Electronic Supplementary Material (ESI) for RSC Advances.

Amphipathic monolith-supported palladium catalysts for chemoselective hydrogenation and cross-coupling reactions

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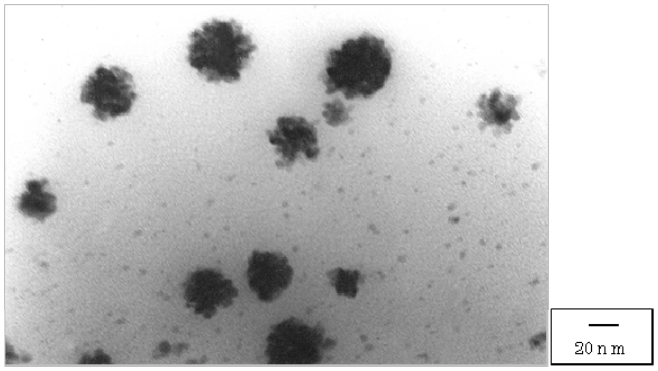
Electronic Supplementary Information

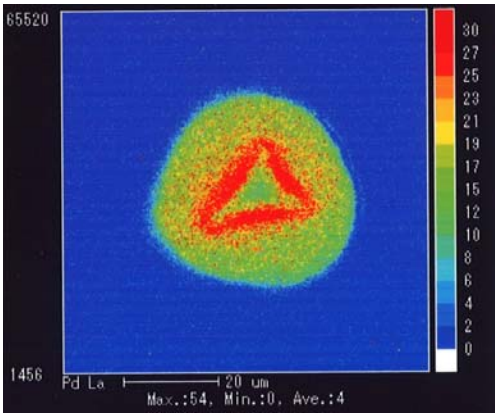
General

Palladium catalyst supported on anion exchange monolithic polymer (-$NMe_3^+NO_3^-$) [Pd/AM] and cation exchange monolithic polymer (-SO_3H) [CM] were obtained from Organo Corporation (Tokyo, Japan). $Pd(OAc)_2$ was obtained from N.E. Chemcat Co. (Tokyo, Japan). MeOH (HPLC grade) and H_2O were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). *i*-PrOH and *N*,*N*-dimethylacetamide (DMA) were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan) and Kishida Chemical Co., Ltd. (Osaka, Japan), respectively. All other reagents were purchased from commercial sources and used without further purification. Flash column chromatography was performed using Silica Gel 60 N (Kanto Chemical Co., Inc., 63–210 μm spherical, neutral). ^1H and ^{13}C NMR spectra were recorded on JEOL ECS-400, AL 400 (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR) or JEOL ECS-500 (500 MHz for ^1H NMR and 125 MHz for ^{13}C NMR). Chemical shifts (δ) were expressed in ppm and internally referenced (δ = 0.00 ppm for TMS/$CDCl_3$, 2.49 ppm for DMSO-d_6, or 3.31 ppm for CD_3OD for ^1H NMR and 77.0 ppm for $CDCl_3$, 39.5 ppm for DMSO-d_6, or 49.0 ppm for CD_3OD for ^{13}C NMR). Mass spectra were measured using JEOL JMS-Q1000 GC MK (EI), JMS-T100TD (ESI), or Shimadzu hybrid LCMS-IT-TOF (ESI-TOF). High resolution mass spectra (EI) were measured by JEOL JMS-100GC. Palladium concentration in solution was determined by AA-7000 atomic absorption spectrophotometer (Shimadzu Co., Kyoto, Japan) or Vista Pro simultaneous ICP-AES (Varian).

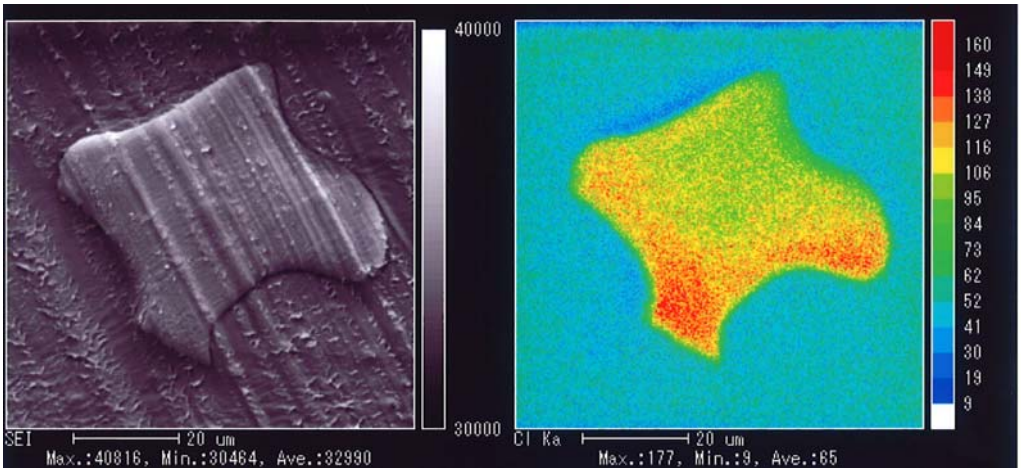
TEM image of 3.9% Pd/AM



EPMA of 3.9% Pd/AM

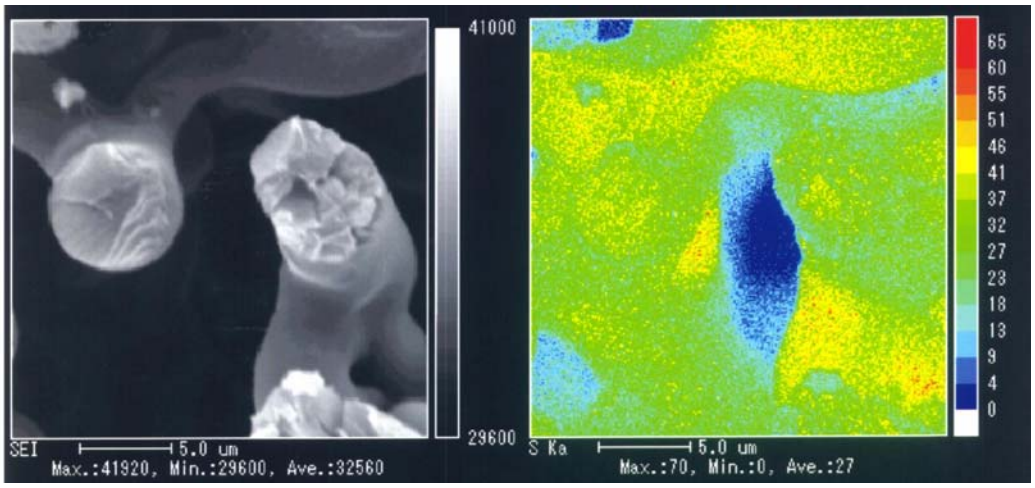


EPMA of AM (as ammonium chloride)



The right figure shows the distribution of chlorine atoms of the ammonium chloride functionalities in the monolithic polymer before the ion-exchange to nitrate by coloring. The uniform dispersion of chlorine atoms in the polymer is indicated.

EPMA of CM



The white parts of the polymer in the left figure are contact with the surface for the measurement, and there are some polymer parts behind the surface (black parts). The right figure shows the distribution of sulfur atoms of the sulfonic acid functionalities on the polymer by coloring. The uniform dispersion of sulfur on the polymer is indicated by the coloring of whole parts.

Typical procedure for the 3.9% Pd/AM- and 5% Pd/CM-catalyzed hydrogenation (Table 1)

A mixture of the substrate (200 μmol) and 3.9% Pd/AM (5.5 mg, 2.00 μmol) or 5% Pd/CM (4.3 mg, 2.00 μmol) in MeOH (1 mL) was stirred under an H_2 atmosphere (balloon) at room temperature for a specific time, then passed through a cotton filter to remove the catalyst. The filtrate was concentrated *in vacuo* to give the analytically pure product. The spectral data of the product were identical to those in the literature.

1,2-Diphenylethane [CAS Reg. No. 103-29-7] (Entries 1 and 2)[1)]

^{1}H NMR [400 MHz (ECS-400), $CDCl_3$]: δ = 7.27 (m, 4H), 7.16–7.20 (m, 6H), 2.91 (s, 4H); ^{13}C NMR [100

MHz (ECS-400), $CDCl_3$]: δ = 141.7, 128.4, 128.3, 125.9, 37.9; MS (EI): *m*/*z* (%): 182 (M^+, 16), 91 (100), 65 (18).

1,2-Dimethoxy-4-propylbenzene [CAS Reg. No. 5888-52-8] (Entries 3 and 4)[1)]

^{1}H NMR [400 MHz (ECS-400), $CDCl_3$]: δ = 6.79 (d, *J* = 10.5 Hz, 1H), 6.71–6.72 (m, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 2.53 (t, *J* = 7.8 Hz, 2H), 1.62 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR [100 MHz (ECS-400), $CDCl_3$]: δ = 148.7, 147.0, 135.3, 120.1, 111.8, 111.1, 55.9, 55.7, 37.6, 24.7, 13.8; MS (EI): *m*/*z* (%): 180 (M^+, 37), 151 (100), 107 (7), 91 (7), 77 (9).

4-Aminobenzoic Acid [CAS Reg. No. 150-13-0] (Entries 5 and 6)[2)]

^{1}H NMR (500 MHz, DMSO-d_6) : δ = 11.97 (br s, 1H), 7.60 (d, *J* = 8.5 Hz, 2H), 6.53 (d, *J* = 8.5 Hz, 2H), 5.87 (br s, 2H); ^{13}C NMR(125 MHz, DMSO-d_6) : δ = 167.6, 153.2, 131.3, 116.9, 112.6; MS (ESI-TOF): *m*/*z* (%): 160 [$(M+Na)^+$, 100].

4-Aminoanisole [CAS Reg. No. 104-94-9] (Entries 7 and 8)[3)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.75 (d, *J* = 8.9 Hz, 2H), 6.65 (d, *J* = 8.9 Hz, 2H), 3.74 (s, 3H), 3.41 (br s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ =152.7, 139.9, 116.4, 114.7, 55.7; MS (EI): *m*/*z* (%): 123 (M^+, 67), 108 (100), 80 (74), 53 (27).

4-*tert*-Butylaniline [CAS Reg. No. 769-92-6] (Entries 9 and 10)[3)]

^{1}H NMR (500 MHz, CD_3OD): δ = 7.14 (d, *J* = 8.5 Hz, 2H), 6.68 (d, *J* = 8.5 Hz, 2H), 4.91 (br s, 2H), 1.26 (s, 9H); ^{13}C NMR (125 MHz, CD_3OD): δ = 145.5, 142.4, 126.7, 116.7, 34.7, 32.0; MS (EI): *m*/*z* (%): 149 (M^+, 28), 134 (100), 119 (9), 106 (29), 94 (27), 77 (14), 65 (12).

Phenethylamine [CAS Reg. No. 64-04-0] (Entries 11 and 12)[4)]

^{1}H NMR [400 MHz (ECS-400), $CDCl_3$]: δ = 7.30 (t, *J* = 7.2 Hz, 2H), 7.19–7.23 (m, 3H), 2.97 (t, *J* = 6.9 Hz, 2H), 2.76 (t, *J* = 6.9 Hz, 2H), 1.97 (br s, 2H); ^{13}C NMR [100 MHz (ECS-400), $CDCl_3$]: δ = 139.6, 128.8, 128.4, 126.2, 43.3, 39.7; MS (ESI-TOF): *m*/*z* (%): 122 [$(M+H)^+$, 100].

***N*-Propylaniline [CAS Reg. No. 622-80-0] (Entries 13 and 14)[5)]**

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.17, (t, *J* = 7.8 Hz, 2H), 6.68 (t, *J* = 7.8 Hz, 1H), 6.60 (t, *J* = 7.8 Hz, 2H), 3.08 (t, *J* = 7.3 Hz, 2H), 1.64 (m, 2H), 1.00 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.5, 129.2, 117.0, 112.6, 45.7, 22.7, 11.6; MS (ESI-TOF): *m*/*z* (%): 136 [$(M+H)^+$, 100].

***N, N*-Dipropylamine [CAS Reg. No. 142-84-7] (Entries 15 and 16)[6)]**

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.65 (t, *J* = 7.8 Hz, 4H), 1.58 (m, 4H), 0.95 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 51.9, 22.6, 11.8; MS (ESI-TOF): *m*/*z* (%): 102 [$(M+H)^+$, 100]. The reaction was carried out in CD_3OD, and the conversion was determined by ^{1}H NMR analysis of the filtrate after the removal of the catalyst due to the volatile nature of the product. The peaks for toluene derived from Cbz group were observed in NMR spectra.

Dihydrocinnamic Acid [CAS Reg. No. 501-52-0] (Entries 17 and 18)[7)]

^{1}H NMR [400 MHz (ECS-400), $CDCl_3$]: δ = 11.42 (br s, 1H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.20–7.24 (m, 3H), 2.96 (t, *J* = 7.9 Hz, 2H), 2.69 (t, *J* = 7.9 Hz, 2H); ^{13}C NMR [100 MHz (ECS-400), $CDCl_3$]: δ = 179.4, 140.1, 128.5, 128.2, 126.4, 35.6, 30.5; MS (ESI-TOF): *m*/*z* (%): 173 [$(M+Na)^+$, 100].

Dihydrocinnamic Acid Methyl Ester [CAS Reg. No. 103-25-3] (Entry 18)[8)]

^{1}H NMR [400 MHz (ECS-400), $CDCl_3$]: δ = 7.28 (m, 2H), 7.17–7.21 (m, 3H), 3.66 (s, 3H), 2.95 (t, J = 7.9 Hz, 2H), 2.63 (t, J = 7.9 Hz, 2H); ^{13}C NMR [100 MHz (ECS-400), $CDCl_3$]: δ = 173.4, 140.5, 128.5, 128.3, 126.2, 51.6, 35.7, 30.9; MS (EI): *m*/*z* (%): 164 (M^+, 35), 133 (6), 104 (100), 91 (77), 77 (26).

2-Methoxy-4-propylphenol [CAS Reg. No. 2785-87-7] (Entries 19 and 20)[1)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.83 (d, J = 8.0 Hz, 1H), 6.68 (s, 1H), 6.67 (d, J = 8.0 Hz, 1H), 5.51 (br s, 1H), 3.86 (s, 3H), 2.51 (t, J = 7.8 Hz, 2H), 1.61 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.2, 143.4, 134.6, 120.9, 114.0, 110.9, 55.8, 37.7, 24.9, 13.8; MS (EI): *m*/*z* (%): 166 (M^+, 40), 137 (100), 122 (9), 94 (7), 77 (10).

4-Hydroxybenzoic Acid [CAS Reg. No. 99-96-7] (Entries 21 and 22)[9)]

^{1}H NMR (500 MHz, DMSO-d_6): δ = 12.4 (br s, 1H), 10.2 (br s, 1H), 7.79 (d, J = 9.3 Hz, 2H), 6.82 (d, J = 9.3 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ =167.3, 161.7, 131.6, 121.4, 115.2; MS (ESI-TOF): *m*/*z* (%): 161 [$(M+Na)^+$, 100].

Benzophenone [CAS Reg. No. 119-61-9] (Entries 23 and 27)[10)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.80 (d, J = 7.7 Hz, 4H), 7.59 (d, J = 7.7 Hz, 2H), 7.48 (d, J = 7.7 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.7, 137.5, 132.4, 130.0, 128.2; MS (EI): *m*/*z* (%): 182 (M^+, 73), 105 (100), 77 (100).

Benzhydrole [CAS Reg. No. 91-01-0] (Entries 23 and 27)[11)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30–7.36 (m, 8H), 7.25 (t, J = 7 Hz, 2H), 5.79 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.7, 128.4, 127.5, 126.5, 76.1; MS (ESI-TOF): *m*/*z* (%): 207 [$(M+Na)^+$, 100].

Diphenylmethane [CAS Reg. No. 101-81-5] (Entry 24)[12)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27 (m, 4H), 7.17–7.20 (m, 6H), 3.97 (s, 2H); ^{13}C NMR (500 MHz, $CDCl_3$): δ = 141.1, 128.9, 128.4, 126.0, 41.9; MS (EI): *m*/*z* (%): 168 (M^+, 100), 153 (30), 91 (18), 65 (12).

1-(4-Hydroxy-3-propylphenyl)ethanone [CAS Reg. No. 61270-28-8] (Entry 25)[13)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.80 (d, J = 2.0 Hz, 1H), 7.74 (dd, J = 2.0, 8.0 Hz, 1H), 7.34 (s, 1H), 6.89 (d, J = 8.0 Hz, 1H), 2.64 (t, J = 7.8 Hz, 2H), 2.59 (s, 3H), 1.67 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 198.6, 159.2, 131.2, 129.5, 129.0, 128.7, 115.0, 32.0, 26.3, 22.7, 13.9; MS (EI): *m*/*z* (%): 178 (M^+, 31), 163 (100), 149 (13), 107 (8), 91 (10), 77 (14).

4-Ethyl-2-propylphenol [CAS Reg. No. 1141348-72-2] (Entry 26)

^{1}H NMR [400 MHz (ECS-400), $CDCl_3$]: δ = 6.94 (d, J = 2.0 Hz, 1H), 6.89 (dd, J = 2.0, 7.9 Hz, 1H), 6.68 (d, J = 7.9 Hz, 1H), 4.67 (br s, 1H), 2.53–2.58 (m, 4H), 1.64 (m, 2H), 1.20 (t, J = 7.6 Hz, 3H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR [100 MHz (ECS-400), $CDCl_3$]: δ = 151.3, 136.4, 129.7, 128.1, 126.1, 115.0, 32.1, 28.0, 23.0, 15.9, 14.0; HRMS (EI): 146.1215 [M^+, 100]; Calcd for $C_{11}H_{16}O_1$: 164.1201.

α-Ethyl α-methylbenzylalcohol [CAS Reg. No. 1565-75-9] (Entry 29)[1)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (d, J = 7.5 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.23 (t, J = 7.5 Hz, 1H), 1.84 (q, J = 7.2 Hz, 2H), 1.54 (s, 3H), 0.79 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.7, 128.0, 126.5, 124.8, 76.9, 36.6, 29.6, 8.3; MS (ESI-TOF): *m*/*z* (%): 173 [$(M+H)^+$, 100].

2-Phenylbutane [CAS Reg. No. 135-98-8] (Entry 30)[14)]

^{1}H NMR [400 MHz (ECS-400), $CDCl_3$]: δ = 7.25 (t, J = 7.6 Hz, 2H), 7.13–7.19 (m, 3H), 2.57 (m, 1H), 1.60

(m, 2H), 1.22 (d, J = 6.8 Hz, 3H), 0.80 (t, J = 7.4 Hz, 3H); ^{13}C NMR [100 MHz (ECS-400), $CDCl_3$]: δ = 129.4, 129.3, 128.0, 126.8, 43.0, 32.2, 22.5, 12.6; MS (EI): m/z (%): 134 (M^+, 16), 105 (100), 91 (16), 77 (16).

Synthesis of substrates for Table 1.

Benzyl 4-*tert*-Butylphenylcarbamate [CAS Reg. No. 916605-92-0] (Entries 8 and 9)[15)]

To a solution of 4-tert-butylaniline (298 mg, 2.00 mmol) in THF (4 mL) at 0 °C under an Ar atmosphere was slowly added benzyl chloroformate (375 mg, 2.20 mmol). After 30 min the mixture was warmed to room temperature, and stirred at room temperature for further 30 min. To the mixture was added 1 M aqueous Na_2CO_3 solution (2.2 mL), and the mixture was concentrated in vacuo. EtOAc (20 mL) and saturated aqueous NH_4Cl (20 mL) were added to the residue, and the organic layer was washed with saturated aqueous NH_4Cl (2 × 20 mL) and brine (20 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexane/EtOAc, 20:1 to 10:1) to give benzyl 4-*tert*-butylphenylcarbamate (547 mg, 97%) as a colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32–7.42 (m, 9H), 6.62 (br s, 1H), 5.20 (s, 2H), 1.30 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.4, 146.5, 136.1, 135.0, 128.6, 128.3, 128.3, 125.9, 118.5, 66.9, 34.2, 31.3; MS (ESI): m/z (%): 306 [$(M+Na)^+$, 100%]

Benzyl Phenethylcarbamate [CAS Reg. No. 70867-38-8] (Entries 10 and 11)[16)]

To a solution of phenethylamine (606 mg, 5.00 mmol) in THF (11.7 mL) at 0 °C under an Ar atmosphere was slowly added benzyl chloroformate (768 mg, 4.50 mmol). After 30 min the mixture was warmed to room temperature, and stirred at room temperature for 1.5 h and at 40 °C for 2.5 h. To the mixture was added $NaHCO_3$ (462 mg, 5.50 mmol), and the mixture was concentrated in vacuo. EtOAc (20 mL) and saturated aqueous NH_4Cl (20 mL) were added to the residue, and the organic layer was washed with saturated aqueous NH_4Cl (2 × 20 mL) and brine (20 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexane/EtOAc, 5:1) to give benzyl phenethylcarbamate (1.14 g, 89%) as a colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.17–7.37 (m, 10H), 5.09 (s, 2H), 4.77 (br s, 1H), 3.47 (q, J = 6.7 Hz, 2H), 2.82 (t, J = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.3, 138.7, 136.5, 128.8, 128.6, 128.5, 128.1, 126.5, 66.6, 42.2, 36.0 (One signal could not be located because of its overlap with other signals); MS (EI): m/z (%): 255 (M^+, 1), 194 (27), 181 (18), 164 (40), 147 (7), 120 (22), 91 (100), 77 (10), 65 (23).

Benzyl Allyl(phenyl)carbamate [CAS Reg. No. 246257-97-6] (Entries 12 and 13)[17)]

To a solution of allylaniline (723 mg, 5.40 mmol) in THF (12 mL) at 0 °C under an Ar atmosphere was slowly added benzyl chloroformate (938 mg, 5.50 mmol). After 30 min the mixture was warmed to room temperature, and stirred at room temperature for 24 h. To the mixture was added 1 M aqueous Na_2CO_3 solution (5.0 mL), and the mixture was concentrated in vacuo. EtOAc (20 mL) and saturated aqueous NH_4Cl (20 mL) were added to the residue, and the organic layer was washed with saturated aqueous NH_4Cl (2 × 20 mL) and brine (20 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexane/EtOAc, 30:1) to give benzyl allyl(phenyl)carbamate (1.23 g, 84%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.22–7.36 (m, 10H), 5.90 (m, 1H), 5.13–5.16 (m, 4H), 4.28 (d, J = 5.5 Hz,

2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.2, 141.9, 136.5, 133.6, 128.8, 128.3, 127.8, 127.6, 126.8, 126.5, 117.1, 67.2, 53.3; MS (EI): *m*/*z* (%): 267 (M^+, 3), 223 (4), 196 (3), 182 (2), 146 (3), 130 (20), 91 (100), 77 (36).

Benzyl Diallylcarbamate [CAS Reg. No. 25070-76-2] (Entries 14 and 15)[18)]

To a solution of diallylamine (486 mg, 5.00 mmol) in THF (5 mL) at 0 °C under an Ar atmosphere was slowly added benzyl chloroformate (869 mg, 5.09 mmol). The mixture was gradually warmed to room temperature, and after 24 h 1 M aqueous Na_2CO_3 solution (7.0 mL) was added. The mixture was concentrated in vacuo, EtOAc (20 mL) and saturated aqueous NH_4Cl (20 mL) were added to the residue, and the organic layer was washed with saturated aqueous NH_4Cl (2 × 20 mL) and brine (20 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexane/EtOAc, 15:1) to give benzyl diallylcarbamate (705 mg, 61%) as a colorless oil.

^{1}H NMR [400 MHz, (ECS-400), $CDCl_3$]: δ = 7.29–7.36 (m, 5H), 5.77 (br s, 2H), 5.15 (s, 2H), 5.13 (br m, 4H), 3.89 (br m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.0, 136.7, 133.4, 128.4, 127.9, 127.7, 117.1, 116.7, 67.1, 49.1, 48.4 (Two sets of signals were observed because of the existence of rotamers); MS (ESI-TOF): *m*/*z* (%): 254 [$(M+Na)^+$, 100%].

Benzy 4-Benzyloxybenzoate [CAS Reg. No. 56442-22-9] (Entries 21 and 22)[19)]

To a solution of 4-hydroxybenzoic acid benzyl ester (1.14 g, 5.00 mmol) in THF (10 mL) at 0 °C under an Ar atmosphere was slowly added NaH [60% dispersion in mineral oil (400 mg, 10.0 mmol)]. After 30 min the mixture was heated at 80 °C, and benzyl bromide (1.58 g, 9.22 mmol) was slowly added. After 21 h saturated aqueous NH_4Cl (20 mL) was added, and the mixture was concentrated in vacuo. Et_2O (20 mL) and H_2O (20 mL) were added to the residue, and the organic layer was washed with H_2O (2 × 20 mL) and brine (2 × 20 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexane/Et_2O, 10:1 to 20:3) to give benzy 4-benzyloxybenzoate (686 mg, 43%) as a colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.0 Hz, 2H), 7.32–7.45 (m, 10H), 6.99 (d, *J* = 8.0 Hz, 2H), 5.33 (s, 2H), 5.11 (s, 2H); ^{13}C NMR (500 MHz, $CDCl_3$): δ =166.1, 162.5, 136.2, 136.2, 131.7, 128.7, 128.5, 128.2, 128.1, 128.1, 127.5, 122.7, 114.4, 70.1, 66.4; MS (ESI-TOF): *m*/*z* (%): 341 [$(M+Na)^+$, 100%].

Typical procedure for the 3.9% Pd/AM- and 5% Pd/CM-catalyzed Suzuki–Miyaura reaction (Table 2)

A mixture of the aryl halide (500 μmol), arylboronic acid (550 μmol), $Na_3PO_4{\cdot}12H_2O$ (665 mg, 1.75 mmol) and Pd/AM (6.8 mg, 2.50 μmol) or Pd/CM (5.3 mg, 2.50 μmol) in H_2O (1 mL)–*i*PrOH (1 mL) or in H_2O (2 mL) in a test tube under an Ar atmosphere was stirred at room temperature or 80 °C. After complete consumption of the aryl halide was confirmed by TLC analyses or after 24 h (if the reaction was incomplete), the mixture was passed through a cotton filter to remove the catalyst. To the filtrate were added EtOAc (20 mL) and saturated aqueous NH_4Cl (20 mL), then the layers were separated. The organic layer was washed with saturated aqueous NH_4Cl (2 × 20 mL) and brine (20 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (*n*-hexane/EtOAc or CH_2Cl_2/MeOH/AcOH) to give the corresponding biaryl. The spectral data of the product were identical to

those in the literature.

4-Nitrobiphenyl [CAS Reg. No. 92-93-3] (Entries 1–3)[20)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.29 (d, J = 8.8 Hz, 2H), 7.73 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 7.5 Hz, 2H), 7.50 (t, J = 7.5 Hz, 2H), 7.45 (t, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.5, 147.0, 138.7, 129.1, 128.9, 127.7, 127.3, 124.0; MS (EI): m/z (%): 199 (M^+, 6), 169 (100), 152 (37).

4-Biphenylcarboxylic Acid Ethyl Ester [CAS Reg. No. 6301-56-0] (Entries 4–6)[20)]

^{1}H NMR [400 MHz (ECS-400), $CDCl_3$]: δ = 8.10 (d, J = 8.8 Hz, 2H), 7.58–7.64 (m, 4H), 7.43 (t, J = 7.3 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 4.38 (q, J = 7.0 Hz, 2H), 1.39 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.4, 145.4, 140.0, 130.0, 129.2, 128.8, 128.0, 127.2, 126.9, 60.9, 14.3; MS (EI): m/z (%): 226 (M^+, 39), 198 (23), 181 (100), 152 (41), 76 (8).

4-Biphenylcarboxylic Acid [CAS Reg. No. 92-92-2] (Entries 7–9)[20)]

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.02 (d, J = 8.3 Hz, 2H), 7.77 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 7.5 Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H), 7.40 (t, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 167.5, 144.6, 139.2, 130.2, 129.8, 129.3, 128.6, 127.2, 127.0; MS (EI): m/z (%): 198 (M^+, 100), 181 (66), 152 (69), 76 (12).

4-Aminobiphenyl [CAS Reg. No. 92-67-1] (Entries 10–12)[20)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, J = 7.5 Hz, 2H), 7.37–7.42 (m, 4H), 7.26 (t, J = 7.3 Hz, 1H), 6.74 (d, J = 7.5 Hz, 2H), 3.71 (br s, 2H); ^{13}C NMR [100 MHz (ECS-400), $CDCl_3$]: δ = 145.8, 141.1, 131.4, 128.6, 127.9, 126.3, 126.2, 115.3; MS (EI): m/z (%): 169 (M^+, 100), 141 (11), 115 (7).

4-Methoxybiphenyl [CAS Reg. No. 613-37-6] (Entries 13–15)[20)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50–7.54 (m, 4H), 7.39 (t, J = 7.7 Hz, 2H), 7.28 (t, J = 7.2 Hz, 1H), 6.95 (d, J = 8.6 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.1, 140.7, 133.7, 128.7, 128.1, 126.7, 126.6, 114.1, 55.2; MS (EI): m/z (%): 184 (M^+, 100), 169 (54), 141 (46), 115 (32).

4-Hydroxybiphenyl [CAS Reg. No. 92-69-3] (Entries 16–18)[20)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.54 (d, J = 7.8 Hz, 2H), 7.48 (t, J = 8.5 Hz, 2H), 7.42 (d, J = 7.8 Hz, 2H), 7.31 (d, J = 7.8 Hz, 1H), 6.91 (t, J = 8.5 Hz, 2H), 4.75 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.0, 140.7, 134.0, 128.7, 128.4, 126.7, 115.6 (One signal could not be located because of its overlap with other signals); MS (EI): m/z (%): 170 (M^+, 100), 141 (26), 115 (14).

2,4'-Dimethoxybiphenyl [CAS Reg. No. 49602-47-3] (Entries 19–21)[20)]

^{1}H NMR [400 MHz (ECS-400), $CDCl_3$]: δ = 7.46 (d, J = 8.6 Hz, 2H), 7.24–7.29 (m, 2H), 6.97–7.00 (m, 2H), 6.93 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H), 3.76 (s, 3H); ^{13}C NMR [100 MHz (AL-400), $CDCl_3$]: δ = 158.6, 156.3, 130.8, 130.6, 130.5, 130.2, 128.1, 120.7, 113.4, 111.1, 55.4, 55.1; MS (EI): m/z (%): 214 (M^+, 100), 199 (54), 184 (43), 168 (25), 156 (14), 139 (18), 128 (39), 115 (10), 102 (8), 63 (10).

4-Acetyl-4'-nitrobiphenyl [CAS Reg. No. 135-69-3] (Entries 22–24)[20)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.33 (d, J = 8.6 Hz, 2H), 8.09 (d, J = 8.6 Hz, 2H), 7.79 (d, J = 8.6 Hz, 2H), 7.73 (d, J = 8.6 Hz, 2H), 2.67 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.4, 147.5, 146.1, 143.0, 137.0, 129.1, 128.0, 127.6, 124.1, 26.7; MS (EI): m/z (%): 241 (M^+, 13), 226 (100), 180 (27), 152 (46).

Typical procedure for the 3.9% Pd/AM- and 5% Pd/CM-catalyzed Mizoroki–Heck reaction (Table 3)

A mixture of the aryl iodide (500 μmol), mono-substituted alkene (600 μmol), Bu_3N (102 mg, 550 μmol), and Pd/AM (2.7 mg, 1.00 μmol) or Pd/CM (2.1 mg, 1.00 μmol) in DMA (2 mL) in a test tube under an Ar atmosphere was stirred at 100 ˚C or 80 ˚C. After complete consumption of the aryl iodide was confirmed by TLC analyses or after 24 h (if the reaction was incomplete), the mixture was passed through a cotton filter to remove the catalyst. To the filtrate were added EtOAc (20 mL) and saturated aqueous NH_4Cl (20 mL), then the layers were separated. The organic layer was washed with saturated aq. NH_4Cl (2 × 20 mL) and brine (20 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography (*n*-hexane/EtOAc) to give the corresponding disubstituted alkene derivative. The spectral data of the product were identical to those in the literature. For entries 19 and 20, the reactions were performed using 2 mol% of Pd/AM (27.3 mg, 10.0 μmol) or Pd/CM (21.3 mg, 10.0 μmol).

Butyl (*E*)-4-Nitrocinnamate [CAS Reg. No. 86622-84-6] (Entries 1–3)[20)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.25 (d, J = 8.6 Hz, 2H), 7.71 (d, J = 16.0 Hz, 1H), 7.69 (d, J = 8.6 Hz, 2H), 6.58 (d, J = 16.0 Hz, 1H), 4.24 (t, J = 6.6 Hz, 2H), 1.71 (m, 2H), 1.45 (m, 2H), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.0, 148.4, 141.5, 140.5, 128.6, 124.1, 122.6, 64.8, 30.6, 19.1, 13.6; MS (EI): *m*/*z* (%): 233 (M^+, 4), 193 (59), 176 (100), 160 (7), 147 (18), 130 (36), 118 (7), 102 (39), 90 (20), 76 (22), 56 (67).

Butyl (*E*)-3-Nitrocinnamate [CAS Reg. No. 440363-15-5] (Entries 4–6)[20)]

^{1}H NMR [400 MHz (ECS-400), $CDCl_3$]: δ = 8.34 (s, 1H), 8.19 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 16.0 Hz, 1H), 7.56 (t, J = 8.0 Hz, 1H), 6.54 (d, J = 16.0 Hz, 1H), 4.20 (t, J = 6.5 Hz, 2H), 1.67 (m, 2H), 1.41 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR [100 MHz (ECS-400), $CDCl_3$]: δ = 166.1, 148.6, 141.5, 136.1, 133.5, 129.9, 124.3, 122.3, 121.4, 64.7, 30.6, 19.1, 13.6; MS (EI): *m*/*z* (%): 194 (M^+, 31), 176 (100), 160 (6), 146 (11), 129 (14), 118 (9), 102 (30) 76 (13), 56 (32).

Butyl (*E*)-4-Methylcinnamate [CAS Reg. No. 123248-21-5] (Entries 7–9)[20)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, J = 16.0 Hz, 1H), 7.40 (d, J = 7.8 Hz, 2H), 7.17 (d, J = 7.8 Hz, 2H), 6.39 (d, J = 16.0 Hz, 1H), 4.19 (t, J = 6.9 Hz, 2H), 2.35 (s, 3H), 1.68 (m, 2H), 1.43 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.1, 144.4, 140.4, 131.6, 129.5, 127.9, 117.1, 64.2, 30.7, 21.3, 19.1, 13.6; MS (EI): *m*/*z* (%): 218 (M^+, 10), 162 (91), 145 (100), 115 (46), 91 (32), 65 (16).

Butyl (*E*)-Cinnamate [CAS Reg. No. 52392-64-0] (Entries 10–12)[20)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67 (d, J = 15.8 Hz, 1H), 7.51 (dd, J = 2.5, 6.5 Hz, 2H), 7.35–7.37 (m, 3H), 6.43 (d, J = 15.8 Hz, 1H), 4.20 (t, J = 6.5 Hz, 2H), 1.69 (m, 2H), 1.43 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.0, 144.4, 134.3, 130.1, 128.8, 127.9, 118.2, 64.3, 30.7, 19.1, 13.7; MS (EI): *m*/*z* (%): 204 (M^+, 6), 148 (100), 132 (89), 103 (60), 77 (32).

(*E*)-Stilbene [CAS Reg. No. 103-30-0] (Entries 13–15)[20)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50 (d, J = 7.5 Hz, 4H), 7.34 (t, J = 7.7 Hz, 4H), 7.24 (d, J = 7.5 Hz, 2H), 7.10 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.3, 128.6, 127.6, 126.5 (One signal could not be located because of its overlap with other signals); MS (EI): *m*/*z* (%): 180 (M^+, 98), 179 (100), 165 (62), 152 (11), 102 (9), 89 (29), 76 (23).

(*E*)-Cinnamamide [CAS Reg. No. 22031-64-7] (Entries 16–18)[20)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, J = 15.5 Hz, 1H), 7.52 (m, 2H), 7.37–7.39 (m, 3H), 6.48 (d, J = 15.5 Hz, 1H), 5.91 (br s, 1H), 5.73 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.9, 142.5, 134.4, 130.0, 128.8, 127.9, 119.5; MS (EI): *m*/*z* (%): 147 (M^+, 0), 146 (100), 131 (34), 103 (61), 77 (61).

(*E*)-Cinnamonitrile [CAS Reg. No. 1885-38-7] (Entries 19–21)[20)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37–7.45 (m, 6H), 5.87 (d, J = 17 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.5, 133.4, 131.1, 129.0, 127.3, 118.1, 96.2; MS (EI): *m*/*z* (%): 129 (M^+, 100), 102 (59), 76 (23).

(*Z*)-Cinnamonitrile [CAS Reg. No. 24840-05-9] (Entries 22–25)[20)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.81 (m, 2H), 7.37–7.45 (m, 3H), 7.13 (d, J = 12 Hz, 1H), 5.45 (d, J = 12 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.7, 130.9, 128.9, 128.8, 117.3, 94.9 (One signal could not be located because of its overlap with other signals); MS (EI): *m*/*z* (%): 129 (M^+, 100), 102 (43), 76 (17).

Typical procedure for the 3.9% Pd/AM- and 5% Pd/CM-catalyzed Sonogashira-type reaction (Table 4)

A mixture of the aryl iodide (500 μmol), the mono-substituted alkyne (600 μmol), $Na_3PO_4{\cdot}12H_2O$ (380 mg, 1.00 mmol) and Pd/AM (5.5 mg, 2.00 μmol) or Pd/CM (4.3 mg, 2.00 μmol) in H_2O (1 mL)–*i*PrOH (1 mL) in a test tube under Ar atmosphere was stirred at 80 °C. After complete consumption of the aryl iodide was confirmed by TLC analyses, the mixture was passed through a cotton filter to remove the catalyst. To the filtrate were added EtOAc (20 mL) and saturated aqueous NH_4Cl (20 mL), then the layers were separated. The organic layer was washed with saturated aqueous NH_4Cl (2 × 20 mL) and brine (20 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (*n*-hexane/EtOAc) to give the corresponding disubstituted alkyne. The spectral data of the product were identical to those in the literature. For entry 5, the reaction was performed using 2 equiv of ethynylbenzene (102 mg, 1.00 mmol).

1-[4-(2-Phenylethynyl)phenyl]ethanone [CAS Reg. No. 1942-31-0] (Entries 1–3)[20)]

^{1}H NMR [400 MHz (ECS-400), $CDCl_3$]: δ = 7.90 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H), 7.54 (m, 2H), 7.33–7.36 (m, 3H); ^{13}C NMR [100 MHz (ECS-400), $CDCl_3$]: δ = 197.1, 136.1, 131.6, 131.6, 128.7, 128.3, 128.2, 128.0, 122.5, 92.6, 88.5, 26.5; MS (EI): *m*/*z* (%): 220 (M^+, 50), 205 (100), 176 (50), 151 (5).

1-[2-(4-Methoxyphenyl)ethynyl]benzene [CAS Reg. No. 7380-78-1] (Entries 4–6)[20)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46–7.52 (m, 4H), 7.30-7.35 (m, 3H), 6.84 (d, J = 8.5 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$): δ = 159.5, 133.0, 131.4, 128.3, 127.9, 123.5, 115.3, 113.9, 89.3, 88.0, 55.2; MS (EI): *m*/*z* (%): 208 (M^+, 100), 193 (60), 165 (44), 139 (7).

Diphenylacetylene [CAS Reg. No. 501-65-5] (Entries 7–9)[20)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.63 (dd, J = 7.5, 1.4 Hz, 4H), 7.36–7.39 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 131.6, 128.3, 128.2, 123.2; MS (EI): *m*/*z* (%): 178 (M^+, 100), 152 (30), 89 (15), 76 (21).

1{4-[2-(2-Trifluoromethylphenyl)ethynyl]phenyl}ethanone [CAS Reg. No. 851279-09-9] (Entries 10–12)[20)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93 (d, J = 8.6 Hz, 2H), 7.66–7.69 (m, 2H), 7.61 (d, J = 8.6 Hz, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 2.59 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.2, 136.5, 133.8, 131.7, 131.5 (q, J_{CF} = 30.2 Hz), 128.4, 128.2, 127.4, 125.9 (q, J_{CF} = 6.0 Hz), 123.5 (q, J_{CF} = 271.9 Hz), 120.8,

93.8, 88.3, 26.5; MS (EI): *m*/*z* (%): 288 (M^+, 40), 273 (100), 245 (41), 225 (36).

1-[4-(4-Hydroxybut-1-ynyl)phenyl]ethanone [CAS Reg. No. 510754-35-5] (Entries 13–15)[20)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 3.85 (q, *J* = 6.3 Hz, 2H), 2.73 (t, *J* = 6.3 Hz, 2H), 2.60 (s, 3H), 1.85 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.5, 135.9, 131.7, 128.3, 128.1, 90.3, 81.6, 60.9, 26.6, 23.8; MS (EI): *m*/*z* (%): 188 (M^+, 49), 173 (100), 143 (23), 115 (12).

1-[4-(*p*-Tolylethynyl)phenyl]ethanone [CAS Reg. No. 123770-66-1] (Entries 16 and 17)[23)]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 7.7 Hz, 2H), 2.60 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.3, 139.0, 135.9, 131.6, 131.2, 129.2, 128.4, 128.2, 119.5, 93.0, 88.0, 26.6, 21.2; MS (EI): *m*/*z* (%): 234 (M^+, 62), 219 (100), 189 (50), 176 (12).

Reuse test of the 3.9% Pd/AM for hydrogenation (Table 5)

A mixture of 1,2-dimethoxy-4-(1-propenyl)benzene (1.25 g, 7.00 mmol) and 3.9% Pd/AM (191 mg, 70.0 μmol) in MeOH (35 mL) in a 100-mL round-bottom flask under an H_2 atmosphere was stirred at room temperature. After 2 h, the mixture was passed through a filter paper [Kiriyama, No. 5C (1 μm), diameter = 40 mm]. The catalyst on the a filter paper was washed with EtOAc (30 mL), and the filtrate was concentrated *in vacuo* to give 1,2-dimethoxy-4-propylbenzene in 100% yield (1.26 g, 7.00 mmol). The recovered catalyst was dried at room temperature under reduced pressure for 24 h, then weighed [184 mg, 96%, 184 ÷ 191 × 100]. The reaction for the second run was carried out in the same manner as the first run, but using 6.75 mmol (1.20 g) of substrate and 67.2 μmol (184 mg) of Pd/AM in MeOH (34 mL). 1,2-Dimethoxy-4-propylbenzene was obtained in 97% yield (1.18 g, 6.55 mmol), and the catalyst was recovered 97% [179 mg, 179 ÷ 184 × 100]. The reactions for the third to fifth runs were also carried out in the same manner as the first run. The results are summarized in the Table S1.

Table S1 Reuse test of Pd/AM in hydrogenation

Run	Quantity			
	Substrate	Used catalyst	Recovered catalyst	Product
1st	1.25 g (7.00 mmol)	191 mg (70.0 μmol)	184 mg (96%)	1.26 g (7.00 mmol), 100%
2nd	1.20 g (6.75 mmol)	184 mg (67.2 μmol)	179 mg (97%)	1.18 g (6.55 mmol), 97%
3rd	1.17 g (6.56 mmol)	179 mg (65.2 μmol)	177 mg (99%)	1.18 g (6.55 mmol), 100%
4th	1.16 g (6.49 mmol)	177 mg (64.5 μmol)	170 mg (96%)	1.15 g (6.43 mmol), 99%
5th	1.11 g (6.23 mmol)	170 mg (61.9 μmol)	170 mg (100%)	1.12 g (6.23 mmol), 100%

Reuse test of the 5% Pd/CM for hydrogenation (Table 5)

A mixture of 1,2-dimethoxy-4-(1-propenyl)benzene (1.25 g, 7.00 mmol) and Pd/CM (149 mg, 70.0 μmol) in MeOH (35.0 mL) in a 100 mL-round bottom flask under an H_2 atmosphere was stirred at room temperature. After 2 h, the mixture was passed through a filter paper [Kiriyama, No. 5C (1 μm), diameter = 40 mm]. The catalyst on the filter paper was washed with EtOAc (30 mL), and the filtrate was concentrated *in vacuo* to give

1,2-dimethoxy-4-propylbenzene in 94% yield (1.19 g, 6.58 mmol). The recovered catalyst was dried at room temperature under reduced pressure for 24 h, then weighed [149 mg, 100%, 149 ÷ 149 × 100]. The reaction for the second run was carried out in the same manner as the first run. 1,2-Dimethoxy-4-propylbenzene was obtained in 99% yield (1.24 g, 6.93 mmol), and the catalyst was recovered 99% [147 mg, 147 ÷ 149 × 100]. The reactions for the third to fifth runs were also carried out in the same manner as the first run. The results are summarized in the Table S2.

Table S2 Reuse test of Pd/CM in hydrogenation

Run	Quantity			
	Substrate	Used catalyst	Recovered catalyst	Product
1st	1.25 g (7.00 mmol)	149 mg (70.0 μmol)	149 mg (100%)	1.19 g (6.58 mmol), 94%
2nd	1.25 g (7.00 mmol)	149 mg (70.0 μmol)	147 mg (99%)	1.24 g (6.93 mmol), 99%
3rd	1.23 g (6.90 mmol)	147 mg (69.0 μmol)	145 mg (99%)	1.24 g (6.93 mmol), 100%
4th	1.21 g (6.80 mmol)	145 mg (68.0 μmol)	143 mg (99%)	1.23 g (6.80 mmol), 100%
5th	1.20 g (6.74 mmol)	143 mg (61.9 μmol)	143 mg (100%)	1.21 g (6.74 mmol), 100%

Reuse test of the 5% Pd/CM for Sonogashira-type reaction (Table 6)

Ten test tubes were prepared, and Pd/CM (4.3 mg, 2.00 μmol), the 4'-iodoacetophenone (123 mg, 500 μmol), ethynylbenzene (61.3 mg, 600 μmol), $Na_2PO_4 \cdot 12H_2O$ (380 mg, 1.00 mmol) and H_2O (1 mL)–*i*PrOH (1 mL) were placed in each tube. The mixture in each test tube was stirred at 80 °C under an Ar atmosphere (balloon) for 1 h, then all the mixtures were filtered using a Kiriyama funnel (1 μm filter paper, diameter = 8 mm). The catalyst on the filter was washed with EtOAc (80 mL), saturated aq. NH_4Cl (40 mL) and H_2O (40 mL). The combined filtrate was separated into two layers. The organic layer was washed with saturated aq. NH_4Cl (2 × 80 mL) and brine (80 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. To the residue were added $CDCl_3$ (ca. 1 mL) and 1,4-dioxane (42.6 μL, 500 μmol) as the internal standard, and the yield of 1-[4-(2-phenylethynyl)phenyl]ethanone was determined to be 100% by ^{1}H NMR. The recovered catalyst was dried at room temperature under reduced pressure for 24 h, then weighed [70.4 mg, >100%, 70.4 ÷ (4.3 × 10) × 100]. The reaction for the second run was carried out in the same manner as the first run, but using the catalyst (7.0 mg) in each test tube. 1-[4-(2-Phenylethynyl)phenyl]ethanone was obtained in 100% yield after 24 h by ^{1}H NMR using 1,4-dixoxane (42.6 μL, 500 μmol) as an internal standard, and the catalyst was recovered (63.9 mg, 91%, 63.9 ÷ (7.0 × 10) × 100). The reactions for the third to fifth runs were also carried out in the same manner as the first run. The results are summarized in Table S3.

Table S3 Reuse test of Pd/CM in Sonogashira-type reaction

Run	Numer of test tubes	Reaction Time (h)	Quantity			
			Substrate & Reagents	Used catalyst	Recovered catalyst	Product yield[a]
1st	10	1	4'-Iodoacetophenone	430 mg (20.0 μmol)	70.4 mg	100%

			1.23 g (5.00 mmol) [123 mg (500 μmol) × 10]	[4.3 mg (2.00 μmol) × 10]	(100% over)	
			Ethynylbenzene 659 μL (6.00 mmol) [65.9 μL (600 μmol) × 10]			
			$Na_3PO_4 \cdot 12H_2O$ 3.80 g (10.0 mmol) [380 mg (1.00 mmol) × 10]			
2nd	10	1	4'-Iodoacetophenone 1.23 g (5.00 mmol) [123 mg (500 μmol) × 10]	70.0 mg [7.0 mg × 10]	63.9 mg (91%)	100%
			Ethynylbenzene 659 μL (6.00 mmol) [65.9 μL (600 μmol) × 10]			
			$Na_3PO_4 \cdot 12H_2O$ 3.80 g (10.0 mmol) [380 mg (1.00 mmol) × 10]			
3rd	10	1	4'-Iodoacetophenone 1.23 g (5.00 mmol) [123 mg (500 μmol) × 10]	63.0 mg [6.3 mg × 10]	59.9 mg (95%)	95% (5%)[b]
			Ethynylbenzene 659 μL (6.00 mmol) [65.9 μL (600 μmol) × 10]			
			$Na_3PO_4 \cdot 12H_2O$ 3.80 g (10.0 mmol) [380 mg (1.00 mmol) × 10]			
4th	10	2	4'-Iodoacetophenone 1.23 g (5.00 mmol) [123 mg (500 μmol) × 10]	59.0 mg [5.9 mg × 10]	52.1 mg (88%)	93% (7%)[b]
			Ethynylbenzene 659 μL (6.00 mmol) [65.9 μL (600 μmol) × 10]			
			$Na_3PO_4 \cdot 12H_2O$ 3.80 g (10.0 mmol) [380 mg (1.00 mmol) × 10]			

[a] Determined by ^{1}H NMR analysis using 1,4-dioxane as an internal standard.

[b] The yield of the recovered 4'-iodoacetophenone is indicated in parentheses.

Assay of residual palladium in the reaction media during the 3.9% Pd/AM-catalyzed hydrogenation

A mixture of 1,2-dimethoxy-4-(1-propenyl)benzene (1.25 g, 7.00 mmol) and Pd/AM (191 mg, 70.0 μmol) in MeOH (35.0 mL) in a 100-mL round-bottom flask under an H_2 atmosphere was stirred at room temperature. After 2 h, the mixture was filtered through a Celite pad, and the pad was washed with MeOH (20 mL). The filtrate was passed through a membrane filter (0.20 μm, Milipore Corporation) and transferred to a 100-mL volumetric flask using MeOH, MeOH was added up to 100 mL of the total volume, and the residual palladium was assayed by atomic absorption spectroscopy using a Shimadzu AA-7000 machine. The palladium leaching from Pd/AM was not observed (detection limit: 1 ppm).

Assay of residual palladium in the reaction media during the 5% Pd/CM-catalyzed hydrogenation

A mixture of 1,2-dimethoxy-4-(1-propenyl)benzene (1.25 g, 7.00 mmol) and Pd/CM (149 g, 70.0 μmol) in MeOH (35.0 mL) in a 100-mL round-bottom flask under an H_2 atmosphere was stirred at room temperature. After 2 h, the mixture was filtered through a Celite pad, and the pad was washed with MeOH (20 mL). The filtrate was passed through a membrane filter (0.20 μm, Milipore Corporation) and transferred to a 100-mL volumetric flask using MeOH, MeOH was added up to 100 mL of the total volume, and the residual palladium was assayed by atomic absorption spectroscopy using a Shimadzu AA-7000 machine. The palladium leaching from Pd/CM was not observed (detection limit: 1 ppm).

Assay of residual palladium in the reaction media during the Pd/AM-catalyzed Sonogashira-type reaction

A mixture of 4'-iodoacetophenone (6.15 g, 25.0 mmol), ethynylbenzene (3.06 mg, 30.0 mmol), 5.5% Pd/AM (194 mg, 100 μmol) and $Na_3PO_4{\cdot}12H_2O$ (1.90 mg, 50.0 mmol) in H_2O (50 mL)–*i*PrOH (50 mL) in a 500-mL round-bottom flask under an Ar atmosphere was stirred at 80 °C. After 1 h, the mixture was passed through a cotton filter to remove the catalyst. To the filtrate were added EtOAc (150 mL) and saturated aq. NH_4Cl (30 mL), and the layers were separated. The organic layer was washed with saturated aq. NH_4Cl (2 × 100 mL). The organic layer and the aqueous layer were filtered through a membrane filter (0.20 μm, Milipore Corporation), and concentrated *in vacuo*. The residue from the organic layer was transferred to a 500-mL volumetric flask using MeOH, MeOH was added up to 500 mL of the total volume, and the residual palladium was assayed by inductively coupled plasma atomic emission spectrometry (ICP-AES) using Vista Pro (Agilent Technologies, CA, USA). The residue from the aqueous layer was also transferred to another 500-mL volumetric flask using H_2O, H_2O was added up to 500 mL of the total volume, and the residual palladium was assayed in the same way. A very small amount of residual palladium was detected in organic layer (0.5 ppm), while no palladium was detected in aqueous layer (< 0.5 ppm). The results are summarized in Table S4.

Assay of residual palladium in the reaction media during the Pd/CM-catalyzed Sonogashira-type reaction

A mixture of 4′-iodoacetophenone (6.15 g, 25.0 mmol), ethynylbenzene (3.06 mg, 30.0 mmol), 5% Pd/CM (213 mg, 100 μmol) and $Na_3PO_4{\cdot}12H_2O$ (1.90 mg, 50.0 mmol) in H_2O (50 mL)–*i*PrOH (50 mL) in a 500

mL-round bottom flask under an Ar atmosphere was stirred at 80 °C. After 1 h, the mixture was passed through a cotton filter to remove the catalyst. To the filtrate were added EtOAc (150 mL) and saturated aq. NH_4Cl (30 mL), and the layers were separated. The organic layer was washed with saturated aq. NH_4Cl (2 × 100 mL). The organic layer and the aqueous layer were filtered through a membrane filter (0.20 μm, Milipore Corporation), and concentrated *in vacuo*. The residue from the organic layer was transferred to a 500-mL volumetric flask using EtOAc, EtOAc was added up to 500 mL of the total volume, and the residual palladium was assayed by ICP-AES using Vista Pro (Agilent Technologies, CA, USA). The residue from the aqueous layer was transferred to another 500-mL volumetric flask using H_2O, H_2O was added up to 500 mL of the total volume, and the residual palladium was assayed in the same way. The total palladium amounts in the organic layer and aqueous layer were negligible (< 0.5 ppm). The results are summarized in Table S4.

