Supporting Information

Ir-Catalyzed Highly Selective Addition of Pyridyl C-H Bonds to Aldehydes Promoted by Triethylsilane

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General Experimental Information

Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with teflon srew cap using standard Schlenk technique. Similarly sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator (water bath temperature 25-40 ℃) with a desktop vacuum pump. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light. Purification of products was accomplished by flash chromatography on silica gel 200-300 mesh.

All GC analyses were conducted with an Agilent 6820 GC equipped with an HP-5 column (25 m x 0.20 mm ID x 0.33 μm film) and an FID detector. The temperature for each run was held at 80 ℃ for 2 min, ramped from 80 ℃ to 280 ℃ at 30 ℃/min, and held at 280 ℃ for 10 min. GC calibration curves for quantifying the amount the C-H silylation product **4** versus dodecane internal standard (Acros, anhydrous) were conducted in triplicate using three calibration points.

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) was registered on Bruker spectrometers with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts are referenced to residual solvent peaks ($CHCl_3$ in $CDCl_3$: 7.26 ppm for ^{1}H, 77.00 ppm for ^{13}C). Data for ^{1}H-NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constant (Hz), and integration.

Infrared spectra were recorded on an AVATAR 330 Fourier transform spectrometer (FT-IR) with an OMNI sampler and are reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI) in the State-authorized Analytical Center in Peking University.

Anhydrous solvents including THF, toluene, benzene and DMF were degassed with nitrogen and passed through a column of activated alumina in a solvent purification system from MBraun.

$Ir_4(CO)_{12}$ and triethylsilane were purchased from Alfa Aesar. Phenanthroline, neocuproine, bathophenanthroline and 4,4'-di-*tert*-butyl-2,2'-bipyridine were purchased from Aldrich without further purification. All the arylaldehydes were commercially available and were distilled prior to use (except **2d**, **2j**, **2k**).

Experimental Procedures and Characterization Data

Synthesis of Substrates:

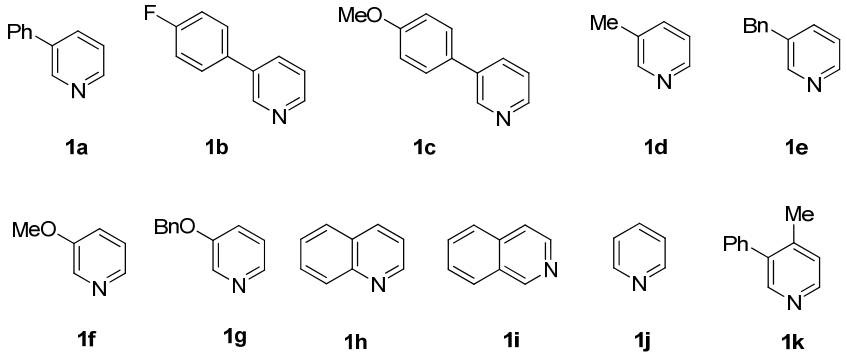
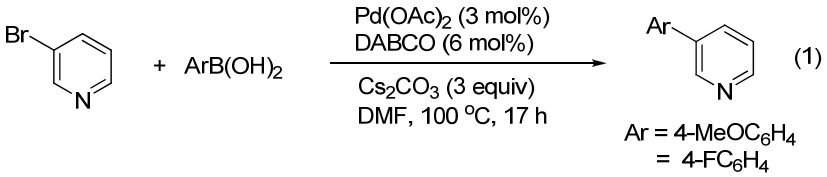
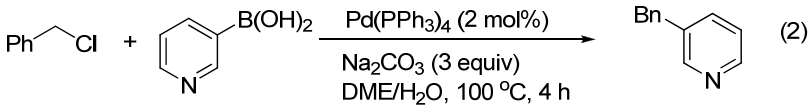
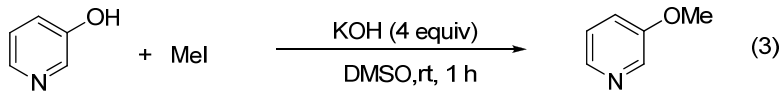


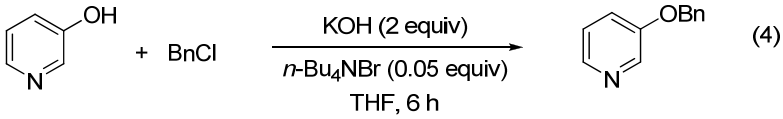
Figure S1. Substrates studied in this reaction.

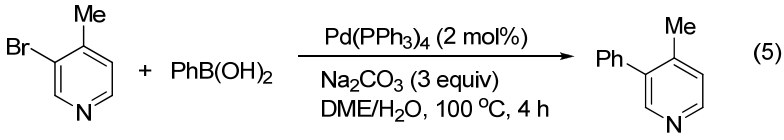
1a (Alfa Aesar), **1d** (Alfa Aesar), **1h** (Acros), **1i** (Acros), **1j** (Acros) are commercially available and are used without further purification. **1b**[1], **1c**[1], **1e**[2], **1f**[3], **1g**[4], **1k**[5] are prepared according to the literature procedure through the following reactions. All these materials are known compounds.











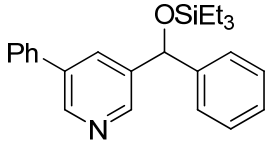
General procedure for the catalytic addition of pyridine derivatives to

arylaldehydes:

To an oven-dried 25 mL Schlenk tube was added $Ir_4(CO)_{12}$ (5.5 mg, 0.005 mmol) and phenanthroline (1.8 mg, 0.01 mmol). The tube was evacuated and refilled with nitrogen. Then 3-phenylpyridine (38.8 mg, 0.25 mmol), benzaldehyde (79.5 mg, 0.75 mmol) and triethylsilane (87.0 mg, 0.75 mmol) were successively added via syringes under a positive stream of dry nitrogen. After the addition of 1 mL of benzene, the tube was tightly sealed and heated to 135 ℃ in an oil bath for 12 h. After cooling to room temperature, the resulting mixture was directly purified by flash chromatography on silica gel eluting with ethyl acetate and petroleum ether.

Charaterization of products

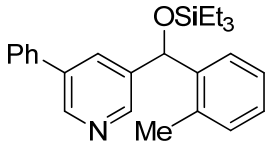
3-phenyl-5-(phenyl(triethylsilyloxy)methyl)pyridine (3a)



Following the general procedure with 3-phenylpyridine (38.8 mg, 0.25 mmol), benzaldehyde (79.5 mg, 0.75 mmol). Flash chromatography eluting with 1:12 ethyl acetate: petroleum ether gave 68.5 mg of product in 73% yield as a gray oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.705 (d, 1 H, *J* = 2.0 Hz), 8.603 (d, 1 H, *J* = 1.6 Hz), 7.856 (t, 1 H, *J* = 2.0 Hz), 7.554-7.526 (m, 2 H), 7.455 (t, 2 H, *J* = 7.2 Hz), 7.403-7.335 (m, 3 H), 7.317 (t, 2 H, *J* = 7.2 Hz), 7.251-7.219 (m, 1 H), 5.861 (s, 1 H), 0.899 (t, 9 H, *J* = 8.0 Hz), 0.599 (q, 6 H, *J* = 8.0 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 146.956, 146.708, 144.014, 140.499, 137.829, 136.157, 132.106, 128.938, 128.386, 127.956, 127.420, 127.094, 126.200, 74.377, 6.678, 4.776. **HRMS** (ESI) ($C_{24}H_{30}NOSi$): Anal. Calcd. ($M+H^+$) 376.20912, Found: 376.20943. **IR** (cm^{-1}): ν 2954, 2875, 1454, 1069.

3-phenyl-5-(o-tolyl(triethylsilyloxy)methyl)pyridine (3b)

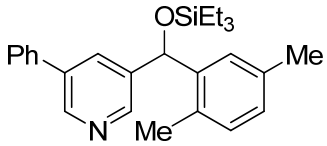


Following the general procedure with 3-phenylpyridine (38.8 mg, 0.25 mmol), 2-methylbenzaldehyde (90.5 mg, 0.75 mmol). Flash chromatography eluting with 1:12 ethyl acetate: petroleum ether gave 76.3 mg of product in 78% yield as a gray oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.697 (d, 1 H, *J* = 2.2 Hz), 8.558 (d, 1 H, *J* = 1.9 Hz), 7.786 (t, 1 H, *J* = 2.0 Hz), 7.631 (d, 1 H, *J* = 7.2 Hz), 7.529-7.506 (m, 2 H), 7.437 (t, 2 H, *J* = 7.2 Hz), 7.383-7.361 (m, 1 H), 7.243 (t, 1 H, *J* = 7.2 Hz), 7.177 (dt, 1 H, *J* = 1.2, 7.2 Hz), 7.094 (d, 1 H, *J* = 7.2 Hz), 6.004 (s, 1 H), 2.253 (s, 3 H), 0.895 (t, 9 H, *J* = 8.0 Hz), 0.599 (q, 6 H, *J* = 8.0 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 147.241, 146.814, 141.458, 139.445, 137.867, 136.041, 134.460, 132.493, 130.658, 128.941, 127.933, 127.509, 127.091, 126.972, 126.072, 72.145, 19.484, 6.668, 4.791. **HRMS** (ESI) ($C_{25}H_{33}NOSi$):

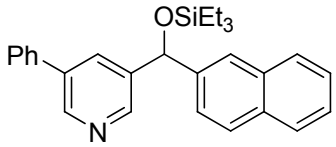
Anal. Calcd. (M+H$^+$) 390.22477, Found: 390.22444. **IR** (cm^{-1}): ν 2954, 2875, 1458, 1113, 1054.

3-((2,5-dimethylphenyl)(triethylsilyloxy)methyl)-5-phenylpyridine (3c)



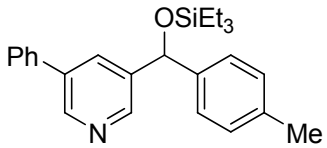
Following the general procedure with 3-phenylpyridine (38.8 mg, 0.25 mmol), 2,5-dimethylbenzaldehyde (100.5 mg, 0.75 mmol). Flash chromatography eluting with 1:12 ethyl acetate: petroleum ether gave 77.7 mg of product in 77% yield as a gray oil.
^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.690 (d, 1 H, *J* = 2.2 Hz), 8.550 (d, 1 H, *J* = 2.0 Hz), 7.789 (t, 1 H, *J* = 2.0 Hz), 7.537-7.514 (m, 2 H), 7.442 (dt, 2 H, *J* = 1.2, 7.2 Hz), 7.407-7.348 (m, 2 H), 6.981 (s, 2 H), 5.975 (s, 1 H), 2.333 (s, 3 H), 2.217 (s, 3 H), 0.901 (t, 9 H, *J* = 8.0 Hz), 0.596 (q, 6 H, *J* = 8.0 Hz). **^{13}C NMR (CDCl$_3$, 100 MHz)**: δ 147.245, 126.739, 141.184, 139.627, 137.958, 136.016, 135.432, 132.432, 131.272, 130.537, 128.942, 128.190, 127.916, 127.687, 127.129, 72.069, 21.097, 19.044, 6.678, 4.810. **HRMS** (ESI) (C$_{26}$H$_{34}$NOSi): Anal. Calcd. (M+H$^+$) 404.24042, Found: 404.24018. **IR** (cm^{-1}): ν 2954, 2875, 1413, 1115, 1003.

3-(naphthalen-2-yl(triethylsilyloxy)methyl)-5-phenylpyridine (3d)



Following the general procedure with 3-phenylpyridine (38.8 mg, 0.25 mmol), 2-naphthylaldehyde (117.0 mg, 0.75 mmol). Flash chromatography eluting with 1:12 ethyl acetate: petroleum ether gave 76.8 mg of product in 72% yield as a gray oil.
^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.718 (d, 1 H, *J* = 1.9 Hz), 8.686 (d, 1 H, *J* = 1.8 Hz), 7.905 (s, 2 H), 7.838 (d, 1 H, *J* = 7.6 Hz), 7.778 (d, 2 H, *J* = 8.4 Hz), 7.521 (d, 2 H, *J* = 7.2 Hz), 7.479-7.397 (m, 5 H), 7.360-7.324 (m, 1 H), 6.034 (s, 1 H), 0.915 (t, 9 H, *J* = 8.0 Hz), 0.629 (q, 6 H, *J* = 8.0 Hz). **^{13}C NMR (CDCl$_3$, 100 MHz)**: δ 147.075, 146.794, 141.403, 140.307, 137.793, 136.216, 133.145, 132.827, 132.205, 128.929, 128.369, 127.964, 127.645, 127.108, 126.124, 125.892, 124.723, 124.433, 74.564, 6.727, 4.820. **HRMS** (ESI) (C$_{28}$H$_{32}$NOSi): Anal. Calcd. (M+H$^+$) 426.22477, Found: 426.22415. **IR** (cm^{-1}): ν 2955, 2874, 1441, 1122, 1004.

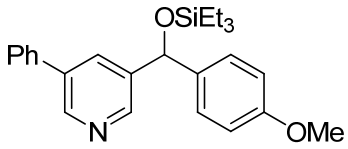
3-phenyl-5-(p-tolyl(triethylsilyloxy)methyl)pyridine (3e)



Following the general procedure with 3-phenylpyridine (38.8 mg, 0.25 mmol),

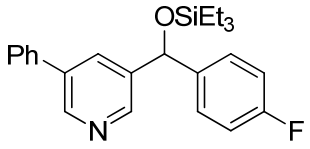
4-methylbenzaldehyde (90.0 mg, 0.75 mmol). Flash chromatography eluting with 1:12 ethyl acetate: petroleum ether gave 74.5 mg of product in 76% yield as a gray oil.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.697 (d, 1 H, *J* = 1.9 Hz), 8.601 (d, 1 H, *J* = 1.8 Hz), 7.853 (s, 1 H), 7.551-7.530 (m, 2 H), 7.463-7.426 (m, 2 H), 7.390-7.351 (m, 1 H), 7.276 (d, 2 H, *J* = 8.0 Hz), 7.128 (d, 2 H, *J* = 8.0 Hz), 5.836 (s, 1 H), 2.307 (s, 3 H), 0.900 (t, 9 H, *J* = 8.0 Hz), 0.596 (q, 6 H, *J* = 8.0 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 146.902, 146.718, 141.151, 140.714, 137.922, 137.057, 136.127, 132.069, 129.078, 128.943, 127.939, 127.127, 126.158, 74.257, 21.044, 6.717, 4.806. **HRMS** (ESI) ($C_{25}H_{31}NOSi$): Anal. Calcd. ($M+H^+$) 390.22477, Found: 390.22467. **IR** (cm^{-1}): ν 2955, 2875, 1439, 1081, 1004.

3-((4-methoxyphenyl)(triethylsilyloxy)methyl)-5-phenylpyridine (3f)



Following the general procedure with 3-phenylpyridine (38.8 mg, 0.25 mmol), 4-methoxybenzaldehyde (102.0 mg, 0.75 mmol). Flash chromatography eluting with 1:8 ethyl acetate: petroleum ether gave 57.2 mg of product in 57% yield as a gray oil.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.698 (d, 1 H, *J* = 2.2 Hz), 8.588 (d, 1 H, *J* = 1.9 Hz), 7.844 (t, 1 H, *J* = 2.0 Hz), 7.543 (t, 2 H, *J* = 7.2 Hz), 7.450 (t, 2 H, *J* = 7.2 Hz), 7.392-7.356 (m, 1 H), 7.296 (d, 2 H, *J* = 8.8 Hz), 6.854 (d, 2 H, *J* = 8.0 Hz), 5.828 (s, 1 H), 3.773 (s, 3 H), 0.901 (t, 9 H, *J* = 8.0 Hz), 0.594 (q, 6 H, *J* = 8.0 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 158.907, 146.845, 146.703, 140.764, 137.909, 136.323, 136.100, 132.045, 128.955, 127.952, 127.523, 127.122, 113.764, 73.992, 55.164, 6.721, 4.806. **HRMS** (ESI) ($C_{25}H_{31}NO_2Si$): Anal. Calcd. ($M+H^+$) 406.21968, Found: 406.21995. **IR** (cm^{-1}): ν 2954, 2875, 1510, 1246, 1055.

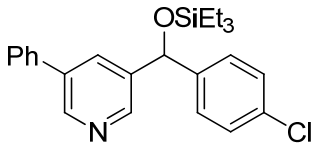
3-((4-fluorophenyl)(triethylsilyloxy)methyl)-5-phenylpyridine (3g)



Following the general procedure with 3-phenylpyridine (38.8 mg, 0.25 mmol), 4-fluorobenzaldehyde (93.0 mg, 0.75 mmol). Flash chromatography eluting with 1:8 ethyl acetate: petroleum ether gave 72.6 mg of product in 74% yield as a gray oil.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.722 (d, 1 H, *J* = 2.2 Hz), 8.588 (d, 1 H, *J* = 2.0 Hz), 7.834 (t, 1 H, *J* = 2.1 Hz), 7.554-7.533 (m, 2 H), 7.503 (dt, 2 H, *J* = 1.2, 6.0 Hz), 7.399-7.346 (m, 3 H), 7.003 (dt, 2 H, *J* = 2.0, 7.2 Hz), 5.852 (s, 1 H), 0.899 (t, 9 H, *J* = 8.0 Hz), 0.600 (q, 6 H, *J* = 8.0 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 162.048 (d, J_0 = 245 Hz), 147.124, 146.637, 140.278, 139.915 (d, J_3 = 3 Hz), 137.744, 136.235, 132.013, 128.983, 128.037, 127.845 (d, J_2 = 22 Hz), 128.096, 115.273 (d, J_1 = 22 Hz), 73.757, 6.662, 4.757. **HRMS** (ESI) ($C_{24}H_{28}NFOSi$): Anal. Calcd. ($M+H^+$) 394.19970, Found:

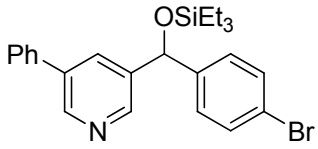
394.19939. **IR** (cm^{-1}): ν 2956, 2876, 1507, 1223, 1081.

3-((4-chlorophenyl)(triethylsilyloxy)methyl)-5-phenylpyridine (3h)



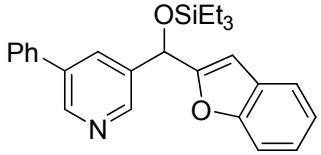
Following the general procedure with 3-phenylpyridine (38.8 mg, 0.25 mmol), 4-chlorobenzaldehyde (105.4 mg, 0.75 mmol). Flash chromatography eluting with 1:8 ethyl acetate: petroleum ether gave 63.3 mg of product in 62% yield as a gray oil.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.722 (d, 1 H, *J* = 2.2 Hz), 8.584 (d, 1 H, *J* = 2.0 Hz), 7.818 (t, 1 H, *J* = 2.0 Hz), 7.549-7.528 (m, 2 H), 7.455 (t, 2 H, *J* = 7.2 Hz), 7.400-7.248 (m, 5 H), 5.834 (s, 1 H), 0.898 (t, 9 H, *J* = 8.0 Hz), 0.600 (q, 6 H, *J* = 8.0 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 147.248, 146.597, 142.630, 140.039, 137.689, 136.308, 133.192, 132.039, 128.999, 128.603, 128.073, 127.514, 127.110, 73.754, 6.681, 4.756. **HRMS** (ESI) ($C_{24}H_{28}NClOSi$): Anal. Calcd. ($M+H^+$) 410.17015, Found: 410.16991. **IR** (cm^{-1}): ν 2955, 2875, 1489, 1106, 1013.

3-((4-bromophenyl)(triethylsilyloxy)methyl)-5-phenylpyridine (3i)



Following the general procedure with 3-phenylpyridine (38.8 mg, 0.25 mmol), 4-bromobenzaldehyde (138.7 mg, 0.75 mmol). Flash chromatography eluting with 1:8 ethyl acetate: petroleum ether gave 68.0 mg of product in 60% yield as a gray oil.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.721 (d, 1 H, *J* = 2.2 Hz), 8.583 (d, 1 H, *J* = 2.1 Hz), 7.814 (t, 1 H, *J* = 2.1 Hz), 7.547-7.518 (m, 2 H), 7.473-7.435 (m, 4 H), 7.400-7.363 (m, 1 H), 7.267 (d, 2 H, *J* = 2.4 Hz), 5.817 (s, 1 H), 0.897 (t, 9 H, *J* = 8.0 Hz), 0.599 (q, 6 H, *J* = 8.0 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 147.273, 146.585, 143.153, 139.961, 137.678, 136.320, 132.034, 131.551, 129.000, 128.078, 127.850, 127.112, 121.336, 73.800, 6.684, 4.758. **HRMS** (ESI) ($C_{24}H_{28}NBrOSi$): Anal. Calcd. ($M+H^+$) 454.11963, Found: 454.11896. **IR** (cm^{-1}): ν 2955, 2875, 1486, 1071.

