L-Proline Promoted Ullmann-Type Reaction of Vinyl Bromides with Imidazoles in Ionic Liquids

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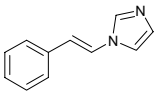
Supporting information

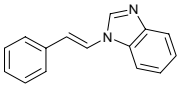
General Methods. All reagents and solvents were pure analytical grade materials purchased from commercial sources and were used without further purification, if not stated otherwise. All *E*-vinyl bromides were prepared according to the known literature.[1] All melting points are uncorrected. The NMR spectra were recorded in $CDCl_3$ or DMSO- d_6 on a 400 MHz instrument with TMS as internal standard. IR spectra were taken as KBr plates. TLC was carried out with 0.2 mm thick silica gel plates (GF254). Visualization was accomplished by UV light. The columns were hand packed with silica gel 60 (200-300). All reactions were carried out in a 10 mL flask equipped with a magnetic stir bar under N_2 atmosphere.

Typical Procedure

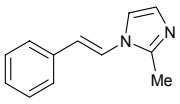
To β-bromostyrene (2 mmol), CuI (0.2 mmol), L-proline (0.4 mmol), K_2CO_3 (5 mmol) and [Bmim]BF_4 (4 mL) mixture, imidazole (2.2 mmol) was added to a 10 mL flask equipped with a magnetic stir bar. Under N_2 atmosphere, the mixture was stirred at 110 °C for 20 h. The resultant product was extracted by ethyl acetate (3×2 mL). The product was further purified by column chromatography (5:1 petroleum ether / ethyl acetate), yield: 87%.



: mp 84-85 °C (Lit.[2] 85-86 °C); ^{1}H NMR (DMSO-d_6) δ 7.01 (d, J = 15.00 Hz, 1H), 7.04 (s, 1H), 7.24 (t, J = 7.60 Hz, 1H), 7.35 (t, J = 7.60 Hz, 2H), 7.48 (d, J = 7.60 Hz, 2H), 7.70 (s, 1H), 7.83 (d, J = 15.00 Hz, 1H), 8.02 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 116.97, 117.36, 124.12, 126.37, 127.81, 129.17, 130.08, 135.45, 137.36; IR 3149, 3099, 3069, 1657cm^{-1}; Anal. Calcd for $C_{11}H_{10}N_2$: C 77.62, H 5.92, N 16.46; Found: C 77.48, H 5.88, N 16.56.

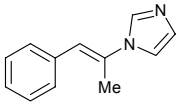


: mp 94-95 °C (Lit.[2] 95-96 °C); ^{1}H NMR (DMSO-d_6) δ 7.25 (d, J = 15.20 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.42 – 7.35 (m, 3H), 7.65 (d, J = 7.60 Hz, 2H), 7.72 (d, J = 7.60 Hz, 1H), 8.01 (d, J = 7.60 Hz, 1H), 8.07 (d, J = 15.20 Hz, 1H), 8.76 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 110.31, 120.00, 120.69, 121.18, 123.12, 123.88, 126.17, 128.09, 128.94, 132.67, 134.59, 140.72, 143.91; IR 3047, 3019, 1697cm^{-1}; Anal. Calcd for $C_{15}H_{12}N_2$: C 81.79, H 5.49, N 12.72; Found: C 81.69, H 5.41, N 12.85.

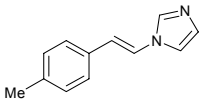


: mp 88-89 °C (Lit.[2] 89-90 °C); ^{1}H NMR (DMSO-d_6) δ 2.41 (s, 3H), 6.84 (s, 1H), 6.87 (d, J = 14.40 Hz, 1H), 7.22 (t, J = 7.60 Hz, 1H), 7.33 (t, J = 7.60 Hz, 2H), 7.54 (d, J = 7.60 Hz,

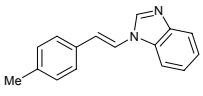
2H), 7.59 (d, J = 14.40 Hz, 1H), 7.60 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.44, 115.64, 119.21, 119.27, 122.10, 126.10, 127.91, 128.41, 128.87, 134.67; IR 3090, 3060, 1655 cm^{-1}; Anal. Calcd for $C_{12}H_{12}N_2$: C 78.23, H 6.57, N 15.21; Found: C 78.41, H 6.59, N 15.40.



