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Tsuji–Trost *N*-Allylation with Allylic Acetates by Using a Cellulose–Palladium Catalyst

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SUPPORTING INFORMATION

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Title: Tsuji–Trost *N*-Allylation with Allylic Acetates by Using a Cellulose–Palladium Catalyst

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1. General Information

The reagents were obtained commercially and used without further purification. Cellulose fiber, medium, was obtained from Sigma-Aldrich. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300 MHz NMR spectrometer using TMS as the internal standard. Chemical shifts are given in parts per million (δ) and coupling constants (J) in Hz. MS data was obtained on Hewlett Packard HP 5973 quadrupole Mass Selective Detector with interface for 6890 series GC. Thin-layer chromatography (TLC) was performed on silica gel 60 F254 precoated glass plates.

2. Experimental Procedures

2.1. Procedure for the catalyst preparation

1 gm of cellulose fiber was dispersed well in 20 mL of water. PdCl₂ (150 mg) was added in small quantities to the suspension. It was stirred at room temperature for 1 h. NaBH₄ (2.5 equiv.) was added in small quantities to the aqueous suspension and was stirred for 15 h at room temperature. The catalyst was centrifuged followed by washing with acetone and was dried under vacuum to obtain black colored powder catalyst.

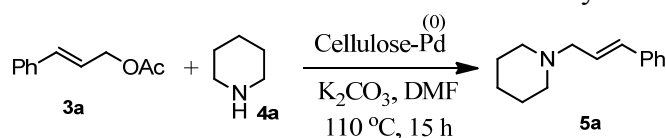
2.2. General procedure for the synthesis of allyl amines

A mixture of allyl acetate (1.0 mmol), nucleophile (1.2 mmol), cellulose-Pd (50 mg) and potassium carbonate (2.0 mmol) in anhydrous DMF (3 mL) is heated at 110 °C under N₂ atmosphere for 15 hours. Upon completion of the reaction as indicated by TLC, the reaction mixture is diluted with water and centrifuged/filtered to separate the catalyst. The decanted liquid is extracted with ethyl acetate (3 x 10 mL). The ethyl acetate layer is dried over anhydrous sodium sulfate and evaporated to get the crude product. The crude product is purified by passing through silica gel column eluting with ethyl acetate-hexane.

2.3 Recovery and reuse of Cellulose-Pd catalyst

After completion of the reaction, the catalyst was separated from the reaction mixture by filtration. The catalyst was washed with acetone, dried under vacuum, and recycled for 5 consecutive reactions without any significant loss in efficiency (Table S1).

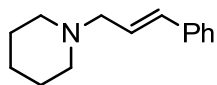
Table S1. Reuse of the cellulose-Pd catalyst.



Cycle	Yield (%)
1	87
2	85
3	85
4	83
5	82

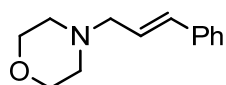
¹H & ¹³C NMR spectra

1-Cinnamylpiperidine (5a)^[1]



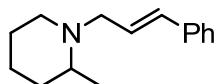
Yield : 87%. ¹H NMR (300 MHz, CDCl₃) δ 1.45 (br s, 2H), 1.61-1.68 (m, 4H), 2.49 (m, 4H), 3.18 (dd, *J* = 6.9 Hz and 6Hz, 2H), 6.32 (dt, *J* = 15.0 and 6.9 Hz, 1H), 6.53 (d, *J* = 15.0 Hz, 1H), 7.20-7.26 (m, 1H), 7.35-7.28 (m, 2H), 7.37-7.41 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 24.2, 25.7, 54.4, 61.6, 126.3, 126.6, 127.4, 128.5, 133.0, 137.0. MS (EI) calcd for C₁₄H₁₉N (M⁺) 201.1517, found 201.1.

4-Cinnamylmorpholine (5b)^[1]



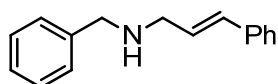
Yield : 90%. ¹H NMR (300 MHz, CDCl₃) δ 2.53 (t, *J* = 6.0 Hz, 4H), 3.18 (dd, *J* = 7.2 and 1.2 Hz, 2H), 3.76 (t, *J* = 6.0 Hz, 4H), 6.28 (dt, *J* = 15.9 and 7.5 Hz, 1H), 6.55 (d, *J* = 15.9 Hz, 1H), 7.22-7.28 (m, 1H), 7.30-7.36 (m, 2H), 7.37-7.41 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 53.7, 61.5, 67.0, 126.0, 126.3, 127.6, 128.6, 133.5, 136.8. MS (EI) calcd for C₁₃H₁₇NO (M⁺) 203.1310, found 203.1.

1-Cinnamyl-2-methylpiperidine (5c)



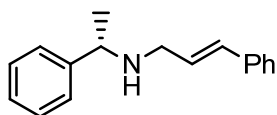
Yield : 95%. ¹H NMR (300 MHz, CDCl₃) δ 1.23 (d, *J* = 6.0 Hz, 3H), 1.28-1.56 (m, 2H), 1.65-1.73 (m, 4H), 2.29-2.38 (m, 1H), 2.49-2.57 (m, 1H), 3.03 (dt, *J* = 12.0 and 6.0 Hz, 1H), 3.27 (dd, *J* = 12.0 and 6.0 Hz, 1H), 3.64 (ddd, *J* = 14.1, 6.0 and 1.5 Hz, 1H), 6.35 (dt, *J* = 15.0 and 5.85 Hz, 1H), 6.55 (d, *J* = 15.0 Hz, 1H), 7.22-7.28 (m, 1H), 7.30-7.36 (m, 2H), 7.38-7.42 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 18.5, 23.5, 25.2, 33.7, 51.9, 56.0, 56.2, 124.6, 126.4, 127.6, 128.6, 134.1, 136.7. MS (EI) calcd for C₁₅H₂₁N (M⁺) 215.1674, found 215.1.

