

Supplementary Materials: Development of Titanium Dioxide-Supported Pd Catalysts for Ligand-Free Suzuki–Miyaura Coupling of Aryl Chlorides

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1. General

All reagents and solvents were obtained from commercial sources and used without further purification. Pd(OAc)₂ was obtained from N.E. Chemcat Co. (Tokyo, Japan). The ¹H NMR and ¹³C NMR spectra were recorded on a JEOL ECZ-400 (400 MHz for ¹H NMR and 100 MHz for ¹³C NMR) spectrometer. CDCl₃ was used as the solvent for NMR measurement. Chemical shifts (δ) are expressed in part per million and internally referenced (0.00 ppm for tetramethylsilane or 7.26 ppm for CHCl₃ for ¹H NMR for CDCl₃ and 77.0 ppm for CDCl₃ for ¹³C NMR). The JEOL JMS Q1000GC Mk II Quad GC/MS was used to determine the area ratio of aryl chlorides and coupling products. The ULVAC-PHI PHI QuanteraSXM was used for the X-ray photoelectron spectroscopy (XPS). All of ¹H and ¹³C NMR spectra of known products were identical with those in the literature.

2. Preparation of Pd/TiO₂ and Pd(red)/TiO₂

5% Pd/TiO₂ (Cat. D, anatase-type): A suspension of anatase-type TiO₂ (3.00 g, colorless powder) in MeCN solution (30 mL) of Pd(OAc)₂ [316 mg, 1.41 mmol (150 mg, palladium quantity)] was stirred under argon atmosphere at 25 °C for 4 days. The resulting light yellow solid was collected by filtration (1 μm filter paper), washed with H₂O (5 mL × 5) and EtOAc (5 mL × 5) and dried in vacuo for 24 h to afford the Pd/TiO₂ (3.15 g, Cat. D, anatase-type). The filtrate was concentrated in vacuo, and then transferred to a 100 mL volumetric flask with H₂O and 15.58 ppm (1.56 mg) of palladium species were observed in the diluted filtrate by the use of atomic absorption spectrometry (SHIMADZU AA-7000). Since the total palladium species which was not absorbed on anatase-type TiO₂ was 1.56 mg, the palladium content of anatase-type Pd/TiO₂ (Cat. D) was approximately 5% (4.7%) [(150 - 1.56)/3150 × 100].

5% Pd(red)/TiO₂ (Cat. A, anatase-type): The collected anatase-type 5% Pd/TiO₂ (Cat. D, 500.0 mg) was stirred with NH₂NH₂·H₂O (29.2 µL, 0.6 mmol) in H₂O (40 mL) under argon atmosphere at 25 °C for 24 h. The grayish white solid was collected by filtration (1 µm filter paper), washed with H₂O (10 mL × 5) and EtOAc (10 mL × 5), and dried in vacuo for 12 h to give Pd(red)/TiO₂ (343 mg, Cat. A, anatase-type).

5% Pd(red)/TiO₂ (Cat. B, anatase-type): The collected anatase-type 5% Pd/TiO₂ (Cat. D, 500.0 mg) was stirred with NaBH₄ (22.7 mg, 0.6 mmol) in H₂O (40 mL) under argon atmosphere at 25 °C for 24 h. The grayish white solid was collected by filtration (1 µm filter paper), washed with H₂O (10 mL × 5) and EtOAc (10 mL × 5), and dried in vacuo for 12 h to give Pd(red)/TiO₂ (442 mg, Cat. B, anatase-type).

5% Pd(red)/TiO₂ (Cat. C, anatase-type): The collected anatase-type 5% Pd/TiO₂ (Cat. D, 500.0 mg) was stirred in H₂O (40 mL) under H₂ atmosphere at 25 °C for 24 h. The grayish white solid was collected by filtration (1 µm filter paper), washed with H₂O (10 mL × 5) and EtOAc (10 mL × 5), and dried in vacuo for 12 h to give Pd(red)/TiO₂ (416 mg, Cat. C, anatase-type).

4% Pd/TiO₂ (Cat. E, anatase-type): A suspension of anatase-type TiO₂ (500 mg, colorless powder) in EtOAc solution (5 mL) of Pd(OAc)₂ [52.8 mg, 235 µmol (25 mg, palladium quantity)] was stirred under argon atmosphere at 25 °C for 4 days. The resulting light yellow solid was collected by filtration (1 µm filter paper), washed with H₂O (5 mL × 5) and EtOAc (5 mL × 5), and dried in vacuo for 24 h to afford the Pd/TiO₂ (525 mg, Cat. E, anatase-type). The filtrate was concentrated in vacuo, and then transferred to a 100 mL volumetric flask with H₂O and 24.235 ppm (2.42 mg) of palladium species were observed in the diluted filtrate by the use of atomic absorption spectrometry (SHIMADZU AA-7000). Since the total palladium species which was not absorbed on anatase-type TiO₂ was 2.42 mg, the palladium content of anatase-type Pd/TiO₂ (Cat. E) was approximately 4% (4.3%) [(25-2.42)/525×100].

5% Pd/TiO₂ (Cat. F, rutile-type): A suspension of rutile-type TiO₂ (500 mg, colorless powder) in MeCN solution (5 mL) of Pd(OAc)₂ [52.8 mg, 235 µmol (25 mg, palladium quantity)] was stirred under argon atmosphere at 25 °C for 4 days. The resulting light yellow solid was collected by filtration (1 µm filter paper), washed with H₂O (5 mL × 5) and EtOAc (5 mL × 5), and dried in vacuo for 24 h to afford the Pd/TiO₂ (527 mg, Cat. F, rutile-type). The filtrate was concentrated in vacuo, and then transferred to a 200 mL volumetric flask with H₂O and 6.650 ppm (1.33 mg) of palladium species were observed in the diluted filtrate by the use of atomic absorption spectrometry (SHIMADZU AA-7000). Since the total palladium species which was not absorbed on anatase-type TiO₂ was 1.56 mg, the palladium content of anatase-type Pd/TiO₂ (Cat. F) was approximately 5% (4.5%) [(25-1.33)/527×100].

5% Pd/TiO₂ (Cat. G, rutile-type): A suspension of rutile-type TiO₂ (500 mg, colorless powder) in EtOAc solution (5 mL) of Pd(OAc)₂ [52.8 mg, 235 µmol (25 mg, palladium quantity)] was stirred under argon atmosphere at 25 °C for 4 days. The resulting light yellow solid was collected by filtration (1 µm filter paper), washed with H₂O (5 mL × 5) and EtOAc (5 mL × 5), and dried in vacuo for 24 h to afford the Pd/TiO₂ (510 mg, Cat. G, rutile-type). The filtrate was concentrated in vacuo, and then transferred to a 100 mL volumetric flask with H₂O and 6.075 ppm (0.61 mg) of palladium species were observed in the diluted filtrate by the use of atomic absorption spectrometry (SHIMADZU AA-7000). Since the total palladium species which was not absorbed on anatase-type TiO₂ was 0.61 mg, the palladium content of anatase-type Pd/TiO₂ (Cat. G) was approximately 5% (4.8%) [(25-0.61)/510×100].

5% Pd/TiO₂ (Cat. H, brookite-type): A suspension of brookite-type TiO₂ (500 mg, colorless powder) in MeCN solution (5 mL) of Pd(OAc)₂ [52.8 mg, 235 µmol (25 mg, palladium quantity)] was stirred under argon atmosphere at 25 °C for 4 days. The resulting light yellow solid was collected by filtration (1 µm filter paper), washed with H₂O (5 mL × 5) and EtOAc (5 mL × 5) and dried in vacuo for 24 h to afford the Pd/TiO₂ (509 mg, Cat. H, brookite-type). The filtrate was concentrated in vacuo, and then transferred to a 100 mL volumetric flask with H₂O and 14.378 ppm (1.44 mg) of palladium species were observed in the diluted filtrate by the use of atomic absorption spectrometry (SHIMADZU AA-

7000). Since the total palladium species which was not absorbed on anatase-type TiO_2 was 1.44 mg, the palladium content of anatase-type Pd/TiO_2 (Cat. **H**) was approximately 5% (4.6%) $[(25-1.44)/509 \times 100]$.

5% Pd/TiO_2 (Cat. **I, brookite-type):** A suspension of brookite-type TiO_2 (500 mg, colorless powder) in EtOAc solution (5 mL) of Pd(OAc)_2 [52.8 mg, 235 μmol (25 mg, palladium quantity)] was stirred under argon atmosphere at 25 °C for 4 days. The resulting light yellow solid was collected by filtration (1 μm filter paper), washed with H_2O (5 mL \times 5) and EtOAc (5 mL \times 5) and dried in vacuo for 24 h to afford the Pd/TiO_2 (471 mg, Cat. **I**, brookite-type). The filtrate was concentrated in vacuo, and then transferred to a 100 mL volumetric flask with H_2O and 12.235 ppm (1.22 mg) of palladium species observed in the diluted filtrate by the use of atomic absorption spectrometry (SHIMADZU AA-7000). Since the total palladium species which was not absorbed on anatase-type TiO_2 was 1.22 mg, the palladium content of anatase-type Pd/TiO_2 (Cat. **I**) was approximately 5% (5.0%) $[(25-1.22)/471 \times 100]$.

3. XPS Spectra of Pd/TiO_2

Area% of Pd(II) and Pd(0) species of the Pd/TiO_2 (Cat. **E–I**) (Figure S1)

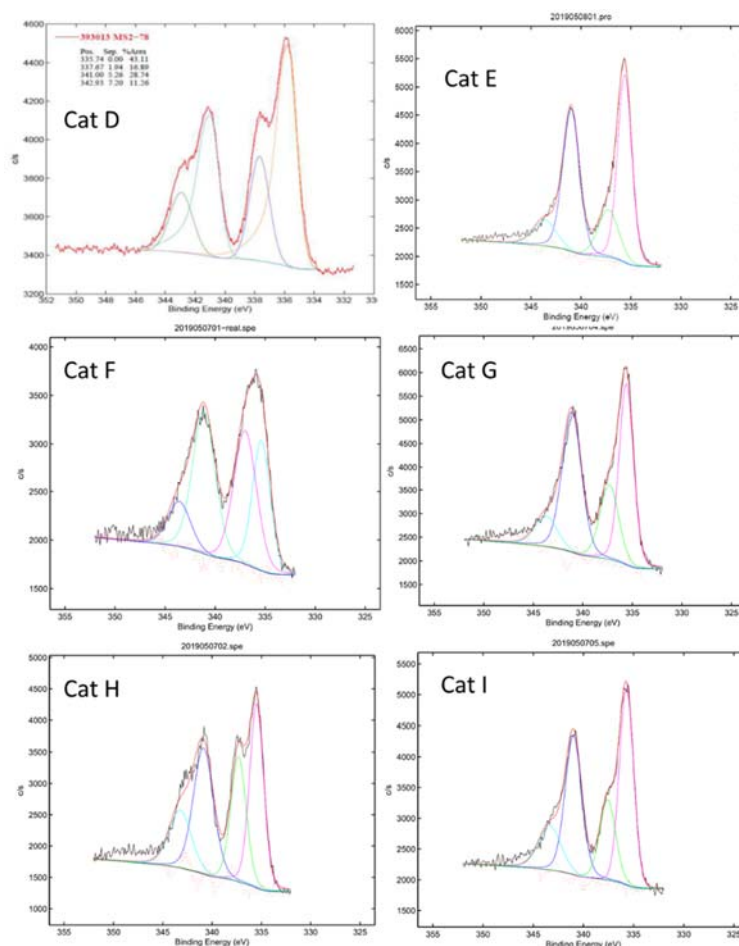


Figure S1. XPS image and curve-fitting of Pd peaks (Cat. **D–I**).

Characteristic peaks and detailed area% of Pd(0) species and Pd(II) ions of Pd/TiO_2 (Cat. **D–I**).

Position (eV)	342.9	341.0	337.7	335.7
Species	Pd(II) 3d3	Pd(0) 3d3	Pd(II) 3d5	Pd(0) 3d5
Area% (Cat. D)	11.26	28.74	16.89	43.11
Area% (Cat. E)	8.82	36.14	14.81	40.23

Area% (Cat. F)	10.60	33.79	31.58	24.04
Area% (Cat. G)	9.20	36.80	18.68	35.33
Area% (Cat. H)	15.47	30.48	22.93	31.12
Area% (Cat. I)	13.85	32.11	17.71	36.32

Area% of Pd(II) and Pd(0) species of 5% Pd/TiO₂ (Cat. D, anatase-type) before and after use (Figure S2).

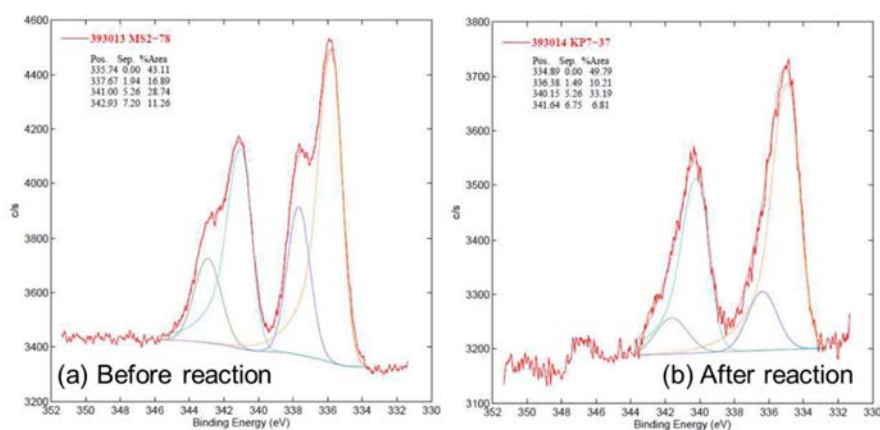


Figure S2. XPS image and curve-fitting of the Pd peaks of 5% Pd/TiO₂ (Cat. D, anatase-type) before and after use.

