Suzuki–Miyaura cross-couplings of arenediazonium tetrafluoroborate salts with arylboronic acids catalyzed by aluminum hydroxide-supported palladium nanoparticles

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Supporting Information

General

All reagents were purchased from commercial sources and used without further purification, unless otherwise indicated. Deuterated solvents were purchased from aladdin. All chromatographically pure reagents were used as solvents. Column chromatography was performed on silica gel (200-300 mesh) with petroleum ether (solvent A)/ethyl acetate (solvent B) gradients, unless otherwise specified. All yields were referred to isolated yields (average of two runs) of compounds. The known compounds were partly characterized by melting points (for solid samples), IR, ^{1}H NMR and ^{13}C NMR, and compared to authentic samples or the literature data. Melting points were measured with a RD-II digital melting point apparatus and are uncorrected. IR spectra (KBr) were recorded on an FT-IR spectrophotometer. ^{1}H NMR data were acquired at 300 K on a Bruker Advance 600 MHz spectrometer or Avarian Inova 500 MHz spectrometer using $CDCl_3$ as solvent. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, = 7.26). Spectra are reported as follows: chemical shift (δ = ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration, and assignment. ^{13}C NMR spectra were collected on commerical instruments (150 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, = 77.0). Mass spectroscopy data of the product was collected on an Agilent 6890-5973N GCMS-EI instrument.

Synthesis of the catalyst 1[1]

A mixture of Pd $(PPh_3)_4$ (260 mg, 0.225 mmol), tetra (ethylene glycol) (418 mg, 2.20 mmol), 1-butanol (3 mL, 32.7 mmol), and aluminum tri-sec-butoxide (9.50 g, 38.5 mmol) was stirred at 110 °C for 10 h, and then the reaction mixture was further stirred at 110 °C for 0.5 h to form a black gel after water was added dropwise. Subsequently, filtering, washing with acetone, and drying the gel at room temperature in the air to give the catalyst **1** as dark greyish-green powder.

Characterization of the catalyst 1

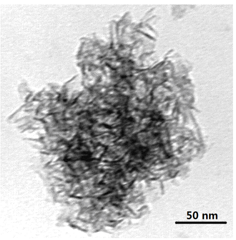


Figure 1. The TEM image of the fresh catalyst **1**

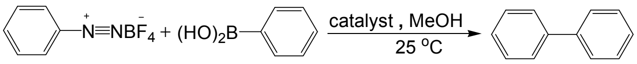
The catalyst **1** was characterized by transmission electron microscopy (TEM). A distinct fibrous morphology is shown in the TEM image (Figure 1).

General procedure for Suzuki cross-coupling reactions

To a tube equipped with a magnetic stir bar were added arenediazonium tetrafluoroborate salt (0.3 mmol, 1.0 equiv.), arylboronic acid (0.36 mmol, 1.2 equiv.) and the catalyst **1** (11.2 mg, 0.3 mol% Pd) in turn. Subsequently, solvent (MeOH, 1.8 mL) was added under air atmosphere. The reaction mixture was then stirred at the specified temperature[2] (Digital display temperature control instrument was used in this process) until the arenediazonium tetrafluoroborate salt was completely consumed. After the solvent (chromatographically pure MeOH) was removed under reduced pressure, the residue was purified by silica gel column chromatography to afford the corresponding pure product.

Screening of palladium catalysts

Table 4 Palladium-Catalyzed Suzuki-Miyaura cross-coupling reaction[a]

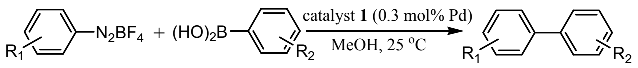


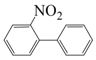
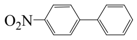
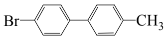
Entry	Cat*	*t* (h)	Yield (%)[b]
1	Cat* 1	4	92
2[c]	Cat* 2	24	26
3	Pd $(PPh_3)_4$	32	31

[a] Reaction conditions: benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), phenylboronic acid (43.9 mg, 1.2 equiv, 0.36 mmol), catalyst (0.3 mol% Pd), MeOH (1.8 mL), 25 °C. [b] Isolated yield. [c] In this process of the preparation of the catalyst 2, aluminium isopropoxide was used instead of aluminum tri-sec-butoxide.

Some cross-couplings at 25 °C

Table 5 Cross-Couplings of arenediazonium tetrafluoroborate salts and arylboronic acids catalyzed by the Palladium nanoparticles catalyst **1**[a]



Entry	R_1	R_2	*t* (h)	Product	Yield (%)[b]
1	2-NO_2	H	3		71
2	4-NO_2	H	1.5		61
3	4-Br	4-CH_3	2		54

[a] Reaction conditions: arenediazonium tetrafluoroborate (0.3 mmol), arylboronic acid (0.36 mmol, 1.2 equiv), catalyst (0.3 mol% Pd, 11.2 mg), MeOH (1.8 mL), 25 °C. [b] Isolated yield.

A typical recycling procedure for Suzuki cross-coupling reactions

The corresponding recycling reaction for 3-nitrobenzenediazonium tetrafluoroborate and phenylboronic acid was carried out with the recovered catalyst **1** that determined the amount of the substrate and reagent as reference in MeOH at 20 °C. Reaction times were 6, 22, and 28 h for cycles 1, 2, and 3, respectively. After the reaction was fully completed, the reaction solvent, MeOH, was concentrated in vacuum to obtain the precipitate. CH_2Cl_2 (1.0 mL) was then added in order to dissolve and extract the coupling products and the remaining materials and to precipitate the catalyst **1**. Subsequently, the resultant mixture was filtered and the filtrate was washed two times with CH_2Cl_2 (0.5

× 2 mL). At last, the remaining precipitate was dried under vacuum to give the catalyst **1** and reused. After the two cycles, the TEM showed that the recycled catalyst **1** remain the same fibrous morphology (Figure 2).

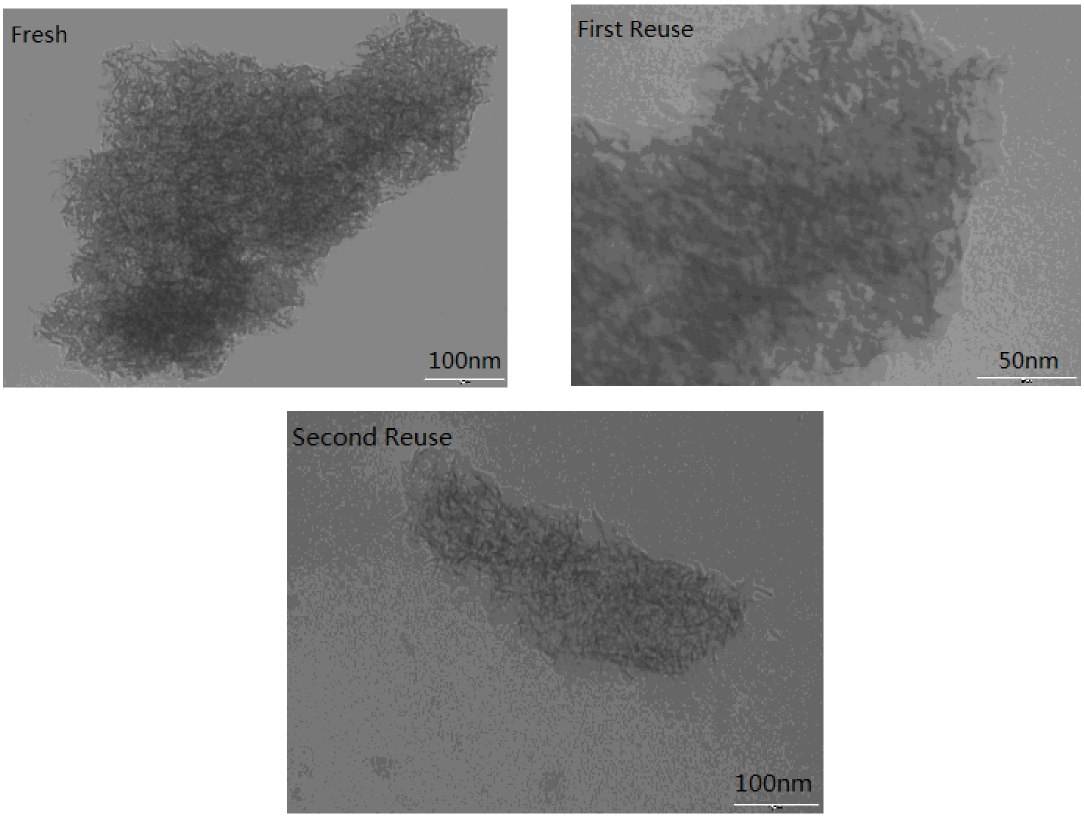
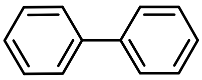


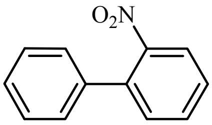
Figure 2. The TEM images of the catalyst **1**

Characterization data for Suzuki cross-coupling products



Biphenyl [3, 5, 9, 13]

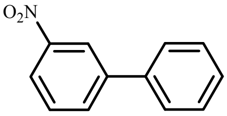
Following the general procedure using benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), and phenylboronic acid (43.9 mg, 0.36 mmol, 1.2 equiv) provided 42.5 mg of the coupling product after purification by column chromatography of the crude product. Yield = 92%; R_f = 0.6 (Petroleum ether); White solid; M.p. = 65-66 °C; IR (cm^{-1}, KBr) ν: 3034, 1608, 1506, 1480, 1430 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.35-7.38 (t, J = 8.0 Hz, 2H), 7.44-7.47 (m, J = 8.0 Hz, 4H), 7.61-7.62 (d, 4H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 141.32, 128.82, 127.32, 127.24 ppm.



2-Nitrobiphenyl [4, 5, 12, 13]

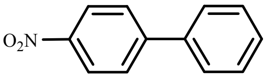
Following the general procedure using 2-nitrobenzenediazonium tetrafluoroborate (71.1 mg, 0.3 mmol), and phenylboronic acid (43.9 mg, 0.36 mmol, 1.2 equiv) provided 56.1 mg of the coupling product after purification by column chromatography of the crude product. Yield = 94%; R_f = 0.2 (Petroleum ether/AcOEt = 50/1 v/v); Yellow oil; IR (cm^{-1}, KBr) ν: 3062, 3031, 2868, 1605, 1568, 1525, 1472, 1452, 1354, 1306, 1162, 1142, 1093, 1075, 917, 852, 782, 770, 740, 698, 666 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.33-7.35

(m, 2H), 7.42-7.47 (m, 4H), 7.48-7.51 (m, 1H), 7.62-7.65 (m, 1H), 7.86-7.88 (q, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 149.35, 137.45, 136.34, 132.00, 132.72, 128.72, 128.26, 128.22, 127.94, 124.08 ppm MS (EI) *m/z* (%) 199 (M^+, 18), 171 (60), 152 (100), 143 (32).



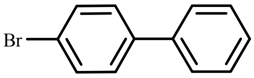
3-Nitrobiphenyl [4, 5, 11, 12]

Following the general procedure using 3-nitrobenzenediazonium tetrafluoroborate (71.1 mg, 0.3 mmol), and phenylboronic acid (43.9 mg, 0.36 mmol, 1.2 equiv) provided 54.9 mg of the coupling product after purification by column chromatography of the crude product. Yield = 92%; R_f = 0.2 (Petroleum ether/AcOEt = 50/1 v/v); Pale yellow solid; M.p. = 57-59 °C; IR (cm^{-1}, KBr) ν: 3081, 2922, 2851, 1577, 1528, 1499, 1472, 1349, 1291, 1043, 993, 897, 873, 812, 767, 731, 695, 675 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.43-7.46 (m, 1H), 7.50-7.53 (m, 2H), 7.61-7.65 (m, 3H), 7.92-7.94 (m, 1H), 8.20-8.22 (m, 1H), 8.46-8.47 (t, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$), δ = 148.76, 142.89, 138.67, 133.04, 129.72, 129.18, 128.56, 127.17, 122.03, 121.95 ppm.



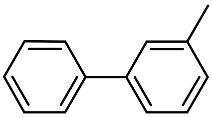
4-Nitrobiphenyl [3, 4, 5, 13]

Following the general procedure using 4-nitrobenzenediazonium tetrafluoroborate (71.1 mg, 0.3 mmol), and phenylboronic acid (43.9 mg, 0.36 mmol, 1.2 equiv) provided 57.9 mg of the coupling product after purification by column chromatography of the crude product. Yield = 97%; R_f = 0.2 (Petroleum ether/AcOEt = 50/1 v/v); Pale yellow solid; M.p. = 113-115 °C; IR (cm^{-1}, KBr): ν: 3077, 1598, 1515, 1345, 1105, 854, 740, 697 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.45-7.48 (m, 1H), 7.50-7.53 (m, 2H), 7.63-7.65 (m, 2H), 7.74-7.76 (m, 2H), 8.30-8.32 (m, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 147.63, 147.11, 138.77, 129.17, 128.94, 127.80, 127.39. 124.11 ppm.



