

Supporting Information

Palladium Nanoparticles on β -Cyclodextrin Functionalized Graphene Nano Sheets: A Supramolecular Based Heterogeneous Catalyst System for C-C Coupling Reactions under Green Reaction Conditions

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Synthesis of Graphene nanosheets (CD-GNS)

Graphene oxide (GO) was prepared from graphite by the Hummers-Offeman method.¹ A CD-GNS hybrid was prepared by the method based on earlier report.² Typically, 20.0 mL, 0.5 mg/mL of GO was dispersed in deionized water by sonication for 30 min. To this homogeneous dispersion, the aqueous solution of β -CD (20.0 mL, 80 mg/mL) and 300.0 μ L of ammonia solution were added followed by the addition of 20 μ L of hydrazine solution with stirring. The mixture was heated to 60°C for 3.5 h with vigorous stirring to give a stable black dispersion. The dispersion was centrifuged at 15,000 rpm to obtain CD-GNS that can be redispersed readily in water (0.25 mg/mL) by ultrasonication.

¹H and ¹³C NMR Spectroscopic data for the products:

Suzuki-Miyaura cross coupling reactions:

Biphenyl [3, 5]:

White solid; ¹H NMR (CDCl₃): δ 7.29 (t, J = 6.78 Hz, 2H), 7.39 (t, J = 7.63 Hz, 4H), 7.53 (d, J = 7.63 Hz, 4H);

¹³C NMR (CDCl₃): δ = 127.10, 127.18, 128.67, 141.15 ppm.

(4-methyl-1,1'-biphenyl) [4, 5, 8]:

Colorless solid; ¹H NMR (CDCl₃, 300 MHz): δ =2.38 (s, 3H; CH₃), 7.17 (d, J = 7.93 Hz, 2H; Ar-H), 7.26 (t, J =7.17, 8.68 Hz, 1H; Ar-H), 7.36 (t, J =7.36, 7.74 Hz 2H; Ar-H), 7.41 (d, J =7.93 Hz, 2H; Ar-H), 7.50 (d, J =7.36 Hz, 2H; Ar-H) ppm.

¹³C NMR (CDCl₃, 75 MHz): δ =21.0, 126.7, 126.9, 128.6, 129.4, 136.6, 136.9, 138.3 and 141.1 ppm.

(2-Phenylpyridine) [5]:

Colorless liquid; ¹H NMR (CDCl₃, 300 MHz): δ =7.17 (dd, J =4.34, 8.30 Hz, 1H; Ar-H), 7.3-7.46 (m, 3H; Ar-H), 7.69 (d, J =3.39 Hz, 2H; Ar-H), 7.95-7.98 (m, 2H; Ar-H), 8.67 (d, J =4.72 Hz, 1H; Ar-H) ppm.

¹³C NMR (CDCl₃, 75 MHz): δ =120.30, 121.9, 126.7, 128.5, 128.7, 136.5, 139.2, 149.4 and 157, ppm.

(4-hydroxy-1,1'-biphenyl) [5]:

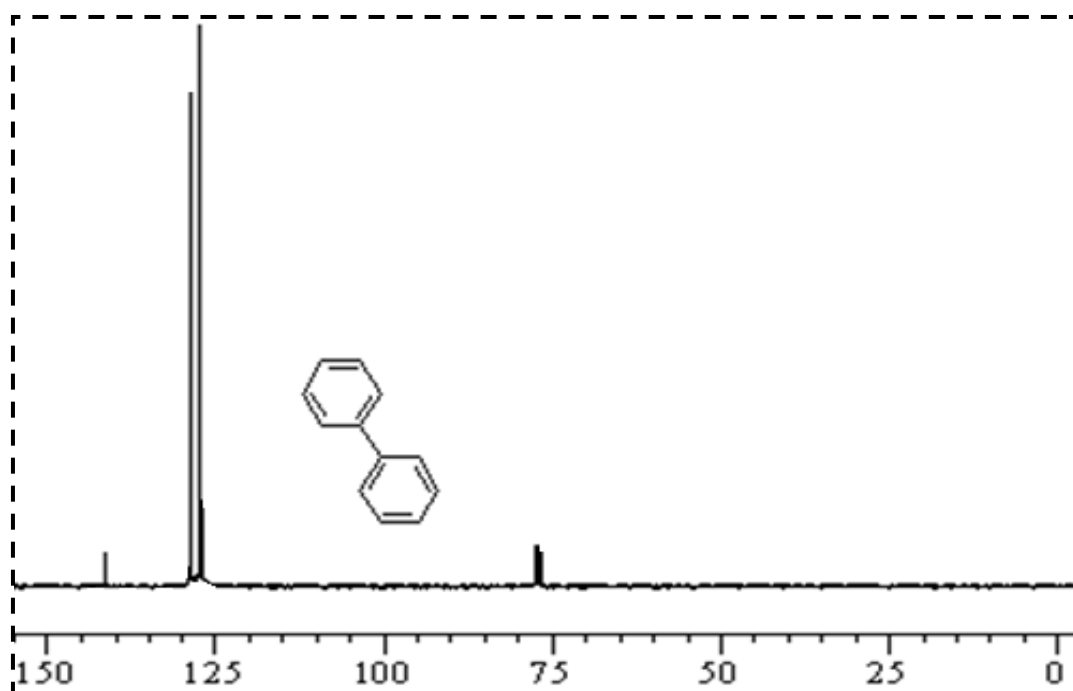
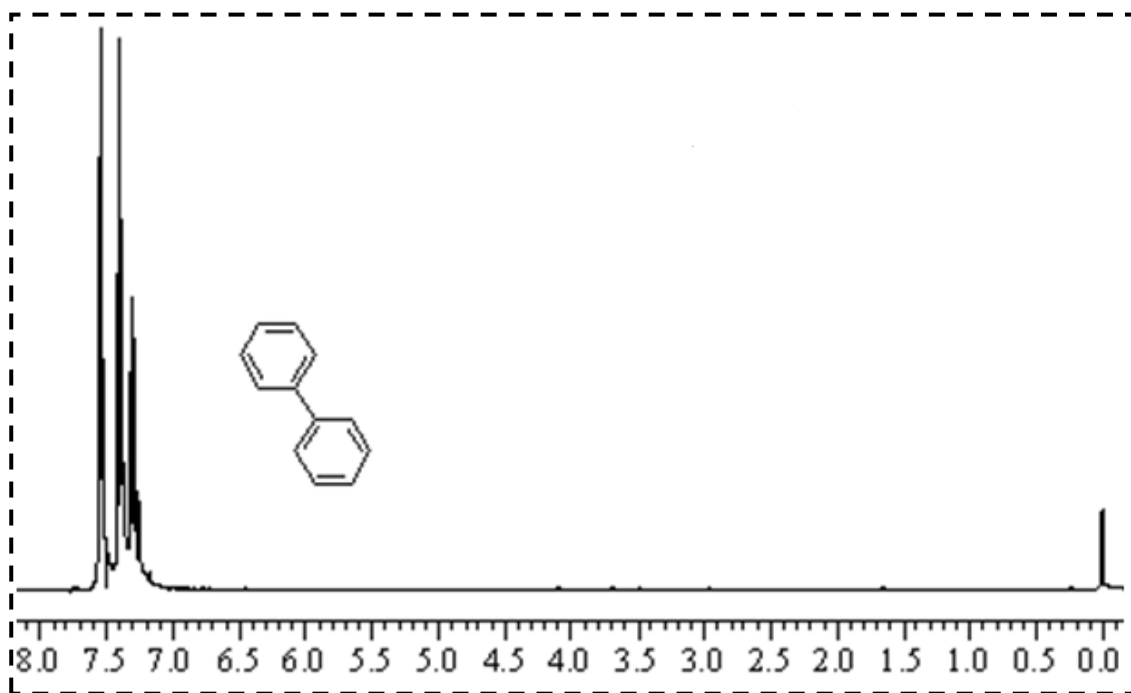
Colorless solid; ^1H NMR (CDCl_3 , 300 MHz): δ =6.83-6.85 (m, 2H; Ar-H), 7.25 (t, J =6.86, 7.84 Hz, 1H; Ar-H), 7.36 (t, J =7.84, 7.84 Hz, 2H; Ar-H), 7.41 (d, J =8.82 Hz, 2H; Ar-H), 7.47 (d, J =6.86 Hz, 2H; Ar-H) ppm.

