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Supporting Information

Transition-Metal-Free Oxidative Cross-Coupling of Tetraarylborates to Biaryls Using Organic Oxidants

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Supporting Information

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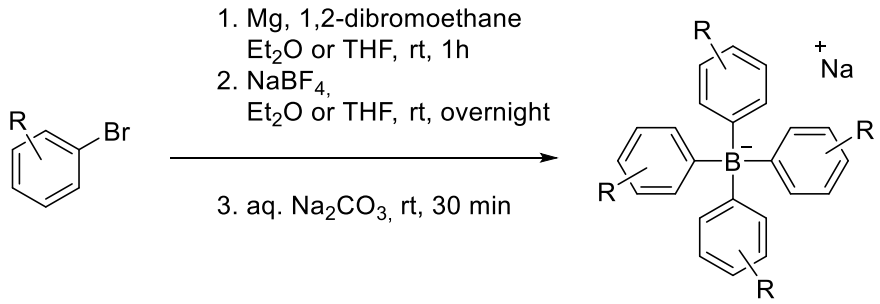
General Information

All reactions involving air or moisture sensitive reagents were carried out in flame-dried glass ware under argon atmosphere using standard Schlenk techniques. Solvents used in reactions were either freshly distilled or obtained in extra-dry grade from commercial sources. Diethyl ether (Et_2O) was refluxed over K and freshly distilled from K-Na-alloy (4:1) afterwards. Tetrahydrofuran (THF) was refluxed over Na and distilled from K afterwards. Acetonitrile (MeCN, 99.9%, Extra Dry over Molecular Sieves) was purchased from *Acros Organics*. Solvents for extraction and for flash chromatography were distilled. *n*-Buthyllithium and phenyllithium were purchased from *Sigma Aldrich*. Sodium tetraphenylborate (**2b**) and potassium tetrakis(2-thienyl)borate (**2g**) were purchased from *Sigma Aldrich*, tetrakis(4-chlorophenyl)borate (**2h**) was purchased from *TCI* and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (**2i**) was purchased from Alfa Aesar. All other chemicals were purchased from *ABCR, Acros Organics, Alfa Aesar, Sigma Aldrich, Fluorochem* and *TCI* and were used as received. Flash chromatography (FC) was performed on Merck silica gel 60 (40 – 63 µm) with an excess argon pressure up to 0.5 bar. Merck silica gel 60 F254 plates were used for thin layer chromatography (TLC) using UV light (254/366 nm) or oxidation with $KMnO_4$ (1.5 g in 200 mL H_2O, 5 g $NaHCO_3$) for detection. Melting points (m.p.) were determined with a Stuart SMP10 and are uncorrected. Infrared spectra (IR) were measured on a Digilab 3100 FT-IR Excalibur Series spectrometer and the position of the absorption bands is given in wave numbers v (cm-1). ^{1}H NMR (300 MHz, 400 MHz and 600 MHz), ^{13}C NMR (75 MHz, 100 MHz and 151 MHz), ^{19}F NMR (282 MHz and 564 MHz) and ^{11}B NMR (96 MHz, 128 MHz and 192 MHz) spectra were measured on a Bruker DPX 300, Bruker AV 300, Bruker AV 400 or an Agilent DD2 600 spectrometer. The multiplicity of all signals were described as *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet) and *m* (multiplet). Chemical shifts (δ in ppm) were referenced on the residual peak of $CDCl_3$ (^{1}H NMR: δ = 7.26; ^{13}C NMR: δ = 77.0), DMSO-d_6 (^{1}H-NMR: δ = 2.50; ^{13}C-NMR: δ = 39.52) or acetone-d_6 (^{1}H-NMR: δ = 2.05; ^{13}C-NMR: δ = 29.84). GC/MS (EI, 70 eV) was conducted on an Agilent 6890N chromatograph with a HP-5 column combined with a WatersMicromass Quatro Micro spectrometer. Helium (1 bar) was used as a carrier gas and the analysis of the data was executed with MassLinx 4.0 from Waters-Micromass. HRMS (ESI) was recorded on a Bruker Daltonics Micro-TOF, or a Thermo Fisher Scientific LTQ Orbitrap XL and peaks are given in m/z. GC-HRMS (EI) was recorded on a Thermo Fisher Scientific Exactive GC-MS. Medium Pressure Liquid Chromatography (MPLC) was used with an automatic flash-system by Reverleris® IES from Grace Davidson with C18 Reverleris® cartridges 4 g as stationary phase. Detection was carried out with UV-absorption (λ = 210 nm, 230 nm).

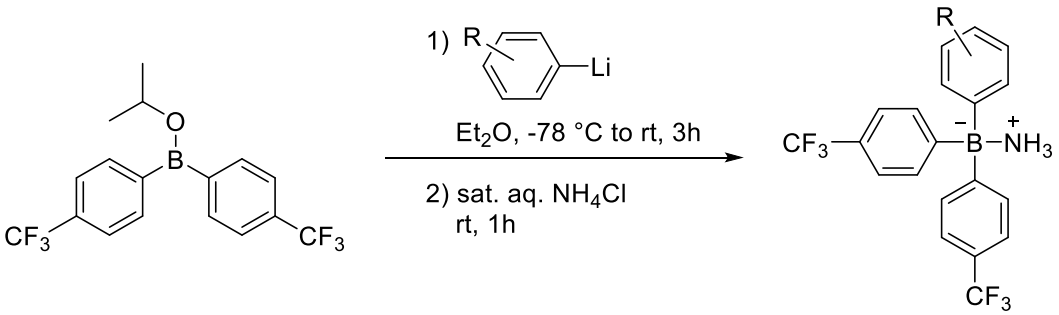
1 General Procedures

1.1 General Procedure for the Synthesis of Tetraarylborates (GP1)



In analogy to a procedure of *Hayashi* et al.,[1] a few drops of 1,2-dibromoethane were added to a suspension of Mg turnings (6.6 or 5.5 equiv.) in THF or Et_2O without stirring. A solution of arylbromide (5.0 or 5.5 equiv.) in THF and/or Et_2O was added slowly. After the start of the reaction (in some cases heating the reaction mixture with a heatgut war necessary) stirring of the solution was started and the arylbromide solution was added dropwise over 60 minutes. The resulting mixture was further stirred for 1 h at room temperature. Sodium tetrafluoroborate (1.0 equiv.) was added and the mixture was stirred for 24 h before pouring it into a solution of Na_2CO_3 in water and stirring for 30 minutes. After filtration the filtrate was extracted with Et_2O, dried over Na_2SO_4 and concentrated *in vacuo.* The resulting solid was washed with pentane/DCM and dried under vacuum to afford the desired sodium tetraarylborate as a white solid.

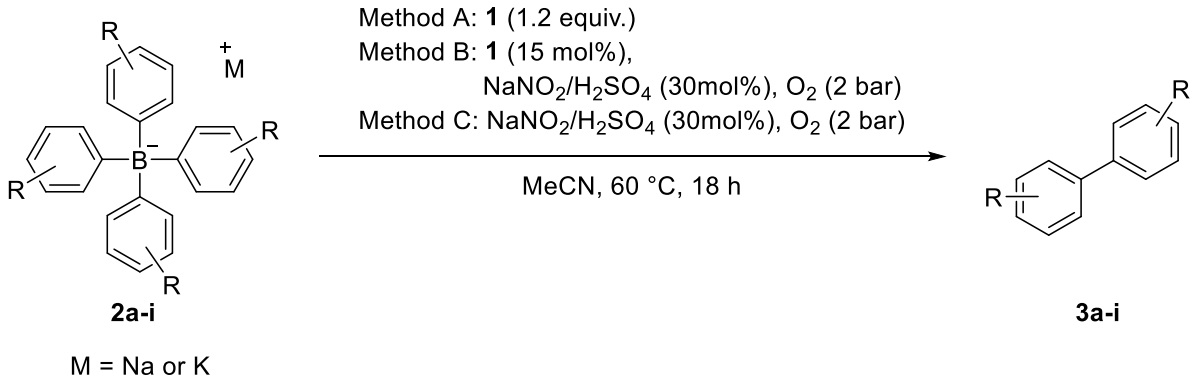
1.2 General Procedure for the Synthesis of Triarylborane-NH_3- Adducts (GP2)



Isopropoxybis(4-(trifluoromethyl)phenyl)borane (**S-1**) (1.0 equiv.) was dissolved in Et_2O and the respective aryllithium solution (1.0 equiv.) [commercially available solution or prepared by addition of *n*BuLi (1.0 equiv.) to arylbromide (1.0 equiv.) in Et_2O at -78 °C and stirring for 1h] was added dropwise. The resulting solution was stirred for 1.5 h, allowed to warm up to room temperature and stirred for another 1.5 h. Sat. aq. NH_4Cl-solution was added and stirring was continued for 1h. The phases were separated and extracted with Et_2O. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure.

The resulting solid was washed with pentane and dried under vacuum to afford the desired triarylborane ammoniate as a white solid.

1.3 General Procedures for the Homocoupling of Tetraarylborates (GP3)



2a-i **3a-i**

M = Na or K

1.3.1 Method A with stochiometric amounts of Bobbitt's salt 1 (GP3-A)

Tetraarylborate **2** (0.30 mmol, 1.0 equiv.) and Bobbitt's salt **1** (0.36 mmol, 1.2 equiv.) were dissolved in MeCN (3.0 mL). The reaction mixture was heated up to 60 °C and stirred for 18 h. After removal of the solvent *in vacuo*, flash column chromatography of the crude material afforded biaryls **3**.

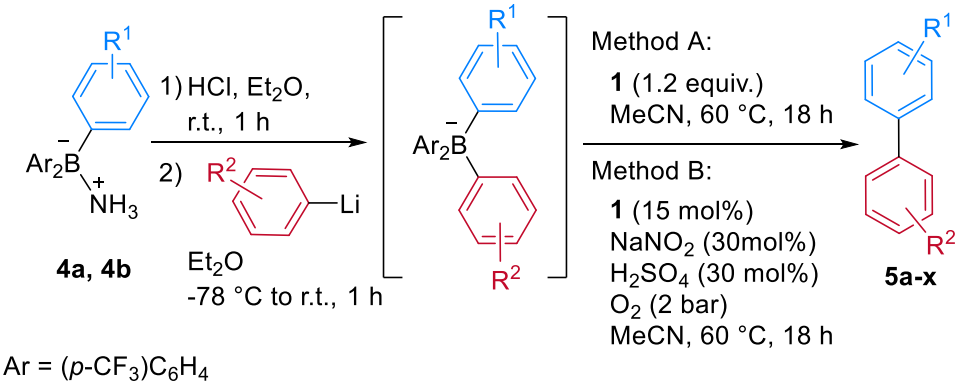
1.3.2 Method B with catalytic amounts of Bobbitt's salt 1 (GP3-B)

A 10 mL *Schlenk* tube was charged with tetraarylborate **2** (0.2 mmol, 1.0 equiv.), Bobbitt's salt **1** (0.03 mmol, 15 mol%) and $NaNO_2$ (0.06 mmol, 30 mol%). The tube was evacuated and filled with O_2. H_2SO_4 (0.06 mmol, 30 mol%) and MeCN (2.0 mL) were added quickly. The tube was charged with O_2 (2 bar) and sealed before the reaction mixture was heated up to 60 °C and stirred for 18 h. After removal of the solvent *in vacuo*, flash column chromatography of the crude material afforded biaryls **3**.

1.3.3 Method C without Bobbitt's salt (GP3-C)

A 10 mL *Schlenk* tube was charged with tetraarylborate **2** (0.1 mmol, 1.0 equiv.) and $NaNO_2$ (0.03 mmol, 30 mol%). The tube was evacuated and filled with O_2. H_2SO_4 (0.03 mmol, 30 mol%) and MeCN (1.0 mL) were added quickly. The tube was charged with O_2 (2 bar) and sealed before the reaction mixture was heated up to 60 °C and stirred for 18 h. After removal of the solvent *in vacuo*, flash column chromatography of the crude material afforded biaryls **3**.

1.4 General Procedures for the Cross-Coupling of Tetraarylborates (GP4)



Ar = (*p*-CF_3)C_6H_4

1.4.1 Method A with stochiometric amounts of Bobbitt's salt 1 (GP4-A)

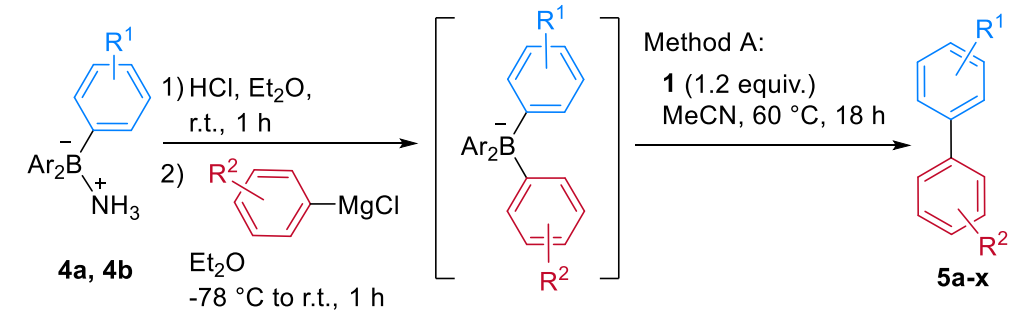
HCl (0.242 mmol, 1.21 equiv.) was added to triarylborane ammoniate **4** (0.22 mmol, 1.1 equiv.) in Et_2O (1 mL) at room temperature and the mixture was stirred for 1 h to let NH_4Cl precipitate. The solution was filtered under argon (using a filter cannula) into a 10 mL *Schlenk*-tube and the residue was washed with Et_2O (2 x 1 mL). Solvent and excess HCl were removed *in vacuo* and the residual triarylborane was redissolved in Et_2O (1 mL).
Arylbromide (0.20 mmol, 1.0 equiv.) was dissolved in THF (1.0 mL) and *n*BuLi (0.20 mmol, 1.0 equiv.) was added dropwise at -78 °C. The mixture was stirred for 1 h at that temperature before it was added to the triarylborane solution at -78 °C. The resulting mixture was stirred for 15 min at -78 °C, was allowed to warm up to room temperature and stirring was continued for 45 min. Subsequently, the solvent was carefully removed *in vacuo* and the resulting residue was taken up in acetonitrile (2.0 mL). After the addition of Bobbitt's salt **1** (0.24 mmol, 1.2 equiv.) the tube was sealed and the mixture was stirred at 60 °C for 18 h. After removal of the solvent *in vacuo*, flash column chromatography of the crude material afforded biaryls **4**.

1.4.2 Method B with catalytic amounts of Bobbitt's salt 1 (GP3-B)

HCl (0.242 mmol, 1.21 equiv.) was added to triarylborane ammoniate **4** (0.22 mmol, 1.1 equiv.) in Et_2O (1 mL) at room temperature and the mixture was stirred for 1 h to let NH_4Cl precipitate. The solution was filtered under argon (using a filter cannula) into a 10 mL *Schlenk*-tube and the residue was washed with Et_2O (2 x 1 mL). Solvent and excess HCl were removed *in vacuo* and the residual triarylborane was redissolved in Et_2O (1 mL).
Arylbromide (0.20 mmol, 1.0 equiv.) was dissolved in THF (1.0 mL) and *n*BuLi (0.20 mmol, 1.0 equiv.) was added dropwise at -78 °C. The mixture was stirred for 1 h at that temperature before it was added to the triarylborane solution at -78 °C. The resulting

mixture was stirred for 15 min at -78 °C, was allowed to warm up to room temperature and stirring was continued for 45 min. Subsequently, the solvent was carefully removed *in vacuo* and the tube was charged with O_2 and the resulting residue was taken up in acetonitrile (2.0 mL). After the addition of Bobbitt's salt **1** (0.24 mmol, 1.2 equiv.), $NaNO_2$ (0.06 mmol, 30 mol%) and H_2SO_4 (0.06 mmol, 30 mol%) the tube was charged with O_2 (2 bar) the tube was sealed and the mixture was stirred at 60 °C for 18 h. After removal of the solvent *in vacuo*, flash column chromatography of the crude material afforded biaryls **4**.

1.5 General Procedures for the Cross-Coupling of Tetraarylborates (GP5)

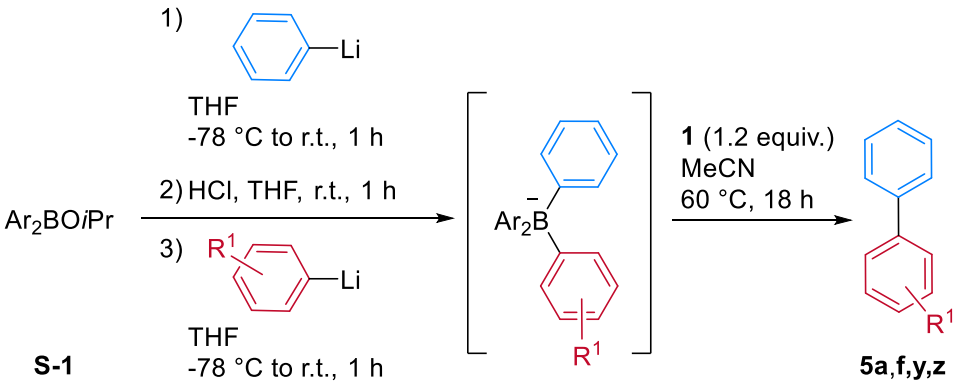


Ar = (*p*-CF_3)C_6H_4

HCl (0.242 mmol, 1.21 equiv.) was added to triarylborane ammoniate **4** (0.22 mmol, 1.1 equiv.) in Et_2O (1 mL) at room temperature and the mixture was stirred for 1 h to let NH_4Cl precipitate. The solution was filtered under argon (using a filter cannula) into a 10 mL *Schlenk*-tube and the residue was washed with Et_2O (2 x 1 mL). Solvent and excess HCl were removed *in vacuo* and the residual triarylborane was redissolved in Et_2O (1 mL).

Aryliodide (0.20 mmol, 1.0 equiv.) was dissolved in THF (1.0 mL) and iPrMgCl•LiCl (0.204 mmol, 1.02 equiv.) was added dropwise at -40 °C. The mixture was stirred for 2.5 h at -40 °C before it was added to the triarylborane solution at the specified temperatur. The resulting mixture was stirred at this temperature for 15 min, was allowed to warm up to room temperature and stirring was continued for 45 min. Subsequently, the solvent was carefully removed *in vacuo* and the resulting residue was taken up in acetonitrile (2.0 mL). After the addition of Bobbitt's salt **1** (0.24 mmol, 1.2 equiv.) the tube was sealed and the mixture was stirred at 60 °C for 18 h. After removal of the solvent *in vacuo*, flash column chromatography of the crude material afforded biaryls **4**.

1.6 General Procedures for the Modular Cross-Coupling of Tetraarylborates (GP6)



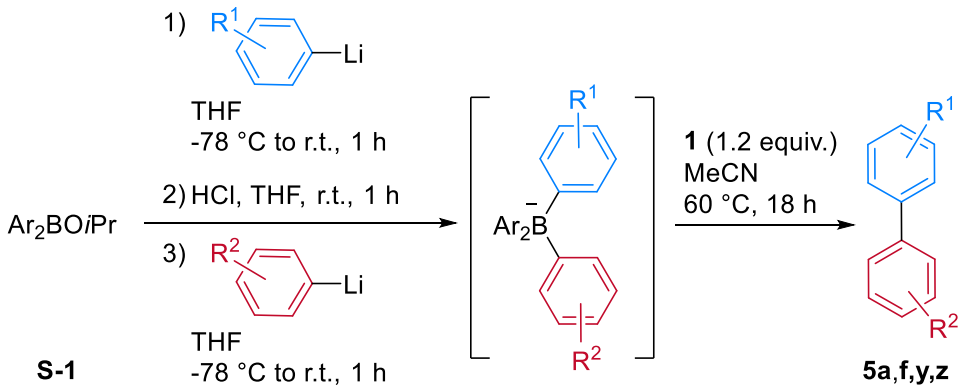
Ar = $p(CF_3)C_6H_4$

Ph-Li (0.22 mmol, 1.1 equiv.) was added to a solution of **S-1** (0.22 mmol, 1.1 equiv.) in THF (1.0 mL) at -78 °C. The mixture was stirred at this temperature for 30 min, was allowed to warm up to room temperature and stirring was continued for 30 min.

HCl (0.242 mmol, 1.21 equiv.) was added and the mixture was stirred for 45 min. Solvent, excess HCl and isopropyl alcohol were removed *in vacuo* and the residual triarylborane was redissolved in THF (1 mL).

R^1Ar-Br (0.20 mmol, 1.0 equiv.) was dissolved in THF (1.0 mL) and *n*BuLi (0.20 mmol, 1.0 equiv.) was added dropwise at -78 °C. The mixture was stirred for 1 h at -78 °C before it was added to the triarylborane solution at -78 °C. The resulting mixture was stirred at -78 °C for 15 min, was allowed to warm up to room temperature and stirring was continued for 45 min. Subsequently, the solvent was carefully removed *in vacuo* and the resulting residue was taken up in acetonitrile (2.0 mL). After the addition of Bobbitt's salt **1** (0.24 mmol, 1.2 equiv.) the tube was sealed and the mixture was stirred at 60 °C for 18 h. After removal of the solvent *in vacuo*, flash column chromatography of the crude material afforded biaryls **4**.

1.7 General Procedures for the Modular Cross-Coupling of Tetraarylborates (GP7)



Ar = *p*(CF_3)C_6H_4

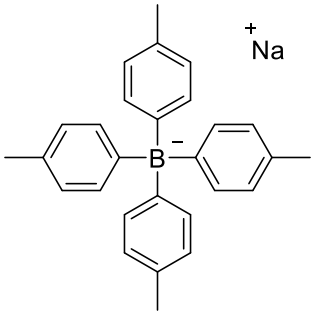
R^1Ar-Br (0.22 mmol, 1.1 equiv.) was dissolved in THF (1.0 mL) and *n*BuLi (0.22 mmol, 1.2 equiv.) was added at -78°C. The mixture was stirred at this temperature for 1 h before it was added to a solution of **S-1** (0.22 mmol, 1.1 equiv.) in THF (1.0 mL) at -78 °C. The mixture was stirred at this temperature for 30 min, was allowed to warm up to room temperature and stirring was continued for 30 min. HCl (0.242 mmol, 1.21 equiv.) was added and the mixture was stirred for 45 min. Solvent, excess HCl and isopropyl alcohol were removed *in vacuo* and the residual triarylborane was redissolved in THF (1 mL).

R^2Ar-Br (0.20 mmol, 1.0 equiv.) was dissolved in THF (1.0 mL) and *n*BuLi (0.20 mmol, 1.0 equiv.) was added dropwise at -78 °C. The mixture was stirred for 1 h at -78 °C before it was added to the triarylborane solution at -78 °C. The resulting mixture was stirred at -78 °C for 15 min, was allowed to warm up to room temperature and stirring was continued for 45 min. Subsequently, the solvent was carefully removed *in vacuo* and the resulting residue was taken up in acetonitrile (2.0 mL). After the addition of Bobbitt's salt **1** (0.24 mmol, 1.2 equiv.) the tube was sealed and the mixture was stirred at 60 °C for 18 h. After removal of the solvent *in vacuo*, flash column chromatography of the crude material afforded biaryls **4**.

2 Analytical Data

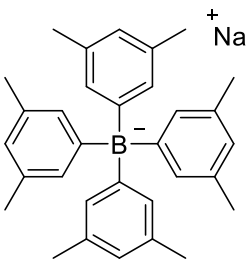
2.1 Synthesis of Starting Materials

Sodium tetra-*p*-tolylborate (2a)



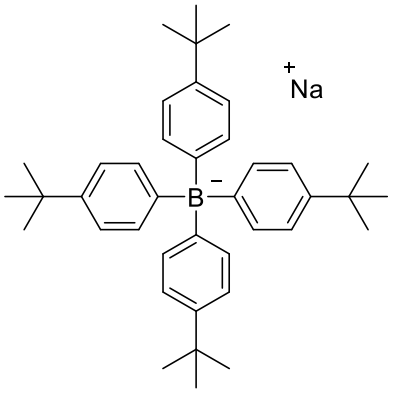
The reaction was performed according to general procedure **GP1** with Mg (256 mg, 10.6 mmol, 6.6 equiv.) in Et_2O (5 mL), 1-bromo-4-methylbenzene (1.51 mg, 8.80 mmol, 5.5 equiv.) in Et_2O (20 mL), $NaBF_4$ (174 mg, 1.60 mmol, 1.0 equiv.) and Na_2CO_3 (4.0 g) in 40 mL H_2O. **2a** was obtained as white solid (465 mg, 1.17 mmol, 73%). **^{1}H NMR** (300 MHz, DMSO-d_6, 300 K): δ (ppm) = 7.09 – 7.00 (m, 8H), 6.73 (*d*, *J* = 7.5 Hz, 8H), 2.16 (*s*, 12H). **^{13}C NMR** (75 MHz, DMSO-d_6, 300 K): δ (ppm) = 160.2 (*q*, $J_{C\text{-}B}$ = 49.7 Hz, 4xC), 135.5 (*q*, $J_{C\text{-}B}$ = 1.4 Hz, 8xCH), 129.1 (4xC), 126.0 (*q*, $J_{C\text{-}B}$ = 2.8 Hz, 8xCH), 20.8 (4xCH_3). **^{11}B NMR** (96 MHz, DMSO-d_6, 300 K): δ (ppm) = -2.5. **HRMS** (ESI) *m/z*: calcd. for $C_{28}H_{28}B^-$ ([M]$^-$): 375.2290, found: 375.2304. **FTIR** (neat): *v* (cm^{-1}) = 3052w, 3002w, 1707w, 1494w, 1257w, 1182w, 1148w, 1100w, 803s, 770m, 554m. **T_d** (decomposition temperature) > 355 °C.

Sodium tetrakis(3,5-dimethylphenyl)borate (2c)



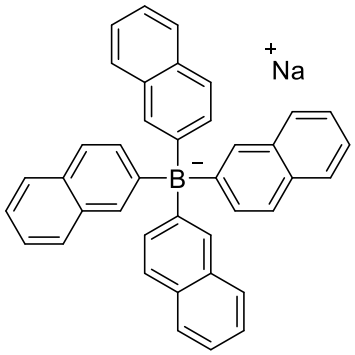
The reaction was performed according to general procedure **GP1** with Mg (559 mg, 23.0 mmol, 5.5 equiv.) in THF (4 mL), 1-bromo-3,5-dimethylbenzene (4.38 mL, 21.0 mmol, 5.0 equiv.) in THF (35 mL), $NaBF_4$ (464 mg, 4.20 mmol, 1.0 equiv.) and Na_2CO_3 (11.0 g) in 110 mL H_2O. **2c** was obtained as white solid (1.85 g, 4.06 mmol, 96%). **^{1}H NMR** (300 MHz, DMSO-d_6, 300 K): δ (ppm) = 6.92 – 6.80 (*m*, 8H), 6.42 (*s*, 4H), 2.10 (*s*, 24H). **^{13}C NMR** (75 MHz, DMSO-d_6, 300 K): δ (ppm) = 163.9 (*q*, $J_{C\text{-}B}$ = 49.1 Hz, 4xC), 133.7 (8xCH) 132.4 (*q*, $J_{C\text{-}B}$ = 2.8 Hz, 8xC), 122.9 (4xCH), 21.7 (8xCH_3)**.** **^{11}B NMR** (96 MHz, DMSO-d_6, 300 K): δ (ppm) = -7.0. **HRMS** (ESI) *m/z*: calcd. for $C_{32}H_{36}B^-$ ([M]$^-$): 431.2916, found: 431.2934. **FTIR** (neat): *v* (cm^{-1}) = 3607w, 3534m, 3008w, 2915w, 2855w, 1717s, 1608w, 1573w, 1464w, 1368m, 1232m, 1152m, 1036w, 883w, 846m, 838m, 741s, 728m. **T_d** (decomposition temperature) = 347 °C

Sodium tetrakis(4-(*tert*-butyl)phenyl)borate (2d)



The reaction was performed according to general procedure **GP1** with Mg (963 mg, 39.6 mmol, 6.6 equiv.) in THF (4 mL), 1-bromo-4-(*tert*-butyl)benzene (5.32 mL, 30.0 mmol, 5.0 equiv.) in THF (50 mL), $NaBF_4$ (659 mg, 6.00 mmol, 1.0 equiv.) and Na_2CO_3 (15.0 g) in 150 mL H_2O. **2d** was obtained as white solid (2.20 g, 3.89 mmol, 65%). **^{1}H NMR** (300 MHz, acetone-d_6, 300 K): δ (ppm) = 7.45 – 7.35 (*m*, 8H), 7.09 – 6.99 (*m*, 8H), 1.29 (*s,* 36H). **^{13}C NMR** (75 MHz, acetone-d_6, 300 K): δ (ppm) = 161.8 (*q*, $J_{C\text{-}B}$ = 49.6 Hz, 4xC), 143.4 (4xC) 136.6 (*q*, $J_{C\text{-}B}$ = 1.5 Hz, 8xCH), 122.5 (*q*, $J_{C\text{-}B}$ = 2.8 Hz, 8xCH), 34.2 (4xC), 32.1 (12xCH_3). **^{11}B NMR** (96 MHz, acetone-d_6, 300 K): δ (ppm) = -7.2. **HRMS** (ESI) *m/z*: calcd. for $C_{40}H_{52}B^-$ ([M]$^-$): 543.4193, found: 543.4168. **FTIR** (neat): *v* (cm^{-1}) = 2965w, 1708s, 1496w, 1419w, 1359s, 1269w, 1221m, 1113w, 1093w, 1021w, 839w, 805m, 692w. **T_d** (decomposition temperature) > 355 °C

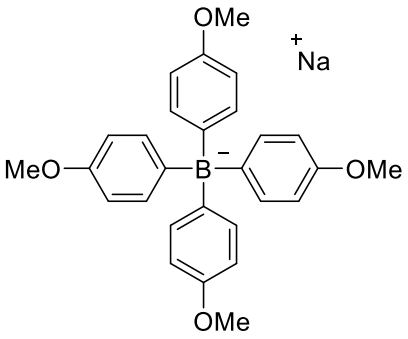
Sodium tetra(naphthalen-2-yl)borate (2e)



In analogy to a procedure of *Bower* et al.[2] a few drops of 1,2-dibromoethane were added to a suspension of Mg turnings (201 mg, 8.25 mmol, 5.5 equiv.) in THF (1 mL) without stirring. A solution of 2-bromonaphthalene (1.53 mg, 7.40 mmol, 5.0 equiv.) in THF (12.5 mL) was added slowly and the reaction mixture was heated with a heatgun to start the reaction. The arylbromide solution was added dropwise over 40 minutes. The resulting mixture was further stirred for 1 h at room temperature. BF_3•OEt_2 (190 µL, 1.50 mmol, 1.0 equiv.) was added and it was stirred for 24 h before pouring the mixture into a solution of Na_2CO_3 (5 g in 50 mL H_2O) and stirring for 30 minutes. After filtration the filtrate was extracted with Et_2O, dried over Na_2SO_4 and coventrated *in vacuo.* The resulting solid was washed with pentane/DCM and dried under vacuum to afford **2e** as white solid (712 mg, 1.31 mmol, 88%). **^{1}H NMR** (300 MHz, DMSO-d_6, 300 K): δ (ppm) = 7.81 (*dd*, *J* = 5.7, 2.6 Hz, 4H), 7.74 – 7.65 (*m*, 4H), 7.63 – 7.44 (*m*, 12H), 7.37 – 7.16 (*m*, 8H). **^{13}C NMR** (75 MHz, DMSO-d_6, 300 K): δ (ppm) = 160.9 (*q*, $J_{C\text{-}B}$ = 49.3 Hz, 4xC), 136.5 (4xCH), 133.1 (*q*, $J_{C\text{-}B}$ = 2.9 Hz, 4xC), 132.2 (4xCH), 130.6 (4xC), 127.0 (4xCH), 126.9 (4xCH), 124.0 (4xCH), 123.7 (*q*, $J_{C\text{-}B}$ = 2.2 Hz, 4xCH), 122.9 (4xCH). **^{11}B NMR** (96 MHz, DMSO-d_6, 300 K): δ (ppm) = -5.9. **HRMS** (ESI) *m/z*: calcd. for $C_{40}H_{28}B^-$ ([M]$^-$): 519.2290, found: 519.2305. **FTIR** (neat): *v* (cm^{-1}) = 3043w, 1706m, 1618w, 1585w, 1494m, 1422w, 1367m, 1324w, 1272w, 1233m, 1199w, 1110w, 1091w, 1016w, 892w, 856w,

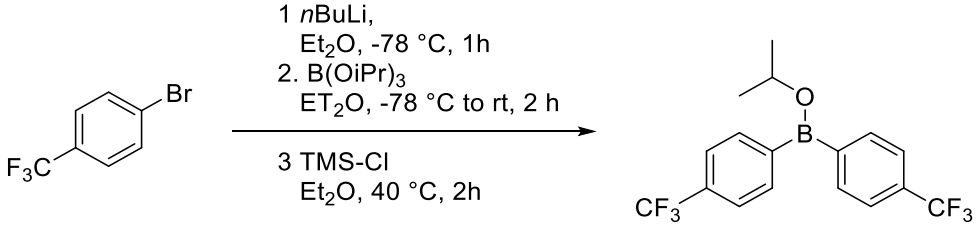
825m, 786s, 761s, 742w. **T_d** (decomposition temperature) = 260 °C. Spectroscopic data are in accordance with those described in the literature.[2]

Sodium tetrakis(4-methoxyphenyl)borate (2f)



The reaction was performed according to general procedure **GP1** with Mg (1.20 g, 49.5 mmol, 6.6 equiv.) in THF (8 mL), 1-bromo-4-methoxybenzene (5.35 mL, 41.3 mmol, 5.5 equiv.) in THF (75 mL) and Et_2O (30 mL), $NaBF_4$ (823 mg, 7.50 mmol, 1.0 equiv.) and Na_2CO_3 (19.0 g) in 190 mL H_2O. **2f** was obtained as white solid (1.01 g, 2.18 mmol, 29%). **^{1}H NMR** (300 MHz, DMSO-d_6, 300 K): δ (ppm) = 7.08 – 6.97 (*m*, 8H), 6.57 – 6.48 (*m*, 8H), 3.63 (*s*, 12H). **^{13}C NMR** (75 MHz, , DMSO-d_6, 300 K): δ (ppm) = 155.1 (*q*, $J_{C\text{-}F}$ = 49.7, 4xC), 154.8 (4xC), 136.0 (*q*, $J_{C\text{-}F}$ = 2.0 Hz, 8xCH), 111.0 (*q*, $J_{C\text{-}F}$ = 3.0 Hz, 8xCH), 54.4 (4xCH_3). **^{11}B NMR** (96 MHz, DMSO-d_6, 300 K): δ (ppm) = -7.8. **FTIR** (neat): *v* (cm^{-1}) = 3637w, 3610w, 3305w, 3011w, 1710w, 1587m, 1564w, 1492s, 1445s, 1267m, 1234s, 1175m, 1100w, 1031m, 900m, 866w, 838w, 812s, 573m. **HRMS** (ESI) *m/z*: calcd. for $C_{28}H_{28}BO_4^-$ ($[M]^-$): 439.20911, found: 439.20843. **T_d** (decomposition temperature) = 308 °C.

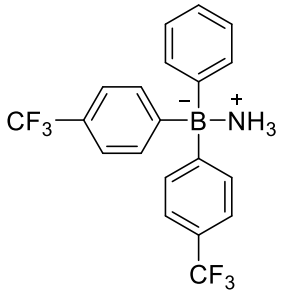
Isopropoxybis(4-(trifluoromethyl)phenyl)borane (S-1)



Based on a procedure of *Luliński* et al.,[3] *n*BuLi (1.6 M in hexane, 26 mL, 42 mmol, 2.1 equiv.) was added dropwise over 40 min to a solution of 1-bromo-4-(trifluoromethyl)benzene (5.9 mL, 42 mmol, 2.1 equiv.) in Et_2O (30 mL) at -78 °C and the resulting mixture was stirred for 1 h at this temperature before $B(OiPr)_3$ (4.6 mL, 20 mmol, 1.0 equiv.) in Et_2O (20 mL) was added dropwise over 45 min. The mixture was stirred for 1 h at -78 °C, allowed to warm up to room temperature and stirred for an additional hour. TMS-Cl (5.9 ml, 46 mmol, 2.3 equiv.) was added and it was heated up to 40 °C for 2 h. After cooling to room temperature, the solution was concentrated *in vacuo* and filtered under argon atmosphere using a filter canula to remove precipitated LiCl. The filtrate was concentrated *in vacuo* and the crude product was purified by distillation under reduced pressure (0.17 mbar, boiling point 102 °C) to give **S-1** as a white solid (5.66 g, 15.7 mmol, 79%). Due to air and moisture sensitivity, the compound was stored under an argon atmosphere. **^{1}H NMR** (600 MHz,

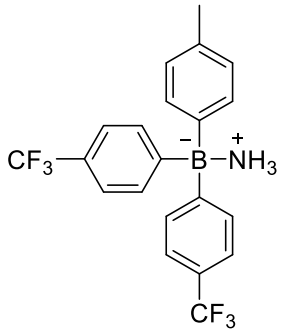
$CDCl_3$, 300 K): δ (ppm) = 7.73 – 7.68 (*m*, 4H), 7.68 – 7.64 (*m*, 4H), 4.61 – 4.54 (*m*, 1H), 1.36 – 1.31 (*m*, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 134.0 (4xCH), 132.2 (*q*, J_{C-F} = 32.1 Hz, 2xC), 124.6 (*q*, J_{C-F} = 3.8 Hz, 4xCH), 124.3 (*q,* J_{C-F} = 273.0, 2xCF_3), 70.8 (1xCH), 24.9 (2xCH_3). The signals of the α-B-carbons were not observed. **^{11}B NMR** (96 MHz, $CDCl_3$, 300 K): δ (ppm) = 44.4. **^{19}F NMR** (564 MHz, CDCl3, 300 K): δ (ppm) = -63.0. **IR** (film) = 1517w, 1403m, 1322s, 1296m, 1270w, 1166m, 1125s, 1106s, 1066s, 1018m, 873m, 762w, 702w, 660w, 642w. **CHN Anal.** calcd for $C_{17}H_{15}BF_6O$: C 56.70; H 4.20; found: C 56.57; H 4.36. **m.p.** = 56 °C.

Phenylbis(4-(trifluoromethyl)phenyl)borane-NH_3 adduct (4a)



The reaction was performed according to general procedure **GP2** with **S-1** (2.6 g, 7.3 mmol, 1.0 equiv.), PhLi (1.9 M in dibutylether, 3.8 mL, 7.3 mmol, 1.0 equiv.) and sat. aq. NH_4Cl-solution (30 mL) in Et_2O (30 mL). **4a** was obtained as white solid (2.7 g, 6.8 mmol, 94%). **^{1}H NMR** (500 MHz, DMSO-d_6, 300 K): δ (ppm) = 7.49 – 7.43 (*m*, 4H), 7.37 – 7.31 (*m*, 4zH), 7.16 – 7.10 (*m*, 4H), 7.09 – 7.03 (*m,* 1H), 5.86 (br, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6, 300 K): δ (ppm) = 133.5 (4xCH), 133.0 (2xCH), 126.6 (2xCH), 125.2 (*q*, J_{C-F} = 30.9 Hz, 2xC), 125.1 (*q*, J_{C-F} = 271.5 Hz, 2xCF_3), 124.5 (CH), 122.8 (*q*, J_{C-F} = 3.8 Hz, 4xCH). The signals of the α-B-carbon atoms was not observed. **^{19}F NMR** (282 MHz, DMSO-d_6, 300 K): δ (ppm) = -55.6 (2xCF_3). **^{11}B NMR** (96 MHz, DMSO-d_6, 300 K): δ (ppm) = -1.9 **IR** (film) = 3296w, 1608w, 398w, 1365w, 1325s, 1275w, 1161m, 1107m, 1066s, 1018m, 831w, 732w, 710w. **GC-HRMS** (EI): *m*: calcd. for $C_{20}H_{13}BF_6$ ([M-NH_3]$^+$): 378.1009, found: 378.1012. **m.p.**: 176 °C.

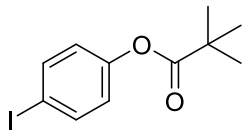
***p*-Tolylbis(4-(trifluoromethyl)phenyl)boran-NH_3 adduct (4b)**



The reaction was performed according to general procedure **GP2** with **S-1** (1.0 g, 2.8 mmol, 1.0 equiv.), 1-bromo-4-methylbenzene (0.48 g, 2.8 mmol, 1.0 equiv.), *n*BuLi (1.6 M in hexane, 1.8 mL, 2.8 mmol, 1.0 equiv.) and sat. aq. NH_4Cl-solution (7.5 mL) in Et_2O (7.5 mL). **4b** was obtained as white solid (0.95 g, 2.3 mmol, 83%). **^{1}H NMR** (600 MHz, DMSO-d_6,300 K): δ (ppm) = 7.50 – 7.42 (*m*, 4H), 7.40 – 7.32 (*m*, 4H), 7.04 – 6.99 (*m*, 2H), 6.99 – 6.94 (*m*, 2H), 5.83 (*s*, 3H), 2.23 (*s*, 3H). **^{13}C NMR** (151 MHz, DMSO-d_6, 300 K): δ (ppm) = 133.5 (4xCH), 133.1 (2xCH), 133.0 (C), 127.4 (2xCH), 125.2 (*q*, J_{C-F} = 31.0 Hz, 2xC), 125.1 (*q*, J_{C-F} = 271.4 Hz, 2xCF_3). 122.8 (*q*, J_{C-F} = 3.8 Hz, 4xCH). 20.8 (CH_3). The signals of the α-B-carbon atoms were not observed. **^{19}F NMR** (564 MHz, DMSO-d_6, 300 K): δ (ppm) = -60.4 (2xCF_3). **^{11}B NMR** (192 MHz, DMSO-d_6, 300 K): δ (ppm) = -5.0. **IR** (film) = 3300w, 1609w, 1397w,

1365w, 1330s, 1275w, 1159m, 1122s, 1067s, 1019m, 964w, 945w, 835m, 824w, 701w. **HRMS** (ESI) *m/z*: calcd. for $C_{21}H_{15}BF_6OH$ ([M-NH_3+OH]$^-$): 409.1208, found: 409.1199. **m.p.**: 200 °C.

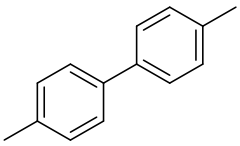
4-Iodophenyl pivalate (S-2)



In analogy to a procedure of *Gagnon* et al.[4] 4-iodophenol (0.88 g, 4.0 mmol, 1.0 equiv.) was dissolved in THF (5.0 ml) and cooled to 0 °C. Triethylamine (0.78 mL, 5.6 mmol, 1.4 equiv.) and pivaloyl chloride (0.49 mL, 4.0 mmol, 1.0 equiv.) were added dropwise. The mixture was allowed to warm up to room temperature and was stirred overnight. After removal of the solvent *in vacuo*, flash column chromatography of the crude product (pentane:ethyl acetate = 10:1) afforded compound **S-2** as white solid (1.17 g, 3.85 mmol, 96%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.75 – 7.61 (*m*, 2H), 6.90 – 6.78 (*m,* 2H), 1.35 (*s*, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 176.8 (C), 151.2 (C), 138.5 (2xCH), 123.9 (2xCH), 89.6 (C), 39.3 (C), 27.2 (3xCH_3). **HRMS** (ESI) *m/z*: calcd. for $C_{11}H_{13}IO_2Na$ ([M+Na]$^+$): 326.9852, found: 326.9846. Spectroscopic data are in accordance with those described in the literature.[4]

2.2 Synthesis of Symmetric Biaryls

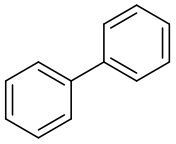
4,4'-Dimethyl-1,1'-biphenyl (3a)



Method A: The reaction was performed according to general procedure **GP3-A** with **2a** (119 mg, 0.300 mmol, 1.0 equiv.) and **1** (108 g, 0.360 mmol, 1.2 equiv.) in MeCN (3.0 mL). Flash column chromatography of the crude product (pentane) afforded **3a** as white solid (48 mg, 0.26 mmol, 88%). **Method B:** The reaction was performed according to general procedure **GP3-B** with **2a** (80 mg, 0.20 mmol, 1.0 equiv.), **1** (9 mg, 0.03 mmol, 15 mol%), $NaNO_2$ (4 mg, 0.06 mmol, 30 mol%) and H_2SO_4 (3 µL, 0.06 mmol, 30 mol%) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **3a** as white solid (31 mg, 0.17 mmol, 85%). **Method C:** The reaction was performed according to general procedure **GP3-C** with **2a** (40 mg, 0.10 mmol, 1.0 equiv.), $NaNO_2$ (1.4 mg, 20 µmol, 20 mol%) and H_2SO_4 (1.1 µL, 20 µmol, 20 mol%) in MeCN (1.0 mL). Flash column chromatography of the crude product (pentane) afforded **3a** as white solid (15.5 mg, 85.0 µmol, 85%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.53 – 7.45 (*m*, 4H), 7.29 – 7.21 (*m*, 4H), 2.40 (*s*, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 138.5 (2xC), 136.8 (2xC), 129.6 (4xCH), 127.0 (4xCH), 21.2 (2xCH_3). **GC-MS** (EI) *m/z* (relative intensity %) =

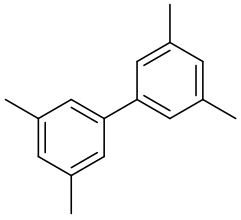
182.1 (M+, 100), 167.1 (50), 165.0 (41), 152.0 (11), 89.1 (14). Spectroscopic data are in accordance with those described in the literature.[5]

1,1'-Biphenyl (3b)



Method A: The reaction was performed according to general procedure **GP3-A** with tetraphenylborate (**2b**) (103 mg, 0.300 mmol, 1.0 equiv.) and **1** (108 g, 0.360 mmol, 1.2 equiv.) in MeCN (3.0 mL). Flash column chromatography of the crude product (pentane) afforded **3b** as white solid (40.5 mg, 0.263 mmol, 88%). **Method B:** The reaction was performed according to general procedure **GP3-B** with tetraphenylborate (**2b**) (68 mg, 0.20 mmol, 1.0 equiv.), **1** (9 mg, 0.03 mmol, 15 mol%), $NaNO_2$ (4 mg, 0.06 mmol, 30 mol%) and H_2SO_4 (3 µL, 0.06 mmol, 30 mol%) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **3b** as white solid (20 mg, 0.13 mmol, 65%). **Method C:** The reaction was performed according to general procedure **GP3-C** with tetraphenylborate (**2b**) (34 mg, 0.10 mmol, 1.0 equiv.), $NaNO_2$ (2 mg, 0.03 mmol, 30 mol%) and H_2SO_4 (1.6 µL, 30 µmol, 30 mol%) in MeCN (1.0 mL). Flash column chromatography of the crude product (pentane) afforded **3b** as white solid (7.0 mg, 45 µmol, 45%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.68 – 7.58 (*m*, 4H), 7.52 – 7.42 (*m,* 4H), 7.42 – 7.32 (*m*, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 141.4 (2xC), 128.9 (4xCH), 127.4 (2xCH), 127.3 (4xCH). **GC-MS** (EI) *m/z* (relative intensity %) = 154.1 (M+, 100), 76.0 (14). Spectroscopic data are in accordance with those described in the literature.[5]

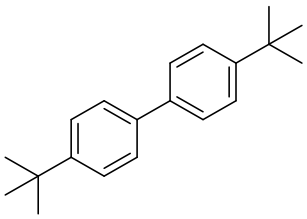
3,3',5,5'-Tetramethyl-1,1'-biphenyl (3c)



Method A: The reaction was performed according to general procedure **GP3-A** with **2c** (136 mg, 0.300 mmol, 1.0 equiv.) and **1** (108 g, 0.360 mmol, 1.2 equiv.) in MeCN (3.0 mL). Flash column chromatography of the crude product (pentane) afforded **3c** as white solid (55.5 mg, 0.264 mmol, 88%). **Method B:** The reaction was performed according to general procedure **GP3-B** with **2c** (91 mg, 0.20 mmol, 1.0 equiv.), **1** (9 mg, 0.03 mmol, 15 mol%), $NaNO_2$ (4 mg, 0.06 mmol, 30 mol%) and H_2SO_4 (3 µL, 0.06 mmol, 30 mol%) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **3c** as white solid (29 mg, 0.14 mmol, 69%). **Method C:** The reaction was performed according to general procedure **GP3-C** with **2c** (45 mg, 0.10 mmol, 1.0 equiv.), $NaNO_2$ (2 mg, 0.03 mmol, 30 mol%) and H_2SO_4 (1.6 µL, 30 µmol, 30 mol%) in MeCN (1.0 mL). Flash column chromatography of the crude product (pentane) afforded **3c** as white solid (12 mg, 57 µmol, 57%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.30 – 7.22 (*m*, 4H), 7.08 – 6.99 (*m*, 2H), 2.44 (*d*, *J* = 0.8 Hz, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$,

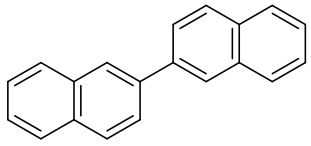
300 K): δ (ppm) = 141.7 (2xC), 138.2 (4xC), 128.9 (2xCH), 125.3 (4xCH), 21.5 (4xCH_3). **GC-MS** (EI) *m/z* (relative intensity %) = 210.2 (M+, 100), 195.1 (35), 179.1 (22), 165.1 (23). Spectroscopic data are in accordance with those described in the literature.[6]

4,4'-Di-*tert*-butyl-1,1'-biphenyl (3d)



Method A: The reaction was performed according to general procedure **GP3-A** with **2d** (170 mg, 0.300 mmol, 1.0 equiv.) and **1** (108 g, 0.360 mmol, 1.2 equiv.) in MeCN (3.0 mL). Flash column chromatography of the crude product (pentane) afforded **3d** as white solid (72 mg, 0.27 mmol, 90%). **Method B:** The reaction was performed according to general procedure **GP3-B** with **2d** (113 mg, 0.200 mmol, 1.0 equiv.), **1** (9 mg, 0.03 mmol, 15 mol%), $NaNO_2$ (4 mg, 0.06 mmol, 30 mol%) and H_2SO_4 (3 µL, 0.06 mmol, 30 mol%) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **3d** as white solid (42.5 mg, 0.16 mmol, 80%). **Method C:** The reaction was performed according to general procedure **GP3-C** with **2d** (57 mg, 0.10 mmol, 1.0 equiv.), $NaNO_2$ (2 mg, 0.03 mmol, 30 mol%) and H_2SO_4 (1.6 µL, 30 µmol, 30 mol%) in MeCN (1.0 mL). Flash column chromatography of the crude product (pentane) afforded **3d** as white solid (21 mg, 79 µmol, 79%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.63 – 7.56 (*m*, 4H), 7.56 – 7.48 (*m*, 4H), 1.43 (*s*, 18H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 150.1 (2xC), 138.4 (2xC), 126.8 (4xCH), 125.8 (4xCH), 34.7 (2xC), 31.6 (6xCH_3). **GC-MS** (EI) *m/z* (relative intensity %) = 266.1 (M+, 44), 251.3 (100), 118.1 (10), 104.0 (10), 90.0 (27), 57.1 (15). Spectroscopic data are in accordance with those described in the literature.[7]

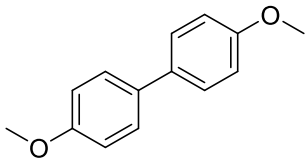
2,2'-Binaphthalene (3e)



Method A: The reaction was performed according to general procedure **GP3-A** with **2e** (162 mg, 0.300 mmol, 1.0 equiv.) and **1** (108 g, 0.360 mmol, 1.2 equiv.) in MeCN (3.0 mL). Flash column chromatography of the crude product (pentane) afforded **3e** as white solid (67 mg, 0.26 mmol, 88%). **Method B:** The reaction was performed according to general procedure **GP3-B** with **2e** (54 mg, 0.10 mmol, 1.0 equiv.), **1** (4.5 mg, 15 µmol, 15 mol%), $NaNO_2$ (2 mg, 0.03 mmol, 30 mol%) and H_2SO_4 (1.6 µL, 30 µmol, 30 mol%) in MeCN (1.0 mL). Flash column chromatography of the crude product (pentane) afforded **3e** as white solid (20 mg, 0.79 mmol, 79%). **Method C:** The reaction was performed according to general procedure **GP3-C** with **2e** (54 mg, 0.10 mmol, 1.0 equiv.), $NaNO_2$ (2 mg, 0.03 mmol, 30 mol%) and H_2SO_4 (1.6 µL, 30 µmol, 30 mol%) in MeCN (1.0 mL). Flash column chromatography of the crude product (pentane) afforded **3e** as white solid (14.5 mg,

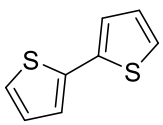
57 µmol, 57%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.23 – 8.14 (*m*, 2H), 8.03 – 7.84 (*m*, 8H), 7.61 – 7.44 (*m*, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 138.6 (2xC), 133.9 (2xC), 132.9 (2xC), 128.7 (2xCH), 128.4 (2xCH), 127.8 (2xCH), 126.5 (2xCH), 126.3 (2xCH), 126.2 (2xCH), 125.9 (2xCH). **GC-MS** (EI) *m/z* (relative intensity %) = 254.1 (M+, 100), 252.1 (34), 126.0 (20). Spectroscopic data are in accordance with those described in the literature.[8]

4,4'-Dimethoxy-1,1'-biphenyl (3f)



Method A: The reaction was performed according to general procedure **GP3-A** with **2f** (139 mg, 0.300 mmol, 1.0 equiv.) and **1** (108 g, 0.360 mmol, 1.2 equiv.) in MeCN (3.0 mL). Flash column chromatography of the crude product (pentane:Et_2O = 50:1) afforded **3f** as white solid (48 mg, 0.22 mmol, 75%). **Method B:** The reaction was performed according to general procedure **GP3-B** with **2f** (92 mg, 0.2 mmol, 1.0 equiv.), **1** (9 mg, 0.03 mmol, 15 mol%), $NaNO_2$ (4 mg, 0.06 mmol, 30 mol%) and H_2SO_4 (3 µL, 0.06 mmol, 30 mol%) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane:Et_2O = 50:1) afforded **3f** as white solid (23.5 mg, 0.11 mmol, 55%). **Method C:** The reaction was performed according to general procedure **GP3-C** with **2f** (46 mg, 0.10 mmol, 1.0 equiv.), $NaNO_2$ (2 mg, 0.03 mmol, 30 mol%) and H_2SO_4 (1.6 µL, 30 µmol, 30 mol%) in MeCN (1.0 mL). Flash column chromatography of the crude product (pentane:Et_2O = 50:1) afforded **3f** as white solid (12 mg, 57 µmol, 57%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.58 – 7.43 (*m*, 4H), 7.07 – 6.90 (*m*, 4H), 3.86 (*s*, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 158.9 (2xC), 133.7 (2xC), 127.9 (4xCH), 114.3 (4xCH), 55.5 (2xCH_3). **GC-MS** (EI) *m/z* (relative intensity %) = 214.1 (M+, 100), 199.1 (90), 171.0 (35), 156.0 (13), 138.9 (14), 128.0 (23), 102.0 (10). Spectroscopic data are in accordance with those described in the literature.[5]

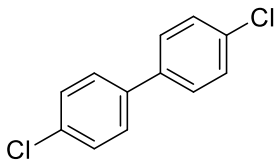
2,2'-Bithiophene (3g)



Method A: The reaction was performed according to general procedure **GP3-A** with potassium tetrakis(2-thienyl)borate (**2g**) (115 mg, 0.300 mmol, 1.0 equiv.) and **1** (108 g, 0.360 mmol, 1.2 equiv.) in MeCN (3.0 mL). Flash column chromatography of the crude product (pentane) afforded **3g** as white solid (25 mg, 0.15 mmol, 50%). **Method B:** The reaction was performed according to general procedure **GP3-B** with potassium tetrakis(2-thienyl)borate (**2g**) (76 mg, 0.20 mmol, 1.0 equiv.), **1** (9 mg, 0.03 mmol, 15 mol%), $NaNO_2$ (4 mg, 0.06 mmol, 30 mol%) and H_2SO_4 (3 µL, 0.06 mmol, 30 mol%) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **3g** as white solid (8.0 mg, 48 µmol, 24%). **Method C:** The reaction was performed

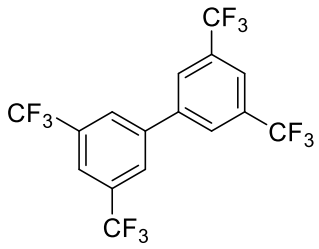
according to general procedure **GP3-C** with potassium tetrakis(2-thienyl)borate (**2g**) (38 mg, 0.10 mmol, 1.0 equiv.), $NaNO_2$ (2 mg, 0.03 mmol, 30 mol%) and H_2SO_4 (1.6 µL, 30 µmol, 30 mol%) in MeCN (1.0 mL). Flash column chromatography of the crude product (pentane) afforded **3g** as white solid (4.0 mg, 24 µmol, 24%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.26 – 7.14 (*m*, 4H), 7.02 (*dd, J* = 5.1, 3.6 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 137.6 (2xC), 127.9 (2xCH), 124.5 (2xCH), 123.9 (2xCH). **GC-MS** (EI) *m/z* (relative intensity %) = 166.0 (M+, 100), 134.0 (16), 121.0 (35), 108 (10), 69.0 (14). Spectroscopic data are in accordance with those described in the literature.[7]

4,4'-Dichloro-1,1'-biphenyl (3h)



Method A: The reaction was performed according to general procedure **GP3-A** with potassium tetrakis(4-chlorophenyl)borate (**2h**) (149 mg, 0.300 mmol, 1.0 equiv.) and **1** (108 g, 0.360 mmol, 1.2 equiv.) in MeCN (3.0 mL). Flash column chromatography of the crude product (pentane) afforded **3h** as white solid (57 mg, 0.25 mmol, 85%). **Method B:** The reaction was performed according to general procedure **GP3-B** with potassium tetrakis(4-chlorophenyl)borate (**2h**) (99 mg, 0.200 mmol, 1.0 equiv.), **1** (9 mg, 0.03 mmol, 15 mol%), $NaNO_2$ (4 mg, 0.06 mmol, 30 mol%) and H_2SO_4 (3 µL, 0.06 mmol, 30 mol%) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **3h** as white solid (25.5 mg, 113 µmol, 57%). **Method C:** The reaction was performed according to general procedure **GP3-C** with potassium tetrakis(4-chlorophenyl)borate (**2h**) (50 mg, 0.10 mmol, 1.0 equiv.), $NaNO_2$ (2 mg, 0.03 mmol, 30 mol%) and H_2SO_4 (1.6 µL, 30 µmol, 30 mol%) in MeCN (1.0 mL). Flash column chromatography of the crude product (pentane) afforded **3h** as white solid (12 mg, 54 µmol, 54%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.54 – 7.37 (*m*, 8H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 138.6 (2xC), 133.9 (2xC), 129.2 (4xCH), 128.4 (4xCH). **GC-MS** (EI) *m/z* (relative intensity %) = 222.0 (M+, 100), 186.0 (10), 152.1 (76), 111.0 (10), 93.0 (15), 75.1 (23). Spectroscopic data are in accordance with those described in the literature.[5]

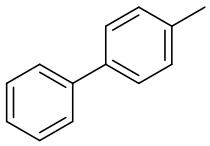
3,3',5,5'-Tetrakis(trifluoromethyl)-1,1'-biphenyl (3i)



Method A: The reaction was performed according to general procedure **GP3-A** with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (**2i**) (266 mg, 0.300 mmol, 1.0 equiv.) and **1** (108 g, 0.360 mmol, 1.2 equiv.) in MeCN (3.0 mL). Only trace amounts of **3i** could be detected by GC-MS. **GC-MS** (EI) *m/z* (relative intensity %) = 426.0 (M+, 100), 407.0 (38), 357.0 (14), 337.0 (15), 169.0 (14).

