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SUPPORTING INFORMATION

Decarboxylative Suzuki-Miyaura Coupling of (hetero)aromatic carboxylic acids using Iodine as the Terminal Oxidant

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General Information

Unless otherwise indicated, all reactions were carried out in 10 mL microwave vials using reagents obtained from commercial sources and used without further purification. K_3PO_4 was kept in a vacuum oven at 200 °C for 24 h prior to use. All other starting materials and solvents were purchased from Acros, Aldrich, Alfa Aesar, Fluorochem, Apollo Scientific and Manchester Organics, and used without further purification unless otherwise stated. Column chromatography was performed on silica gel (40–63 μm). Thin layer chromatography (TLC) was carried out on pre-coated silica gel F254 plates with visualization under UV light or using an aqueous basic $KMnO_4$ solution. Melting points were obtained using a Stuart SMP11 apparatus and are uncorrected. IR spectra were recorded using a Thermo Scientific Nicolet iS5 FTIR machine, relevant bands are quoted in cm^{-1}. High resolution mass spectra were performed by the School of Chemistry Mass Spectrometry Service (University of Manchester) employing a Thermo Finnigan MAT95XP or Thermo Exactive Plus EMR spectrometer. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded at 400 or 500 MHz on Bruker machines. ^{1}H NMR are referenced to the residual solvent peak at 7.26 ppm ($CDCl_3$) and quoted in ppm to 2 decimal places with coupling constants (*J*) to the nearest 0.1 Hz. ^{13}C NMR spectra, recorded at 101 MHz or 126 MHz, are referenced to the solvent peak at 77.16 ppm ($CDCl_3$) and quoted in ppm to 1 decimal place with coupling constants (*J*) to the nearest 0.1 Hz. ^{19}F NMR spectra were recorded at 376 or 471 MHz in $CDCl_3$ and quoted in ppm to 2 decimal places and with coupling constants (*J*) to the nearest 0.1 Hz.

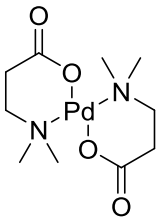
General Procedure A for the Decarboxylative Iodination/Suzuki-Miyaura Coupling

A 10 mL microwave vial was charged with K_3PO_4 (106.1 mg, 0.5 mmol, 1.0 equiv), put under vacuum and flame dried. Under a nitrogen funnel benzoic acid (0.5 mmol, 1.0 equiv) and a given amount of I_2 were added. The vial was flushed with nitrogen, capped and MeCN (0.75 mL, 0.66 M) was added. The reaction was stirred for a given time at a given temperature. Upon completion the reaction was cooled and the excess iodine quenched with a given amount of Et_3N and stirred at 120 ˚C for 5 h. After this time the reaction was cooled and Pd(N,N-dimethyl β-alaninate)$_2$ (3.4 mg, 0.01 mmol, 2 mol %), K_3PO_4 (212.2 mg, 1.0 mmol, 2 equiv), boronic acid (0.75 mmol, 1.5 equiv) and EtOH/H_2O 1:1 (1.5 mL, 0.22M) were added. The vial was then capped and stirred under air at 100 ˚C for 5h, after this time the crude mixture was cooled and adsorbed directly onto silica gel then purified by column chromatography. Removal of the solvents *in vacuo* yielded the desired product.

General Procedure B for the Decarboxylative Bromination/Suzuki-Miyaura Coupling

A 10 mL microwave vial was charged with K_3PO_4 (106.1 mg, 0.5 mmol, 1.0 equiv), benzoic acid (0.5 mmol, 1.0 equiv), Bu_4NBr_3 (482.18, 1.0 mmol 2.0 equiv) and MeCN (0.75 mL 0.66 M). The reaction was stirred for a given time at a 100 °C. Upon completion the reaction was cooled and the solvents removed *in vacuo.* After removal of the solvents Pd(N,N-dimethyl β-alaninate)$_2$ (3.4 mg, 0.01 mmol, 2 mol %), K_3PO_4 (212.2 mg, 1.0 mmol, 2 equiv), boronic acid (0.75 mmol, 1.5 equiv) and EtOH/H_2O 1:1 (1.5 mL, 0.22M) were added. The vial was then capped and stirred under air at 100 ˚C for 5h, after this time the crude mixture was cooled and adsorbed directly onto silica gel then purified by column chromatography. Removal of the solvents *in vacuo* yielded the desired product.

Preparation of Pd(*N*,*N*-Dimethyl-β-alaninate)$_2$

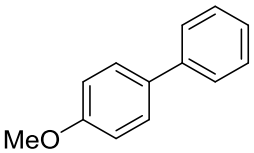


Following the reported procedure.[1] A mixture of *N*,*N*-dimethyl-β-alanine (2 equiv) and K_2PdCl_4 (1 equiv) was stirred in H_2O at r.t. for 10 min. The solution was adjusted to pH 8 with aq 10 % NaOH whereupon a precipitate was formed. The yellow solid obtained was collected by filtration and dried under vacuum; yield: 72%.

Spectroscopic data matched those previously reported

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.57 (s, 12 H), 2.56 (m, 4 H), 2.45 (t, *J* = 5.25 Hz, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.0, 60.1, 49.0, 34.5.

Experimental Details, Spectroscopic data and Analytical data

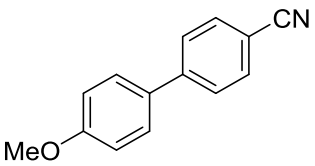


4-methoxy-1,1'-biphenyl (3a)

The general procedure **A** was carried out with 4-methoxybenzoic acid (76.0 mg, 0.5 mmol, 1.0 equiv) and I_2 (380.7 mg, 1.5 mmol, 3 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with phenylboronic acid (91.4 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (93.0 mg, 92%).

Spectroscopic data matched those previously reported[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 4H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 140.9, 133.9, 128.9, 128.3, 126.9, 126.8, 114.3, 55.5.



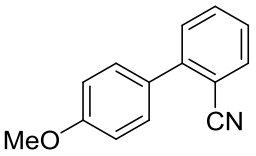
4'-methoxy-[1,1'-biphenyl]-4-carbonitrile (3b)

The general procedure **A** was carried out with 4-methoxybenzoic acid (76.0 mg, 0.5 mmol, 1.0 equiv) and I_2 (380.7 mg, 1.5 mmol, 3 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with (4-cyanophenyl)boronic acid (110.2 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient).

Removal of the solvent *in vacuo* gave the desired product as a colourless solid (98.3 mg, 94%).

Spectroscopic data matched those previously reported[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 145.3, 132.7, 131.6, 128.5, 127.2, 119.2, 114.6, 110.2, 55.5.

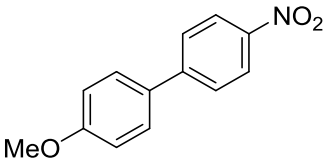


4'-methoxy-[1,1'-biphenyl]-2-carbonitrile (3c)

The general procedure **A** was carried out with 4-methoxybenzoic acid (76.0 mg, 0.5 mmol, 1.0 equiv) and I_2 (380.7 mg, 1.5 mmol, 3 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with (2-cyanophenyl)boronic acid (111.0 mg, 0.75 mmol, 1.5 equiv) and stirred for 15 h. After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (64.9 mg, 62%).

Spectroscopic data matched those previously reported[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.62 (app td, *J* = 7.8, 1.4 Hz, 1H), 7.55 – 7.45 (m, 2H), 7.40 (app td, *J* = 7.6, 1.2 Hz, 1H), 7.02 (d, *J* = 8.8 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 145.3, 133.9, 132.9, 130.6, 130.1, 123.0, 127.2, 119.1, 114.3, 111.1, 55.5.

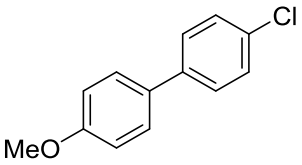


4-methoxy-4'-nitro-1,1'-biphenyl (3d)

The general procedure **A** was carried out with 4-methoxybenzoic acid (76.0 mg, 0.5 mmol, 1.0 equiv) and I_2 (380.7 mg, 1.5 mmol, 3 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with (4-nitrophenyl)boronic acid (125.9 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a yellow solid (110.0, 96%).

Spectroscopic data matched those previously reported[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.7 Hz, 2H), 7.69 (d, *J* = 8.7 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 147.3, 146.7, 131.2, 128.7, 127.2, 124.3, 114.7, 55.6.

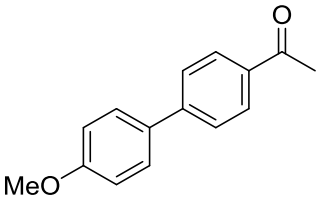


4-chloro-4'-methoxy-1,1'-biphenyl (3e)

The general procedure **A** was carried out with 4-methoxybenzoic acid (76.0 mg, 0.5 mmol, 1.0 equiv) and I_2 (380.7 mg, 1.5 mmol, 3 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with (4-chlorophenyl)boronic acid (117.3 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (106.1, 97%).

Spectroscopic data matched those previously reported[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.6, 6.4 Hz, 4H), 7.39 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 139.4, 132.8, 132.6, 129.0, 128.1, 128.1, 114.4, 55.5.

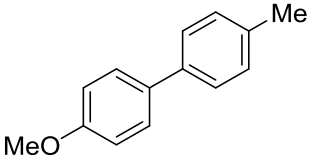


1-(4'-methoxy-[1,1'-biphenyl]-4-yl)ethan-1-one (3f)

The general procedure **A** was carried out with 4-methoxybenzoic acid (76.0 mg, 0.5 mmol, 1.0 equiv) and I_2 (380.7 mg, 1.5 mmol, 3 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with (4-acetylphenyl)boronic acid (123.0 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (87.1 mg, 77%).

Spectroscopic data matched those previously reported[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 160.0, 145.4, 135.3, 132.3, 129.0, 128.4, 126.7, 114.5, 55.5, 26.7.



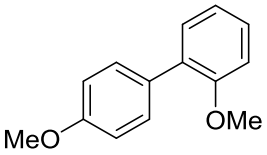
4-methoxy-4'-methyl-1,1'-biphenyl (3g)

The general procedure **A** was carried out with 4-methoxybenzoic acid (76.0 mg, 0.5 mmol, 1.0 equiv) and I_2 (380.7 mg, 1.5 mmol, 3 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with *p*-tolylboronic acid (102.0 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the

crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (89.2 mg, 90%).

Spectroscopic data matched those previously reported[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 138.0, 136.5, 133.8, 129.6, 128.1, 126.7, 114.3, 55.4, 21.2.

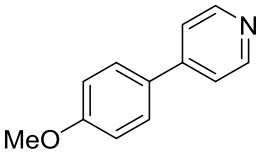


2,4'-dimethoxy-1,1'-biphenyl (3h)

The general procedure **A** was carried out with 4-methoxybenzoic acid (76.0 mg, 0.5 mmol, 1.0 equiv) and I_2 (380.7 mg, 1.5 mmol, 3 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with (2-methoxyphenyl)boronic acid (114.0 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (98.6 mg, 92%).

Spectroscopic data matched those previously reported[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.40 – 7.32 (m, 2H), 7.08 (app td, *J* = 7.5, 1.1 Hz, 1H), 7.03 (m, 3H), 3.89 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 156.5, 131.0, 130.8, 130.7, 130.4, 128.3, 120.9, 113.6, 111.2, 55.6, 55.3.

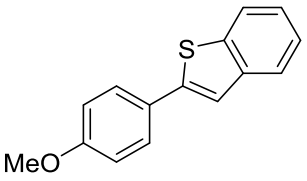


4-(4-methoxyphenyl)pyridine (3i)

The general procedure **A** was carried out with 4-methoxybenzoic acid (76.0 mg, 0.5 mmol, 1.0 equiv) and I_2 (380.7 mg, 1.5 mmol, 3 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with pyridin-4-ylboronic acid (122.9 mg, 1.0 mmol, 2.0 equiv) and stirred for 15 h. After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (85.2 mg, 92%).

Spectroscopic data matched those previously reported[9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 6.0 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 6.2 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 150.3, 147.9, 130.4, 128.2, 121.1, 114.6, 55.5.

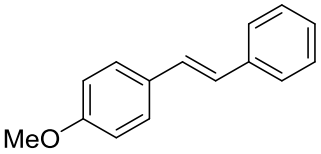


2-(4-methoxyphenyl)benzo[b]thiophene (3j)

The general procedure **A** was carried out with 4-methoxybenzoic acid (76.0 mg, 0.5 mmol, 1.0 equiv) and I_2 (380.7 mg, 1.5 mmol, 3 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with benzo[b]thiophen-2-ylboronic acid (178.0 mg, 1.0 mmol, 2.0 equiv) and stirred for 15 h. After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (72.1 mg, 60%).

Spectroscopic data matched those previously reported[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.4 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.43 (s, 1H), 7.33 (app td, *J* = 7.7, 1.1 Hz, 1H), 7.29 (app td, *J* = 7.6, 1.3 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 144.3, 141.0, 139.3, 127.9, 127.2, 124.6, 124.1, 123.4, 122.3, 118.3, 114.5, 55.5.

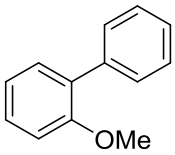


(E)-1-methoxy-4-styrylbenzene (3k)

The general procedure **A** was carried out with 4-methoxybenzoic acid (76.0 mg, 0.5 mmol, 1.0 equiv) and I_2 (380.7 mg, 1.5 mmol, 3 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with (E)-styrylboronic acid (111.0 mg, 0.75 mmol, 1.5 equiv) and stirred for 15 h. After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (88.3 mg, 84%) (E/Z >99:1).

Spectroscopic data matched those previously reported[11]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.37 (app t, *J* = 7.5 Hz, 2H), 7.26 (app t, *J* = 7.0 Hz, 1H), 7.10 (d, *J* = 16.3 Hz, 1H), 7.00 (d, *J* = 16.3 Hz, 1H), 6.92 (d, *J* = 8.2 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 137.8, 130.2, 128.8, 128.3, 127.8, 127.3, 126.7, 126.4, 114.2, 55.4.

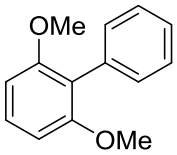


2-methoxy-1,1'-biphenyl (3l)

The general procedure **A** was carried out with 2-methoxybenzoic acid (76.0 mg, 0.5 mmol, 1.0 equiv) and I_2 (213.3 mg, 1.25 mmol, 2.5 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with phenylboronic acid (91.4 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (75.5 mg, 82%).

Spectroscopic data matched those previously reported[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.1 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.31 (m, 3H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 138.6, 131.0, 130.8, 129.7, 128.7, 128.1, 127.0, 120.9, 111.3, 55.6.

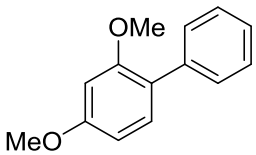


2,6-dimethoxy-1,1'-biphenyl (3m)

The general procedure **A** was carried out with 2,6-dimethoxybenzoic acid (91.1 mg, 0.5 mmol, 1.0 equiv) and I_2 (380.7 mg, 1.5 mmol, 3.0 equiv) and was stirred at ~18 °C for 20 h. The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with phenylboronic acid (91.4 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (86.8 mg, 81%).

Spectroscopic data matched those previously reported[13]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.28 (t, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 2H), 3.72 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 134.2, 131.0, 128.7, 127.8, 126.9, 119.6, 104.3, 56.0.



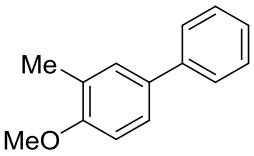
2,4-dimethoxy-1,1'-biphenyl (2n)

The general procedure **A** was carried out with 2,4-dimethoxybenzoic acid (91.1 mg, 0.5 mmol, 1.0 equiv) and I_2 (380.7 mg, 1.5 mmol, 3 equiv) and was stirred at ~18 °C for 6 h. The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with phenylboronic acid (91.4 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate

gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (105.0 mg, 98%).

Spectroscopic data matched those previously reported[14]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.16 (d, *J* = 8.9 Hz, 1H), 6.52 – 6.38 (m, 2H), 3.75 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4, 157.6, 138.5, 131.4, 129.6, 128.1, 126.6, 123.7, 104.7, 99.1, 55.6, 55.5.

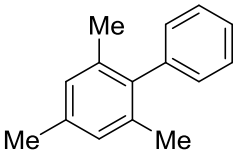


4-methoxy-3-methyl-1,1'-biphenyl (3o)

The general procedure **A** was carried out with 4-methoxy-3-methylbenzoic acid (83.1 mg, 0.5 mmol, 1.0 equiv) and I_2 (380.7 mg, 1.5 mmol, 3 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with phenylboronic acid (121.9 mg, 1.0 mmol, 2.0 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (72.4 mg, 73%).

Spectroscopic data matched those previously reported[15]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.50 – 7.43 (m, 4H), 7.36 (tt, *J* = 6.9, 1.2 Hz, 1H), 6.95 (d, *J* = 9.0 Hz, 1H), 3.92 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 141.08, 133.4, 129.5, 128.7, 126.9, 126.8, 126.6, 125.4, 110.2, 55.5, 16.5.

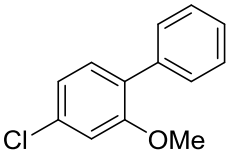


2,4,6-trimethyl-1,1'-biphenyl (3p)

The general procedure **A** was carried out with 2,4,6-trimethylbenzoic acid (82.1 mg, 0.5 mmol, 1.0 equiv) and I_2 (380.7 mg, 1.5 mmol, 3.0 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with phenylboronic acid (91.4 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless oil (76.6 mg, 78%).

Spectroscopic data matched those previously reported[16]

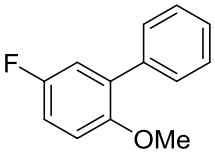
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (t, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.0 Hz, 2H), 7.02 (s, 2H), 2.41 (s, 3H), 2.08 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 139.2, 136.7, 136.1, 129.4, 128.5, 128.2, 126.6, 21.2, 20.9.



4-chloro-2-methoxy-1,1'-biphenyl (3q)

The general procedure **A** was carried out with 4-chloro-2-methoxybenzoic acid (93.3 mg, 0.5 mmol, 1.0 equiv) and I_2 (380.7 mg, 1.5 mmol, 3.0 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with phenylboronic acid (91.4 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (106.2 mg, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.0 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 1H), 7.05 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.00 (d, *J* = 1.9 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 137.6, 134.0, 131.7, 129.5, 129.3, 128.2, 127.4, 121.0, 112.0, 55.9; m.p. 37-41°C; IR(ATR) 2969 1502 1497 1390 1238 1029; HRMS (EI) m/z calcd. $C_{13}H_{12}OCl$: 219.0571; found $[M]^+$ 219.1574.

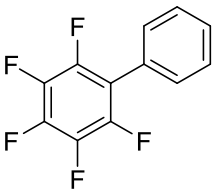


5-fluoro-2-methoxy-1,1'-biphenyl (3r)

The general procedure **A** was carried out with 5-fluoro-2-methoxybenzoic acid (85.1 mg, 0.5 mmol, 1.0 equiv) and I_2 (380.7 mg, 1.5 mmol, 3 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with phenylboronic acid (91.4 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless oil (81.9 mg, 81%).

Spectroscopic data matched those previously reported[17]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.08 (dd, *J* = 9.1, 3.1 Hz, 1H), 7.02 (ddd, *J* = 8.9, 7.9, 3.1 Hz, 1H), 6.92 (dd, *J* = 9.0, 4.6 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3 (d, *J* = 238.5 Hz), 152.8, 137.6, 132.1 (d, *J* = 7.5 Hz), 129.5, 128.2, 127.5, 117.5 (d, *J* = 23.4 Hz), 114.4 (d, *J* = 22.6 Hz), 112.4 (d, *J* = 8.3 Hz), 56.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -124.02.



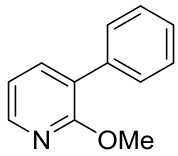
2,3,4,5,6-pentafluoro-1,1'-biphenyl (3s)

The general procedure **A** was carried out with 2,3,4,5,6-pentafluorobenzoic acid (106.0 mg, 0.5 mmol, 1.0 equiv) and I_2 (380.7 mg, 1.5 mmol, 3.0 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with phenylboronic acid (91.4 mg, 0.75 mmol, 1.5 equiv) and stirred for 15 h. After completion of the reaction the crude mixture was purified by column chromatography

(Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (103.8 mg, 85%).

Spectroscopic data matched those previously reported[18]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.40 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.14 (dddt, *J* = 247.6, 10.9, 7.4, 3.8 Hz), 140.37 (dtt, *J* = 253.5, 13.3, 5.0 Hz), 137.83 (ddddd, *J* = 250.4, 17.6, 12.6, 5.2, 2.2 Hz), 130.14, 129.29, 128.71, 126.40, 115.93 (td, *J* = 17.4, 4.1 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -143.28 (dd, *J* = 22.9, 8.2 Hz), -155.67 (t, *J* = 21.0 Hz), -162.30 (td, *J* = 22.4, 8.2 Hz).

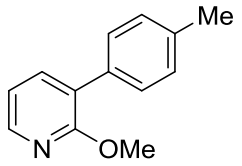


2-methoxy-3-phenylpyridine (3t)

The general procedure **A** was carried out with 2-methoxynicotinic acid (76.6 mg, 0.5 mmol, 1.0 equiv) and I_2 (507.6 mg, 2.0 mmol, 4 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with phenylboronic acid (91.4 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a yellow oil (74.1 mg, 80%).

Spectroscopic data matched those previously reported[19]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.62 (dd, *J* = 7.3, 1.9 Hz, 1H), 7.57 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 6.98 (dd, *J* = 7.3, 5.0 Hz, 1H), 3.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 145.8, 138.7, 136.9, 129.3, 128.4, 127.7, 124.8, 117.2, 53.6.

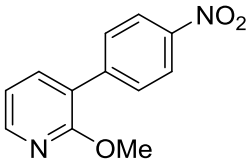


2-methoxy-3-(p-tolyl)pyridine (3u)

The general procedure **A** was carried out with 2-methoxynicotinic acid (76.6 mg, 0.5 mmol, 1.0 equiv) and I_2 (507.6 mg, 2.0 mmol, 4 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with *p*-tolylboronic acid (102.0 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless oil (81.6 mg, 82%).

Spectroscopic data matched those previously reported[20]

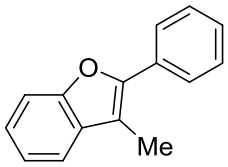
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 4.9 Hz, 1H), 7.60 (d, *J* = 7.3 Hz, 1H), 7.46 (d, *J* = 7.3 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 2H), 6.97 (t, *J* = 6.0 Hz, 1H), 3.98 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.1, 145.6, 138.5, 137.5, 134.0, 129.2 129.1, 124.8, 117.2, 53.6, 21.4.



2-methoxy-3-(4-nitrophenyl)pyridine (3v)

The general procedure **A** was carried out with 2-methoxynicotinic acid (76.6 mg, 0.5 mmol, 1.0 equiv) and I_2 (507.6 mg, 2.0 mmol, 4 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with (4-nitrophenyl)boronic acid (125.3 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a yellow solid (93.2 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.9 Hz, 2H), 8.23 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.72 (d, *J* = 8.9 Hz, 2H), 7.64 (dd, *J* = 7.3, 1.9 Hz, 1H), 7.02 (dd, *J* = 7.3, 5.0 Hz, 1H), 3.98 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.7, 147.4, 147.1, 143.7, 138.8, 130.1, 123.5, 122.4, 117.4, 53.8. m.p. 99-102 °C IR (ATR) 2943 1580 1462 1391 1346 1253 1022; HRMS (EI) m/z calcd. $C_{12}H_{10}O_3N_2$: 231.0764; found $[M]^+$ 231.0766.

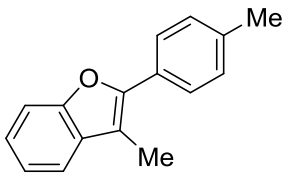


3-methyl-2-phenylbenzofuran (3w)

The general procedure **A** was carried out with 3-methylbenzofuran-2-carboxylic acid (88.1 mg, 0.5 mmol, 1.0 equiv) and I_2 (253.81 mg, 1.0 mmol, 2.0 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with phenylboronic acid (91.4 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (100.0 mg, 96%).

Spectroscopic data matched those previously reported[21]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 3H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.37 – 7.27 (m, 2H), 2.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 150.8, 131.5, 131.3, 128.7, 128.0, 126.8, 124.4, 122.5, 119.4, 111.4, 111.1, 9.6.



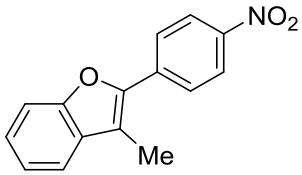
3-methyl-2-(p-tolyl)benzofuran (3x)

The general procedure **A** was carried out with 3-methylbenzofuran-2-carboxylic acid (88.1 mg, 0.5 mmol, 1.0 equiv) and I_2 (253.81 mg,

1.0 mmol, 2.0 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with *p*-tolylboronic acid (102.0 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (100.0 mg, 90%).

Spectroscopic data matched those previously reported[22]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.31 – 7.21 (m, 4H), 2.45 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.8, 151.0, 137.9, 131.4, 129.4, 128.7, 126.8, 124.2, 122.4, 119.2, 111.0, 110.7, 21.5, 9.6.

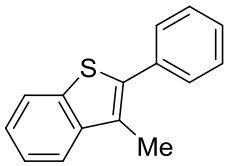


3-methyl-2-(4-nitrophenyl)benzofuran (3y)

The general procedure **A** was carried out with 3-methylbenzofuran-2-carboxylic acid (88.1 mg, 0.5 mmol, 1.0 equiv) and I_2 (253.81 mg, 1.0 mmol, 2.0 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with (4-nitrophenyl)boronic acid (125.2 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a yellow solid (108.9 mg, 86%).

Spectroscopic data matched those previously reported[23]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.5 Hz, 2H), 7.94 – 7.89 (m, 2H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.37 (app t, *J* = 7.7 Hz, 1H), 7.29 (app t, *J* = 7.5 Hz, 1H), 2.52 (d, *J* = 1.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2, 148.2, 146.5, 137.4, 130.8, 126.5, 125.9, 124.1, 123.0, 112.0, 115.5, 111.3, 10.0.

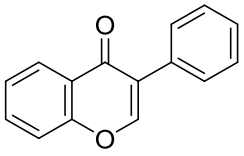


3-methyl-2-phenylbenzo[b]thiophene (3z)

The general procedure **A** was carried out with 3-methylbenzo[b]thiophene-2-carboxylic acid (96.1 mg, 0.5 mmol, 1.0 equiv) and I_2 (279.2 mg, 1.1 mmol, 2.2 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with phenylboronic acid (91.4 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (99.8 mg, 89%).

Spectroscopic data matched those previously reported[24]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 7.1 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.46 – 7.34 (m, 3H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 139.0, 138.2, 134.9, 129.9, 128.7, 127.9, 127.6, 124.4, 124.3, 122.3 (2C), 12.8.

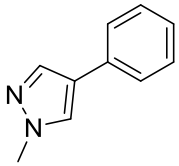


3-phenyl-4H-chromen-4-one (3aa)

The general procedure **A** was carried out with 4-oxo-4*H*-chromene-3-carboxylic acid (95.1 mg, 0.5 mmol, 1.0 equiv) and I_2 (380.7 mg, 1.5 mmol, 3 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with phenylboronic acid (91.4 mg, 0.75 mmol, 1.5 equiv) and stirred for 15 h. After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (92.2 mg, 83%).

Spectroscopic data matched those previously reported[25]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.03 (s, 1H), 7.69 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.58 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.48 – 7.35 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 156.3, 153.2, 133.8, 132.0, 129.1, 128.6, 128.3, 126.6, 125.5, 125.4, 124.7, 118.2.

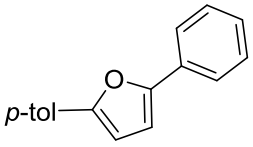


1-methyl-4-phenyl-1H-pyrazole (3ab)

The general procedure **A** was carried out with 1-methyl-1H-pyrazole-4-carboxylic acid (63.1 mg, 0.5 mmol, 1.0 equiv) and I_2 (507.6 mg, 2.0 mmol, 4 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with phenylboronic acid (91.4 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a yellow solid (55.4 mg, 70%).

Spectroscopic data matched those previously reported[26]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.60 (s, 1H), 7.47 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8, 132.7, 128.9, 127.0, 126.4, 125.6, 123.3, 39.2.

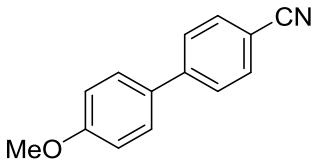


2-phenyl-5-(p-tolyl)furan (3ac)

The general procedure **A** was carried out with 5-(p-tolyl)furan-2-carboxylic acid (106.0 mg, 0.5 mmol, 1.0 equiv) and I_2 (380.7 mg, 1.5 mmol, 3.0 equiv). The reaction was quenched with Et_3N (0.63 mL, 2.25 mmol, 4.5 equiv) for 5 h. The remainder of procedure **A** was then followed with phenylboronic acid (91.4 mg, 0.75 mmol, 1.5 equiv) and stirred for 16 h. After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (76.1 mg, 65%).

Spectroscopic data matched those previously reported[27]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.3 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.31 – 7.25 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 3.4 Hz, 1H), 6.69 (d, *J* = 3.4 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.7, 153.1, 137.4, 131.0, 129.5, 128.8, 128.3, 127.3, 123.8, 123.8, 107.3, 106.6, 21.5.

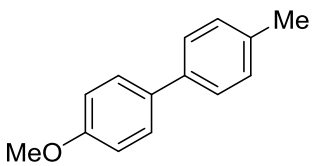


4'-methoxy-[1,1'-biphenyl]-4-carbonitrile (3b')

The general procedure **B** was carried out with 4-methoxybenzoic acid (76.0 mg, 0.5 mmol, 1.0 equiv) and ^{n}Bu$_4$NBr$_3$ (241.1 mg, 0.5 mmol, 1 equiv). After the given amount of time the solvents were removed and the remainder of procedure **B** was then followed with (4-cyanophenyl)boronic acid (110.2 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (94.2 mg, 90%).

