Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Preparation of Polyfunctional Biaryl Derivatives by Cyclolanthanation of 2-Bromobiaryls and Heterocyclic Analogues Using *n*Bu_2LaCl·4 LiCl

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Supporting Information

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1. General Considerations

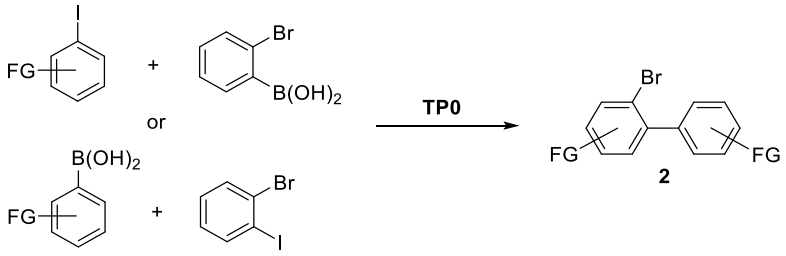
All reactions were carried out under an argon atmosphere in flame-dried glassware with magnetic stirring. Syringes used to transfer anhydrous solvents or reagents were purged with argon prior to use. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Reactions were monitored by gas chromatography (GC and GC-MS) or thin layer chromatography (TLC). GC was performed on instruments of the type Hewlett-Packard 6890 or 5890 Series II, using a column of the type HP 5 and a flame ionization detector. TLC was performed using aluminum plates covered with SiO_2 (Merck 60, F-254) and visualized by UV detection. Purification by column chromatography was performed using Merck silica gel 60 (0.040–0.063 mm, 230–400 mesh ASTM). Yields refer to yields of isolated compounds estimated to be >95% pure as determined by ^{1}H-NMR (25 °C) and GC-analysis. NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer. Chemical shifts are reported as δ-values in ppm relative to the deuterated solvent residual peak ($CDCl_3$: δ = 7.26 ppm for ^{1}H-NMR and 77.0 ppm for ^{13}C-NMR; d^8-THF: δ = 3.58 for ^{1}H-NMR and 67.57 ppm for ^{13}C-NMR). ^{7}Li-NMR spectra were recorded on a 500 MHz spectrometer (195 MHz for ^{7}Li) with saturated THF solution of LiCl as the internal standard (0 ppm). For the characterization of the observed signal multiplicities, the following abbreviations were used: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), dd (doublet of doublet), ddd (doublet of doublet of doublet), dt (doublet of triplet), dq (doublet of quartet), m (multiplet) and br (broad). Melting points were measured using a Büchi B-540 apparatus and are uncorrected. Infrared spectra were recorded in 4000−400 cm^{-1} on a Perkin Elmer Spectrum BX-59343 instrument using a Smiths Detection DuraSampl IR II Diamond ATR sensor. Mass spectra and high-resolution mass spectra (HRMS) were recorded on a Thermo Finnigan LTQ FT Ultra High Performance Mass Spectrometer using electro ionization (EI). $LaCl_3$·2LiCl (ca. 15% in THF, ca. 0.50 mol/L) and *n*BuLi (ca. 23% in hexane) were purchased from Rockwood Lithium company. *n*BuLi was titrated at regular intervals to ensure its accurate concentration. All reagents obtained from commercial sources were used without further purification unless otherwise stated.

Preparation of *n*Bu_2LaCl·4LiCl:

A dry and argon-flushed *Schlenk*-tube was charged with $LaCl_3$·2LiCl (2.0 mL, 1.1 mmol, 1.1 equiv, 0.55 M in THF) and THF (1.0 mL). After cooling to −50 °C, *n*BuLi (0.95 mL, 2.2 mmol, 2.2 equiv, 2.34 M in hexane) was added dropwise, and the resulting solution was stirred at −50 °C for 0.5 h. By this procedure, an orange and turbid solution of *n*Bu_2LaCl·4LiCl was obtained, which can be stored at −50 °C under argon prior to use. (For its NMR analysis, see the attached ^{1}H-NMR and ^{7}Li-NMR spectra for details.)

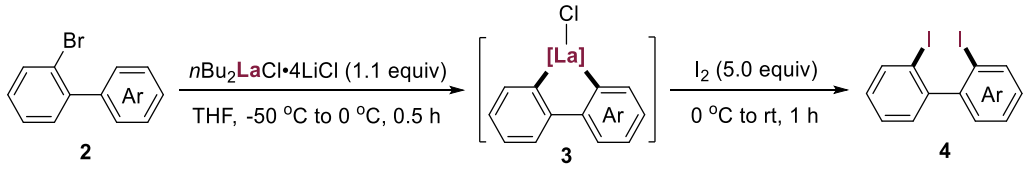
2. Typical Procedures

Typical Procedure for the Synthesis of 2-Bromobiaryls of Type 2 (TP0)



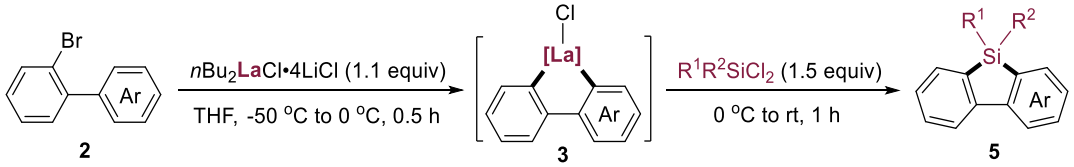
Following a reported procedure,[1] a flask was charged with the corresponding iodobenzene (1.0 equiv), the corresponding boronic acid (1.2 equiv), potassium carbonate (2.0−3.0 equiv), and bis(triphenylphosphine)palladium(II) dichloride (1.5 mol%) or tetrakis(triphenylphosphine)palladium(0) (2.0 mol%). The reactants were dissolved in a degassed mixture of 1,2-dimethoxyethane/water (v/v = 6:1) or a mixture of toluene/ethanol/water (v/v/v = 4:1:1), and the reaction mixture was stirred with heat for 3−24 h. After cooling to room temperature, water was added and the aqueous phase was extracted with ethyl acetate (3 × 15 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Finally, the residue was purified by column chromatography using the indicated mixture of solvents as eluent to give 2-bromobiaryls of type **2.**

Typical Procedure for the Conversion of 2-Bromobiaryls into 2,2'-Diiodobiaryls of Type 4 Using *n*Bu$_2$LaCl·4LiCl (TP1)



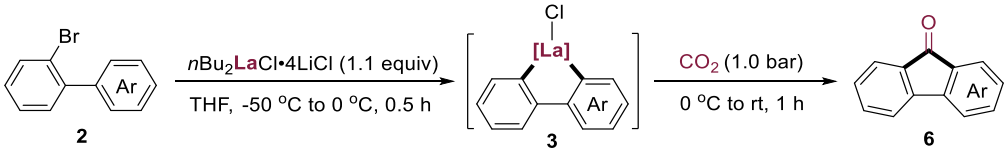
A dry and argon-flushed *Schlenk*-tube was charged with $LaCl_3$·2LiCl (2.0 mL, 1.1 mmol, 1.1 equiv, 0.55 M in THF) and THF (1.0 mL). After cooling to −50 °C, *n*BuLi (0.95 mL, 2.2 mmol, 2.2 equiv, 2.34 M in hexane) was added dropwise, and the resulting orange solution was stirred at −50 °C for 0.5 h. Subsequently, 2-bromobiaryl (**2**, 1.0 mmol, 1.0 equiv) was added at −50 °C. After 5 min, the reaction solution was gradually warmed up to 0 °C. After 0.5 h, the reaction solution was quenched by adding I_2 (1.27 g, 5.0 mmol, 5.0 equiv) at 0 °C and was further stirred at room temperature for 1 h. Then, saturated aqueous $Na_2S_2O_3$ solution (5.0 mL) was added and the reaction mixture was stirred until the brown colour faded away. The aqueous phase was extracted with ethyl acetate (3 × 10 mL) and the combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Finally, the residue was purified by column chromatography using the indicated mixture of solvents as eluent to give the desired product of type **4**.

Typical Procedure for the Direct Synthesis of Silafluorene Derivatives of Type 5 from 2-Bromobiaryls Using *n*Bu$_2$LaCl·4LiCl (TP2)



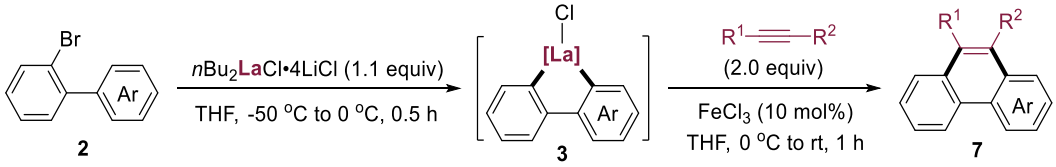
A dry and argon-flushed *Schlenk*-tube was charged with $LaCl_3$·2LiCl (2.0 mL, 1.1 mmol, 1.1 equiv, 0.55 M in THF) and THF (1.0 mL). After cooling to −50 °C, *n*BuLi (0.95 mL, 2.2 mmol, 2.2 equiv, 2.34 M in hexane) was added dropwise, and the resulting orange solution was stirred at −50 °C for 0.5 h. Subsequently, 2-bromobiaryl (**2**, 1.0 mmol, 1.0 equiv) was added at −50 °C. After 5 min, the reaction solution was gradually warmed up to 0 °C. After 0.5 h, the reaction solution was quenched by adding dichlorosilane (1.5 mmol, 1.5 equiv) at 0 °C and was further stirred at room temperature for 1 h. Then, water (5.0 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Finally, the residue was purified by column chromatography using the indicated mixture of solvents as eluent to give the desired product of type **5**. (Other heterofluorenes **10** and **11** were also prepared according to this procedure.)

Typical Procedure for the Synthesis of Fluoren-9-one Derivatives of Type 6 from 2-Bromobiaryls Using *n*Bu$_2$LaCl·4LiCl (TP3)



A dry and argon-flushed *Schlenk*-tube was charged with $LaCl_3$·2LiCl (2.0 mL, 1.1 mmol, 1.1 equiv, 0.55 M in THF) and THF (1.0 mL). After cooling to −50 °C, *n*BuLi (0.95 mL, 2.2 mmol, 2.2 equiv, 2.34 M in hexane) was added dropwise, and the resulting orange solution was stirred at −50 °C for 0.5 h. Subsequently, 2-bromobiaryl (**2**, 1.0 mmol, 1.0 equiv) was added at −50 °C. After 5 min, the reaction solution was gradually warmed up to 0 °C. After 0.5 h, CO_2 was bubbled into the reaction solution at 0 °C for 0.5 h and the reaction solution was further stirred at room temperature for 0.5 h. Then, water (5.0 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Finally, the residue was purified by column chromatography using the indicated mixture of solvents as eluent to give the desired product of type **6**.

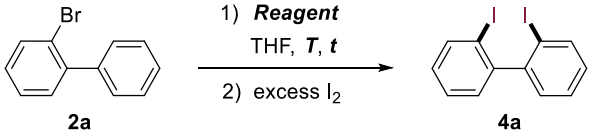
Typical Procedure for the Synthesis of Phenanthrene Derivatives of Type 7 from 2-Bromobiaryls Using *n*Bu$_2$LaCl·4LiCl (TP4)



A dry and argon-flushed *Schlenk*-tube was charged with $LaCl_3$·2LiCl (2.0 mL, 1.1 mmol, 1.1 equiv, 0.55 M in THF) and THF (1.0 mL). After cooling to −50 °C, *n*BuLi (0.95 mL, 2.2 mmol, 2.2 equiv, 2.34 M in hexane) was added dropwise, and the resulting orange solution was stirred at −50 °C for 0.5 h. Subsequently, 2-bromobiaryl (**2**, 1.0 mmol, 1.0 equiv) was added at −50 °C. After 5 min, the reaction solution was gradually warmed up to 0 °C. After 0.5 h, $FeCl_3$ (0.1 mmol, 0.1 equiv) and alkyne (2.0 mmol, 2.0 equiv) were added and the reaction solution was stirred at room temperature for 1 h. Then, water (5.0 mL) was added and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Finally, the residue was purified by column chromatography using the indicated mixture of solvents as eluent to give the desired product of type **7**.

3. Detailed Tables and Proposed Reaction Pathways

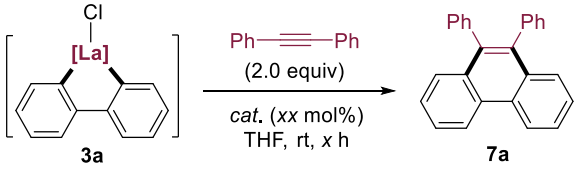
Table S1. Optimization of Conditions for Cyclometalation of 2-Bromobiphenyl **(2a)**



Entry	***Reagent***	***T*** (°C)	***t*** (min)	Conv. of **2a** (%)[a]	Yield of **4a** (%)[a,b]
1	*n*Bu**Li** (2.2 equiv)	−50	30	100	0
2	nBu$_2$**Mg** (1.1 equiv)	rt	60	23	0
3	*n*BuLi (1.1 equiv) then TMP**Mg**Cl·LiCl (1.1 equiv)	−50 to rt	60	100	0
4	nBu$_3$**Sm**·5LiCl (1.1 equiv)	−30	5	100	10
5	nBu$_3$**Sm**·5LiCl (1.1 equiv)	−30 to rt	30	100	31[c]
6	nBu$_2$**Sm**Me·5LiCl (1.1 equiv)	−30 to rt	30	100	31[c]
7	nBu$_2$**Sm**Cl·4LiCl (1.1 equiv)	−30 to rt	30	100	40[c]
8	nBu$_3$**La**·5LiCl (1.1 equiv)	−50 to rt	30	100	49[c]
9	nBu$_2$**La**Cl·4LiCl (1.1 equiv)	−50	15	93	33[d]
10	nBu$_2$**La**Cl·4LiCl (1.1 equiv)	−50	60	100	61[d]
11	nBu$_2$**La**Cl·4LiCl (1.1 equiv)	−50 to rt	30	100	89[d]
12	nBu$_2$**La**Cl·4LiCl (1.1 equiv)	−50 to 0	30	100	90(79[e])
13	nBu$_2$**La**Cl·4LiCl (1.1 equiv)	−50 to 0	60	100	80
14	nBu$_2$**La**Cl·4LiCl (1.1 equiv)	−30 to 0	30	100	84

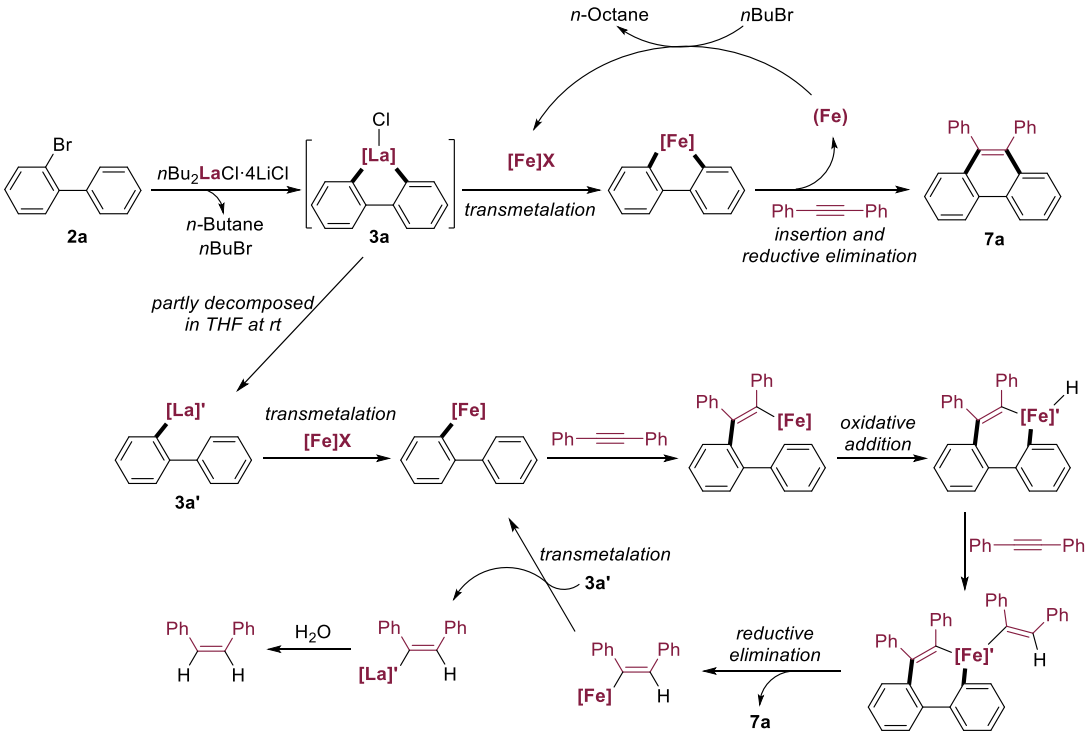
[a] Determined by GC-analysis. [b] The observed by-products were mostly biphenyl, 2-butylbiphenyl and 2-iodobiphenyl. [c] 2-butylbiphenyl was mainly generated. [d] 2-butylbiphenyl was almost not observed. [e] Isolated yield of analytically pure product.

Table S2. Evaluation of Transtion Metal Salts for the Annulation of Alkynes



Entry	***Catalyst***	***t*** (h)	Yield (%)[a]
1	none	12	0
2	$CrCl_2$ (10 mol%)	12	0
3	$CrCl_2$ (10 mol%) / bpy (20 mol%)	12	0
4	$CrCl_3$ (10 mol%)	12	49
5	$CrCl_3$ (100 mol%)	5	75
6	$Fe(acac)_3$ (10 mol%)	5	77
7	$FeCl_3$ (10 mol%)	1	85(79[b])
8	$FeCl_3$ (10 mol%) / bpy (20 mol%)	1	85
9	$FeCl_2$ (10 mol%)	1	83

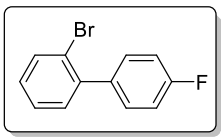
[a] Yields were determined by GC-analysis. [b] Isolated yield of analytically pure product.



Scheme S1. Proposed Role of Fe Catalyst in the Annulation Reaction

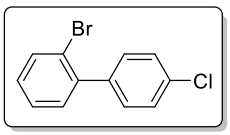
4. Reaction Details and Characterization Data of Compounds

Preparation of 2-bromo-4'-fluoro-1,1'-biphenyl (2b):



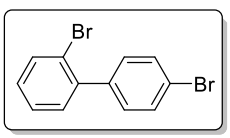
According to **TP0**, a flask was charged with 1-bromo-2-iodobenzene (1.00 g, 3.54 mmol, 1.0 equiv), (4-fluorophenyl)boronic acid (594 mg, 4.25 mmol, 1.2 equiv), K_2CO_3 (1.22 g, 8.85 mmol, 2.5 equiv) and $Pd(PPh_3)_2Cl_2$ (40 mg, 0.053 mmol, 1.5 mol%) in a degassed mixture of DME / H_2O (12 : 2 mL). The reaction mixture was stirred at 80 °C for 6 h. After work-up, purification by column chromatography (SiO_2, *i*-hexane) yielded **2b** (711 mg, 2.83 mmol, 80%) as a colorless oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.70 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.43 − 7.32 (m, 4H), 7.23 (ddd, *J* = 8.0, 6.8, 2.0 Hz, 1H), 7.17 − 7.12 (m, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 162.3 (d, $^1J_{C-F}$ = 245 Hz), 141.6, 137.0 (d, $^4J_{C-F}$ = 3.3 Hz), 133.1, 131.2, 131.0 (d, $^3J_{C-F}$ = 8.0 Hz), 128.8, 127.4, 122.7, 114.9 (d, $^2J_{C-F}$ = 21.3 Hz). **^{19}F-NMR (376 MHz, $CDCl_3$)** δ = −114.4. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3054, 1890, 1606, 1511, 1464, 1221, 1157, 1026, 1005, 833, 753. **MS (EI, 70 eV)** m/z (%) = 252 (87), 250 (90), 171 (45), 170 (100). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{12}H_8BrF$] 249.9793, found 249.9787.

Preparation of 2-bromo-4'-chloro-1,1'-biphenyl (2c):



According to **TP0**, a flask was charged with 1-bromo-2-iodobenzene (1.37 g, 4.83 mmol, 1.0 equiv), (4-chlorophenyl)boronic acid (906 mg, 5.79 mmol, 1.2 equiv), K_2CO_3 (1.67 g, 12.1 mmol, 2.5 equiv) and $Pd(PPh_3)_2Cl_2$ (51 mg, 0.073 mmol, 1.5 mol%) in a degassed mixture of DME / H_2O (15 : 2.5 mL). The reaction mixture was stirred at 80 °C for 8 h. After work-up, purification by column chromatography (SiO_2, *i*-hexane) yielded **2c** (1.02 g, 3.82 mmol, 79%) as a colorless oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.70 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.45 − 7.41 (m, 2H), 7.40 − 7.36 (m, 3H), 7.32 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.24 (ddd, *J* = 8.0, 7.2, 2.0 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 141.2, 139.3, 133.6, 133.2, 131.1, 130.7, 129.0, 128.2, 127.4, 122.4. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3052, 1597, 1495, 1462, 1395, 1090, 1018, 1002, 826, 751, 682. **MS (EI, 70 eV)** m/z (%) = 268 (75), 266 (59), 152 (100). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{12}H_8BrCl$] 265.9498, found 265.9491.

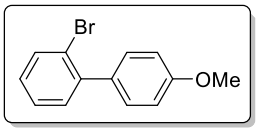
Preparation of 2,4'-dibromo-1,1'-biphenyl (2d):



According to **TP0**, a flask was charged with 1-bromo-4-iodobenzene (849 mg, 3.0 mmol, 1.0 equiv), (2-bromophenyl)boronic acid (663 mg, 3.3 mmol, 1.1 equiv), K_2CO_3 (830 mg, 6.0 mmol, 2.0 equiv) and $Pd(PPh_3)_4$ (70 mg, 0.060 mmol, 2.0 mol%) in a degassed mixture of toluene / ethanol / water (16 : 4 : 4 mL). The reaction mixture was stirred at 80 °C for 5 h. After work-up, purification by column chromatography (SiO_2, *i*-hexane) yielded **2d** (810 mg, 2.60 mmol, 86%) as a colorless oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.67 (dd, *J* = 8.0, 1.2

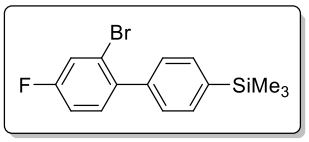
Hz, 1H), 7.58 − 7.55 (m, 2H), 7.37 (td, *J* = 7.6, 1.2 Hz, 1H), 7.31 − 7.28 (m, 3H), 7.22 (ddd, *J* = 7.8, 7.2, 2.0 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 141.3, 139.9, 133.2, 131.1, 131.0, 129.0, 127.5, 122.4, 121.9. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3051, 1898, 1494, 1460, 1390, 1073, 1014, 1000, 822, 750, 671. **MS (EI, 70 eV)** m/z (%) = 312 (80), 310 (43), 152 (100). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{12}H_8Br_2$] 309.8993, found 309.8987.

Preparation of 2-bromo-4'-methoxy-1,1'-biphenyl (2e):



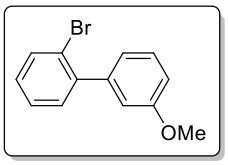
According to **TP0**, a flask was charged with 1-iodo-4-methoxybenzene (936 mg, 4.0 mmol, 1.0 equiv), (2-bromophenyl)boronic acid (884 mg, 4.4 mmol, 1.1 equiv), K_2CO_3 (1.11 g, 8.0 mmol, 2.0 equiv) and $Pd(PPh_3)_4$ (92 mg, 0.080 mmol, 2.0 mol%) in a degassed mixture of toluene / ethanol / water (20 : 5 : 5 mL). The reaction mixture was stirred at 80 °C for 24 h. After work-up, purification by column chromatography (SiO_2, *i*-hexane) yielded **2e** (874 mg, 3.32 mmol, 83%) as a colorless oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.68 − 7.66 (m, 1H), 7.39 − 7.31 (m, 4H), 7.19 (ddd, *J* = 8.0, 6.4, 2.8 Hz, 1H), 7.00 − 6.96 (m, 2H), 3.87 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 159.0, 142.1, 133.5, 133.1, 131.3, 130.5, 128.4, 127.3, 122.9, 113.3, 55.2. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3034, 2834, 1888, 1609, 1514, 1463, 1295, 1241, 1176, 1024, 829, 753, 731. **MS (EI, 70 eV)** m/z (%) = 264 (97), 262 (100), 247 (29), 219 (21), 139 (54). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{13}H_{11}BrO$] 261.9993, found 261.9987.

Preparation of (2'-bromo-4'-fluoro-[1,1'-biphenyl]-4-yl)trimethylsilane (2f):



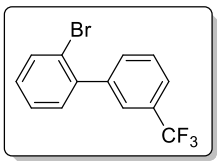
According to **TP0**, a flask was charged with 2-bromo-4-fluoro-1-iodobenzene (690 mg, 2.29 mmol, 1.0 equiv), (4-(trimethylsilyl)phenyl)boronic acid (535 mg, 2.75 mmol, 1.2 equiv), K_2CO_3 (792 mg, 5.74 mmol, 2.5 equiv) and $Pd(PPh_3)_2Cl_2$ (25 mg, 0.035 mmol, 1.5 mol%) in a degassed mixture of DME / H_2O (9 : 1.5 mL). The reaction mixture was stirred at 80 °C for 5 h. After work-up, purification by column chromatography (SiO_2, *i*-hexane) yielded **2f** (550 mg, 1.70 mmol, 74%) as a white solid. **M.p.**: 44 − 45 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.61 (d, *J* = 8.0 Hz, 2H), 7.44 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.32 (dd, *J* = 8.4, 6.0 Hz, 1H), 7.10 (td, *J* = 8.0, 2.8 Hz, 1H), 0.35 (s, 9H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 161.6 (d, $^1J_{C-F}$ = 249 Hz), 140.5, 139.9, 138.8 (d, $^4J_{C-F}$ = 3.6 Hz), 133.8, 133.0, 132.0 (d, $^3J_{C-F}$ = 8.2 Hz), 128.7, 126.5, 122.6 (d, $^3J_{C-F}$ = 9.4 Hz), 120.2 (d, $^2J_{C-F}$ = 24.1 Hz), 114.5 (d, $^2J_{C-F}$ = 20.7 Hz), −1.1. **^{19}F-NMR (376 MHz, $CDCl_3$)** δ = −113.5. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3067, 2955, 1593, 1475, 1376, 1246, 1114, 1002, 828, 806, 754, 692. **MS (EI, 70 eV)** m/z (%) = 324 (16), 322 (17), 309 (99), 307 (100), 165 (18). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{15}H_{16}BrFSi$] 322.0189, found 322.0180.

Preparation of 2-bromo-3'-methoxy-1,1'-biphenyl (2g):



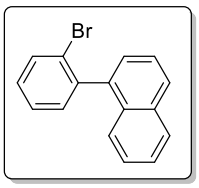
According to **TP0**, a flask was charged with 1-bromo-2-iodobenzene (863 mg, 3.05 mmol, 1.0 equiv), (3-methoxyphenyl)boronic acid (556 mg, 3.66 mmol, 1.2 equiv), K_2CO_3 (1.05g, 7.62 mmol, 2.5 equiv) and $Pd(PPh_3)_2Cl_2$ (35 mg, 0.046 mmol, 1.5 mol%) in a degassed mixture of DME / H_2O (9 : 1.5 mL). The reaction mixture was stirred at 80 °C for 5 h. After work-up, purification by column chromatography (SiO_2, *i*-hexane / ethyl acetate = 10 : 1) yielded **2g** (690 mg, 2.62 mmol, 86%) as a colorless oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.68 − 7.66 (m, 1H), 7.38 − 7.32 (m, 3H), 7.21 (ddd, *J* = 8.0, 6.8, 2.4 Hz, 1H), 7.00 − 6.92 (m, 3H), 3.85 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 159.0, 142.4, 133.1, 131.2, 129.0, 128.8, 127.3, 122.5, 121.8, 115.0, 113.2, 55.3. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3055, 2832, 1924, 1602, 1579, 1465, 1413, 1318, 1209, 1177, 1043, 1015, 860, 751, 696, 658. **MS (EI, 70 eV)** m/z (%) = 264 (97), 262 (100), 168 (25), 152 (35), 139 (45). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{13}H_{11}BrO$] 261.9993, found 261.9987.

Preparation of 2-bromo-3'-trifluoromethyl-1,1'-biphenyl (2h):



According to **TP0**, a flask was charged with 1-iodo-3-(trifluoromethyl)benzene (1.09 g, 4.0 mmol, 1.0 equiv), (2-bromophenyl)boronic acid (884 mg, 4.4 mmol, 1.1 equiv), K_2CO_3 (1.11 g, 8.0 mmol, 2.0 equiv) and $Pd(PPh_3)_4$ (93 mg, 0.08 mmol, 2.0 mol%) in a degassed mixture of toluene / EtOH / H_2O (16 : 4 : 4 mL). The reaction mixture was stirred at 80 °C for 4 h. After work-up, purification by column chromatography (SiO_2, *i*-hexane) yielded **2h** (1.05 g, 4.0 mmol, 87%) as a colorless oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.73 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.70 − 7.64 (m, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H), 7.36 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.28 (ddd, *J* = 8.0, 7.2, 2.0 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 141.7, 141.1, 133.3, 132.8 (d, $^4J_{C-F}$ = 1.2 Hz), 131.1, 130.5 (q, $^2J_{C-F}$ = 32.1 Hz), 129.4, 128.5, 127.6, 126.3 (q, $^3J_{C-F}$ = 3.8 Hz), 124.4 (q, $^3J_{C-F}$ = 3.8 Hz), 124.1 (q, $^1J_{C-F}$ = 271 Hz), 122.4. **^{19}F-NMR (376 MHz, $CDCl_3$)** δ = −62.6. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3062, 1562, 1420, 1332, 1242, 1163, 1118, 1065, 1017, 904, 802, 752, 701, 666. **MS (EI, 70 eV)** m/z (%) = 302 (63), 300 (66), 201 (100), 152 (36). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{13}H_8BrF_3$] 299.9761, found 299.9753.

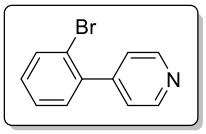
Preparation of 1-(2-bromophenyl)naphthalene (2i):



According to **TP0**, a flask was charged with 1-iodonaphthalene (1.27 g, 5.0 mmol, 1.0 equiv), (2-bromophenyl)boronic acid (1.10 g, 5.5 mmol, 1.1 equiv), K_2CO_3 (1.38 g, 10.0 mmol, 2.0 equiv) and $Pd(PPh_3)_4$ (115 mg, 0.10 mmol, 2.0 mol%) in a degassed mixture of toluene / EtOH / H_2O (20 : 5 : 5 mL). The reaction mixture was stirred at 80 °C for 5 h. After work-up, purification by column chromatography (SiO_2, *i*-hexane) yielded **2i** (1.26 g, 4.45 mmol, 89%) as a white solid. **M.p.**: 87 − 88 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.94 (d, *J* = 8.4 Hz, 2H), 7.76 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.59 − 7.49 (m, 3H), 7.46 − 7.38 (m, 4H), 7.33 (td, *J*

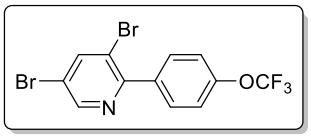
= 7.6, 2.0 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 141.3, 139.0, 133.4, 132.7, 131.9, 131.5, 129.1, 128.2, 128.2, 127.1, 126.9, 126.1, 125.9, 125.8, 125.1, 124.3. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3053, 1931, 1595, 1505, 1474, 1424, 1392, 1254, 1026, 800, 779, 758, 657. **MS (EI, 70 eV)** m/z (%) = 284 (27), 282 (30), 203 (96), 202 (100), 200 (30). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{16}H_{11}Br$] 282.0044, found 282.0037.

Preparation of 4-(2-bromophenyl)pyridine (2j):



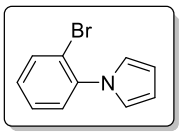
According to **TP0**, a flask was charged with 4-iodopyridine (820 mg, 4.0 mmol, 1.0 equiv), (2-bromophenyl)boronic acid (884 mg, 4.4 mmol, 1.1 equiv), K_2CO_3 (1.10 g, 8.0 mmol, 2.0 equiv) and $Pd(PPh_3)_4$ (92 mg, 0.08 mmol, 2.0 mol%) in a degassed mixture of toluene / EtOH / H_2O (18 : 4.5 : 4.5 mL). The reaction mixture was stirred at 80 °C for 5 h. After work-up, purification by column chromatography (SiO_2, *i*-hexane / ethyl acetate = 2 : 1) yielded **2j** (904 mg, 3.84 mmol, 96%) as an orange oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.65 (dd, *J* = 4.4, 1.6 Hz, 2H), 7.66 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.37 (td, *J* = 7.4, 1.2 Hz, 1H), 7.32 (dd, *J* = 4.4, 1.6 Hz, 2H), 7.28 − 7.22 (m, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 149.5, 148.4, 139.7, 133.3, 130.7, 129.7, 127.6, 124.1, 121.6. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3025, 1931, 1596, 1540, 1464, 1404, 1217, 1072, 1012, 822, 753, 657. **MS (EI, 70 eV)** m/z (%) = 235 (96), 233 (100), 154 (33), 126 (25). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{11}H_8BrN$] 232.9840, found 232.9833.

Preparation of 3,5-dibromo-2-(4-(trifluoromethoxy)phenyl)pyridine (2k):



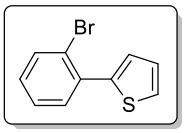
According to a similar procedure,[2] to a solution of 3,5-dibromopyridine (2.37 g, 10.0 mmol, 1.0 equiv) in THF (60 mL) was added dropwise TMPMgCl·LiCl (1.15 M in THF, 9.13 mL, 10.5 mmol, 1.05 equiv) at 0 °C. The solution was stirred at 0 °C for 1 h, and $ZnCl_2$ (1.0 M in THF, 10.5 mL, 10.5 mmol, 1.05 equiv) was subsequently added. The reaction mixture was warmed to room temperature and stirred for 1 h. Then, $Pd(PPh_3)_4$ (462 mg, 0.40 mmol, 4.0 mol%) and 1-iodo-4-(trifluoromethoxy)benzene (2.74 g, 9.5 mmol, 0.95 equiv) were added and the reaction mixture was heated at 50 °C overnight. After work-up, purification by column chromatography (SiO_2, *i*-hexane / ethyl acetate = 15 : 1) yielded **2k** (2.38 g, 6.0 mmol, 63%) as a white solid. **M.p.**: 78 – 79 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.68 (d, *J* = 2.0 Hz, 1H), 8.18 (d, *J* = 1.6 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 155.2, 149.7 (q, $^4J_{C-F}$ = 1.7 Hz), 149.2, 143.4, 136.8, 131.0, 120.4 (d, $^4J_{C-F}$ = 0.7 Hz), 120.4 (q, $^1J_{C-F}$ = 256 Hz), 119.7, 119.2. **^{19}F-NMR (376 MHz, $CDCl_3$)** δ = −57.7. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3041, 2455, 1900, 1607, 1507, 1428, 1359, 1242, 1150, 1060, 1006, 923, 894, 837, 789, 755, 669. **MS (EI, 70 eV)** m/z (%) = 397 (43), 395 (22), 318 (96), 316 (100), 237 (77), 140 (51). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{12}H_6Br_2F_3NO$] 394.8768, found 394.8760.

Preparation of 1-(2-bromophenyl)-1*H*-pyrrole (2l):



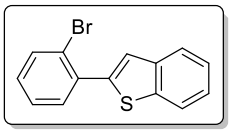
According to a reported procedure,[3] a flask was charged with 2,5-dimethoxytetrahydrofuran (1.46 g, 11.0 mmol, 1.1 equiv), 2-bromoaniline (1.72 g, 10.0 mmol, 1.0 equiv), $CuCl_2$ (135 mg, 1.0 mmol, 10 mol%) and H_2O (30 mL). The reaction mixture was stirred at reflux for 1 h. After work-up, purification by column chromatography (SiO_2, *i*-hexane / ethyl acetate = 8 : 1) yielded **2l** (1.96 g, 8.8 mmol, 88%) as a colorless oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.73 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.44 − 7.36 (m, 2H), 7.27 (ddd, *J* = 8.0, 7.2, 2.0 Hz, 1H), 6.93 (t, *J* = 2.0 Hz, 2H), 6.40 (t, *J* = 2.0 Hz, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 140.2, 133.6, 128.7, 128.2, 128.0, 122.1, 119.7, 109.1. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3102, 1721, 1588, 1493, 1441, 1332, 1115, 1071, 1012, 923, 756, 714. **MS (EI, 70 eV)** m/z (%) = 223 (97), 221 (100), 142 (38), 115 (99). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{10}H_8BrN$] 220.9840, found 220.9833.

Preparation of 2-(2-bromophenyl)thiophene (2m):



According to a reported procedure,[4] to a solution of thiophene (2.52 g, 30.0 mmol, 3.0 equiv) in THF (30 mL) was added dropwise *n*BuLi (12.8 mL, 30.0 mmol, 3.0 equiv, 2.34 M in hexane) at −30 °C. The solution was then stirred at 0 °C for 1 h, and 1,2-dibromobenzene (2.36 g, 10.0 mmol, 1.0 equiv) was subsequently added to the solution. The reaction mixture was warmed to room temperature and stirred for 1 h. After work-up, purification by column chromatography (SiO_2, *i*-hexane) yielded **2m** (2.10 g, 8.79 mmol, 88%) as a colorless oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.70 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.51 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.41 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.37 − 7.32 (m, 2H), 7.22 − 7.18 (m, 1H), 7.14 (dd, *J* = 5.2, 3.6 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 141.7, 135.2, 133.6, 131.9, 129.0, 127.7, 127.4, 126.9, 126.0, 122.8. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3064, 1798, 1587, 1466, 1433, 1261, 1208, 1024, 959, 849, 752, 692. **MS (EI, 70 eV)** m/z (%) = 240 (99), 238 (100), 159 (25), 115 (75). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{10}H_7BrS$] 237.9452, found 237.9444.

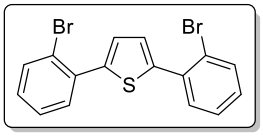
Preparation of 2-(2-bromophenyl)benzo[b]thiophene (2n):



According to a reported procedure,[4] to a solution of benzo[b]thiophene (4.03 g, 30.0 mmol, 3.0 equiv) in THF (30 mL) was added dropwise *n*BuLi (12.8 mL, 30.0 mmol, 3.0 equiv, 2.34 M in hexane) at −30 °C. The solution was then stirred at 0 °C for 1 h, and 1,2-dibromobenzene (2.36 g, 10.0 mmol, 1.0 equiv) was subsequently added to the solution. The reaction mixture was warmed to room temperature and stirred for 1 h. After work-up, purification by column chromatography (SiO_2, *i*-hexane) yielded **2n** (2.34 g, 8.10 mmol, 81%) as a white solid. **M.p.**: 65 − 66 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.89 − 7.84 (m, 2H), 7.73 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.57 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.52 (d, *J* = 0.4 Hz, 1H), 7.43 − 7.35 (m, 3H), 7.27 − 7.22 (m, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 141.9, 140.2, 139.7, 135.3, 133.7, 132.2, 129.6, 127.4, 124.5,

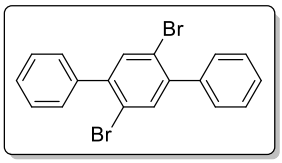
124.4, 124.4, 123.9, 123.0, 122.1. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3053, 1584, 1465, 1432, 1244, 1183, 1027, 940, 860, 833, 756, 726, 668. **MS (EI, 70 eV)** m/z (%) = 290 (99), 288 (100), 208 (34), 165 (92). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{14}H_9BrS$] 287.9608, found 287.9601.

Preparation of 2,5-bis(2-bromophenyl)thiophene (2o):



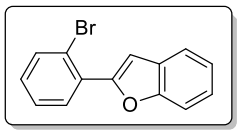
According to **TP0**, a flask was charged with 2,5-diiodothiophene (1.68 g, 5.0 mmol, 1.0 equiv), (2-bromophenyl)boronic acid (2.21 g, 11.0 mmol, 2.2 equiv), K_2CO_3 (2.07 g, 15.0 mmol, 3.0 equiv) and $Pd(PPh_3)_4$ (173 mg, 0.15 mmol, 3.0 mol%) in a degassed mixture of toluene / EtOH / H_2O (30 : 7.5 : 7.5 mL). The reaction mixture was stirred at 80 °C for 8 h. After work-up, purification by column chromatography (SiO_2, *i*-hexane) yielded **2o** (1.62 g, 4.1 mmol, 82%) as a white solid. **M.p.**: 72 − 73 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.70 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.56 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.35 (td, *J* = 7.6, 1.2 Hz, 2H), 7.33 (s, 2H), 7.19 (td, *J* = 7.8, 1.6 Hz, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 142.3, 134.9, 133.8, 131.8, 129.0, 127.6, 127.5, 122.6. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 2354, 1589, 1459, 1252, 1020, 938, 811, 743, 721. **MS (EI, 70 eV)** m/z (%) = 394 (100), 392 (53), 234 (99), 232 (20), 202 (40), 189 (36). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{16}H_{10}Br_2S$] 391.8870, found 391.8864.

Preparation of 1,4-dibromo-2,5-diphenylbenzene (2p):



According to **TP0**, a flask was charged with 1,4-dibromo-2,5-diiodobenzene (1.46 g, 3.0 mmol, 1.0 equiv), phenylboronic acid (805 mg, 6.6 mmol, 2.2 equiv), K_2CO_3 (1.24 g, 9.0 mmol, 3.0 equiv) and $Pd(PPh_3)_4$ (104 mg, 0.09 mmol, 3.0 mol%) in a degassed mixture of toluene / ethanol / water (20 : 5 : 5 mL). The reaction mixture was stirred at 110 °C for 3 h. After work-up, purification by column chromatography (SiO_2, *i*-hexane) yielded **2p** (1.02 g, 2.64 mmol, 88%) as a white solid. **M.p.**: 216 − 217 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.65 (s, 2H), 7.48 − 7.42 (m, 10H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 142.9, 139.4, 135.2, 129.3, 128.1, 128.1, 121.3. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3060, 1767, 1457, 1347, 1241, 1085, 1033, 1007, 890, 758, 695. **MS (EI, 70 eV)** m/z (%) = 388 (100), 386 (52), 228 (81), 226 (74), 113 (30). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{18}H_{12}Br_2$] 385.9306, found 385.9299.

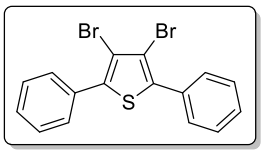
Preparation of 2-(2-bromophenyl)benzofuran (2q):



According to a similar procedure,[4] to a solution of 2,3-benzofuran (3.54 g, 30.0 mmol, 3.0 equiv) in THF (30 mL) was added dropwise *n*BuLi (12.8 mL, 30.0 mmol, 3.0 equiv, 2.34 M in hexane) at −30 °C. The solution was then stirred at 0 °C for 1 h, and 1,2-dibromobenzene (2.36 g, 10.0 mmol, 1.0 equiv) was subsequently added to the solution. The reaction mixture was warmed to room temperature and stirred for 1 h. After work-up,

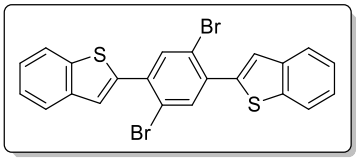
purification by column chromatography (SiO_2, *i*-hexane) yielded **2q** (1.52 g, 5.56 mmol, 56%) as a colorless oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.00 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.73 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.68 − 7.66 (m, 1H), 7.57 − 7.55 (m, 2H), 7.46 − 7.42 (m, 1H), 7.38 − 7.33 (m, 1H), 7.30 − 7.26 (m, 1H), 7.22 (ddd, *J* = 8.0, 7.4, 1.8 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 154.2, 153.1, 134.2, 130.9, 129.7, 129.4, 128.8, 127.4, 124.8, 122.9, 121.4, 120.7, 111.1, 107.0. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3062, 1570, 1452, 1308, 1257, 1207, 1171, 1108, 1010, 920, 886, 804, 742, 699. **MS (EI, 70 eV)** m/z (%) = 274 (98), 272 (100), 193 (18), 165 (84), 164 (20), 163 (23). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{14}H_9BrO$] 271.9837, found 271.9831.

Preparation of 3,4-dibromo-2,5-diphenylthiophene (2r):



According to **TP0**, a flask was charged with perbromothiophene (1.6 g, 4.0 mmol, 1.0 equiv), phenylboronic acid (1.17 g, 9.6 mmol, 2.4 equiv), K_2CO_3 (1.94 g, 14.0 mmol, 3.5 equiv) and $PdCl_2(PPh_3)_2$ (196 mg, 0.28 mmol, 7.0 mol%) in a degassed mixture of DMF / ethanol (16 : 4 mL). The reaction mixture was stirred at 65 °C for 6 h. After work-up, purification by column chromatography (SiO_2, *i*-hexane) yielded **2r** (863 mg, 2.20 mmol, 55%) as a white solid. **M.p.**: 95 − 96 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.69 − 7.66 (m, 4H), 7.50 − 7.40 (m, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 138.1, 132.8, 129.0, 128.8, 128.6, 112.2. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3048, 1594, 1474, 1438, 1288, 1264, 1153, 1072, 1029, 863, 742, 686. **MS (EI, 70 eV)** m/z (%) = 394 (49), 392 (26), 234 (100), 202 (22), 189 (46). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{16}H_{10}Br_2S$] 391.8870, found 391.8863.

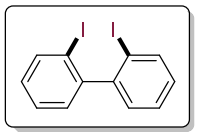
Preparation of 1,4-dibromo-2,5-bis(benzo[b]thiophen-2-yl)benzene (2s):



To a solution of benzo[b]thiophene (1.61 g, 12.0 mmol, 2.4 equiv) in THF (20 mL) was added dropwise *n*BuLi (5.2 mL, 12.0 mmol, 2.4 equiv, 2.34 M in hexane) at −30 °C. The solution was stirred at 0 °C for 1 h and $ZnCl_2$ (1.0 M in THF, 12.0 mL, 12.0 mmol, 2.4 equiv) was subsequently added. The reaction mixture was warmed to room temperature and stirred for 1 h. Then, $Pd(PPh_3)_4$ (578 mg, 0.50 mmol, 10 mol%) and 1,4-dibromo-2,5-diiodobenzene (2.44 g, 5.0 mmol, 1.0 equiv) were added and the reaction mixture was heated at 60 °C overnight. After cooling to room temperature, water was added and the aqueous phase was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Finally, the residue was washed by ethyl acetate to give **2s** (1.45 g, 2.9 mmol, 58%) as a light yellow solid. **M.p.**: 228 − 229 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.91 − 7.85 (m, 6H), 7.60 (s, 2H), 7.44 − 7.37 (m, 4H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 140.3, 139.7, 139.5, 136.4, 136.4, 125.2, 125.0, 124.7, 124.1, 122.1, 121.5. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3054, 1524, 1464, 1430, 1240, 1156, 1066,

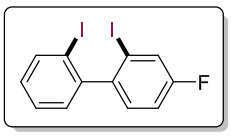
942, 882, 834, 748, 720. **MS (EI, 70 eV)** m/z (%) = 500 (44), 498 (22), 340 (13), 126 (23), 58 (44), 43 (100). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{22}H_{12}Br_2S_2$] 497.8747, found 497.8753.

Synthesis of 2,2'-diiodo-1,1'-biphenyl (4a):



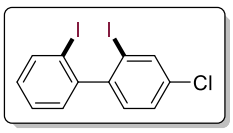
According to **TP1**, 2-bromobiphenyl (**2a**, 233 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **4a** (320 mg, 0.79 mmol, 79%) as a white solid. **M.p.**: 110 − 111 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.98 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.44 (td, *J* = 7.4, 1.2 Hz, 2H), 7.22 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.12 (td, *J* = 7.6, 1.6 Hz, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 148.8, 138.8, 129.8, 129.3, 127.9, 99.6. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 2918, 1556, 1450, 1428, 1254, 1014, 997, 942, 753, 719. **MS (EI, 70 eV)** m/z (%) = 406 (5), 280 (13), 279 (100), 152 (62), 151 (16), 150 (15). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{12}H_8I_2$] 405.8715, found 405.8710.

Synthesis of 4-fluoro-2,2'-diiodo-1,1'-biphenyl (4b):



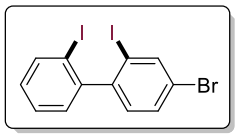
According to **TP1**, 2-bromo-4'-fluoro-1,1'-biphenyl (**2b**, 251 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **4b** (348 mg, 0.82 mmol, 82%) as a white solid. **M.p.**: 61 − 62 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.96 − 7.94 (m, 1H), 7.68 − 7.65 (m, 1H), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H), 7.20 − 7.14 (m, 3H), 7.12 − 7.08 (m, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 161.4 (d, $^1J_{C-F}$ = 251 Hz), 148.0, 145.2 (d, $^4J_{C-F}$ = 3.6 Hz), 138.9, 130.6 (d, $^3J_{C-F}$ = 8.2 Hz), 130.1, 129.6, 128.1, 125.8 (d, $^2J_{C-F}$ = 23.5 Hz), 115.2 (d, $^2J_{C-F}$ = 21.0 Hz), 100.0, 99.1 (d, $^3J_{C-F}$ = 8.1 Hz). **^{19}F-NMR (376 MHz, $CDCl_3$)** δ = −112.7. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 2921, 1890, 1573, 1490, 1455, 1380, 1248, 1194, 999, 855, 822, 759, 718. **MS (EI, 70 eV)** m/z (%) = 424 (4), 297 (12), 170 (12), 61 (12), 45 (13), 43 (100). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{12}H_7FI_2$] 423.8621, found 423.8610.

Synthesis of 4-chloro-2,2'-diiodo-1,1'-biphenyl (4c):



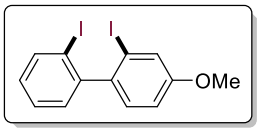
According to **TP1**, 2-bromo-4'-chloro-1,1'-biphenyl (**2c**, 268 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **4c** (370 mg, 0.84 mmol, 84%) as a white solid. **M.p.**: 70 − 71 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.96 − 7.93 (m, 2H), 7.45 − 7.40 (m, 2H), 7.17 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.13 − 7.08 (m, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 147.8, 147.4, 138.9, 138.2, 134.1, 130.4, 129.9, 129.6, 128.3, 128.1, 99.7, 99.4. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3050, 2922, 1892, 1574, 1478, 1450, 1368, 1248, 1095, 1018, 996, 820, 753, 688. **MS (EI, 70 eV)** m/z (%) = 440 (5), 313 (100), 186 (58), 150 (20). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{12}H_7ClI_2$] 439.8326, found 439.8320.

Synthesis of 4-bromo-2,2'-diiodo-1,1'-biphenyl (4d):



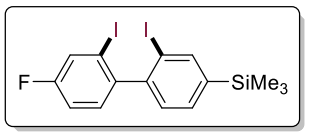
According to **TP1**, 2,4'-dibromo-1,1'-biphenyl (**2d**, 312 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **4d** (296 mg, 0.61 mmol, 61%) as a white solid. **M.p.**: 74 − 75 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.10 (d, *J* = 2.0 Hz, 1H), 7.94 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.56 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.42 (td, *J* = 7.4, 1.2 Hz, 1H), 7.16 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.10 (td, *J* = 7.8, 1.6 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 147.8, 147.8, 140.8, 139.0, 131.2, 130.8, 129.8, 129.6, 128.1, 122.1, 100.2, 99.3. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3046, 2923, 1568, 1448, 1364, 1244, 1082, 1015, 994, 878, 818, 754, 676. **MS (EI, 70 eV)** m/z (%) = 486 (8), 484 (9), 357 (100), 230 (36), 151 (36), 150 (38). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{12}H_7BrI_2$] 483.7820, found 483.7818.

Synthesis of 2,2'-diiodo-4-methoxy-1,1'-biphenyl (4e):



According to **TP1**, 2-bromo-4'-methoxy-1,1'-biphenyl (**2e**, 263 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane / ethyl acetate = 10 : 1) yielded the desired product **4e** (349 mg, 0.80 mmol, 80%) as a light yellow solid. **M.p.**: 87 − 88 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.94 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.46 (d, *J* = 2.8 Hz, 1H), 7.40 (td, *J* = 7.4, 1.2 Hz, 1H), 7.20 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.10 − 7.05 (m, 2H), 6.97 (dd, *J* = 8.6, 2.6 Hz, 1H), 3.85 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 159.2, 148.6, 141.6, 138.8, 130.4, 130.1, 129.2, 128.0, 123.7, 114.1, 100.7, 99.6, 55.5. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3053, 2834, 1593, 1491, 1455, 1285, 1220, 1025, 876, 809, 750, 722. **MS (EI, 70 eV)** m/z (%) = 436 (16), 309 (100), 182 (37), 167 (29), 139 (47). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{13}H_{10}I_2O$] 435.8821, found 435.8814.

Synthesis of 4-fluoro-4'-trimethylsilyl-2,2'-diiodo-1,1'-biphenyl (4f):

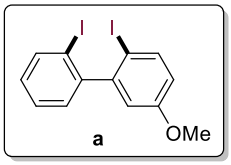


According to **TP1**, (2'-bromo-4'-fluoro-[1,1'-biphenyl]-4-yl)trimethylsilane (**2f**, 323 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **4f** (376 mg, 0.76 mmol, 76%) as a colorless oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.05 (d, *J* = 0.8 Hz, 1H), 7.68 − 7.65 (m, 1H), 7.53 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.17 − 7.13 (m, 3H), 0.32 (s, 9H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 161.3 (d, $^1J_{C-F}$ = 251 Hz), 148.0, 145.2 (d, $^4J_{C-F}$ = 3.5 Hz), 143.5 (d, $^3J_{C-F}$ = 8.4 Hz), 132.9, 130.6 (d, $^3J_{C-F}$ = 8.2 Hz), 129.6, 129.6, 125.8 (d, $^2J_{C-F}$ = 23.5 Hz), 115.2 (d, $^2J_{C-F}$ = 21.0 Hz), 100.8, 98.9 (d, $^3J_{C-F}$ = 8.1 Hz), −1.2. **^{19}F-NMR (376 MHz, $CDCl_3$)** δ = −112.8. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 2954, 1593, 1493, 1358, 1248, 1199, 1112, 1060, 998, 815,

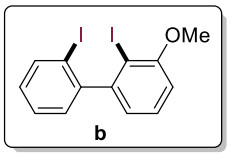
753, 656. **MS (EI, 70 eV)** m/z (%) = 496 (1), 369 (100), 227 (27). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{15}H_{15}FI_2Si$] 495.9016, found 495.9008.

Synthesis of 2,2'-diiodo-(5 or 3)-methoxy-1,1'-biphenyl (4g):

According to **TP1**, 2-bromo-3'-methoxy-1,1'-biphenyl (**2g**, 263 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane / ethyl acetate = 8 : 1) yielded the desired product **4g** (379 mg, 0.87 mmol, 87%), which contains **4ga** (305 mg, 0.70 mmol) and **4gb** (74 mg, 0.17 mmol).

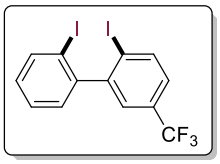


White solid. **M.p.**: 89 − 90 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.94 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.42 (td, *J* = 7.5, 1.2 Hz, 1H), 7.20 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.09 (td, *J* = 7.8, 1.6 Hz, 1H), 6.77 (d, *J* = 2.8 Hz, 1H), 6.70 (dd, *J* = 8.6, 3.0 Hz, 1H), 3.81 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 159.6, 149.6, 148.7, 139.4, 138.9, 129.8, 129.3, 128.0, 115.8, 115.6, 99.4, 88.1, 55.4. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3059, 2936, 2834, 1561, 1455, 1412, 1310, 1262, 1124, 1006, 851, 779, 753, 714. **MS (EI, 70 eV)** m/z (%) = 436 (28), 309 (99), 182 (29), 167 (37), 139 (100). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{13}H_{10}I_2O$] 435.8821, found 435.8812.



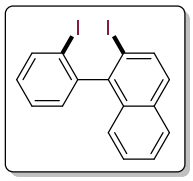
Colorless oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.94 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.42 (td, *J* = 7.4, 1.2 Hz, 1H), 7.37 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.18 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.08 (td, *J* = 7.8, 1.6 Hz, 1H), 6.83 (td, *J* = 8.0, 1.2 Hz, 2H), 3.95 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 158.2, 150.8, 149.1, 138.8, 129.8, 129.2, 129.0, 128.0, 122.3, 109.7, 99.5, 91.9, 56.5. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3049, 2932, 2834, 1561, 1457, 1297, 1209, 1176, 1015, 853, 804, 754, 723. **MS (EI, 70 eV)** m/z (%) = 436 (6), 309 (100), 182 (13), 167 (15), 152 (14), 139 (63). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{13}H_{10}I_2O$] 435.8821, found 435.8811.

Synthesis of 2,2'-diiodo-5-trifluoromethyl-1,1'-biphenyl (4h):



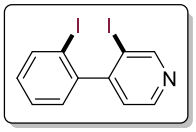
According to **TP1**, 2-bromo-3'-trifluoromethyl-1,1'-biphenyl (**2h**, 300 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **4h** (341 mg, 0.72 mmol, 72%) as a yellow solid. **M.p.**: 62 − 63 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.08 (dd, *J* = 8.4, 0.4 Hz, 1H), 7.98 − 7.96 (m, 1H), 7.47 − 7.43 (m, 2H), 7.35 − 7.32 (m, 1H), 7.21 − 7.19 (m, 1H), 7.13 (ddd, *J* = 8.0, 7.6, 1.6 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 149.6, 147.6, 139.6, 139.1, 130.6 (q, $^2J_{C-F}$ = 32.8 Hz), 129.9, 129.8, 128.2, 126.5 (q, $^3J_{C-F}$ = 3.7 Hz), 125.8 (q, $^3J_{C-F}$ = 3.6 Hz), 123.8 (q, $^1J_{C-F}$ = 271 Hz), 104.2, 99.0. **^{19}F-NMR (376 MHz, $CDCl_3$)** δ = −62.8. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 2929, 1916, 1604, 1426, 1398, 1331, 1282, 1254, 1175, 1131, 1082, 1064, 1003, 895, 825, 755, 719. **MS (EI, 70 eV)** m/z (%) = 474 (2), 347 (100), 220 (55), 201 (13), 170 (11). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{13}H_7F_3I_2$] 473.8589, found 473.8581.

Synthesis of 2-iodo-1-(2-iodophenyl)naphthalene (4i):



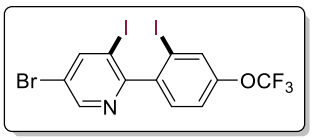
According to **TP1**, 1-(2-bromophenyl)naphthalene (**2i**, 283 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **4i** (260 mg, 0.57 mmol, 57%) as a white solid. **M.p.**: 100 − 101 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.09 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.58 − 7.53 (m, 2H), 7.45 − 7.41 (m, 1H), 7.30 − 7.20 (m, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 147.5, 146.0, 139.2, 135.3, 132.7, 132.6, 130.7, 129.5, 129.4, 128.5, 128.0, 127.0, 126.5, 126.4, 100.3, 98.7. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3052, 1576, 1499, 1421, 1312, 1250, 1126, 1092, 1014, 959, 819, 796, 753, 725, 658. **MS (EI, 70 eV)** m/z (%) = 456 (34), 329 (53), 202 (100), 200 (31). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{16}H_{10}I_2$] 455.8872, found 455.8866.

Synthesis of 3-iodo-4-(2-iodophenyl)pyridine (4j):



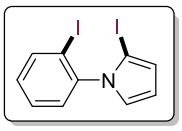
According to **TP1**, 4-(2-bromophenyl)pyridine (**2j**, 117 mg, 0.5 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane / ethyl acetate = 1 : 1) yielded the desired product **4j** (134 mg, 0.33 mmol, 66%) as an organge solid. **M.p.**: 125 − 126 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 9.05 (s, 1H), 8.60 (d, *J* = 4.8 Hz, 1H), 7.97 − 7.94 (m, 1H), 7.47 − 7.43 (m, 1H), 7.18 − 7.12 (m, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 157.4, 156.0, 148.8, 146.2, 139.2, 130.1, 129.1, 128.3, 125.0, 99.0, 97.3. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 2924, 1935, 1569, 1442, 1392, 1264, 1172, 1082, 1001, 834, 756, 684. **MS (EI, 70 eV)** m/z (%) = 407 (13), 280 (100), 153 (39), 126 (37). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{11}H_7I_2N$] 406.8668, found 406.8663.

Synthesis of 5-bromo-3-iodo-2-(2-iodo-4-(trifluoromethoxy)phenyl)pyridine (4k):



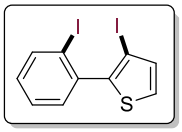
According to **TP1**, 3,5-dibromo-2-(4-(trifluoromethoxy)phenyl)pyridine (**2k**, 100 mg, 0.25 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane / ethyl acetate = 15 : 1) yielded the desired product **4k** (112 mg, 0.20 mmol, 79%) as an orange oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.70 (d, *J* = 2.0 Hz, 1H), 8.39 (d, *J* = 2.4 Hz, 1H), 7.78 (dd, *J* = 2.0, 1.2 Hz, 1H), 7.33 − 7.30 (m, 1H), 7.27 − 7.24 (m, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 161.2, 149.6, 148.9, 148.3, 144.6, 131.2, 130.1, 120.7, 120.3 (q, $^1J_{C-F}$ = 257 Hz), 119.9, 97.1, 96.0. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3045, 2958, 1593, 1545, 1487, 1422, 1359, 1246, 1160, 1101, 1004, 891, 822, 782, 761, 666. **MS (EI, 70 eV)** m/z (%) = 571 (11), 569 (12), 444 (95), 442 (100), 317 (27), 315 (29), 139 (22). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{12}H_5BrF_3I_2NO$] 568.7596, found 568.7599.

Synthesis of 2-iodo-1-(2-iodophenyl)-1*H*-pyrrole (4l):



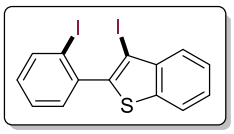
According to **TP1**, 1-(2-bromophenyl)-1*H*-pyrrole (**2l**, 222 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **4l** (319 mg, 0.81 mmol, 81%) as a grey solid. **M.p.**: 80 − 81 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.95 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.46 (td, *J* = 7.6, 1.2 Hz, 1H), 7.31 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.19 (ddd, *J* = 7.8, 7.4, 1.6 Hz, 1H), 6.89 (dd, *J* = 3.2, 1.6 Hz, 1H), 6.53 (dd, *J* = 3.6, 2.0 Hz, 1H), 6.34 (dd, *J* = 3.6, 3.2 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 143.8, 139.4, 130.5, 129.8, 128.8, 125.2, 119.3, 111.8, 99.6, 70.2. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3060, 1714, 1579, 1474, 1439, 1378, 1320, 1192, 1048, 1016, 940, 759, 708. **MS (EI, 70 eV)** m/z (%) = 395 (100), 268 (72), 141 (94), 140 (39), 114 (28). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{10}H_7I_2N$] 394.8668, found 394.8663.

Synthesis of 3-iodo-2-(2-iodophenyl)thiophene (4m):



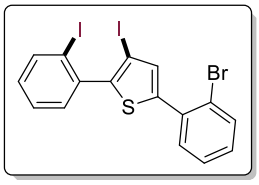
According to **TP1**, 2-(2-bromophenyl)thiophene (**2m**, 239 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **4m** (330 mg, 0.80 mmol, 80%) as a white solid. **M.p.**: 106 − 107 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.96 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.42 (td, *J* = 7.4, 1.2 Hz, 1H), 7.36 − 7.34 (m, 2H), 7.14 − 7.10 (m, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 144.9, 139.5, 139.2, 134.8, 131.7, 130.4, 128.0, 127.4, 101.4, 82.6. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3104, 1581, 1458, 1414, 1333, 1136, 1014, 963, 854, 755, 712. **MS (EI, 70 eV)** m/z (%) = 412 (8), 285 (16), 158 (16), 43 (100). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{10}H_6I_2S$] 411.8280, found 411.8270.

Synthesis of 3-iodo-2-(2-iodophenyl)benzo[b]thiophene (4n):



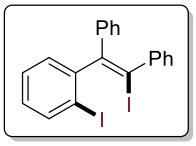
According to **TP1**, 2-(2-bromophenyl)benzo[b]thiophene (**2n**, 289 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **4n** (342 mg, 0.74 mmol, 74%) as a white solid. **M.p.**: 141 − 142 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.00 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.84 − 7.82 (m, 2H), 7.53 − 7.39 (m, 4H), 7.19 − 7.15 (m, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 144.5, 140.7, 139.9, 139.2, 131.5, 130.6, 128.0, 126.0, 125.8, 125.5, 122.3, 100.4, 83.7. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3046, 1538, 1456, 1428, 1246, 1159, 1013, 968, 874, 744, 722. **MS (EI, 70 eV)** m/z (%) = 462 (23), 335 (70), 208 (100), 163 (24). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{14}H_8I_2S$] 461.8436, found 461.8433.

Synthesis of 5-(2-bromophenyl)-3-iodo-2-(2-iodophenyl)thiophene (4o):



According to **TP1**, 2,5-bis(2-bromophenyl)thiophene (**2o**, 394 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **4o** (469 mg, 0.83 mmol, 83%) as an orange oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.98 (d, *J* = 8.0 Hz, 1H), 7.69 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.53 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.45 − 7.43 (m, 2H), 7.36 (td, *J* = 7.6, 1.2 Hz, 1H), 7.33 (s, 1H), 7.22 (td, *J* = 7.8, 1.6 Hz, 1H), 7.14 (ddd, *J* = 8.0, 6.0, 3.0 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 145.5, 143.5, 139.3, 139.3, 134.8, 133.8, 133.8, 131.8, 131.6, 130.5, 129.6, 128.0, 127.6, 122.6, 101.3, 82.2. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3051, 1918, 1582, 1455, 1314, 1253, 1136, 1016, 970, 904, 835, 749, 726. **MS (EI, 70 eV)** m/z (%) = 568 (46), 566 (47), 441 (38), 439 (39), 314 (38), 312 (38), 233 (40), 232 (63), 189 (100). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{16}H_9BrI_2S$] 565.7698, found 565.7701.

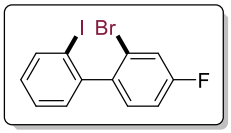
Synthesis of (Z)-(1-iodo-2-(2-iodophenyl)ethene-1,2-diyl)dibenzene (4p):



A dry and argon-flushed *Schlenk*-tube was charged with 2-bromo-1,1,2-triphenylethylene (**2p**, 168 mg, 0.5 mmol, 1.0 equiv), $LaCl_3$·2LiCl (1.0 mL, 0.55 mmol, 1.1 equiv, 0.55 M in THF) and THF (0.5 mL). After cooling to −78 °C, *t*BuLi (0.92 mL, 1.65 mmol, 3.3 equiv, 1.80 M in hexane) was added dropwise, and the resulting orange solution was stirred at −78 °C for 10 min and then was gradually warmed up to 0 °C. After 0.5 h, the reaction solution was quenched by adding I_2 (635 mg, 2.5 mmol, 5.0 equiv) at 0 °C and was further stirred at room temperature for 1 h. Then, saturated aqueous $Na_2S_2O_3$ solution (5.0 mL) was added and the reaction mixture was stirred until the brown colour faded away. The aqueous phase was extracted with ethyl acetate (3 × 10 mL) and the combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Finally, the residue was purified by column chromatography (SiO_2, *i*-hexane) to give the desired product **4p** (147 mg, 0.29 mmol, 58%) as a colorless solid. **M.p.**: 171 − 172 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.96 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.46 – 7.38 (m, 3H), 7.31 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.24 – 7.17 (m, 3H), 7.09 – 7.03 (m, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 151.3, 150.3, 143.8, 139.6, 138.0, 130.3, 129.9, 129.8, 129.0, 128.6, 128.1, 128.0, 127.7, 127.1, 105.2, 99.3. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 2918, 1574, 1484, 1428, 1220, 1156, 1078, 1013, 954, 789, 738, 692. **MS (EI, 70 eV)** m/z (%) = 508 (2), 381 (37), 254 (100), 252 (44). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{20}H_{14}I_2$] 507.9185, found 507.9181.

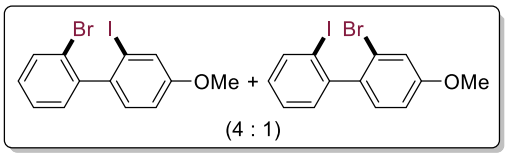
Synthesis of 2-bromo-4-fluoro-2'-iodo-1,1'-biphenyl (8a):

A dry and argon-flushed *Schlenk*-tube was charged with 4-fluoro-2,2'-diiodo-1,1'-biphenyl (**4b**, 212 mg, 0.5 mmol, 1.0 equiv) in THF (2.0 mL). After cooling to −40 °C, *i*PrMgCl·LiCl (0.41 mL, 0.5 mmol, 1.0 equiv, 1.22 M in THF) was added dropwise, and the resulting solution was stirred at −40 °C for 1 h. Subsequently, 1,2-dibromotetrachloroethane (195 mg, 0.6 mmol, 1.2 equiv) was added and the reaction



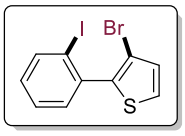
solution was further stirred at room temperature for 1 h. After work-up, purification by column chromatography (SiO_2, *i*-hexane) yielded **8a** (158 mg, 0.42 mmol, 84%) as a colorless oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.96 − 7.94 (m, 1H), 7.44 − 7.40 (m, 2H), 7.23 − 7.17 (m, 2H), 7.13 − 7.07 (m, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 161.8 (d, $^1J_{C\text{-}F}$ = 250 Hz), 145.1, 141.1 (d, $^4J_{C\text{-}F}$ = 3.6 Hz), 138.9, 131.8 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 130.1, 129.5, 128.0, 123.6 (d, $^3J_{C\text{-}F}$ = 9.6 Hz), 119.8 (d, $^2J_{C\text{-}F}$ = 24.3 Hz), 114.4 (d, $^2J_{C\text{-}F}$ = 21.0 Hz), 99.8. **^{19}F-NMR (376 MHz, $CDCl_3$)** δ = −111.9. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3050, 1599, 1578, 1495, 1458, 1384, 1258, 1199, 1068, 1001, 873, 817, 754, 722. **MS (EI, 70 eV)** m/z (%) = 378 (16), 376 (17), 297 (63), 251 (24), 249 (24), 170 (100). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{12}H_7BrFI$] 375.8760, found 375.8751.

Synthesis of 2'-bromo-2-iodo-4-methoxy-1,1'-biphenyl (8b):



A dry and argon-flushed *Schlenk*-tube was charged with 2,2'-diiodo-4-methoxy-1,1'-biphenyl (**4e**, 218 mg, 0.5 mmol, 1.0 equiv) in THF (2.0 mL). After cooling to −40 °C, *i*PrMgCl·LiCl (0.41 mL, 0.5 mmol, 1.0 equiv, 1.22 M in THF) was added dropwise, and the resulting solution was stirred at −40 °C for 1 h. Subsequently, 1,2-dibromotetrachloroethane (195 mg, 0.6 mmol, 1.2 equiv) was added and the reaction solution was further stirred at room temperature for 1 h. After work-up, purification by column chromatography (SiO_2, *i*-hexane / ethyl acetate = 10 : 1) yielded **8b** (174 mg, 0.45 mmol, 89%) as a white solid. **M.p.**: 87 − 88 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.94 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.66 (dd, *J* = 8.0, 1.2 Hz, 0.23 H), 7.47 (d, *J* = 2.4 Hz, 0.24H), 7.42 − 7.35 (m, 1.60H), 7.27 − 7.19 (m, 2.92H), 7.14 − 7.05 (m, 2.33H), 6.96 (dd, *J* = 8.4, 2.4 Hz, 0.25H), 6.93 (dd, *J* = 8.4, 2.6 Hz, 1.06H), 3.86 (s, 3.15H), 3.84 (s, 0.75H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 159.6, 159.1, 145.8, 144.6, 138.8, 138.6, 137.5, 132.5, 131.5, 131.3, 130.4, 130.1, 129.6, 129.3, 129.2, 127.9, 127.1, 123.7, 123.6, 117.5, 114.0, 113.3, 100.5, 99.4, 55.6, 55.5. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3058, 2958, 2835, 1747, 1601, 1558, 1499, 1458, 1418, 1290, 1220, 1032, 996, 877, 809, 752, 724. **MS (EI, 70 eV)** m/z (%) = 390 (50), 388 (51), 309 (92), 263 (28), 261 (29), 182 (95), 139 (100). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{13}H_{10}BrIO$] 387.8960, found 387.8954.

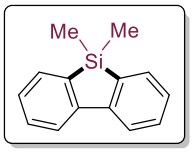
Synthesis of 3-bromo-2-(2-iodophenyl)thiophene (8c):



A dry and argon-flushed *Schlenk*-tube was charged with 3-iodo-2-(2-iodophenyl)thiophene (**4m**, 195 mg, 0.47 mmol, 1.0 equiv) in THF (2.0 mL). After cooling to −40 °C, *i*PrMgCl·LiCl (0.39 mL, 0.47 mmol, 1.0 equiv, 1.22 M in THF) was added dropwise, and the resulting solution was stirred at −40 °C for 1 h. Subsequently, 1,2-dibromotetrachloroethane (185 mg, 0.57 mmol, 1.2 equiv) was added and the reaction solution was further stirred at room temperature for 1 h. After work-up, purification by column chromatography (SiO_2,

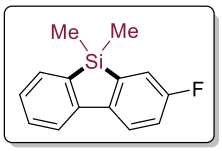
i-hexane) yielded **8c** (133 mg, 0.36 mmol, 78%) as a colorless solid. **M.p.**: 98 − 99 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.96 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.44 − 7.35 (m, 3H), 7.12 (ddd, *J* = 7.8, 7.2, 1.8 Hz, 1H), 7.06 (d, *J* = 5.6 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 140.4, 139.2, 137.9, 131.7, 130.4, 130.0, 127.9, 125.8, 110.9, 101.2. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3103, 1582, 1528, 1460, 1416, 1340, 1148, 1015, 858, 756, 713. **MS (EI, 70 eV)** m/z (%) = 366 (32), 364 (32), 285 (98), 158 (100). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{10}H_6BrIS$] 363.8418, found 363.8411.

Synthesis of 9,9-dimethyl-9-silafluorene (5a):



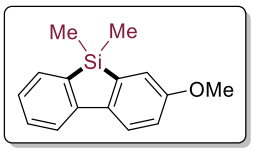
According to **TP2**, 2-bromobiphenyl (**2a**, 233 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **5a** (178 mg, 0.85 mmol, 85%) as a white solid. **M.p.**: 60 − 61 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.90 (d, *J* = 8.0 Hz, 2H), 7.72 − 7.70 (m, 2H), 7.50 (td, *J* = 7.6, 1.6 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 0.51 (s, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 147.8, 138.9, 132.7, 130.1, 127.3, 120.8, −3.3. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3042, 2919, 1590, 1426, 1256, 1127, 1060, 841, 786, 744, 709. **MS (EI, 70 eV)** m/z (%) = 210 (37), 195 (100), 165 (35). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{14}H_{14}Si$] 210.0865, found 210.0857.

Synthesis of 2-fluoro-9,9-dimethyl-9-silafluorene (5b):



According to **TP2**, 2-bromo-4'-fluoro-1,1'-biphenyl (**2b**, 160 mg, 0.64 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **5b** (116 mg, 0.51 mmol, 80%) as a white solid. **M.p.**: 54 − 55 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.78 − 7.74 (m, 2H), 7.63 − 7.61 (m, 1H), 7.43 (td, *J* =7.7, 1.2 Hz, 1H), 7.30 − 7.24 (m, 2H), 7.10 (ddd, *J* = 8.8, 8.4, 2.8 Hz, 1H), 0.43 (s, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 162.7 (d, $^1J_{C-F}$ = 247 Hz), 147.0, 143.6 (d, $^4J_{C-F}$ = 2.8 Hz), 141.9 (d, $^3J_{C-F}$ = 5.1 Hz), 138.4, 132.8, 130.3, 127.0, 122.2 (d, $^3J_{C-F}$ = 7.3 Hz), 120.6, 119.0 (d, $^2J_{C-F}$ = 19.6 Hz), 116.9 (d, $^2J_{C-F}$ = 22.3 Hz), −3.4. **^{19}F-NMR (376 MHz, $CDCl_3$)** δ = −115.9. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3045, 2956, 1588, 1469, 1433, 1253, 1192, 1127, 1053, 894, 839, 772, 748, 716. **MS (EI, 70 eV)** m/z (%) = 228 (55), 213 (100), 183 (12), 165 (23). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{14}H_{13}FSi$] 228.0771, found 228.0763.