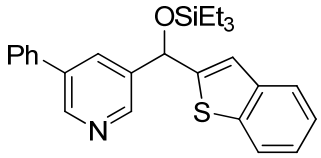
3-(benzofuran-2-yl(triethylsilyloxy)methyl)-5-phenylpyridine (3j)



Following the general procedure with 3-phenylpyridine (38.8 mg, 0.25 mmol), benzofuran-2-carbaldehyde (109.5 mg, 0.75 mmol). Flash chromatography eluting with 1:12 ethyl acetate: petroleum ether gave 56.8 mg of product in 55% yield as a gray oil.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.783 (d, 1 H, *J* = 2.4 Hz), 8.703 (d, 1 H, *J* = 2.0 Hz), 8.021 (t, 1 H, *J* = 2.0 Hz), 7.575 (d, 2 H, *J* = 4.0 Hz), 7.508 (dd, 1 H, *J* = 0.8, 8.0 Hz),

7.453 (t, 2 H, *J* = 8.0 Hz), 7.395 (t, 2 H, *J* = 8.0 Hz), 7.223 (dt, 1 H, *J* = 0.8, 7.2 Hz), 7.176 (dt, 1 H, *J* = 0.8, 7.2 Hz), 6.611 (s, 1 H), 5.999 (s, 1 H), 0.941 (t, 9 H, *J* = 8.0 Hz), 0.666 (q, 6 H, *J* = 8.0 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 158.550, 155.050, 147.687, 146.898, 137.635, 137.092, 136.292, 132.432, 129.007, 128.089, 127.934, 127.145, 124.196, 122.758, 121.066, 111.265, 103.492, 68.910, 6.660, 4.702. **HRMS** (ESI) ($C_{26}H_{29}NO_2Si$): Anal. Calcd. ($M+H^+$) 416.20403, Found: 416.20427. **IR** (cm^{-1}): ν 2954, 2875, 1453, 1254, 1005.

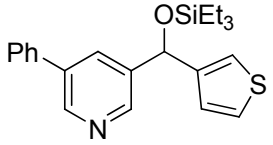
3-(benzo[b]thiophen-2-yl(triethylsilyloxy)methyl)-5-phenylpyridine (3k)



Following the general procedure with 3-phenylpyridine (38.8 mg, 0.25 mmol), benzo[b]thiophene-2-carbaldehyde (121 mg, 0.75 mmol). Flash chromatography eluting with 1:12 ethyl acetate: petroleum ether gave 51.1 mg of product in 54% yield as a gray oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.790 (d, 1 H, *J* = 2.4 Hz), 8.710 (d, 1 H, *J* = 1.6 Hz), 8.027 (t, 1 H, *J* = 2.0 Hz), 7.758 (dd, 1 H, *J* = 1.2, 6.8 Hz), 7.670 (dd, 1 H, *J* = 1.2, 6.8 Hz), 7.578-7.553 (m, 2 H), 7.450 (dt, 2 H, *J* = 1.2, 6.8 Hz), 7.398-7.377 (m, 1 H), 7.299-7.232 (m, 2 H), 7.104 (s, 1 H), 6.164 (s, 1 H), 0.945 (t, 9 H, *J* = 8.0 Hz), 0.660 (q, 6 H, *J* = 8.0 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 149.691, 147.636, 146.509, 139.729, 139.378, 139.282, 137.596, 126.373, 132.152, 129.002, 128.104, 127.136, 124.187, 124.115, 123.507, 122.357, 120.257, 71.277, 6.718, 4.773. **HRMS** (ESI) ($C_{26}H_{29}NOSSi$): Anal. Calcd. ($M+H^+$) 432.18119, Found: 432.18135. **IR** (cm^{-1}): ν 2954, 2874, 1457, 1126, 1005.

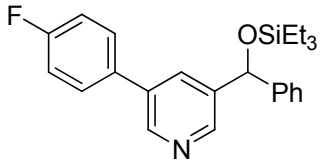
3-phenyl-5-(thiophen-3-yl(triethylsilyloxy)methyl)pyridine (3l)



Following the general procedure with 3-phenylpyridine (38.8 mg, 0.25 mmol), thiophene-2-carbaldehyde (84.0 mg, 0.75 mmol). Flash chromatography eluting with 1:12 ethyl acetate: petroleum ether gave 64.8 mg of product in 68% yield as a gray oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.738 (d, 1 H, *J* = 2.0 Hz), 8.606 (d, 1 H, *J* = 2.4 Hz), 7.884 (t, 1 H, *J* = 2.0 Hz), 7.555 (d, 2 H, *J* = 8.4 Hz), 7.451 (t, 1 H, *J* = 7.2 Hz), 7.393-7.355 (m, 1 H), 7.243-7.197 (m, 2 H), 6.968 (dd, 1 H, *J* = 1.2, 4.8 Hz), 5.943 (s, 1 H), 0.911 (t, 9 H, *J* = 8.0 Hz), 0.608 (q, 6 H, *J* = 8.0 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 147.106, 146.634, 145.503, 139.849, 137.731, 136.176, 132.130, 128.951, 127.990, 127.072, 126.198, 126.010, 121.128, 70.946, 6.674, 4.752. **HRMS** (ESI) ($C_{22}H_{27}NOSSi$): Anal. Calcd. ($M+H^+$) 382.16554, Found: 382.16534. **IR** (cm^{-1}): ν 2954, 2874, 1441, 1147, 1077.

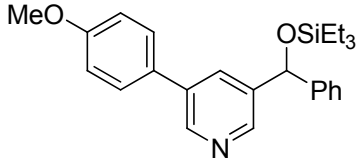
3-(4-fluorophenyl)-5-(phenyl(triethylsilyloxy)methyl)pyridine (3n)



Following the general procedure with 3-(4-fluorophenyl)pyridine (43.3 mg, 0.25 mmol), benzaldehyde (79.5 mg, 0.75 mmol). Flash chromatography eluting with 1:8 ethyl acetate: petroleum ether gave 66.8 mg of product in 68% yield as a gray oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.660 (d, 1 H, *J* = 2.2 Hz), 8.610 (d, 1 H, *J* = 1.9 Hz), 7.815 (t, 1 H, *J* = 2.0 Hz), 7.511-7.476 (m, 2 H), 7.396 (d, 2 H, *J* = 7.2 Hz), 7.318 (t, 2 H, *J* = 7.2 Hz), 7.255-7.218 (m, 1 H), 7.134 (dt, 1 H, *J* = 2.0, 7.2 Hz), 5.863 (s, 1 H), 0.899 (t, 9 H, *J* = 8.0 Hz), 0.601 (q, 6 H, *J* = 8.0 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 142.813 (d, J_0 = 246 Hz), 146.787, 146.743, 143.963, 140.568, 135.244, 133.950 (d, J_3 = 3 Hz), 131.907, 128.762 (d, J_2 = 8 Hz), 128.417, 127.471, 126.198, 115.772 (d, J_1 = 22 Hz), 74.329, 6.670, 4.772. **HRMS** (ESI) ($C_{24}H_{28}NOSi$): Anal. Calcd. ($M+H^+$) 394.19970, Found: 394.19999. **IR** (cm^{-1}): ν 2955, 2875, 1513, 1453, 1069.

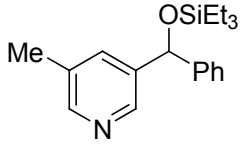
3-(4-methoxyphenyl)-5-(phenyl(triethylsilyloxy)methyl)pyridine (3o)



Following the general procedure with 3-(4-methoxyphenyl)pyridine (46.3 mg, 0.25 mmol), benzaldehyde (79.5 mg, 0.75 mmol). Flash chromatography eluting with 1:8 ethyl acetate: petroleum ether gave 66.3 mg of product in 66% yield as a gray oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.669 (d, 1 H, *J* = 2.2 Hz), 8.555 (d, 1 H, *J* = 1.9 Hz), 7.810 (t, 1 H, *J* = 1.8 Hz), 7.478 (dt, 2 H, *J* = 2.0, 8.8 Hz), 7.404-7.383 (m, 2 H), 7.312 (t, 2 H, *J* = 7.6 Hz), 7.247-7.211 (m, 1 H), 6.984 (dt, 2 H, *J* = 2.0, 8.8 Hz), 5.848 (s, 1 H), 3.833 (s, 3 H), 0.897 (t, 9 H, *J* = 8.0 Hz), 0.596 (q, 6 H, *J* = 8.0 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 159.688, 146.648, 146.148, 144.098, 140.425, 135.784, 131.625, 130.266, 128.386, 128.186, 127.405, 126.227, 114.455, 74.415, 55.300, 6.700, 4.804. **HRMS** (ESI) ($C_{25}H_{31}NO_2Si$): Anal. Calcd. ($M+H^+$) 406.21968, Found: 406.21916. **IR** (cm^{-1}): ν 2954, 2875, 1516, 1249, 1069.

3-methyl-5-(phenyl(triethylsilyloxy)methyl)pyridine (3p)

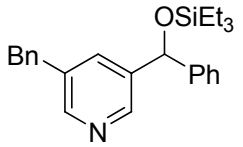


Following the general procedure with 3-picoline (23.3 mg, 0.25 mmol), benzaldehyde (79.5 mg, 0.75 mmol). Flash chromatography eluting with 1:8 ethyl acetate: petroleum ether gave 47.4 mg of product in 61% yield as a gray oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.445 (d, 1 H, *J* = 1.2 Hz), 8.290 (d, 1 H, *J* = 1.2 Hz),

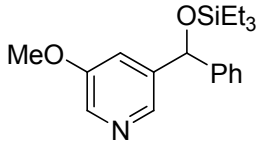
7.432 (s, 1 H), 7.365-7.344 (m, 2 H), 7.299 (t, 2 H, *J* = 7.2 Hz), 7.239-7.221 (m, 1 H), 5.760 (s, 1 H), 2.274 (s, 3 H), 0.878 (t, 9 H, *J* = 8.0 Hz), 0.570 (q, 6 H, *J* = 8.0 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 149.023, 145.180, 144.239, 139.973, 134.268, 132.658, 128.297, 127.274, 126.145, 74.297, 18.372, 6.656, 4.756. **HRMS** (ESI) ($C_{19}H_{27}NOSi$): Anal. Calcd. ($M+H^+$) 314.19347, Found: 314.19350. **IR** (cm^{-1}): ν 2954, 2875, 1454, 1028, 1004.

3-benzyl-5-(phenyl(triethylsilyloxy)methyl)pyridine (3q)



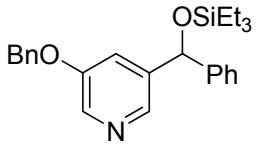
Following the general procedure with 3-benzylpyridine (63.6 mg, 0.25 mmol), benzaldehyde (79.5 mg, 0.75 mmol). Flash chromatography eluting with 1:8 ethyl acetate: petroleum ether gave 63.6 mg of product in 66% yield as a gray oil.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.446 (d, 1 H, *J* = 1.4 Hz), 8.330 (d, 1 H, *J* = 1.4 Hz), 7.474 (s, 1 H), 7.329-7.177 (m, 8 H), 7.125 (d, 2 H, *J* = 7.2 Hz), 5.744 (s, 1 H), 3.932 (s, 2 H), 0.830 (t, 9 H, *J* = 8.0 Hz), 0.521 (q, 6 H, *J* = 8.0 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 148.849, 145.975, 144.070, 140.279, 139.718, 135.965, 134.158, 128.757, 128.535, 128.300, 127.311, 126.332, 126.182, 74.248, 38.932, 6.625, 4.734. **HRMS** (ESI) ($C_{25}H_{31}NOSi$): Anal. Calcd. ($M+H^+$) 390.22477, Found: 390.22435. **IR** (cm^{-1}): ν 2952, 2875, 1454, 1089, 1004.

3-methoxy-5-(phenyl(triethylsilyloxy)methyl)pyridine (3r)



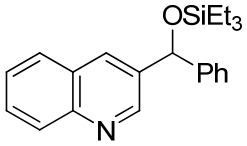
Following the general procedure with 3-methoxypyridine (27.3 mg, 0.25 mmol), benzaldehyde (79.5 mg, 0.75 mmol). Flash chromatography eluting with 1:5 ethyl acetate: petroleum ether gave 44.5 mg of product in 53% yield as a gray oil.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.219 (d, 1 H, *J* = 1.2 Hz), 8.164 (d, 1 H, *J* = 2.8 Hz), 7.364-7.363 (m, 2 H), 7.302 (t, 2 H, *J* = 8.0 Hz), 7.259-7.208 (m, 2 H), 7.239-7.221 (m, 1 H), 5.783 (s, 1 H), 3.808 (s, 3 H), 0.886 (t, 9 H, *J* = 8.0 Hz), 0.578 (q, 6 H, *J* = 8.0 Hz).
^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.593, 144.035, 141.384, 140.337, 136.185, 128.344, 127.381, 126.154, 118.184, 74.039, 55.421, 6.679, 4.769. **HRMS** (ESI) ($C_{19}H_{27}NO_2Si$): Anal. Calcd. ($M+H^+$) 330.18838, Found: 330.18822. **IR** (cm^{-1}): ν 2954, 2875, 1586, 1285, 1016.

3-(benzyloxy)-5-(phenyl(triethylsilyloxy)methyl)pyridine (3s)



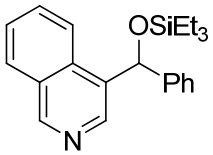
Following the general procedure with 3-benzyloxypyridine (46.2 mg, 0.25 mmol), benzaldehyde (79.5 mg, 0.75 mmol). Flash chromatography eluting with 1:8 ethyl acetate: petroleum ether gave 55.5 mg of product in 55% yield as a gray oil.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.236-8.228 (m, 2 H), 7.398-7.204 (m, 11 H), 5.763 (s, 1 H), 5.052 (s, 3 H), 0.869 (t, 9 H, *J* = 8.0 Hz), 0.557 (q, 6 H, *J* = 8.0 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 154.773, 144.008, 141.400, 140.551, 136.952, 136.099, 128.609, 128.343, 128.170, 127.530, 127.373, 126.139, 119.254, 74.013, 70.215, 6.681, 4.750. **HRMS** (ESI) ($C_{25}H_{31}NO_2Si$): Anal. Calcd. ($M+H^+$) 406.21968, Found: 406.21929. **IR** (cm^{-1}): ν 2954, 2874, 1432, 1286, 1088.

3-(phenyl(triethylsilyloxy)methyl)quinoline (3t)



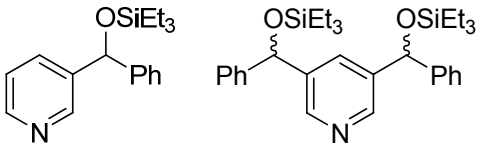
Following the general procedure with quinoline (32.3 mg, 0.25 mmol), benzaldehyde (79.5 mg, 0.75 mmol). Flash chromatography eluting with 1:15 ethyl acetate: petroleum ether gave 23.3 mg of product in 27% yield as a gray oil.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.915 (d, 1 H, *J* = 2.1 Hz), 8.104 (t, 1 H, *J* = 2.0 Hz), 8.066 (d, 1 H, *J* = 8.4 Hz), 8.794 (d, 1 H, *J* = 8.4 Hz), 7.665 (dt, 1 H, *J* = 1.2, 7.2 Hz), 7.518 (dt, 1 H, *J* = 1.2, 7.2 Hz), 7.409 (d, 2 H, *J* = 7.2 Hz), 7.314 (dt, 1 H, *J* = 1.2, 7.2 Hz), 7.255-7.236 (m, 1 H), 5.973 (s, 1 H), 0.898 (t, 9 H, *J* = 8.0 Hz), 0.607 (q, 6 H, *J* = 8.0 Hz).
^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.043, 147.386, 143.958, 137.886, 132.341, 129.196, 129.072, 128.443, 127.867, 127.771, 127.501, 126.618, 126.407, 74.755, 6.727, 4.837. **HRMS** (ESI) ($C_{22}H_{27}NOSi$): Anal. Calcd. ($M+H^+$) 350.19347, Found: 350.19339. **IR** (cm^{-1}): ν 2955, 2875, 1496, 1067, 1005.

4-(phenyl(triethylsilyloxy)methyl)isoquinoline (3u)



Following the general procedure with isoquinoline (32.3 mg, 0.25 mmol), benzaldehyde (79.5 mg, 0.75 mmol). Flash chromatography eluting with 1:8 ethyl acetate: petroleum ether gave 52.7 mg of product in 62% yield as a gray oil.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.190 (s, 1 H), 8.756 (s, 1 H), 8.091 (d, 1 H, *J* = 8.4 Hz), 7.915 (d, 1 H, *J* = 7.6 Hz), 7.536 (dt, 1 H, *J* = 1.2, 7.2 Hz), 7.484 (t, 1 H, *J* = 8.0 Hz), 7.421 (d, 2 H, *J* = 8.0 Hz), 7.261 (t, 2 H, *J* = 7.2 Hz), 7.175 (t, 1 H, *J* = 7.2 Hz), 6.286 (s, 1 H), 0.843 (t, 9 H, *J* = 8.0 Hz), 0.600 (m, 6 H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 152.933, 143.771, 141.835, 133.164, 132.870, 129.902, 128.722, 128.124, 128.040, 126.993, 126.676, 126.133, 124.381, 74.032, 6.643, 4.743. **HRMS** (ESI) ($C_{22}H_{27}NOSi$): Anal. Calcd. ($M+H^+$) 350.19347, Found: 350.19338. **IR** (cm^{-1}): ν 2955, 2875, 1086, 1068, 1006.

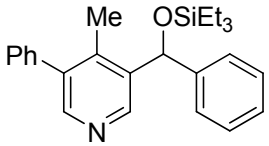
3-(phenyl(triethylsilyloxy)methyl)pyridine (3v)
3,5-bis(phenyl(triethylsilyloxy)methyl)pyridine (3v')



Following the general procedure with pyridine (19.8 mg, 0.25 mmol), benzaldehyde (79.5 mg, 0.75 mmol). Flash chromatography eluting with 1:40 to 1:10 ethyl acetate: petroleum ether gave 28.0 mg of **3s** in 37% yield as a gray oil, and 26.8 mg of **3v'** in 21% yield as a gray oil (**3v'** is a 3:2 ratio mixture of diastereoisomers as determined by NMR).
3v: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.625 (d, 1 H, *J* = 2.0 Hz), 8.461 (dd, 1 H, *J* = 1.5, 4.8 Hz), 7.651 (dt, 1 H, *J* = 1.8, 8.0 Hz), 7.365-7.344 (m, 2 H), 7.302 (t, 2 H, *J* = 6.4 Hz), 7.258-7.187 (m, 2 H), 5.789 (s, 1 H), 0.878 (t, 9 H, *J* = 8.0 Hz), 0.574 (q, 6 H, *J* = 8.0 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 148.429, 148.013, 144.117, 140.559, 133.814, 128.361, 127.387, 126.208, 123.221, 74.380, 6.666, 4.778. **HRMS** (ESI) ($C_{18}H_{25}NOSi$): Anal. Calcd. ($M+H^+$) 300.17782, Found: 300.17796. **IR** (cm^{-1}): ν 2954, 2875, 1423, 1024.

