Supplementary Information

Bimetallic quantum dots (Cu-Pd, Ni-Pd) catalyzed reaction of bromo arenes with alkenes and aryl boronic acids

Pallavi K Raut[a], Heena K Meroliya[c], Swapnil R Dumbre[a], Vaishali N Patil[c], Bhanupratap S Solanki[b,d], Shobha A Waghmode*[c] & Suresh Iyer*[a,b]

[a] Organic Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pashan, Pune 411 008, Maharashtra, India

[b] Academy of Scientific and Innovative Research (AcSIR), CSIR-HRDC Campus, Postal Staff College Area, Sector 19, Kamla Nehru Nagar, Ghaziabad 201 002, Uttar Pradesh, India

[c] Abasaheb Garware College, Karve Road, Pune 411 004, India

[d] Chemical Engineering and Process Development Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pashan, Pune 411 008, Maharashtra, India

E-mail: drsureshiyer@yahoo.com

Received 12 July 2022; accepted (revised) 17 July 2023

Supporting Information File 1

LIST OF CONTENTS

A. General method

All reagents were purchased from commercial sources (Sigma-Aldrich, Merck and Lancaster) and were used without further purification. Solvents used as reaction media were purchased from local sources and were used after distillation. QDs were prepared following patented and literature procedure[1, 2]. Reactions were monitored using commercially available, pre-coated thin-layer chromatography (TLC) plates (Merck, silica gel 60 F_{254}, 0.25 mm) and compounds were visualized under ultraviolet light (254 nm) and/or by staining with iodine. Silica gel (100 - 200 and 230-400 mesh) was used for column chromatography. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance 200, instrument operating at 200 MHz (^{1}H), (^{13}C). Chemical shifts (δ) are quoted in ppm and referenced to internal TMS (δ 0.00 for ^{1}H NMR) or $CDCl_3$ (δ 77.0 for ^{13}C NMR); coupling constants (*J*) are quoted in Hz. High-resolution mass spectra (ESI) were obtained with a Q – Exactive (Thermo Fisher scientific) instrument. IR spectra were recorded on Shimadzu 8300, FT-IR spectrometer and absorption is expressed in cm^{-1}. TEM and EDAX was recorded on Tecnai G2 20 S-Twin and SEM on ESEM FEI QUANTA 200 3D. – UV-Visible spectrum was recorded on Shimadzu UV 1800.

B. General Procedure

a. Synthesis of bimetallic quantum dots (QDs).

i) Preparation of natural neem extract: Powder of neem plant i.e. Azadirachta indica, dried leaves in sunlight, were used as reducing agent for QD synthesis. 10gm leaf powder was added to 100 ml distilled water and then boiled for 20 mins. After cooling, this mixture was then filtered through ordinary filter paper. Filtrate was used as reducing agent, green approach towards quantum dot synthesis.

ii) Procedure for bimetallic quantum dots synthesis:

Synthesis of CuPd quantum dots (10:1): 10 mmol (0.241 g for 100 ml) solution of copper (II) nitrate trihydrate and 1 mmol (0.017 g for 100 ml) palladium (II) chloride were prepared in distilled water. Then 100 ml of each solution was taken into two separate flasks. To each flask of metal solution, 5ml of natural extract of neem powder was added and flasks were sonicated for 30 minutes, at room temperature individually. After sonication and keeping overnight, both solutions of $Cu(NO_3)_2$ & $PdCl_2$ were mixed together and again sonicated for 30 minutes. After sonication the pH was adjusted to 8 by using 1M NaOH and kept overnight. After 1 day Cu-Pd (10:1 ratio) quantum dots were formed and characterized by UV, XRD, TEM-EDAX and further used as a catalyst for coupling reactions.

Synthesis of NiPd quantum dots (10:1): 10 mmol (0.290 g for 100 ml) solutions of Nickel (II) nitrate trihydrate ($Ni(NO_3)_2.3H_2O$) and 1 mmol (0.017 g for 100 ml) palladium (II) chloride ($PdCl_2$) were prepared in distilled water. Then 100 ml of each solution was taken into two different flasks. Into each flask of metal solution, 5 ml of natural neem powder extract was added, and both the flasks were sonicated for 30 minutes at room temperature individually. After sonication both solutions of $Ni(NO_3)_2$ & $PdCl_2$ were mixed together and again sonicated for 30 minutes. After sonication, the pH was adjusted to 8 by using 1M NaOH and kept overnight. After 24 hours NiPd (10:1 ratio) QDs were formed and characterized by UV, TEM-EDAX and further used as a catalyst for coupling reactions.

b. General procedure for bimetallic QD catalysis of Mizoroki-Heck reaction

To a solution of aryl halide (0.157 g, 1 mmol), ethyl acrylate (0.2 g, 2 mmol), TBABr (0.322 g, 1 mmol) and K_2CO_3 (0.165 g, 1.2 mmol) in NMP (5 ml) was added Cu-Pd QDs (0.010 g, 0.06 mmol). The resulting mixture was heated with stirring at 150 ^{o}C for 2 - 6 h under argon.

After completion of reaction (monitored by TLC), the reaction mixture was quenched by adding water. The solution was extracted with ethyl acetate (3 x 20 ml) the combined extract was washed with saturated brine and dried over anhydrous Na_2SO_4. The organic layer was concentrated under vacuum and the crude product purified by column chromatography on silica gel (100-200 mesh, Petroleum Ether: 2 % Ethyl acetate) to give pure product.

A1 2-Propenoic acid, 3-phenyl-, ethyl ester (2E) (4a) (2 h, 0.126 g, 0.72 mmol, 72 % yield, colourless oil) CAS Registry Number 4192-77-2, ^{1}H NMR (200 MHz, $CDCl_3$, δ ppm) 7.65-7.73 (d, J=16 Hz, 1H), 7.32 - 7.57 (m, 5H), 6.40-6.48 (d, J=16 Hz, 1H), 4.14 - 4.38 (q, J=7.2 Hz, 2H), 1.20-1.44 (t, *J*=7.1 Hz, 3H) ^{13}C NMR ($CDCl_3$, d, 200 MHz): d 166.9, 144.48, 134.36, 130.13, 126.76, 127.96, 118.18, 60.40, 14.24; IR (cm $^{-1}$) 3715, 3679, 3582, 3386, 2953, 2924, 2825, 1721, 1658, 1640, 1547, 1512, 1461, 1378, 1219, 1165, 1020, 772; HRMS-ESI : $[M]^+$ calcd for $C_{11}H_{12}O_2$ $[M]^+$ 177.0910, found: 177.0912

A2 Benzene, 1,1'-(1E)-1,2-ethenediylbis (4b) (4h, 0.175 g, 97 %, 0.97 mmol, white solid, 124 ^{o}C) CAS Registry Number 103-30-0 ^{1}H NMR (200 MHz, $CDCl_3$, δ) –7.54-7.2 (m,10H),7.11(s, 2H), ^{13}C NMR (200 MHz, $CDCl_3$, δ) –137.29, 128.66, 127.6, 126.48, IR (cm $^{-1}$) – HRMS-ESI : $[M]^+$ calcd for $C_{14}H_{12}$ $[M]^+$ 181.1012, found: 181.1014

A3 2-Propenoic acid, 3-(4-methoxyphenyl),- ethyl ester, (2E)- (4c) (25 h, 0.173 g, 0.5 mmol, 50 %, Colourless oil) CAS Registry Number 24393-56-4 ^{1}H NMR (200 MHz, $CDCl_3$, δ) 7.67-7.59 (d, J = 15.9 Hz, 1 H), 7.49-7.44 (d, J = 8.7 Hz, 2 H), 6.91 - 6.87 (d, J = 8.9 Hz, 2H), 6.34 - 6.26 (d, J = 16 Hz, 1 H), 4.30 – 4.19 (q, J = 7 Hz, 2 H), 3.83 (s, 3 H), 1.36 - 1.26 (t, J = 7.2 Hz, 3 H), ^{13}C NMR (200 MHz, $CDCl_3$, δ) 167.30, 161.28, 144.20, 129.64, 127.15, 115.70, 114.26, 60.28, 55.32, 14.31 IR (cm $^{-1}$) HRMS-ESI : $[M^++H]^+$ calcd for $C_{12}H_{15}0_3$ $[M^++H]^+$ 207.1016, found: 207.1019

A4 Benzene, 1-methoxy-4-[(1E)-2-phenylethenyl]- (4d) (5h, 0.166 g, 79 %, 0.79 mmol, White solid, MP-136 ^{o}C) CAS Registry Number 1694-19-5, ^{1}H NMR (200 MHz, $CDCl_3$, δ) 7.52-7.23 (m, 7 H), 7.05-7.01 (d, J = 7.45 Hz, 2 H), 6.92-6.88 (d, J = 8.45 Hz, 2H), 6.35-6.27 (d, J = 16 Hz, 1 H), 4.31 – 4.20 (q, J = 7.2 Hz, 2 H), 3.83 (s, 3 H), 1.37 – 1.26 (t, J = 7.2 Hz, 3 H) ^{13}C NMR (200 MHz, $CDCl_3$, δ) 159.25, 137.60, 130.09, 128.60, 128.16, 127.68, 127.17, 126.56, 126.21, 114.09, 55.26, IR (cm $^{-1}$) HRMS-ESI : calcd for $C_{15}H_{15}O$ $[M^++H]^+$ 211.1117, found 211.1119

A5 Benzene, 1-chloro-4-[(1E)-2-phenylethenyl]- (4e) (4h, 0.163 g, 86 %, 0.76 mmol, White solid, MP – 129 ^{o}C) CAS Registry Number 1657-50-7 ^{1}H NMR (200 MHz, $CDCl_3$, δ) 7.53-7.25 (m, 9 H), 7.07- (s, 2 H), ^{13}C NMR (200 MHz, $CDCl_3$, δ) 136.95, 135.81, 133.14, 129.29, 128.82, 128.71, 127.64, 126.53, IR (cm $^{-1}$) 3418, 3082, 3022, 2925, 2857, 1904, 1642, 1490, 1452, 1404, 1376, 1329, 1305, 1216, 1095, 967, 865, 817, 760, 696, 665; HRMS-ESI : $[M^++H]^+$ calcd for $C_{14}H_{12}Cl$ $[M+H]^+$ 215.0622, found: 215.0622

A6 2-Propenoic acid, 3-(1-naphthalenyl)-, ethyl ester, (2E)- (4f) (6h, 0.113 g, 50 %, 0.5 mmol, Colourless oil) CAS Registry Number 98978-43-9 ^{1}H NMR (200 MHz, $CDCl_3$, δ)

8.58-8.50 (d, J = 15.67 Hz, 1H), 8.24-8.19 (m, 1 H), 7.93 – 7.76 (m, 2H), 7.79 - 7.75 (m, 1H), 7.63 – 7.46 (m, 3 H), 6.58 - 6.50 (d, J = 15.79 Hz, 1H), 4.38-4.28 (q, J = 7.07 Hz, 2 H), 1.43 – 1.35 (t, J = 7.07 Hz, 3 H), ^{13}C NMR (200 MHz, $CDCl_3$, δ) 166.87, 141.60, 133.65, 131.83, 130.42, 128.69, 126.82, 126.19, 125.43, 124.97, 123.40, 120.94, 60.59, 14.35, IR (cm^{-1}) 3404, 3056, 2925, 2860, 2321, 1939, 1713, 1630, 1511, 1455, 1362, 1304, 1258, 1171, 1094, 1038, 977, 861, 779, 723; HRMS-ESI : $[M^{+}+H]^{+}$ calcd for $C_{15}H_{15}O_2$ $[M+H]^{+}$ 227.1067, found: 227.1064

A7 Naphthalene, 1-[(1E)-2-phenylethenyl]- (4g) (5h, 0.115 g, 63 %, 0.67 mmol, White solid, MP – 70 °C) CAS Registry Number 2840-87-1 ^{1}H NMR (200 MHz, $CDCl_3$, δ) 8.26 - 8.21 (m, 1 H), 7.94 – 7.74 (m, 4 H), 7.65 – 7.31 (m, 8H), 7.21 - 7.13 (d, J = 15.92 Hz, 1H), ^{13}C NMR (200 MHz, $CDCl_3$, δ) 166.87, 141.60, 133.65, 131.83, 130.42, 128.69, 126.82, 126.19, 125.43, 124.97, 123.40, 120.94, 60.59, 14.35, IR (cm^{-1}) 3377, 3047, 2852, 2724, 1935, 1802, 1709, 1591, 1456, 1377, 1308, 1160, 1075, 1022, 961, 852, 782, 759, 739, 691; HRMS-ESI : $[M]^{+}$ calcd for $C_{18}H_{14}$ $[M]^{+}$ 230.110, found: 230.1090

A8 2-Propenoic acid,3-(4-methylphenyl)-ethyl ester (2E) (4h) (5 h, 0.107 g, 56 %, 0.56 mmol, colourless oil) CAS Registry Number 24393-49-5 ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.56 (d, *J*=16.0 Hz, 1H), 7.30 (d, *J*=8.0 Hz, 2H), 7.06 (d, *J*=7.8 Hz, 2H), 6.28 (d, *J*=15.9 Hz, 1H), 4.15 (q, *J*=7.1 Hz, 2H), 2.24 (s, 3H), 1.22 (t, *J*=7.1 Hz, 3H); ^{13}C NMR (CHLOROFORM-d ,50MHz): δ (ppm) 167.2, 144.6, 140.6, 131.7, 129.6, 128.0, 117.2, 77.6, 76.4, 60.4, 21.4, 14.3; IR (cm^{-1}) 2920, 2856, 2347, 2286, 1711, 1610, 1383, 1314, 1267, 1169, 1118, 1038, 811, 767, 664; HRMS : $[M^{+}+H]^{+}$ calcd for $C_{12}H_{15}O_2$ $[M+H]^{+}$ 191.1067, found: 191.1068 $C_{12}H_{15}O_2$

c. General procedure for Bimetallic QD catalysis of Suzuki coupling

To a solution of aryl halide (0.078 g, 0.5 mmol), aryl boronic acid (0.073 g, 0.6 mmol), TBABr (0.161 g, 0.5 mmol) and K_3PO_4 (0.127 g, 0.6 mmol) in dioxane and water (1:1, 10 ml) was added Ni-Pd QDs (0.005 g, 0.03 mmol). The resulting mixture was heated with stirring at 130 °C for 2 - 6 h under argon. After completion of reaction (monitored by TLC), the reaction mixture was quenched by adding water. The solution was extracted with ethyl acetate (3 x 20 ml) the combined extract was washed with saturated brine and dried over anhydrous Na_2SO_4. The organic layer was concentrated under vacuum and the crude product purified by column chromatography on silica gel (100-200 mesh, Petroleum Ether) to give pure product.