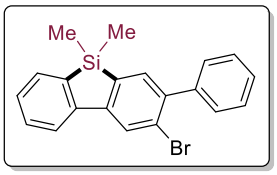
Synthesis of 2-methoxy-9,9-dimethyl-9-silafluorene (5c):



According to **TP2**, 2-bromo-4'-methoxy-1,1'-biphenyl (**2e**, 263 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **5c** (219 mg, 0.91 mmol, 91%) as a yellow oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.77 (dd, *J* = 8.0, 6.4 Hz, 2H), 7.64 (ddd, *J* = 7.0, 1.2, 0.6 Hz, 1H), 7.44 (td, *J* = 7.6, 1.2 Hz, 1H), 7.28 − 7.24 (m, 1H),

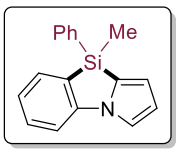
7.21 (d, *J* = 2.4 Hz, 1H), 6.99 (dd, *J* = 8.4, 2.8 Hz, 1H), 3.90 (s, 3H), 0.47 (s, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 159.2, 147.8, 140.9, 140.6, 138.1, 132.7, 130.2, 126.3, 121.9, 120.1, 117.7, 115.5, 55.4, −3.2. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3048, 2954, 1588, 1464, 1429, 1268, 1214, 1180, 1129, 1041, 867, 799, 772, 747, 716. **MS (EI, 70 eV)** m/z (%) = 240 (88), 225 (100), 210 (11), 182 (20). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{15}H_{16}OSi$] 240.0970, found 240.0963.

Synthesis of 3-bromo-2-phenyl-9,9-dimethyl-9-silafluorene (5d):



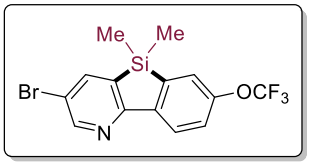
According to **TP2**, 1,4-dibromo-2,5-diphenylbenzene (**2p**, 582 mg, 1.5 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **5d** (432 mg, 1.18 mmol, 79%) as a light yellow solid. **M.p.**: 174 − 175 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.13 (s, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.68 − 7.66 (m, 1H), 7.59 (s, 1H), 7.52 − 7.45 (m, 5H), 7.44 − 7.39 (m, 1H), 7.34 (td, *J* = 7.4, 0.8 Hz, 1H), 0.46 (s, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 148.6, 146.2, 141.2, 141.0, 139.2, 138.2, 135.2, 132.8, 130.4, 129.4, 127.9, 127.5, 125.5, 125.3, 121.2, −3.3. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3054, 1589, 1430, 1358, 1247, 1129, 1063, 1024, 906, 854, 766, 702. **MS (EI, 70 eV)** m/z (%) = 366 (72), 364 (73), 351 (98), 349 (100), 269 (14), 267 (22), 239 (40). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{20}H_{17}BrSi$] 364.0283, found 364.0276.

Synthesis of 9-methyl-9-phenyl-benzo[d]pyrroloazasilole (5e):



According to **TP2**, 1-(2-bromophenyl)-1*H*-pyrrole (**2l**, 222 mg, 1.0 mmol, 1.0 equiv) and $PhMeSiCl_2$ (287 mg, 1.5 mmol, 1.5 equiv) were used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **5e** (183 mg, 0.70 mmol, 70 %) as a grey solid. **M.p.**: 75 − 76 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.62 − 7.60 (m, 2H), 7.57 − 7.55 (m, 1H), 7.47 (dd, *J* = 2.6, 1.0 Hz, 1H), 7.42 − 7.34 (m, 5H), 7.12 (td, *J* = 7.2, 1.2 Hz, 1H), 6.63 (dd, *J* = 3.4, 1.0 Hz, 1H), 6.47 (dd, *J* = 3.2, 2.8 Hz, 1H), 0.78 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 147.5, 134.5, 134.0, 133.9, 130.9, 130.0, 129.0, 128.6, 128.0, 124.1, 118.0, 117.3, 113.5, 111.5, −4.2. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3051, 2956, 1716, 1598, 1450, 1332, 1281, 1110, 1085, 955, 794, 723, 697. **MS (EI, 70 eV)** m/z (%) = 261 (64), 246 (100). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{17}H_{15}NSi$] 261.0974, found 261.0966.

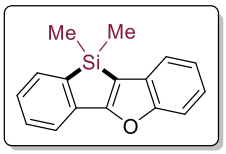
Synthesis of 3-bromo-5,5-dimethyl-7-(trifluoromethoxy)-benzosilolo[3,2-b]pyridine (5f):



According to **TP2**, 3,5-dibromo-2-(4-(trifluoromethoxy)phenyl)pyridine (**2k**, 159 mg, 0.4 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane / ethyl acetate = 15 : 1) yielded the desired product **5f** (103 mg, 0.28 mmol, 69 %) as a white solid. **M.p.**: 91 − 92 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.65 (d, *J* = 2.4 Hz, 1H), 8.23 − 8.21 (m, 1H),

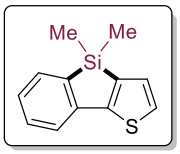
7.99 (d, J = 2.4 Hz, 1H), 7.44 (d, J = 1.2 Hz, 1H), 7.34 (ddd, J = 8.4, 2.4, 1.0 Hz, 1H), 0.48 (s, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 162.2, 151.8, 150.3 (q, $^4J_{C-F}$ = 1.7 Hz), 145.4, 142.8, 141.4, 134.8, 124.4, 124.1, 123.3, 120.5 (q, $^1J_{C-F}$ = 256 Hz), 120.2, −3.8. **^{19}F-NMR (376 MHz, $CDCl_3$)** δ = −57.6. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 2928, 1738, 1572, 1458, 1402, 1246, 1204, 1150, 1120, 1020, 944, 859, 780, 716, 662. **MS (EI, 70 eV)** m/z (%) = 375 (78), 373 (78), 360 (100), 358 (99), 139 (20). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{14}H_{11}BrF_3NOSi$] 372.9745, found 372.9736.

Synthesis of 10,10-dimethyl-benzosilolo[3,2-b]benzofuran (5g):



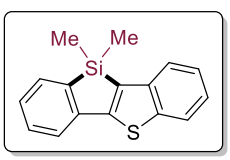
According to **TP2**, 2-(2-bromophenyl)benzofuran (**2q**, 273 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **5g** (167 mg, 0.67 mmol, 67%) as a colorless oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.65 (d, J = 7.6 Hz, 1H), 7.58 − 7.54 (m, 3H), 7.42 (td, J = 7.6, 1.2 Hz, 1H), 7.31 − 7.28 (m, 1H), 7.27 − 7.24 (m, 2H), 0.50 (s, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 169.3, 158.4, 142.1, 138.8, 132.6, 130.7, 129.8, 127.7, 123.8, 123.2, 121.8, 119.4, 113.2, 111.7, −3.5. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3052, 2956, 1580, 1514, 1432, 1344, 1256, 1108, 1082, 1008, 840, 783, 740, 689. **MS (EI, 70 eV)** m/z (%) = 250 (100), 235 (99), 189 (16). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{16}H_{14}OSi$] 250.0814, found 250.0807.

Synthesis of 4,4-dimethyl-benzosilolo[3,2-b]thiophene (5h):



According to **TP2**, 2-(2-bromophenyl)thiophene (**2m**, 239 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **5h** (168 mg, 0.78 mmol, 78%) as a white solid. **M.p.**: 97 − 98 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.54 (d, J = 6.8 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.37 (td, J = 7.6, 1.2 Hz, 1H), 7.32 (d, J = 4.8 Hz, 1H), 7.23 − 7.19 (m, 1H), 7.16 (d, J = 4.8 Hz, 1H), 0.44 (s, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 156.6, 143.6, 140.7, 140.6, 132.4, 130.1, 129.2, 126.5, 126.4, 120.6, −3.3. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3064, 2964, 1588, 1469, 1386, 1250, 1178, 1062, 894, 843, 768, 711. **MS (EI, 70 eV)** m/z (%) = 216 (65), 201 (100), 141 (14). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{12}H_{12}SSi$] 216.0429, found 216.0421.

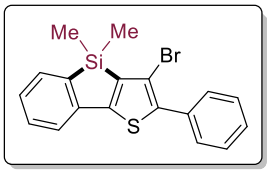
Synthesis of 10,10-dimethyl-benzo[b]benzosilolo[2,3-d]thiophene (5i):



According to **TP2**, 2-(2-bromophenyl)benzo[b]thiophene (**2n**, 290 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **5i** (200 mg, 0.76 mmol, 76%) as a white solid. **M.p.**: 91 − 92 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.93 − 7.91 (m, 1H), 7.80 − 7.78 (m, 1H), 7.63 − 7.61 (m, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.46 − 7.38 (m, 2H), 7.35 − 7.28 (m, 2H), 0.56 (s, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 156.6, 143.7, 143.1, 141.8,

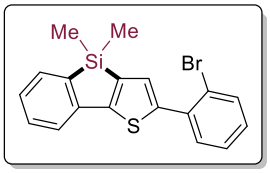
140.8, 137.2, 132.3, 130.2, 127.2, 124.7, 124.0, 123.9, 123.2, 121.6, −3.5. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 2356, 1589, 1453, 1304, 1246, 1129, 1069, 997, 840, 784, 760, 732. **MS (EI, 70 eV)** m/z (%) = 266 (87), 251 (100), 189 (15). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{16}H_{14}SSi$] 266.0585, found 266.0577.

Synthesis of 3-bromo-4,4-dimethyl-2-phenyl-benzosilolo[3,2-b]thiophene (5j):



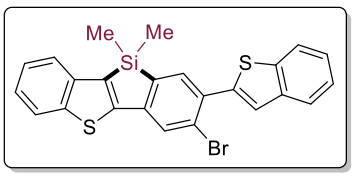
According to **TP2**, 3,4-dibromo-2,5-diphenylthiophene (**2r**, 390 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **5j** (155 mg, 0.42 mmol, 42%) as a colorless solid. **M.p.**: 131 − 132 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.79 − 7.75 (m, 2H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.51 − 7.40 (m, 5H), 7.29 (td, *J* = 7.2, 1.2 Hz, 1H), 0.57 (s, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 154.2, 145.1, 142.8, 139.6, 138.7, 133.1, 132.5, 130.2, 128.9, 128.5, 128.1, 127.0, 120.5, 110.8, −4.3. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3052, 2958, 1585, 1510, 1440, 1350, 1246, 1124, 1064, 989, 877, 791, 744, 693. **MS (EI, 70 eV)** m/z (%) = 372 (100), 370 (98), 357 (52), 355 (51), 275 (36), 215 (29). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{18}H_{15}BrSSi$] 369.9847, found 369.9839.

Synthesis of 2-(2-bromophenyl)-4,4-dimethyl-benzosilolo[3,2-b]thiophene (5k):



According to **TP2**, 2,5-bis(2-bromophenyl)thiophene (**2o**, 788 mg, 2.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **5k** (528 mg, 0.71 mmol, 71%) as a colorless oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.69 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.56 − 7.52 (m, 2H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.38 − 7.32 (m, 3H), 7.24 − 7.16 (m, 2H), 0.46 (s, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 157.1, 143.6, 143.1, 141.0, 140.3, 135.4, 133.8, 132.3, 131.8, 130.1, 130.0, 128.8, 127.4, 126.6, 122.6, 120.7, −3.3. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3055, 2949, 1587, 1444, 1246, 1163, 1124, 1024, 859, 780, 748, 686. **MS (EI, 70 eV)** m/z (%) = 372 (100), 370 (98), 357 (65), 355 (60), 275 (19), 215 (38). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{18}H_{15}BrSSi$] 369.9847, found 369.9840.

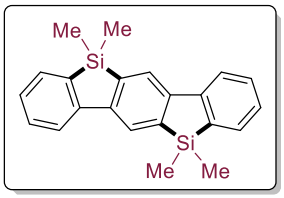
Synthesis of 2-(benzo[b]thiophen-2-yl)-3-bromo-10,10-dimethyl-benzo[b]benzosilolo[2,3-d]thiophene (5l):



According to **TP2**, 1,4-dibromo-2,5-bis(benzo[b]thiophen-2-yl)benzene (**2s**, 500 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **5l** (282 mg, 0.59 mmol, 59%) as a light yellow solid. **M.p.**: 181 − 182 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.93 − 7.91 (m, 1H), 7.89 − 7.83 (m, 3H), 7.78 (dd, *J* = 7.0, 0.6 Hz, 1H), 7.74 (s, 1H), 7.56 (s, 1H), 7.43 − 7.33 (m, 4H), 0.57 (s, 6H).

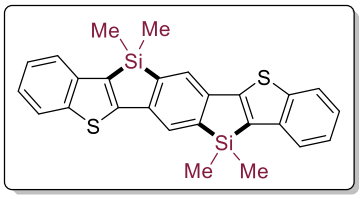
^{13}C-NMR (100 MHz, $CDCl_3$) δ = 154.2, 145.0, 143.5, 142.1, 141.5, 140.2, 140.1, 139.7, 139.2, 135.6, 133.6, 126.4, 125.3, 125.0, 124.6, 124.5, 124.5, 124.4, 124.3, 123.8, 123.3, 122.0, −3.5. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3049, 2921, 2852, 1579, 1454, 1308, 1246, 1065, 1008, 836, 779, 744, 722. **MS (EI, 70 eV)** m/z (%) = 478 (100), 476 (86), 463 (40), 461 (35). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{24}H_{17}BrS_2Si$] 475.9724, found 475.9728.

Synthesis of [2,3]-benzosilolo-9,9-dimethyl-9-silafluorene (9a):



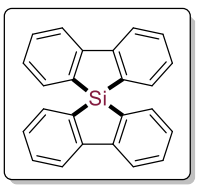
According to **TP2**, **5d** (92 mg, 0.25 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **9a** (70 mg, 0.21 mmol, 82%) as a white solid. **M.p.**: 203 − 204 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.12 (s, 2H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.67 − 7.65 (m, 2H), 7.46 (td, *J* = 7.6, 1.2 Hz, 2H), 7.30 (td, *J* = 7.4, 0.8 Hz, 2H), 0.49 (s, 12H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 147.8, 146.7, 141.4, 138.9, 132.8, 130.2, 127.1, 124.8, 120.7, −3.2. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3026, 2363, 1588, 1362, 1244, 1130, 1086, 831, 767, 745, 698. **MS (EI, 70 eV)** m/z (%) = 342 (98), 327 (100), 207 (22). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{22}H_{22}Si_2$] 342.1260, found 342.1252.

Synthesis of ladder π-conjugated compound 9b:



According to **TP2**, **5l** (143 mg, 0.30 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **9b** (118 mg, 0.26 mmol, 87%) as a yellow solid. **M.p.**: 364 − 365 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.92 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.72 (s, 2H), 7.39 (td, *J* = 7.6, 1.2 Hz, 2H), 7.34 − 7.30 (m, 2H), 0.59 (s, 12H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 156.5, 143.6, 143.1, 142.8, 141.9, 137.0, 125.4, 124.8, 124.0, 123.9, 123.2, −3.5. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3050, 2958, 1590, 1454, 1353, 1243, 1080, 1001, 832, 777, 722, 677. **MS (EI, 70 eV)** m/z (%) = 454 (100), 439 (23), 212 (16). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{26}H_{22}S_2Si_2$] 454.0701, found 454.0695.

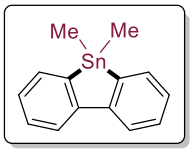
Synthesis of 9,9'-spiro-9-silabifluorene (9c):



According to **TP2**, 2-bromobiphenyl (**2a**, 117 mg, 0.5 mmol, 1.0 equiv) and $SiCl_4$ (39 mg, 0.225 mmol, 0.45 equiv) were used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **9c** (50 mg, 0.15 mmol, 67%) as a colorless solid. **M.p.**: 215 – 216 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.95 (d, *J* = 8.0 Hz, 4H), 7.52 (td, *J* = 7.6, 1.2 Hz, 4H), 7.44 – 7.42 (m, 4H), 7.23 (td, *J* = 7.2, 0.8 Hz, 4H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 149.9, 134.3, 132.6, 131.3, 127.9, 121.0. **IR (Diamond-**

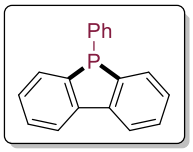
ATR, neat) $\tilde{\nu}$ / cm = 3060, 1934, 1590, 1428, 1257, 1130, 1064, 769, 750, 725. **MS (EI, 70 eV)** m/z (%) = 332 (100), 302 (10). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{24}H_{16}Si$] 332.1021, found 332.1013.

Synthesis of 9,9-dimethyl-9-stannafluorene (10):



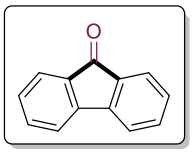
According to **TP2**, 2-bromobiphenyl (**2a**, 233 mg, 1.0 mmol, 1.0 equiv) and Me_2SnCl_2 (264 mg, 1.2 mmol, 1.2 equiv) were used for the reaction. Finally, purification by recrystallization of the residue in *i*-hexane yielded the desired product **10** (245 mg, 0.81 mmol, 81%) as a colorless solid. **M.p.**: 123 − 124 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.01 − 7.96 (m, 2H), 7.76 − 7.65 (m, 2H), 7.47 − 7.41 (m, 2H), 7.36 − 7.28 (m, 2H), 0.64 − 0.49 (m, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 148.2, 140.9, 136.3, 129.1, 127.4, 122.4, −8.5. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3050, 1580, 1456, 1426, 1288, 1252, 1110, 781, 744, 706. **MS (EI, 70 eV)** m/z (%) = 302 (10), 287 (100), 285 (72), 152 (29). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{14}H_{14}Sn$] 302.0117, found 302.0106.

Synthesis of 9-phenyl-9-phosphafluorene (11):



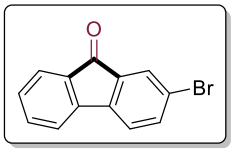
According to **TP2**, 2-bromobiphenyl (**2a**, 233 mg, 1.0 mmol, 1.0 equiv) and $PhPCl_2$ (268 mg, 1.5 mmol, 1.5 equiv) were used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **11** (161 mg, 0.62 mmol, 62%) as a white solid. **M.p.**: 91 − 92 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.97 (dd, *J* = 7.8, 0.6 Hz, 2H), 7.74 − 7.71 (m, 2H), 7.49 (td, *J* = 7.6, 1.2 Hz, 2H), 7.37 − 7.22 (m, 7H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 143.6 (d, $^3J_{C-P}$ = 3.0 Hz), 142.5 (d, $^3J_{C-P}$ = 2.5 Hz), 136.1 (d, $^1J_{C-P}$ = 18.7 Hz), 132.6 (d, $^1J_{C-P}$ = 20.0 Hz), 130.4 (d, $^1J_{C-P}$ = 21.7 Hz), 129.2 (d, $^4J_{C-P}$ = 0.8 Hz), 128.6, 128.6 (d, $^2J_{C-P}$ = 7.6 Hz), 127.6 (d, $^2J_{C-P}$ = 7.6 Hz), 121.3. **^{31}P-NMR (162 MHz, $CDCl_3$)** δ = −10.1. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3047, 1596, 1472, 1434, 1262, 1202, 1129, 1025, 870, 751, 692. **MS (EI, 70 eV)** m/z (%) = 260 (100), 228 (31), 183 (65). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{18}H_{13}P$] 260.0755, found 260.0747.

Synthesis of fluoren-9-one (6a):



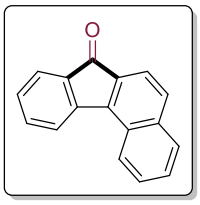
According to **TP3**, 2-bromobiphenyl (**2a**, 233 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane / ethyl acetate = 10 : 1) yielded the desired product **6a** (133 mg, 0.74 mmol, 74%) as a yellow solid. **M.p.**: 82 − 83 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.64 (dt, *J* = 7.4, 0.8 Hz, 2H), 7.50 − 7.44 (m, 4H), 7.27 (td, *J* = 7.2, 1.6 Hz, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 193.8, 144.4, 134.6, 134.1, 129.0, 124.2, 120.2. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3058, 1835, 1712, 1598, 1449, 1296, 1186, 1150, 1097, 917, 733, 670. **MS (EI, 70 eV)** m/z (%) = 180 (100), 152 (42), 150 (14). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{13}H_8O$] 180.0575, found 180.0569.

Synthesis of 2-bromo-fluoren-9-one (6b):



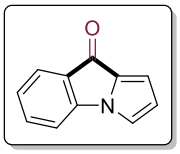
According to **TP3**, 2,4'-dibromo-1,1'-biphenyl (**2d**, 312 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane / ethyl acetate = 12 : 1) yielded the desired product **6b** (137 mg, 0.53 mmol, 53%) as a yellow solid. **M.p.**: 141 − 142 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.73 (d, *J* = 1.6 Hz, 1H), 7.63 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.58 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.49 − 7.47 (m, 2H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.30 (ddd, *J* = 7.4, 5.5, 3.0 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 192.3, 143.6, 142.9, 137.0, 135.7, 135.0, 133.6, 129.4, 127.5, 124.6, 122.7, 121.7, 120.4. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3062, 1716, 1593, 1441, 1292, 1256, 1187, 1150, 1109, 1052, 820, 735, 658. **MS (EI, 70 eV)** m/z (%) = 260 (97), 258 (100), 151 (50), 150 (37). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{13}H_7BrO$] 257.9680, found 257.9674.

Synthesis of benzo[c]fluoren-9-one (6c):



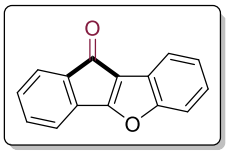
According to **TP3**, 1-(2-bromophenyl)naphthalene (**2i**, 283 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane / ethyl acetate = 10 : 1) yielded the desired product **6c** (115 mg, 0.50 mmol, 50%) as an orange solid. **M.p.**: 160 − 161 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.46 − 8.43 (m, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.86 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.73 (q, *J* = 8.4 Hz, 2H), 7.66 (dd, *J* = 7.2, 0.4 Hz, 1H), 7.62 − 7.54 (m, 2H), 7.50 (td, *J* = 7.6, 1.2 Hz, 1H), 7.31 − 7.27 (m, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 194.4, 144.9, 142.8, 137.9, 134.4, 134.4, 131.8, 129.9, 129.6, 128.7, 128.7, 128.2, 127.7, 124.8, 124.0, 123.3, 119.8. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3062, 1707, 1602, 1578, 1462, 1368, 1172, 1100, 934, 824, 779, 740, 701. **MS (EI, 70 eV)** m/z (%) = 230 (100), 202 (66), 200 (37). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{17}H_{10}O$] 230.0732, found 230.0725.

Synthesis of pyrrolo[1,2-a]indol-9-one (6d):



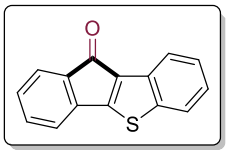
According to **TP3**, 1-(2-bromophenyl)-1*H*-pyrrole (**2l**, 222 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane / ethyl acetate = 10 : 1) yielded the desired product **6d** (120 mg, 0.71 mmol, 71%) as an orange solid. **M.p.**: 121 − 122 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.54 (d, *J* = 7.6 Hz, 1H), 7.40 (td, *J* = 7.6, 1.2 Hz, 1H), 7.12 − 7.05 (m, 3H), 6.76 (dd, *J* = 3.6, 0.4 Hz, 1H), 6.28 (dd, *J* = 3.8, 2.6 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 179.6, 143.7, 134.1, 131.8, 130.1, 125.4, 124.4, 119.4, 115.8, 113.9, 110.2. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3125, 3056, 1674, 1616, 1523, 1478, 1403, 1358, 1311, 1248, 1181, 1076, 1021, 909, 870, 745, 699. **MS (EI, 70 eV)** m/z (%) = 169 (100), 140 (22), 114 (15). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{11}H_7NO$] 169.0528, found 169.0521.

Synthesis of indeno[1,2-b]benzofuran-10-one (6e):



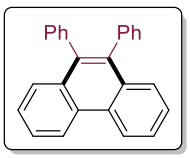
According to **TP3**, 2-(2-bromophenyl)benzofuran (**2q**, 273 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane / ethyl acetate = 10 : 1) yielded the desired product **6e** (138 mg, 0.63 mmol, 63%) as an orange solid. **M.p.**: 159 − 160 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.75 − 7.73 (m, 1H), 7.54 − 7.49 (m, 2H), 7.38 − 7.34 (m, 1H), 7.33 − 7.25 (m, 4H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 185.0, 178.4, 160.8, 138.6, 133.5, 132.8, 130.4, 125.3, 125.0, 123.6, 122.2, 121.0, 118.5, 118.3, 112.5. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3056, 1721, 1697, 1538, 1475, 1404, 1302, 1178, 1140, 1052, 915, 855, 754, 714. **MS (EI, 70 eV)** m/z (%) = 220 (100), 163 (44). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{15}H_8O_2$] 220.0524, found 220.0518.

Synthesis of benzo[b]indeno[2,1-d]thiophen-10-one (6f):



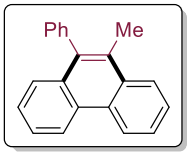
According to **TP3**, 2-(2-bromophenyl)benzo[b]thiophene (**2n**, 289 mg, 1.0 mmol, 1.0 equiv) was used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane / ethyl acetate = 10 : 1) yielded the desired product **6f** (170 mg, 0.72 mmol, 72%) as a red solid. **M.p.**: 204 − 205 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.11 (dd, *J* = 7.4, 0.6 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.44 − 7.40 (m, 1H), 7.37 − 7.29 (m, 2H), 7.25 − 7.21 (m, 1H), 7.17 (d, *J* = 7.2 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 187.2, 162.2, 143.9, 138.6, 136.8, 134.7, 133.5, 132.4, 129.5, 126.5, 125.2, 123.4, 123.1, 122.9, 120.1. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3062, 1714, 1688, 1596, 1462, 1349, 1226, 1155, 1078, 1042, 850, 744, 698. **MS (EI, 70 eV)** m/z (%) = 236 (100), 208 (28), 163 (23). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{15}H_8OS$] 236.0296, found 236.0289.

Synthesis of 9,10-diphenylphenanthrene (7a):



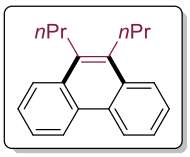
According to **TP4**, 2-bromobiphenyl (**2a**, 117 mg, 0.5 mmol, 1.0 equiv) and diphenylacetylene (178 mg, 1.0 mmol, 2.0 equiv) were used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **7a** (130 mg, 0.40 mmol, 79%) as a white solid. **M.p.**: 234 − 235 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.83 (d, *J* = 8.4 Hz, 2H), 7.71 − 7.66 (m, 2H), 7.59 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.53 − 7.49 (m, 2H), 7.28 − 7.22 (m, 5H), 7.22 − 7.16 (m, 5H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 139.5, 137.2, 131.8, 131.0, 129.9, 127.8, 127.6, 126.6, 126.4, 126.4, 122.5. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 1486, 1440, 1418, 1072, 1028, 758, 725, 700. **MS (EI, 70 eV)** m/z (%) = 330 (100), 329 (21), 253 (22), 252 (30). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{26}H_{18}$] 330.1409, found 330.1399.

Synthesis of 9-methyl-10-phenylphenanthrene (7b):



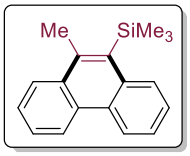
According to **TP4**, 2-bromobiphenyl (**2a**, 117 mg, 0.5 mmol, 1.0 equiv) and 1-phenyl-1-propyne (116 mg, 1.0 mmol, 2.0 equiv) were used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **7b** (90 mg, 0.34 mmol, 67%) as a white solid. **M.p.**: 100 − 101 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.83 − 8.79 (m, 1H), 8.76 (d, *J* = 8.4 Hz, 1H), 8.20 − 8.16 (m, 1H), 7.74 − 7.67 (m, 2H), 7.62 − 7.53 (m, 3H), 7.51 − 7.39 (m, 3H), 7.35 − 7.32 (m, 2H), 2.49 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 140.7, 137.0, 132.3, 131.8, 130.3, 129.9, 129.8, 129.3, 128.4, 127.4, 127.0, 126.8, 126.3, 126.2, 125.6, 125.1, 122.8, 122.3, 17.3. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3060, 2918, 1590, 1488, 1440, 1317, 1238, 1072, 1004, 856, 752, 723, 700. **MS (EI, 70 eV)** m/z (%) = 268 (100), 253 (36), 252 (36). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{21}H_{16}$] 268.1252, found 268.1244.

Synthesis of 9,10-dipropylphenanthrene (7c):



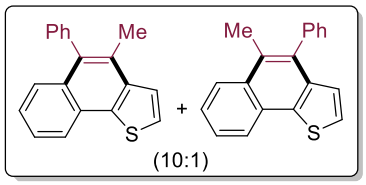
According to **TP4**, 2-bromobiphenyl (**2a**, 117 mg, 0.5 mmol, 1.0 equiv) and 4-octyne (110 mg, 1.0 mmol, 2.0 equiv) were used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **7c** (67 mg, 0.26 mmol, 51%) as a colorless solid. **M.p.**: 95 − 96 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.77 − 8.72 (m, 2H), 8.16 − 8.12 (m, 2H), 7.66 − 7.60 (m, 4H), 3.19 − 3.15 (m, 4H), 1.84 − 1.74 (m, 4H), 1.20 (t, *J* = 7.2 Hz, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 133.8, 131.3, 129.8, 126.5, 125.3, 124.7, 122.9, 31.5, 24.0, 14.8. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3079, 2953, 2868, 1588, 1493, 1430, 1376, 1240, 1088, 1046, 888, 756, 723. **MS (EI, 70 eV)** m/z (%) = 262 (80), 233 (100), 218 (24), 203 (33), 191 (40). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{20}H_{22}$] 262.1722, found 262.1714.

Synthesis of 9-methyl-10-(trimethylsilyl)phenanthrene (7d):



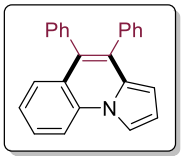
According to **TP4**, 2-bromobiphenyl (**2a**, 117 mg, 0.5 mmol, 1.0 equiv) and 1-trimethylsilyl-1-propyne (112 mg, 1.0 mmol, 2.0 equiv) were used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **7d** (69 mg, 0.26 mmol, 52%) as a colorless oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.70 (dt, *J* = 7.2, 2.0 Hz, 2H), 8.23 − 8.21 (m, 1H), 8.17 − 8.14 (m, 1H), 7.70 − 7.62 (m, 2H), 7.60 − 7.53 (m, 2H), 2.90 (s, 3H), 0.61 (s, 9H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 140.9, 135.4, 134.5, 131.9, 130.8, 129.3, 128.8, 126.7, 126.5, 125.4, 125.0, 124.5, 122.9, 122.6, 21.9, 4.1. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3071, 2950, 1563, 1488, 1434, 1376, 1251, 1043, 916, 834, 749, 722. **MS (EI, 70 eV)** m/z (%) = 264 (72), 249 (78), 233 (100). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{18}H_{20}Si$] 264.1334, found 264.1325.

Synthesis of 4(5)-methyl-5(4)-phenylnaphtho[1,2-b]thiophene (7e):



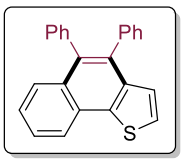
According to **TP4**, 2-(2-bromophenyl)thiophene (**2m**, 120 mg, 0.5 mmol, 1.0 equiv) and 1-phenyl-1-propyne (116 mg, 1.0 mmol, 2.0 equiv) were used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **7e** (89 mg, 0.32 mmol, 65%) as an orange oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.22 − 8.15 (m, 2.01H), 7.62 − 7.59 (m, 2.14H), 7.54 − 7.49 (m, 2.36H), 7.47 − 7.43 (m, 1.28H), 7.39 − 7.31 (m, 3.53H), 7.03 − 6.98 (m, 1H), 2.54 (s, 3H), 2.45 (s, 0.35H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 140.6, 139.8, 137.9, 137.8, 136.7, 135.5, 135.4, 135.1, 131.1, 130.8, 130.6, 129.9, 128.7, 128.4, 128.3, 128.2, 128.0, 127.6, 127.6, 127.1, 127.0, 126.1, 125.8, 125.7, 125.5, 125.5, 124.9, 124.1, 124.0, 123.5, 18.0, 16.3. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3052, 3024, 2920, 1947, 1886, 1601, 1575, 1494, 1442, 1378, 1323, 1270, 1094, 1072, 847, 745, 723, 690. **MS (EI, 70 eV)** m/z (%) = 274 (100), 259 (12), 239 (10), 197 (14). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{19}H_{14}S$] 274.0816, found 274.0805.

Synthesis of 4,5-diphenylpyrrolo[1,2-a]quinoline (7f):



According to **TP4**, 1-(2-bromophenyl)-1*H*-pyrrole (**2l**, 111 mg, 0.5 mmol, 1.0 equiv) and diphenylacetylene (178 mg, 1.0 mmol, 2.0 equiv) were used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **7f** (144 mg, 0.45 mmol, 90%) as a grey solid. **M.p.**: 210 − 211 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.00 − 7.96 (m, 2H), 7.55 − 7.50 (m, 1H), 7.43 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.29 − 7.16 (m, 11H), 6.79 (dd, *J* = 4.0, 2.8 Hz, 1H), 6.25 (dd, *J* = 4.0, 1.6 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 137.7, 137.6, 132.7, 131.9, 131.5, 130.8, 130.2, 128.4, 128.1, 127.8, 127.7, 127.6, 126.9, 126.7, 124.7, 123.4, 114.0, 112.9, 112.2, 104.2. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3056, 2358, 1591, 1482, 1442, 1365, 1321, 1159, 1098, 1073, 1026, 908, 751, 696. **MS (EI, 70 eV)** m/z (%) = 319 (9), 281 (25), 225 (16), 207 (100), 191 (17). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{24}H_{17}N$] 319.1361, found 319.1354.

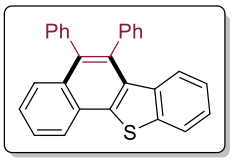
Synthesis of 4,5-diphenylnaphtho[1,2-b]thiophene (7g):



According to **TP4**, 2-(2-bromophenyl)thiophene (**2m**, 120 mg, 0.5 mmol, 1.0 equiv) and diphenylacetylene (178 mg, 1.0 mmol, 2.0 equiv) were used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **7g** (124 mg, 0.37 mmol, 74%) as a white solid. **M.p.**: 216 − 217 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.27 (dd, *J* = 8.2, 0.6 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.64 − 7.60 (m, 1H), 7.48 − 7.43 (m, 2H), 7.33 − 7.18 (m, 11H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 139.8, 138.9, 137.5, 136.9, 135.4, 134.8, 131.5, 130.6, 130.5, 128.4, 128.1, 127.6, 127.6, 126.6, 126.5, 126.4, 125.8, 124.6, 123.6. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3055, 2364, 1490, 1443, 1394, 1316, 1094, 1073, 1029, 850, 756,

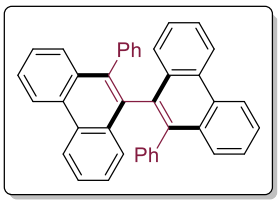
740, 696. **MS (EI, 70 eV)** m/z (%) = 336 (100), 302 (11), 259 (16). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{24}H_{16}S$] 336.0973, found 336.0964.

Synthesis of 5,6-diphenylbenzo[b]naphtho[2,1-d]thiophene (7h):



According to **TP4**, 2-(2-bromophenyl)benzo[b]thiophene (**2n**, 145 mg, 0.5 mmol, 1.0 equiv) and diphenylacetylene (178 mg, 1.0 mmol, 2.0 equiv) were used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **7h** (127 mg, 0.33 mmol, 66%) as a white solid. **M.p.**: 218 − 219 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.27 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.66 − 7.61 (m, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.49 − 7.45 (m, 1H), 7.37 − 7.16 (m, 11H), 7.07 − 7.03 (m, 1H), 6.59 (d, *J* = 8.4 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 139.8, 139.3, 138.8, 137.5, 137.2, 136.8, 135.8, 131.4, 131.3, 131.0, 130.3, 128.1, 128.0, 127.5, 127.1, 126.5, 126.4, 125.5, 124.9, 124.4, 123.9, 122.6. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3057, 2358, 1493, 1441, 1378, 1315, 1158, 1072, 1030, 751, 730, 696. **MS (EI, 70 eV)** m/z (%) = 386 (10), 281 (27), 225 (26), 207 (100), 191 (17). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{28}H_{18}S$] 386.1129, found 386.1124.

Synthesis of 10,10'-diphenyl-9,9'-biphenanthrene (7i):



According to **TP4**, 2-bromobiphenyl (**2a**, 117 mg, 0.5 mmol, 1.0 equiv) and 1,4-diphenylbuta-1,3-diyne (46 mg, 0.225 mmol, 0.45 equiv) were used for the reaction. Finally, purification by column chromatography (SiO_2, *i*-hexane) yielded the desired product **7i** (62 mg, 0.12 mmol, 54%) as a white solid. **M.p.**: 300 − 301 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.79 (d, *J* = 8.4 Hz, 4H), 7.66 − 7.62 (m, 4H), 7.47 (ddd, *J* = 8.0, 3.2, 1.2 Hz, 4H), 7.42 − 7.37 (m, 4H), 7.21 (td, *J* = 7.4, 0.8 Hz, 2H), 7.07 (tt, *J* = 7.2, 1.4 Hz, 2H), 6.86 − 6.78 (m, 4H), 6.64 (d, *J* = 7.6 Hz, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 138.4, 137.5, 133.9, 133.3, 132.2, 132.0, 130.5, 129.6, 128.8, 128.5, 127.7, 127.4, 126.8, 126.8, 126.6, 126.3, 126.3, 126.2, 122.5, 122.4. **IR (Diamond-ATR, neat)** $\tilde{\nu}$ / cm = 3060, 2356, 1600, 1486, 1444, 1416, 1178, 1074, 1042, 914, 856, 759, 724, 700. **MS (EI, 70 eV)** m/z (%) = 507 (47), 506 (100), 127 (13). **HRMS (EI, 70 eV)** m/z: calcd for [$C_{40}H_{26}$] 506.2035, found 506.2016.

5. X-ray Crystallographic Studies

Single crystals of $LaCl_3 \cdot 2LiCl$ suitable for X-ray analysis were grown in THF at -10 °C for a week. Data collections were performed at 180 K on a XtaLAB Pro: Kappa single diffractometer using Mo Kα radiation (λ = 0.71073 Å). Using Olex2, the structure was solved with Superflip solution program using Charge Flipping or ShelXS-97 solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. In the structure, the commands DELU, SIMU and ISOR were applied to mostly restrain the disorders of coordinated THF molecules. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1936794. Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

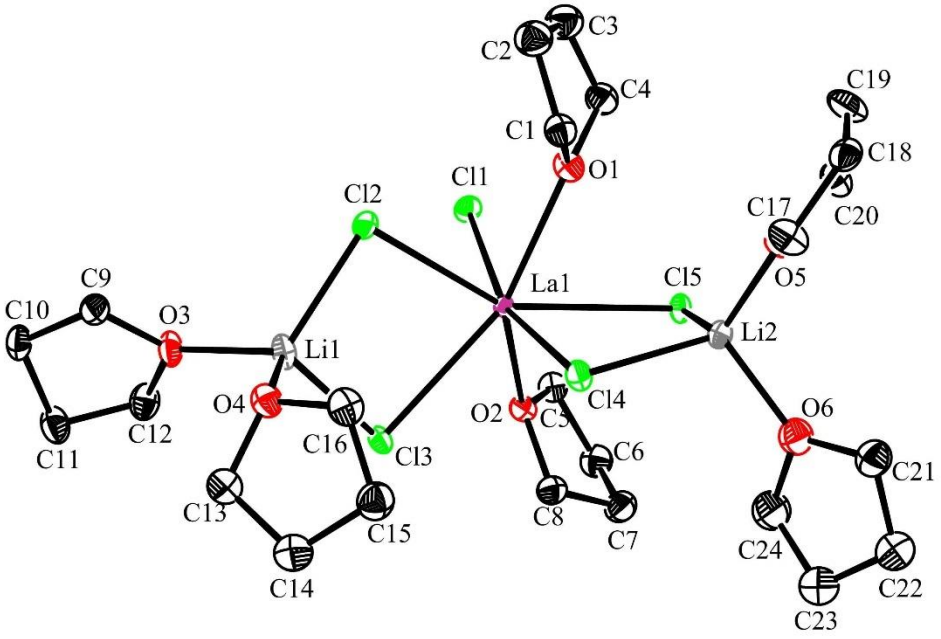


Figure S1. ORTEP drawing of $LaCl_3 \cdot 2LiCl$ with 20% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Table S3. Crystal data and structure refinement for $LaCl_3 \cdot 2LiCl$.

Identification code	$LaCl_3 \cdot 2LiCl$
Empirical formula	$C_{24}H_{48}Cl_5LaLi_2O_6$
Formula weight	762.66

Temperature/K	179.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.5244(3)
b/Å	32.2985(8)
c/Å	11.1418(3)
α/°	90
β/°	113.212(4)
γ/°	90
Volume/Å^3	3480.77(19)
Z	4
ρ_{calc}g/cm^3	1.455
μ/mm^{-1}	1.643
F(000)	1552.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.71 to 52.042
Index ranges	$-12 \leq h \leq 12$, $-39 \leq k \leq 39$, $-13 \leq l \leq 13$
Reflections collected	63768
Independent reflections	6835 [R_{int} = 0.0471, R_{sigma} = 0.0215]
Data/restraints/parameters	6835/280/343
Goodness-of-fit on F^2	1.155
Final R indexes [I>=2σ (I)]	R_1 = 0.0624, wR_2 = 0.1384
Final R indexes [all data]	R_1 = 0.0647, wR_2 = 0.1397
Largest diff. peak/hole / e Å^{-3}	1.93/-1.76

6. X-ray Absorption Fine Structure (XAFS) Studies

Extended X-ray absorption fine structure (EXAFS) measurements (La solution) were performed at the La L_3-edge in fluorescence mode. Data collections were performed at beamline Taiwan Photon Source (TPS) 44A at National Synchrotron Radiation Research Center (NSSRC) in Taiwan. Internal energy calibration was made with a vanadium metal foil assigned to 5465 eV (V K-edge). The JAQ program (by Oliver Müller, Bergische Universität Wuppertal) was used for EXAFS data treatment. Artemis software (Demeter 0.9.26) was used to fit the EXAFS data. The coordination parameters were obtained by fitting the R-space which was k^2-weighted Fourier transform data.

First, the Fourier transform data for $LaCl_3 \cdot 2LiCl$ in THF [La001] appears as one peak corresponding to La−O and La−Cl bonds. The best fit revealed that each La atom is bound to two oxygen atoms with 2.63 Å La−O bond distance and five chlorine atoms with 2.84 Å La−Cl bond distance on average, (Figure S2, Table S4). These parameters are in good accordance with the crystal structure of $LaCl_3 \cdot 2LiCl$.

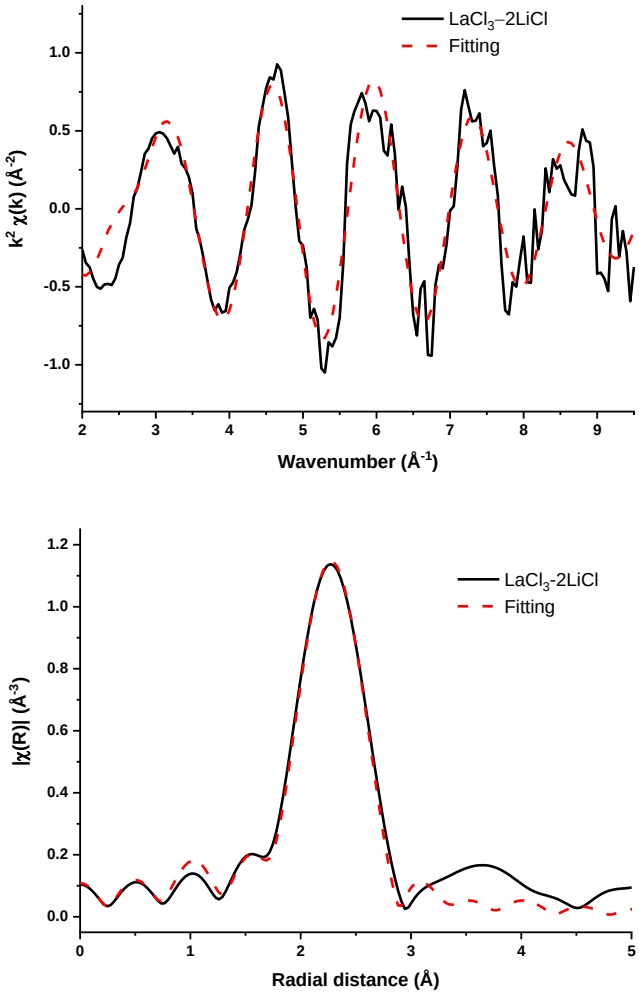


Figure S2. La L_3-edge k^2-weighted EXAFS spectra and Fourier transforms for $LaCl_3 \cdot 2LiCl$ in THF. Solid black lines show the experimental data and dashed red lines are the best fitting result. (2.7 $Å^{-1}$ < k < 9 $Å^{-1}$ and 1.3 Å < R < 3.2 Å)

Then, to the solution of $LaCl_3$·2LiCl in THF was added *n*BuLi (2.0 equiv) at -50 °C, and K-space and R-space revealed that the coordination environment of La changed immediately and carbon and chlorine atoms were detected around La atom. The EXAFS fitting is an average of various La species and their best fits are shown in Figure S3. The average coordination numbers (CN) of La−C and La−Cl are 1.96 and 4.22, respectively. Meanwhile, the La−C and La−Cl bond distances determined from EXAFS refinements are 2.36 Å and 3.00 Å, respectively (Table S4). These results indicated that the transmetalation occurred upon the addition of *n*BuLi to $LaCl_3$·2LiCl in THF, affording some new organolanthanum species [La002]. One possible structure of [La002] was proposed in Scheme S2. The flexible coordination of LiCl around La in [La002] might also have led to the average CN_{La-Cl} (4.22) lying in between 4-5.

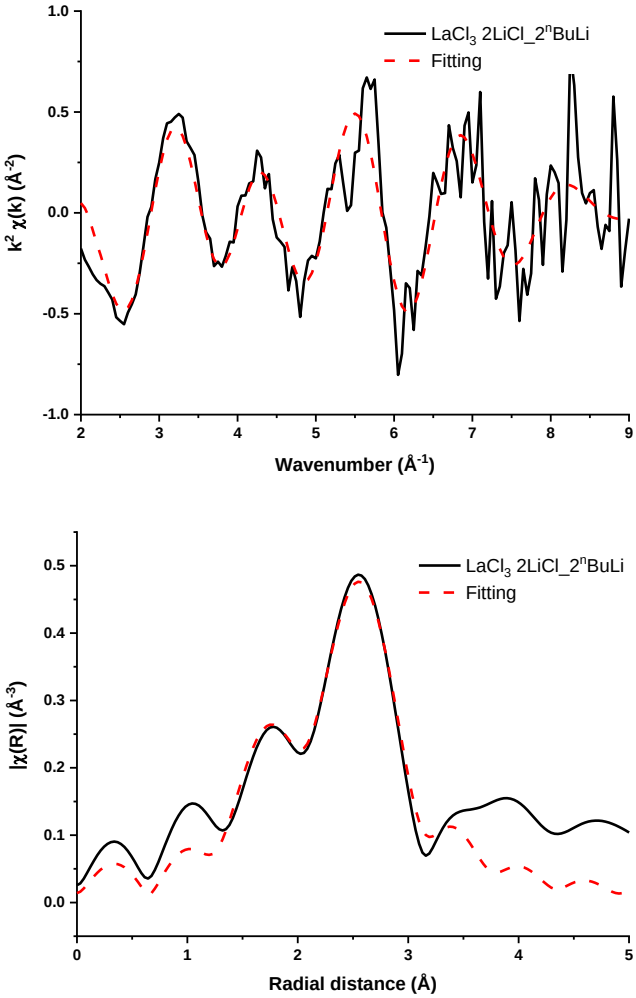


Figure S3. La L_3-edge k^2-weighted EXAFS spectra and Fourier transforms after addition of 2.0 equiv of *n*BuLi to $LaCl_3$·2LiCl in THF (the formulated *n*Bu_2LaCl·4LiCl). Solid black lines show the experimental data and dashed red lines are the best fitting result. (2.7 $Å^{-1}$ < k < 8 $Å^{-1}$ and 1.3 Å < R < 3.2 Å)

Next, after addition of 2-bromobiphenyl to the above solution (the formulated *n*Bu$_2$LaCl·4LiCl) at -50 °C, X-ray absorption fine structure (XAFS) measurement was started with 0.5 second/scan in quick-scan mode and structural changes occurred. All EXAFS spectra were recorded during the operando experiment and spectra were nearly identical from over 30 min. The fitting results reveal that the CN of La−C and La−Cl are about 3.63 and 4.26 and the bond distances are 2.50 Å and 2.91 Å, respectively. (Figure S4, Table S4). These results indicated that some new organolanthanum species [La003] were formed upon the addition of 2-bromobiphenyl into *n*Bu$_2$LaCl·4LiCl. The average CN_{La-C} (3.63) and CN_{La-Cl} (4.26) revealed that there were several proportional La species in [La003]. Three possible structures in [La003] were proposed in Scheme S2 and one structure was shown as a representative in Ref. 5b.

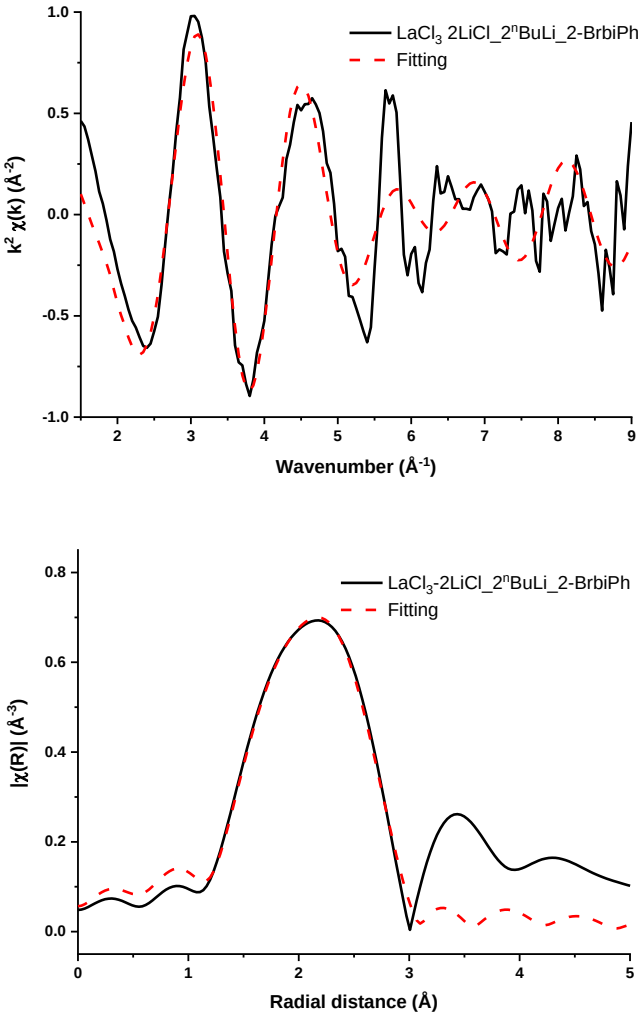


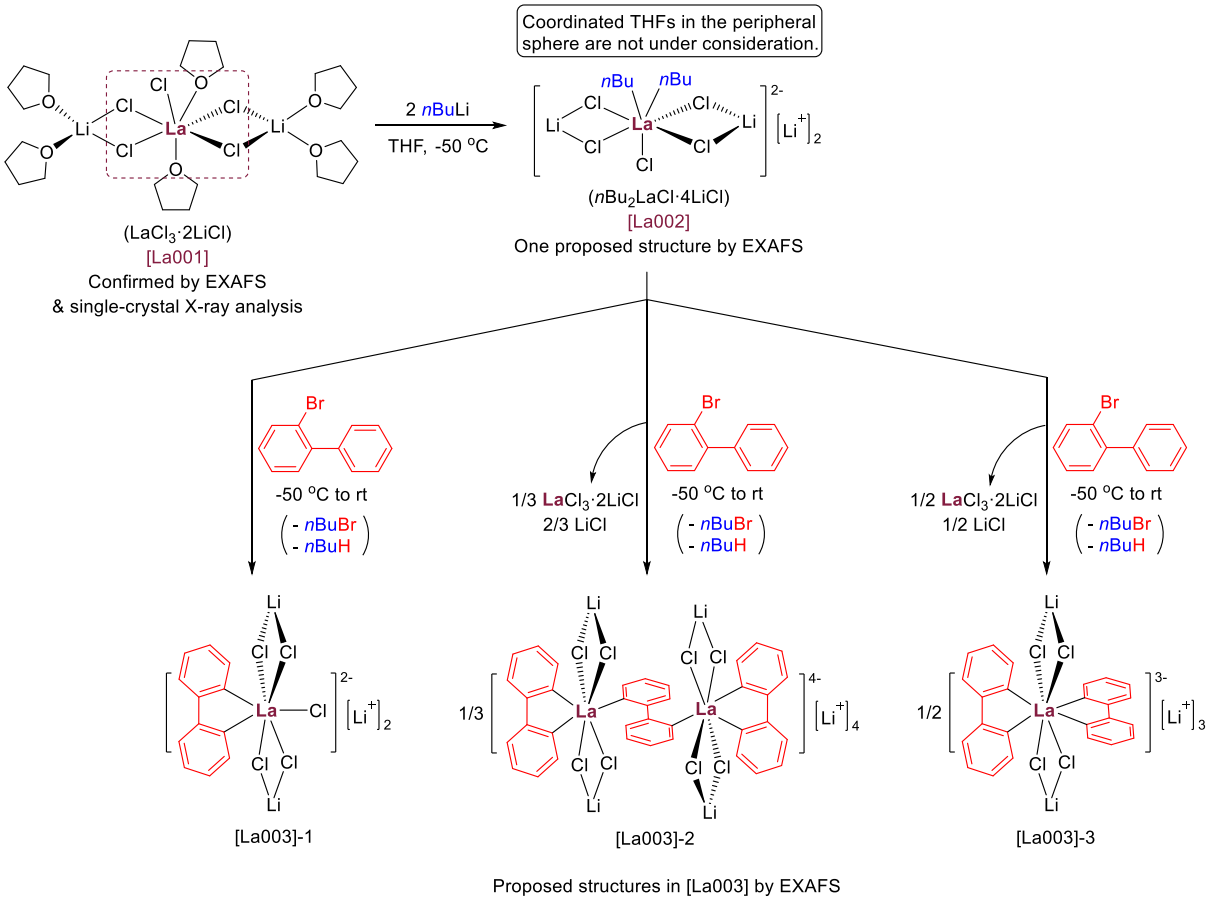
Figure S4. La L_3-edge k^2-weighted EXAFS spectra and Fourier transforms after addition of 2-bromobiphenyl to the formulated *n*Bu$_2$LaCl·4LiCl in THF. Solid black lines show the experimental data and dashed red lines are the best fitting result. (2 Å^{-1} < k < 7 Å^{-1} and 1.3 Å < R < 3 Å)

Table S4. EXAFS fitting results

La001_$LaCl_3$·2LiCl in THF $S_0^2 = 1.05$ $\Delta E_0 = 6.009$ eV			
	Coordination Number	**Bond Distance (Å)**	**σ^2(Å^2)**
La–Cl	5	2.84(1)	0.00851
La–O	2	2.56(1)	0.00351

La002_$LaCl_3$·2LiCl_2*n*BuLi in THF $S_0^2 = 1.05$ $\Delta E_0 = 1.253$ eV			
	Coordination Number	**Bond Distance (Å)**	**σ^2(Å^2)**
La–Cl	4.22	2.99(3)	0.01508
La–C	1.96	2.36(2)	0.00342

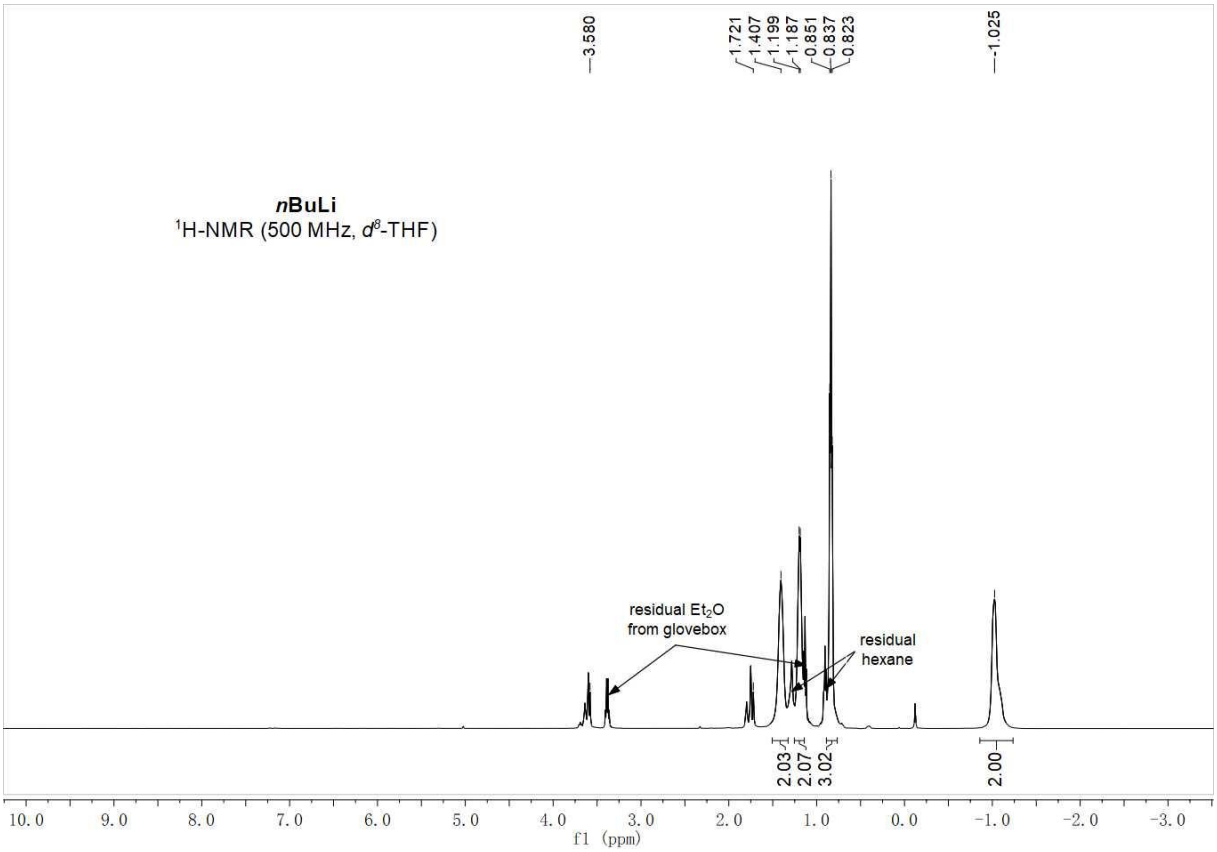
La003_$LaCl_3$·2LiCl_2*n*BuLi_2-BrbiPh in THF $S_0^2 = 1.05$ $\Delta E_0 = 6.203$ eV			
	Coordination Number	**Bond Distance (Å)**	**σ^2(Å^2)**
La–Cl	4.26	2.90(2)	0.013
La–C	3.63	2.49(2)	0.00349

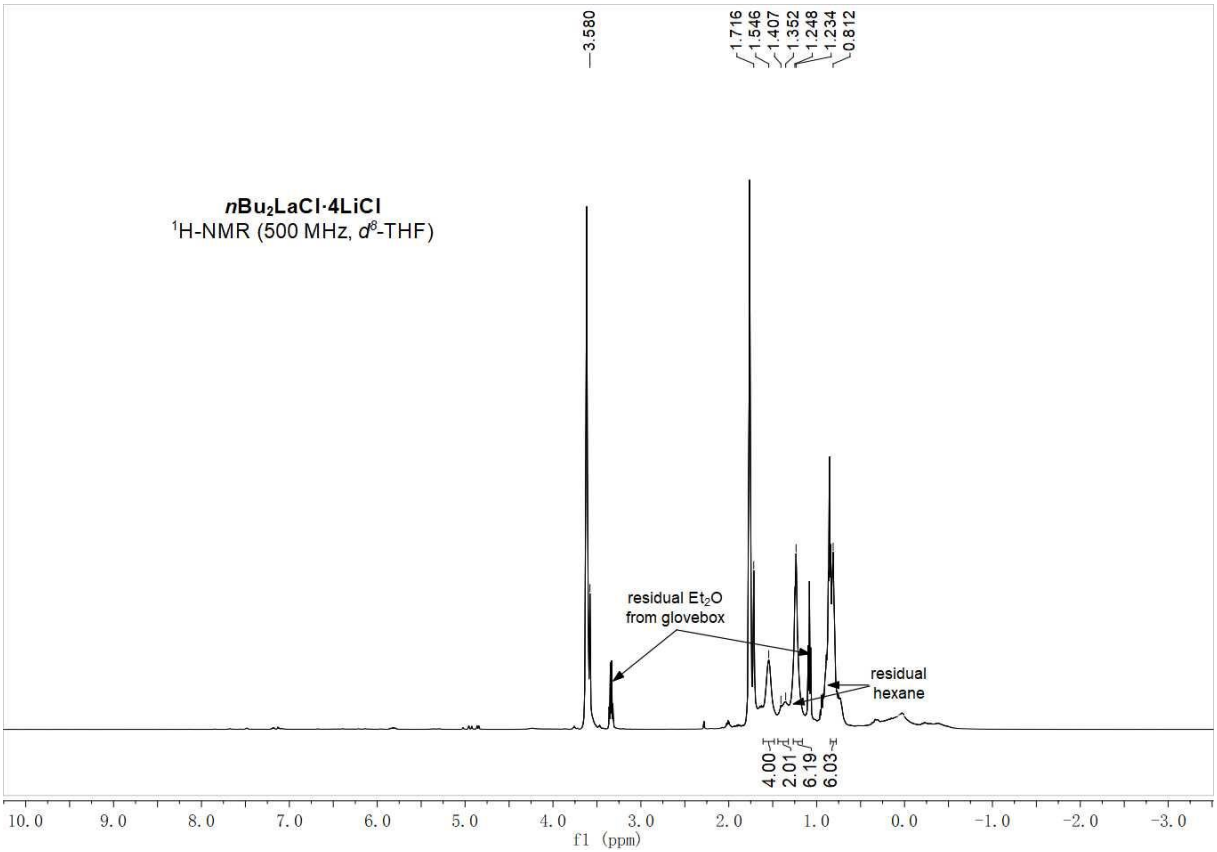


Scheme S2. Proposed structures of the involved organolanthanum species

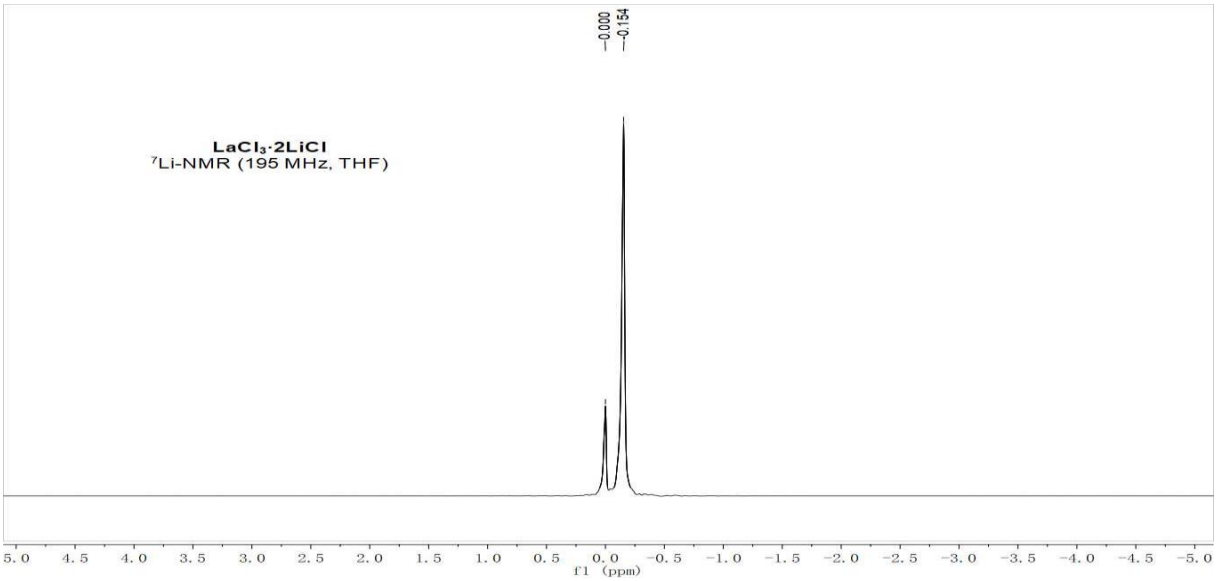
7. NMR Spectra

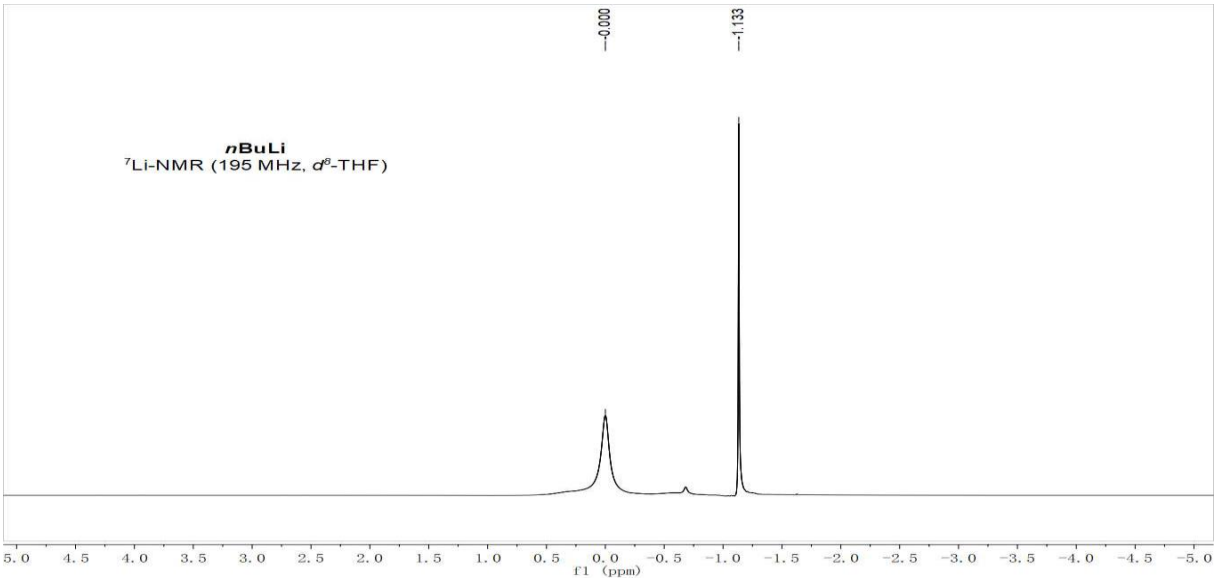
^{1}H-NMR analysis of *n*BuLi and *n*Bu$_2$LaCl·4LiCl