(*E*)-*N*-Benzyl-3-phenylprop-2-en-1-amine (5d)^[2]



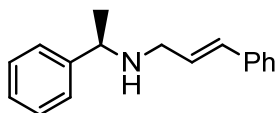
Yield : 85%. ¹H NMR (300 MHz, CDCl₃) δ 3.48 (dd, *J* = 6.30 and 1.35 Hz, 2H), 3.88 (s, 2H), 6.35 (dt, *J* = 15.0 and 7.20 Hz, 1H), 6.57 (d, *J* = 15 Hz, 1H), 7.22-7.42 (m, 10H). ¹³C NMR (75 MHz, CDCl₃) δ 51.0, 53.1, 126.3, 127.1, 127.4, 128.0, 128.3, 128.5, 128.6, 131.8, 137.1, 139.8. MS (EI) calcd for C₁₆H₁₇N (M⁺) 223.1361, found 223.1.

(*S,E*)-3-Phenyl-*N*-(1-phenylethyl)prop-2-en-1-amine (5e)^[3]



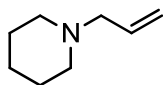
Yield : 89%. ^1H NMR (300 MHz, CDCl_3) δ 1.43 (d, $J = 6.0$ Hz, 3H), 3.30 (dt, $J = 6.30$ and 1.2 Hz, 2H), 3.89 (dd, $J = 12.0$ and 6.0 Hz, 1H), 6.31 (dt, $J = 15.0$ and 6.6 Hz, 1H), 6.50 (d, $J = 15$ Hz, 1H), 7.21-7.41 (m, 10H). ^{13}C NMR (75 MHz, CDCl_3) δ 24.23, 49.67, 57.60, 126.25, 126.66, 126.98, 127.30, 128.50, 128.52, 128.61, 131.19, 137.21, 145.44. MS (EI) calcd for $\text{C}_{17}\text{H}_{19}\text{N}$ (M^+) 237.1517, found 237.1.

(R,E)-3-Phenyl-N-(1-phenylethyl)prop-2-en-1-amine (5f) ^[4]



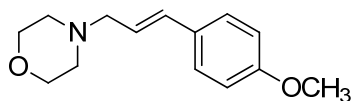
Yield : 90%. ^1H NMR (300 MHz, CDCl_3) δ 1.43 (d, $J = 6.0$ Hz, 3H), 3.31 (dt, $J = 6.30$ and 1.2 Hz, 2H), 3.89 (dd, $J = 12.0$ and 6.0 Hz, 1H), 6.31 (dt, $J = 15.0$ and 6.6 Hz, 1H), 6.50 (d, $J = 15$ Hz, 1H), 7.20-7.42 (m, 10H). ^{13}C NMR (75 MHz, CDCl_3) δ 24.23, 49.67, 57.60, 126.25, 126.66, 126.98, 127.30, 128.50, 128.52, 128.61, 131.19, 137.21, 145.44. MS (EI) calcd for $\text{C}_{17}\text{H}_{19}\text{N}$ (M^+) 237.1517, found 237.1.

1-Allylpiperidine (5g) ^[5]



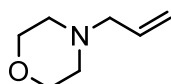
Yield : 96%. ^1H NMR (300 MHz, CDCl_3): δ 1.32-1.60 (m, 6H), 2.17-2.40 (m, 4H), 2.85-3.01 (m, 2H), 5.03-5.15 (m, 2H), 5.80-5.92 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ 24.4, 26.0, 54.3, 62.7, 117.7, 135.5. MS (EI) calcd for $\text{C}_8\text{H}_{15}\text{N}$ (M^+) 125.1204, found 125.1.

(E)-4-(3-(4-Methoxyphenyl)allyl)morpholine (5h) ^[6]



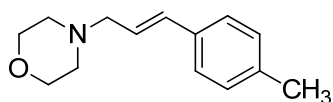
Yield : 86%. ^1H NMR (300 MHz, CDCl_3) δ 2.48 (s, 4H), 3.12 (d, $J = 6.5$ Hz, 2H), 3.75 (dd, $J = 4.6$ and 4.5 Hz, 4H), 3.79 (s, 3H), 6.12 (dt, $J = 16.0$ and 6.5 Hz, 1H), 6.48 (d, $J = 16.0$ Hz, 1H), 6.82-6.83 (m, 2H), 7.28-7.33 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 53.5, 55.2, 61.4, 67.0, 114.0, 123.5, 127.4, 129.5, 132.7, 159.1. MS (EI) calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_2$ (M^+) 233.1416, found 233.1.

4-Allylmorpholine (5i) ^[5]



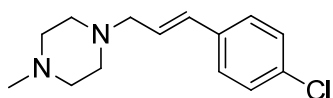
Yield : 93%. ^1H NMR (300 MHz, CDCl_3): δ 2.21-2.45 (m, 4H), 2.88-3.03 (m, 2H), 3.55-3.72 (m, 4H), 5.06-5.22 (m, 2H), 5.65-5.82 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ 53.5, 62.1, 67.0, 118.4, 134.5. MS (EI): m/z calcd for $\text{C}_7\text{H}_{13}\text{NO}$ [M^+]: 127.0997; found: 127.1.