B1 1,1'-Biphenyl (5a) (1.5 h, 0.112 g, 0.36 mmol, 72 % yield, white solid, MP – 68 °C) CAS Registry Number 92-52-4 ^{1}H NMR (200 MHz, $CDCl_3$, δ) –7.62-7.56 (m,4 H),7.49-7.3 (m, 6 H) IR (cm^{-1}) – 3383, 2965, 2725, 1947, 1879, 1711, 1570, 1457, 1374, 1307, 1163, 1080, 968, 729; HRMS-ESI : $[M]^{+}$ calcd for $C_{12}H_{10}$ $[M]^{+}$ 154.0777, found: 154.0776

B2 1,1'-Biphenyl, 4, 4'-dimethoxy- (5b) (2.5 h, 0.2 g, 0.46 mmol, 92 % yield, white solid, MP – 176 °C) CAS Registry Number 2132-80-1 ^{1}H NMR (200 MHz, $CDCl_3$, δ) –7.51-7.47 (d, J = 8.97 Hz, 4 H), 6.99-6.95 (d, J = 8.84 Hz, 4H), 3.85 (s, 6H) ^{13}C NMR (200 MHz, $CDCl_3$, δ) –158.70, 133.50, 127.73, 114.16, 55.34 IR (cm^{-1}) - 3378, 2923, 2858, 2065, 1896, 1606, 1571, 1455, 1373, 1268, 1137, 1031, 812, 724, 660; HRMS-ESI : $[M]^+$ calcd for $C_{14}H_{14}O_2$ $[M]^+$ 214.0988, found: 214.0987

B3 1,1'-Biphenyl, 4-methoxy- (5c) (6.5 h, 0.083 g, 0.45 mmol, 90 % yield, white solid, MP – 90 °C) CAS Registry Number 613-37-6 ^{1}H NMR (200 MHz, $CDCl_3$, δ) –7.59-7.52 (m,4 H),7.47-7.31 (m, 3H), 7.02 – 6.97 (d, J = 8.84 Hz, 2H), 3.87 (s, 3 H); ^{13}C NMR (200 MHz, $CDCl_3$, δ) –128.71, 128.14, 126.73, 126.64, 114.19, 55.34; IR (cm $^{-1}$) – 3383, 2923, 2858, 2725, 1947, 1883, 1713, 1651, 1603, 1520, 1455, 1374, 1282, 1252, 1187, 1120, 1035, 831, 758, 687; HRMS-ESI : $[M]^+$ calcd for $C_{13}H_{12}O$ $[M]^+$ 184.0883, found: 184.0882

B4 Naphthalene, 1-phenyl (5d) (2.5 h, 0.098 g, 0.48 mmol, 96 % yield, white solid, MP – 45 °C) CAS Registry Number 605-02-7 ^{1}H NMR (200 MHz, $CDCl_3$, δ) –7.93-7.84 (m,3 H),7.57-7.39 (m, 9 H); ^{13}C NMR (200 MHz, $CDCl_3$, δ) –143.4, 142.6, 140.3, 137.4, 130.4, 129.5,128.6, 128.2, 127.9, 127.6, 127.5, 127.4, 126.7, 116.5, 87.5, 83.1, 68.8, 65.1, 64.6, IR (cm $^{-1}$) – 3381, 3050, 2957, 2855, 2725, 1936, 1809, 1711, 1590, 1457, 1377, 1163, 1070, 1025, 964, 855, 770, 705, 657; HRMS-ESI : $[M]^+$ calcd for $C_{16}H_{12}$ $[M]^+$ 204.0934, found: 204.0934

B5 1,1'-Biphenyl, 4-chloro-4'-methyl- (5e) (3 h, 0.069 g, 0.34 mmol, 68 % yield, white solid, MP – 122 °C) CAS Registry Number 19482-11-2 ^{1}H NMR (200 MHz, $CDCl_3$, δ) – 7.54-7.42 (m,6 H),7.24 – 7.23 (m, 2 H), 2.41 (s, 3 H) ^{13}C NMR (200 MHz, $CDCl_3$, δ) –143.4, 142.6, 140.3, 137.4, 130.4, 129.5,128.6, 128.2, 127.9, 127.6, 127.5, 127.4, 126.7, 116.5, 87.5, 83.1, 68.8, 65.1, 64.6, IR (cm $^{-1}$) – 3387, 2923, 2858, 1571, 1455, 1372, 1030, 842, 777, 724, 658; HRMS-ESI : $[M^++H]^+$ calcd for $C_{13}H_{12}Cl$ $[M+H]^+$ 203.0622, found: 203.0625

B6 Naphthalene, 1-(4-methoxyphenyl)- (5f) (3 h, 0.112 g, 0.48 mmol, 96 % yield, white solid, MP – 115 °C) CAS Registry Number 27331-33-5 ^{1}H NMR (200 MHz, $CDCl_3$, δ) –7.96 - 7.84 (m, 3H),7.53 -7.4 (m, 6H), 7.07 – 7.03 (d, J = 8.84 Hz, 2H), 3.91 (s, 3 H); ^{13}C NMR (200 MHz, $CDCl_3$, δ) 131.11, 128.25, 127.32, 126.9, 126.07, 125.9, 125.68, 125.39, 113.72, 55.36; IR (cm $^{-1}$) – 3686, 3620, 3021, 2969, 2841, 2403, 2360, 1609, 1513, 1430, 1287, 1217, 1111, 1034, 928, 772, 673; HRMS-ESI : $[M]^+$ calcd for $C_{17}H_{14}O$ $[M]^+$ 234.1039 found: 234.1035

B7 1,1'-Binaphthalene (5g) (6 h, 0.108 g, 0.425 mmol, 85 % yield, white solid, MP – 160 °C) CAS Registry Number 604-53-5 ^{1}H NMR (200 MHz, $CDCl_3$, δ) –7.99-7.93 (m, 4H),7.64-7.25 (m, 10 H); ^{13}C NMR (200 MHz, $CDCl_3$, δ) – 128.13, 127.87, 127.81, 126.54, 125.96, 125.78, 125.36; IR (cm $^{-1}$) – 3050, 2924, 2859, 2670, 2410, 1928, 1812, 1735, 1586, 1536, 1499, 1459, 1377, 1332, 1247, 1209, 1166, 1017, 961, 773; HRMS-ESI : $[M]^+$ calcd for $C_{20}H_{14}$ $[M]^+$ 254.1090 found: 254.1088

B8 1,1'-Biphenyl, 4-chloro- (5h) (2 h, 0.089 g, 0.475 mmol, 95 % yield, white solid, MP – 79 °C) CAS Registry Number 2051-62-9 ^{1}H NMR (200 MHz, $CDCl_3$, δ) –7.60 - 7.37 (m, 9 H); ^{13}C NMR (200 MHz, $CDCl_3$, δ) – 139.98, 139.65, 133.35, 128.88, 128.37, 126.97; IR (cm $^{-1}$) – 3381, 2846, 2725, 1712, 1602, 1460, 1376, 1308, 1216, 1161, 1094, 1011, 970, 832, 761, 726, 666; HRMS-ESI : $[M]^+$ calcd for $C_{12}H_9Cl$ $[M]^+$ 188.0387, found: 188.0386

B9 Naphthalene, 2-[1,1'-biphenyl]-4-yl- (5i) (6 h, 0.097 g, 0.345 mmol, 69 % yield, white solid, MP – 223 °C) CAS Registry Number 68862-02-2 ^{1}H NMR (200 MHz, $CDCl_3$, δ) –8.02 - 7.87 (m, 3 H),7.77 - 7.69 (m, 4H), 7.62 – 7.43 (m, 9 H) ^{13}C NMR (200 MHz, $CDCl_3$, δ) – 140.00, 139.67, 133.37, 130,49, 128.89, 128.38, 126.96, 126.02; IR (cm $^{-1}$) – 3384, 2924, 2857, 1589, 1460, 1376, 1219, 1122, 772, 722; HRMS-ESI : $[M+H]^+$ calcd for $C_{22}H_{17}$ $[M+H]^+$ 281.1325, found: 281.1328

Characterization of bimetallic quantum dots :

a. UV-Visible Spectra

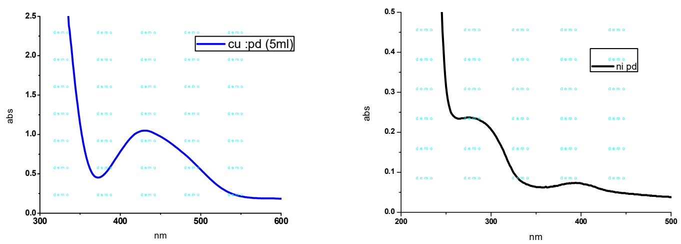
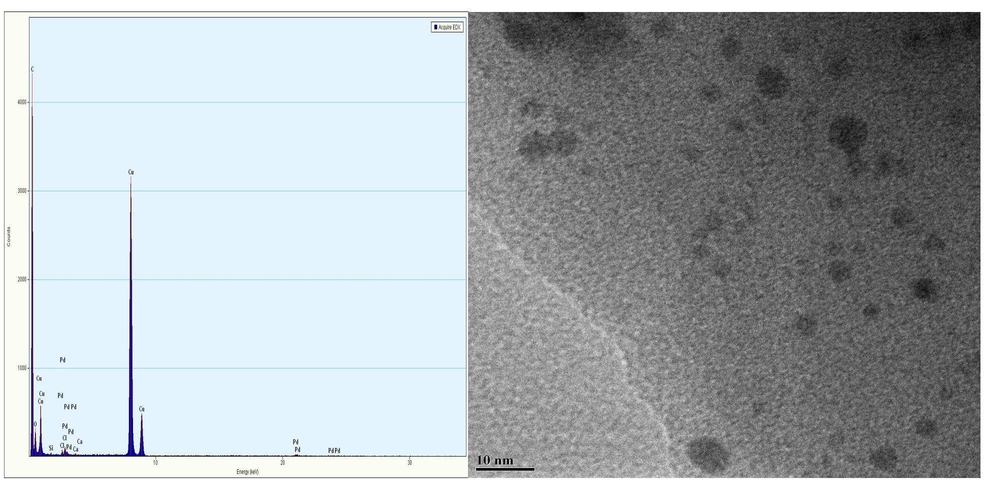


Figure.1 UV-visible spectra of Cu:Pd quantum dots: In above figure UV-visible spectra of Cu:Pd QDs (10:1) ratio is given and it shows two peaks at 432 nm at 1.04 absorbance and other peak at 319 nm with 2.8 absorbance which is characteristic Surface Plasmon Resonance for CuPd bimetaliic quantum dots. NiPd shows absorption at 400nm and extract protein peak at 290nm.

b) TEM image and EDAX spectra for bimetallic quantum dots:



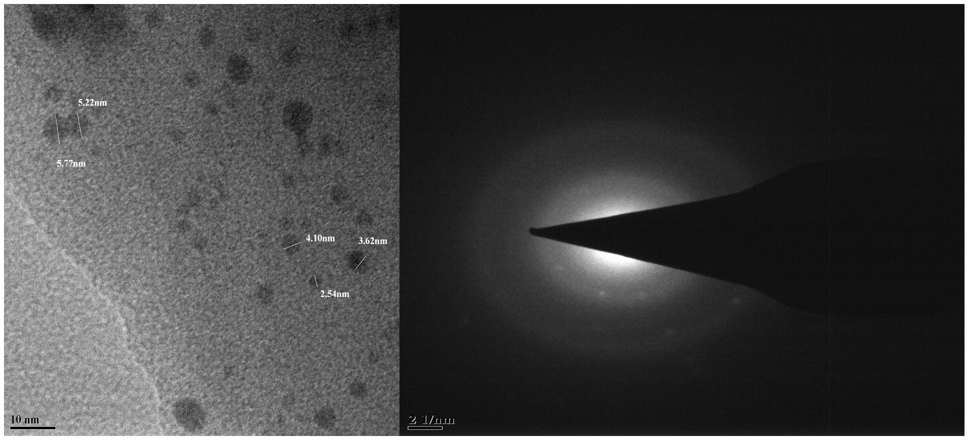


Figure 2 : TEM data shows images with bimetallic CuPd quantum dots with crystalline nature. The size variation is seen with different sizes one with 5.7 nm and other with around 3.5 nm which also confirms bimetallic nature. EDS data explains presence of Cu as well as Pd.

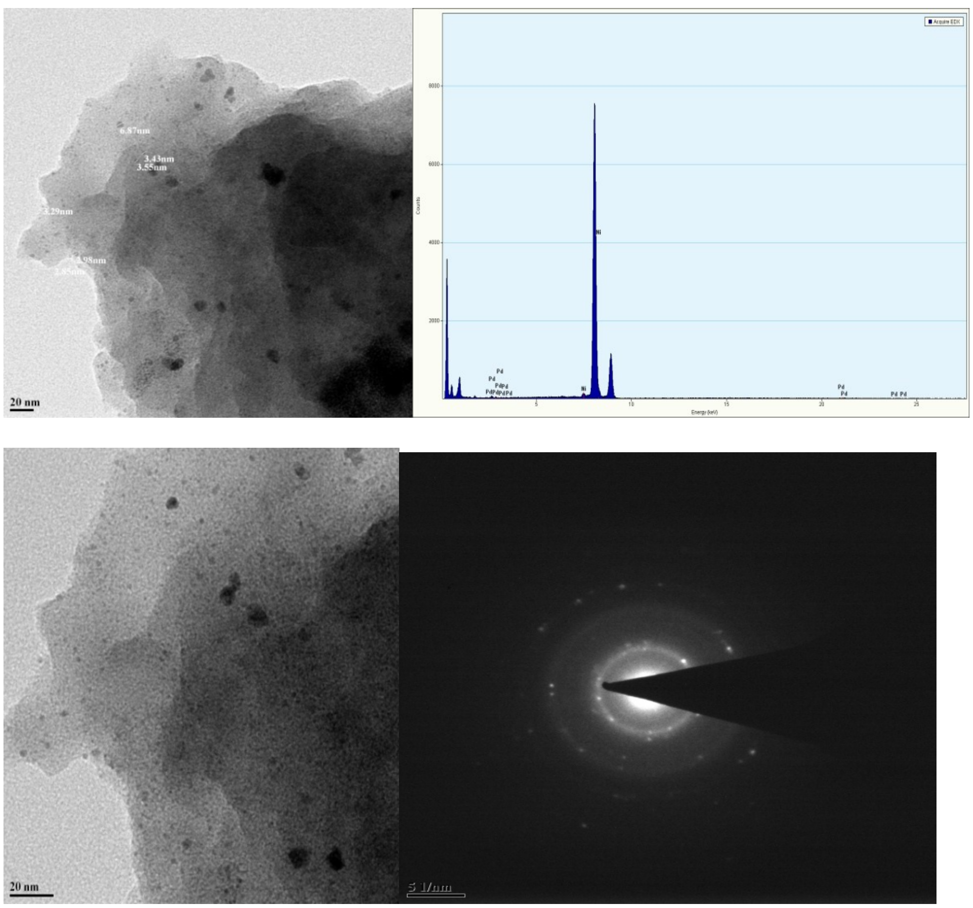


Figure 3 TEM, EDAX data for NiPd quantum dots **:** TEM data shows images with bimetallic NiPd quantum dots with crystalline nature. The size variation is seen with different sizes one with 6.8 nm and other with around 3.4 nm which also confirms bimetallic nature. EDS data explains presence of Nickel as well as Palladium.

XPS analysis

Surface species of only Ni and Cu obtained in the deconvoluted XPS spectra of Pd-Ni and Pd-Cu quantum dots. The figure 1.a represents the Cu2p3/2 analysis of Pd-Cu QDs where binding energy of 932.35 eV represents metallic Cu/Cu^{+1} along with Cu^{+2} represented at 934.6 eV[3]. The presence of strong bimodal satellite peaks also reaffirms this finding. To get the clear idea of chemical composition Cu was also analysed by its LM2 auger analysis as shown in figure 4.b which clearly suggest that proportion of metallic Cu is higher than Cu_2O.

