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Supporting Information

Easy Access to Polyhalogenated Biaryls: Regioselective (Di)Halogenation of hypervalent bromines and chlorines.

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1. General experimental

1.1. Materials and methods

All reactions and manipulations were conducted under inert atmosphere of argon using standard Schlenk techniques and oven-dried or flame-dried glassware, unless otherwise stated. Liquids and solutions were transferred with argon-purged syringes or cannulae. Air- and moisture-sensitive reagents were stored and handled under argon atmosphere. Anhydrous solvents were commercially supplied (THF, DMF, Me-THF, TBME, DME, anisole) or distilled prior to use and stored over molecular sieves (toluene, Et_2O, MeCN, DCM). Technical grade solvents for extraction and column chromatography (Cy, EtOAc, DCM, PE) were used without further purification. All reagents were purchased from commercial sources (Sigma Aldrich, TCI, Alfa Aesar, BLD Pharmatech, Fluorochem, Apollo scientific, ABCR) and used as received, or synthesized according to the procedures given. Reactions were cooled using acetone/dry ice baths (-30 °C to -78 °C) and heated using paraffin oil baths equipped with magnetic stirrers or DrySyn® heating blocks.

1.2. Analysis and instrumentation

Flash column chromatography purifications were carried out by hand using VWR silica gel (40-63 µm) using the indicated eluents, or by a Biotage® Isolera™ One automated system equipped with simultaneous UV-detection (254 and 280 nm) and Biotage® Sfär columns of appropriate size and loading capacity, using the indicated eluent gradients.

Thin layer chromatography (TLC) was performed on Merck® Kieselgel 60 F_{254} fluorescent treated silica on aluminium plates (0.25 mm), and visualized under 254 nm UV light irradiation, or by staining with an aqueous basic $KMnO_4$ solution, followed by heating.

Preparative layer chromatography (PLC) was performed on Merck® Kieselgel 60 F_{254} fluorescent treated silica on glass plates (20 × 20 cm). Samples were deposited as a band across the width of the plate, eluted using the indicated eluents, visualized under 254 nm UV light irradiation, and isolated by scraping and extraction of the desired band.

Tandem Gas Chromatography – Mass Spectrometry (GC-MS) analyses were carried out using an Agilent 5977E Series Mass Selective Detector (MSD) with a 7820A Gas Chromatograph (GC) system, or with an Agilent 5977B Series MSD with an 8060 GC system. Column specifications: HP5-MS-USI 30m × 0.25 mm × 0.25 µm. Injection parameters: T_{inj} = 250 °C; split = 1/50; flowrate = 1.2 mL/min; vector gas = He; V_{inj} = 1 µL. Mass detector parameters: solvent delay = 3 min; mass range = 50-650 Da; frequency = 2.5 scans/s; cycle = 406.61 ms; T_{source} = 230 °C; T_{quad} = 150 °C; electron ionisation = 70 eV. Oven parameters: 80 °C (1 min), 80-300 °C linear slope (30 °C/min), 300 °C (8 min). Blanks carried out with anthracene as internal standard.

Nuclear Magnetic Resonance (NMR) spectra were recorded at various field strengths, as indicated, using Bruker Advance III HD 400 and 500 MHz instruments for ^{1}H, ^{13}C and ^{19}F acquisitions. All NMR spectra were recorded at 25 °C, unless otherwise stated. Chemical shifts (δ) are reported in parts per million (ppm) and referred to partially deuterated chloroform ($CDCl_3$, $\delta[^{1}H]$ = 7.26 ppm, $\delta[^{13}C]$ = 77.0 ppm), DMSO (DMSO-d6, $\delta[^{1}H]$ = 2.50 ppm, $\delta[^{13}C]$ = 39.5 ppm) and benzene (C_6D_6, $\delta[^{1}H]$ = 7.16 ppm, $\delta[^{13}C]$ = 128.1 ppm). Coupling constants (*J*) are given in Hertz (Hz) and refer to apparent multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal, dd = doublet of

doublets, etc.). The ^{1}H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of protons). NMR assignments, if reported, were made using two-dimensional NMR spectroscopy (COSY, HSQC, HMBC) to assist the assignment. NMR yields were determined using dibromomethane as an internal standard.

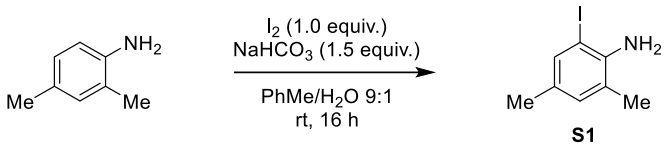
High resolution mass spectra (HRMS) were recorded on Bruker Daltonics MicrOTOF or Thermo Fisher Orbitrap mass analysers, by Electrospray Ionisation (ESI) or Atmospheric Pressure Chemical Ionisation (APCI), by the mass spectrometry facility at the University of Strasbourg.

X-Ray Diffraction (XRD) crystallographic structure analysis was performed by the radiocrystallography facility at the University of Strasbourg using a Bruker PHOTON III DUO CPAD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo K_α radiation (λ = 0.71073 Å).

2. Preparation of Starting Materials

2.1. Synthesis of non-commercial precursors

- **2-iodo-4,6-dimethylaniline (S1)**



S1

Following a literature reported procedure,[1] to a flame-dried round bottom flask were added 2,4-dimethylaniline (1.0 equiv., 9 mmol, 1.09 g), iodine (1.0 equiv., 9 mmol, 2.28 g) and $NaHCO_3$ (1.5 equiv., 13.5 mmol, 1.13 g). The solids were dissolved in a mixture of toluene (9 mL) and water (1 mL), and the mixture was stirred under argon at room temperature for 16 h.

Upon completion, the reaction was diluted with EtOAc (30 mL), the phases were separated, the organic phase was washed with sat. aq. $Na_2S_2O_3$ (2 x 20 mL), and the aqueous phase was extracted with EtOAc (2 x 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude was purified by flash column chromatography (SiO_2, Cy/DCM 3:1) to give the title compound as a light brown solid (1.84 g, 83%).

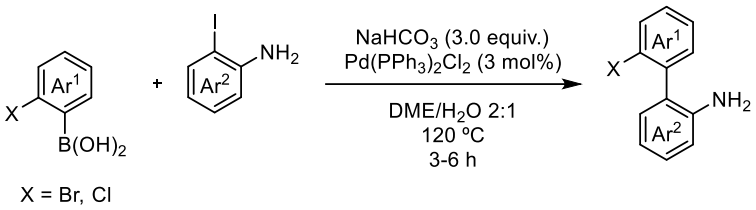
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (s, 1H), 6.84 (s, 1H), 3.92 (br, 2H), 2.20 (s, 3H), 2.18 (s, 3H).

Characterisation data is consistent with that reported in the literature.[1]

2.2. Synthesis of bromo- and chloro-biaryl anilines

2.2.1. General Procedures

General Procedure 1A



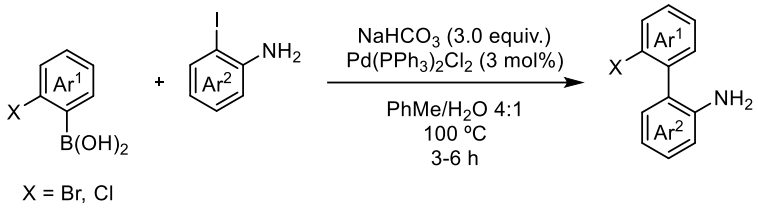
X = Br, Cl

Following a literature-reported procedure,[2] to a round bottom flask equipped with a magnetic stirrer and a reflux condenser were added 2-iodoaniline (1.0 equiv.), 2-chloro or 2-bromoarylboronic acid (1.2 equiv.), $NaHCO_3$ (3.0 equiv.) and $Pd(PPh_3)_2Cl_2$ (3 mol%). The reaction vessel was evacuated and backfilled with argon three times. Then, 1,2-dimethoxyethane, DME (0.35 M) was added and the resulting mixture was stirred at room temperature for 5 min. Then, H_2O (DME/H_2O 2:1) was added and the reaction was stirred under argon at 120 °C for 3-6 h.

Upon completion, the reaction was allowed to cool to room temperature, the mixture was filtered over a pad of Celite®, washing with EtOAc. The phases were separated, the organic phase was washed with brine, and the aqueous phase was extracted twice with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude was purified by flash column chromatography (SiO_2, Cy/EtOAc or PE/EtOAc, loaded pre-adsorbed on silica gel) to give the desired product.

Further purification to remove traces of Pd may be carried out *via* high vacuum Kugelrohr distillation (50 rpm, 150-200 °C, horizontal stirring, collection vessel cooled to -78 °C).

General Procedure 1B



Following an adapted literature-reported procedure,[2] to a flame-dried round bottom flask equipped with a magnetic stirrer and a reflux condenser were added 2-iodoaniline (1 equiv.), 2-chloro or 2-bromoarylboronic acid (1.2 equiv.), $NaHCO_3$ (3 equiv.) and $Pd(PPh_3)_2Cl_2$ (3 mol%). The reaction vessel was evacuated and backfilled with argon three times. Then, toluene (0.35 M) was added and the resulting mixture was stirred at room temperature for 5 min. Then, H_2O (toluene/H_2O 4:1) was added and the reaction was stirred under argon at 100 °C for 3-6 h.

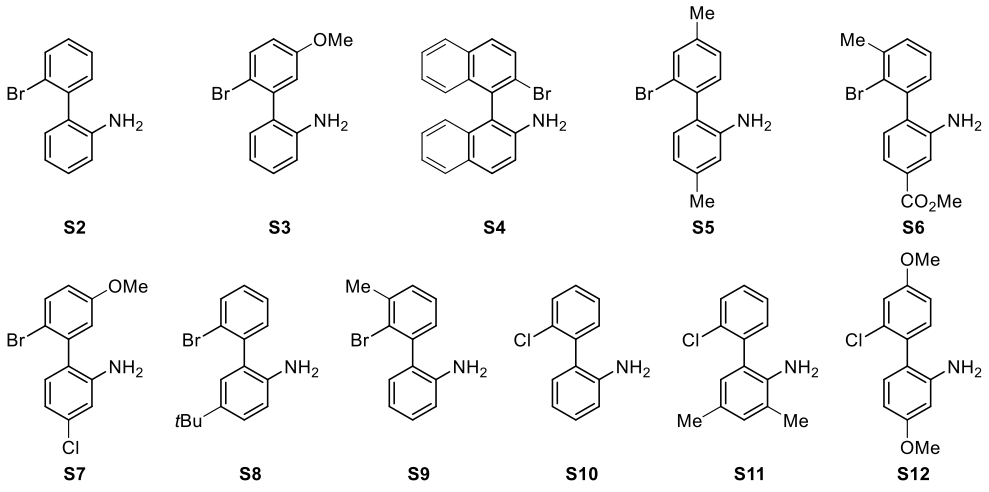
Upon completion, the reaction was allowed to cool to room temperature, the mixture was filtered over a pad of Celite®, washing with EtOAc. The phases were separated, the organic phase was washed with brine, and the aqueous phase was extracted twice with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude was purified by flash column chromatography (SiO_2, Cy/EtOAc or PE/EtOAc, loaded pre-adsorbed on silica gel) to give the desired product.

Further purification to remove traces of Pd may be carried out *via* high vacuum Kugelrohr distillation (50 rpm, 150-200 °C, horizontal stirring, collection vessel cooled to -78 °C).

2.2.2. Prepared Compounds

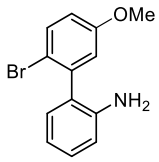
The following bromo- and chloro-biaryl anilines were prepared according to literature known or adapted procedures and were stored at 4 °C.

Figure S1: Bromo- and chloro-biaryl aniline precursors used in the manuscript.



- Biaryl anilines **S2**,[2] **S5-S9**,[2] and **S10**[3] were synthesized according to literature procedure **GP-1A**.

- **2'-bromo-5'-methoxy-[1,1'-biphenyl]-2-amine (S3)**

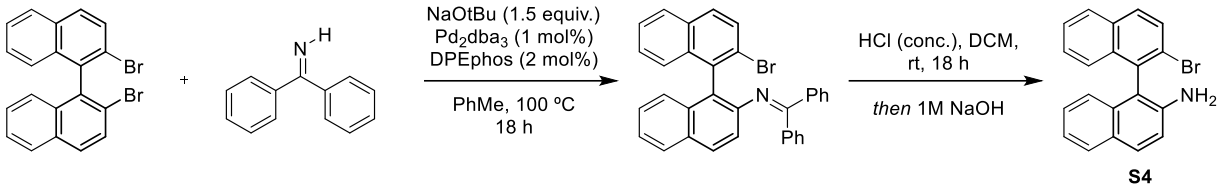


Following **GP-1B** using 2-iodoaniline (1.50 mmol, 329 mg) and (2-bromo-5-methoxyphenyl)boronic acid, reaction time: 3 h. Purification by flash column chromatography (Cy/EtOAc 4:1) yielded the title compound as a brown oil (338 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 8.8 Hz, 1H), 7.21 (ddd, *J* = 8.0, 7.4, 1.6 Hz, 1H), 7.03 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.88 (d, *J* = 3.1 Hz, 1H), 6.86 – 6.74 (m, 3H), 3.80 (s, 3H), 3.57 (br, 2H).

Characterisation data is consistent with that reported in the literature.[3]

- **2'-bromo-[1,1'-binaphthalen]-2-amine (S4)**



S4

Following a literature-reported procedure,[4] to a flame-dried round bottom flask equipped with a magnetic stirrer and a reflux condenser were added 2,2'-dibromo-1,1'-binapthalene (1.0 equiv., 4.85 mmol, 2.00 g), benzophenone imine (1.3 equiv., 6.31 mmol, 1.06 mL), NaO*t*Bu (1.5 equiv., 7.28 mmol, 700 mg), Pd_2dba_3 (1 mol%, 0.05 mmol, 39 mg) and bis[(2-diphenylphosphino)phenyl] ether, DPEphos (2 mol%, 0.10 mmol, 52 mg). The reaction vessel was evacuated and backfilled with argon three times. Toluene (20 mL) was added and the resulting mixture was stirred under argon at 100 °C for 18 h.

After cooling to room temperature, two-thirds of the solvent was removed under reduced pressure. Upon adding EtOH (25 mL) and water (3 mL), yellow crystals of the benzophenone imine biaryl adduct were formed. They were collected by Büchner filtration, washing with small volumes of cold EtOH, to be used in the subsequent hydrolysis step without further purification.

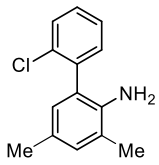
The collected crude imine adduct was suspended in DCM (100 mL) in a round bottom flask. Concentrated 37% HCl (3.0 equiv., 14.56 mmol, 1.21 mL) was added dropwise while stirring, and the suspension became homogeneous within 15 min. After stirring for a further 18 h at room temperature, the hydrochloride salt of product **S4** precipitated and was thus treated with 1 M NaOH (25 mL).

The neutralized and solubilized crude product was poured in a separating funnel, and the phases were separated. The organic phase was washed with brine, and the aqueous phase was extracted twice with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude was purified by flash column chromatography (SiO_2, PE/EA 10-30% gradient, loaded pre-adsorbed on silica gel) to give the title compound as white crystals (1.06 g, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 – 7.90 (m, 1H), 7.87 – 7.82 (m, 3H), 7.82 – 7.79 (m, 1H), 7.51 (ddd, *J* = 8.2, 5.9, 2.1 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.25 – 7.16 (m, 2H), 7.14 (dd, *J* = 8.8, 1.9 Hz, 1H), 6.91 – 6.85 (m, 1H), 3.57 (br, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 141.5, 134.6, 133.8, 133.3, 132.9, 130.5, 129.7, 129.7, 128.3, 128.1, 128.0, 127.5, 126.8, 126.5, 126.2, 124.0, 123.7, 122.5, 118.2, 116.6. **HRMS** (ESI) m/z: Calcd. for $C_{20}H_{15}BrN$ ($[M+H]^+$) 348.0382; found 348.0379.

The ^{1}H NMR spectrum of the title compound was also measured in C_6D_6, which resulted in an improved resolution and integration of the peaks: **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.71 – 7.66 (m, 2H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.57 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.14 – 7.00 (m, 4H), 6.92 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 1H), 6.68 (d, *J* = 8.7 Hz, 1H), 2.92 (br, 2H). *See NMR spectra*.

- **2'-chloro-3,5-dimethyl-[1,1'-biphenyl]-2-amine (S11)**

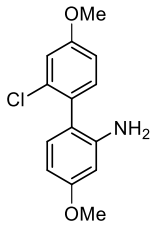


Following **GP-1B** using 2-iodo-4,6-dimethylaniline **S1** (1.30 mmol, 321 mg) and (2-chlorophenyl)boronic acid, reaction time: 4 h. Purification by flash column chromatography (Cy/EtOAc 5-20% gradient) yielded the title compound as a yellow oil, (152 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 – 7.47 (m, 1H), 7.38 – 7.27 (m, 3H), 6.96 (s, 1H), 6.76 (s, 1H), 3.38 (br, 2H), 2.27 (s, 3H), 2.22 (s, 3H).

Characterisation data is consistent with that reported in the literature.[5]

- **2'-chloro-4,4'-dimethoxy-[1,1'-biphenyl]-2-amine (S12)**

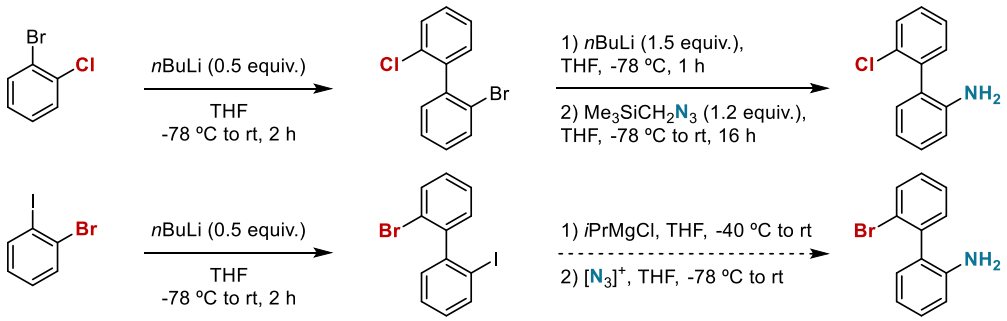


Following **GP-1A** using 2-bromo-5-methoxyaniline[a] (3.0 mmol, 671 mg) and (2-chloro-4-methoxyphenyl)boronic acid, reaction time: 3 h. Purification by flash column chromatography (Cy/EtOAc 5-35% gradient) yielded the title compound as a brown oil, (722 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23 (d, *J* = 8.5 Hz, 1H), 7.04 (d, *J* = 2.6 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.88 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.40 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.33 (d, *J* = 2.5 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 3.57 (br, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 160.5, 159.7, 145.4, 135.0, 132.9, 131.8, 129.9, 118.2, 115.2, 113.5, 104.1, 101.0, 55.7, 55.3. **HRMS** (ESI) m/z: Calcd. for $C_{14}H_{15}ClNO_2$ ([M+H]$^+$) 264.0786; found 264.0779. *See NMR spectra*.

2.2.3. Transition metal free alternative procedure

Alternative literature-reported, transition metal free strategies towards the synthes of chloro-biaryl aniline precursors can also be carried out. This route involves an initial aryne coupling step,[6] followed by lithium-bromine exchange and trapping with a masked amine electrophile.[3] A similar strategy to prepare analogous bromo-biaryl anilines can likewise be envisaged, as summarized in the scheme below.

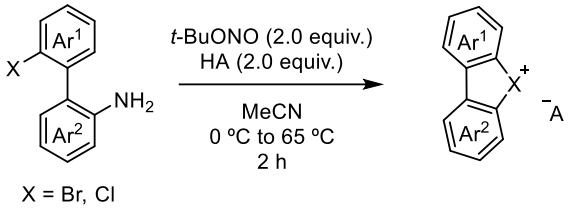


[a] In the case of the synthesis of chloro biaryl anilines, 2-bromoanilines may be used as substrates instead of 2-iodoanilines.

2.3. Synthesis of cyclic biaryl hypervalent Br(III) and Cl(III) compounds

2.3.1. General Procedures

General Procedure 2



X = Br, Cl

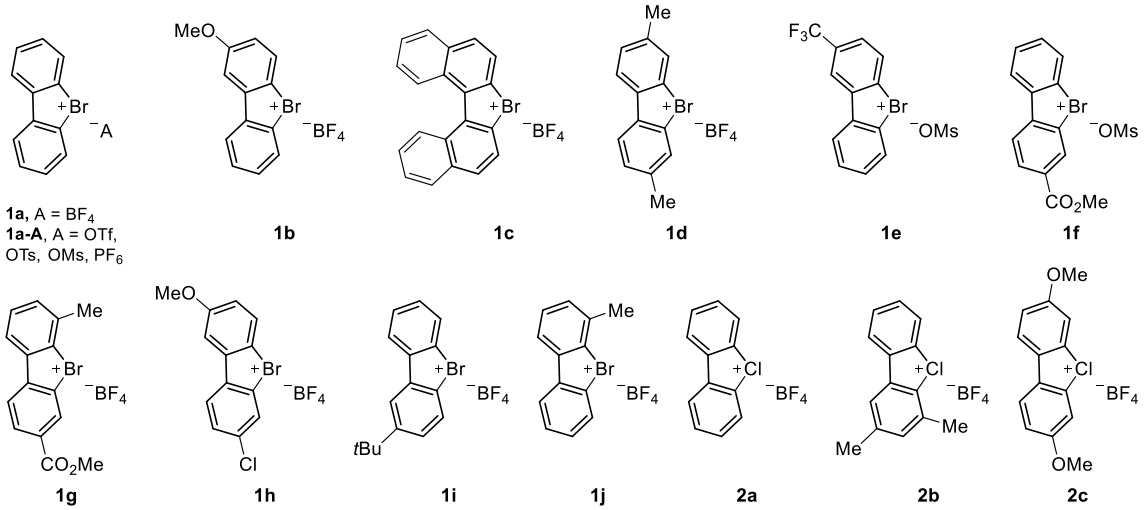
Following a literature reported procedure,[2] to a flame-dried two-necked round bottom flask equipped with a magnetic stirrer was added the bromo or chloro biaryl aniline (1.0 equiv.), and the vessel was evacuated and backfilled with argon three times. MeCN (0.1 M) was added and the solution was cooled to 0 °C in an ice/water bath. Then, *t*-BuONO (2.0 equiv.) and the selected acid HA (2.0 equiv.) were added dropwise, the resulting mixture was stirred at 0 °C for 1 h, and then heated to 65 °C for 1 h.

After cooling to room temperature, the reaction was poured slowly into cold Et_2O (3 × V_{MeCN}) stirred gently at 0 °C for 1-2 min until full formation of a precipitate is observed.[b] The filtrate was decanted, the solid was isolated by Büchner filtration and washed with small quantities of cold Et_2O. The solid was finally dried under vacuum to afford the desired product without further purification.

2.3.2. Prepared Compounds

The following cyclic biaryl hypervalent Br(III) and Cl(III) compounds were prepared according to literature known procedures and were stored at 4 °C.

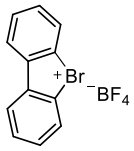
Figure S2: Hypervalent Br(III) and Cl(III) compounds used in the manuscript.



- Hypervalent compounds **1a**,[2] **1a-OTf**,[2] **1a-OTs**,[2] **1a-OMs**,[2] **1a-PF_6**,[2] **1e**,[2] **1f**[2] and **2a**[3] were synthesized according to literature procedure **GP-2**.

[b] If precipitation does not work with the substrate, remove the solvent and add cold Et_2O gradually until a precipitate forms. If that still is ineffective, try storing the mixture in the freezer overnight. If none of these methods work, the reaction likely failed.

- **dibenzo[*b,d*]bromol-5-ium tetrafluoroborate (1a)**

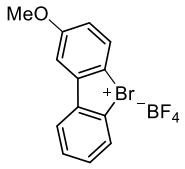


Following **GP-2** using 2'-bromo-[1,1'-biphenyl]-2-amine **S2** (4.37 mmol, 1.09 g) and HBF_4 (48% aq. soln.), the title compound was isolated as a fluffy white solid (944 mg, 68%).

^{1}H NMR (400 MHz, DMSO-d6) δ: 8.60 (dd, *J* = 7.8, 1.6 Hz, 2H), 8.48 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.95 (td, *J* = 7.5, 1.0 Hz, 2H), 7.85 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 2H).

Characterisation data is consistent with that reported in the literature.[2]

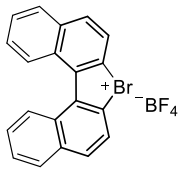
- **2-methoxydibenzo[*b,d*]bromol-5-ium tetrafluoroborate (1b)**



Following **GP-2** using 2'-bromo-5'-methoxy-[1,1'-biphenyl]-2-amine **S3** (2.36 mmol, 656 mg) and HBF_4 (48% aq. soln.), the title compound was isolated as a yellow powder (506 mg, 61%).

^{1}H NMR (400 MHz, DMSO-d6) δ: 8.64 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.45 (dd, *J* = 8.5, 1.0 Hz, 1H), 8.31 (d, *J* = 9.4 Hz, 1H), 8.15 (d, *J* = 2.9 Hz, 1H), 7.94 (td, *J* = 7.5, 1.0 Hz, 1H), 7.84 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 1H), 7.41 (dd, *J* = 9.4, 2.9 Hz, 1H), 3.96 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d6) δ: 161.6, 137.0, 136.8, 135.3, 131.9, 131.1, 126.9, 126.6, 126.2, 125.6, 118.8, 110.4, 56.4. **^{19}F NMR** (377 MHz, DMSO-d6) δ: -148.22 (s), -148.28 (s). **HRMS** (ESI) m/z: Calcd. for $C_{13}H_{10}BrO$ ($[M\text{-}BF_4]^+$) 260.9910; found 260.9924. *See NMR spectra*.

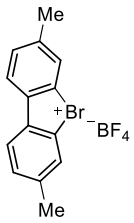
- **dinaphtho[2,1-*b*:1',2'-*d*]bromol-7-ium tetrafluoroborate (1c)**



Following **GP-2** using 2'-bromo-[1,1'-binaphthalen]-2-amine **S4** (2.30 mmol, 800 mg) and HBF_4 (48% aq. soln.), the title compound was isolated as a yellow powder (155 mg, 16%).

^{1}H NMR (400 MHz, DMSO-d6) δ: 8.61 (dd, *J* = 9.2, 1.1 Hz, 2H), 8.51 (d, *J* = 9.5 Hz, 2H), 8.47 (d, *J* = 8.4 Hz, 2H), 8.34 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.88 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 2H), 7.80 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 2H). **^{13}C NMR** (101 MHz, DMSO-d6) δ: 137.0, 134.1, 132.6, 132.3, 130.0, 129.3, 128.5, 127.2, 126.8, 120.8. **^{19}F NMR** (377 MHz, DMSO-d6) δ: -148.18 (s), -148.24 (s). **HRMS** (ESI) m/z: Calcd. for $C_{20}H_{12}Br$ ($[M\text{-}BF_4]^+$) 331.0117; found 331.0105. *See NMR spectra*.

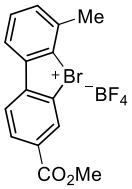
- **3,7-dimethyldibenzo[*b,d*]bromol-5-ium tetrafluoroborate (1d)**



Following **GP-2**, using 2'-bromo-4,4'-dimethyl-[1,1'-biphenyl]-2-amine **S5** (1.14 mmol, 316 mg) and HBF_4 (48% aq. soln.), the title compound was isolated as a light brown powder (268 mg, 67%).

^{1}H NMR (400 MHz, DMSO-d6) δ: 8.42 (d, *J* = 8.0 Hz, 2H), 8.24 (s, 2H), 7.75 (d, *J* = 7.9 Hz, 2H), 2.54 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d6) δ: 142.1, 136.5, 132.7, 132.1, 125.5, 125.2, 21.4. **^{19}F NMR** (377 MHz, DMSO-d6) δ: -148.23 (s), -148.29 (s). **HRMS** (ESI) m/z: Calcd. for $C_{14}H_{12}Br$ ($[M\text{-}BF_4]^+$) 259.0117; found 259.0117. *See NMR spectra*.

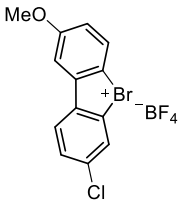
- **3-(methoxycarbonyl)-6-methyldibenzo[*b,d*]bromol-5-ium tetrafluoroborate (1g)**



Following **GP-2**, using methyl 2-amino-2'-bromo-3'-methyl-[1,1'-biphenyl]-4-carboxylate **S6** (0.62 mmol, 200 mg) and HBF_4 (48% aq. soln.), the title compound was isolated as a white powder (186 mg, 76%).

^{1}H NMR (400 MHz, DMSO-d6) δ: 9.25 (d, *J* = 1.4 Hz, 1H), 8.74 (d, *J* = 8.2 Hz, 1H), 8.53 (d, *J* = 7.8 Hz, 1H), 8.47 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.93 (t, *J* = 7.6 Hz, 1H), 7.80 (ddd, *J* = 7.5, 1.6, 0.9 Hz, 1H), 3.98 (s, 3H), 2.79 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d6) δ: 164.2, 140.0, 139.8, 137.3, 134.8, 134.2, 133.8, 132.2, 131.9, 131.8, 127.0, 126.9, 125.0, 53.1, 21.4. **^{19}F NMR** (377 MHz, DMSO-d6) δ: -148.22 (s), -148.28 (s). **HRMS** (ESI) m/z: Calcd. for $C_{15}H_{12}BrO_2$ ([M-BF_4]$^+$) 303.0015; found 303.0013. *See NMR spectra*.

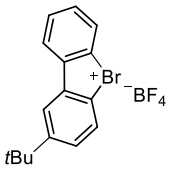
- **7-chloro-2-methoxydibenzo[*b,d*]bromol-5-ium tetrafluoroborate (1h)**



Following **GP-2**, using 2'-bromo-4-chloro-5'-methoxy-[1,1'-biphenyl]-2-amine **S7** (0.64 mmol, 200 mg) and HBF_4 (48% aq. soln.), the title compound was isolated as a brown powder (124 mg, 51%).

^{1}H NMR (400 MHz, DMSO-d6) δ: 8.68 (d, *J* = 8.5 Hz, 1H), 8.52 (d, *J* = 1.9 Hz, 1H), 8.30 (d, *J* = 9.5 Hz, 1H), 8.20 (d, *J* = 2.9 Hz, 1H), 8.09 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.44 (dd, *J* = 9.5, 2.9 Hz, 1H), 3.96 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d6) δ: 161.7, 136.5, 135.9, 134.9, 134.6, 131.6, 127.6, 127.4, 126.2, 125.3, 119.1, 110.6, 56.5. **^{19}F NMR** (377 MHz, DMSO-d6) δ: -148.22 (s), -148.28 (s). **HRMS** (ESI) m/z: Calcd. for $C_{13}H_9BrClO$ ([M-BF_4]$^+$) 294.9520; found 294.9548. *See NMR spectra*.

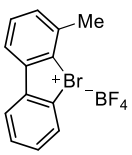
- **2-(*tert*-butyl)dibenzo[*b,d*]bromol-5-ium tetrafluoroborate (1i)**



Following **GP-2**, using 2'-bromo-5-(*tert*-butyl)-[1,1'-biphenyl]-2-amine **S8** (2.15 mmol, 655 mg) and HBF_4 (48% aq. soln.), the title compound was isolated as a fluffy white solid (190 mg, 24%).

^{1}H NMR (400 MHz, DMSO-d6) δ: 8.75 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.58 (d, *J* = 2.3 Hz, 1H), 8.46 (dd, *J* = 8.6, 1.0 Hz, 1H), 8.37 (d, *J* = 9.1 Hz, 1H), 7.97 – 7.92 (m, 1H), 7.90 (dd, *J* = 9.1, 2.3 Hz, 1H), 7.83 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 1H), 1.42 (s, 9H). **^{13}C NMR APT** (126 MHz, DMSO-d6) δ: 154.7, 136.8, 135.5, 135.1, 133.7, 131.7, 131.0, 129.3, 126.6, 125.5, 125.0, 123.3, 35.3, 31.0. **^{19}F NMR** (377 MHz, DMSO-d6) δ: -148.23 (s), -148.29 (s). **HRMS** (ESI) m/z: Calcd. for $C_{16}H_{16}Br$ ([M-BF_4]$^+$) 287.0430; found 287.0426. *See NMR spectra*.

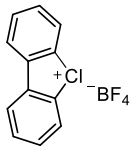
- **4-methyldibenzo[*b,d*]bromol-5-ium tetrafluoroborate (1j)**



Following **GP-2**, using 2'-bromo-3'-methyl-[1,1'-biphenyl]-2-amine **S9** (0.76 mmol, 200 mg) and HBF_4 (48% aq. soln.), the title compound was isolated as a beige powder (145 mg, 57%).

^{1}H NMR (400 MHz, DMSO-d6) δ: 8.64 – 8.58 (m, 2H), 8.44 (ddd, *J* = 7.7, 1.5, 0.7 Hz, 1H), 7.98 (td, *J* = 7.5, 1.0 Hz, 1H), 7.91 – 7.84 (m, 2H), 7.73 (ddd, *J* = 7.4, 1.6, 0.9 Hz, 1H), 2.76 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d6) δ: 138.5, 137.6, 135.8, 135.1, 134.5, 132.6, 132.2, 131.6, 131.5, 127.1, 125.8, 124.0, 21.4. **^{19}F NMR** (377 MHz, DMSO-d6) δ: -148.19 (s), -148.25 (s). **HRMS** (ESI) m/z: Calcd. for $C_{13}H_{10}Br$ ([M-BF_4]$^+$) 244.9960; found 244.9958. *See NMR spectra*.

- **dibenzo[*b,d*]chlorol-5-ium tetrafluoroborate (2a)**

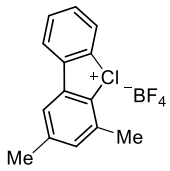


Following **GP-2**, using 2'-chloro-[1,1'-biphenyl]-2-amine **S10** (6.51 mmol, 1.33 g) and HBF_4 (48% aq. soln.), the title compound was isolated as a fluffy white solid (946 mg, 53%).

^{1}H NMR (400 MHz, DMSO-d6) δ: 8.67 (ddd, *J* = 8.5, 2.9, 1.4 Hz, 4H), 8.01 (td, *J* = 7.5, 1.1 Hz, 2H), 7.95 (ddd, *J* = 8.9, 7.3, 1.7 Hz, 2H).

Characterisation data is consistent with that reported in the literature.[3]

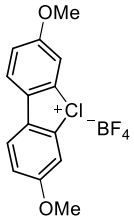
- **2,4-dimethyldibenzo[*b,d*]chlorol-5-ium tetrafluoroborate (2b)**



Following **GP-2**, using 2'-chloro-3,5-dimethyl-[1,1'-biphenyl]-2-amine **S11** (5.6 mmol, 1.30 g) and HBF_4 (48% aq. soln.), the title compound was isolated as a fluffy white solid (1.09 g, 64%).

^{1}H NMR (400 MHz, DMSO-d6) δ: 8.68 – 8.60 (m, 2H), 8.36 (d, *J* = 2.0 Hz, 1H), 8.03 (td, *J* = 7.5, 1.1 Hz, 1H), 7.96 (ddd, *J* = 8.9, 7.3, 1.7 Hz, 1H), 7.67 (dt, *J* = 1.8, 0.9 Hz, 1H), 2.70 (s, 3H), 2.54 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d6) δ: 142.6, 140.4, 137.7, 133.7, 132.4, 132.3, 132.1, 131.5, 131.1, 126.0, 123.4, 122.9, 20.7, 18.9. **^{19}F NMR** (377 MHz, DMSO-d6) δ: -148.22 (s), -148.28 (s). **HRMS** (ESI) m/z: Calcd. for $C_{14}H_{12}Cl$ ($[M\text{-}BF_4]^+$) 215.0622; found 215.0623. *See NMR spectra*.

- **3,7-dimethoxydibenzo[*b,d*]chlorol-5-ium tetrafluoroborate (2c)**



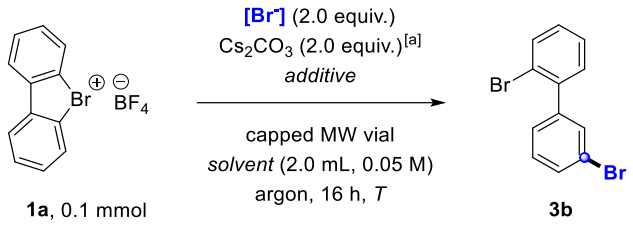
Following **GP-2**, using 2'-chloro-4,4'-dimethoxy-[1,1'-biphenyl]-2-amine **S12** (2.7 mmol, 720 mg) and HBF_4 (48% aq. soln.), the title compound was isolated as a golden yellow powder (462 mg, 51%).

^{1}H NMR (400 MHz, DMSO-d6) δ: 8.45 (d, *J* = 8.7 Hz, 2H), 8.27 (d, *J* = 2.3 Hz, 2H), 7.55 (dd, *J* = 8.8, 2.4 Hz, 2H), 3.94 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d6) δ: 160.4, 140.9, 124.8, 124.4, 119.0, 107.7, 56.6. **^{19}F NMR** (377 MHz, DMSO-d6) δ: -148.21 (s), -148.27 (s). **HRMS** (ESI) m/z: Calcd. for $C_{14}H_{12}ClO_2$ ($[M\text{-}BF_4]^+$) 247.0520; found 247.0521. *See NMR spectra*.

3. Optimization and regioselectivity studies

3.1. Optimization for monobromination

Table S1: Summary of optimization reactions for mono-bromination of **1a**.



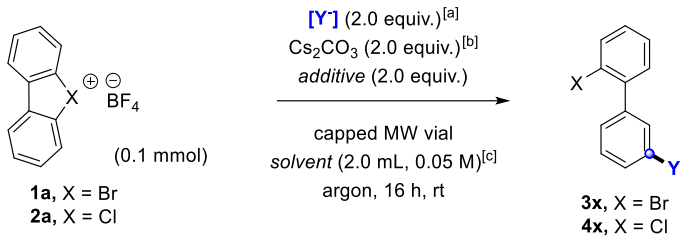
1a, 0.1 mmol — **3b**

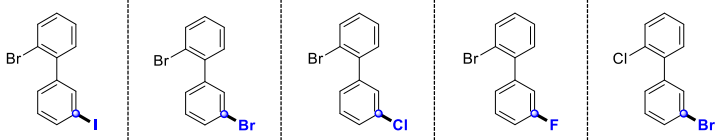
Entry	[Br⁻]	Additive (equiv.)	Solvent[b]	Temp / °C	% Yield 3b[c]
1[d]	KBr	-	DCM	rt	(42)
2[d,e]	KBr	-	DCM	rt	(54)
3[d]	KBr	**18-crown-6 (2)**	DCM	rt	(71)
4	**NaBr**	**15-crown-5** (2)	DCM	rt	56
5	**LiBr**	**12-crown-4** (2)	DCM	rt	99 (87)
6	LiBr	-	DCM	rt	67
7	LiBr	-	DCM (**1.0 mL**)	rt	(40)
8	LiBr	-	DCM	**40**	43
9	LiBr	-	**DCM/H_2O 1:1**	rt	78
10	LiBr	-	**THF**	rt	78
11	LiBr	-	**MeCN**	rt	(77)
12	LiBr	-	**MeCN/H_2O 1:1**	rt	40 + 24[f]
13	LiBr	-	**MeTHF**	rt	0 + 6[f]
14	**NH_4Br**	-	**DCM/H_2O 1:1**	rt	3 + 34[f]
15	**TBAB**	-	**DCM/H_2O 1:1**	rt	20 + 24[f]
16	**TBAB**	-	DCM	rt	30 + 24[f]
17	**TBAB**	-	**MeCN**	rt	72
18	**TBAB**	-	**MeCN/H_2O 1:1**	rt	99 (99)
19	**TBAB**	-	**THF**	rt	99 (99)
20	**TBAB**	-	**EtOH** (not dist.)	rt	26
21	**TBAB**	-	**AcOEt** (not dist.)	rt	99
22	**TBAB**	-	**Et_2O**	rt	85
23	**TBAB**	-	**MeTHF**	rt	97
24	**TBAB**	-	**TBME**	rt	75
25	**TBAB**	-	**DME**	rt	99
26	**TBAB**	-	**anisole**	rt	99

[a] Commercial puratronic 99.994% metal based Cs_2CO_3 from TCI Chemicals, unless otherwise specified. [b] Distilled or stored over 4 Å molecular sieves, unless otherwise specified. [c] Isolated yield in parentheses, otherwise crude NMR yield was determined by integration relative to CH_2Br_2 internal standard. [d] 0.2 mmol scale. [e] 10 equiv. of KBr. [f] Unwanted *ortho*-brominated side-product.

3.2. Extension to other monohalogenations

Table S2: Summary of optimization reactions for other monohalogenations of **1a** or **2a**.



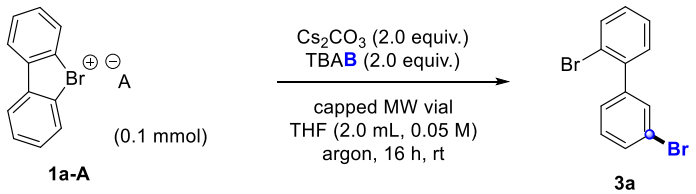


		3a	3b	3c	3d	4b
Entry	**Conditions**	**% Yield[c]**				
1	**LiY, 12-crown-4, DCM**	38	99 (87)	0	n.d.[e]	n.d.
2	**NaY, 15-crown-5, DCM**	86	56	56 (49)	n.d.	n.d.
3	**KY, 18-crown-6, DCM**	(73)	(71)	(75)	n.d.	n.d.
4	**TBAY[e], MeCN**	33	(72)	(53)	(59)	n.d.
5	**TBAY, DCM**	85 (81)	30	99 (88)	n.d.	43
6	**TBAY, MeCN/H_2O 1:1**	32 (38)	99 (99)	(51)	0	84 (85)
7	**TBAY, AcOEt**	74	99	99	68	79
8	**TBAY, THF**	**99 (99)**	**99 (99)**	**99 (99)**	**80 (82)**	**99 (99)**

[a] Y = generic halide (I, Br, Cl or F), thus LiY refers to any lithium halide salt, NaY to any sodium halide salt, etc. [b] Commercial puratronic 99.994% metal based Cs_2CO_3 from TCI Chemicals, unless otherwise specified. [c] Distilled and stored over 4 Å molecular sieves, unless otherwise specified. [d] Isolated yield in parentheses, otherwise crude NMR yield was determined by integration relative to CH_2Br_2 internal standard. [e] n.d. = not determined. [f] TBAY = tetra-*n*-butylammonium halide.

3.3. Compatibility with other counter anions

Table S3: Compatibility of monobromination of 1a with different counter anions.



Counter anion	**1a-OTf[a]**	**1a-OTs[b]**	**1a-OMs[c]**	**1a-PF_6**
% Yield **3b**[d]	98	99	91	90

[a] Triflate or trifluoromethanesulfonate anion. [b] Tosylate or *p*-toluenesulfonate anion [c] Mesylate or methanesulfonate anion. [d] Yield determined by crude NMR analysis relative to CH_2Br_2 as internal standard.

3.4. Confirmation of regioselectivity of monohalogenation

The regioselectivity of the reaction was first assessed through comparative analysis by gas chromatography-mass spectrometry (GC-MS). For instance, for the monobromination we examined the GC-MS profiles of our reaction crudes, which were expected to contain *meta*-selective product **3b** (2,3'-dibromo-1,1'-biphenyl), and compared them with the GC-MS profile of commercially available 2,2'-dibromo-1,1'-biphenyl, which would represent the alternative *ortho*-brominated product.

Figure S3: GC chromatogram (top) and MS spectrum (bottom) of 2,2'-dibromo-1,1'-biphenyl.

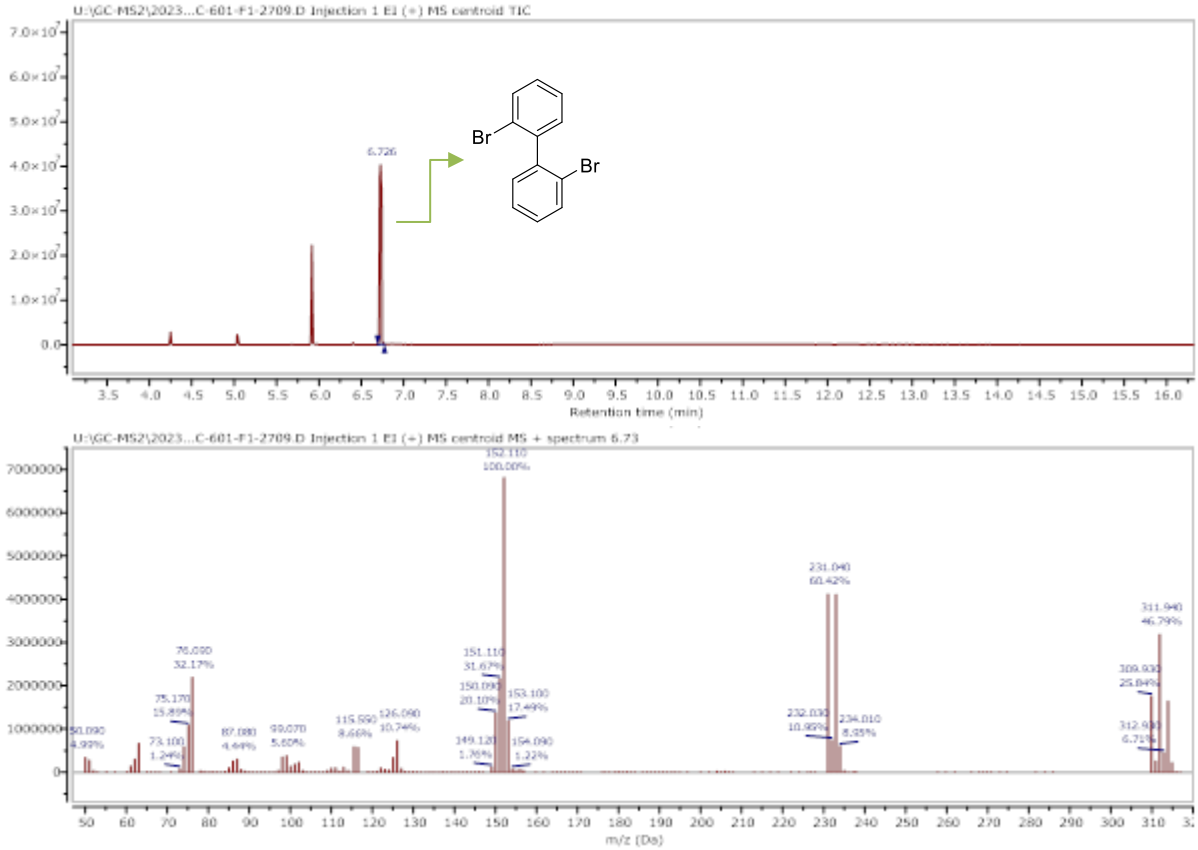
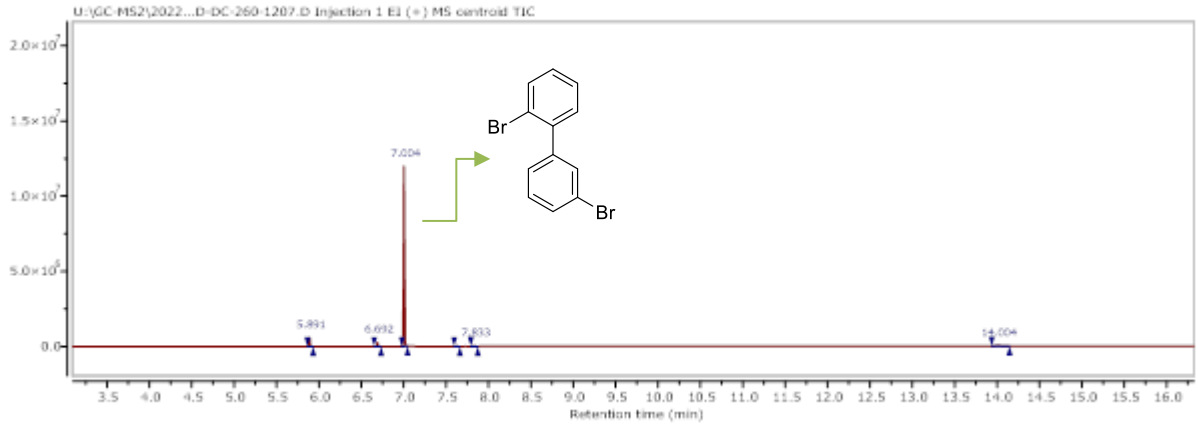
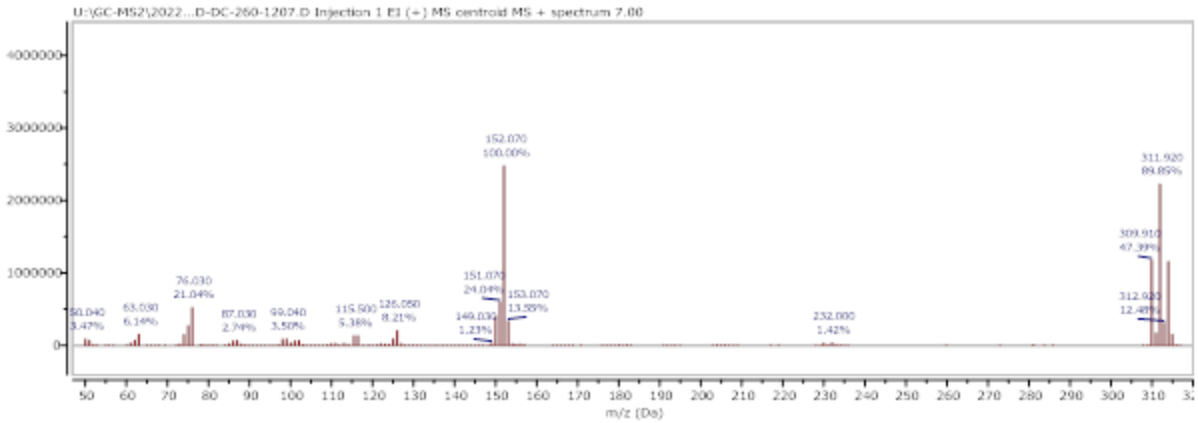


Figure S4: GC chromatogram (top) and MS spectrum (bottom) of **1a**.





While the mass spectra of both compounds exhibited identical m/z values and isotopic patterns for the molecular ion, their fragmentations and retention times were distinct. To further substantiate the regioselectivity of our reaction and eliminate any ambiguities, we turned to NMR spectroscopy:

- Both the ^{1}H and ^{13}C NMR spectra displayed an asymmetric pattern, unequivocally ruling out the possibility of the C_2-symmetric *ortho*-brominated product (Figure S3, compound A). In addition, this compound is already literature-reported and its NMR profile does not match that of our product.[7]
- Under the premise that base-promoted aryne formation occurs between the *ortho* and *meta* carbons, in line with established research by Lanzi *et al.*,[2,3,8] this means the only plausible structure is the expected *meta*-brominated product (Figure S3, compound B).

Additional confirmation may be found by examining the 2D NMR spectra:

- Within the ^{1}H-^{1}H COSY spectrum, the triplet signal at 7.56 ppm displayed no pronounced coupling to any other signal. Typical aromatic $^{1}J_{ortho}$ couplings within the range of 7-8 Hz seem the only ones strong enough to be observed in this spectrum. This indicates the presence of an "isolated" aromatic proton with no other neighbouring protons in *ortho* position.
- Alternative structural scenarios (Figure S5, compounds D, F, or G) would be characterized by a lack of such isolated peaks in the COSY spectrum, with all protons exhibiting coupling to at least one other *ortho* proton. Therefore, we can rule out these possibilities.
- In the unlikely event that the correct structure is compound E (see Figure S5), we would expect an "isolated" signal for proton 3 which, within the HMBC spectrum, should also be coupled to both quaternary C-Br carbons, at 122.5 and 122.1 ppm. However, our HMBC spectrum revealed that the isolated triplet proton at 7.56 ppm was coupled to one quaternary C-Br carbon at 122.1 ppm, and another quaternary carbon from the biaryl axis, at 141.2 ppm.

Figure S5: All possible regioisomers arising from the bromination of hypervalent bromine **1a**.

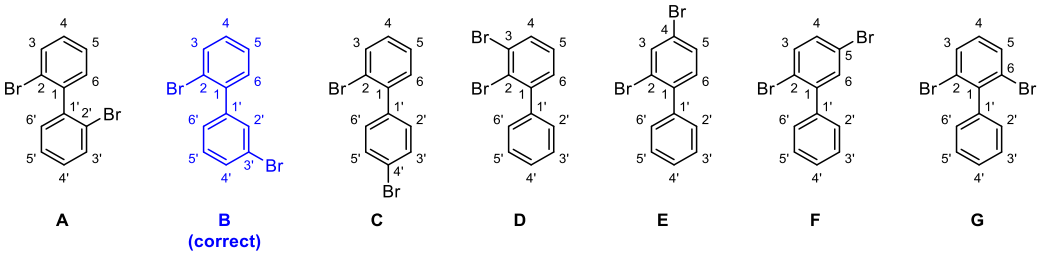


Figure S6: ^{1}H NMR (400 MHz, $CDCl_3$) of **3b.** Aromatic region, key triplet at 7.56 ppm highlighted.

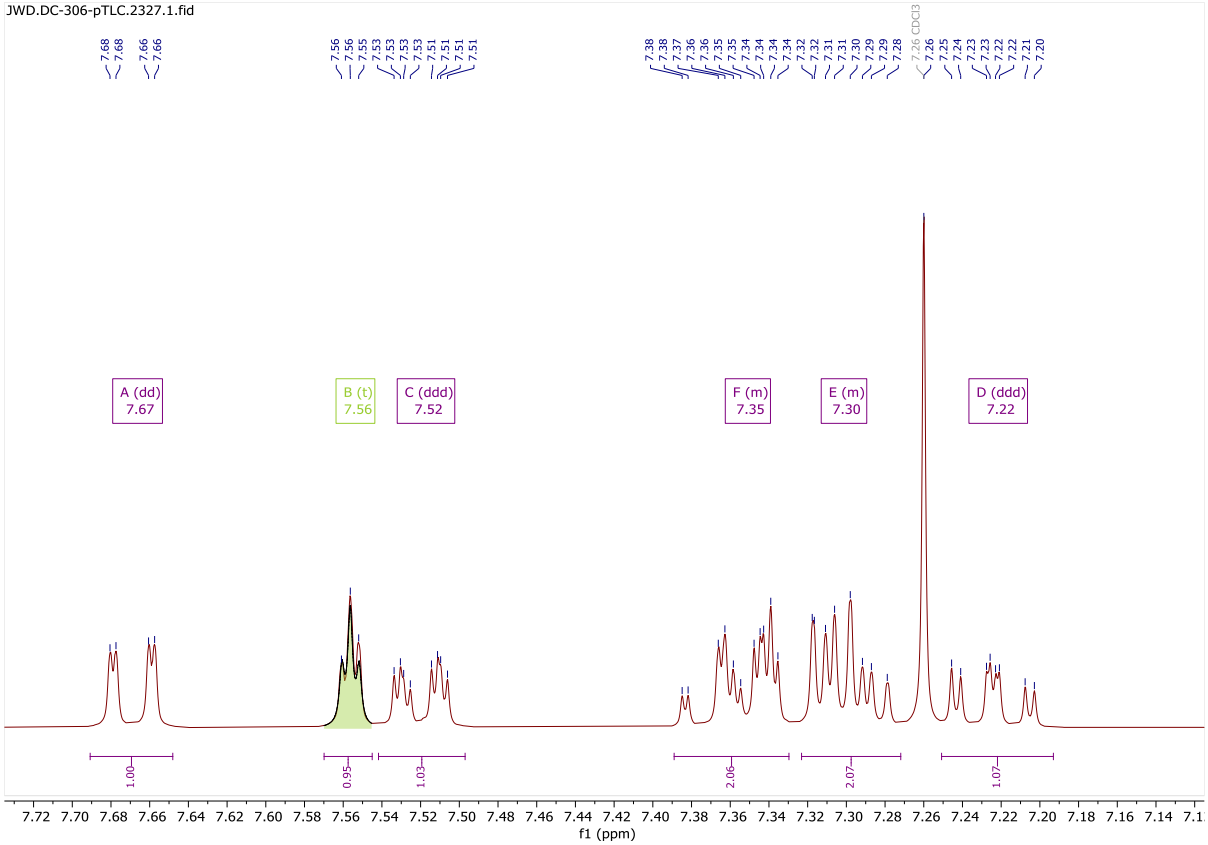


Figure S7: ^{13}C NMR (101 MHz, $CDCl_3$) of **3b.** Aromatic region, quaternary carbons highlighted.

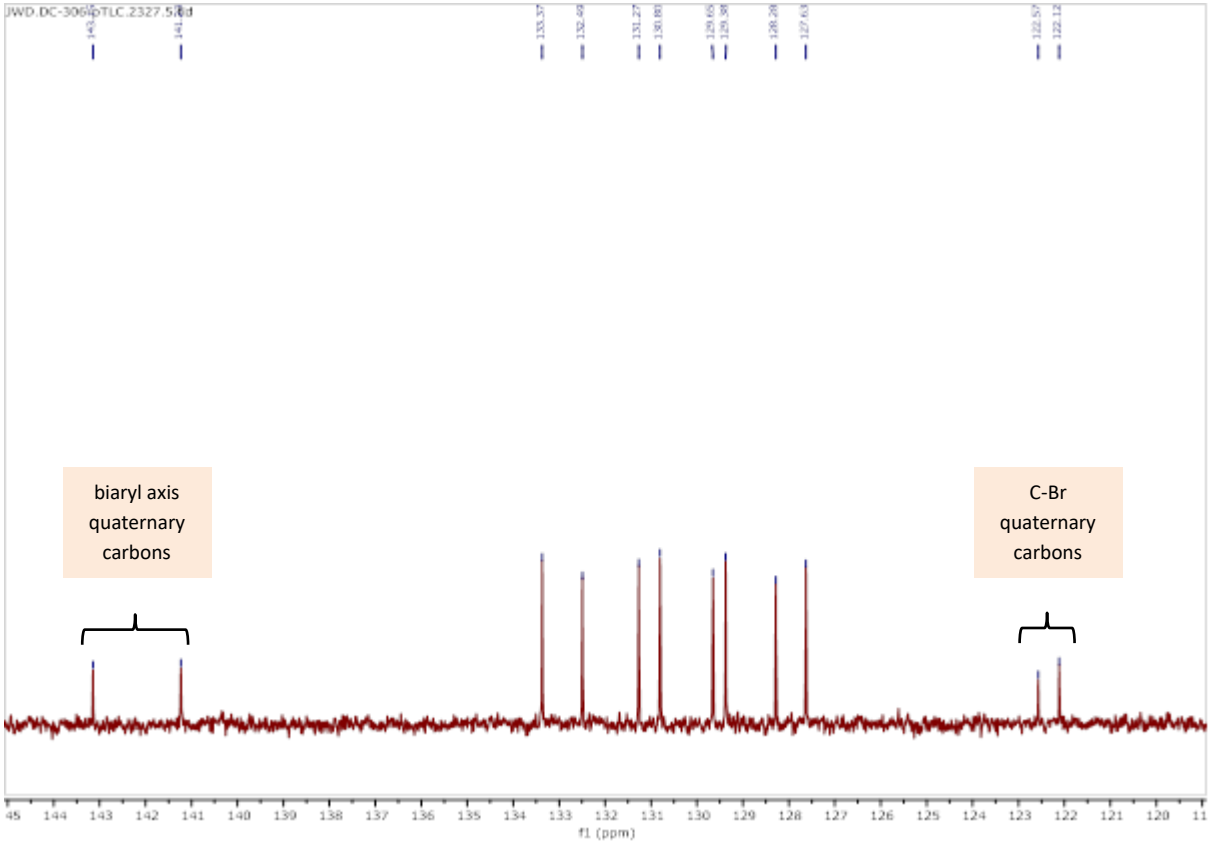


Figure S8: 2D ^{1}H-^{1}H COSY NMR (400 MHz, $CDCl_3$) of **3b.** Isolated triplet at 7.56 ppm highlighted.

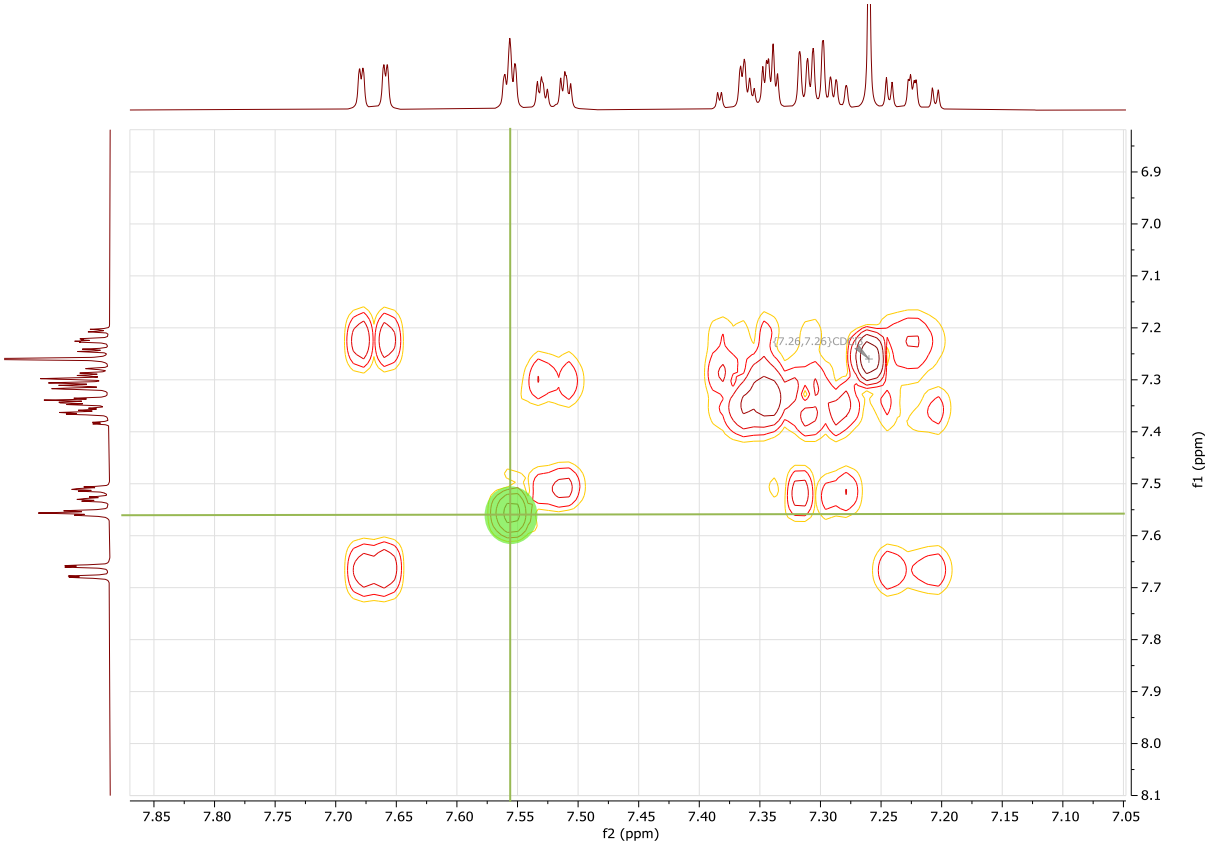


Figure S9: 2D ^{1}H-^{13}C HSQC NMR (400 MHz, $CDCl_3$) of **3b.** Matching C signal for key triplet highlighted.

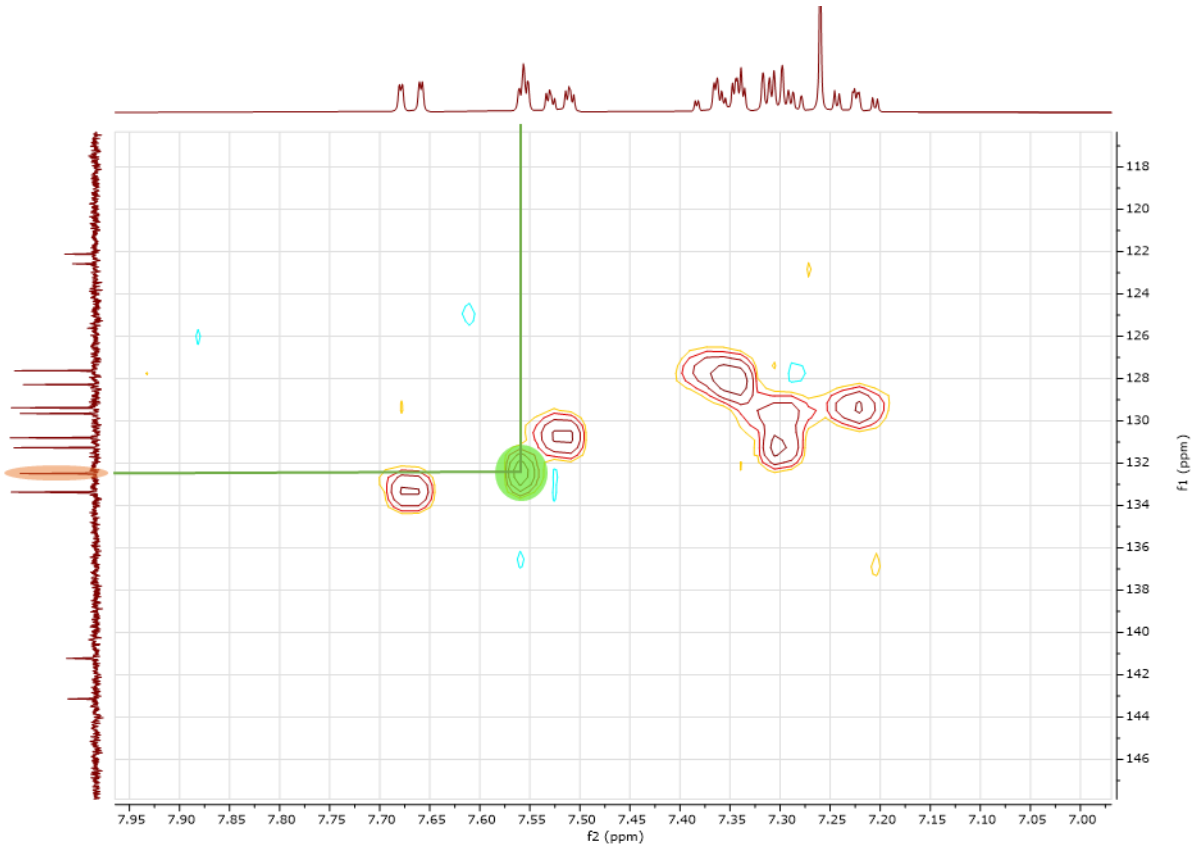
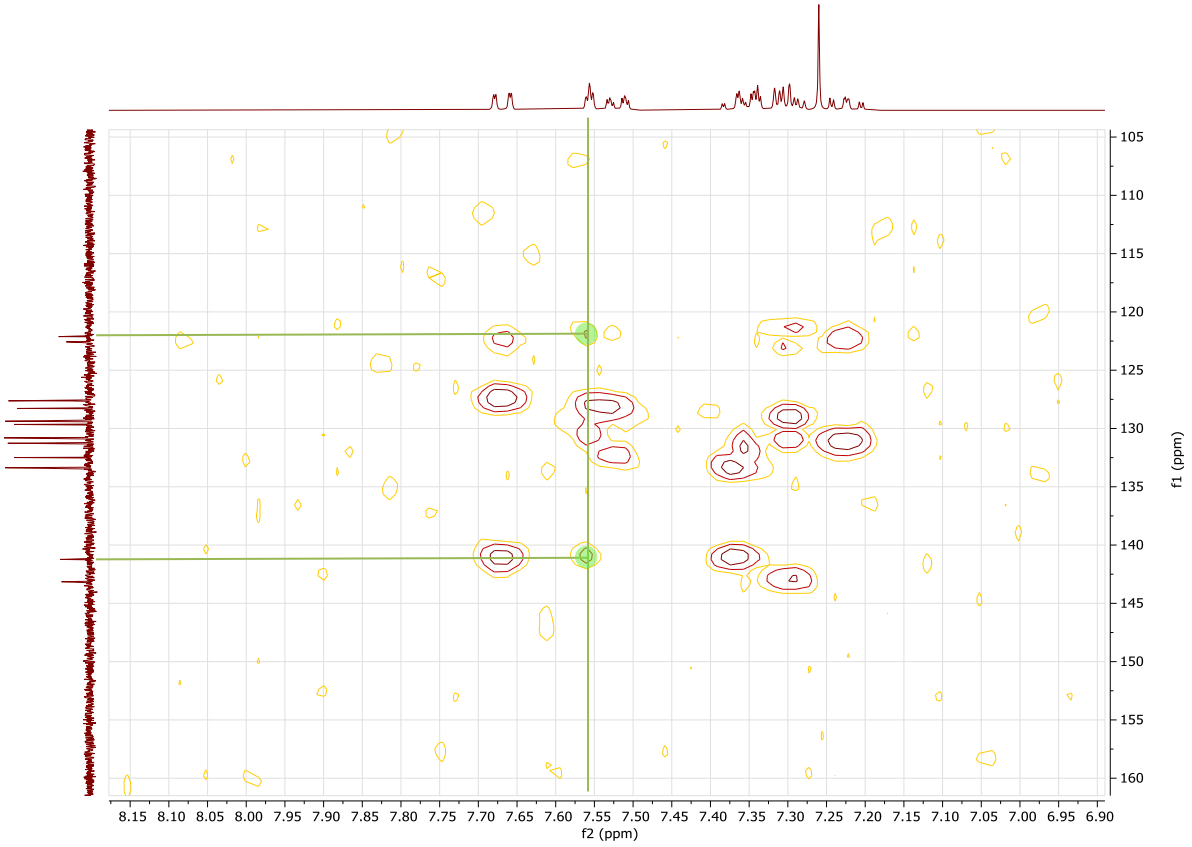
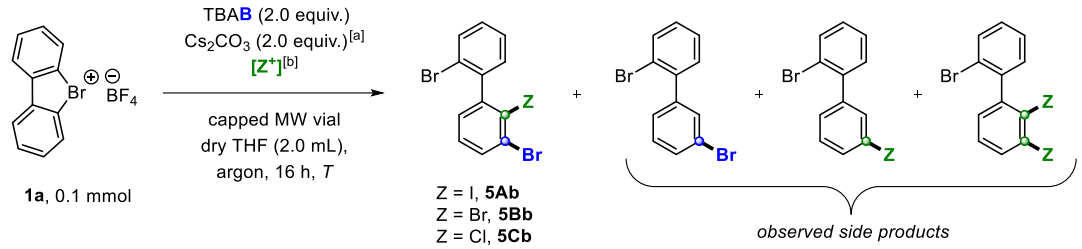


Figure S10: 2D ^{1}H-^{13}C HMBC NMR (400 MHz, $CDCl_3$) of **3b.** Couplings of quaternary Cs to triplet.



3.5. Optimization for electrophilic trapping

Table S4: Optimization for electrophilic trapping with other halogens



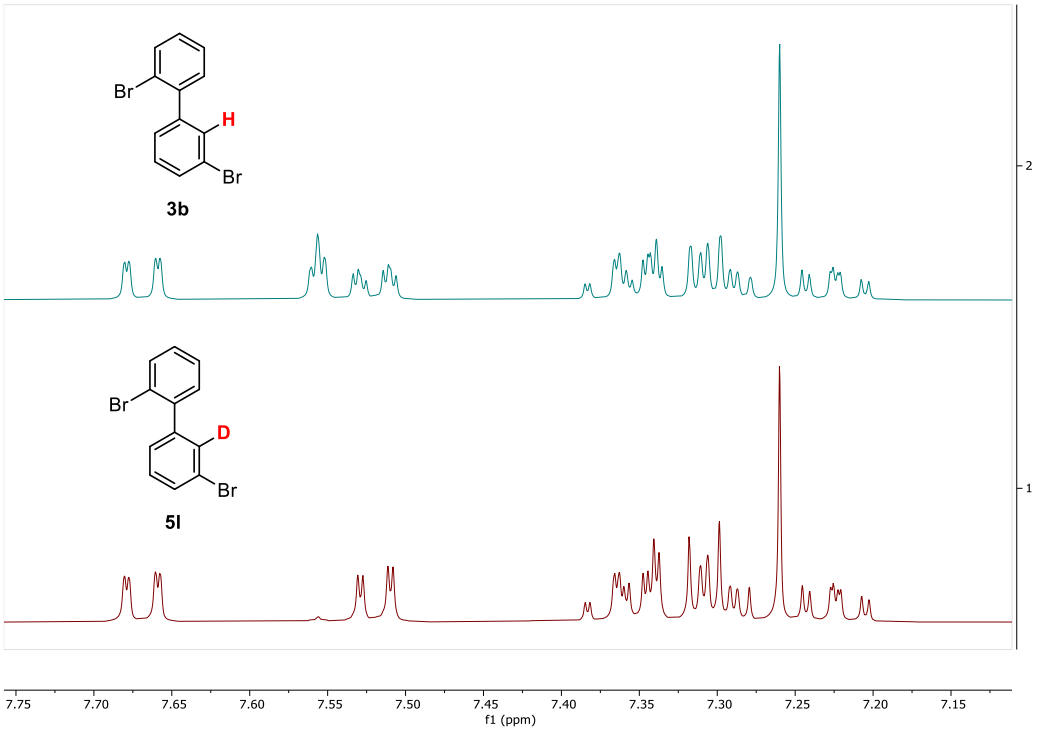
Entry	Z	[Z⁺] (equiv.)	Temp / °C	GCMS analysis[c]	% Yield 5[d]
1	I	I_2 (1.2)	rt	traces of **5**	n.d.[e]
2		**NIS (3.0)**	rt	traces of **5**	n.d.
3		**I-Cl** (3.0)	rt	traces of **5**	n.d.
4		**CHI_3** (3.0)	rt	no product	n.r.[f]
5		**Ethyl iodoacetate** (3.0)	rt	complex mixture	n.r.
6		***n*C_6F_{13}-I** (3.0)	rt	no product	n.r.
7		***n*C_4F_9-I (5.0)**	rt	Only **5**	(86)
8		*n*C_4F_9-I (**5.0**), sequential addition after 20 min	rt	complex mixture	n.d.
9	Br	CBr_4 (5.0)	rt	traces of **5**	n.d.
10		**CCl_3Br** (5.0)	rt	traces of **5**	n.d.
11		**NBS** (5.0)	rt	traces of **5**	n.d.
12		**1,2-dibromotetrafluoroethane** (5.0)	rt	traces of **5**	n.d.
13		**1,2-dibromoethane** (2.0 mL, solvent)[g]	rt	no product	n.r.
14		**TBATB** (5.0)[h]	rt	no product	n.r.
15		***n*C_6F_{13}-Br** (5.0)	rt	**5** + side products	6
16		***n*C_8F_{17}-Br** (5.0)	rt	**5** + side products	10
17		**C_6F_5-Br (20)**	rt	**5** + side products	17
18		*n*C_6F_{13}-Br **(15)**	**50**	traces of **5**	n.d.
19		*n*C_8F_{17}-Br **(15)**	**50**	**5** + side products	(16)
20		C_6F_5-Br **(15)**	**50**	Only **5**	(91)
21	Cl	CCl_4 (5.0)	rt	traces of **5**	n.d.
22		CCl_4 **(1.0 mL)**	rt	no product	n.r.
23		**PCl_5** (5.0)	rt	complex mixture	n.d.
24		**NCS** (5.0)	rt	complex mixture	n.r.
25		**trichlorocyanuric acid** (5.0)	rt	complex mixture	n.d.
26		**C_6F_5-Cl** (5.0)	rt	traces of **5**	n.d.
27		C_6F_5-Cl **(15)**	**50**	**5** + side products	(30)
28		CCl_4 **(15)**	**50**	Only **5**	(53)

[a] Commercial puratronic 99.994% metal based Cs_2CO_3 from TCI Chemicals, unless otherwise specified. [b] Z = generic halogen (I, Br or Cl). Electrophilic [Z⁺] reagent added simultaneously to other reagents, unless otherwise specified. [c] Qualitative observation by GCMS analysis of formation of desired product **5** vs formation of side products. [d] Isolated yield in parentheses, crude NMR yield determined by integration relative to CH_2Br_2 internal standard. [e] n.d. = not determined. [f] n.r. = no reaction. [g] Using KBr (2.0 equv.) + 18-crown-6 (2.0 equiv.) as nucleophilic bromine source. [h] No TBAB added, tetra-*n*-butylammonium tribromide (TBATB) used as both nucleophilic and electrophilic source of bromine, in MeCN.