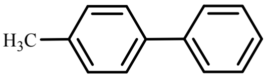
4-Bromobiphenyl [6, 12]

Following the general procedure using 4-bromobenzenediazonium tetrafluoroborate (82.4 mg, 0.3 mmol), and phenylboronic acid (43.9 mg, 0.36 mmol, 1.2 equiv) provided 51.2 mg of the coupling product after purification by column chromatography of the crude product. At the same time, using benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), and 4-bromophenylboronic acid (72.3 mg, 0.36 mmol, 1.2 equiv) provided 54.8 mg of product. Yield = 73% and 78%, respectively; R_f = 0.7 (Petroleum ether); White solid; M.p. = 89-90 °C; IR (cm^{-1}, KBr) ν: 3128, 3031, 1668, 1587, 1477, 1449, 1393, 1366, 1310, 1275, 1108, 1080, 1003, 830, 767, 691 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.37-7.40 (t, 1H), 7.45-7.49 (m, 4H), 7.57-7.60 (m, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 140.16, 140.02, 132.04, 131.87, 128.91, 128.76, 128.52, 127.65, 126.95, 121.54 ppm.



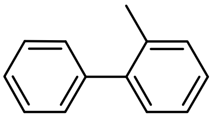
3-Methyldiphenyl [10, 12, 13]

Following the general procedure using 3-methylbenzenediazonium tetrafluoroborate (61.8 mg, 0.3 mmol), and phenylboronic acid (43.9 mg, 0.36 mmol, 1.2 equiv) provided 22.7 mg of the coupling product after purification by column chromatography of the crude product. At the same time, using benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), and 3-methylphenylboronic acid (49.9 mg, 0.36 mmol, 1.2 equiv) provided 44.4 mg of product. Yield = 45% and 88%, respectively; R$_f$ = 0.6 (Petroleum ether); Colourless liquid; IR (cm^{-1}, KBr) ν: 3060, 3030, 2949, 2863, 1607, 1589, 1482, 1411, 1377, 1076, 1026, 882, 753, 727, 699, 617, 576 cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.66-7.65 (q, 2H), 7.50-7.46 (m, 4H), 7.41-7.38 (m, 2H), 7.24-7.22 (d, 1H), 2.49 (s, 3H) ppm; ^{13}C NMR (150 MHz, CDCl$_3$): δ = 141.50, 141.38, 138.43, 128.83, 128.80, 128.14, 128.11, 127.31, 127.29, 124.42, 21.67 ppm; MS (EI) *m/z* (%) 168 (M$^+$, 100), 152 (22).



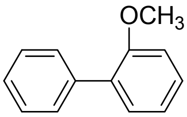
4-Methylbiphenyl [3, 5, 9, 10, 12]

Following the general procedure using 4-methylbenzenediazonium tetrafluoroborate (61.8 mg, 0.3 mmol), and phenylboronic acid (43.9 mg, 0.36 mmol, 1.2 equiv) provided 36.8 mg of the coupling product after purification by column chromatography of the crude product. At the same time, using benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), and 4-methylphenylboronic acid (49.9 mg, 0.36 mmol, 1.2 equiv) provided 37.3 mg of product. Yield = 73% and 74%, respectively; R$_f$ = 0.5 (Petroleum ether); White solid; M.p. = 41-43 °C; IR (cm^{-1}, KBr) ν: 3067, 3033, 2917, 2860, 1602, 1567, 1522, 1488, 1378, 1340, 1044, 823, 766, 706, 481 cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$): δ = 2.43 (s, 3H), 7.28-7.29 (d, J = 7.8 Hz, 2H), 7.34-7.37 (m, 1H), 7.44-7.47 (t, 2H), 7.52-7.54 (d, J = 7.8 Hz, 2H), 7.61-7.62 (q, 2H) ppm; ^{13}C NMR (150 MHz, CDCl$_3$): δ = 141.20, 138.40, 137.04, 129.51, 128.74, 127.02, 127.00, 21.12 ppm.



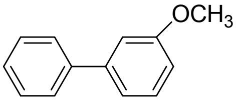
2-Methyldiphenyl [9, 10, 12]

Following the general procedure using benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), and 2-methylphenylboronic acid (49.9 mg, 0.36 mmol, 1.2 equiv) provided 34.8 mg of the coupling product after purification by column chromatography of the crude product. Yield = 69%; R$_f$ = 0.5 (Petroleum ether); Colourless liquid; IR (cm^{-1}, KBr) ν: 3068, 3038, 2919, 2850, 1610, 1467, 1406, 1378, 1369, 1051, 848, 797, 721, 666 cm^{-1} ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.52-7.51 (m, 2H), 7.45-7.42 (t, 2H, J = 1.2 Hz), 7.37-7.35 (m, 2H), 7.34 (t, 2H, J = 1.2 Hz), 2.38 (s, 3H) ppm; ^{13}C NMR (150 MHz, CDCl$_3$): δ = 135.82, 135.36, 130.31, 129.80, 129.20, 128.07, 127.25, 127.15, 126.77, 125.76, 125.54, 20,47 ppm; MS (EI) *m/z* (%) 168 (M$^+$, 100), 152 (22).



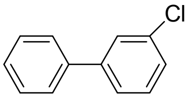
2-Methoxylbiphenyl [9, 10]

Following the general procedure using benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), and 2-methoxylphenylboronic acid (55.8 mg, 0.36 mmol, 1.2 equiv) provided 53.5 mg of the coupling product after purification by column chromatography of the crude product. Yield = 97%; R_f = 0.2 (Petroleum ether); Yellow transparent liquid; IR (cm^{-1}, KBr) ν: 3059, 3025, 2955, 2833, 1597, 1584, 1504, 1483, 1463, 1430, 1260, 1236, 1180, 1123, 1056, 1028, 1009, 754, 732, 699 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.84 (s, 3H), 7.02-7.03 (dd, J=8.4, 0.6 Hz, 1H), 7.06-7.08 (td, J=7.2, 0.6 Hz, 1H), 7.34-7.35 (d, J=1.8 Hz, 1H), 7.36 (q, J=1.2 Hz, 1H), 7.37 (t, J=1.8 Hz, 1H), 7.43-7.46 (dd, J=7.2, 1.8 Hz, 2H), 7.56-7.58 (dd, J=8.4, 1.2 Hz, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 156.50, 138.58, 130.91, 130.77, 129.57, 128.62, 127.99, 126.92, 120.85, 111,27, 55.57 ppm.



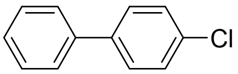
3-Methoxylbiphenyl [9]

Following the general procedure using benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), and 3-methoxylphenylboronic acid (55.8 mg, 0.36 mmol, 1.2 equiv) provided 37 mg of the coupling product after purification by column chromatography of the crude product. Yield = 67%; R_f = 0.2 (Petroleum ether); Canary yellow liquid; IR (cm^{-1}, KBr) ν: 3064, 3033, 3005, 2957, 2940, 2833, 1604, 1569, 1480, 1424, 1293, 1214, 1176, 1058 1013, 786, 673 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.89 (s, 3H), 6.92-6.94 (ddd, J=8.4, 3.0, 1.2 Hz, 1H), 7.16 (m, 1H), 7.21-7.22 (m, 1H), 7.36-7.39 (m, 2H), 7.45-7.48 (m, 2H), 7.61 (t, J=1.2 Hz, 1H), 7.62-7.63 (d, J=1.2 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.97, 142.81, 141.14, 129.77, 128.76, 127.44, 127.22, 119.71, 112.93, 112.71, 55.32 ppm; MS (EI) *m/z* (%) 184 (M$^+$, 100), 169 (43), 77 (7).



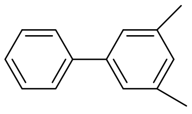
3-chlorobiphenyl [12, 13]

Following the general procedure using benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), and 3-chlorophenylboronic acid (56.3 mg, 0.36 mmol, 1.2 equiv) provided 45.1 mg of the coupling product after purification by column chromatography of the crude product. Yield = 80%; R_f = 0.6 (Petroleum ether); Colorless transparent liquid; IR (cm^{-1}, KBr): ν: 3057, 3033, 2924, 1380, 1494, 1464, 1425, 1130, 1072, 1038, 1011, 771, 746, 697 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.34-7.41 (m, 3H), 7.45-7.50 (m, 3H), 7.57-7.63 (m, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 139.83, 134.67, 130.00, 128.91, 127.91, 127.88, 127.31, 127.28, 127.13, 125.31, 125.29 ppm; MS (EI) *m/z* (%) 188 (M$^+$, 100), 152 (47), 76 (11).



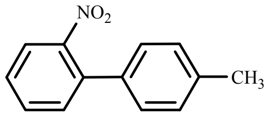
4-chlorobiphenyl [4, 5, 11, 12]

Following the general procedure using benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), and 4-chlorophenylboronic acid (56.3 mg, 0.36 mmol, 1.2 equiv) provided 47.9 mg of the coupling product after purification by column chromatography of the crude product. Yield = 85%; R_f = 0.6 (Petroleum ether); White solid; M.p. = 32 °C; IR (cm^{-1}, KBr) ν: 3065, 2922, 1656, 1586, 1473, 1393, 1095, 1002, 831, 756, 686, 618 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.37-7.40 (ddd, J=8.4, 2.4, 1.2 Hz, 1H), 7.42 (t, J=1.8 Hz, 1H), 7.43 (t, J=1.8 Hz, 1H), 7.44-7.46 (m, 1H), 7.47-7.48 (dd, J=4.8, 1.8 Hz, 1H), 7.52-7.55 (dt, J=8.4, 2.4 Hz, 2H), 7.57-7.58 (m, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 140.02, 139.69, 133.40, 129.06, 128.92, 128.90, 128.41, 127.60, 127.00 ppm.



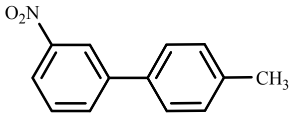
3,5-dimethylbiphenyl [9]

Following the general procedure using benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), and 3,5-dimethylphenylboronic acid (54.0 mg, 0.36 mmol, 1.2 equiv) provided 50.2 mg of the coupling product after purification by column chromatography of the crude product. Yield = 92%; R_f = 0.6 (Petroleum ether); Colorless transparent liquid; IR (cm^{-1}, KBr) ν: 3068, 3038, 2919, 2850, 2837, 1610, 1583, 1467, 1406, 1378, 1369, 1051, 848, 797, 729, 673 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.41-2.42 (d, 6H), 7.01-7.04 (d, 1H), 7.23-7.25 (d, 2H), 7.35-7.37 (t, J=7.2 Hz, 1H), 7.44-7.47 (m, 2H), 7.61-7.62 (d, J=7.2 Hz, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 141.50, 141.29, 138.26, 128.91, 128.65, 127.21, 127.09, 125.13, 21.42 ppm; MS (EI) *m/z* (%) 182 (M$^+$, 100), 167 (79), 152 (14).



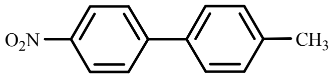
4-Methyl-2'-nitrobiphenyl [7]

Following the general procedure using 2-nitrobenzenediazonium tetrafluoroborate (71.1 mg, 0.3 mmol), and 4-methylphenylboronic acid (49.9 mg, 0.36 mmol, 1.2 equiv) provided 50.5 mg of the coupling product after purification by column chromatography of the crude product. Yield = 79%; Rf = 0.6 (Petroleum ether); Yellow oily liquid; IR (cm^{-1}, KBr) ν: 3027, 2921, 2867, 1613, 1566, 1525, 1475, 1355, 1305, 1283, 1041, 853, 819, 781, 749, 721, 704, 656, 639 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 7.23-7.27 (m, 4H), 7.44-7.48 (m, 2H), 7.59-7.62 (m, 1H), 7.83-7.84 (q, 1H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$), δ = 149.2, 138.0, 136.0, 134.3, 132.1, 131.8, 129.3, 127.8, 127.6, 123.8, 21.1 ppm; MS (EI) *m/z* (%) 213 (M$^+$, 42), 196 (48), 152 (82), 77 (68).



4-Methyl-3'-nitrobiphenyl [4]

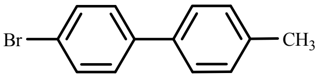
Following the general procedure using 3-nitrobenzenediazonium tetrafluoroborate (71.1 mg, 0.3 mmol), and 4-methylphenylboronic acid (49.9 mg, 0.36 mmol, 1.2 equiv) provided 52.4 mg of the coupling product after purification by column chromatography of the crude product. Yield = 82%; R_f = 0.6 (Petroleum ether); White solid; M.p. = 75-76 ^{o}C; IR (cm^{-1}, KBr) ν: 3087, 3025, 2922, 2854, 1582, 1529, 1380, 1346, 1293, 1260, 1186, 1084, 1037, 967, 899, 874, 804, 739, 681 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.43 (s, 3H), 7.31-7.32 (d, 2H), 7.53-7.54 (q, 2H), 7.58-7.61 (t, 1H), 7.90-7.91 (m, 1H), 8.17-8.19 (m, 1H), 8.44-8.45 (t, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 148.74, 142.77, 138.58, 135.72, 132.78, 129.90, 129.65, 126.95, 121.70, 121.62, 21.16 ppm.



