



Supporting Information

for

An atom-economical addition of methyl azaarenes with aromatic aldehydes via benzylic C(sp³)–H bond functionalization under solvent- and catalyst-free conditions

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Experimental procedures, compound characterization data, and NMR spectra

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1. Experimental section

i) Chemicals

Ammonium β zeolite ($\text{NH}_4\beta$) ($\text{Si}/\text{Al} = 19$) was purchased from Alfa Aesar, England and calcined at $500\text{ }^\circ\text{C}$ for 10 h to afford $\text{H}\beta$. MCM-41 ($\text{Si}/\text{Al} = 30$) was synthesized [1], and H-mordenite ($\text{Si}/\text{Al} = 12.5$) was purchased from Zeolyst C. V. Azaarenes and benzaldehyde derivatives were purchased from Sigma-Aldrich. All remaining chemicals used in this study were used as received.

ii) General information

^1H NMR spectra were recorded at 300, 400, or 500 MHz and ^{13}C NMR spectra at 75, 100, or 125 MHz in CDCl_3 . The chemical shifts (δ) are described in ppm relative to TMS as an internal standard for ^1H NMR and CDCl_3 for ^{13}C NMR spectra. Coupling constants (J) are reported in Hz, and multiplicities are indicated as follows: s (singlet), br s (broad singlet), d (doublet), dd (doublet of doublet), t (triplet), m (multiplet). The mass spectrometric analysis was performed using a high-resolution Q-TOF mass spectrometer. The GC analysis was carried out using a GC Shimadzu (GC-2014) gas chromatograph equipped with an FID detector and a capillary column (EB-5, length 30 m, inner diameter 0.25 mm, film 0.25 mm). TLC inspections were

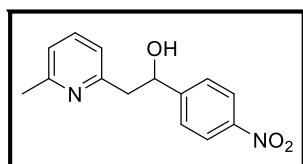
carried out on silica gel 60 F₂₅₄ plates. Column chromatography was performed on silica gel (100–200 mesh) using *n*-hexane/EtOAc as an eluent.

iii) General procedure

Reactions were performed in a magnetically stirred 15 mL sealed vial and placed in a temperature-controlled oil bath. The appropriate benzaldehyde (1 mmol) was added to a pyridine or quinoline compounds (2 mmol), and the reaction mixture was allowed to stir at 135 °C for 24 hours. After the disappearance of the starting materials (as monitored by TLC analysis) or after the appropriate time, the reaction mixture was cooled to room temperature. The crude residue was further purified by column chromatography using silica gel (100–200 mesh) to afford pure products. All the products were identified on the basis of NMR and mass spectral data.

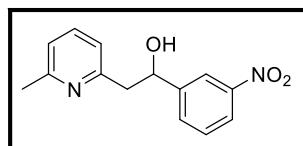
2. Spectroscopic data of all products

2-(6-Methylpyridin-2-yl)-1-(4-nitrophenyl)ethan-1-ol (3a)^[2]



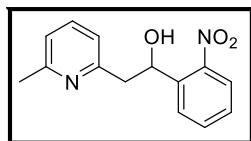
¹H NMR (300 MHz, CDCl₃) δ (ppm) = 8.20 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 7.4 Hz, 1H), 5.25 (dd, *J* = 3.0, 8.5 Hz, 1H), 3.15-2.99 (m, 2H), 2.57 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 158.12, 157.42, 151.62, 147.03, 137.41, 126.54, 123.50, 121.61, 120.59, 72.50, 44.46, 24.25.

2-(6-Methylpyridin-2-yl)-1-(3-nitrophenyl)ethan-1-ol (3b)^[2]



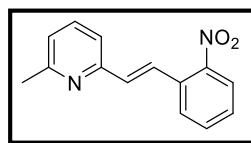
¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.30 (s, 1H), 8.13-8.10 (m, 1H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.53 (qt, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 5.24 (dd, *J* = 3.2, 8.6 Hz, 1H), 3.15-3.02 (m, 2H), 2.57 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ (ppm) = 158.22, 157.47, 148.24, 146.42, 137.40, 131.96, 129.18, 122.14, 121.60, 120.95, 120.59, 72.39, 44.56, 24.31.

2-(6-Methylpyridin-2-yl)-1-(2-nitrophenyl)ethan-1-ol (3c)^[2]



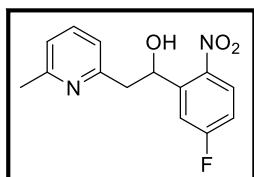
¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.97 (dd, *J* = 7.9, 16.9 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.89 (brs, 1H), 5.63 (dd, *J* = 2.1, 9.0 Hz, 1H), 3.30 (dd, *J* = 2.1, 14.8 Hz, 1H), 3.02-2.97 (m, 1H), 2.57 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) = 158.70, 157.31, 147.53, 139.67, 137.45, 133.43, 128.55, 127.83, 124.17, 121.52, 120.60, 69.16, 44.19, 24.32.

(E)-2-Methyl-6-(2-nitrostyryl)pyridine (4c)



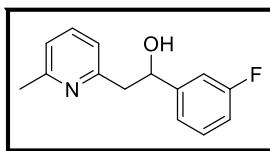
¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.99-7.95 (m, 2H), 7.81-7.79 (m, 1H), 7.62-7.56 (m, 2H), 7.45-7.40 (m, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 16.0 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 2.58 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 158.49, 154.28, 148.24, 136.74, 133.65, 133.09, 132.54, 128.42, 127.27, 124.72, 122.50, 118.93, 24.57; HRMS (ESI): m/z calculated for C₁₄H₁₃O₂N₂[M+H]⁺, 241.09715, found: 241.09674.

1-(5-Fluoro-2-nitrophenyl)-2-(6-methylpyridin-2-yl)ethan-1-ol (3d)



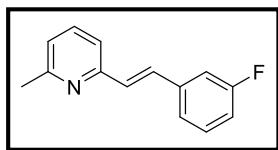
¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.08 (dd, *J* = 5.0, 9.0 Hz, 1H), 7.72 (dd, *J* = 2.8, 9.7 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.11-7.06 (m, 2H), 6.98 (d, *J* = 7.7 Hz, 1H), 5.68 (d, *J* = 9.7 Hz, 1H), 3.30 (dd, *J* = 2.2, 14.9 Hz, 1H), 2.94 (dd, *J* = 8.9, 14.9 Hz, 1H), 2.57 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 166.74, 164.18, 158.37, 157.34, 144.15 (d, *J* = 8.7 Hz), 143.20, 137.56, 127.40 (d, *J* = 9.8 Hz), 121.67, 120.57, 115.7 (d, *J* = 25.0 Hz), 114.90 (d, *J* = 23.9 Hz), 69.13, 43.76, 24.29; HRMS (ESI): m/z calculated for C₁₄H₁₄O₃N₂F[M+H]⁺, 277.0983, found: 277.0978.

1-(3-Fluorophenyl)-2-(6-methylpyridin-2-yl)ethan-1-ol (3e)^[2]



¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.51 (t, *J* = 7.7 Hz, 1H), 7.32-7.26 (m, 1H), 7.18-7.15 (m, 2H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.96-6.89 (m, 2H), 5.13 (dd, *J* = 4.6, 7.4 Hz, 1H), 3.06-3.04 (m, 2H), 2.56 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) = 162.95 (d, *J* = 245.7 Hz), 158.72, 157.37, 146.94 (d, *J* = 7.2 Hz), 137.23, 129.67 (d, *J* = 8.03 Hz), 121.37, 120.56, 114.04, 113.76, 112.93, 112.64, 72.71, 44.95, 24.32.

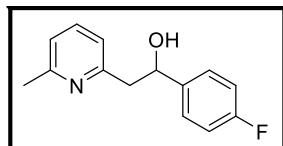
(E)-2-(3-Fluorostyryl)-6-methylpyridine (4e)^[2]



¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.58-7.53 (m, 2H), 7.35-7.28 (m, 3H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 16.1 Hz, 1H), 7.04 (d, *J* = 7.7 Hz, 1H), 7.00-6.95 (m, 1H), 2.59 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) = 163.09 (d, *J* = 244.9 Hz), 158.36, 154.51, 139.14 (d, *J*

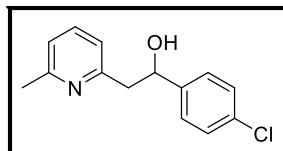
$= 8.0$ Hz), 136.69, 131.07, 130.05 (d, $J = 8.8$ Hz), 129.59, 122.96, 122.01, 119.12, 114.90 (d, $J = 21.6$ Hz), 113.25 (d, $J = 21.6$ Hz), 24.61.

1-(4-Fluorophenyl)-2-(6-methylpyridin-2-yl)ethan-1-ol (3f)^[2]



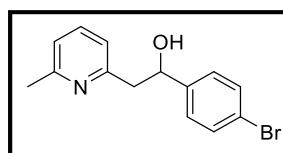
^1H NMR (500 MHz, CDCl_3) δ (ppm) = 7.50 (t, $J = 7.6$ Hz, 1H), 7.40-7.37 (m, 2H), 7.05-7.00 (m, 3H), 6.89 (d, $J = 7.6$ Hz, 1H), 5.11 (dd, $J = 3.9, 8.0$ Hz, 1H), 3.08-3.00 (m, 2H), 2.55 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) = 161.95 (d, $J = 244.2$ Hz), 158.84, 157.36, 139.91 (d, $J = 2.7$ Hz), 137.21, 127.37 (d, $J = 8.2$ Hz), 121.33, 120.58, 115.13, 114.86, 72.73, 45.26, 24.29.

1-(4-Chlorophenyl)-2-(6-methylpyridin-2-yl)ethan-1-ol (3g)^[2]



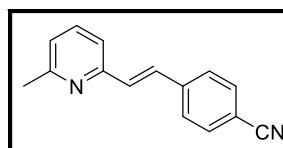
^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.51 (t, $J = 7.7$ Hz, 1H), 7.37-7.29 (m, 4H), 7.04 (d, $J = 7.7$ Hz, 1H), 6.89 (d, $J = 7.5$ Hz, 1H), 5.11 (t, $J = 6.1$ Hz, 1H), 3.03 (d, $J = 5.8$ Hz, 2H), 2.55 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) = 158.76, 157.38, 142.70, 137.24, 132.73, 128.36, 127.19, 121.37, 120.57, 72.69, 45.04, 24.33.

1-(4-Bromophenyl)-2-(6-methylpyridin-2-yl)ethan-1-ol (3h)



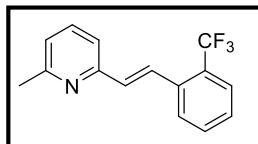
^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.51 (t, $J = 7.6$ Hz, 1H), 7.47-7.44 (m, 2H), 7.32-7.29 (m, 2H), 7.05 (d, $J = 7.6$ Hz, 1H), 6.89 (d, $J = 7.6$ Hz, 1H), 5.09 (t, $J = 5.9$ Hz, 1H), 3.06-2.98 (m, 2H), 2.55 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) = 158.73, 157.38, 143.23, 137.24, 131.30, 127.56, 121.37, 120.57, 72.72, 44.98, 24.33; HRMS (ESI): m/z calculated for $\text{C}_{14}\text{H}_{15}\text{ONBr}[\text{M}+\text{H}]^+$, 292.03315, found: 292.03254.

(E)-4-(2-(6-Methylpyridin-2-yl)vinyl)benzonitrile (4i)^[2]



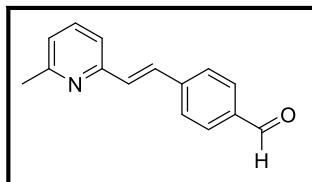
¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.64 (s, 4H), 7.62-7.57 (m, 2H), 7.26-7.22 (m, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 2.59 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) = 158.55, 153.84, 141.25, 136.79, 132.39, 131.72, 130.19, 127.31, 122.56, 119.66, 118.86, 111.02, 24.58.

(E)-2-Methyl-6-(2-(trifluoromethyl)styryl)pyridine (4j)^[2]



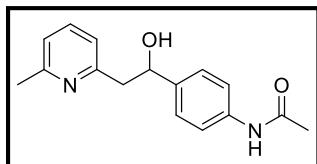
¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.89-7.82 (m, 2H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.59-7.52 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 15.8 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 2.59 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 158.40, 154.73, 136.67, 135.89, 132.78, 131.89, 128.04, 127.72, 127.65, 127.30, 125.99-125.72 (m), 122.99, 122.18, 118.52, 24.57.

(E)-4-(2-(6-Methylpyridin-2-yl)vinyl)benzaldehyde (4k)



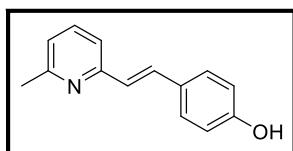
¹H NMR (400 MHz, CDCl₃) δ (ppm) = 10.00 (s, 1H), 7.89-7.87 (m, 2H), 7.72-7.70 (m, 2H), 7.67-7.63 (m, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.31-7.24 (m, 2H), 7.07 (d, *J* = 7.5 Hz, 1H), 2.60 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 191.54, 158.53, 154.15, 142.83, 136.76, 135.64, 131.58, 130.85, 130.13, 127.41, 122.42, 119.55, 24.60; HRMS (ESI): m/z calculated for C₁₅H₁₄ON[M+H]⁺, 224.10699, found: 224.10648.

***N*-(4-(1-Hydroxy-2-(6-methylpyridin-2-yl)ethyl)phenyl)acetamide (3l)**



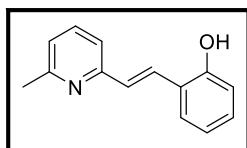
¹H NMR (500 MHz, CDCl₃+DMSO-d₆) δ (ppm) = 7.51 (t, *J* = 7.7 Hz, 1H), 7.46-7.35 (m, 4H), 7.04 (d, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 7.7 Hz, 1H), 5.09 (dd, *J* = 4.0, 8.1 Hz, 1H), 3.11-3.01 (m, 2H), 2.55 (s, 3H), 2.16 (s, 3H); ¹³C NMR (75 MHz, CDCl₃+DMSO-d₆) δ (ppm) = 168.03, 157.97, 156.28, 138.90, 137.14, 136.12, 125.34, 120.25, 120.04, 118.66, 72.02, 45.26, 39.47, 23.50, 23.39; HRMS (ESI): m/z calculated for C₁₆H₁₉O₂N₂ [M+H]⁺, 271.1441 found: 271.1434.

(E)-4-(2-(6-Methylpyridin-2-yl)vinyl)phenol (4m)



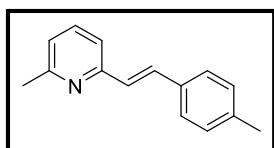
¹H NMR (400 MHz, CDCl₃+DMSO-d₆) δ (ppm) = 7.62 (t, *J* = 7.7 Hz, 1H), 7.54-7.46 (m, 3H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.06-7.01 (m, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 2.47 (s, 3H); ¹³C NMR (75 MHz, CDCl₃+DMSO-d₆) δ (ppm) = 157.19, 154.76, 136.03, 131.61, 127.71, 127.30, 124.54, 120.50, 117.62, 115.17, 23.85; HRMS (ESI): m/z calculated for C₁₄H₁₄ON[M+H]⁺, 212.1070 found: 212.1066.

(E)-2-(2-(6-Methylpyridin-2-yl)vinyl)phenol (4n)



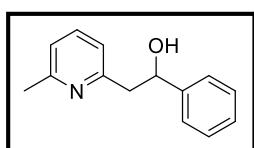
¹H NMR (400 MHz, CDCl₃+DMSO-d₆) δ (ppm) = 7.88 (d, *J* = 16.2 Hz, 1H), 7.65-7.53 (m, 2H), 7.28-7.24 (m, 1H), 7.14-6.76 (m, 5H), 2.49 (s, 3H); ¹³C NMR (75 MHz, CDCl₃+DMSO-d₆) δ (ppm) = 157.48, 155.39, 154.78, 136.85, 129.11, 127.32, 126.85, 123.13, 121.29, 119.21, 115.80, 24.19; HRMS (ESI): m/z calculated for C₁₄H₁₆O₂N[M+H+H₂O]⁺, 230.1176, found: 230.1170.

(E)-2-Methyl-6-(4-methylstyryl)pyridine (4o)^[2]



¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.56-7.51 (m, 2H), 7.48-7.46 (m, 2H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.18-7.10 (m, 3H), 7.00 (d, *J* = 7.5 Hz, 1H), 2.58 (s, 3H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 158.19, 155.31, 138.14, 136.58, 134.00, 132.30, 129.37, 127.46, 126.97, 121.46, 118.58, 24.64, 21.28.

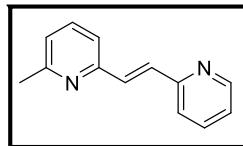
2-(6-Methylpyridin-2-yl)-1-phenylethan-1-ol (3p)^[2]



¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.52 (t, *J* = 7.5 Hz, 1H), 7.44-7.41 (m, 2H), 7.35-7.31 (m, 2H), 7.27-7.23 (m, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 7.5 Hz, 1H), 5.16-5.12 (m,

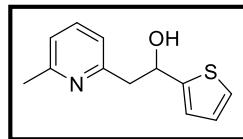
1H), 3.13-3.11 (m, 2H), 2.57 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) = 158.72, 157.17, 144.02, 137.42, 132.90, 129.95, 128.23, 127.17, 125.77, 121.46, 120.86, 73.44, 45.28, 23.94.

(E)-2-Methyl-6-(2-(pyridin-2-yl)vinyl)pyridine (4q)



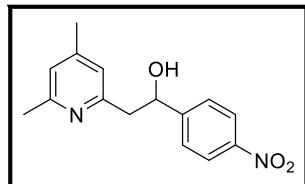
^1H NMR (400 MHz, CDCl_3) δ (ppm) = 8.62 (d, J = 4.7 Hz, 1H), 7.71-7.62 (m, 3H), 7.56 (t, J = 7.7 Hz, 1H), 7.46 (d, J = 7.8 Hz, 1H), 7.26 (d, J = 6.8 Hz, 1H), 7.17 (dd, J = 1.1, 4.8 Hz, 1H), 7.05 (d, J = 7.7 Hz, 1H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 158.37, 155.19, 154.33, 149.64, 136.73, 136.53, 132.09, 131.45, 122.88, 122.44, 122.32, 120.16, 24.63; HRMS (ESI): m/z calculated for $\text{C}_{13}\text{H}_{13}\text{N}_2[\text{M}+\text{H}]^+$, 197.1073, found: 197.1071.

2-(6-Methylpyridin-2-yl)-1-(thiophen-2-yl)ethan-1-ol (3r)



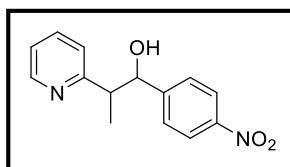
^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.51 (t, J = 7.7 Hz, 1H), 7.21 (dd, J = 1.3, 4.8 Hz, 1H), 7.04 (d, J = 7.7 Hz, 1H), 6.98-6.93 (m, 3H), 5.40 (dt, J = 0.7, 5.9 Hz, 1H), 3.20 (d, J = 5.7 Hz, 2H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 158.59, 157.34, 148.36, 137.18, 126.43, 124.06, 122.88, 121.35, 120.68, 69.64, 44.98, 24.27; HRMS (ESI): m/z calculated for $\text{C}_{12}\text{H}_{14}\text{ONS}[\text{M}+\text{H}]^+$, 220.07906, found: 220.07861.