3.6. Confirmation of regioselectivity of double halogenations

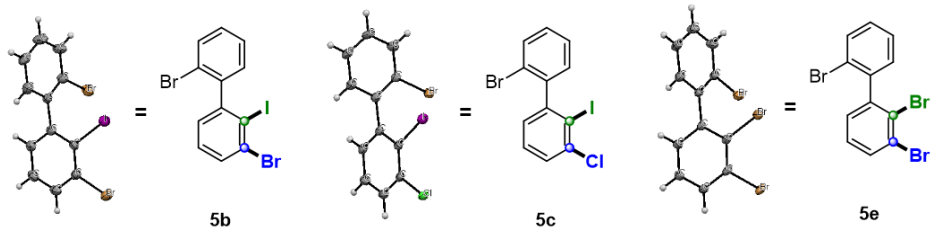
We confirmed the correct mass and isotopic pattern of our desired products through GC-MS analysis, though this evidence, while supportive, was not an absolute confirmation of structure. Additionally, while 2D NMR analyses may offer some insight, it cannot be used to unambiguously assign all ^{1}H and ^{13}C signals. We thus performed a deuteration experiment of **1a** using TBAB as the nucleophile and MeOH-*d* as the electrophile, revealing that the target *ortho* proton was 92% deuterated in product **5l**. Comparison with the corresponding triplet peak at 7.56 ppm in the ^{1}H NMR spectrum of non-deuterated product **3b** (see Section 3.3, Figure S6) confirmed that this was the correct position being trapped by our halogen electrophiles (Figure S11).

Figure S11: Comparison of ^{1}H NMR aromatic peaks of non-deuterated **3b** and deuterated **5l.**



Our unequivocal source of proof lies, however, in X-Ray analysis: Figure S12 illustrates the crystal structures of three different compounds obtained through our optimized double halogenation methodology. These structures unambiguously demonstrate that the nucleophilic [Y^{-}] reagent selectively halogenates the biaryl aryne in the *meta* position, while the electrophilic [Z^{+}] reagent exclusively functionalizes the adjoining *ortho* position.

Figure S12: Crystal structures of **5b**, **5c** and **5e.**

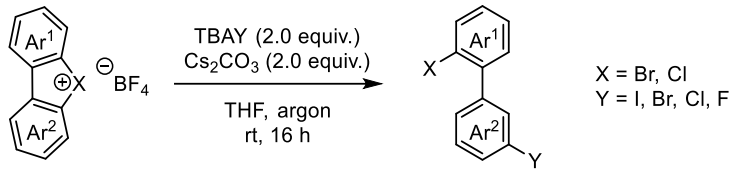


4. Halogenation reactions

4.1. Monohalogenations

4.1.1. General Procedures

General Procedure 3



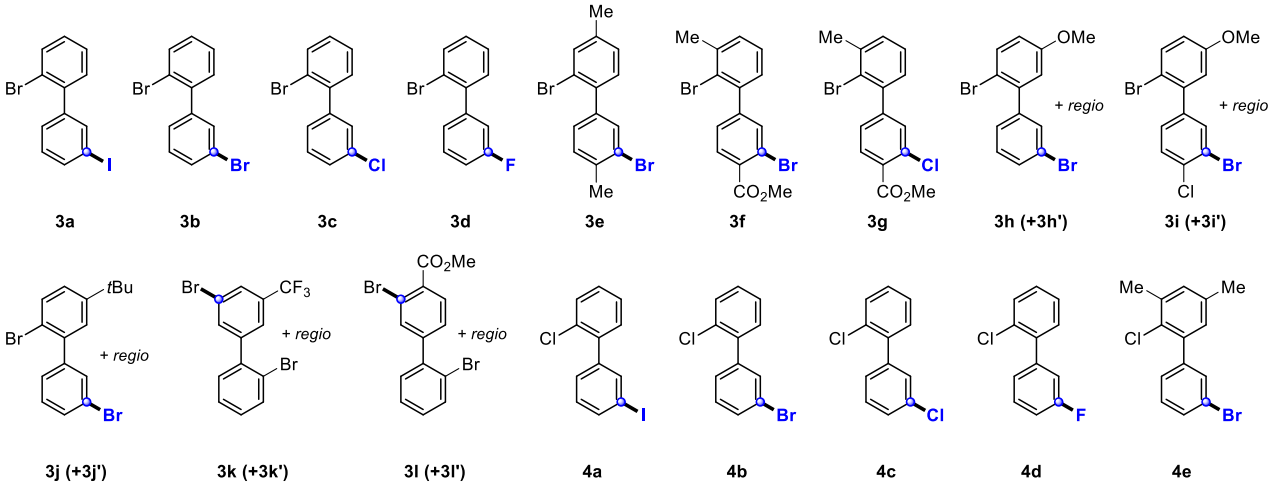
To a Schlenk tube or microwave vial, equipped with a stirrer bar, was added the hypervalent bromine/chlorine salt (1.0 equiv.), Cs_2CO_3 (2.0 equiv.) and the corresponding tetrabutylammonium halide salt, TBAY (2.0 equiv.). In the case of fluorination, TBAF (2.0 equiv., 1 M in THF) was added dropwise after addition of the solvent. Dry THF (0.05 M) was added and the reaction tube was flushed with argon and sealed. The resulting suspension was stirred at room temperature overnight.[c]

Upon completion, the reaction mixture was filtered through a pad of Celite® washing with EtOAc, and the solvent was removed under reduced pressure. The resulting crude was purified by flash column chromatography (SiO_2, loaded pre-adsorbed on silica gel) to afford the pure compound.[d]

4.1.2. Prepared Compounds

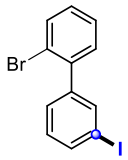
The following monohalogenation products were prepared and stored at 4 °C.

Figure S13: *Meta*-selective monohalogenations prepared in the manuscript.



[c] Heterogeneous reaction. Ensuring an adequate mixing (high stirring speeds, use of tubular reaction vessels) leads to improved yields, reproducibilities, and minimized side products.
[d] Most halogenated biaryls are very apolar. Long columns and low polarity eluents such as petroleum ether, pentane or hexane are recommended.

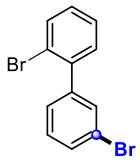
- **2-bromo-3'-iodo-1,1'-biphenyl (3a)**



Following **GP-3**, using dibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1a** (0.10 mmol, 31.9 mg) and TBAI. Purification by flash column chromatography (PE 100%) yielded the title compound as a yellow oil (35.3 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (t, *J* = 1.7 Hz, 1H), 7.72 (ddd, *J* = 7.9, 1.8, 1.1 Hz, 1H), 7.66 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.39 (ddd, *J* = 7.7, 1.7, 1.0 Hz, 1H), 7.35 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.29 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.22 (ddd, *J* = 8.0, 7.2, 1.9 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 143.2, 141.1, 138.3, 136.7, 133.4, 131.3, 129.8, 129.4, 128.9, 127.6, 122.6, 93.9. **HRMS** (ESI) m/z: Calcd. for $C_{12}H_8BrI$ (M^+) 357.8849; found 357.8821. *See NMR spectra*

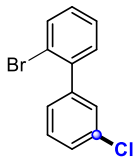
- **2,3'-dibromo-1,1'-biphenyl (3b)**



Following **GP-3**, using dibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1a** (0.10 mmol, 31.9 mg) and TBAB. Purification by flash column chromatography (100% PE) yielded the title compound as a colourless oil (30.8 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.56 (t, *J* = 1.8 Hz, 1H), 7.52 (ddd, *J* = 7.7, 2.0, 1.4 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.32 – 7.27 (m, 2H), 7.22 (ddd, *J* = 8.0, 7.2, 1.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 143.1, 141.2, 133.4, 132.5, 131.3, 130.8, 129.7, 129.4, 128.3, 127.6, 122.6, 122.1. **HRMS** (ESI) m/z: Calcd. for $C_{12}H_8Br_2$ (M^+) 309.8987; found 309.8997. *See NMR spectra*

- **2-bromo-3'-chloro-1,1'-biphenyl (3c)**

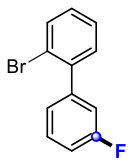


Following **GP-3**, using dibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1a** (0.10 mmol, 31.9 mg) and TBAC. Purification by flash column chromatography (PE 100%) yielded the title compound as a colourless oil (26.4 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.42 – 7.33 (m, 4H), 7.32 – 7.27 (m, 2H), 7.22 (ddd, *J* = 8.1, 7.2, 1.9 Hz, 1H).

Characterization data is consistent with that reported in the literature.[9]

- **2-bromo-3'-fluoro-1,1'-biphenyl (3d)**

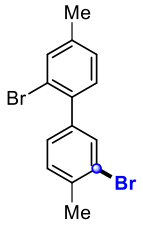


Following **GP-3**, using dibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1a** (0.10 mmol, 31.9 mg) and TBAF (1 M in THF). Purification by flash column chromatography (PE 100%) yielded the title compound as a colourless oil (20.5 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.36 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.31 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.22 (ddd, *J* = 8.0, 7.2, 1.9 Hz, 1H), 7.18 (ddd, *J* = 7.7, 1.6, 1.1 Hz, 1H), 7.15 – 7.03 (m, 2H).

Characterization data is consistent with that reported in the literature.[10]

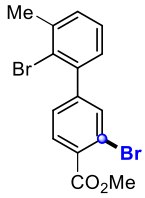
- **2,3'-dibromo-4,4'-dimethyl-1,1'-biphenyl (3e)**



Following **GP-3**, using 3,7-dimethyldibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1d** (0.10 mmol, 35.5 mg) and TBAB. Purification by flash column chromatography (100% Cy) yielded the title compound as a pale-yellow oil (16.8 mg, 49%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, J = 1.5 Hz, 1H), 7.49 (s, 1H), 7.30 – 7.22 (m, 2H), 7.21 – 7.12 (m, 2H), 2.45 (s, 3H), 2.37 (s, 3H).. **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 140.4, 139.39, 138.2, 137.1, 133.7, 133.2, 131.0, 130.3, 128.6, 128.4, 124.5, 122.3, 22.83, 20.9. **HRMS** (ESI) m/z: Calcd. for $C_{14}H_{12}Br_2$ (M^+) 337.9300; found 337.9311. *See NMR spectra*

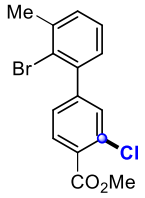
- **methyl 2',3-dibromo-3'-methyl-[1,1'-biphenyl]-4-carboxylate (3f)**



Following **GP-3**, using 3-(methoxycarbonyl)-6-methyldibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1g** (0.10 mmol, 39.1 mg) and TBAB. Purification by flash column chromatography (PE/DCM 5%) yielded the title compound as a colourless oil (30.5 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (d, *J* = 1.7 Hz, 1H), 7.99 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.29 – 7.22 (m, 3H), 7.02 – 6.98 (m, 1H), 3.92 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 165.8, 147.4, 141.9, 139.0, 133.9, 131.2, 131.1, 130.7, 128.4, 128.0, 127.0, 125.4, 123.8, 52.6, 23.9. **HRMS** (ESI) m/z: Calcd. for $C_{15}H_{13}Br_2O_2$ ($[M+H]^+$) 382.9277; found 382.9277. *See NMR spectra*

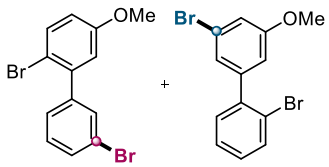
- **methyl 2'-bromo-3-chloro-3'-methyl-[1,1'-biphenyl]-4-carboxylate (3g)**



Following **GP-3**, using 3-(methoxycarbonyl)-6-methyldibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1g** (0.10 mmol, 39.1 mg) and TBAC. Purification by flash column chromatography (PE 100%) yielded the title compound as a white solid (18.8 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12 (d, *J* = 1.6 Hz, 1H), 7.95 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.32 – 7.20 (m, 3H), 7.05 – 6.98 (m, 1H), 3.92 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 166.0, 145.4, 140.3, 139.0, 133.9, 131.3, 131.2, 130.8, 130.7, 128.1, 127.8, 127.0, 125.6, 52.6, 24.0. **HRMS** (ESI) m/z: Calcd. for $C_{15}H_{13}BrClO_2$ ($[M+H]^+$) 338.9782; found 338.9772. *See NMR spectra*

- **2,3'-dibromo-5-methoxy-1,1'-biphenyl (3h) + 2,3'-dibromo-5'-methoxy-1,1'-biphenyl (3h')**



Following **GP-3**, using 2-methoxydibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1b** (0.10 mmol, 34.9 mg) and TBAB. Purification by flash column chromatography (PE 100%) yielded the title compounds as a mixture of regioisomers (confirmed by GC-MS analysis and NMR, 2.5:1 ratio), in the form of a white solid (25.3 mg, 74%).

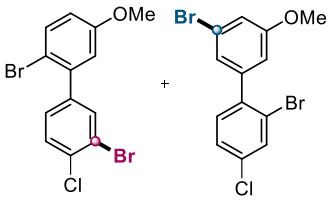
Additional purification by PLC (PE 100%) separated the major regioisomer **3h**, confirmed by 2D NMR analysis. Analysis of **3h'** was possible by comparing the NMRs of **3h** and the mixture.

Regioisomer **3h** (major): **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.57 – 7.49 (m, 3H), 7.35 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 6.84 (d, *J* = 3.1 Hz, 1H), 6.79 (dd, *J* = 8.7, 3.1 Hz, 1H), 3.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 159.0, 143.2, 142.0, 134.0, 132.4, 130.9, 129.7, 128.2, 122.1, 116.7, 115.4, 112.9, 55.7.

Regioisomer **3h'** (minor): **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.66 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.32 – 7.27 (m, 1H), 7.22 (ddd, *J* = 8.0, 7.2, 1.9 Hz, 1H), 7.13 (t, *J* = 1.6 Hz, 1H), 7.08 (t, *J* = 2.1 Hz, 1H), 6.88 (t, *J* = 2.0 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 160.0, 143.8, 141.2, 133.4, 131.2, 129.4, 127.6, 124.9, 122.5, 122.4, 116.5, 114.6, 55.8.

HRMS (ESI) m/z: Calcd. for $C_{13}H_{10}Br_2O$ (M^+) 339.9093; found 339.9111. *See NMR spectra*

- **2,3'-dibromo-4'-chloro-5-methoxy-1,1'-biphenyl (3i) + 2,3'-dibromo-4-chloro-5'-methoxy-1,1'-biphenyl (3i')**



Following **GP-3**, using 7-chloro-2-methoxydibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1h** (0.10 mmol, 38.3 mg) and TBAB. Purification by flash column chromatography (PE 100%), and additional purification by PLC (PE 100%), yielded the title compounds as an inseparable mixture of regioisomers (confirmed by GC-MS analysis and NMR, 1.5:1 ratio), in the form of a colourless oil (34.7 mg, 92%).

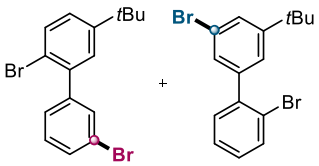
The characterization of each regioisomer is determined by the relative integrations and intensities of each NMR peak in the mixture, with the aid of 2D NMR. The major product was identified as **3i**.

Regioisomer **3i** (major): **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.69 (d, *J* = 2.1 Hz, 1H), 7.54 (dd, *J* = 8.8, 1.0 Hz, 1H), 7.36 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 1H), 6.88 – 6.74 (m, 2H), 3.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 158.7, 141.7, 140.5, 134.5, 133.3, 132.3, 131.6, 127.5, 123.9, 116.4, 115.6, 113.8, 55.6.

Regioisomer **3i'** (minor): **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.67 (d, *J* = 2.1 Hz, 1H), 7.54 (dd, *J* = 8.8, 1.0 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.31 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.88 – 6.74 (m, 2H), 3.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 158.9, 141.0, 140.8, 134.4, 134.0, 129.8, 129.5, 122.0, 116.6, 115.4, 112.7, 55.6. One quaternary carbon is not visible.

HRMS (ESI) m/z: Calcd. for $C_{13}H_9Br_2ClO$ (M^+) 373.8703; found 373.8724. *See NMR spectra*

- **2,3'-dibromo-5-(*tert*-butyl)-1,1'-biphenyl (3j) + 2,3'-dibromo-5'-(*tert*-butyl)-1,1'-biphenyl (3j')**



Following **GP-3**, using 2-(*tert*-butyl)dibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1i** (0.075 mmol, 28.3 mg) and TBAB. Purification by flash column chromatography (PE 100%), and additional purification by PLC (PE 100%), yielded the title compounds as an inseparable mixture of regioisomers (confirmed by GC-MS analysis and NMR, 3.3:1 ratio), in the form of a colourless oil (25.0 mg, 90%).

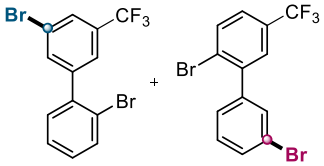
The characterization below is reported separately for **3h** (major) and **3h'** (minor), determined by the relative integrations and intensities of each NMR peak in the mixture, with the help of 2D NMR.

Regioisomer **3j** (major): **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.52 – 7.47 (m, 2H), 7.46 – 7.42 (m, 1H), 7.30 – 7.26 (m, 1H), 7.26 – 7.19 (m, 2H), 7.17 (dd, *J* = 8.2, 2.6 Hz, 1H), 1.25 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 151.0, 143.7, 140.6, 132.9, 132.5, 130.7, 129.6, 128.4, 128.4, 126.7, 122.1, 119.3, 34.8, 31.4.

Regioisomer **3j'** (minor): **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.59 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.30 (t, *J* = 1.6 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.26 – 7.19 (m, 1H), 7.15 – 7.10 (m, 1H), 7.27 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 153.1, 142.6, 141.7, 133.4, 131.3, 129.4, 129.2, 127.9, 127.6, 126.0, 122.7, 122.0, 35.1, 31.3.

HRMS (ESI) m/z: Calcd. for $C_{16}H_{16}Br_2$ (M^+) 365.9613; found 365.9625. *See NMR spectra*

- **2,3'-dibromo-5'-(trifluoromethyl)-1,1'-biphenyl (3k) + 2,3'-dibromo-5-(trifluoromethyl)-1,1'-biphenyl (3k')**

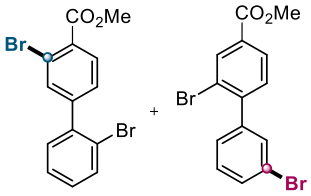


Following **GP-3**, using 2-(trifluoromethyl)dibenzo[*b,d*]bromol-5-ium methanesulfonate **1e** (0.10 mmol, 39.5 mg) and TBAB. Purification by flash column chromatography (PE 100%) yielded the title compounds as a mixture of regioisomers (confirmed by GC-MS analysis and NMR, 10:1 ratio), in the form of a white solid (25.2 mg, 66%).

The major regioisomer is the only easily discernible compound by NMR analysis, and has been identified through 2D NMR analysis as compound **3k**:

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (dt, *J* = 14.7, 1.9 Hz, 2H), 7.69 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.62 (d, *J* = 1.3 Hz, 1H), 7.40 (td, *J* = 7.5, 1.2 Hz, 1H), 7.31 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.29 – 7.24 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 143.5, 139.7, 135.8, 135.8, 133.4z, 132.1 (q, only two central peaks visible, $^2J_{CF}$ = 33.0 Hz), 131.0, 129.9, 127.7, 127.6 (q, $^3J_{CF}$ = 3.9 Hz), 125.2 (d, $^3J_{CF}$ = 3.7 Hz), 123.1 (q, only two central peaks visible, $^1J_{CF}$ = 273.3 Hz), 122.2. **^{19}F NMR** (377 MHz, $CDCl_3$) δ: -62.72 (s). **HRMS** (ESI) m/z: Calcd. for $C_{13}H_7Br_2F_3$ (M^+) 377.8861; found 377.8884. *See NMR spectra*

- **methyl 2',3-dibromo-[1,1'-biphenyl]-4-carboxylate (3l) + methyl 2,3'-dibromo-[1,1'-biphenyl]-4-carboxylate (3l')**

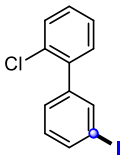


Following **GP-3**, using 3-(methoxycarbonyl)dibenzo[*b,d*]bromol-5-ium methanesulfonate **1f** (0.10 mmol, 38.5 mg) and TBAB. Purification by automated column chromatography (Biotage® Isolera™ One, Cy/EtOAc 5-25% gradient) yielded the title compounds as a mixture of regioisomers (confirmed by GC-MS analysis and NMR, 17:1), in the form of a white solid (27.0 mg, 73%).

Additional purification by PLC (Cy/EtOAc 10%) separated the major regioisomer, identified through 2D NMR analysis as **3l**.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35 (d, *J* = 1.7 Hz, 1H), 8.04 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.69 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.40 (td, *J* = 7.5, 1.2 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.29 (ddd, *J* = 8.0, 7.5, 1.8 Hz, 1H), 7.23 (dd, *J* = 7.5, 1.8 Hz, 1H), 3.96 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 165.6, 146.4, 141.3, 133.8, 132.7, 131.3, 131.0, 130.6, 129.8, 128.2, 127.2, 123.7, 122.9. **HRMS** (ESI) m/z: Calcd. for $C_{14}H_{10}Br_2O_2Na$ ($[M+Na]^+$) 390.8940; found 390.8928. *See NMR spectra*

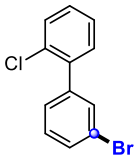
- **2-chloro-3'-iodo-1,1'-biphenyl (4a)**



Following **GP-3**, using dibenzo[*b,d*]chlorol-5-ium tetrafluoroborate **2a** (0.10 mmol, 27.5 mg) and TBAI. Purification by flash column chromatography (PE 100%) yielded the title compound as a yellow oil (15.8 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (t, *J* = 1.7 Hz, 1H), 7.72 (ddd, *J* = 7.9, 1.8, 1.1 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.42 (ddd, *J* = 7.7, 1.7, 1.1 Hz, 1H), 7.33 – 7.29 (m, 3H), 7.17 (t, *J* = 7.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 141.6, 139.1, 138.4, 136.7, 132.5, 131.3, 130.2, 129.8, 129.2, 128.9, 127.1, 93.9. **HRMS** (ESI) m/z: Calcd. for $C_{12}H_8ClI$ (M^+) 313.9354; found 313.9361. *See NMR spectra*

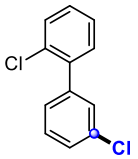
- **3'-bromo-2-chloro-1,1'-biphenyl (4b)**



Following **GP-3**, using dibenzo[*b,d*]chlorol-5-ium tetrafluoroborate **2a** (0.10 mmol, 27.5 mg) and TBAB. Purification by flash column chromatography (PE 100%) yielded the title compound as a colourless oil (26.4 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (t, *J* = 1.7 Hz, 1H), 7.46 (ddd, *J* = 7.9, 2.0, 1.2 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.32 (ddd, *J* = 7.7, 1.7, 1.2 Hz, 1H), 7.28 – 7.19 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 141.5, 139.2, 132.6, 132.5, 131.4, 130.8, 130.2, 129.7, 129.2, 128.3, 127.1, 122.2. **HRMS** (ESI) m/z: Calcd. for $C_{12}H_8BrCl$ (M^+) 265.9492; found 265.9486. *See NMR spectra*

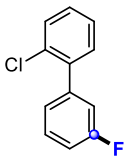
- **2,3'-dichloro-1,1'-biphenyl (4c)**



Following **GP-3**, using dibenzo[*b,d*]chlorol-5-ium tetrafluoroborate **2a** (0.10 mmol, 27.5 mg) and TBAC. Purification by flash column chromatography (PE 100%) yielded the title compound as a colourless oil (22.0 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 – 7.39 (m, 1H), 7.38 (dt, *J* = 2.5, 1.1 Hz, 1H), 7.33 – 7.26 (m, 4H), 7.26 – 7.19 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 141.2, 139.3, 134.1, 132.6, 131.3, 130.2, 129.7, 129.4, 129.2, 127.9, 127.9, 127.1. **HRMS** (ESI) m/z: Calcd. for $C_{12}H_8Cl_2$ (M^+) 221.9997; found 221.9985. *See NMR spectra*

- **2-chloro-3'-fluoro-1,1'-biphenyl (4d)**

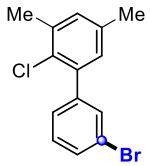


Following **GP-3**, using dibenzo[*b,d*]chlorol-5-ium tetrafluoroborate **2a** (0.10 mmol, 27.5 mg) and TBAF (1 M in THF). Purification by flash column chromatography (PE 100%) yielded the title compound as a colourless oil (88% ^{1}H NMR yield, 6.4 mg, 30%[e]).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 – 7.39 (m, 1H), 7.33 (td, *J* = 8.0, 6.0 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.25 – 7.19 (m, 1H), 7.15 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.10 (ddd, *J* = 9.8, 2.6, 1.5 Hz, 1H), 7.02 (tdd, *J* = 8.4, 2.6, 1.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 162.5 (d, $^{1}J_{CF}$ = 245.8 Hz), 141.6 (d, $^{3}J_{CF}$ = 8.0 Hz), 139.4 (d, $^{4}J_{CF}$ = 2.2 Hz), 132.5, 131.4, 130.2, 129.7 (d, $^{3}J_{CF}$ = 8.4 Hz), 129.1, 127.1, 125.4 (d, $^{4}J_{CF}$ = 2.9 Hz), 116.7 (d, $^{2}J_{CF}$ = 22.1 Hz), 114.7 (d, $^{2}J_{CF}$ = 20.9 Hz). **^{19}F NMR** (377 MHz, $CDCl_3$) δ: -113.45 (s). **HRMS** (ESI) m/z: Calcd. for $C_{12}H_8ClF$ (M^+) 206.0293; found 206.0292. *See NMR spectra*

[e] ^{1}H NMR yield was determined using CH_2Br_2 as internal standard. The compound is volatile and is easily lost under high vacuum, leading to poor isolated yields.

- **3'-bromo-2-chloro-3,5-dimethyl-1,1'-biphenyl (4e)**



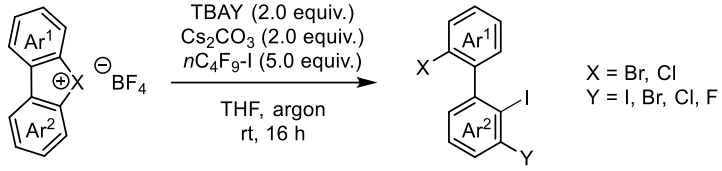
Following **GP-3**, using 2,4-dimethyldibenzo[*b,d*]chlorol-5-ium tetrafluoroborate **2b** (0.10 mmol, 30.3 mg) and TBAB. Purification by flash column chromatography (PE 100%) yielded the title compound as a colourless oil (27.1 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (t, *J* = 1.8 Hz, 1H), Z7.49 (ddd, *J* = 7.8, 2.1, 1.2 Hz, 1H), 7.34 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.07 (dt, *J* = 2.2, 0.7 Hz, 1H), 6.95 (dt, *J* = 2.3, 0.7 Hz, 1H), 2.41 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 142.4, 139.3, 136.9, 136.2, 132.6, 131.4, 130.5, 129.7, 129.6, 129.6, 128.3, 122.1, 21.0, 20.8. **HRMS** (ESI) m/z: Calcd. for $C_{14}H_{12}BrCl$ (M^+) 293.9805; found 293.9800. *See NMR spectra*

4.2. Dihalogenations *via* electrophilic trapping

4.2.1. General Procedures

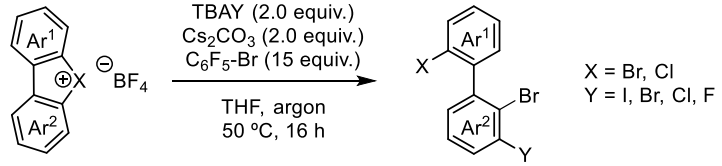
General Procedure 4A – Trapping with iodine



To flame-dried Schlenk flask or microwave vial, equipped with a stirrer bar, was added the hypervalent bromine/chlorine salt (1.0 equiv.), Cs_2CO_3 (2.0 equiv.) and the corresponding tetrabutylammonium halide salt, TBAY (2.0 equiv.) or TBAF (2.0 equiv., 1 M in THF) in the case of fluorination. Then, dry THF (0.05 M) was added and, in quick succession, the electrophile nonafluoro-1-iodobutane (5.0 equiv.) was added.[f] The flask was flushed with argon, sealed, and the mixture was stirred at room temperature overnight.

Upon completion, the reaction mixture was filtered through a pad of Celite® washing with EtOAc, and the solvent was removed under reduced pressure. The resulting crude was purified by flash column chromatography (SiO_2, loaded pre-adsorbed on silica gel) to afford the pure compound.[g]

General Procedure 4B – Trapping with bromine



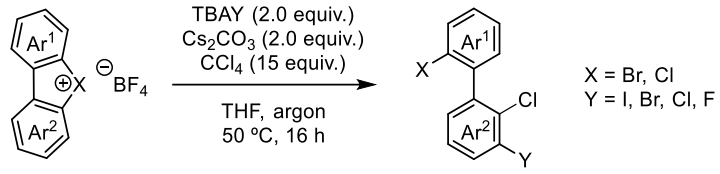
To flame-dried Schlenk flask or microwave vial, equipped with a stirrer bar, was added the hypervalent bromine/chlorine salt (1.0 equiv.), Cs_2CO_3 (2.0 equiv.) and the corresponding tetrabutylammonium halide salt, TBAY (2.0 equiv.) or TBAF (2.0 equiv., 1 M in THF) in the case of fluorination. Then, dry THF (0.05 M) was added and, in quick succession, the electrophile bromopentafluorobenzene (15 equiv.) was added.[f] The flask was flushed with argon, sealed, and the mixture was stirred at 50 °C overnight.

Upon completion, the reaction mixture was filtered through a pad of Celite® washing with EtOAc, and the solvent was removed under reduced pressure. The resulting crude was purified by flash column chromatography (SiO_2, loaded pre-adsorbed on silica gel) to afford the pure compound.[g]

[f] It is important that the electrophile is added immediately after, or preferably simultaneously to the solvent. Delay can lead to mixtures of mono- and dihalogenations, and other unwanted side products. Ensuring thorough mixing (high rotation speed, tubular vessels), a tight argon atmosphere, as well as using dry, pure solvents and reagents also enhances selectivity and yield.

[g] Most halogenated biaryls are very apolar. Long columns and low polarity eluents such as petroleum ether, pentane or hexane are recommended.

General Procedure 4C – Trapping with chlorine



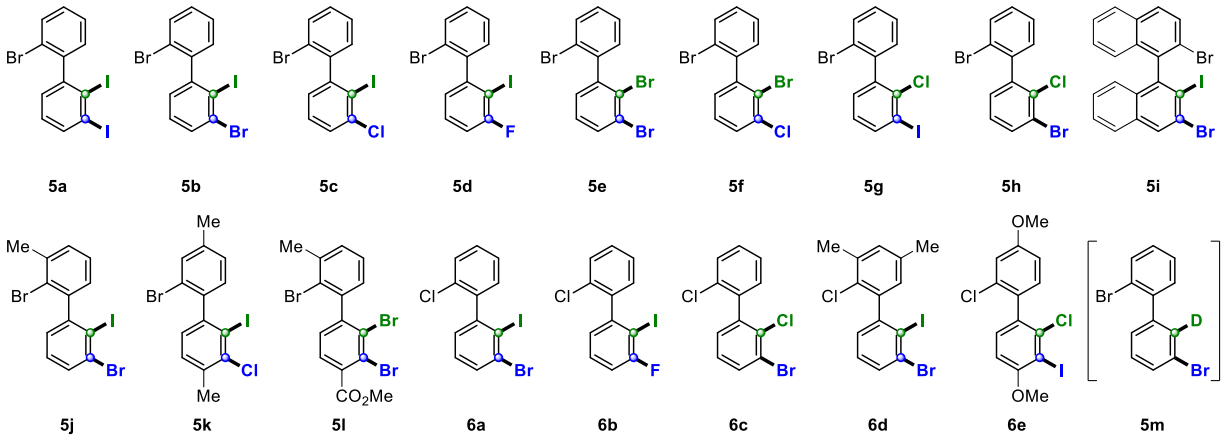
To flame-dried Schlenk flask or microwave vial, equipped with a stirrer bar, was added the hypervalent bromine/chlorine salt (1.0 equiv.), Cs_2CO_3 (2.0 equiv.) and the corresponding tetrabutylammonium halide salt, TBAY (2.0 equiv.) or TBAF (2.0 equiv., 1 M in THF) in the case of fluorination. Then, dry THF (0.05 M) was added and, in quick succession, the electrophile carbon tetrachloride (15 equiv.) was added.[f] The flask was flushed with argon, sealed, and the mixture was stirred at 50 °C overnight.

Upon completion, the reaction mixture was filtered through a pad of Celite® washing with EtOAc, and the solvent was removed under reduced pressure. The resulting crude was purified by flash column chromatography (SiO_2, loaded pre-adsorbed on silica gel) to afford the pure compound.[g]

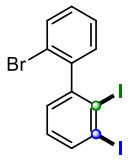
4.2.2. Prepared Compounds

The following dihalogenation products were prepared and stored at 4 °C.

Figure S14: Dihalogenation [and halo-deuteration] products prepared in the manuscript.



- **2'-bromo-2,3-diiodo-1,1'-biphenyl (5a)**

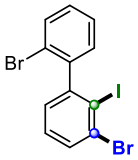


Following **GP-4A**, using dibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1a** (0.10 mmol, 31.9 mg) and TBAI. Purification by flash column chromatography (100% PE) yielded the title compound as a pale-yellow solid (47.7 mg, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (dd, *J* = 7.2, 2.2 Hz, 1H), 7.66 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.38 (td, *J* = 7.5, 1.1 Hz, 1H), 7.26 (td, *J* = 8.1, 1.7 Hz, 1H), 7.18 – 7.09 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 148.7, 147.1, 139.0, 132.8, 130.7, 129.7, 129.4, 128.7, 127.4, 123.2, 113.4, 109.6.

HRMS (ESI) m/z: Calcd. for $C_{12}H_7BrI_2$ (M^+) 483.7815; found 483.7784. *See NMR spectra*

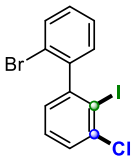
- **2',3-dibromo-2-iodo-1,1'-biphenyl (5b)**



Following **GP-4A**, using dibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1a** (0.10 mmol, 31.9 mg) and TBAB. Purification by flash column chromatography (100% PE) yielded the title compound as an off-white solid (37.8 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (ddd, *J* = 8.0, 6.9, 1.3 Hz, 2H), 7.39 (td, *J* = 7.5, 1.2 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.18 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.12 (dd, *J* = 7.6, 1.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 149.4, 146.2, 132.8, 132.1, 130.9, 130.8, 129.8, 129.3, 128.1, 127.5, 123.3, 107.1. **HRMS** (ESI) m/z: Calcd. for $C_{12}H_7Br_2I$ (M^+) 435.7954; found 435.7932. *See NMR spectra*, *See X-Ray*

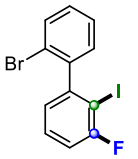
- **2'-bromo-3-chloro-2-iodo-1,1'-biphenyl (5c)**



Following **GP-4A**, using dibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1a** (0.10 mmol, 31.9 mg) and TBAC. Purification by flash column chromatography (100% PE) yielded the title compound as an off-white solid (18.1 mg, 46%).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.67 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.47 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.39 (td, *J* = 7.5, 1.2 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.18 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.08 (dd, *J* = 7.6, 1.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 149.2, 145.7, 139.5, 132.8, 130.8, 129.8, 129.1, 128.6, 127.7, 127.5, 123.3, 104.2. **HRMS** (ESI) m/z: Calcd. for $C_{12}H_7BrClI$ (M^+) 391.8459; found 391.8462. *See NMR spectra*, *See X-Ray*

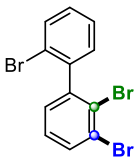
- **2'-bromo-3-fluoro-2-iodo-1,1'-biphenyl (5d)**



Following **GP-4A**, using dibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1a** (0.10 mmol, 31.9 mg) and TBAF (1 M in THF). Purification by flash column chromatography (100% PE) yielded the title compound as an off-white solid (22.3 mg, 59%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.42 – 7.33 (m, 2H), 7.29 (td, *J* = 7.7, 1.7 Hz, 1H), 7.19 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.08 (td, *J* = 8.0, 1.4 Hz, 1H), 7.03 (ddd, *J* = 7.6, 1.5, 0.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 161.9 (d, $^{1}J_{CF}$ = 245.4 Hz), 148.5 (d, $^{4}J_{CF}$ = 2.3 Hz), 144.0 (d, $^{5}J_{CF}$ = 1.2 Hz), 132.9, 131.0, 129.8, 129.7 (d, $^{3}J_{CF}$ = 8.4 Hz), 127.4, 125.7 (d, $^{4}J_{CF}$ = 2.9 Hz), 123.4, 114.7 (d, $^{2}J_{CF}$ = 24.2 Hz), 87.6 (d, $^{2}J_{CF}$ = 25.3 Hz). **^{19}F NMR** (377 MHz, $CDCl_3$) δ: -89.82 (s). **HRMS** (ESI) m/z: Calcd. for $C_{12}H_7BrFI$ (M^+) 375.8754; found 375.8773. *See NMR spectra*

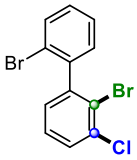
- **2,2',3-tribromo-1,1'-biphenyl (5e)**



Following **GP-4B**, using dibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1a** (0.10 mmol, 31.9 mg) and TBAB. Purification by flash column chromatography (100% PE) yielded the title compound as a colourless oil (35.7 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (t, *J* = 1.4 Hz, 1H), 7.66 (t, *J* = 1.5 Hz, 1H), 7.38 (td, *J* = 7.5, 1.3 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.24 – 7.20 (m, 2H), 7.17 (dd, *J* = 7.6, 1.7 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 144.6, 142.6, 133.4, 132.8, 130.8, 129.7, 129.7, 128.2, 127.4, 126.3, 125.9, 123.3. **HRMS** (ESI) m/z: Calcd. for $C_{12}H_7Br_3$ (M^+) 387.8092; found 387.8090. *See NMR spectra*, *See X-Ray*

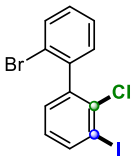
- **2,2'-dibromo-3-chloro-1,1'-biphenyl (5f)**



Following **GP-4B**, using dibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1a** (0.10 mmol, 31.9 mg) and TBAC. Purification by flash column chromatography (100% PE) yielded the title compound as a colourless oil (30.6 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.51 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.39 (td, *J* = 7.5, 1.2 Hz, 1H), 7.34 – 7.25 (m, 2H), 7.22 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.13 (dd, *J* = 7.6, 1.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 144.6, 142.3, 135.4, 132.8, 130.8, 129.9, 129.8, 129.1, 128.0, 127.4, 124.1, 123.4. **HRMS** (ESI) m/z: Calcd. for $C_{12}H_7Br_2Cl$ (M^+) 343.8598; found 343.8608. *See NMR spectra*

- **2'-bromo-2-chloro-3-iodo-1,1'-biphenyl (5g)**

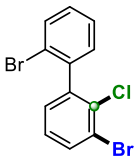


Following **GP-4C**, using dibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1a** (0.10 mmol, 31.9 mg) and TBAI. Purification by flash column chromatography (100% PE) yielded the title compound as a pale-yellow oil (28.3 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.67 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.38 (td, *J* = 7.5, 1.3 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.22 (dt, *J* = 7.5, 1.5 Hz, 2H), 7.03 (t, *J* = 7.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 141.2, 141.2, 140.2, 137.6, 132.8, 131.0, 130.8, 129.7, 127.9, 127.4, 123.4, 99.3. **HRMS** (ESI) m/z: Calcd. for $C_{12}H_7BrClI$ (M^+) 391.8459; found 391.8440. *See NMR spectra*

Gram scale: **GP-4C** was followed without variations, using dibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1a** (4.70 mmol, 1.50 g) and TBAI. The reaction was carried out in a large tubular Schlenk flask under argon and rapid stirring, ensuring simultaneous addition of the electrophile and the solvent in order to minimize formation of side products. Purification by flash column chromatography (100% PE) yielded the title compound as a pale-yellow oil (1.10 g, 59%).

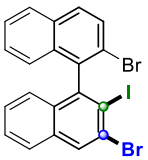
- **2',3-dibromo-2-chloro-1,1'-biphenyl (5h)**



Following **GP-4C**, using dibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1a** (0.10 mmol, 31.9 mg) and TBAB. Purification by flash column chromatography (100% PE) yielded the title compound as a colourless oil (18.5 mg, 53%). Product mixed with minor inseparable impurities.

^{1}H NMR (400 MHz, $CDCl_3$) δ: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.64 (m, 2H), 7.44 – 7.33 (m, 2H), 7.28 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.21 – 7.18 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 142.0, 140.5, 133.4, 132.7, 130.8, 129.9, 129.6, 129.4, 128.0, 127.4, 127.2, 123.3. **HRMS** (ESI) m/z: Calcd. for $C_{12}H_7Br_2Cl$ (M^+) 343.8598; found 343.8604. *See NMR spectra*

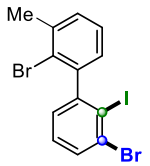
- **2',3-dibromo-2-iodo-1,1'-binaphthalene (5i)**



Following **GP-4A**, using dinaphtho[2,1-*b*:1',2'-*d*]bromol-7-ium tetrafluoroborate **1c** (0.10 mmol, 41.9 mg) and TBAB. Purification by flash column chromatography (100% PE) yielded the title compound as a pale-yellow oil (37.2 mg, 69%). Product mixed with inseparable 2'-bromo-2-iodo-1,1'-binaphthalene.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.99 – 7.90 (m, 2H), 7.90 – 7.79 (m, 3H), 7.55 – 7.47 (m, 2H), 7.37 – 7.26 (m, 2H), 7.12 – 7.07 (m, 1H), 7.07 – 7.01 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 134.1, 133.5, 133.4, 133.2, 133.0, 132.6, 132.5, 131.3, 130.2, 130.1, 129.9, 128.4, 128.4, 127.5, 126.5, 126.0, 122.9. **HRMS** (ESI) m/z: Calcd. for $C_{20}H_{11}Br_2I$ (M^+) 535.8267; found 535.8266. *See NMR spectra*

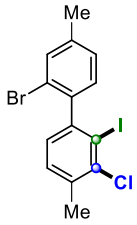
- **2,3'-dibromo-2'-iodo-3-methyl-1,1'-biphenyl (5j)**



Following **GP-4A**, using 4-methyldibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1j** (0.10 mmol, 33.3 mg) and TBAB. Purification by flash column chromatography (100% PE) yielded the title compound as an off-white solid (30.9 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.29 – 7.19 (m, 3H), 7.09 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.96 (dd, *J* = 6.1, 3.2 Hz, 1H), 2.46 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 150.2, 146.7, 138.9, 131.8, 130.8, 130.5, 129.3, 128.1, 128.1, 127.0, 125.7, 107.2, 24.0. **HRMS** (ESI) m/z: Calcd. for $C_{13}H_9Br_2I$ (M^+) 449.8110; found 449.8110. *See NMR spectra*

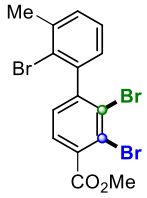
- **2'-bromo-3-chloro-2-iodo-4,4'-dimethyl-1,1'-biphenyl (5k)**



Following **GP-4A**, using 3,7-dimethyldibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1d** (0.10 mmol, 34.7 mg) and TBAC. Purification by flash column chromatography (100% PE) yielded the title compound as an off-white solid (30.6 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (dd, *J* = 1.7, 0.9 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.18 (ddd, *J* = 7.8, 1.7, 0.8 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 2.52 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 146.8, 143.1, 139.9, 138.9, 136.7, 133.2, 130.7, 130.4, 128.2, 127.7, 123.2, 105.4, 22.6, 21.1. **HRMS** (ESI) m/z: Calcd. for $C_{14}H_{11}BrClI$ (M^+) 419.8772; found 419.8753. *See NMR spectra*

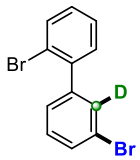
- **methyl 2,2',3-tribromo-3'-methyl-[1,1'-biphenyl]-4-carboxylate (5l)**



Following **GP-4B**, using 3-(methoxycarbonyl)-6-methyldibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1g** (0.10 mmol, 39.1 mg and TBAB. Purification by flash column chromatography (Cy/EtOAc 5%) yielded the title compound as a colourless oil (13.5 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 7.9 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.02 – 6.98 (m, 1H), 3.98 (s, 3H), 2.48 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 167.0, 147.7, 142.8, 139.1, 135.2, 130.8, 129.4, 128.8, 128.6, 127.8, 127.1, 125.3, 124.3, 53.0, 23.9. **HRMS** (ESI) m/z: Calcd. for $C_{15}H_{12}Br_3O_2$ ($[M+H]^+$) 460.8382; found 460.8394. *See NMR spectra*

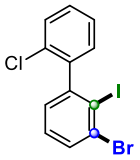
- **3-bromo-2,2'-dichloro-1,1'-biphenyl-2'-*d* (5m)**



Following a modified **GP-4B**, using dibenzo[*b,d*]bromol-5-ium tetrafluoroborate **1a** (0.10 mmol, 27.5 mg) and MeOH-*d* (30 equiv.) as electrophile. Purification by flash column chromatography (100% PE) yielded the title compound as a white solid (27.3 mg, 87%). Deuterium incorporation (NMR analysis): 92%.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.52 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.32 – 7.28 (m, 2H), 7.22 (ddd, *J* = 8.0, 7.2, 1.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 143.1, 141.2, 133.4, 131.3, 130.8, 129.7, 129.4, 128.3, 127.6, 122.6, 122.0. The quaternary C-D carbon is not visible. **HRMS** (ESI) m/z: Calcd. for $C_{12}H_7Br_2D$ (M^+) 310.9050; found 310.9060. *See NMR spectra*

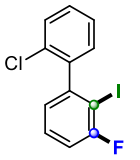
- **3-bromo-2'-chloro-2-iodo-1,1'-biphenyl (6a)**



Following **GP-4A**, using dibenzo[*b,d*]chlorol-5-ium tetrafluoroborate **2a** (0.10 mmol, 27.5 mg) and TBAB. Purification by flash column chromatography (100% PE) yielded the title compound as a white solid (17.5 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.37 – 7.33 (m, 2H), 7.27 (t, *J* = 7.7 Hz, 1H), 7.19 – 7.16 (m, 1H), 7.13 (dd, *J* = 7.6, 1.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 147.8, 144.2, 133.1, 132.1, 131.0, 130.9, 129.7, 129.6, 129.3, 128.2, 126.8, 107.1. **HRMS** (ESI) m/z: Calcd. for $C_{12}H_7BrClI$ (M^+) 391.8459; found 391.8473. *See NMR spectra*

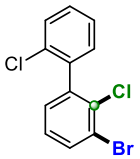
- **2'-chloro-3-fluoro-2-iodo-1,1'-biphenyl (6b)**



Following **GP-4A**, using dibenzo[*b,d*]chlorol-5-ium tetrafluoroborate **2a** (0.10 mmol, 27.5 mg) and TBAF (1 M in THF). Purification by flash column chromatography (100% PE) yielded the title compound as a colourless oil (10.4 mg, 31%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 – 7.45 (m, 1H), 7.41 – 7.30 (m, 3H), 7.22 – 7.01 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 161.9 (d, $^{1}J_{CF}$ = 245.4 Hz), 139.0, 133.3, 131.1, 130.8 (d, $^{3}J_{CF}$ = 10.4 Hz), 129.7, 129.7, 129.6 (d, $^{3}J_{CF}$ = 8.1 Hz), 128.7, 126.8, 125.8 (d, $^{4}J_{CF}$ = 2.9 Hz), 114.7 (d, $^{2}J_{CF}$ = 24.2 Hz). **^{19}F NMR** (377 MHz, $CDCl_3$) δ: -89.73 (s). **HRMS** (ESI) m/z: Calcd. for $C_{12}H_7ClFI$ (M^+) 331.9260; found 331.9266. *See NMR spectra*

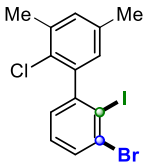
- **3-bromo-2,2'-dichloro-1,1'-biphenyl (6c)**



Following **GP-4C**, using dibenzo[*b,d*]chlorol-5-ium tetrafluoroborate **2a** (0.10 mmol, 27.5 mg) and TBAB. Purification by flash column chromatography (100% PE) yielded the title compound as a colourless oil (22.3 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (dd, *J* = 7.4, 2.2 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.37 – 7.33 (m, 2H), 7.26 – 7.16 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 140.6, 138.6, 134.0, 133.5, 133.5, 131.0, 130.2, 129.7. 129.7, 127.5, 126.8, 123.5. **HRMS** (ESI) m/z: Calcd. for $C_{12}H_7BrCl_2$ (M^+) 299.9103; found 299.9120. *See NMR spectra*

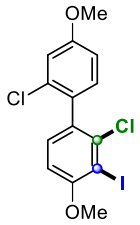
- **3'-bromo-2-chloro-2'-iodo-3,5-dimethyl-1,1'-biphenyl (6d)**



Following **GP-4A**, using 2,4-dimethyldibenzo[*b,d*]chlorol-5-ium tetrafluoroborate **2b** (0.10 mmol, 30.3 mg) and TBAB. Purification by flash column chromatography (100% PE) yielded the title compound as an off white solid (23.8 mg, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.13 – 7.07 (m, 2H), 6.84 – 6.80 (m, 1H), 2.40 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 148.7, 144.2, 136.5, 136.1, 131.8, 131.6, 130.8, 130.0, 129.2, 128.9, 128.1, 107.3, 20.9, 20.7. **HRMS** (ESI) m/z: Calcd. for $C_{14}H_{11}BrClI$ (M^+) 419.8772; found 419.8770. *See NMR spectra*

- **2,2'-dichloro-3-iodo-4,4'-dimethoxy-1,1'-biphenyl (6e)**

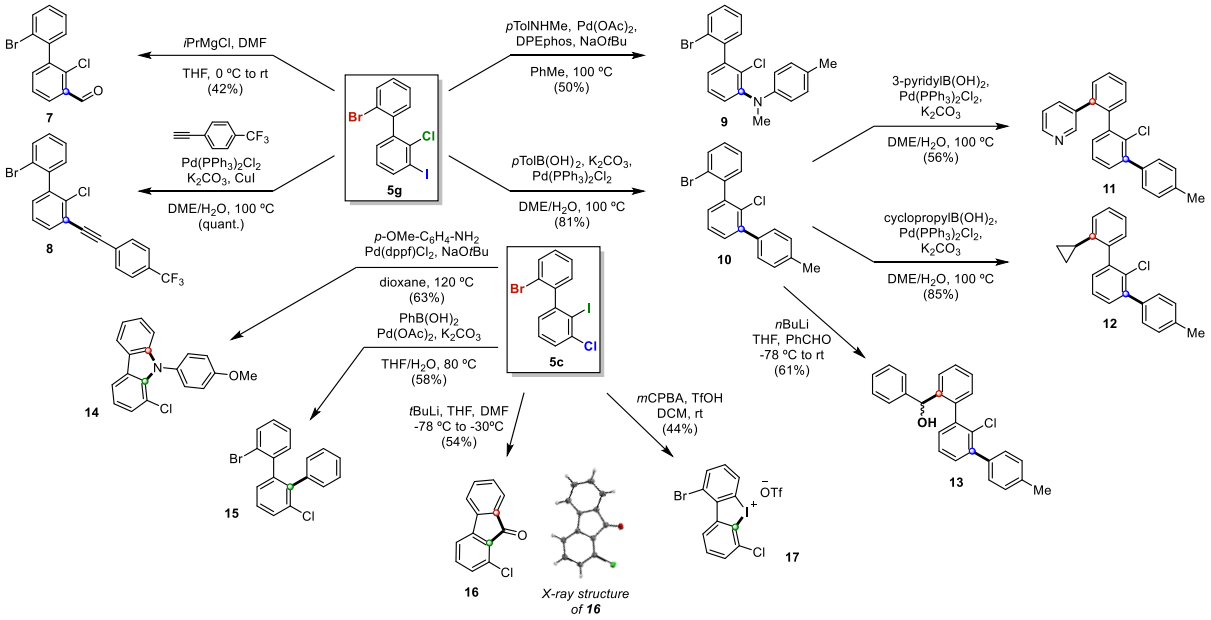


Following **GP-4C**, using 3,7-dimethoxydibenzo[*b,d*]chlorol-5-ium tetrafluoroborate **2c** (0.10 mmol, 33.5 mg) and TBAI. Purification by flash column chromatography (Cy/EtOAc 5-10%) yielded the title compound as a white solid (27.6 mg, 67%).

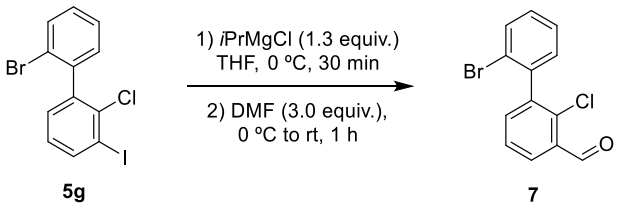
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.12 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 8.5 Hz, 1H), 7.01 (d, *J* = 2.6 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.87 (dd, *J* = 8.5, 2.6 Hz, 1H), 3.94 (s, 3H), 3.85 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 160.0, 154.6, 138.9, 136.2, 134.3, 132.0, 128.6, 114.7, 114.6, 112.9, 111.3, 107.0, 56.7, 55.7. **HRMS** (ESI) m/z: Calcd. for $C_{14}H_{11}Cl_2IO_2$ (M^+) 407.9175; found 407.9151. *See NMR spectra*

5. Post-functionalization studies

Figure S15: Post-functionalizations performed on substrates **5c** and **5g**.



- **2'-bromo-2-chloro-[1,1'-biphenyl]-3-carbaldehyde (7)**

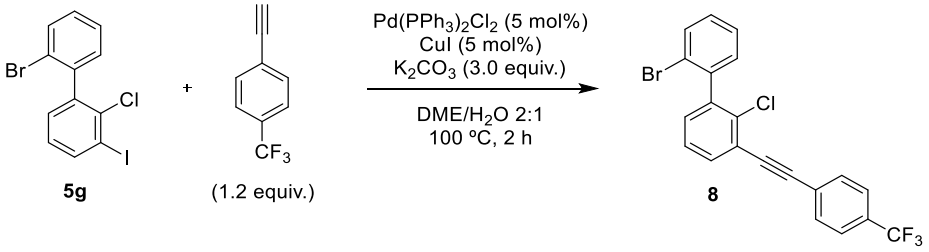


To a flame-dried Schlenk flask equipped with a stirrer bar was added 2'-bromo-2-chloro-3-iodo-1,1'-biphenyl **5g** (1 equiv., 0.10 mmol, 39.3 mg) and dissolved in THF (0.8 mL). The solution was cooled to 0 °C, and freshly titrated isopropylmagnesium chloride (2.0 M solution in THF) (1.2 equiv., 0.12 mmol, 59 µL) was added dropwise. After stirring at 0 °C for 30 min, dry DMF (1.0 M in THF) (3.0 equiv., 0.30 mmol, 0.30 mL) was added in one shot. The mixture was stirred for a further 15 min at 0 °C and then warmed to room temperature for 1 h.

Upon completion, the reaction was diluted with EtOAc (10 mL) and washed with 1 M HCl solution (2 × 10 mL). The phases were separated, the aqueous phase was extracted with EtOAc (2 × 10 mL), the combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude was purified by flash column chromatography (SiO_2, PE/EtOAc 5%) to give the title compound as a white solid (12.3 mg, 42%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.57 (d, *J* = 0.7 Hz, 1H), 7.99 (dd, *J* = 7.3, 2.3 Hz, 1H), 7.71 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.42 (td, *J* = 7.5, 1.3 Hz, 1H), 7.31 (td, *J* = 7.8, 1.8 Hz, 1H), 7.28 – 7.24 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 190.3, 141.8, 139.3, 137.2, 136.6, 133.1, 132.9, 131.1, 130.0, 129.1, 127.5, 127.0, 123.7. **HRMS** (ESI) m/z: Calcd. for $C_{13}H_8OBrClNa$ ([M+Na]$^+$) 316.9339; found 316.9336. *See NMR spectra*

- **2'-bromo-2-chloro-3-((4-(trifluoromethyl)phenyl)ethynyl)-1,1'-biphenyl (8)**

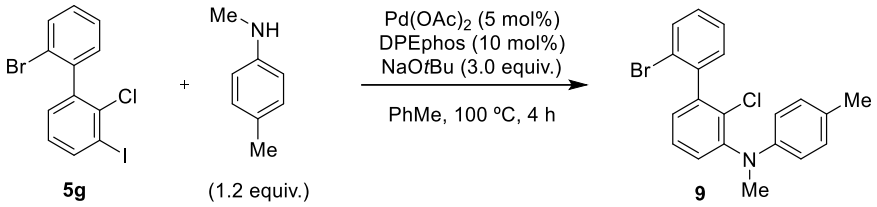


To a microwave vial equipped with a stirrer bar were added 2'-bromo-2-chloro-3-iodo-1,1'-biphenyl **5g** (1 equiv., 0.10 mmol, 39.3 mg), 1-ethynyl-4-(trifluoromethyl)benzene (1.2 equiv., 0.12 mmol, 20 µL), K_2CO_3 (3.0 equiv., 0.30 mmol, 41.5 mg), $Pd(PPh_3)_2Cl_2$ (5 mol%, 0.005 mmol, 3.5 mg) and CuI (5 mol%, 0.005 mmol, 1.0 mg). DME (1.0 mL) was added and the mixture was stirred at room temperature for 5 min. Then, water (0.5 mL) was added, the vial was sealed, and the reaction was stirred at 100 °C for 2 hours.

Upon completion, the reaction was diluted with EtOAc (10 mL), the phases were separated, the organic phase was washed with sat. aq. NaCl (2 × 10 mL), and the aqueous phase was extracted with EtOAc (2 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude was purified by flash column chromatography (SiO_2, Cy/EtOAc 4:1) to give the title compound as a yellow oil (43.5 mg, quant.).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 – 7.57 (m, 6H), 7.40 (td, *J* = 7.5, 1.3 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.31 – 7.23 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 141.0, 140.2, 135.4, 133.1, 132.9, 132.1, 131.5, 131.0, 130.5 (q, only two central peaks visible, $^2J_{CF}$ = 32.6 Hz), 129.8, 127.4, 126.9 (q, only two central peaks visible, $^4J_{CF}$ = 1.6 Hz), 126.5, 125.5 (q, $^3J_{CF}$ = 3.8 Hz), 124.1 (q, first peak not visible, second peak under multiplet at 125.5 ppm, third and fourth peaks visible, $^1J_{CF}$ = 271.7 Hz), 123.6, 123.4, 93.1, 88.8. **^{19}F NMR** (377 MHz, $CDCl_3$) δ: -62.82 (s). **HRMS** (ESI) m/z: Calcd. for $C_{21}H_{11}BrClF_3$ (M^+) 433.9679; found 433.9681. *See NMR spectra*

- **2'-bromo-2-chloro-*N*-methyl-*N*-(*p*-tolyl)-[1,1'-biphenyl]-3-amine (9)**

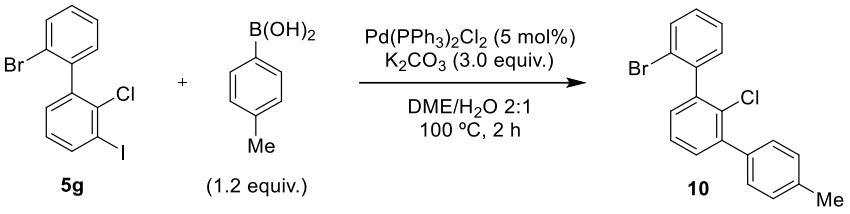


To a microwave vial equipped with a stirrer bar were added 2'-bromo-2-chloro-3-iodo-1,1'-biphenyl **5g** (1 equiv., 0.10 mmol, 39.3 mg), *N*-methyl-*p*-toluidine (1.2 equiv., 0.12 mmol, 15 µL), NaO*t*Bu (3.0 equiv., 0.30 mmol, 28.8 mg), $Pd(OAc)_2$ (5 mol%, 0.005 mmol, 1.1 mg) and bis[(2-diphenylphosphino)phenyl] ether DPEphos (10 mol%, 0.01 mmol, 5.4 mg). The solids were dissolved in toluene (1.5 mL), the vial was sealed, and the mixture was stirred at 100 °C for 4 hours.

Upon completion, the reaction was diluted with EtOAc (10 mL), the phases were separated, the organic phase was washed with sat. aq. NaCl (2 × 10 mL), and the aqueous phase was extracted with EtOAc (2 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude was purified by flash column chromatography (SiO_2, PE 100%) to give the title compound as a yellow solid (19.2 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.38 (td, *J* = 7.5, 1.3 Hz, 1H), 7.36 – 7.29 (m, 3H), 7.29 – 7.22 (m, 2H), 7.14 (dd, *J* = 7.0, 2.2 Hz, 1H), 7.06 – 6.98 (m, 2H), 6.63 – 6.55 (m, 2H), 3.28 (s, 3H), 2.26 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 146.6, 146.4, 142.4, 140.8, 133.1, 132.7, 131.0, 129.7, 129.5, 129.3, 128.4, 127.6, 127.3, 127.3, 123.9, 114.1, 39.5, 20.5. **HRMS** (ESI) m/z: Calcd. for $C_{20}H_{17}BrClN$ (M^+) 385.0227; found 385.0221. *See NMR spectra*

- **2-bromo-2'-chloro-4''-methyl-1,1':3',1''-terphenyl (10)**



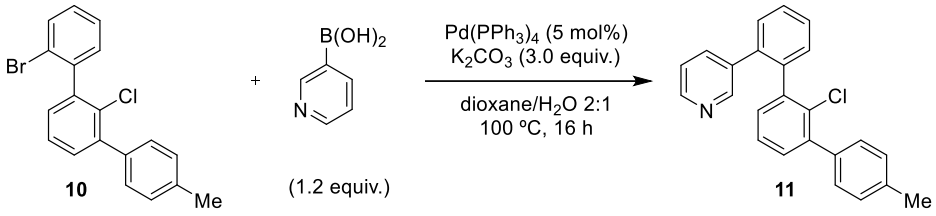
To a microwave vial equipped with a stirrer bar were added 2'-bromo-2-chloro-3-iodo-1,1'-biphenyl **5g** (1 equiv., 0.10 mmol, 39.3 mg), *p*-tolylboronic acid (1.2 equiv., 0.12 mmol, 16.3 mg), K_2CO_3 (3.0 equiv., 0.30 mmol, 41.5 mg) and $Pd(PPh_3)_2Cl_2$ (5 mol%, 0.005 mmol, 3.5 mg). The solids were dissolved in DME (1.0 mL) and the mixture was stirred at room temperature for 5 minutes. Then, water (0.5 mL) was added, the vial was sealed, and the reaction was stirred at 100 °C for 2 hours.

Upon completion, the reaction was diluted with EtOAc (10 mL), the phases were separated, the organic phase was washed with sat. aq. NaCl (2 × 10 mL), and the aqueous phase was extracted with EtOAc (2 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude was purified by flash column chromatography (SiO_2, PE 100%) to give the title compound as white crystals (29.0 mg, 81%).

Scale-up: Following the above procedure using 2'-bromo-2-chloro-3-iodo-1,1'-biphenyl **5Ca** (1 equiv., 1.27 mmol, 500 mg), the resulting crude reaction mixture was purified by flash column chromatography (100% PE) to yield the title compound as white crystals (255 mg, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.41 – 7.35 (m, 5H), 7.32 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.29 – 7.24 (m, 3H), 7.22 (dd, *J* = 6.0, 3.3 Hz, 1H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 141.4, 141.3, 141.1, 137.5, 137.0, 132.7, 131.9, 131.2, 131.1, 129.9, 129.6, 129.4, 128.9, 127.3, 126.4, 123.9, 21.4. **HRMS** (ESI) m/z: Calcd. for $C_{19}H_{14}BrCl$ (M^+) 355.9962; found 355.9955. *See NMR spectra*

- **3-(2'-chloro-4''-methyl-[1,1':3',1''-terphenyl]-2-yl)pyridine (11)**

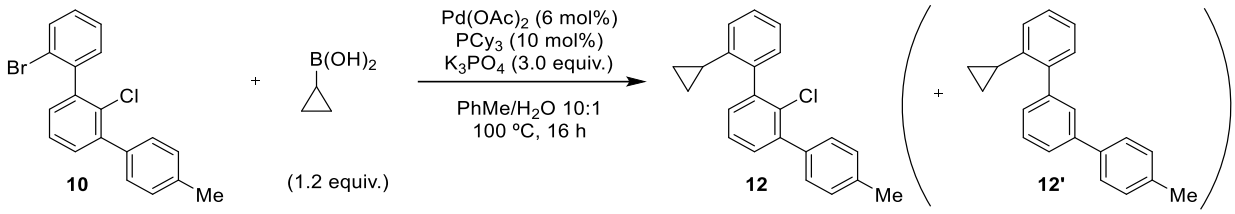


To a microwave vial equipped with a stirrer bar were added 2-bromo-2'-chloro-4''-methyl-1,1':3',1''-terphenyl **10** (1 equiv., 0.10 mmol, 35.8 mg), 3-pyridylboronic acid (1.2 equiv., 0.12 mmol, 14.8 mg), K_2CO_3 (3.0 equiv., 0.30 mmol, 41.5 mg) and $Pd(PPh_3)_4$ (5 mol%, 0.005 mmol, 5.8 mg). 1,4-Dioxane (1.0 mL) was added and the mixture was stirred at room temperature for 5 min. Then, water (0.5 mL) was added, the vial was sealed, and the reaction was stirred at 100 °C overnight.

Upon completion, the reaction was diluted with EtOAc (10 mL), the phases were separated, the organic phase was washed with sat. aq. NaCl (2 × 10 mL), and the aqueous phase was extracted with EtOAc (2 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude was purified by flash column chromatography (SiO_2, Cy/EtOAc 4:1) to give the title compound as an off-white solid (19.9 mg, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (d, *J* = 1.8 Hz, 1H), 8.44 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.55 – 7.42 (m, 5H), 7.24 – 7.09 (m, 8H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 150.2, 147.9, 141.5, 140.6, 139.2, 137.9, 137.5, 137.0, 136.9, 136.6, 131.7, 131.0, 131.0, 130.7, 130.0, 129.4, 128.8, 128.5, 128.1, 126.3, 122.7, 21.4. **HRMS** (ESI) m/z: Calcd. for $C_{24}H_{19}NCl$ ($[M+H]^+$) 356.1201; found 356.1199. *See NMR spectra*

- **2'-chloro-2-cyclopropyl-4''-methyl-1,1':3',1''-terphenyl (12)**

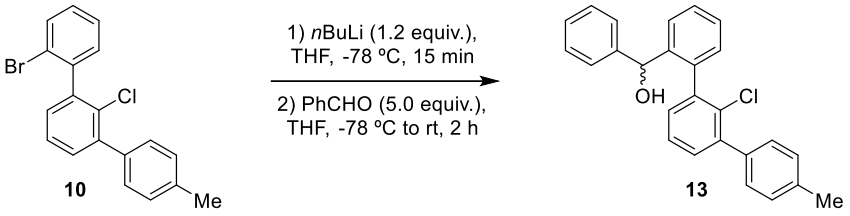


To a flame-dried microwave vial equipped with a stirrer bar were added 2-bromo-2'-chloro-4''-methyl-1,1':3',1''-terphenyl **10** (1 equiv., 0.10 mmol, 35.8 mg), cyclopropylboronic acid (1.2 equiv., 0.12 mmol, 10.3 mg), K_3PO_4 (3.0 equiv., 0.30 mmol, 63.7 mg) and $Pd(OAc)_2$ (6 mol%, 0.006 mmol, 1.3 mg). The vessel was evacuated and backfilled with argon thrice, then tricyclohexylphosphine (10 mol%, 0.01 mmol, 2.8 mg) was added in the glovebox. Toluene (0.9 mL) was added and the mixture was stirred under argon at room temperature for 5 min. Then, water (0.1 mL) was added, the vial was sealed, and the reaction was stirred at 100 °C overnight.

Upon completion, the reaction was diluted with EtOAc (10 mL), the phases were separated, the organic phase was washed with sat. aq. NaCl (2 × 10 mL), and the aqueous phase was extracted with EtOAc (2 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude was purified by flash column chromatography (SiO_2, PE 100%) to give the title compound as a white solid (26.9 mg, 85%). The compound was found to be mixed with a minor inseparable impurity **12'** by GC-MS and NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 – 7.37 (m, 2H), 7.36 – 7.17 (m, 8H), 6.97 – 6.94 (m, 1H), 2.42 (s, 3H), 1.69 (tt, *J* = 8.0, 5.6 Hz, 1H), 0.80 – 0.71 (m, 2H), 0.66 – 0.56 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 141.6, 141.5, 141.1, 140.5, 137.3, 137.1, 132.1, 130.3, 130.3, 129.5, 129.5, 129.4, 128.7, 128.7, 128.0, 126.1, 125.0, 123.5, 21.3, 13.2, 9.0, 8.6. **HRMS** (ESI) m/z: Calcd. for $C_{22}H_{19}Cl$ (M^+) 318.1170; found 318.1171. *See NMR spectra*

- **(2'-chloro-4''-methyl-[1,1':3',1''-terphenyl]-2-yl)(phenyl)methanol (13)**



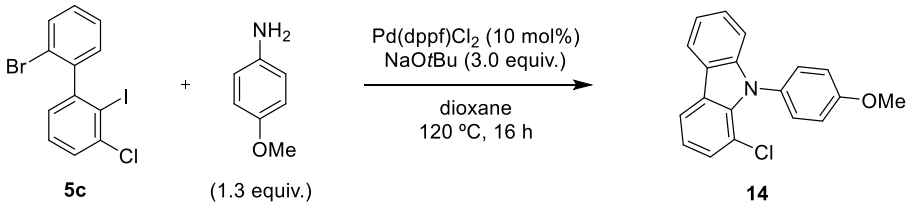
To a flame-dried Schlenk flask equipped with a stirrer bar was added 2-bromo-2'-chloro-4''-methyl-1,1':3',1''-terphenyl **10** (1 equiv., 0.10 mmol, 35.8 mg) and dissolved in THF (1.0 mL). The solution was cooled to -78 °C, and freshly titrated *n*-butyllithium (1.6 M solution in hexanes) (1.2 equiv., 0.12 mmol, 91 µL) was added dropwise. After stirring at -78 °C for 15 min, benzaldehyde (5.0 equiv., 0.50 mmol, 51 µL) was added dropwise. The mixture was stirred for a further 15 min at -78 °C and then warmed to room temperature for 2 h.

Upon completion, the reaction was quenched with 1M HCl (10 mL), diluted with EtOAc (10 mL) and washed with brine (2 × 10 mL). The phases were separated, the aqueous phase was extracted with EtOAc (2 × 10 mL), the combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude was purified by flash column chromatography (SiO_2, Cy/EtOAc 5-10%) to give the title compound as a colourless oil and a mixture of two atropodiastereomers (55:45 NMR ratio, 23.4 mg, 61%).