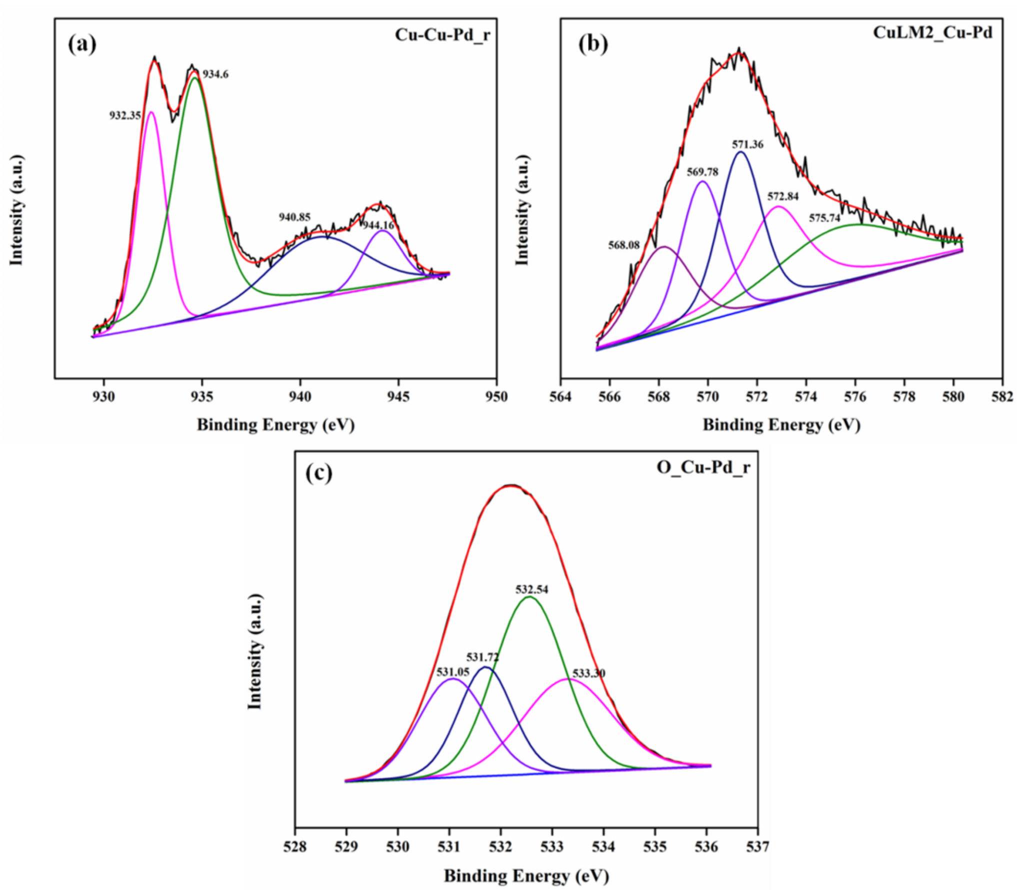


Figure 4: XPS deconvolution of (a) $Cu_2p3/2$ core of Cu in Pd-Cu QDs (b) Cu-LM2 auger spectra (c) O1s core spectra of Cu in Pd-Cu

Higher binding energy impressions like 572.84 eV, 575.74 eV and 571.36 eV which have almost 66.94% chunk of CuLM2 auger spectra are attributed to Cu(0) whereas lower binding energy values like 569.78 eV and 568.08 eV correspond to Cu_2O[4]. Adsorbed Oxygen and lattice Oxygen with different chemical environment is also observed in O1s spectra of Pd-Cu QDs at 531.97 eV and 530.42 and 531.16 eVs respectively[5]. Figure 5 depicts the XPS deconvolution of Ni2p3/2 core level of Ni in Pd-Ni variant suggesting presence of metal-metal oxide pair as Ni(0) was observed at 855.58 eV and Ni(+2) at 859.76 eV[6]. Appearance of multiple peaks in Ni XPS analysis also inferred the presence of various oxide form of Ni on surface.

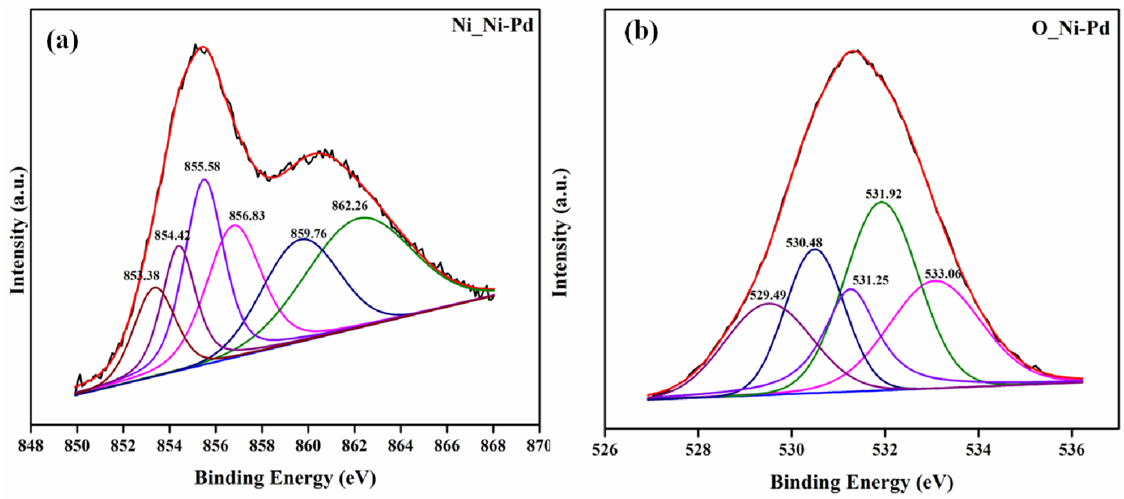


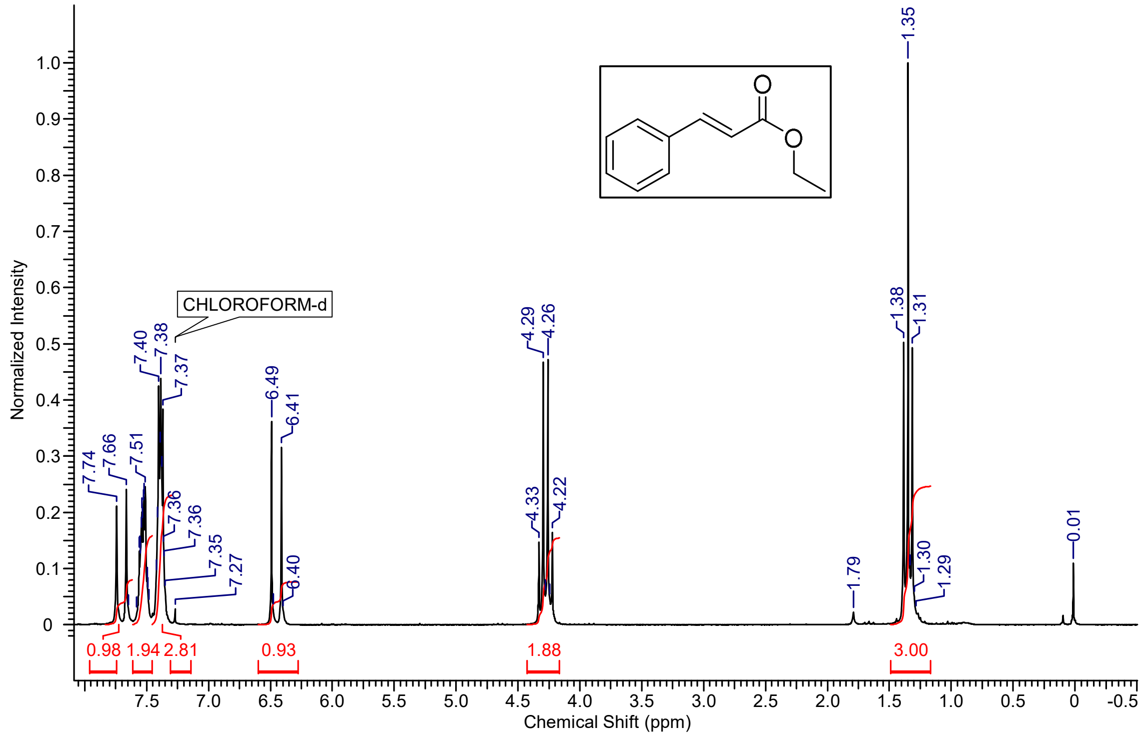
Figure 5: XPS deconvolution of (a) Ni2p3/2 core level spectra of Ni in Pd-Ni (b) O1s core level spectra of Ni in Pd-Ni

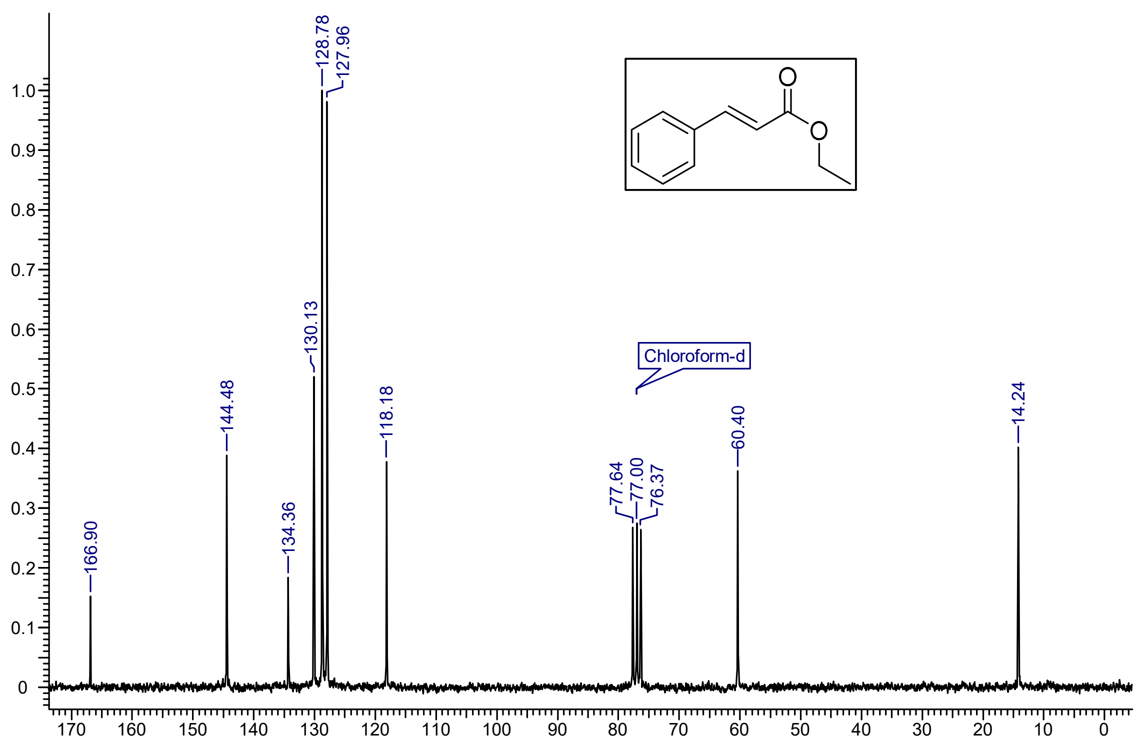
References

1. Waghmode S A, Arora B, Lokhande V 2017 *Indian Pat. Appl*. IN 201721016134 A 20170602
2. Shivshankar S, Rai A, Ahmad A, Sastry M 2004 Rapid synthesis of Au, Ag, and bimetallic Au core–Ag shell nanoparticles using Neem (Azadirachta indica) leaf broth *J. Colloid. Interface Sci.* **275 (2)** 496
3. Chusuei C C, Brookshier M A, Goodman D W 1999 Correlation of Relative X-ray Photoelectron Spectroscopy Shake-up Intensity with CuO Particle Size *Langmuir* **15** 2806
4. Li D, Wang G, Cheng L, Wang C, Mei X 2018 Engineering the Self-Assembly Induced Emission of Copper Nanoclusters as 3D Nanomaterials with Mesoporous Sphere Structures by the Crosslinking of Ce^{3+} *ACS Omega* **3** 14755
5. Gao Y, Yang F, Yu Q, Fan R, Yang M, Rao, S, Lan Q, Yang Z, Yang Z 2019 Three-dimensional porous Cu@Cu_2O aerogels for direct voltammetric sensing of glucose *Microchim. Acta.* **186** 192
6. Hosseini M G, Hosseinzadeh F, Zardari P, Mermer O 2018 Pd-Ni nanoparticle supported on reduced graphene oxide and multi-walled carbon nanotubes as electrocatalyst for oxygen reduction reaction *Fullerenes, Nanotubes and Carbon Nanostructures* **26**, 675

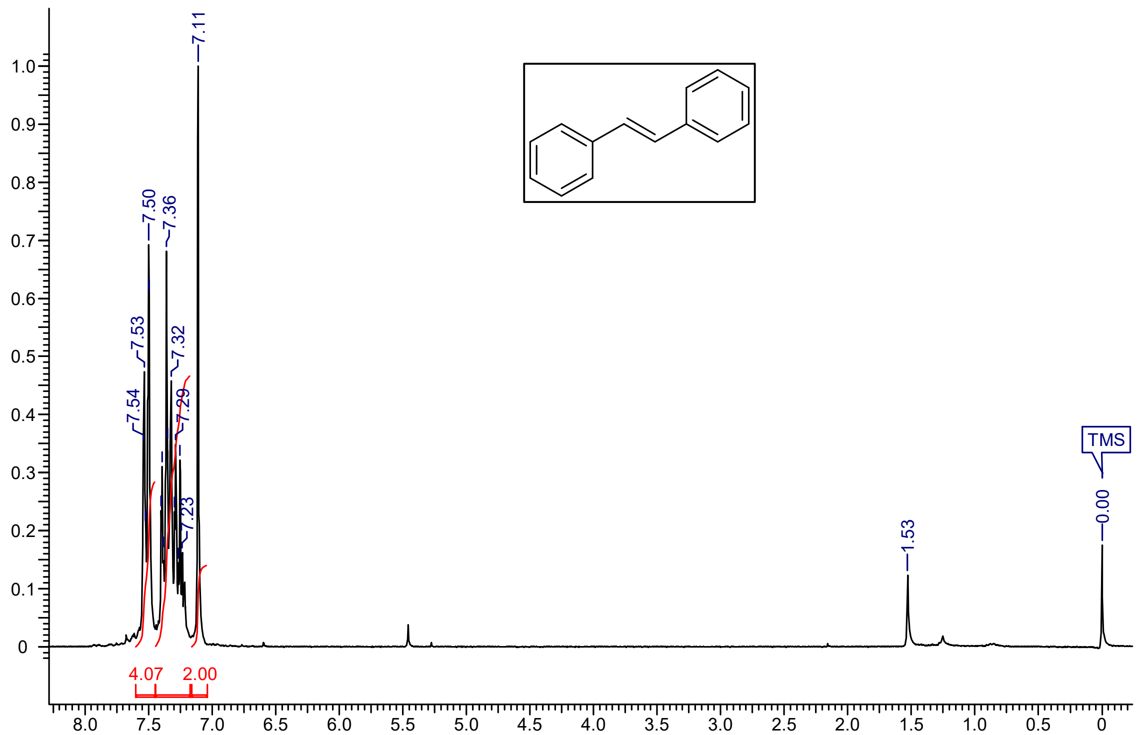
b) Characterization of organic reaction products: i) NMR Spectra-

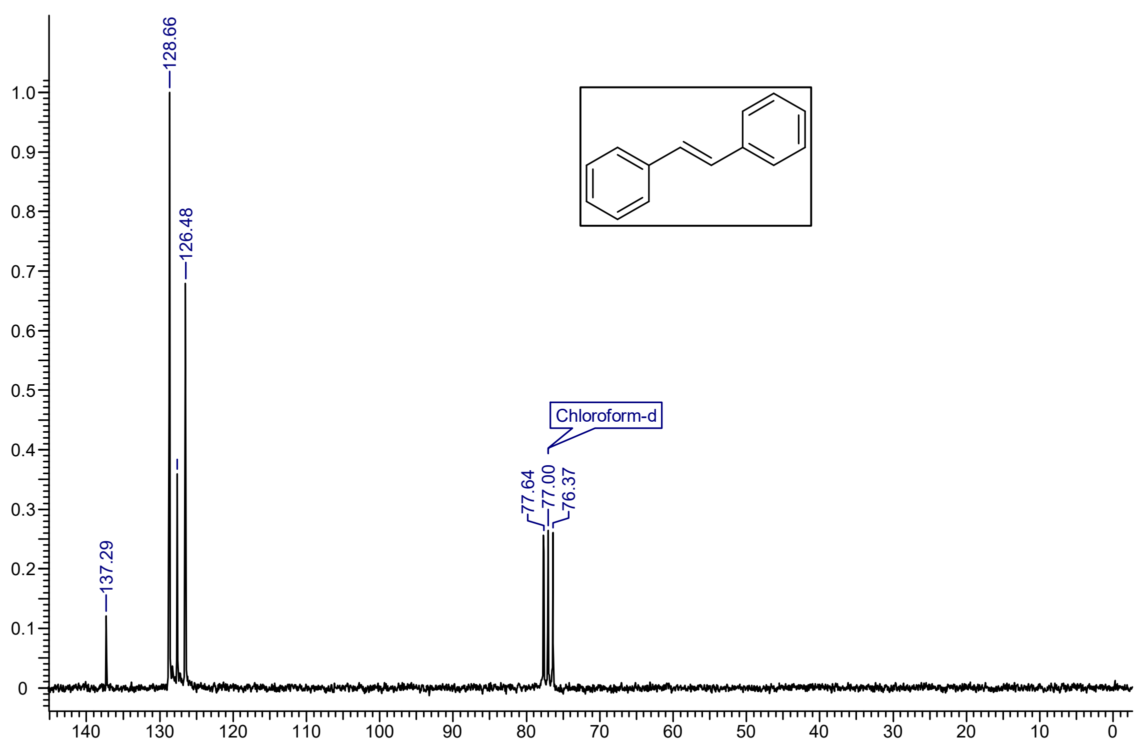
A1 2-Propenoic acid, 3-phenyl-, ethyl ester (2E) (4a)