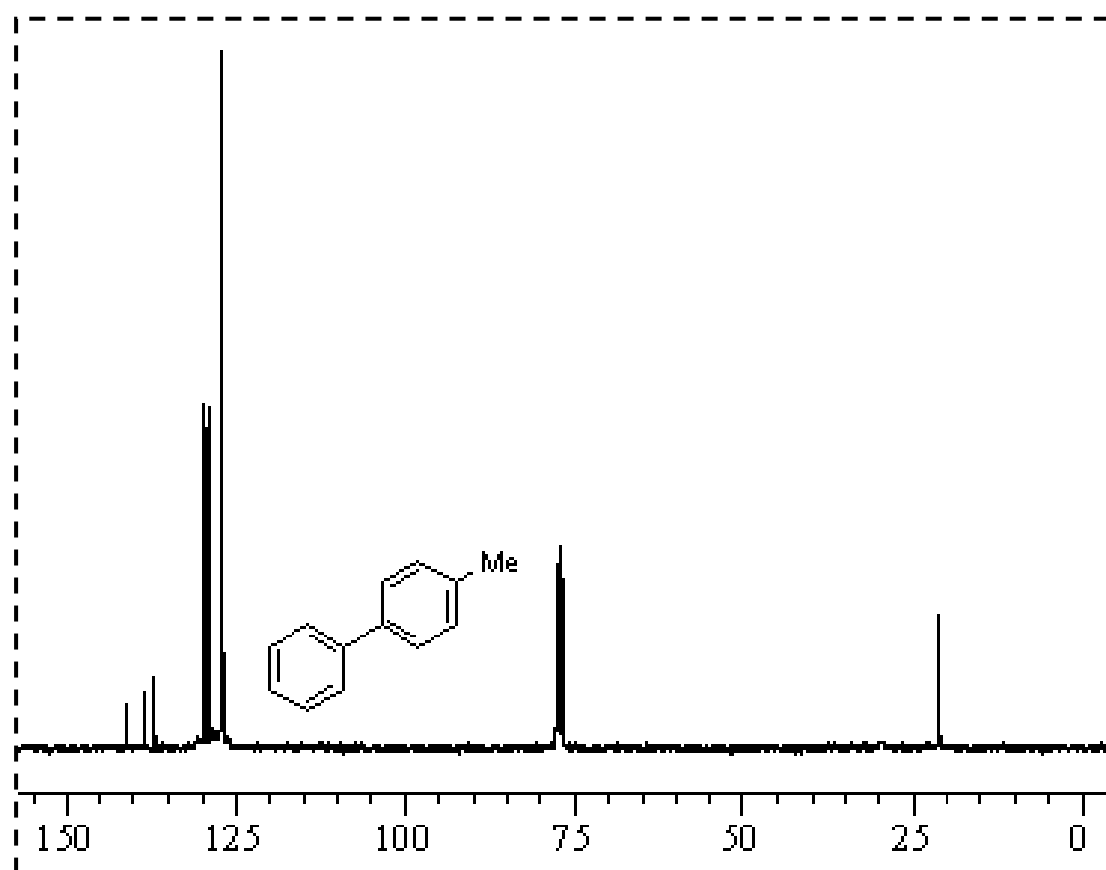
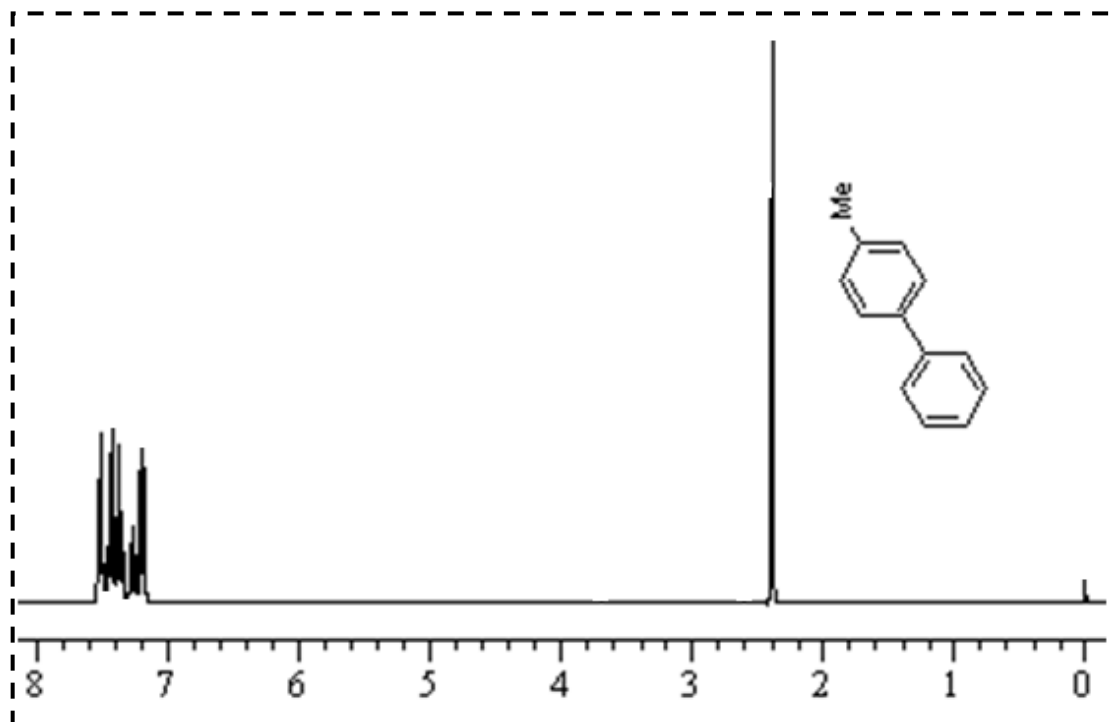
^{13}C NMR (CDCl_3 +DMSO, 75 MHz): δ =115.30, 125.76, 125.82, 127.40, 128.09, 131.51, 140.38 and 156.39.ppm.