(a) Before reaction

Position (eV)	342.9	341.0	337.7	335.7
Species	Pd(II) 3d3	Pd(0) 3d3	Pd(II) 3d5	Pd(0) 3d5
Area%	11.26	28.74	16.89	43.11

(b) After reaction

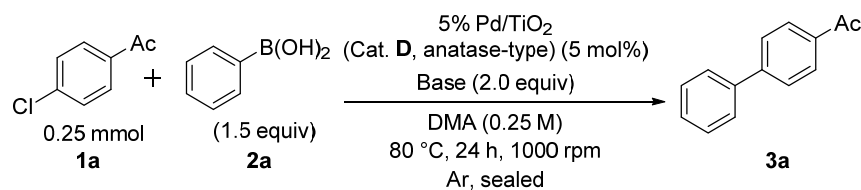
Position (eV)	341.6	340.2	336.4	334.9
Species	Pd(II) 3d3	Pd(0) 3d3	Pd(II) 3d5	Pd(0) 3d5
Area%	6.81	33.19	10.21	47.79

4. Typical procedure for the coupling reaction between aryl chlorides and arylboronic acids

A mixture of 5% Pd/TiO₂ (30.0 mg, 12.5 μ mol), an aryl chloride (250 μ mol), an arylboronic acid (375 μ mol), Cs₂CO₃ (163 mg, 500 μ mol) in DMA (1 mL) was stirred at 80 °C in a test tube tightly sealed under argon. After 24 h, the mixture was cooled to 25 °C, diluted with EtOAc (10 mL) and H₂O (10 mL), and filtered through a membrane filter (pore size: 0.2 μ m). The catalyst on the filter was washed with EtOAc (10 mL) and H₂O (10 mL), and combined filtrates were separated to two layers. The aqueous layer was extracted with EtOAc (15 mL \times 3), and combined EtOAc layers were washed with H₂O (20 mL \times 3) and brine (20 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using hexane/EtOAc as eluents to afford the corresponding biaryl derivative.

5. Optimization of 5% Pd/TiO₂ (anatase-type)-catalyzed Suzuki–Miyaura coupling reaction

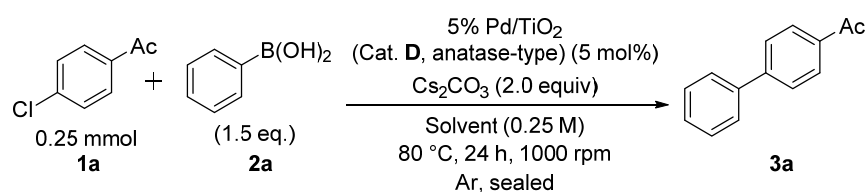
Table S1. Base efficiency.



Entry	Base	Ratio of 1a and 3a ^a
1	Cs ₂ CO ₃	0:100 (99) ^b
2	Na ₂ CO ₃	18:82
3	K ₂ CO ₃	33:73
4	NaHCO ₃	22:78
5	NaOtBu	27:73
6	KOtBu	0:100 (75) ^b
7	Na ₃ PO ₄ · 12H ₂ O	6:94
8	K ₃ PO ₄	22:78

^a Ratios were determined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard. ^b Isolated yield is indicated in parenthesis.

Table S2. Solvent efficiency.



Entry	Solvent	Ratio of 1a and 3a ^a
1	DMA	0:100 (99) ^b
2	DMF	27:73
3	1,4-Dioxane	93:7
4	CPME	90:10
5	Toluene	90:10
7	H ₂ O	94:6
6	CH ₃ OH	85:15
8	2-PrOH	59:41
9	50% 2-PrOH	89:11
10	50% DMA	33:67
11	DMA	100:0 ^c

^a Ratios were determined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard. ^b Isolated yield is indicated in parenthesis. ^c At 25 °C.

Table S3. Time course study.

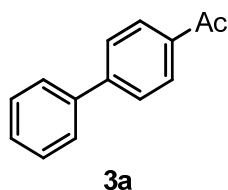
Time	Ratio of 1a and 3a ^a
6 h	62:38
12 h	39:61
20 h	2:98
24 h	0:100 (99) ^b

^a Ratios were determined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard. ^b Isolated yield is indicated in parenthesis.

6. Spectroscopic Data of Products

4-Acetylbiphenyl (**3a**) [CAS Reg. No. 92-91-1]¹

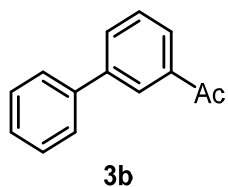
Obtained in 99% yield (48.6 mg, 248 μmol) from 4'-chloroacetophenone (38.6 mg, 250 μmol) and phenylboronic acid (45.7 mg, 375 μmol).



¹H NMR [400 MHz (ECZ-400, CDCl₃)] δ 8.04 (2H d, *J* = 8.0 Hz), 7.69 (2H, d, *J* = 8.0 Hz), 7.63 (2H, d, *J* = 7.6 Hz), 7.48 (2H, t, *J* = 6.8 Hz), 7.41 (1H t, *J* = 6.8 Hz), 2.65 (3H, s); ¹³C NMR (100 MHz, CDCl₃) δ 197.7, 145.7, 139.8, 135.7, 128.9, 128.8, 128.2, 127.2, 127.1, 26.6.

3-Acetylbiphenyl (**3b**) [CAS Reg. No. 3112-01-4]¹

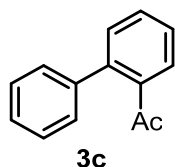
Obtained in 68% yield (33.4 mg, 170 μmol) from 3'-chloroacetophenone (38.6 mg, 250 μmol), phenylboronic acid (61.0 mg, 500 μmol) using 5% Pd/TiO₂ (60mg, 25.0 μmol, Cat. **D**, anatase-type) and Cs₂CO₃ (244.5 mg, 500 μmol).



¹H NMR [400 MHz (ECZ-400, CDCl₃)] δ 8.18 (1H, s), 7.94 (1H, dt, *J* = 1.4 Hz, 8.0 Hz), 7.79 (1H, dt, *J* = 1.6 Hz, *J* = 8.0 Hz), 7.62 (2H, d, *J* = 7.2 Hz), 7.54 (1H, t, *J* = 7.8 Hz), 7.47 (2H, t, *J* = 7.4 Hz), 7.40 (1H, d, *J* = 7.2 Hz), 2.66 (3H, s); ¹³C NMR [100 MHz (ECZ-400, CDCl₃)] δ 198.1, 141.7, 140.2, 137.6, 131.7, 129.0, 128.9, 127.8, 127.2, 126.9 (2C), 26.8.

2-Acetylbiphenyl (**3c**) [CAS Reg. No. 2142-66-7]¹

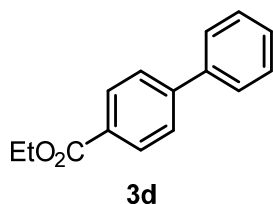
Obtained in 85% yield (41.9 mg, 213 μmol) from 2'-chloroacetophenone (38.6 mg, 250 μmol), phenylboronic acid (61.0 mg, 500 μmol) using 5% Pd/TiO₂ (60mg, 25.0 μmol, Cat. **D**, anatase-type), and Cs₂CO₃ (244.5 mg, 500 μmol).



^1H NMR [400 MHz (ECZ-400, CDCl_3)] δ 7.56–7.49 (2H, m), 7.44–7.34 (7H, m), 2.00 (3H, s); ^{13}C NMR [100 MHz (ECZ-400, CDCl_3)] δ 204.9, 140.8, 140.6, 140.4, 130.7, 130.2, 128.8, 128.6, 127.8, 127.8, 127.4, 30.4.

Ethyl biphenyl-4-carboxylate (3d) [CAS Reg. No. 6301-56-0]¹

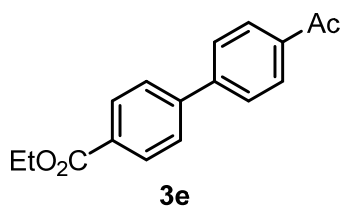
Obtained in 76% yield (43.2 mg, 191 μmol) from ethyl 4-chlorobenzoate (46.2 mg, 250 μmol) and phenylboronic acid (45.7 mg, 375 μmol).



^1H NMR [400 MHz (ECZ-400, CDCl_3)] δ 8.11 (2H, d, J = 8.0 Hz), 7.67–7.61 (4H, m), 7.47 (2H, t, J = 7.4 Hz), 7.39 (1H, t, J = 7.2 Hz), 4.40 (2H, q, J = 7.1 Hz), 1.41 (3H, t, J = 7.1 Hz); ^{13}C NMR [100 MHz (ECZ-400, CDCl_3)] δ 166.4, 145.4, 140.0, 130.0, 129.1, 128.8, 128.0, 127.2, 126.9, 60.9, 14.3.

Ethyl 4'-acetyl-[1,1'-biphenyl]-4-carboxylate(3e) [CAS Reg. No. 119838-61-8]¹

Obtained in 84% yield (56.6 mg, 211 μmol) from ethyl 4'-chlorobenzoate (46.2 mg, 250 μmol) and 4-acetylphenylboronic acid (61.5 mg, 375 μmol).



^1H NMR [400 MHz (ECZ-400, CDCl_3)] δ 8.14 (2H, d, J = 8.2 Hz), 8.05 (2H, d, J = 8.2 Hz), 7.73–7.68 (4H, m), 4.41 (2H, q, J = 6.8 Hz), 2.65 (3H, s), 1.42 (3H, t, J = 6.8 Hz); ^{13}C NMR [100 MHz (ECZ-400, CDCl_3)] δ 197.6, 166.2, 144.5, 144.0, 136.4, 130.1, 130.1, 128.9, 127.3, 127.1, 61.1, 26.7, 14.3.

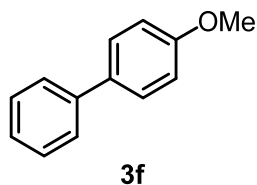
4-Methoxybiphenyl (3f) [CAS Reg. No. 613-37-6]¹

Obtained in 17% yield (7.9 mg, 42.9 μmol) from chlorobenzene (28.0 mg, 250 μmol) and 4-methoxyphenylboronic acid (57.1 mg, 375 μmol) using 5% Pd/TiO₂ (60mg, 25.0 μmol , Cat. **D**, anatase-type) and Cs₂CO₃ (163.0 mg, 500 μmol) in Scheme 1.

Obtained in 42% yield (18.9 mg, 105 μmol) from chlorobenzene (28.0 mg, 250 μmol) and 4-methoxyphenylboronic acid (57.1 mg, 375 μmol) using KO^tBu (56.1 mg, 500 μmol) instead of Cs₂CO₃ in Scheme 1.

Obtained in 24% yield (11.0 mg, 59.7 μmol) from 4-chloroanisole (35.6 mg, 250 μmol) and phenylboronic acid (61.3 mg, 500 μmol) using 5% Pd/TiO₂ (60mg, 25.0 μmol , Cat. **D**, anatase-type) and Cs₂CO₃ (244.7 mg, 750 μmol) in Eq. 1.

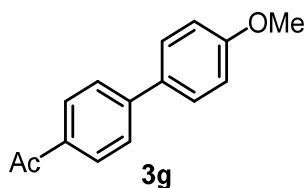
Obtained in 85% yield (39.2 mg, 213 μmol) from 4-bromoanisole (46.8 mg, 250 μmol) and phenylboronic acid (45.7 mg, 375 μmol) in Eq. 1.



^1H NMR [400 MHz (ECZ-400, CDCl_3)] δ 7.54 (4H, t, $J = 9.0$ Hz), 7.43 (2H, t, $J = 7.6$ Hz), 7.32–7.29 (1H, m), 6.99 (2H, d, $J = 8.4$ Hz), 3.86 (3H, s); ^{13}C NMR [100 MHz (ECZ-400, CDCl_3)] δ 159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.

4-Acetyl-4'-methoxybiphenyl (3g) [CAS Reg. No. 13021-18-6]¹

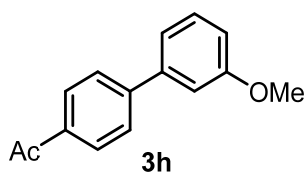
Obtained in 62% yield (34.8 mg, 154 μmol) from 4'-chloroacetophenone (38.6 mg, 250 μmol) and 4-methoxyphenylboronic acid (57.0 mg, 375 μmol).



^1H NMR [400 MHz (ECZ-400, CDCl_3)] δ 8.00 (2H, d, $J = 8.2$ Hz), 7.63 (2H, d, $J = 8.2$ Hz), 7.57 (2H, d, $J = 8.8$ Hz), 6.99 (2H, d, $J = 8.8$ Hz), 3.85 (3H, s), 2.62 (3H, s); ^{13}C NMR [100 MHz (ECZ-400, CDCl_3)] δ 197.7, 159.8, 145.3, 135.2, 132.1, 128.9, 128.3, 126.5, 114.3, 55.3, 26.6.

4-Acetyl-3'-methoxybiphenyl (3h) [CAS Reg. No. 76650-30-1]¹

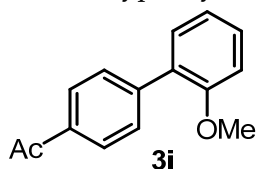
Obtained in 56% yield (31.7 mg, 140 μmol) from 4'-chloroacetophenone (38.6 mg, 250 μmol) and 3-methoxyphenylboronic acid (57.0 mg, 375 μmol).



^1H NMR [400 MHz (ECZ-400, CDCl_3)] δ 8.02 (2H, d, $J = 8.4$ Hz), 7.67 (2H, d, $J = 8.4$ Hz), 7.38 (1H, t, $J = 8.0$ Hz), 7.20 (1H, d, $J = 8.2$ Hz), 7.14 (1H, t, $J = 1.8$ Hz), 6.94 (1H, dd, $J = 8.2$ Hz, 1.8 Hz), 3.87 (3H, s), 2.63 (3H, s); ^{13}C NMR [100 MHz (ECZ-400, CDCl_3)] δ 197.7, 160.0, 145.6, 141.3, 135.9, 129.9, 128.8, 127.2, 119.7, 113.5, 113.0, 55.3, 26.6.

