1.26-1.42 [4H, m, $CH_2(C\underline{H}_2)_2CH_3$], 1.66-1.71 (2H, m, $CH_2C\underline{H}_2CH_3$), 2.46 [2H, t, *J* 7.9, $C\underline{H}_2CH_2CH_3$], 2.76 [2H, t, *J* 7.9, $C\underline{H}_2(CH_2)_2CH_3$], 7.11-7.14 (2H, m, Ph-H), 7.18 (1H, s, Py-H), 7.26-7.31 (3H, m, Ph-H); ^{13}C NMR (75.45 MHz; $CDCl_3$; Me_4Si) 13.97, 14.28, 22.88, 23.93, 30.92, 31.74, 34.81, 119.04, 120.04, 123.67, 127.07, 127.38, 127.96, 128.29, 128.57, 128.83, 129.04, 136.48, 139.33, 145.31, 151.12, 162.09; δ_F(282.38 MHz; $CDCl_3$; $CFCl_3$) -68.00 (s, CF_3); MS *m/z* 321 (M^+, 88) and 252 (100); HRMS calcd for M+H ($C_{19}H_{23}NF_3$): 322.1789, found 322.1797.

2-Pentyl-4,6-diphenylpyridine (4a): (0.265 g, 44%) as colorless oil. IR υ_{max} (liq. film) 3056, 2958,

1560, 1540, 1480, 1436, 760, 694 cm^{-1}; ^{1}H NMR (300.13 MHz; $CDCl_3$; Me_4Si) 0.88 [3H, t, *J* 7.2, $(CH_2)_4C\underline{H}_3$], 1.27-1.41 [6H, m, $CH_2(C\underline{H}_2)_3CH_3$], 2.58 [2H, *J* 7.9, $C\underline{H}_2(CH_2)_3CH_3$], 7.28-7.48 (10H, m, Ph-H and Py-H), 8.03-8.06 (2H, m, Ph-H); ^{13}C NMR (75.45 MHz; $CDCl_3$; Me_4Si) 13.98, 21.90, 22.88, 30.90, 34.68, 120.24, 123.86, 127.89, 128.38, 128.60, 128.98, 129.44, 131.48, 133.90, 136.40, 140.34, 145.31, 152.12; MS *m/z* 302 (M+1, 100), 301 (M^+, 18), 258 (32); HRMS calcd for M+H ($C_{22}H_{24}N$): 302.1908, found 302.1917.

3-Butyl-2-methyl-4,6-diphenylpyridine (4b): (0.109 g, 18%) as colorless oil. IR υ_{max}(liq. film) 3048, 2950, 1557, 1543, 1480, 1440, 764, 694 cm^{-1}; ^{1}H NMR (300.13 MHz; $CDCl_3$; Me_4Si) 0.77 [3H, t, *J* 7.2, $(CH_2)_3C\underline{H}_3$], 1.18-1.47 [4H, m, $CH_2(C\underline{H}_2)_2CH_3$], 2.52 [2H, *J* 7.9, $C\underline{H}_2(CH_2)_2CH_3$], 2.72 (3H, s, CH_3), 7.19-7.49 (9H, m, Ph-H and Py-H), 8.01-8.03 (2H, m, Ph-H); ^{13}C NMR (75.45 MHz; $CDCl_3$; Me_4Si) 13.90, 22.88, 24.10, 30.09, 32.68, 121.24, 123.68, 127.98, 128.38, 128.66, 128.88, 129.34, 131.38, 133.88, 136.60, 141.34, 145.31, 152.42; MS *m/z* 302 (M+1, 48), 301 (M^+, 22) and 258 (16); HRMS calcd for M+H ($C_{22}H_{24}N$): 302.1908, found 302.1895.