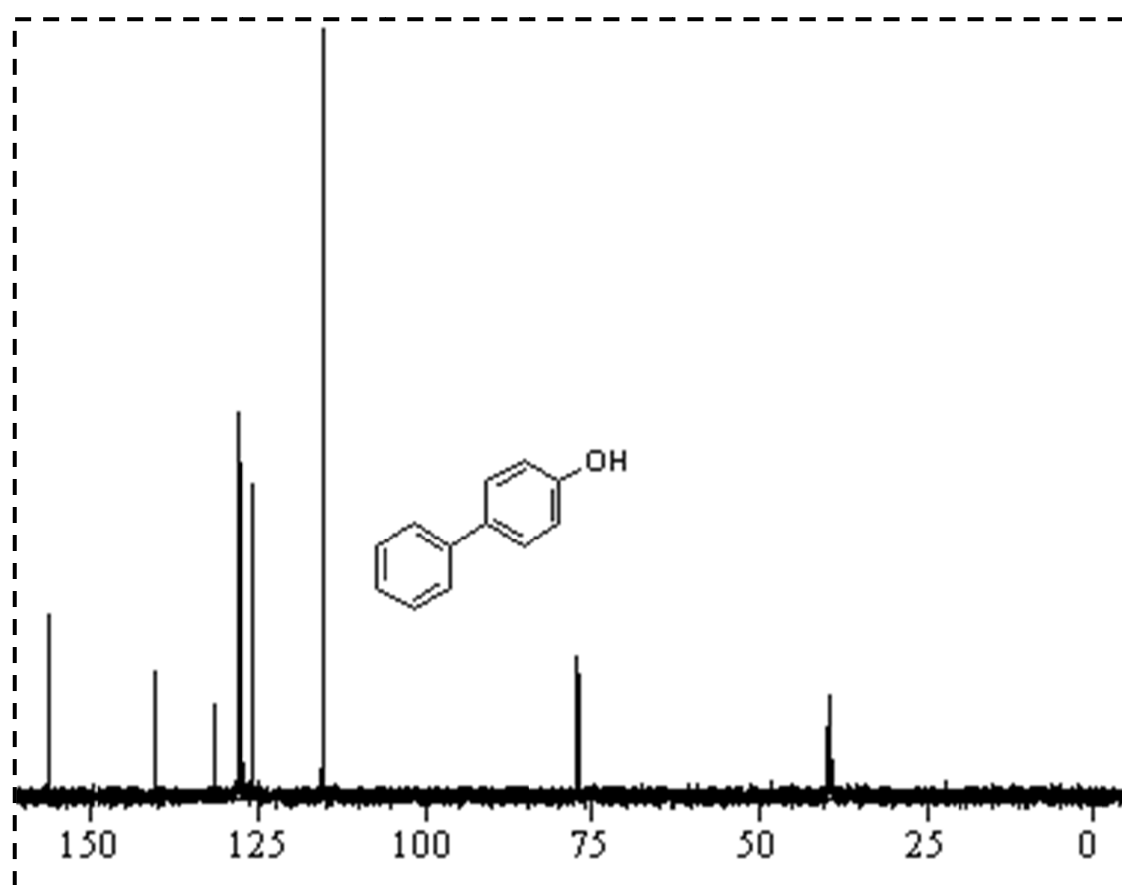
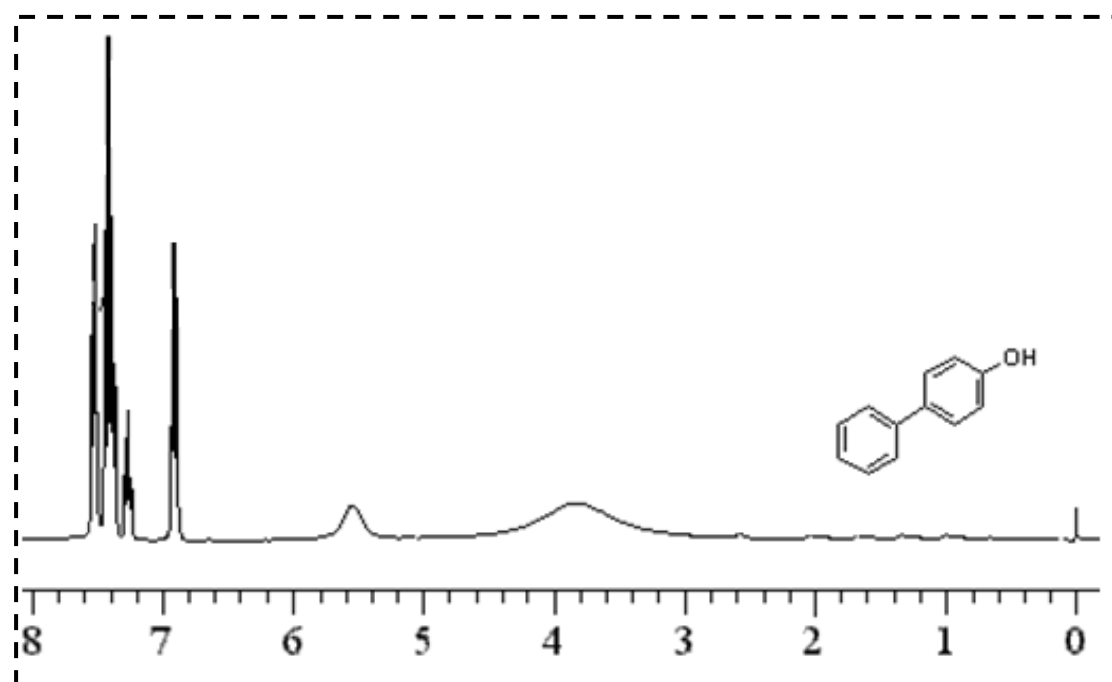
(1,1'-Biphenyl)-4-carboxaldehyde [5]:

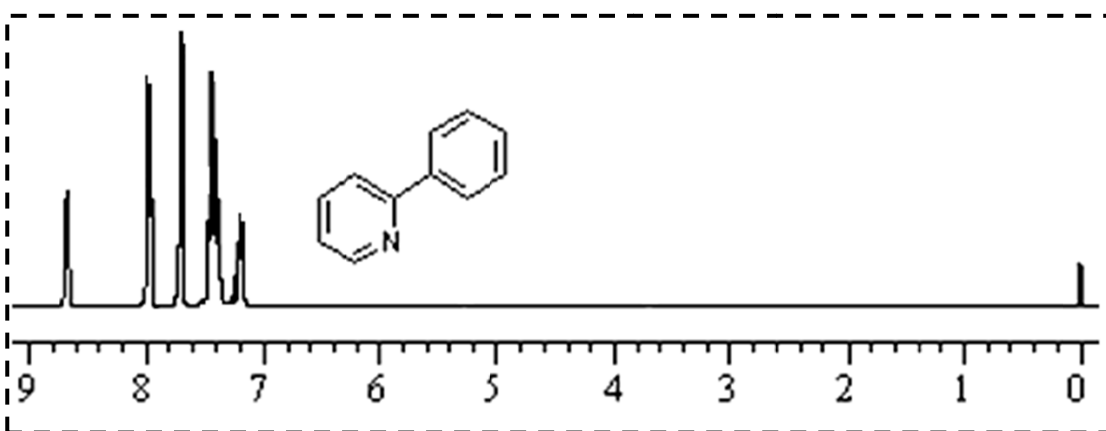
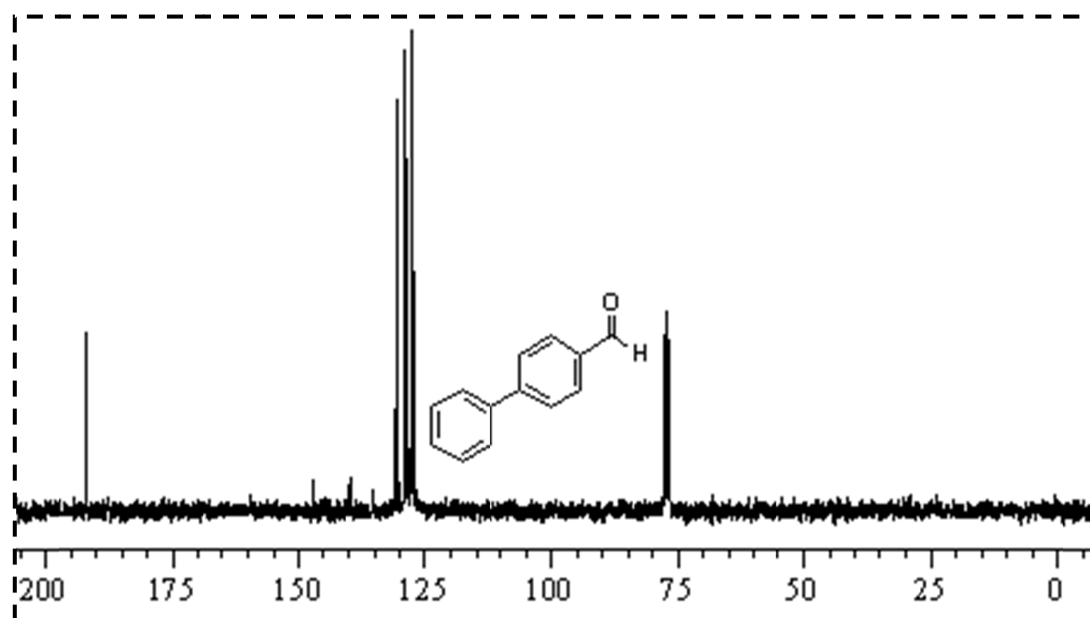
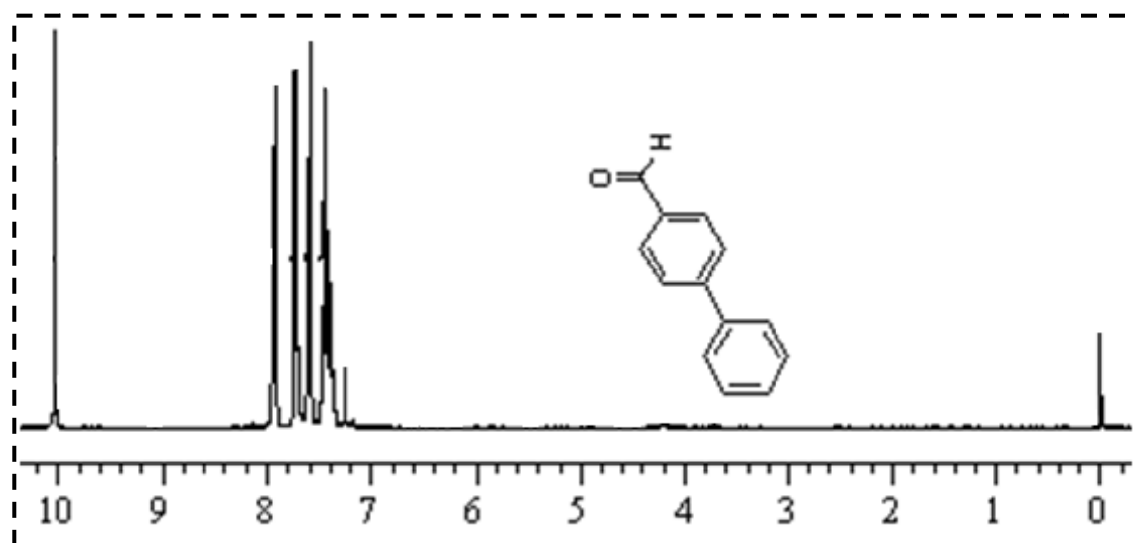
Colorless solid; ^1H NMR (CDCl_3 , 300 MHz): δ =7.35-7.47 (m, 3H; Ar-H), 7.60 (d, J =6.98 Hz, 2H; Ar-H), 7.73 (d, J =8.30 Hz, 2H; Ar-H), 7.94 (d, J =8.30 Hz, 2H; Ar-H), 10.03 (s, 1H; -CHO) ppm.