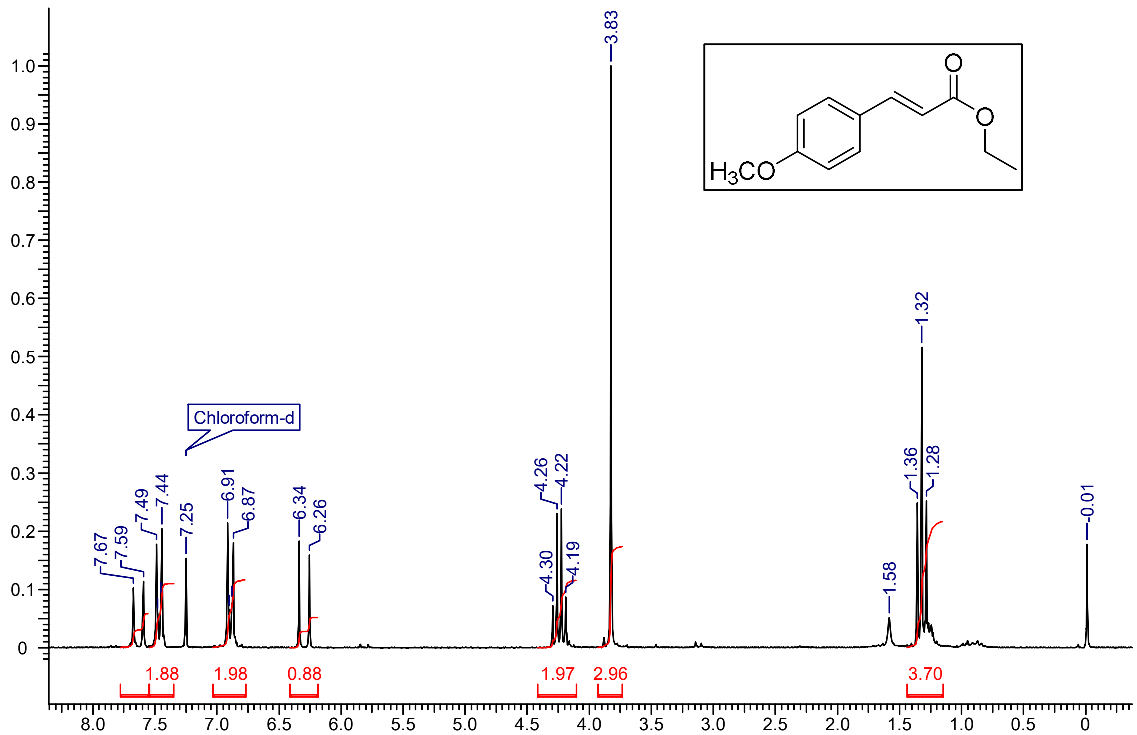


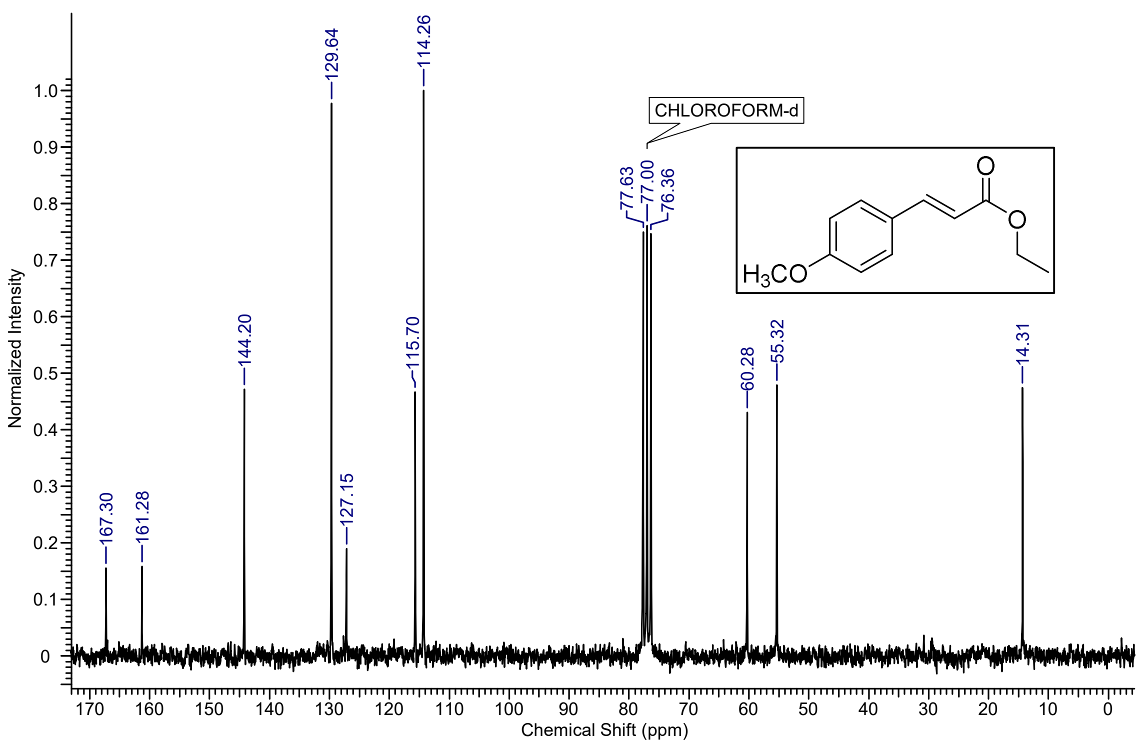
A2 Benzene, 1,1'-(1E)-1,2-ethenediylbis (4b)



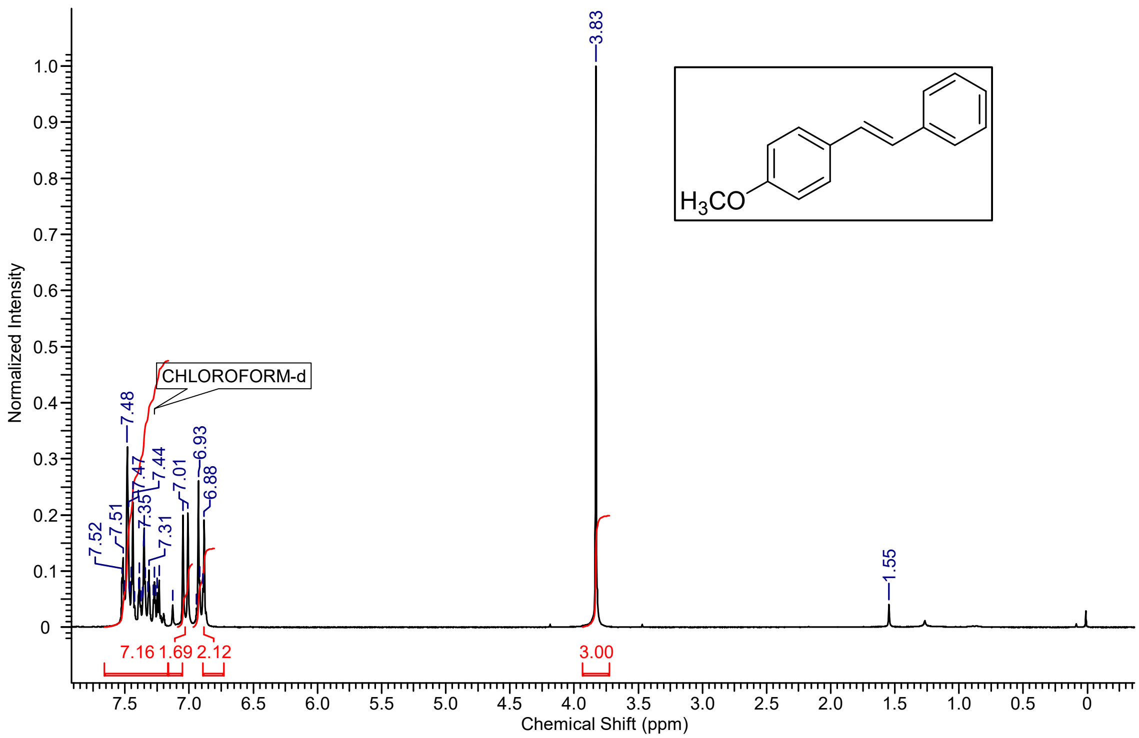


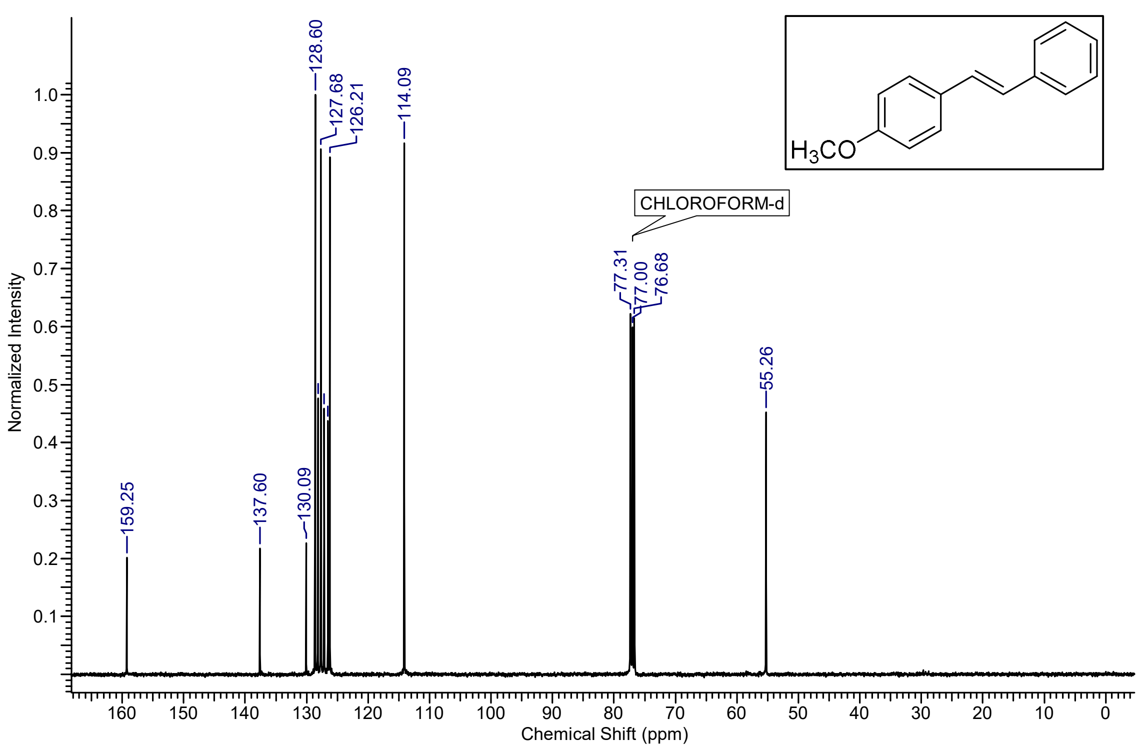
A3 2-Propenoic acid, 3-(4-methoxyphenyl)-, ethyl ester, (2E)- (4c)



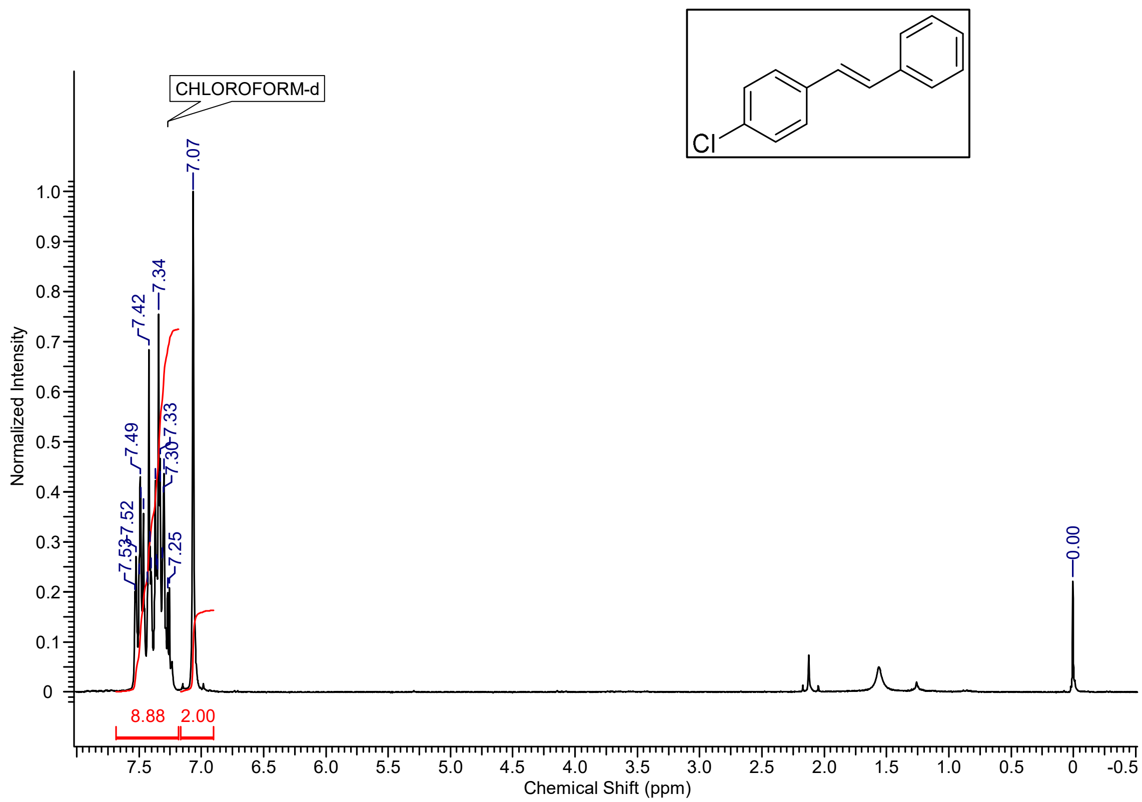


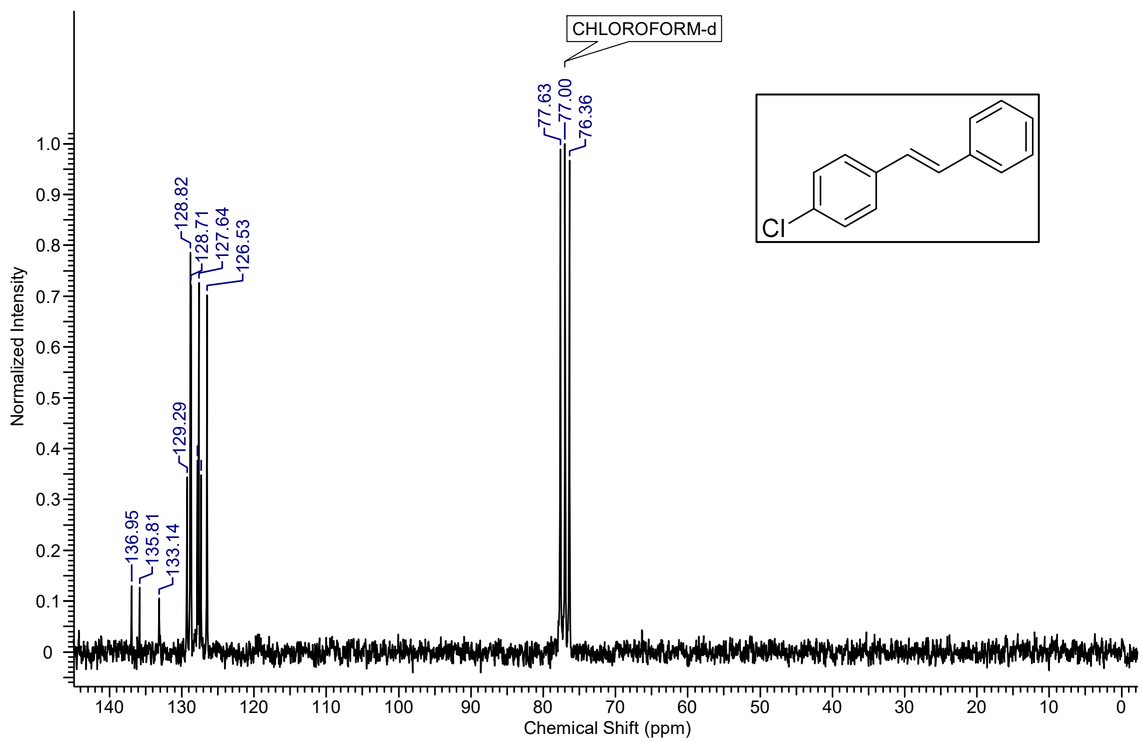
A4 Benzene, 1-methoxy-4-[(1E)-2-phenylethenyl]- (4d)



