Supporting Information

Synthesis of 2,2'-Dihalobiaryls via Cu-Catalyzed Halogenation of Cyclic Diaryliodonium Salts

Kai Zhu, Zongqiang Song, Yi Wang, and Fengzhi Zhang*

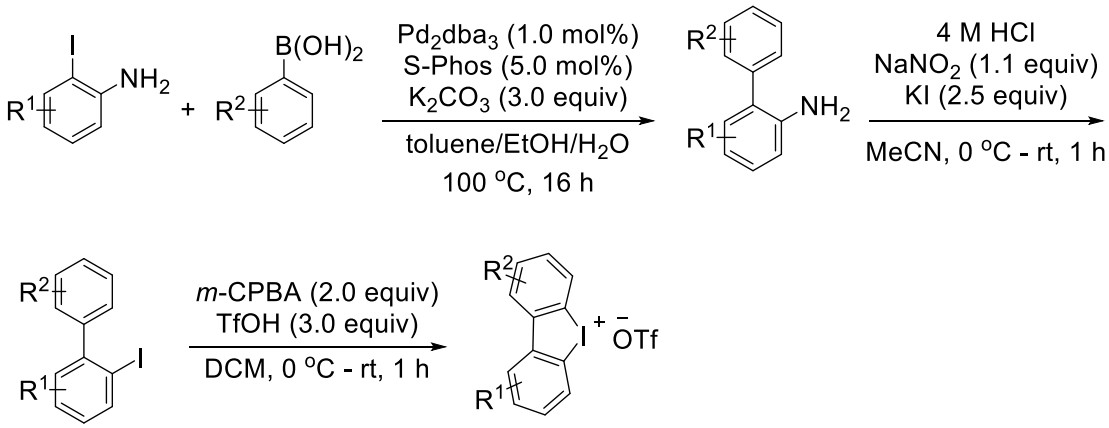
Email: zhangfengzhi@zjut.edu.cn

Contents

1. General information

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ADNANCE III 500 MHz instrument. Reference values for residual solvents were taken as δ = 7.26 ppm ($CDCl_3$), 2.50 ppm (DMSO-d_6), 3.31 ppm (CD_3OD) for ^1H NMR; δ = 77.0 ppm ($CDCl_3$), δ = 39.0 ppm (DMSO-d_6), δ = 48.8 ppm (CD_3OD) for ^{13}C NMR. Signals are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and coupling constants are expressed in hertz. Optical rotations were obtained with Rudolph Autopol V polarimeter (589 nm). HRMS were recorded on Agilent 6210TOF LC/MS mass spectrometer. Reactions were monitored by thin layer chromatography (TLC) using UV light. All reagents were obtained from commercial suppliers and used without further purification. Ligand **L1** – **L6** were purchased from DAICEL CHIRAL TECHNOLOGIES (CHINA) CO. LTD. The cyclic diaryliodoniums with triflate anion were synthesized according to the reported literature.[1-2]

2. Synthesis and characterization of diaryliodonium salts (Typical Procedure A)



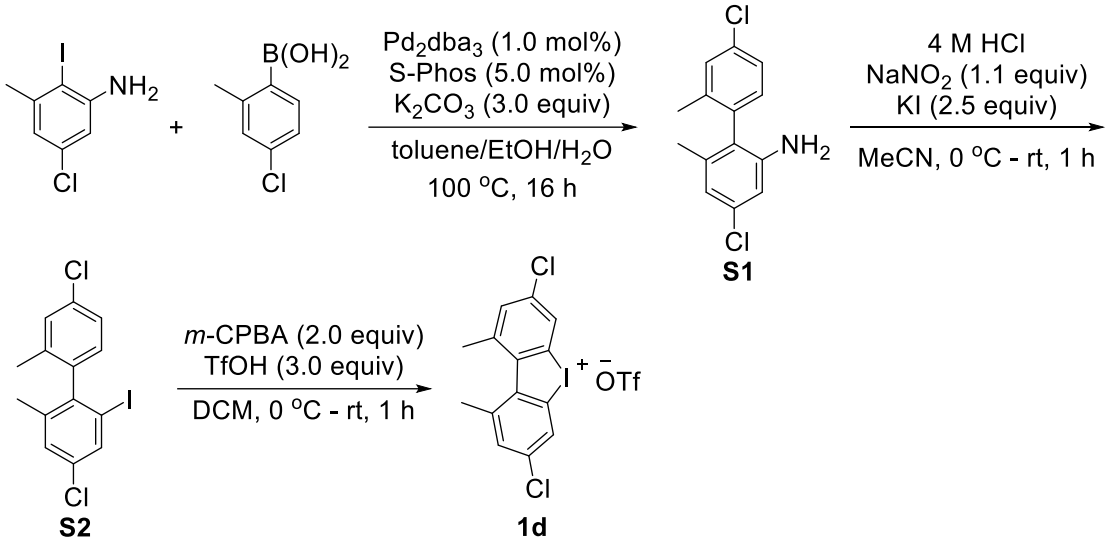
An round-bottomed flask containing a suspension of the appropriate 2-iodo aniline (1.0 equiv), boronic acid (1.5 equiv), Pd_2dba_3 (1.0 mol %), *S*-Phos (5.0 mol %) and K_2CO_3 (3.0 equiv) in toluene/EtOH/H_2O (8: 2: 2, 0.2 M) was backfilled with N_2 for 3 times. The reaction was stirred at 100 °C in an oil bath for 16 h under N_2 before being allowed to cool to room temperature. The reaction mixture was filtered and extracted with ethyl acetate, the combined organic layers were washed with H_2O and brine, dried over anhydrous Na_2SO_4, concentrated by rotary evaporation. The crude material was purified by flash chromatography on silica gel to give the product.

To a stirred mixture of 2-aminobiphenyl (1.0 equiv) and 4 M HCl (10.0 equiv) in MeCN (1.0 M) was added an aqueous solution of $NaNO_2$ (1 M, 1.1 equiv) dropwise at 0 °C and stirred for 45 min. Aqueous KI (2 M, 2.5 equiv) was added dropwise at 0 °C and stirred for 5 min at 0 °C and 2 h at room temperature. The mixture was extracted with ethyl acetate, and the combined organic layers were washed with H_2O, brine and saturated $NaHSO_3$ solution. The organic phase was dried over anhydrous Na_2SO_4, filtrated and concentrated by rotary evaporation. The crude product was purified by flash chromatography on silica gel to give the product.

To a stirred solution of above product in DCM (0.25 M) was added *m*-CPBA (85%, 2.0 equiv) in one portion. After *m*-CPBA being completely dissolved, TfOH (3.0 equiv) was added

dropwise at 0 °C, and was stirred at room temperature for 2 h. DCM was removed by rotary evaporation before the addition of Et_2O. The mixture was stirred for 30 min, and the solid was collected by filtration. The crude solid was washed with Et_2O three times, dried under vacuum to afford the appropriate cyclic diaryliodonium salt.

3,7-dichloro-1,9-dimethyldibenzo[*b*,*d*]-cyclic iodonium triflate (1d)

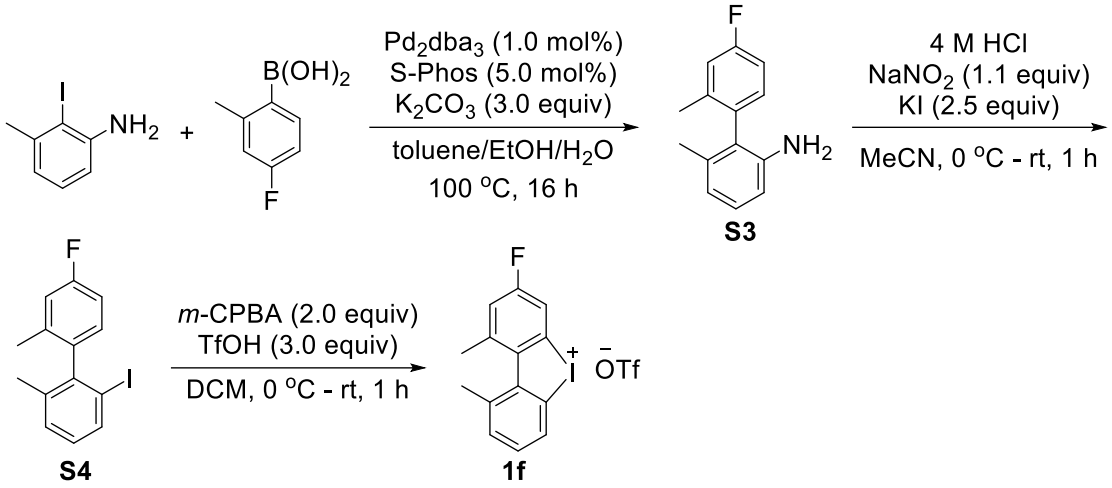


The reaction was performed by following the general procedure **A**. The reaction of 5-chloro-2-iodo-3-methylaniline (2.14 g, 8.0 mmol, 1.0 equiv) and (4-chloro-2-methylphenyl) boronic acid (2.04 g, 12.0 mmol, 1.5 equiv) afforded **S1** (1.91 g, 90%) as yellowish oil, which was purified by column chromatography on silica gel (ethyl acetate/haxanes = 1:40).

The reaction of **S1** (1.91 g, 7.2 mmol) afforded **S2** (2.49 g, 92%) as yellowish oil, which was purified by column chromatography on silica gel (ethyl acetate/haxanes = 1:200).

The reaction of **S2** (2.49 g, 6.6 mmol) afforded **1d** (3.13 g, 90%) as a white solid. Mp = 258.2-259.5 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.08 (d, J = 2.1 Hz, 2H), 7.83 (d, J = 2.1 Hz, 2H), 2.52 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 141.6, 139.3, 133.8, 133.5, 126.8, 121.8, 23.4. HRMS (ESI) m/z: $[M\text{-}TfO^-]^+$ Calcd for $C_{14}H_{10}Cl_2I^+$ 374.9199; Found 374.9186.

3-fluoro-1,9-dimethyldibenzo[*b*,*d*]-cyclic iodonium triflate (1f)

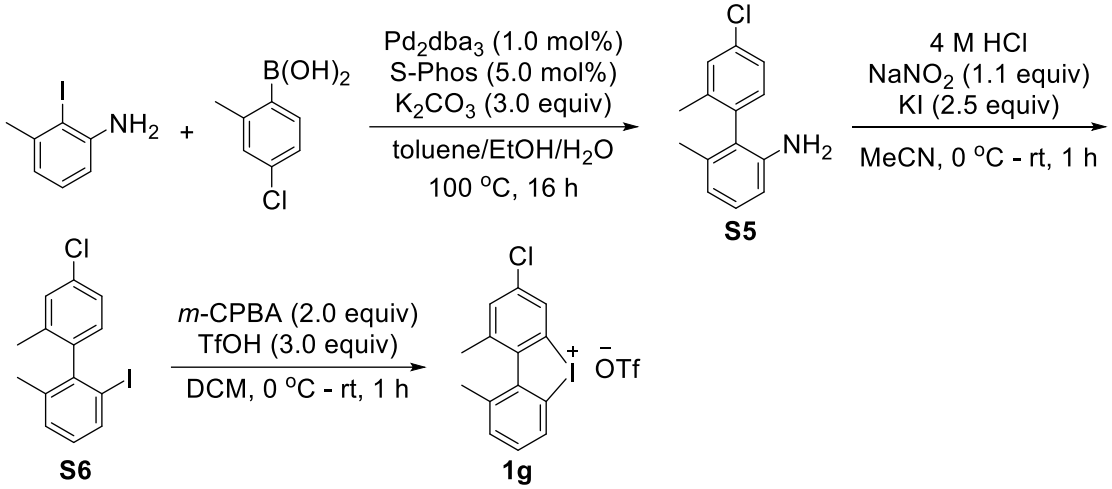


The reaction was performed by following the general procedure **A**. The reaction of 2-iodo-3-methylaniline (1.16 g, 5.0 mmol, 1.0 equiv) and (4-fluoro-2-methylphenyl)boronic acid (1.16 g, 7.5 mmol, 1.5 equiv) afforded **S3** (0.98 g, 91%) as yellowish oil, which was purified by column chromatography on silica gel (ethyl acetate/haxanes = 1:20).

The reaction of **S3** (0.98 g, 4.6 mmol) afforded **S4** (1.36 g, 92%) as yellowish oil, which was purified by column chromatography on silica gel (ethyl acetate/haxanes = 1:200).

The reaction of **S4** (1.36 g, 4.19 mmol) afforded **1f** (1.81 g, 91%) as a white solid. Mp = 185.1-186.1 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.07 (dd, J = 8.0, 1.2 Hz, 1H), 7.92 (dd, J = 7.1, 2.6 Hz, 1H), 7.71 (d, J = 7.5 Hz, 1H), 7.67 – 7.62 (m, 2H), 2.54 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 161.0 (d, $J_{C\text{-}F}$ = 253.2 Hz), 142.1 (d, $J_{C\text{-}F}$ = 8.2 Hz), 140.0 (d, $J_{C\text{-}F}$ = 7.2 Hz), 138.2 (d, $J_{C\text{-}F}$ = 2.9 Hz), 133.8, 129.7, 127.5, 121.3, 121.2, 121.0 (d, $J_{C\text{-}F}$ = 1.6 Hz), 120.6 (d, $J_{C\text{-}F}$ = 21.9 Hz), 115.1 (d, $J_{C\text{-}F}$ = 27.2 Hz), 23.7, 23.5. HRMS (ESI) m/z: $[M\text{-}TfO^-]^+$ Calcd for $C_{14}H_{11}FI^+$ 324.9884; Found 324.9874.

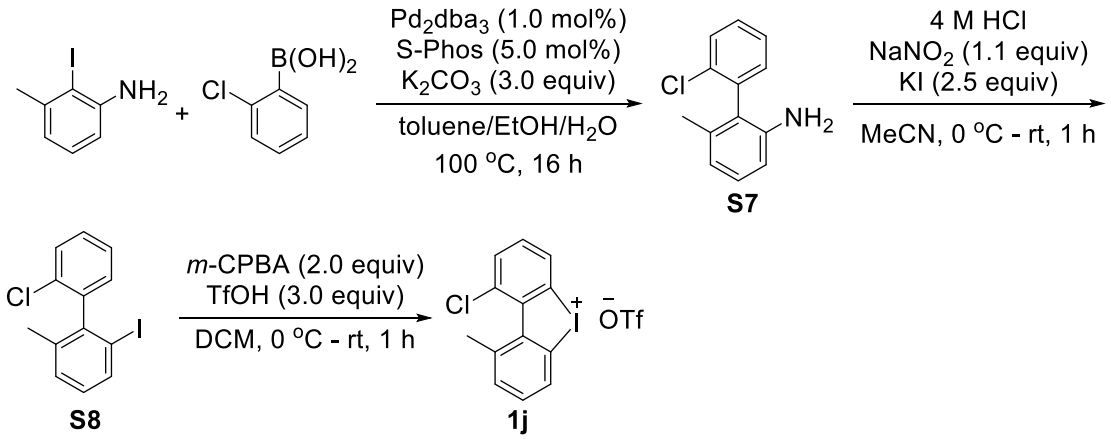
3-chloro-1,9-dimethyldibenzo[*b*,*d*]-cyclic iodonium triflate (1g)



The reaction was performed by following the general procedure **A**. The reaction of 2-iodo-3-methylaniline (1.16 g, 5.0 mmol, 1.0 equiv) and (4-fluoro-2-methylphenyl)boronic acid (1.28

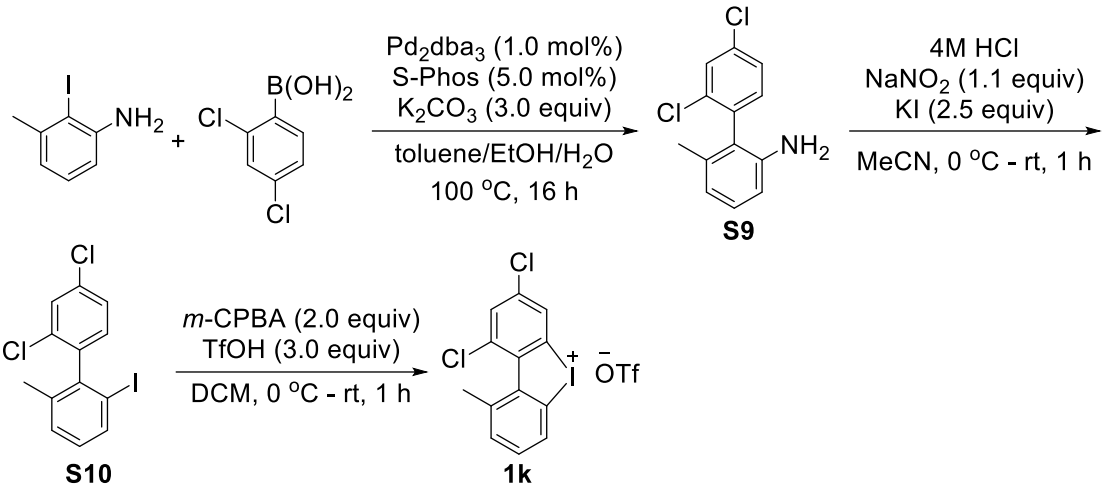
g, 7.5 mmol, 1.5 equiv) afforded **S5** (1.06 g, 92%) as yellowish oil, which was purified by column chromatography on silica gel (ethyl acetate/haxanes = 1:20).
The reaction of **S5** (1.06 g, 4.6 mmol) afforded **S6** (1.45 g, 92%) as yellowish oil, which was purified by column chromatography on silica gel (ethyl acetate/haxanes = 1:200).
The reaction of **S6** (1.45 g, 4.23 mmol) afforded **1g** (1.87 g, 90%) as a white solid. Mp = 212.1-212.4 °C; ^{1}H NMR (500 MHz, CD_3OD) δ 8.02 (d, *J* = 2.1 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 2.0 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 2.62 (s, 6H); ^{13}C NMR (126 MHz, CD_3OD) δ 143.4, 142.6, 142.3, 142.0, 136.3, 135.5, 135.2, 131.4, 128.7, 128.3, 120.65, 120.62, 24.2, 24.1. HRMS (ESI) m/z: $[M\text{-}TfO^-]^+$ Calcd for $C_{14}H_{11}ClI$ 340.9588; Found 340.9578.

1-chloro-9-methyldibenzo[*b*,*d*]-cyclic iodonium triflate (1j)



The reaction was performed by following the general procedure **A**. The reaction of 2-iodo-3-methylaniline (1.16 g, 5.0 mmol, 1.0 equiv) and (2-chlorophenyl)boronic acid (1.17 g, 7.5 mmol, 1.5 equiv) afforded **S7** (0.98 g, 90%) as yellowish oil, which was purified by column chromatography on silica gel (ethyl acetate/haxanes = 1:20).
The reaction of **S7** (0.98 g, 4.5 mmol) afforded **S8** (1.33 g, 90%) as yellowish oil, which was purified by column chromatography on silica gel (ethyl acetate/haxanes = 1:200).
The reaction of **S8** (1.33 g, 4.05 mmol) afforded **1j** (1.75 g, 91%) as a white solid. Mp = 194.4-195.1 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.24 (dd, *J* = 8.1, 1.1 Hz, 1H), 8.09 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.96 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.76 – 7.67 (m, 3H), 2.64 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 141.2, 140.0, 139.1, 133.9, 133.3, 132.9, 131.2, 130.6, 129.2, 127.4, 121.7, 121.1, 24.7. HRMS (ESI) m/z: $[M\text{-}TfO^-]^+$ Calcd for $C_{13}H_9ClI$ 326.9432; Found 326.9423.

1,3-dichloro-9-methyldibenzo[*b*,*d*]-cyclic iodonium triflate (1k)

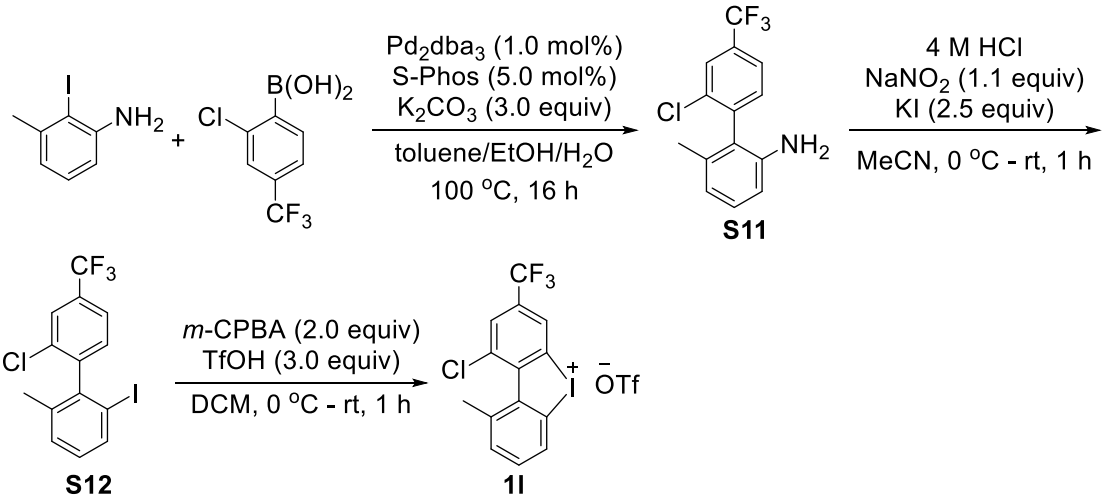


The reaction was performed by following the general procedure **A**. The reaction of 2-iodo-3-methylaniline (1.16 g, 5.0 mmol, 1.0 equiv) and (2,4-dichlorophenyl)boronic acid (1.42 g, 7.5 mmol, 1.5 equiv) afforded **S9** (1.1 g, 88%) as yellowish oil, which was purified by column chromatography on silica gel (ethyl acetate/haxanes = 1:20).

The reaction of **S9** (1.1 g, 4.4 mmol) afforded **S10** (1.39 g, 87%) as yellowish oil, which was purified by column chromatography on silica gel (ethyl acetate/haxanes = 1:200).

The reaction of **S10** (1.39 g, 3.83 mmol) afforded **1k** (1.74 g, 89%) as a white solid. Mp = 219.4-220.1 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.24 (d, J = 1.9 Hz, 1H), 8.18 (d, J = 2.0 Hz, 1H), 8.08 (dd, J = 7.8, 1.5 Hz, 1H), 7.78 – 7.69 (m, 2H), 2.63 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 141.8, 140.0, 138.7, 134.7, 134.5, 134.2, 132.9, 131.3, 129.0, 127.8, 123.0, 121.9, 25.2. HRMS (ESI) m/z: $[M\text{-}TfO^-]^+$ Calcd for $C_{13}H_8Cl_2I$ 360.9042; Found 360.9044.

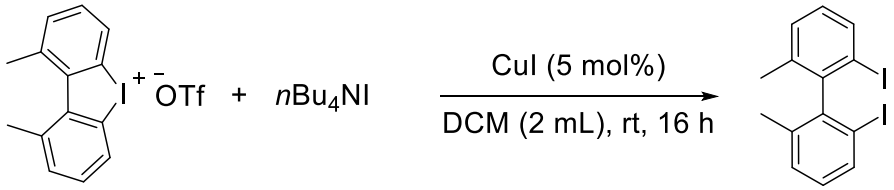
1,3-dichloro-9-methyldibenzo[*b*,*d*]-cyclic iodonium triflate (1l)



The reaction was performed by following the general procedure **A**. The reaction of 2-iodo-3-methylaniline (1.16 g, 5.0 mmol, 1.0 equiv) and (2-chloro-4-(trifluoromethyl)phenyl) boronic acid (1.68 g, 7.5 mmol, 1.5 equiv) afforded **S11** (1.25 g, 88%) as yellowish oil, which was purified by column chromatography on silica gel (ethyl acetate/haxanes = 1:20).

The reaction of **S11** (1.25 g, 4.4 mmol) afforded **S12** (1.52 g, 87%) as yellowish oil, which was purified by column chromatography on silica gel (ethyl acetate/haxanes = 1:200).
The reaction of **S12** (1.52 g, 3.83 mmol) afforded **1l** (1.83 g, 88%) as a white solid. Mp = 233.2-234.5 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.54 (d, J = 1.7 Hz, 1H), 8.43 (d, J = 1.7 Hz, 1H), 8.13 (dd, J = 7.2, 2.0 Hz, 1H), 7.85 – 7.74 (m, 2H), 2.67 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 144.1, 142.1, 137.9, 134.1, 133.9, 131.5, 130.0 (q, $J_{C\text{-}F}$ = 34.8 Hz), 129.7 (q, $J_{C\text{-}F}$ = 4.4 Hz), 127.5, 125.5 (q, $J_{C\text{-}F}$ = 4.4 Hz), 122.8, 122.6 (q, $J_{C\text{-}F}$ = 273.2 Hz), 122.2, 24.7. HRMS (ESI) m/z: $[M\text{-}TfO^-]^+$ Calcd for $C_{14}H_8F_3ClI$ 394.9305; Found 394.9291.

3. Synthesis and characterization of 2a (Typical Procedure B)

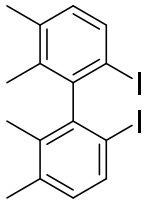


1a **2a**

To the stirred solution of cyclic diaryliodonium salts **1a** (91.2 mg, 0.2 mmol), CuI (1.9 mg, 5 mol%) in DCM (2 mL) was added nBu$_4$NI (88.6 mg, 0.24 mmol). The reaction mixture was stirred at room temperature for 16 h. Then the solvent was concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 200:1) on silica gel to obtain the desired product **2a** (85.9 mg, 99%) as a white solid. Mp = 68.1-69.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 2H), 7.30 (dt, J = 7.6, 0.9 Hz, 2H), 7.03 (t, J = 7.7 Hz, 2H), 2.04 (s, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.5, 137.6, 136.8, 130.0, 129.4, 100.7, 21.4. The spectra data was consistent with that reported.[3]

Gram scale procedure: To the stirred solution of cyclic diaryliodonium salts **1a** (1.37 g, 3 mmol), CuI (28.5 mg, 5 mol%) in DCM (20 mL) was added nBu$_4$NI (1.33 g, 3.6 mmol). The reaction mixture was stirred at room temperature for 16 h. Then the solvent was concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 200:1) on silica gel to obtain the desired product **2a** (1.28 g, 99%) as a white solid.

6,6'-diiodo-2,2',3,3'-tetramethyl-1,1'-biphenyl (2b)

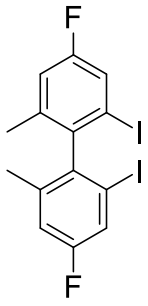


2b

Following the procedure **B**, **2b** was purified by PE/EtOAc (200:1) and obtained as a white solid (89.6 mg, 97%). Mp = 123.6-124.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 2.31 (s, 6H), 1.93 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 137.1,

136.3, 136.1, 130.8, 97.6, 20.3, 17.8. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{16}I_2$ 461.9342; Found 461.9357.

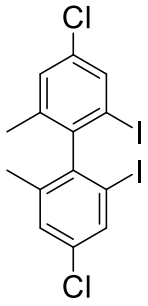
4,4'-difluoro-2,2'-diiodo-6,6'-dimethyl-1,1'-biphenyl (2c)



2c

Following the procedure **B**, **2c** was purified by PE/EtOAc (200:1) and obtained as a white solid (90.2 mg, 96%). Mp = 90.8-91.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.8, 2.5 Hz, 2H), 7.09 – 6.98 (m, 2H), 2.02 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5 (d, J_{C-F} = 251.6 Hz), 142.7 (d, J_{C-F} = 3.4 Hz), 139.3 (d, J_{C-F} = 8.1 Hz), 123.8 (d, J_{C-F} = 23.4 Hz), 117.2 (d, J_{C-F} = 21.2 Hz), 100.4 (d, J_{C-F} = 8.9 Hz), 21.7 (d, J_{C-F} = 1.6 Hz). HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{10}F_2I_2$ 469.8840; Found 469.8838.

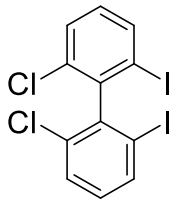
4,4'-dichloro-2,2'-diiodo-6,6'-dimethyl-1,1'-biphenyl (2d)



2d

Following the procedure **B**, **2d** was purified by PE/EtOAc (200:1) and obtained as a white solid (95.3 mg, 95%). Mp = 130.7-131.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 2.0 Hz, 2H), 7.31 (d, *J* = 2.0 Hz, 2H), 2.00 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 138.7, 136.3, 134.3, 130.3, 100.5, 21.4. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{10}Cl_2I_2$ 501.8249; Found 501.8253.

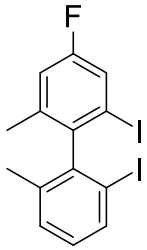
2,2'-dichloro-6,6'-diiodo-1,1'-biphenyl (2e)



2e

Following the procedure **B**, **2e** was purified by PE/EtOAc (200:1) and obtained as a white solid (89.1 mg, 94%). Mp = 148.5-149.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.0, 1.1 Hz, 2H), 7.53 (dd, *J* = 8.0, 1.1 Hz, 2H), 7.09 (td, *J* = 8.0, 1.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.1, 137.6, 133.6, 130.9, 129.5, 100.2. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{12}H_6Cl_2I_2$ 473.7936; Found 473.7950.

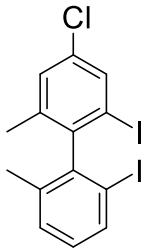
4-fluoro-2,2'-diiodo-6,6'-dimethyl-1,1'-biphenyl (2f)



2f

Following the procedure **B**, **2f** was purified by PE/EtOAc (200:1) and obtained as a white solid (87.7 mg, 97%). Mp = 72.5-73.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.9 Hz, 1H), 7.55 (dd, *J* = 7.9, 2.6 Hz, 1H), 7.31 – 7.28 (m, 1H), 7.07 – 6.99 (m, 2H), 2.02 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4 (d, J_{C-F} = 251.0 Hz), 146.5, 143.7 (d, J_{C-F} = 3.5 Hz), 139.0 (d, J_{C-F} = 8.0 Hz), 137.8, 136.9, 130.1, 129.6, 123.7 (d, J_{C-F} = 23.8 Hz), 117.2 (d, J_{C-F} = 20.7 Hz), 101.1, 99.9 (d, J_{C-F} = 8.5 Hz), 21.7, 21.4. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{11}FI_2$ 451.8934; Found 451.8939.

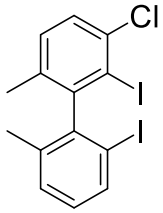
4-chloro-2,2'-diiodo-6,6'-dimethyl-1,1'-biphenyl (2g)



2g

Following the procedure **B**, **2g** was purified by PE/EtOAc (200:1) and obtained as a white solid (88.9 mg, 95%). Mp = 76.4-77.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 2H), 7.33 – 7.31 (m, 1H), 7.30 – 7.28 (m, 1H), 7.03 (t, *J* = 7.7 Hz, 1H), 2.02 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.4, 146.0, 138.7, 137.6, 136.9, 136.2, 133.9, 130.20, 130.15, 129.7, 100.6, 100.5, 21.42, 21.38. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{11}ClI_2$ 467.8639; Found 467.8657.

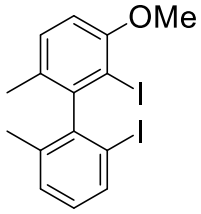
3-chloro-2,2'-diiodo-6,6'-dimethyl-1,1'-biphenyl (2h)



2h

Following the procedure **B**, **2h** was purified by PE/EtOAc (200:1) and obtained as a white solid (91.7 mg, 98%). Mp = 123.8-124.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.26 – 7.22 (m, 1H), 7.03 (t, *J* = 7.7 Hz, 1H), 2.01 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.0, 147.9, 137.3, 136.9, 136.8, 135.4, 131.2, 130.2, 129.6, 128.3, 104.8, 100.2, 21.3, 21.0. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{11}ClI_2$ 467.8639; Found 467.8650.

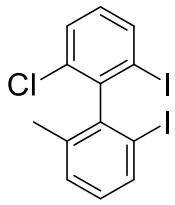
2,2'-diiodo-3-methoxy-6,6'-dimethyl-1,1'-biphenyl (2i)



2i

Following the procedure **B**, **2i** was purified by PE/EtOAc (50:1) and obtained as a colourless oil (90.9 mg, 98%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.9 Hz, 1H), 7.30 (s, 1H), 7.25 (d, *J* = 8.3 Hz, 1H), 7.02 (t, *J* = 7.7 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 3.95 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.8, 149.0, 147.6, 137.5, 136.8, 130.8, 130.0, 129.30, 129.26, 110.0, 100.6, 92.4, 56.5, 21.3, 20.4. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{14}OI_2$ 463.9134; Found 463.9144.