2-Butyl-3-ethyl-4,6-diphenylpyridine (4c): (0.303 g, 48%) as colorless oil. IR υ_{max}(liq. film) 3059, 2954, 1568, 1540, 1478, 1449, 760, 690 cm^{-1}; ^{1}H NMR (300.13 MHz; $CDCl_3$; Me_4Si) 0.75 [3H, t, *J* 7.2, $(CH_2)_3C\underline{H}_3$], 1.03 (3H, t, *J* 7.0, $CH_2C\underline{H}_3$), 1.37-1.87 [4H, m, $CH_2(C\underline{H}_2)_2CH_3$], 2.37 (2H, q, $C\underline{H}_2CH_3$), 2.79 (2H, t, *J* 7.9, $C\underline{H}_2(CH_2)_2CH_3$], 7.28-7.53 (9H, m, Ph-H and Py-H), 7.93-7.96 (2H, m, Ph-H); ^{13}C NMR (75.45 MHz; $CDCl_3$; Me_4Si) 13.90, 14.40, 22.68, 23.8, 30.88, 34.80, 122.24, 123.38, 127.66, 128.33, 128.67, 129.64, 131.78, 134.28, 136.60, 141.84, 143.87, 146.87, 152.24; MS *m/z* 316 (M+1, 100), 315 (M^+, 28) and 286 (16); HRMS calcd for M+H ($C_{23}H_{26}N$): 316.2064, found 316.2070.

2,3-Dipropyl-4,6-diphenylpyridine (4d): (0.221 g, 35%) as colorless oil. IR υ_{max}(liq. film) 3060, 2959, 2930, 1588, 1540, 1467, 1428, 764, 700 cm^{-1}; ^{1}H NMR (300.13 MHz; $CDCl_3$; Me_4Si) 0.81-1.13 (6H, m, $CH_2CH_2C\underline{H}_3$), 1.42-1.93 (4H, m, $CH_2C\underline{H}_2CH_3$), 2.41-2.92 (4H, m, $C\underline{H}_2CH_2CH_3$), 7.29-7.58 (9H, m, Ph-H and Py-H), 7.99-8.02 (2H, m, Ph-H); ^{13}CNMR(75.45 MHz; $CDCl_3$; Me_4Si) 13.34, 13.98, 21.40, 22.87, 32.19, 33.41, 122.18, 123.38, 127.89, 128.38, 128.89, 129.34, 131.56, 134.08, 135.90, 140.84, 143.87, 145.87, 152.29; MS *m/z* 316 (M+1, 100), 315 (M^+, 20) and 286(14); HRMS calcd for M+H ($C_{23}H_{26}N$): 316.2064, found 316.2055.

2-Butyl-3-propyl-4,6-diphenylpyridine (4e): (0.540 g, 82%) as colorless oil. IR υ_{max}(liq. film) 3058, 2956, 1591, 1495, 1456, 1429, 765, 702 cm^{-1}; ^{1}H NMR (300.13 MHz; $CDCl_3$; Me_4Si) 0.82 [3H, t, *J* 7.2, $(CH_2)_3C\underline{H}_3$], 1.02 [3H, t, *J* 7.2, $(CH_2)_2C\underline{H}_3$], 1.44-1.55 [4H, m, $CH_2(C\underline{H}_2)_2CH_3$], 1.87-2.19 (2H, m, $CH_2C\underline{H}_2CH_3$), 2.56 [2H, t, *J* 7.9, $C\underline{H}_2CH_2CH_3$], 2.93 [2H, t, *J* 7.9, $C\underline{H}_2(CH_2)_2CH_3$], 7.35 (1H, s, Py-H), 7.39-7.50 (8H, m, Ph-H), 8.03-8.06 (2H, m, Ph-H); ^{13}C NMR (75.45 MHz; $CDCl_3$; Me_4Si) 14.13, 14.47, 22.94, 24.05, 30.90, 32.19, 34.51, 119.10, 127.98, 128.28, 128.63, 128.98, 129.33, 131.32, 134.09, 136.61, 140.73, 150.60, 153.24, 160.72; MS *m/z* 330 (M+1, 100), 329 (M^+, 24) and 286 (23); HRMS calcd for M+H ($C_{24}H_{28}N$): 330.2222, found 330.2223.