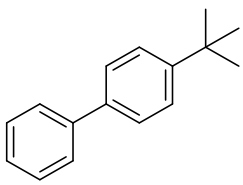
2.3 Synthesis of Unsymmetric Biaryls

4-Methyl-1,1'-biphenyl (5a)



Method A: The reaction was performed according to general procedure **GP4-A** with **4a** (87 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), 1-bromo-4-methylbenzene (34 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5a** as white solid (25 mg, 0.15 mmol, 74%). **Method B:** The reaction was performed according to general procedure **GP4-B** with **4a** (87 mg, 0.22 mmol, 1.1 equiv.), HCl (235 µL, 0.242 mmol, 1.2 equiv.), 1-bromo-4-methylbenzene (34 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.), Bobbitt's salt **1** (9 mg, 0.03 mmol, 15 mol%), $NaNO_2$ (4 mg, 0.06 mmol, 30 mol%) and H_2SO_4 (3 µL, 0.06 mmol, 30 mol%) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5a** as white solid (23 mg, 0.14 mmol, 68%)**. Modular strategy:** The reaction was performed according to general procedure **GP6** with **S-1** (79 mg, 0.22 mmol, 1.1 equiv.), Ph-Li (1.9 M in dibutylether, 116 µL 0.220 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.21 equiv.), 1-bromo-4-methylbenzene (34 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5a** as white solid (19 mg, 0.11 mmol, 56%)**. ^{1}H NMR** (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.56 – 7.48 (*m*, 2H), 7.47 – 7.41 (*m*, 2H), 7.40 – 7.31 (*m*, 2H), 7.30 – 7.22 (*m,* 1H), 7.22 – 7.14 (*m*, 2H), 2.33 (*s*, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 141.4 (C), 138.5 (C), 137.2 (C), 129.6 (2xCH), 128.9 (2xCH), 127.1 (2xCH), 127.1 (2xCH), 127.1 (1xCH), 21.2 (CH_3). **GC-MS** (EI) *m/z* (relative intensity %) = 168.1 (M+, 100), 152.0 (28), 115.0 (11), 82.8 (14). Spectroscopic data are in accordance with those described in the literature.[9]

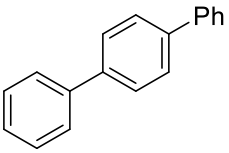
4-(*Tert*-butyl)-1,1'-biphenyl (5b)



Method A: The reaction was performed according to general procedure **GP4-A** with **4a** (87 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), 1-bromo-4-(*tert*-butyl)benzene (43 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5b** as white solid (28 mg, 0.13 mmol, 67%). **Method B:** The reaction was performed according to general procedure **GP4-B** with **4a** (87 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O,

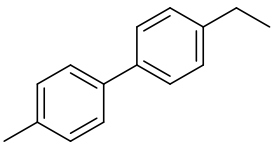
235 µL, 0.242 mmol, 1.2 equiv.), 1-bromo-4-(*tert*-butyl)benzene (43 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.), Bobbitt's salt **1** (9 mg, 0.03 mmol, 15 mol%), $NaNO_2$ (4 mg, 0.06 mmol, 30 mol%) and H_2SO_4 (3 µL, 0.06 mmol, 30 mol%) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5b** as white solid (25 mg, 0.12 mmol, 59%)**.** **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.64 – 7.54 (*m*, 4H), 7.52 – 7.41 (*m*, 4H), 7.39 – 7.31 (*m*, 1H), 1.39 (*s*, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 150.4 (C), 141.3 (C), 138.5 (C), 128.8 (2xCH), 127.2 (2xCH), 127.1 (CH), 126.9 (2xCH), 125.9 (2xCH), 34.7 (C), 31.5 (3xCH_3). **GC-MS** (EI) *m/z* (relative intensity %) = 210.1 (M+, 40), 195.1 (100) 178.1 (12), 167.1 (30), 165.1 (14), 152.0 (14), 83.5 (14). Spectroscopic data are in accordance with those described in the literature.[10]

1,1':4',1''-Terphenyl (5c)



The reaction was performed according to general procedure **GP4-A** with **4a** (87 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), 4-bromo-1,1'-biphenyl (47 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5c** as white solid (29 mg, 0.13 mmol, 63%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.74 – 7.62 (*m*, 8H), 7.52 – 7.43 (*m*, 4H), 7.42 – 7.34 (*m*, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 140.9 (2xC), 140.3 (2xC), 129.0 (4xCH), 127.7 (4xCH), 127.5 (2xCH), 127.2 (4xCH). **GC-MS** (EI) *m/z* (relative intensity %) = 230.1 (M+, 100), 152.0 (10), 115.0 (20). Spectroscopic data are in accordance with those described in the literature.[9]

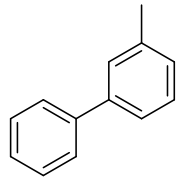
4-Ethyl-4'-methyl-1,1'-biphenyl (5d)



The reaction was performed according to general procedure **GP4-A** with **4b** (90 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), 1-bromo-4-ethylbenzene (28 µL, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5d** as white solid (28 mg, 0.14 mmol, 71%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.58 – 7.46 (*m*, 4H), 7.33 – 7.22 (*m*, 4H), 2.71 (*q*, *J* = 7.6 Hz, 2H), 2.41 (*s*, 3H), 1.30 (*t*, *J* = 7.6 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 143.2 (C), 138.7 (C), 138.5 (C), 136.8 (C), 129.6 (2xCH), 128.4 (2xCH), 127.0 (2xCH), 127.0 (2xCH), 28.7 (CH_2), 21.2 (CH_3), 15.7 (CH_3). **GC-MS** (EI)

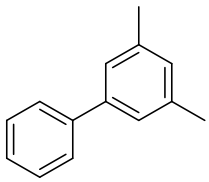
m/z (relative intensity %) = 196.1 (M+, 56), 181.1 (100), 165.1 (32). Spectroscopic data are in accordance with those described in the literature.[11]

3-Methyl-1,1'-biphenyl (5e)



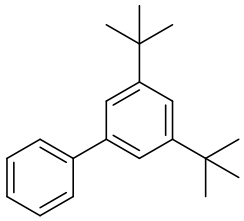
The reaction was performed according to general procedure **GP4-A** with **4a** (87 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), 1-bromo-3-methylbenzene (24 µL, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5e** as colorless oil (20 mg, 0.12 mmol, 60%).**^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.67 – 7.54 (*m*, 2H), 7.50 – 7.39 (*m*, 4H), 7.39 – 7.30 (*m*, 2H), 7.23 – 7.12 (*m*, 1H), 2.44 (*s*, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 141.6 (C), 141.4 (C), 138.5 (C), 128.8 (2xCH), 128.8 (1xCH), 128.1 (2xCH), 127.3 (2xCH), 127.3 (1xCH), 124.4 (1xCH), 21.7 (CH_3). **GC-MS** (EI) *m/z* (relative intensity %) = 168.1 (M+, 100), 152.0 (24), 115.0 (10), 82.9 (14). Spectroscopic data are in accordance with those described in the literature.[12]

3,5-Dimethyl-1,1'-biphenyl (5f)



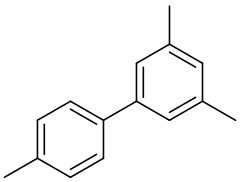
The reaction was performed according to general procedure **GP4-A** with **4a** (87 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), 1-bromo-3,5-dimethylbenzene (37 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5f** as white solid (24.5 mg, 134 µmol, 67%). **Modular strategy:** The reaction was performed according to general procedure **GP6** with **S-1** (79 mg, 0.22 mmol, 1.1 equiv.), Ph-Li (1.9 M in dibutylether, 116 µL 0.220 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.21 equiv.), 1-bromo-3,5-dimethylbenzene (37 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5f** as white solid (20 mg, 0.11 mmol, 55%)**. ^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.64 – 7.56 (*m*, 2H), 7.48 – 7.40 (*m*, 2H), 7.39 – 7.31 (*m*, 1H), 7.26 – 7.22 (*m,* 2H), 7.07 – 6.97 (*m*, 1H), 2.41 *(d*, *J* = 0.7 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 141.6 (C), 141.4 (C), 138.4 (2xC), 129.0 (CH), 128.8 (2xCH), 127.3 (2xCH), 127.2 (CH), 125.3 (2xCH), 21.5 ($2xCH_3$). **GC-MS** (EI) *m/z* (relative intensity %) = 182.1 (M+, 100), 167.1 (62), 165.1 (42), 152.1 (17), 89.0 (11). Spectroscopic data are in accordance with those described in the literature.[13]

3,5-Di-*tert*-butyl-1,1'-biphenyl (5g)



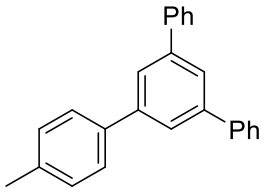
The reaction was performed according to general procedure **GP4-A** with **4a** (87 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), 1-bromo-3,5-di-*tert*-butylbenzene (54 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5g** as white solid (37.5 mg, 141 µmol, 70%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.66 – 7.59 (*m*, 2H), 7.51 – 7.42 (*m*, 5H), 7.40 – 7.32 (*m*, 1H), 1.42 (*s*, 18H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 151.3 (2xC), 142.7 (C), 140.9 (C), 128.8 (2xCH), 127.6 (2xCH), 127.1 (CH), 121.9 (2xCH), 121.5 (CH), 35.1 (2xC), 31.7 (6xCH_3). **GC-MS** (EI) *m/z* (relative intensity %) = 266.1 (M+, 40), 251.2 (100), 104.0 (10), 57.1 (41). Spectroscopic data are in accordance with those described in the literature.[14]

3,4',5-Trimethyl-1,1'-biphenyl (5h)



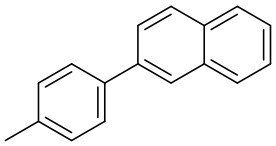
Method A: The reaction was performed according to general procedure **GP4-A** with **4b** (90 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), 1-bromo-3,5-dimethylbenzene (37 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5h** as white solid (30 mg, 0.15 mmol, 76%). **Method B:** The reaction was performed according to general procedure **GP4-B** with **4b** (90 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), 1-bromo-3,5-dimethylbenzene (37 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.), Bobbitt's salt **1** (9 mg, 0.03 mmol, 15 mol%), $NaNO_2$ (4 mg, 0.06 mmol, 30 mol%) and H_2SO_4 (3 µL, 0.06 mmol, 30 mol%) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5h** as white solid (26.5 mg, 0.135 mol, 68%). **^{1}H NMR** (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.49 – 7.46 (*m*, 2H), 7.24 – 7.20 (*m*, 2H), 7.20 – 7.18 (*m*, 2H), 6.99 – 6.95 (*m*, 1H), 2.38 (*s*, 3H), 2.38 – 2.36 (*m*, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 141.3 (C), 138.7 (C), 138.3 (2xC), 137.0 (C), 129.5 (2xCH), 128.8 (CH), 127.2 (2xCH), 125.1 (2xCH), 21.6 (2xCH_3), 21.2 (CH_3). **GC-MS** (EI) *m/z* (relative intensity %) = 196.1 (M+, 100), 181.1 (50), 165.1 (40), 89.1 (13). Spectroscopic data are in accordance with those described in the literature.[15]

4-Methyl-5'-phenyl-1,1':3',1''-terphenyl (5i)



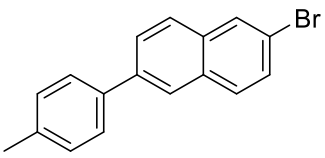
The reaction was performed according to general procedure **GP4-A** with **4b** (90 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), 5'-bromo-1,1':3',1''-terphenyl (62 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5i** as white solid (36 mg, 0.11 mmol, 56%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.84 – 7.78 (*m*, 3H), 7.77 – 7.70 (*m*, 4H), 7.67 – 7.60 (*m*, 2H), 7.55 – 7.48 (*m*, 4H), 7.46 – 7.38 (*m*, 2H), 7.36 – 7.29 (*m*, 2H), 2.45 (*s*, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.5 (2xC), 142.4 (C), 141.4 (2xC), 138.4 (C), 137.5 (C), 129.7 (2xCH), 129.0 (4xCH), 127.7 (2xCH), 127.5 (4xCH), 127.3 (2xCH), 125.1 (2xCH), 125.1 (CH), 21.3 (CH_3). **GC-MS** (EI) *m/z* (relative intensity %) = 320.1 (M+, 100). Spectroscopic data are in accordance with those described in the literature.[16]

2-(*p*-Tolyl)naphthalene (5j)



The reaction was performed according to general procedure **GP4-A** with **4b** (90 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), 2-bromonaphthalene (41 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5j** as white solid (29.5 mg, 135 µmol, 67%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.05 (*d*, *J* = 1.8 Hz, 1H), 7.97 – 7.85 (*m*, 3H), 7.77 (*dd*, *J* = 8.6, 1.9 Hz, 1H), 7.69 – 7.60 (*m*, 2H), 7.57 – 7.44 (*m*, 2H), 7.32 (*dd*, *J* = 7.3, 1.3 Hz, 2H), 2.45 (*s*, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 138.7 (C), 138.4 (C), 137.3 (C), 133.9 (C), 132.7 (C), 129.7 (2xCH), 128.5 (CH), 128.3 (CH), 127.8 (CH), 127.4 (2xCH), 126.4 (CH), 125.9 (CH), 125.7 (CH), 125.6 (CH), 21.3 (CH_3). **GC-MS** (EI) *m/z* (relative intensity %) = 218.1 (M+, 100), 202.1 (32), 108.9 (13) 107.8 (14). Spectroscopic data are in accordance with those described in the literature.[10]

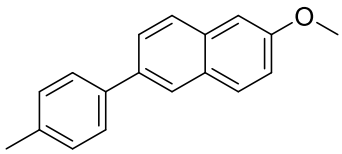
2-Bromo-6-(*p*-tolyl)naphthalene (5k)



The reaction was performed according to general procedure **GP4-A** with **4b** (90 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), 2,6-dibromonaphthalene (57 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5k** as white solid

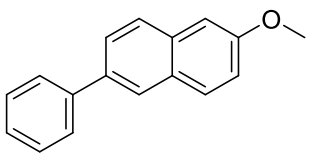
(33 mg, 0.11 mmol, 56%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.06 – 7.95 (*m*, 2H), 7.85 – 7.71 (*m*, 3H), 7.66 – 7.52 (*m*, 3H), 7.35 – 7.27 (*m*, 2H), 2.43 (*s*, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 139.1 (C), 137.9 (C), 137.6 (C), 133.7 (C), 132.3 (C), 129.9 (CH), 129.8 (CH), 129.8 (2xCH), 129.8 (CH), 127.6 (CH), 127.3 (2xCH), 126.7 (CH), 125.4 (CH), 119.8 (C), 21.3 (CH_3). **IR** (film) = 2914w, 2853w, 1610w, 1584w, 1519w, 1493w, 1460w, 1377w, 1357w, 1333w, 1272w, 1215w, 1167w, 1139w, 1065m, 1016w, 943w, 888s, 868m, 810s, 797m, 681w, 651w, 637w, 557m. **GC-HRMS** (EI) *m*: calcd. for $C_{12}H_8BFO_2$ (M^+): 296.0195, found: 296.0196. **m.p.**: 163 °C.

2-Methoxy-6-(*p*-tolyl)naphthalene (5l)



The reaction was performed according to general procedure **GP4-A** with **4b** (90 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), 2-bromo-6-methoxynaphthalene (47 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane:Et_2O = 100:1) afforded **5l** as white solid (36.5 mg, 147 µmol, 73%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.96 (*dd*, *J* = 1.9, 0.8 Hz, 1H), 7.83 – 7.77 (*m*, 2H), 7.74 – 7.68 (*m*, 1H), 7.67 – 7.55 (*m*, 2H), 7.33 – 7.27 (*m*, 2H), 7.21 – 7.14 (*m*, 2H), 3.95 (*s*, 3H), 2.42 (*s*, 3H).**^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 157.9 (C), 138.5 (C), 137.0 (C), 136.5 (C), 133.8 (C), 129.8 (CH9, 129.7 (2xCH), 129.4 (C) 127.3 (CH), 127.20 (2xCH), 126.2 (CH), 125.4 (CH), 119.2 (CH), 105.8 (CH), 55.5 (CH_3), 21.2 (CH_3). **GC-MS** (EI) *m/z* (relative intensity %) = 248.1 (M^+, 100), 233.1 (19), 205.1 (58), 189.1 (15), 124.0 (13), 101.0 (11). Spectroscopic data are in accordance with those described in the literature.[17]

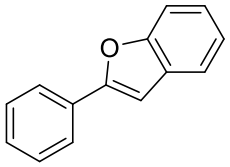
2-Methoxy-6-phenylnaphthalene (5m)



The reaction was performed according to general procedure **GP4-A** with **4a** (87 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), 2-bromo-6-methoxynaphthalene (47 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane:Et_2O = 100:1) afforded **5m** as white solid (36 mg, 0.15 mmol, 77%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.02 – 7.97 (*m*, 1H), 7.84 – 7.79 (*m*, 2H), 7.76 – 7.70 (*m*, 3H), 7.58 – 7.43 (*m*, 2H), 7.43 – 7.31 (*m*, 1H), 7.23 – 7.16 (*m*, 2H), 3.95 (*s*, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 158.0 (C), 141.4 (C), 136.6 (C), 134.0 (C), 129.9 (CH), 129.4 (C), 129.0 (2xCH), 127.4 (CH), 127.4 (2xCH), 127.2 (CH), 126.2 (CH), 125.8 (CH), 119.3 (CH), 105.8 (CH), 55.5 (CH_3).

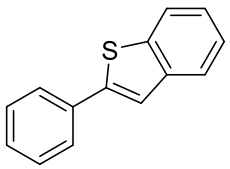
GC-MS (EI) *m/z* (relative intensity %) = 234.1 (M+, 100), 219.1 (25), 191.1 (75), 165.0 (12), 117.0 (12), 94.6 (10). Spectroscopic data are in accordance with those described in the literature.[18]

2-Phenylbenzofuran (5n)



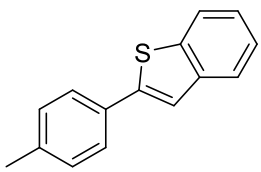
The reaction was performed according to general procedure **GP4-A** with **4a** (87 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), benzofuran (21 µL, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5n** as white solid (20 mg, 0.10 mmol, 51%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 – 7.80 (*m*, 2H), 7.61 – 7.49 (*m*, 2H), 7.48 – 7.39 (*m*, 2H), 7.38 – 7.18 (*m*, 3H), 7.01 (*d*, *J* = 0.9 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 156.1 (C), 155.1 (C), 130.7 (C), 129.4 (C), 128.9 (2xCH), 128.7 (CH), 125.1 (2xCH), 124.4 (CH), 123.1 (CH), 121.1 (CH), 111.3 (CH), 101.5 (CH). **GC-MS** (EI) *m/z* (relative intensity %) = 194.1 (M+, 100), 165.0 (54), 97.0 (11), 82.2 (13). Spectroscopic data are in accordance with those described in the literature.[19]

2-Phenylbenzo[b]thiophene (5o)



The reaction was performed according to general procedure **GP4-A** with **4a** (87 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), benzo[b]thiophene (27 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5o** as white solid (24 mg, 0.11 mmol, 57%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.84 (*ddd*, *J* = 7.2, 1.9, 0.8 Hz, 1H), 7.82 – 7.70 (*m*, 3H), 7.56 (*d*, *J* = 0.8 Hz, 1H), 7.48 – 7.41 (*m*, 2H), 7.40 – 7.29 (*m*, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 144.4 (C), 140.9 (C), 139.7 (C), 134.5 (C), 129.1 (2xCH), 128.4 (CH), 126.7 (2xCH), 124.7 (CH), 124.5 (CH), 123.7 (CH), 122.4 (CH), 119.6 (CH). **GC-MS** (EI) *m/z* (relative intensity %) = 210.1 (M+, 100), 178.1 (13), 165.0 (33), 105.0 (14). Spectroscopic data are in accordance with those described in the literature.[20]

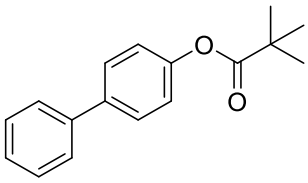
2-(*p*-Tolyl)benzo[b]thiophene (5p)



Method A: The reaction was performed according to general procedure **GP4-A** with **4b** (90 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), benzo[b]thiophene (27 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL,

0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5p** as white solid (29.5 mg, 131 µmol, 66%). **Method B:** The reaction was performed according to general procedure **GP4-B** with **4b** (90 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), benzo[b]thiophene (27 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.), Bobbitt's salt **1** (9 mg, 0.03 mmol, 15 mol%), $NaNO_2$ (4 mg, 0.06 mmol, 30 mol%) and H_2SO_4 (3 µL, 0.06 mmol, 30 mol%) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5p** as white solid (20 mg, 89 µmol, 45%)**.** **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.87 – 7.74 (*m*, 2H), 7.67 – 7.60 (*m*, 2H), 7.51 (*d*, *J* = 0.8 Hz, 1H), 7.40 – 7.28 *(m*, 2H), 7.28 – 7.22 (*m*, 2H), 2.41 (*s*, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 144.6 (C), 141.0 (C), 139.5 (C), 138.4 (C), 131.7 (C), 129.8 (2xCH), 126.5 (2xCH), 124.6 (CH), 124.3 (CH), 123.6 (CH), 122.4 (CH), 119.0 (CH), 21.4 (CH_3). **GC-MS** (EI) *m/z* (relative intensity %) = 224.1 (M+, 100), 112.0 (10). Spectroscopic data are in accordance with those described in the literature.[20]

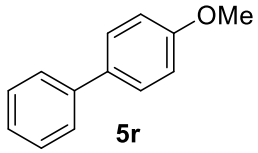
[1,1'-Biphenyl]-4-yl pivalate (5q)



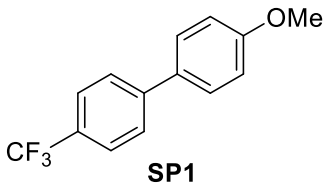
The reaction was performed according to general procedure **GP5** with **4a** (87 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), **S-2** (61 mg, 0.20 mmol, 1.0 equiv.), iPrMgCl•LiCl (1.27 M in THF, 160 µL, 0.204 mmol, 1.02 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL) at -20 °C. Flash column chromatography of the crude product (pentane:Et_2O = 40:1) afforded **5q** as white solid (37 mg, 0.15 mmol, 73%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.65 – 7.53 (*m*, 4H), 7.50 – 7.40 (*m*, 2H), 7.39 – 7.31 (*m*, 1H), 7.19 – 7.10 (*m*, 2H), 1.40 (*s*, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 177.2 (C), 150.7 (C), 140.6 (C), 138.9 (C), 128.9 (2xCH), 128.2 (2xCH), 127.4 (CH), 127.3 (2xCH), 121.9 (2xCH), 39.3 (C), 27.3 (3xCH_3). **GC-MS** (EI) *m/z* (relative intensity %) = 254.1 (M^+, 15), 170.1 (100), 141.0 (14), 115.0 (15), 57.1 (45). Spectroscopic data are in accordance with those described in the literature[21]

4-Methoxy-1,1'-biphenyl (5r) and

4-Methoxy-4'-(trifluoromethyl)-1,1'-biphenyl (SP1)



5r

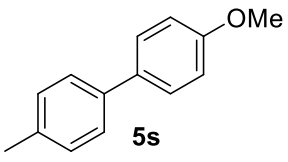


SP1

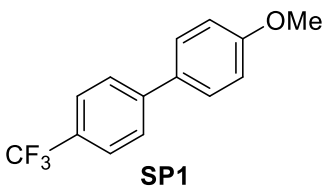
The reaction was performed according to general procedure **GP4-A** with **4a** (87 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), 1-bromo-4-methoxybenzene (25 µl, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). MPLC (Reveleris® C18 (4 g) flash cartidges, 5%-90% MeCN in H_2O over 40 min) afforded **5r** (12.5 mg, 67.8 µmol, 34%) and **SP1** (17.5 mg, 69.4 µmol, 35%) as white solids. Spectroscopic data for **5r**: **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.60 – 7.50 (*m*, 4H), 7.47 – 7.37 (*m*, 2H), 7.35 – 7.27 (*m*, 1H), 7.06 – 6.92 (*m,* 2H), 3.86 (*s*, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 159.3 (C), 141.0 (C), 134.0 (C), 128.9 (2xCH), 128.3 (2xCH), 126.9 (2xCH), 126.8 (1xCH), 114.4 (2xCH), 55.5 (CH_3). **GC-MS** (EI) *m/z* (relative intensity %) = 184.1 (M^+, 100), 169.0 (50), 141.0 (50), 139.0 (14), 115 (39). Spectroscopic data are in accordance with those described in the literature[22] Spectroscopic data for **SP1**: **^{1}H NMR** (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.71 – 7.62 (*m*, 4H), 7.57 – 7.52 (*m*, 2H), 7.03 – 6.99 (*m*, 2H), 3.87 (*s*, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 159.8 (C), 144.3 (C), 132.2 (C), 128.7 (*q*, *J* = 32.6 Hz, C),128.3 (2xCH), 126.8 (2xCH), 125.7 (*q*, *J* = 3.7 Hz, CF_3), 124.4 (*q*, *J* = 271.9 Hz, 2xCH). 114.4 (2xCH), 55.4 (CH_3). **^{19}F NMR** (282 MHz, CDCl3, 300 K): δ (ppm) = -62.3 (CF_3). **GC-MS** (EI) *m/z* (relative intensity %) = 252.1 (M^+,100), 237.0 (28), 209.0 (56), 188.0 (10), 183.0 (14), 139.0 (14). Spectroscopic data are in accordance with those described in the literature[22]

4-Methoxy-4'-methyl-1,1'-biphenyl (5s) and

4-Methoxy-4'-(trifluoromethyl)-1,1'-biphenyl (SP1)



5s

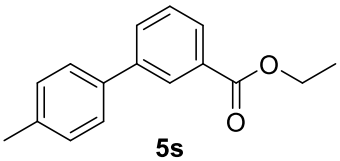


SP1

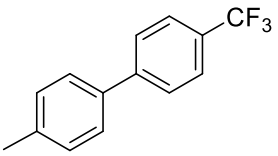
The reaction was performed according to general procedure **GP4-A** with **4b** (90 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), 1-bromo-4-methoxybenzene (25 µL, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). MPLC (Reveleris® C18 (4 g) flash cartidges, 5%-90% MeCN in H_2O over 50 min) afforded **5s** (21.5 mg, 108 µmol, 54%) and **SP1** (11 mg, 44 µmol, 22%) as white solids. Spectroscopic data for **5s**: **^{1}H NMR** (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.54 – 7.48 (*m*, 2H), 7.47 – 7.42 (*m*, 2H),

7.25 – 7.20 (*m*, 2H), 6.99 – 6.94 (*m*, 2H), 3.85 (*s*, 3H), 2.38 (*s*, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 159.1 (C), 138.1 (C), 136.5 (C), 133.9 (C), 129.6 (2xCH), 128.1 (2xCH), 126.7 (2xCH), 114.3 (2xCH), 55.5 (CH_3), 21.2 (CH_3). **GC-MS** (EI) *m/z* (relative intensity %) =198.1 (M+, 100), 183.1 (59), 155.1 (35), 128.0 (13), 115.0 (10). Spectroscopic data are in accordance with those described in the literature.[22] Spectroscopic data for **SP2**: see together with **5r**.

Ethyl 4'-methyl-[1,1'-biphenyl]-3-carboxylate (5t) and
4-Methyl-4'-(trifluoromethyl)-1,1'-biphenyl (SP2)



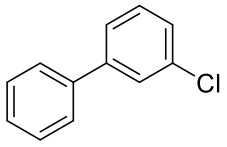
5s



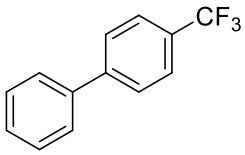
SP2

The reaction was performed according to general procedure **GP5** with **4b** (90 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), ethyl 3-iodobenzoate (55 mg, 0.20 mmol, 1.0 equiv.), iPrMgCl•LiCl (1.27 M in THF, 160 µL, 0.204 mmol, 1.02 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL) at 0 °C. Flash column chromatography of the crude product (pentane → pentane:Et_2O = 10:1) afforded **5t** (22 mg, 92 µmol, 46%) and **SP2** (12 mg, 51 µmol, 25%) as white solids. Spectroscopic data for **5t:** **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.10 – 8.01 (*m*, 1H), 7.84 – 7.75 (*m*, 1H), 7.59 – 7.52 (*m*, 1H), 7.40 – 7.28 (*m*, 3H), 7.10 – 7.03 (*m*, 2H), 4.21 (*q*, *J* = 7.1 Hz, 2H), 2.20 (*s*, 3H), 1.21 (*t, J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.8 (C), 141.5 (C), 137.7 (C), 137.5 (C), 131.4 (CH), 131.2 (C), 129.7 (2xCH), 128.9 (CH), 128.2 (2xCH), 127.2 (2xCH), 61.2 (CH_2), 21.2 (CH_3), 14.5 (CH_3). **GC-MS** (EI) *m/z* (relative intensity %) = 240.1 (M+, 100), 212.1 (24), 195.0 (92), 167.0 (44), 165.0 (46), 152.0 (56), 97.3 (13), 82.3 (11). Spectroscopic data are in accordance with those described in the literature.[23] Spectroscopic data for **SP2: ^{1}H NMR** (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.70 – 7.65 (*m*, 4H), 7.52 – 7.49 (*m*, 2H), 7.31 – 7.27 (*m,* 2H), 2.42 (*s*, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 144.8 (C), 138.3 (C), 137.0 (C), 129.9 (2xCH), 129.2 (q, J_{C-F} = 32.4 Hz, 2xCH), 127.3 (2xCH), 127.2 (2xCH), 125.8 (q, J_{C-F} = 3.8 Hz, C), 124.5 (q, J_{C-F} = 271.9 Hz, CF_3), 21.3 (CH_3). **^{19}F NMR** (282 MHz, CDCl3, 300 K): δ (ppm) = -62.4 (CF_3). **GC-MS** (EI) *m/z* (relative intensity %) = 236.1 (M+, 100), 217.1 (10), 167.0 (44), 152.0 (11). Spectroscopic data are in accordance with those described in the literature[22]

3-Chloro-1,1'-biphenyl (5u) and
4-(Trifluoromethyl)-1,1'-biphenyl (SP3)



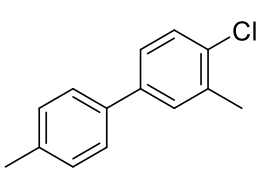
5t



SP3

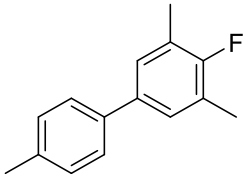
The reaction was performed according to general procedure **GP4-A** with **4a** (87 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), 1-bromo-3-chlorobenzene (23 µL, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5u** (10.5 mg, 55.5 µmol, 28%) and **SP3** (7.0 mg, 33 µmol, 16%) as an inseparable mixture (17.7 mg, **5u**:**SP3** = 1.7:1). Above assigned yields are calculated back. Spectroscopic data for the mixture of **5u** and **SP2:** **^{1}H NMR** (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.70 (*s*, $4H_{SP3}$), 7.62 – 7.55 (*m*, $3H_{5u}$, $2H_{SP3}$), 7.50 – 7.35 (*m*, $5H_{5u}$, $3H_{SP3}$), 7.34 – 7.31 (*m*, $1H_{5u}$). **^{13}C NMR {^{19}F}** (151 MHz, $CDCl_3$, 300 K): δ (ppm) = 144.9 (C_{SP3}), 143.2 (C_{5u}), 140.0 (C_{5u}), 139.9 (C_{SP3}), 134.8 (C_{5u}), 130.1 (CH_{5u}), 129.5 (C_{SP3}), 129.1 ($2xCH_{SP3}$), 129.04 ($2xCH_{5u}$), 128.3 (CH_{SP3}), 128.0 (CH_{5u}), 127.6 ($2xCH_{SP3}$), 127.5 (CH_{5u}), 127.4 ($2xCH_{SP3}$), 127.4 (CH_{5u}), 127.3 ($2xCH_{5u}$), 125.9 ($2xCH_{SP3}$), 125.5 (CH_{5u}), 124.5 (C_{SP3}). **^{19}F NMR** (564 MHz, DMSO-d_6, 300 K): δ (ppm) = -62.4. (CF_3). **GC-MS** (EI) *m/z* (relative intensity %) of **5u** = 188.0 (M+, 100), 152.0 (56), 76.0 (27), 63.0 (13). **GC-MS** (EI) *m/z* (relative intensity %) of **SP3** = 222.0 (M+, 100), 201.0 (10), 152.0 (26). Spectroscopic data are in accordance with those described in the literature[24,25]

4-Chloro-3,4'-dimethyl-1,1'-biphenyl (5v)



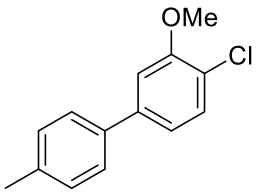
The reaction was performed according to general procedure **GP4-A** with **4b** (90 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), 4-bromo-1-chloro-2-methylbenzene (41 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5v** as white solid (26 mg, 0.12 mmol, 60%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.49 – 7.42 (*m*, 3H), 7.41 – 7.30 (*m*, 2H), 7.28 – 7.21 (*m*, 2H), 2.44 (*s*, 3H), 2.40 (*s*, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 139.9 (C), 137.5 (C), 137.4 (C), 136.3 (C), 133.4 (C), 129.7 (2xCH), 129.6 (CH), 129.5 (CH), 127.0 (2xCH), 125.8 (CH), 21.2 (CH_3), 20.3 (CH_3). **IR** (film) = 3027w, 2919w, 2860w, 1611w, 1564w, 1479m, 1444w, 1380w, 1326w, 1196w, 1161w, 1127w, 1062m, 1039m, 881w, 806s, 704w. **GC-HRMS** (EI) *m/z*: calcd. for $C_{14}H_{13}Cl$ (M^+): 216.0700, found: 216.0701. **m.p.**: 48°C.

4-Fluoro-3,4',5-trimethyl-1,1'-biphenyl (5w)



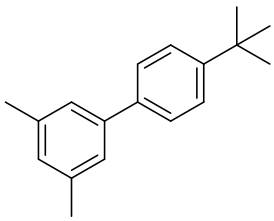
The reaction was performed according to general procedure **GP4-A** with **4b** (90 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), 5-bromo-2-fluoro-1,3-dimethylbenzene (41 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5w** as white solid (27.5 mg, 128 µmol, 64%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.47 – 7.41 (*m*, 2H), 7.26 – 7.18 (*m*, 4H), 2.40 (*s*, 3H), 2.33 (*d*, *J* = 2.2 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 159.6 (*d*, $J_{C\text{-}F}$ = 243.7 Hz, C), 138.0 (C), 136.9 (C), 136.6 (*d*, $J_{C\text{-}F}$ = 4.2 Hz, C), 129.6 (2xCH), 127.5 (*d*, $J_{C\text{-}F}$ = 4.9 Hz, 2xCH), 127.0 (2xCH), 124.7 (*d*, $J_{C\text{-}F}$ = 18.2 Hz, 2xC), 21.2 (CH_3), 14.9 (d, $J_{C\text{-}F}$ = 4.2 Hz, 2xCH_3). **^{19}F NMR** (282 MHz, CDCl3, 300 K): δ (ppm) = -124.7. **IR** (film) = 3030w, 2921w, 2859w, 1617w, 1479m, 1381w, 1326w, 1236m, 1208w, 1173m, 1128w, 1115w, 1072w, 1037w, 1017w, 986w, 959w, 908w, 890w, 878w, 816s, 734w, 719m. **GC-HRMS** (EI) *m/z*: calcd. for $C_{15}H_{15}F$ (M^+): 214.11523, found: 214.11513.

4-Chloro-3-methoxy-4'-methyl-1,1'-biphenyl (5x)



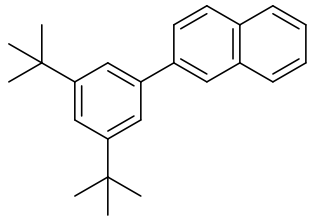
The reaction was performed according to general procedure **GP4-A** with **4b** (90 mg, 0.22 mmol, 1.1 equiv.), HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.2 equiv.), 4-bromo-1-chloro-2-methoxybenzene (44 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5x** as colorless oil (22.5 mg, 96.7 µmol, 48%).**^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.50 – 7.43 (*m*, 2H), 7.43 – 7.37 (*m*, 1H), 7.30 – 7.22 (*m*, 2H), 7.15 – 7.07 (*m*, 2H), 3.97 (*s*, 3H), 2.41 (*s*, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 155.3 (C), 141.5 (C), 137.7 (C), 137.7 (C), 130.5 (CH), 129.7 (2xCH), 127.1 (2xCH), 121.6 (C), 120.1 (CH), 111.1 (CH), 56.3 (CH_3), 21.2 (CH_3). **IR** (film) = 2922w, 1594w, 1562w, 1482s, 1464m, 1447w, 1415w, 1391m, 1306m, 1227s, 1188w, 1145w, 1117w, 1075m, 1029m, 858w, 825w, 804s, 706w. **HRMS** (ESI) *m/z*: calcd. for $C_{14}H_{13}OClNa$ ([M+Na]$^+$): 255.0547, found: 255.0548.

4'-(*Tert*-butyl)-3,5-dimethyl-1,1'-biphenyl (5y)



The reaction was performed according to general procedure **GP7** with **S-1** (79 mg, 0.22 mmol, 1.1 equiv.), 1-bromo-3,5-dimethylbenzene (41 mg, 0.22 mmol, 1.1 equiv.), *n*BuLi (1.51 M in hexane, 0.15 mL, 0.22 mmol, 1.1 equiv.) HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.21 equiv.), 1-bromo-4-(*tert*-butyl)benzene (43 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5y** as white solid (20.5 mg, 86.0 µmol, 43%). **^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.57 – 7.43 (*m*, 4H), 7.25 – 7.18 (*m*, 2H), 7.05 – 6.92 (*m*, 1H), 2.42 – 2.36 (*m*, 6H), 1.38 (*s*, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 150.2 (C), 141.3 (C), 138.7 (C), 138.3 (2xC), 128.8 (CH), 127.0 (2xCH), 125.7 (2xCH), 125.2 (2xCH), 34.7 (C), 31.5 (3xCH_3), 21.6 (2xCH_3). **GC-MS** (EI) *m/z* (relative intensity %) = 238.2 (M+, 33), 223.2 (100), 195.1 (11), 165.0 (14), 90.0 (13). Spectroscopic data are in accordance with those described in the literature[13]

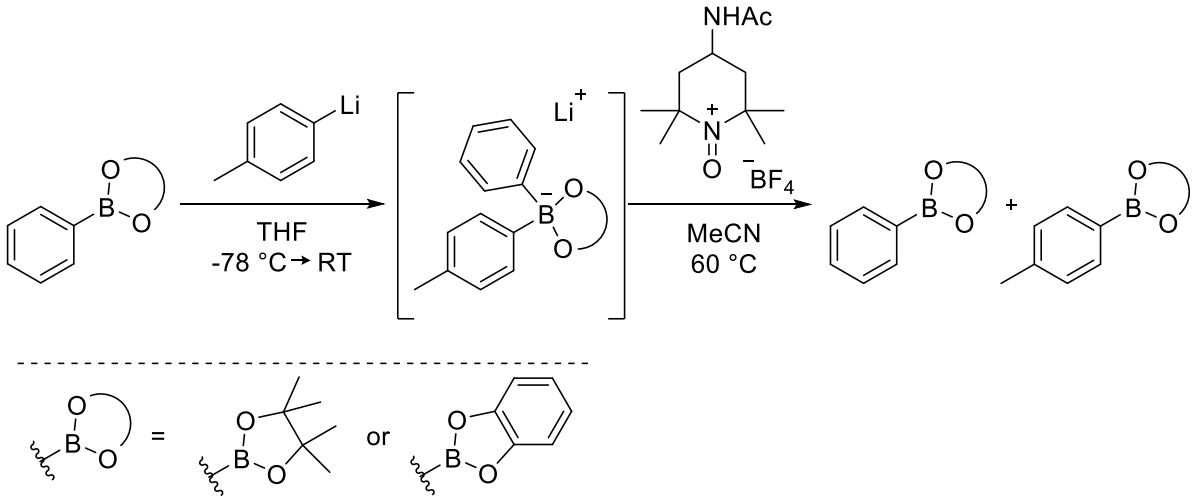
2-(3,5-Di-*tert*-butylphenyl)naphthalene (5z)



The reaction was performed according to general procedure **GP7** with **S-1** (79 mg, 0.22 mmol, 1.1 equiv.), 1-bromo-3,5-di-*tert*-butylbenzene (59 mg, 0.22 mmol, 1.1 equiv.), *n*BuLi (1.51 M in hexane, 0.15 mL, 0.22 mmol, 1.1 equiv.) HCl (1.03 M in Et_2O, 235 µL, 0.242 mmol, 1.21 equiv.), 2-bromonaphthalene (41 mg, 0.20 mmol, 1.0 equiv.), *n*BuLi (1.51 M in hexane, 0.13 mL, 0.20 mmol, 1.0 equiv.) and Bobbitt's salt **1** (72 mg, 0.24 mmol, 1.2 equiv.) in MeCN (2.0 mL). Flash column chromatography of the crude product (pentane) afforded **5z** as white solid (25.5 mg, 80.6 µmol, 40%).**^{1}H NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.08 – 8.03 (*m*, 1H), 7.97 – 7.86 (*m*, 3H), 7.78 (*dd*, *J* = 8.5, 1.8 Hz, 1H), 7.58 (*d*, *J* = 1.9 Hz, 2H), 7.55 – 7.45 (*m*, 3H), 1.45 (*s*, 18H). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 151.4 (2xC), 140.8 (C), 140.0 (C), 133.9 (C), 132.7 (C), 128.4 (CH), 128.3 (CH), 127.8 (CH), 126.3 (CH), 126.3 (CH), 126.0 (CH), 125.9 (CH), 122.1 (2xCH), 121.7 (CH), 35.2 (2xC), 31.7 (6xCH_3). **IR** (film) = 2962s, 2902w, 2867w, 1593m, 1506w, 1476w, 1460w, 1426w, 1393w, 1362m, 1325w, 1247m, 1224w, 1202w, 1131w, 1071w, 1018w, 902w, 889w, 875m, 853s, 816s, 745s, 712s. **GC-HRMS** (EI) *m/z*: calcd. for $C_{24}H_{28}$ (M^+): 316.2186, found: 316.2185. **m.p.**: 139 °C

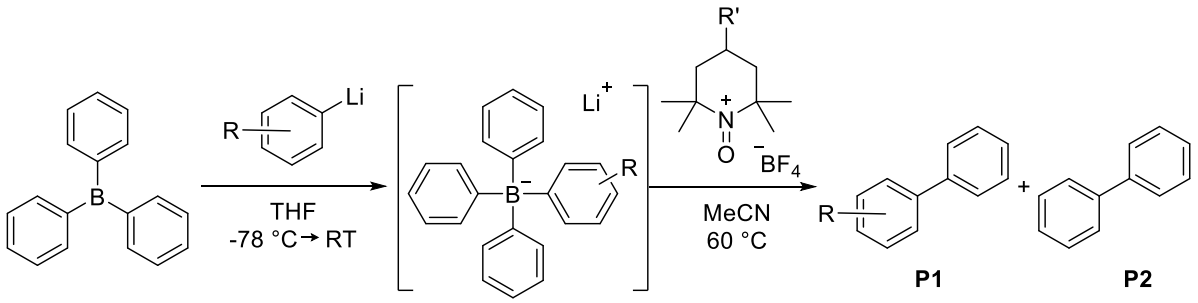
3 Preliminary studies towards the selective cross-coupling of tetraaryl-borates

Attempted coupling with pinacol and catechol aryl boronic esters:



Procedure: *n*BuLi (1.6 M in hexane, 125 µL, 0.200 mmol, 1.0 equiv.) was added to 1-bromo-4-methylbenzene (34 mg, 0.20 mmol, 1.0 equiv.) in THF (1.5 mL) at -78 °C and the mixture was stirred for 30 min before addition of PhBpin or PhBcat (0.30 mmol, 1.0 equiv.) at -78 °C. The mixture was stirred for 10 min, allowed to warm up to room temperature and stirring was continued for 30 min. $TEMPO^+BF_4^-$ (73 mg, 0.30 mmol, 1.0 equiv.) was added, the tube was sealed and the reaction mixture was heated up to 60 °C and stirred for 18 h. After removal of the solvent *in vacuo*, the crude mixture was analyzed by GC-MS analysis. In both cases, the desired biaryl formation was not observed but both the respective phenyl boronic esters and *p*-methylphenyl boronic esters could be detected.

Identifying an ideal "dummy" ligand:

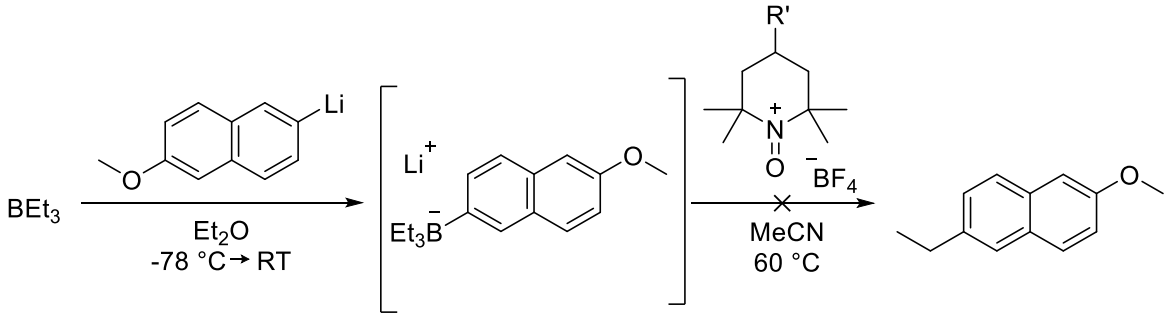


Procedure: *n*BuLi (1.6 M in hexane, 0.19 mL, 0.30 mmol, 1.0 equiv.) was added to the respective arylbromide (0.30 mmol, 1.0 equiv.) in THF (1.5 mL) at -78 °C and the mixture was stirred for 30 min before addition of BPh_3 (0.25 M in THF, 1.2 mL, 0.30 mmol,

1.0 equiv.) at -78 °C. The mixture was stirred for 10 min, allowed to warm up to room temperature and stirring was continued for 30 min. $TEMPO^+BF_4^-$ (73 mg, 0.30 mmol, 1.0 equiv.) was added, the tube was sealed and the reaction mixture was heated up to 60 °C and stirred for 18 h. After removal of the solvent *in vacuo*, flash column chromatography (pentane) of the crude material afforded an inseparable mixture of **P1** and **P2**. Ratio and yields determined *via* ^{1}H-NMR analysis (600 MHz).
For R = *p*-OMe **P1** and **P2** could be separated via FC (pentane/Et_2O = 100:1).

	R	R'	Yield of **P1** [%]	Yield of **P2** [%]
1	*p*-Me	H	53	9
2	*p*-OMe	H	52	6
3	*p*-CF_3	H	1	52
4	*p*-CF_3	NHAc	1	57
5	*p*-CN	H	Traces	35
6	*p*-F	H	14	25

Attempted alkyl/aryl coupling:



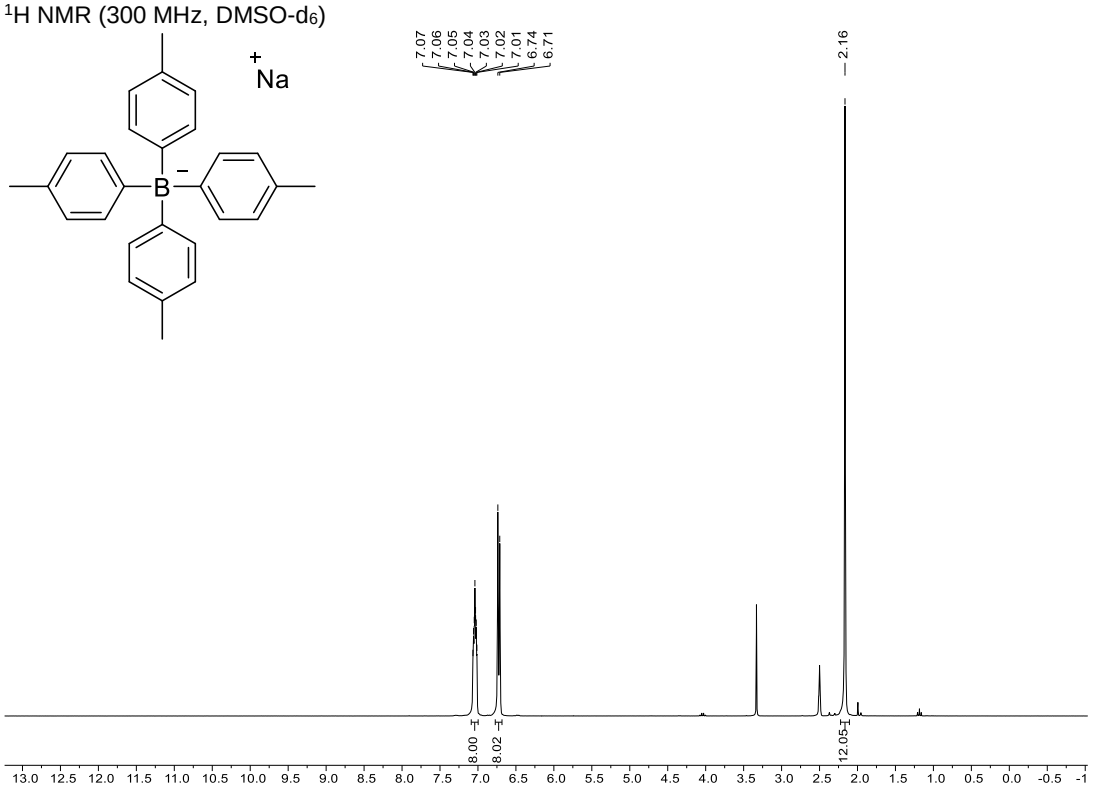
Procedure: *n*BuLi (1.51 M in hexane, 0.12 mL, 0.30 mmol, 1.0 equiv.) was added to 2-bromo-6-methoxynaphthalene (71 mg, 0.30 mmol, 1.0 equiv.) in Et_2O (1.5 mL) at -78 °C and the mixture was stirred for 30 min before addition of BEt_3 (1.0 M in hexane, 0.30 mL, 0.30 mmol, 1.0 equiv.) at -78 °C. The mixture was stirred for 10 min, allowed to warm up to room temperature and stirring was continued for 30 min. Bobbitt's salt (108 mg, 0.360 mmol, 1.2 equiv.) was added, the tube was sealed and the reaction mixture was heated up to 60 °C and stirred for 18 h. After removal of the solvent *in vacuo*, the crude mixture was analyzed by GC-MS analysis. The targeted 2-ethyl-6-methoxynaphthalene could not be detected.