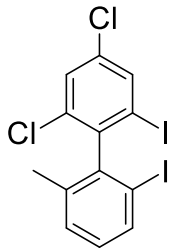
2-chloro-2',6-diiodo-6'-methyl-1,1'-biphenyl (2j)



2j

Following the procedure **B**, **2j** was purified by PE/EtOAc (200:1) and obtained as a white solid (86.2 mg, 95%). Mp = 93.5-94.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.52 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.06 (td, *J* = 7.9, 3.9 Hz, 2H), 2.08 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.33, 146.25, 137.83, 137.78, 136.7, 133.4, 130.4, 129.95, 129.93, 129.6, 100.9, 100.0, 21.2. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{13}H_9ClI_2$ 453.8482; Found 453.8483.

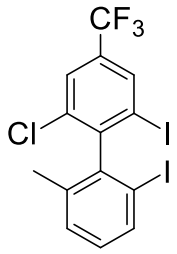
2,4-dichloro-2',6-diiodo-6'-methyl-1,1'-biphenyl (2k)



2k

Following the procedure **B**, **2k** was purified by PE/EtOAc (200:1) and obtained as a colourless oil (95.6 mg, 98%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 2.0 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 2.1 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.8 Hz, 1H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.3, 145.0, 137.8, 137.4, 136.7, 134.8, 133.7, 130.2, 130.0, 129.7, 100.7, 99.9, 21.2. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{13}H_8Cl_2I_2$ 487.8093; Found 487.8102.

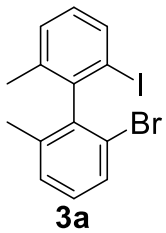
2-chloro-2',6-diiodo-6'-methyl-4-(trifluoromethyl)-1,1'-biphenyl (2l)



2l

Following the procedure **B**, **2l** was purified by PE/EtOAc (200:1) and obtained as a colourless oil (96.4 mg, 94%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.80 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.33 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 2.07 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.0, 145.3, 137.4, 136.9, 134.6 (q, $J_{C\text{-}F}$ = 3.5 Hz), 134.1, 132.5 (q, $J_{C\text{-}F}$ = 33.9 Hz), 130.4, 130.1, 126.7 (q, $J_{C\text{-}F}$ = 3.5 Hz), 122.1 (q, $J_{C\text{-}F}$ = 273.4 Hz), 101.1, 98.9, 21.1. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_8ClI_2F_3$ 521.8356; Found 521.8376.

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

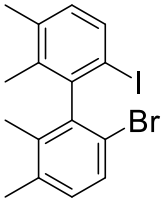


3a

To the stirred solution of cyclic diaryliodonium salts **1a** (91.2 mg, 0.2 mmol), CuBr (1.4 mg, 5 mol %) in DCM (2 mL) was added *n*Bu_4NBr (77.4 mg, 0.24 mmol). The reaction mixture was stirred at room temperature for 16 h. Then the solvent was concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 200:1) on silica gel to obtain the desired product **3a** (76.4 mg, 99%) as a white solid. Mp = 78.5-79.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ

7.84 – 7.80 (m, 1H), 7.57 – 7.52 (m, 1H), 7.31 – 7.26 (m, 2H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.02 (t, *J* = 7.7 Hz, 1H), 2.05 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.6, 143.8, 138.2, 137.7, 136.7, 130.3, 129.9, 129.3, 129.2, 129.1, 123.9, 100.4, 21.3, 20.6. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{12}BrI$ 385.9167; Found 385.9173.

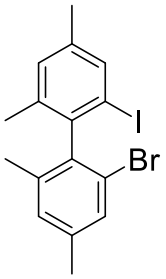
6-bromo-6'-iodo-2,2',3,3'-tetramethyl-1,1'-biphenyl (3b)



3b

Following the procedure of **3a**, **3b** was purified by PE/EtOAc (200:1) and obtained as a white solid (80.3 mg, 97%). Mp = 91.4-92.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 2.31 (s, 6H), 1.95 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 144.3, 137.0, 136.8, 136.5, 136.2, 136.0, 130.8, 130.5, 129.6, 121.3, 97.3, 20.35, 20.33, 17.7, 17.1. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{16}BrI$ 413.9480; Found 413.9499.

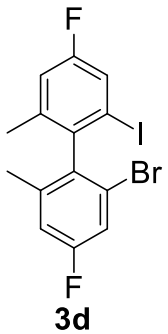
2-bromo-2'-iodo-4,4',6,6'-tetramethyl-1,1'-biphenyl (3c)



3c

Following the procedure of **3a**, **3c** was purified by PE/EtOAc (200:1) and obtained as a white solid (78.7 mg, 95%). Mp = 111.5-112.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 1H), 7.17 (d, *J* = 1.2 Hz, 2H), 7.08 (dt, *J* = 1.7, 0.8 Hz, 1H), 2.51 (s, 3H), 2.38 (s, 3H), 2.00 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.1, 141.9, 139.8, 139.0, 137.7, 134.7, 130.7, 130.1, 129.6, 128.7, 123.7, 107.6, 29.4, 21.04, 20.96, 20.6. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{16}BrI$ 413.9480; Found 413.9496.

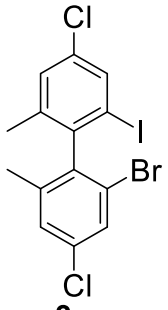
2-bromo-4,4'-difluoro-2'-iodo-6,6'-dimethyl-1,1'-biphenyl (3d)



3d

Following the procedure of **3a**, **3d** was purified by PE/EtOAc (200:1) and obtained as a white solid (79.3 mg, 94%). Mp = 66.3-67.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.8, 2.6 Hz, 1H), 7.31 (dd, *J* = 8.1, 2.6 Hz, 1H), 7.07 – 7.00 (m, 2H), 2.03 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8 (d, J_{C-F} = 250.5 Hz), 161.5 (d, J_{C-F} = 251.4 Hz), 140.2 (d, J_{C-F} = 7.6 Hz), 139.8 (d, J_{C-F} = 3.2 Hz), 139.4 (d, J_{C-F} = 7.4 Hz), 139.0 (d, J_{C-F} = 3.2 Hz), 124.4 (d, J_{C-F} = 10.4 Hz), 123.7 (d, J_{C-F} = 22.5 Hz), 117.6 (d, J_{C-F} = 24.2 Hz), 117.1 (d, J_{C-F} = 21.1 Hz), 116.4 (d, J_{C-F} = 20.8 Hz), 100.1 (d, J_{C-F} = 7.8 Hz), 21.5, 20.9. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{10}F_2BrI$ 421.8979; Found 421.8970.

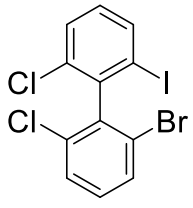
2-bromo-4,4'-dichloro-2'-iodo-6,6'-dimethyl-1,1'-biphenyl (3e)



3e

Following the procedure of **3a**, **3e** was purified by PE/EtOAc (200:1) and obtained as a white solid (89.0 mg, 98%). Mp = 126.7-127.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 2.0 Hz, 1H), 7.57 (d, *J* = 2.0 Hz, 1H), 7.30 (dd, *J* = 9.7, 2.0 Hz, 2H), 2.01 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 141.4, 139.5, 138.9, 136.2, 134.3, 134.2, 130.2, 130.1, 129.5, 124.3, 100.2, 21.2, 20.6. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{10}Cl_2BrI$ 453.8388; Found 453.8399.

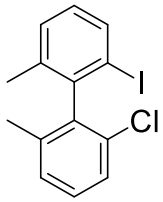
2-bromo-2',6-dichloro-6'-iodo-1,1'-biphenyl (3f)



3f

Following the procedure of **3a**, **3f** was purified by PE/EtOAc (200:1) and obtained as a white solid (79.2 mg, 93%). Mp = 164.7-165.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.65 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.51 (ddd, *J* = 9.4, 8.1, 1.1 Hz, 2H), 7.27 (t, *J* = 8.1 Hz, 1H), 7.09 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.3, 141.7, 137.6, 134.7, 133.6, 131.2, 130.8, 130.6, 129.4, 128.7, 124.8, 99.9. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{12}H_6Cl_2BrI$ 425.8075; Found 425.8084.

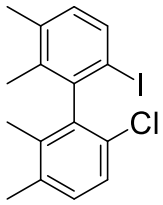
2-chloro-2'-iodo-6,6'-dimethyl-1,1'-biphenyl (4a)



4a

To the stirred solution of cyclic diaryliodonium salts **1a** (91.2 mg, 0.2 mmol), CuCl (1.0 mg, 5 mol %) in DCM (2 mL) was added *n*Bu_4NCl (66.7 mg, 0.24 mmol). The reaction mixture was stirred at room temperature for 16 h. Then the solvent was concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 200:1) on silica gel to obtain the desired product **4a** (66.3 mg, 97%) as a white solid. Mp = 58.2-59.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.9 Hz, 1H), 7.37 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.23 (ddd, *J* = 7.6, 1.5, 0.8 Hz, 1H), 7.02 (t, *J* = 7.7 Hz, 1H), 2.05 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 142.0, 138.0, 137.9, 136.7, 133.3, 129.9, 129.3, 128.8, 128.5, 127.0, 100.4, 21.2, 20.2. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{12}ClI$ 341.9672; Found 341.9665.

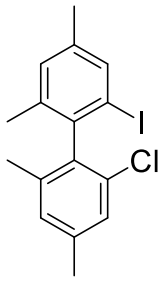
6-chloro-6'-iodo-2,2',3,3'-tetramethyl-1,1'-biphenyl (4b)



4b

Following the procedure of **4a**, **4b** was purified by PE/EtOAc (200:1) and obtained as a white solid (72.5 mg, 98%). Mp = 80.0-81.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 1H), 7.15 (d, *J* = 8.2 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 1.95 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 142.6, 137.0, 136.6, 136.5, 136.0, 135.5, 130.8, 130.2, 126.4, 97.2, 20.32, 20.30, 17.7, 16.7. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{16}ClI$ 369.9985; Found 369.9974.

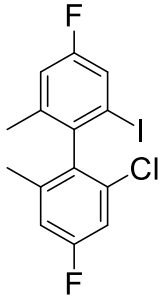
2-chloro-2'-iodo-4,4',6,6'-tetramethyl-1,1'-biphenyl (4c)



4c

Following the procedure of **4a**, **4c** was purified by PE/EtOAc (200:1) and obtained as a white solid (71.0 mg, 96%). Mp = 112.3-113.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 – 7.16 (m, 1H), 7.15 (s, 2H), 7.04 – 7.01 (m, 1H), 2.49 (s, 3H), 2.37 (s, 3H), 1.98 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 140.1, 139.8, 138.7, 137.6, 134.8, 132.9, 129.6, 129.5, 128.7, 127.5, 107.6, 29.4, 21.1, 20.9, 20.1. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{16}ClI$ 369.9985; Found 369.9987.

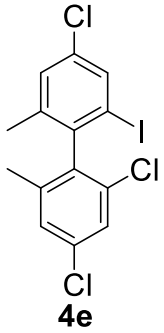
2-chloro-4,4'-difluoro-2'-iodo-6,6'-dimethyl-1,1'-biphenyl (4d)



4d

Following the procedure of **4a**, **4d** was purified by PE/EtOAc (200:1) and obtained as a white solid (74.1 mg, 98%). Mp = 60.0-60.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (dd, J = 7.7, 2.9 Hz, 1H), 7.12 (dt, J = 5.7, 2.8 Hz, 1H), 7.08 – 7.01 (m, 1H), 6.97 (dt, J = 5.8, 2.9 Hz, 1H), 2.03 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9 (d, J_{C-F} = 250.0 Hz), 161.5 (d, J_{C-F} = 251.5 Hz), 140.1 (d, J_{C-F} = 8.6 Hz), 139.6 (d, J_{C-F} = 8.2 Hz), 138.2 (d, J_{C-F} = 4.2 Hz), 137.2 (d, J_{C-F} = 3.6 Hz), 134.4 (d, J_{C-F} = 6.9 Hz), 123.8 (d, J_{C-F} = 23.3 Hz), 117.1 (d, J_{C-F} = 20.7 Hz), 115.8 (d, J_{C-F} = 21.4 Hz), 114.5 (d, J_{C-F} = 24.6 Hz), 100.0, 21.4, 20.4. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{10}F_2ClI$ 377.9484; Found 377.9487.

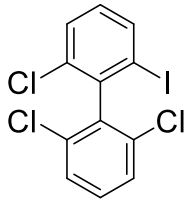
2,4,4'-trichloro-2'-iodo-6,6'-dimethyl-1,1'-biphenyl (4e)



4e

Following the procedure of **4a**, **4e** was purified by PE/EtOAc (200:1) and obtained as a white solid (79.5 mg, 97%). Mp = 114.5-115.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 2.0 Hz, 1H), 7.39 (d, *J* = 2.0 Hz, 1H), 7.31 (t, *J* = 1.4 Hz, 1H), 7.25 (d, *J* = 1.8 Hz, 1H), 2.02 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.6, 139.6, 139.5, 139.0, 136.2, 134.24, 134.19, 134.1, 130.1, 128.9, 127.1, 100.2, 21.1, 20.1. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{10}Cl_3I$ 409.8893; Found 409.8884.

2,2',6-trichloro-6'-iodo-1,1'-biphenyl (4f)

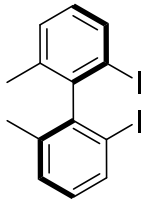


4f

Following the procedure of **4a**, **4f** was purified by PE/EtOAc (200:1) and obtained as a white solid (72.6 mg, 95%). Mp = 166.2-166.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.53 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.35 (dd, *J* = 8.6, 7.5 Hz, 1H), 7.09 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.7, 140.0, 137.5, 134.9, 133.7, 130.8, 130.2, 129.4, 128.0, 99.9. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{12}H_6Cl_3I$ 381.8580; Found 381.8576.

4. Examples of enantioselective halogenative of cyclic diaryliodonium salts

(*R*)-2,2'-diiodo-6,6'-dimethyl-1,1'-biphenyl (2a')

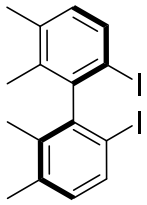


2a'

To the stirred solution of cyclic diaryliodonium salts **1a** (91.2 mg, 0.2 mmol), CuI (1.9 mg, 5 mol %), **L6** (5.0 mg, 7.5 mol %) in DCM (2 mL) was added NaI (36.0 mg, 0.24 mmol). The reaction mixture was stirred at room temperature for 20 h. Then the solvent was concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 200:1) on silica

gel to obtain the desired product **2a'** (85.0 mg, 98%, 98% ee) as a white solid. Mp = 68.1-69.0 °C; HPLC conditions: Chiralpak IC, isopropanol/hexanes = 0.5:99.5, flow: 0.4 mL/min, λ = 254 nm, t_R = 8.521 min (minor), 9.027 min (major). $[\alpha]_D^{20}$ –29.6 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 2H), 7.30 (dt, *J* = 7.6, 0.9 Hz, 2H), 7.03 (t, *J* = 7.7 Hz, 2H), 2.04 (s, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.5, 137.6, 136.8, 130.0, 129.4, 100.7, 21.4. The spectra data was consistent with that reported.[3]

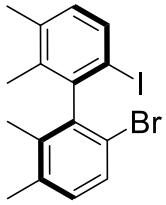
(*R*)-6,6'-diiodo-2,2',3,3'-tetramethyl-1,1'-biphenyl (2b')



2b'

Following the procedure of **2a'**, **2b'** was purified by PE/EtOAc (200:1) and obtained as a white solid (86.8 mg, 94%, 97% ee). Mp = 123.6-124.5 °C; HPLC conditions: Chiralpak IC, isopropanol/hexanes = 0.5:99.5, flow: 0.4 mL/min, λ = 254 nm, t_R = 9.602 min (minor), 10.610 min (major). $[\alpha]_D^{20}$ –44.0 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 2.31 (s, 6H), 1.93 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 137.1, 136.3, 136.1, 130.8, 97.6, 20.3, 17.8. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{16}I_2$ 461.9342; Found 461.9357.

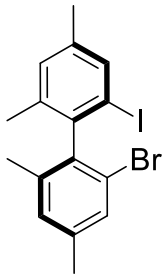
(*R*)-6-bromo-6'-iodo-2,2',3,3'-tetramethyl-1,1'-biphenyl (3b')



3b'

To the stirred solution of cyclic diaryliodonium salts **1a** (91.2 mg, 0.2 mmol), CuBr (1.4 mg, 5 mol%), **L6** (5.0 mg, 7.5 mol%) in DCM (2 mL) was added LiBr (20.8 mg, 0.24 mmol). The reaction mixture was stirred at room temperature for 20 h. Then the solvent was concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 200:1) on silica gel to obtain the desired product **3b'** (80.3 mg, 97%, 97% ee) as a white solid. Mp = 91.4-92.3 °C; HPLC conditions: Chiralpak IC, isopropanol/hexanes = 0.5:99.5, flow: 0.4 mL/min, λ = 254 nm, t_R = 9.659 min (minor), 11.320 min (major). $[\alpha]_D^{20}$ –18.0 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 2.31 (s, 6H), 1.95 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 144.3, 137.0, 136.8, 136.5, 136.2, 136.0, 130.8, 130.5, 129.6, 121.3, 97.3, 20.35, 20.33, 17.7, 17.1. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{16}BrI$ 413.9480; Found 413.9499.

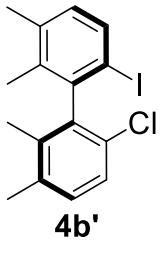
(*R*)-2-bromo-2'-iodo-4,4',6,6'-tetramethyl-1,1'-biphenyl (3c')



3c'

Following the procedure of **3b'**, **3c'** was purified by PE/EtOAc (200:1) and obtained as a white solid (78.7 mg, 95%, 97% ee). Mp = 111.5-112.3 °C; HPLC conditions: Chiralpak IC, isopropanol/hexanes = 0.5:99.5, flow: 0.4 mL/min, λ = 254 nm, t_R = 9.943 min (minor), 10.982 min (major). $[\alpha]_D^{20}$ –14.0 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 1H), 7.17 (d, *J* = 1.2 Hz, 2H), 7.08 (dt, *J* = 1.7, 0.8 Hz, 1H), 2.51 (s, 3H), 2.38 (s, 3H), 2.00 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.1, 141.9, 139.8, 139.0, 137.7, 134.7, 130.7, 130.1, 129.6, 128.7, 123.7, 107.6, 29.4, 21.04, 20.96, 20.6. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{16}BrI$ 413.9480; Found 413.9496.

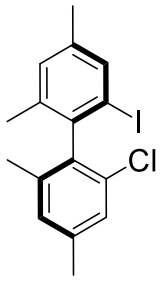
(*R*)-6-bromo-6'-iodo-2,2',3,3'-tetramethyl-1,1'-biphenyl (4b')



4b'

To the stirred solution of cyclic diaryliodonium salts **1a** (91.2 mg, 0.2 mmol), CuCl (1.0 mg, 5 mol%), **L6** (5.0 mg, 7.5 mol%) in DCM (2 mL) was added LiBr (10.2 mg, 0.24 mmol). The reaction mixture was stirred at room temperature for 20 h. Then the solvent was concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 200:1) on silica gel to obtain the desired product **4b'** (73.3 mg, 99%, 97% ee) as a white solid. Mp = 80.0-81.2 °C; HPLC conditions: Chiralpak IC, isopropanol/hexanes = 0.5:99.5, flow: 0.4 mL/min, λ = 254 nm, t_R = 9.558 min (minor), 11.192 min (major). $[\alpha]_D^{20}$ –30.0 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 1H), 7.15 (d, *J* = 8.2 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 1.95 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 142.6, 137.0, 136.6, 136.5, 136.0, 135.5, 130.8, 130.2, 126.4, 97.2, 20.32, 20.30, 17.7, 16.7. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{16}ClI$ 369.9985; Found 369.9974.

(*R*)-2-chloro-2'-iodo-4,4',6,6'-tetramethyl-1,1'-biphenyl (4c')



4c'

Following the procedure of **4b'**, **4c'** was purified by PE/EtOAc (200:1) and obtained as a white solid (70.3 mg, 95%, 95% ee). Mp = 112.3-113.0 °C; HPLC conditions: Chiralpak IC, isopropanol/hexanes = 0.5:99.5, flow: 0.4 mL/min, λ = 254 nm, t_R = 8.930 min (minor), 9.441 min (major). $[\alpha]_D^{20}$ –6.0 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 – 7.16 (m, 1H), 7.15 (s, 2H), 7.04 – 7.01 (m, 1H), 2.49 (s, 3H), 2.37 (s, 3H), 1.98 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 140.1, 139.8, 138.7, 137.6, 134.8, 132.9, 129.6, 129.5, 128.7, 127.5, 107.6, 29.4, 21.1, 20.9, 20.1. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{16}ClI$ 369.9985; Found 369.9987.

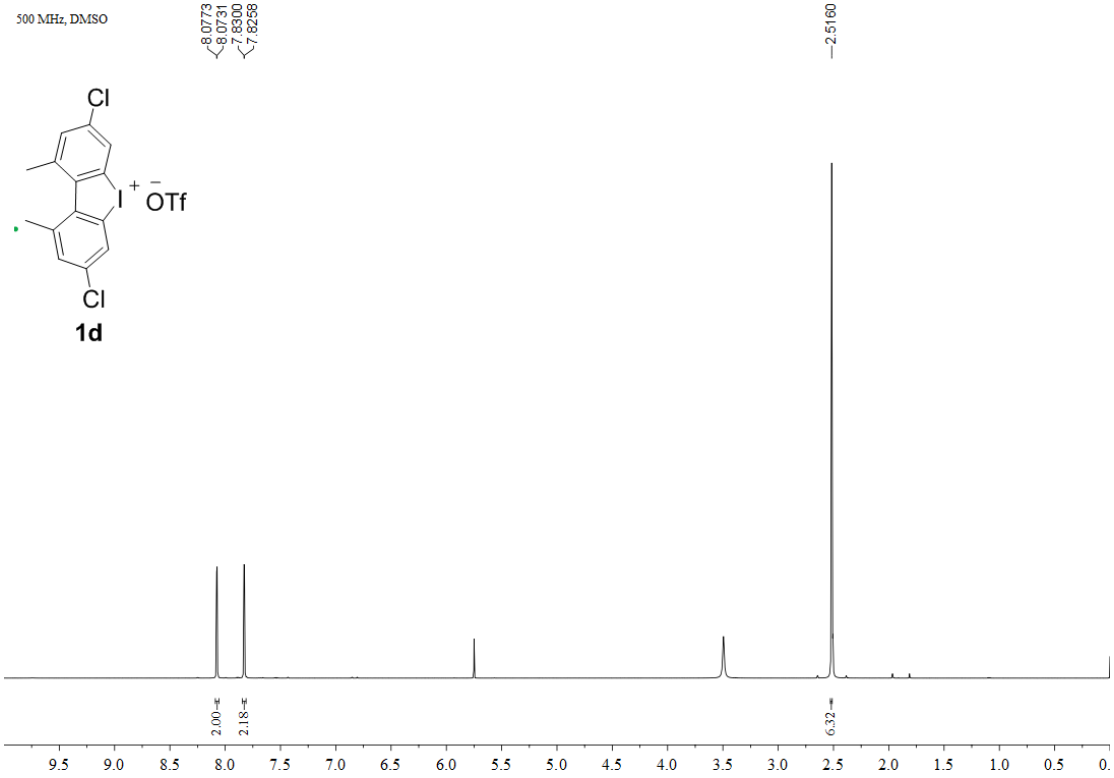
5. References

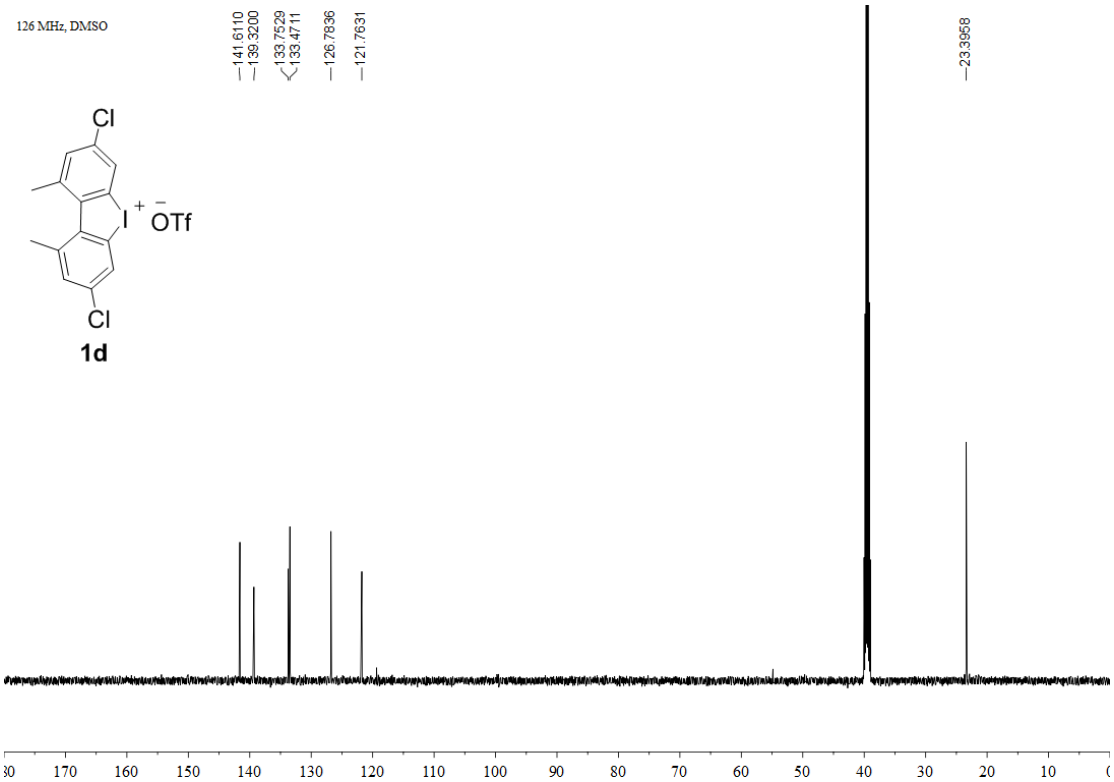
[1] Zhao, K.; Duan, L.-H.; Xu, S.-B.; Jiang, J.-L.; Fu, Y;, Gu, Z.-H. Enhanced Reactivity by Torsional Strain of Cyclic Diaryliodonium in Cu-Catalyzed Enantioselective Ring-Opening Reaction. *Chem*. **2018**, *4*, 599-612.

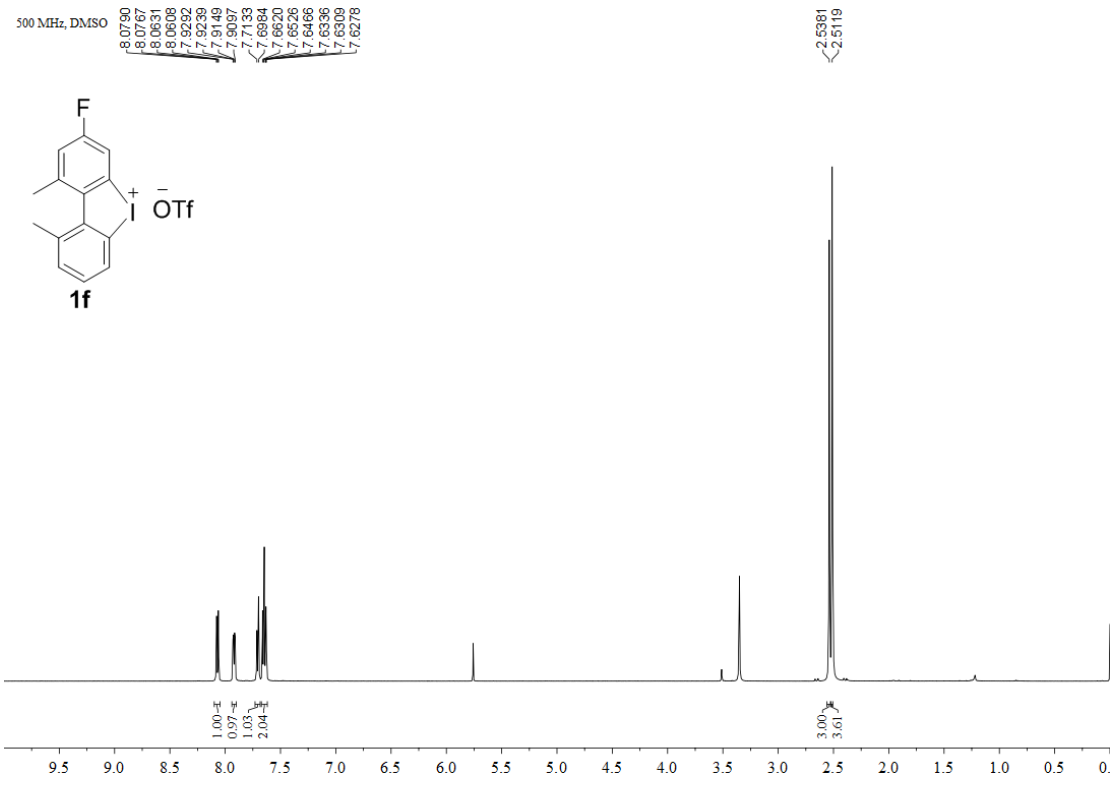
[2] Zhu, K.; Xu, K.; Fang, Q.; Wang, Y.; Tang, B.; Zhang, F. Enantioselective Synthesis of Axially Chiral Biaryls via Cu-Catalyzed Acyloxylation of Cyclic Diaryliodonium Salts. *ACS Catal*. **2019**, *9*, 4951-4957.

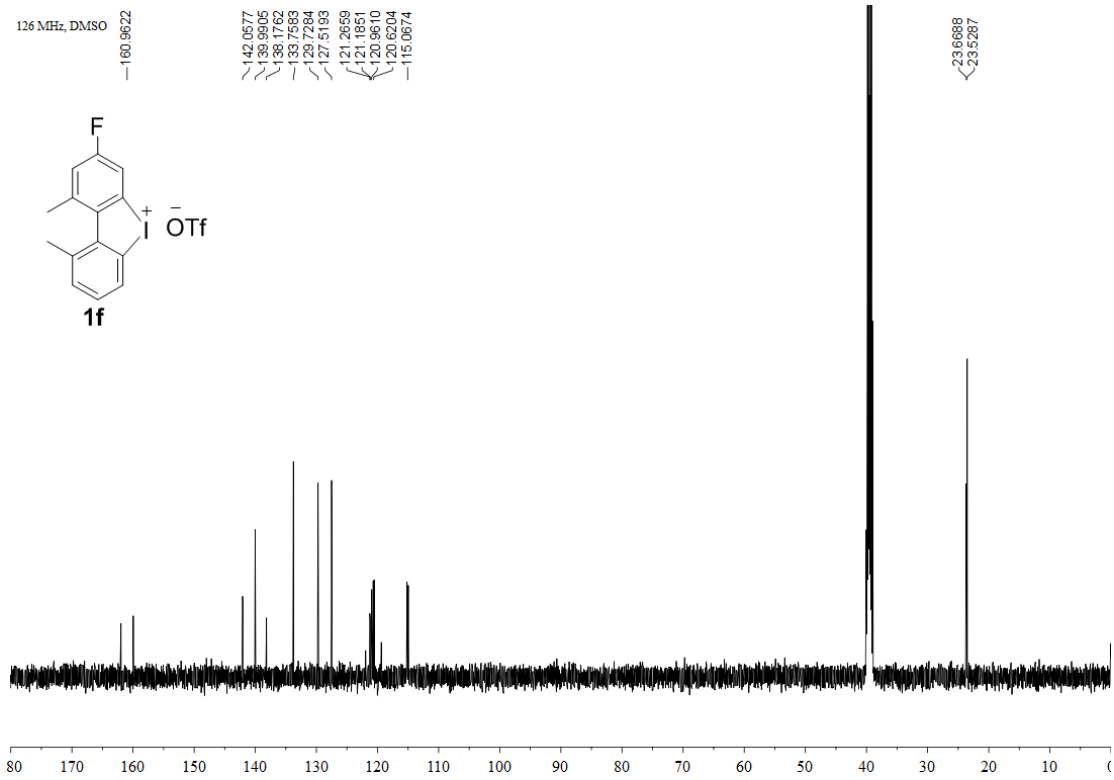
[3] Deng, R.; Zhan, S.; Li, C.; Gu, Z.-H. Hypervalent Iodine-Mediated Carbon-Carbon Bond Cleavage and Dearomatization of 9H-Fluoren-9-ols. *Angew. Chem. Int. Ed*. **2020**, *59*, 3093-3098.