4-Acetyl-2'-methoxybiphenyl (3i) [CAS Reg. No. 52807-17-7]¹

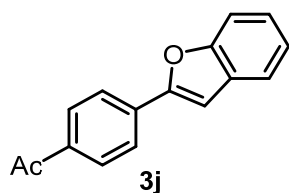
Obtained in 43% yield (24.5 mg, 108 μmol) from 4'-chloroacetophenone (38.6 mg, 250 μmol) and 2-methoxyphenylboronic acid (57.0 mg, 375 μmol).



^1H NMR [400 MHz (ECZ-400, CDCl_3)] δ 8.00 (2H, d, $J = 8.6$ Hz), 7.63 (2H, d, $J = 8.6$ Hz), 7.38–7.32 (2H, m), 7.07–6.99 (2H, m), 3.82 (3H, s), 2.63 (3H, s); ^{13}C NMR [100 MHz (ECZ-400, CDCl_3)] δ 197.9, 156.4, 143.5, 135.4, 130.7, 129.7, 129.4, 129.4, 128.0, 120.9, 111.2, 55.5, 26.6.

1-[4-(2-Benzofuranyl)phenyl]ethanone (3j) [CAS Reg. No. 132932-61-7]¹

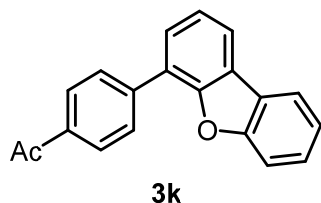
Obtained in 51% yield (29.9 mg, 127 μmol) from 4'-chloroacetophenone (38.6 mg, 250 μmol) and benzofuran-2-boronic acid (60.5 mg, 375 μmol).



^1H NMR [400 MHz (ECZ-400, CDCl_3)] δ 8.03 (2H, d, $J = 8.0$ Hz), 7.93 (2H, d, $J = 8.4$ Hz), 7.61 (1H, d, $J = 7.6$ Hz), 7.54 (1H, d, $J = 7.6$ Hz), 7.33 (1H, dt, $J = 1.2$ Hz, $J = 7.8$ Hz), 7.26 (1H, t, $J = 7.4$ Hz), 7.16 (1H, s), 2.63 (3H, s); ^{13}C NMR [100 MHz (ECZ400, CDCl_3)] δ 197.3, 155.1, 154.5, 136.5, 134.5, 128.9, 128.8, 125.1, 124.7, 123.2, 121.3, 111.3, 103.6, 26.6.

1-[4-(4-dibenzofuranyl)phenyl]ethanone (3k) [CAS Reg. No.756484-37-4]²

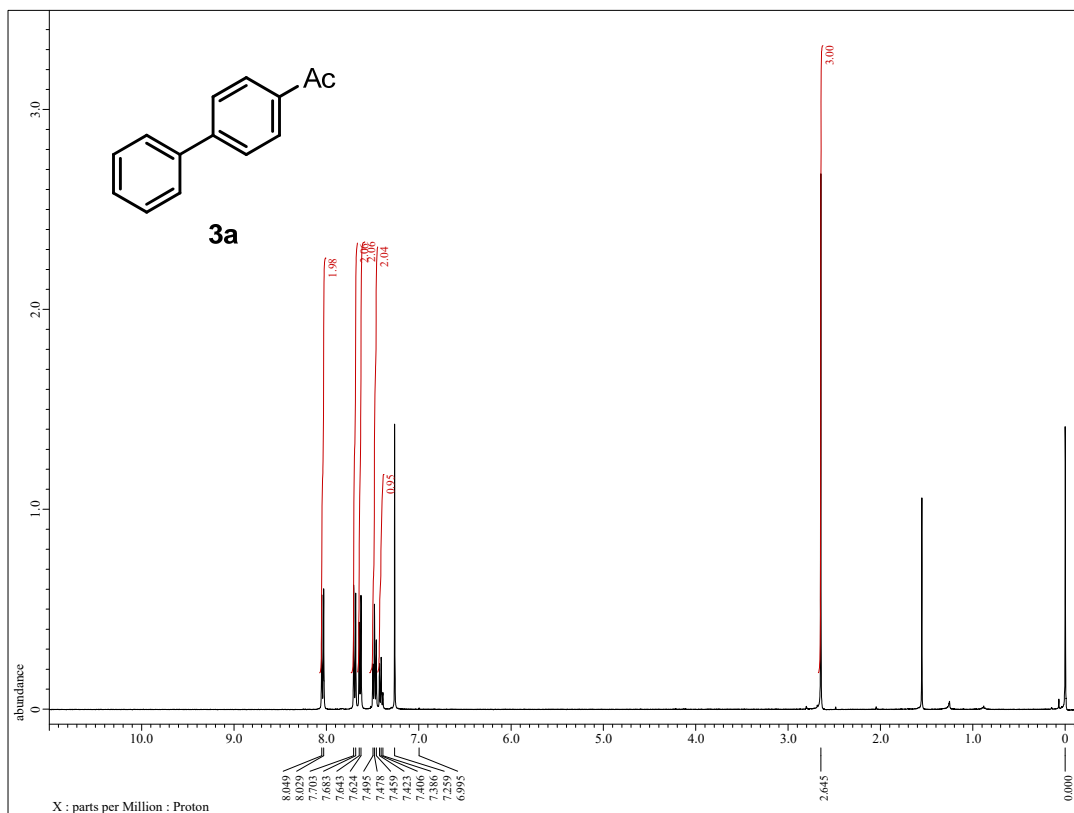
Obtained in 98% yield (70.2 mg, 245 μmol) from ethyl 4'-chloroacetophenone (38.6 mg, 250 μmol) and 4-dibenzofurylboronic acid (79.5 mg, 375 μmol).



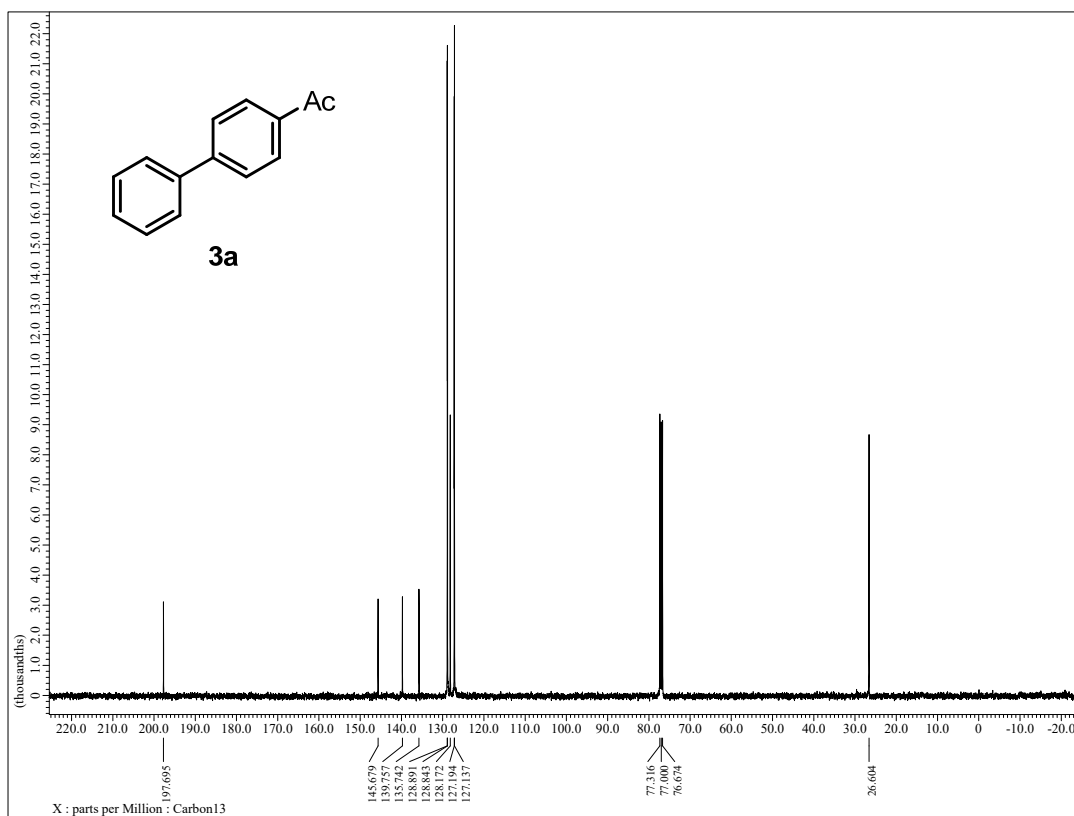
^1H NMR [400 MHz (ECZ-400, CDCl_3)] δ 8.09 (2H, d, $J = 8.8$ Hz), 8.00–7.94 (4H, m), 7.59 (2H, t, $J = 6.2$ Hz), 7.48–7.34 (3H, m), 2.65 (3H, s); ^{13}C NMR [100 MHz (ECZ-400, CDCl_3)] δ 197.7, 156.0, 153.2, 141.1, 136.0, 128.8, 128.6, 127.4, 126.7, 125.1, 124.4, 123.9, 123.2, 122.9, 120.7, 120.6, 111.8, 26.6.

7. ^1H and ^{13}C NMR spectra of products

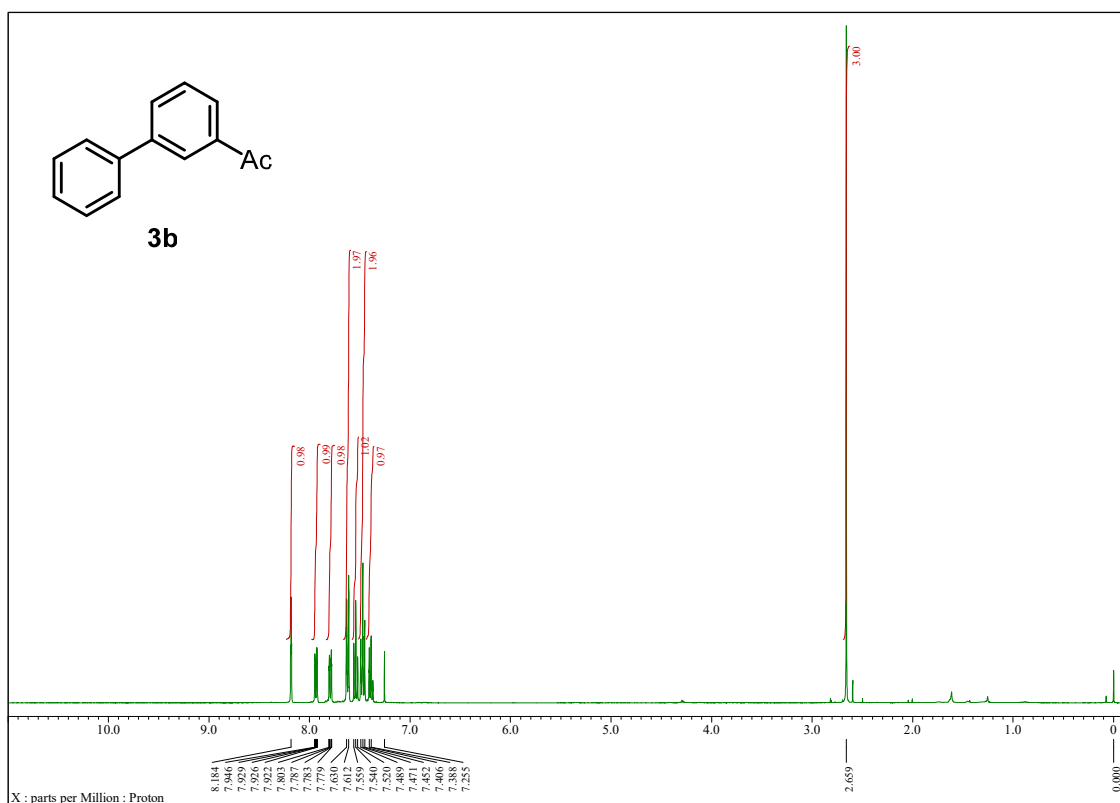
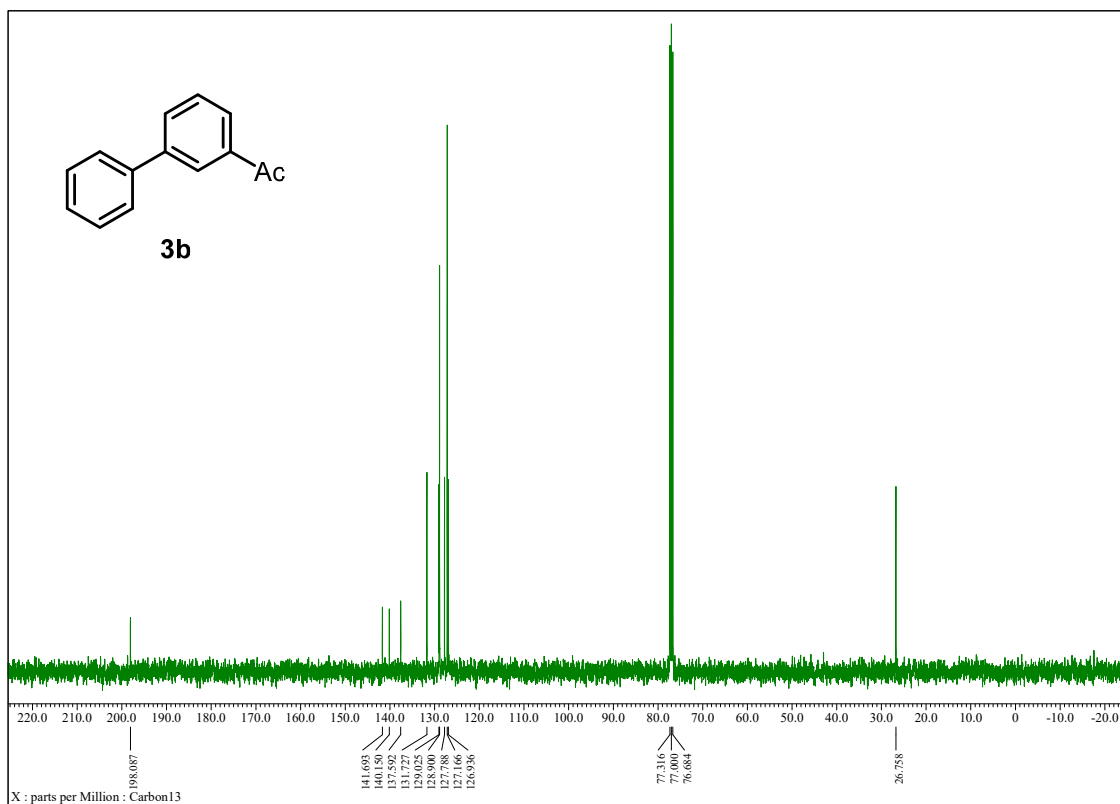
^1H NMR of 4-acetylbiphenyl (3a)