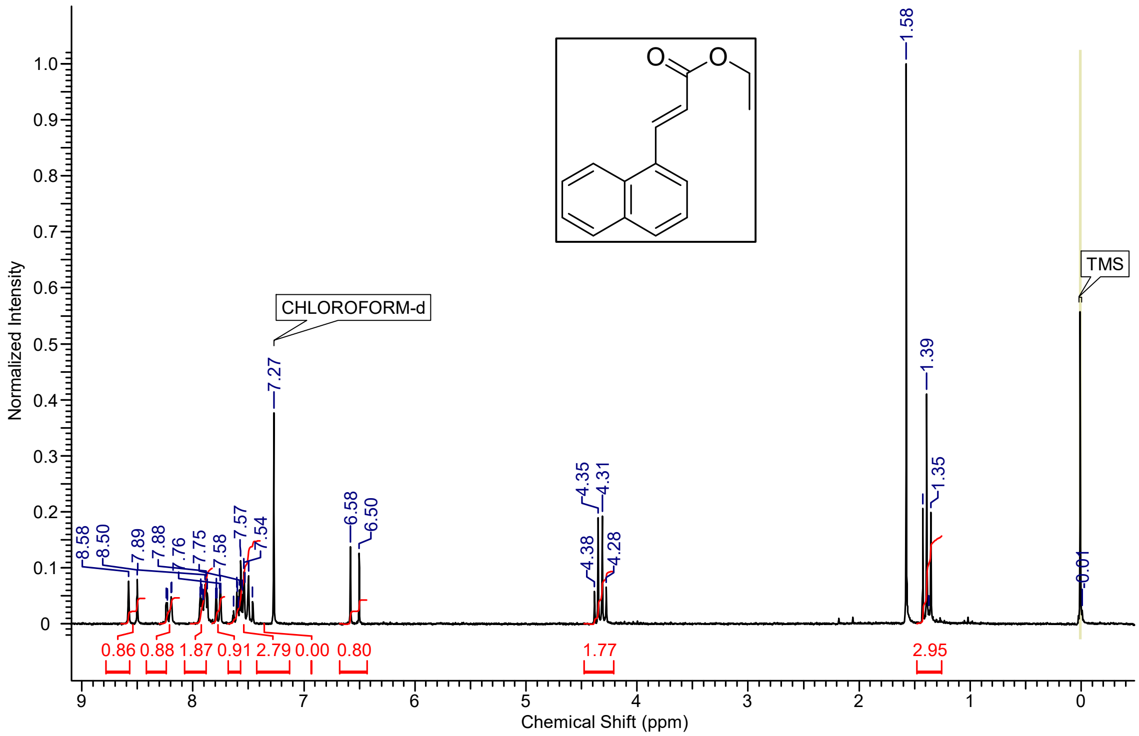


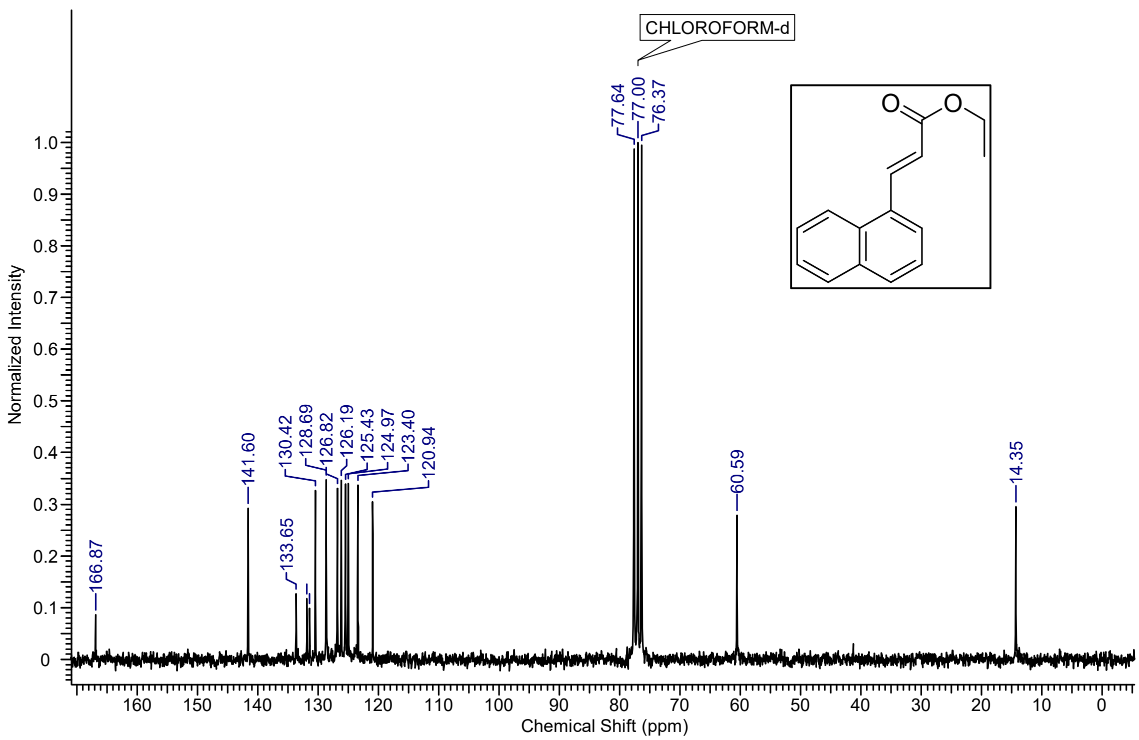
A5 Benzene, 1-chloro-4-[(1E)-2-phenylethenyl]- (4e)



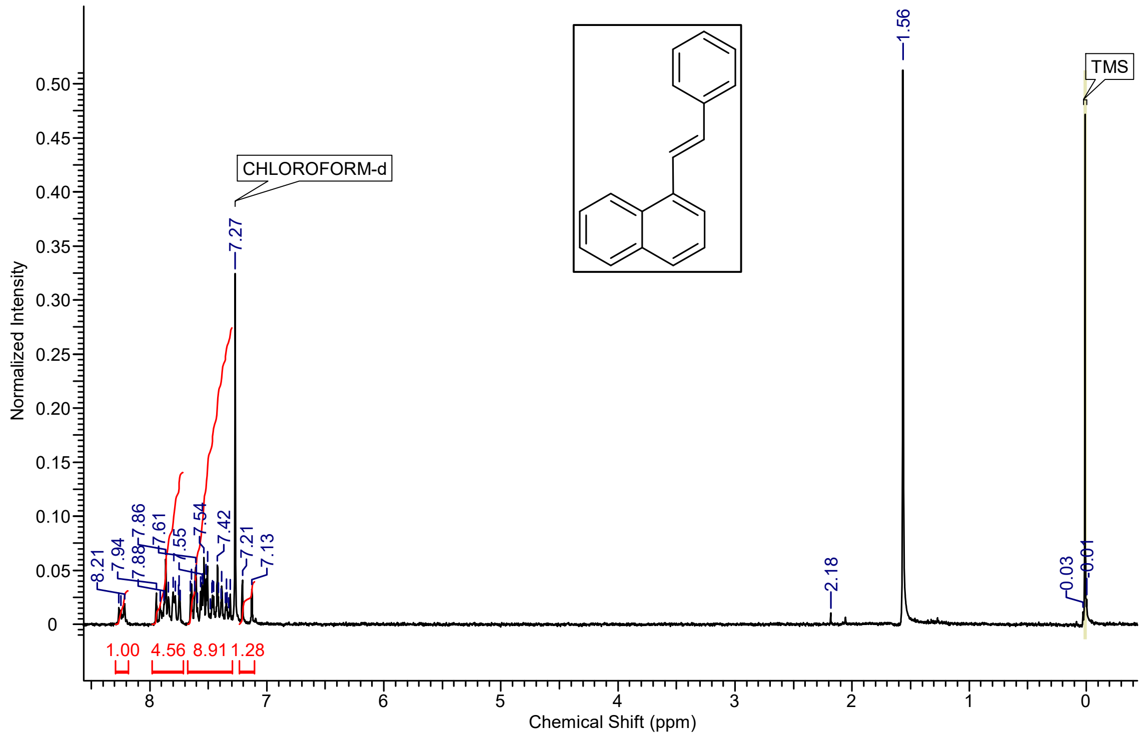


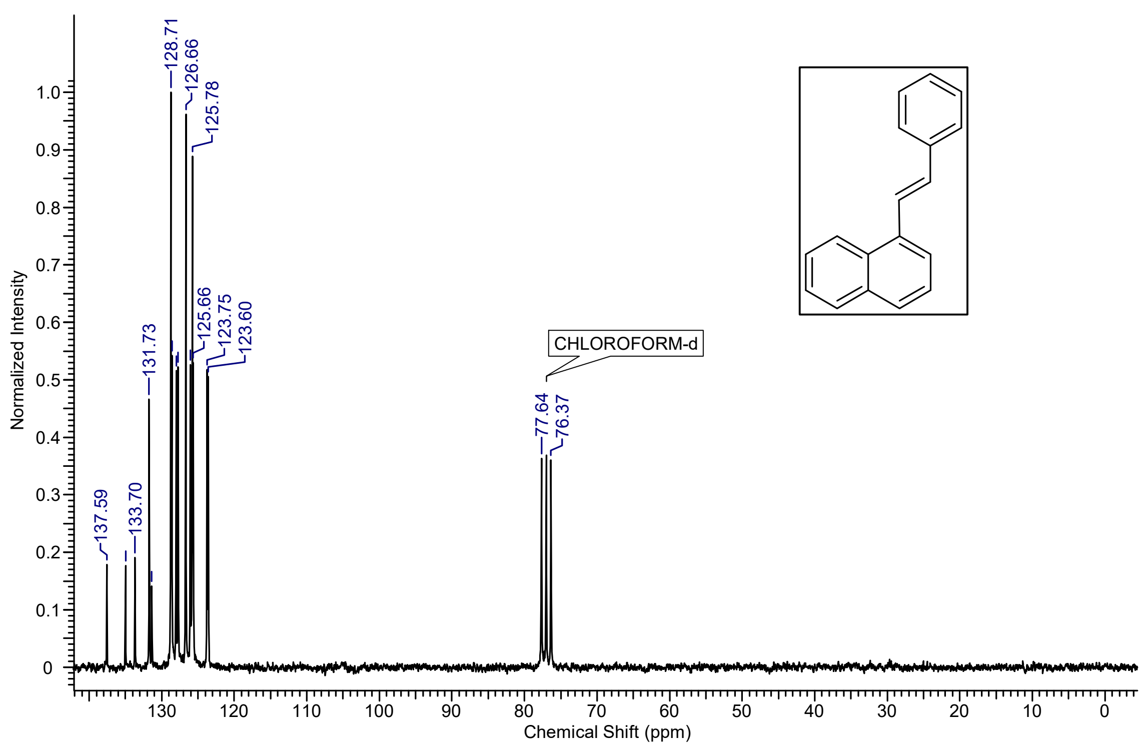
A6 2-Propenoic acid, 3-(1-naphthalenyl)-, ethyl ester, (2E)-(4f)