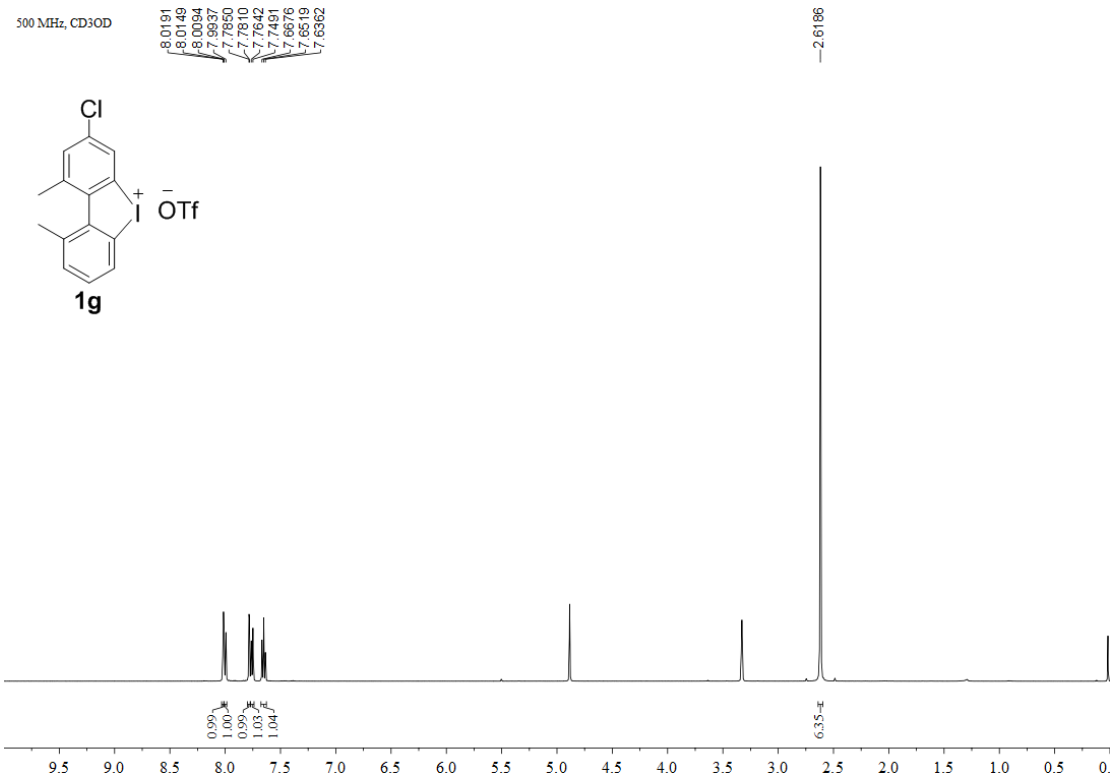
6. Copies of NMR spectra

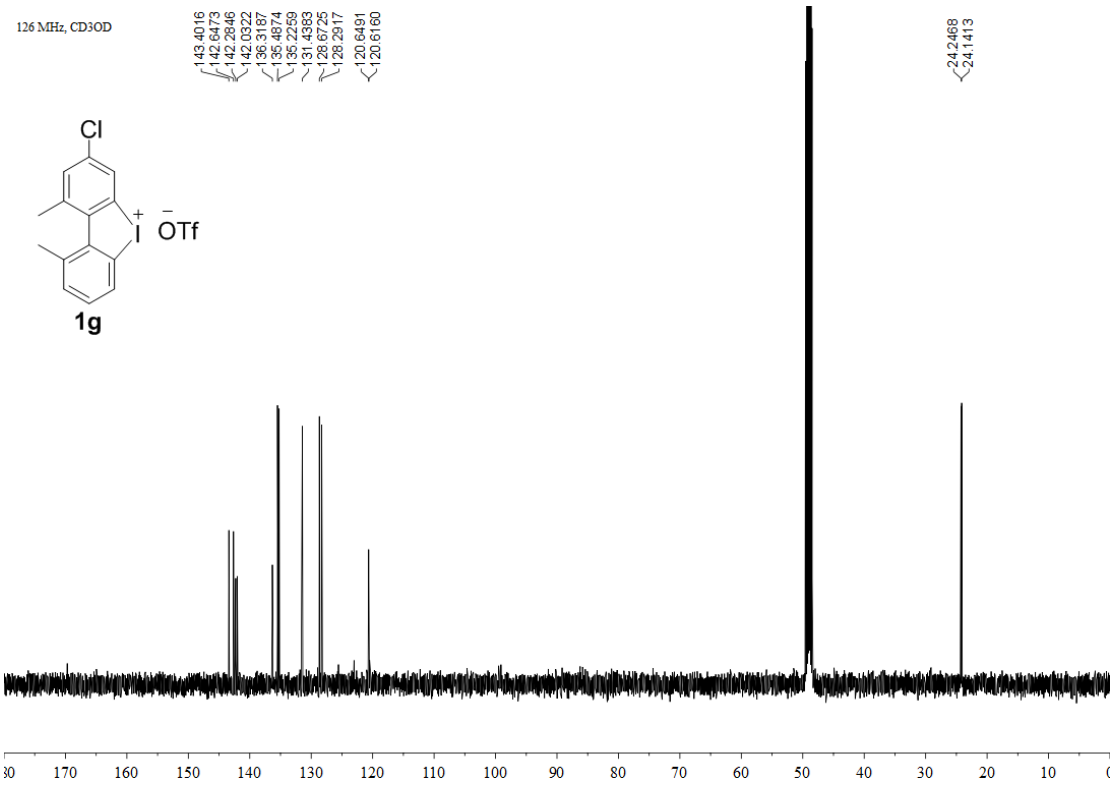


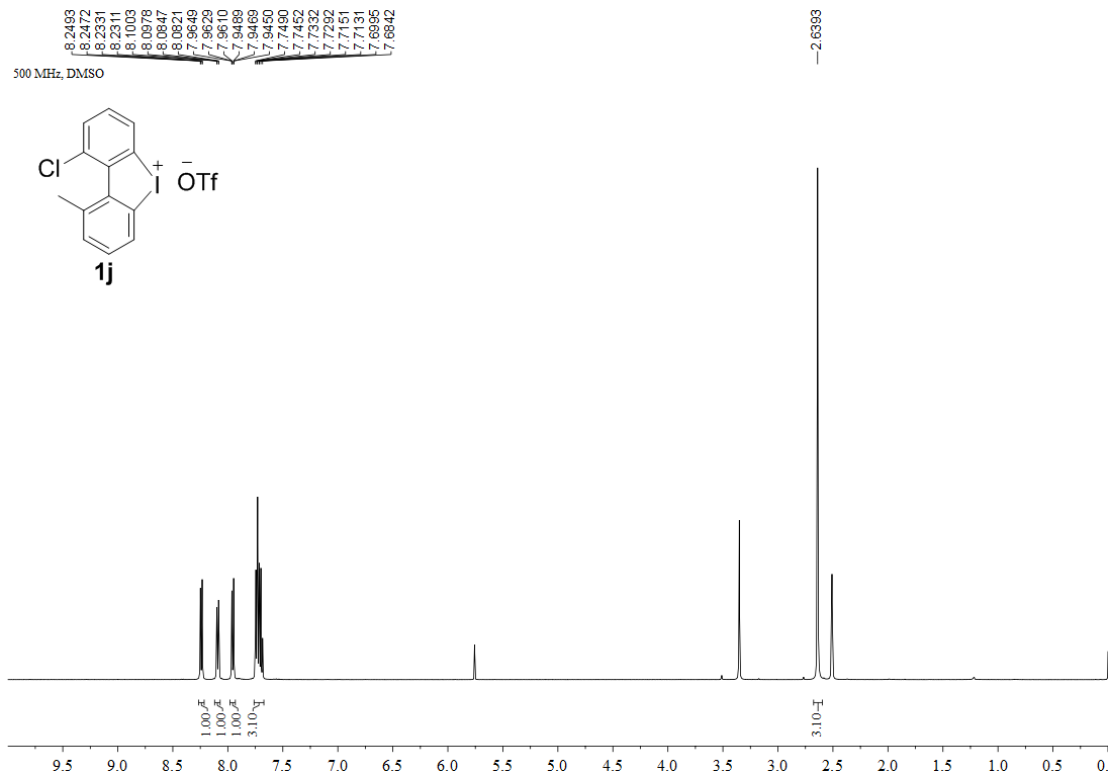


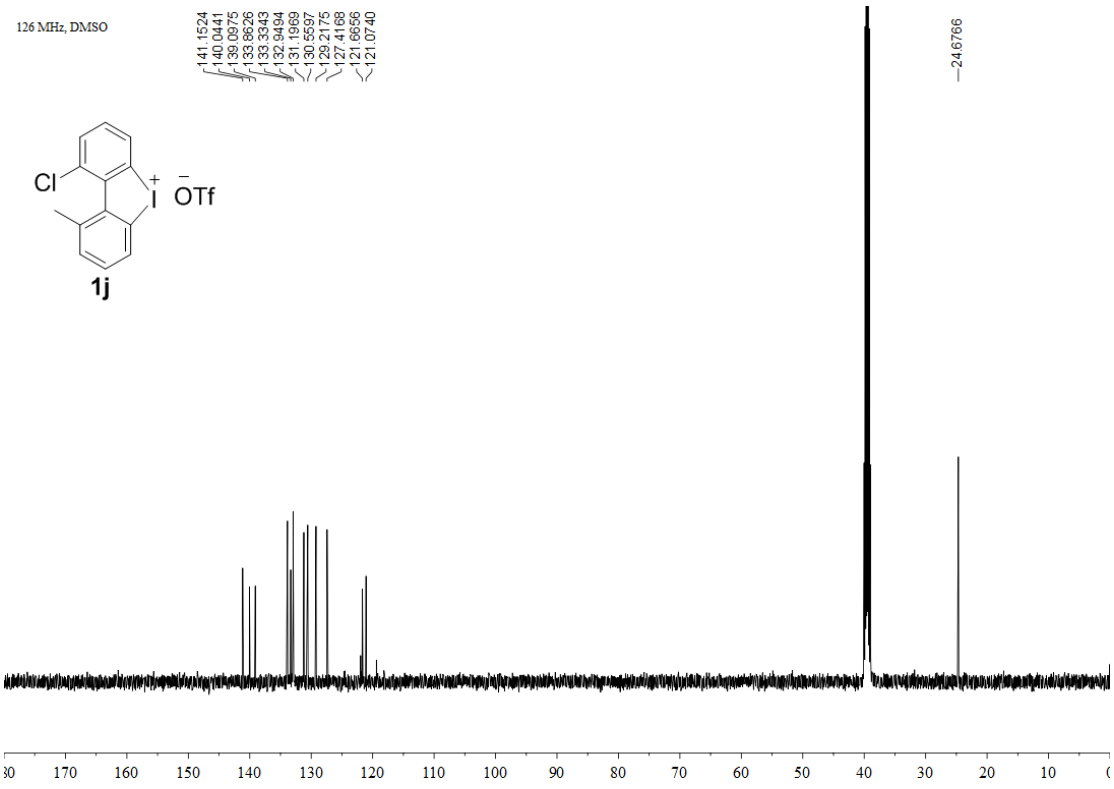

500 MHz, DMSO
8.0790
8.0767
8.0631
8.0608
7.9292
7.9239
7.9149
7.9097
7.7133
7.6984
7.6620
7.6526
7.6466
7.6336
7.6309
7.6278
2.5381
2.5119
F
I
OTf
1f
1.00
0.97
1.03
2.04
3.00
3.61
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

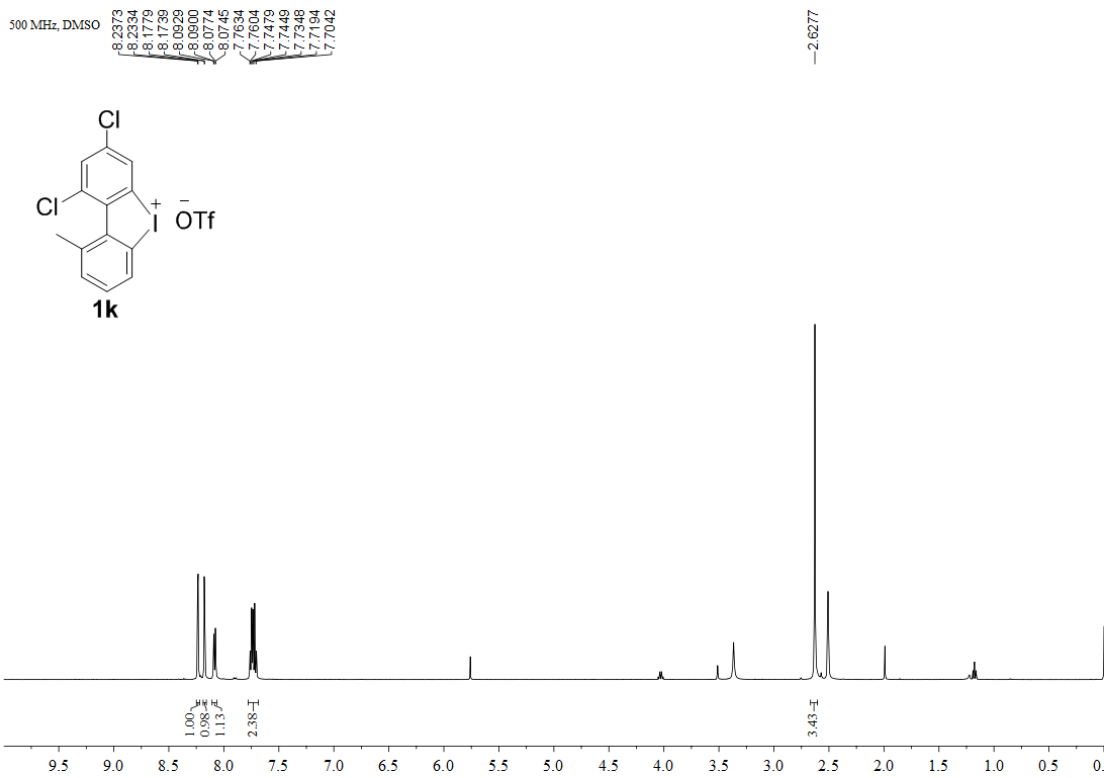

126 MHz, DMSO
160.9622
142.0577
139.9905
138.1762
133.7583
129.7284
127.5193
121.2659
121.1851
120.9610
120.6204
115.0674
39.6688
39.5287
F
I
OTf
1f
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

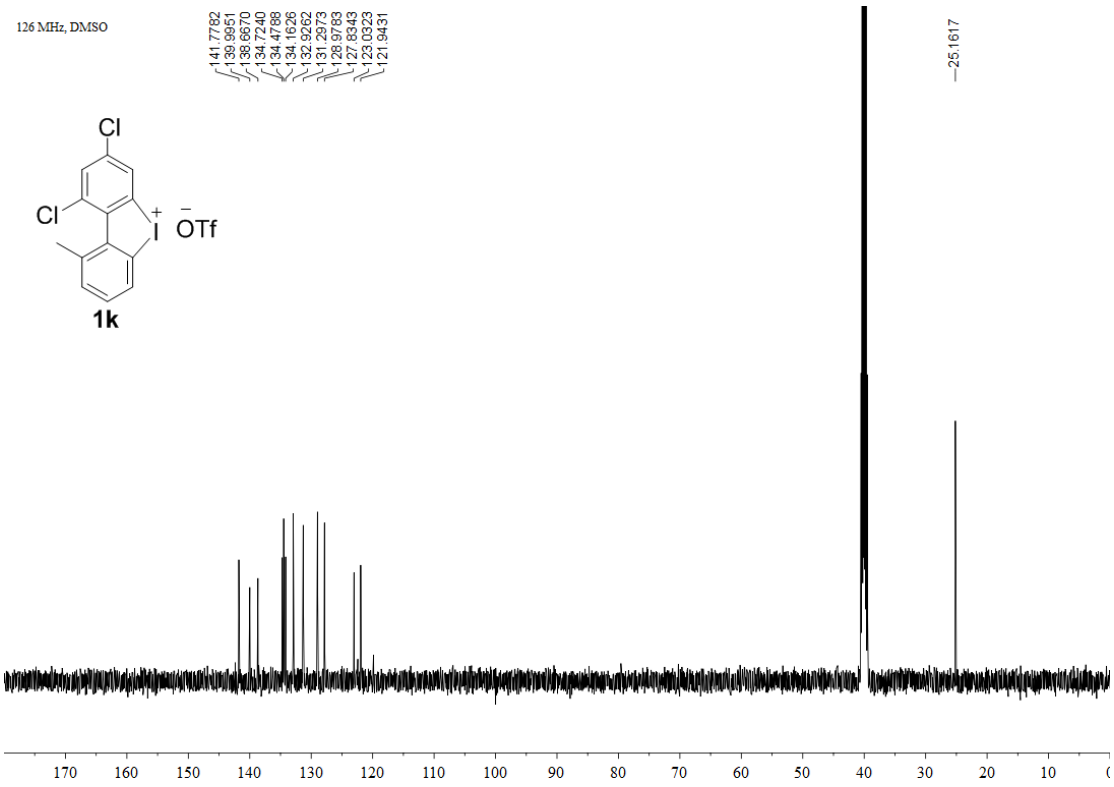

500 MHz, CD3OD
8.0191
8.0149
8.0094
7.9937
7.7850
7.7810
7.7642
7.7491
7.6676
7.6519
7.6362
2.6186
Cl
I
OTf
1g
0.99
1.00
0.99
1.03
1.04
6.35
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

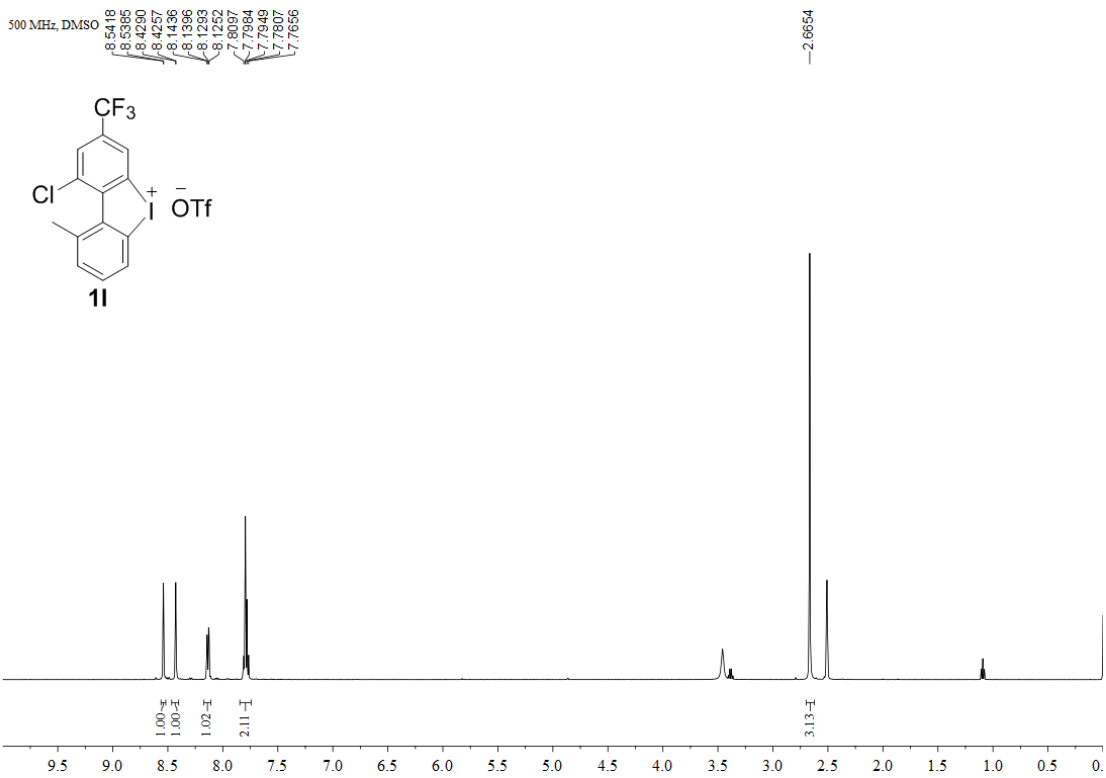

126 MHz, CD3OD
143.4016
142.6473
142.2846
142.0322
136.3187
135.4874
135.2259
131.4383
128.6725
128.2917
120.6491
120.6160
24.2468
24.1413
Cl
I
OTf
1g
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

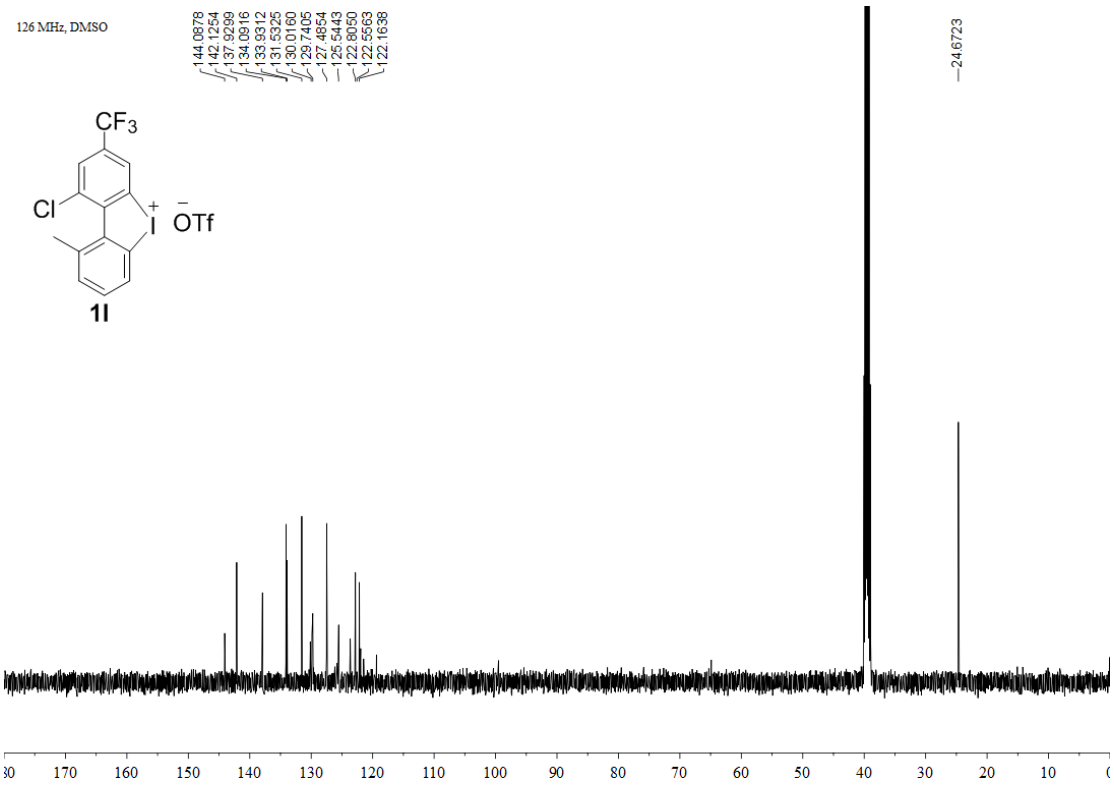

8.2493
8.2472
8.2331
8.2311
8.1003
8.0978
8.0847
8.0821
7.9649
7.9629
7.9610
7.9489
7.9469
7.9450
7.7490
7.7452
7.7332
7.7292
7.7151
7.7131
7.6995
7.6842
2.6393
500 MHz, DMSO
Cl
I
OTf
1j
1.00
1.00
1.00
3.10
3.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

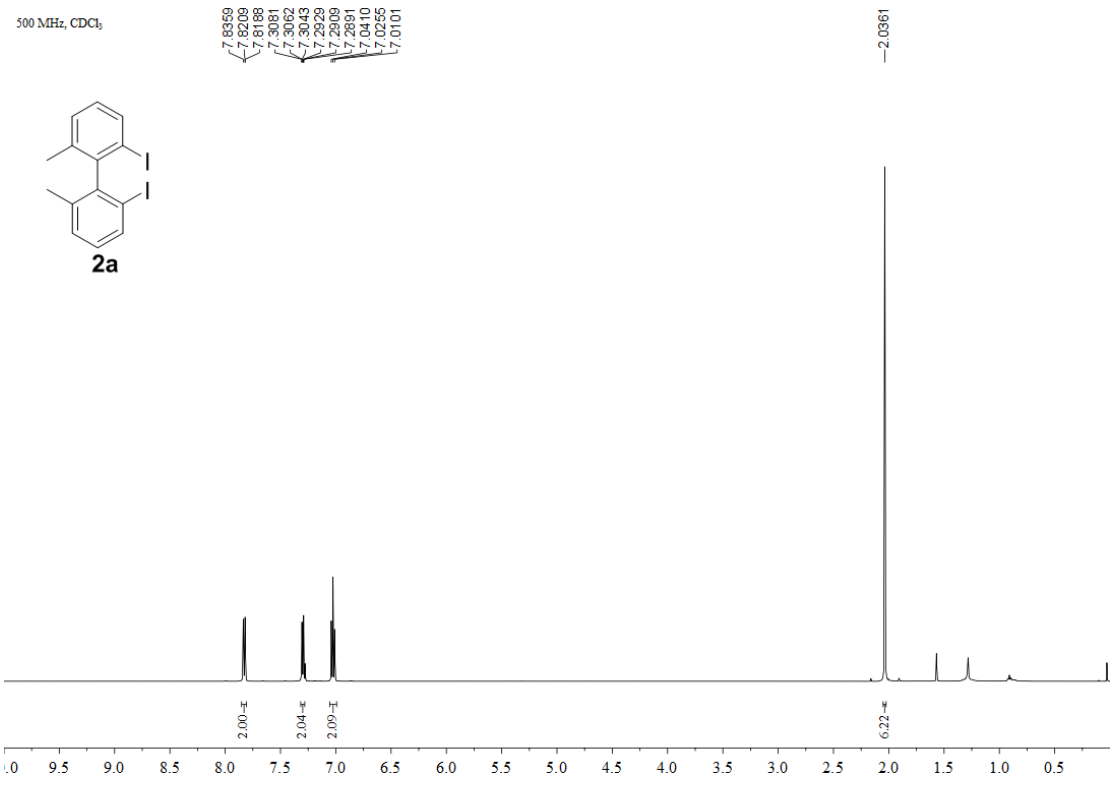

126 MHz, DMSO
141.1524
140.0441
139.0975
133.8626
133.3343
132.9494
131.1969
130.5597
129.2175
127.4168
121.6656
121.0740
24.6766
Cl
I
OTf
1j
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

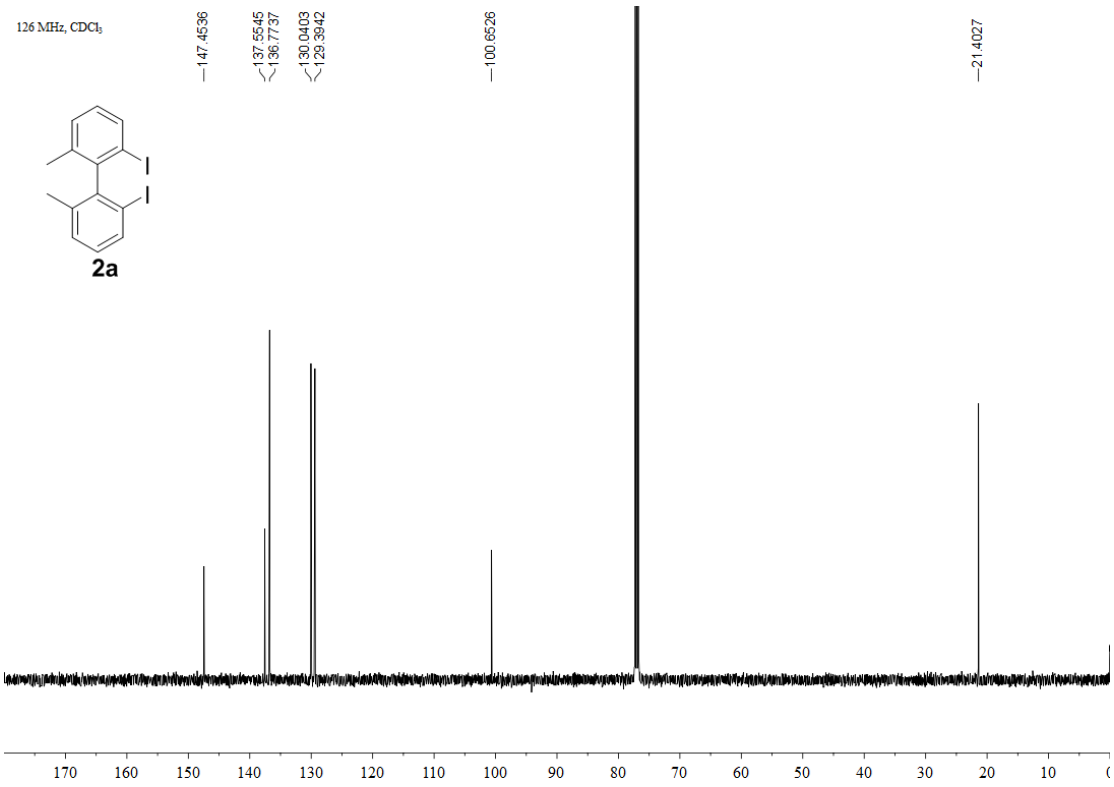

500 MHz, DMSO
8.2373
8.2334
8.1779
8.1738
8.0929
8.0900
8.0774
8.0745
7.7634
7.7604
7.7479
7.7449
7.7348
7.7194
7.7042
2.6277
Cl
Cl
I
OTf
1k
1.00
0.98
1.13
2.38
3.43
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

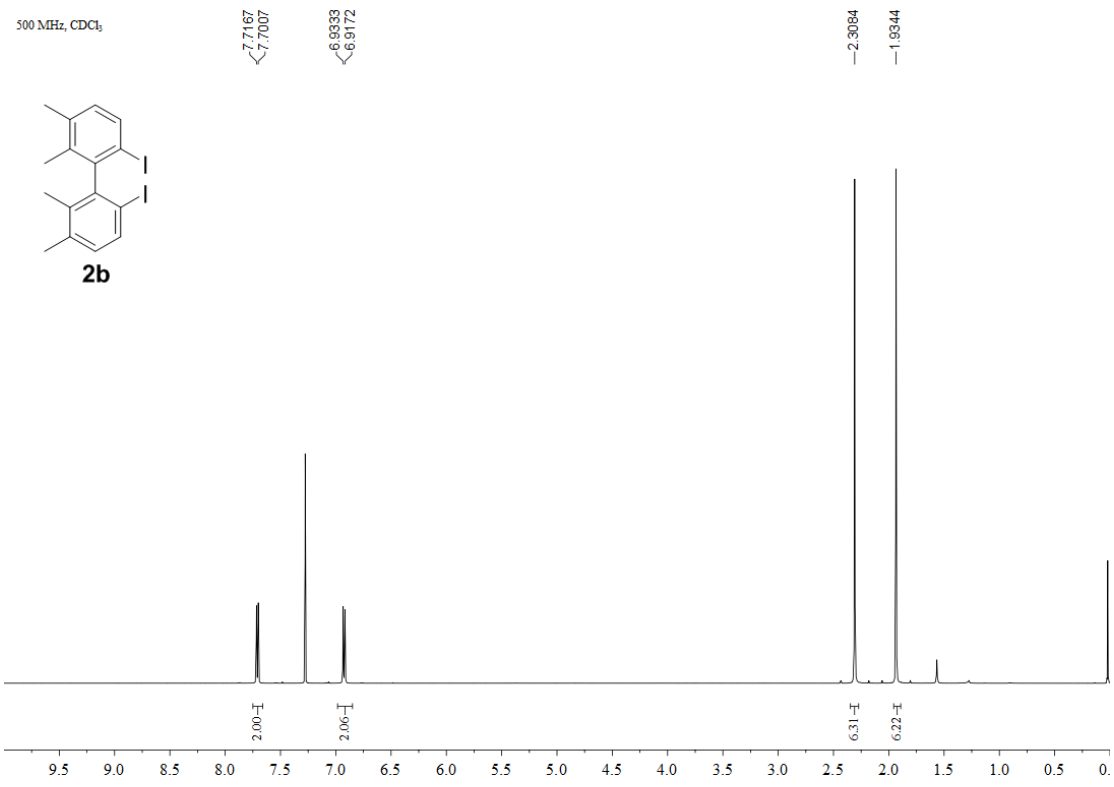

126 MHz, DMSO
141.7782
139.9951
138.6670
134.7240
134.4788
134.1626
132.9262
131.2973
128.9783
127.8343
123.0323
121.9431
25.1617
Cl
Cl
I
OTf
1k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