4-Methyl-4'-nitrobiphenyl [8]

Following the general procedure using 4-nitrobenzenediazonium tetrafluoroborate (71.1 mg, 0.3 mmol), and 4-methylphenylboronic acid (49.9 mg, 0.36 mmol, 1.2

equiv) provided 46.6 mg of the coupling product after purification by column chromatography of the crude product. Yield = 73%; R_f = 0.1 (Petroleum ether); White solid; M.p. = 140-142 °C; IR (cm^{-1}, KBr) ν: 3078, 2924, 2852, 1595, 1513, 1483, 1397, 1338, 1294, 1189, 1107, 1004, 853, 824, 753, 720, 696 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 2.44 (s, 3H), 7.31-7.32 (q, 2H), 7.53-7.55 (m, 2H), 7.71-7.74 (m, 2H), 8.27-8.30 (m, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 149.35, 137.45, 136.34, 132.34, 132.00, 128.72, 128.26, 128.22, 127.94, 124.08, 21.21 ppm.



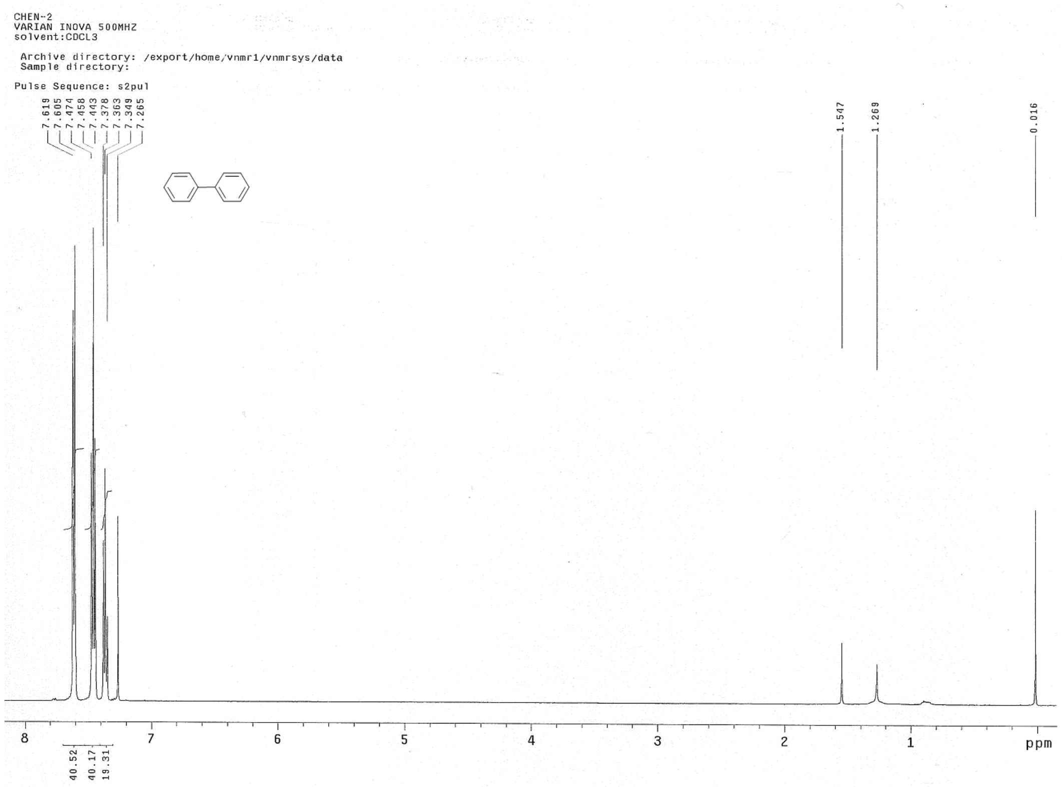
4-Methyl-4'-bromobiphenyl [11]

Following the general procedure using 4-bromobenzenediazonium tetrafluoroborate (82.4 mg, 0.3 mmol), and 4-methylphenylboronic acid (49.9 mg, 0.36 mmol, 1.2 equiv) provided 38.2 mg of the coupling product after purification by column chromatography of the crude product. Yield = 78%; R_f = 0.6 (Petroleum ether); White solid; M.p. = 129-130 °C; IR (cm^{-1}, KBr) ν: 3022, 2915, 2848, 1476, 1388, 1071, 1001, 805, 720, 543, 501 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 2.41 (s, 3H), 7.25-7.27 (t, 2H), 7.44-7.47 (m, 4H), 7.54-7.57 (m, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 140.10, 137.54, 137.15, 131.86, 129.68, 128.58, 126.82, 121.24, 21.18 ppm.

References:

[1] M. S. Kwon, N. Kim, C. M. Park, J. S. Lee, K. Y. Kang and J. Park, *Org. Lett.,* 2005, **7**, 1077.
[2] Unless otherwise specified, digital display temperature control instrument was used in this process.
[3] J. Lemo, K. Heuzé and D. Astruc, *Org. Lett.,* 2005, **7**, 2253.
[4] D. Srimani and A. Sarkar, *Tetrahedron,* 2008, **64**, 5762-5772.
[5] J. H. Li, W. J. Liu and Y. X. Xie, *J. Org. Chem.,* 2005, **70**, 5409.
[6] F.X. Felpin, and E. Fouquet, *Adv. Synth. Catal*., 2008, **350**, 863.
[7] J. T. Kuethe and K. G. Childers, *Adv. Synth. Catal.,* 2008, **350**, 1577.
[8] S. H. Li, Y. j. Lin, J. G. Cao and S. B. Zhang *J. Org. Chem.*, 2007, **72**, 4071.
[9] F. Li and T. S. A. Hor *Adv. Synth. Catal.,* 2008, **350**, 2391.
[10] H. E. Moll, D. S. meril, D. Matt and L. Toupet, *Adv. Synth. Catal.*, 2010, **352**, 901.
[11] Y. C. Qin, W. Wei and M. M. Luo, *Synlett,* **2007**, 2410.
[12] J. Wen, J. Zhang, S. Y. Chen, J. Li and X. Q. Yu, *Angew. Chem. Int. Ed.*, 2008, **47**, 8897.
[13] K. Karami, C. Rizzoli, M. M. Salah, *Journal of Organometallic Chemistry,* **2011**, 940.

Spectra



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CHEN-2
VARIAN INOVA 500MHZ
solvent:CDCL3

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 Sample directory:

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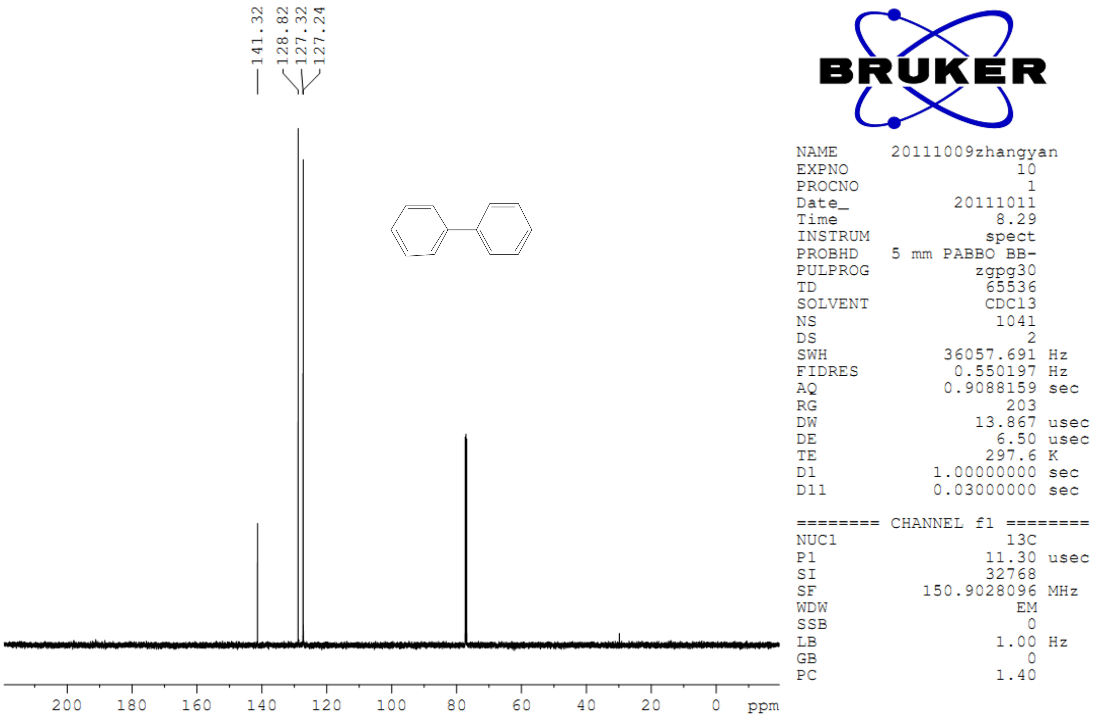

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FIDRES           0.550197 Hz
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RG                     203
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DE                    6.50 usec
TE                   297.6 K
D1              1.00000000 sec
D11             0.03000000 sec

======== CHANNEL f1 ========
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SSB                      0
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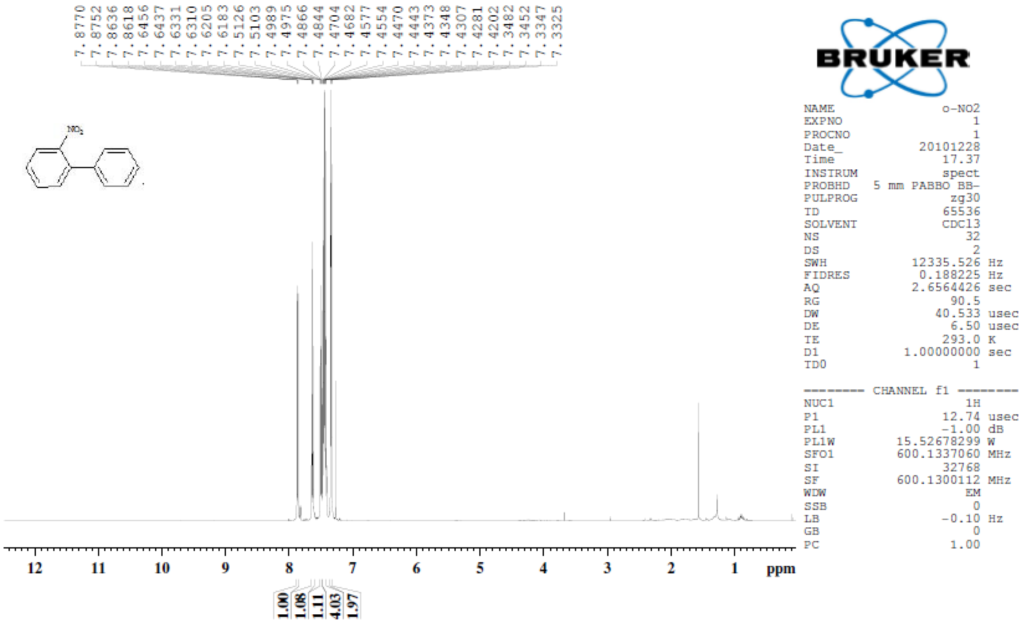

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PROCNO                  1
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PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             12335.526 Hz
FIDRES           0.188225 Hz
AQ              2.6564426 sec
RG                   90.5
DW                 40.533 usec
DE                   6.50 usec
TE                  293.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
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P1                  12.74 usec
PL1                 -1.00 dB
PL1W          15.52678299 W
SFO1          600.1337060 MHz
SI                  32768
SF            600.1300112 MHz
WDW                    EM
SSB                     0
LB                  -0.10 Hz
GB                      0
PC                   1.00
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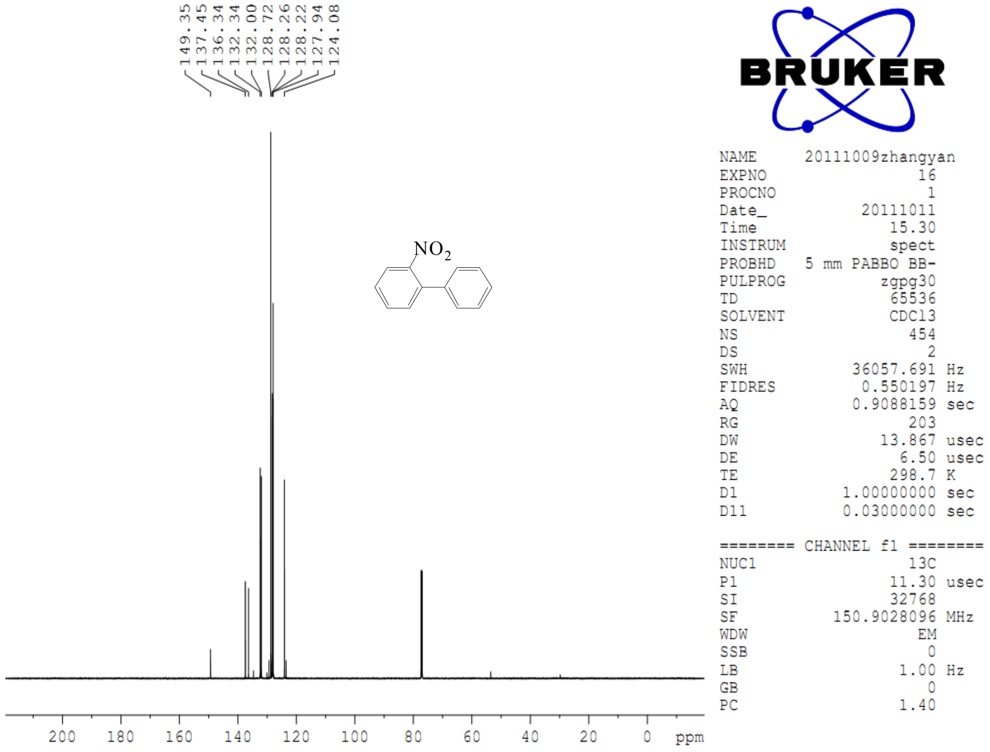