(E)-4-(3-(p-Tolyl)allyl)morpholine (5j) ^[6]



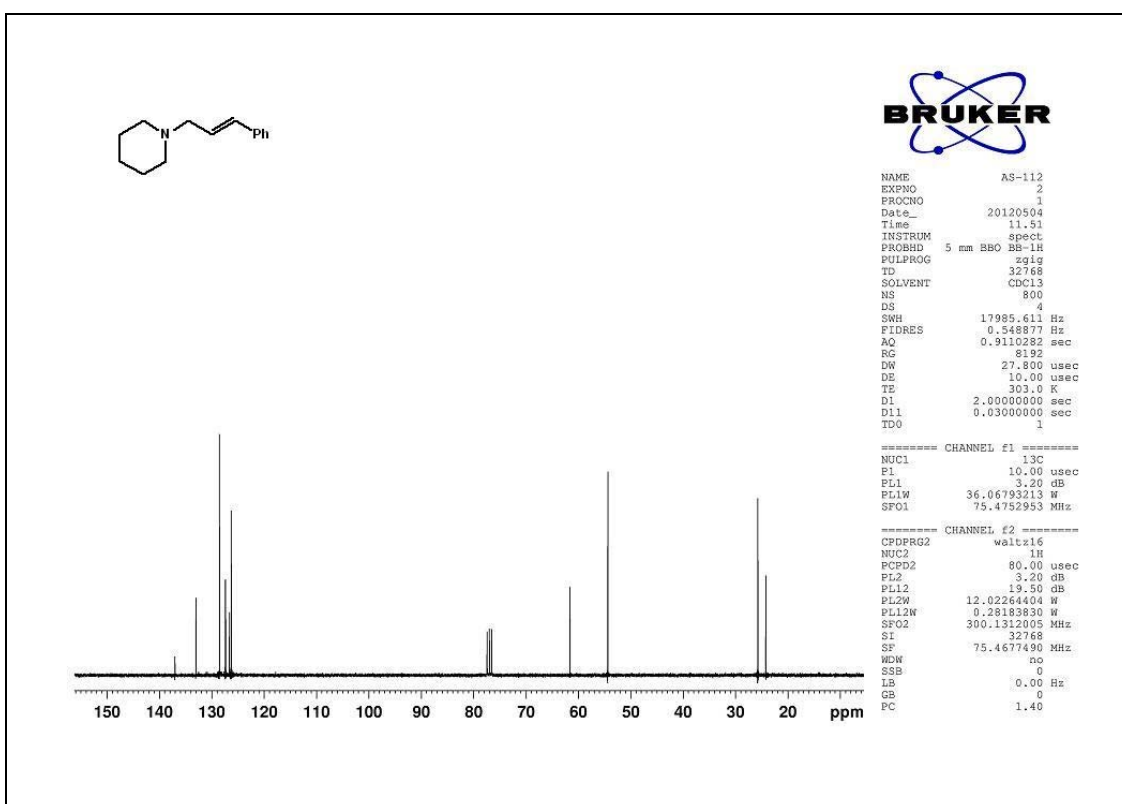
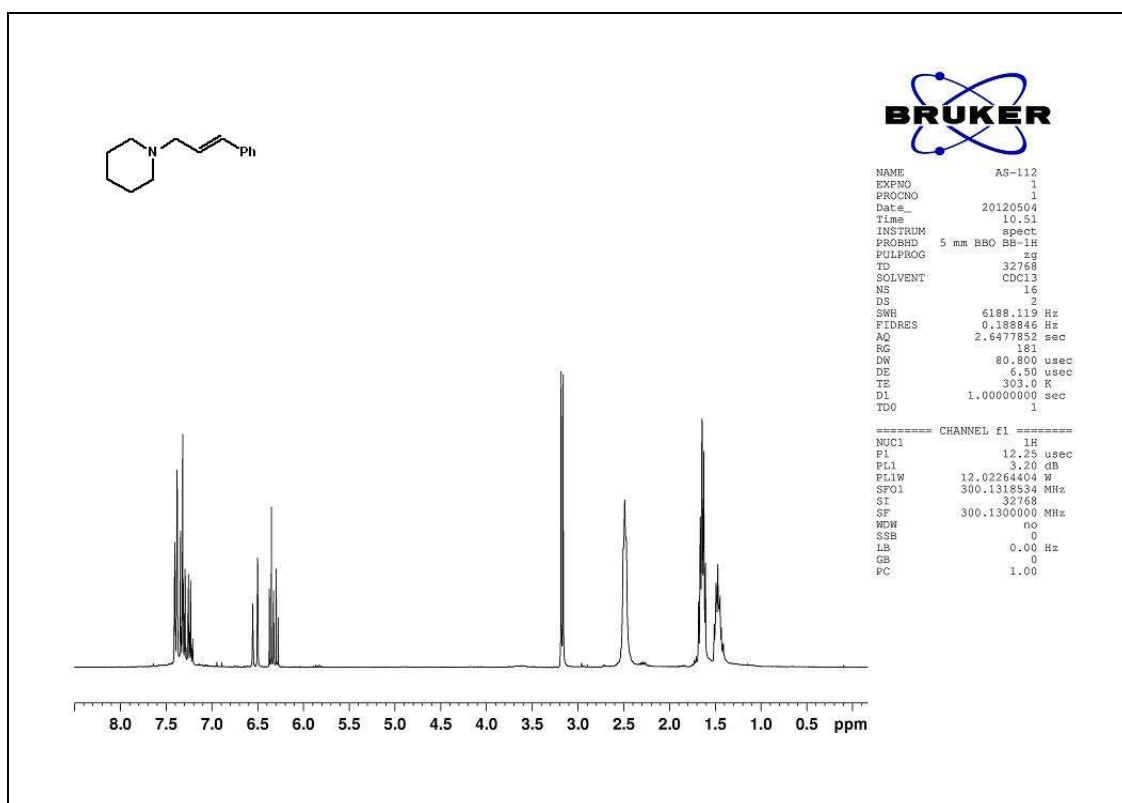
Yield : 88%. ^1H NMR (300 MHz, CDCl_3): δ 2.33 (s, 3H), 2.42–2.56 (m, 4H), 3.10 (dd, $J = 6.6$ and 1.2 Hz, 2H), 3.68–3.73 (m, 4H), 6.18 (dt, $J = 16.0$ and 6.5 Hz, 1H), 6.48 (d, $J = 16.0$ Hz, 1H), 7.10 (d, $J = 8.0$ Hz, 2H), 7.25 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (75 Hz, CDCl_3): $\delta = 21.4, 53.7, 61.5, 67.2, 124.9, 126.4, 129.3, 133.4, 134.1, 137.5$. MS (EI): m/z calcd for $\text{C}_{14}\text{H}_{19}\text{NO}$ [M^+]: 217.1467; found: 217.1.