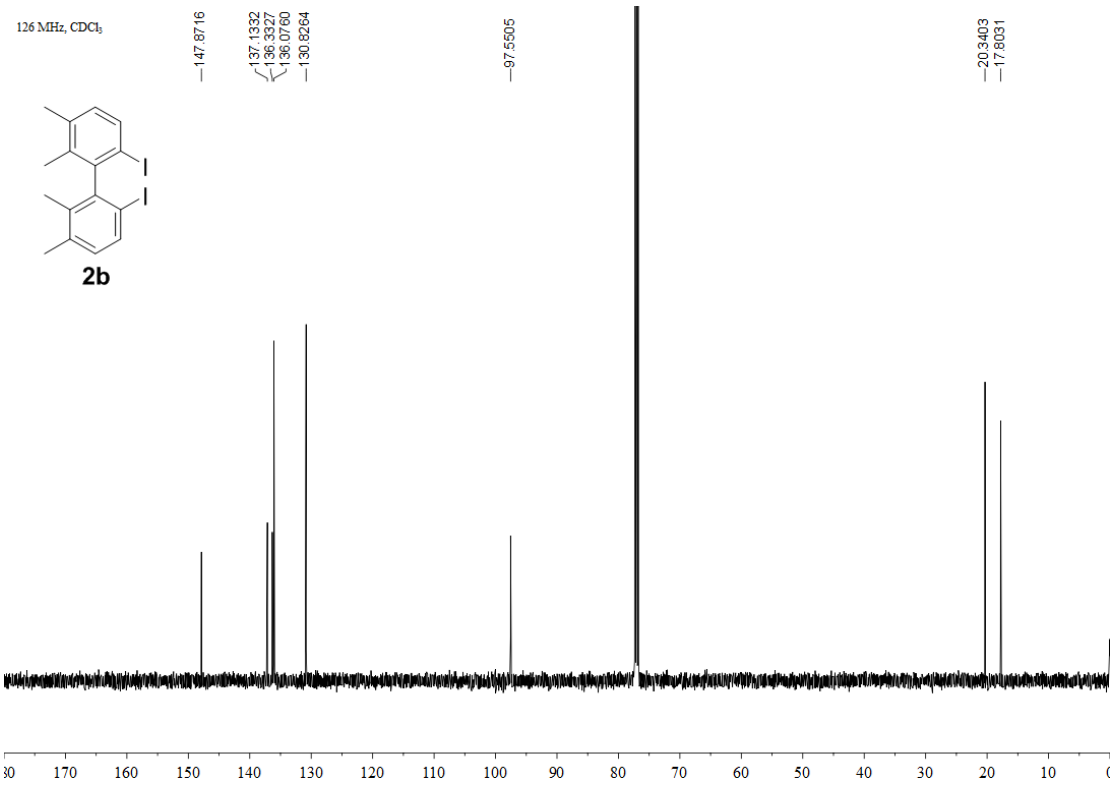

500 MHz, DMSO
8.5418
8.5385
8.4290
8.4257
8.1436
8.1396
8.1293
8.1252
7.8097
7.7984
7.7949
7.7807
7.7656
2.6654
CF3
Cl
I
OTf
1l
1.00
1.00
1.02
2.11
3.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

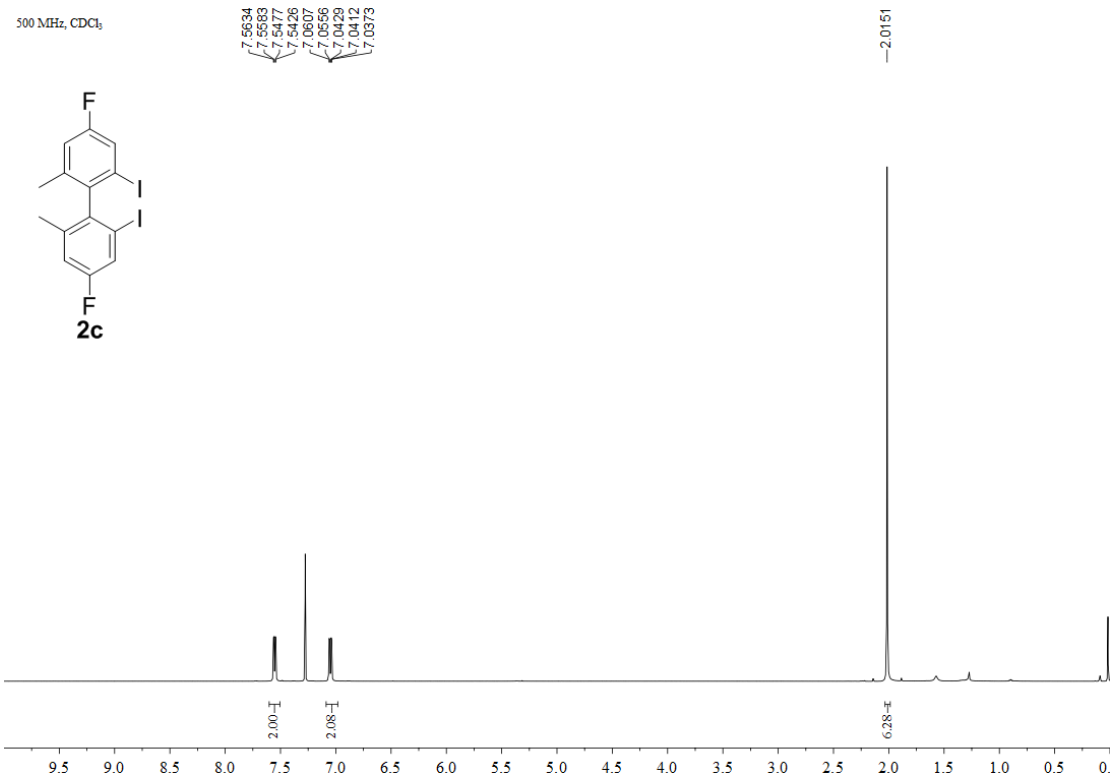

126 MHz, DMSO
144.0878
142.1254
137.9299
134.0916
133.9312
131.5325
130.0160
129.7405
127.4854
125.5443
122.8050
122.5563
122.1638
24.6723
CF3
Cl
I
OTf
1l
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

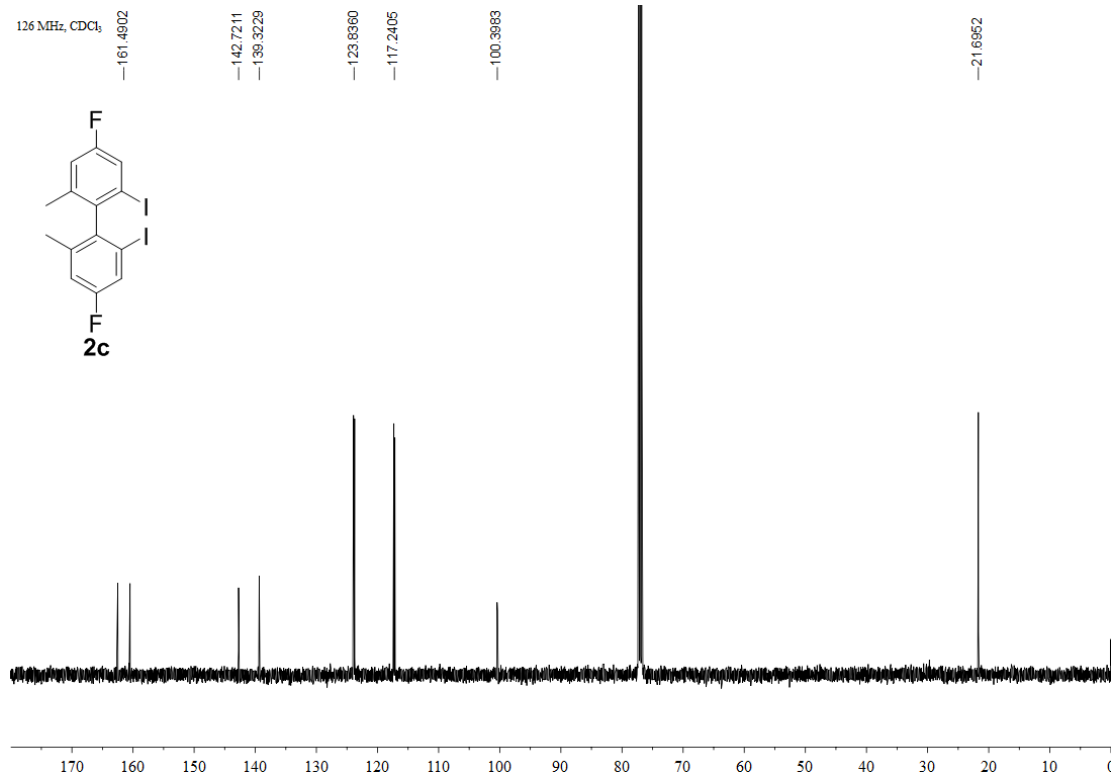

500 MHz, CDCl3
7.8359
7.8209
7.8188
7.3081
7.3062
7.3043
7.2929
7.2909
7.2891
7.0410
7.0255
7.0101
2.0361
2a
2.00
2.04
2.09
6.22

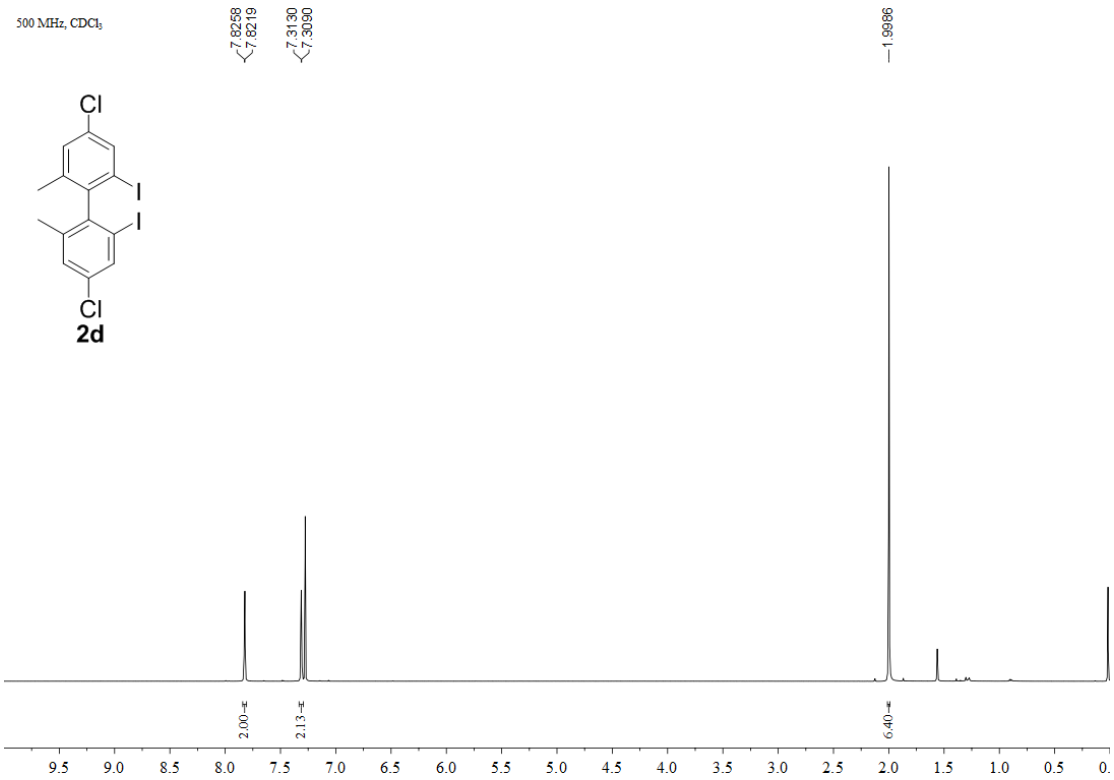

126 MHz, CDCl3
147.4536
137.5545
136.7737
130.0403
129.3942
100.6526
21.4027
2a

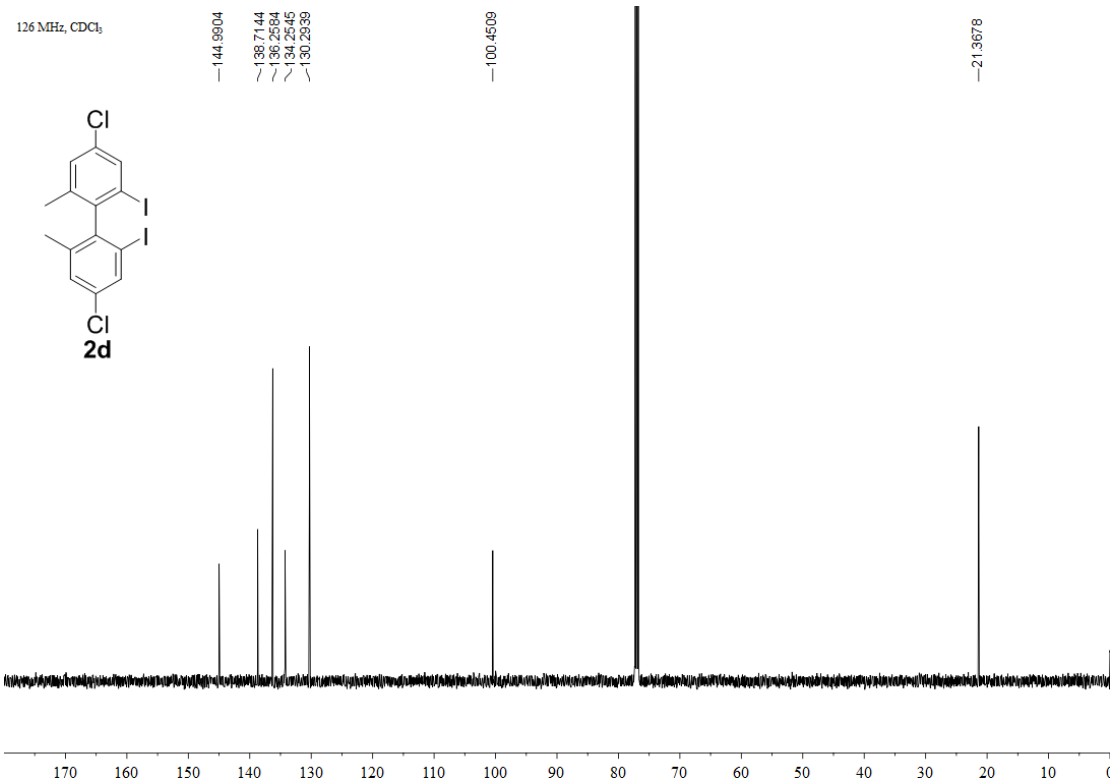

500 MHz, CDCl3
7.7167
7.7007
6.9333
6.9172
2.3084
1.9344
2b
2.00
2.06
6.31
6.22
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

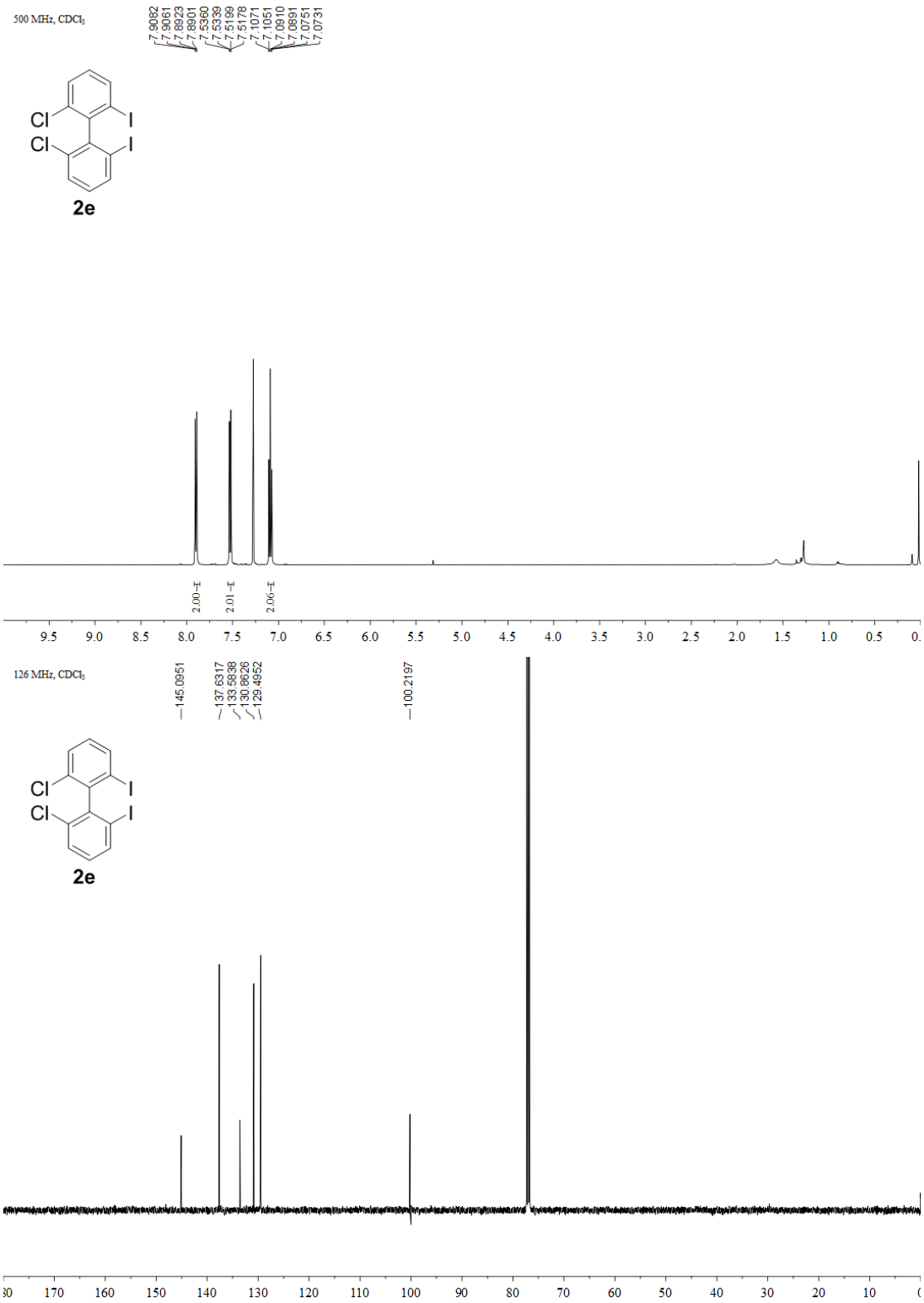

126 MHz, CDCl3
147.8716
137.1332
136.3327
136.0760
130.8264
97.5505
20.3403
17.8031
2b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

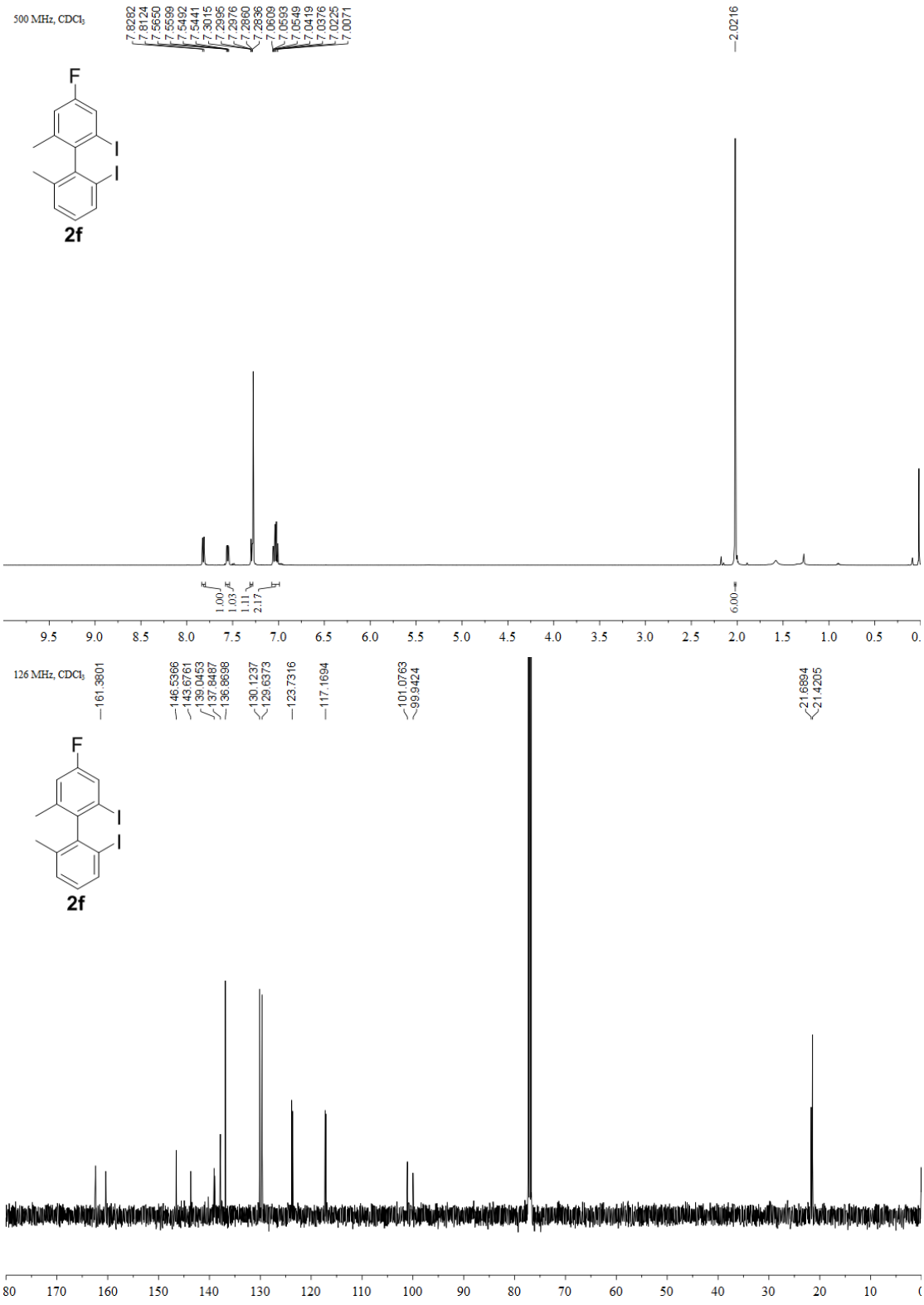

500 MHz, CDCl3
7.5634
7.5583
7.5477
7.5426
7.0607
7.0556
7.0429
7.0412
7.0373
2.0151
F
I
I
F
2c
2.00
2.08
6.28
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.

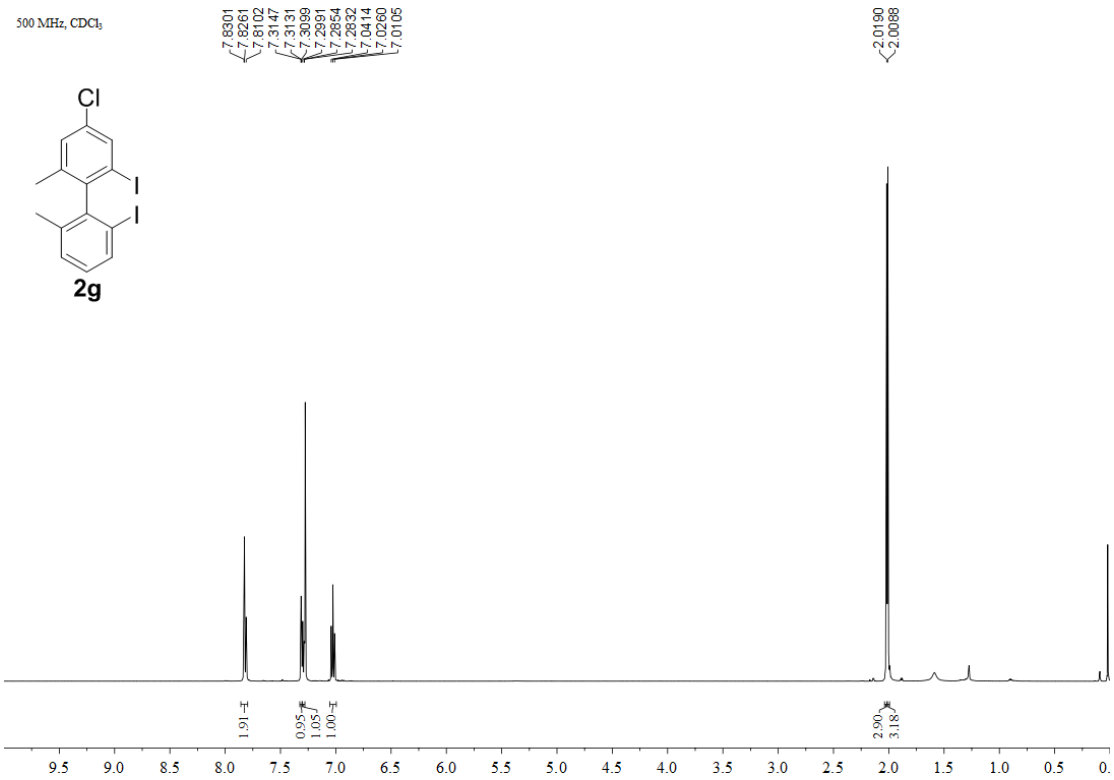

126 MHz, CDCl3
161.4902
142.7211
139.3229
123.8360
117.2405
100.3983
21.6952
F
I
I
F
2c
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

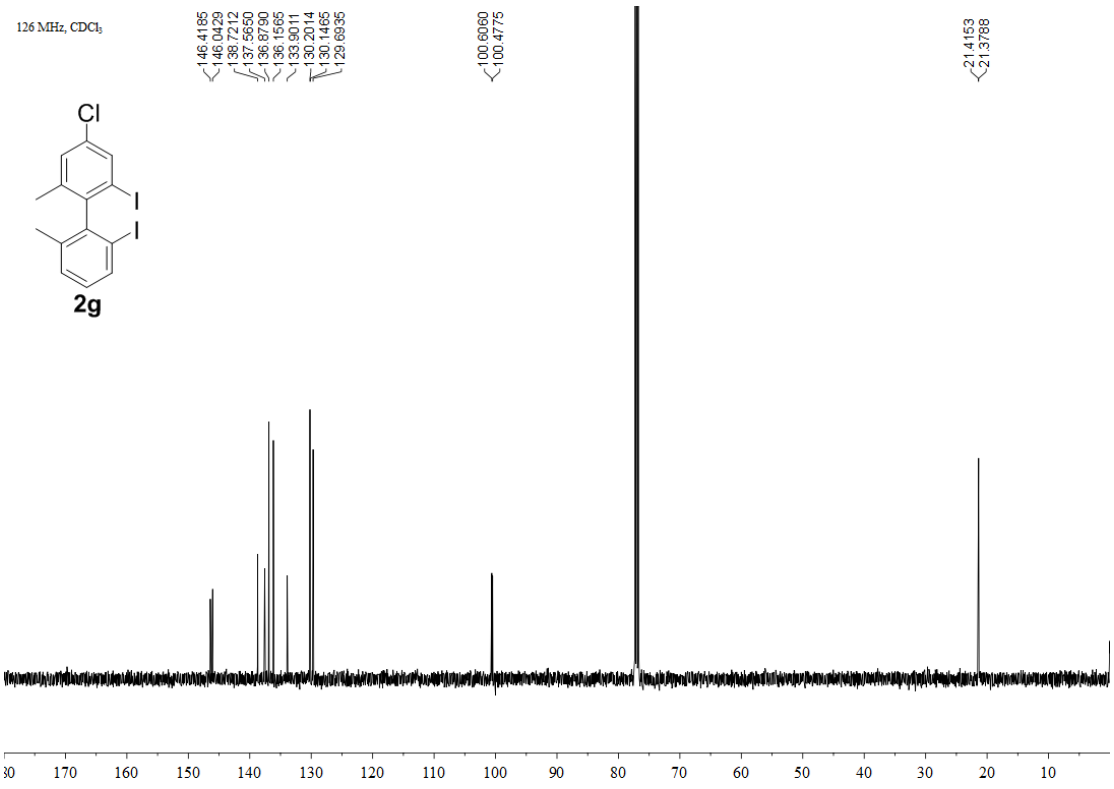

500 MHz, CDCl3
7.8258
7.8219
7.3130
7.3090
1.9986
Cl
I
I
Cl
2d
2.00
2.13
6.40
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

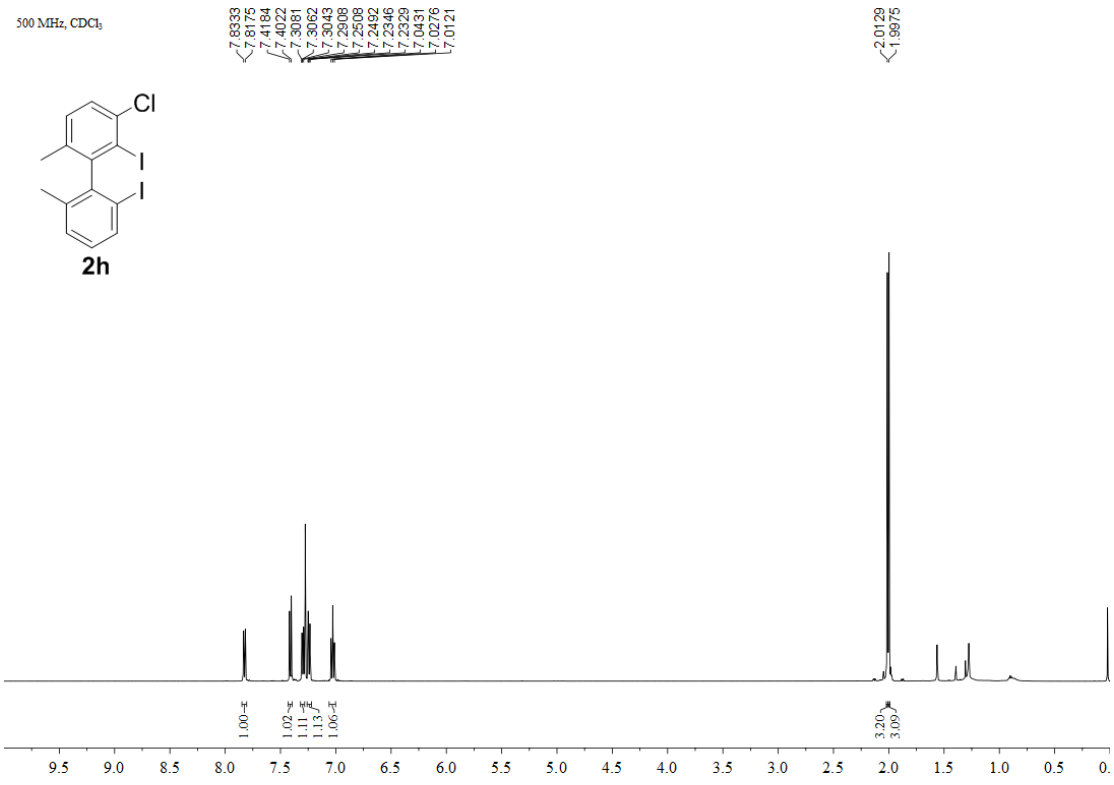

126 MHz, CDCl3
144.9904
138.7144
136.2584
134.2545
130.2939
100.4509
21.3678
Cl
I
I
Cl
2d
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