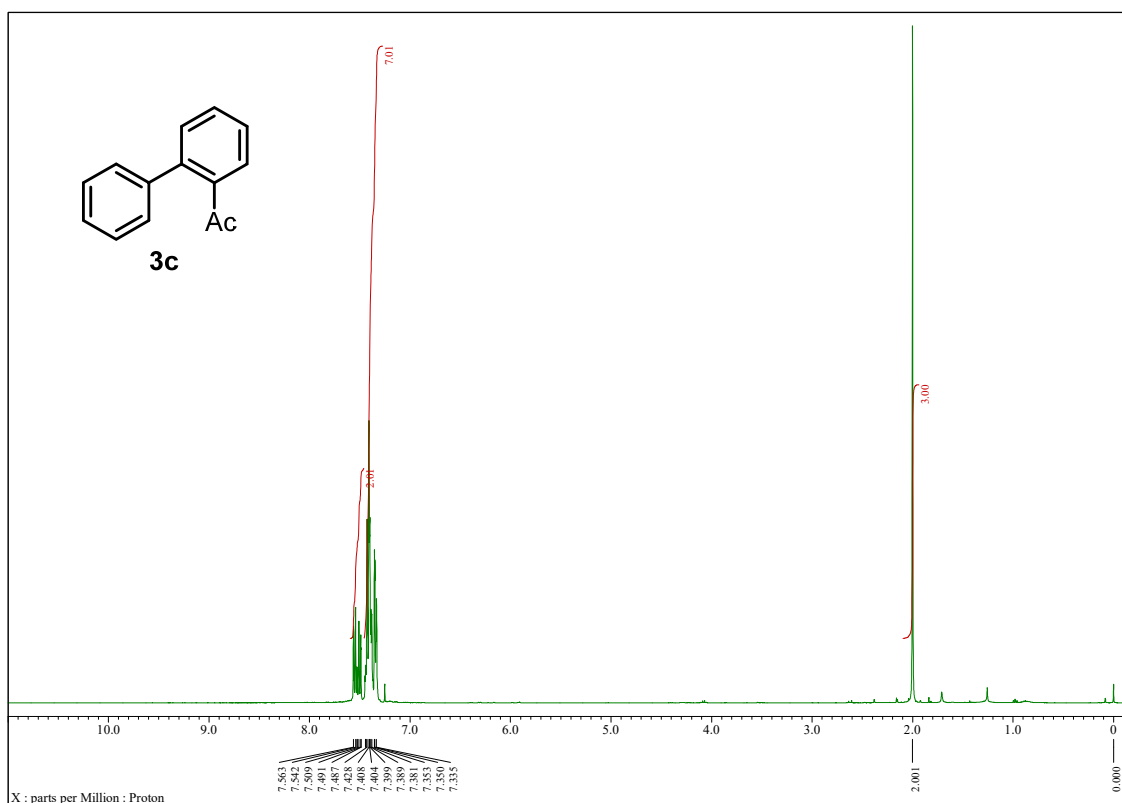
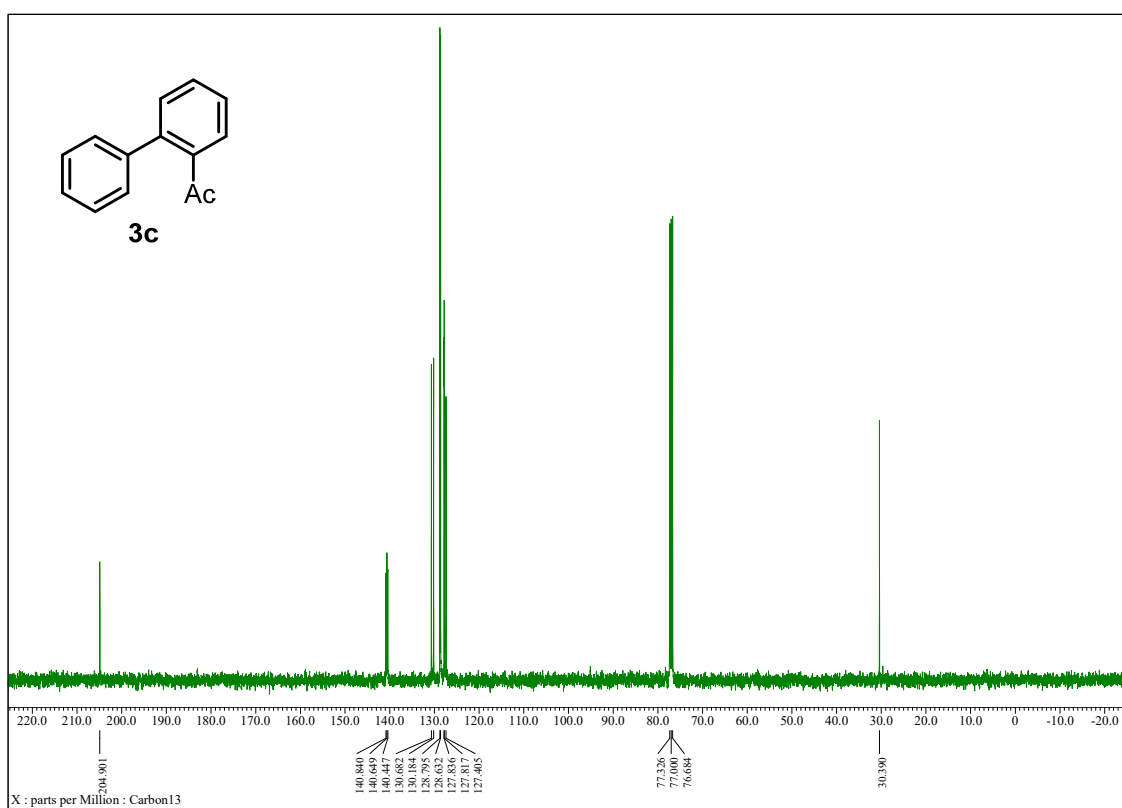


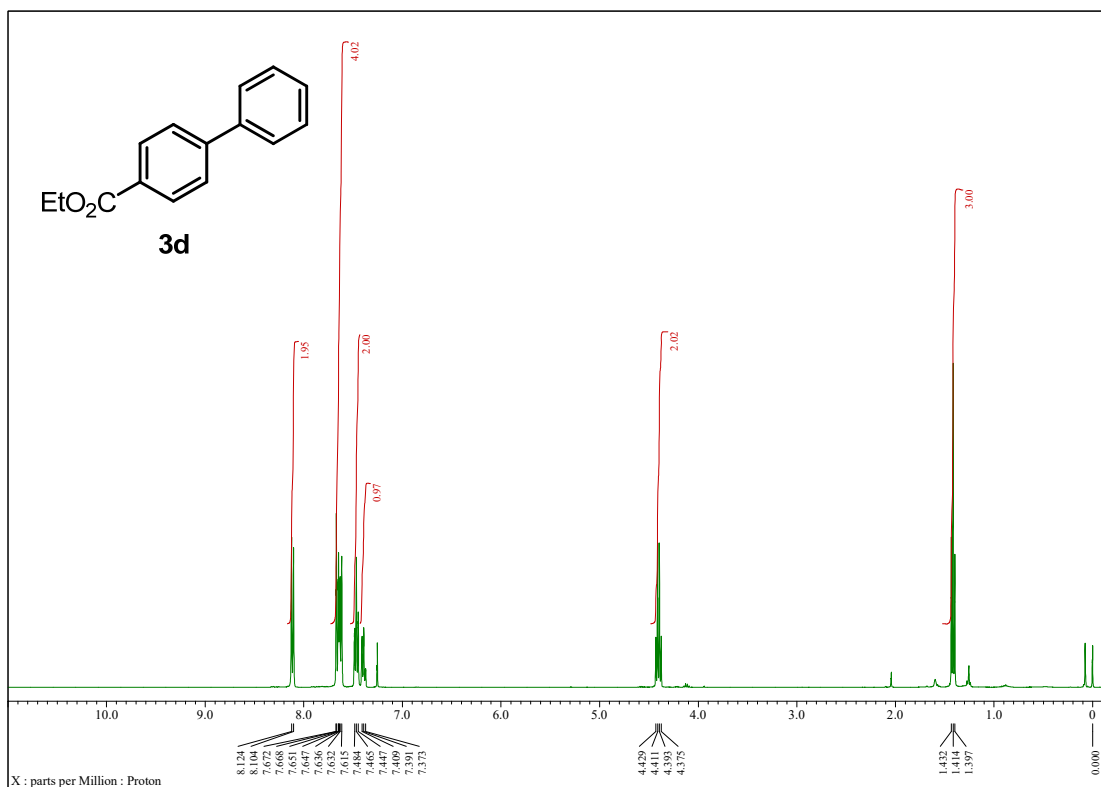
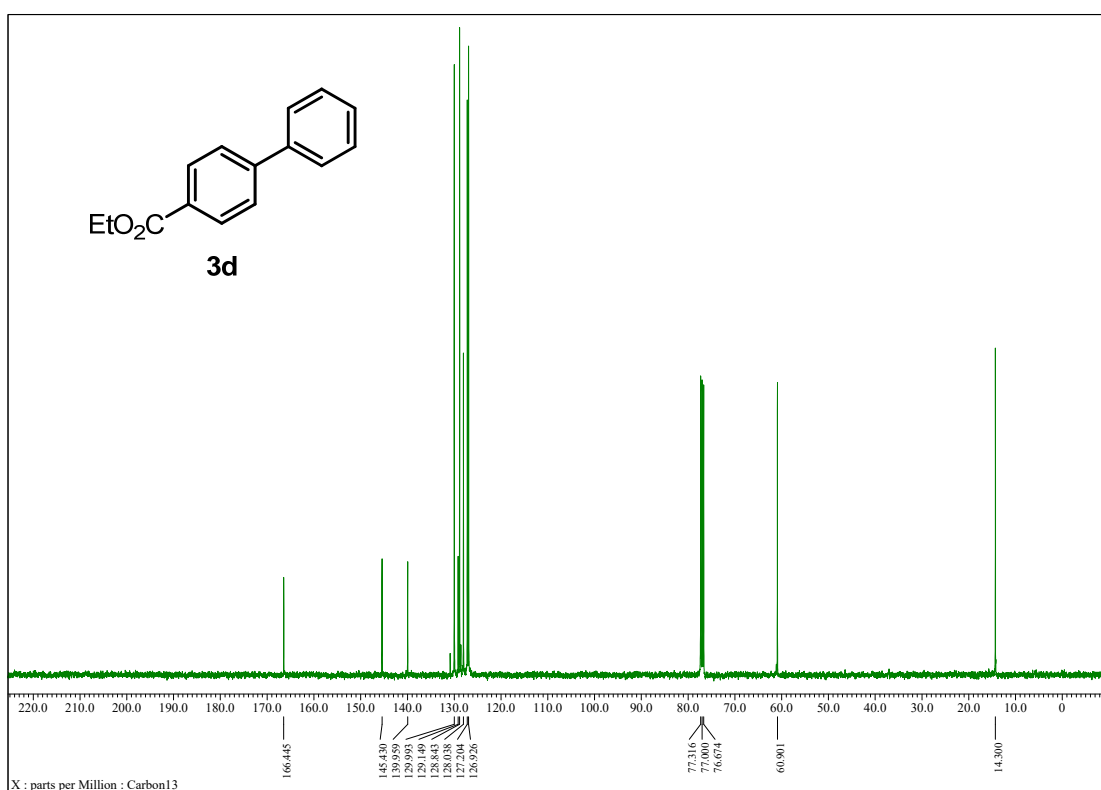
^{13}C NMR of 4-acetylbiphenyl (3a)

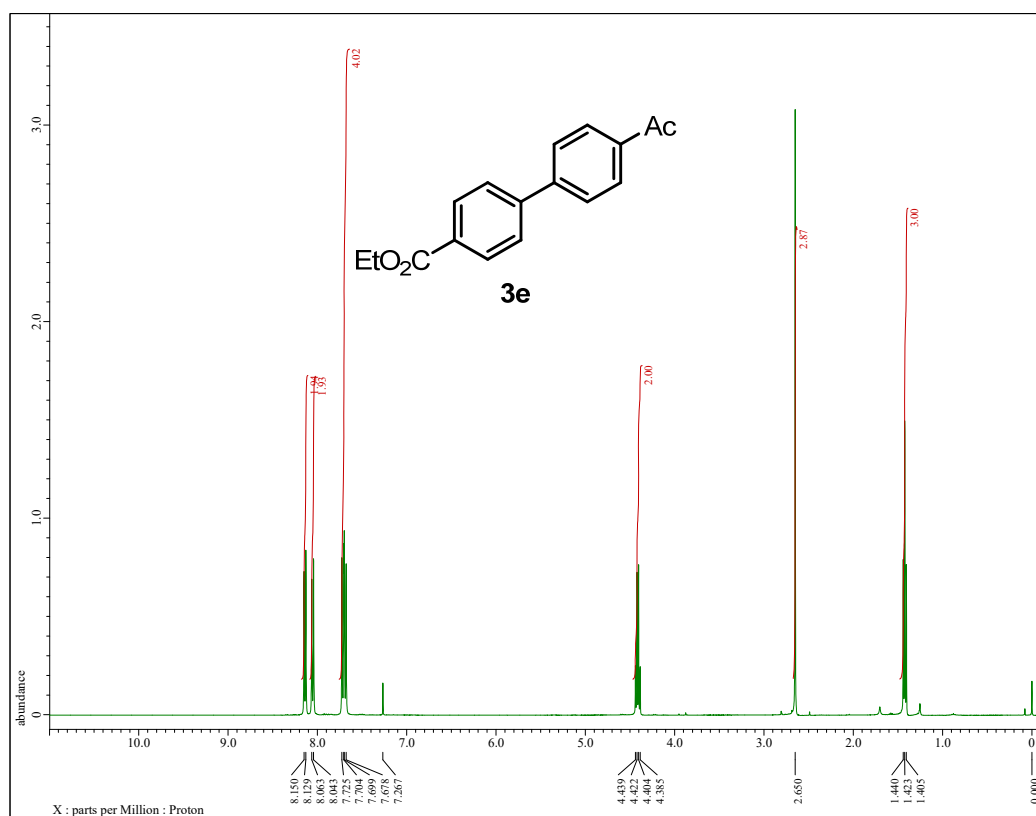


^1H NMR of 3-acetylbiphenyl (3b)