2-(4,6-Dimethylpyridin-2-yl)-1-(4-nitrophenyl)ethan-1-ol (5b)^[3]



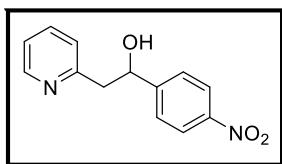
^1H NMR (400 MHz, CDCl_3) δ (ppm) = 8.19 (d, J = 8.6 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 6.89 (s, 1H), 6.72 (s, 1H), 5.22 (dd, J = 3.0, 8.8 Hz, 1H), 3.08-2.94 (m, 2H), 2.51 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 157.91, 157.09, 151.80, 148.67, 147.03, 126.56, 123.53, 122.57, 121.56, 72.59, 44.31, 24.06, 20.90.

1-(4-Nitrophenyl)-2-(pyridin-2-yl)propan-1-ol (**5c**)



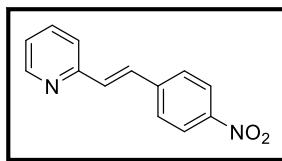
¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.52-8.50 (m, 1H), 8.09-8.06 (m, 2H), 7.53 (dt, J = 1.9, 7.7 Hz, 1H), 7.40-7.36 (m, 2H), 7.17-7.13 (m, 1H), 6.90 (d, J = 8.5 Hz, 1H), 5.04 (d, J = 4.5 Hz, 1H), 3.22-3.15 (m, 1H), 1.47 (d, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 162.79, 151.94, 148.29, 146.84, 137.20, 126.74, 123.21, 122.00, 77.51, 46.64, 19.31; HRMS (ESI): m/z calculated for C₁₄H₁₅O₃N₂[M+H]⁺, 259.10772, found: 259.10724.

1-(4-Nitrophenyl)-2-(pyridin-2-yl)ethan-1-ol (**5d**)^[3]



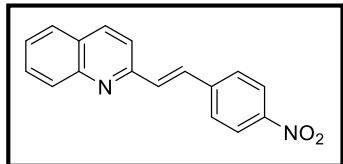
¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.55-8.53 (m, 1H), 8.21-8.17 (m, 2H), 7.65 (dt, J = 1.8, 7.7 Hz, 1H), 7.59 (d, J = 8.3 Hz, 2H), 7.25-7.22 (m, 1H), 7.10 (d, J = 7.8 Hz, 1H), 5.29 (dd, J = 3.3, 8.6 Hz, 1H), 3.22-3.08 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 158.66, 151.39, 148.33, 137.32, 126.57, 123.91, 123.57, 122.14, 72.50, 44.77.

(E)-2-(4-Nitrostyryl)pyridine (**6d**)



¹H NMR (500 MHz, CDCl₃) δ (ppm) = 8.64 (d, J = 5.6 Hz, 1H), 8.24 (d, J = 8.8 Hz, 2H); 7.73-7.69 (m, 4H), 7.42 (d, J = 7.7 Hz, 1H), 7.30 (d, J = 16.0 Hz, 1H), 7.24-7.21 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 154.34, 149.92, 143.10, 136.78, 132.10, 130.22, 127.50, 124.13, 123.05; HRMS (ESI): m/z calculated for C₁₃H₁₁O₂N₂ [M+H]⁺, 227.08150, found: 227.08111.

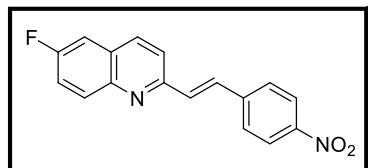
(E)-2-(4-Nitrostyryl)quinoline (**6f**)^[3]



¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.26 (d, J = 8.8 Hz, 2H), 8.18 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.83-7.72 (m, 5H), 7.67 (d, J = 8.5 Hz, 1H), 7.56-7.50 (m, 2H); ¹³C NMR

(100 MHz, CDCl_3) δ (ppm) = 154.61, 148.24, 147.36, 142.92, 136.67, 133.11, 131.65, 130.04, 129.35, 127.62, 127.55, 126.76, 124.15, 119.70.

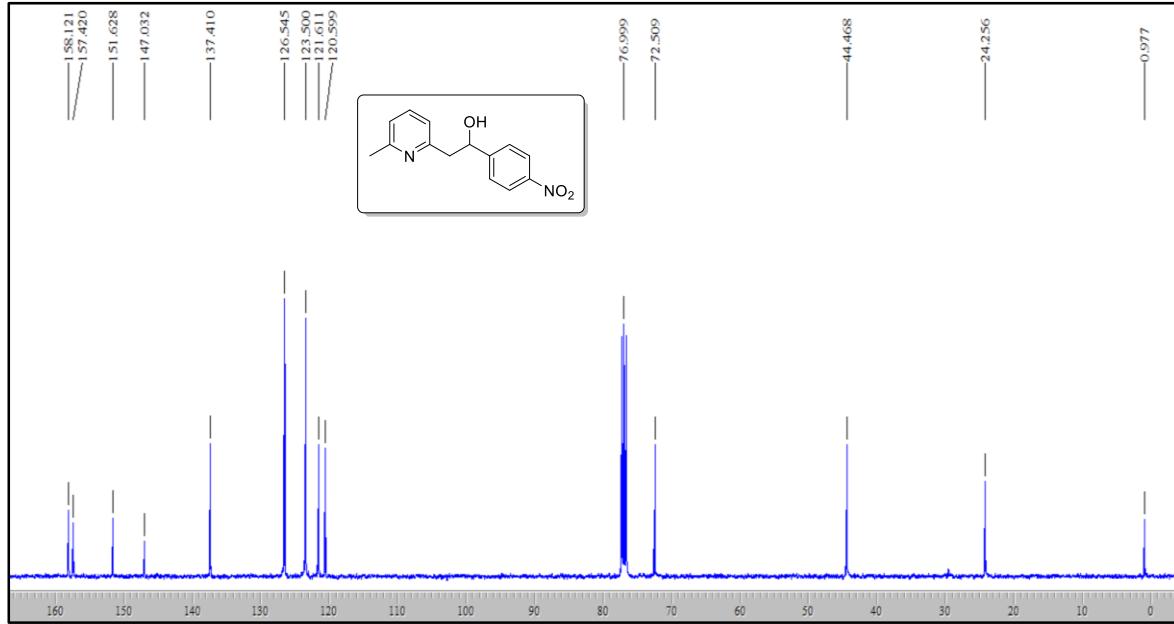
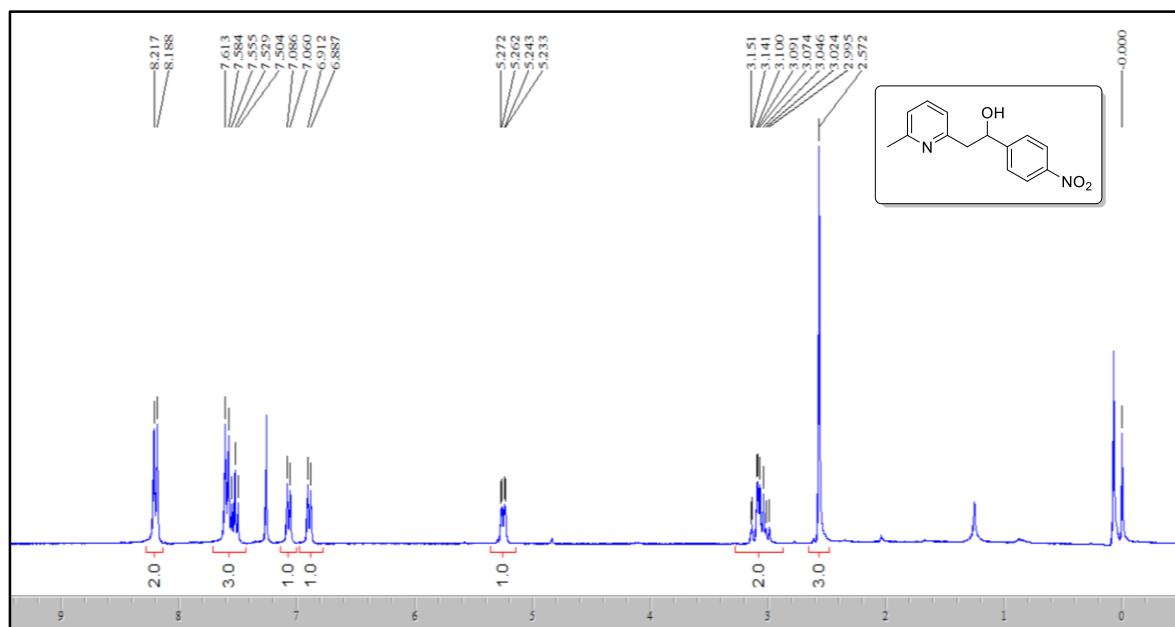
(E)-6-Fluoro-2-(4-nitrostyryl)quinoline (6g)



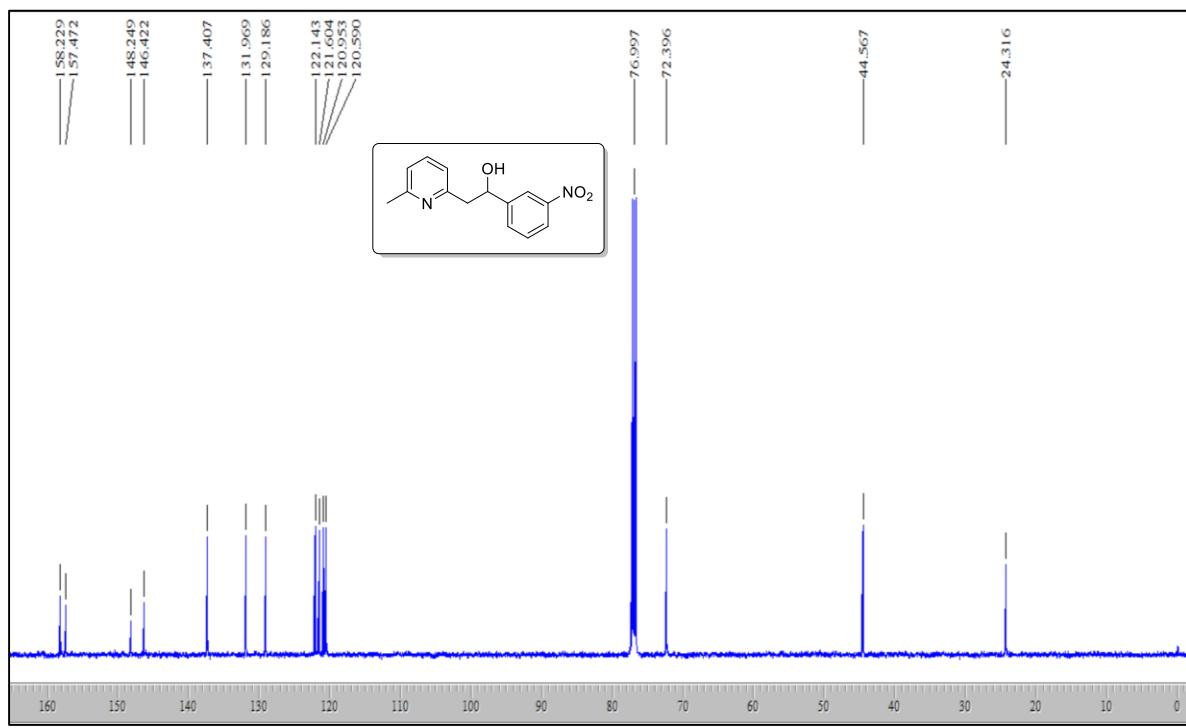
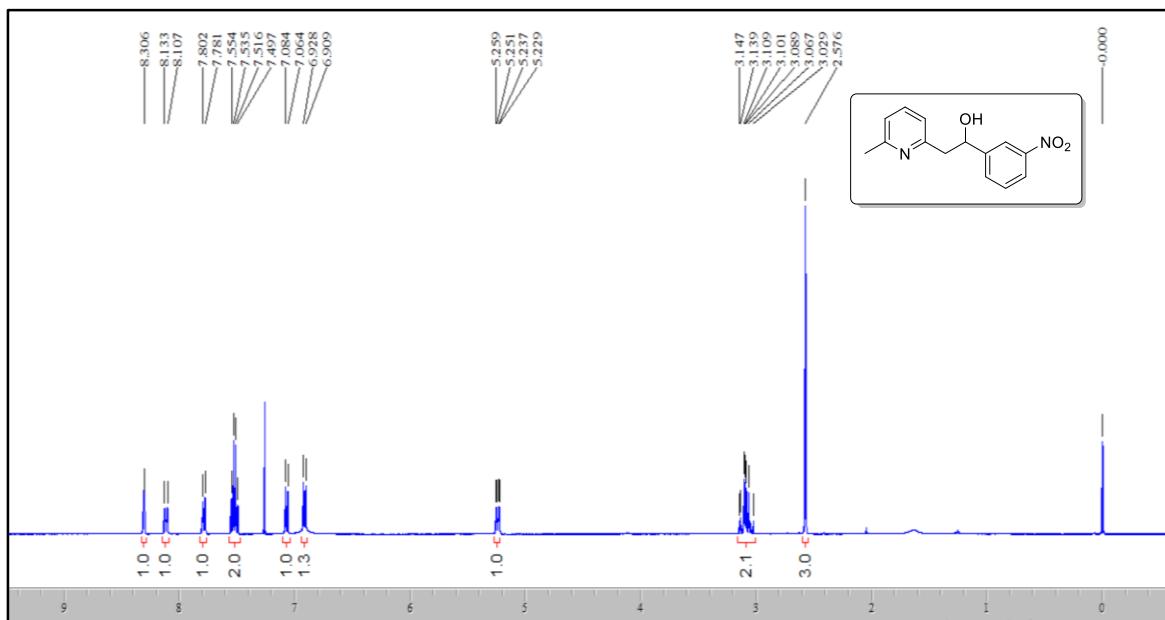
^1H NMR (400 MHz, CDCl_3) δ (ppm) = 8.27 (d, J = 8.8 Hz, 2H), 8.14-8.08 (m, 2H), 7.78-7.74 (m, 3H), 7.68 (d, J = 8.5 Hz, 1H), 7.54-7.42 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 154.04, 147.42, 145.37, 142.85, 136.03 (d, J = 5.5 Hz), 132.77, 131.87 (d, J = 8.8 Hz), 131.66, 128.21 (d, J = 9.9 Hz), 127.65, 124.19, 120.51, 120.12, 110.68 (d, J = 21.4 Hz); HRMS (ESI): m/z calculated for $\text{C}_{17}\text{H}_{12}\text{O}_2\text{N}_2\text{F}[\text{M}+\text{H}]^+$, 295.0877, found: 295.0873.

3. Copies of ^1H and ^{13}C NMR spectra of all products

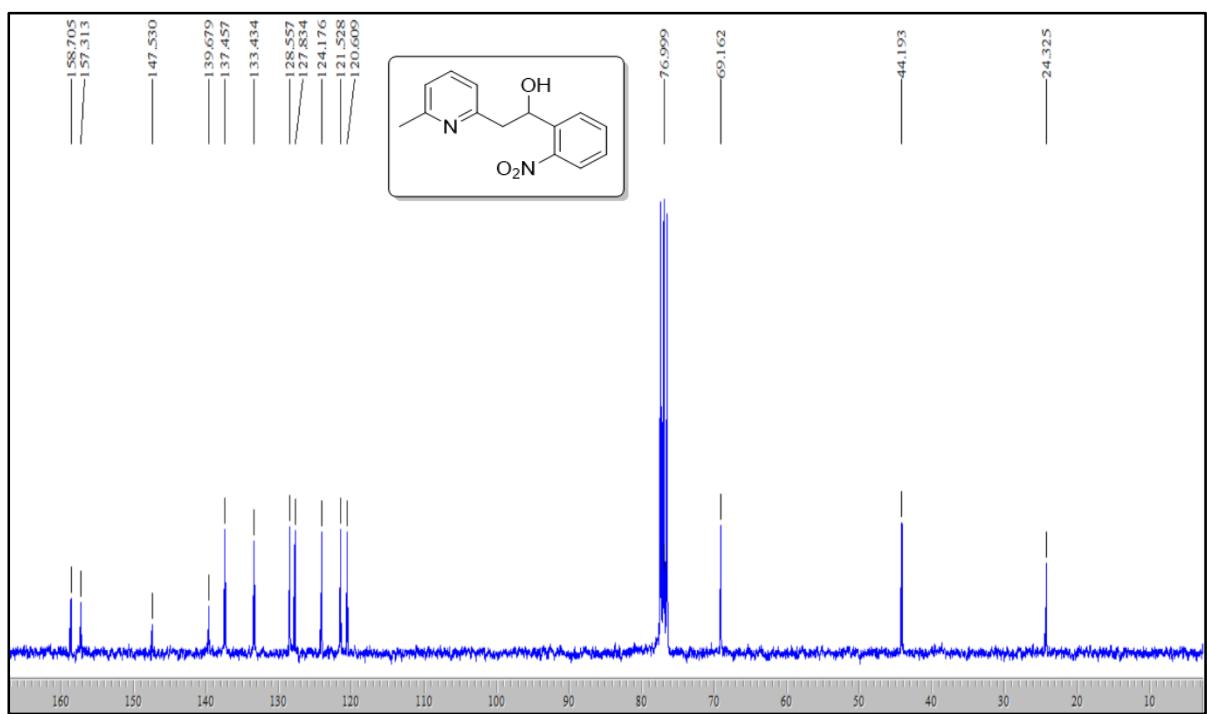
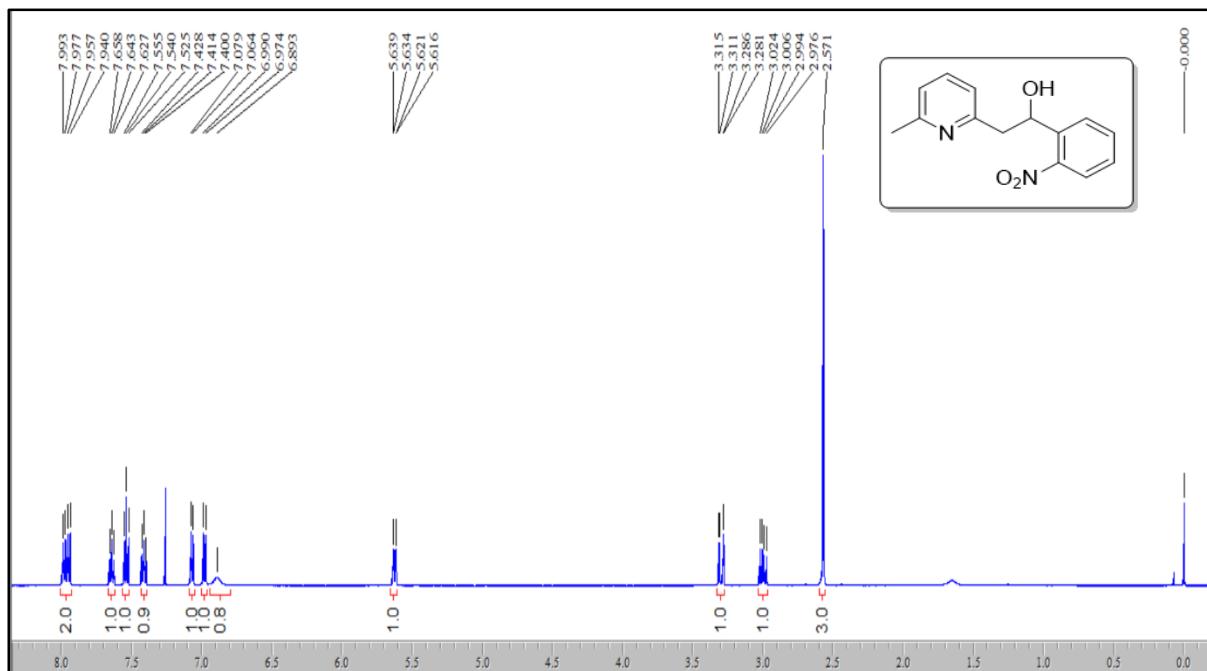
2-(6-Methylpyridin-2-yl)-1-(4-nitrophenyl)ethan-1-ol (3a)