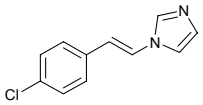
: mp 59-60 °C (Lit.[3] 60-61 °C); ^{1}H NMR ($CDCl_3$) δ 2.29 (s, 3H), 6.62 (s, 1H), 7.10 (s, 1H), 7.19 (s, 1H), 7.23 – 7.27 (m, 3H), 7.34 (t, J = 7.20 Hz, 2H), 7.76 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 17.16, 117.68, 121.70, 126.56, 127.66, 128.51, 128.99, 132.37, 134.47, 134.78; IR 3084, 2996, 1699cm^{-1}; Anal. Calcd for $C_{12}H_{12}N_2$: C 78.23, H 6.57, N 15.21; Found: C 78.19, H 6.66, N 15.33.



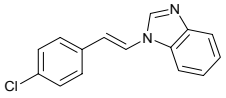
: mp 96-97 °C; ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3H), 6.70 (d, J = 14.80 Hz, 1H), 7.14 (s, 1H), 7.17 (d, J = 7.60 Hz, 2H), 7.25 (s, 1H), 7.28 (d, J = 14.80 Hz, 1H), 7.29 (d, J = 7.60 Hz, 2H), 7.74 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.20, 116.19, 118.79, 121.85, 126.01, 129.57, 130.30, 131.43, 136.28, 137.98; IR 3112, 3095, 2922, 1653cm^{-1}; ES$^+$MS m/z (relative intensity, %): 185 [M^++1, 100]; Anal. Calcd for $C_{12}H_{12}N_2$: C 78.23, H 6.57, N 15.21; Found: C 78.26, H 6.80, N 15.11.



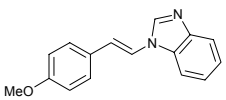
: mp 113-114 °C; ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3H), 6.95 (d, J = 14.60 Hz, 1H), 7.23 (d, J = 8.00 Hz, 2H), 7.41 – 7.36 (m, 4H), 7.48 (d, J = 14.60 Hz, 1H), 7.62 (d, J = 7.60 Hz, 1H), 7.88 (d, J = 7.60 Hz, 1H), 8.26 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.24, 110.35, 120.30, 120.32, 120.58, 123.06, 123.82, 126.09, 129.64, 131.66, 132.69, 138.14, 140.71, 143.75; IR 3124, 3052, 3022, 2917, 1656 cm^{-1}; ES$^+$MS m/z (relative intensity, %): 235 [M^++1, 100]; Anal. Calcd for $C_{16}H_{14}N_2$: C 82.02, H 6.02, N 11.96; Found: C 81.95, H 6.28, N 11.87.



: mp 206-207 °C; ^{1}H NMR (DMSO-d_6) δ 7.54 (d, J = 8.40 Hz, 2H), 7.60 (d, J = 14.40 Hz, 1H), 7.63 (d, J = 8.40 Hz, 2H), 7.88 (s, 1H), 8.16 (d, J = 14.40 Hz, 1H), 8.35 (s, 1H), 9.60 (s, 1H),; ^{13}C NMR (DMSO-d_6) δ 119.33, 121.54, 122.34, 123.46, 128.81, 129.43, 132.87, 133.54, 135.08; IR 3085, 3061, 1659 cm^{-1}; ES$^+$MS m/z (relative intensity, %): 205 [M^++1, 100]; Anal. Calcd for $C_{11}H_9ClN_2$: C 64.56, H 4.43, N 13.69; Found: C 64.68, H 4.55, N 13.51.



: mp 150-151 °C; ^{1}H NMR ($CDCl_3$) δ 6.95 (d, J = 14.40 Hz, 1H), 7.44 – 7.36 (m, 6H), 7.53 (d, J = 14.40 Hz, 1H), 7.64 (d, J = 8.00 Hz, 1H), 7.87 (d, J = 8.00 Hz, 1H), 8.26 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 110.30, 118.58, 120.72, 121.64, 123.28, 124.02, 127.34, 129.12, 132.55, 133.11, 133.74, 140.76, 143.94; IR 3090, 3029, 2909, 1666 cm^{-1}; ES$^+$MS m/z (relative intensity, %): 255 [M^++1, 100]; Anal. Calcd for $C_{15}H_{11}ClN_2$: C 70.73, H 4.35, N 11.00; Found: C 70.49, H 4.50, N 11.20.