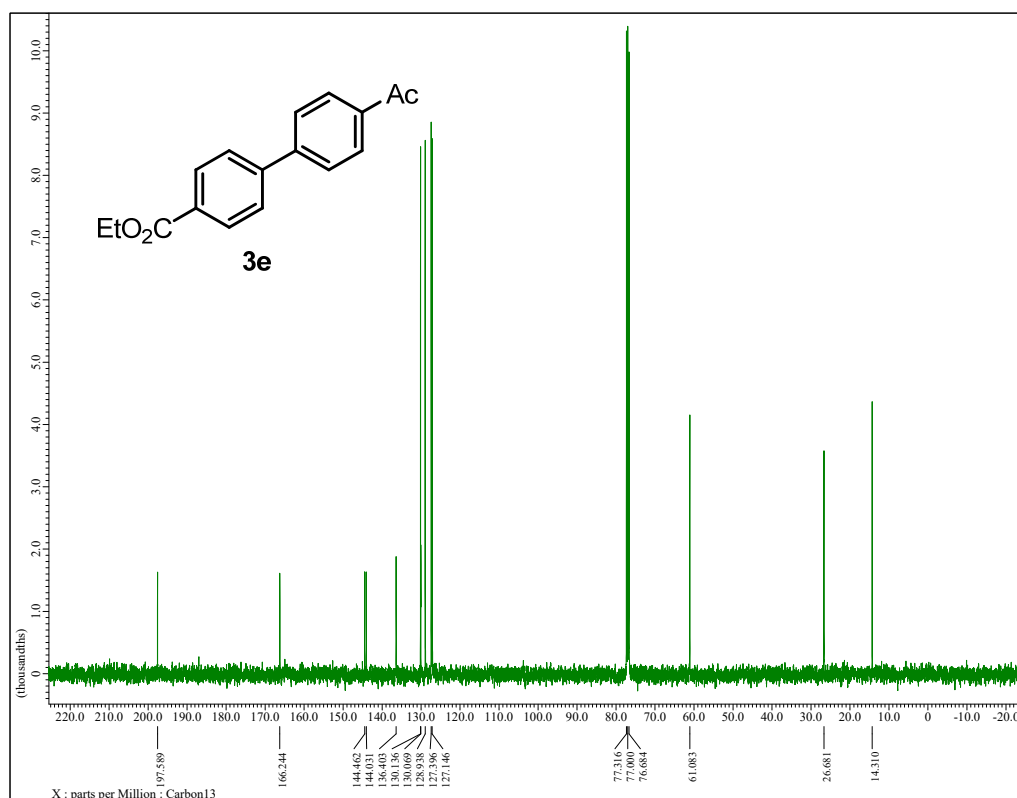
¹³C NMR of 3-acetylbiphenyl (3b)¹H NMR of 2-acetylbiphenyl (3c)

**¹³C NMR of 2-acetylbiphenyl (3c)****¹H NMR of ethyl biphenyl-4-carboxylate (3d)**

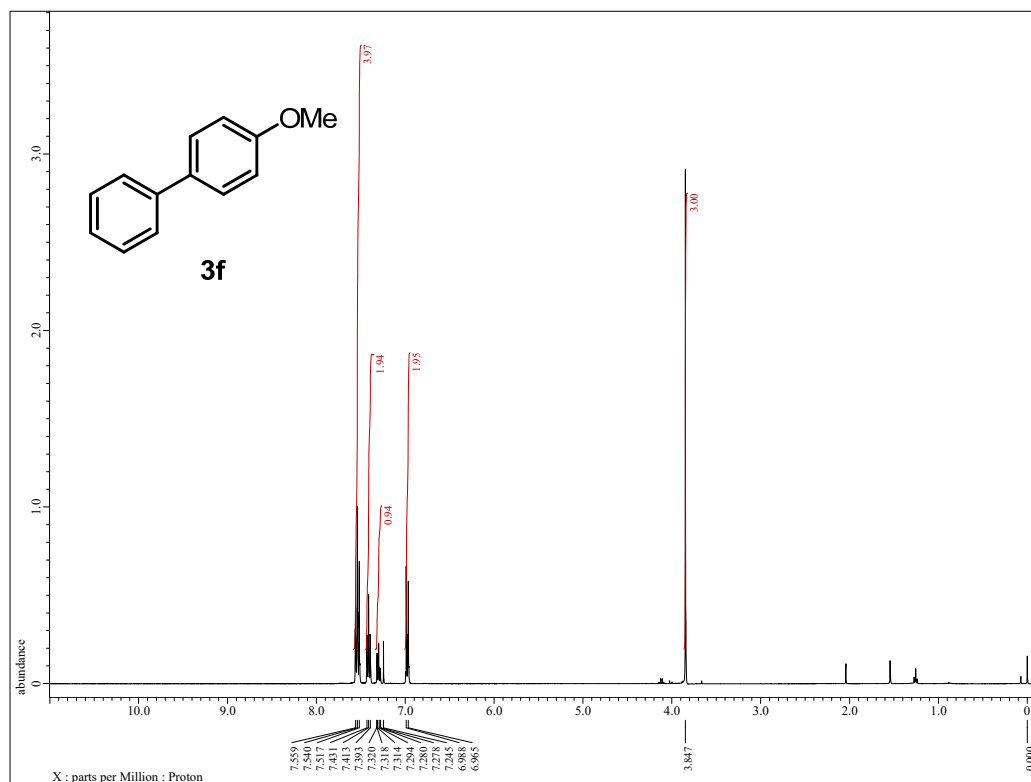
**¹³C NMR of ethyl biphenyl-4-carboxylate (3d)****¹H NMR of ethyl 4'-acetyl-[1,1'-biphenyl]-4-carboxylate (3e)**



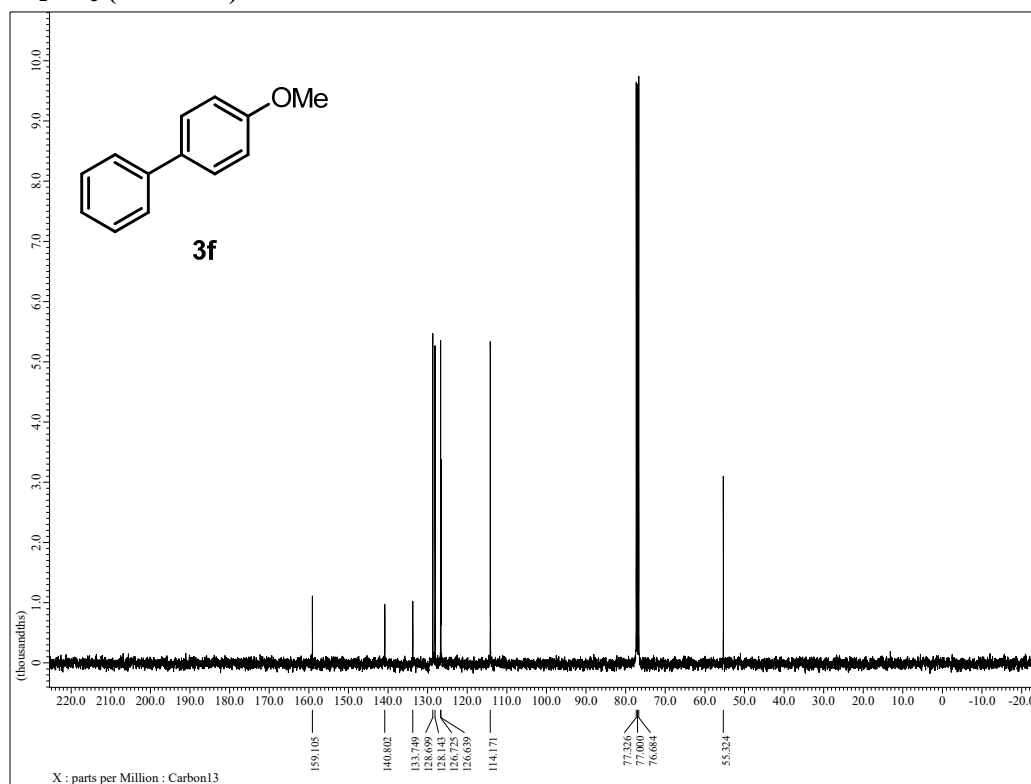
¹³C NMR of ethyl 4'-acetyl-[1,1'-biphenyl]-4-carboxylate (3e)



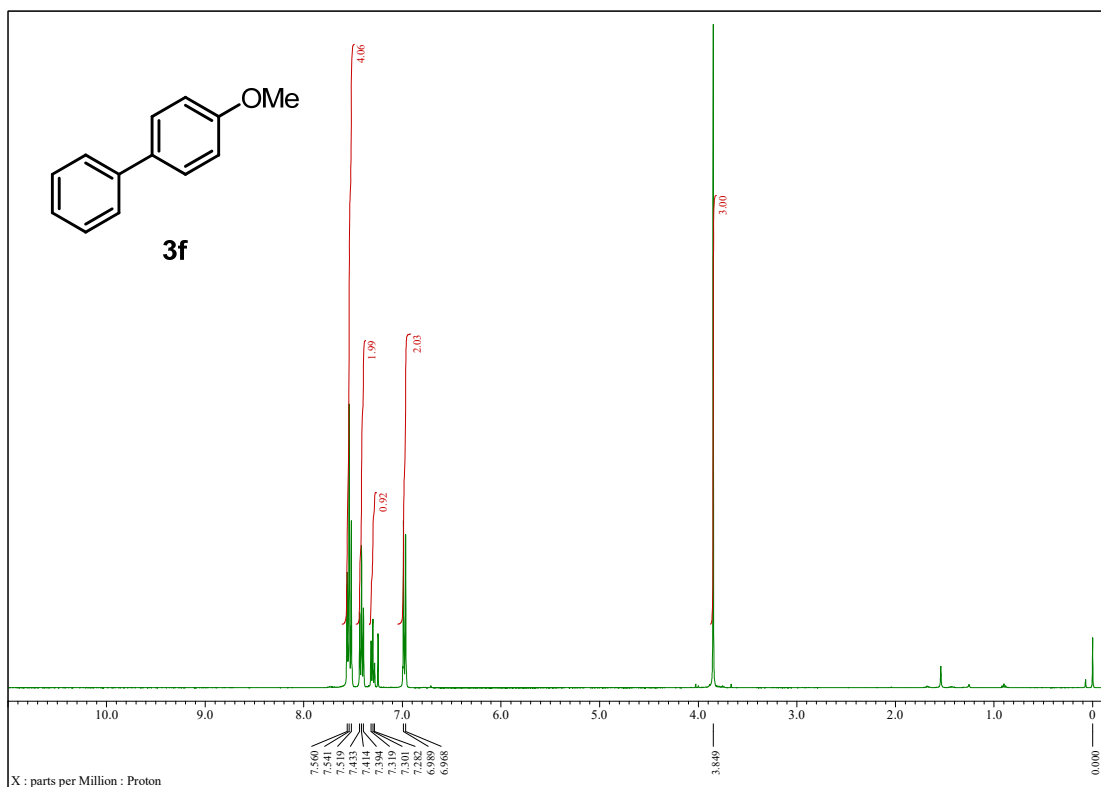
¹H NMR of 4-methoxybiphenyl (3f) from chlorobenzene and 4-methoxyphenylboronic acid using Cs₂CO₃ (Scheme 1)