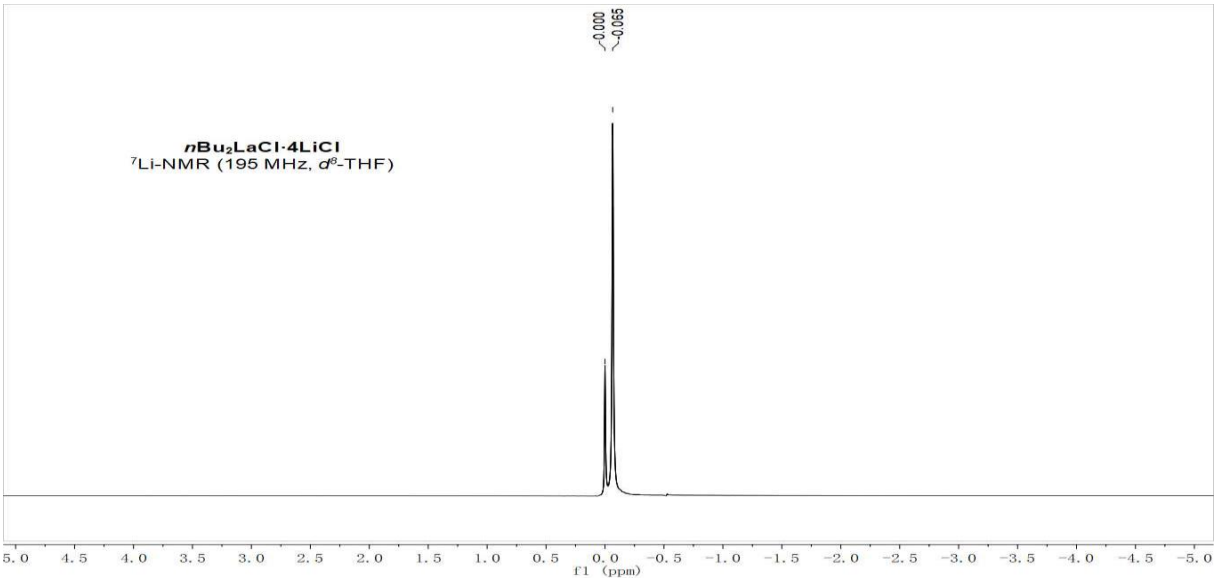


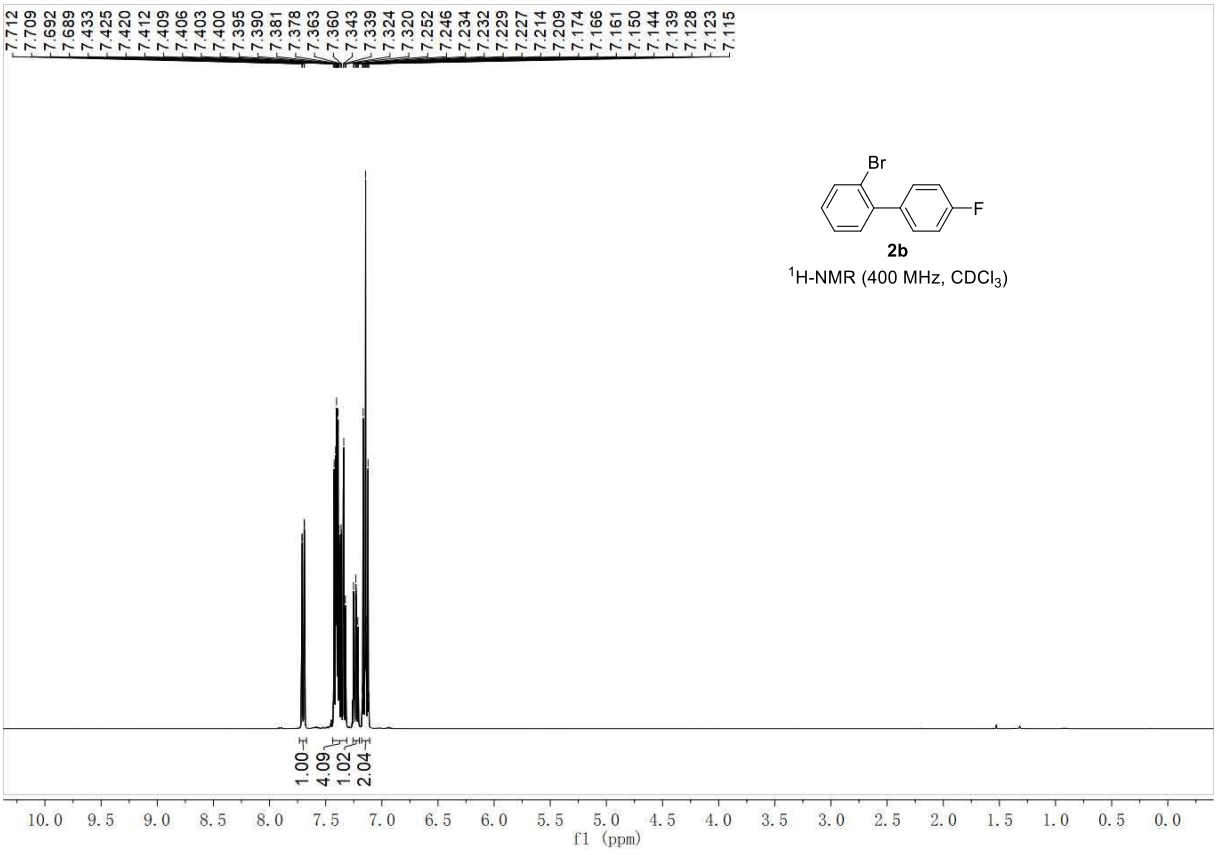


^{7}Li-NMR analysis of $LaCl_3 \cdot 2LiCl$, *n*BuLi and $nBu_2LaCl \cdot 4LiCl$





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7.709
7.692
7.689
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7.425
7.420
7.412
7.409
7.406
7.403
7.400
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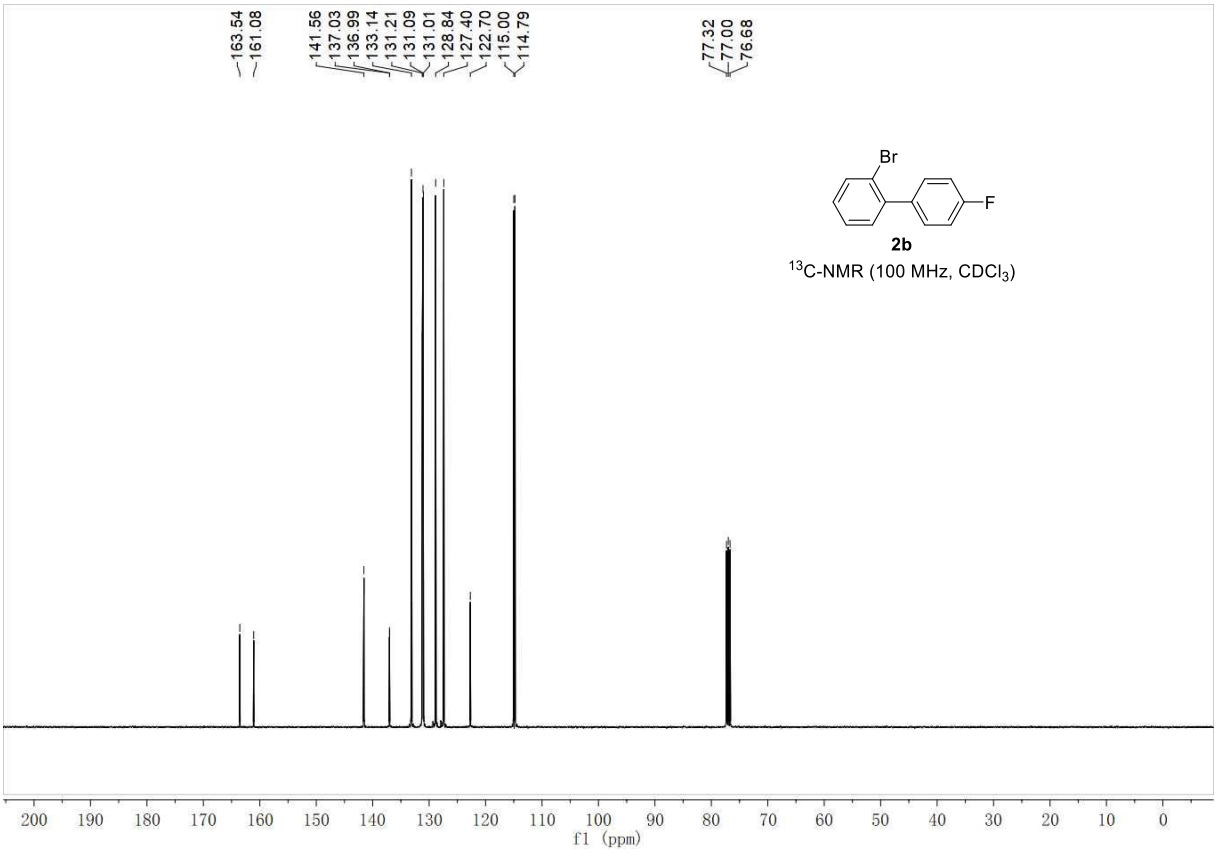
7.390
7.381
7.378
7.363
7.360
7.343
7.339
7.324
7.320
7.252
7.246
7.234
7.232
7.229
7.227
7.214
7.209
7.174
7.166
7.161
7.150
7.144
7.139
7.128
7.123
7.115
Br
F
2b
1H-NMR (400 MHz, CDCl3)
1.00
4.09
1.02
2.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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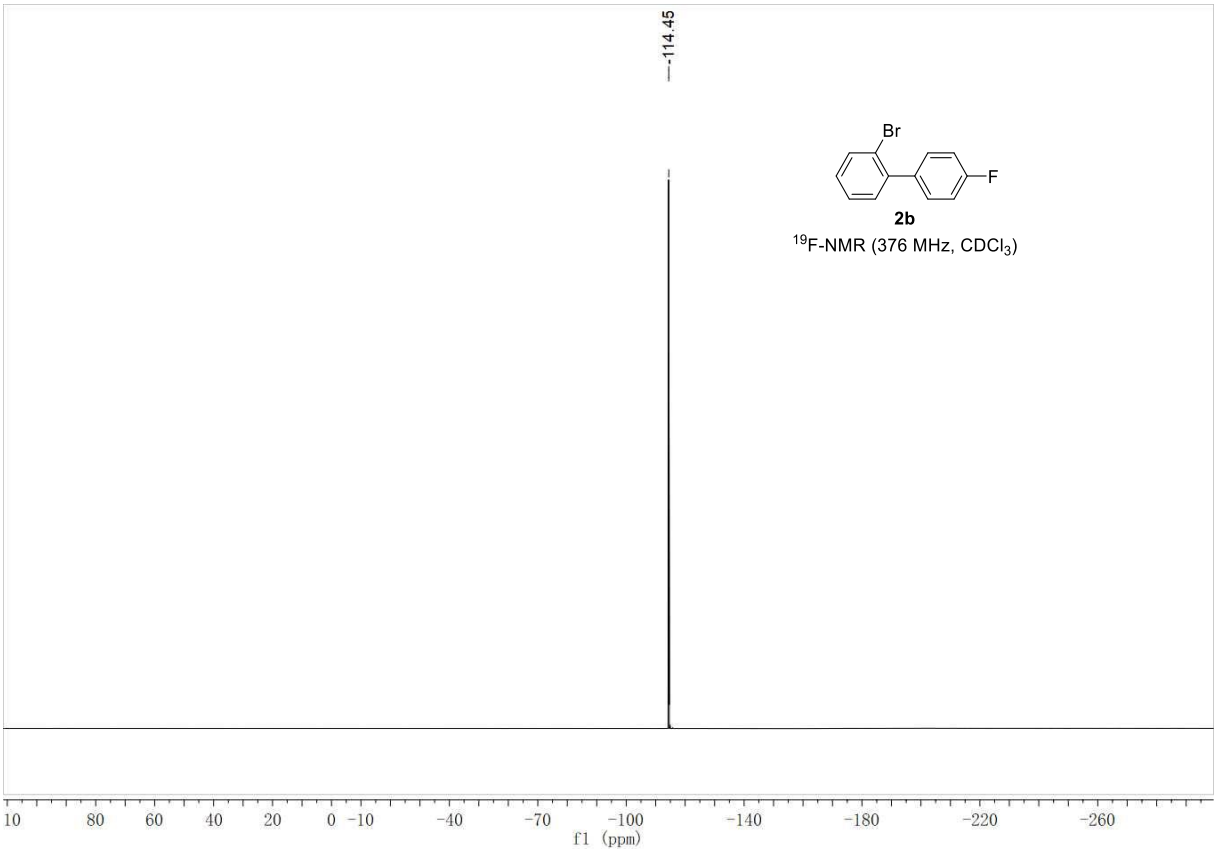
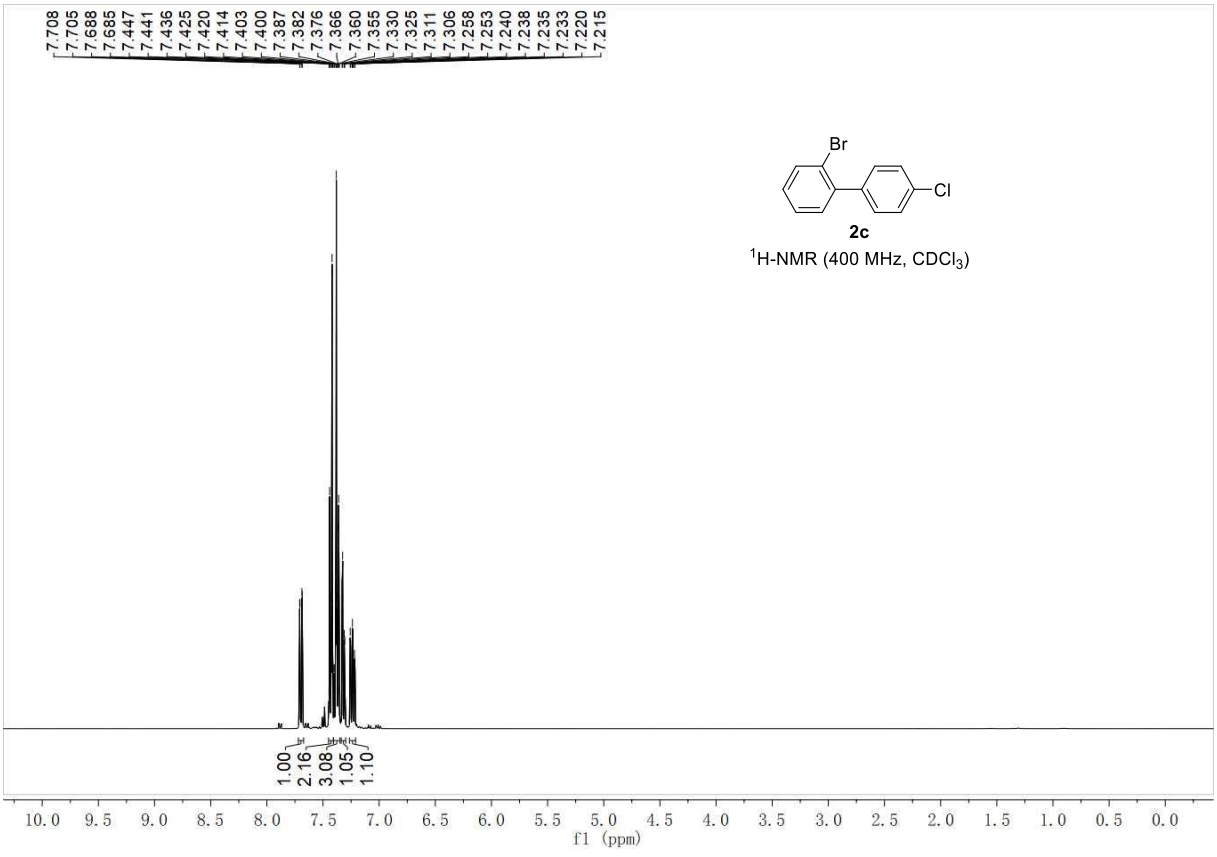
161.08
141.56
137.03
136.99
133.14
131.21
131.09
131.01
128.84
127.40
122.70
115.00
114.79
77.32
77.00
76.68
Br
F
2b
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-114.45
Br
F
2b
19F-NMR (376 MHz, CDCl3)
10
80
60
40
20
0
-10
-40
-70
-100
-140
-180
-220
-260
f1 (ppm)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7.685
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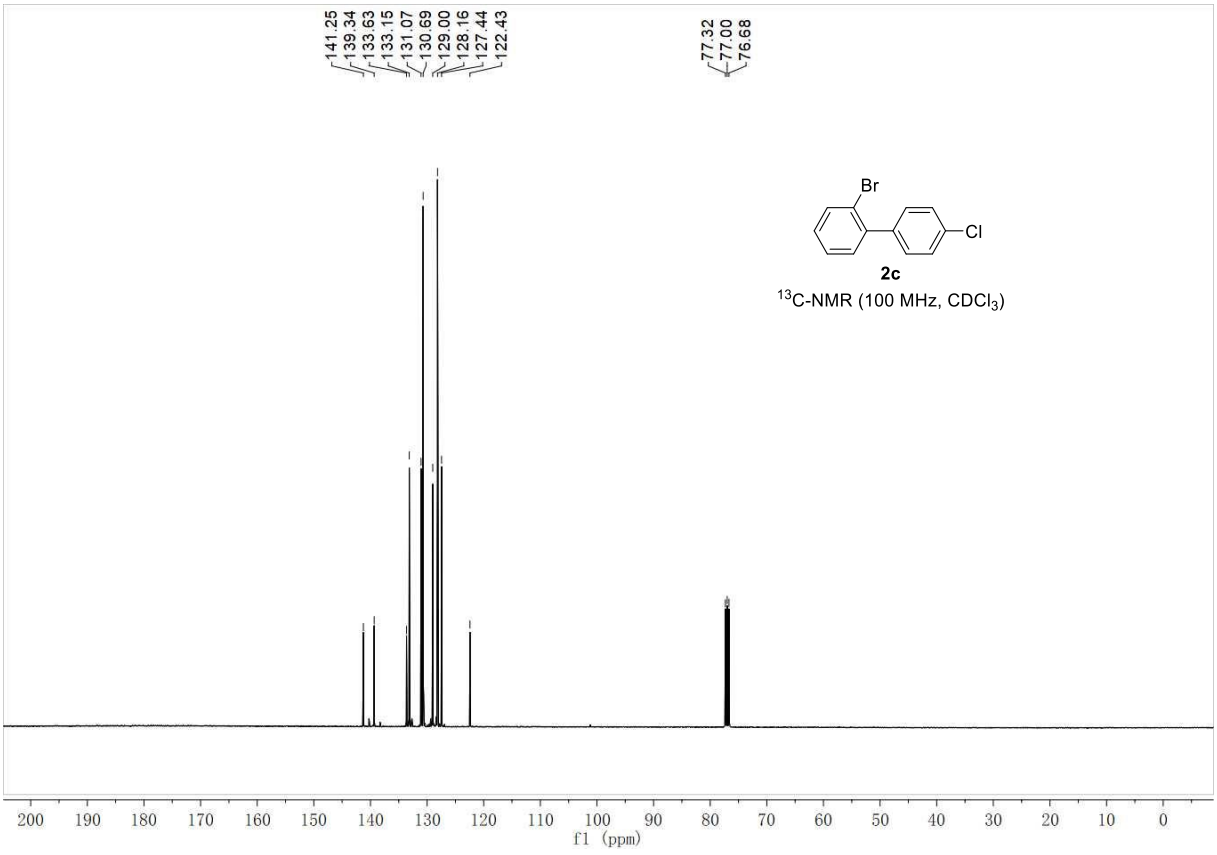
7.441
7.436
7.425
7.420
7.414
7.403
7.400
7.387
7.382
7.376
7.366
7.360
7.355
7.330
7.325
7.311
7.306
7.258
7.253
7.240
7.238
7.235
7.233
7.220
7.215
Br
Cl
2c
1H-NMR (400 MHz, CDCl3)
1.00
2.16
3.08
1.05
1.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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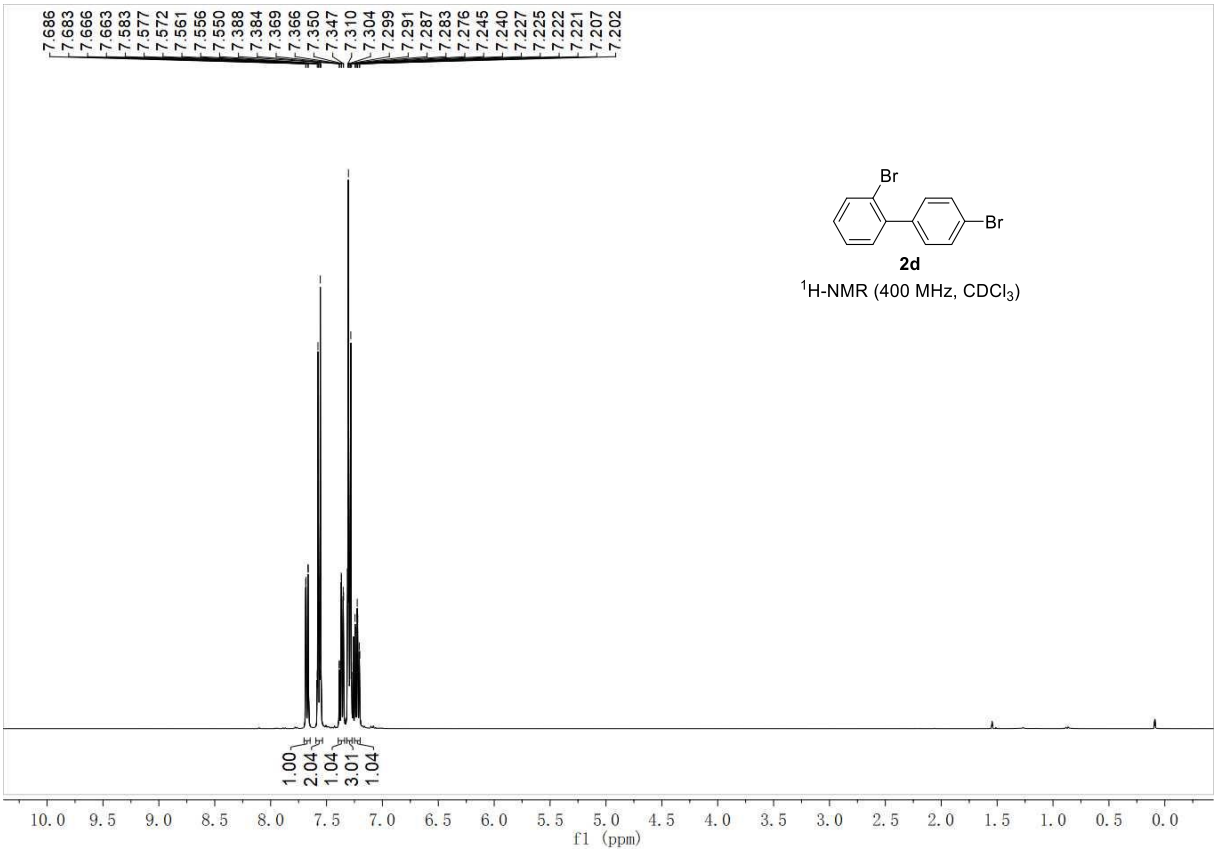
139.34
133.63
133.15
131.07
130.69
129.00
128.16
127.44
122.43
77.32
77.00
76.68
Br
Cl
2c
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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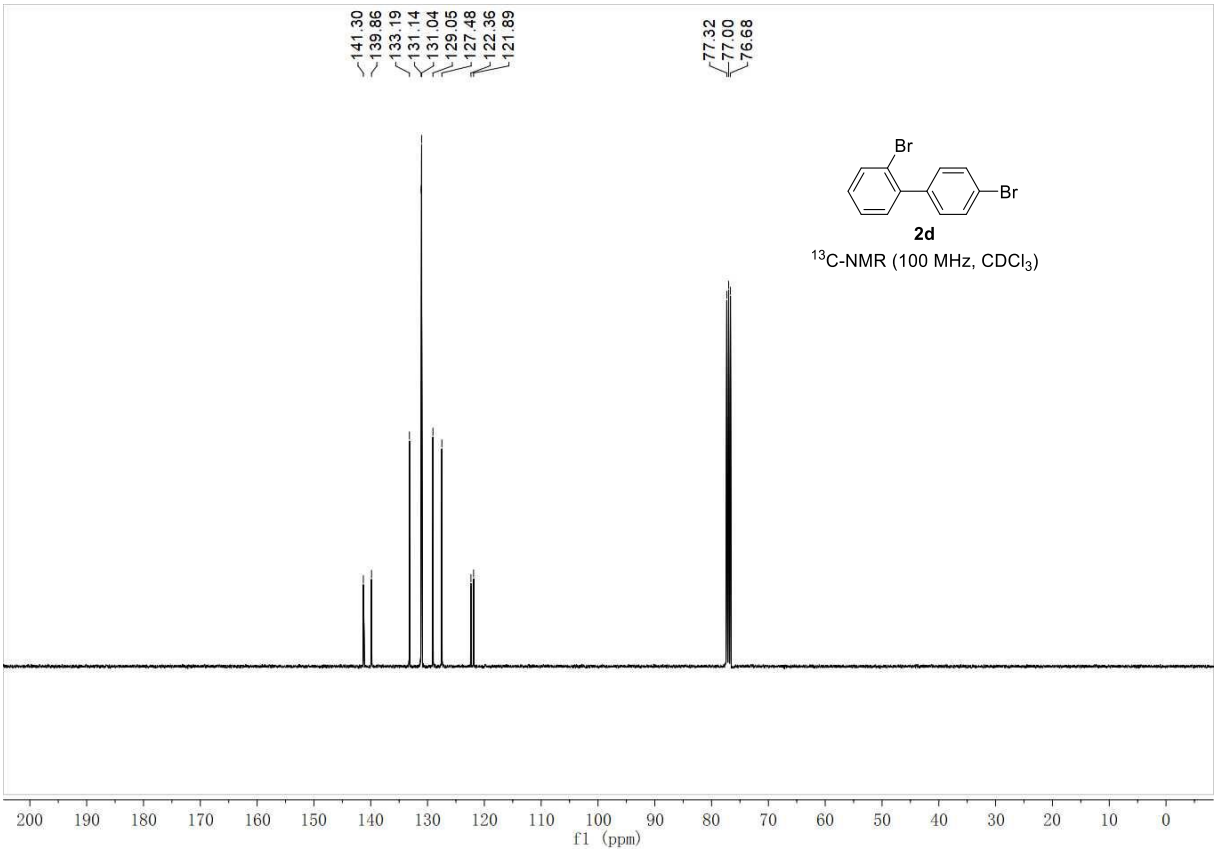
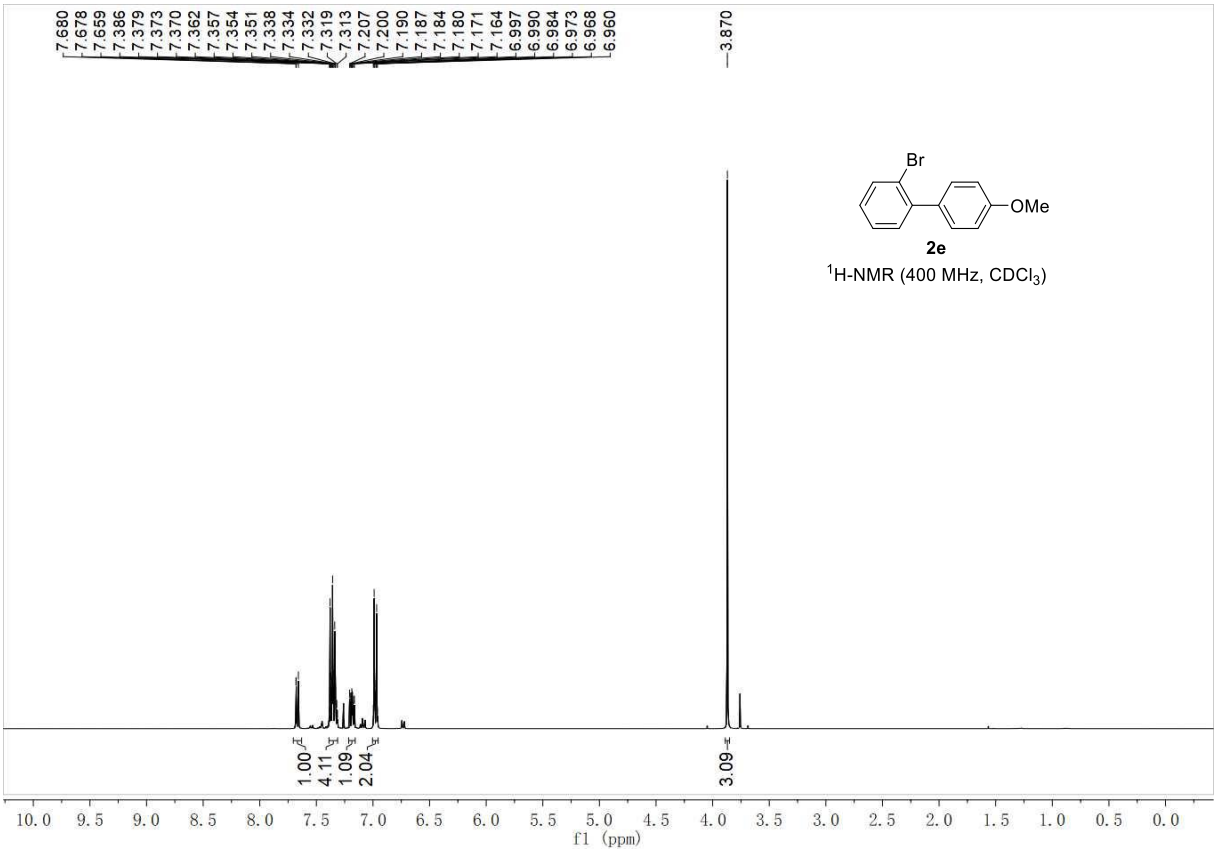
7.683
7.666
7.663
7.583
7.577
7.572
7.561
7.556
7.550
7.388
7.384
7.369
7.366
7.350
7.347
7.310
7.304
7.299
7.291
7.287
7.283
7.276
7.245
7.240
7.227
7.225
7.222
7.221
7.207
7.202
1.00
2.04
1.04
3.01
1.04
Br
Br
2d
1H-NMR (400 MHz, CDCl3)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


141.30
139.86
133.19
131.14
131.04
129.05
127.48
122.36
121.89
77.32
77.00
76.68
Br
Br
2d
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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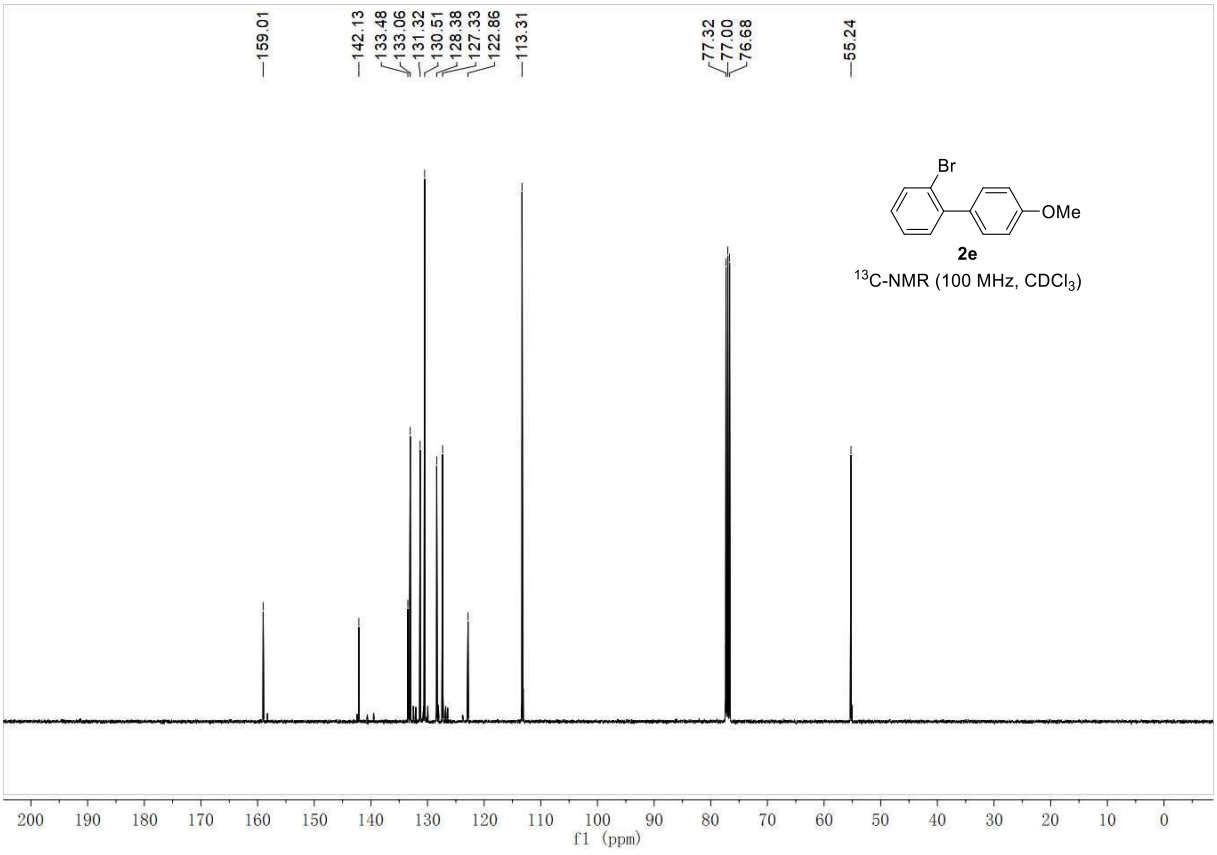
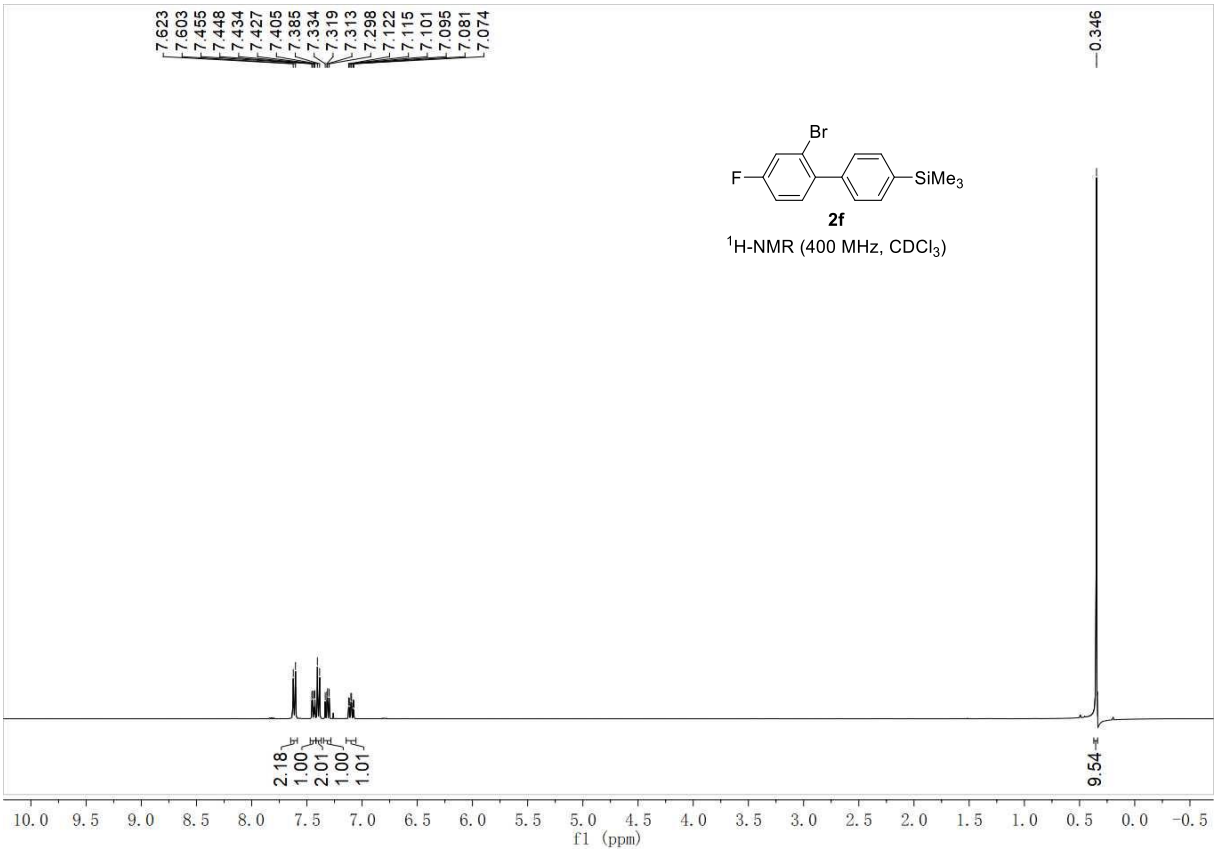
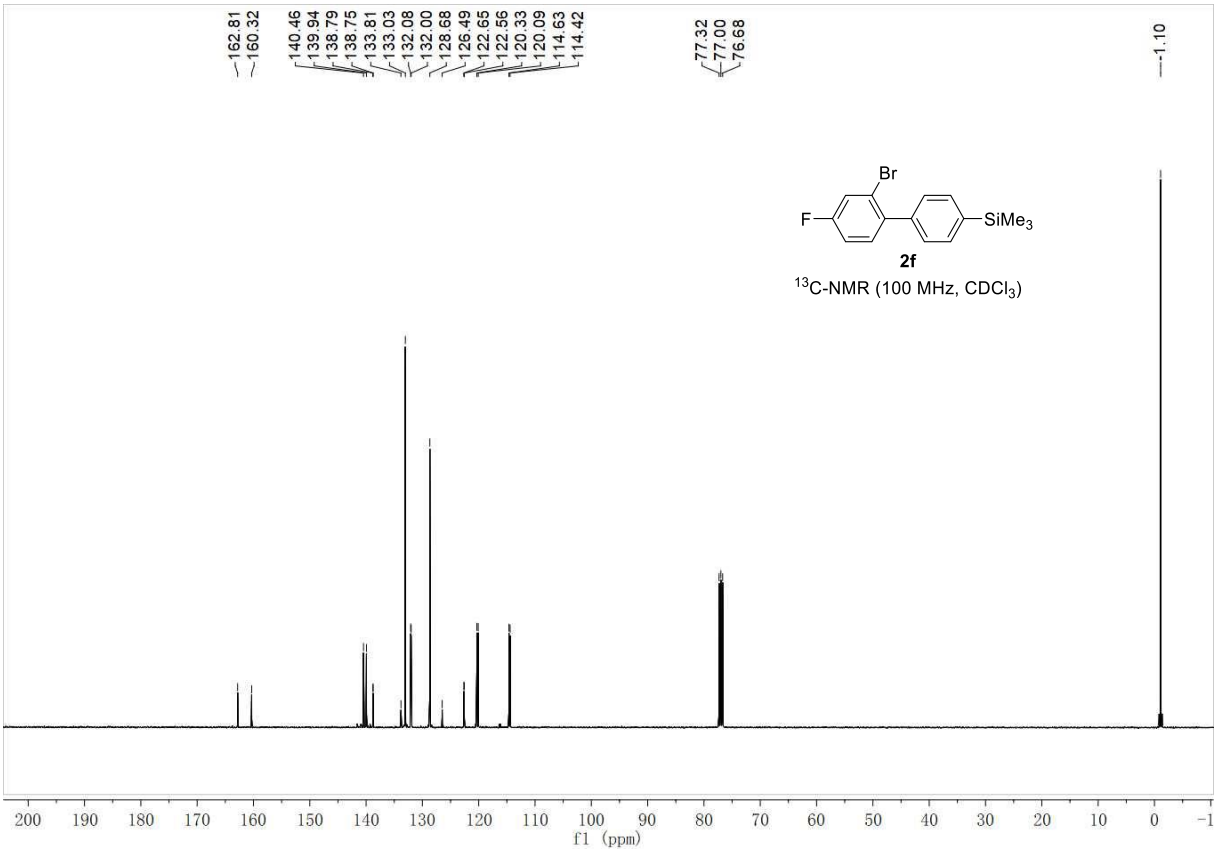
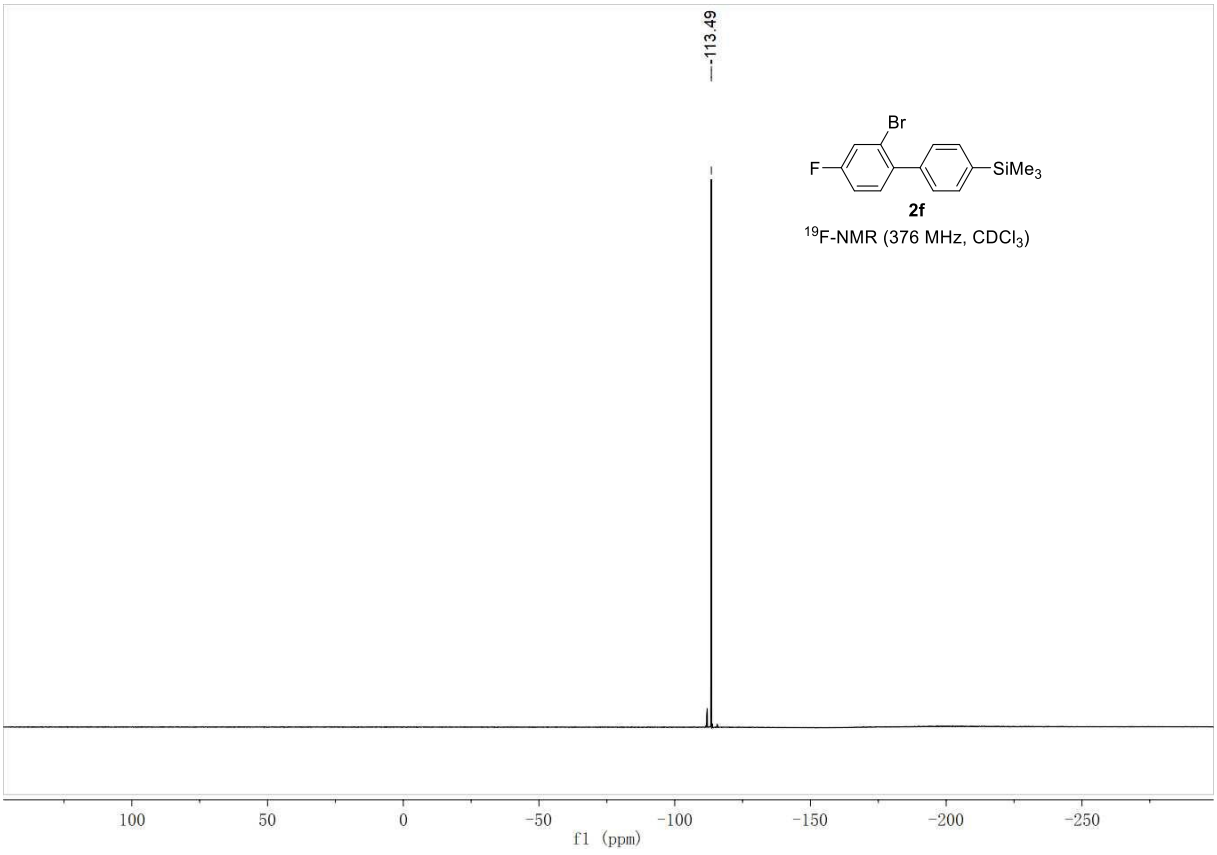
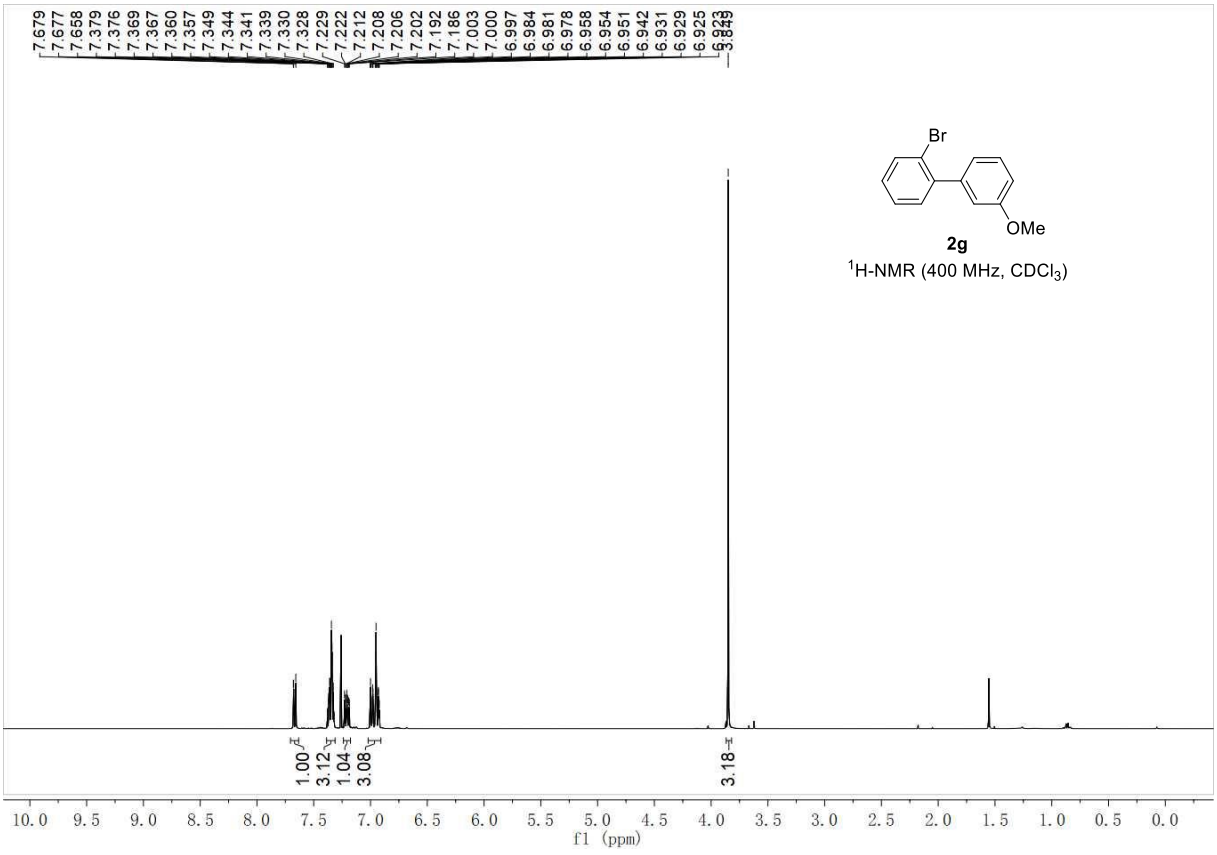
7.678
7.659
7.386
7.379
7.373
7.370
7.362
7.357
7.354
7.351
7.338
7.334
7.332
7.319
7.313
7.207
7.200
7.190
7.187
7.184
7.180
7.171
7.164
6.997
6.990
6.984
6.973
6.968
6.960
3.870
Br
OMe
2e
1H-NMR (400 MHz, CDCl3)
1.00
4.11
1.09
2.04
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

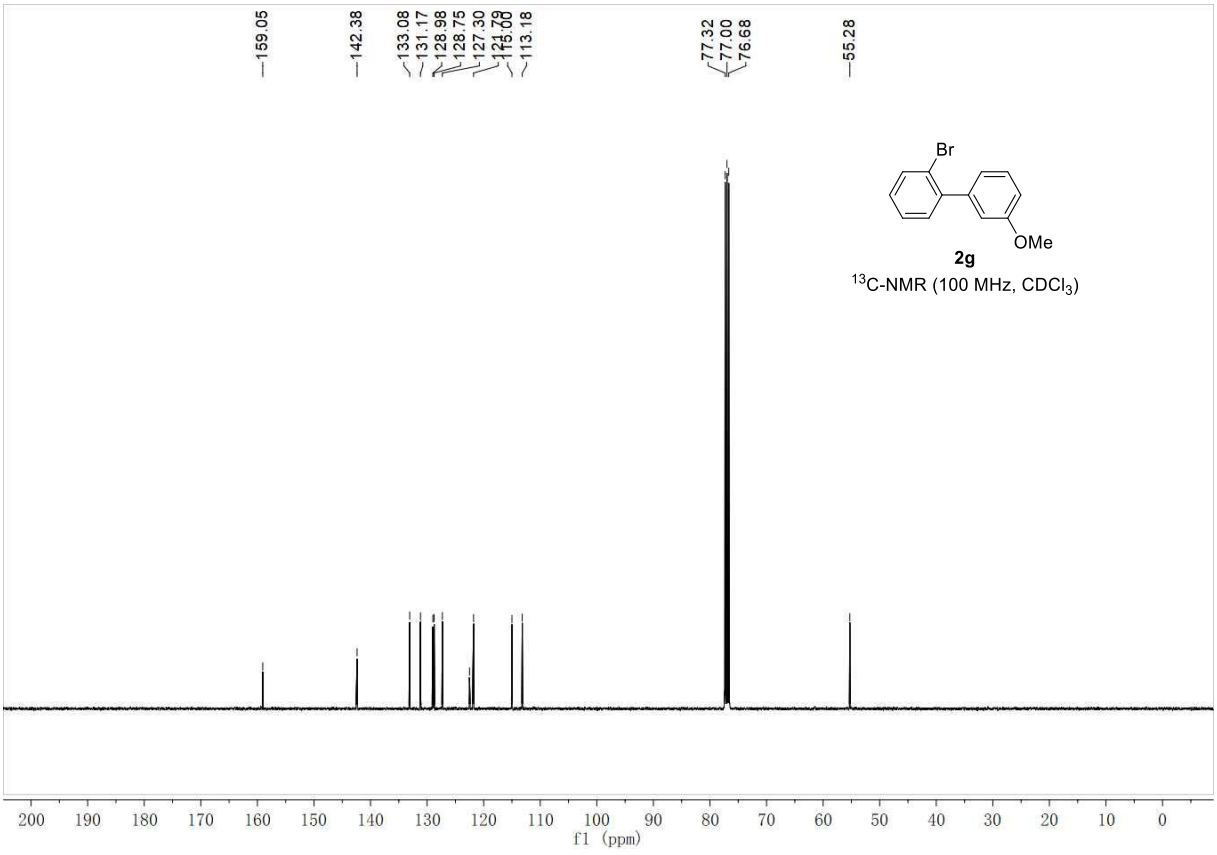

159.01
142.13
133.48
133.06
131.32
130.51
128.38
127.33
122.86
113.31
77.32
77.00
76.68
55.24
Br
OMe
2e
13C-NMR (100 MHz, CDCl3)
f1 (ppm)

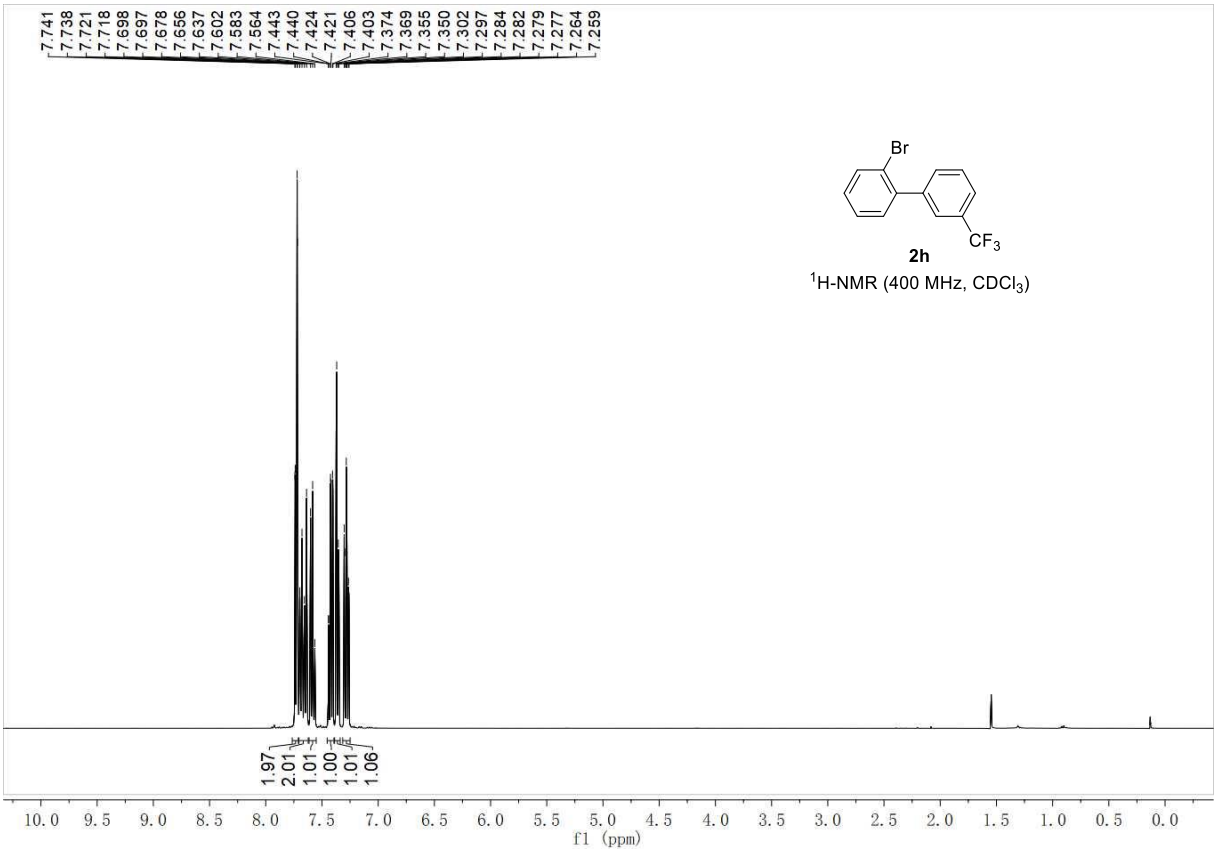

7.623
7.603
7.455
7.448
7.434
7.427
7.405
7.385
7.334
7.319
7.313
7.298
7.122
7.115
7.101
7.095
7.081
7.074
0.346
Br
F
SiMe3
2f
1H-NMR (400 MHz, CDCl3)
2.18
1.00
2.01
1.00
1.01
9.54
f1 (ppm)

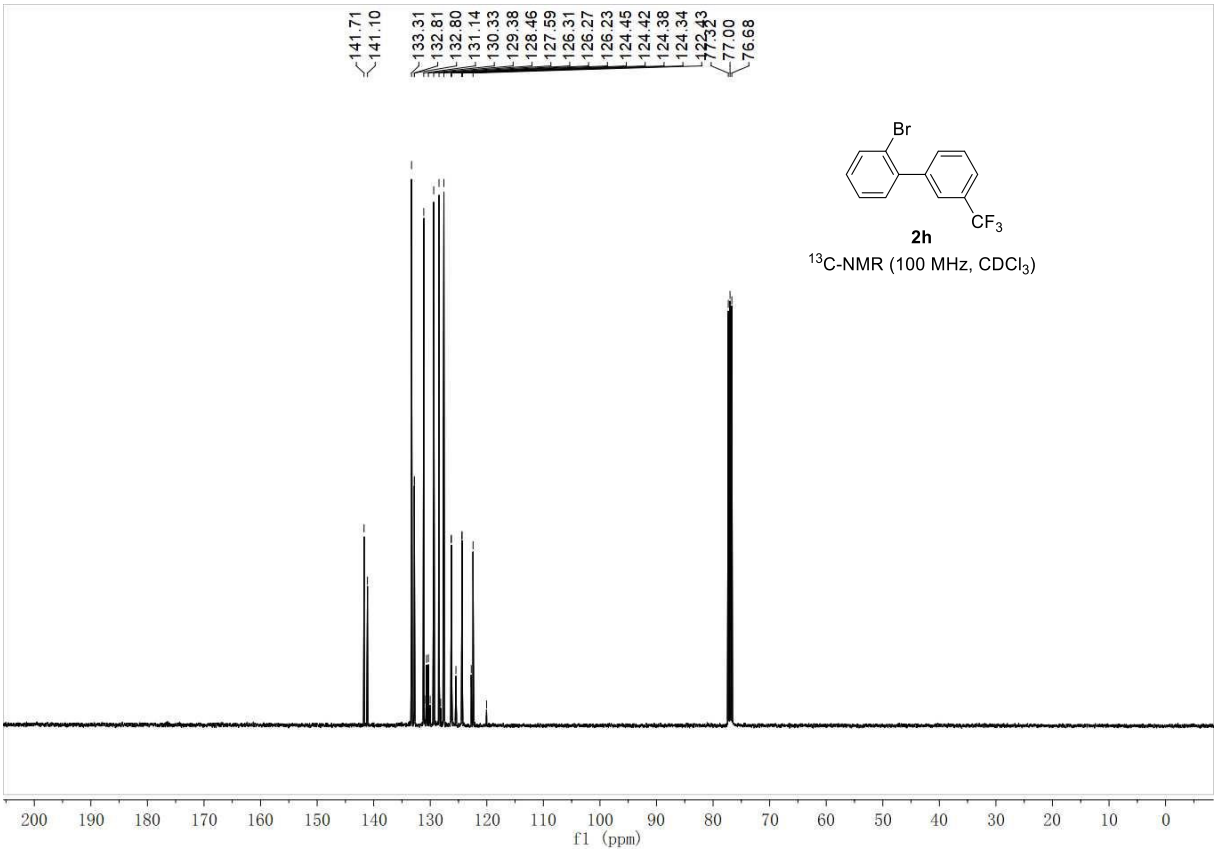

162.81
160.32
140.46
139.94
138.79
138.75
133.81
133.03
132.08
132.00
128.68
126.49
122.65
122.56
120.33
120.09
114.63
114.42
77.32
77.00
76.68
1.10
Br
F
SiMe3
2f
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

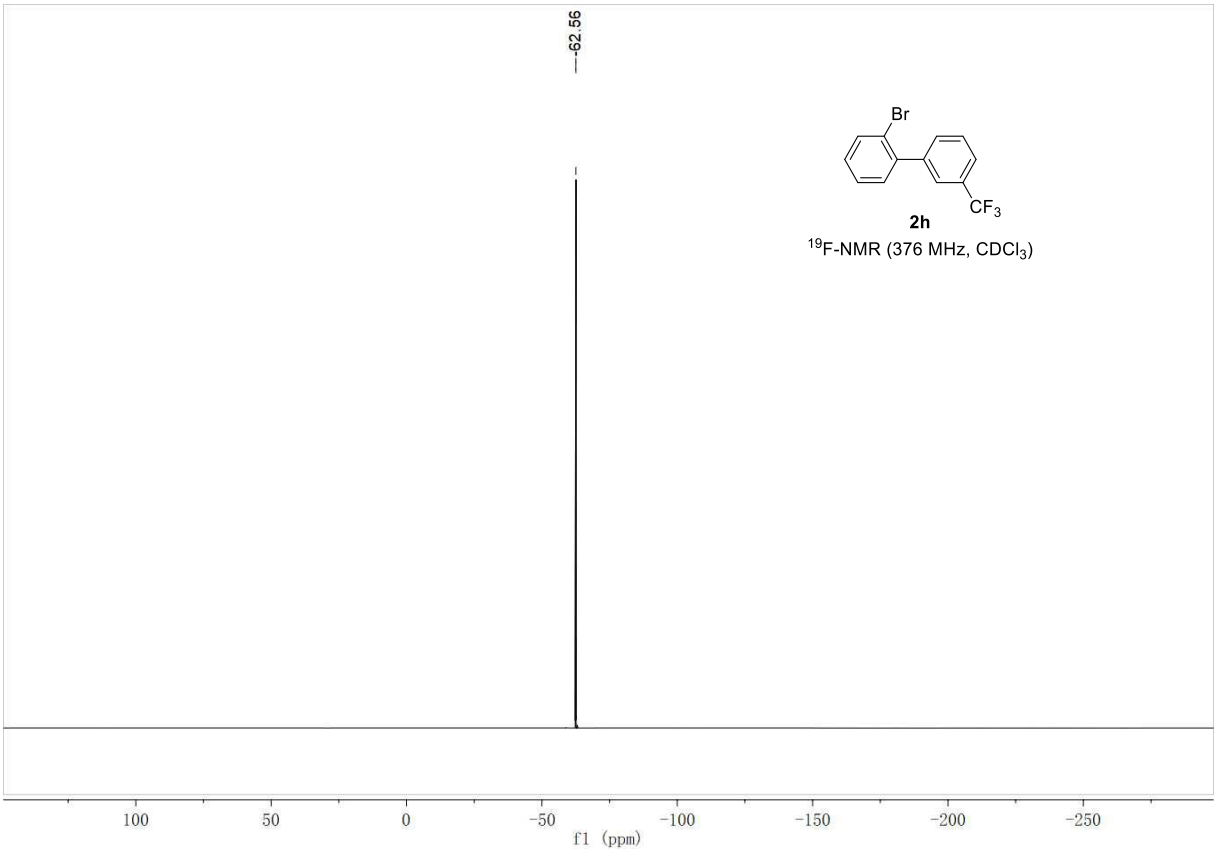

113.49
Br
F
SiMe3
2f
19F-NMR (376 MHz, CDCl3)
100 50 0 -50 -100 -150 -200 -250
f1 (ppm)


7.679
7.677
7.658
7.379
7.376
7.369
7.367
7.360
7.357
7.349
7.344
7.341
7.339
7.330
7.328
7.229
7.222
7.212
7.208
7.206
7.202
7.192
7.186
7.003
7.000
6.997
6.984
6.981
6.978
6.958
6.954
6.951
6.942
6.931
6.929
6.925
6.923
6.849
Br
OMe
2g
1H-NMR (400 MHz, CDCl3)
1.00
3.12
1.04
3.08
3.18
10.0 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 0.0
f1 (ppm)


159.05
142.38
133.08
131.17
128.98
128.75
127.30
121.79
115.00
113.18
77.32
77.00
76.68
55.28
Br
OMe
2g
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

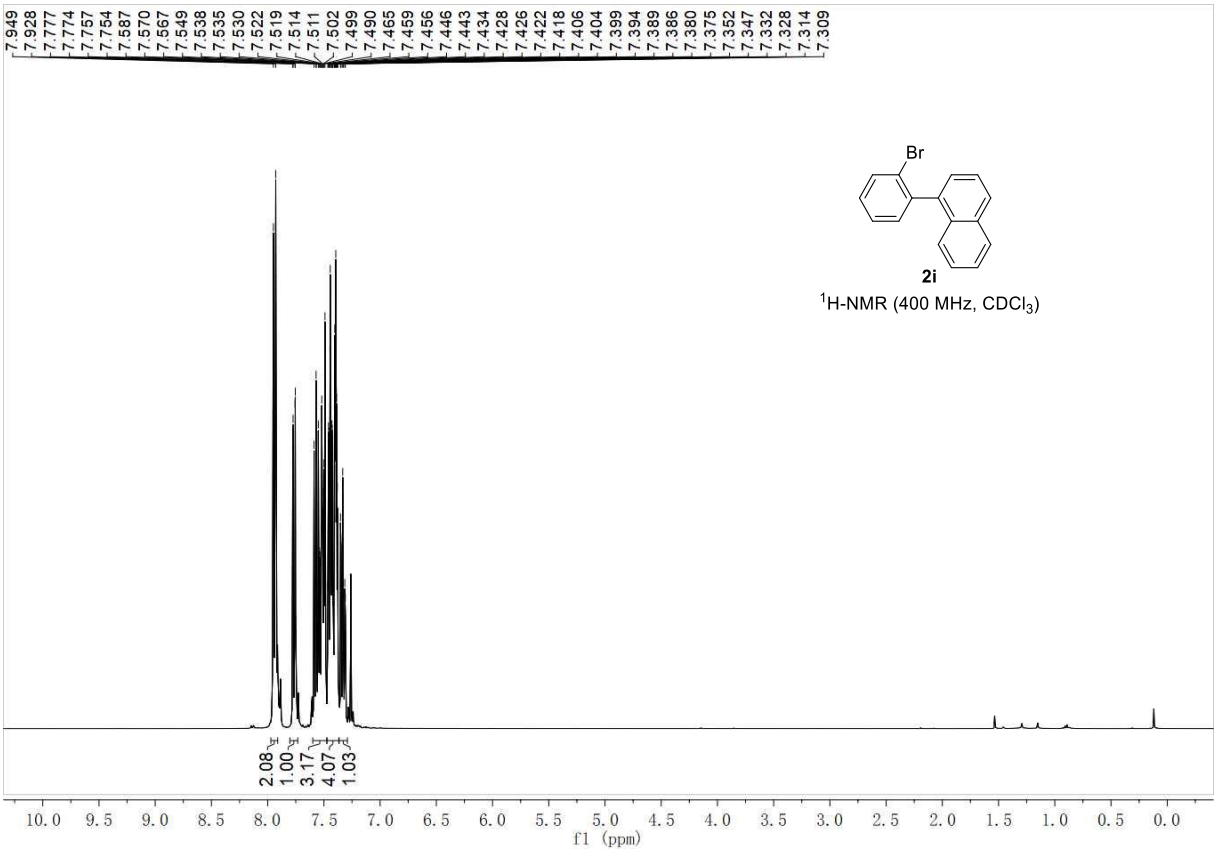

7.741
7.738
7.721
7.718
7.698
7.697
7.678
7.656
7.637
7.602
7.583
7.564
7.443
7.440
7.424
7.421
7.406
7.403
7.374
7.369
7.355
7.350
7.302
7.297
7.284
7.282
7.279
7.277
7.264
7.259
Br
CF3
2h
1H-NMR (400 MHz, CDCl3)
1.97
2.01
1.01
1.00
1.01
1.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


141.71
141.10
133.31
132.81
132.80
131.14
130.33
129.38
128.46
127.59
126.31
126.27
126.23
124.45
124.42
124.38
124.34
123.43
77.32
77.00
76.68
Br
CF3
2h
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



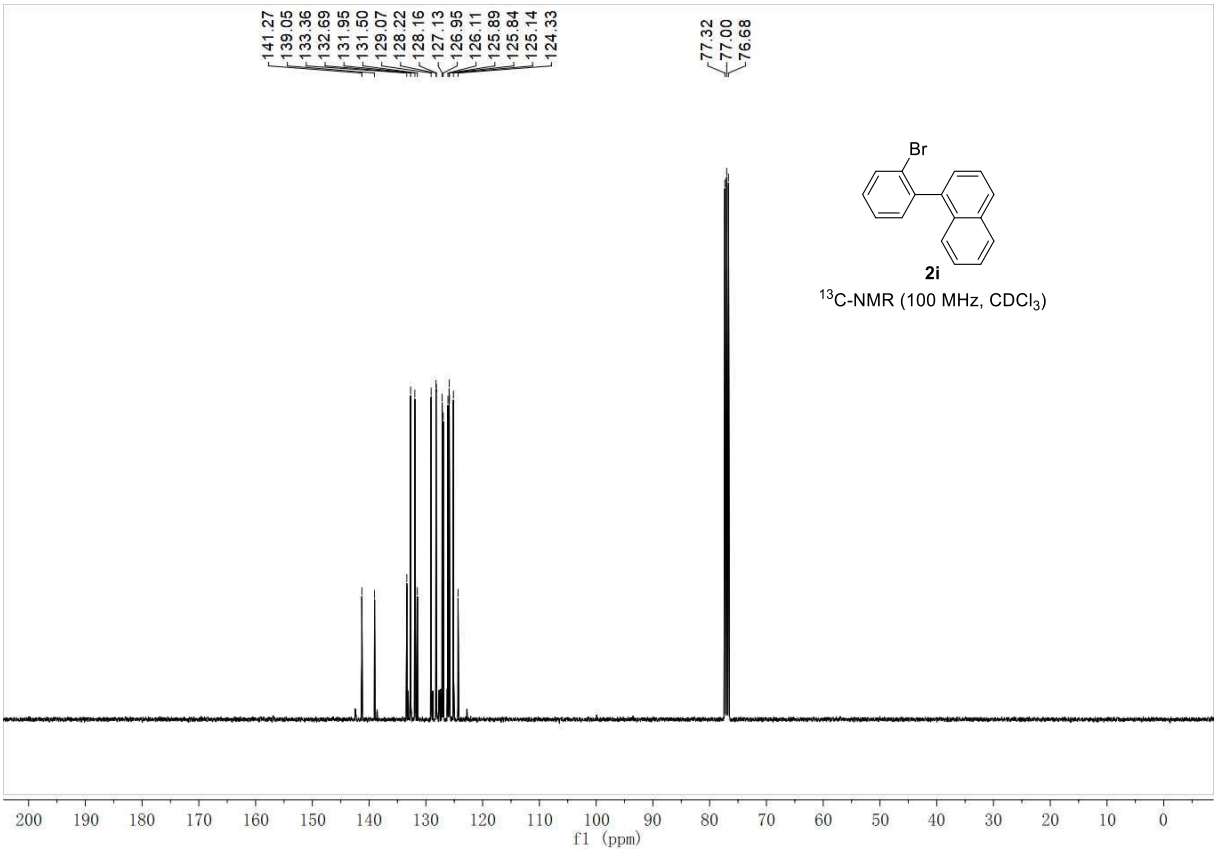
2h

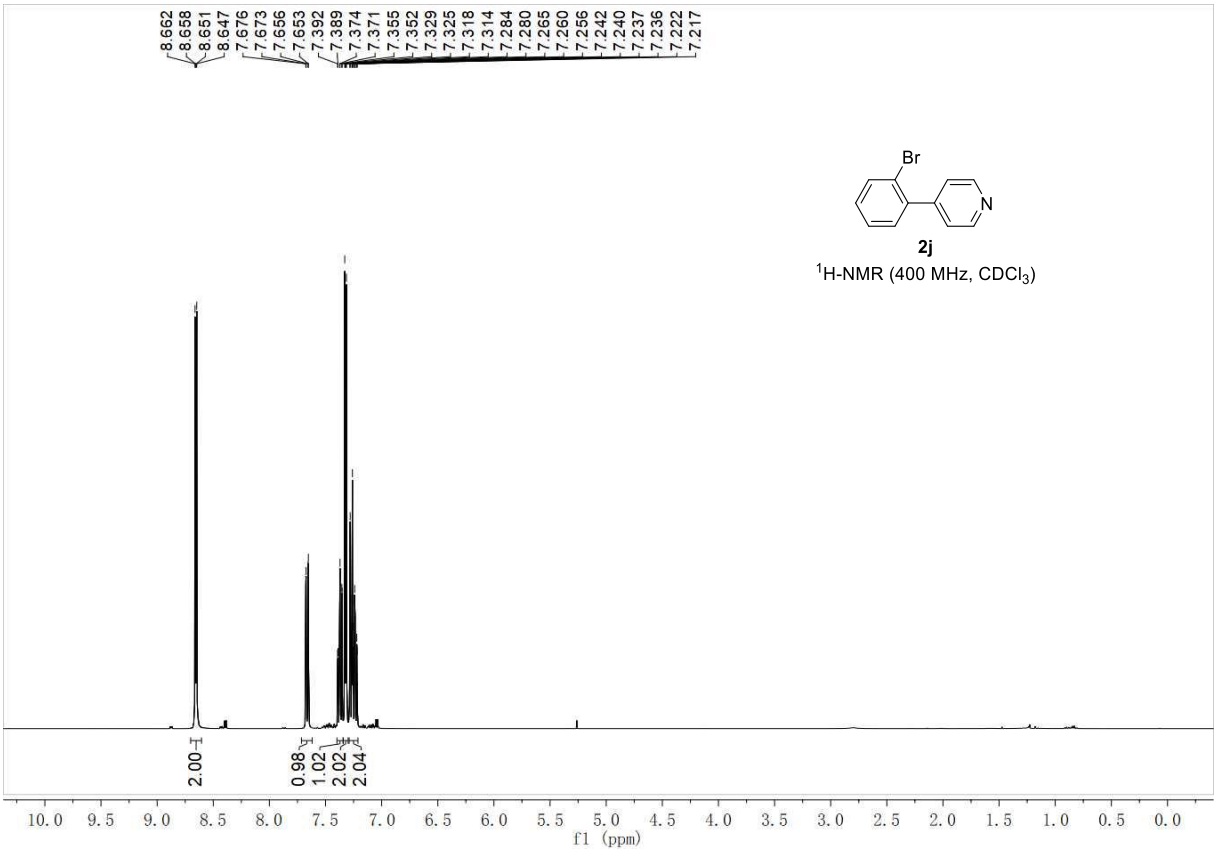
^{19}F-NMR (376 MHz, $CDCl_3$)



2i

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


141.27
139.05
133.36
132.69
131.95
131.50
129.07
128.22
128.16
127.13
126.95
126.11
125.89
125.84
125.14
124.33
77.32
77.00
76.68
Br
2i
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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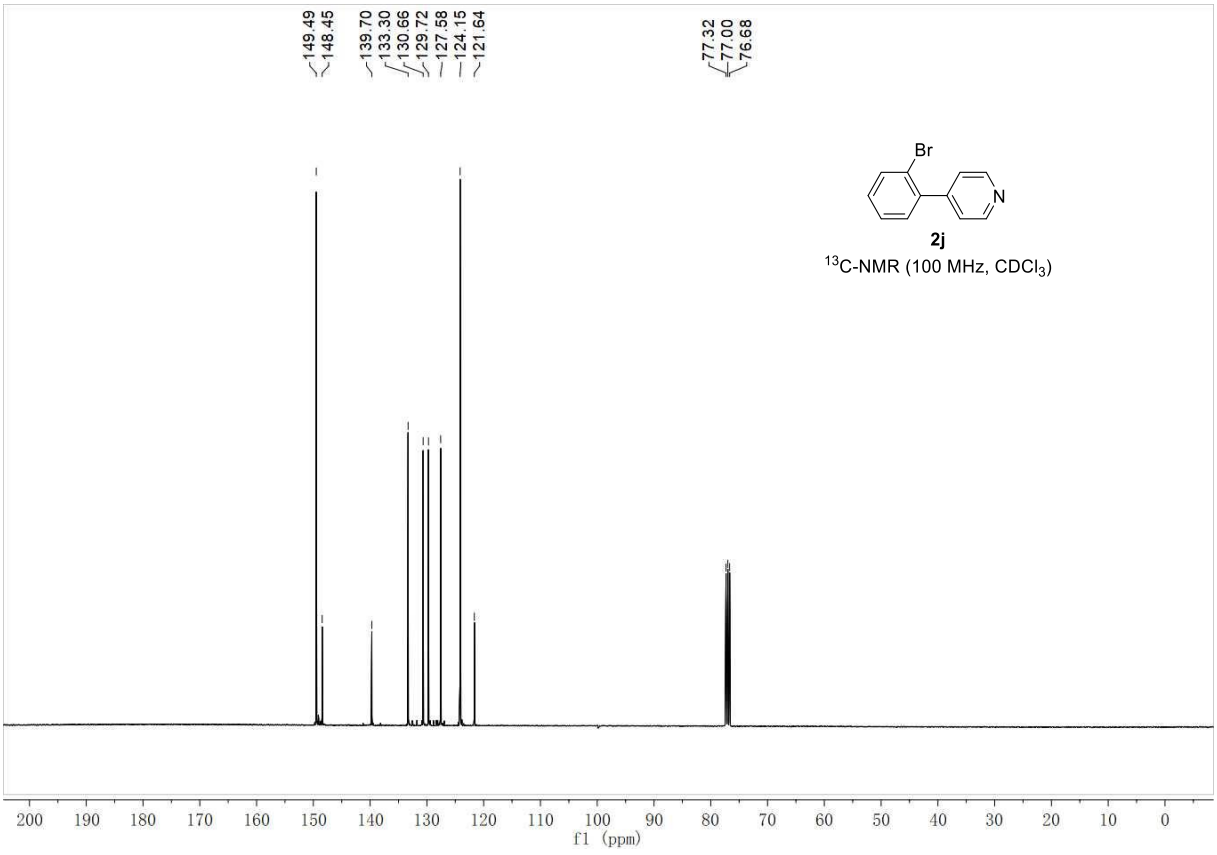
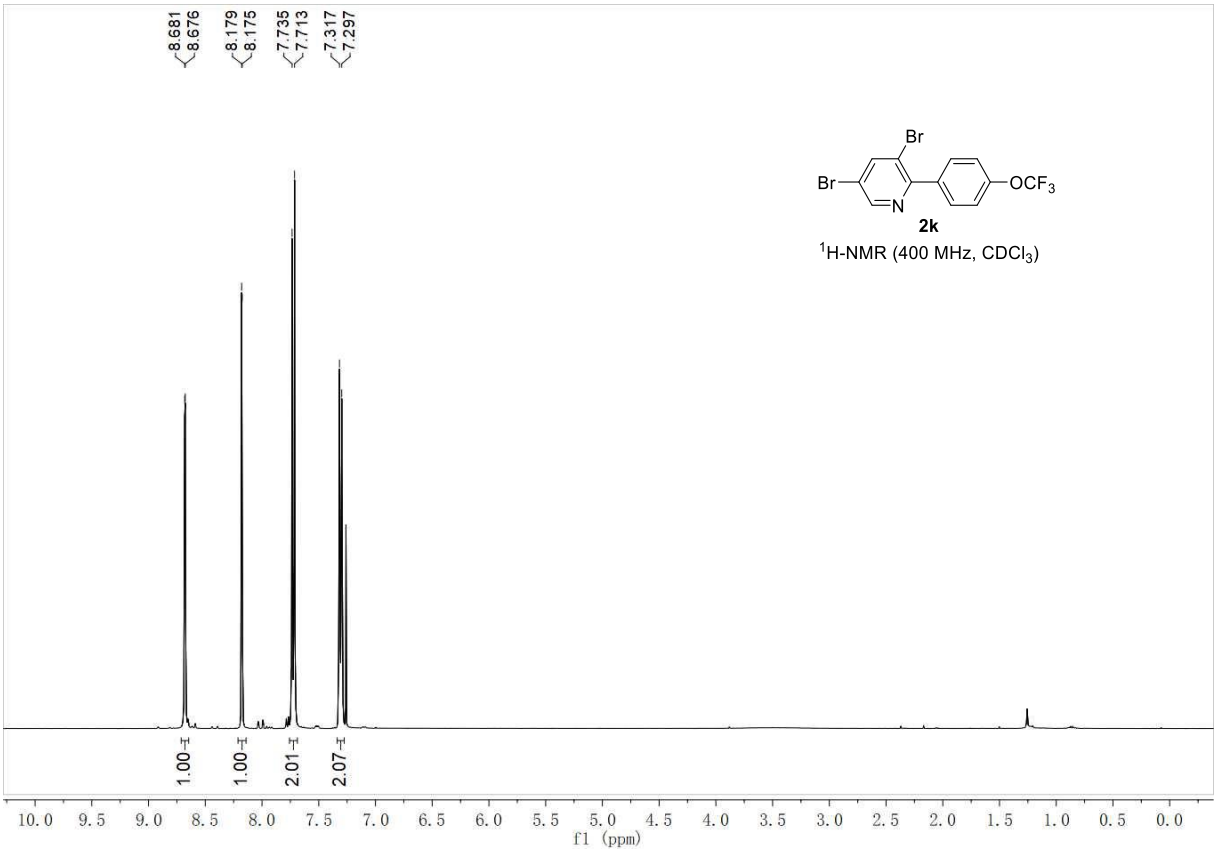
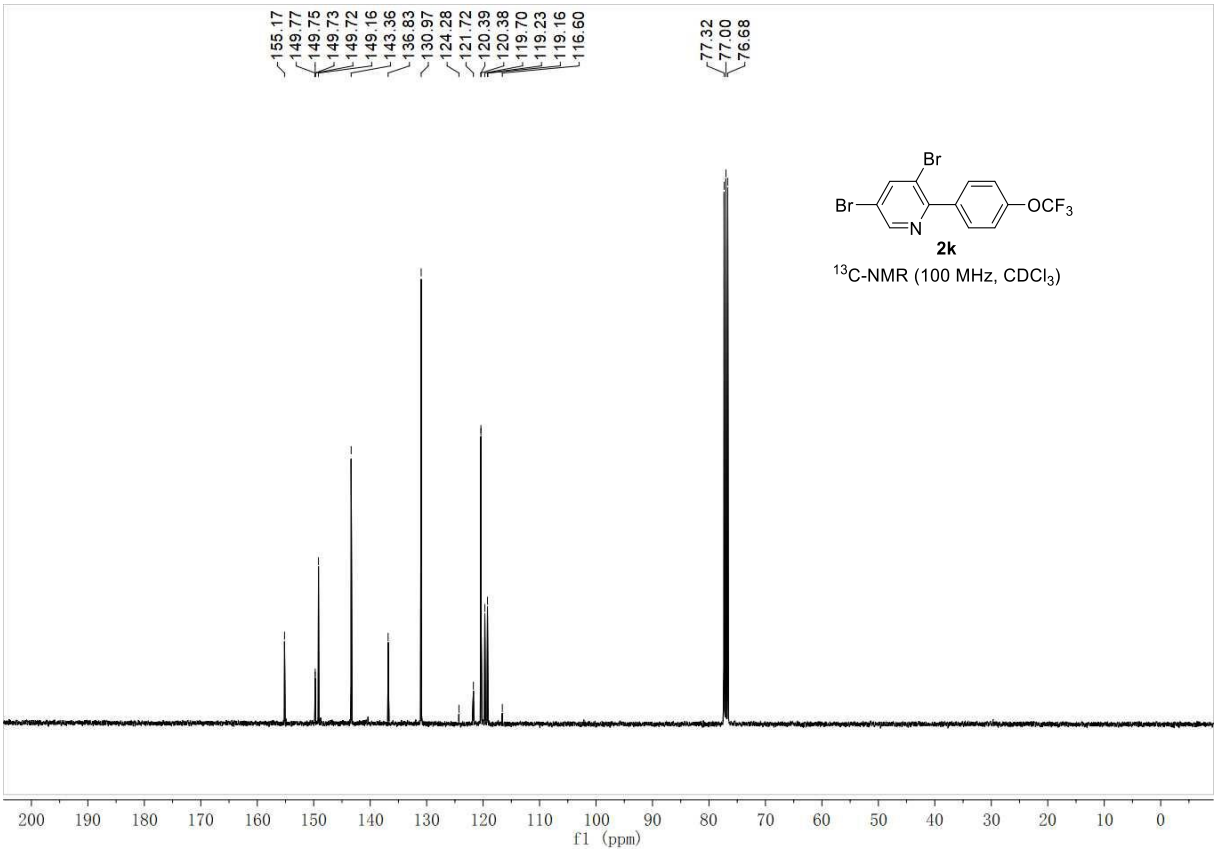
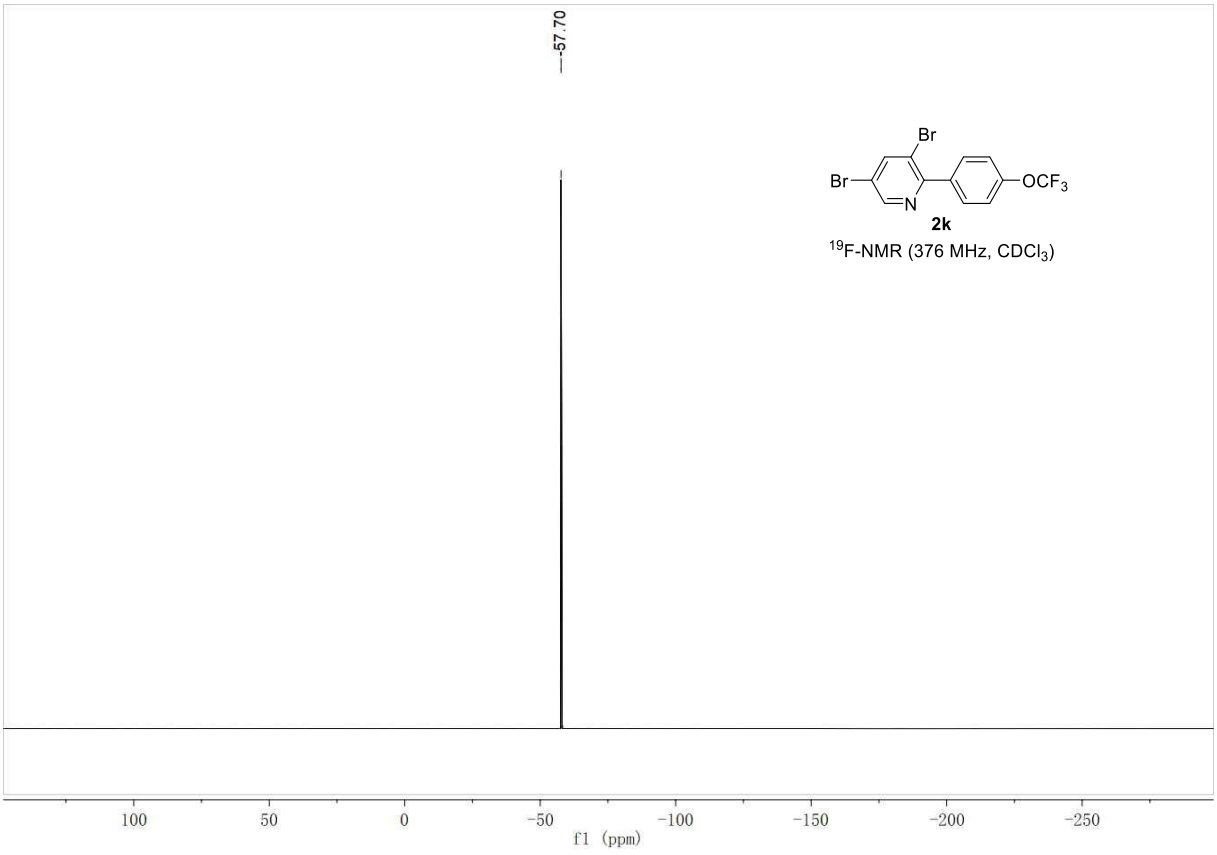
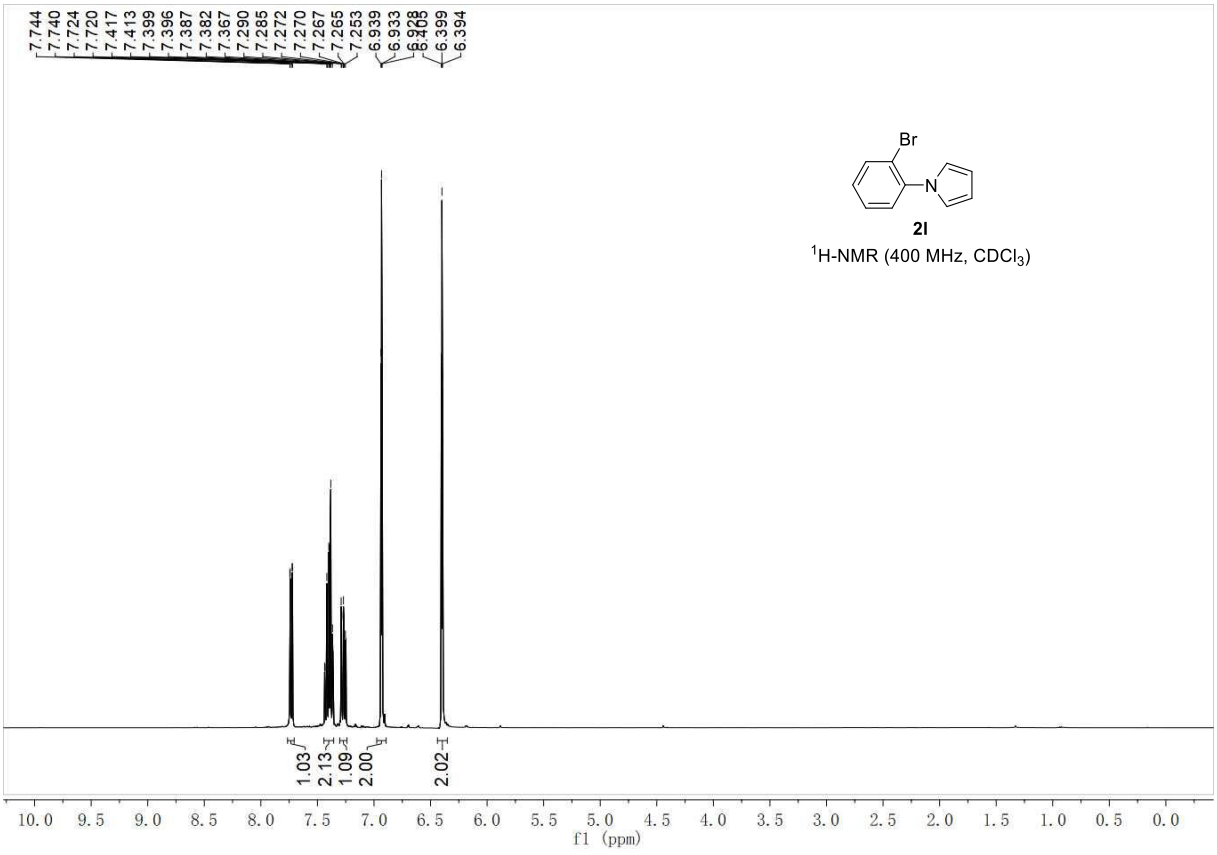
8.658
8.651
8.647
7.676
7.673
7.656
7.653
7.392
7.389
7.374
7.371
7.355
7.352
7.329
7.325
7.318
7.314
7.284
7.280
7.265
7.260
7.256
7.242
7.240
7.237
7.236
7.222
7.217
Br
N
2j
1H-NMR (400 MHz, CDCl3)
2.00
0.98
1.02
2.02
2.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