Table S4 Assay of residual palladium in the reaction media during the Pd/AM- and Pd/CM-catalyzed Sonogashira-type reaction

	Pd/AM		Pd/CM	
	Organic	Aqueous	Organic	Aqueous
ppm	0.5	< 0.5	< 0.5	< 0.5
g/mL (density of sample)	0.791	1.037	0.895	1.016
μg/mL	0.3955	< 0.5185	< 0.4475	< 0.508
%	1.89%	< 2.44%	< 2.10%	< 2.39%

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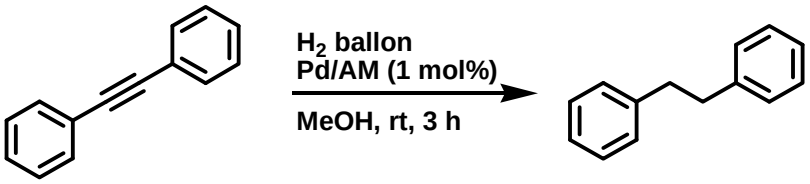
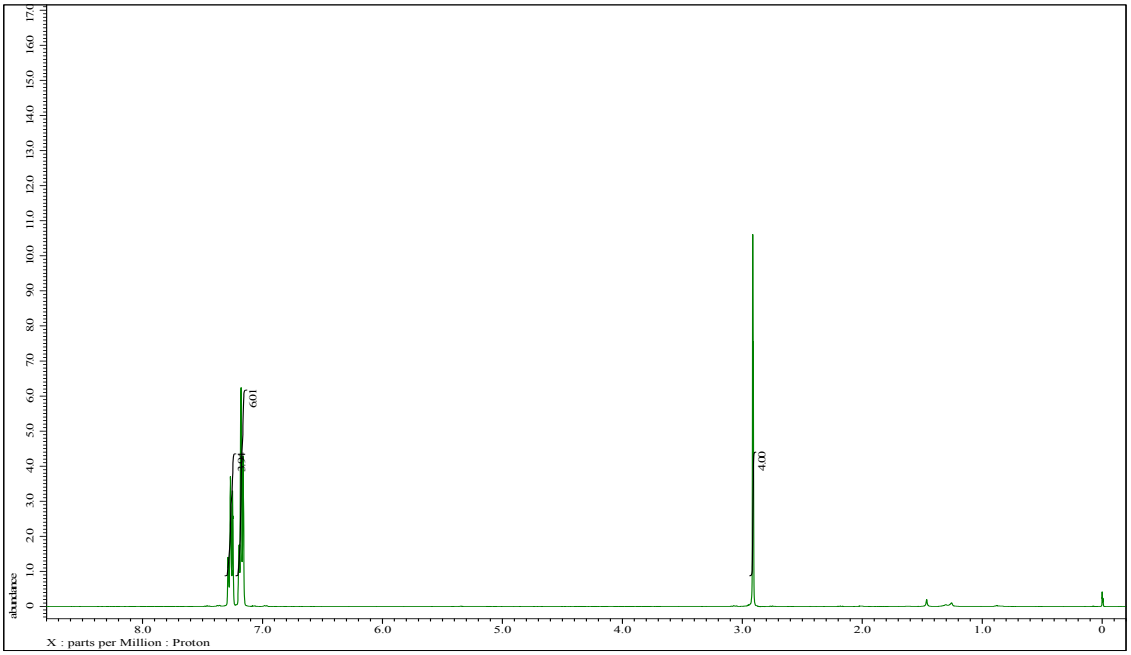
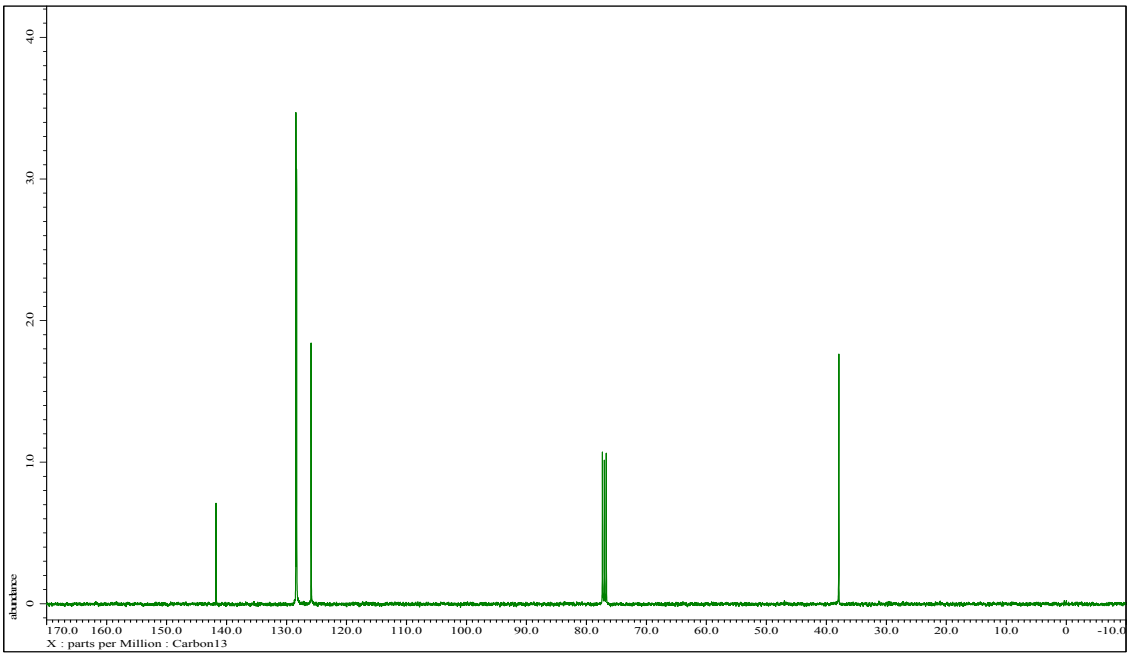
1,2-Diphenylethane (Table 1, Entry 1)







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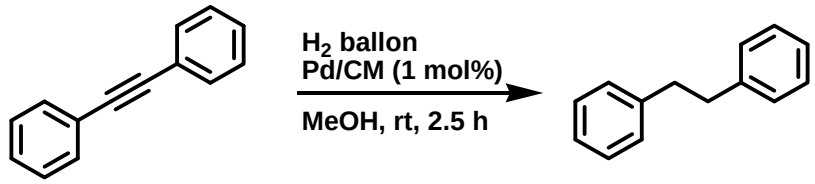
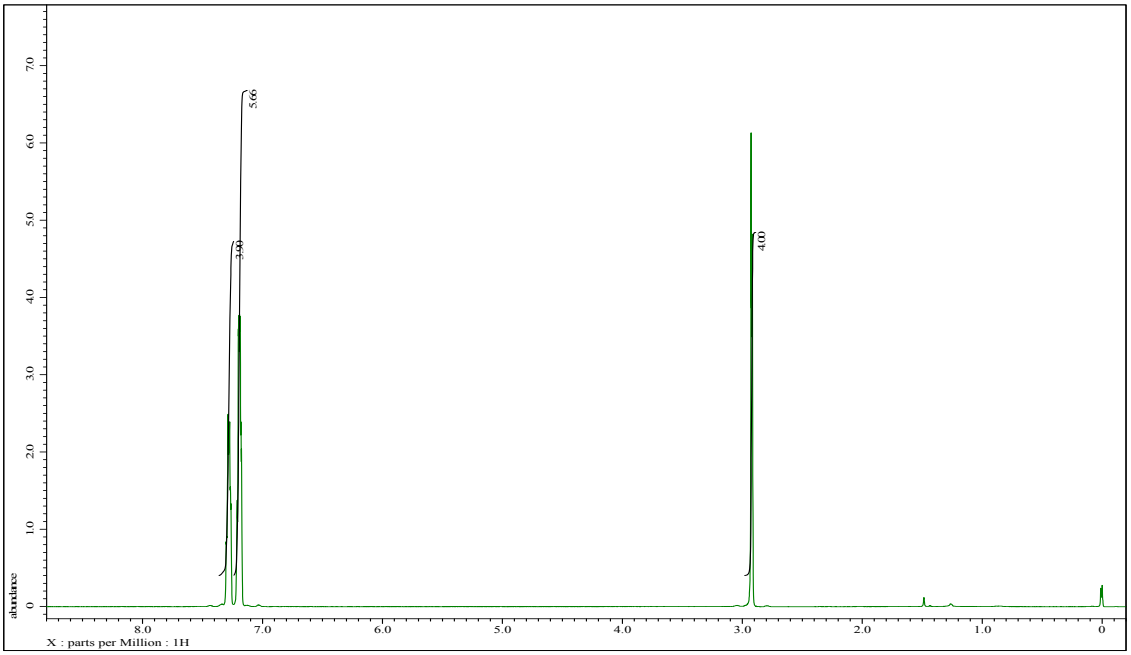
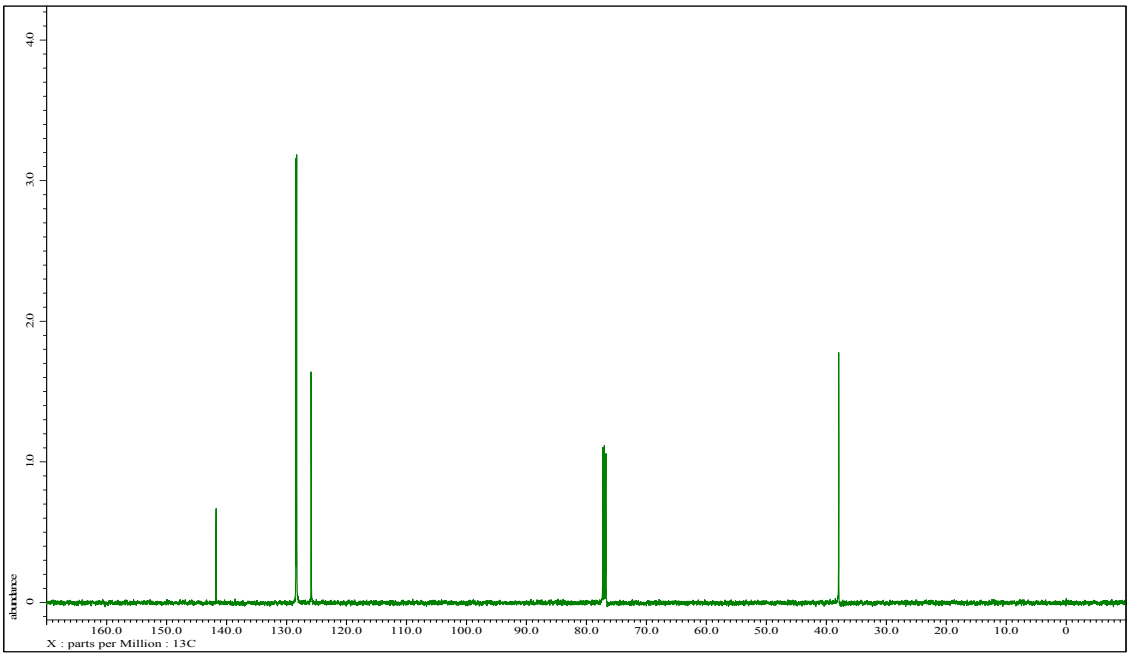
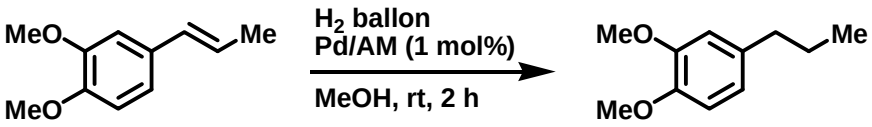
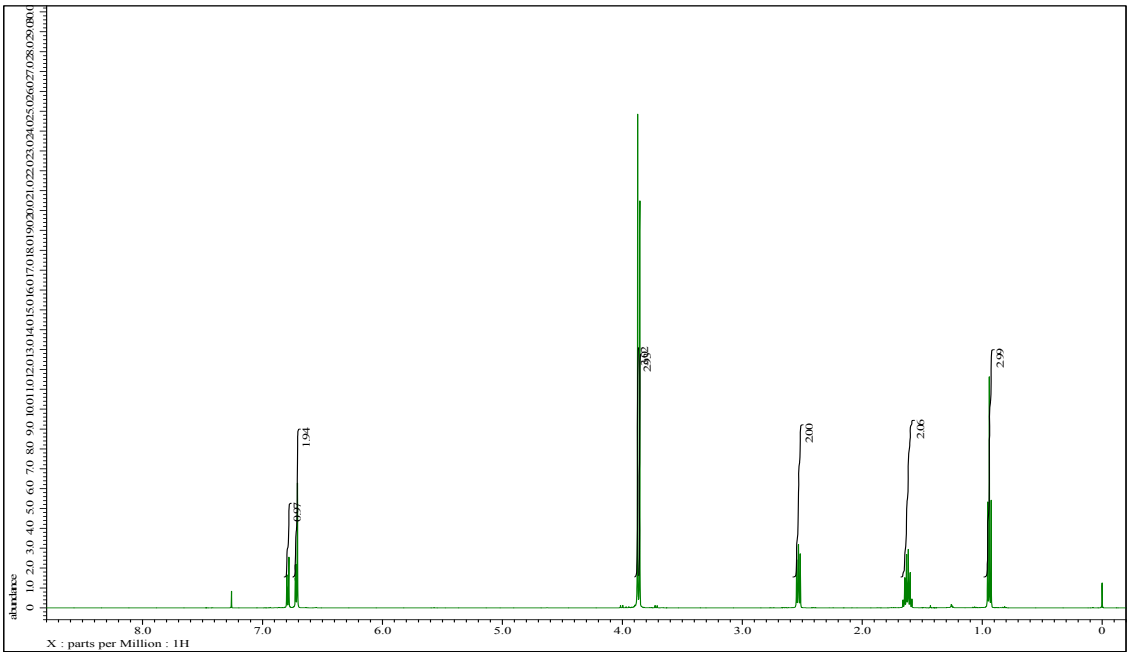


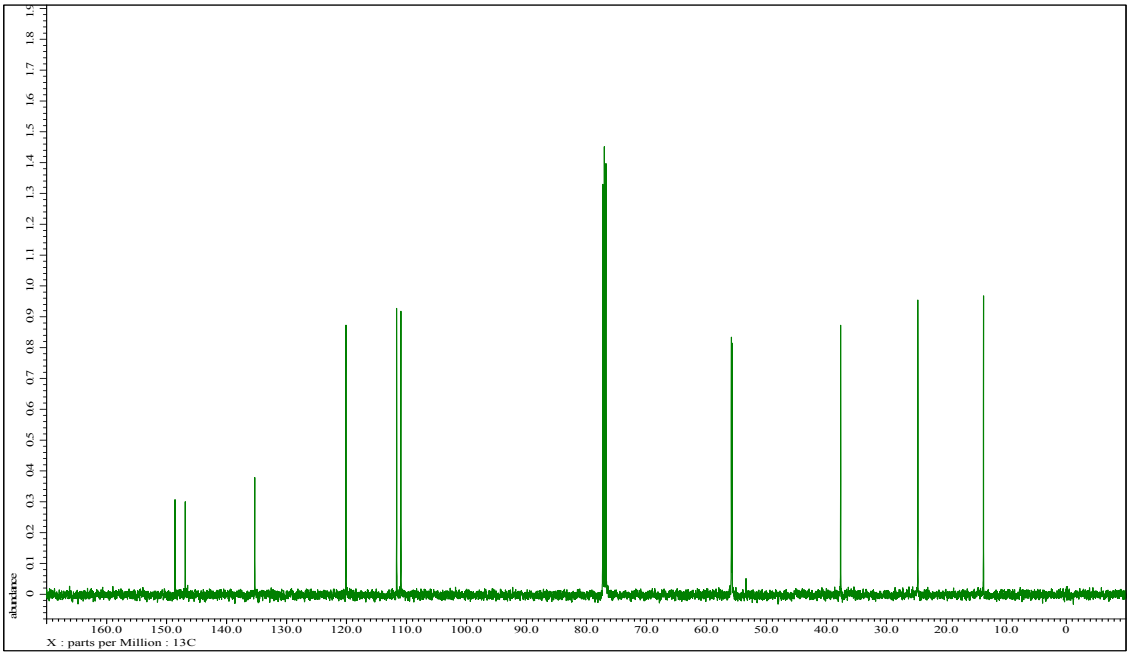




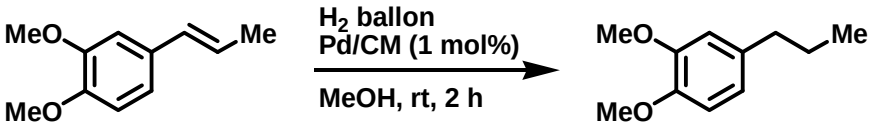
1,2-Dimethoxy-4-propylbenzene (Table 1, Entry 3)

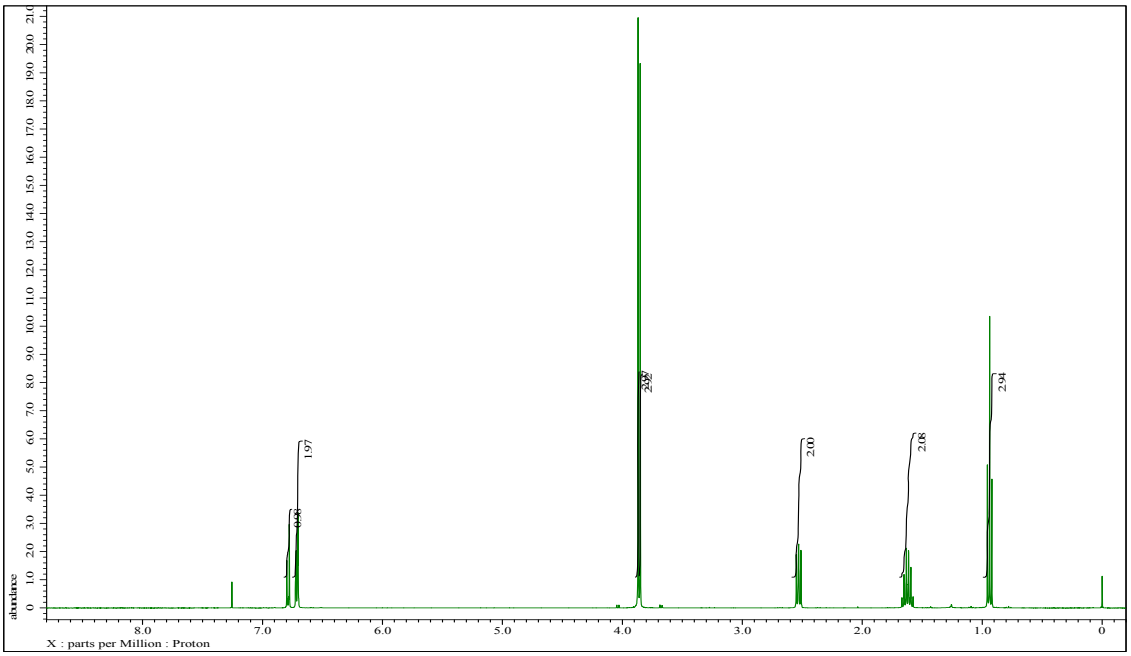


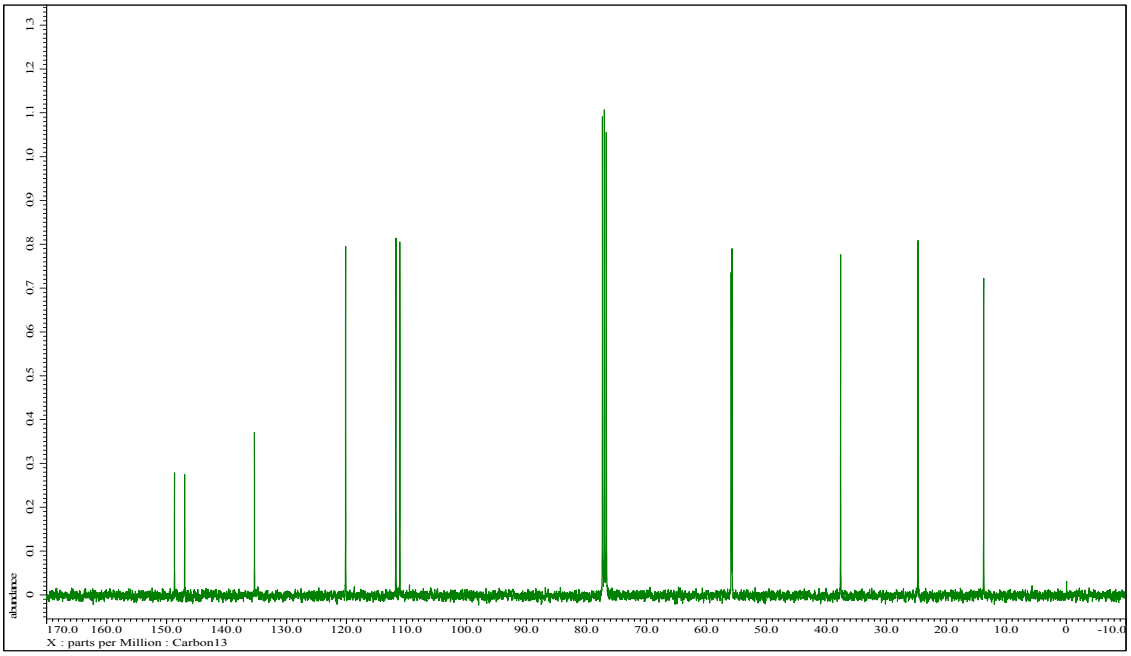




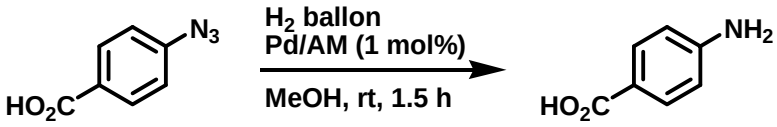
1,2-Dimethoxy-4-propylbenzene (Table 1, Entry 4)

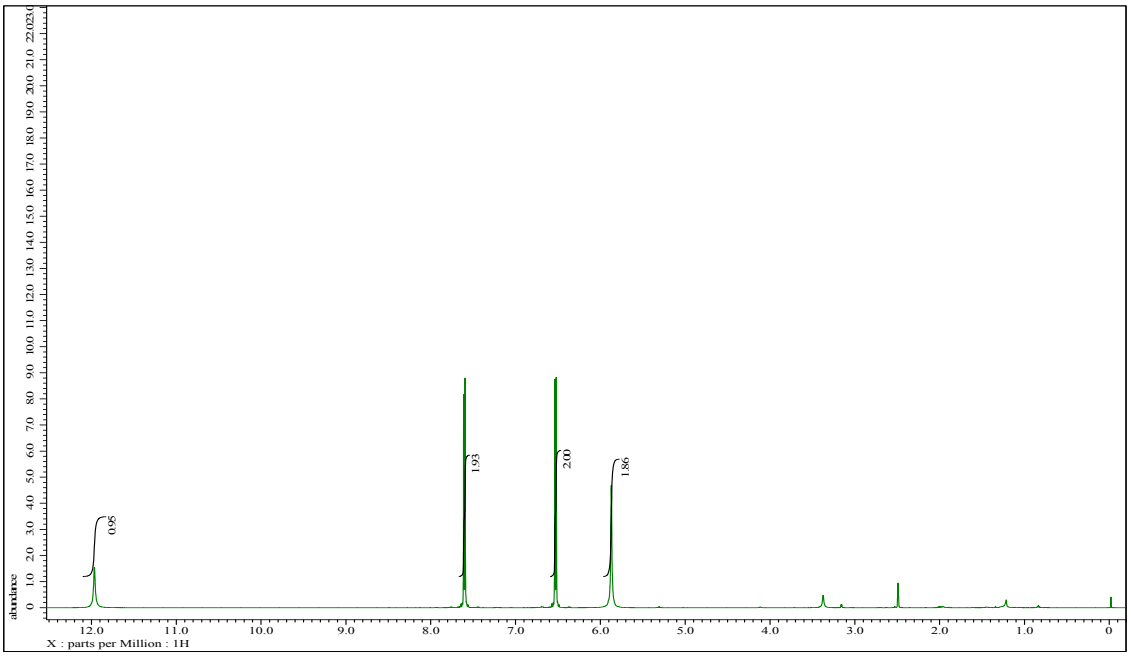


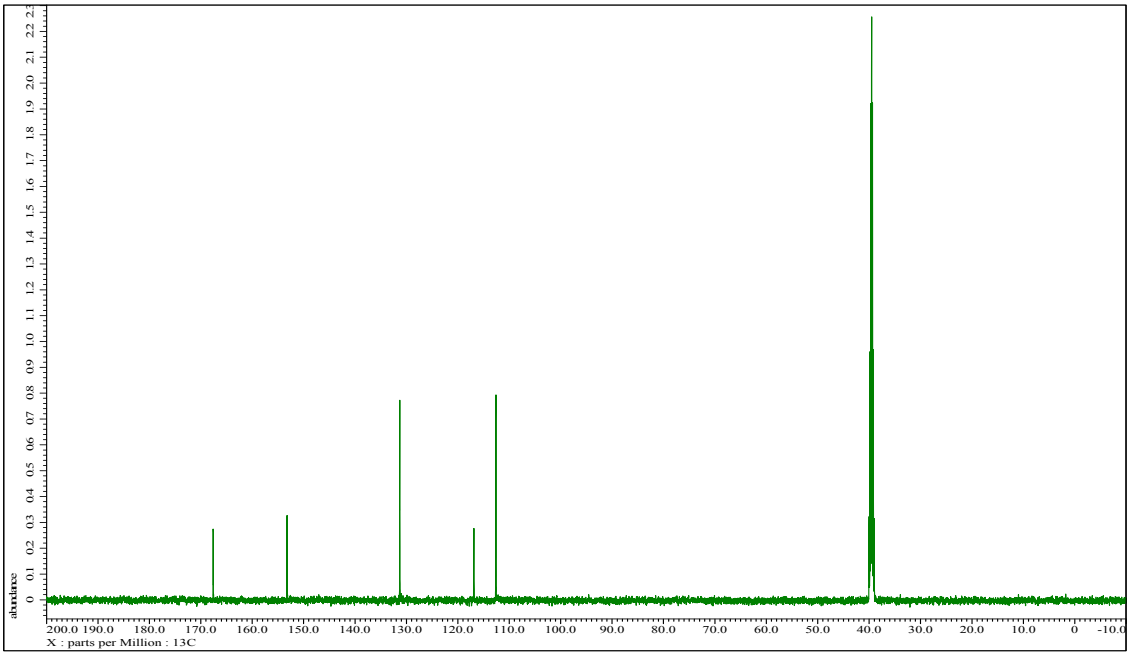




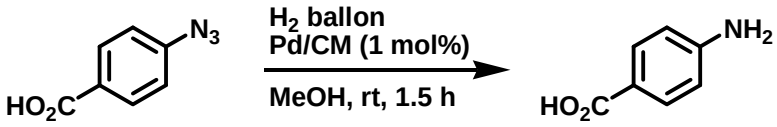
4-Aminobenzoic Acid (Table 1, Entry 5)

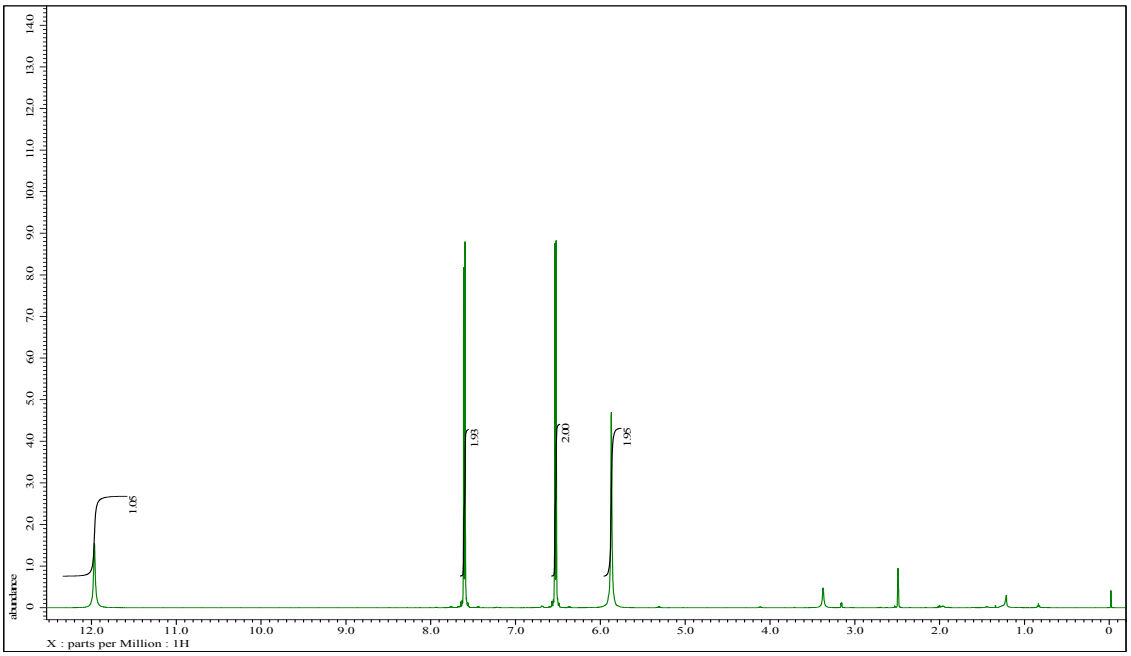


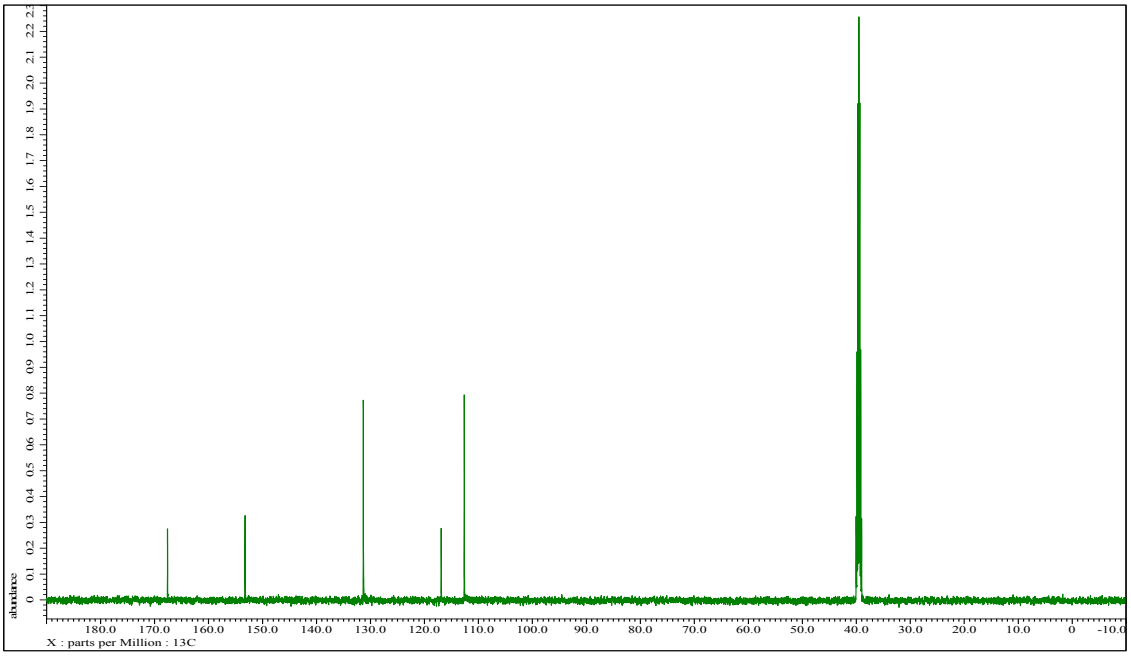




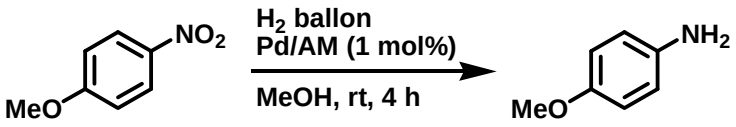
4-Aminobenzoic Acid (Table 1, Entry 6)

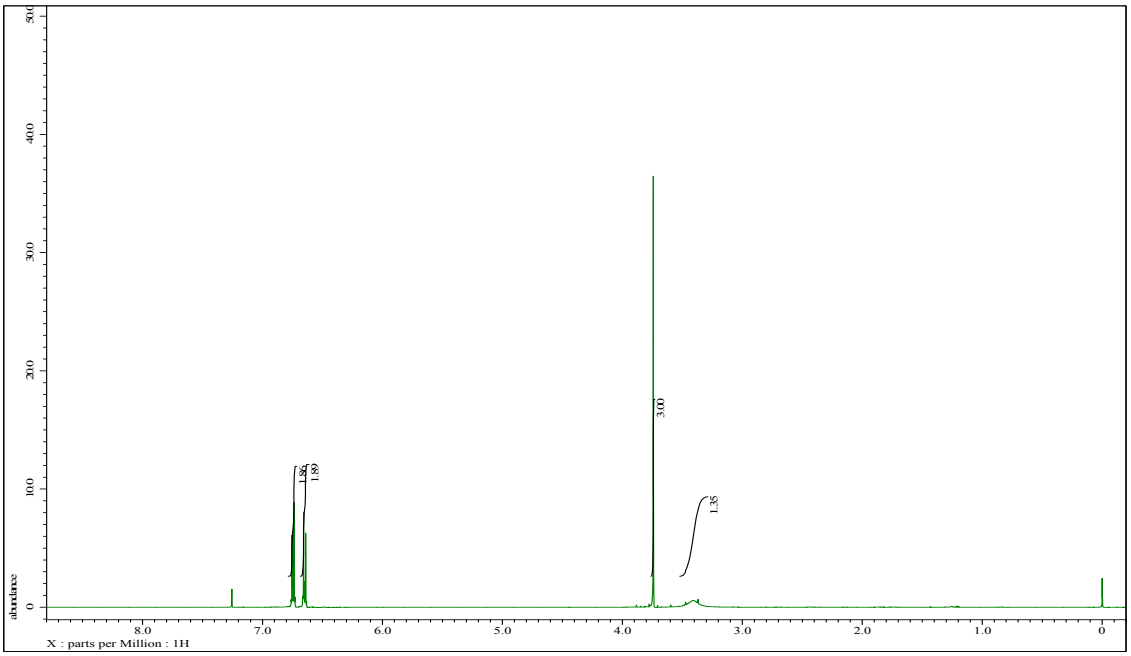


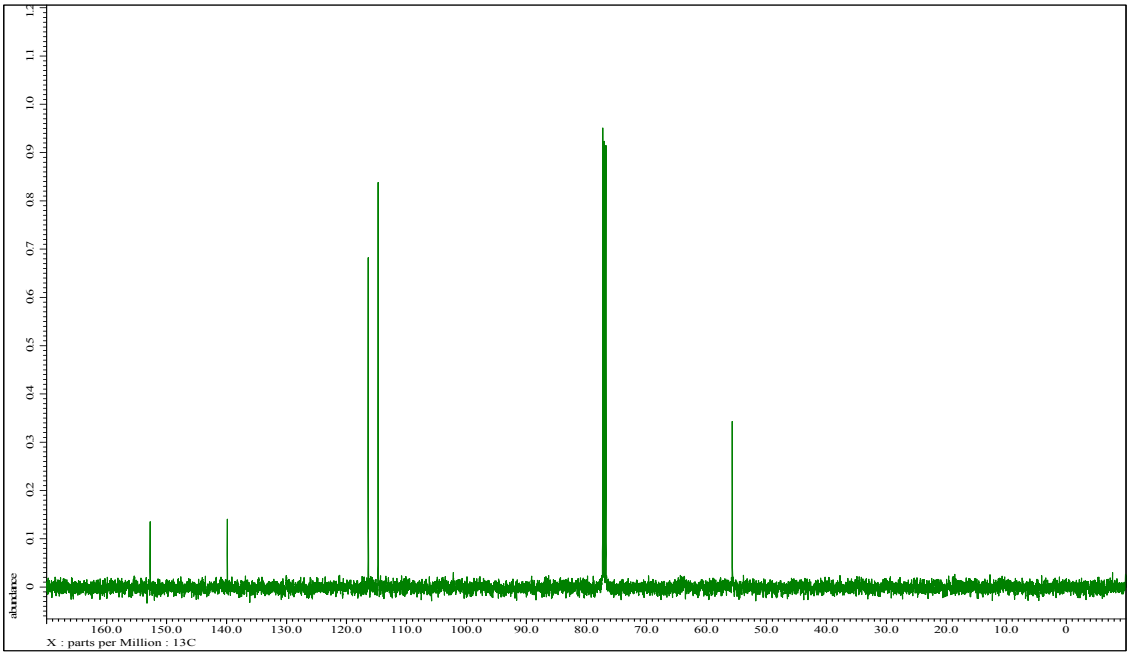




4-Aminoanisole (Table 1, Entry 7)







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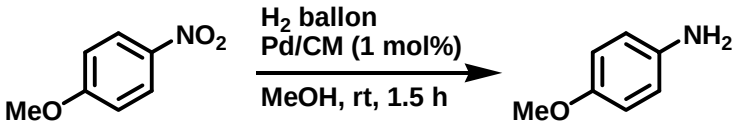
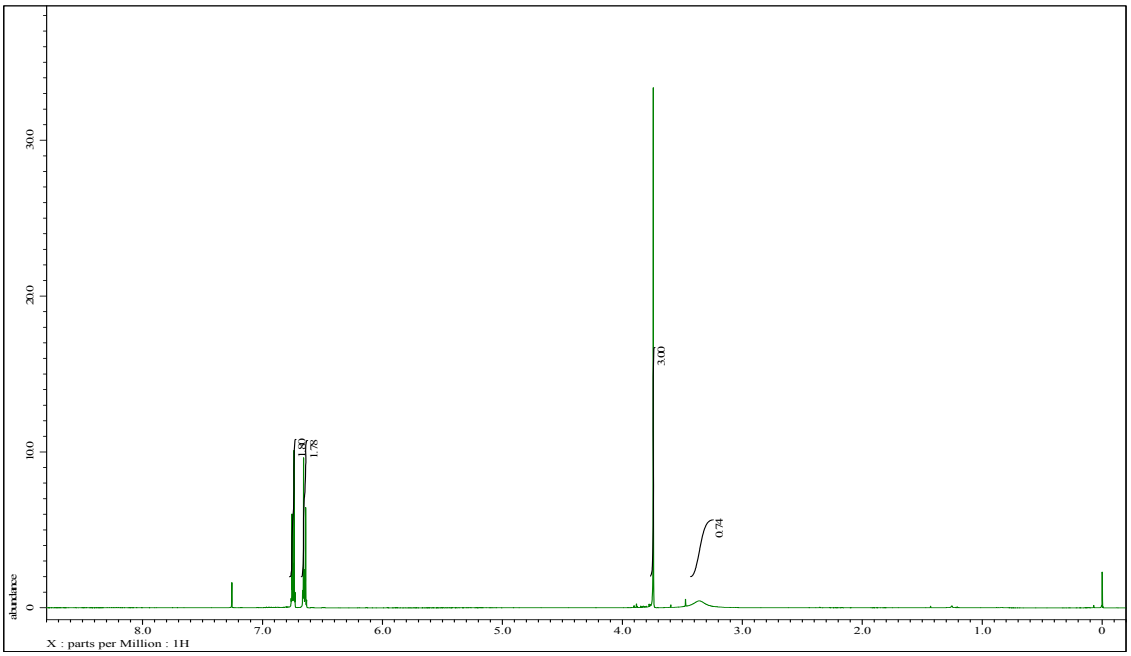
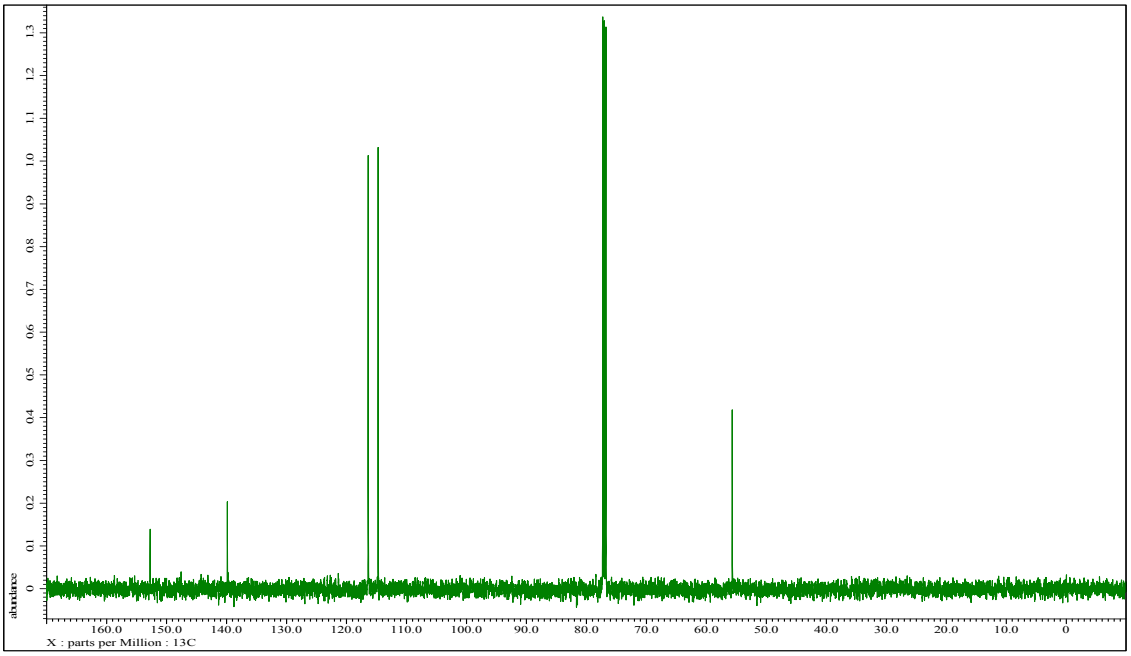
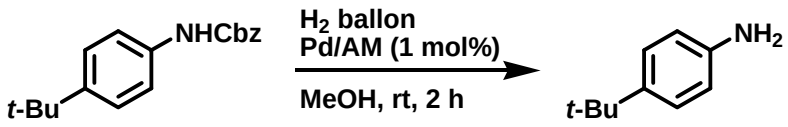
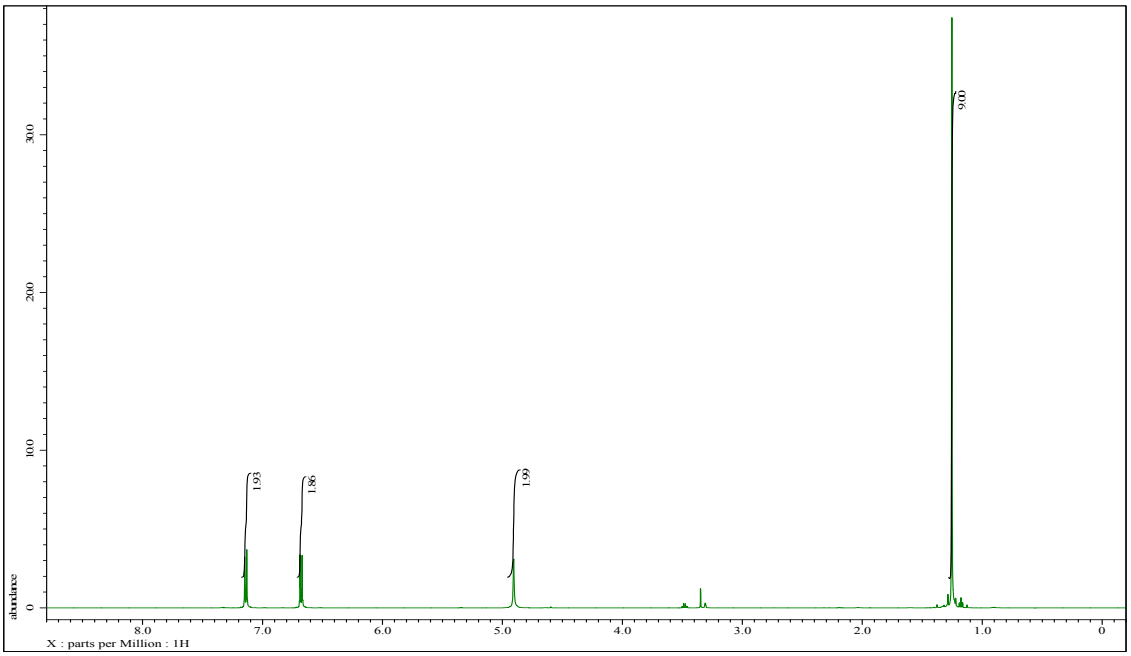


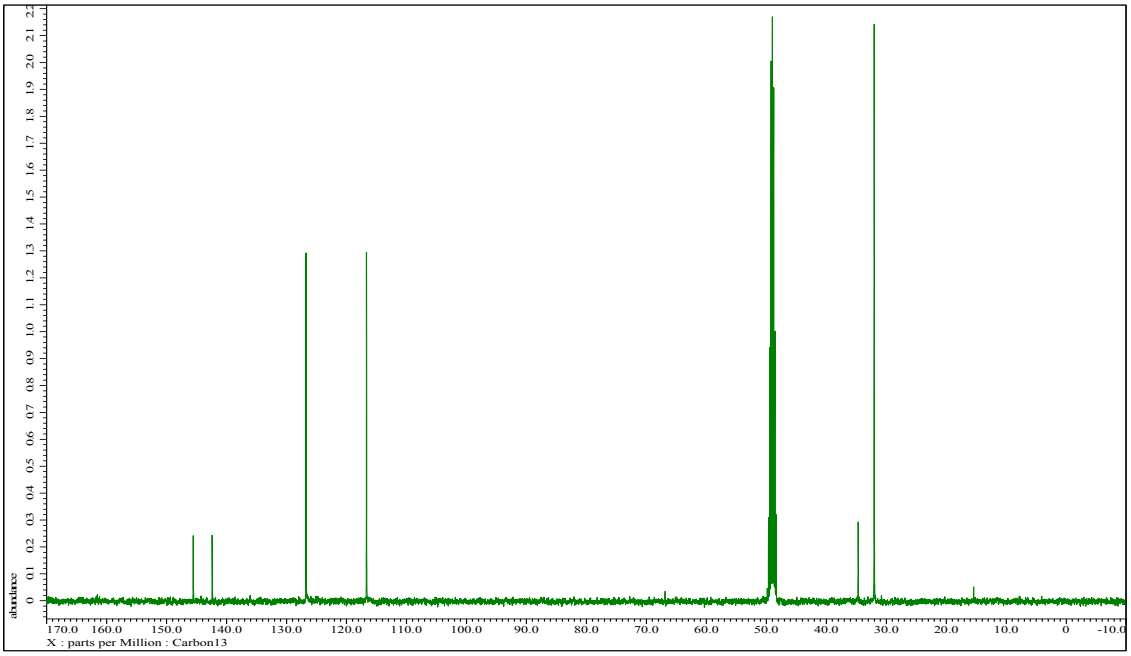




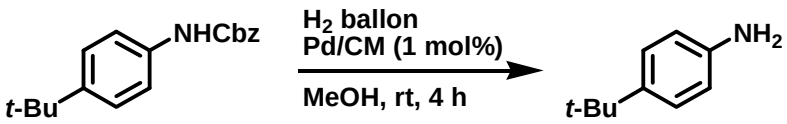
4-*tert*-Butylaniline (Table 1, Entry 9)

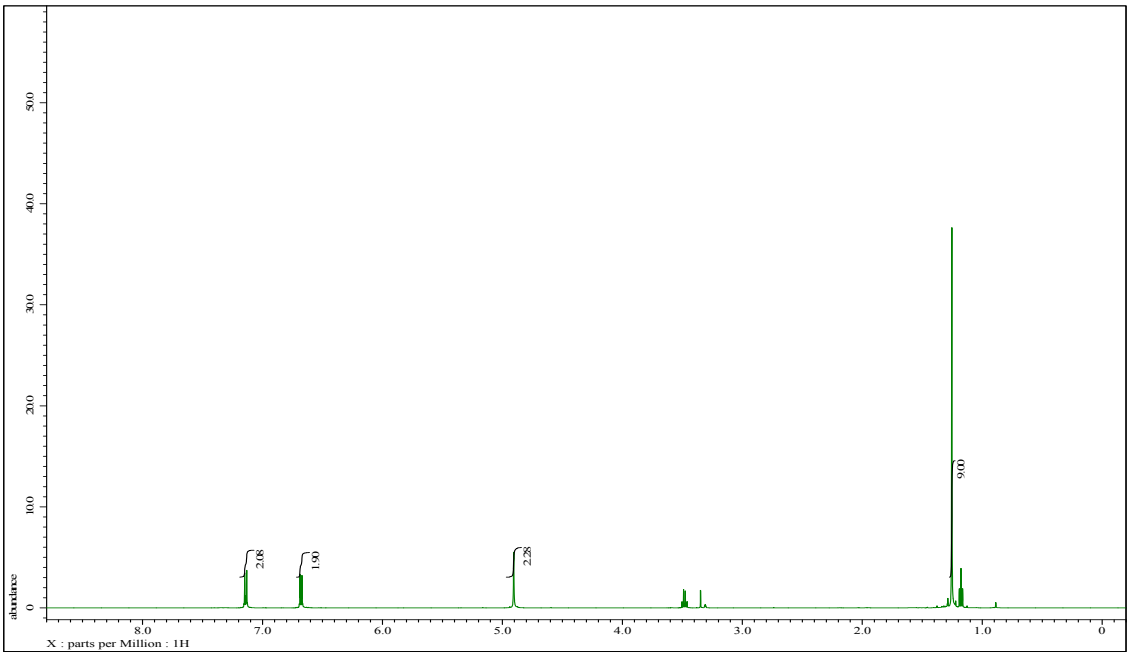


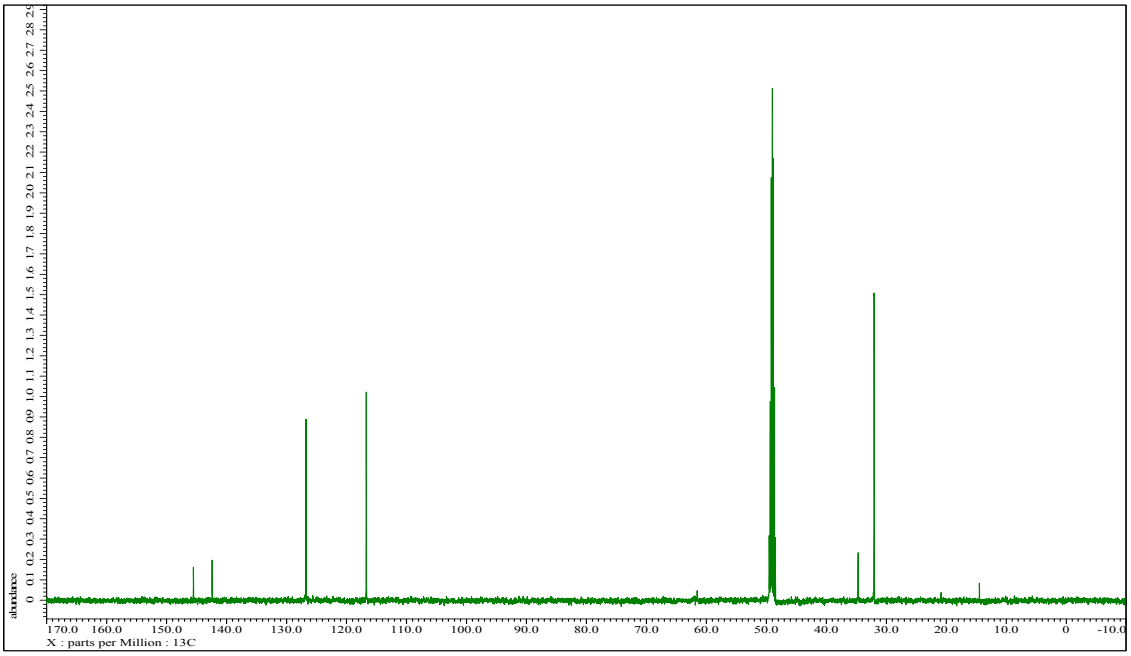




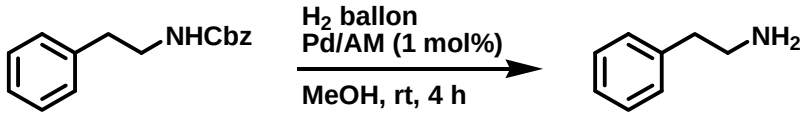
4-*tert*-Butylaniline (Table 1, Entry 10)

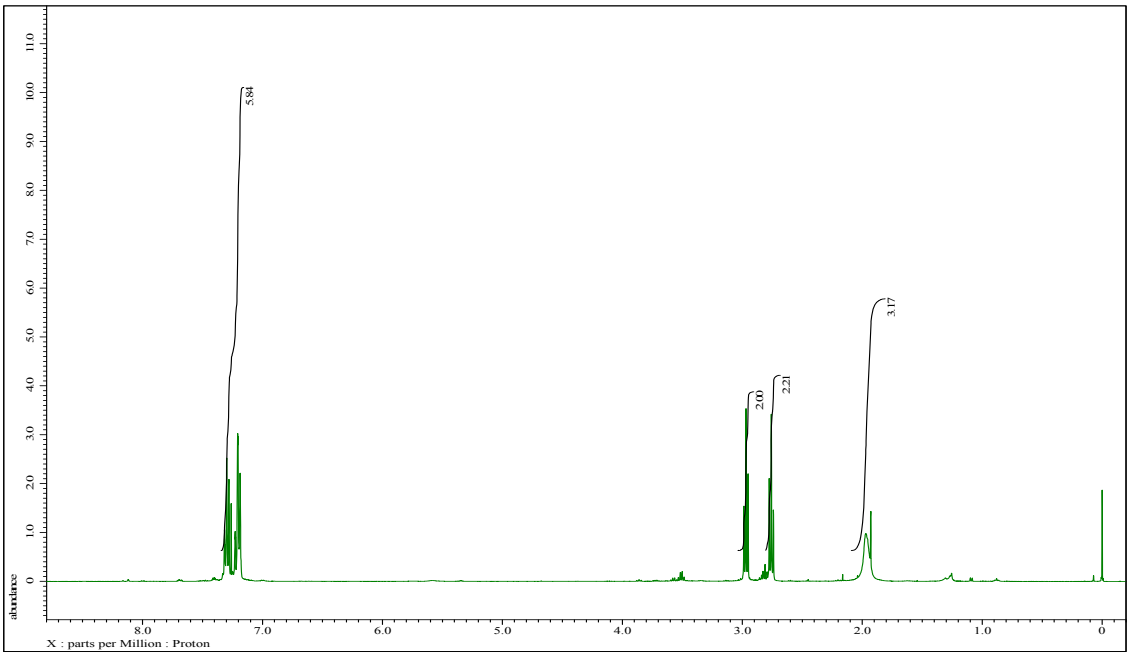


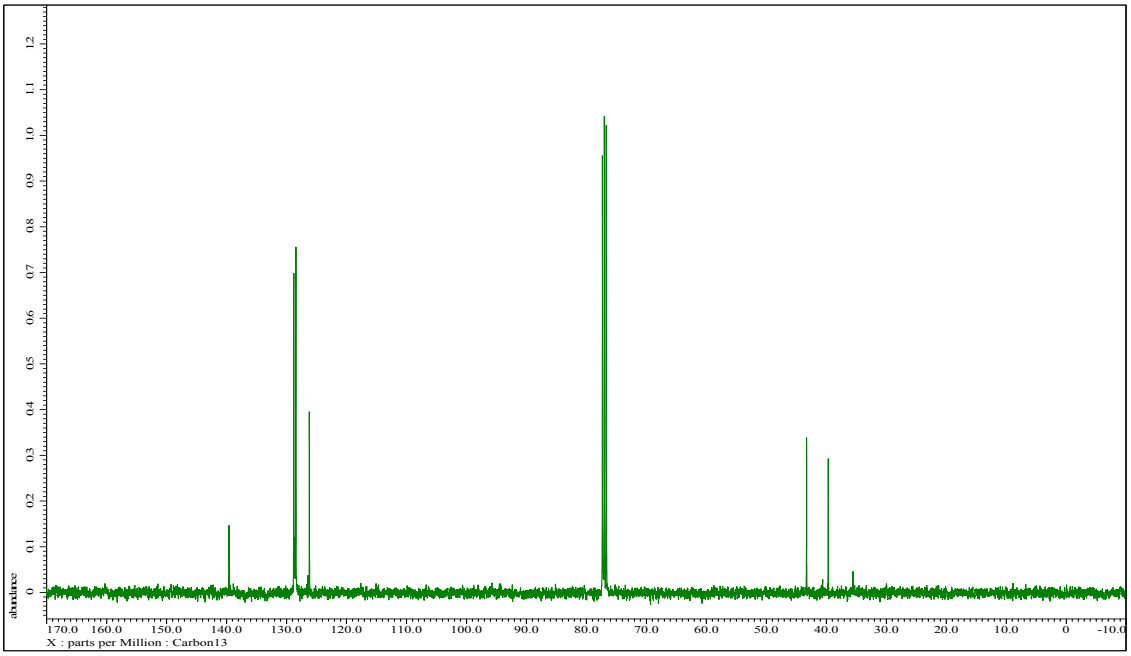




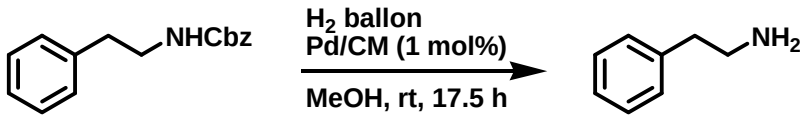
Phenethylamine (Table 1, Entry 11)

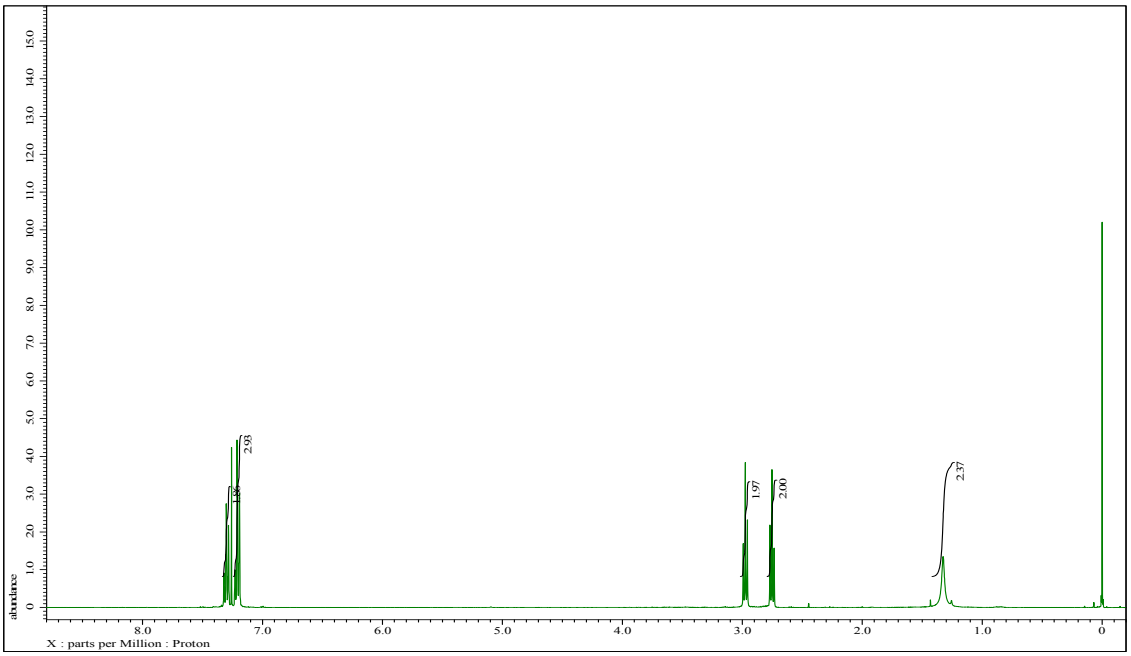


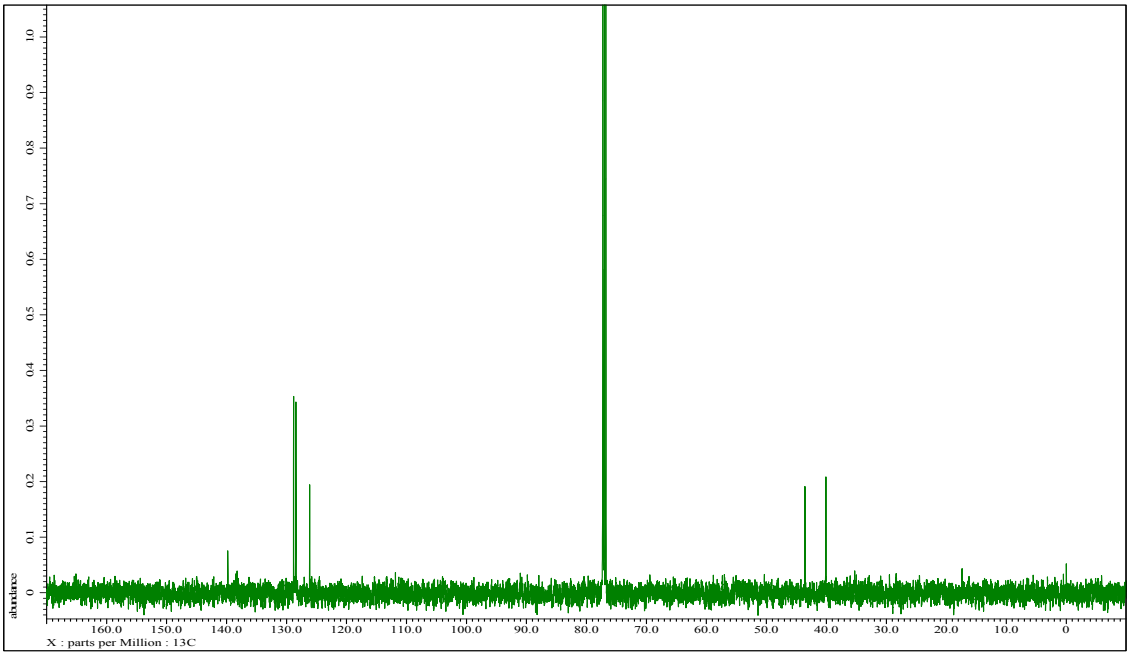




Phenethylamine (Table 1, Entry 12)