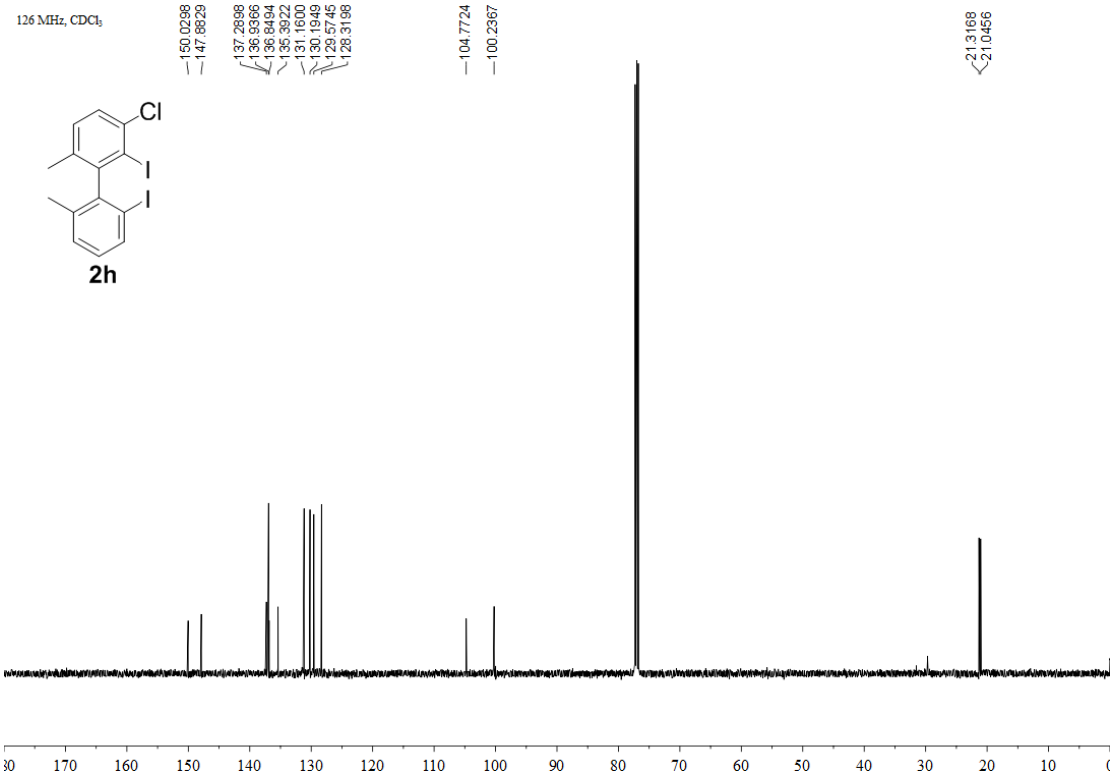

500 MHz, CDCl3
7.9082
7.9061
7.8923
7.8901
7.5360
7.5339
7.5199
7.5178
7.1071
7.1051
7.0910
7.0891
7.0751
7.0731
Cl
Cl
I
I
2e
2.00
2.01
2.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
126 MHz, CDCl3
145.0951
137.6317
133.5838
130.8626
129.4952
100.2197
Cl
Cl
I
I
2e
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

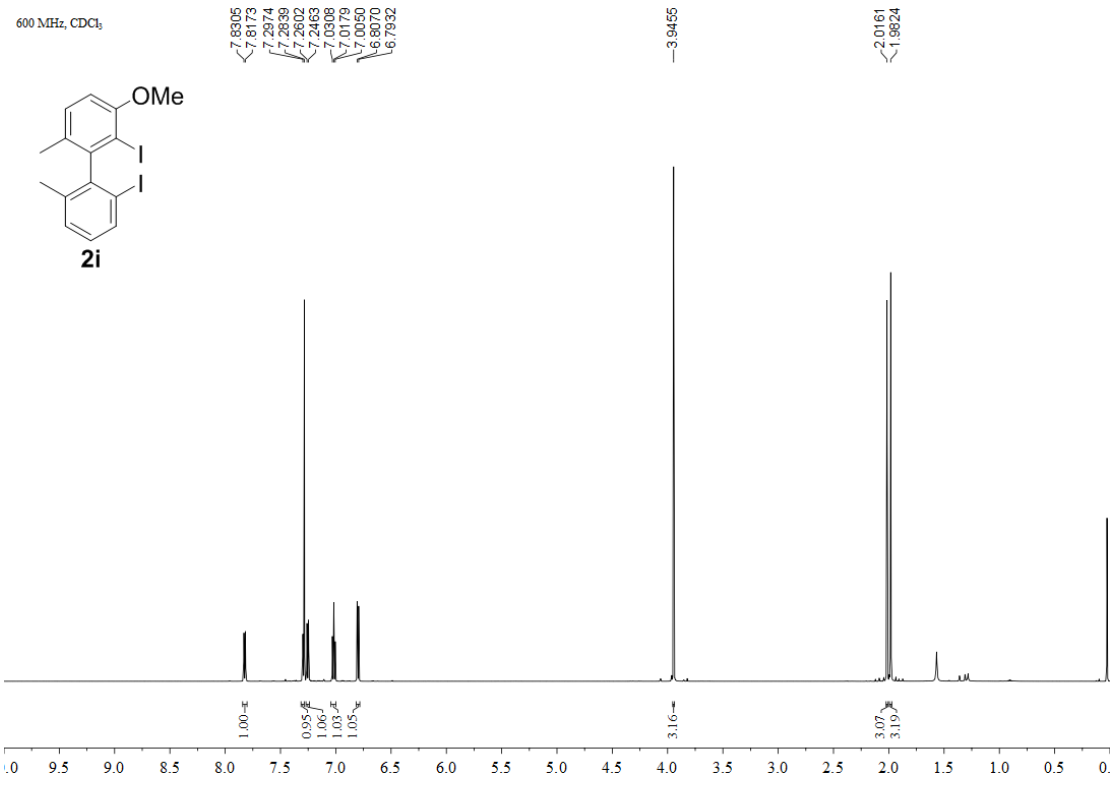

500 MHz, CDCl3
7.8282
7.8124
7.5650
7.5599
7.5492
7.5441
7.3015
7.2995
7.2976
7.2860
7.2836
7.0609
7.0593
7.0549
7.0419
7.0376
7.0225
7.0071
2.0216
F
I
I
2f
1.00
1.03
1.11
2.17
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
126 MHz, CDCl3
161.3801
146.5366
143.6761
139.0453
137.8487
136.8698
130.1237
129.6373
123.7316
117.1694
101.0763
99.9424
21.6894
21.4205
F
I
I
2f
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

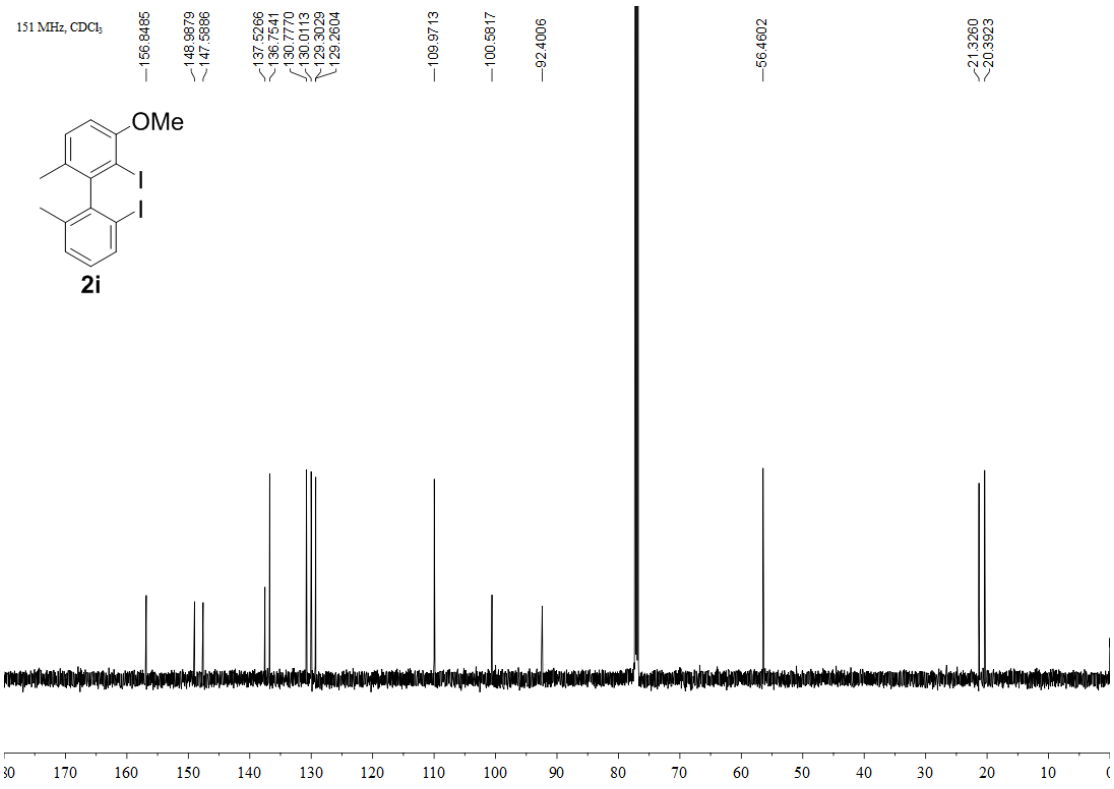

500 MHz, CDCl3
7.8301
7.8261
7.8102
7.3147
7.3131
7.3099
7.2991
7.2854
7.2832
7.0414
7.0260
7.0105
2.0190
2.0088
Cl
I
I
2g
1.91
0.95
1.05
1.00
2.90
3.18
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.

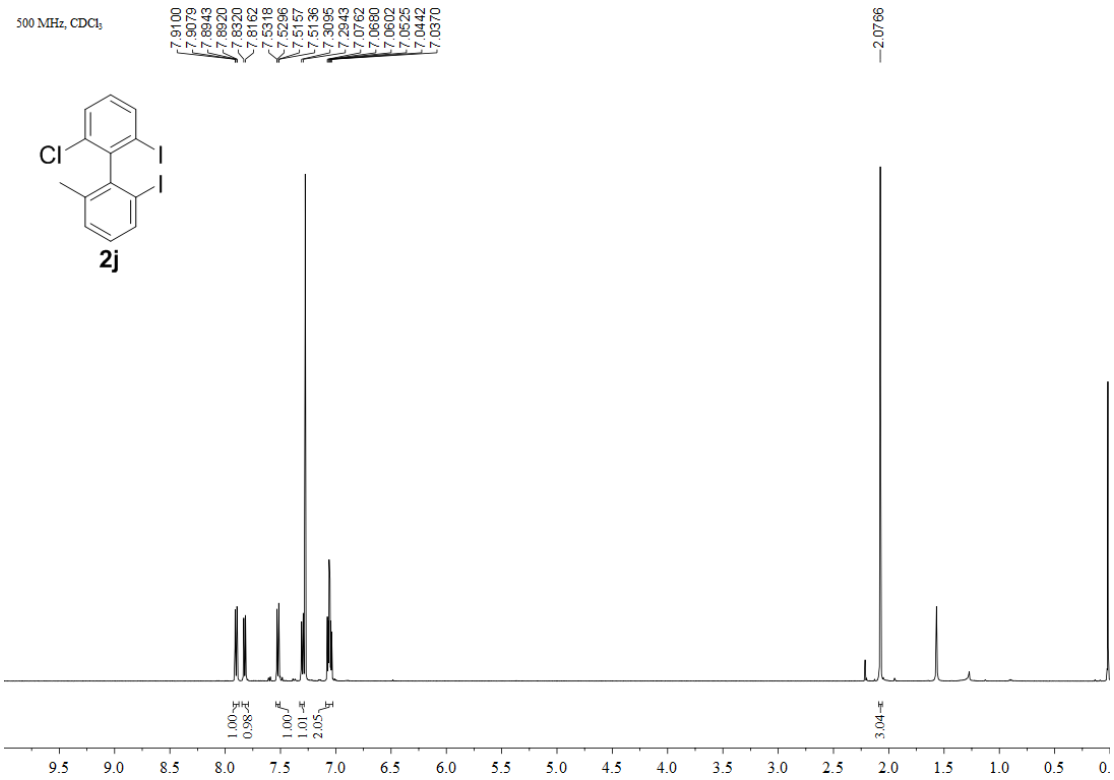

126 MHz, CDCl3
146.4185
146.0429
138.7212
137.5650
136.8790
136.1565
133.9011
130.2014
130.1465
129.6935
100.6060
100.4775
21.4153
21.3788
Cl
I
I
2g
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

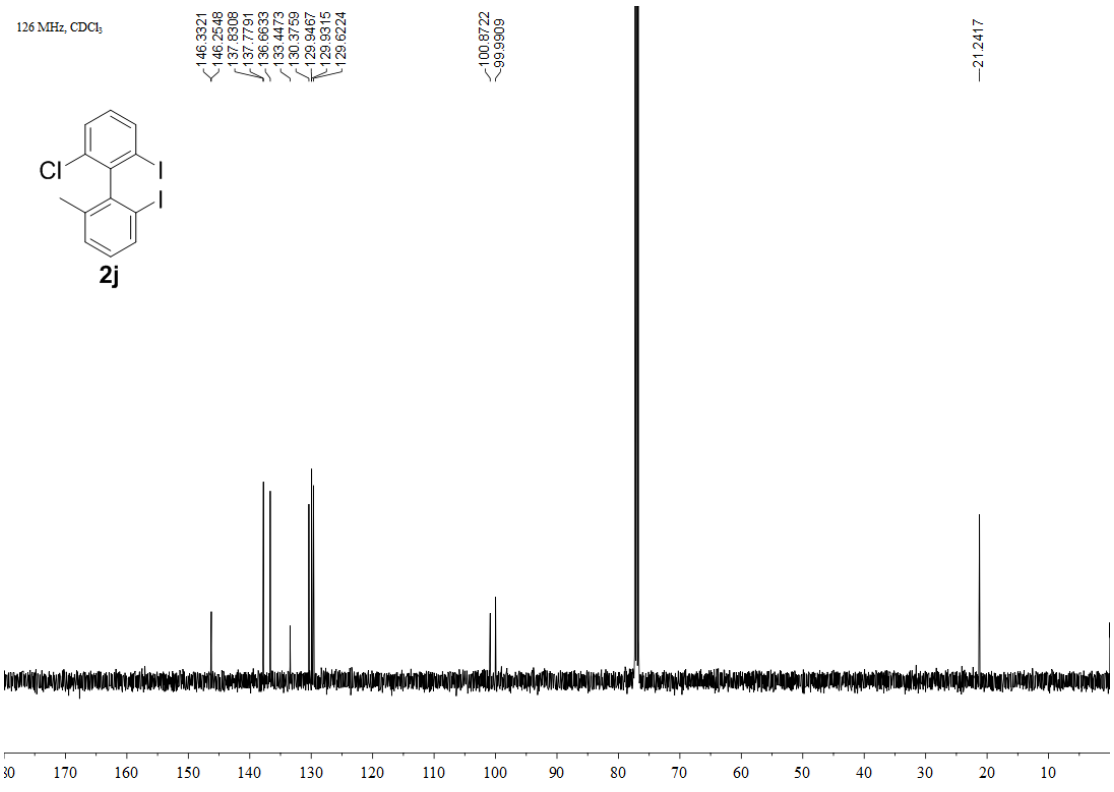

500 MHz, CDCl3
7.8333
7.8175
7.4184
7.4022
7.3081
7.3062
7.3043
7.2908
7.2508
7.2492
7.2346
7.2329
7.0431
7.0276
7.0121
2.0129
1.9975
Cl
I
I
2h
1.00
1.02
1.11
1.13
1.06
3.20
3.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

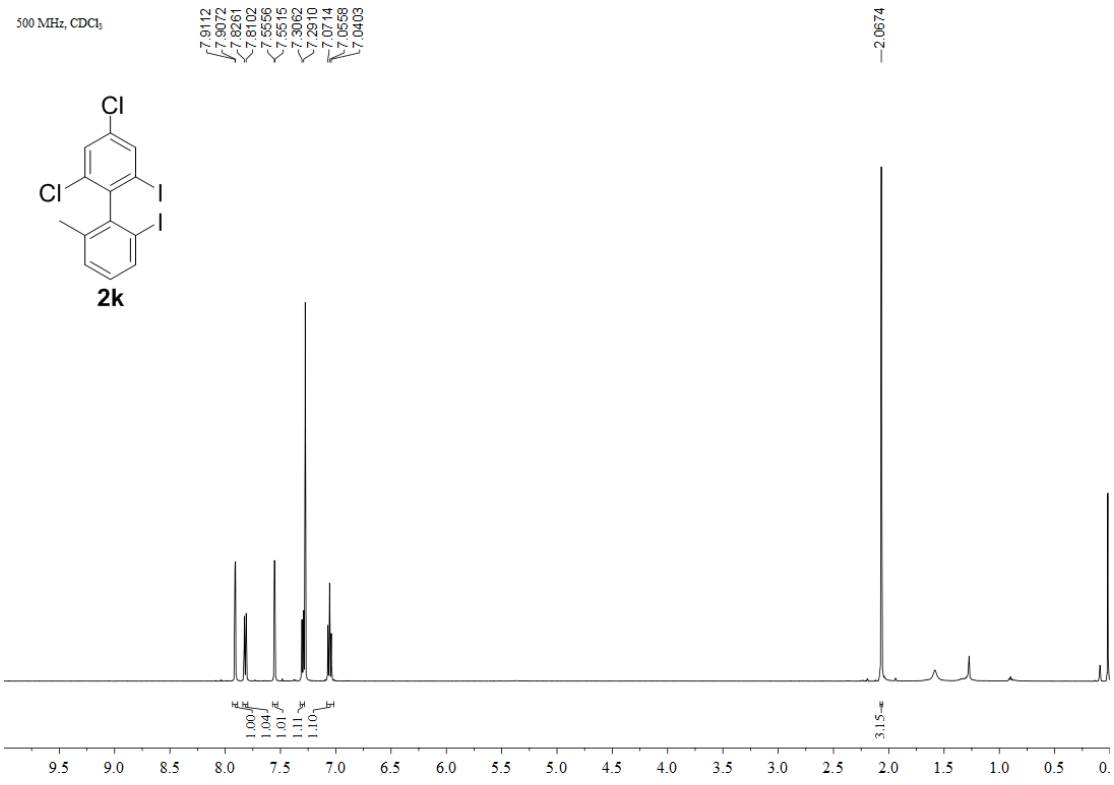

126 MHz, CDCl3
150.0298
147.8829
137.2898
136.9366
136.8494
135.3922
131.1600
130.1949
129.5745
128.3198
104.7724
100.2367
21.3168
21.0456
Cl
I
I
2h
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

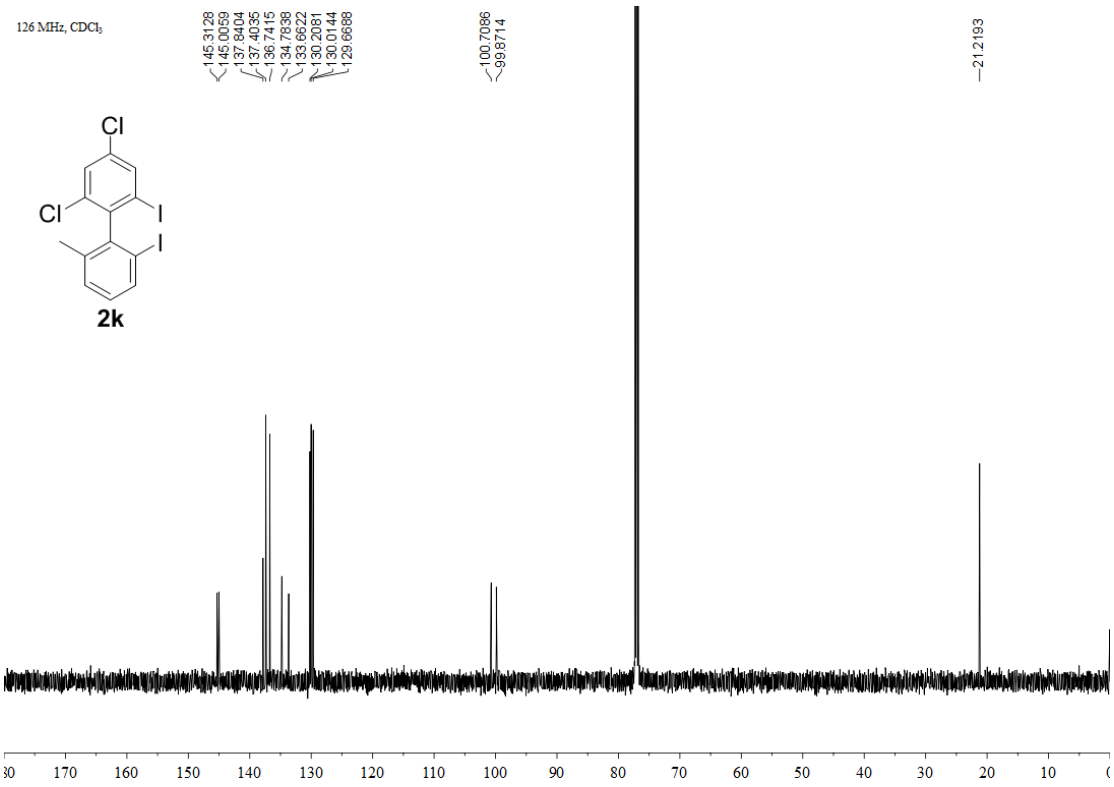

600 MHz, CDCl3
7.8305
7.8173
7.2974
7.2839
7.2602
7.2463
7.0308
7.0179
7.0050
6.8070
6.7932
3.9455
2.0161
1.9824
OMe
I
I
2i
1.00
0.95
1.06
1.03
1.05
3.16
3.07
3.19

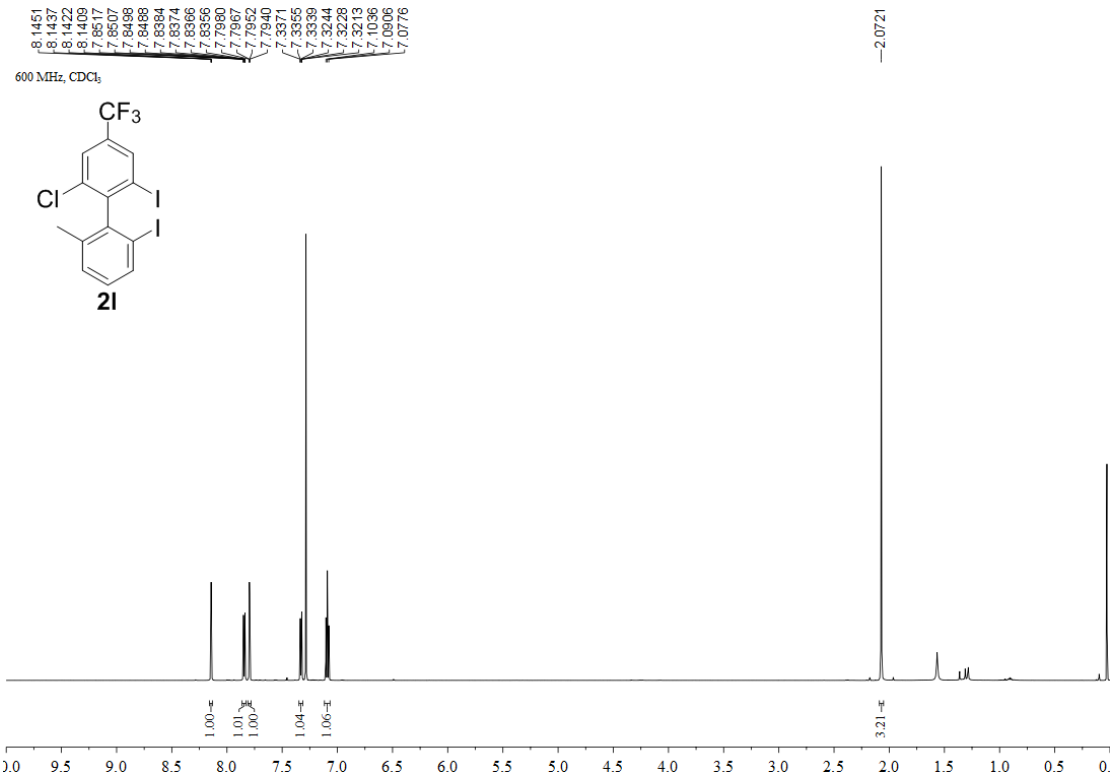

151 MHz, CDCl3
156.8485
148.9879
147.5886
137.5266
136.7541
130.7770
130.0113
129.3029
129.2604
109.9713
100.5817
92.4006
56.4602
21.3260
20.3923
OMe
I
I
2i

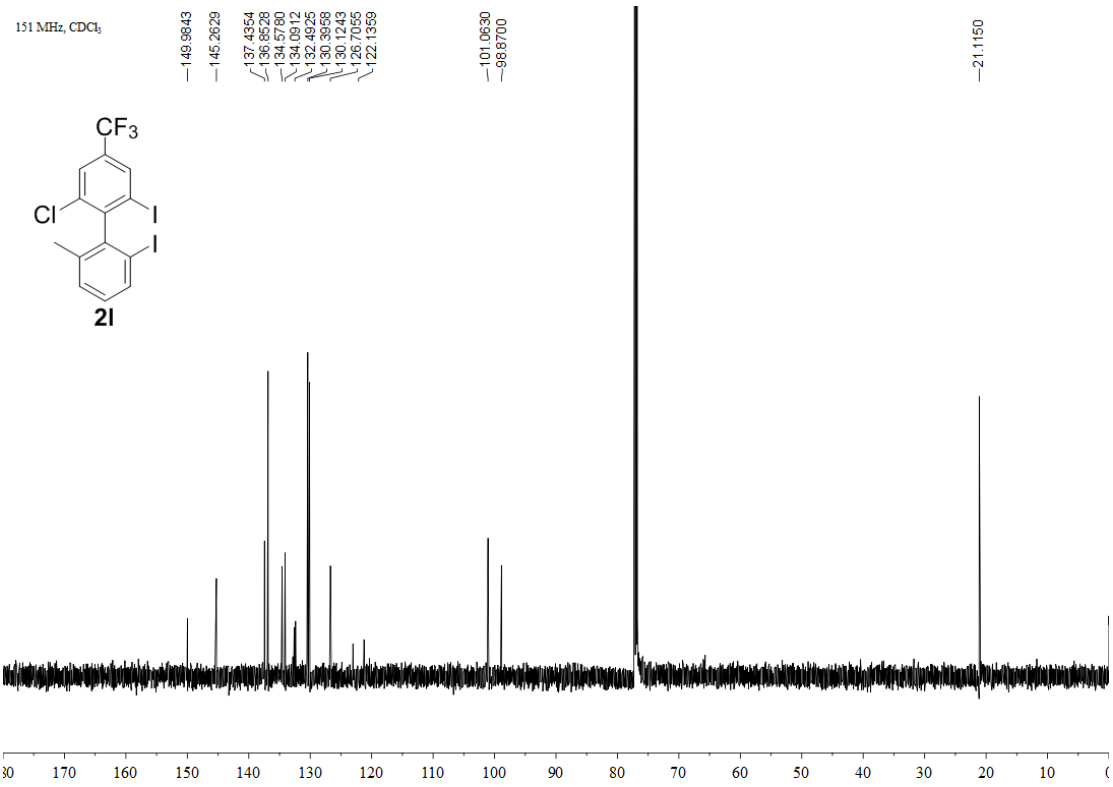

500 MHz, CDCl3
7.9100
7.9079
7.8943
7.8920
7.8320
7.8162
7.5318
7.5296
7.5157
7.5136
7.3095
7.2943
7.0762
7.0680
7.0602
7.0525
7.0442
7.0370
2.0766
Cl
I
I
2j
1.00
0.98
1.00
1.01
2.05
3.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

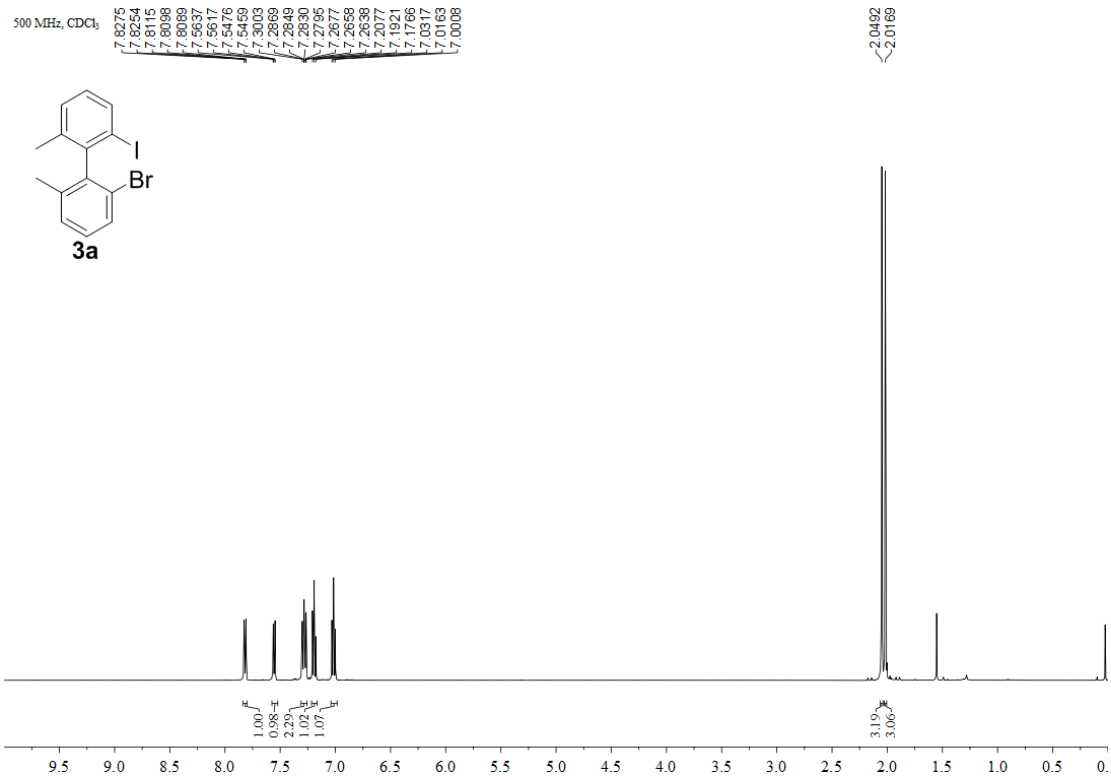

126 MHz, CDCl3
146.3321
146.2548
137.8308
137.7791
136.6633
133.4473
130.3759
129.9467
129.9315
129.6224
100.8722
99.9909
21.2417
Cl
I
I
2j
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

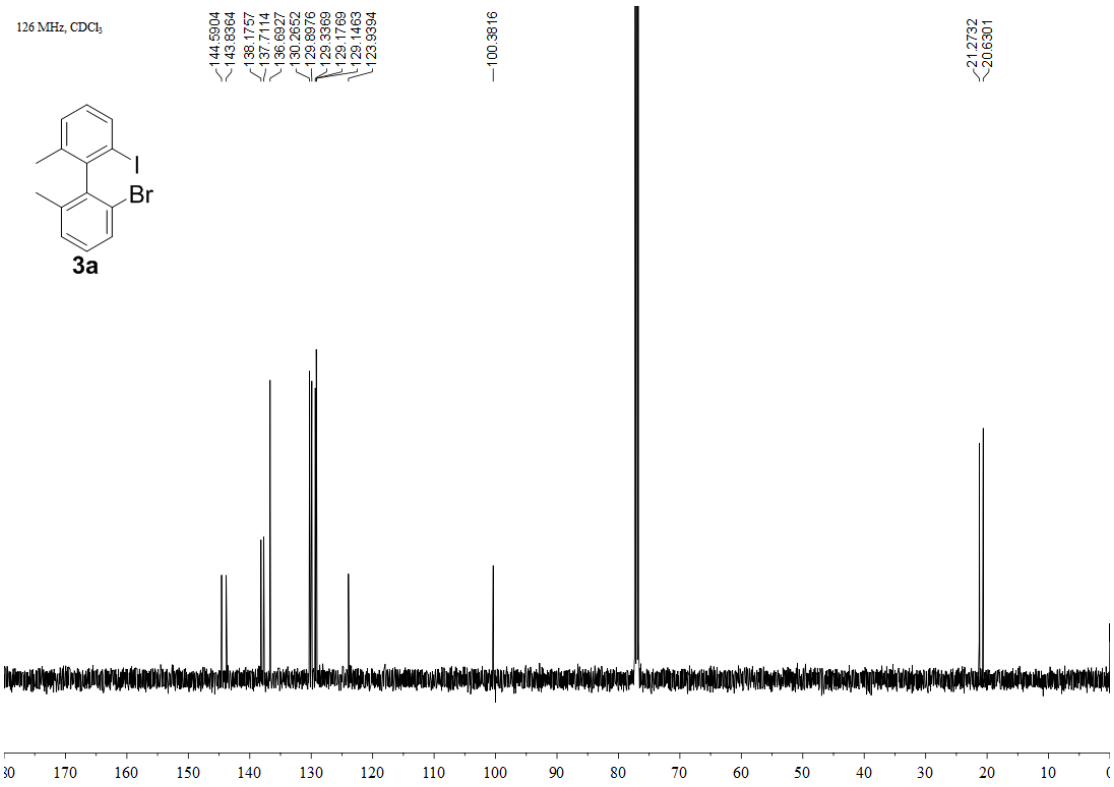

500 MHz, CDCl3
7.9112
7.9072
7.8261
7.8102
7.5556
7.5515
7.3062
7.2910
7.0714
7.0558
7.0403
2.0674
Cl
Cl
I
I
2k
1.00
1.04
1.01
1.11
1.10
3.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