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SWH               36057.691 Hz
FIDRES             0.550197 Hz
AQ                0.9088159 sec
RG                      203
DW                   13.867 usec
DE                     6.50 usec
TE                    298.7 K
D1               1.00000000 sec
D11              0.03000000 sec

======== CHANNEL f1 ========
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PC                     1.40
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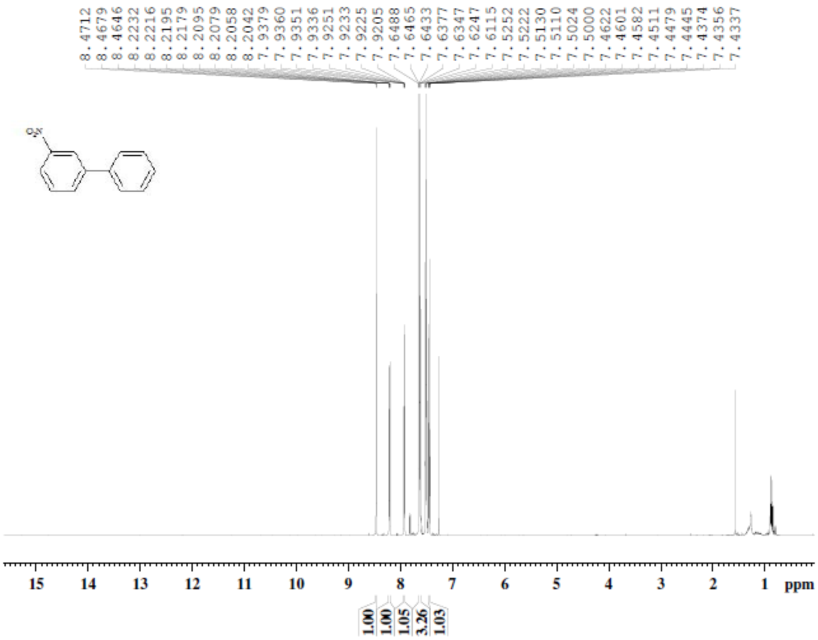

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FIDRES        0.188225 Hz
AQ           2.6564426 sec
RG                90.5
DW              40.533 usec
DE                6.50 usec
TE               293.0 K
D1          1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               12.74 usec
PL1              -1.00 dB
PL1W       15.52678299 W
SFO1       600.1337060 MHz
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WDW                 EM
SSB                  0
LB               -0.10 Hz
GB                   0
PC                1.00
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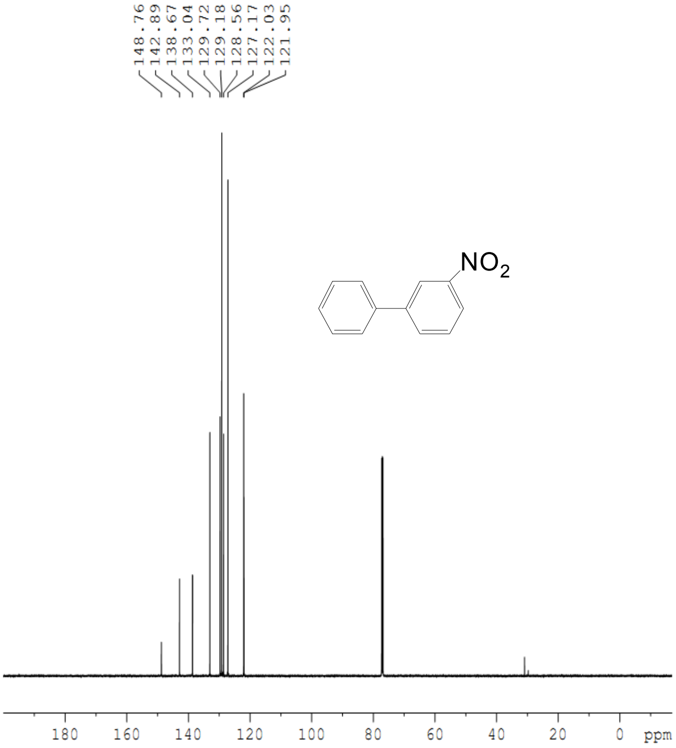

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TE                297.3 K
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D11          0.03000000 se

======== CHANNEL f1 ======
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LB                 1.00 Hz
GB                    0
PC                 1.40
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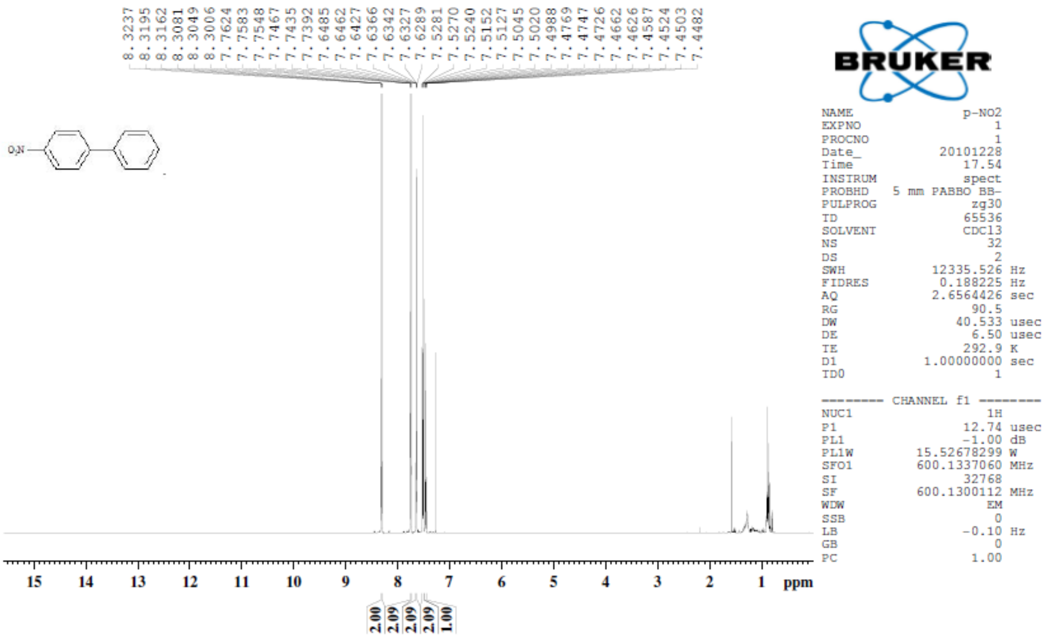

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TD               65536
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NS                  32
DS                   2
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FIDRES        0.188225 Hz
AQ           2.6564426 sec
RG                90.5
DW              40.533 usec
DE                6.50 usec
TE               292.9 K
D1          1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               12.74 usec
PL1              -1.00 dB
PL1W       15.52678299 W
SFO1       600.1337060 MHz
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WDW                 EM
SSB                  0
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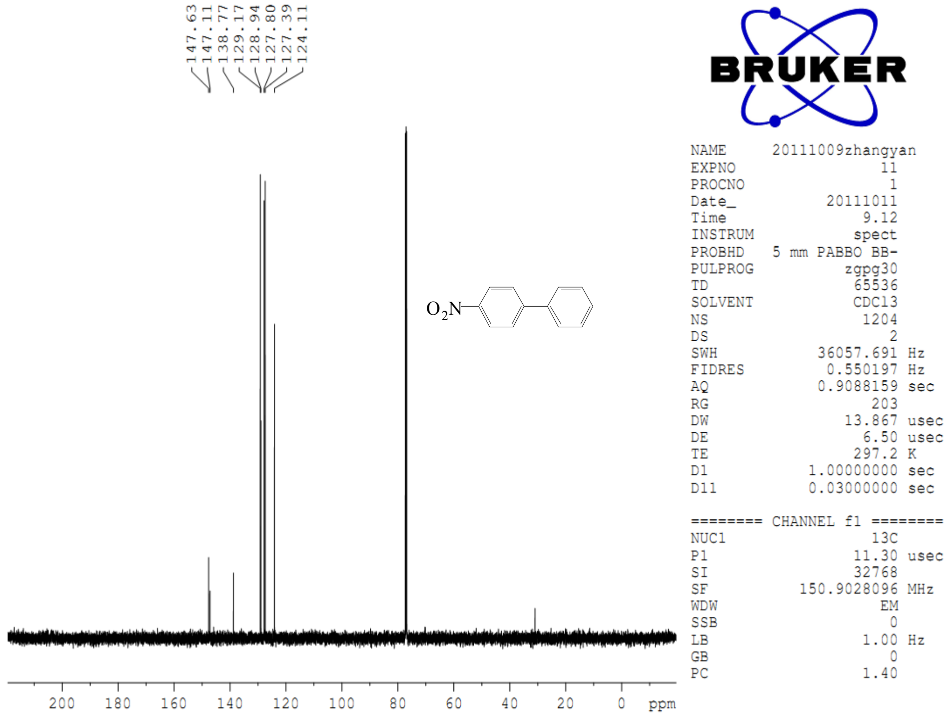

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D11          0.03000000 sec

======== CHANNEL f1 ========
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GB                    0
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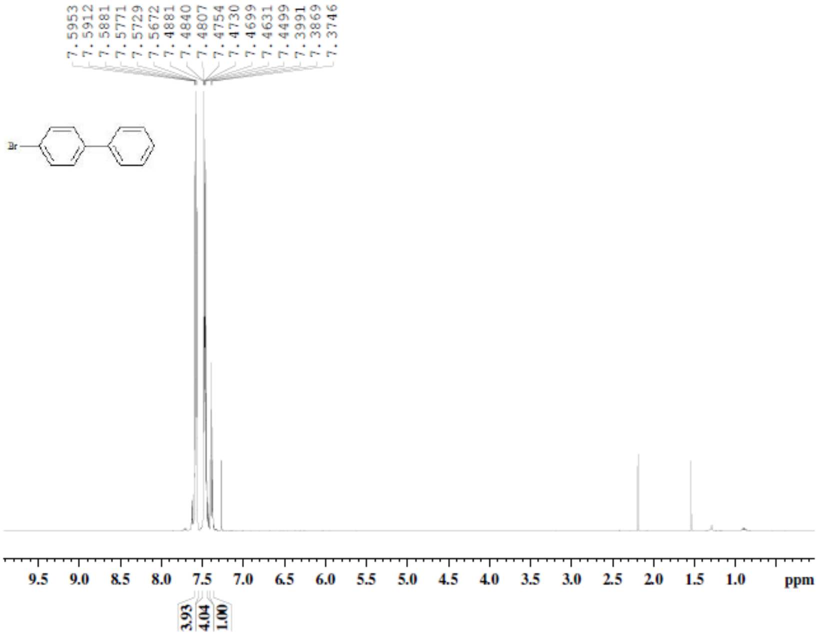

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======== CHANNEL f1 ========
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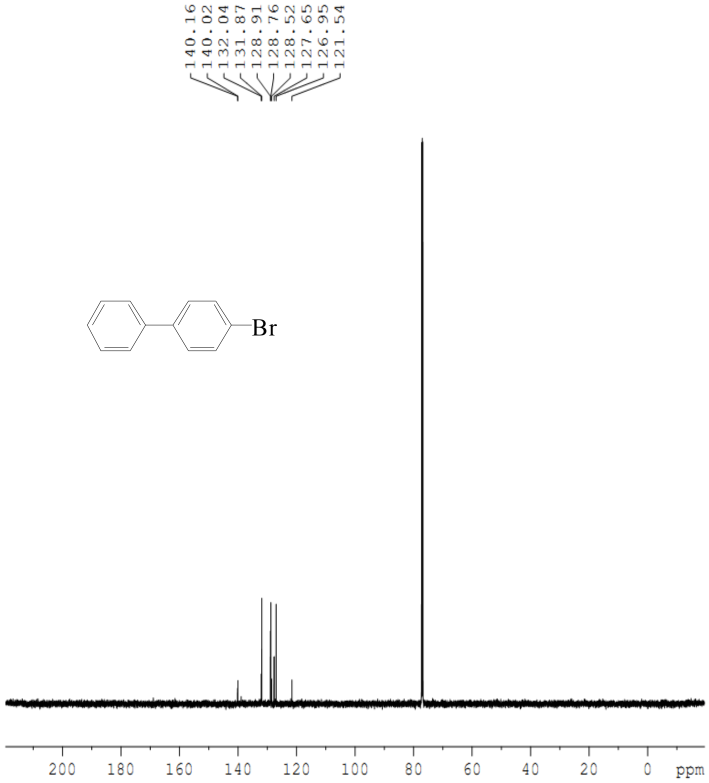