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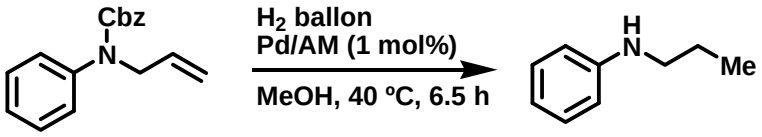
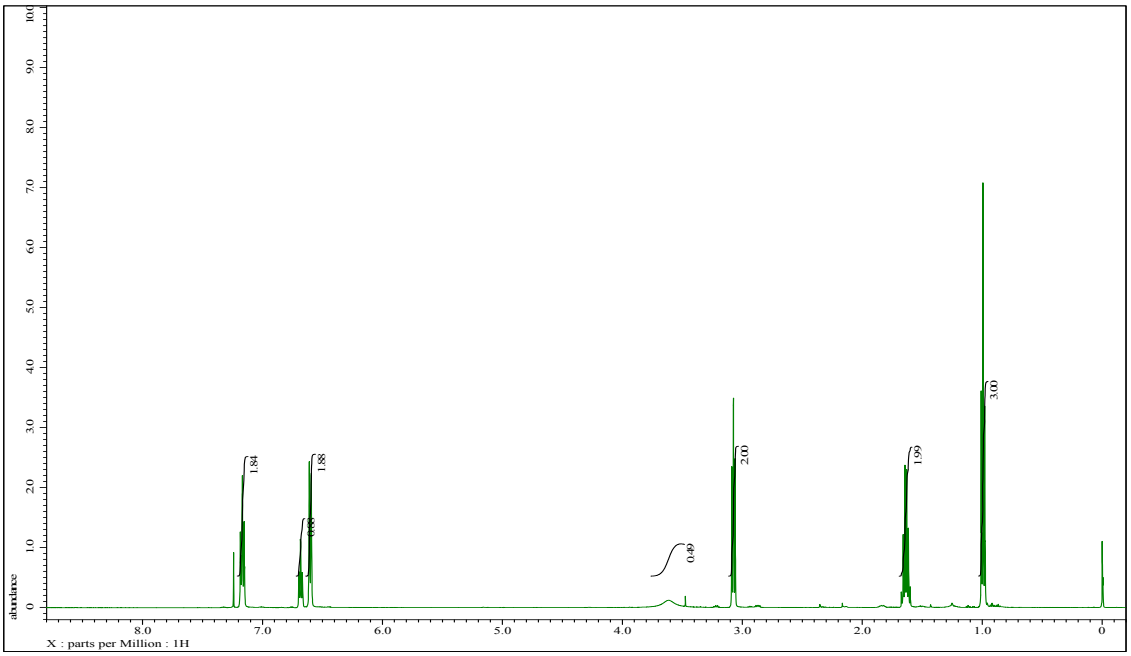
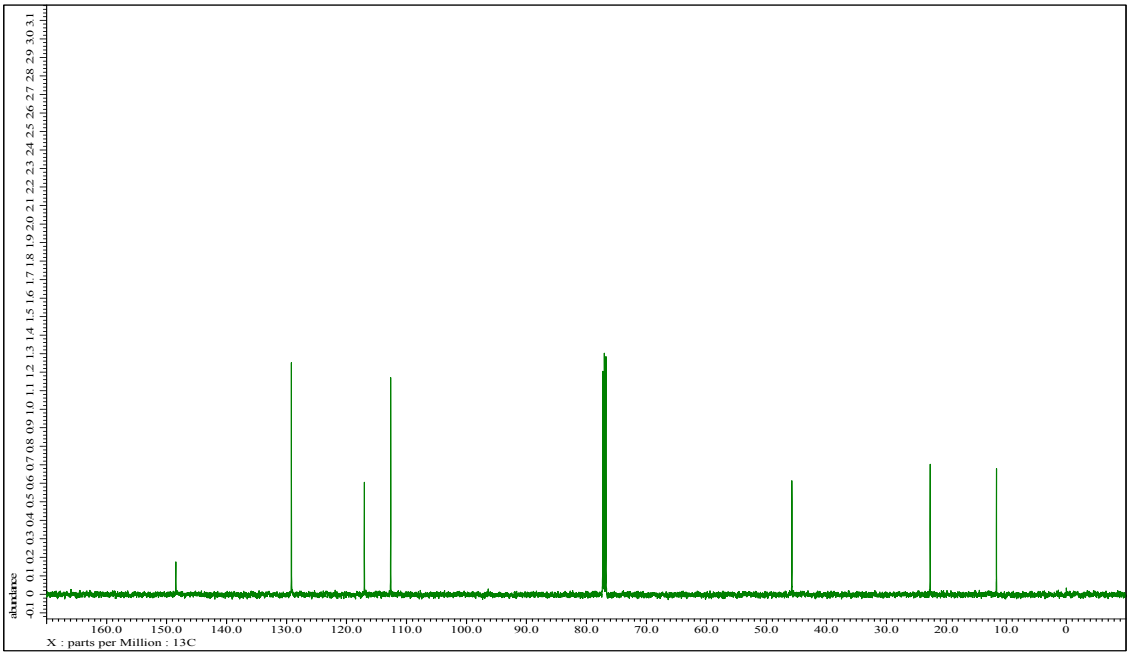
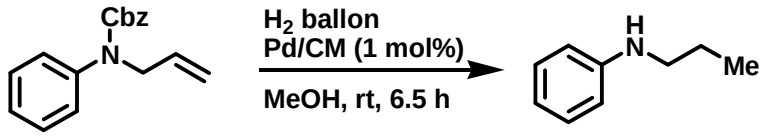
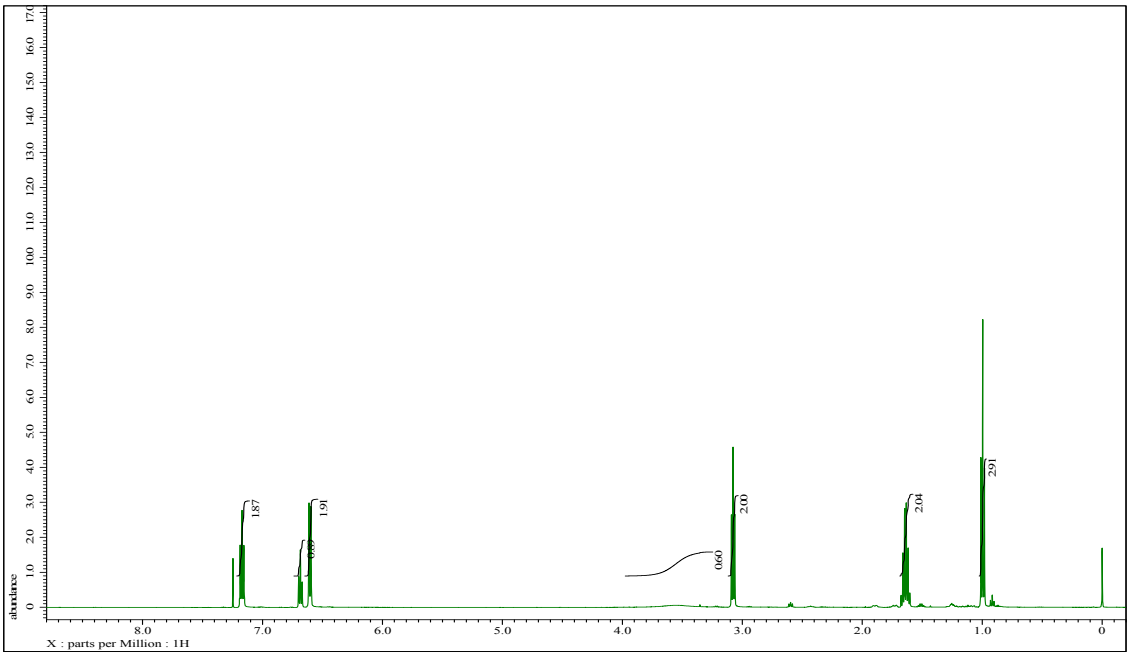


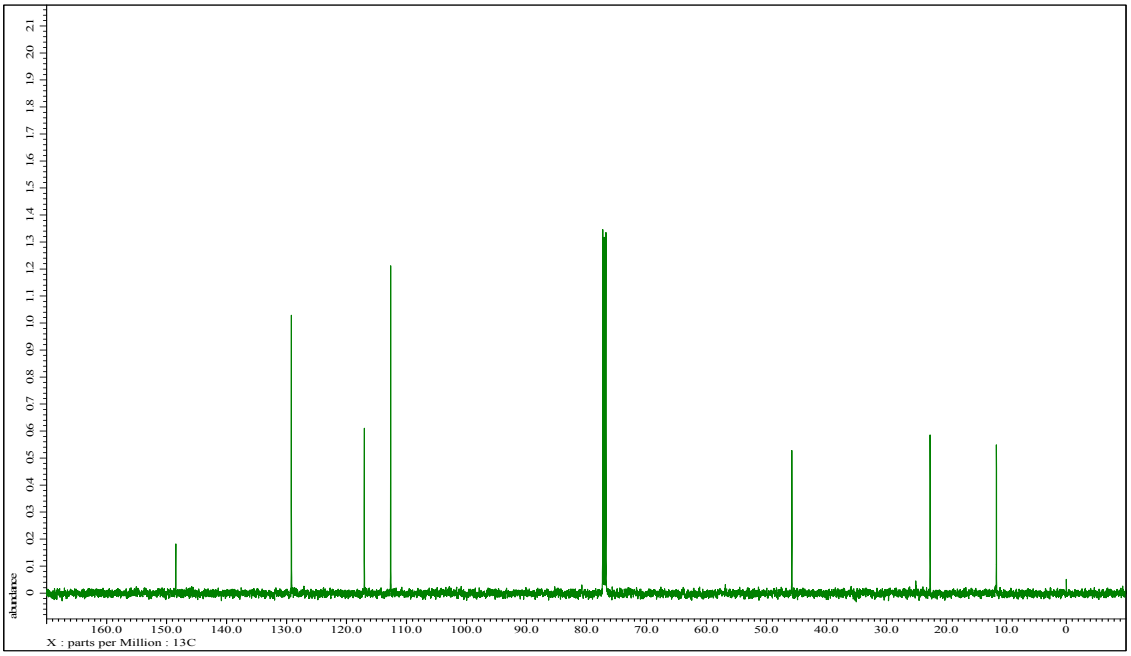




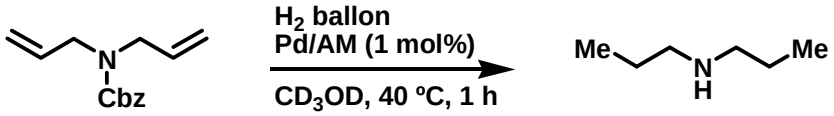
N-Propylaniline (Table 1, Entry 14)

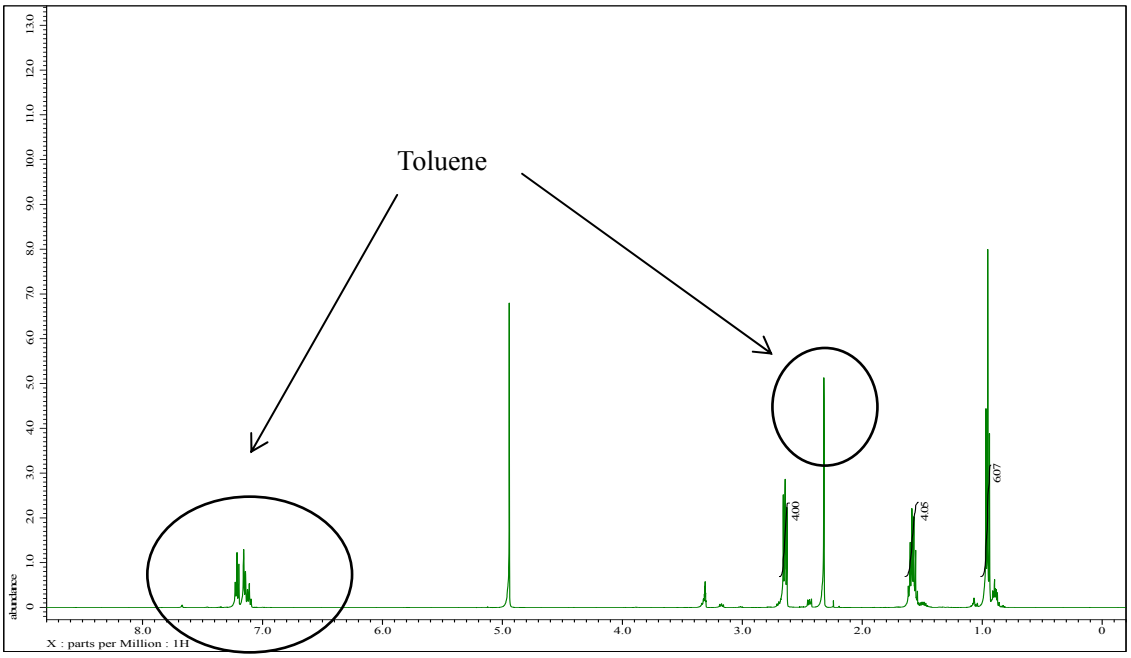


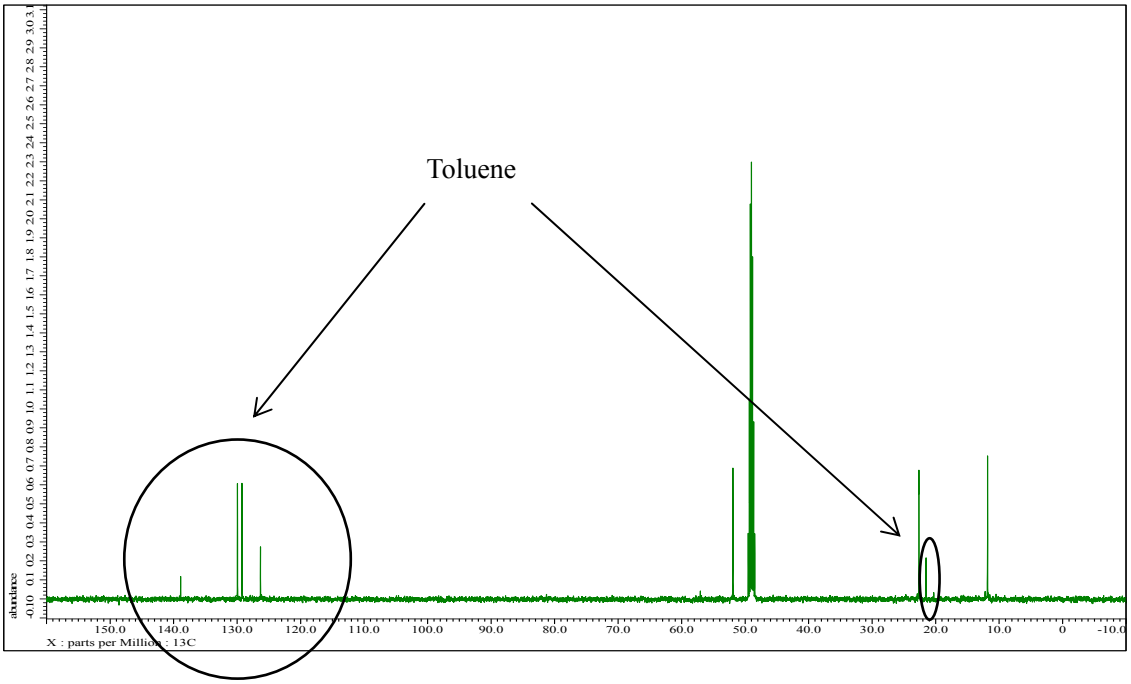




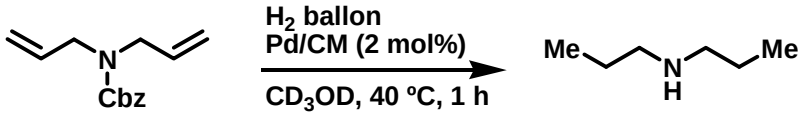
***N, N*-Dipropylamine (Table 1, Entry 15)**

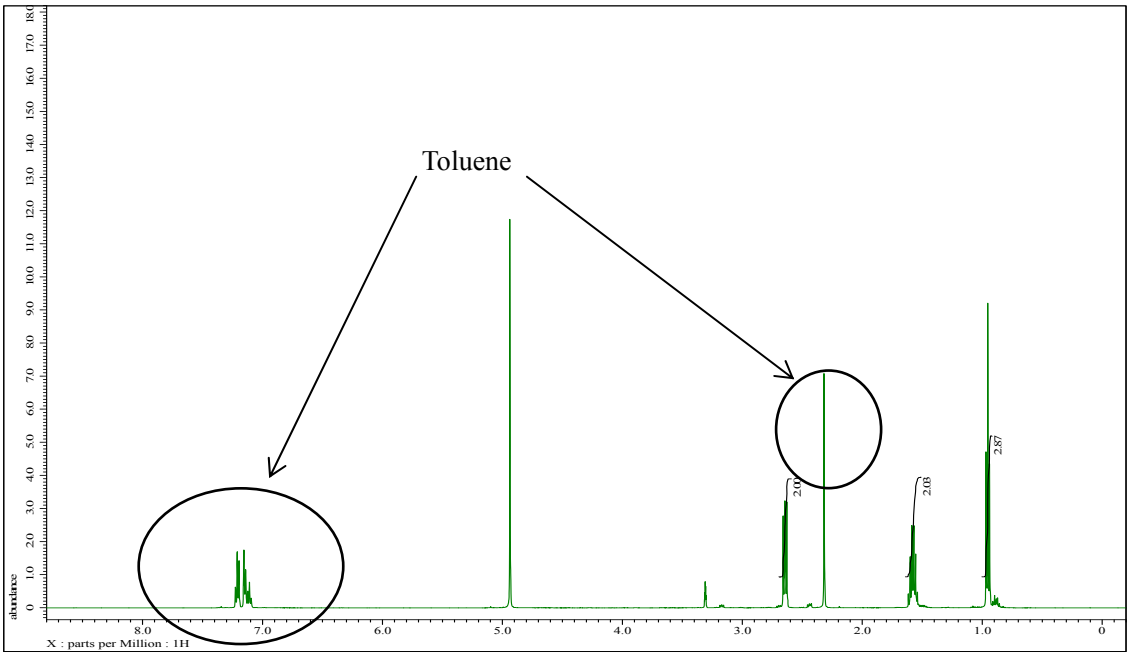


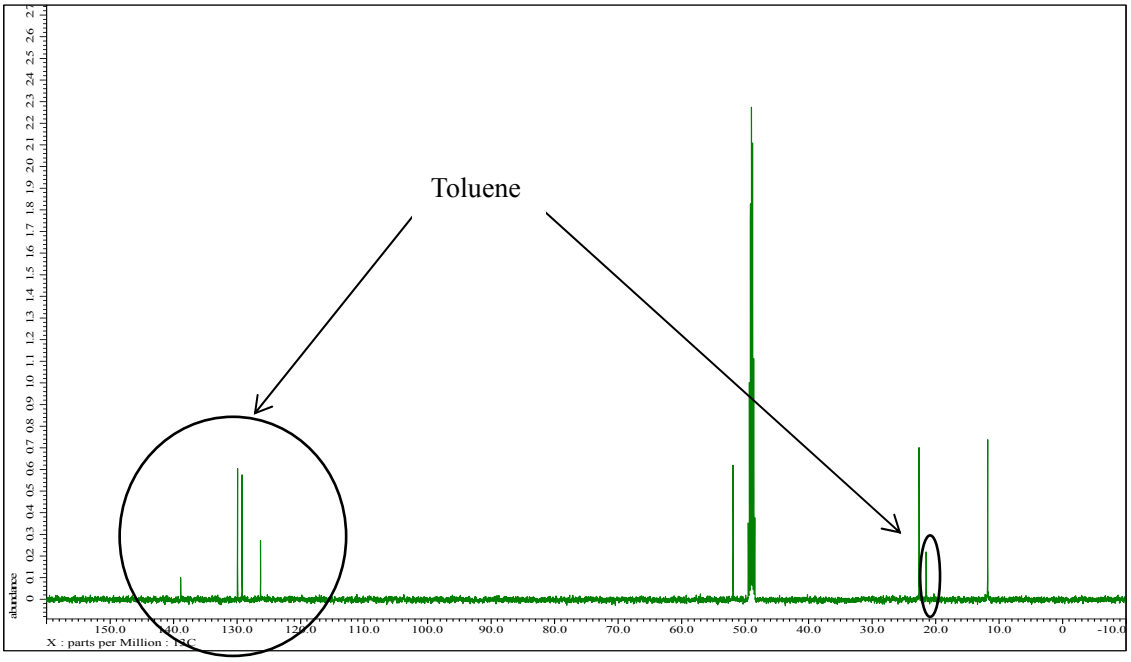




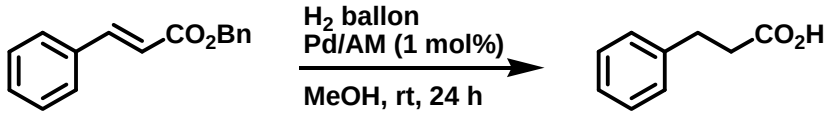
***N, N*-Dipropylamine (Table 1, Entry 16)**

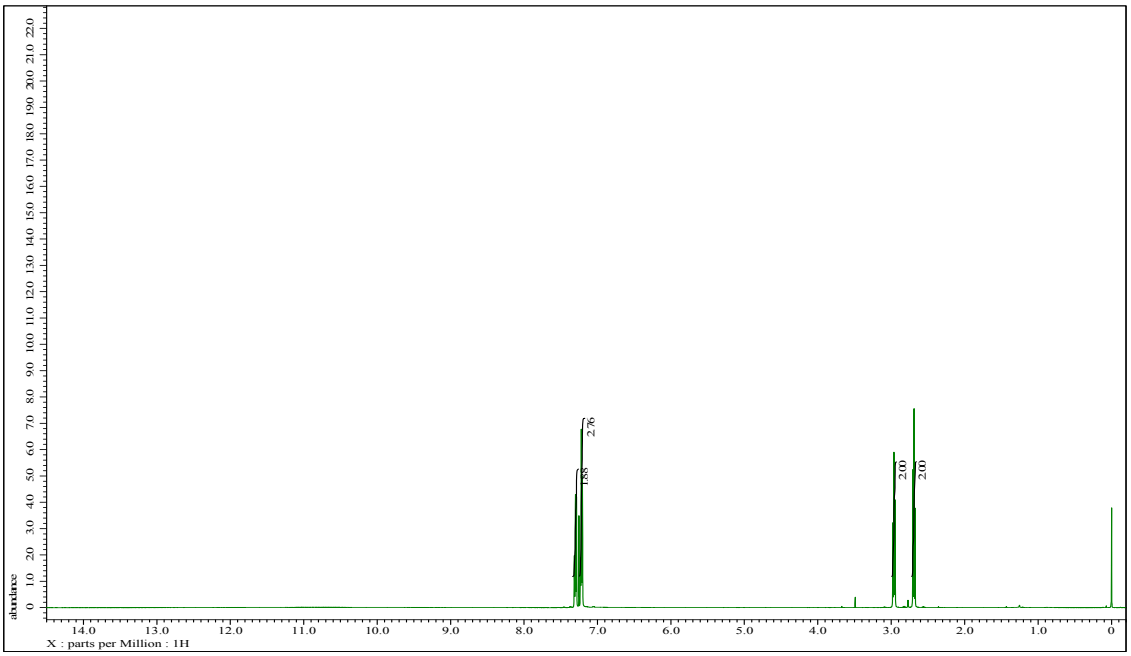


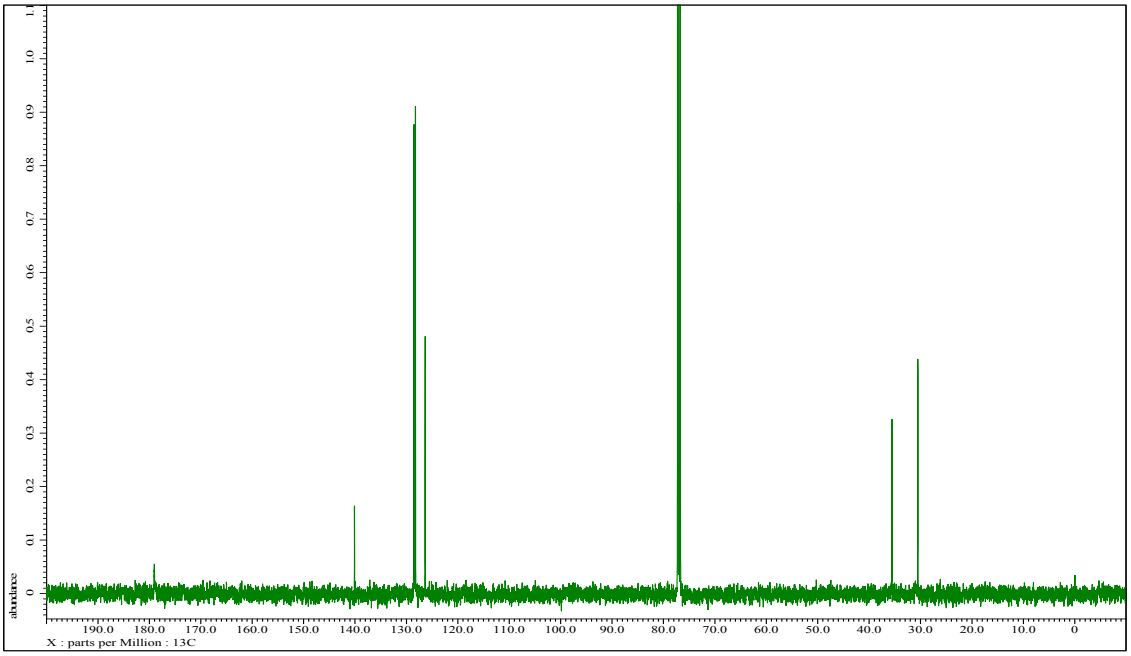




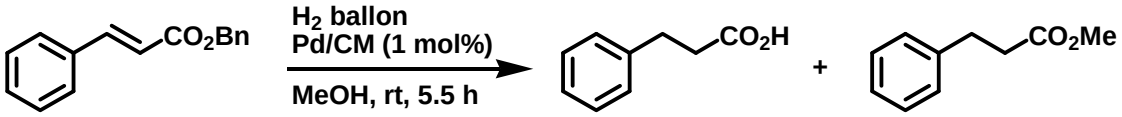
Dihydrocinnamic Acid (Table 1, Entry 17)



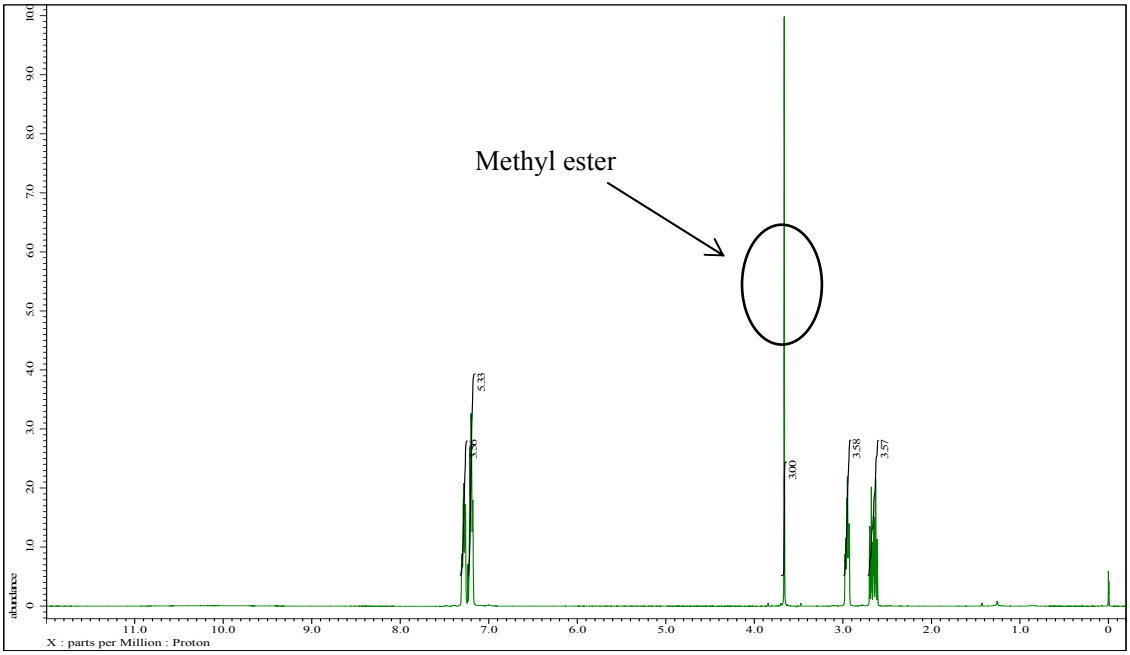


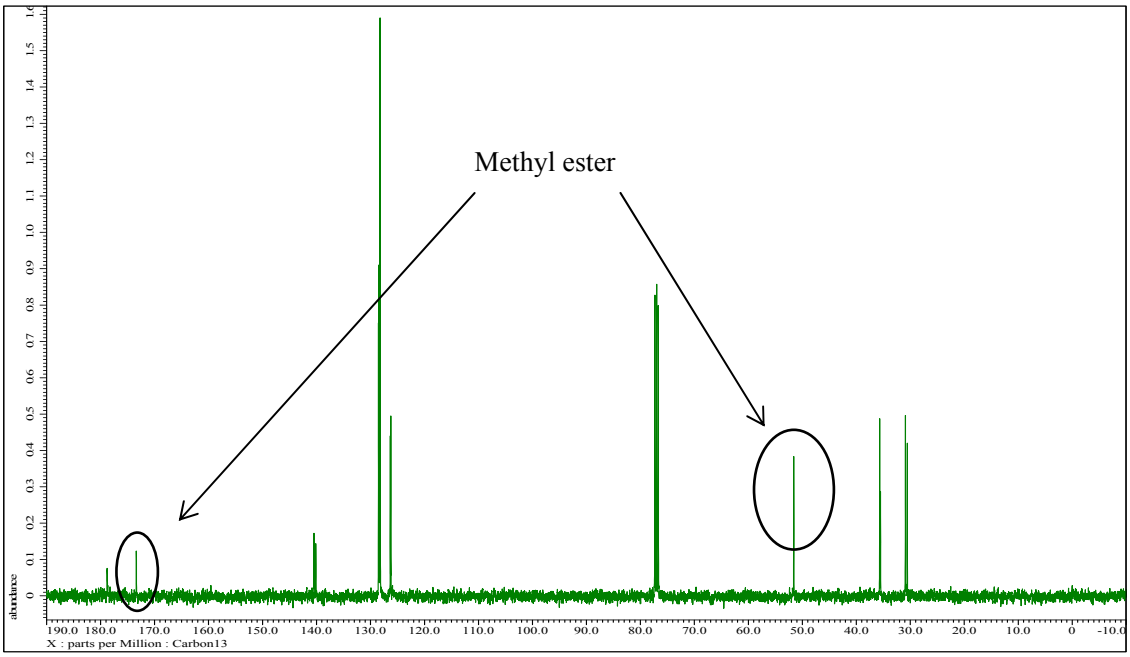


Dihydrocinnamic Acid and Dihydrocinnamic Acid Methyl Ester (Table 1, Entry 18)

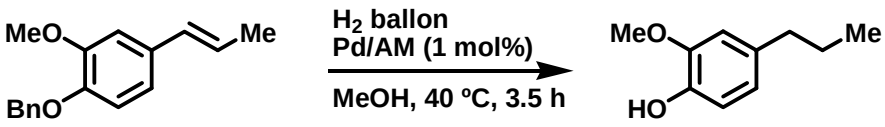


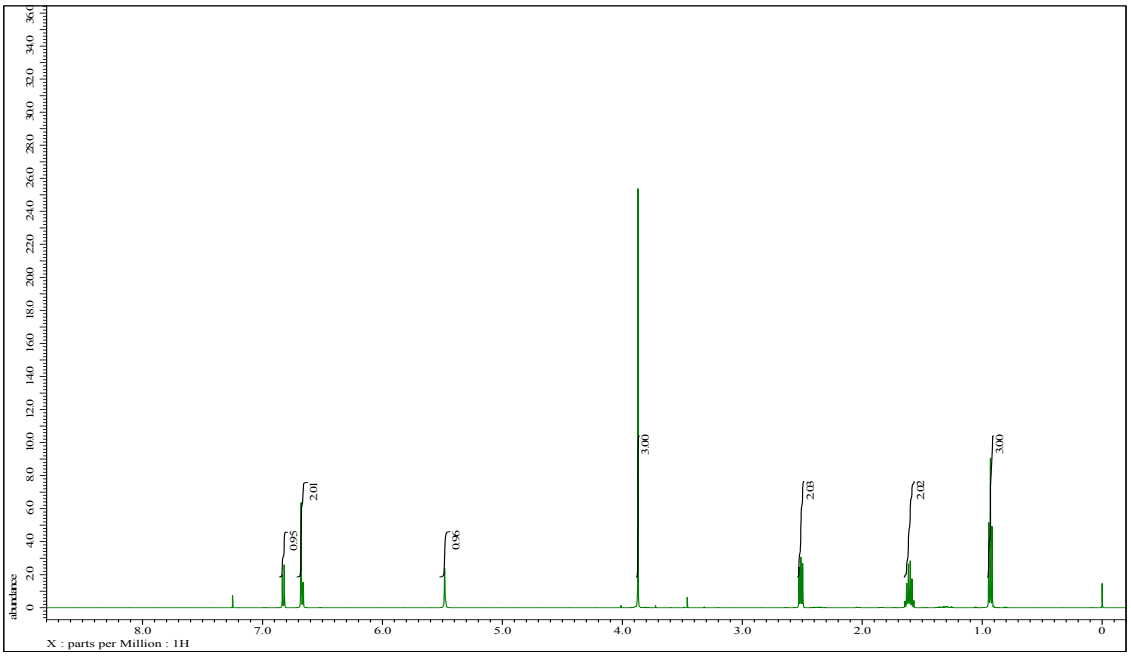
44 : 56

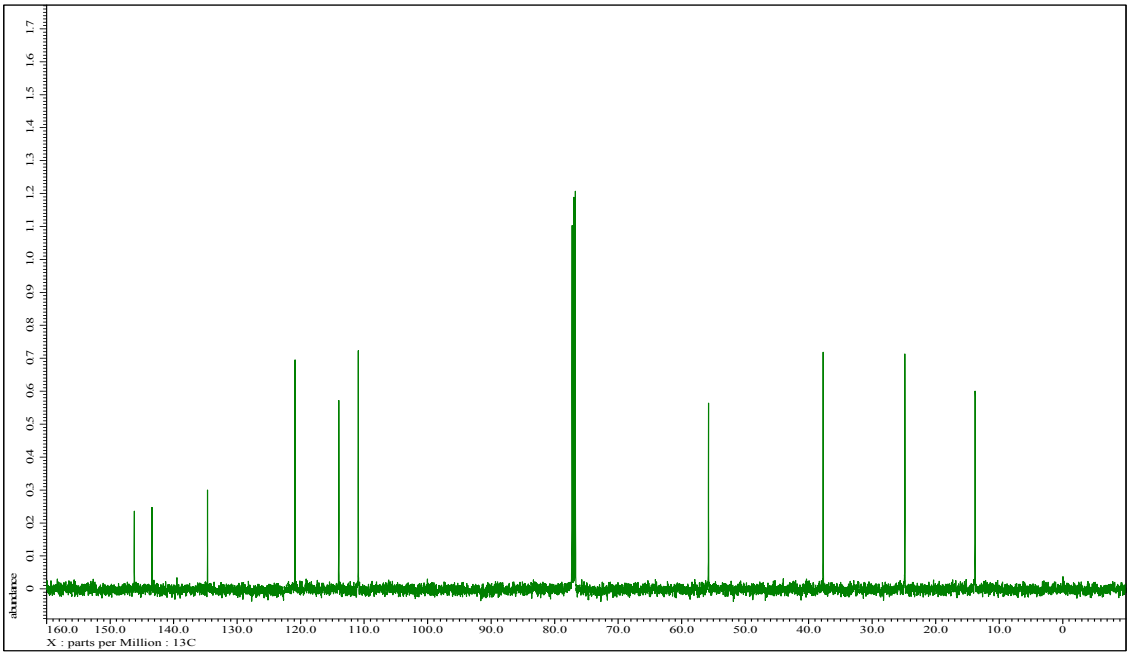




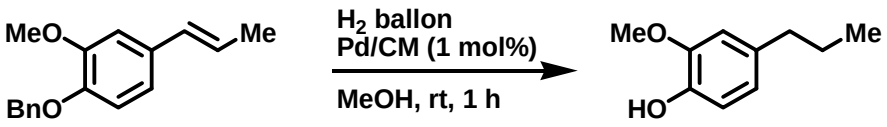
2-Methoxy-4-propylphenol (Table 1, Entry 19)

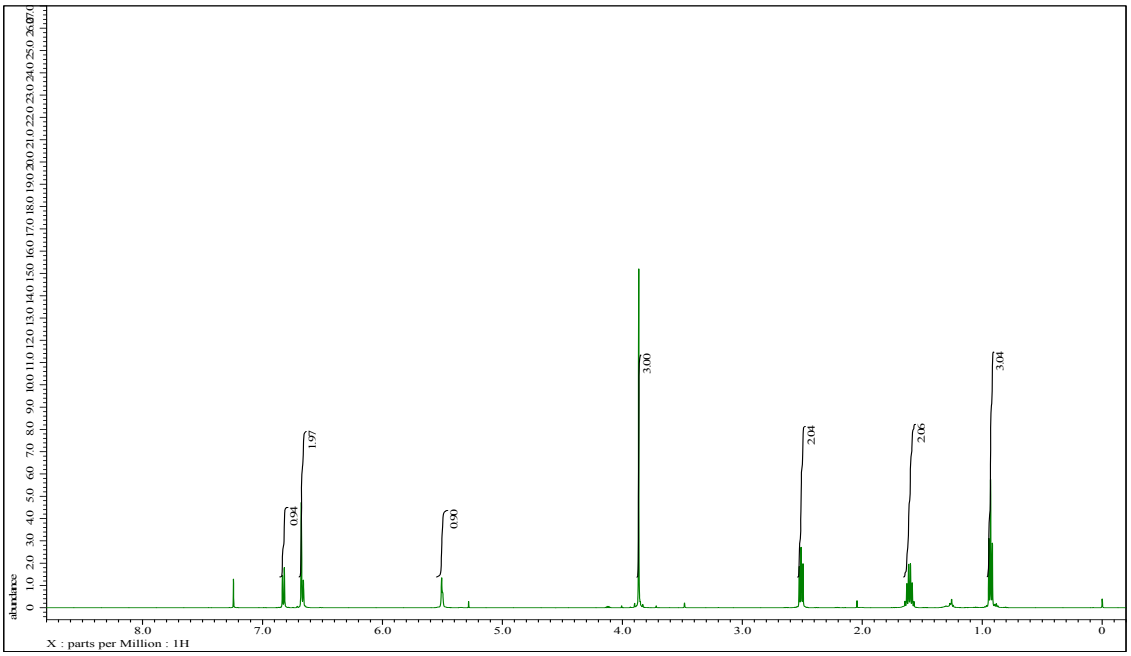


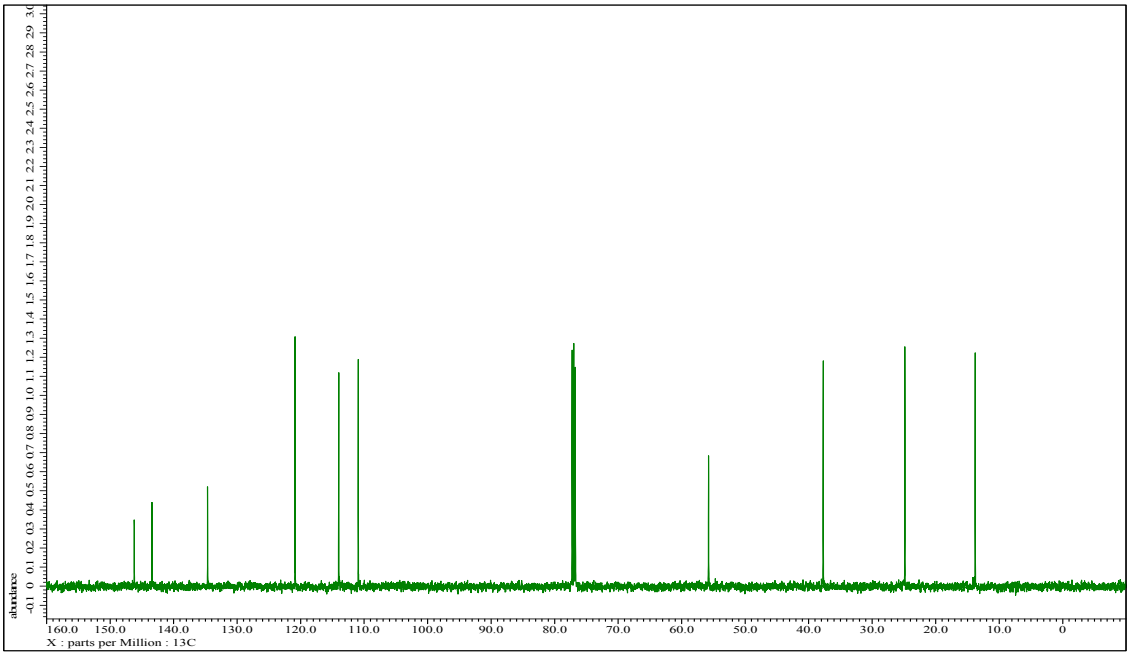




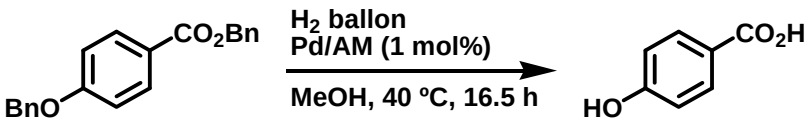
2-Methoxy-4-propyl phenol (Table 1, Entry 20)

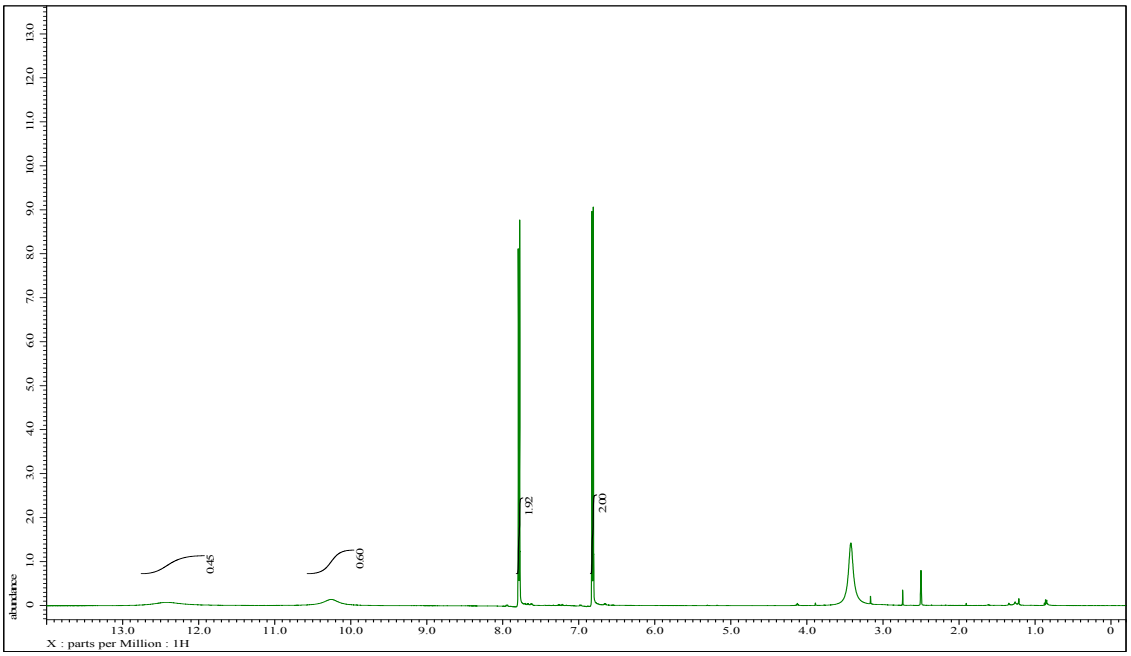


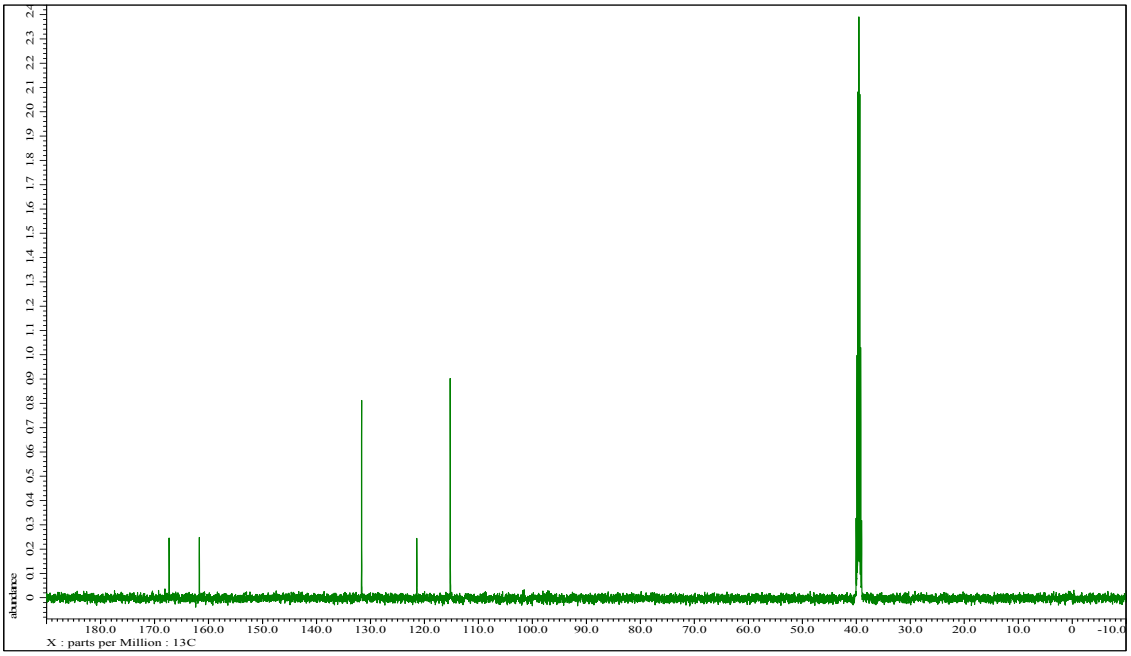




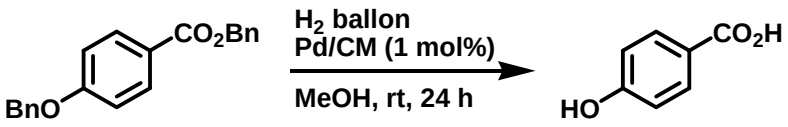
4-Hydroxybenzoic Acid (Table 1, Entry 21)

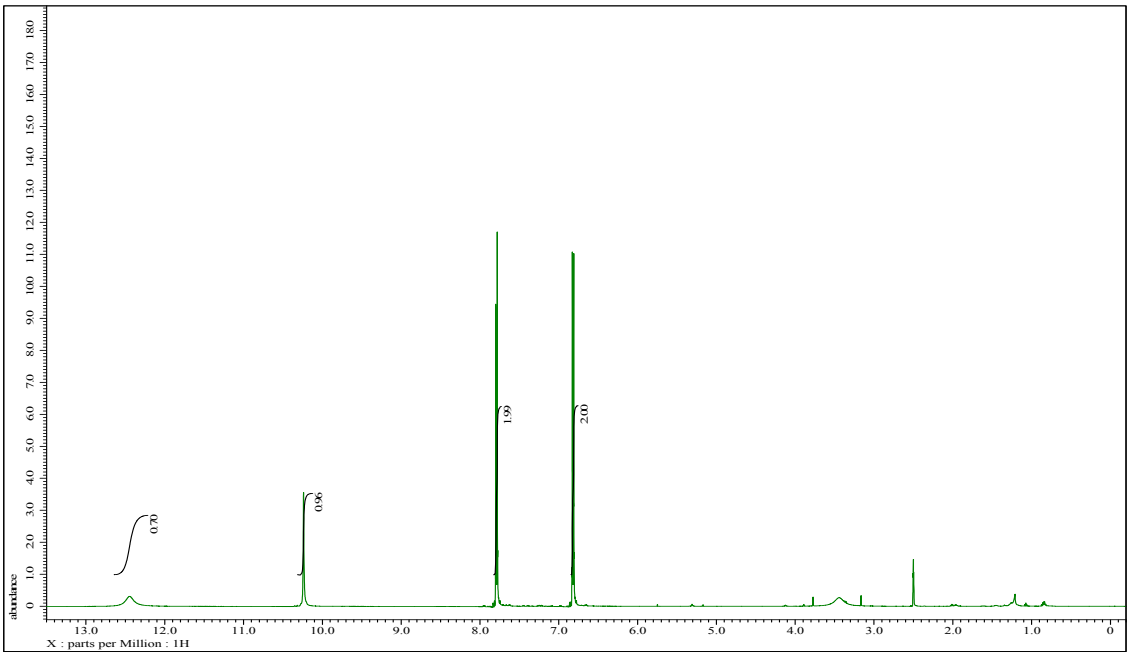


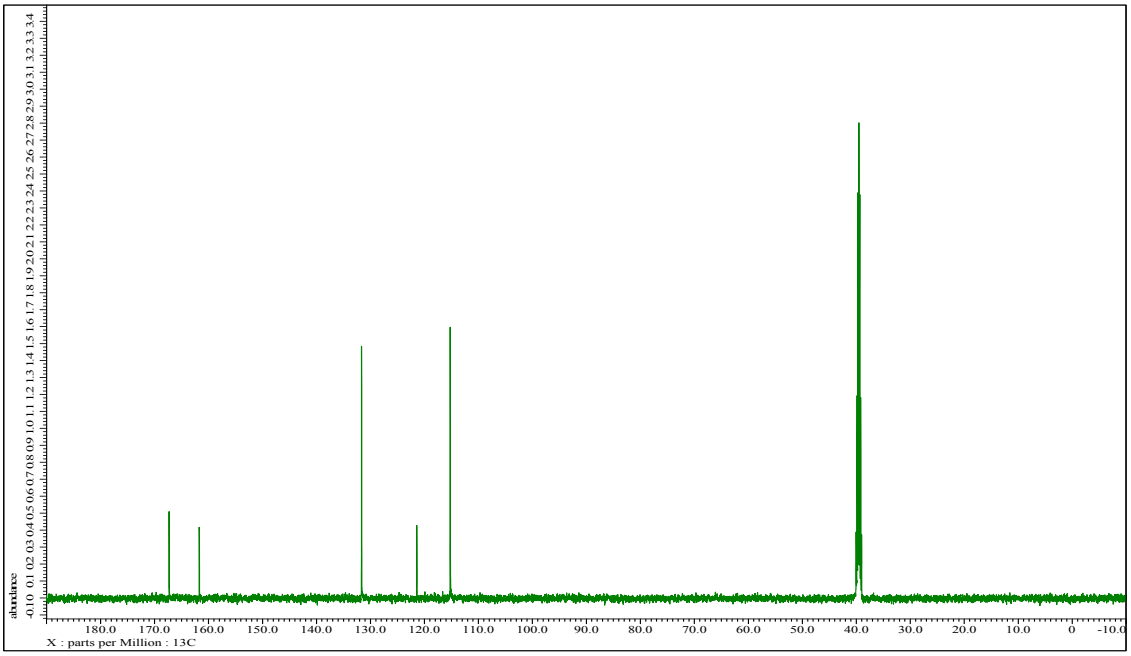




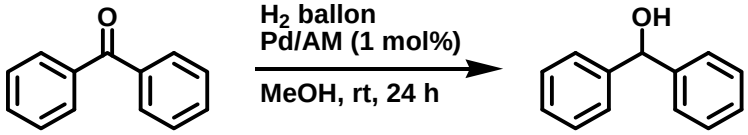
4-Hydroxybenzoic Acid (Table 1, Entry 21)







Benzophenone and Benzhydrole (Table 1, Entry 22)