(E)-1-(3-(4-chlorophenyl)allyl)-4-methylpiperazine (5k)^[7]

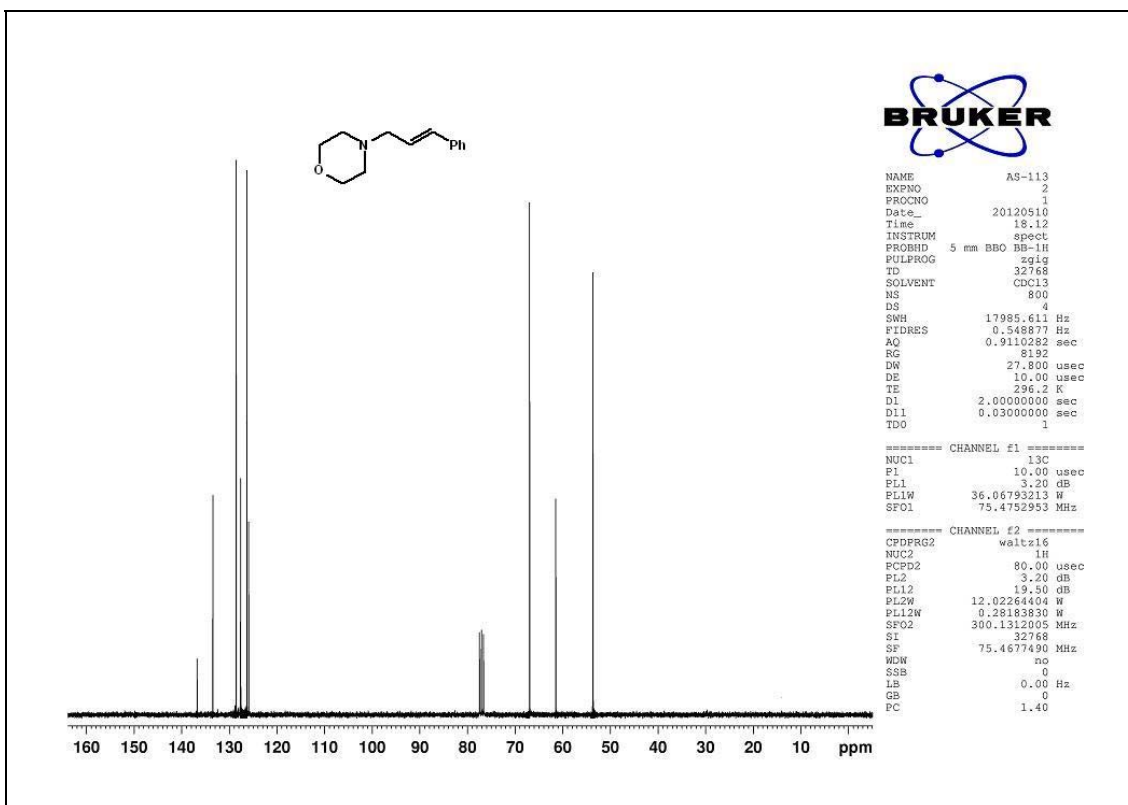
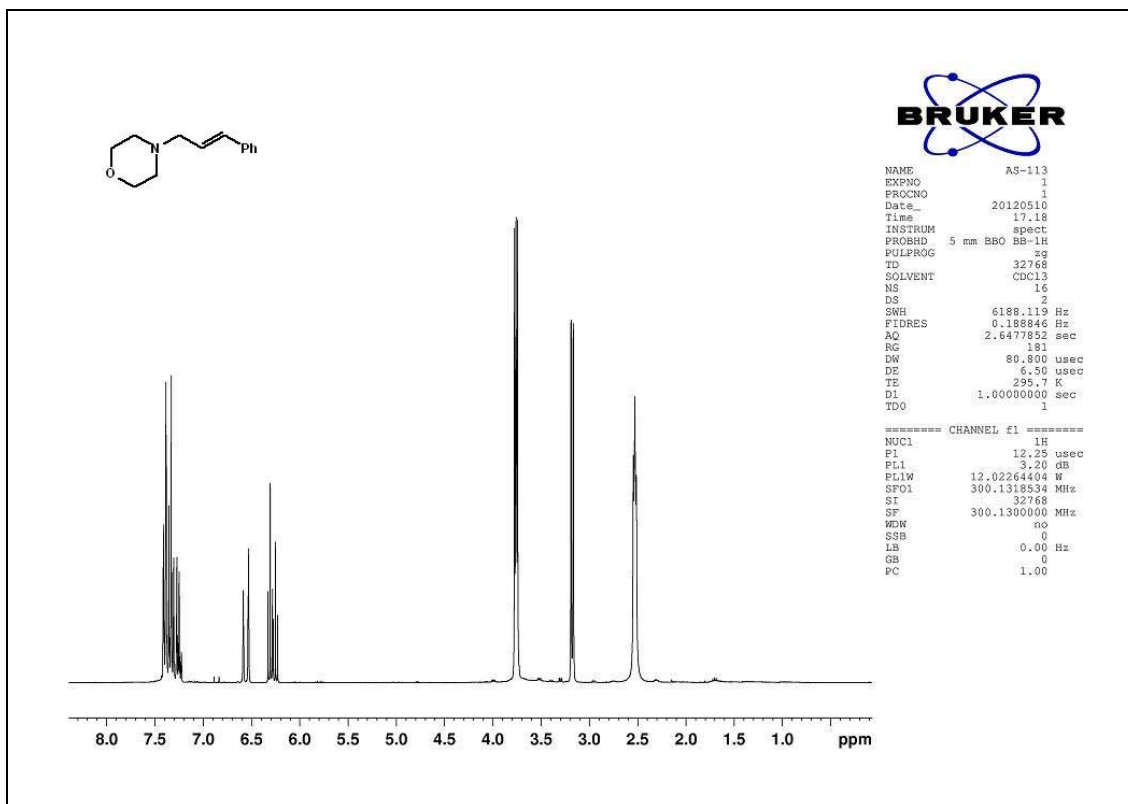