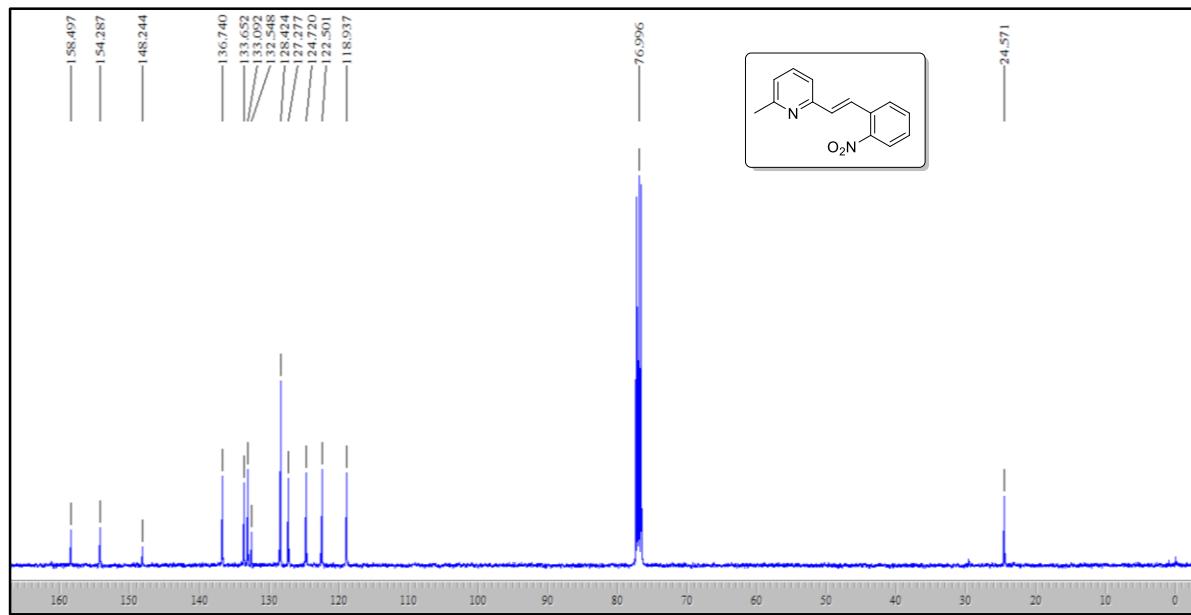
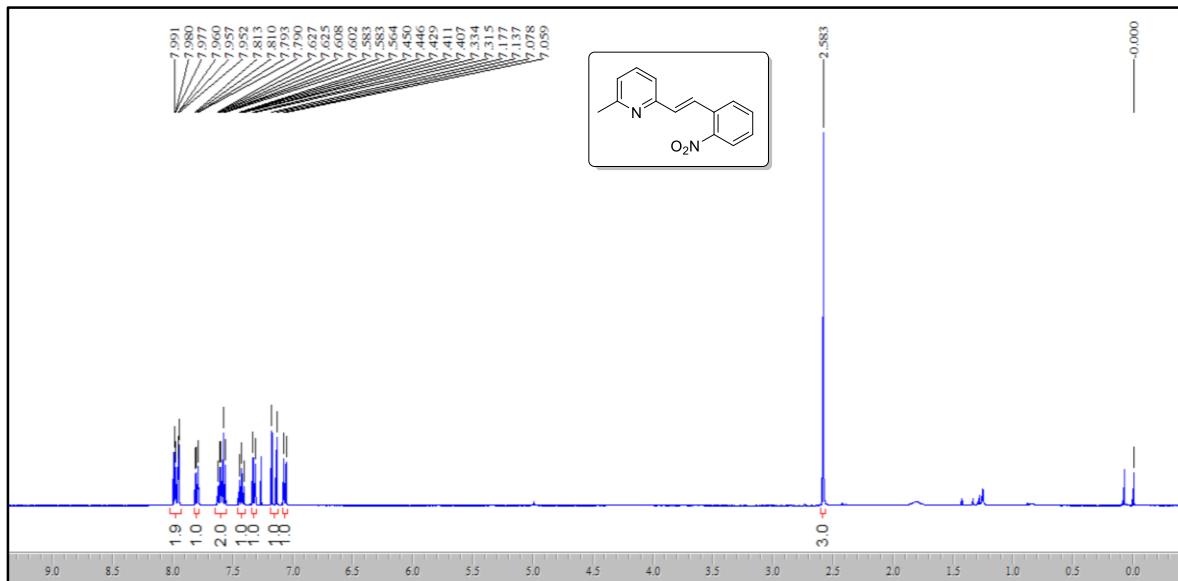
2-(6-Methylpyridin-2-yl)-1-(3-nitrophenyl)ethan-1-ol (3b)



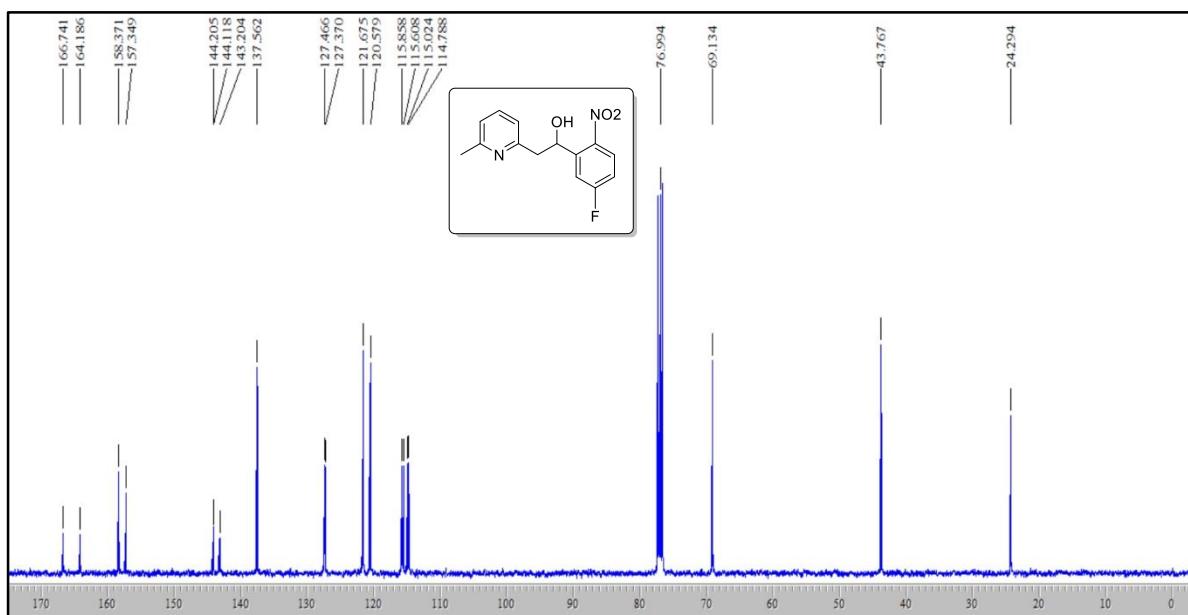
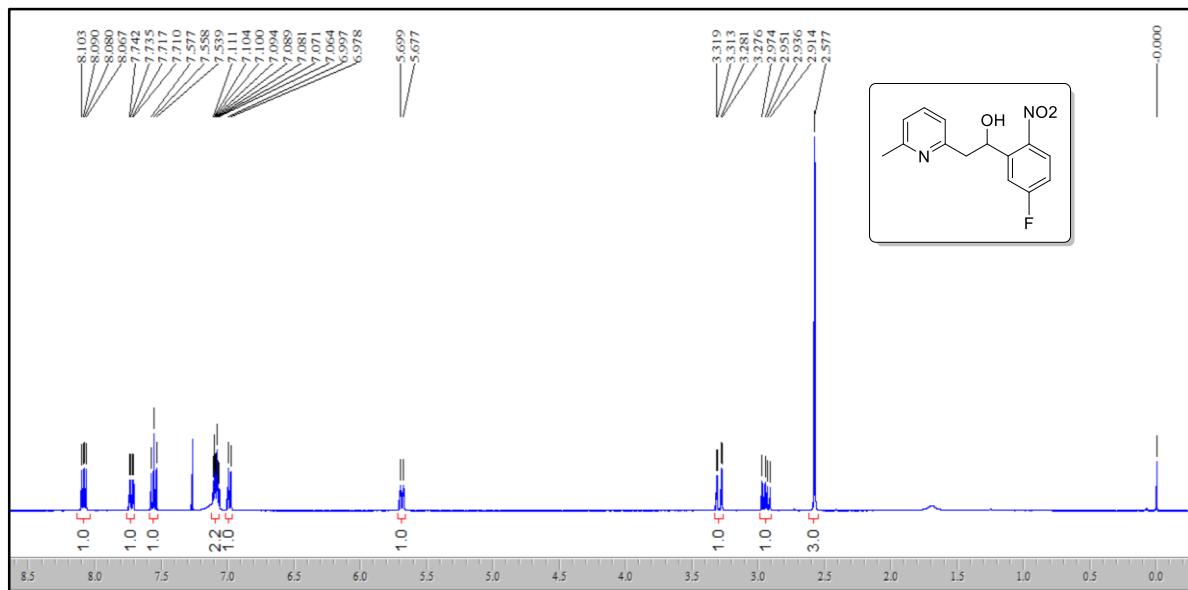
2-(6-Methylpyridin-2-yl)-1-(2-nitrophenyl)ethan-1-ol (3c)



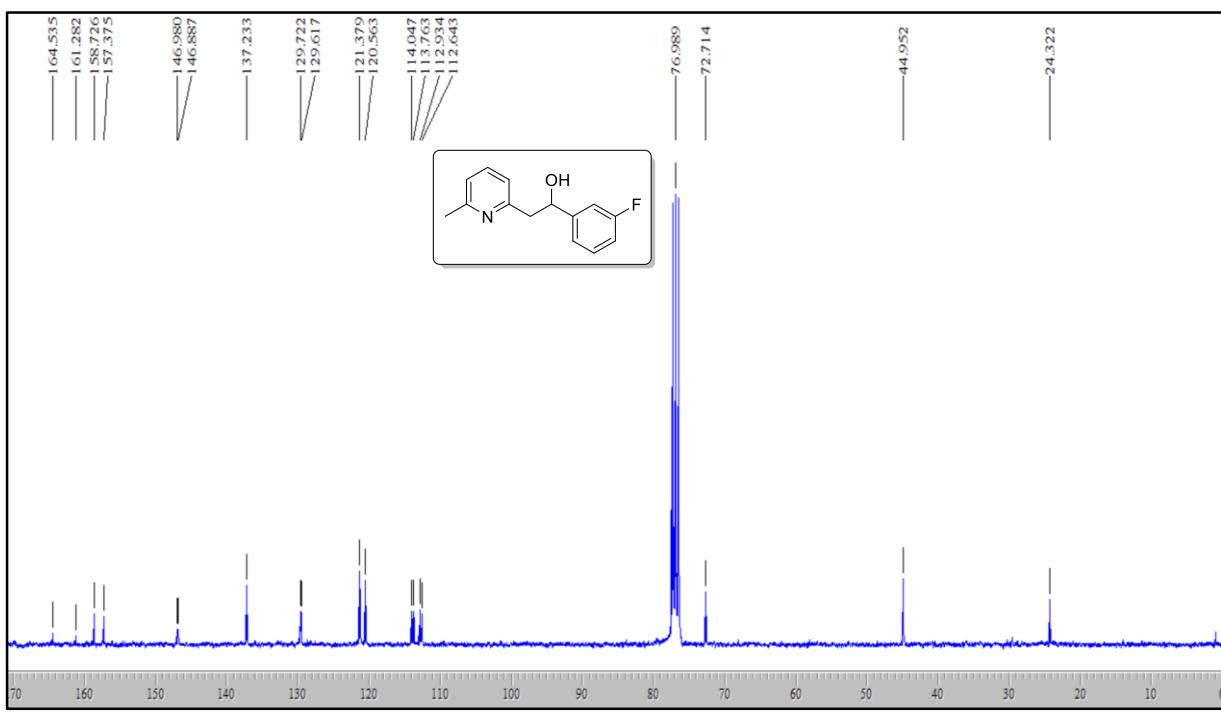
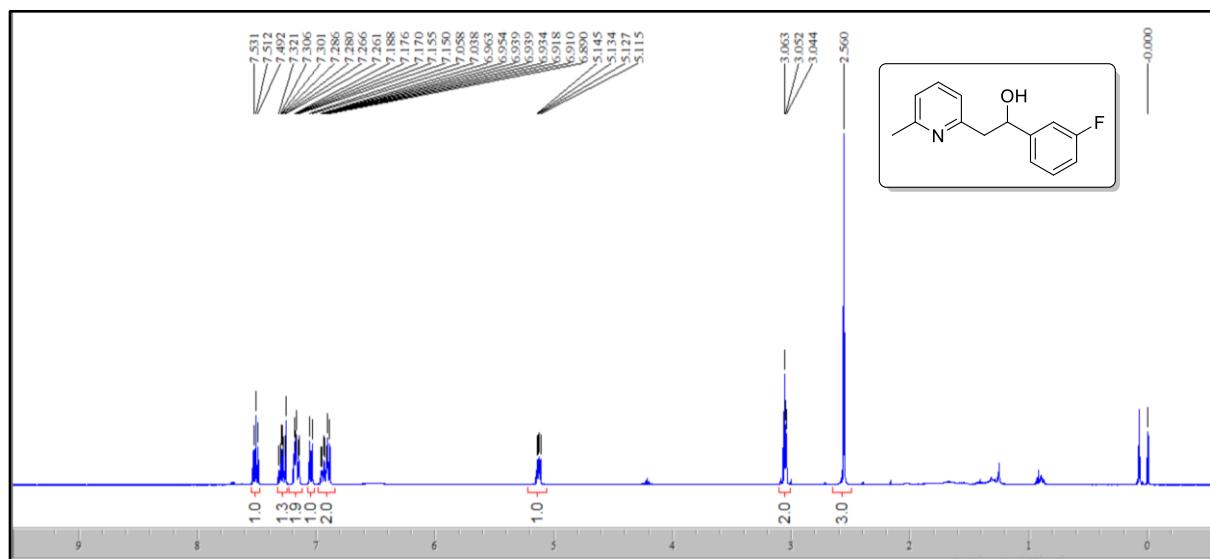
(E)-2-Methyl-6-(2-nitrostyryl)pyridine (4c)



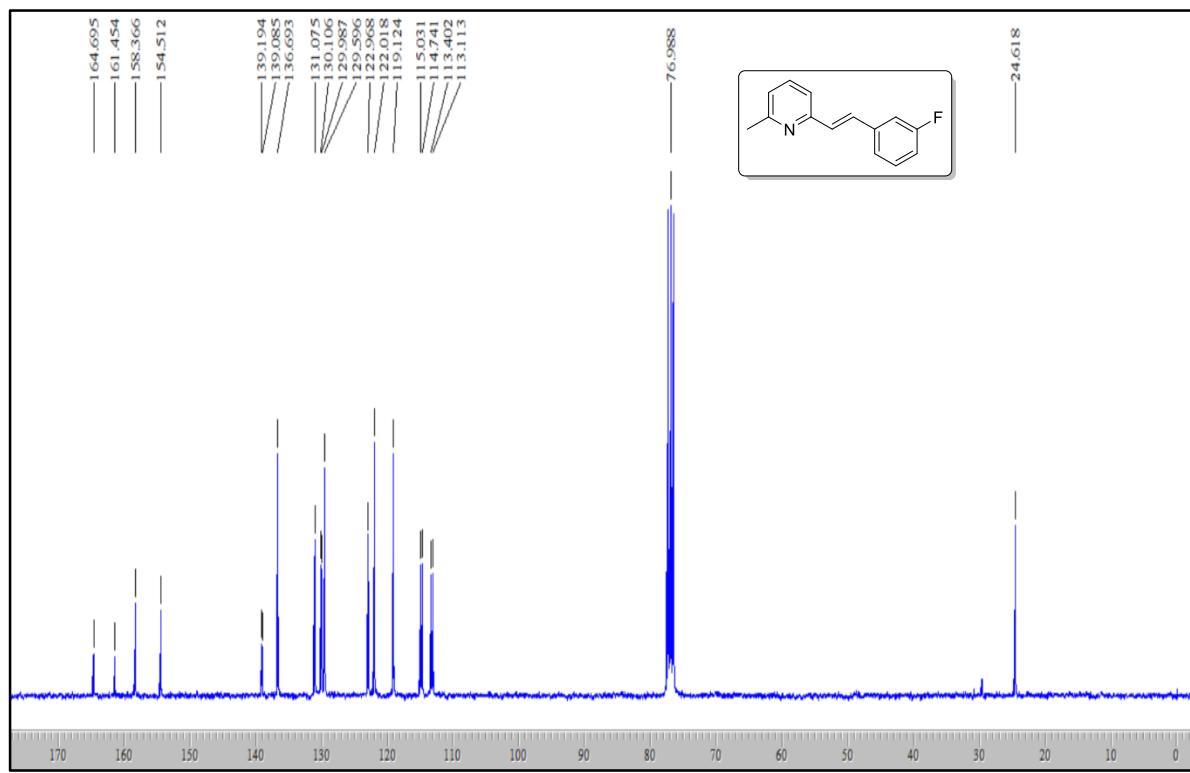
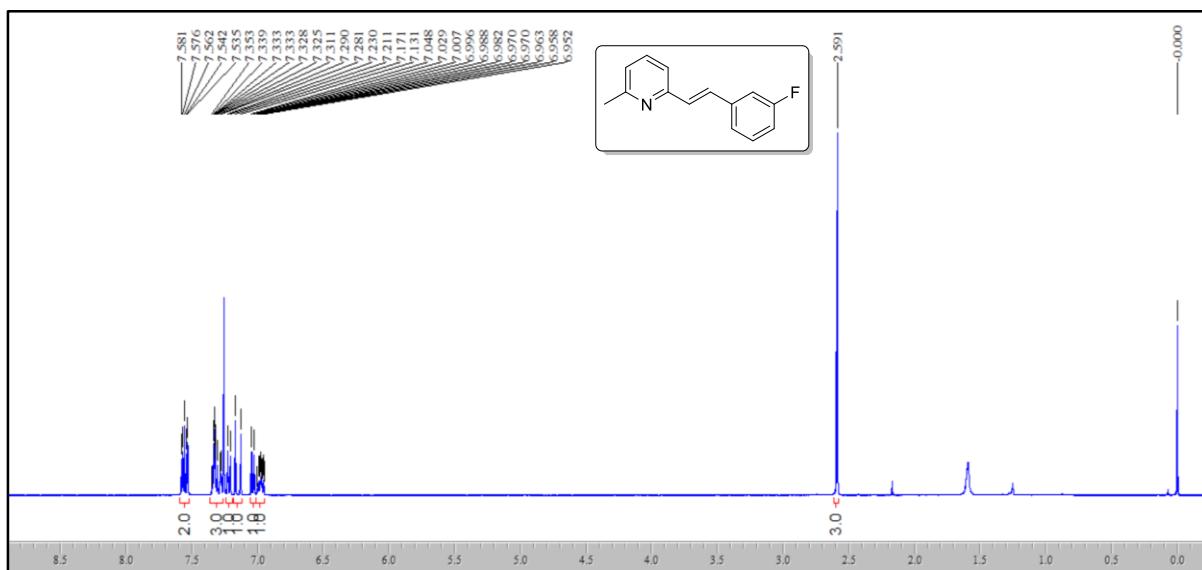
1-(5-Fluoro-2-nitrophenyl)-2-(6-methylpyridin-2-yl)ethan-1-ol (3d)