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D11            0.03000000 sec

======== CHANNEL f1 ========
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SI                  32768
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PC                   1.40
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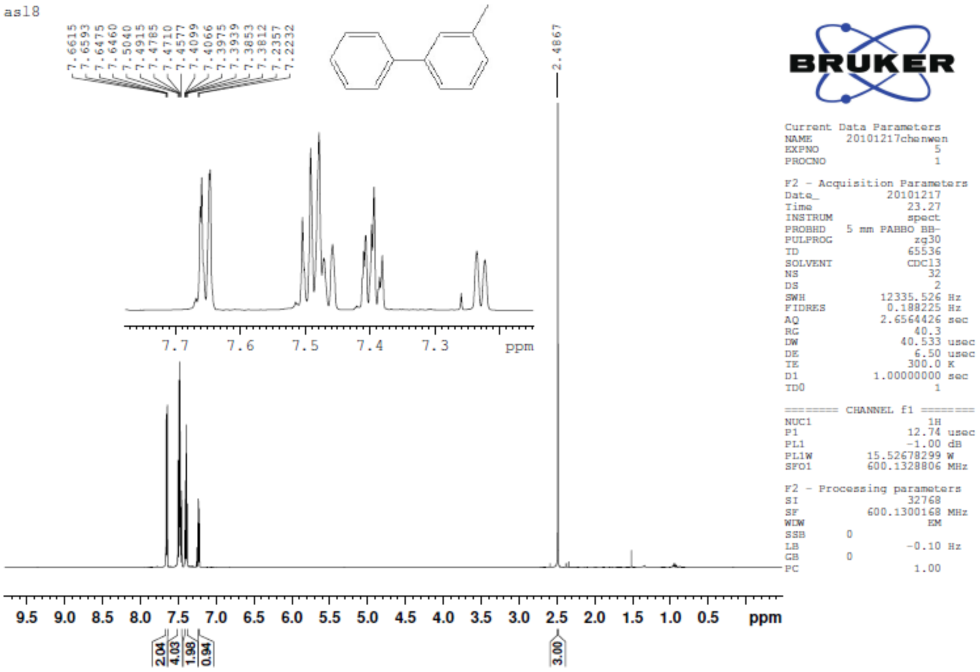

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NS                      32
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FIDRES            0.188225 Hz
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TD0                      1

======== CHANNEL f1 ========
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SFO1           600.1328806 MHz

F2 - Processing parameters
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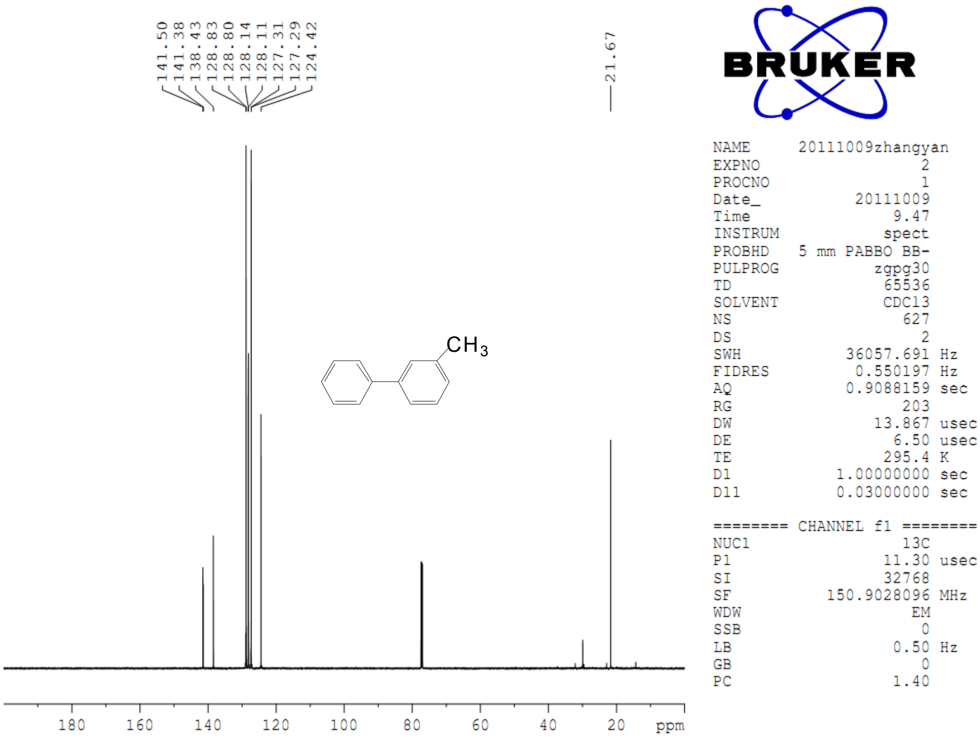

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RG                     203
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D11             0.03000000 sec

======== CHANNEL f1 ========
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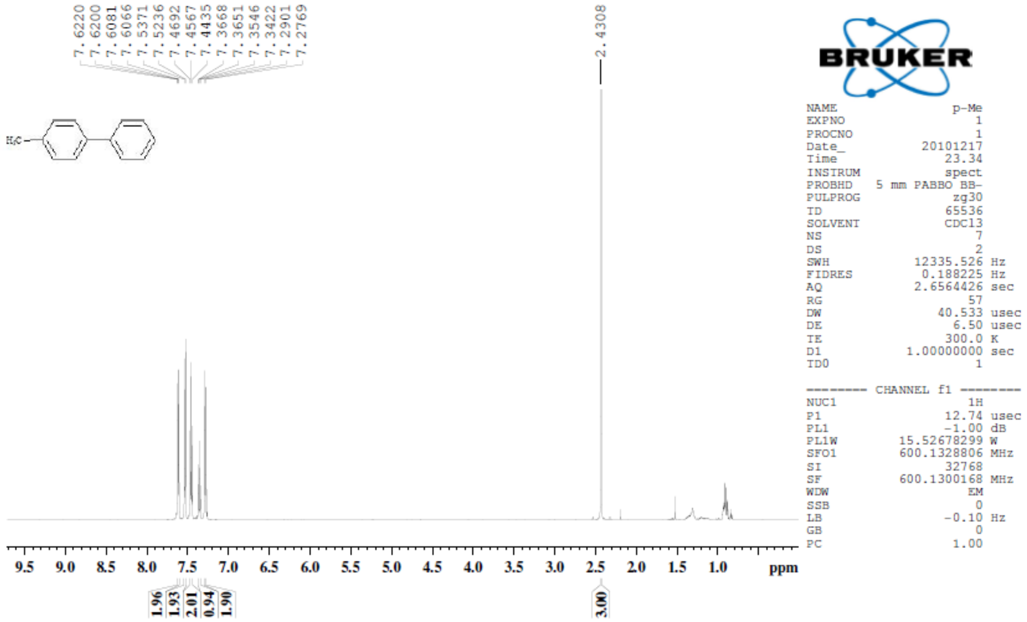

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======== CHANNEL f1 ========
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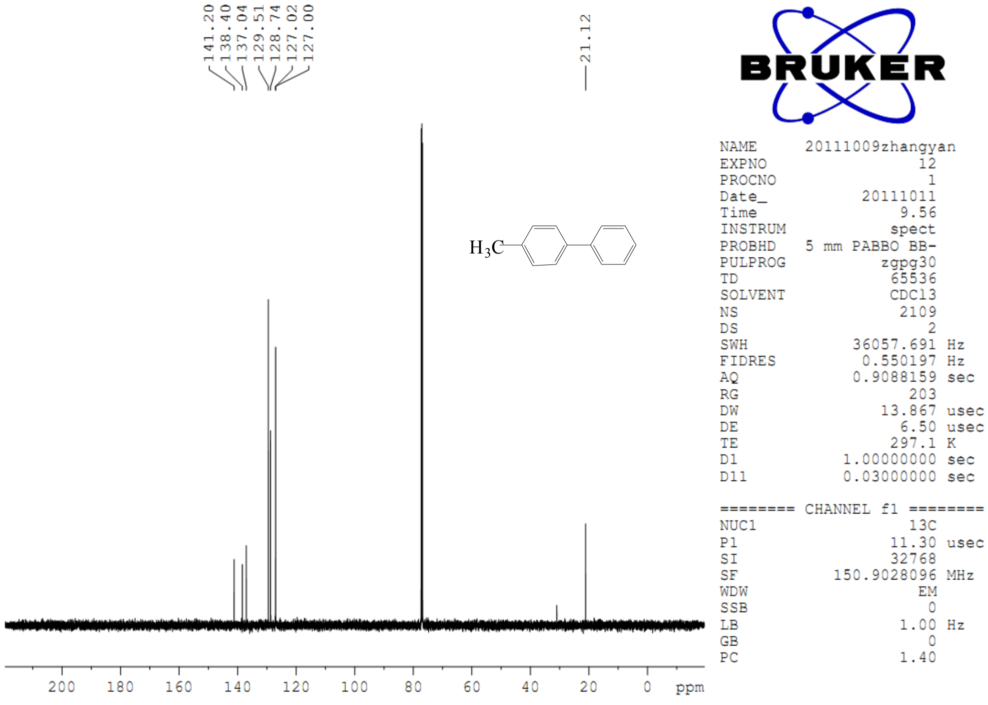

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DE                     6.50 usec
TE                    297.1 K
D1               1.00000000 sec
D11              0.03000000 sec

======== CHANNEL f1 ========
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WDW                      EM
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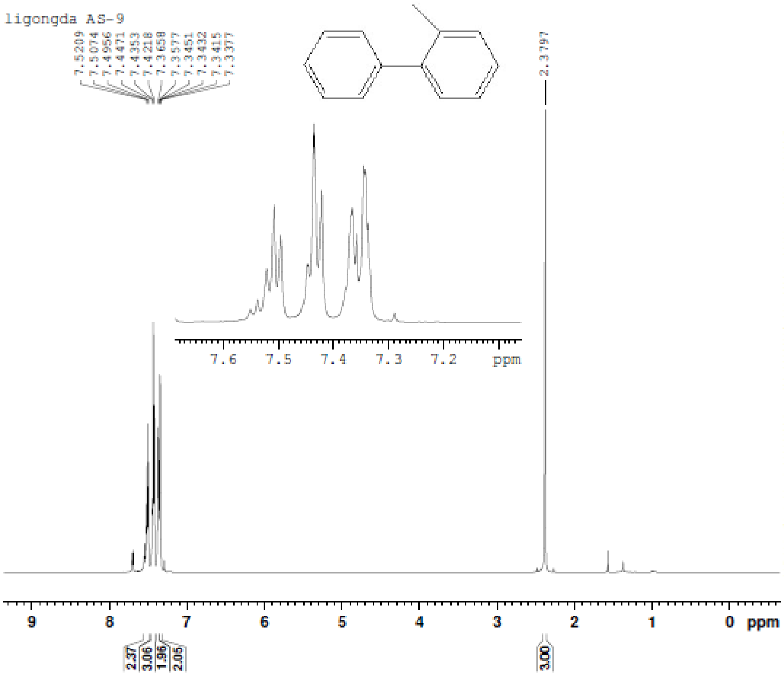

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PROCNO                 1

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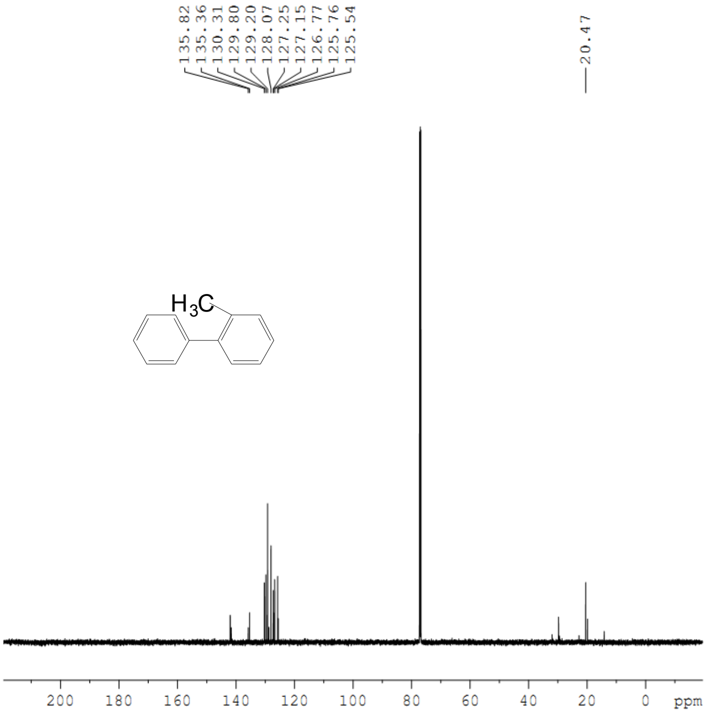
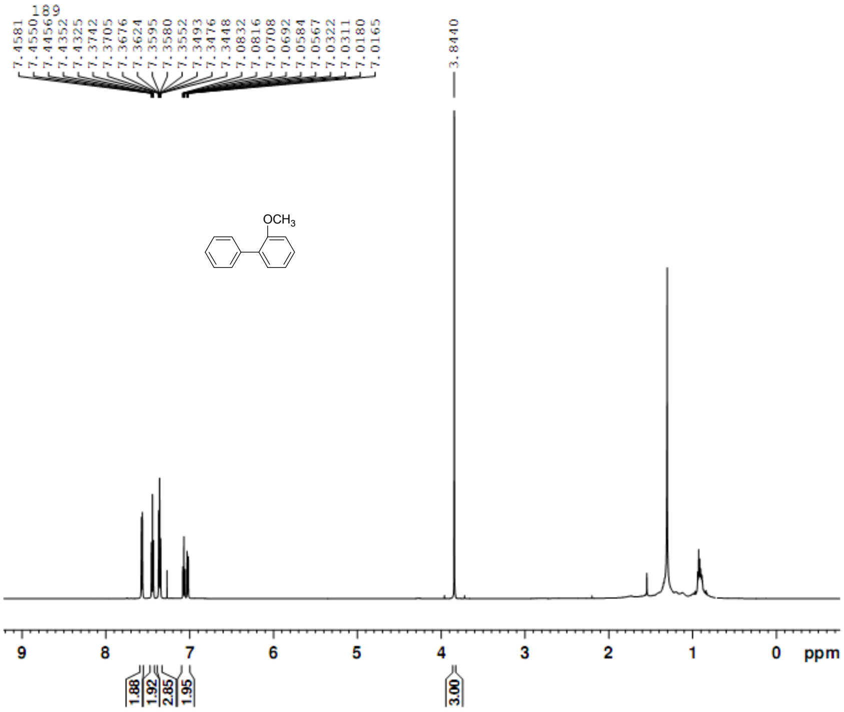
GB       0
PC                  1.00
```