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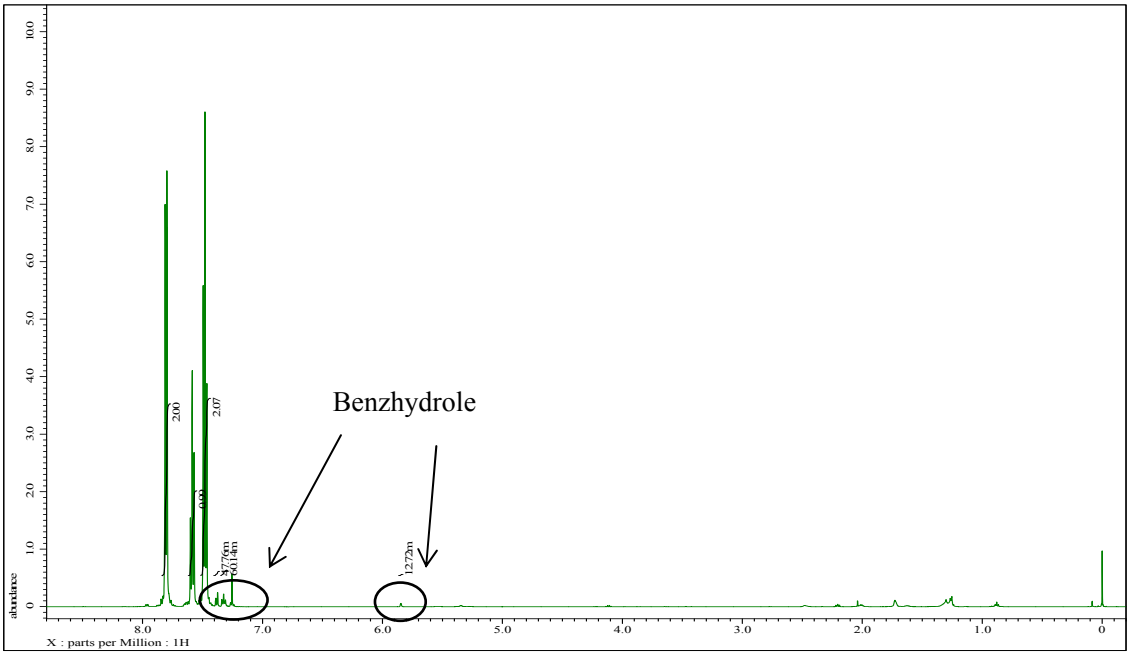
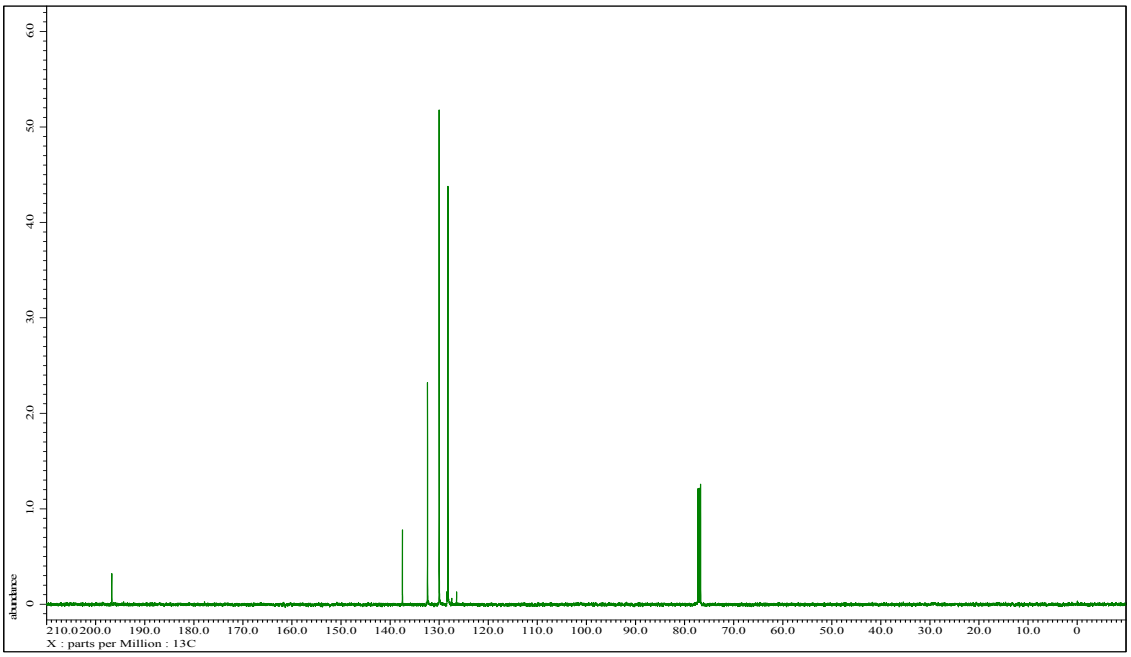
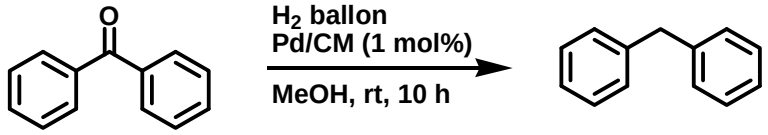
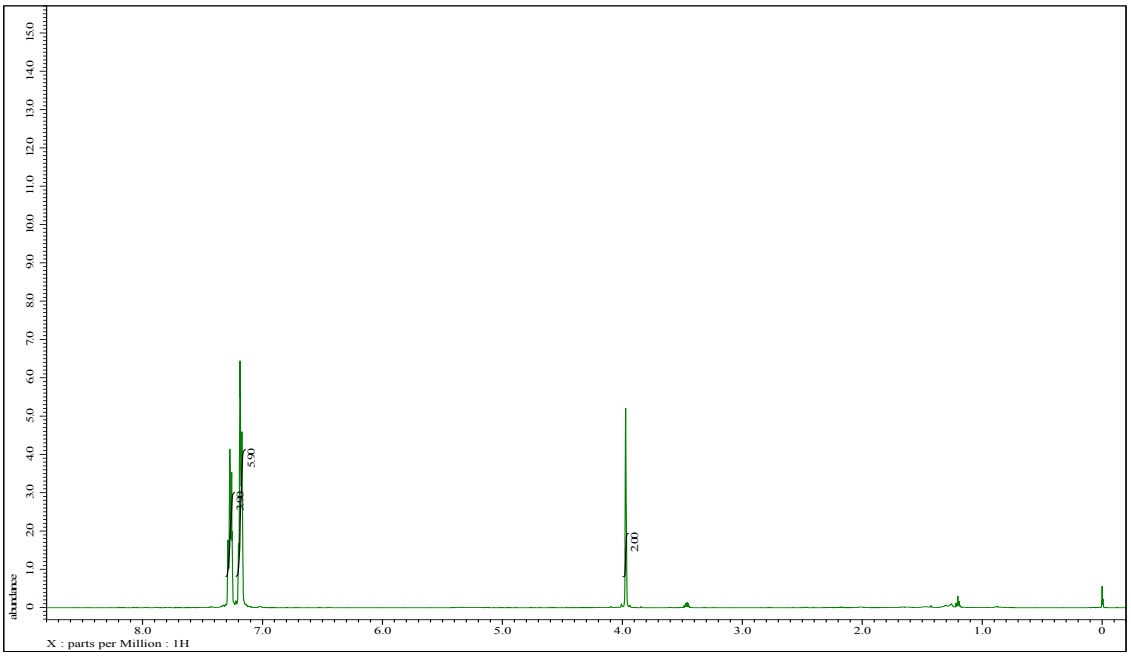
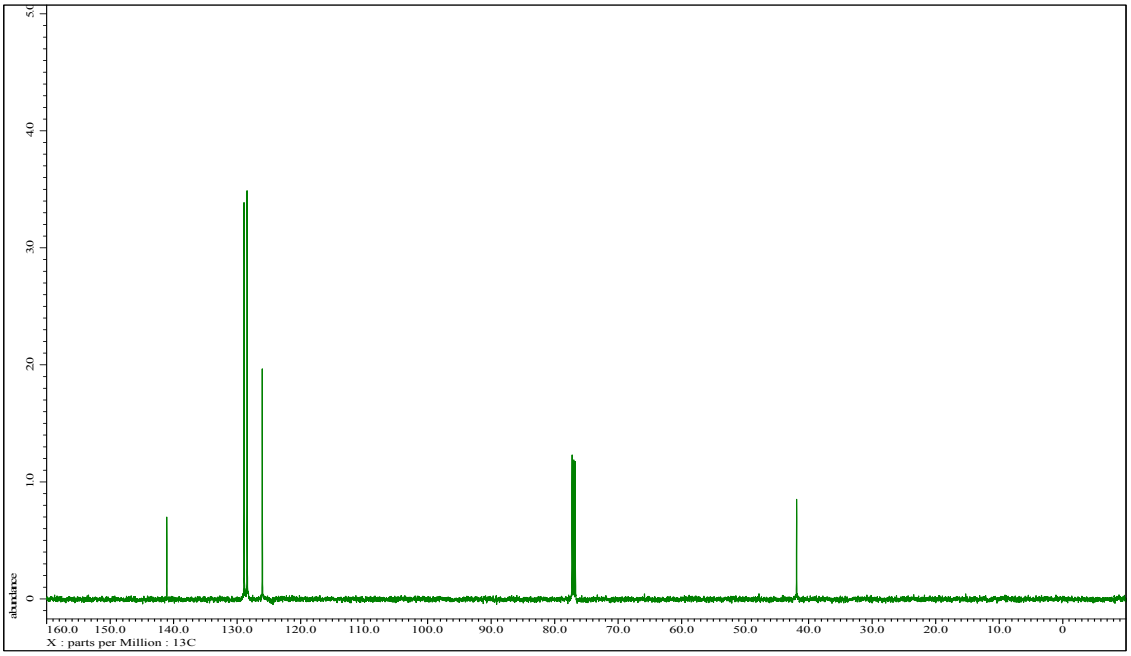




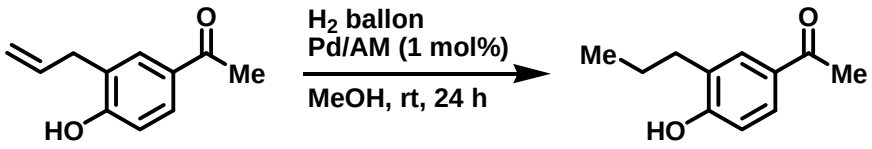
Diphenylmethane (Table 1, Entry 24)

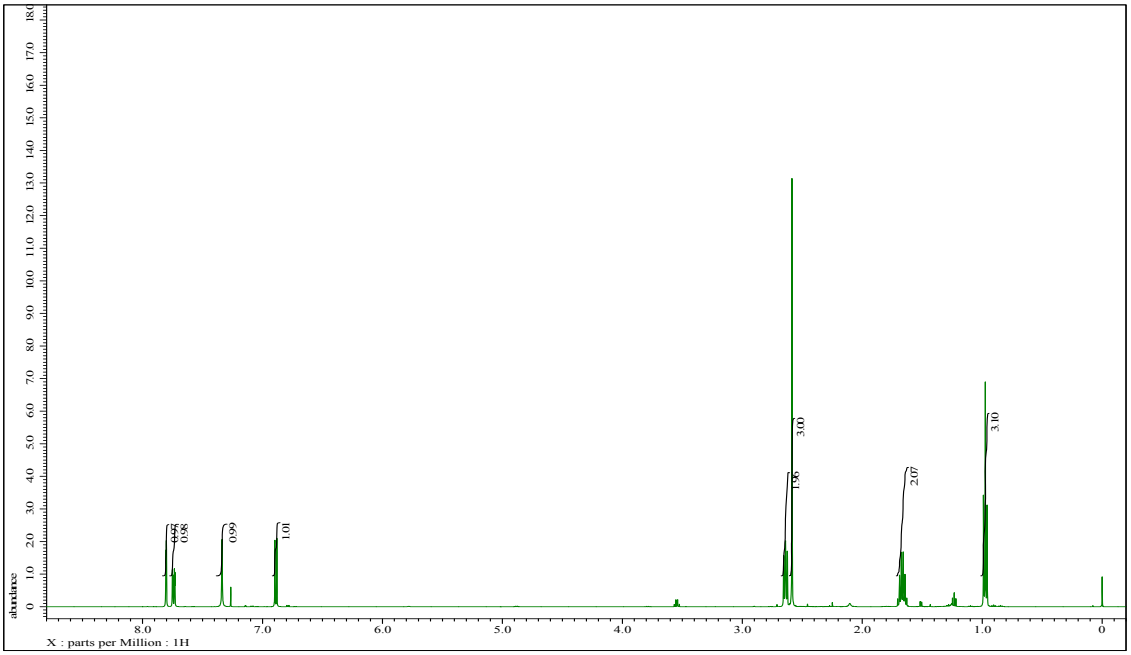


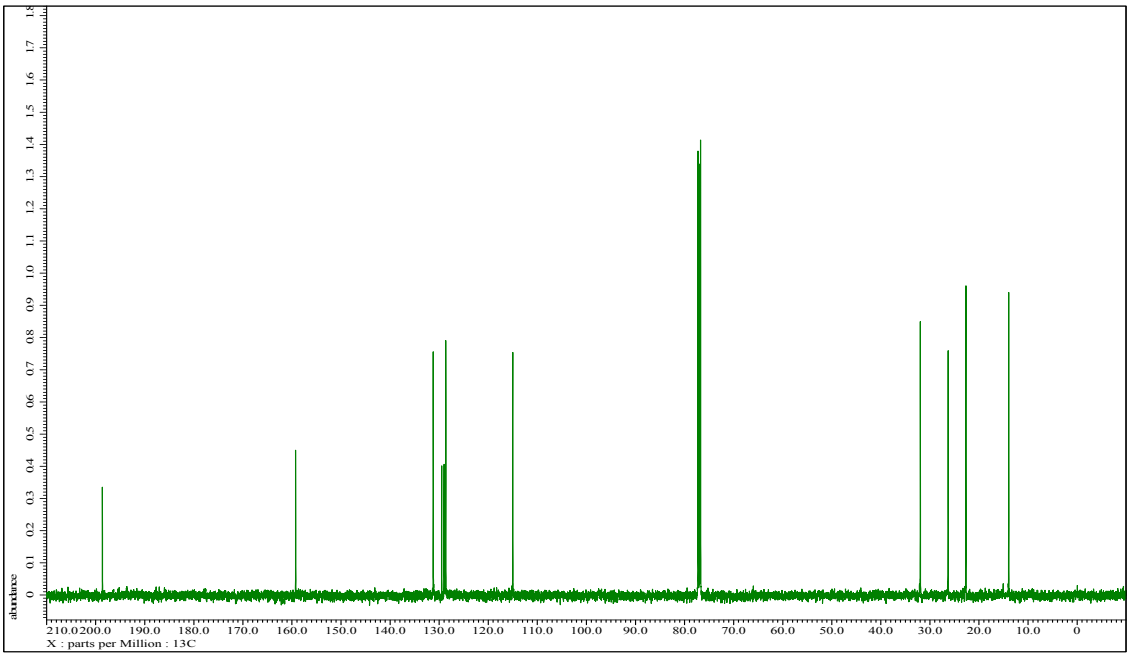




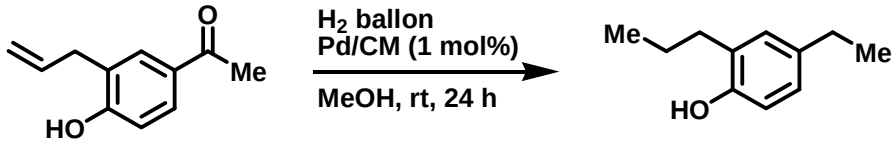
1-(4-Hydroxy-3-propylphenyl)ethanone (Table 1, Entry 25)

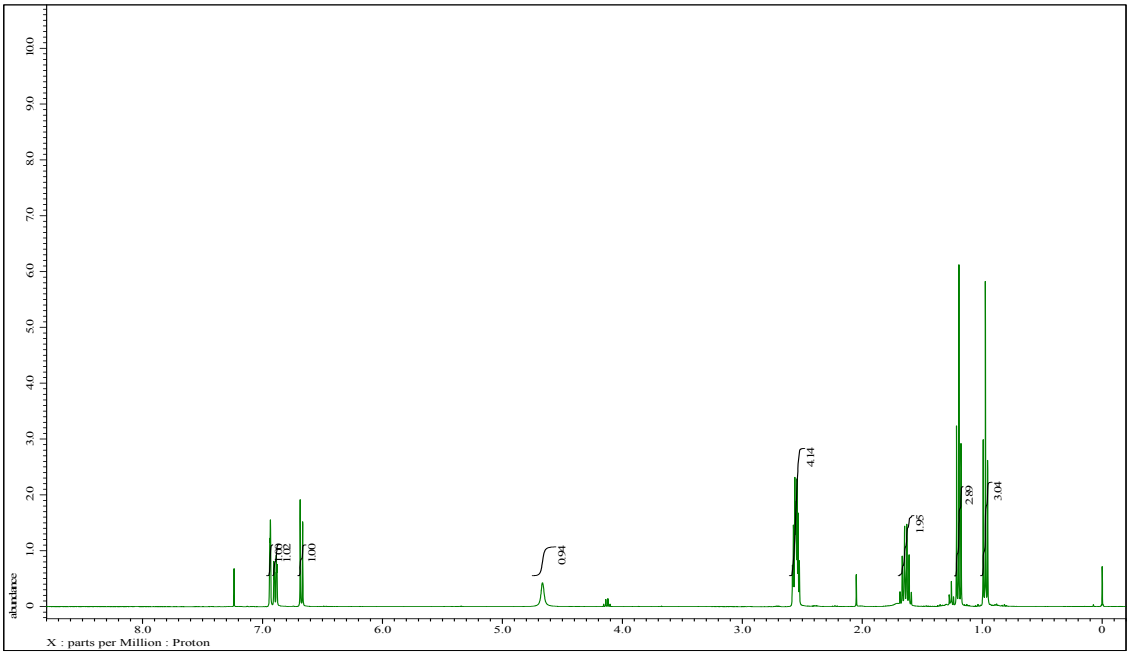


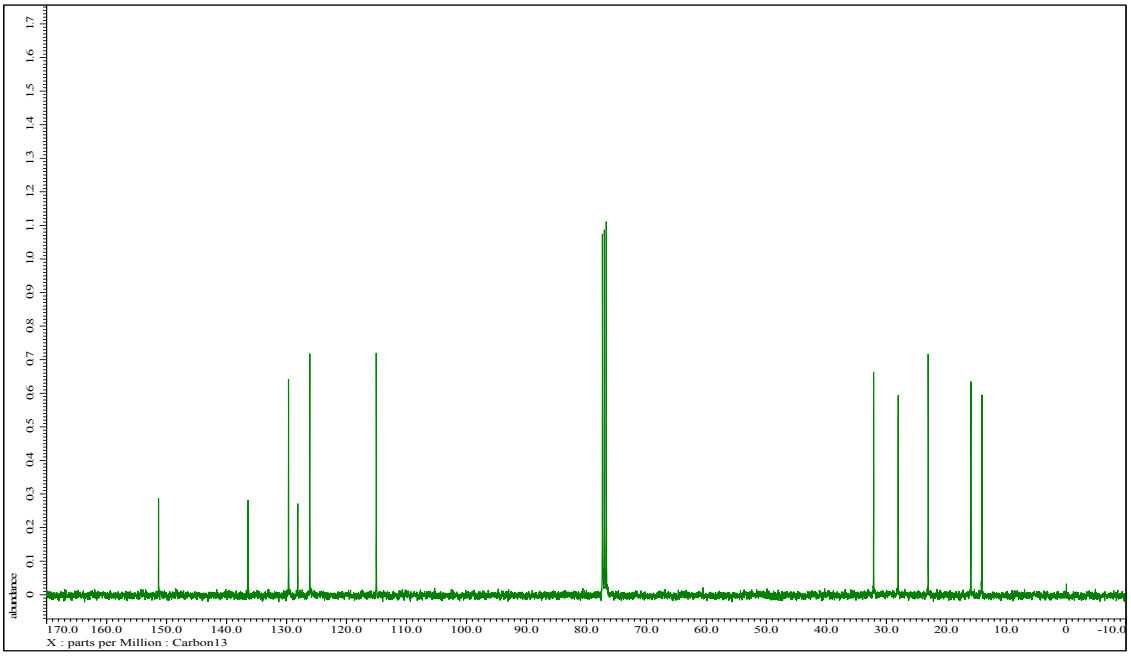




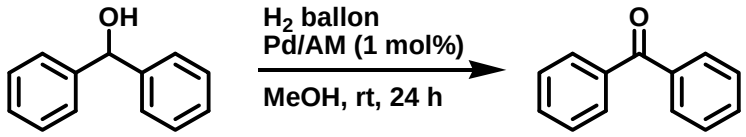
4-Ethyl-2-propylphenol (Table 1, Entry 26)



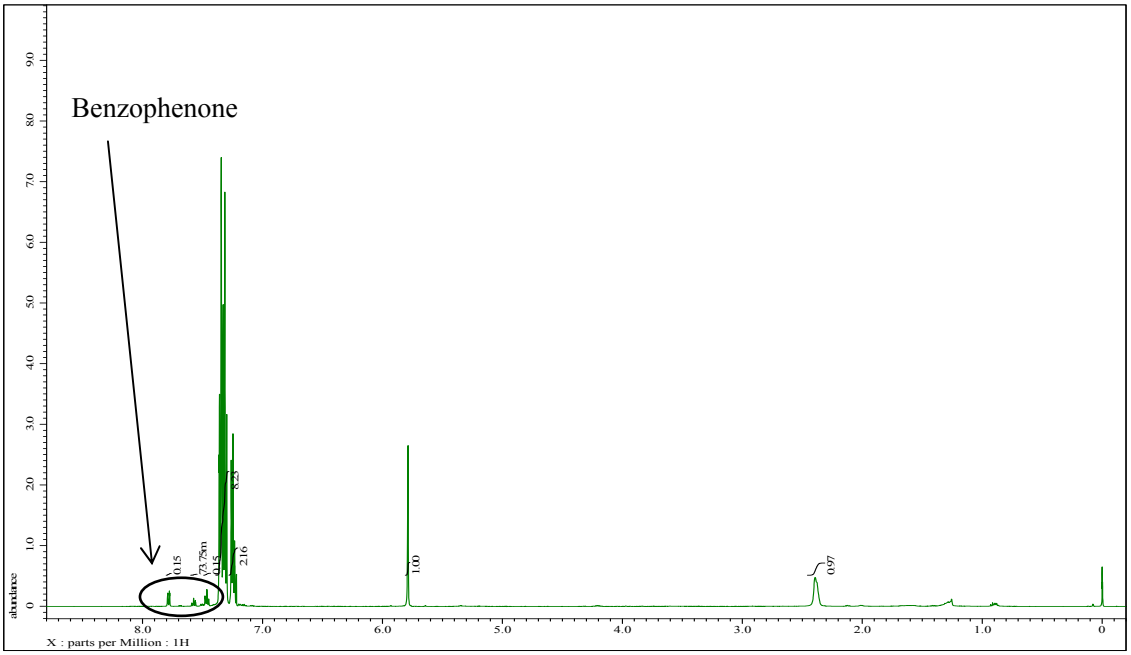


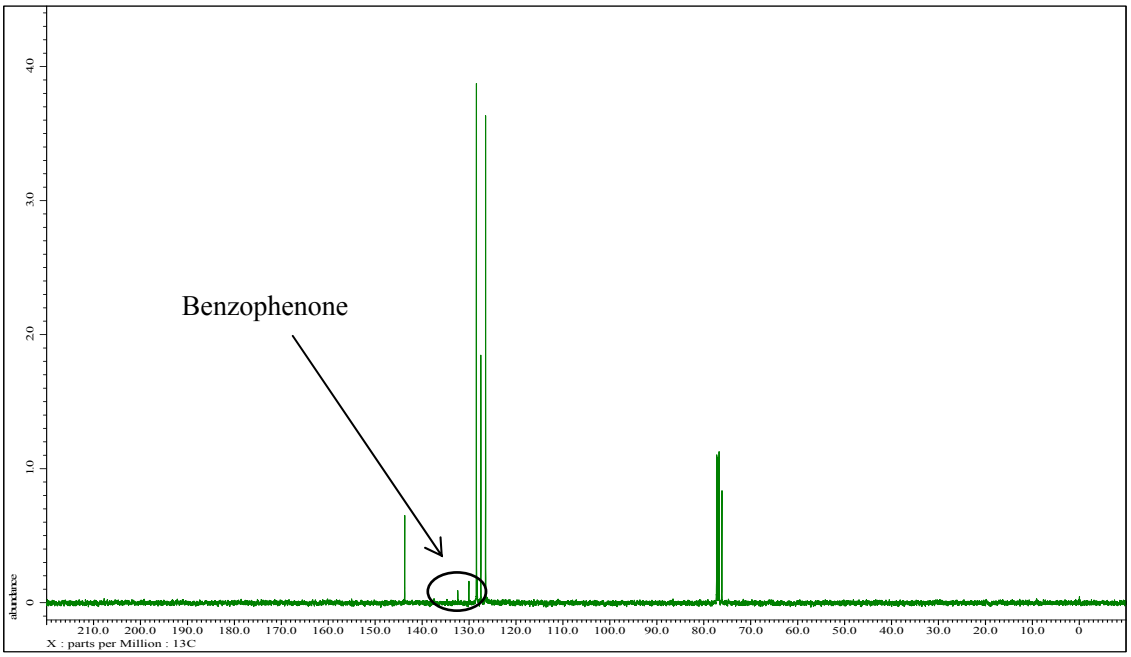


Benzhydrole and Benzophenone (Table 1, Entry 27)

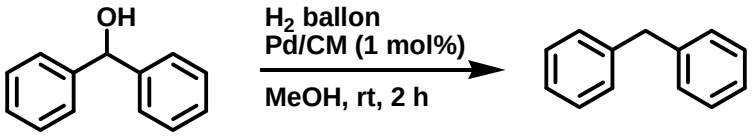


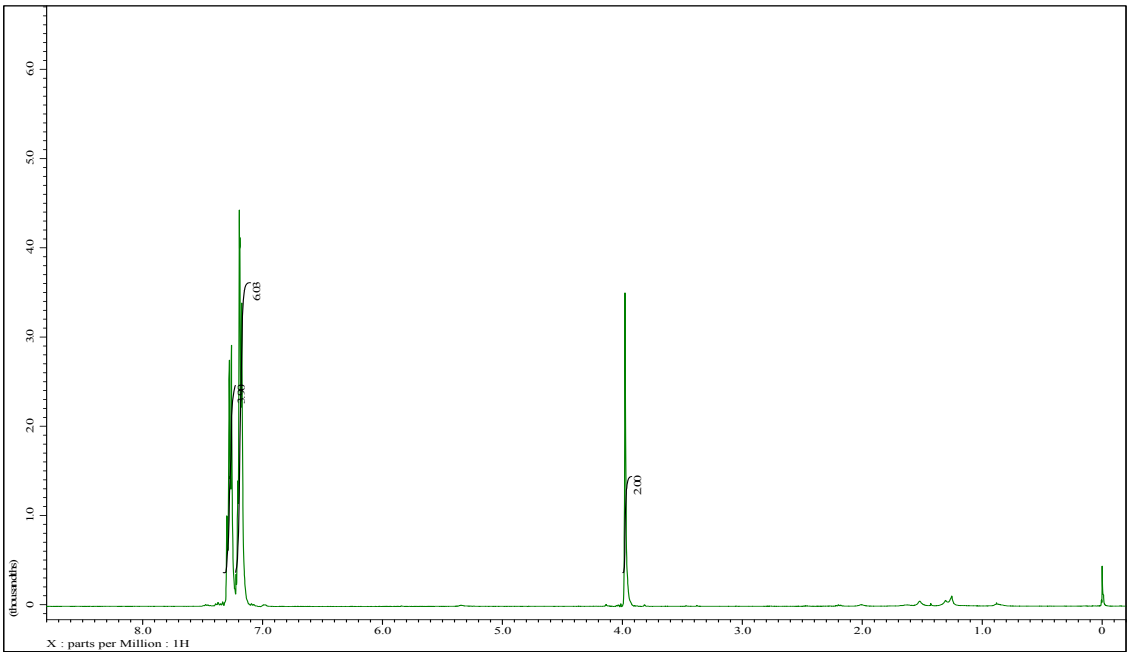
97 3

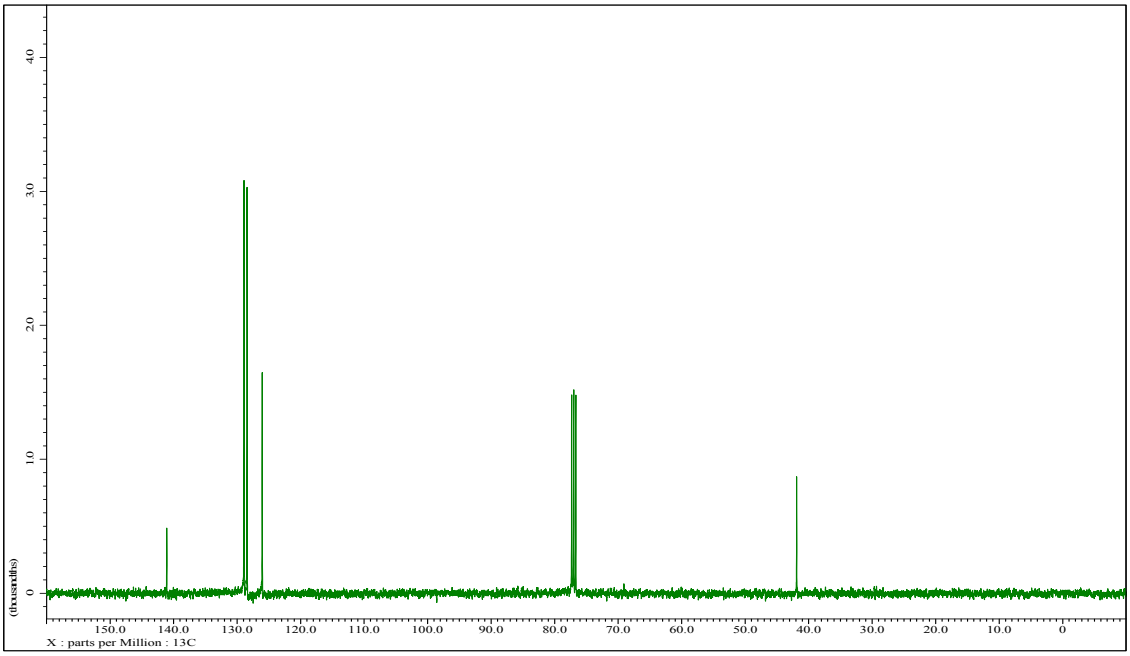




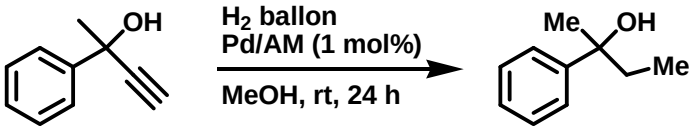
Diphenylmethane (Table 1, Entry 28)

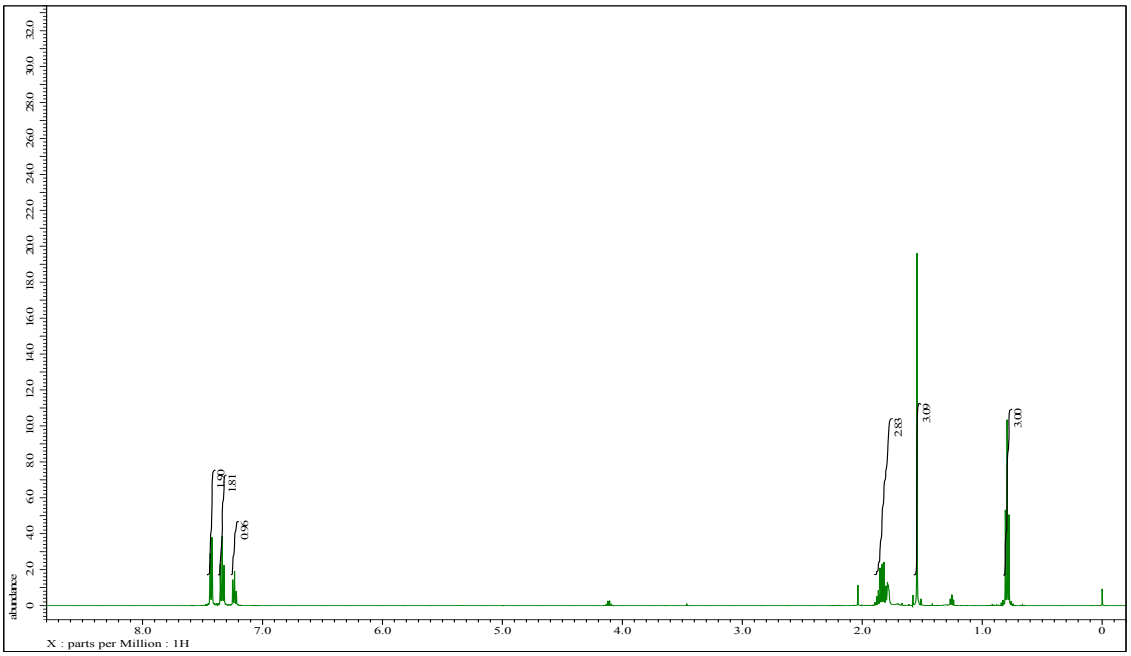


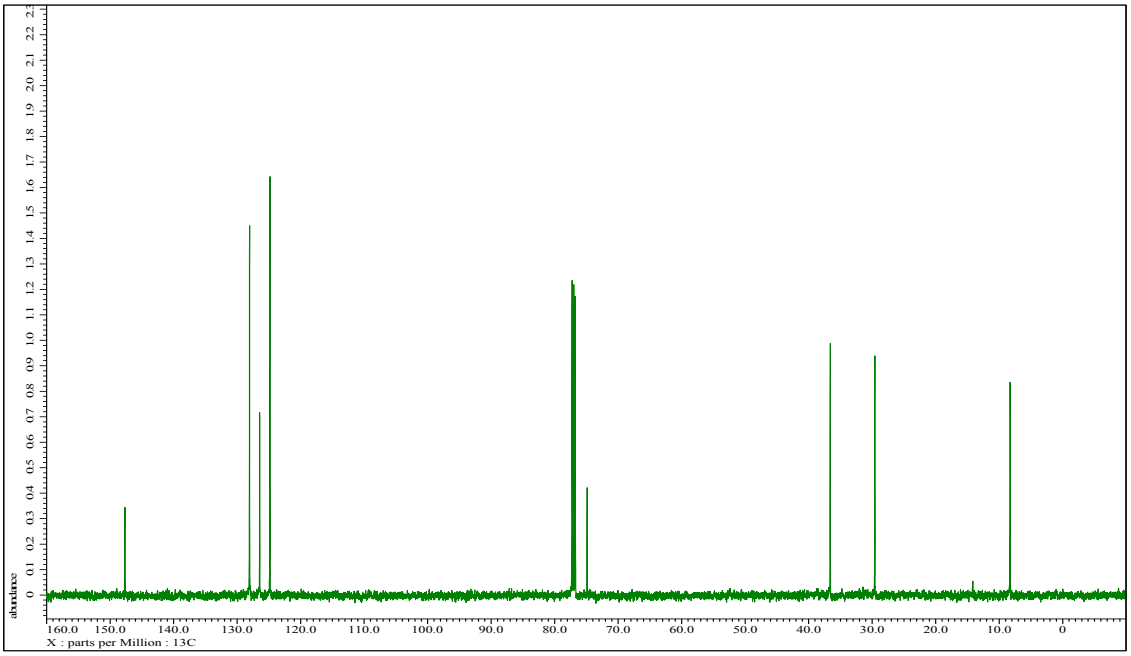




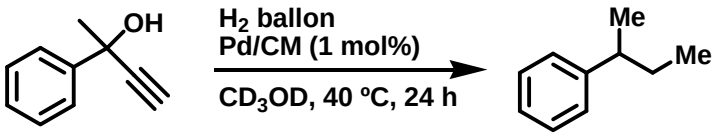
α-Ethyl α-methyl benzylalcohol (Table 1, Entry 29)

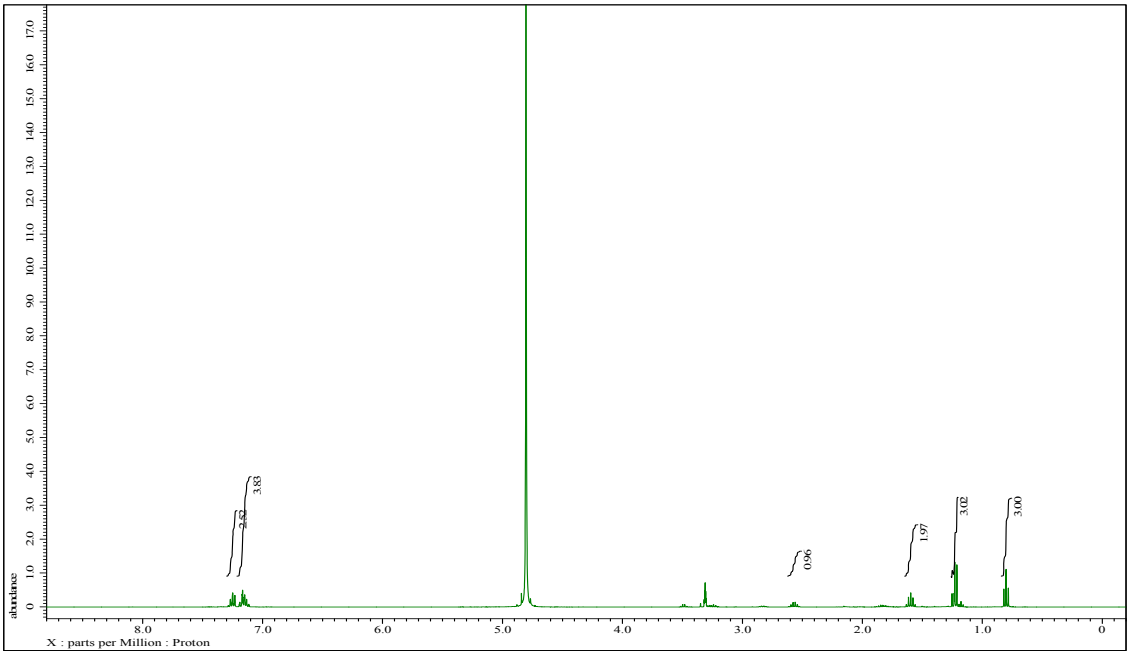


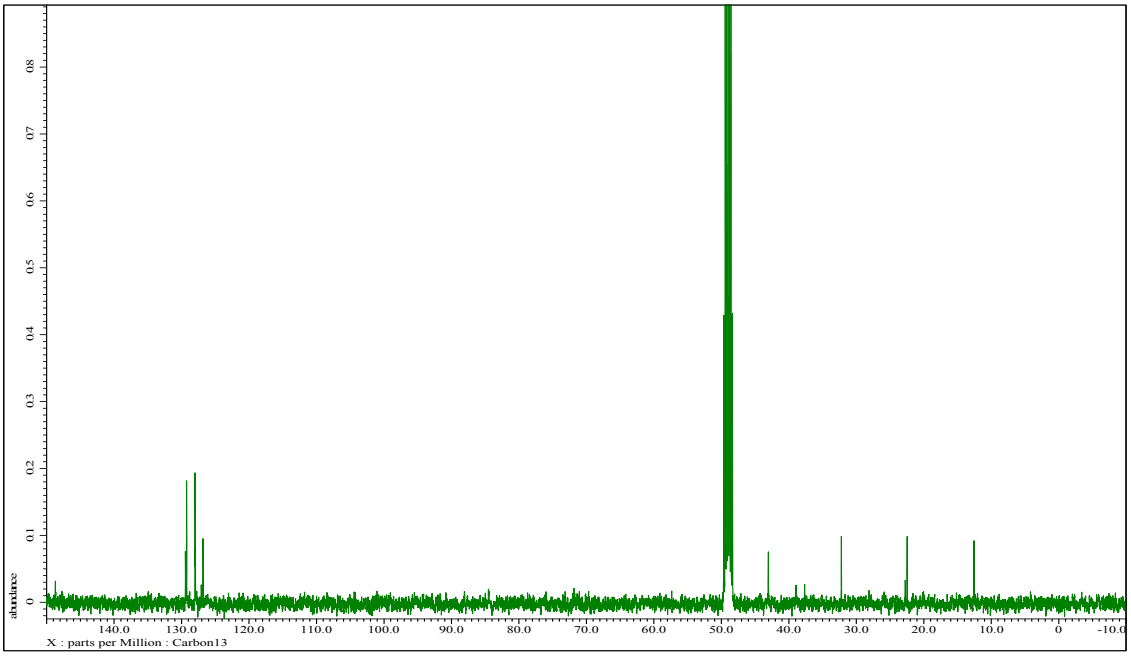




2-Phenyl butane (Table 1, Entry 30)

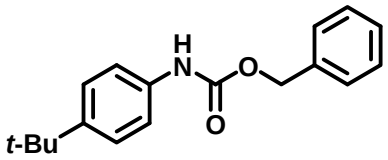


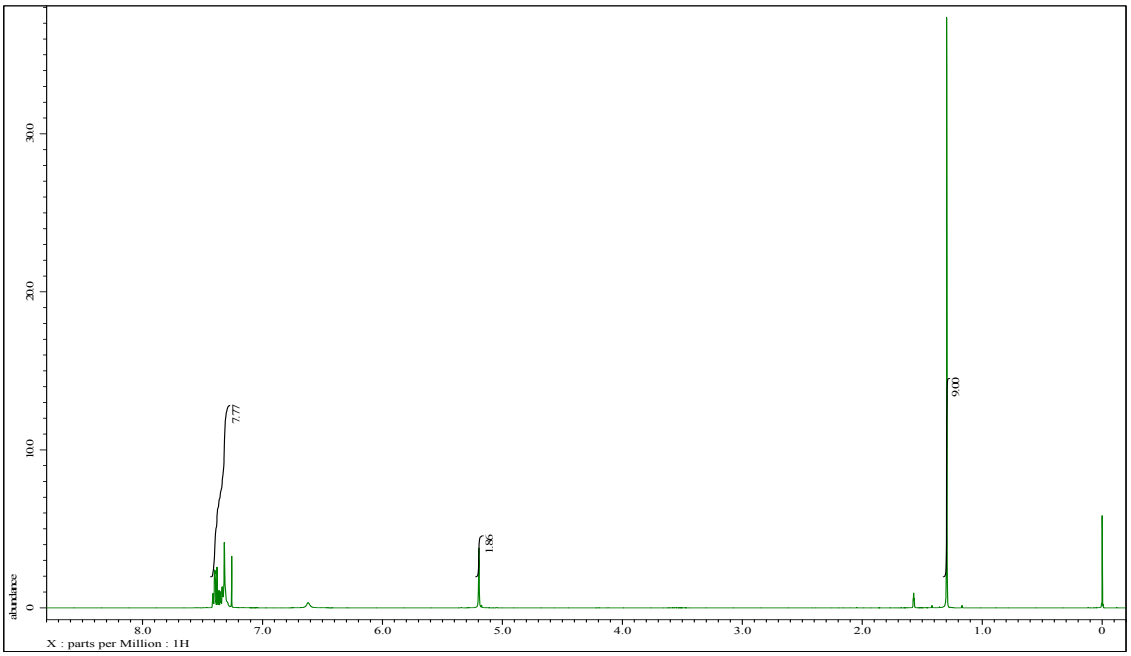


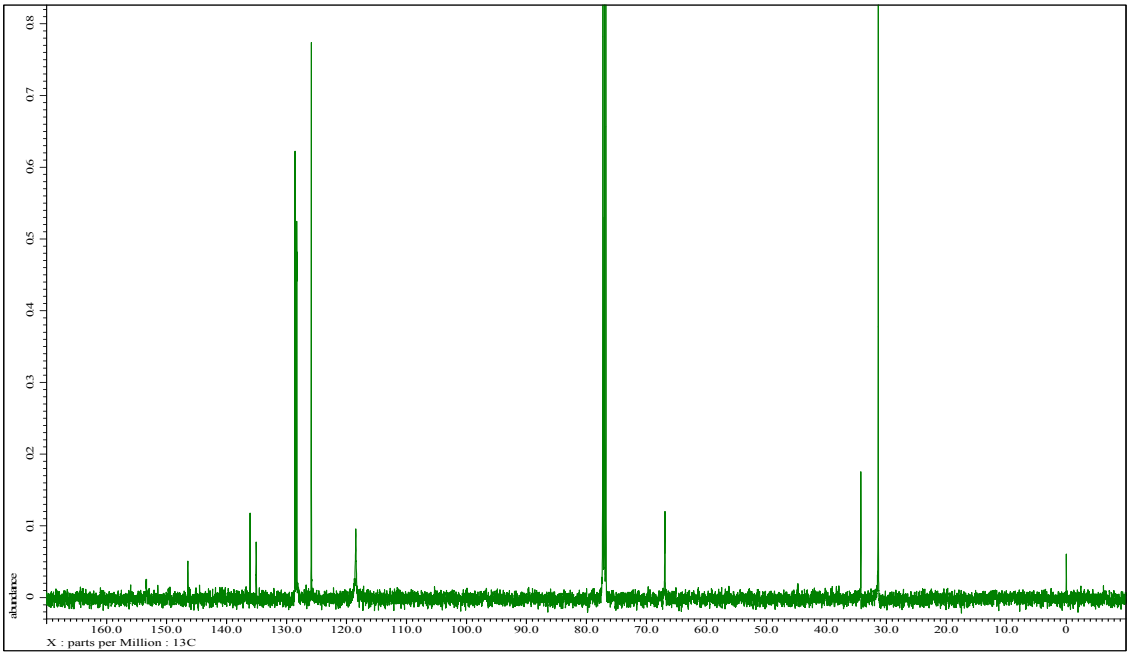


Substrates

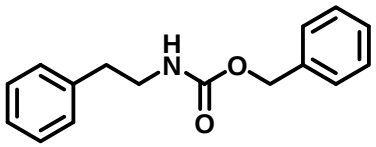
Benzyl 4-*tert*-Butylphenylcarbamate (for Table 1, Entries 9 and 10)

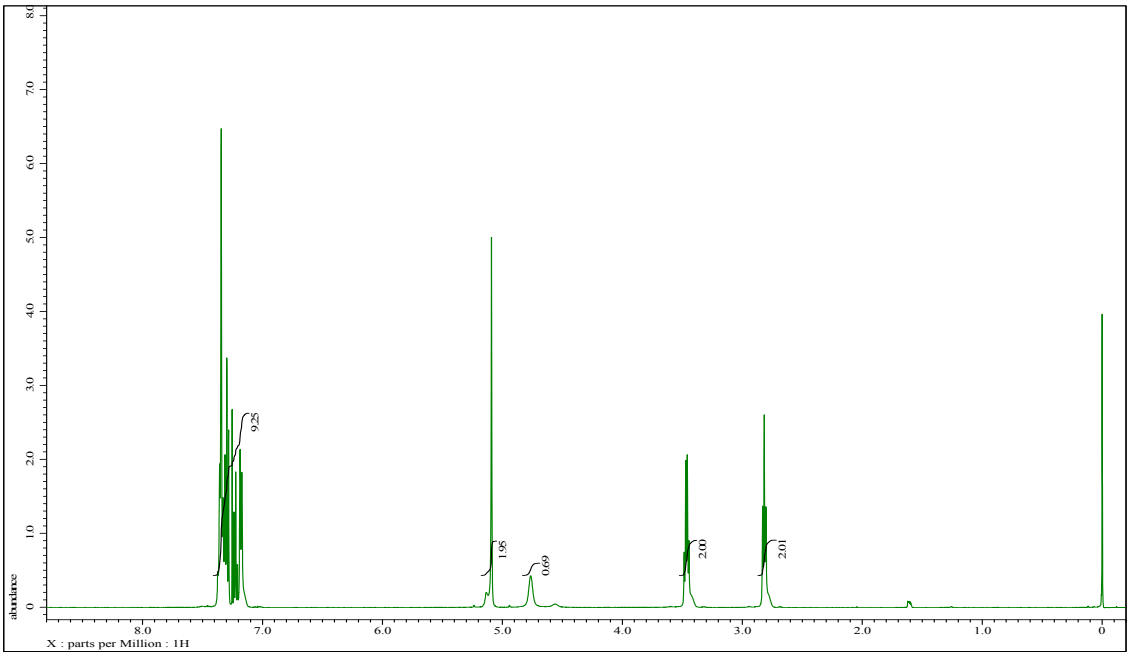


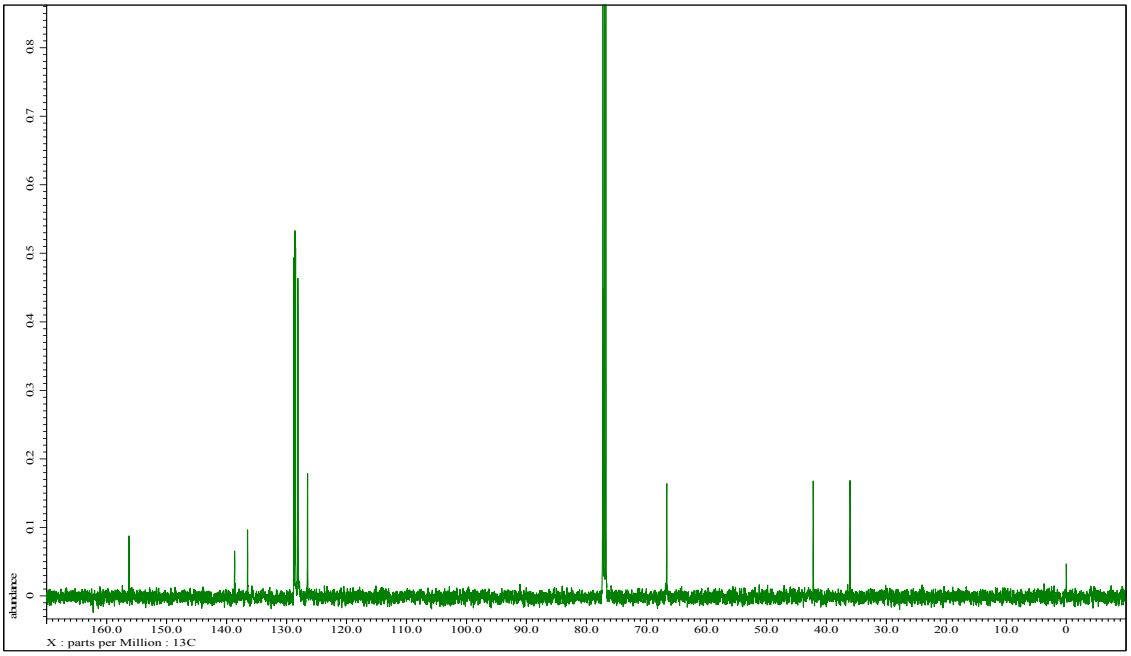




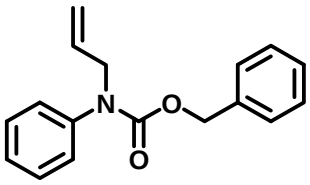
Benzyl Phenethylcarbamate (for Table 1, Entries 11 and 12)

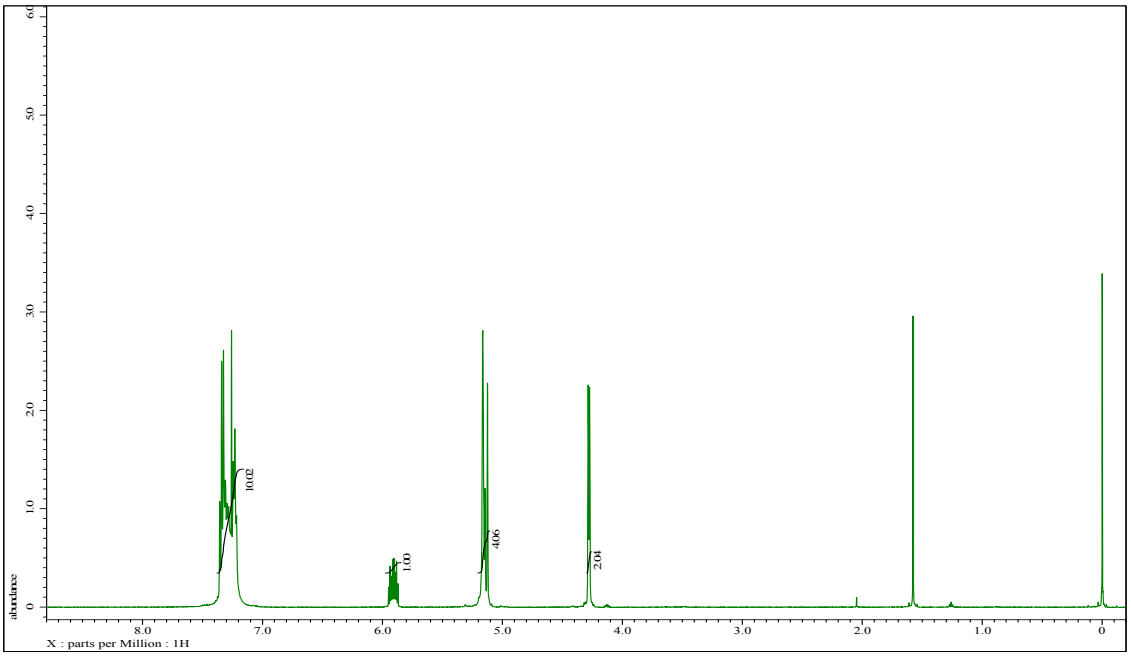


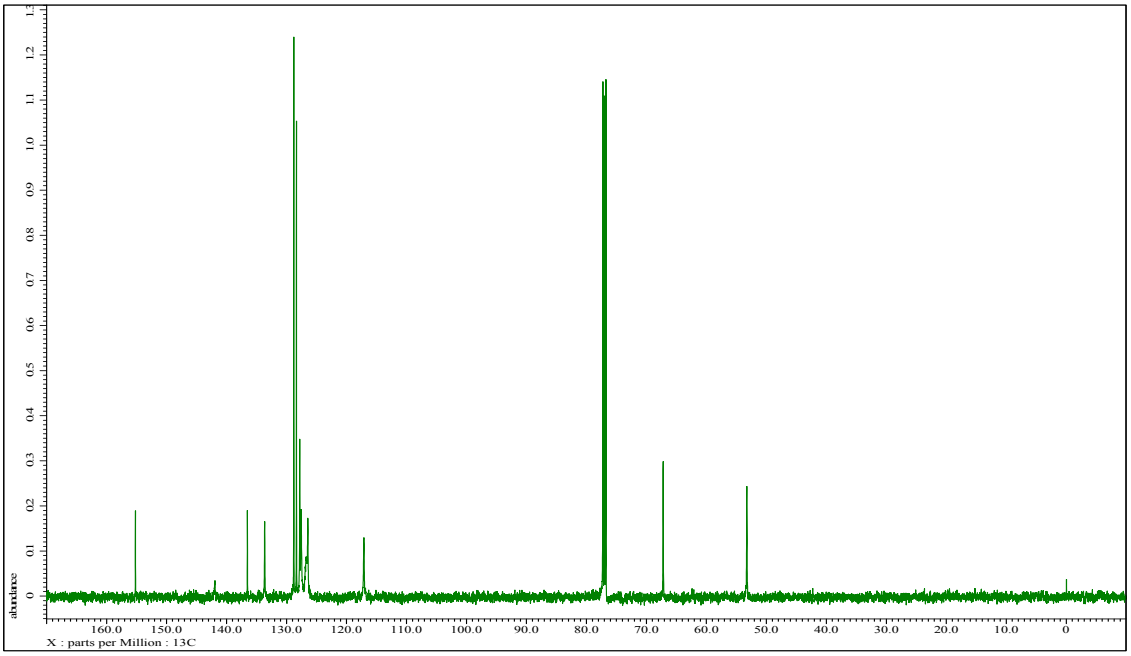




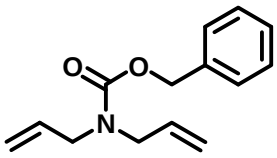
Benzyl Allyl(phenyl)carbamate (for Table 1, Entries 12 and 13)

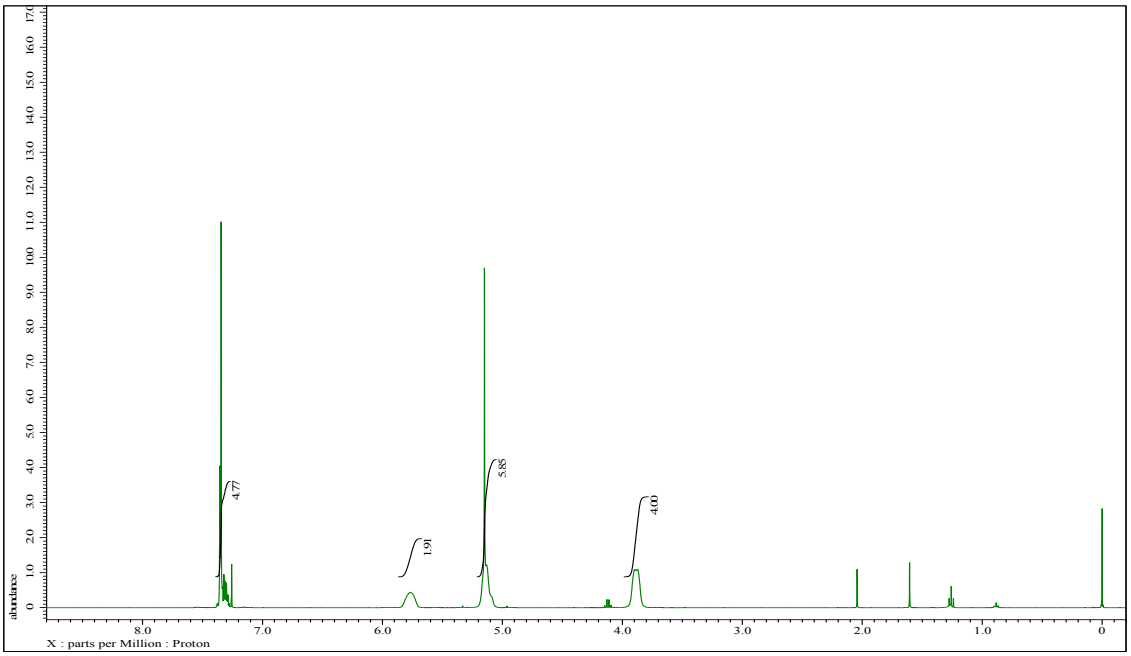


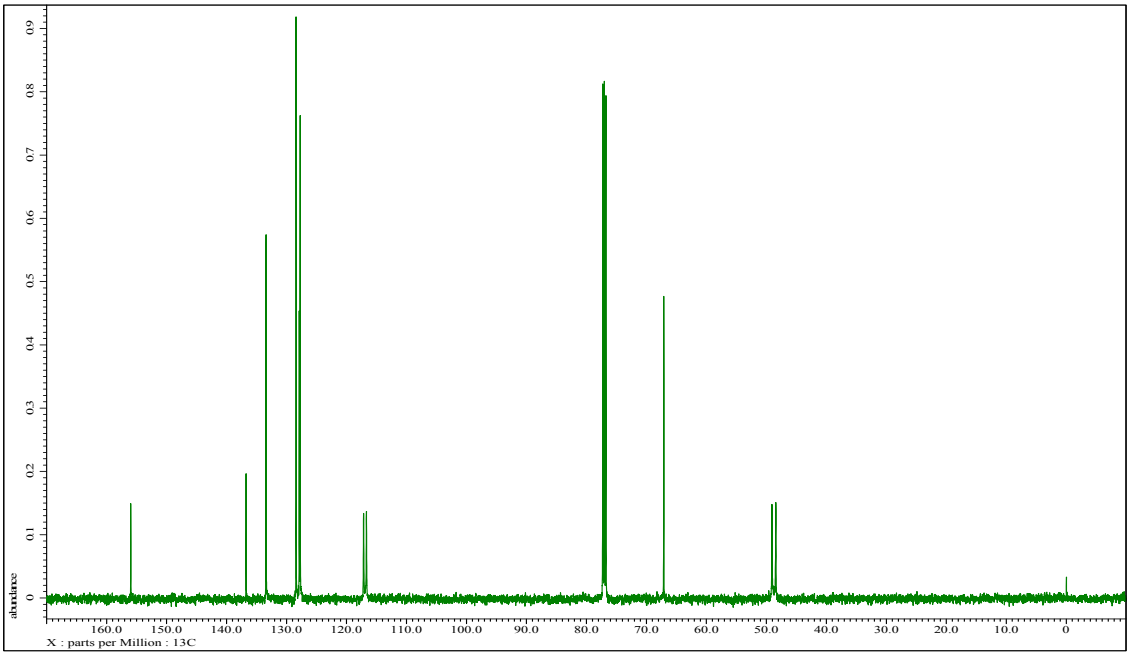




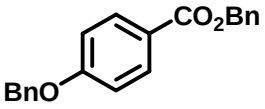
Benzyl Diallylcarbamate (for Table 1, Entries 14 and 15)