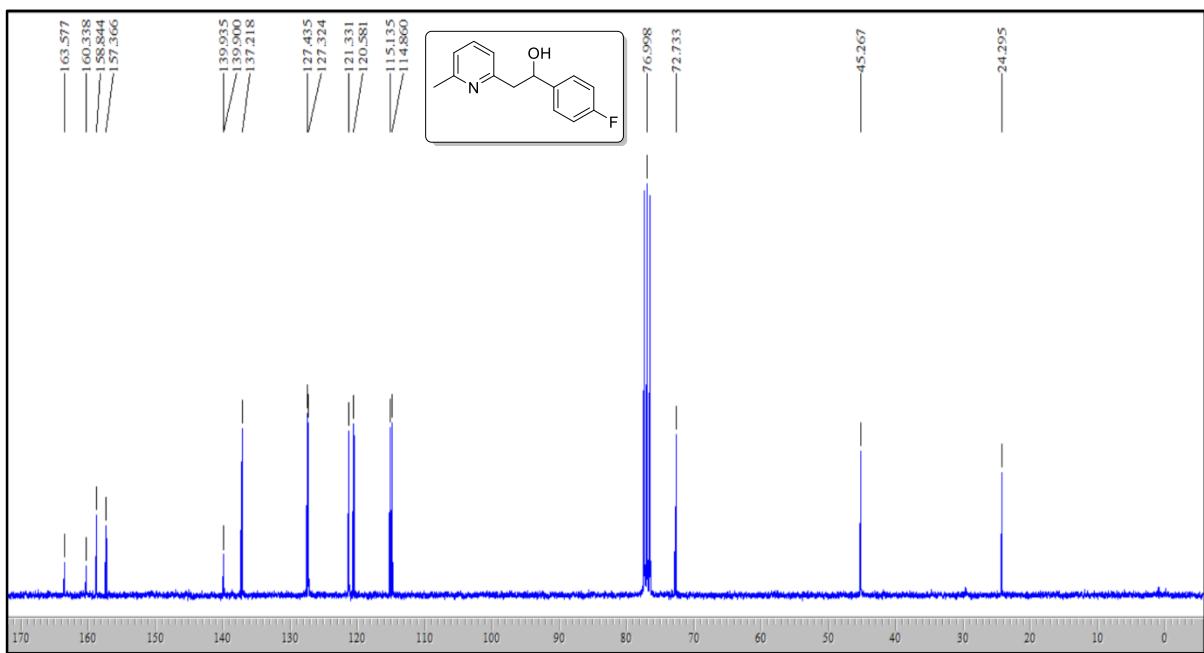
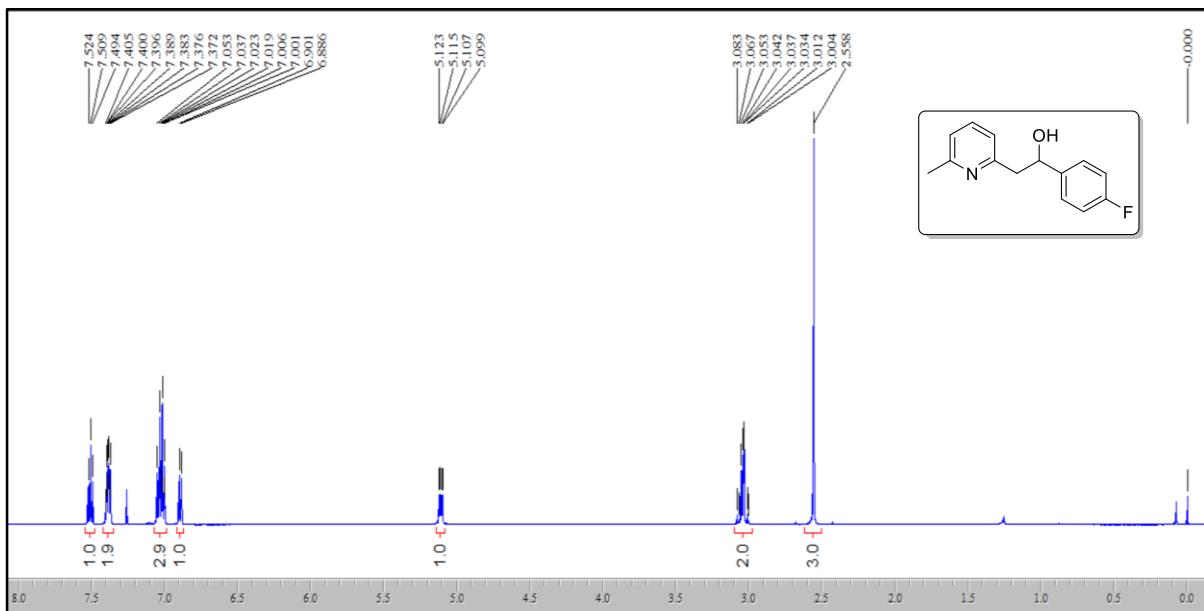
1-(3-Fluorophenyl)-2-(6-methylpyridin-2-yl)ethan-1-ol (3e)



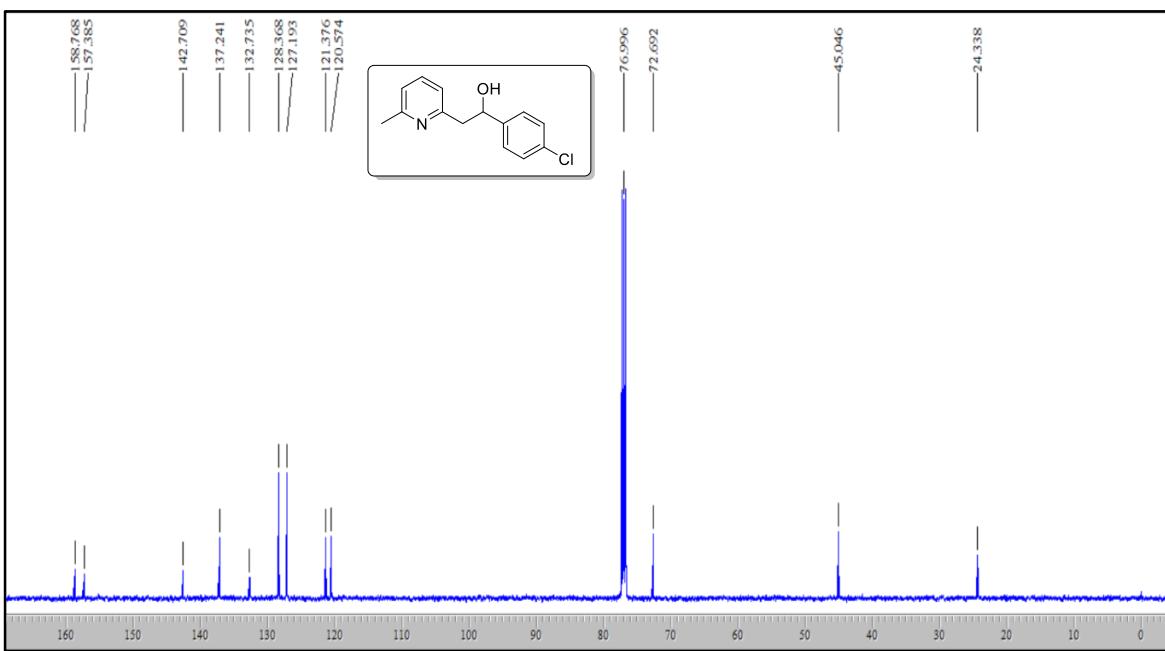
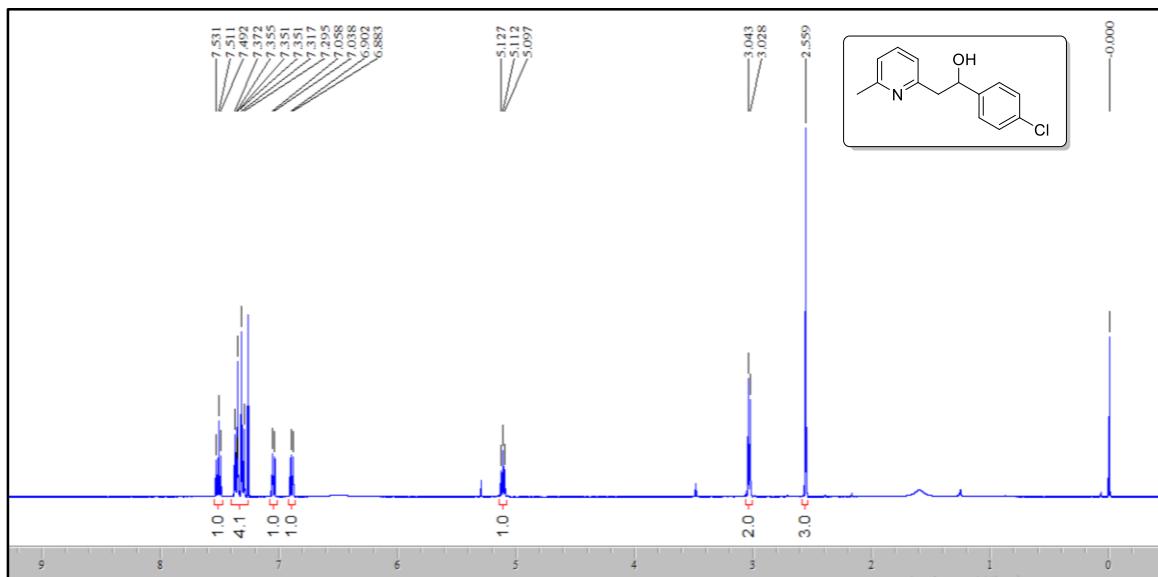
(E)-2-(3-Fluorostyryl)-6-methylpyridine (4e)



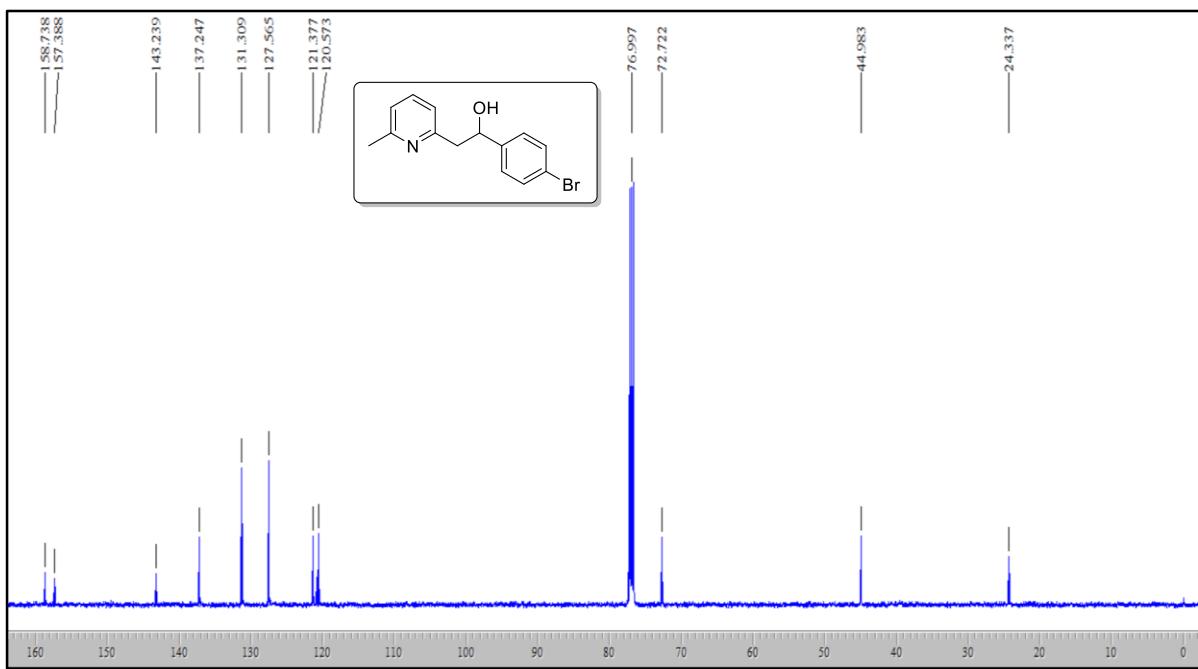
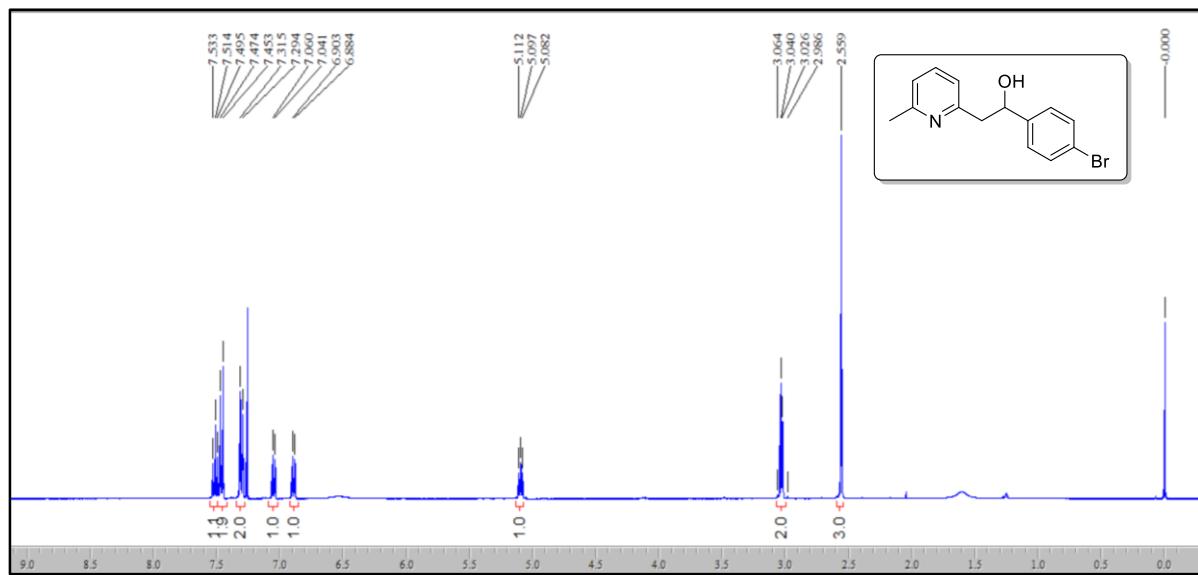
1-(4-Fluorophenyl)-2-(6-methylpyridin-2-yl)ethan-1-ol (3f)



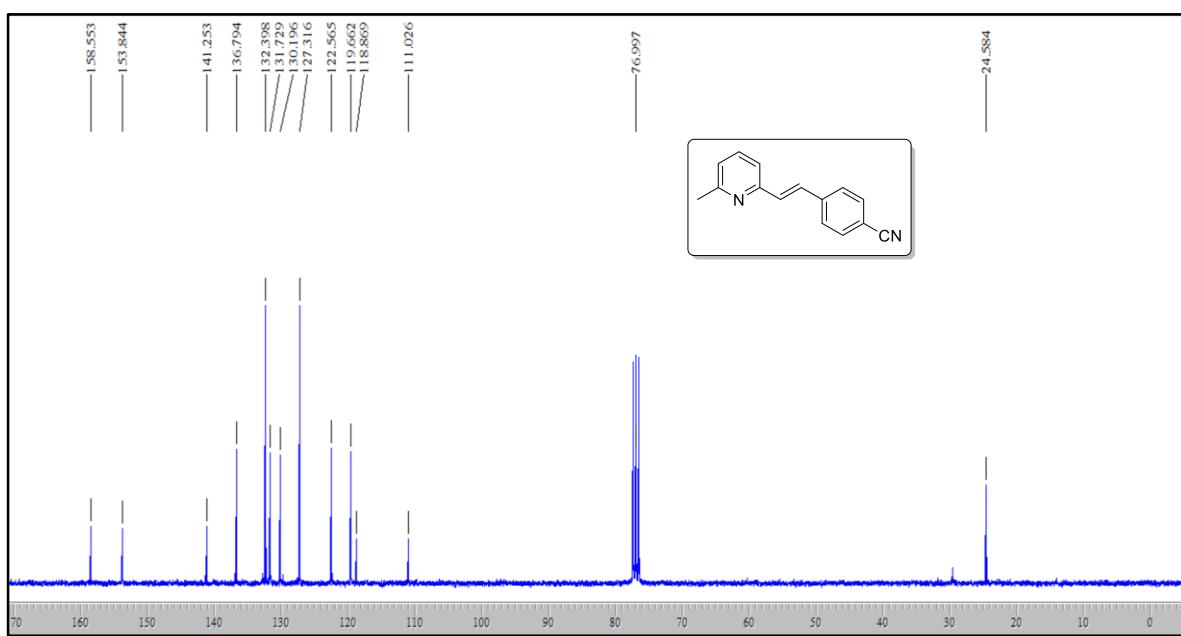
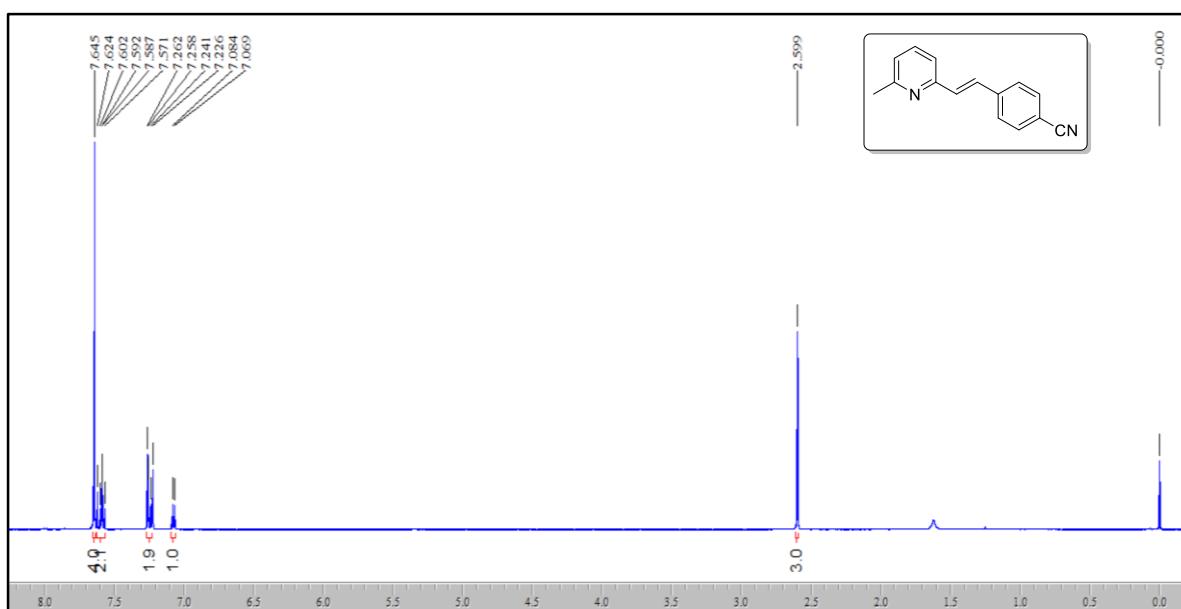
1-(4-Chlorophenyl)-2-(6-methylpyridin-2-yl)ethan-1-ol (3g)