```
NAME       20111009zhangyan
EXPNO                     6
PROCNO                    1
Date_              20111010
Time                  10.22
INSTRUM               spect
PROBHD      5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     7748
DS                        2
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9088159 sec
RG                      203
DW                   13.867 usec
DE                     6.50 usec
TE                    298.2 K
D1               2.00000000 sec
D11              0.03000000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                    11.30 usec
SI                    32768
SF           150.9028096 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

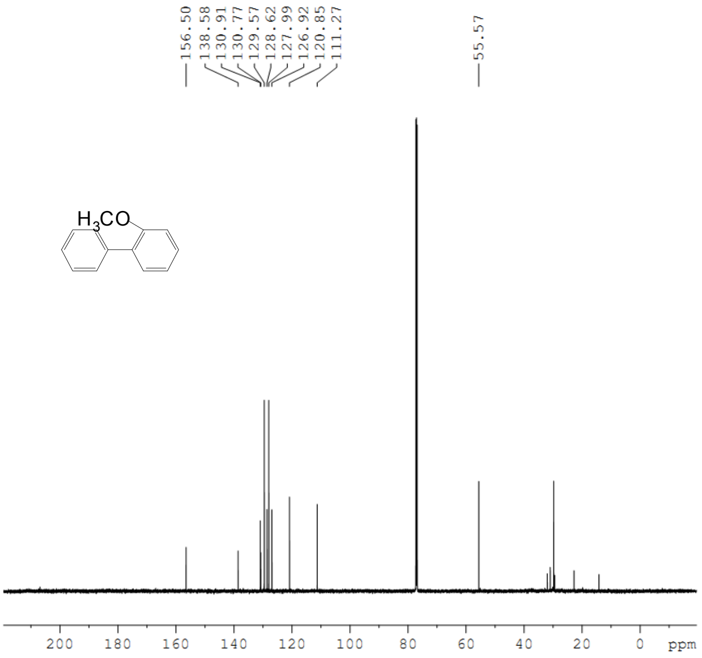


```
Current Data Parameters
NAME     20110826ligong
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20110826
Time              16.05
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           12335.526 Hz
FIDRES         0.188225 Hz
AQ            2.6564426 sec
RG                 25.4
DW               40.533 usec
DE                 6.50 usec
TE                298.3 K
D1           1.00000000 sec

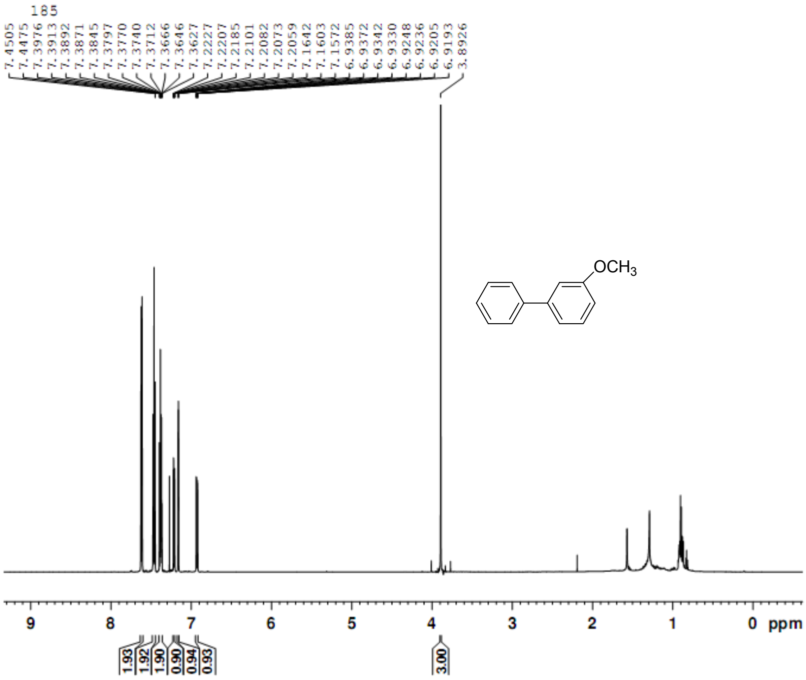
======== CHANNEL f1 ========
NUC1                 1H
P1                12.60 usec
PLW1        13.99600029 W
SFO1        600.1328806 MHz

F2 - Processing parameters
SI                32768
SF          600.1300098 MHz
WDW                  EM
SSB      0
LB                -0.10 Hz
GB       0
PC                 1.00
```



```
NAME      20111009zhangyan
EXPNO                    9
PROCNO                   1
Date_             20111010
Time                 21.10
INSTRUM              spect
PROBHD      5 mm PABBO BB-
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                   13612
DS                       2
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9088159 sec
RG                     203
DW                  13.867 usec
DE                    6.50 usec
TE                   298.0 K
D1              2.00000000 sec
D11             0.03000000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                   11.30 usec
SI                   32768
SF             150.9028096 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

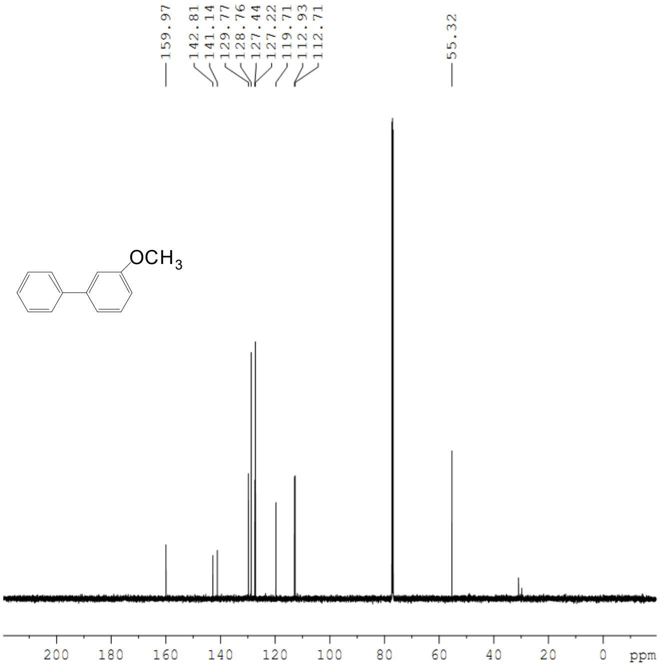


```
Current Data Parameters
NAME      20110826ligong
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110826
Time               15.45
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            12335.526 Hz
FIDRES          0.188225 Hz
AQ             2.6564426 sec
RG                  71.8
DW                40.533 usec
DE                  6.50 usec
TE                 298.3 K
D1            1.00000000 sec

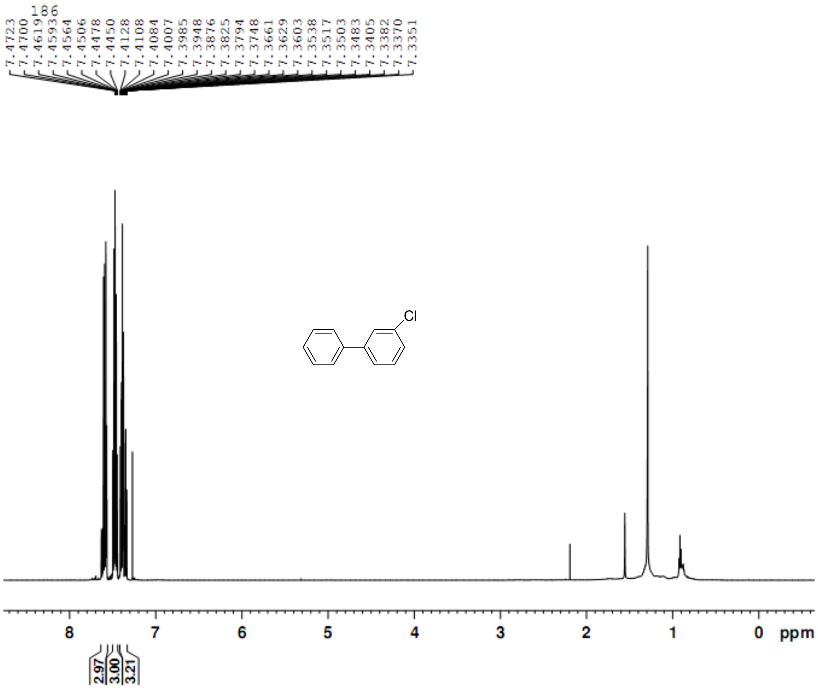
======== CHANNEL f1 ========
NUC1                  1H
P1                 12.60 usec
PLW1         13.99600029 W
SFO1         600.1328806 MHz

F2 - Processing parameters
SI                 32768
SF           600.1300098 MHz
WDW                   GM
SSB      0
LB                 -0.10 Hz
GB                   0.1
PC                  1.00
```



```
NAME       20111009zhangyan
EXPNO                     3
PROCNO                    1
Date_              20111009
Time                  11.28
INSTRUM               spect
PROBHD      5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     5196
DS                        2
SWH               36057.691 Hz
FIDRES             0.550197 Hz
AQ                0.9088159 sec
RG                      203
DW                   13.867 usec
DE                     6.50 usec
TE                    296.7 K
D1               1.00000000 sec
D11              0.03000000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                    11.30 usec
SI                    32768
SF              150.9028096 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