Spectroscopic data matched those previously reported[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 145.3, 132.7, 131.6, 128.5, 127.2, 119.2, 114.6, 110.2, 55.5.

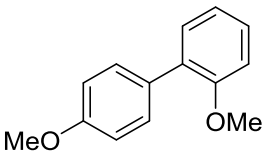


4-methoxy-4'-methyl-1,1'-biphenyl (3g')

The general procedure **B** was carried out with 4-methoxybenzoic acid (76.0 mg, 0.5 mmol, 1.0 equiv) ^{n}Bu$_4$NBr$_3$ (241.1 mg, 0.5 mmol, 1 equiv). After the given amount of time the solvents were removed and the remainder of procedure **B** was then followed with *p*-tolylboronic acid (102.0 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (74.4 mg, 75%).

Spectroscopic data matched those previously reported[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 138.0, 136.5, 133.8, 129.6, 128.1, 126.7, 114.3, 55.4, 21.2.

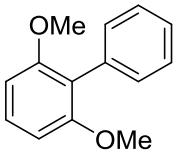


2,4'-dimethoxy-1,1'-biphenyl (3h')

The general procedure **B** was carried out with 4-methoxybenzoic acid (76.0 mg, 0.5 mmol, 1.0 equiv) and ^{n}Bu$_4$NBr$_3$ (241.1 mg, 0.5 mmol, 1 equiv). After the given amount of time the solvents were removed and the remainder of procedure **B** was then followed with (2-methoxyphenyl)boronic acid (114.0 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (98.6 mg, 92%).

Spectroscopic data matched those previously reported[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.40 – 7.32 (m, 2H), 7.08 (app td, *J* = 7.5, 1.1 Hz, 1H), 7.03 (m, 3H), 3.89 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 156.5, 131.0, 130.8, 130.7, 130.4, 128.3, 120.9, 113.6, 111.2, 55.6, 55.3.

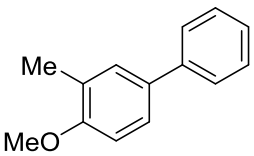


2,6-dimethoxy-1,1'-biphenyl (3m')

The general procedure **B** was carried out with 2,6-dimethoxybenzoic acid (91.1 mg, 0.5 mmol, 1.0 equiv) and ^{n}Bu$_4$NBr$_3$ (241.1 mg, 0.5 mmol, 1 equiv). After the given amount of time the solvents were removed and the remainder of procedure **B** was then followed with phenylboronic acid (91.4 mg, 0.75 mmol, 1.5 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (91.1 mg, 85%).

Spectroscopic data matched those previously reported[13]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.28 (t, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 2H), 3.72 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 134.2, 131.0, 128.7, 127.8, 126.9, 119.6, 104.3, 56.0.



4-methoxy-3-methyl-1,1'-biphenyl (3o')

The general procedure **B** was carried out with 4-methoxy-3-methylbenzoic acid (83.1 mg, 0.5 mmol, 1.0 equiv) and $^{n}Bu_4NBr_3$ (241.1 mg, 0.5 mmol, 1 equiv). After the given amount of time the solvents were removed and the remainder of procedure **B** was then followed with phenylboronic acid (121.9 mg, 1.0 mmol, 2.0 equiv). After completion of the reaction the crude mixture was purified by column chromatography (Hexane/Ethyl Acetate gradient). Removal of the solvent *in vacuo* gave the desired product as a colourless solid (91.2 mg, 92%).

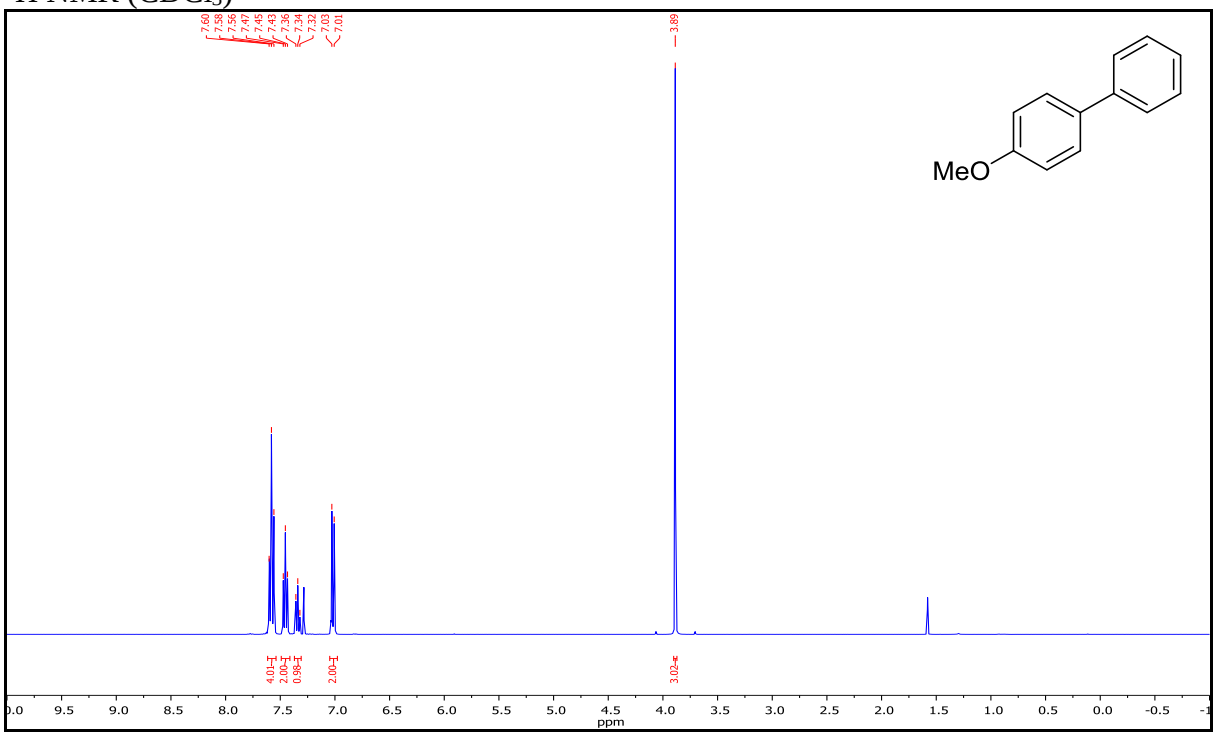
Spectroscopic data matched those previously reported[15]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.50 – 7.43 (m, 4H), 7.36 (tt, *J* = 6.9, 1.2 Hz, 1H), 6.95 (d, *J* = 9.0 Hz, 1H), 3.92 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 141.08, 133.4, 129.5, 128.7, 126.9, 126.8, 126.6, 125.4, 110.2, 55.5, 16.5.

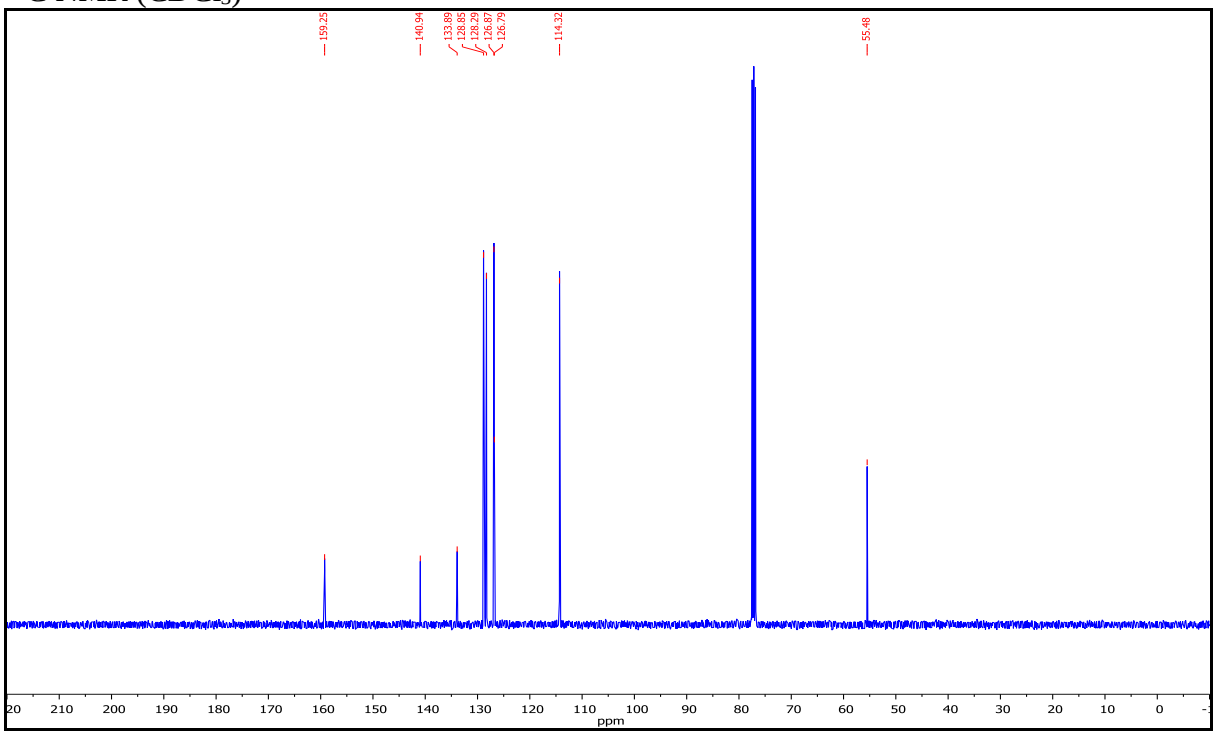
NMR Spectra

4-methoxy-1,1'-biphenyl (3a)

^{1}H NMR ($CDCl_3$)

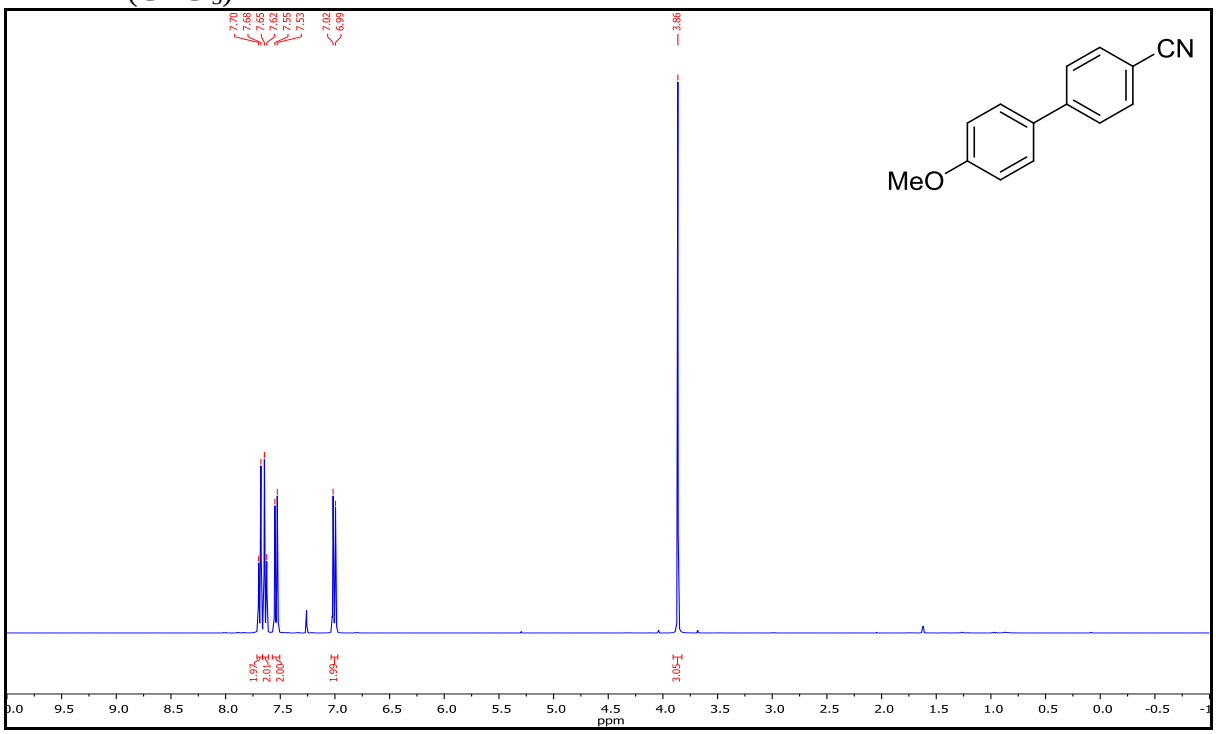


^{13}C NMR ($CDCl_3$)

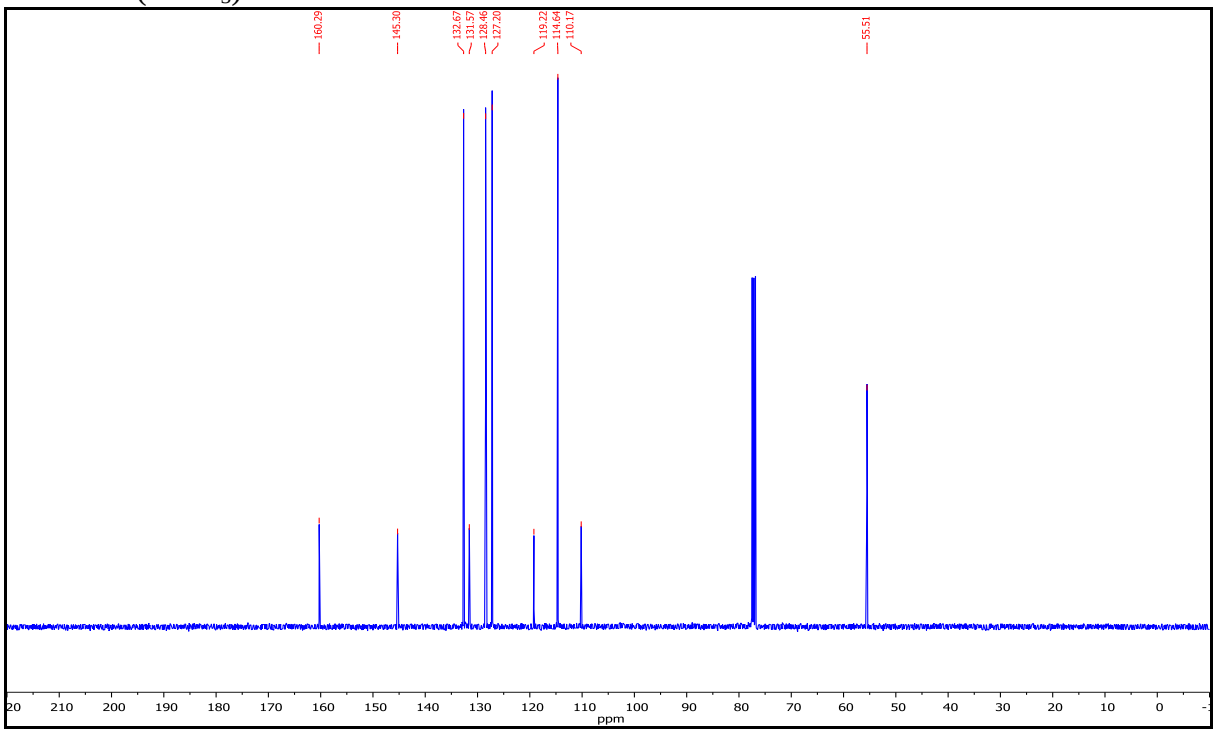


4'-methoxy-[1,1'-biphenyl]-4-carbonitrile (2b)

^{1}H NMR ($CDCl_3$)

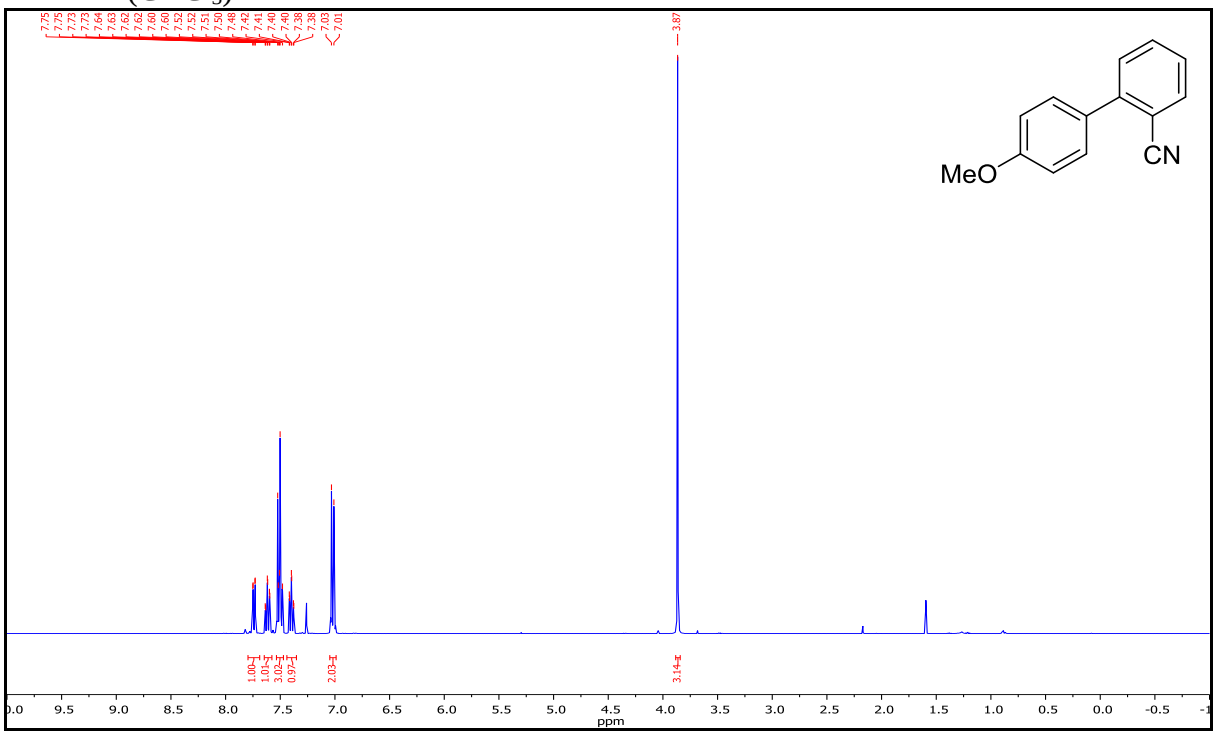


^{13}C NMR ($CDCl_3$)

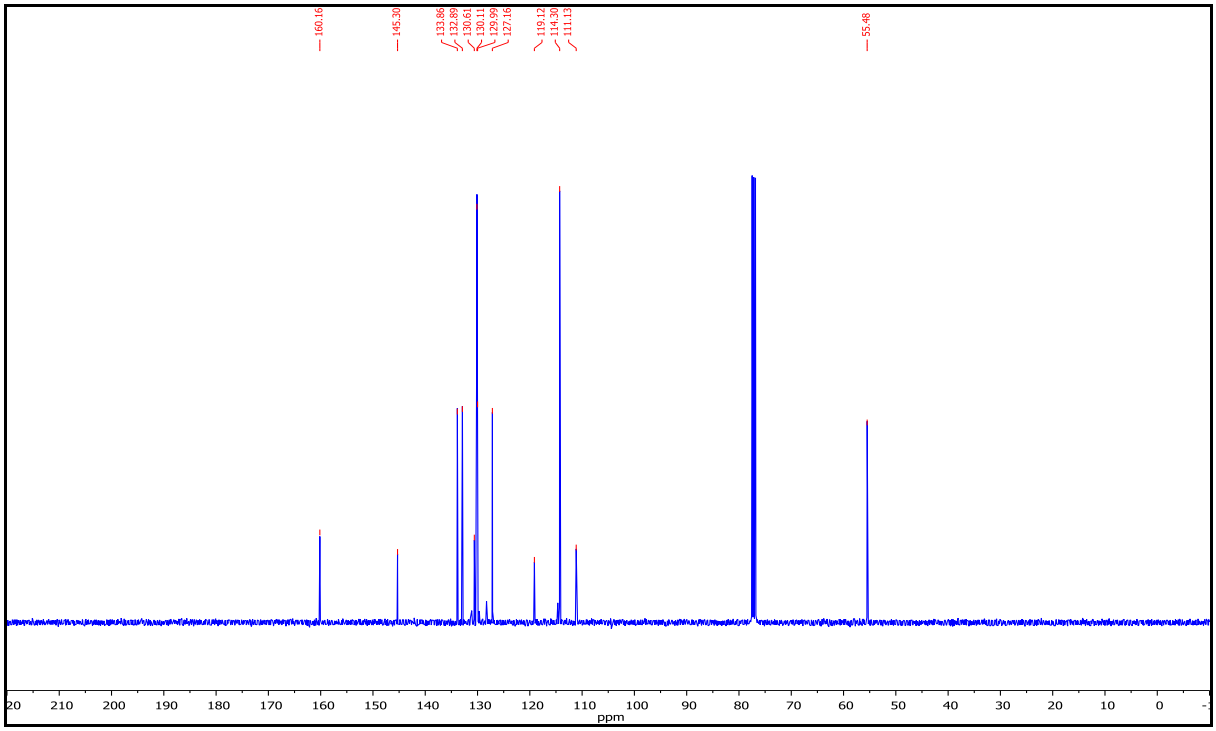


4'-methoxy-[1,1'-biphenyl]-2-carbonitrile (3c)

^{1}H NMR ($CDCl_3$)

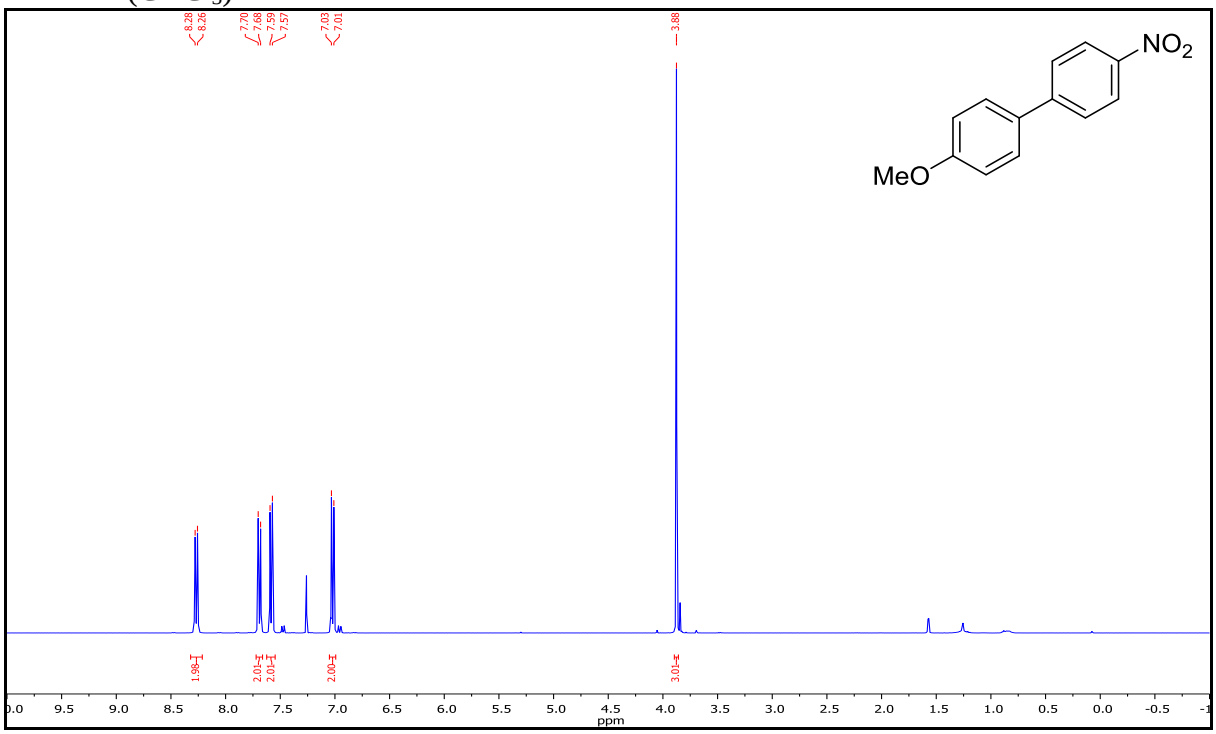


^{13}C NMR ($CDCl_3$)

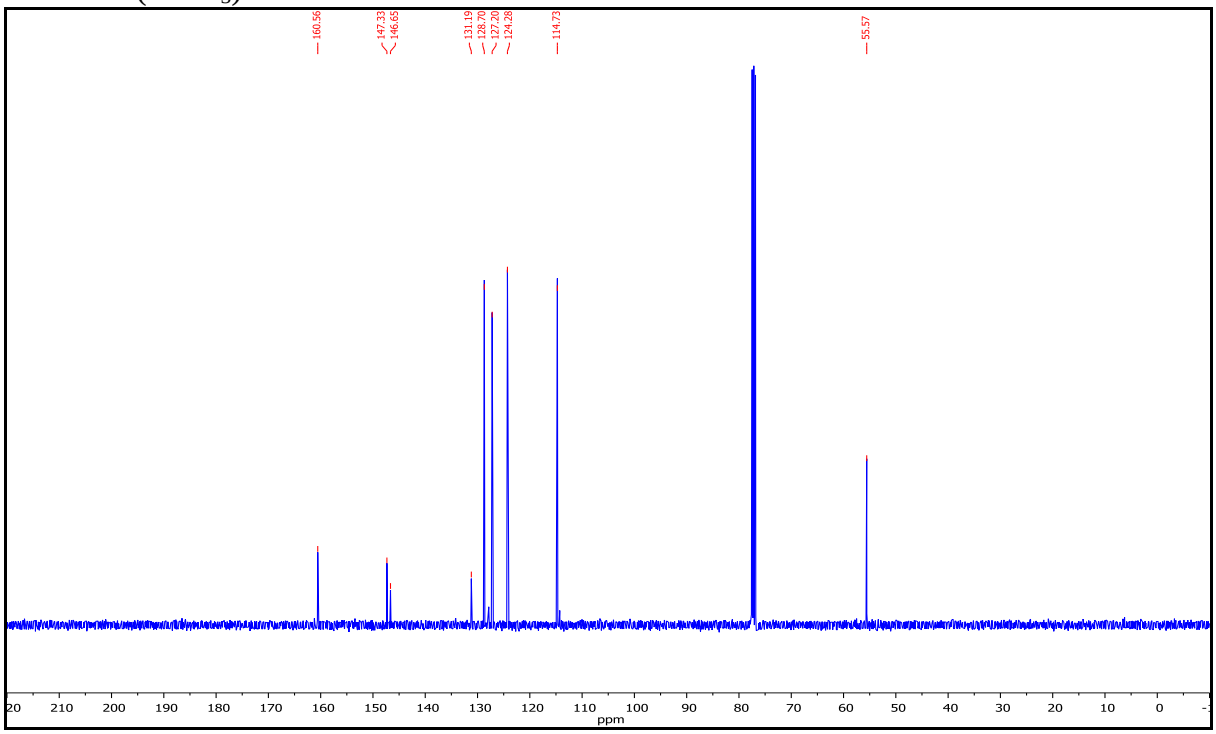


4-methoxy-4'-nitro-1,1'-biphenyl (3d)

^{1}H NMR ($CDCl_3$)

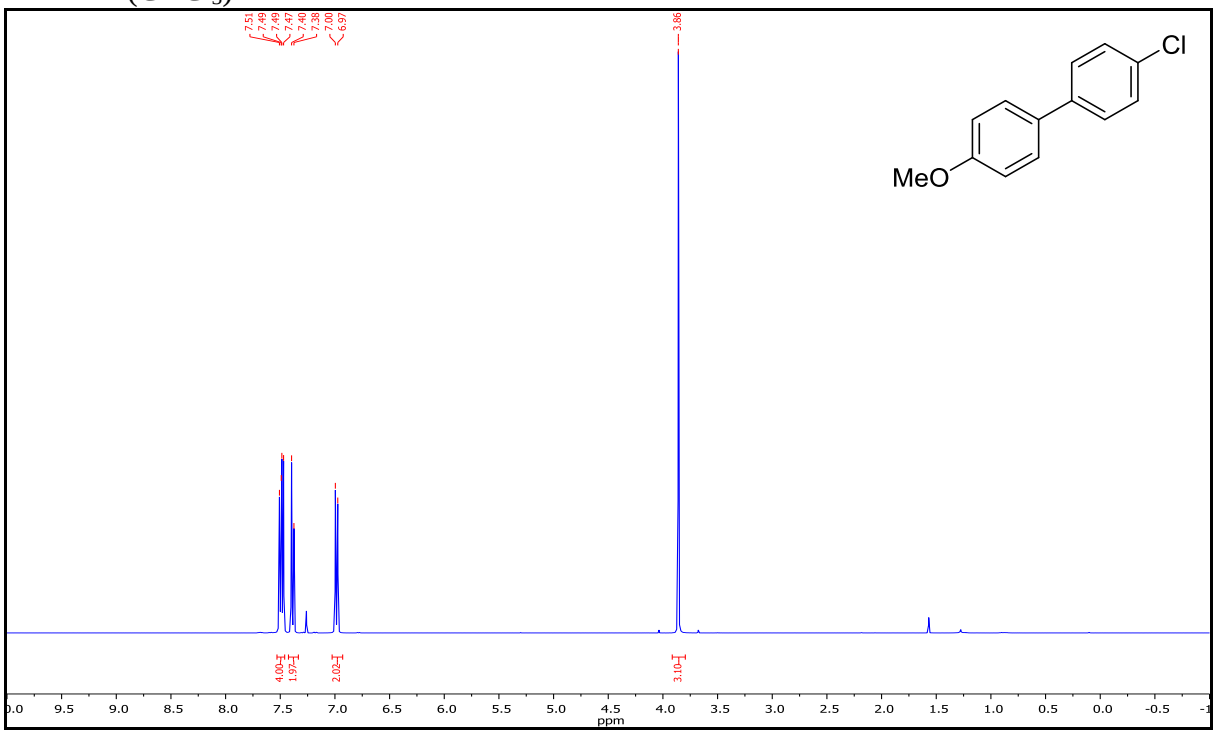


^{13}C NMR ($CDCl_3$)