Yield : 92%. ^1H NMR (300 MHz, CDCl_3): δ 2.23 (s, 3H), 2.44 (br s, 8H), 3.11 (d, $J = 6.5$ Hz, 2H), 6.14–6.23 (m, 1H), 6.42 (d, $J = 16.0$ Hz, 1H), 7.14–7.25 (m, 4H); ^{13}C NMR (75 Hz, CDCl_3): δ 46.2, 53.3, 55.2, 60.9, 127.4, 127.6, 128.8, 131.8, 133.2, 135.4; MS (EI): m/z calcd for $\text{C}_{14}\text{H}_{19}\text{ClN}_2$ [M^+]: 250.1237; Found: 250.1.

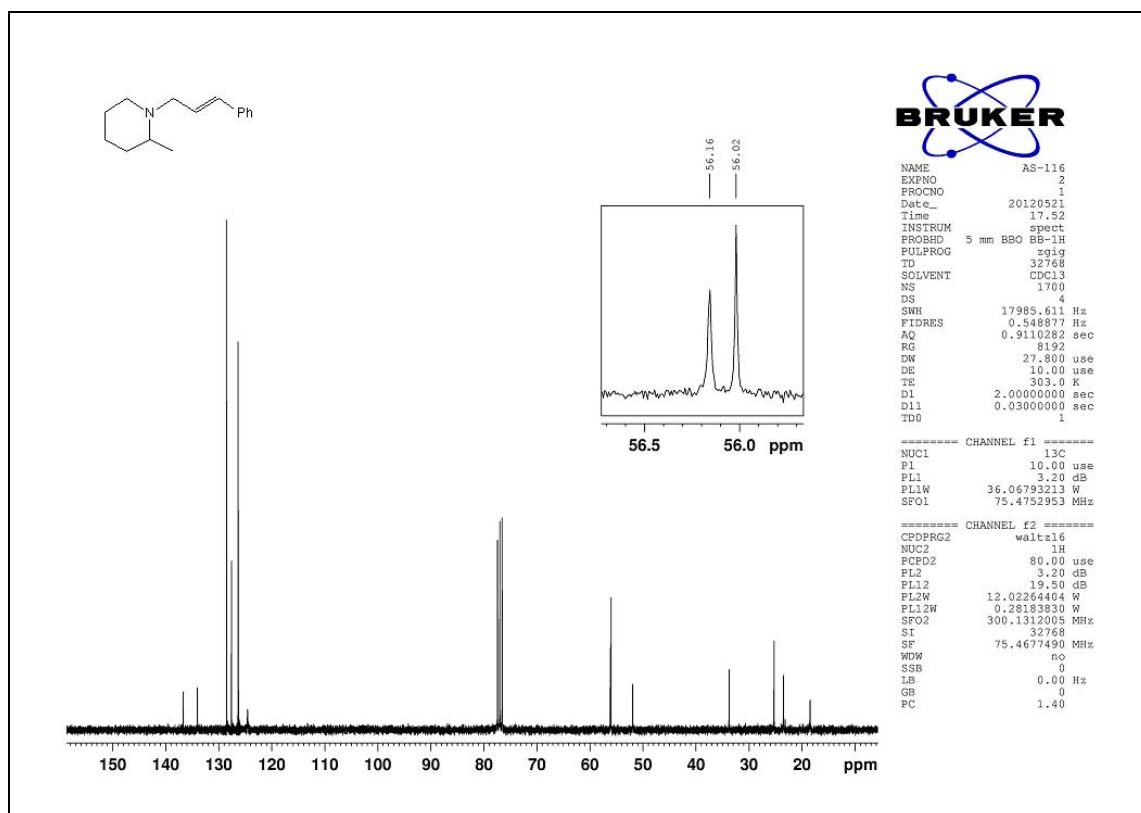
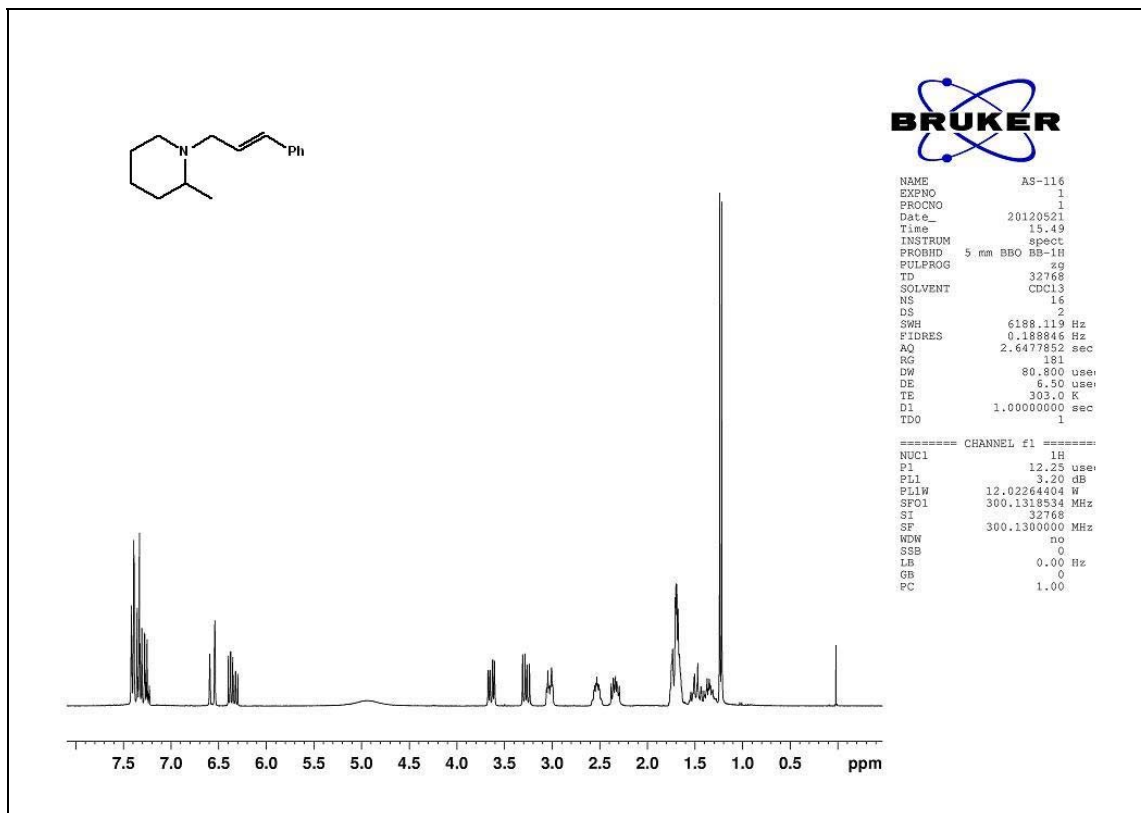
^1H & ^{13}C NMR spectra of the representative compounds
1-Cinnamylpiperidine (5a)