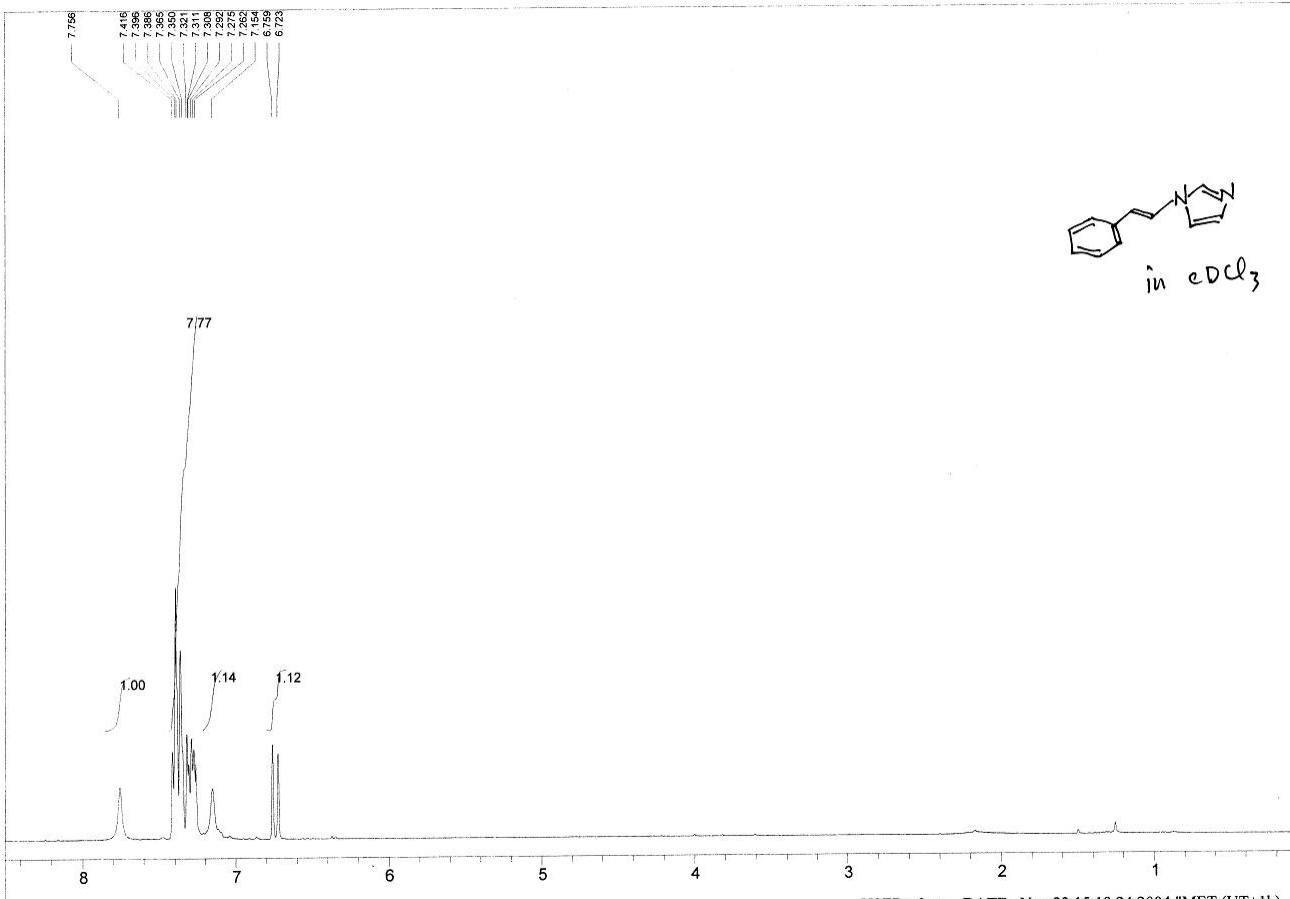


: mp 108-109°C; ^{1}H NMR ((DMSO-d_6) δ 3.77 (s, 3H), 6.97 (d, J = 7.80 Hz,

2H), 7.19 (d, *J* = 14.80Hz, 1H), 7.28 (t, *J* = 8.00 Hz, 1H), 7.35 (t, *J* = 8.00 Hz, 1H), 7.58 (d, *J* = 7.80 Hz, 2H), 7.71 (d, *J* = 8.00 Hz, 1H), 7.93 (d, *J* = 14.80 Hz, 1H), 7.97 (d, *J* = 8.00 Hz, 1H), 8.71 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 55.31, 110.25, 114.36, 119.38, 120.23, 120.61, 122.92, 123.70, 127.10, 127.45, 132.74, 140.73, 143.88, 159.59; IR 3105, 2959, 2837, 1732 cm^{-1}; ES^+MS m/z (relative intensity, %): 251 [M^++1, 100]; Anal. Calcd for $C_{16}H_{14}N_2O$: C 76.78, H 5.64, N 11.19; Found: C 76.89, H 5.46, N 11.22.