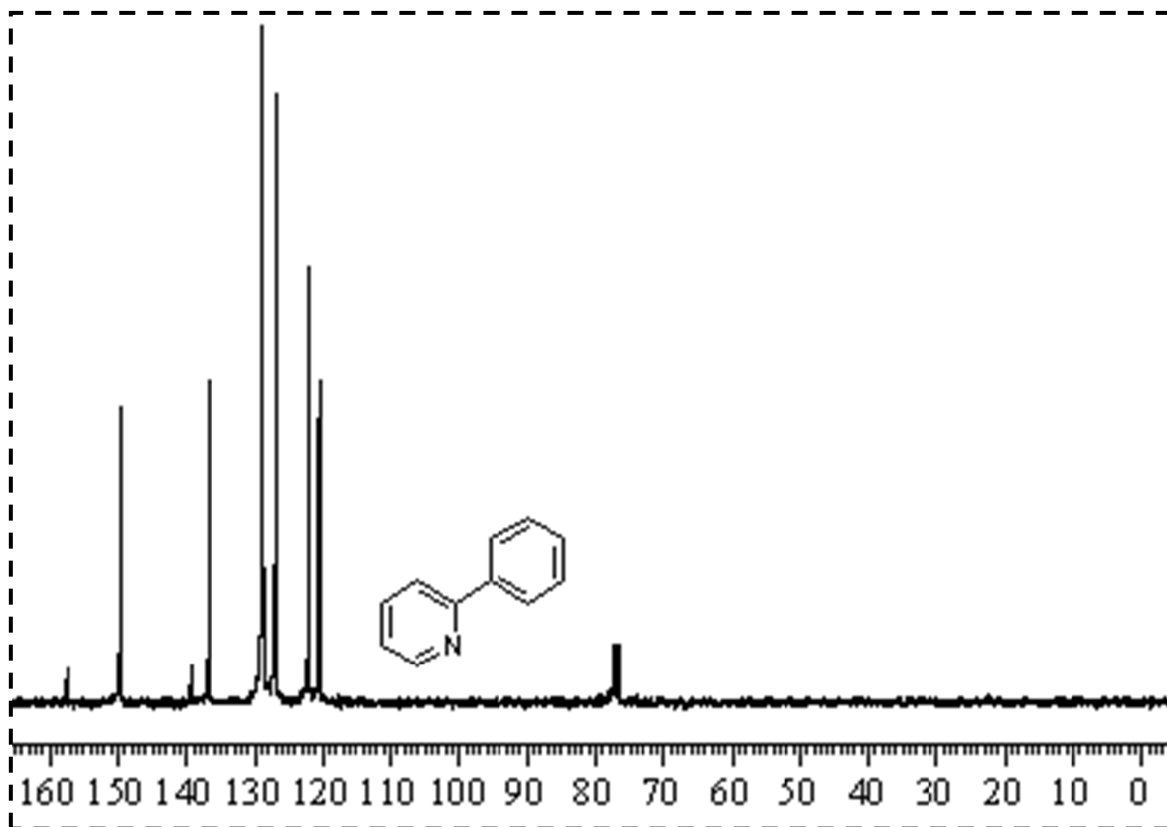
^{13}C NMR (CDCl_3 , 75 MHz): δ =127.32, 127.64, 128.43, 128.97, 130.24, 135.13, 139.66, 147.16 and 192.1.ppm.











Heck- Mizoroki cross coupling reactions

^1H and ^{13}C NMR Spectroscopic data for the products:

(E)-1,2-Diphenylethene [6,7]:

White crystalline solid, mp 122–124 °C; ^1H NMR (CDCl_3): δ 7.04 (s, 2H), 7.16–7.21 (m, 2H), 7.29 (t, J = 6.78 Hz, 4H), 7.46 (d, J = 7.17 Hz, 4H) ppm;

^{13}C NMR (CDCl_3): δ 126.4, 127.5, 128.5, 128.6, 137.2 ppm.

(E)-1-Methoxy-4-styrylbenzene [6]:

White crystalline solid, mp 131–134 °C; ^1H NMR (CDCl_3): δ 3.81 (s, 3H), 6.82 (d, J = 9.06 Hz, 2H), 6.88–7.04 (dd, J = 15.86, 16.61 Hz, 2H), 7.18 (t, J = 6.79 Hz, 1H), 7.29 (t, J = 6.79 Hz, 2H), 7.38–7.45 (m, 4H) ppm.

^{13}C NMR (CDCl_3): δ 55.2, 114.0, 126.2, 126.5, 127.1, 127.6, 128.1, 128.5, 130.0, 137.6, 159.2 ppm.

(E)-1-tert-Butyl-4-styrylbenzene:

White crystalline solid, mp 94–96 °C; ^1H NMR (CDCl_3): δ 1.33 (s, 9H), 7.02 (s, 2H), 7.16–7.23 (m, 1H), 7.27–7.33 (m, 4H), 7.39 (d, J = 8.30 Hz, 2H), 7.46 (d, J = 7.55 Hz, 2H) ppm;

^{13}C NMR (CDCl_3): δ 31.3, 34.5, 125.5, 126.1, 126.3, 127.3, 127.8, 128.4, 128.5, 134.5, 137.4, 150.7 ppm.