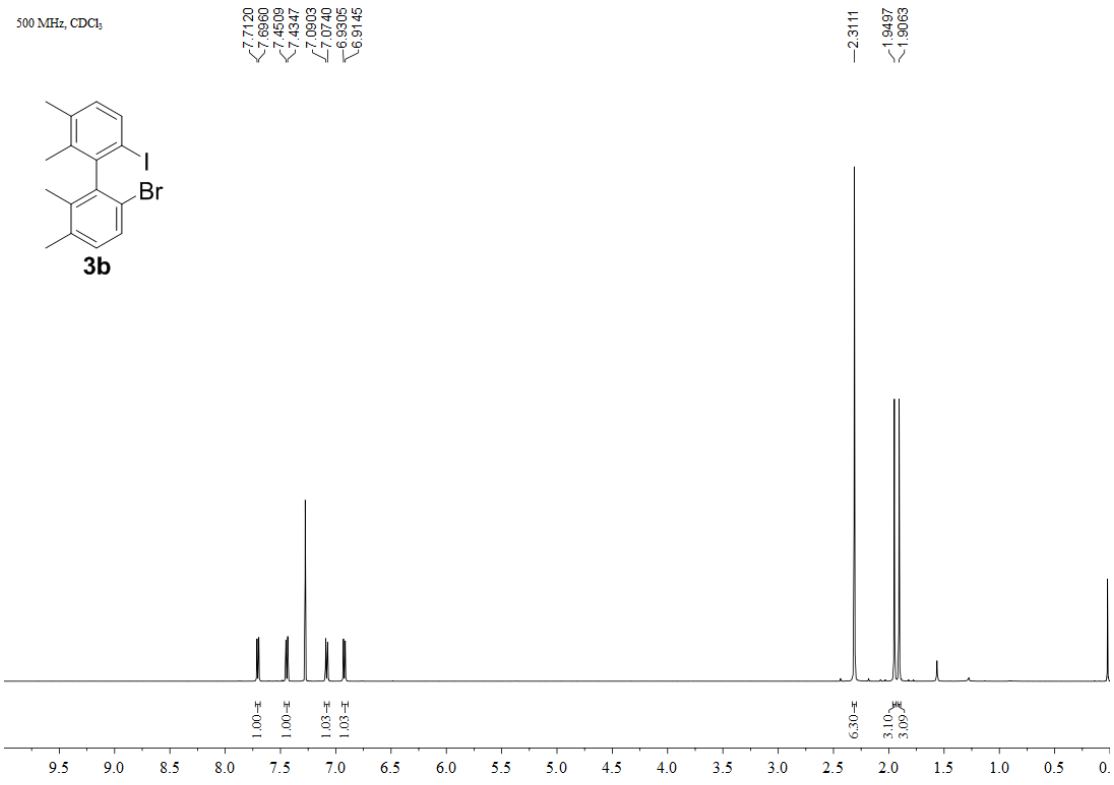

126 MHz, CDCl3
145.3128
145.0059
137.8404
137.4035
136.7415
134.7838
133.6622
130.2081
130.0144
129.6688
100.7086
99.8714
21.2193
Cl
Cl
I
I
2k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

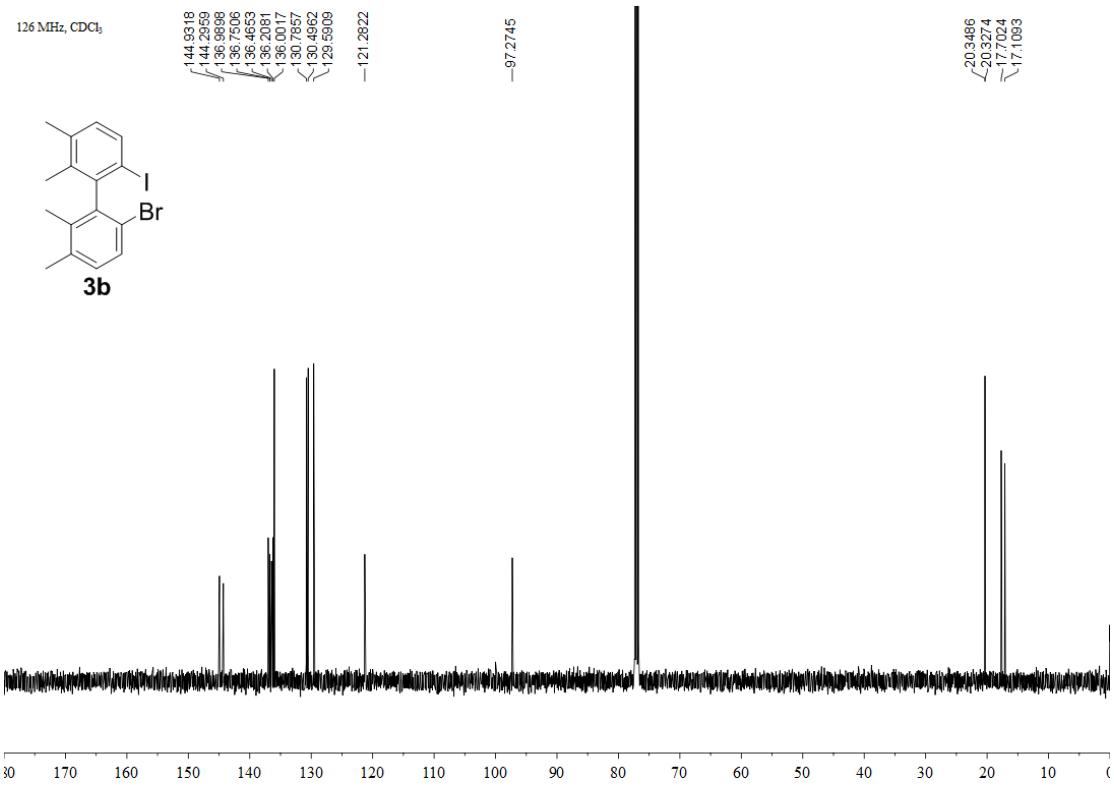

8.1451
8.1437
8.1422
8.1406
7.8517
7.8507
7.8498
7.8488
7.8384
7.8374
7.8366
7.8356
7.7980
7.7967
7.7952
7.7940
7.3371
7.3355
7.3339
7.3244
7.3228
7.3213
7.1036
7.0906
7.0776
2.0721
600 MHz, CDCl3
CF3
Cl
I
I
2l
1.00
1.01
1.00
1.04
1.06
3.21

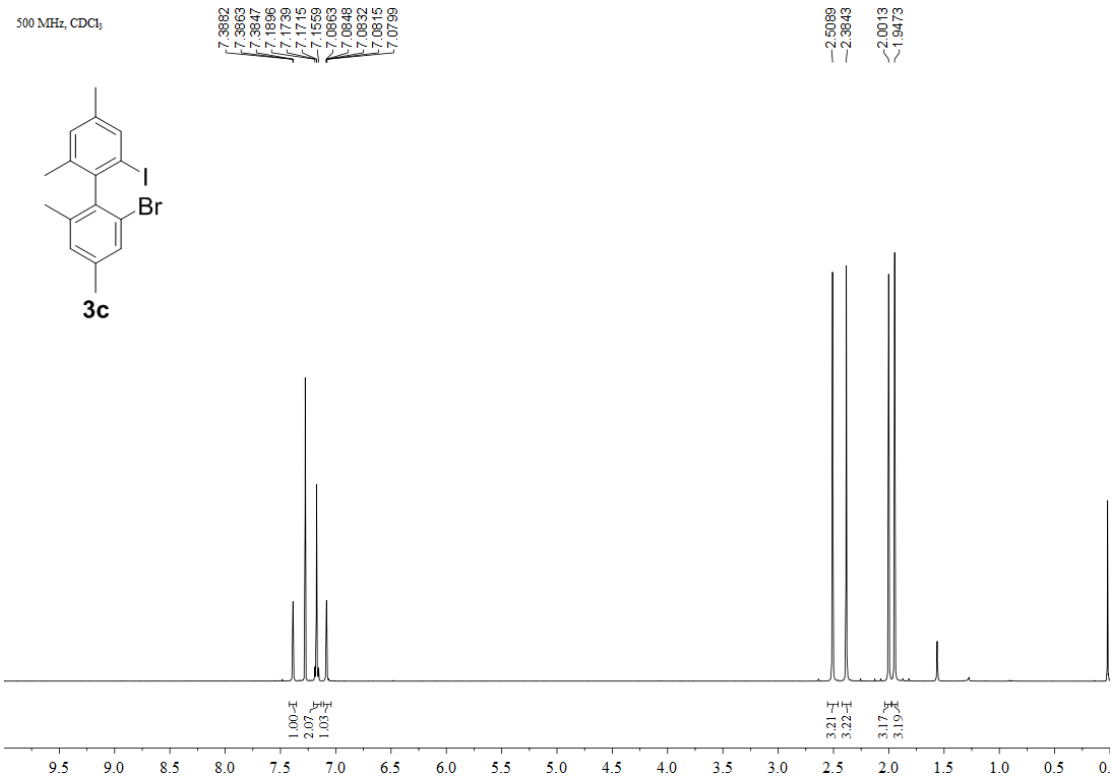

151 MHz, CDCl3
149.9843
145.2629
137.4354
136.8528
134.5780
134.0912
132.4925
130.3958
130.1243
126.7055
122.1359
101.0630
98.8700
21.1150
CF3
Cl
I
I
2l

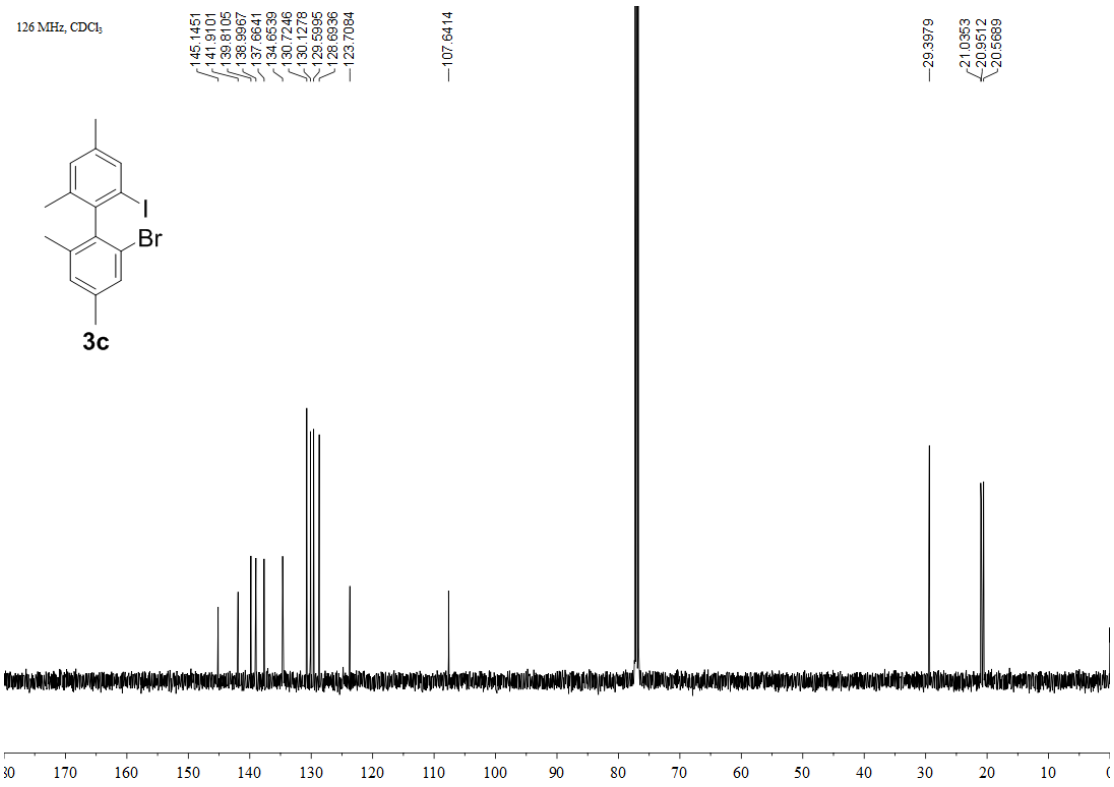

500 MHz, CDCl3
7.8275
7.8254
7.8115
7.8098
7.8089
7.5637
7.5617
7.5476
7.5459
7.3003
7.2869
7.2849
7.2830
7.2795
7.2677
7.2658
7.2638
7.2077
7.1921
7.1766
7.0317
7.0163
7.0008
2.0492
2.0169
I
Br
3a
1.00
0.98
2.29
1.02
1.07
3.19
3.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

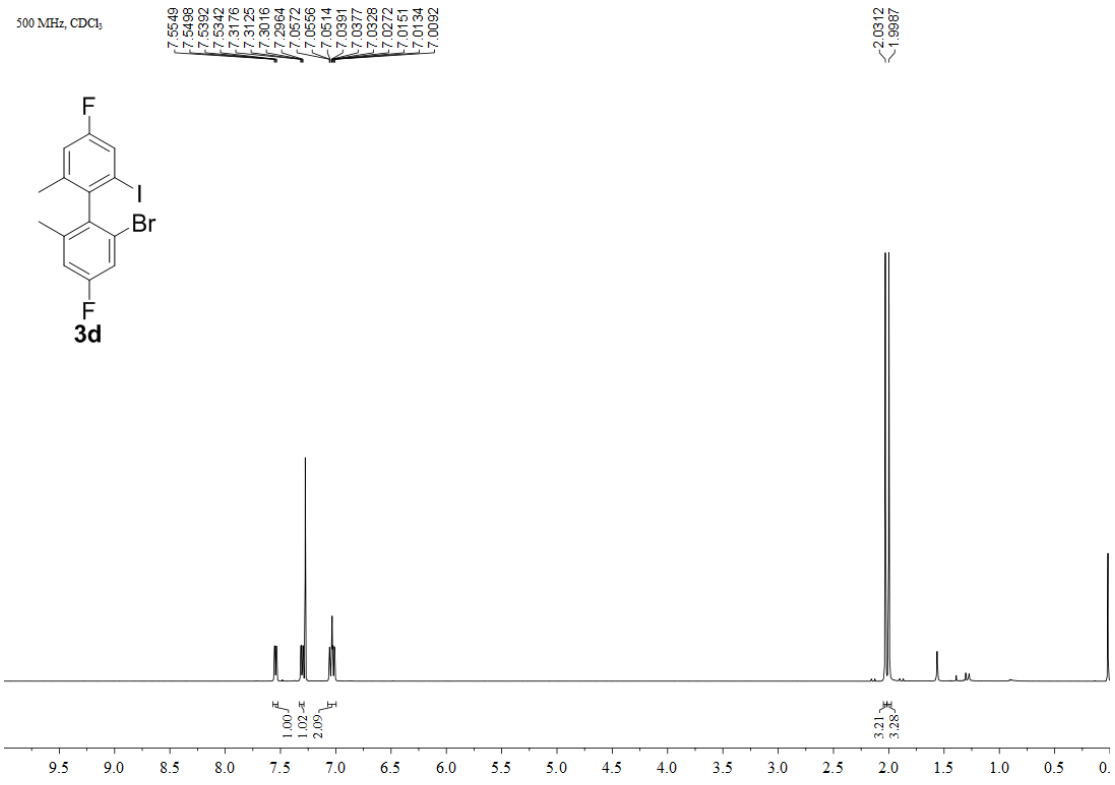

126 MHz, CDCl3
144.5904
143.8364
138.1757
137.7114
136.6927
130.2652
129.8976
129.3369
129.1769
129.1463
123.9394
100.3816
21.2732
20.6301
I
Br
3a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

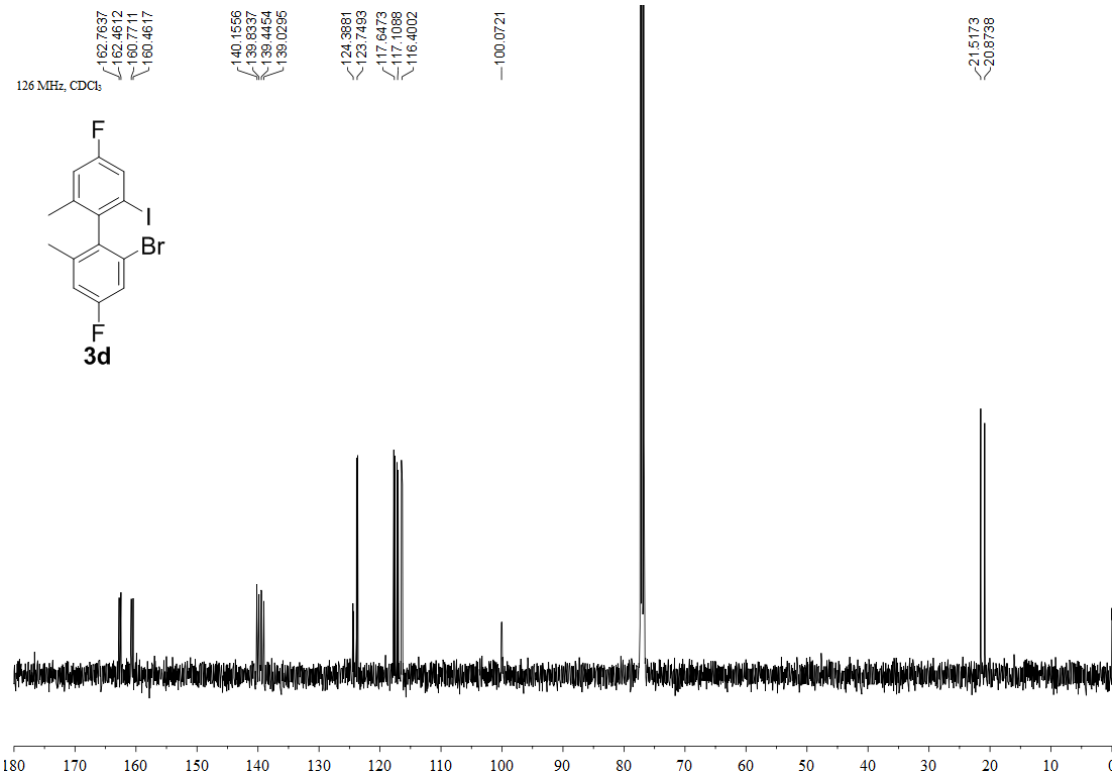

500 MHz, CDCl3
7.7120
7.6960
7.4509
7.4347
7.0903
7.0740
6.9305
6.9145
2.3111
1.9497
1.9063
I
Br
3b
1.00
1.00
1.03
1.03
6.30
3.10
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

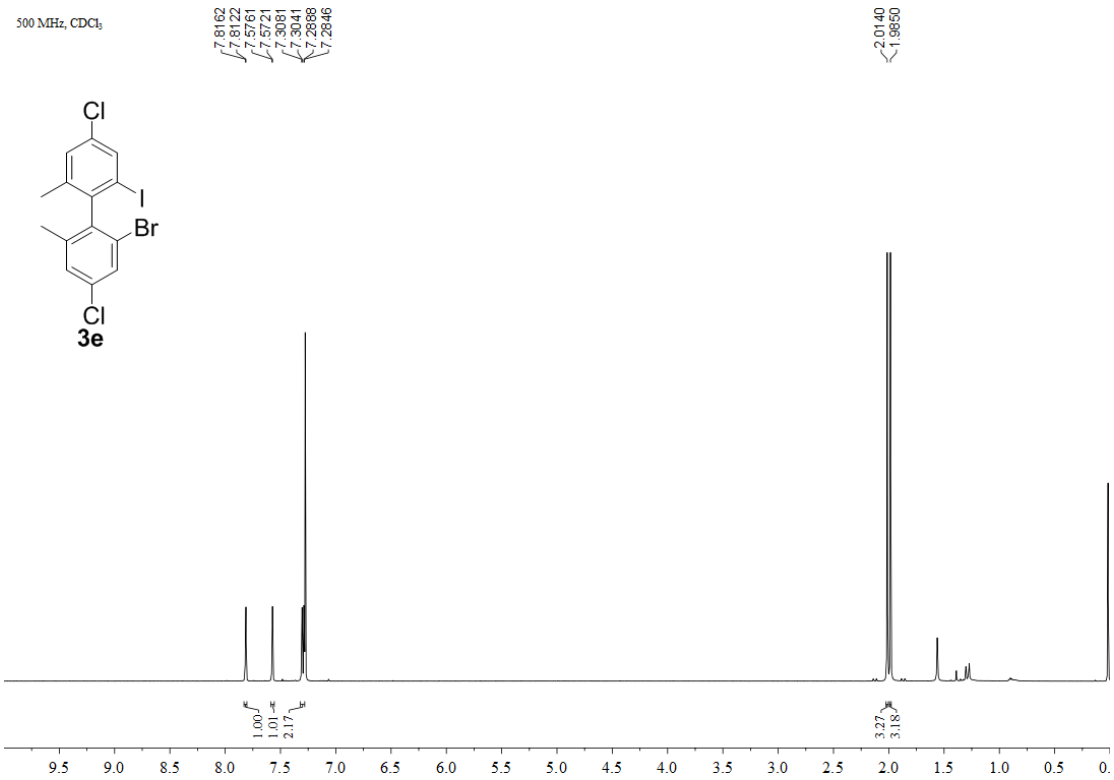

126 MHz, CDCl3
144.9318
144.2959
136.9898
136.7506
136.4653
136.2081
136.0017
130.7857
130.4962
129.5909
121.2822
97.2745
20.3486
20.3274
17.7024
17.1093
I
Br
3b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

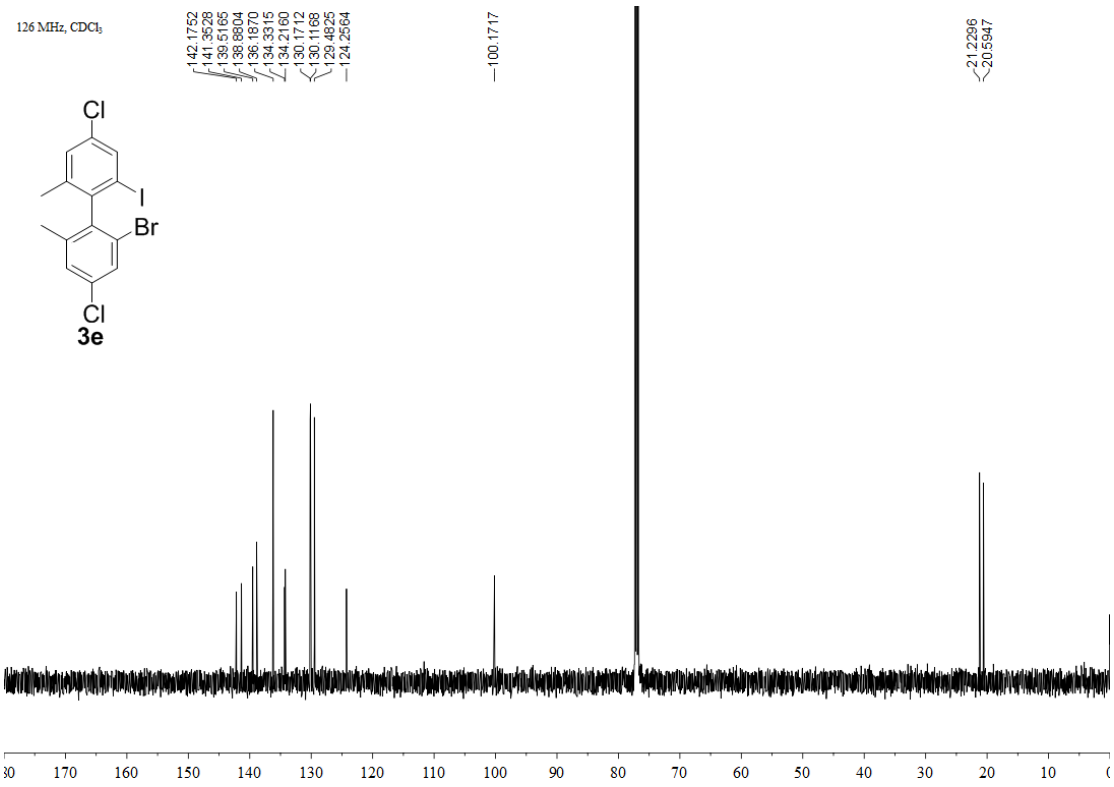

500 MHz, CDCl3
7.3882
7.3863
7.3847
7.1896
7.1739
7.1715
7.1559
7.0863
7.0848
7.0832
7.0815
7.0799
2.5089
2.3843
2.0013
1.9473
I
Br
3c
1.00
2.07
1.03
3.21
3.22
3.17
3.19
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

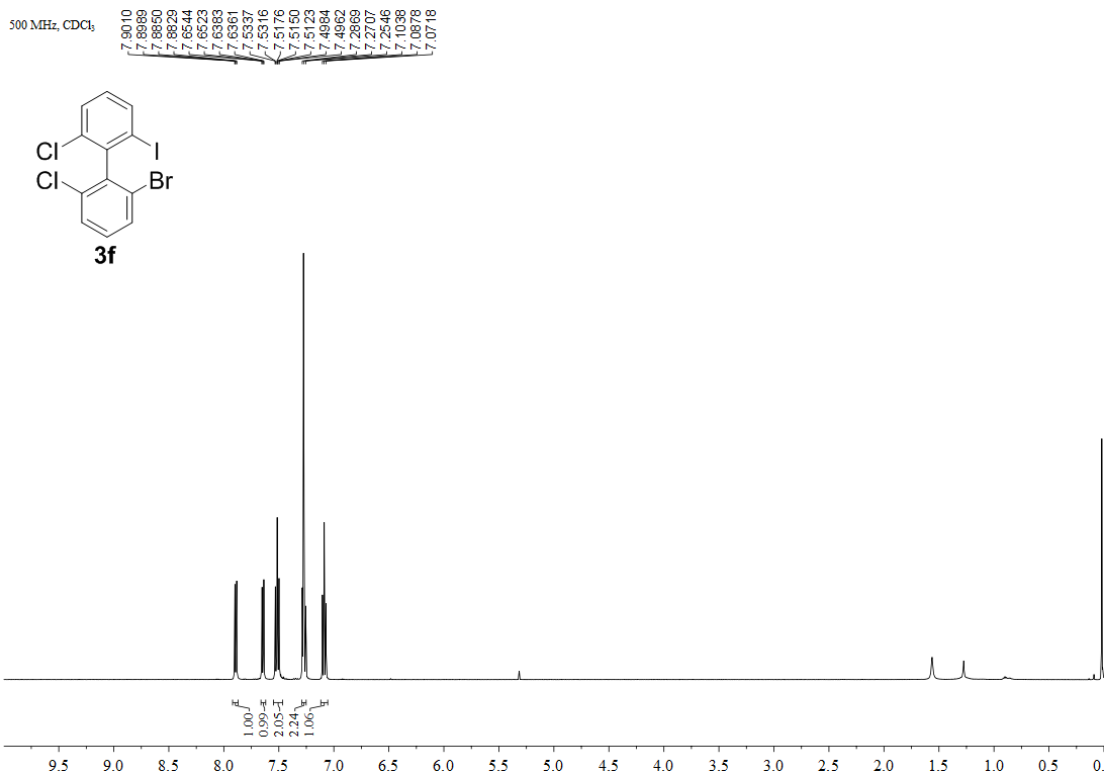

126 MHz, CDCl3
145.1451
141.9101
139.8105
139.9967
137.6641
134.6539
130.7246
130.1278
129.5995
128.6936
123.7084
107.6414
29.3979
21.0353
20.9512
20.5689
I
Br
3c
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

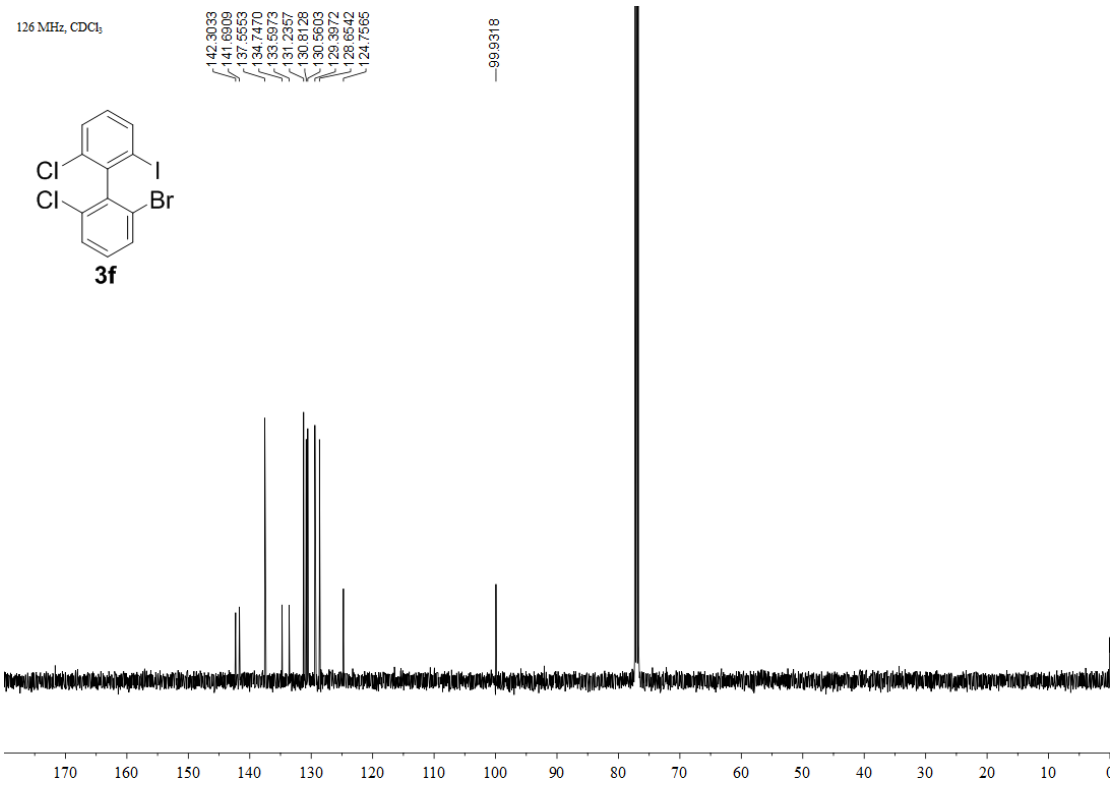

500 MHz, CDCl3
7.5549
7.5498
7.5392
7.5342
7.3176
7.3125
7.3016
7.2964
7.0572
7.0556
7.0514
7.0391
7.0377
7.0328
7.0272
7.0151
7.0134
7.0092
2.0312
1.9987
F
I
Br
F
3d
1.00
1.02
2.09
3.21
3.28
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