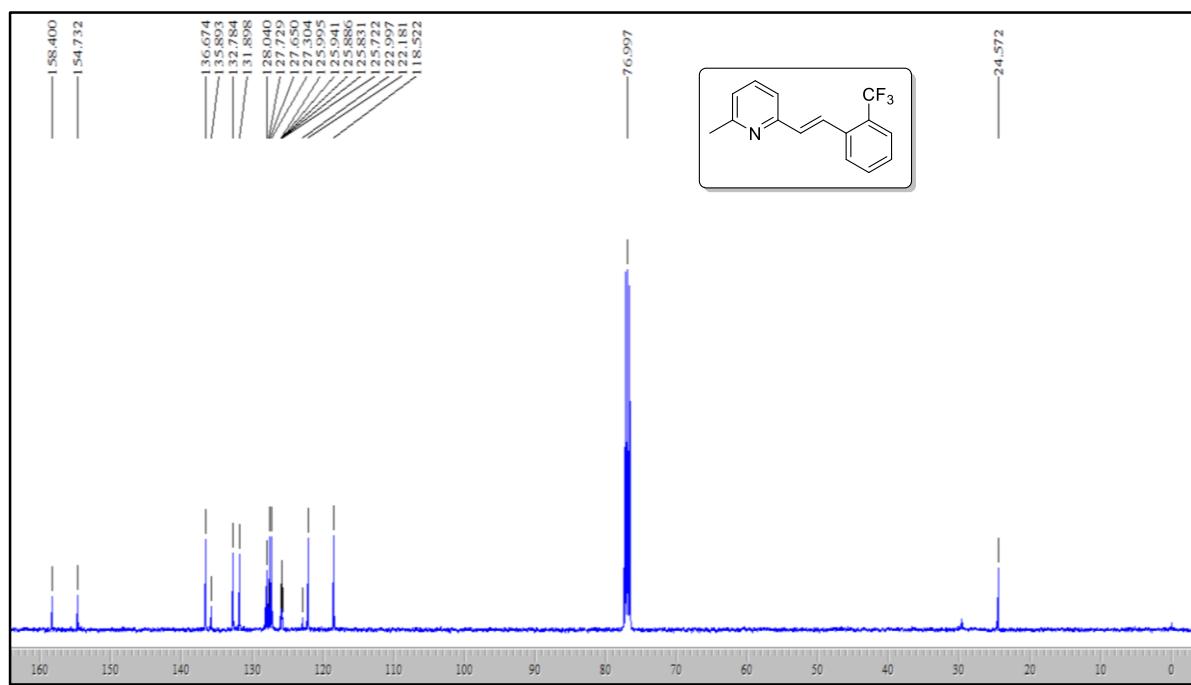
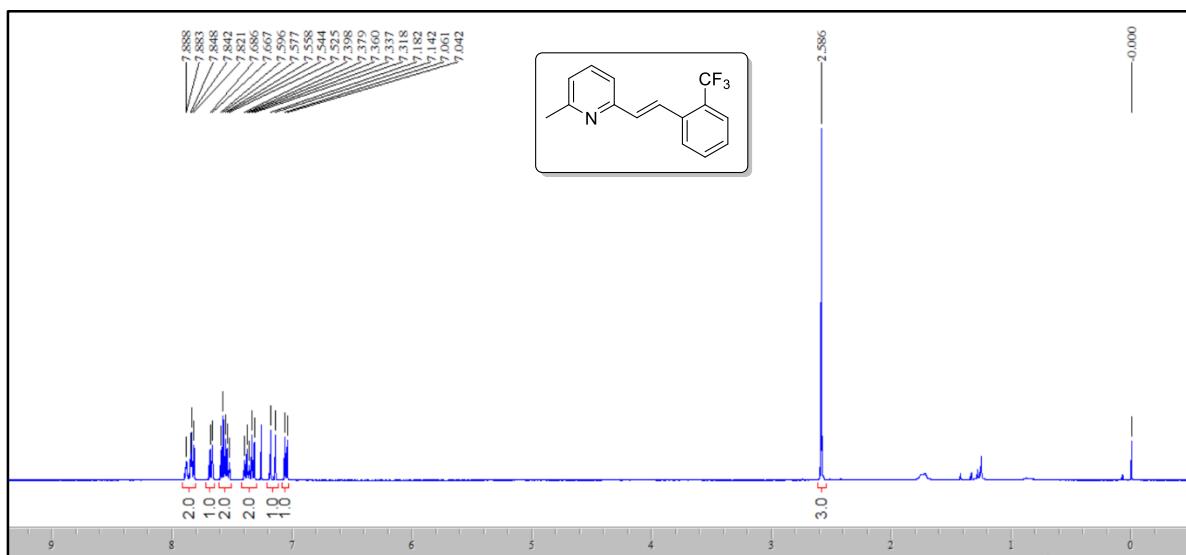
1-(4-Bromophenyl)-2-(6-methylpyridin-2-yl)ethan-1-ol (3h)



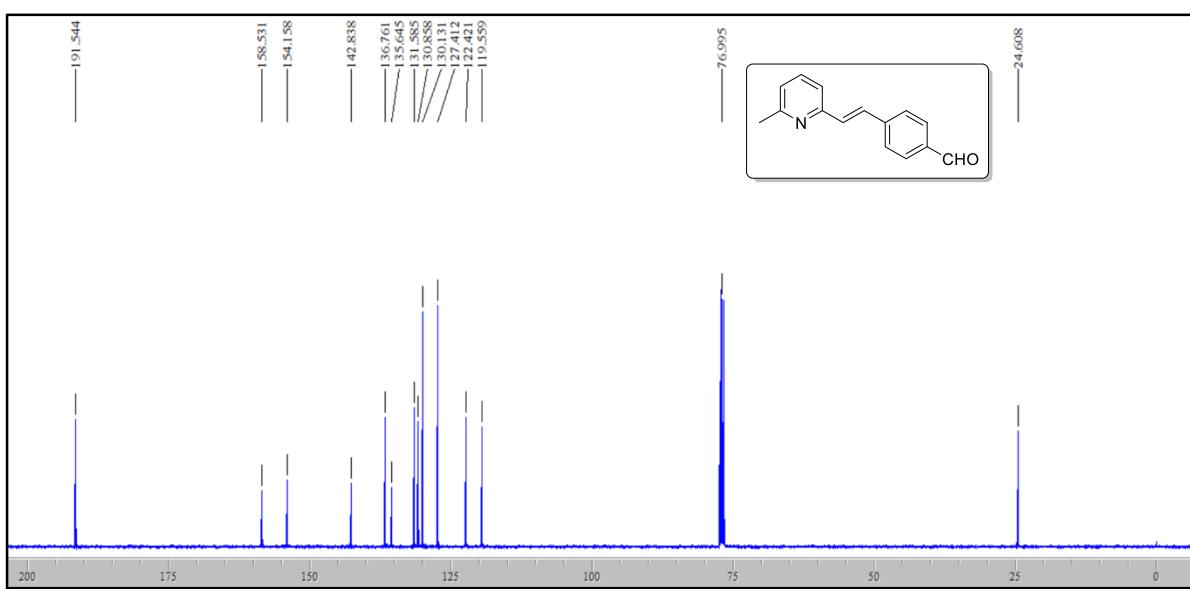
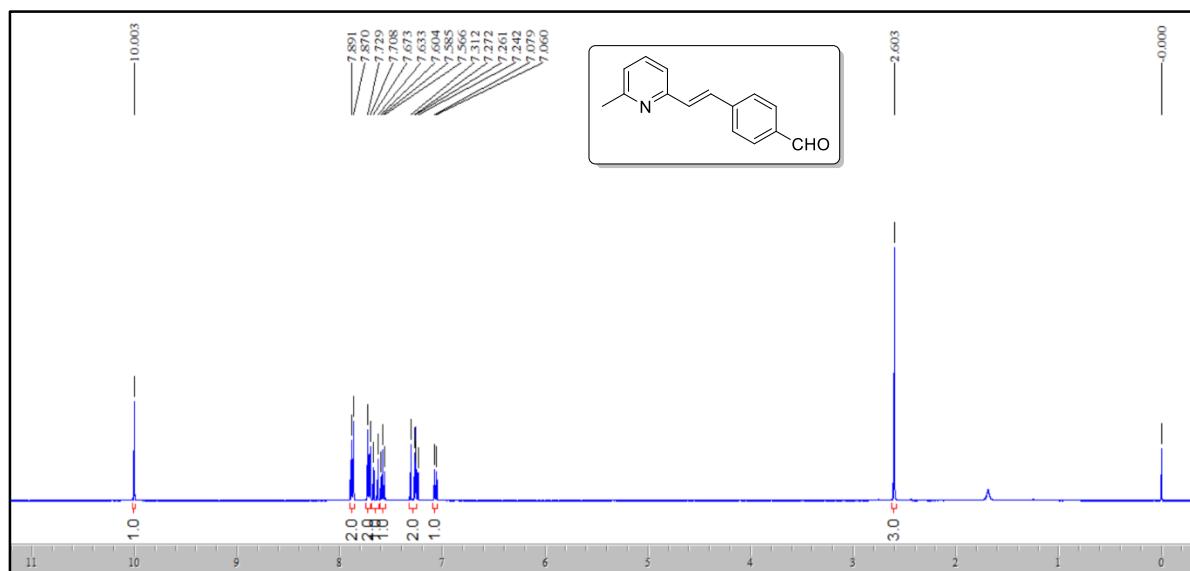
(E)-4-(2-(6-Methylpyridin-2-yl)vinyl)benzonitrile (4i)



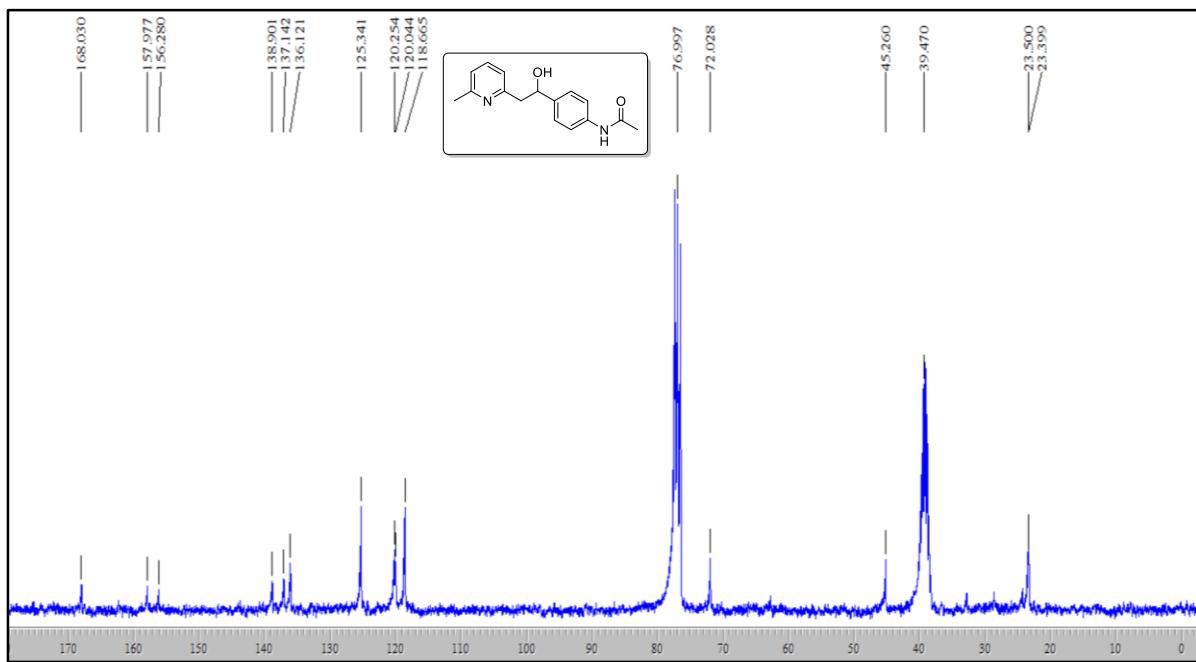
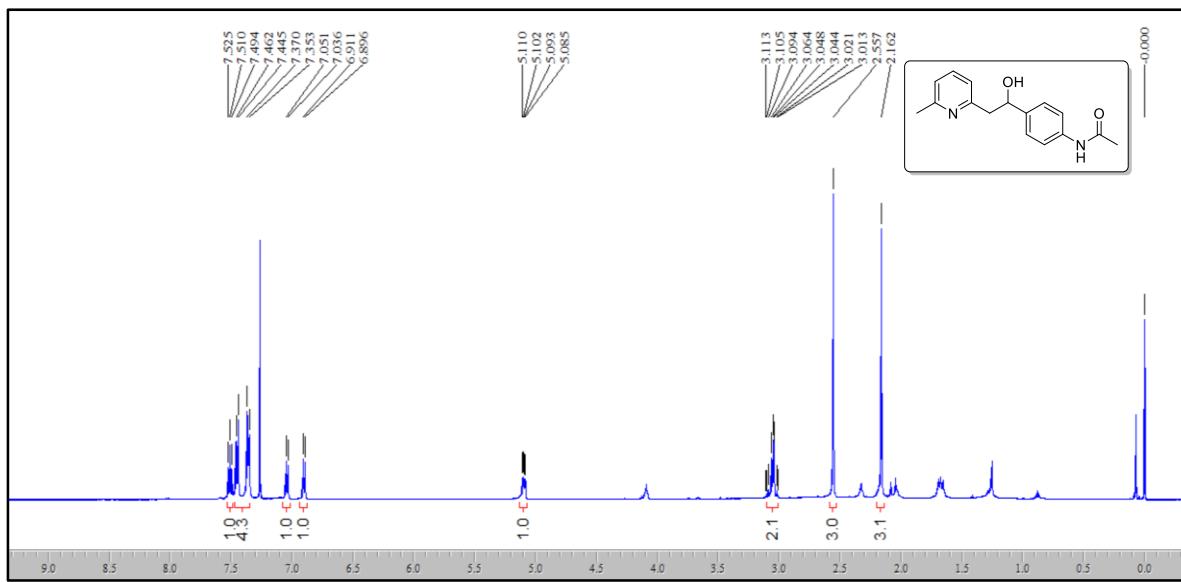
(E)-2-Methyl-6-(2-(trifluoromethyl)styryl)pyridine (4j)



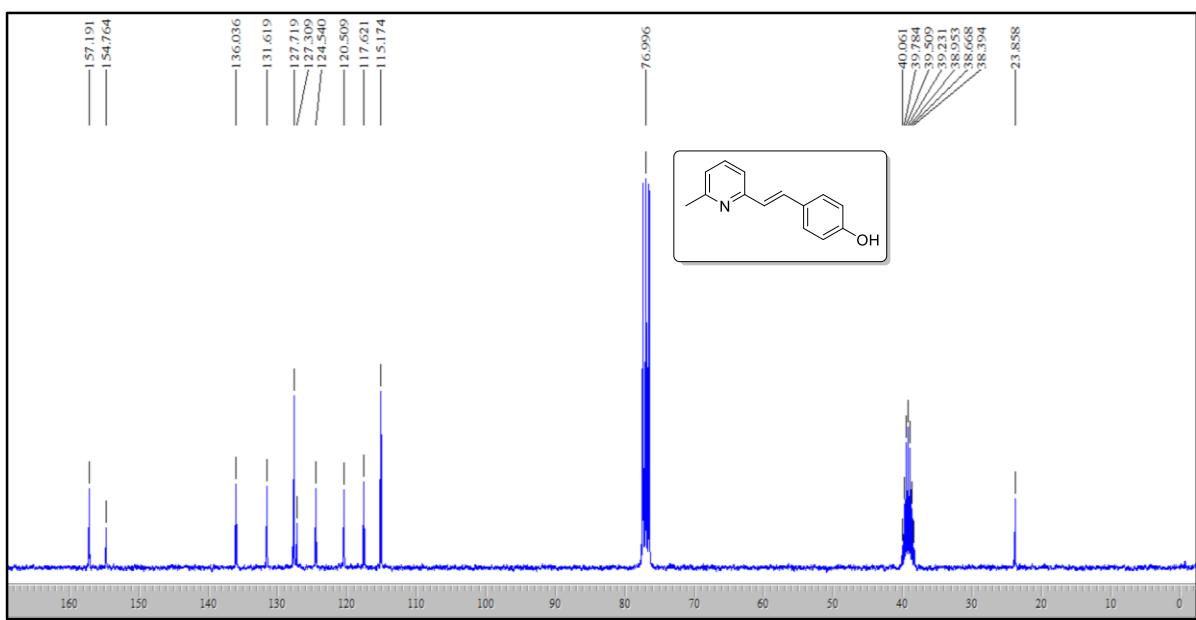
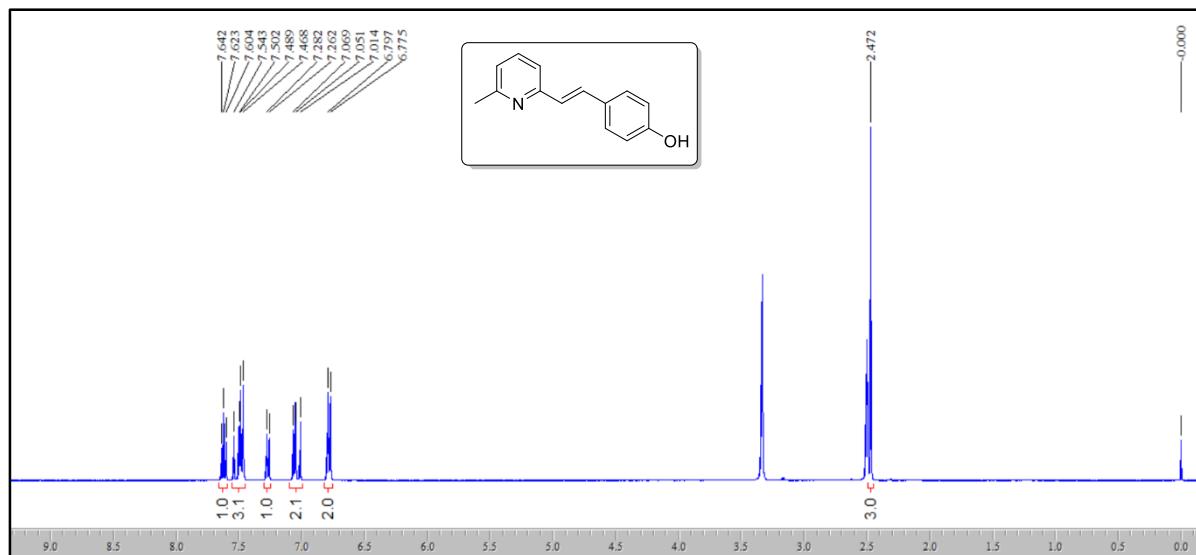
(E)-4-(2-(6-Methylpyridin-2-yl)vinyl)benzaldehyde (4k)