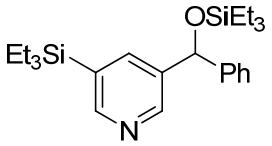
3v': ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.440 (d, 1.2 H, *J* = 2.0 Hz), 8.410 (d, 0.8 H, *J* = 2.0 Hz), 7.718 (t, 0.4 H, *J* = 2.0 Hz), 7.657 (t, 0.6 H, *J* = 2.0 Hz), 7.319-7.194 (m, 10 H), 5.749 (s, 1 H), 0.831 (t, 7.2 H, *J* = 8.0 Hz), 0.824 (t, 10.8 H, *J* = 8.0 Hz), 0.518 (q, 4.8 H, *J* = 8.0 Hz), 0.512 (q, 7.2 H, *J* = 8.0 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 146.859, 146.701, 144.109, 144.070, 140.239, 140.112, 131.930, 131.826, 128.307, 127.338, 127.300, 126.309, 126.217, 74.404, 74.355, 6.660, 4.787. **HRMS** (ESI) ($C_{31}H_{45}NO_2Si_2$): Anal. Calcd. ($M+H^+$) 520.30616, Found: 520.30717. **IR** (cm^{-1}): ν 2954, 2875, 1454, 1026.

4-methyl-3-phenyl-5-(phenyl(triethylsilyloxy)methyl)pyridine (3w)



Following the general procedure with 3-phenyl-4-methylpyridine (42.3 mg, 0.25 mmol), benzaldehyde (79.5 mg, 0.75 mmol). Flash chromatography eluting with 1:15 ethyl acetate: petroleum ether gave 30.5 mg of product in 31% yield as a gray oil.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.802 (s, 1 H), 8.369 (s, 1 H), 7.856 (t, 1 H, *J* = 2 Hz), 7.421-7.302 (m, 7 H), 7.287-7.220 (m, 3 H), 5.976 (s, 1 H), 0.894 (t, 9 H, *J* = 8.0 Hz), 0.596 (q, 6 H, *J* = 8.0 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 149.149, 147.615, 143.103, 142.008, 138.106, 138.011, 129.541, 128.238, 128.223, 127.441, 127.176, 126.690, 73.519, 16.114, 6.704, 4.835. **HRMS** (ESI) ($C_{22}H_{31}NOSi$): Anal. Calcd. ($M+H^+$) 390.22477, Found: 390.22477. **IR** (cm^{-1}): ν 2954, 2875, 1434, 1006.

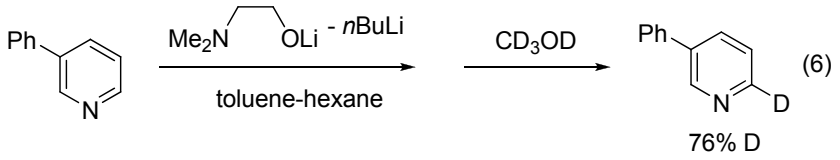
3-(phenyl(triethylsilyloxy)methyl)-5-(triethylsilyl)pyridine (3x)

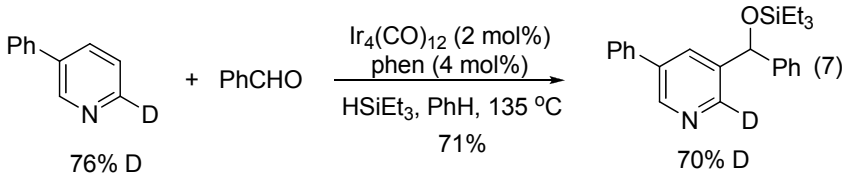


Following the general procedure with 3-triethylsilylpyridine (48.3 mg, 0.25 mmol), benzaldehyde (79.5 mg, 0.75 mmol). Flash chromatography eluting with 1:40 to 1:20 ethyl acetate: petroleum ether gave 45.9 mg of product in 45% yield as a gray oil.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.518 (d, 1 H, *J* = 2.2 Hz), 8.5065 (d, 1 H, *J* = 1.6 Hz), 7.780 (t, 1 H, *J* = 1.8 Hz), 7.355-7.296 (m, 4 H), 7.258-7.221 (m, 1 H), 5.774 (s, 1 H), 0.934 (t, 9 H, *J* = 8 Hz), 0.876 (t, 9 H, *J* = 8 Hz), 0.778 (dq, 6 H, *J* = 1.5, 8.0 Hz), 0.596 (q, 6 H, *J* = 8.0 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 153.146, 148.387, 144.182, 139.683, 139.510, 131.551, 128.307, 127.304, 126.222, 74.600, 7.156, 6.663, 4.822, 3.090. **HRMS** (ESI) ($C_{24}H_{39}NOSi_2$): Anal. Calcd. ($M+H^+$) 414.26429, Found: 414.26433. **IR** (cm^{-1}): ν 2954, 2875, 1455, 1115, 1066.

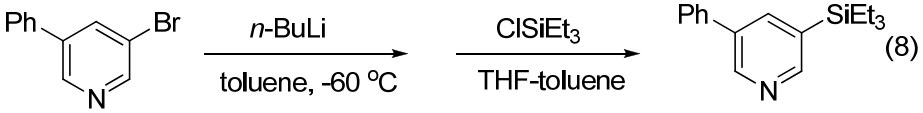
Synthesis of 6-D-3-Phenylpyridine:

The D-labeled 3-phenylpyridine was synthesized according to the literature procedure[6].



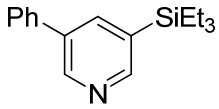


Synthesis of 3-phenyl-5-(triethylsilyl)pyridine 4[7]:



To a cold solution of *n*-BuLi (2.2 mL, 1.6 M in hexane) in 12 mL of toluene (-60℃) was added dropwise a solution of 3-phenyl-3-bromo-pyridine[8] (3.0 mmol) in 6 mL of toluene. The resulting solution was stirred at that temperature for 0.5 h. Then 6 mL of THF was added slowly and the brown solution was stirred for another 15 min. After the addition of triethylchlorosilane (3.6 mmol), the mixture was slowly brought to room temperature. The reaction was quenched by water and extracted by ethyl acetate. The organic layer was dried over $MgSO_4$ and evaporated. Purification of the residue by flash column chromatography on neutral aluminia provided the desired product in 35% yield.

3-phenyl-5-(triethylsilyl)pyridine (4)



^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.806 (d, 1 H, *J* = 2.4 Hz), 8.638 (d, 1 H, *J* = 1.6 Hz), 7.810 (dd, 1 H, *J* = 1.9, 2.0 Hz), 7.592-7.584 (m, 2 H), 7.487 (d, 2 H, *J* = 8.0 Hz), 7.424-7.406 (m, 1 H), 0.995 (t, 9 H, *J* = 4.0 Hz), 0.596 (q, 6 H, *J* = 8 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 153.240, 148.454, 140.230, 138.313, 135.867, 132.053, 129.018, 127.931, 127.210, 7.268, 3.137. **HRMS** (ESI) ($C_{17}H_{23}NSi$): Anal. Calcd. ($M+H^+$) 270.16725, Found: 270.16729. **IR** (cm^{-1}): ν 2934, 2865, 1254, 1126.

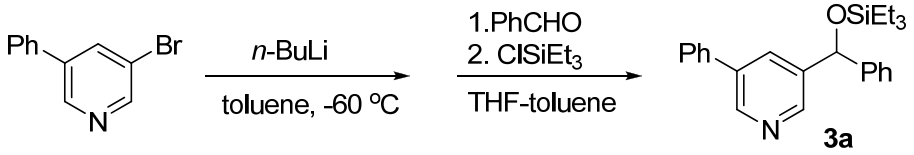
Procedure for the catalytic C-H silylation (Eq 2)

To an oven-dried 25 mL Schlenk tube was added $Ir_4(CO)_{12}$ (5.5 mg, 0.005 mmol) and phenanthroline (1.8 mg, 0.01 mmol). The tube was evacuated and refilled with nitrogen. Then 3-phenylpyridine (38.8 mg, 0.25 mmol), the corresponding additive (0.75 mmol) and triethylsilane (87.0 mg, 0.75 mmol) were successively added via syringes under a positive stream of dry nitrogen. After the addition of 1 mL of benzene, the tube was tightly sealed and heated to 135 ℃ in an oil bath for 12 h. After cooling to room temperature, the resulting mixture was applied to GC analysis with dodecane as an internal standard.

Procedure for the addition of 4 to benzaldehyde (Eq 3)

To an oven-dried 25 mL Schlenk tube was added, if indicated, $Ir_4(CO)_{12}$ (5.5 mg, 0.005 mmol) and phenanthroline (1.8 mg, 0.01 mmol). The tube was evacuated and refilled with nitrogen. Then 3-phenylpyridyl triethylsilane **4** (0.25 mmol), benzaldehyde (80 mg, 0.75 mmol) and triethylsilane (87.0 mg, 0.75 mmol, if indicated) were successively added via syringes under a positive stream of dry nitrogen. After the addition of 1 mL of benzene, the tube was tightly sealed and heated to 135 ℃ in an oil bath for 12 h. After cooling to room temperature, the resulting mixture was applied to GC and GC-MS analysis.

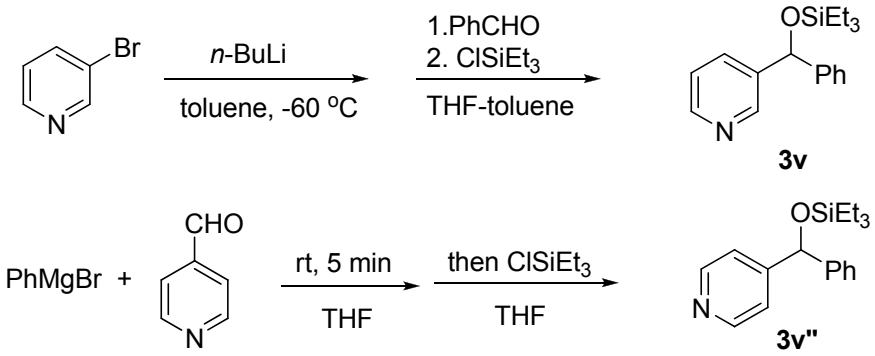
Independent synthesis of standard products[7]:



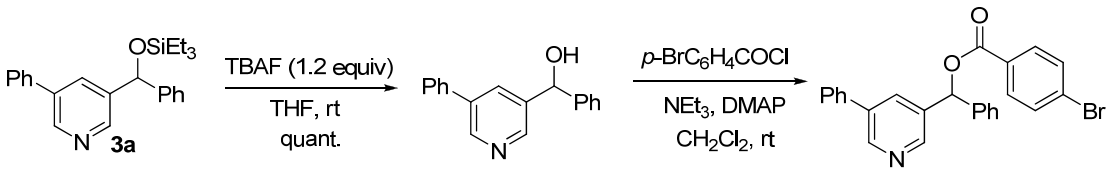
To a cold solution of *n*-BuLi (2.2 mL, 1.6 M in hexane) in 12 mL toluene (-60℃) was added dropwise a solution of 3-phenyl-3-bromo-pyridine[8] (3.0 mmol) in 6 mL of toluene. The resulting solution was stirred at that temperature for 0.5 h. Then 6 mL of THF was added slowly and the brown solution was stirred for another 15 min. After the addition of

benzaldehyde (3.6 mmol), the mixture was slowly brought to room temperature. Then triethylchlorosilane (3.6 mmol) was added and the mixture was stirred for an additional 1 h. The reaction was quenched by water and extracted by ethyl acetate. The organic layer was dried over $MgSO_4$ and evaporated. Purification of the residue by flash column chromatography on silica gel provided the desired product in 78% yield. This product was identical in every aspect (including ^1H NMR, ^{13}C NMR and retention time on GC and GC-MS) with the product obtained by the iridium-catalyzed reaction.

Similarly, the structure of **3v** was confirmed by the following independent synthesis (80% yield). The absence of the functionalization product at the 4-position of pyridine was confirmed by comparison of the crude NMR with **3v** and **3v"**.



Preparation of *p*-bromobenzoyl ester of the deprotected alcohol of 3a

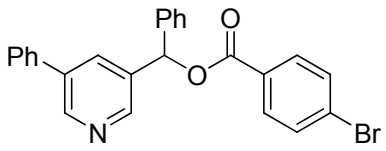


To a solution of **3a** (112 mg, 0.3 mmol) in 5 mL of THF was added 0.36 mL of a solution of TBAF in THF (1.0 M) at room temperature. After 5 min, the solvent was removed and the residue was directly applied to the next step.

A mixture of the alcohol (78 mg, 0.3 mmol), *p*-bromobenzoyl chloride (100 mg, 0.45 mmol), triethylamine (60 mg, 0.6 mmol), 4-(N,-N-dimethylamino)pyridine (10 mg) in 10 mL of dichloromethane was stirred at room temperature for 1 h. The mixture was washed by water and dried over $MgSO_4$. Removal of the solvent followed by flash chromatography on silica gel eluting with 1:4 ethyl acetate: petroleum ether provided 120 mg of the product in 90% yield.

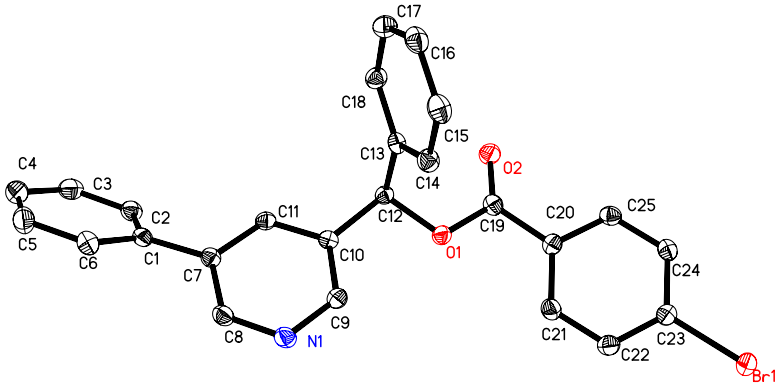
The crystal suitable for X-ray analysis was grown by slow evaporation of a solution of the product in ethyl acetate at room temperature.

phenyl(5-phenylpyridin-3-yl)methyl 4-bromobenzoate



^1H NMR ($CDCl_3$, 400 MHz): δ 8.796 (d, 1 H, *J* = 2.1 Hz), 8.704 (d, 1 H, *J* = 1.9 Hz),

7.966 (d, 2 H, *J* = 8.4 Hz), 7.862 (t, 1 H, *J* = 2.0 Hz), 7.602 (d, 2 H, *J* = 8.4 Hz), 7.537 (d, 2 H, *J* = 7.2 Hz), 7.476-7.440 (m, 4 H), 7.397 (t, 3 H, *J* = 7.2 Hz), 7.356-7.320 (m, 1 H), 7.198 (s, 1 H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 164.696, 147.983, 147.284, 138.820, 137.299, 136.521, 135.609, 133.074, 131.873, 131.241, 129.063, 128.863, 128.585, 128.511, 128.274, 127.191, 126.997, 75.666. **HRMS** (ESI) ($C_{26}H_{19}BrO_2$): Anal. Calcd. ($M+H^+$) 444.05937, Found: 444.05898. **IR** (cm^{-1}): ν 3033, 1720, 1589, 1261, 1097.



ORTEP diagram at 50% thermal ellipsoids (CCDC 773152).

X-ray Data for p-bromobenzoyl ester of deprotected 3a

ORTEP diagram of complex **3** at 50% thermal ellipsoids

Table 1. Crystal data and structure refinement for SA693.

Identification code	sa693
Empirical formula	C25 H18 Br N O2
Formula weight	444.31
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 6.1156(12) A alpha = 90 deg. b = 21.353(4) A beta = 95.378(3) deg. c = 15.092(3) A gamma = 90 deg.

Volume	1962.1(7) A^3
Z, Calculated density	4, 1.504 Mg/m^3
Absorption coefficient	2.117 mm^-1
F(000)	904
Crystal size	0.23 x 0.10 x 0.10 mm
Theta range for data collection	2.87 to 27.49 deg.
Limiting indices	-7<=h<=7, -24<=k<=27, -13<=l<=19
Reflections collected / unique	17238 / 4477 [R(int) = 0.0443]
Completeness to theta = 27.49	99.7 %
Absorption correction	Numerical
Max. and min. transmission	0.8162 and 0.6417
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4477 / 0 / 262
Goodness-of-fit on F^2	1.198
Final R indices [I>2sigma(I)]	R1 = 0.0565, wR2 = 0.1094
R indices (all data)	R1 = 0.0631, wR2 = 0.1126
Largest diff. peak and hole	0.638 and -0.530 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for SA693.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)

Br(1)	861(1)	5376(1)	8508(1)	40(1)
O(1)	-2765(3)	8370(1)	8435(1)	29(1)
O(2)	-6066(4)	7924(1)	8047(2)	37(1)
N(1)	1674(4)	9803(1)	8878(2)	33(1)
C(1)	-2005(5)	11199(1)	9071(2)	30(1)
C(2)	-3882(5)	11328(2)	9498(2)	34(1)
C(3)	-4608(6)	11943(2)	9567(2)	43(1)
C(4)	-3492(7)	12438(2)	9231(3)	49(1)
C(5)	-1570(7)	12309(2)	8819(3)	46(1)
C(6)	-851(6)	11698(2)	8743(2)	37(1)
C(7)	-1310(5)	10543(1)	8942(2)	27(1)
C(8)	906(5)	10378(2)	9009(2)	32(1)
C(9)	185(5)	9357(2)	8650(2)	30(1)
C(10)	-2067(5)	9467(1)	8550(2)	24(1)
C(11)	-2803(5)	10064(1)	8711(2)	27(1)
C(12)	-3689(5)	8978(1)	8178(2)	26(1)
C(13)	-4012(5)	9018(1)	7169(2)	27(1)
C(14)	-2363(5)	8814(2)	6660(2)	33(1)
C(15)	-2638(6)	8873(2)	5740(2)	40(1)
C(16)	-4522(6)	9139(2)	5328(2)	39(1)
C(17)	-6160(6)	9341(2)	5830(2)	39(1)
C(18)	-5911(5)	9282(2)	6749(2)	33(1)
C(19)	-4124(5)	7874(2)	8254(2)	30(1)
C(20)	-2898(5)	7274(1)	8346(2)	29(1)
C(21)	-728(5)	7246(2)	8728(2)	33(1)
C(22)	376(5)	6681(2)	8783(2)	34(1)
C(23)	-681(5)	6147(2)	8447(2)	30(1)
C(24)	-2837(5)	6165(2)	8059(2)	33(1)
C(25)	-3939(5)	6728(2)	8015(2)	31(1)

Table 3. Bond lengths [A] and angles [deg] for SA693.