A separate characterization of each atropodiastereomer was not possible, therefore a combined analysis was carried out. Some peaks in ^{1}H NMR were identifiable as belonging to either one or the other diastereomer (labelled below as *dia*^{A} or *dia*^{B}), whereas the rest were undistinguishable (*dia*$^{A+B}$).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (dd, *J* = 7.8, 1.4 Hz, 1H, *dia*^{B}), 7.53 (dd, *J* = 7.8, 1.5 Hz, 1H, *dia*^{A}), 7.45 (dd, *J* = 7.6, 1.5 Hz, 1H, *dia*^{B}), 7.43 – 7.32 (m, 5H, *dia*$^{A+B}$), 7.31 – 7.27 (m, 1H, *dia*$^{A+B}$ + 1H, *dia*^{A}), 7.25 – 7.11 (m, 7H, *dia*$^{A+B}$ + 1H, *dia*^{A}), 6.99 (dd, *J* = 7.5, 1.8 Hz, 1H, *dia*^{B}), 5.80 (d, *J* = 3.6 Hz, 1H, *dia*^{A}), 5.76 (d, *J* = 2.6 Hz, 1H, *dia*^{B}), 2.42 (s, 3H, *dia*^{B}), 2.40 (s, 3H, *dia*^{A}), 2.28 (d, *J* = 2.9 Hz, 1H, *dia*^{B}), 2.00 (d, *J* = 4.2 Hz, 1H, *dia*^{A}). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 143.5, 143.0, 142.4, 141.6, 141.6, 141.4, 140.5, 140.2, 139.3, 138.7, 137.7, 137.5, 137.0, 136.9, 132.4, 131.6, 130.9, 130.9, 130.8, 130.3, 130.2, 129.6, 129.6, 129.5, 129.0, 128.9, 128.8, 128.5, 128.3, 128.3, 127.7, 127.5, 127.5, 127.3, 127.0, 127.0, 126.9, 126.6, 126.3, 73.2, 73.1, 21.4. **HRMS** (ESI) m/z: Calcd. for $C_{26}H_{21}ClO$ ([M-H]$^+$) 383.1197; found 383.1212. *See NMR spectra*

- **1-chloro-9-(4-methoxyphenyl)-9*H*-carbazole (14)**

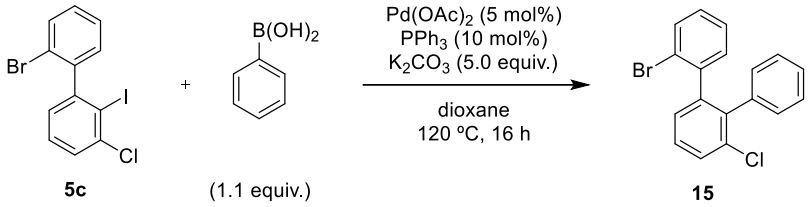


To a flame-dried microwave vial equipped with a stirrer bar were added 2'-bromo-3-chloro-2-iodo-1,1'-biphenyl **5c** (1 equiv., 0.10 mmol, 39.3 mg), *p*-anisidine (1.3 equiv., 0.13 mmol, 16.0 mg), NaO*t*Bu (3.0 equiv., 0.30 mmol, 28.8 mg) and $Pd(dppf)_2Cl_2$ (10 mol%, 0.01 mmol, 7.3 mg). The vessel was evacuated and backfilled with argon thrice, 1,4-dioxane (1.0 mL) was added and the mixture was stirred under argon at 120 °C overnight.

Upon completion, the reaction was diluted with EtOAc (10 mL), the phases were separated, the organic phase was washed with sat. aq. NaCl (2 × 10 mL), and the aqueous phase was extracted with EtOAc (2 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude was purified by flash column chromatography (SiO_2, Cy/EtOAc 5%) to give the title compound as a yellow oil (19.3 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (dt, *J* = 7.7, 1.0 Hz, 1H), 8.05 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.42 – 7.33 (m, 4H), 7.31 – 7.26 (m, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.08 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.06 – 7.02 (m, 2H), 3.92 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 159.7, 143.5, 136.8, 131.0, 130.8, 127.6, 126.7, 126.2, 122.5, 120.4, 120.3, 120.3, 118.9, 116.8, 114.2, 110.6, 55.7. **HRMS** (ESI) m/z: Calcd. for $C_{19}H_{15}ClNO$ ($[M+H]^+$) 308.0837; found 308.0835. *See NMR spectra*

- **2-bromo-3'-chloro-1,1':2',1''-terphenyl (15)**

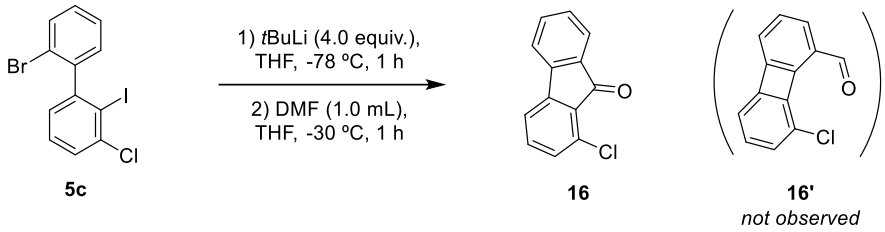


To a flame-dried microwave vial equipped with a stirrer bar were added 2'-bromo-3-chloro-2-iodo-1,1'-biphenyl **5c** (1 equiv., 0.10 mmol, 39.3 mg), phenylboronic acid (1.1 equiv., 0.11 mmol, 13.4 mg), K_2CO_3 (5.0 equiv., 0.50 mmol, 69.1 mg), $Pd(OAc)_2$ (5 mol%, 0.005 mmol, 1.1 mg) and PPh_3 (10 mol%, 0.01 mmol, 2.6 mg). The vessel was evacuated and backfilled with argon thrice, 1,4-dioxane (1.0 mL) was added and the mixture was stirred under argon at 120 °C overnight.

Upon completion, the reaction was diluted with EtOAc (10 mL), the phases were separated, the organic phase was washed with sat. aq. NaCl (2 × 10 mL), and the aqueous phase was extracted with EtOAc (2 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude was purified by flash column chromatography (SiO_2, PE 100%) to give the title compound as an off-white solid (21.7 mg, 63%).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.54 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.46 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.23 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.22 – 7.13 (m, 5H), 7.07 (td, *J* = 7.4, 1.3 Hz, 1H), 7.00 (td, *J* = 7.6, 2.1 Hz, 1H), 6.97 (dd, *J* = 7.3, 1.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 142.7, 141.6, 139.9, 137.7, 134.0, 132.4, 131.9, 130.4, 129.8, 129.3, 128.9, 128.7, 128.1, 127.8, 127.3, 126.6, 123.6. **HRMS** (ESI) m/z: Calcd. for $C_{18}H_{12}BrCl$ (M^+) 341.9805; found 341.9809. *See NMR spectra*

- **1-chloro-9*H*-fluoren-9-one (16)**



5c **16** **16'** *not observed*

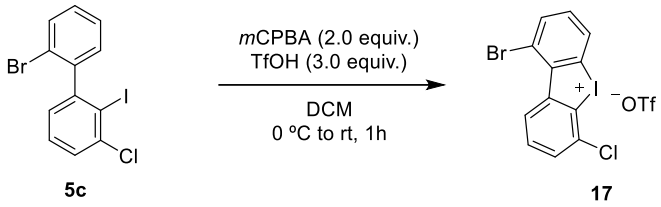
Following a literature-reported procedure,[11] to a flame-dried Schlenk flask equipped with a stirrer bar was added 2'-bromo-3-chloro-2-iodo-1,1'-biphenyl **5c** (1 equiv., 0.20 mmol, 78.7 mg) and dissolved in THF (1.0 mL). The solution was cooled to -78 °C and *tert*-butyllithium (1.4 M in pentane) (4.0 equiv., 0.80 mmol, 0.57 mL) was added dropwise, and the reaction was stirred at the same temperature for 1 h. After diluting with toluene (3.0 mL), the reaction was warmed up to -30 °C, maintained at the same temperature for 1 h, and treated with excess DMF (1.0 mL). The reaction was stirred at said temperature for 1 h.

Upon completion, the reaction was diluted with water (5.0 mL), the phases were separated, the organic phase was washed with sat. aq. NaCl (2 × 10 mL), and the aqueous phase was extracted with EtOAc (2 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude was purified by flash column chromatography (SiO_2, Cy/EtOAc 5%) to give the title compound as a yellow solid (23.2 mg, 54%).[h]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (dt, *J* = 7.4, 1.0 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.44 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.38 – 7.29 (m, 1H), 7.22 (dd, *J* = 7.8, 1.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 191.0, 146.7, 142.8, 135.4, 134.9, 134.1, 132.9, 131.1, 129.8, 124.7, 120.6, 118.8. **HRMS** (ESI) m/z: Calcd. for $C_{17}H_7ClNaO$ ([M+Na]$^+$) 237.0078; found 237.0079. *See NMR spectra*, *See X-Ray*

[h] The expected structure according to the followed literature procedure, compound **16'**, was not observed by GC-MS or NMR analysis. Confirmation of the structure of compound **16** was obtained by 2D-NMR analysis and X-Ray diffraction.

- **1-bromo-6-chlorodibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (17)**



Following a literature-reported procedure,[12] to a solution of 2'-bromo-3-chloro-2-iodo-1,1'-biphenyl **5c** (1 equiv., 0.50 mmol, 197 mg) in DCM (2.0 mL) was added *m*CPBA 70% (2.0 equiv., 1.0 mmol, 247 mg) in one portion. After the *m*CPBA fully dissolved, TfOH (3.0 equiv., 1.5 mmol, 133 µL) was added dropwise at 0 °C. The resulting pale green suspension was stirred at room temperature for 1 h, after which time it became yellow.

Upon completion, the solvent was removed under reduced pressure and cold Et_2O was added (approx. 10 mL). The mixture was stirred for 20 min, during which time a yellow precipitate formed. The solid was collected *via* Büchner filtration, washing with small amounts of cold Et_2O. The resulting product was dried under vacuum to afford the title compound, without further purification, as a pale yellow powder (50 mg, 19%).

^{1}H NMR (400 MHz, DMSO-d6) δ: 9.30 – 9.24 (m, 1H), 8.53 (dd, *J* = 8.4, 1.1 Hz, 1H), 8.26 (dd, *J* = 7.9, 1.1 Hz, 1H), 8.03 – 7.96 (m, 2H), 7.63 (t, *J* = 8.1 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO-d6) δ: 142.6, 138.8, 138.0, 133.0, 132.2, 131.1, 131.1, 130.3, 128.5, 125.3, 124.3, 122.0, 119.1. **^{19}F NMR** (377 MHz, DMSO-d6) δ: -77.74 (s). **HRMS** (ESI) m/z: Calcd. for $C_{12}H_6BrClI$ ($[M\text{-}OTf]^+$) 390.8381; found 390.8383. *See NMR spectra*

6. References

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7. Crystallographic Data

- **2',3-dibromo-2-iodo-1,1'-biphenyl (5b)** *See procedure.*

Crystal preparation: The pure compound was dissolved in a minimum amount of *i*Pr_2O. After 3 days of slow evaporation, colourless crystals could be harvested.

The crystal structure and refinement data are given in Table S5. Crystallographic data for compound **5Ab** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC XXXXXXX. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

Figure S16: Crystal structure of **5Ab**.

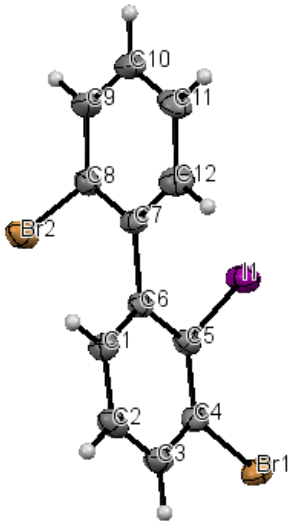


Table S5: Crystal data and structure refinement for **5Ab**.

Property	Value
Identification code	ejwddc230223
Empirical formula	$C_{12}H_7Br_2I$
Formula weight	437.90
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 7.5376(9) Å, α = 82.325(4)° b = 7.9320(9) Å, β = 74.766(4)° c = 11.5935(12) Å, γ = 65.240(3)°
Volume	607.10(12) $Å^3$
Z, Calculated density	2, 2.395 mg/m^3
Absorption coefficient	9.182 mm^{-1}

F(000)	404
Crystal size	0.160 x 0.140 x 0.100 mm
Theta range for data collection	2.829° to 27.898°
Limiting indices	-9 ≤ h ≤ 9, -10 ≤ k ≤ 9, -15 ≤ l ≤ 15
Reflections collected / unique	6603 / 2883 [R(int) = 0.0250]
Completeness to theta = 25.242	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.4594
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2883 / 0 / 136
Goodness-of-fit on F^2	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0288, wR2 = 0.0641
R indices (all data)	R1 = 0.0399, wR2 = 0.0688
Extinction coefficient	n/a
Largest diff. peak and hole	0.781 and -0.794 e·$Å^{-3}$

- **2'-bromo-3-chloro-2-iodo-1,1'-biphenyl (5c)** *See procedure*.

Crystal preparation: The pure compound was dissolved in a minimum amount of DCM. After 3 days of slow evaporation, colourless crystals could be harvested.

The crystal structure and refinement data are given in Table S6. Crystallographic data for compound **5Ac** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC XXXXXXX. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

Figure S17: Crystal structure of **5Ac**.

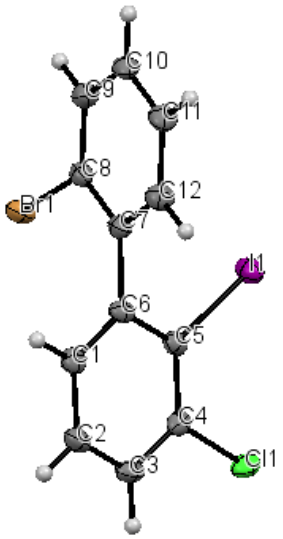


Table S6: Crystal data and structure refinement for **5Ac**.

Property	Value
Identification code	jwddcm230706
Empirical formula	$C_{12}H_7BrClI$
Formula weight	393.44
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 7.5445(3) Å, α = 81.1650(10)° b = 7.7965(3) Å, β = 73.5190(10)° c = 11.5759(4) Å, γ = 64.5410(10)°
Volume	589.13(4) $Å^3$
Z, Calculated density	2, 2.218 mg/m^3
Absorption coefficient	6.298 mm^{-1}
F(000)	368

Crystal size	0.120 x 0.100 x 0.080 mm
Theta range for data collection	2.896° to 28.034°
Limiting indices	$-9 \leq h \leq 9$, $-10 \leq k \leq 10$, $-15 \leq l \leq 15$
Reflections collected / unique	19446 / 2812 [R(int) = 0.0244]
Completeness to theta = 25.242	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6427
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2812 / 0 / 136
Goodness-of-fit on F^2	1.094
Final R indices [I>2sigma(I)]	R1 = 0.0202, wR2 = 0.0425
R indices (all data)	R1 = 0.0234, wR2 = 0.0439
Extinction coefficient	n/a
Largest diff. peak and hole	0.696 and -0.833 $e \cdot Å^{-3}$

- **2,2',3-tribromo-1,1'-biphenyl (5e)** *See procedure*.

Crystal preparation: The pure compound was dissolved in a minimum amount of *i*Pr_2O. After 3 days of slow evaporation, colourless crystals could be harvested.

The crystal structure and refinement data are given in Table S7. Crystallographic data for compound **5Ba** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC XXXXXXX. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

Figure S18: Crystal structure of **5Ba**.

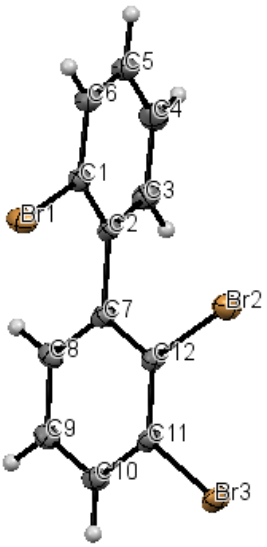


Table S7: Crystal data and structure refinement for **5Ba**.

Property	Value
Identification code	ejwddc230712
Empirical formula	$C_{12}H_7Br_3$
Formula weight	390.91
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 7.4022(3) Å, α = 83.9920(10)° b = 7.8572(3) Å, β = 76.4460(10)° c = 11.3380(4) Å, γ = 65.0730(10)°
Volume	581.33(4) $Å^3$
Z, Calculated density	2, 2.233 mg/m^3
Absorption coefficient	10.370 mm^{-1}
F(000)	368

Crystal size	0.160 x 0.140 x 0.100 mm
Theta range for data collection	2.859° to 27.928°
Limiting indices	-9 ≤ h ≤ 9, -10 ≤ k ≤ 10, -14 ≤ l ≤ 14
Reflections collected / unique	24581 / 2772 [R(int) = 0.0469]
Completeness to theta = 25.242	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.4154
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2772 / 0 / 136
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0236, wR2 = 0.0550
R indices (all data)	R1 = 0.0287, wR2 = 0.0574
Extinction coefficient	n/a
Largest diff. peak and hole	0.853 and -0.835 e·$Å^{-3}$

- **1-chloro-9*H*-fluoren-9-one (16)** *See procedure*.

  Crystal preparation: The pure compound was dissolved in a minimum amount of DCM. After 3 days of slow evaporation, orange crystals could be harvested.

  The crystal structure and refinement data are given in Table S8. Crystallographic data for compound **17** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC XXXXXXX. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

Figure S19: Crystal structure of **17**.

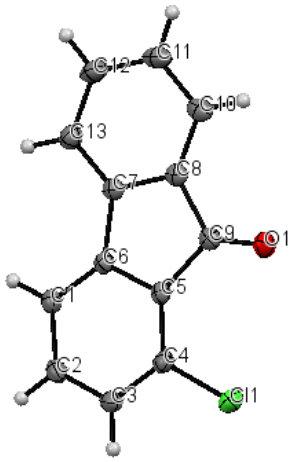


Table S8: Crystal data and structure refinement for **17**.

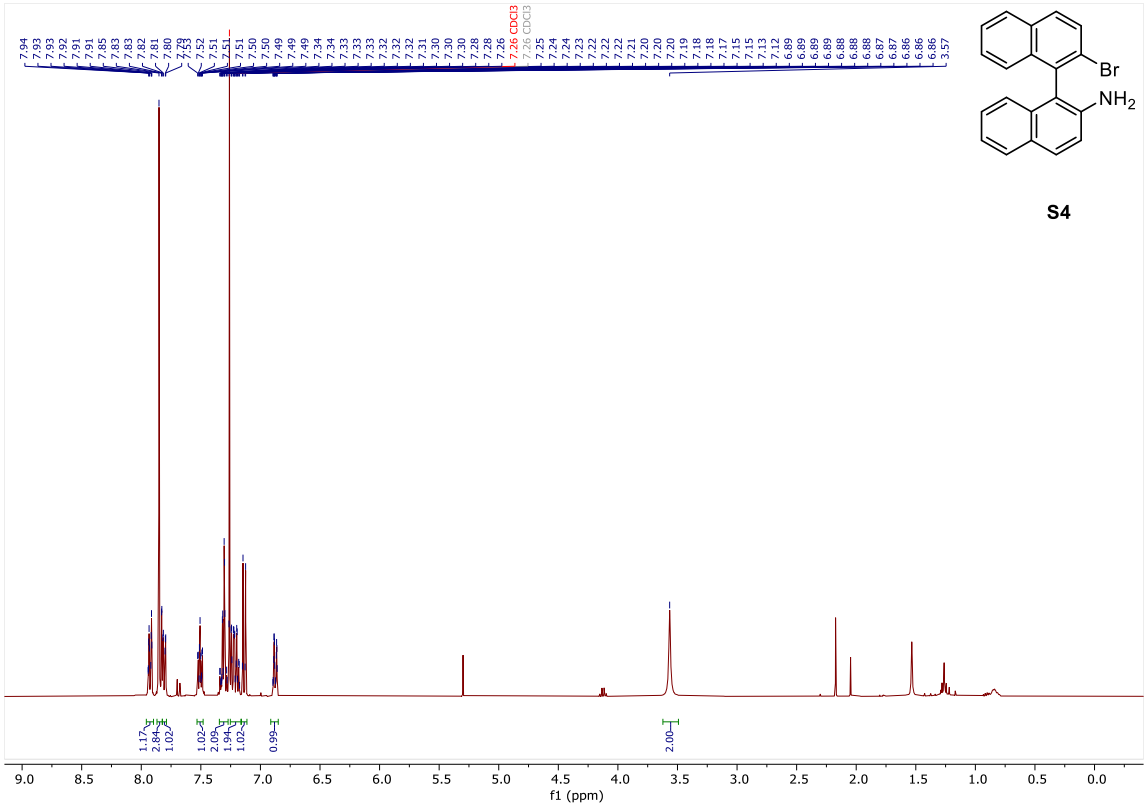
Property	Value
Identification code	ejwddc230704
Empirical formula	$C_{13}H_7ClO$
Formula weight	214.64
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 7.3449(2) Å, α = 90° b = 15.5390(3) Å, β = 104.8270(10)° c = 8.8357(2) Å, γ = 90°
Volume	974.86(4) Å³
Z, Calculated density	4, 1.462 Mg/m³
Absorption coefficient	0.355 mm^{-1}
F(000)	440

Crystal size	0.180 x 0.160 x 0.140 mm
Theta range for data collection	2.622° to 27.898°
Limiting indices	-9 ≤ h ≤ 9, -20 ≤ k ≤ 18, -11 ≤ l ≤ 11
Reflections collected / unique	19777 / 2335 [R(int) = 0.0233]
Completeness to theta = 25.242	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.7059
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2335 / 0 / 136
Goodness-of-fit on F^2	1.059
Final R indices [I>2sigma(I)]	R1 = 0.0308, wR2 = 0.0850
R indices (all data)	R1 = 0.0324, wR2 = 0.0865
Extinction coefficient	n/a
Largest diff. peak and hole	0.603 and -0.284 $e \cdot Å^{-3}$

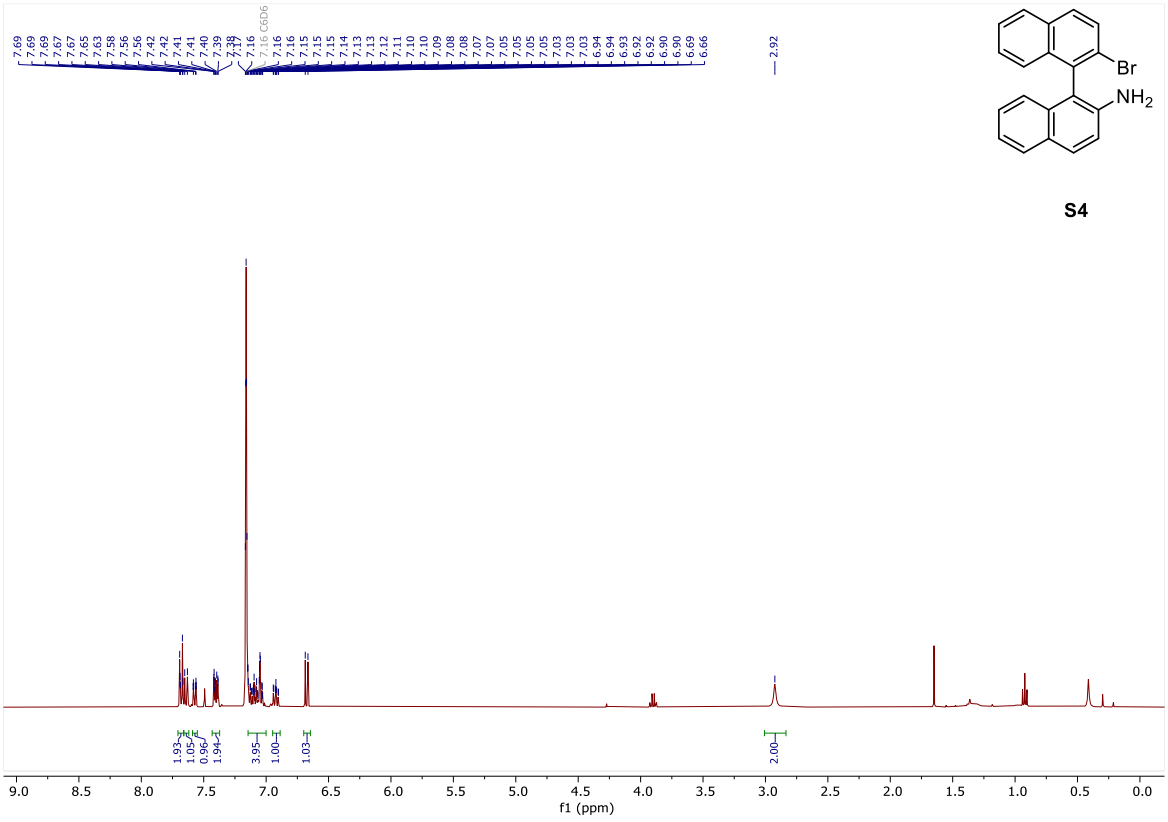
8. Spectroscopic Data

2'-bromo-[1,1'-binaphthalen]-2-amine (S4) *See procedure*.

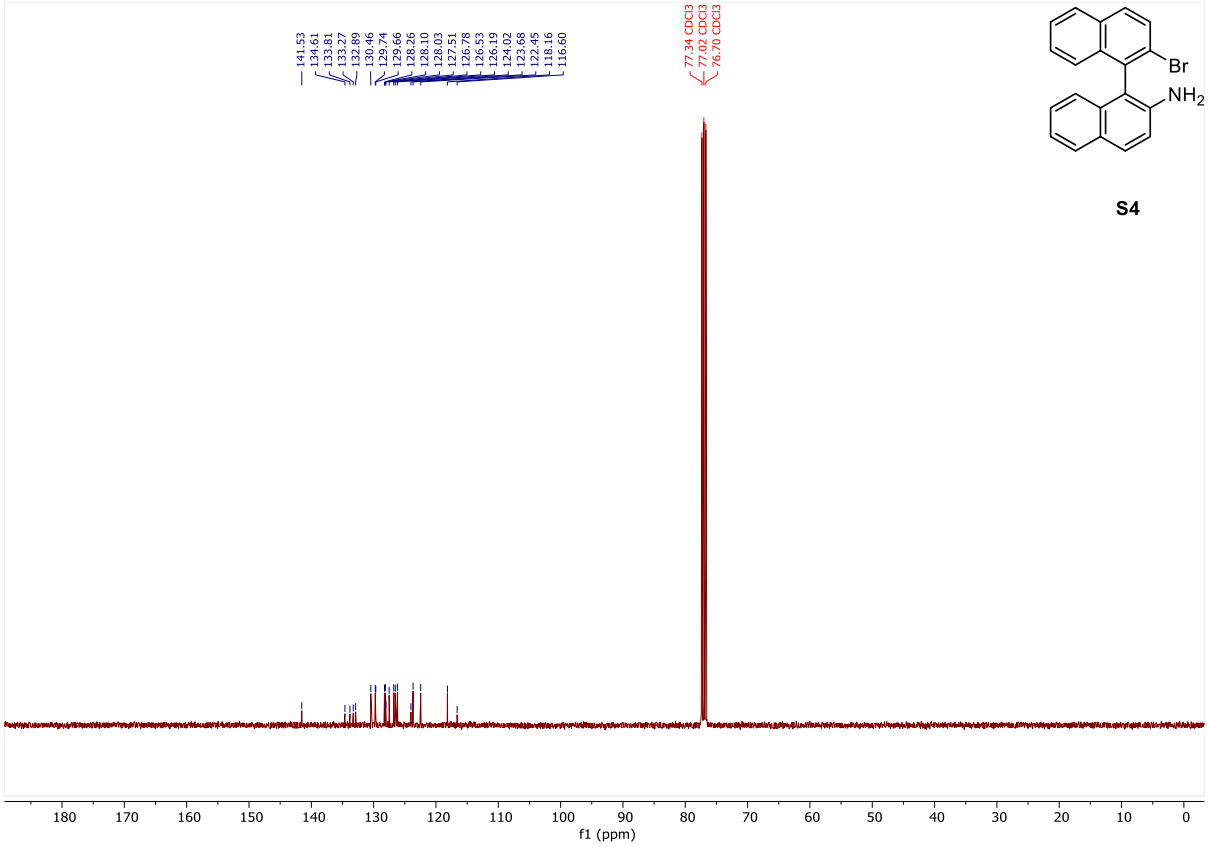
^{1}H NMR (400 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, C_6D_6)

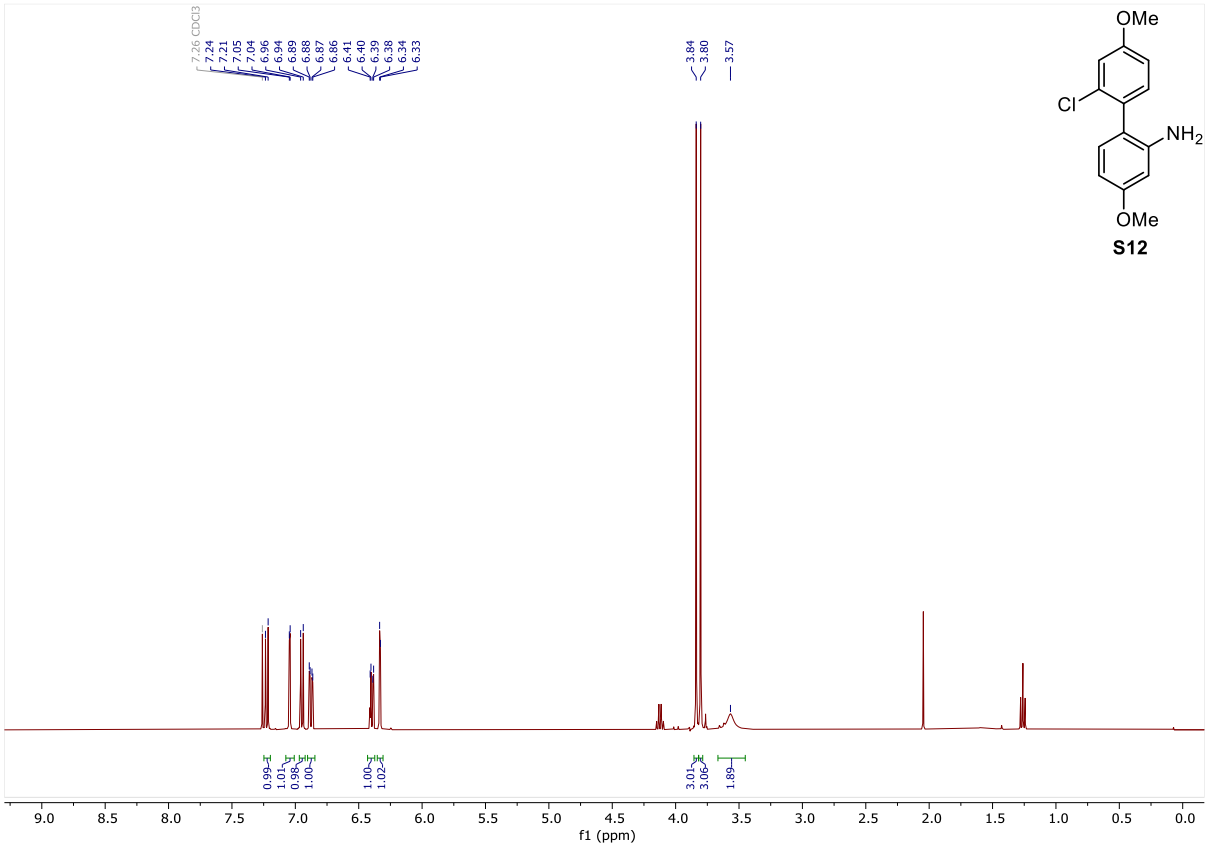


^{13}C NMR (101 MHz, $CDCl_3$)

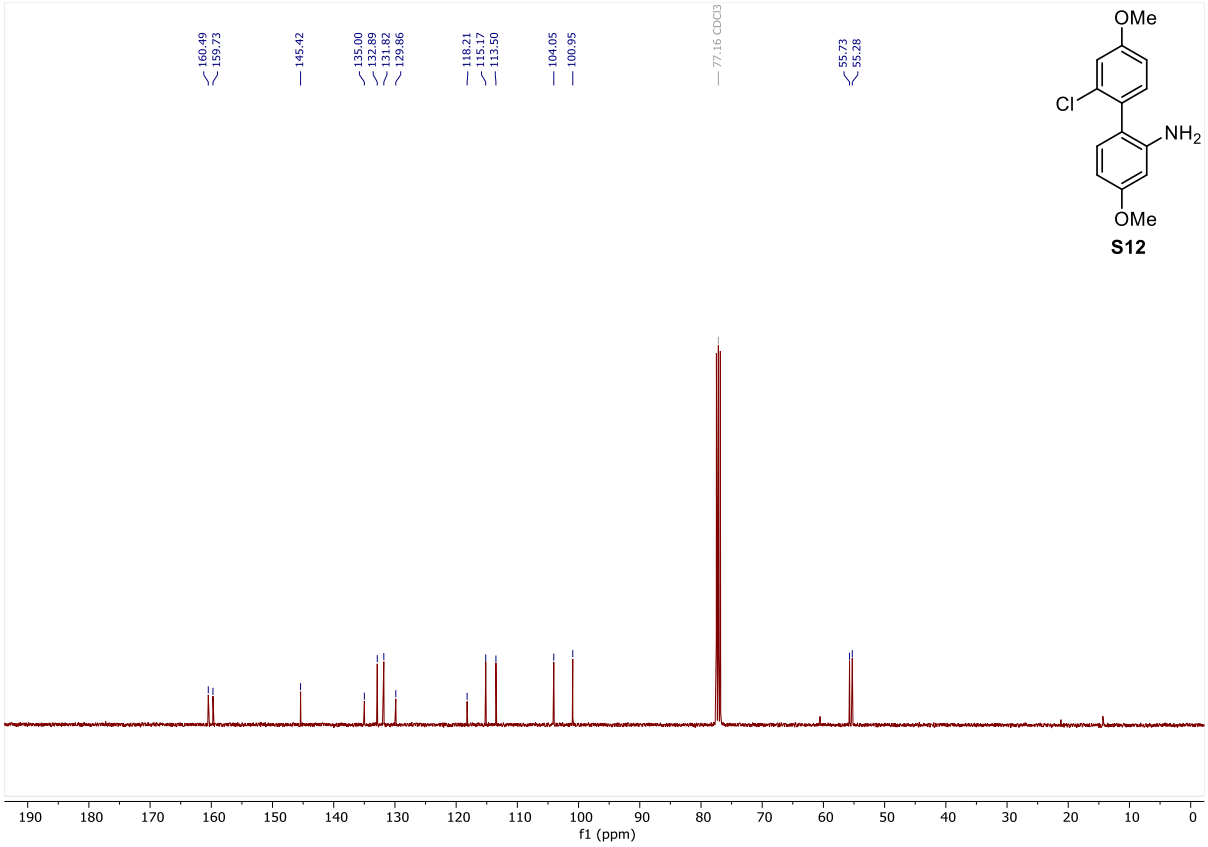


2'-chloro-4,4'-dimethoxy-[1,1'-biphenyl]-2-amine (S12) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

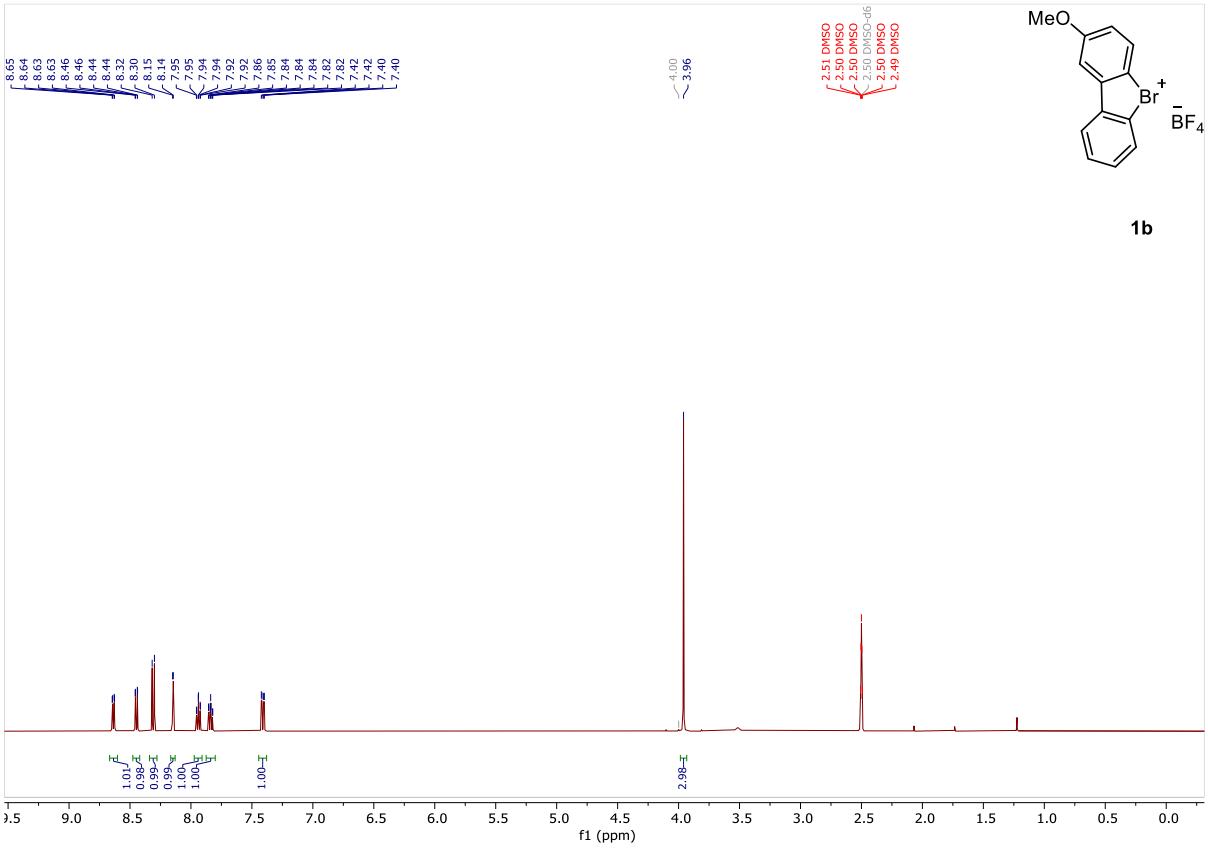


^{13}C NMR (101 MHz, $CDCl_3$)

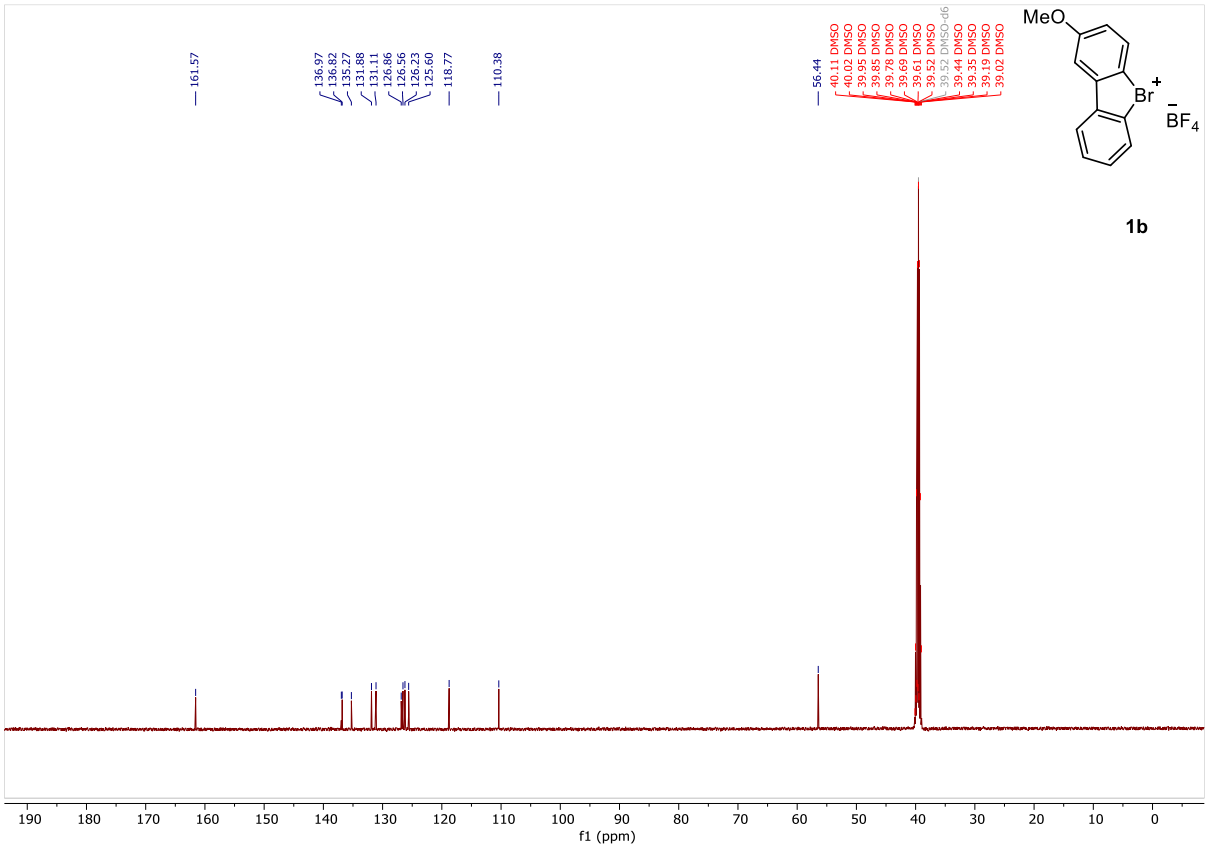


2-methoxydibenzo[*b,d*]bromol-5-ium tetrafluoroborate (1b) *See procedure*.

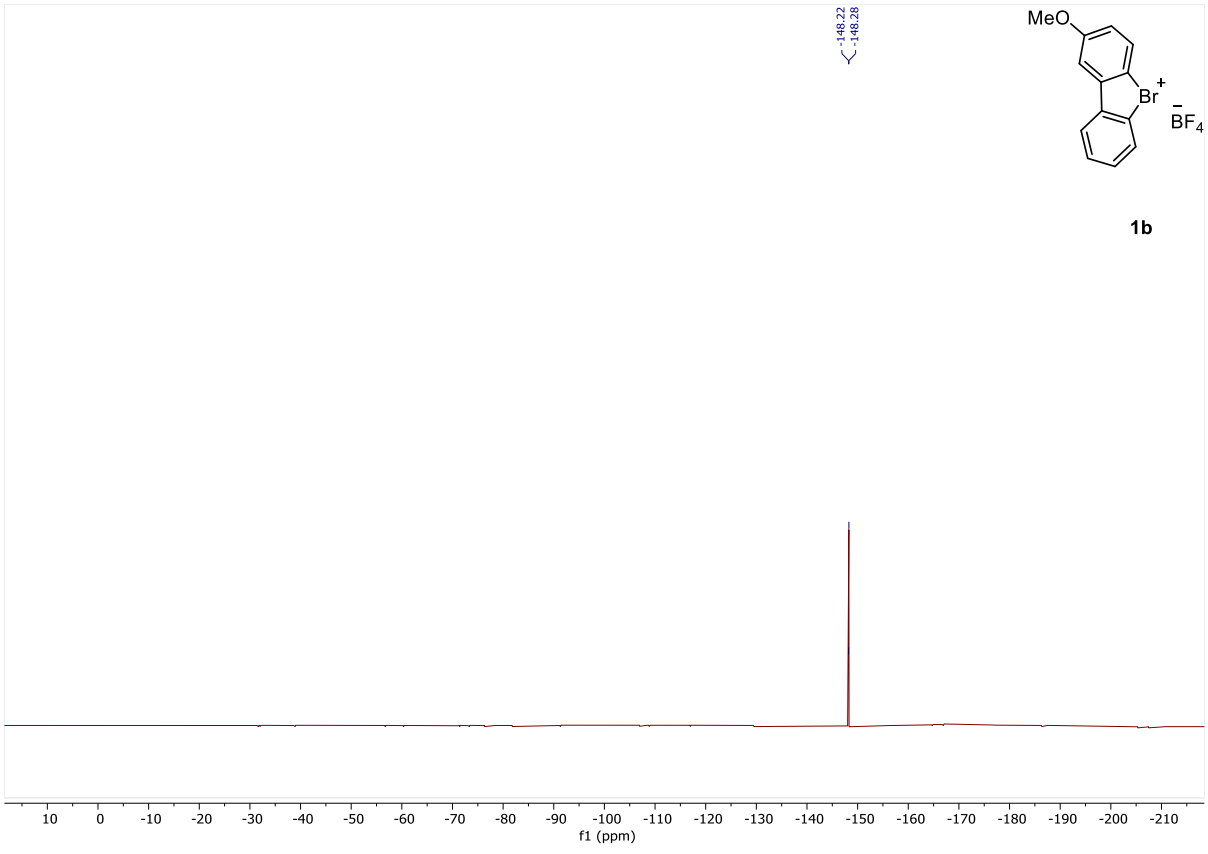
^{1}H NMR (400 MHz, DMSO-d6)



^{13}C NMR (101 MHz, DMSO-d6)

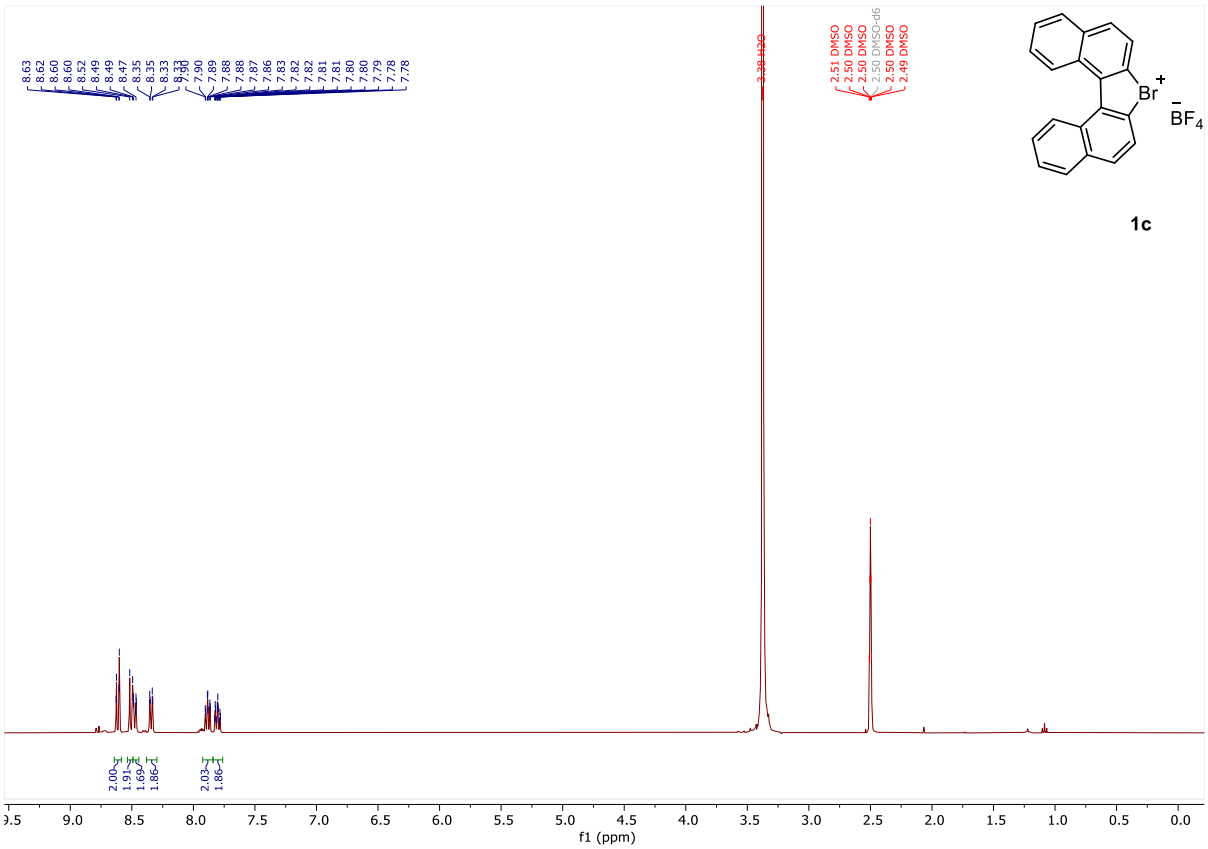


^{19}F NMR (377 MHz, DMSO-d6)

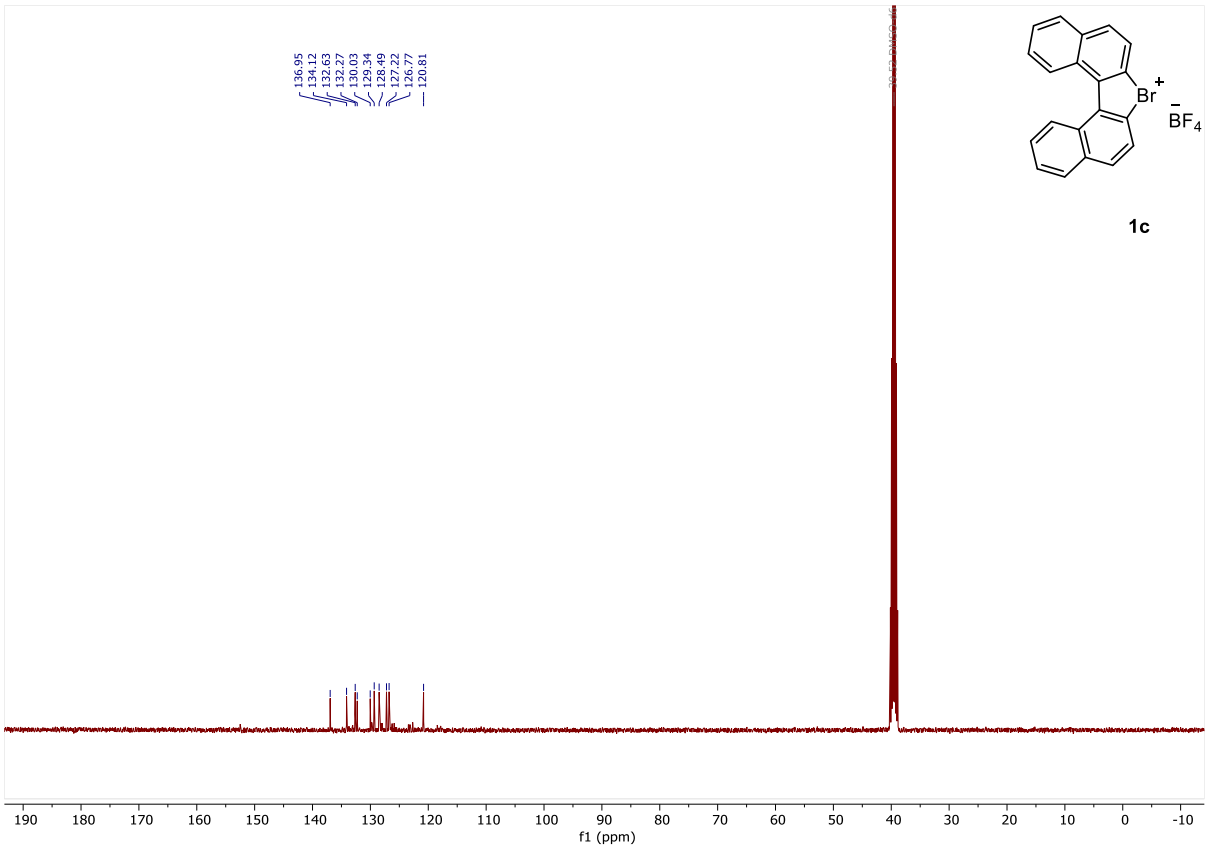


dinaphtho[2,1-*b*:1',2'-*d*]bromol-7-ium tetrafluoroborate (1c) *See procedure*.

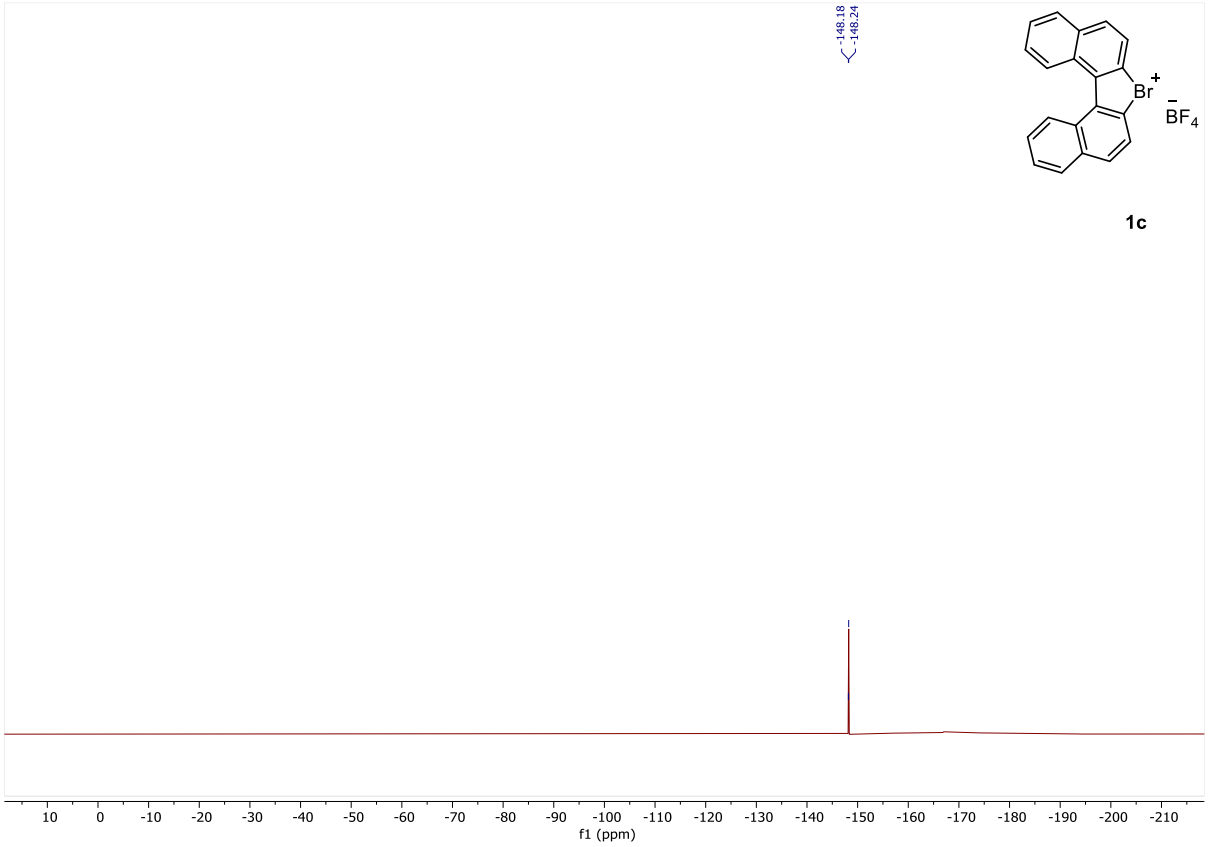
^{1}H NMR (400 MHz, DMSO-d6)



^{13}C NMR (101 MHz, DMSO-d6)

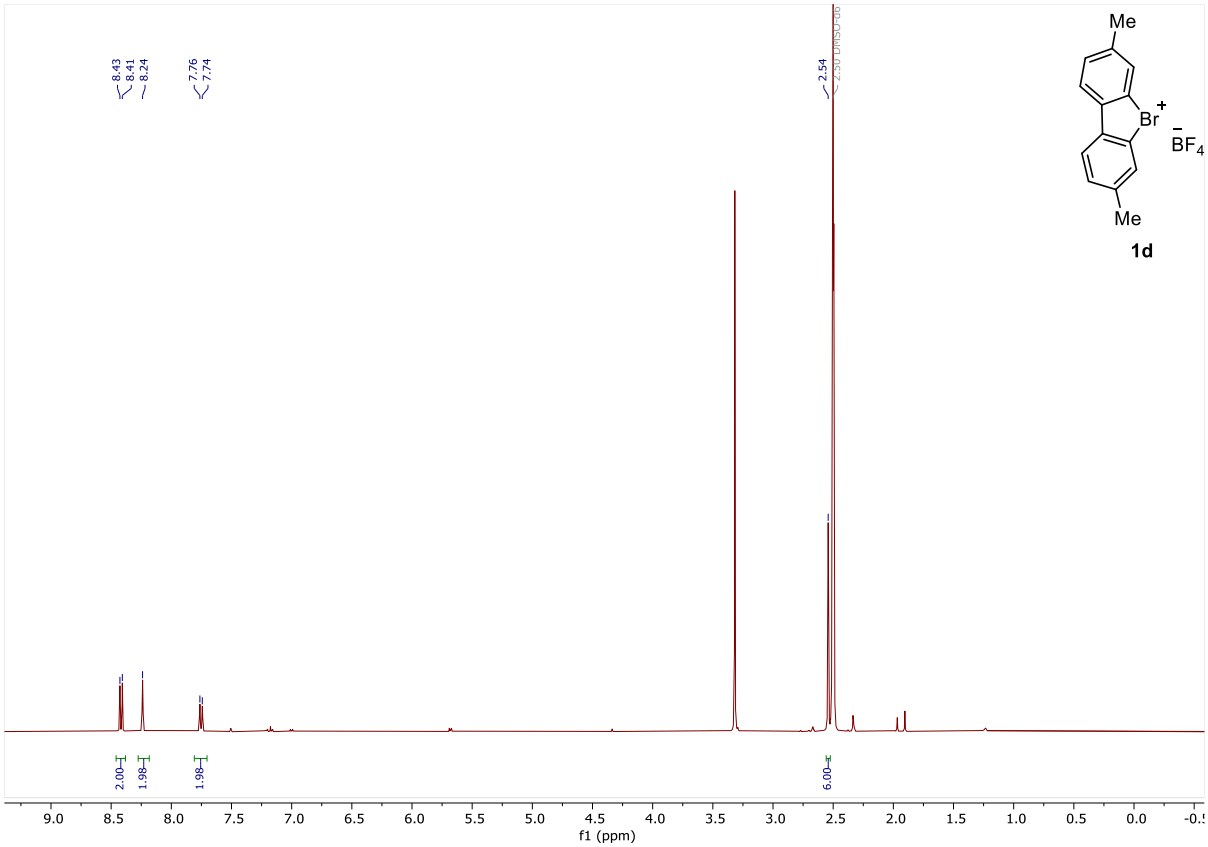


^{19}F NMR (377 MHz, DMSO-d6)

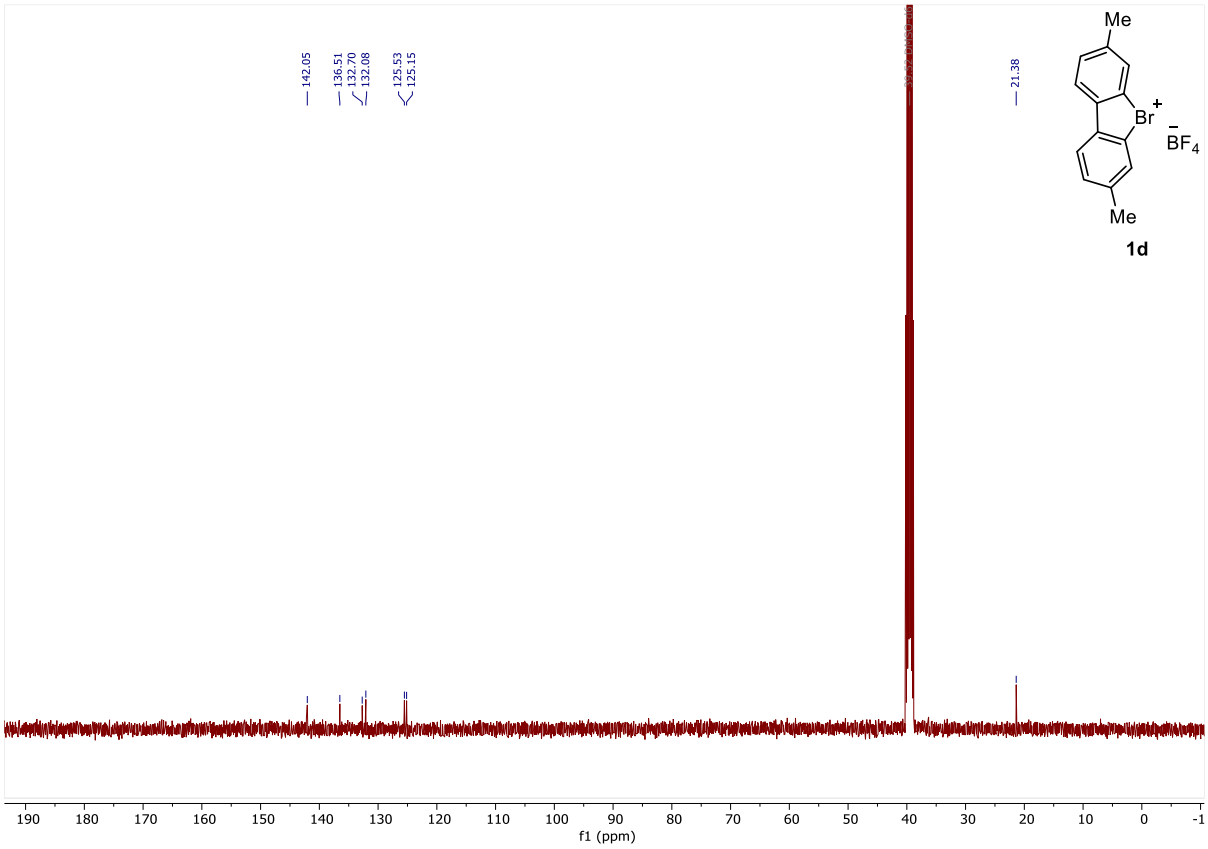


3,7-dimethyldibenzo[*b,d*]bromol-5-ium tetrafluoroborate (1d) *See procedure*.

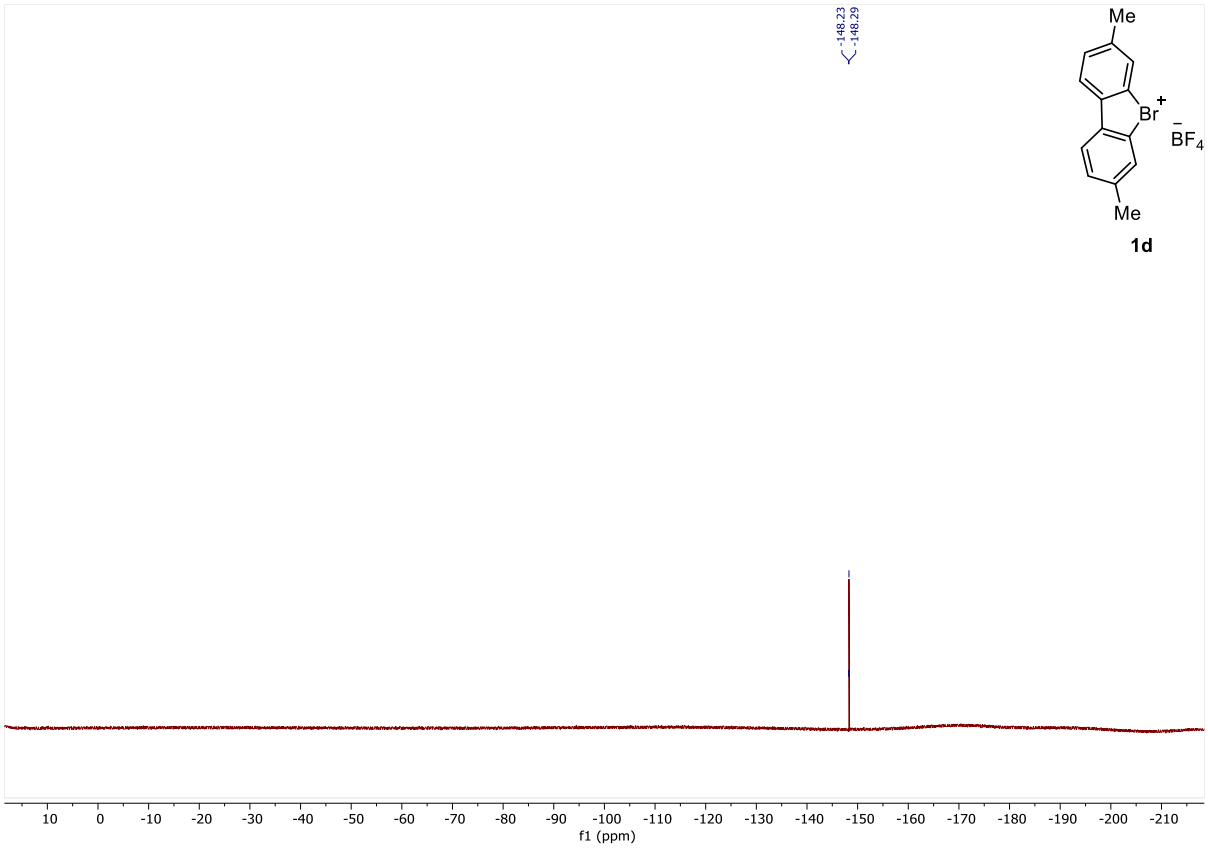
^{1}H NMR (400 MHz, DMSO-d6)



^{13}C NMR (101 MHz, DMSO-d6)

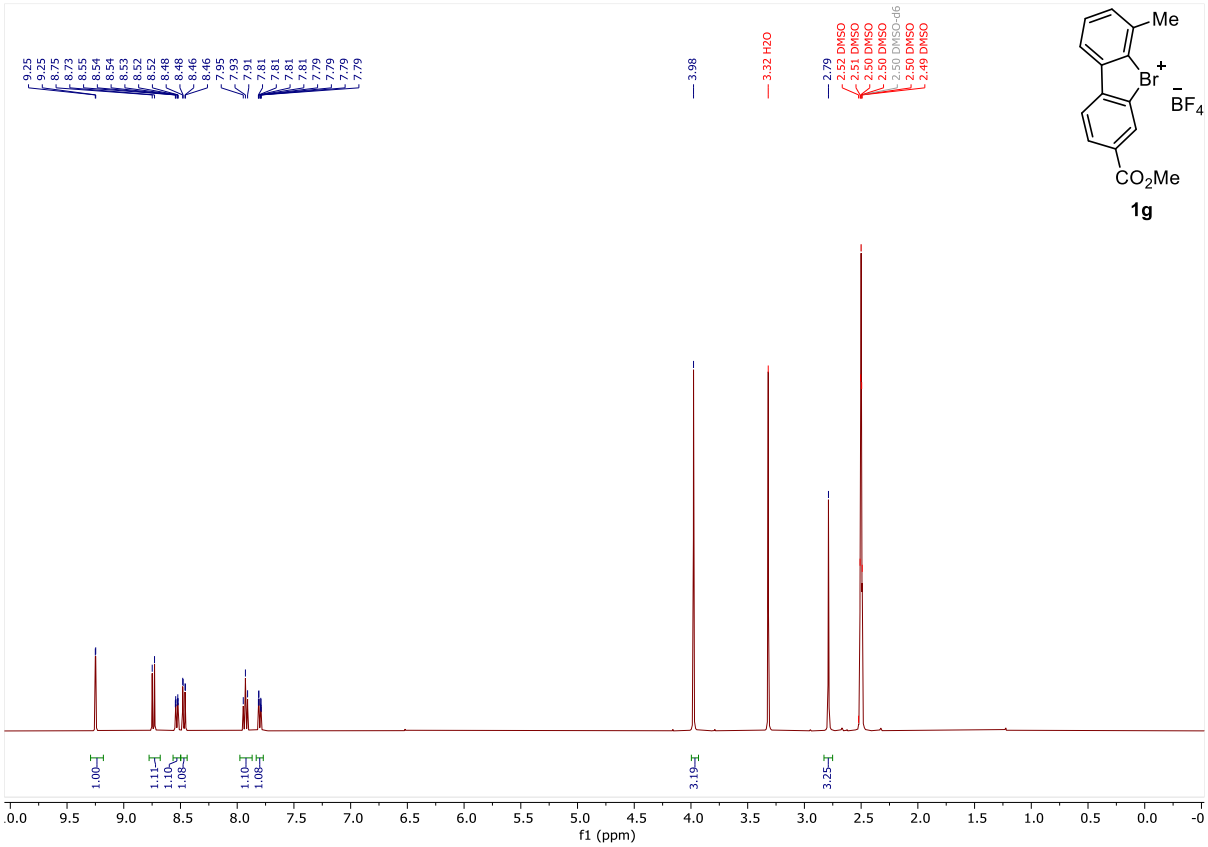


^{19}F NMR (377 MHz, DMSO-d6)

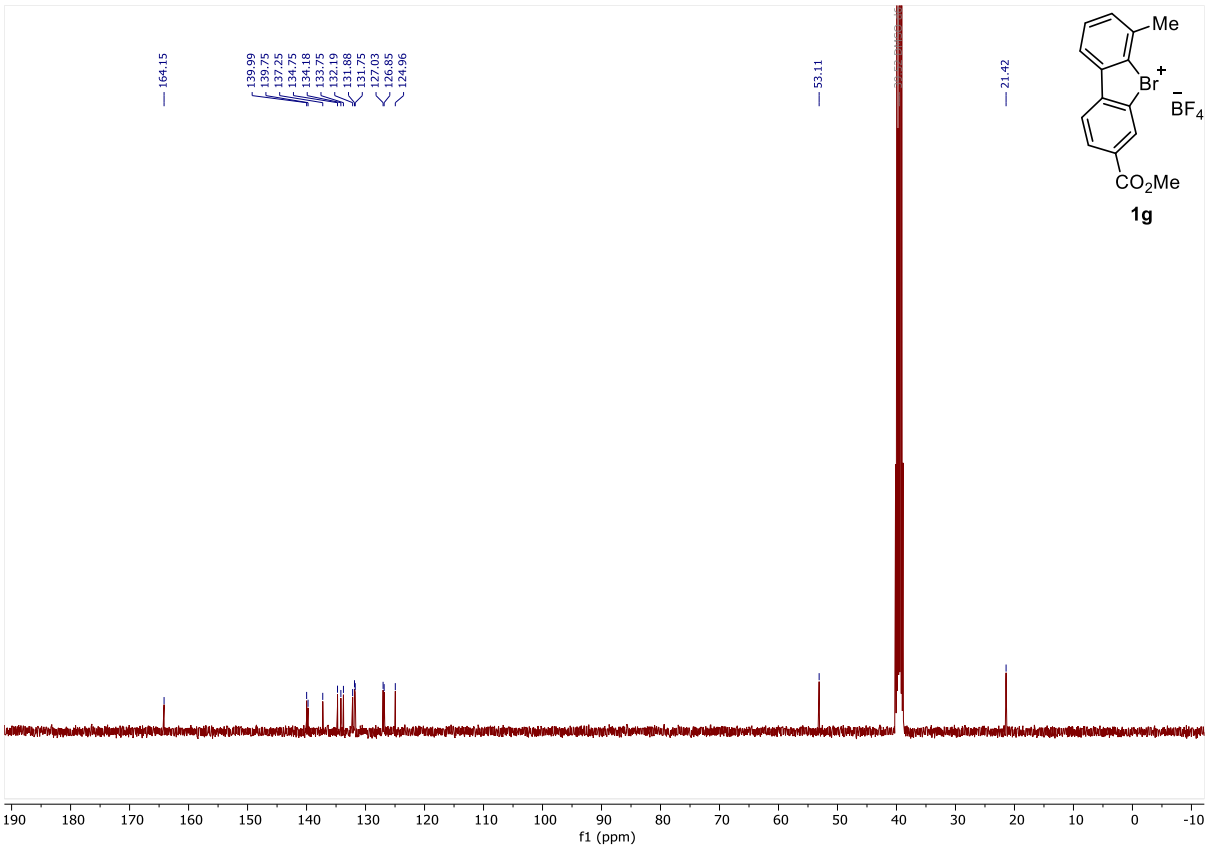


3-(methoxycarbonyl)-6-methyldibenzo[*b,d*]bromol-5-ium tetrafluoroborate (1g) *See procedure*.