References:

1. S. Chowdhury, and S. Roy, *J. Org. Chem.*, 1997, **62**, 199.
2. G. Cooper, and W. J. Irwin, *J. Chem. Soc., Perkin Trans. 1*, 1976, 545.
3. B. Paul, L. Jacqueline, and D. Jacques, *J. Heteroc. Chem*., 1978, **15**, 1543.



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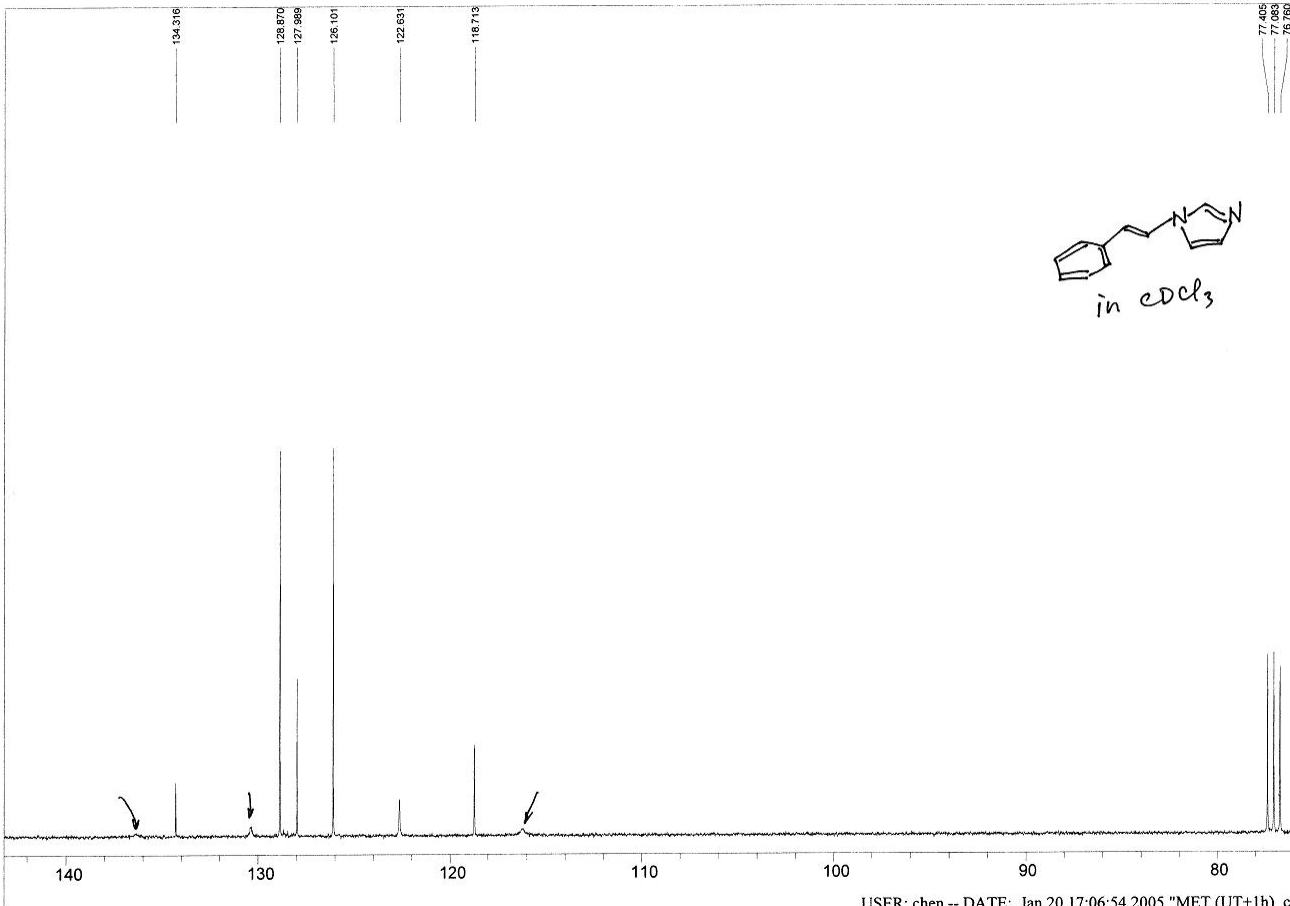