Br(1)-C(23)	1.895(3)
O(1)-C(19)	1.357(4)
O(1)-C(12)	1.454(3)
O(2)-C(19)	1.204(4)
N(1)-C(8)	1.335(4)
N(1)-C(9)	1.340(4)
C(1)-C(6)	1.394(5)
C(1)-C(2)	1.395(4)

C(1)-C(7)	1.483(4)
C(2)-C(3)	1.393(5)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.380(6)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.408(6)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.385(5)
C(5)-H(5A)	0.9500
C(6)-H(6A)	0.9500
C(7)-C(11)	1.393(4)
C(7)-C(8)	1.395(4)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.392(4)
C(9)-H(9A)	0.9500
C(10)-C(11)	1.381(4)
C(10)-C(12)	1.512(4)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.520(4)
C(12)-H(12A)	1.0000
C(13)-C(18)	1.389(4)
C(13)-C(14)	1.394(4)
C(14)-C(15)	1.388(5)
C(14)-H(14A)	0.9500
C(15)-C(16)	1.380(5)
C(15)-H(15A)	0.9500
C(16)-C(17)	1.382(5)
C(16)-H(16A)	0.9500
C(17)-C(18)	1.387(4)
C(17)-H(17A)	0.9500
C(18)-H(18A)	0.9500
C(19)-C(20)	1.486(4)
C(20)-C(25)	1.397(4)
C(20)-C(21)	1.397(4)
C(21)-C(22)	1.382(4)
C(21)-H(21A)	0.9500
C(22)-C(23)	1.383(4)
C(22)-H(22A)	0.9500
C(23)-C(24)	1.392(4)
C(24)-C(25)	1.378(4)
C(24)-H(24A)	0.9500
C(25)-H(25A)	0.9500

C(19)-O(1)-C(12)	115.3(2)

C(8)-N(1)-C(9)	116.9(3)
C(6)-C(1)-C(2)	118.7(3)
C(6)-C(1)-C(7)	120.9(3)
C(2)-C(1)-C(7)	120.4(3)
C(3)-C(2)-C(1)	120.1(3)
C(3)-C(2)-H(2A)	120.0
C(1)-C(2)-H(2A)	120.0
C(4)-C(3)-C(2)	121.5(4)
C(4)-C(3)-H(3A)	119.2
C(2)-C(3)-H(3A)	119.2
C(3)-C(4)-C(5)	118.3(4)
C(3)-C(4)-H(4A)	120.8
C(5)-C(4)-H(4A)	120.8
C(6)-C(5)-C(4)	120.4(4)
C(6)-C(5)-H(5A)	119.8
C(4)-C(5)-H(5A)	119.8
C(5)-C(6)-C(1)	120.9(3)
C(5)-C(6)-H(6A)	119.5
C(1)-C(6)-H(6A)	119.5
C(11)-C(7)-C(8)	116.3(3)
C(11)-C(7)-C(1)	122.5(3)
C(8)-C(7)-C(1)	121.2(3)
N(1)-C(8)-C(7)	125.0(3)
N(1)-C(8)-H(8A)	117.5
C(7)-C(8)-H(8A)	117.5
N(1)-C(9)-C(10)	123.3(3)
N(1)-C(9)-H(9A)	118.3
C(10)-C(9)-H(9A)	118.3
C(11)-C(10)-C(9)	118.2(3)
C(11)-C(10)-C(12)	119.3(3)
C(9)-C(10)-C(12)	122.1(3)
C(10)-C(11)-C(7)	120.3(3)
C(10)-C(11)-H(11A)	119.9
C(7)-C(11)-H(11A)	119.9
O(1)-C(12)-C(10)	107.1(2)
O(1)-C(12)-C(13)	109.2(2)
C(10)-C(12)-C(13)	110.6(2)
O(1)-C(12)-H(12A)	110.0
C(10)-C(12)-H(12A)	110.0
C(13)-C(12)-H(12A)	110.0
C(18)-C(13)-C(14)	119.5(3)
C(18)-C(13)-C(12)	120.3(3)
C(14)-C(13)-C(12)	120.1(3)
C(15)-C(14)-C(13)	119.8(3)

C(15)-C(14)-H(14A)	120.1
C(13)-C(14)-H(14A)	120.1
C(16)-C(15)-C(14)	120.4(3)
C(16)-C(15)-H(15A)	119.8
C(14)-C(15)-H(15A)	119.8
C(15)-C(16)-C(17)	119.9(3)
C(15)-C(16)-H(16A)	120.0
C(17)-C(16)-H(16A)	120.0
C(16)-C(17)-C(18)	120.2(3)
C(16)-C(17)-H(17A)	119.9
C(18)-C(17)-H(17A)	119.9
C(17)-C(18)-C(13)	120.2(3)
C(17)-C(18)-H(18A)	119.9
C(13)-C(18)-H(18A)	119.9
O(2)-C(19)-O(1)	123.6(3)
O(2)-C(19)-C(20)	125.3(3)
O(1)-C(19)-C(20)	111.1(3)
C(25)-C(20)-C(21)	119.7(3)
C(25)-C(20)-C(19)	118.5(3)
C(21)-C(20)-C(19)	121.7(3)
C(22)-C(21)-C(20)	120.1(3)
C(22)-C(21)-H(21A)	120.0
C(20)-C(21)-H(21A)	120.0
C(21)-C(22)-C(23)	119.3(3)
C(21)-C(22)-H(22A)	120.4
C(23)-C(22)-H(22A)	120.4
C(22)-C(23)-C(24)	121.6(3)
C(22)-C(23)-Br(1)	119.0(2)
C(24)-C(23)-Br(1)	119.4(2)
C(25)-C(24)-C(23)	118.9(3)
C(25)-C(24)-H(24A)	120.5
C(23)-C(24)-H(24A)	120.5
C(24)-C(25)-C(20)	120.4(3)
C(24)-C(25)-H(25A)	119.8
C(20)-C(25)-H(25A)	119.8

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for SA693.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	44(1)	33(1)	41(1)	-3(1)	-1(1)	7(1)
O(1)	26(1)	25(1)	35(1)	3(1)	1(1)	-1(1)
O(2)	27(1)	34(1)	49(1)	2(1)	1(1)	-2(1)
N(1)	23(1)	36(2)	41(2)	-8(1)	2(1)	1(1)
C(1)	29(2)	29(2)	29(2)	-6(1)	-3(1)	1(1)
C(2)	32(2)	36(2)	33(2)	-7(1)	1(1)	2(1)
C(3)	40(2)	49(2)	39(2)	-13(2)	-4(2)	12(2)
C(4)	60(3)	37(2)	45(2)	-5(2)	-13(2)	2(2)
C(5)	59(2)	33(2)	46(2)	-2(2)	0(2)	-6(2)
C(6)	38(2)	34(2)	37(2)	-3(1)	3(1)	-5(1)
C(7)	27(2)	29(2)	25(2)	-3(1)	3(1)	0(1)
C(8)	26(2)	33(2)	36(2)	-3(1)	1(1)	-5(1)
C(9)	28(2)	29(2)	33(2)	-2(1)	2(1)	4(1)
C(10)	23(1)	28(2)	22(1)	0(1)	3(1)	-1(1)
C(11)	22(1)	31(2)	27(2)	0(1)	3(1)	2(1)
C(12)	24(1)	25(2)	29(2)	0(1)	2(1)	2(1)
C(13)	29(2)	23(2)	28(2)	-3(1)	5(1)	-4(1)
C(14)	33(2)	34(2)	34(2)	-4(1)	5(1)	1(1)
C(15)	45(2)	39(2)	36(2)	-7(2)	14(2)	-6(2)
C(16)	55(2)	35(2)	27(2)	-1(1)	5(2)	-7(2)
C(17)	45(2)	38(2)	31(2)	2(2)	-2(1)	2(2)
C(18)	32(2)	33(2)	33(2)	-1(1)	4(1)	4(1)
C(19)	31(2)	29(2)	29(2)	1(1)	5(1)	-5(1)
C(20)	29(2)	27(2)	31(2)	4(1)	7(1)	-2(1)
C(21)	35(2)	29(2)	36(2)	-1(1)	1(1)	-4(1)
C(22)	32(2)	35(2)	34(2)	3(1)	0(1)	0(1)
C(23)	34(2)	31(2)	27(2)	1(1)	5(1)	3(1)
C(24)	37(2)	29(2)	32(2)	-3(1)	3(1)	-4(1)
C(25)	28(2)	34(2)	32(2)	4(1)	1(1)	-4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for SA693.

	x	y	z	U(eq)
H(2A)	-4666	10996	9743	41
H(3A)	-5901	12023	9851	52
H(4A)	-4007	12855	9277	59
H(5A)	-761	12642	8592	56
H(6A)	448	11617	8462	44
H(8A)	1950	10699	9160	38
H(9A)	693	8945	8553	36
H(11A)	-4335	10149	8663	32
H(12A)	-5127	9036	8433	31
H(14A)	-1055	8635	6942	40
H(15A)	-1522	8728	5393	47
H(16A)	-4693	9182	4699	47
H(17A)	-7461	9522	5546	46
H(18A)	-7042	9421	7092	39
H(21A)	-11	7617	8949	40
H(22A)	1844	6659	9050	41
H(24A)	-3538	5794	7830	39
H(25A)	-5415	6746	7757	37

Table 6. Torsion angles [deg] for SA693.

C(6)-C(1)-C(2)-C(3)	1.9(5)
C(7)-C(1)-C(2)-C(3)	-175.8(3)
C(1)-C(2)-C(3)-C(4)	-1.0(5)
C(2)-C(3)-C(4)-C(5)	-0.5(5)
C(3)-C(4)-C(5)-C(6)	1.0(6)
C(4)-C(5)-C(6)-C(1)	-0.1(5)
C(2)-C(1)-C(6)-C(5)	-1.4(5)
C(7)-C(1)-C(6)-C(5)	176.3(3)
C(6)-C(1)-C(7)-C(11)	-137.9(3)
C(2)-C(1)-C(7)-C(11)	39.8(4)
C(6)-C(1)-C(7)-C(8)	39.2(4)
C(2)-C(1)-C(7)-C(8)	-143.1(3)
C(9)-N(1)-C(8)-C(7)	1.1(5)
C(11)-C(7)-C(8)-N(1)	-0.7(5)
C(1)-C(7)-C(8)-N(1)	-178.0(3)

C(8)-N(1)-C(9)-C(10)	-0.1(5)
N(1)-C(9)-C(10)-C(11)	-1.3(5)
N(1)-C(9)-C(10)-C(12)	171.8(3)
C(9)-C(10)-C(11)-C(7)	1.7(4)
C(12)-C(10)-C(11)-C(7)	-171.6(3)
C(8)-C(7)-C(11)-C(10)	-0.8(4)
C(1)-C(7)-C(11)-C(10)	176.5(3)
C(19)-O(1)-C(12)-C(10)	172.1(2)
C(19)-O(1)-C(12)-C(13)	-68.1(3)
C(11)-C(10)-C(12)-O(1)	-155.6(3)
C(9)-C(10)-C(12)-O(1)	31.4(4)
C(11)-C(10)-C(12)-C(13)	85.6(3)
C(9)-C(10)-C(12)-C(13)	-87.5(3)
O(1)-C(12)-C(13)-C(18)	137.9(3)
C(10)-C(12)-C(13)-C(18)	-104.6(3)
O(1)-C(12)-C(13)-C(14)	-44.7(4)
C(10)-C(12)-C(13)-C(14)	72.8(3)
C(18)-C(13)-C(14)-C(15)	-0.3(5)
C(12)-C(13)-C(14)-C(15)	-177.7(3)
C(13)-C(14)-C(15)-C(16)	0.8(5)
C(14)-C(15)-C(16)-C(17)	-0.8(5)
C(15)-C(16)-C(17)-C(18)	0.4(5)
C(16)-C(17)-C(18)-C(13)	0.1(5)
C(14)-C(13)-C(18)-C(17)	-0.1(5)
C(12)-C(13)-C(18)-C(17)	177.3(3)
C(12)-O(1)-C(19)-O(2)	-13.0(4)
C(12)-O(1)-C(19)-C(20)	167.0(2)
O(2)-C(19)-C(20)-C(25)	12.7(5)
O(1)-C(19)-C(20)-C(25)	-167.3(3)
O(2)-C(19)-C(20)-C(21)	-169.3(3)
O(1)-C(19)-C(20)-C(21)	10.7(4)
C(25)-C(20)-C(21)-C(22)	-0.5(5)
C(19)-C(20)-C(21)-C(22)	-178.5(3)
C(20)-C(21)-C(22)-C(23)	0.9(5)
C(21)-C(22)-C(23)-C(24)	-0.5(5)
C(21)-C(22)-C(23)-Br(1)	179.0(2)
C(22)-C(23)-C(24)-C(25)	-0.2(5)
Br(1)-C(23)-C(24)-C(25)	-179.7(2)
C(23)-C(24)-C(25)-C(20)	0.6(5)
C(21)-C(20)-C(25)-C(24)	-0.2(5)
C(19)-C(20)-C(25)-C(24)	177.9(3)

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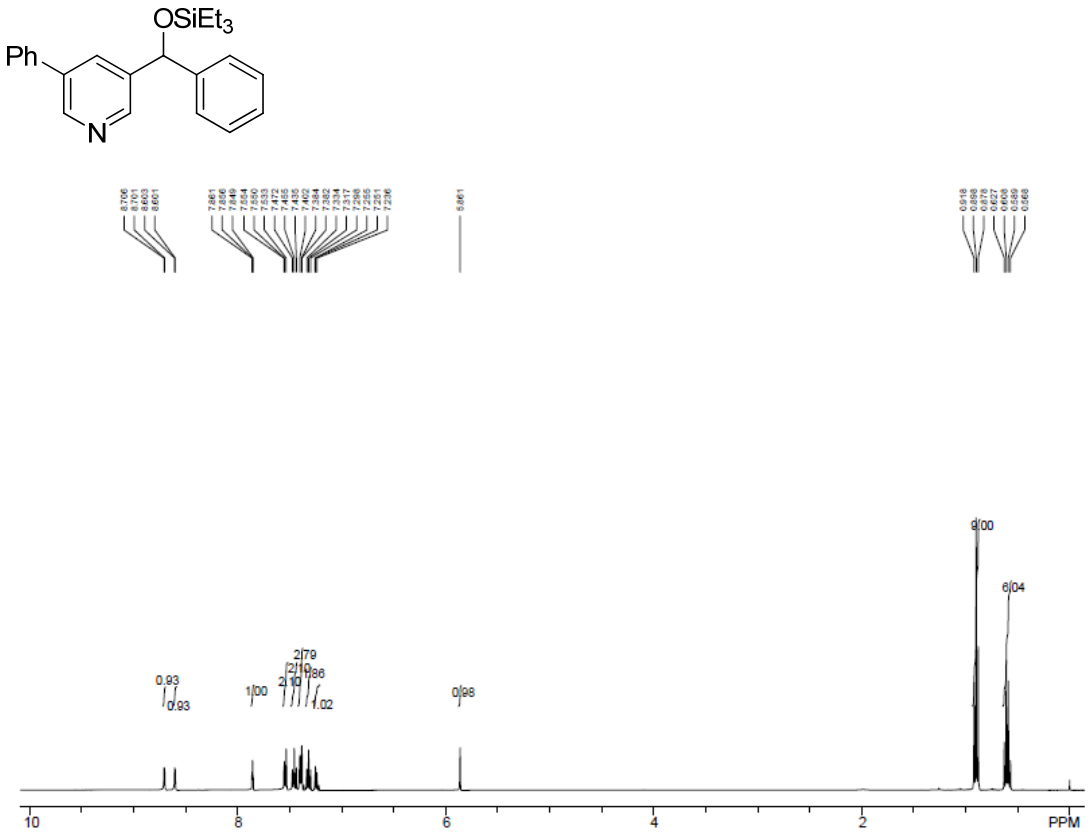
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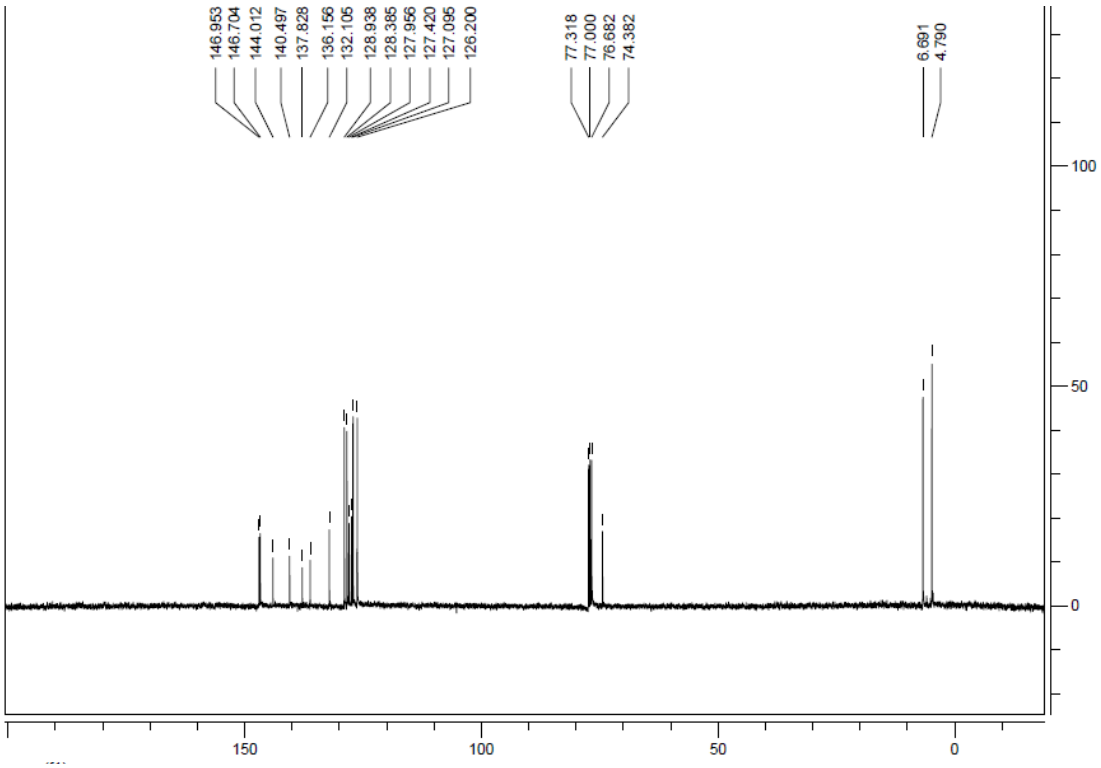
6
4
2
PPM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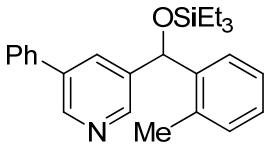
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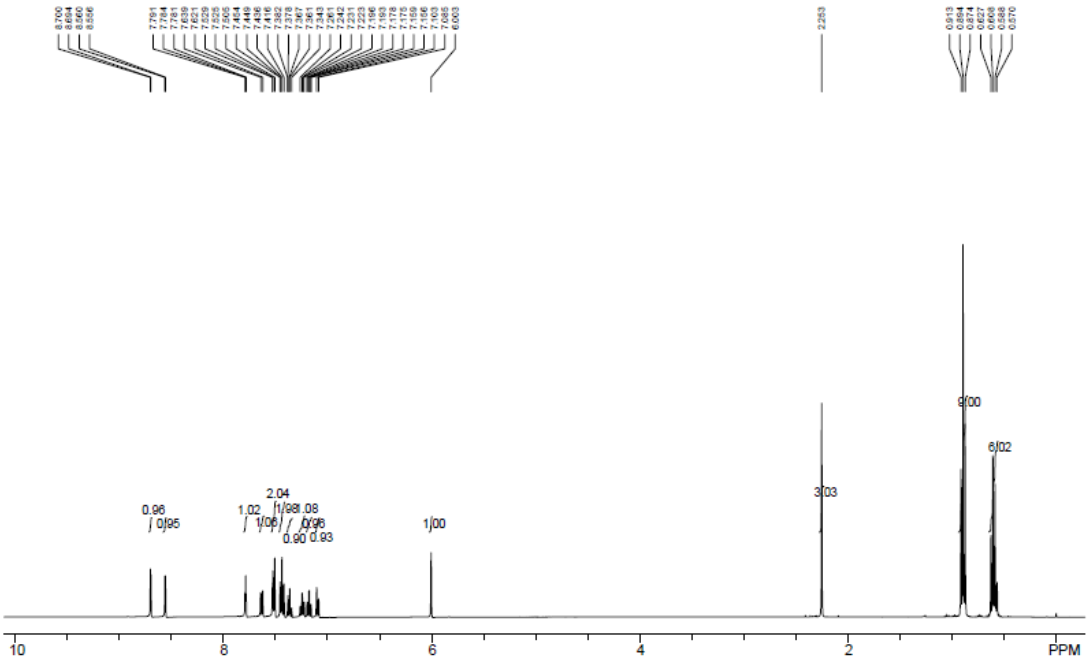
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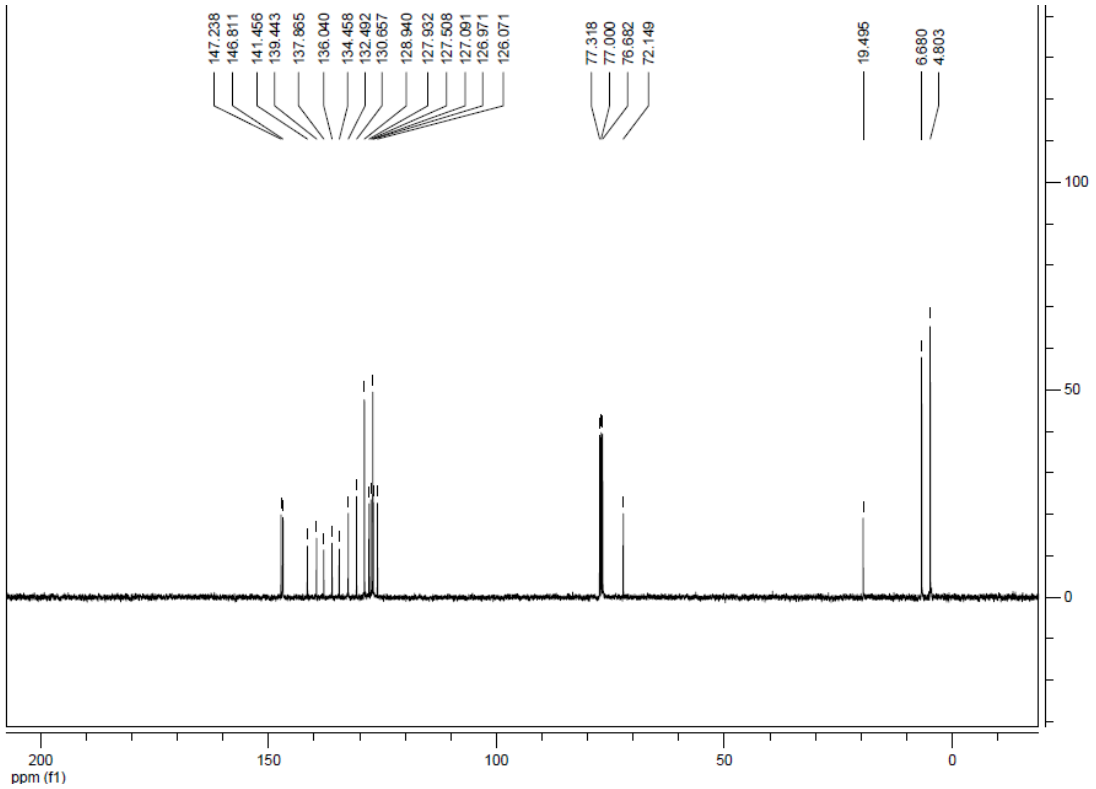