(E)-1-Methyl-4-styrylbenzene [6-8]:

White crystalline solid, mp 119–122 °C; ^1H NMR (CDCl_3): δ 2.36 (s, 3H), 7.02 (s, 2H), 7.11 (d, $J = 7.93$ Hz, 2H), 7.16–7.24 (m, 1H), 7.29 (t, $J = 7.74$, 7.11 Hz, 2H), 7.34 (d, $J = 8.12$ Hz, 2H), 7.45 (d, $J = 7.74$ Hz, 2H) ppm.

^{13}C NMR (CDCl_3): δ 21.2, 126.3, 127.3, 127.6, 128.6, 129.3, 134.5, 137.4 ppm.

(*E*)-Methyl cinnamate:

^1H NMR (CDCl_3): δ 3.79 (s, 3H), 6.38 (d, $J = 15.53$ Hz, 1H), 7.34–7.37 (m, 3H), 7.49–7.50 (m, 2H), 7.65 (d, $J = 16.45$ Hz, 1H) ppm.

^{13}C NMR (CDCl_3): δ 51.5, 117.6, 127.9, 128.7, 130.1, 134.1, 144.6, 167.2 ppm.

(*E*)-*n*-Butyl cinnamate:

Yellow liquid, ^1H NMR (CDCl_3): δ 0.98 (t, $J = 7.36$ Hz, 3H), 1.38–1.93 (m, 2H), 1.63–1.73 (m, 2H), 4.18 (t, $J = 6.61$ Hz, 2H), 6.39 (d, $J = 15.86$ Hz, 1H), 7.32–7.38 (m, $J = 3$ Hz), 7.49 (dd, $J = 4.15$, 2.07, Hz, 2H), 7.60 (d, $J = 16.05$ Hz, 1H) ppm.

^{13}C NMR (CDCl_3): δ 13.5, 18.9, 30.5, 64.1, 118.0, 127.8, 128.6, 129.9, 134.2, 144.3, 166.8 ppm.

(*E*)-*t*-Butyl cinnamate:

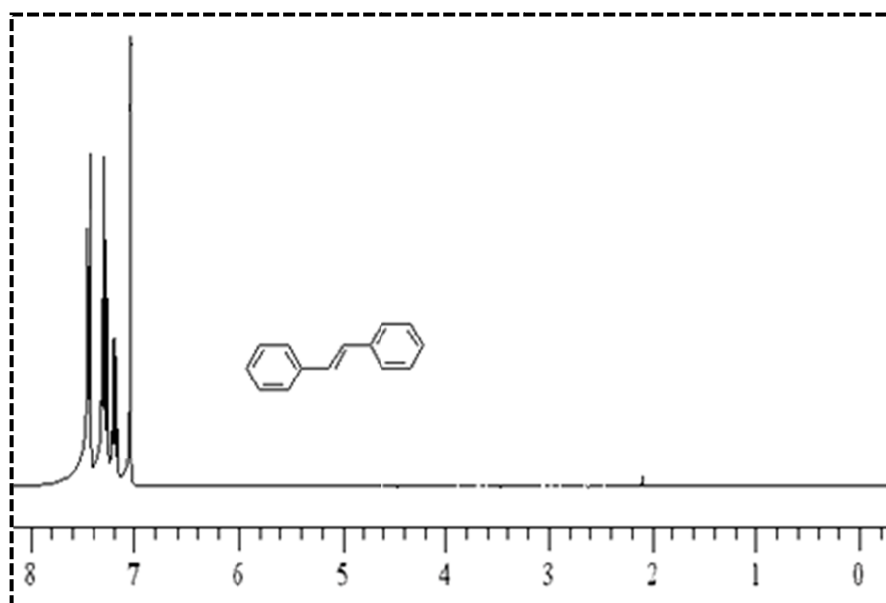
Yellow liquid, ^1H NMR (CDCl_3): δ 1.52 (s, 9H), 6.32 (d, $J = 15.86$ Hz, 1H), 7.32–7.37 (m, 3H), 7.46–7.56 (m, 3H) ppm.

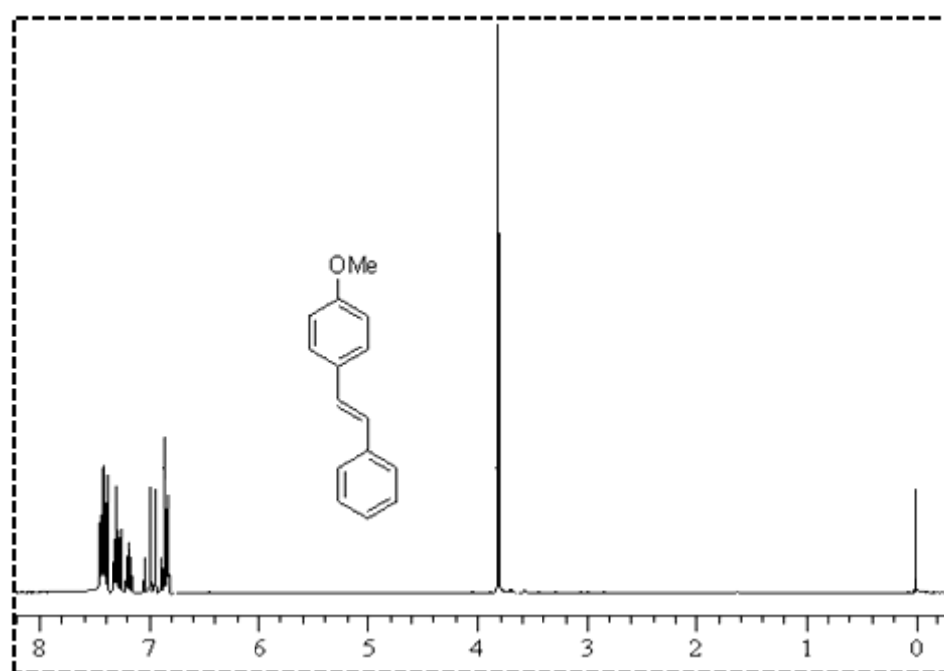
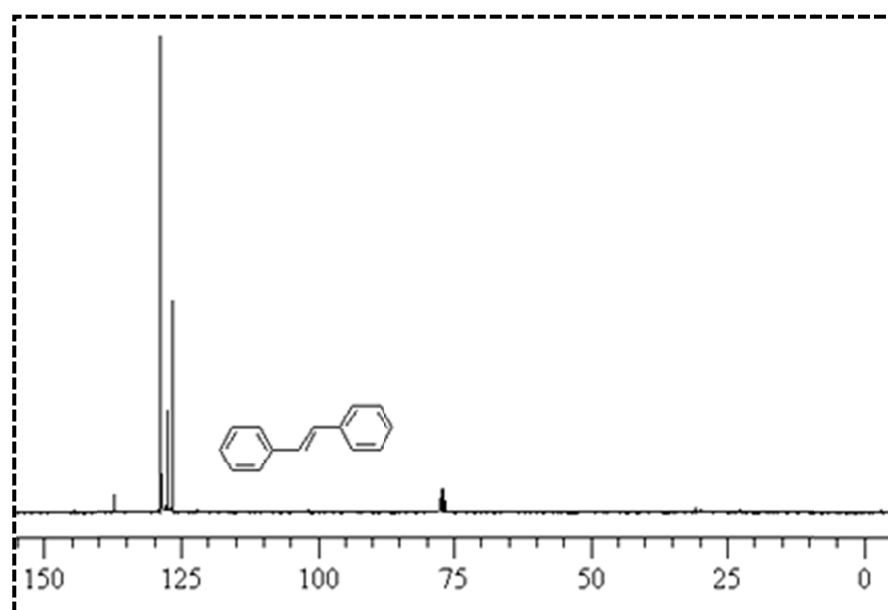
^{13}C NMR (CDCl_3): δ 28.1, 80.4, 120.1, 127.8, 128.7, 129.8, 134.5, 143.4, 166.2 ppm.