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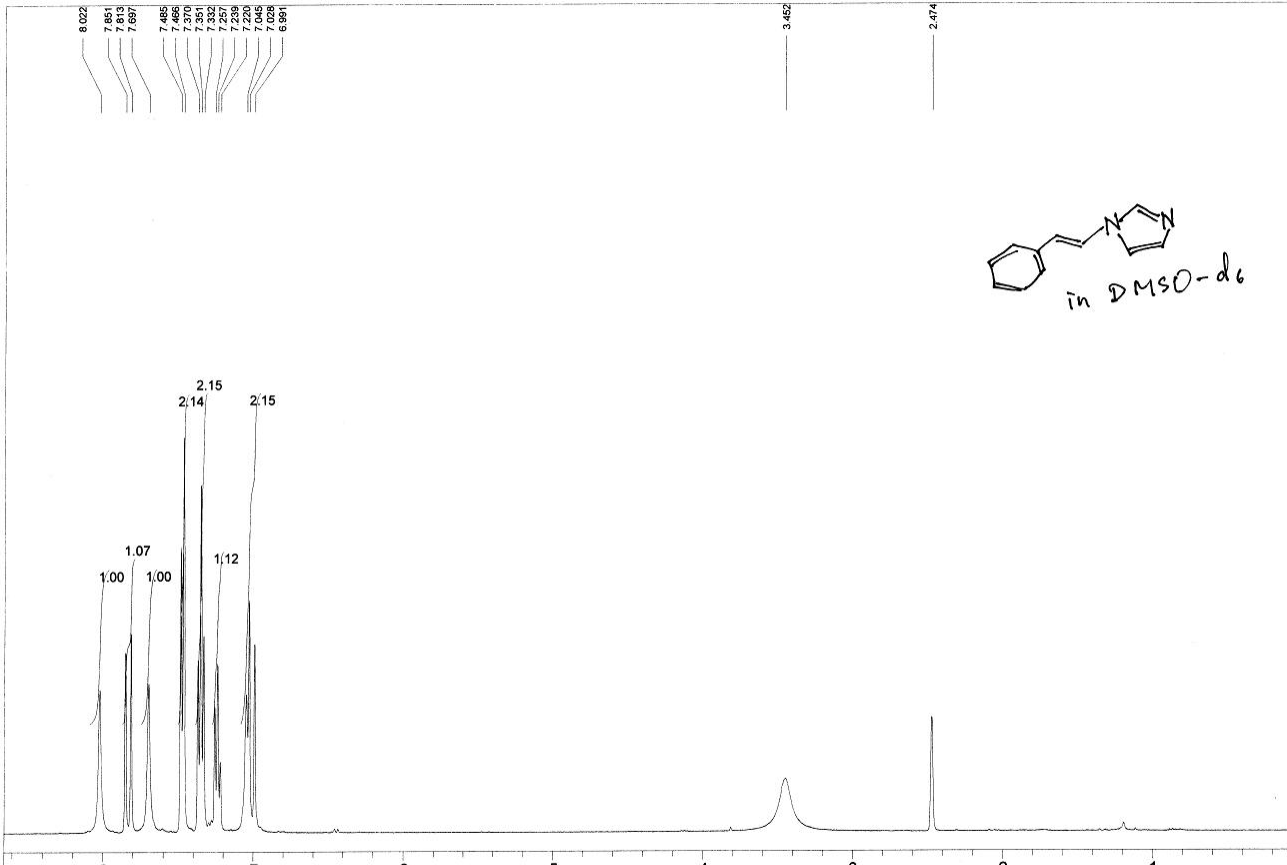