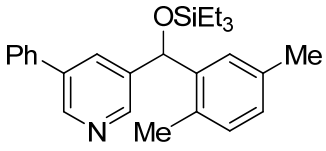

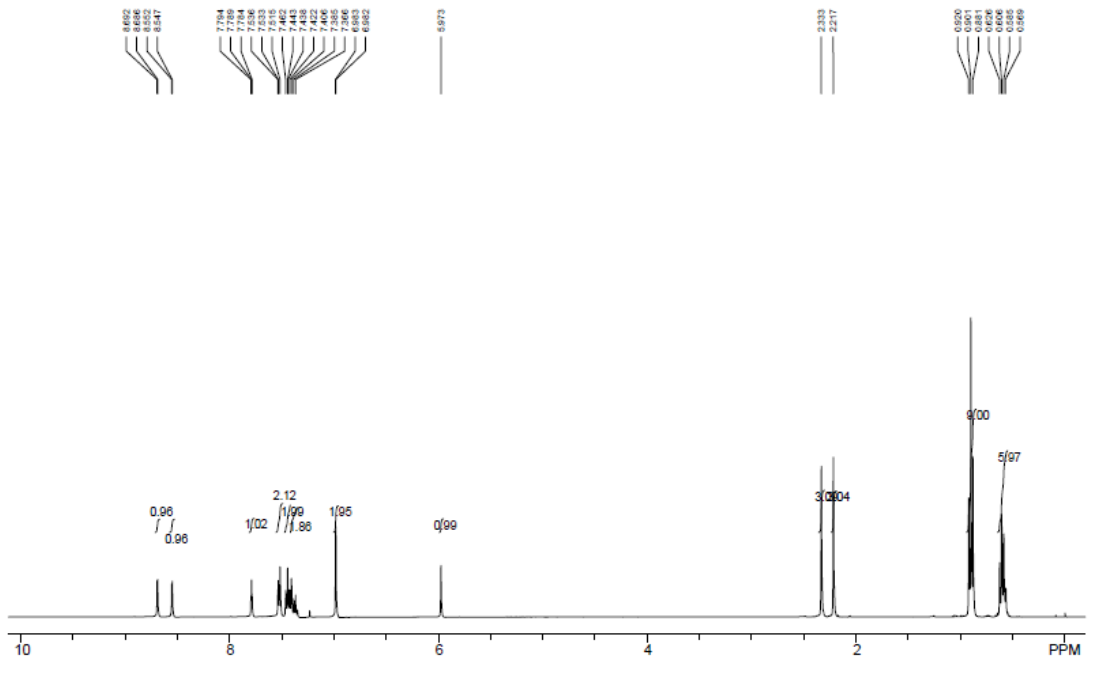

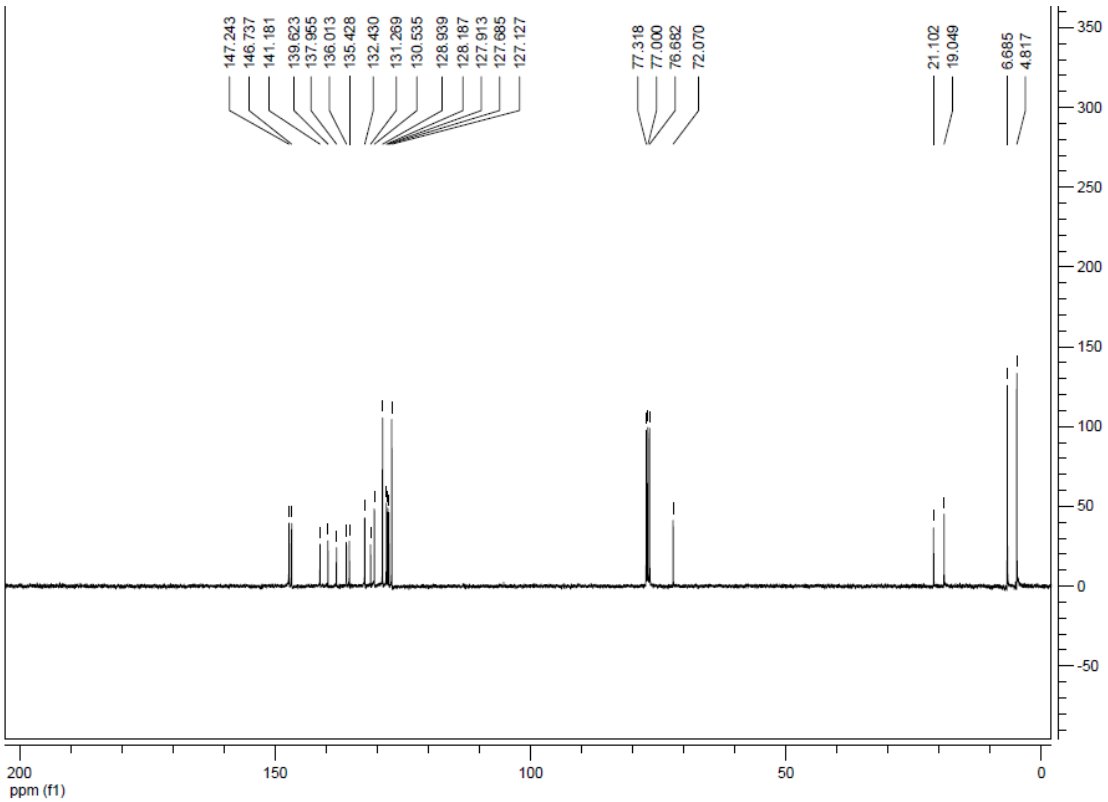

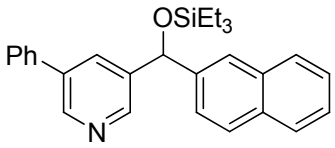

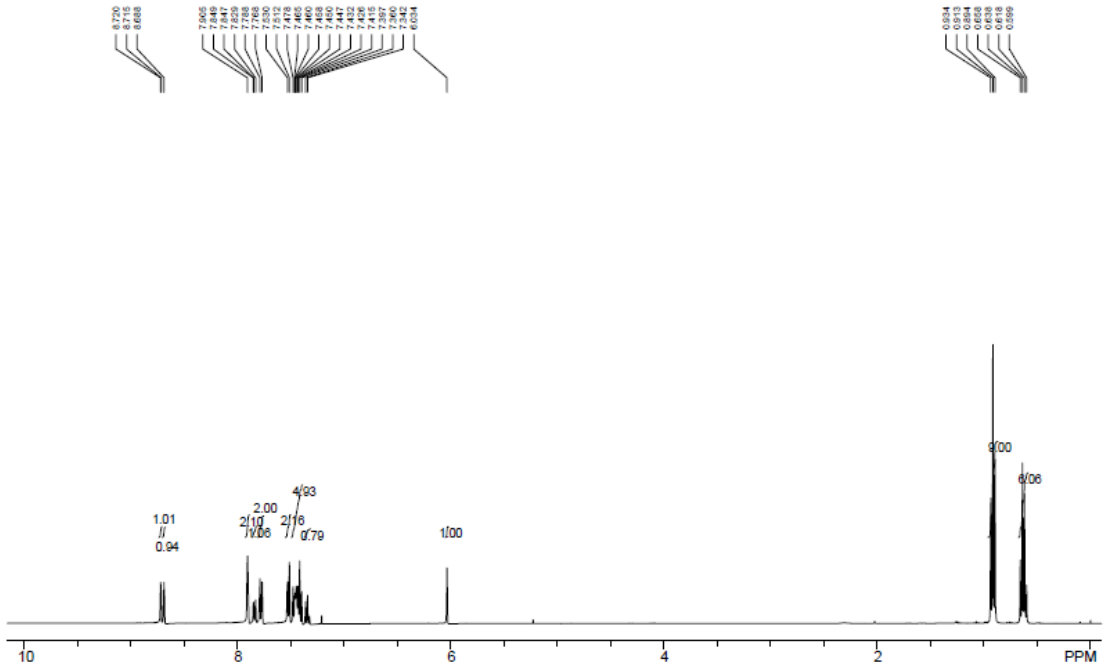

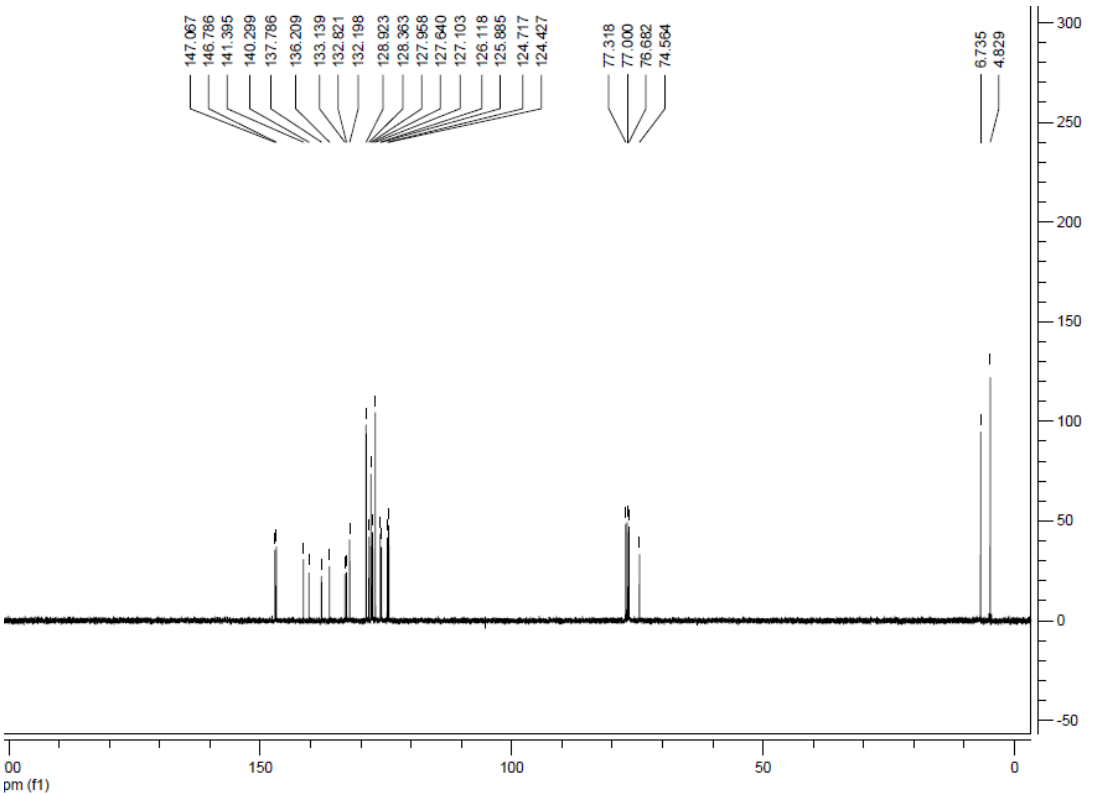

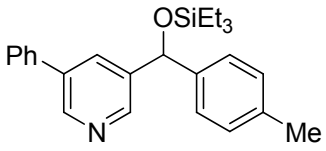

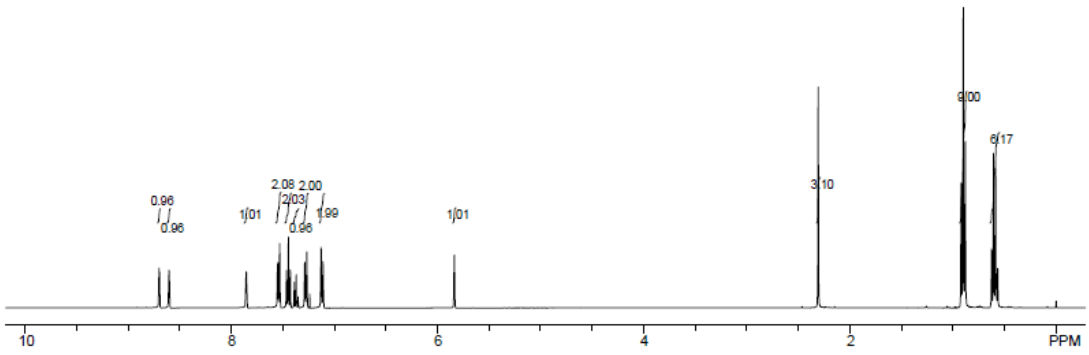

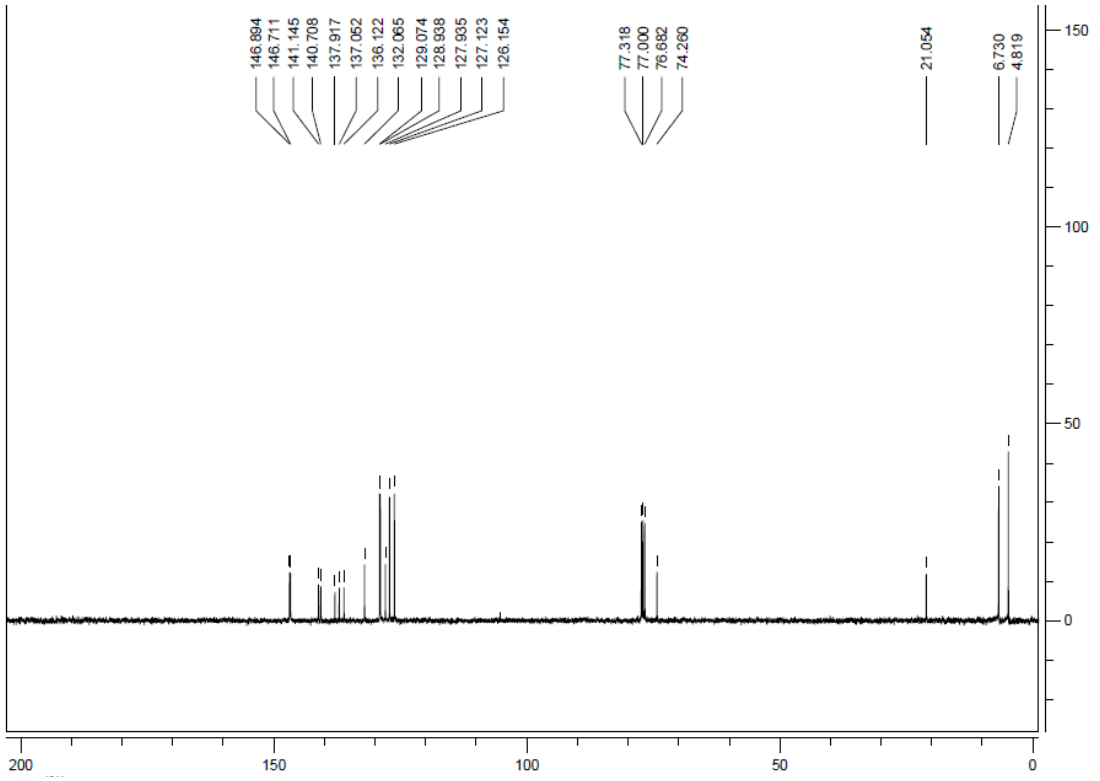
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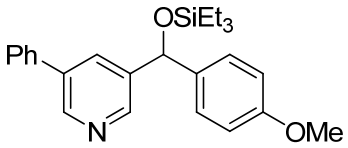
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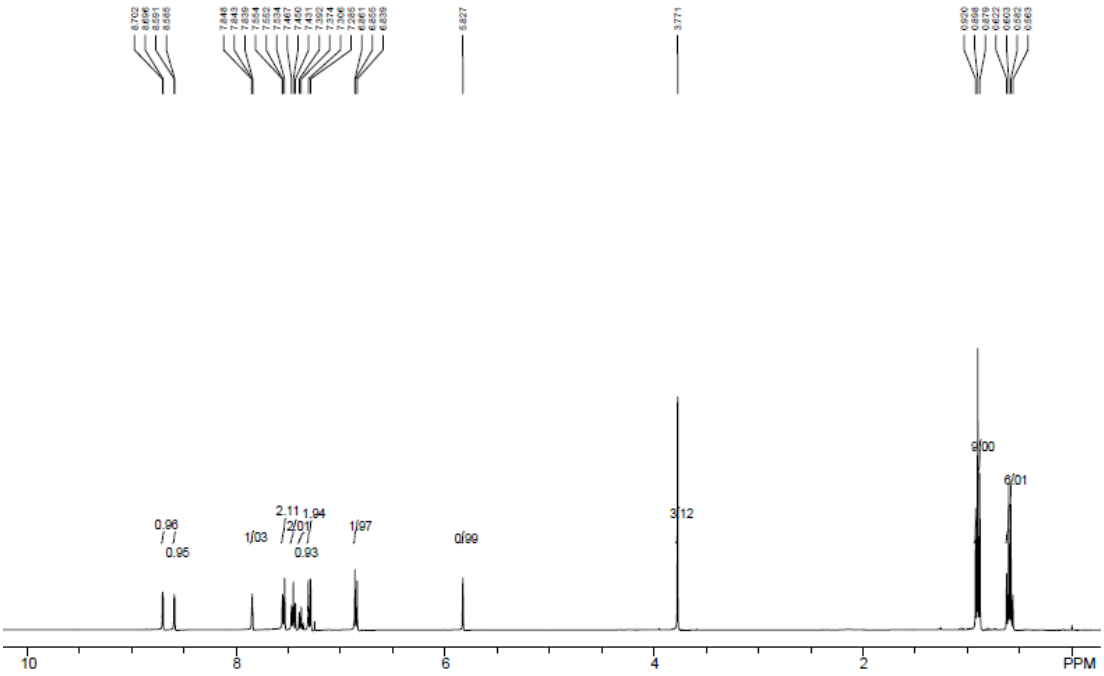
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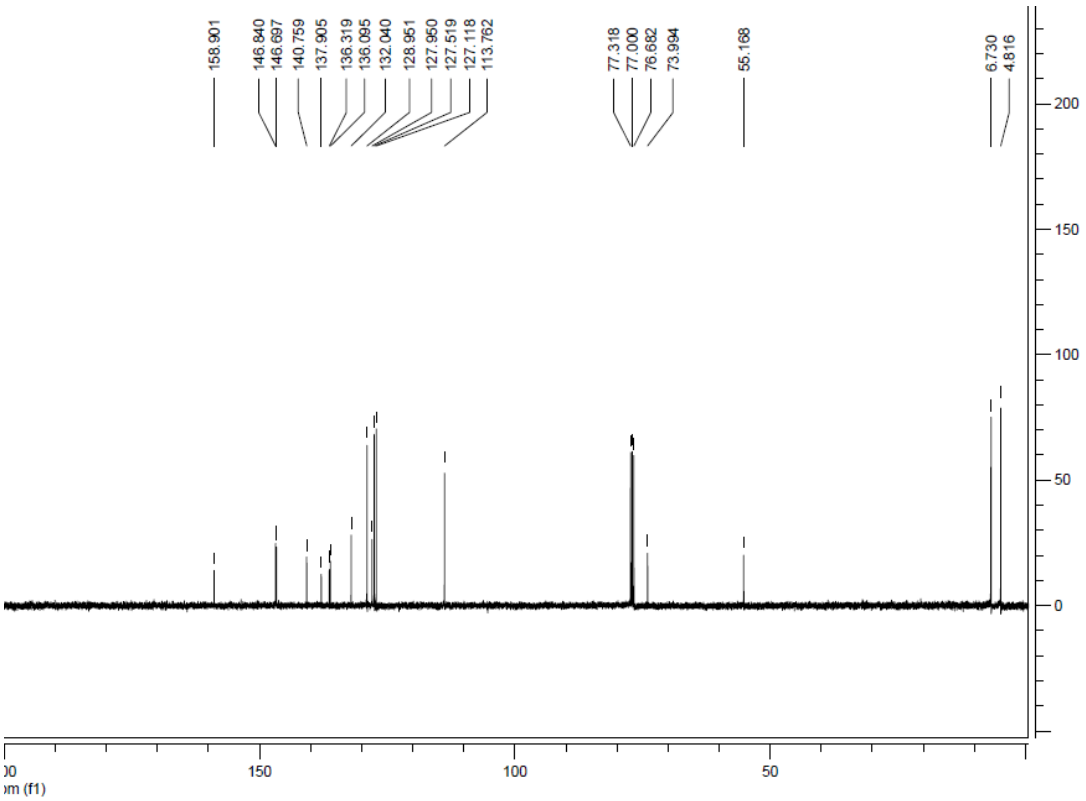