2-Butyl-3-propyl-4-(2-tolyl)-6-phenylpyridine (4f): (0.550 g, 80%) as colorless oil. IR υ_{max}(liq. film) 3060, 2946, 2956, 1598, 1560, 1478, 1429, 765, 698 cm^{-1}; ^{1}H NMR (300.13 MHz; $CDCl_3$; Me_4Si) 0.88 [3H, t, *J* 7.2, $(CH_2)_3C\underline{H}_3$], 1.13 [3H, t, *J* 7.2, $(CH_2)_2C\underline{H}_3$], 1.43-1.51 [4H, m, $CH_2(C\underline{H}_2)_2CH_3$], 1.61-1.68 (2H, m, $CH_2C\underline{H}_2CH_3$), 2.20 (3H, s, CH_3), 2.62 [2H, t, *J* 7.9, $C\underline{H}_2CH_2CH_3$], 2.99 [2H, t, *J* 7.9, $C\underline{H}_2(CH_2)_2CH_3$], 7.13-7.49 (8H, m, Ph-H and Py-H), 8.11-8.14 (2H, m, Ph-H); ^{13}C NMR (75.45 MHz; $CDCl_3$; Me_4Si) 14.13, 14.45, 19.95, 22.94, 23.67, 30.97, 31.84, 34.94, 118.69, 125.44, 126.64, 127.65, 128.32, 128.79, 129.94, 131.99, 135.01, 139.97, 150.09, 153.32, 160.76; MS *m/z* 344 (M+1, 100), 343 (M^+, 18) and 288 (20); HRMS calcd for M+H ($C_{25}H_{30}N$): 344.2382, found 344.2393.

2-Butyl-3-propyl-4-phenyl-6-(2-tolyl)pyridine(4g): (0.522 g, 76%) as colorless oil. IR υ_{max}(liq. film) 3060, 2948, 2959, 1589, 1560, 1478, 1429, 765, 700 cm^{-1}; ^{1}H NMR (300.13 MHz; $CDCl_3$; Me_4Si) 0.84 [3H, t, *J* 7.2, $(CH_2)_3C\underline{H}_3$], 0.99 [3H, t, *J* 7.2, $(CH_2)_2C\underline{H}_3$], 1.43-1.52 [4H, m, $CH_2(C\underline{H}_2)_2CH_3$], 1.83-1.88 (2H, m, $CH_2C\underline{H}_2CH_3$), 2.46 (3H, s, CH_3), 2.59 [2H, t, *J* 7.9, $C\underline{H}_2CH_2CH_3$], 2.92 [2H, t, *J* 7.9, $C\underline{H}_2(CH_2)_2CH_3$], 7.11-7.82 (10H, m, Ph-H and Py-H); ^{13}C NMR (75.45 MHz; $CDCl_3$; Me_4Si) 14.19, 14.45, 20.86, 22.78, 24.12, 30.95, 32.19, 34.51, 121.37, 127.58, 128.11, 128.69, 129.33, 129.78, 131.40, 134.11, 136.66, 141.44, 144.56, 152.57, 159.88; MS *m/z* 345 (M+2, 100), 344 (M+1, 15), 343 (M^+, 22) and 301 (15); HRMS calcd for M+H ($C_{25}H_{30}N$): 344.2382, found 344.2392.

3-Cyano-2-methyl-4,6-diphenylpyridine (6): (0.194 g, 36%) as colorless needles. mp 119.8-120.6 ^{o}C (EtOH) (lit., [17] mp 117.5-118 ^{o}C); IR υ_{max} 3032, 2956, 2208, 1598, 1496, 1218, 1001, 753, 700 cm^{-1}; ^{1}H NMR (300.13 MHz; $CDCl_3$; Me_4Si) 2.78 (3H, s, CH_3), 7.21-7.56 (9H, m, Ph-H and Py-H), 7.91-7.93

(2H, m, Ph-H; *m/z* 271 (M+1, 100), 270 (M^+; 36).

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