149.49
148.45
139.70
133.30
130.66
129.72
127.58
124.15
121.64
77.32
77.00
76.68
Br
N
2j
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.681
8.676
8.179
8.175
7.735
7.713
7.317
7.297
Br
Br
N
OCF3
2k
1H-NMR (400 MHz, CDCl3)
1.00
1.00
2.01
2.07
10.0 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 0.0
f1 (ppm)


155.17
149.77
149.75
149.73
149.72
149.16
143.36
136.83
130.97
124.28
121.72
120.39
120.38
119.70
119.23
119.16
116.60
77.32
77.00
76.68
Br
Br
N
OCF3
2k
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-57.70
Br
Br
N
OCF3
2k
19F-NMR (376 MHz, CDCl3)
100 50 0 -50 -100 -150 -200 -250
f1 (ppm)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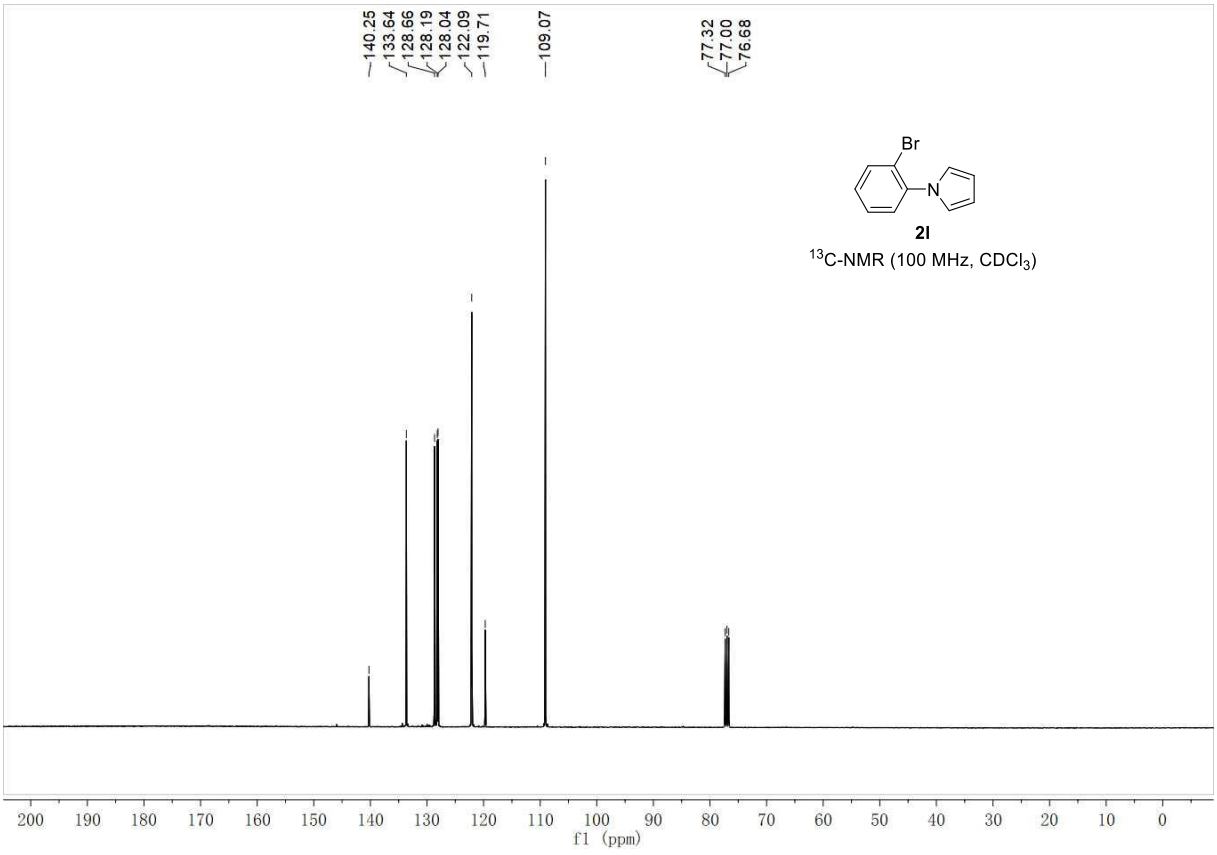
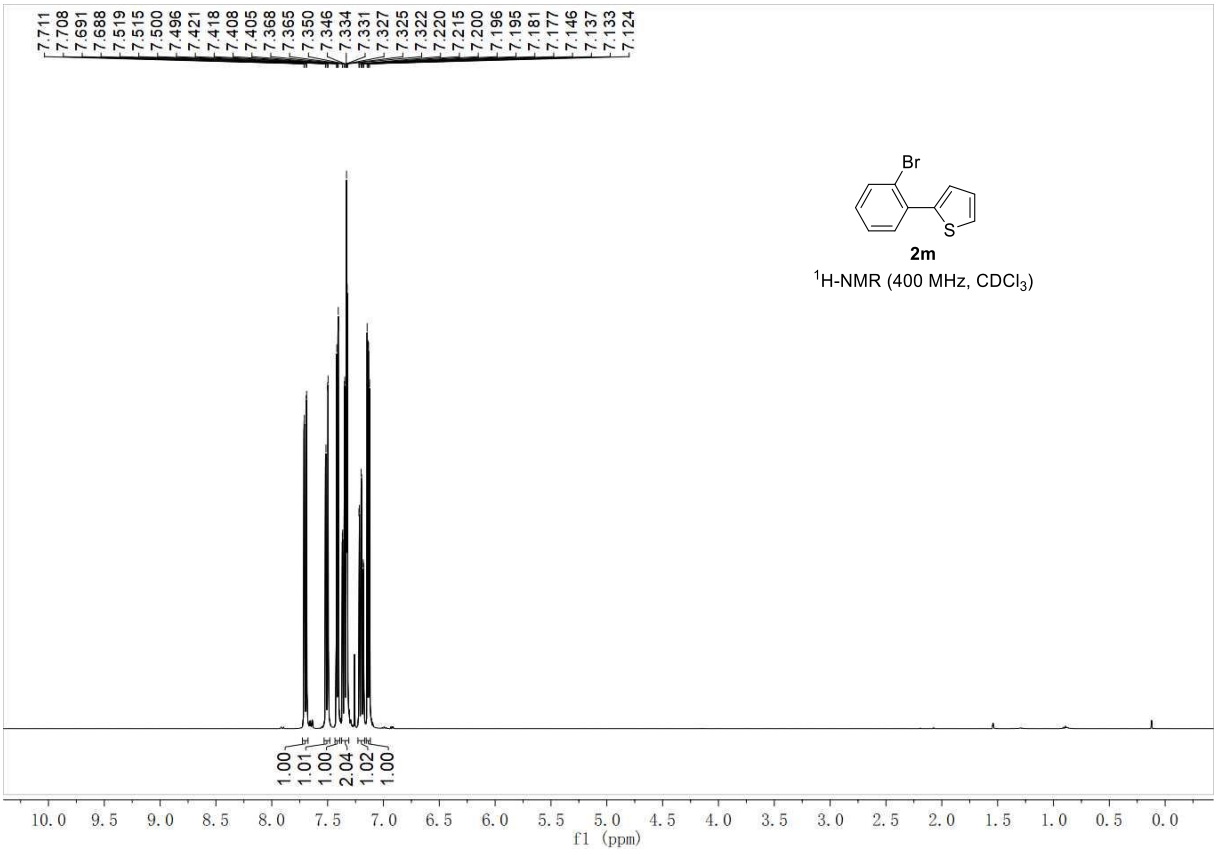
7.724
7.720
7.417
7.413
7.399
7.396
7.387
7.382
7.367
7.290
7.285
7.272
7.270
7.267
7.265
7.253
6.939
6.933
6.928
6.405
6.399
6.394
Br
N
2l
1H-NMR (400 MHz, CDCl3)
1.03
2.13
1.09
2.00
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


140.25
133.64
128.66
128.19
128.04
122.09
119.71
109.07
77.32
77.00
76.68
Br
N
2l
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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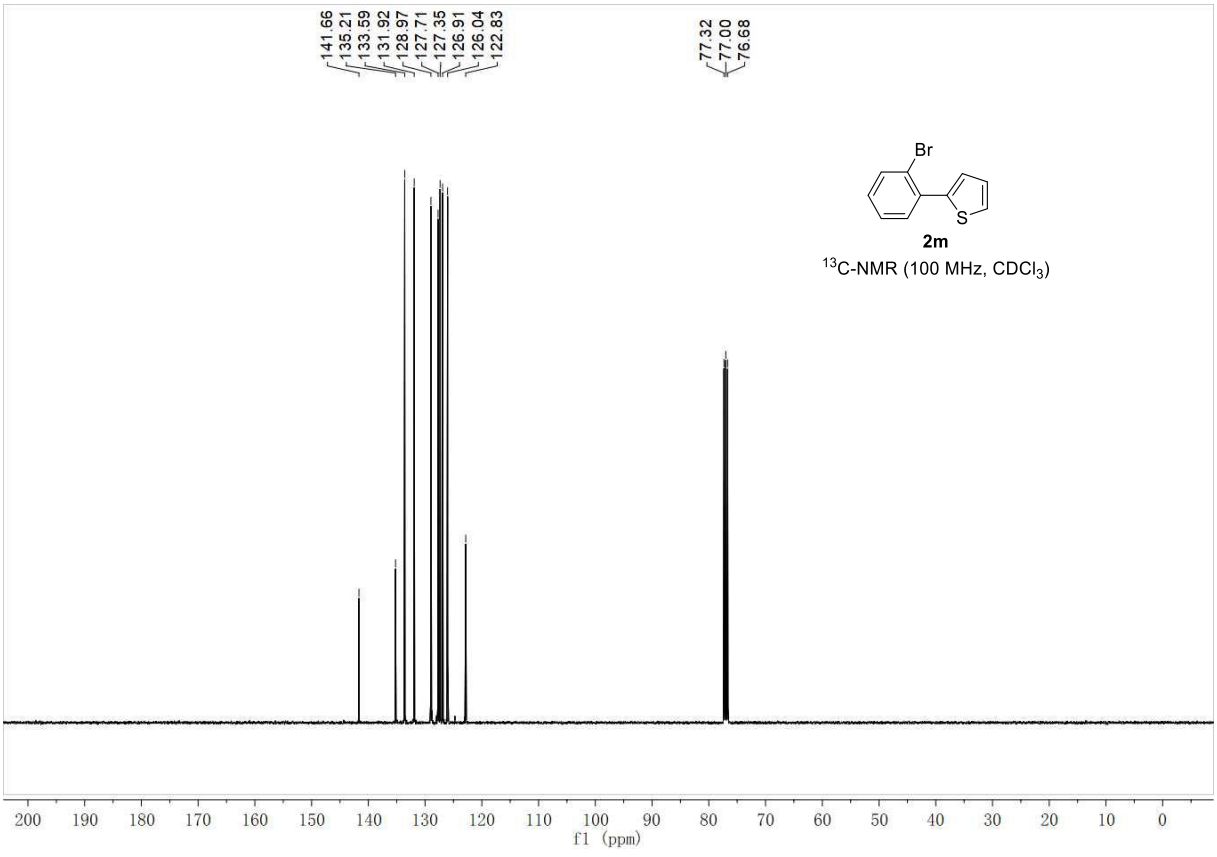
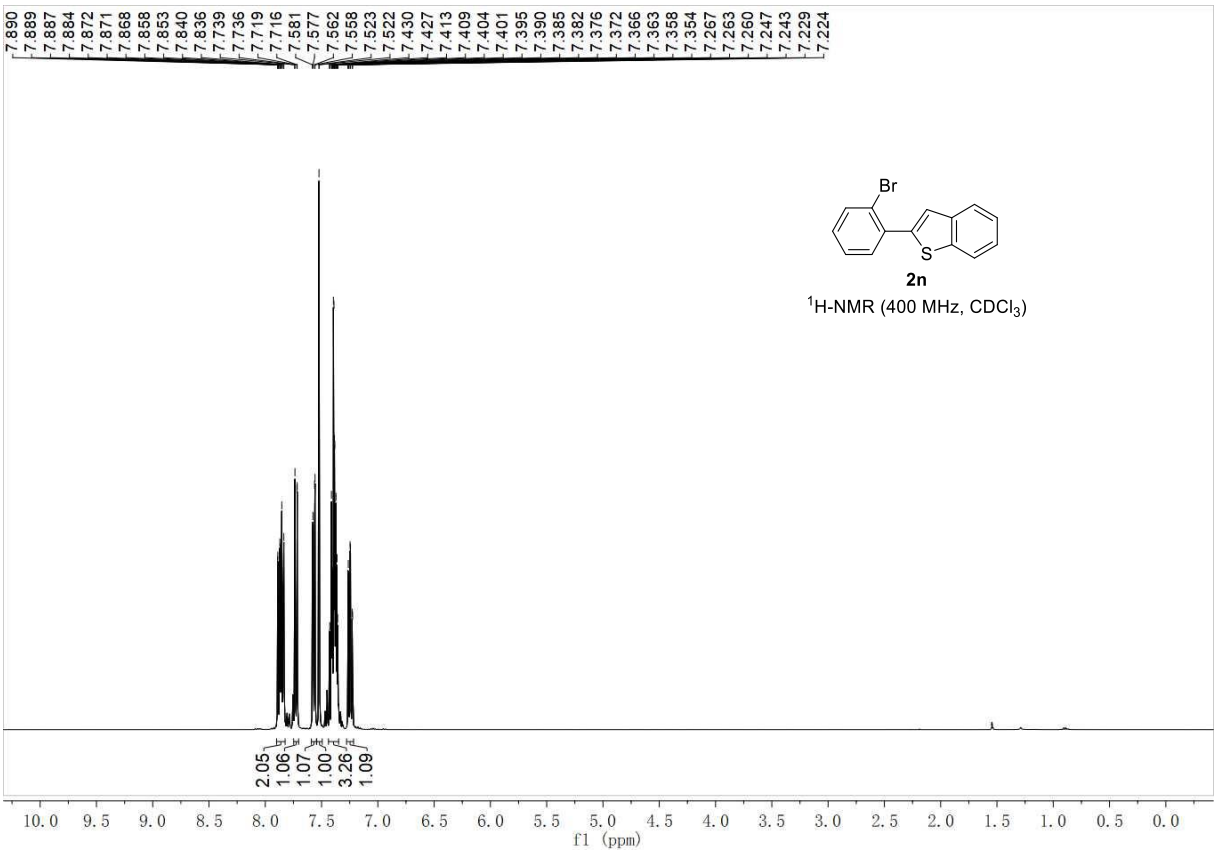
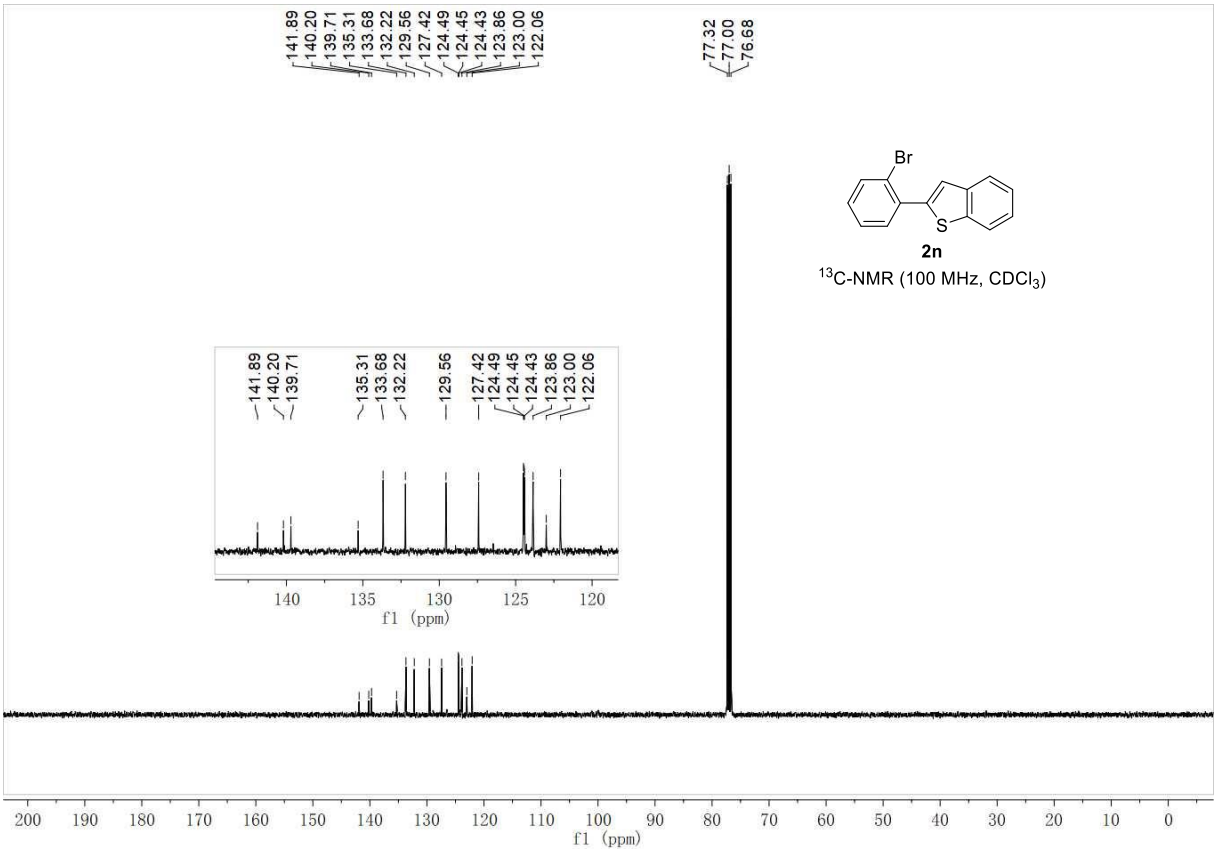
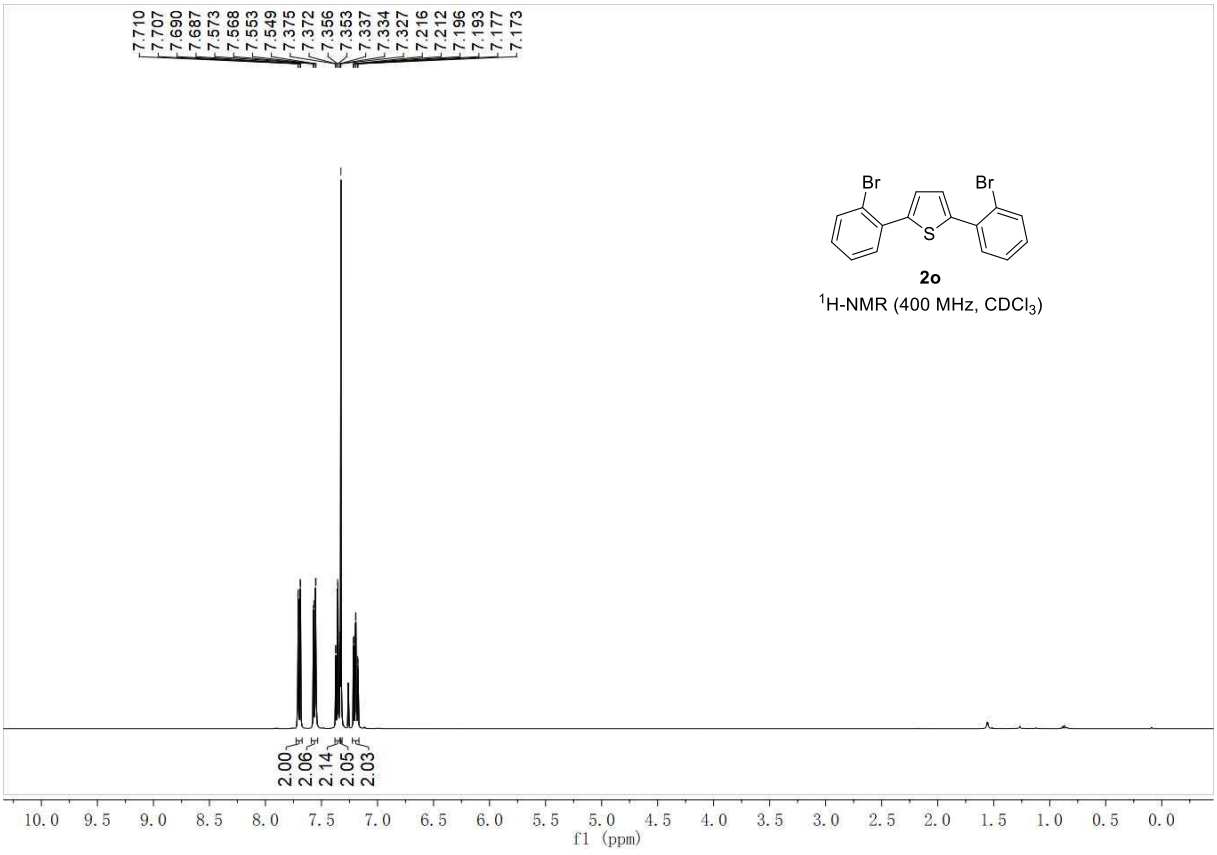
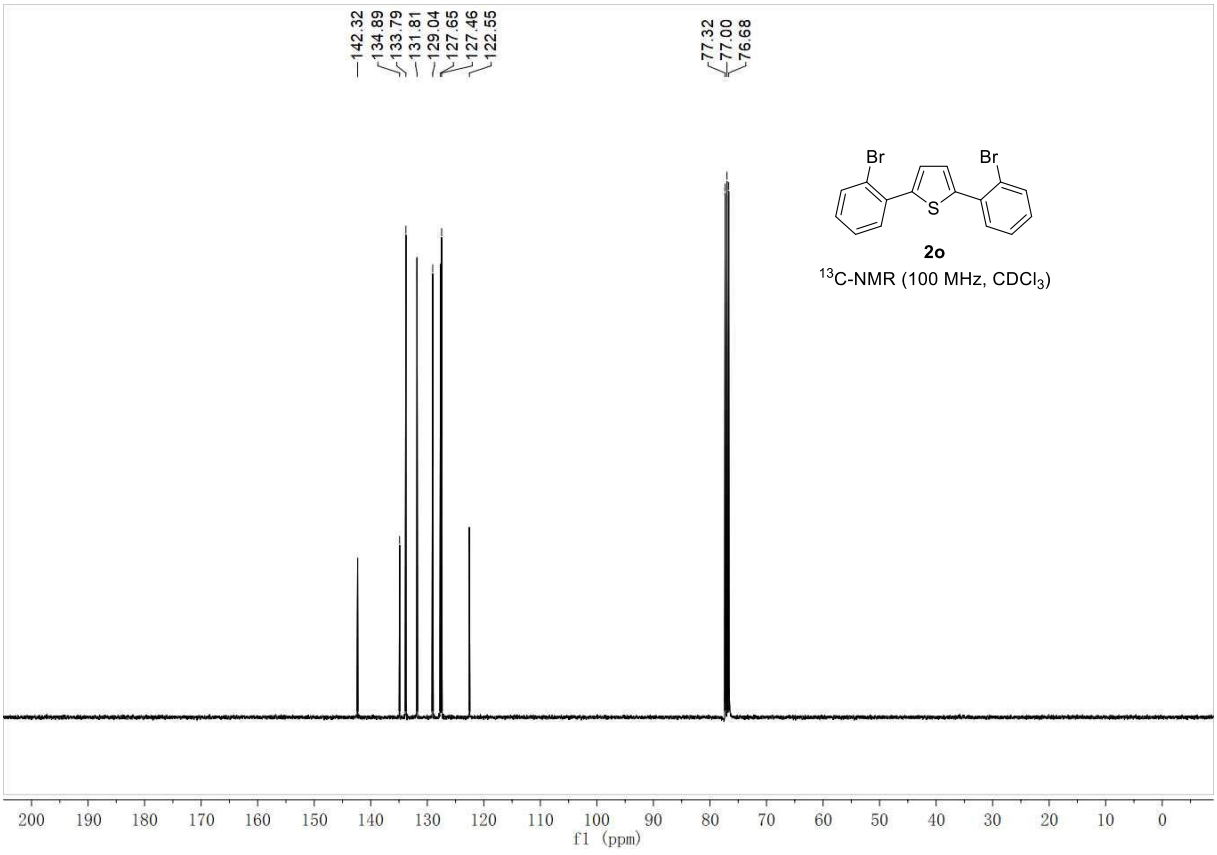
7.688
7.519
7.515
7.500
7.496
7.421
7.418
7.408
7.405
7.368
7.365
7.350
7.346
7.334
7.331
7.327
7.325
7.322
7.220
7.215
7.200
7.196
7.195
7.181
7.177
7.146
7.137
7.133
7.124
Br
S
2m
1H-NMR (400 MHz, CDCl3)
1.00
1.01
1.00
2.04
1.02
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

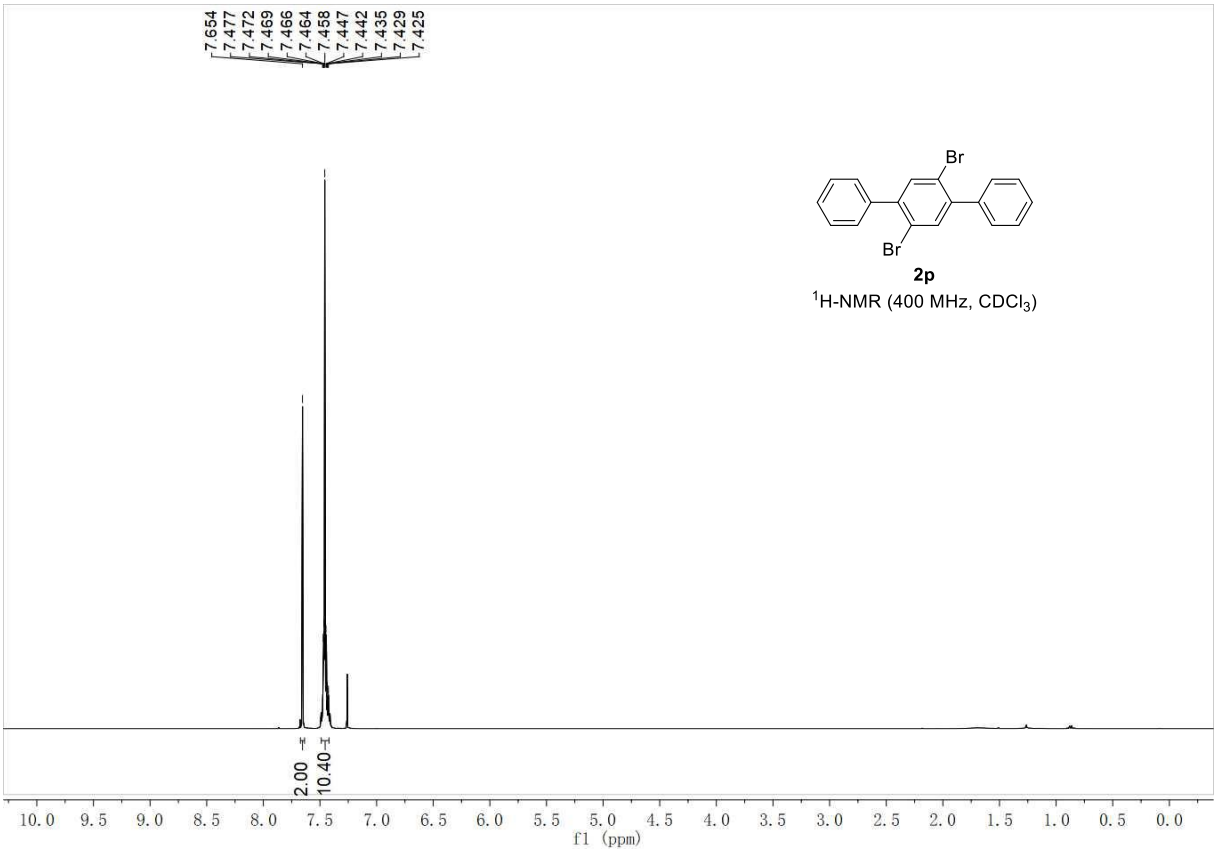

141.66
135.21
133.59
131.92
128.97
127.71
127.35
126.91
126.04
122.83
77.32
77.00
76.68
Br
S
2m
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

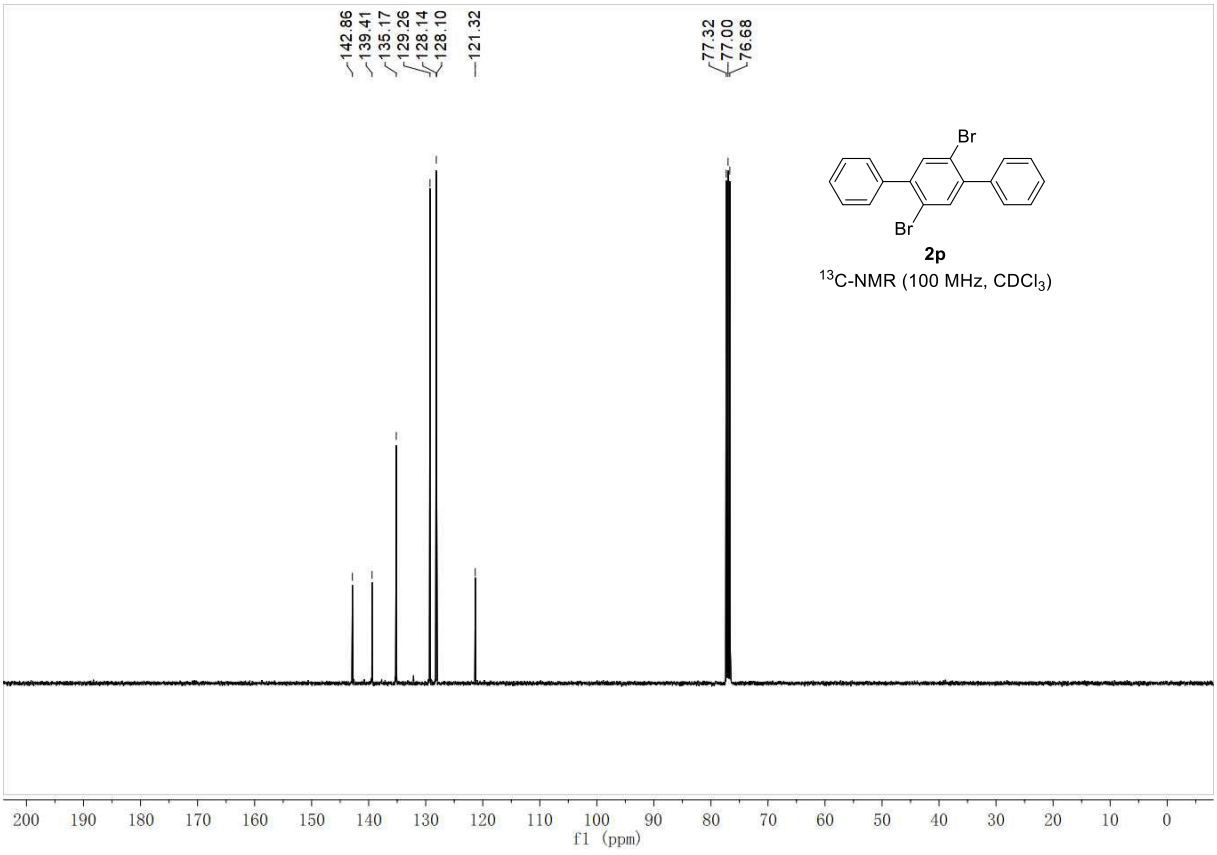

7.890
7.889
7.887
7.884
7.872
7.871
7.868
7.858
7.853
7.840
7.836
7.739
7.736
7.719
7.716
7.581
7.577
7.562
7.558
7.523
7.522
7.430
7.427
7.413
7.409
7.404
7.401
7.395
7.390
7.385
7.382
7.376
7.372
7.366
7.363
7.358
7.354
7.267
7.263
7.260
7.247
7.243
7.229
7.224
Br
S
2n
1H-NMR (400 MHz, CDCl3)
2.05
1.06
1.07
1.00
3.26
1.09
f1 (ppm)

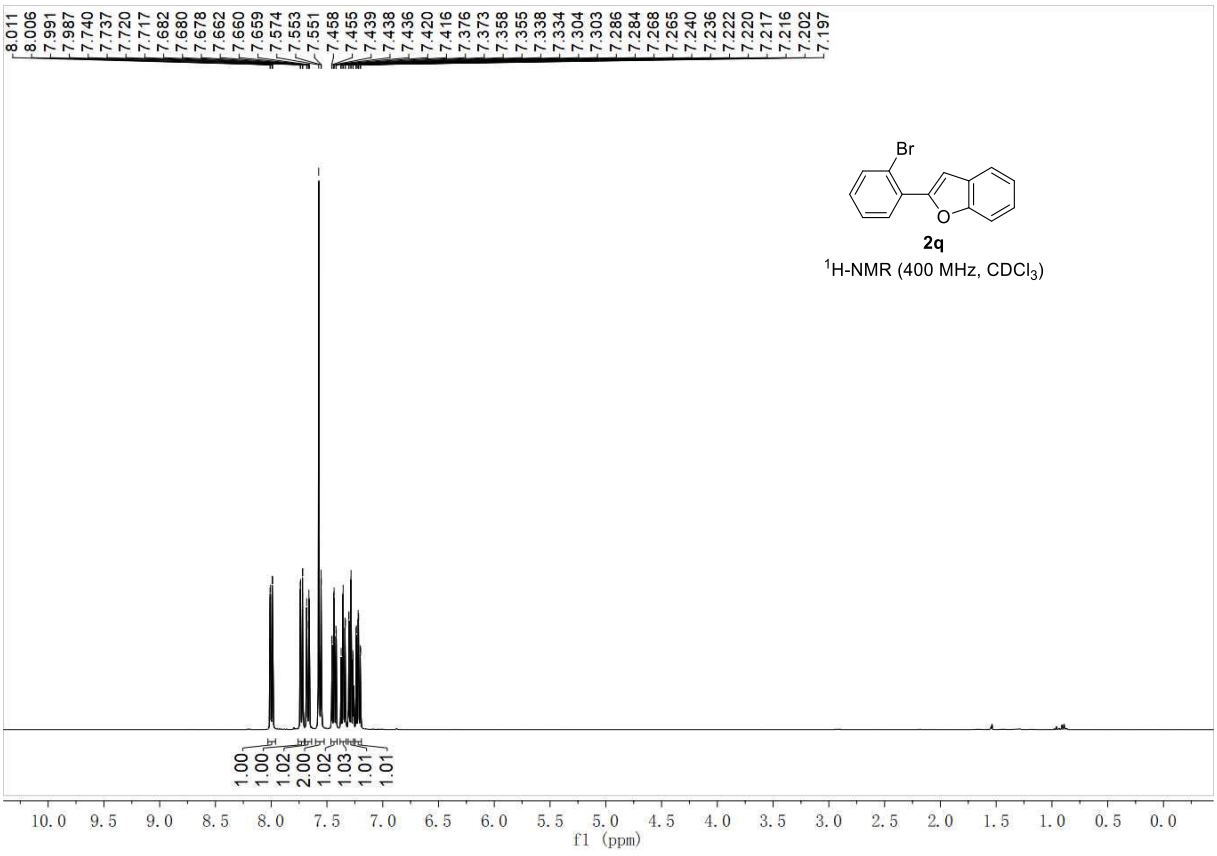

141.89
140.20
139.71
135.31
133.68
132.22
129.56
127.42
124.49
124.45
124.43
123.86
123.00
122.06
77.32
77.00
76.68
Br
S
2n
13C-NMR (100 MHz, CDCl3)
f1 (ppm)

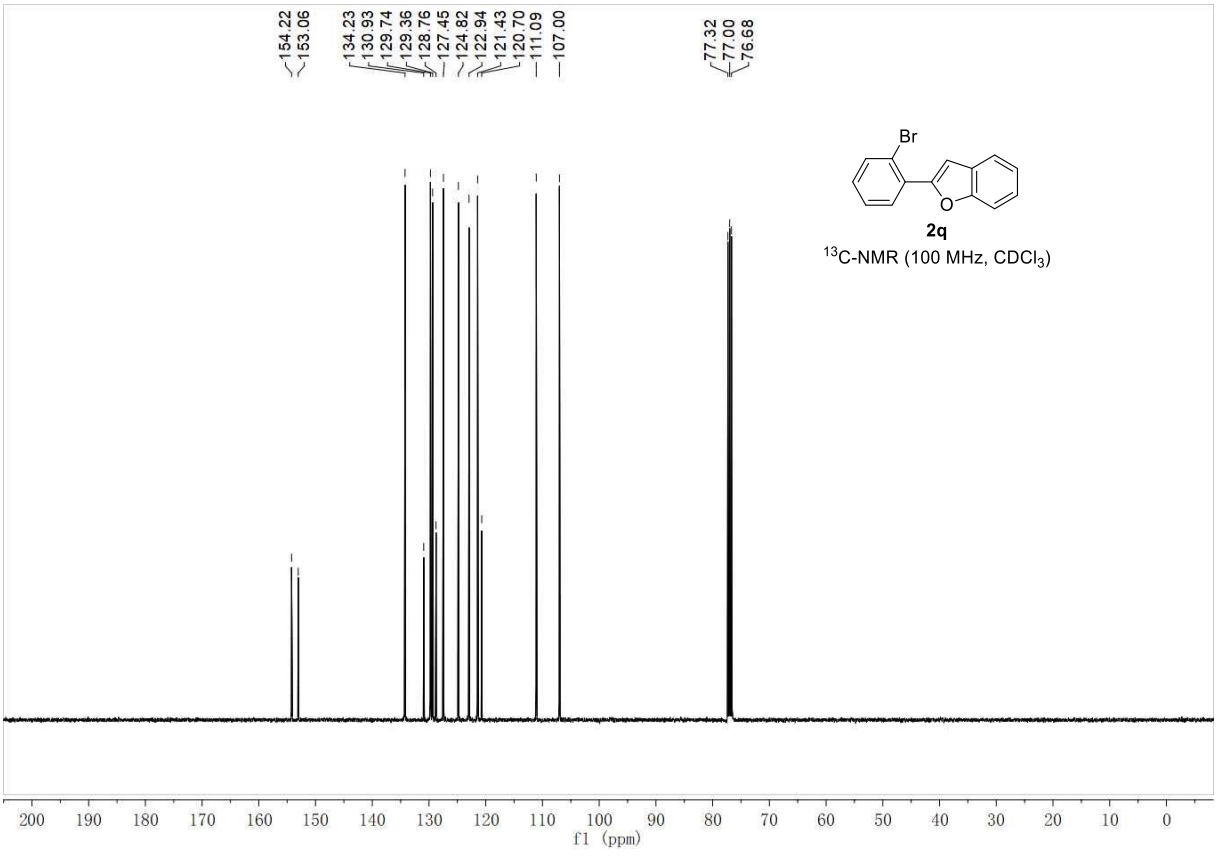

7.710
7.707
7.690
7.687
7.573
7.568
7.553
7.549
7.375
7.372
7.356
7.353
7.337
7.334
7.327
7.216
7.212
7.196
7.193
7.177
7.173
Br
Br
S
2o
1H-NMR (400 MHz, CDCl3)
2.00
2.06
2.14
2.05
2.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

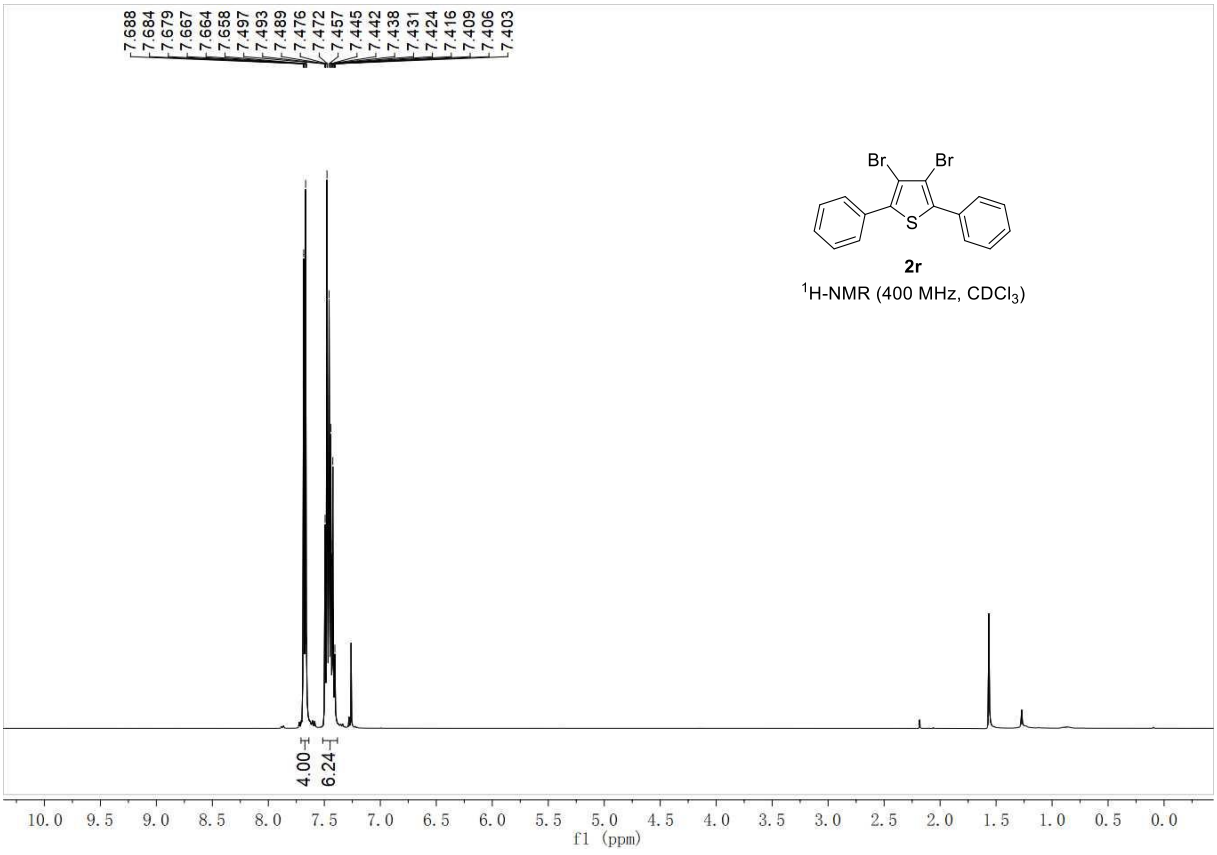

142.32
134.89
133.79
131.81
129.04
127.65
127.46
122.55
77.32
77.00
76.68
Br
Br
S
2o
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.654
7.477
7.472
7.469
7.466
7.464
7.458
7.447
7.442
7.435
7.429
7.425
Br
Br
2p
^{1}H-NMR (400 MHz, $CDCl_3$)
2.00
10.40
10.0 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 0.0
f1 (ppm)


142.86
139.41
135.17
129.26
128.14
128.10
121.32
77.32
77.00
76.68
Br
Br
2p
^{13}C-NMR (100 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

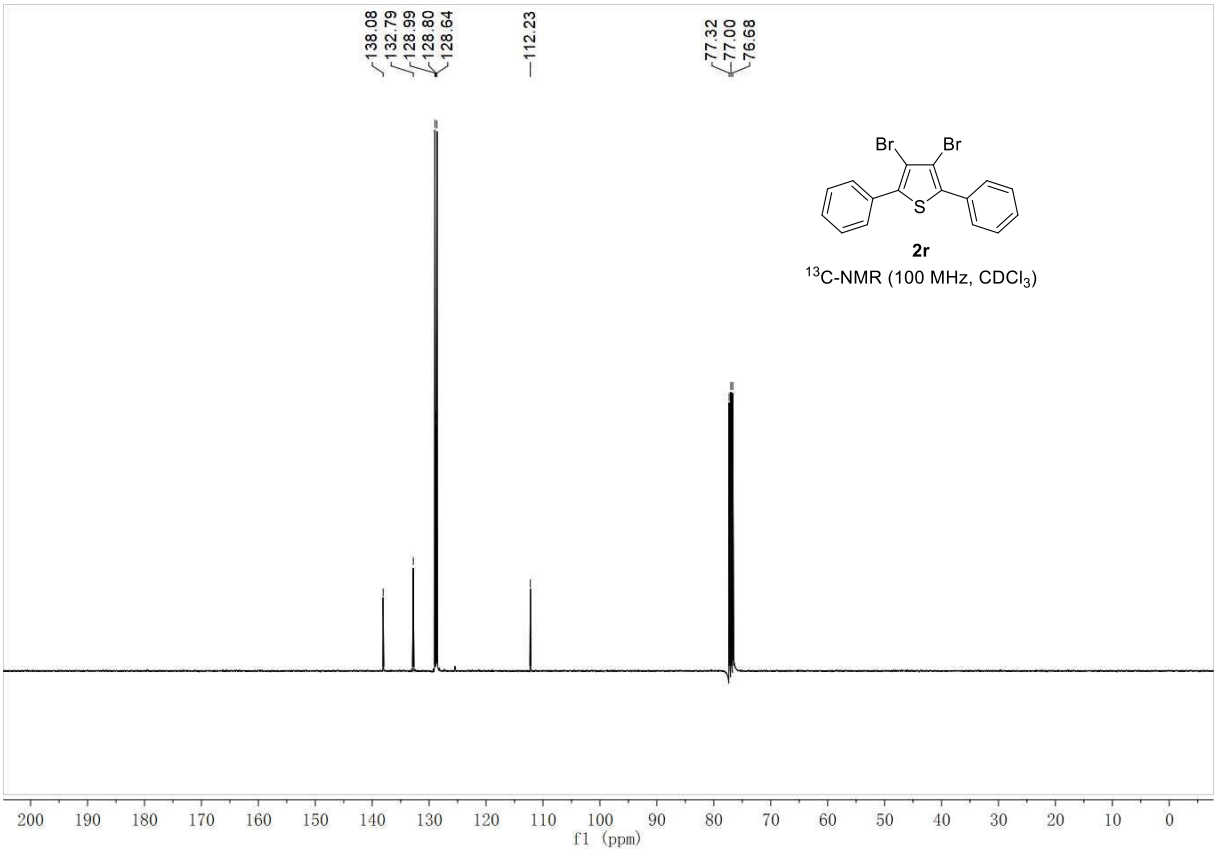

8.011
8.006
7.991
7.987
7.740
7.737
7.720
7.717
7.682
7.680
7.678
7.662
7.660
7.659
7.574
7.553
7.551
7.458
7.455
7.439
7.438
7.436
7.420
7.416
7.376
7.373
7.358
7.355
7.338
7.334
7.304
7.303
7.286
7.284
7.268
7.265
7.240
7.236
7.222
7.220
7.217
7.216
7.202
7.197
Br
O
2q
1H-NMR (400 MHz, CDCl3)
1.00
1.00
1.02
2.00
1.02
1.03
1.01
1.01
10.0 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 0.0
f1 (ppm)


154.22
153.06
134.23
130.93
129.74
129.36
128.76
127.45
124.82
122.94
121.43
120.70
111.09
107.00
77.32
77.00
76.68
Br
O
2q
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



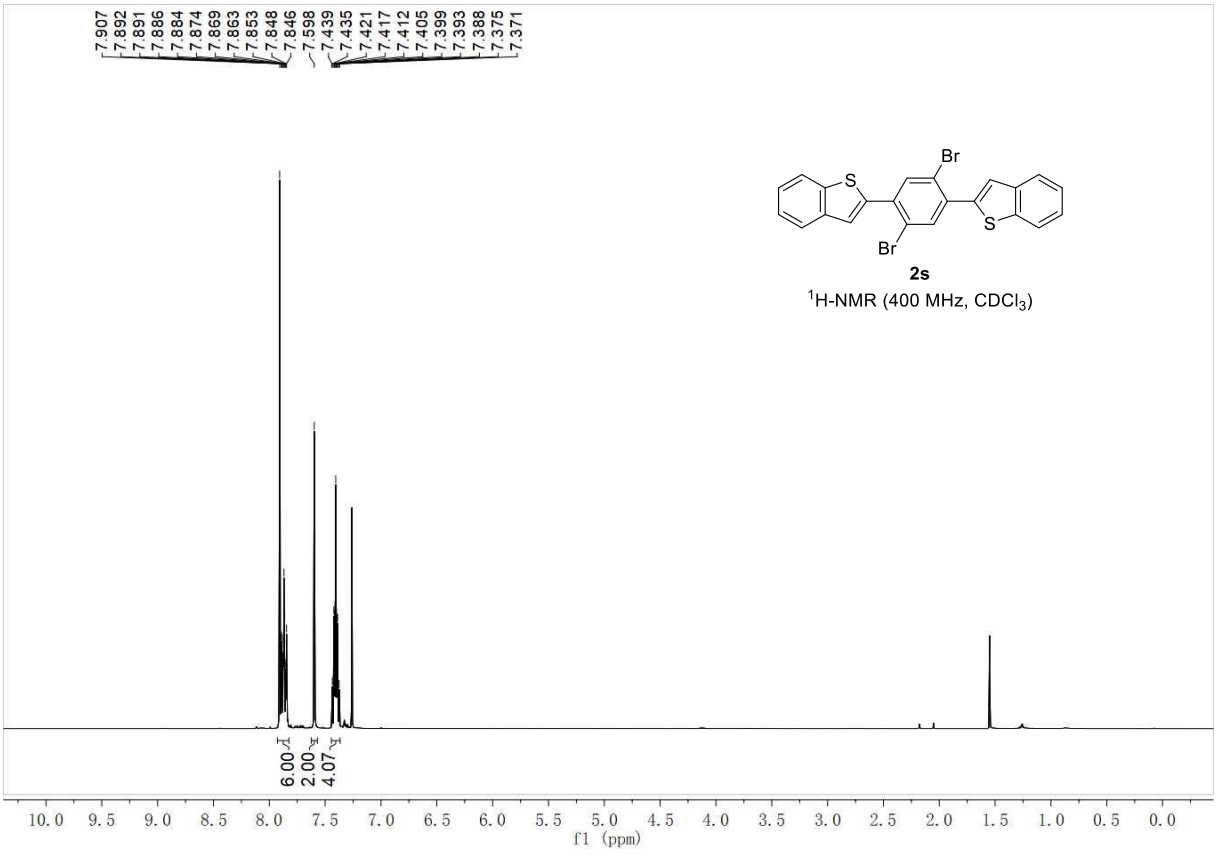
2r

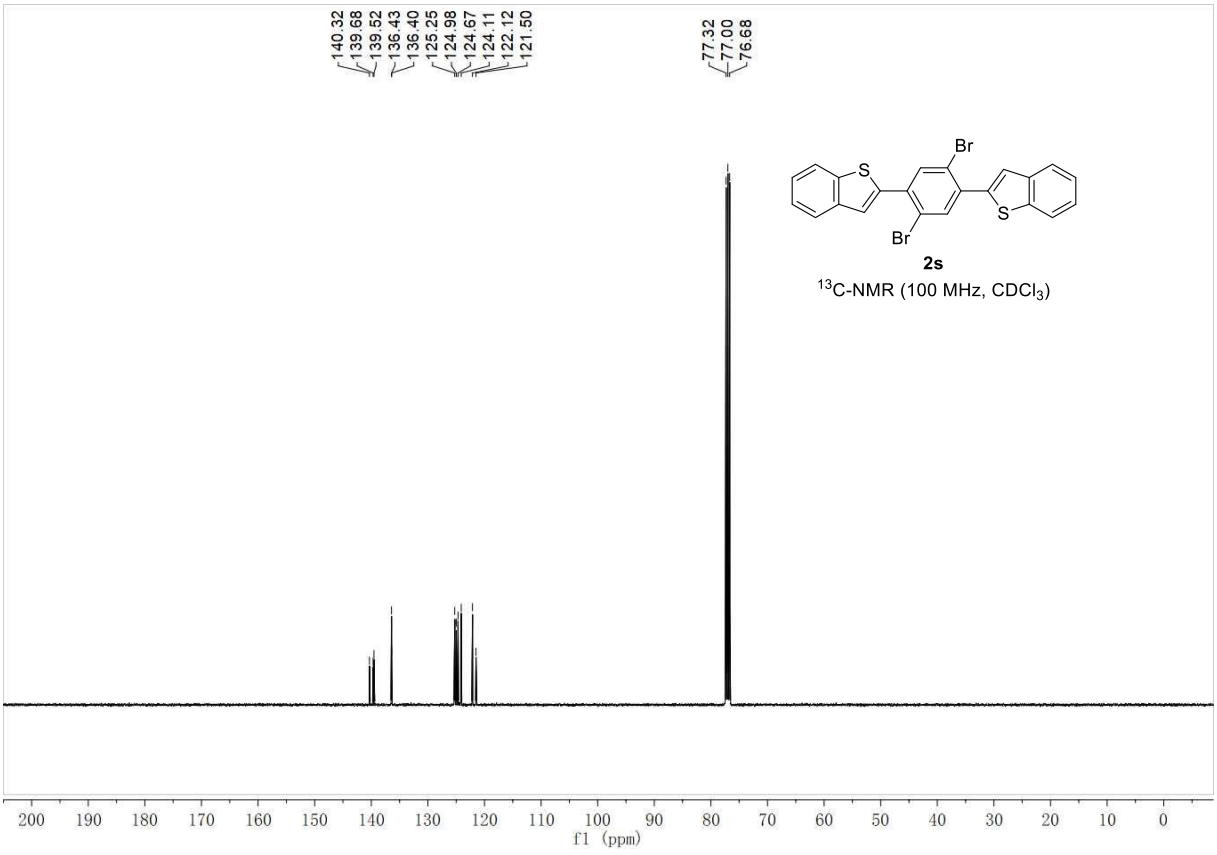
^{1}H-NMR (400 MHz, $CDCl_3$)

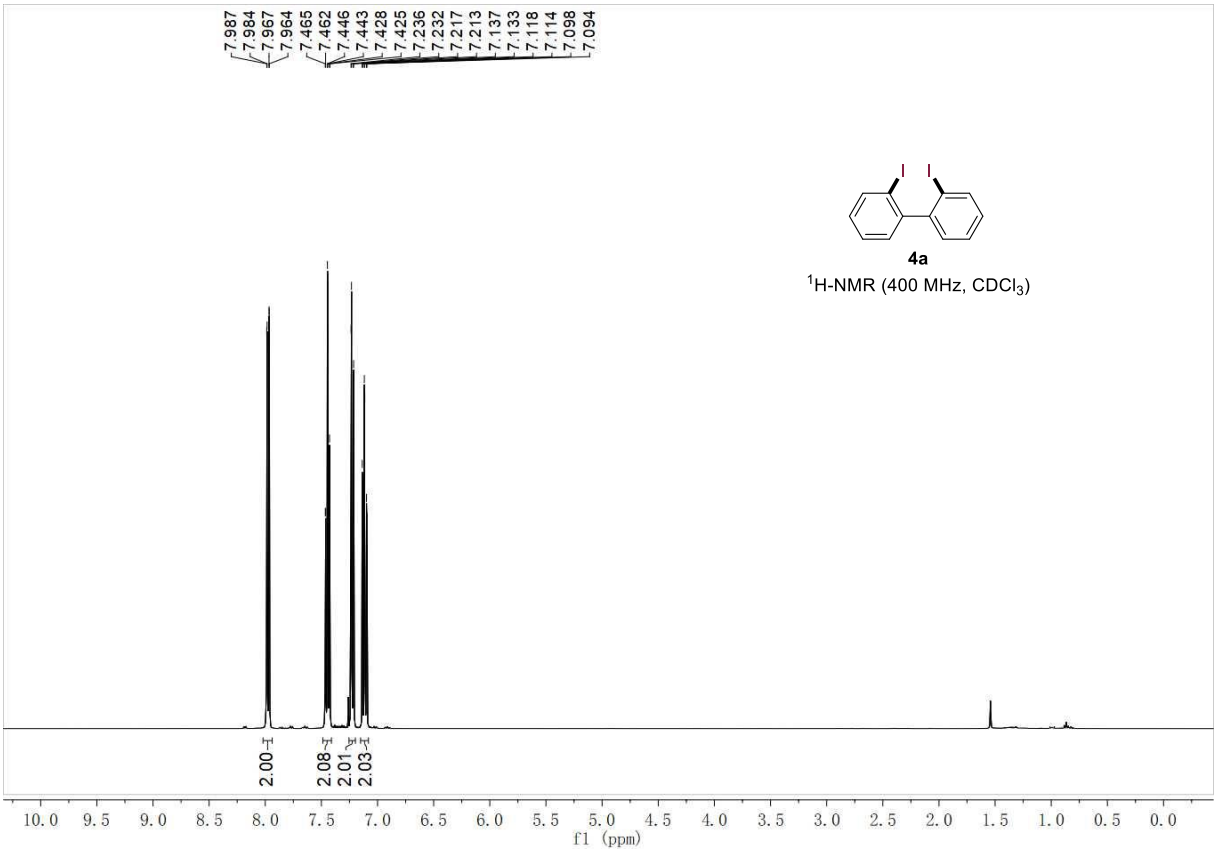


2r

^{13}C-NMR (100 MHz, $CDCl_3$)

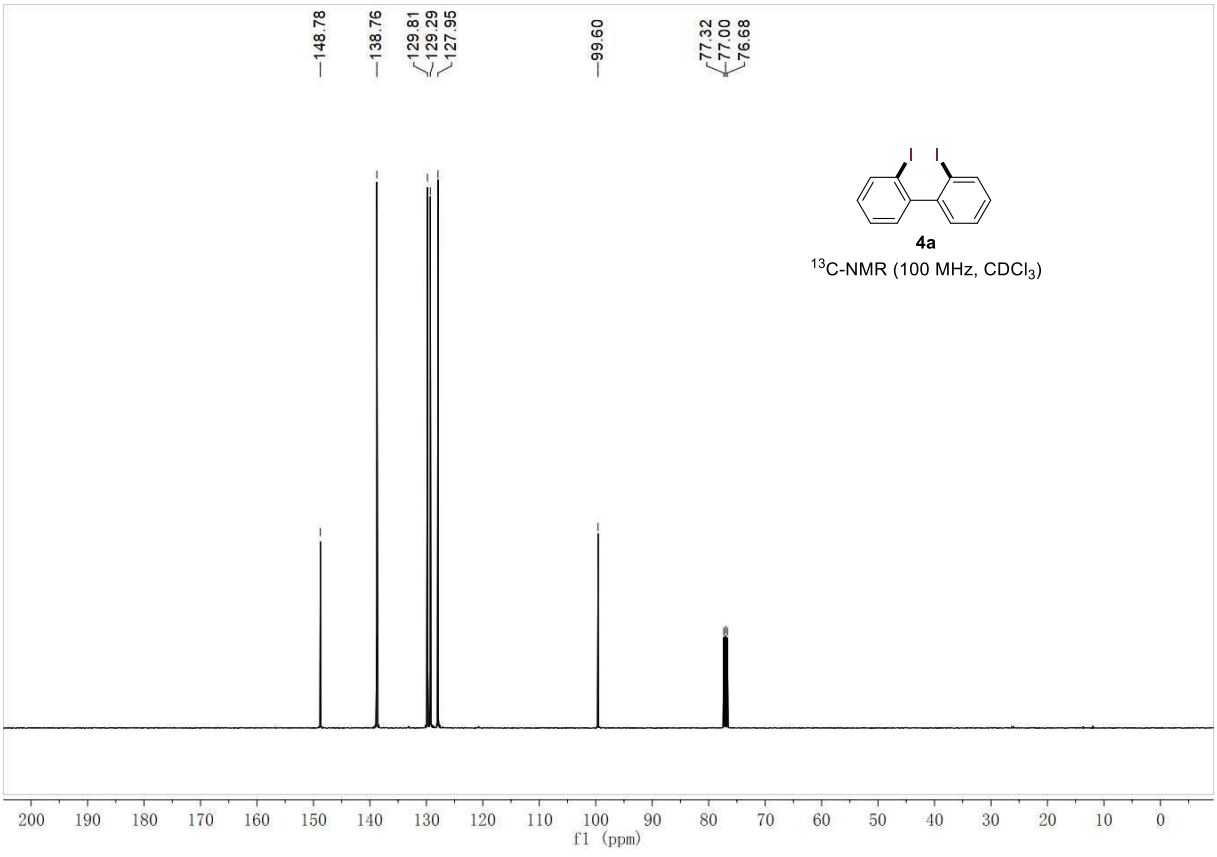

7.907
7.892
7.891
7.886
7.884
7.874
7.869
7.863
7.853
7.848
7.846
7.598
7.439
7.435
7.421
7.417
7.412
7.405
7.399
7.393
7.388
7.375
7.371
Br
S
S
Br
2s
1H-NMR (400 MHz, CDCl3)
6.00
2.00
4.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


140.32
139.68
139.52
136.43
136.40
125.25
124.98
124.67
124.11
122.12
121.50
77.32
77.00
76.68
Br
S
S
Br
2s
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



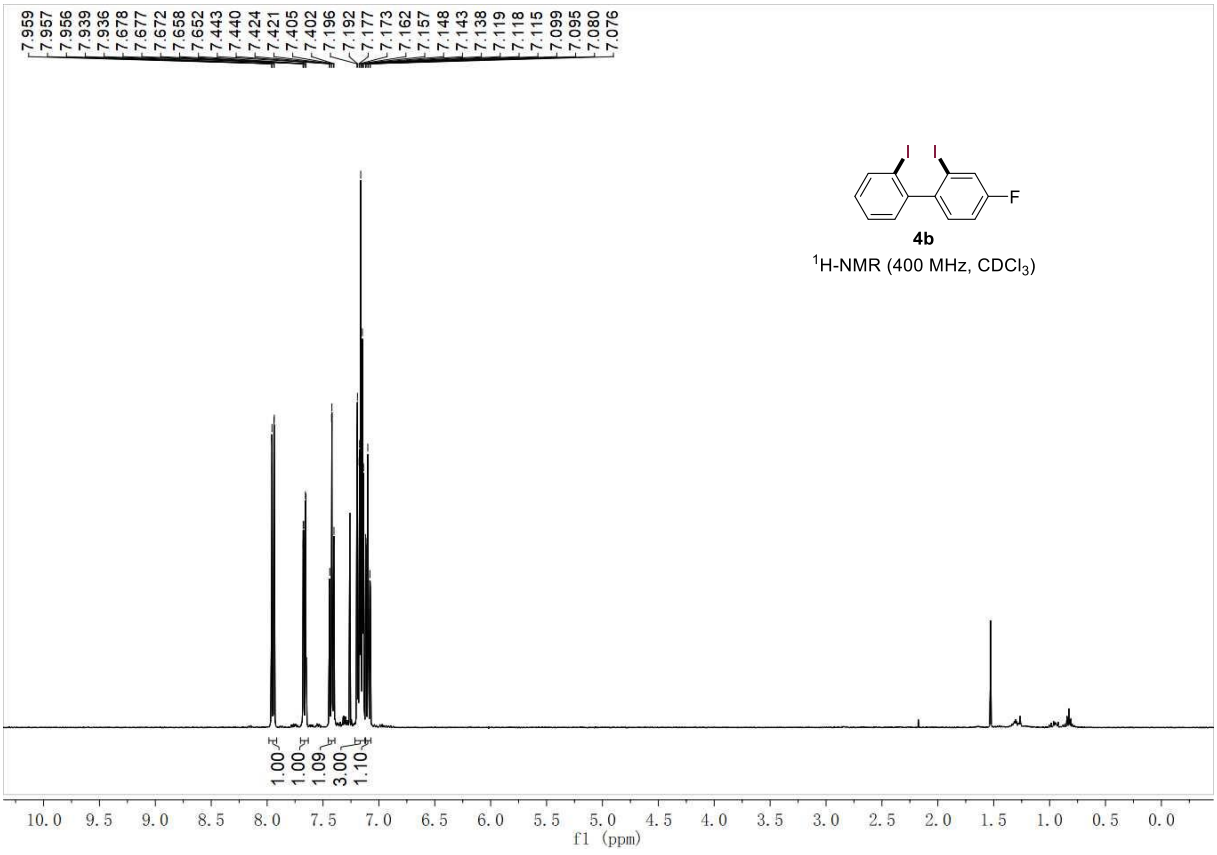
4a

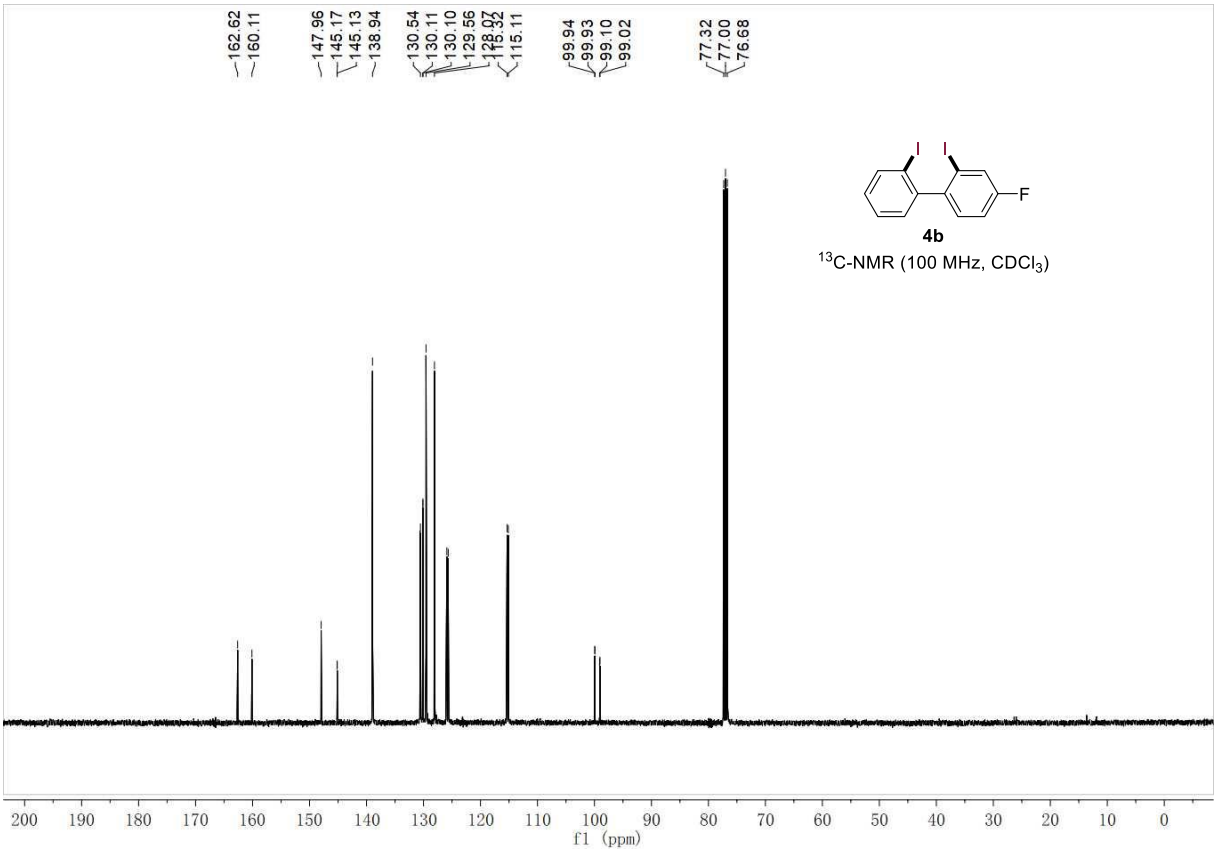
^{1}H-NMR (400 MHz, $CDCl_3$)

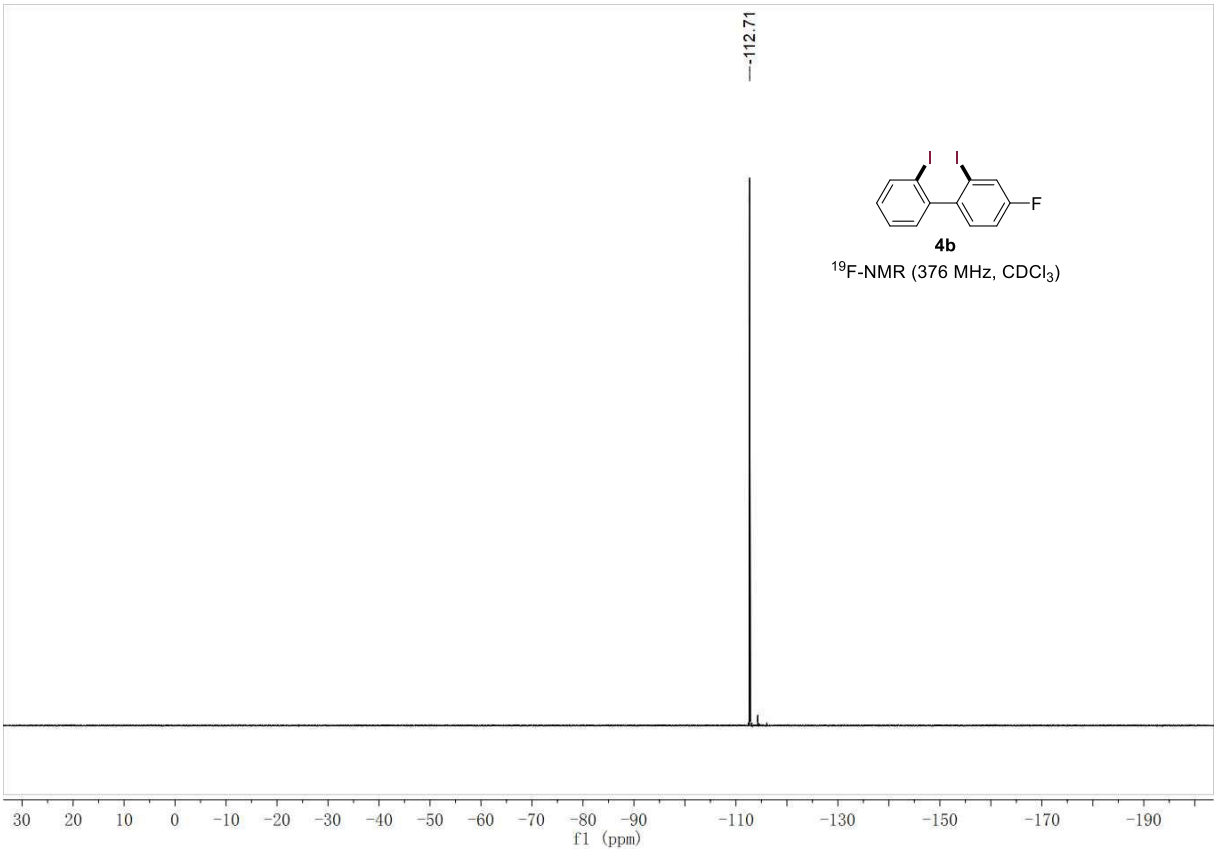


4a

^{13}C-NMR (100 MHz, $CDCl_3$)

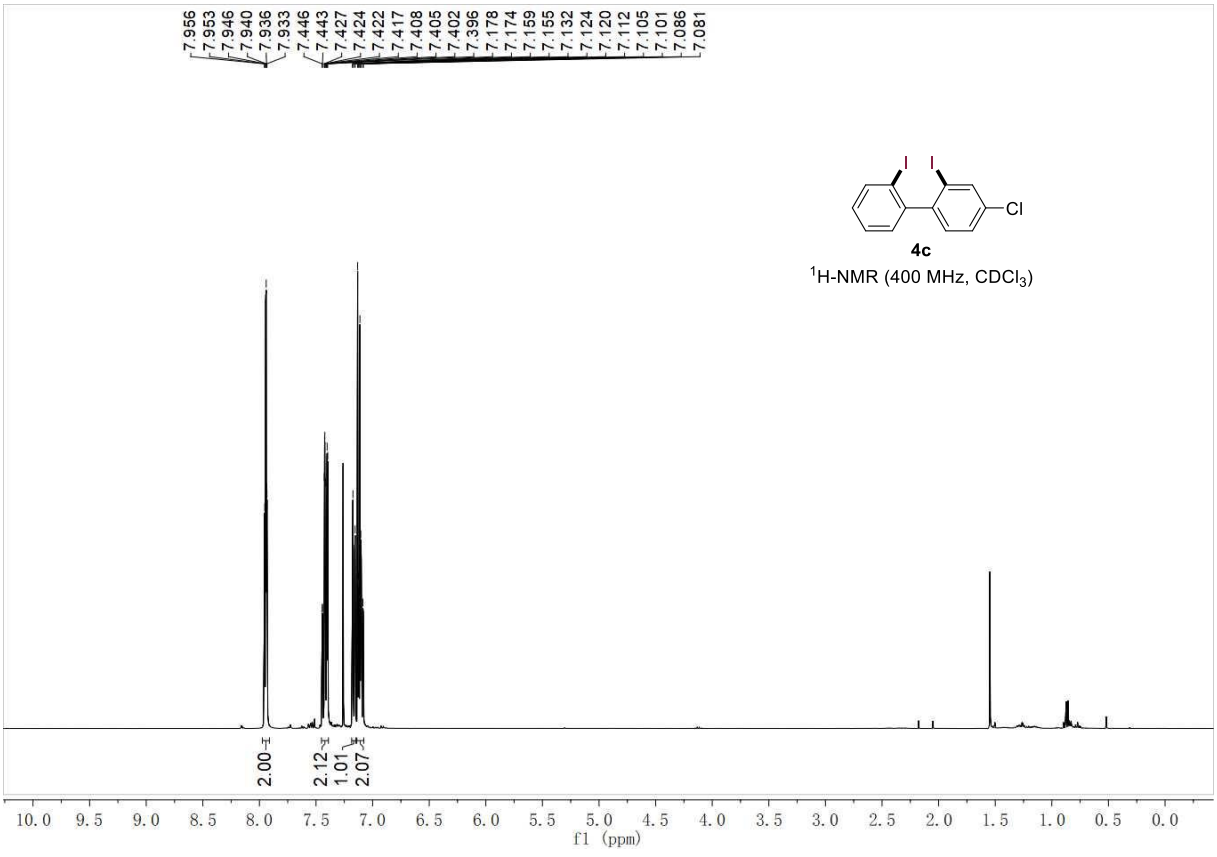

7.959
7.957
7.956
7.939
7.936
7.678
7.677
7.672
7.658
7.652
7.443
7.440
7.424
7.421
7.405
7.402
7.196
7.192
7.177
7.173
7.162
7.157
7.148
7.143
7.138
7.119
7.118
7.115
7.099
7.095
7.080
7.076
I
I
F
4b
1H-NMR (400 MHz, CDCl3)
1.00
1.00
1.09
3.00
1.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