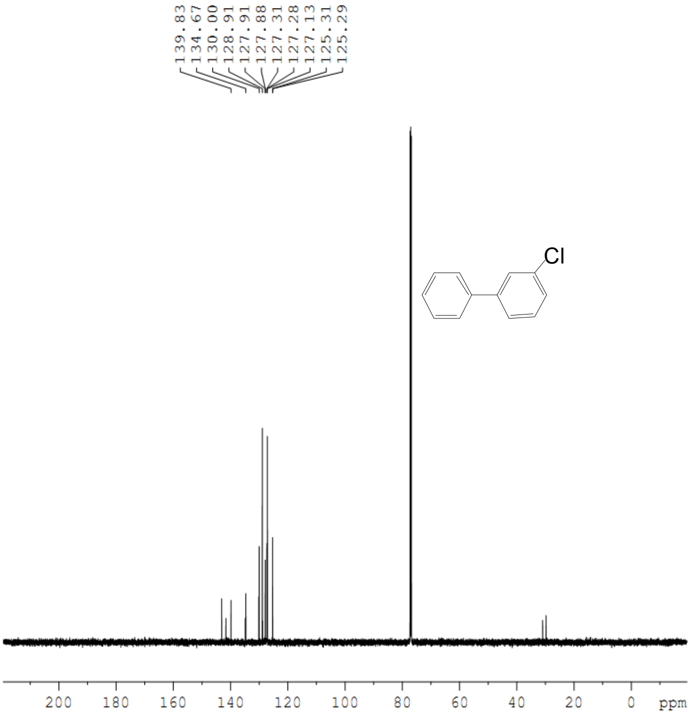


```
Current Data Parameters
NAME       20110826ligong
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20110826
Time                15.50
INSTRUM             spect
PROBHD     5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             12335.526 Hz
FIDRES           0.188225 Hz
AQ              2.6564426 sec
RG                     64
DW                 40.533 usec
DE                   6.50 usec
TE                  298.3 K
D1             1.00000000 sec

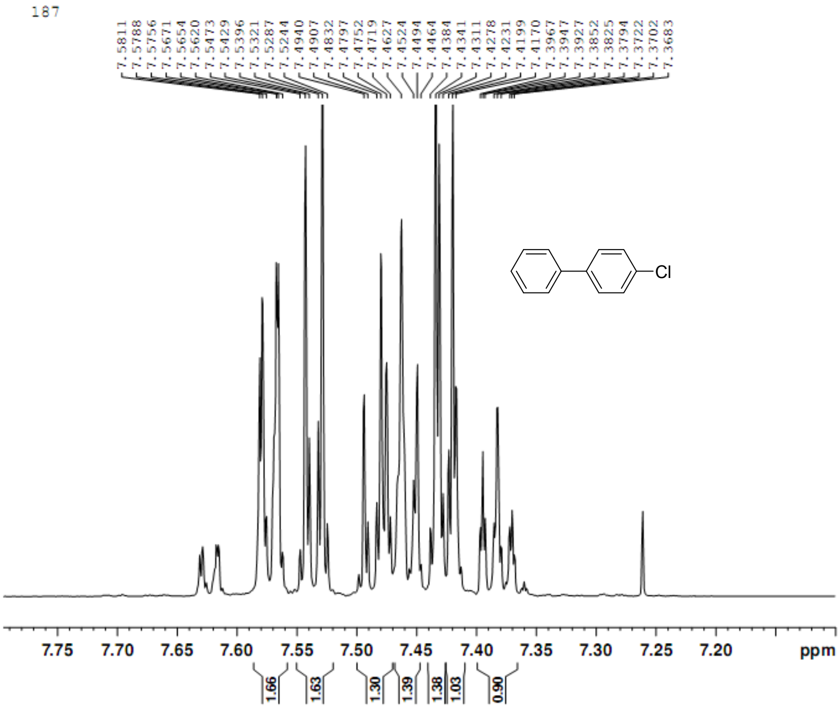
======== CHANNEL f1 ========
NUC1                   1H
P1                  12.60 usec
PLW1          13.99600029 W
SFO1          600.1328806 MHz

F2 - Processing parameters
SI                  32768
SF            600.1300098 MHz
WDW                    EM
SSB        0
LB                  -0.10 Hz
GB         0
PC                   1.00
```



```
NAME      20111009zhangyan
EXPNO                    4
PROCNO                   1
Date_             20111009
Time                 13.52
INSTRUM              spect
PROBHD      5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    5120
DS                       2
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9088159 sec
RG                     203
DW                  13.867 usec
DE                    6.50 usec
TE                   296.4 K
D1              1.00000000 sec
D11             0.03000000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                   11.30 usec
SI                   32768
SF             150.9028096 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

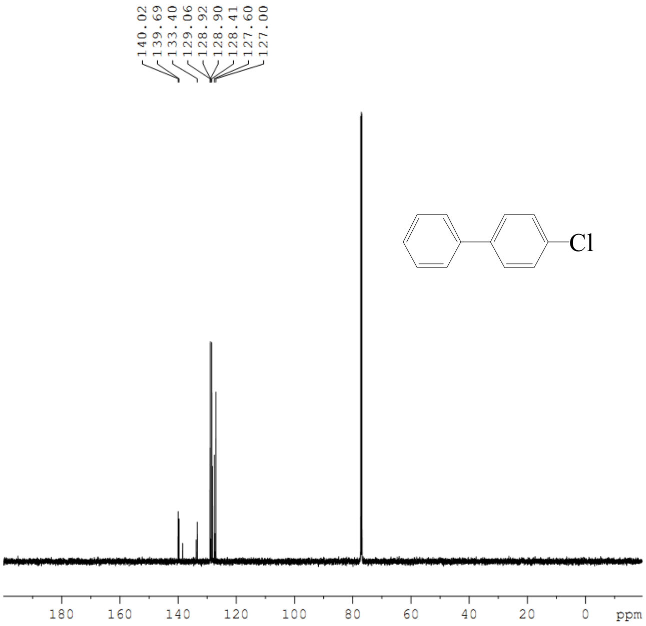


```
Current Data Parameters
NAME      20110826ligong
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110826
Time               15.55
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            12335.526 Hz
FIDRES          0.188225 Hz
AQ             2.6564426 sec
RG                    64
DW                40.533 usec
DE                  6.50 usec
TE                 298.3 K
D1            1.00000000 sec

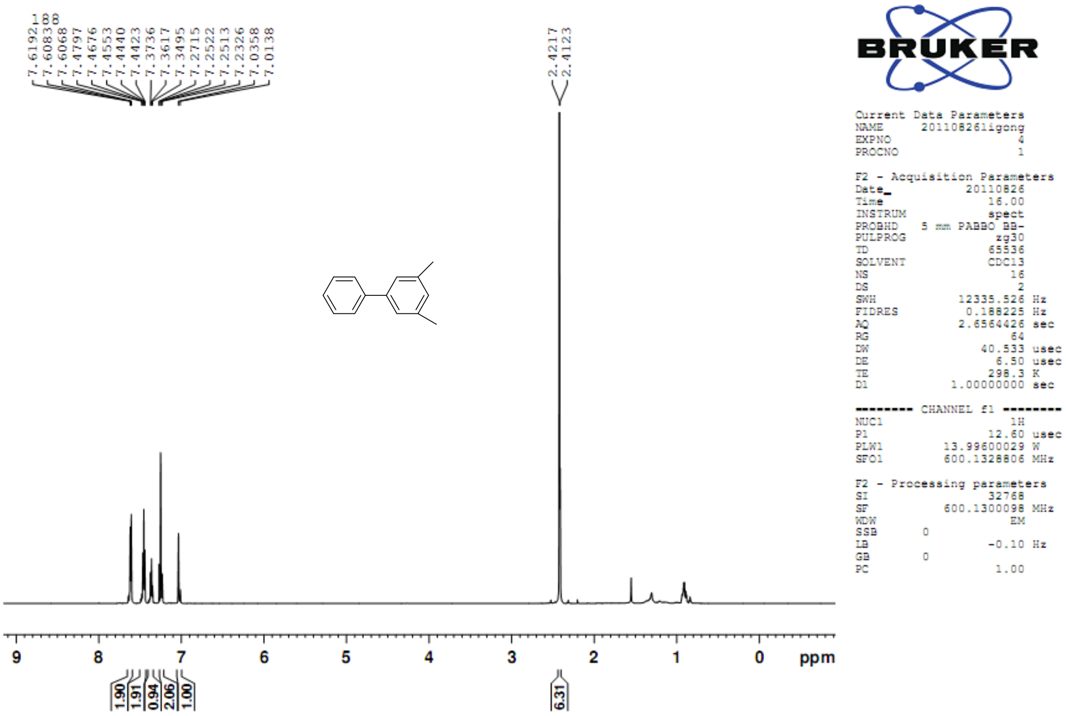
======== CHANNEL f1 ========
NUC1                  1H
P1                 12.60 usec
PLW1         13.99600029 W
SFO1         600.1328806 MHz

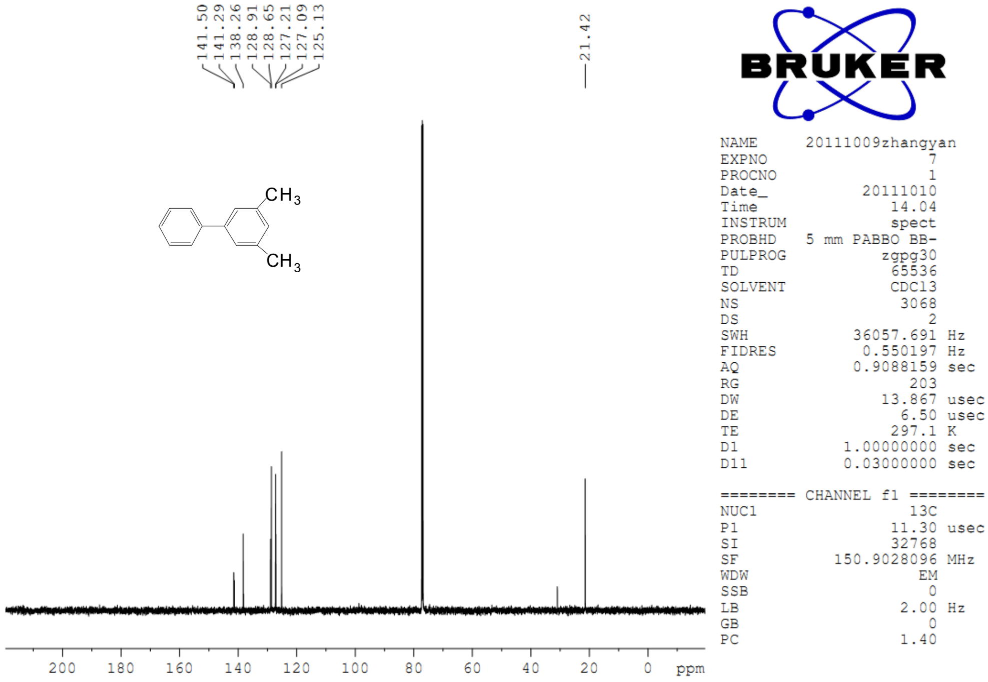
F2 - Processing parameters
SI                 32768
SF           600.1300158 MHz
WDW                   EM
SSB      0
LB                 -0.10 Hz
GB       0
PC                  1.00
```

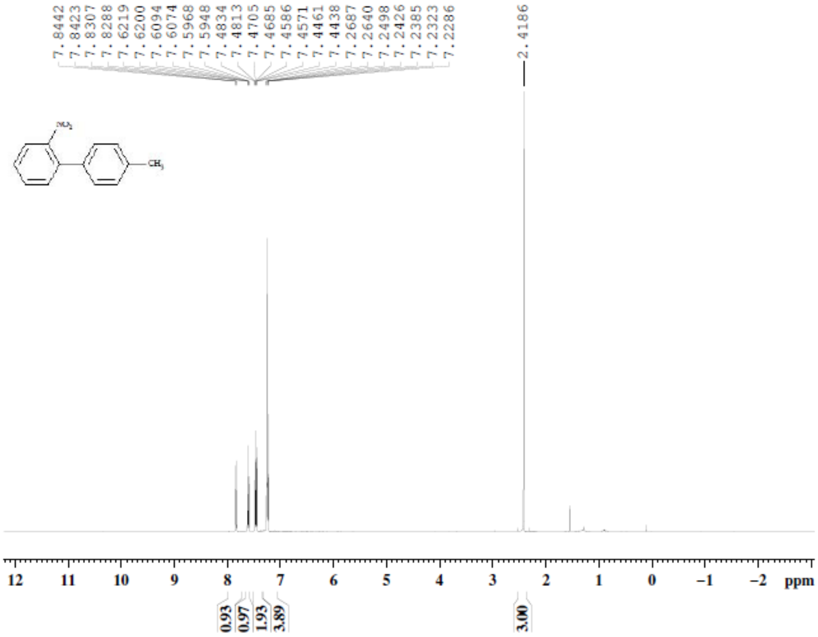


```
NAME      20111009zhangyan
EXPNO                  5
PROCNO                 1
Date_           20111009
Time               16.52
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  5120
DS                     2
SWH            36057.691 Hz
FIDRES          0.550197 Hz
AQ             0.9088159 sec
RG                   203
DW                13.867 usec
DE                  6.50 usec
TE                 297.0 K
D1            1.00000000 sec
D11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 11.30 usec
SI                 32768
SF           150.9028096 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

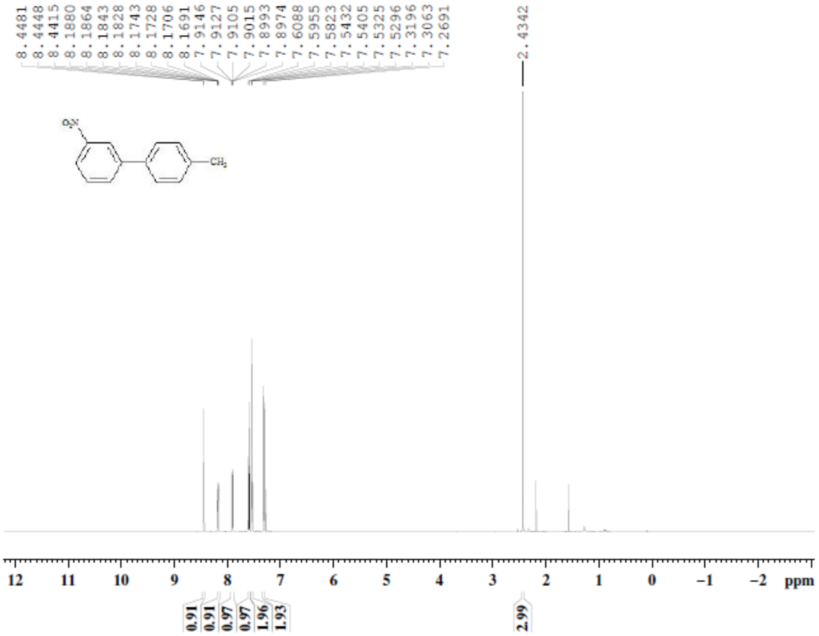

188
7.6192
7.6083
7.6068
7.4797
7.4676
7.4553
7.4440
7.4423
7.3736
7.3617
7.3495
7.2715
7.2522
7.2513
7.2326
7.0358
7.0138
2.4217
2.4123
Current Data Parameters
NAME 20110826ligong
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110826
Time 16.00
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 12335.526 Hz
FIDRES 0.188225 Hz
AQ 2.6564426 sec
RG 64
DW 40.533 usec
DE 6.50 usec
TE 298.3 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.60 usec
PLW1 13.99600029 W
SFO1 600.1328806 MHz
F2 - Processing parameters
SI 32768
SF 600.1300098 MHz
WDW EM
SSB 0
LB -0.10 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
0
ppm
1.90
1.91
0.94
2.06
1.00
6.31