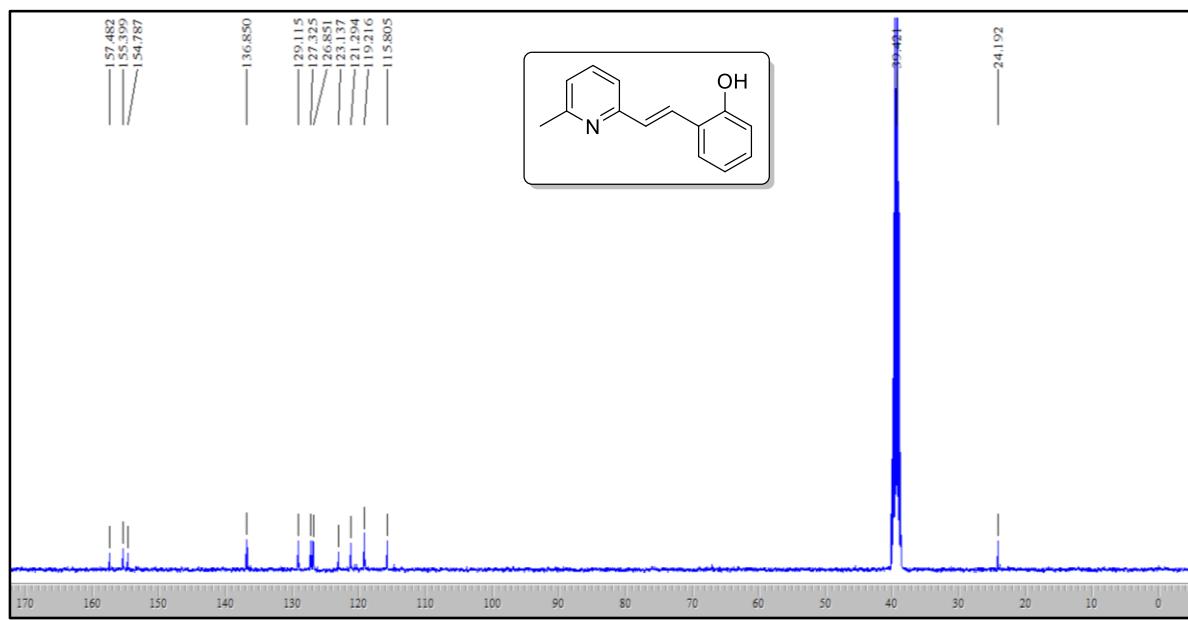
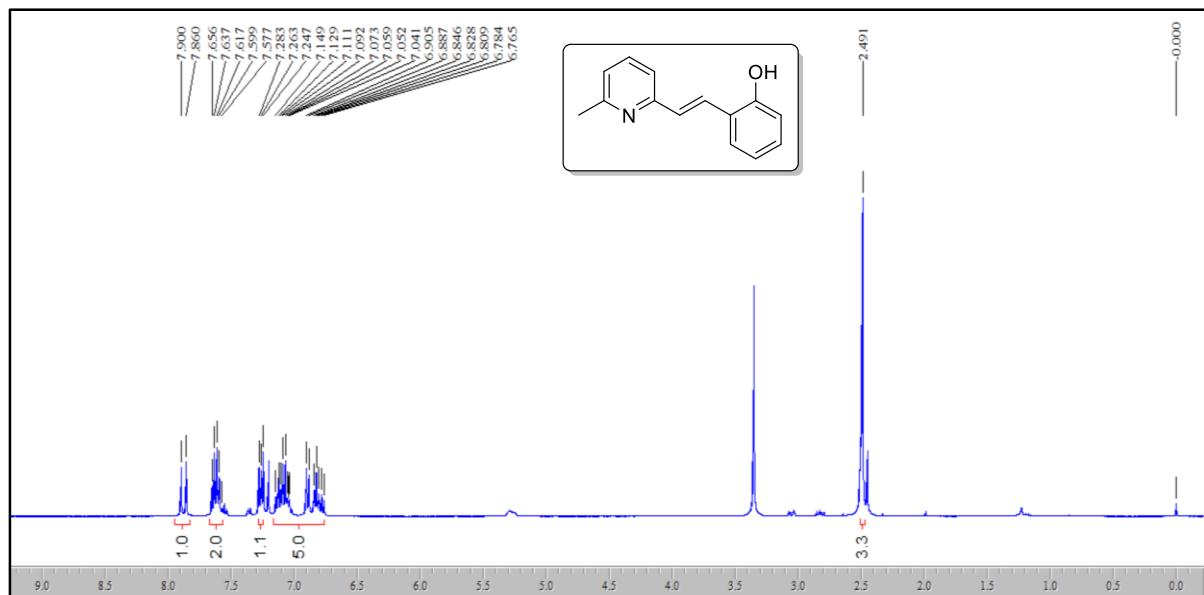
N-(4-(1-Hydroxy-2-(6-methylpyridin-2-yl)ethyl)phenyl)acetamide (3l)



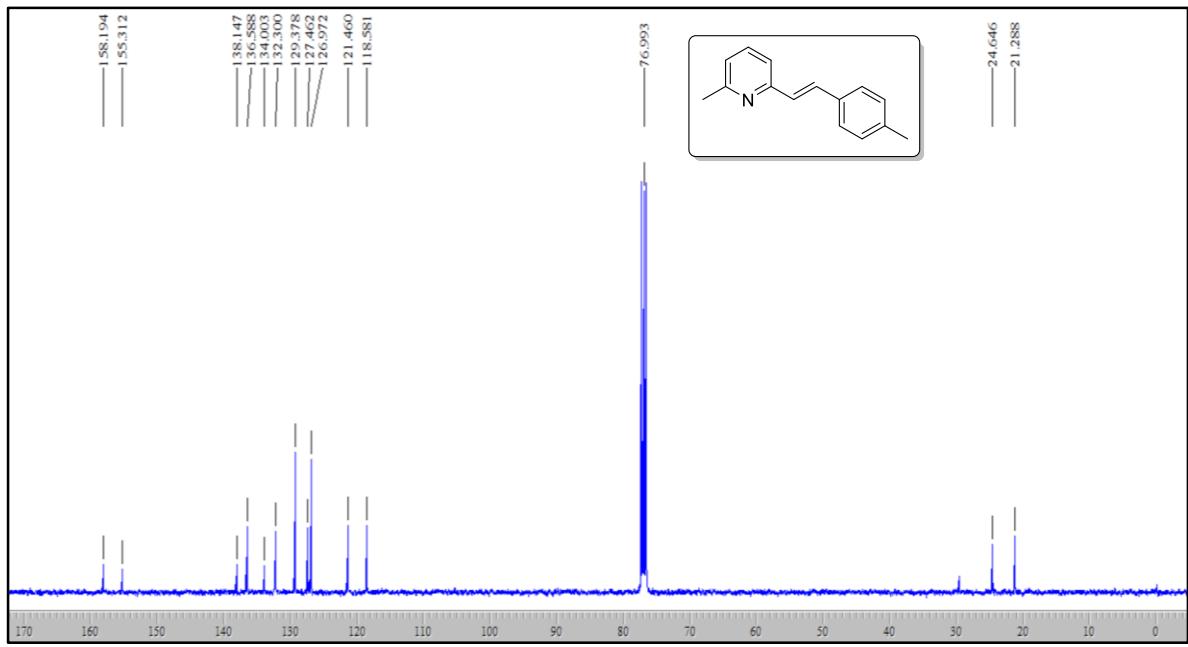
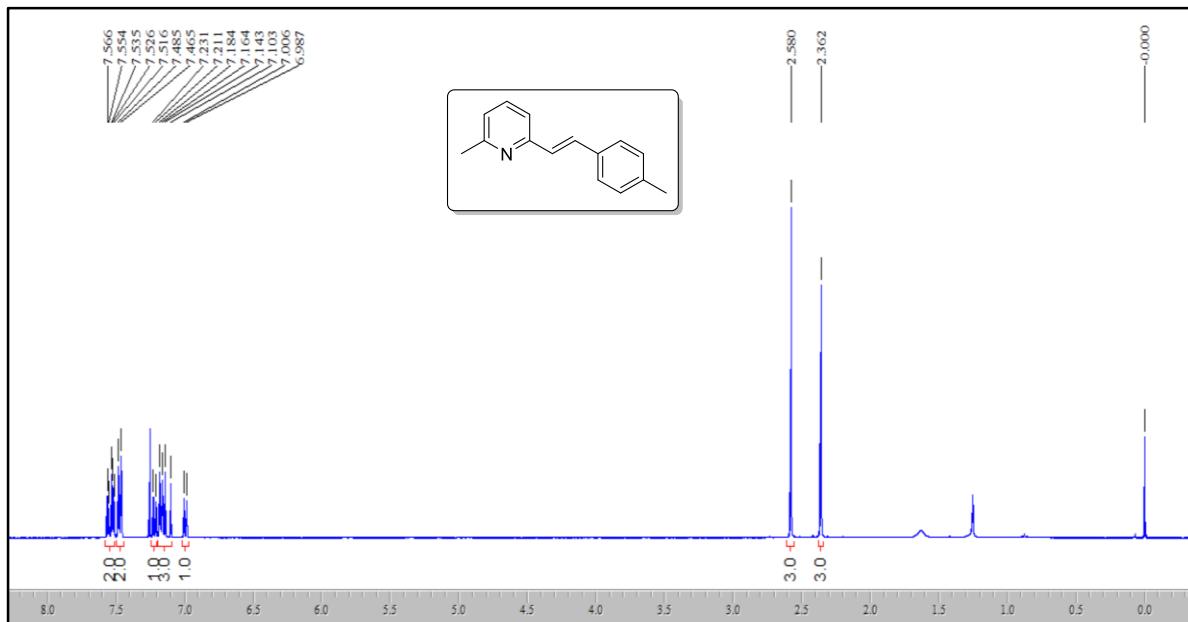
(E)-4-(2-(6-Methylpyridin-2-yl)vinyl)phenol (4m)



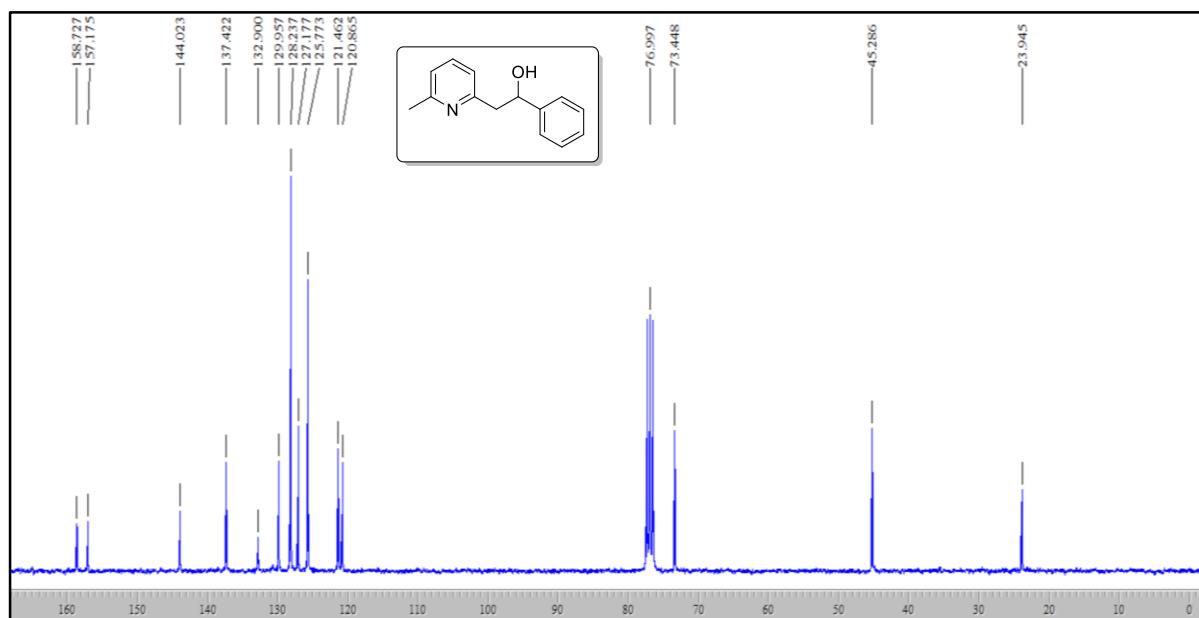
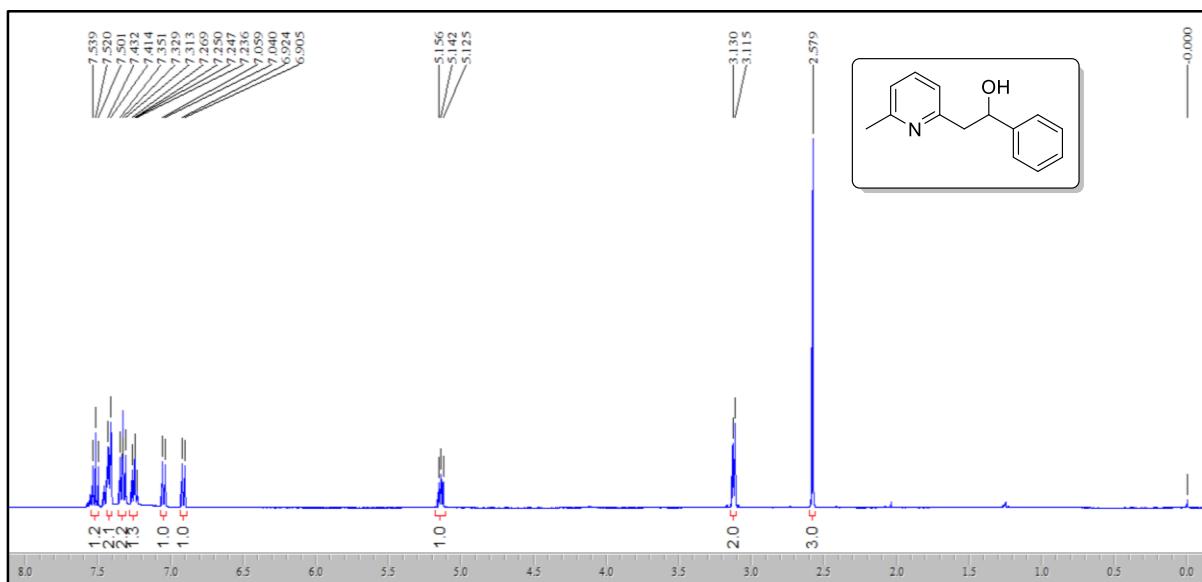
(E)-2-(2-(6-Methylpyridin-2-yl)vinyl)phenol (4n)



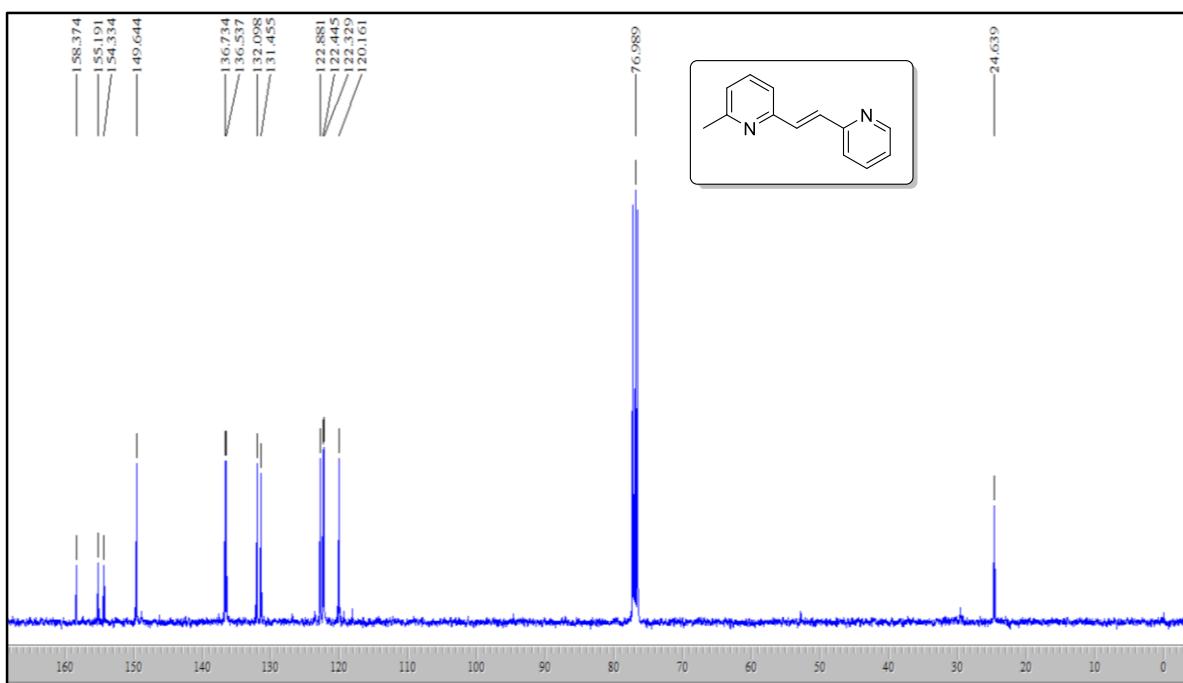
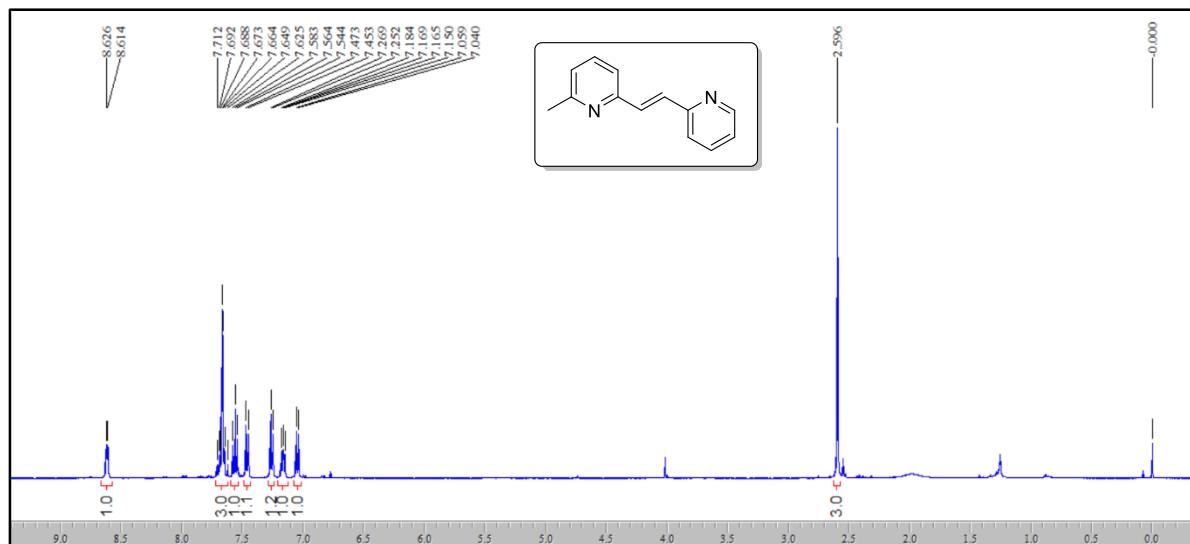
(E)-2-Methyl-6-(4-methylstyryl)pyridine (4o)