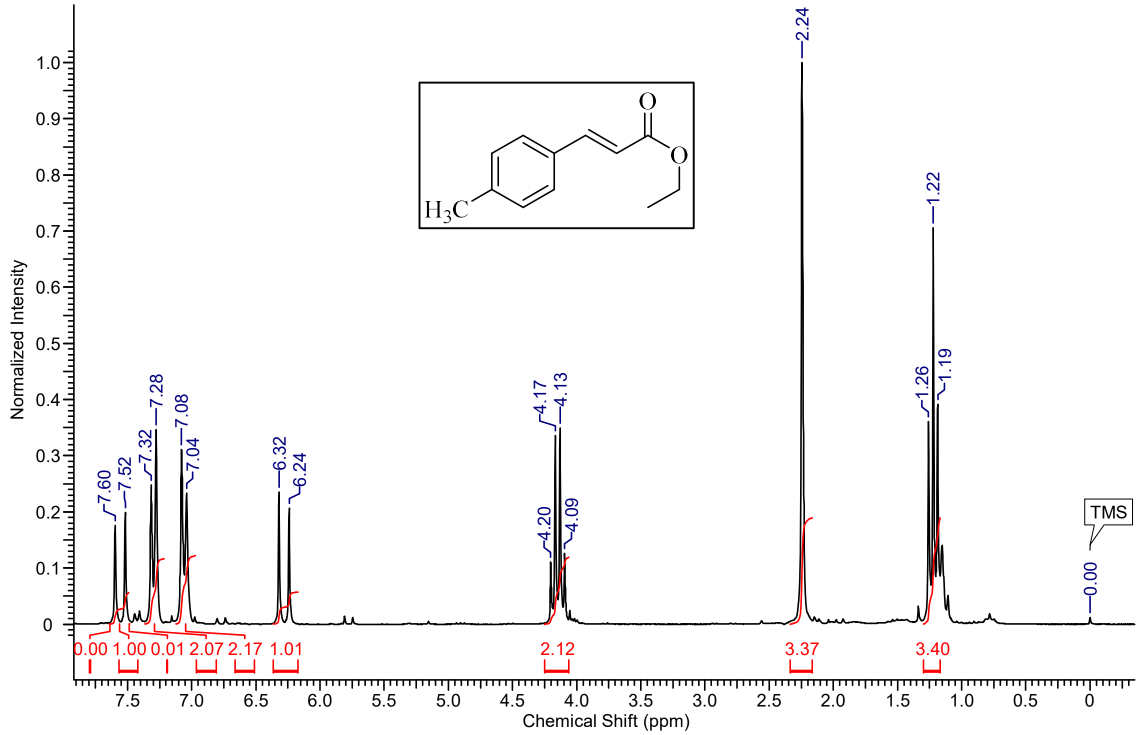


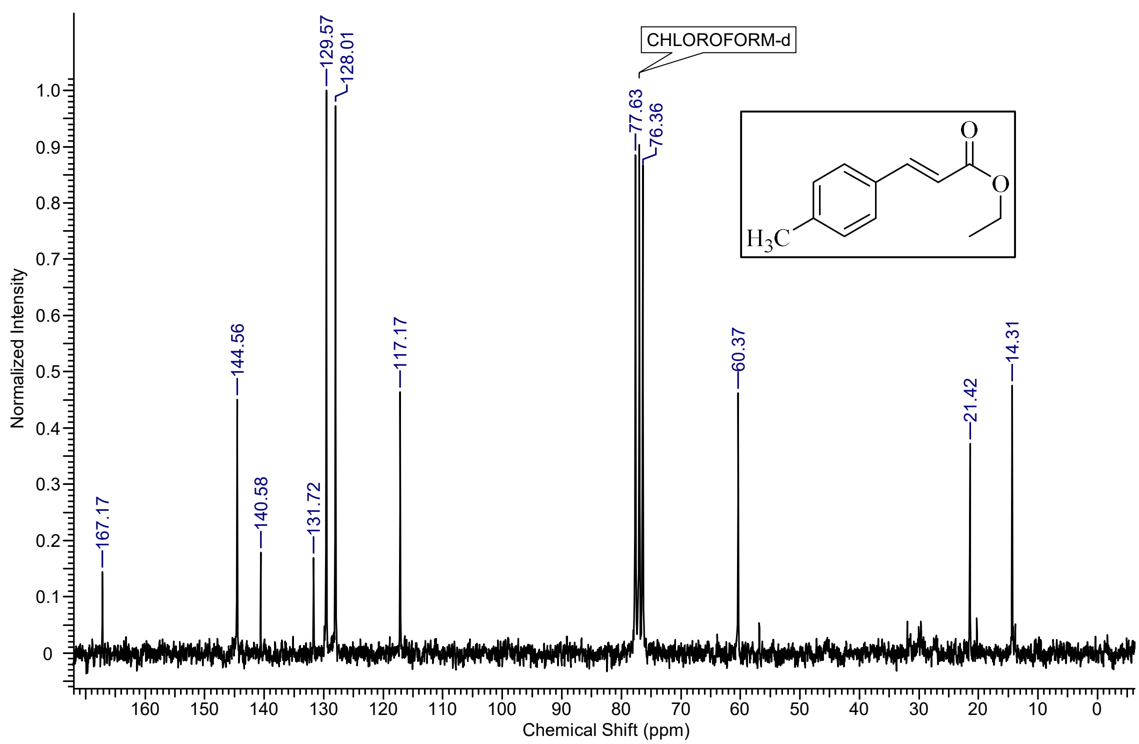
A7 Naphthalene,1-[(1E)-2-phenylethenyl]- (4g)



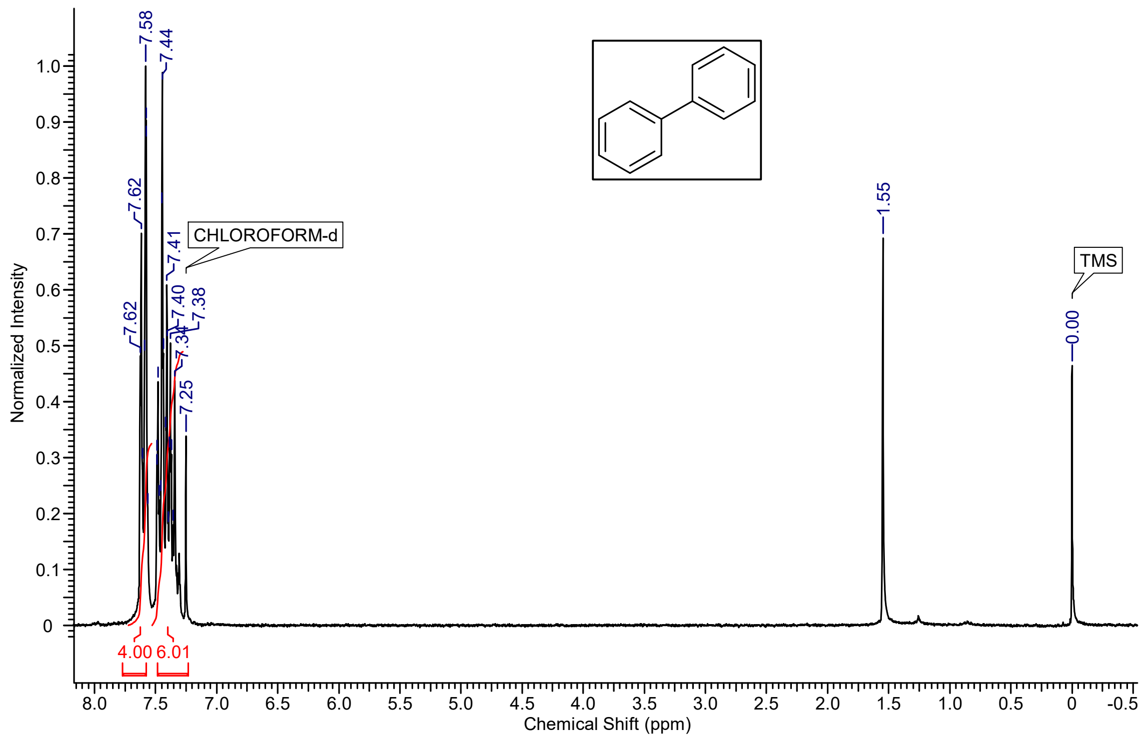


A8 2-Propenoic acid, 3-(4-methylphenyl)-ethyl ester (2E) (4h)

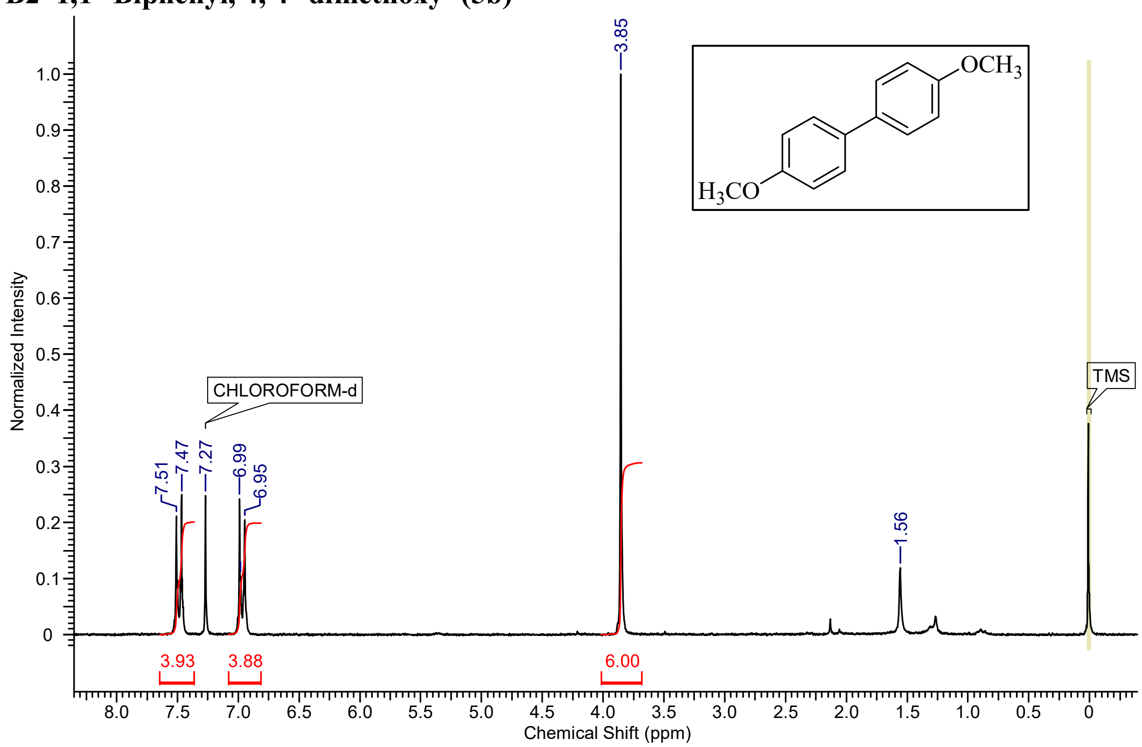




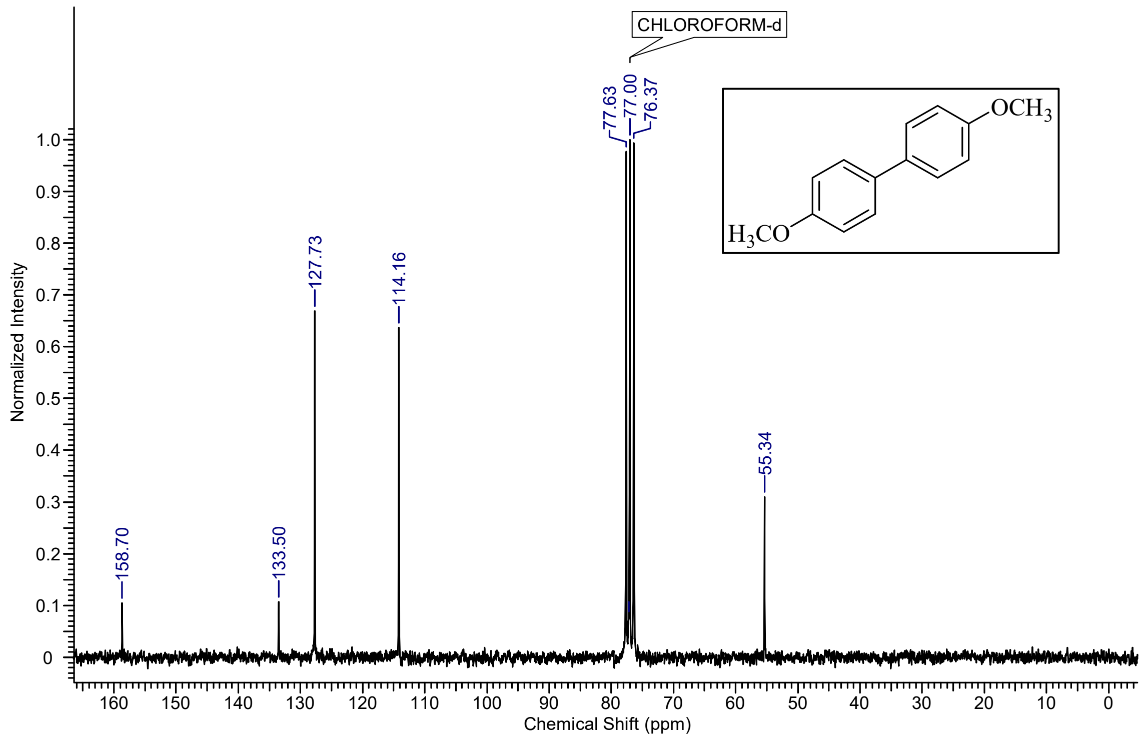
B1 1,1'-Biphenyl (5a)



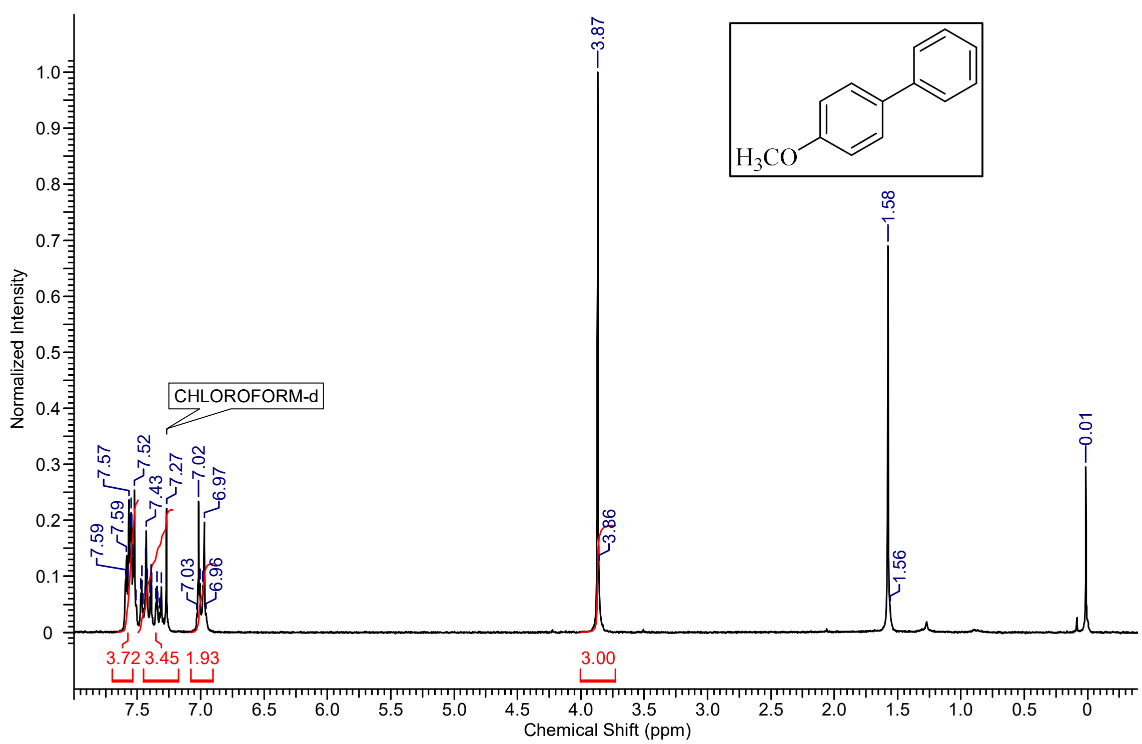
B2 1,1'-Biphenyl, 4, 4'-dimethoxy- (5b)



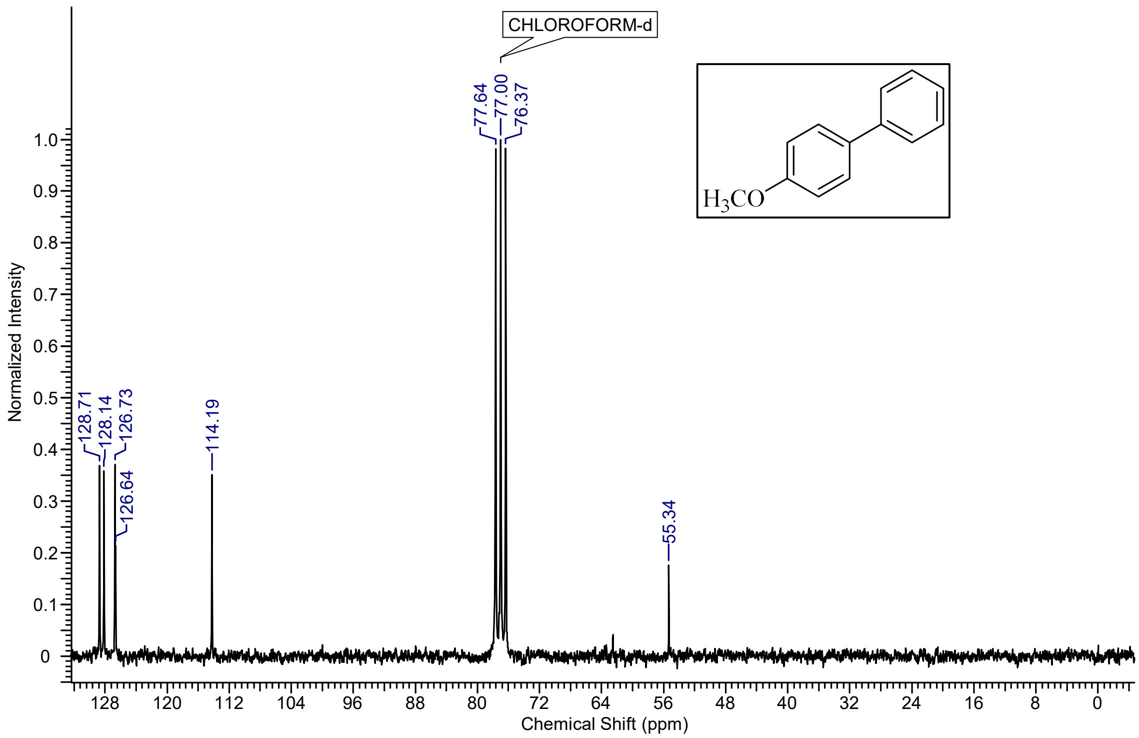
B2 1,1'-Biphenyl, 4, 4'-dimethoxy- (5b)