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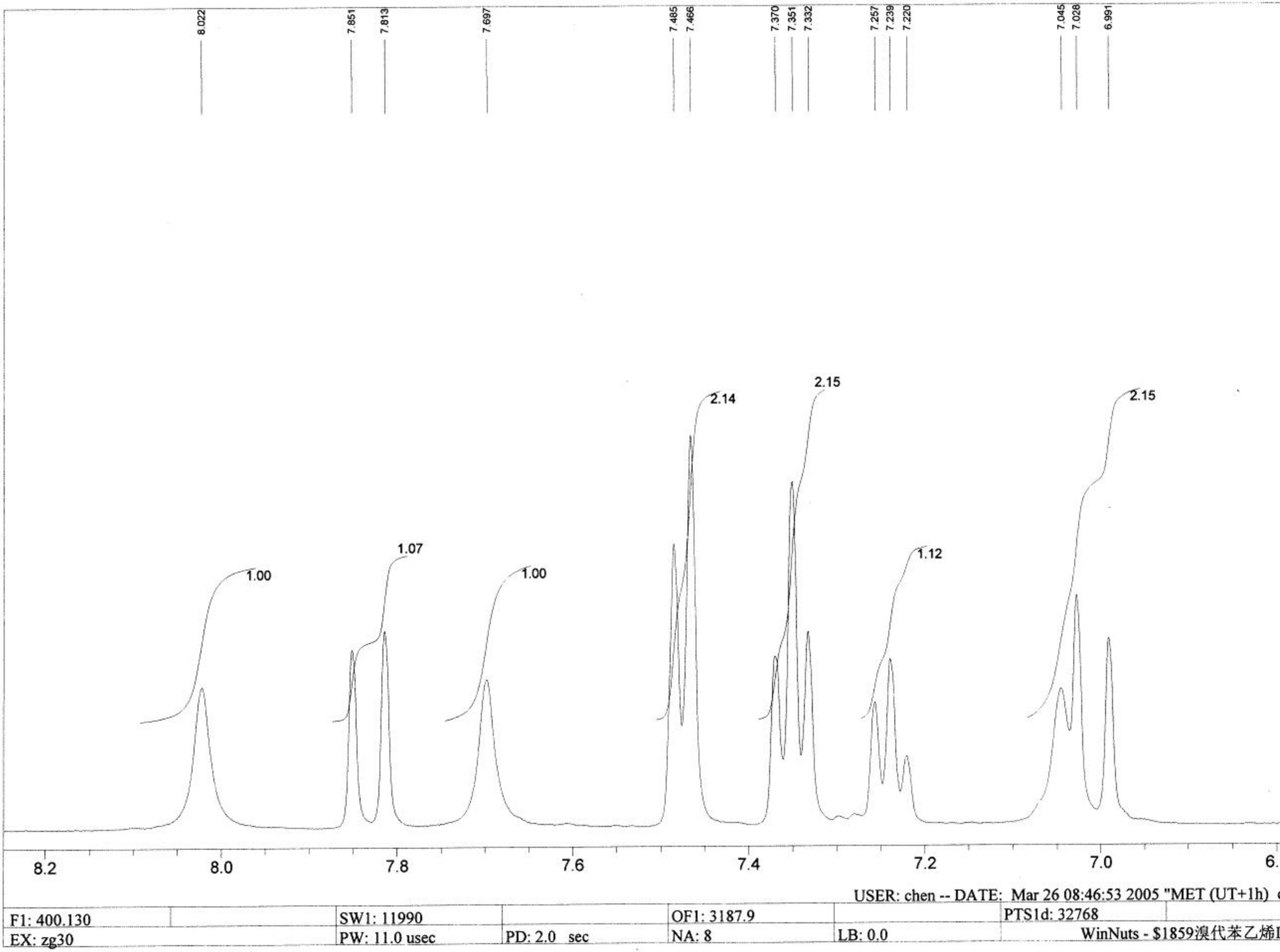