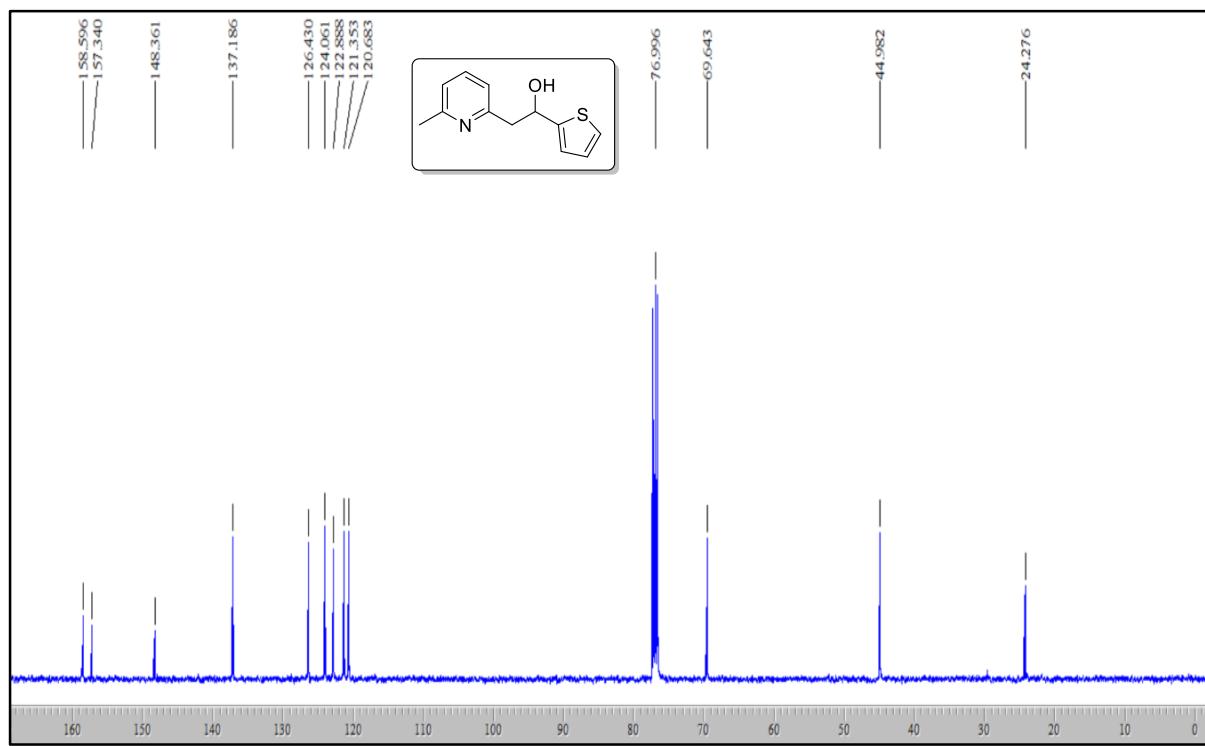
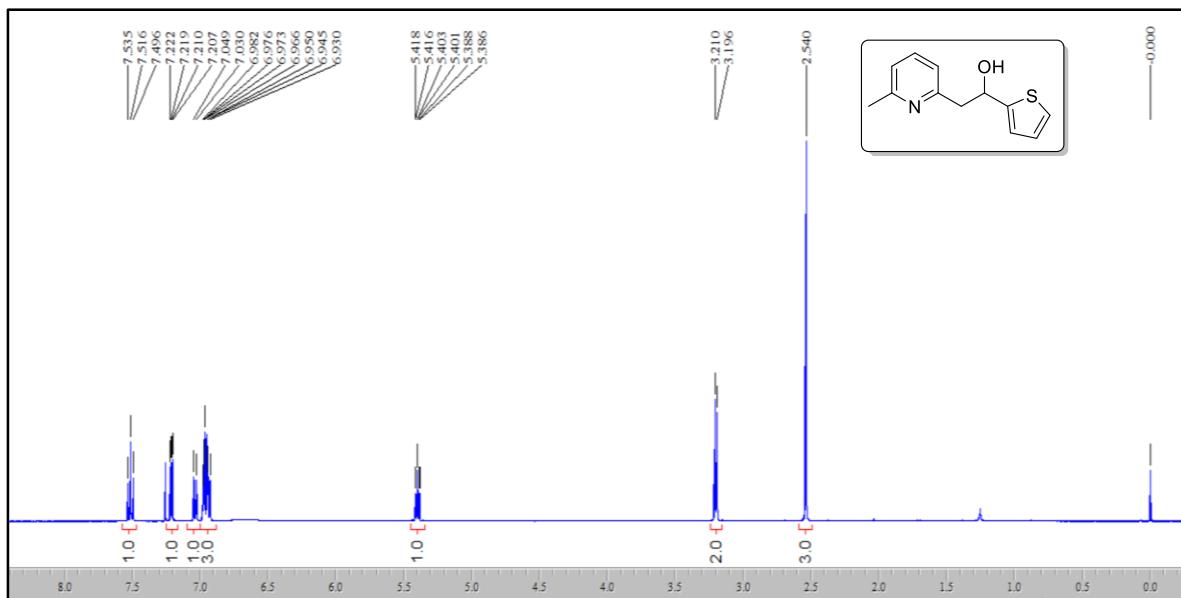
2-(6-Methylpyridin-2-yl)-1-phenylethan-1-ol (3p)



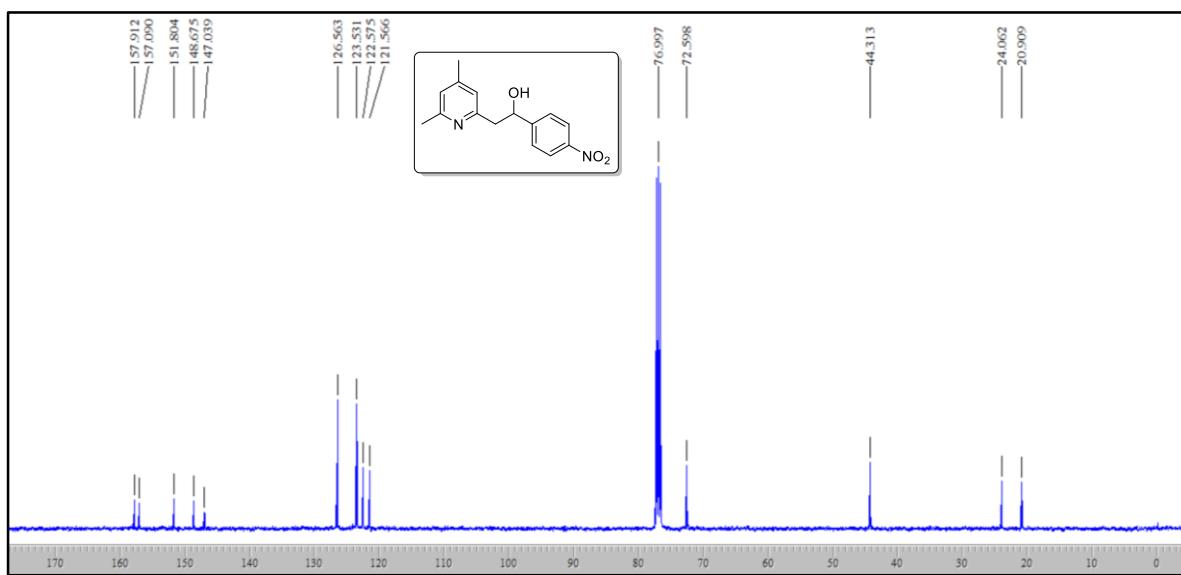
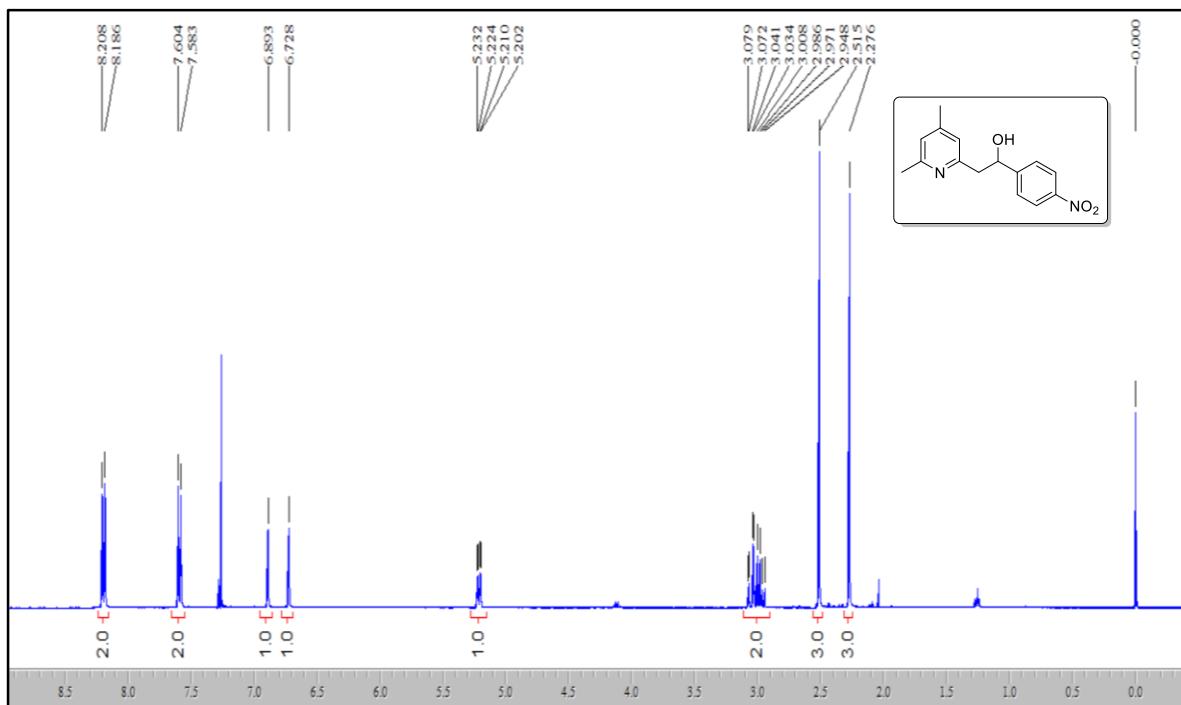
(E)-2-Methyl-6-(2-(pyridin-2-yl)vinyl)pyridine (4q)



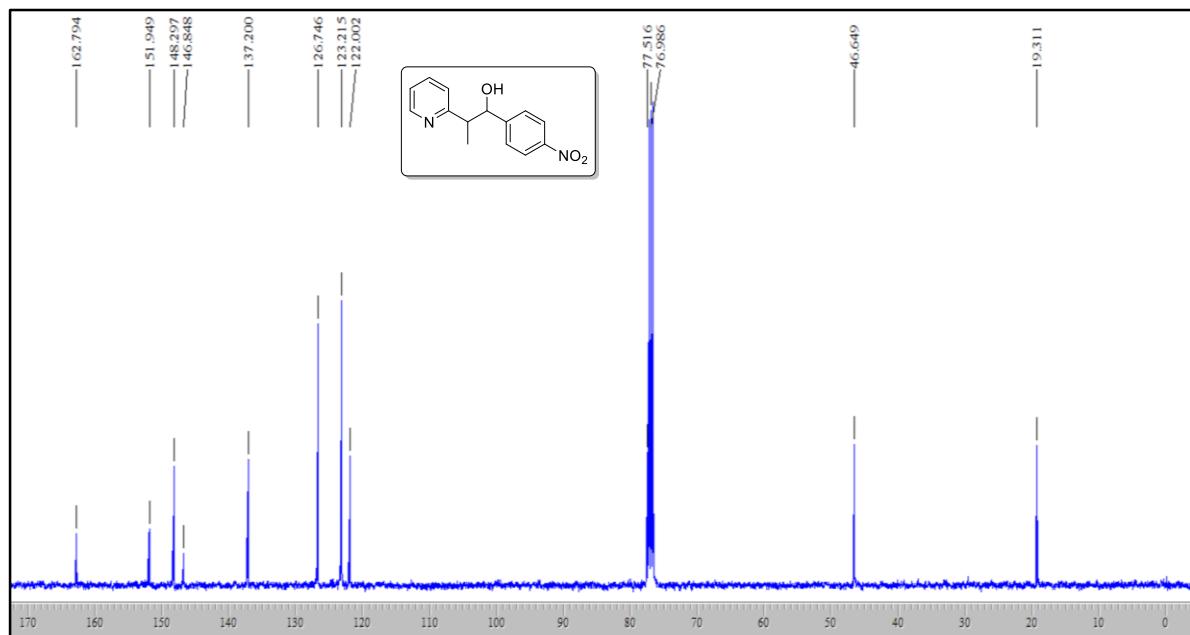
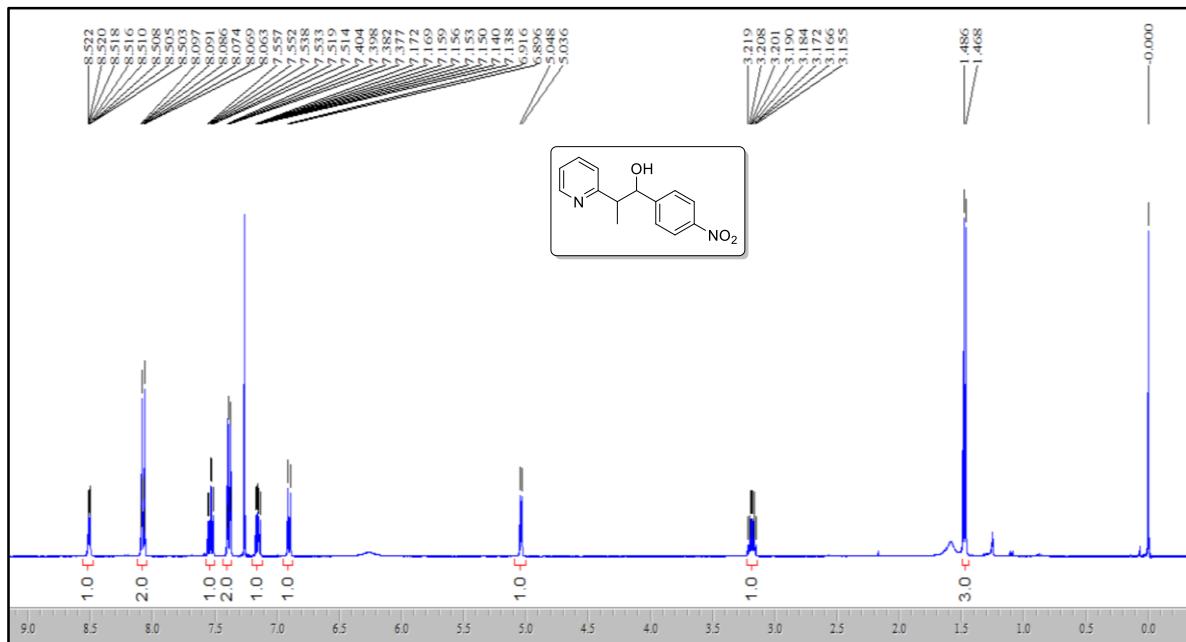
2-(6-Methylpyridin-2-yl)-1-(thiophen-2-yl)ethan-1-ol (3r)