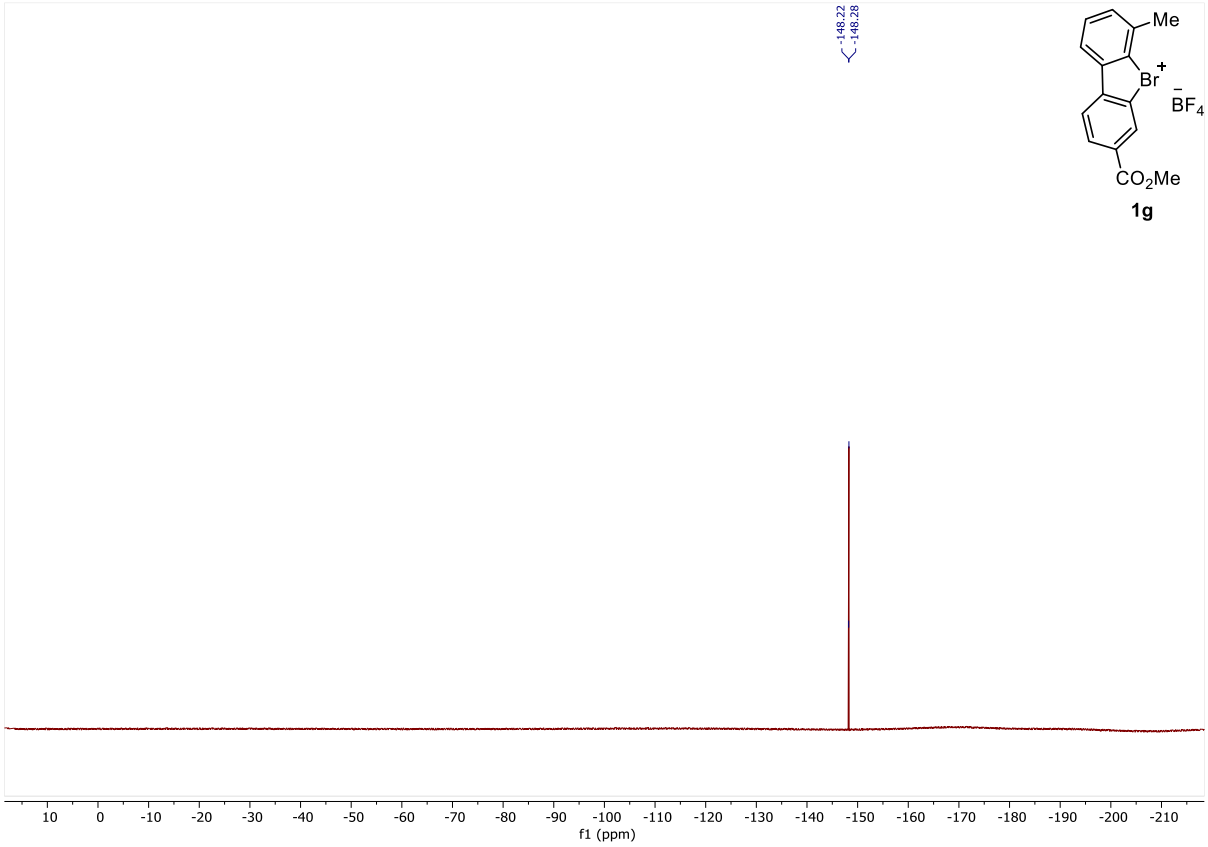
^{1}H NMR (400 MHz, DMSO-d6)



^{13}C NMR (101 MHz, DMSO-d6)

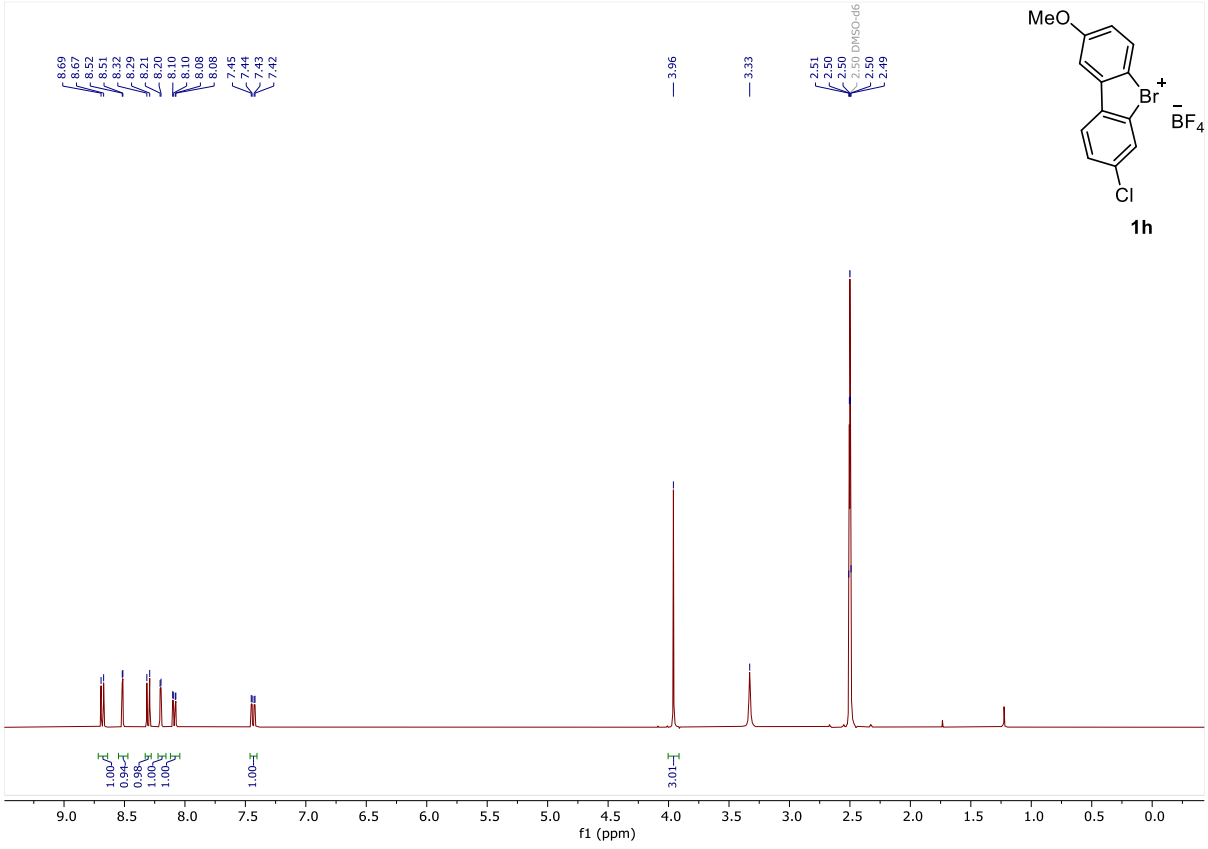


^{19}F NMR (377 MHz, DMSO-d6)

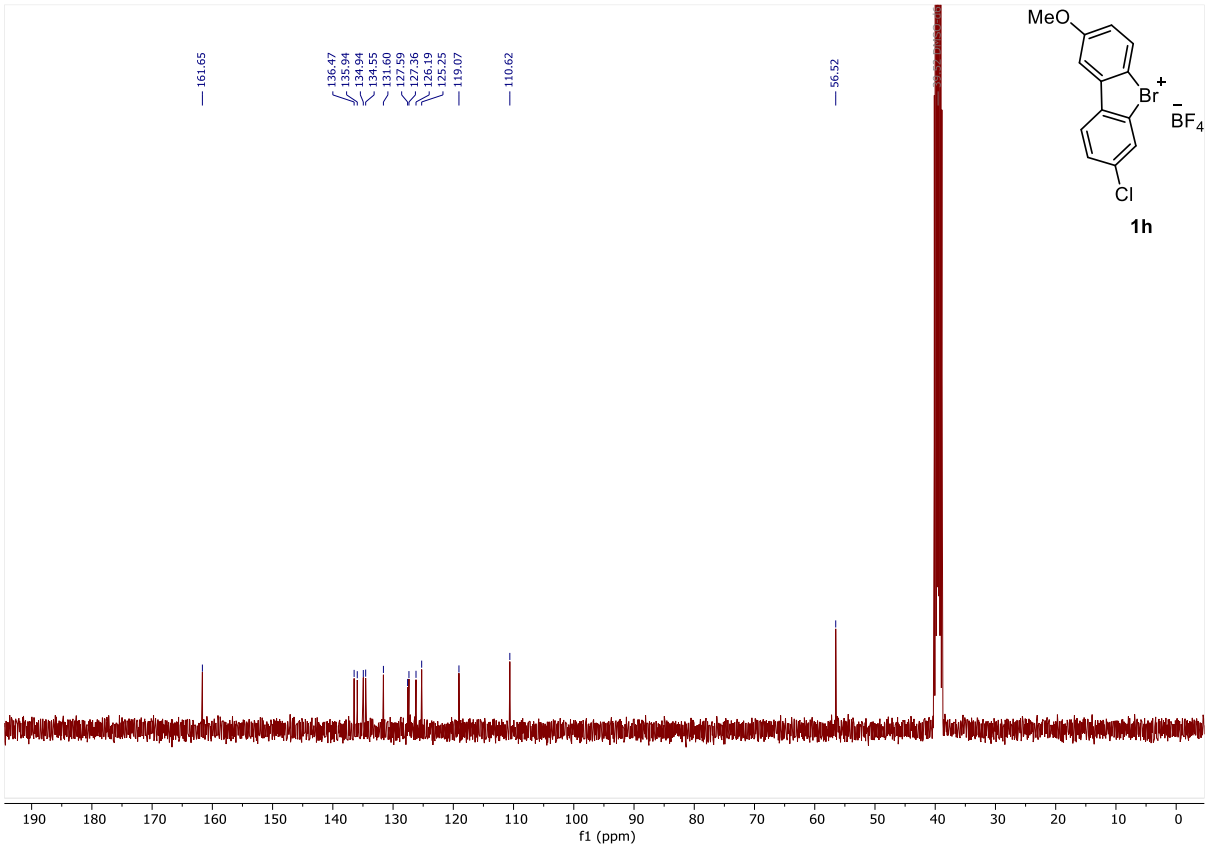


7-chloro-2-methoxydibenzo[*b,d*]bromol-5-ium tetrafluoroborate (1h) *See procedure*.

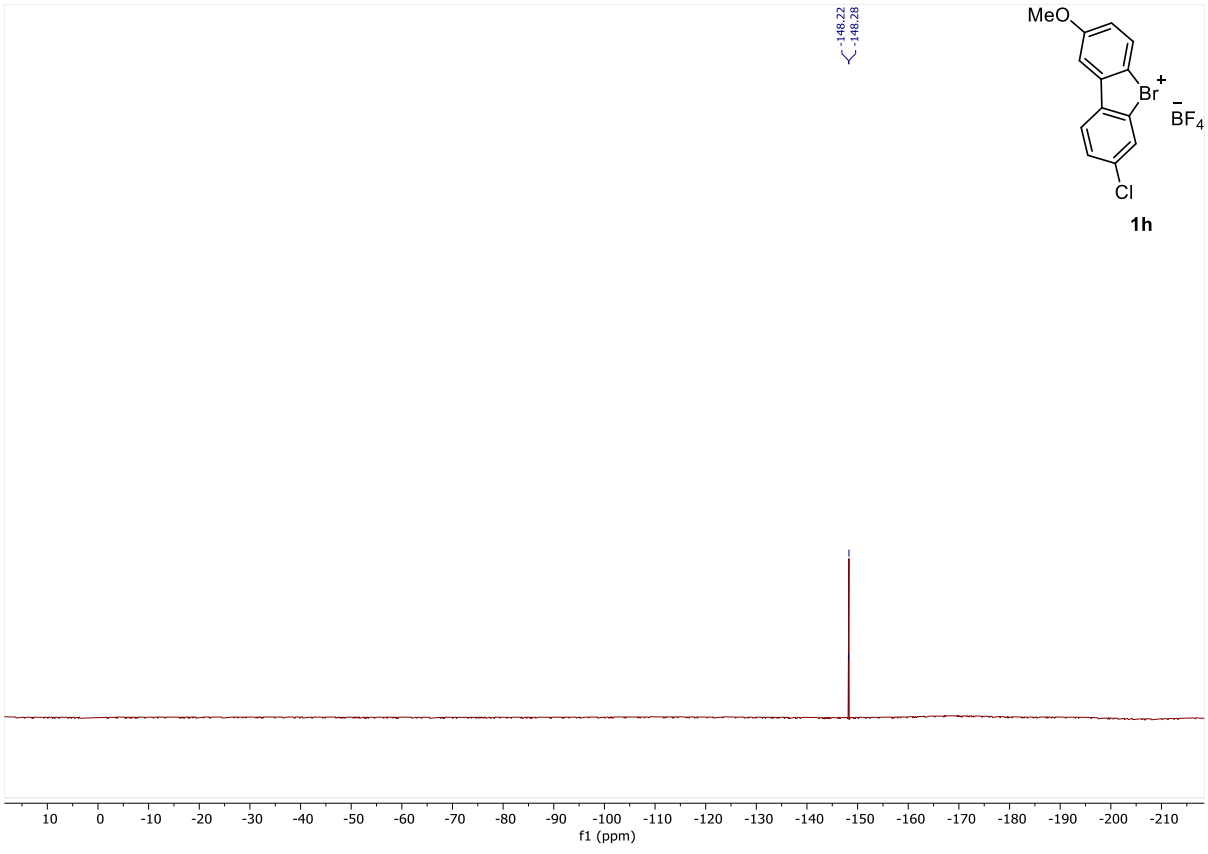
^{1}H NMR (400 MHz, DMSO-d6)



^{13}C NMR (101 MHz, DMSO-d6)

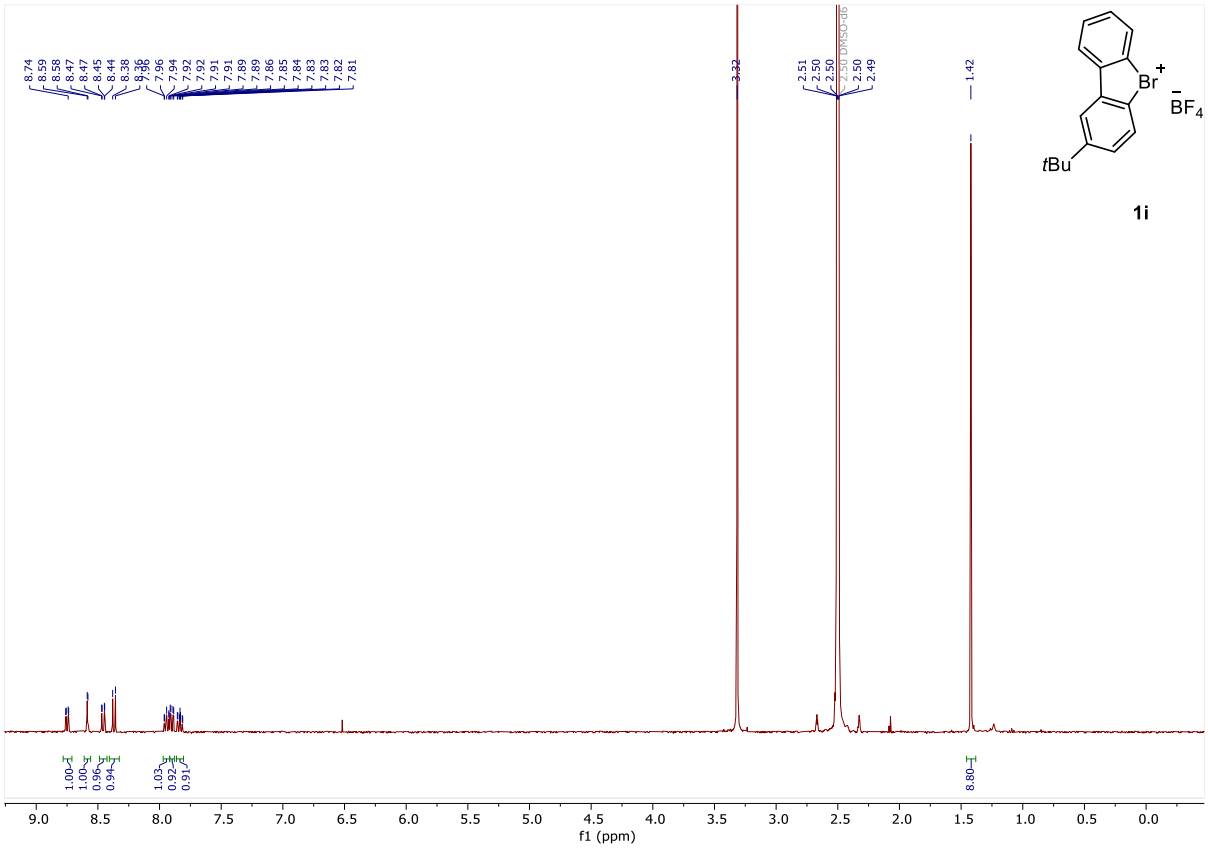


^{19}F NMR (377 MHz, DMSO-d6)

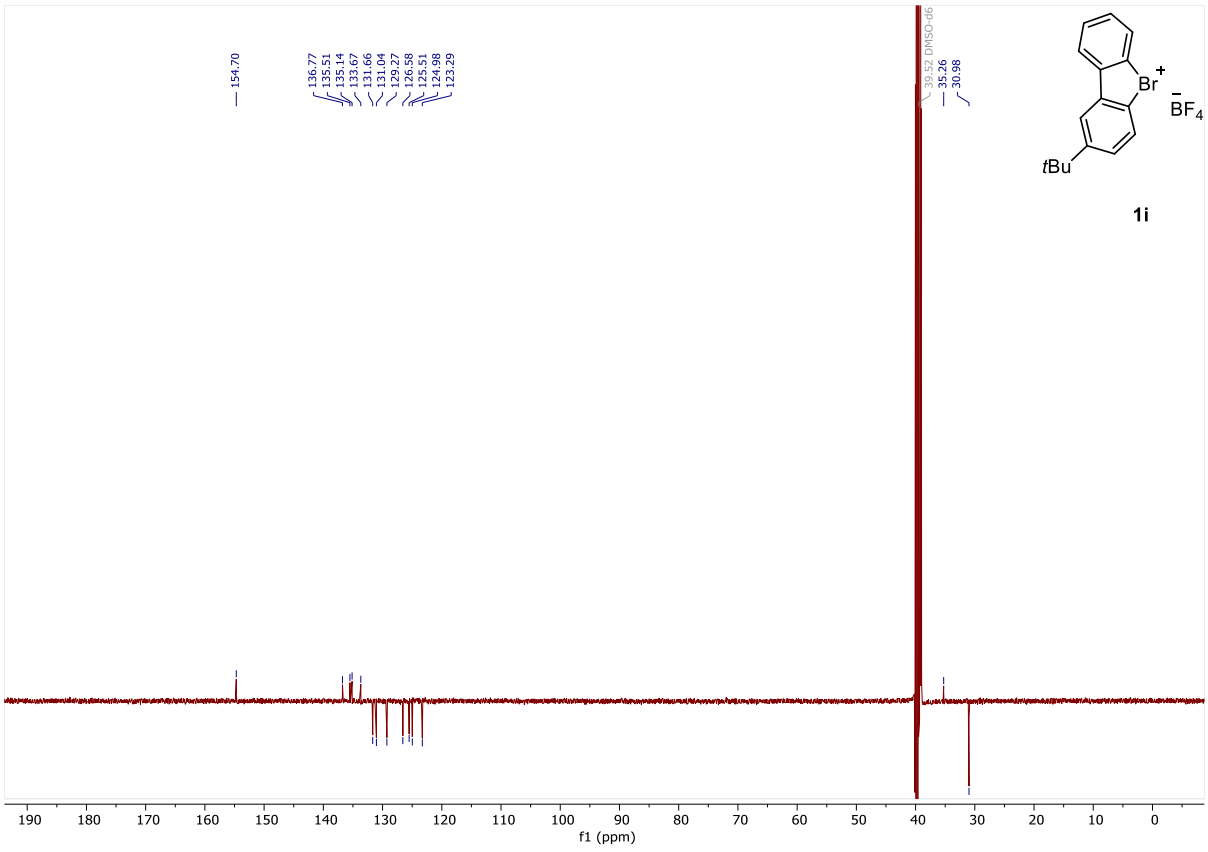


2-(*tert*-butyl)dibenzo[*b,d*]bromol-5-ium tetrafluoroborate (1i) *See procedure*.

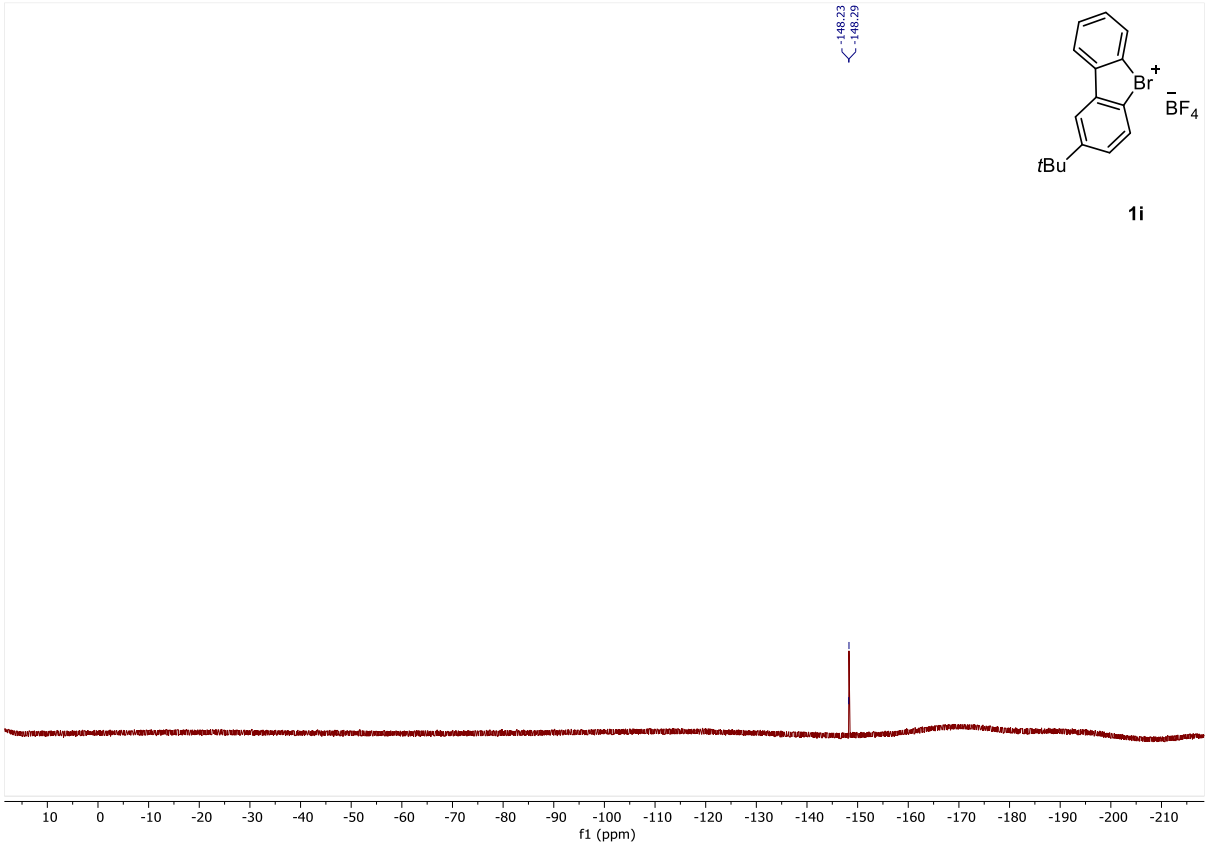
^{1}H NMR (400 MHz, DMSO-d6)



^{13}C NMR APT (126 MHz, DMSO-d6)

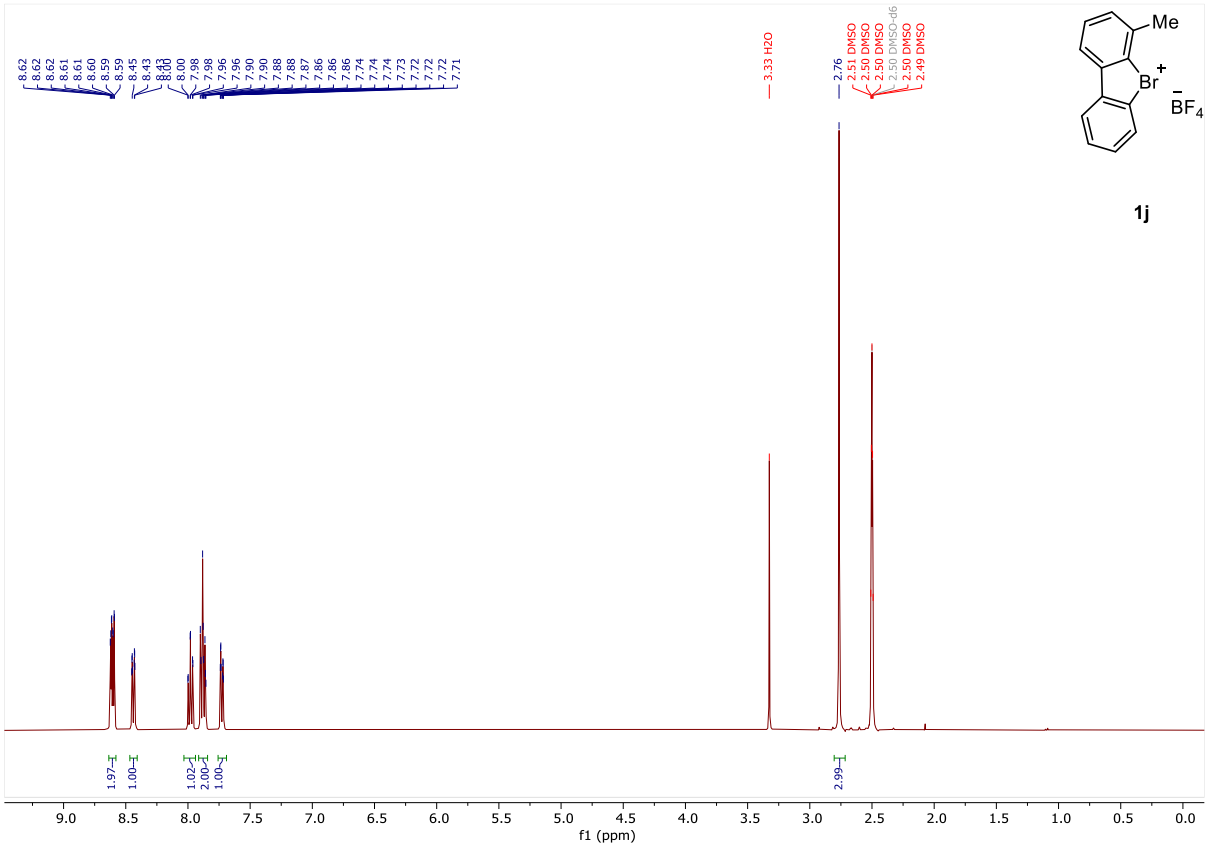


^{19}F NMR (377 MHz, DMSO-d6)

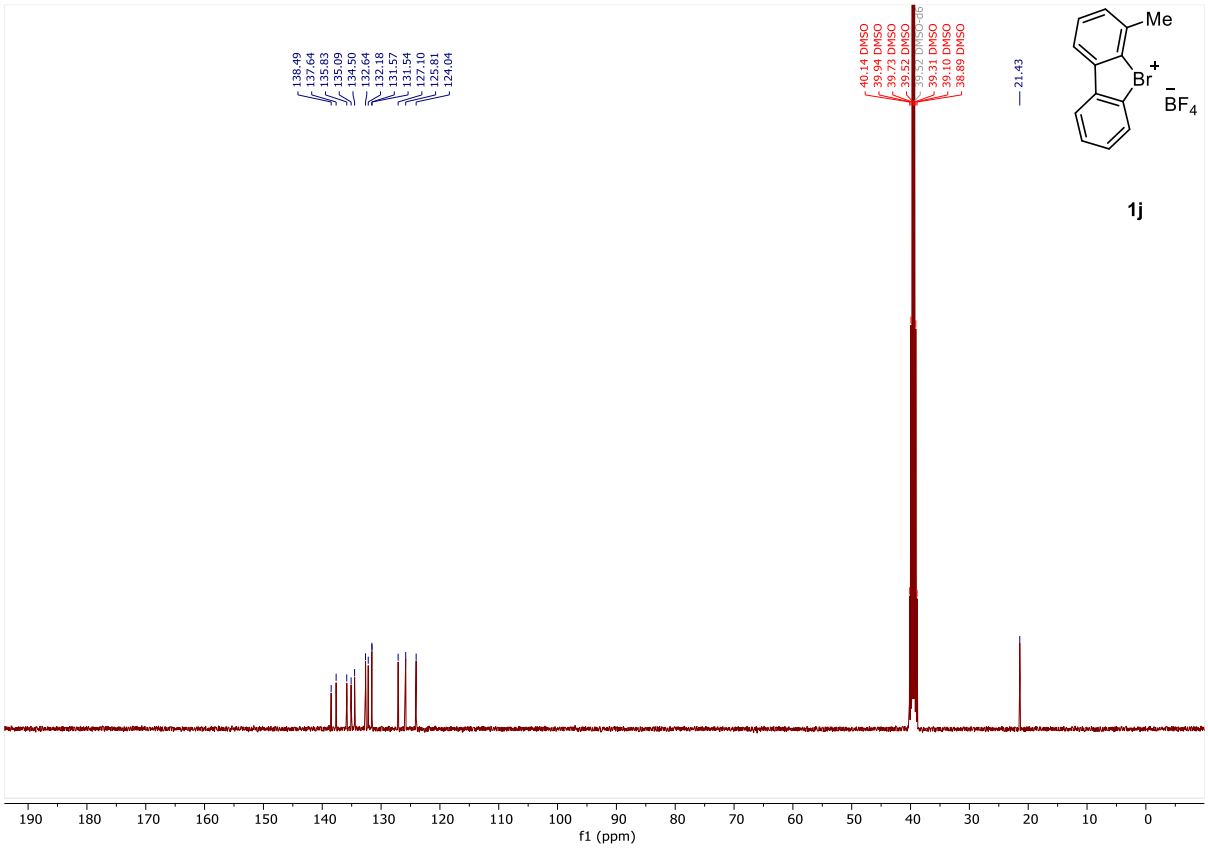


4-methyldibenzo[*b,d*]bromol-5-ium tetrafluoroborate (1j) *See procedure*.

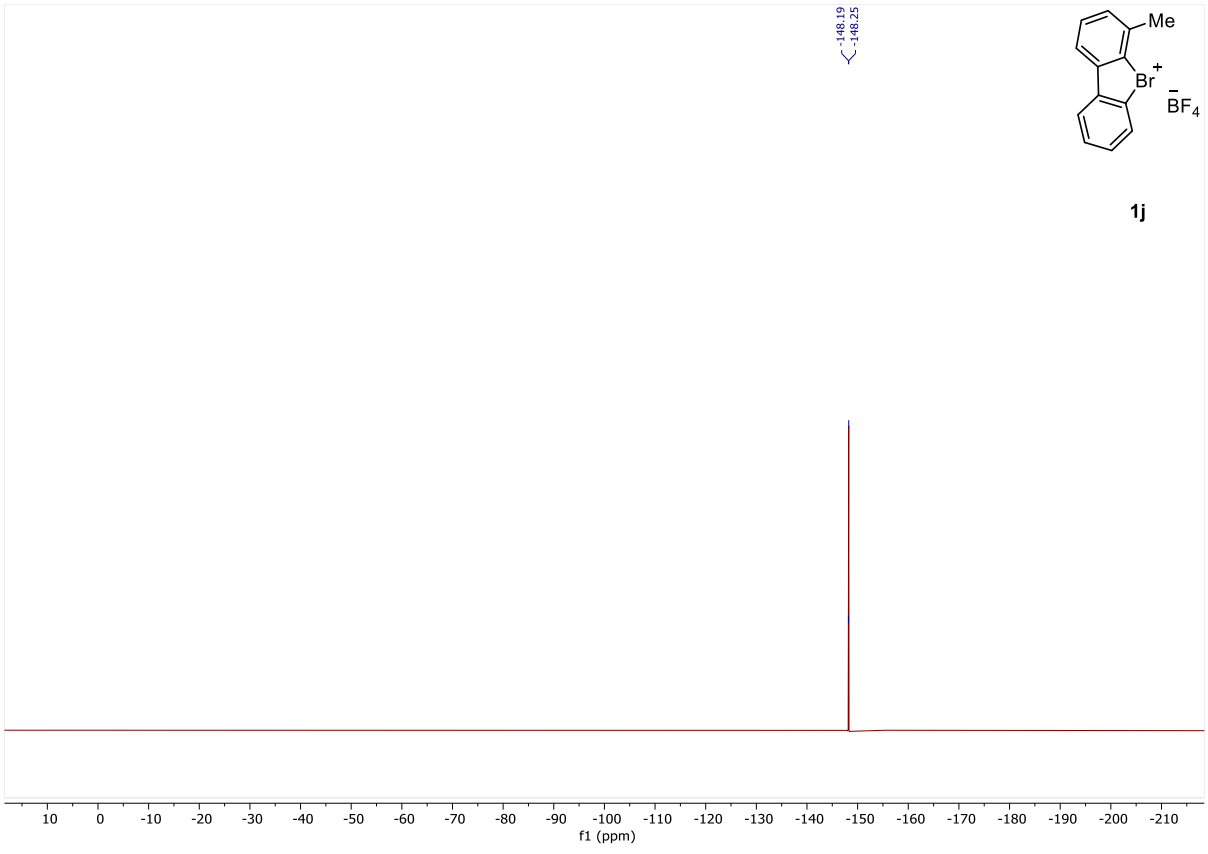
^{1}H NMR (400 MHz, DMSO-d6)



^{13}C NMR (101 MHz, DMSO-d6)

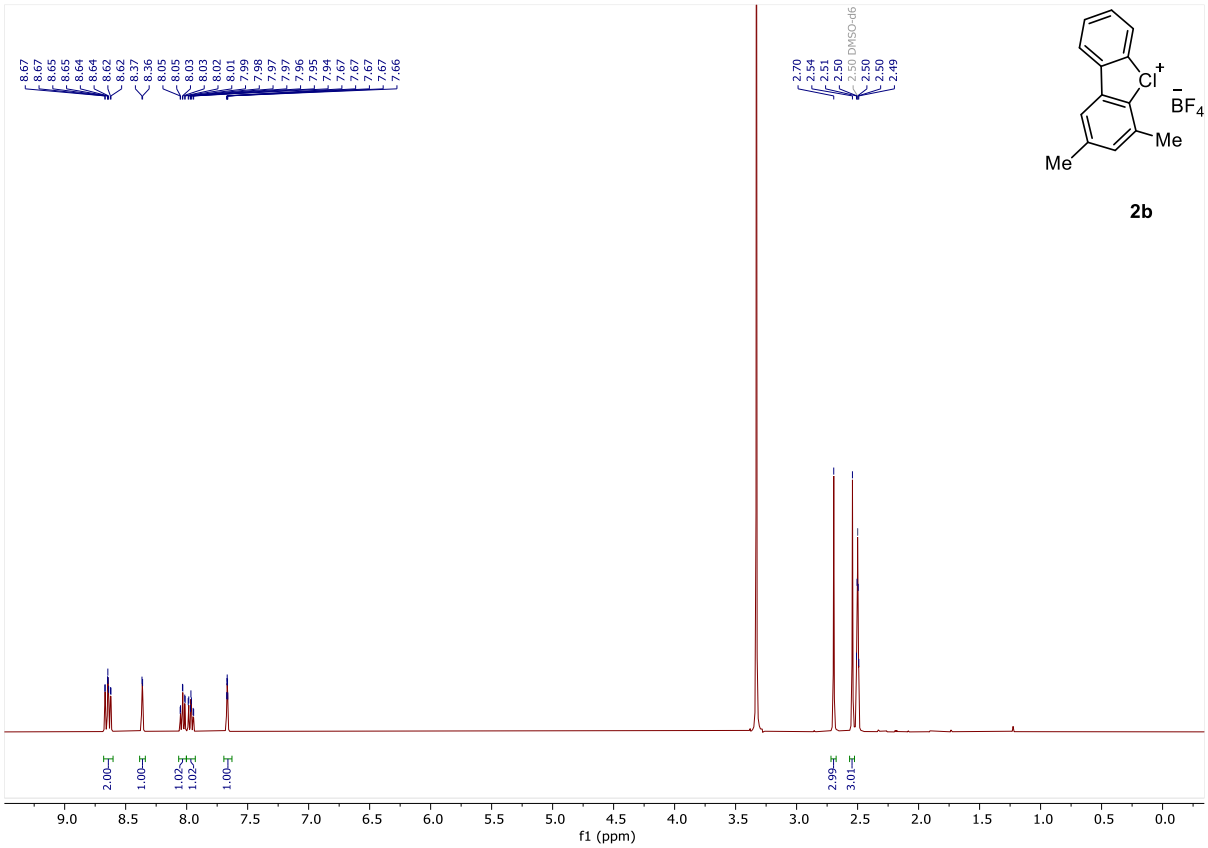


^{19}F NMR (377 MHz, DMSO-d6)

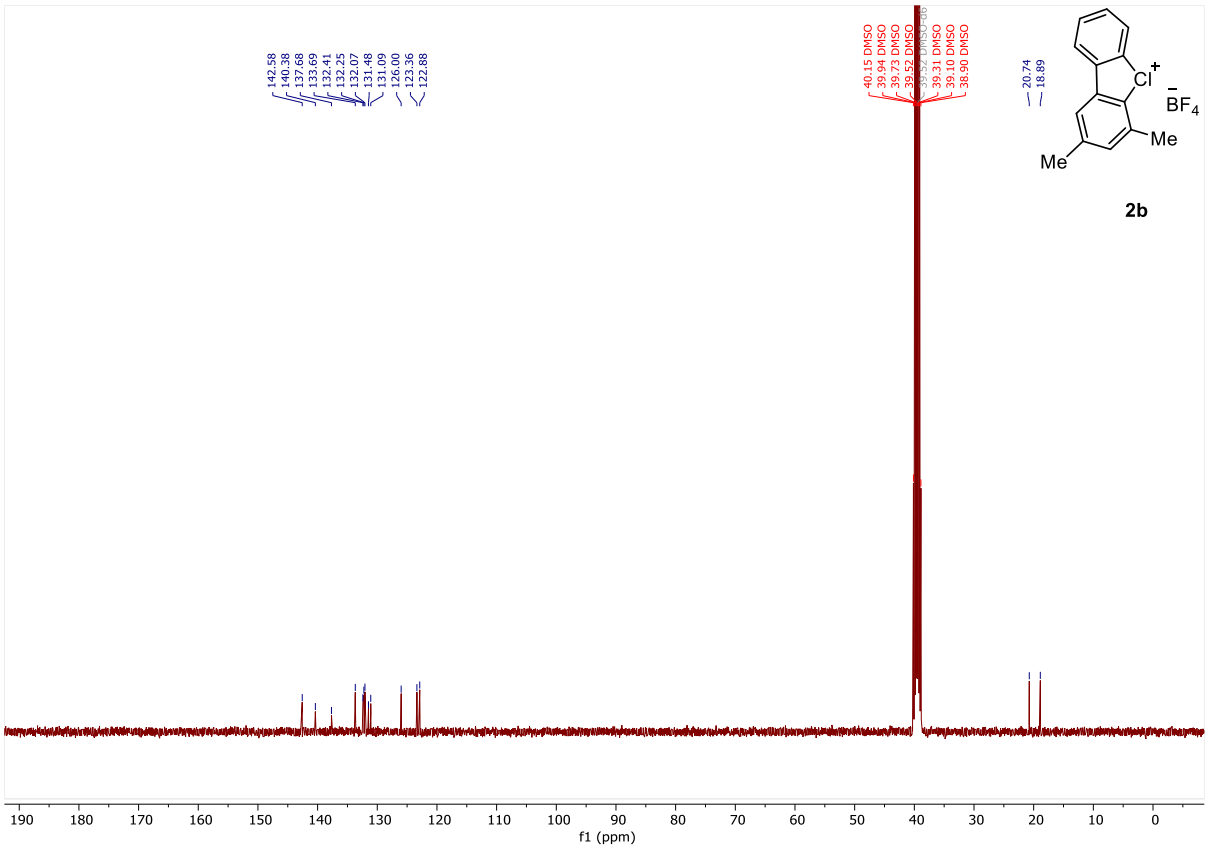


2,4-dimethyldibenzo[*b,d*]chlorol-5-ium tetrafluoroborate (2b) *See procedure*.

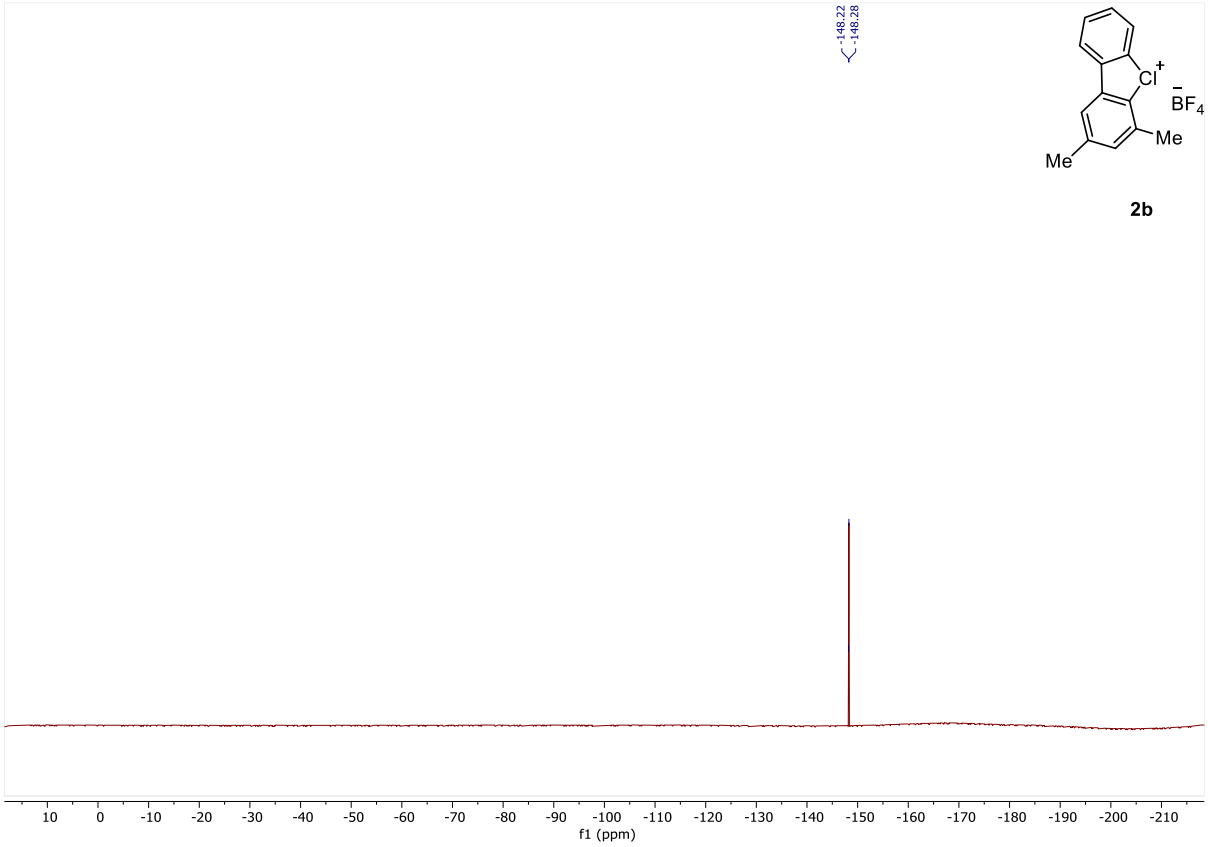
^{1}H NMR (400 MHz, DMSO-d6)



^{13}C NMR (101 MHz, DMSO-d6)

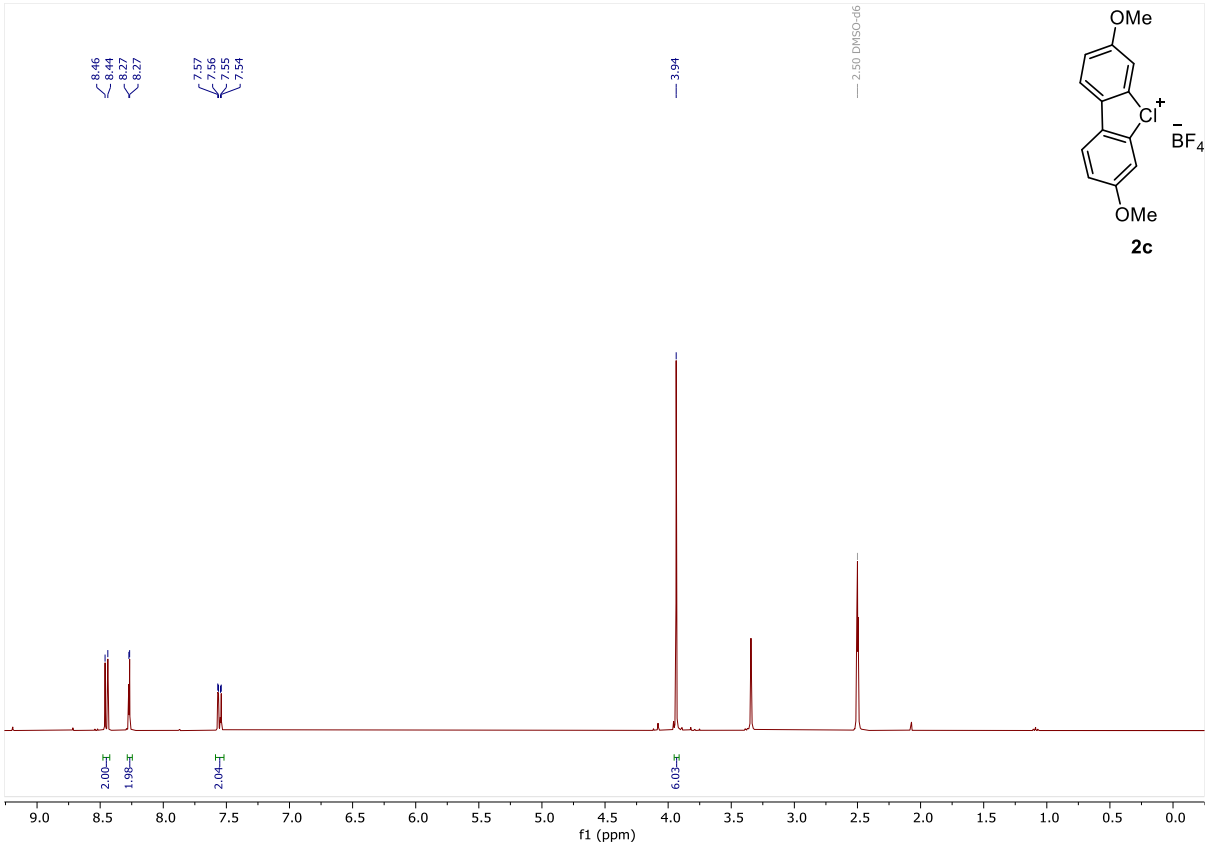


^{19}F NMR (377 MHz, DMSO-d6)

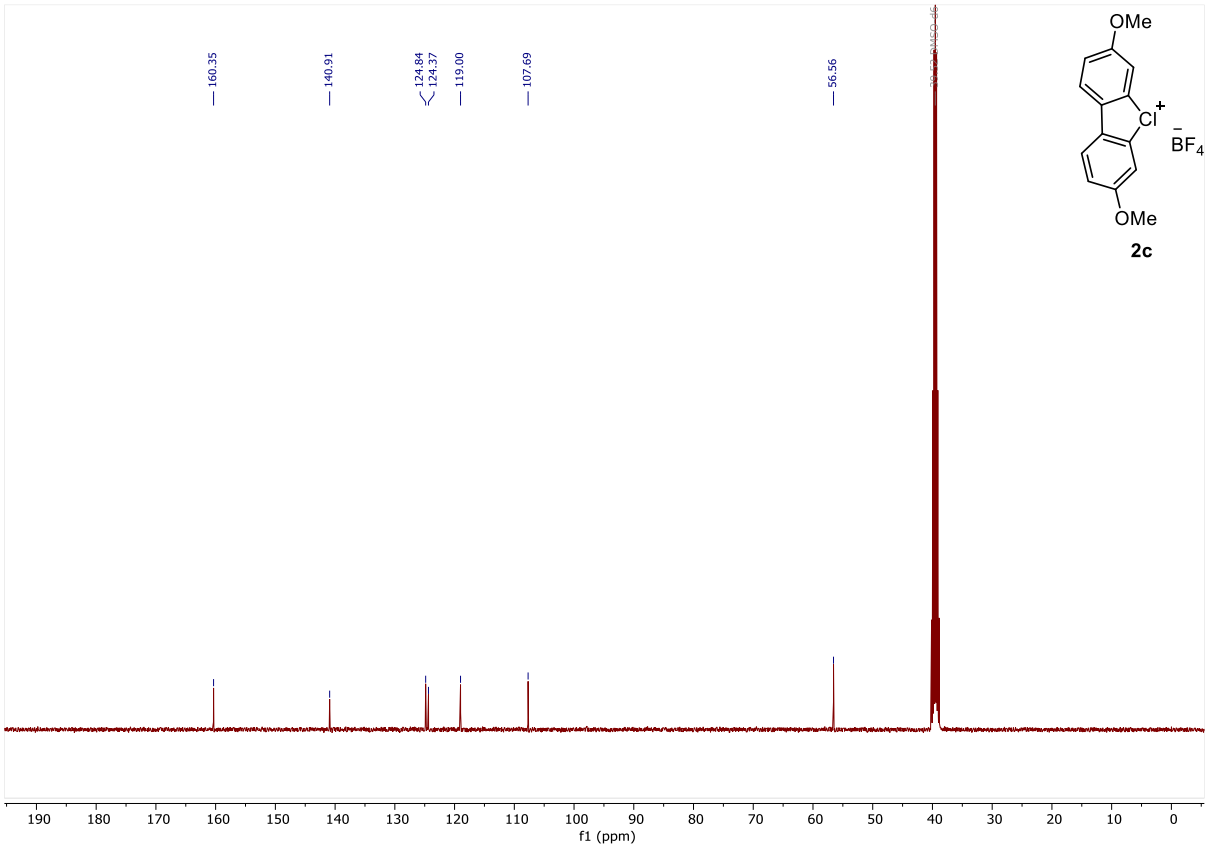


3,7-dimethoxydibenzo[*b,d*]chlorol-5-ium tetrafluoroborate (2c) *See procedure*.

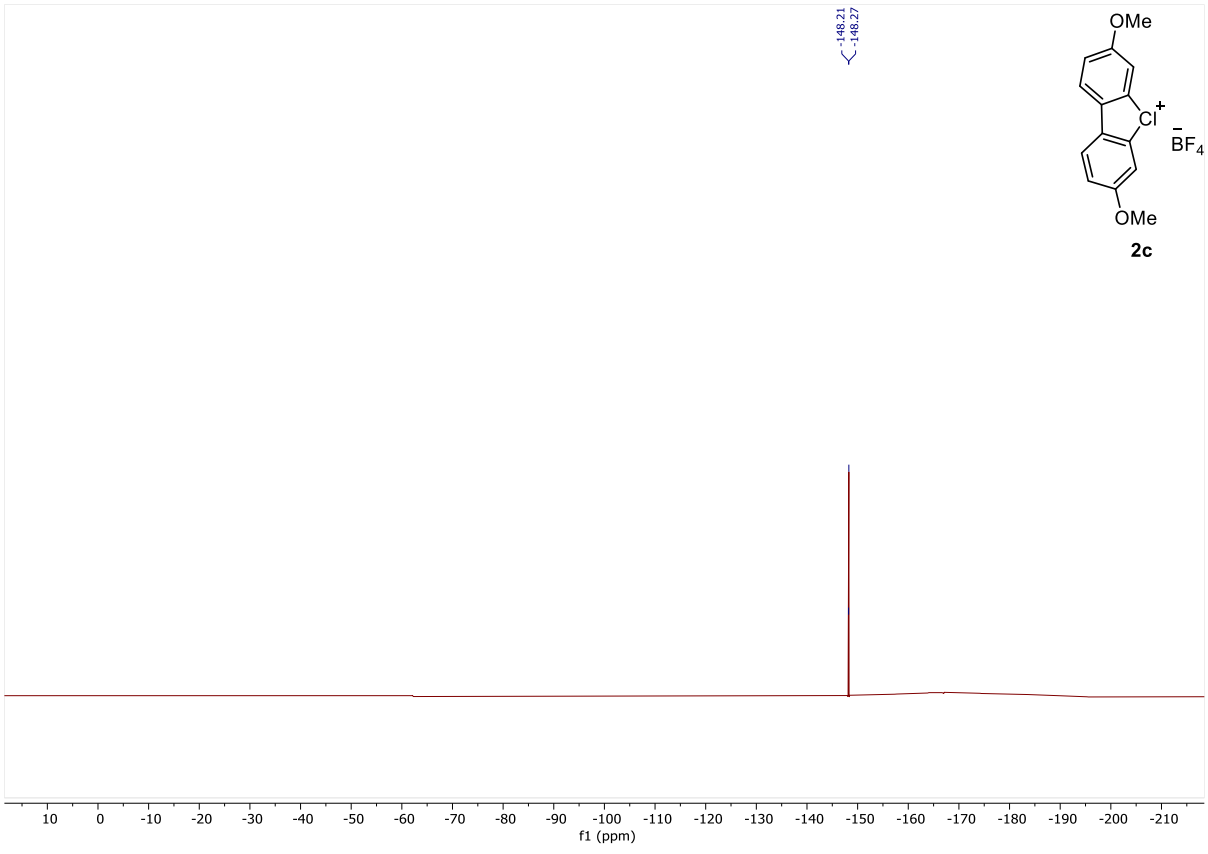
^{1}H NMR (400 MHz, DMSO-d6)



^{13}C NMR (101 MHz, DMSO-d6)

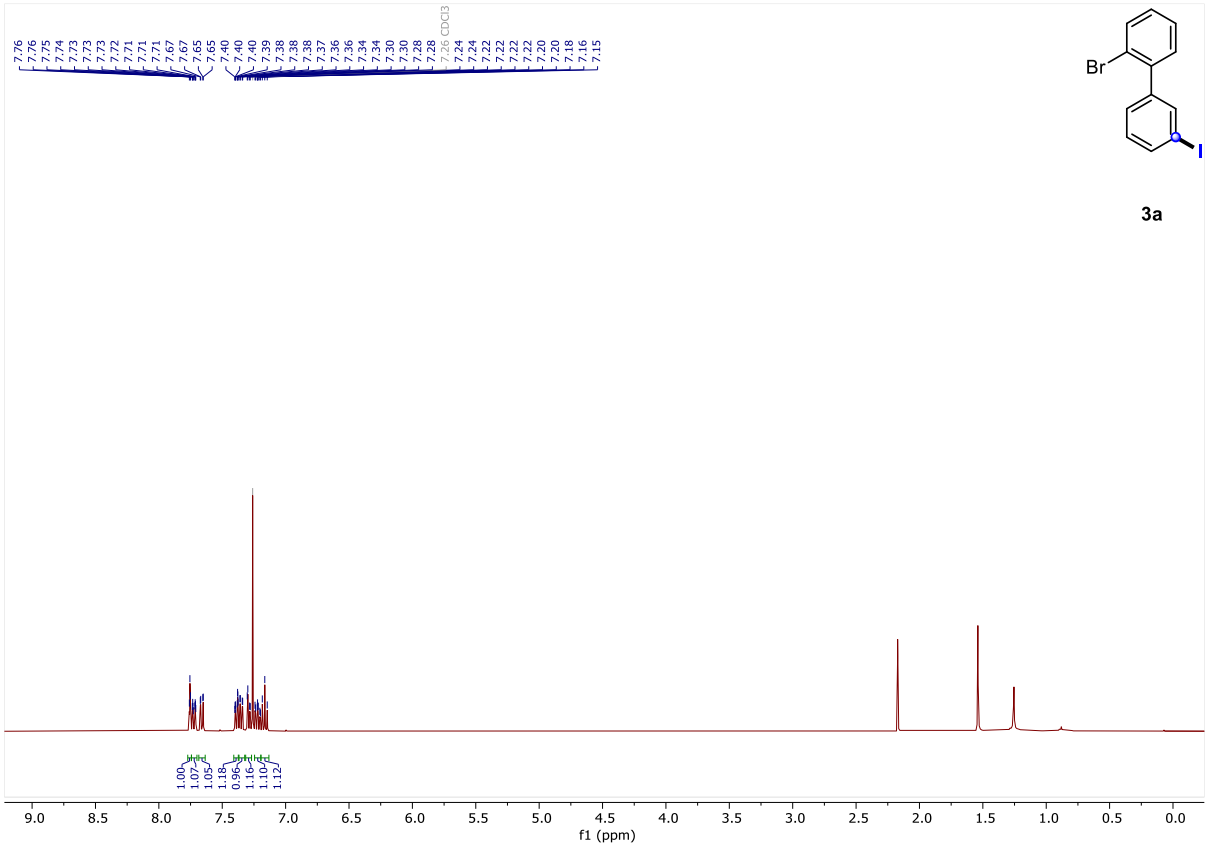


^{19}F NMR (377 MHz, DMSO-d6)

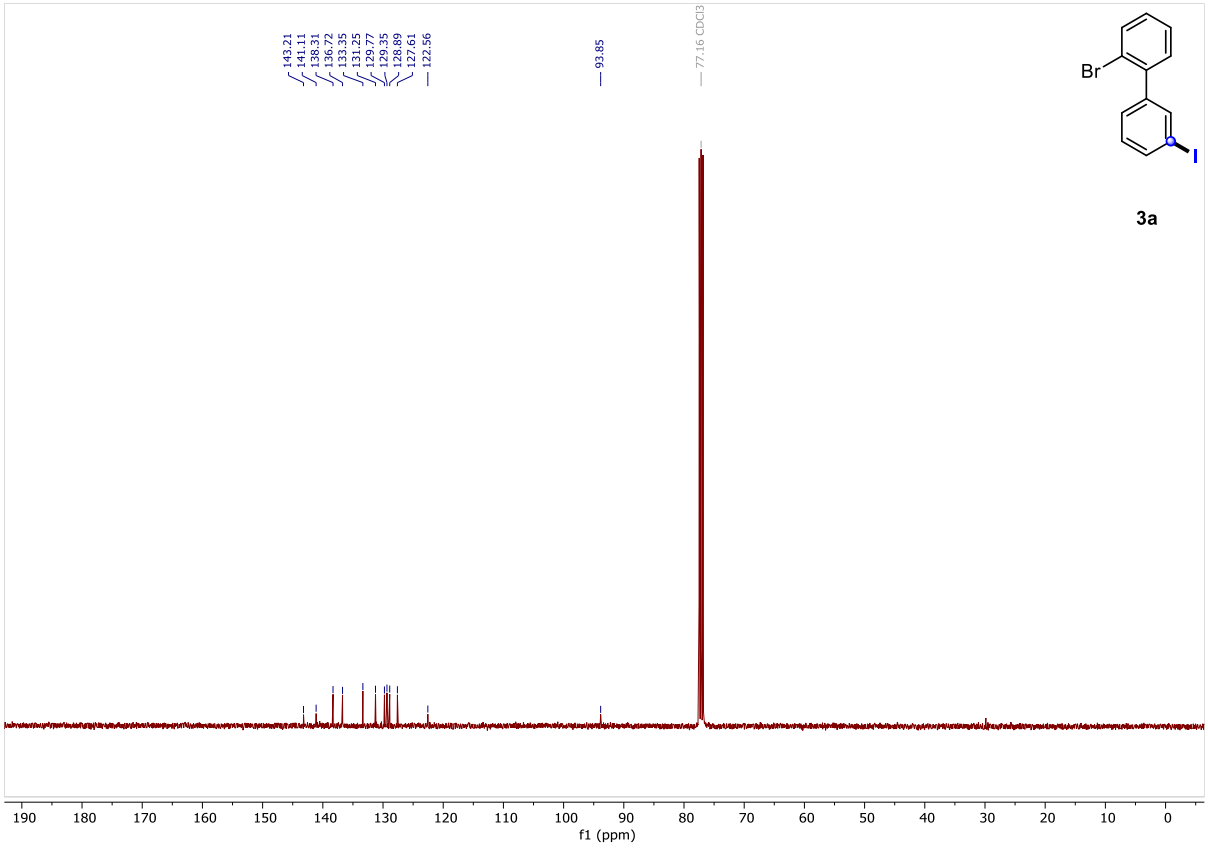


2-bromo-3'-iodo-1,1'-biphenyl (3a) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

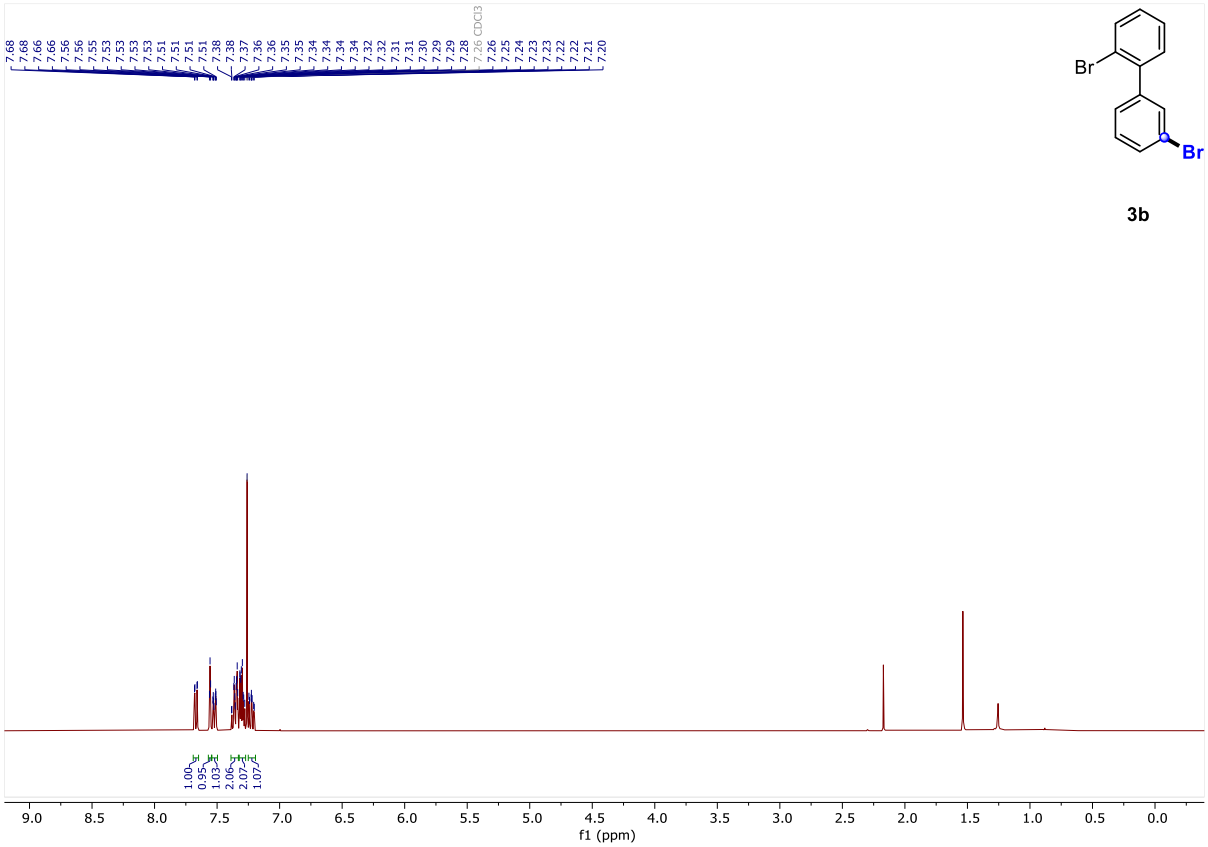


^{13}C NMR (101 MHz, $CDCl_3$)

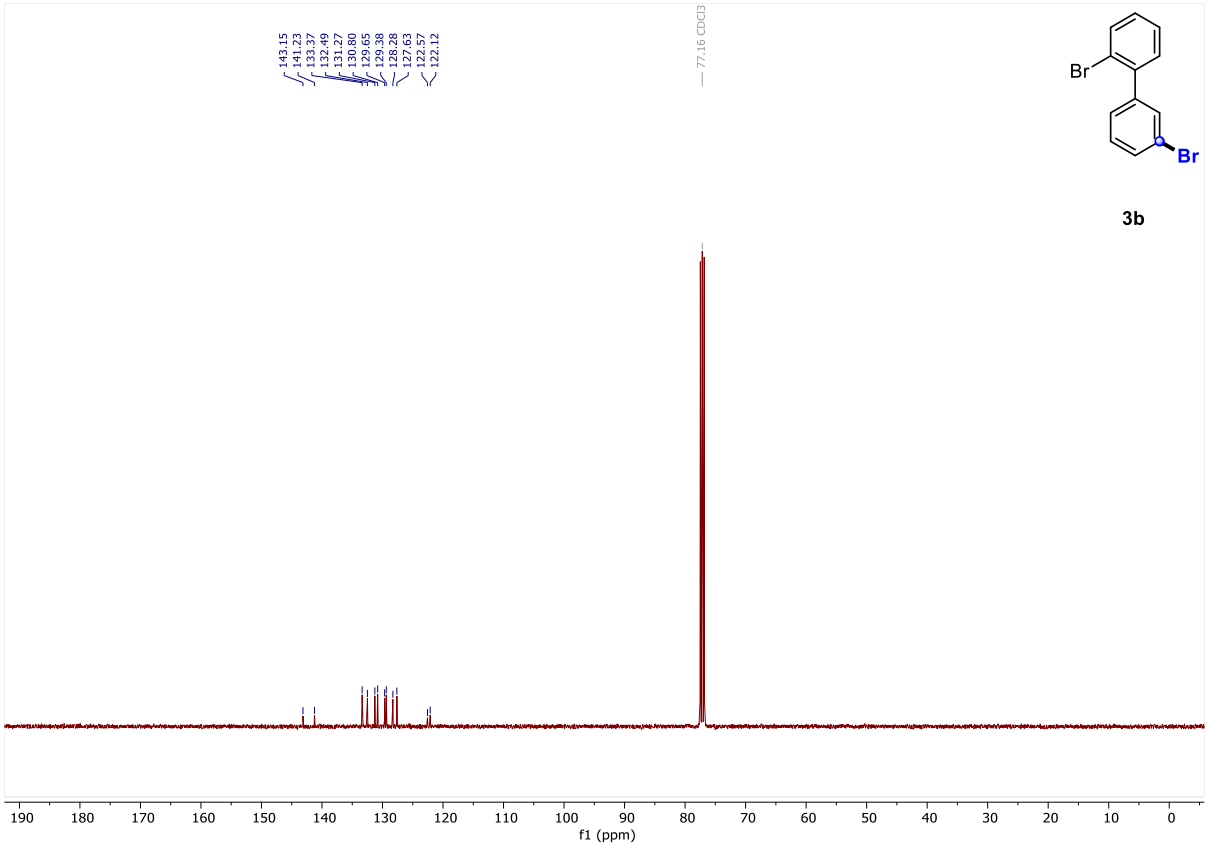


2,3'-dibromo-1,1'-biphenyl (3b) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

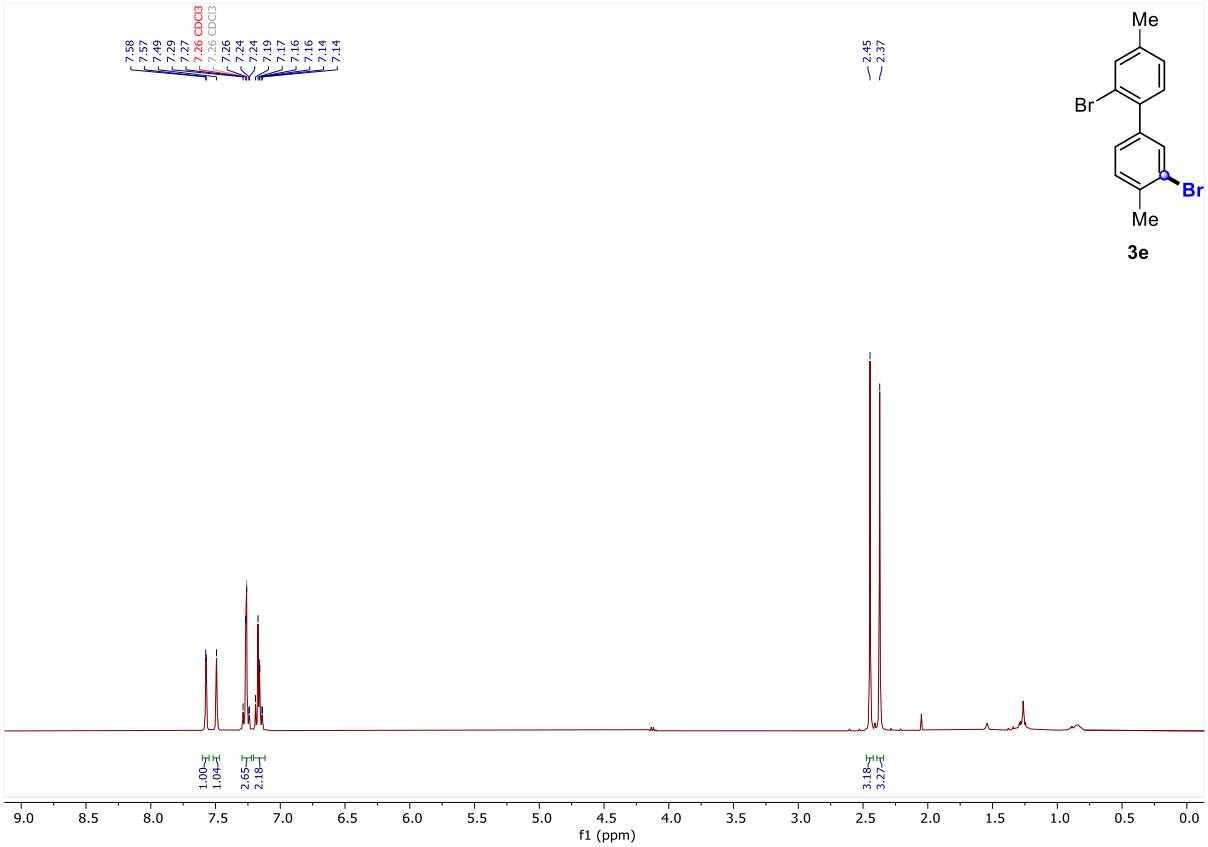


^{13}C NMR (101 MHz, $CDCl_3$)

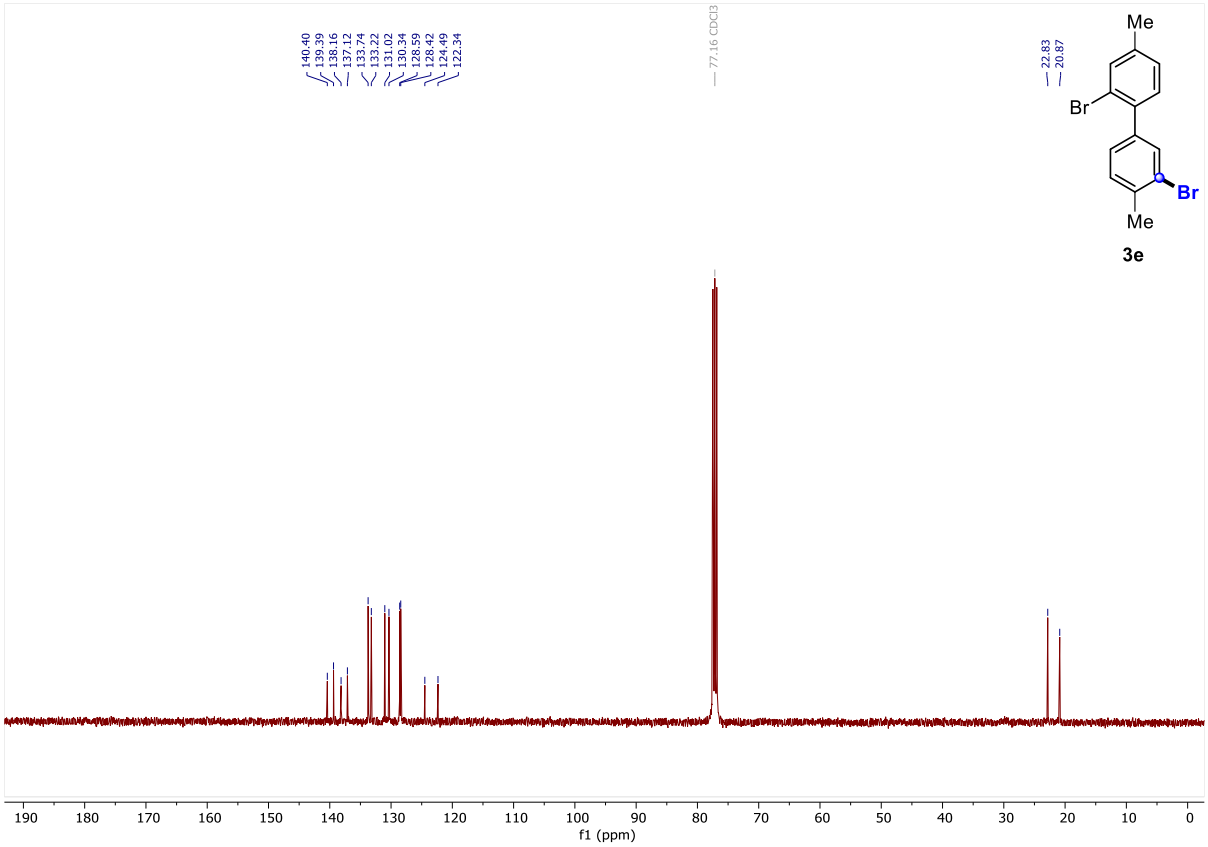


2,3'-dibromo-4,4'-dimethyl-1,1'-biphenyl (3e) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

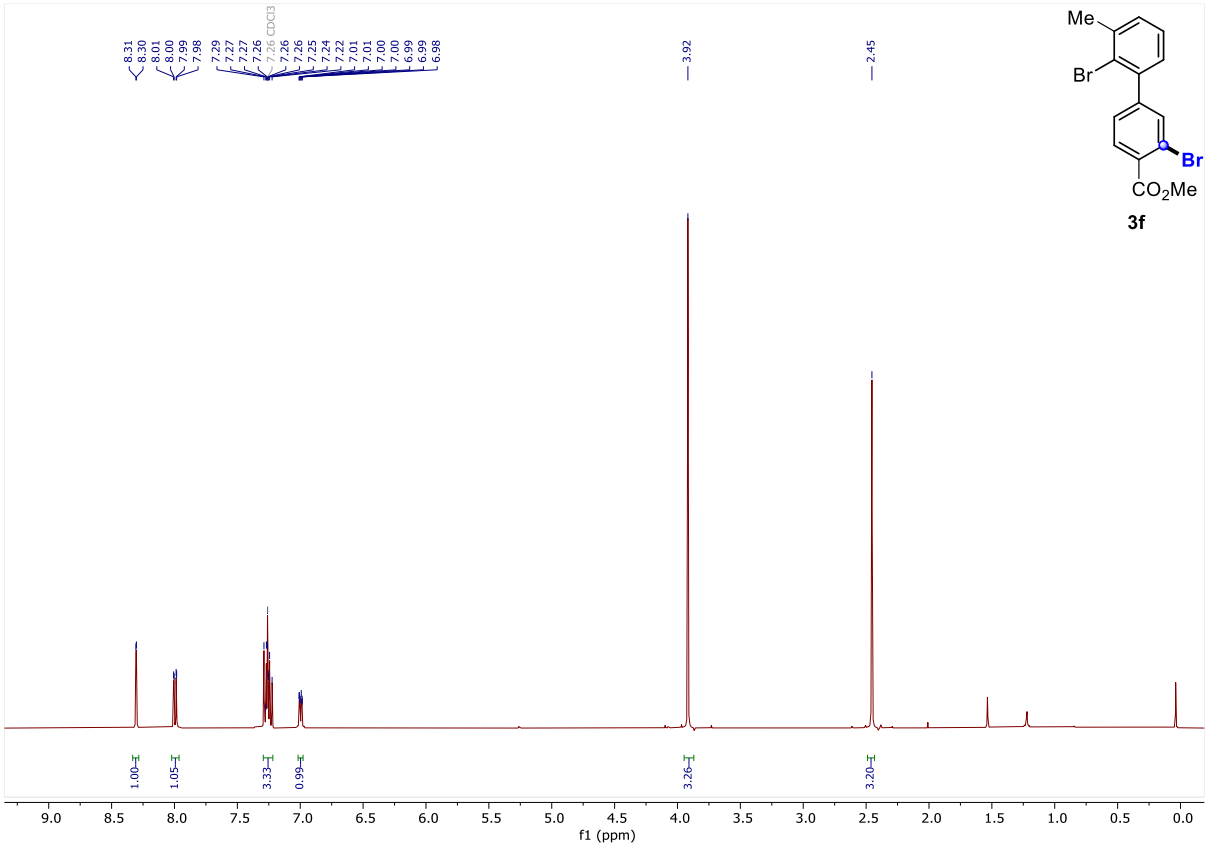


^{13}C NMR (101 MHz, $CDCl_3$)