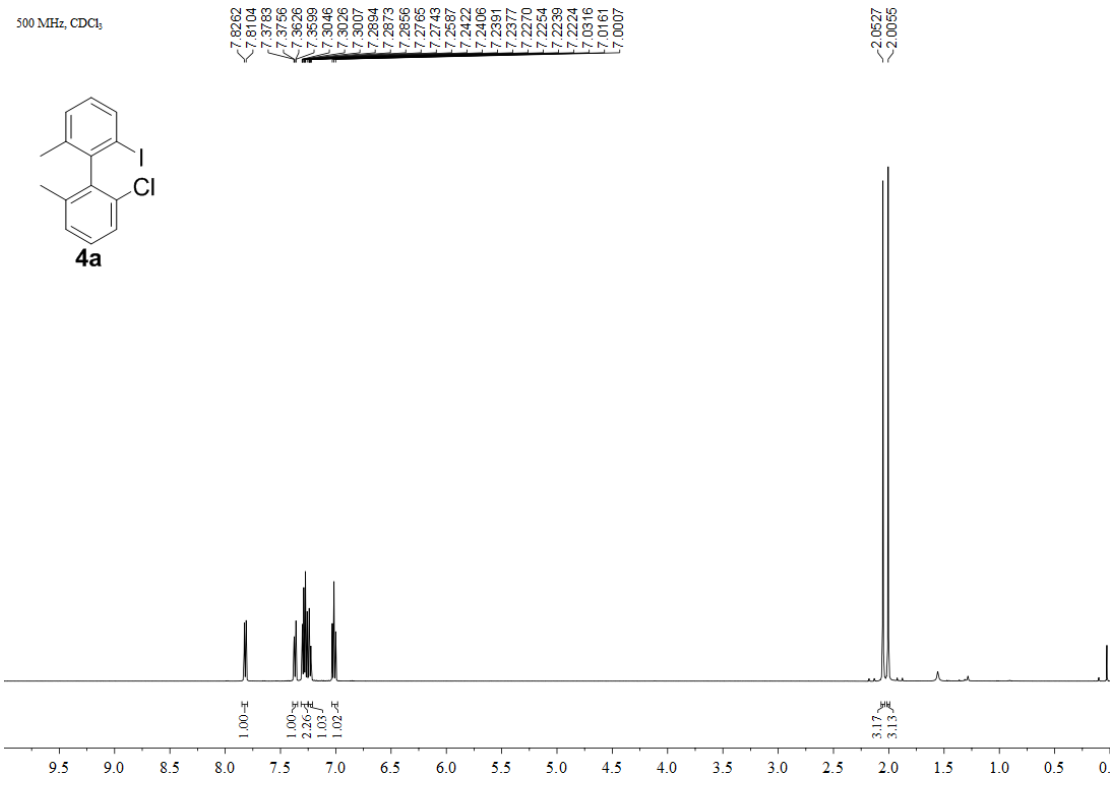

126 MHz, CDCl3
162.7637
162.4612
160.7711
160.4617
140.1556
139.8337
139.4454
139.0295
124.3881
123.7493
117.6473
117.1088
116.4002
100.0721
21.5173
20.8738
F
I
Br
F
3d
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

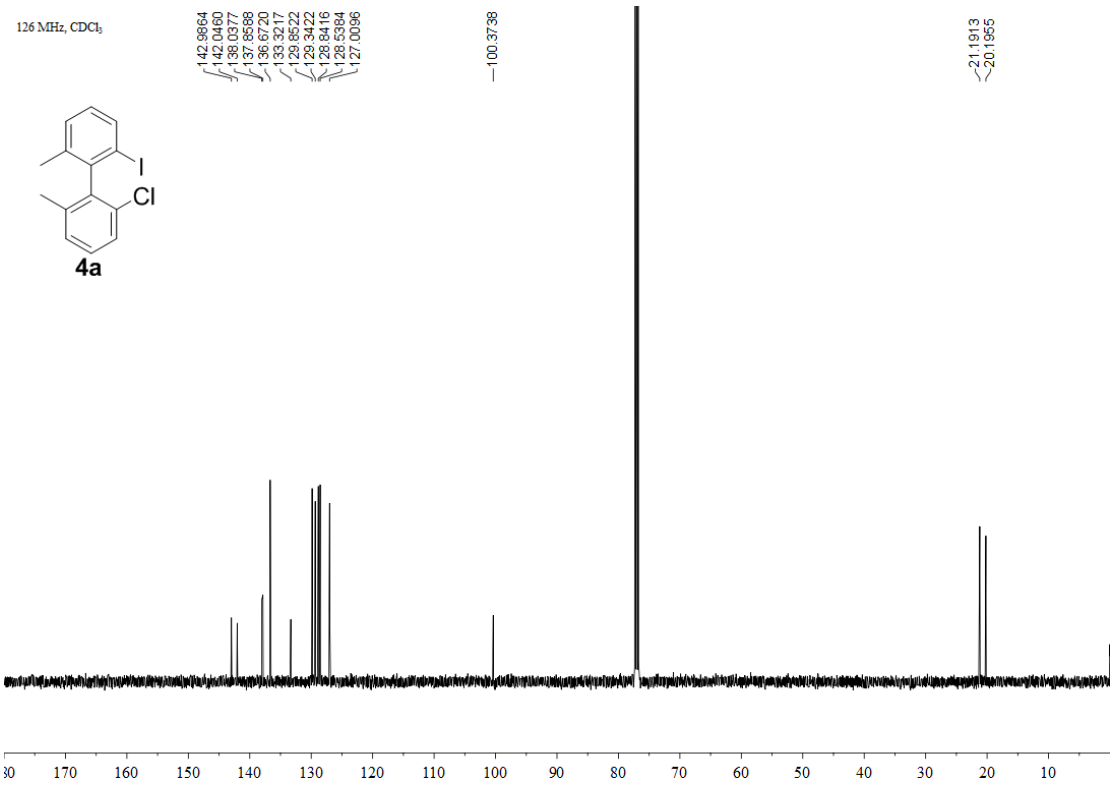

500 MHz, CDCl3
7.8162
7.8122
7.5761
7.5721
7.3081
7.3041
7.2888
7.2846
2.0140
1.9850
Cl
I
Br
Cl
3e
1.00
1.01
2.17
3.27
3.18
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.

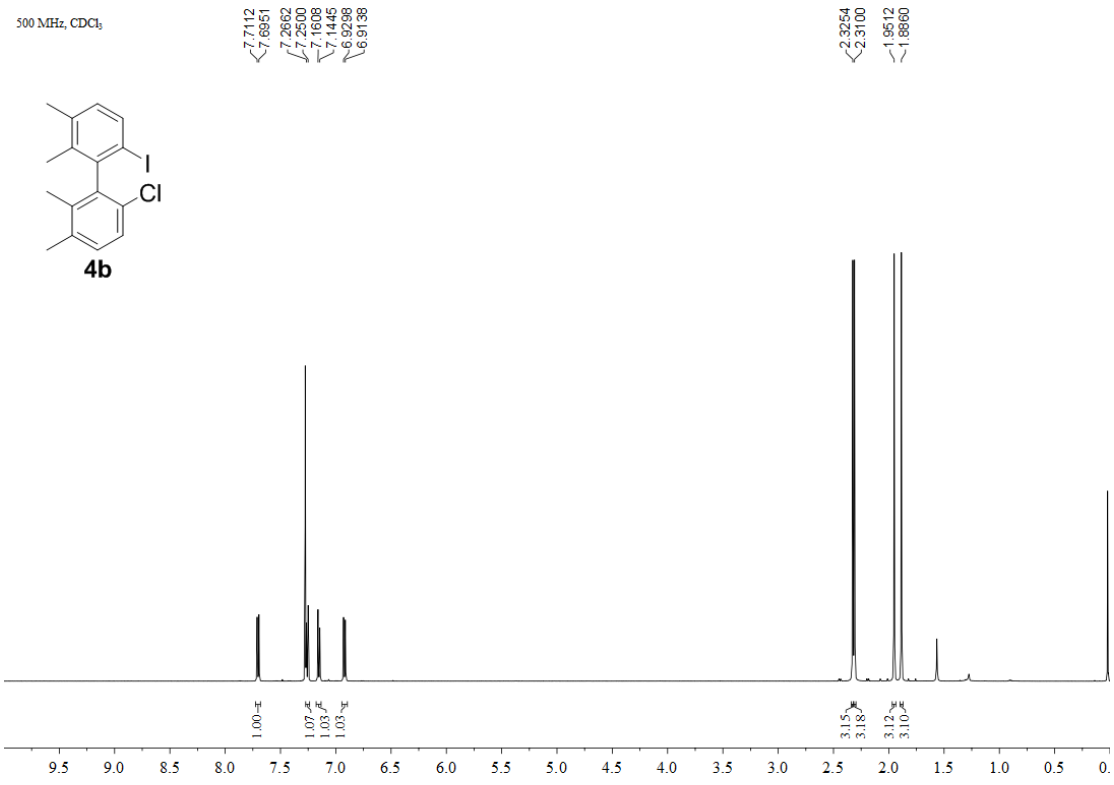

126 MHz, CDCl3
142.1752
141.3528
139.5165
138.8804
136.1870
134.3315
134.2160
130.1712
130.1168
129.4825
124.2564
100.1717
21.2296
20.5947
Cl
I
Br
Cl
3e
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

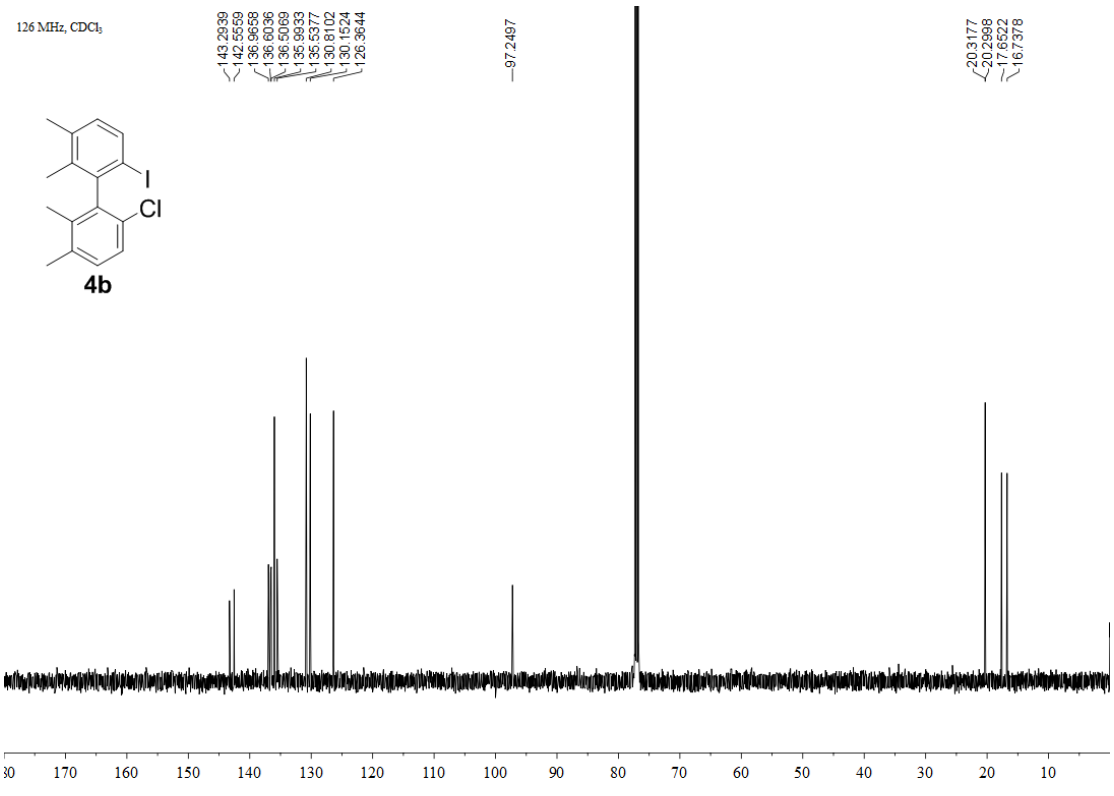

500 MHz, CDCl3
7.9010
7.8989
7.8850
7.8829
7.6544
7.6523
7.6383
7.6361
7.5337
7.5316
7.5176
7.5150
7.5123
7.4984
7.4962
7.2869
7.2707
7.2546
7.1038
7.0878
7.0718
Cl
Cl
I
Br
3f
1.00
0.99
2.05
2.24
1.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

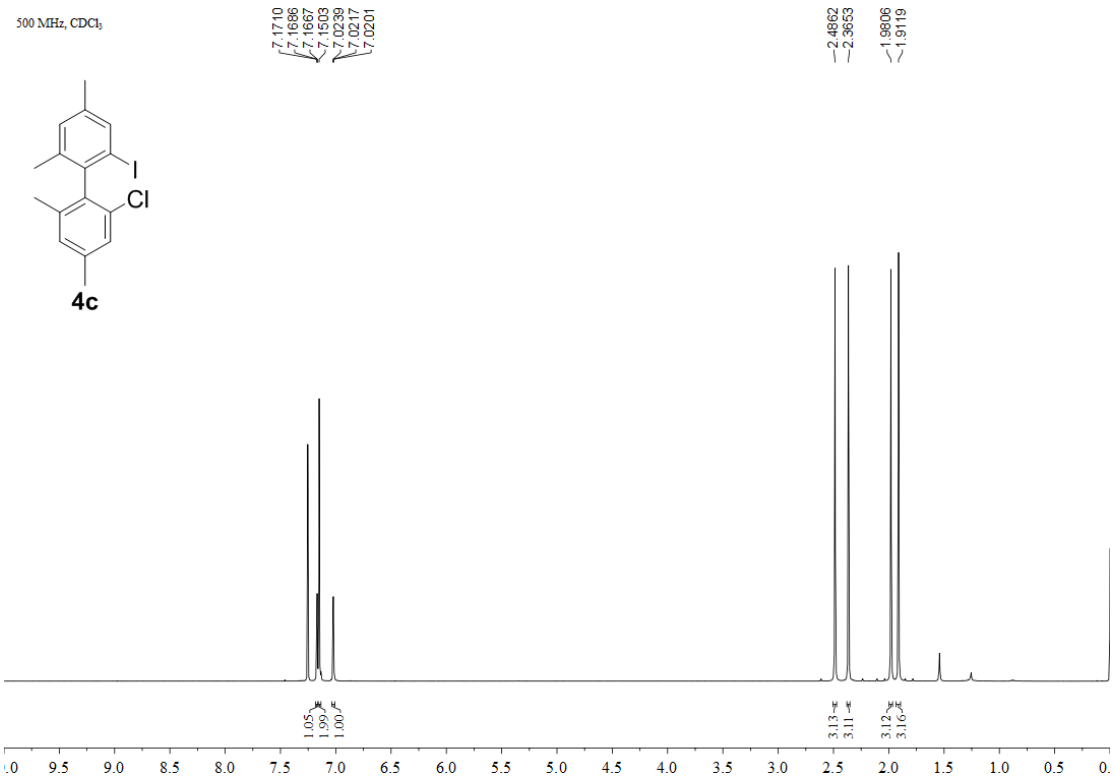

126 MHz, CDCl3
142.3033
141.6909
137.5553
134.7470
133.5973
131.2357
130.8128
130.5603
129.3972
128.6542
124.7565
99.9318
Cl
Cl
I
Br
3f
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

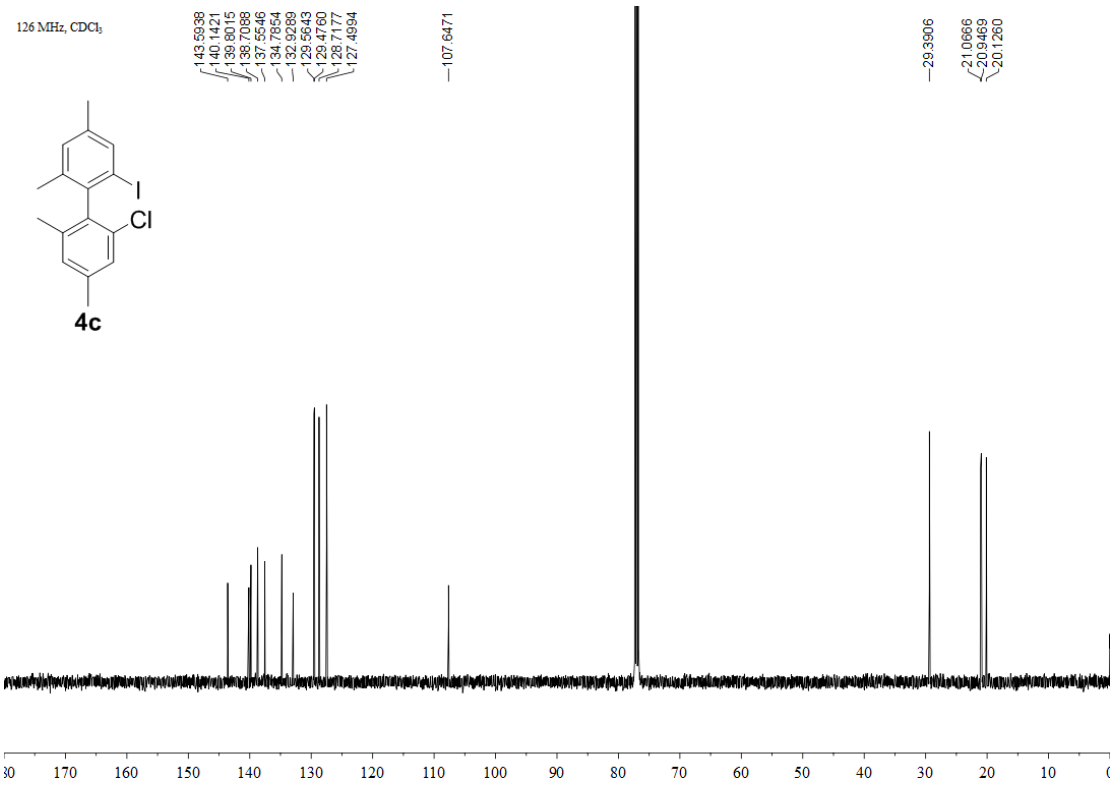

500 MHz, CDCl3
7.8262
7.8104
7.3783
7.3756
7.3626
7.3599
7.3046
7.3026
7.3007
7.2894
7.2873
7.2856
7.2765
7.2743
7.2587
7.2422
7.2406
7.2391
7.2377
7.2270
7.2254
7.2239
7.2224
7.0161
7.0007
2.0527
2.0055
I
Cl
4a
1.00
1.00
2.26
1.03
1.02
3.17
3.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

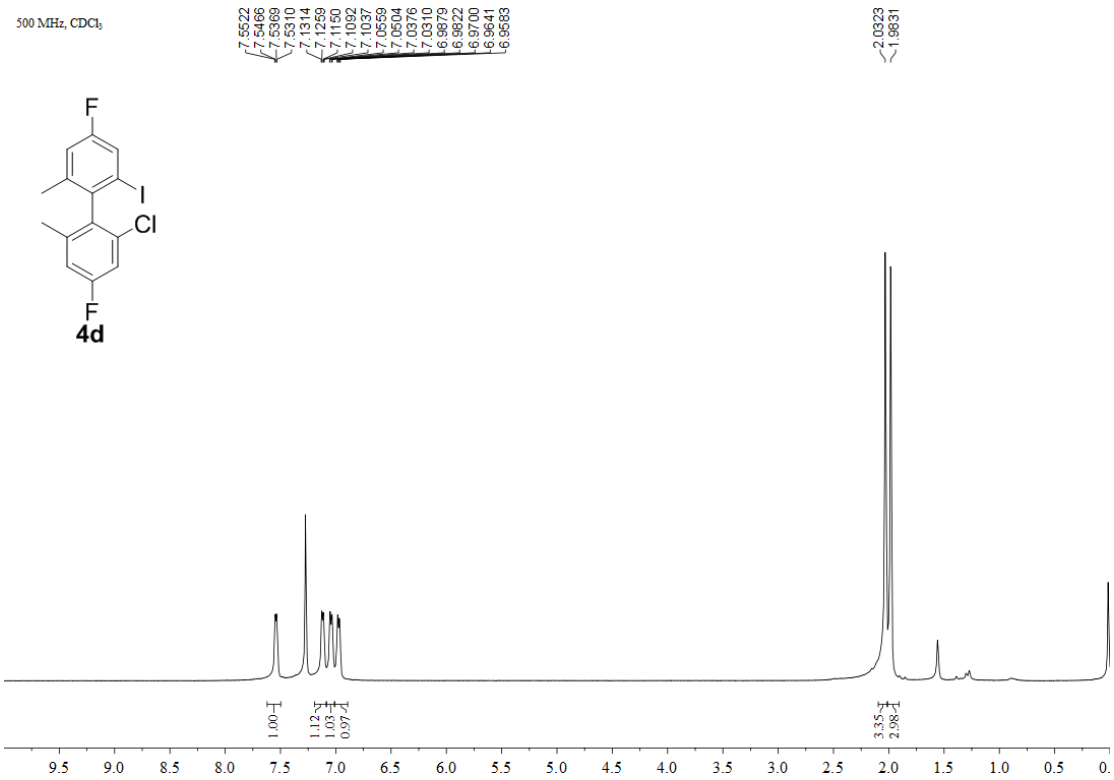

126 MHz, CDCl3
142.9864
142.0460
138.0377
137.8588
136.6720
133.3217
129.8522
129.3422
128.8416
128.5384
127.0096
100.3738
21.1913
20.1955
I
Cl
4a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

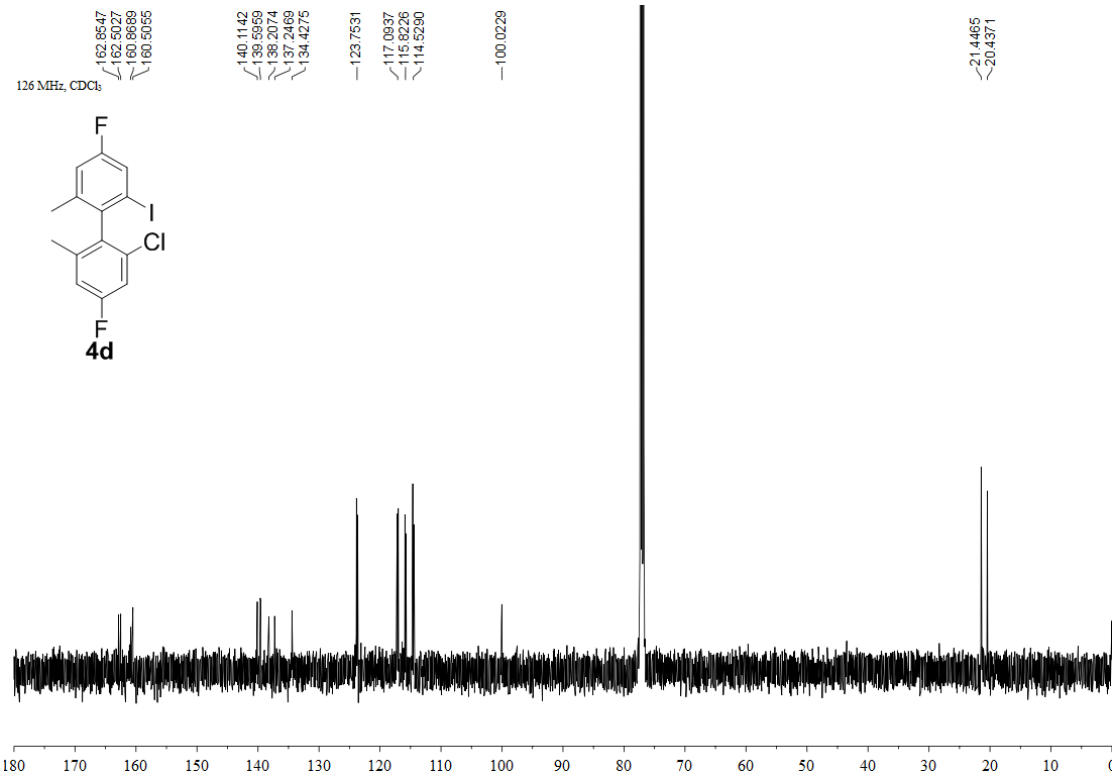

500 MHz, CDCl3
7.7112
7.6951
7.2662
7.2500
7.1608
7.1445
6.9298
6.9138
2.3254
2.3100
1.9512
1.8860
I
Cl
4b
1.00
1.07
1.03
1.03
3.15
3.18
3.12
3.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.

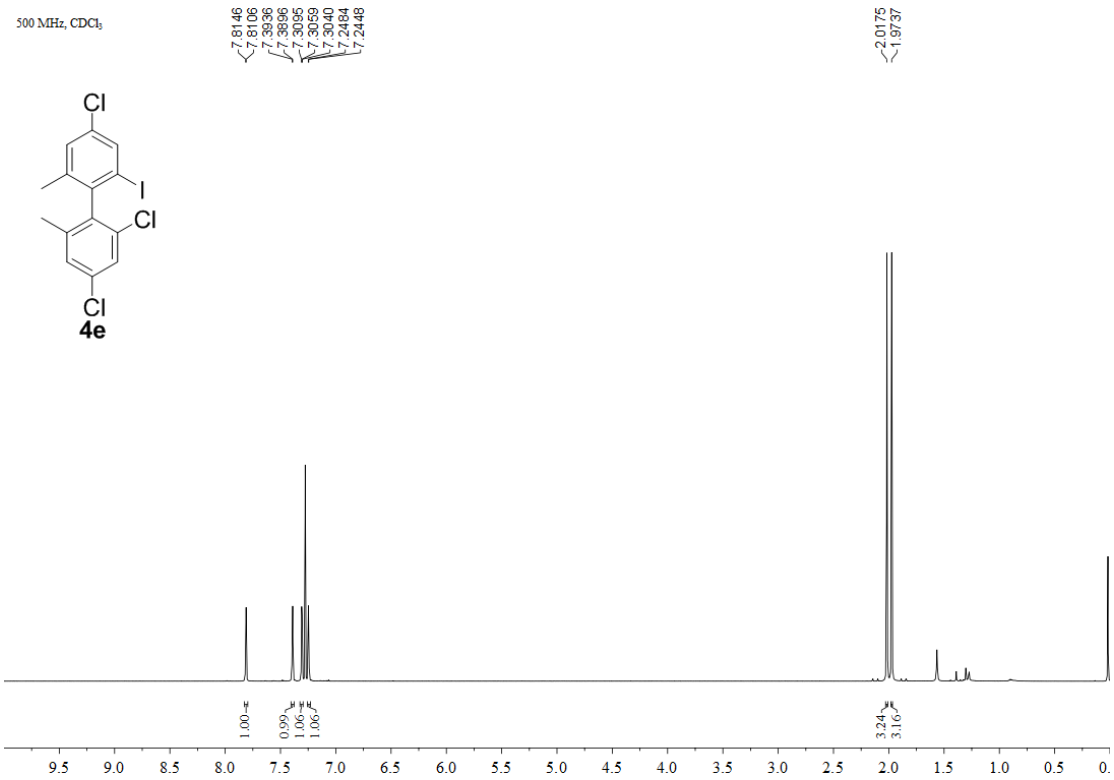

126 MHz, CDCl3
143.2939
142.5559
136.9658
136.6036
136.5069
135.9933
135.5377
130.8102
130.1524
126.3644
97.2497
20.3177
20.2998
17.6522
16.7378
I
Cl
4b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

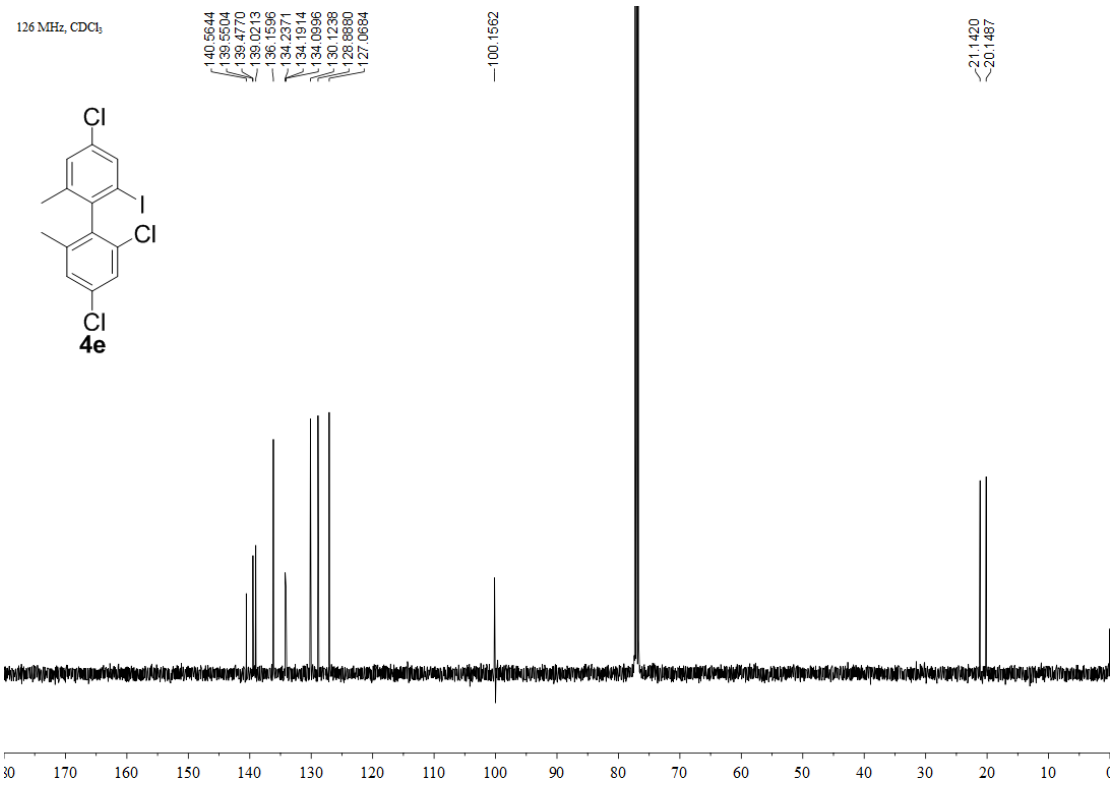

500 MHz, CDCl3
7.1710
7.1686
7.1667
7.1503
7.0239
7.0217
7.0201
2.4862
2.3653
1.9806
1.9119
I
Cl
4c
1.05
1.99
1.00
3.13
3.11
3.12
3.16

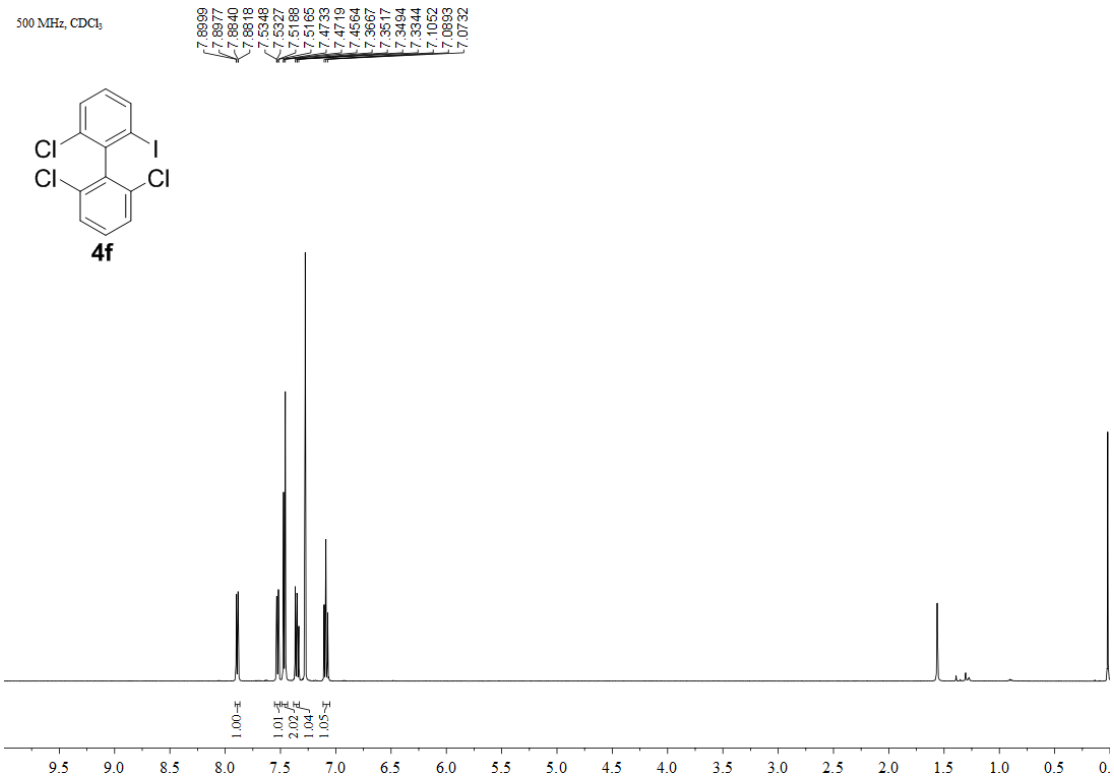

126 MHz, CDCl3
143.5938
140.1421
139.8015
138.7088
137.5546
134.7854
132.9289
129.5643
129.4760
128.7177
127.4994
107.6471
29.3906
21.0666
20.9469
20.1260
I
Cl
4c

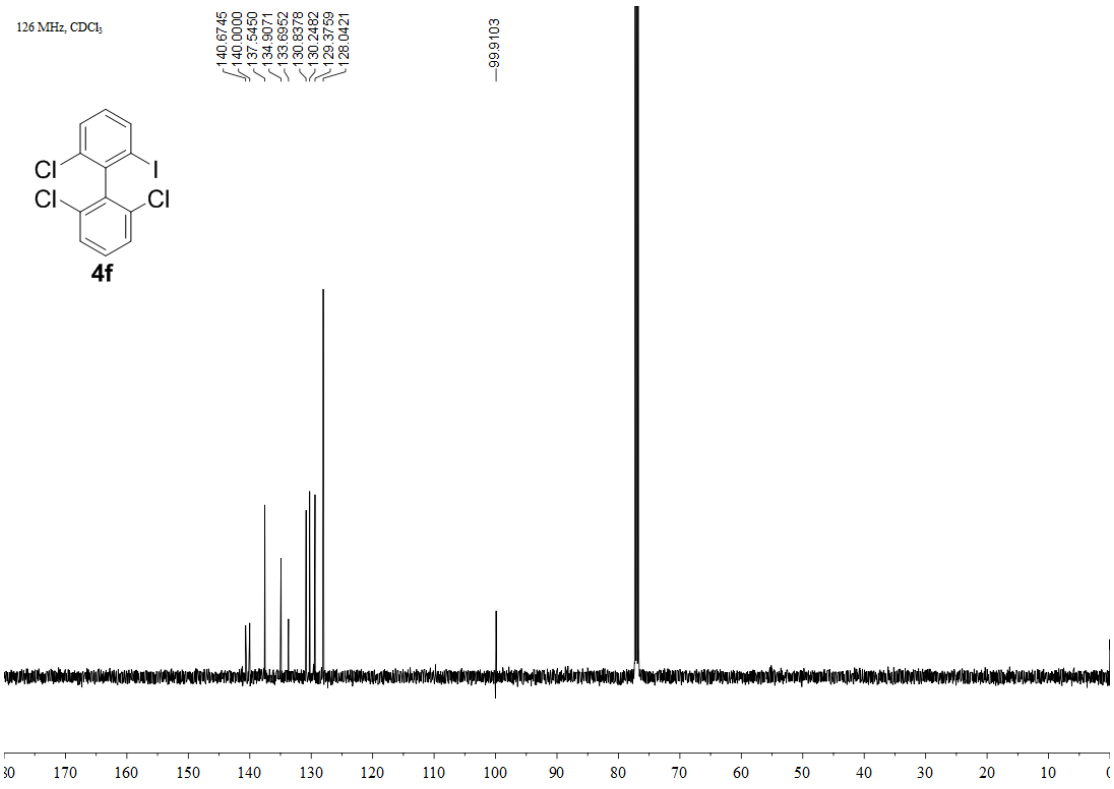

500 MHz, CDCl3
7.5522
7.5466
7.5369
7.5310
7.1314
7.1259
7.1150
7.1092
7.1037
7.0559
7.0504
7.0376
7.0310
6.9879
6.9822
6.9700
6.9641
6.9583
2.0323
1.9831
F
I
Cl
F
4d
1.00
1.12
1.03
0.97
3.35
2.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.