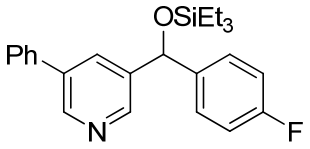

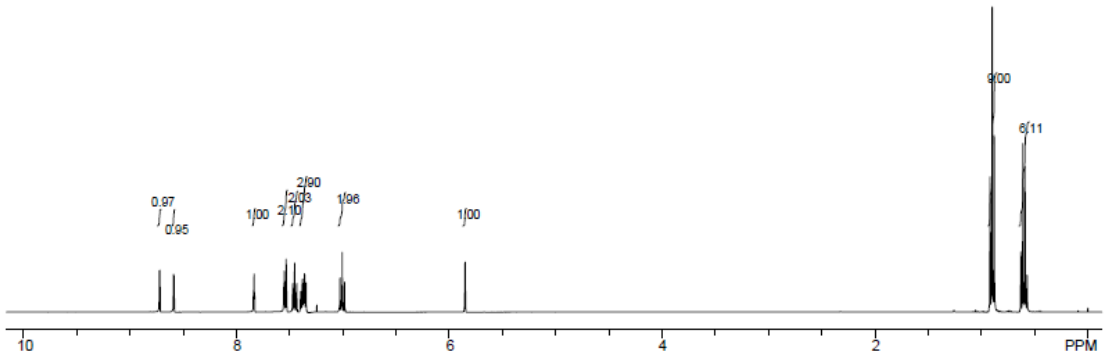

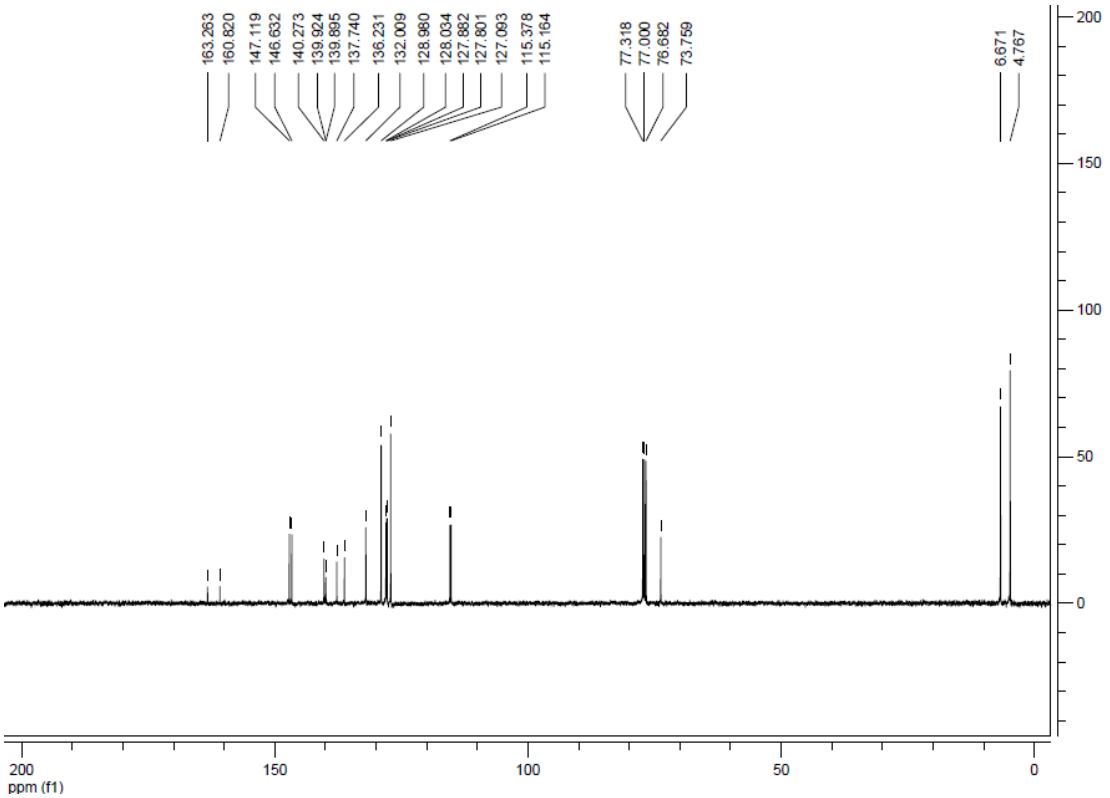

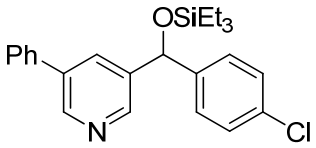

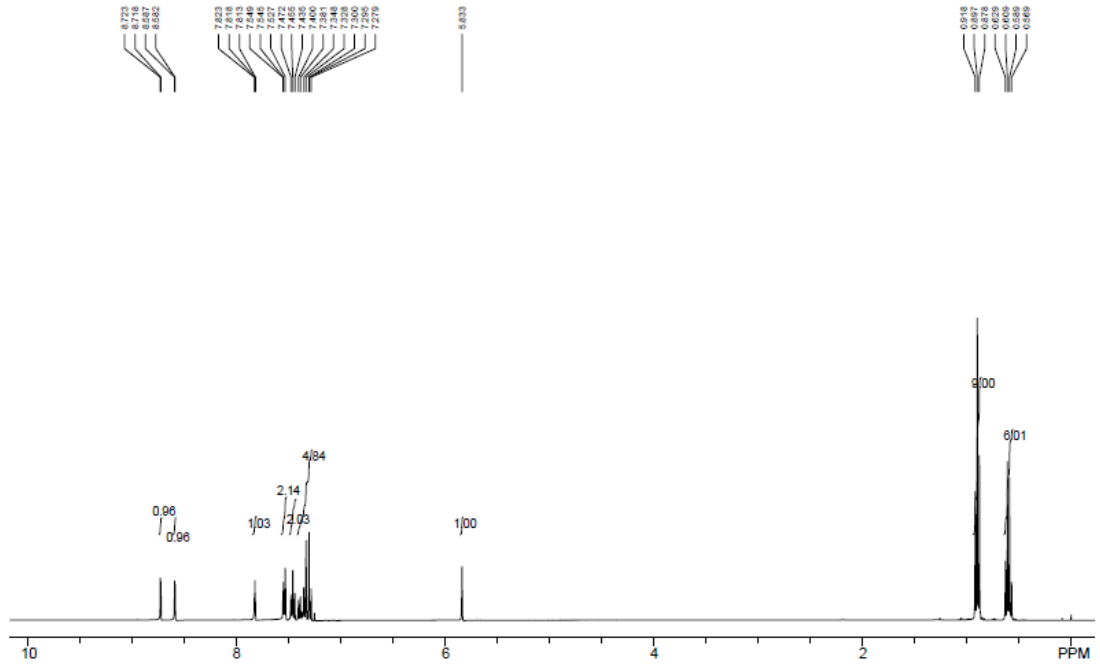

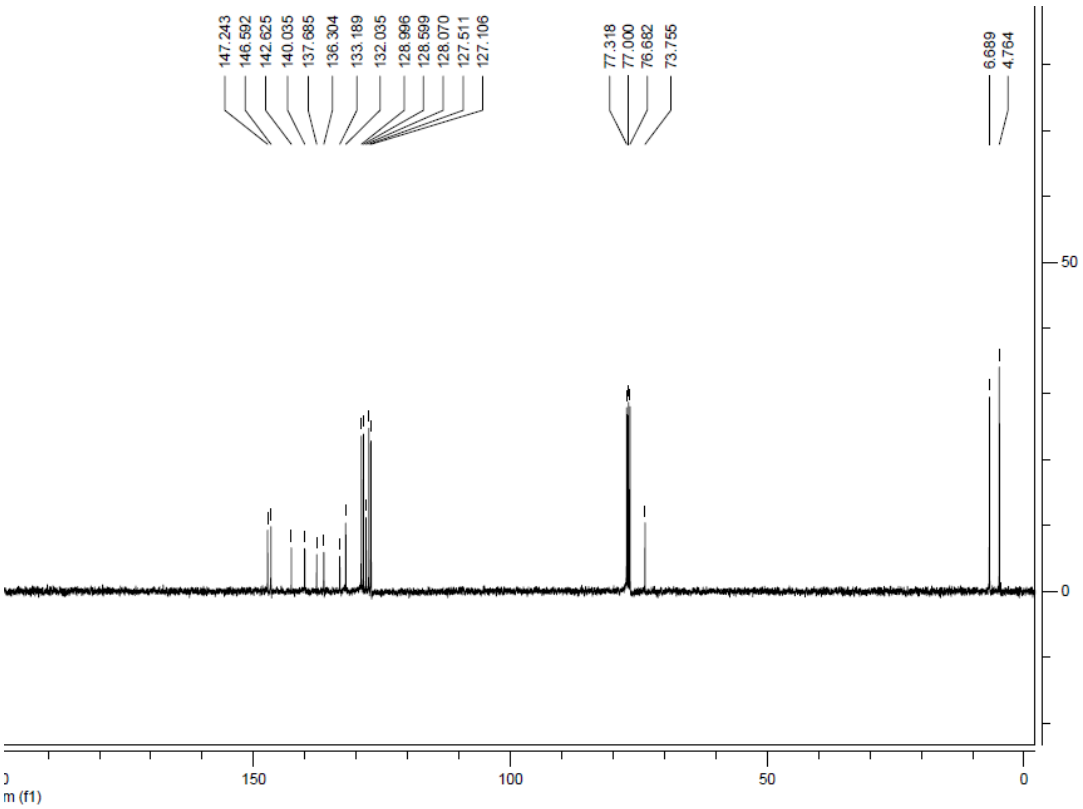

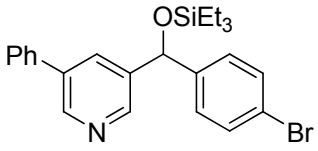

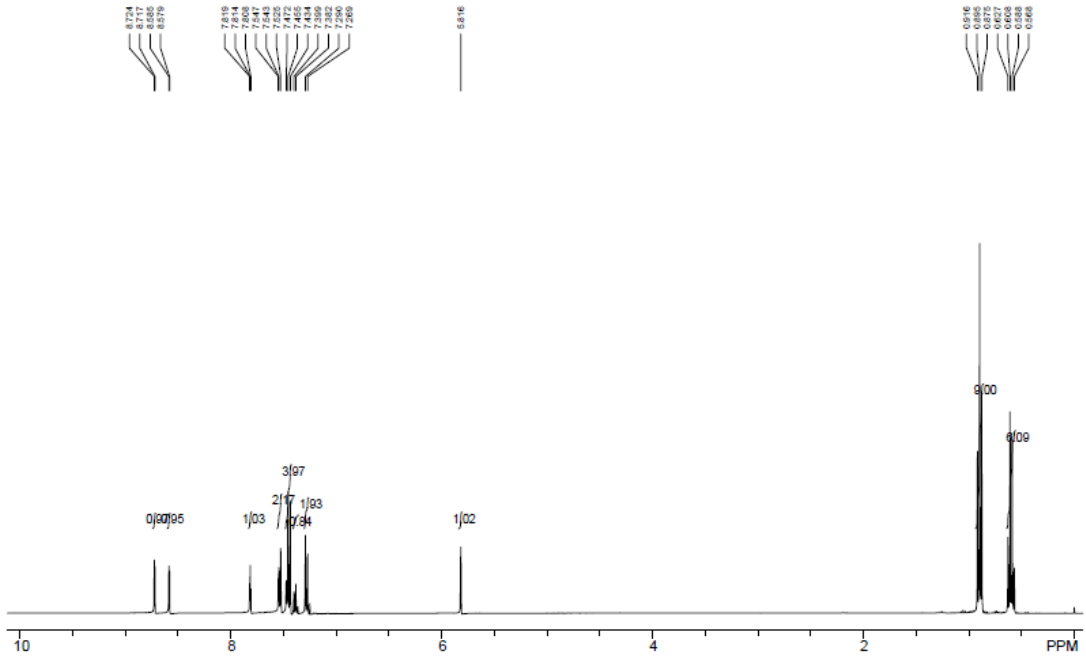

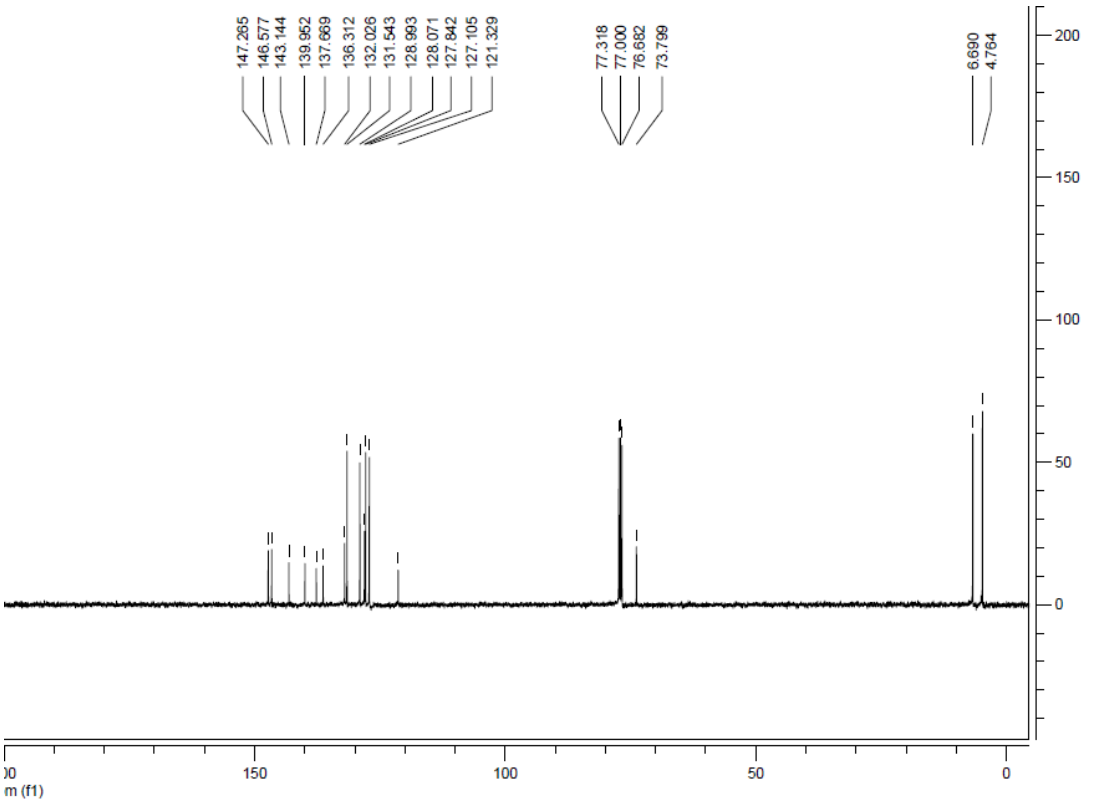

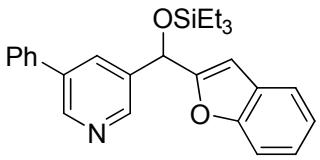

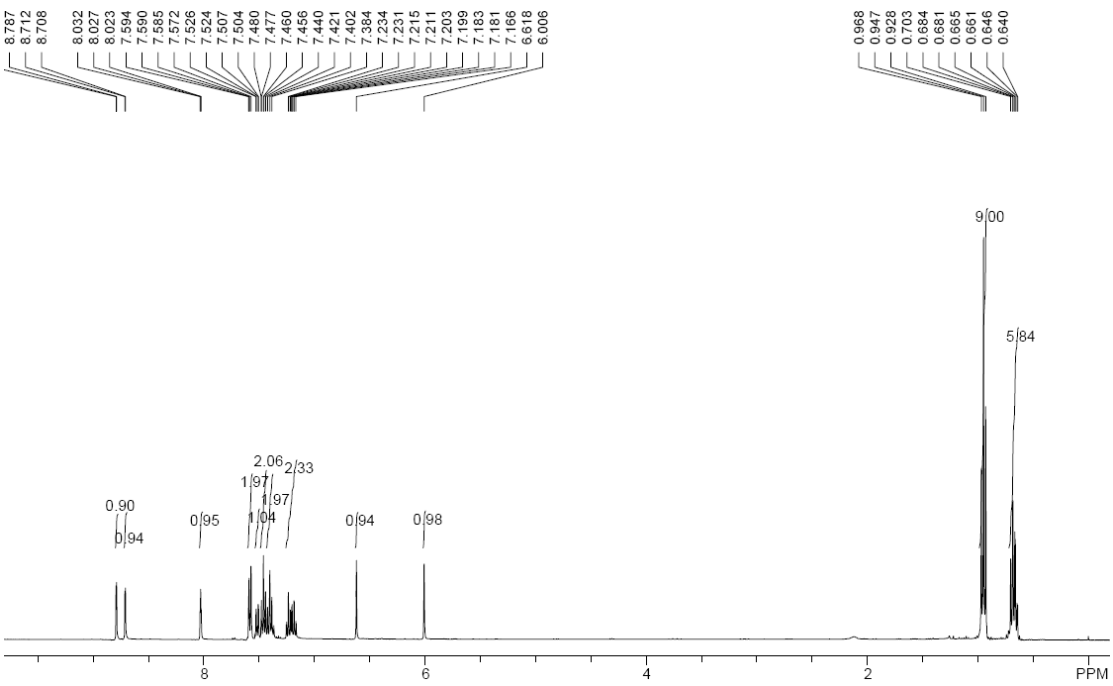

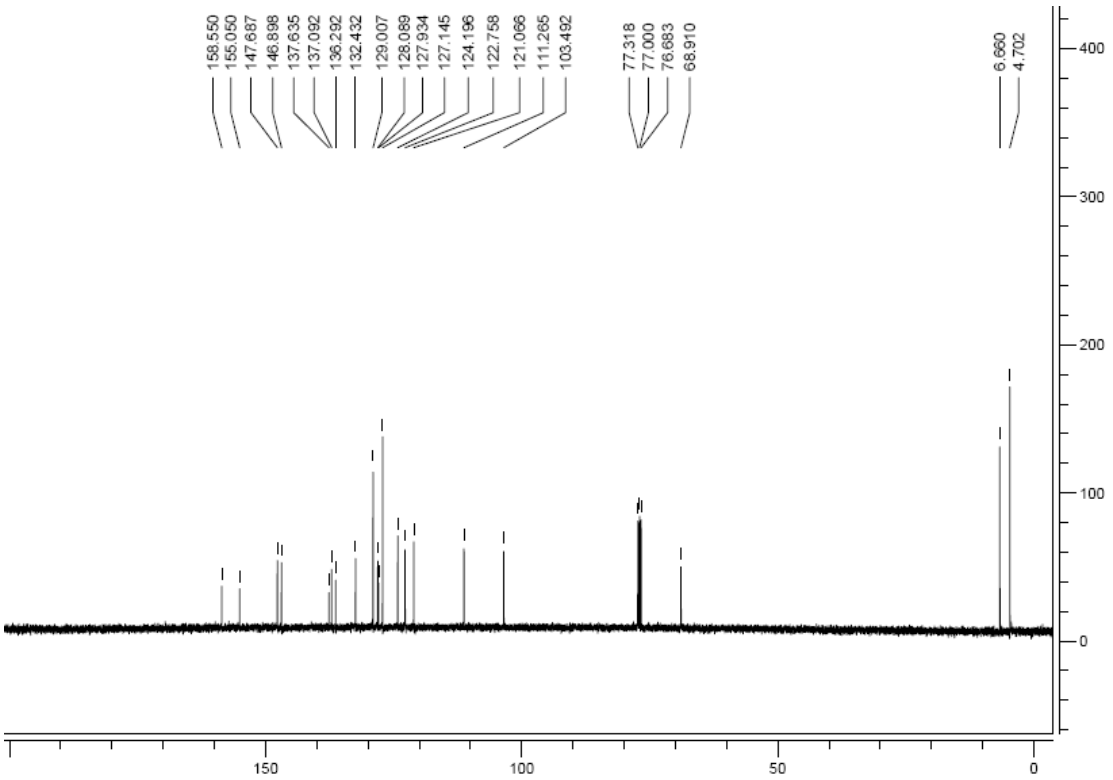

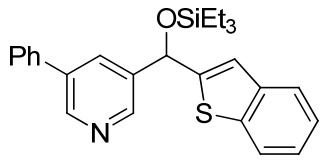