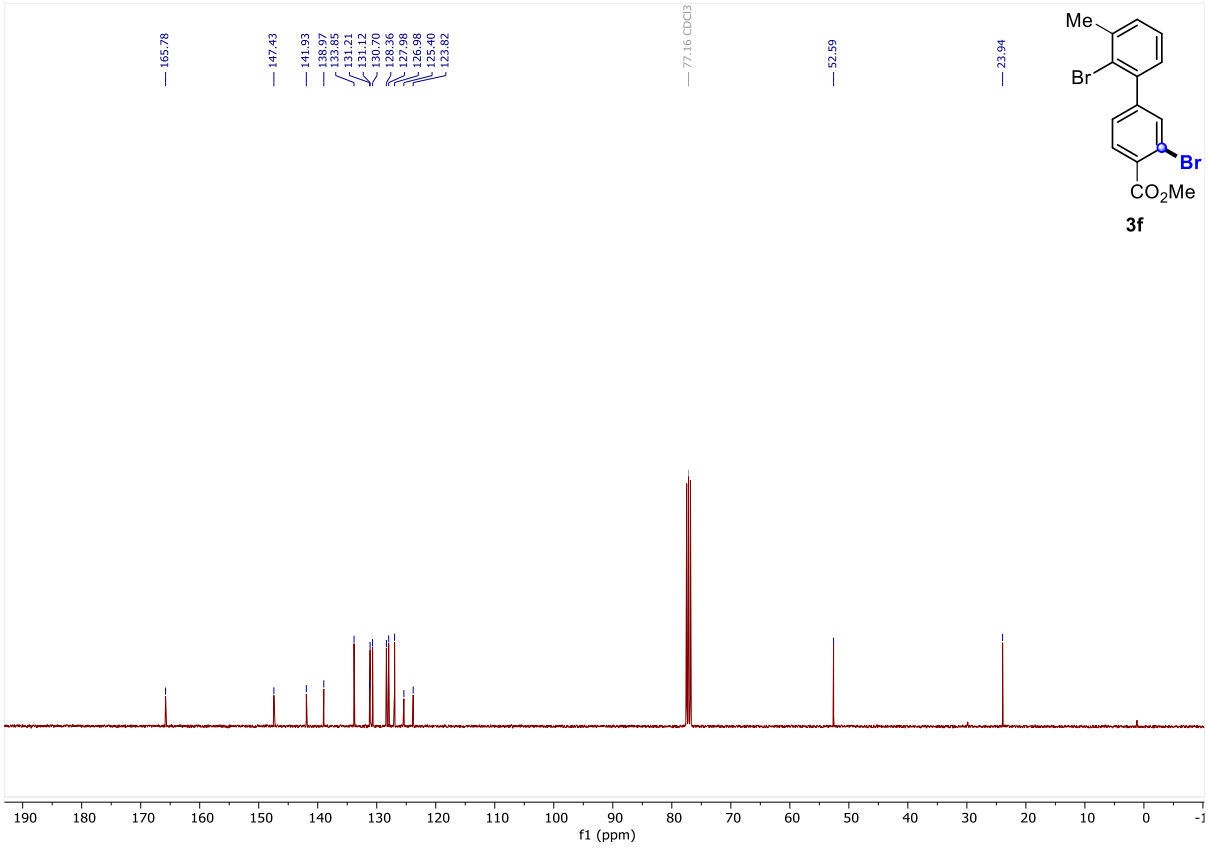


methyl 2',3-dibromo-3'-methyl-[1,1'-biphenyl]-4-carboxylate (3f) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

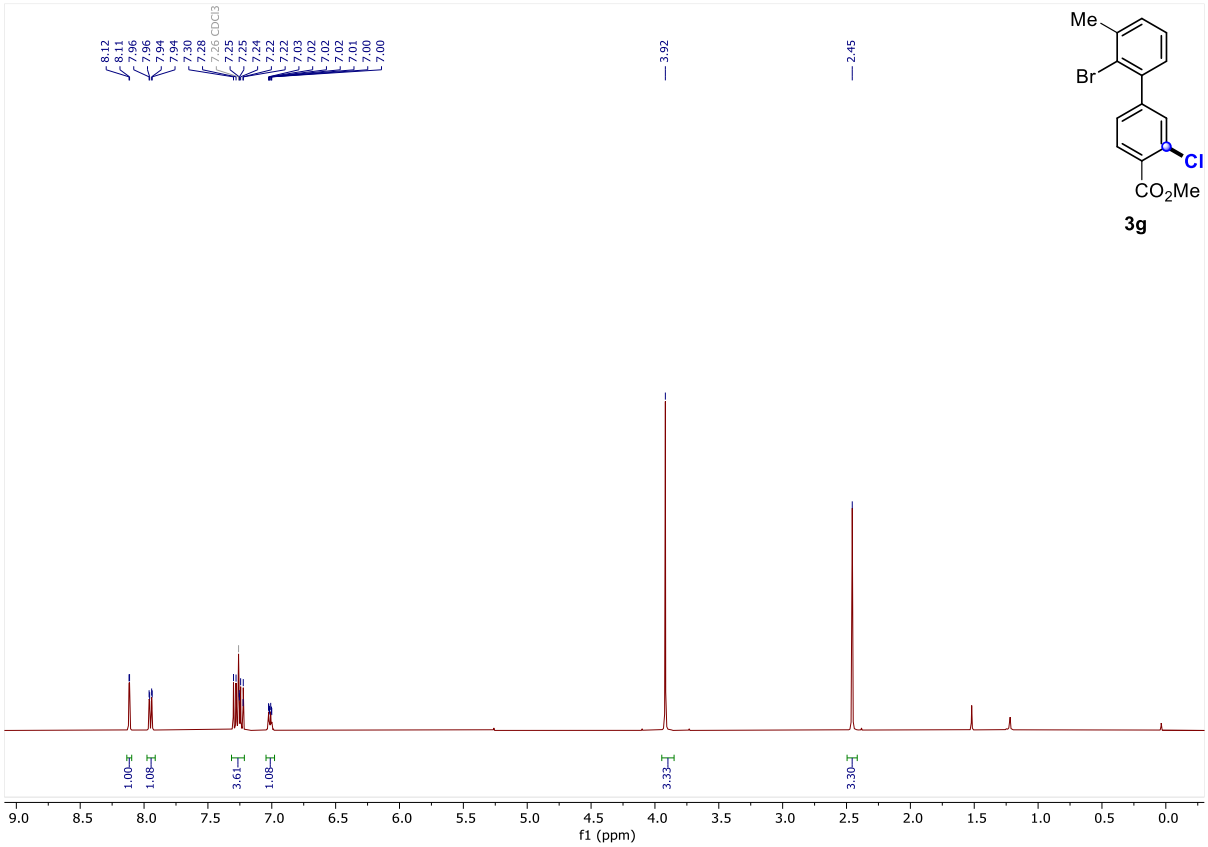


^{13}C NMR (101 MHz, $CDCl_3$)

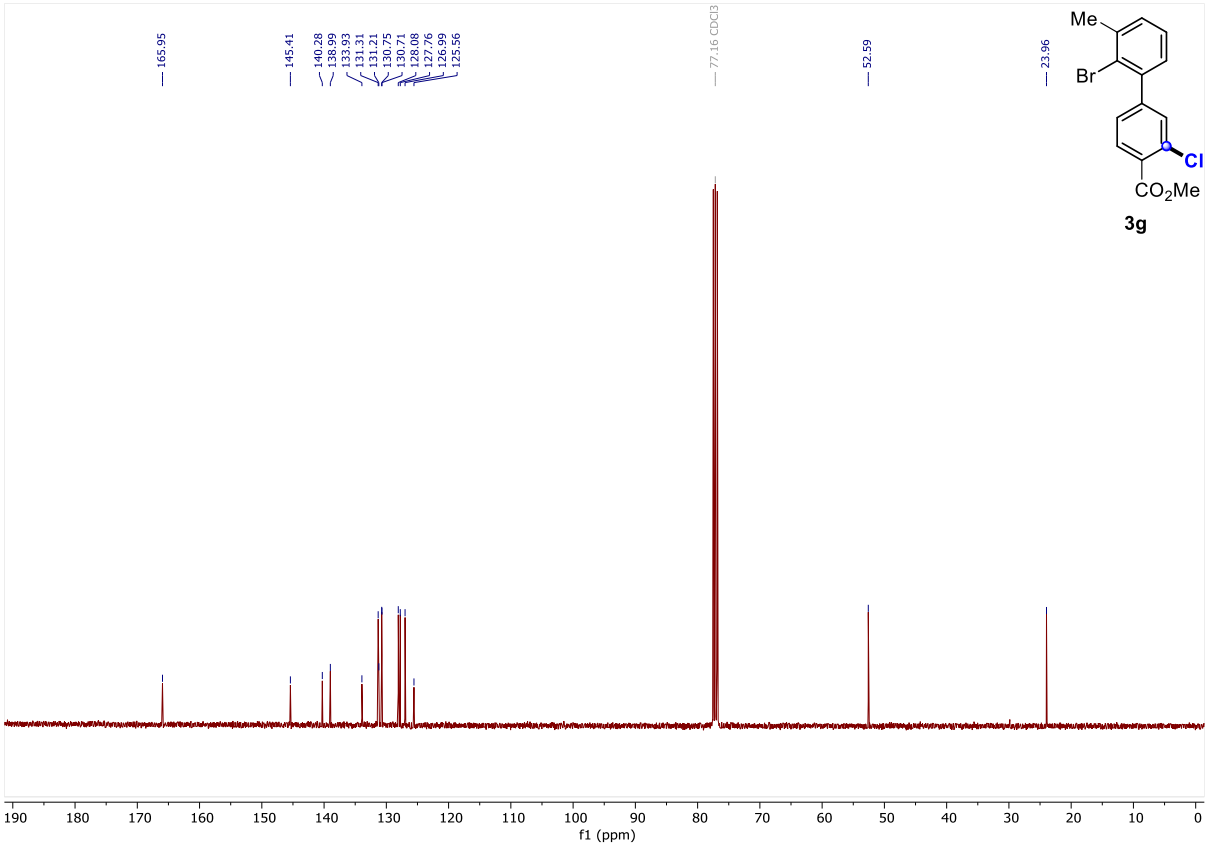


methyl 2'-bromo-3-chloro-3'-methyl-[1,1'-biphenyl]-4-carboxylate (3g) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

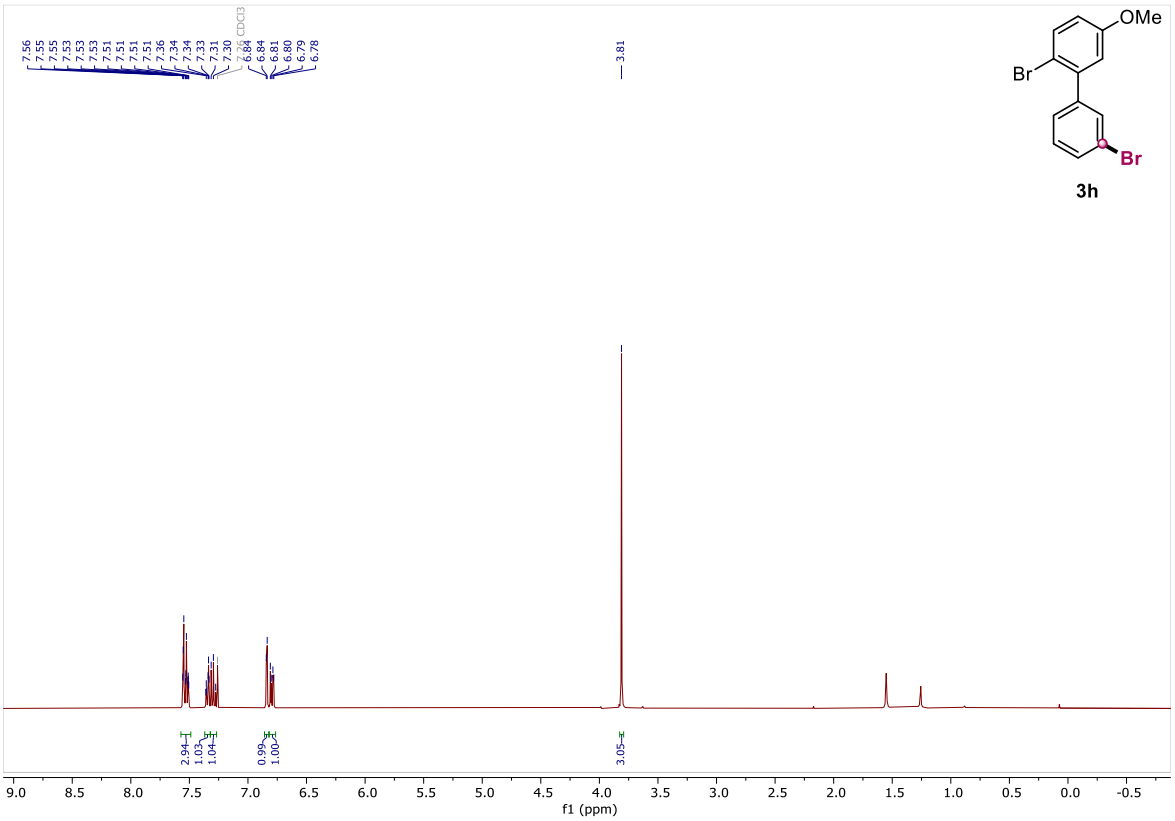


^{13}C NMR (101 MHz, $CDCl_3$)

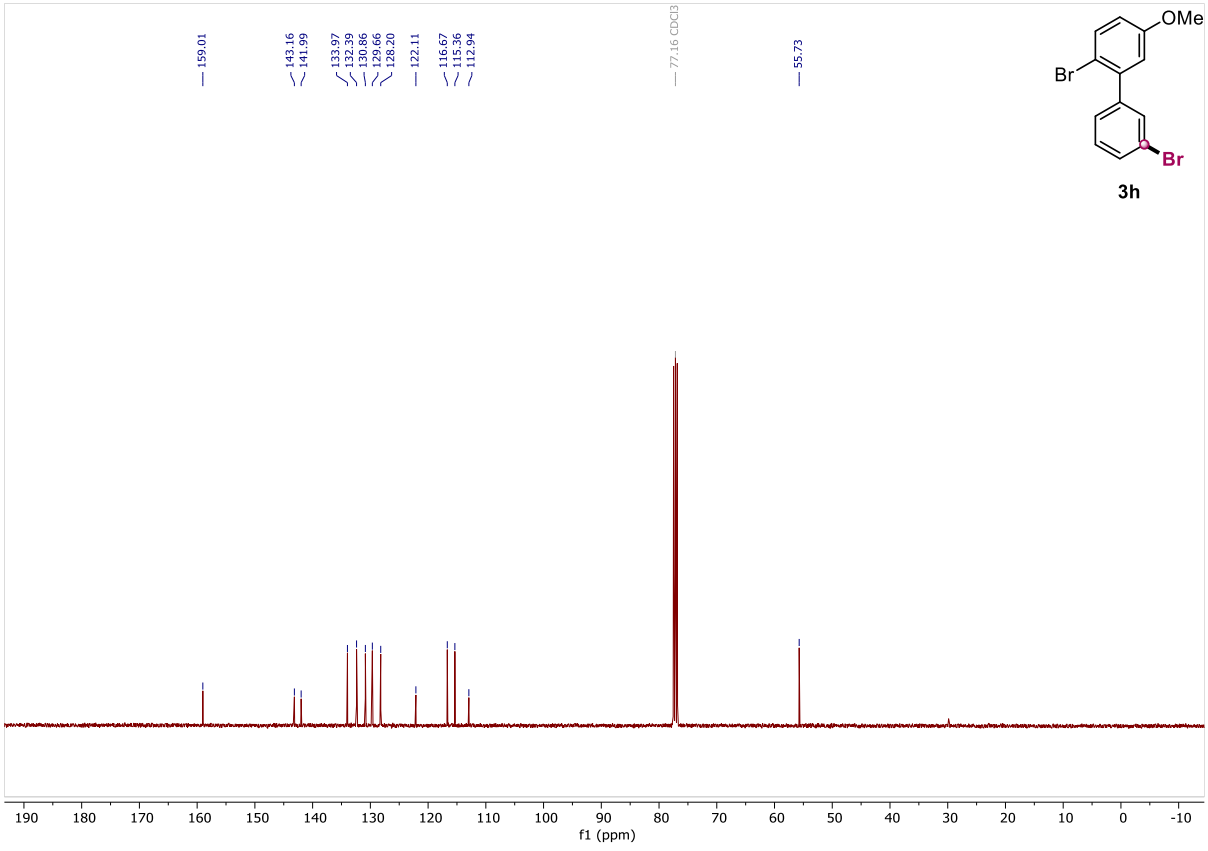


2,3'-dibromo-5-methoxy-1,1'-biphenyl (3h) + 2,3'-dibromo-5'-methoxy-1,1'-biphenyl (3h') *See procedure*.

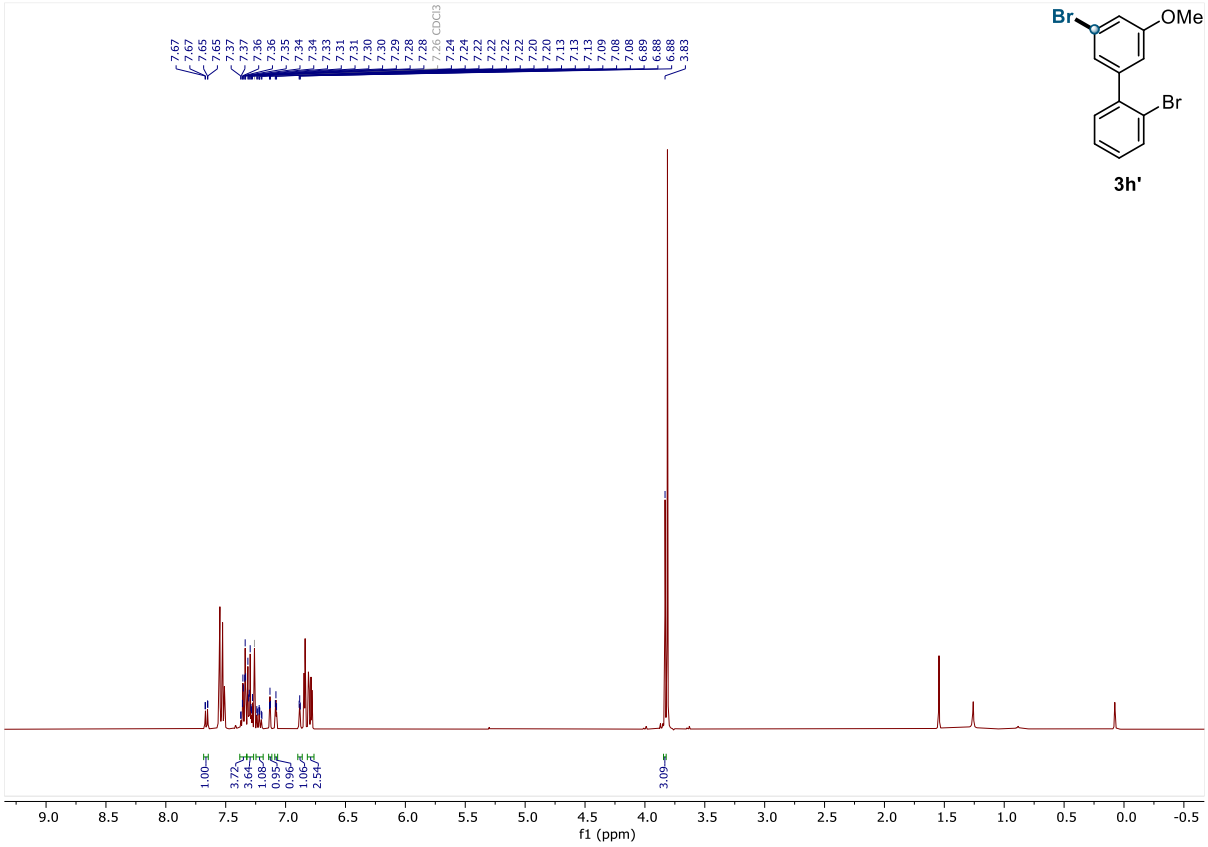
^{1}H NMR (400 MHz, $CDCl_3$), regioisomer **3h** (major)



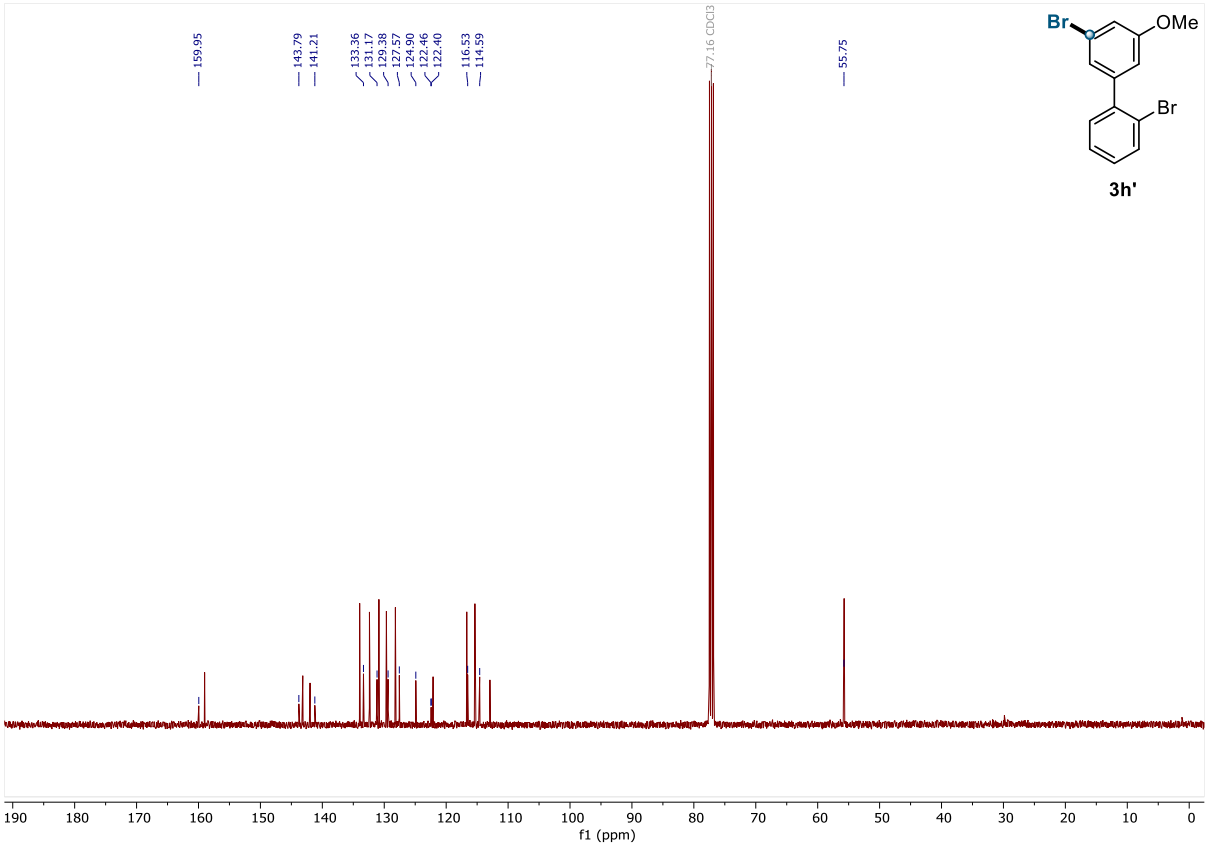
^{13}C NMR (101 MHz, $CDCl_3$), regioisomer **3h** (major)



^{1}H NMR (400 MHz, $CDCl_3$), mixture of regioisomers **3h** and **3h'** (2.5:1 ratio). Assignment of **3h'** shown

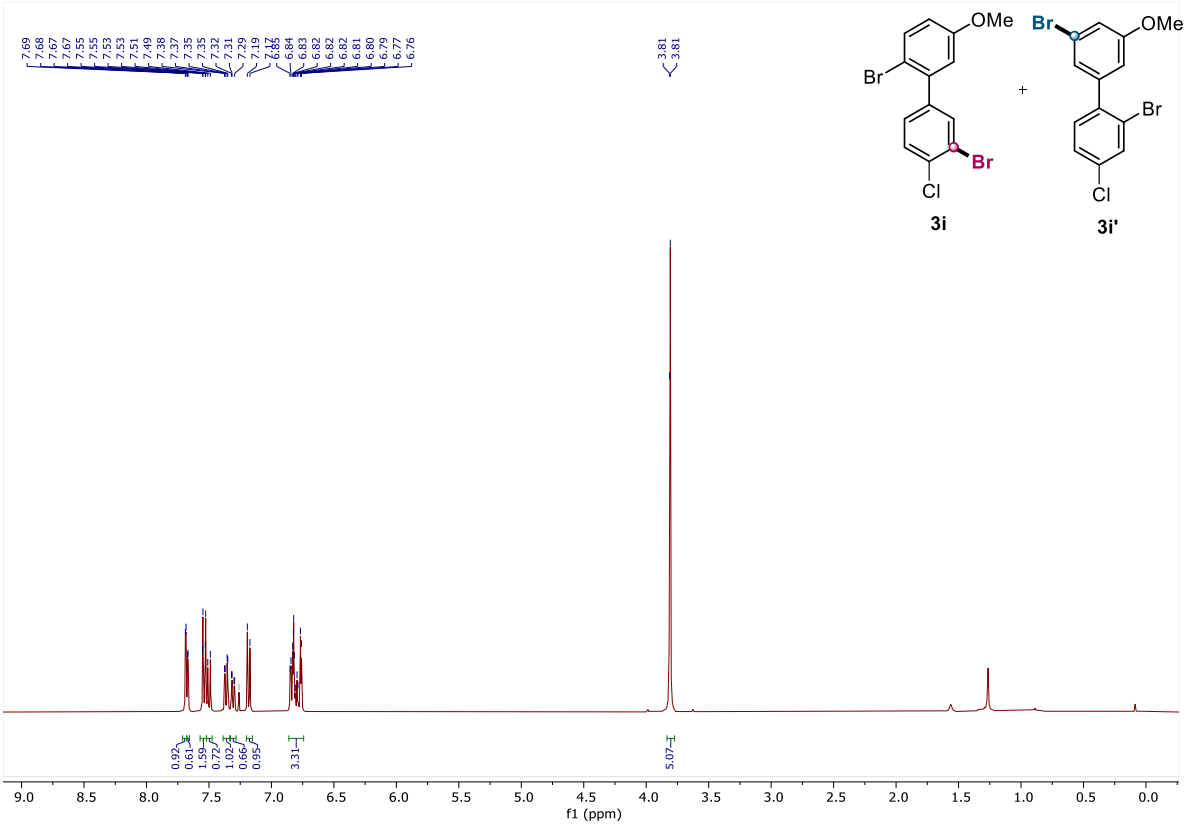


^{13}C NMR (101 MHz, $CDCl_3$), mixture of regioisom. **3h** and **3h'** (2.5:1 ratio). Assignment of **3h'** shown

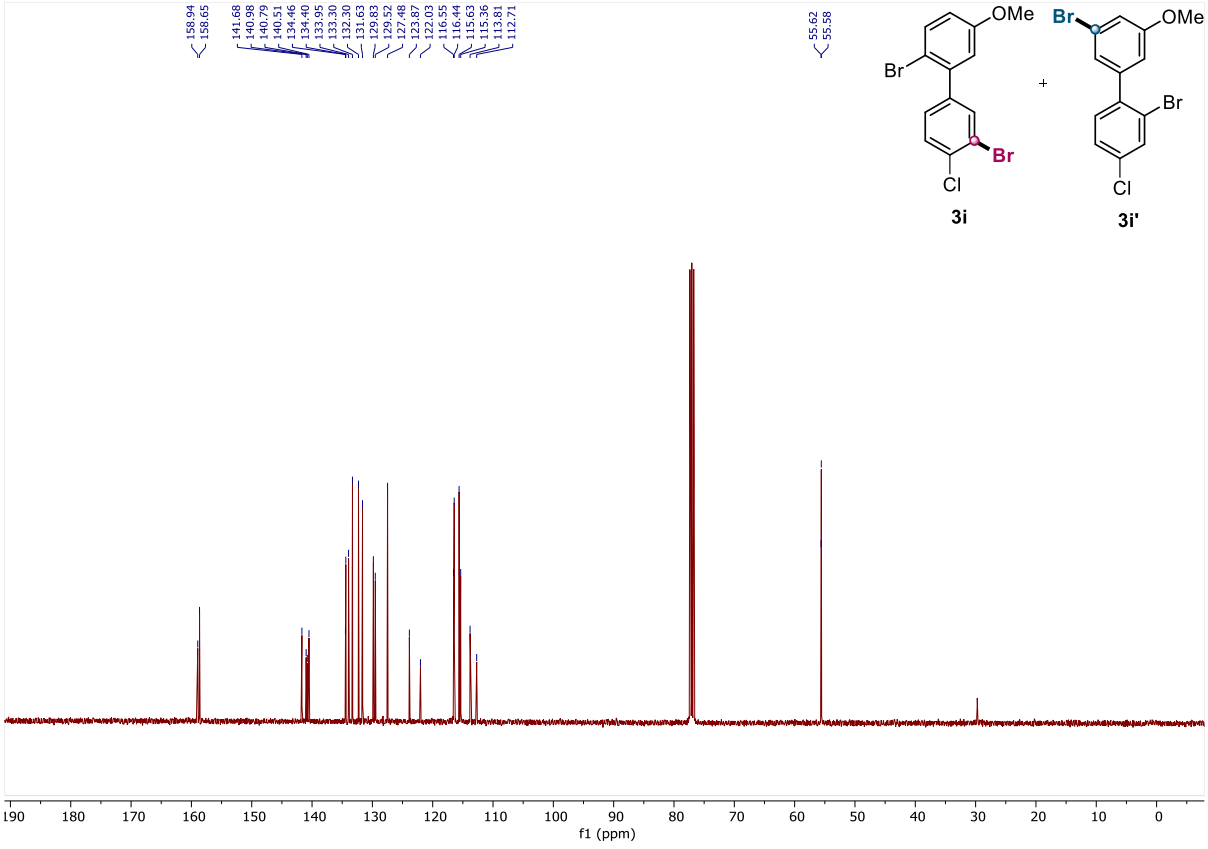


2,3'-dibromo-4'-chloro-5-methoxy-1,1'-biphenyl (3i) + 2,3'-dibromo-4-chloro-5'-methoxy-1,1'-biphenyl (3i') *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$), mixture of **3i** and **3i'** (1.5:1 ratio)

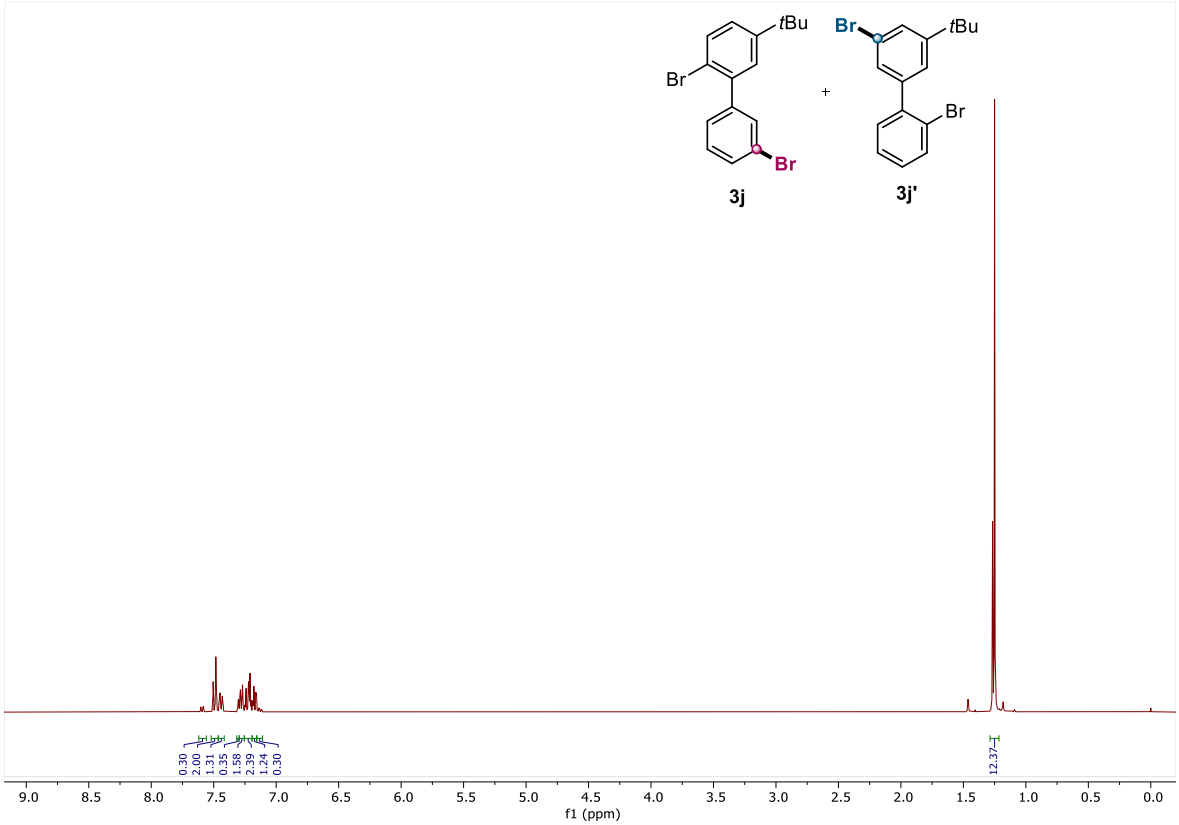


^{13}C NMR (101 MHz, $CDCl_3$), mixture of **3i** and **3i'** (1.5:1 ratio)

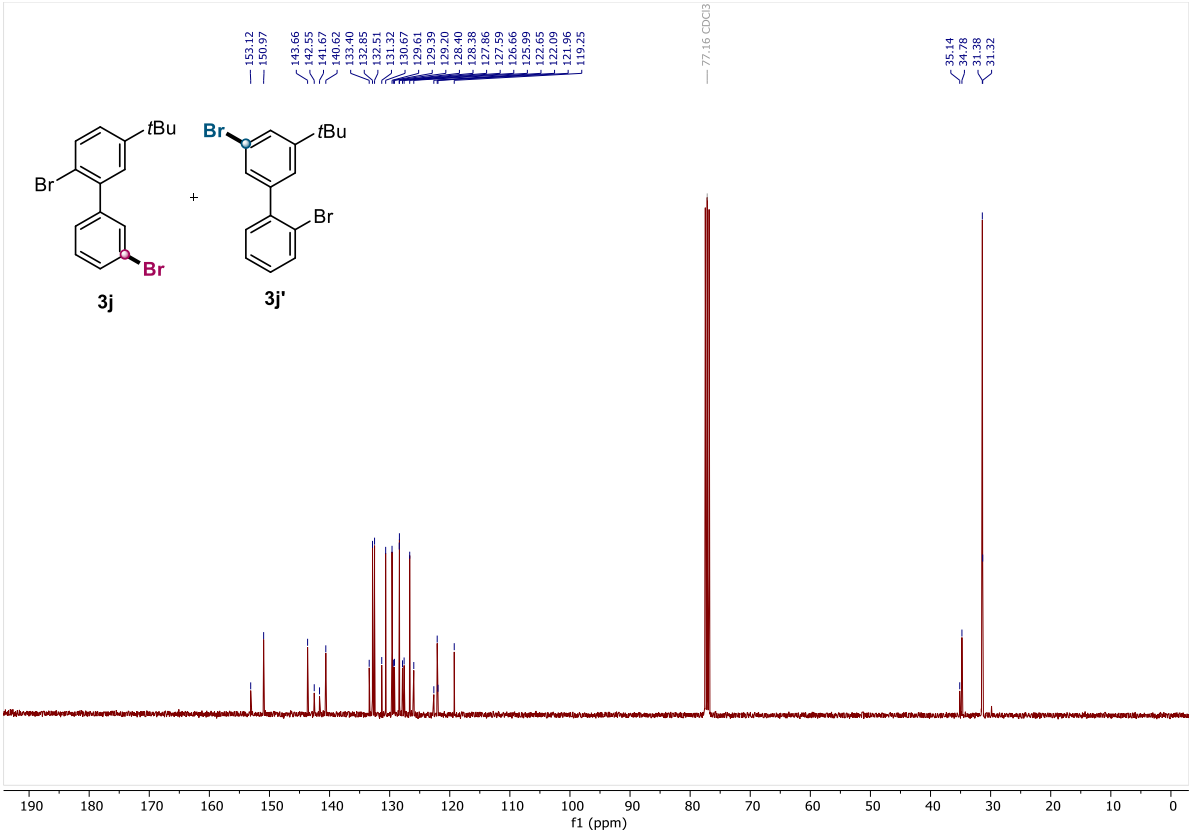


2,3'-dibromo-5'-(*tert*-butyl)-1,1'-biphenyl (3j) + 2,3'-dibromo-5-(*tert*-butyl)-1,1'-biphenyl (3j') *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$), mixture of regioisomers **3j** and **3j'** (3.3:1 ratio)

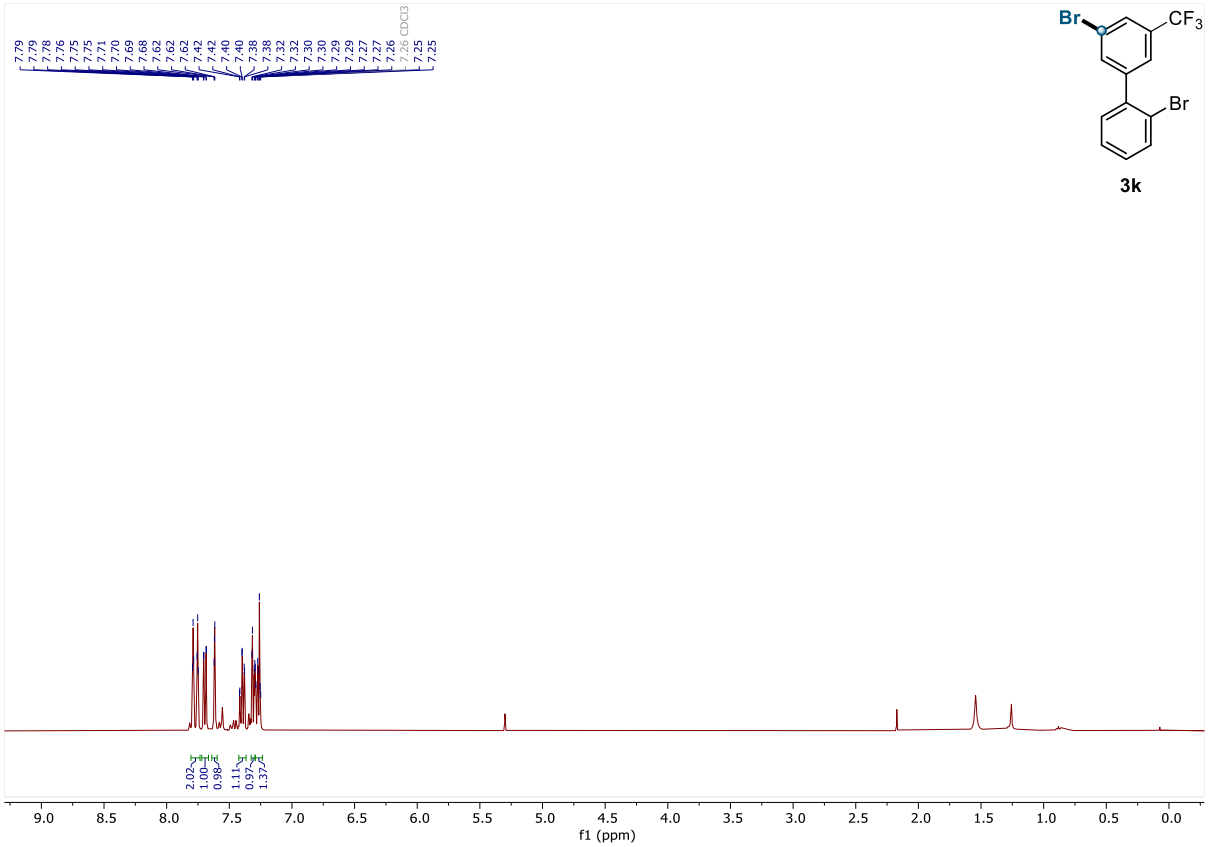


^{13}C NMR (101 MHz, $CDCl_3$), mixture of regioisomers **3j** and **3j'** (3.3:1 ratio)

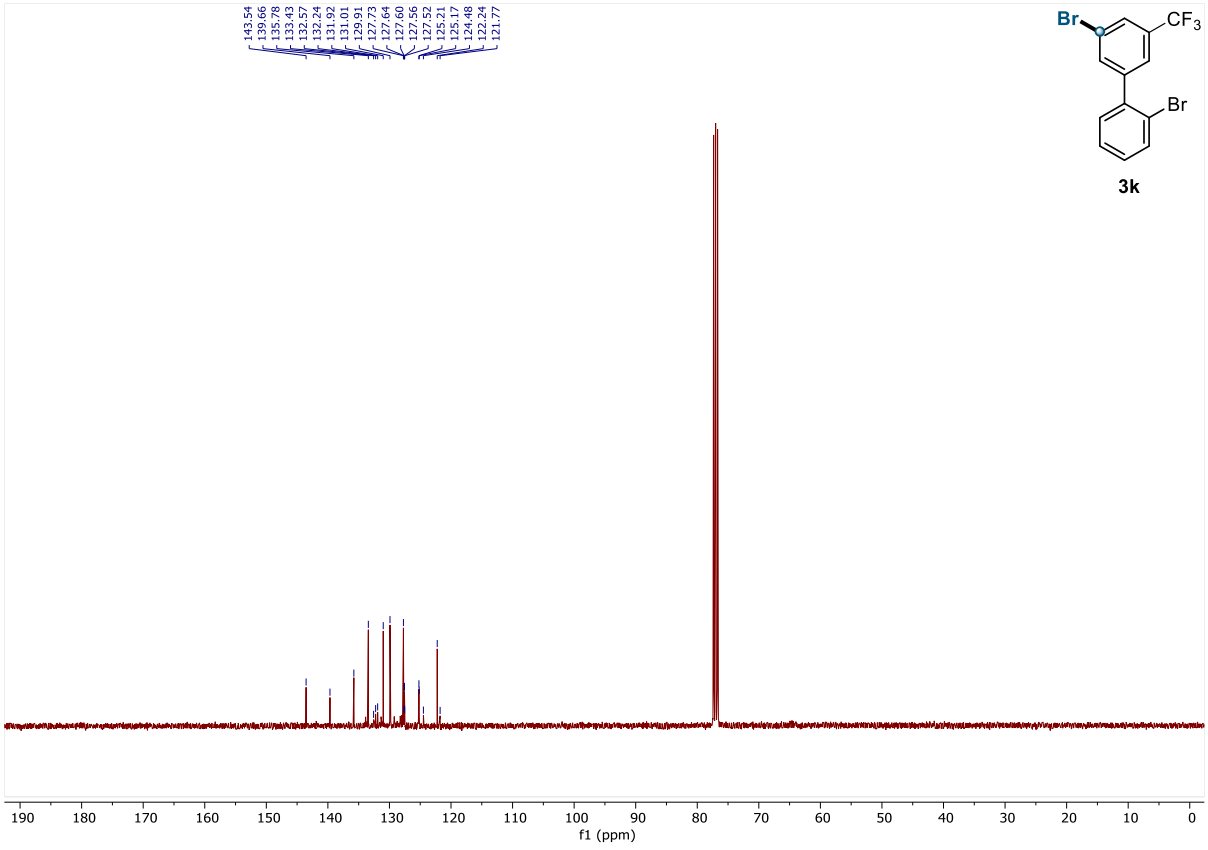


2,3'-dibromo-5'-(trifluoromethyl)-1,1'-biphenyl (3k) *See procedure*.

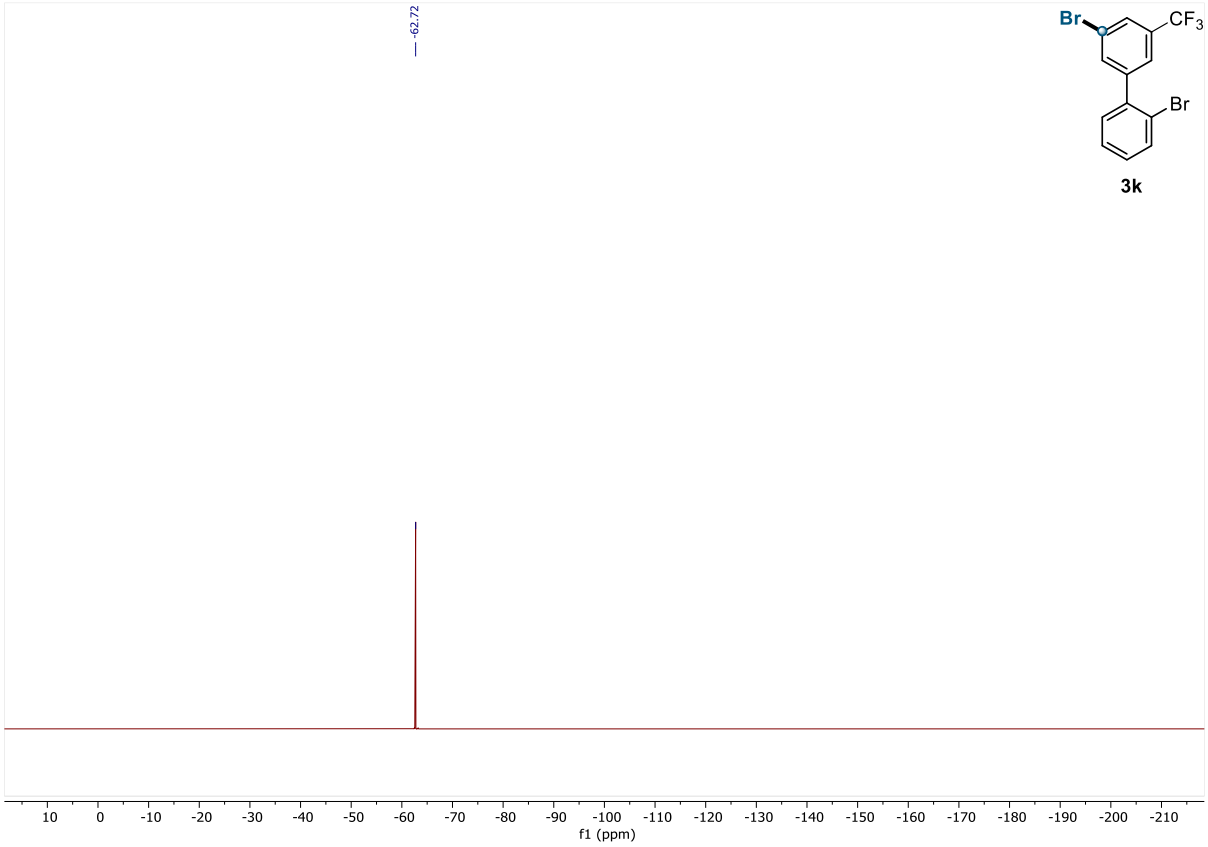
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

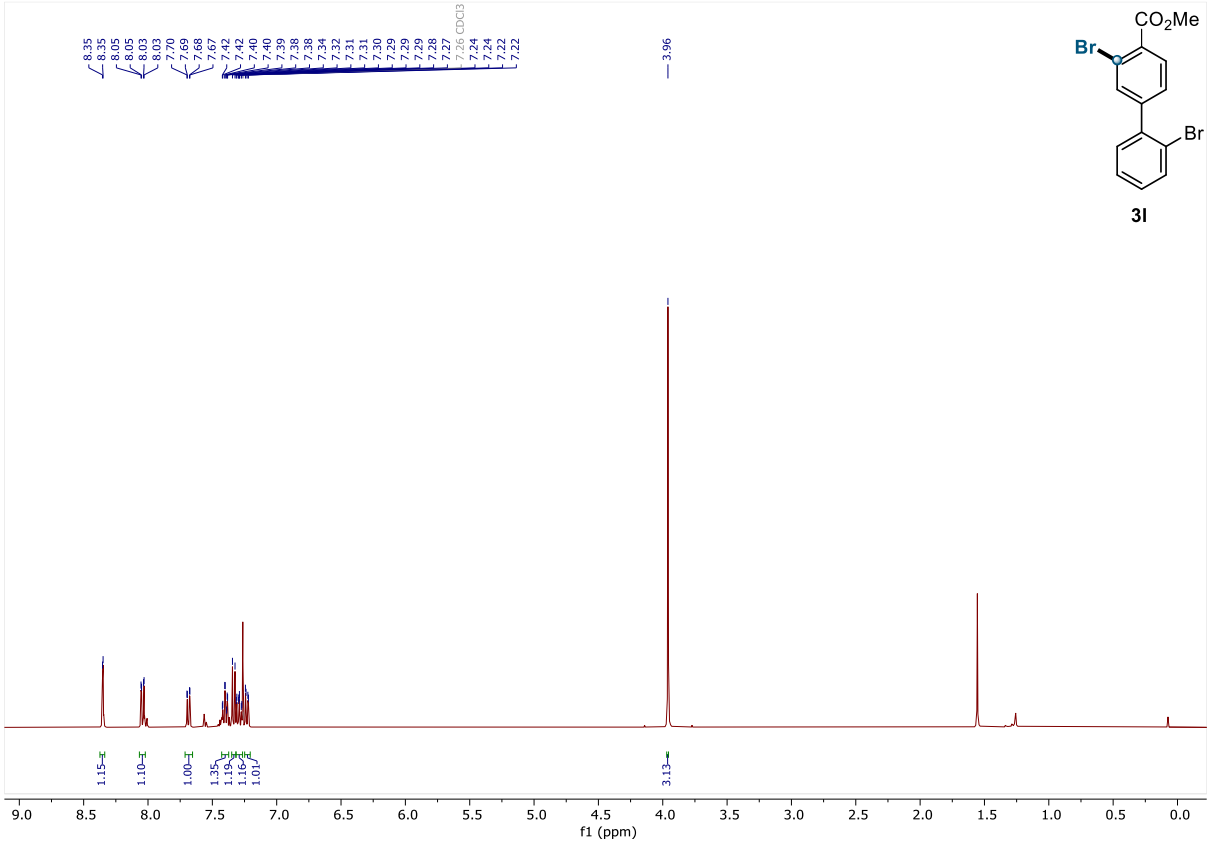


^{19}F NMR (377 MHz, $CDCl_3$)

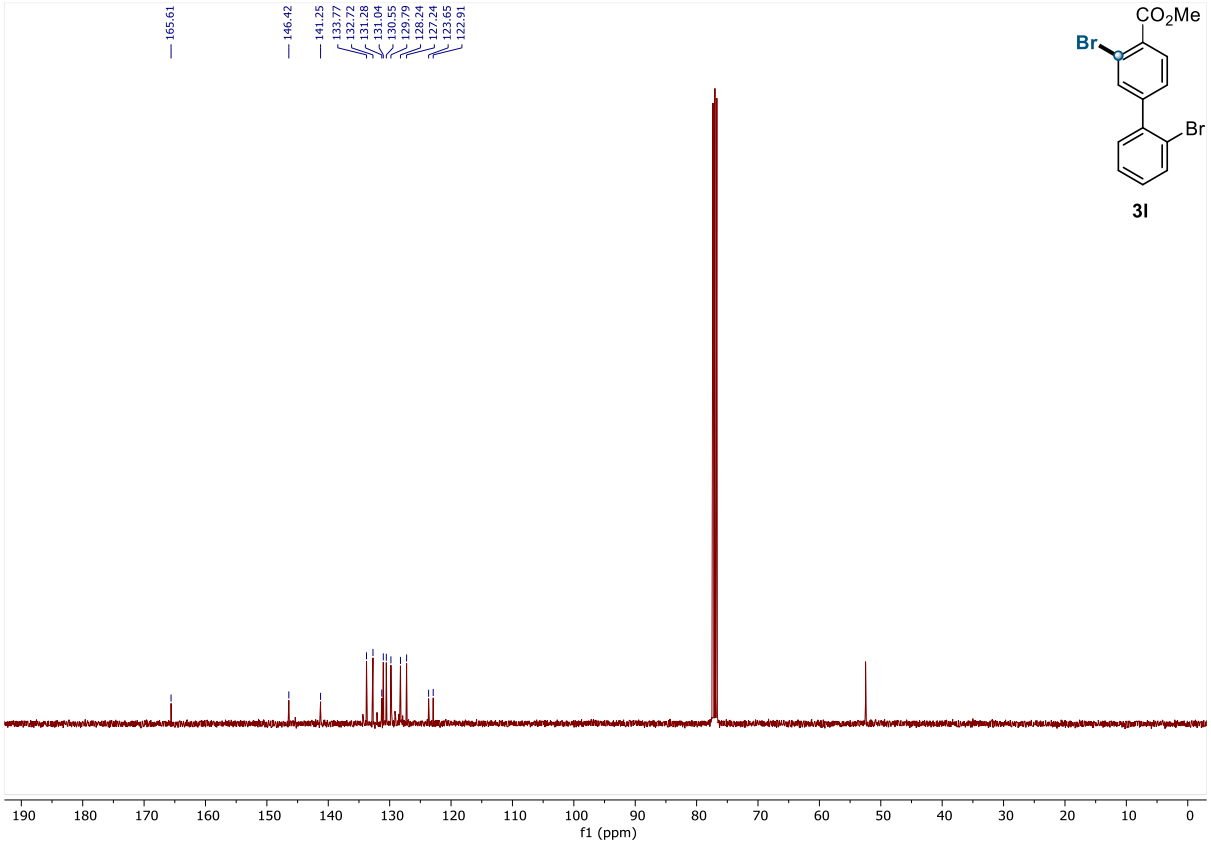


methyl 2',3-dibromo-[1,1'-biphenyl]-4-carboxylate (3l) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

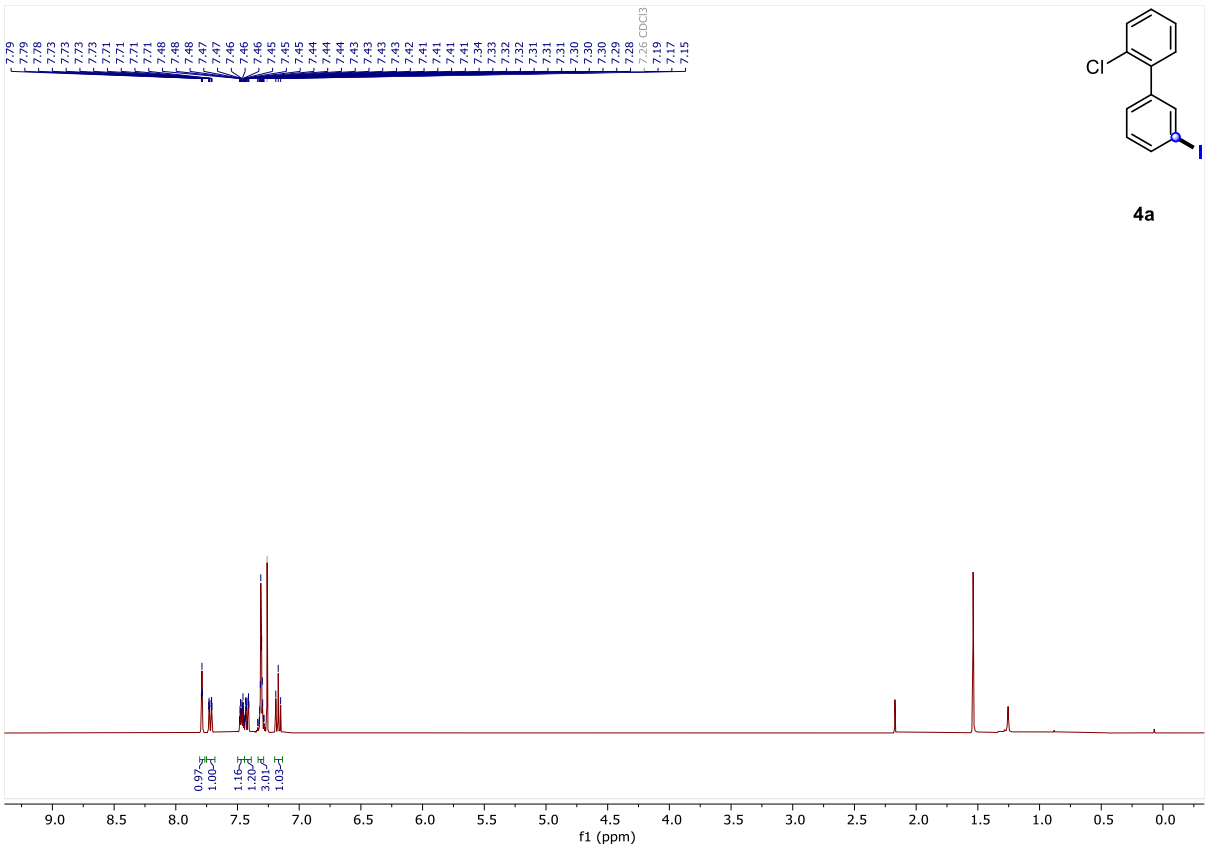


^{13}C NMR (101 MHz, $CDCl_3$)

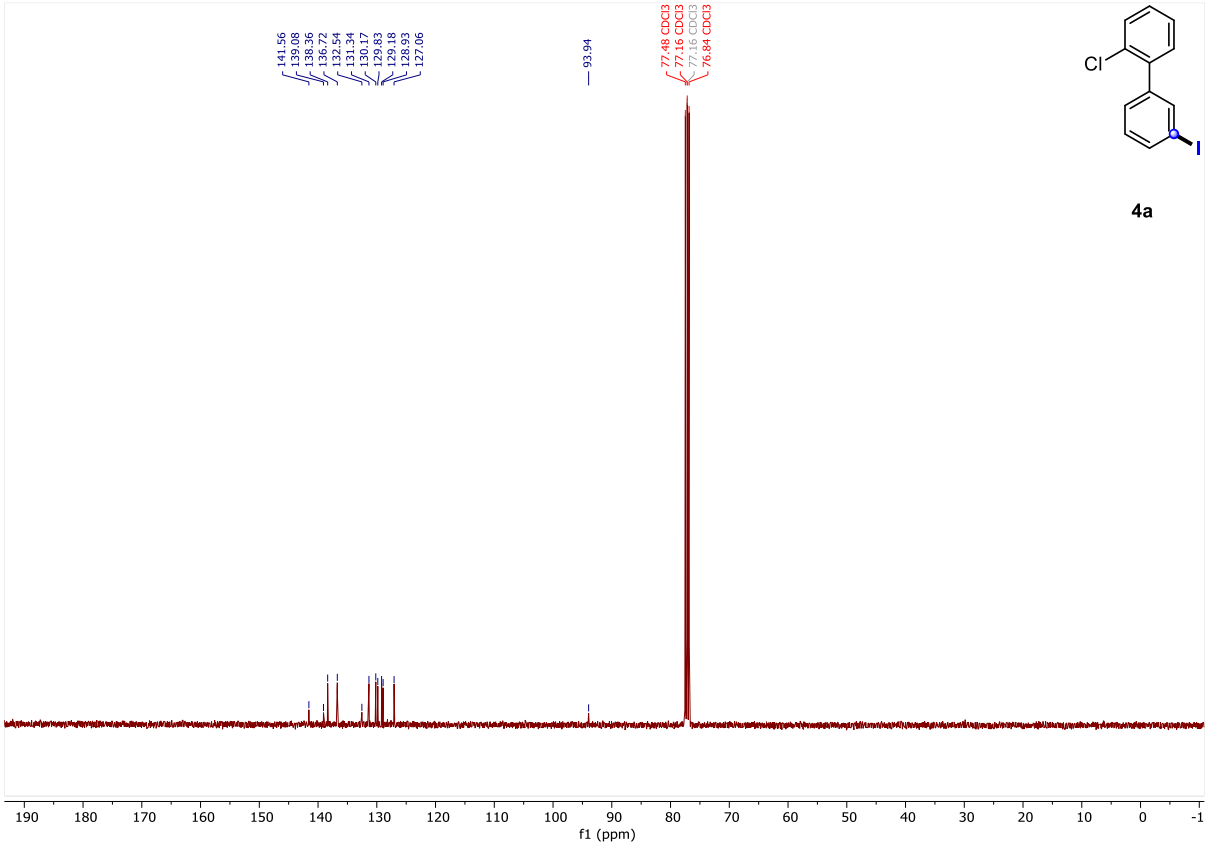


2-chloro-3'-iodo-1,1'-biphenyl (4a) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

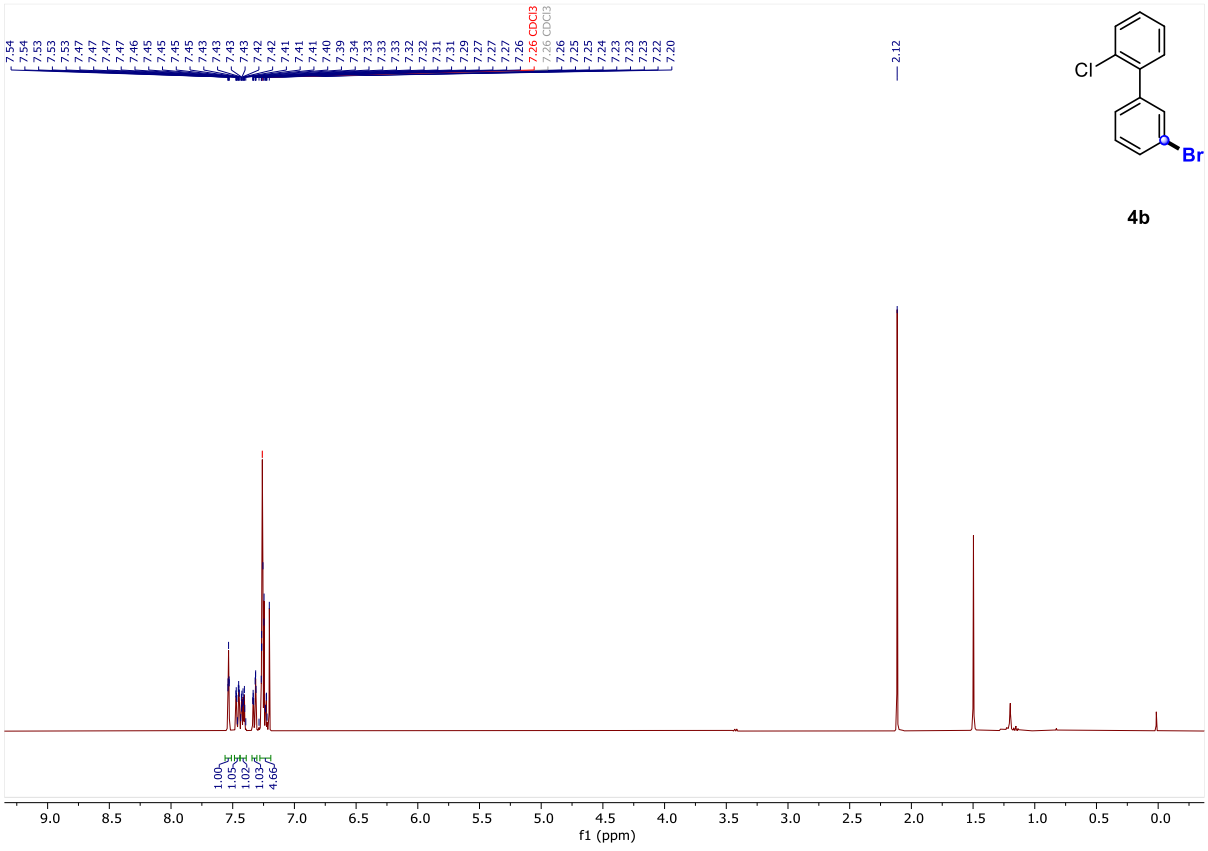


^{13}C NMR (101 MHz, $CDCl_3$)

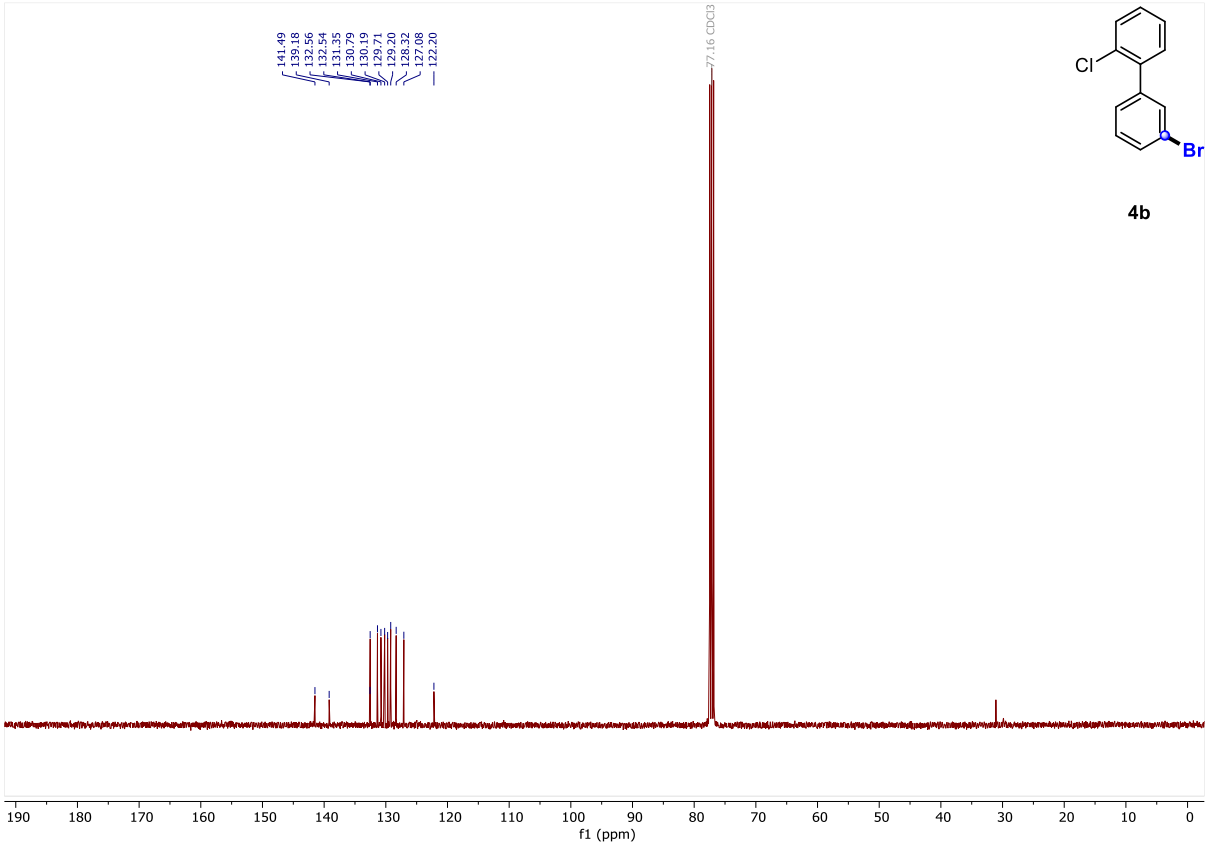


3'-bromo-2-chloro-1,1'-biphenyl (4b) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

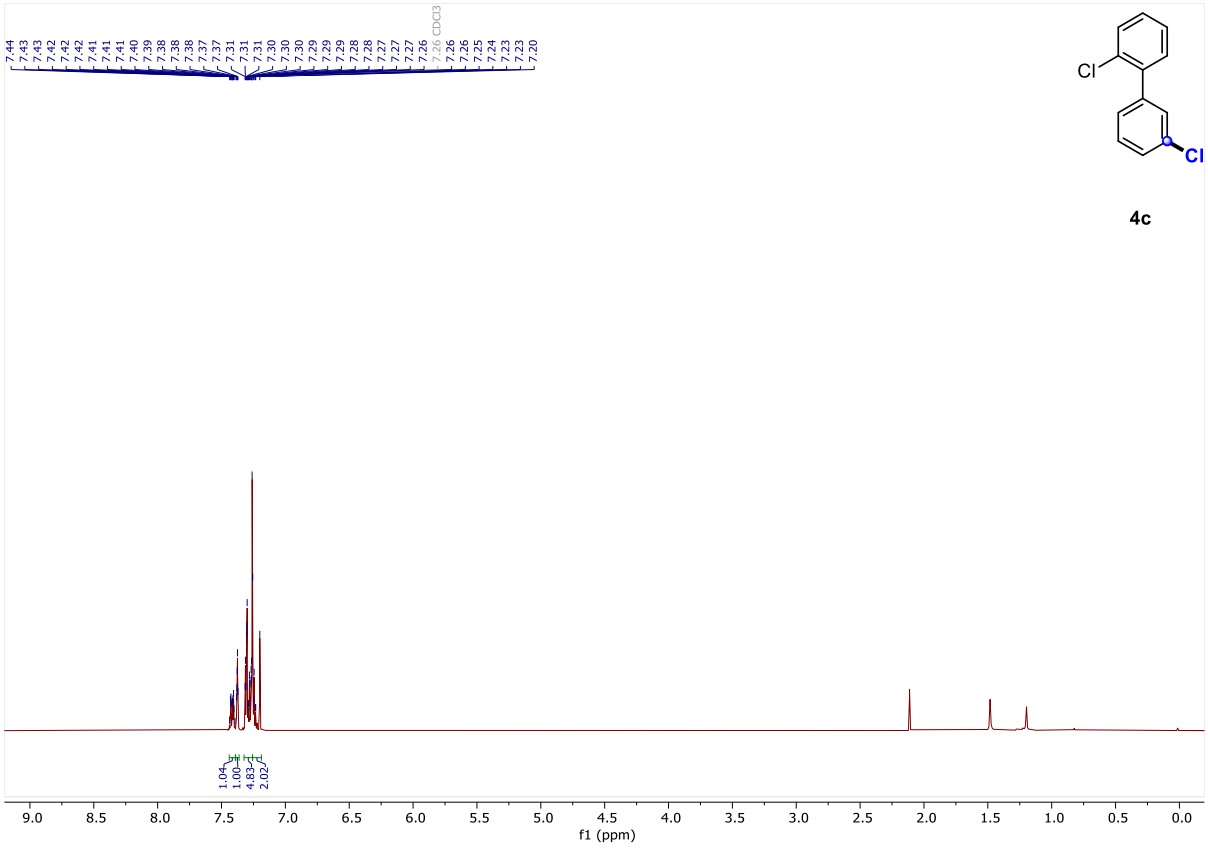


^{13}C NMR (101 MHz, $CDCl_3$)

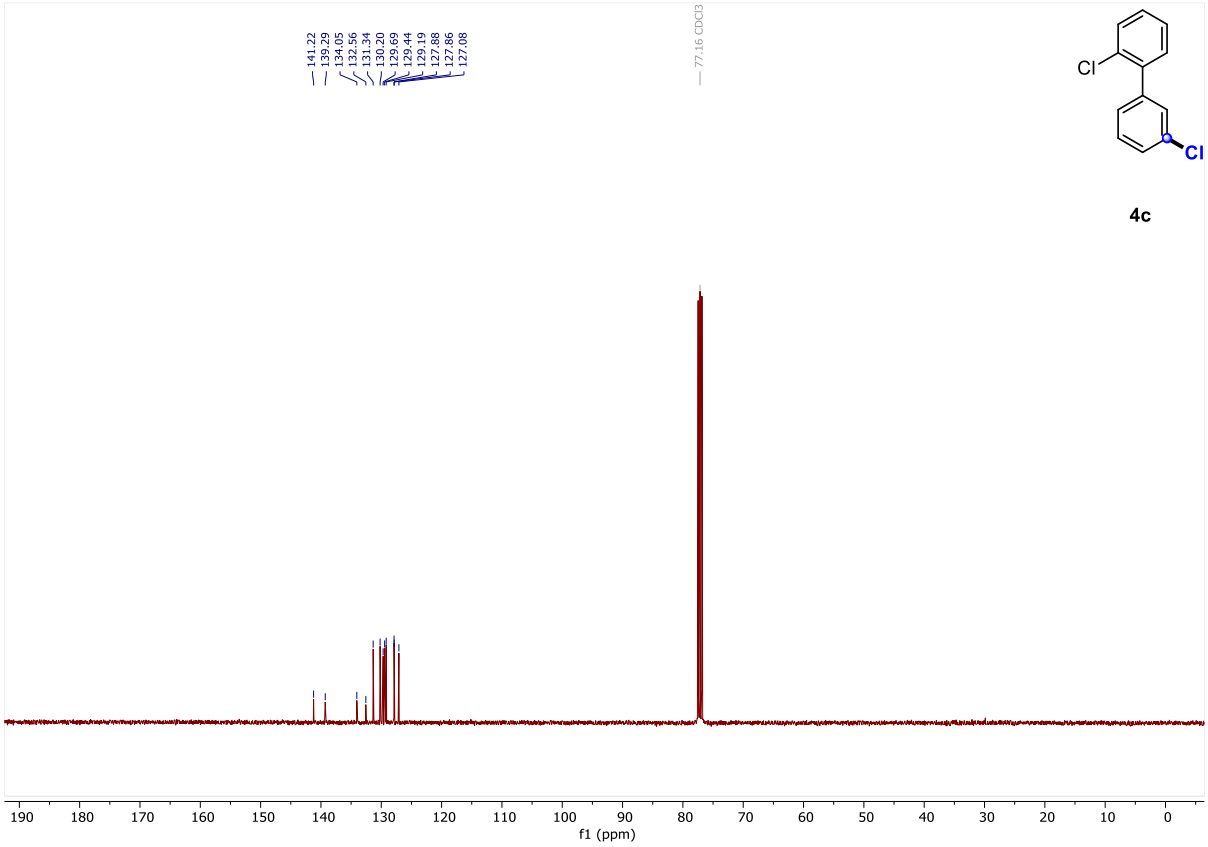


2,3'-dichloro-1,1'-biphenyl (4c) See procedure.