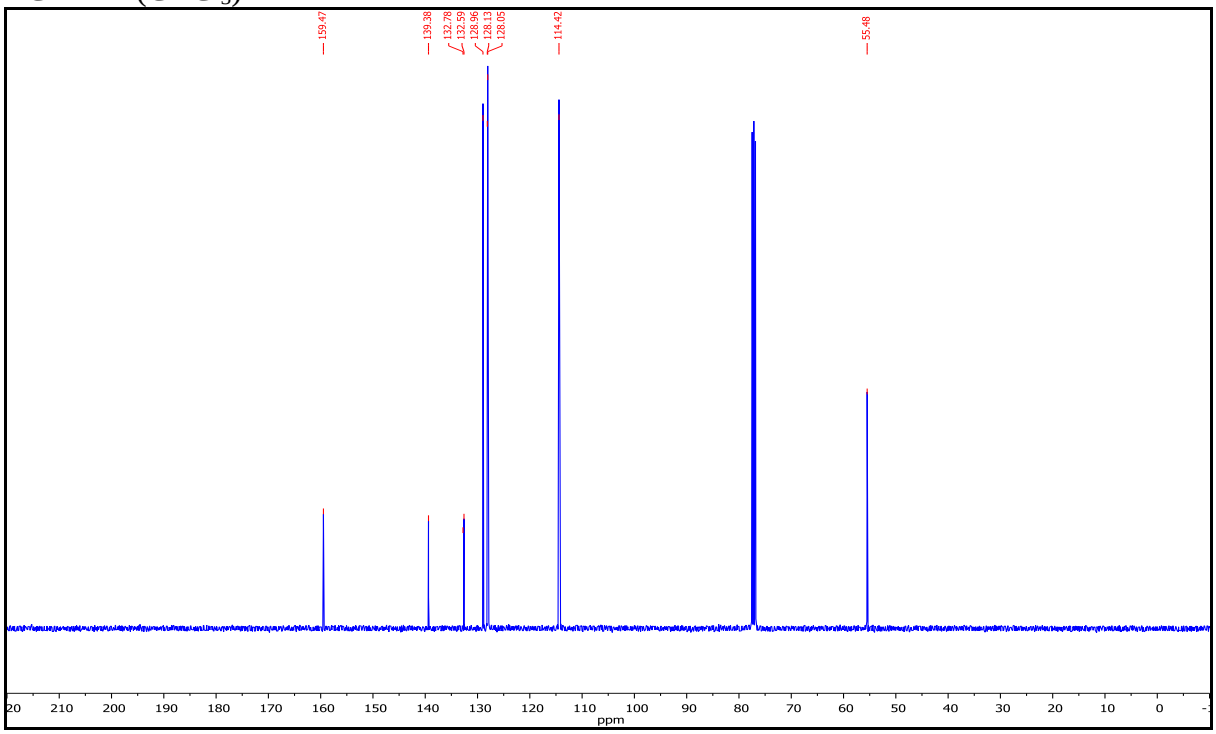


4-chloro-4'-methoxy-1,1'-biphenyl (3e)

^{1}H NMR ($CDCl_3$)

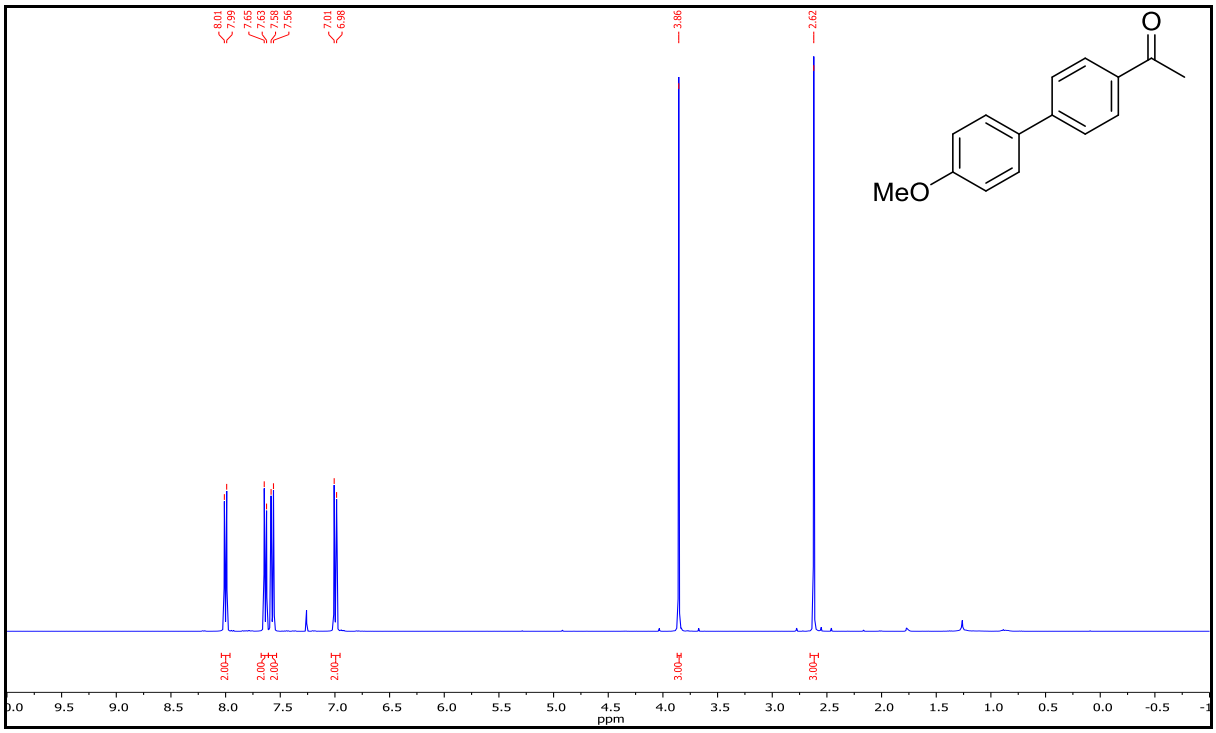


^{13}C NMR ($CDCl_3$)

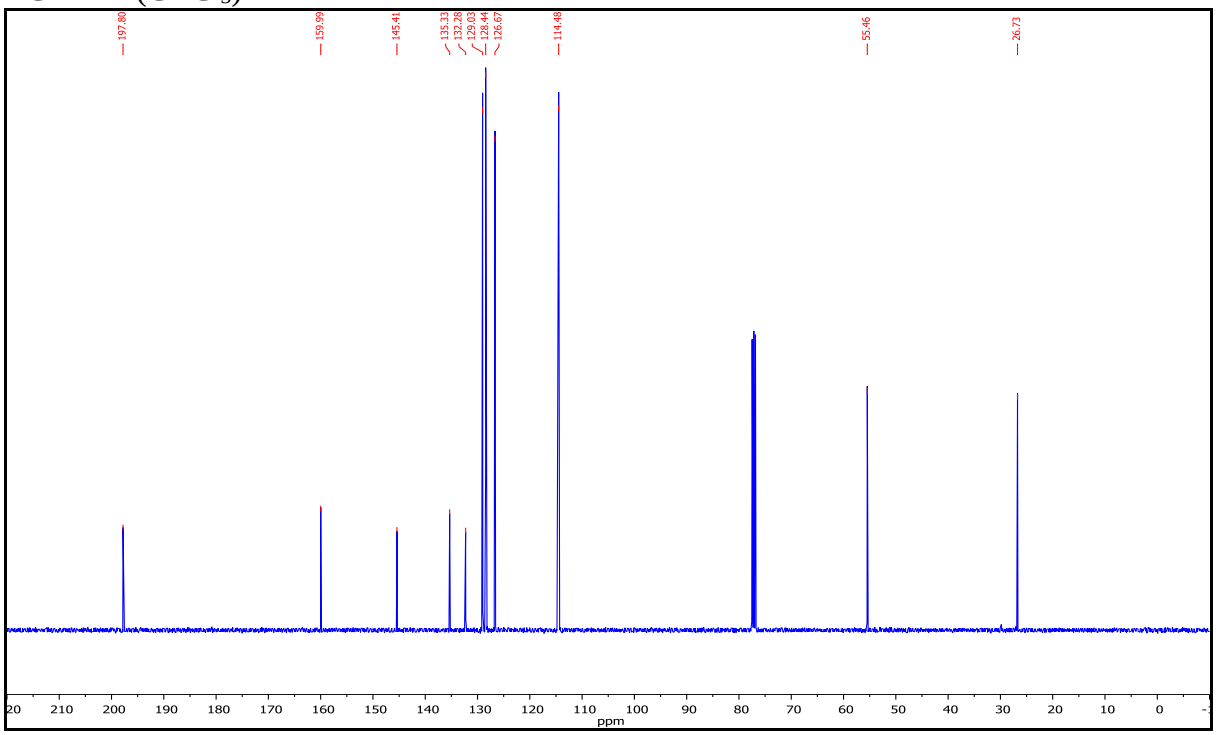


1-(4'-methoxy-[1,1'-biphenyl]-4-yl)ethan-1-one (3f)

^{1}H NMR ($CDCl_3$)

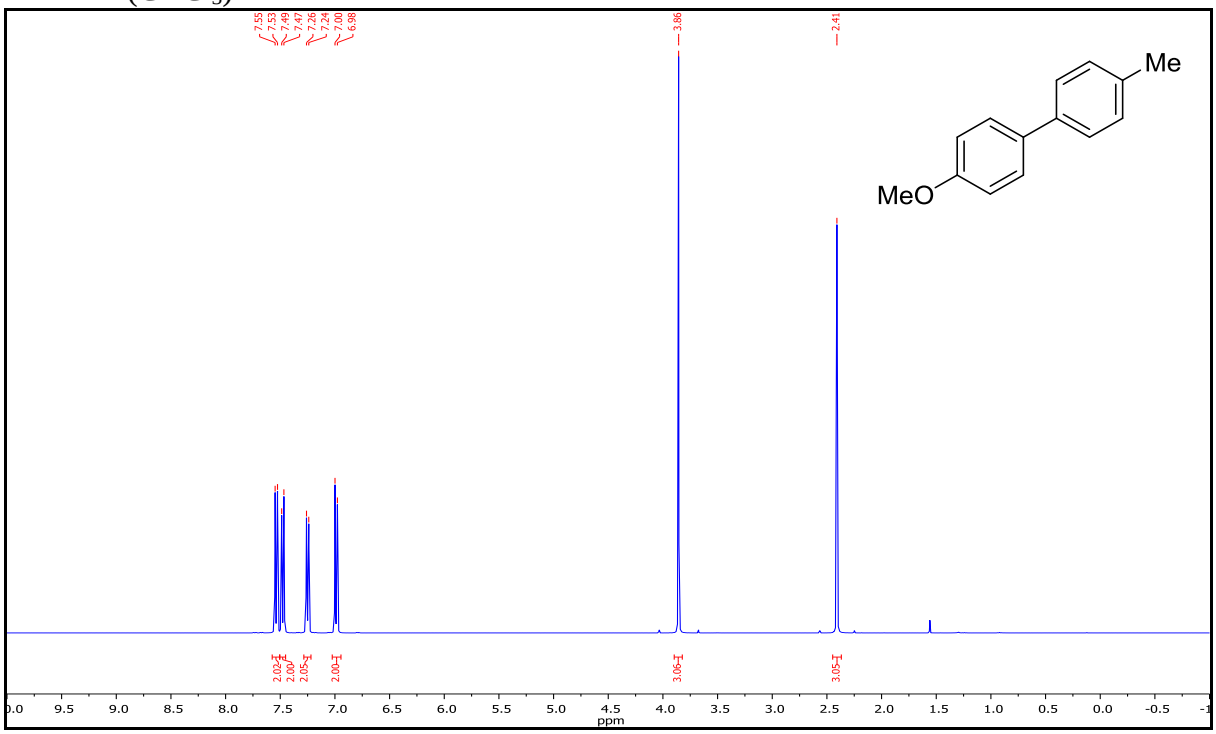


^{13}C NMR ($CDCl_3$)

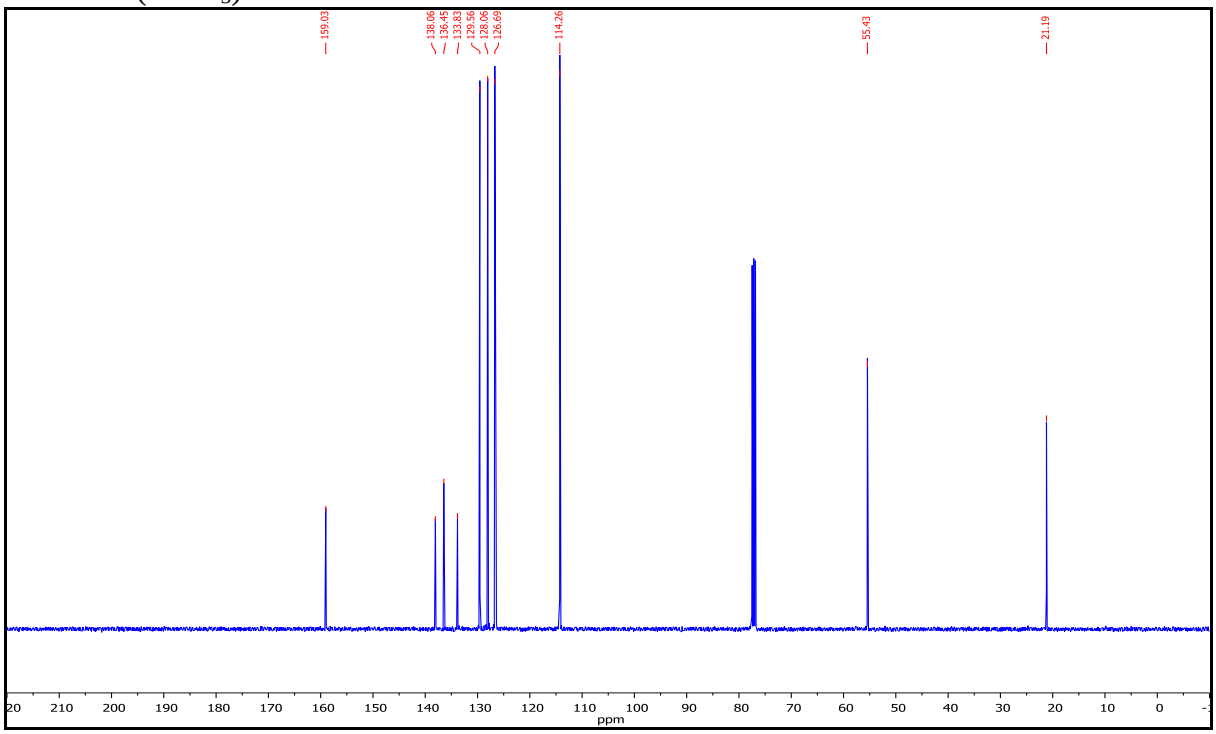


4-methoxy-4'-methyl-1,1'-biphenyl (3g)

^{1}H NMR ($CDCl_3$)

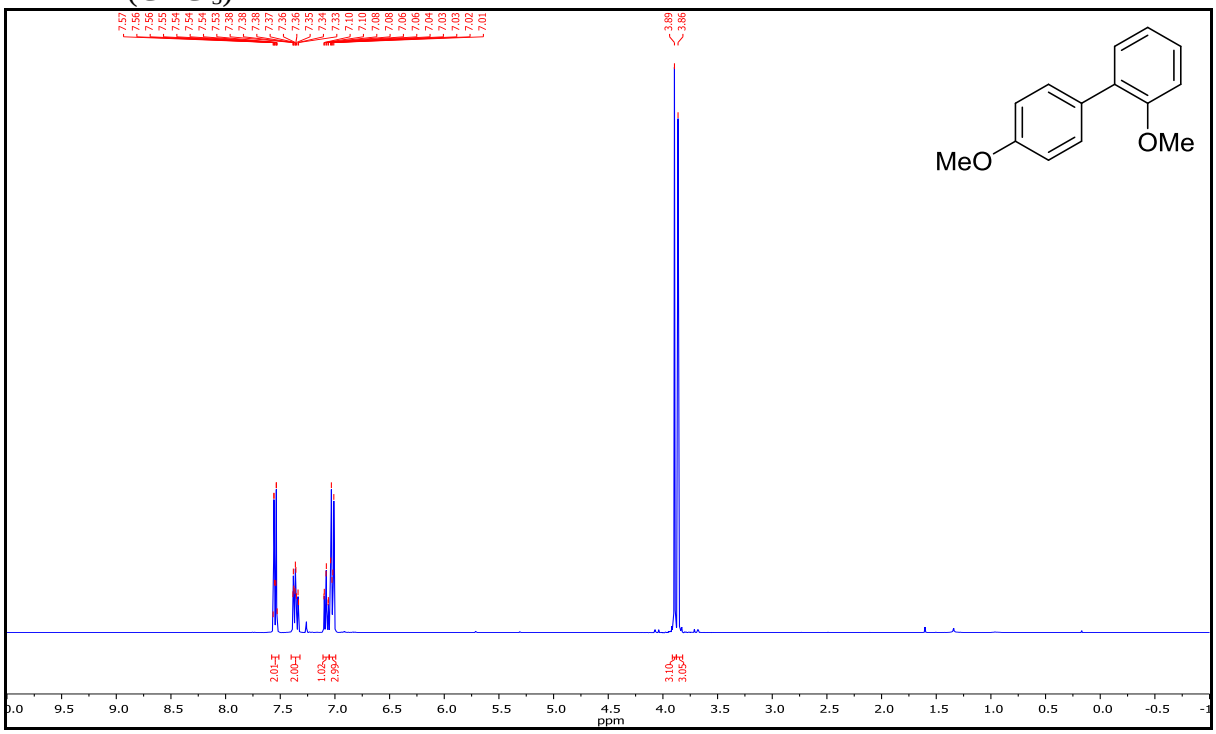


^{13}C NMR ($CDCl_3$)

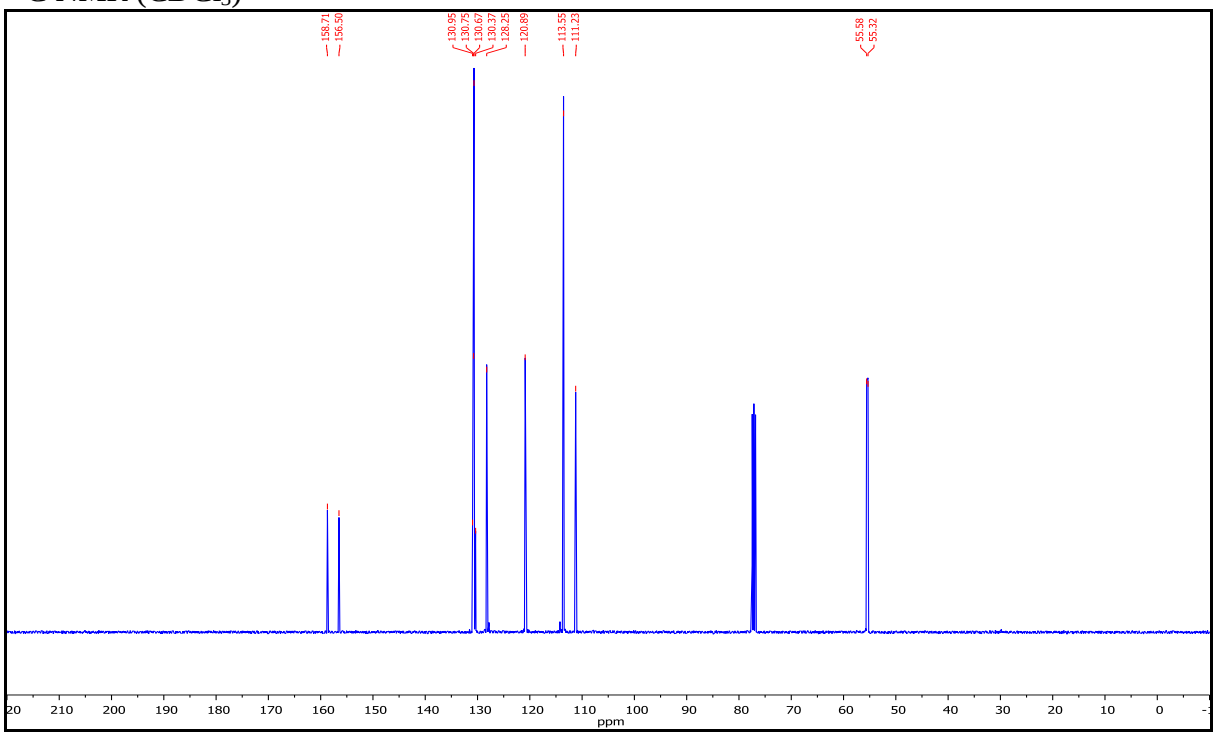


2,4'-dimethoxy-1,1'-biphenyl (3h)

^{1}H NMR ($CDCl_3$)

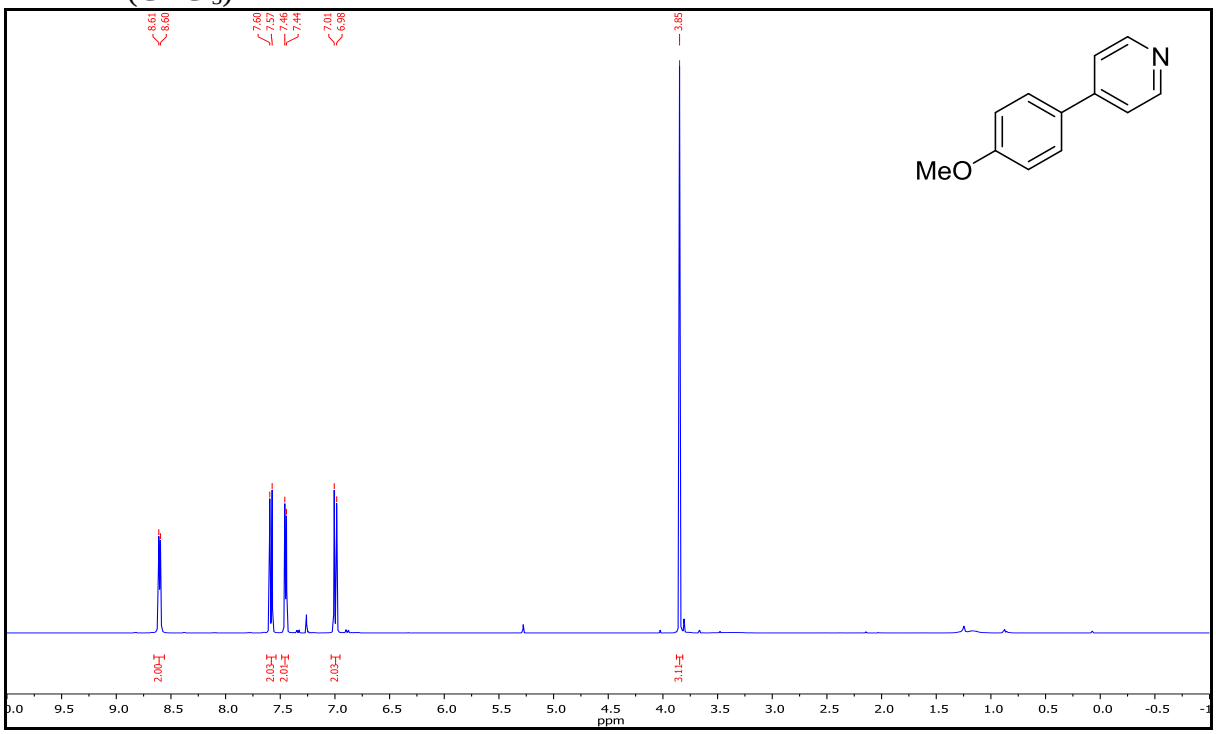


^{13}C NMR ($CDCl_3$)

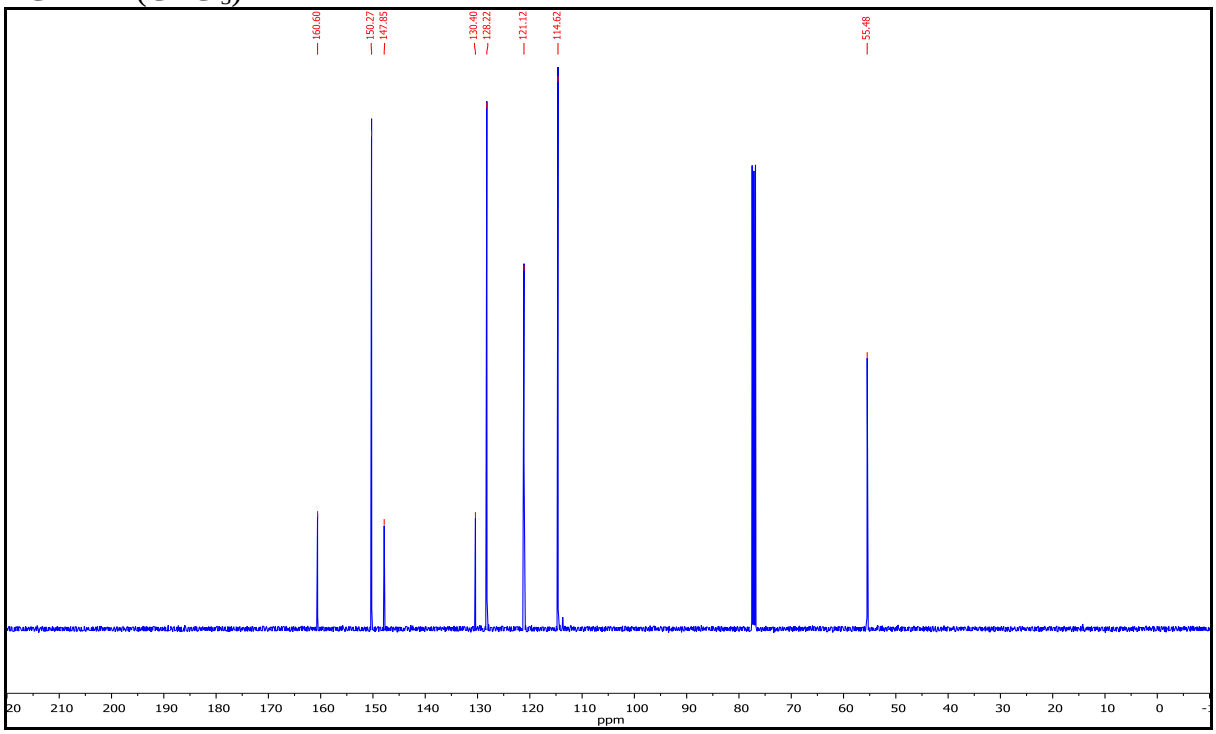


4-(4-methoxyphenyl)pyridine (3i)

^{1}H NMR ($CDCl_3$)

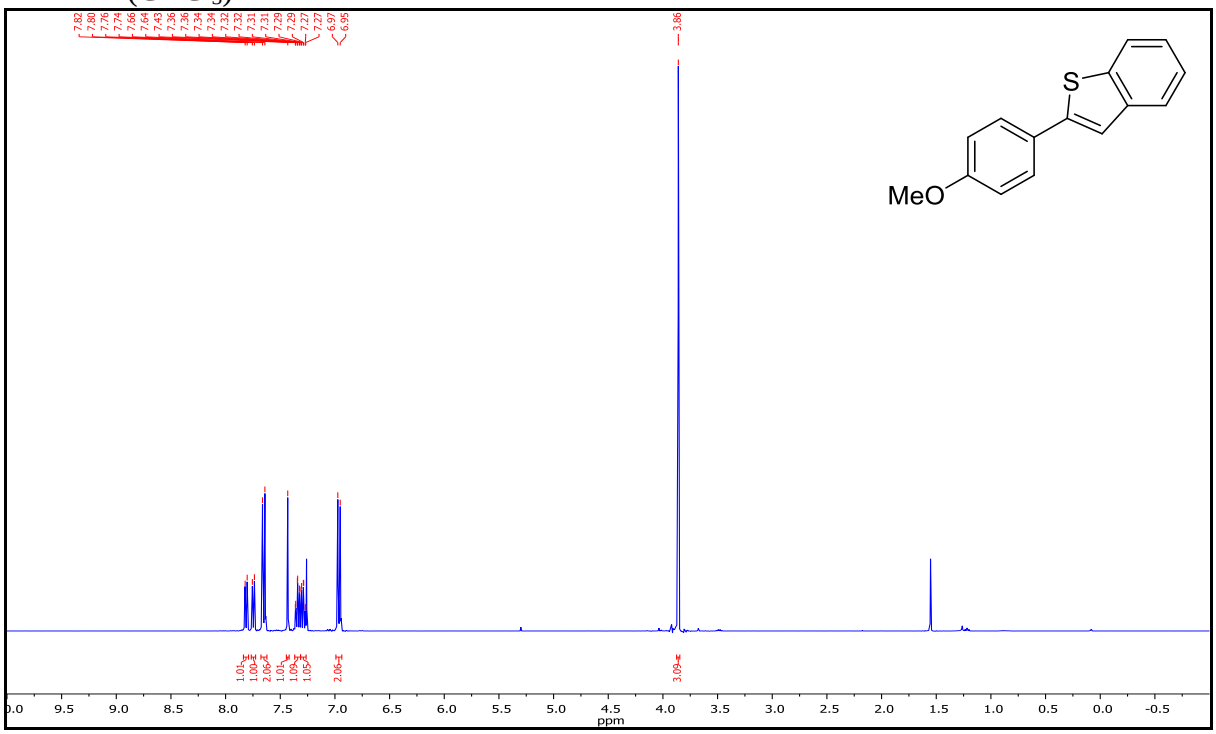


^{13}C NMR ($CDCl_3$)