4 Spectral Data

4.1 Spectral Data for Starting Materials

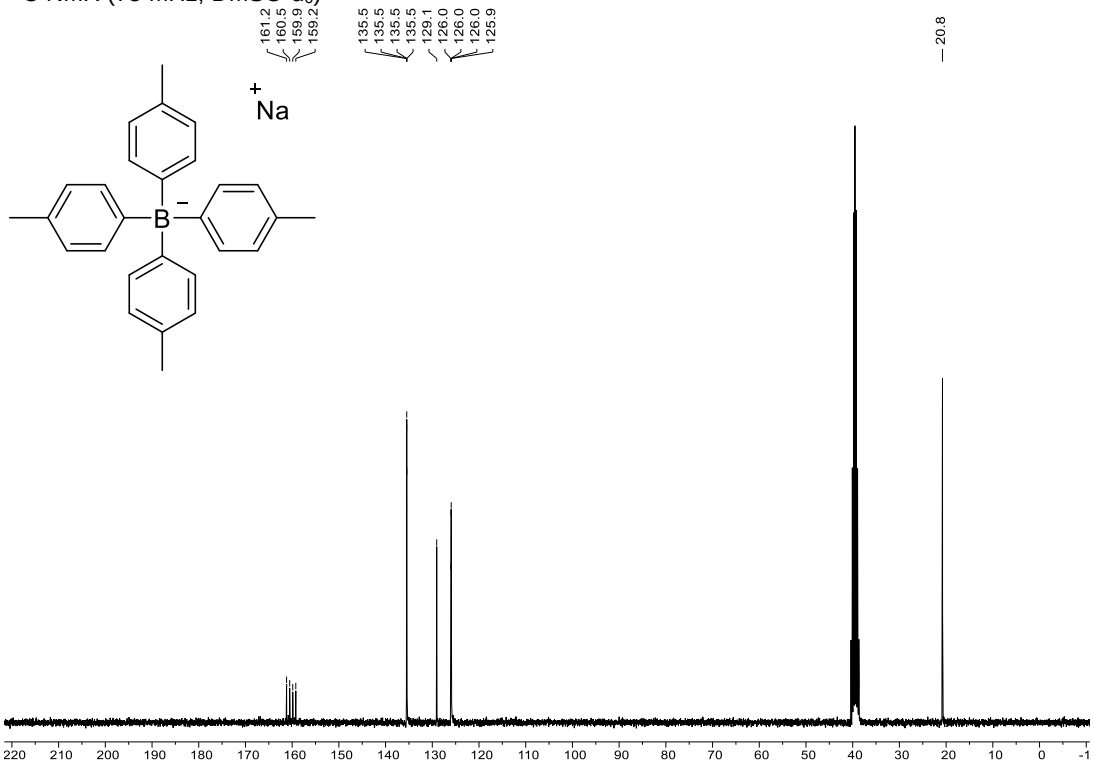
Sodium tetra-*p*-tolylborate (2a)

^{1}H NMR (300 MHz, DMSO-d$_6$)



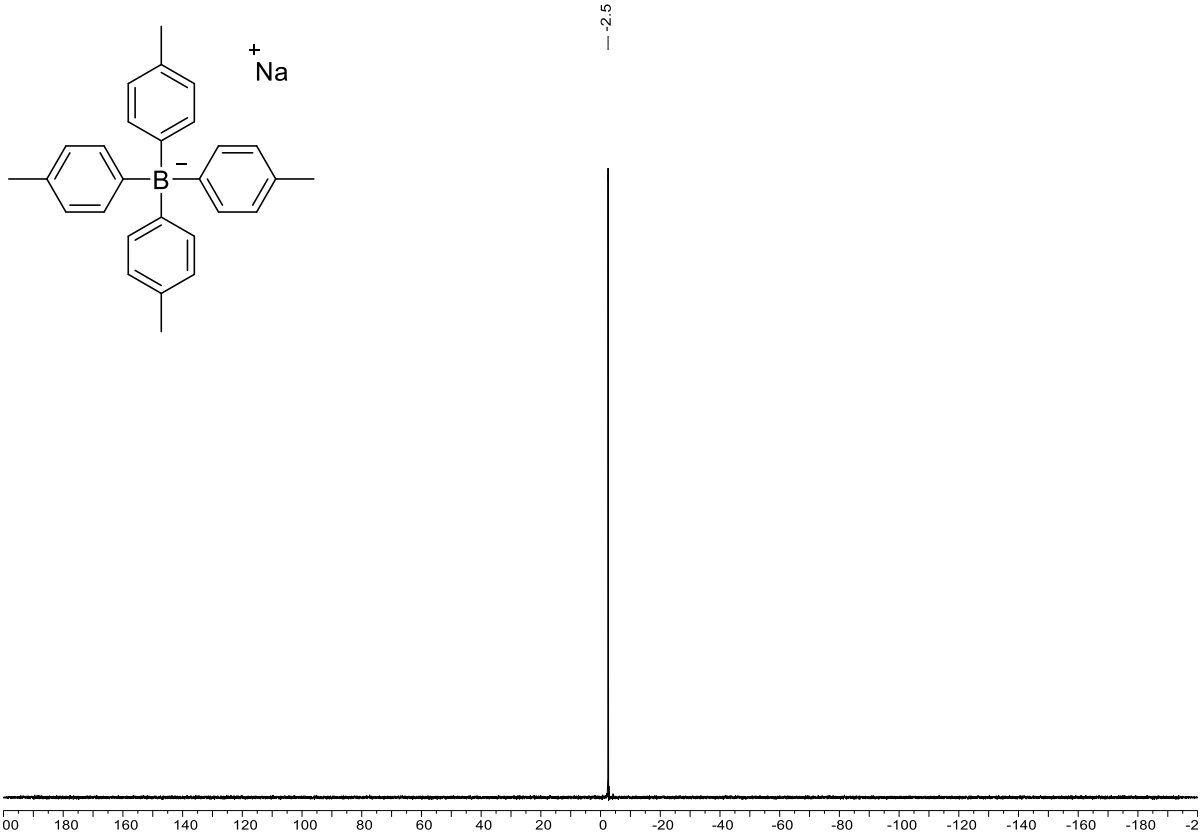
Sodium tetra-*p*-tolylborate (2a)

^{13}C NMR (75 MHz, DMSO-d$_6$)



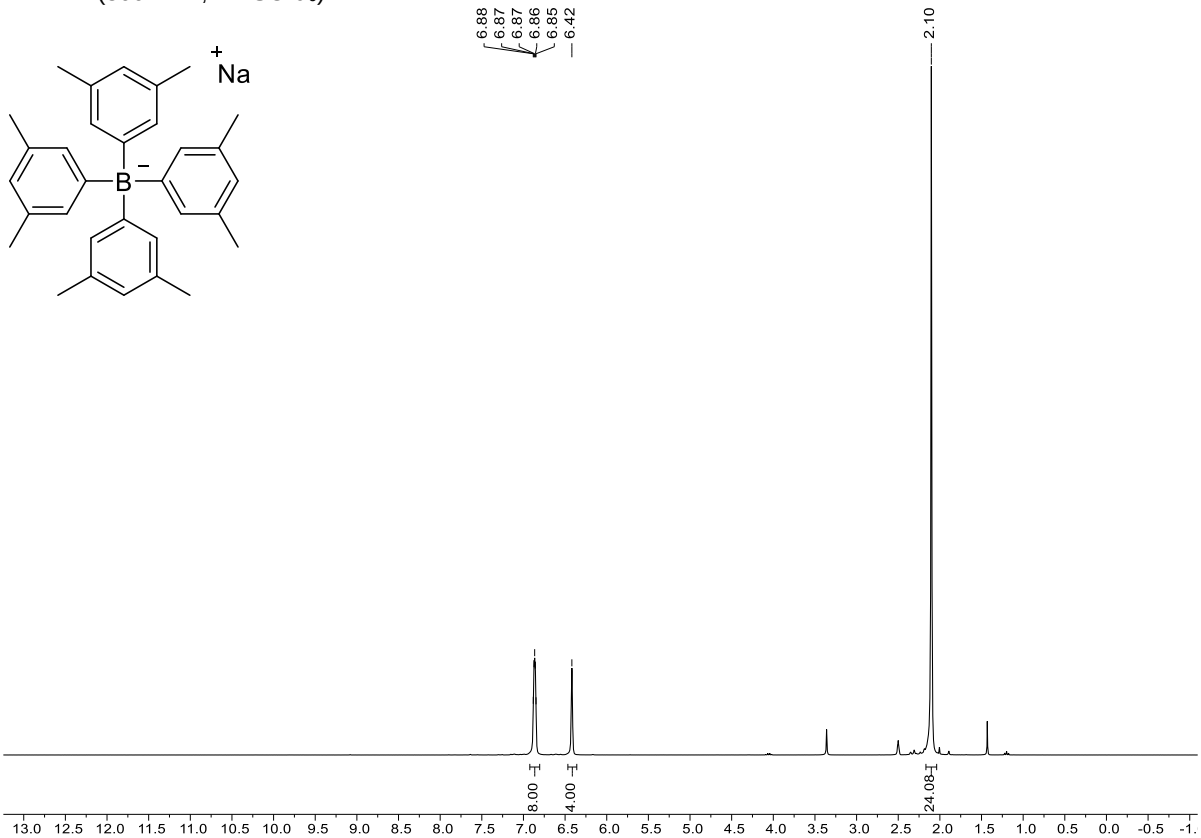
Sodium tetra-*p*-tolylborate (2a)

^{11}B NMR (96 MHz, DMSO-d_6)



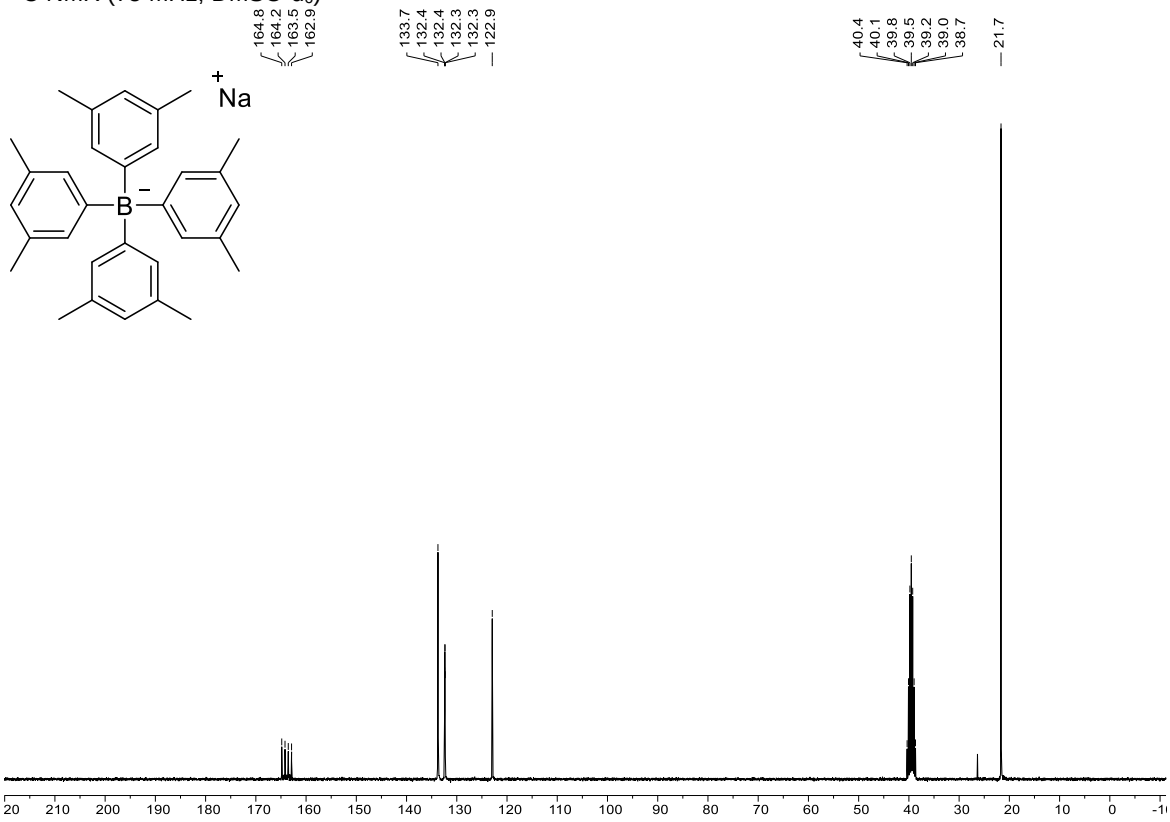
Sodium tetrakis(3,5-dimethylphenyl)borate (2c)

^{1}H NMR (300 MHz, DMSO-d_6)



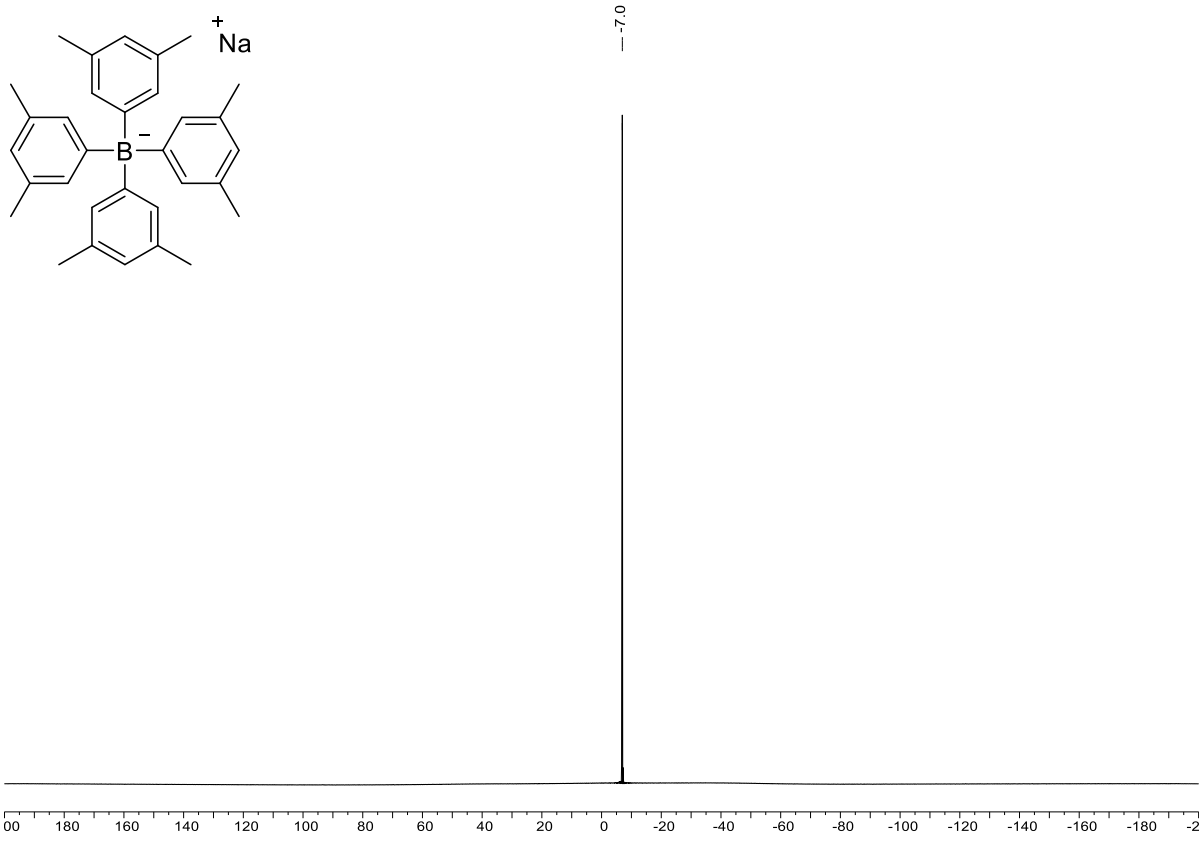
Sodium tetrakis(3,5-dimethylphenyl)borate (2c)

^{13}C NMR (75 MHz, DMSO-d_6)



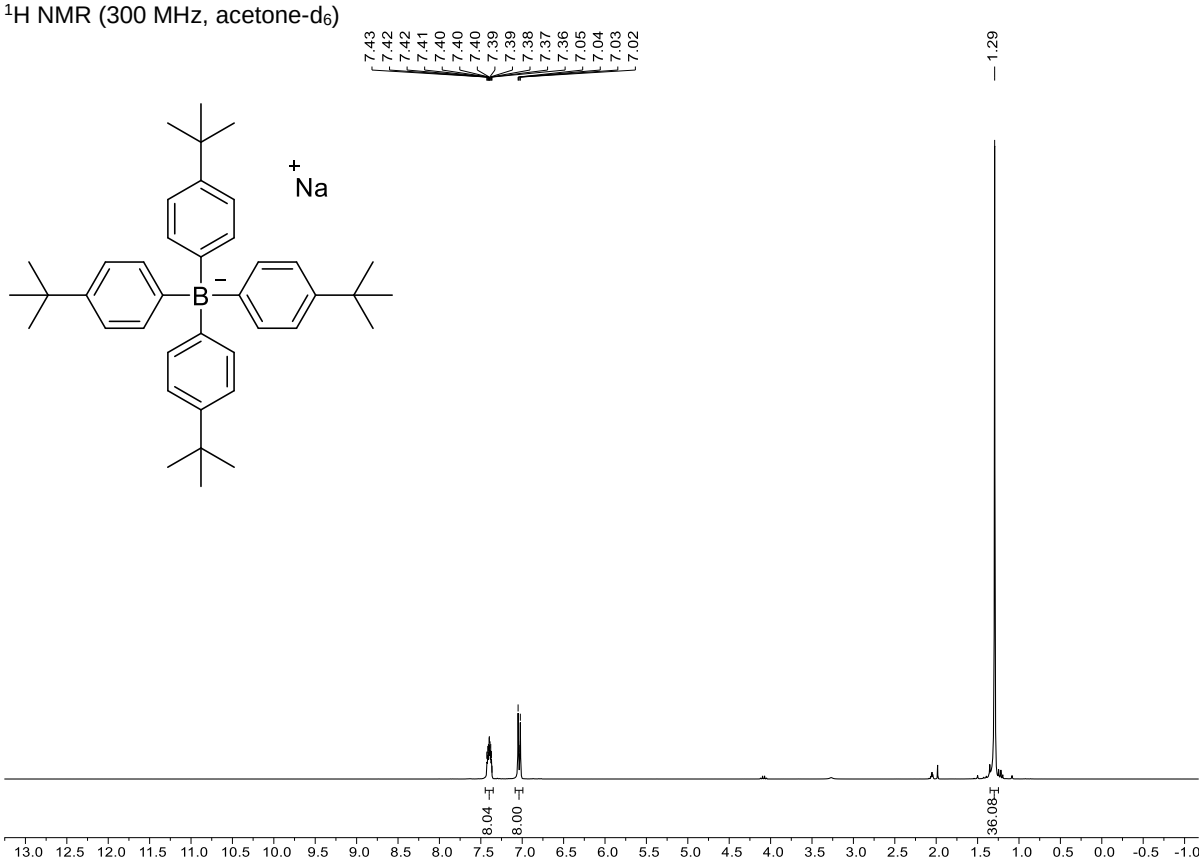
Sodium tetrakis(3,5-dimethylphenyl)borate (2c)

^{11}B NMR (96 MHz, DMSO-d_6)



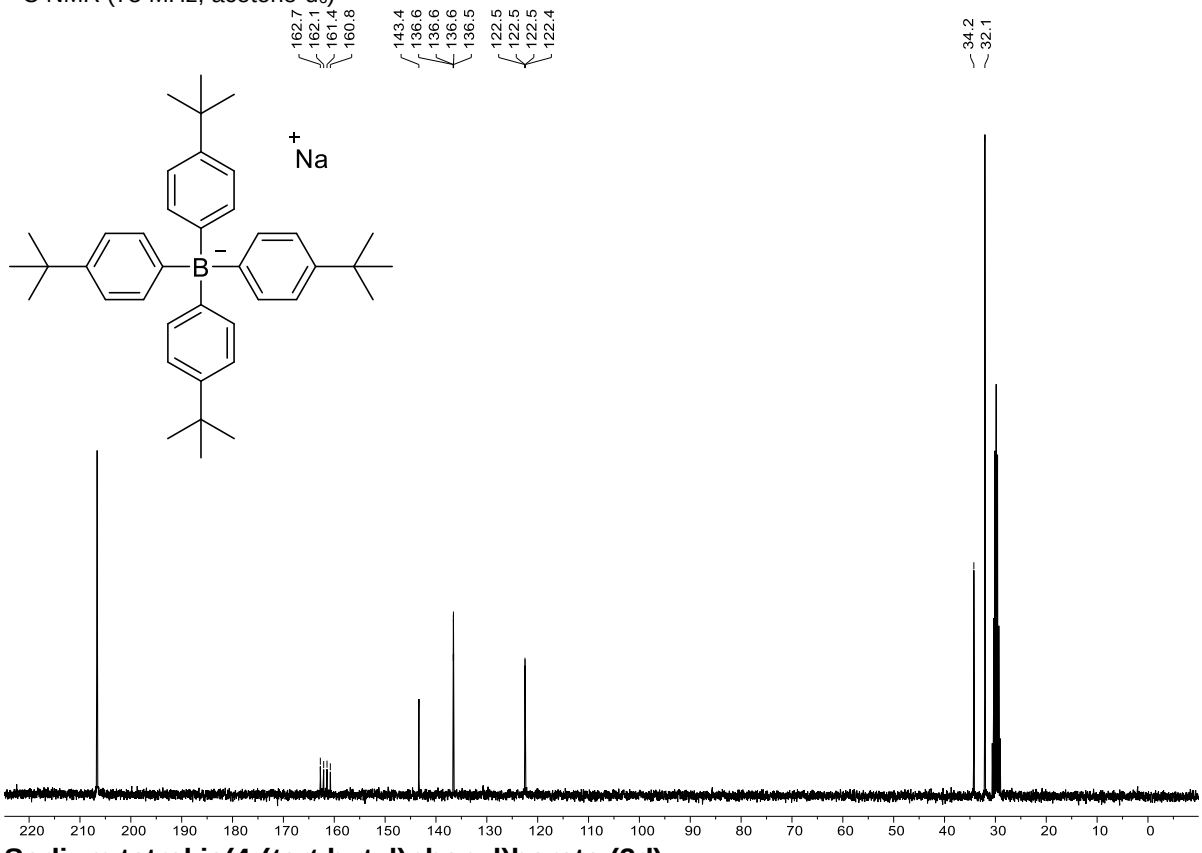
Sodium tetrakis(4-(*tert*-butyl)phenyl)borate (2d)

^{1}H NMR (300 MHz, acetone-d_6)



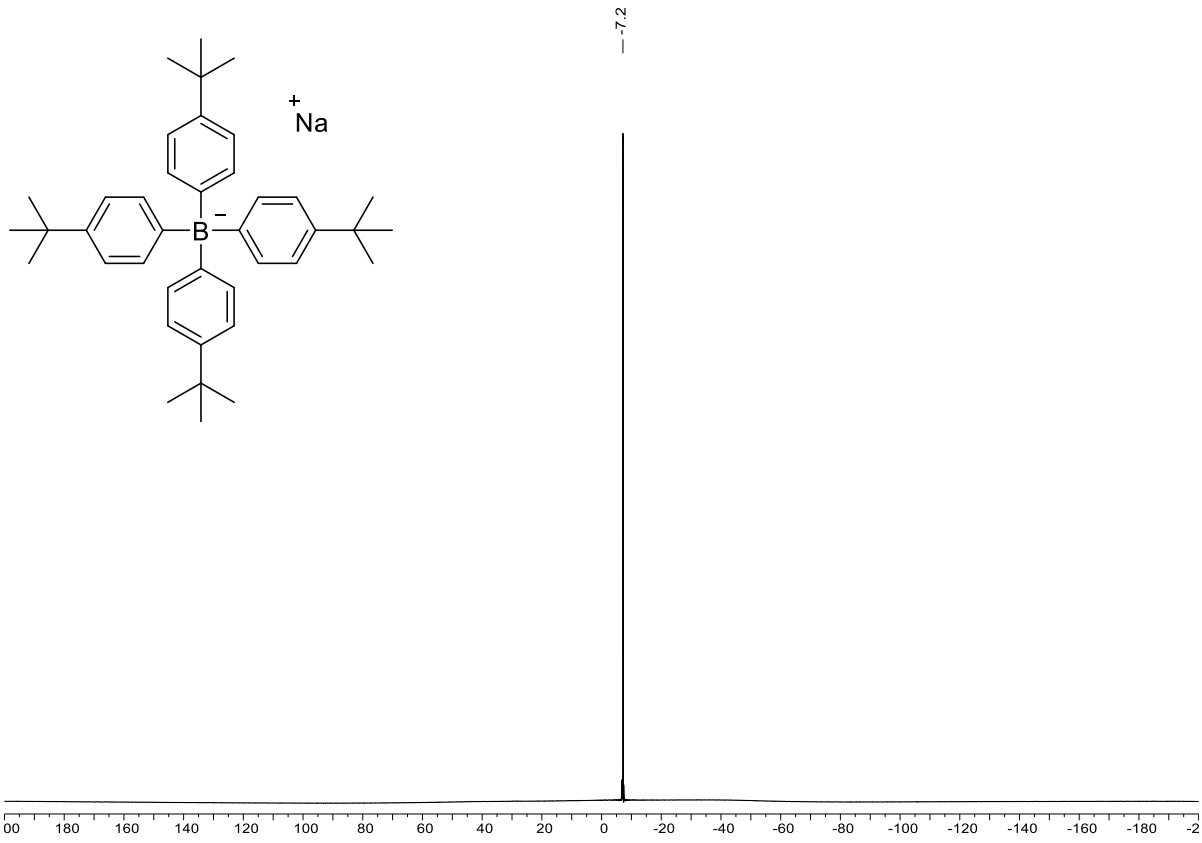
Sodium tetrakis(4-(*tert*-butyl)phenyl)borate (2d)

^{13}C NMR (75 MHz, acetone-d_6)



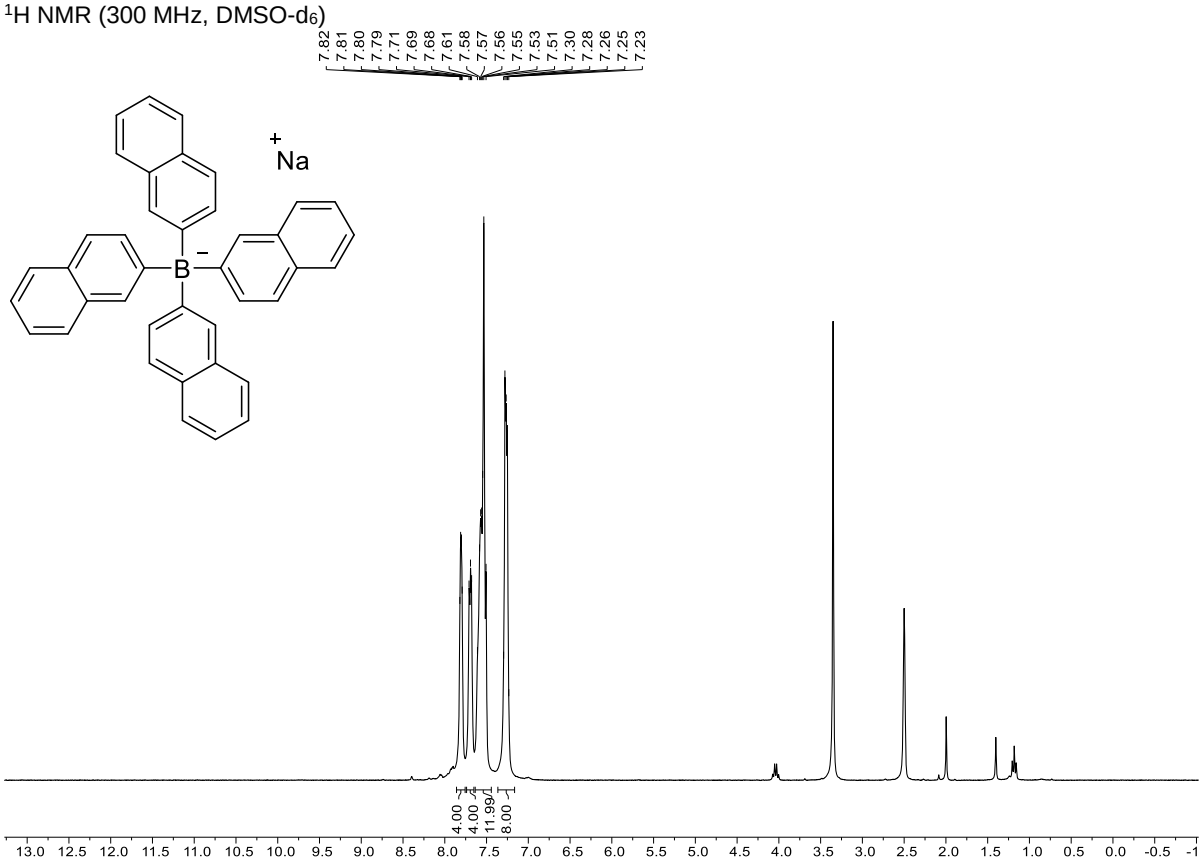
Sodium tetrakis(4-(*tert*-butyl)phenyl)borate (2d)

^{11}B NMR (96 MHz, acetone-d_6)



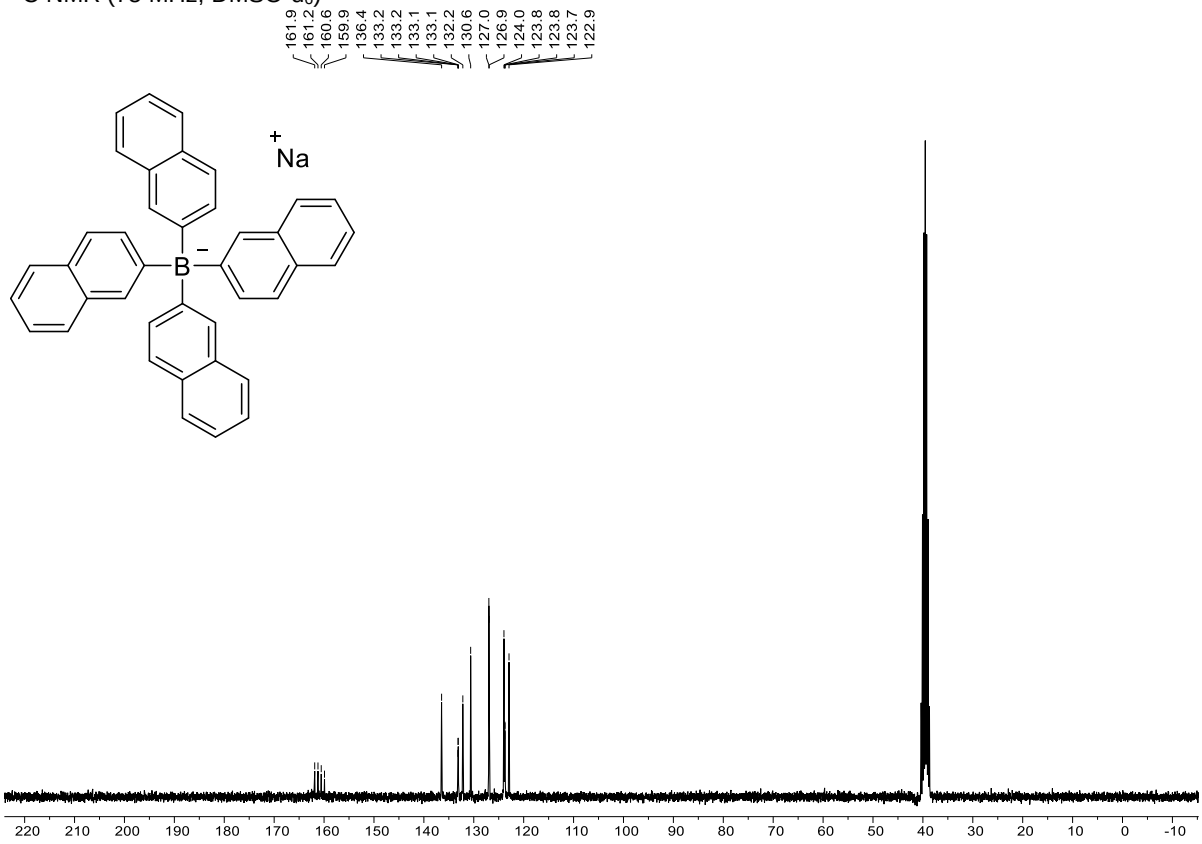
Sodium tetra(naphthalen-2-yl)borate (2e)

^{1}H NMR (300 MHz, DMSO-d_6)



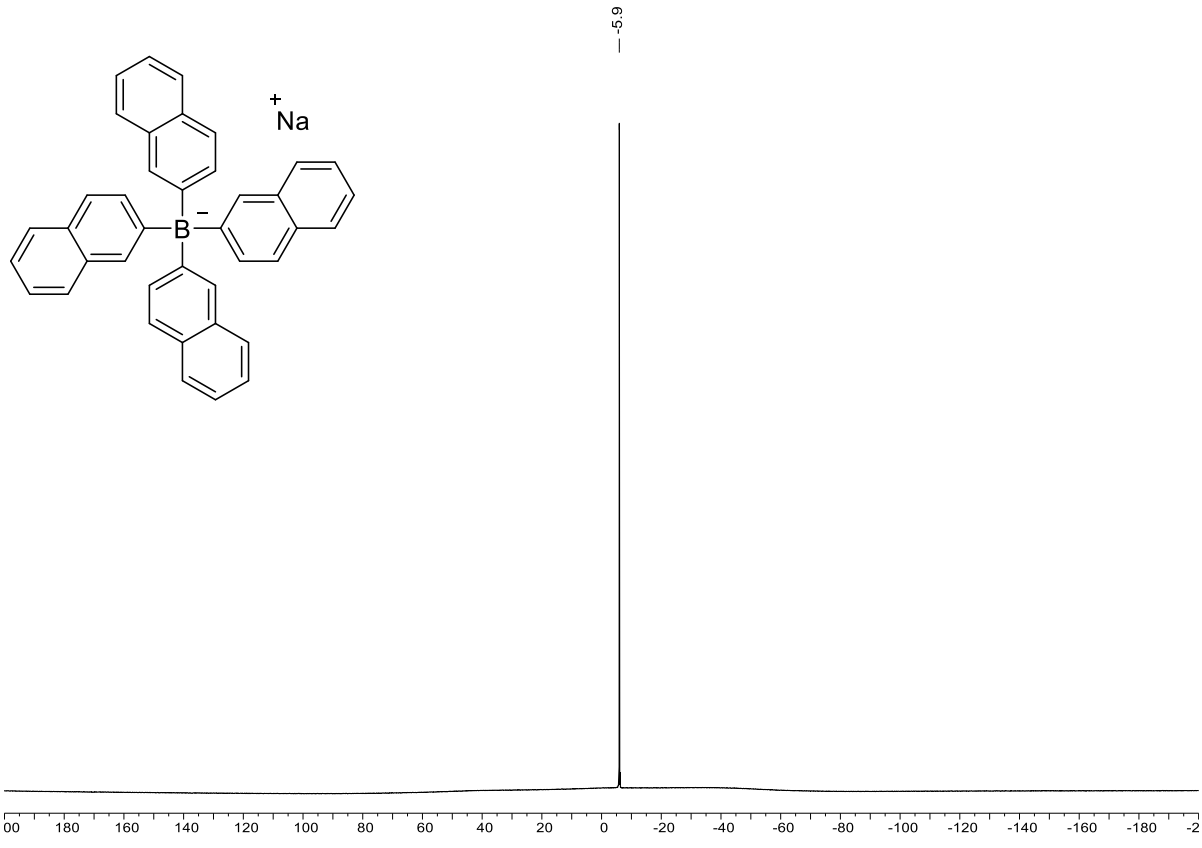
Sodium tetra(naphthalen-2-yl)borate (2e)

^{13}C NMR (75 MHz, DMSO-d_6)



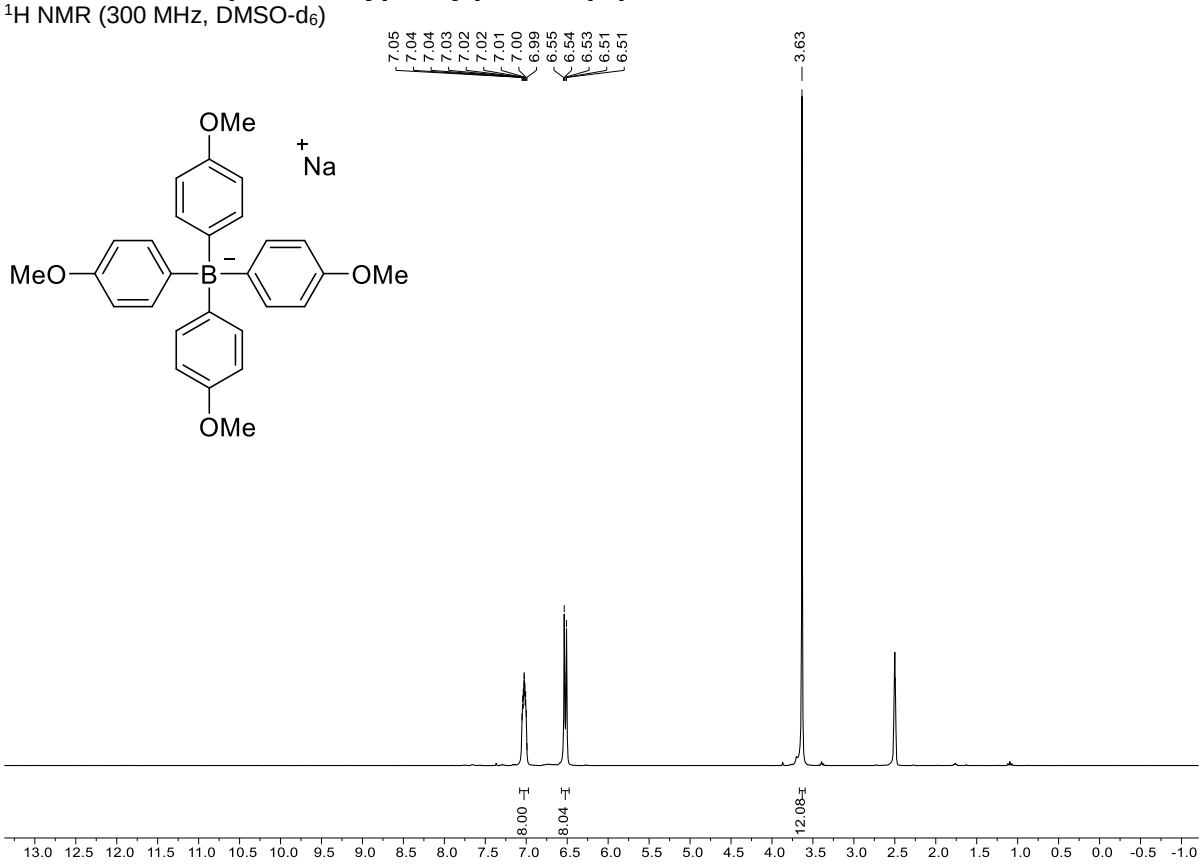
Sodium tetra(naphthalen-2-yl)borate (2e)

^{11}B NMR (96 MHz, DMSO-d_6)



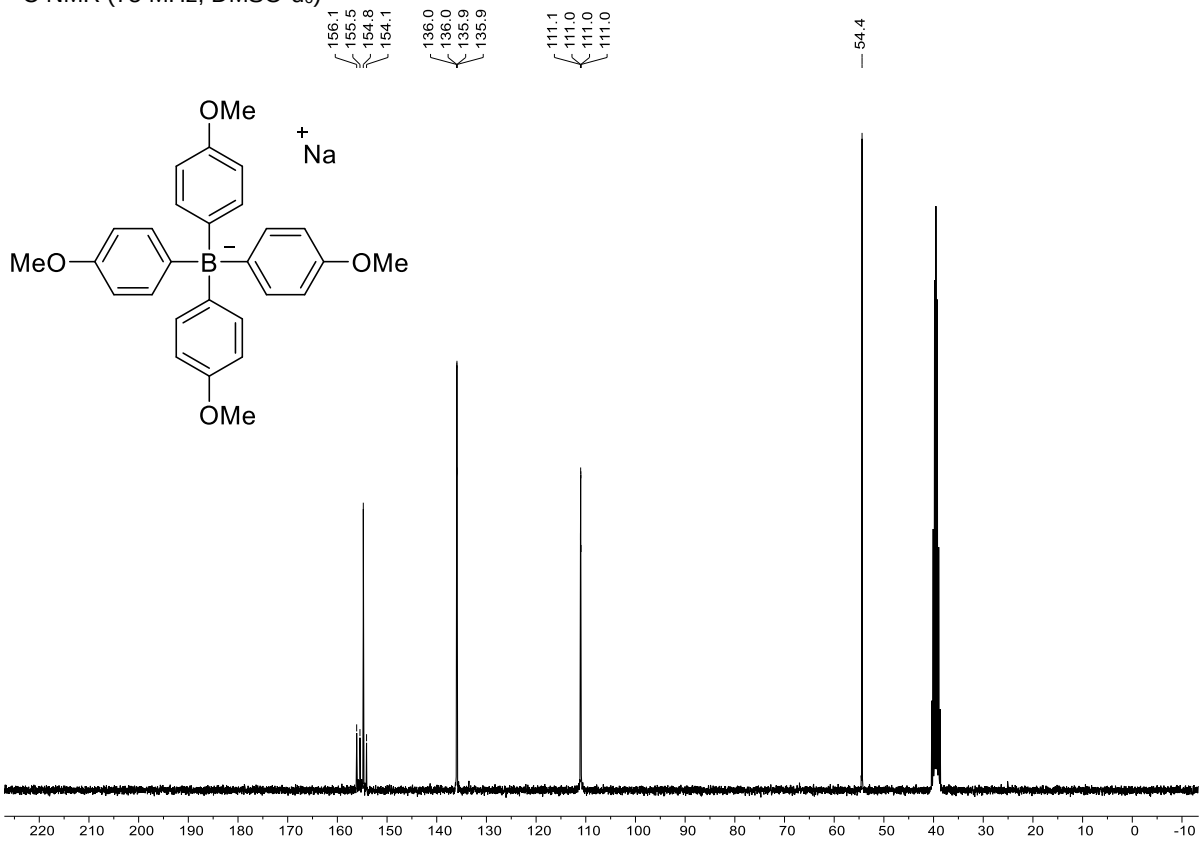
Sodium tetrakis(4-methoxyphenyl)borate (2f)

^{1}H NMR (300 MHz, DMSO-d_6)



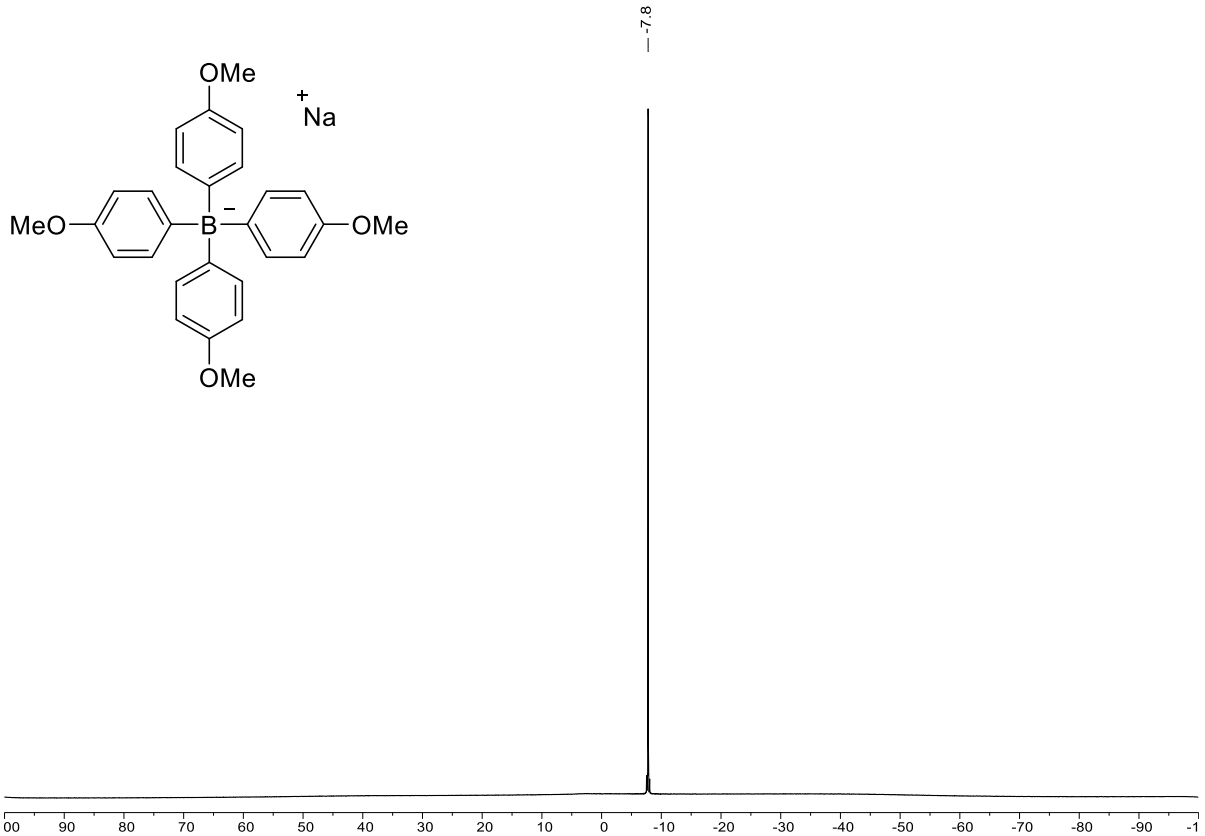
Sodium tetrakis(4-methoxyphenyl)borate (2f)

^{13}C NMR (75 MHz, DMSO-d_6)



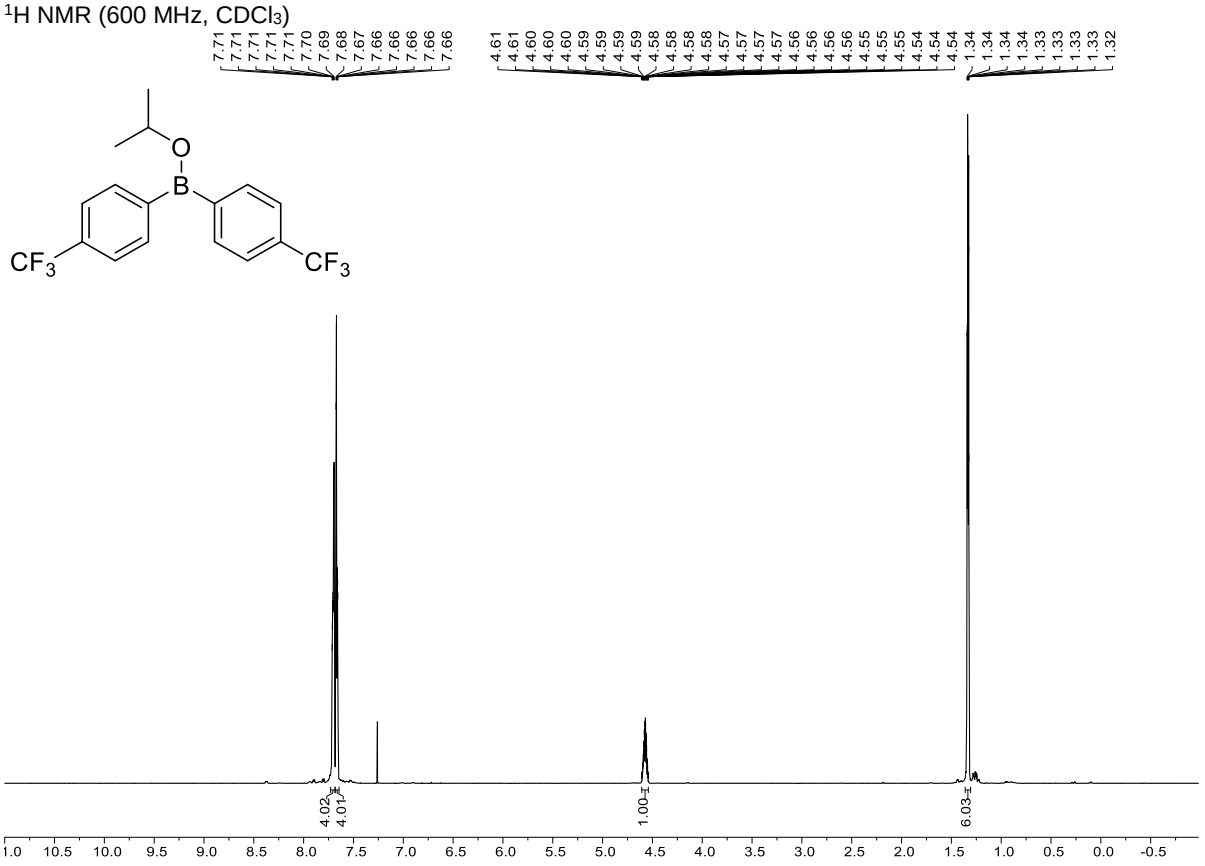
Sodium tetrakis(4-methoxyphenyl)borate (2f)

^{11}B NMR (96 MHz, DMSO-d_6)



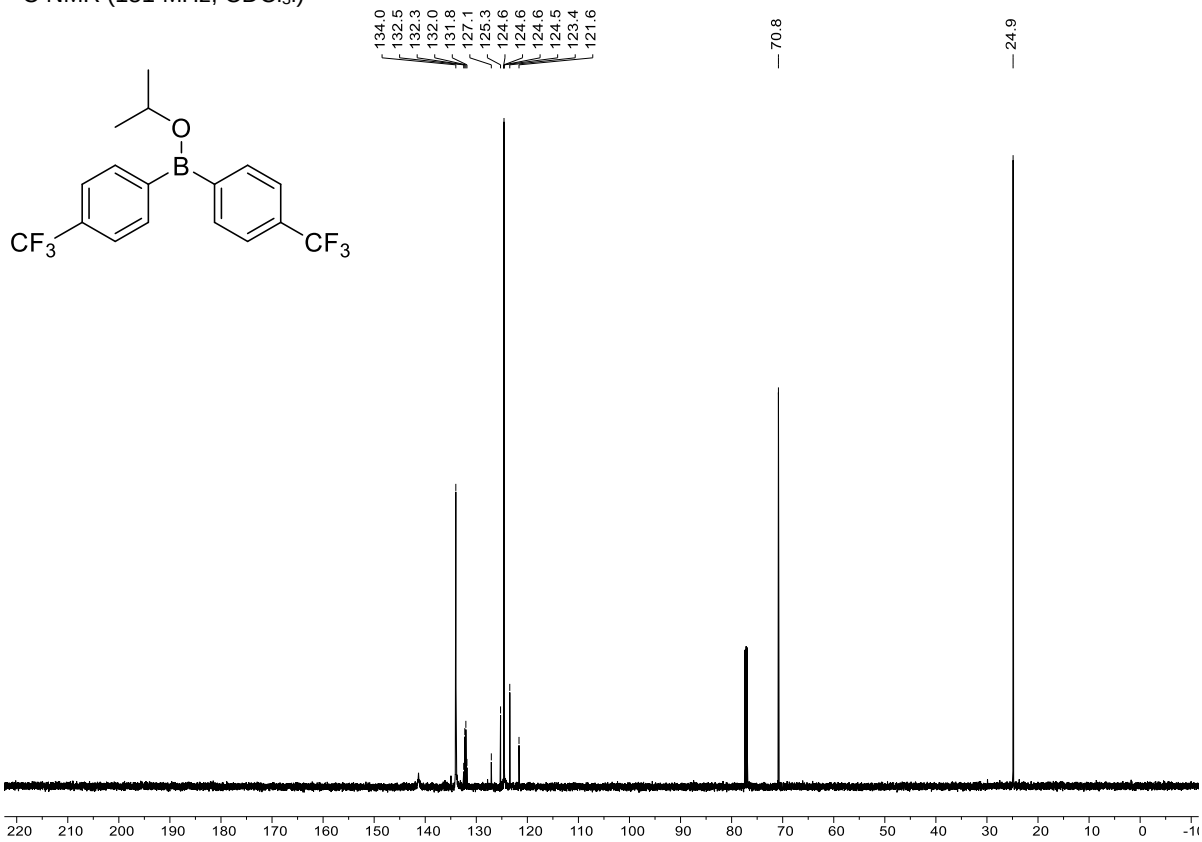
Isopropoxybis(4-(trifluoromethyl)phenyl)borane (S-1)

^{1}H NMR (600 MHz, $CDCl_3$)