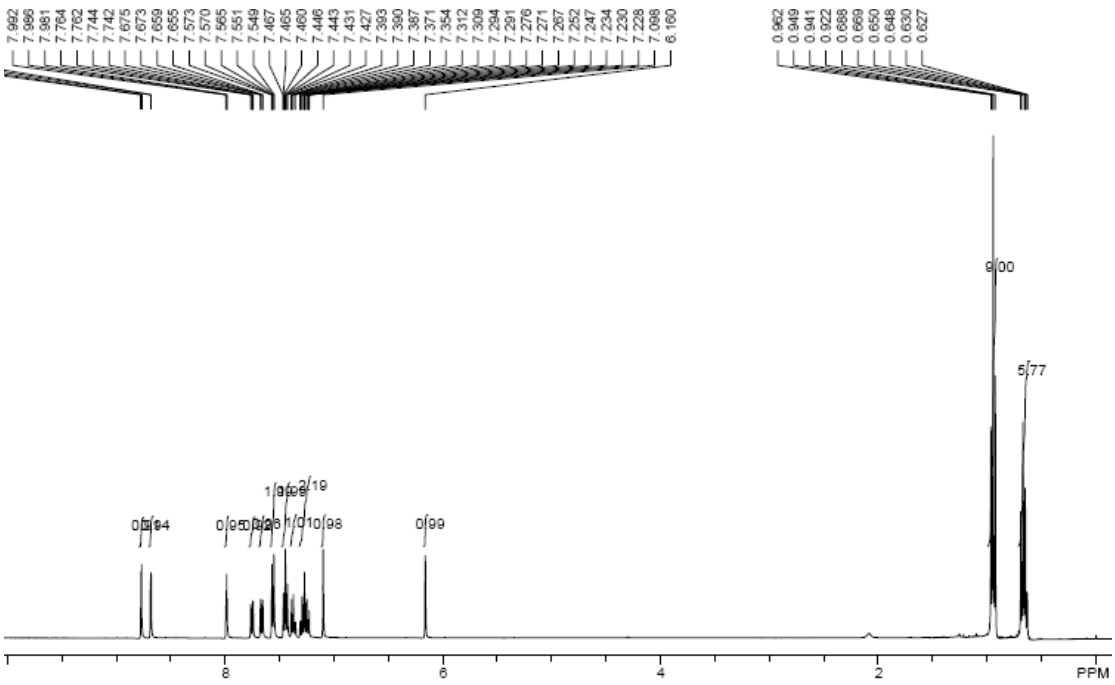

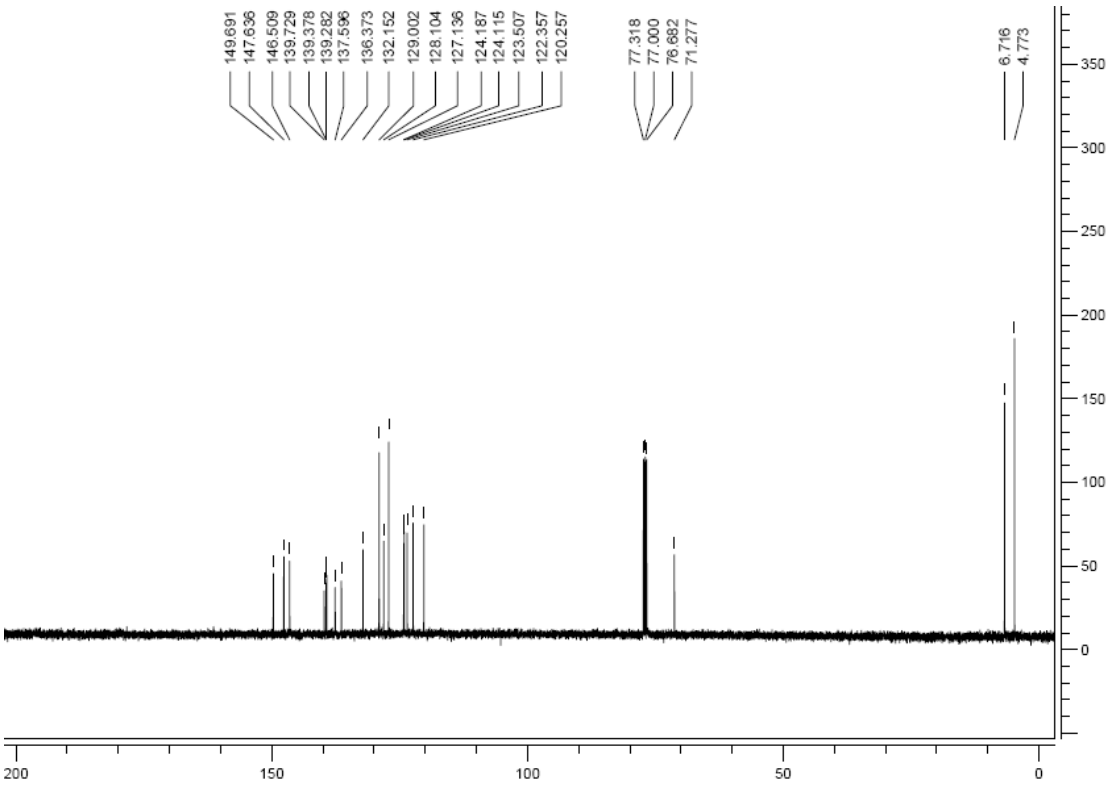

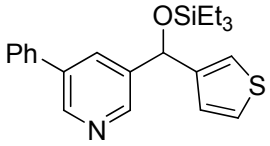

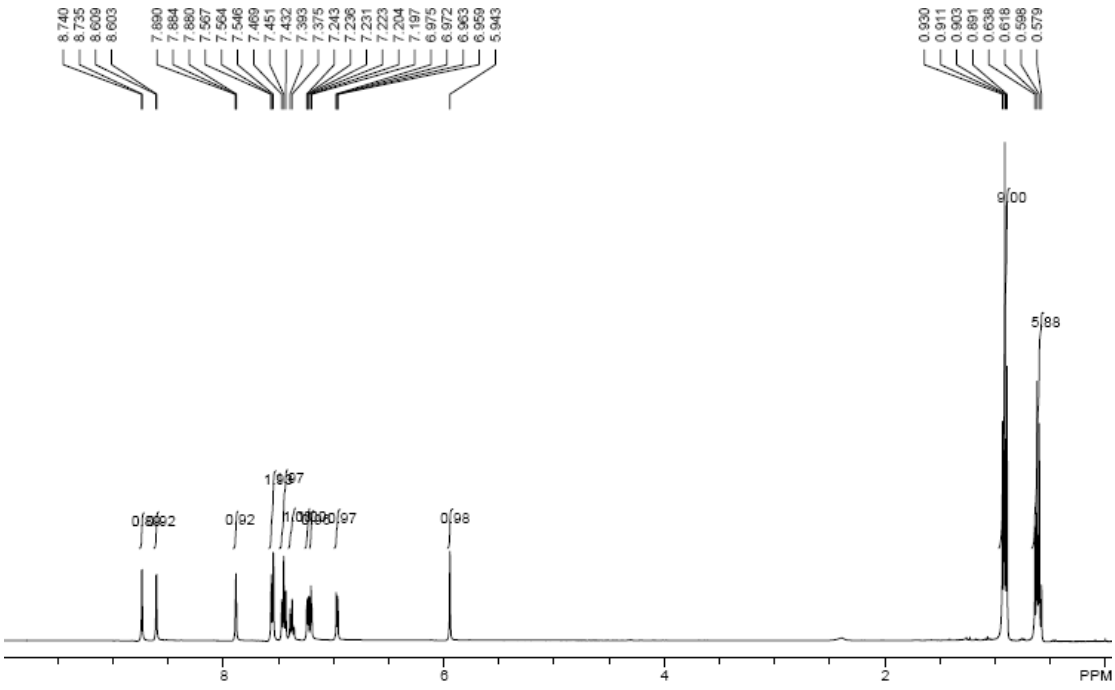

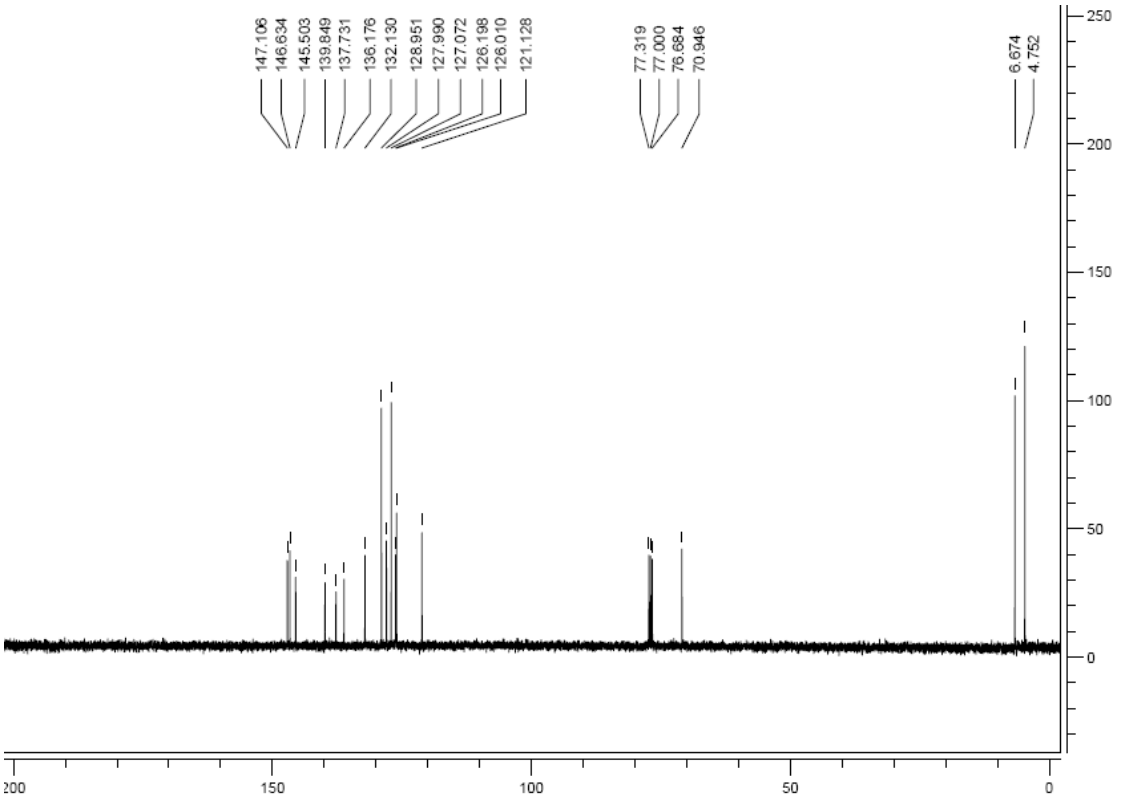

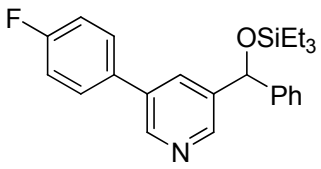

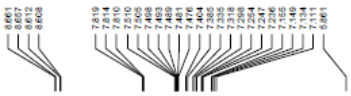

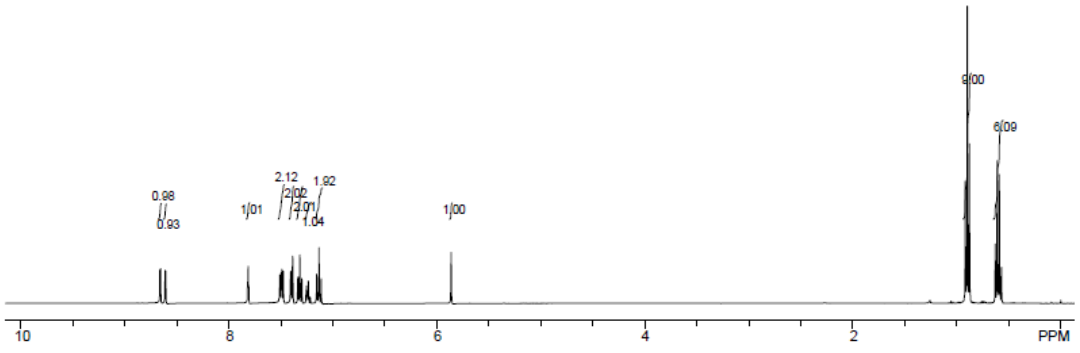

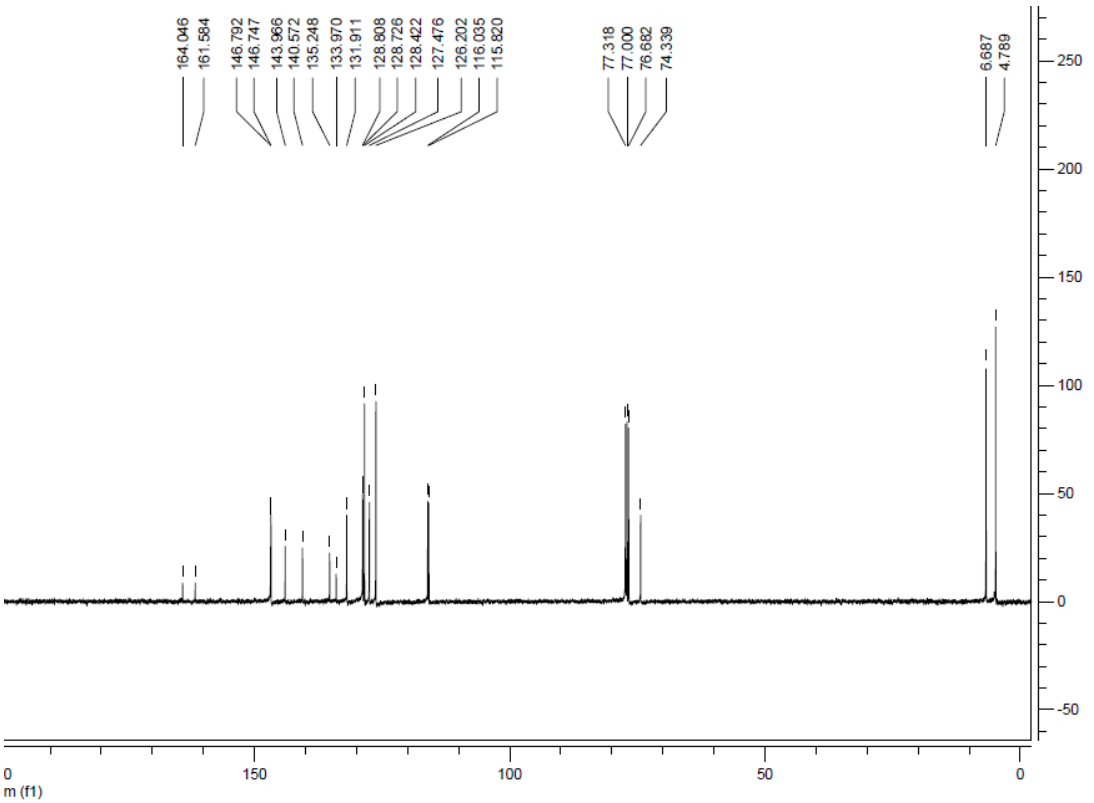

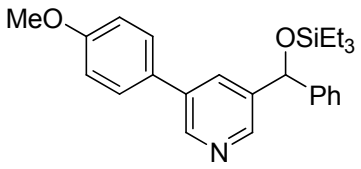

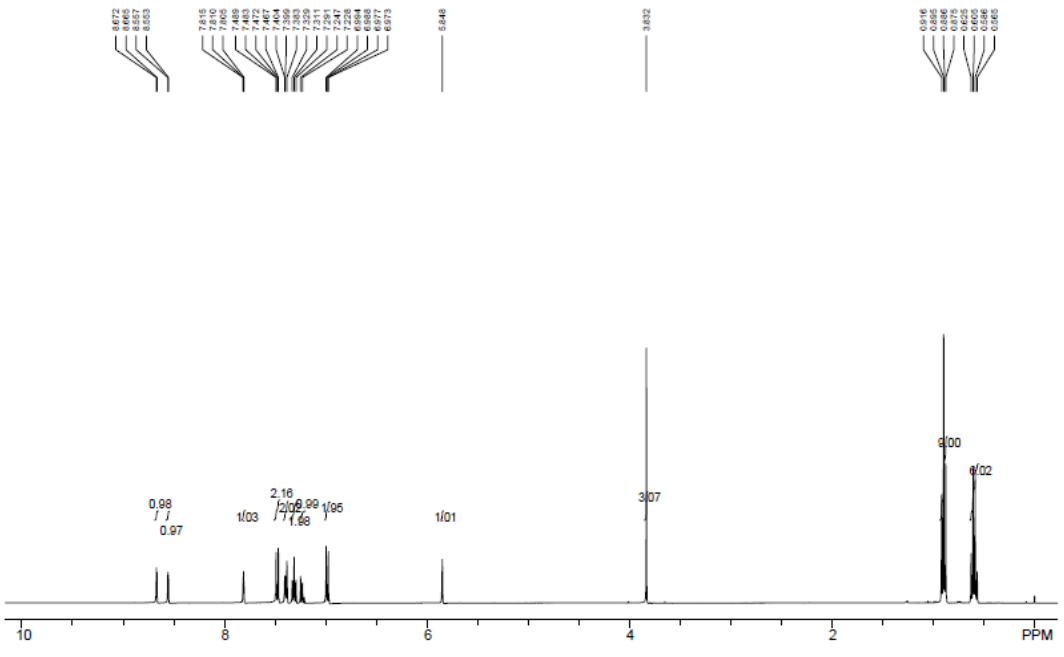

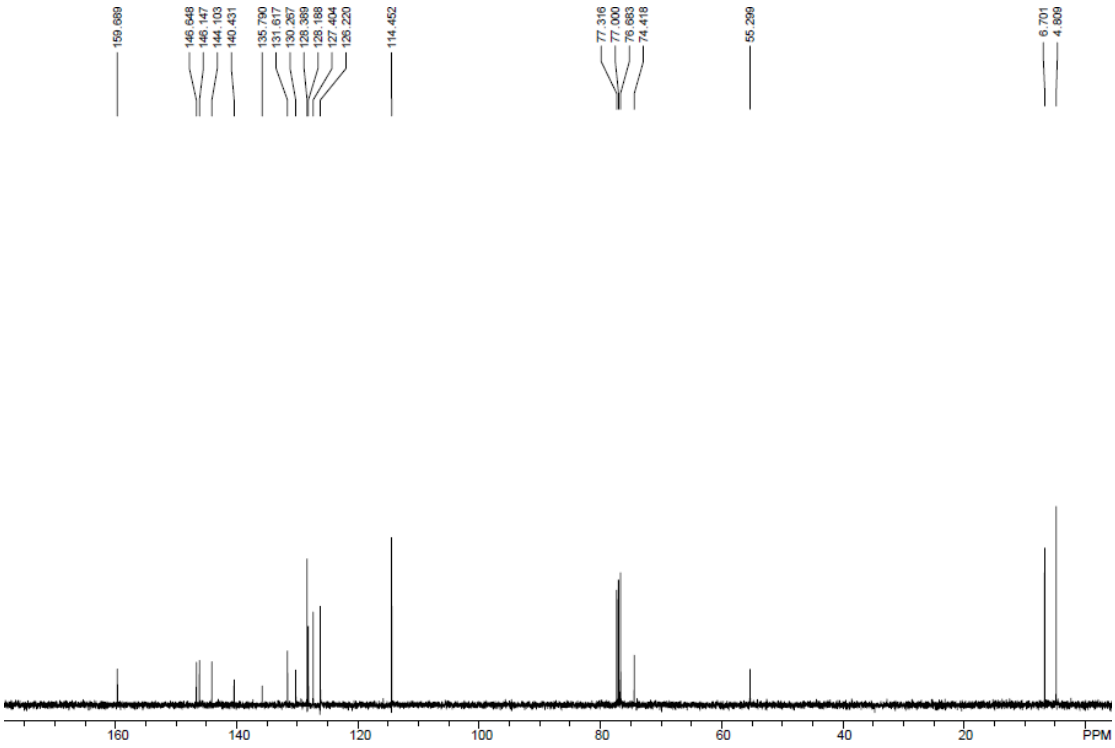

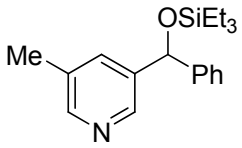