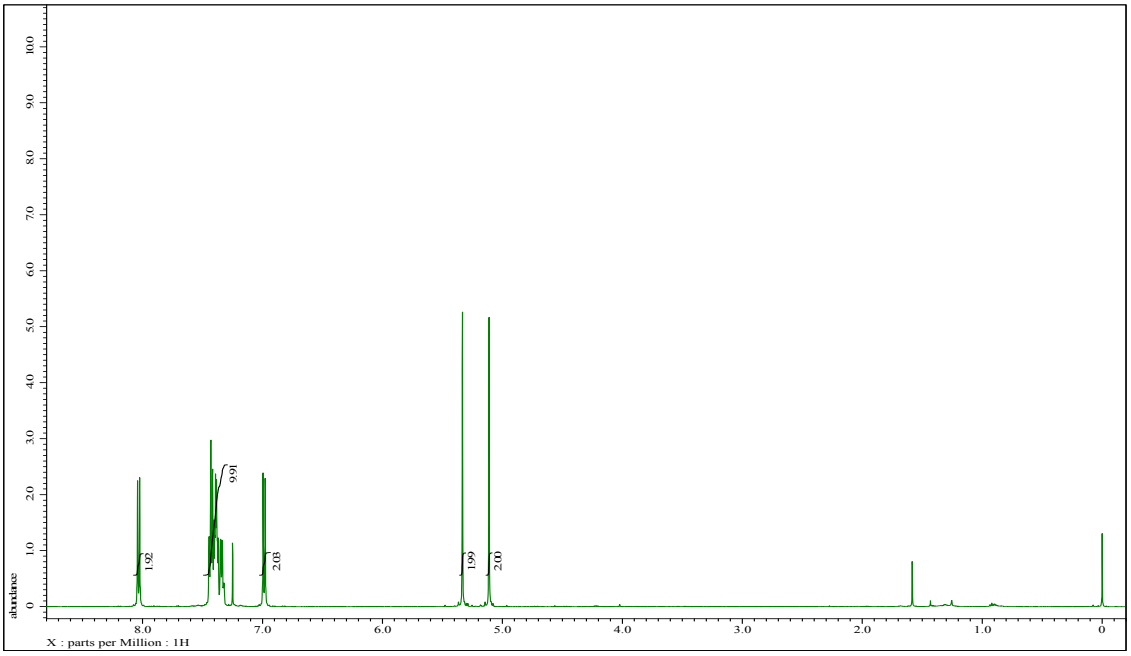


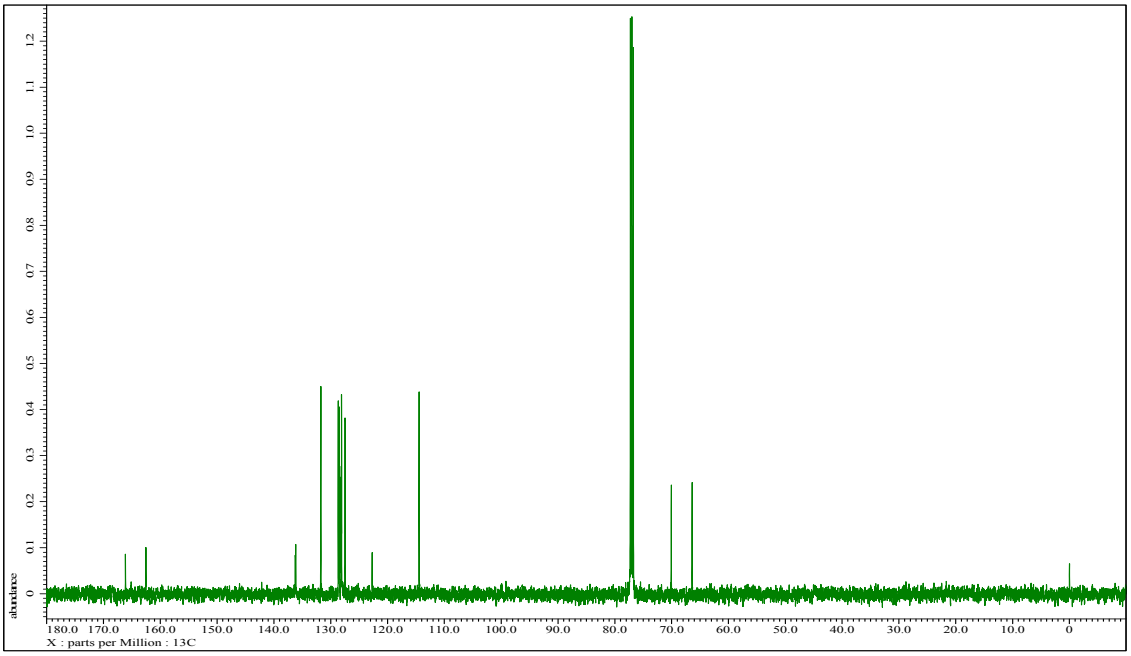




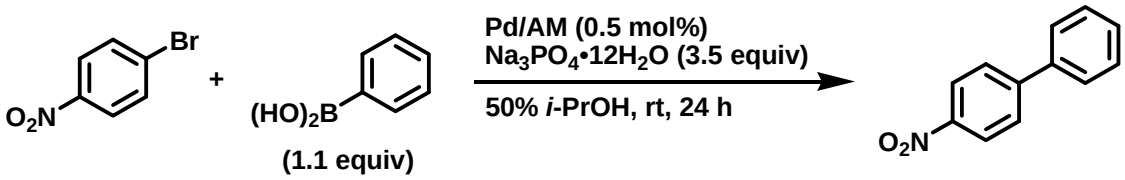
Benzyl 4-Benzyloxybenzoate (for Table 1, Entries 21 and 22)

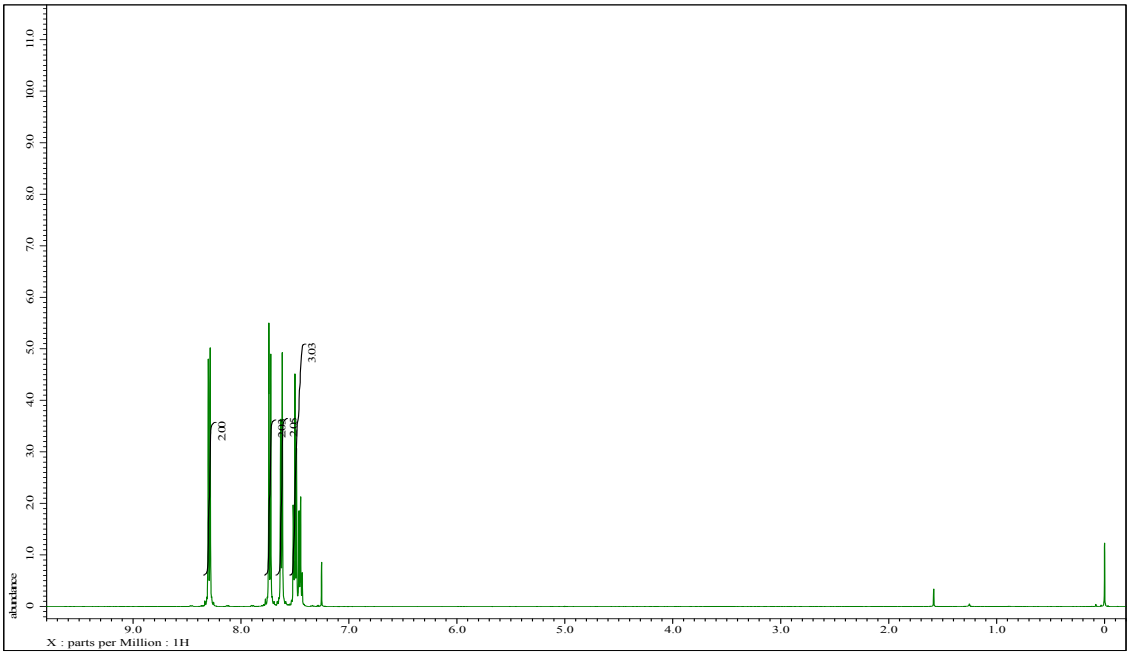


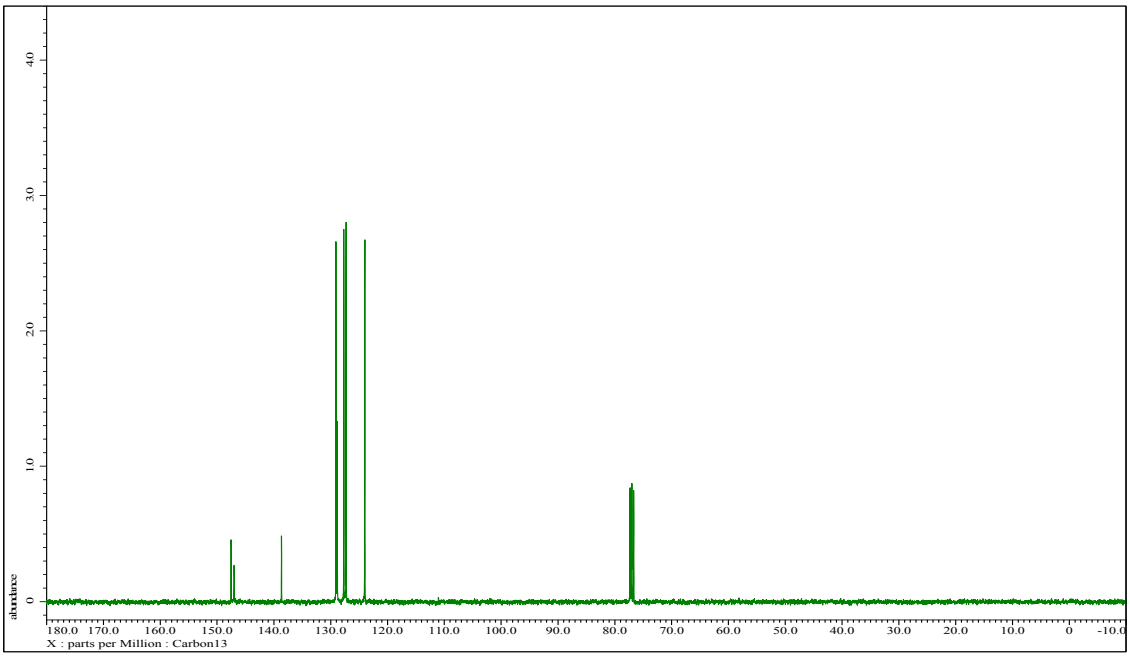




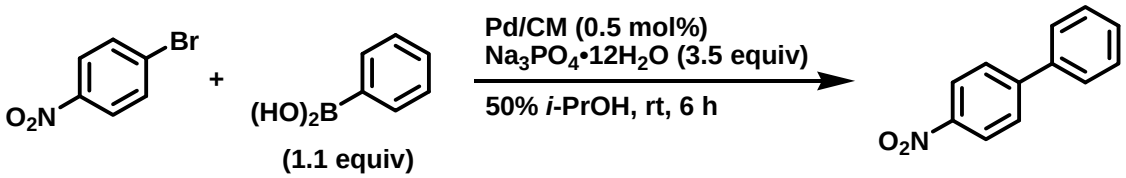
4-Nitrobiphenyl (for Table 2, Entry 1)

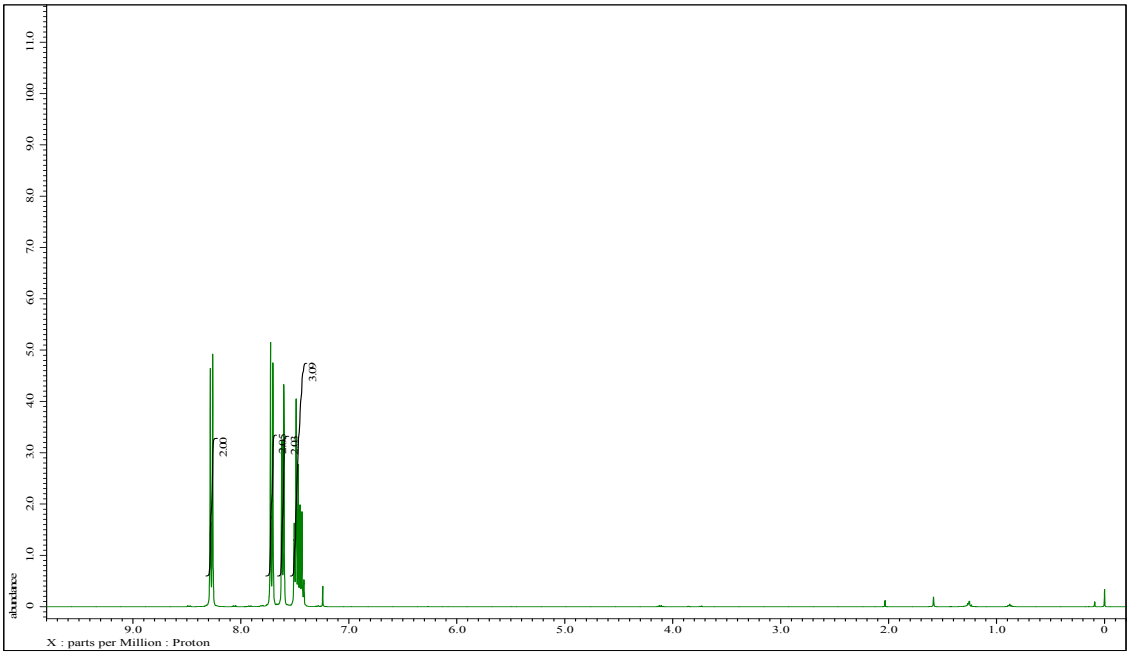


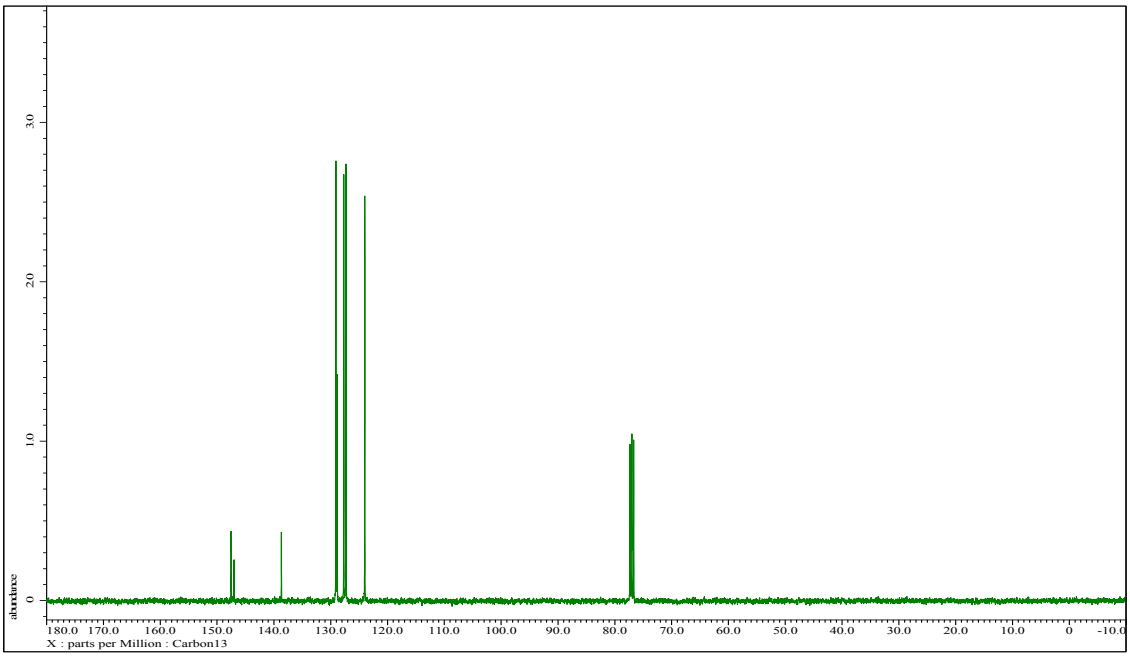




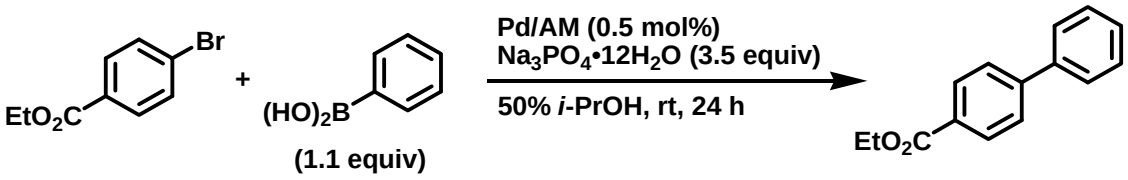
4-Nitrobiphenyl (Table 2, Entry 2)

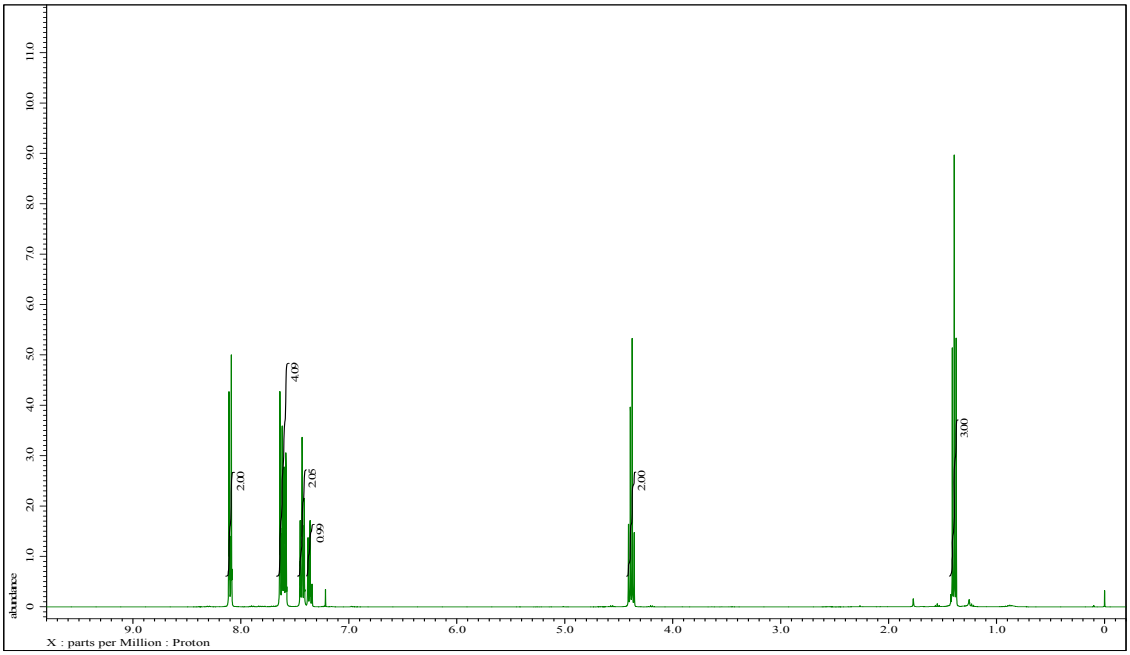


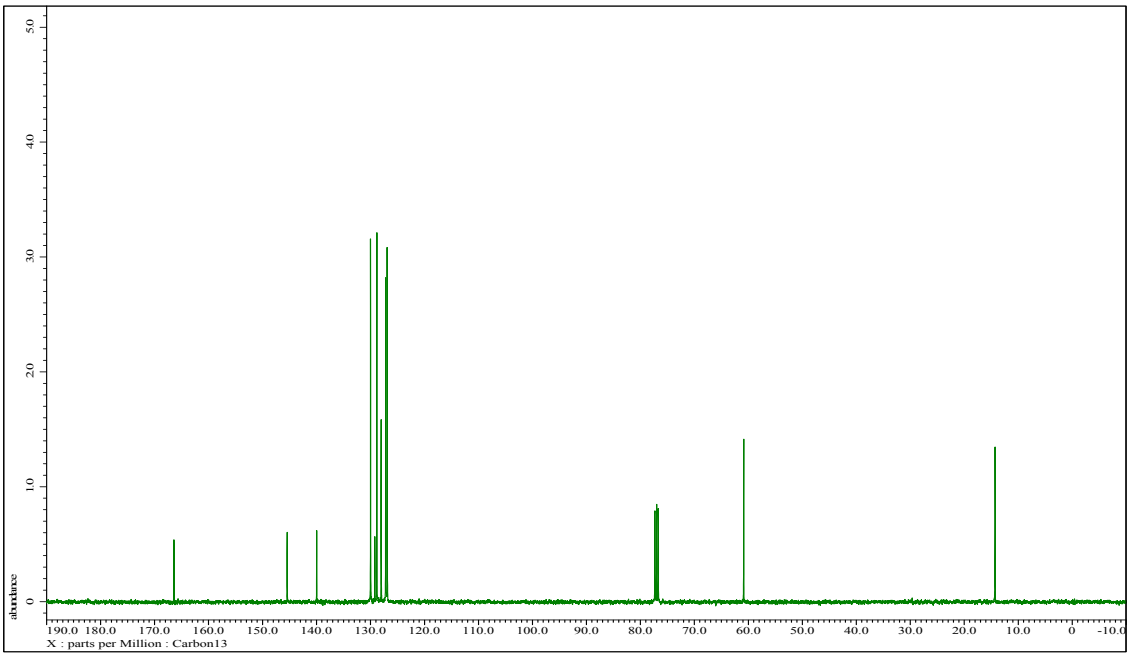




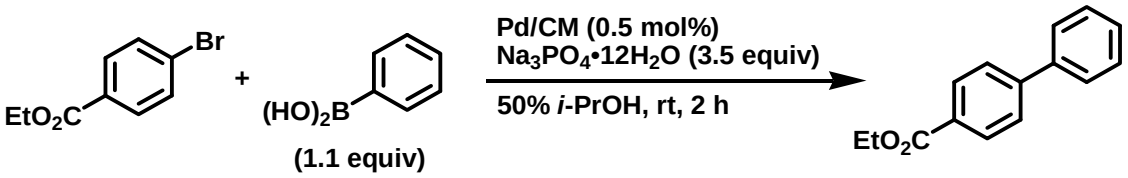
4-Biphenylcarboxylic Acid Ethyl Ester (Table 2, Entry 4)

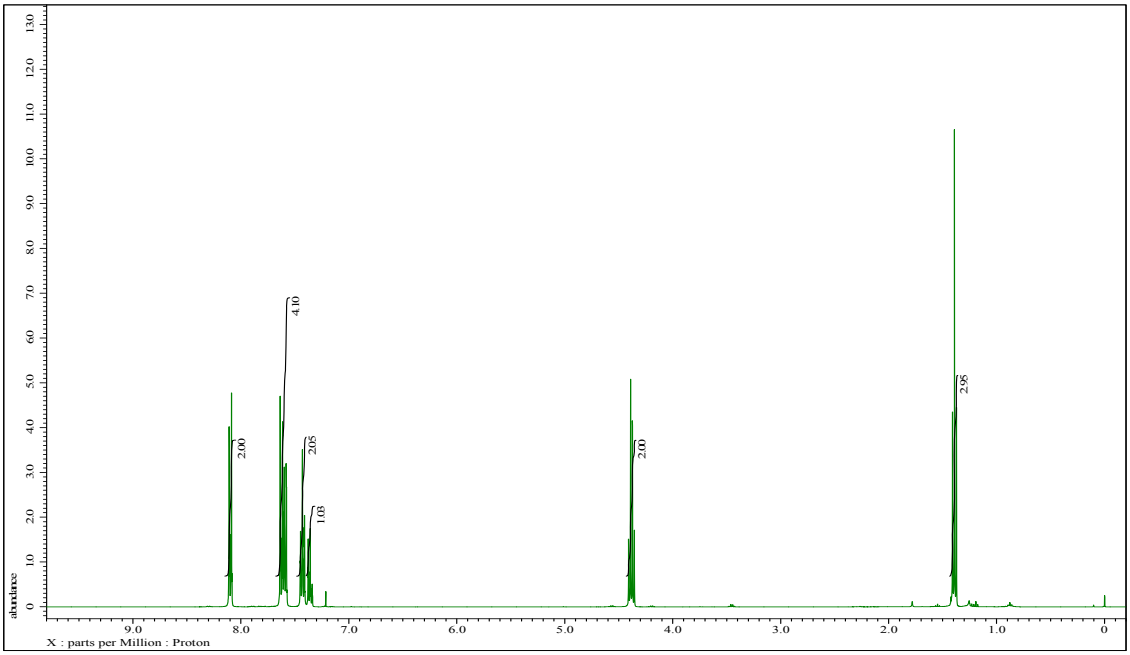


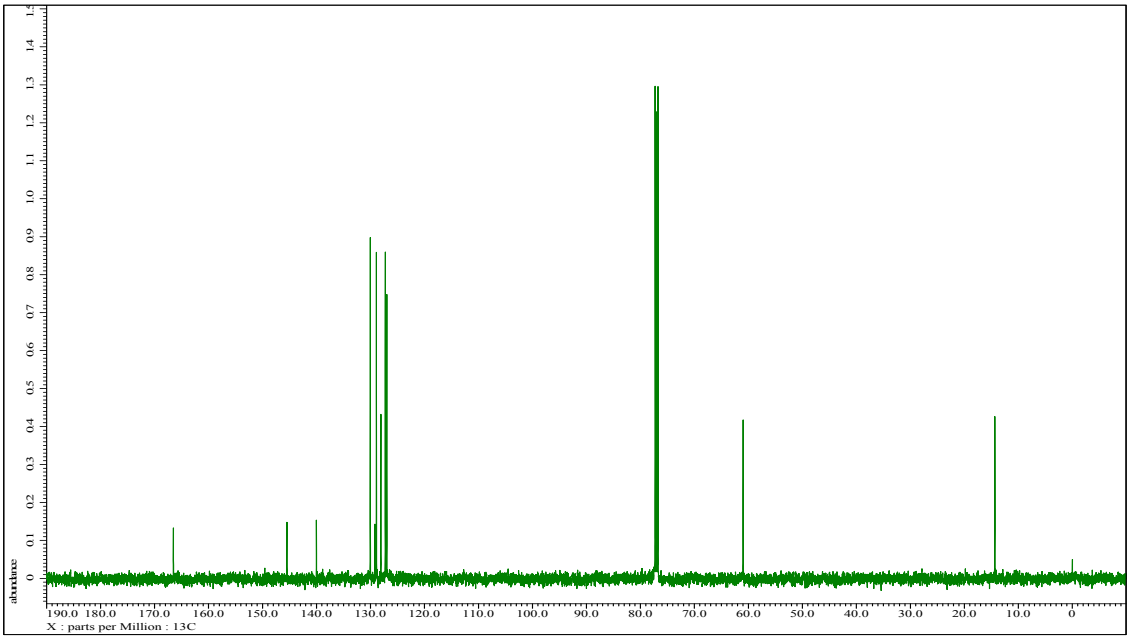




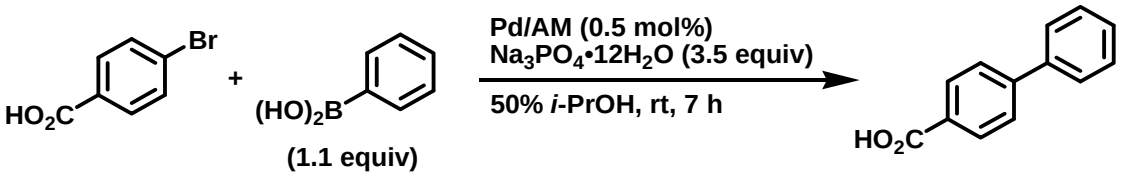
4-Biphenylcarboxylic Acid Ethyl Ester (Table 2, Entry 5)

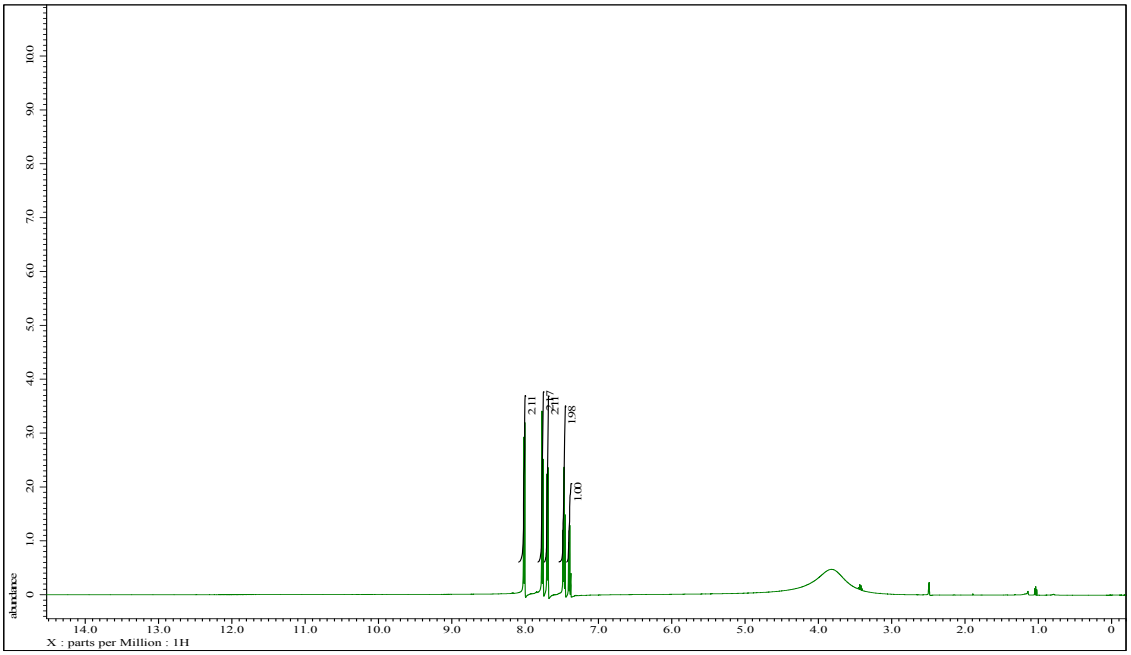


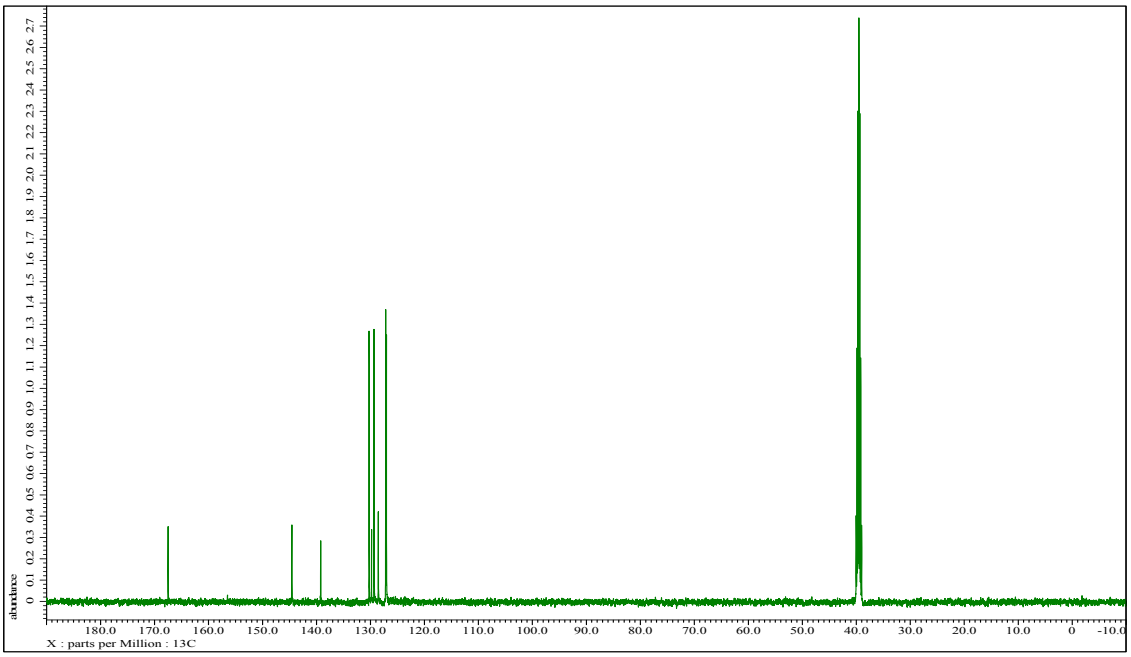




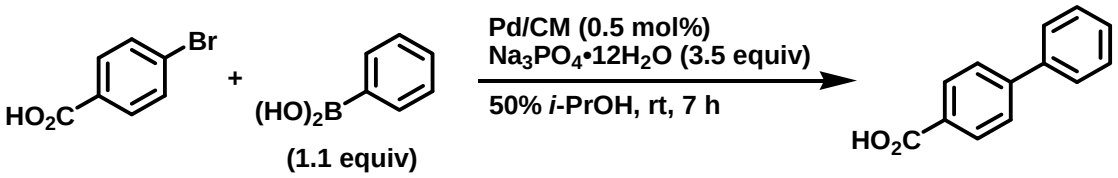
4-Biphenylcarboxylic Acid (Table 2, Entry 7)

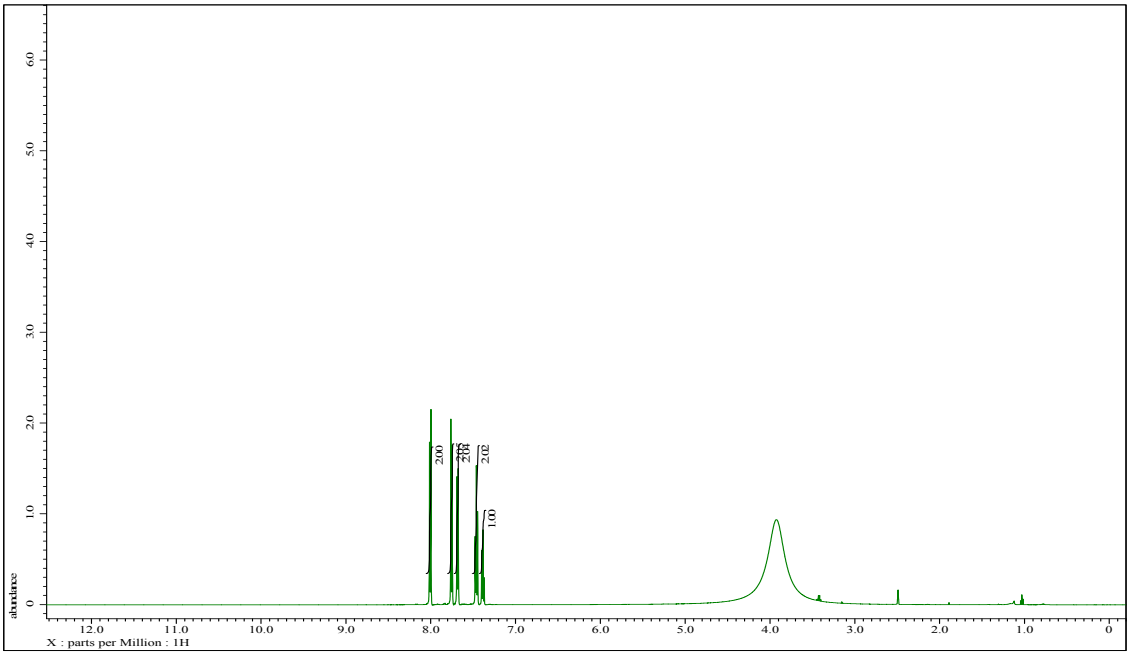


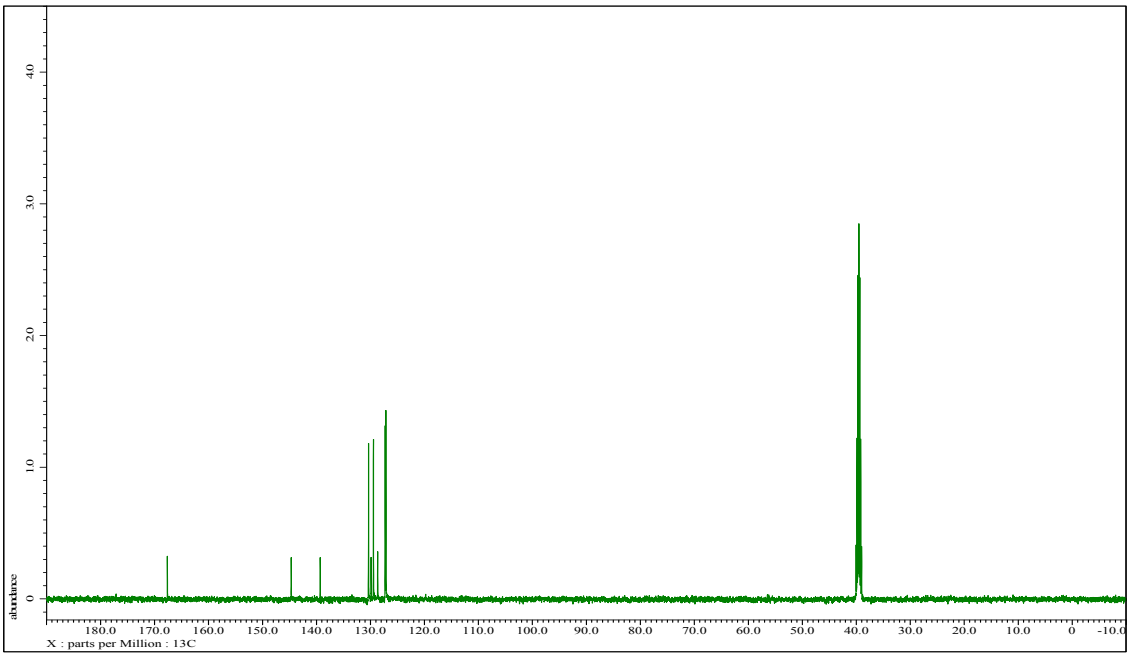




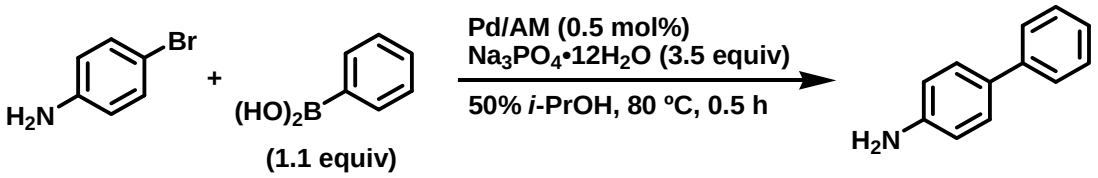
4-Biphenylcarboxylic Acid (Table 2, Entry 8)

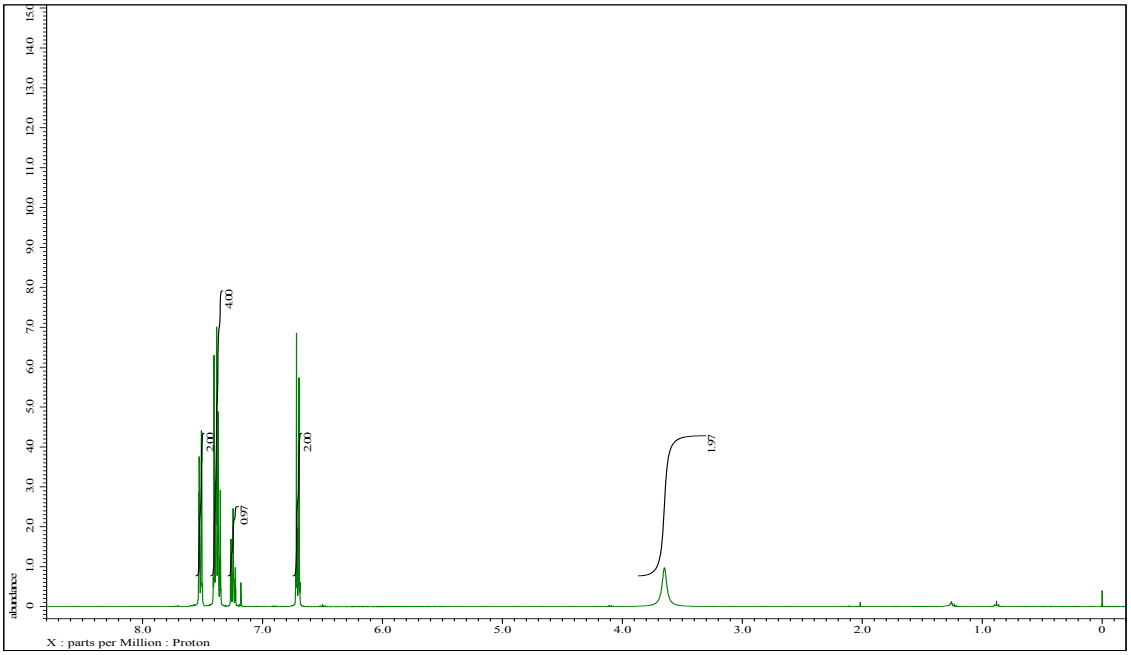


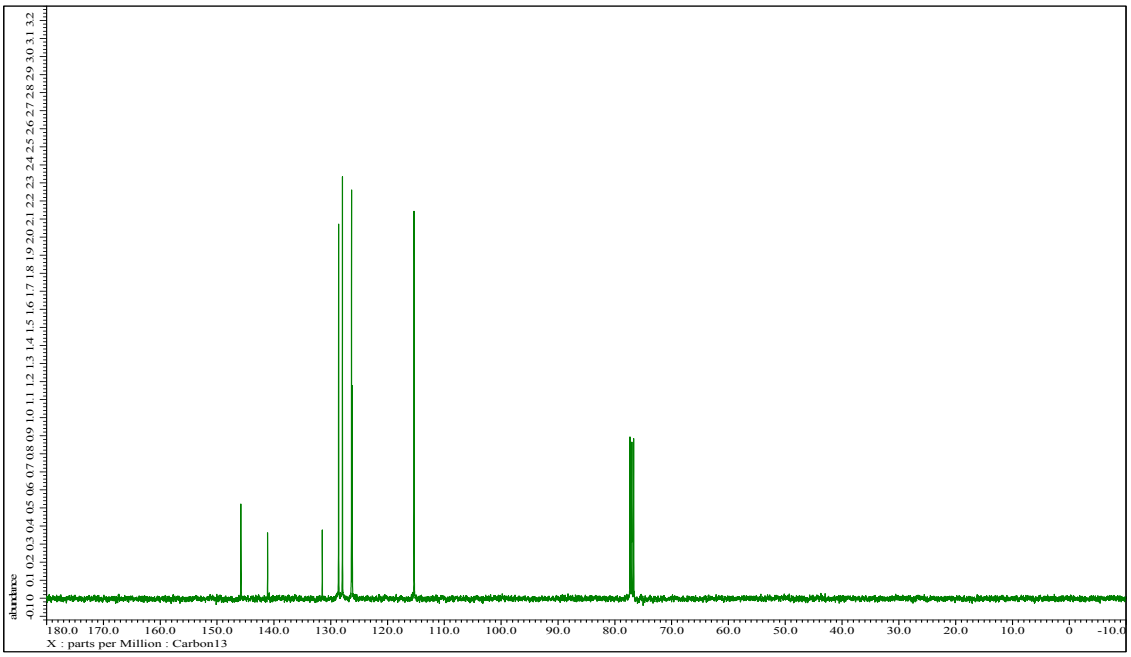




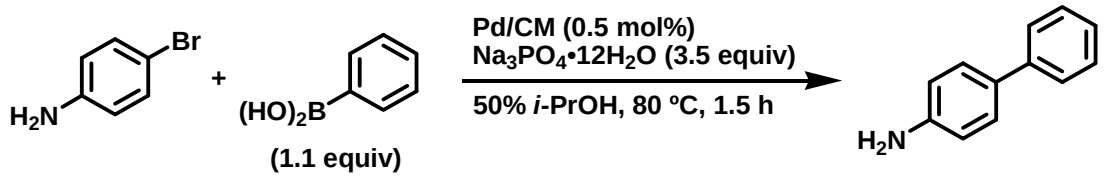
4-Aminobiphenyl (Table 2, Entry 10)

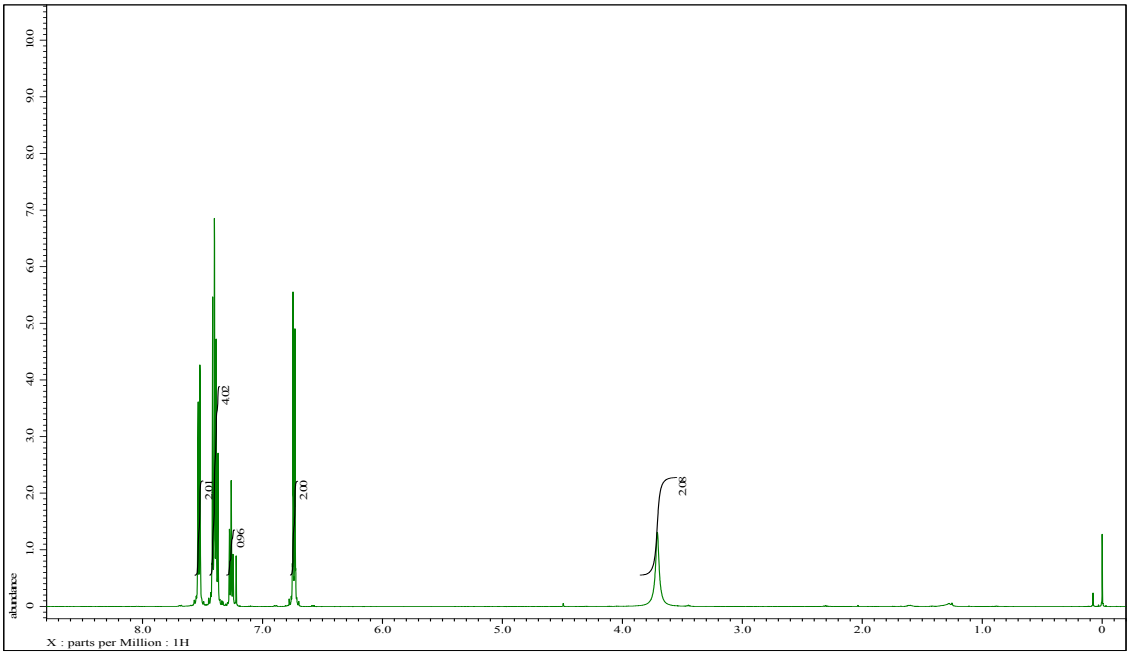


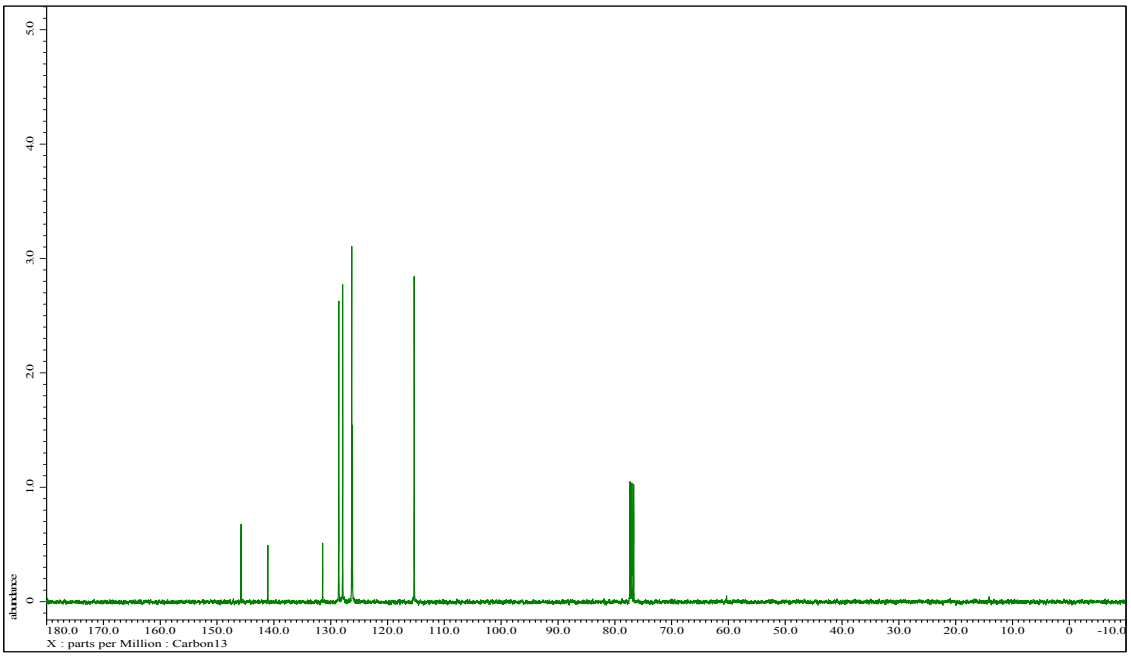




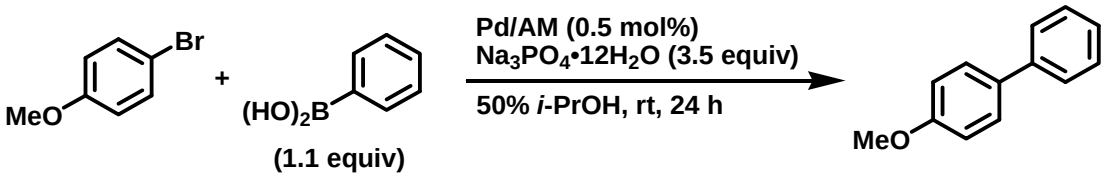
4-Aminobiphenyl (Table 2, Entry 11)

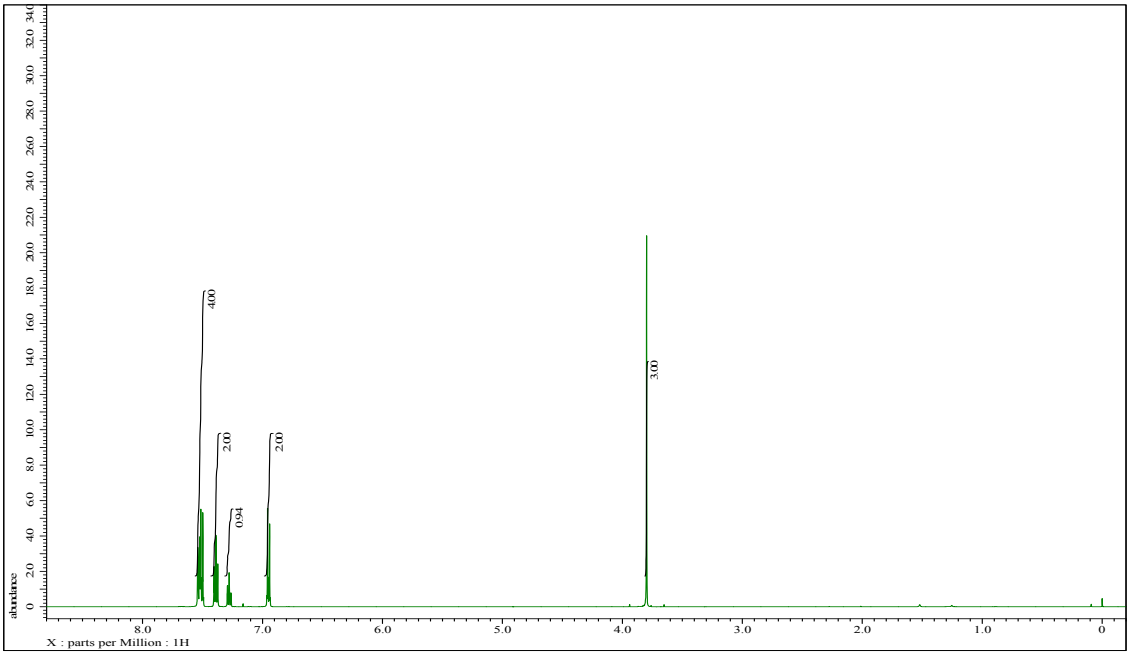


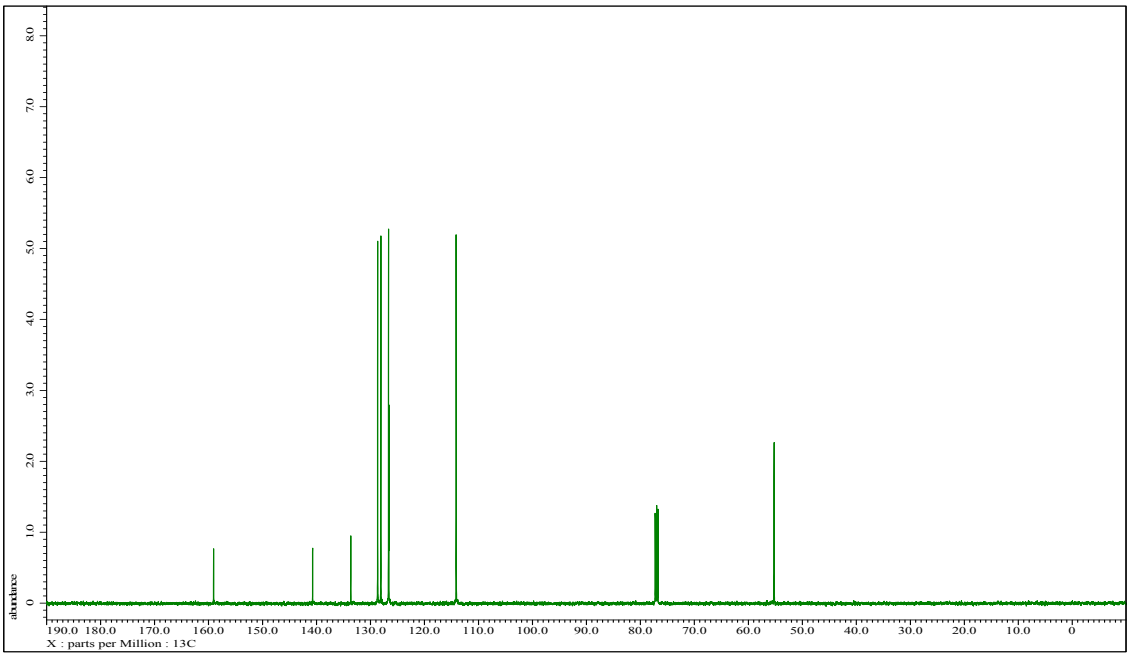




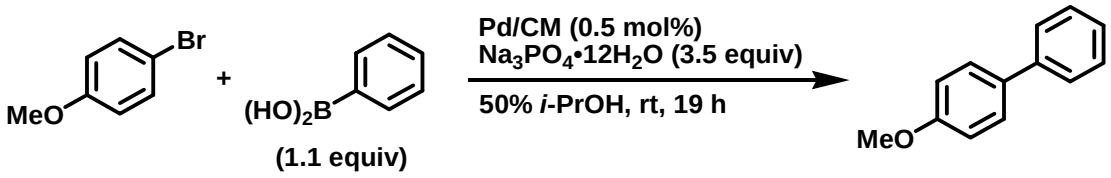
4-Methoxybiphenyl (Table 2, Entry 13)