141.50
141.29
138.26
128.91
128.65
127.21
127.09
125.13
21.42
CH3
CH3
NAME 20111009zhangyan
EXPNO 7
PROCNO 1
Date_ 20111010
Time 14.04
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3068
DS 2
SWH 36057.691 Hz
FIDRES 0.550197 Hz
AQ 0.9088159 sec
RG 203
DW 13.867 usec
DE 6.50 usec
TE 297.1 K
D1 1.00000000 sec
D11 0.03000000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 11.30 usec
SI 32768
SF 150.9028096 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm



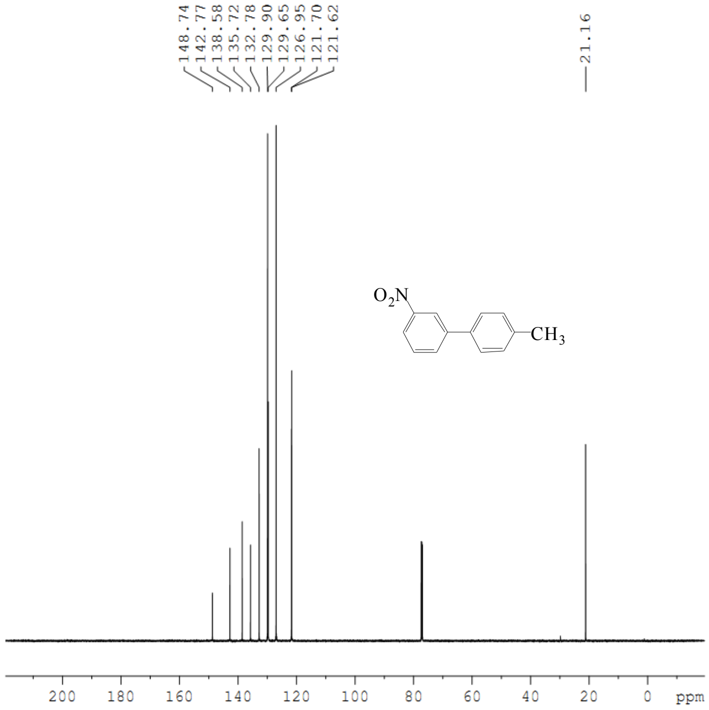
```
NAME            4-Me-2'-NO2
EXPNO                     1
PROCNO                    1
Date_              20110119
Time                  17.01
INSTRUM               spect
PROBHD     5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        2
SWH              12335.526 Hz
FIDRES            0.188225 Hz
AQ               2.6564426 sec
RG                       57
DW                   40.533 usec
DE                     6.50 usec
TE                    300.1 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    12.74 usec
PL1                   -1.00 dB
PL1W            15.52678299 W
SFO1            600.1337060 MHz
SI                    32768
SF              600.1300112 MHz
WDW                      EM
SSB                       0
LB                    -0.10 Hz
GB                        0
PC                     1.00
```



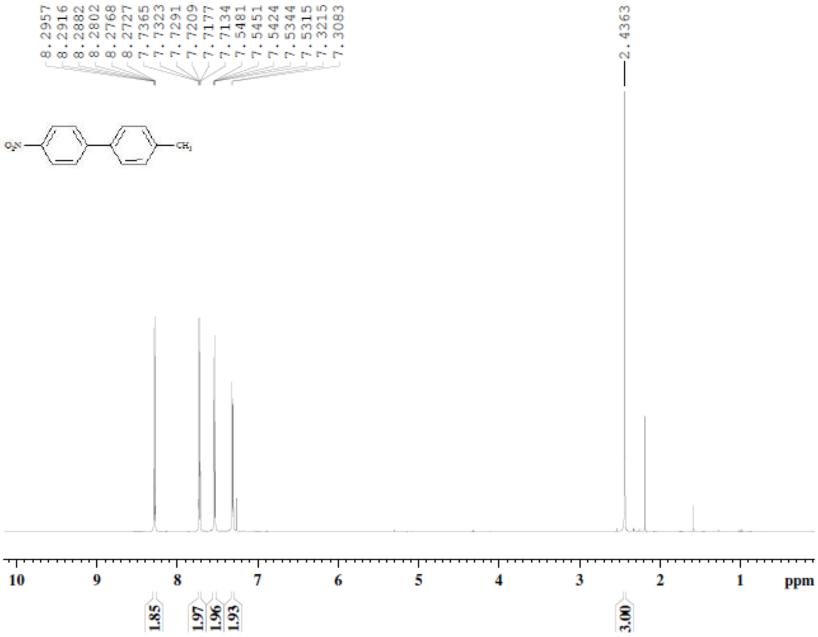
```
NAME          4-Me-3’-NO2
EXPNO                   1
PROCNO                  1
Date_            20110119
Time                17.10
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             12335.526 Hz
FIDRES           0.188225 Hz
AQ              2.6564426 sec
RG                     57
DW                 40.533 usec
DE                   6.50 usec
TE                  300.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.74 usec
PL1                 -1.00 dB
PL1W          15.52678299 W
SFO1          600.1337060 MHz
SI                  32768
SF            600.1300112 MHz
WDW                    EM
SSB                     0
LB                  -0.10 Hz
GB                      0
PC                   1.00
```



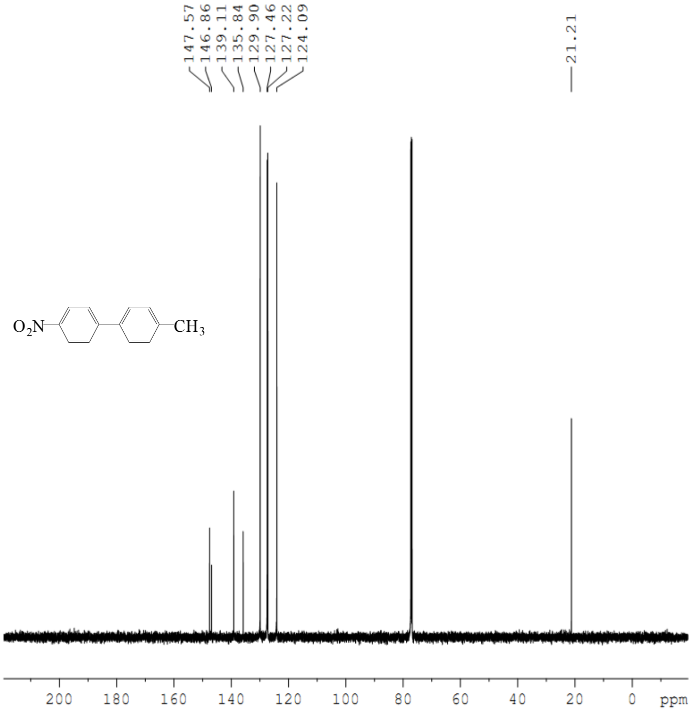
```
NAME     20111009zhangyan
EXPNO                  15
PROCNO                  1
Date_            20111011
Time                15.13
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    211
DS                      2
SWH             36057.691 Hz
FIDRES           0.550197 Hz
AQ              0.9088159 sec
RG                    203
DW                 13.867 usec
DE                   6.50 usec
TE                  297.3 K
D1             1.00000000 sec
D11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                  11.30 usec
SI                  32768
SF            150.9028096 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



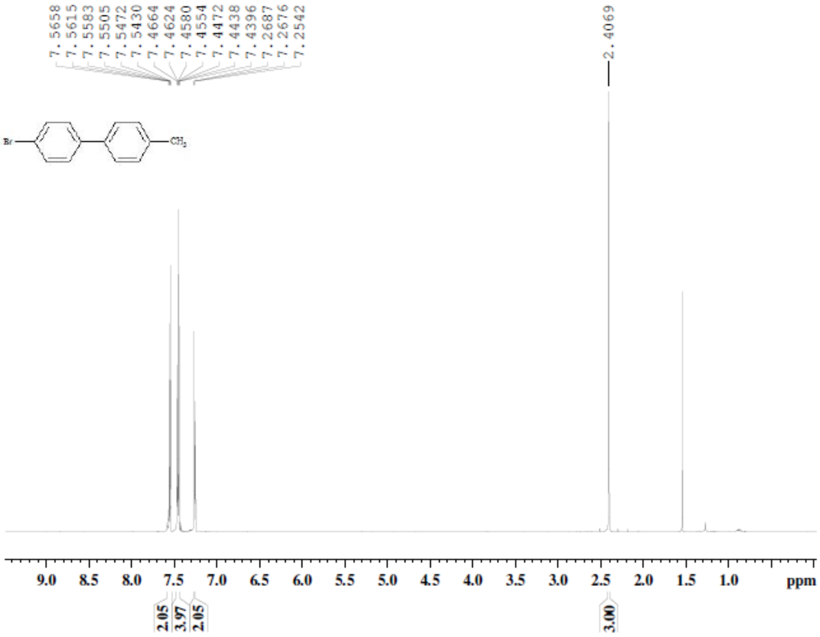
```
NAME          4-Me-4'-NO2
EXPNO                   1
PROCNO                  1
Date_            20110124
Time                16.56
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             12335.526 Hz
FIDRES           0.188225 Hz
AQ              2.6564426 sec
RG                     64
DW                 40.533 usec
DE                   6.50 usec
TE                  300.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.74 usec
PL1                 -1.00 dB
PL1W          15.52678299 W
SFO1          600.1337060 MHz
SI                  32768
SF            600.1300112 MHz
WDW                    EM
SSB                     0
LB                  -0.10 Hz
GB                      0
PC                   1.00
```



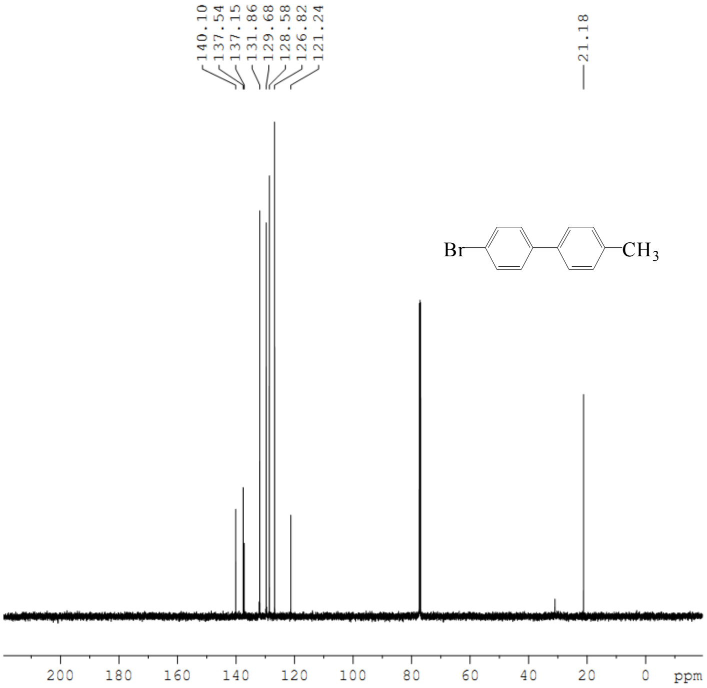
```
NAME     20111009zhangyan
EXPNO                  13
PROCNO                  1
Date_            20111011
Time                11.14
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   5141
DS                      2
SWH             36057.691 Hz
FIDRES           0.550197 Hz
AQ              0.9088159 sec
RG                    203
DW                 13.867 usec
DE                   6.50 usec
TE                  296.9 K
D1             1.00000000 sec
D11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                  11.30 usec
SI                  32768
SF            150.9028096 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



```
NAME          4-Me-4'-Br
EXPNO                  1
PROCNO                 1
Date_           20110119
Time               17.29
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            12335.526 Hz
FIDRES          0.188225 Hz
AQ             2.6564426 sec
RG                  90.5
DW                40.533 usec
DE                  6.50 usec
TE                 300.1 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.74 usec
PL1                -1.00 dB
PL1W         15.52678299 W
SFO1         600.1337060 MHz
SI                 32768
SF           600.1300112 MHz
WDW                   EM
SSB                    0
LB                 -0.10 Hz
GB                     0
PC                  1.00
```



```
NAME       20111009zhangyan
EXPNO                    14
PROCNO                    1
Date_              20111011
Time                  14.13
INSTRUM               spect
PROBHD       5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1615
DS                        2
SWH               36057.691 Hz
FIDRES             0.550197 Hz
AQ                0.9088159 sec
RG                      203
DW                   13.867 usec
DE                     6.50 usec
TE                    298.6 K
D1               1.00000000 sec
D11              0.03000000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                    11.30 usec
SI                    32768
SF              150.9028096 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```