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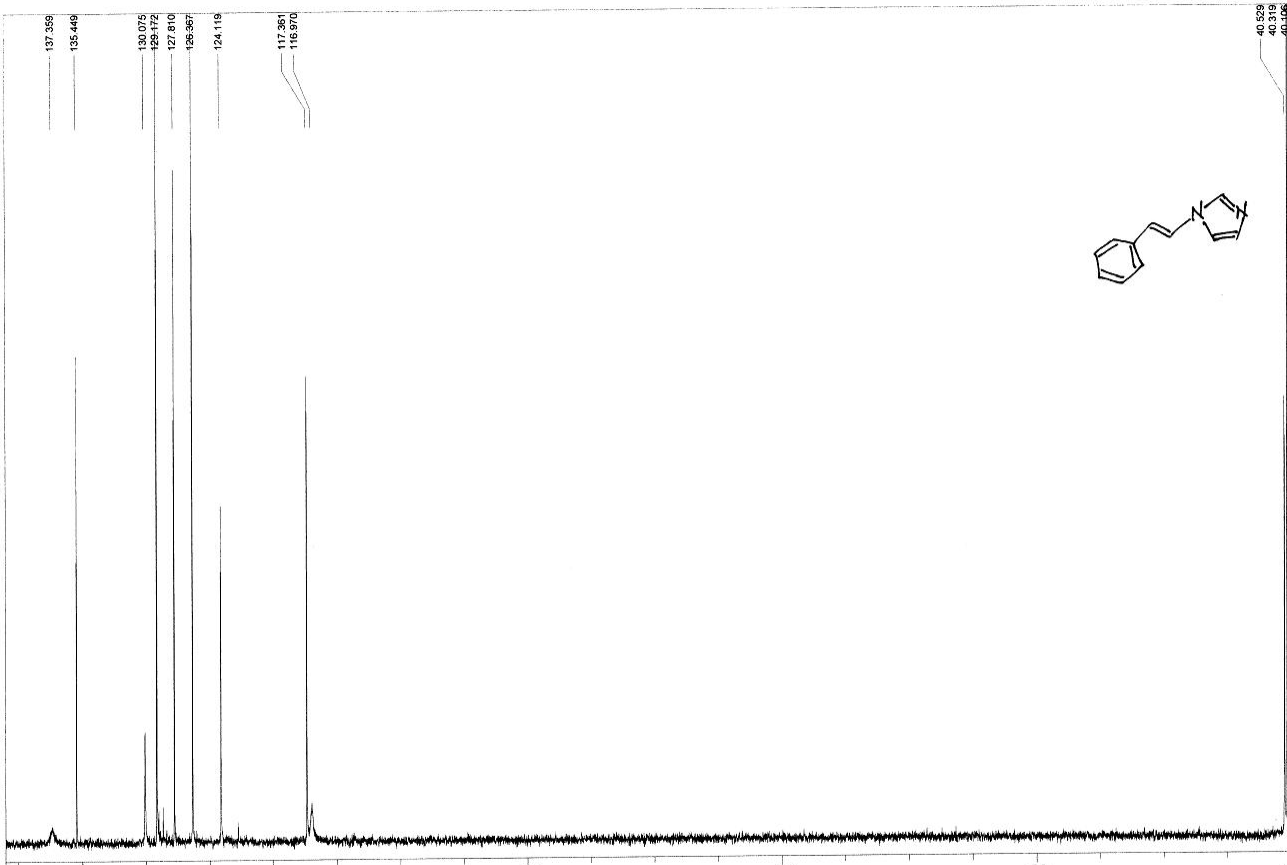