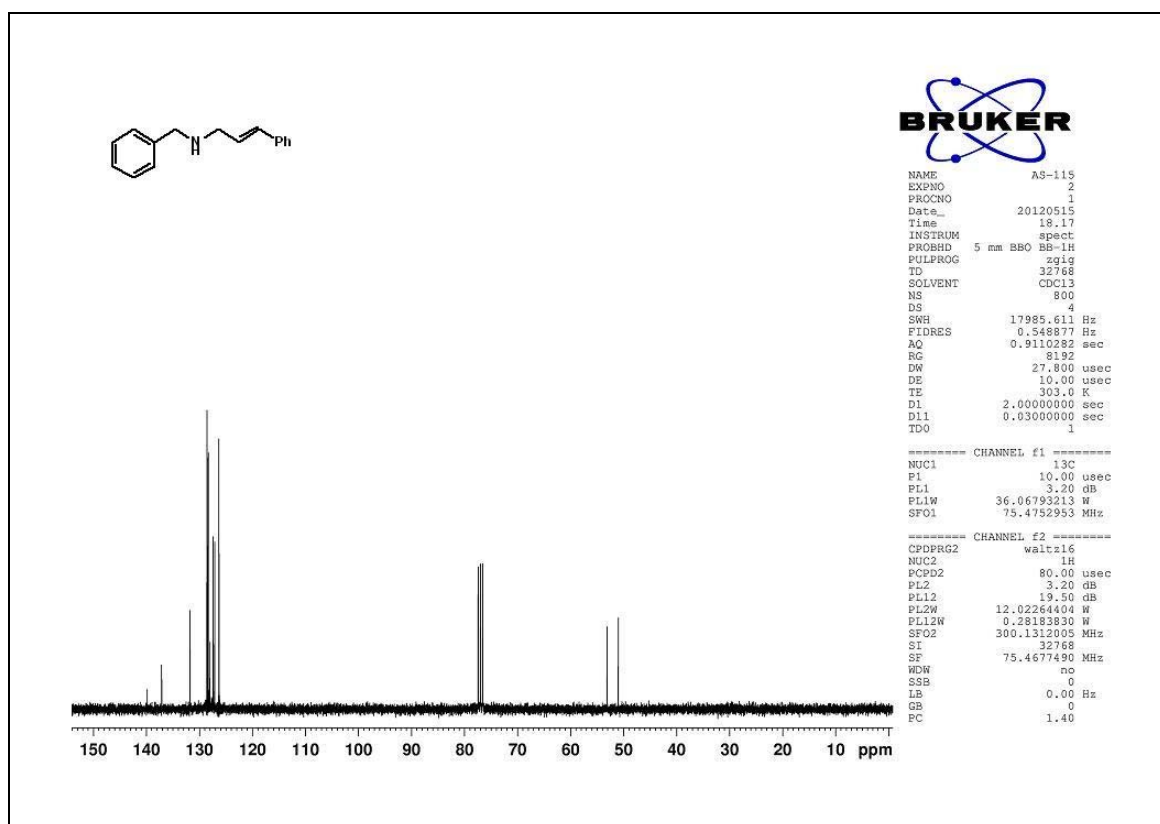
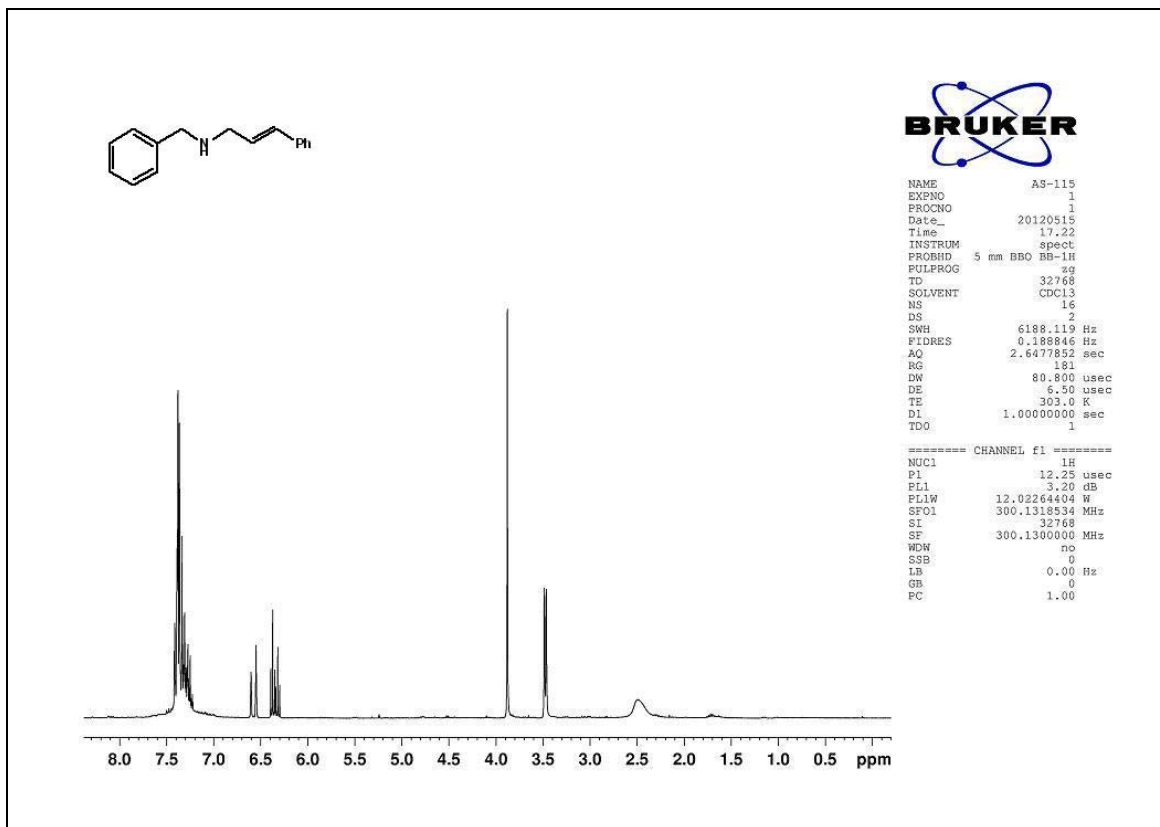
4-Cinnamylmorpholine (5b)