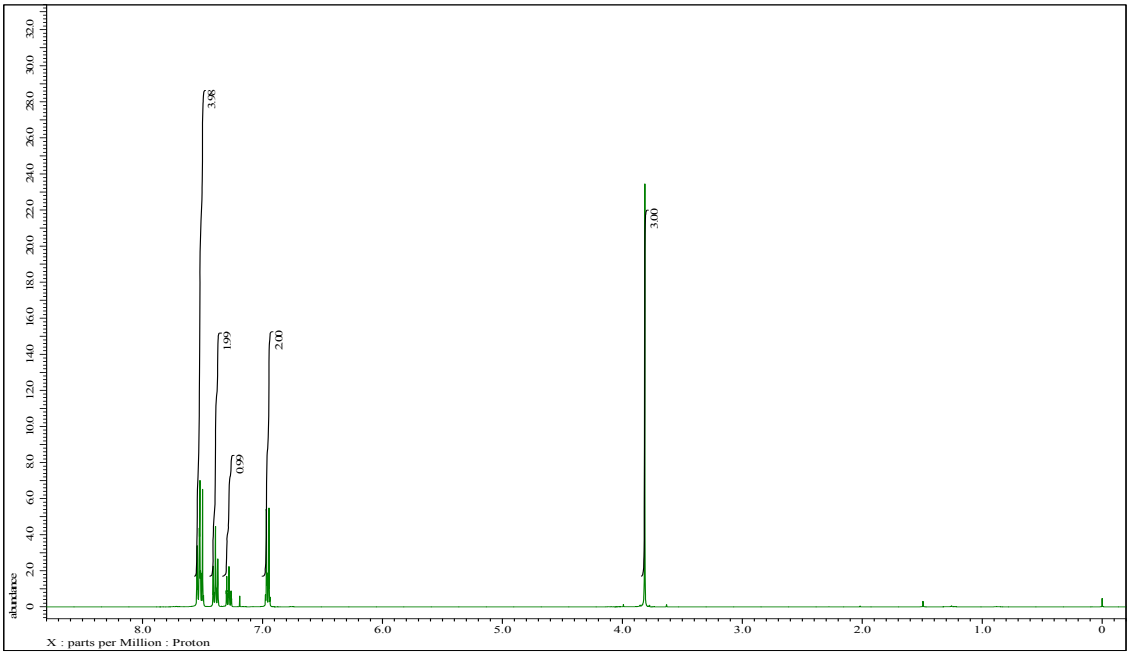


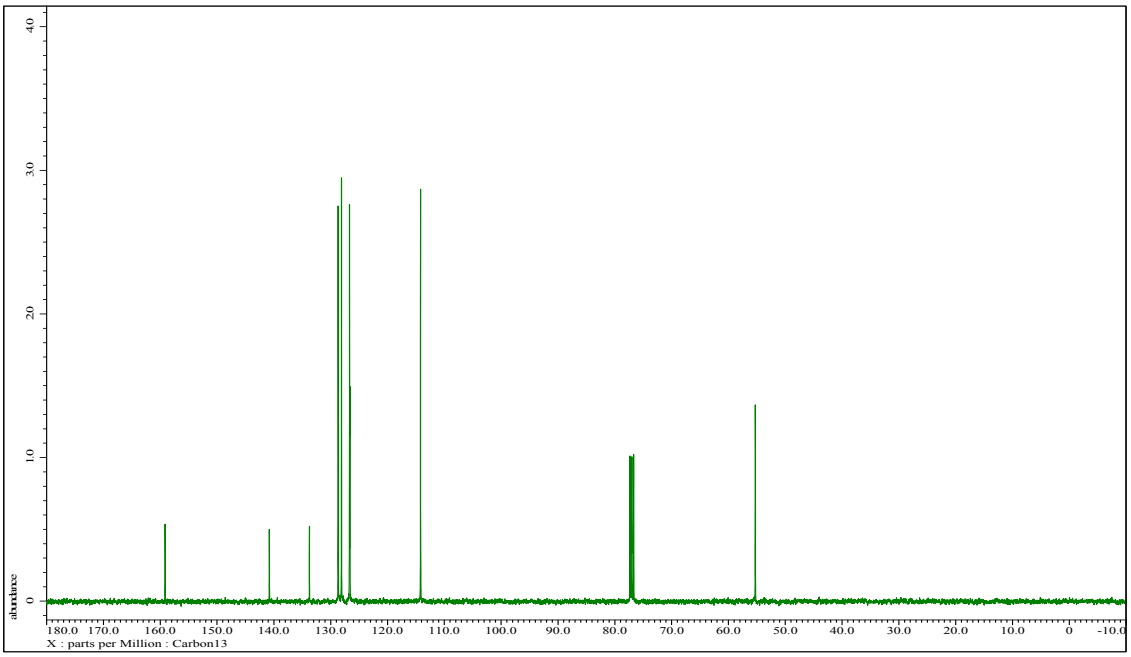




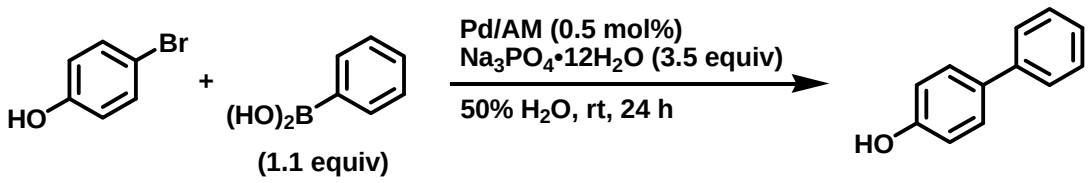
4-Methoxybiphenyl (Table 2, Entry 14)

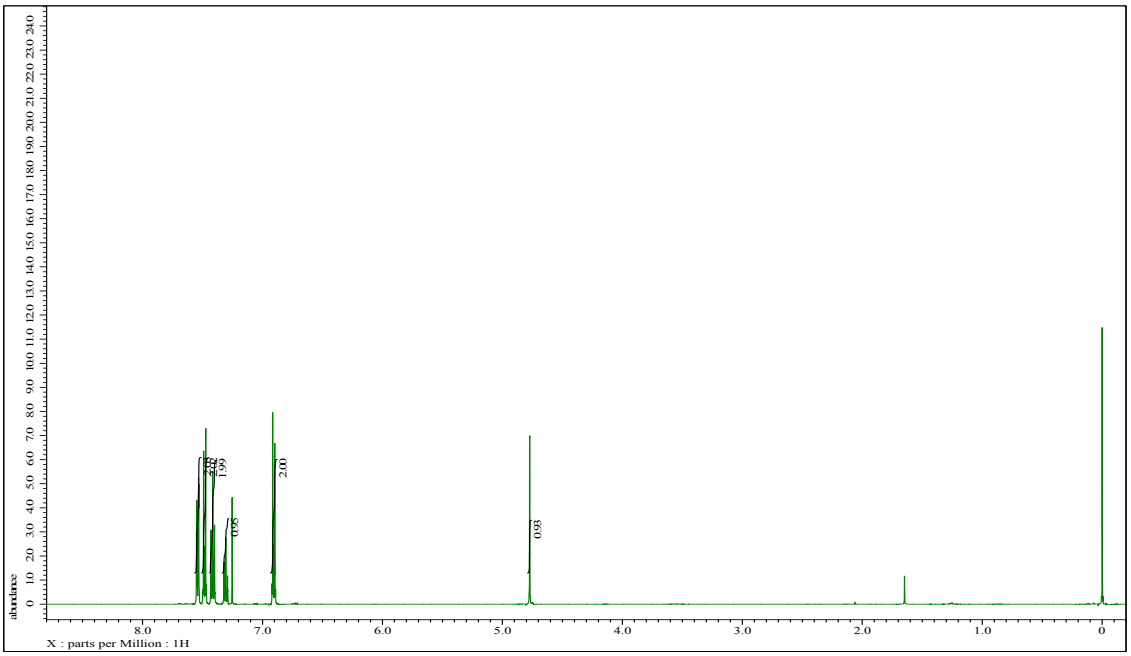


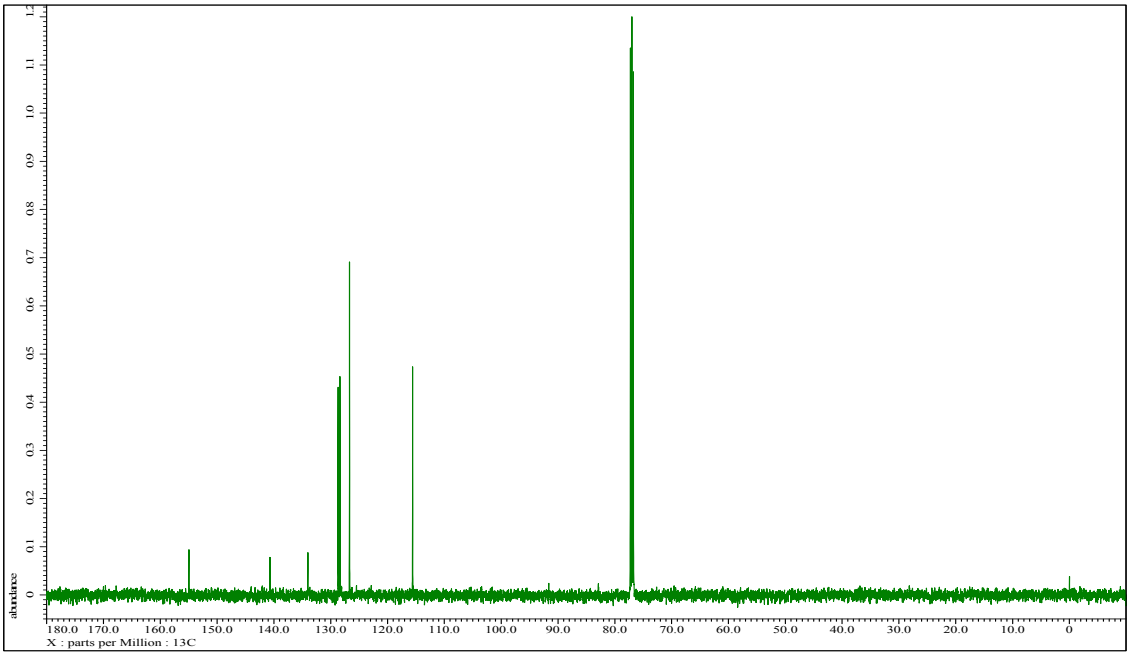




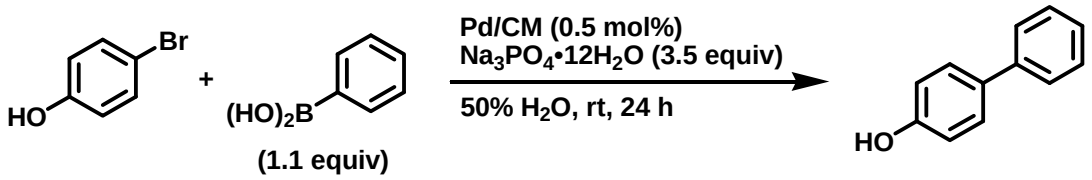
4-Hydroxybiphenyl (Table 2, Entry 16)

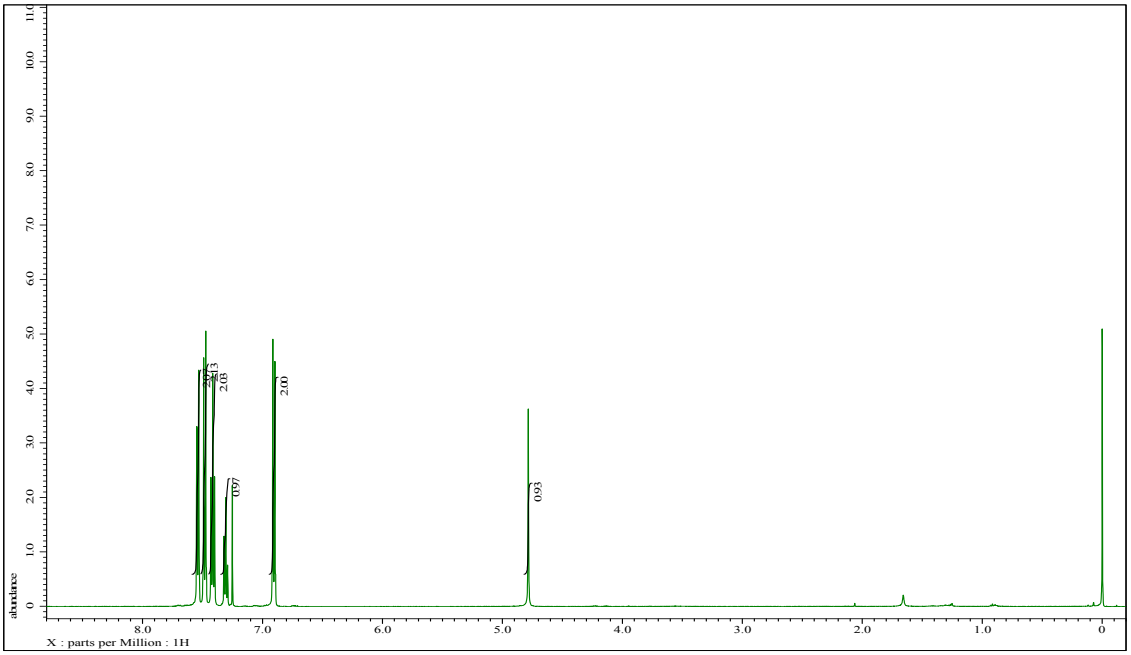


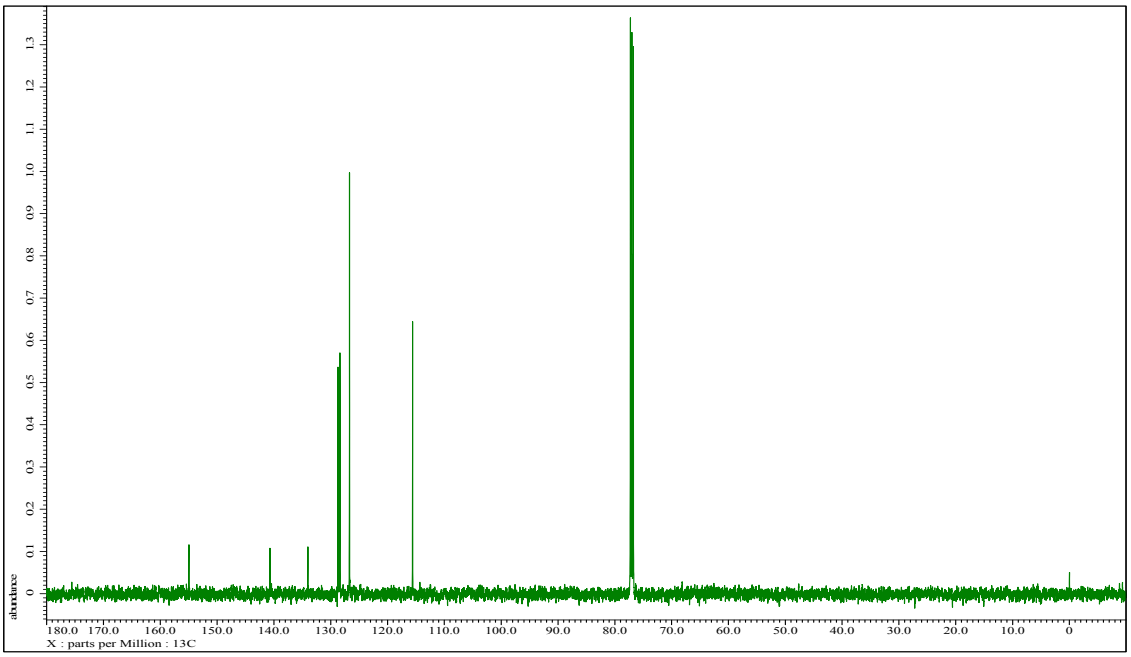




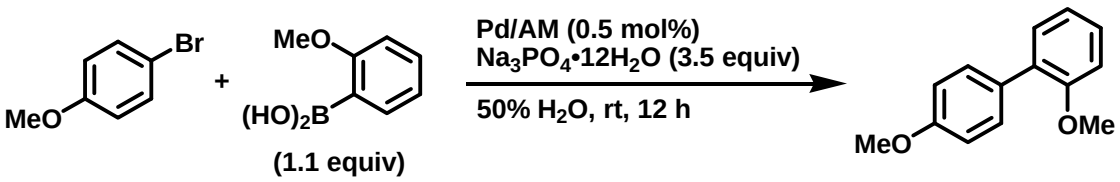
4-Hydroxybiphenyl (Table 2, Entry 17)

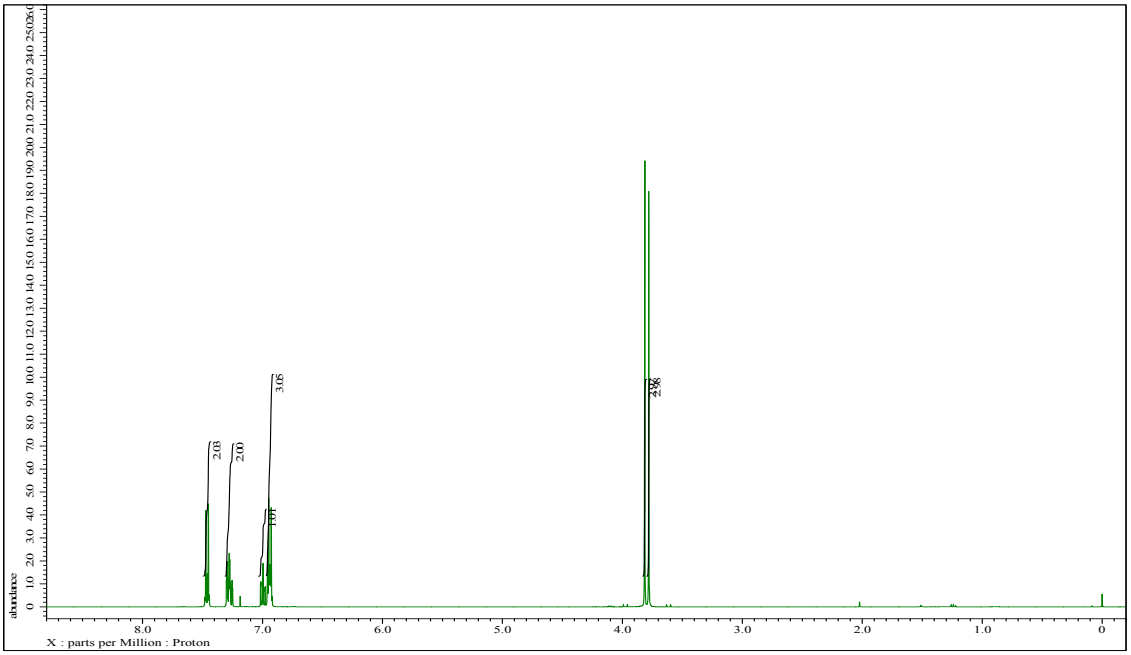


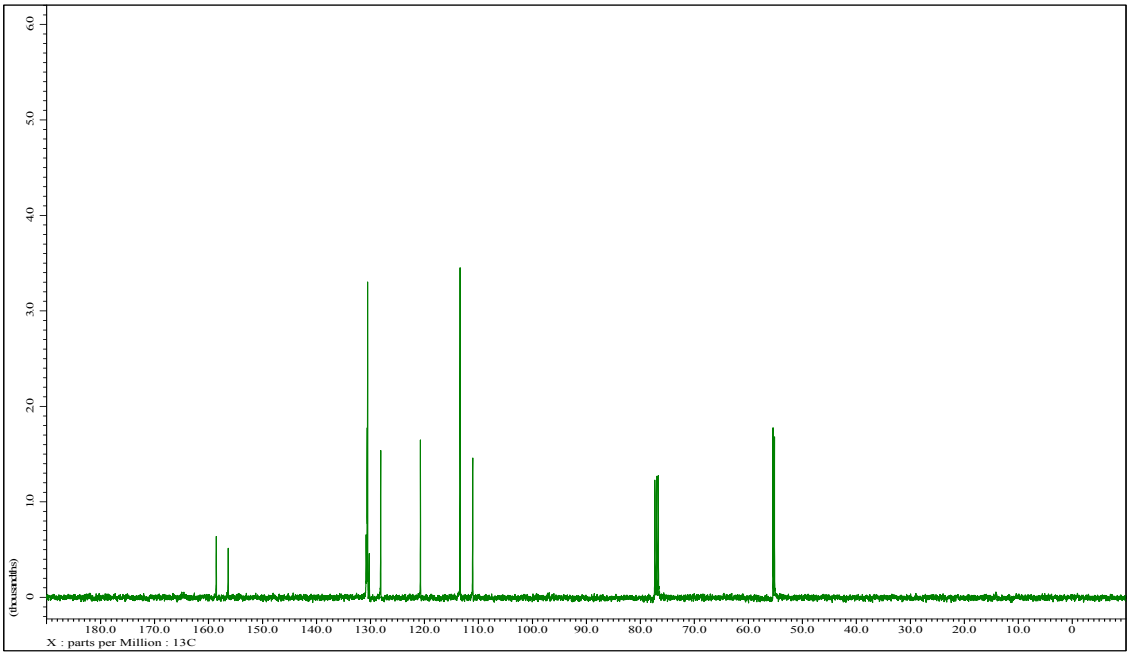




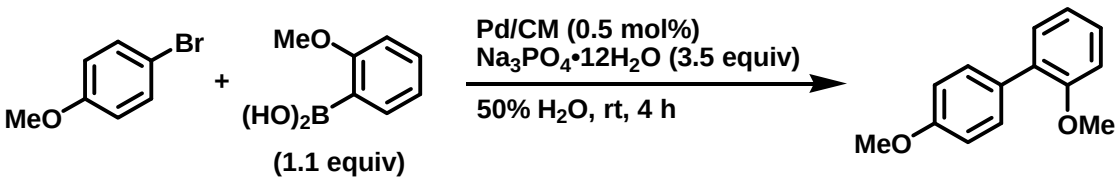
2,4'-Dimethoxybiphenyl (Table 2, Entry 19)

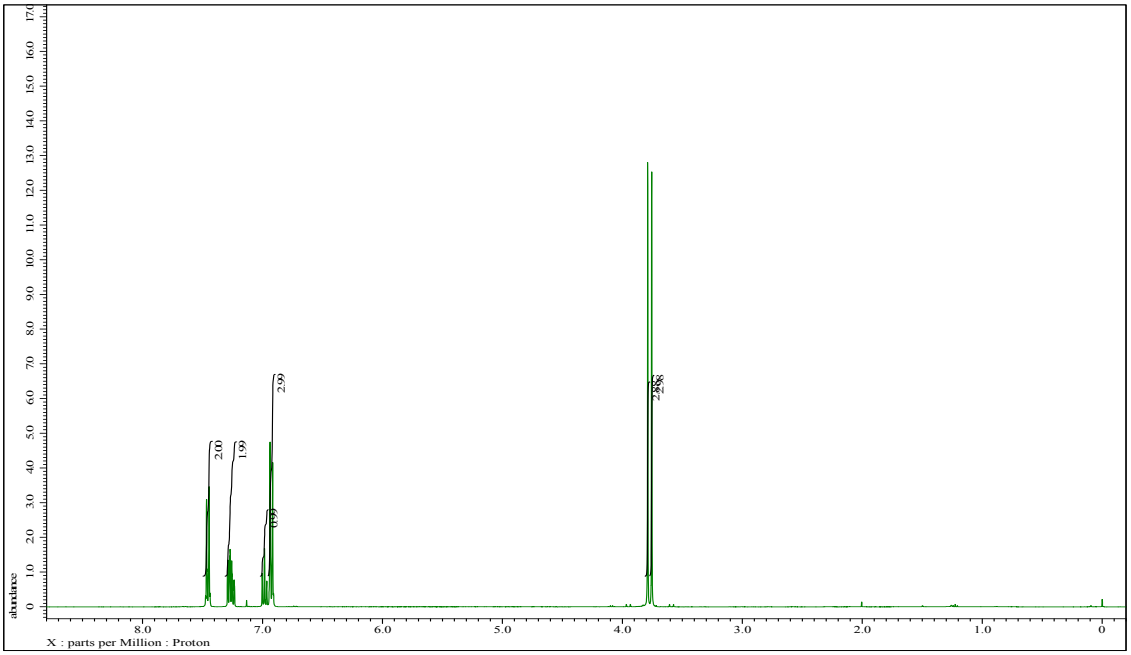


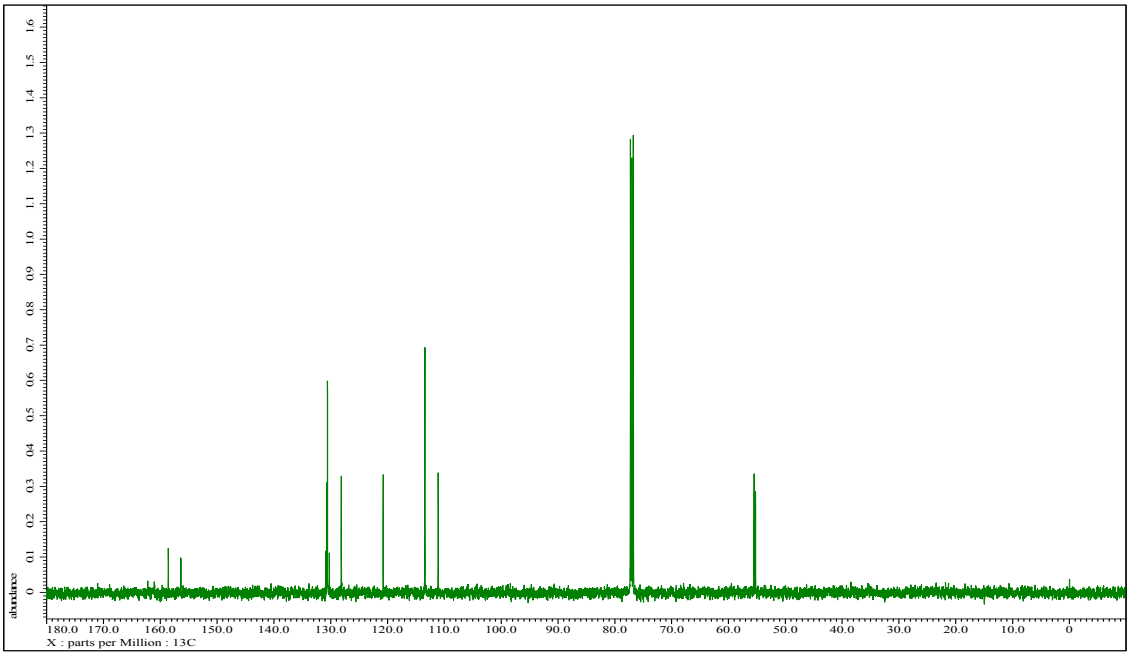




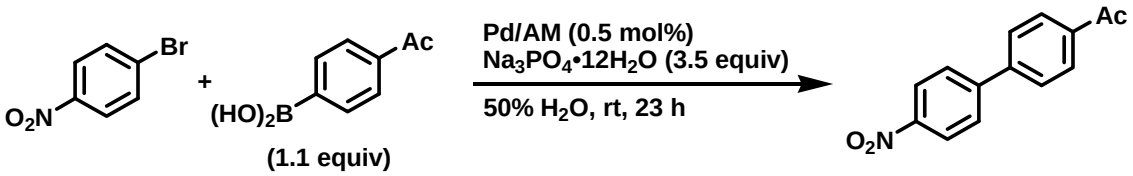
2,4'-Dimethoxybiphenyl (Table 2, Entry 20)

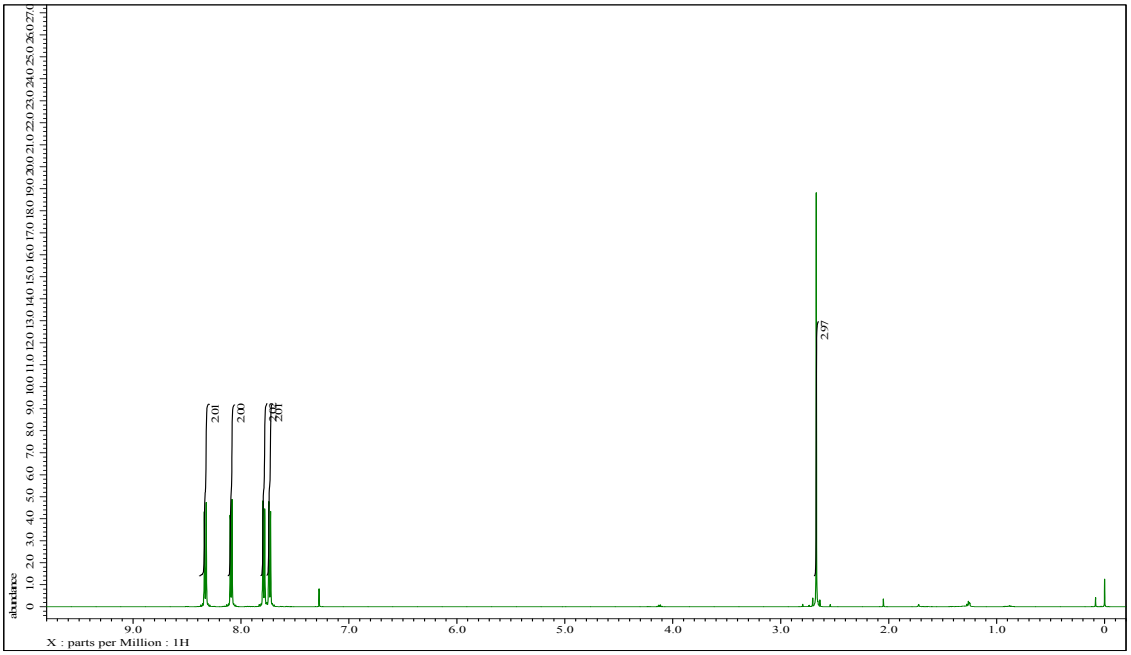


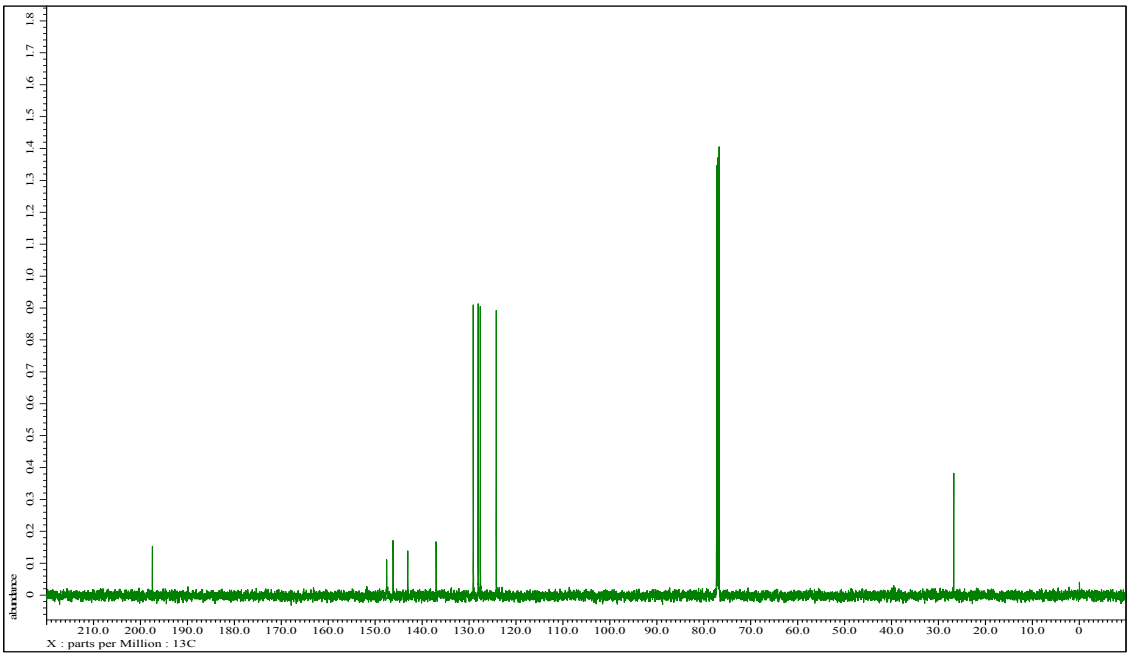




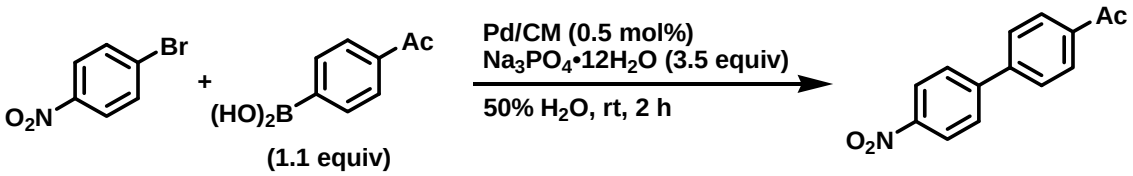
4-Acetyl-4'-nitrobiphenyl (Table 2, Entry 22)

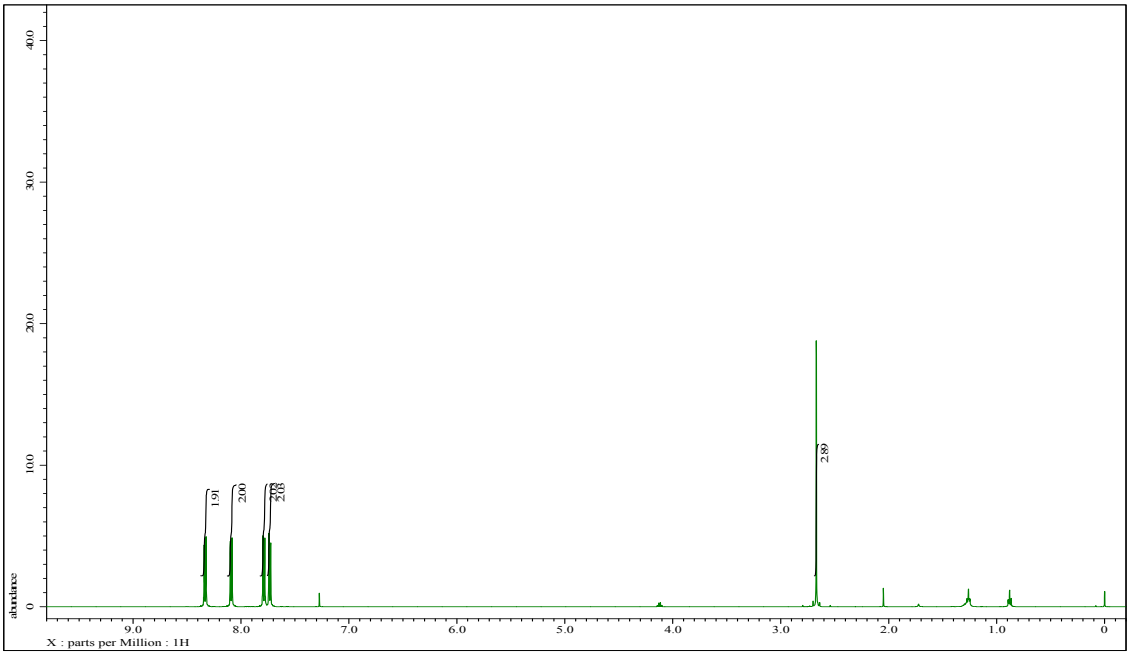


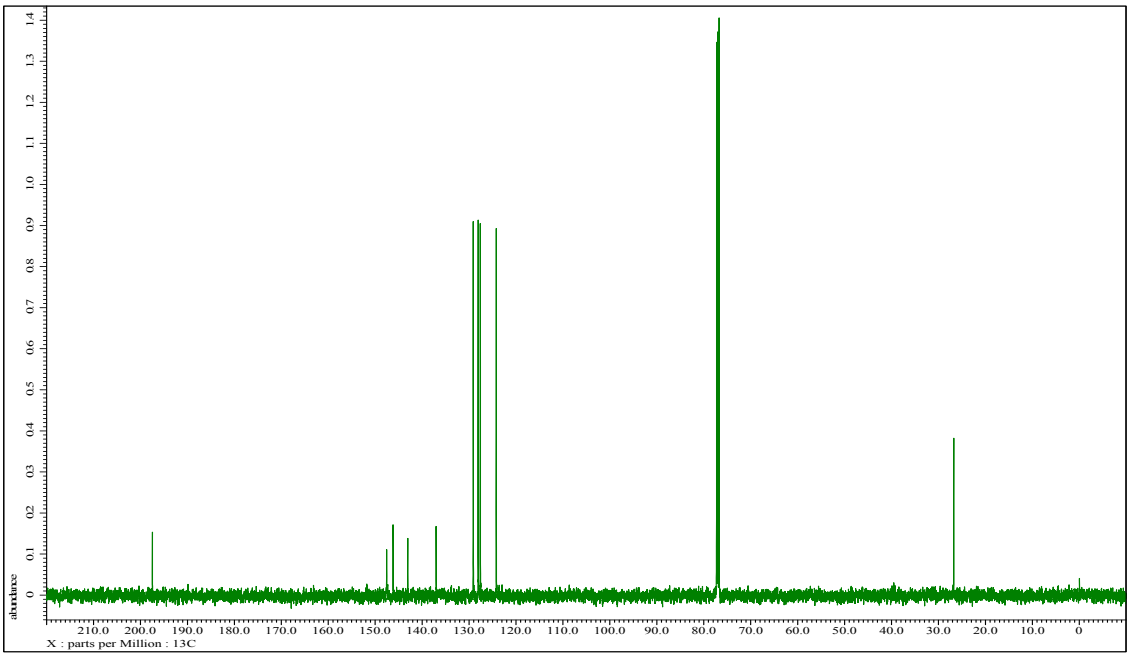




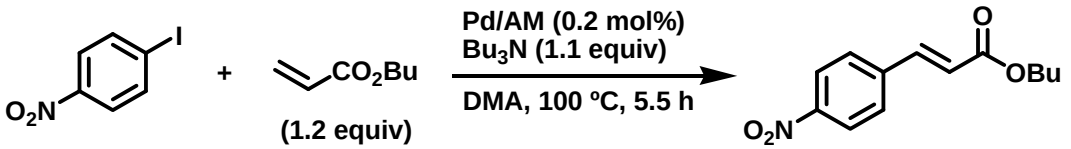
4-Acetyl-4'-nitrobiphenyl (Table 2, Entry 23)

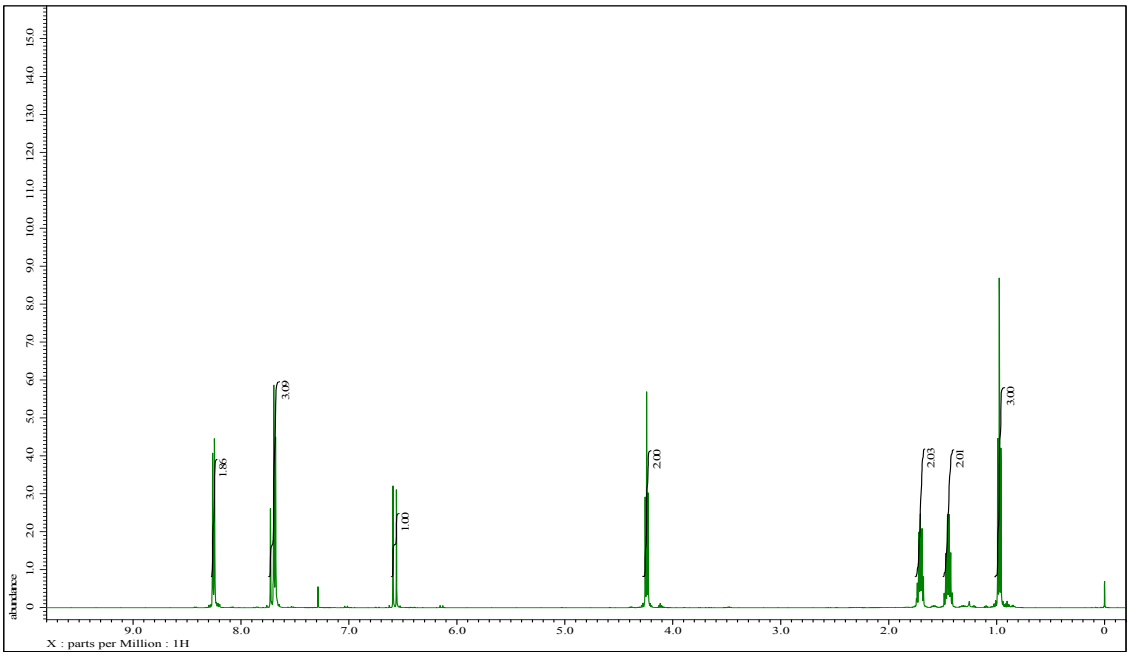


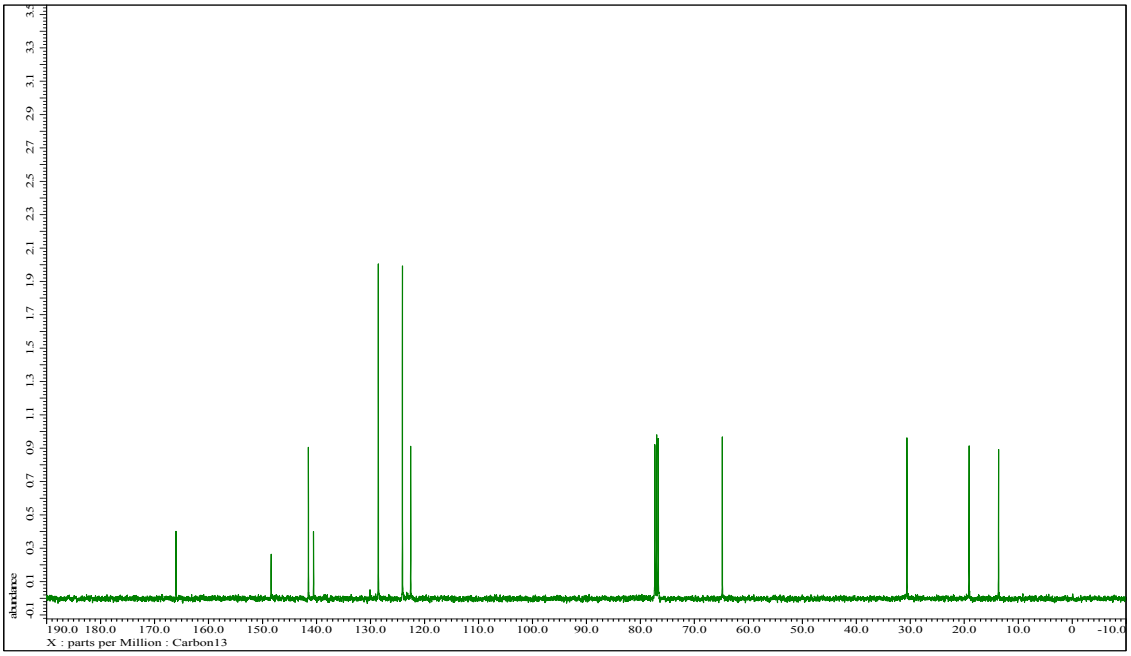




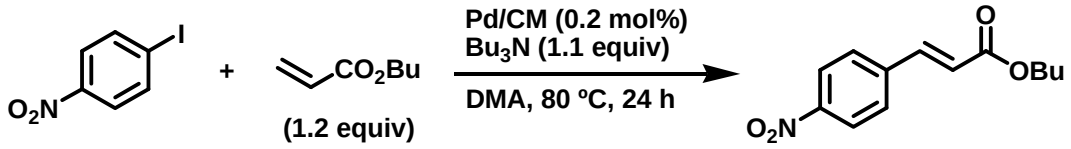
Butyl (*E*)-4-Nitrocinnamate (Table 3, Entry 1)

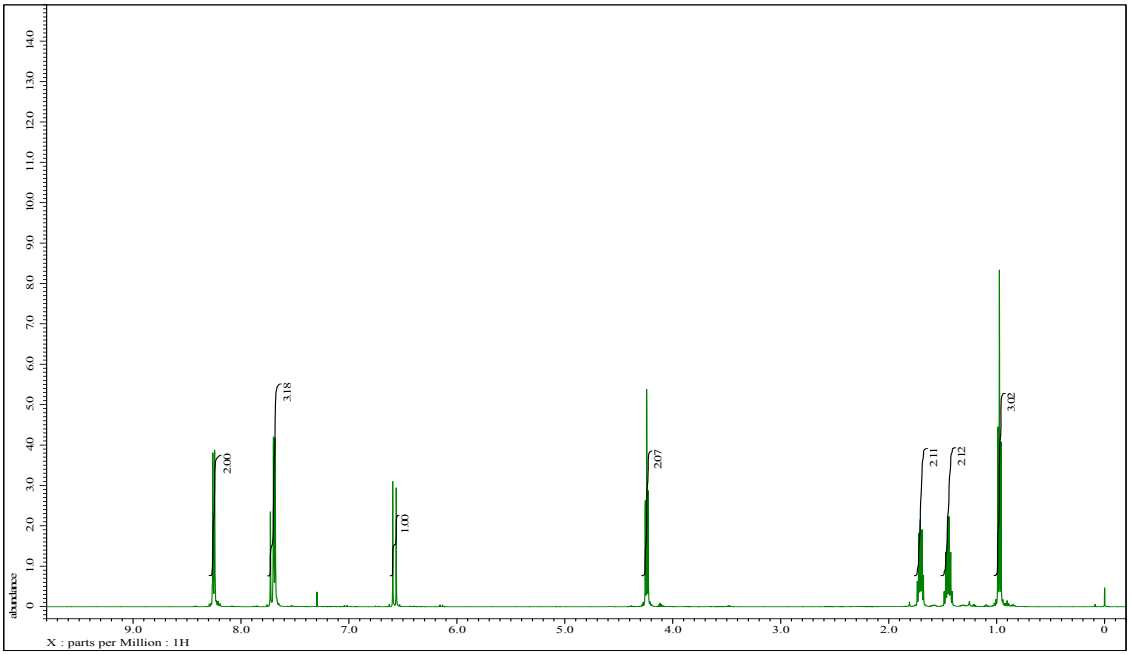


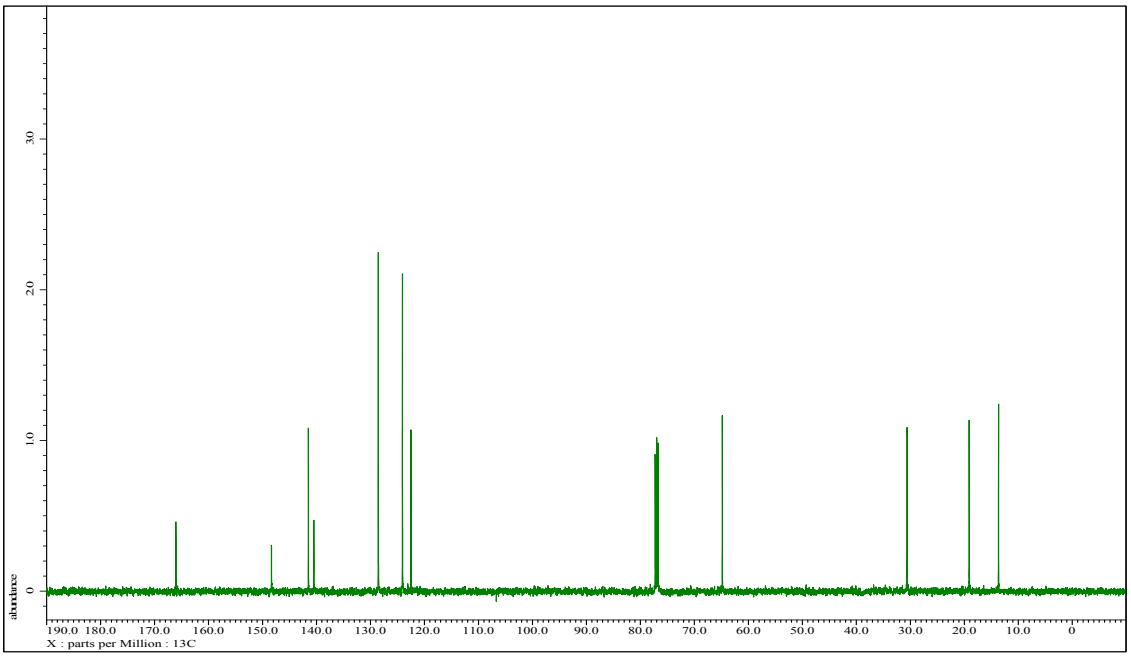




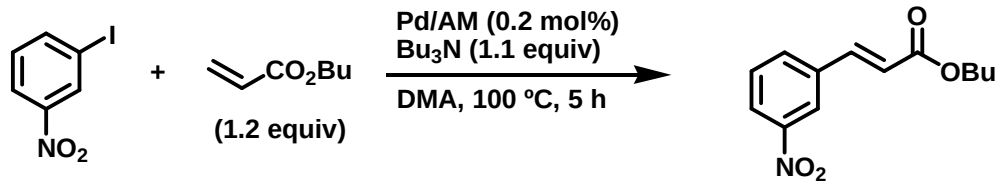
Butyl (*E*)-4-Nitrocinnamate (Table 3, Entry 2)

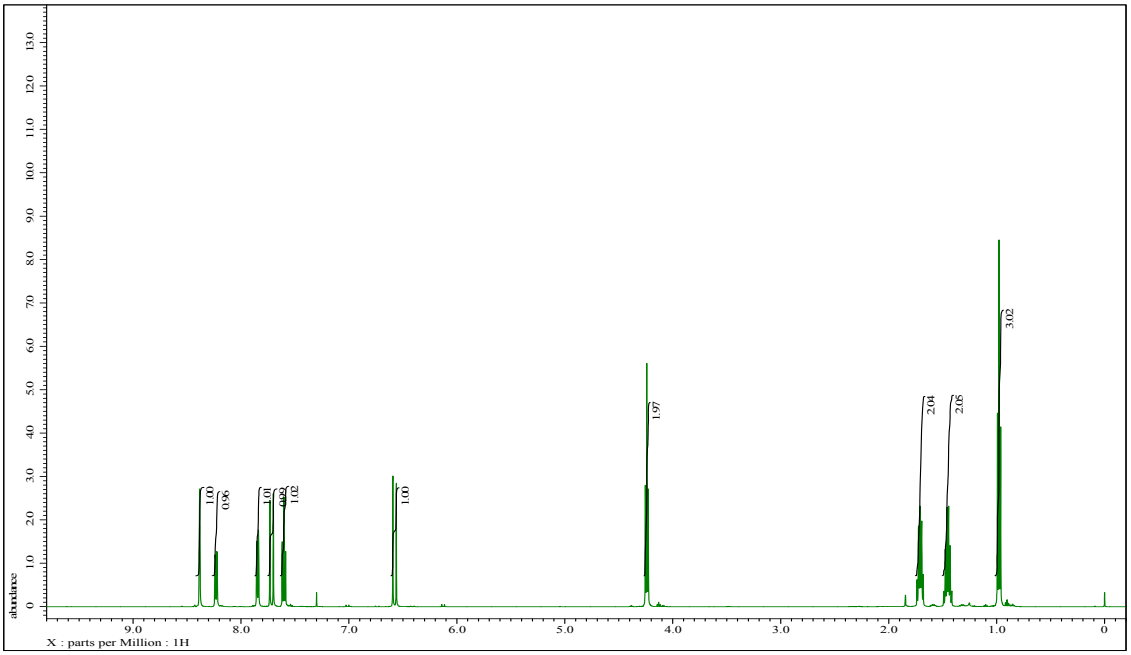


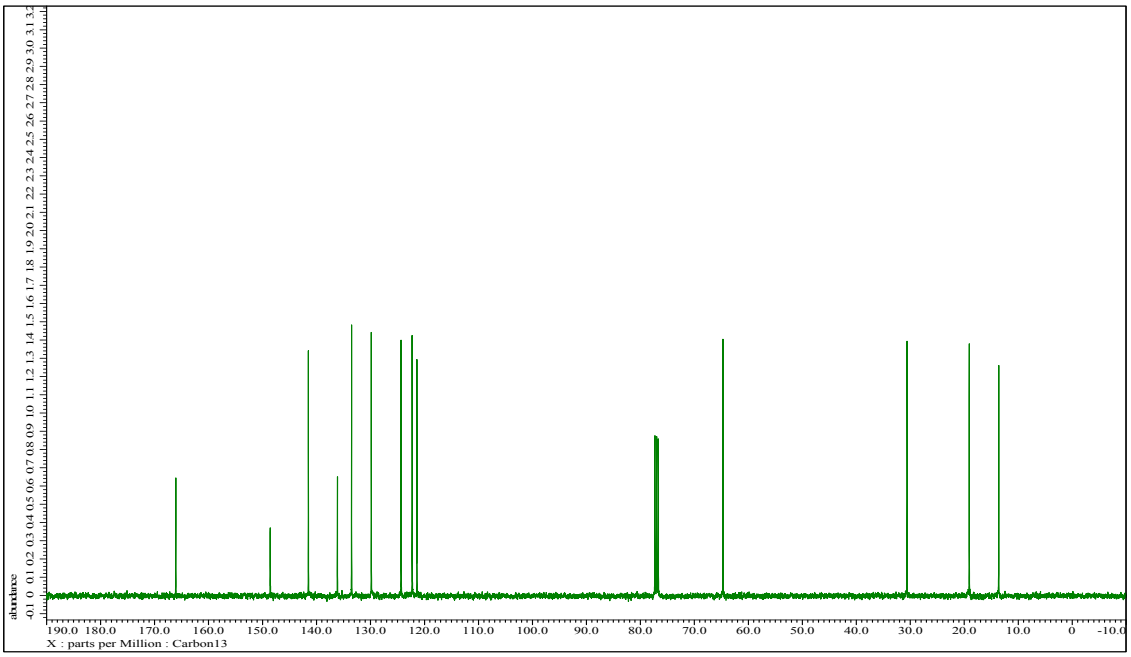




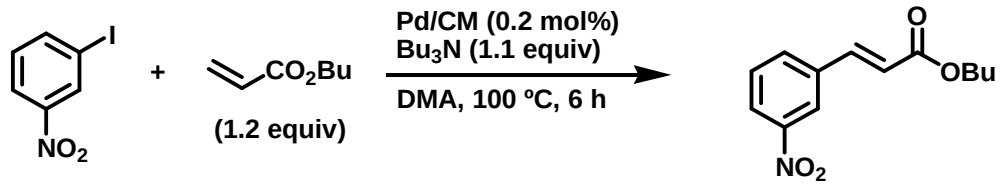
Butyl (*E*)-3-Nitrocinnamate (Table 3, Entry 4)

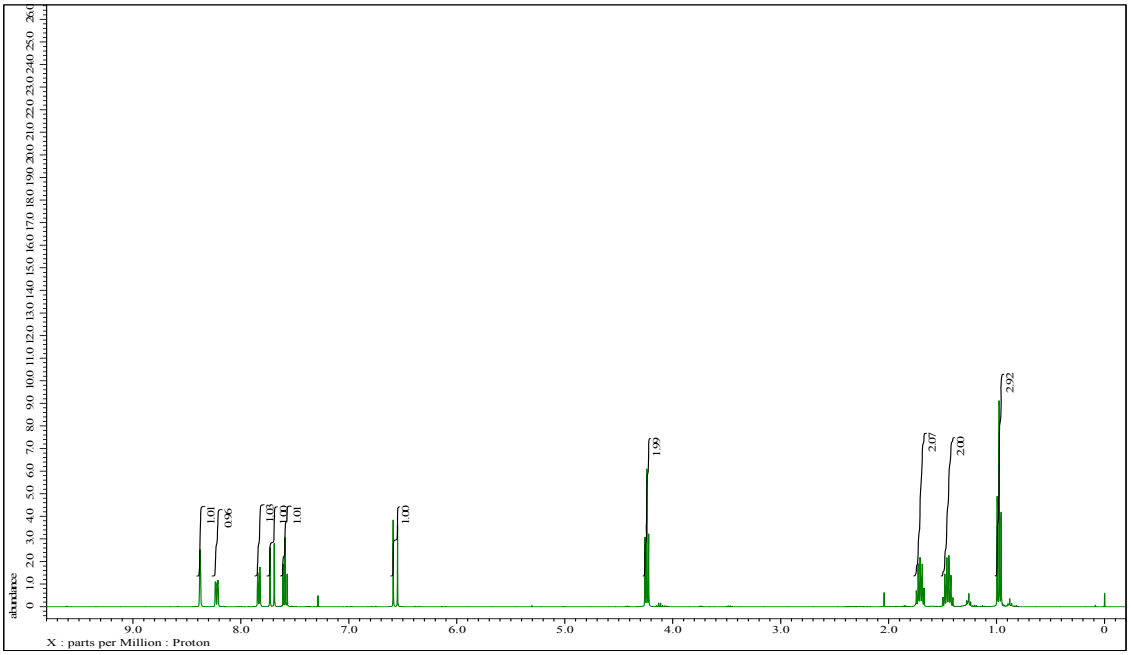


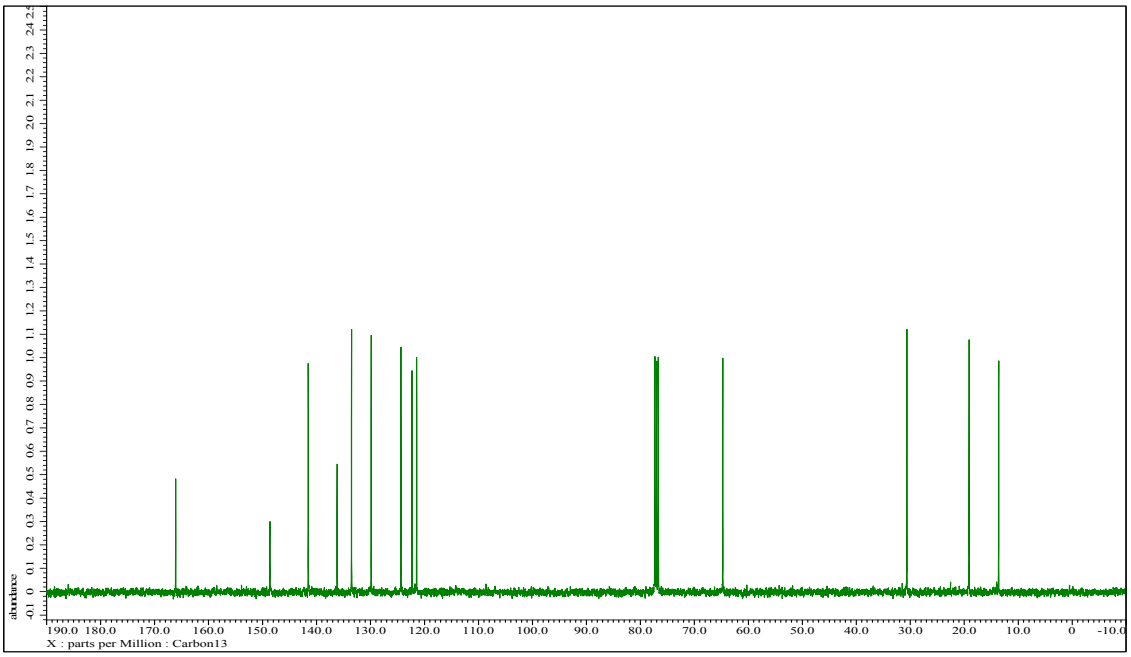




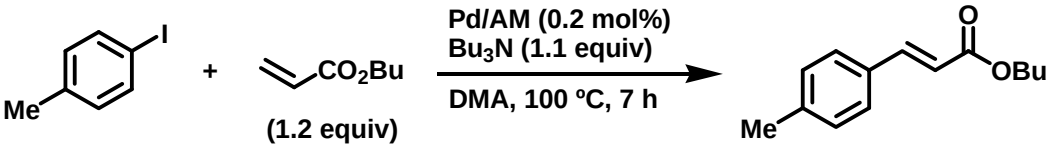
Butyl (*E*)-3-Nitrocinnamate (Table 3, Entry 5)