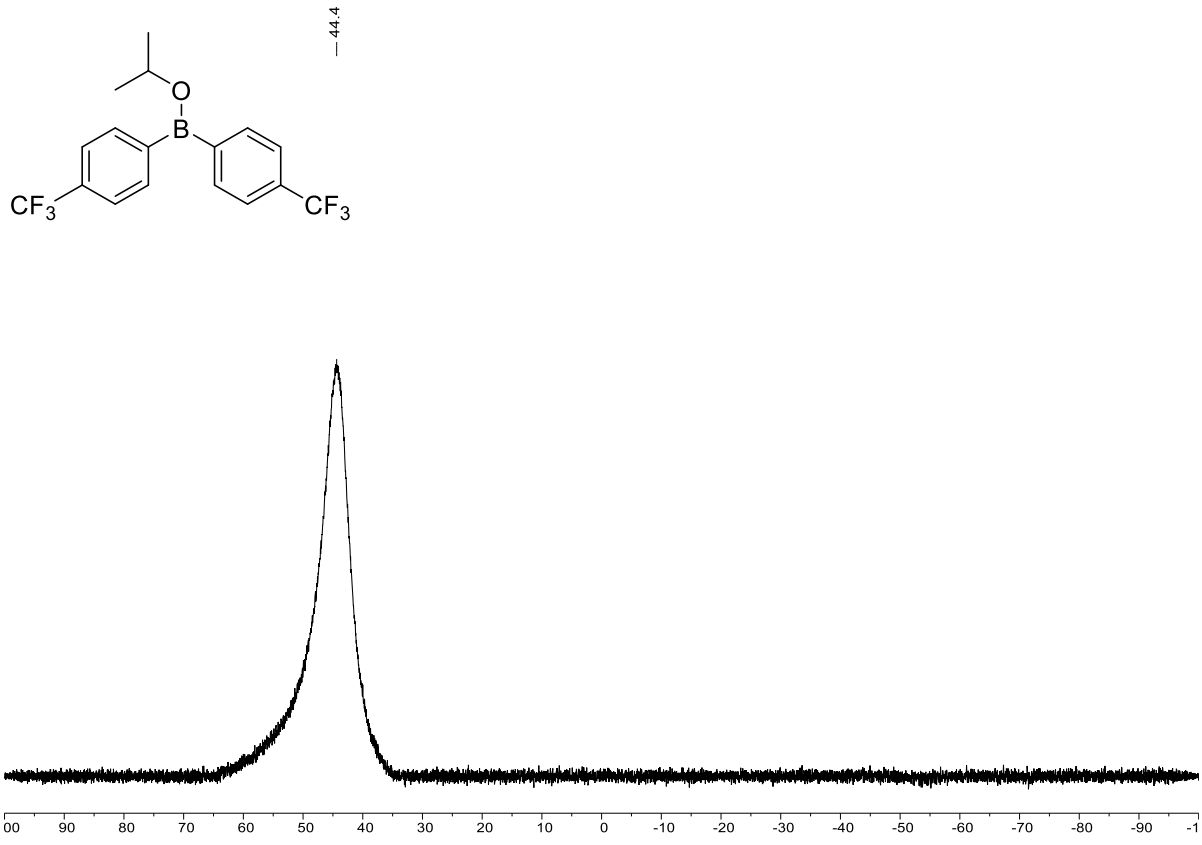
Isopropoxybis(4-(trifluoromethyl)phenyl)borane (S-1)

^{13}C NMR (151 MHz, $CDCl_3$i)



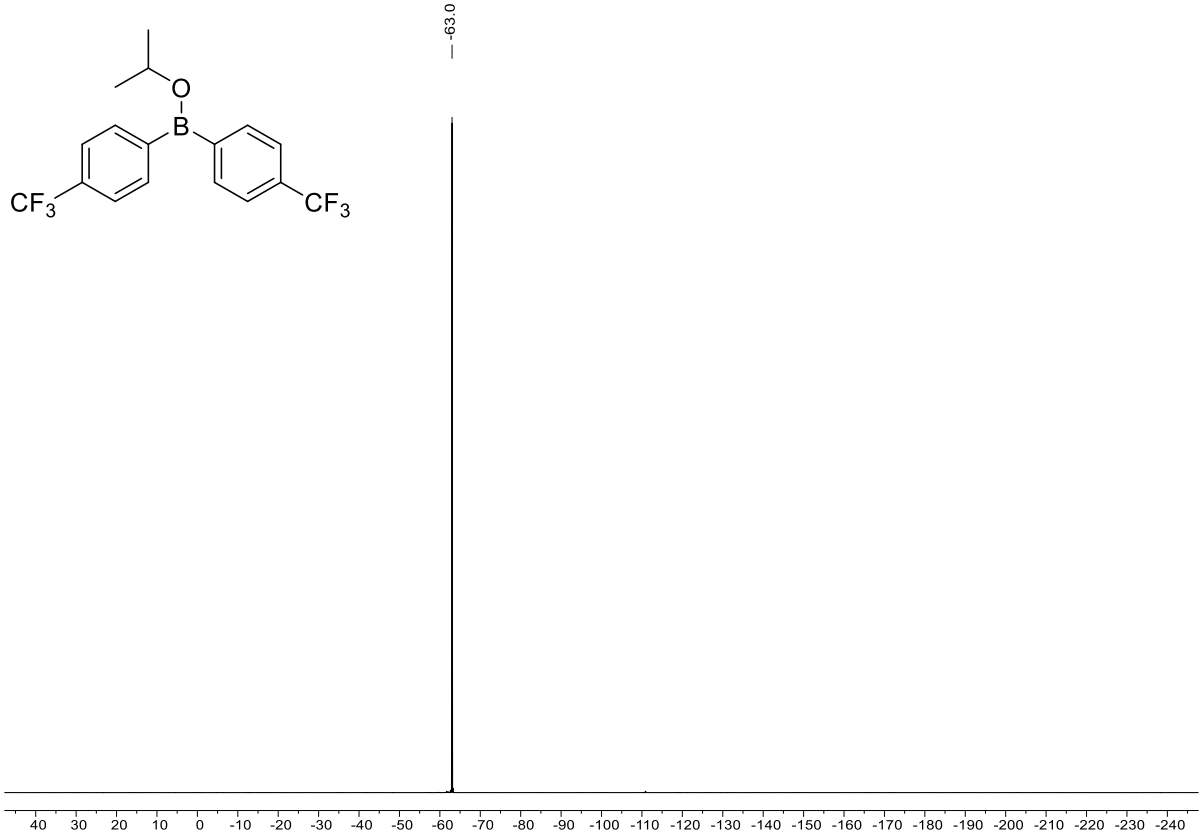
Isopropoxybis(4-(trifluoromethyl)phenyl)borane (S-1)

^{11}B NMR (96 MHz, $CDCl_3$i)



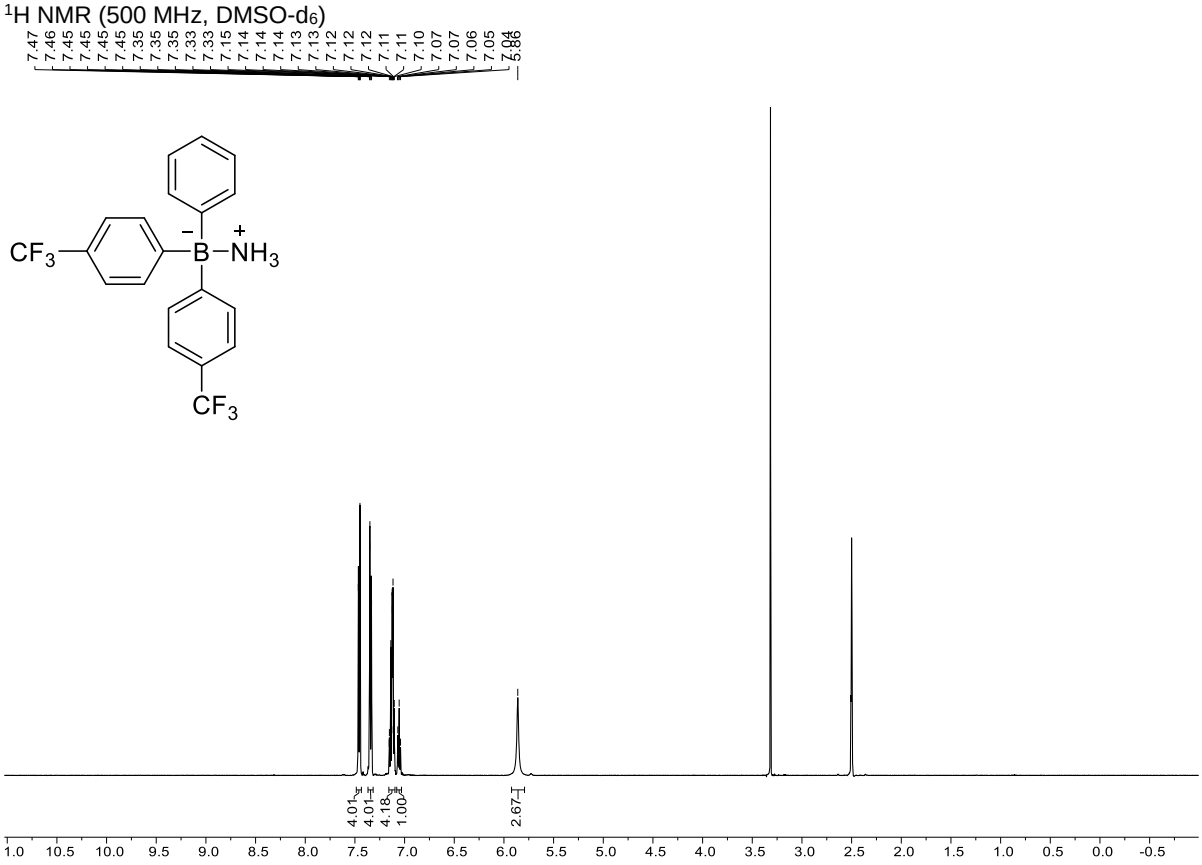
Isopropoxybis(4-(trifluoromethyl)phenyl)borane (S-1)

^{19}F NMR (564 MHz, $CDCl_3$i)



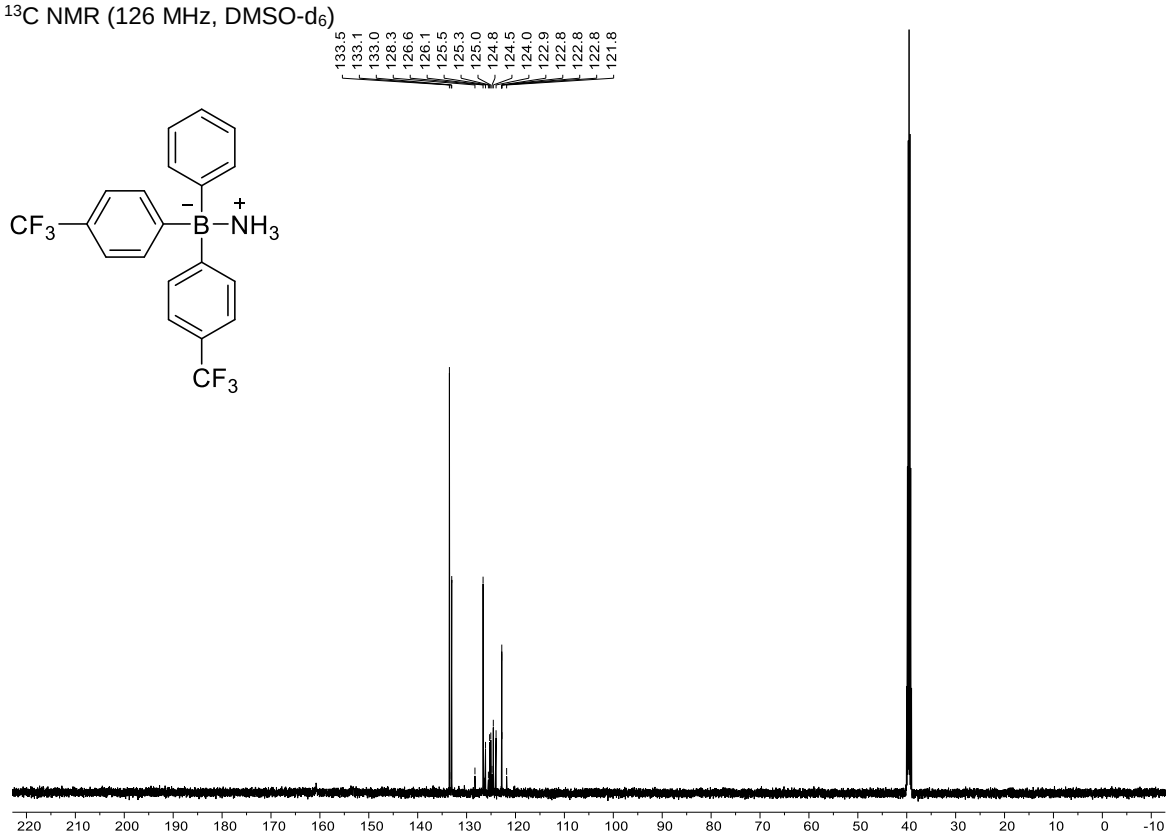
Phenylbis(4-(trifluoromethyl)phenyl)borane-NH_3 adduct (4a)

^{1}H NMR (500 MHz, DMSO-d_6)



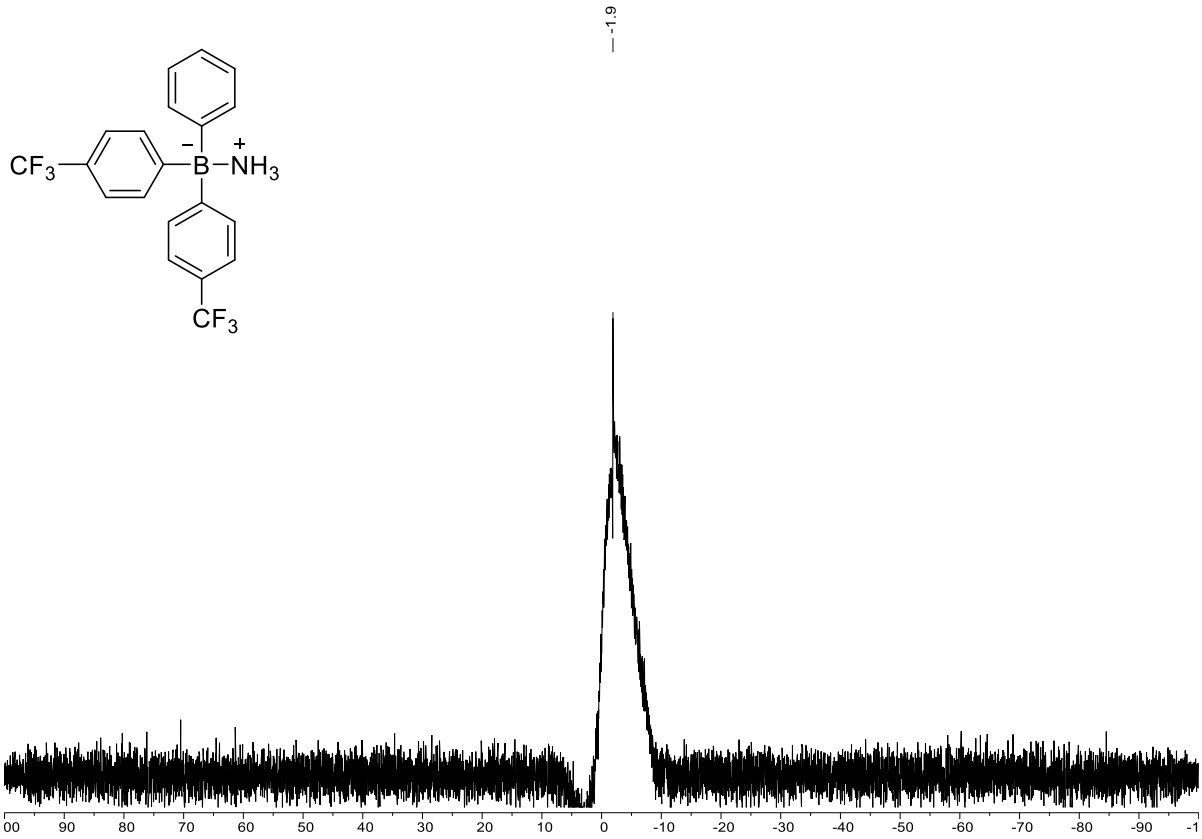
Phenylbis(4-(trifluoromethyl)phenyl)borane-NH_3 adduct (4a)

^{13}C NMR (126 MHz, DMSO-d_6)



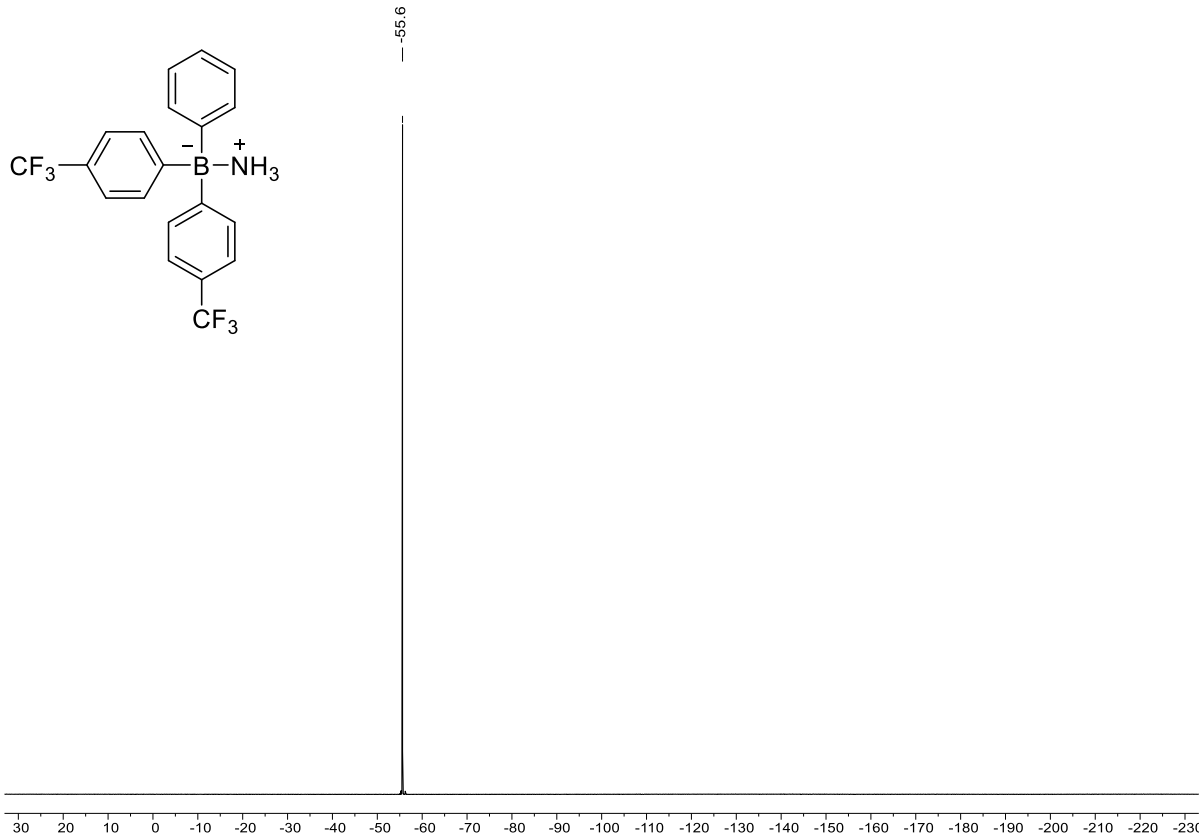
Phenylbis(4-(trifluoromethyl)phenyl)borane-NH_3 adduct (4a)

^{11}B NMR (96 MHz, DMSO-d_6)



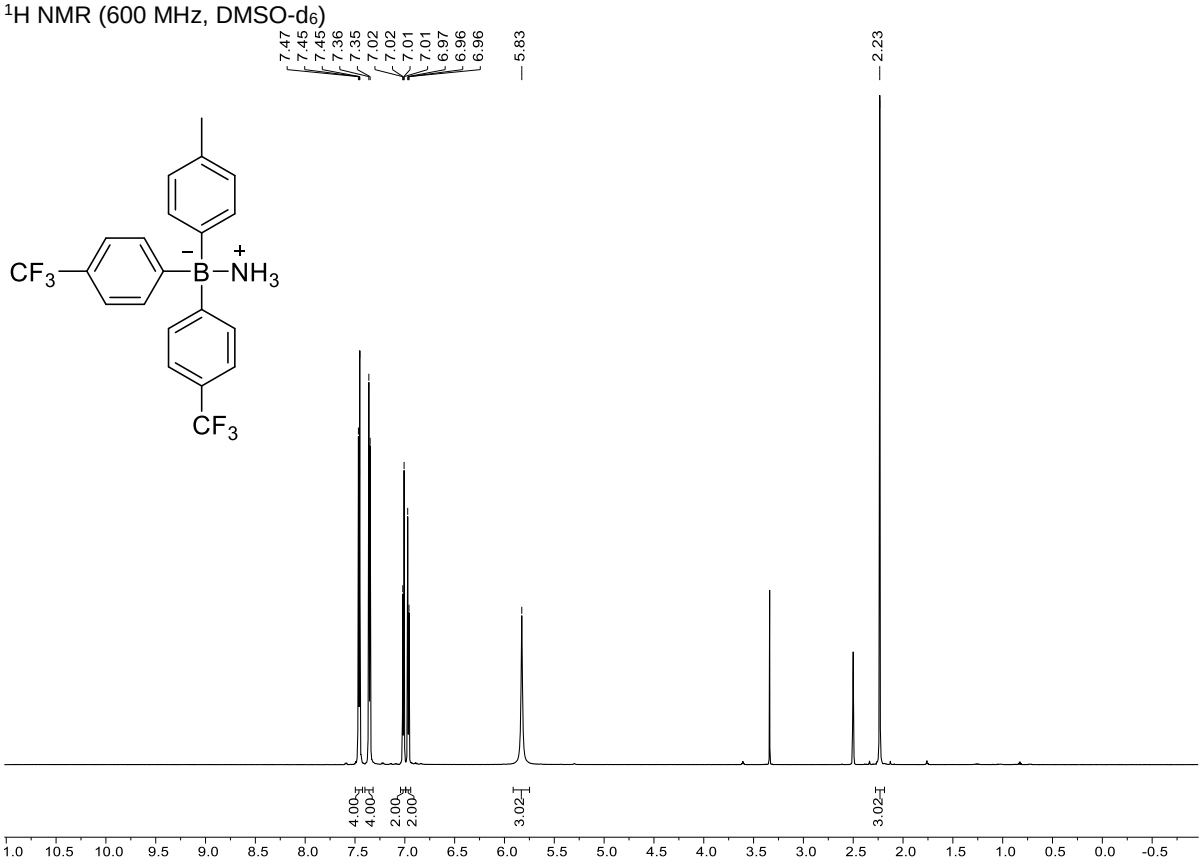
Phenylbis(4-(trifluoromethyl)phenyl)borane-NH_3 adduct (4a)

^{19}F NMR (282 MHz, DMSO-d_6)



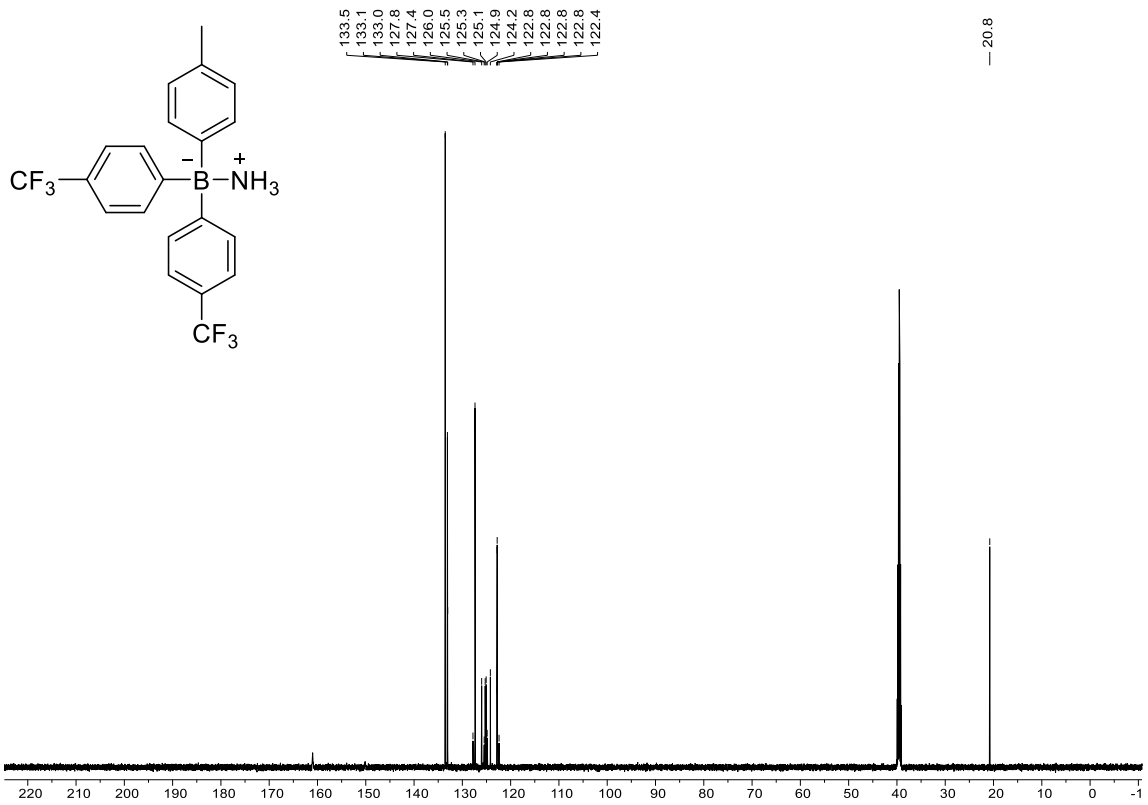
***p*-Tolylbis(4-(trifluoromethyl)phenyl)boran ammoniate (4b)**

^{1}H NMR (600 MHz, DMSO-d_6)



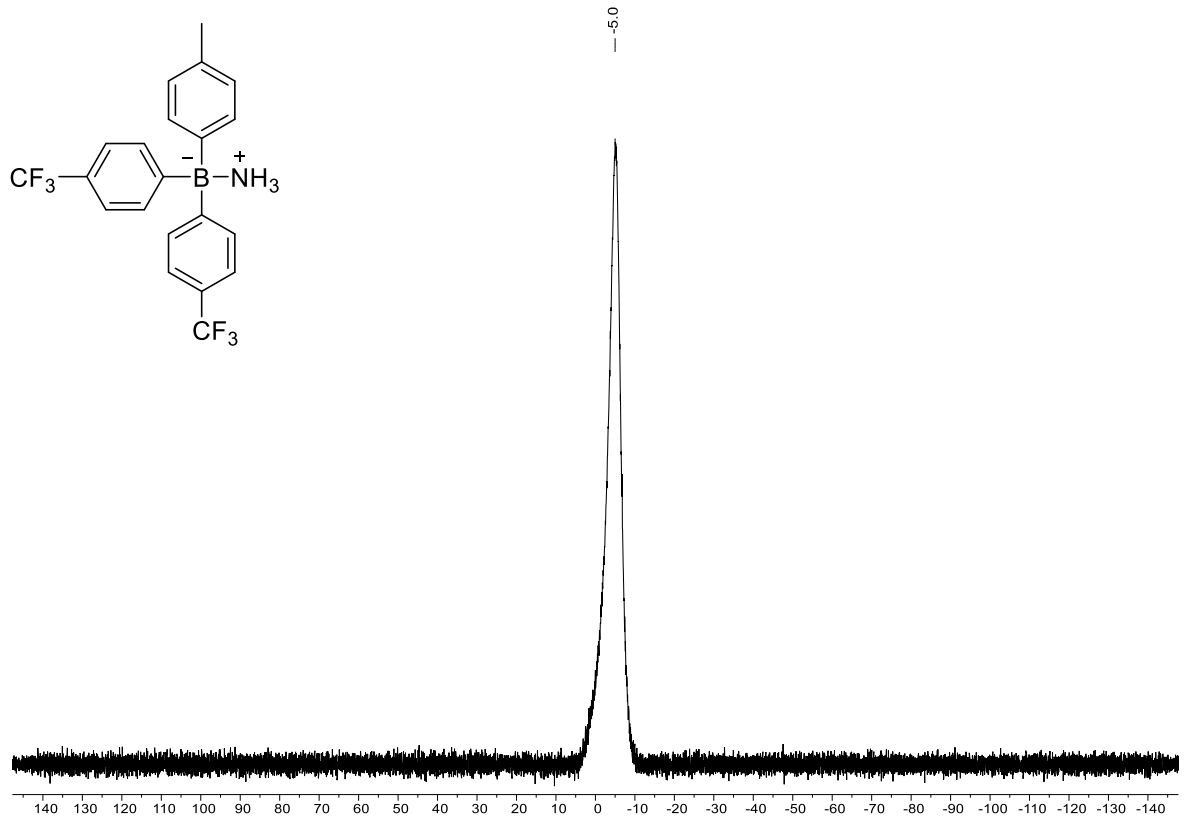
p-Tolylbis(4-(trifluoromethyl)phenyl)boran ammoniate (4b)

^{13}C NMR (151 MHz, DMSO-d_6)



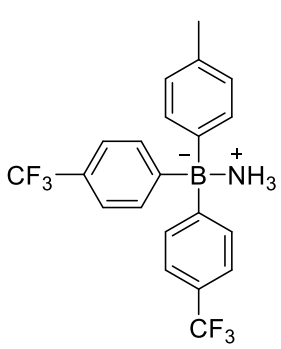
p-Tolylbis(4-(trifluoromethyl)phenyl)boran ammoniate (4b)

^{11}B NMR (192 MHz, DMSO-d_6)



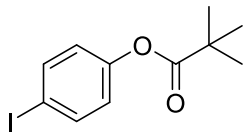
p-Tolylbis(4-(trifluoromethyl)phenyl)boran ammoniate (4b)

^{19}F NMR (564 MHz, DMSO-d_6)



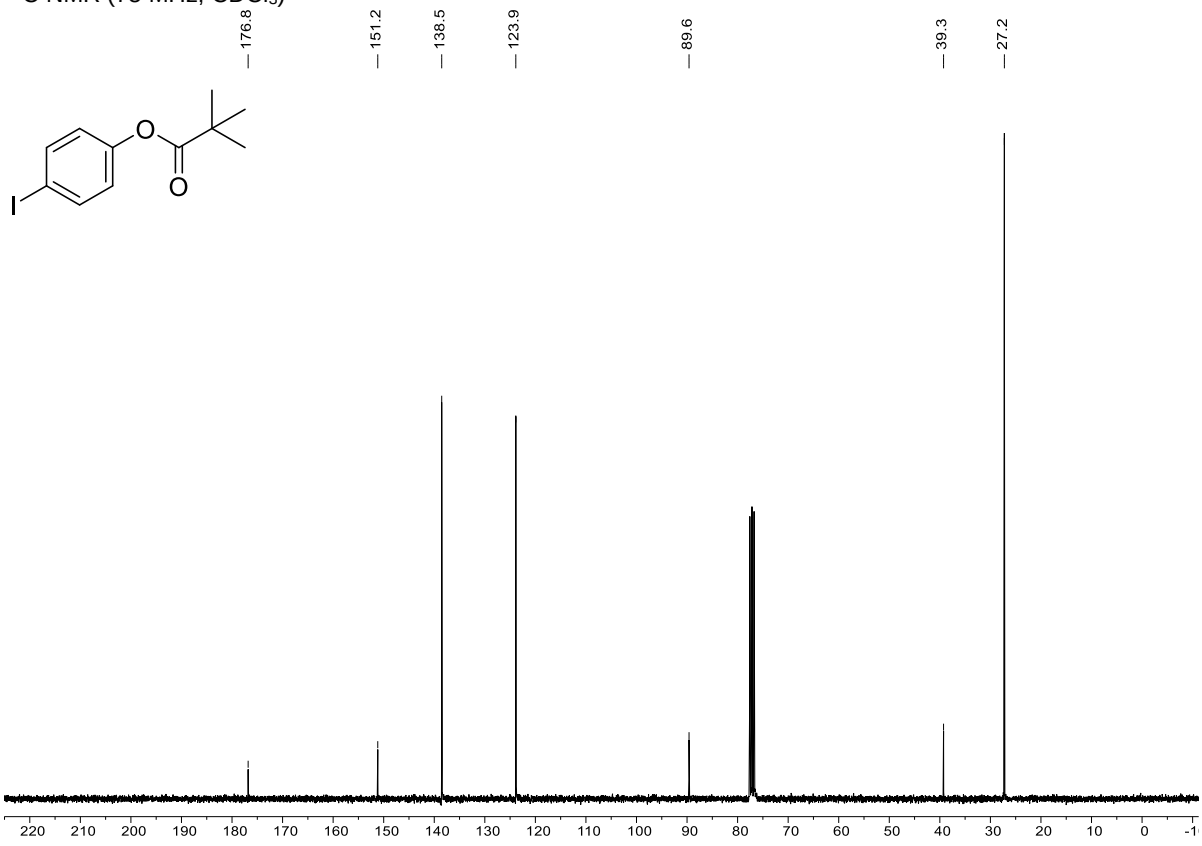
4-Iodophenyl pivalate (S-2)

^{1}H NMR (300 MHz, $CDCl_3$)



4-Iodophenyl pivalate (S-2)

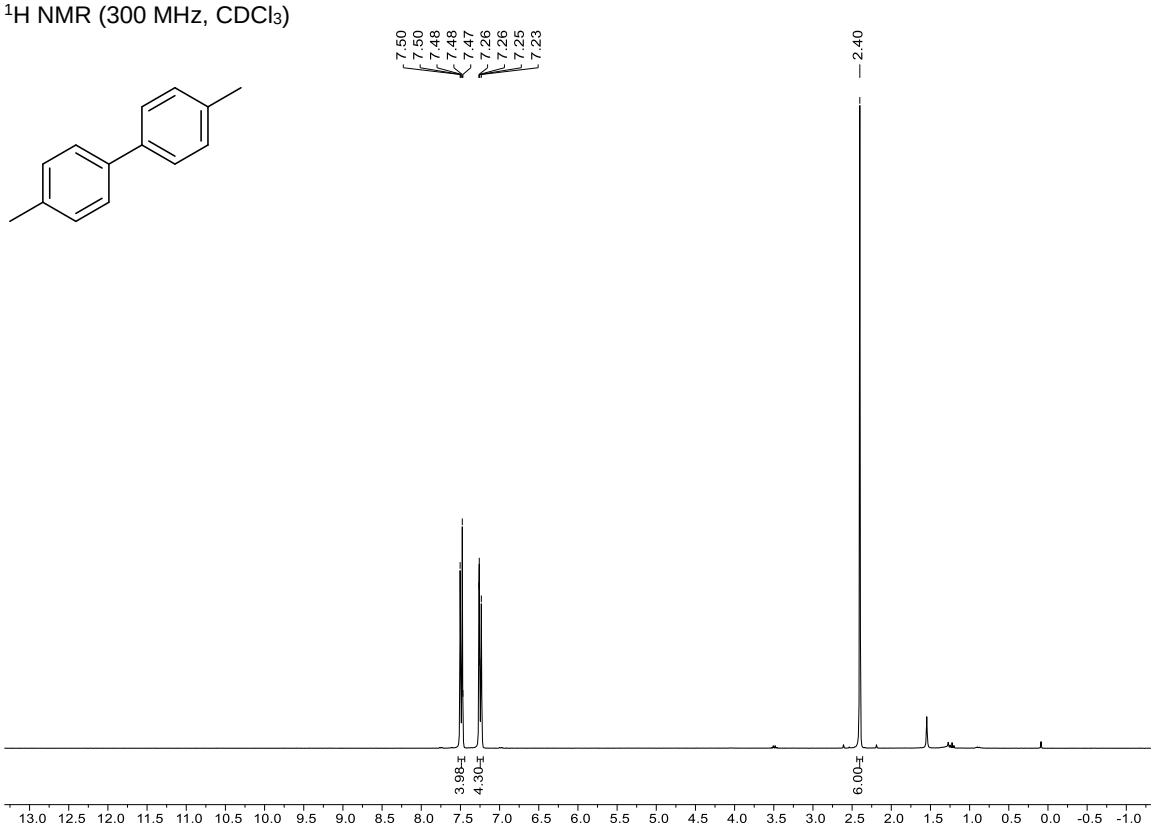
^{13}C NMR (75 MHz, $CDCl_3$)



4.2 Spectral Data for Symmetric Biaryls

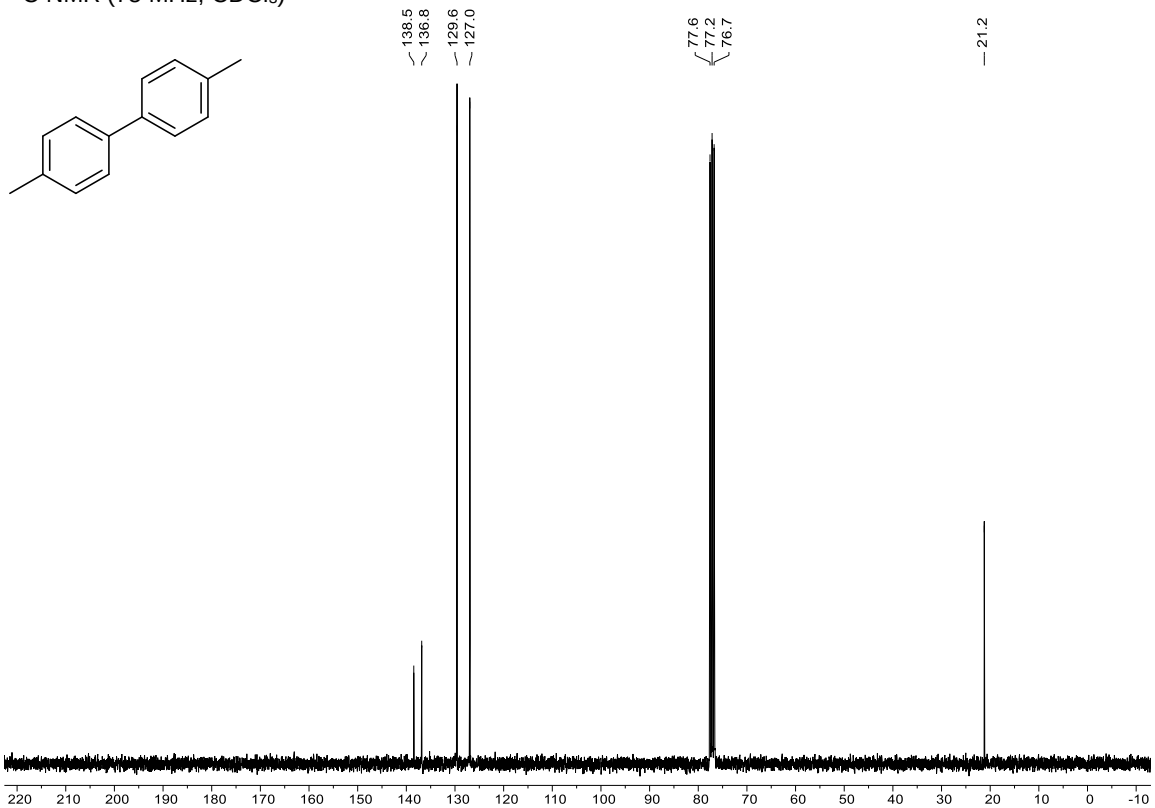
4,4'-Dimethyl-1,1'-biphenyl (3a)

^{1}H NMR (300 MHz, $CDCl_3$)



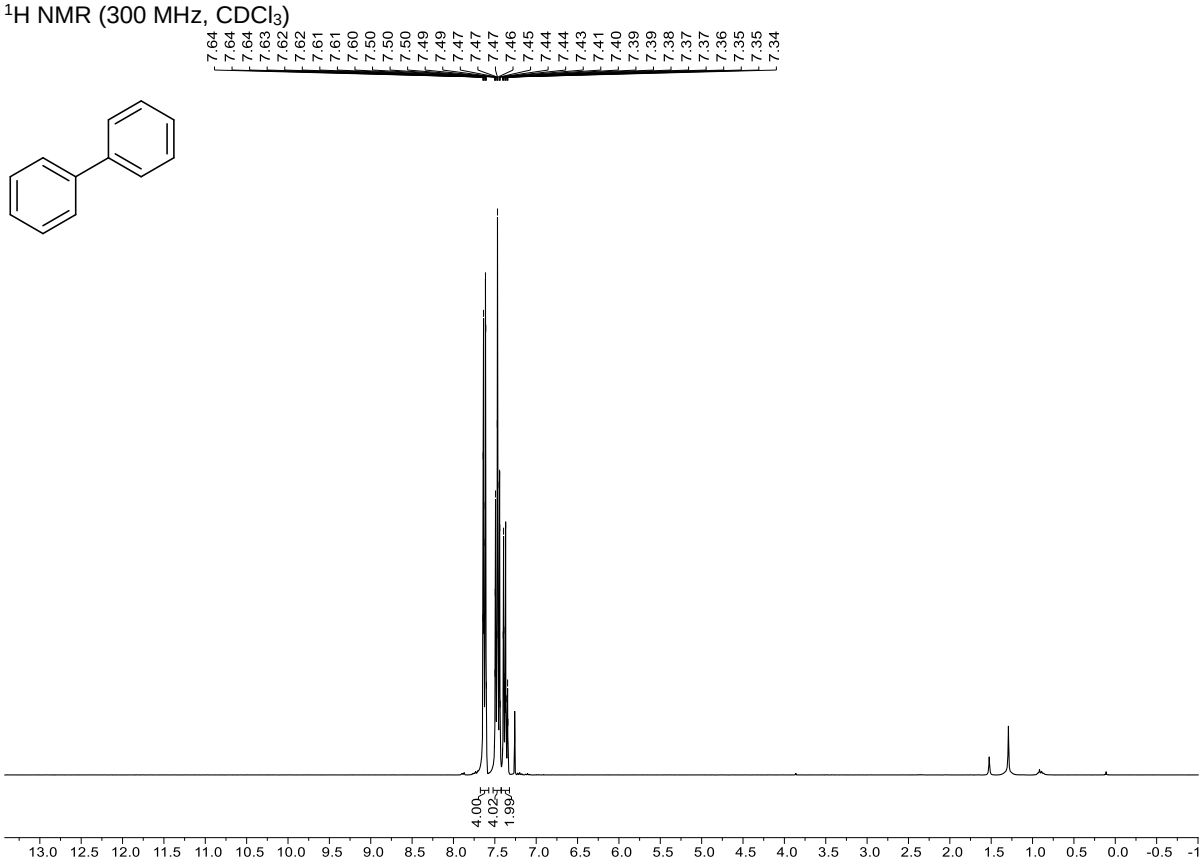
4,4'-Dimethyl-1,1'-biphenyl (3a)

^{13}C NMR (75 MHz, $CDCl_3$)



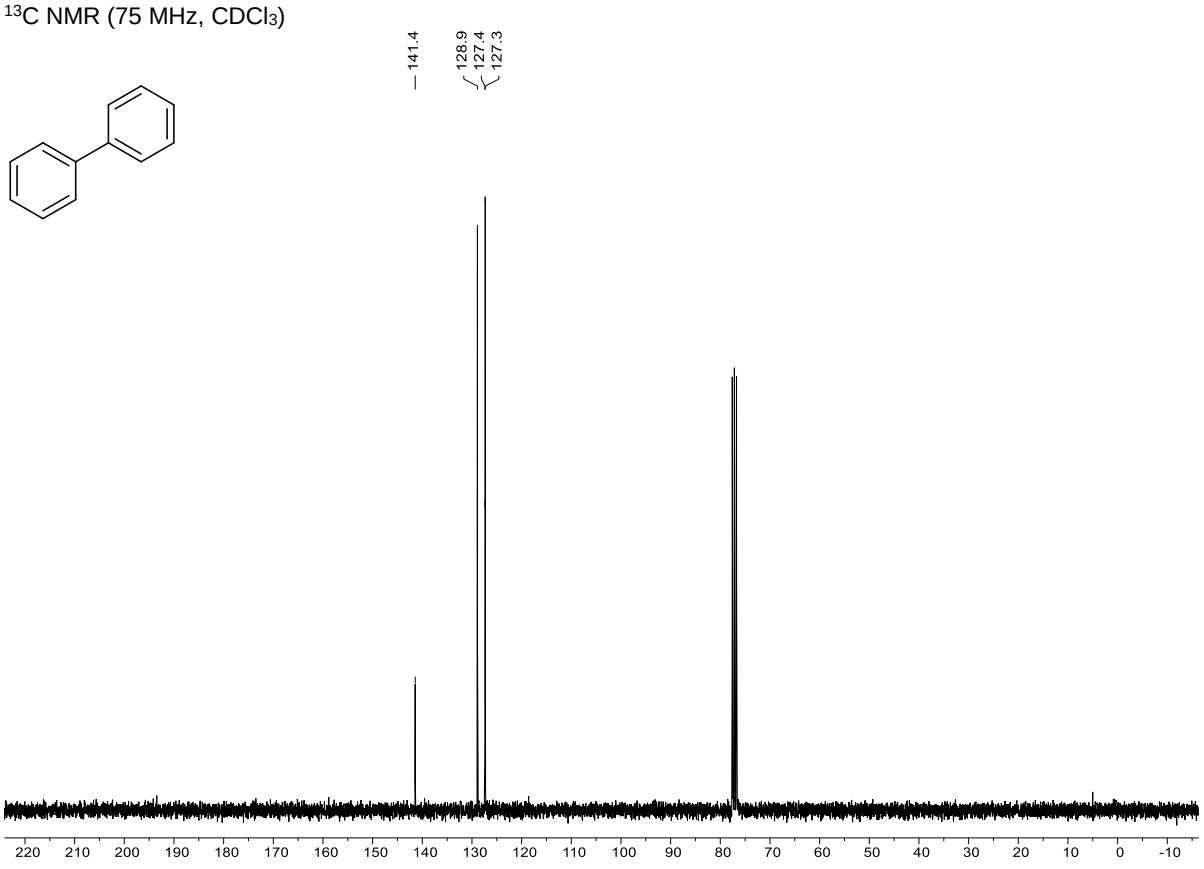
1,1'-Biphenyl (3b)

^{1}H NMR (300 MHz, $CDCl_3$)



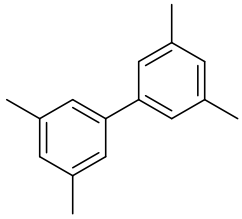
1,1'-Biphenyl (3b)

^{13}C NMR (75 MHz, $CDCl_3$)



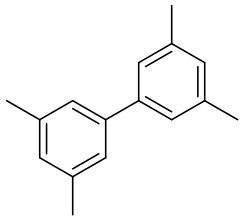
3,3',5,5'-Tetramethyl-1,1'-biphenyl (3c)

^{1}H NMR (300 MHz, $CDCl_3$)



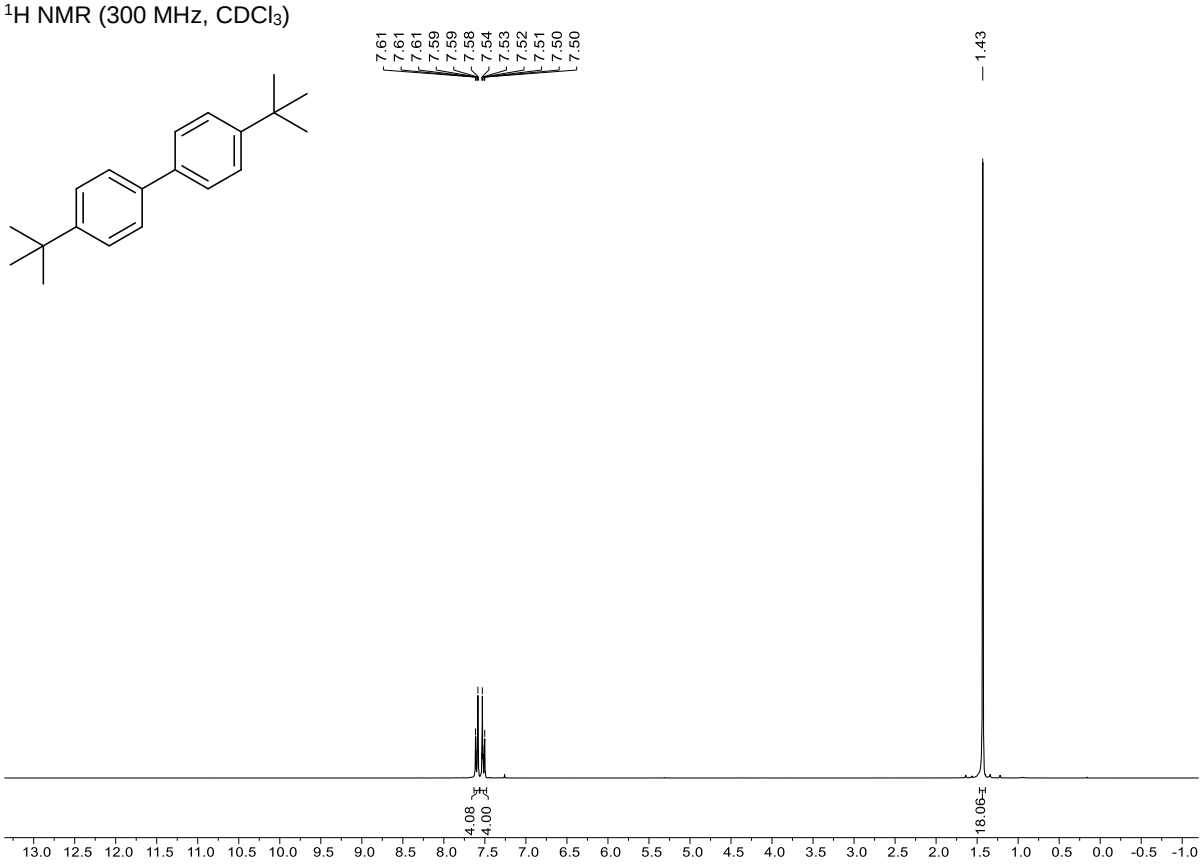
3,3',5,5'-Tetramethyl-1,1'-biphenyl (3c)

^{13}C NMR (75 MHz, $CDCl_3$)



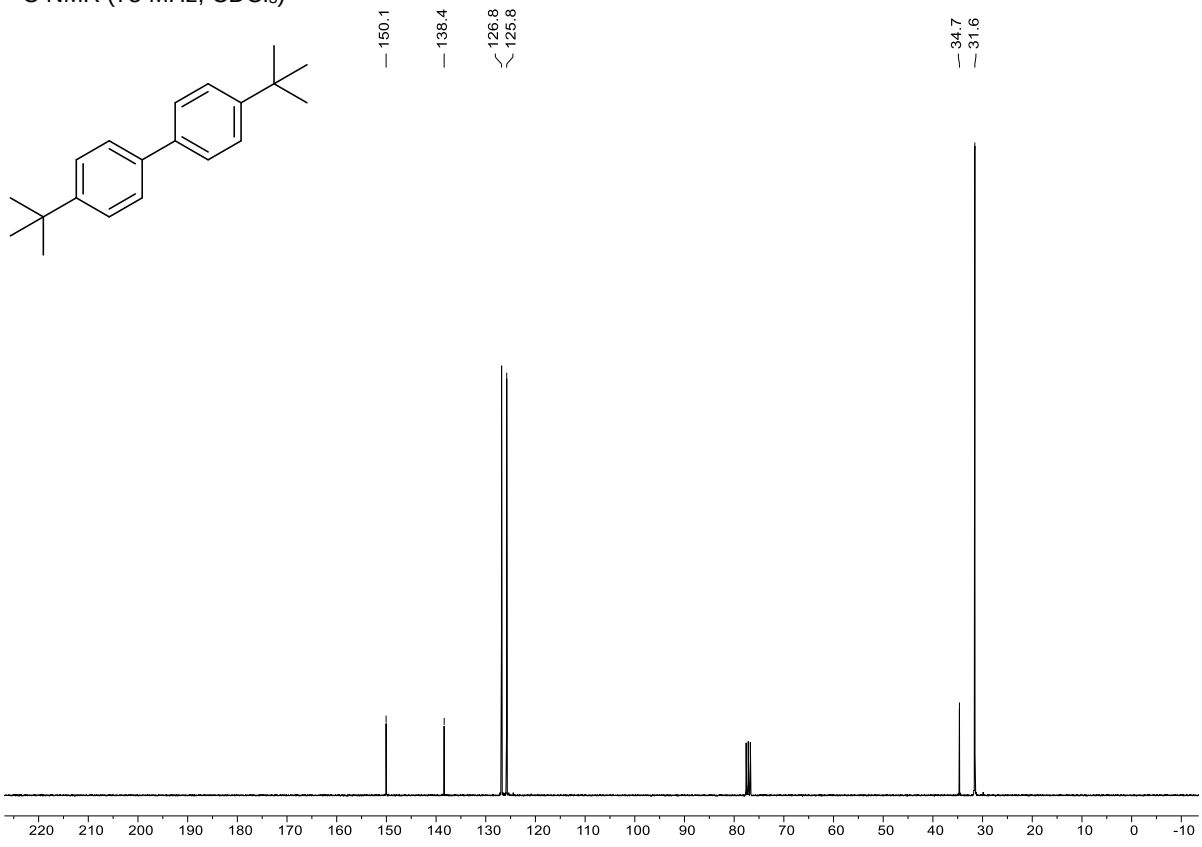
4,4'-Di-*tert*-butyl-1,1'-biphenyl (3d)

^{1}H NMR (300 MHz, $CDCl_3$)