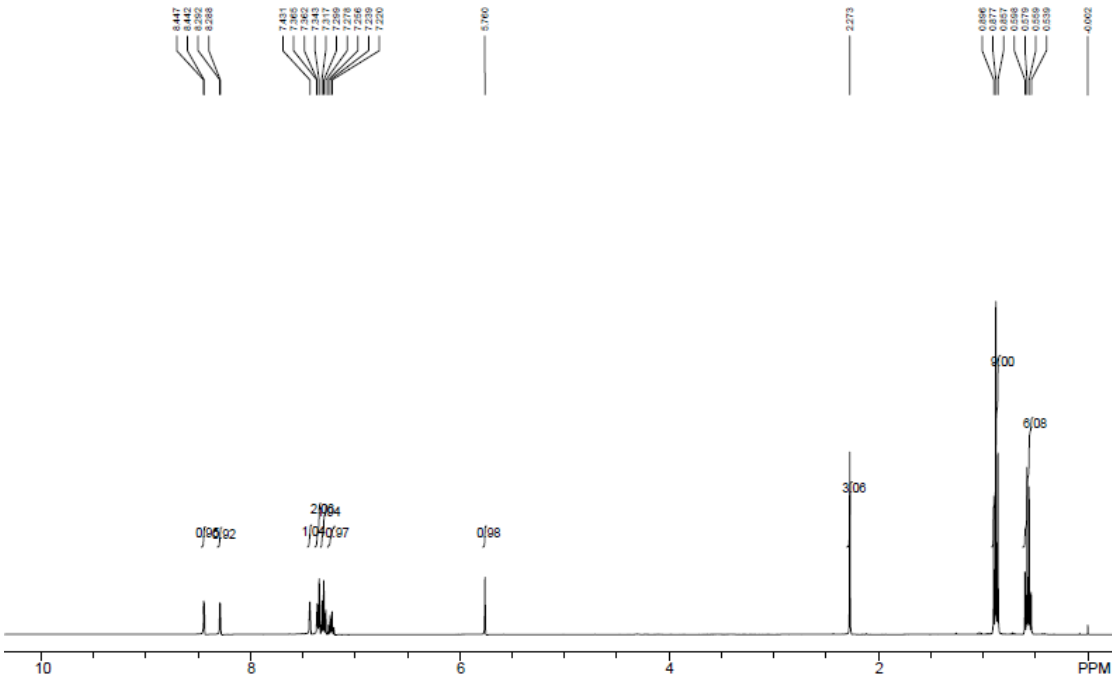

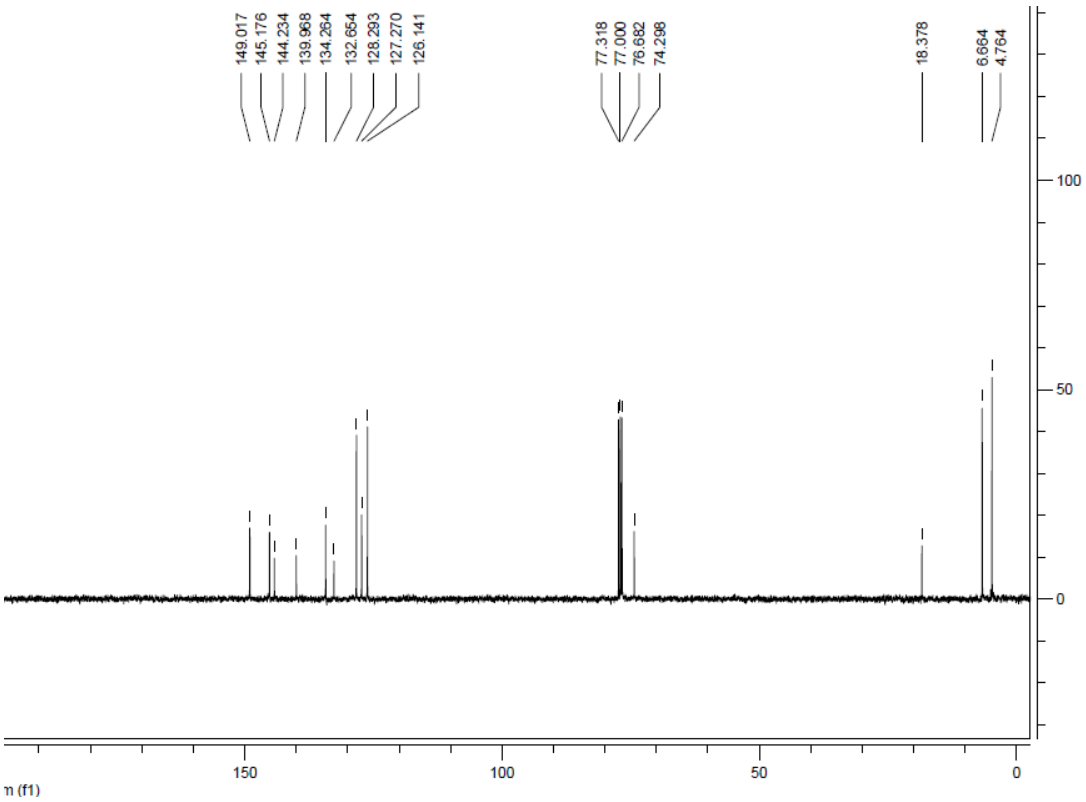

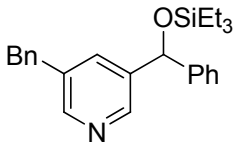

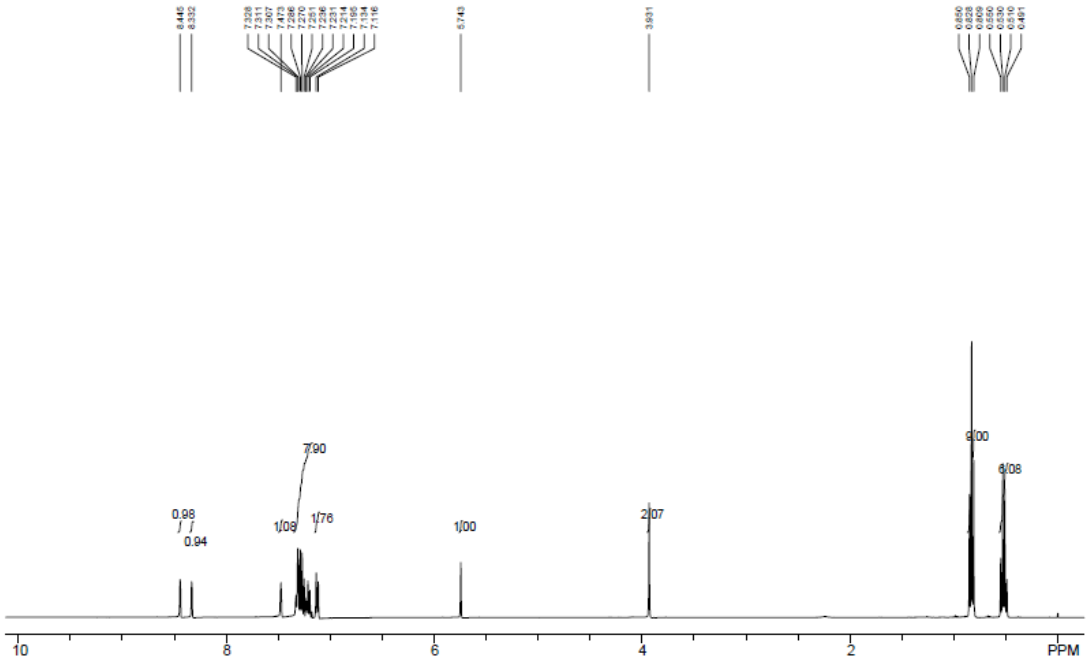

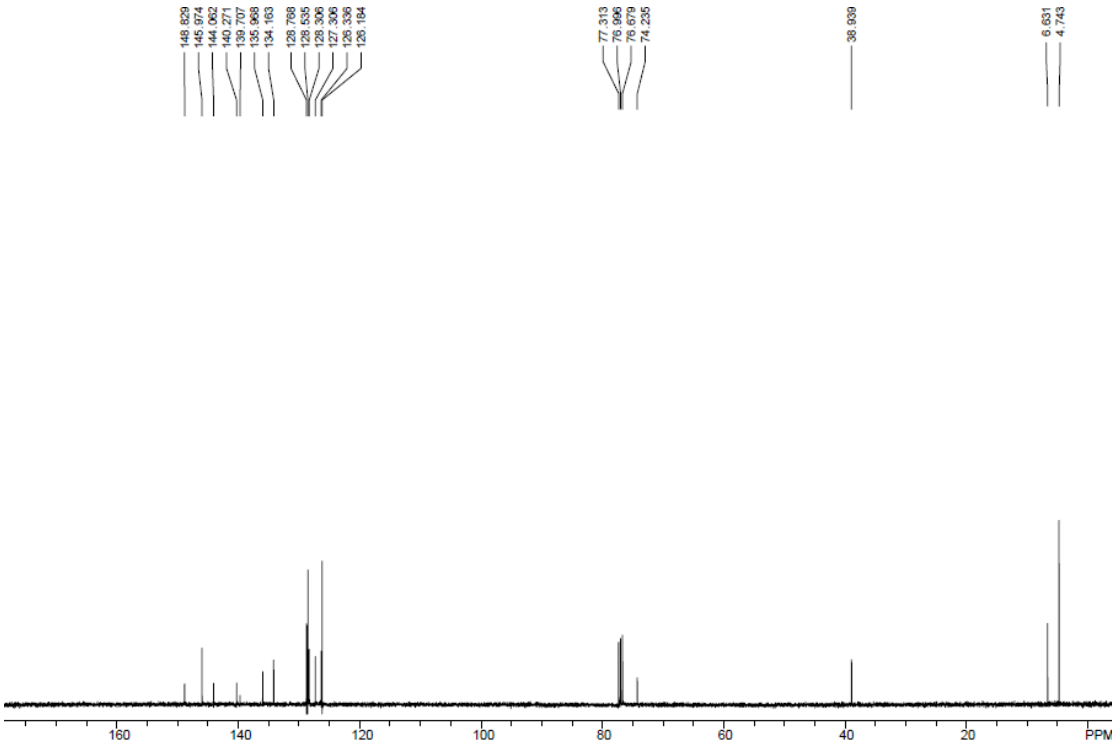

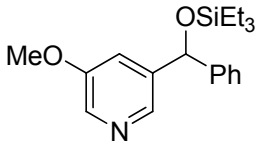

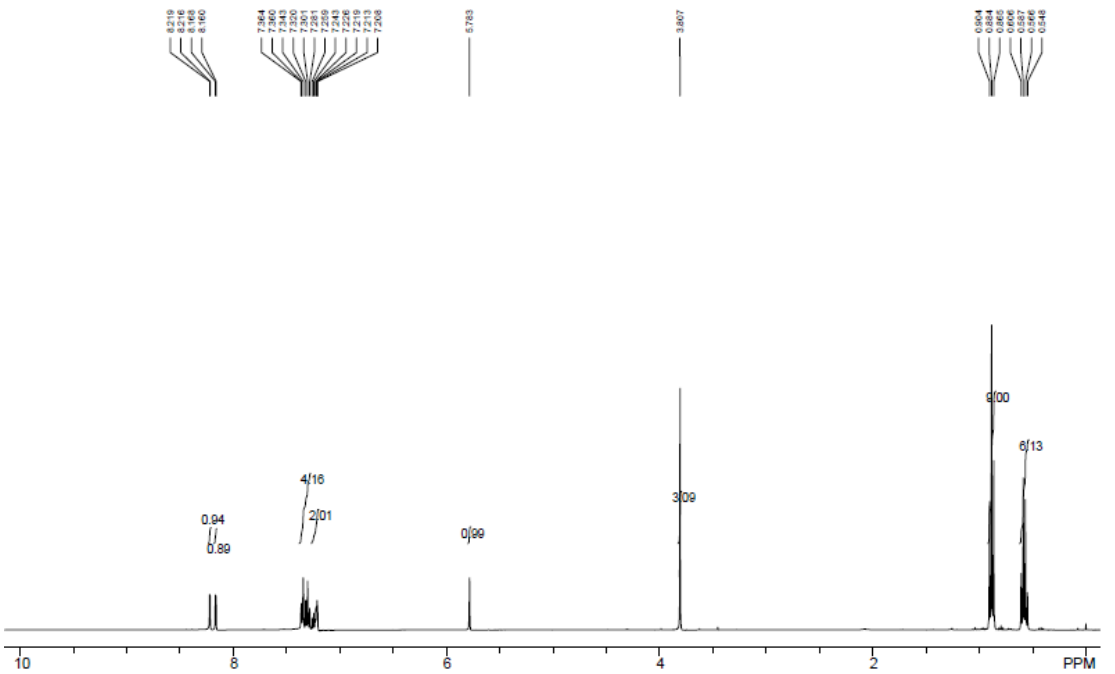

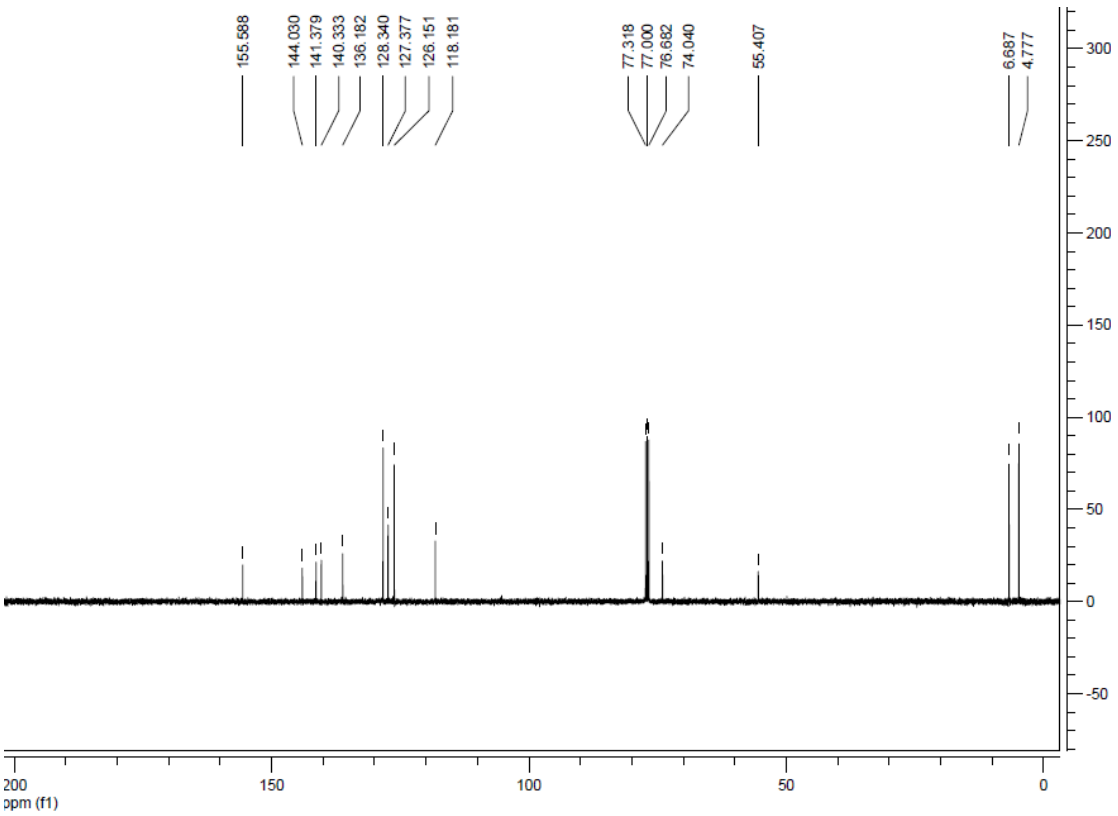
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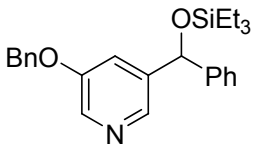
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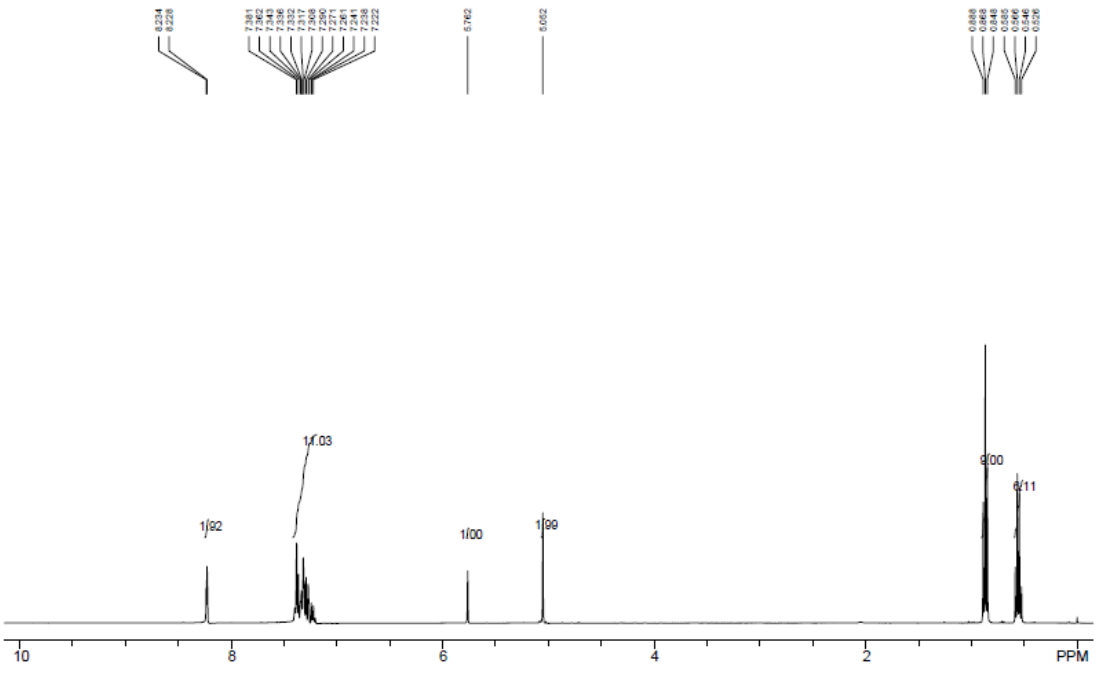
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