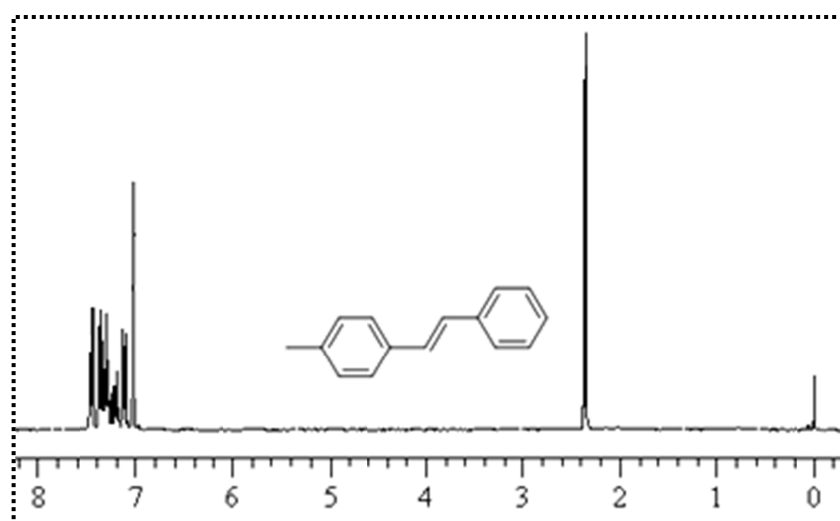
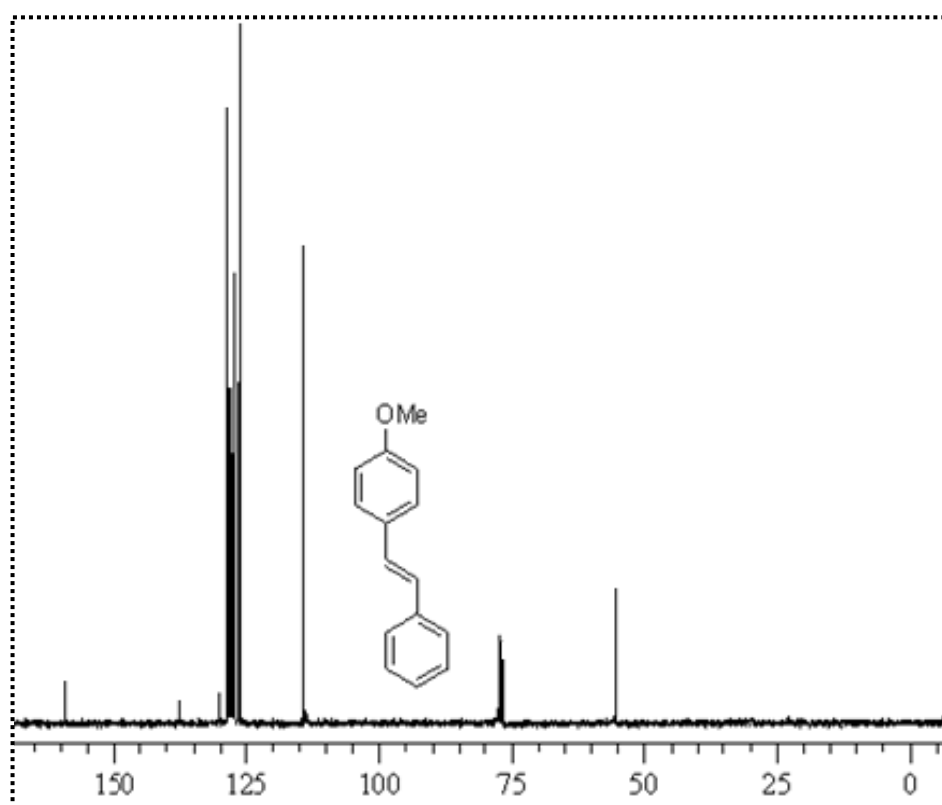
***trans*-Cinnamic acid [6]:**

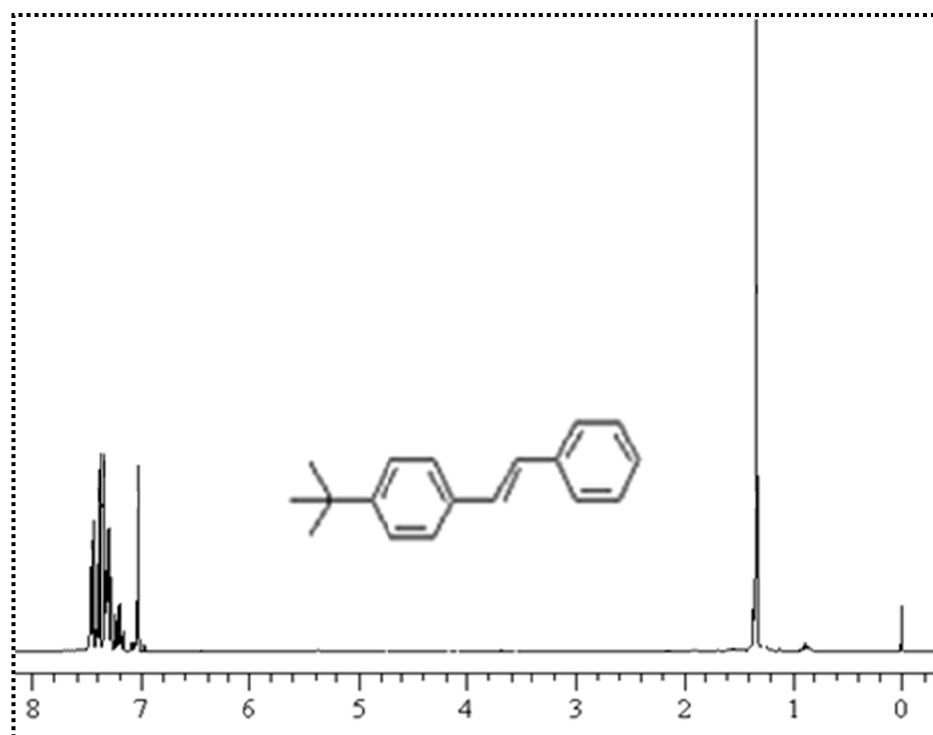
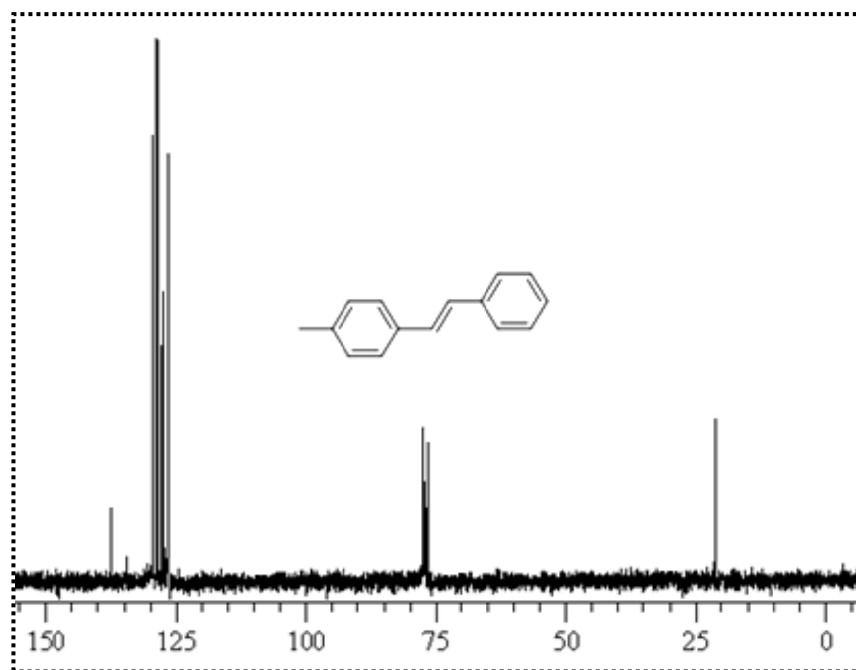
White crystalline solid, ^1H NMR (CDCl_3): δ 6.43 (d, $J = 15.86$ Hz, 1H), 7.34–7.41 (m, 3H), 7.52–7.55 (m, 2H), 7.79 (d, $J = 15.86$ Hz, 1H) ppm;

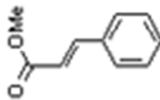
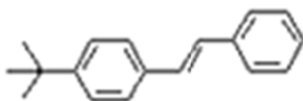
^{13}C NMR (CDCl_3): δ 117.3, 128.3, 128.8, 130.6, 133.9, 147.0, 172.7 ppm.