^{1}H NMR (400 MHz, $CDCl_3$)

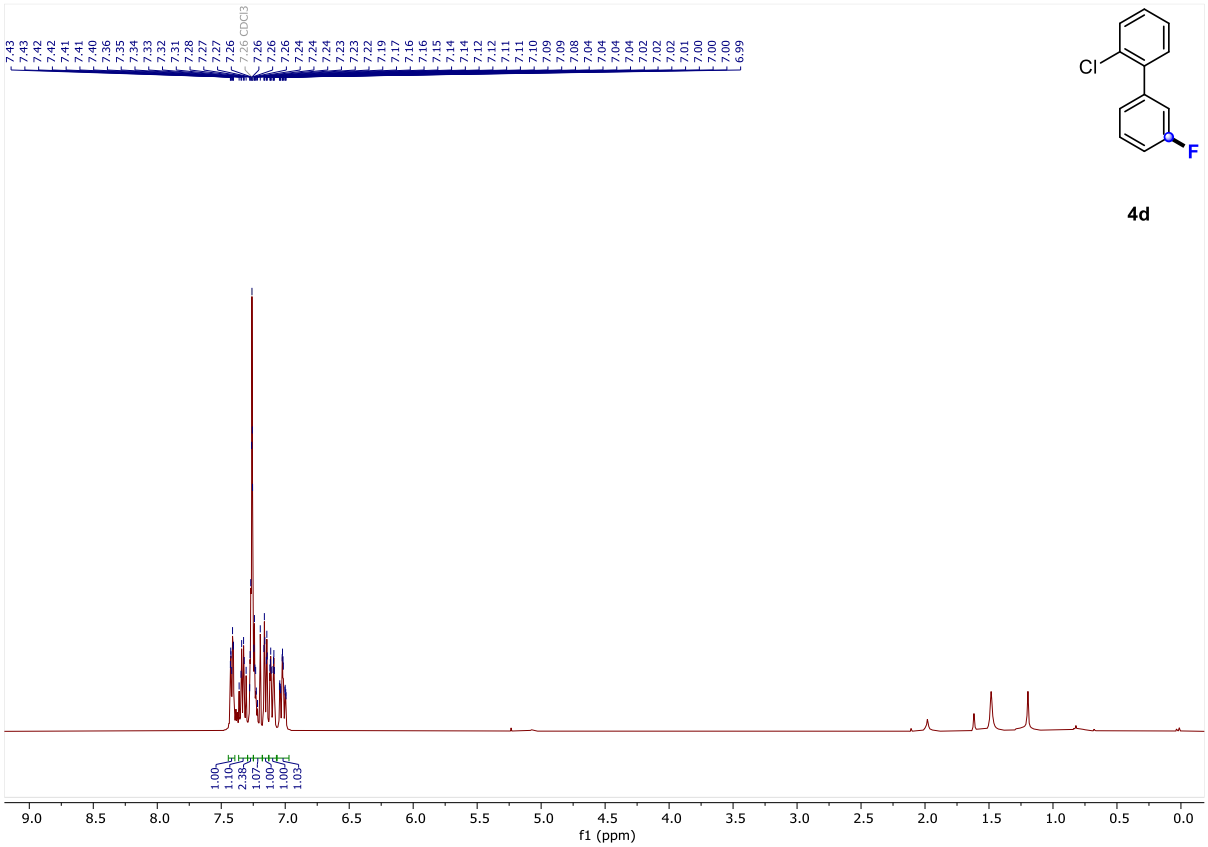


^{13}C NMR (101 MHz, $CDCl_3$)

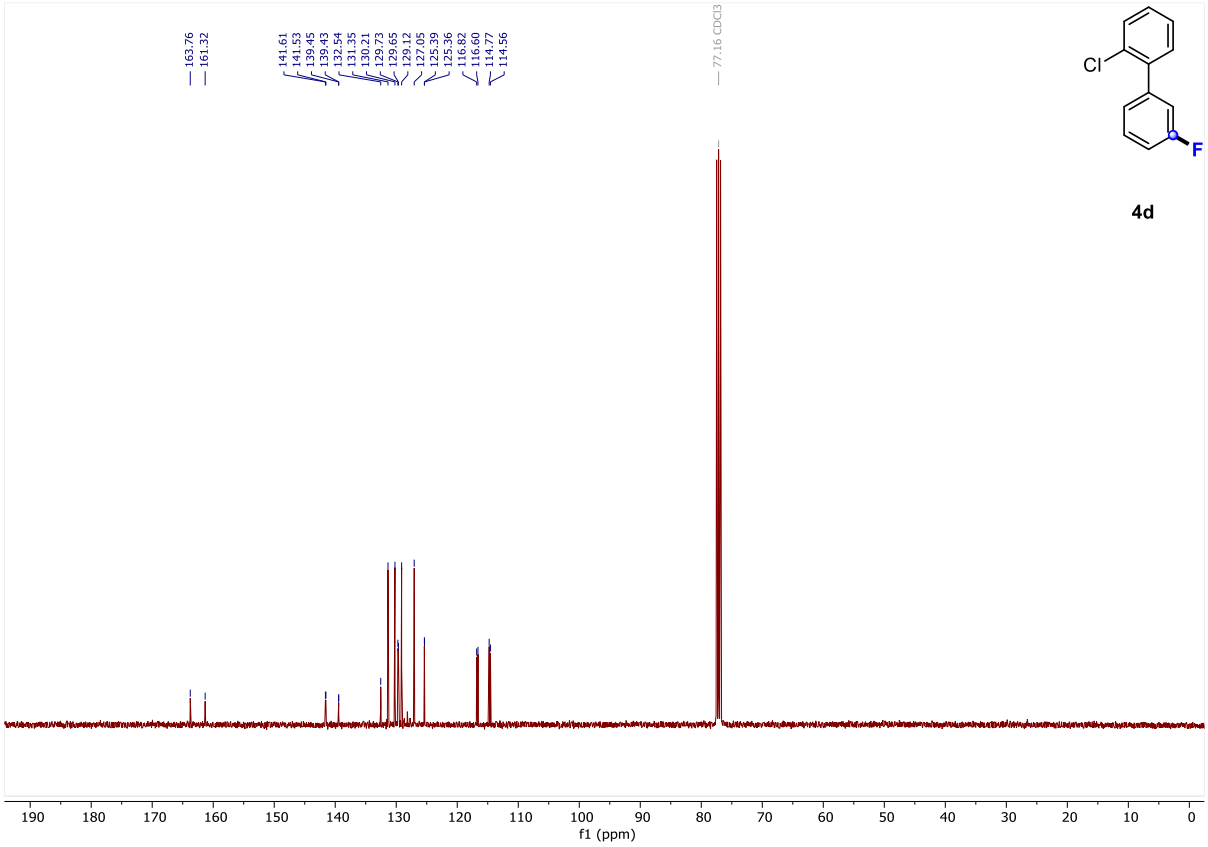


2-chloro-3'-fluoro-1,1'-biphenyl (4d) *See procedure*.

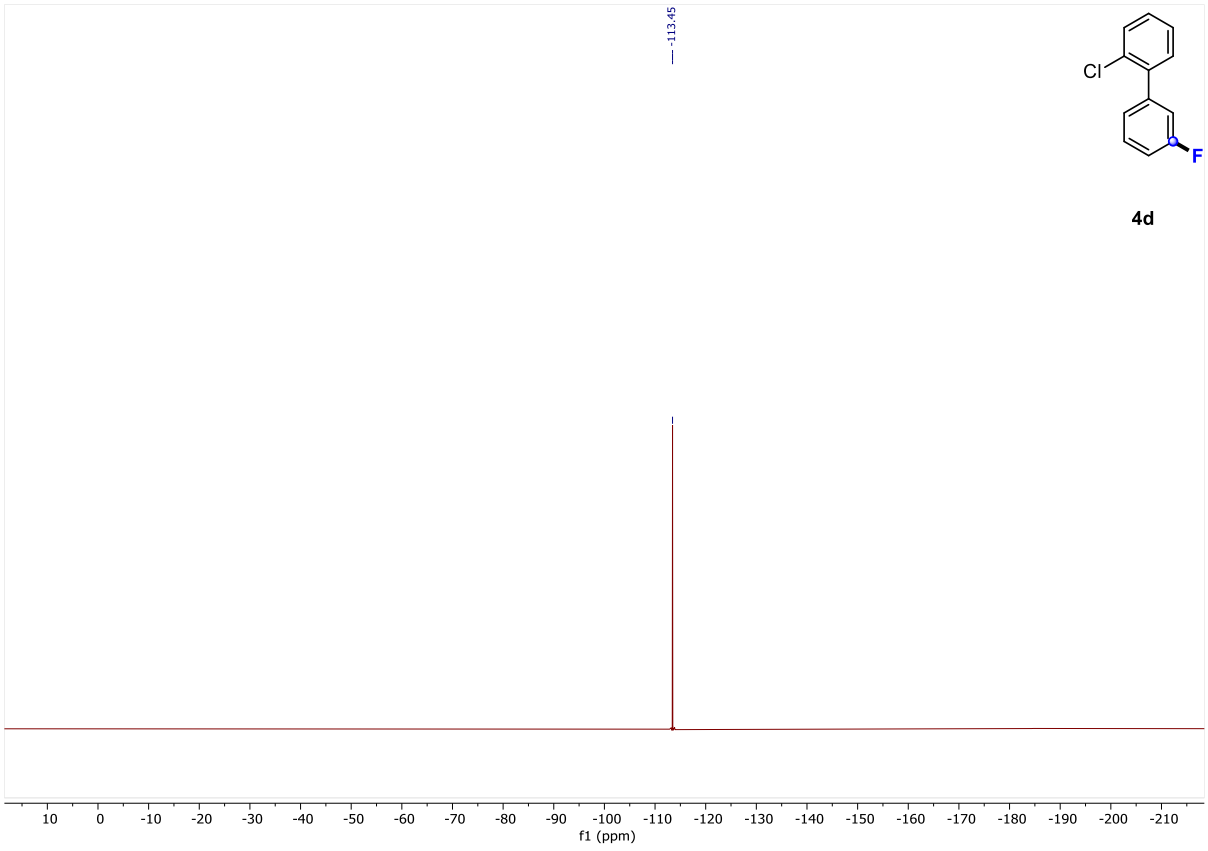
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

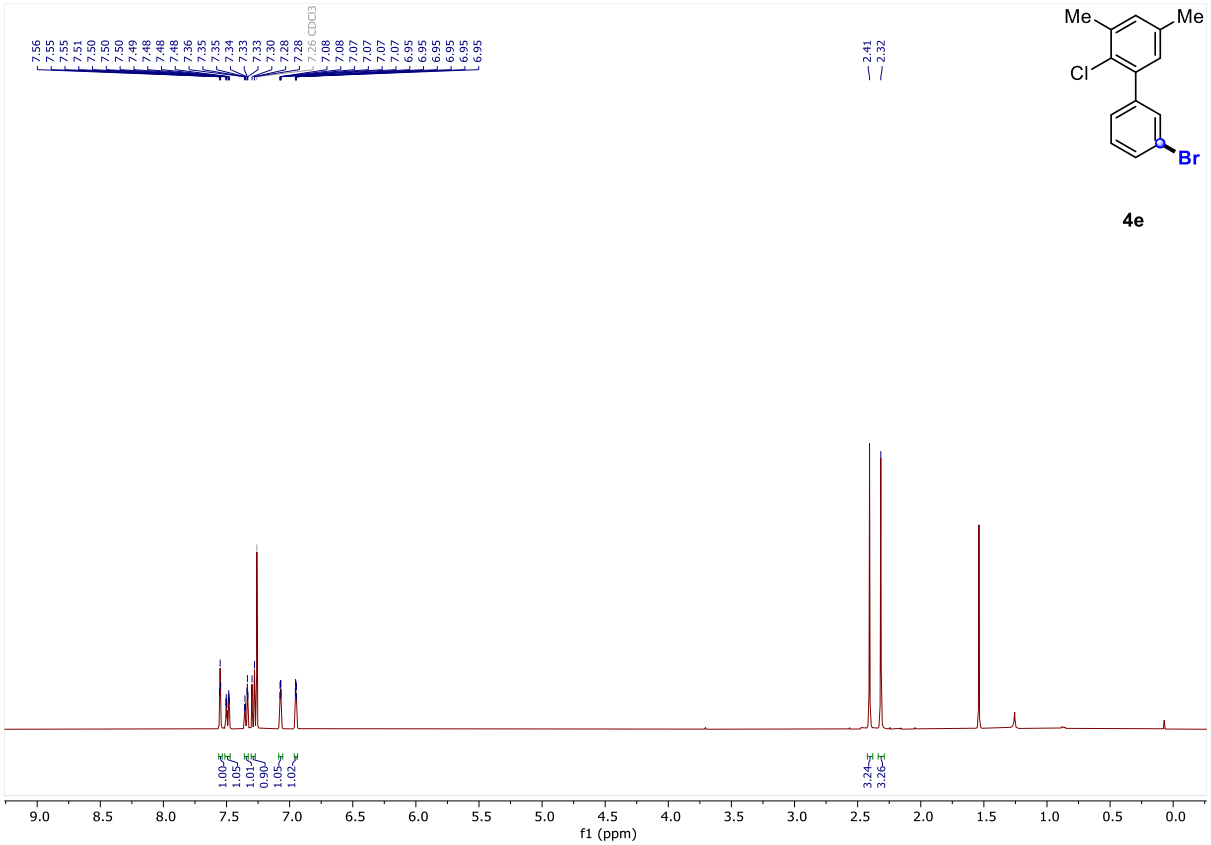


^{19}F NMR (377 MHz, $CDCl_3$)

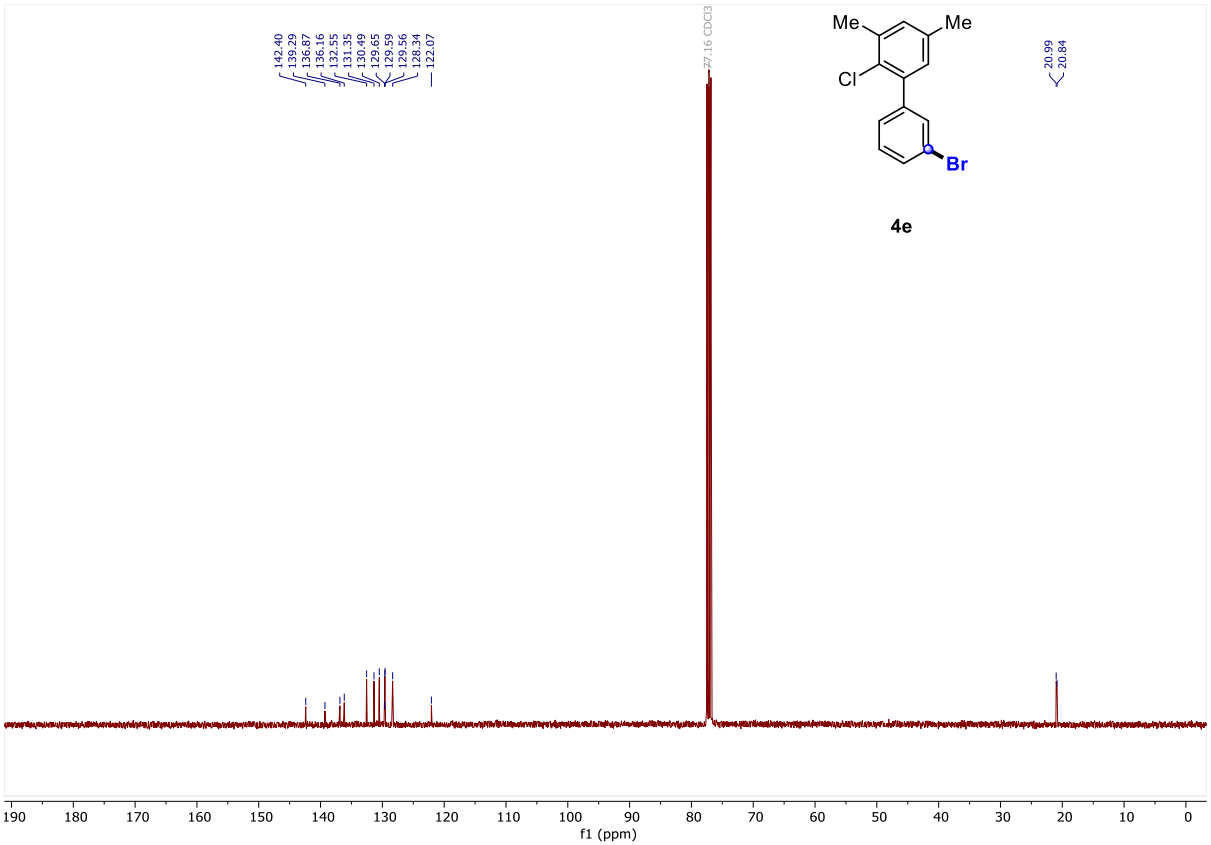


3'-bromo-2-chloro-3,5-dimethyl-1,1'-biphenyl (4e) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

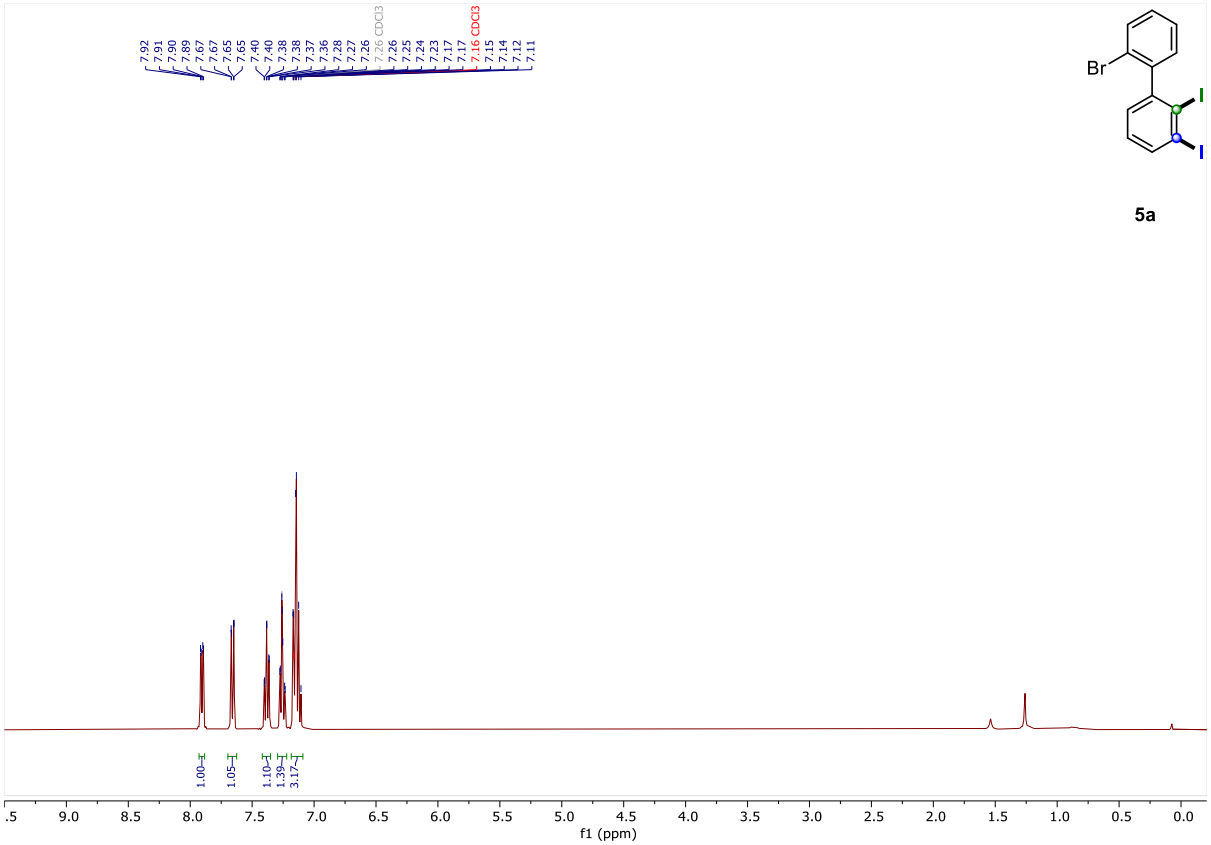


^{13}C NMR (101 MHz, $CDCl_3$)

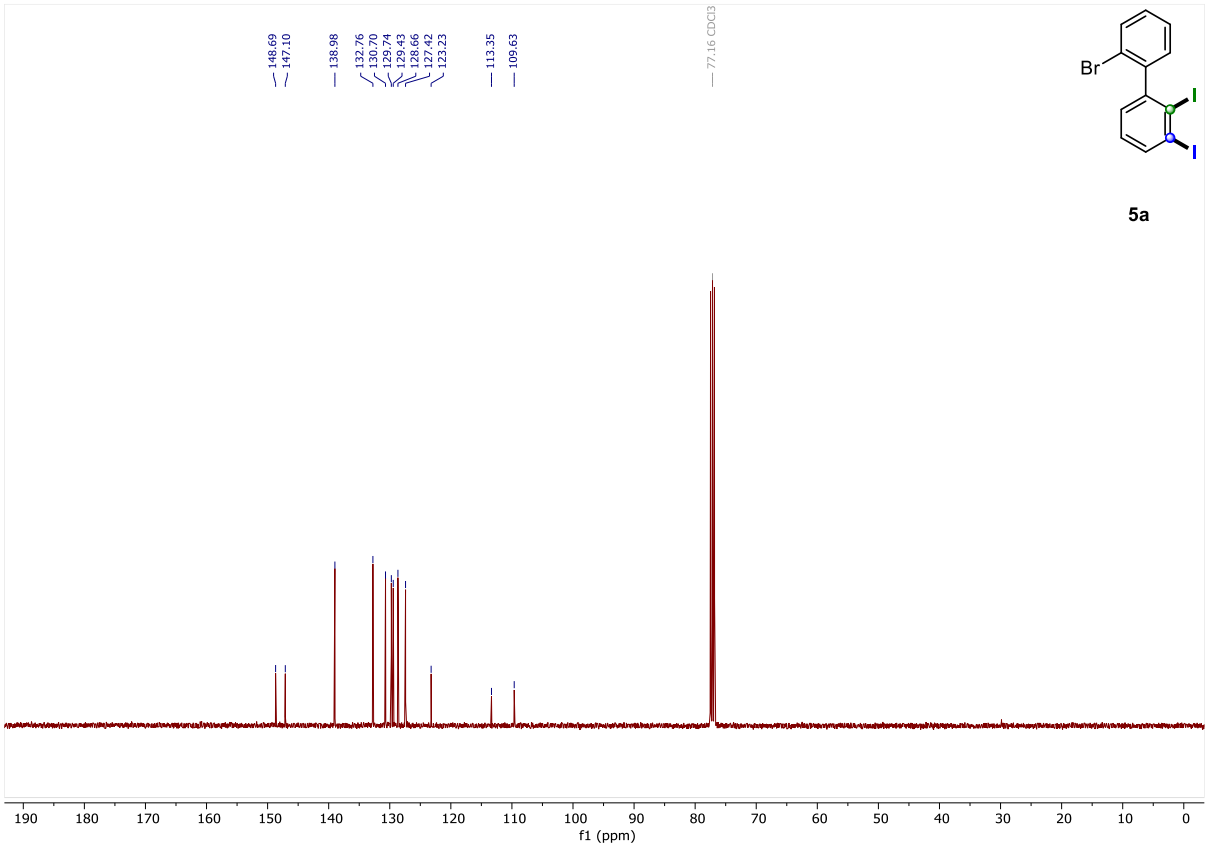


2'-bromo-2,3-diiodo-1,1'-biphenyl (5a) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

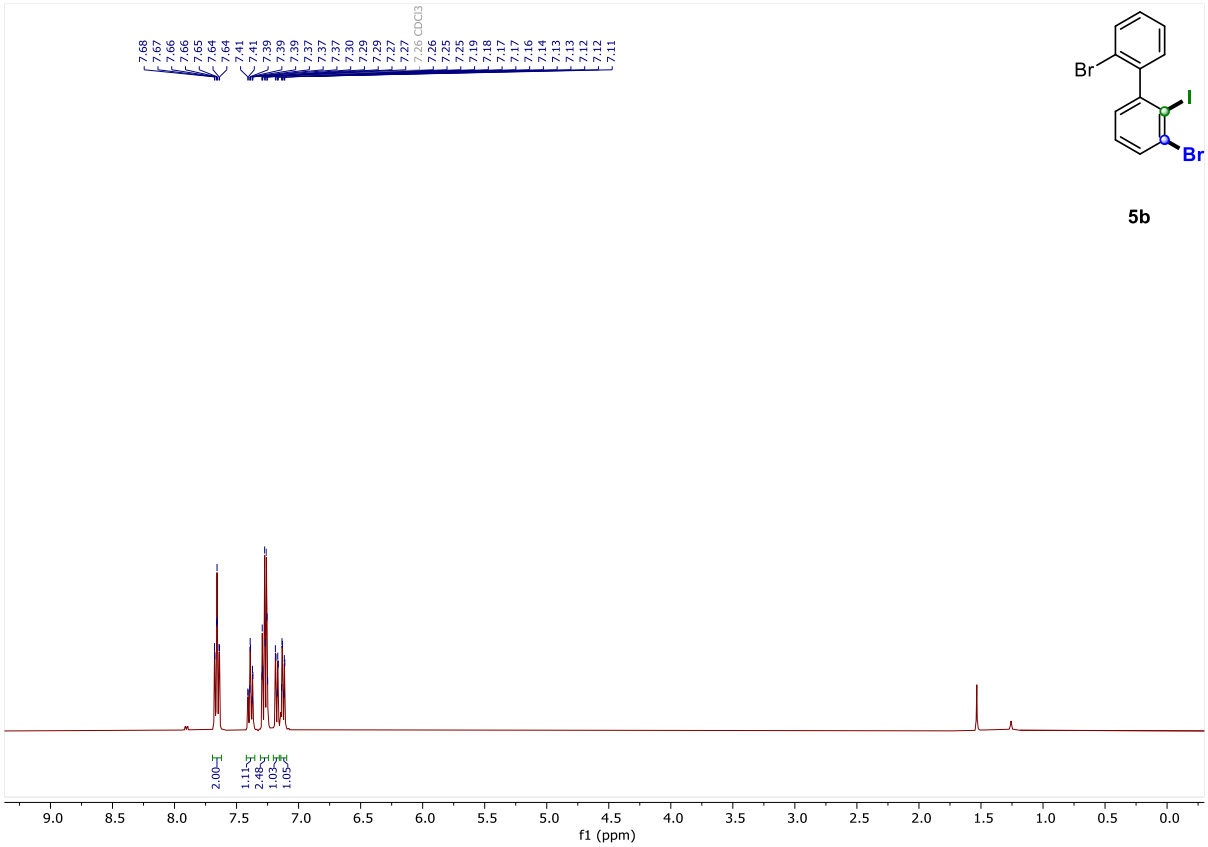


^{13}C NMR (101 MHz, $CDCl_3$)

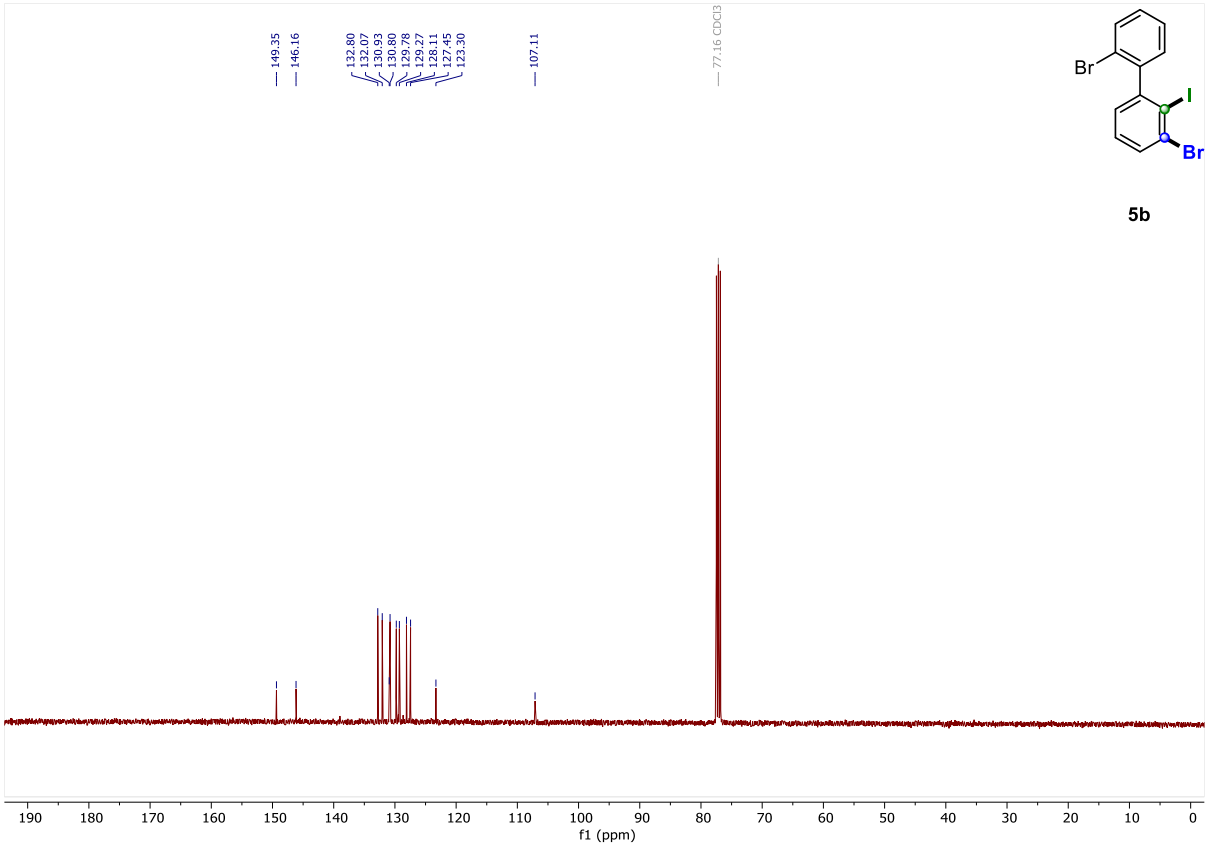


2',3-dibromo-2-iodo-1,1'-biphenyl (5b) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

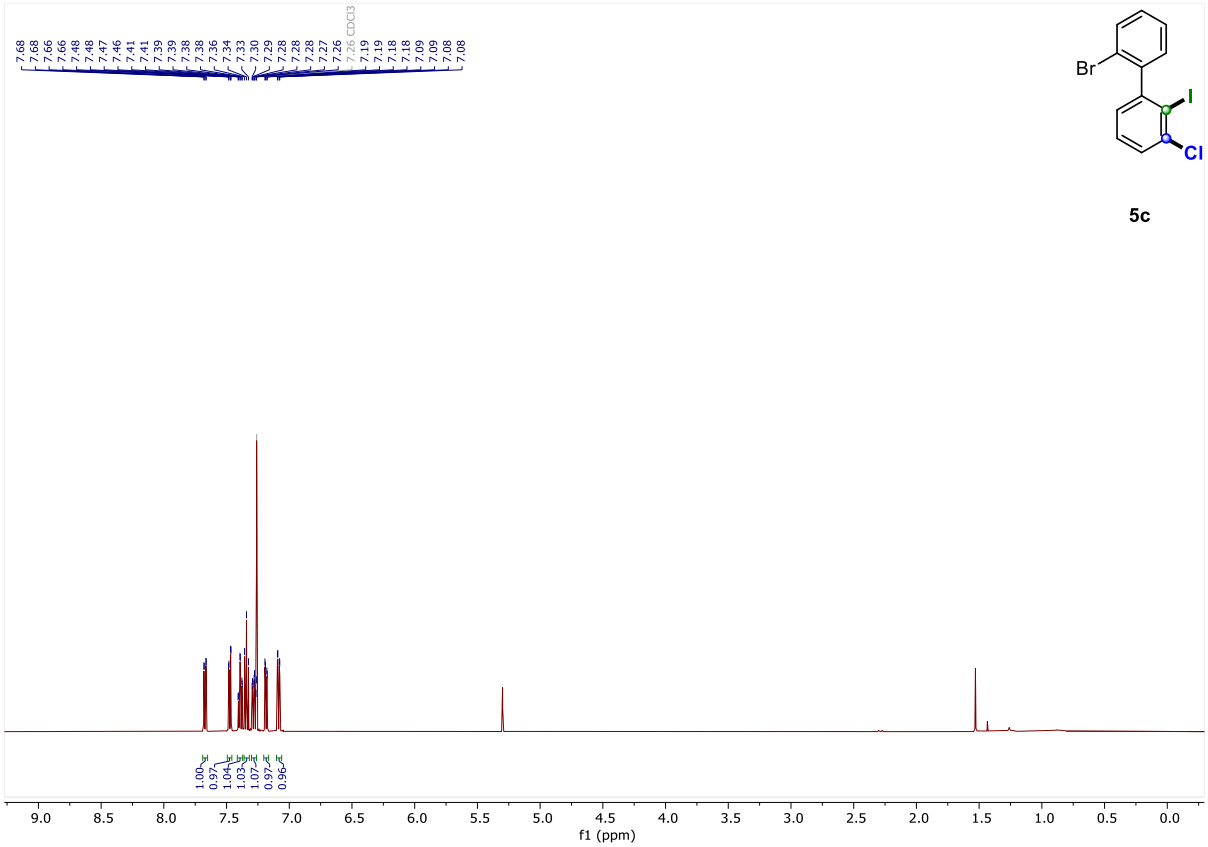


^{13}C NMR (101 MHz, $CDCl_3$)

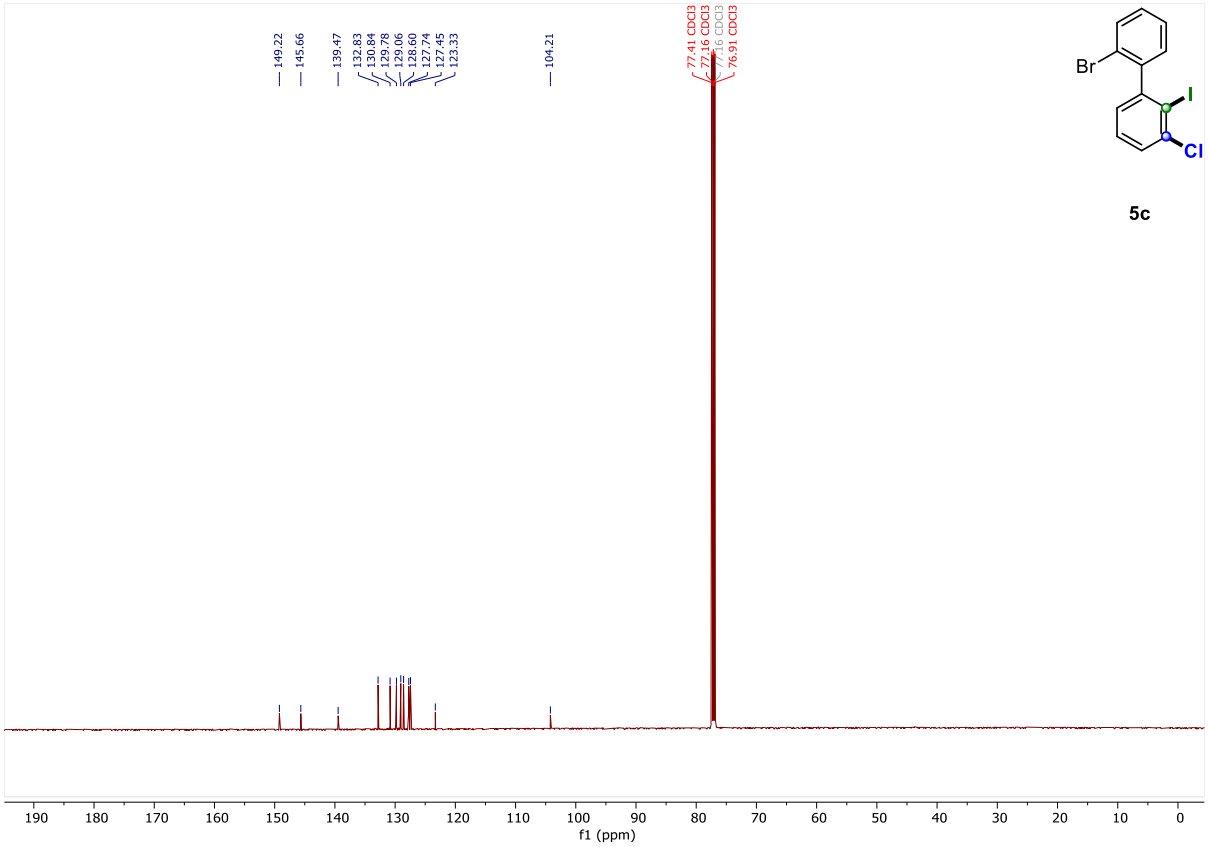


2'-bromo-3-chloro-2-iodo-1,1'-biphenyl (5c) *See procedure*.

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

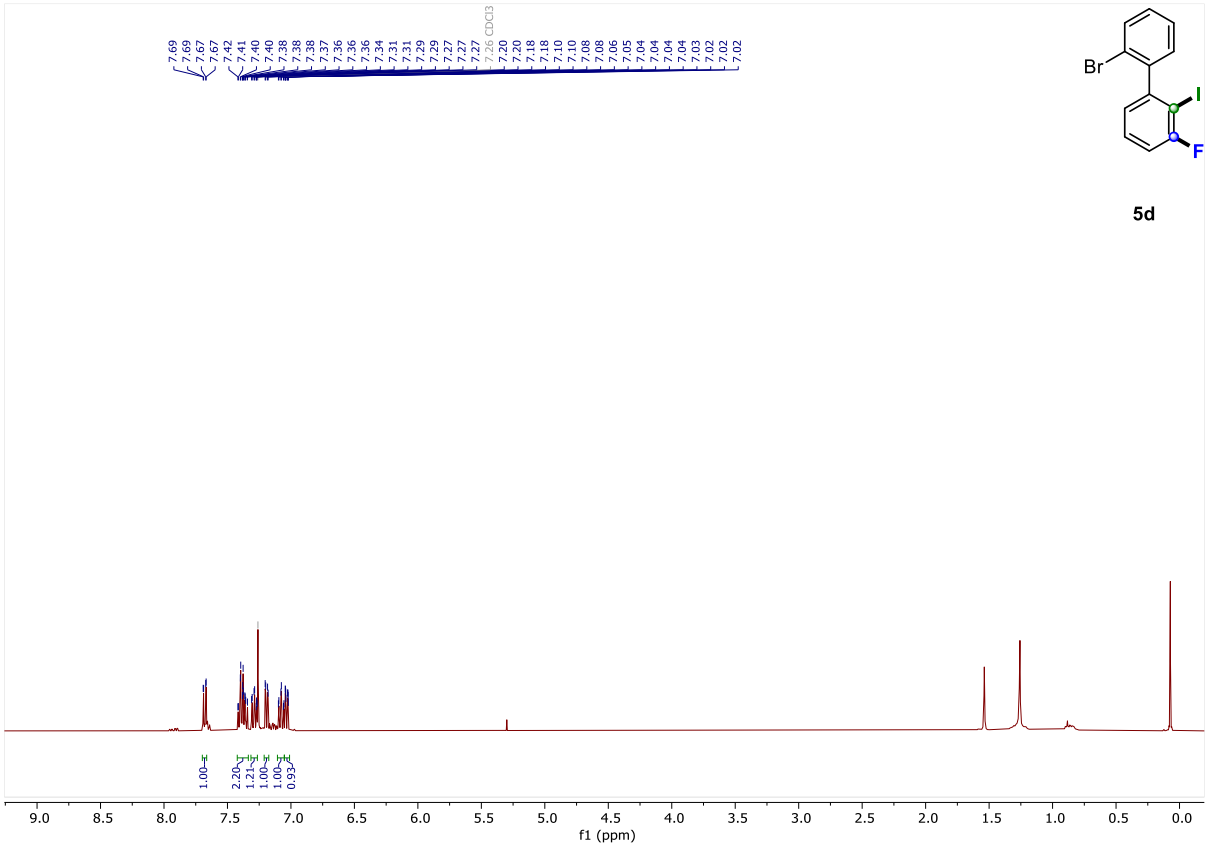


^{13}C NMR (126 MHz, $CDCl_3$)

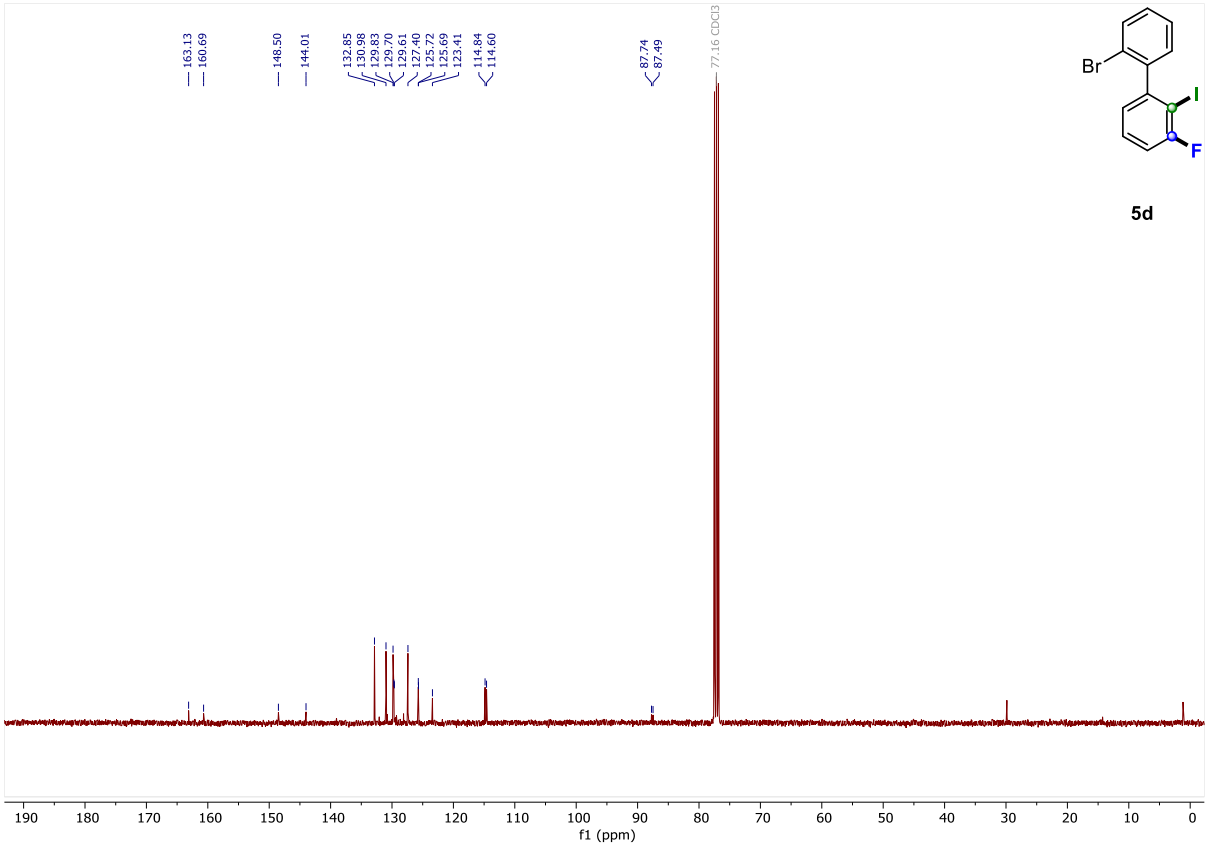


2'-bromo-3-fluoro-2-iodo-1,1'-biphenyl (5d) *See procedure*.

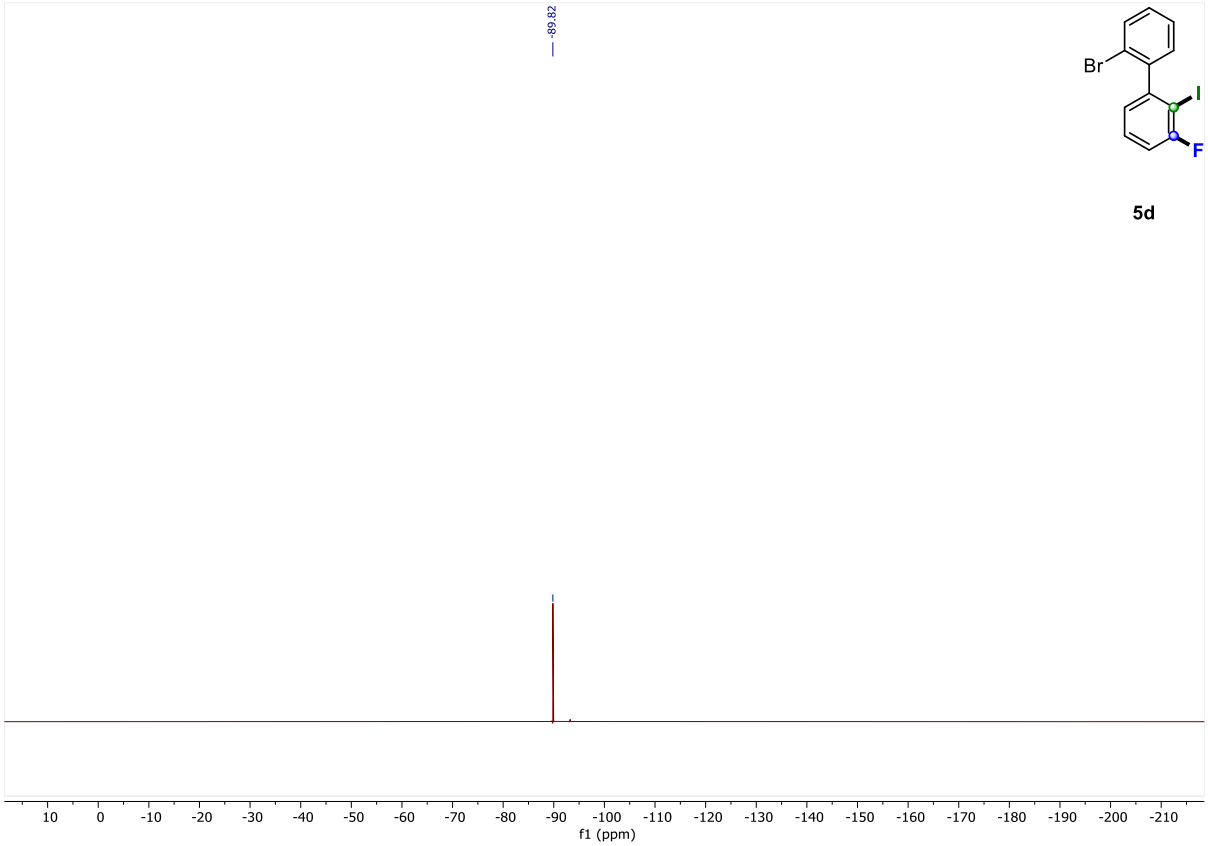
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

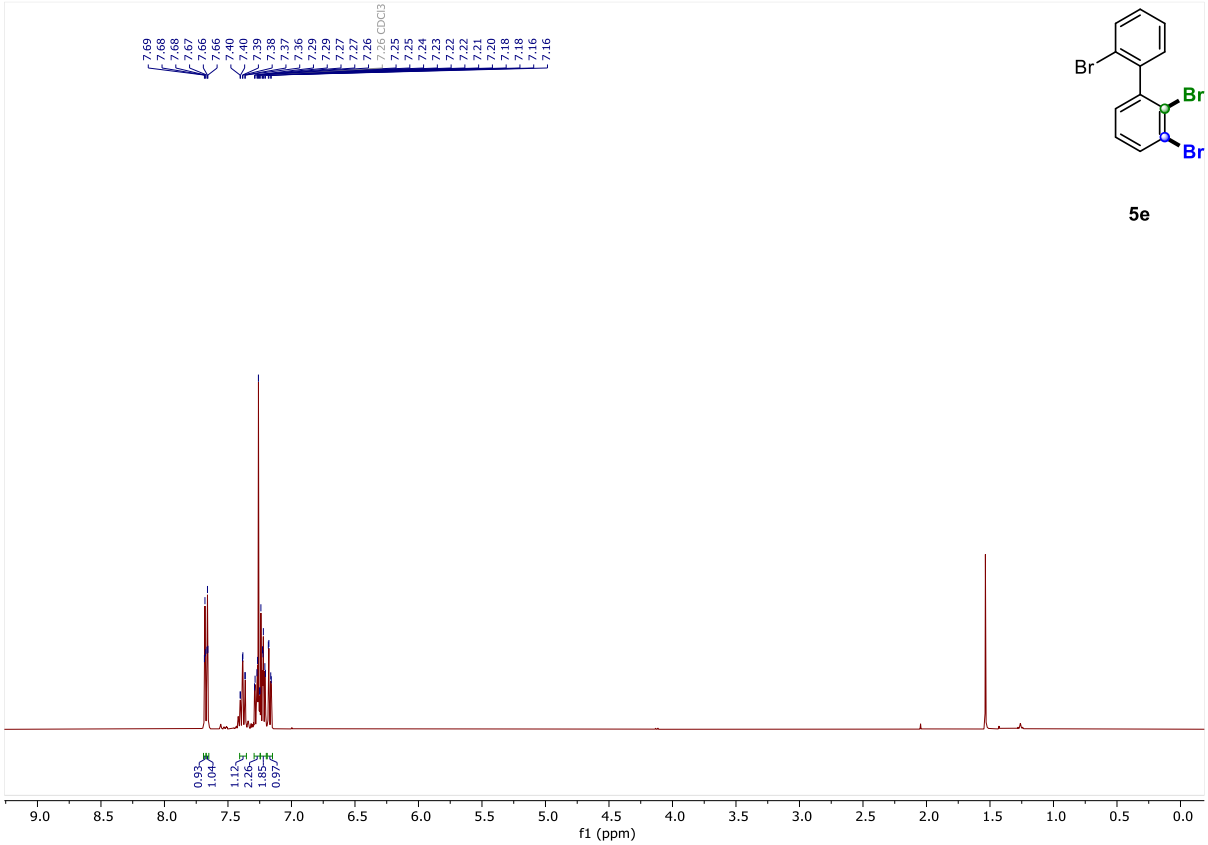


^{19}F NMR (377 MHz, $CDCl_3$)

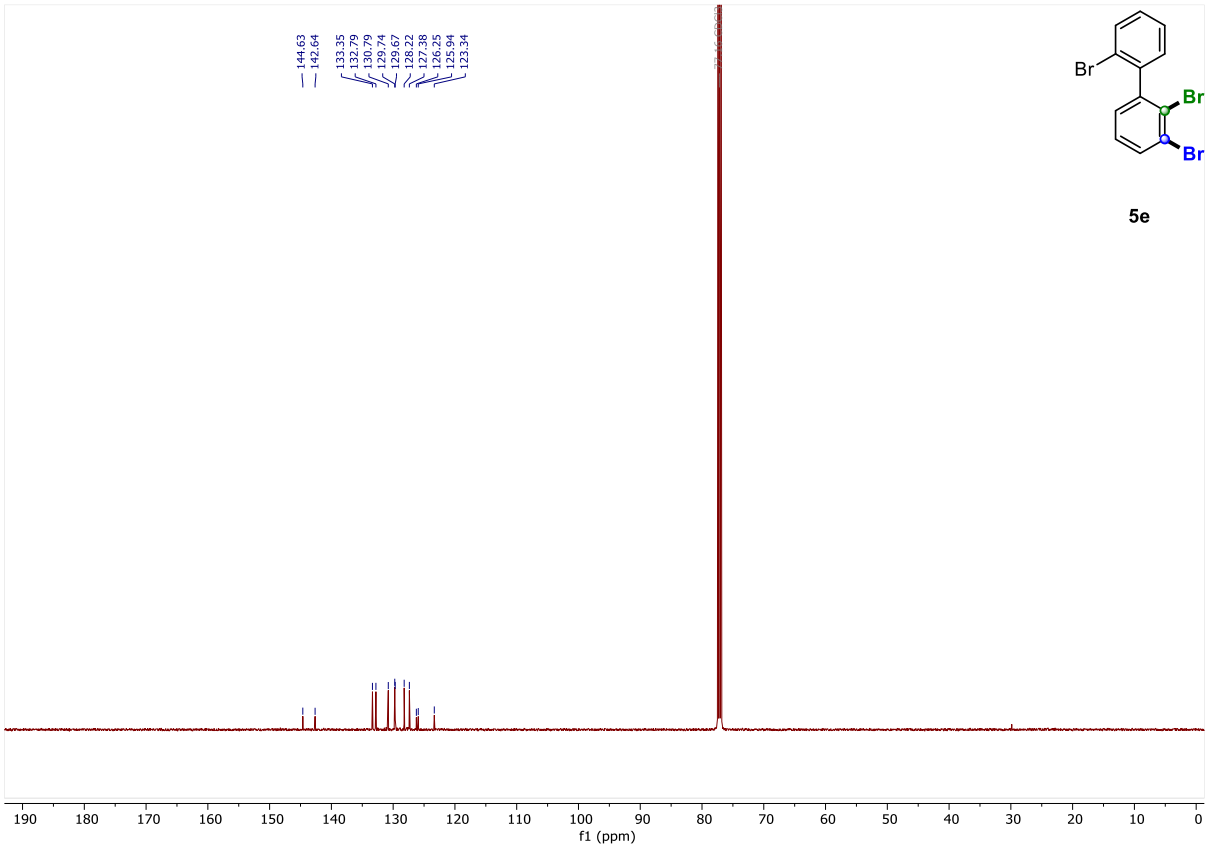


2,2',3-tribromo-1,1'-biphenyl (5e) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

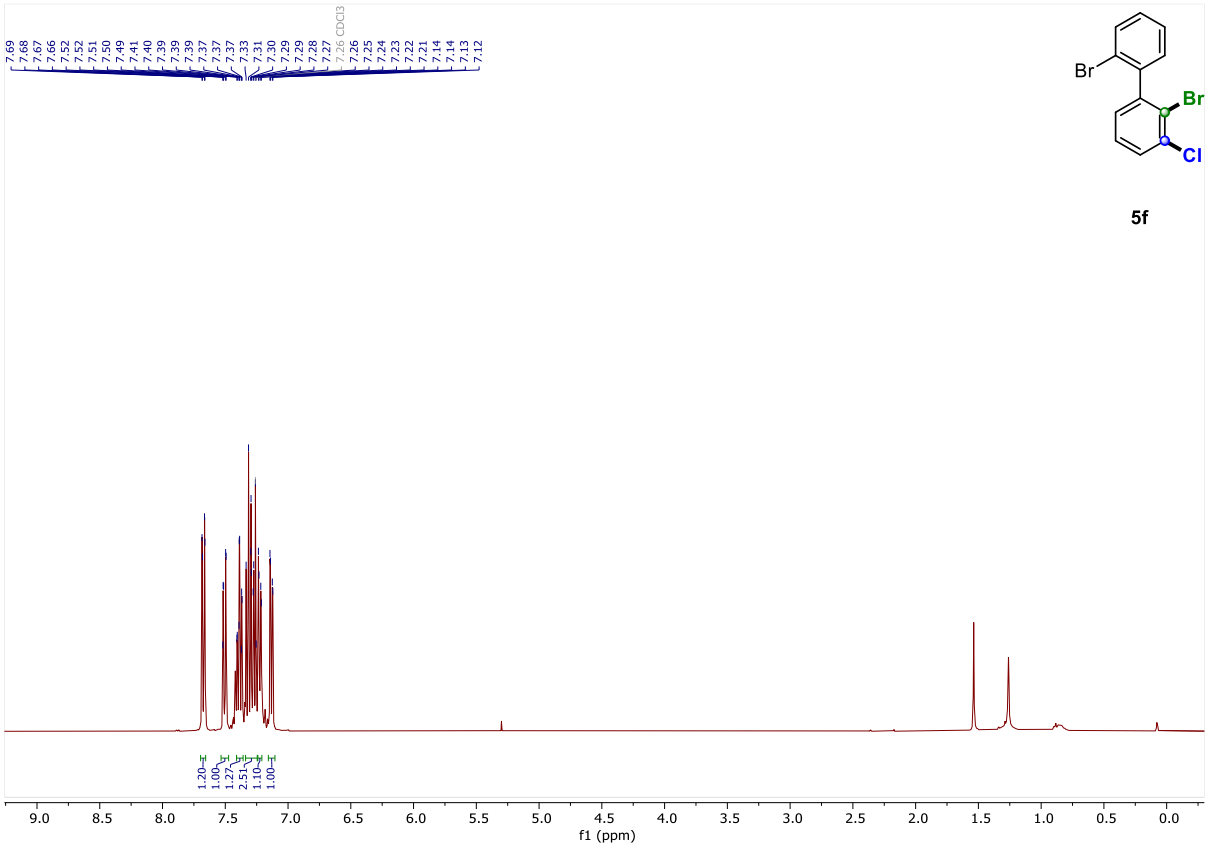


^{13}C NMR (126 MHz, $CDCl_3$)

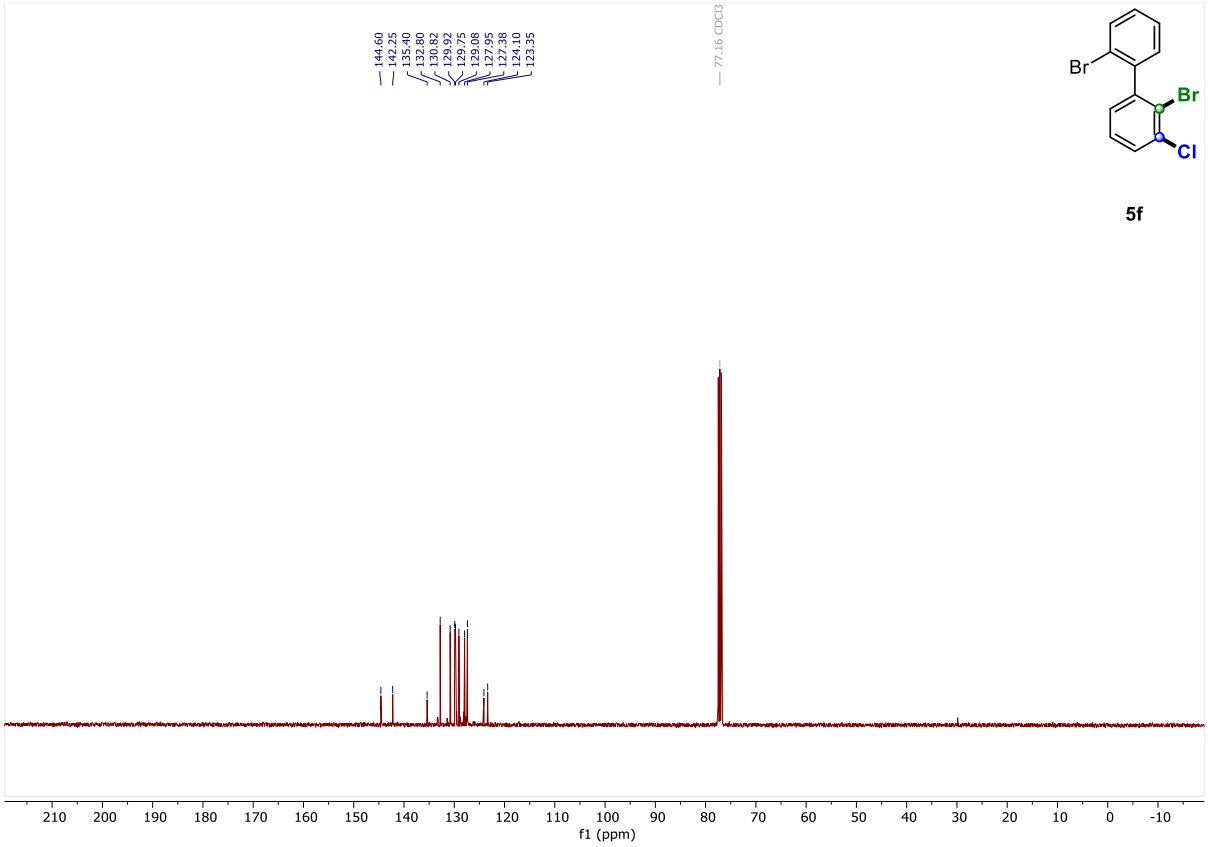


2,2'-dibromo-3-chloro-1,1'-biphenyl (5f) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

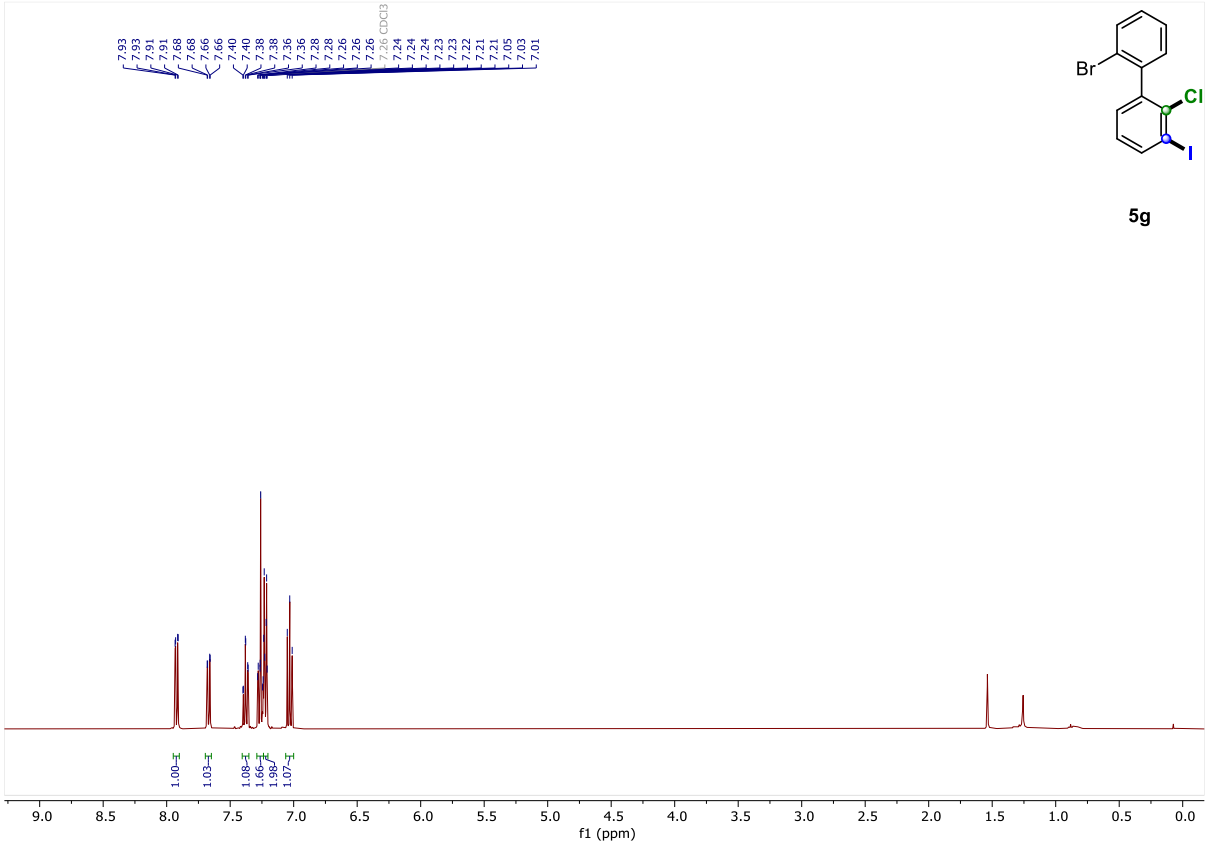


^{13}C NMR (101 MHz, $CDCl_3$)

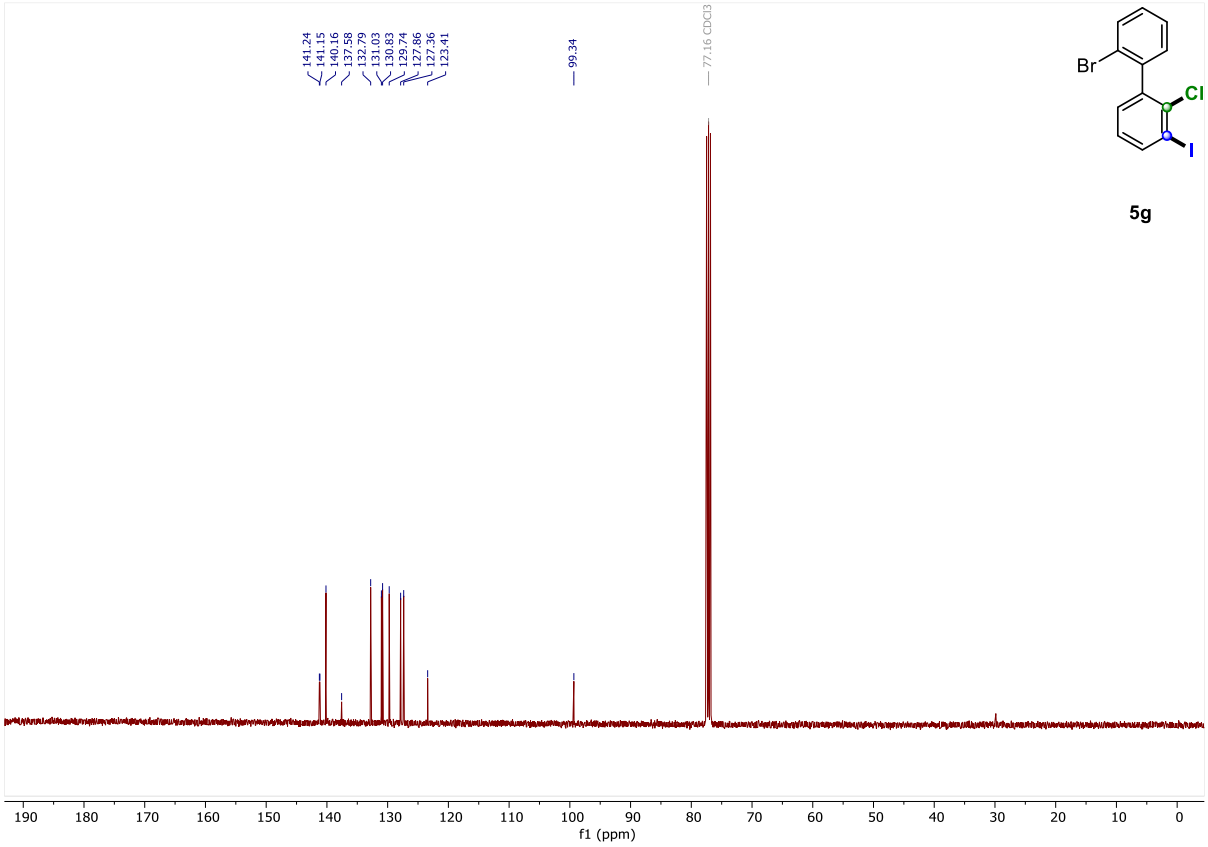


2'-bromo-2-chloro-3-iodo-1,1'-biphenyl (5g) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

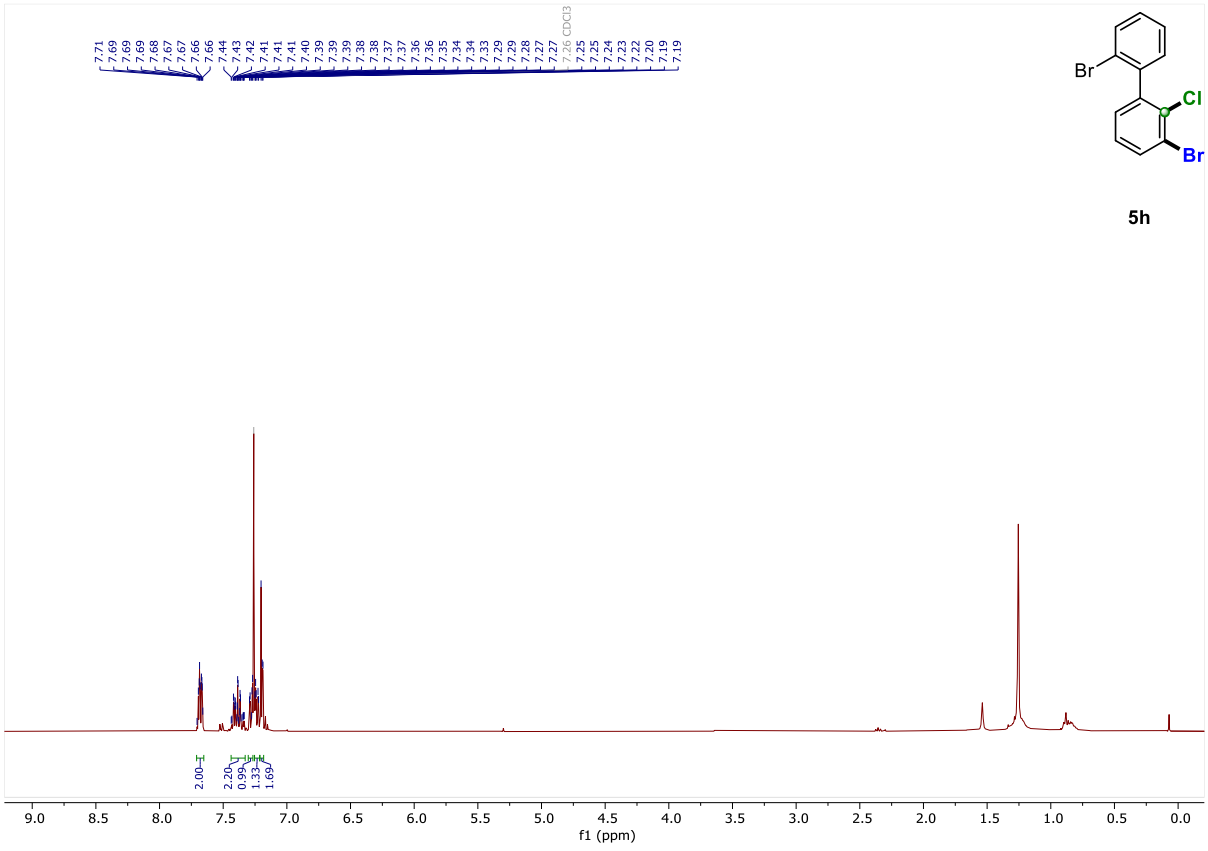


^{13}C NMR (101 MHz, $CDCl_3$)

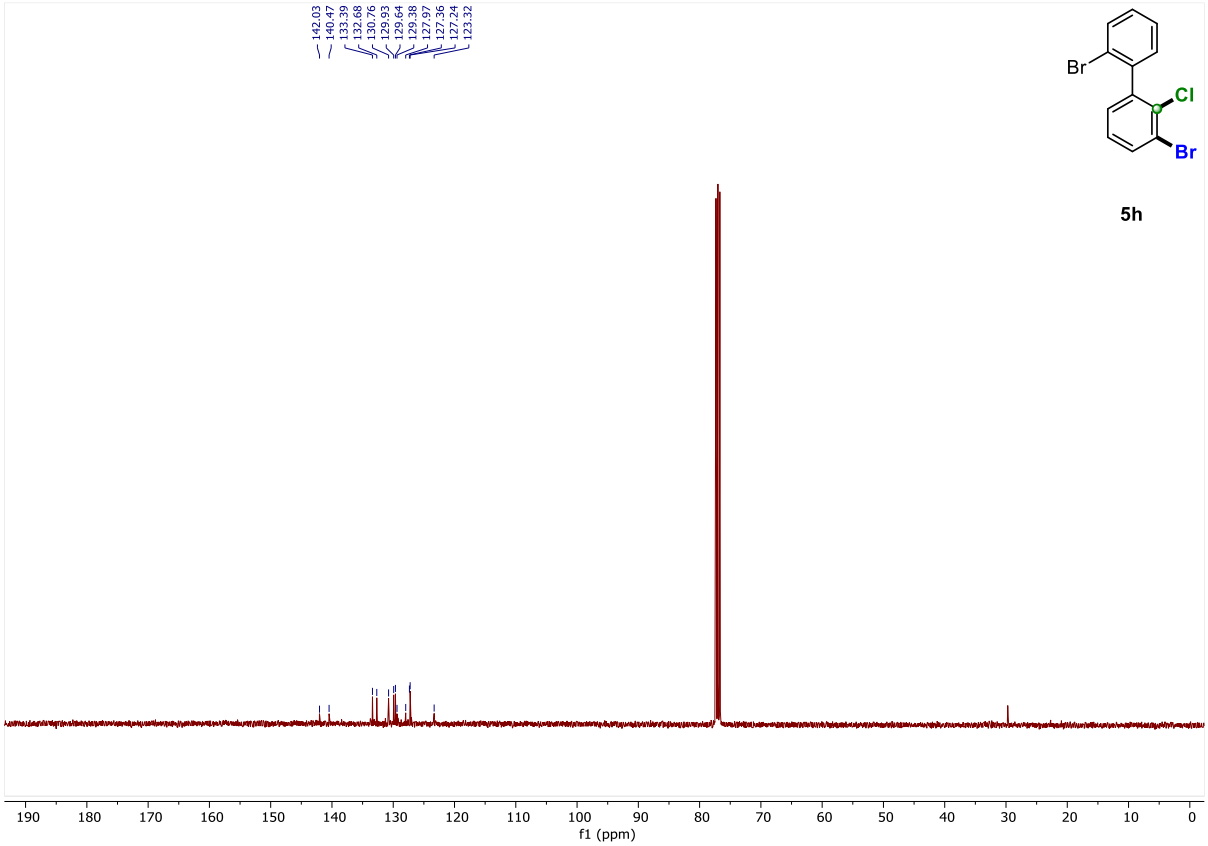


2',3-dibromo-2-chloro-1,1'-biphenyl (5h) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

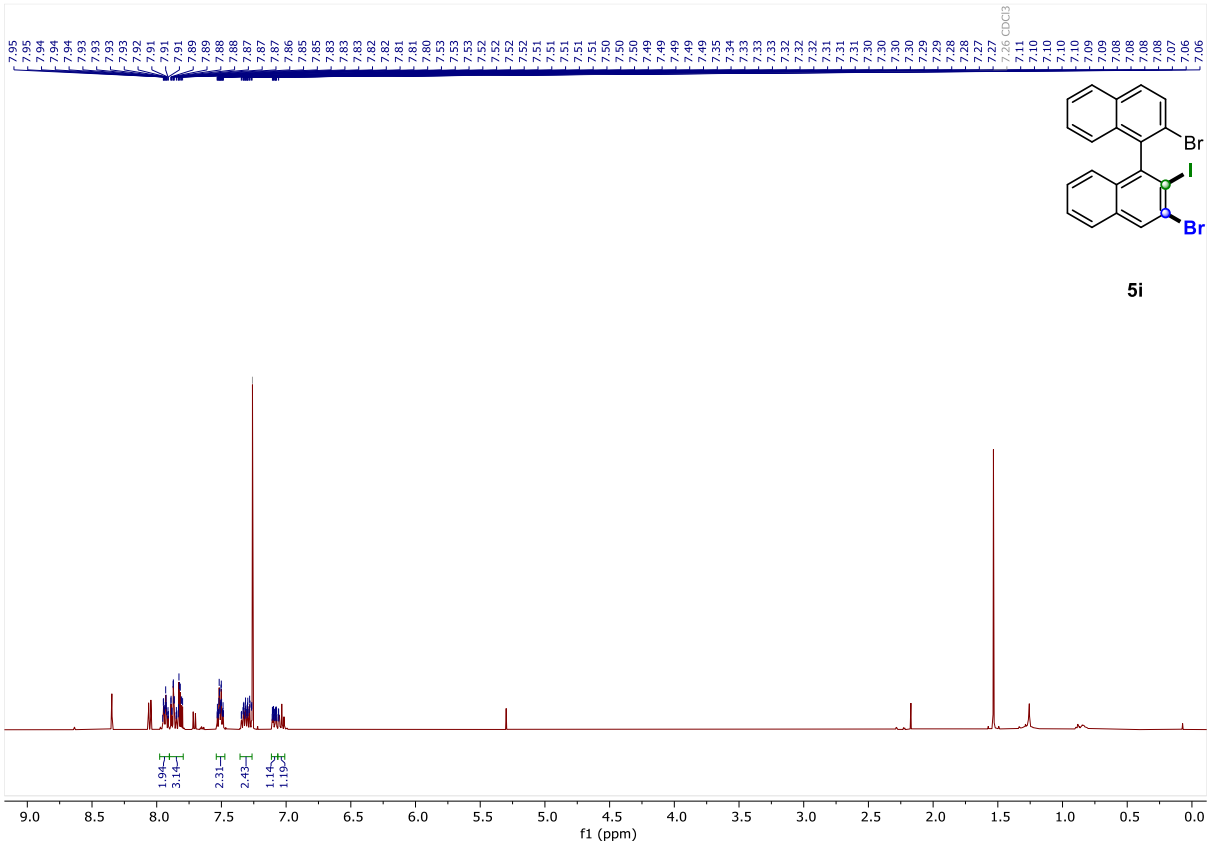


^{13}C NMR (101 MHz, $CDCl_3$)

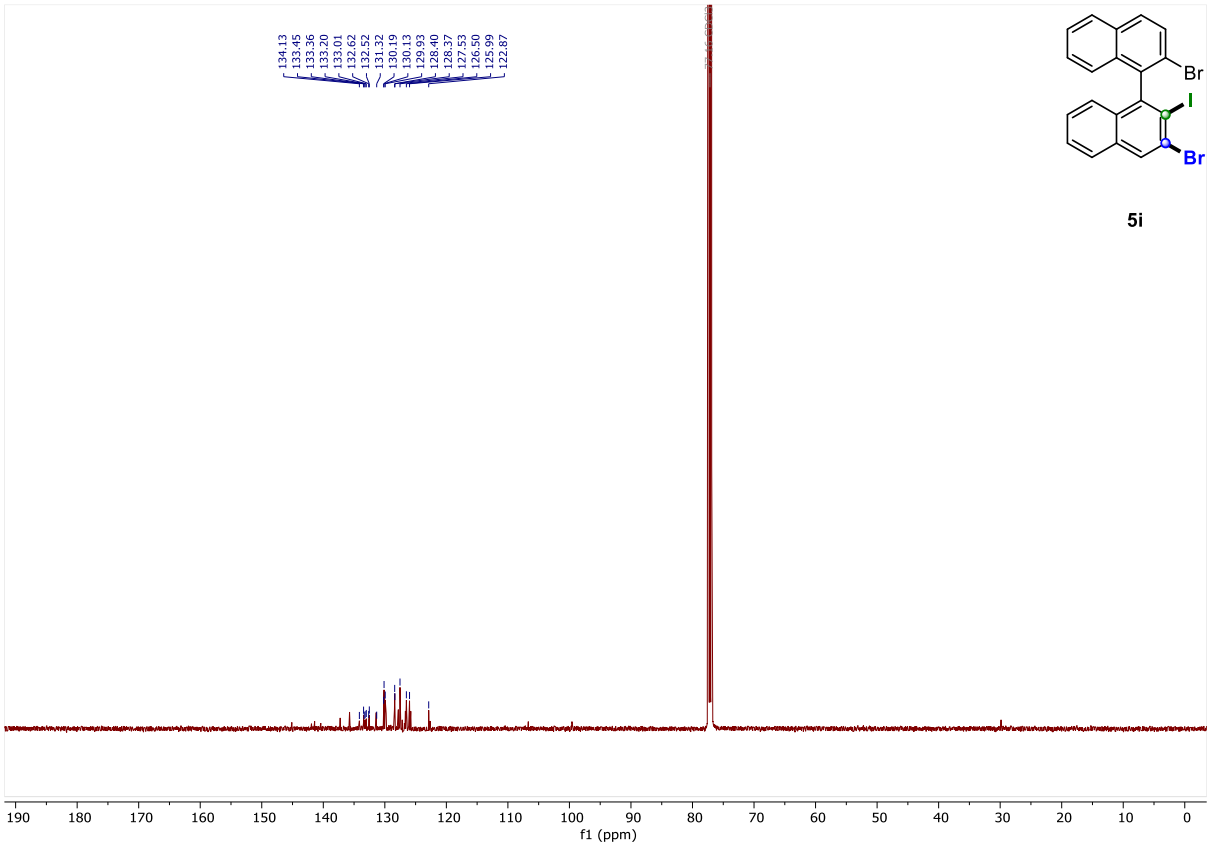


2',3-dibromo-2-iodo-1,1'-binaphthalene (5i) *See procedure*.