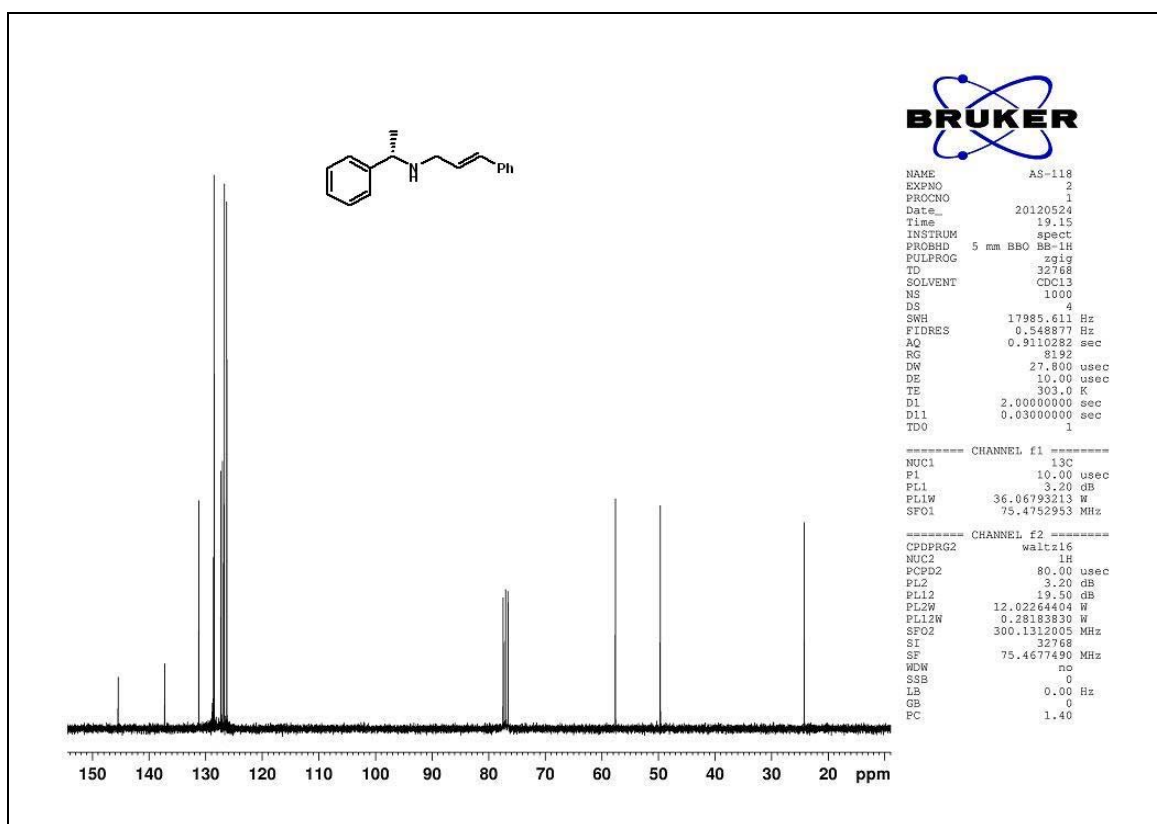
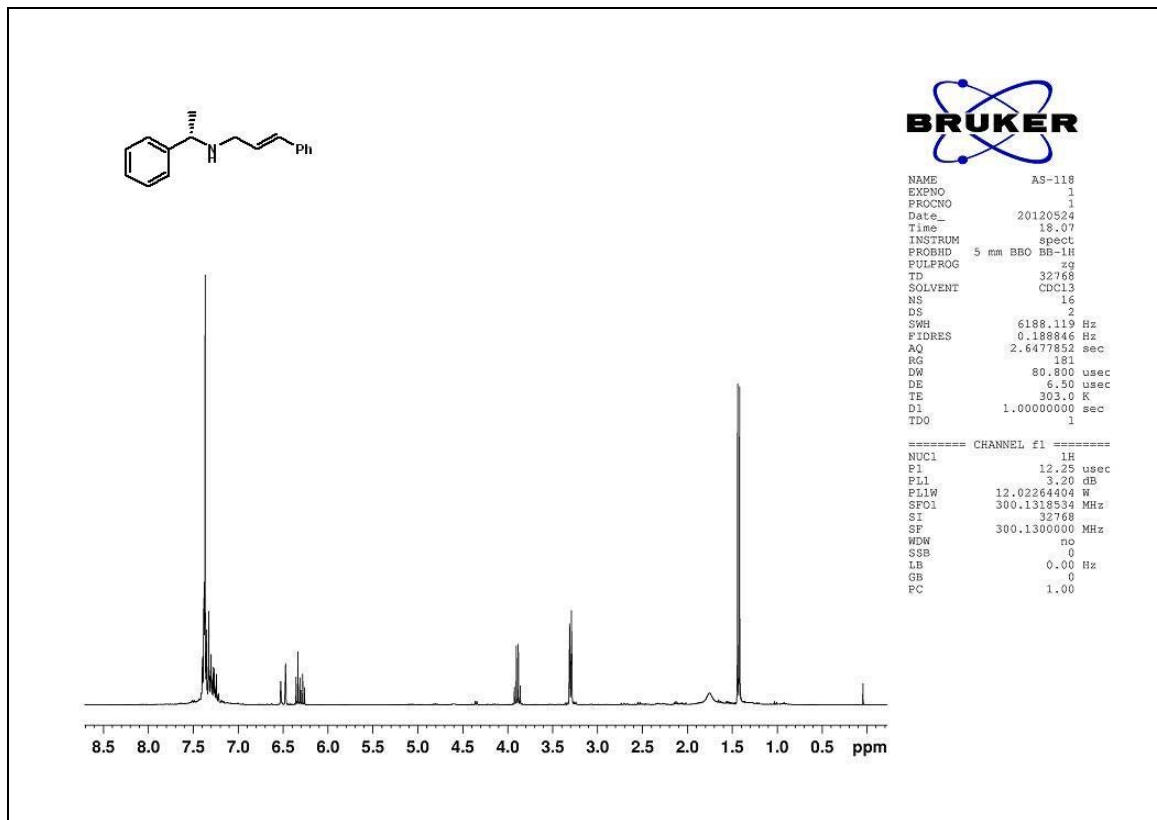
1-Cinnamyl-2-methylpiperidine (5c)



(E)-N-Benzyl-3-phenylprop-2-en-1-amine (5d)



(*S,E*)-3-Phenyl-*N*-(1-phenylethyl)prop-2-en-1-amine (5e)



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