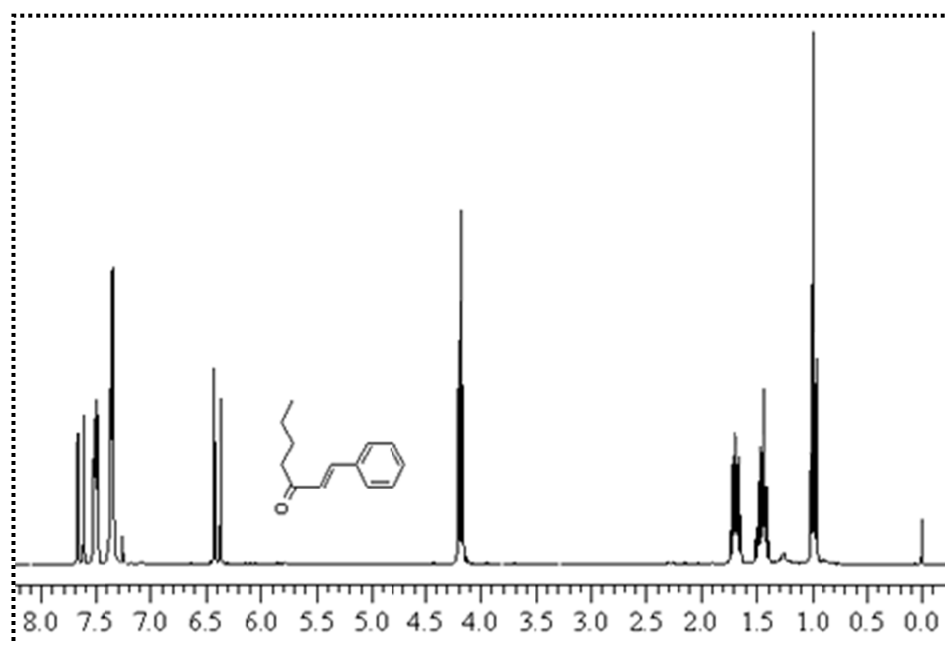
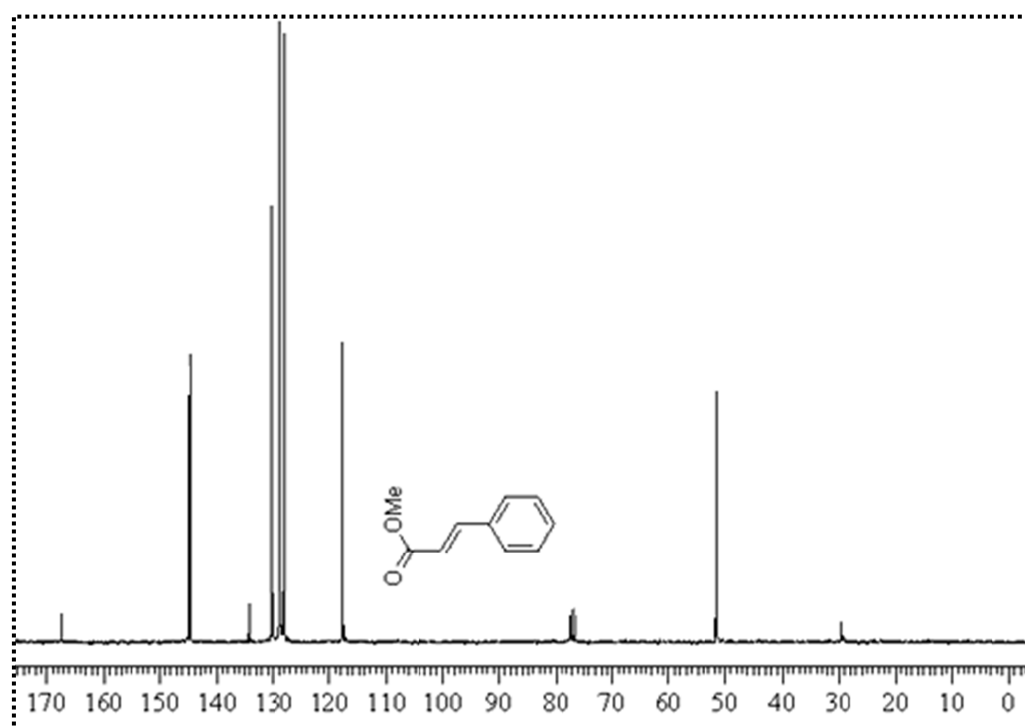


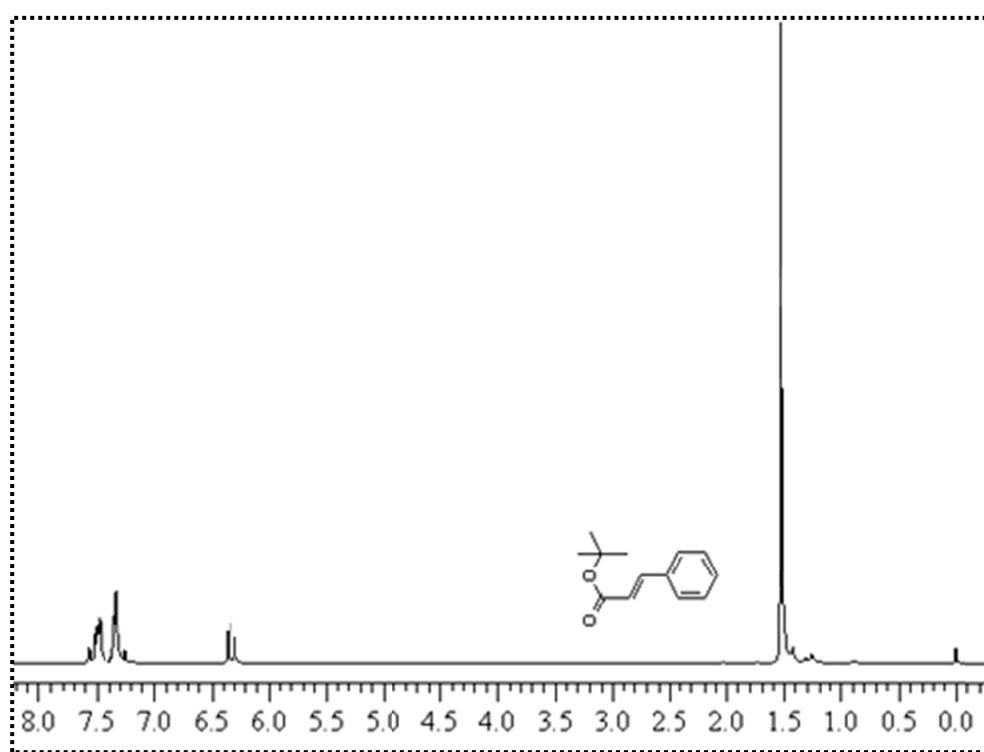
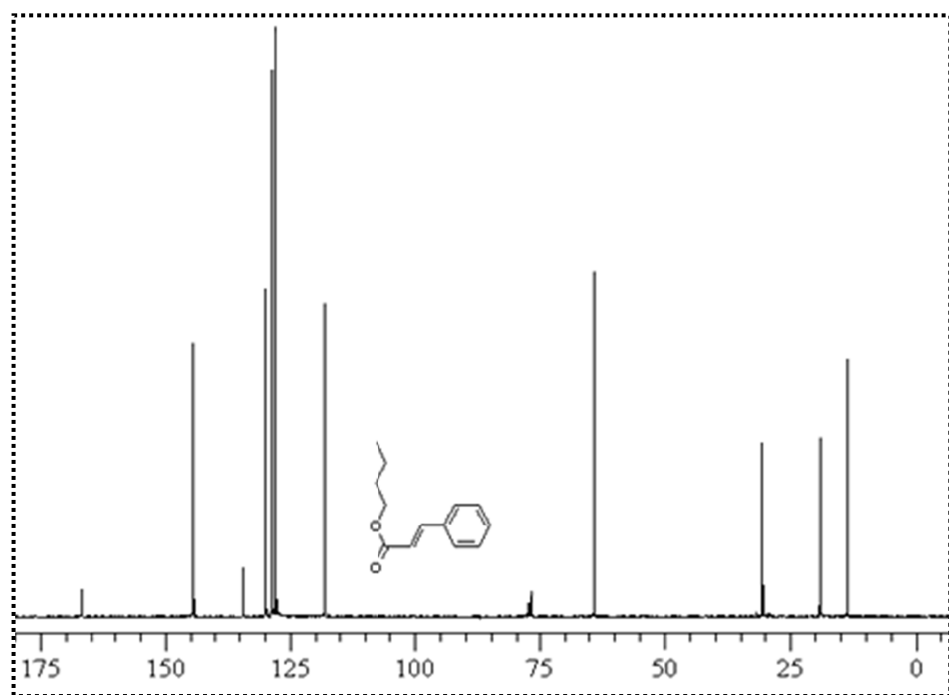