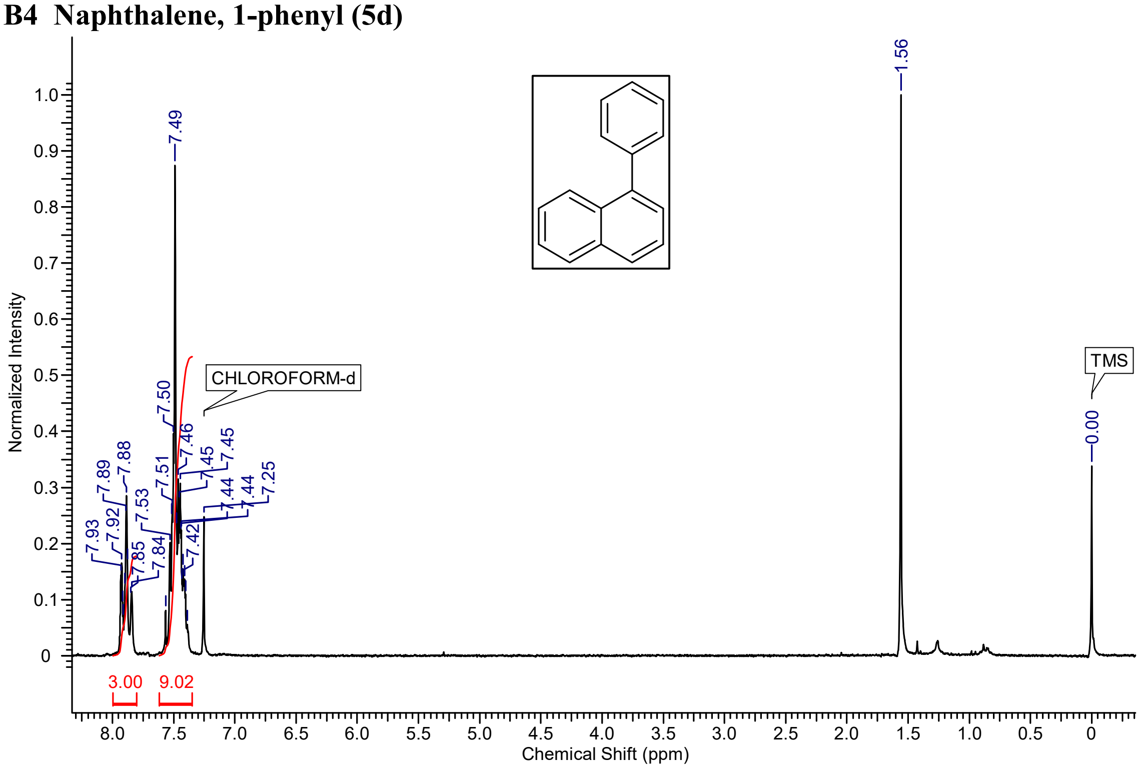
B3 1,1'-Biphenyl, 4-methoxy- (5c)



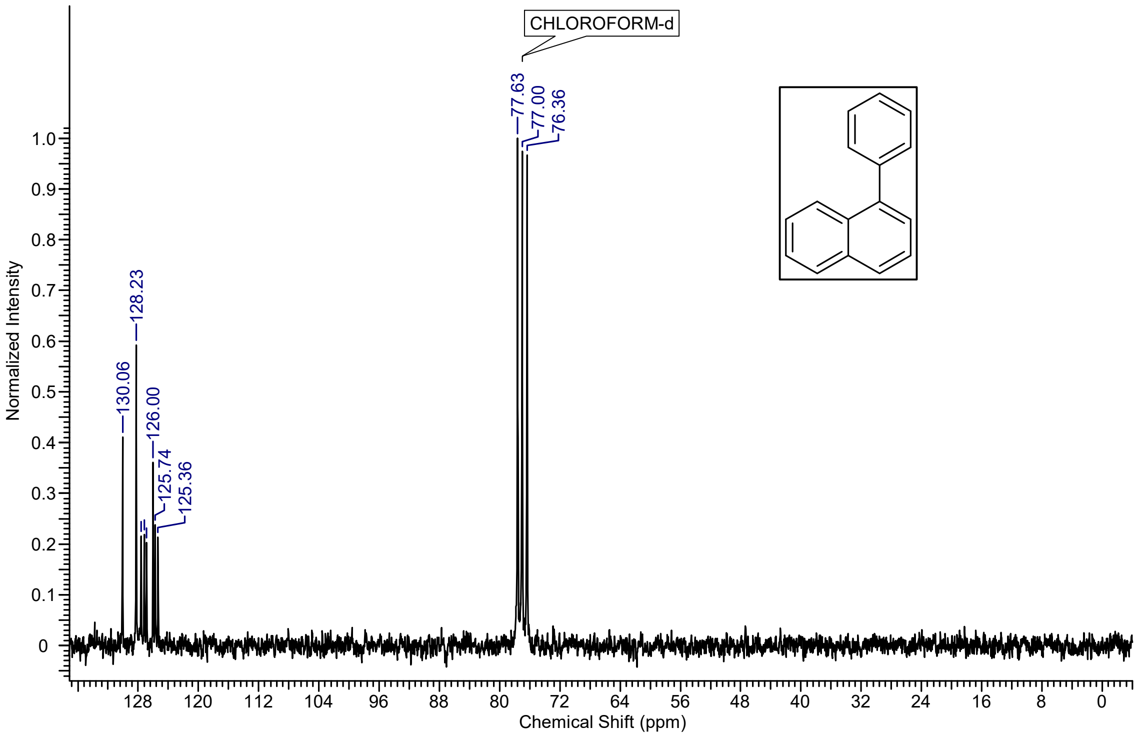
B3 1,1’-Biphenyl, 4-methoxy- (5c)



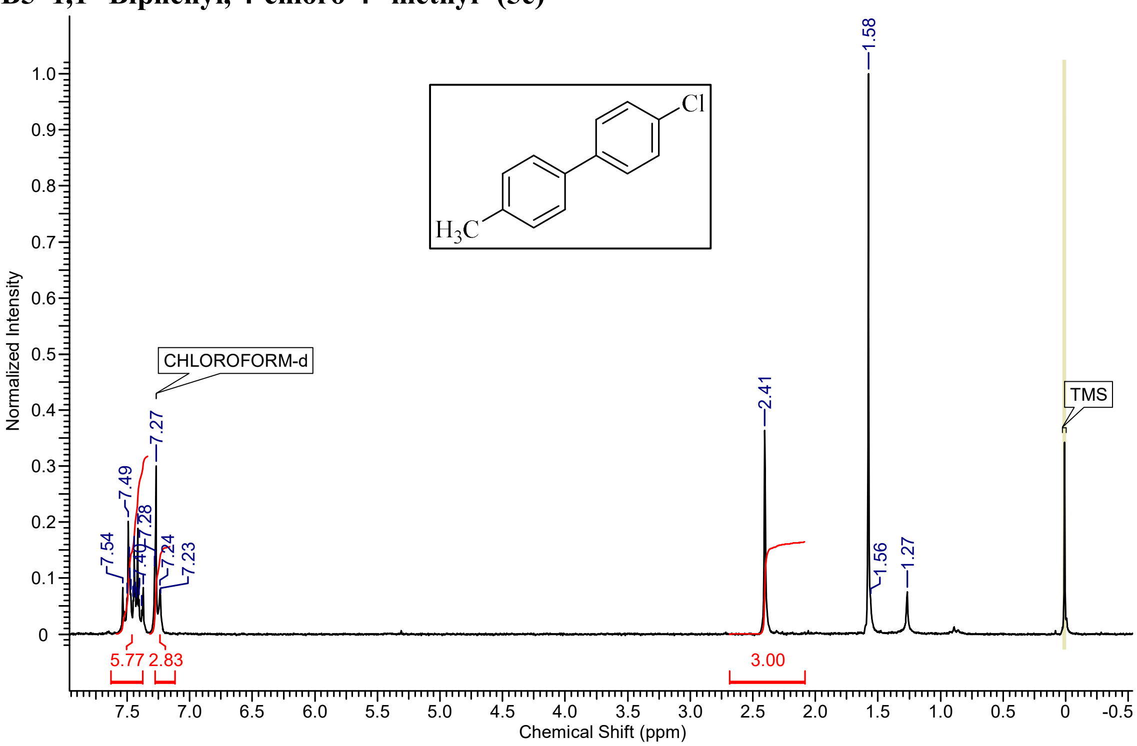
B4 Naphthalene, 1-phenyl (5d)



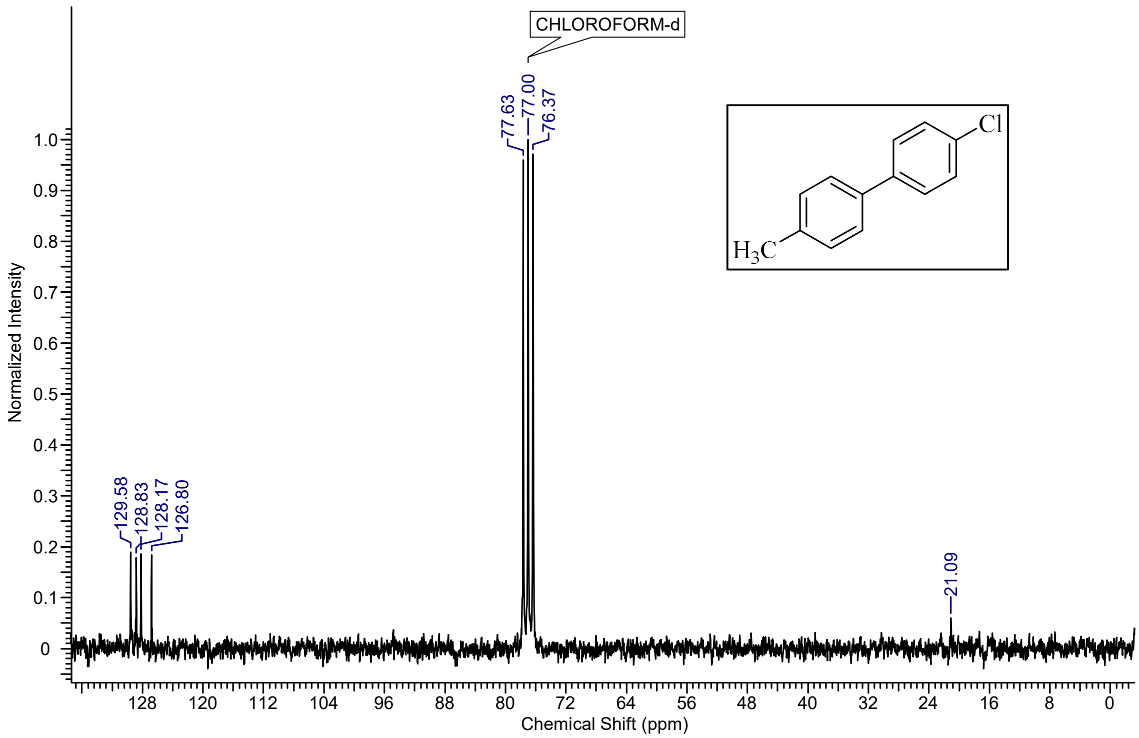
B4 Naphthalene, 1-phenyl (5d)



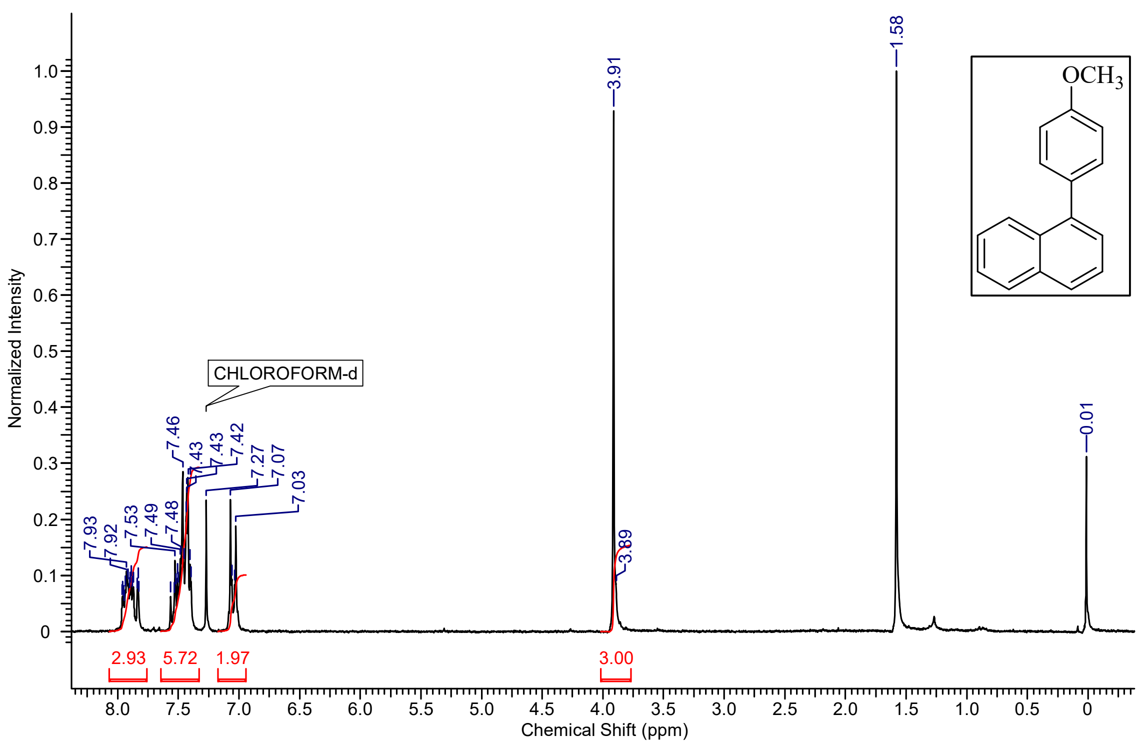
B5 1,1'-Biphenyl, 4-chloro-4'-methyl- (5e)