162.62
160.11
147.96
145.17
145.13
138.94
130.54
130.11
130.10
129.56
128.07
115.32
115.11
99.94
99.93
99.10
99.02
77.32
77.00
76.68
I
I
F
4b
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



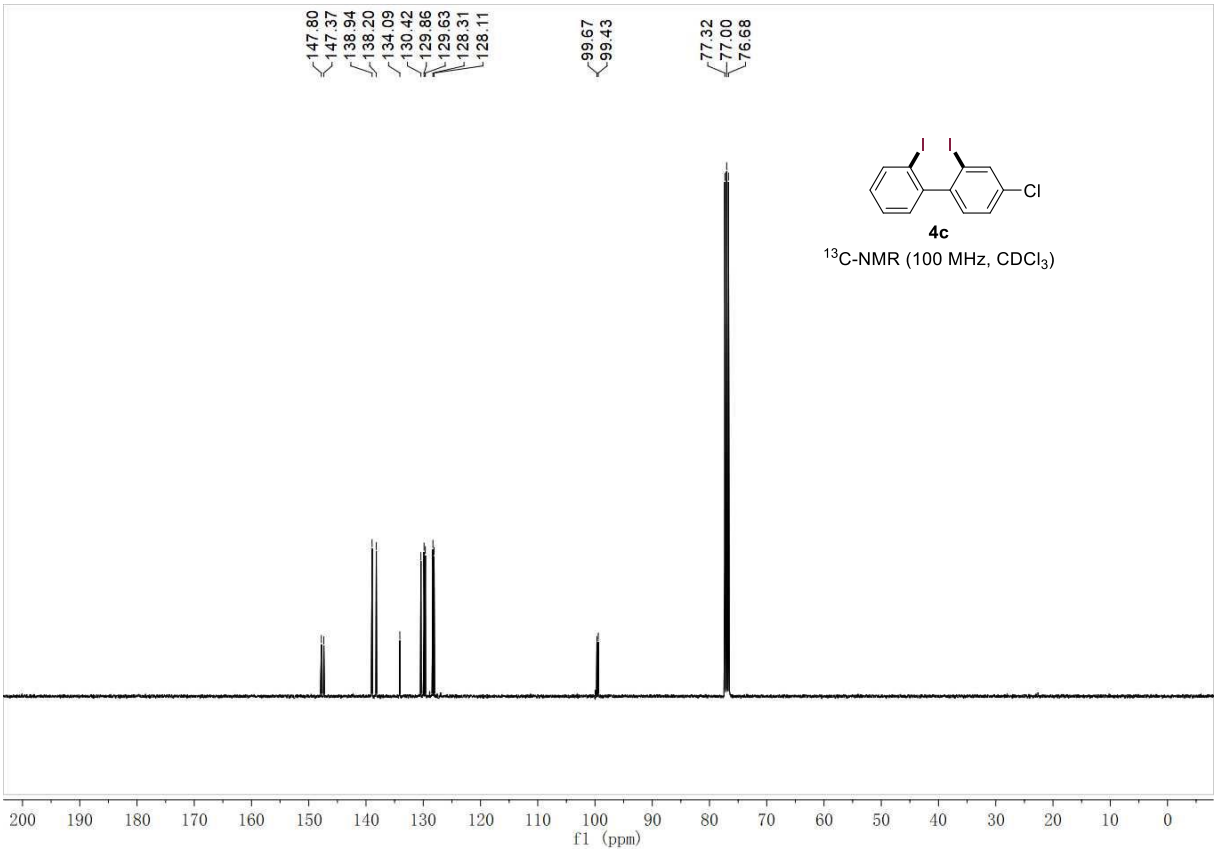
4b

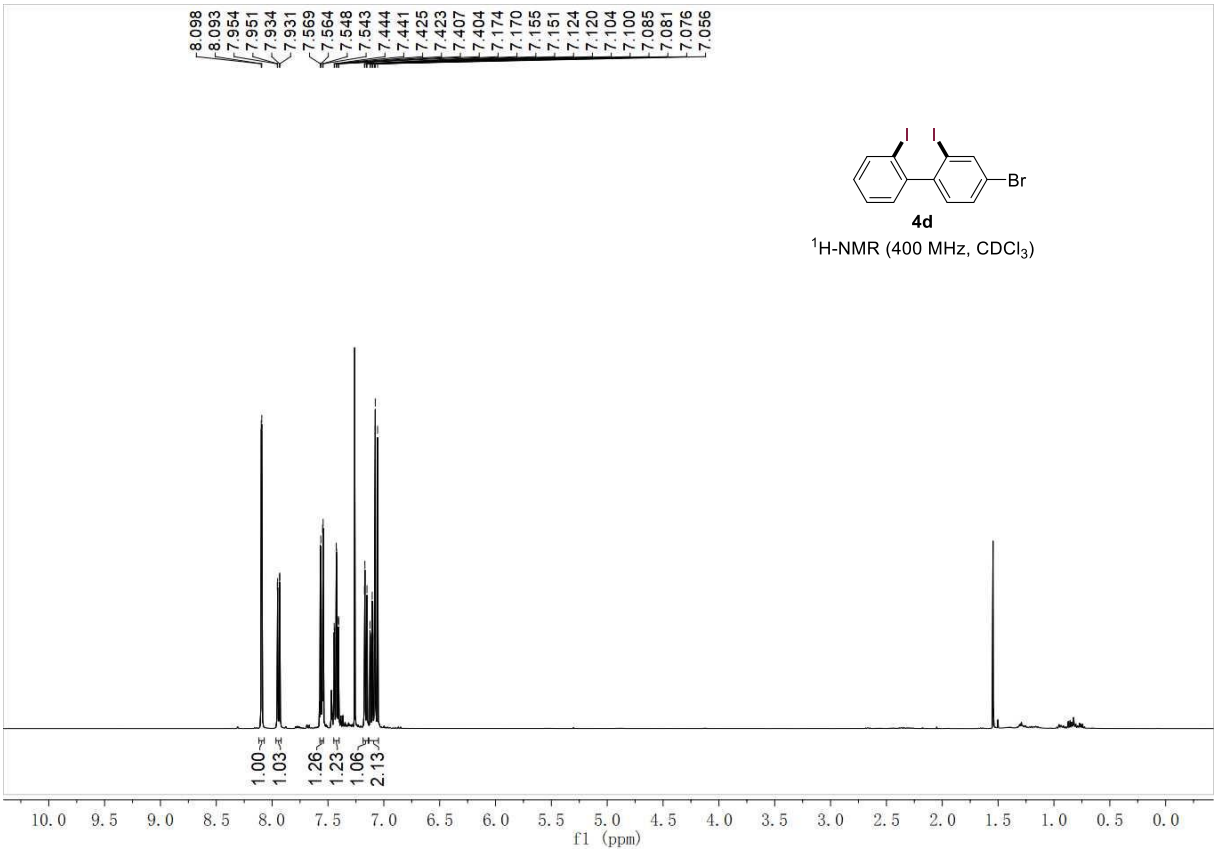
^{19}F-NMR (376 MHz, $CDCl_3$)

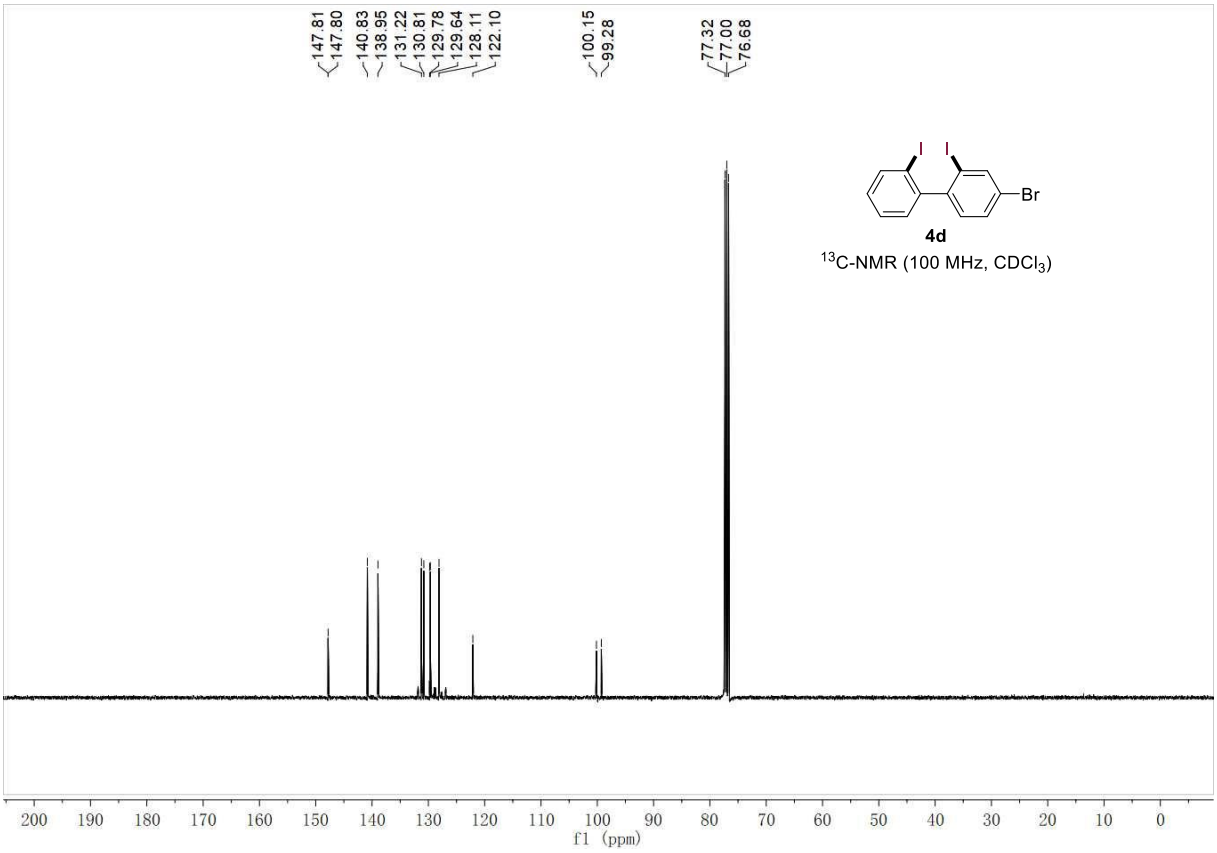


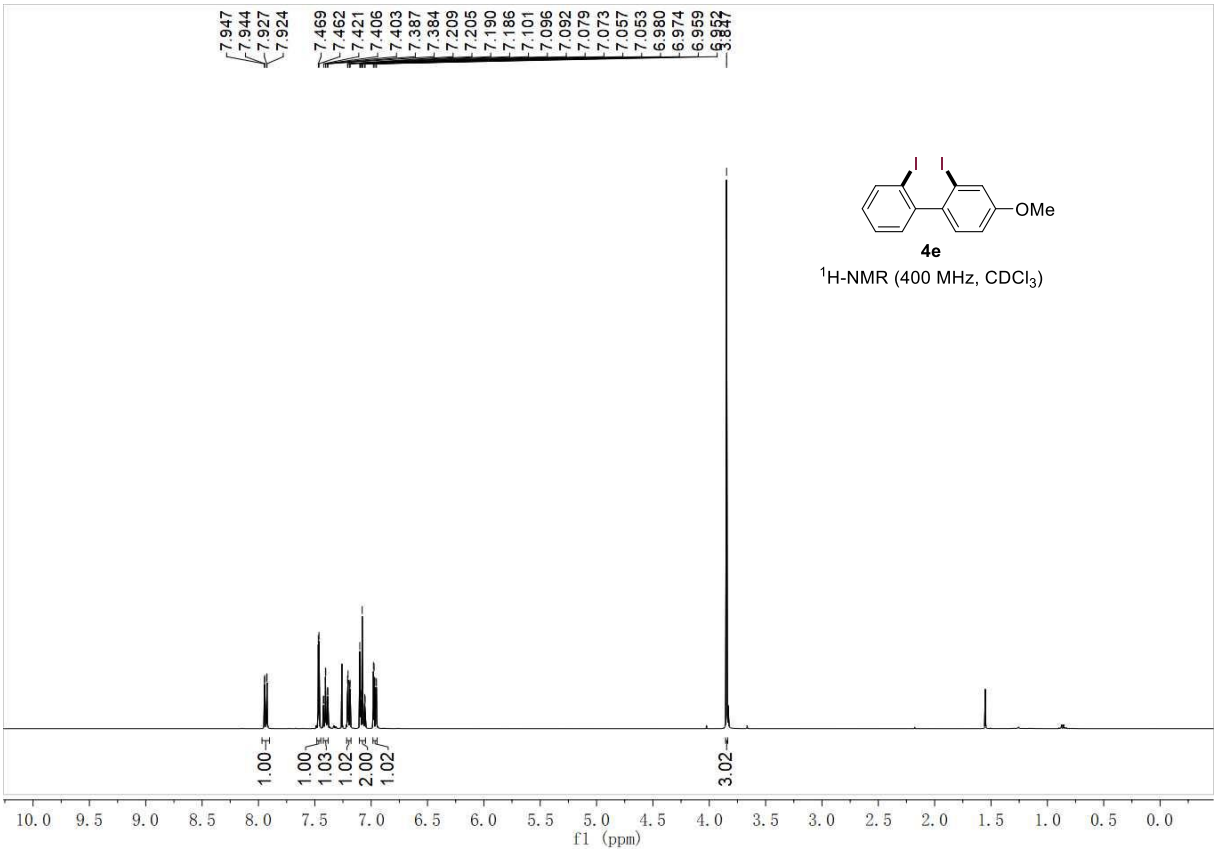
4c

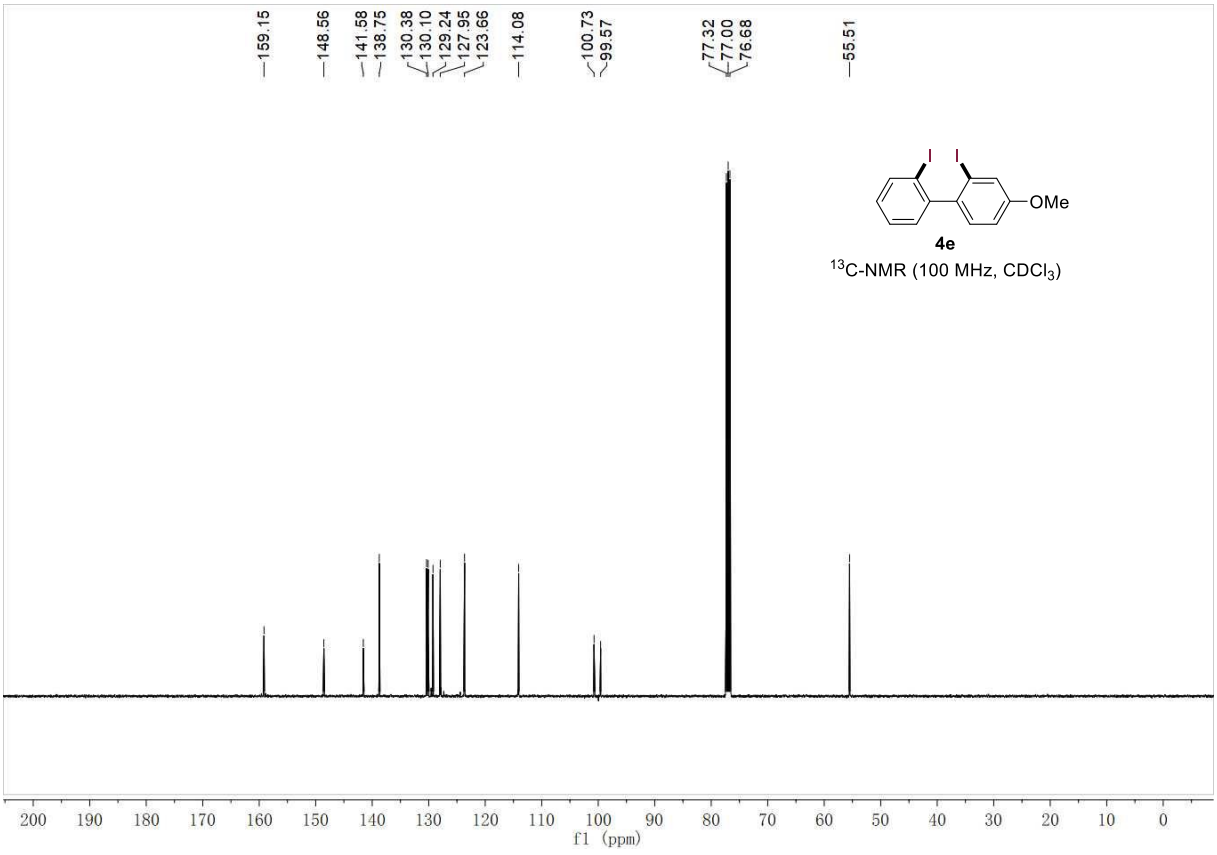
^{1}H-NMR (400 MHz, $CDCl_3$)

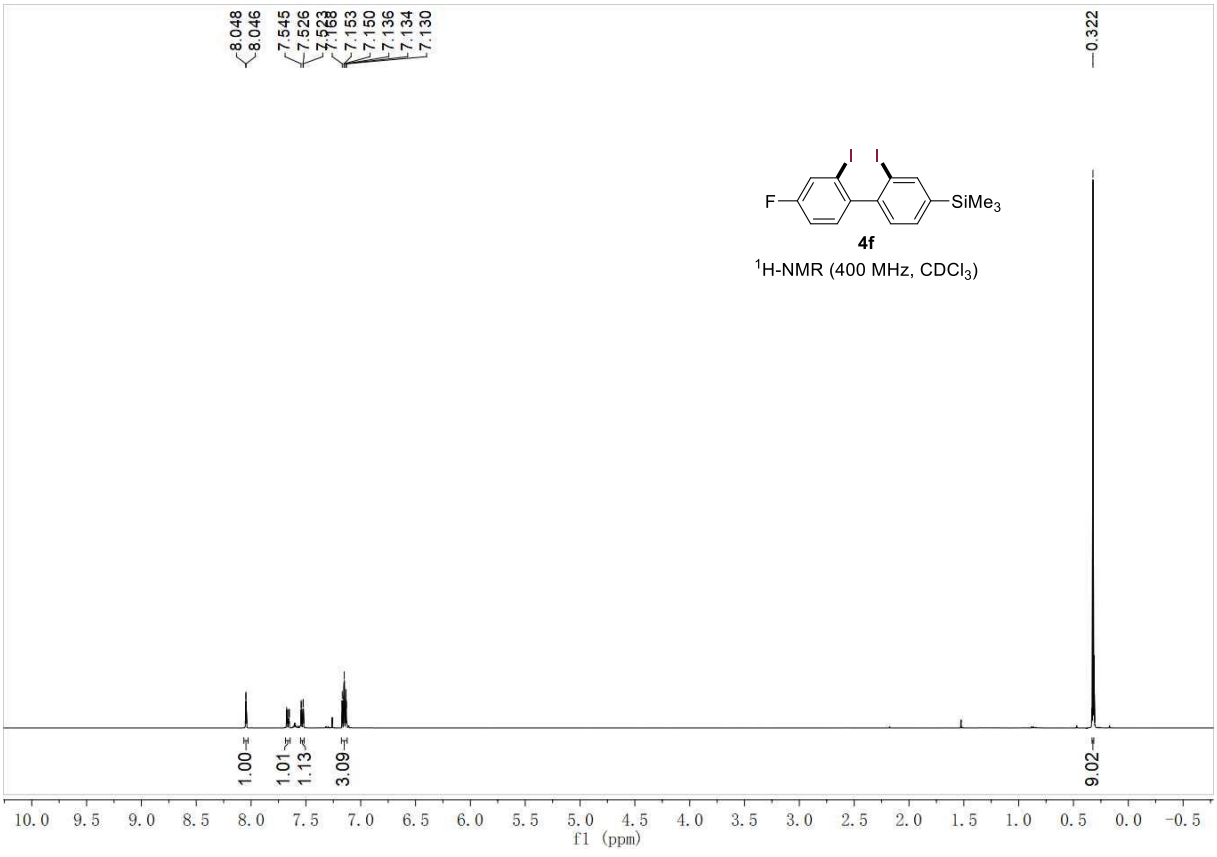

147.80
147.37
138.94
138.20
134.09
130.42
129.86
129.63
128.31
128.11
99.67
99.43
77.32
77.00
76.68
I
I
Cl
4c
^{13}C-NMR (100 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

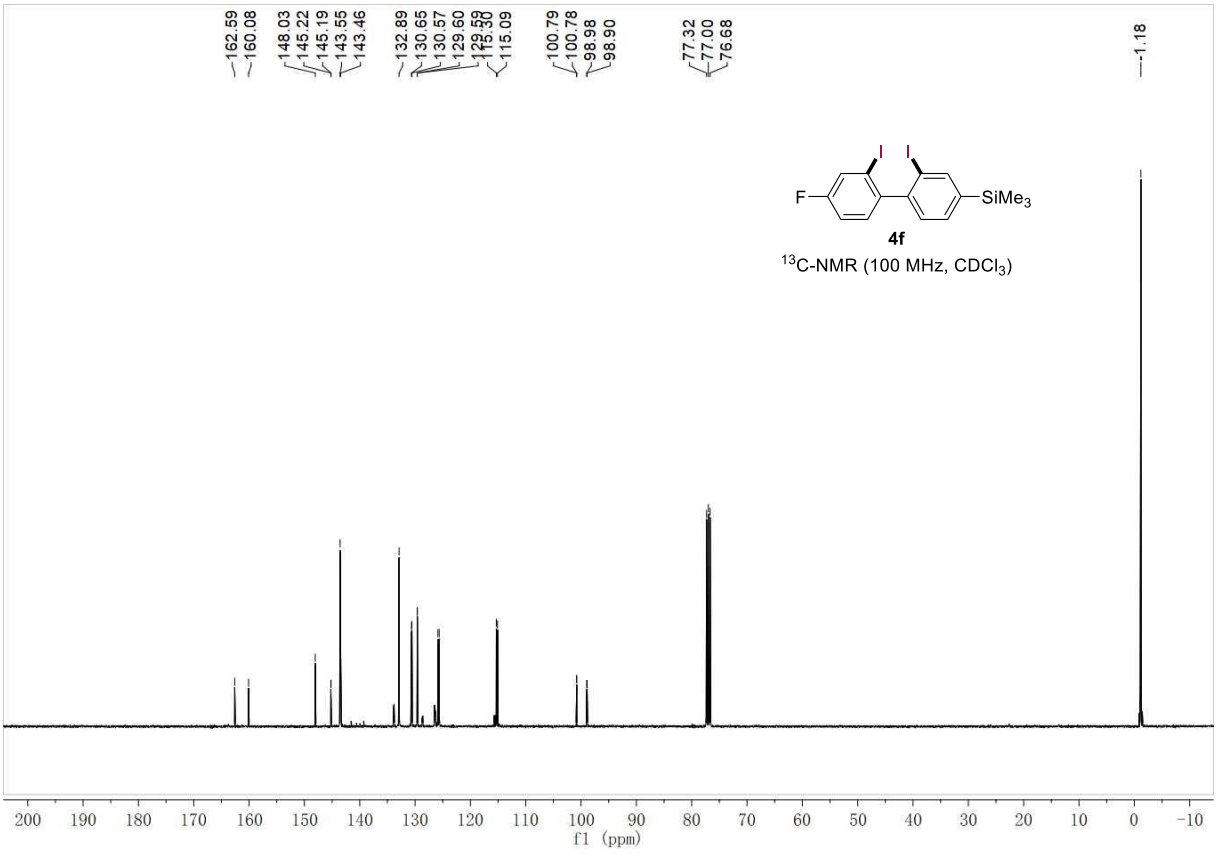

8.098
8.093
7.954
7.951
7.934
7.931
7.569
7.564
7.548
7.543
7.444
7.441
7.425
7.423
7.407
7.404
7.174
7.170
7.155
7.151
7.124
7.120
7.104
7.100
7.085
7.081
7.076
7.056
I
I
Br
4d
^{1}H-NMR (400 MHz, $CDCl_3$)
1.00
1.03
1.26
1.23
1.06
2.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

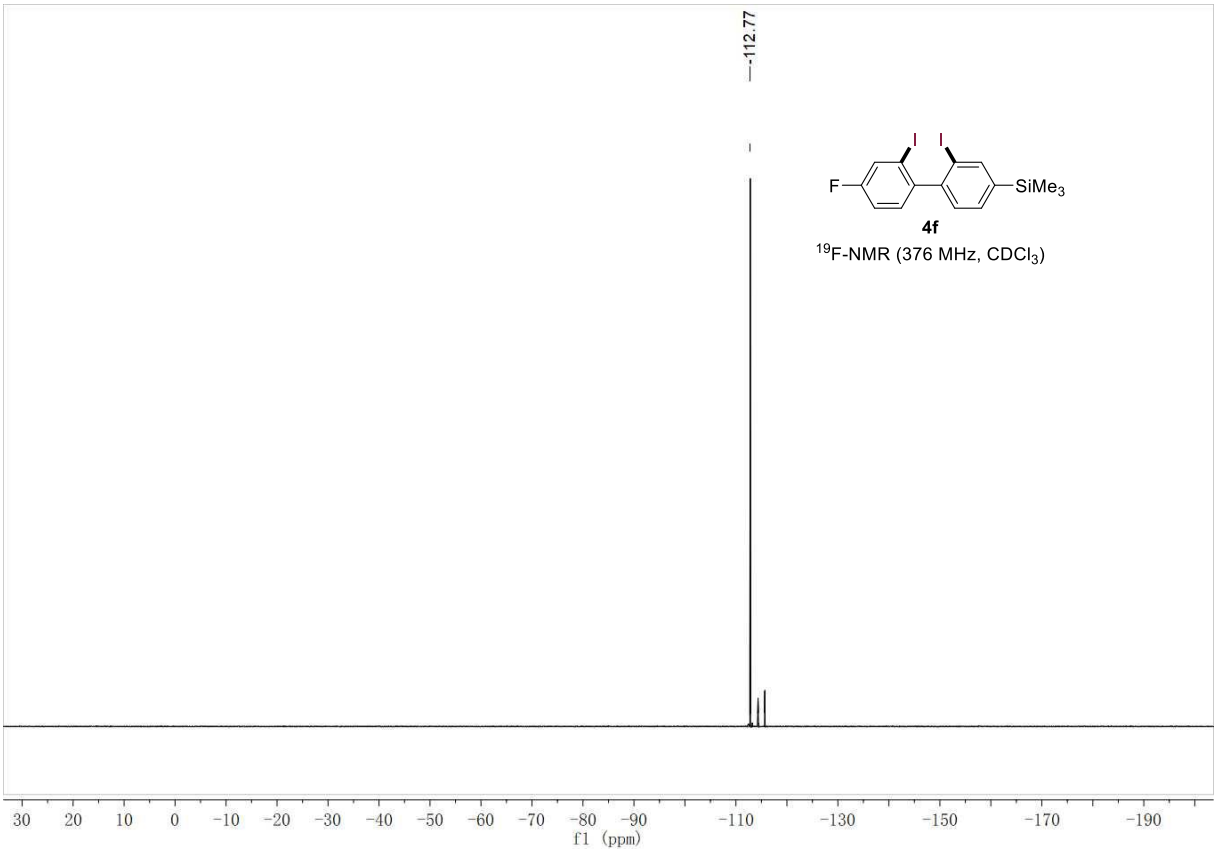

147.81
147.80
140.83
138.95
131.22
130.81
129.78
129.64
128.11
122.10
100.15
99.28
77.32
77.00
76.68
I
I
Br
4d
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

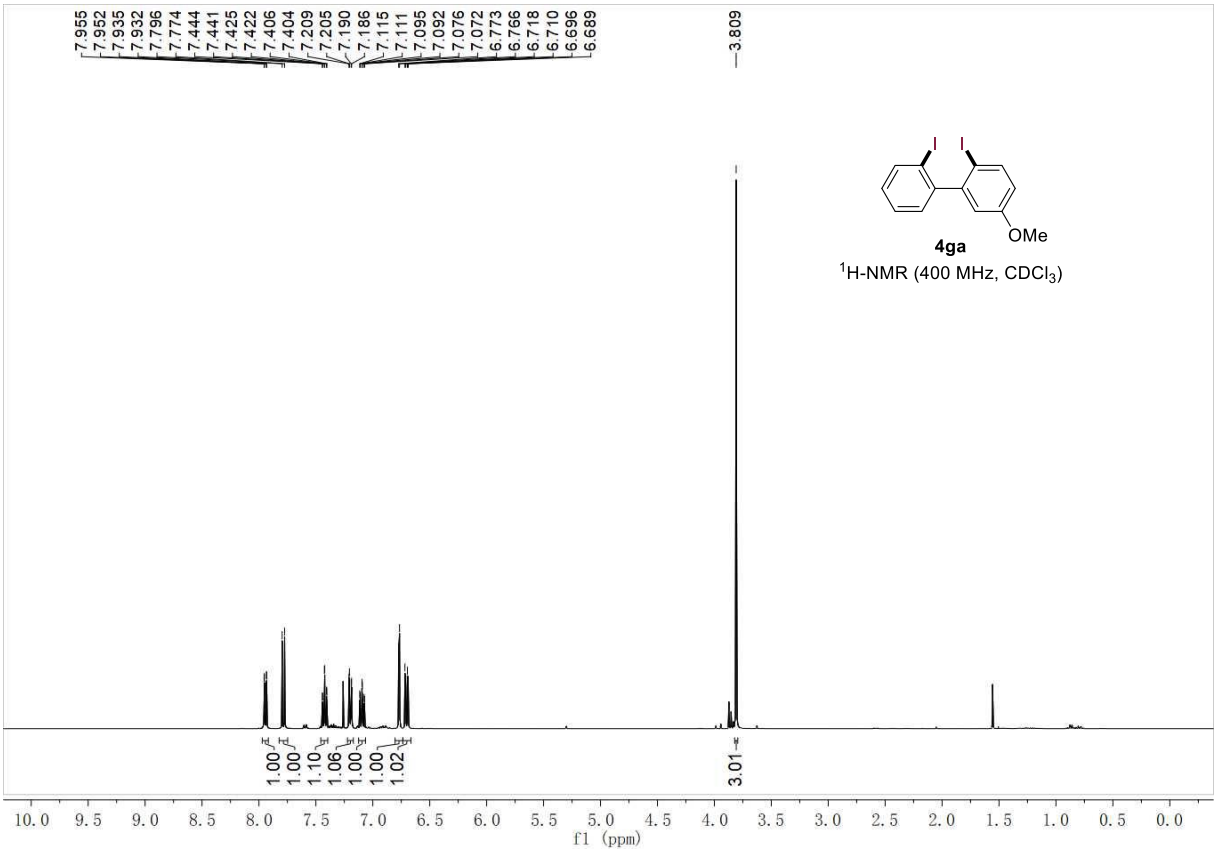

7.947
7.944
7.927
7.924
7.469
7.462
7.421
7.406
7.403
7.387
7.384
7.209
7.205
7.190
7.186
7.101
7.096
7.092
7.079
7.073
7.057
7.053
6.980
6.974
6.959
3.847
I
I
OMe
4e
1H-NMR (400 MHz, CDCl3)
1.00
1.00
1.03
1.02
2.00
1.02
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

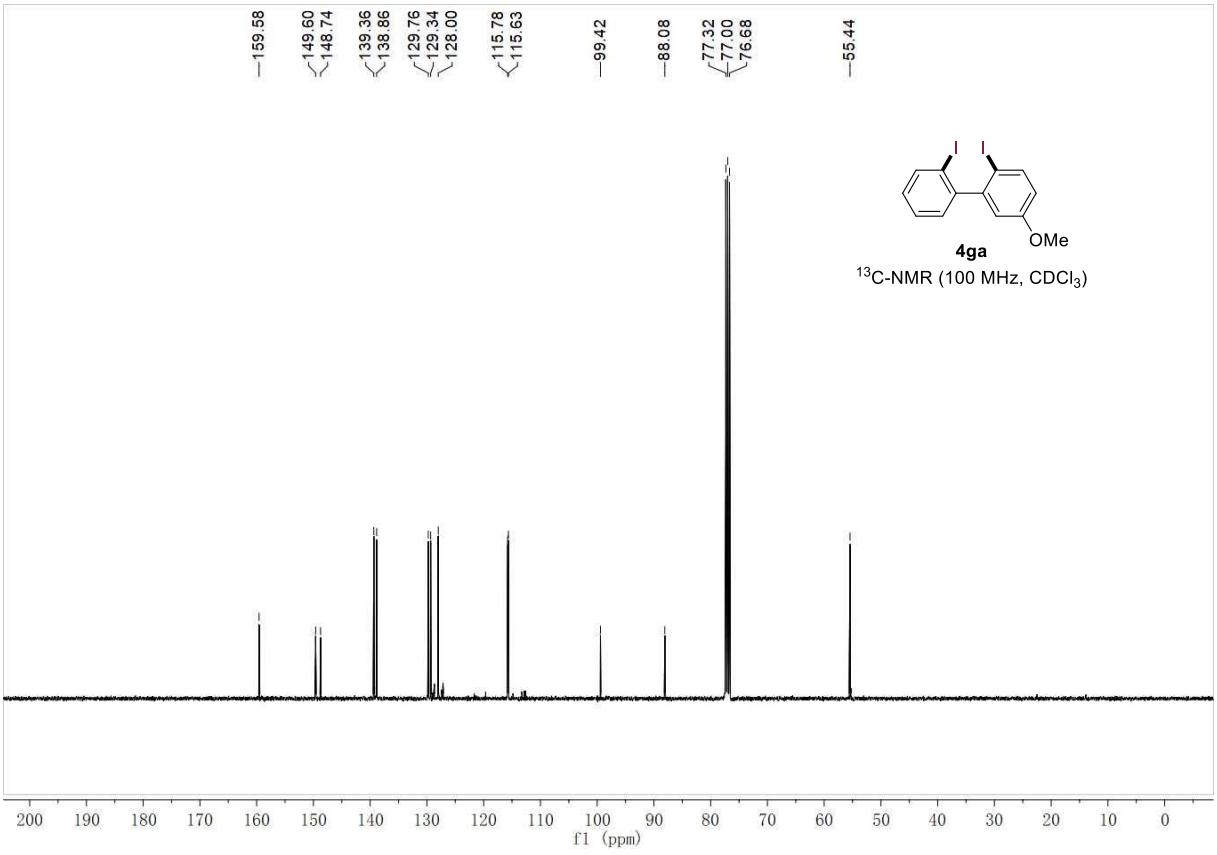

159.15
148.56
141.58
138.75
130.38
130.10
129.24
127.95
123.66
114.08
100.73
99.57
77.32
77.00
76.68
55.51
I
I
OMe
4e
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

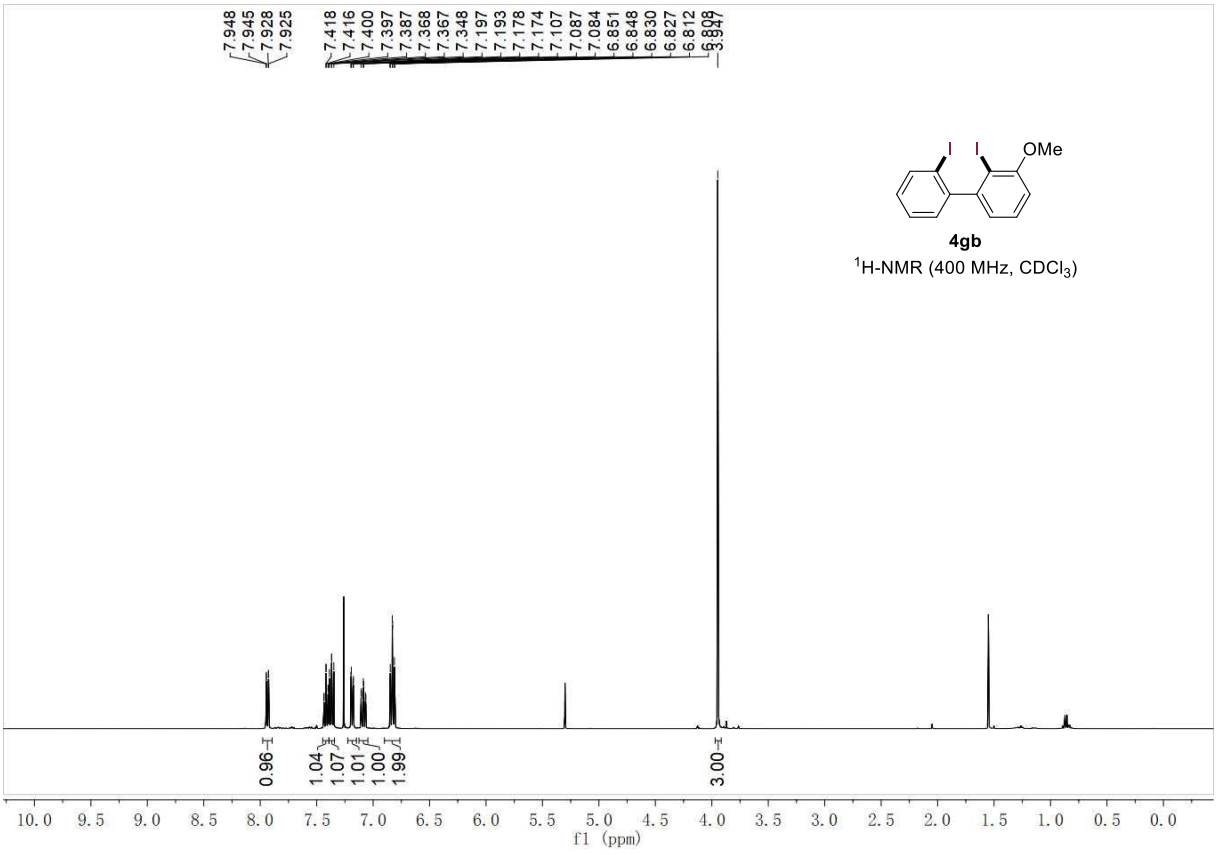

8.048
8.046
7.545
7.526
7.153
7.150
7.136
7.134
7.130
0.322
I
I
F
SiMe3
4f
1H-NMR (400 MHz, CDCl3)
1.00
1.01
1.13
3.09
9.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


162.59
160.08
148.03
145.22
145.19
143.55
143.46
132.89
130.65
130.57
129.60
125.30
115.09
100.79
100.78
98.98
98.90
77.32
77.00
76.68
-1.18
F
I
I
SiMe3
4f
13C-NMR (100 MHz, CDCl3)
f1 (ppm)


-112.77
F
I
I
SiMe3
4f
19F-NMR (376 MHz, CDCl3)
f1 (ppm)

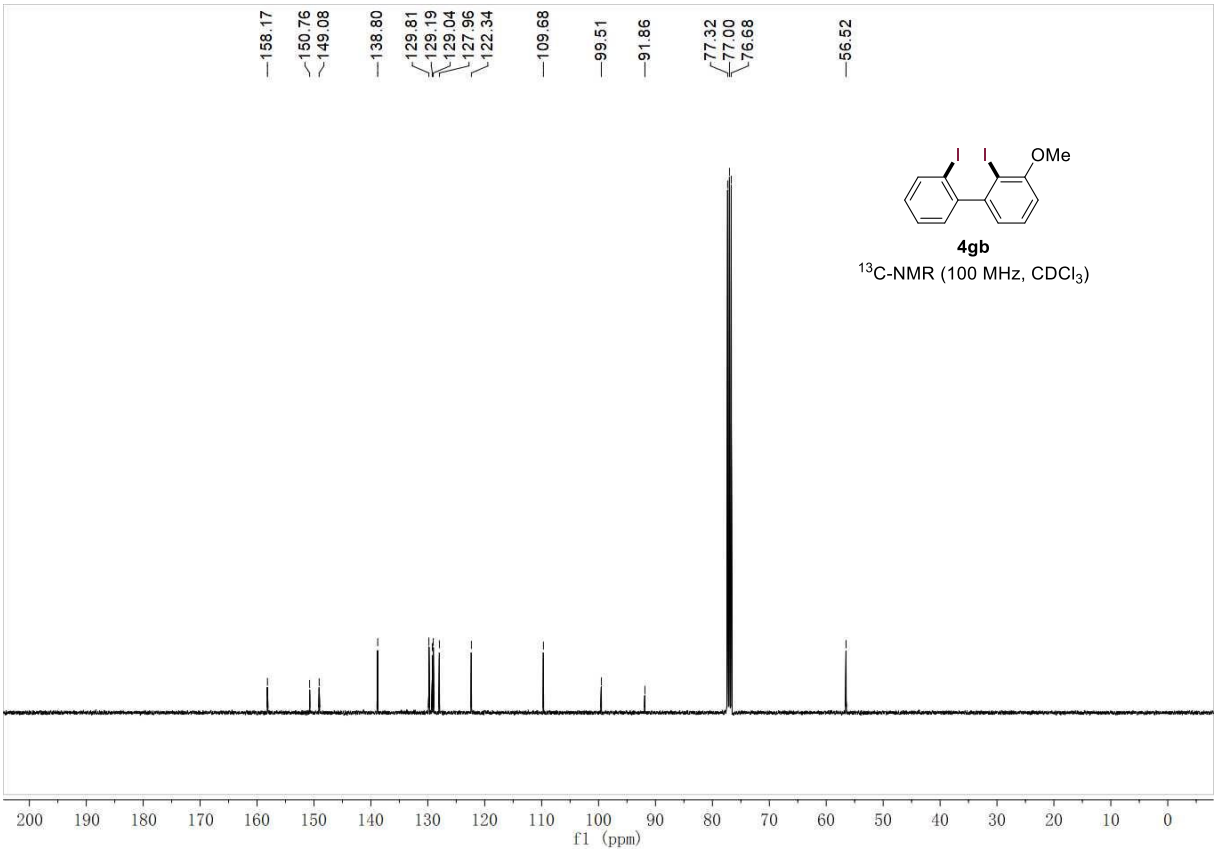

7.955
7.952
7.935
7.932
7.796
7.774
7.444
7.441
7.425
7.422
7.406
7.404
7.209
7.205
7.190
7.186
7.115
7.111
7.095
7.092
7.076
7.072
6.773
6.766
6.718
6.710
6.696
6.689
3.809
1.00
1.00
1.10
1.06
1.00
1.00
1.02
3.01
I
I
OMe
4ga
^{1}H-NMR (400 MHz, $CDCl_3$)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.58
149.60
148.74
139.36
138.86
129.76
129.34
128.00
115.78
115.63
99.42
88.08
77.32
77.00
76.68
55.44
I
I
OMe
4ga
^{13}C-NMR (100 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



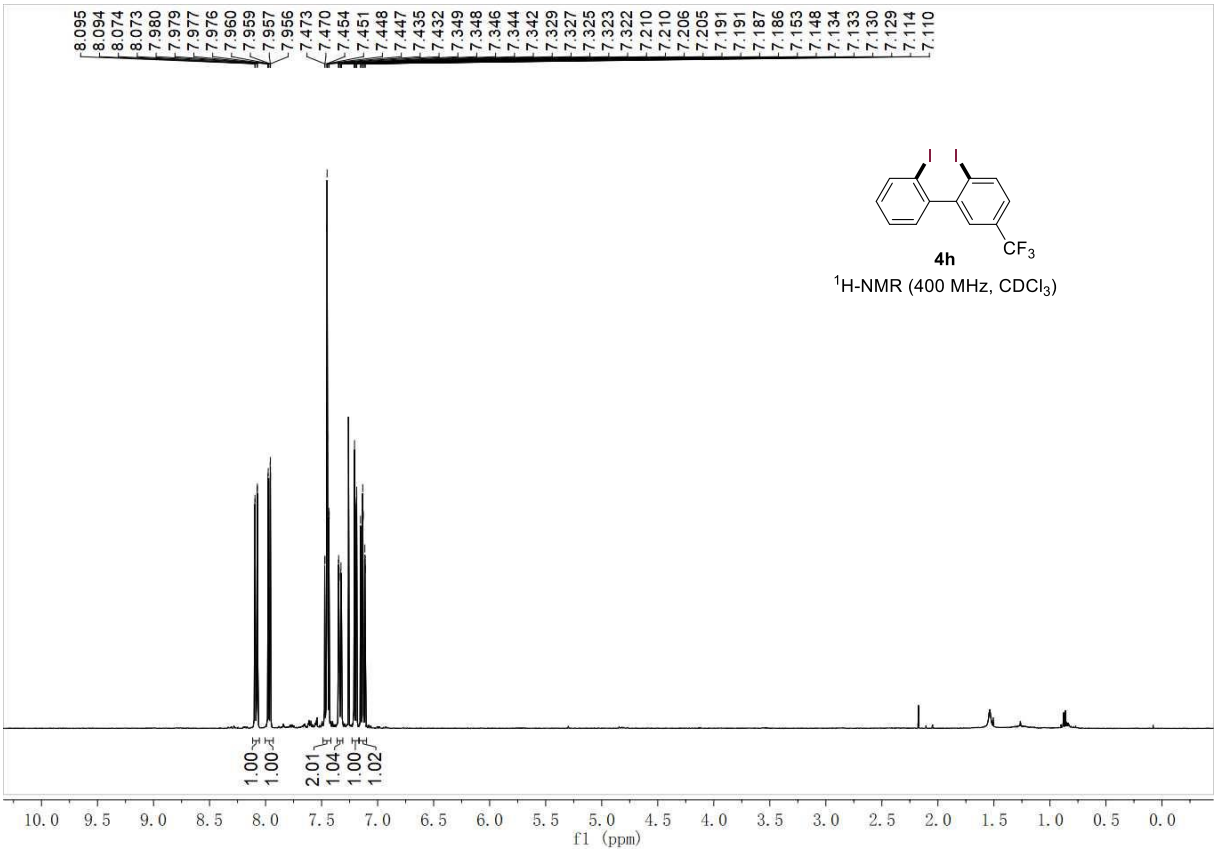
4gb

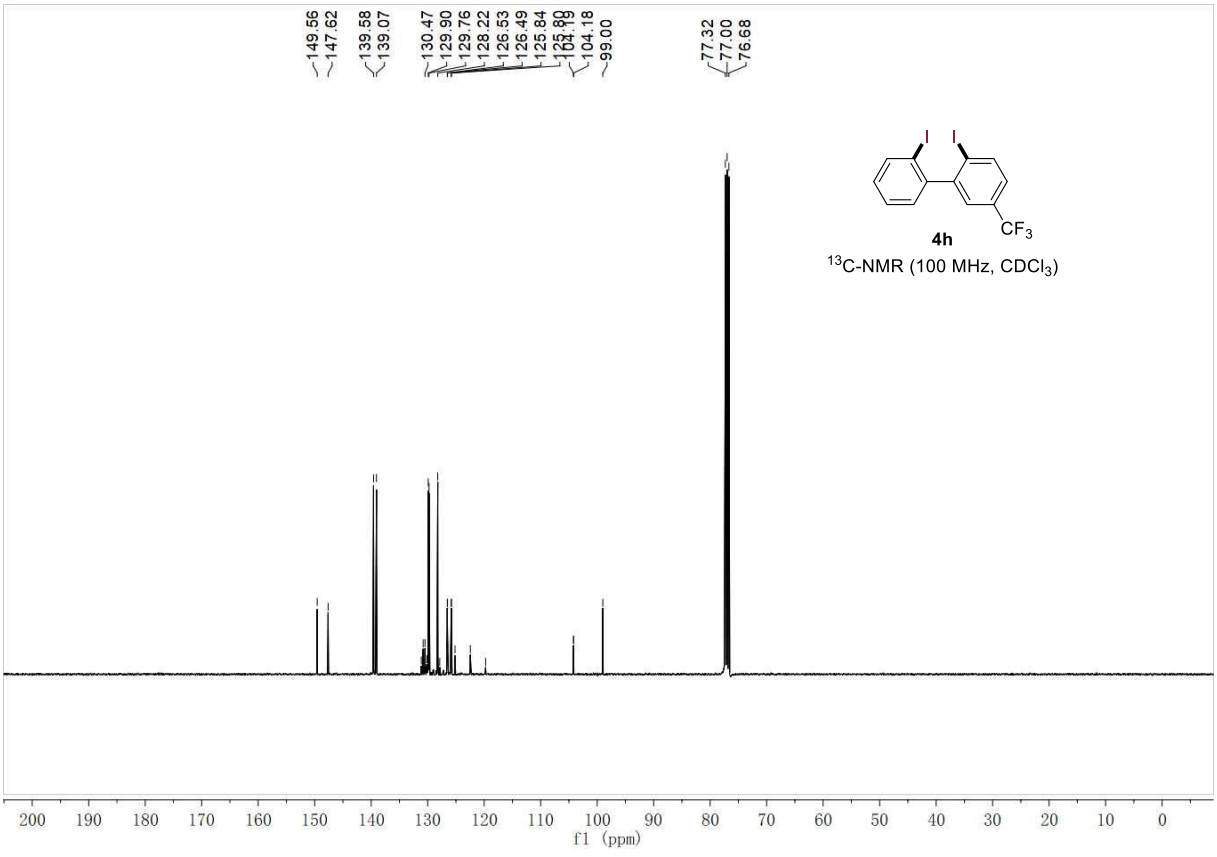
^{1}H-NMR (400 MHz, $CDCl_3$)

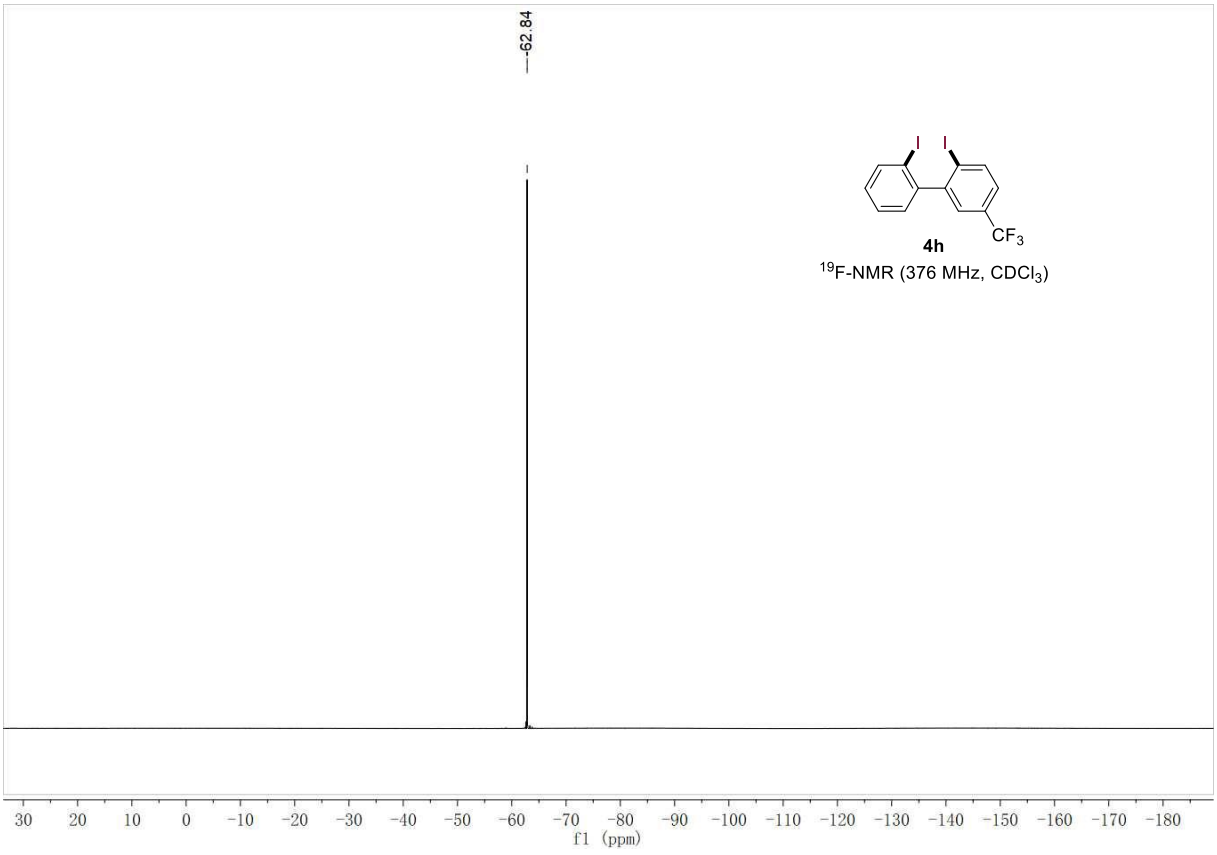


4gb

^{13}C-NMR (100 MHz, $CDCl_3$)

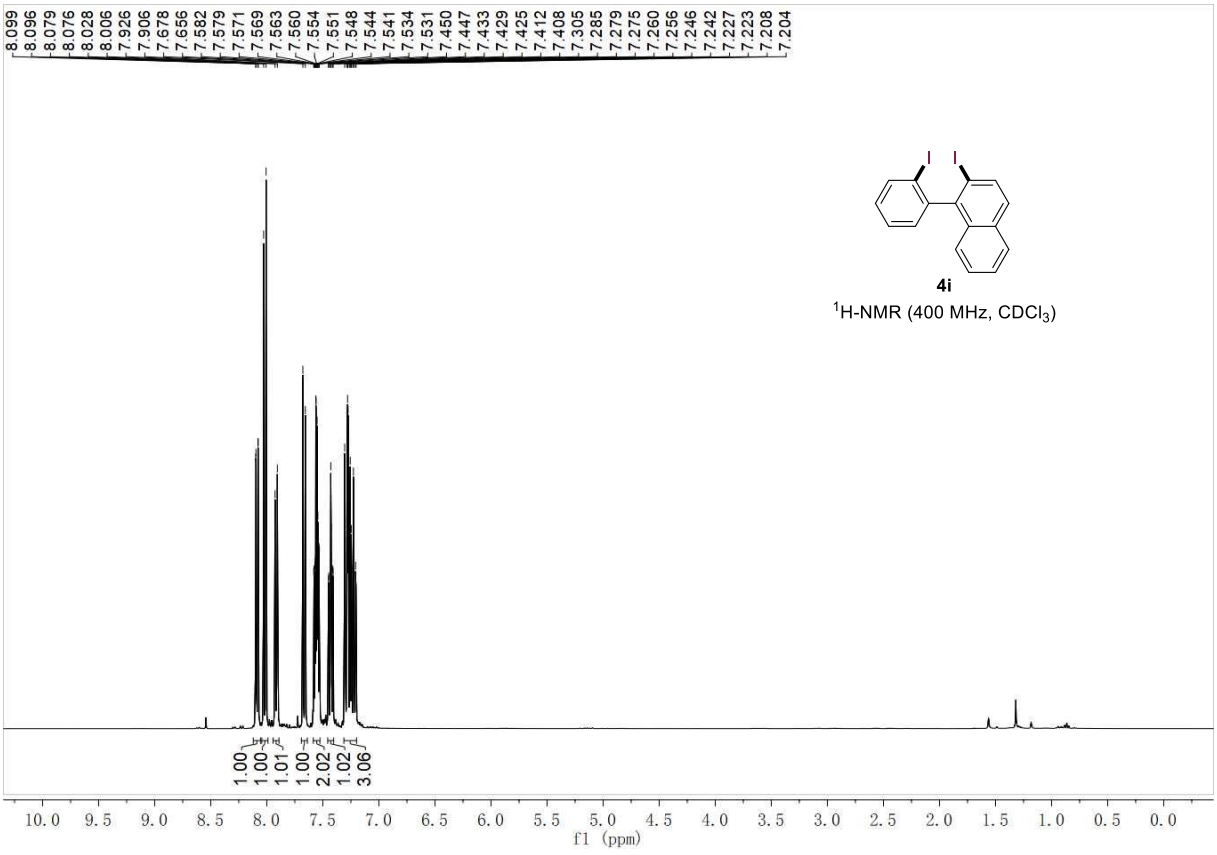

8.095
8.094
8.074
8.073
7.980
7.979
7.977
7.976
7.960
7.959
7.957
7.956
7.473
7.470
7.454
7.451
7.448
7.447
7.435
7.432
7.349
7.348
7.346
7.344
7.342
7.329
7.327
7.325
7.323
7.322
7.210
7.210
7.206
7.205
7.191
7.191
7.187
7.186
7.153
7.148
7.134
7.133
7.130
7.129
7.114
7.110
I
I
CF3
4h
1H-NMR (400 MHz, CDCl3)
1.00
1.00
2.01
1.04
1.00
1.02
10.0 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 0.0
f1 (ppm)


149.56
147.62
139.58
139.07
130.47
129.90
129.76
128.22
126.53
126.49
125.84
104.18
99.00
77.32
77.00
76.68
I
I
CF3
4h
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



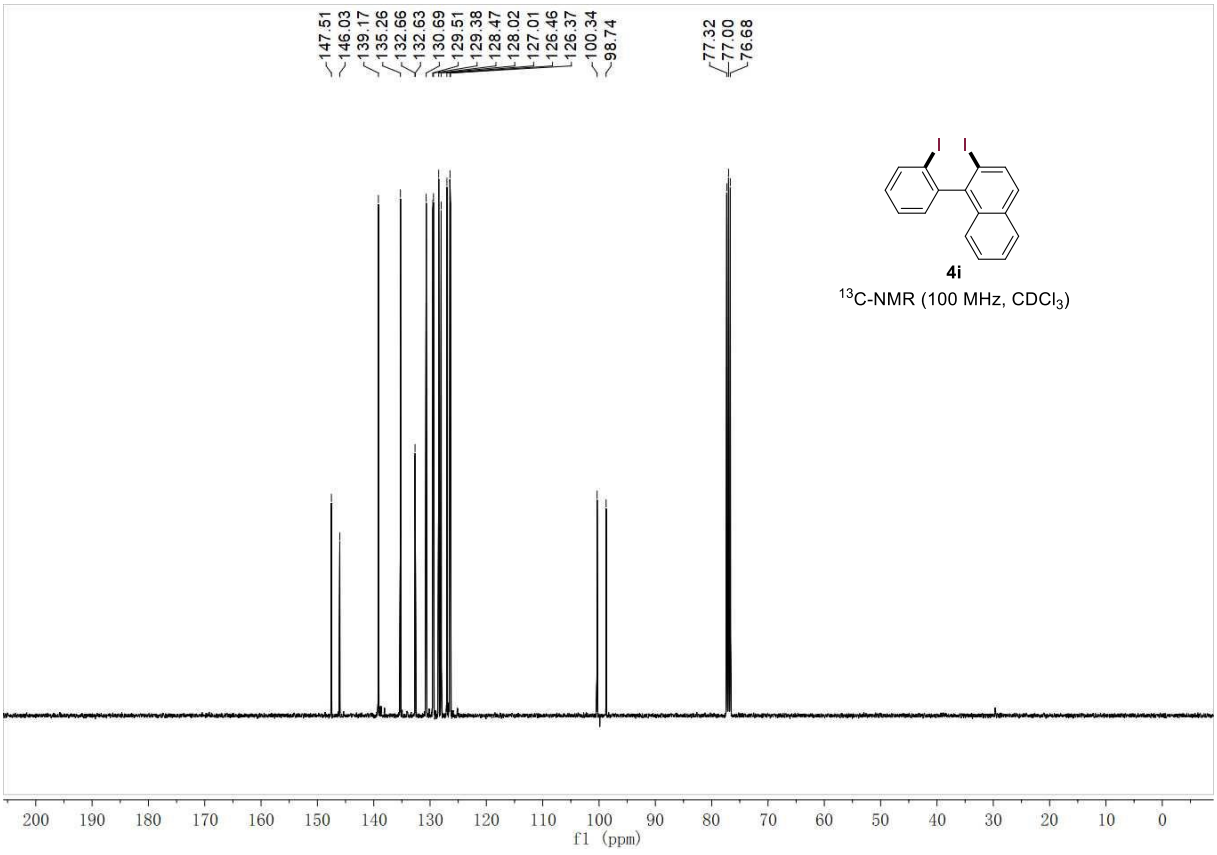
4h

^{19}F-NMR (376 MHz, $CDCl_3$)



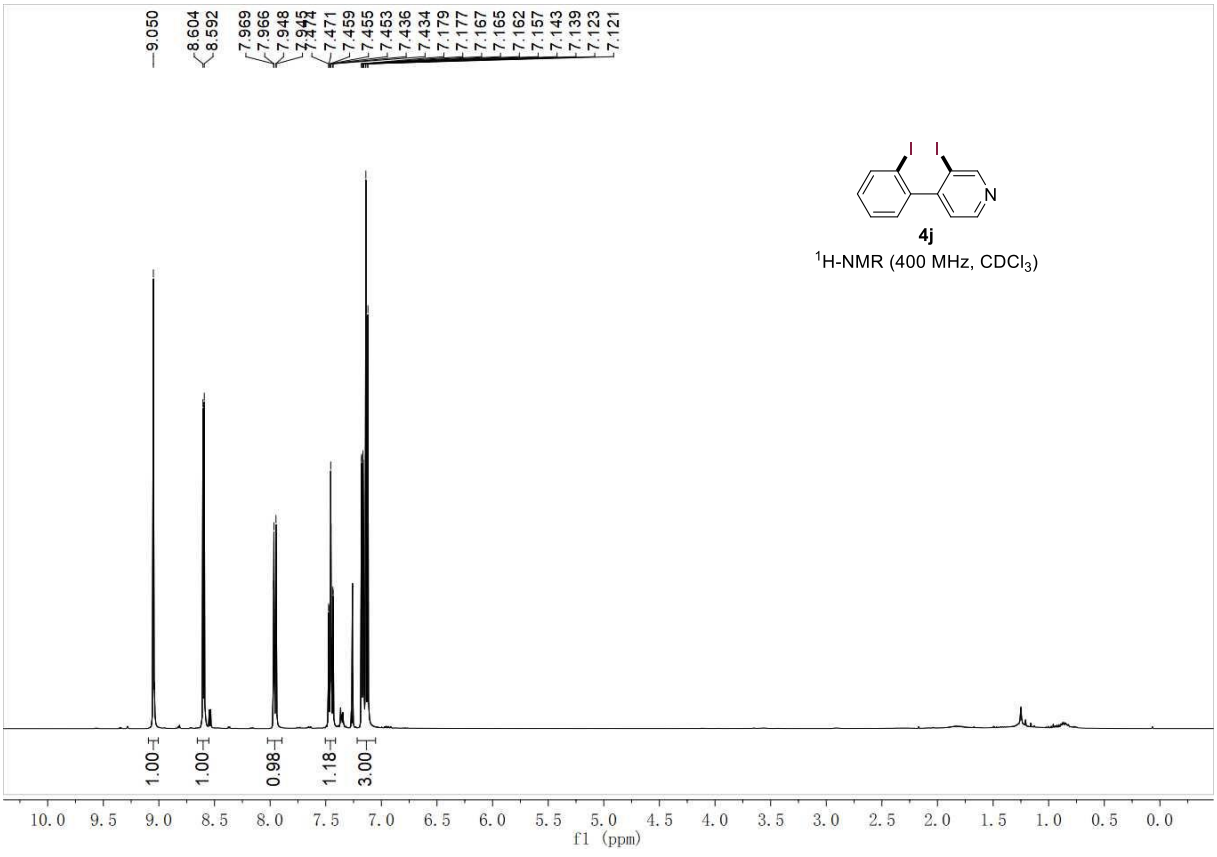
4i

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



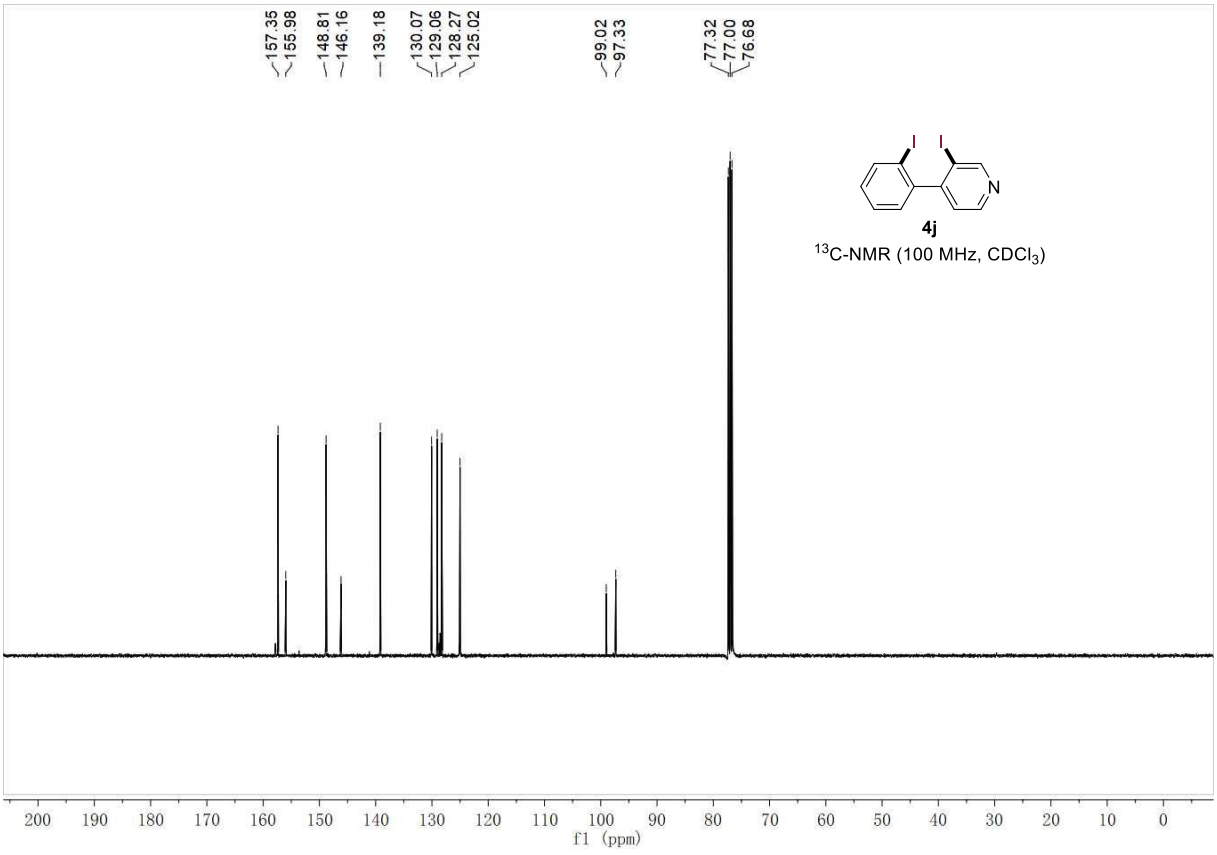
4i

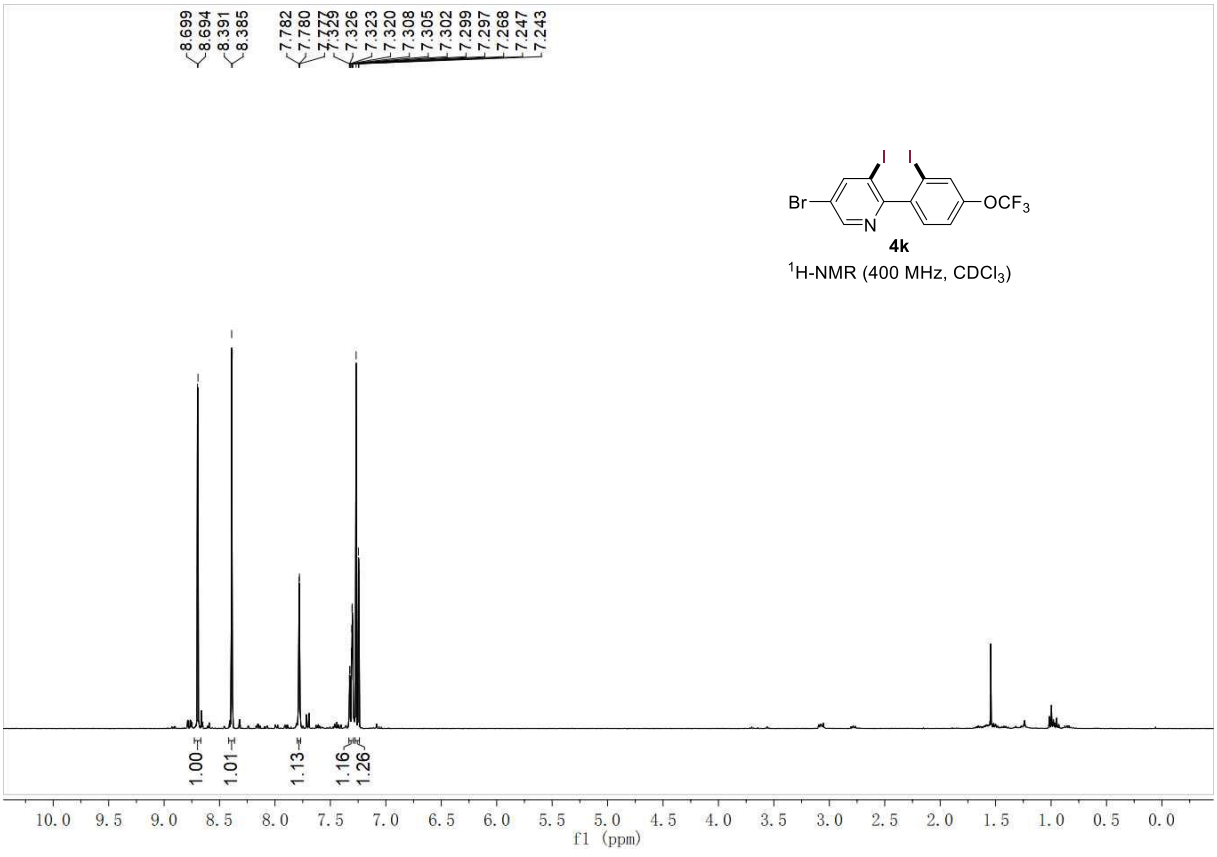
^{13}C-NMR (100 MHz, $CDCl_3$)

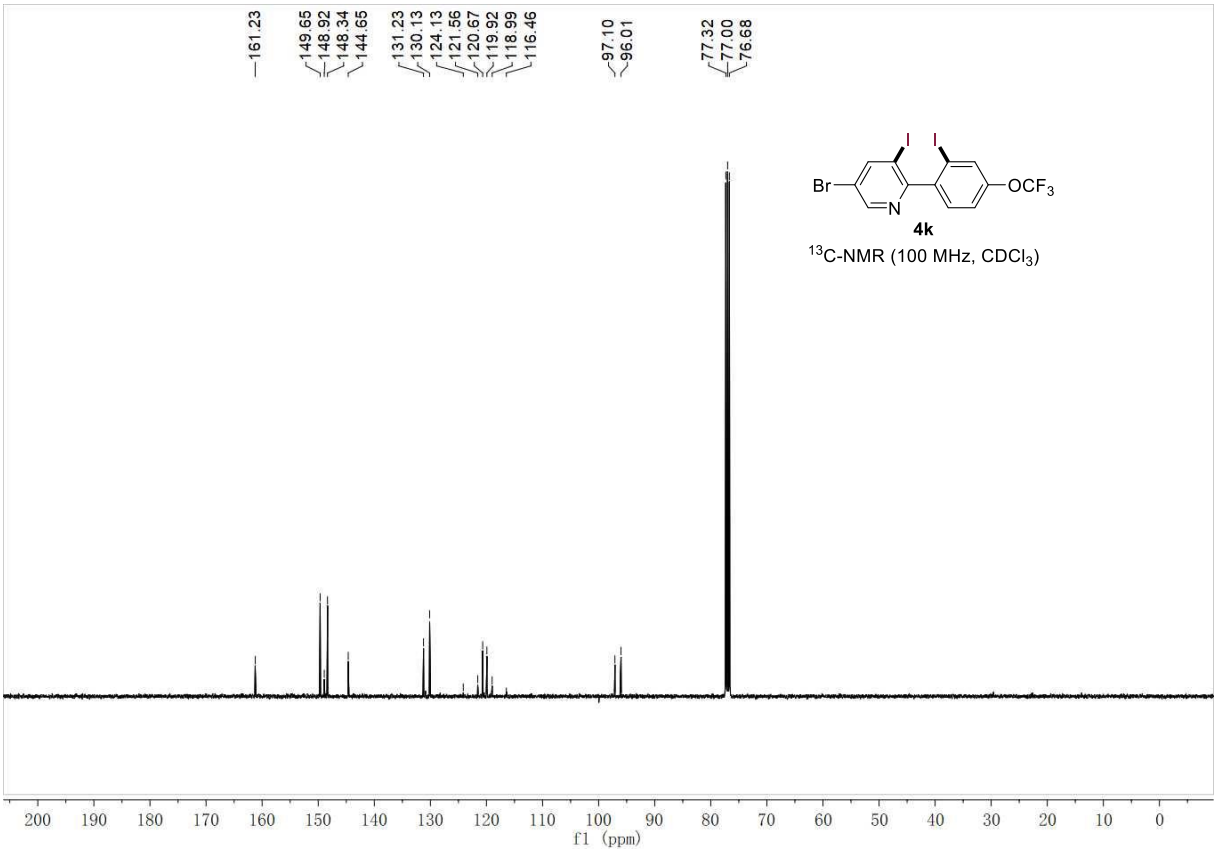


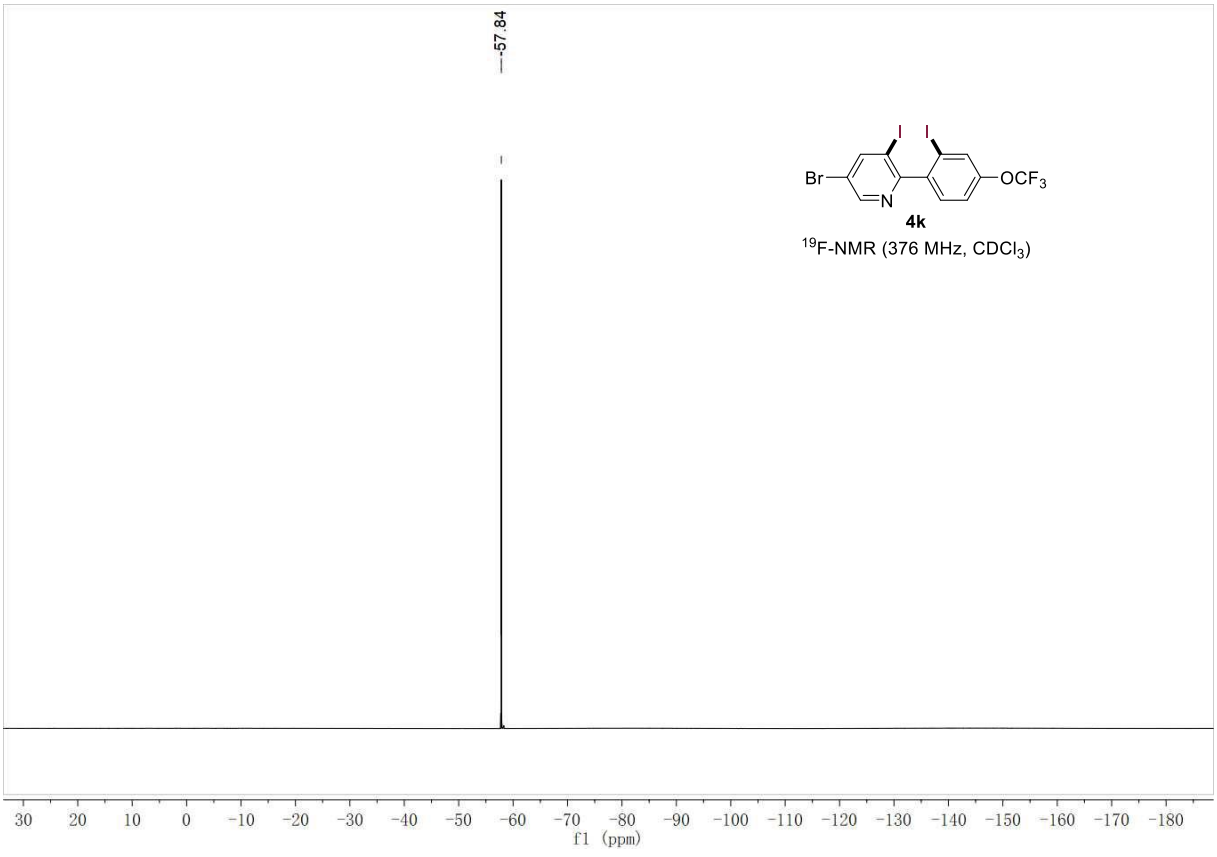
4j

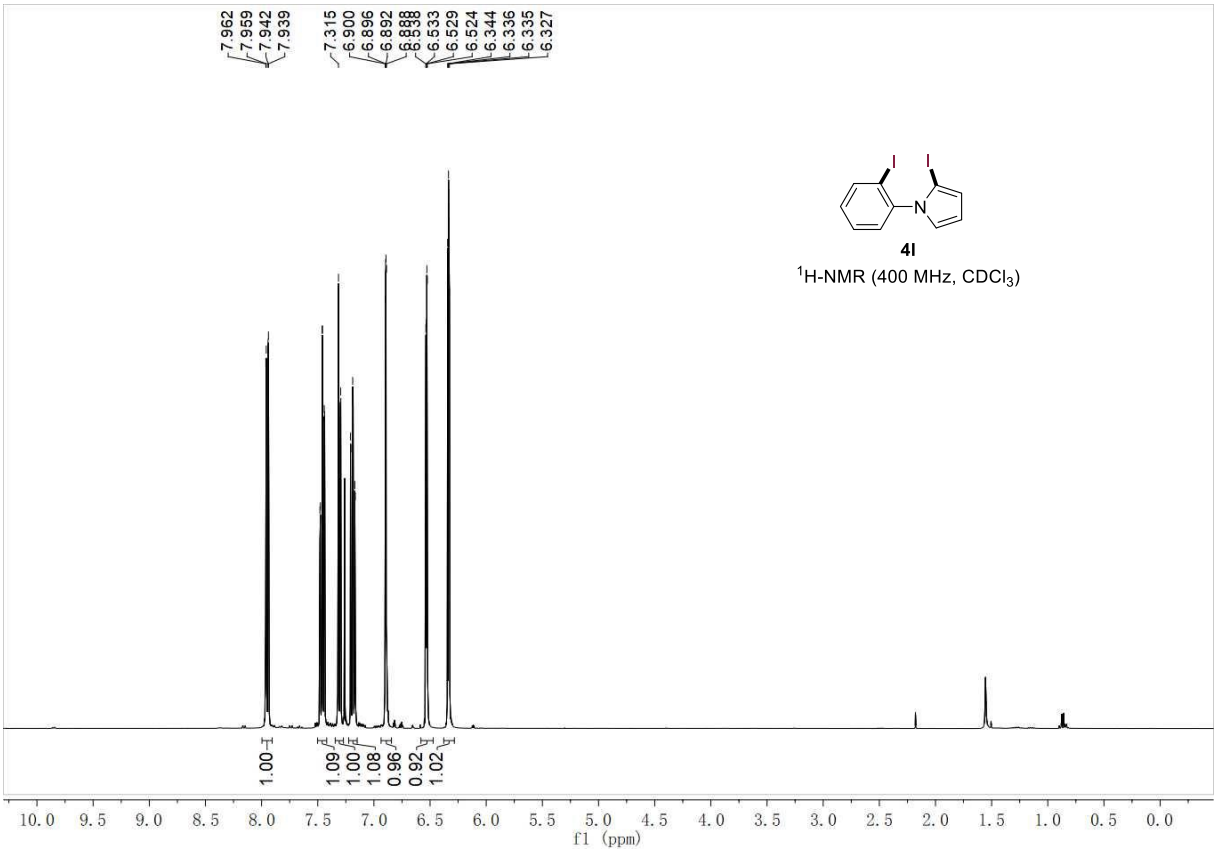
^{1}H-NMR (400 MHz, $CDCl_3$)