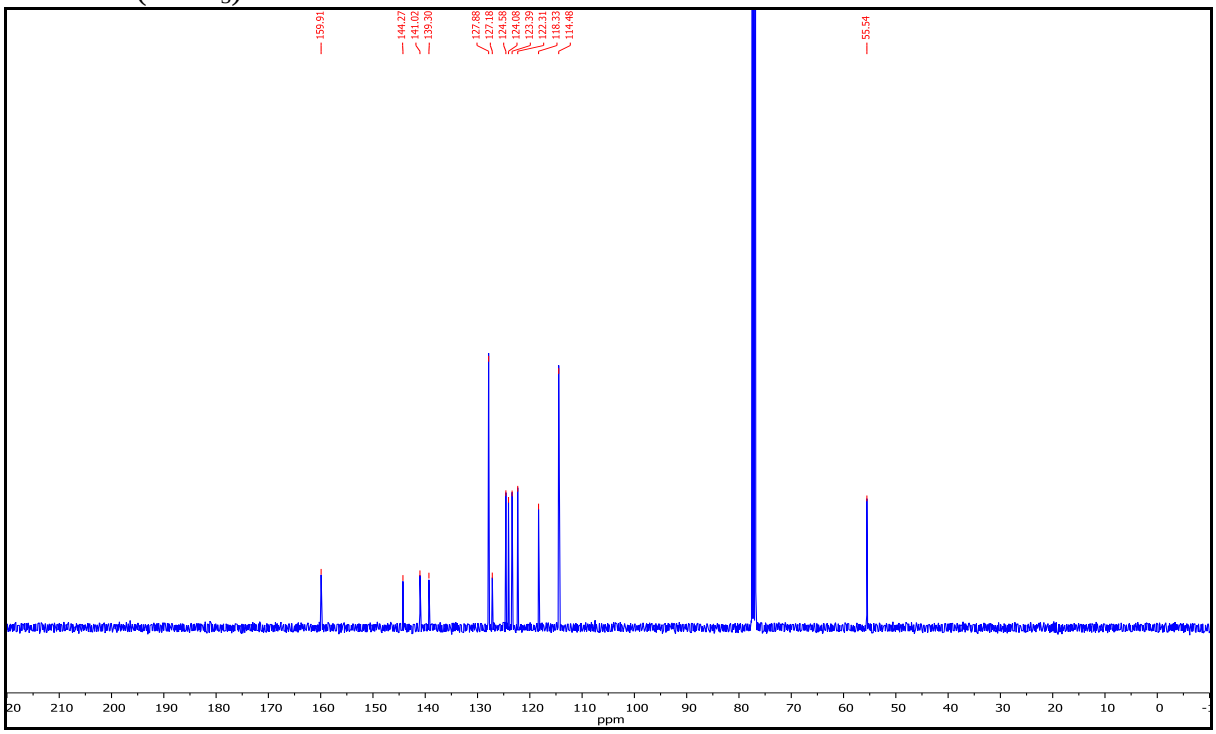


2-(4-methoxyphenyl)benzo[b]thiophene (3j)

^{1}H NMR ($CDCl_3$)

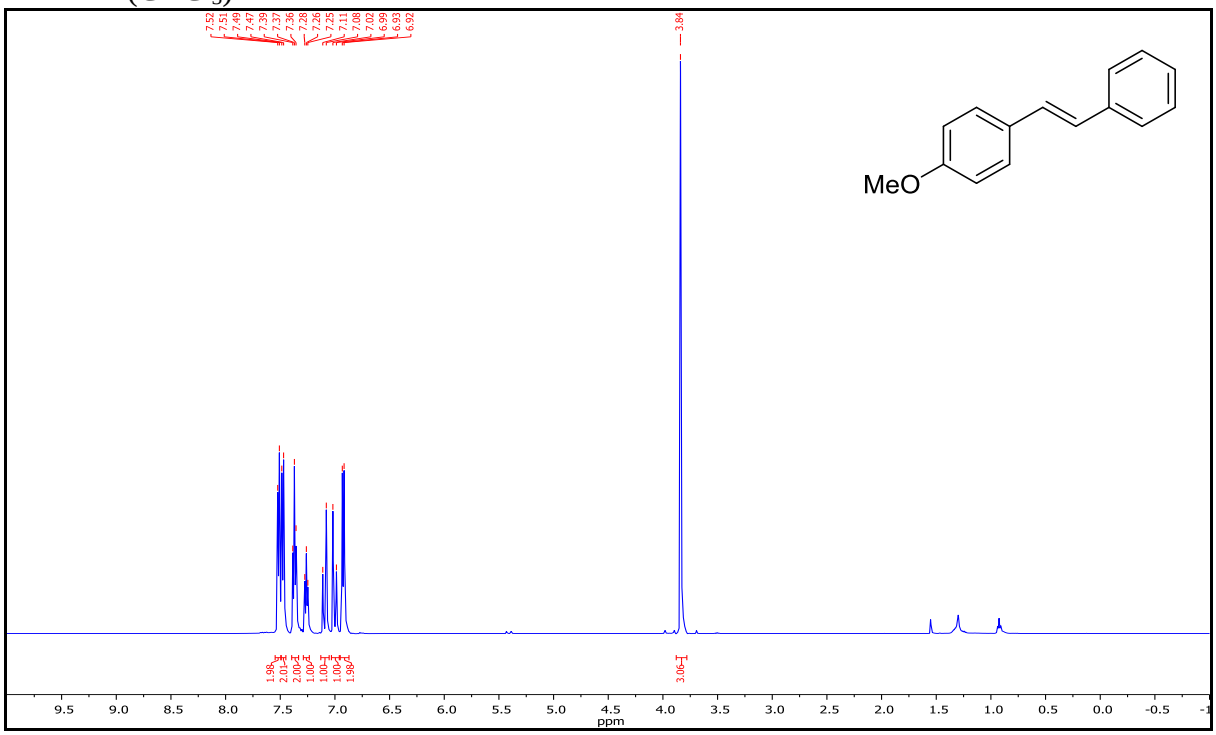


^{13}C NMR ($CDCl_3$)

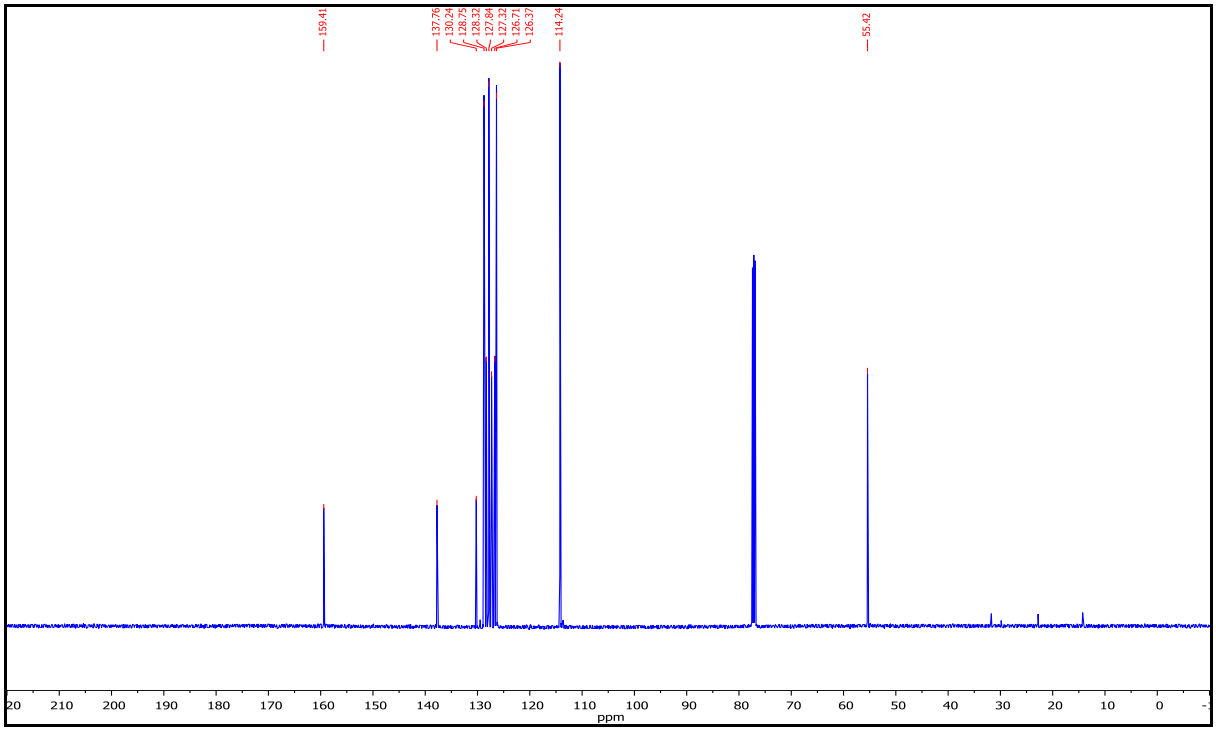


(E)-1-methoxy-4-styrylbenzene (3k)

^{1}H NMR ($CDCl_3$)

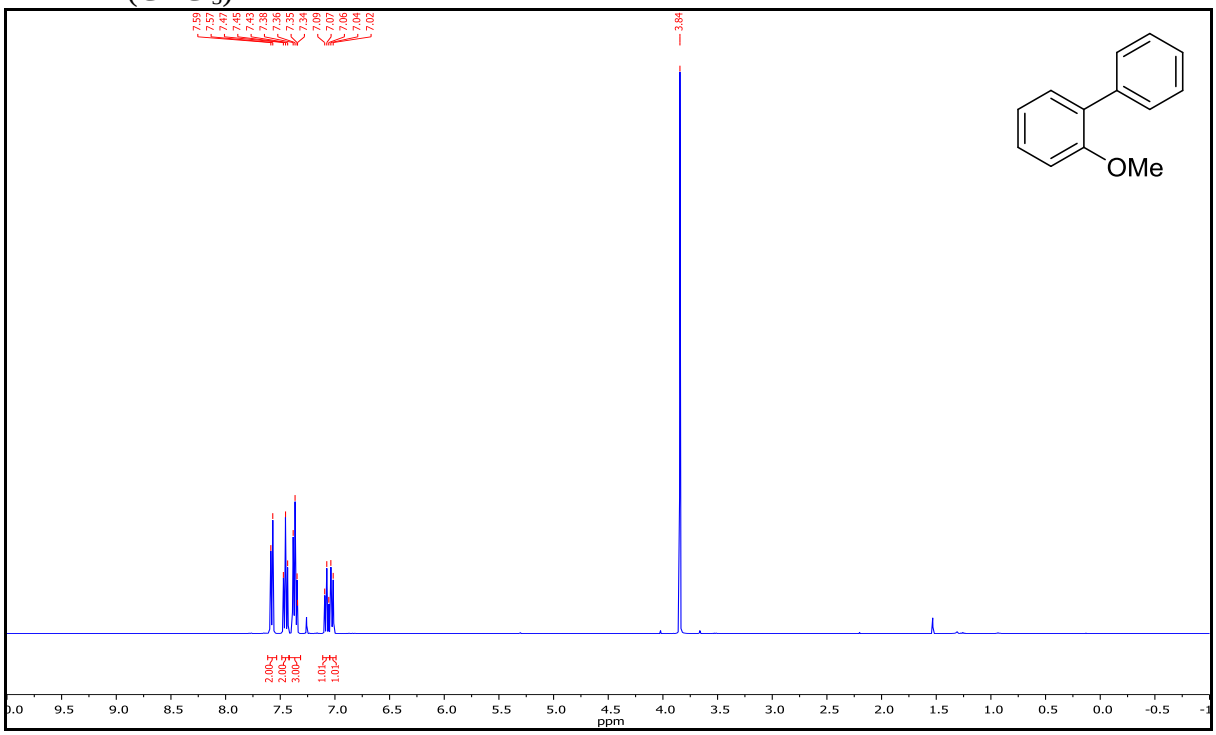


^{13}C NMR ($CDCl_3$)

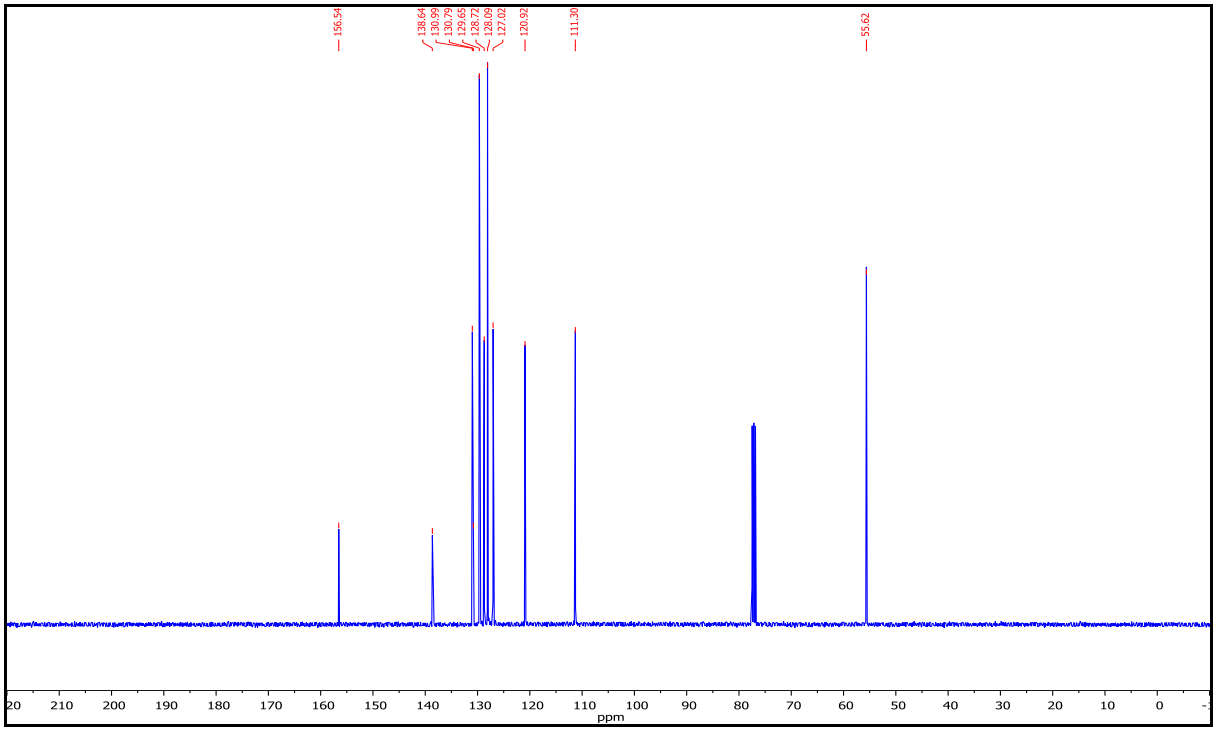


2-methoxy-1,1'-biphenyl (3l)

^{1}H NMR ($CDCl_3$)

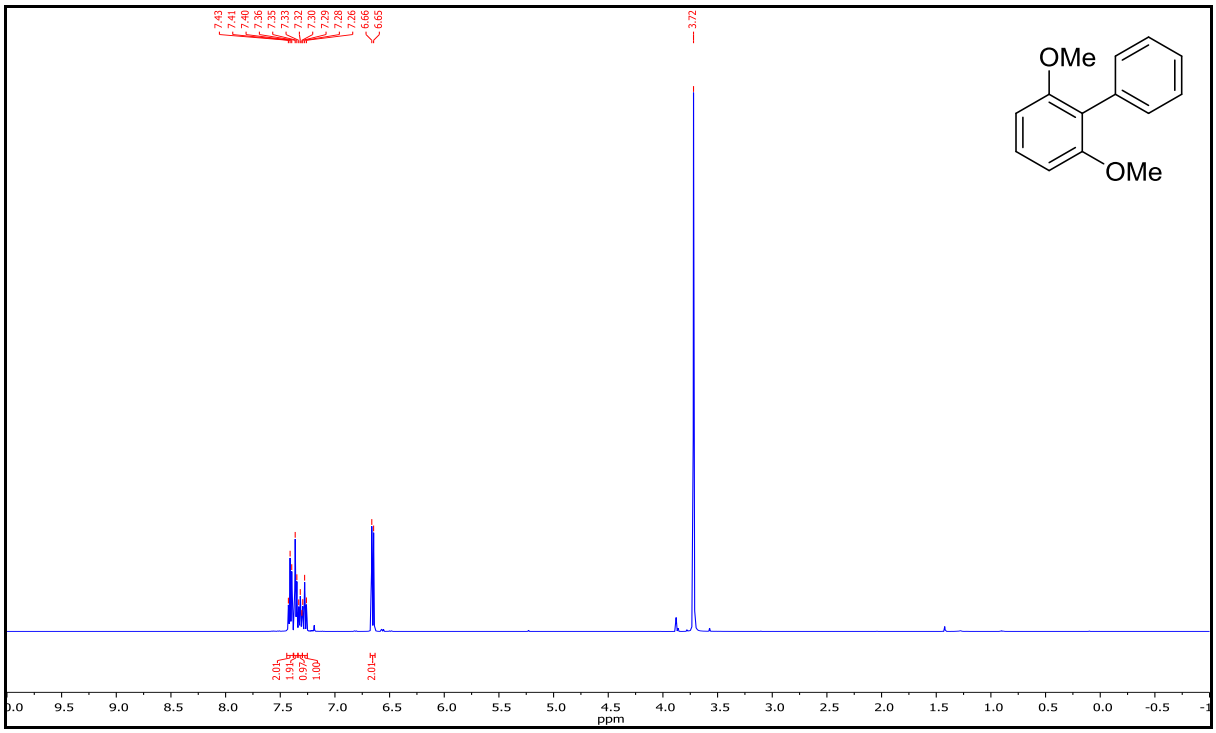


^{13}C NMR ($CDCl_3$)

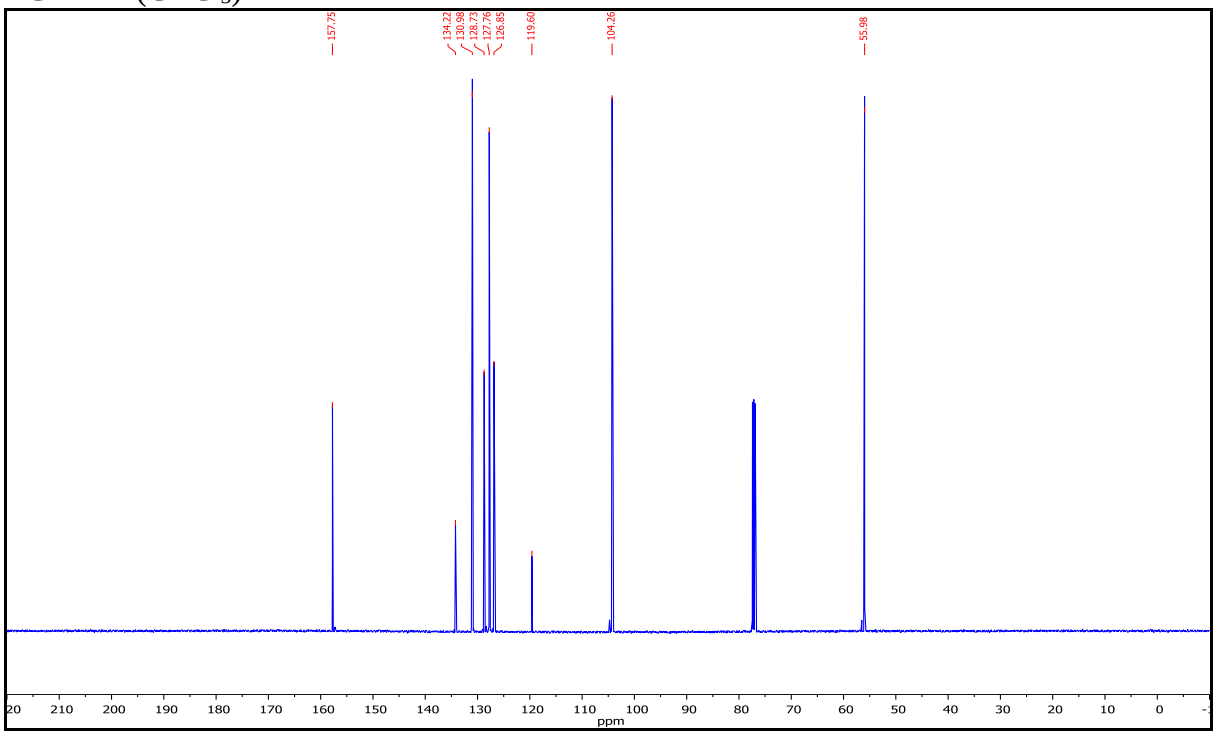


2,6-dimethoxy-1,1'-biphenyl (3m)

^{1}H NMR ($CDCl_3$)

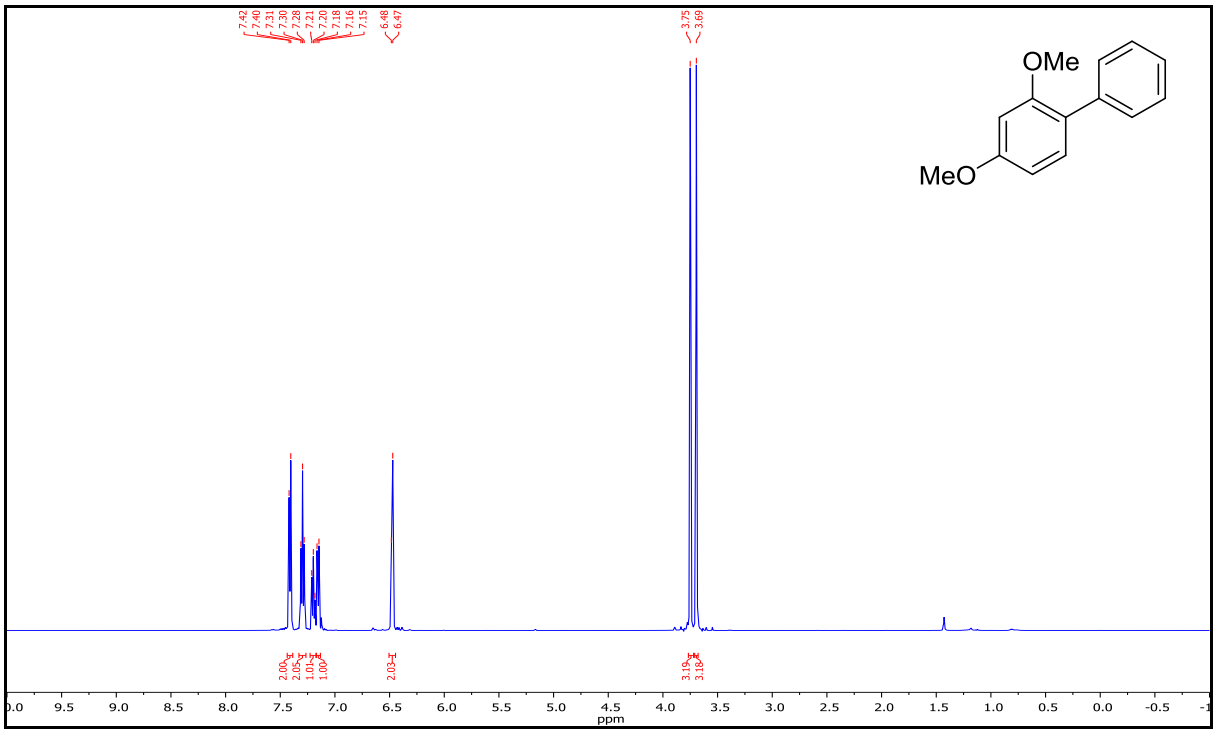


^{13}C NMR ($CDCl_3$)

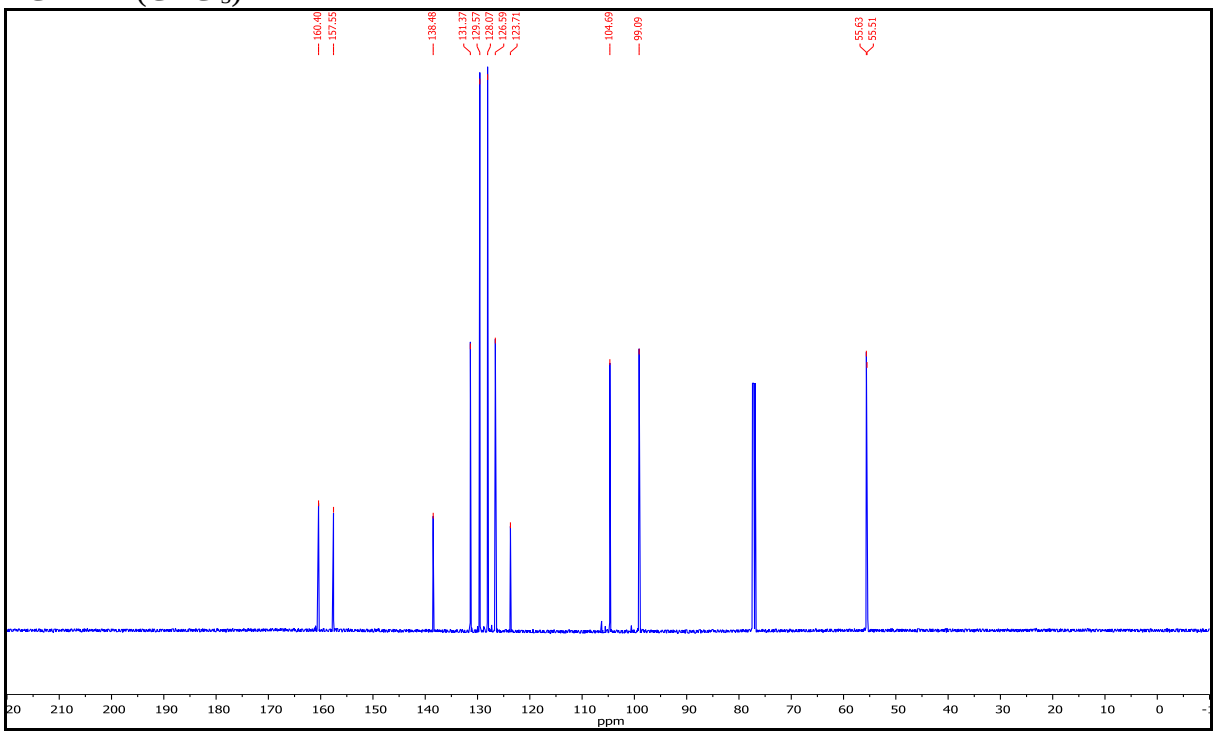


2,4-dimethoxy-1,1'-biphenyl (3n)

^{1}H NMR ($CDCl_3$)

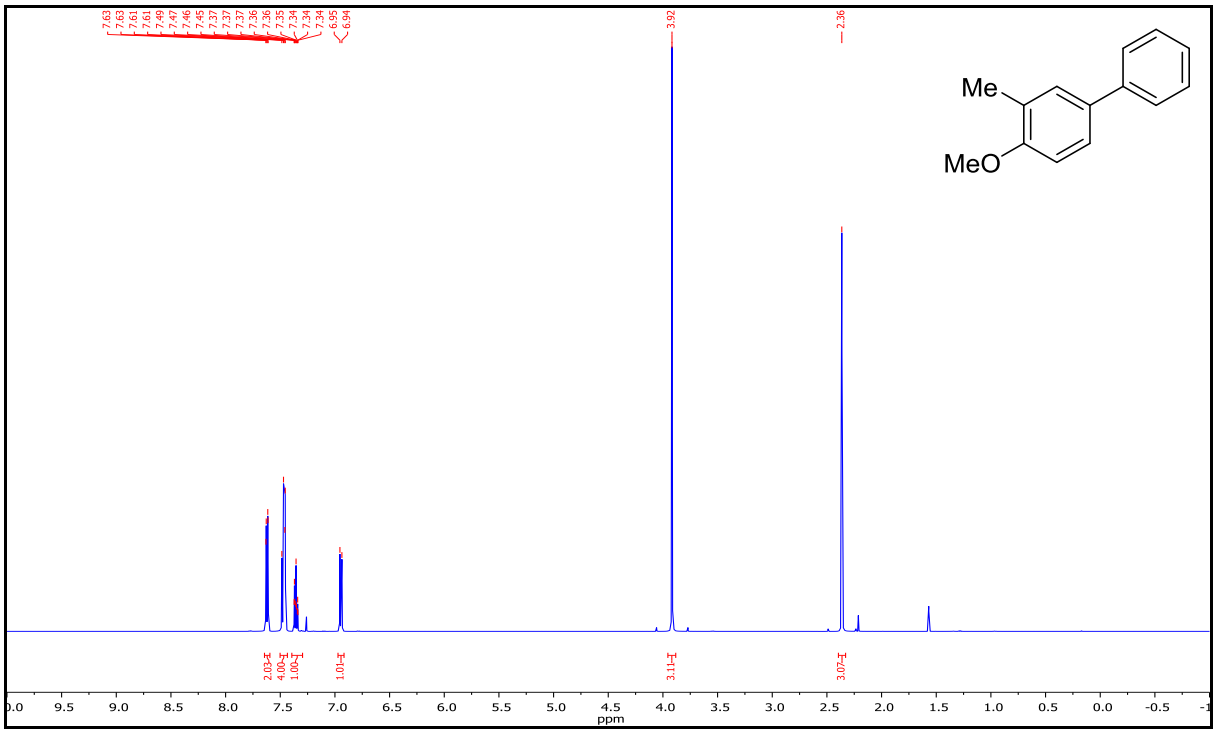


^{13}C NMR ($CDCl_3$)