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

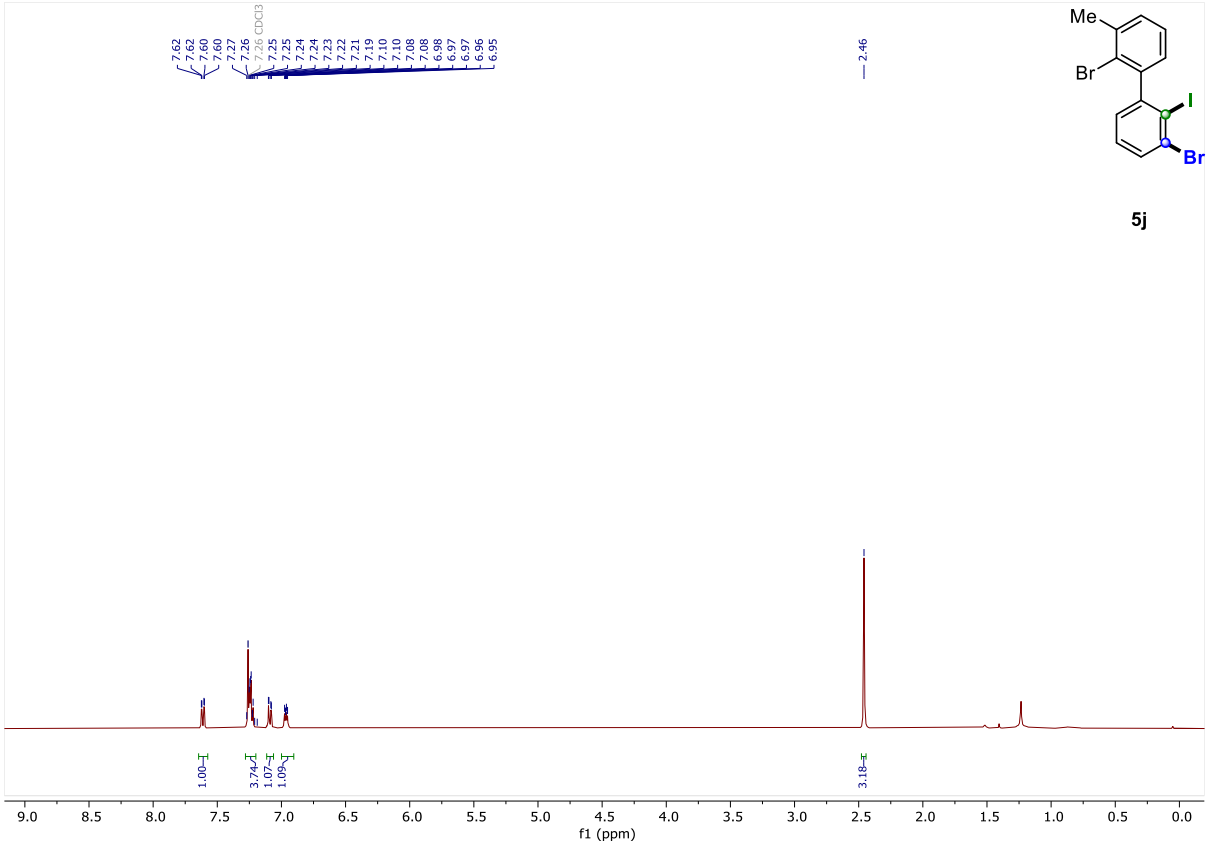


^{13}C NMR (126 MHz, $CDCl_3$)

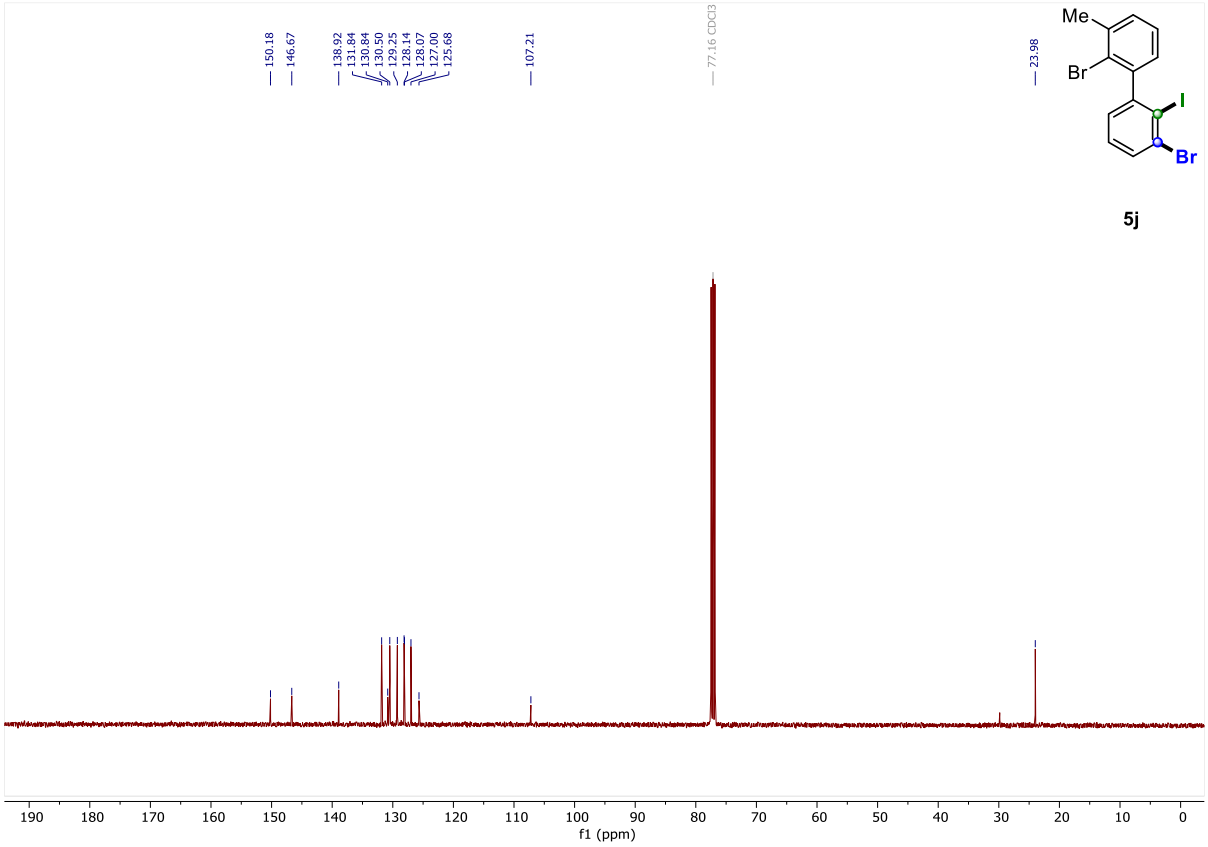


2,3'-dibromo-2'-iodo-3-methyl-1,1'-biphenyl (5j) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

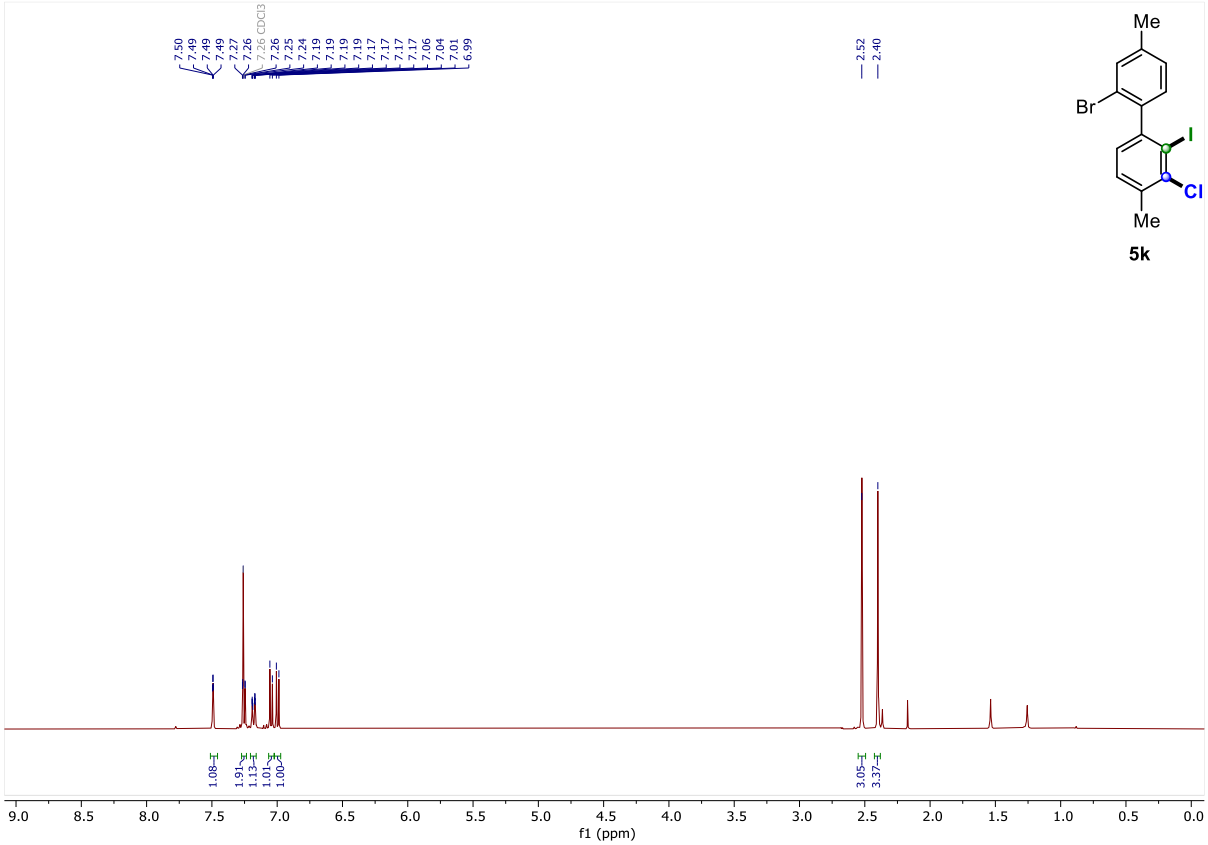


^{13}C NMR (101 MHz, $CDCl_3$)

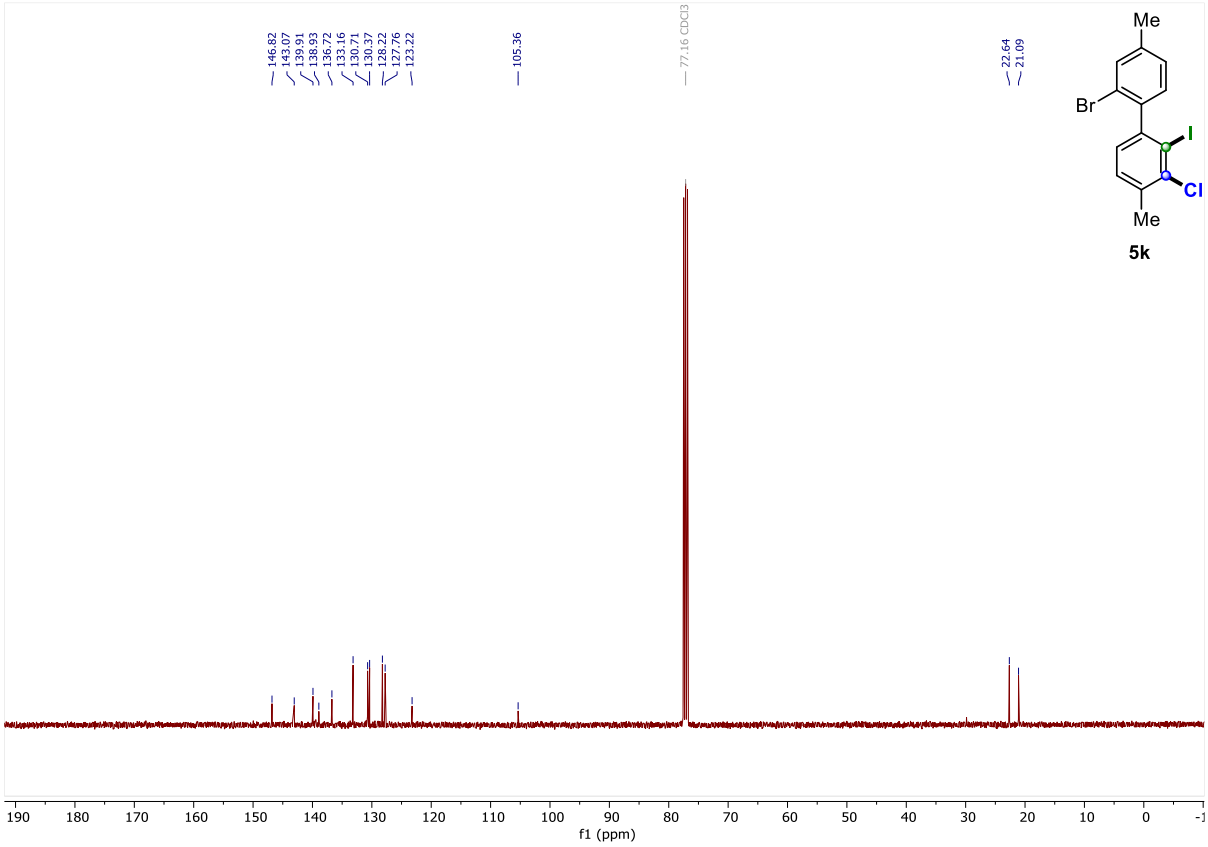


2'-bromo-3-chloro-2-iodo-4,4'-dimethyl-1,1'-biphenyl (5k) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

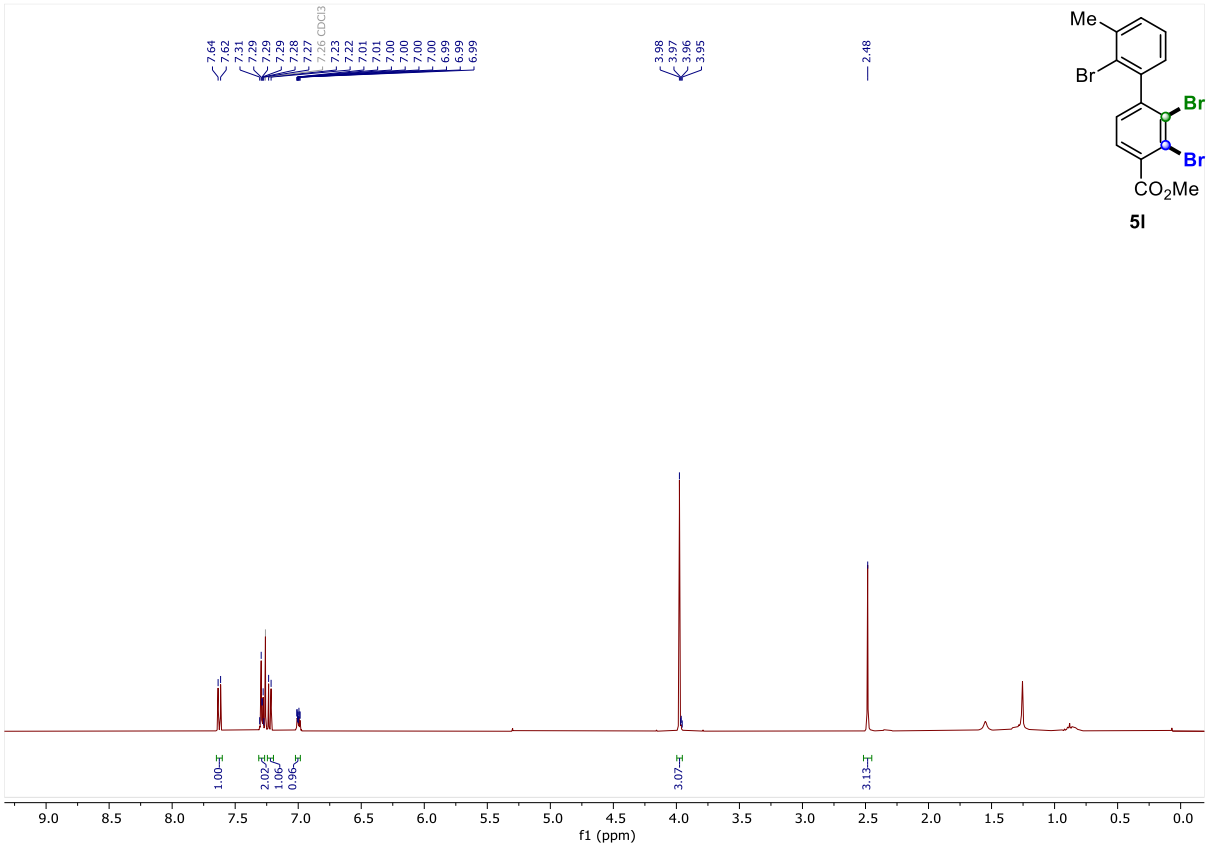


^{13}C NMR (101 MHz, $CDCl_3$)

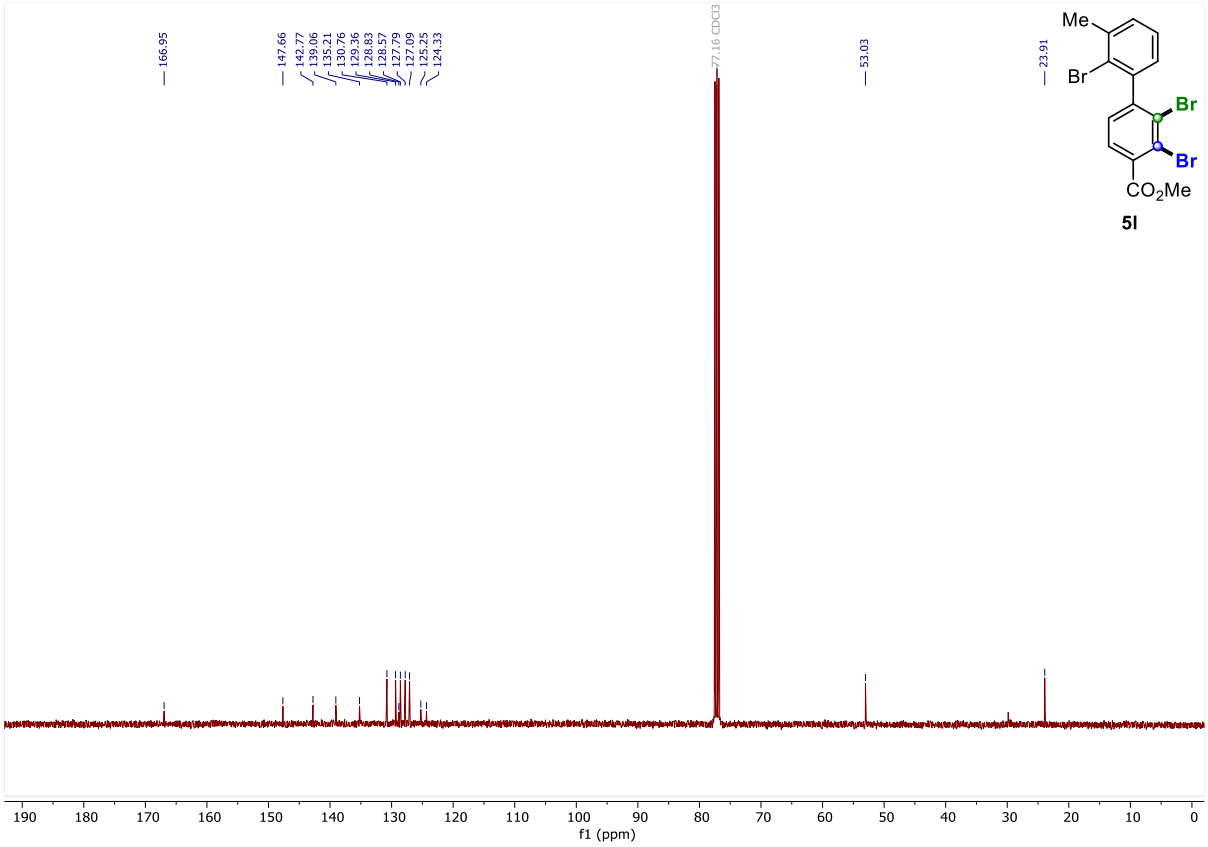


methyl 2,2',3-tribromo-3'-methyl-[1,1'-biphenyl]-4-carboxylate (5l) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

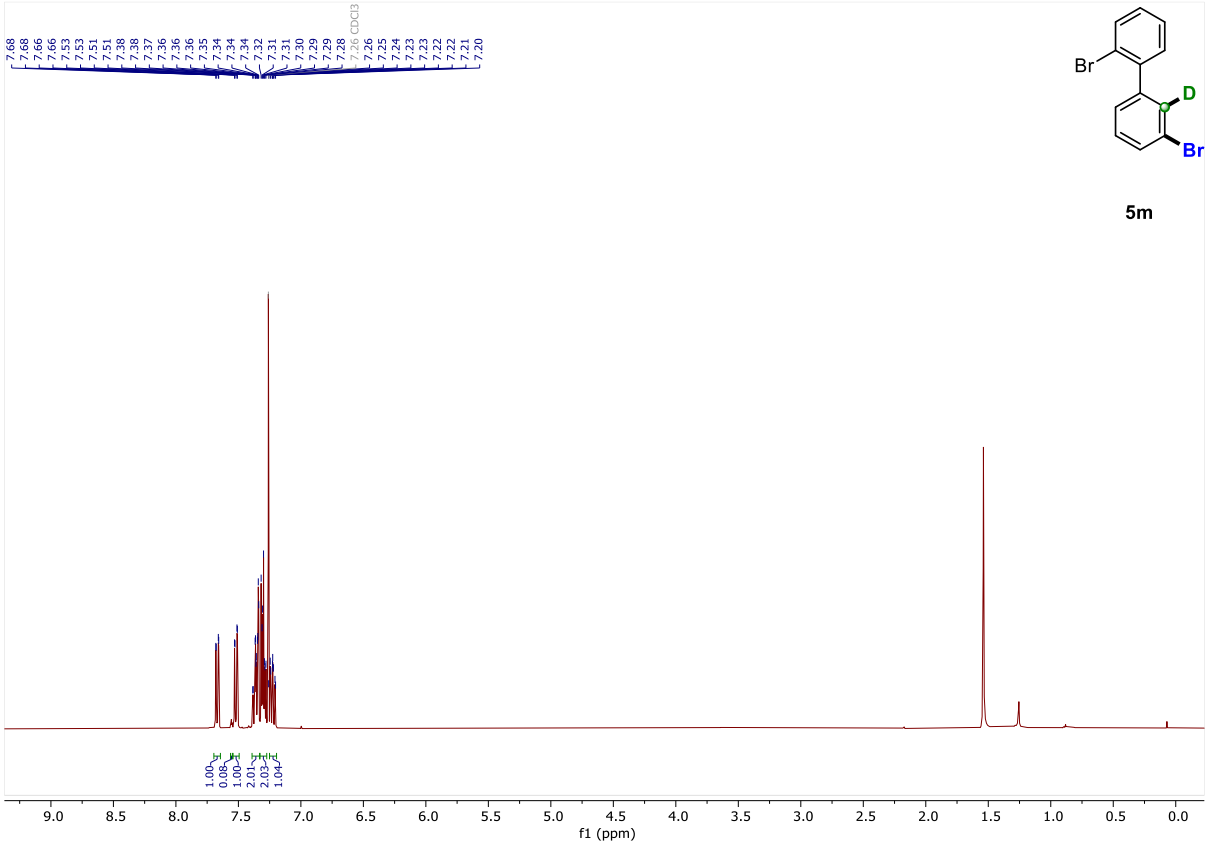


^{13}C NMR (101 MHz, $CDCl_3$)

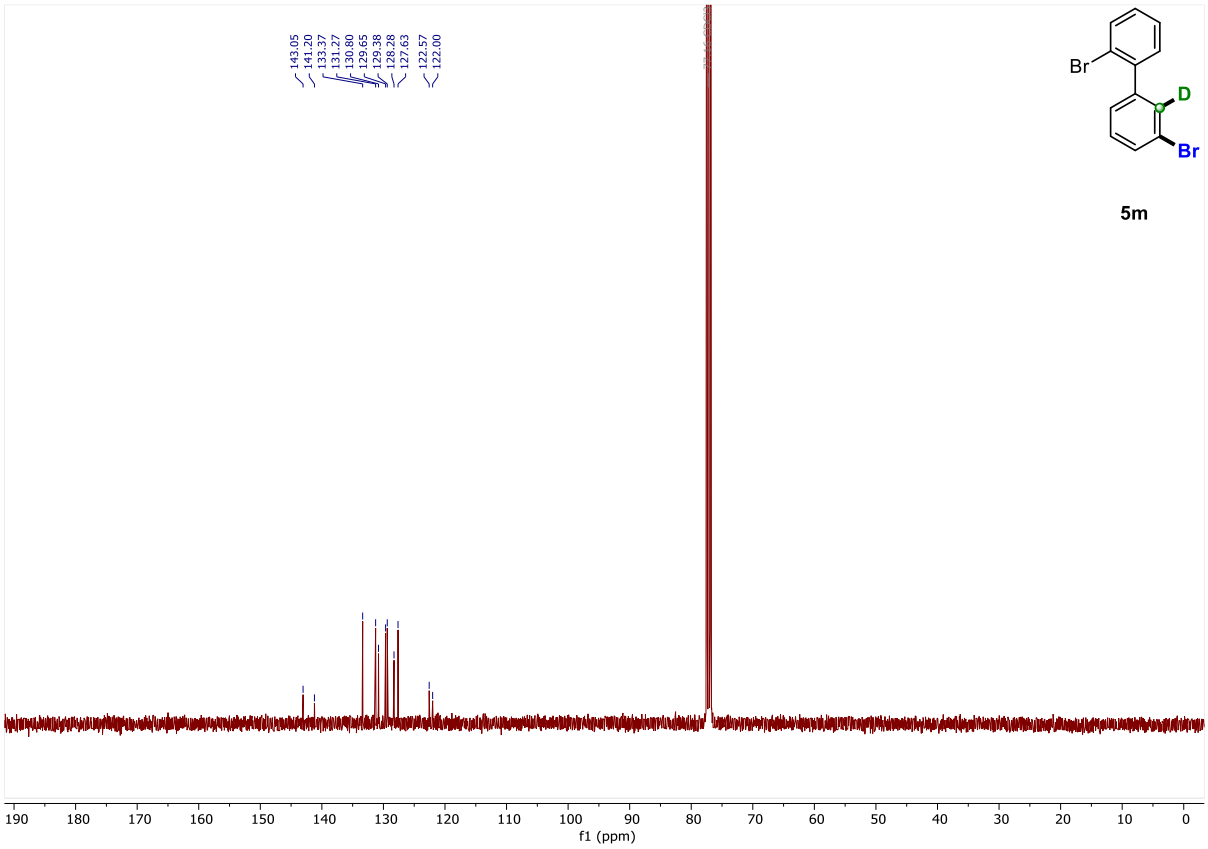


3-bromo-2,2'-dichloro-1,1'-biphenyl-2'-*d* (5m) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

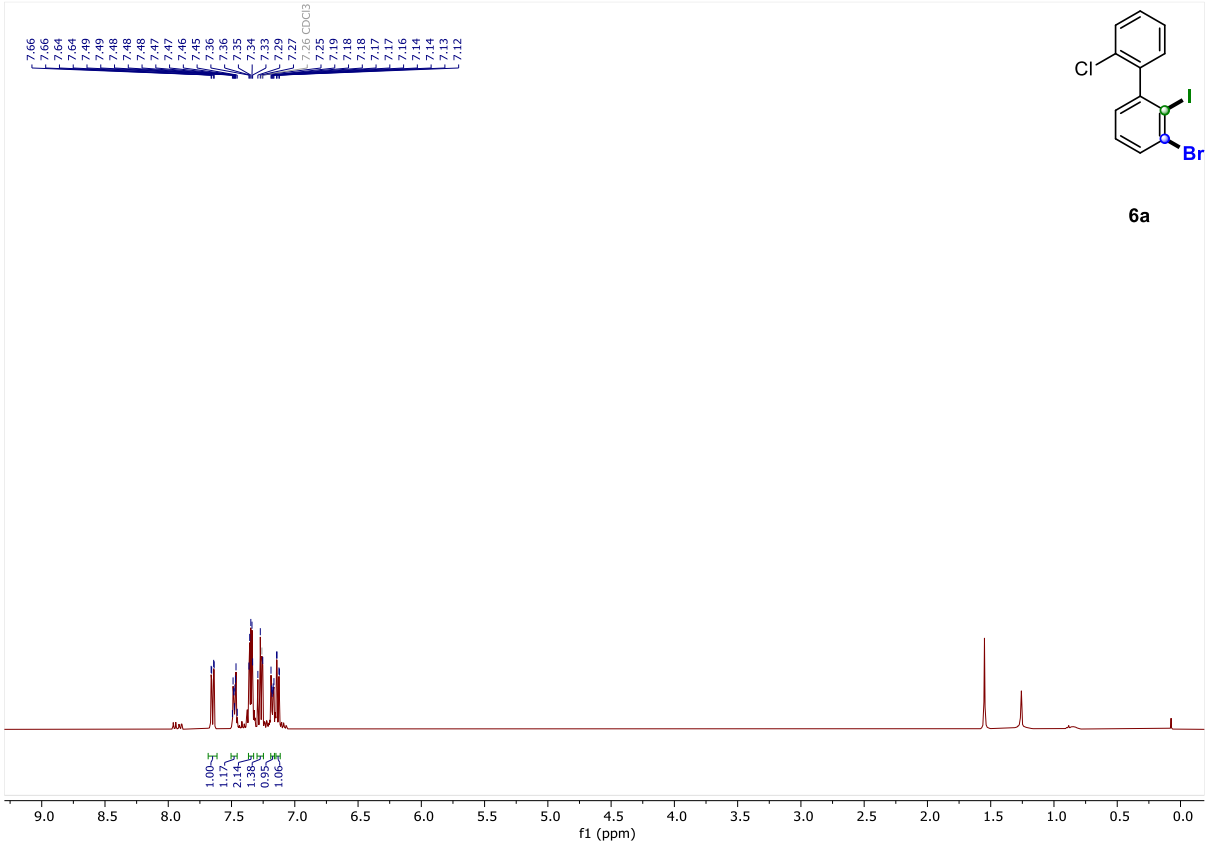


^{13}C NMR (101 MHz, $CDCl_3$)

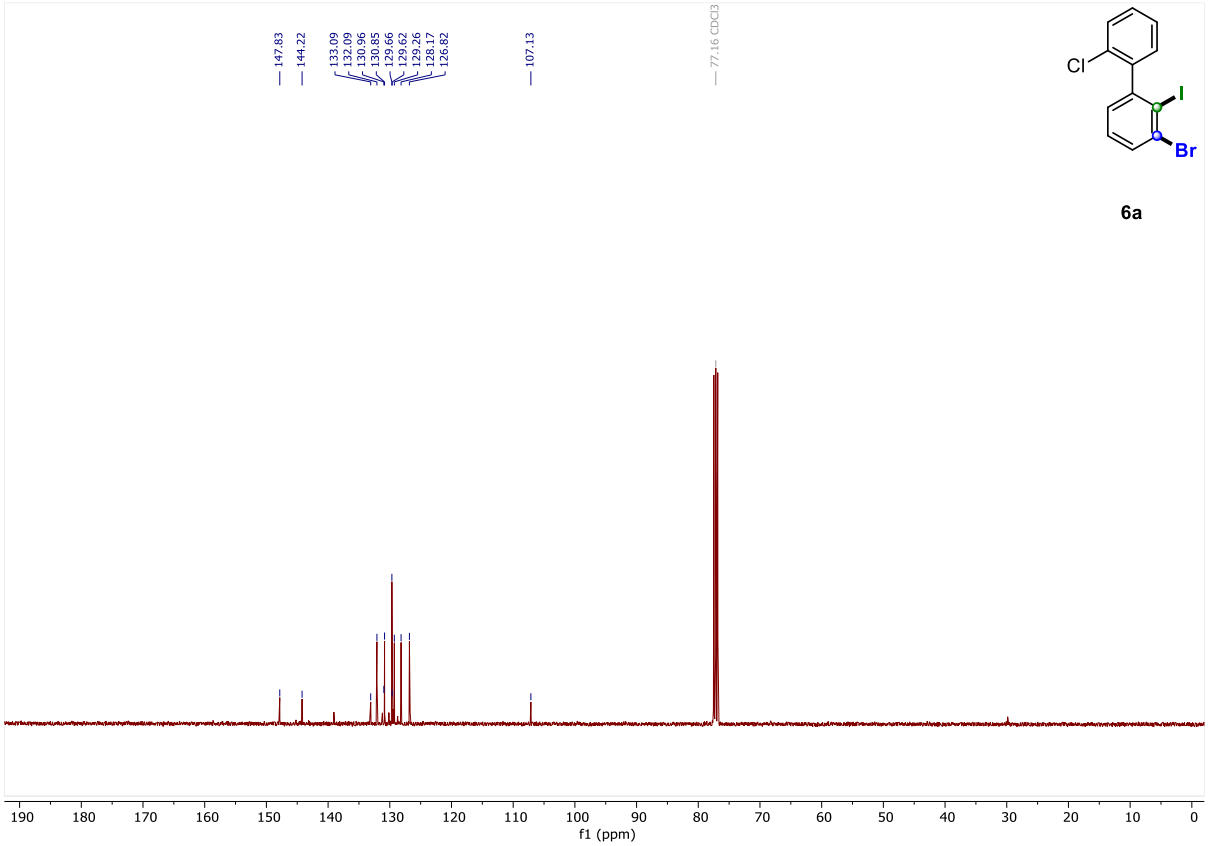


3-bromo-2'-chloro-2-iodo-1,1'-biphenyl (6a) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

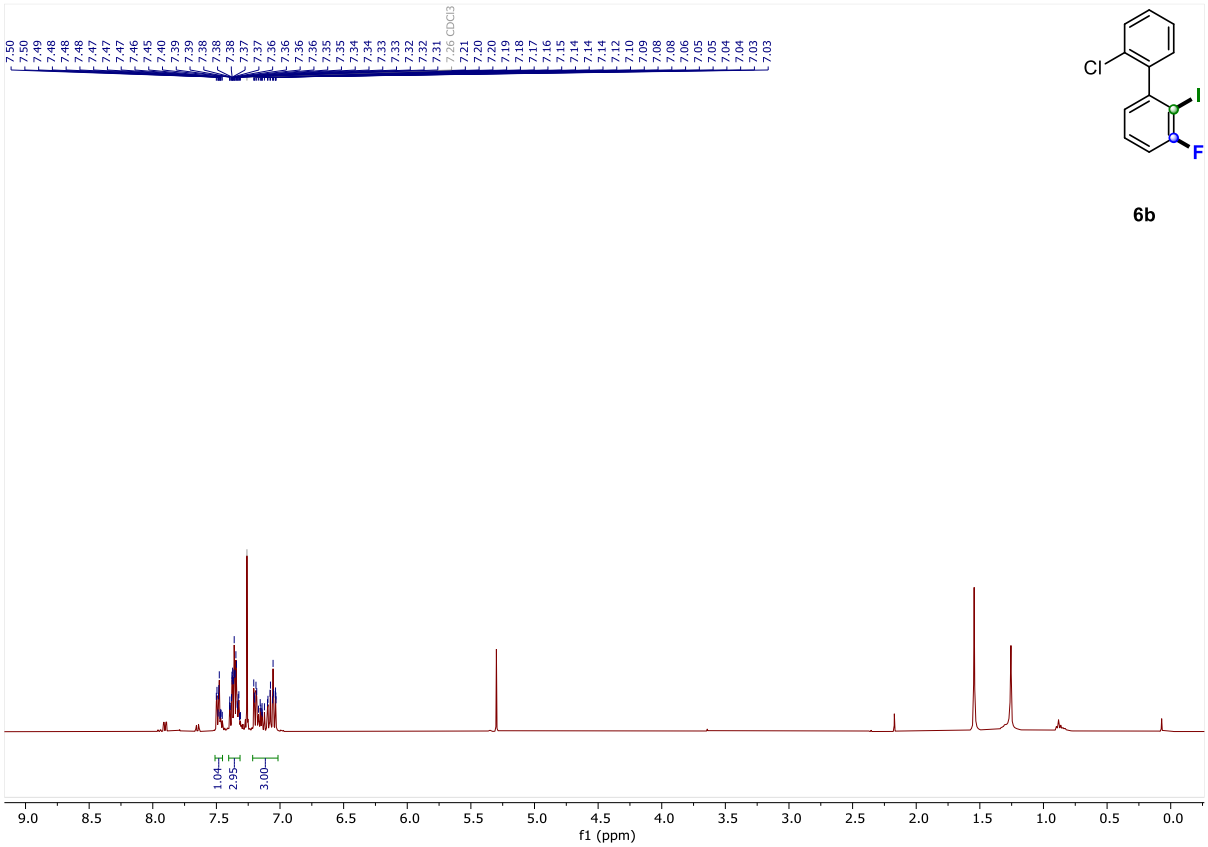


^{13}C NMR (101 MHz, $CDCl_3$)

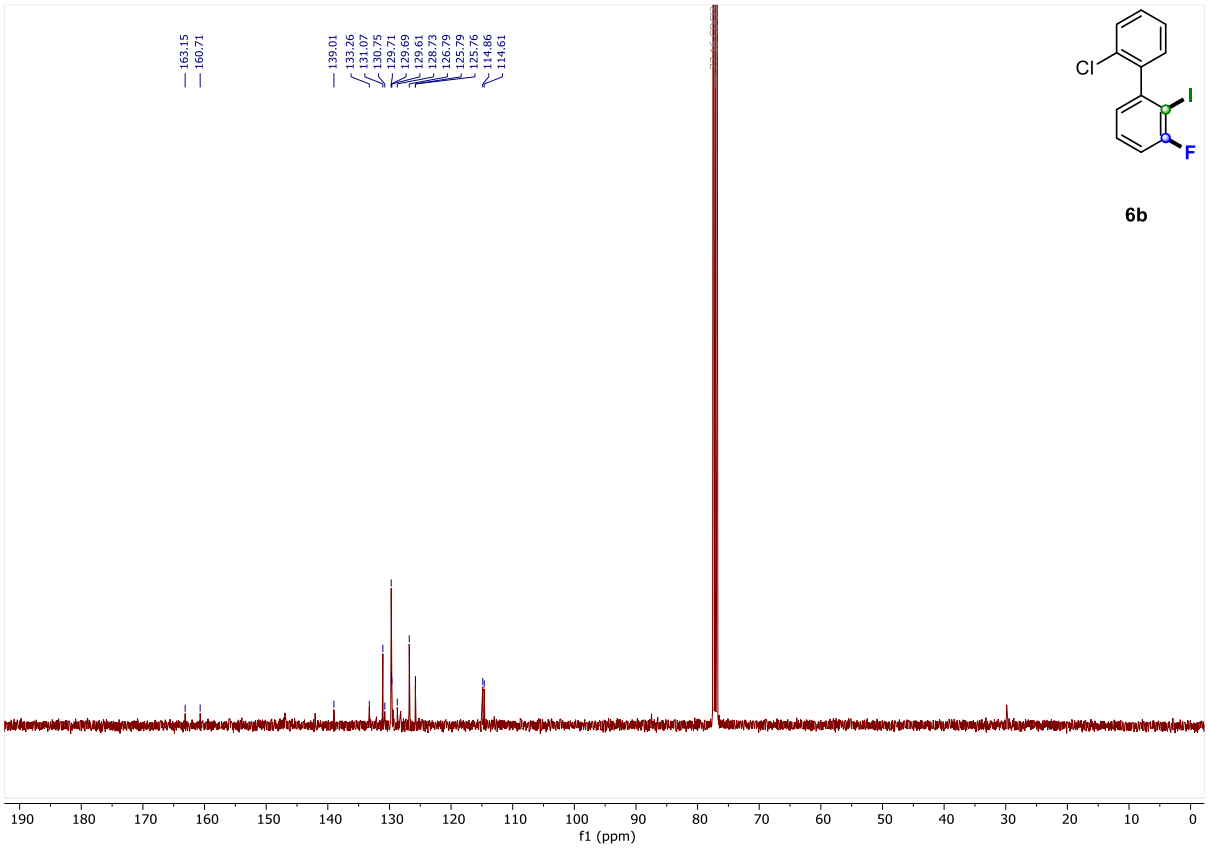


2'-chloro-3-fluoro-2-iodo-1,1'-biphenyl (6b) *See procedure*.

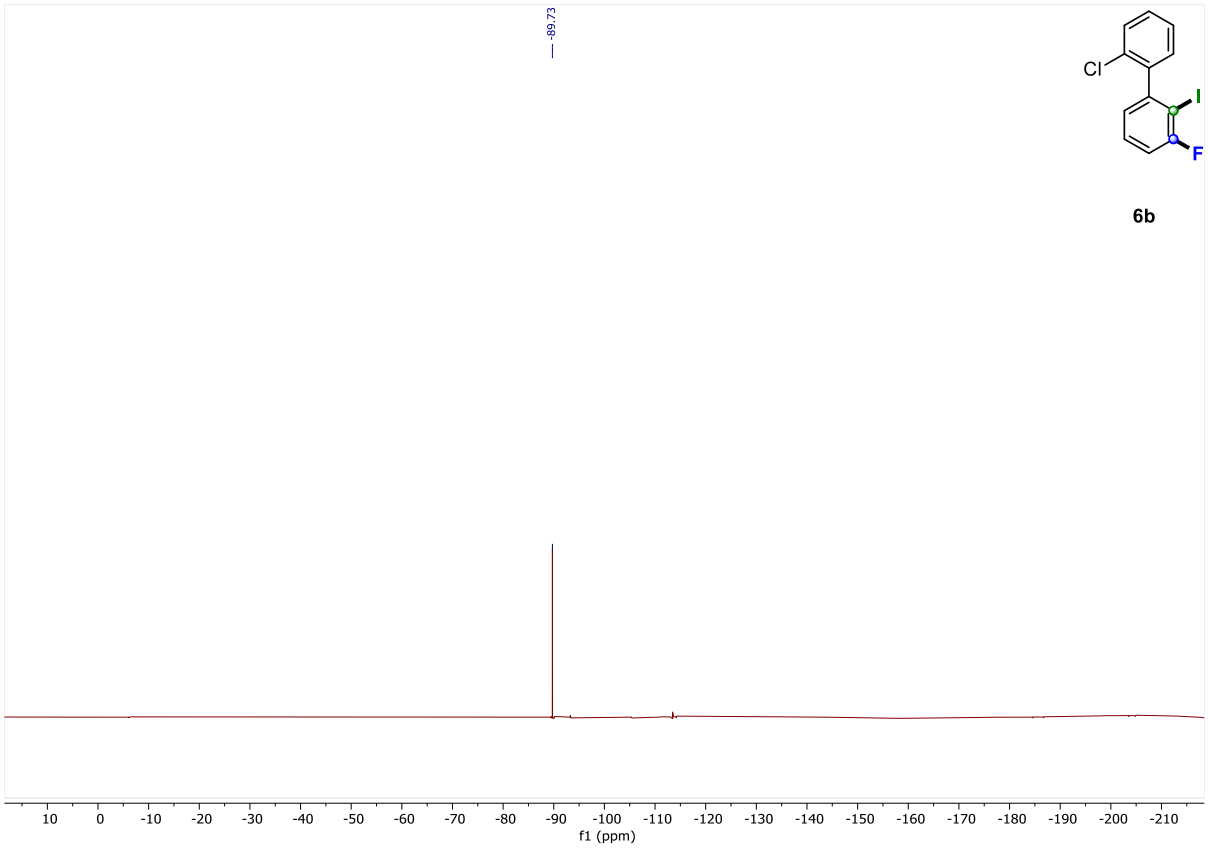
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

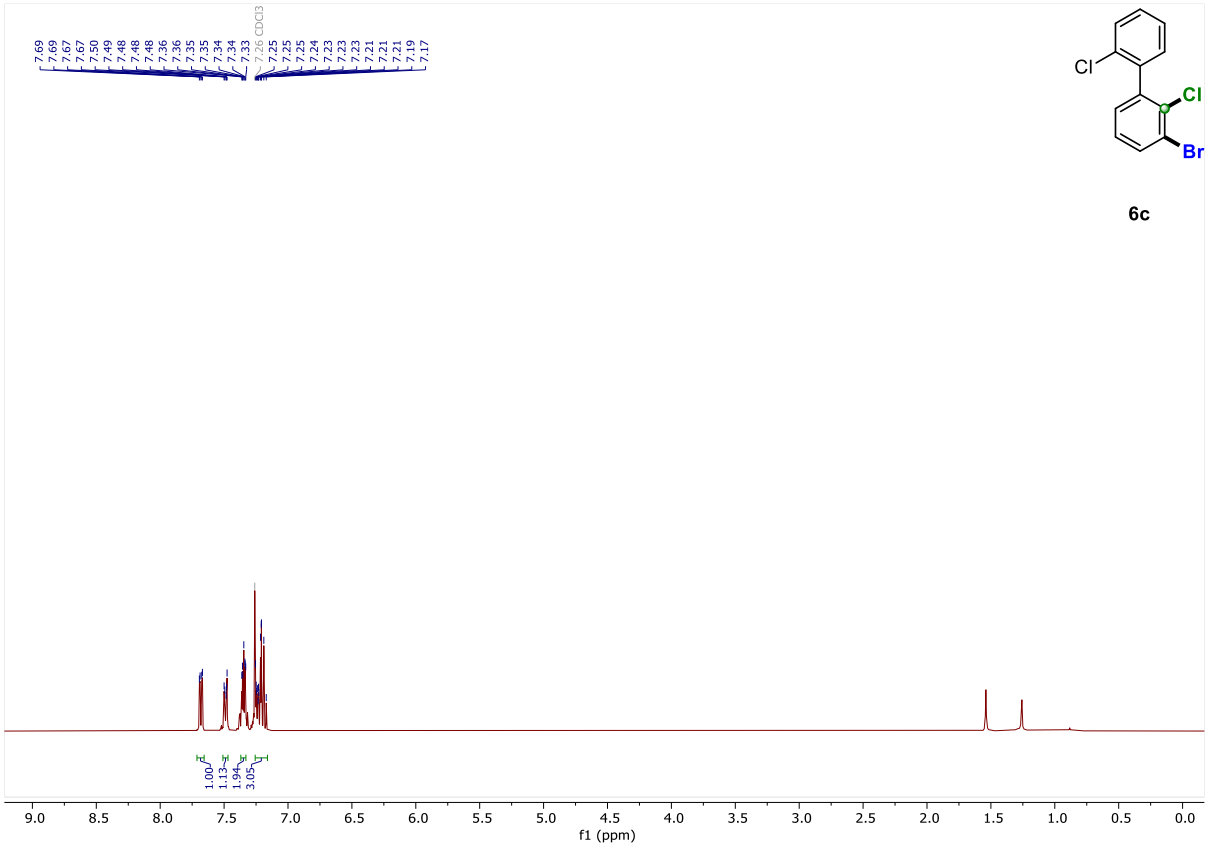


^{19}F NMR (377 MHz, $CDCl_3$)

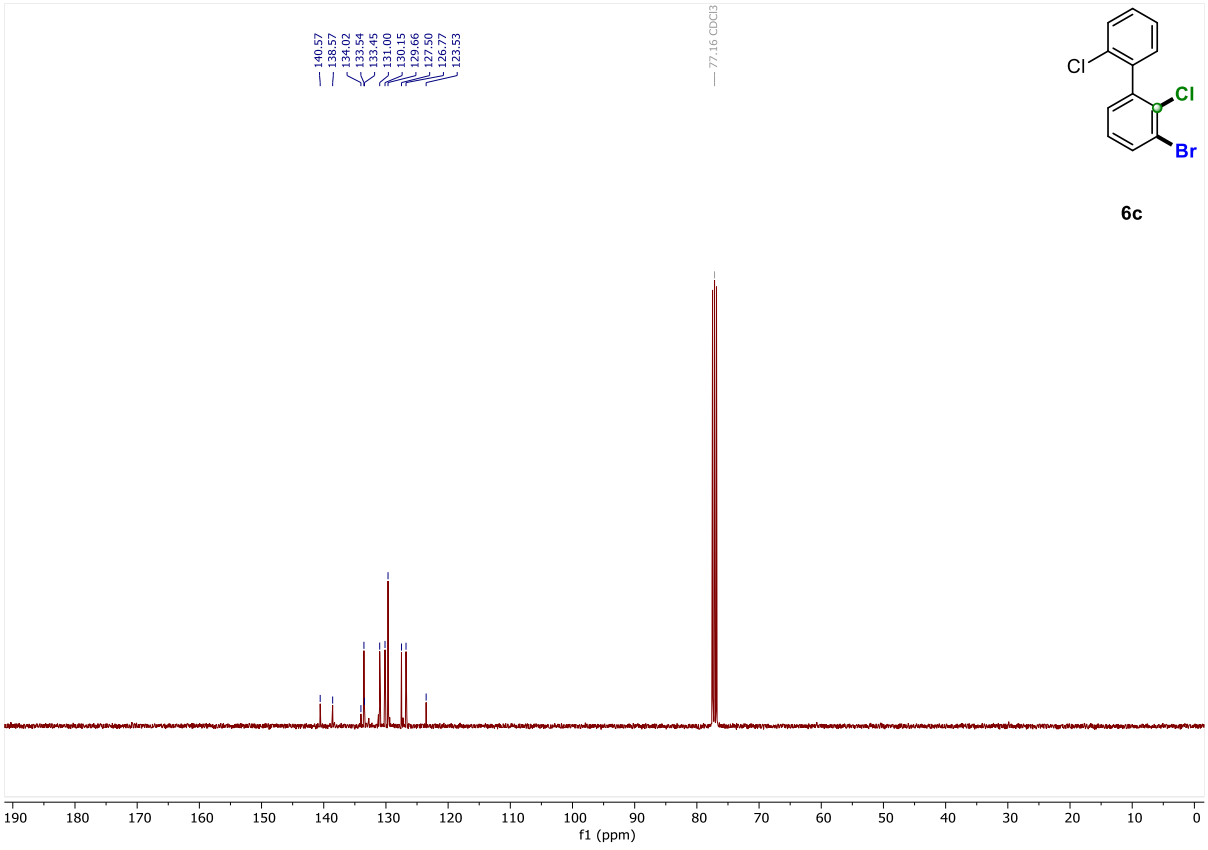


3-bromo-2,2'-dichloro-1,1'-biphenyl (6c) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

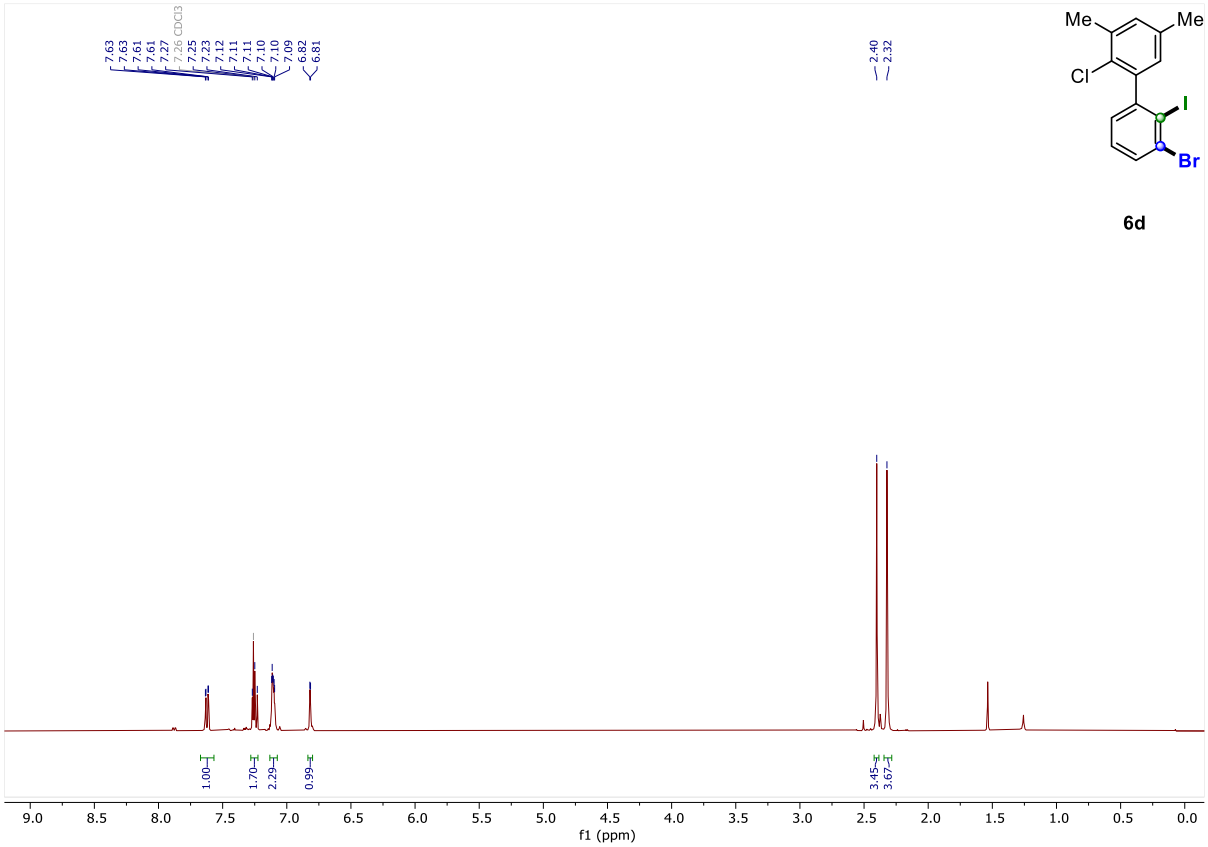


^{13}C NMR (101 MHz, $CDCl_3$)

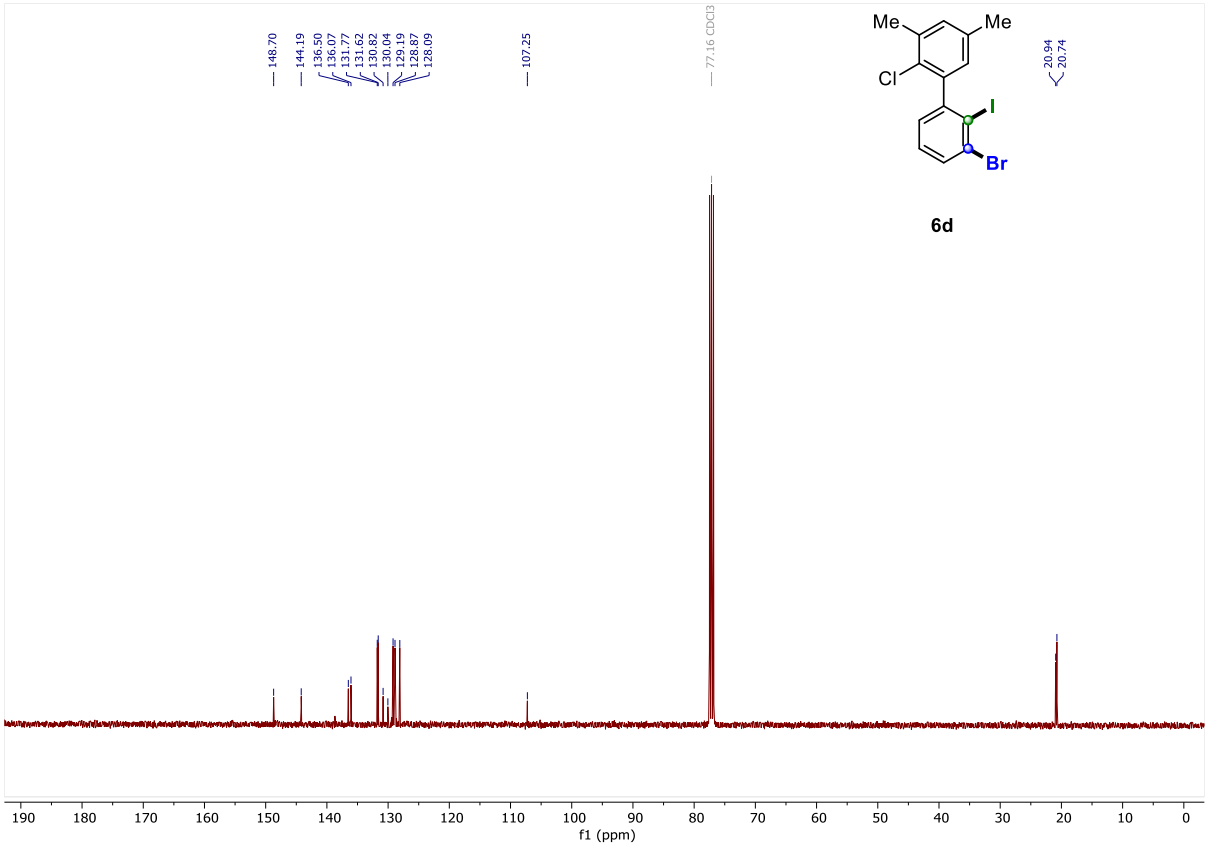


3'-bromo-2-chloro-2'-iodo-3,5-dimethyl-1,1'-biphenyl (6d) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

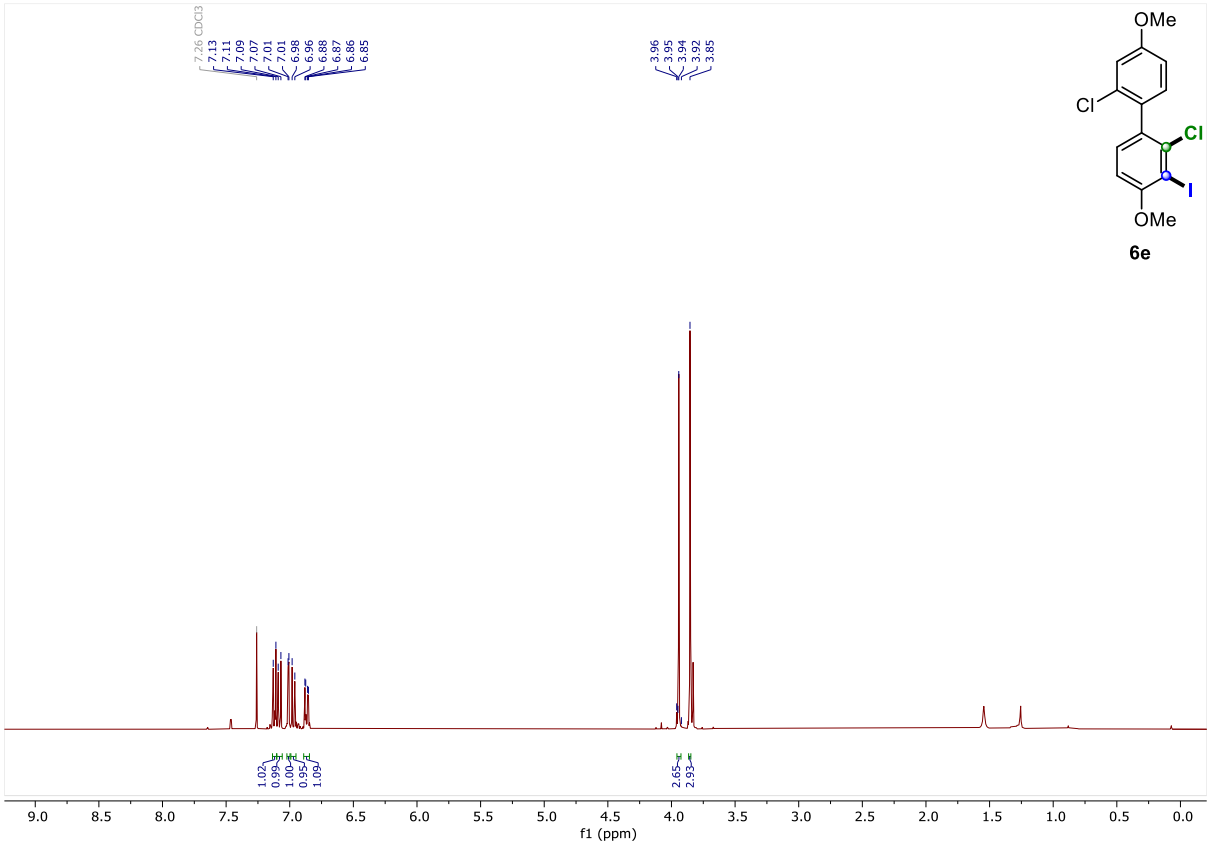


^{13}C NMR (101 MHz, $CDCl_3$)

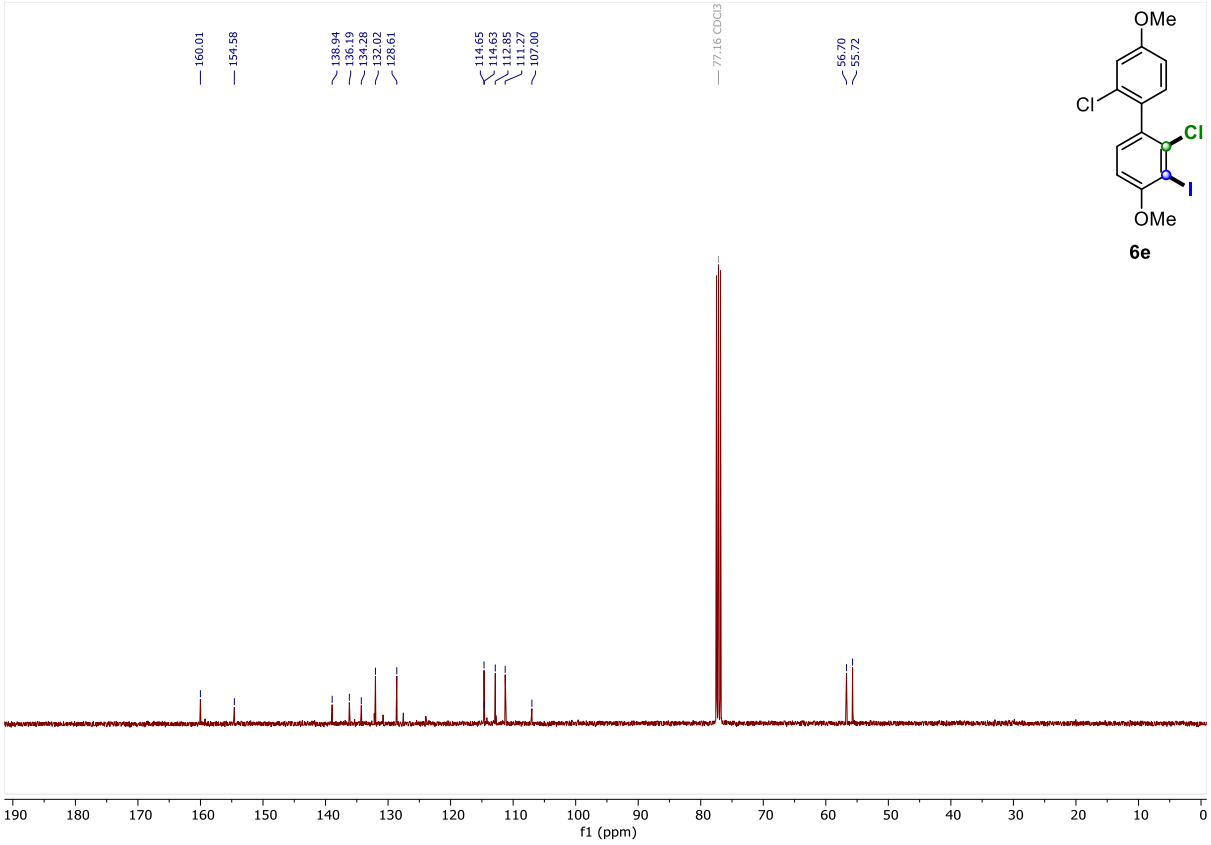


2,2'-dichloro-3-iodo-4,4'-dimethoxy-1,1'-biphenyl (6e) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

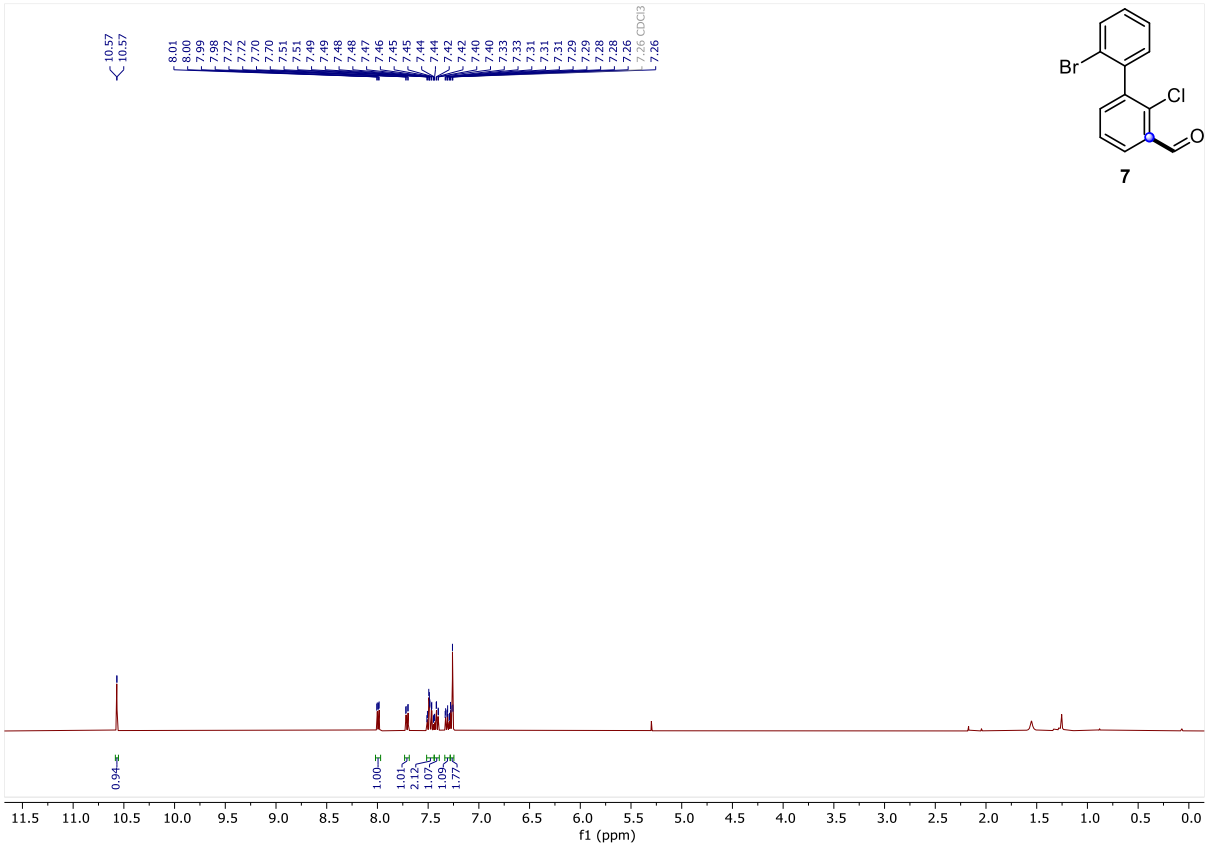


^{13}C NMR (101 MHz, $CDCl_3$)

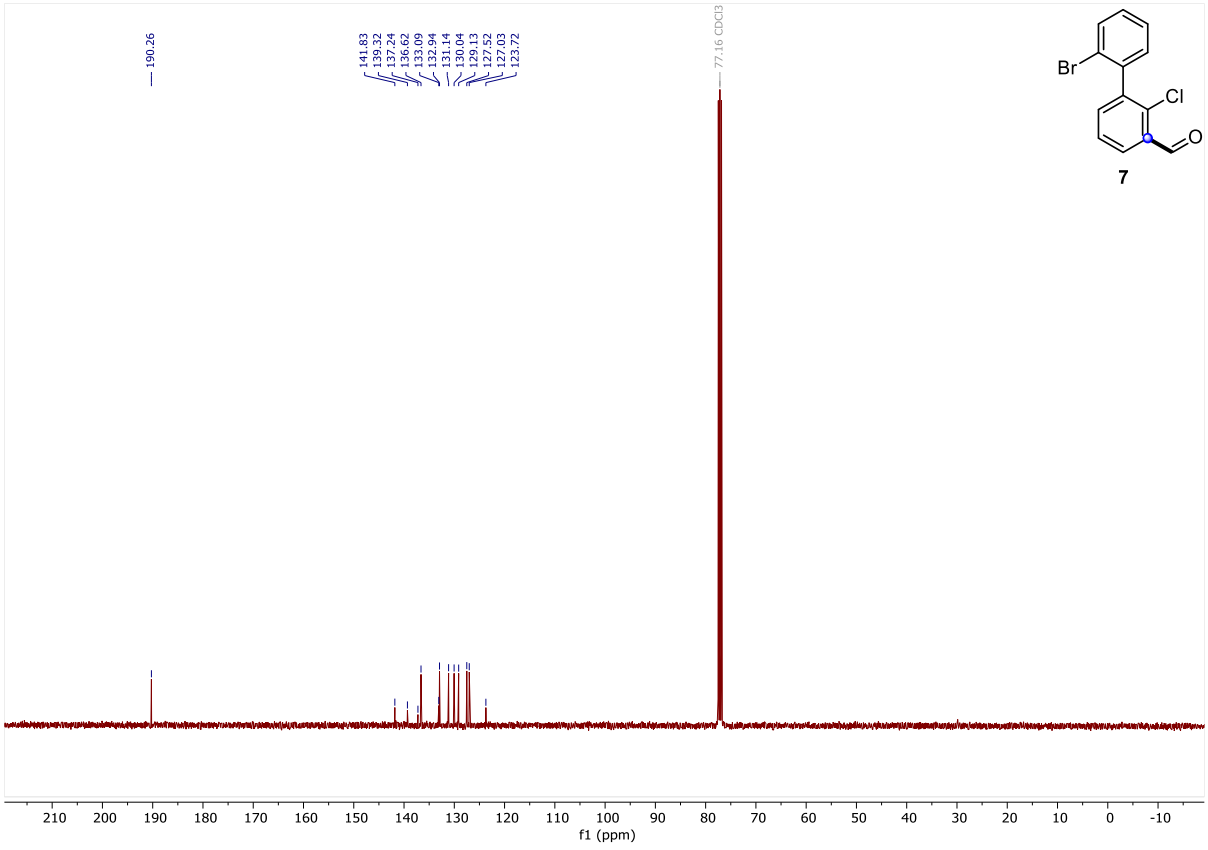


2'-bromo-2-chloro-[1,1'-biphenyl]-3-carbaldehyde (7) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

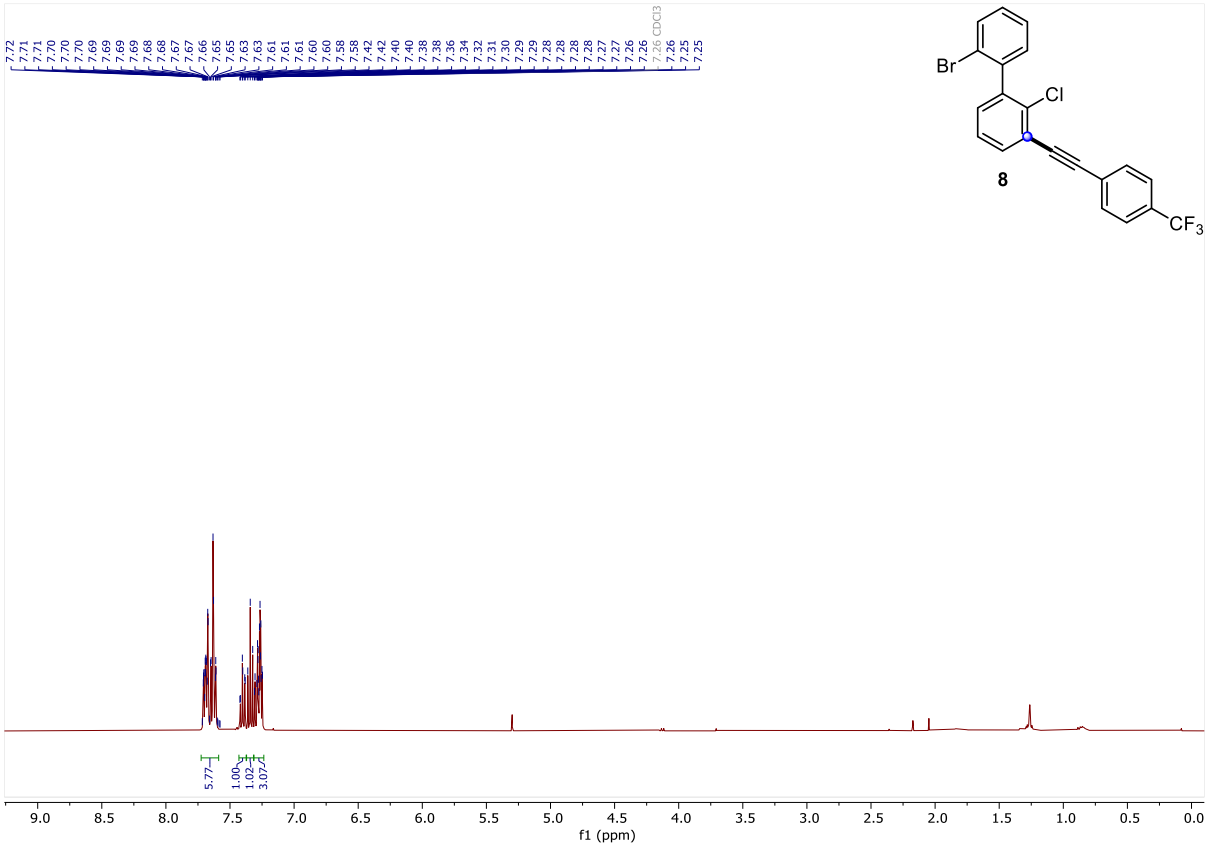


^{13}C NMR (101 MHz, $CDCl_3$)

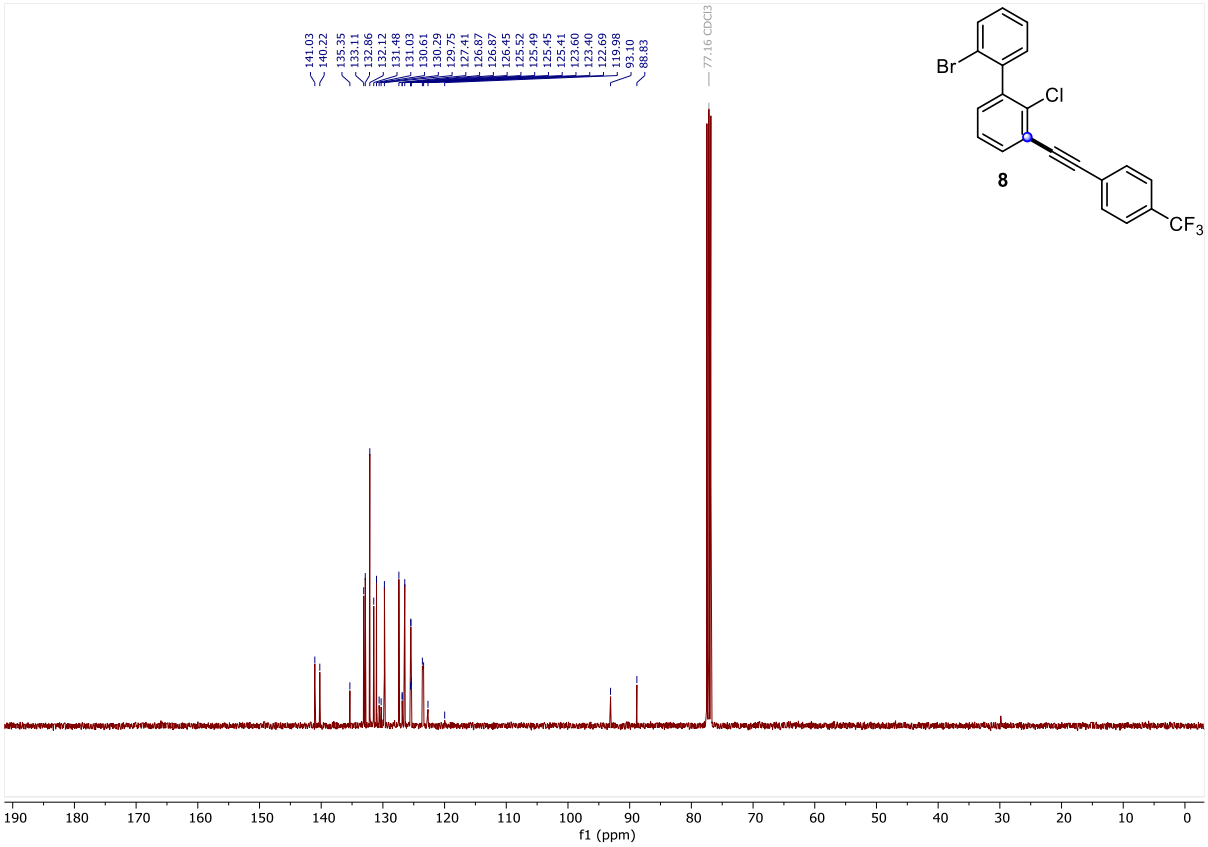


2'-bromo-2-chloro-3-((4-(trifluoromethyl)phenyl)ethynyl)-1,1'-biphenyl (8) *See procedure*.