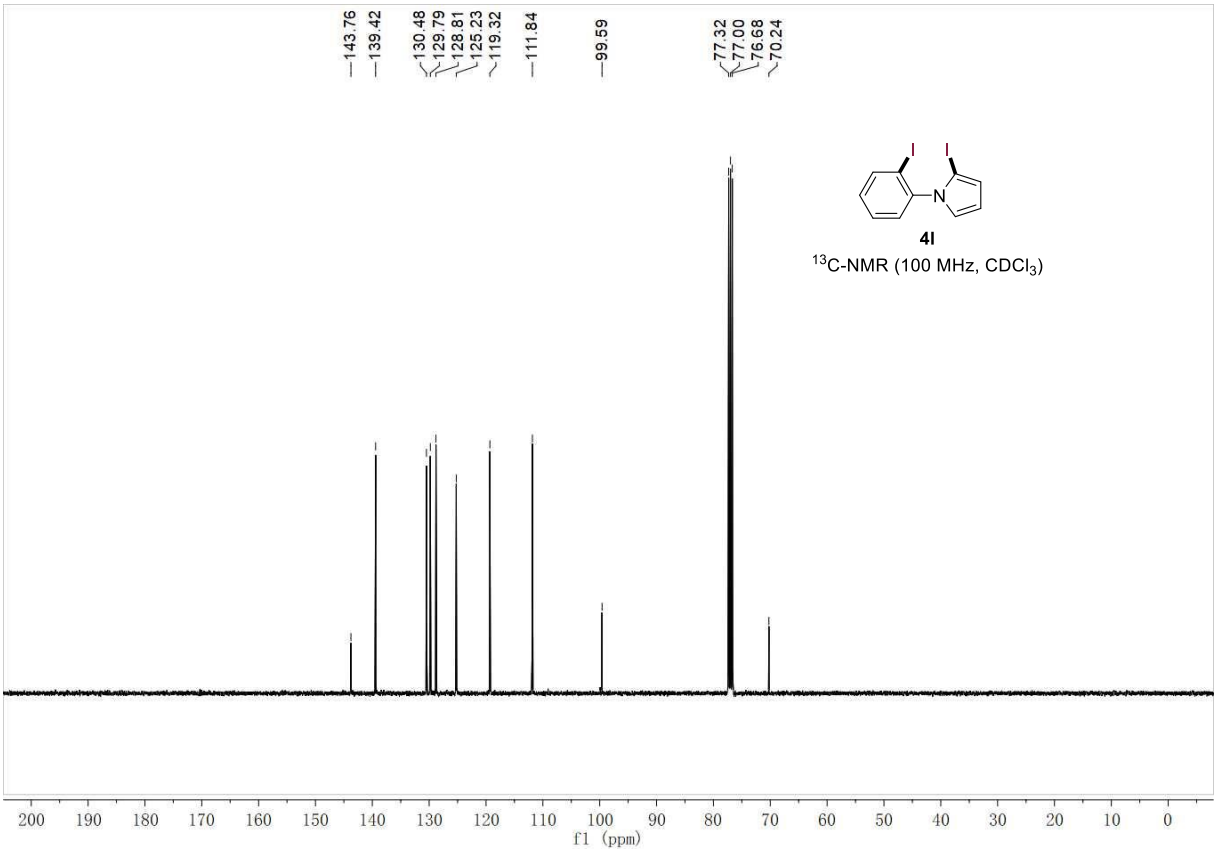

157.35
155.98
148.81
146.16
139.18
130.07
129.06
128.27
125.02
99.02
97.33
77.32
77.00
76.68
I
I
N
4j
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

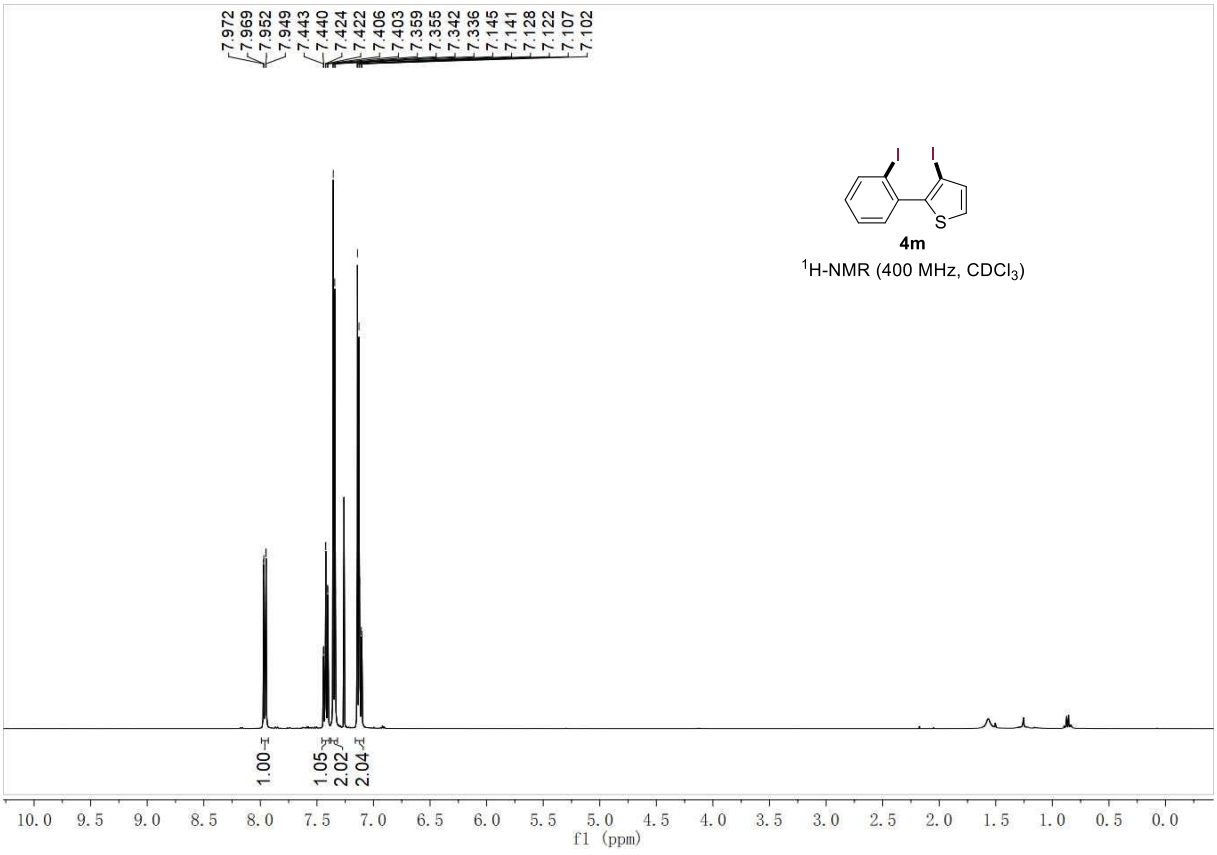

8.699
8.694
8.391
8.385
7.782
7.780
7.326
7.323
7.320
7.308
7.305
7.302
7.299
7.297
7.268
7.247
7.243
I
I
Br
N
OCF3
4k
1H-NMR (400 MHz, CDCl3)
1.00
1.01
1.13
1.16
1.26
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

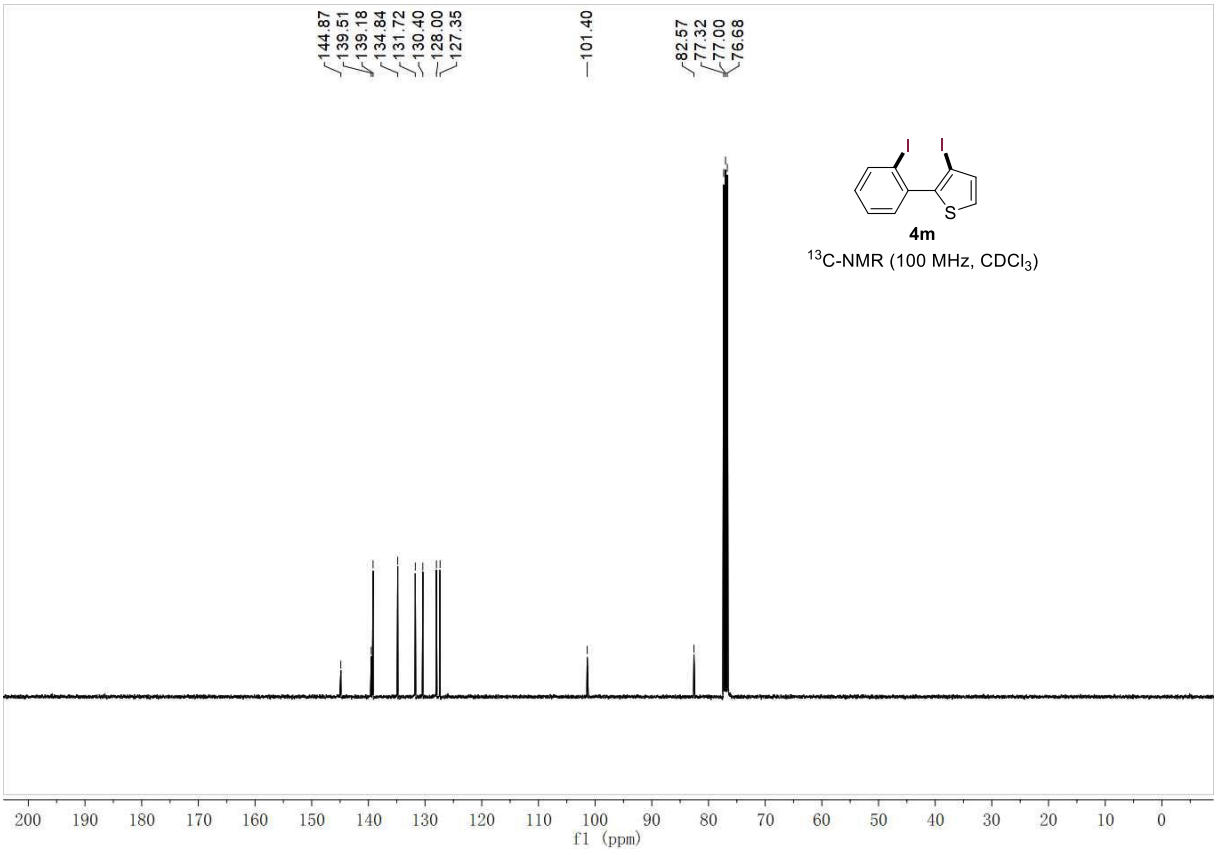

161.23
149.65
148.92
148.34
144.65
131.23
130.13
124.13
121.56
120.67
119.92
118.99
116.46
97.10
96.01
77.32
77.00
76.68
Br
N
I
I
OCF3
4k
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

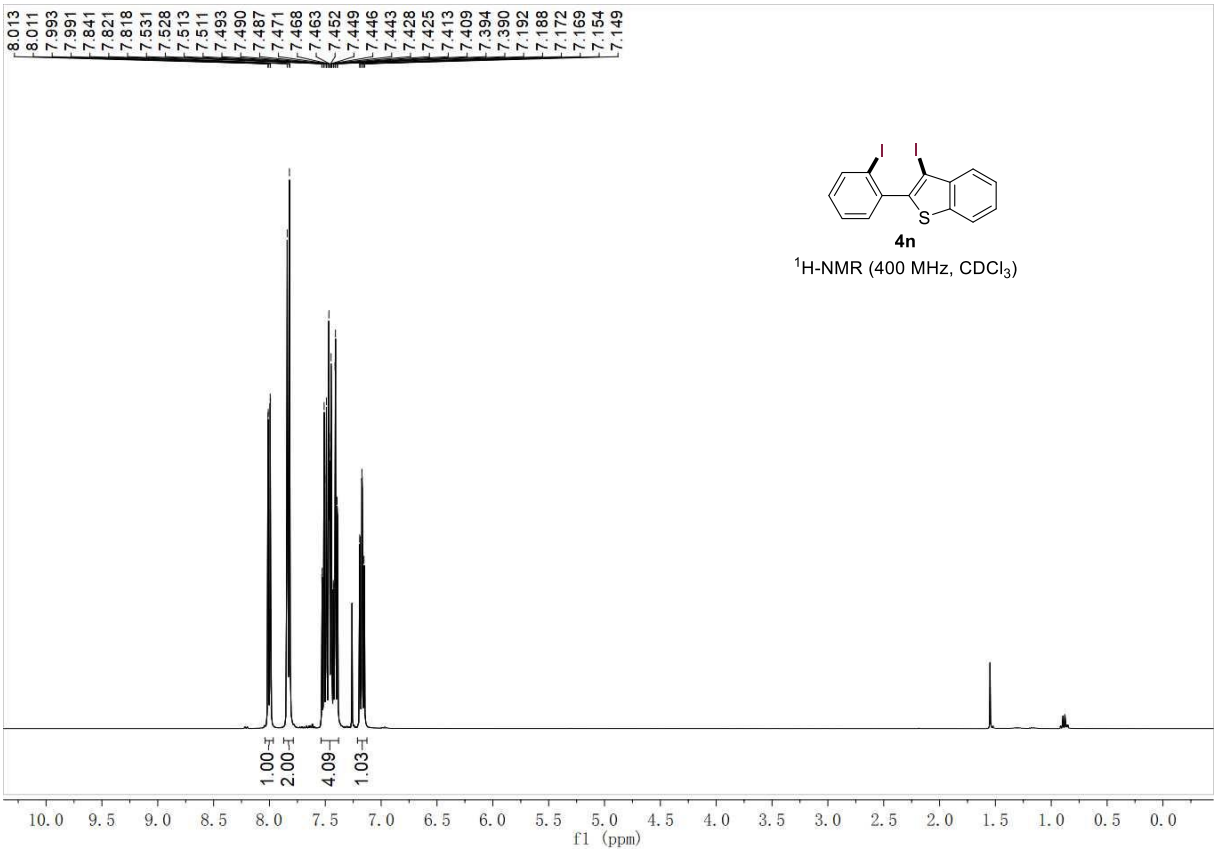

-57.84
Br
N
I
I
OCF3
4k
19F-NMR (376 MHz, CDCl3)
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

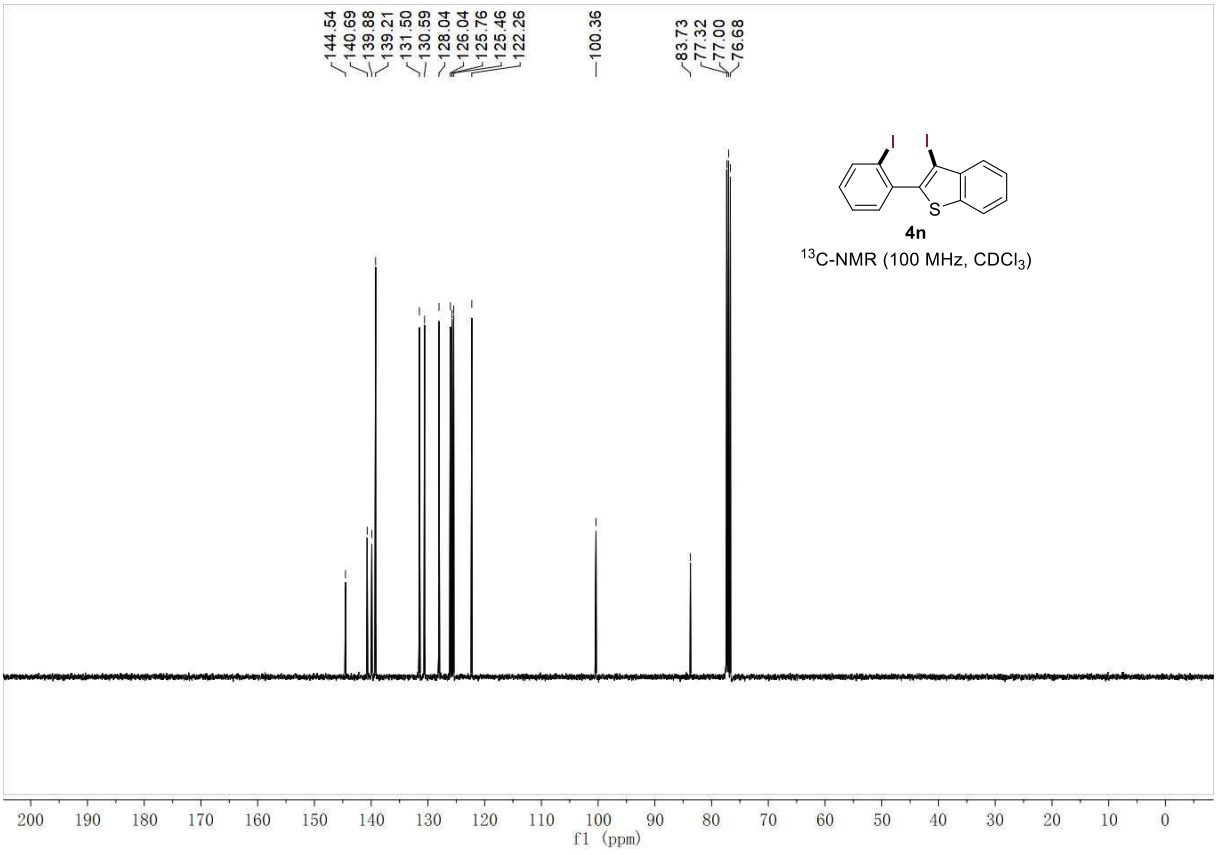

7.962
7.959
7.942
7.939
7.315
6.900
6.896
6.892
6.533
6.529
6.524
6.344
6.336
6.335
6.327
1.00
1.09
1.00
1.08
0.96
0.92
1.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
I
I
N
4l
^{1}H-NMR (400 MHz, $CDCl_3$)

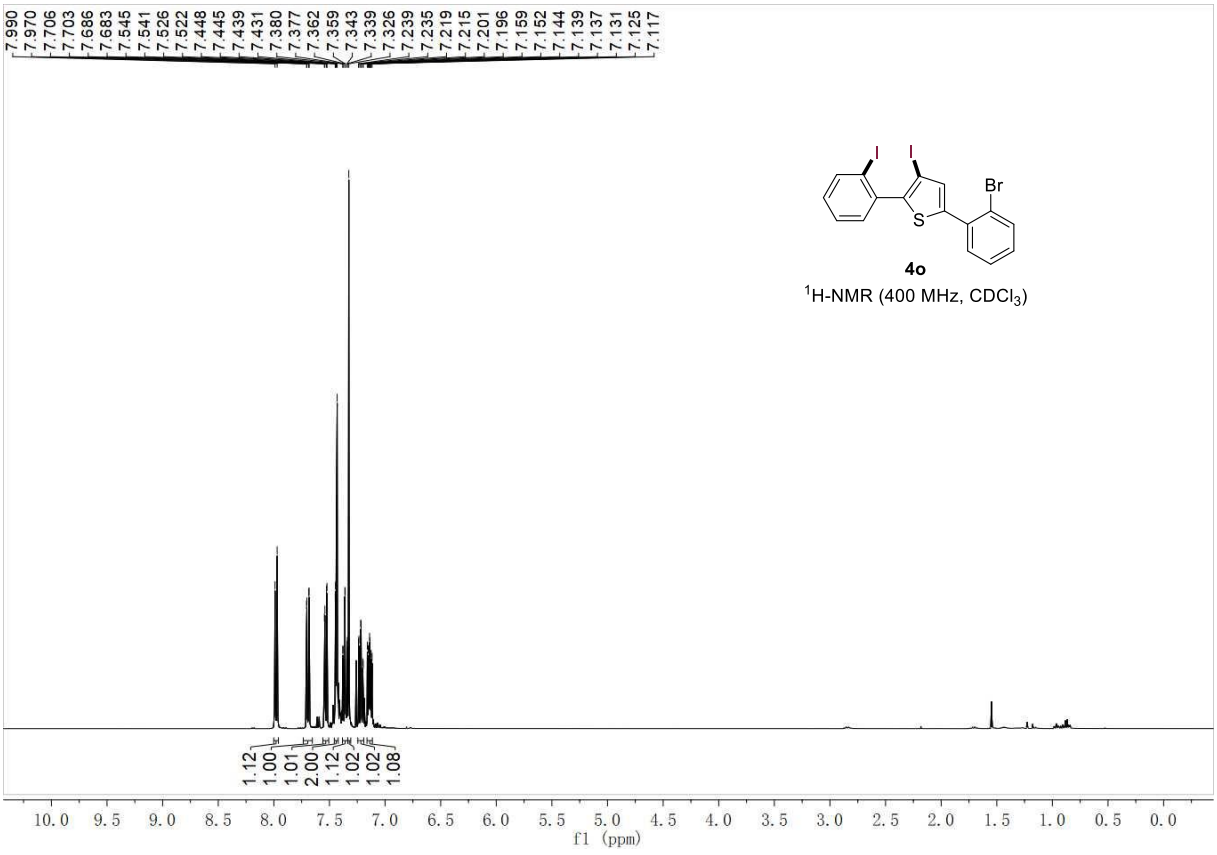

143.76
139.42
130.48
129.79
128.81
125.23
119.32
111.84
99.59
77.32
77.00
76.68
70.24
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
I
I
N
4l
^{13}C-NMR (100 MHz, $CDCl_3$)

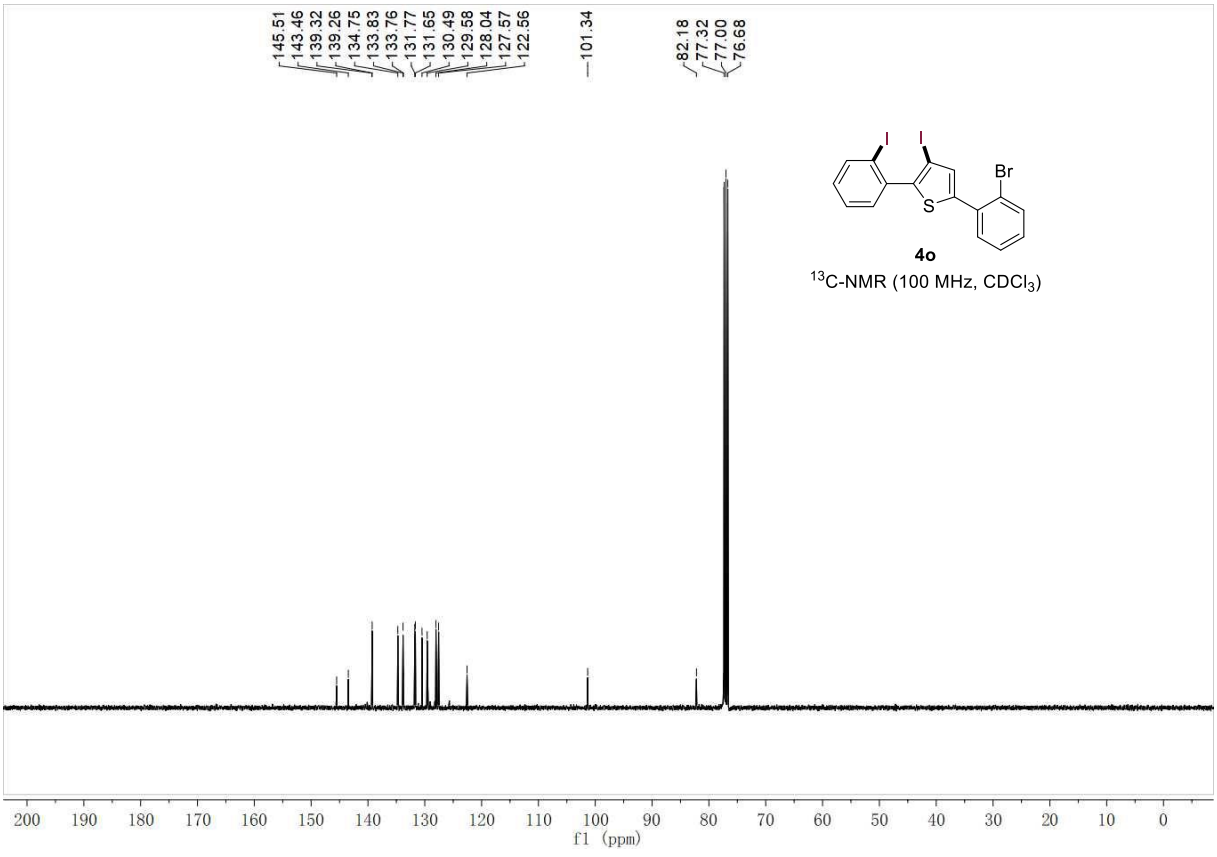

7.972
7.969
7.952
7.949
7.443
7.440
7.424
7.422
7.406
7.403
7.359
7.355
7.342
7.336
7.145
7.141
7.128
7.122
7.107
7.102
1.00
1.05
2.02
2.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
I
I
S
4m
^{1}H-NMR (400 MHz, $CDCl_3$)

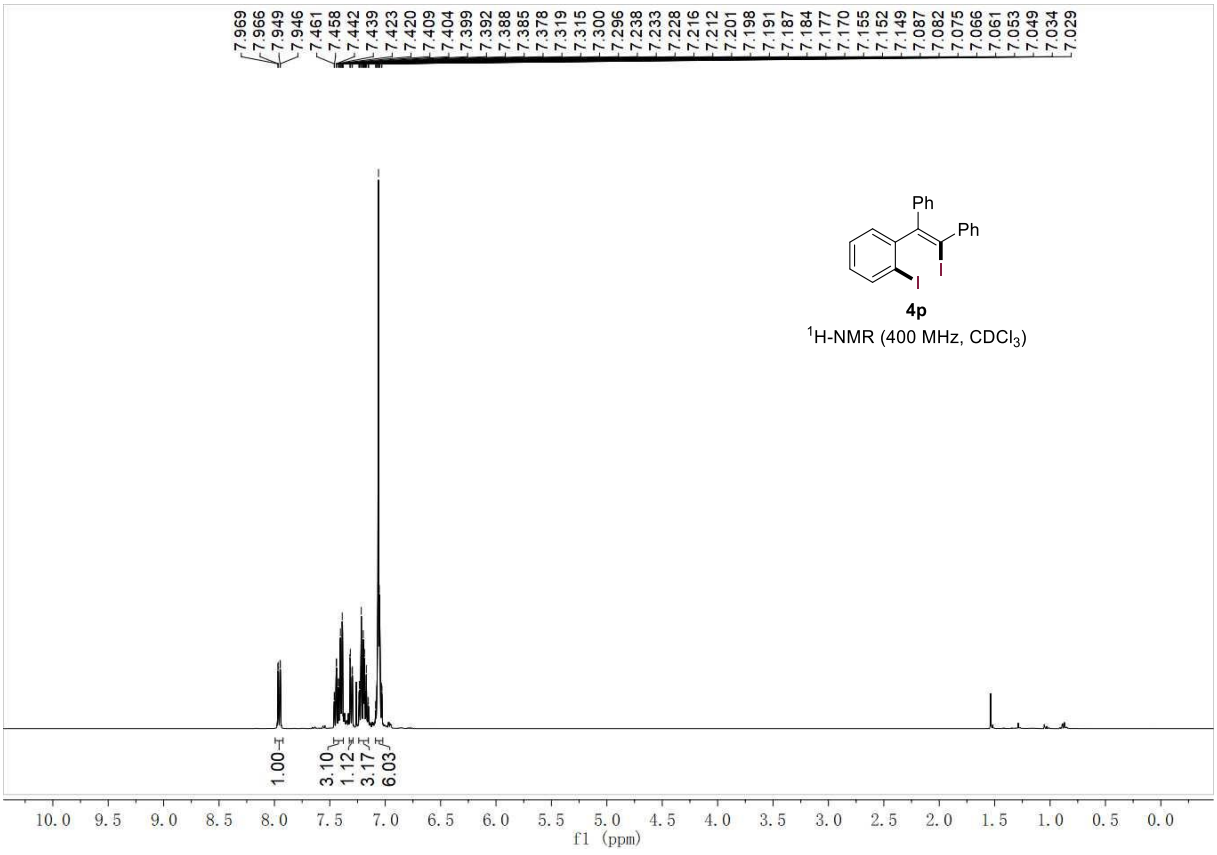

144.87
139.51
139.18
134.84
131.72
130.40
128.00
127.35
101.40
82.57
77.32
77.00
76.68
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
I
I
S
4m
^{13}C-NMR (100 MHz, $CDCl_3$)

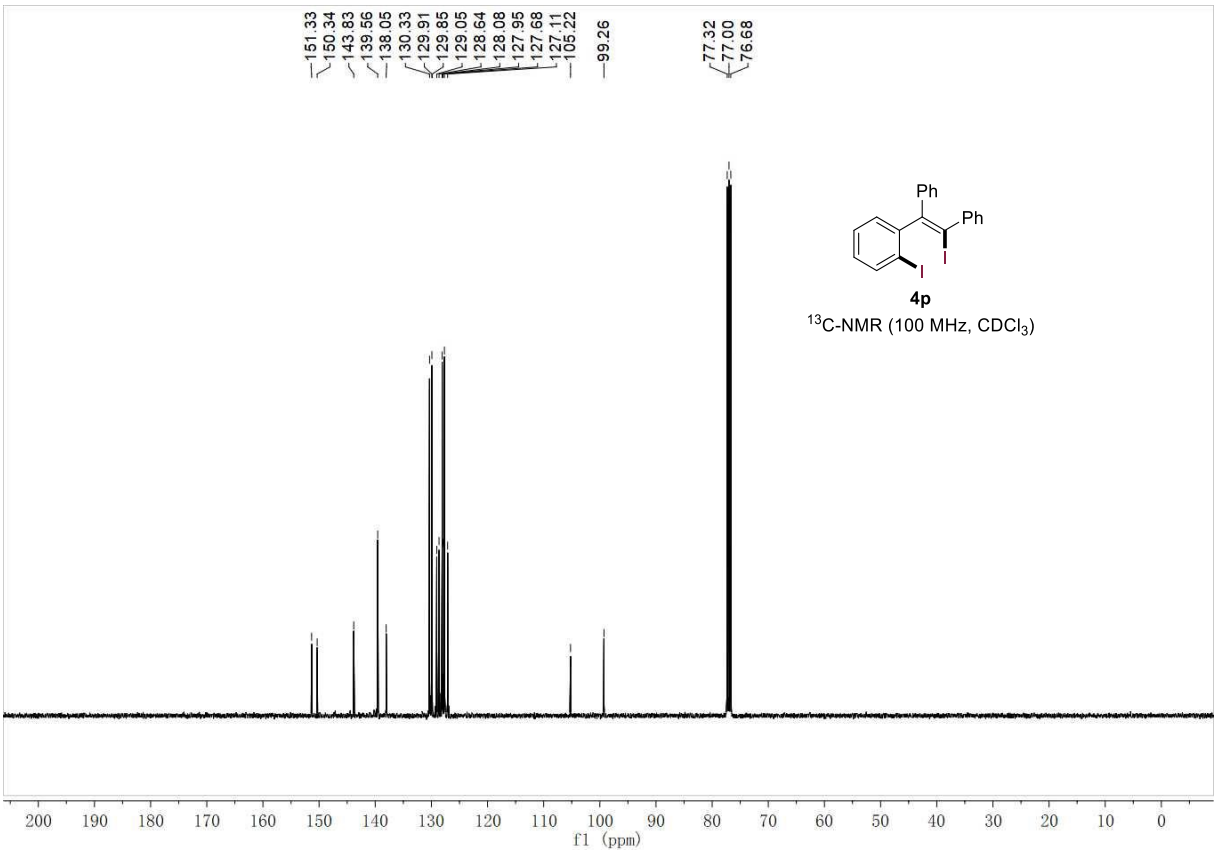

8.013
8.011
7.993
7.991
7.841
7.821
7.818
7.531
7.528
7.513
7.511
7.493
7.490
7.487
7.471
7.468
7.463
7.452
7.449
7.446
7.443
7.428
7.425
7.413
7.409
7.394
7.390
7.192
7.188
7.172
7.169
7.154
7.149
I
I
S
4n
1H-NMR (400 MHz, CDCl3)
1.00
2.00
4.09
1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

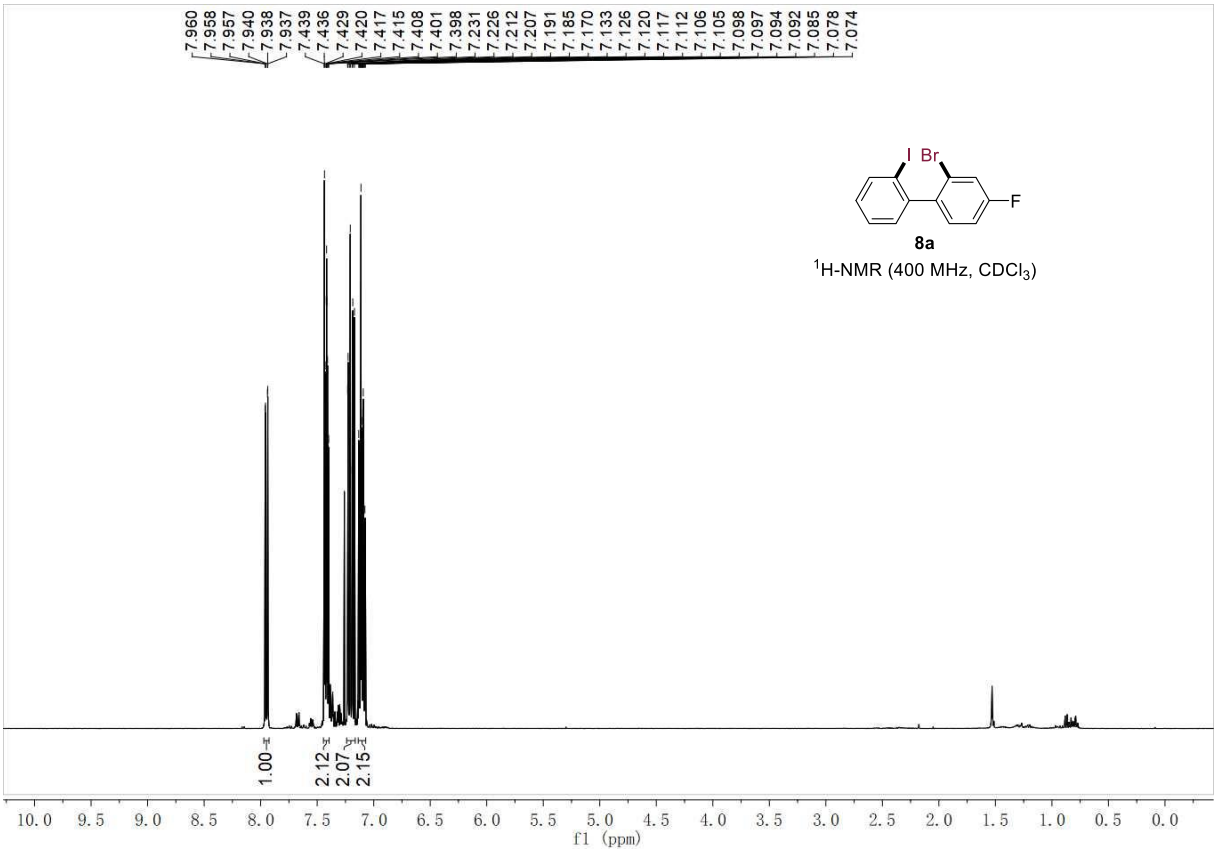

144.54
140.69
139.88
139.21
131.50
130.59
128.04
126.04
125.76
125.46
122.26
100.36
83.73
77.32
77.00
76.68
I
I
S
4n
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

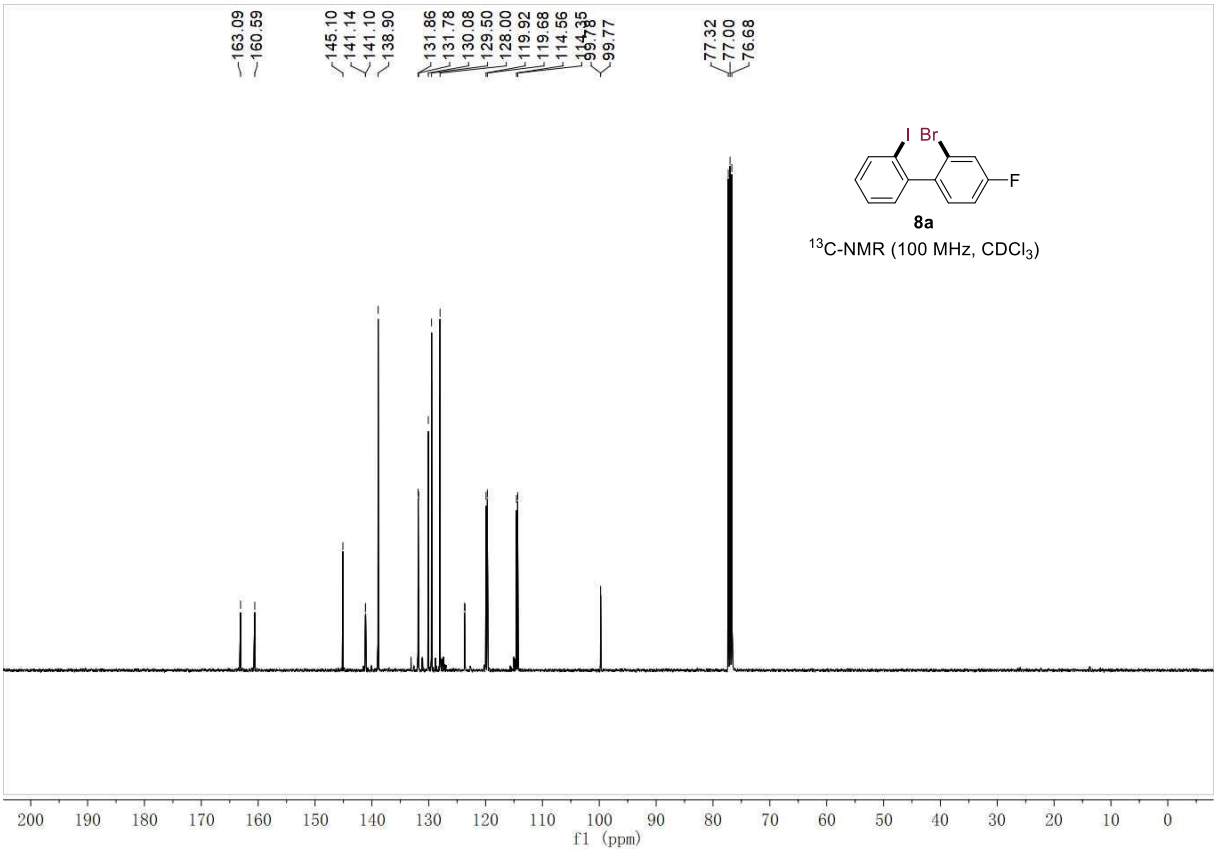

7.990
7.970
7.706
7.703
7.686
7.683
7.545
7.541
7.526
7.522
7.448
7.445
7.439
7.431
7.380
7.377
7.362
7.359
7.343
7.339
7.326
7.239
7.235
7.219
7.215
7.201
7.196
7.159
7.152
7.144
7.139
7.137
7.131
7.125
7.117
I
I
Br
S
4o
1H-NMR (400 MHz, CDCl3)
1.12
1.00
1.01
2.00
1.12
1.02
1.02
1.08
10.0 9.5 9.0 8.5 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 0.0
f1 (ppm)

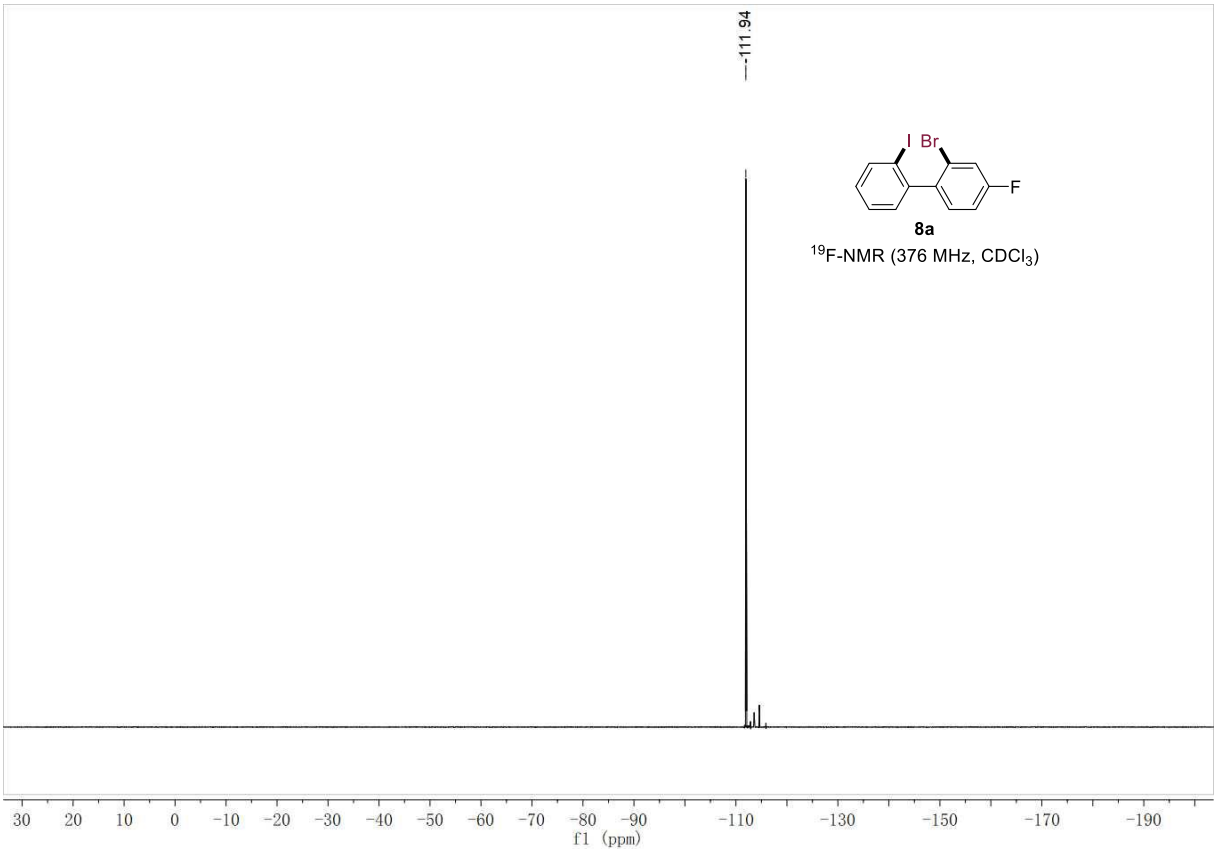

145.51
143.46
139.32
139.26
134.75
133.83
133.76
131.77
131.65
130.49
129.58
128.04
127.57
122.56
101.34
82.18
77.32
77.00
76.68
I
I
Br
S
4o
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.969
7.966
7.949
7.946
7.461
7.458
7.442
7.439
7.423
7.420
7.409
7.404
7.399
7.392
7.388
7.385
7.378
7.319
7.315
7.300
7.296
7.238
7.233
7.228
7.216
7.212
7.201
7.198
7.191
7.187
7.184
7.177
7.170
7.155
7.152
7.149
7.087
7.082
7.075
7.066
7.061
7.053
7.049
7.034
7.029
Ph
Ph
I
4p
1H-NMR (400 MHz, CDCl3)
1.00
3.10
1.12
3.17
6.03
10.0 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 0.0
f1 (ppm)


151.33
150.34
143.83
139.56
138.05
130.33
129.91
129.85
129.05
128.64
128.08
127.95
127.68
127.11
105.22
99.26
77.32
77.00
76.68
Ph
Ph
I
4p
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

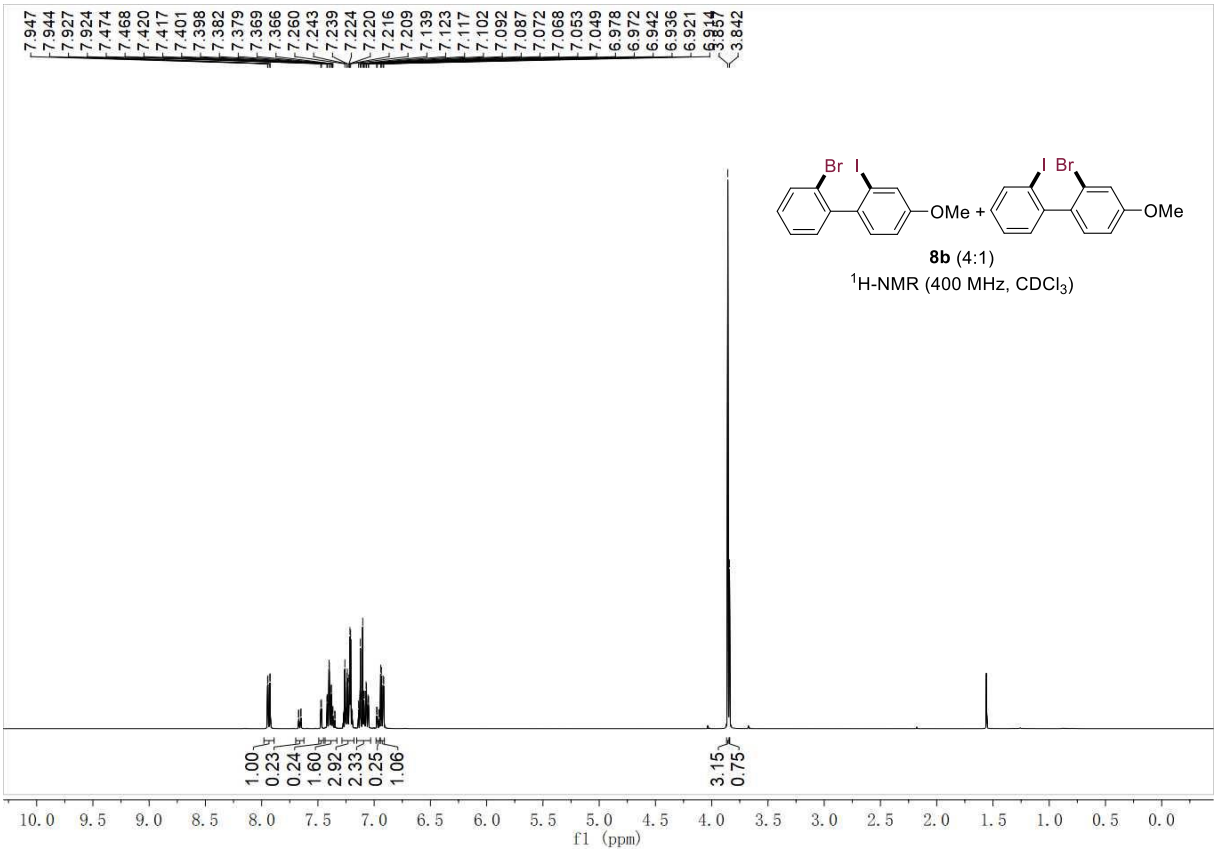

7.960
7.958
7.957
7.940
7.938
7.937
7.439
7.436
7.429
7.420
7.417
7.415
7.408
7.401
7.398
7.231
7.226
7.212
7.207
7.191
7.185
7.170
7.133
7.126
7.120
7.117
7.112
7.106
7.105
7.098
7.097
7.094
7.092
7.085
7.078
7.074
I Br
F
8a
1H-NMR (400 MHz, CDCl3)
1.00
2.12
2.07
2.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


163.09
160.59
145.10
141.14
141.10
138.90
131.86
131.78
130.08
129.50
128.00
119.92
119.68
114.56
114.35
99.78
99.77
77.32
77.00
76.68
I Br
F
8a
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



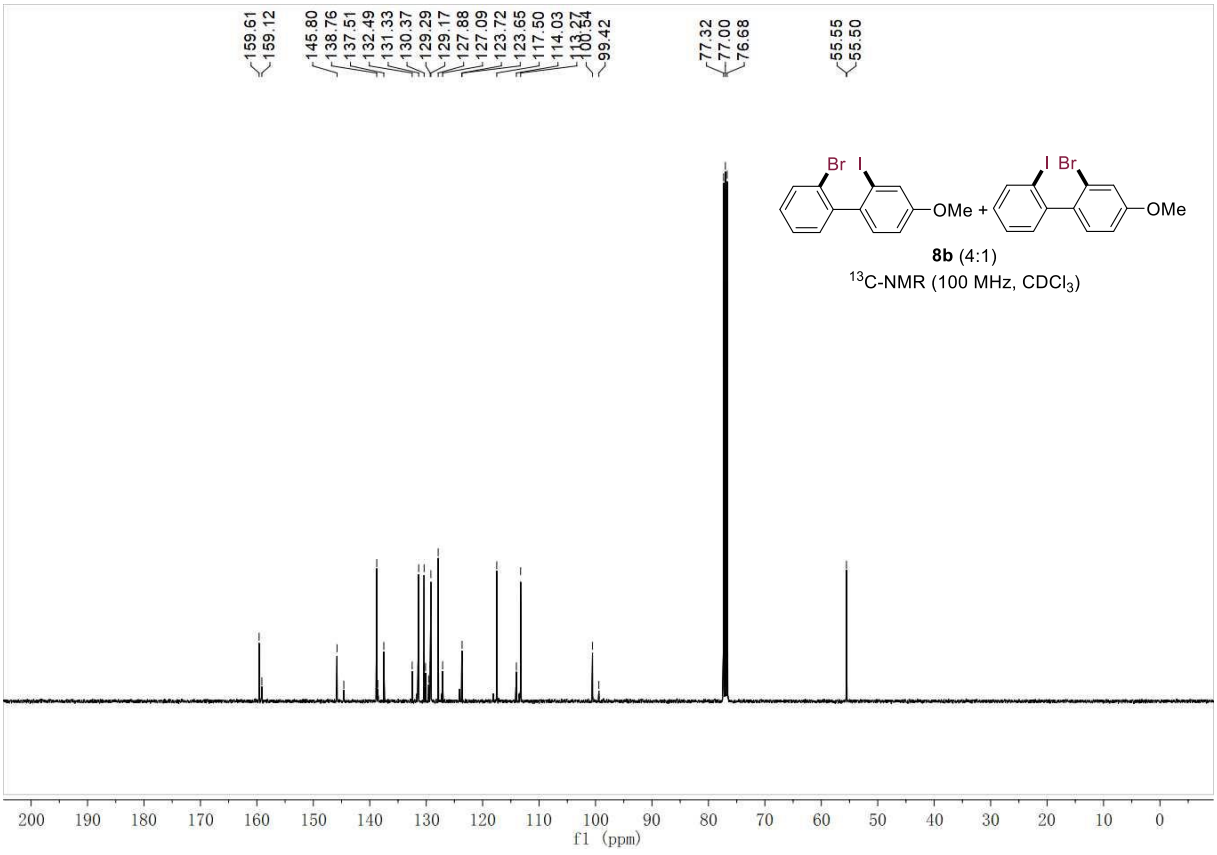
8a

^{19}F-NMR (376 MHz, $CDCl_3$)



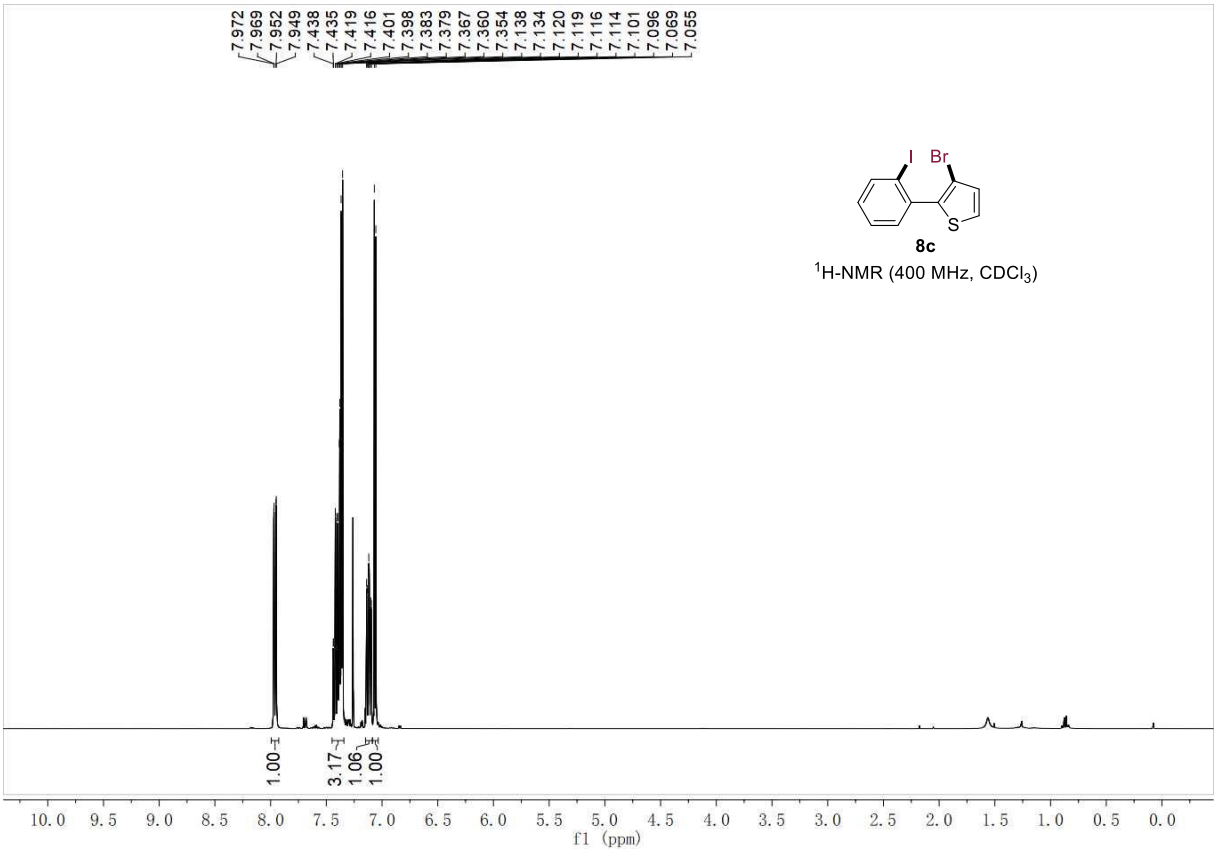
8b (4:1)

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



8b (4:1)

^{13}C-NMR (100 MHz, $CDCl_3$)

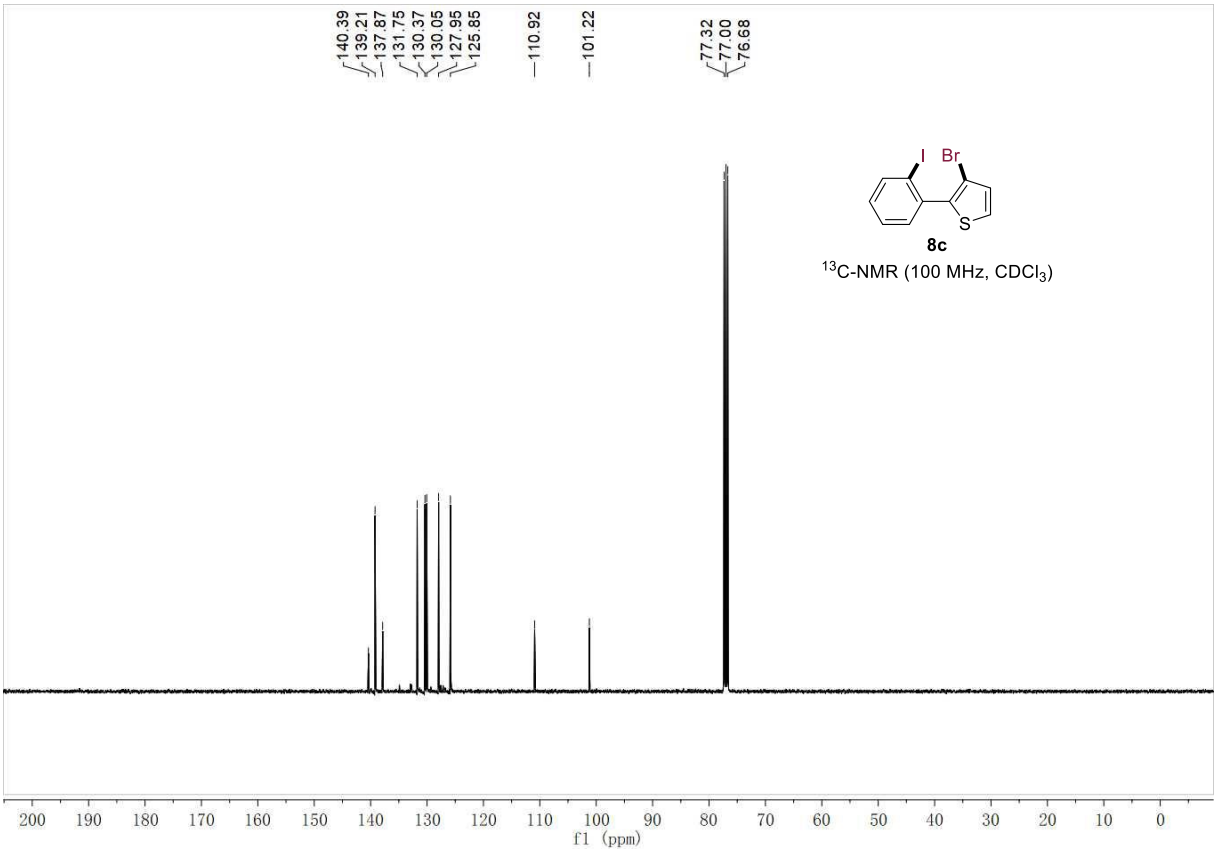


I Br

S

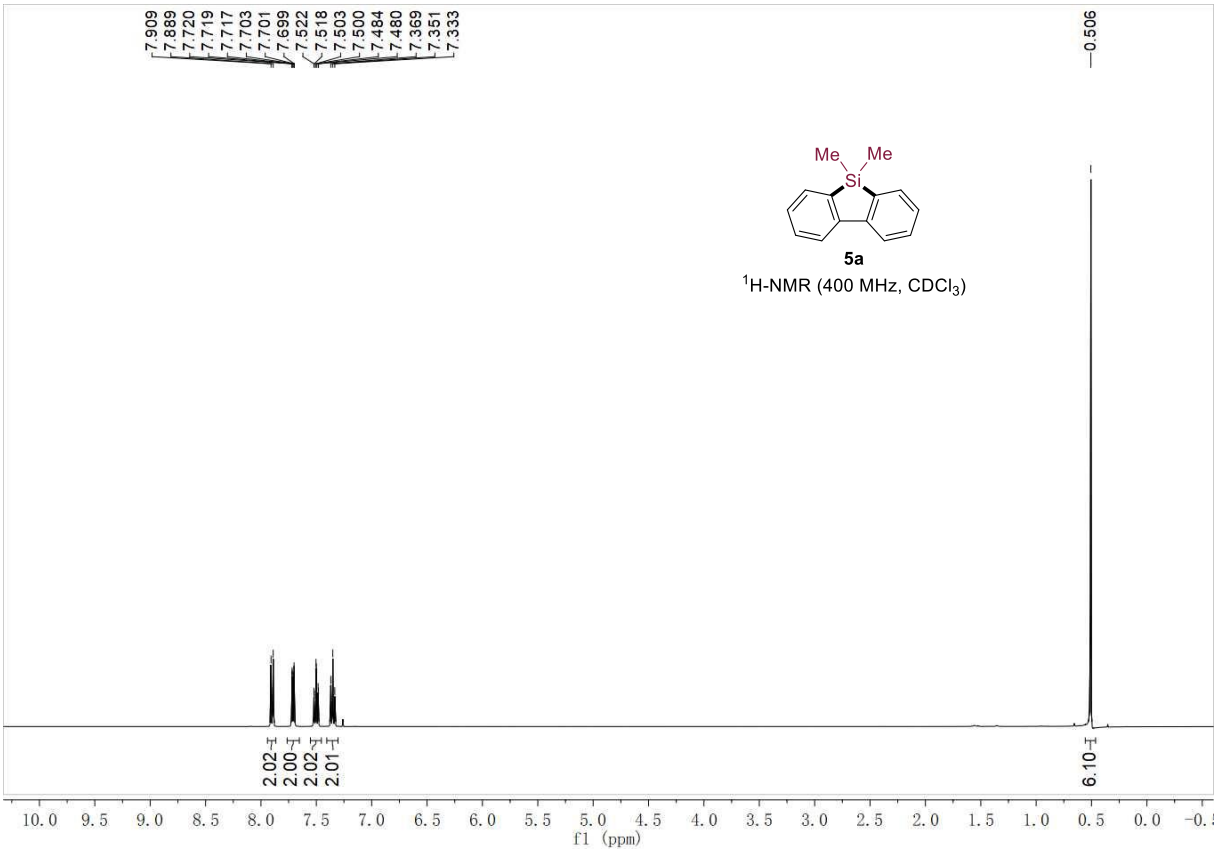
8c

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



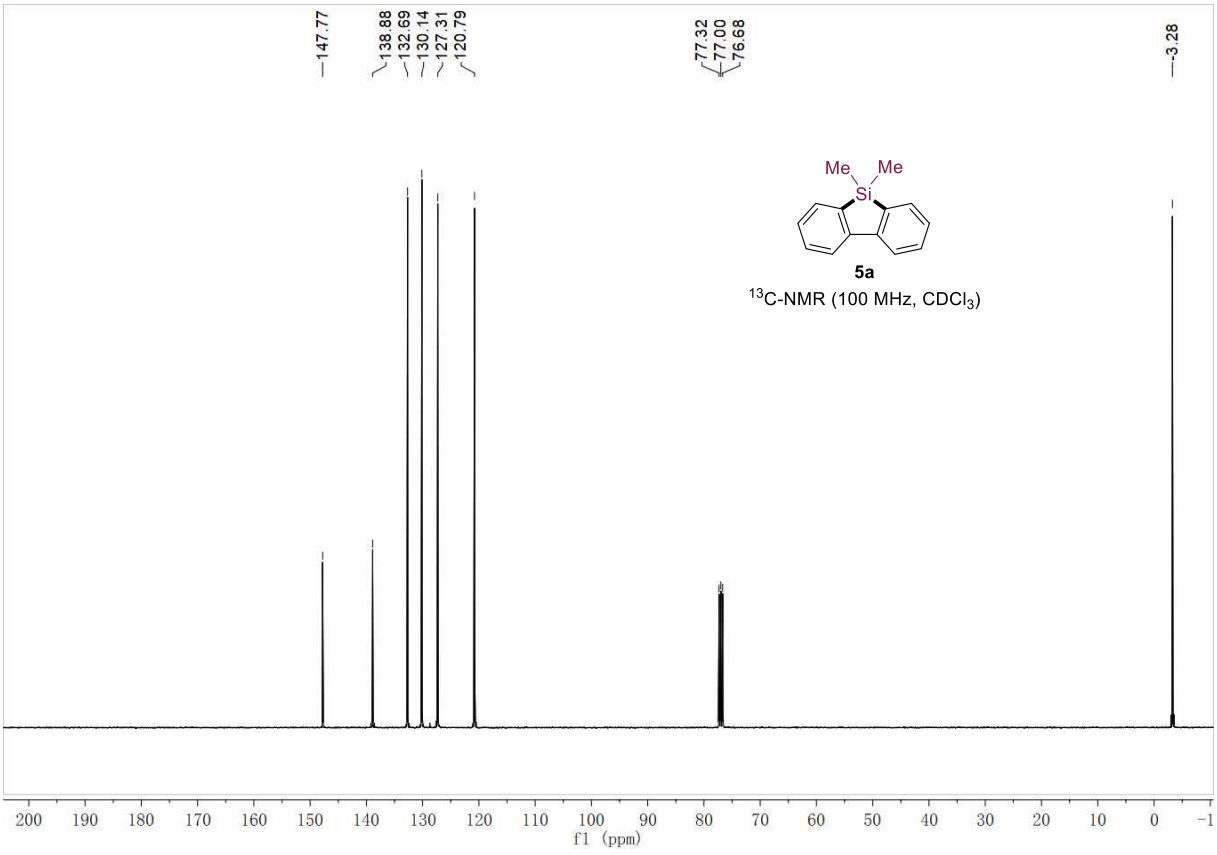
8c

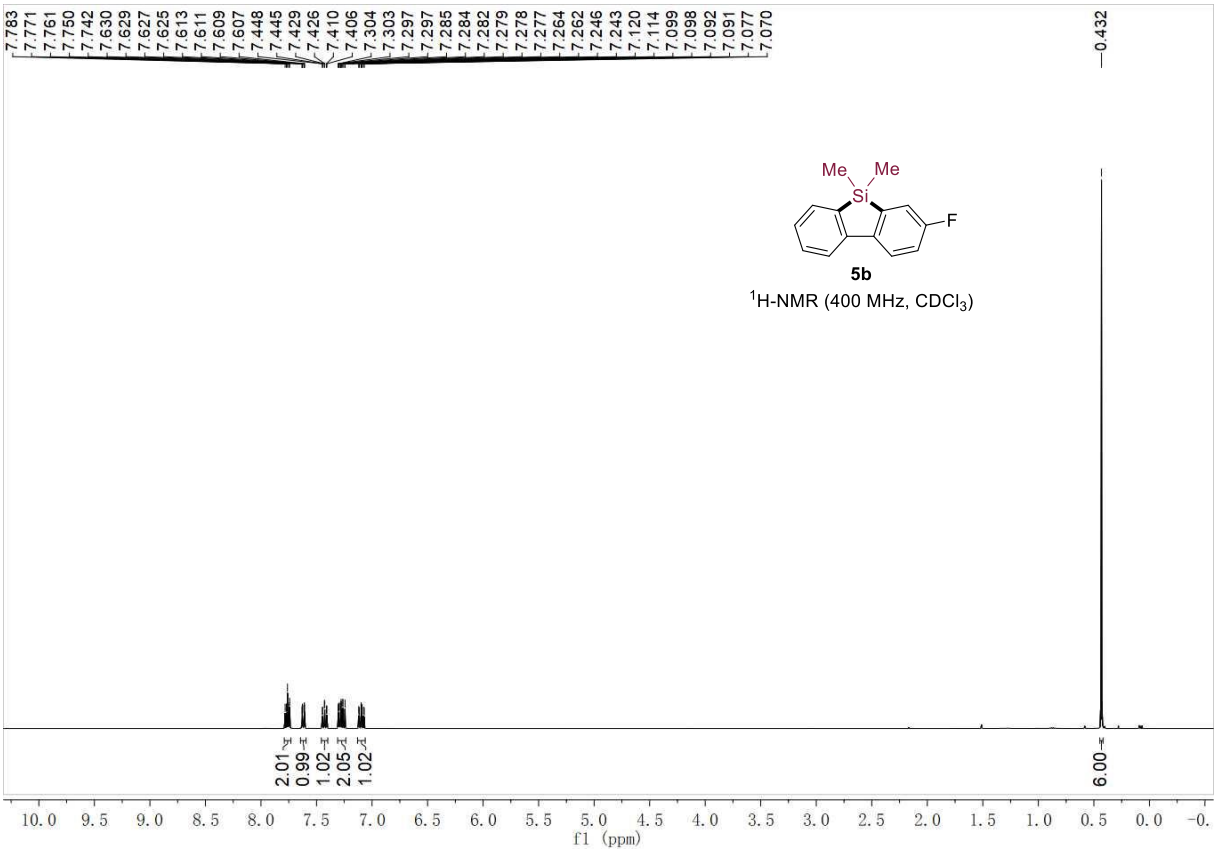
^{13}C-NMR (100 MHz, $CDCl_3$)

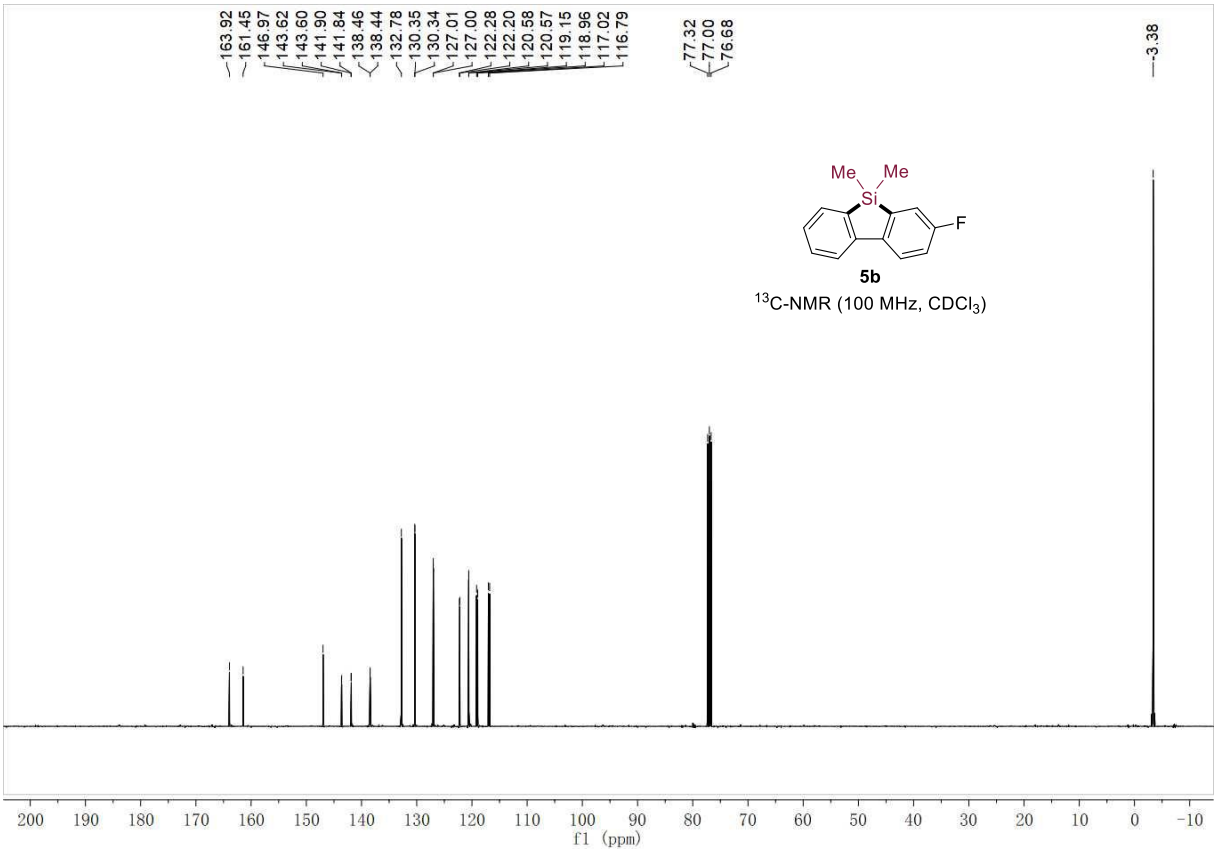


5a

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

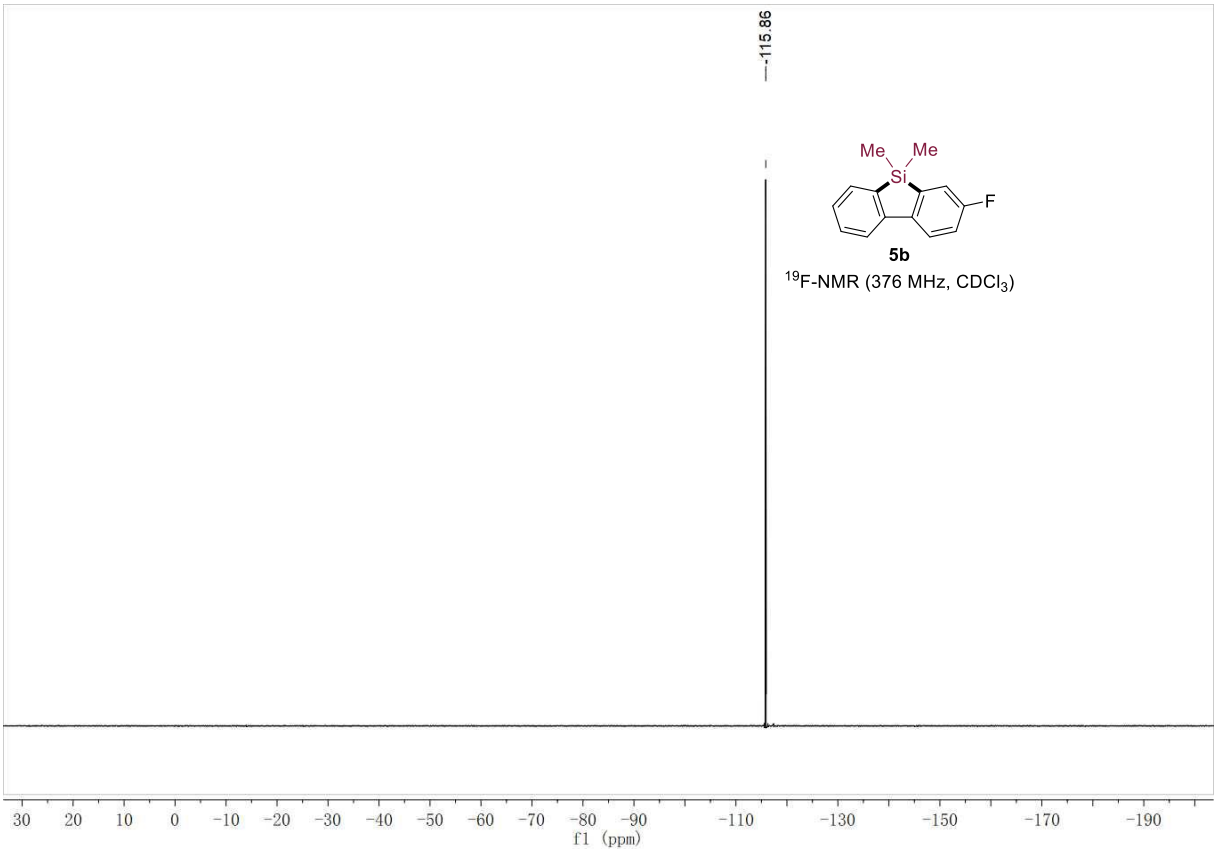

147.77
138.88
132.69
130.14
127.31
120.79
77.32
77.00
76.68
-3.28
Me
Me
Si
5a
13C-NMR (100 MHz, CDCl3)
f1 (ppm)