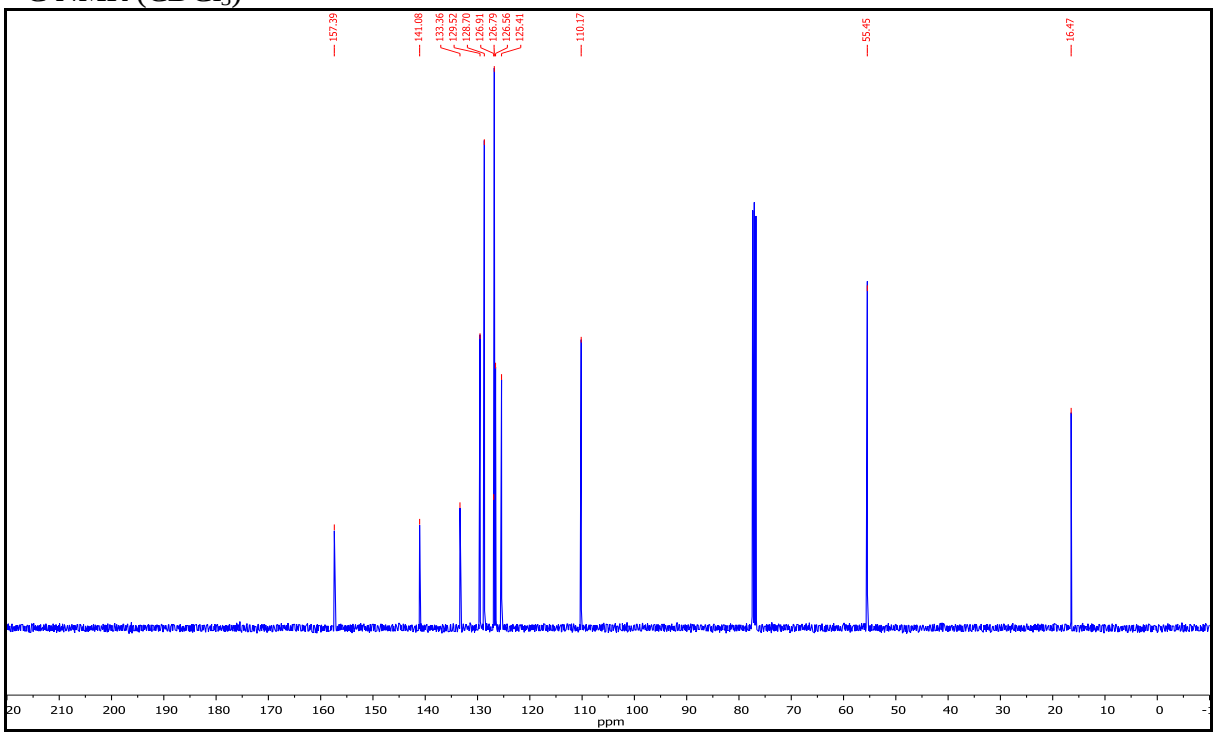


4-methoxy-3-methyl-1,1'-biphenyl (3o)

^{1}H NMR ($CDCl_3$)

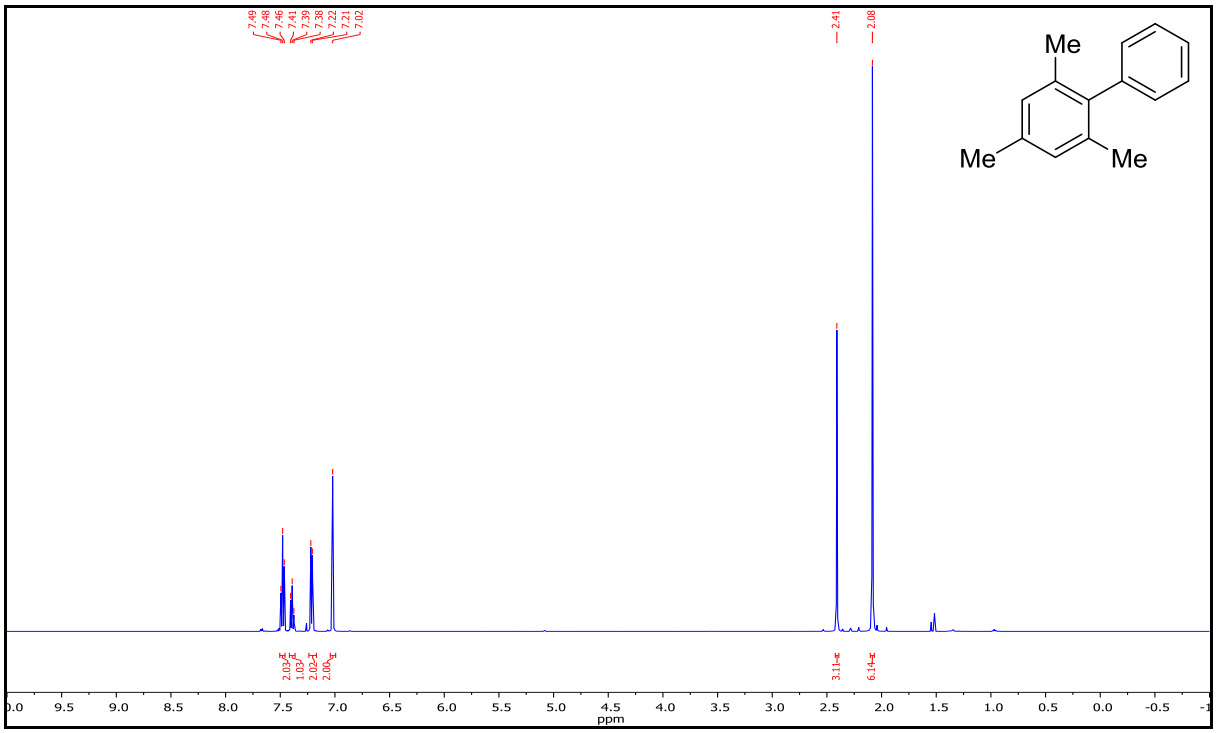


^{13}C NMR ($CDCl_3$)

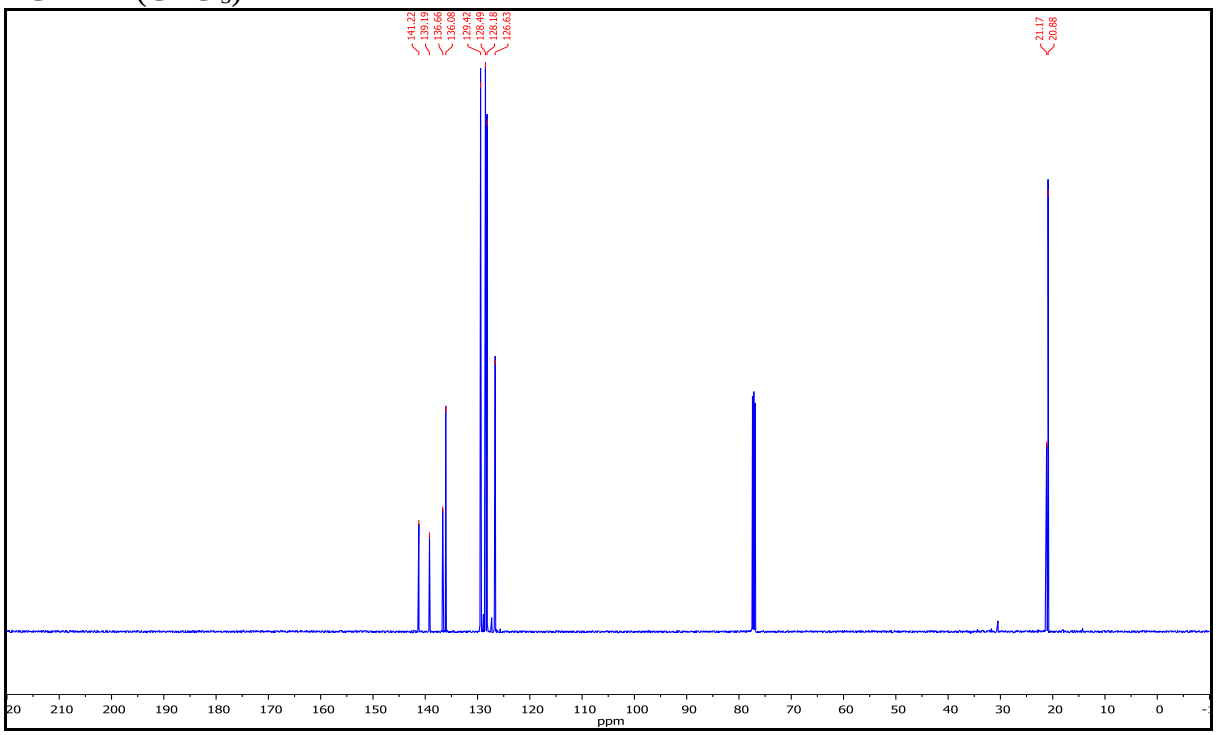


2,4,6-trimethyl-1,1'-biphenyl (3p)

^{1}H NMR ($CDCl_3$)

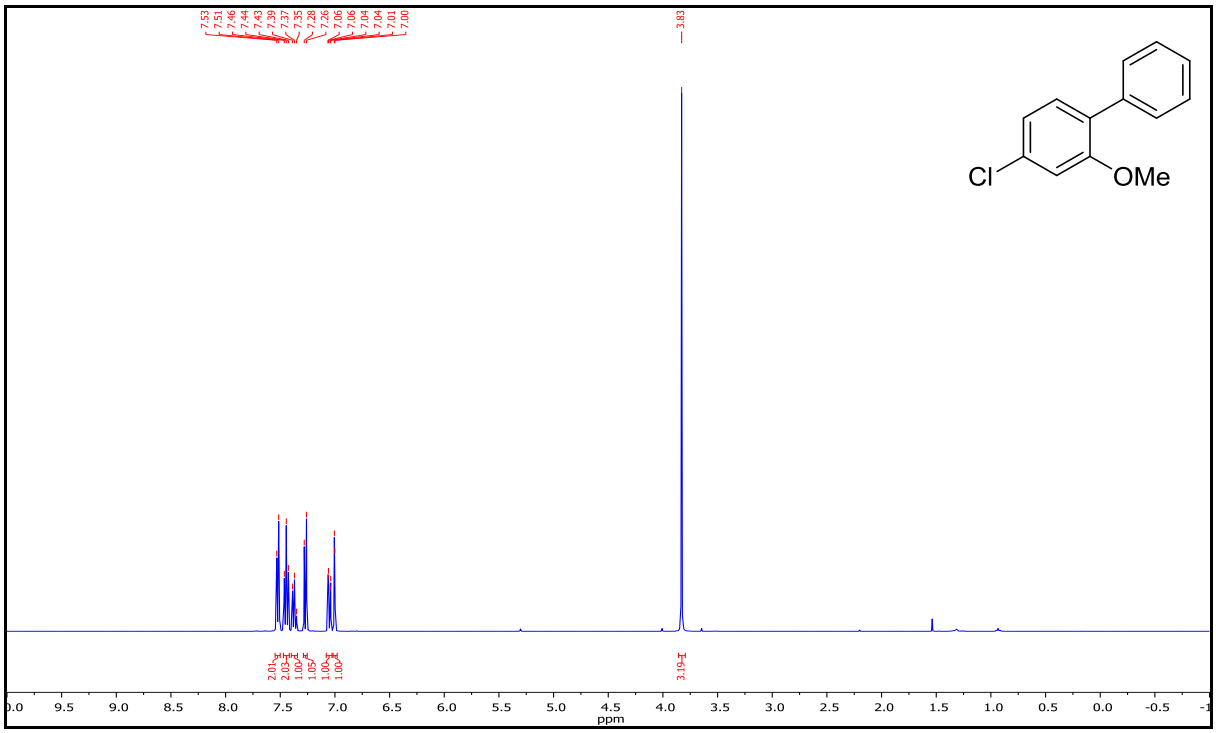


^{13}C NMR ($CDCl_3$)

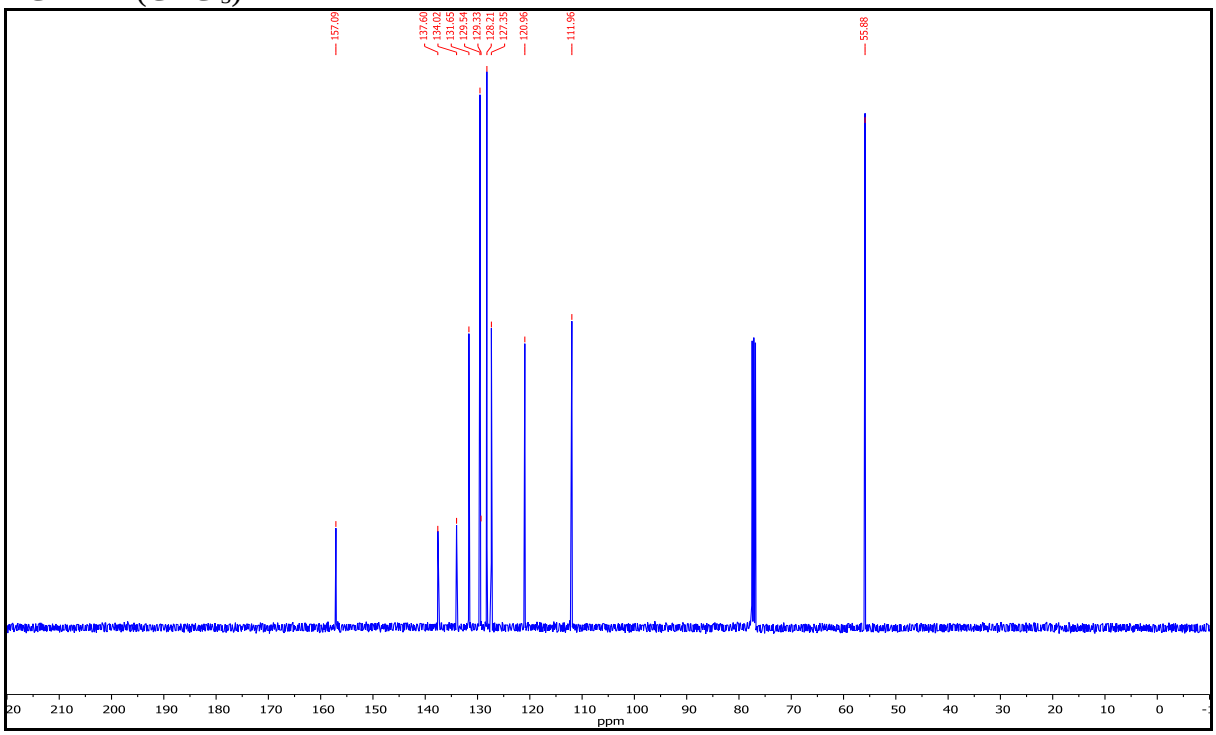


4-chloro-2-methoxy-1,1'-biphenyl (3q)

^{1}H NMR ($CDCl_3$)

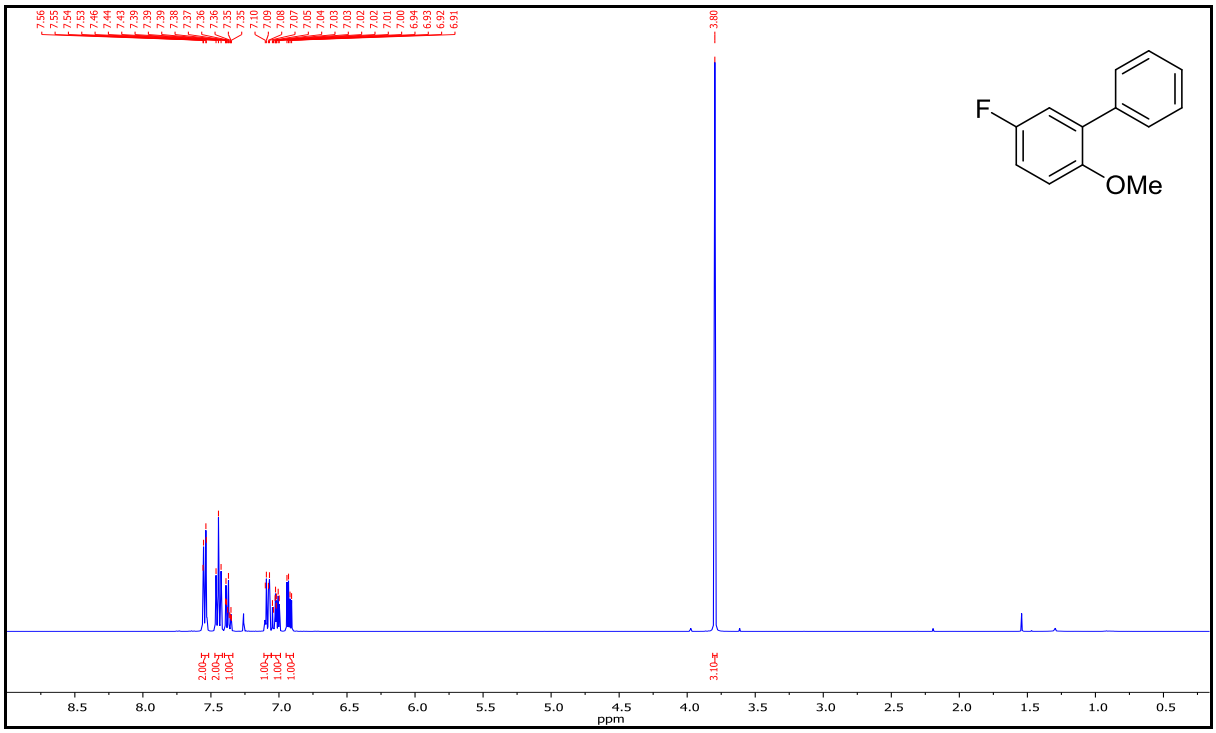


^{13}C NMR ($CDCl_3$)

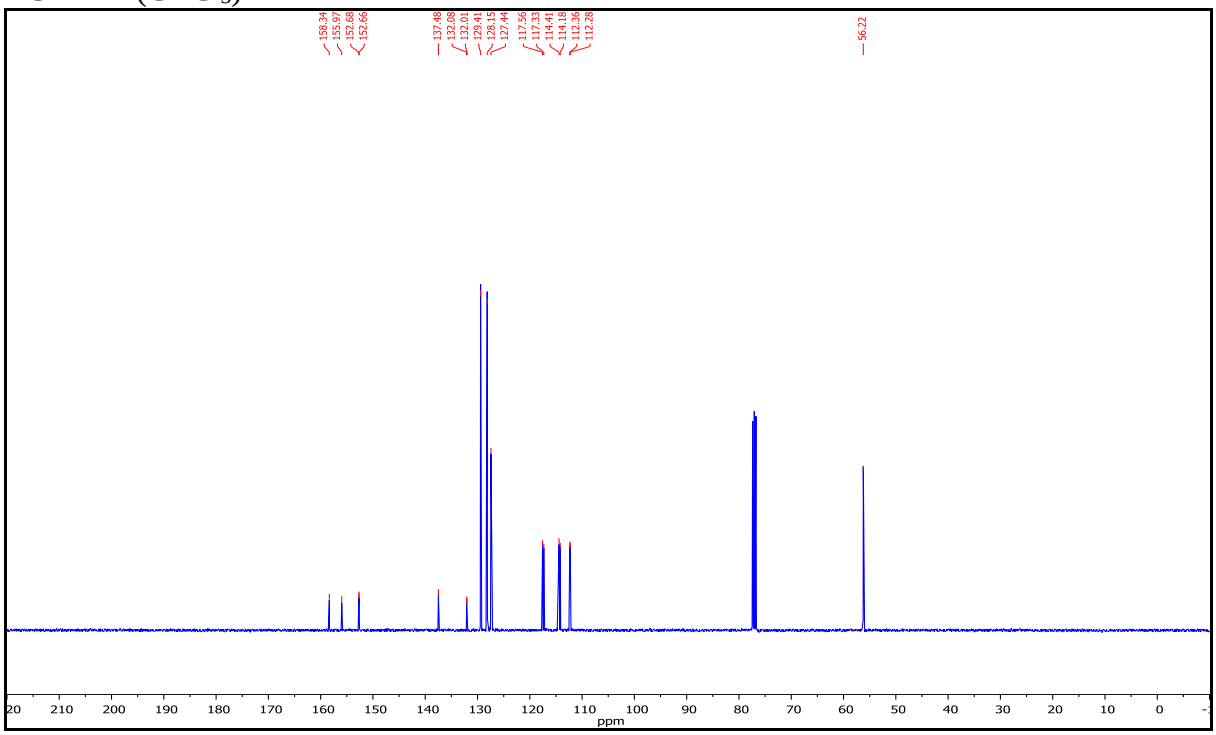


5-fluoro-2-methoxy-1,1'-biphenyl (3r)

^{1}H NMR ($CDCl_3$)

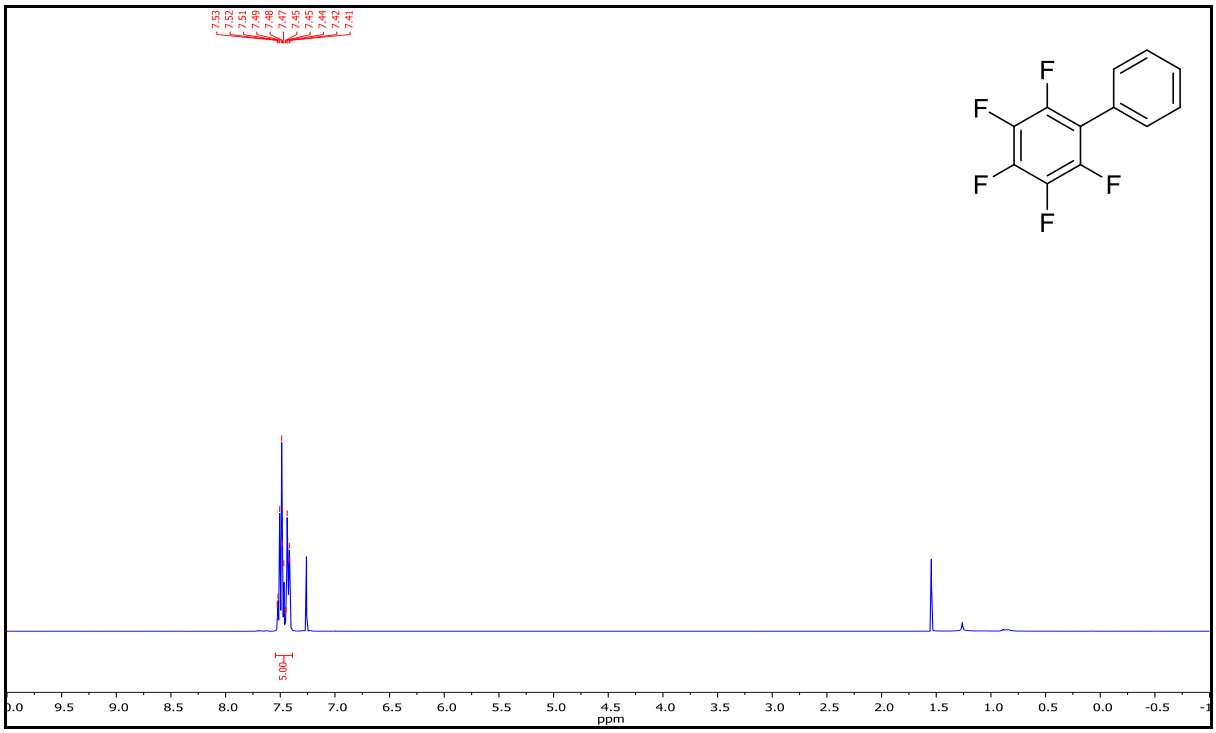


^{13}C NMR ($CDCl_3$)

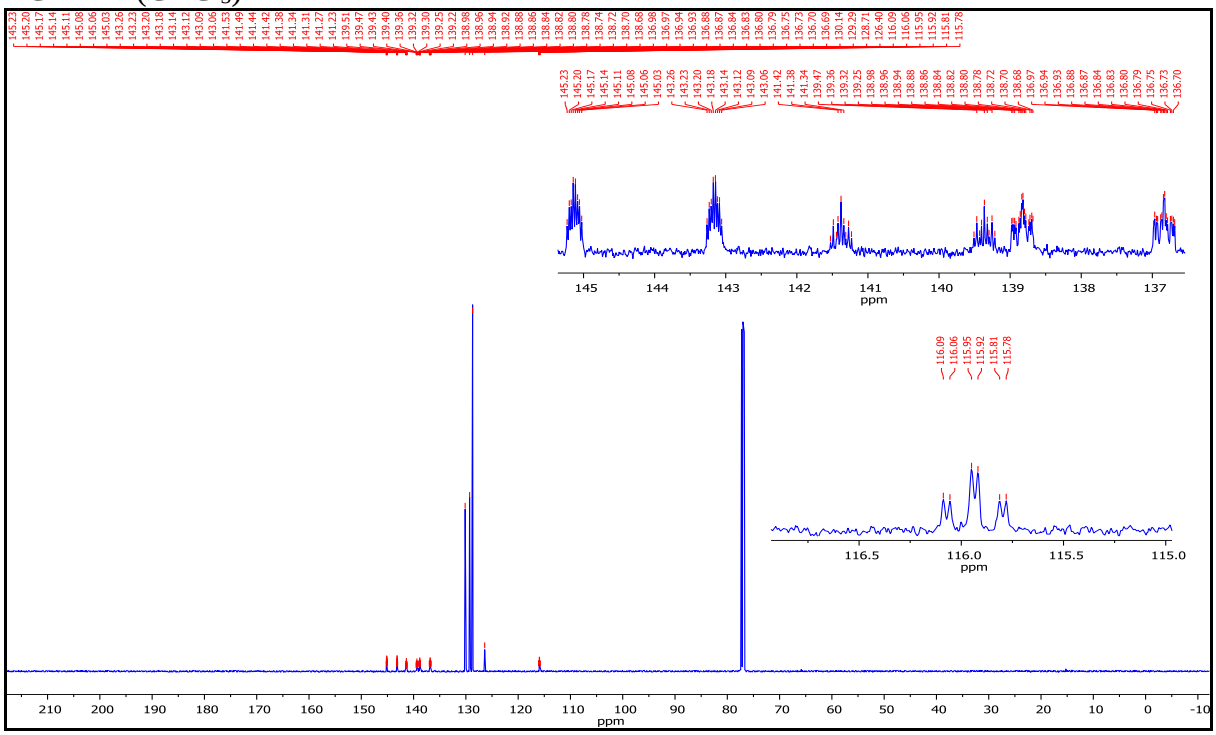


2,3,4,5,6-pentafluoro-1,1'-biphenyl (3s)

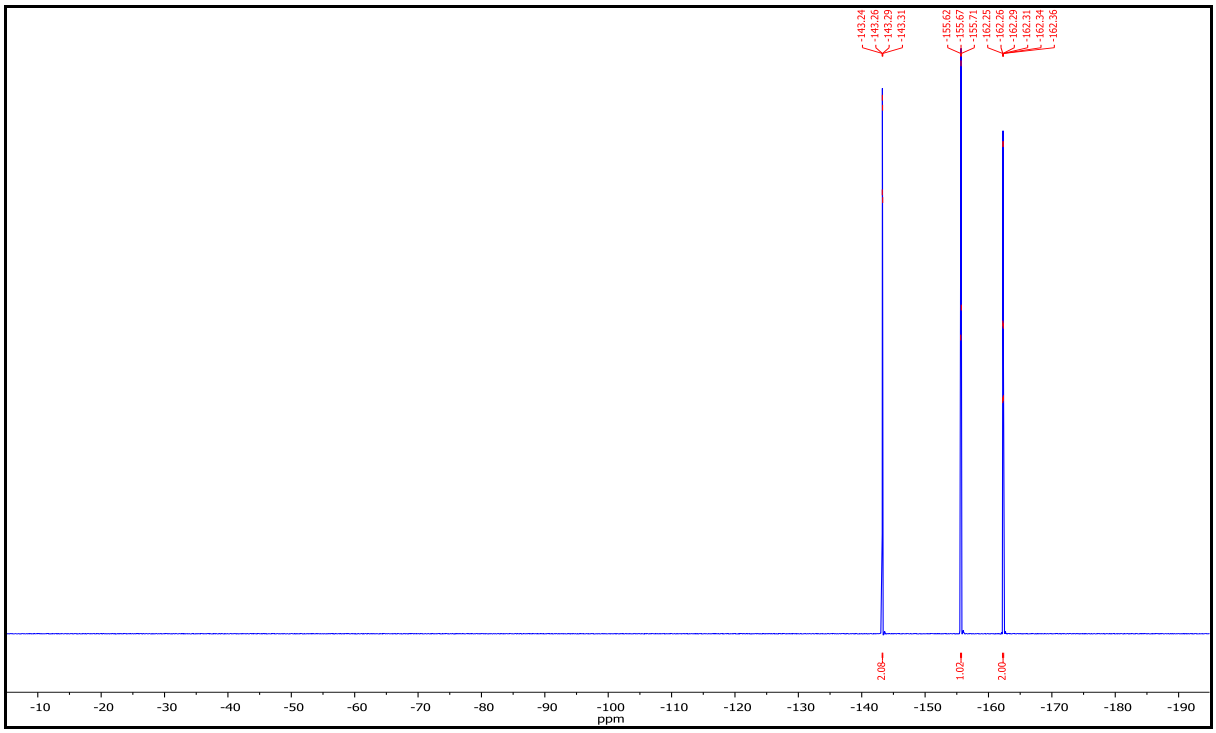
^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