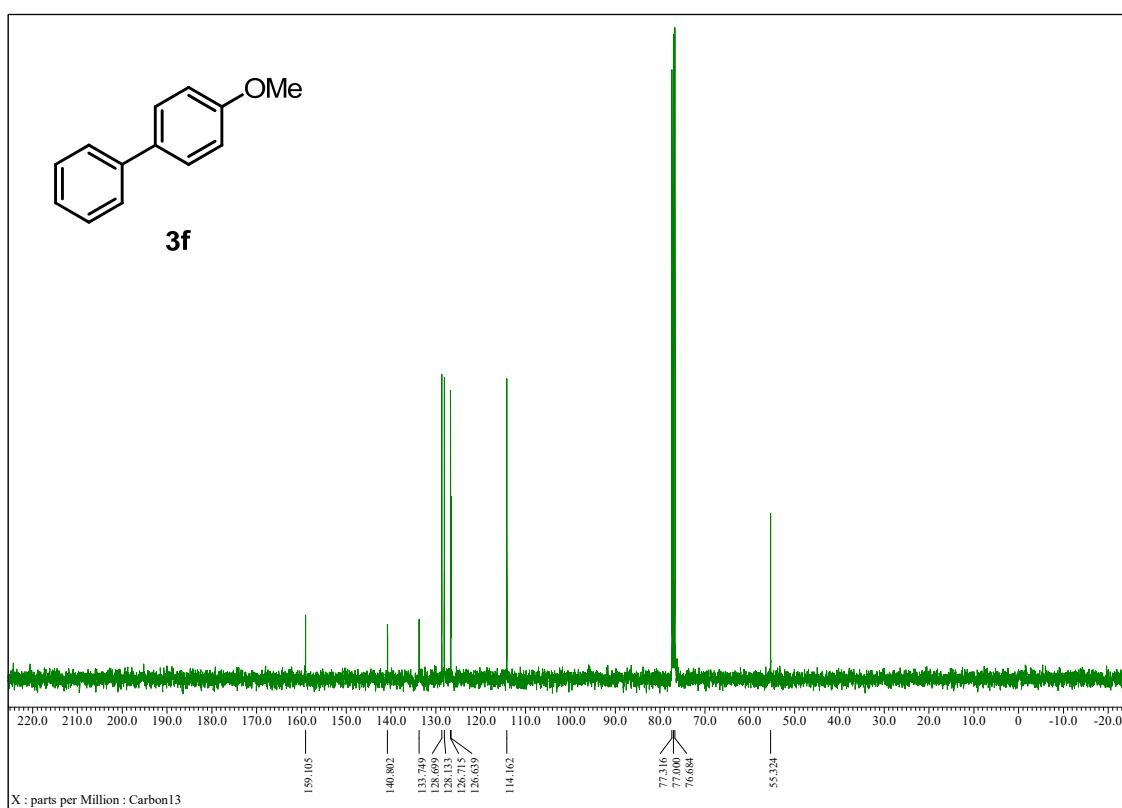
¹H NMR of 4-methoxybiphenyl (3f) from chlorobenzene and 4-methoxyphenylboronic acid using Cs₂CO₃ (Scheme 1)



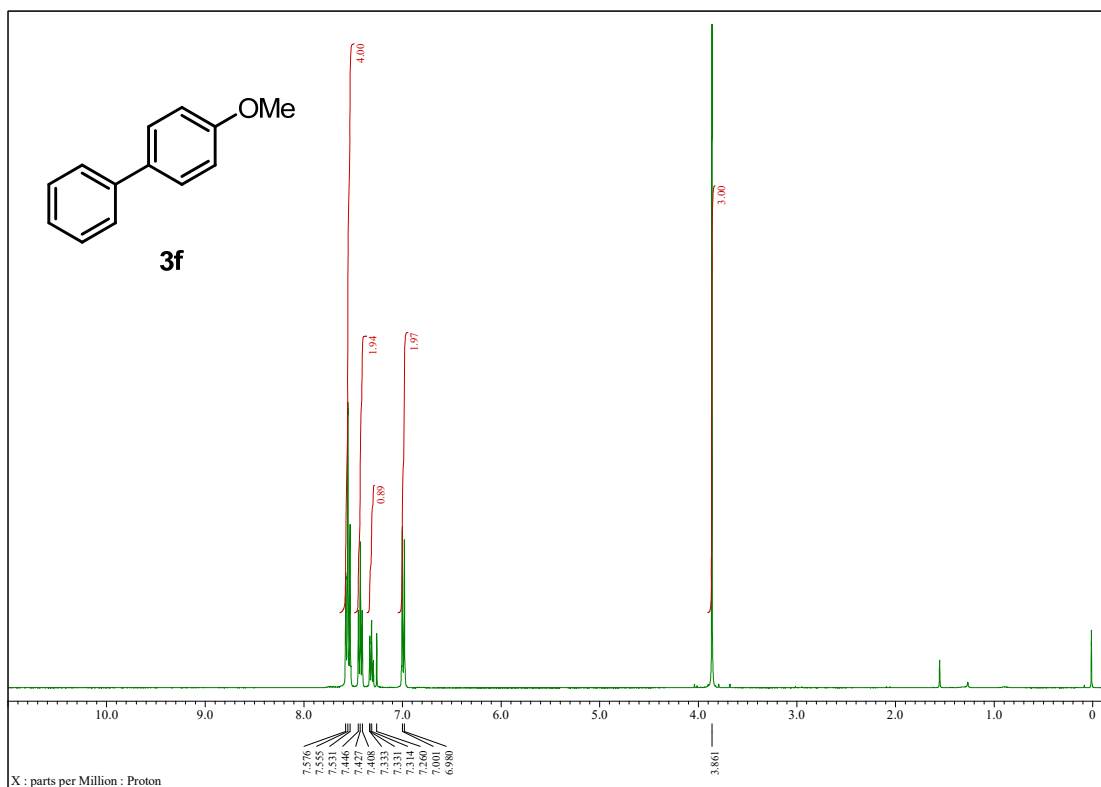
¹³C NMR of 4-methoxybiphenyl (3f) from chlorobenzene and 4-methoxyphenylboronic acid using KOtBu instead of Cs₂CO₃ (Scheme 1)



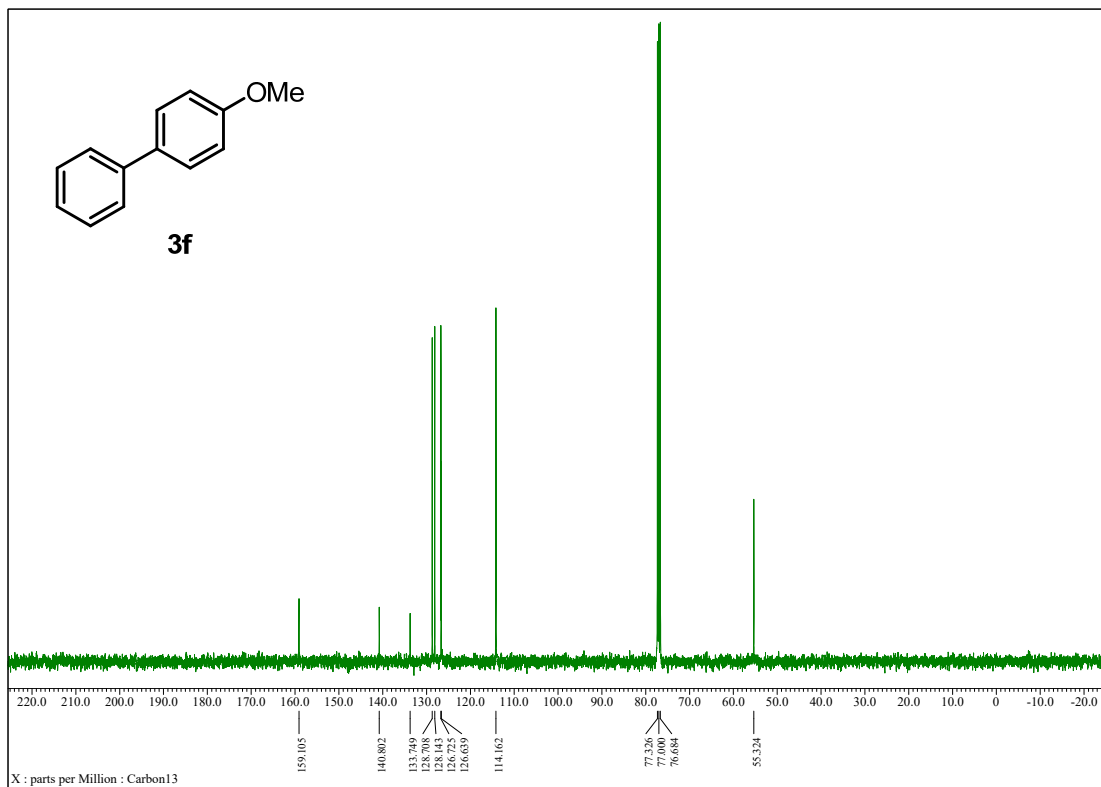
¹H NMR of 4-methoxybiphenyl (3f) from chlorobenzene and 4-methoxyphenylboronic acid using KO^tBu instead of Cs₂CO₃ (Scheme 1)

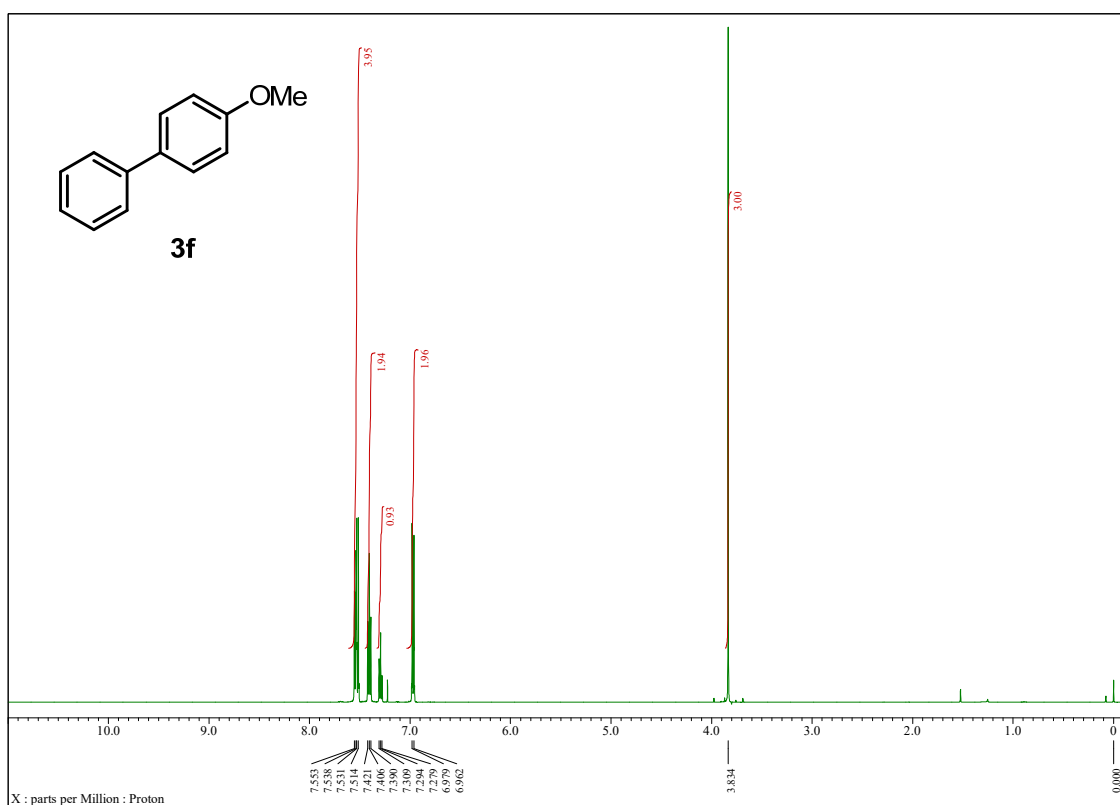
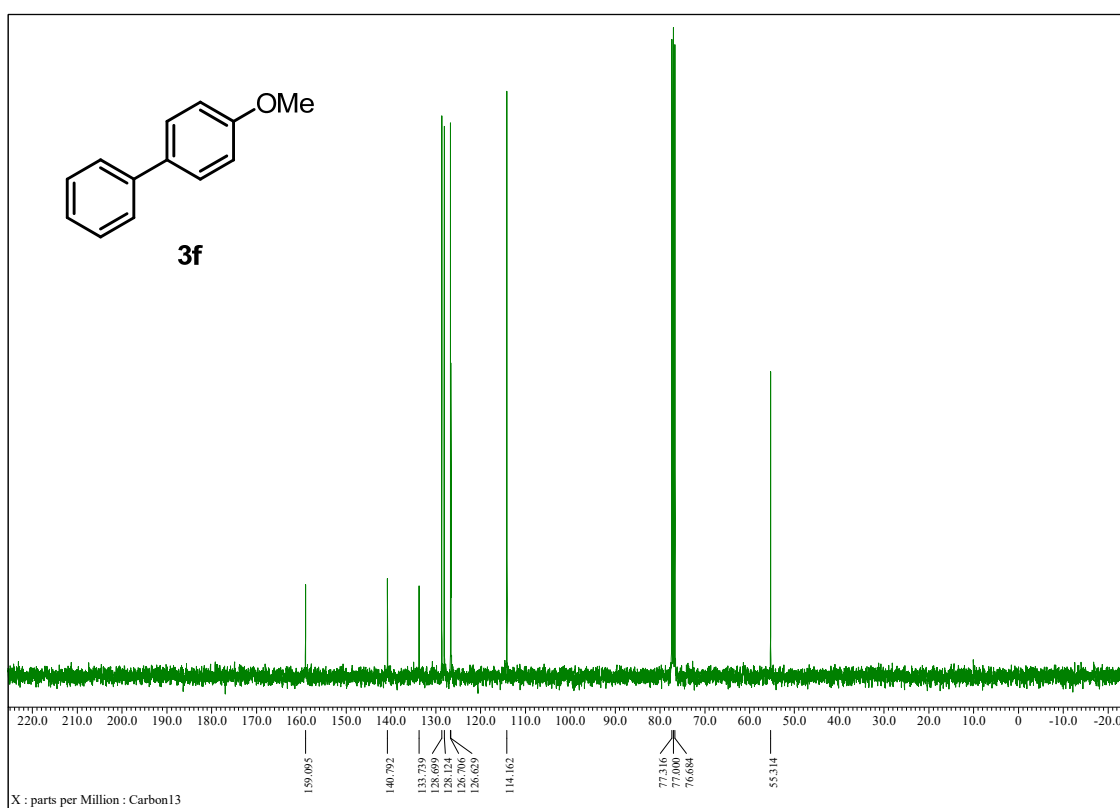