7.783
7.771
7.761
7.750
7.742
7.630
7.629
7.627
7.625
7.613
7.611
7.609
7.607
7.448
7.445
7.429
7.426
7.410
7.406
7.304
7.303
7.297
7.297
7.285
7.284
7.282
7.279
7.278
7.277
7.264
7.262
7.246
7.243
7.120
7.114
7.099
7.098
7.092
7.091
7.077
7.070
0.432
Me
Me
Si
F
5b
1H-NMR (400 MHz, CDCl3)
2.01
0.99
1.02
2.05
1.02
6.00
f1 (ppm)



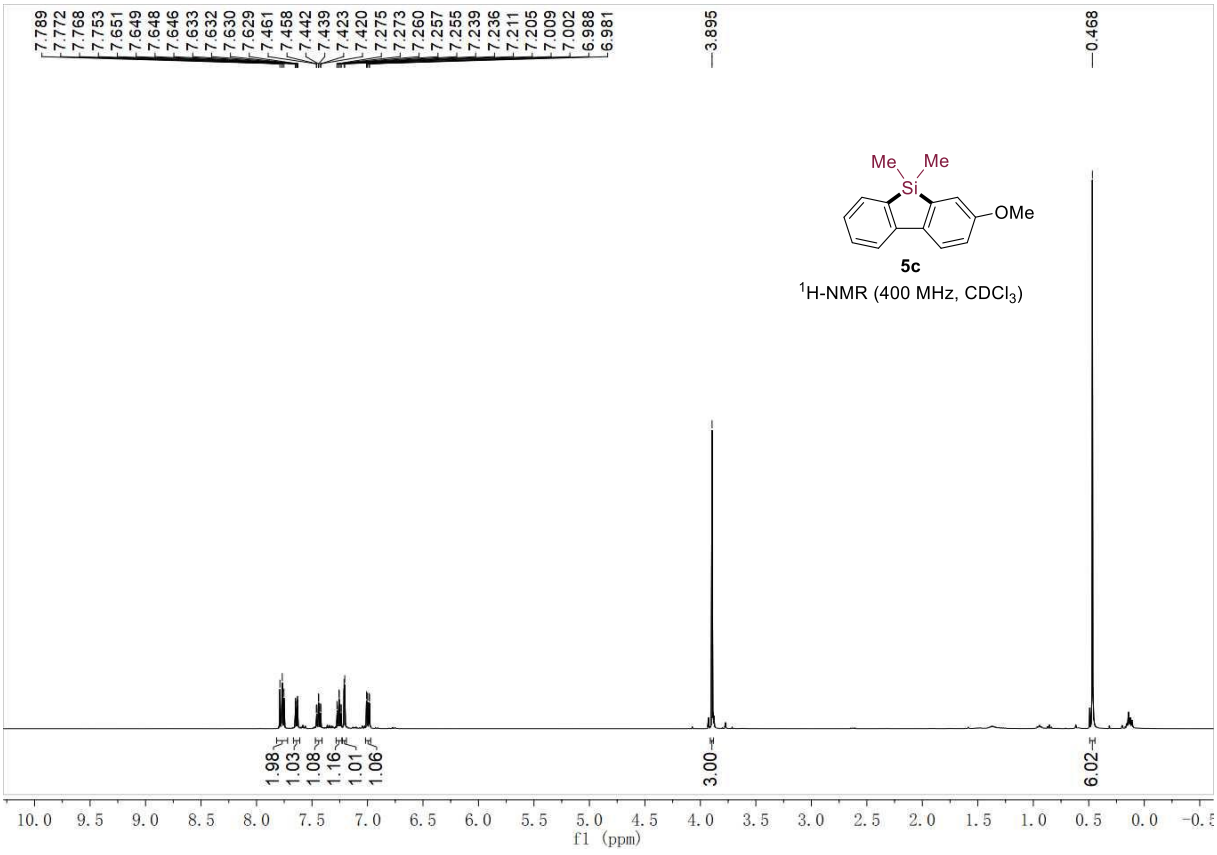
5b

^{13}C-NMR (100 MHz, $CDCl_3$)



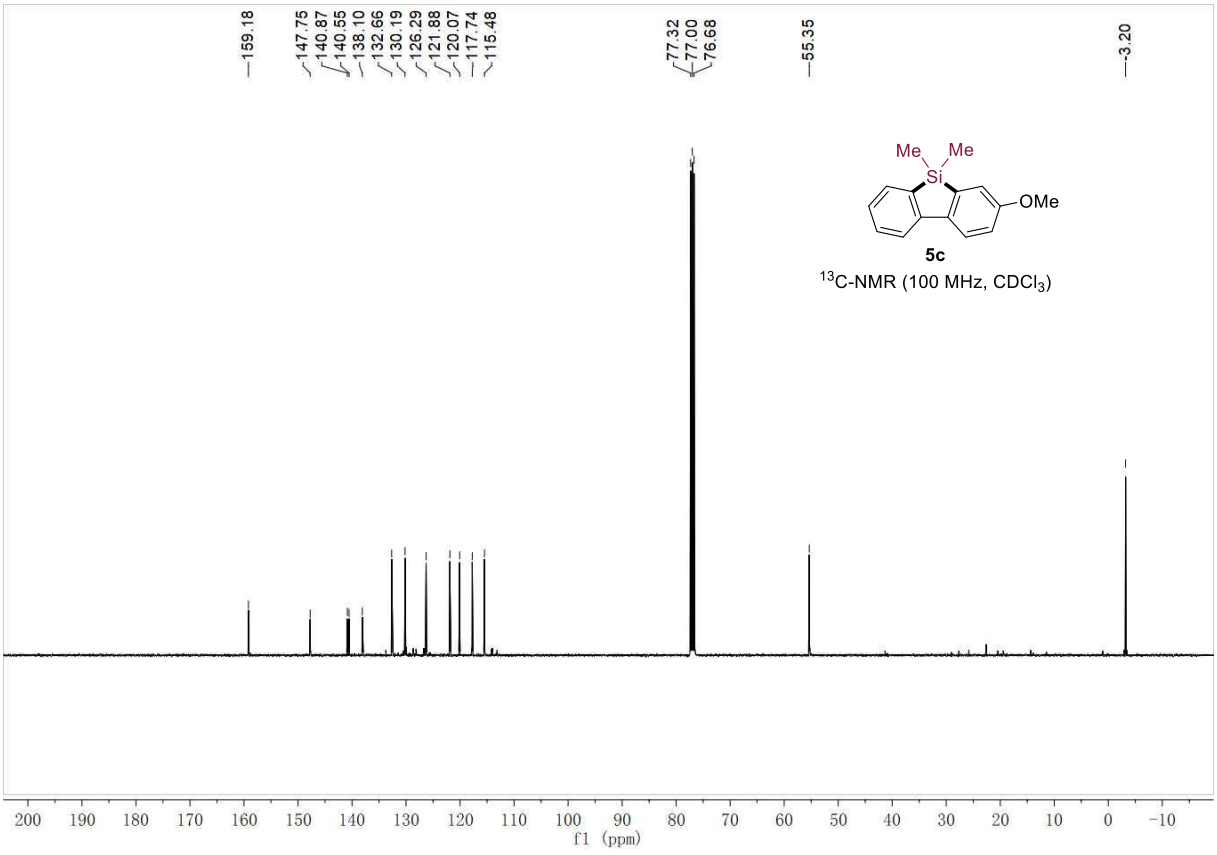
5b

^{19}F-NMR (376 MHz, $CDCl_3$)



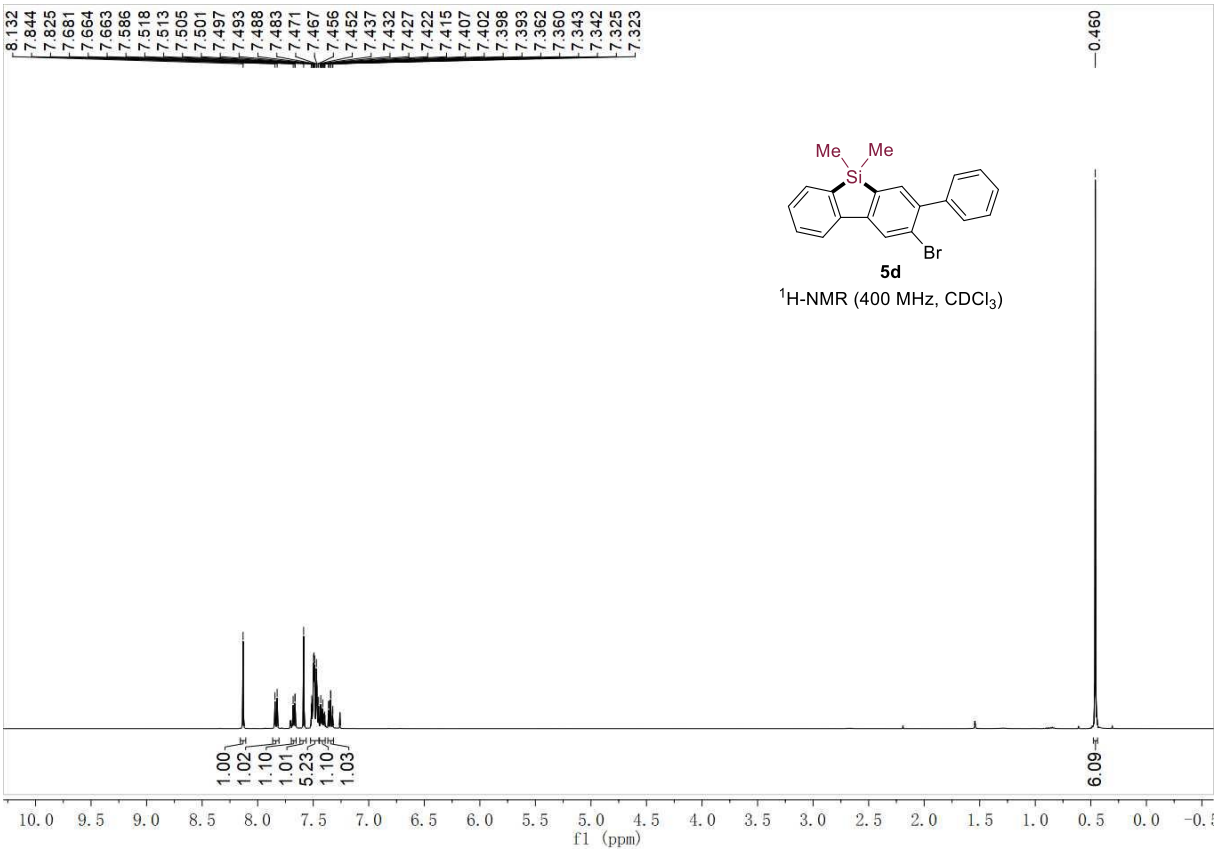
5c

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



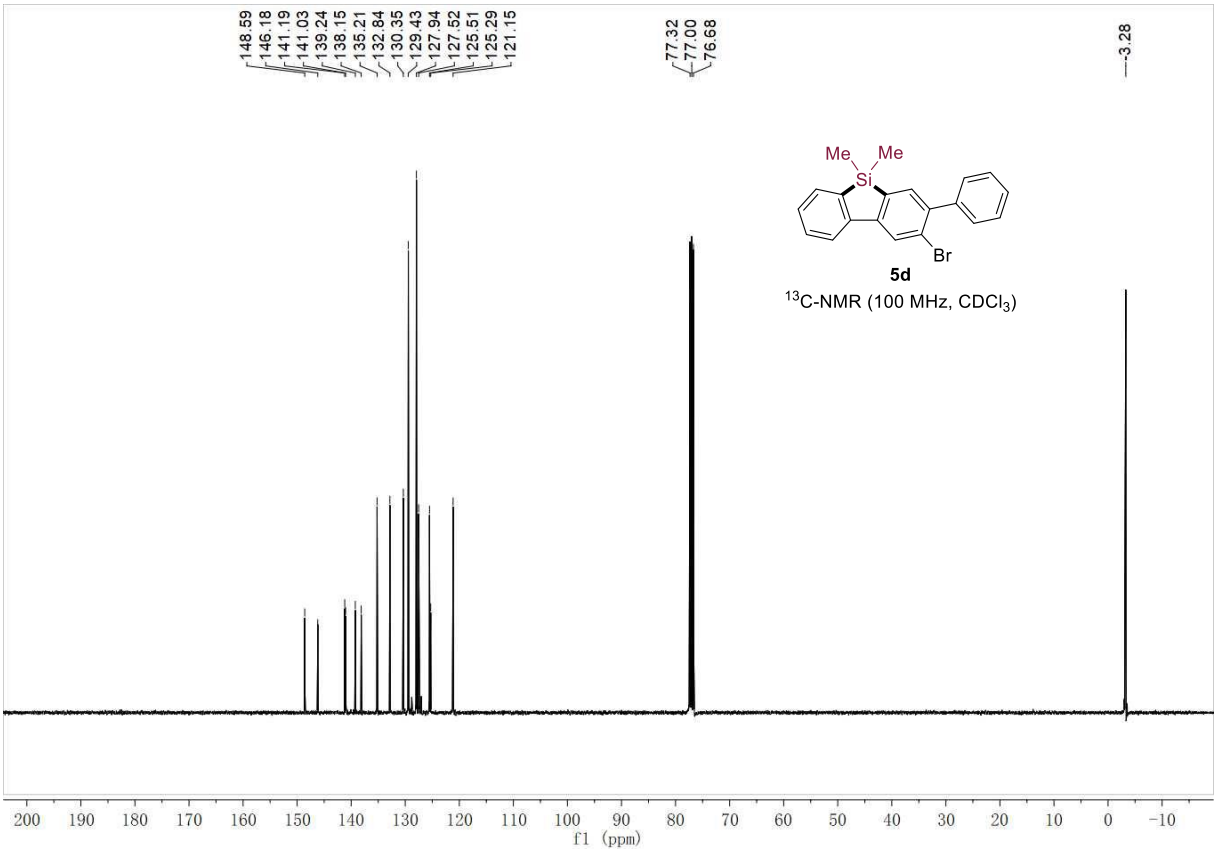
5c

^{13}C-NMR (100 MHz, $CDCl_3$)



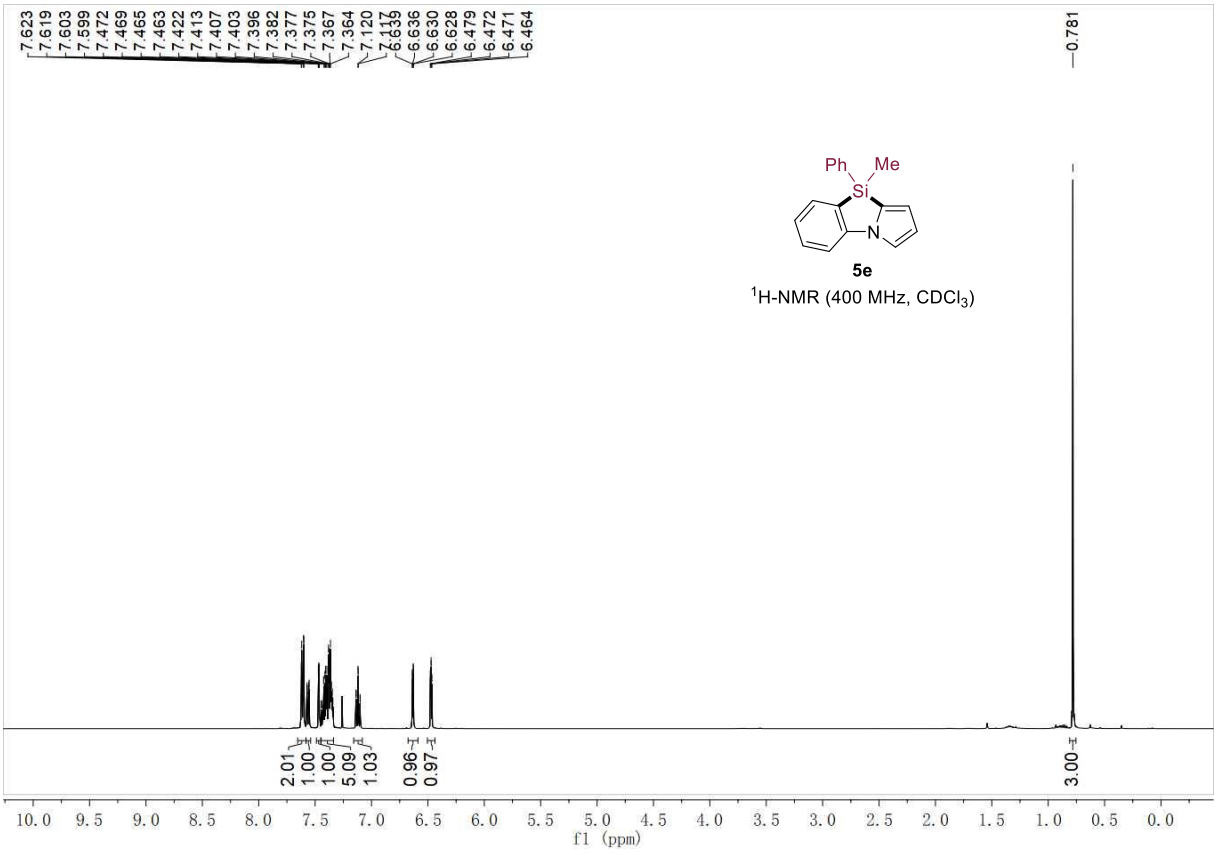
5d

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



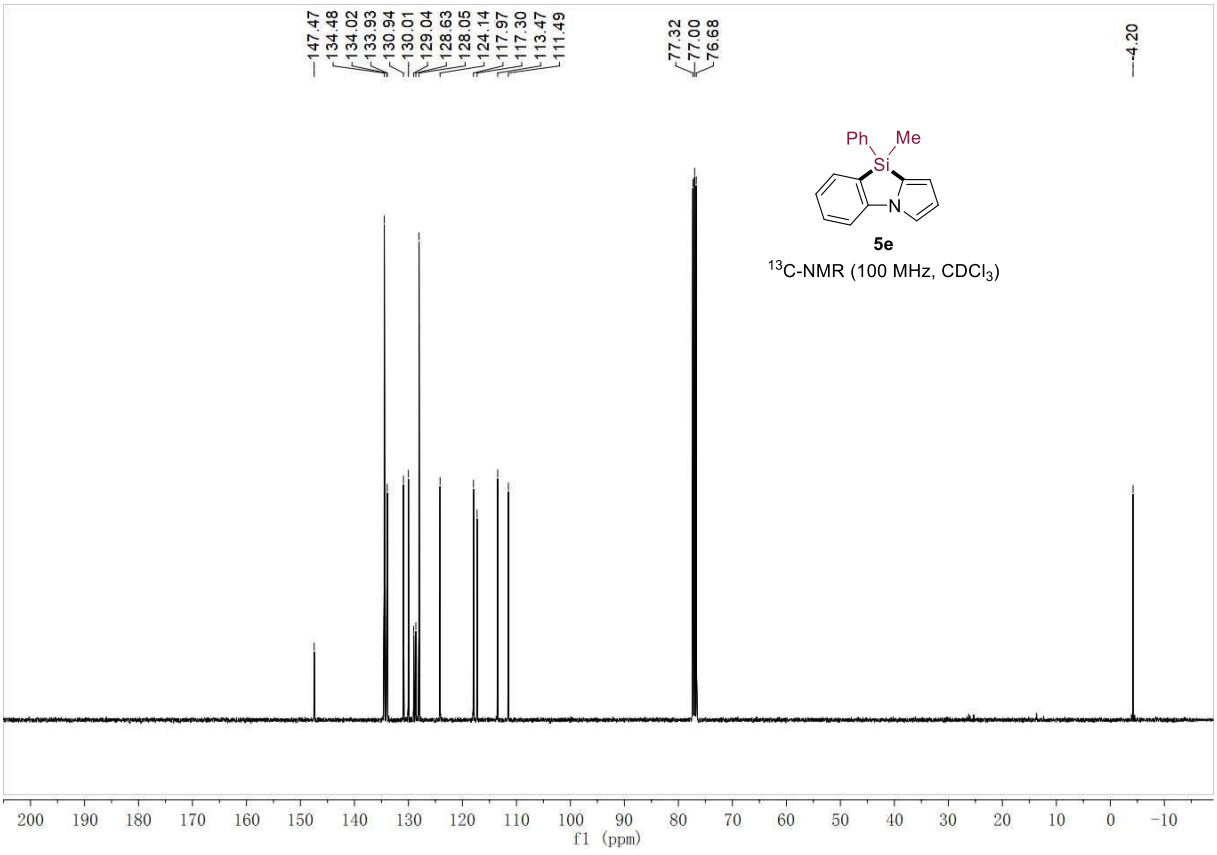
5d

^{13}C-NMR (100 MHz, $CDCl_3$)



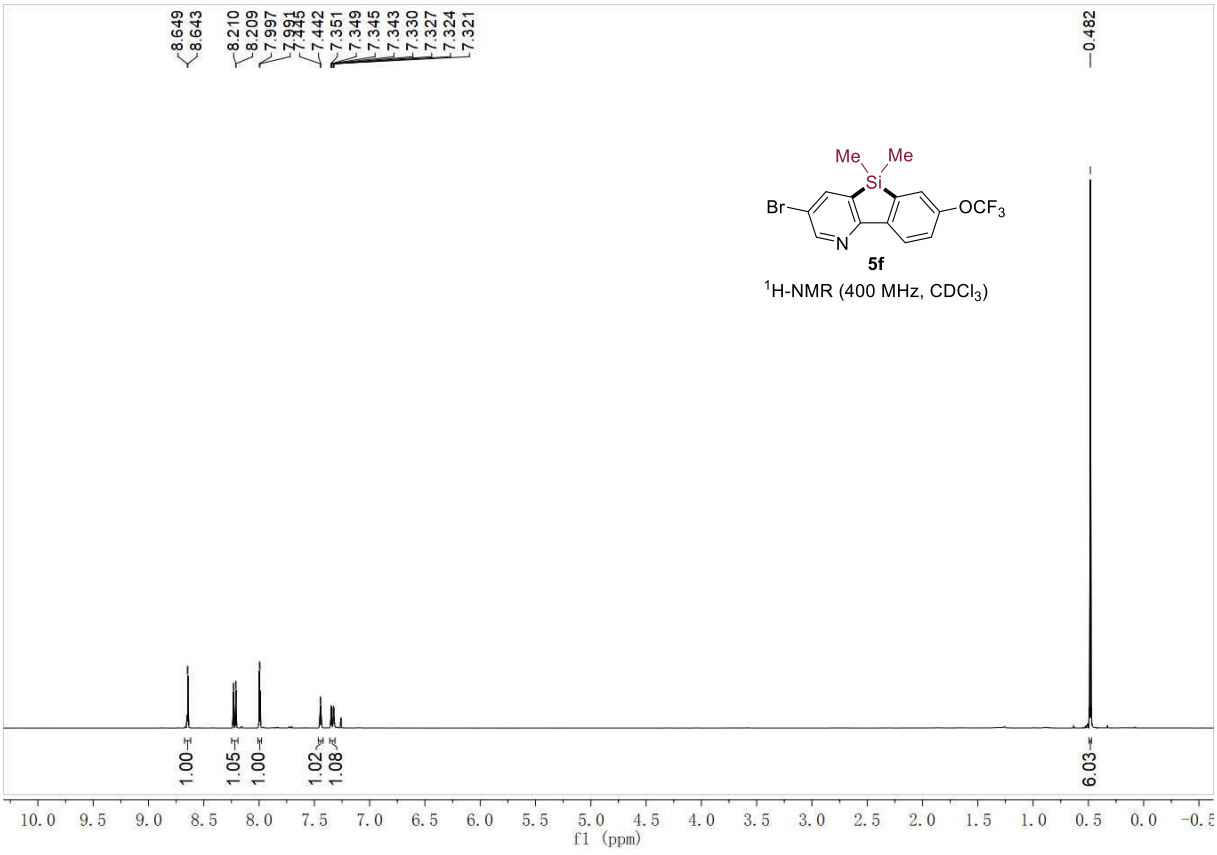
5e

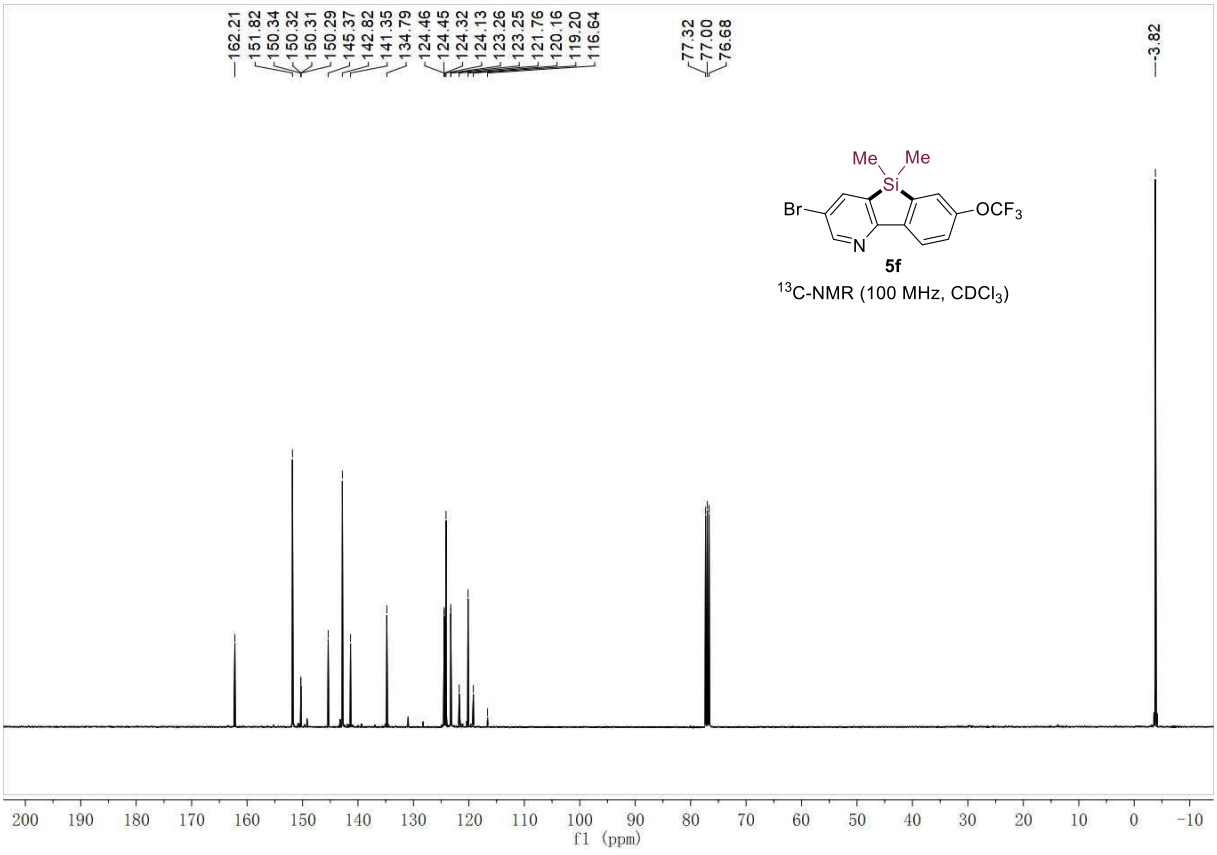
^{1}H-NMR (400 MHz, $CDCl_3$)

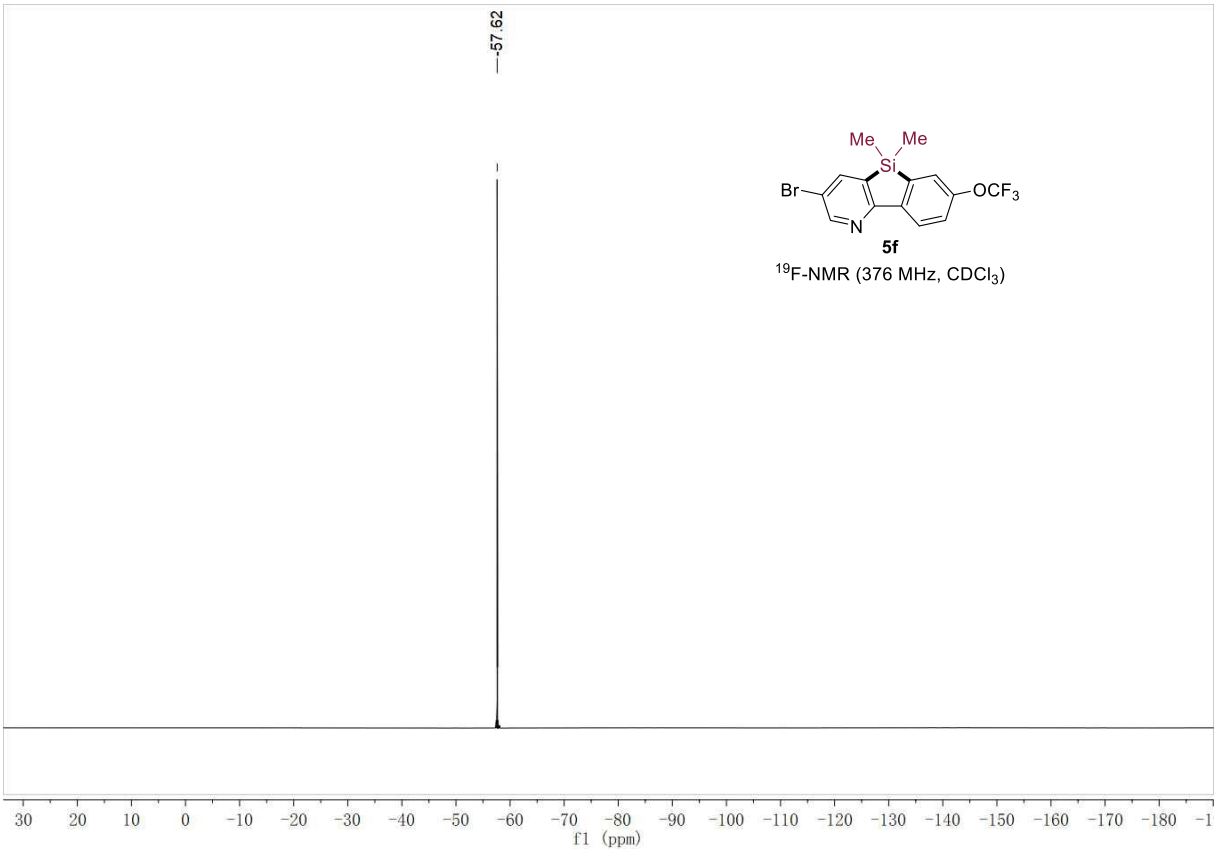


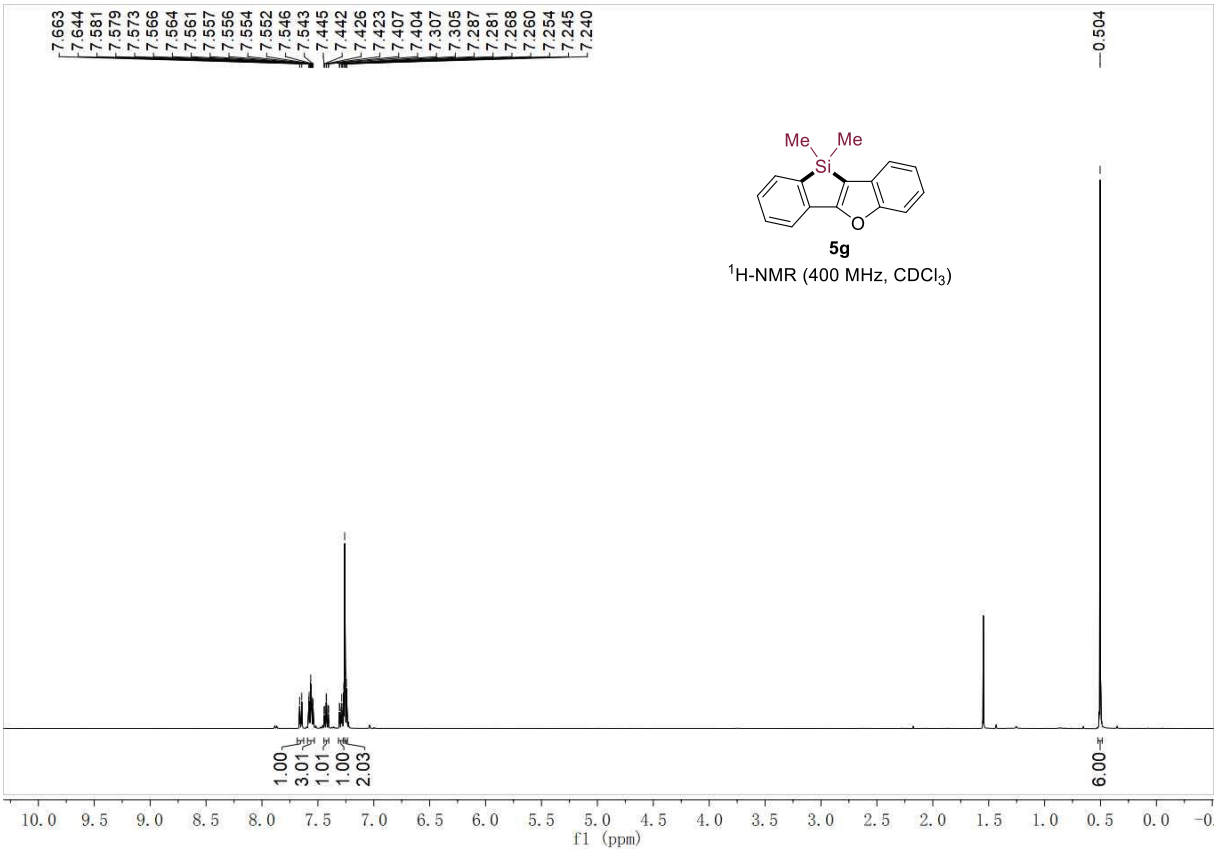
5e

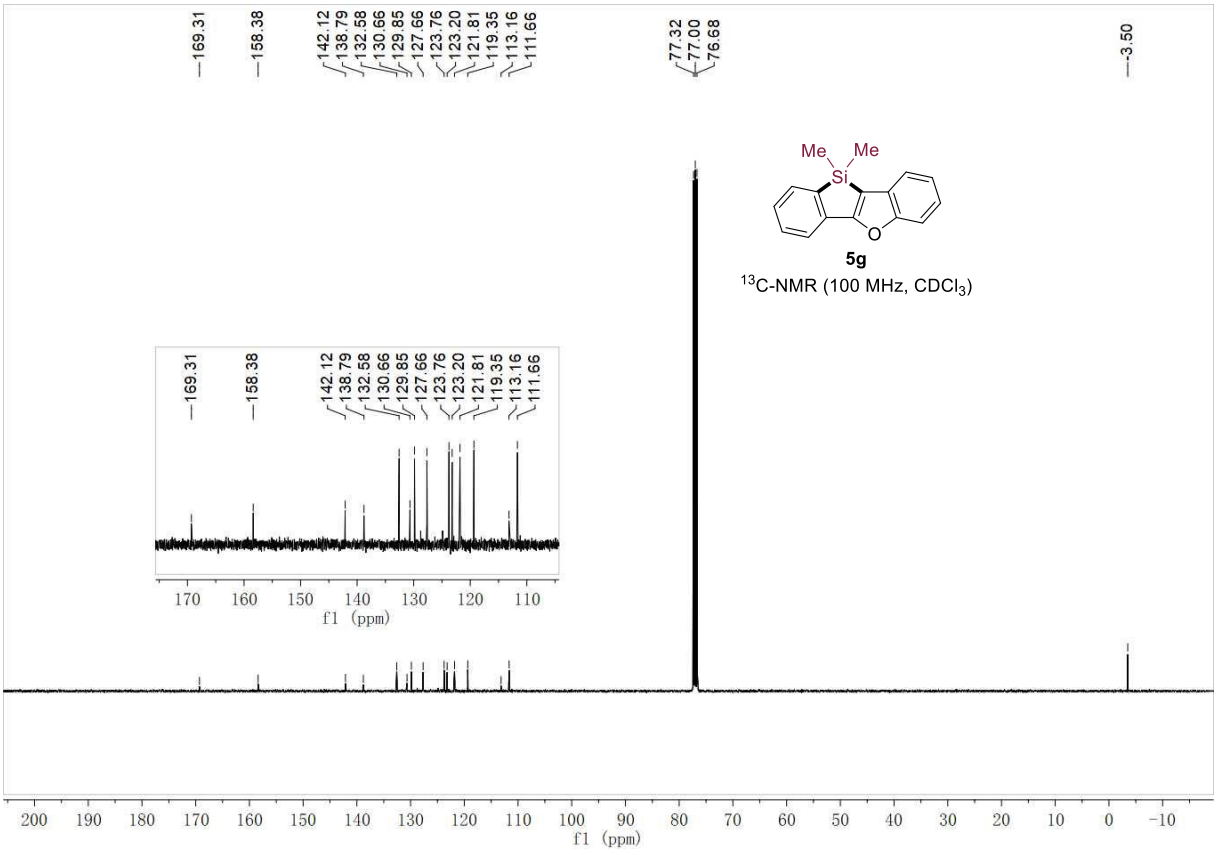
^{13}C-NMR (100 MHz, $CDCl_3$)

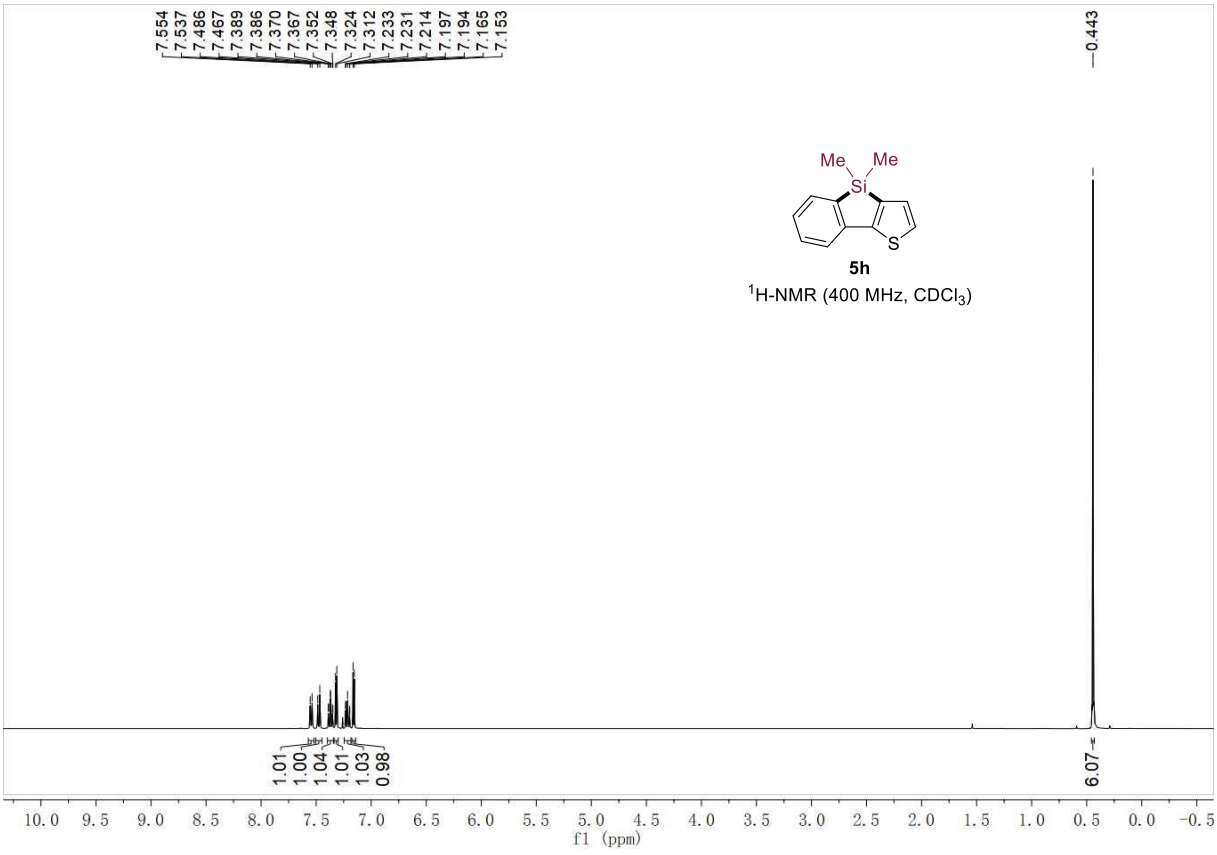

8.649
8.643
8.210
8.209
7.997
7.991
7.445
7.442
7.351
7.349
7.345
7.343
7.330
7.327
7.324
7.321
0.482
Me
Me
Si
Br
OCF3
N
5f
1H-NMR (400 MHz, CDCl3)
1.00
1.05
1.00
1.02
1.08
6.03
f1 (ppm)

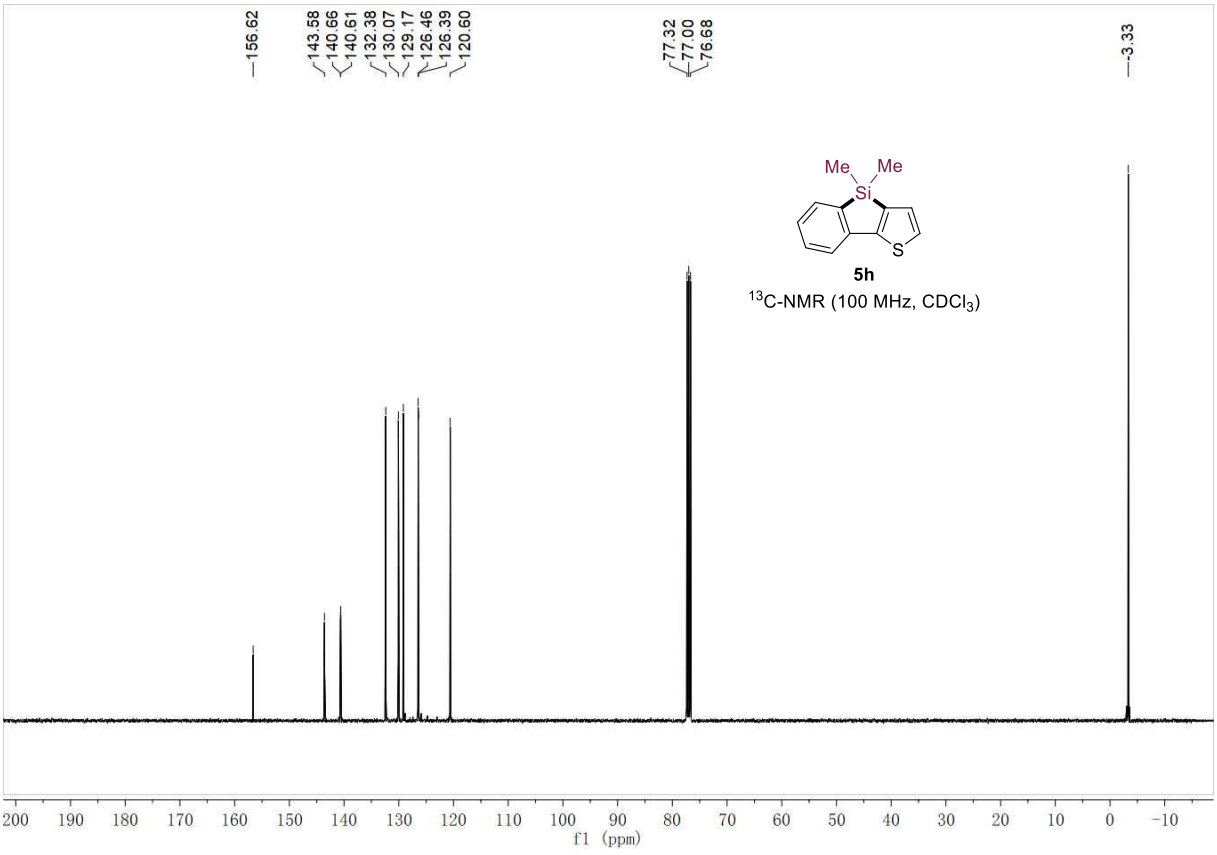

162.21
151.82
150.34
150.32
150.31
150.29
145.37
142.82
141.35
134.79
124.46
124.45
124.32
124.13
123.26
123.25
121.76
120.16
119.20
116.64
77.32
77.00
76.68
3.82
Me
Me
Si
Br
OCF3
N
5f
13C-NMR (100 MHz, CDCl3)
f1 (ppm)

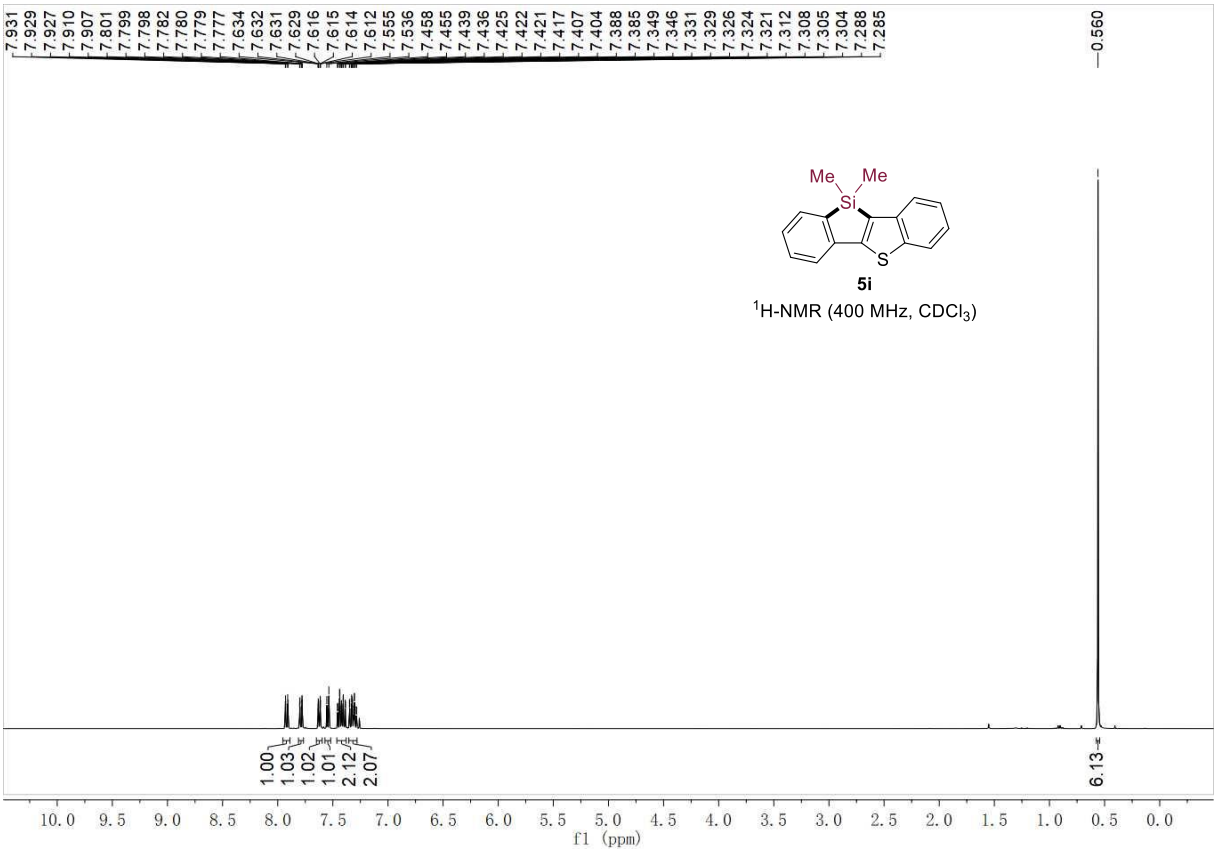

-57.62
Me
Me
Si
Br
N
OCF3
5f
19F-NMR (376 MHz, CDCl3)
f1 (ppm)

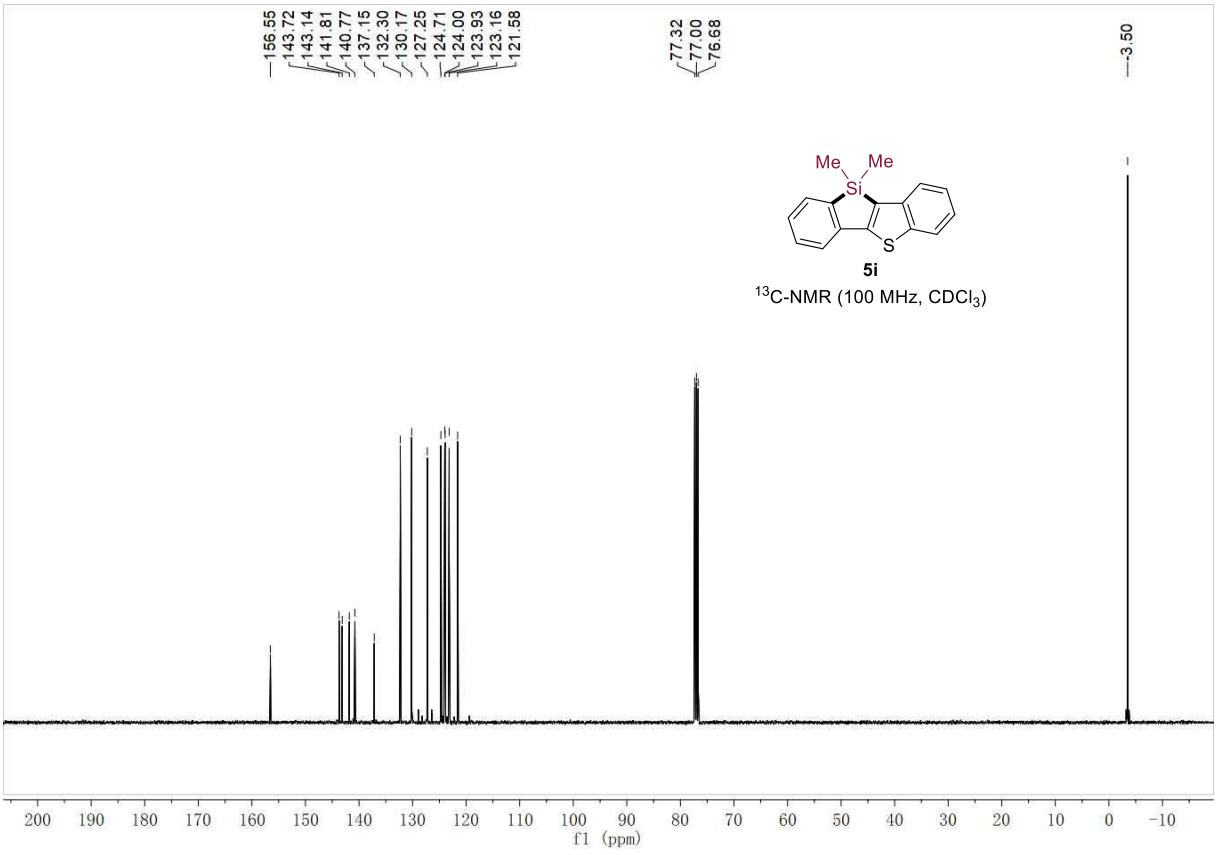

7.663
7.644
7.581
7.579
7.573
7.566
7.564
7.561
7.557
7.556
7.554
7.552
7.546
7.543
7.445
7.442
7.426
7.423
7.407
7.404
7.307
7.305
7.287
7.281
7.268
7.260
7.254
7.245
7.240
0.504
Me
Me
Si
O
5g
1H-NMR (400 MHz, CDCl3)
1.00
3.01
1.01
1.00
2.03
6.00
f1 (ppm)


169.31
158.38
142.12
138.79
132.58
130.66
129.85
127.66
123.76
123.20
121.81
119.35
113.16
111.66
77.32
77.00
76.68
3.50
Me
Me
Si
O
5g
13C-NMR (100 MHz, CDCl3)
f1 (ppm)


7.554
7.537
7.486
7.467
7.389
7.386
7.370
7.367
7.352
7.348
7.324
7.312
7.233
7.231
7.214
7.197
7.194
7.165
7.153
0.443
Me
Me
Si
S
5h
1H-NMR (400 MHz, CDCl3)
1.01
1.00
1.04
1.01
1.03
0.98
6.07
f1 (ppm)

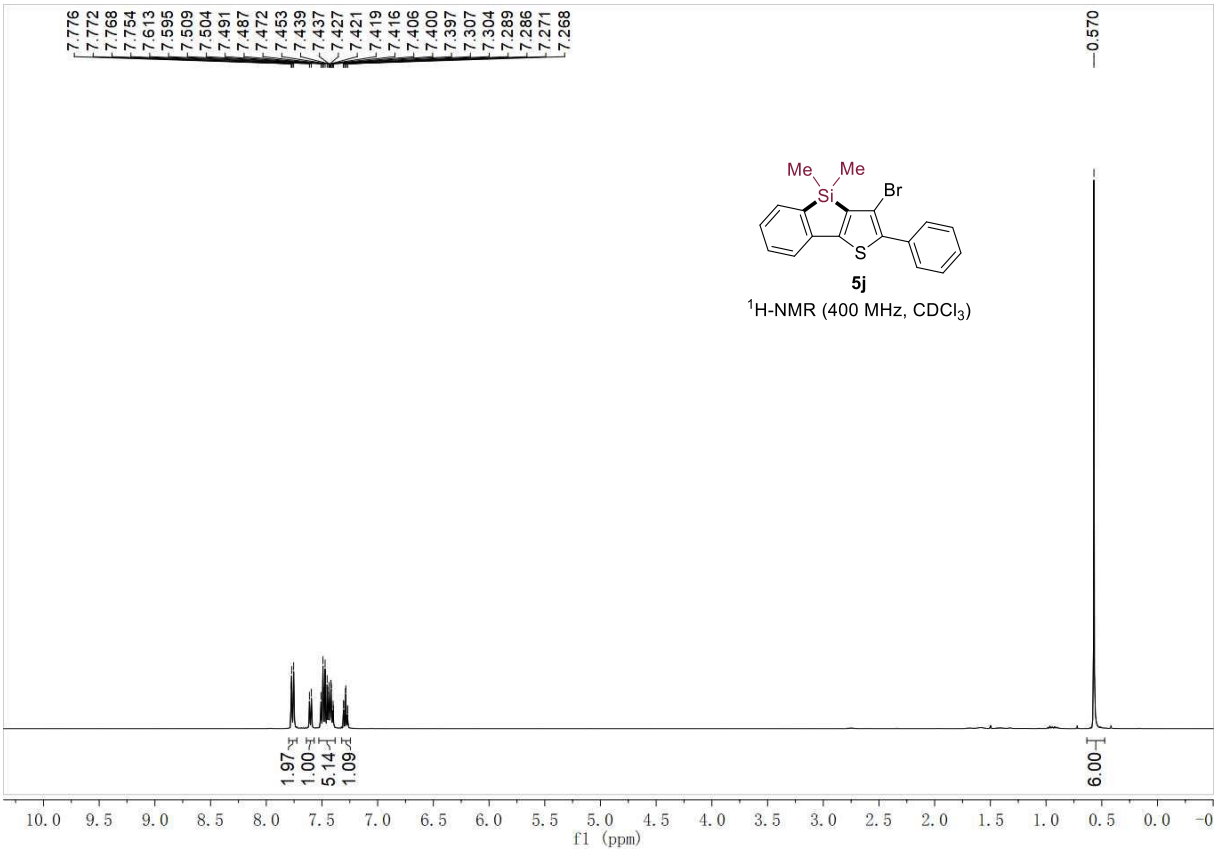

156.62
143.58
140.66
140.61
132.38
130.07
129.17
126.46
126.39
120.60
77.32
77.00
76.68
-3.33
Me
Me
Si
S
5h
^{13}C-NMR (100 MHz, $CDCl_3$)
f1 (ppm)


7.931
7.929
7.927
7.910
7.907
7.801
7.799
7.798
7.782
7.780
7.779
7.777
7.634
7.632
7.631
7.629
7.616
7.615
7.614
7.612
7.555
7.536
7.458
7.455
7.439
7.436
7.425
7.422
7.421
7.417
7.407
7.404
7.388
7.385
7.349
7.346
7.331
7.329
7.326
7.324
7.321
7.312
7.308
7.305
7.304
7.288
7.285
0.560
Me
Me
Si
S
5i
^{1}H-NMR (400 MHz, $CDCl_3$)
1.00
1.03
1.02
1.01
2.12
2.07
6.13
f1 (ppm)



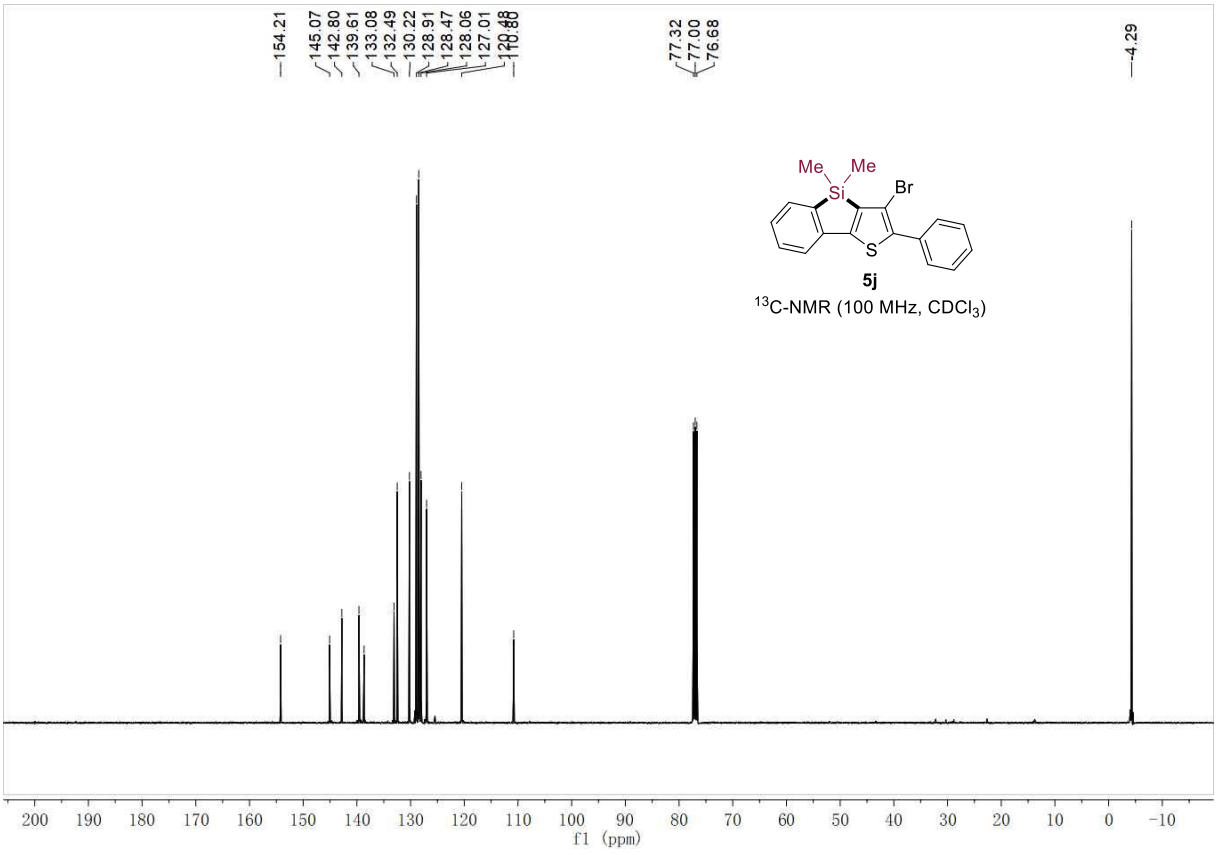
5i

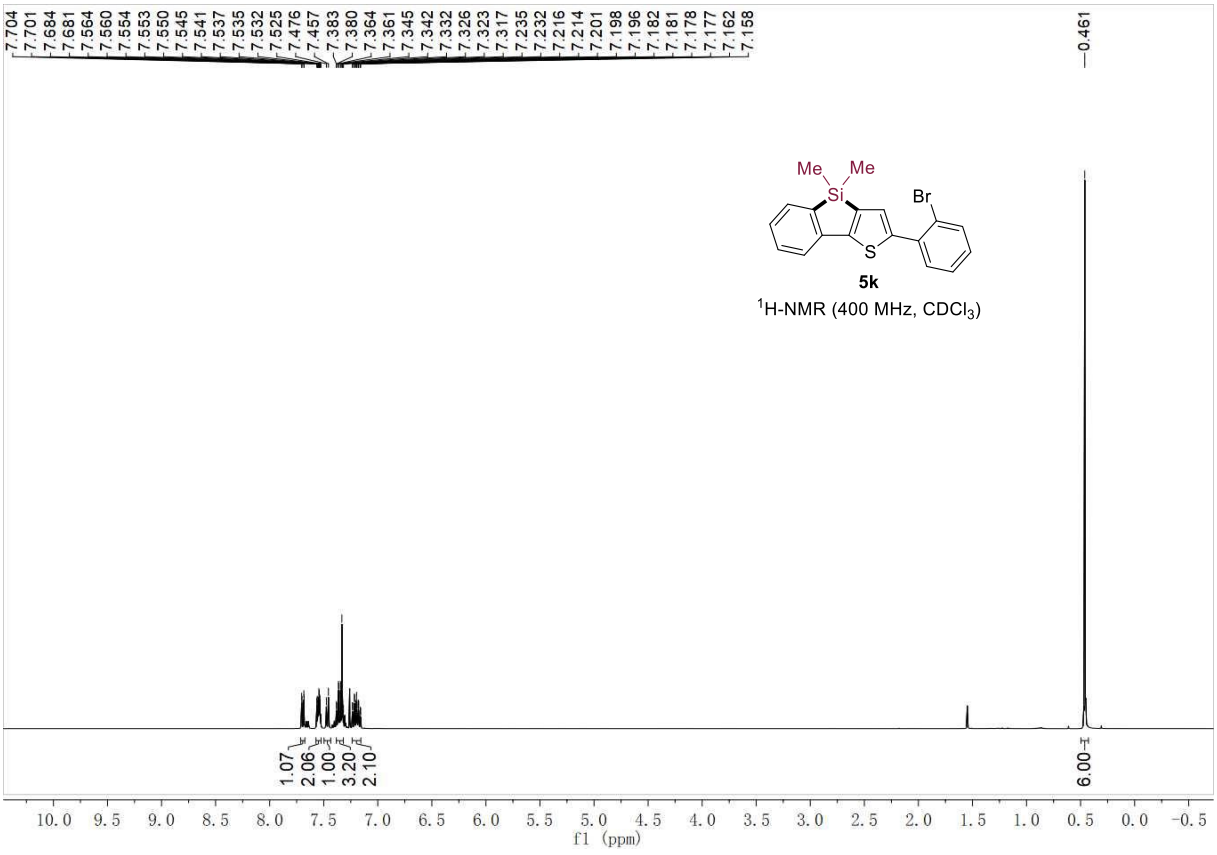
^{13}C-NMR (100 MHz, $CDCl_3$)

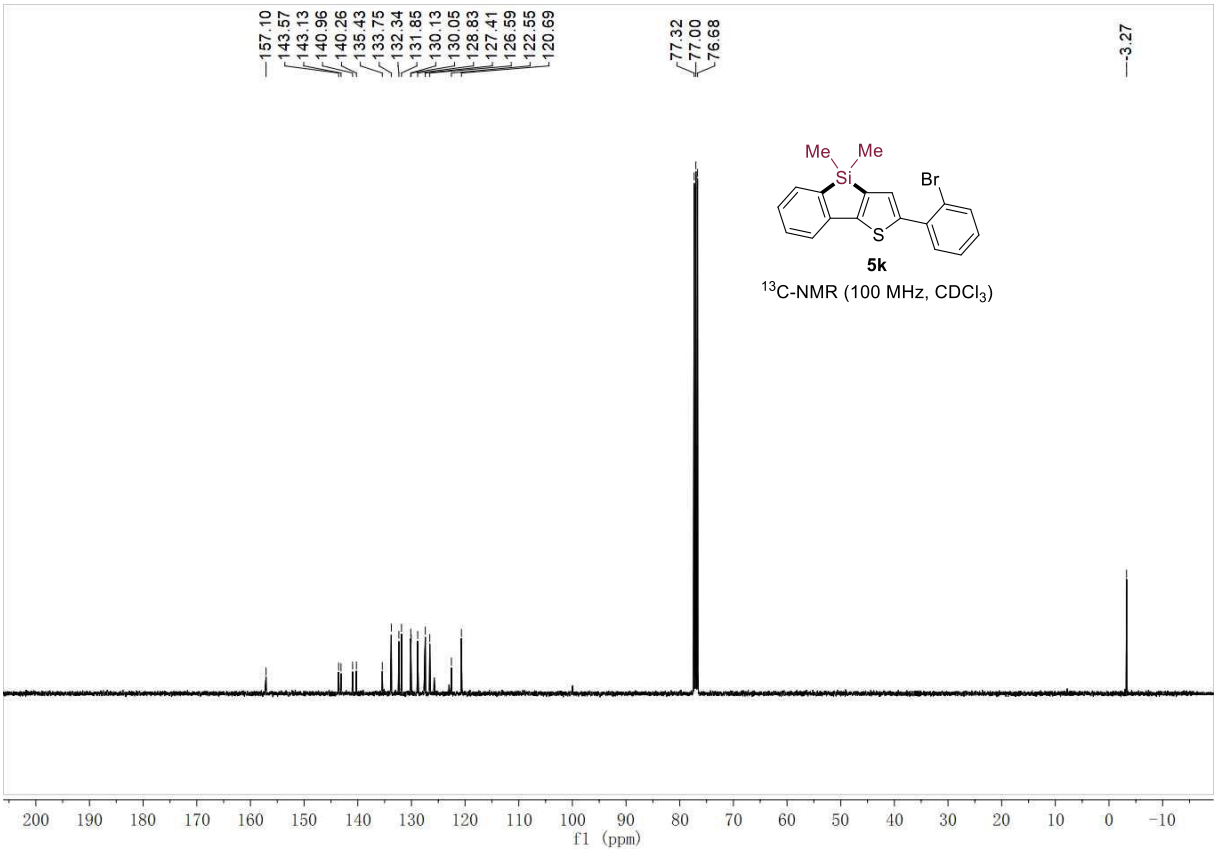


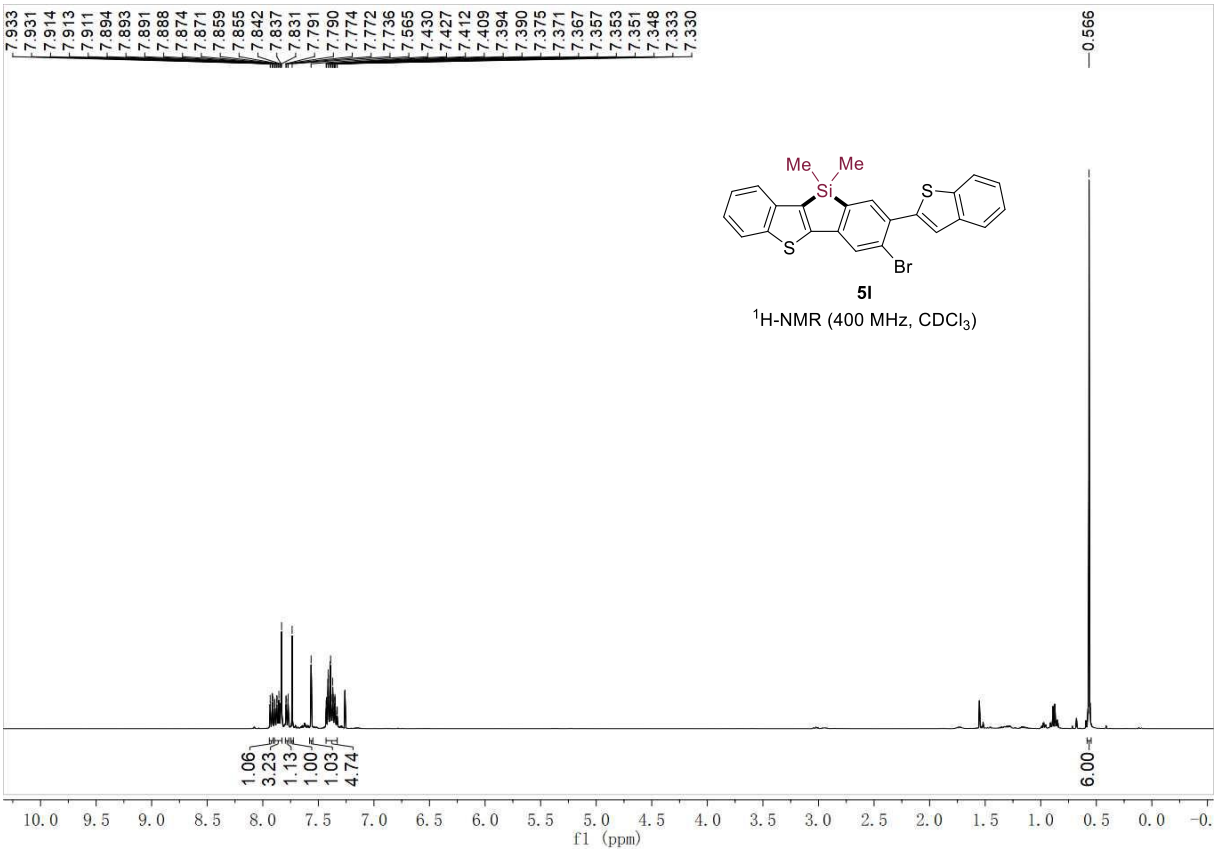
5j

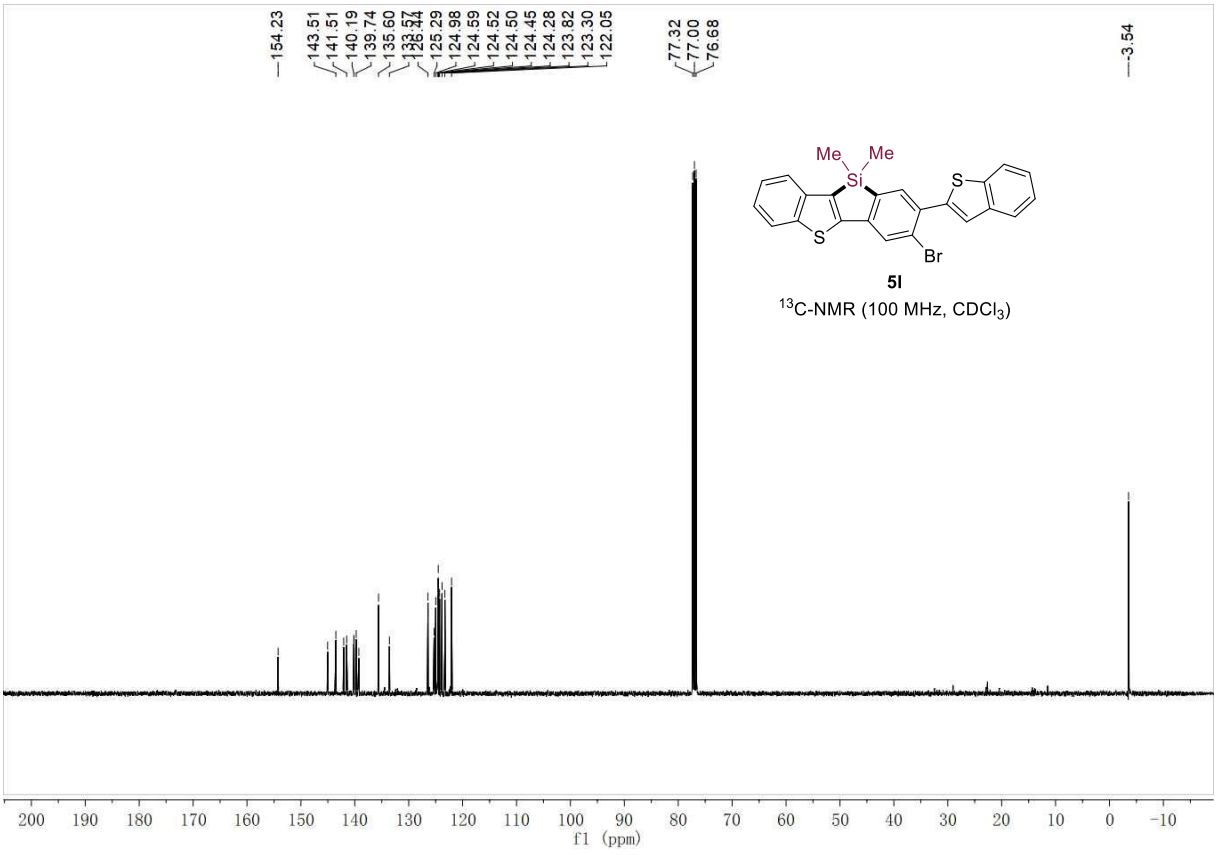
^{1}H-NMR (400 MHz, $CDCl_3$)


154.21
145.07
142.80
139.61
133.08
132.49
130.22
128.91
128.47
128.06
127.01
77.32
77.00
76.68
4.29
Me
Me
Si
Br
S
5j
13C-NMR (100 MHz, CDCl3)
f1 (ppm)


7.704
7.701
7.684
7.681
7.564
7.560
7.554
7.553
7.550
7.545
7.541
7.537
7.535
7.532
7.525
7.476
7.457
7.383
7.380
7.364
7.361
7.345
7.342
7.332
7.326
7.323
7.317
7.235
7.232
7.216
7.214
7.201
7.198
7.196
7.182
7.181
7.178
7.177
7.162
7.158
0.461
Me
Me
Si
Br
S
5k
1H-NMR (400 MHz, CDCl3)
1.07
2.06
1.00
3.20
2.10
6.00
f1 (ppm)

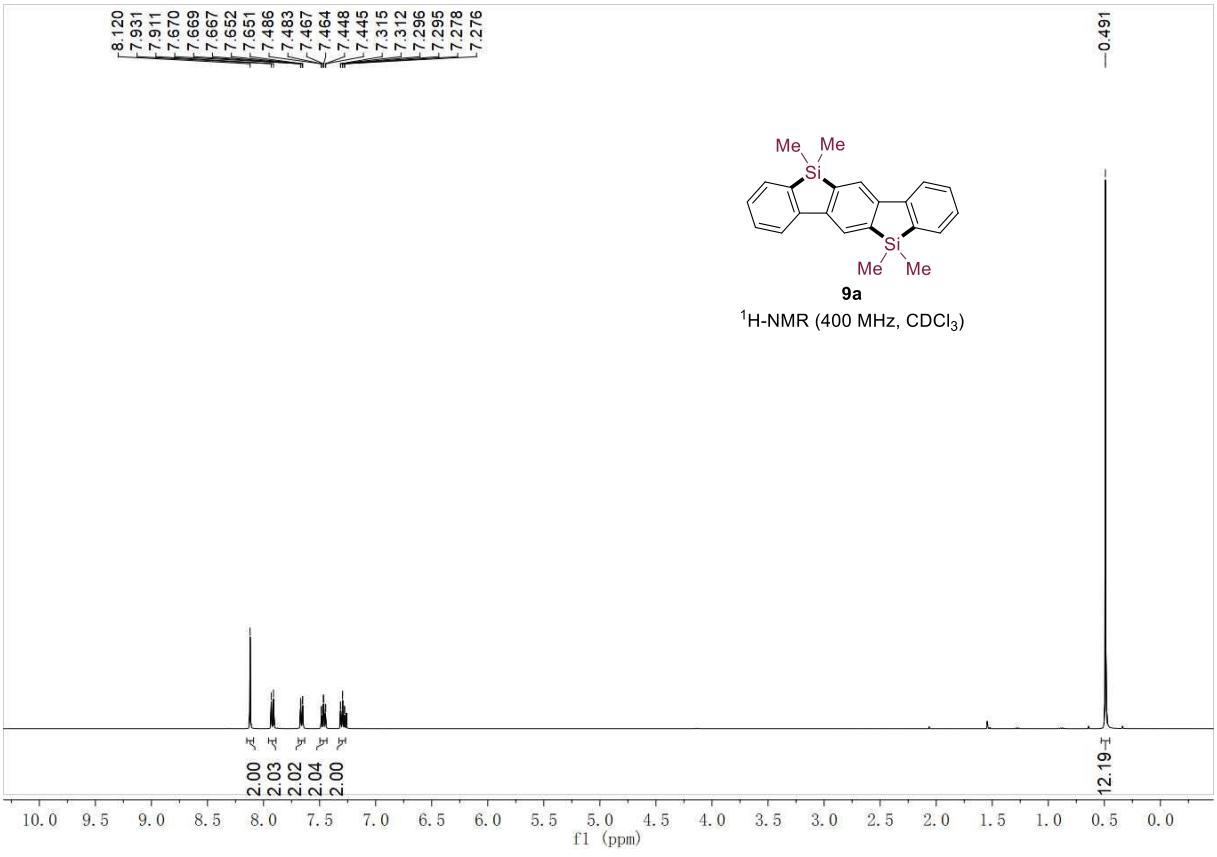

157.10
143.57
143.13
140.96
140.26
135.43
133.75
132.34
131.85
130.13
130.05
128.83
127.41
126.59
122.55
120.69
77.32
77.00
76.68
3.27
Me
Me
Si
Br
S
5k
^{13}C-NMR (100 MHz, $CDCl_3$)
f1 (ppm)