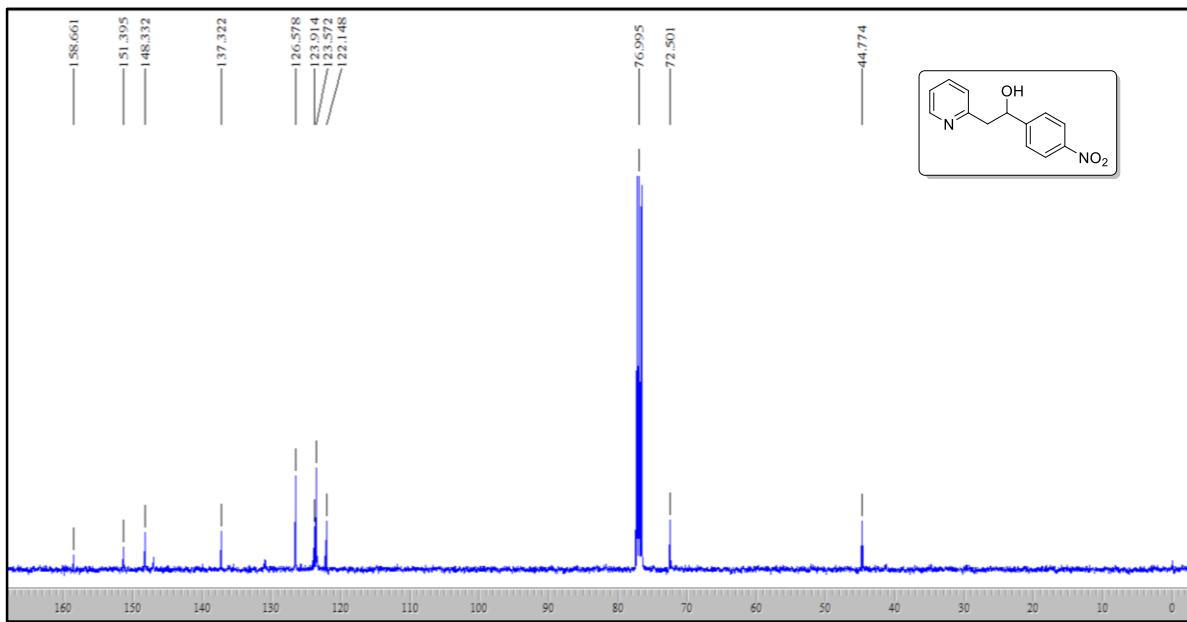
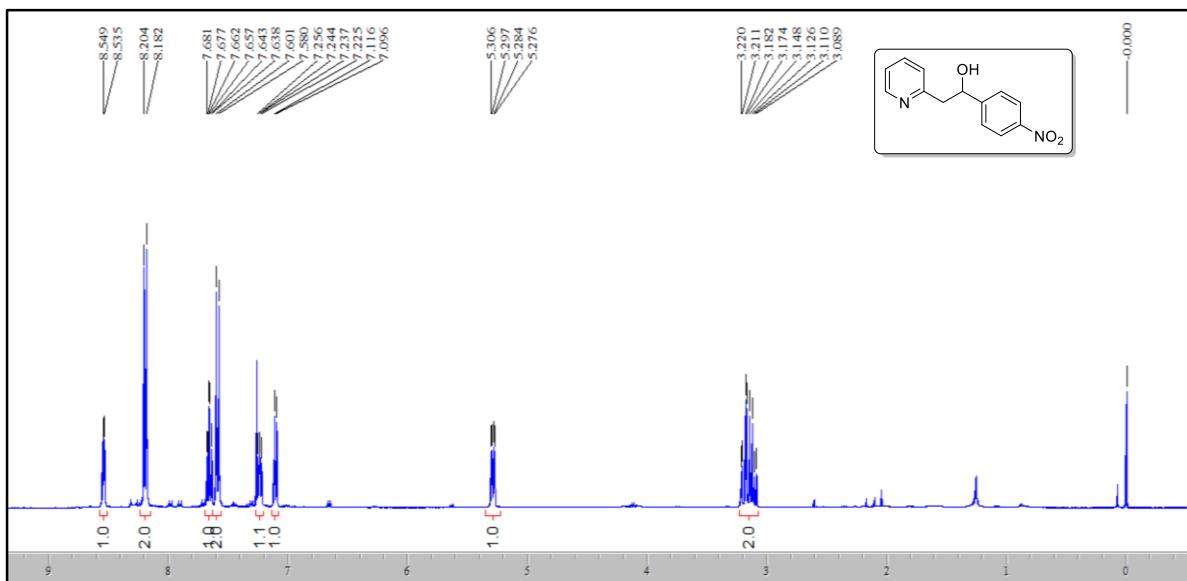
2-(4,6-Dimethylpyridin-2-yl)-1-(4-nitrophenyl)ethan-1-ol (5b)



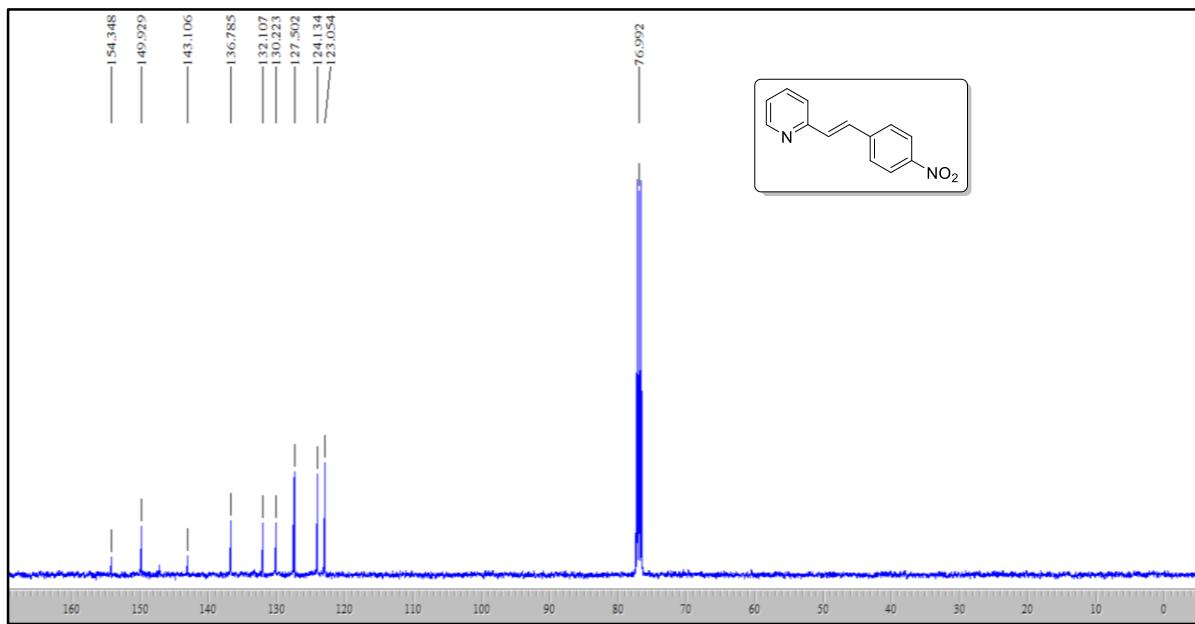
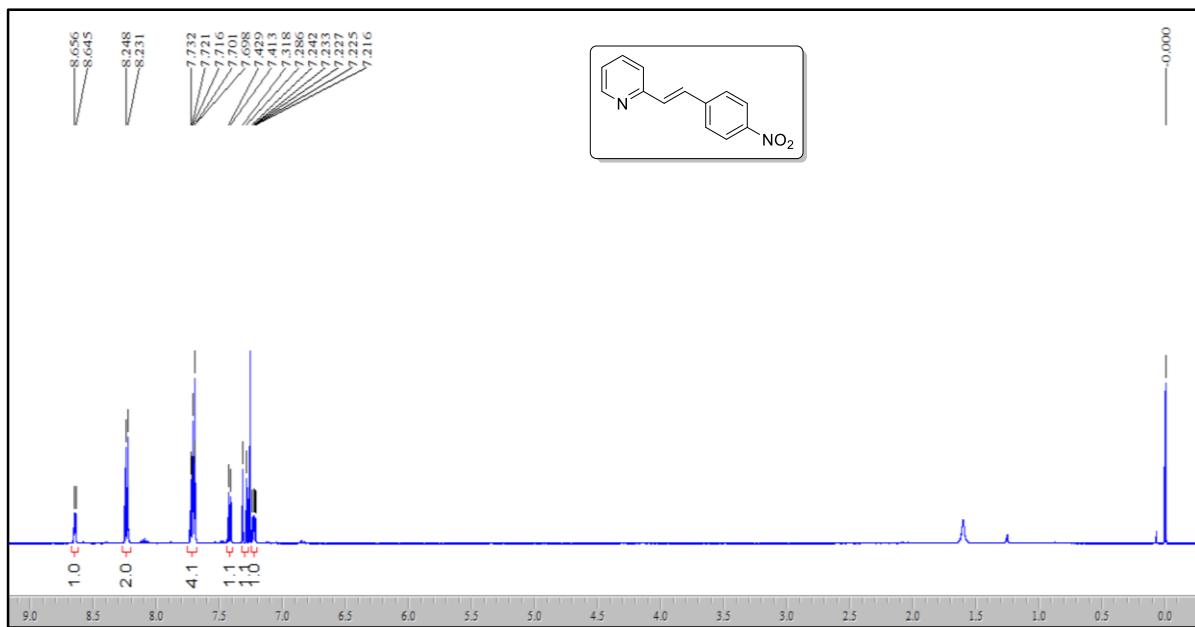
1-(4-Nitrophenyl)-2-(pyridin-2-yl)propan-1-ol (5c)



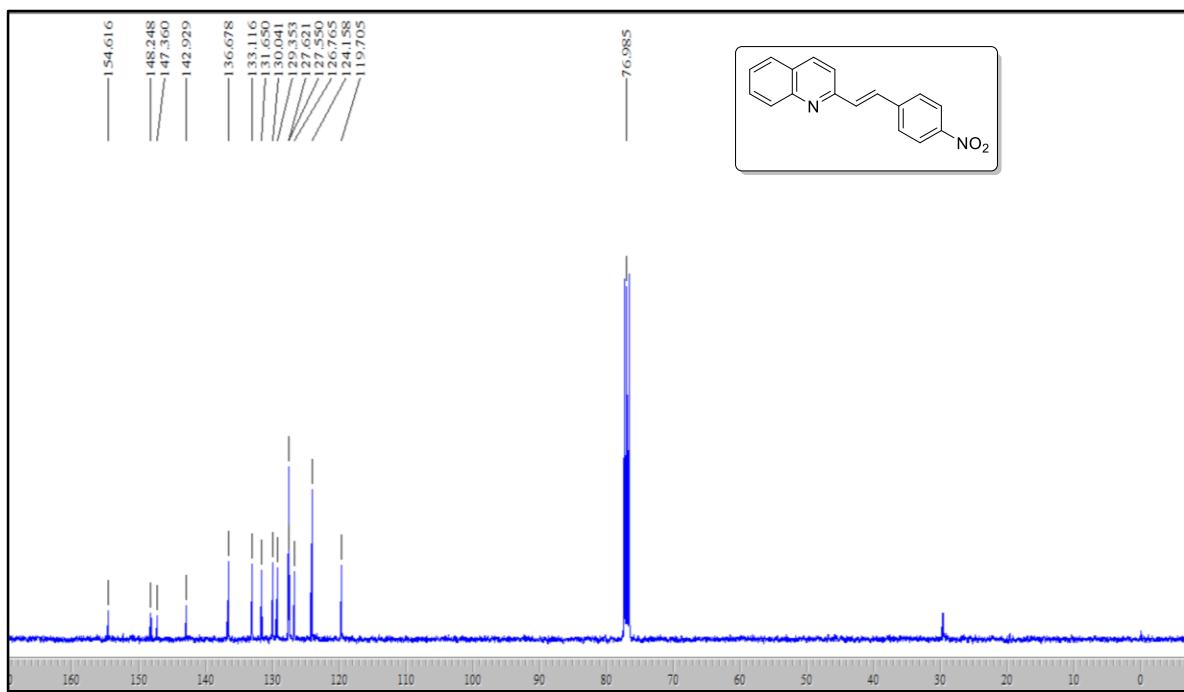
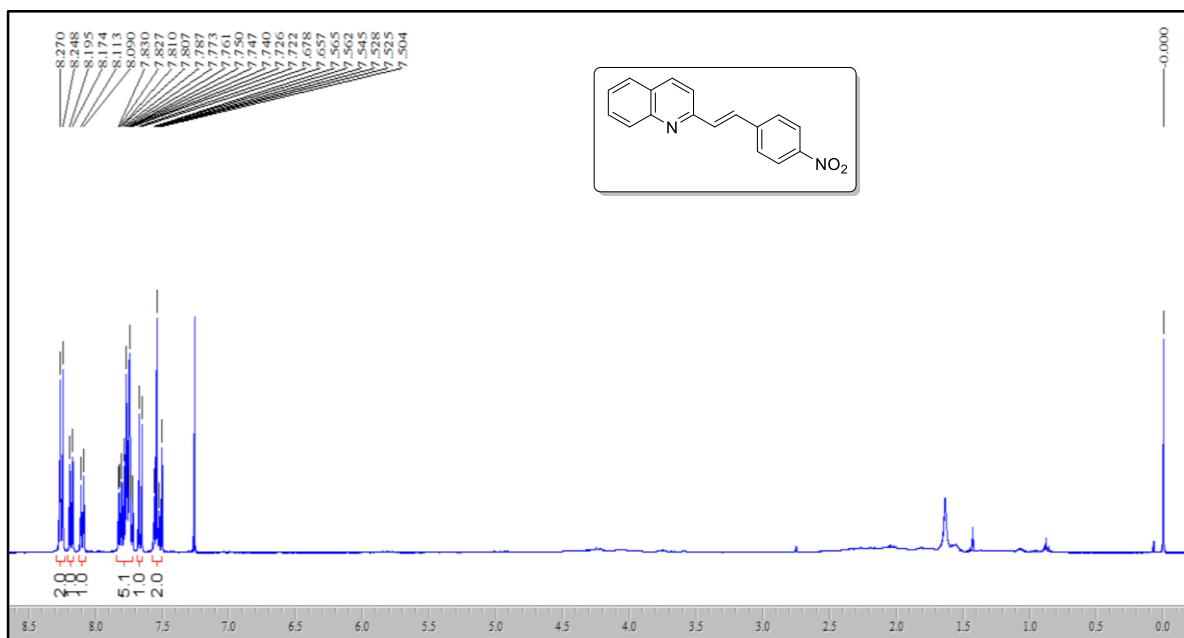
1-(4-Nitrophenyl)-2-(pyridin-2-yl)ethan-1-ol (5d)



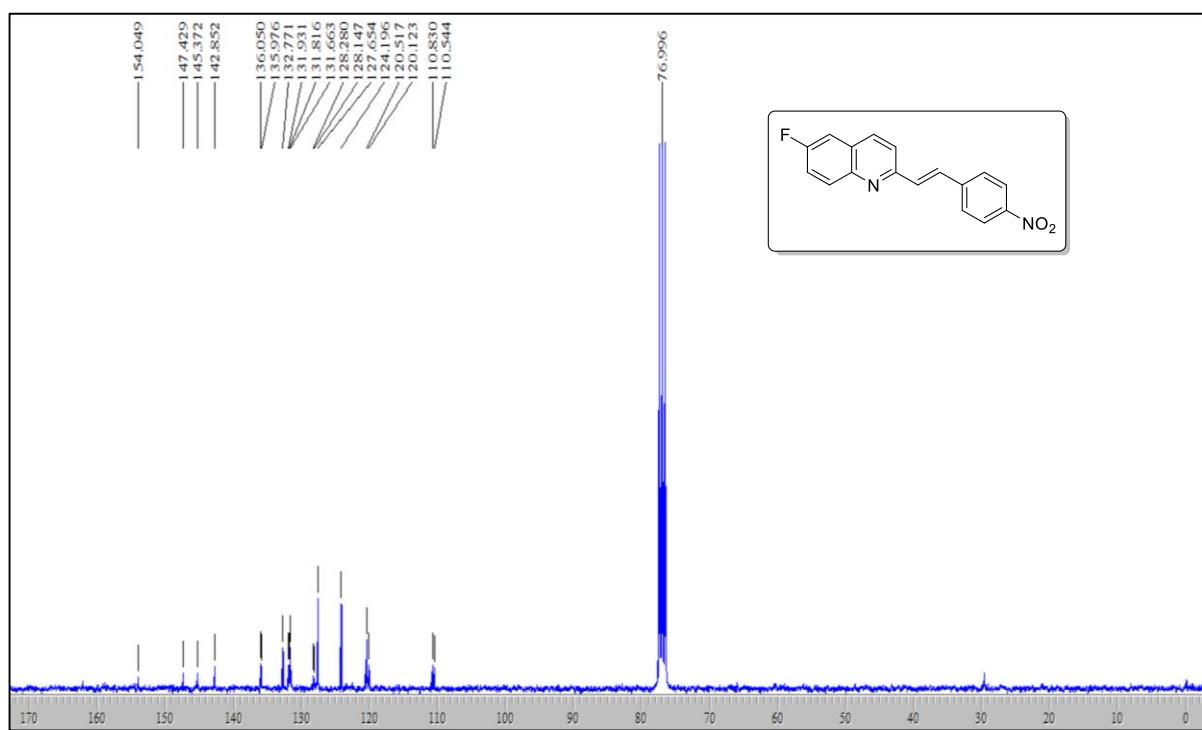
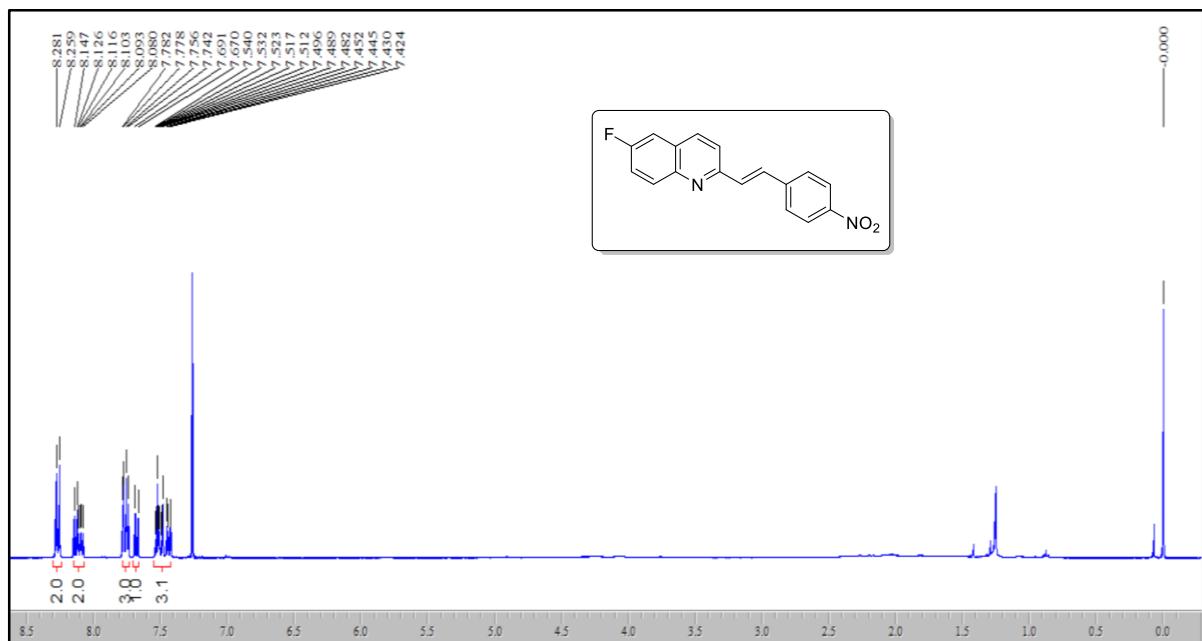
(E)-2-(4-Nitrostyryl)pyridine (6d)



(E)-2-(4-Nitrostyryl)quinoline (6f)



(E)-6-Fluoro-2-(4- nitrostyryl)quinoline (6g)



4. References

1. Ortalm, A.; Rathousky, J.; Ekloff, G. S.; Zukal, A. *Microporous Mater.*, **1996**, *6*, 171-180.
2. Dan, M.; Gang, H.; Shengying, W.; Xin, L.; Jianjun, Y.; Limin, W. *Eur. J. Org. Chem.*, **2014**, *2014*, 3009–3019.
3. Wang, F. F.; Luo, C. P.; Wang, Y.; Deng, G.; Yang, L. *Org. Biomol. Chem.*, **2012**, *10*, 8605–8608.