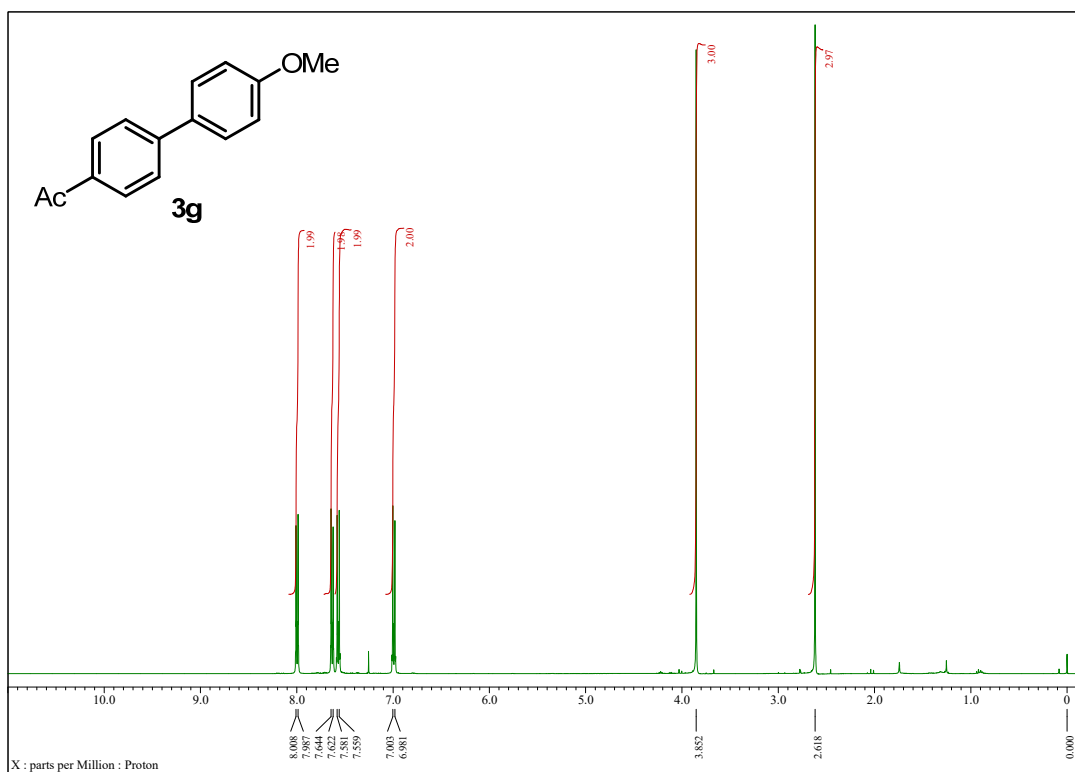
¹³C NMR of 4-methoxybiphenyl (3f) from 4-chloroanisole and phenylboronic acid using Cs₂CO₃ (eq. 1)



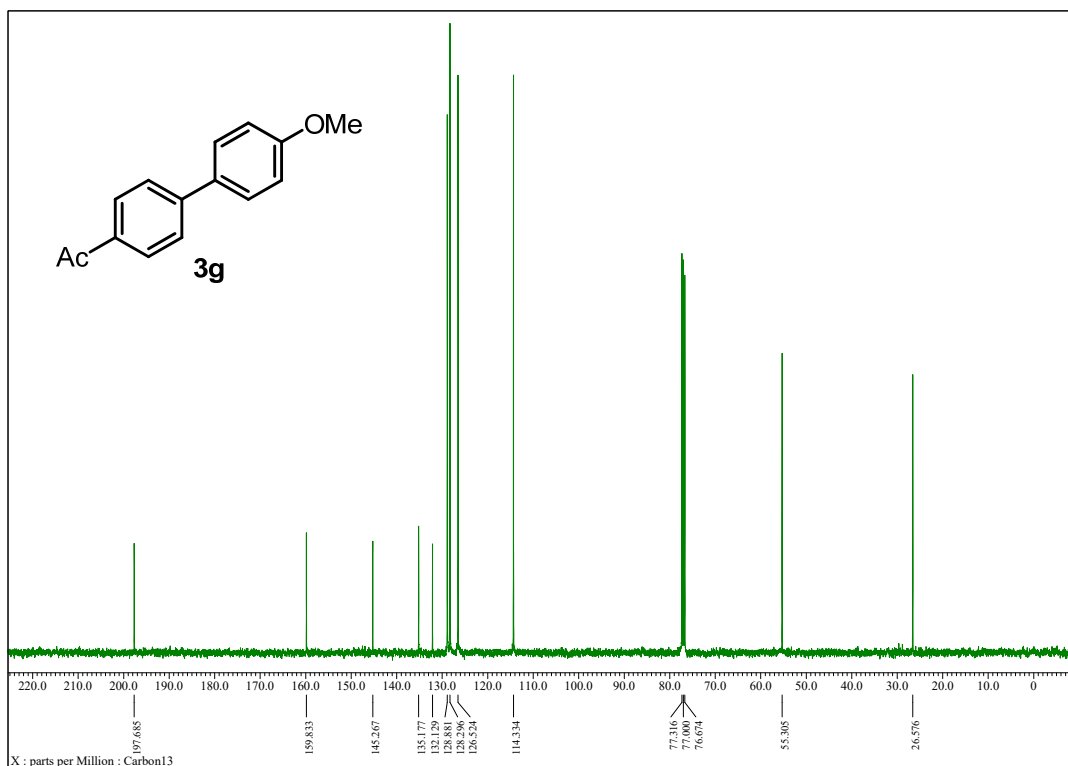
¹³C NMR of 4-methoxybiphenyl (3f) from 4-chloroanisole and phenylboronic acid using Cs₂CO₃ (eq. 1)



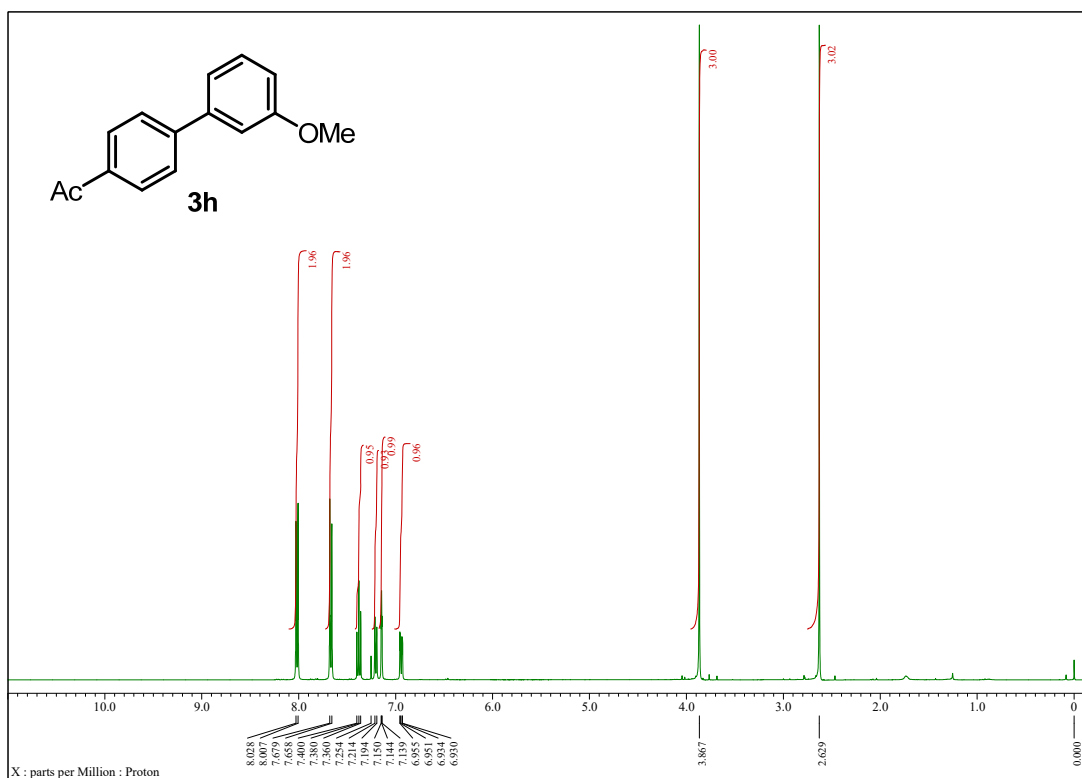
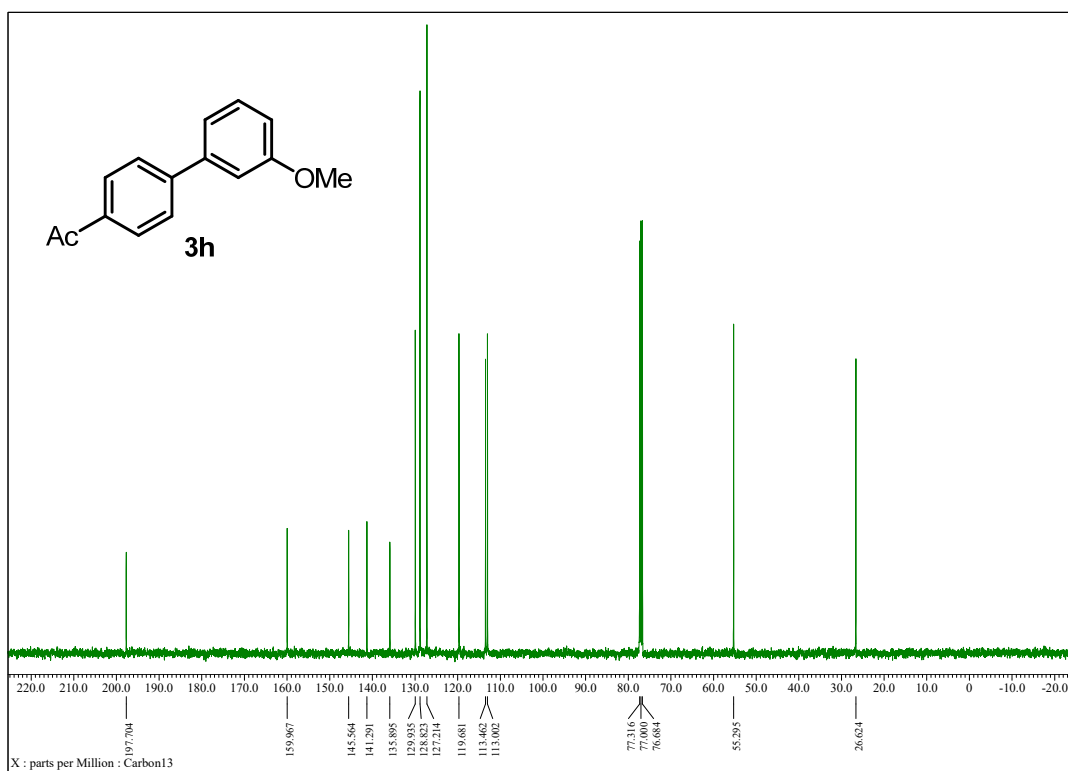
¹H NMR of 4-methoxybiphenyl (3f) from 4-bromoanisole and phenylboronic acid (eq. 1)**¹³C NMR of 4-methoxybiphenyl (3f) from 4-bromoanisole and phenylboronic acid (eq. 1)****¹H NMR of 4-acetyl-4'-methoxybiphenyl (3g)**

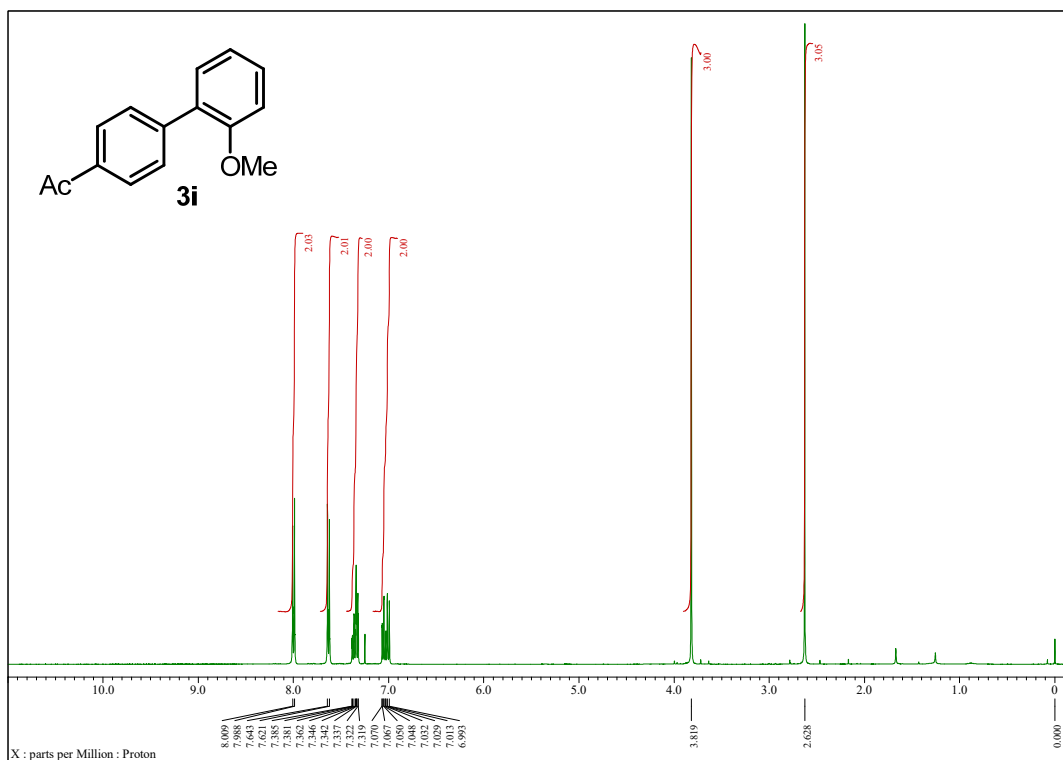
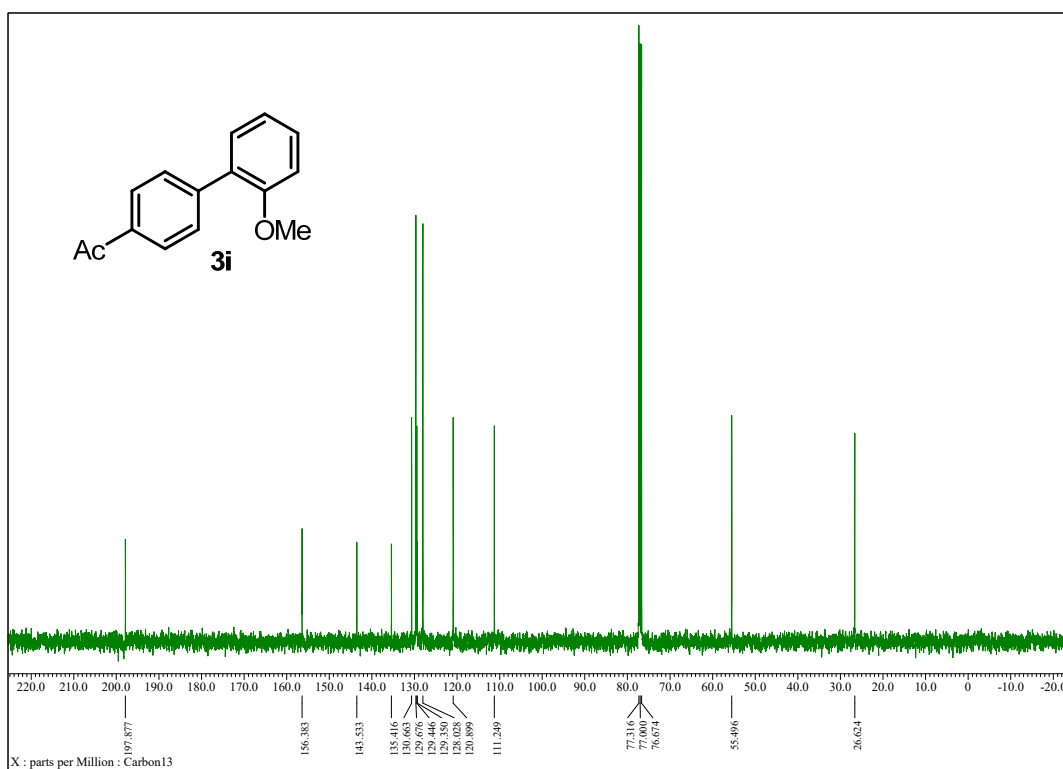