126 MHz, CDCl3
162.8547
162.5027
160.8689
160.5055
140.1142
139.5959
138.2074
137.2469
134.4275
123.7531
117.0937
115.8226
114.5290
100.0229
21.4465
20.4371
F
I
Cl
F
4d
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

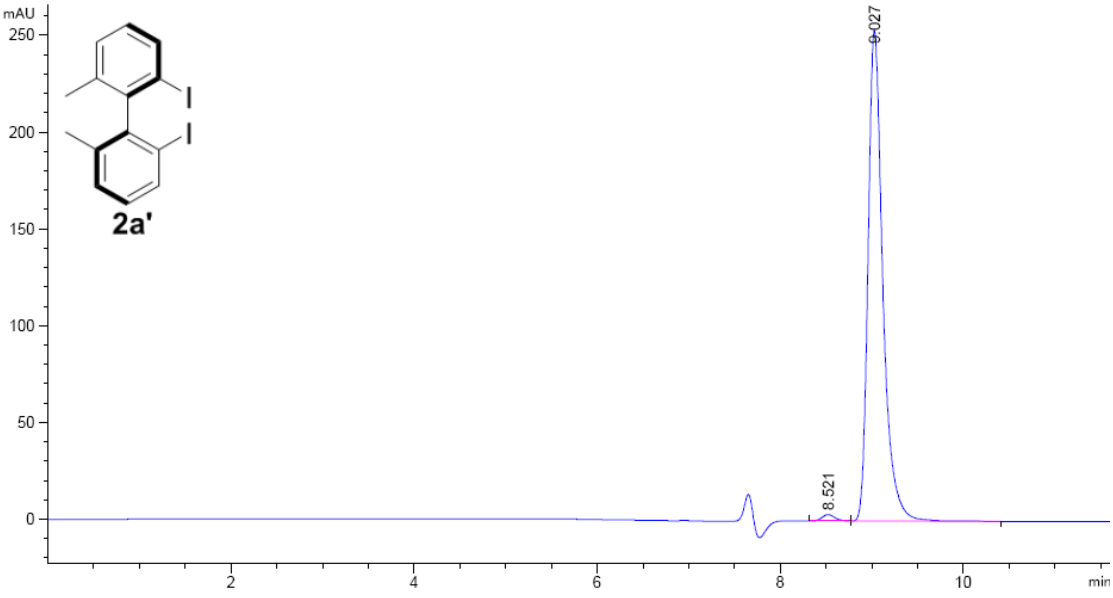

500 MHz, CDCl3
7.8146
7.8106
7.3936
7.3896
7.3095
7.3059
7.3040
7.2484
7.2448
2.0175
1.9737
Cl
I
Cl
Cl
4e
1.00
0.99
1.06
1.06
3.24
3.16
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5


126 MHz, CDCl3
140.5644
139.5504
139.4770
139.0213
136.1596
134.2371
134.1914
134.0996
130.1238
128.8880
127.0664
100.1562
21.1420
20.1487
Cl
I
Cl
Cl
4e
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

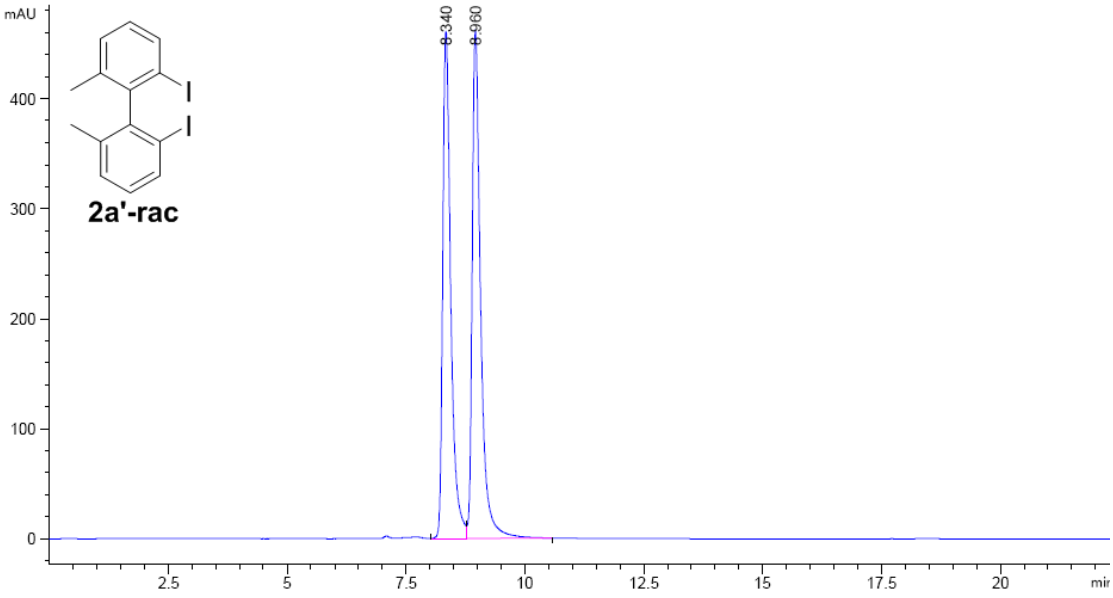

500 MHz, CDCl3
7.8999
7.8977
7.8840
7.8818
7.5348
7.5327
7.5188
7.5165
7.4733
7.4719
7.4564
7.3667
7.3517
7.3494
7.3344
7.1052
7.0893
7.0732
Cl
Cl
I
Cl
4f
1.00
1.01
2.02
1.04
1.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


126 MHz, CDCl3
140.6745
140.0000
137.5450
134.9071
133.6952
130.8378
130.2482
129.3759
128.0421
99.9103
Cl
Cl
I
Cl
4f
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

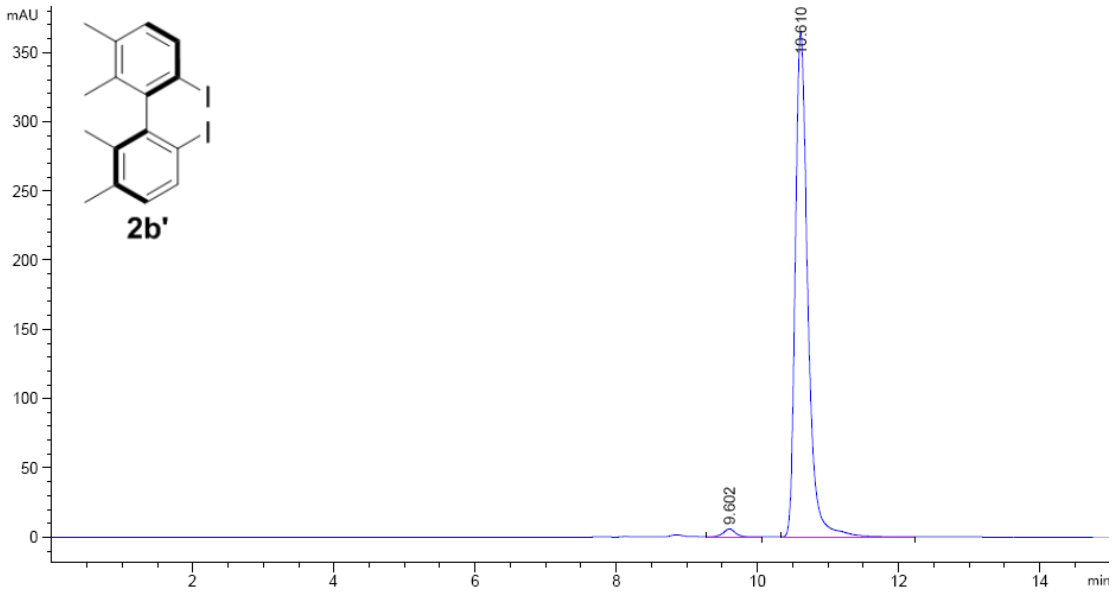
7. Copies of HPLC traces



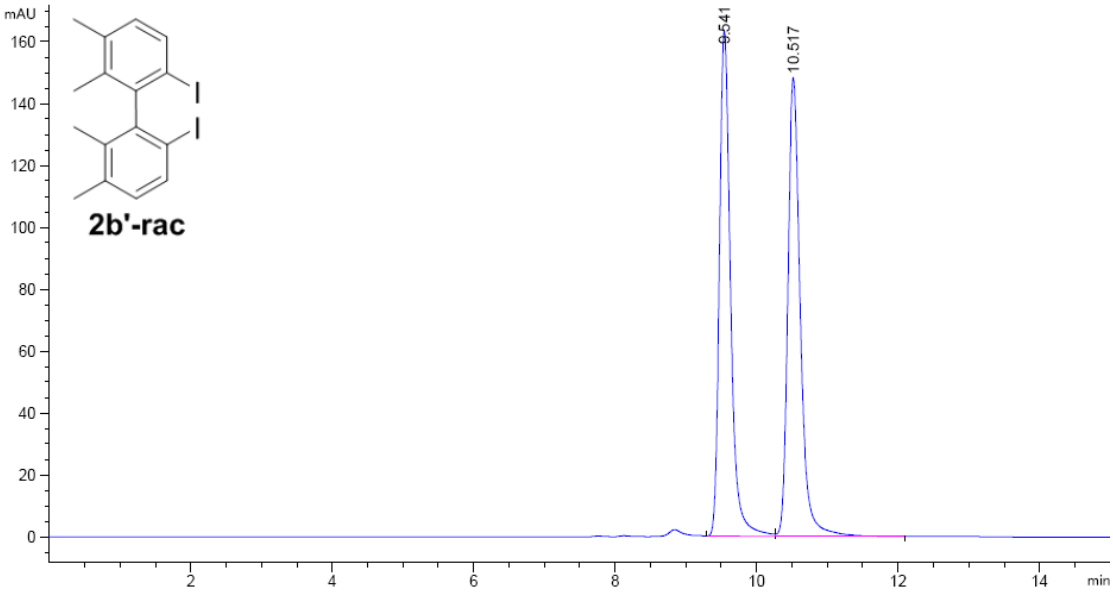
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.521	BB	0.1507	32.22519	3.30797	1.1242
2	9.027	BB	0.1684	2834.33887	253.52258	98.8758



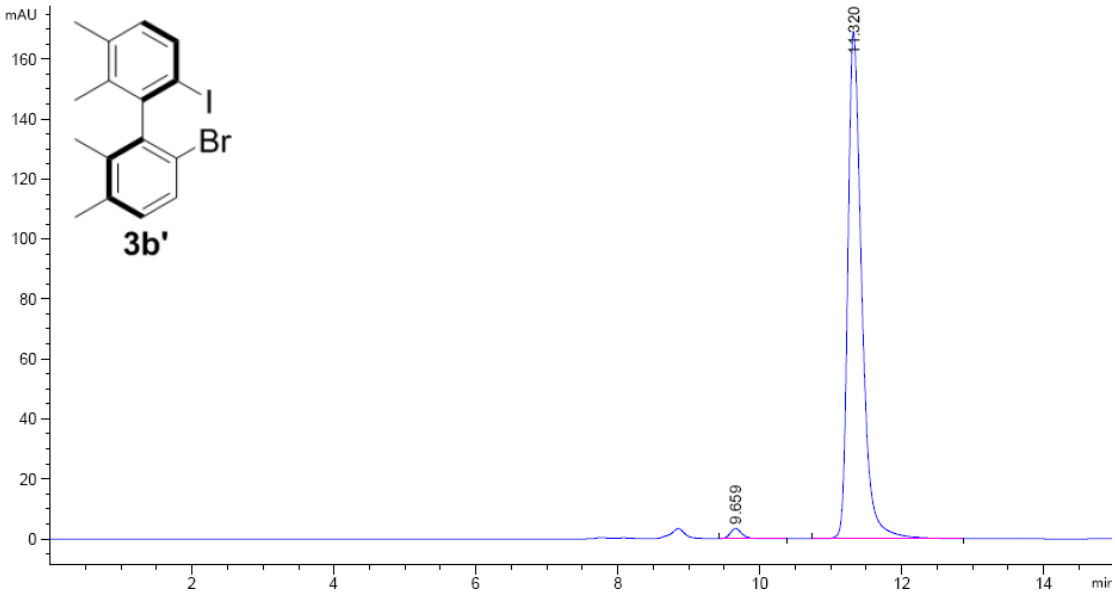
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.340	BV	0.1757	5402.46143	461.12976	48.6453
2	8.960	VB	0.1854	5703.36572	460.92227	51.3547



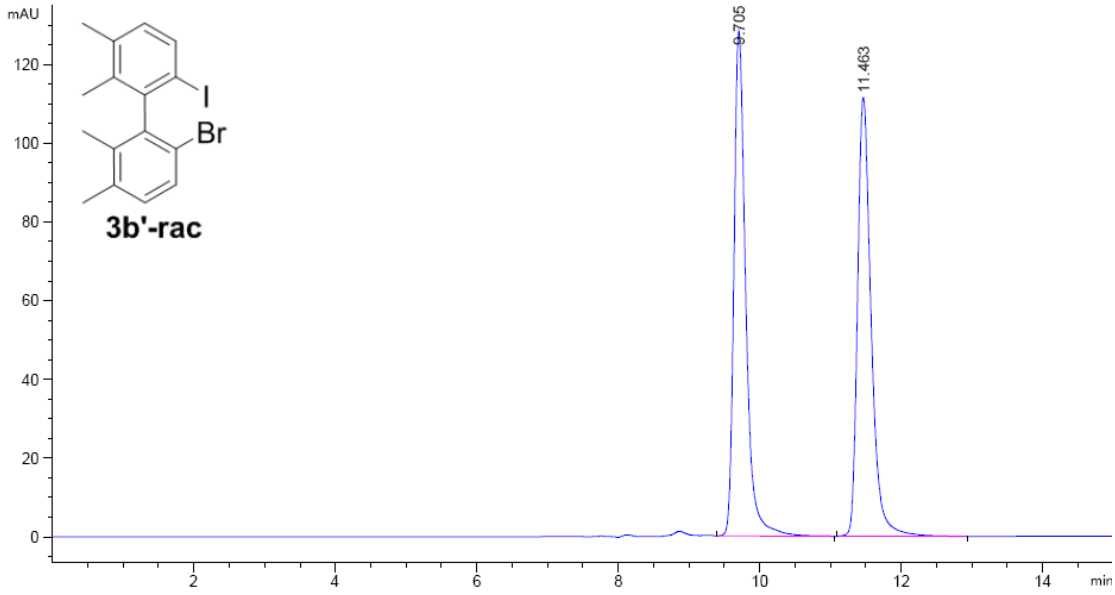
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.602	BB	0.1780	69.10201	5.75862	1.5213
2	10.610	VB	0.1871	4473.06641	364.59198	98.4787



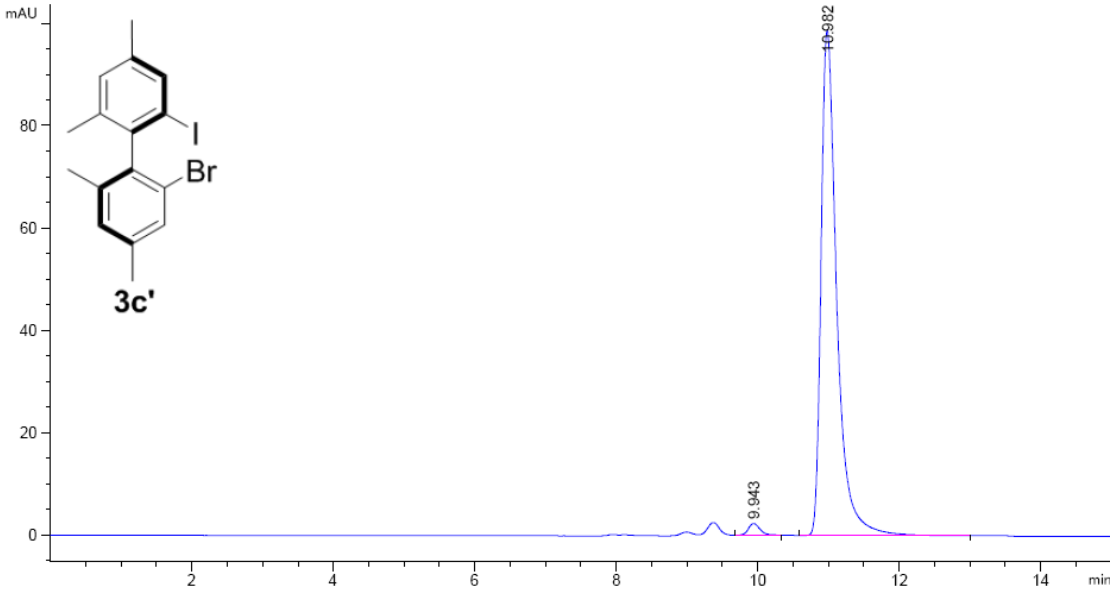
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.541	BV	0.1666	1787.32117	163.39067	49.6819
2	10.517	VB	0.1855	1810.21143	148.19119	50.3181



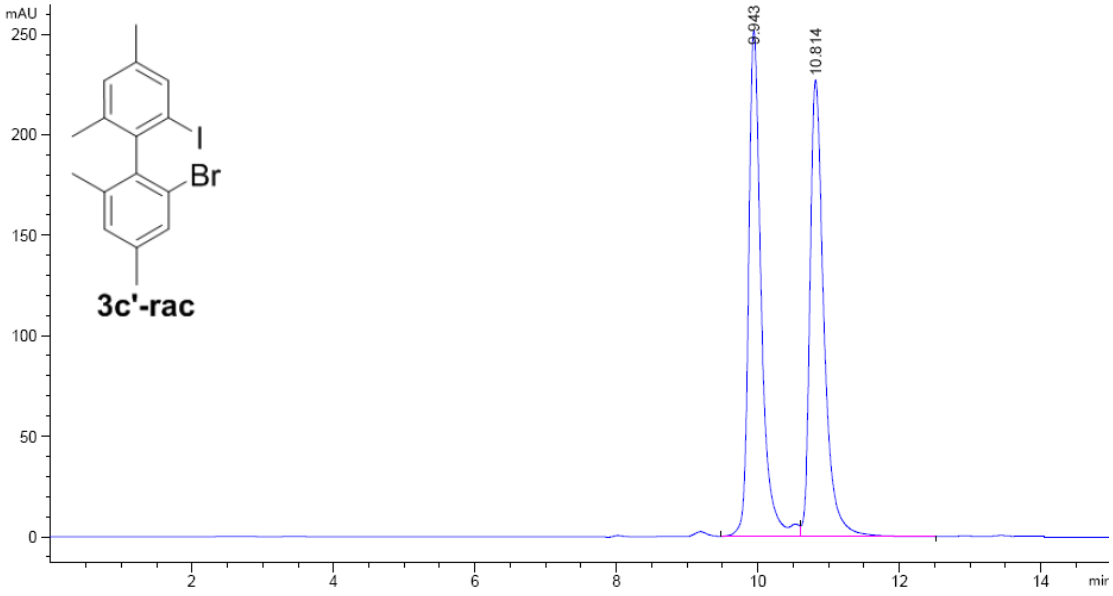
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.659	BB	0.1738	39.48143	3.44281	1.6810
2	11.320	BB	0.2083	2309.24438	169.07312	98.3190



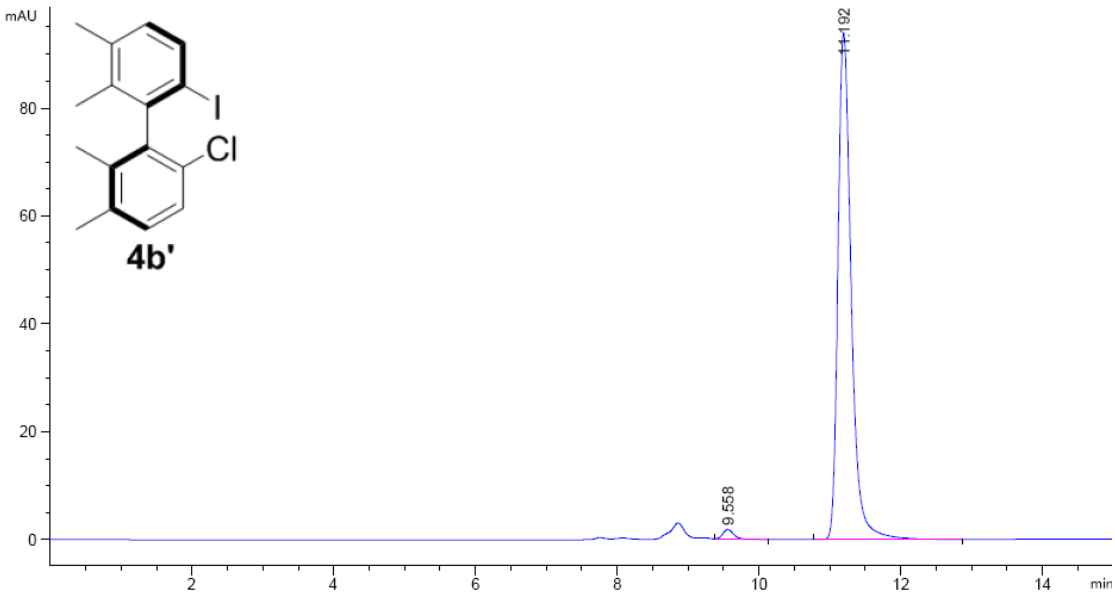
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.705	BB	0.1750	1485.30127	128.35703	49.9959
2	11.463	BB	0.2034	1485.54224	111.50239	50.0041



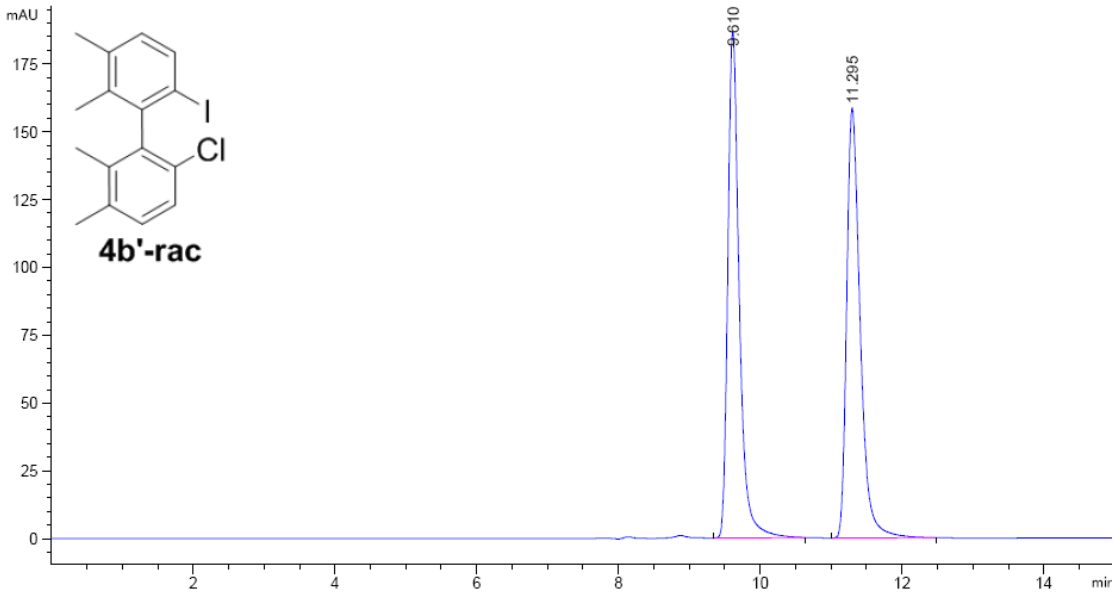
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.943	BB	0.1724	25.73260	2.28467	1.6652
2	10.982	BB	0.2315	1519.54126	98.78271	98.3348



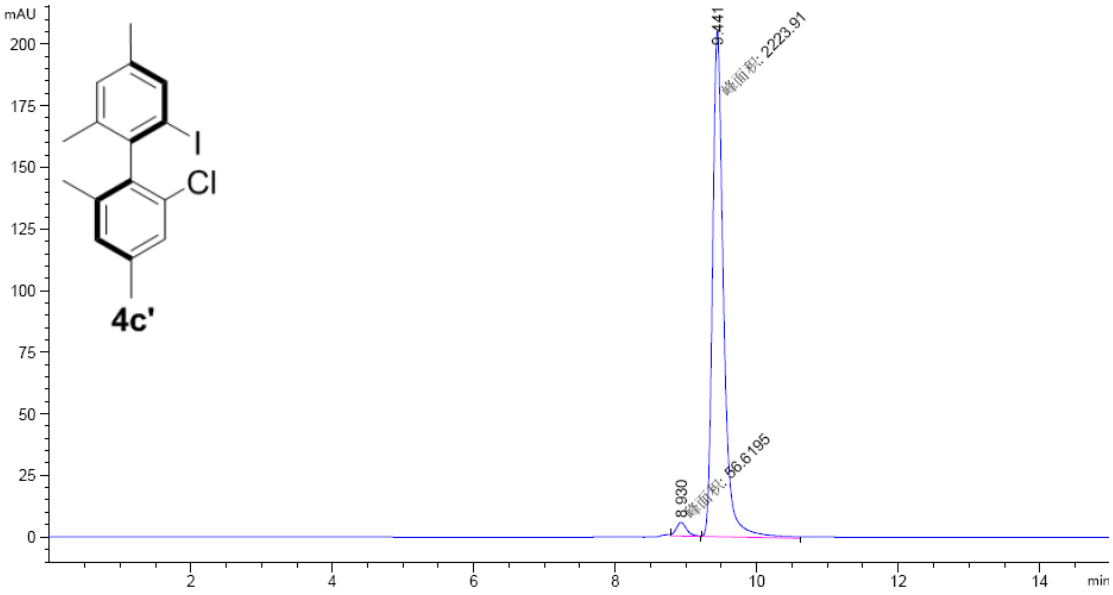
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.943	BV R	0.1843	3137.03638	251.59924	50.3610
2	10.814	VB	0.2059	3092.06519	227.09006	49.6390



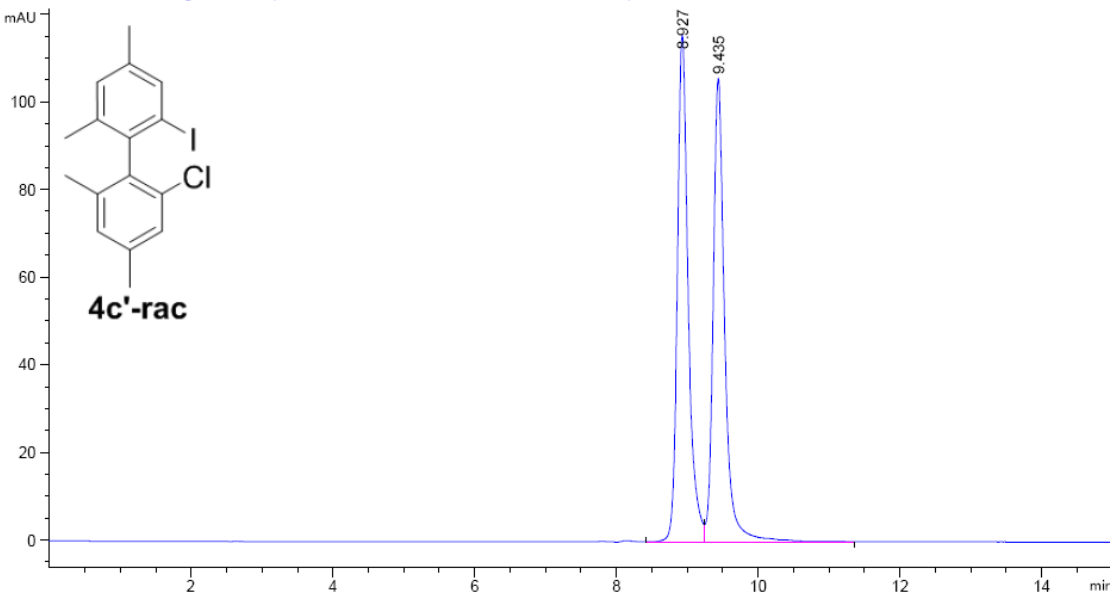
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.558	BB	0.1629	18.72320	1.76256	1.5128
2	11.192	BB	0.1974	1218.89856	93.93652	98.4872



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.610	VB	0.1698	2092.04590	186.60672	49.9456
2	11.295	BB	0.2012	2096.60132	158.67679	50.0544



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.930	MM	0.1716	56.61953	5.50059	2.4827
2	9.441	MM	0.1806	2223.91333	205.29053	97.5173



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.927	BV	0.1572	1220.94690	115.65438	50.6209
2	9.435	VB	0.1694	1190.99744	105.71049	49.3791