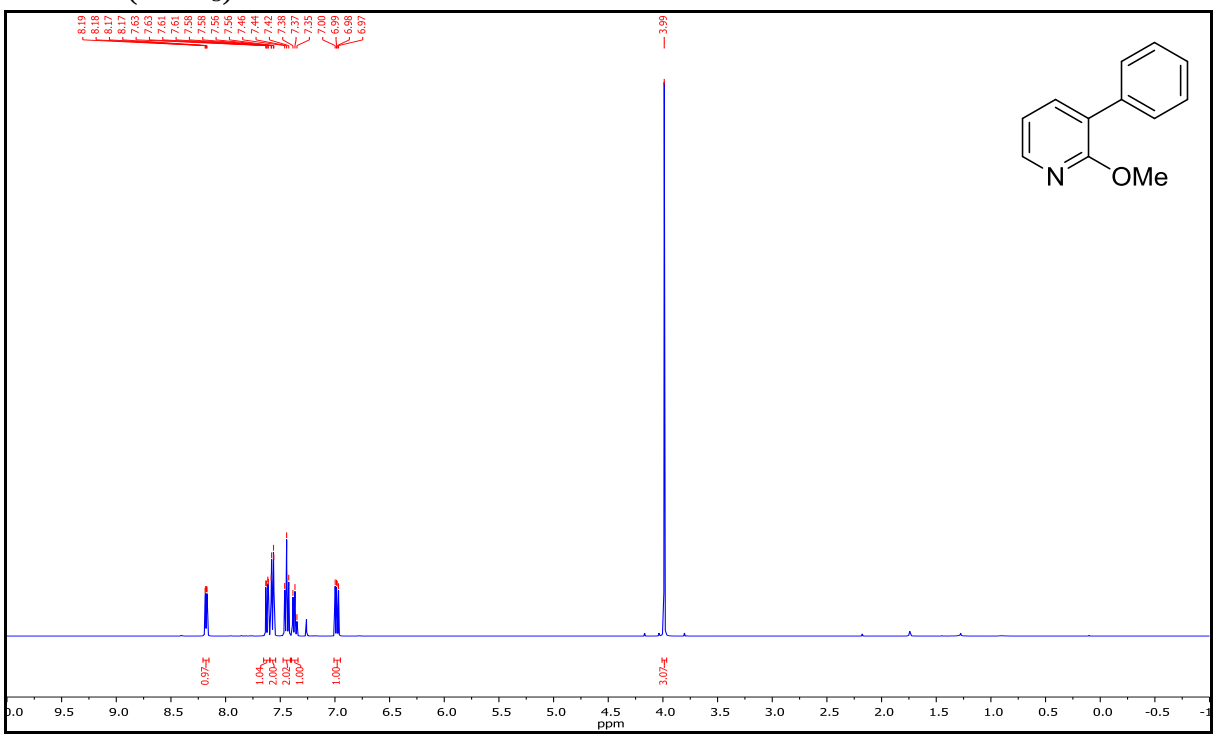


^{19}F NMR ($CDCl_3$)

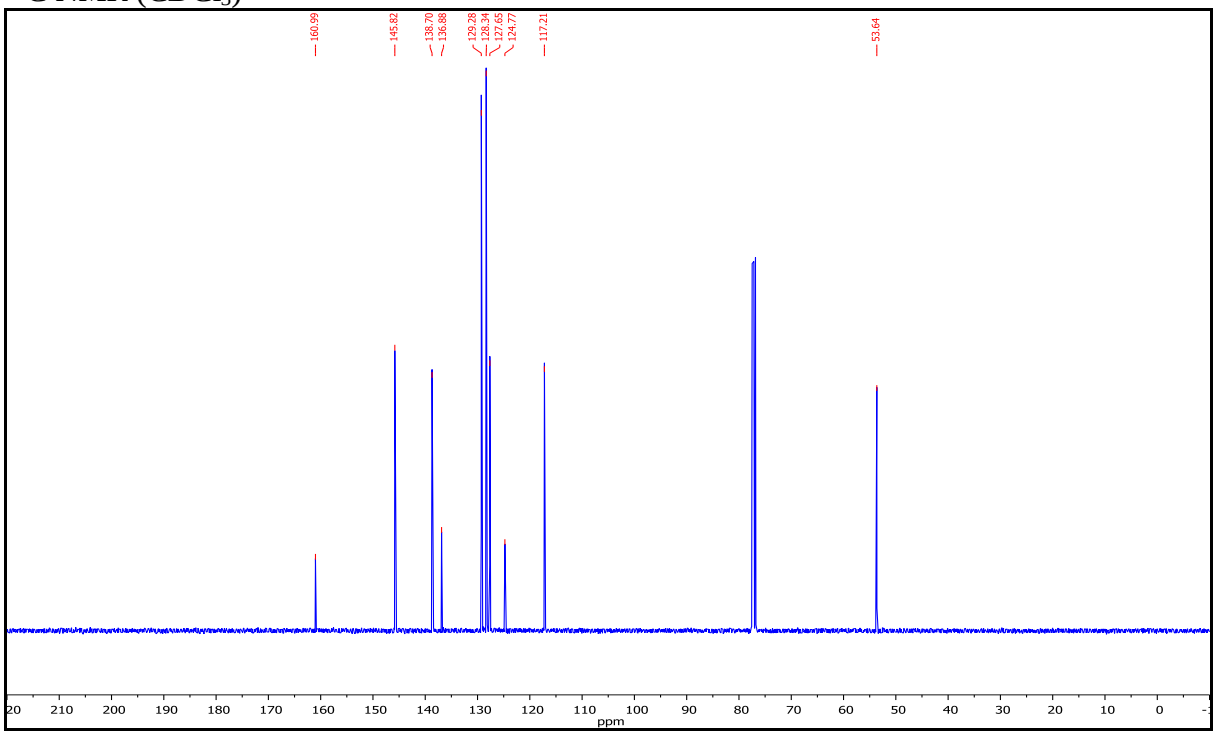


2-methoxy-3-phenylpyridine (3t)

^{1}H NMR ($CDCl_3$)

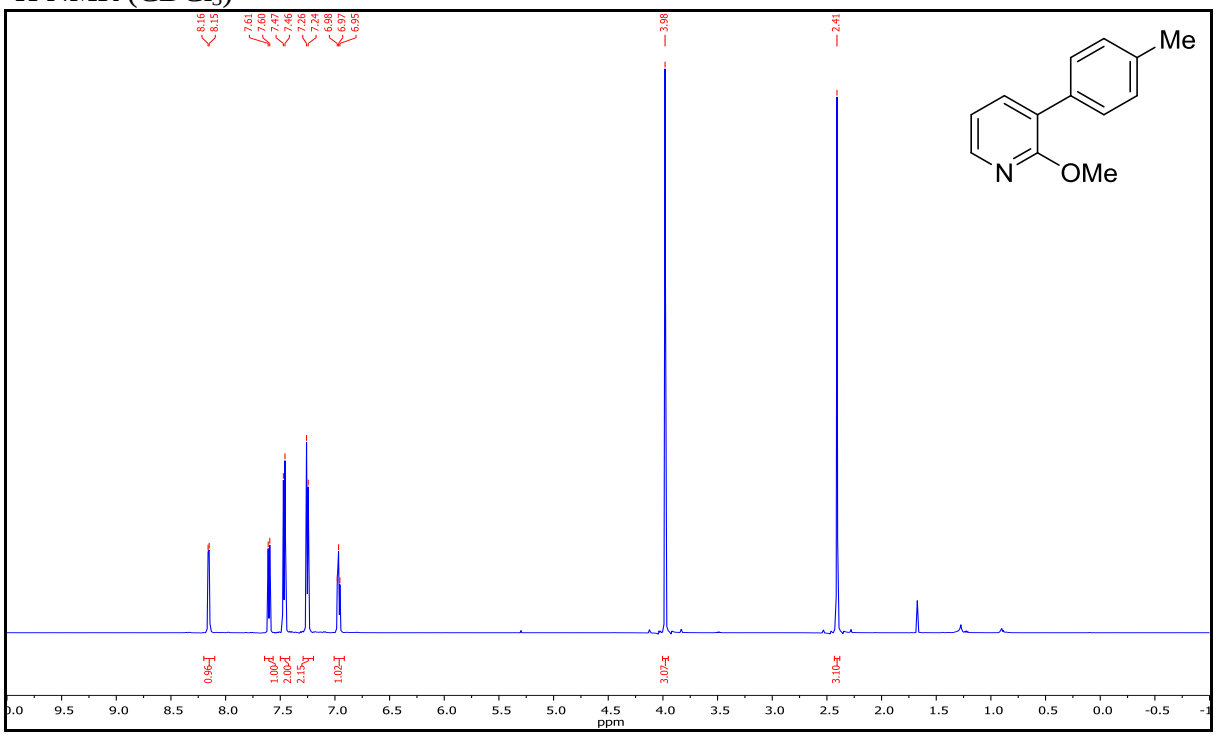


^{13}C NMR ($CDCl_3$)

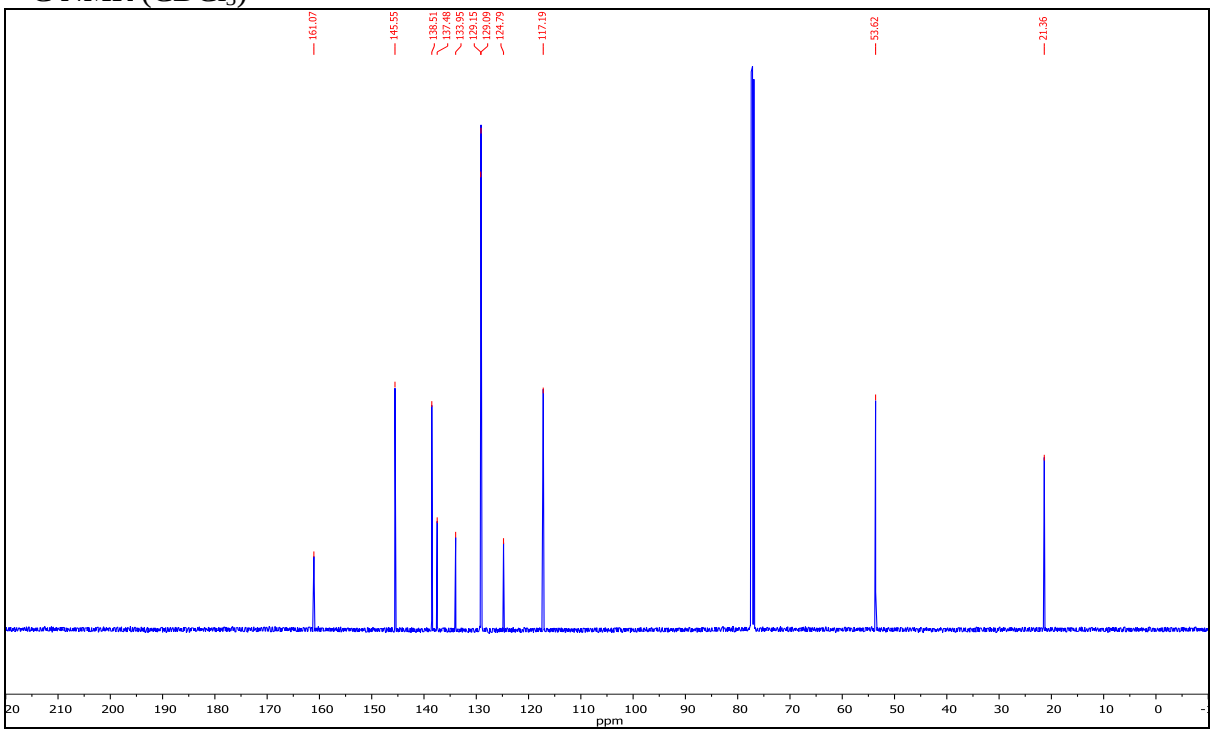


2-methoxy-3-(p-tolyl)pyridine (3u)

^{1}H NMR ($CDCl_3$)

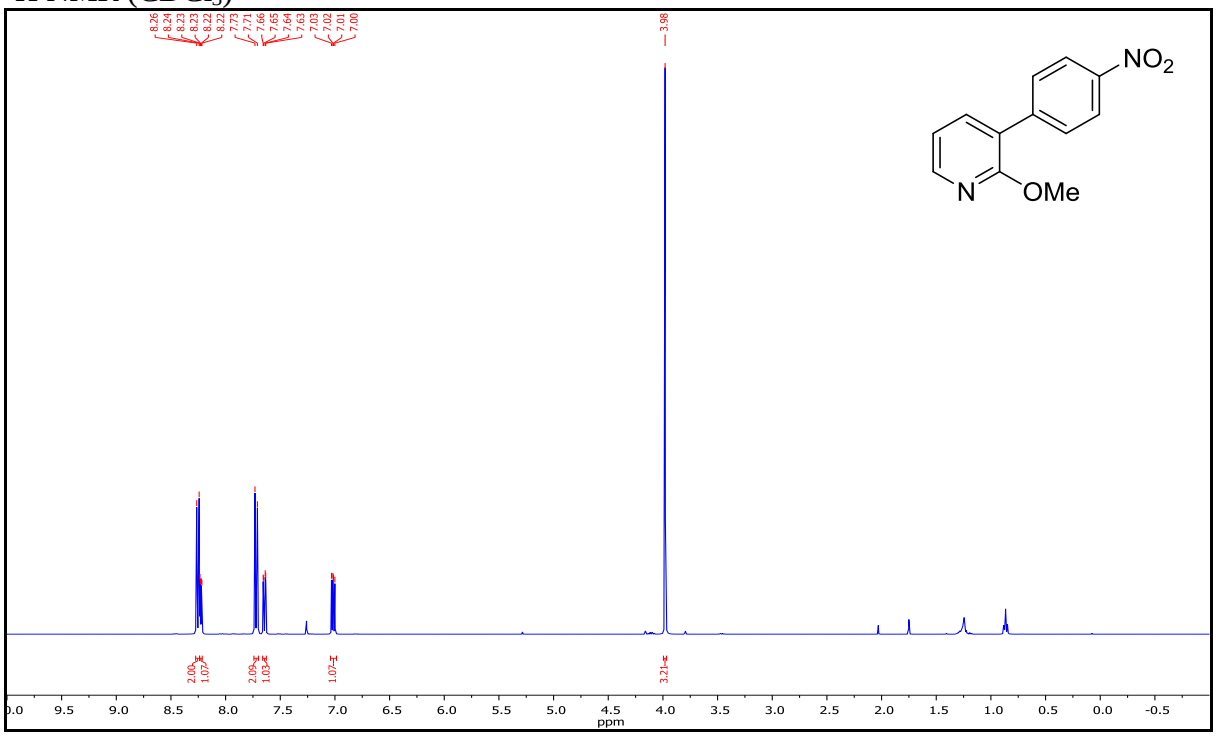


^{13}C NMR ($CDCl_3$)

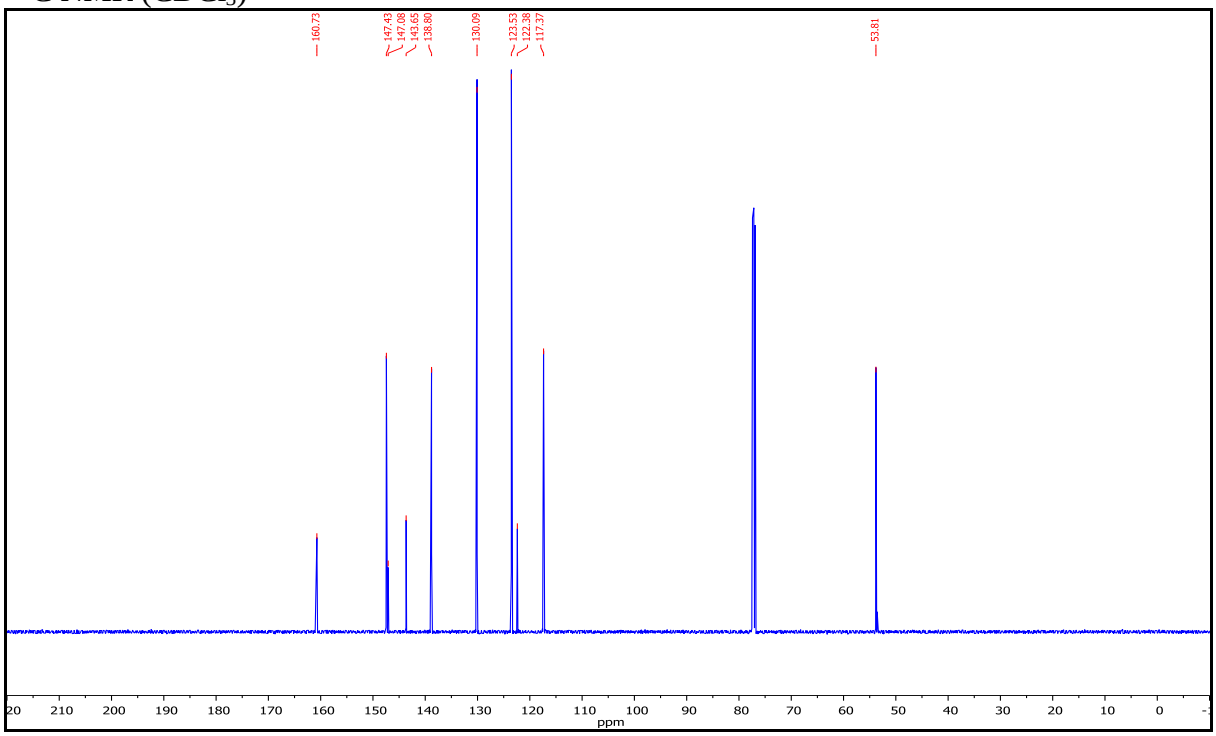


2-methoxy-3-(4-nitrophenyl)pyridine (3v)

^{1}H NMR ($CDCl_3$)

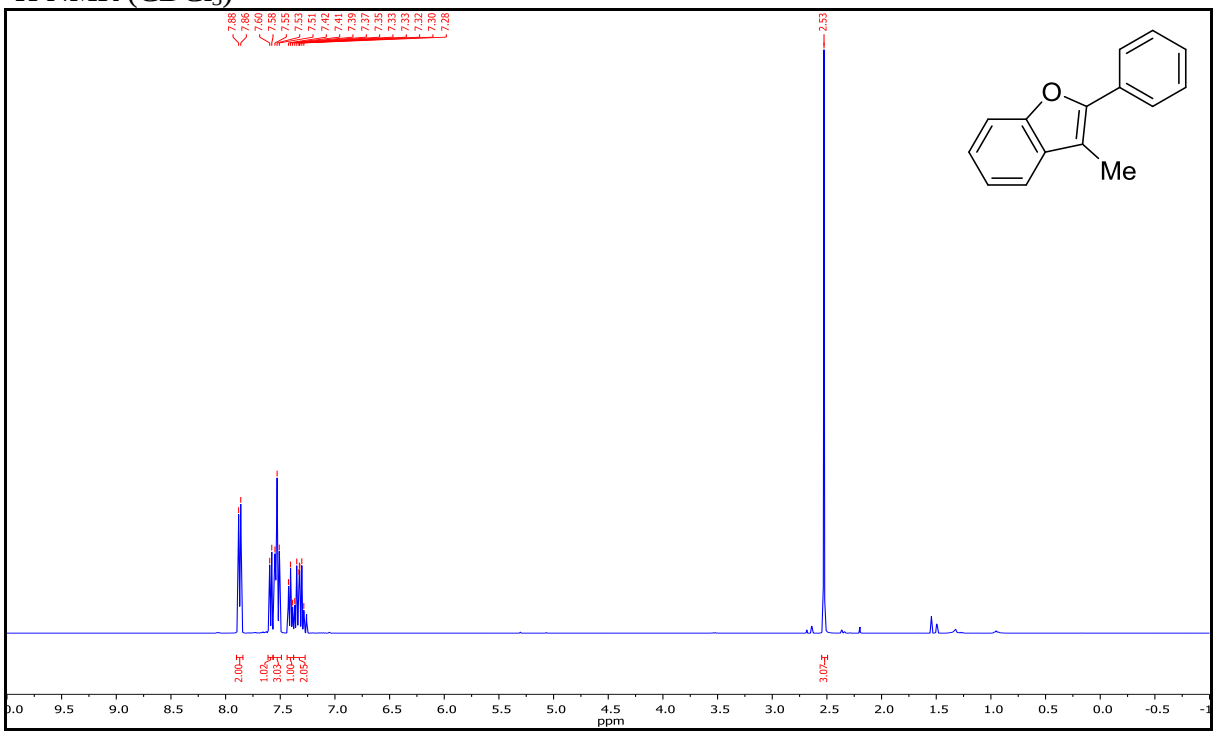


^{13}C NMR ($CDCl_3$)

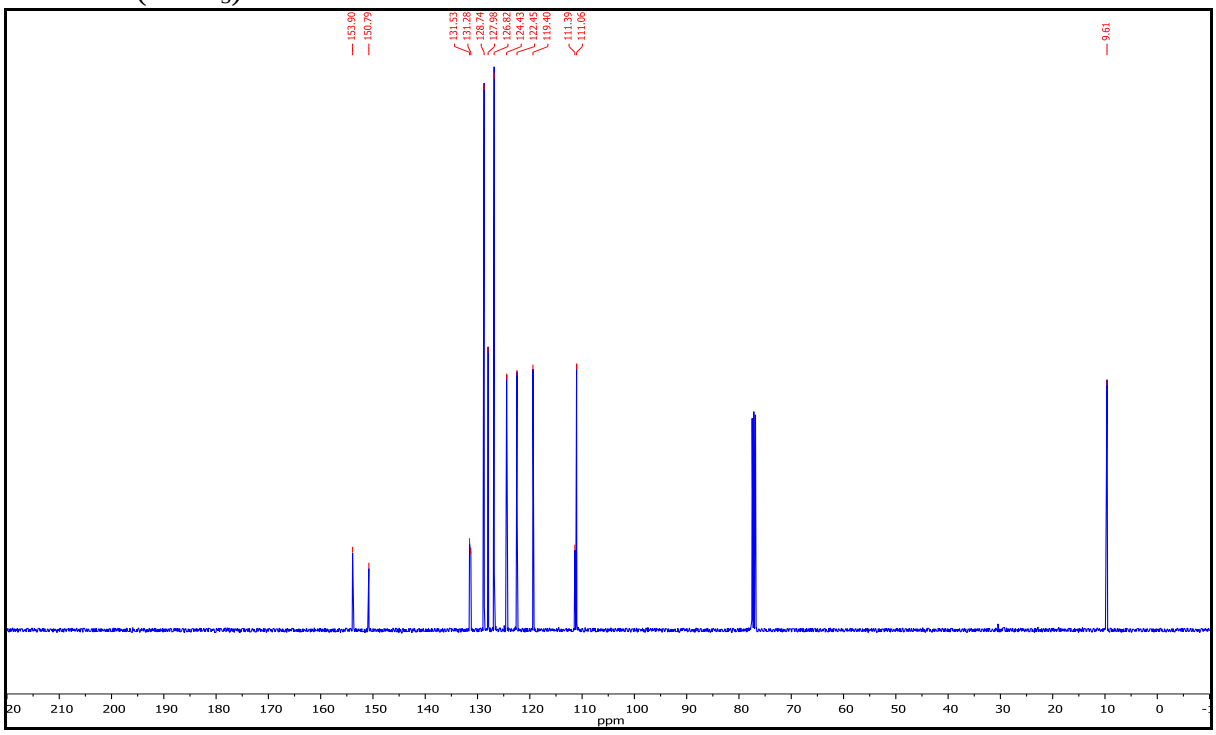


3-methyl-2-phenylbenzofuran (3w)

^{1}H NMR ($CDCl_3$)

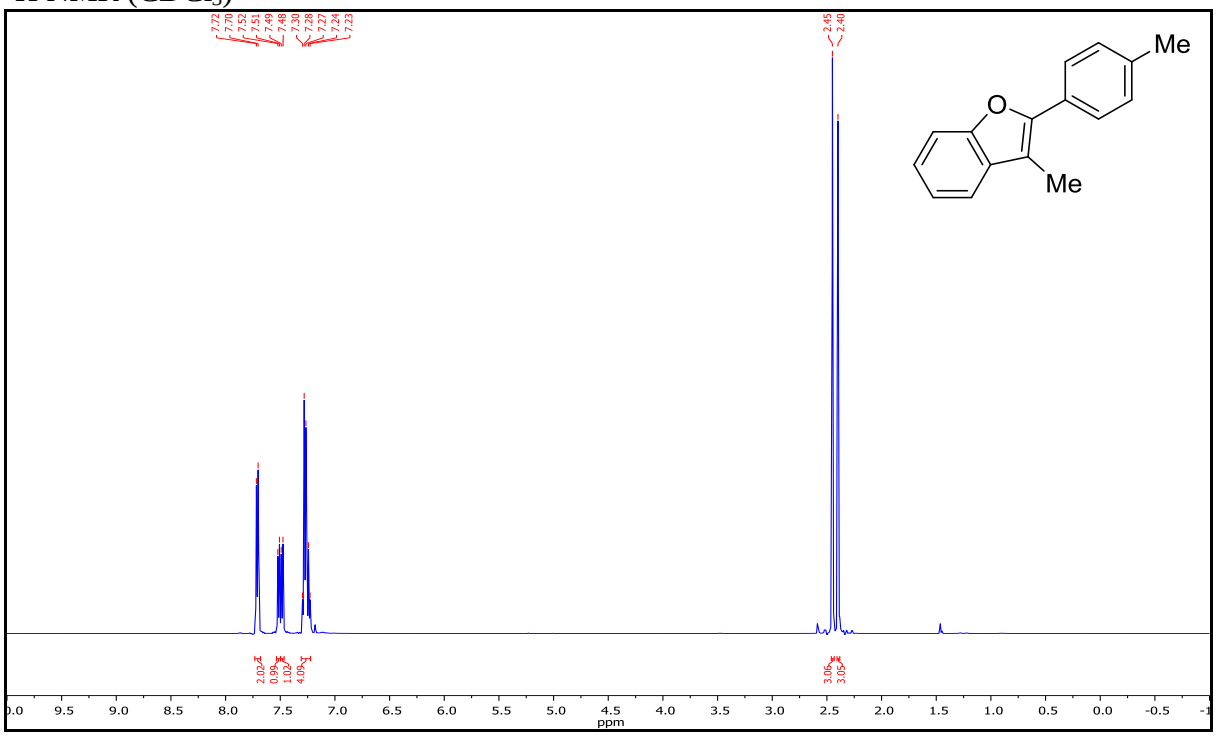


^{13}C NMR ($CDCl_3$)

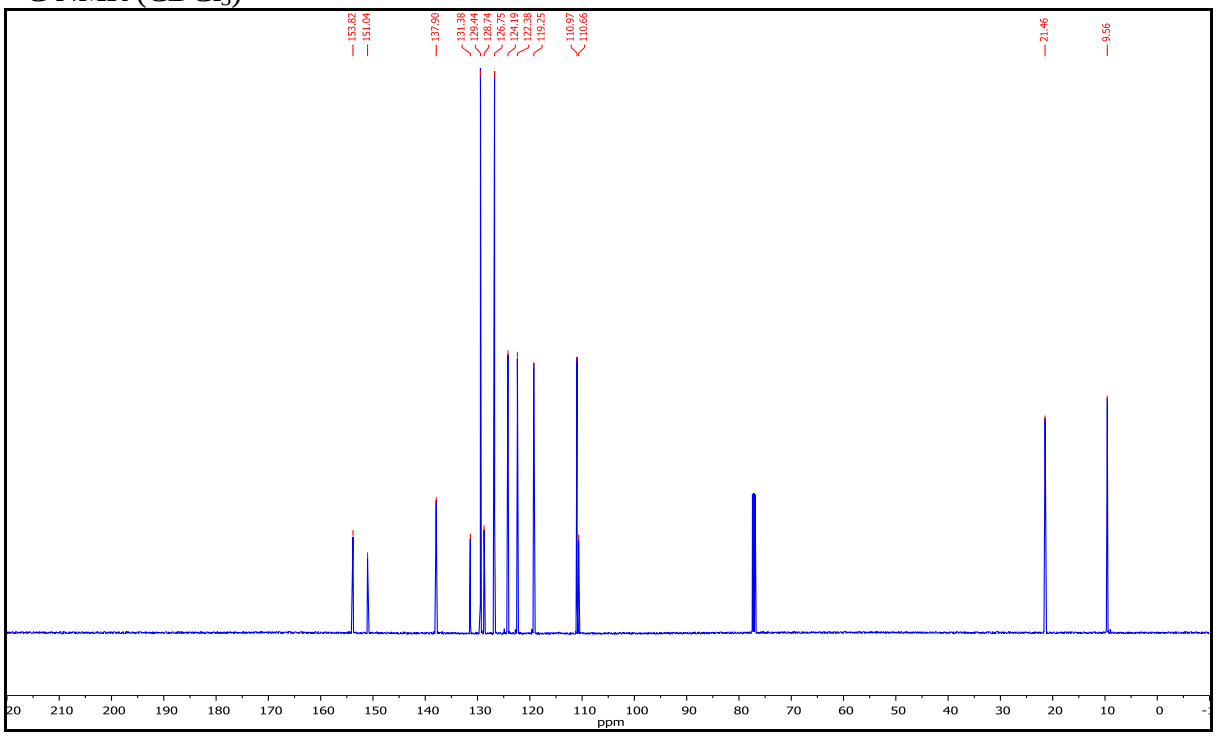


3-methyl-2-(p-tolyl)benzofuran (3x)

^{1}H NMR ($CDCl_3$)