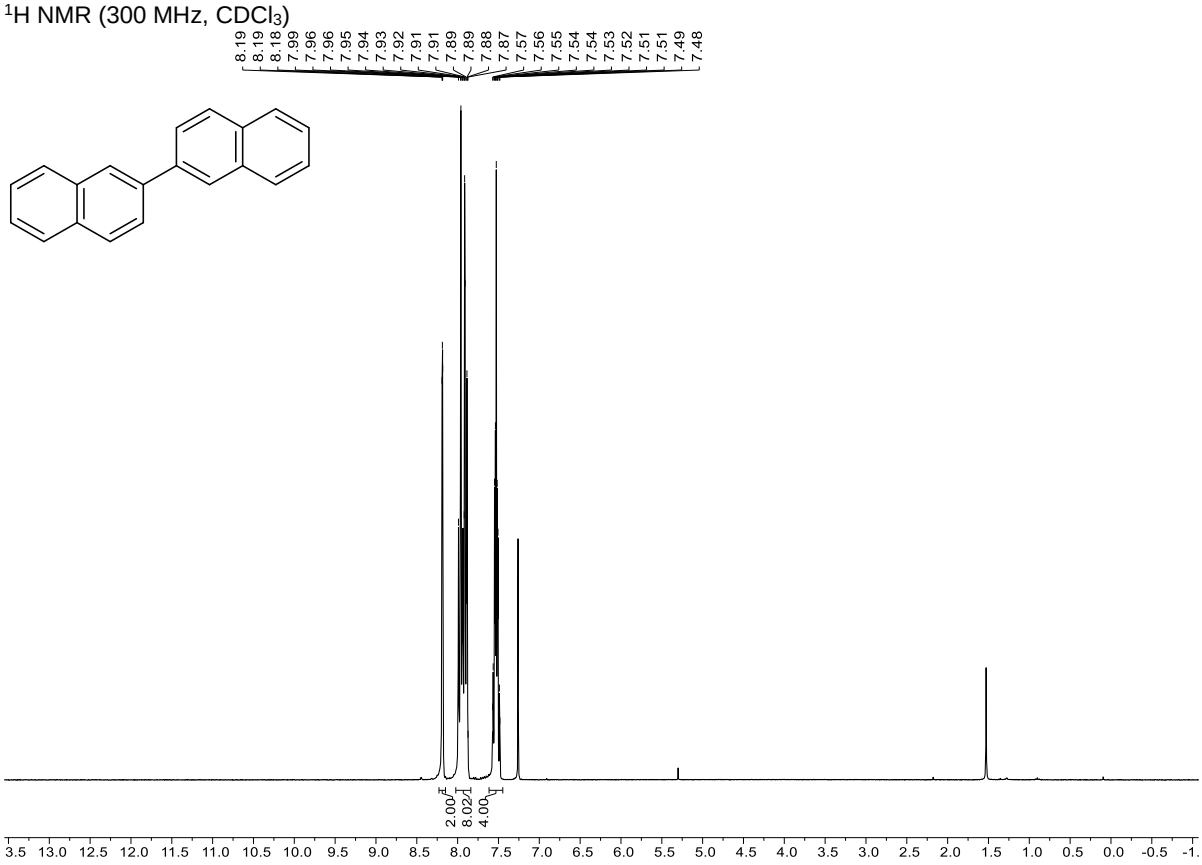
4,4'-Di-*tert*-butyl-1,1'-biphenyl (3d)

^{13}C NMR (75 MHz, $CDCl_3$)



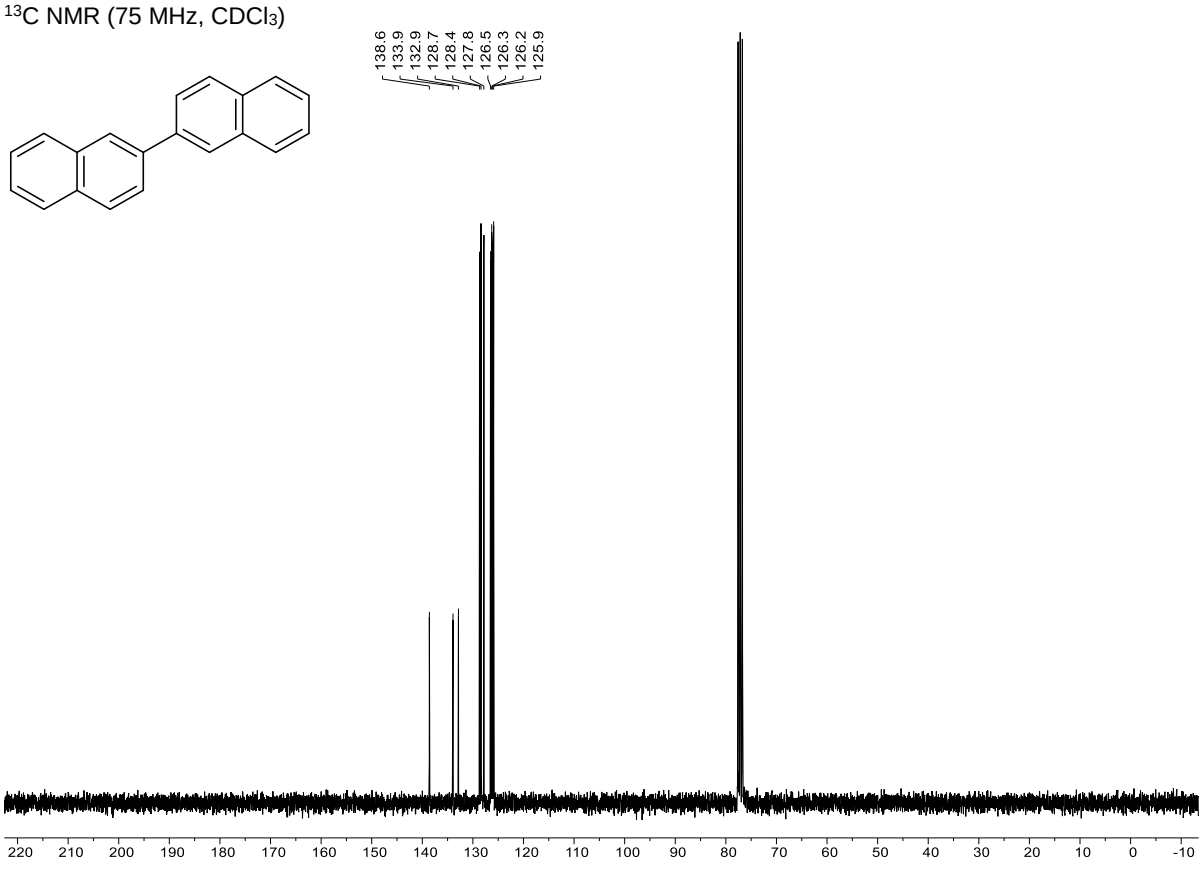
2,2'-Binaphthalene (3e)

^{1}H NMR (300 MHz, $CDCl_3$)



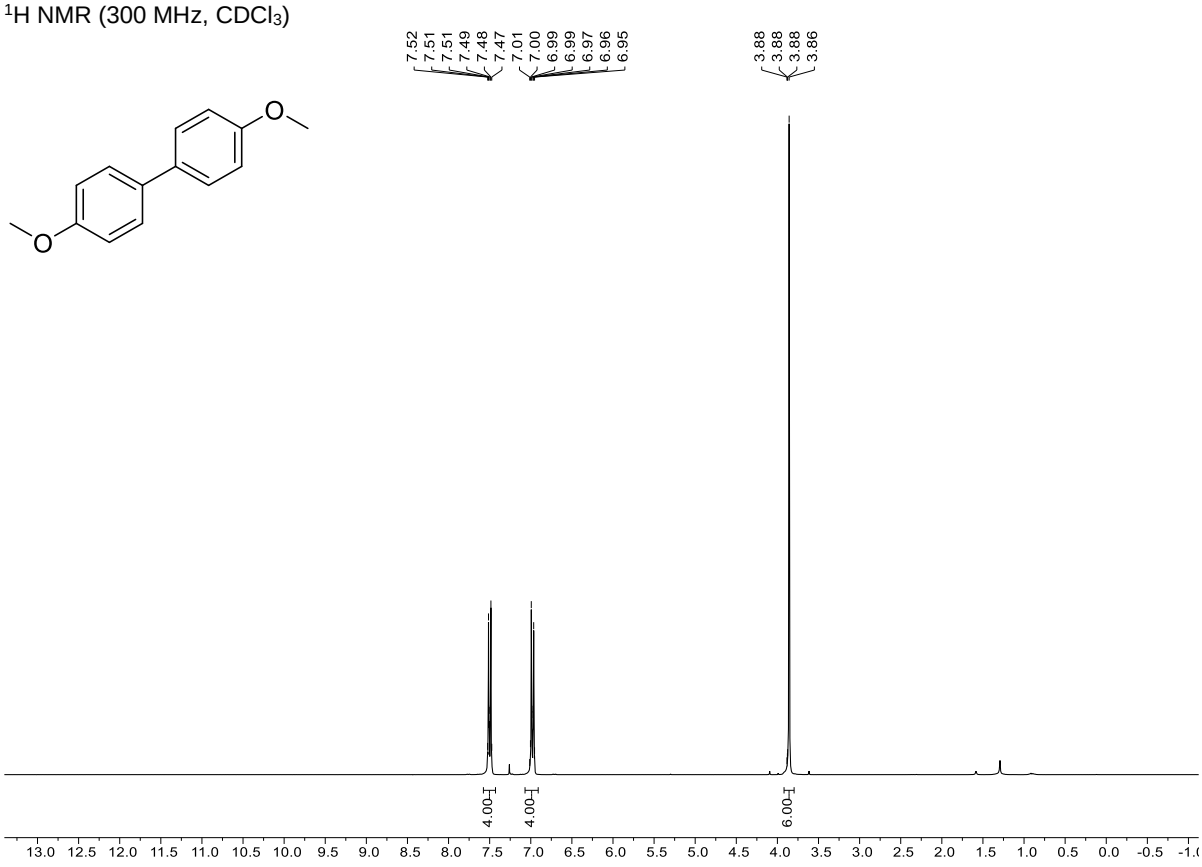
2,2'-Binaphthalene (3e)

^{13}C NMR (75 MHz, $CDCl_3$)



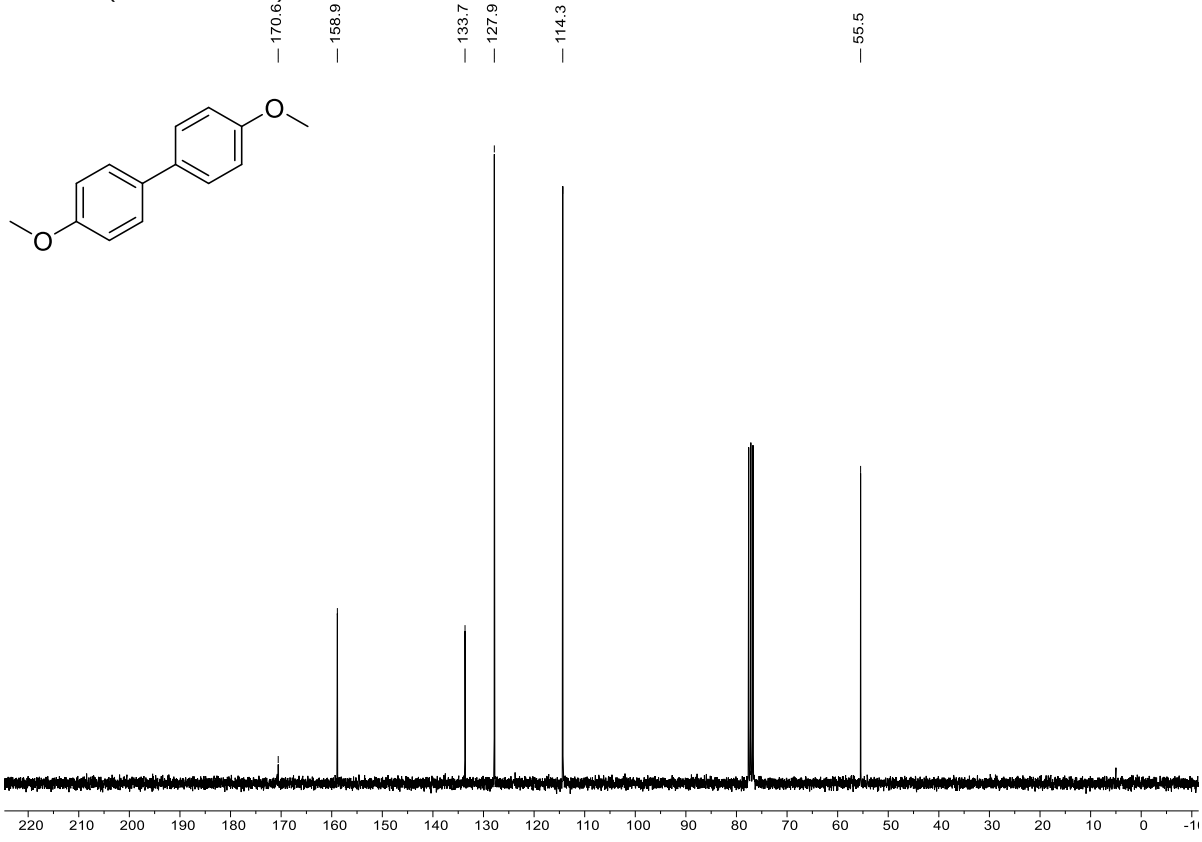
4,4'-Dimethoxy-1,1'-biphenyl (3f)

^{1}H NMR (300 MHz, $CDCl_3$)



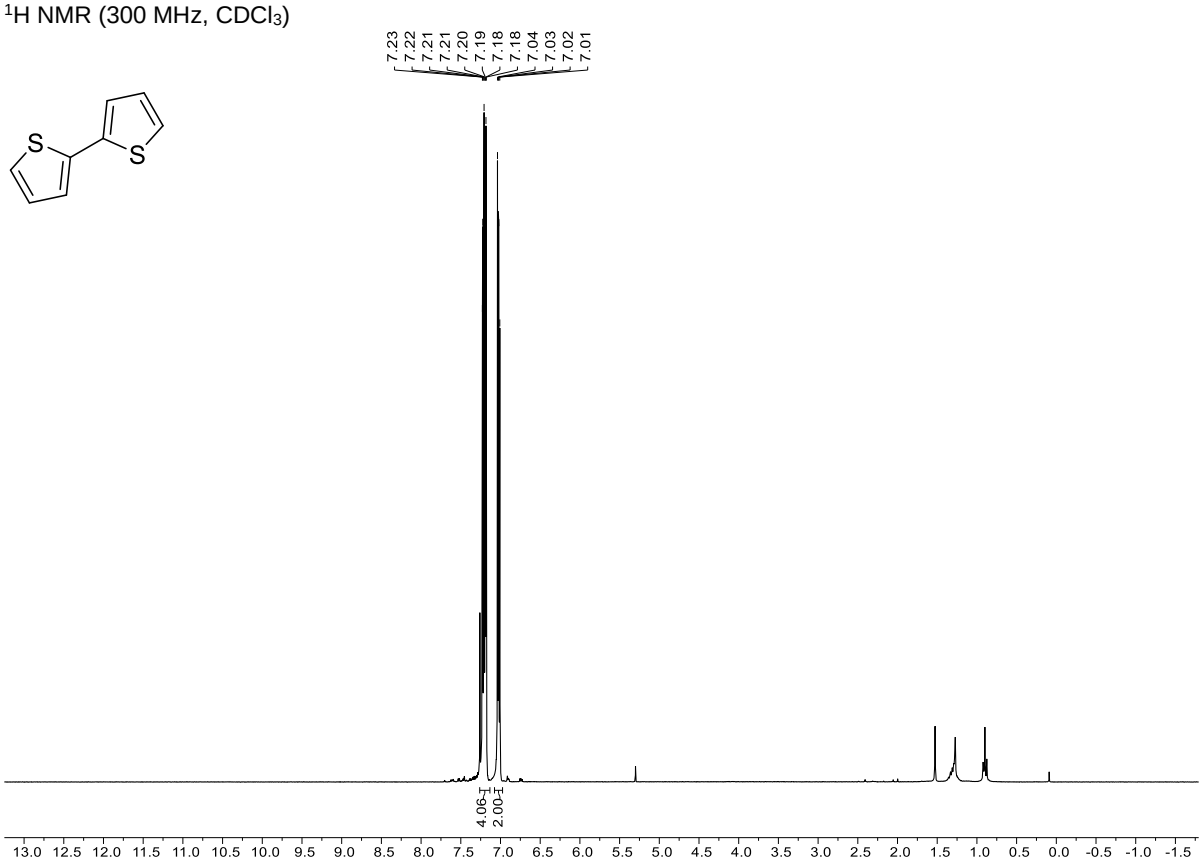
4,4'-Dimethoxy-1,1'-biphenyl (3f)

^{13}C NMR (75 MHz, $CDCl_3$)



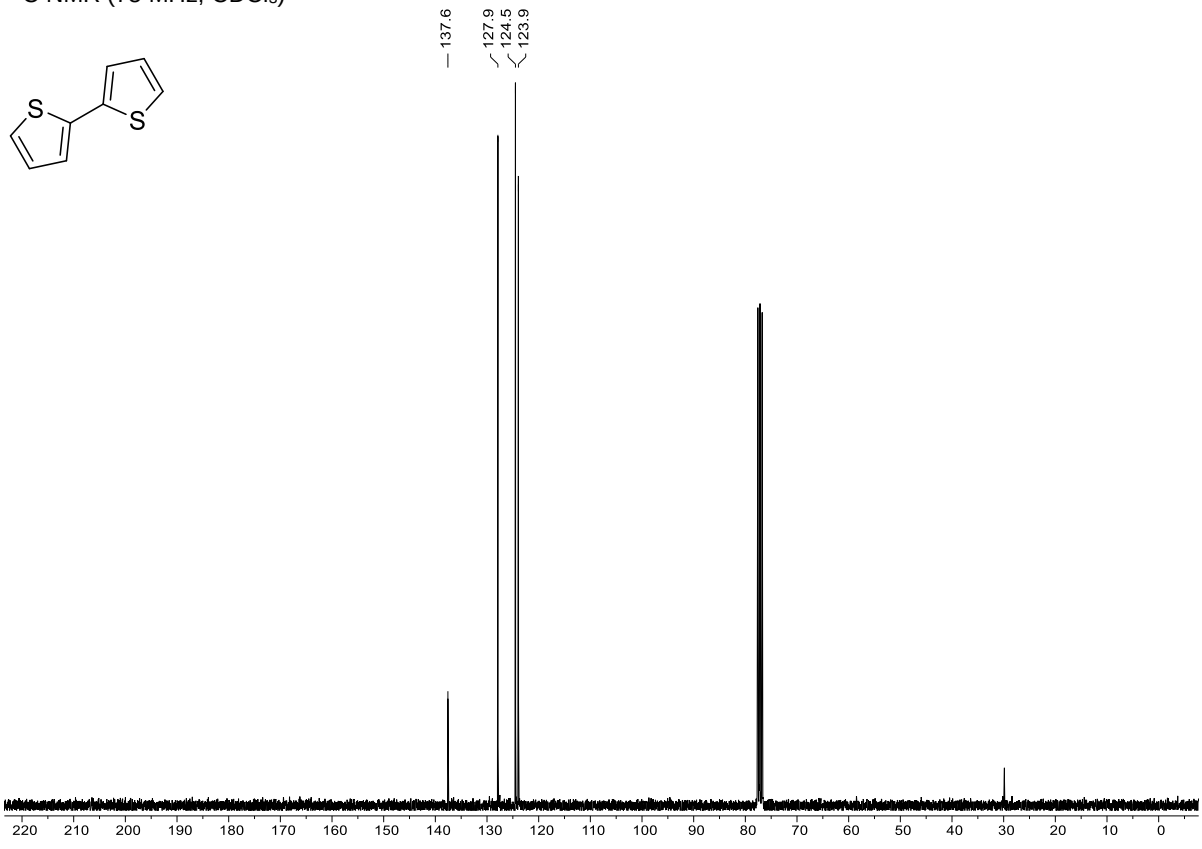
2,2'-Bithiophene (3g)

^{1}H NMR (300 MHz, $CDCl_3$)



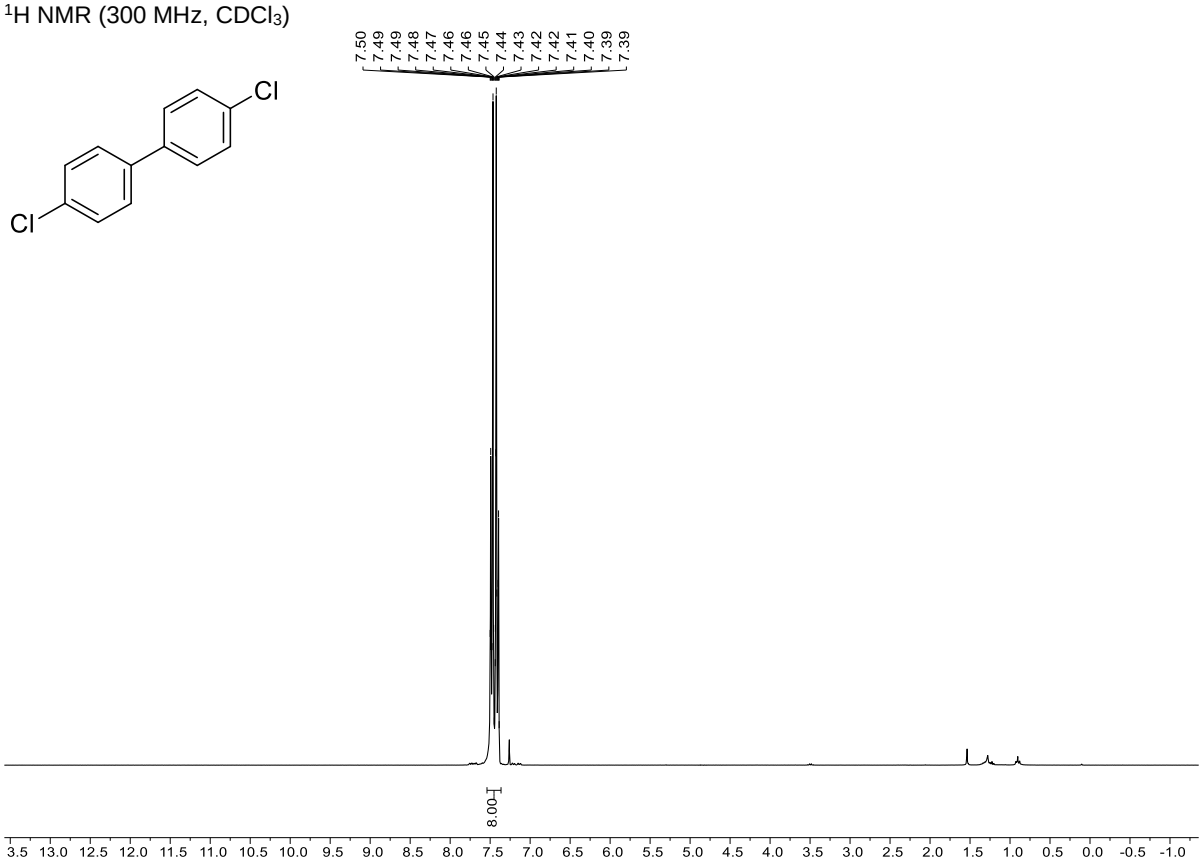
2,2'-Bithiophene (3g)

^{13}C NMR (75 MHz, $CDCl_3$)



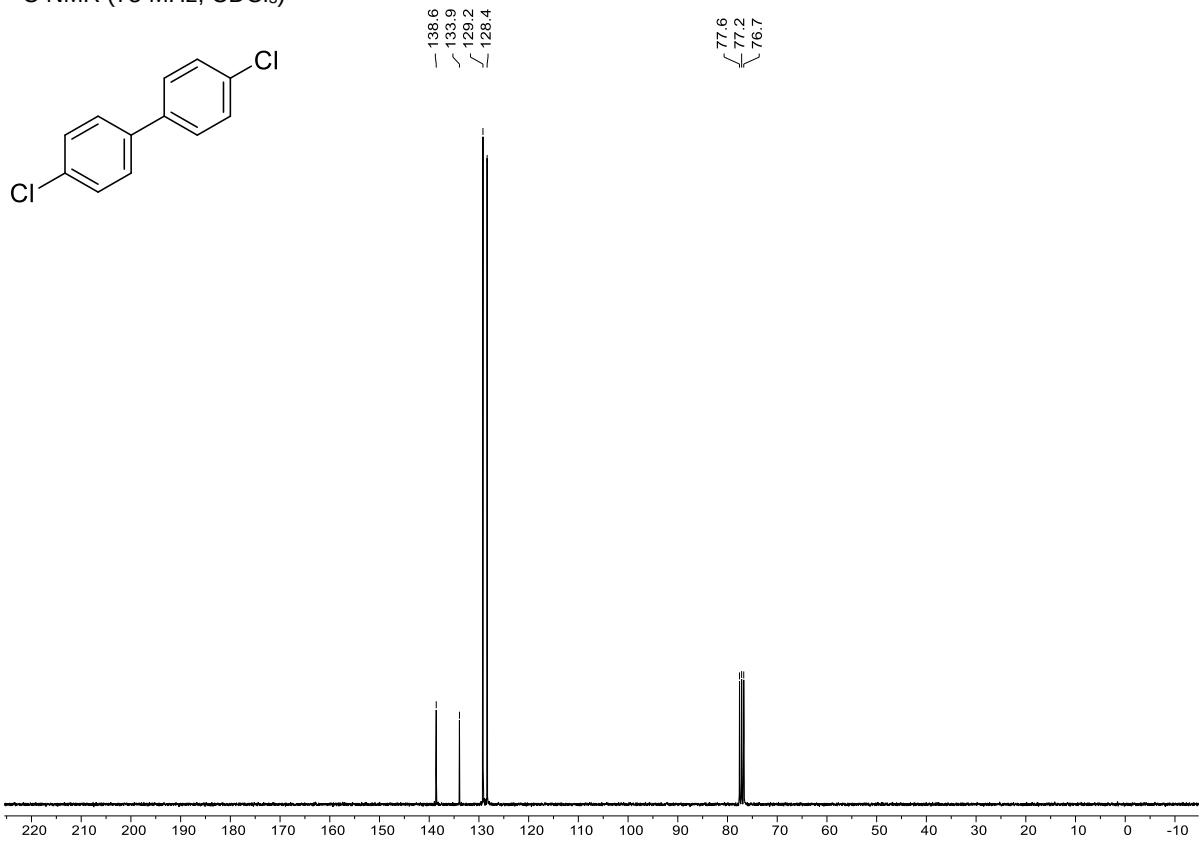
4,4'-Dichloro-1,1'-biphenyl (3h)

^{1}H NMR (300 MHz, $CDCl_3$)



4,4'-Dichloro-1,1'-biphenyl (3h)

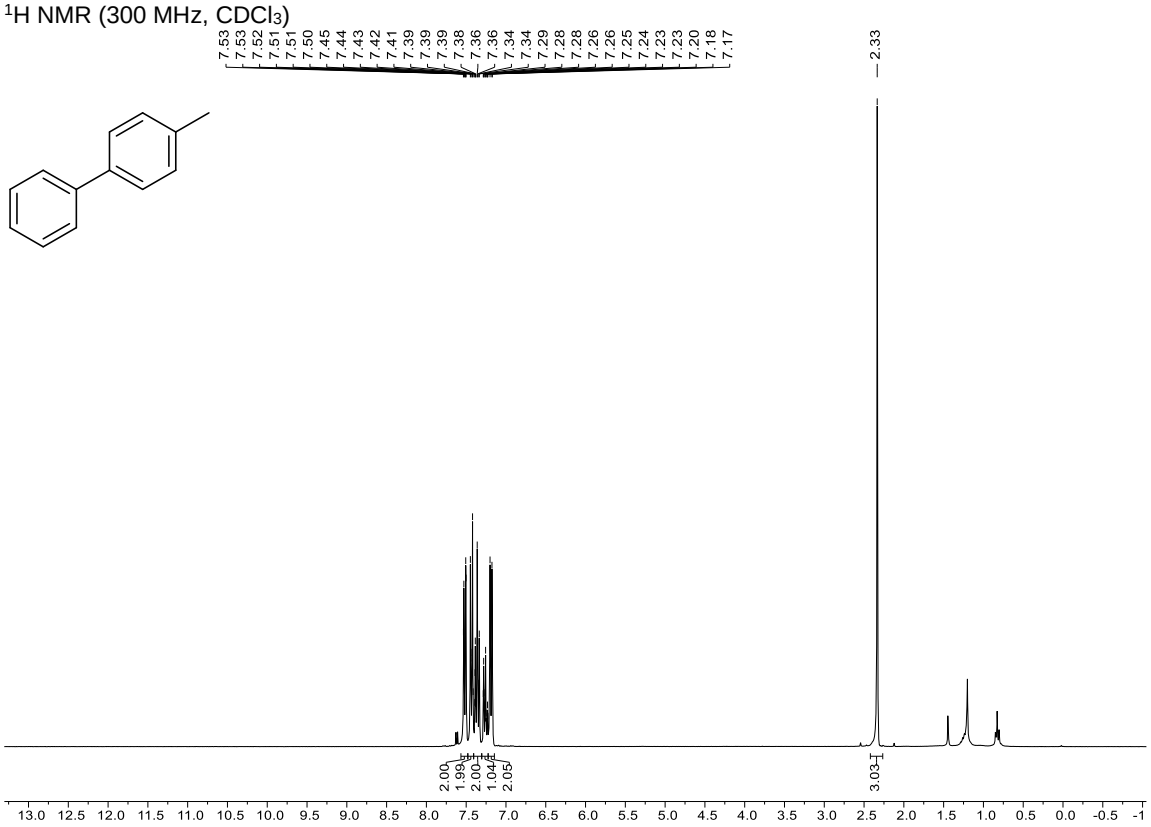
^{13}C NMR (75 MHz, $CDCl_3$)



4.3 Spectral Data for Unsymmetric Biaryls

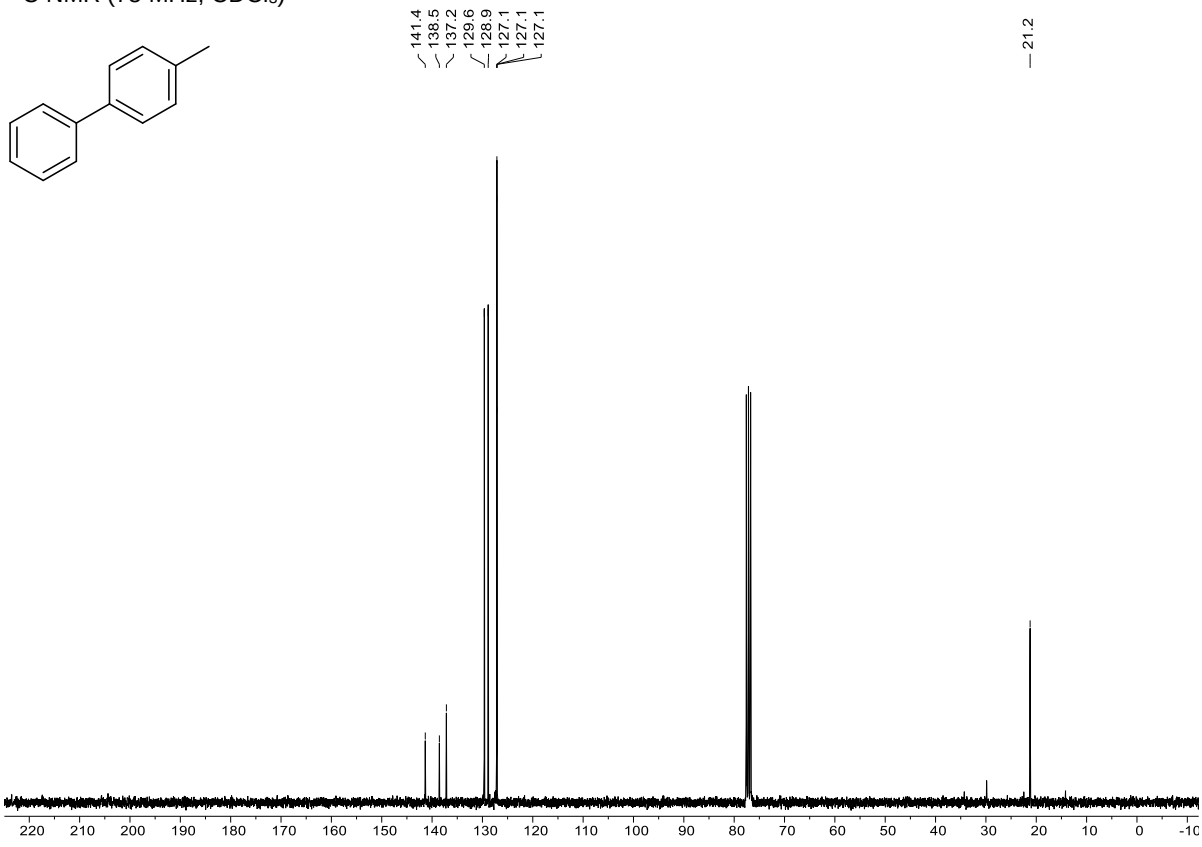
4-Methyl-1,1'-biphenyl (5a)

^{1}H NMR (300 MHz, $CDCl_3$)



4-Methyl-1,1'-biphenyl (5a)

^{13}C NMR (75 MHz, $CDCl_3$)

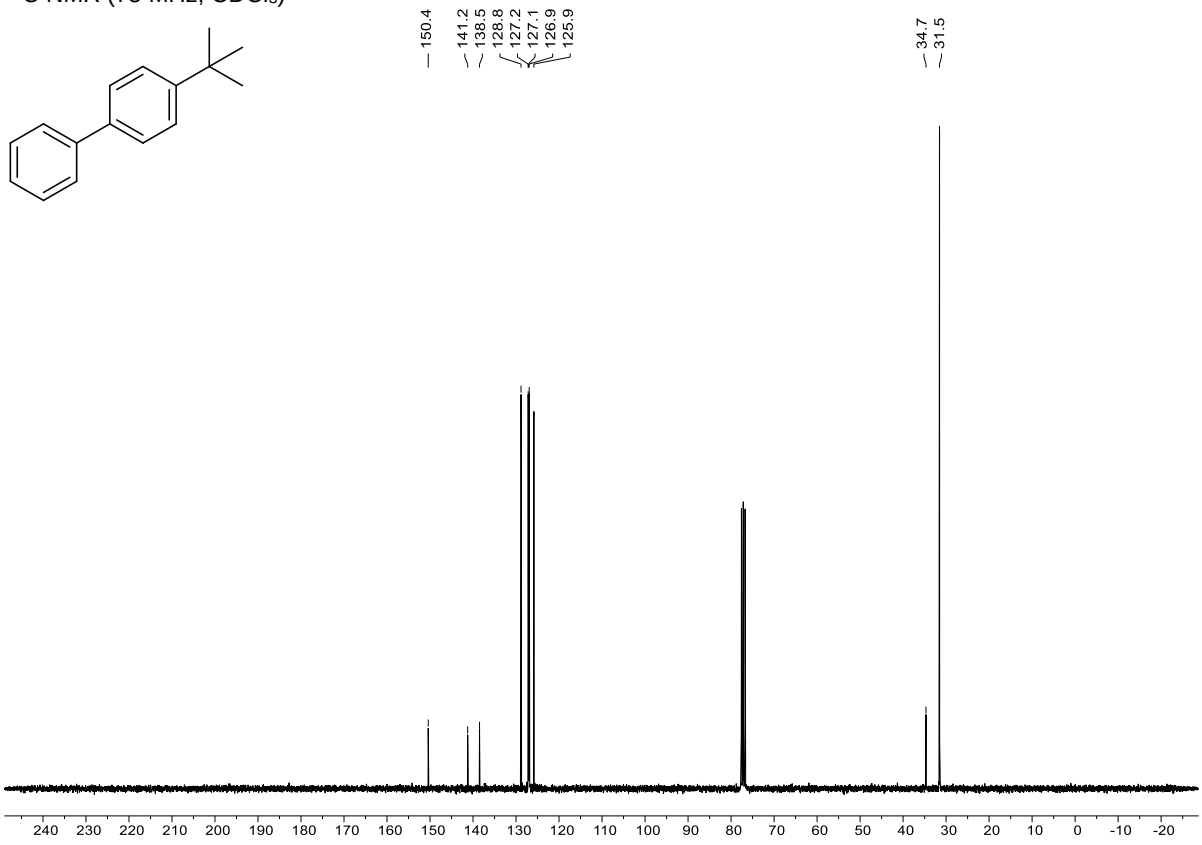


4-(*Tert*-butyl)-1,1'-biphenyl (5b)

^{1}H NMR (300 MHz, $CDCl_3$)

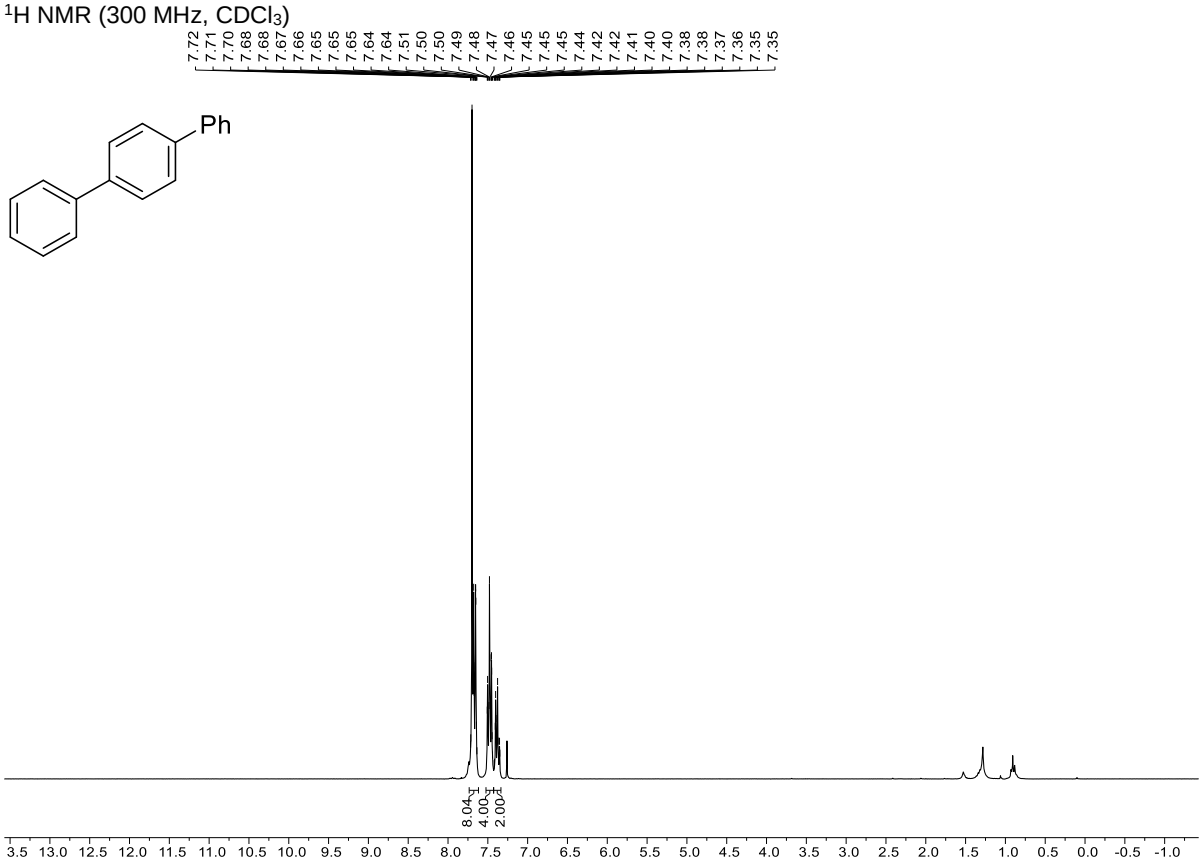
4-(*Tert*-butyl)-1,1'-biphenyl (5b)

^{13}C NMR (75 MHz, $CDCl_3$)



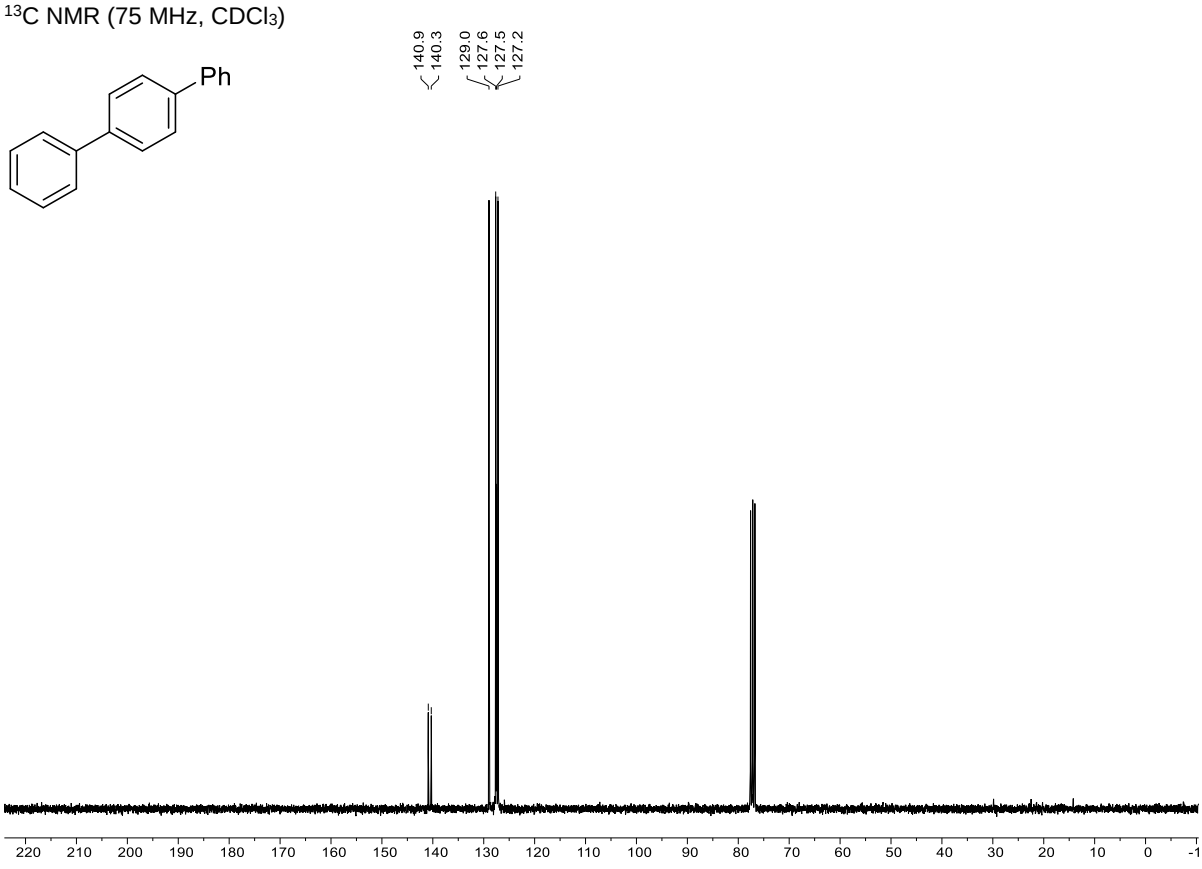
1,1':4',1''-Terphenyl (5c)

^{1}H NMR (300 MHz, $CDCl_3$)



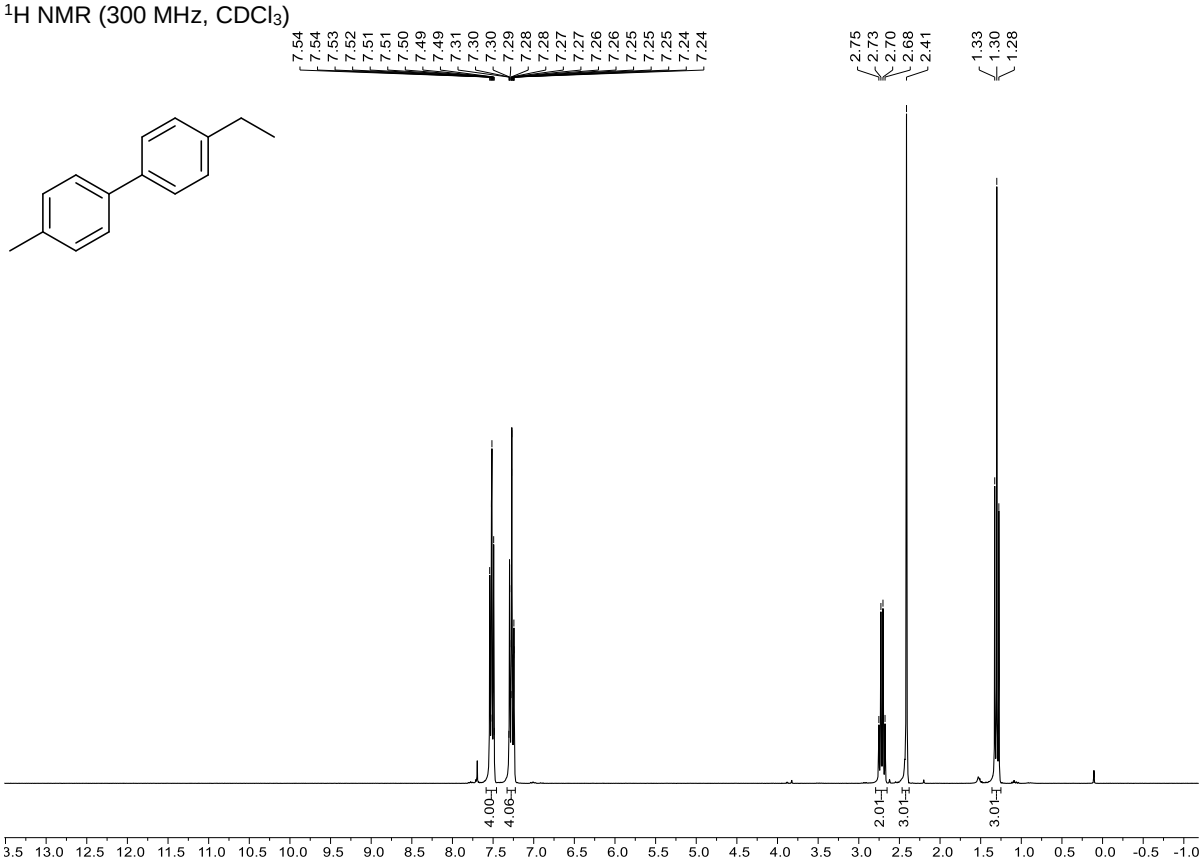
1,1':4',1''-Terphenyl (5c)

^{13}C NMR (75 MHz, $CDCl_3$)



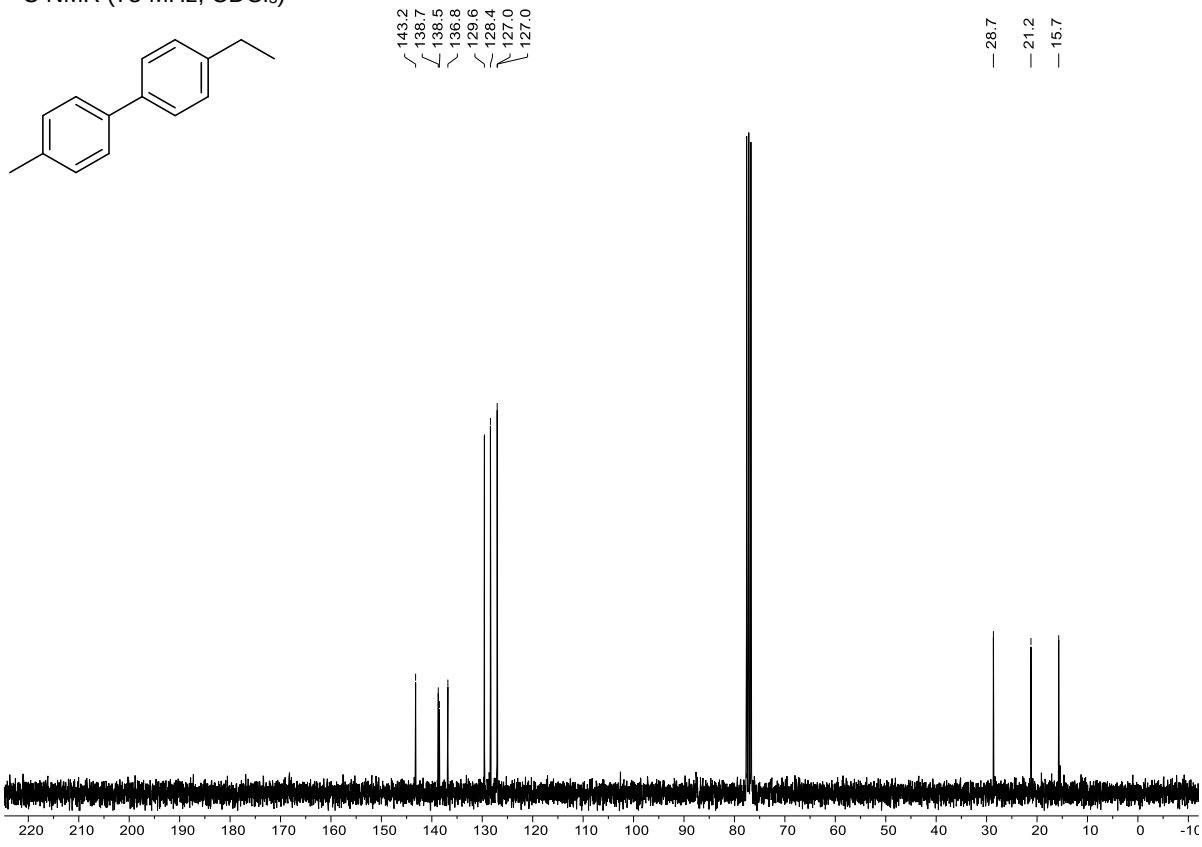
4-Ethyl-4'-methyl-1,1'-biphenyl (5d)

^{1}H NMR (300 MHz, $CDCl_3$)



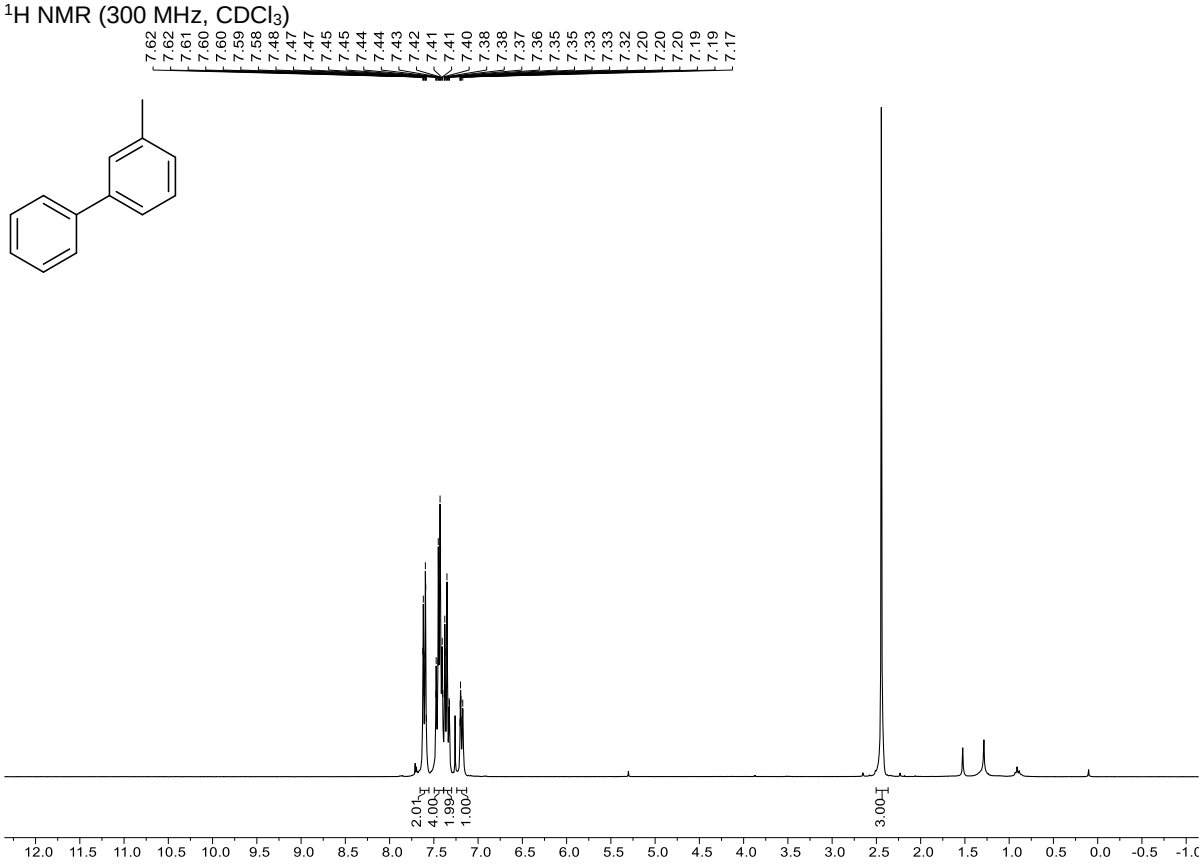
4-Ethyl-4'-methyl-1,1'-biphenyl (5d)

^{13}C NMR (75 MHz, $CDCl_3$)



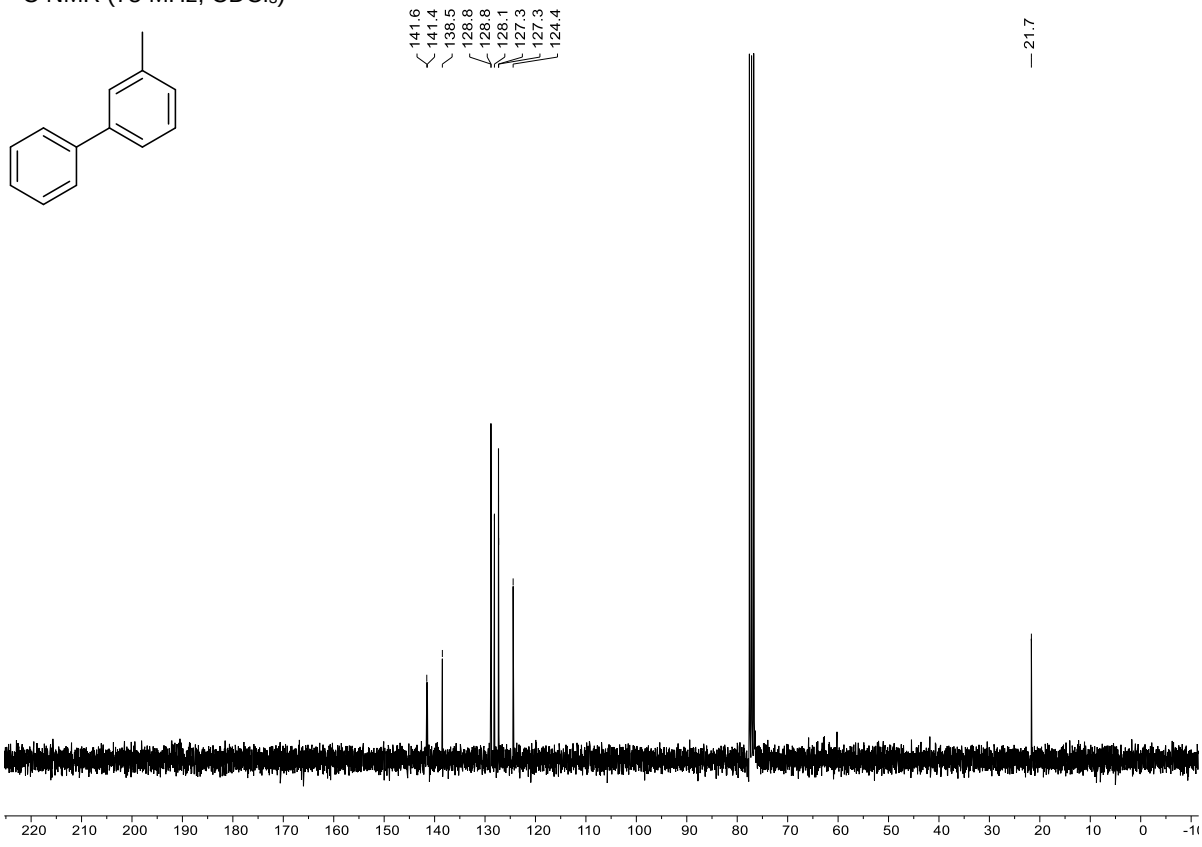
3-Methyl-1,1'-biphenyl (5e)