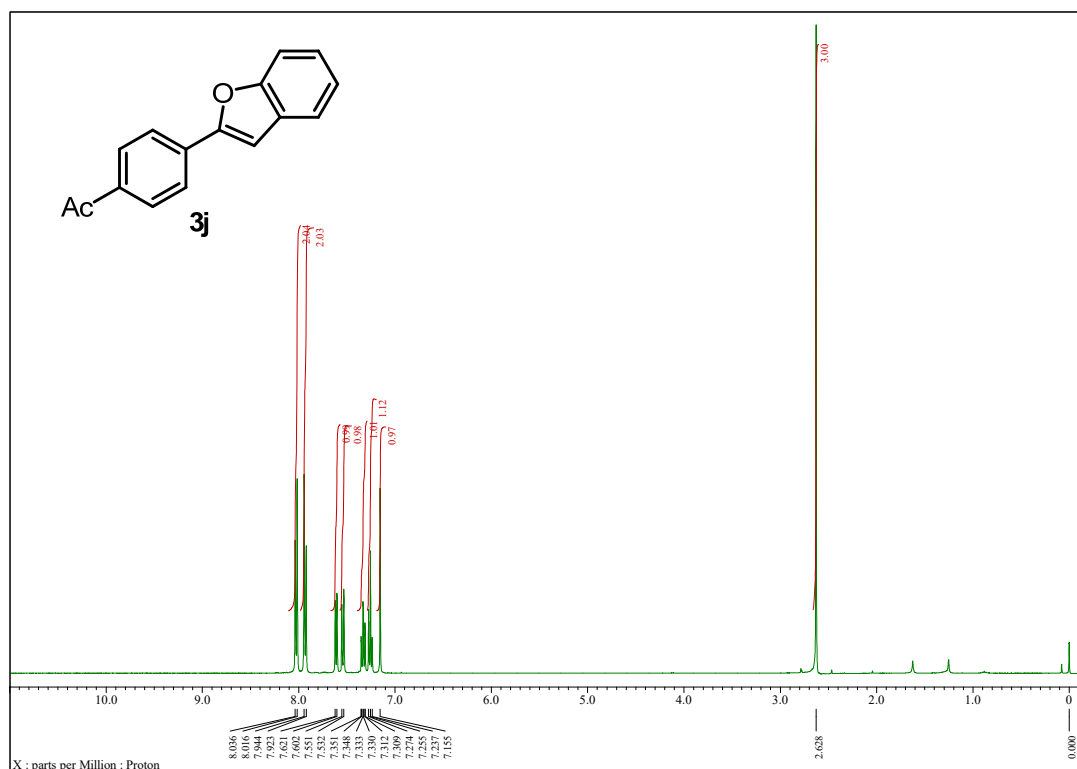
¹³C NMR of 4-acetyl-4'-methoxybiphenyl (**3g**)



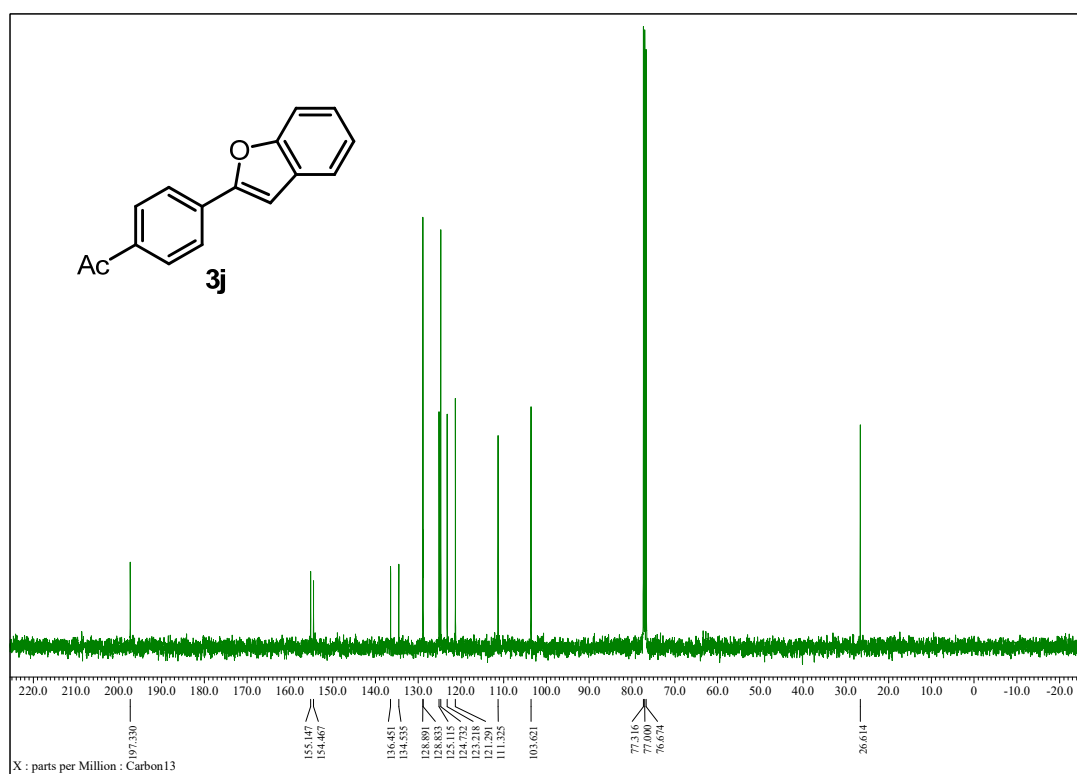
¹H NMR of 4-acetyl-3'-methoxybiphenyl (**3h**)

**¹³C NMR of 4-acetyl-3'-methoxybiphenyl (3h)****¹H NMR of 4-acetyl-2'-methoxybiphenyl (3i)**

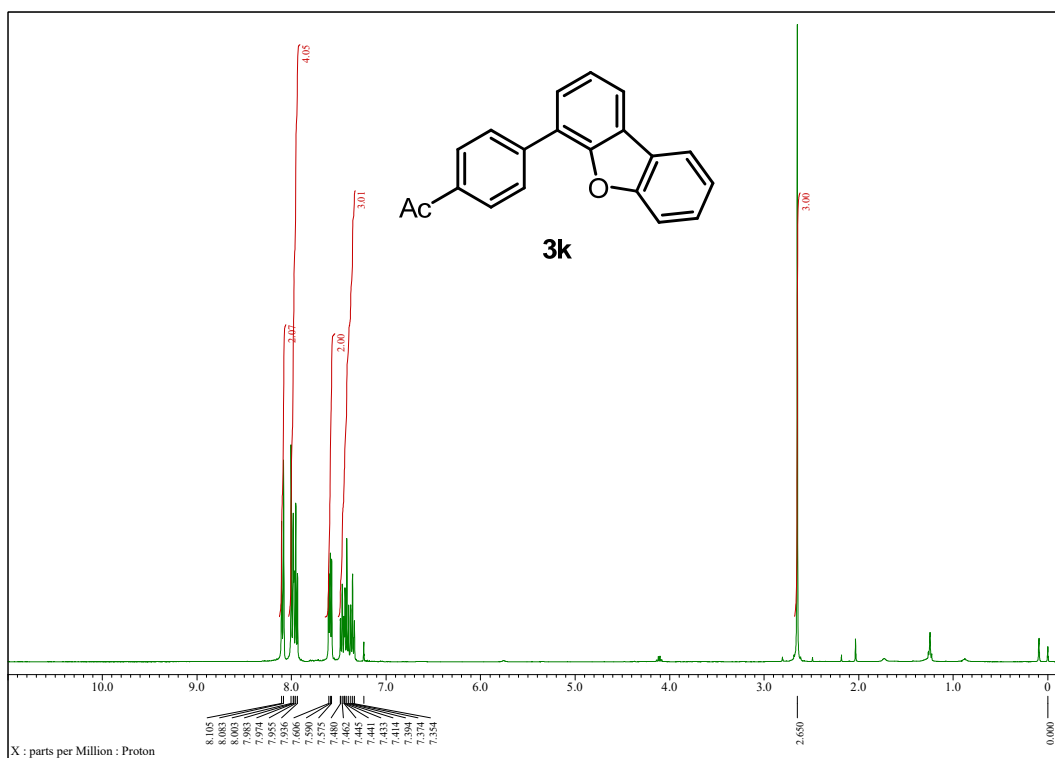
**¹³C NMR of 4-acetyl-2'-methoxybiphenyl (3i)****¹H NMR of 1-[4-(2-benzofuranyl)phenyl]ethanone (3j)**



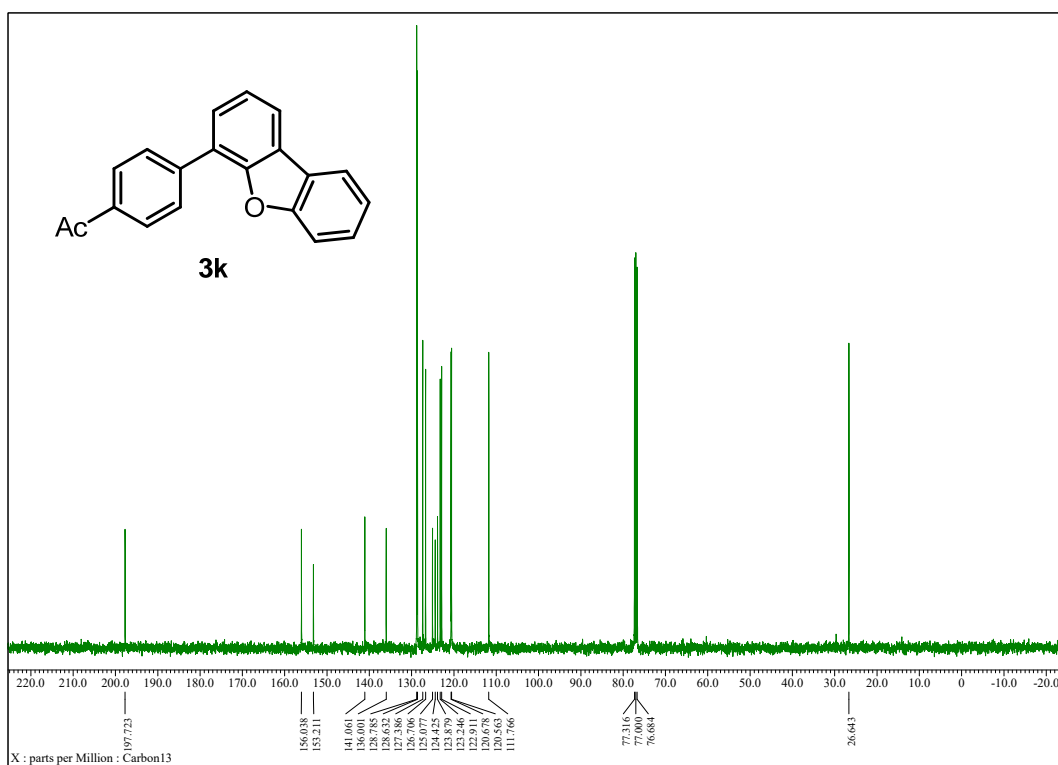
¹³C NMR of 1-[4-(2-benzofuranyl)phenyl]ethanone (3j)



¹H NMR of 1-[4-(4-dibenzofuranyl)phenyl]ethanone (3k)



¹³C NMR of 1-[4-(4-dibenzofuranyl)phenyl]ethanone (3k)



8. References

- 1) Tomohiro, I.; Moeko Netsu, Masahiro Mizuno, Tomoteru Mizusaki, Yukio Takagi, Yoshinari Sawama, Yasunari Monguchi, Hironao Sajiki, *Adv. Synth. Catal.* **2017**, 359, 2269–2279.
- 2) Visannagari Ramakrishna, Morla Jhansi Rani, Nareddula Dastagiri Reddy, *Eur. J. Org. Chem.* **2017**, 7238–7255.