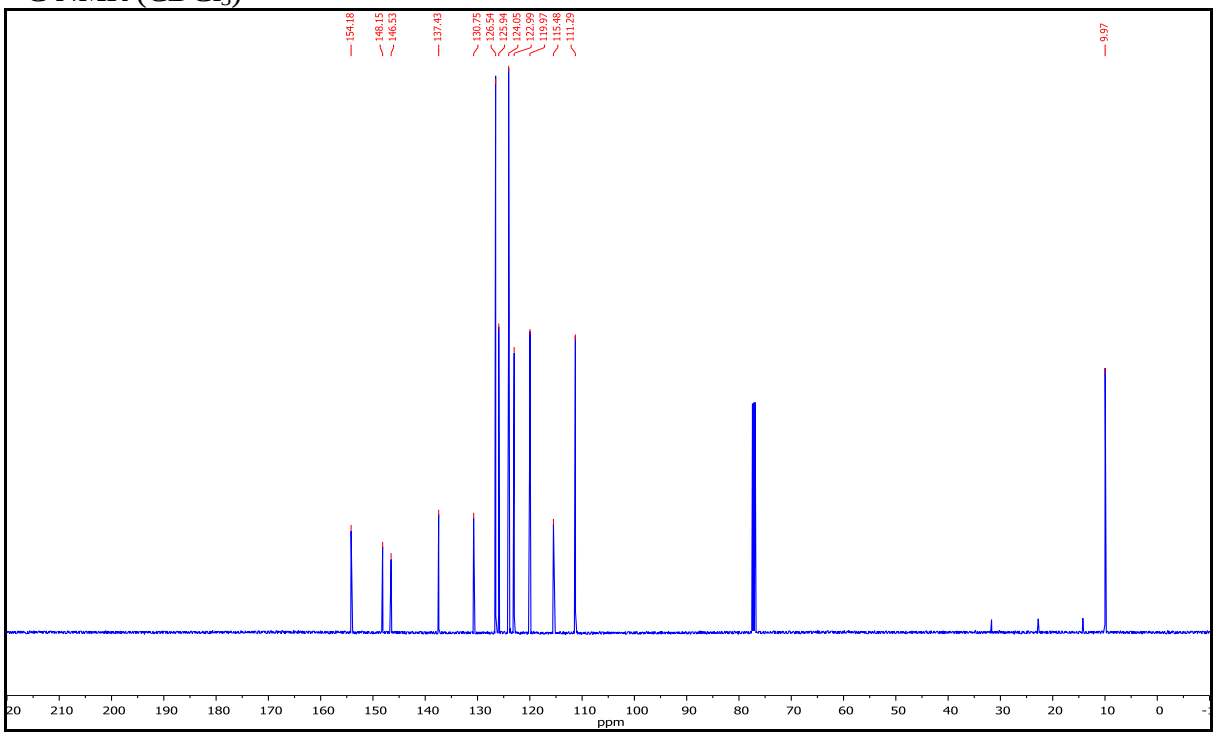
^{13}C NMR ($CDCl_3$)



3-methyl-2-(4-nitrophenyl)benzofuran (3y)

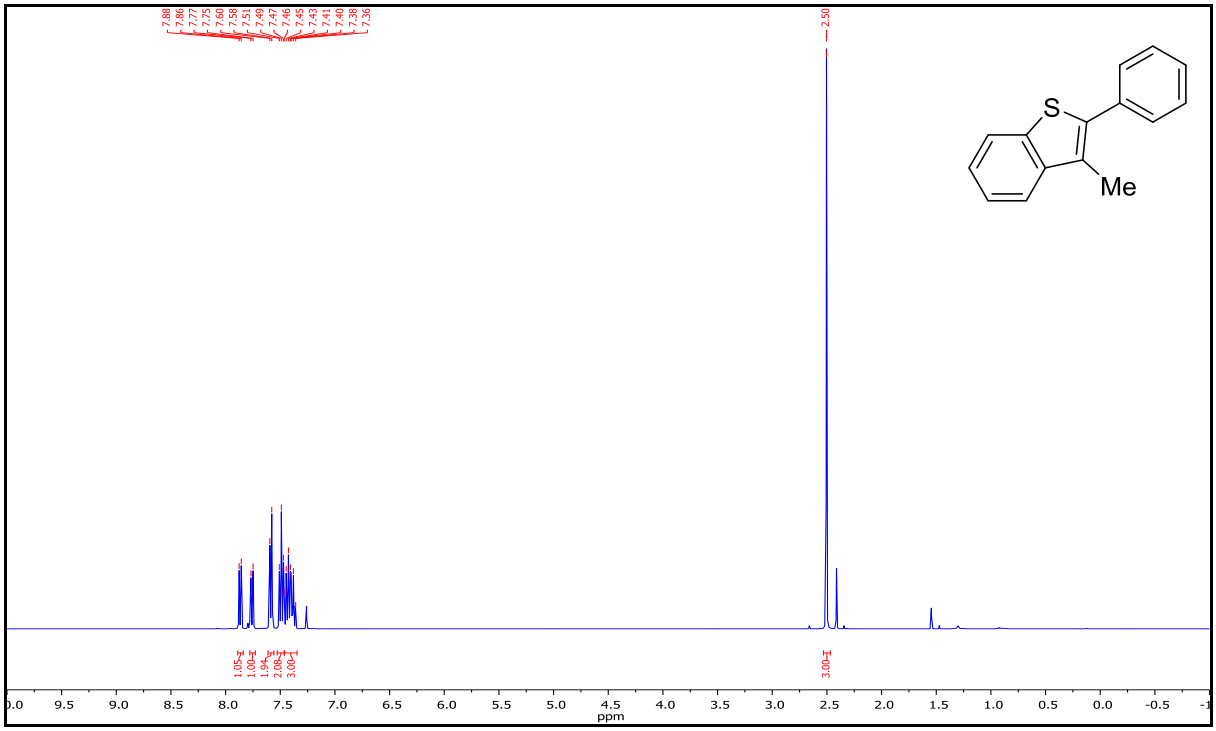
^{1}H NMR ($CDCl_3$)

^{13}C NMR ($CDCl_3$)

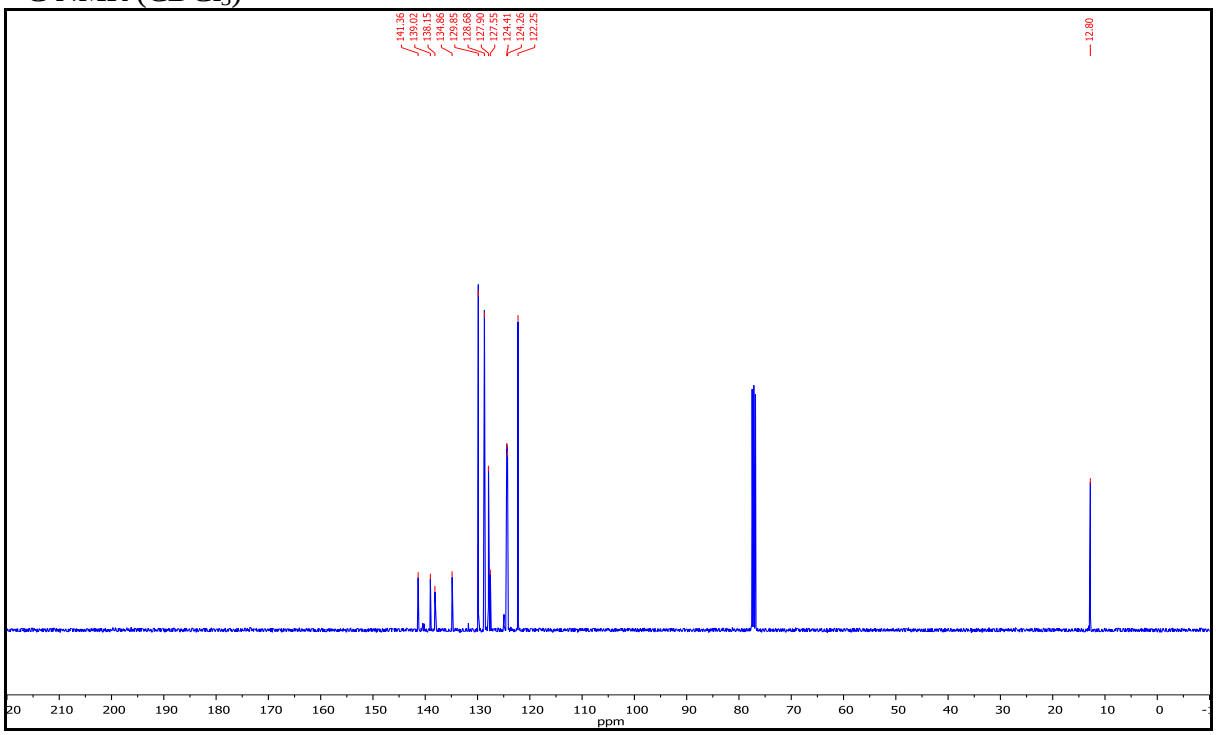


3-methyl-2-phenylbenzo[b]thiophene (3z)

^{1}H NMR ($CDCl_3$)

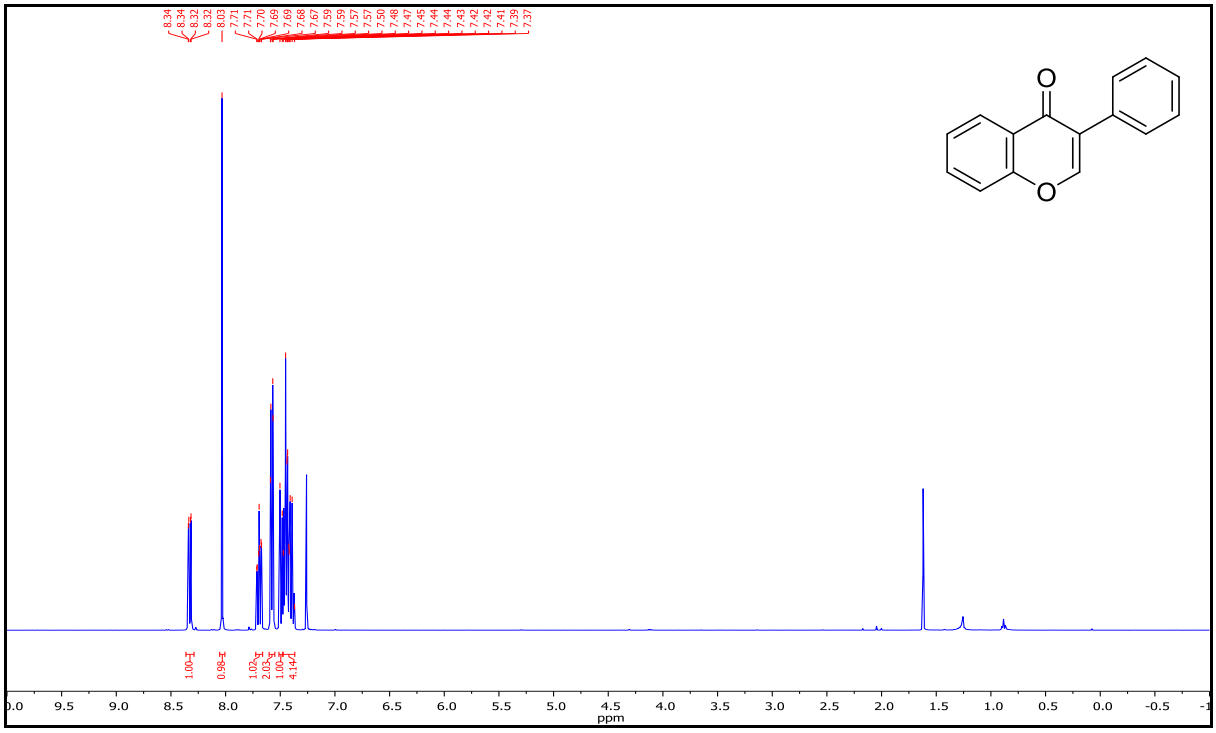


^{13}C NMR ($CDCl_3$)

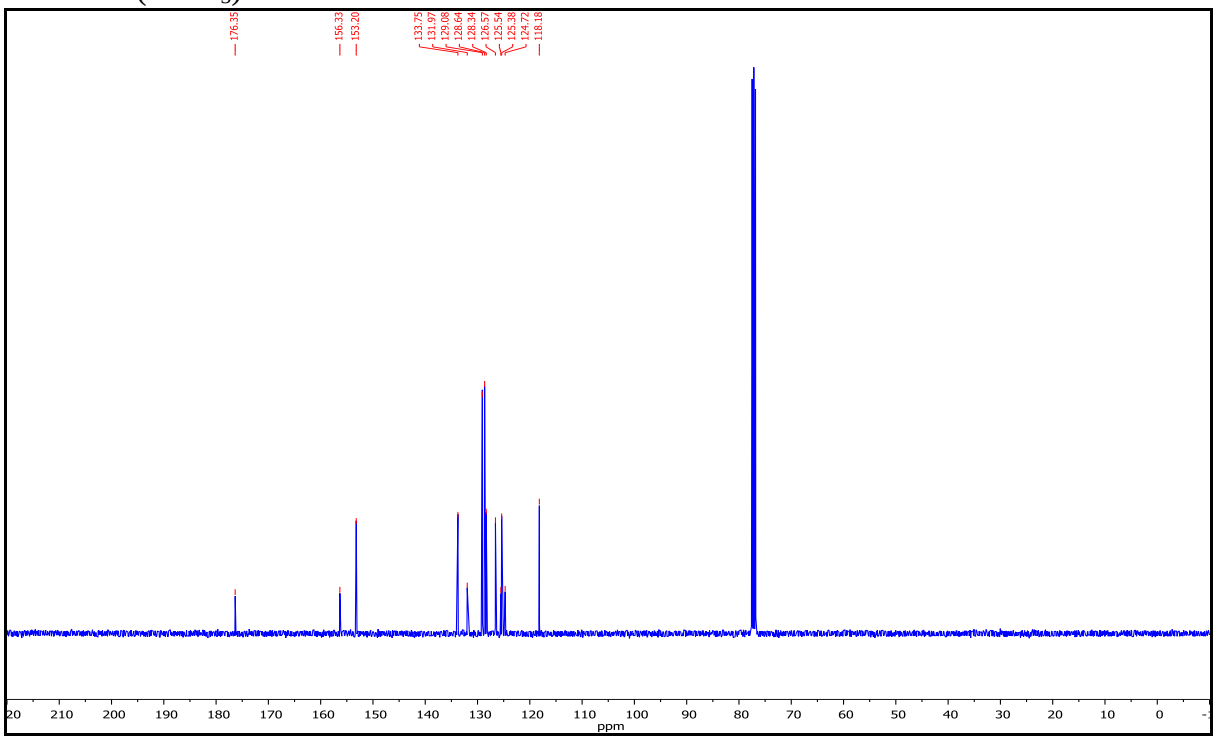


3-phenyl-4H-chromen-4-one (3aa)

^{1}H NMR ($CDCl_3$)

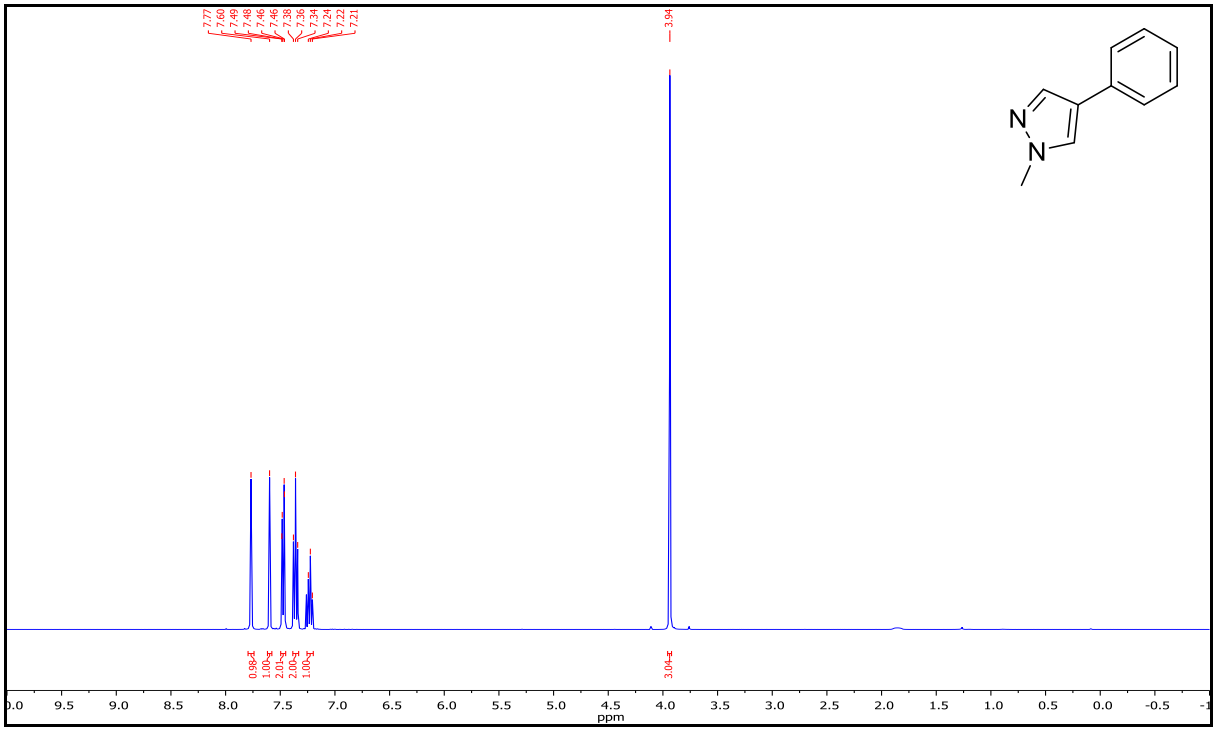


^{13}C NMR ($CDCl_3$)

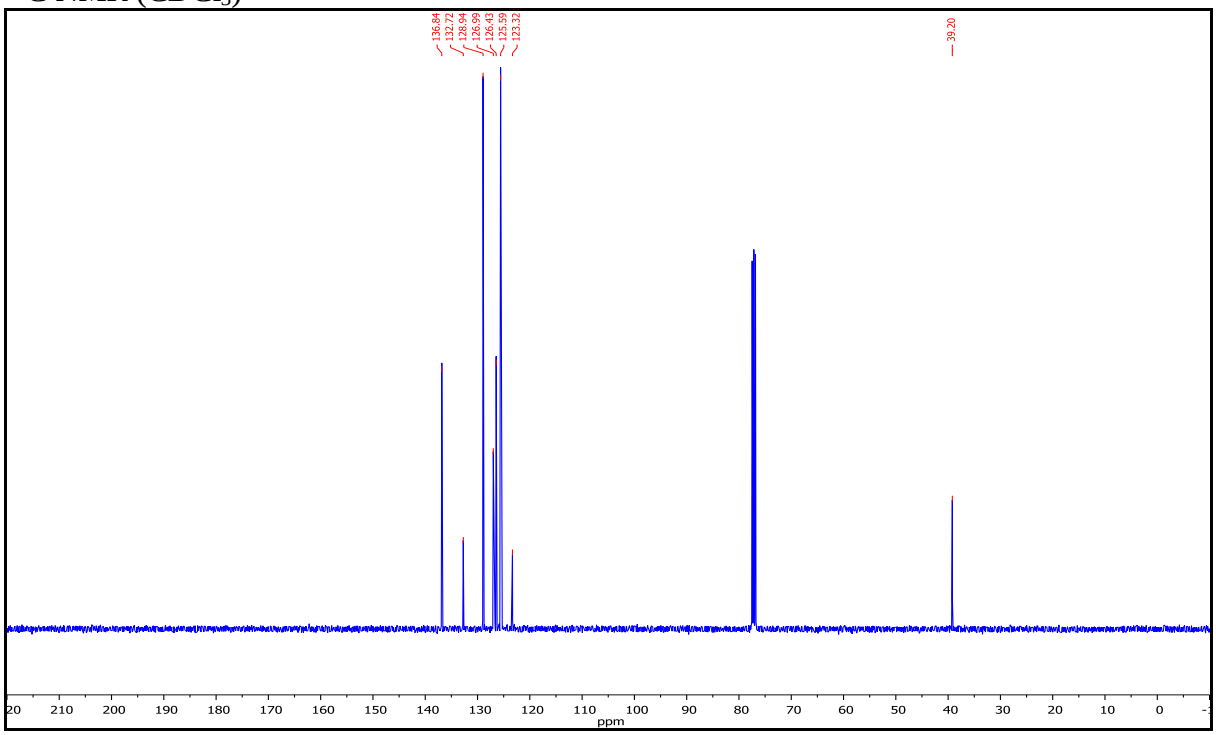


1-methyl-4-phenyl-1H-pyrazole (3ab)

^{1}H NMR ($CDCl_3$)

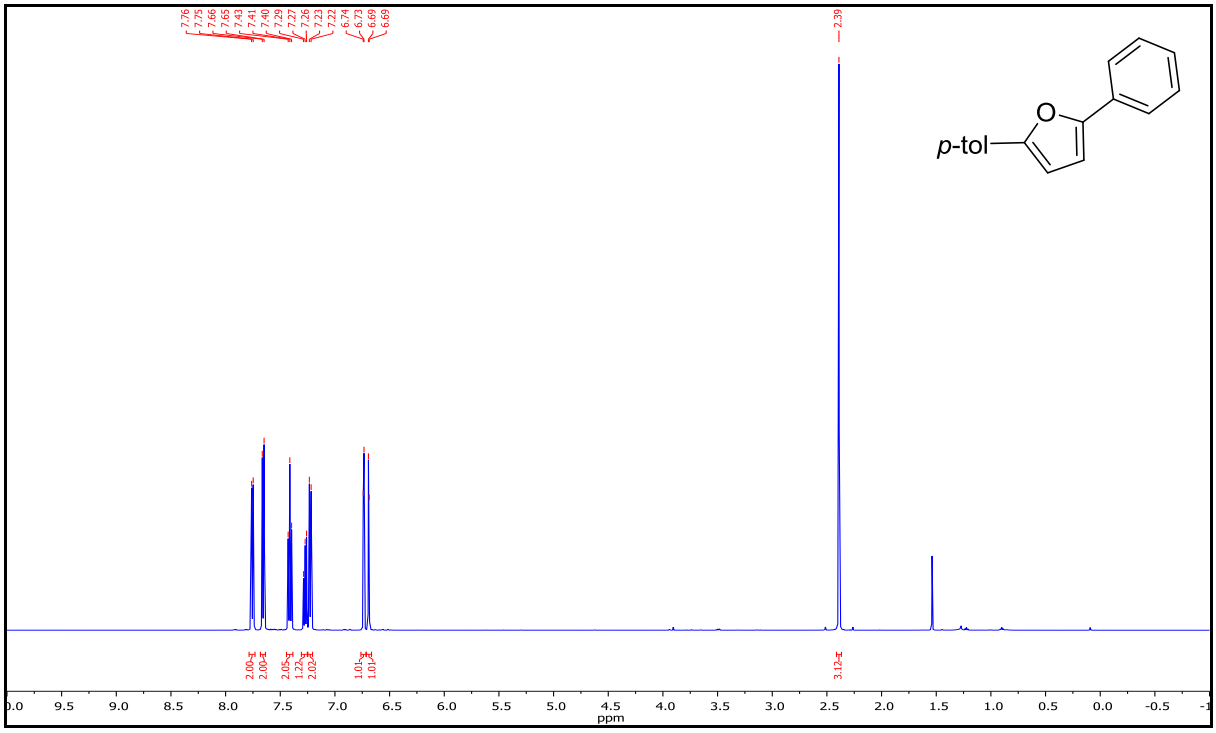


^{13}C NMR ($CDCl_3$)

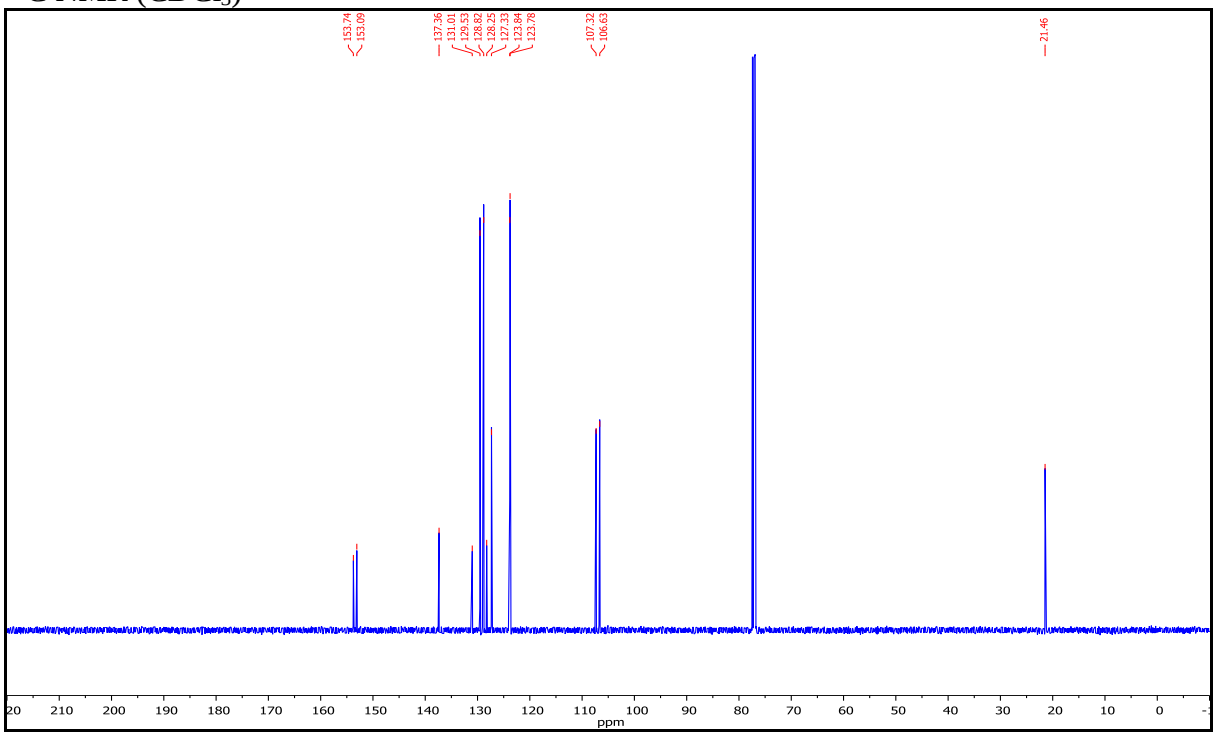


2-phenyl-5-(p-tolyl)furan (3ac)

^{1}H NMR ($CDCl_3$)

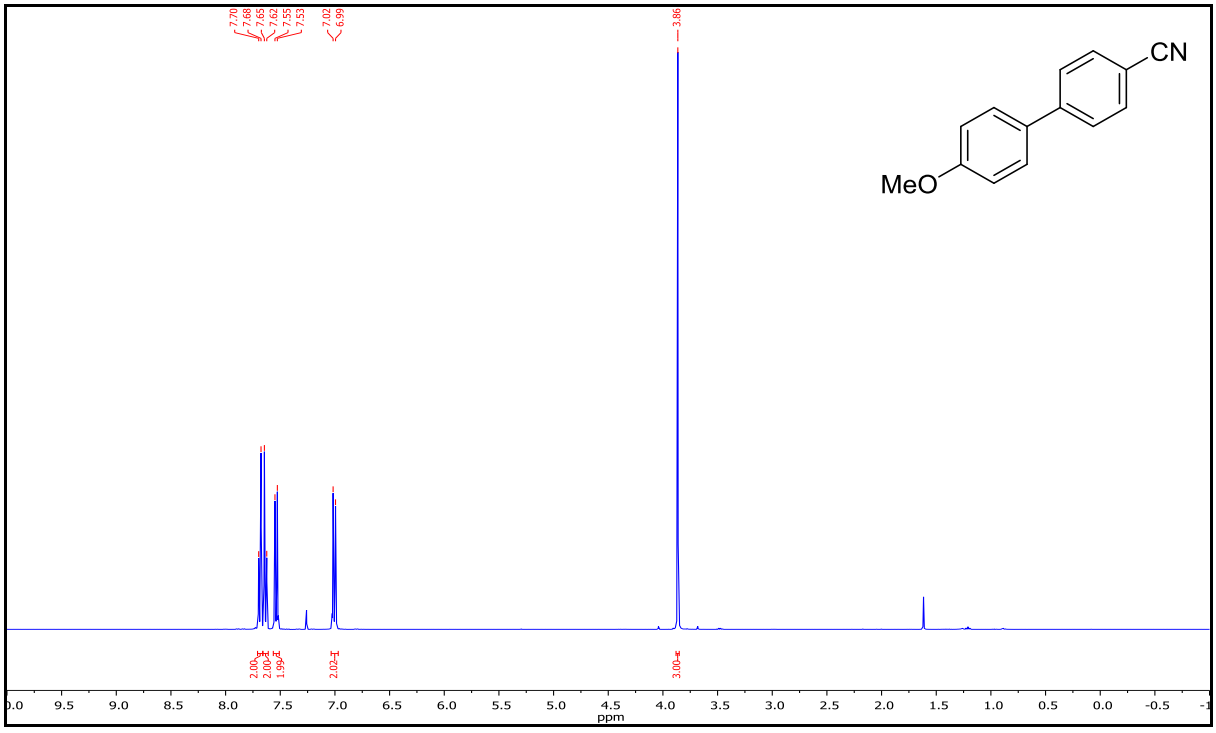


^{13}C NMR ($CDCl_3$)