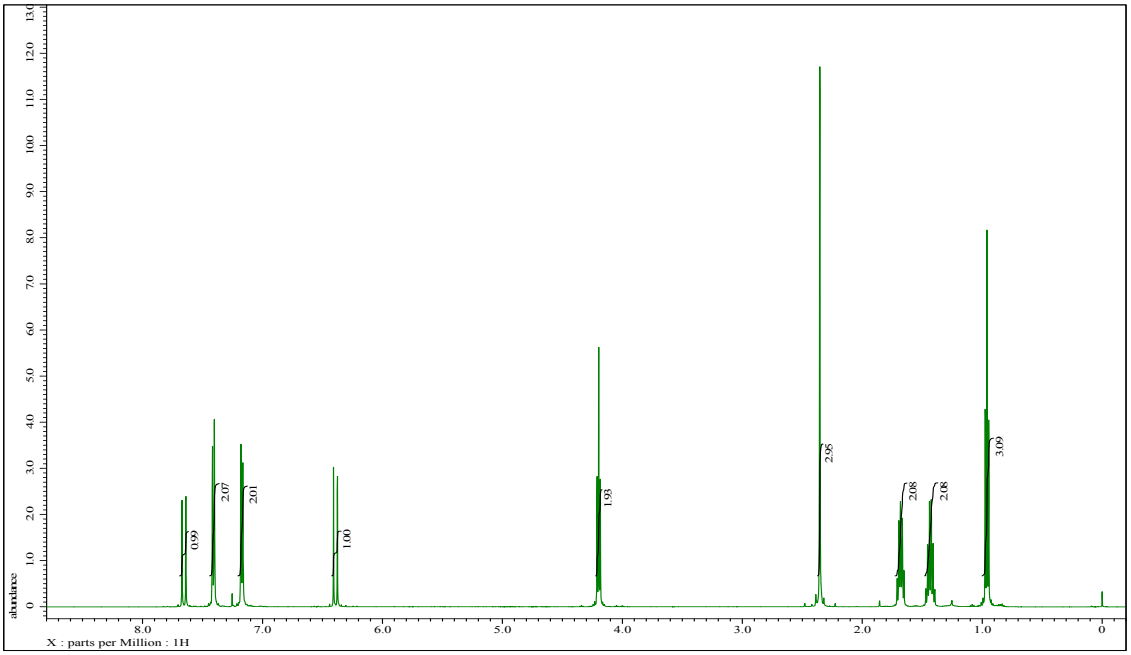


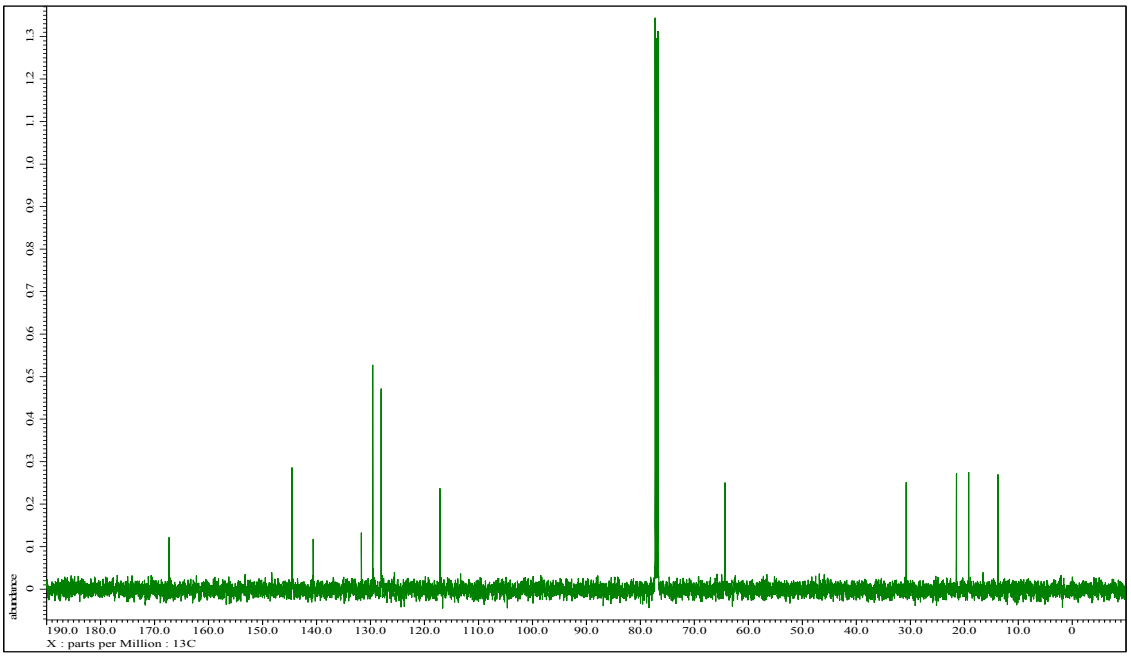




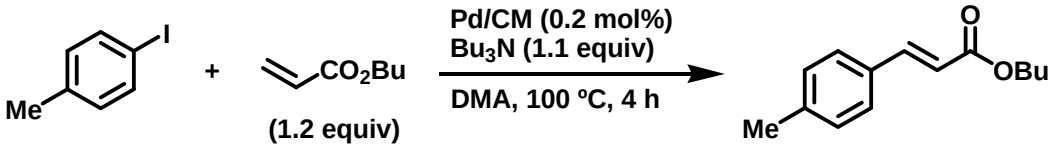
Butyl (*E*)-4-Methylcinnamate (Table 3, Entry 7)

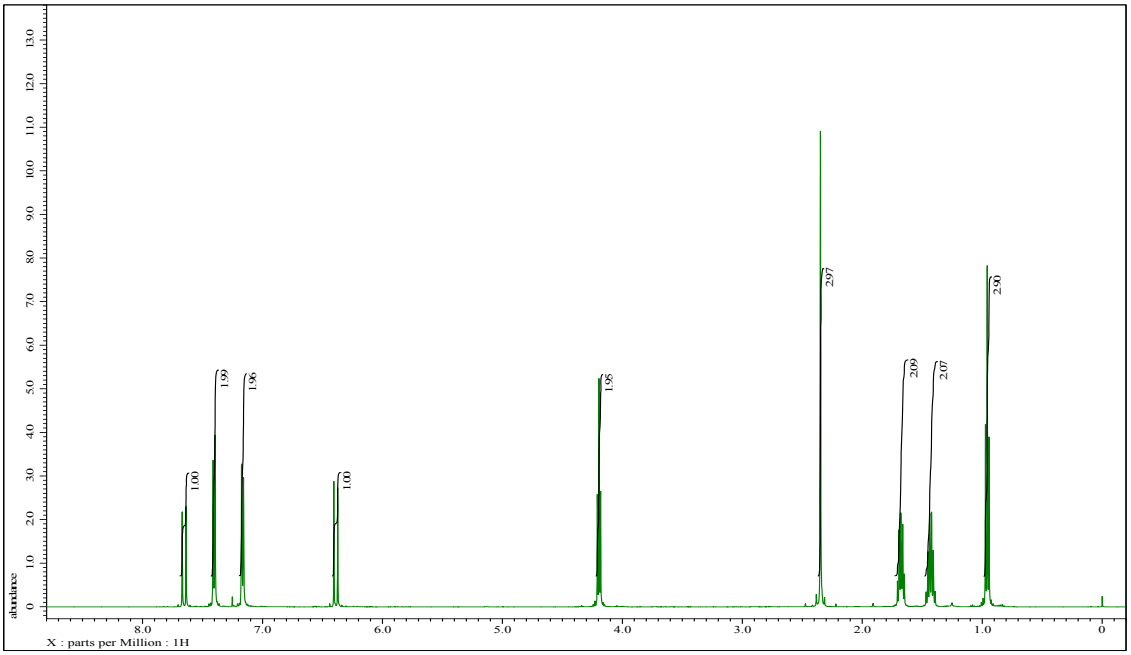


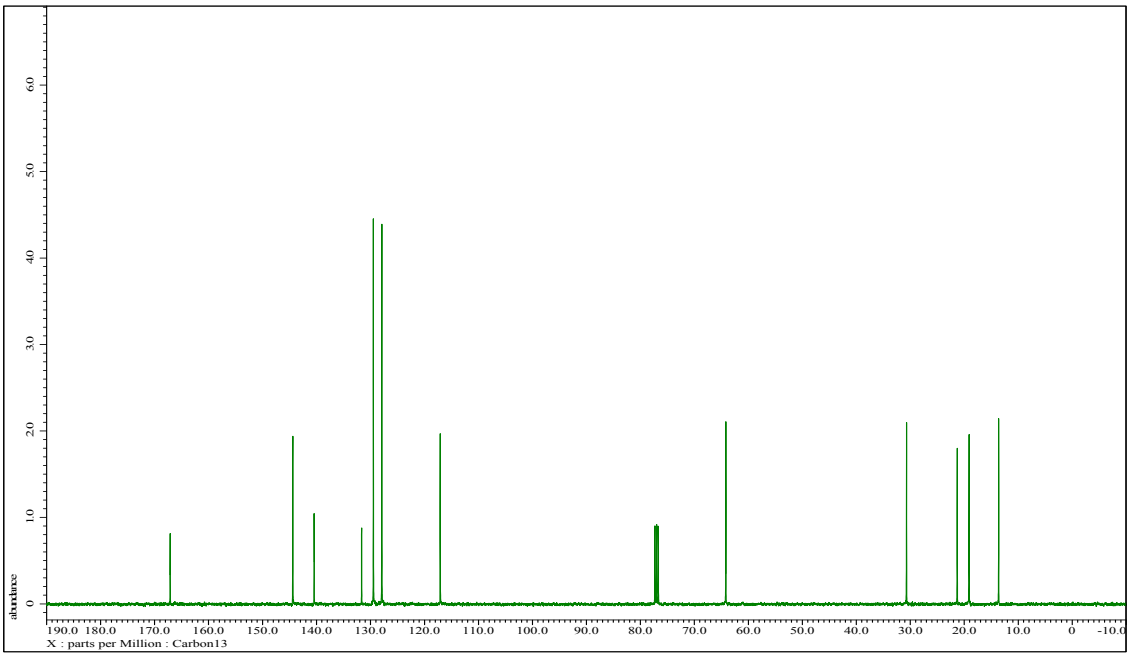




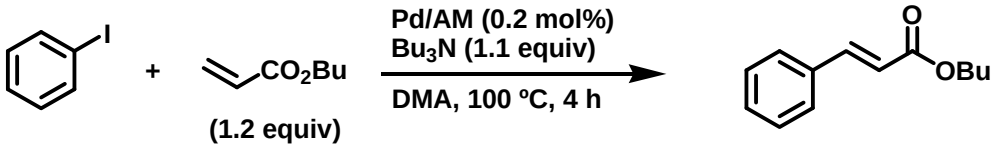
Butyl (*E*)-4-Methylcinnamate (Table 3, Entry 8)

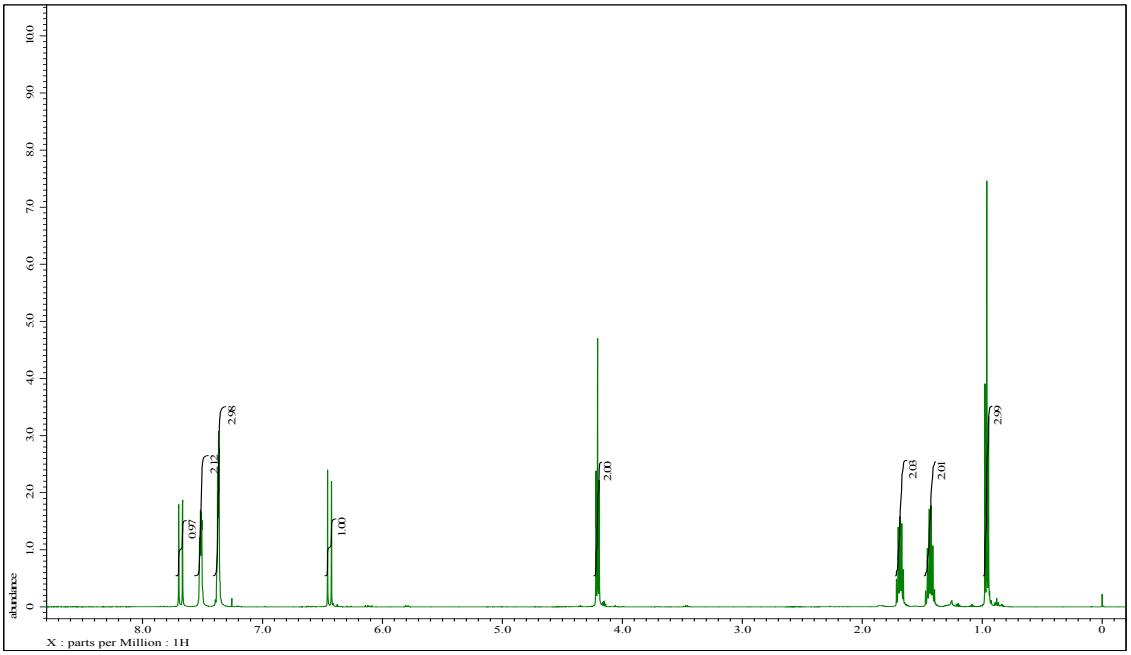


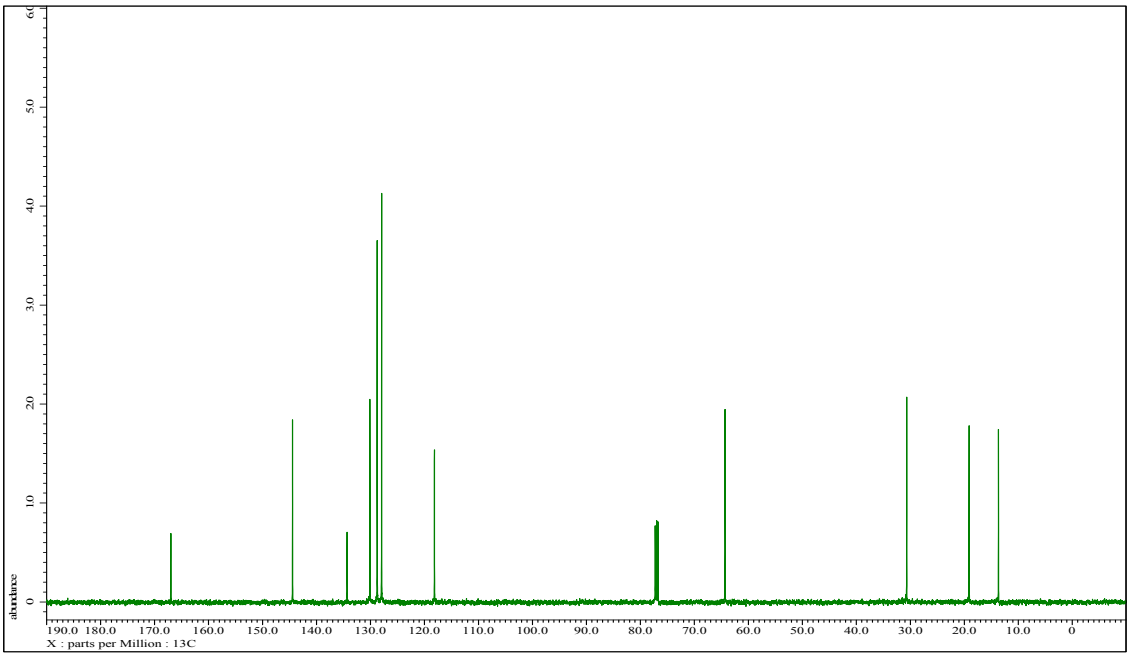




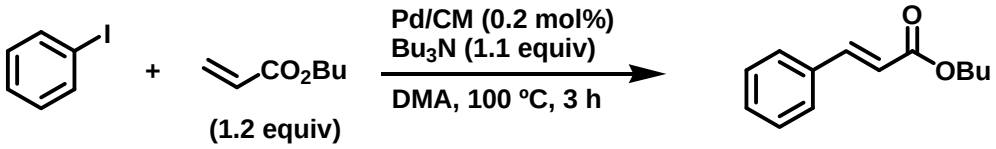
Butyl (*E*)-Cinnamate (Table 3, Entry 10)

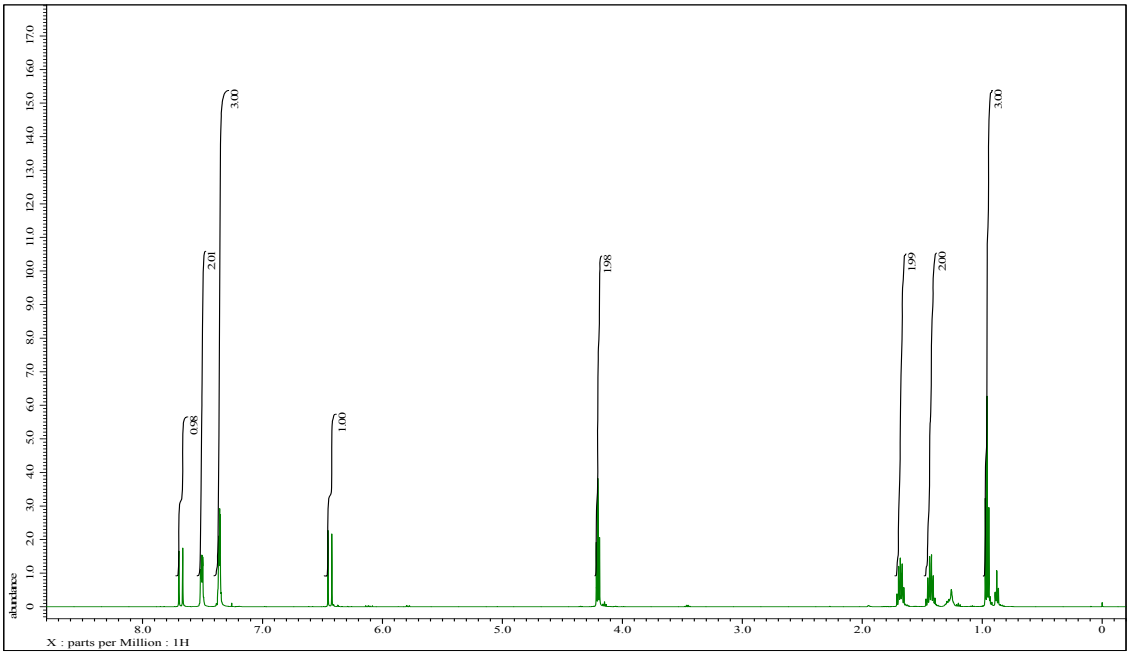


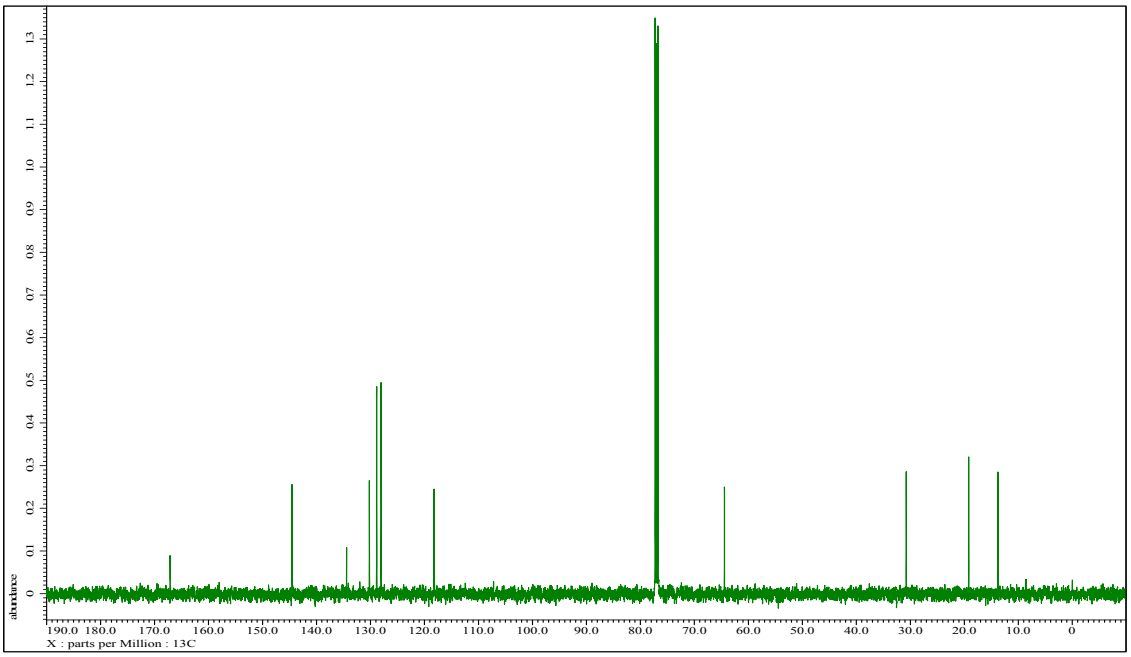




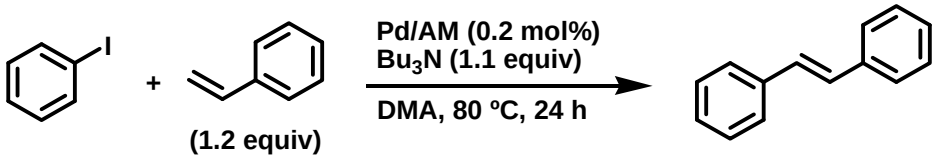
Butyl (*E*)-Cinnamate (Table 3, Entry 11)

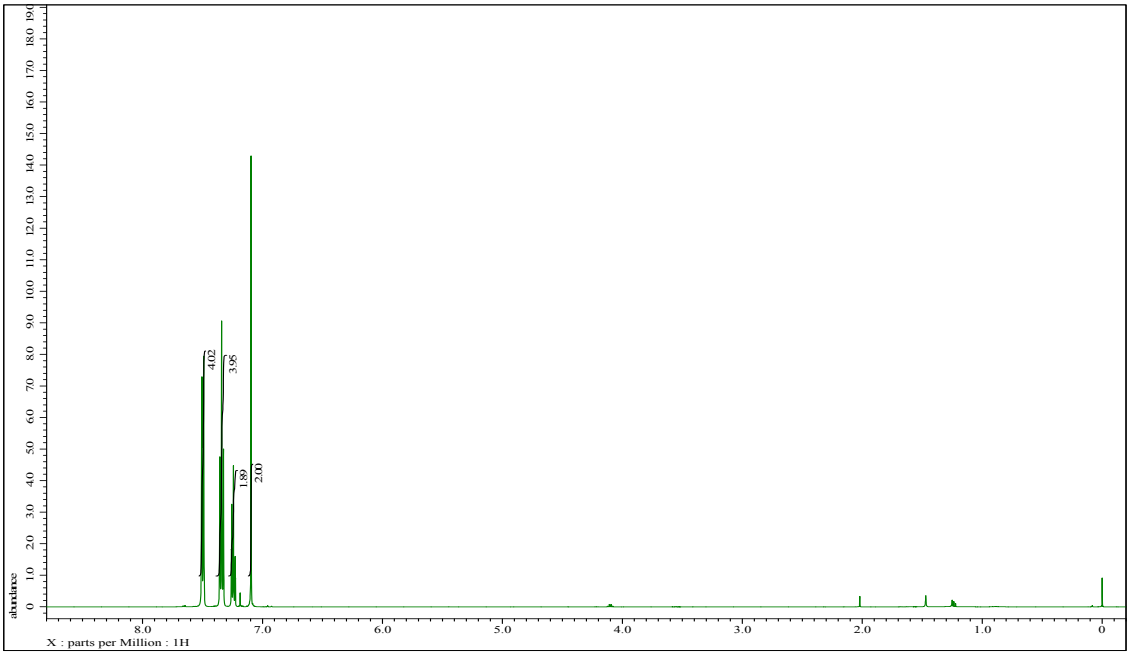


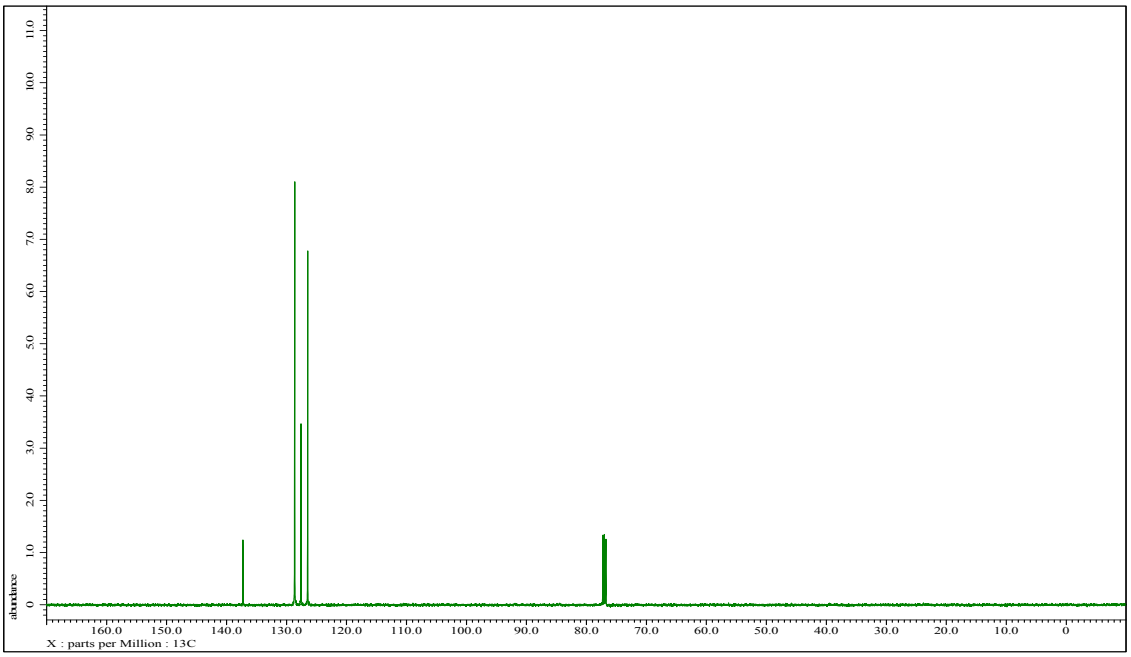




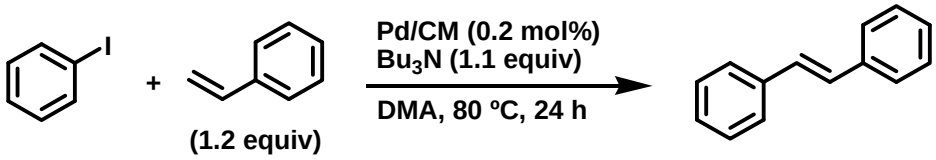
(*E*)-Stilbene (Table 3, Entry 13)

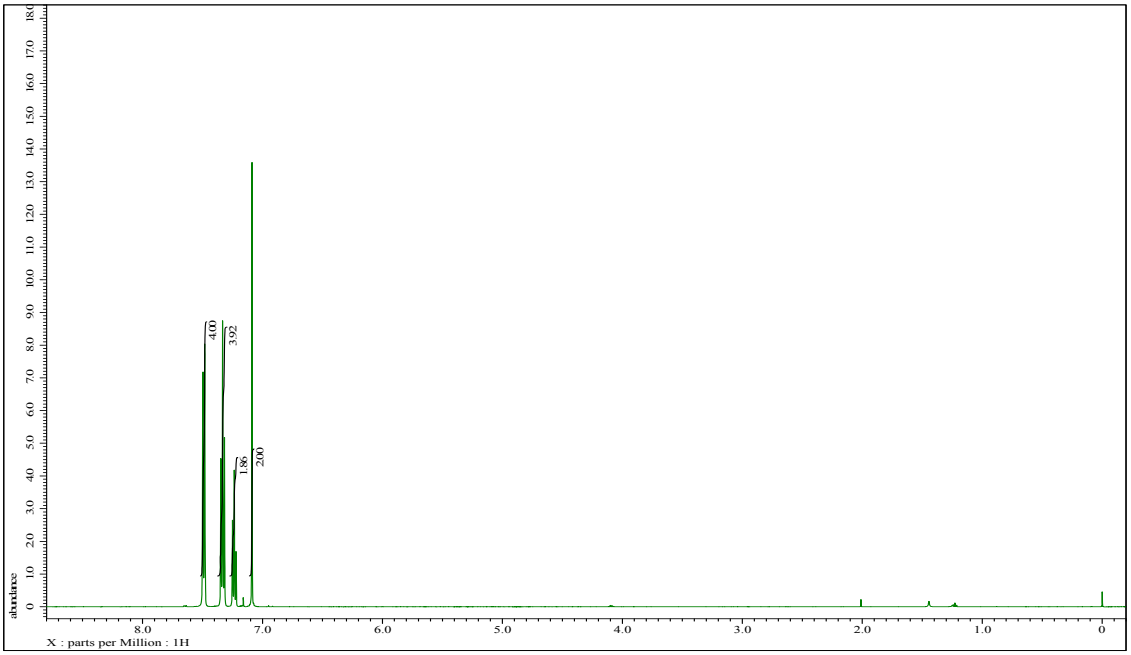


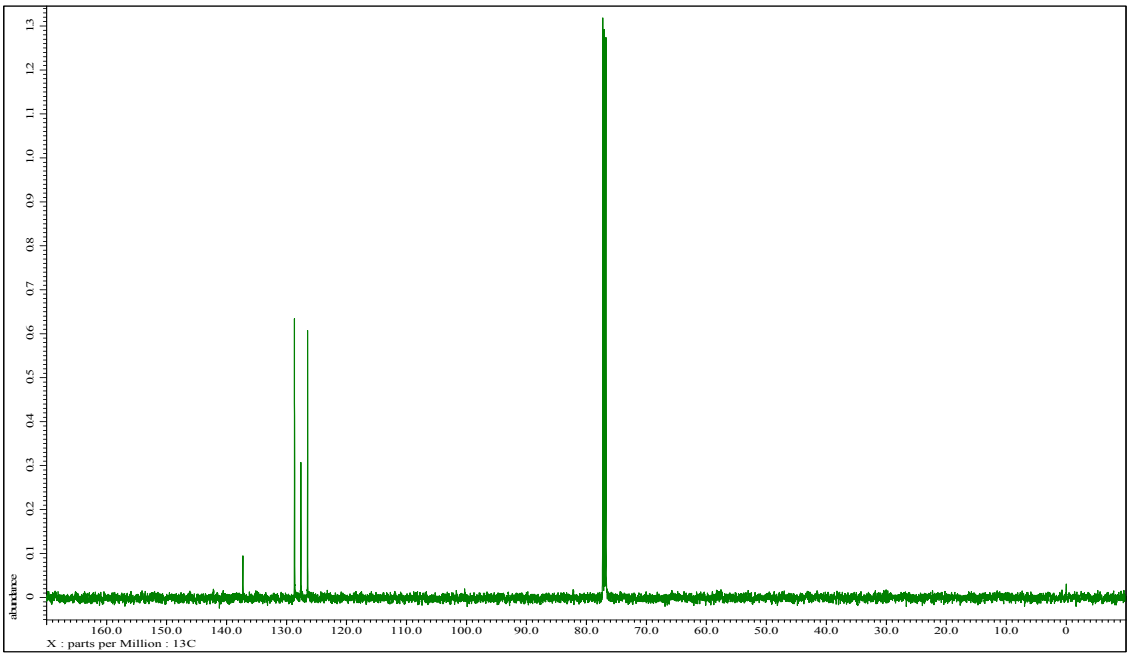




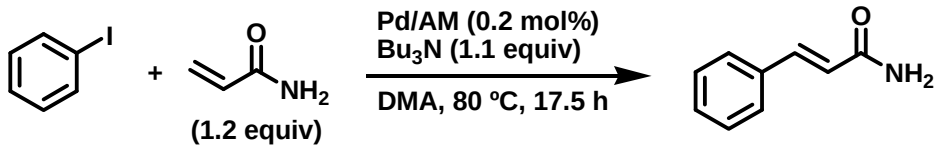
(*E*)-Stilbene (Table 3, Entry 14)

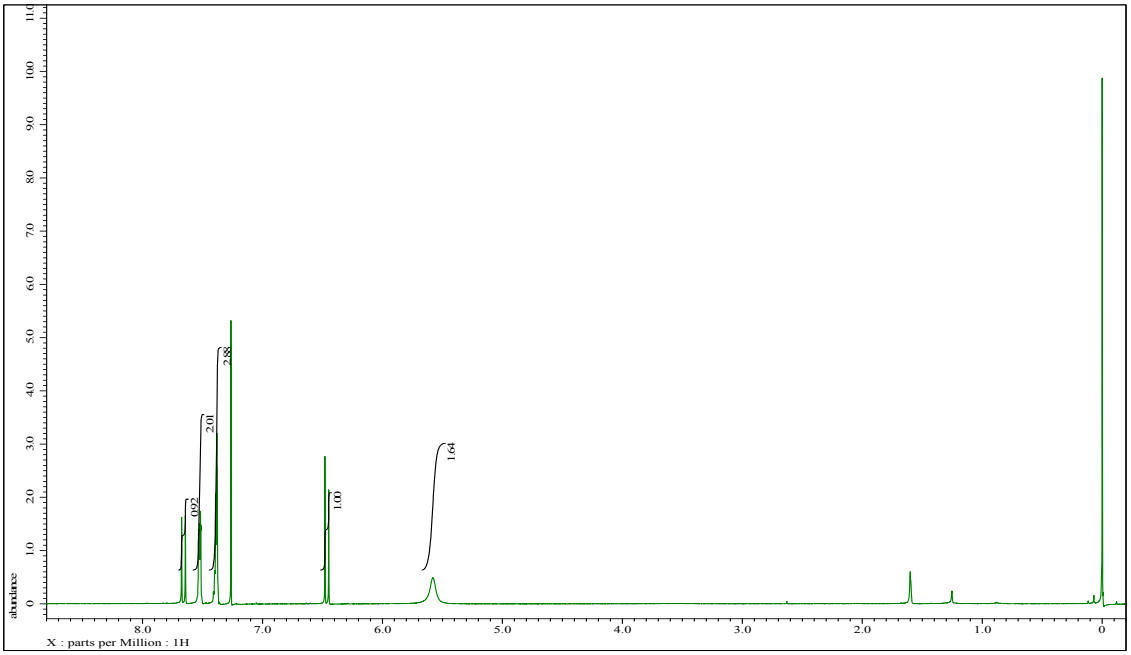


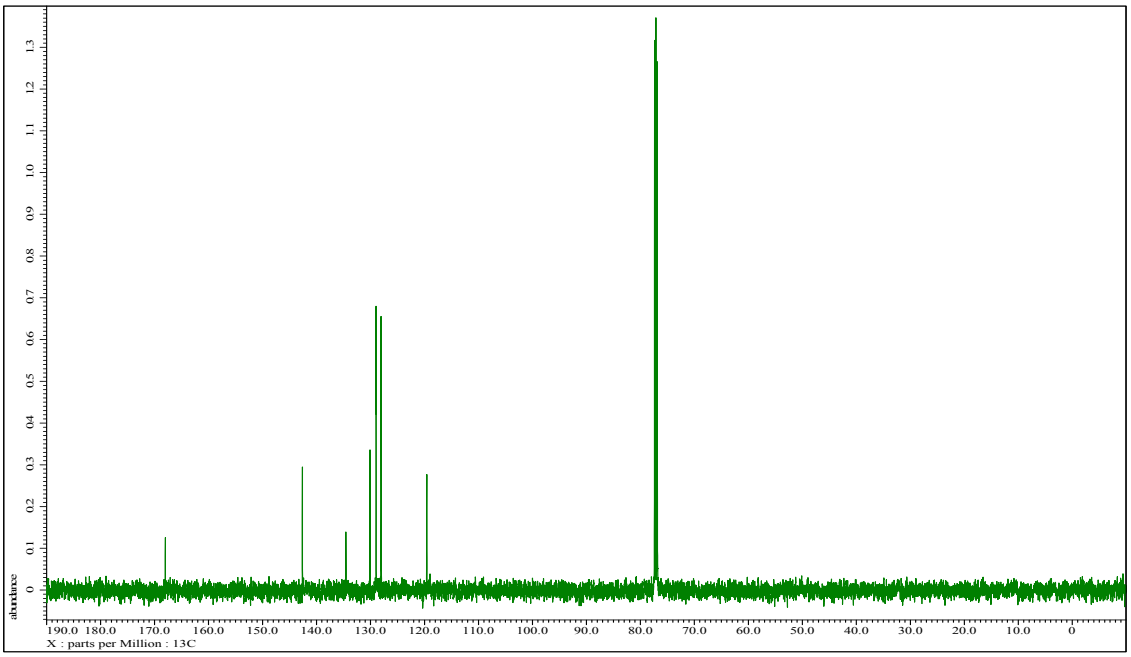




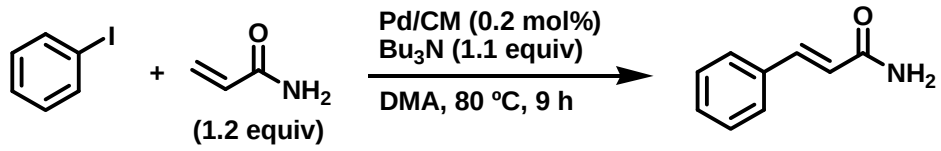
(*E*)-Cinnamamide (Table 3, Entry 16)

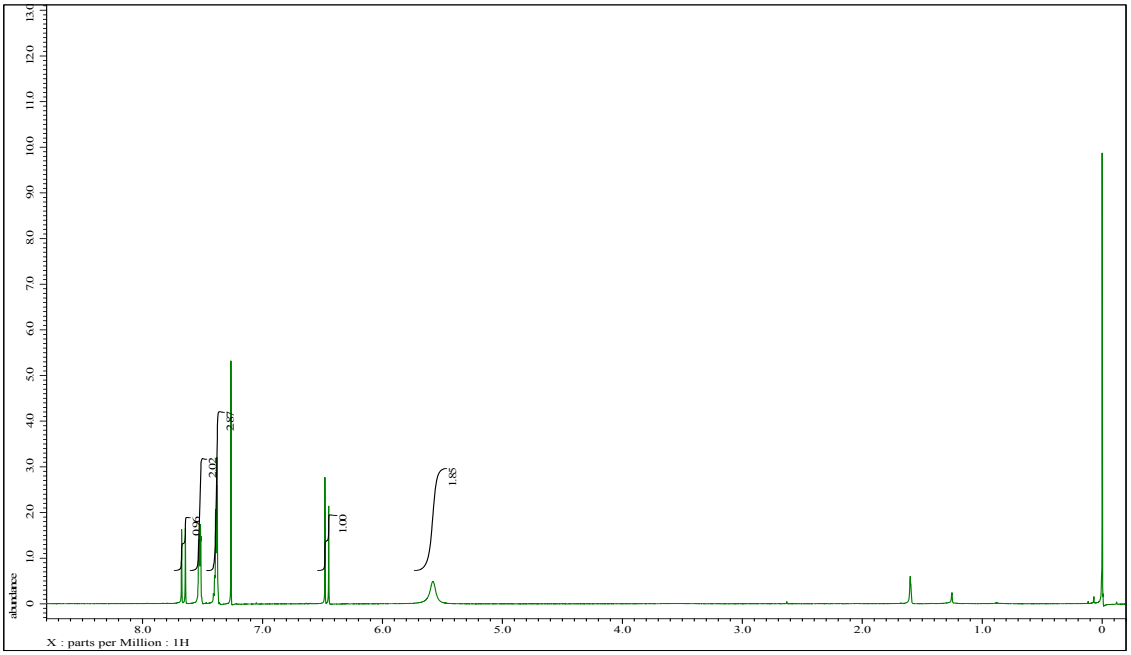


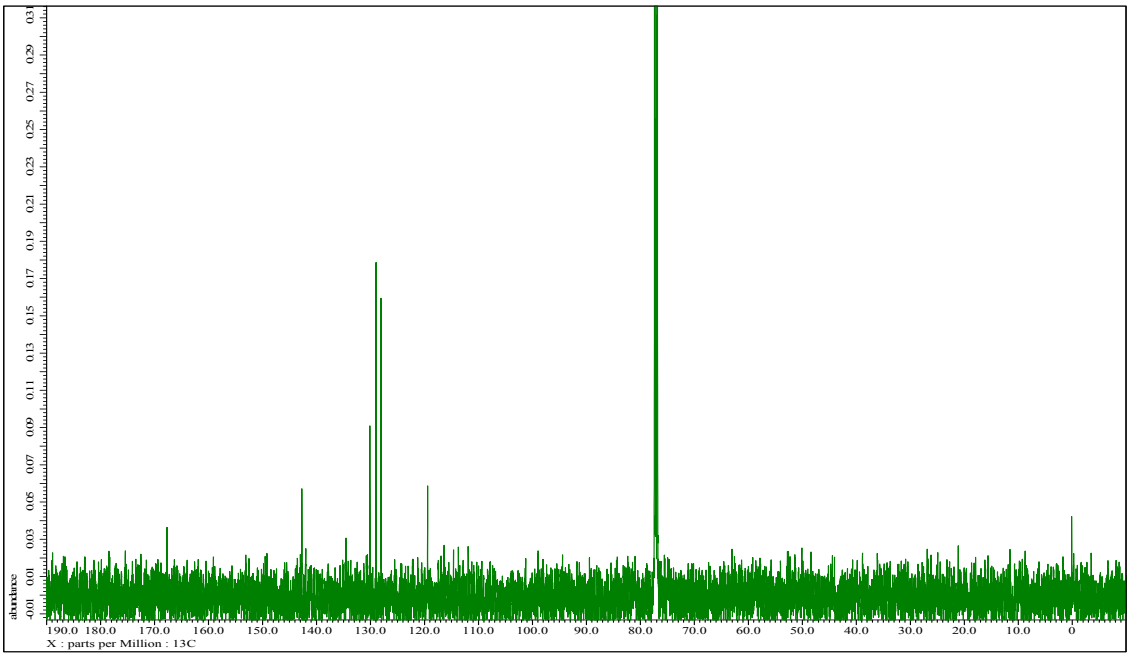




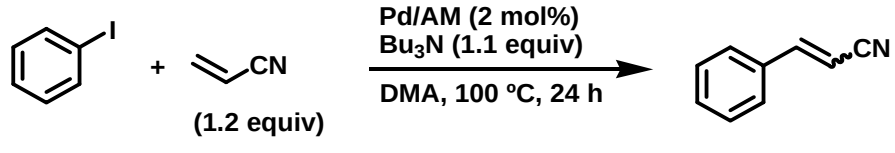
(*E*)-Cinnamamide (Table 3, Entry 17)



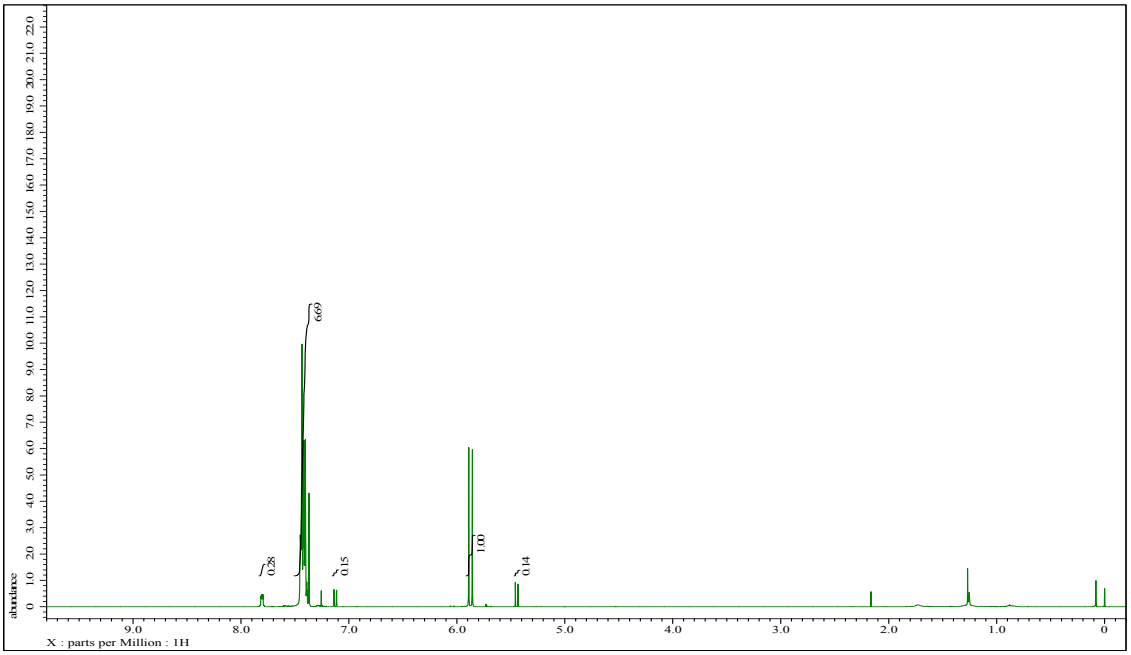


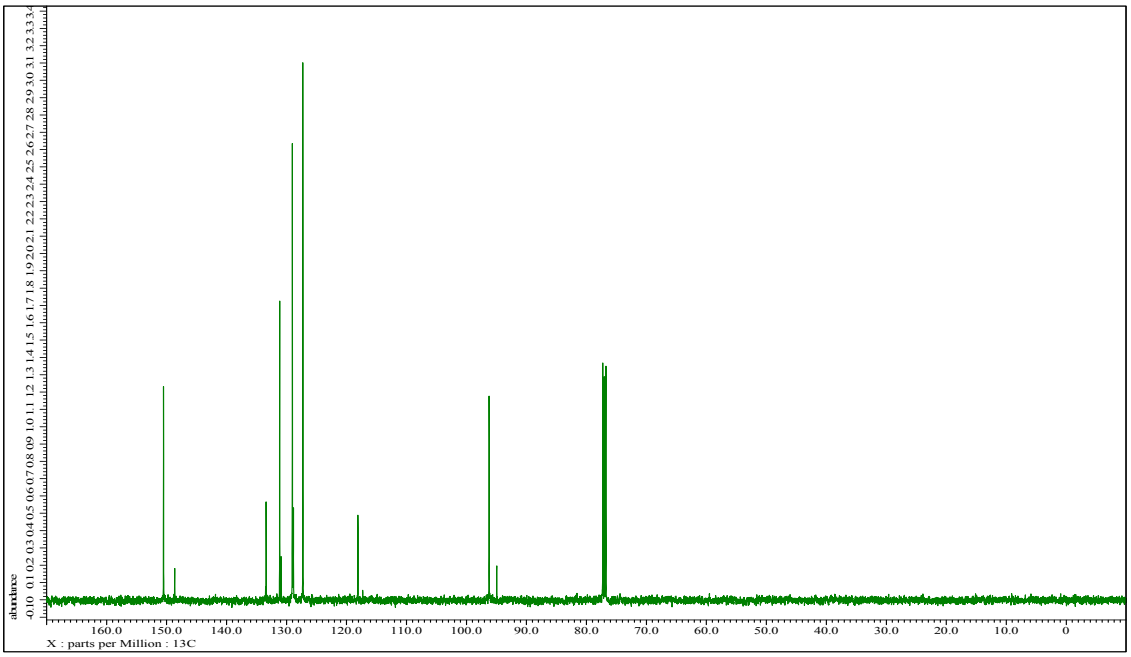


Cinnamonitrile (Table 3, Entry 19)

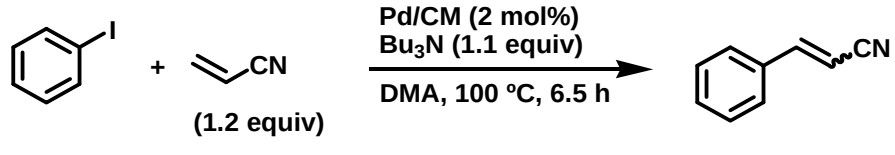


(E : Z = 85 : 15)

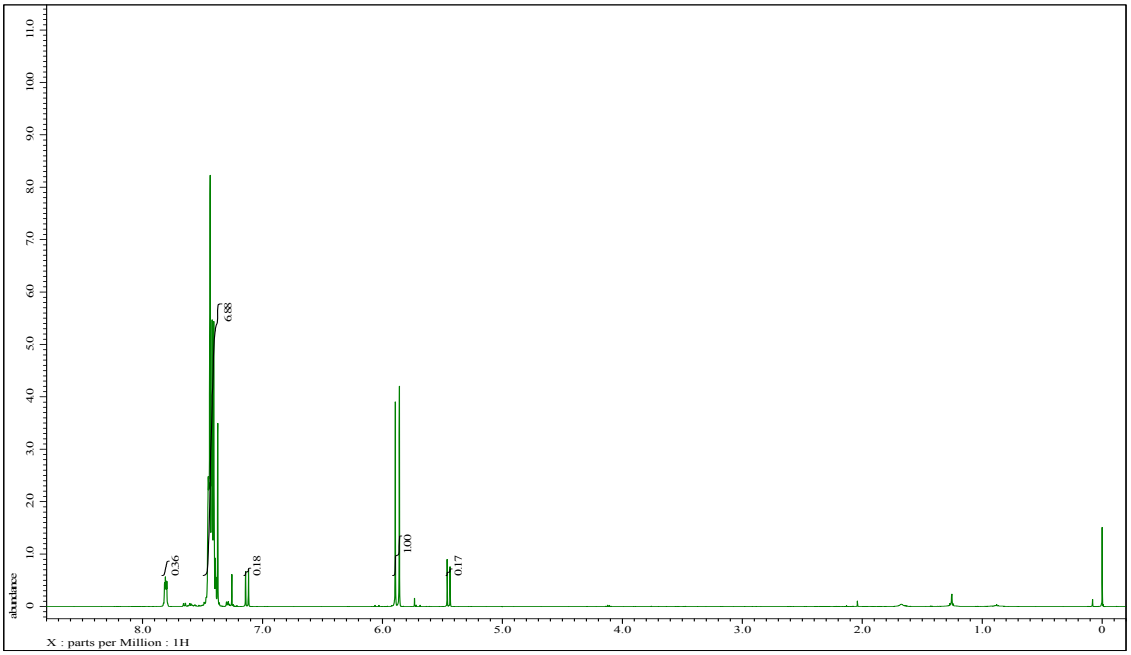


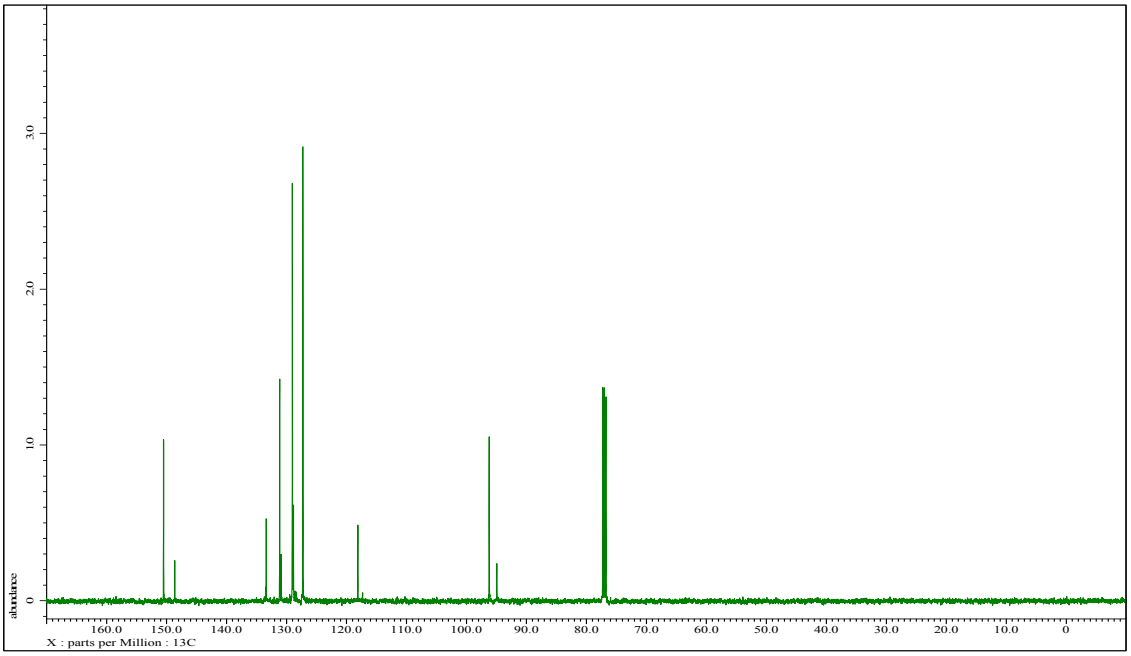


Cinnamonitrile (Table 3, Entry 20)

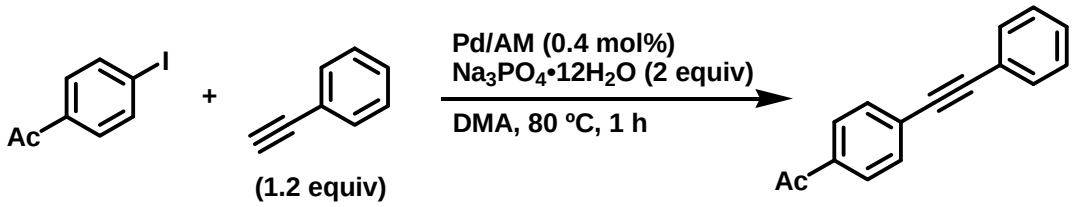


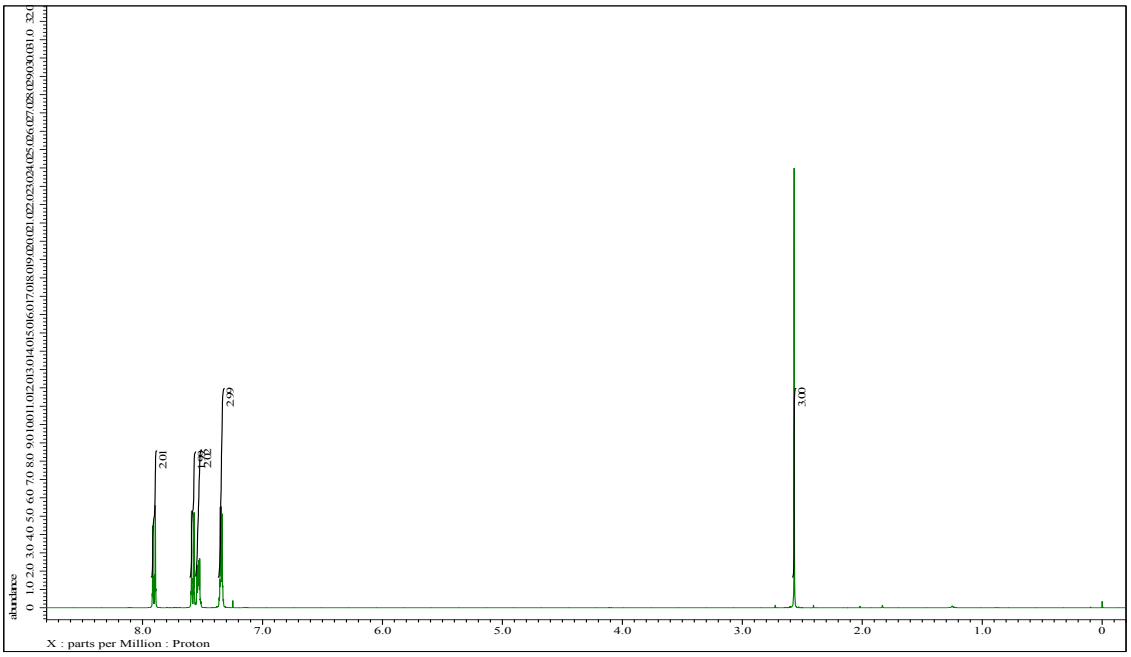
(E : Z = 86 : 14)