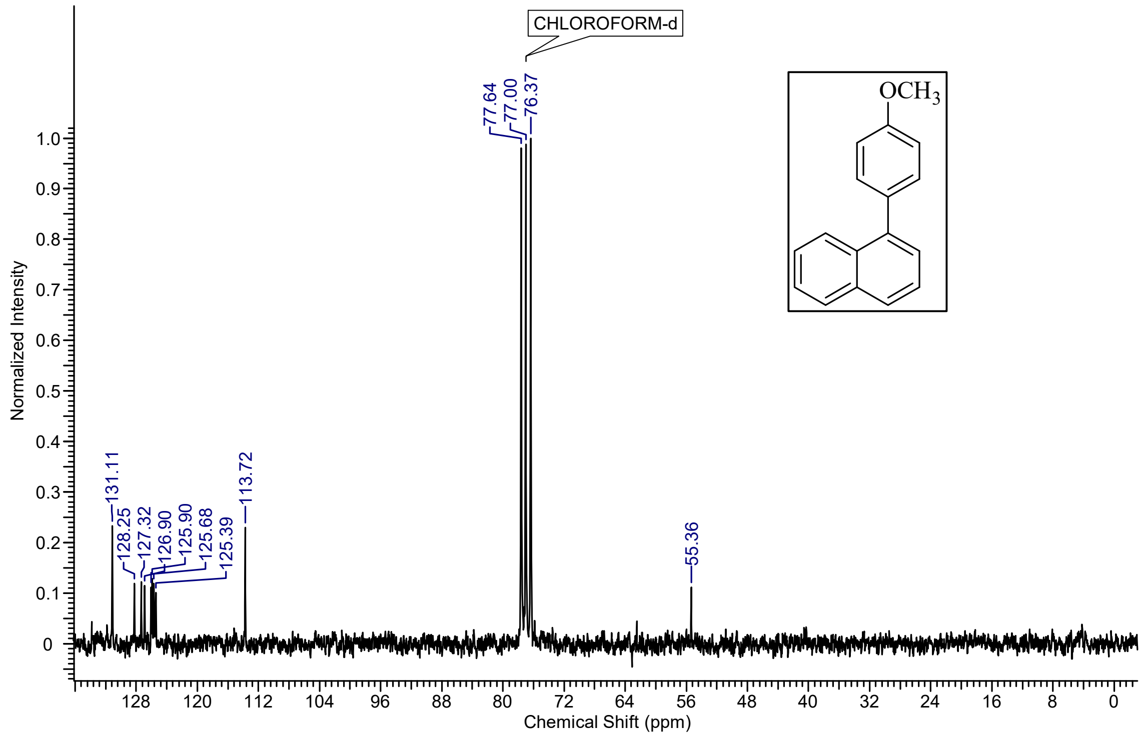
B5 1,1'-Biphenyl, 4-chloro-4'-methyl- (5e)



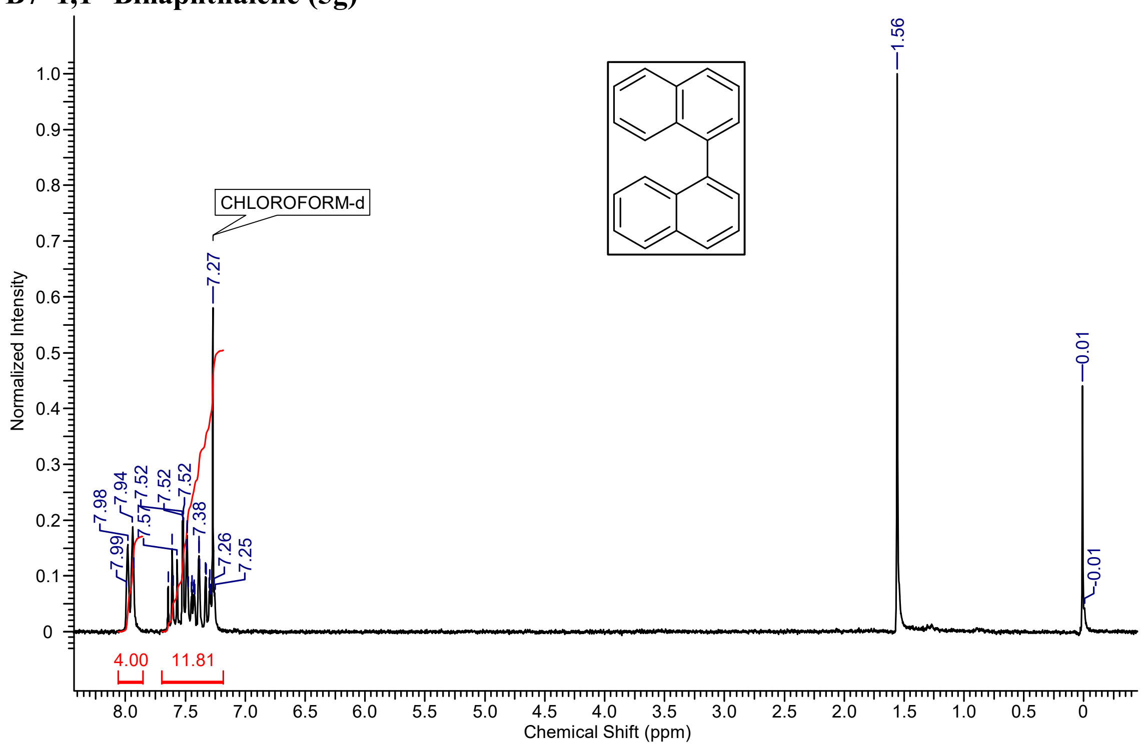
B6 Naphthalene, 1-(4-methoxyphenyl)- (5f)



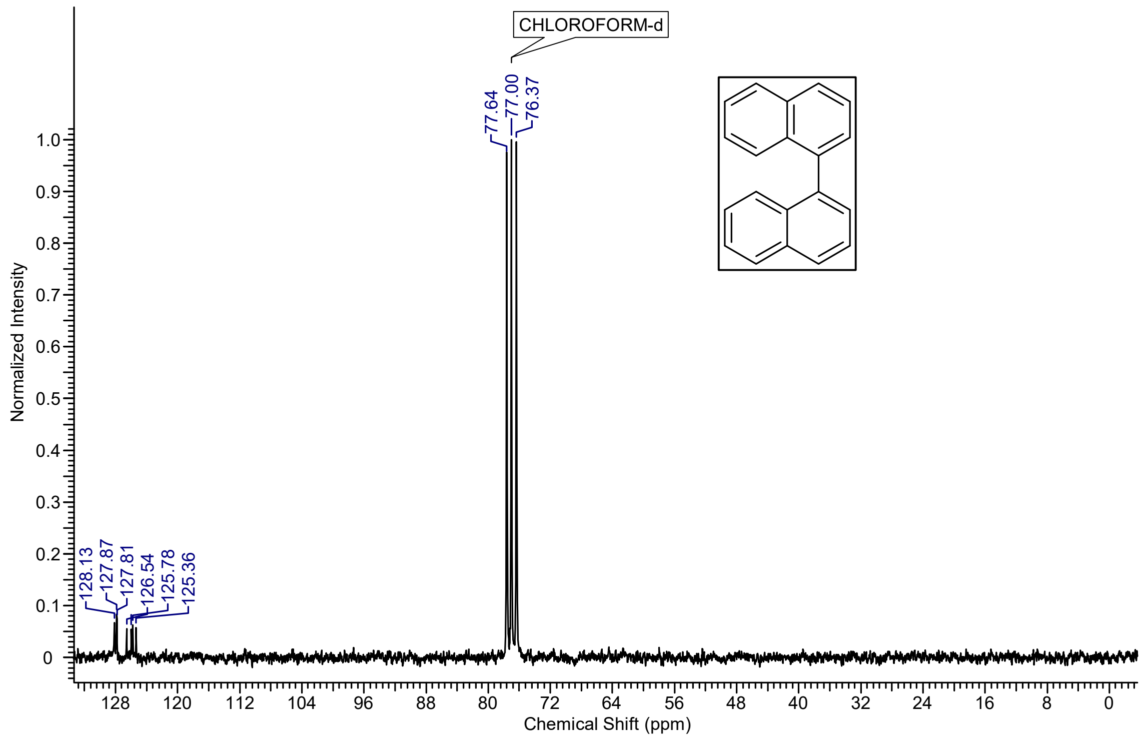
B6 Naphthalene, 1-(4-methoxyphenyl)- (5f)



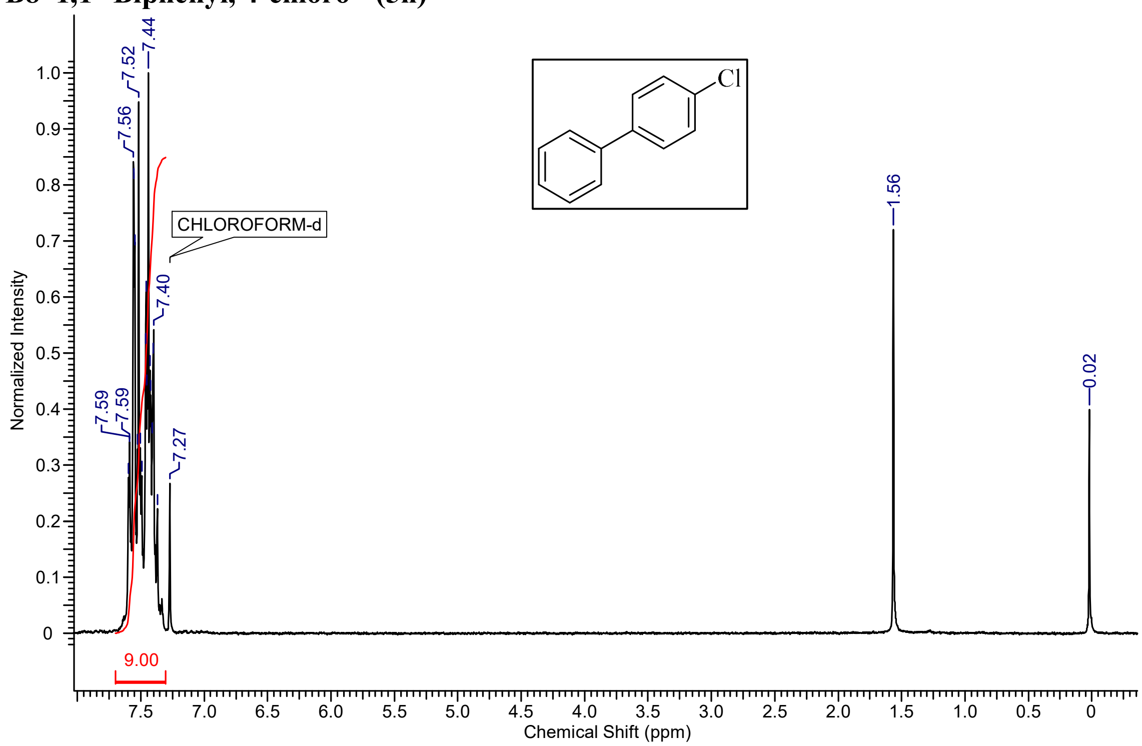
B7 1,1'-Binaphthalene (5g)



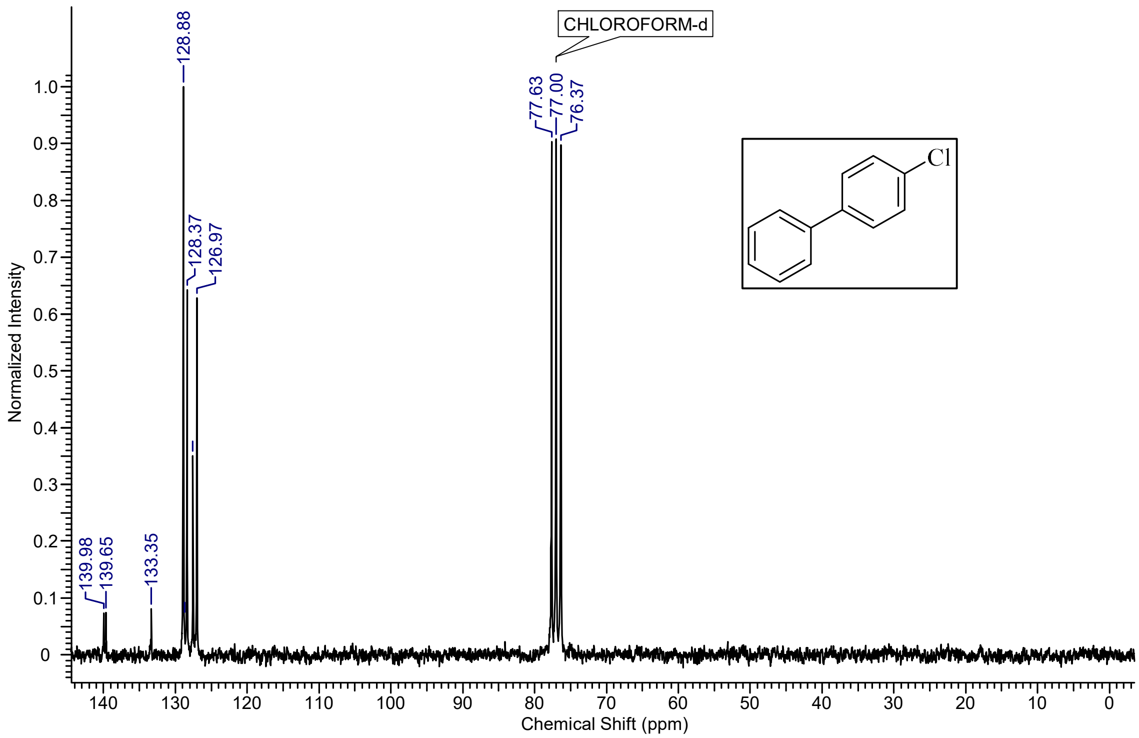
B7 1,1'-Binaphthalene (5g)



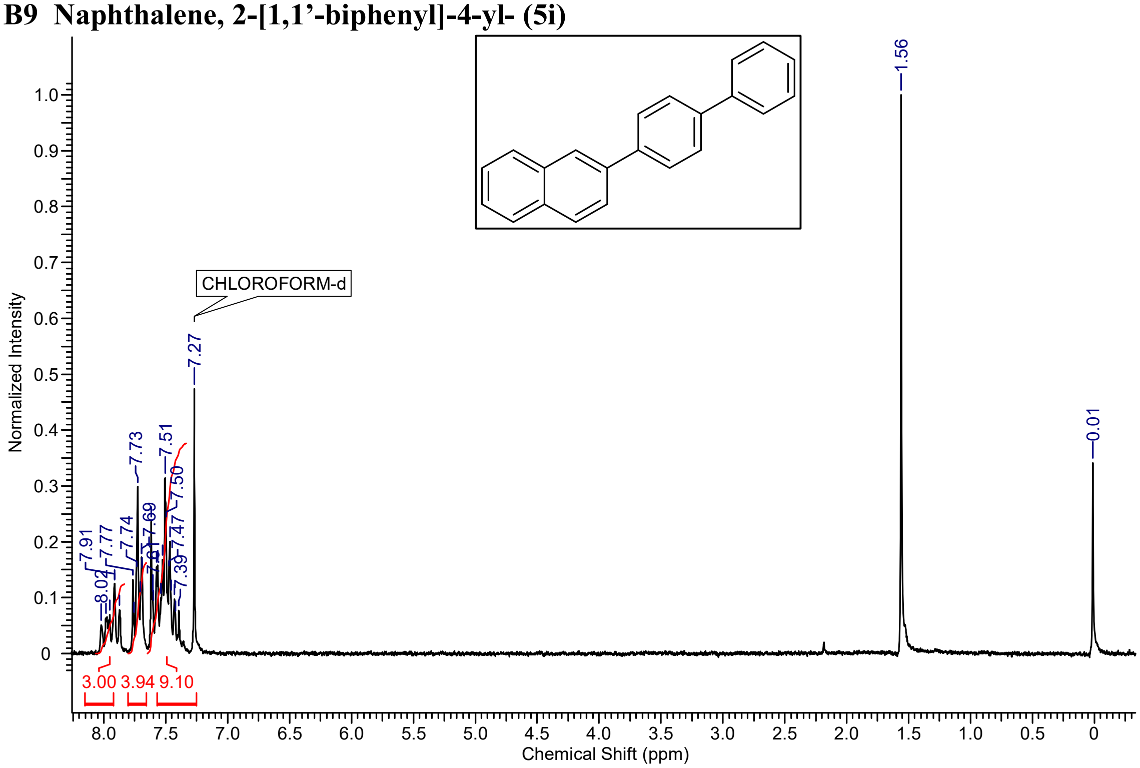
B8 1,1'-Biphenyl, 4-chloro- (5h)



B8 1,1'-Biphenyl, 4-chloro- (5h)



B9 Naphthalene, 2-[1,1'-biphenyl]-4-yl- (5i)



B9 Naphthalene, 2-[1,1'-biphenyl]-4-yl- (5i)