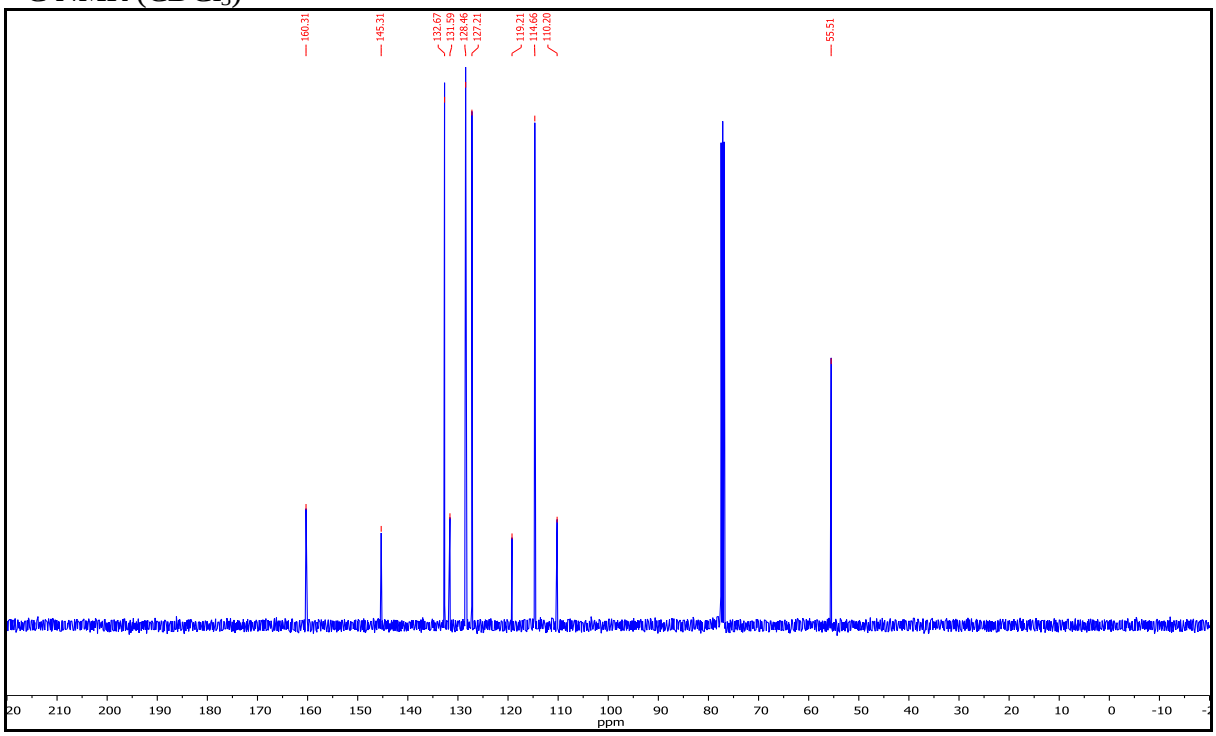


4'-methoxy-[1,1'-biphenyl]-4-carbonitrile (3b')

^{1}H NMR ($CDCl_3$)

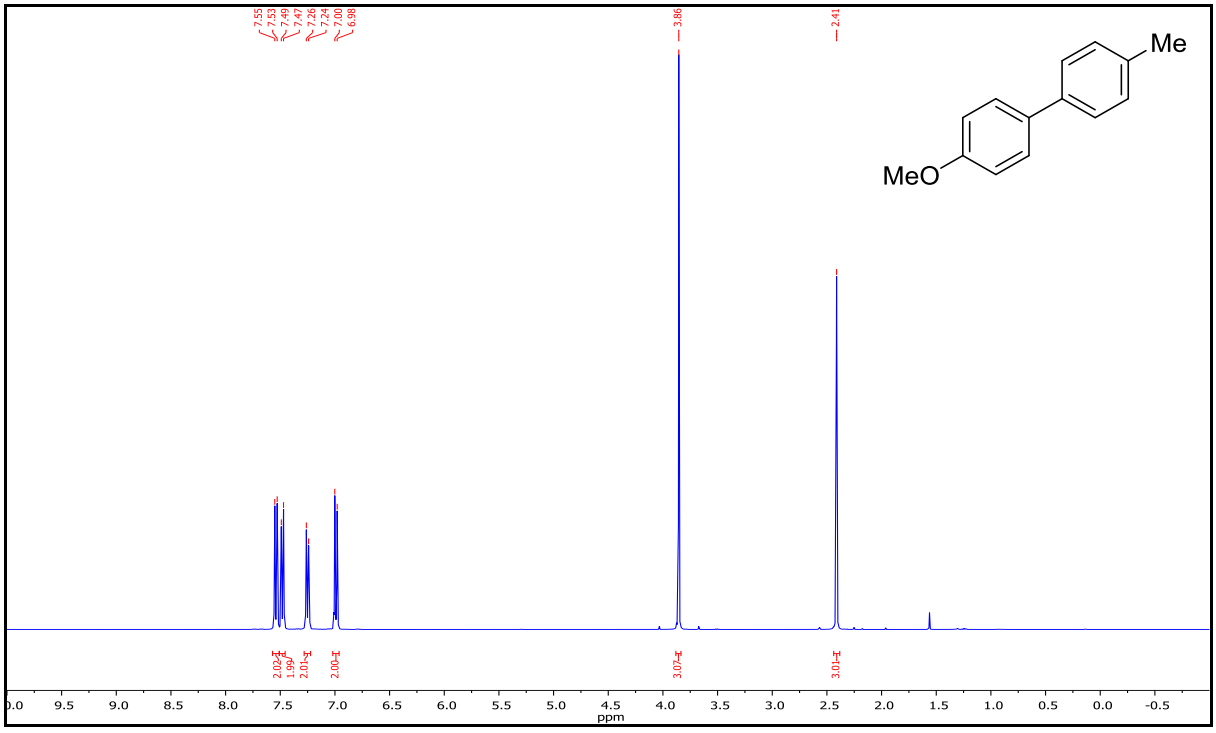


^{13}C NMR ($CDCl_3$)

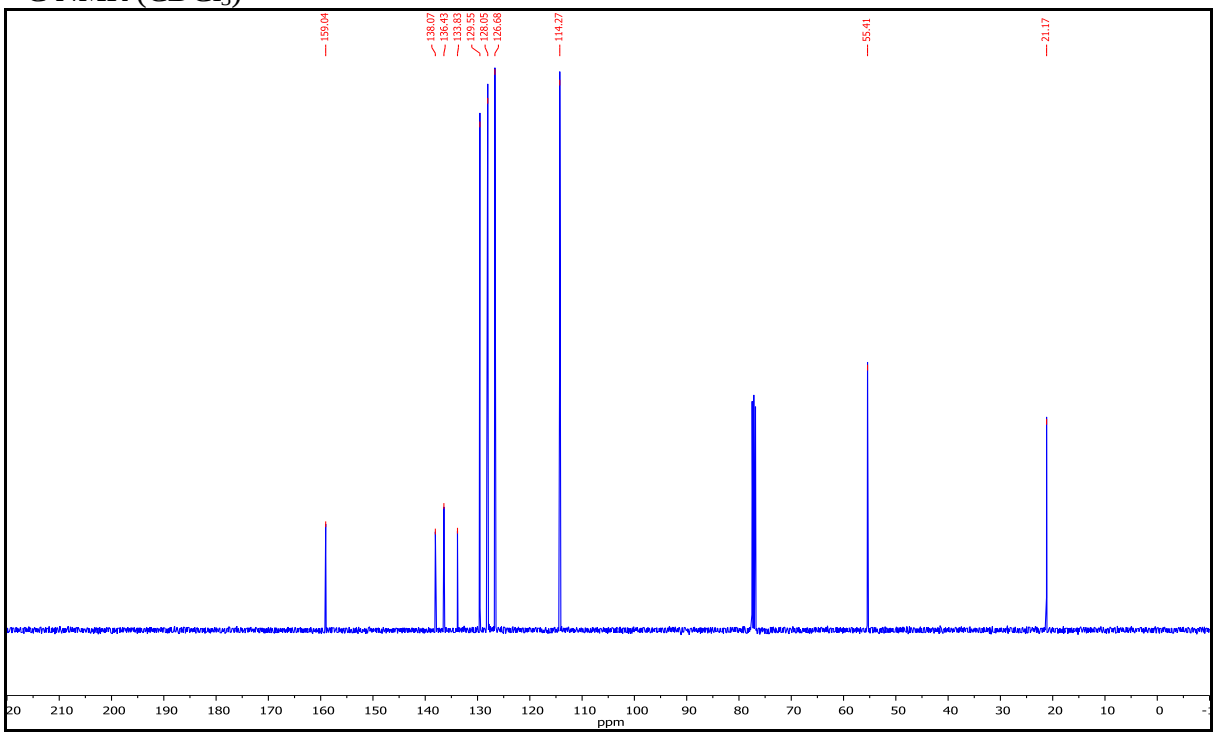


4-methoxy-4'-methyl-1,1'-biphenyl (3g')

^{1}H NMR ($CDCl_3$)

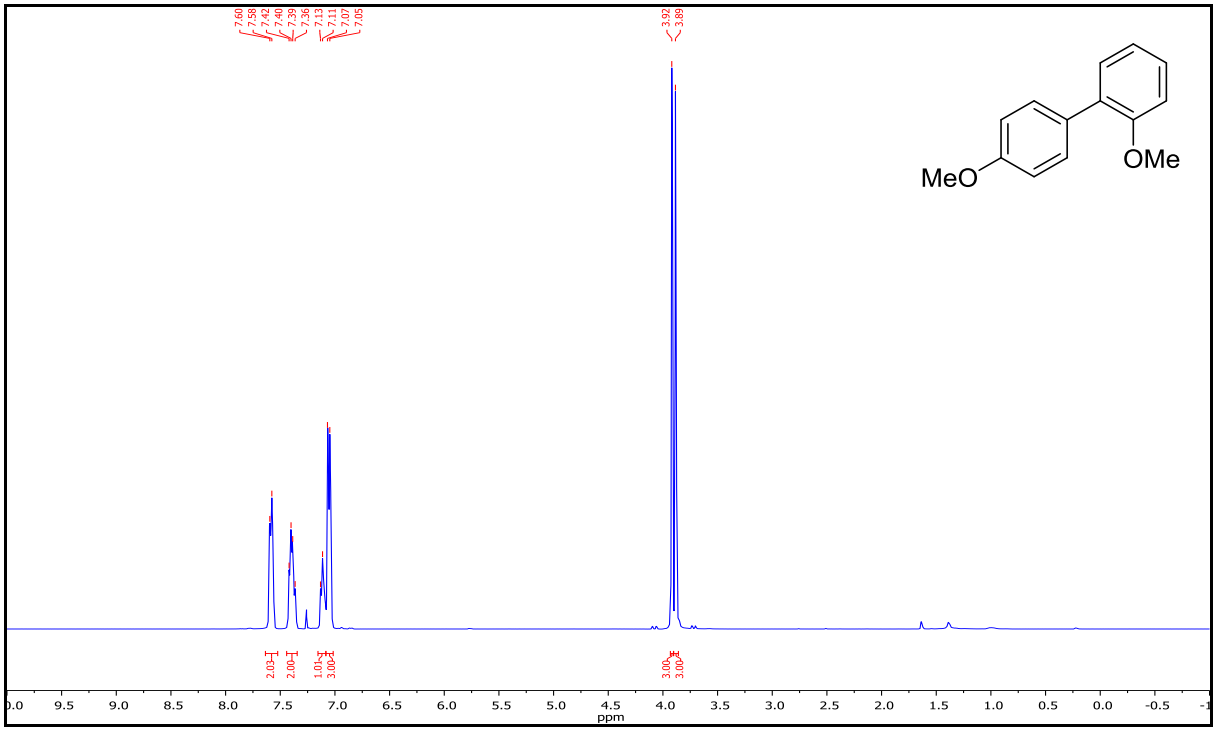


^{13}C NMR ($CDCl_3$)

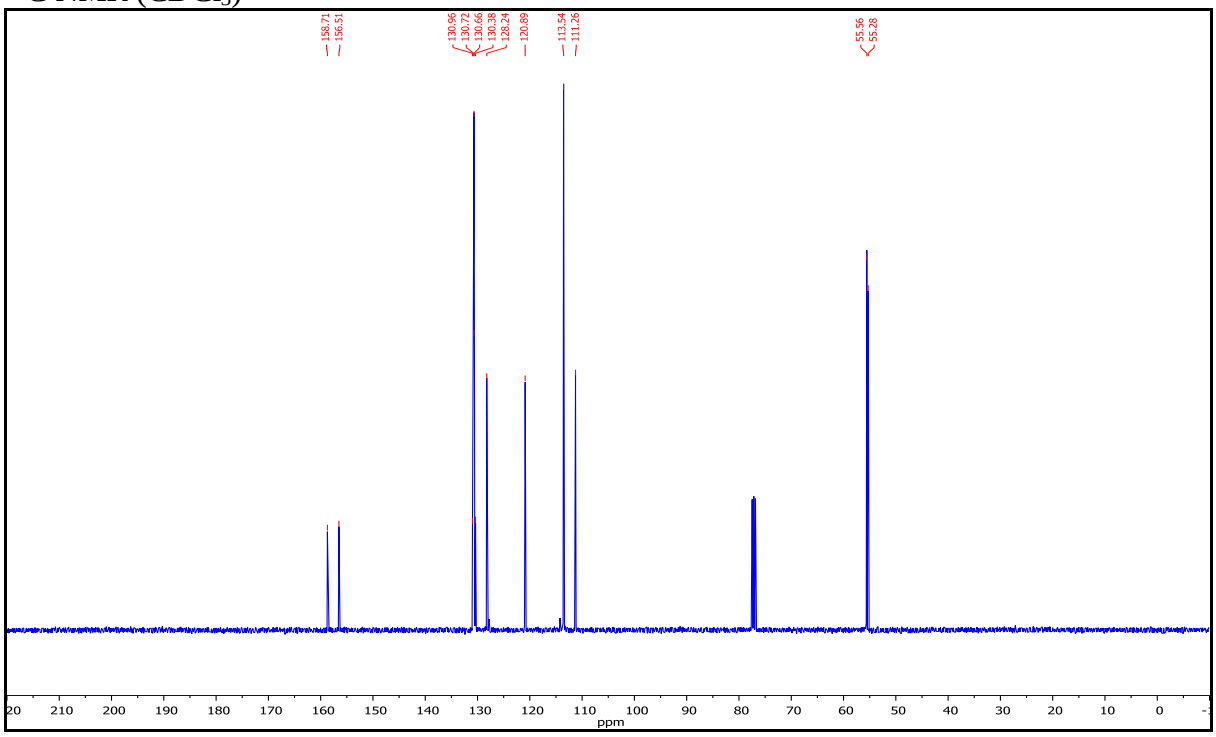


2,4'-dimethoxy-1,1'-biphenyl (3h')

^{1}H NMR ($CDCl_3$)

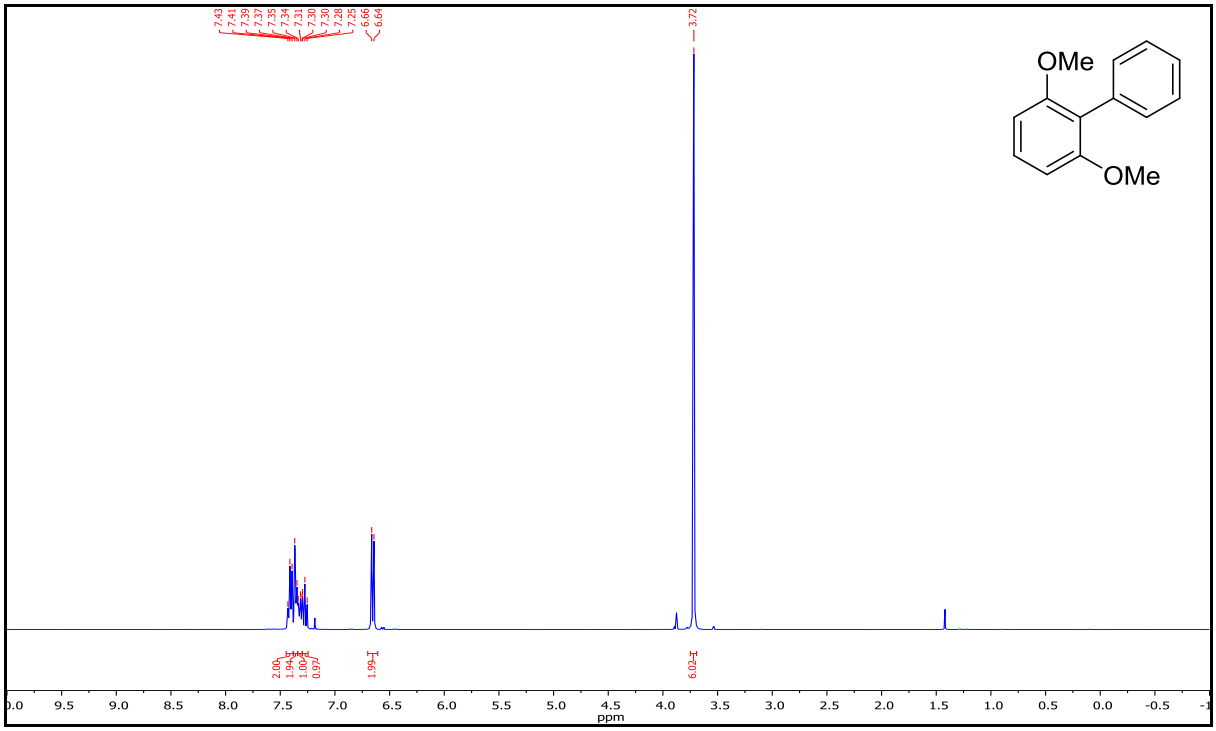


^{13}C NMR ($CDCl_3$)

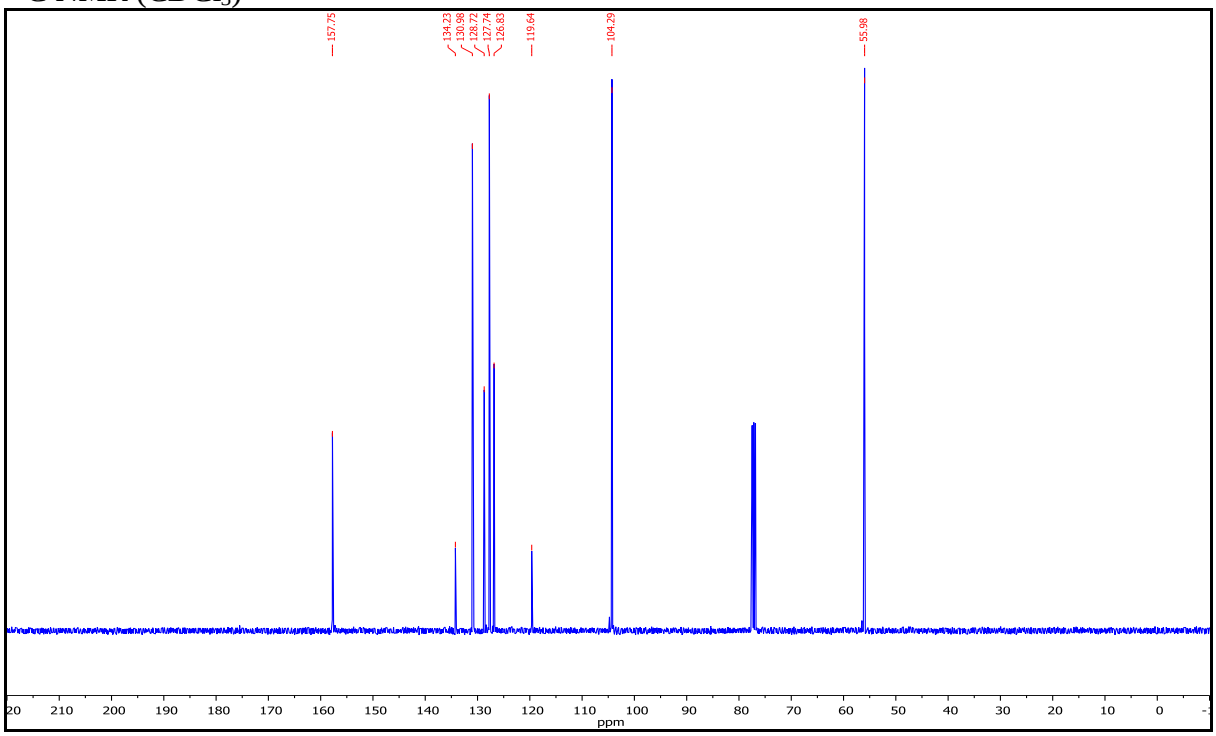


2,6-dimethoxy-1,1'-biphenyl (3m')

^{1}H NMR ($CDCl_3$)

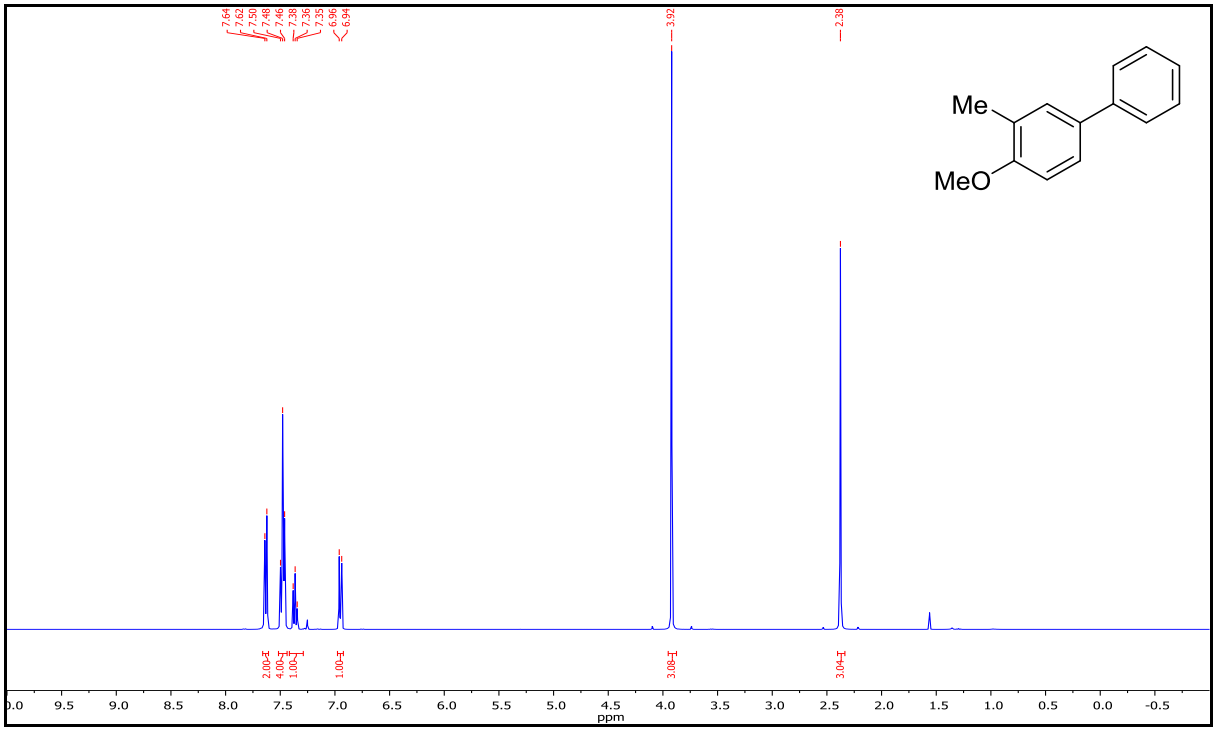


^{13}C NMR ($CDCl_3$)

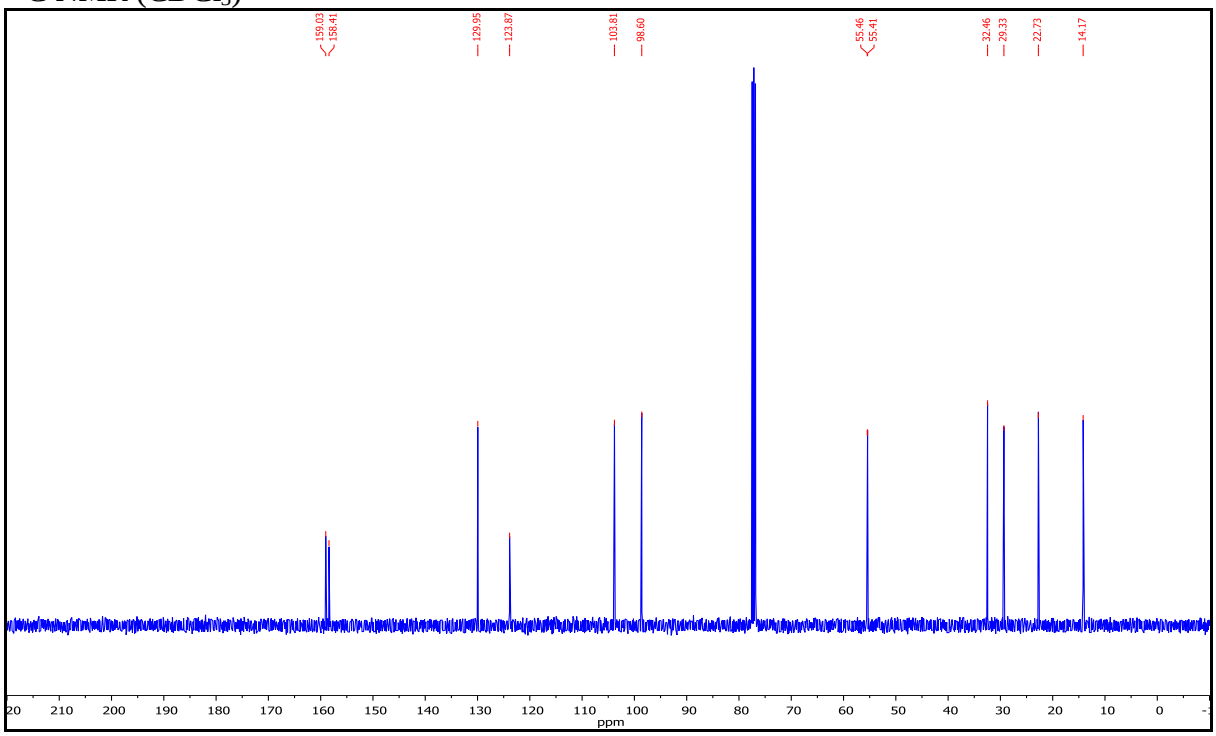


4-methoxy-3-methyl-1,1'-biphenyl (3o')

^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)



References

1 X. Cui, T. Qin, J.-R. Wang, L. Liu and Q.-X. Guo, *Synthesis*, 2007, **2007**, 393–399.
2 B. Karimi and P. F. Akhavan, *Chem. Commun.*, 2009, 3750–3752.
3 S. Shi and M. Szostak, *Org. Lett.*, 2017, **19**, 3095–3098.
4 J. M. Hammann, F. H. Lutter, D. Haas and P. Knochel, *Angew. Chem. Int. Ed.*, 2017, **56**, 1082–1086.
5 W. Erb, M. Albini, J. Rouden and J. Blanchet, *J. Org. Chem.*, 2014, **79**, 10568–10580.
6 Z.-J. Jiang, Z.-H. Li, J.-B. Yu and W.-K. Su, *J. Org. Chem.*, 2016, **81**, 10049–10055.
7 W.-J. Guo and Z.-X. Wang, *J. Org. Chem.*, 2013, **78**, 1054–1061.
8 S. Asghar, S. B. Tailor, D. Elorriaga and R. B. Bedford, *Angew. Chem. Int. Ed.*, 2017, **56**, 16367–16370.
9 I. Peñafiel, I. M. Pastor, M. Yus, M. A. Esteruelas, M. Oliván and E. Oñate, *Eur. J. Org. Chem.*, 2011, **2011**, 7174–7181.
10 R. Cai, M. Lu, E. Y. Aguilera, Y. Xi, N. G. Akhmedov, J. L. Petersen, H. Chen and X. Shi, *Angew. Chem. Int. Ed.*, 2015, 54, 8772–8776.
11 N. Zhang, Z.-J. Quan, Z. Zhang, Y.-X. Da and X.-C. Wang, *Chem. Commun.*, 2016, **52**, 14234–14237.
12 R. Fareghi-Alamdari, M. Golestanzadeh and O. Bagheri, *RSC Adv.*, 2016, **6**, 108755–108767.
13 A. Wang, X. Li, J. Liu, Q. Gui, X. Chen, Z. Tan and K. Xie, *Synth. Commun.*, 2014, **44**, 289–295.
14 W. Shi-Meng, W. Xiao-Yan, Q. Hua-Li and Z. Cheng-Pan, *Chem. – Eur. J.*, 2016, **22**, 6542–6546.

15 B. Basu, S. Das, P. Das, B. Mandal, D. Banerjee and F. Almqvist, *Synthesis*, 2009, **2009**, 1137–1146.
16 P. Huo, J. Li, W. Liu, X. He and G. Mei, *Chem. Lett.*, 2016, 45, 454–456.
17 E. J. Milton and M. L. Clarke, *Green Chem.*, 2010, **12**, 381–383.
18 L. Davin, R. McLellan, A. R. Kennedy and E. Hevia, *Chem. Commun.*, 2017, **53**, 11650–11653.
19 T. Truong, M. Mesgar, K. K. A. Le and O. Daugulis, *J. Am. Chem. Soc.*, 2014, **136**, 8568–8576.
20 M. A. Pena, J. Pérez Sestelo and L. A. Sarandeses, *J. Org. Chem.*, 2007, **72**, 1271–1275.
21 R.-C. M. A, L.-P. Antonio and C. Avelino, *Chem. – Eur. J.*, 2017, **23**, 1702–1708.
22 P. P. Lange, L. J. Gooßen, P. Podmore, T. Underwood and N. Sciammetta, *Chem. Commun.*, 2011, **47**, 3628–3630.
23 D. Hellwinkel and K. Göke, *Synthesis*, 1995, **1995**, 1135–1141.
24 K. Nobushige, K. Hirano, T. Satoh and M. Miura, *Org. Lett.*, 2014, **16**, 1188–1191.
25 P. Mutai, E. Pavadai, I. Wiid, A. Ngwane, B. Baker and K. Chibale, *Bioorg. Med. Chem. Lett.*, 2015, **25**, 2510–2513.
26 H. Cheng, Q.-Y. Wu, F. Han and G.-F. Yang, *Chin. Chem. Lett.*, 2014, **25**, 705–709.
27 L. Chen, Y. Du, X.-P. Zeng, T.-D. Shi, F. Zhou and J. Zhou. *Org. Lett.* 2015, **17**, 1557−1560.
28 K.-F. Zhang, F. Christoffel and O. Baudoin, *Angew. Chem. Int. Ed.*, 2018, **57**, 1982–1986.