^{1}H NMR (300 MHz, $CDCl_3$)



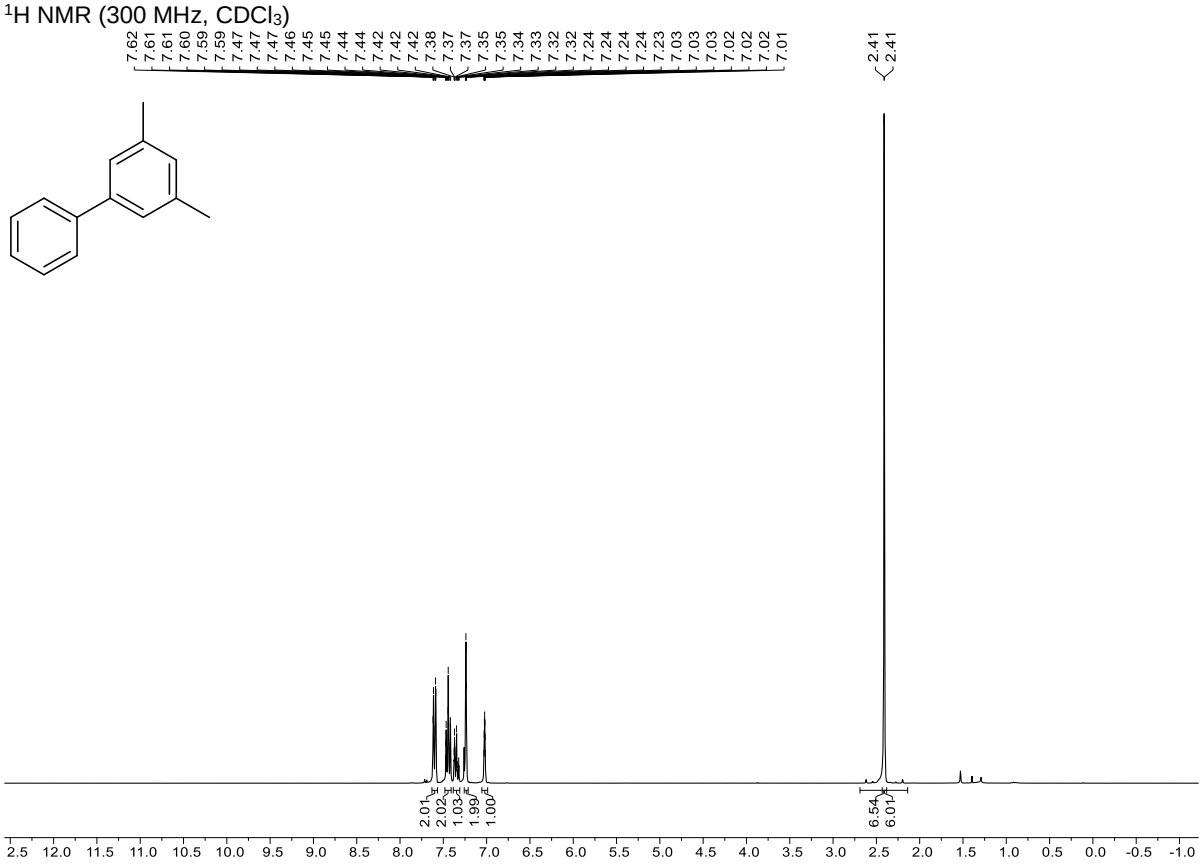
3-Methyl-1,1'-biphenyl (5e)

^{13}C NMR (75 MHz, $CDCl_3$)



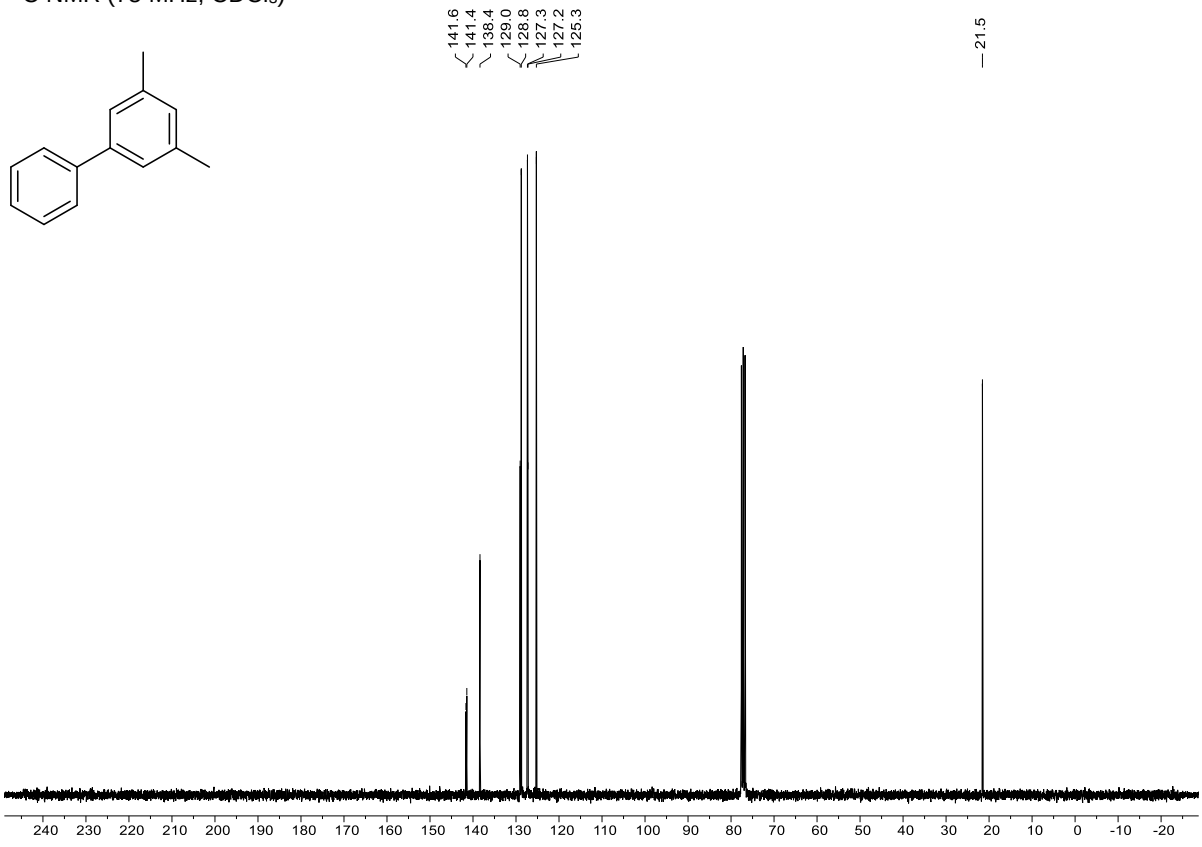
3,5-Dimethyl-1,1'-biphenyl (5f)

^{1}H NMR (300 MHz, $CDCl_3$)



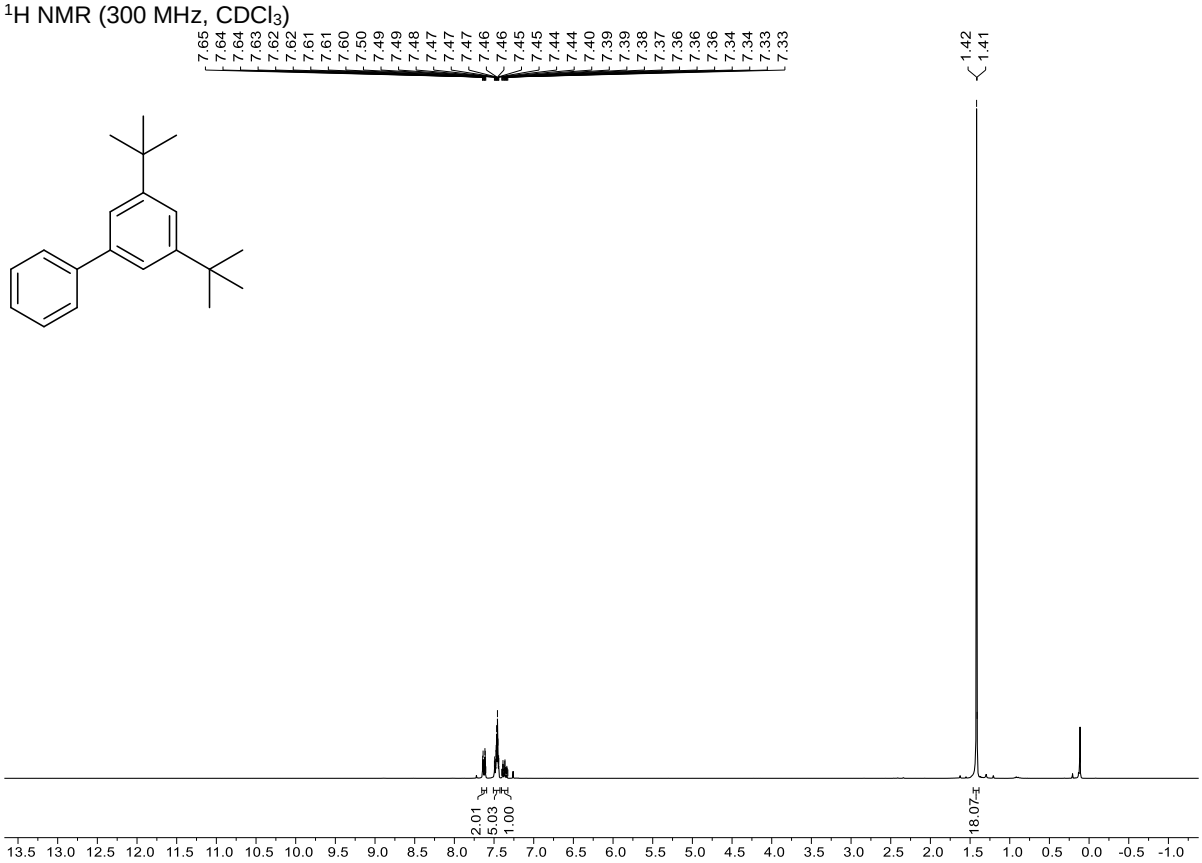
3,5-Dimethyl-1,1'-biphenyl (5f)

^{13}C NMR (75 MHz, $CDCl_3$)



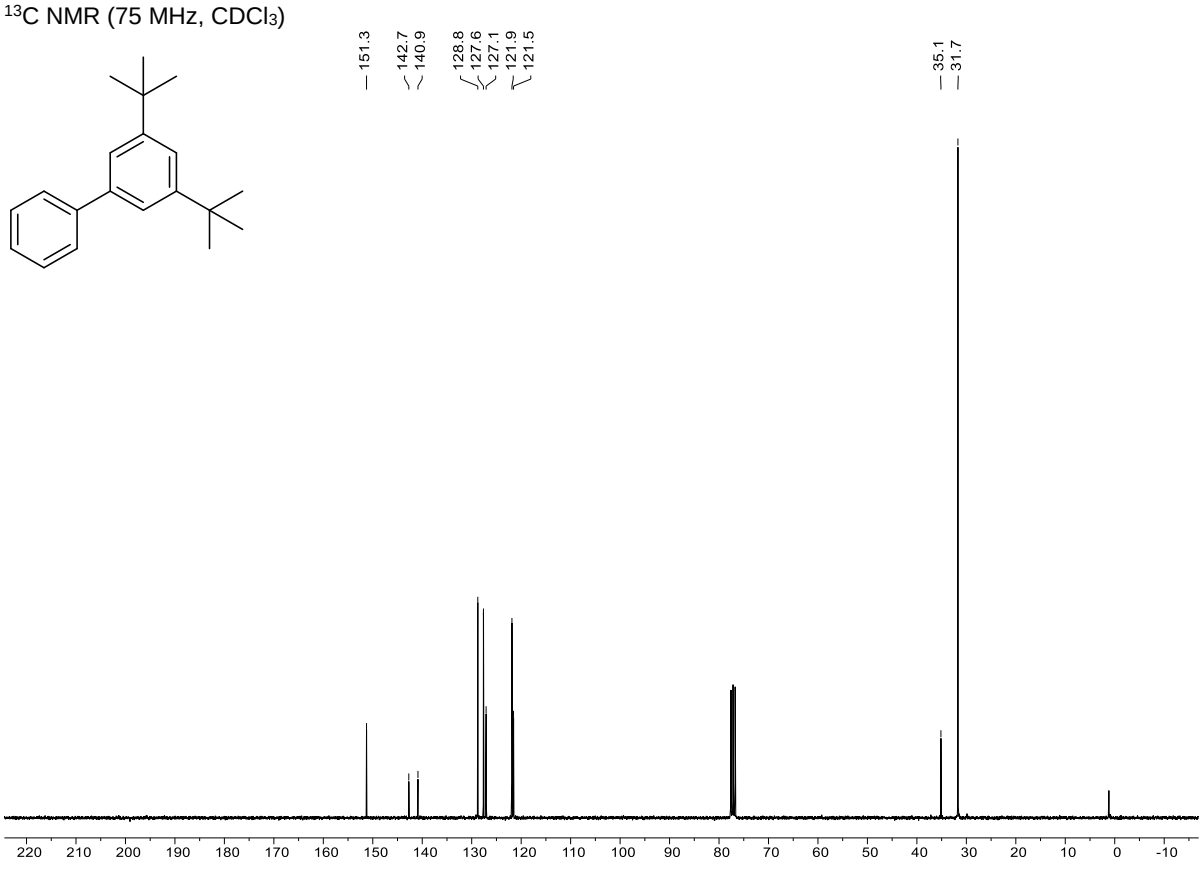
3,5-Di-*tert*-butyl-1,1'-biphenyl (5g)

^{1}H NMR (300 MHz, $CDCl_3$)



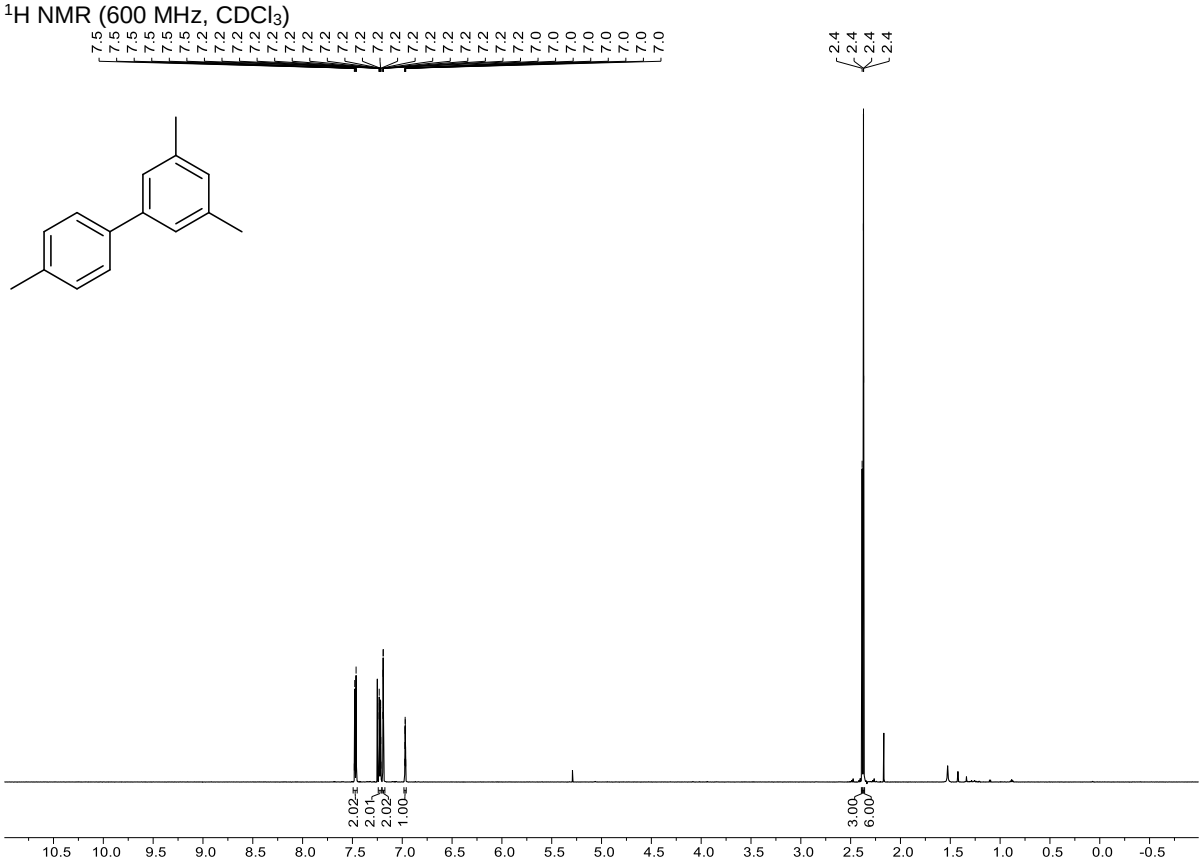
3,5-Di-*tert*-butyl-1,1'-biphenyl (5g)

^{13}C NMR (75 MHz, $CDCl_3$)



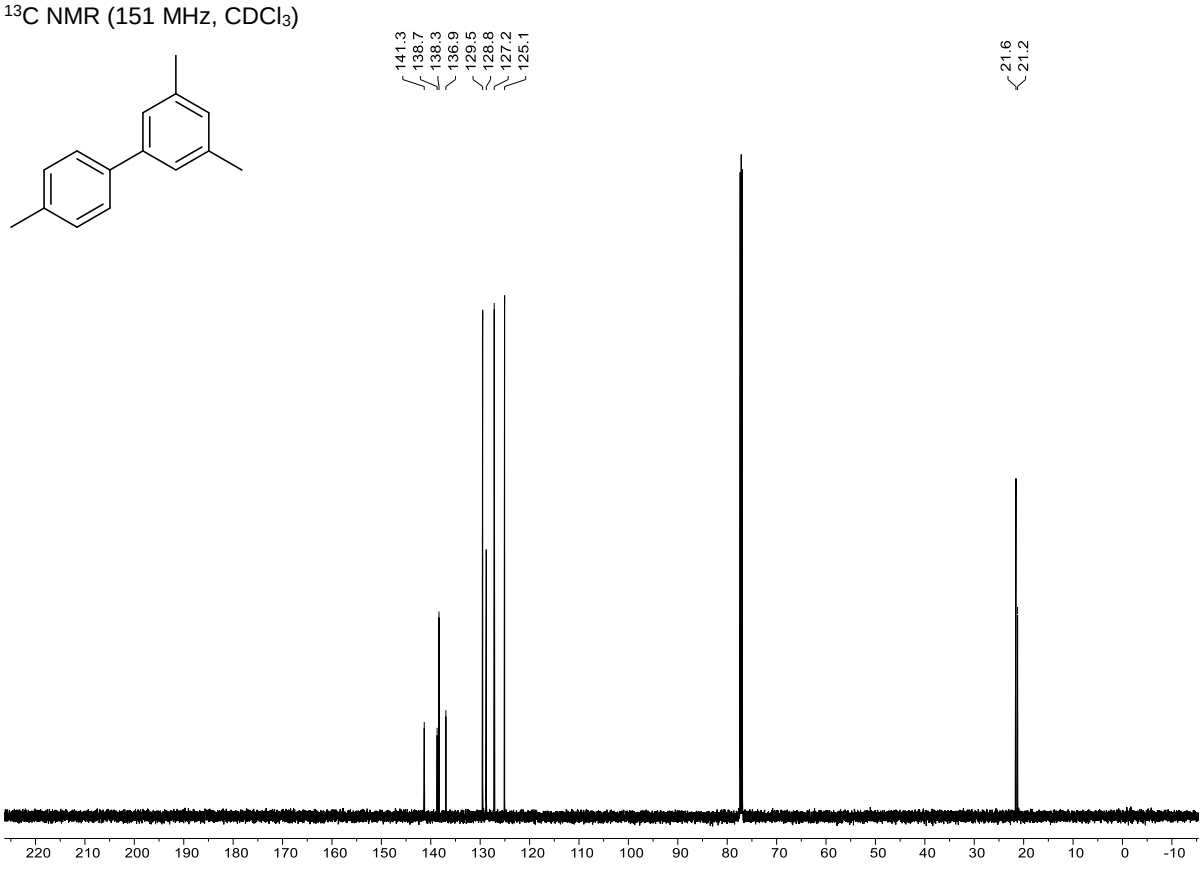
3,4',5-Trimethyl-1,1'-biphenyl (5h)

^{1}H NMR (600 MHz, $CDCl_3$)



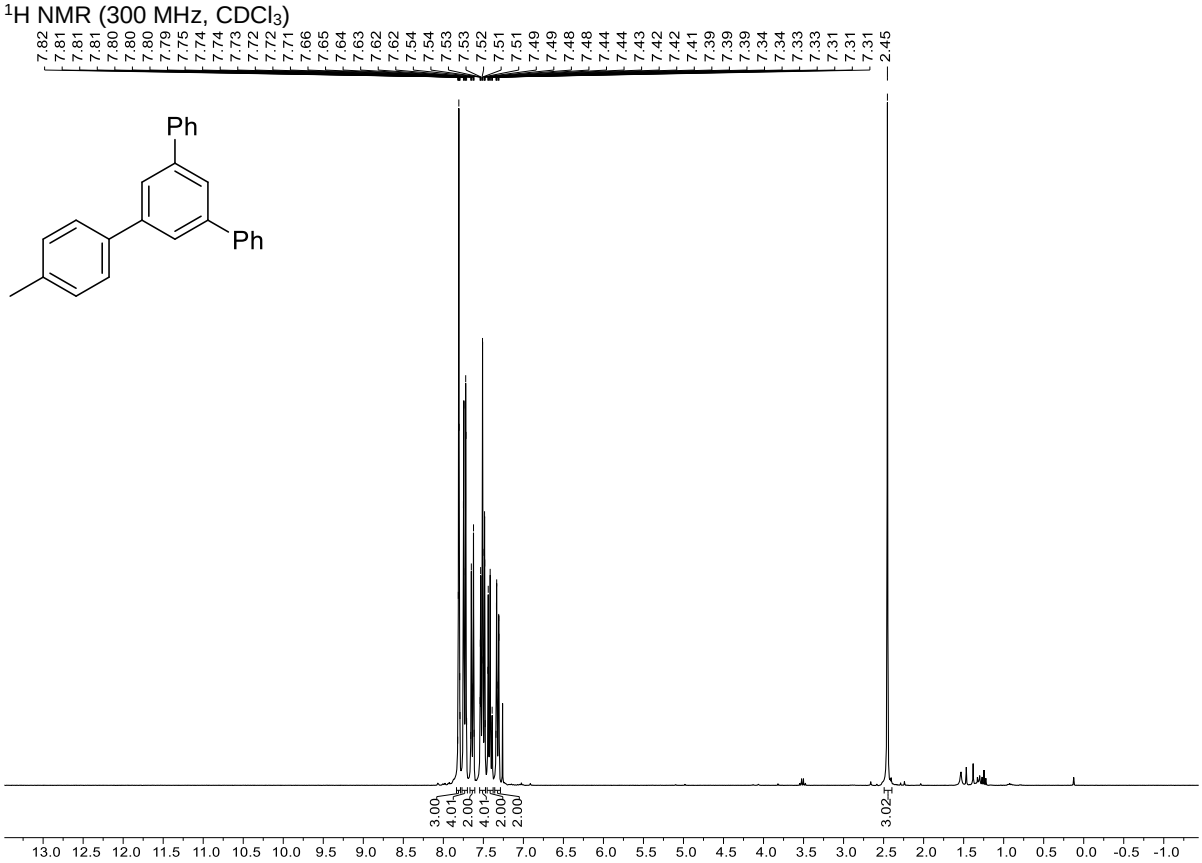
3,4',5-Trimethyl-1,1'-biphenyl (5h)

^{13}C NMR (151 MHz, $CDCl_3$)



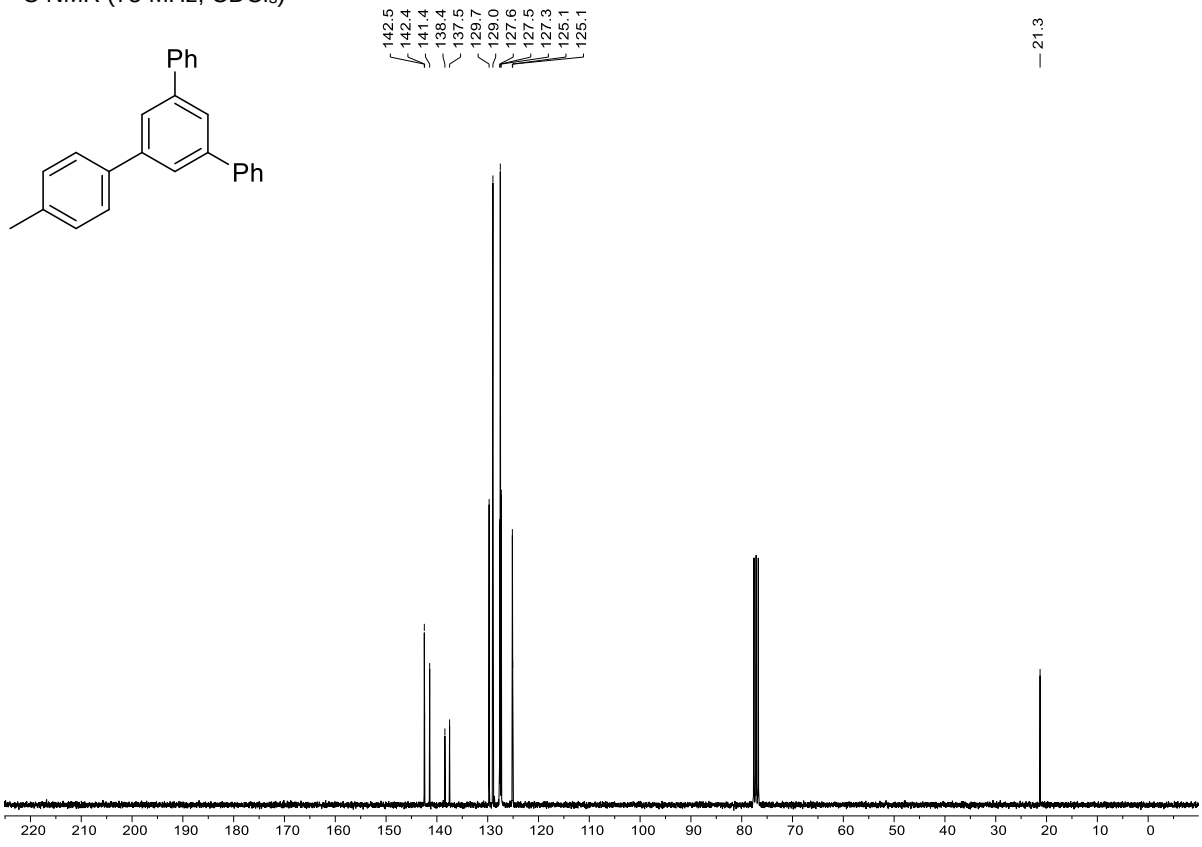
4-Methyl-5'-phenyl-1,1':3',1''-terphenyl (5i)

^{1}H NMR (300 MHz, $CDCl_3$)



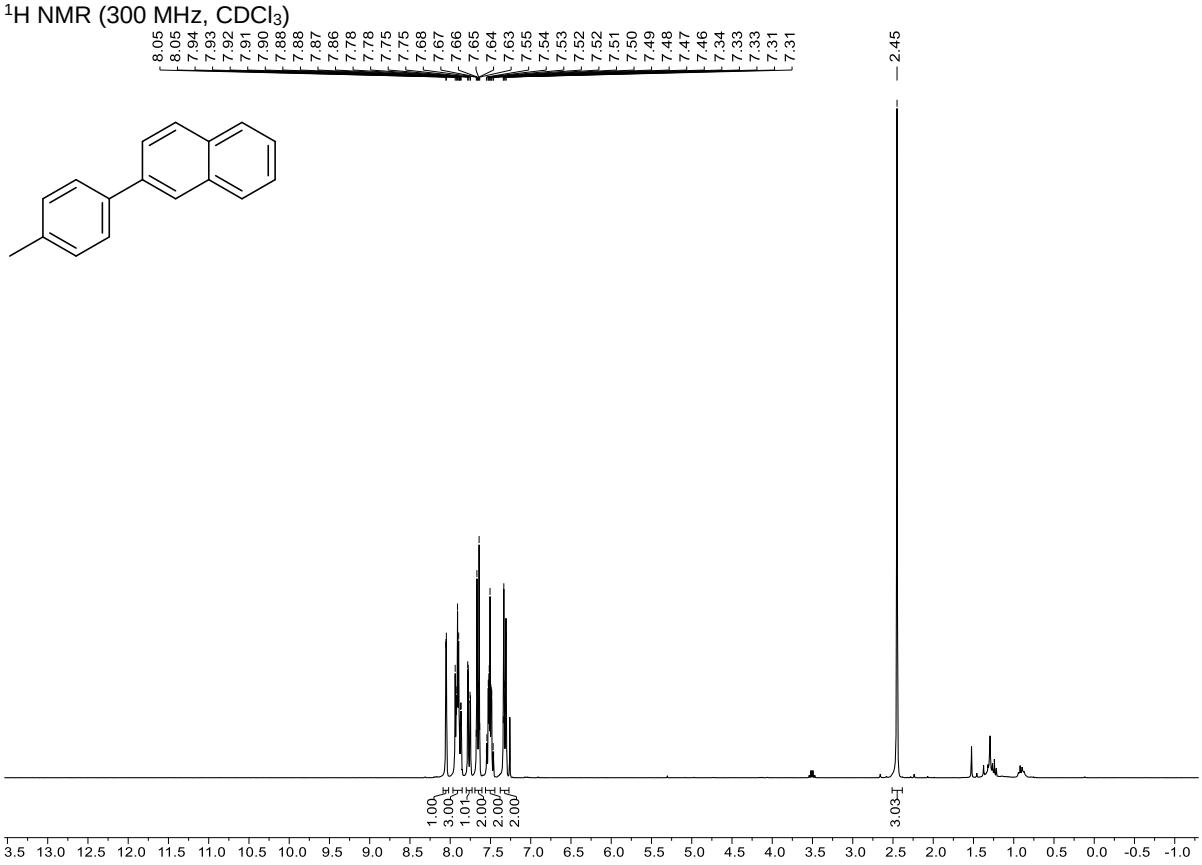
4-Methyl-5'-phenyl-1,1':3',1''-terphenyl (5i)

^{13}C NMR (75 MHz, $CDCl_3$)



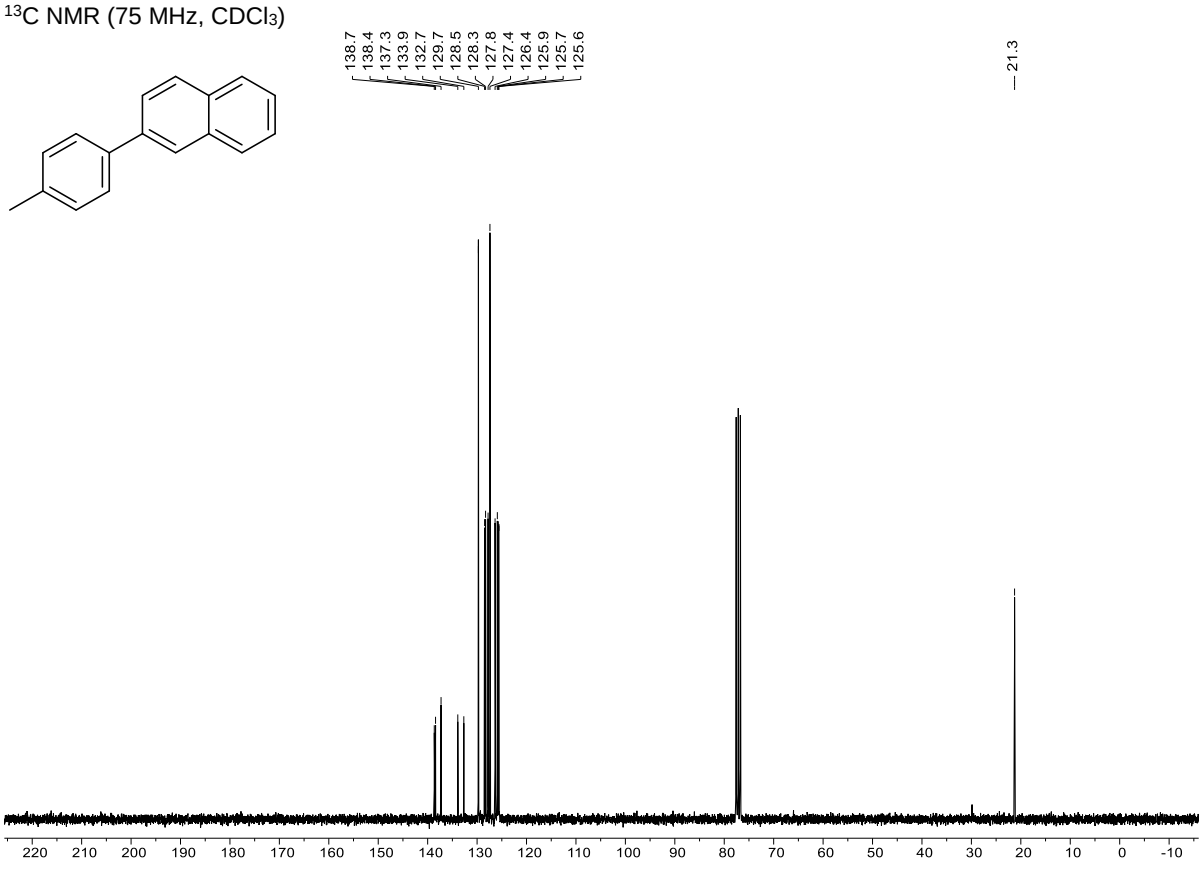
2-(*p*-Tolyl)naphthalene (5j)

^{1}H NMR (300 MHz, $CDCl_3$)



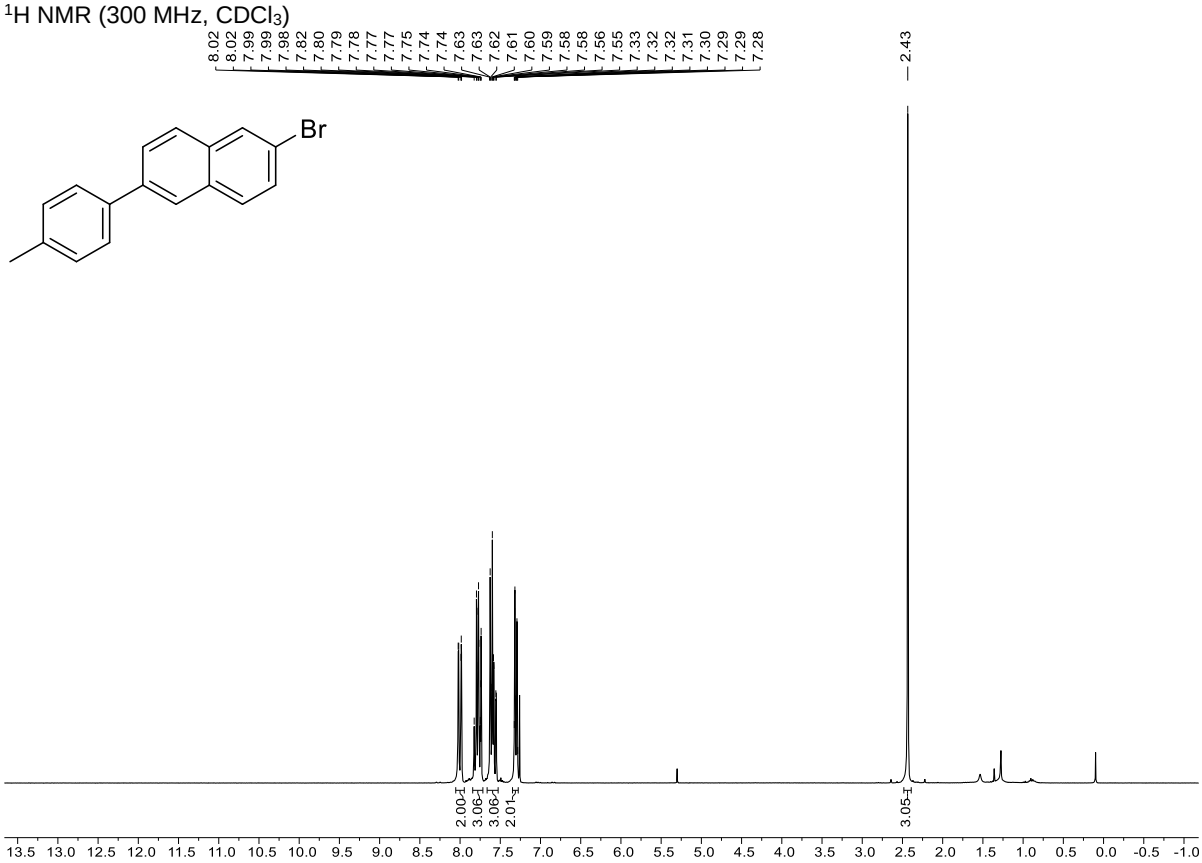
2-(*p*-Tolyl)naphthalene (5j)

^{13}C NMR (75 MHz, $CDCl_3$)



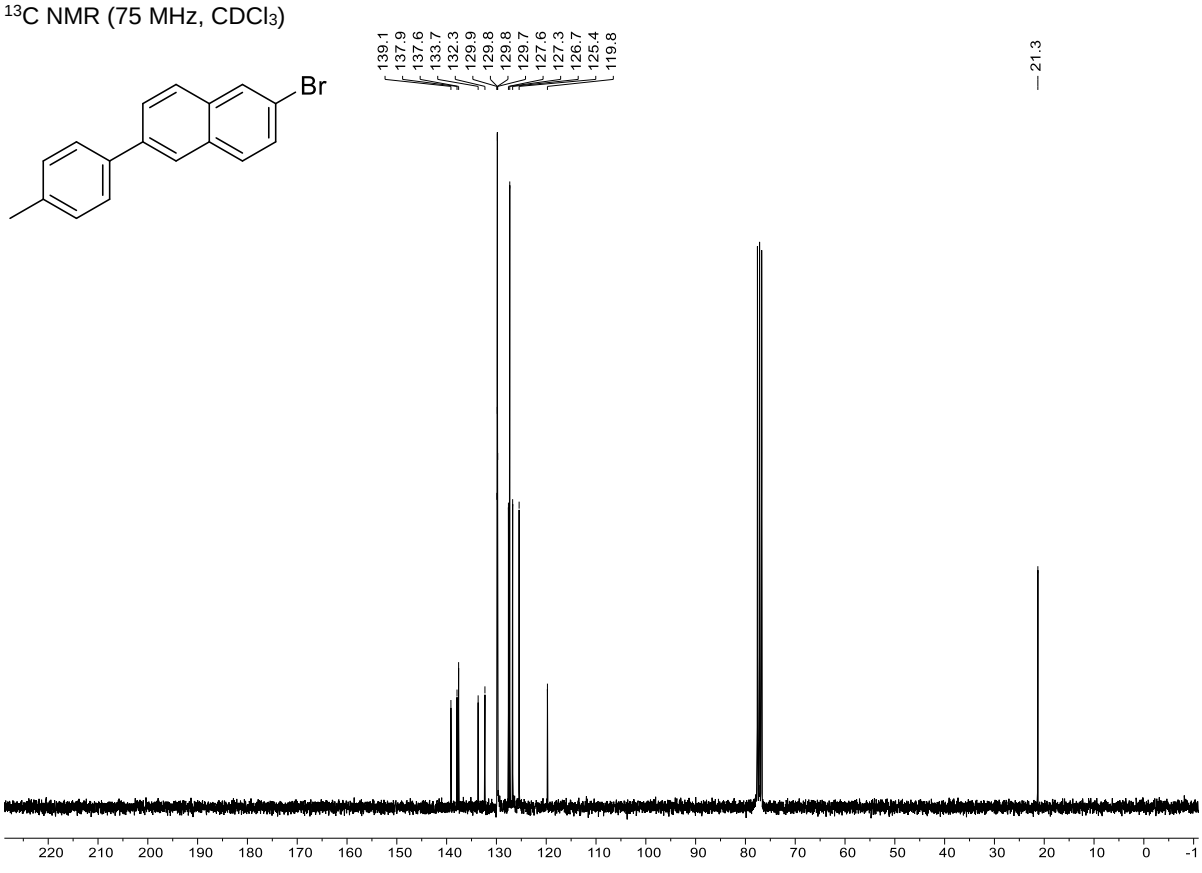
2-Bromo-6-(*p*-tolyl)naphthalene (5k)

^{1}H NMR (300 MHz, $CDCl_3$)



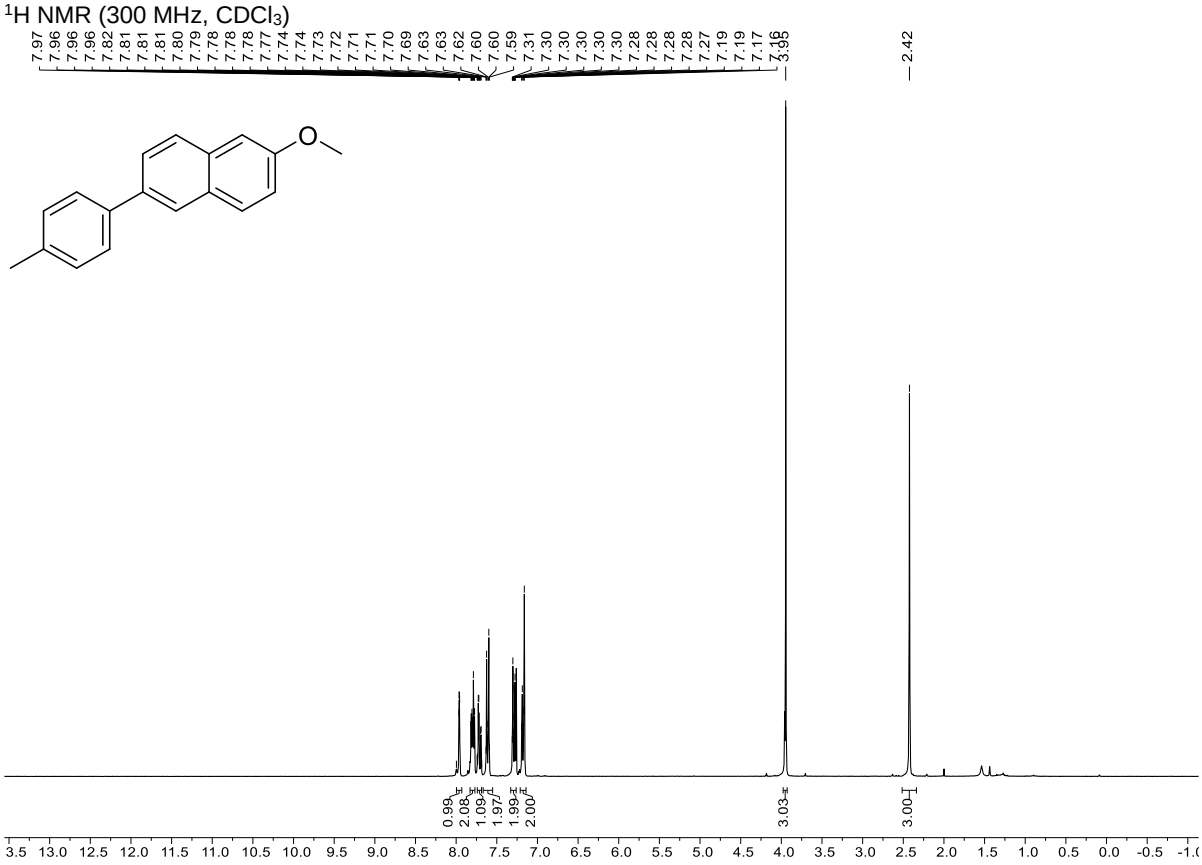
2-Bromo-6-(*p*-tolyl)naphthalene (5k)

^{13}C NMR (75 MHz, $CDCl_3$)



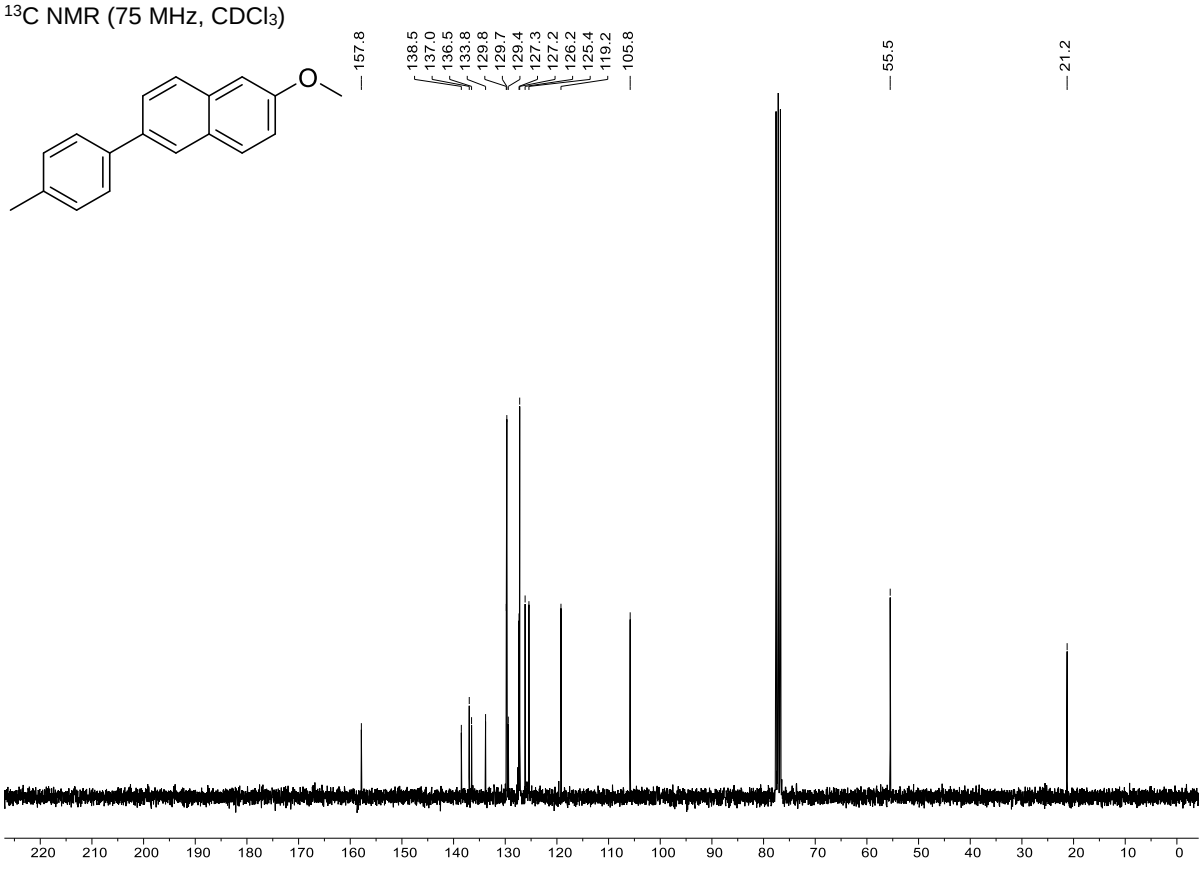
2-Methoxy-6-(*p*-tolyl)naphthalene (5l)

^{1}H NMR (300 MHz, $CDCl_3$)



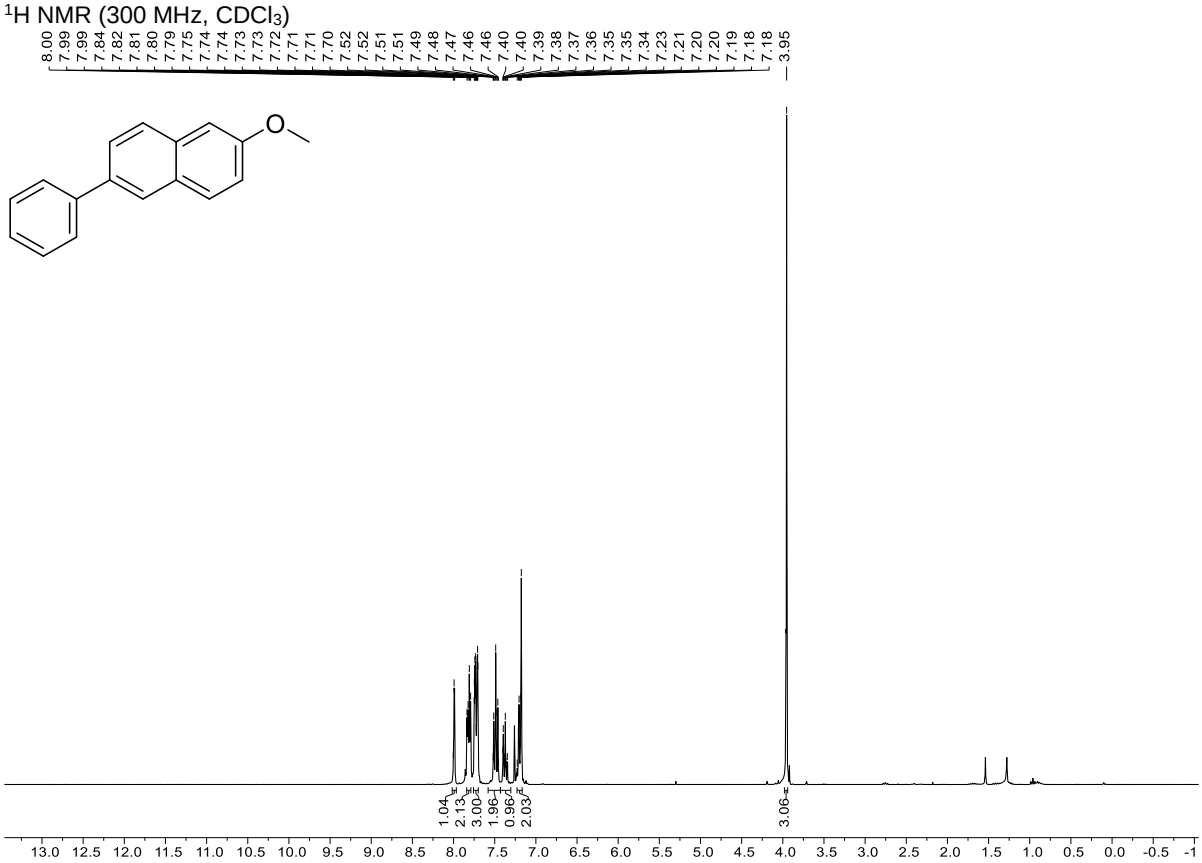
2-Methoxy-6-(*p*-tolyl)naphthalene (5l)

^{13}C NMR (75 MHz, $CDCl_3$)



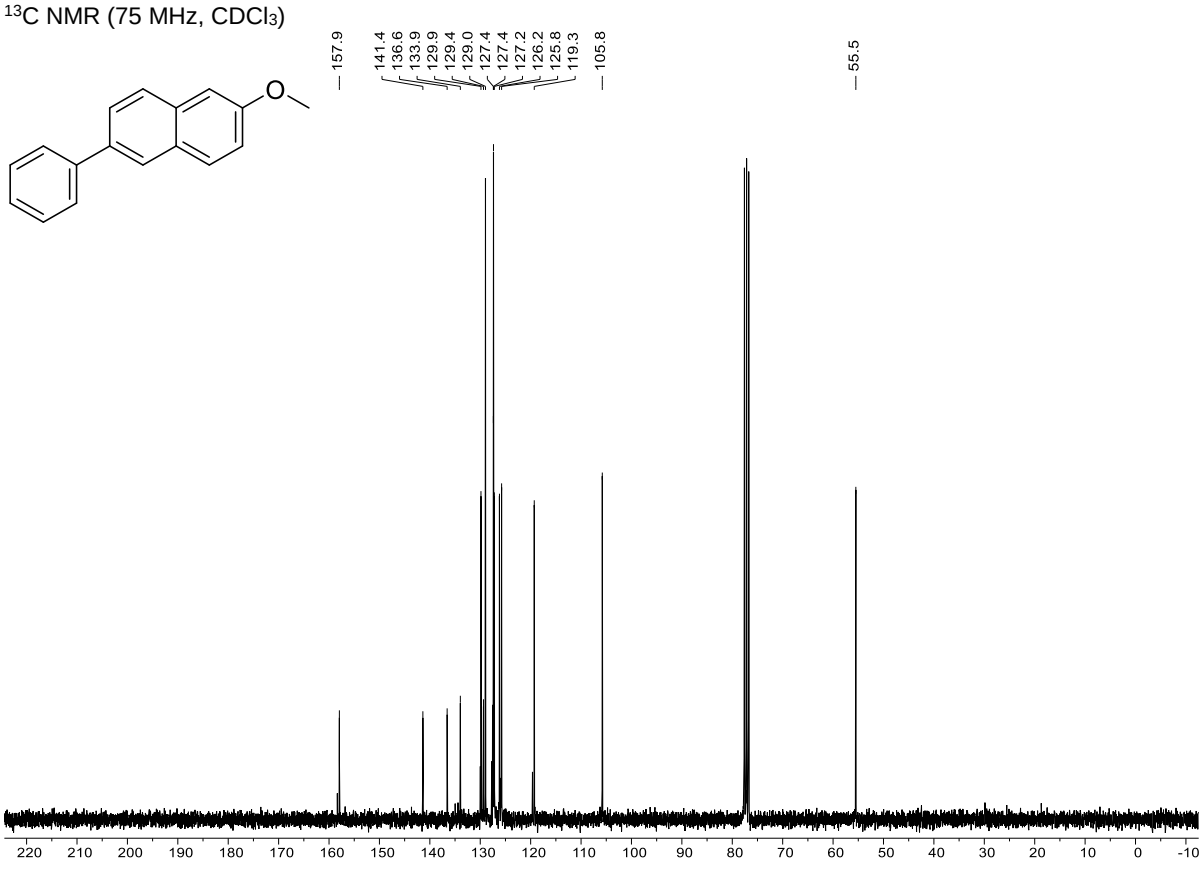
2-Methoxy-6-phenylnaphthalene (5m)