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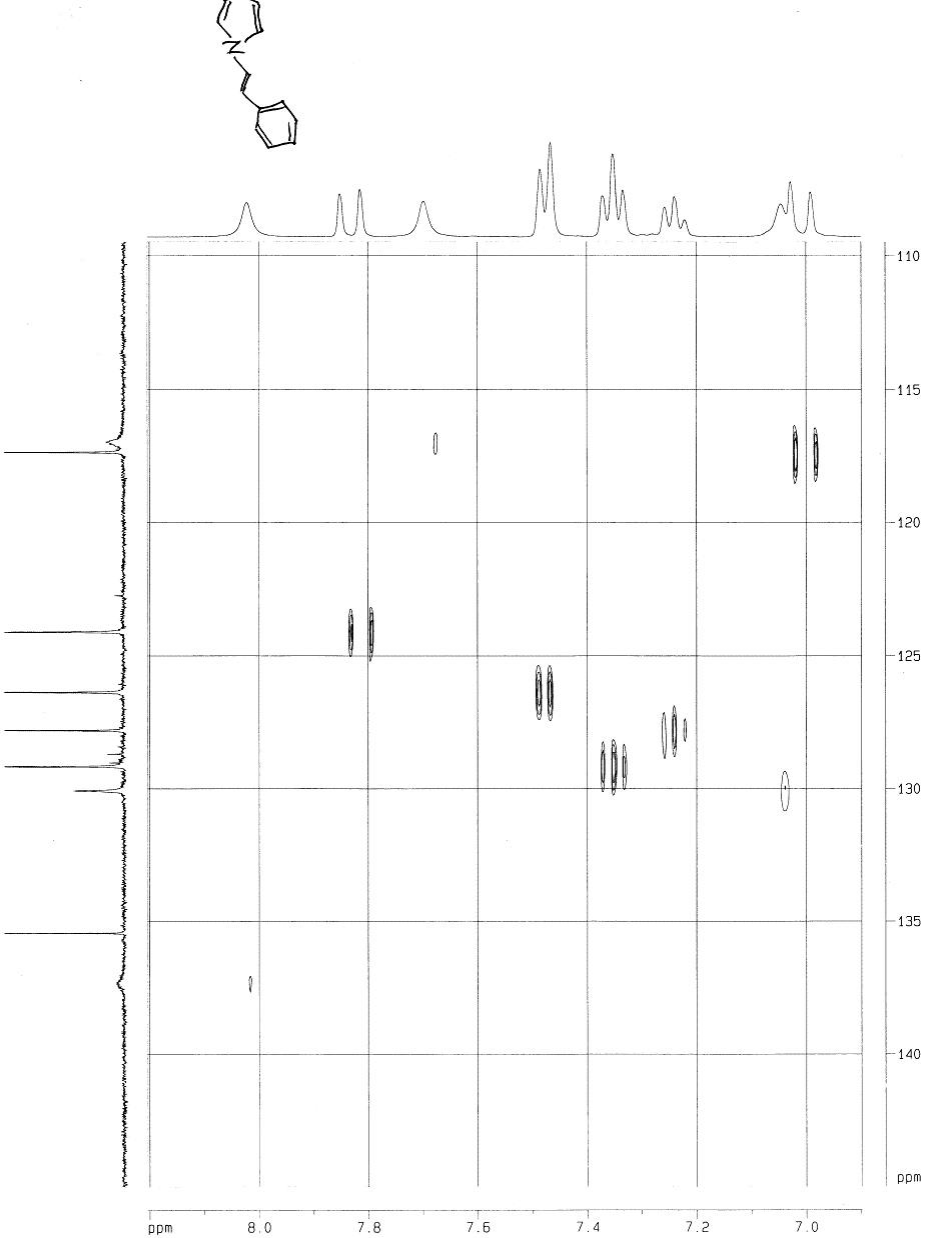
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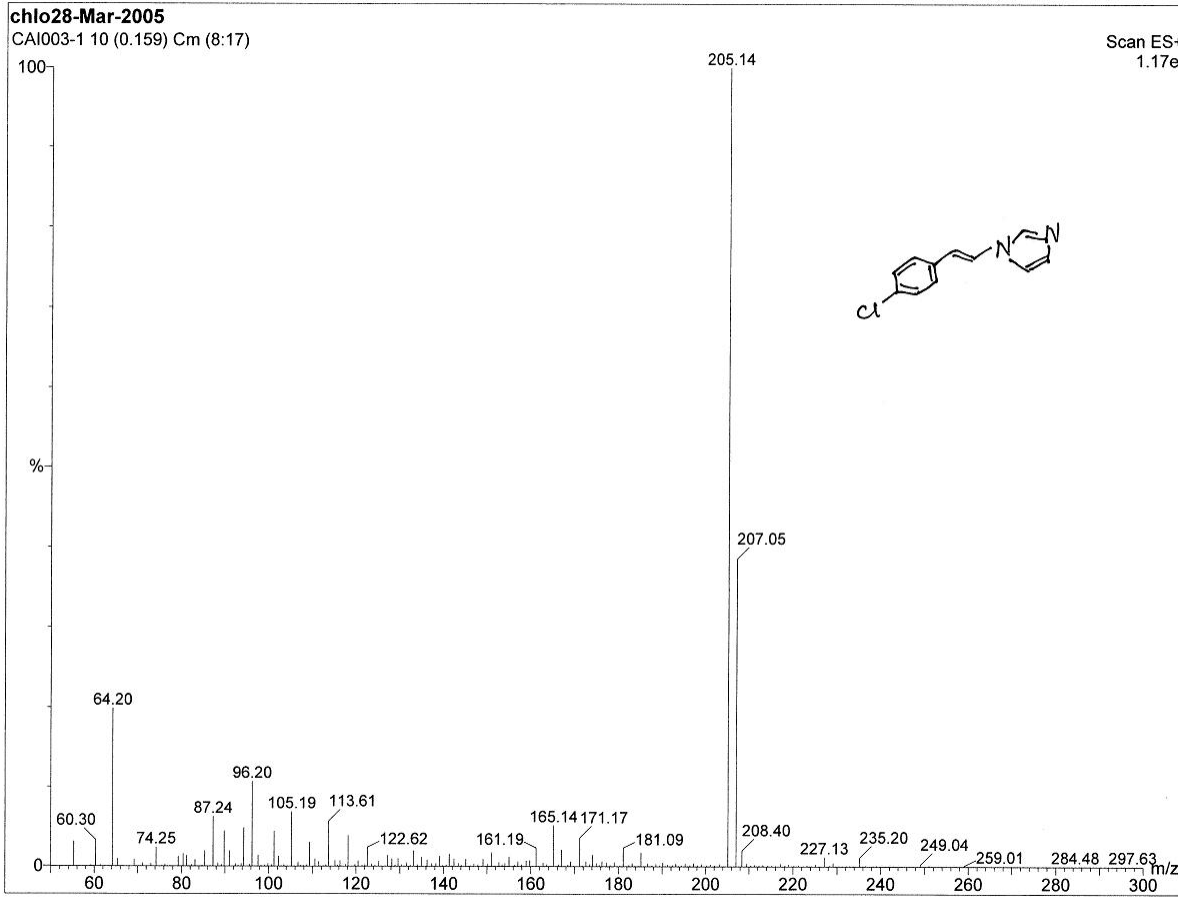
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