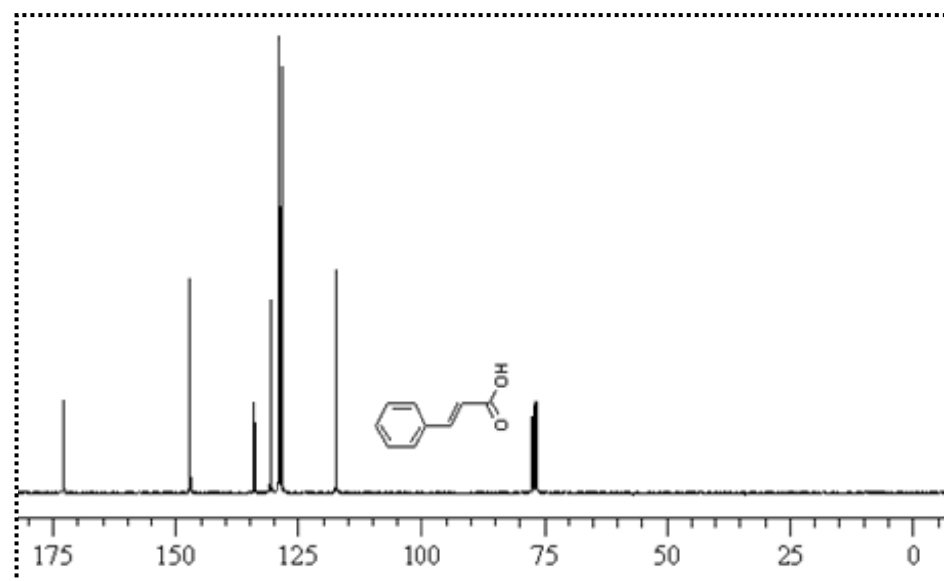
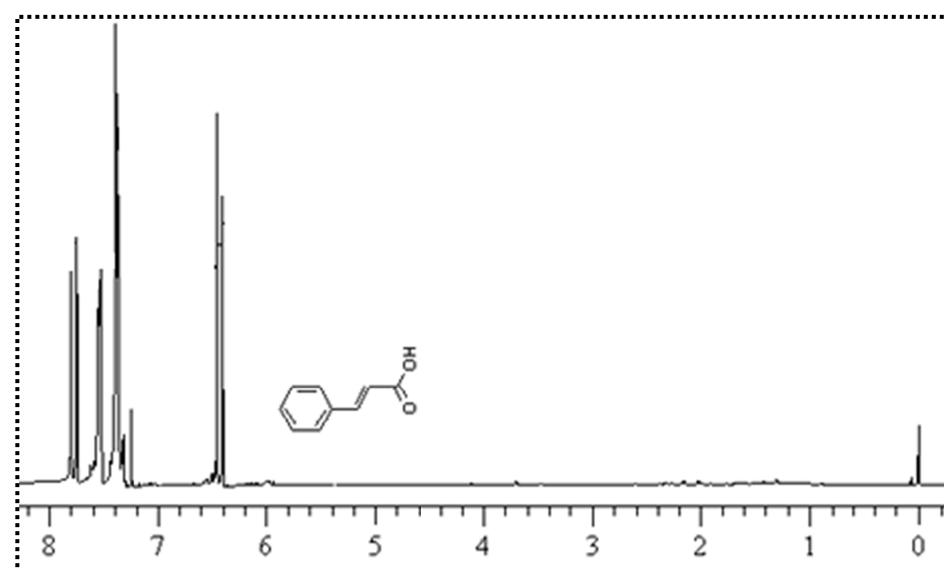
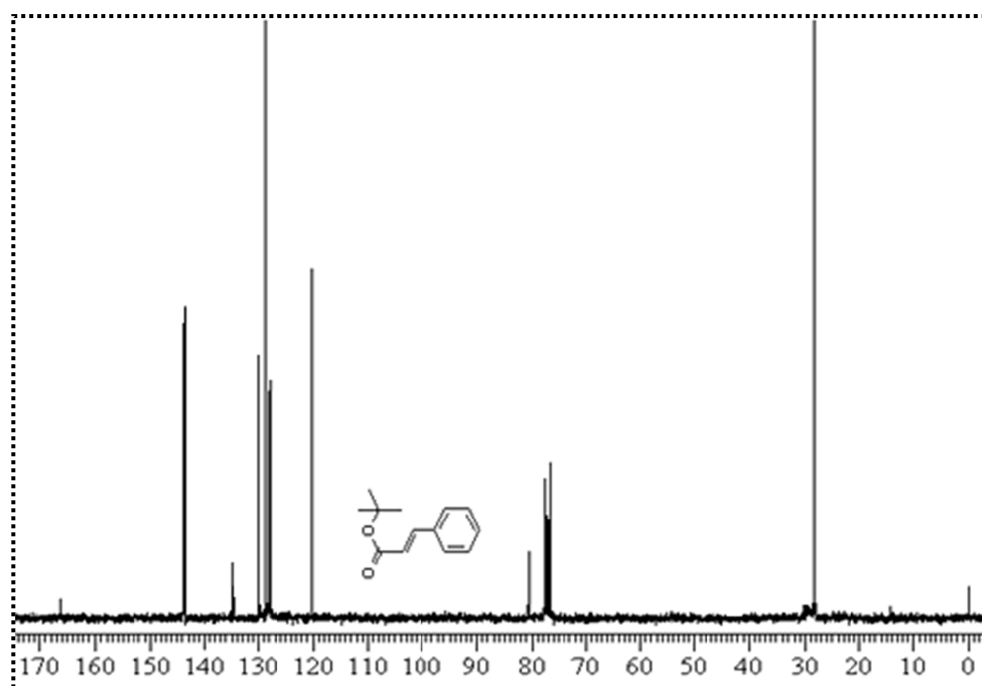












References

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