^{1}H NMR (300 MHz, $CDCl_3$)



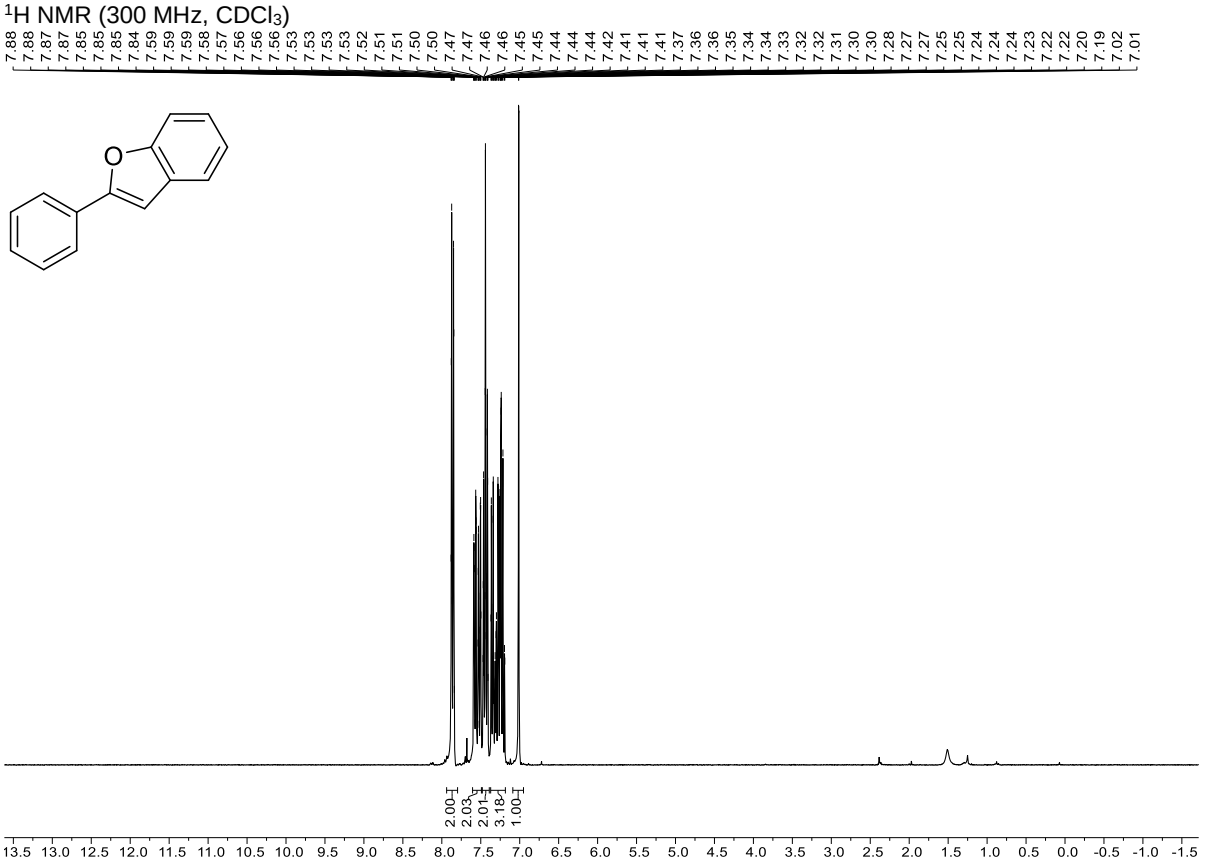
2-Methoxy-6-phenylnaphthalene (5m)

^{13}C NMR (75 MHz, $CDCl_3$)



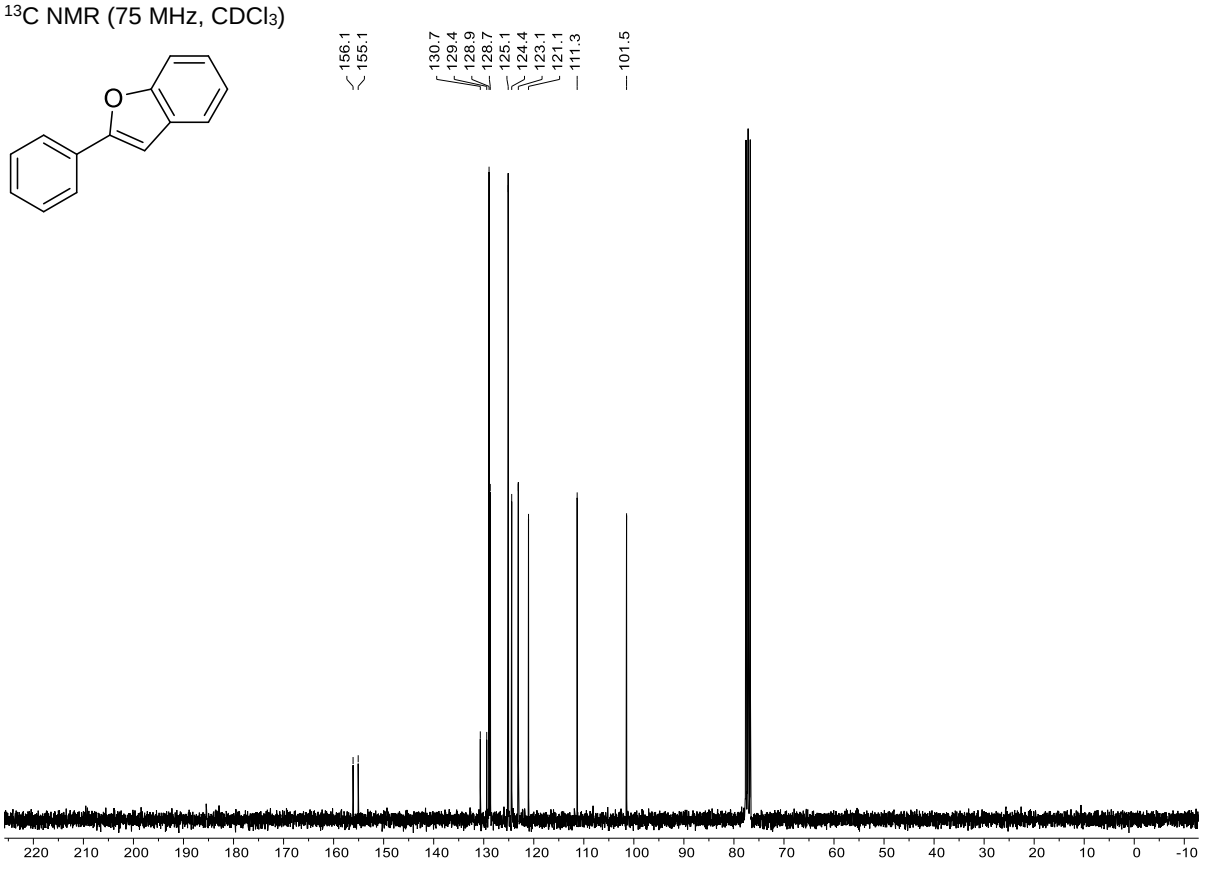
2-Phenylbenzofuran (5n)

^{1}H NMR (300 MHz, $CDCl_3$)



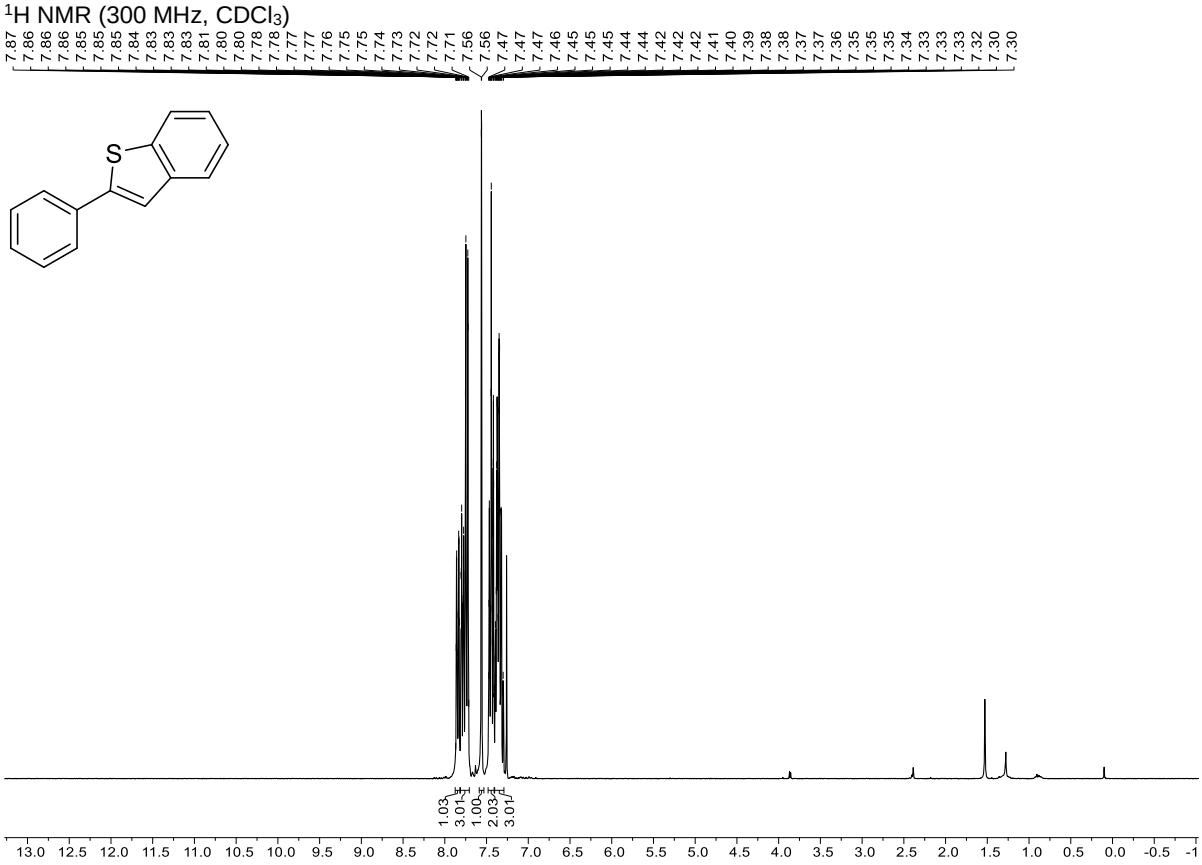
2-Phenylbenzofuran (5n)

^{13}C NMR (75 MHz, $CDCl_3$)



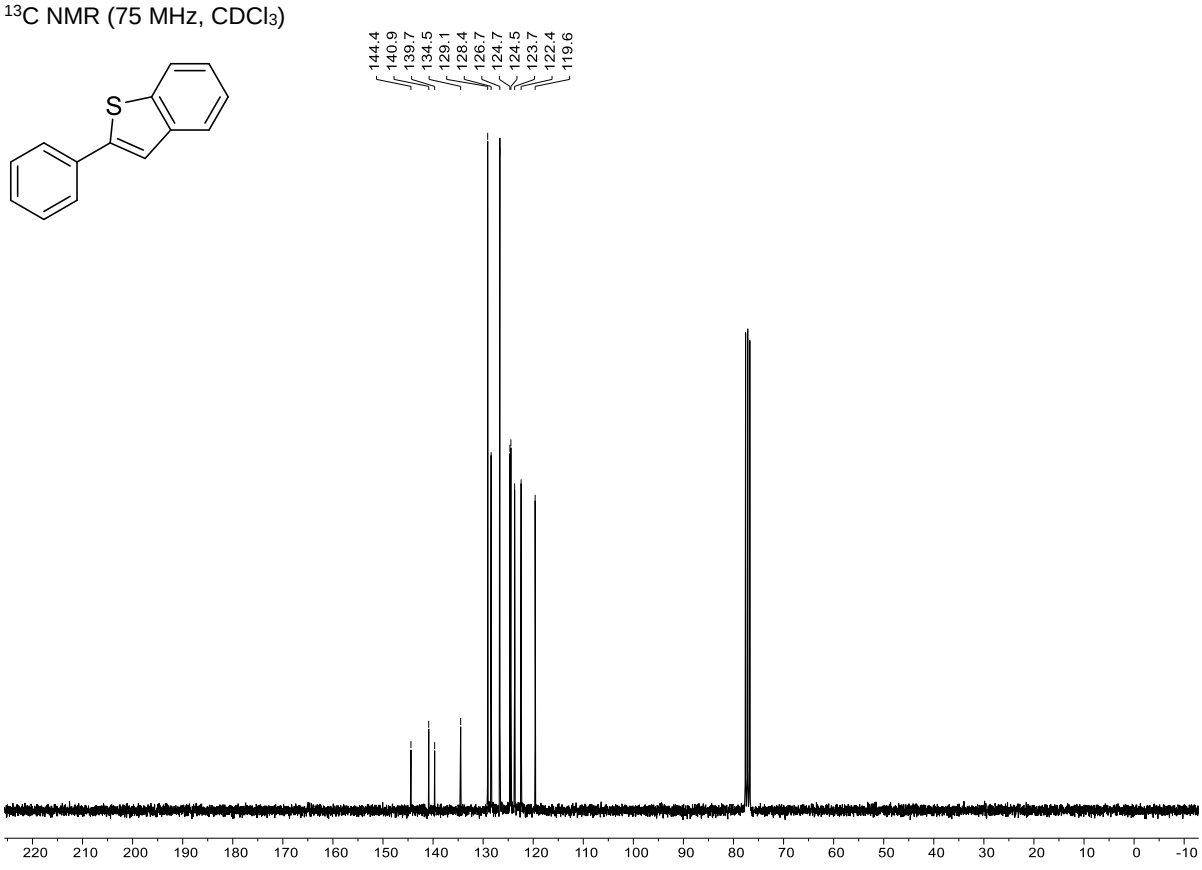
2-Phenylbenzo[b]thiophene (5o)

^{1}H NMR (300 MHz, $CDCl_3$)



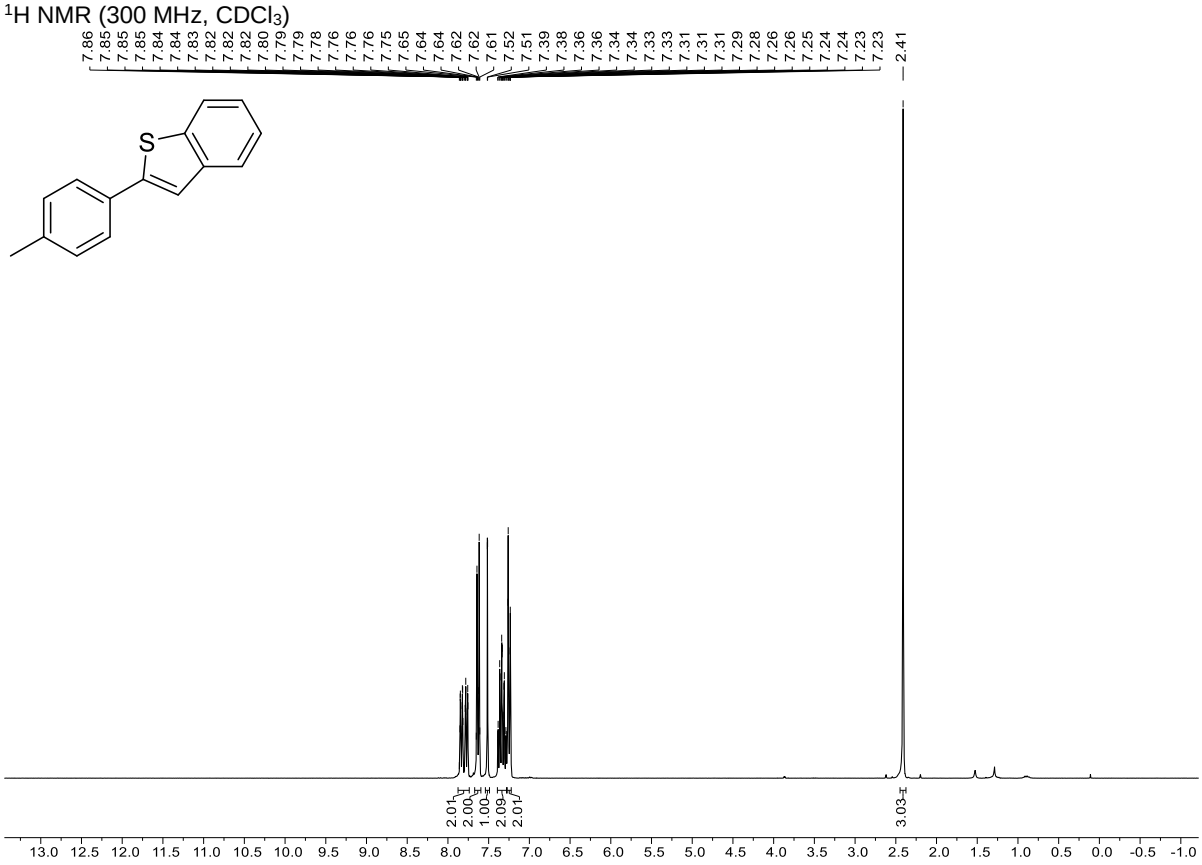
2-Phenylbenzo[b]thiophene (5o)

^{13}C NMR (75 MHz, $CDCl_3$)



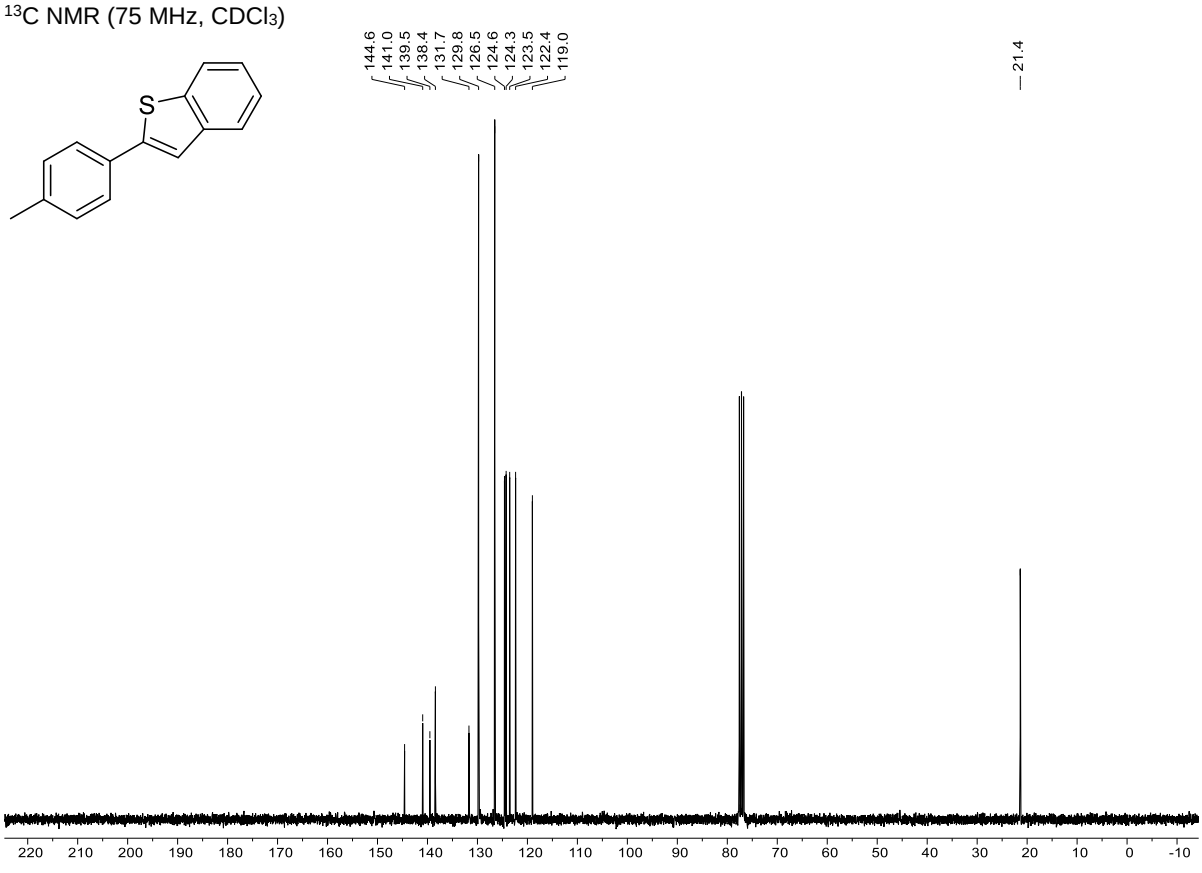
2-(*p*-Tolyl)benzo[b]thiophene (5p)

^{1}H NMR (300 MHz, $CDCl_3$)



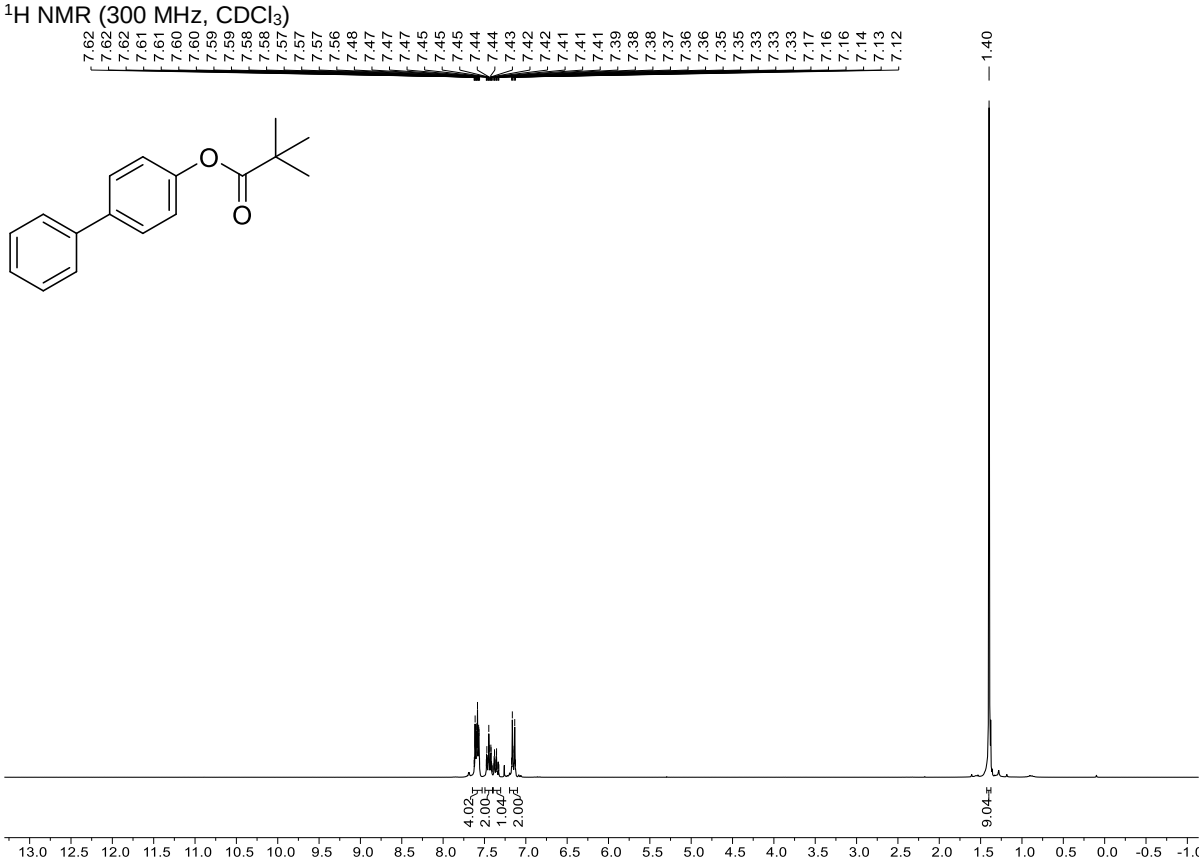
2-(*p*-Tolyl)benzo[b]thiophene (5p)

^{13}C NMR (75 MHz, $CDCl_3$)



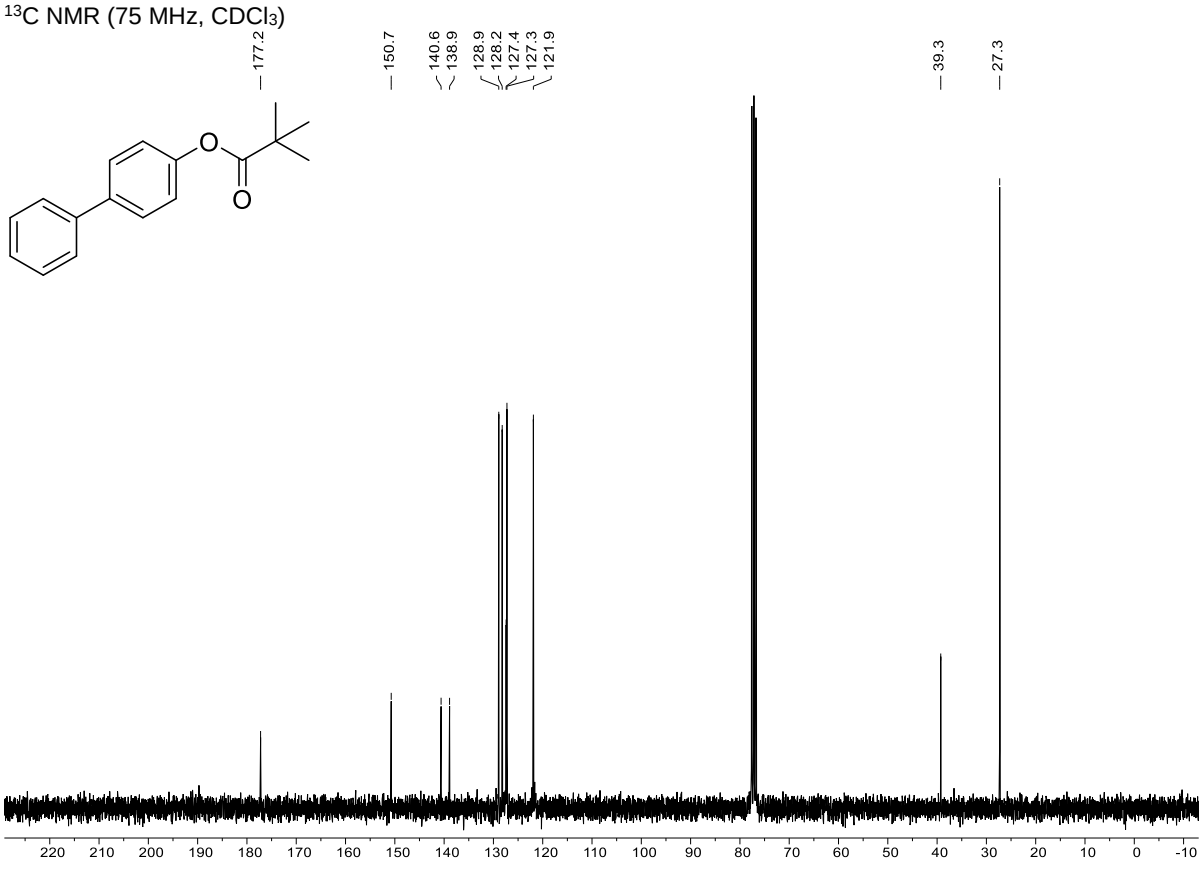
[1,1'-Biphenyl]-4-yl pivalate (5q)

^{1}H NMR (300 MHz, $CDCl_3$)



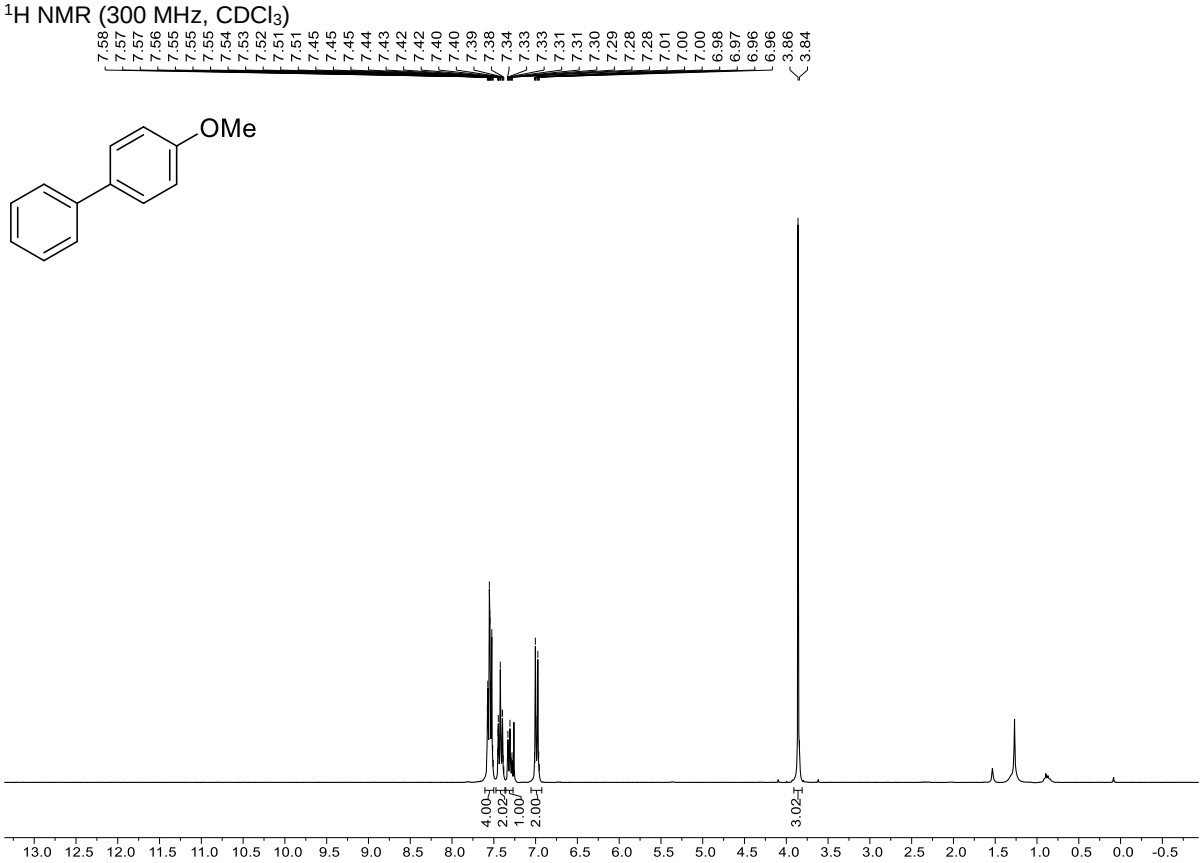
[1,1'-Biphenyl]-4-yl pivalate (5q)

^{13}C NMR (75 MHz, $CDCl_3$)



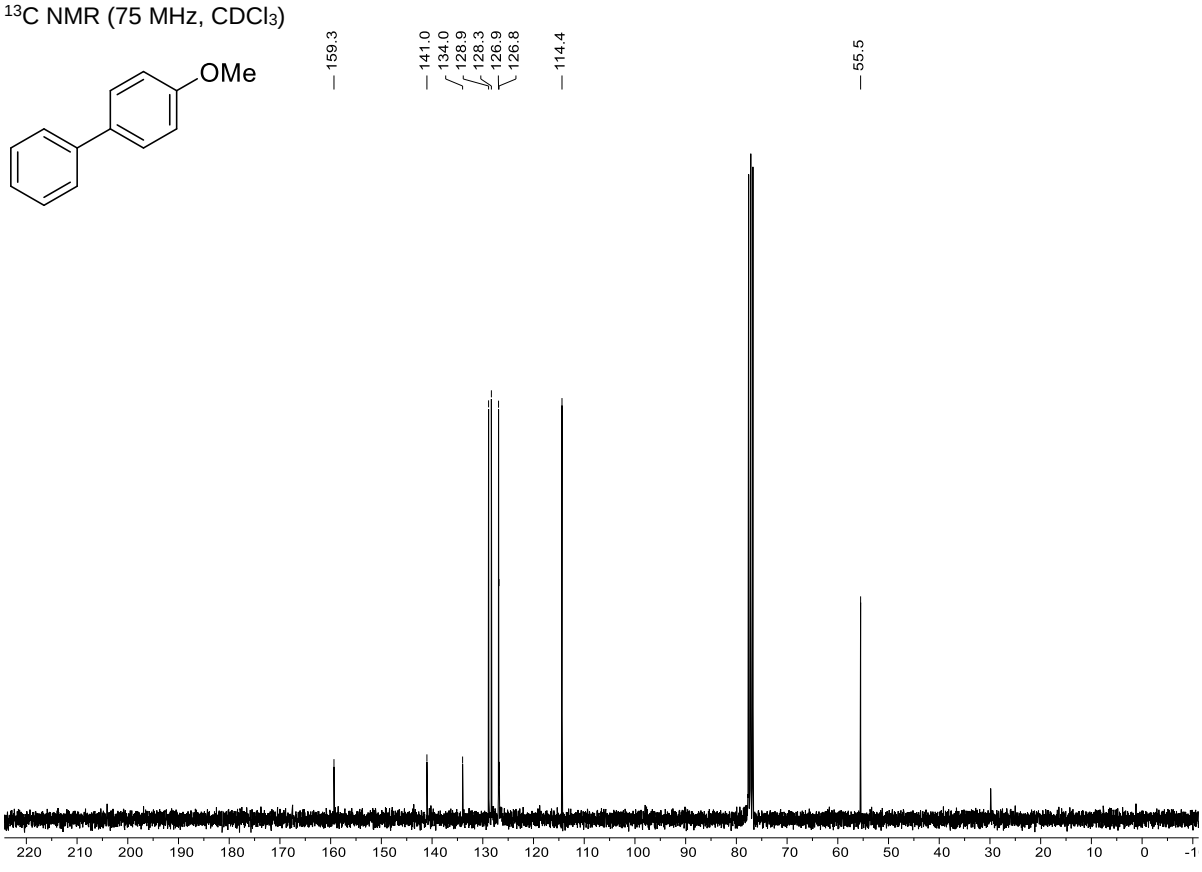
4-Methoxy-1,1'-biphenyl (5r)

^{1}H NMR (300 MHz, $CDCl_3$)



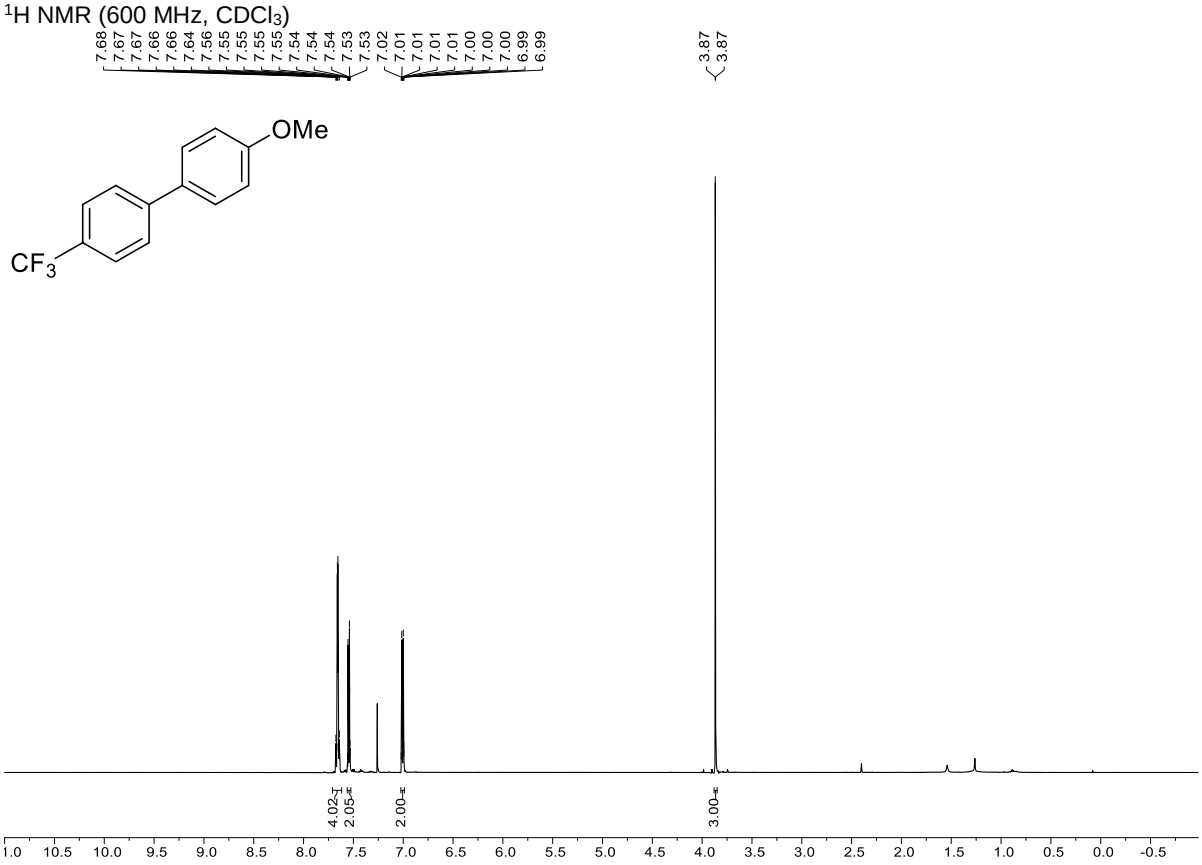
4-Methoxy-1,1'-biphenyl (5r)

^{13}C NMR (75 MHz, $CDCl_3$)



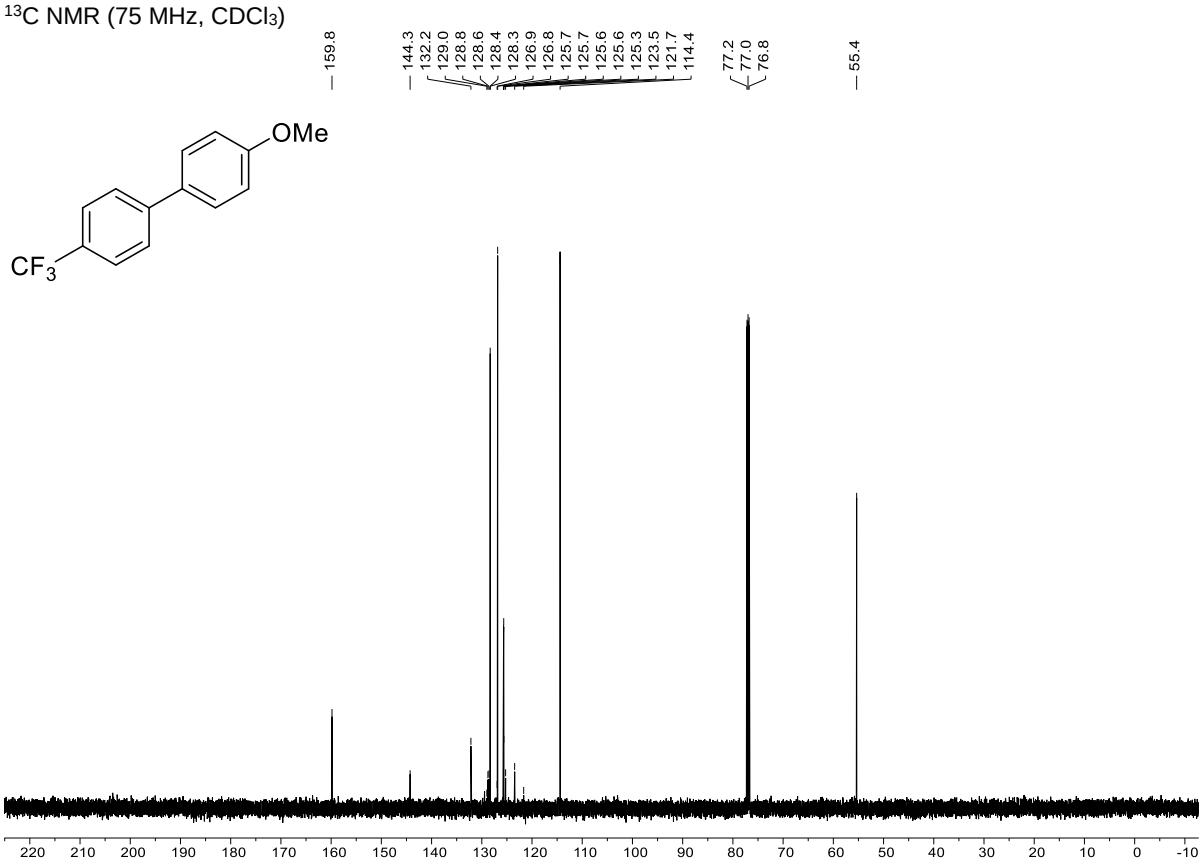
4-Methoxy-4'-(trifluoromethyl)-1,1'-biphenyl (SP1)

^{1}H NMR (600 MHz, $CDCl_3$)



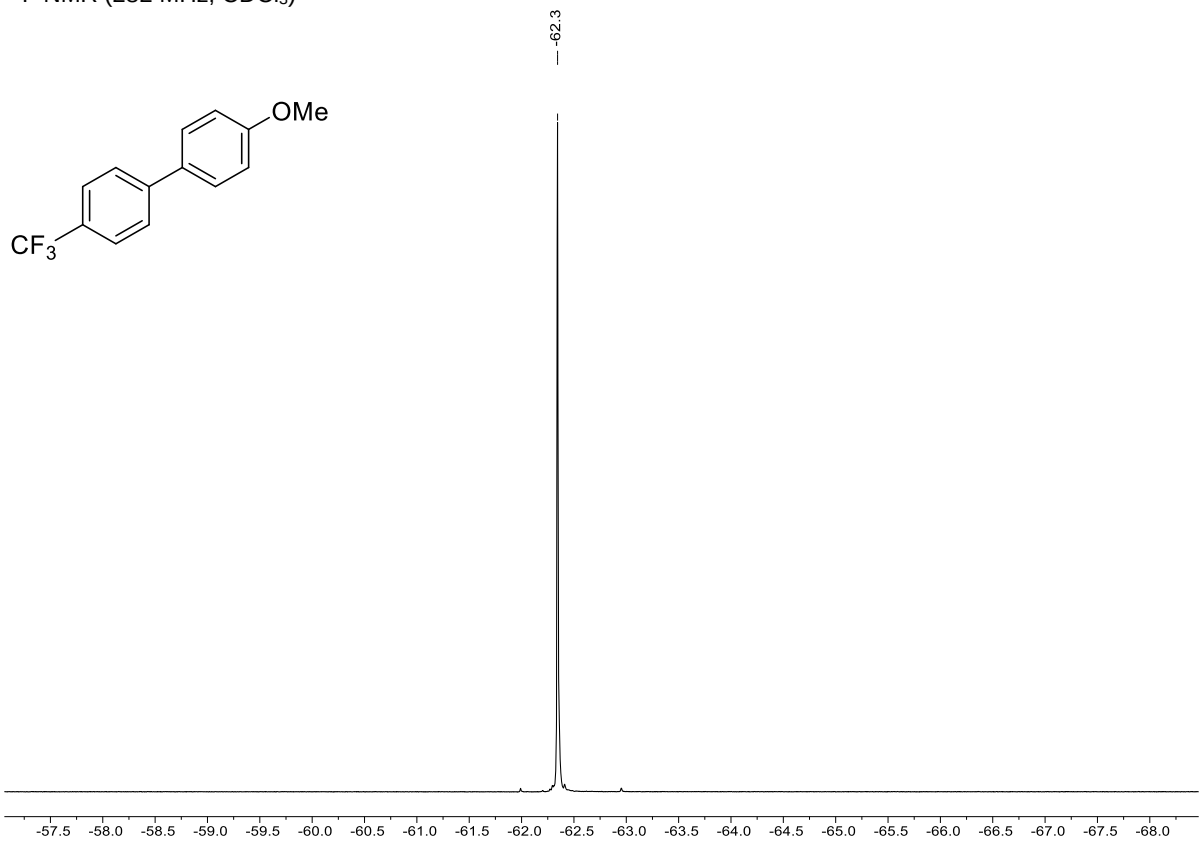
4-Methoxy-4'-(trifluoromethyl)-1,1'-biphenyl (SP1)

^{13}C NMR (75 MHz, $CDCl_3$)



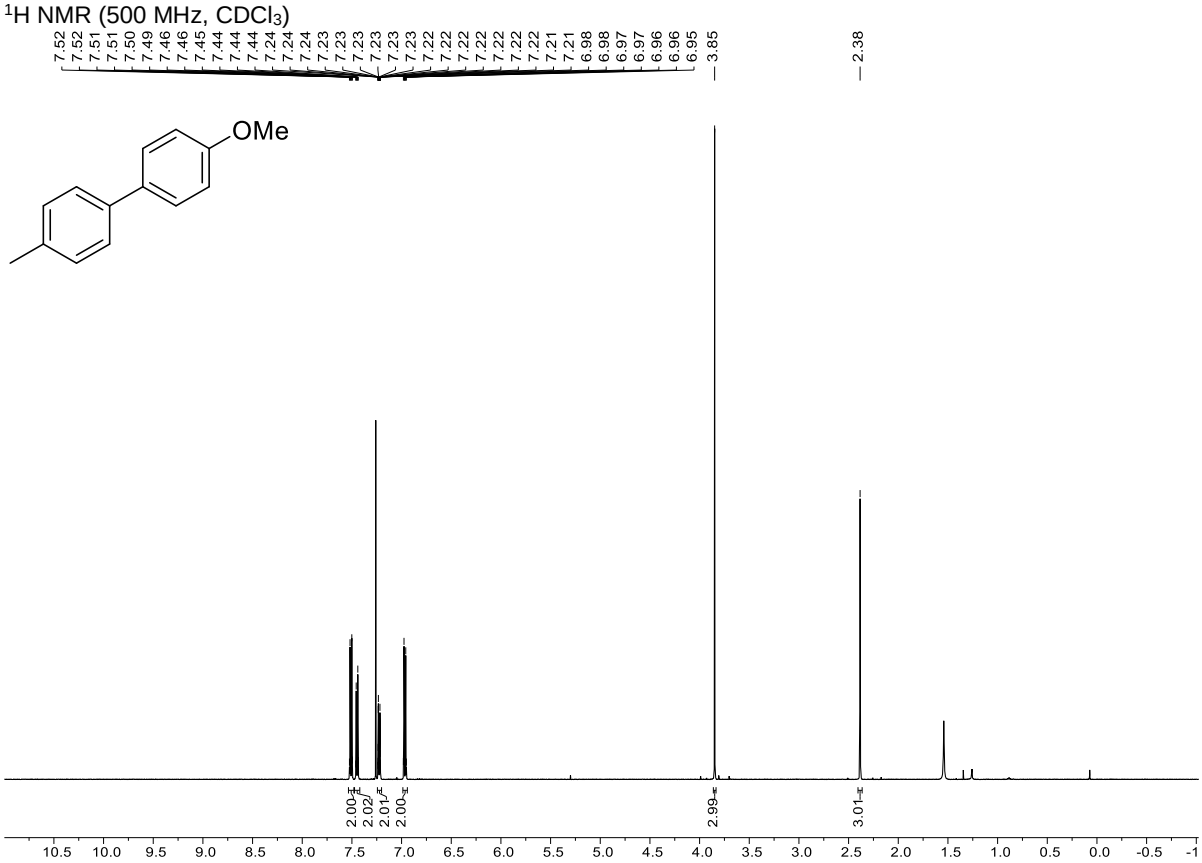
4-Methoxy-4'-(trifluoromethyl)-1,1'-biphenyl (SP1)

^{19}F NMR (282 MHz, $CDCl_3$)



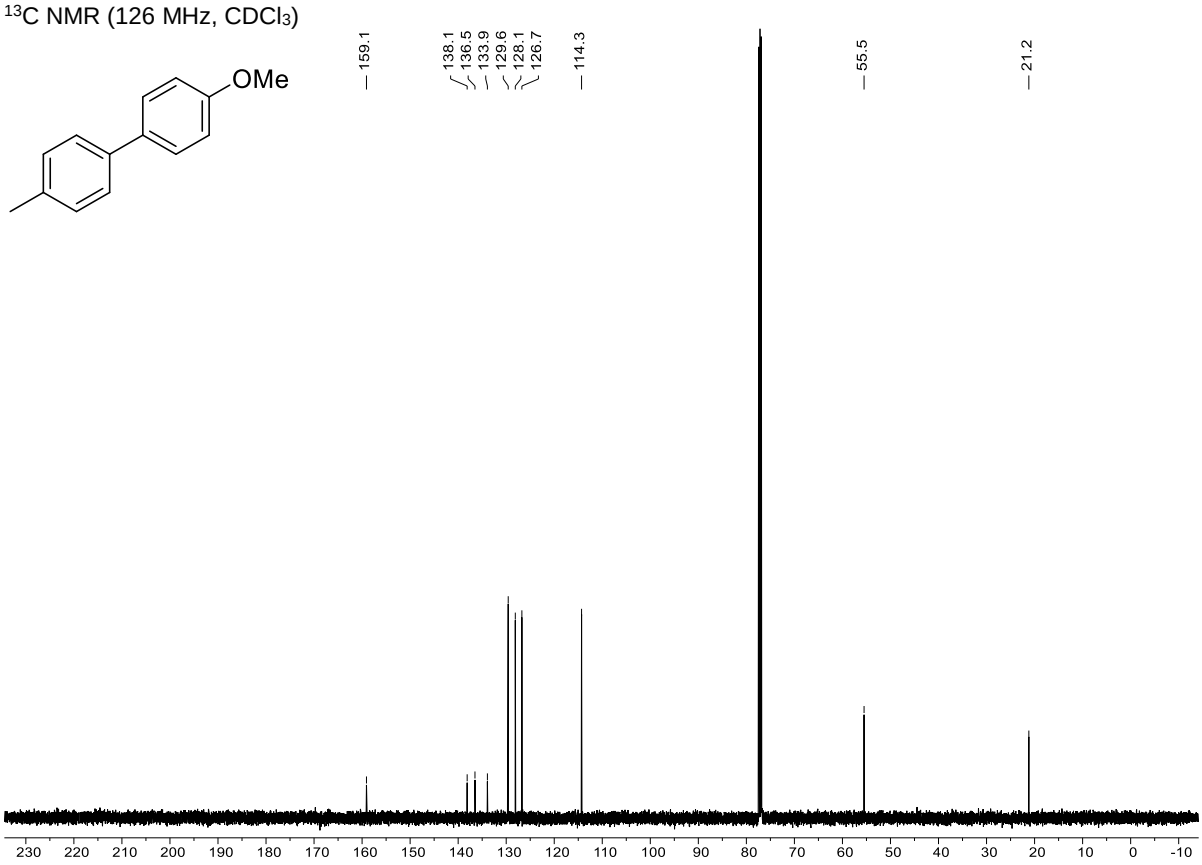
4-Methoxy-4'-methyl-1,1'-biphenyl (5s)

^{1}H NMR (500 MHz, $CDCl_3$)



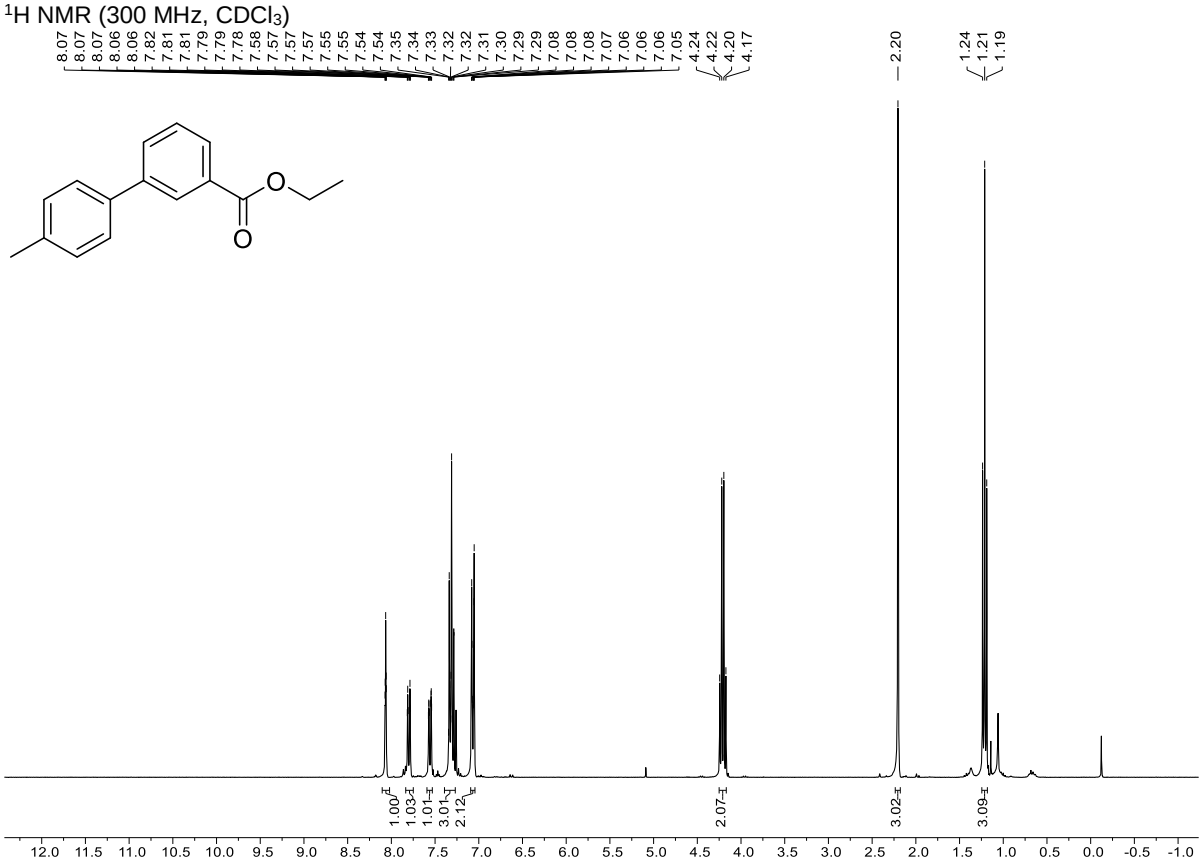
4-Methoxy-4'-methyl-1,1'-biphenyl (5s)

^{13}C NMR (126 MHz, $CDCl_3$)