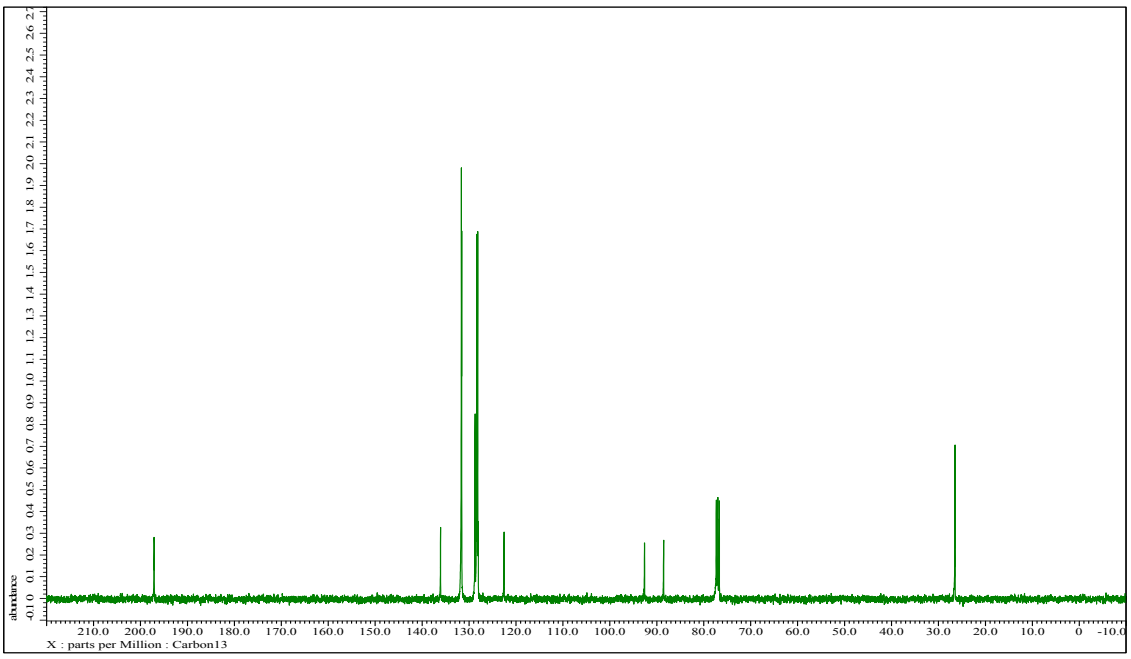




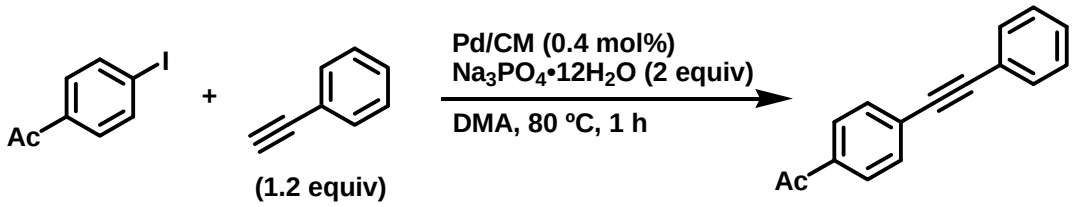
1-[4-(2-Phenylethynyl)phenyl]ethanone (Table 4, Entry 1)

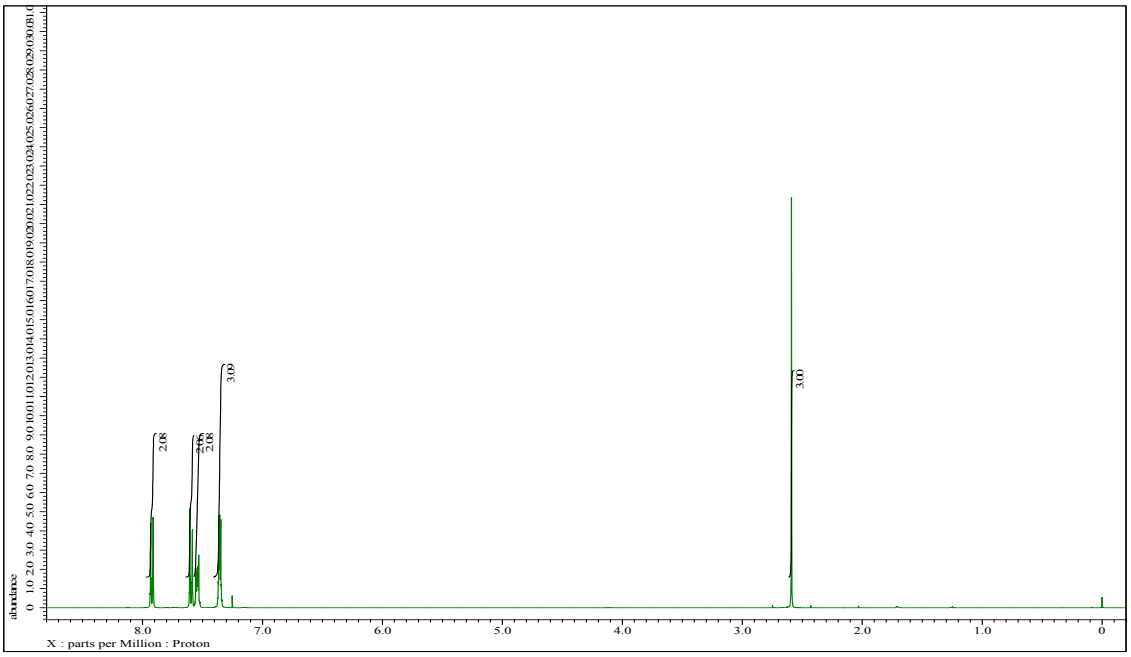


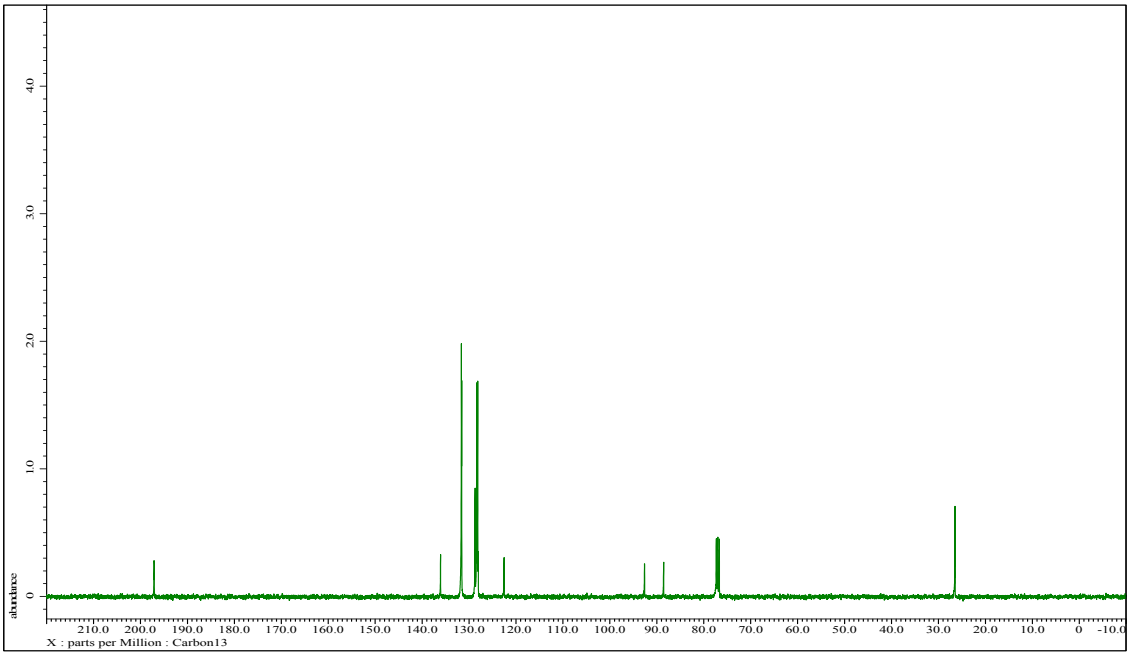




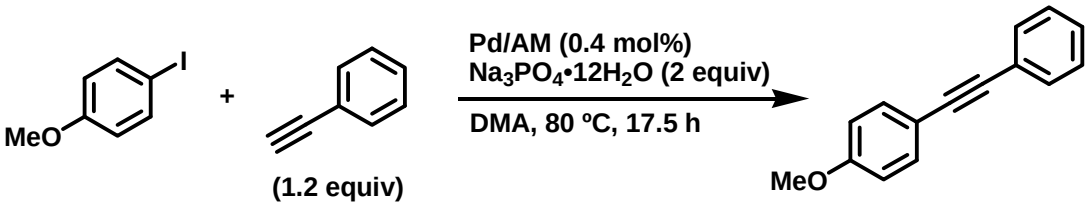
1-[4-(2-Phenylethynyl)phenyl]ethanone (Table 4, Entry 2)

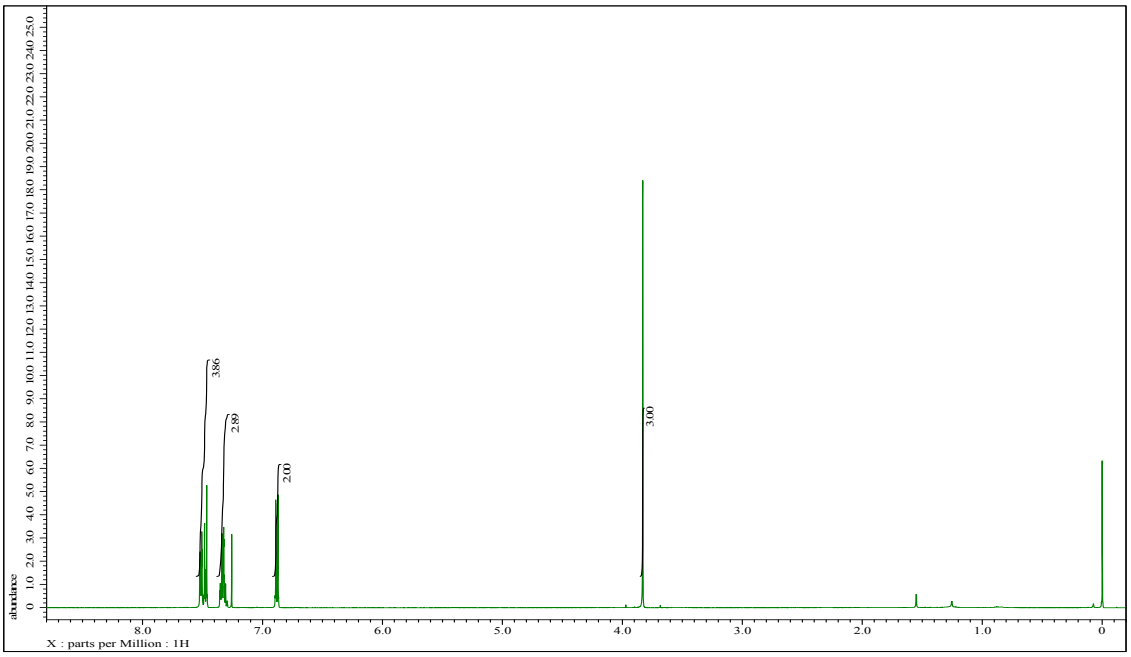


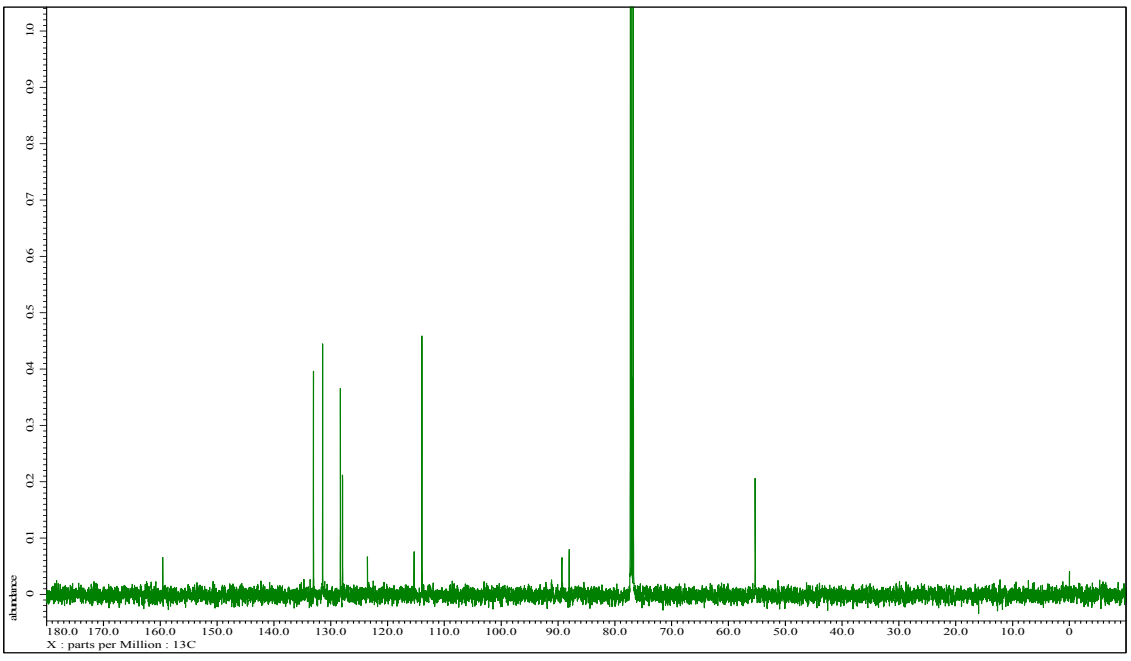




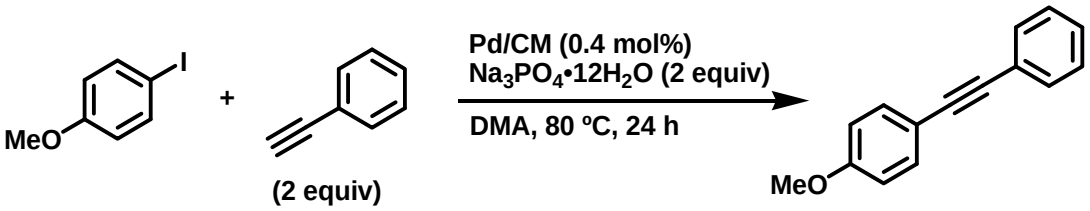
1-[2-(Methoxyphenyl)ethynyl]benzene (Table 4, Entry 4)

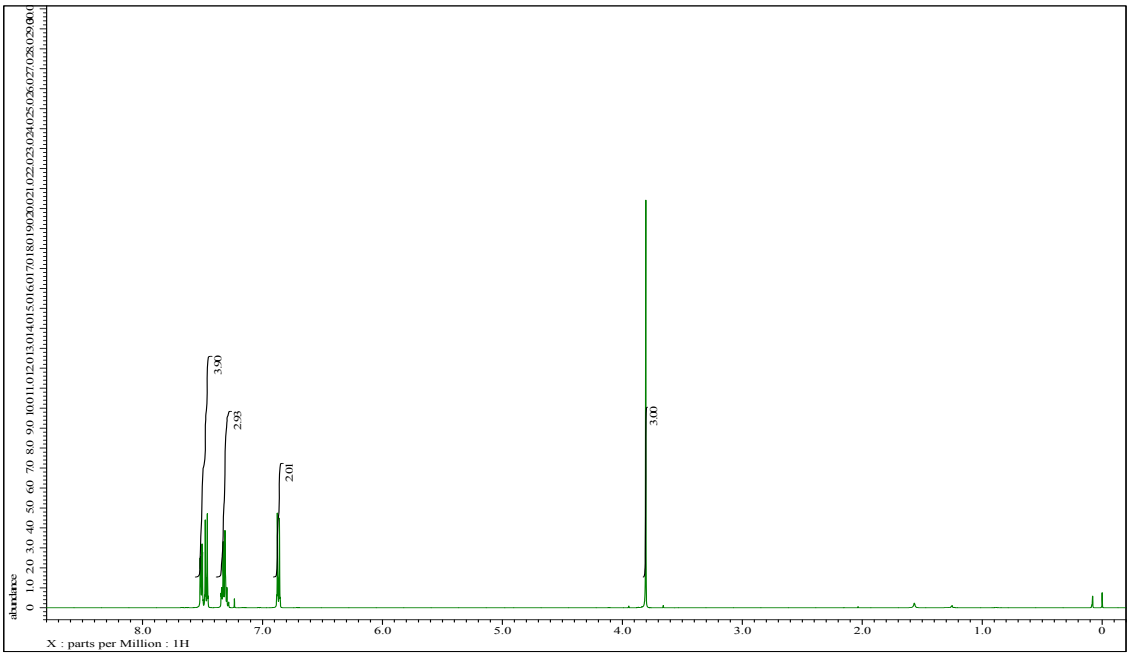


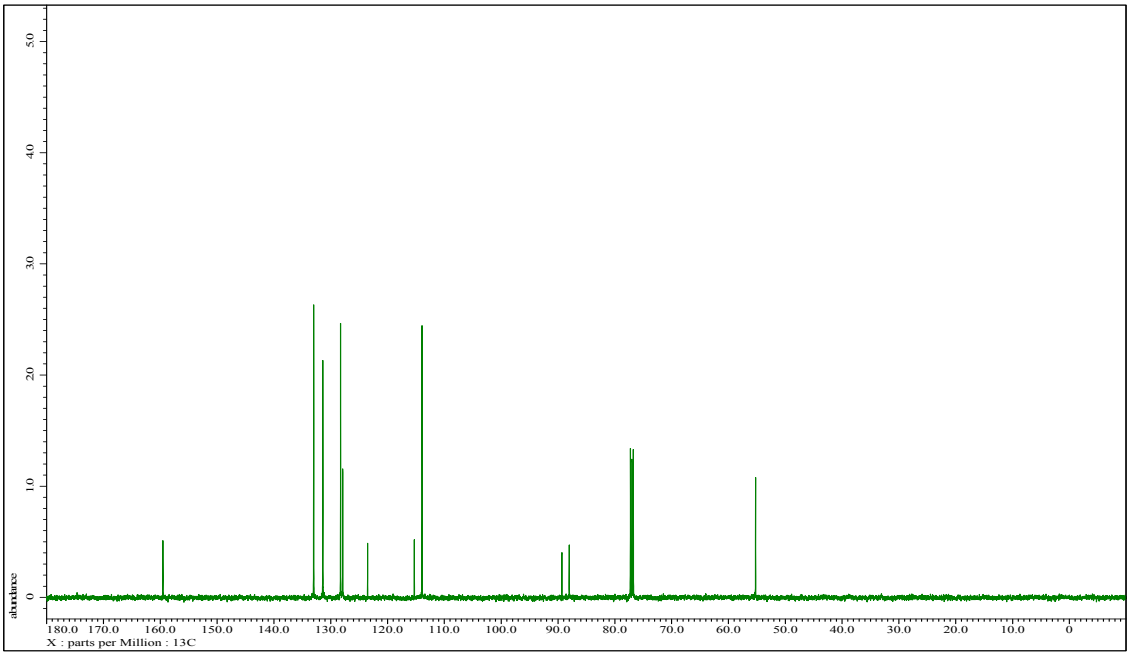




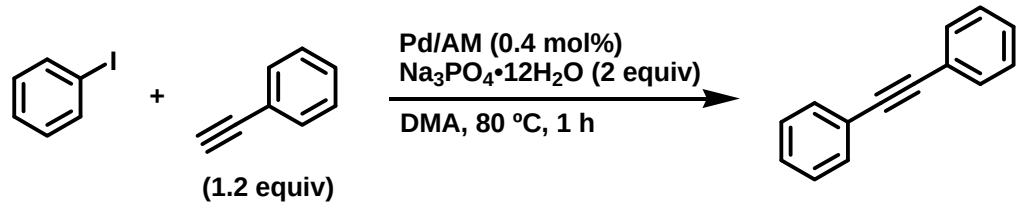
1-[2-(Methoxyphenyl)ethynyl]benzene (Table 4, Entry 5)

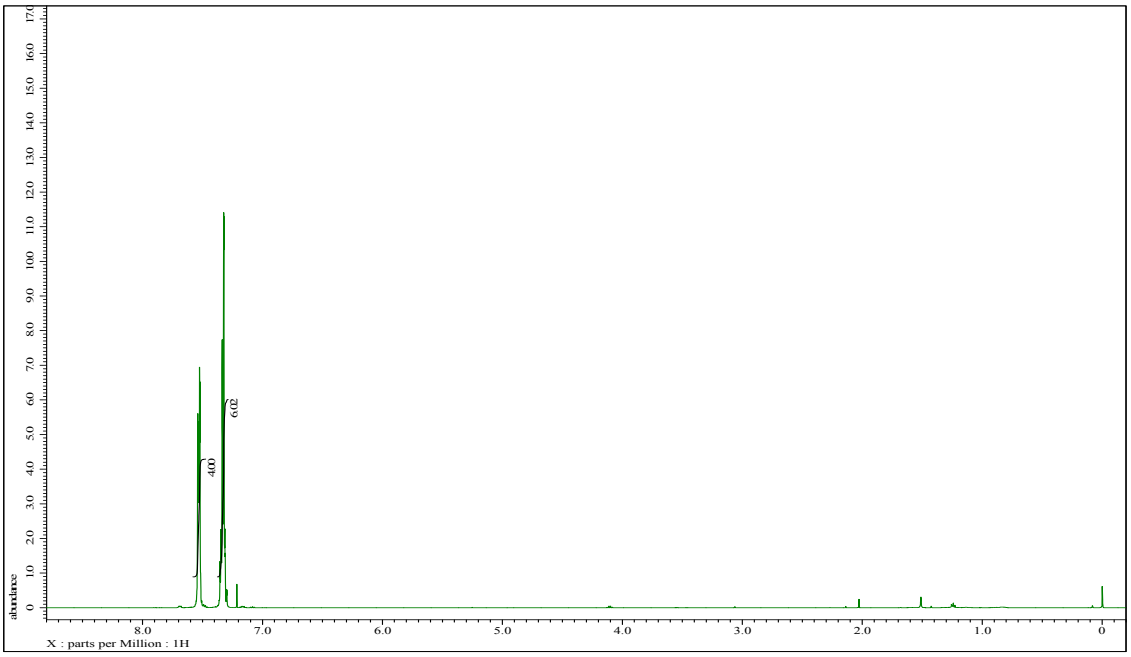


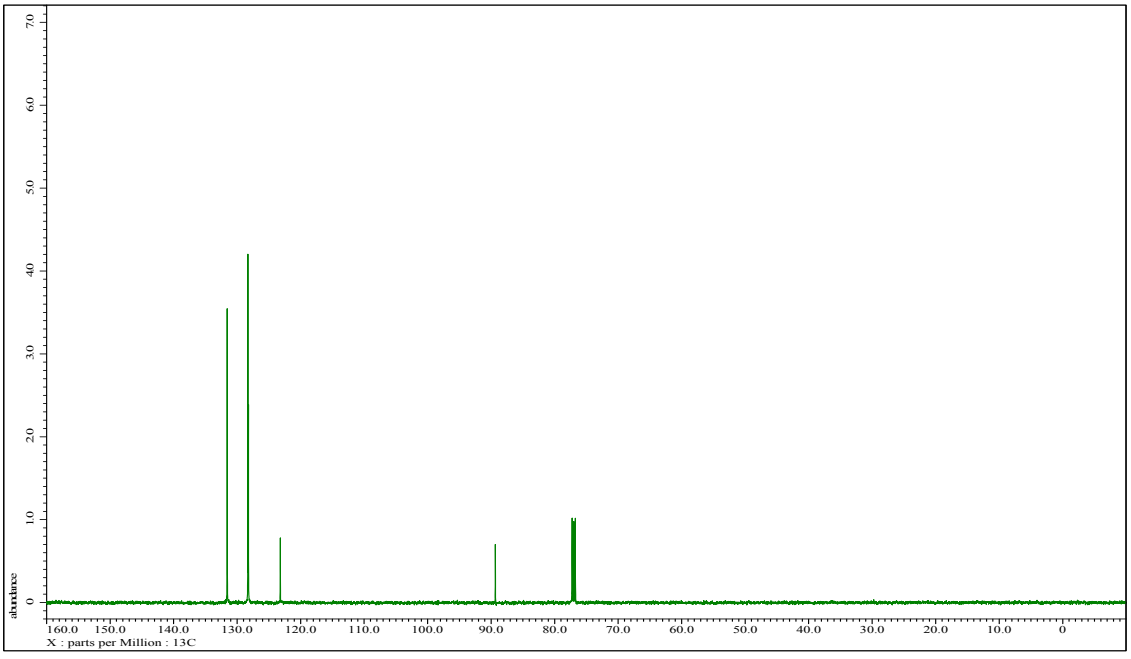




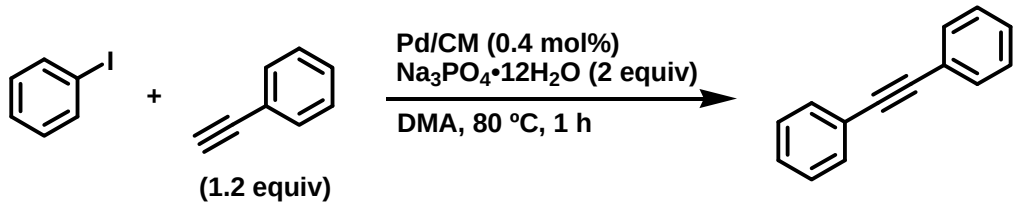
Diphenylacetylene (Table 4, Entry 7)

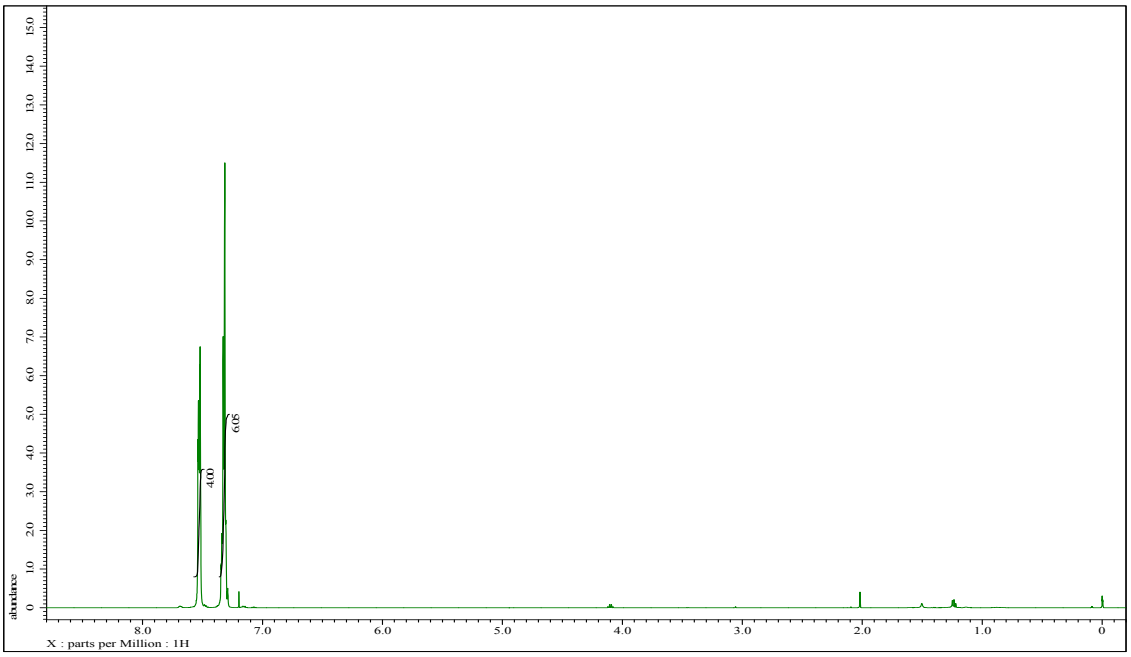


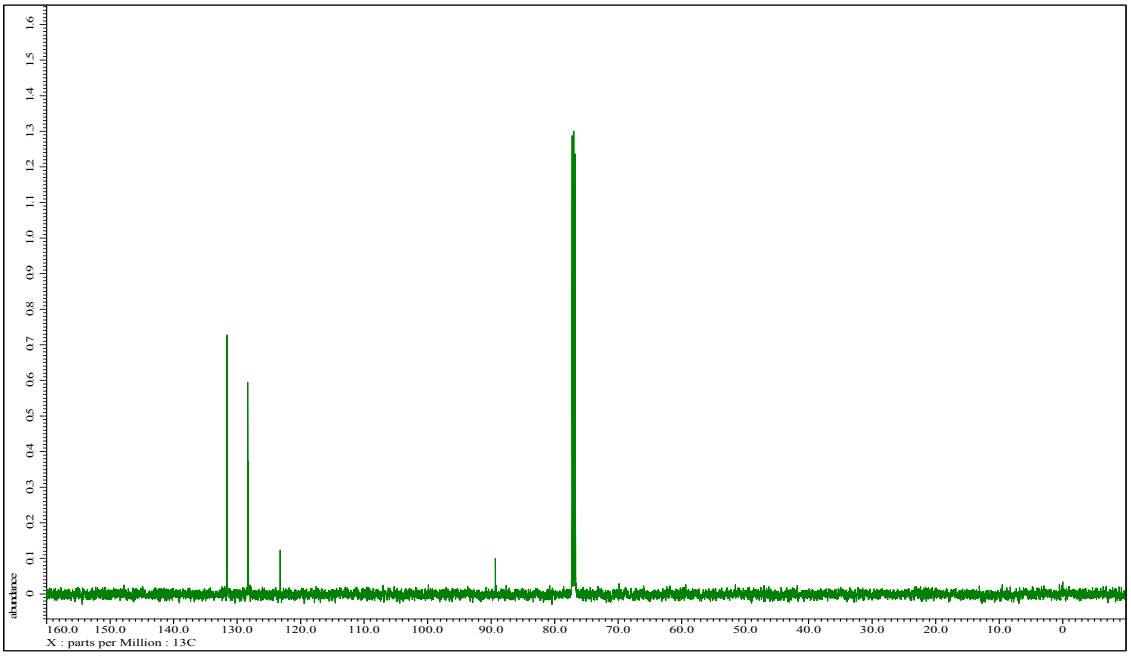




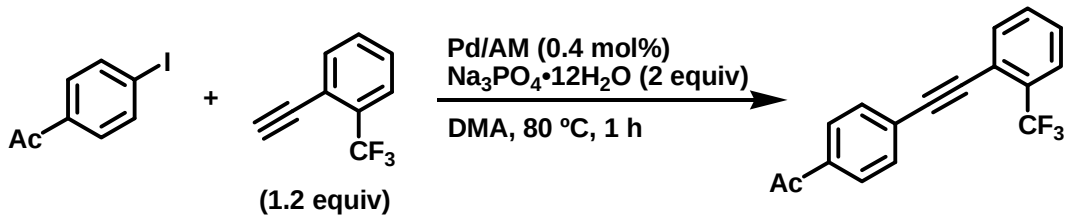
Diphenylacetylene (Table 4, Entry 8)

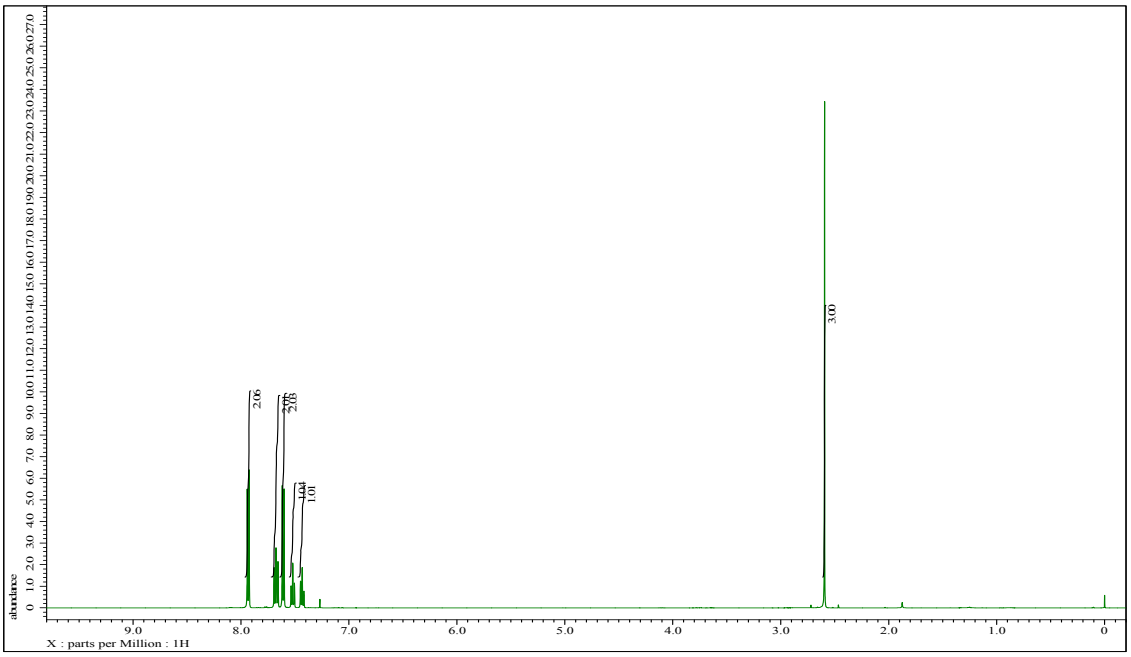


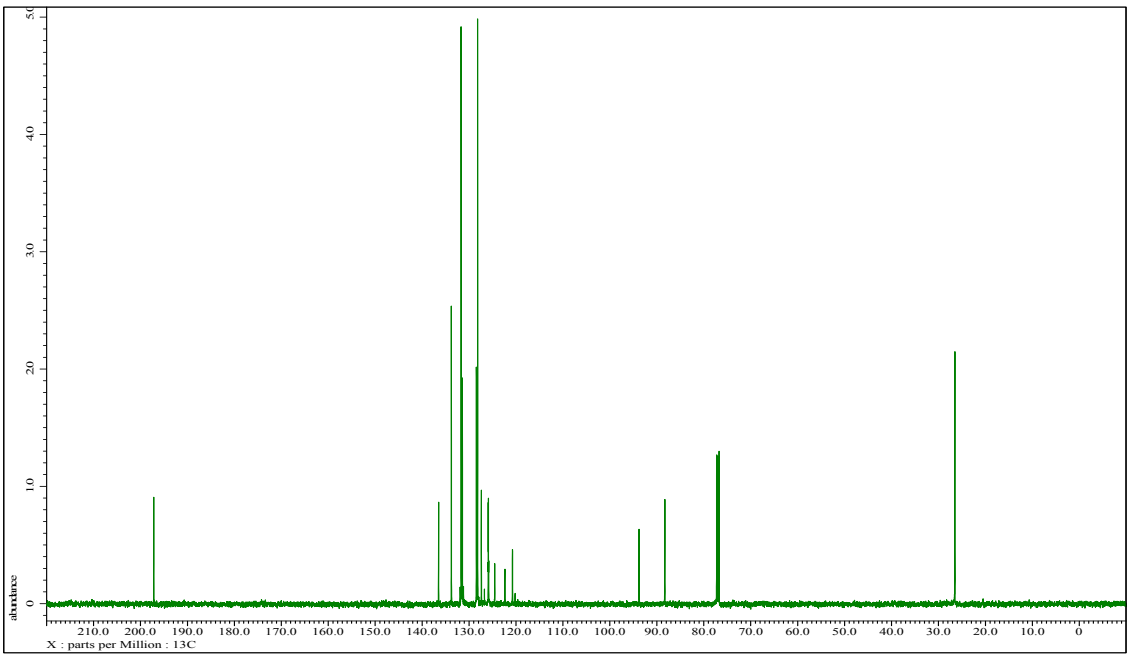




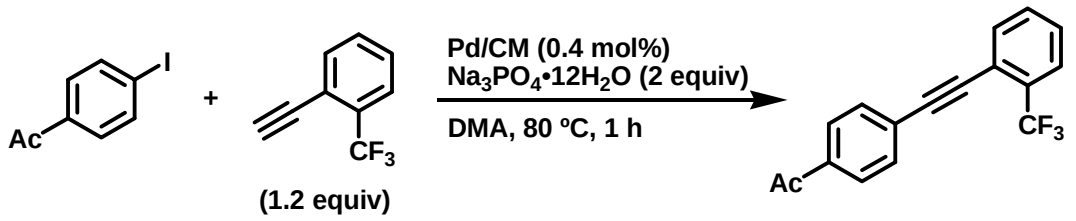
1{4-[2-(2-Trifluoromethylphenyl)ethynyl]phenyl}ethanone (Table 4, Entry 10)

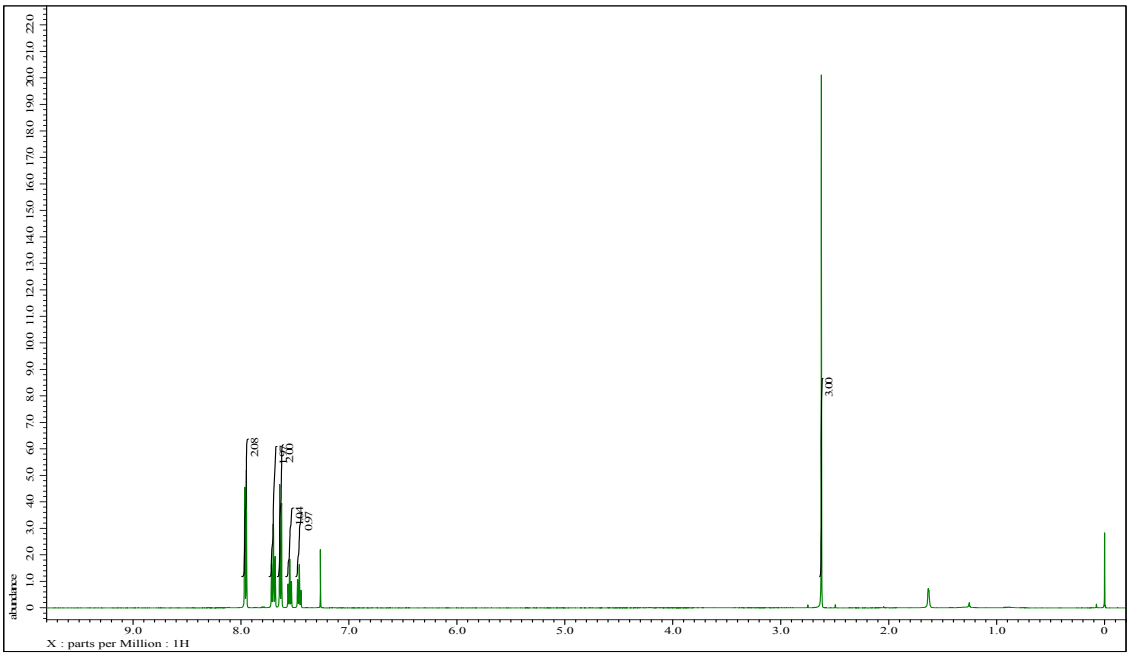


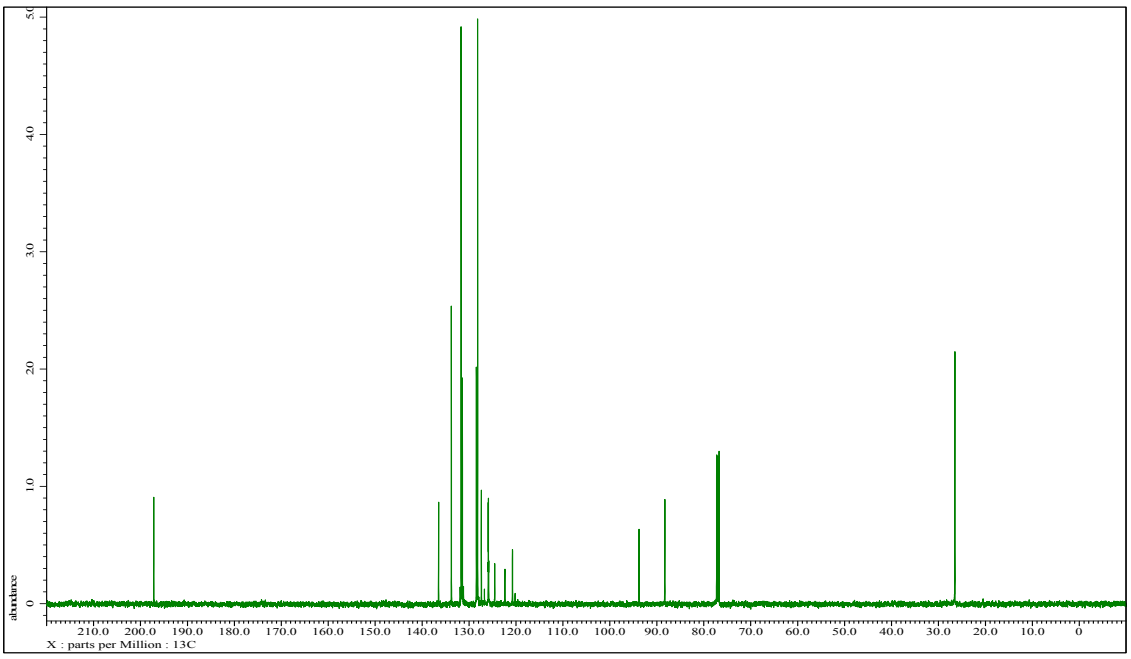




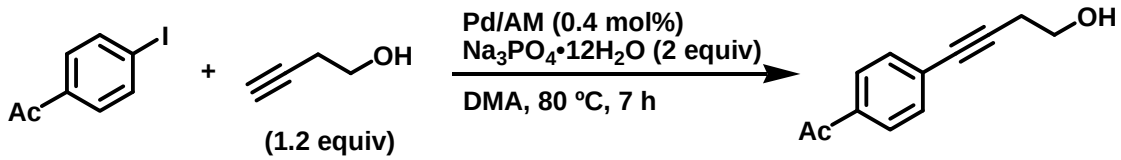
1{4-[2-(2-Trifluoromethylphenyl)ethynyl]phenyl}ethanone (Table 4, Entry 11)

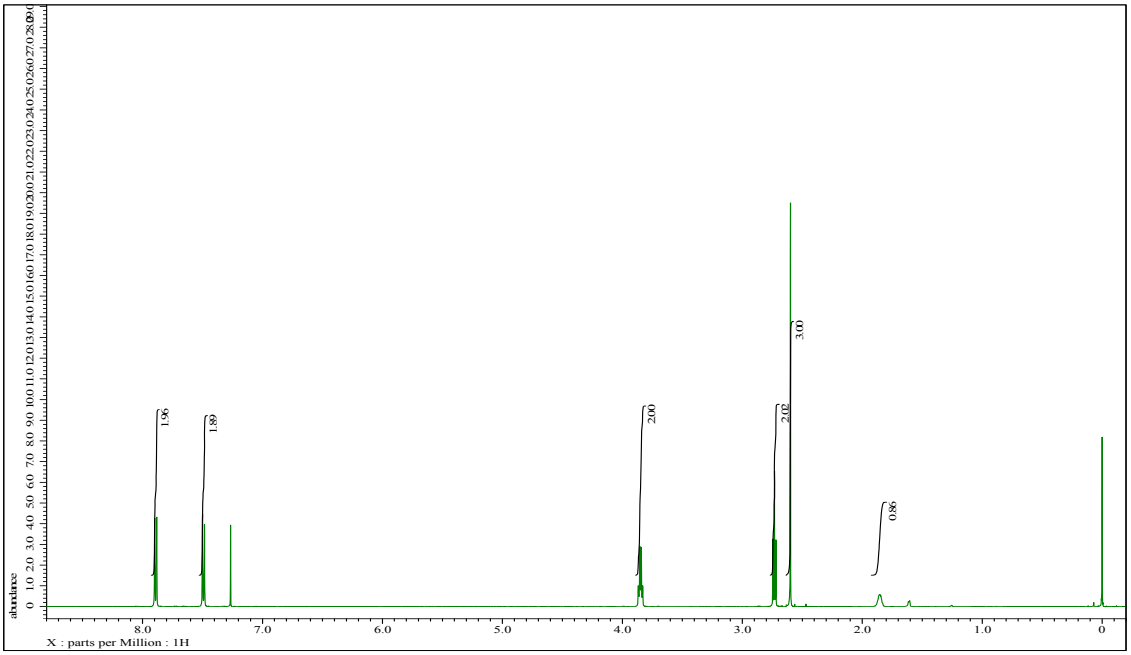


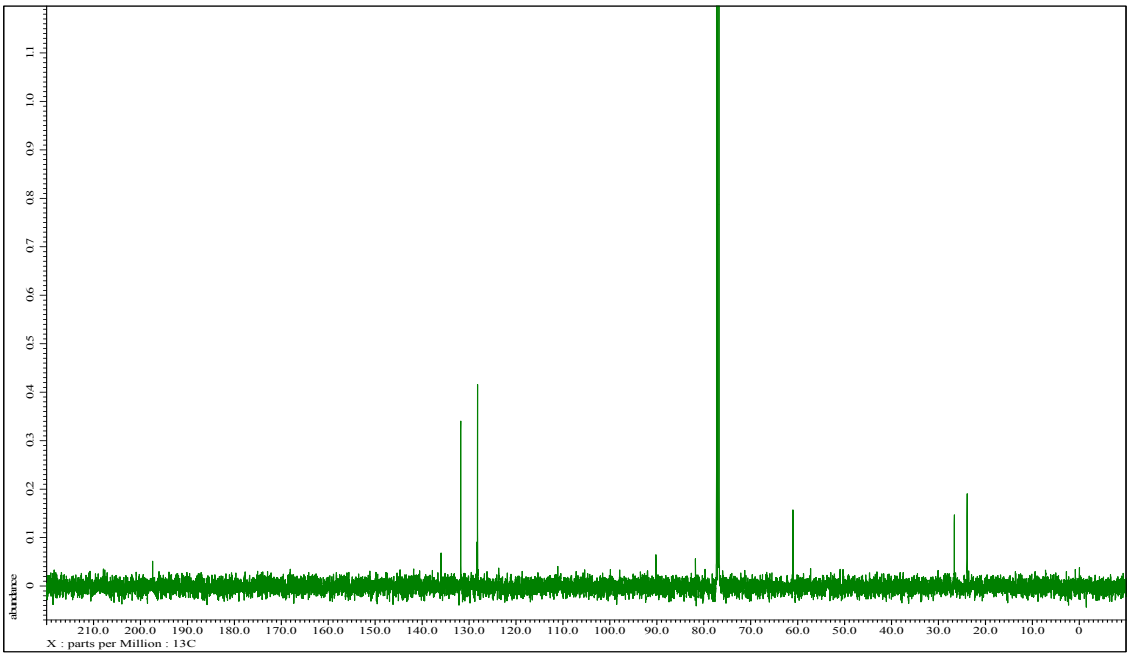




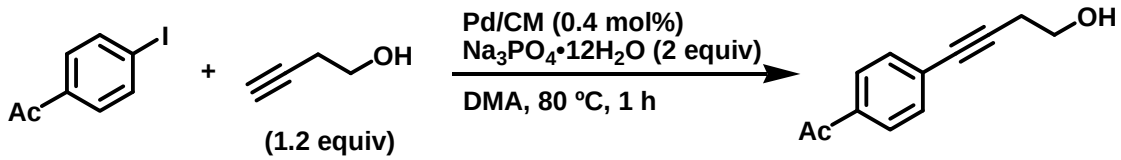
1-[4-(4-Hydroxybut-1-ynyl)phenyl]ethanone (Table 4, Entry 13)

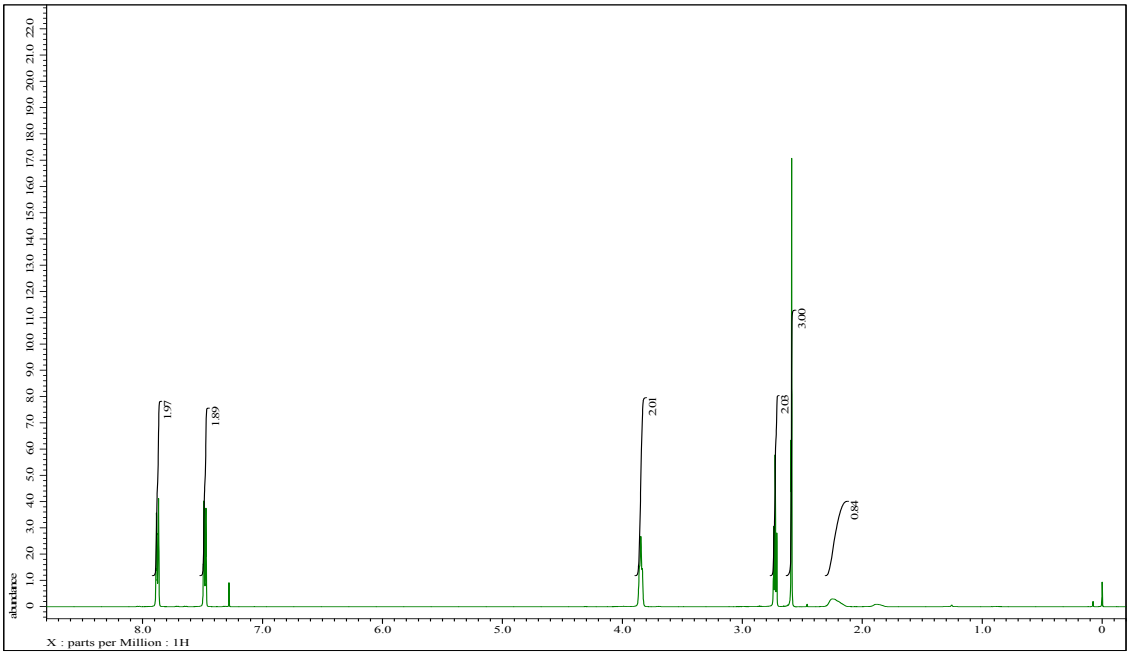


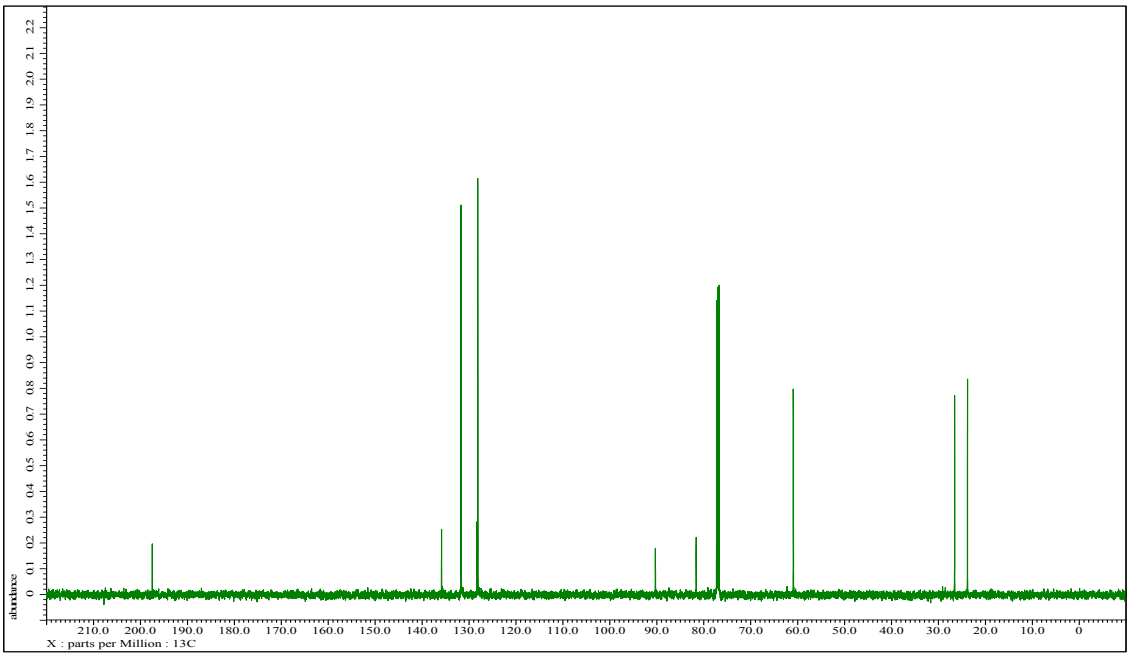




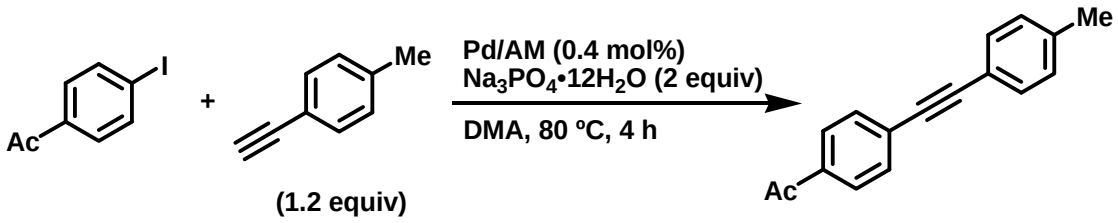
1-[4-(4-Hydroxybut-1-ynyl)phenyl]ethanone (Table 4, Entry 14)

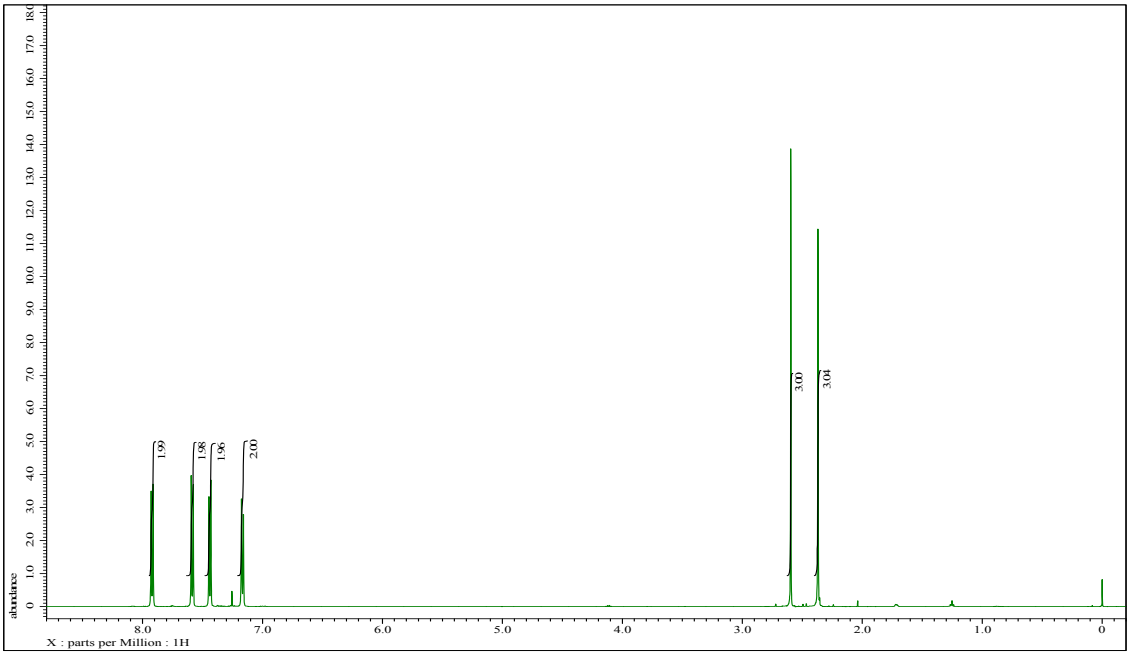


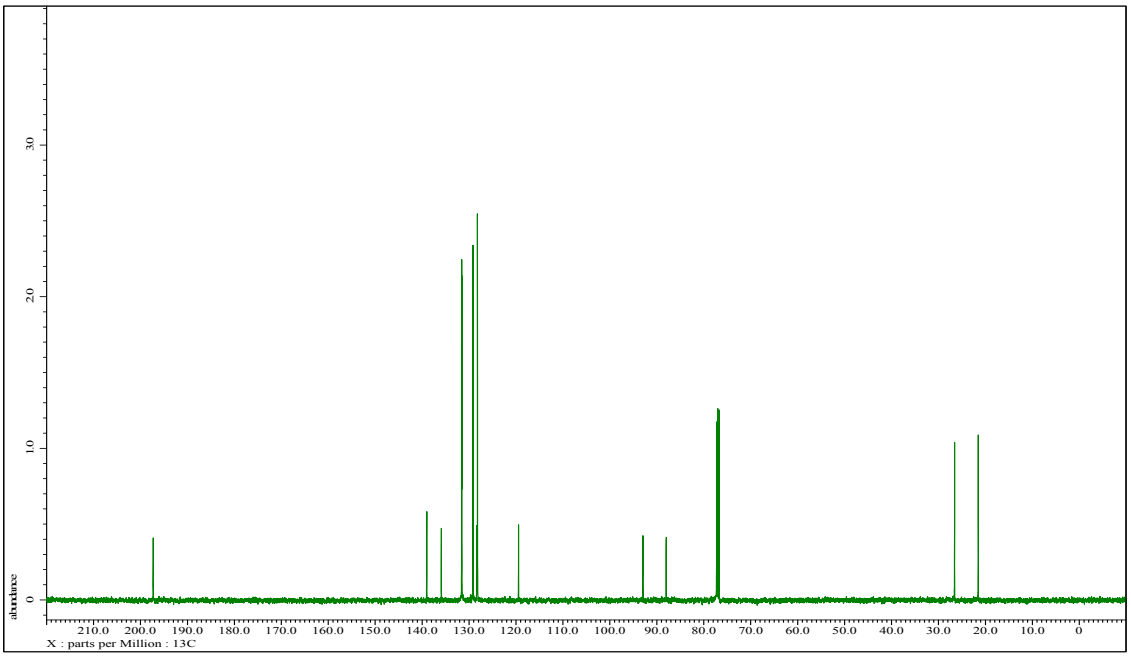




1-[4-(*p*-Tolylethynyl)phenyl]ethanone (Table 4, Entry 16)







1-[4-(*p*-Tolylethynyl)phenyl]ethanone (Table 4, Entry 17)