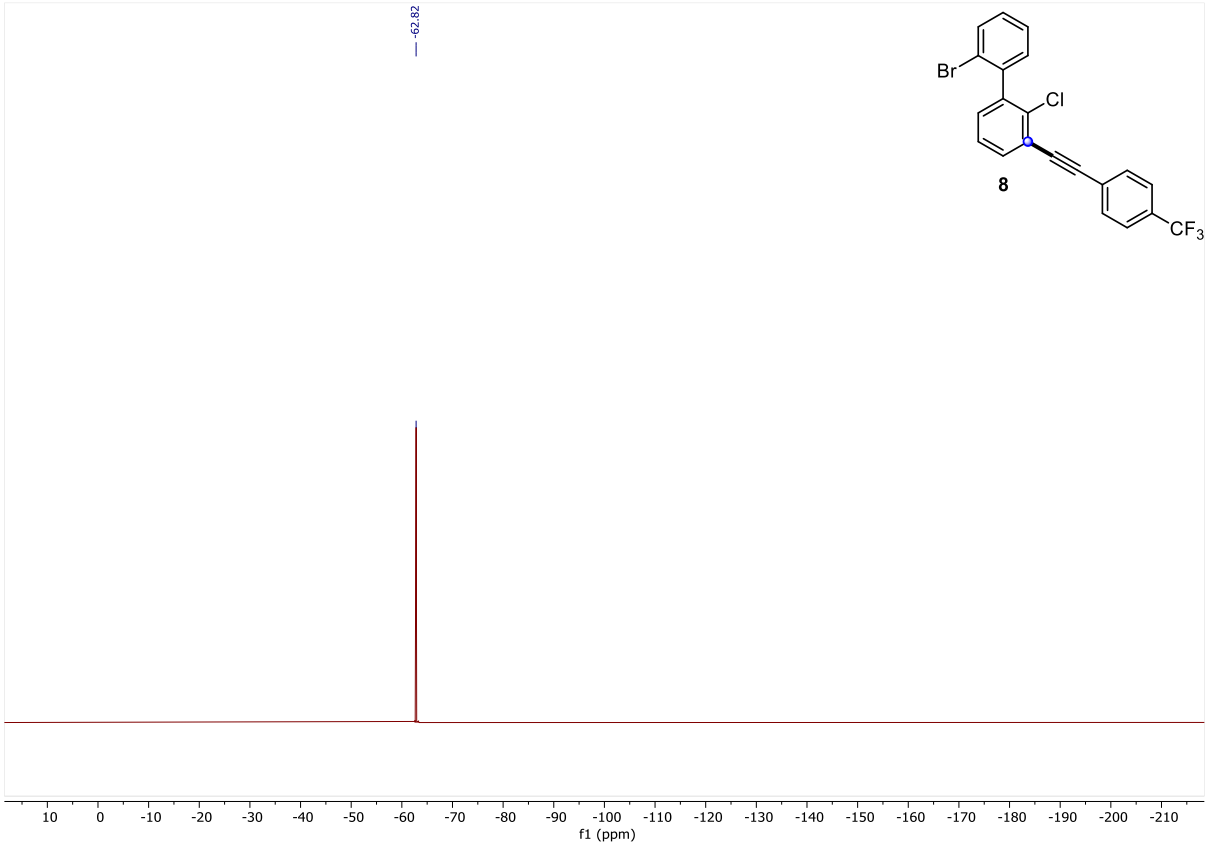
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

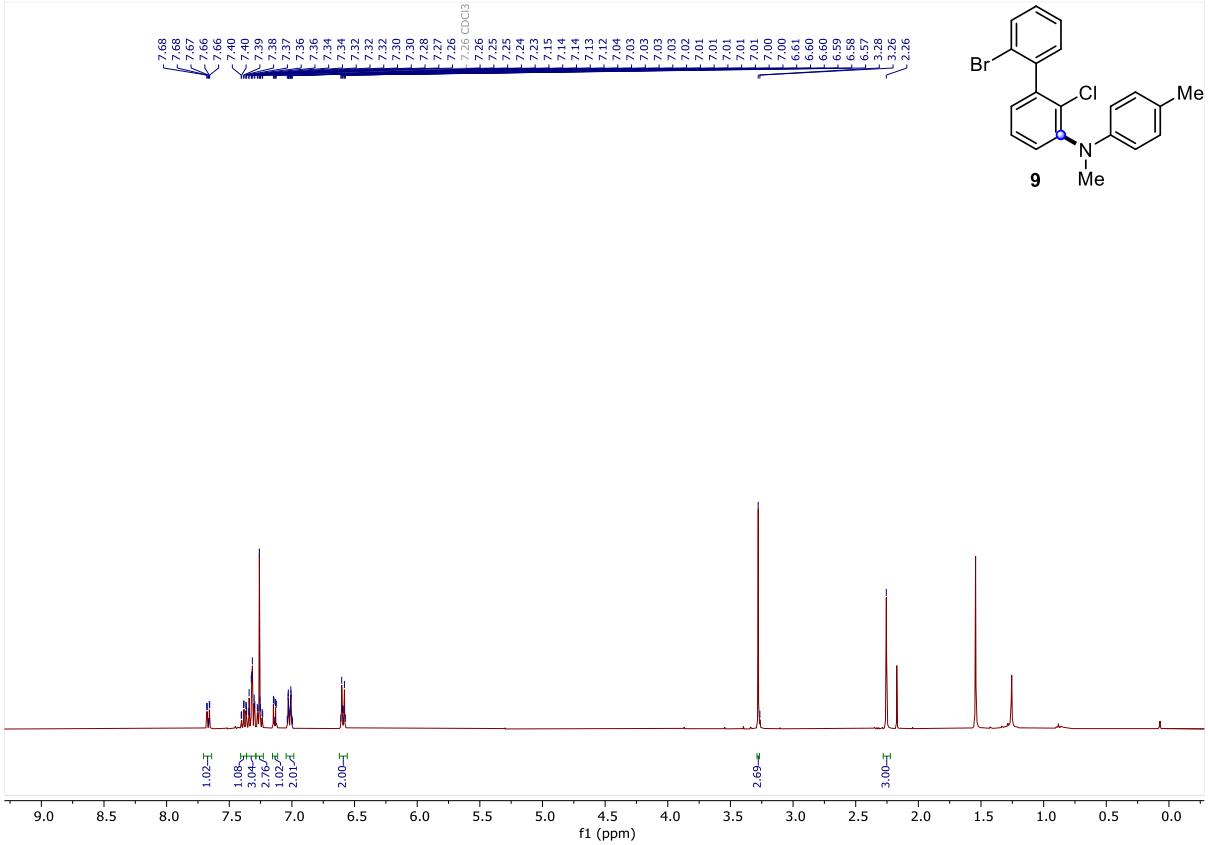


^{19}F NMR (377 MHz, $CDCl_3$)

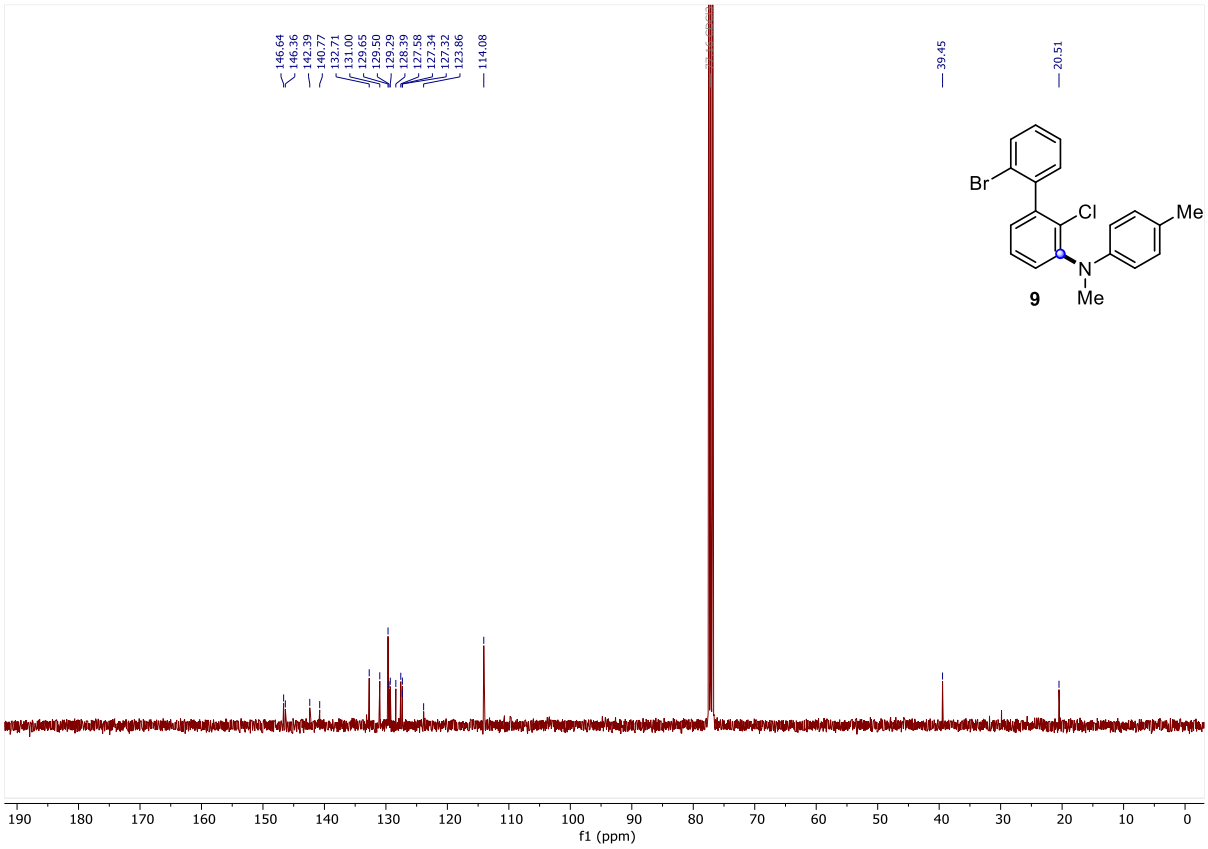


2'-bromo-2-chloro-*N*-methyl-*N*-(*p*-tolyl)-[1,1'-biphenyl]-3-amine (9) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

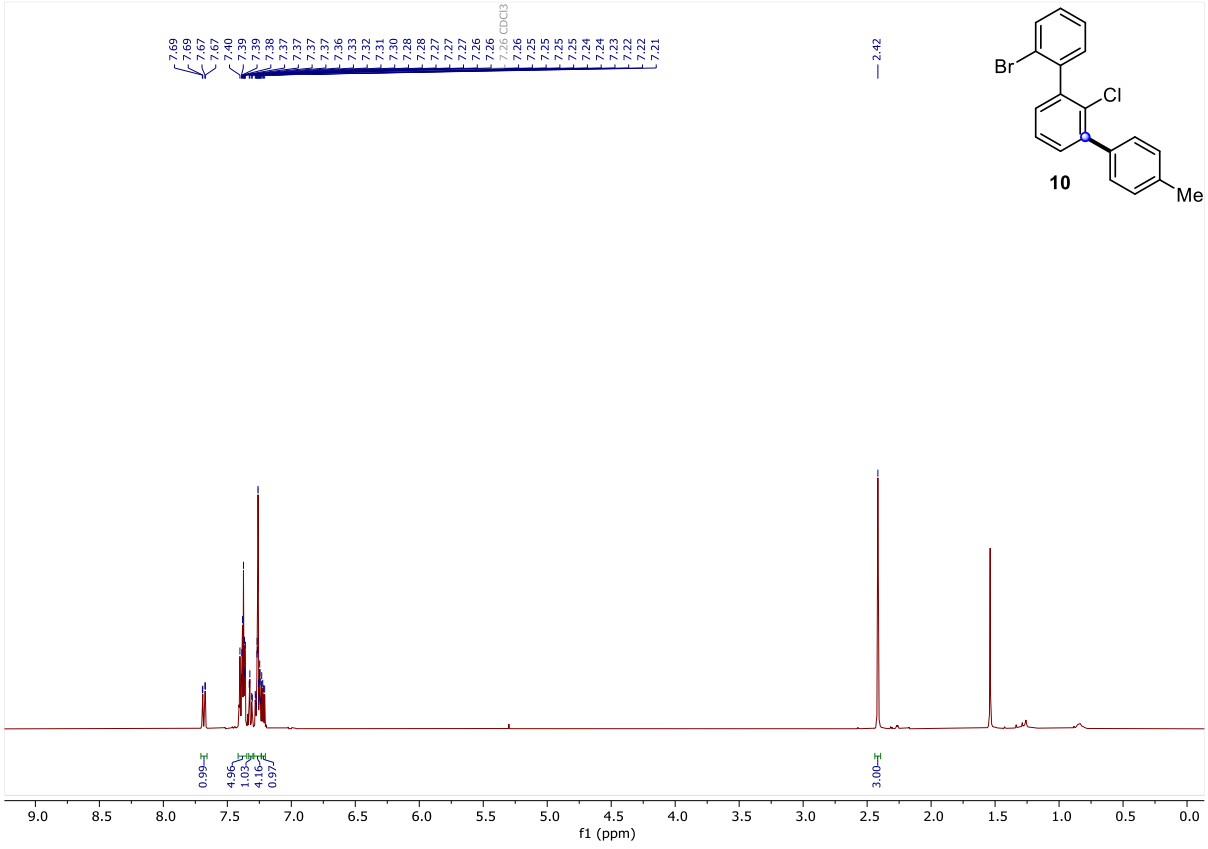


^{13}C NMR (101 MHz, $CDCl_3$)

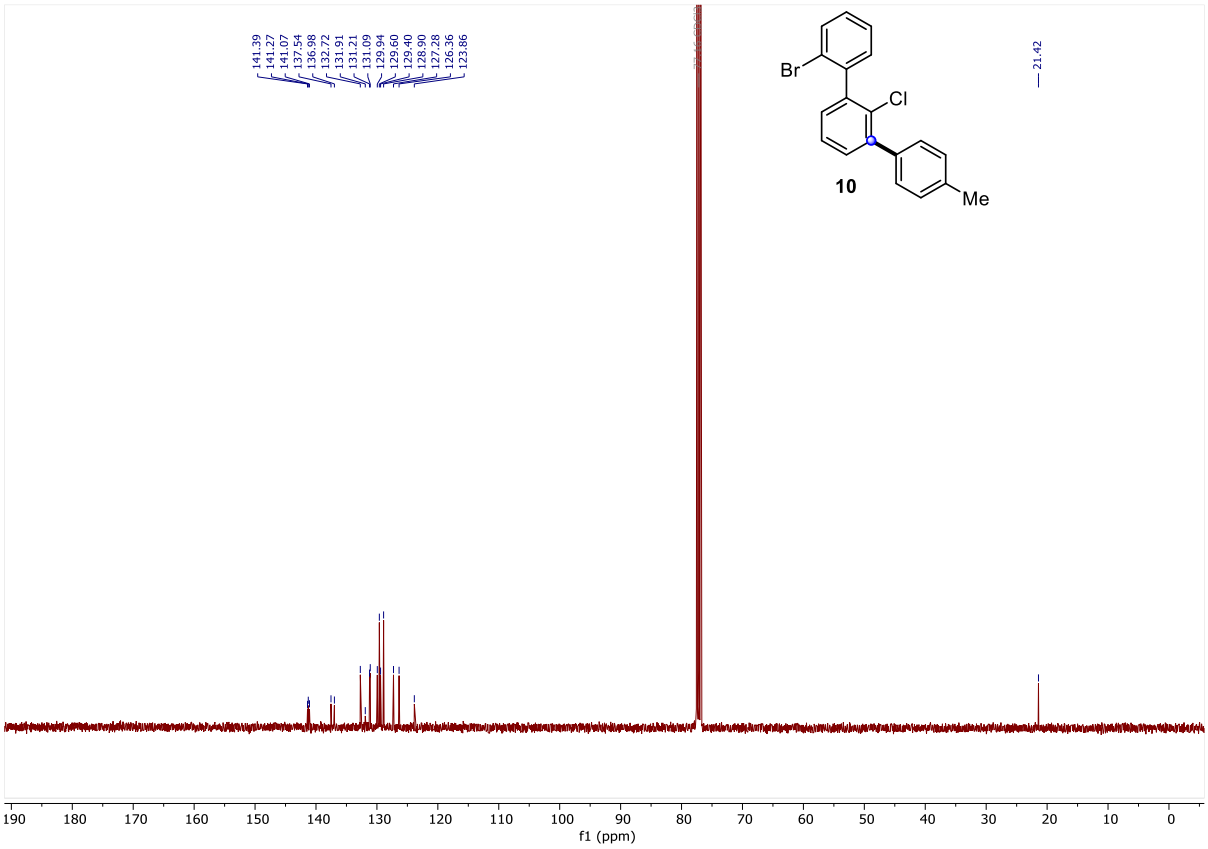


2-bromo-2'-chloro-4''-methyl-1,1':3',1''-terphenyl (10) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

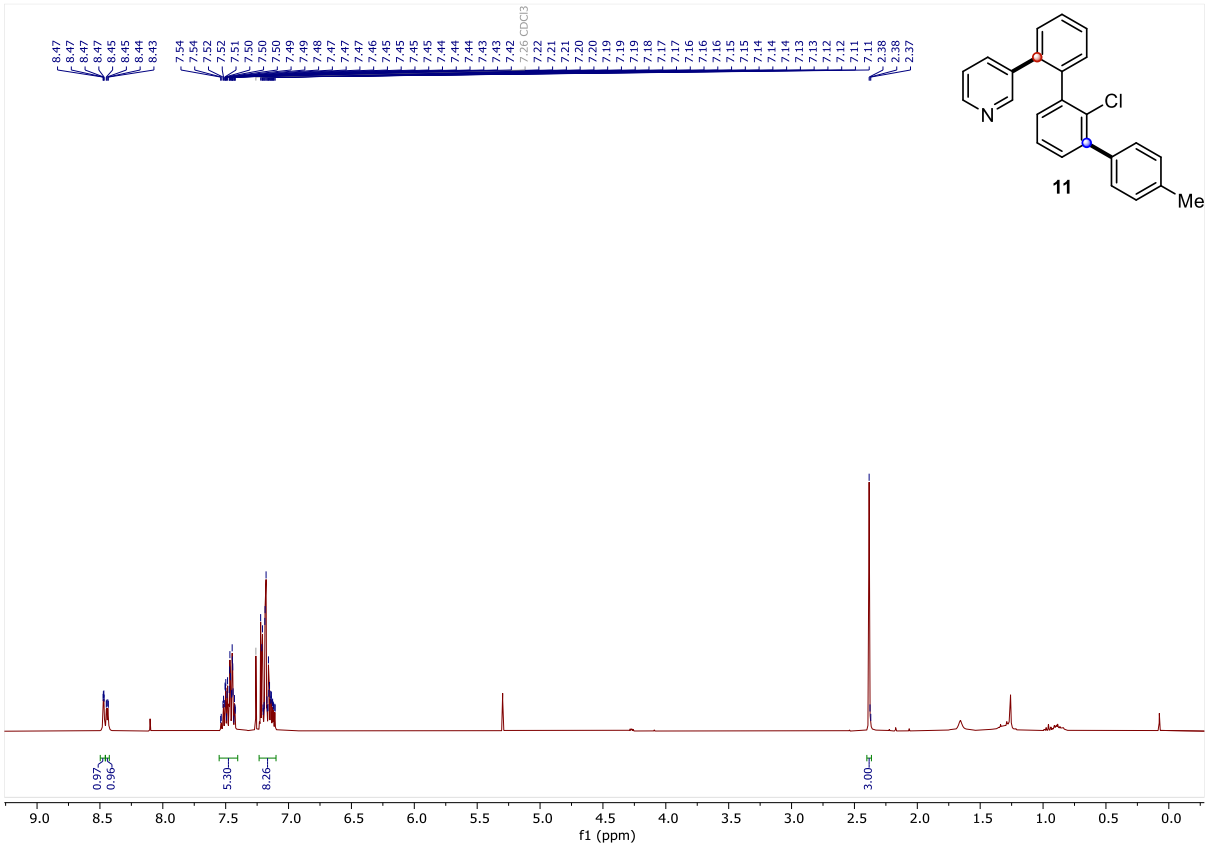


^{13}C NMR (101 MHz, $CDCl_3$)

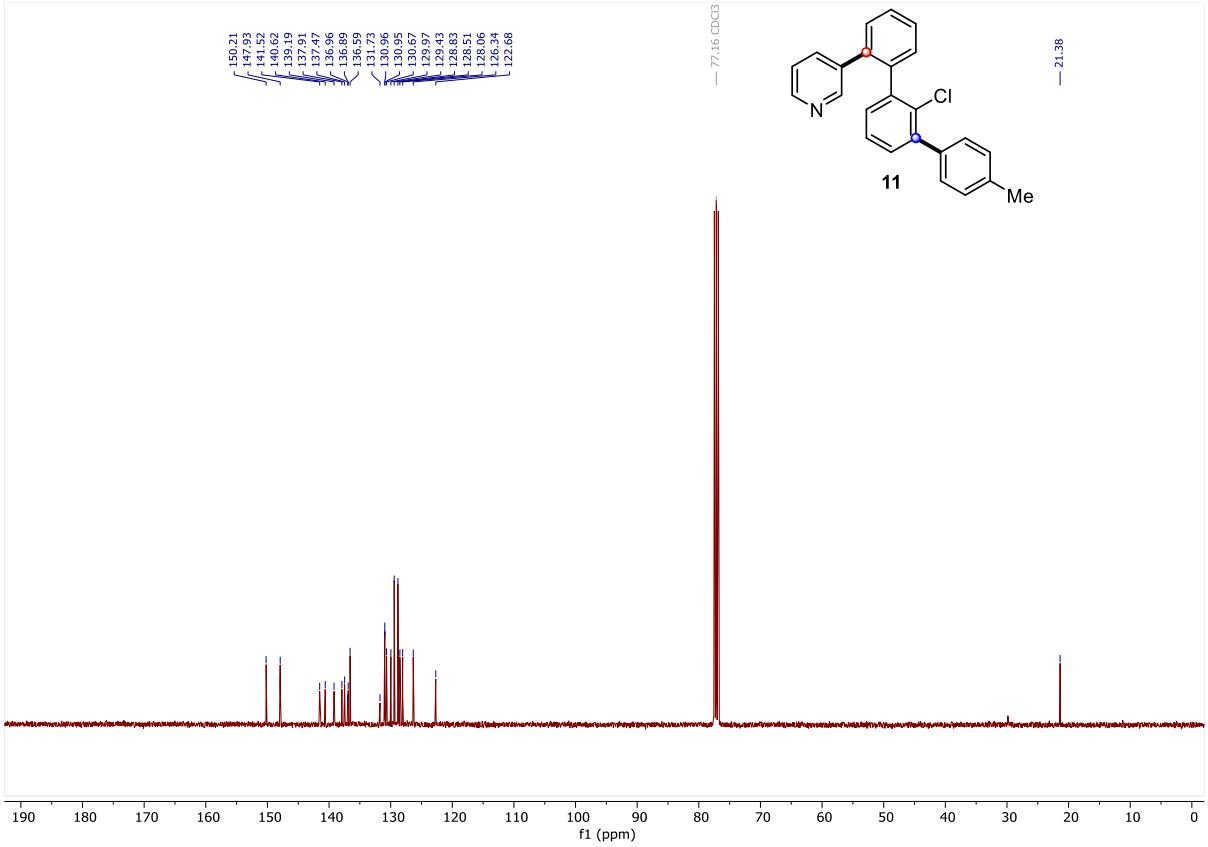


3-(2'-chloro-4''-methyl-[1,1':3',1''-terphenyl]-2-yl)pyridine (11) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

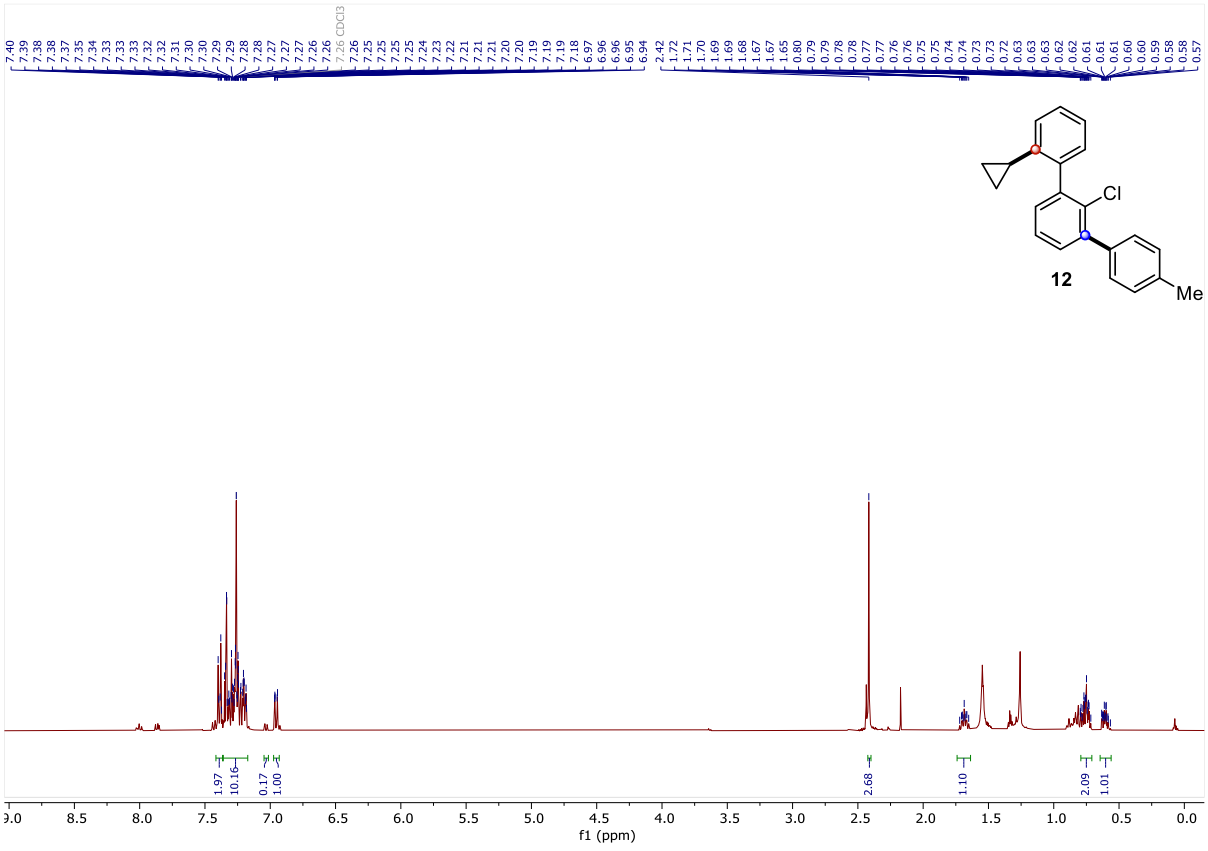


^{13}C NMR (101 MHz, $CDCl_3$)

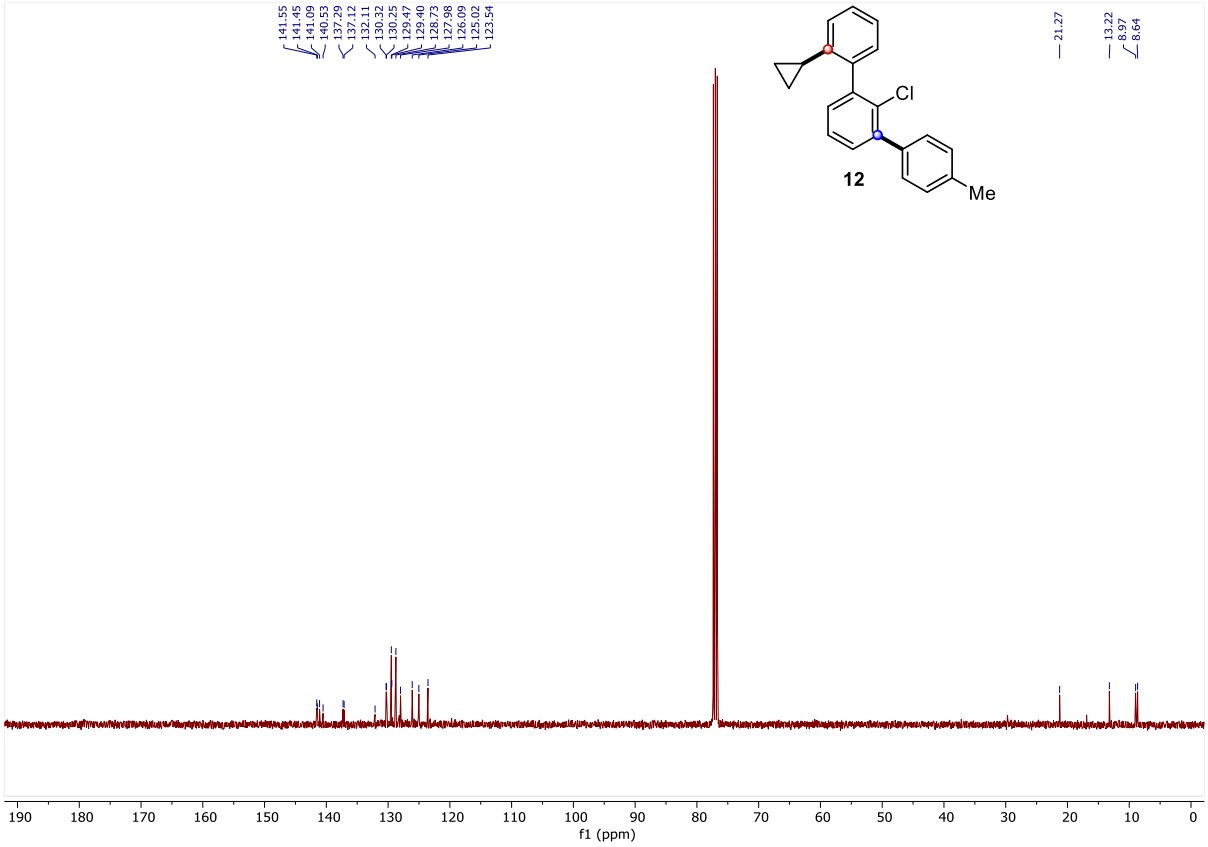


2'-chloro-2-cyclopropyl-4''-methyl-1,1':3',1''-terphenyl (12) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

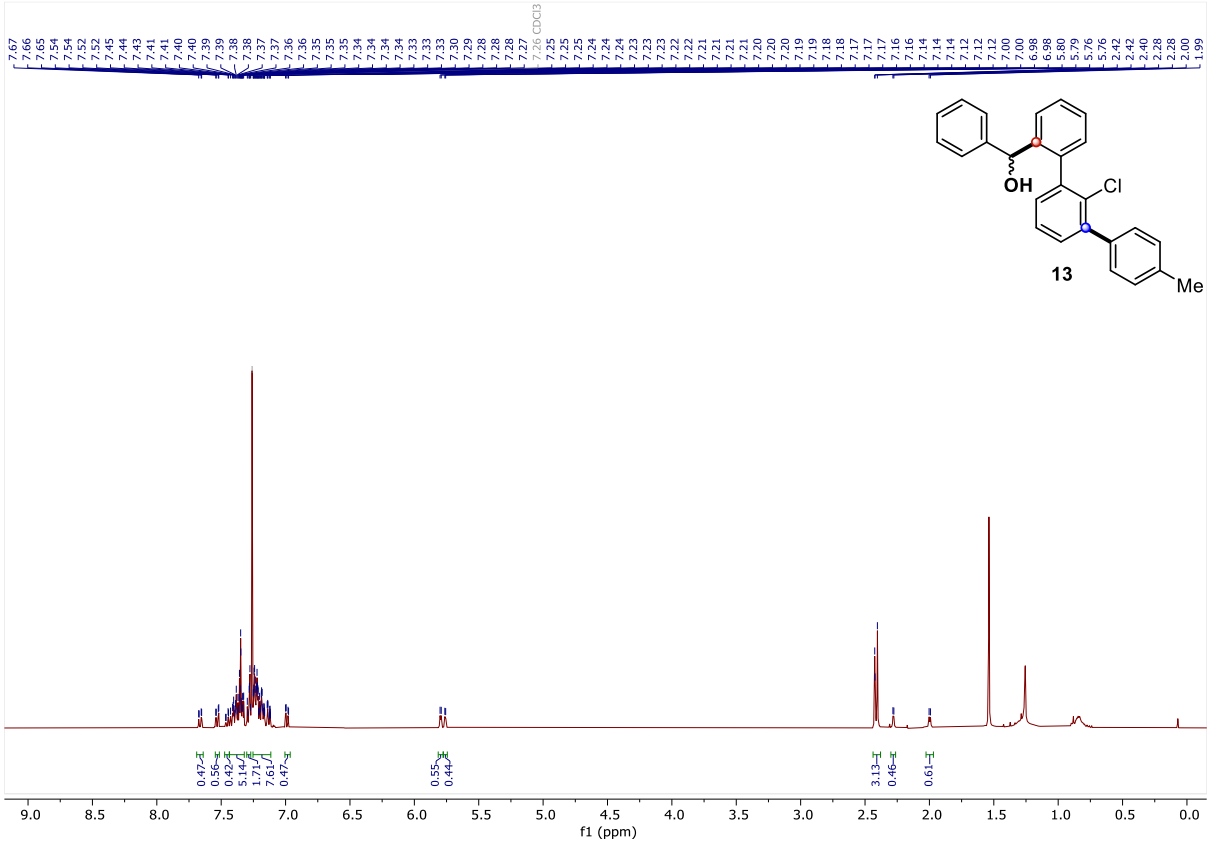


^{13}C NMR (101 MHz, $CDCl_3$)

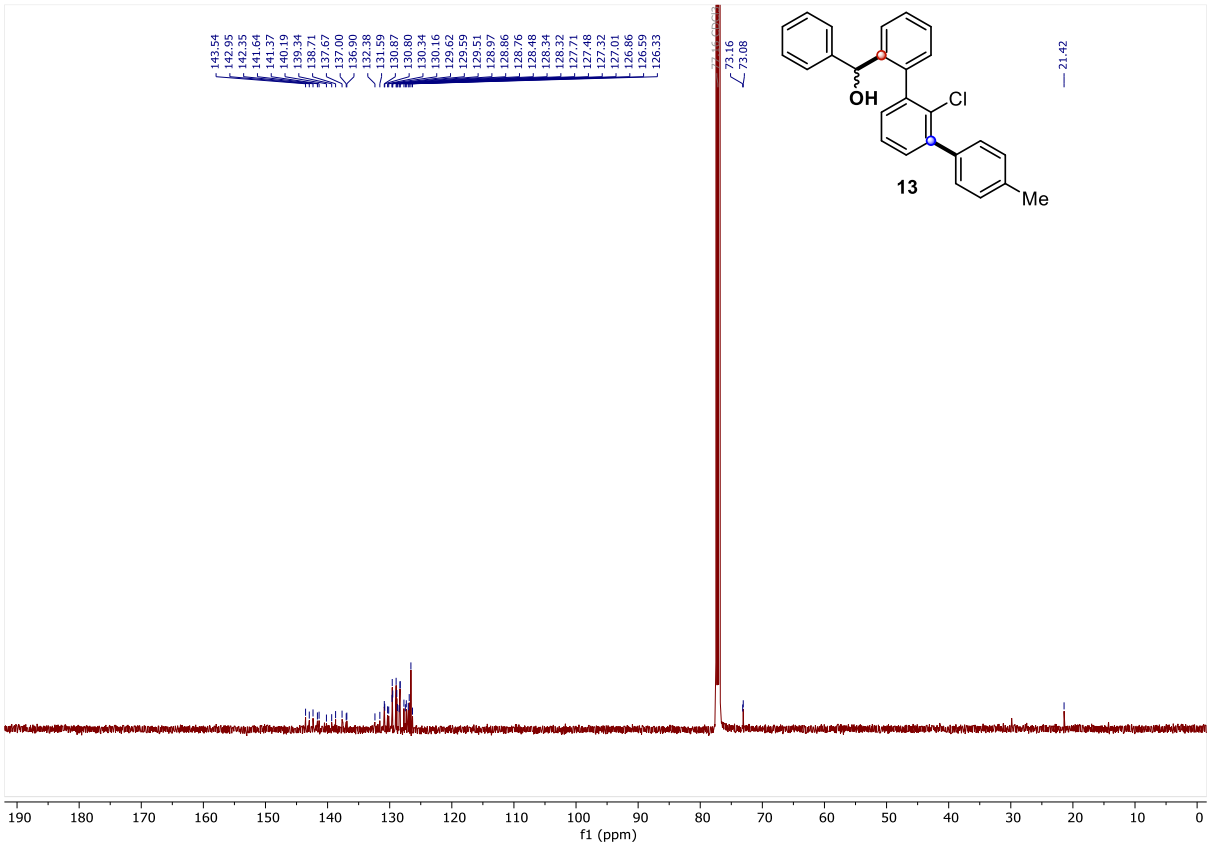


(2'-chloro-4''-methyl-[1,1':3',1''-terphenyl]-2-yl)(phenyl)methanol (13) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$), mixture of atropodiastereomers (55:45 ratio)

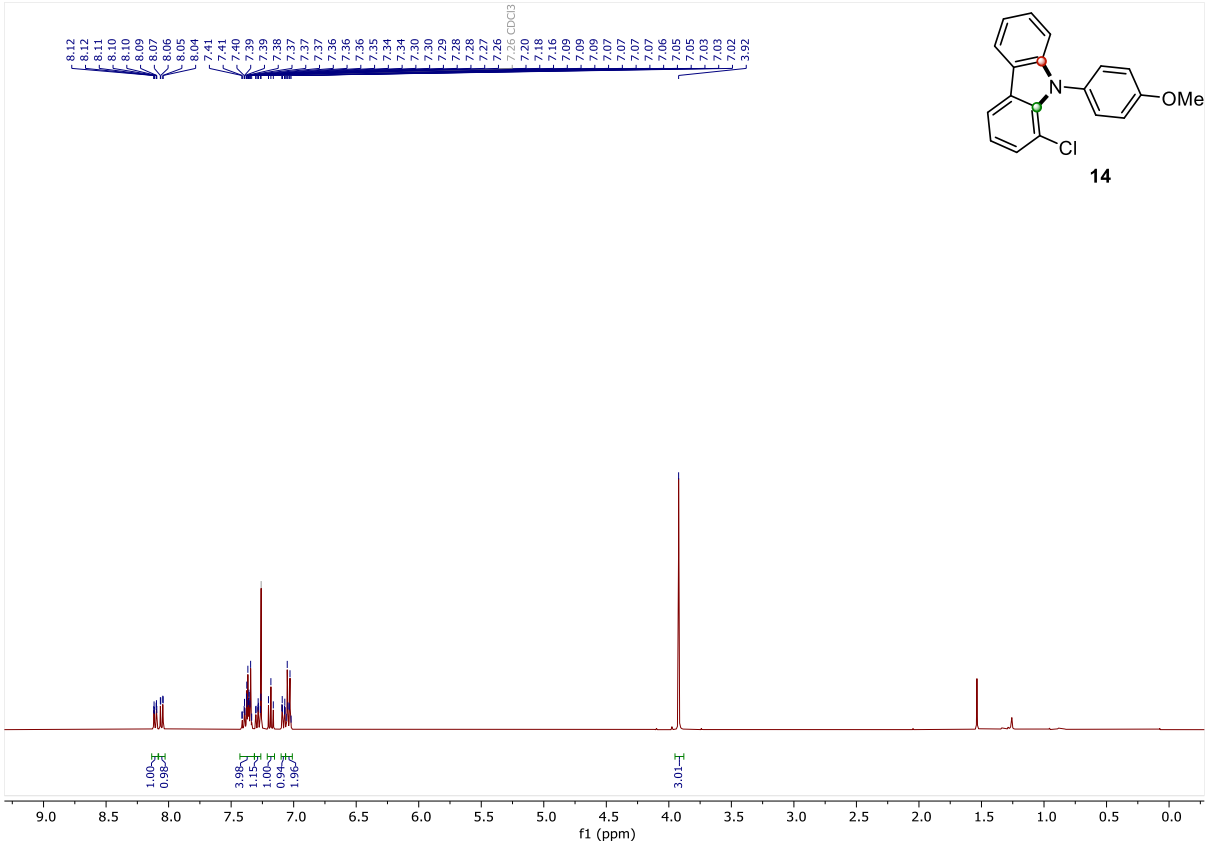


^{13}C NMR (126 MHz, $CDCl_3$), mixture of atropodiastereomers (55:45 ratio)

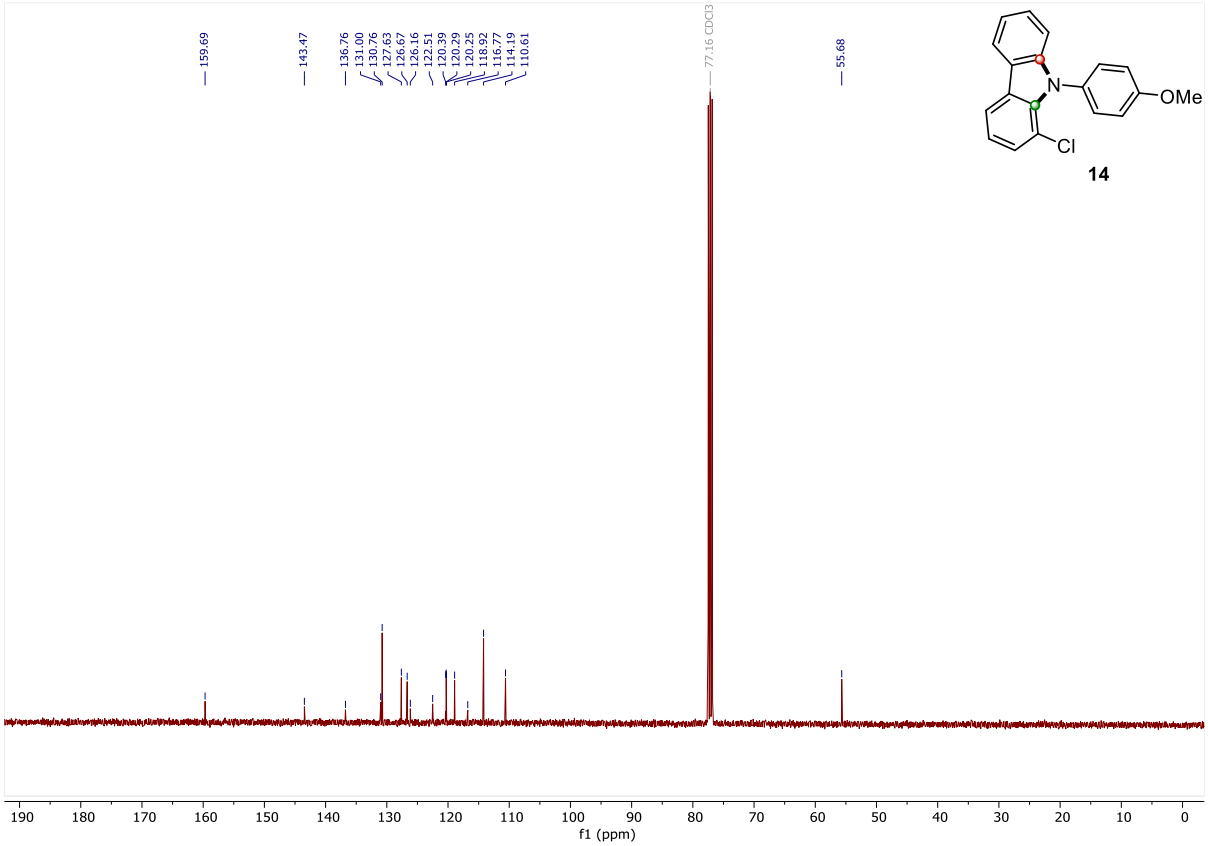


1-chloro-9-(4-methoxyphenyl)-9*H*-carbazole (14) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

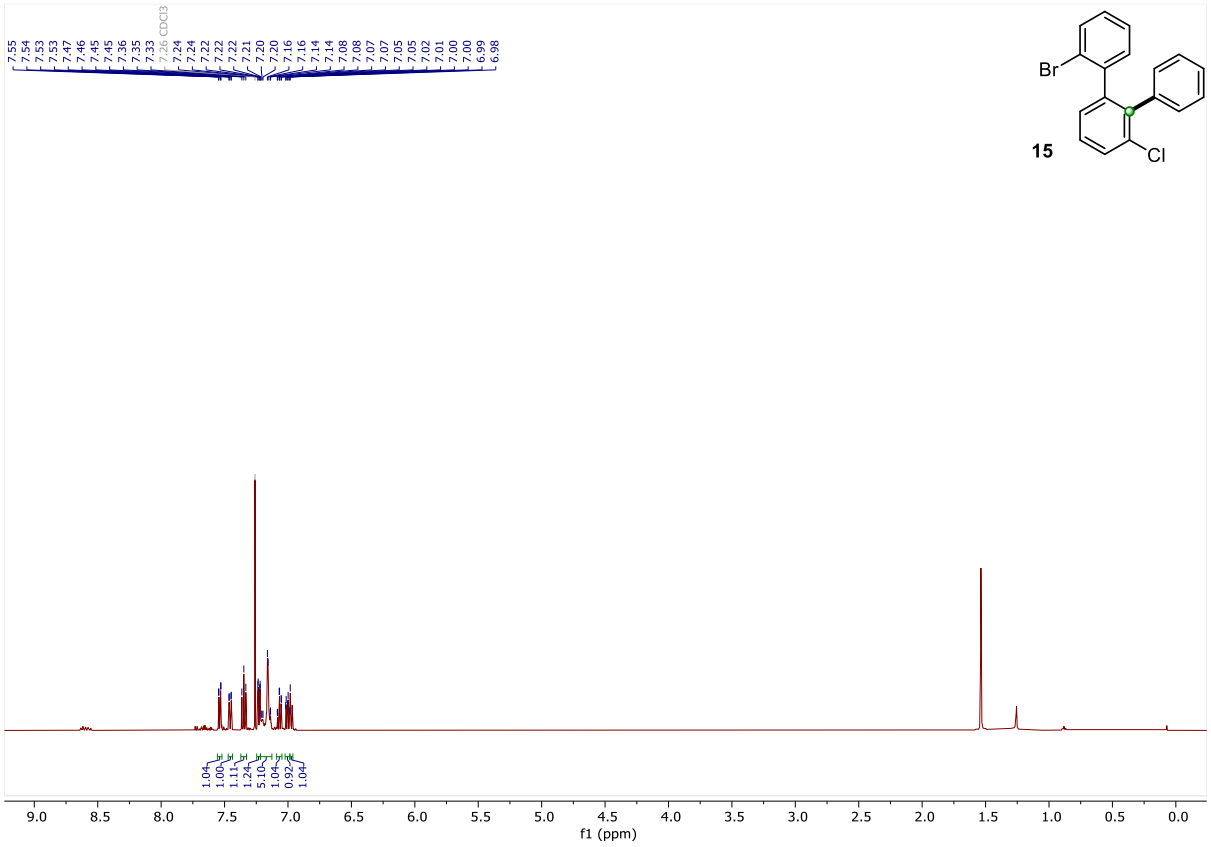


^{13}C NMR (101 MHz, $CDCl_3$)

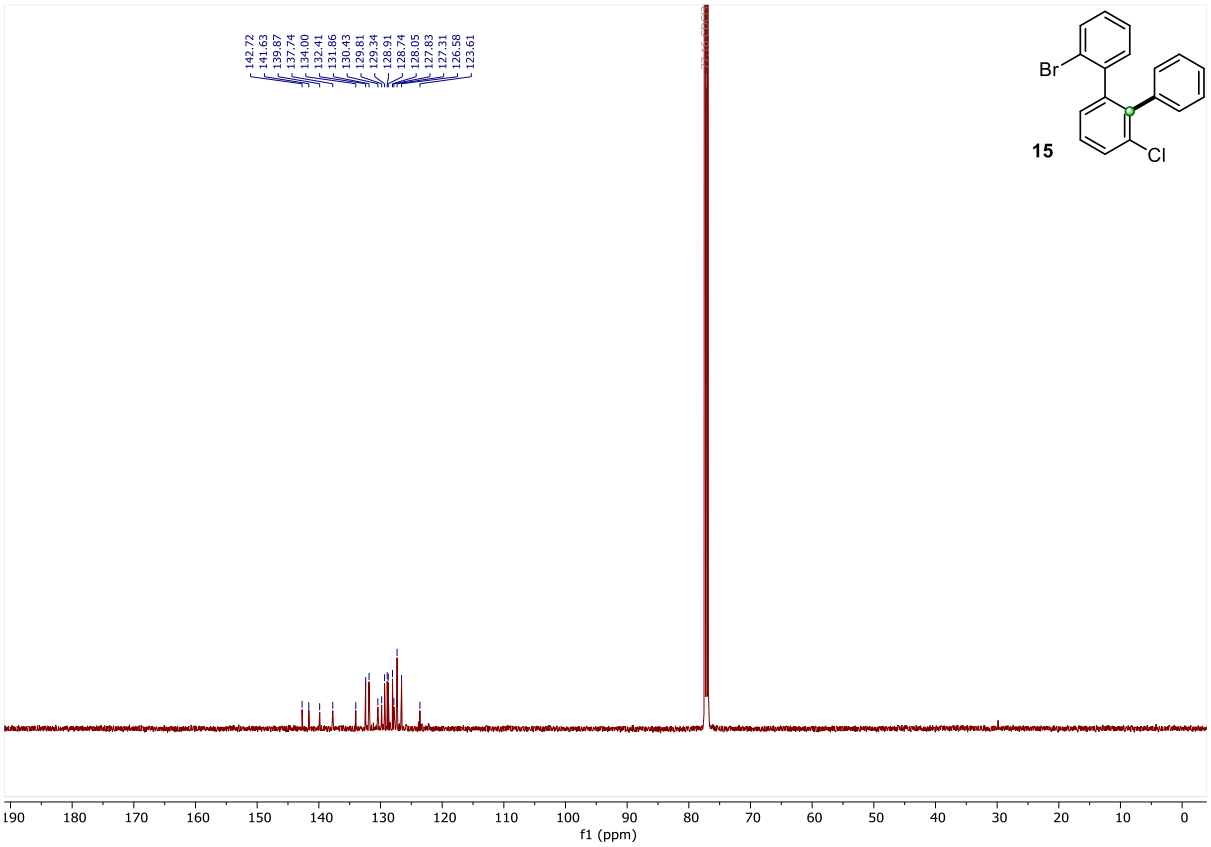


2-bromo-3'-chloro-1,1':2',1''-terphenyl (15) *See procedure*.

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

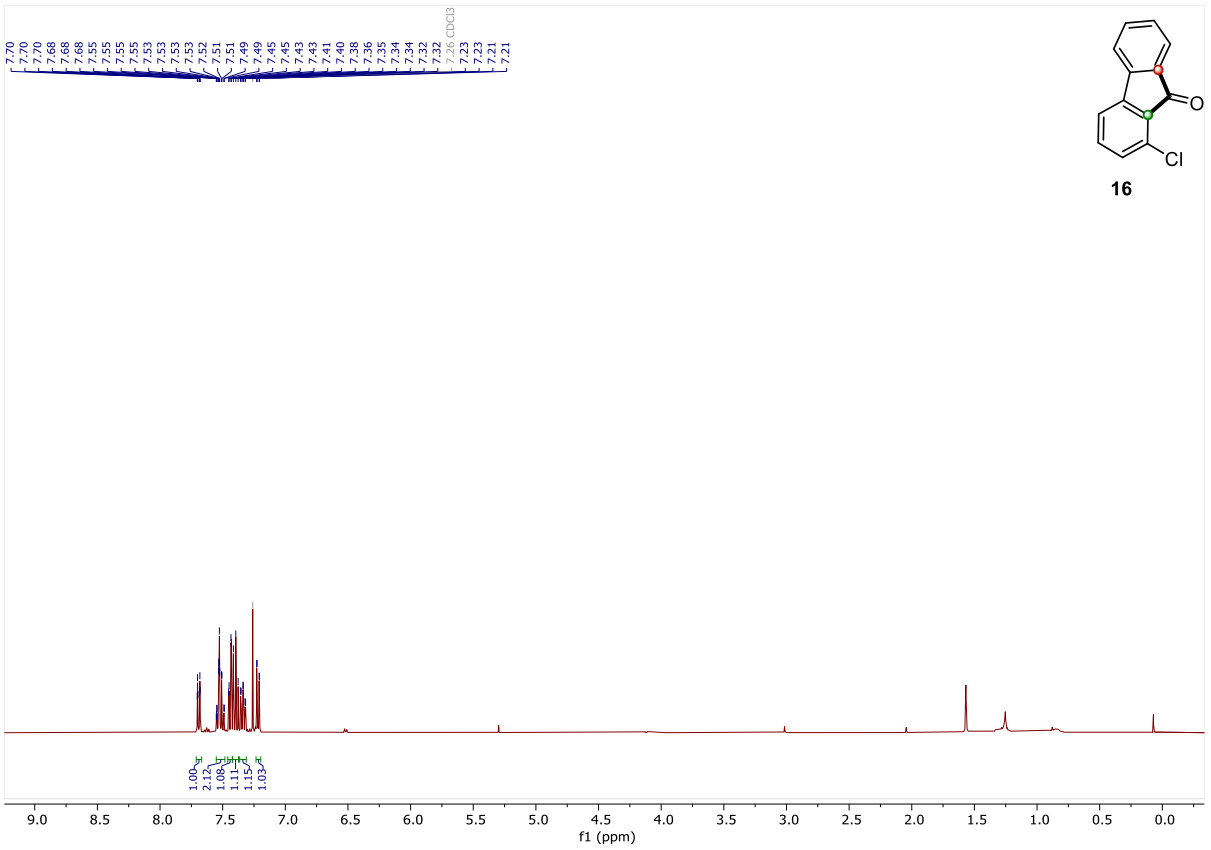


^{13}C NMR (126 MHz, $CDCl_3$)

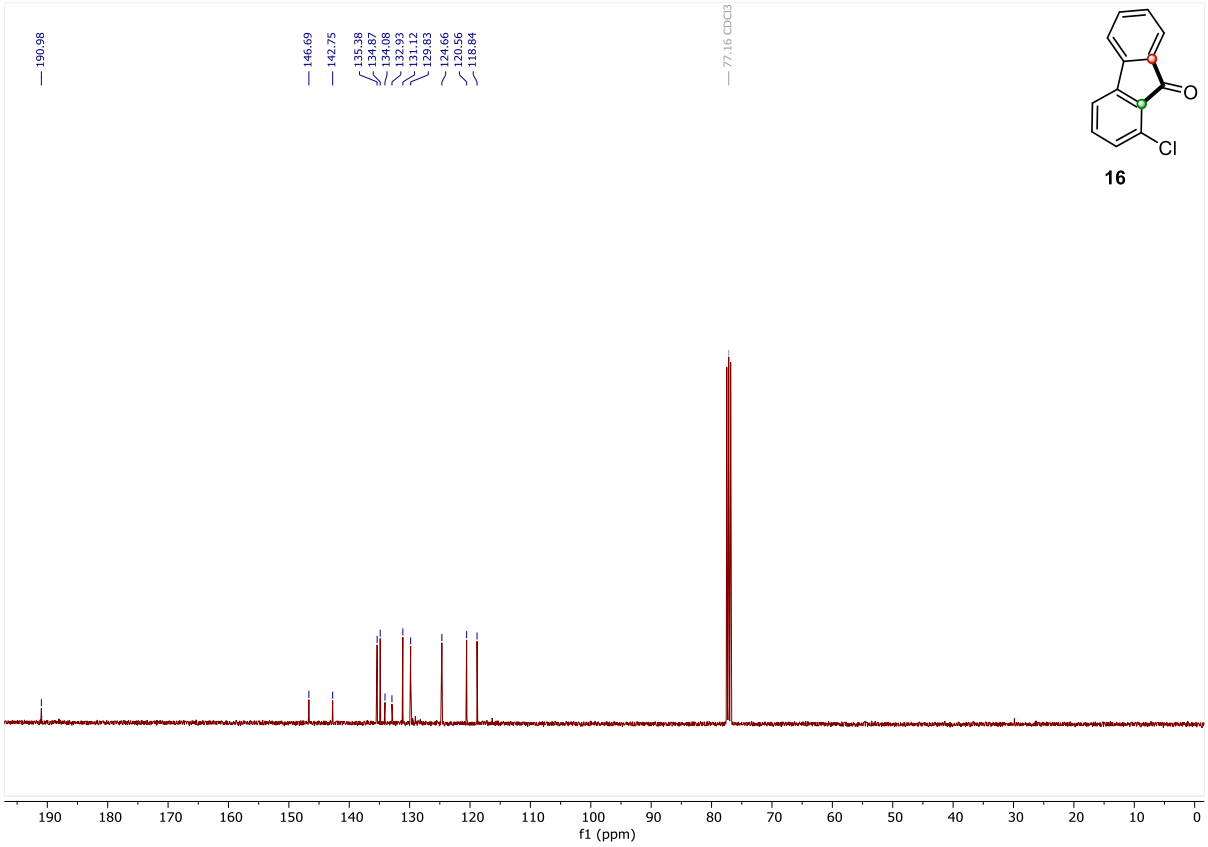


1-chloro-9*H*-fluoren-9-one (16) *See procedure*.

^{1}H NMR (400 MHz, $CDCl_3$)

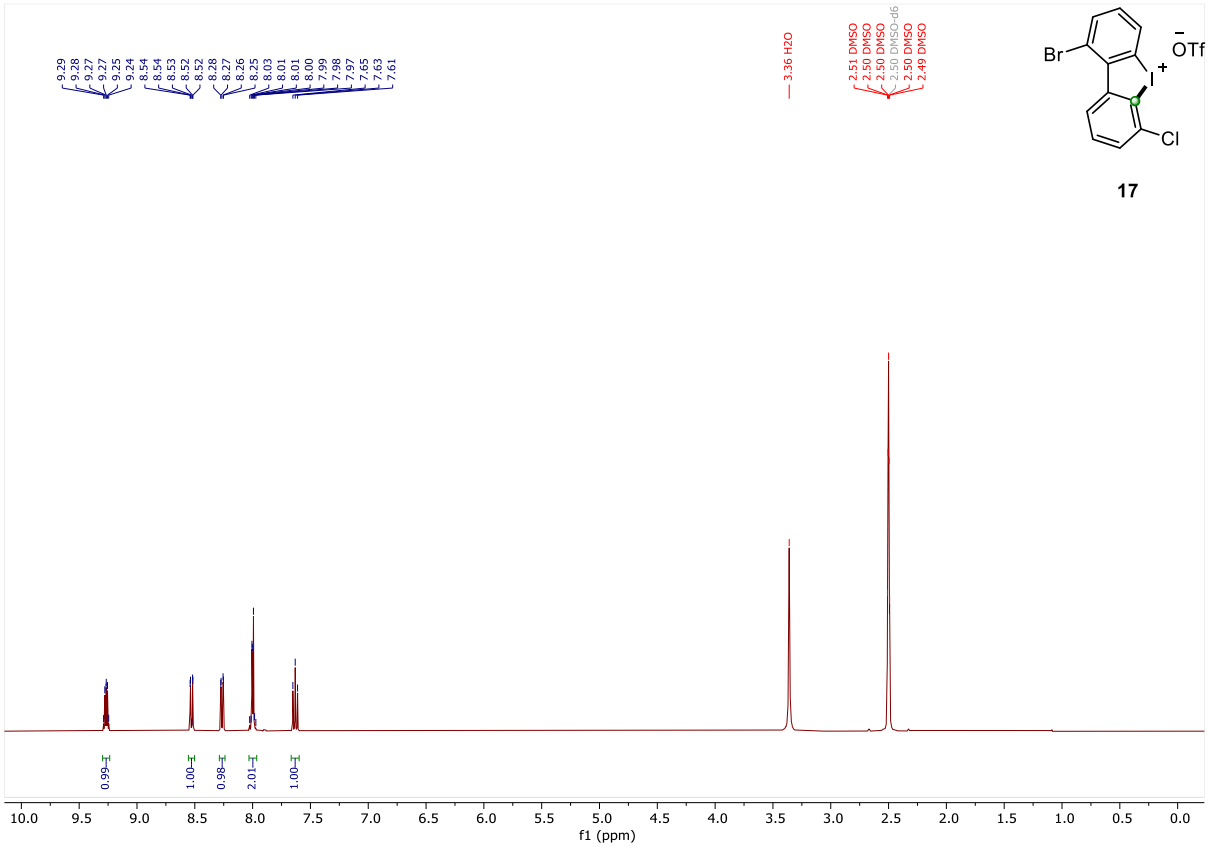


^{13}C NMR (101 MHz, $CDCl_3$)

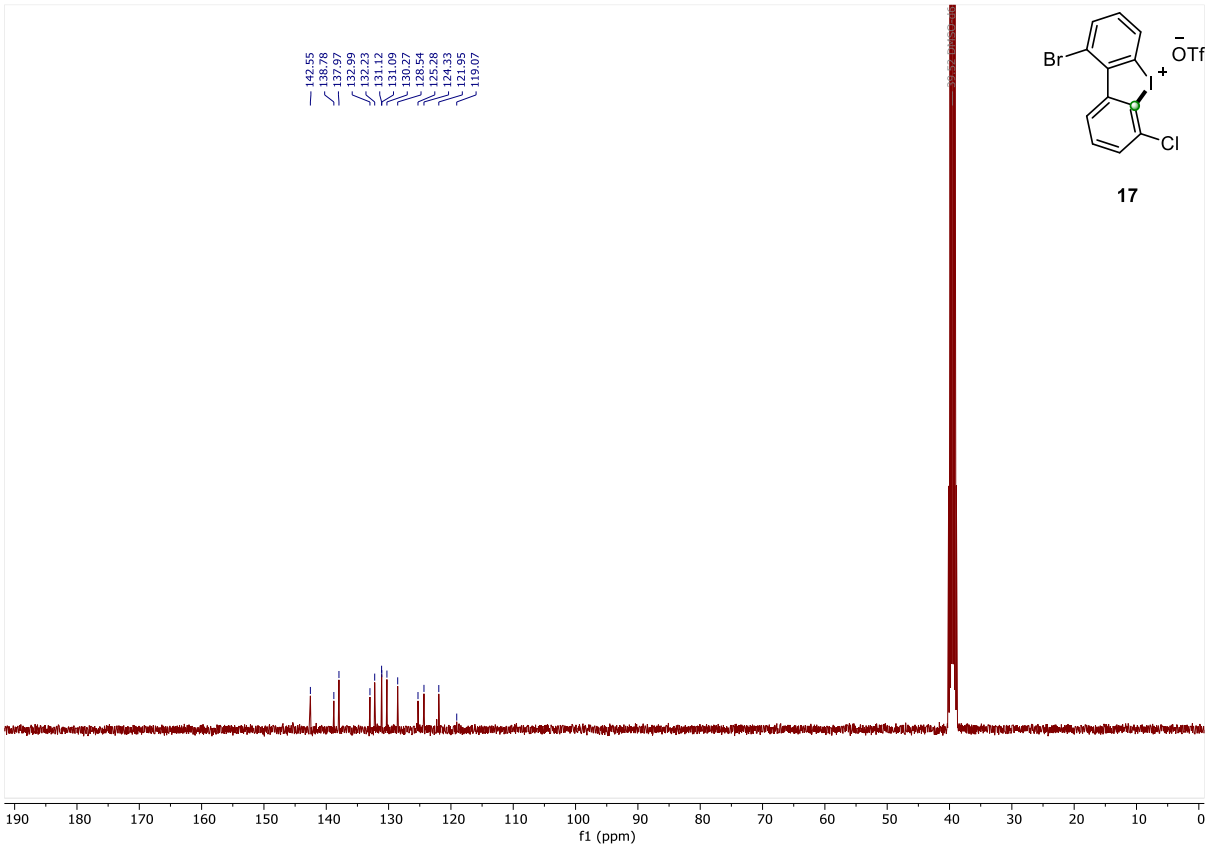


1-bromo-6-chlorodibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (17) *See procedure*.

^{1}H NMR (400 MHz, DMSO-d6)



^{13}C NMR (101 MHz, DMSO-d6)



^{19}F NMR (377 MHz, DMSO-d6)