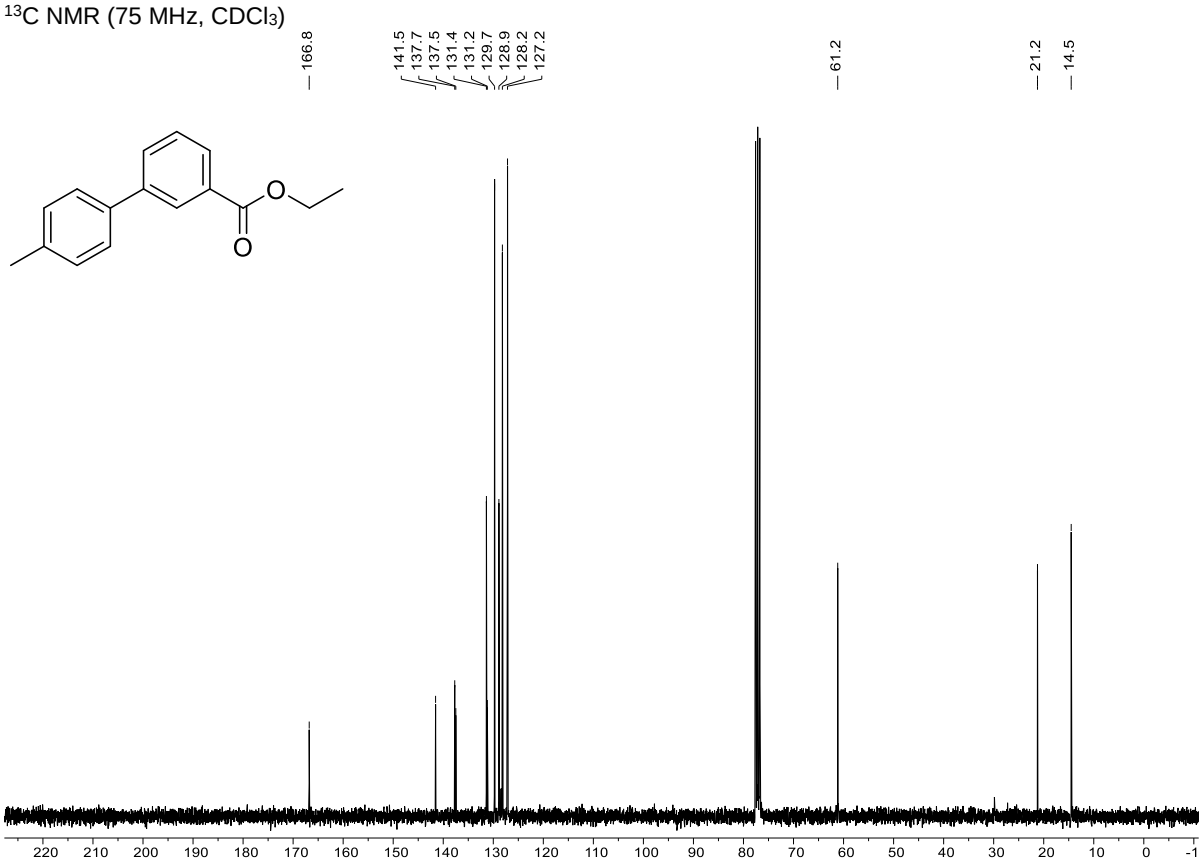
Ethyl 4'-methyl-[1,1'-biphenyl]-3-carboxylate (5t)

^{1}H NMR (300 MHz, $CDCl_3$)



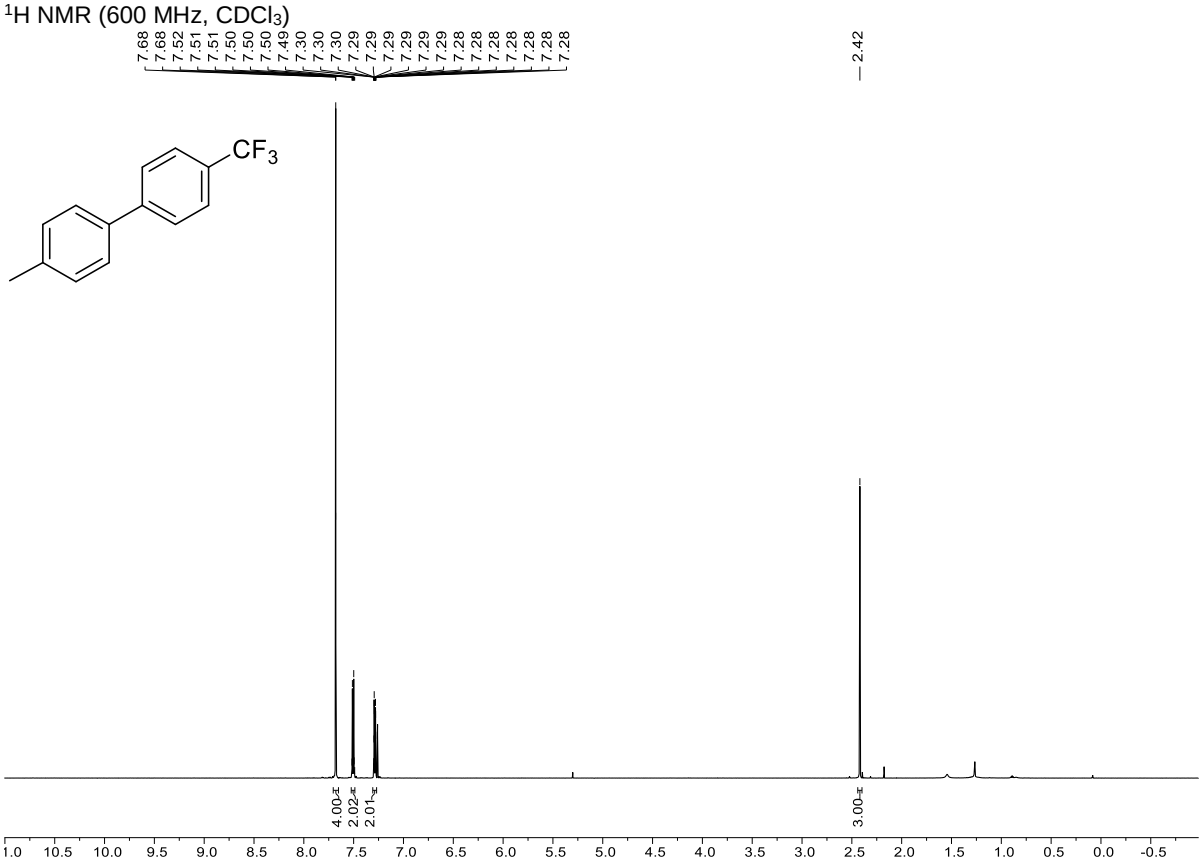
Ethyl 4'-methyl-[1,1'-biphenyl]-3-carboxylate (5t)

^{13}C NMR (75 MHz, $CDCl_3$)



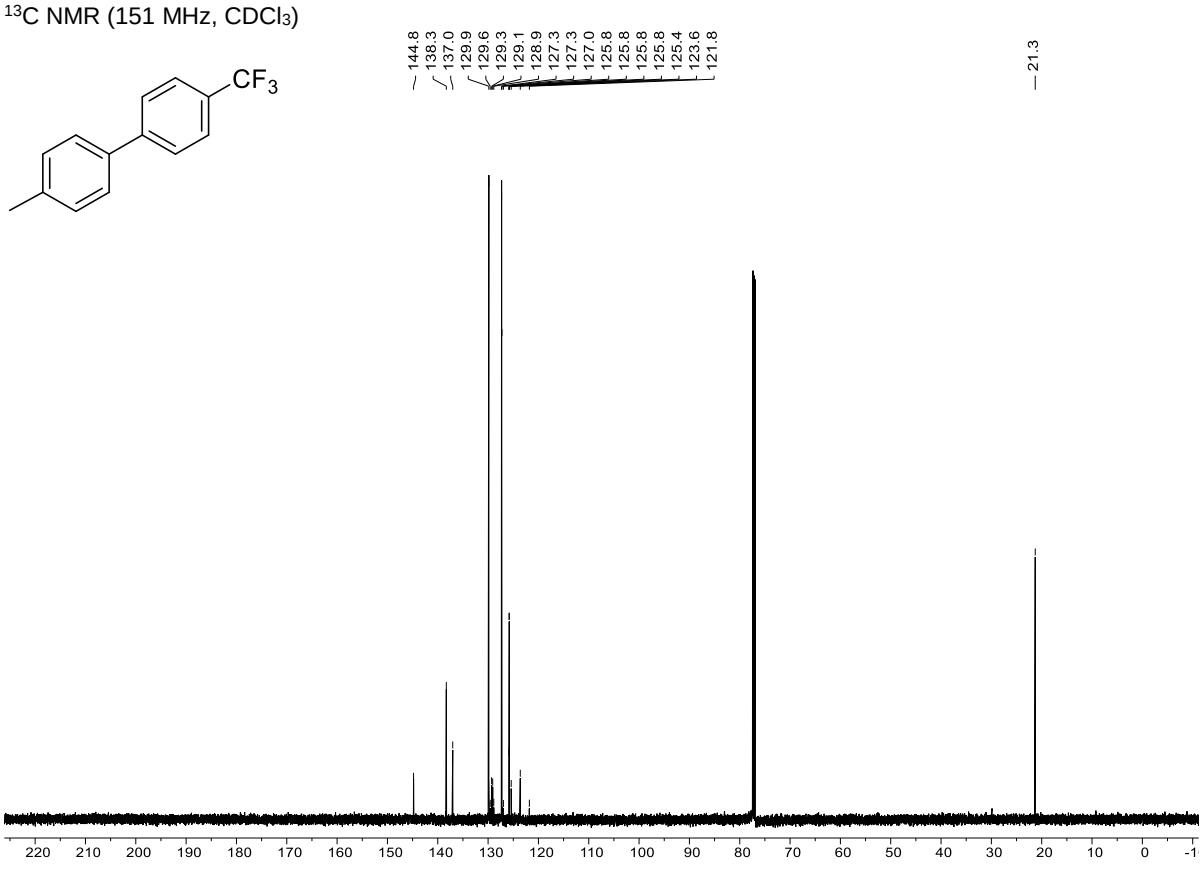
4-Methyl-4'-(trifluoromethyl)-1,1'-biphenyl (SP2)

^{1}H NMR (600 MHz, $CDCl_3$)



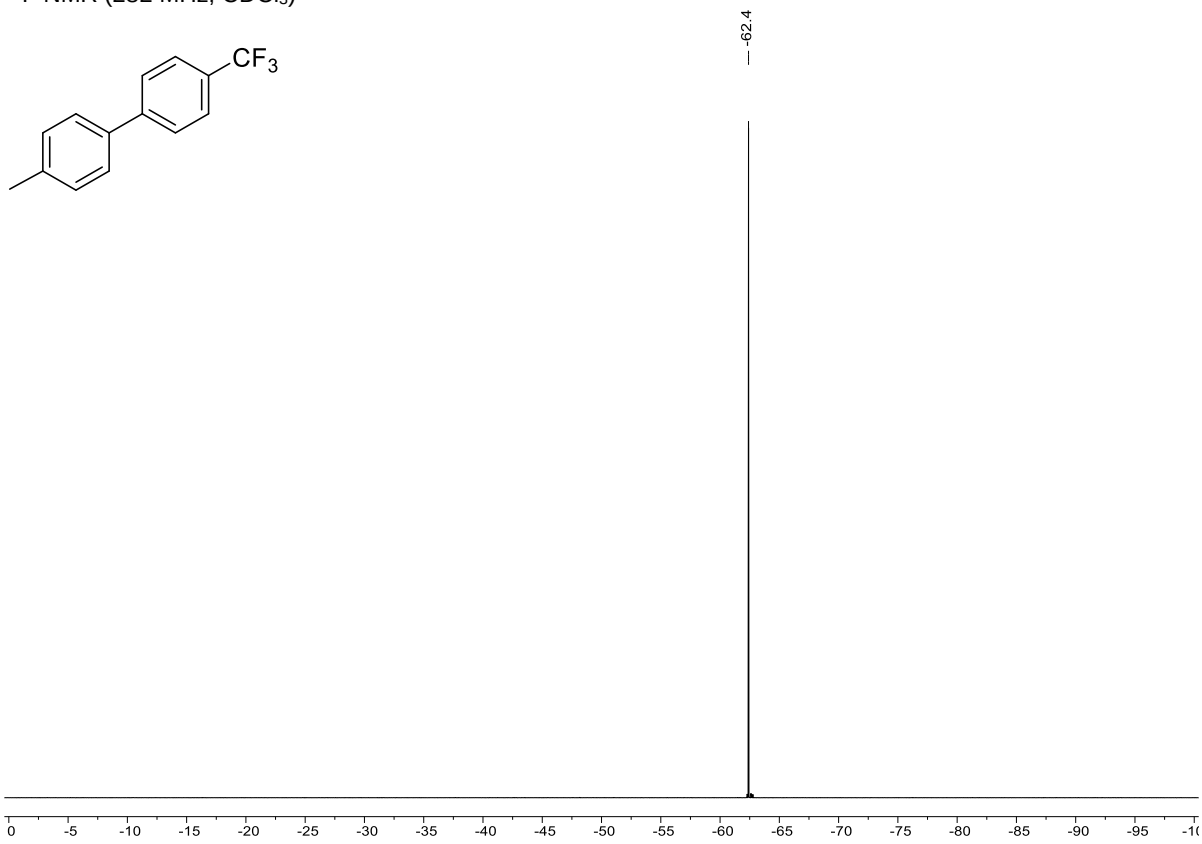
4-Methyl-4'-(trifluoromethyl)-1,1'-biphenyl (SP2)

^{13}C NMR (151 MHz, $CDCl_3$)



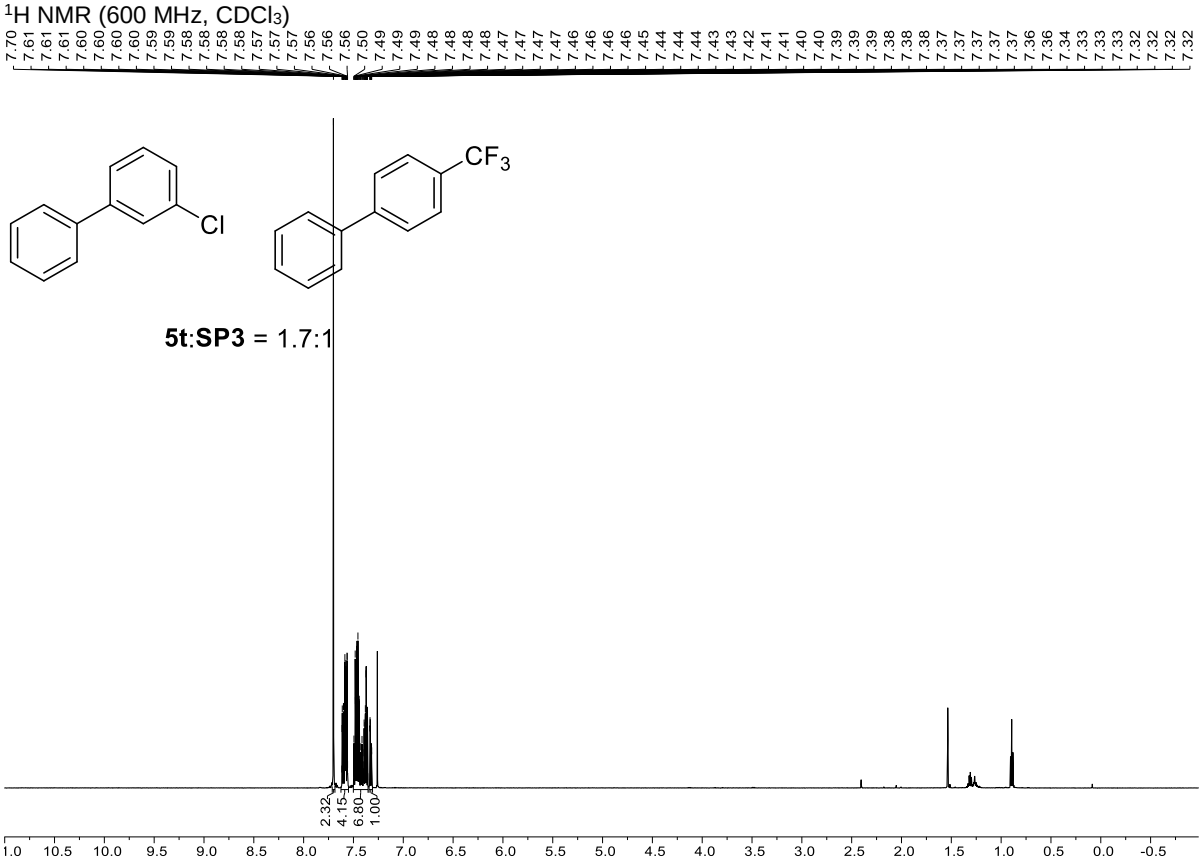
4-Methyl-4'-(trifluoromethyl)-1,1'-biphenyl (SP2)

^{19}F NMR (282 MHz, $CDCl_3$)



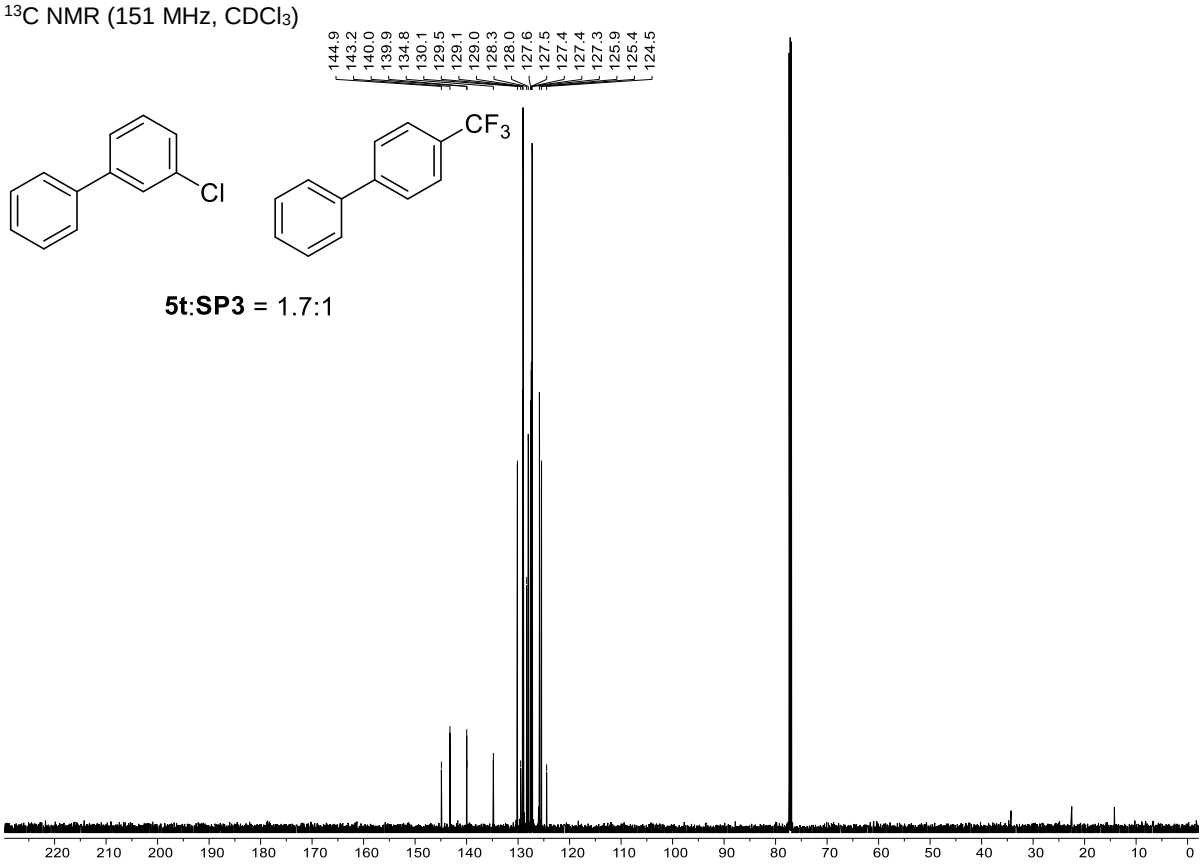
3-Chloro-1,1'-biphenyl (5u) and 4-(Trifluoromethyl)-1,1'-biphenyl (SP3)

^{1}H NMR (600 MHz, $CDCl_3$)



3-Chloro-1,1'-biphenyl (5u) and **4-(Trifluoromethyl)-1,1'-biphenyl (SP3)**

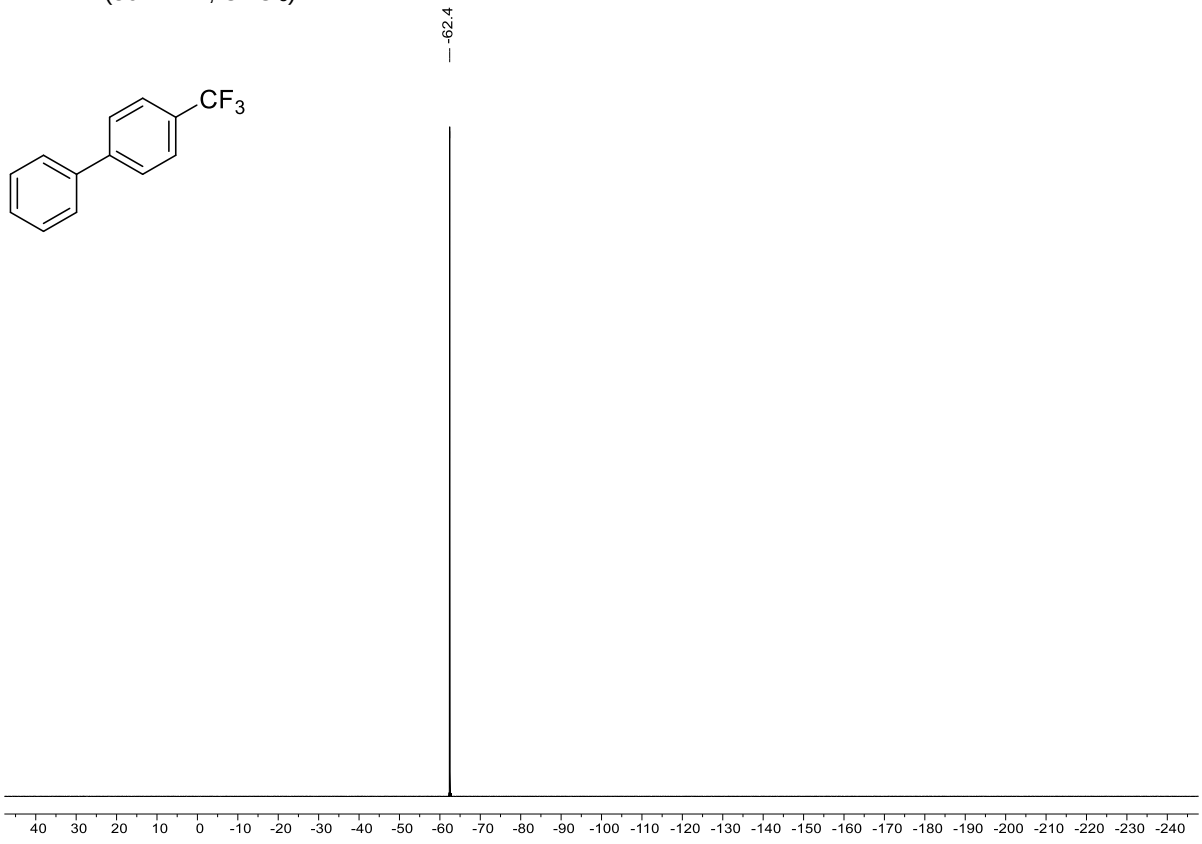
^{13}C NMR (151 MHz, $CDCl_3$)



5t:**SP3** = 1.7:1

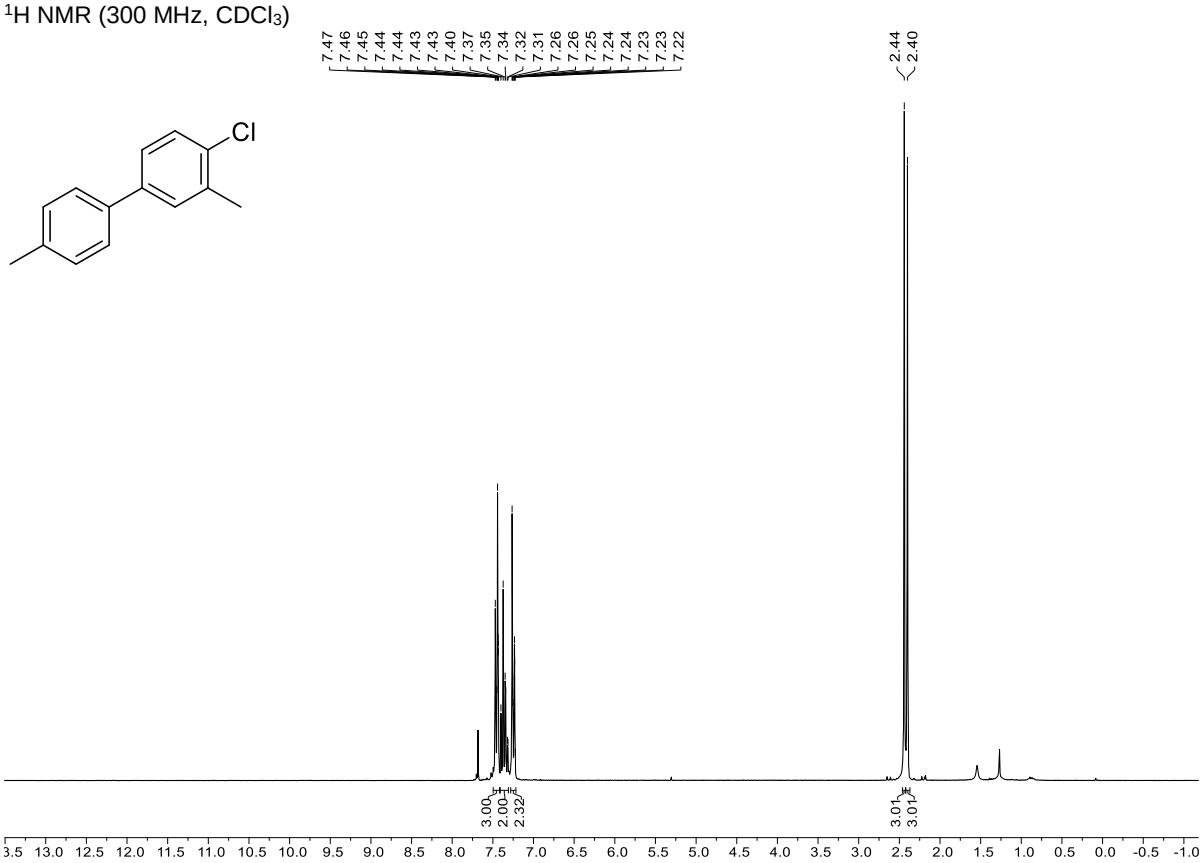
4-(Trifluoromethyl)-1,1'-biphenyl (SP3)

^{19}F NMR (564 MHz, $CDCl_3$)



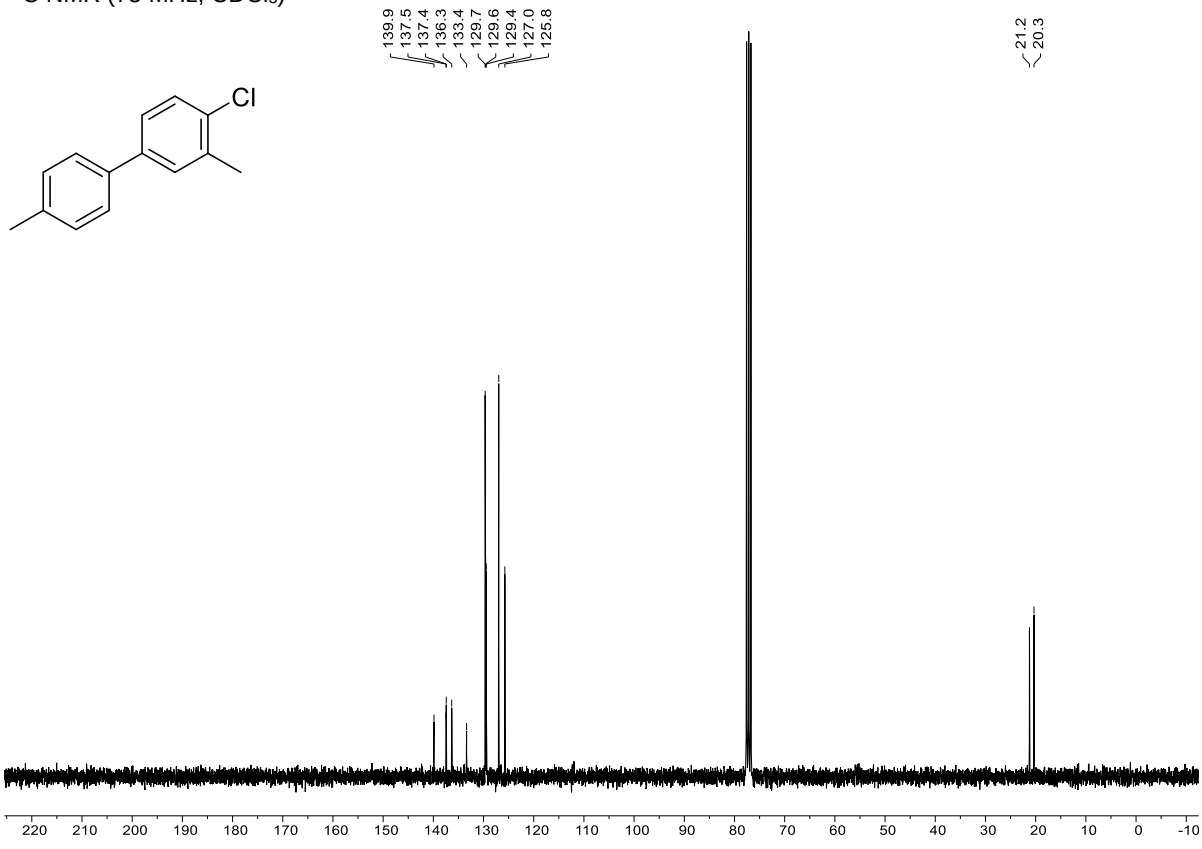
4-Chloro-3,4'-dimethyl-1,1'-biphenyl (5v)

^{1}H NMR (300 MHz, $CDCl_3$)



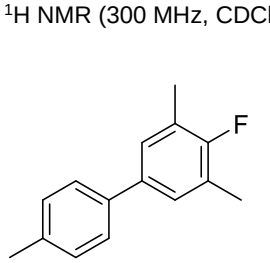
4-Chloro-3,4'-dimethyl-1,1'-biphenyl (5v)

^{13}C NMR (75 MHz, $CDCl_3$)



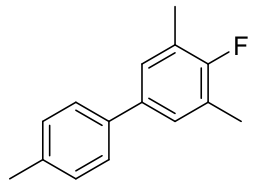
4-Fluoro-3,4',5-trimethyl-1,1'-biphenyl (5w)

^{1}H NMR (300 MHz, $CDCl_3$)



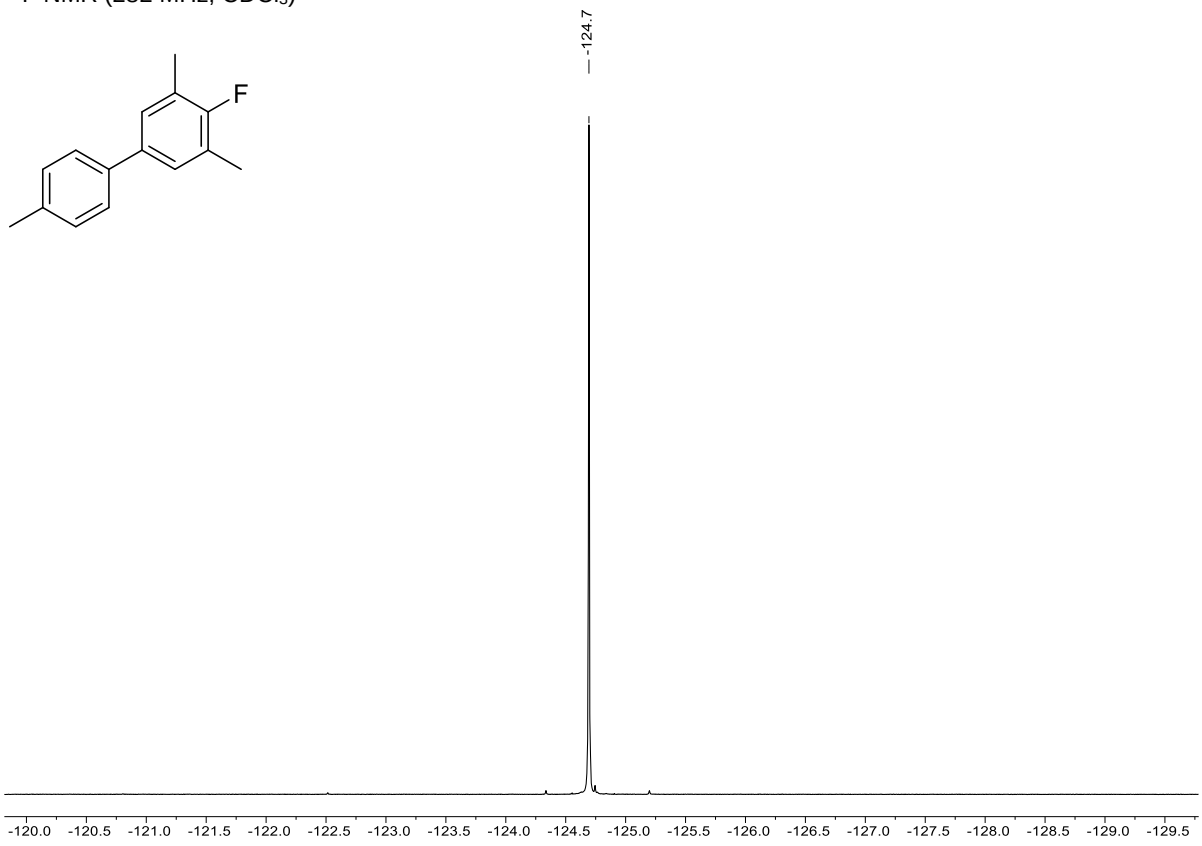
4-Fluoro-3,4',5-trimethyl-1,1'-biphenyl (5w)

^{13}C NMR (75 MHz, $CDCl_3$)



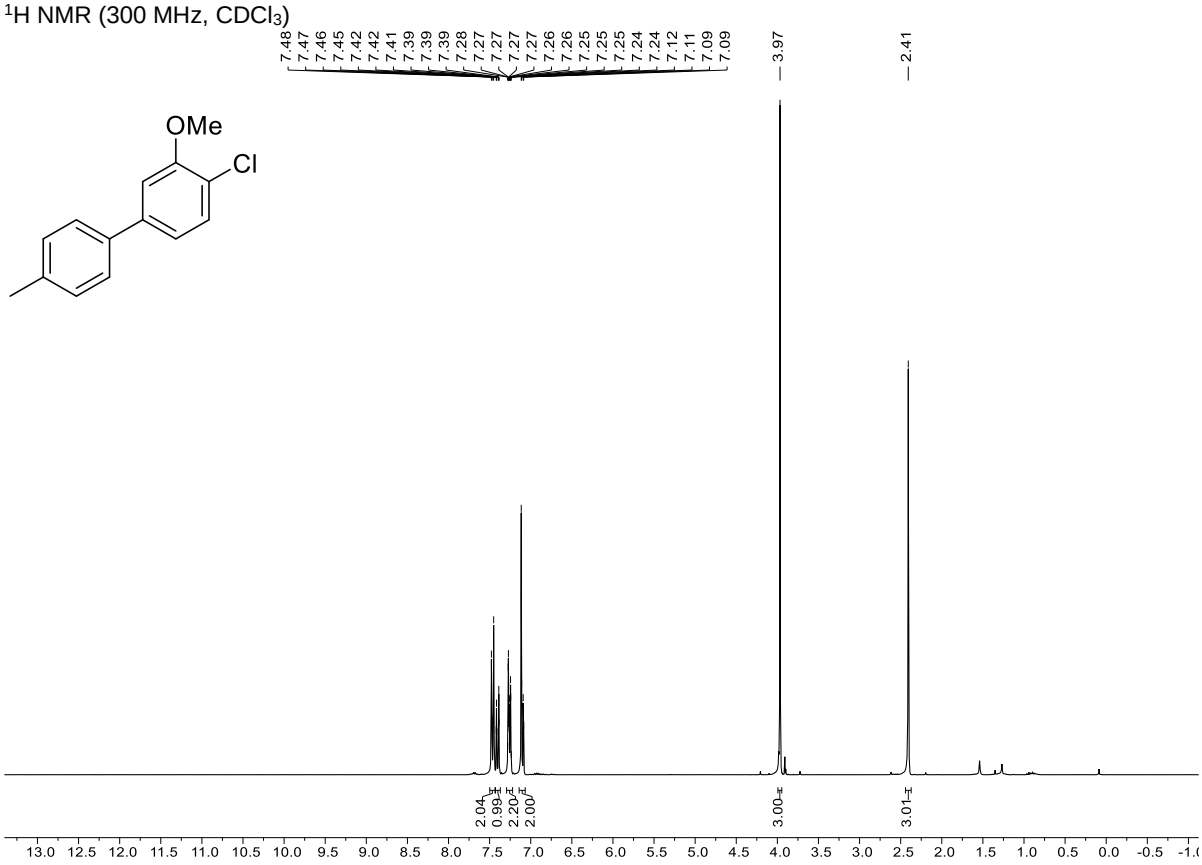
4-Fluoro-3,4',5-trimethyl-1,1'-biphenyl (5w)

^{19}F NMR (282 MHz, $CDCl_3$)



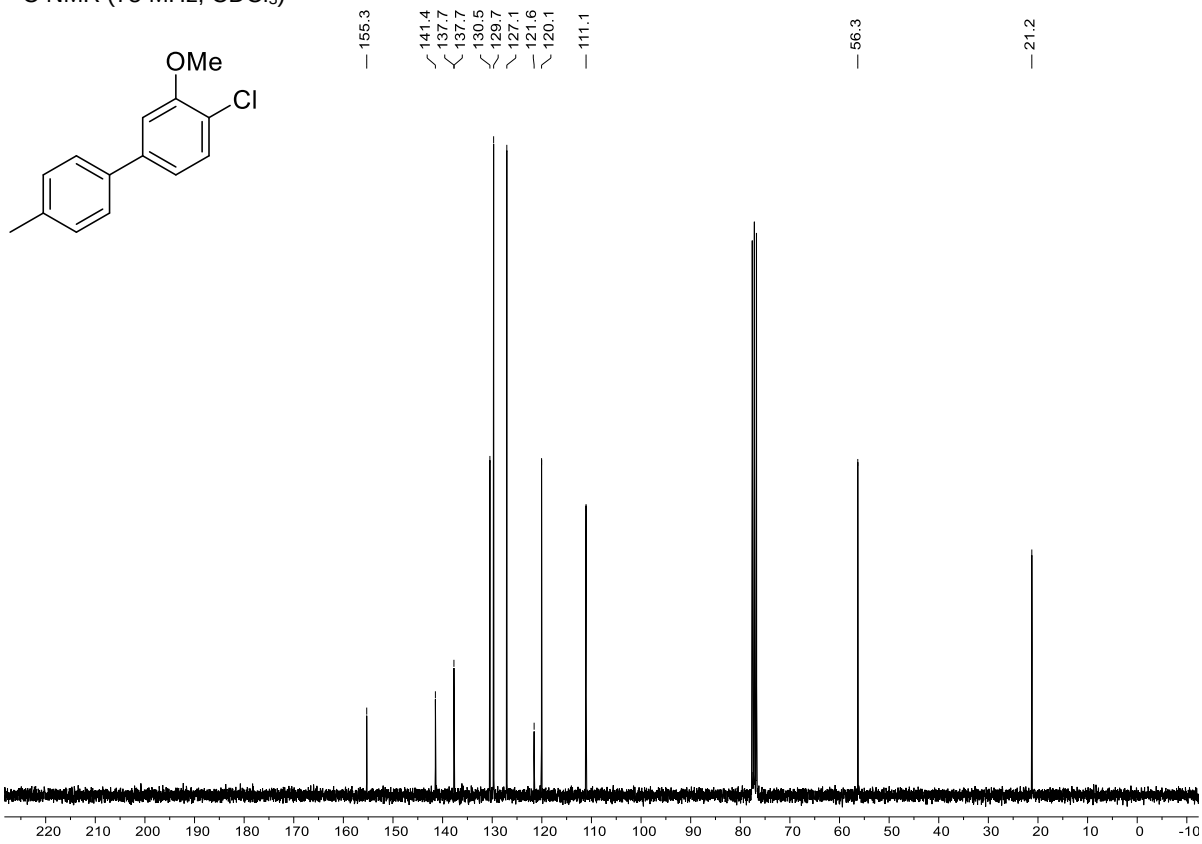
4-Chloro-3-methoxy-4'-methyl-1,1'-biphenyl (5x)

^{1}H NMR (300 MHz, $CDCl_3$)



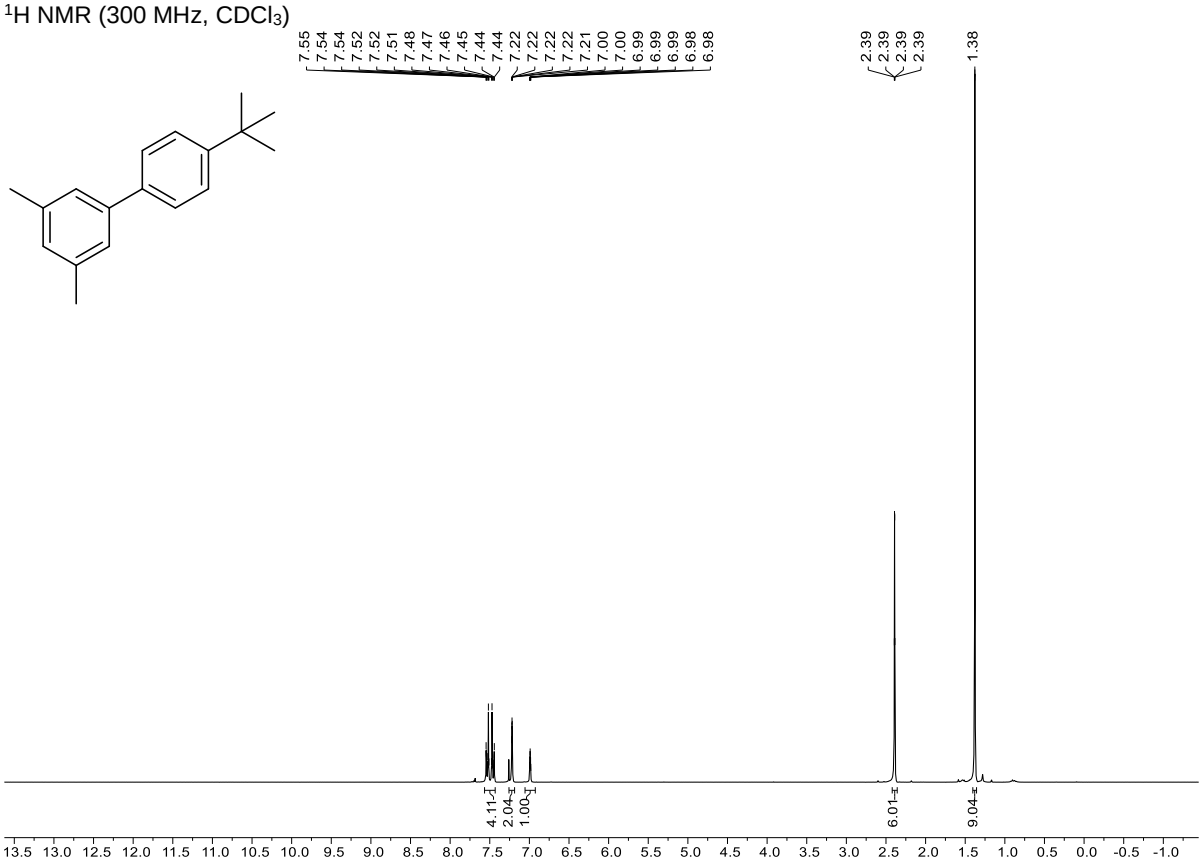
4-Chloro-3-methoxy-4'-methyl-1,1'-biphenyl (5x)

^{13}C NMR (75 MHz, $CDCl_3$)



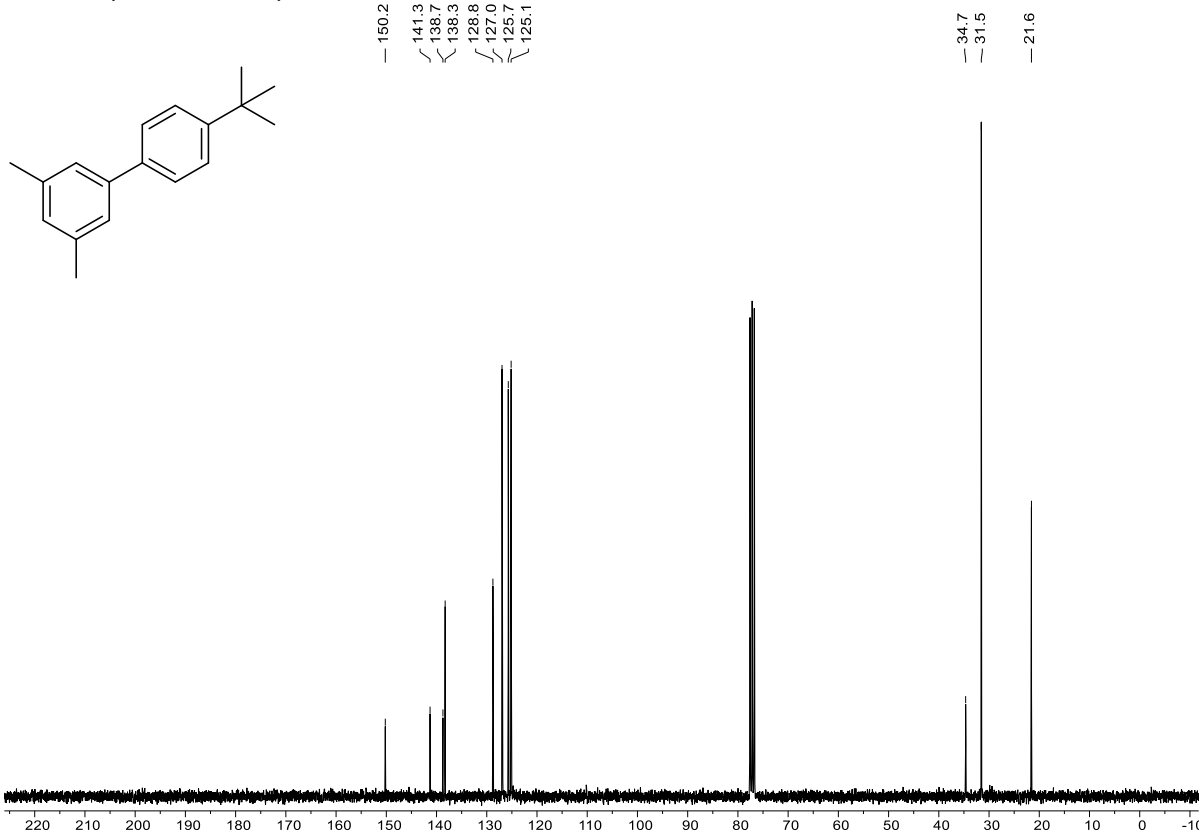
4'-(*Tert*-butyl)-3,5-dimethyl-1,1'-biphenyl (5y)

^{1}H NMR (300 MHz, $CDCl_3$)



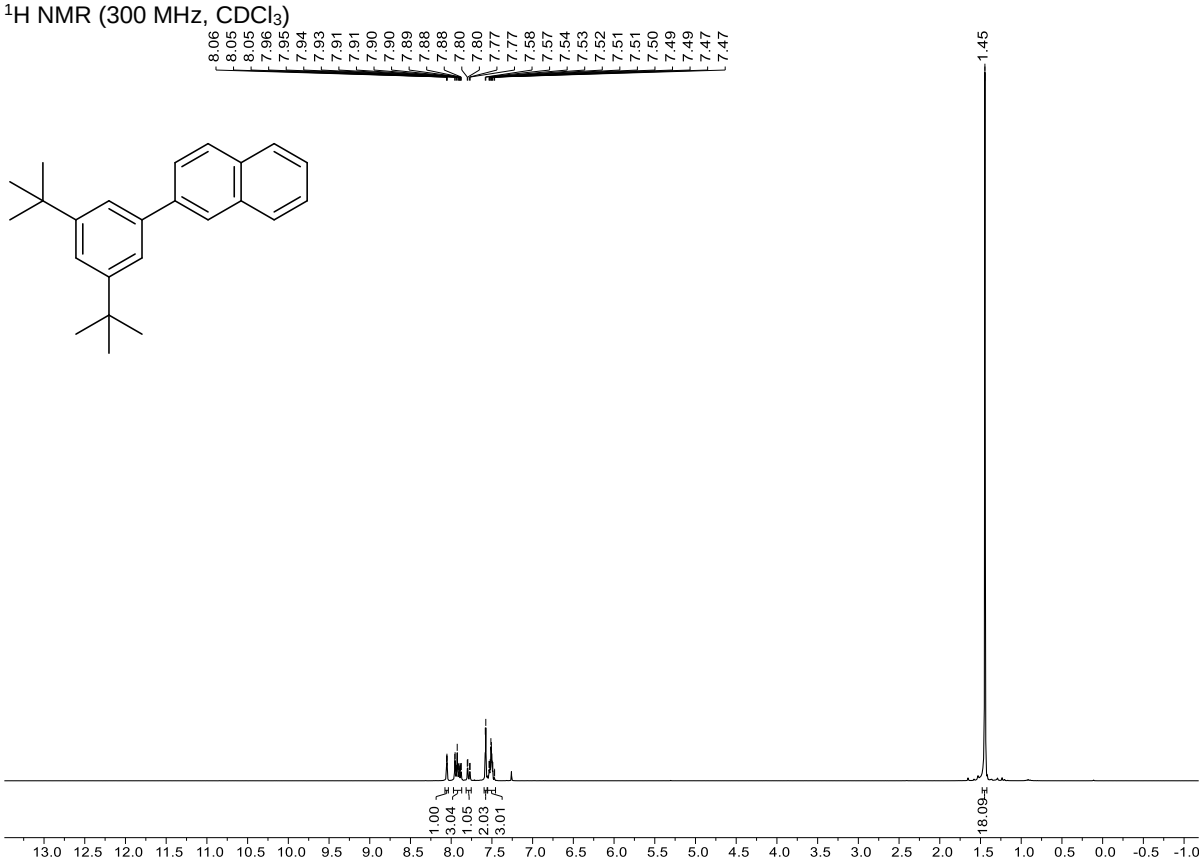
4'-(*Tert*-butyl)-3,5-dimethyl-1,1'-biphenyl (5y)

^{13}C NMR (75 MHz, $CDCl_3$)



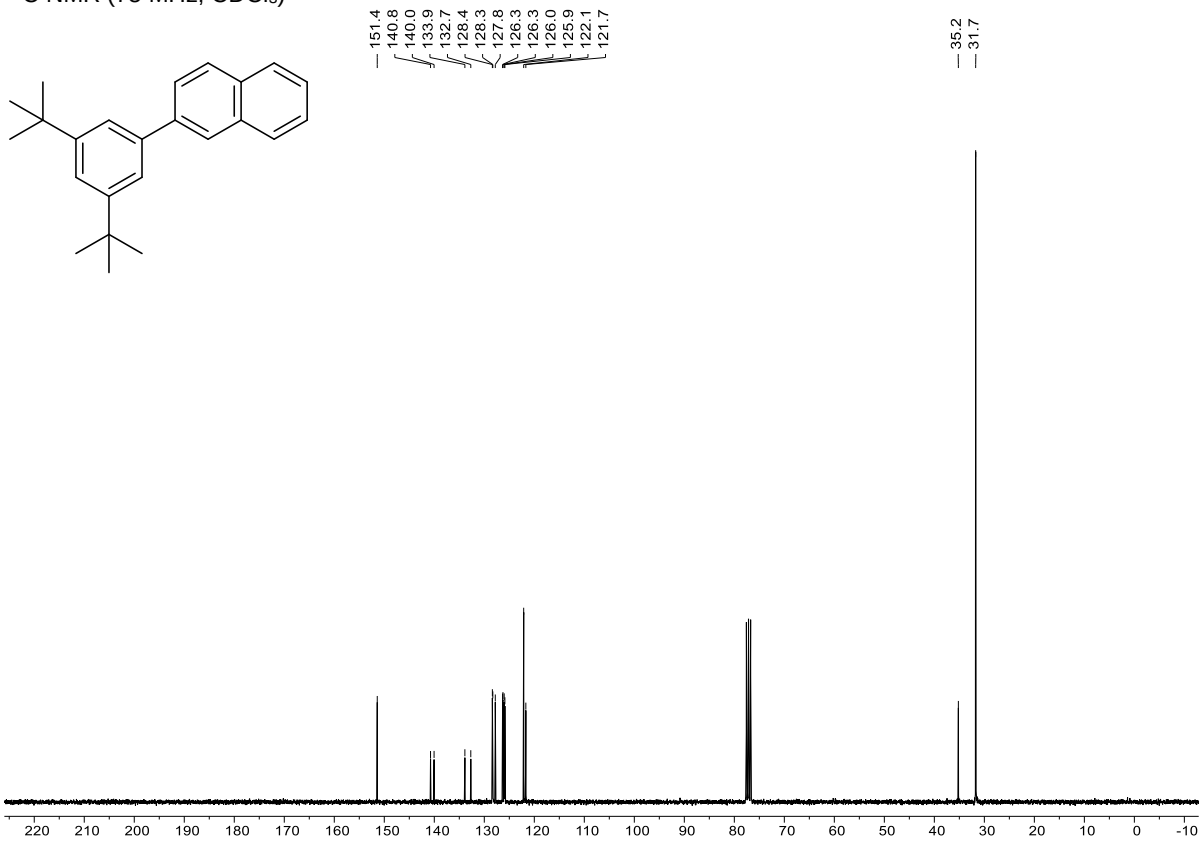
2-(3,5-Di-*tert*-butylphenyl)naphthalene (5z)

^{1}H NMR (300 MHz, $CDCl_3$)



2-(3,5-Di-*tert*-butylphenyl)naphthalene (5z)

^{13}C NMR (75 MHz, $CDCl_3$)



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