7.933
7.931
7.914
7.913
7.911
7.894
7.893
7.891
7.888
7.874
7.871
7.859
7.855
7.842
7.837
7.831
7.791
7.790
7.774
7.772
7.736
7.565
7.430
7.427
7.412
7.409
7.394
7.390
7.375
7.371
7.367
7.357
7.353
7.351
7.348
7.333
7.330
0.566
Me
Me
Si
S
S
Br
5l
^{1}H-NMR (400 MHz, $CDCl_3$)
1.06
3.23
1.13
1.00
1.03
4.74
6.00
f1 (ppm)



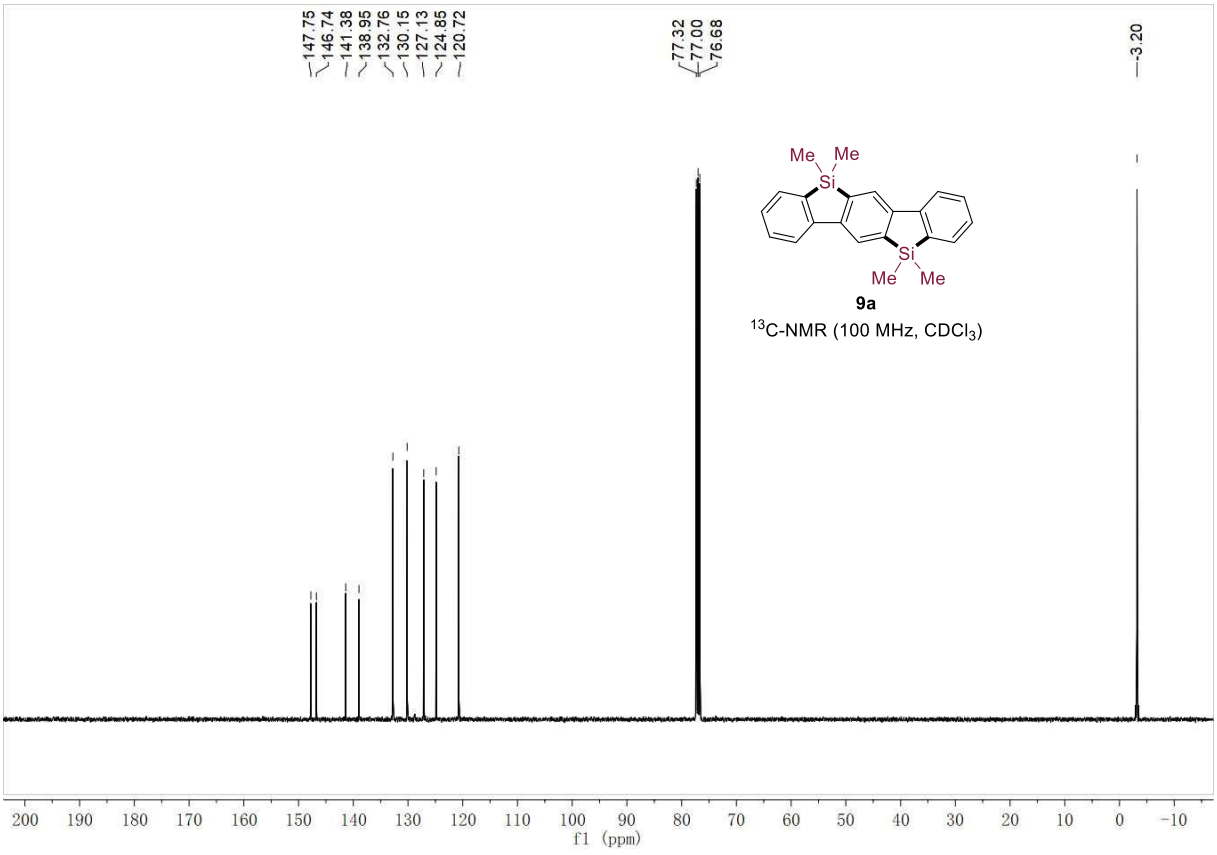
5l

^{13}C-NMR (100 MHz, $CDCl_3$)



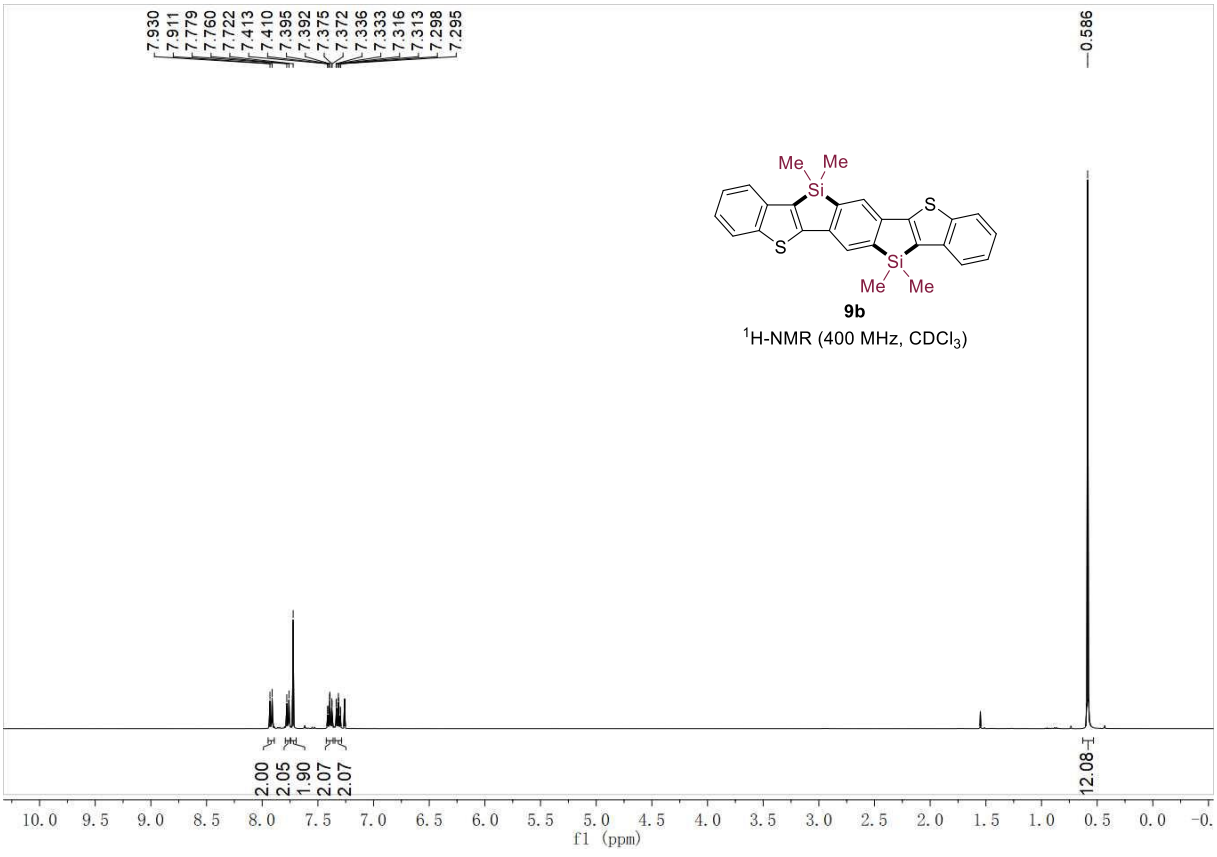
9a

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



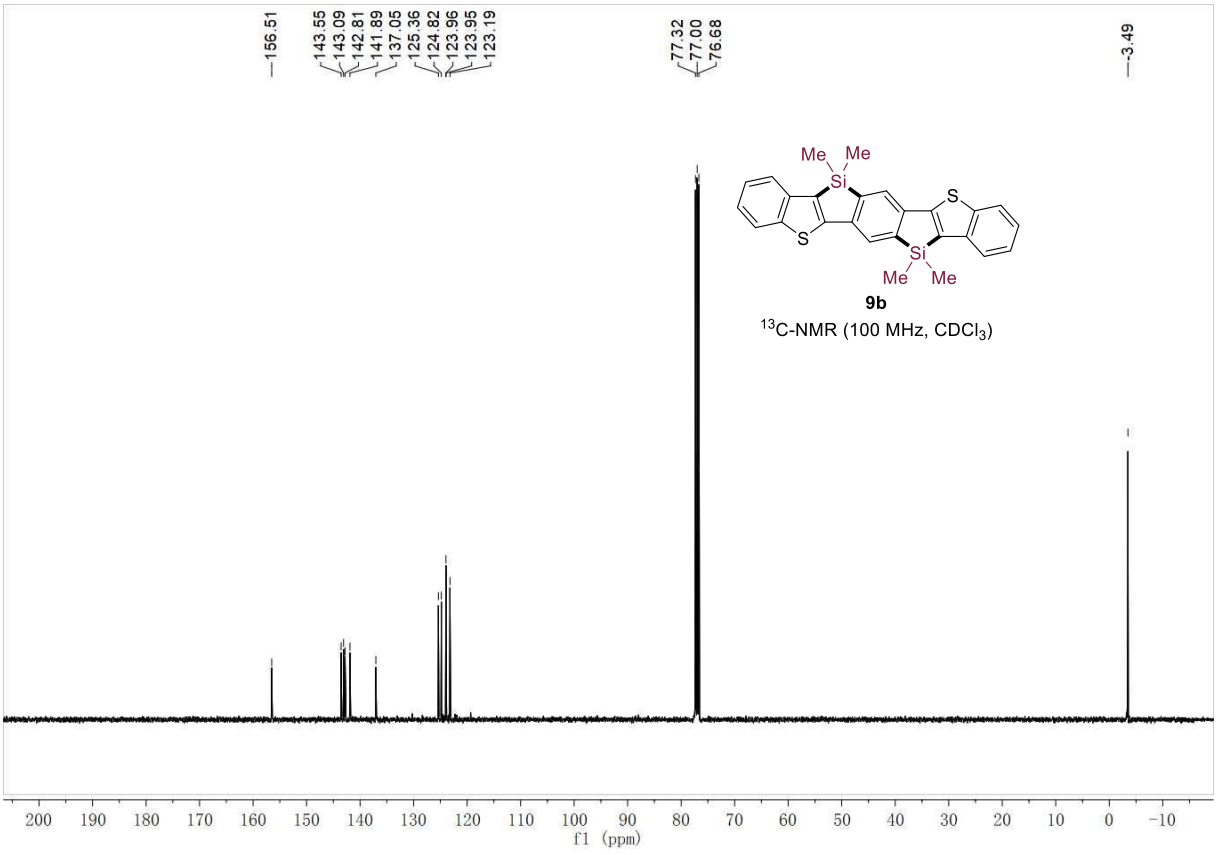
9a

^{13}C-NMR (100 MHz, $CDCl_3$)



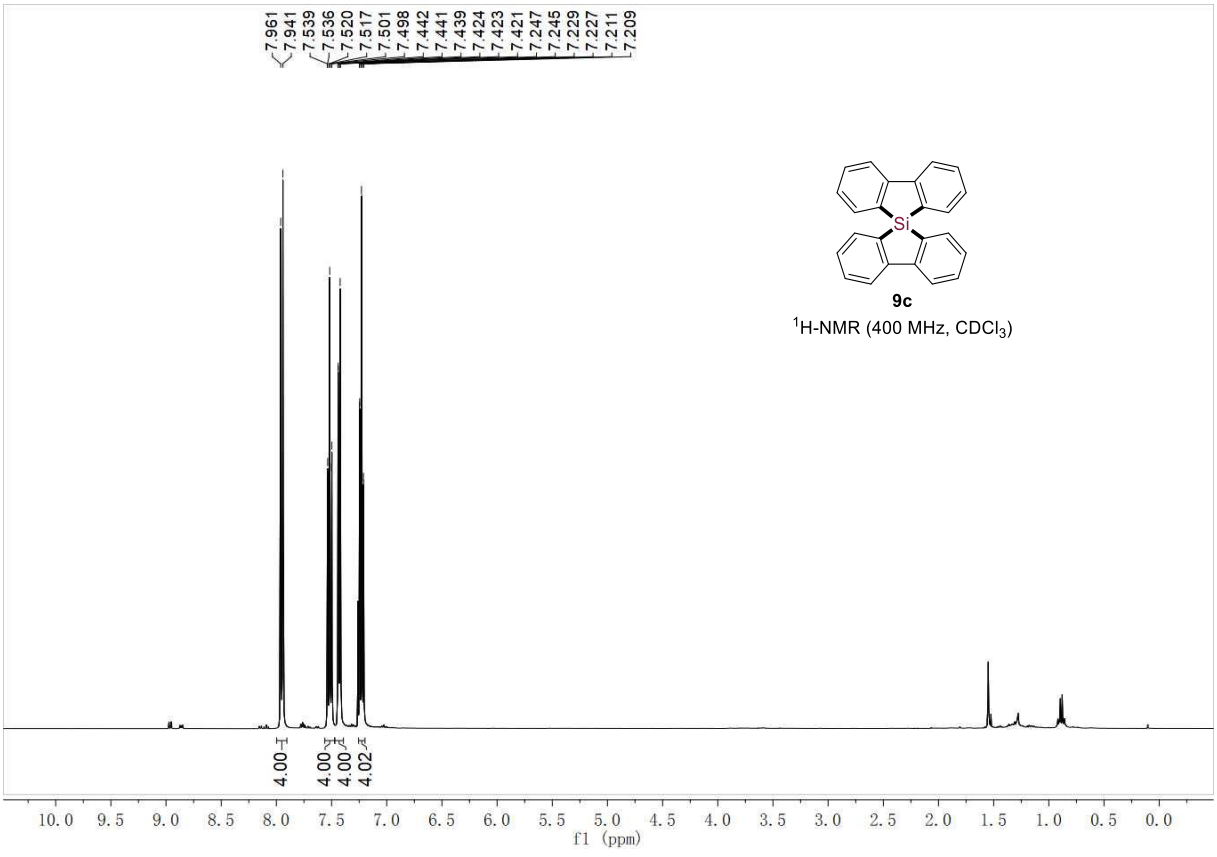
9b

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



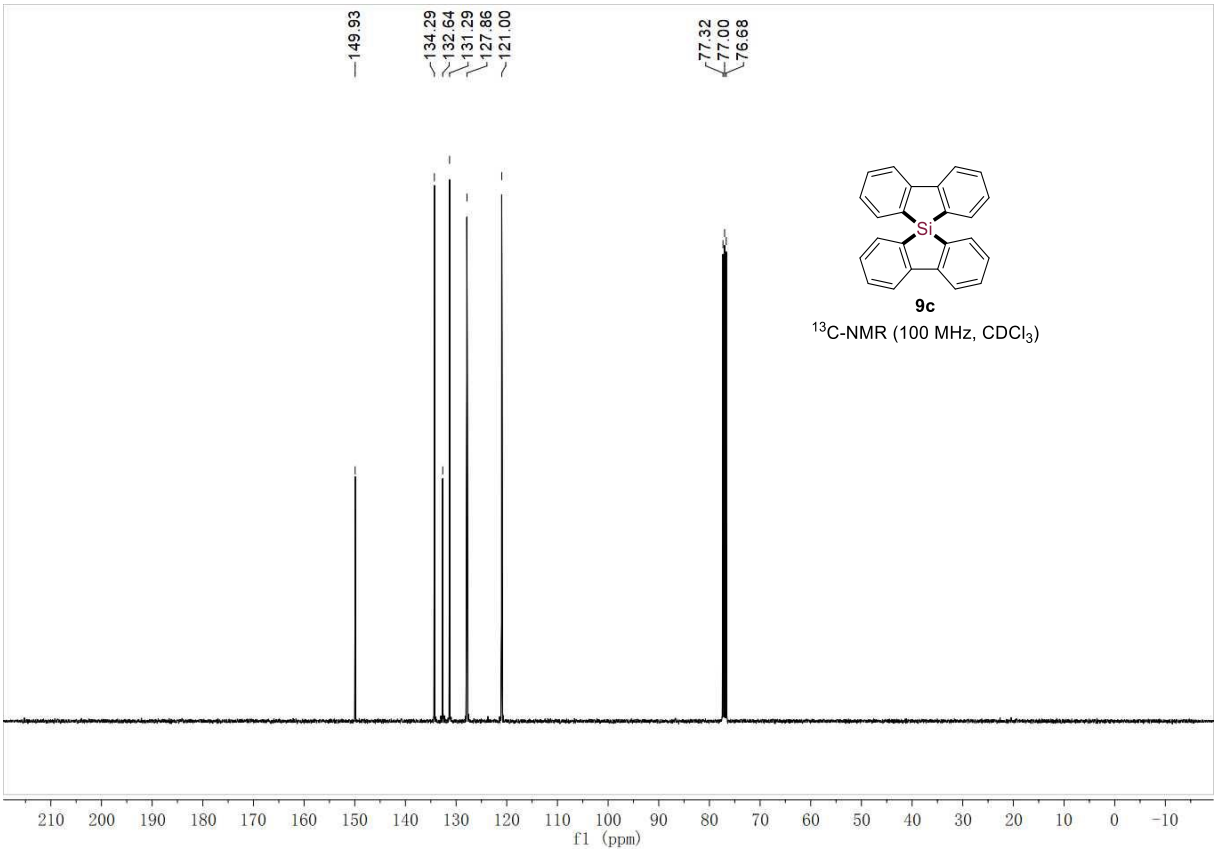
9b

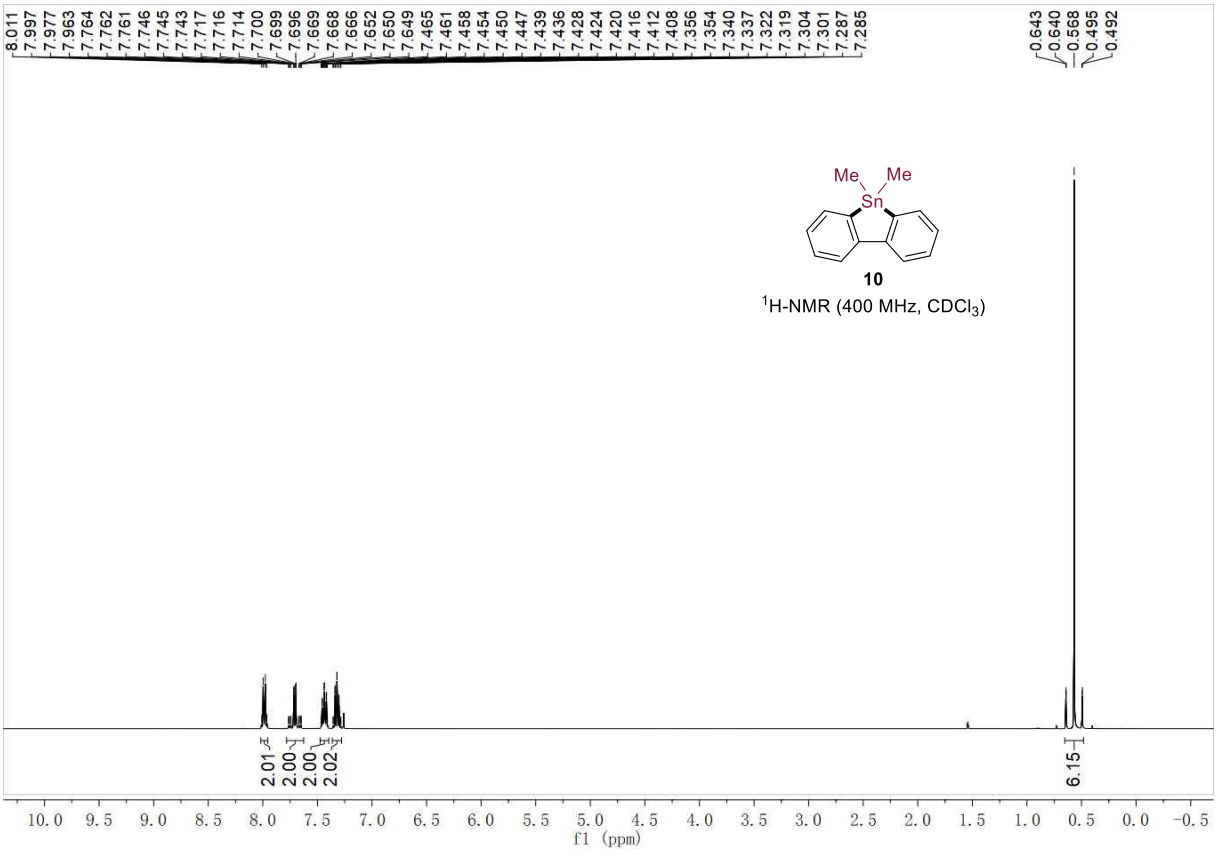
^{13}C-NMR (100 MHz, $CDCl_3$)

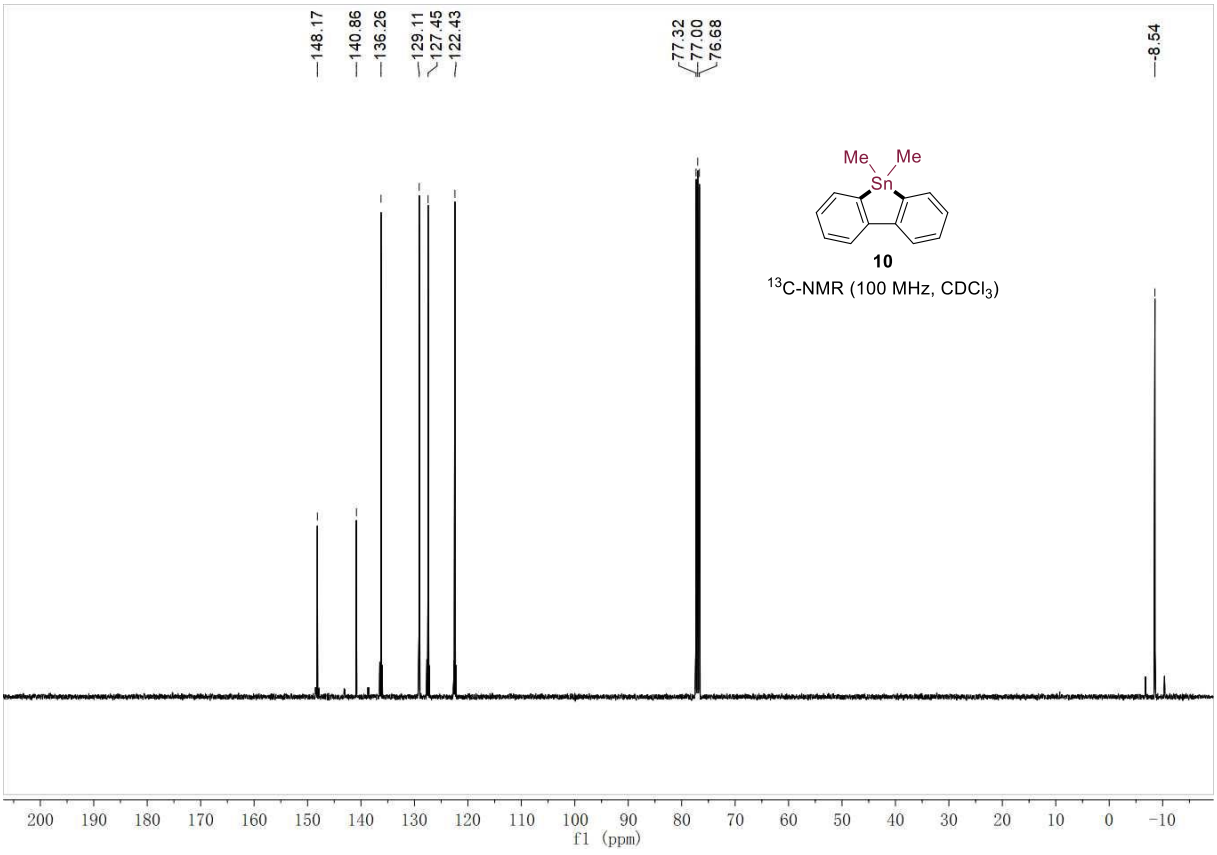


9c

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

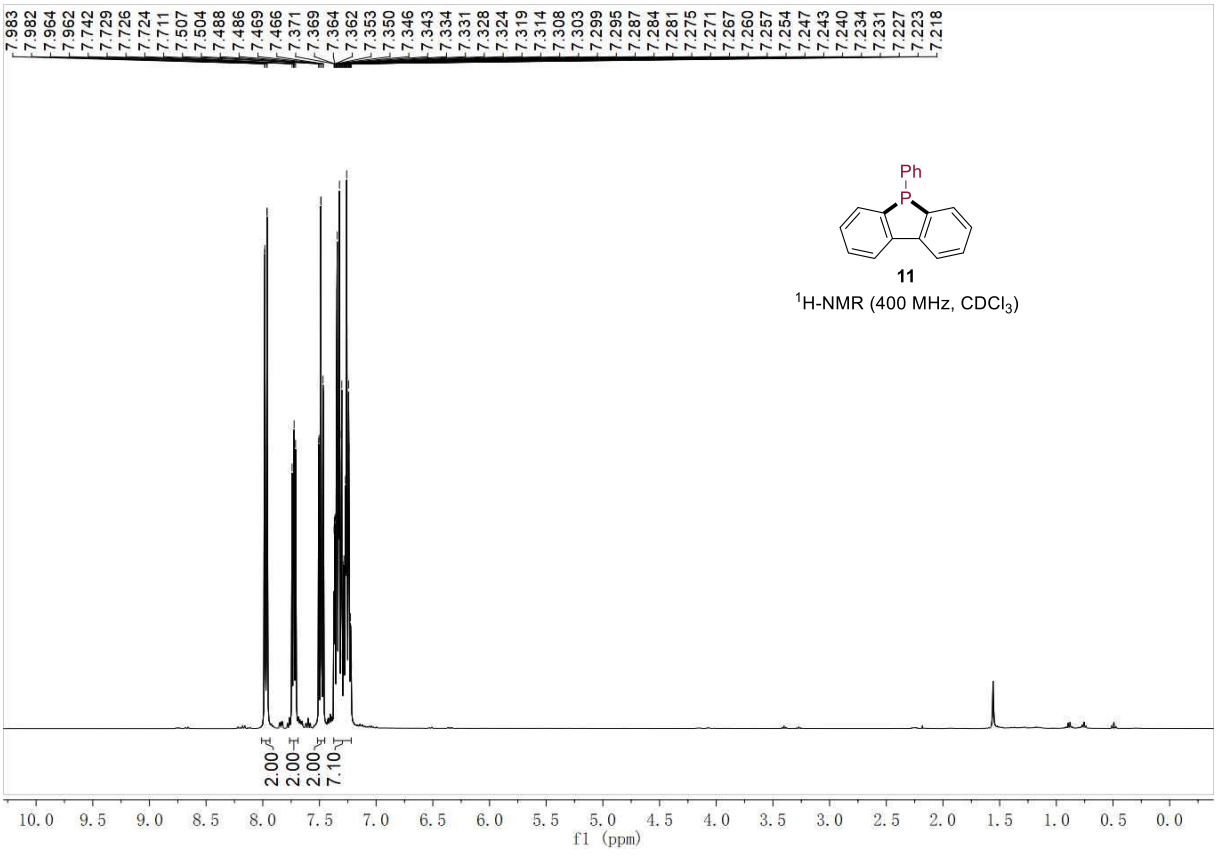

149.93
134.29
132.64
131.29
127.86
121.00
77.32
77.00
76.68
Si
9c
13C-NMR (100 MHz, CDCl3)
f1 (ppm)


8.011
7.997
7.977
7.963
7.764
7.762
7.761
7.746
7.745
7.743
7.717
7.716
7.714
7.700
7.699
7.696
7.669
7.668
7.666
7.652
7.650
7.649
7.465
7.461
7.458
7.454
7.450
7.447
7.439
7.436
7.428
7.424
7.420
7.416
7.412
7.408
7.356
7.354
7.340
7.337
7.322
7.319
7.304
7.301
7.287
7.285
0.643
0.640
0.568
0.495
0.492
Me
Me
Sn
10
1H-NMR (400 MHz, CDCl3)
2.01
2.00
2.00
2.02
6.15
f1 (ppm)



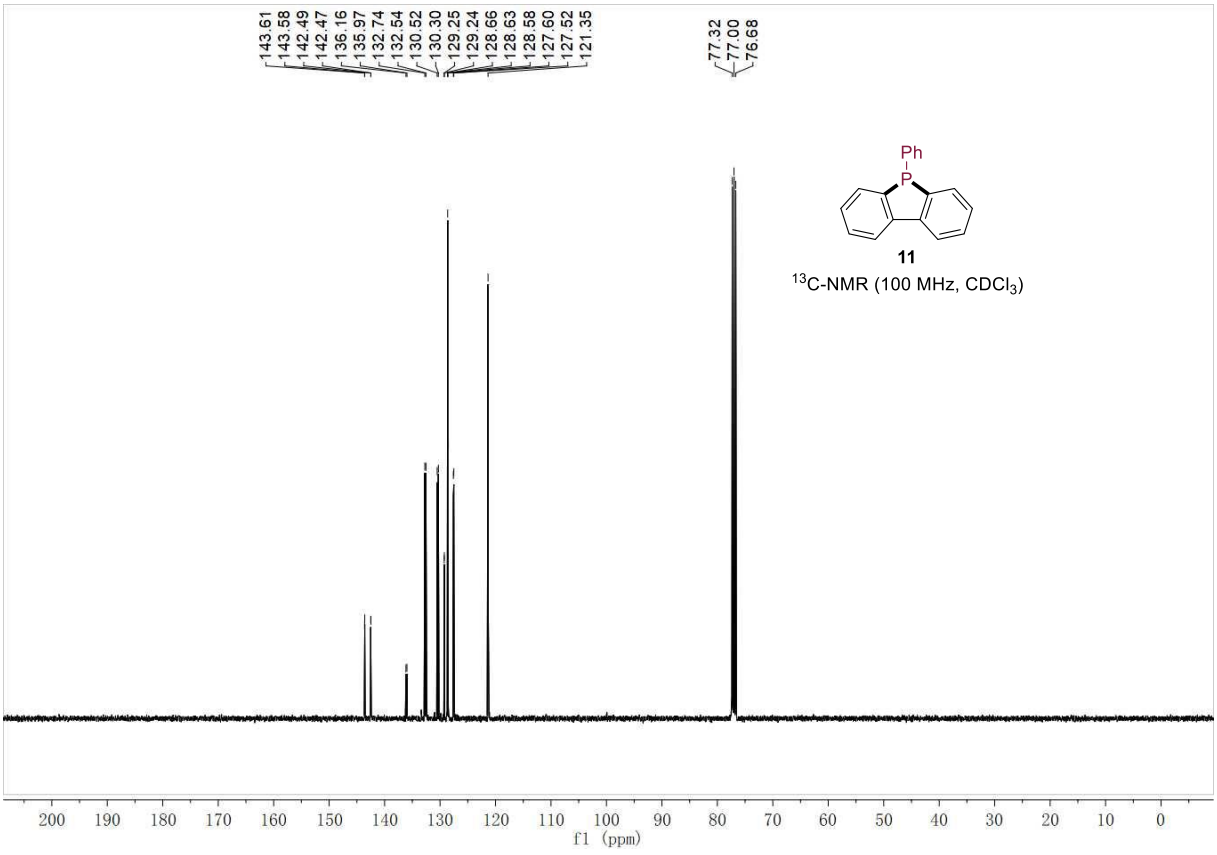
10

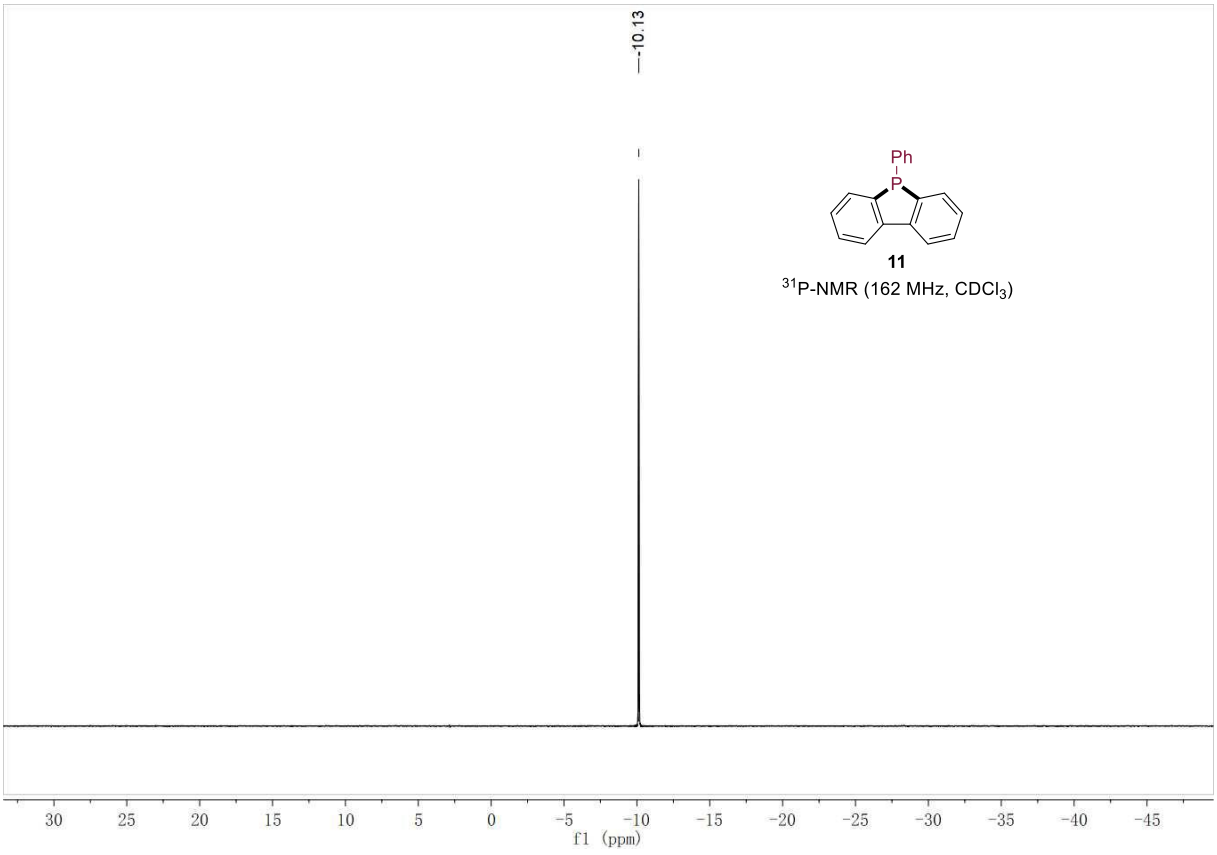
^{13}C-NMR (100 MHz, $CDCl_3$)

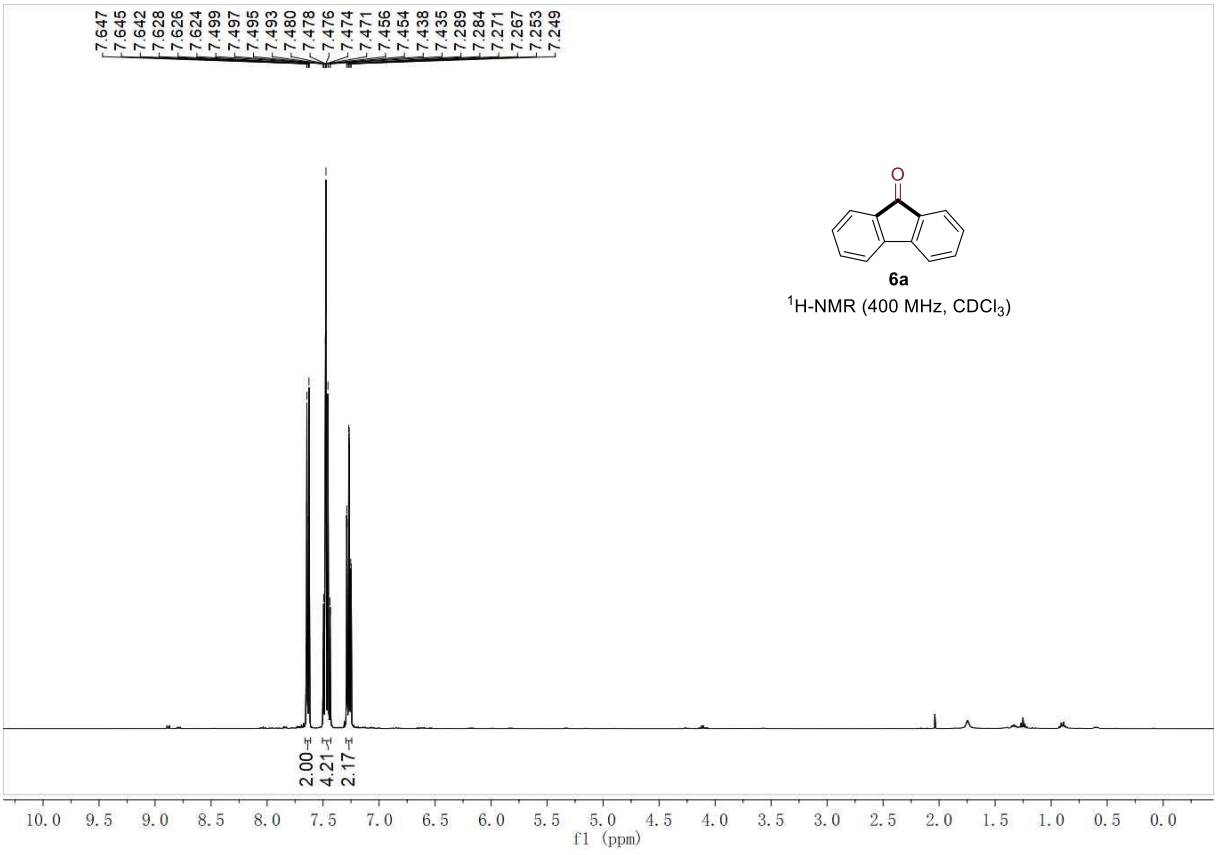


11

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

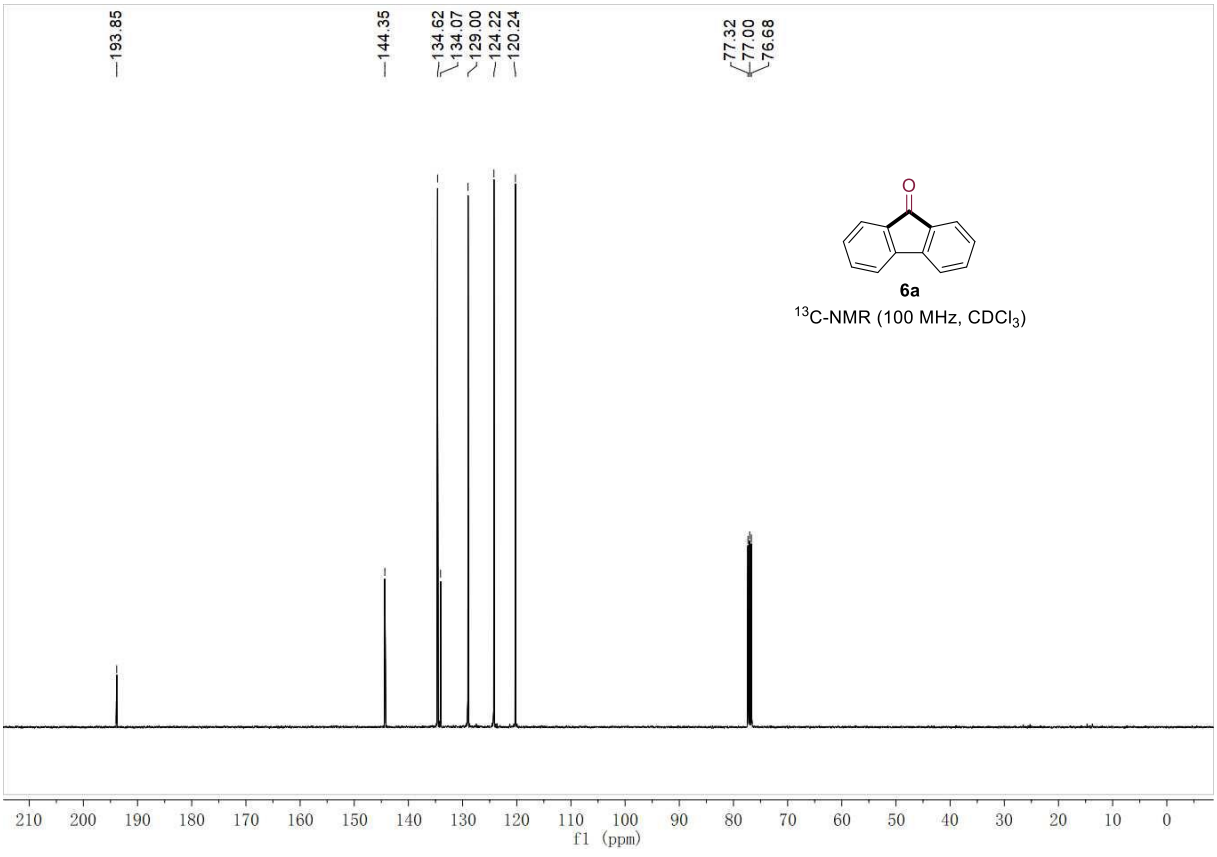

143.61
143.58
142.49
142.47
136.16
135.97
132.74
132.54
130.52
130.30
129.25
129.24
128.66
128.63
128.58
127.60
127.52
121.35
77.32
77.00
76.68
Ph
P
11
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-10.13
Ph
P
11
31P-NMR (162 MHz, CDCl3)
30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45
f1 (ppm)



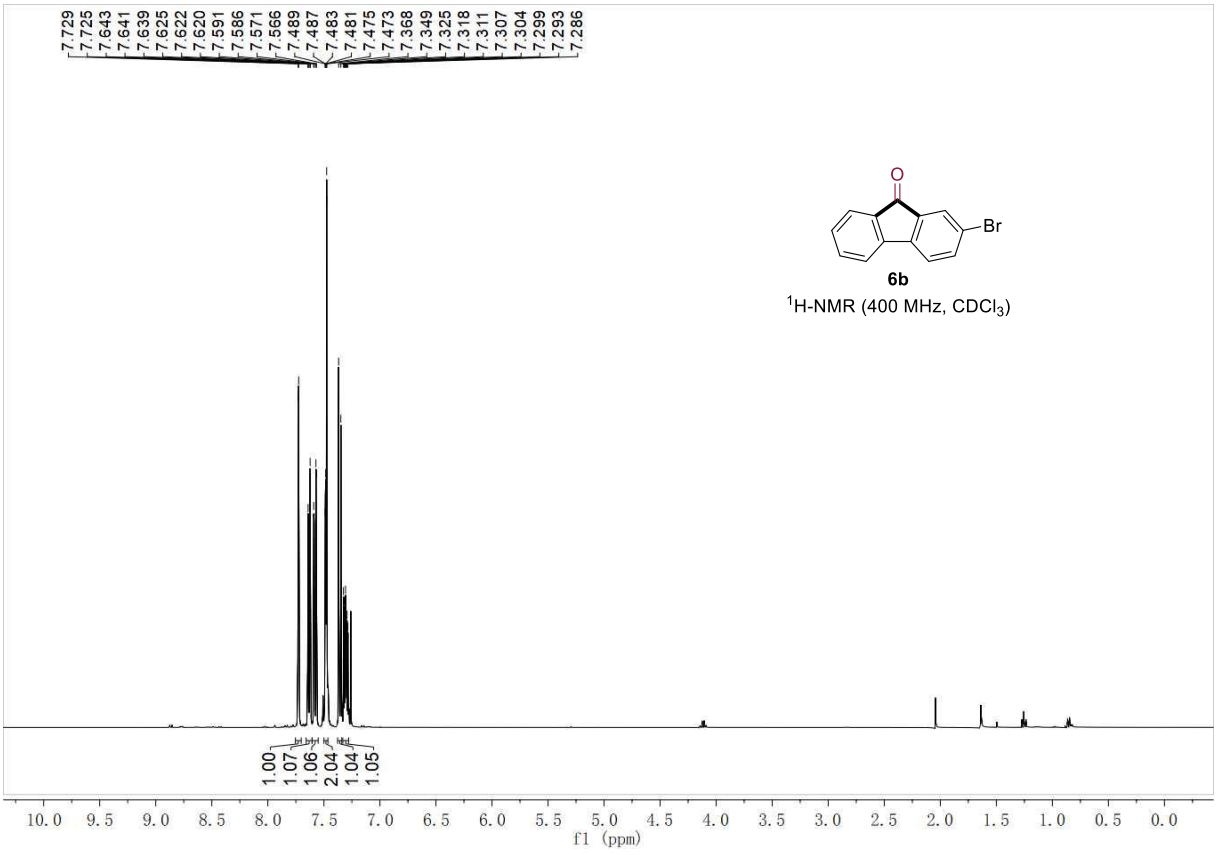
6a

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



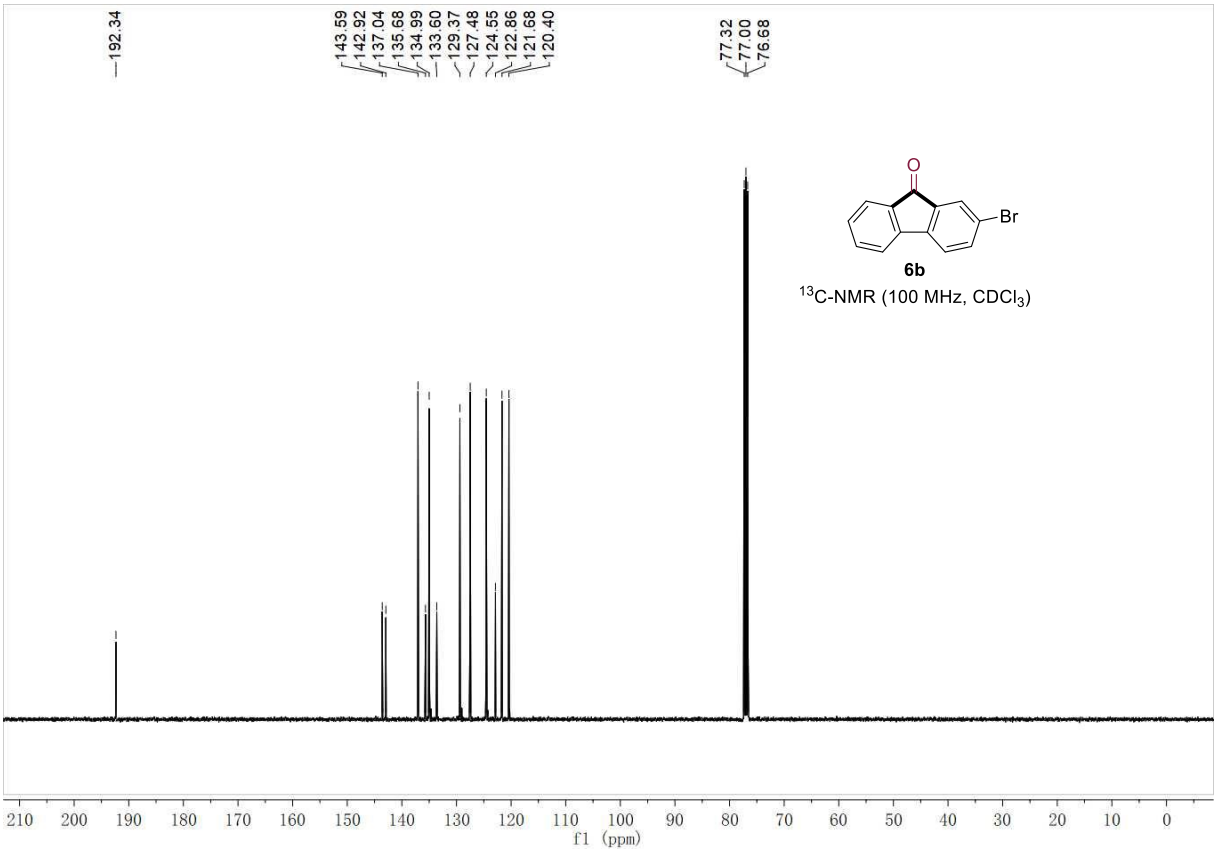
6a

^{13}C-NMR (100 MHz, $CDCl_3$)



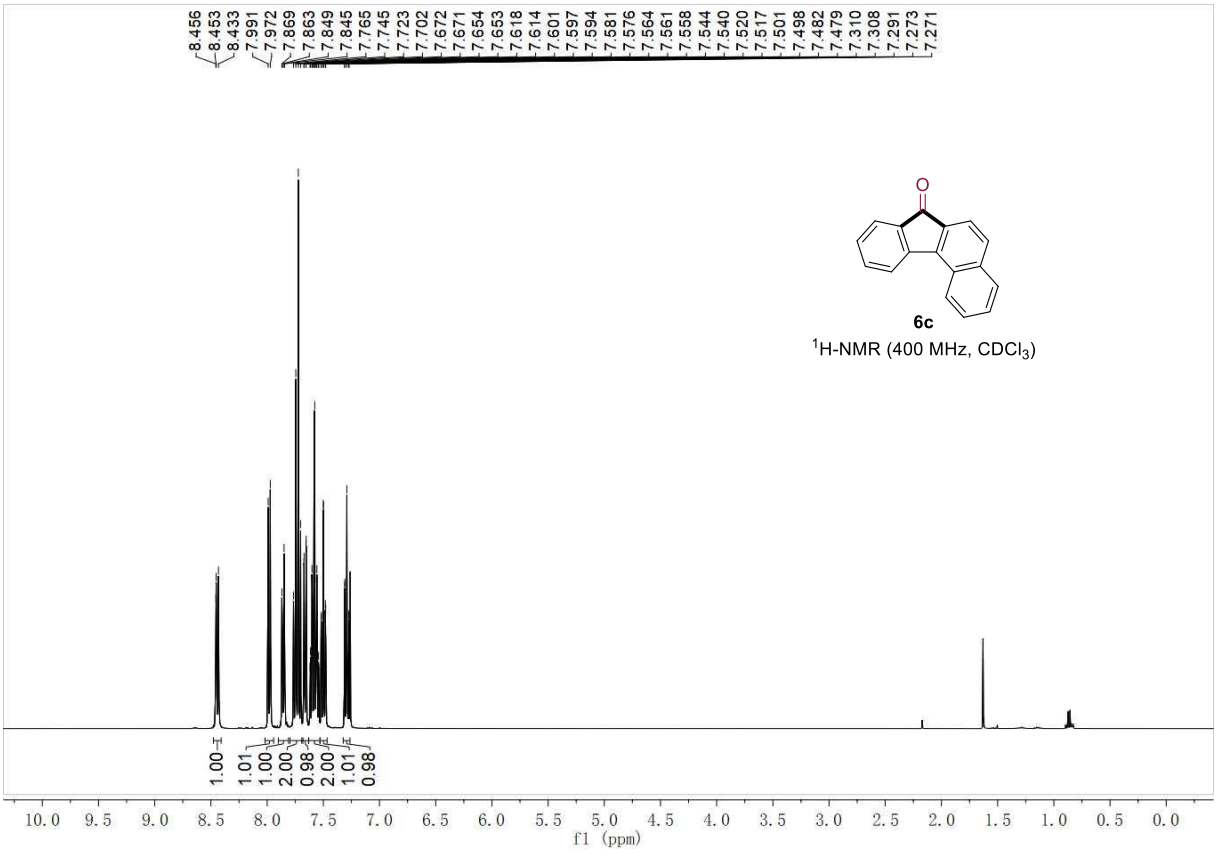
6b

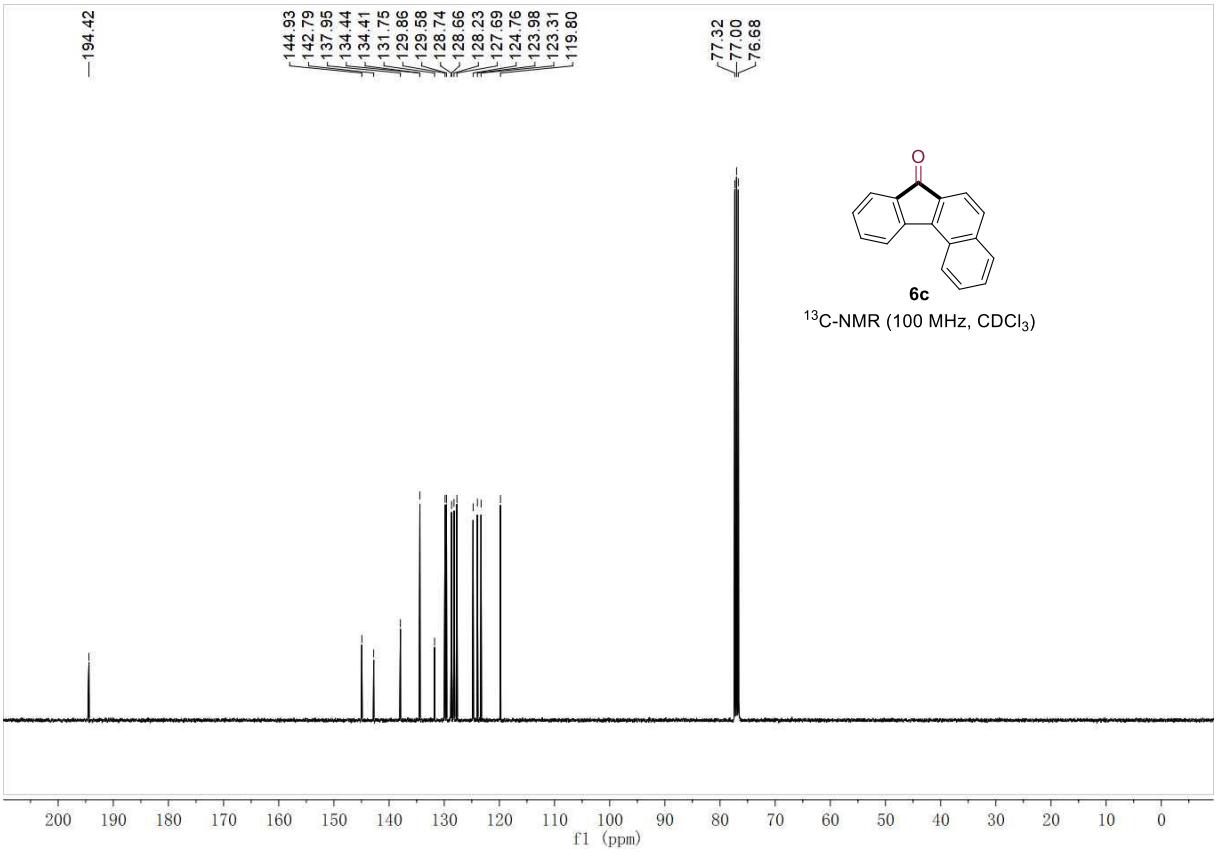
^{1}H-NMR (400 MHz, $CDCl_3$)

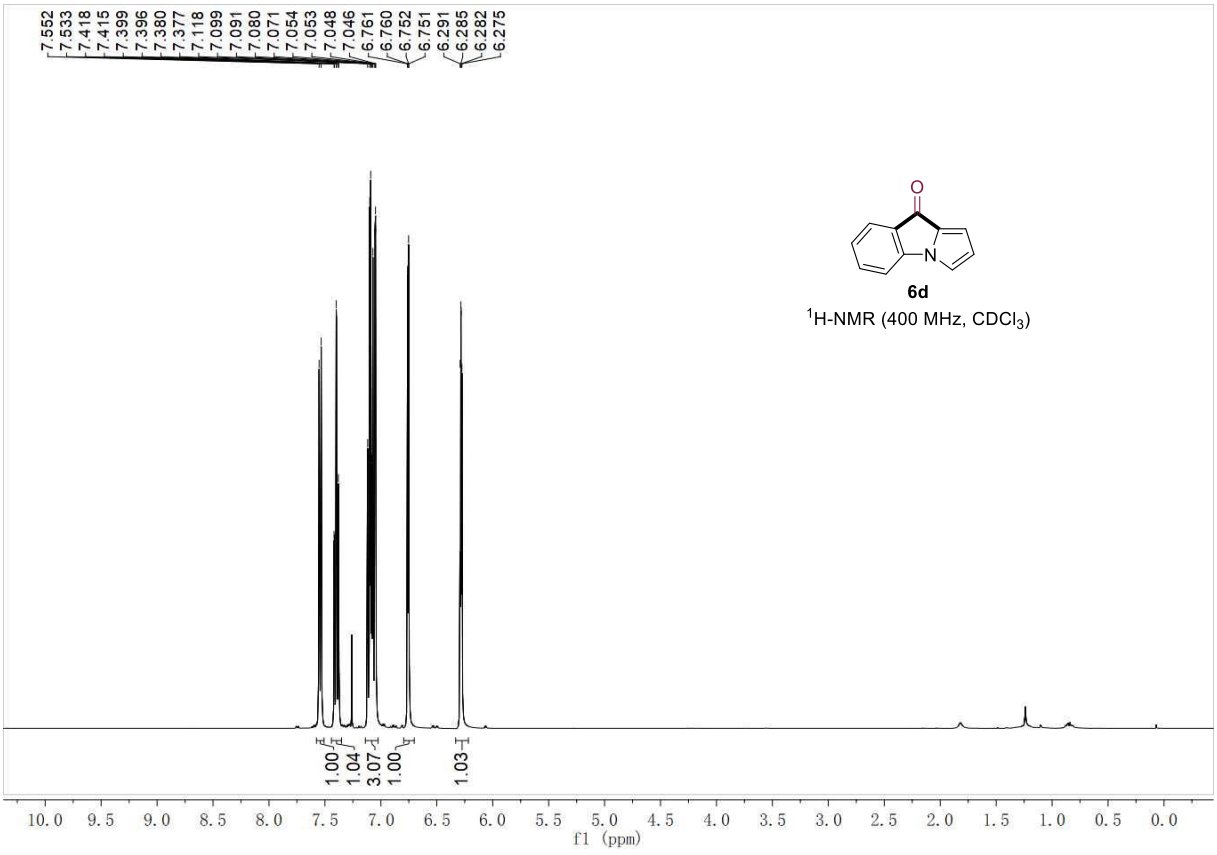


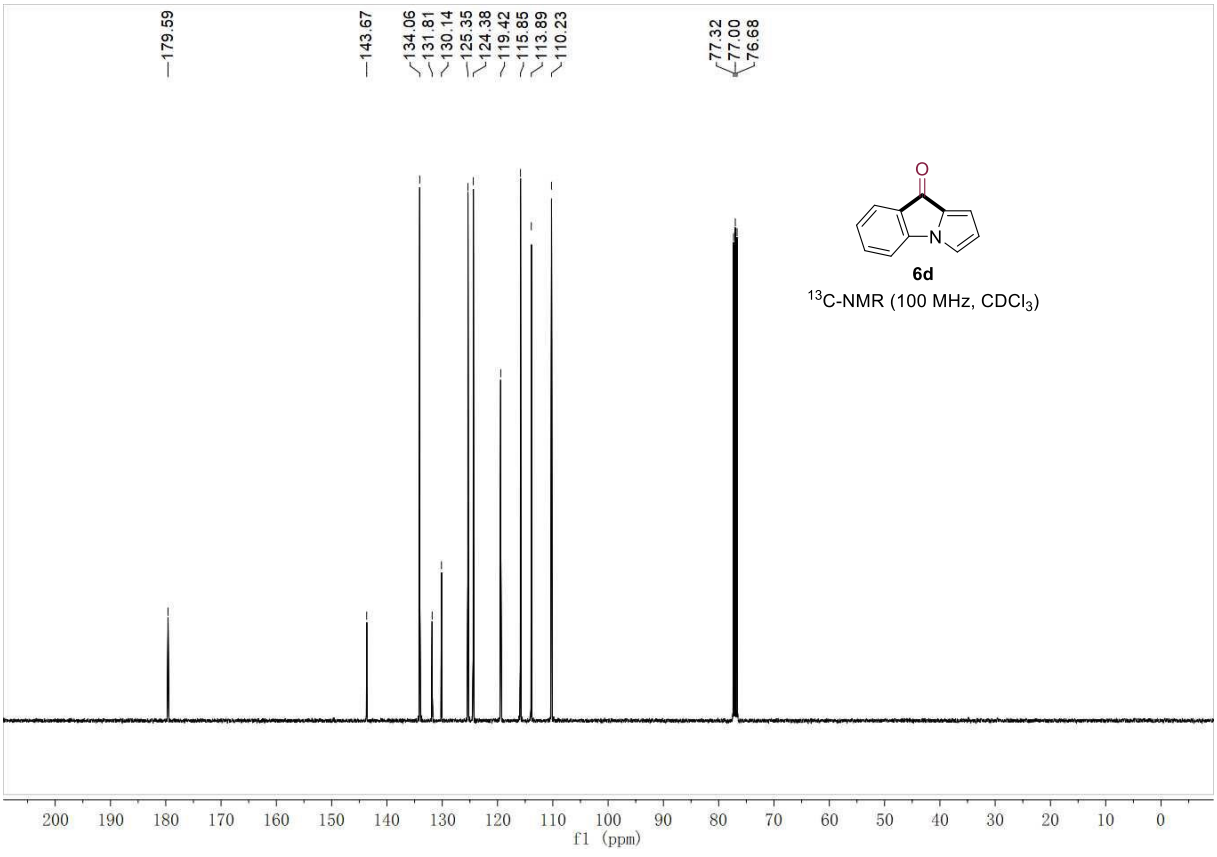
6b

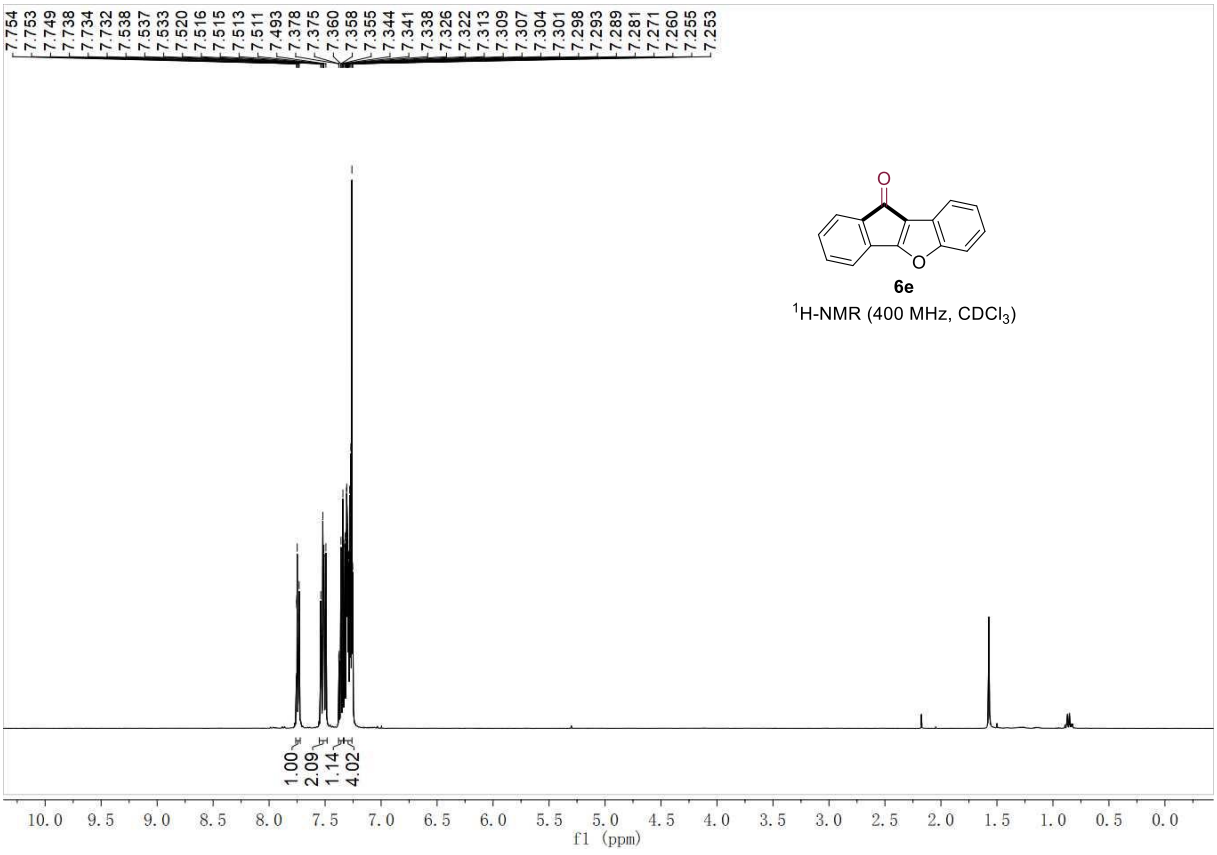
^{13}C-NMR (100 MHz, $CDCl_3$)


8.456
8.453
8.433
7.991
7.972
7.869
7.863
7.849
7.845
7.765
7.745
7.723
7.702
7.672
7.671
7.654
7.653
7.618
7.614
7.601
7.597
7.594
7.581
7.576
7.564
7.561
7.558
7.544
7.540
7.520
7.517
7.501
7.498
7.482
7.479
7.310
7.308
7.291
7.273
7.271
1.00
1.01
1.00
2.00
0.98
2.00
1.01
0.98
10.0 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 0.0
f1 (ppm)
O
6c
^{1}H-NMR (400 MHz, $CDCl_3$)


194.42
144.93
142.79
137.95
134.44
134.41
131.75
129.86
129.58
128.74
128.66
128.23
127.69
124.76
123.98
123.31
119.80
77.32
77.00
76.68
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
6c
^{13}C-NMR (100 MHz, $CDCl_3$)

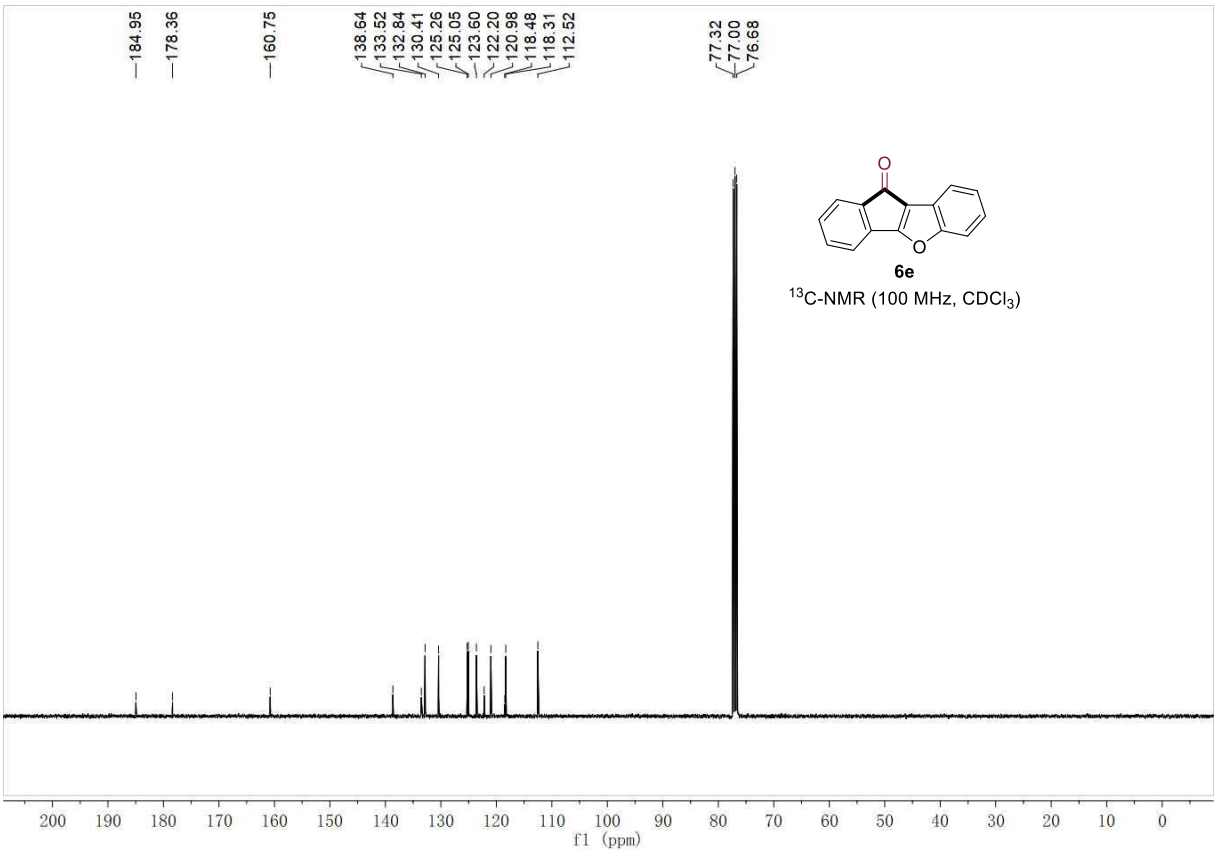

7.552
7.533
7.418
7.415
7.399
7.396
7.380
7.377
7.118
7.099
7.091
7.080
7.071
7.054
7.053
7.048
7.046
6.761
6.760
6.752
6.751
6.291
6.285
6.282
6.275
1.00
1.04
3.07
1.00
1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O
N
6d
1H-NMR (400 MHz, CDCl3)


179.59
143.67
134.06
131.81
130.14
125.35
124.38
119.42
115.85
113.89
110.23
77.32
77.00
76.68
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
N
6d
13C-NMR (100 MHz, CDCl3)



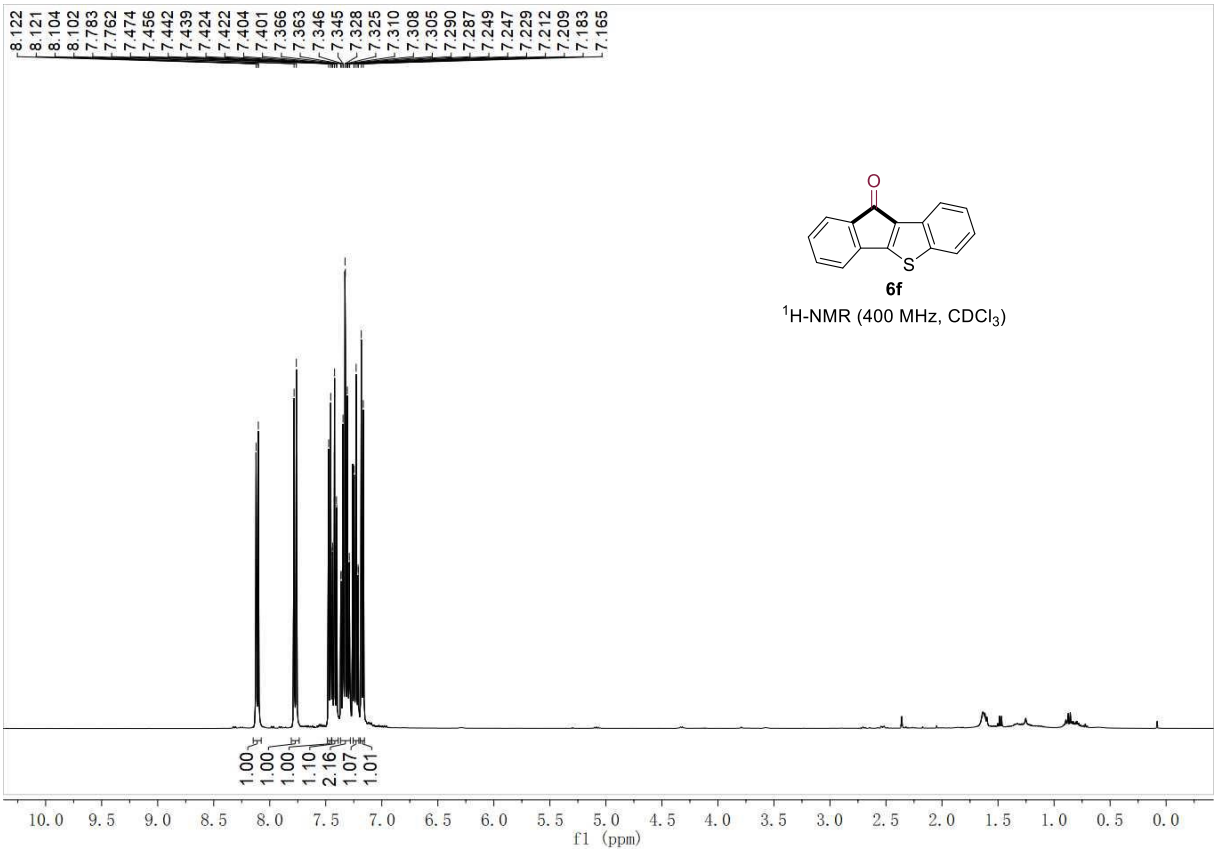
6e

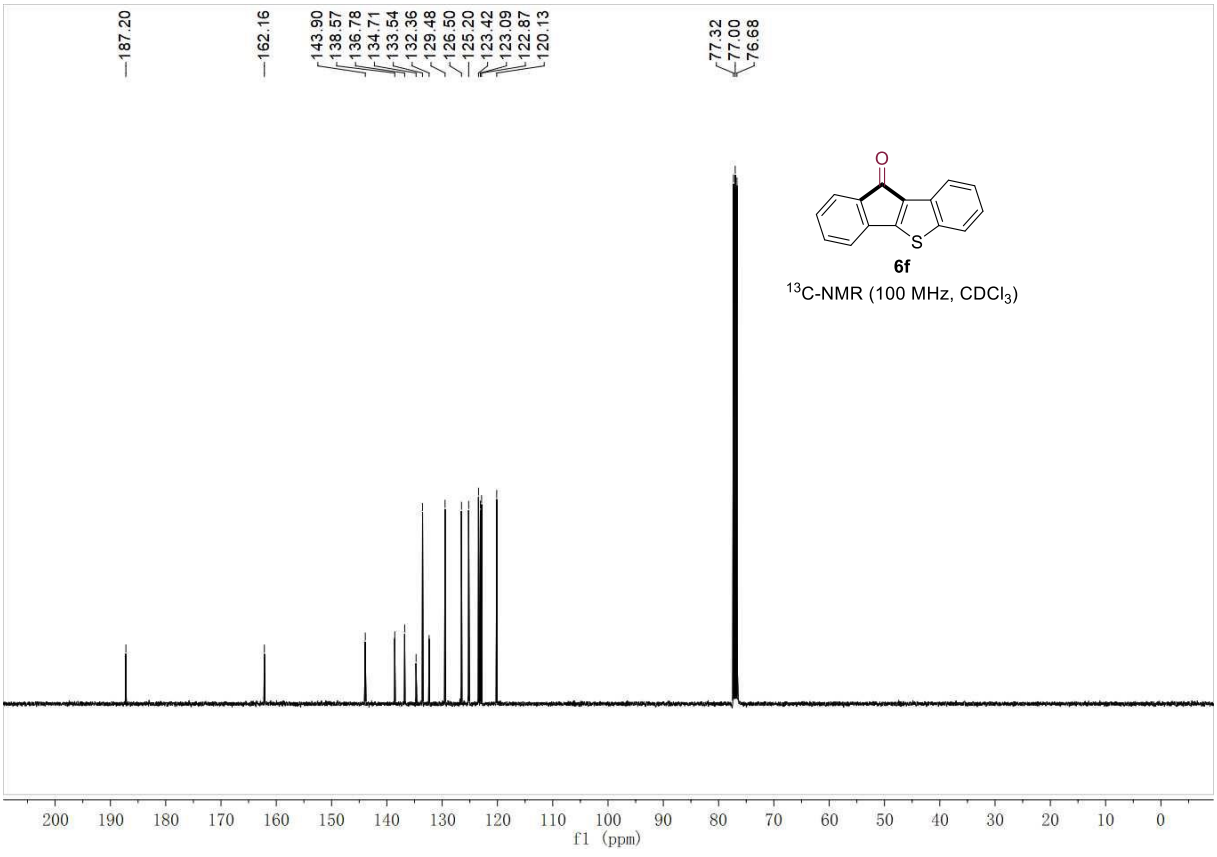
^{1}H-NMR (400 MHz, $CDCl_3$)

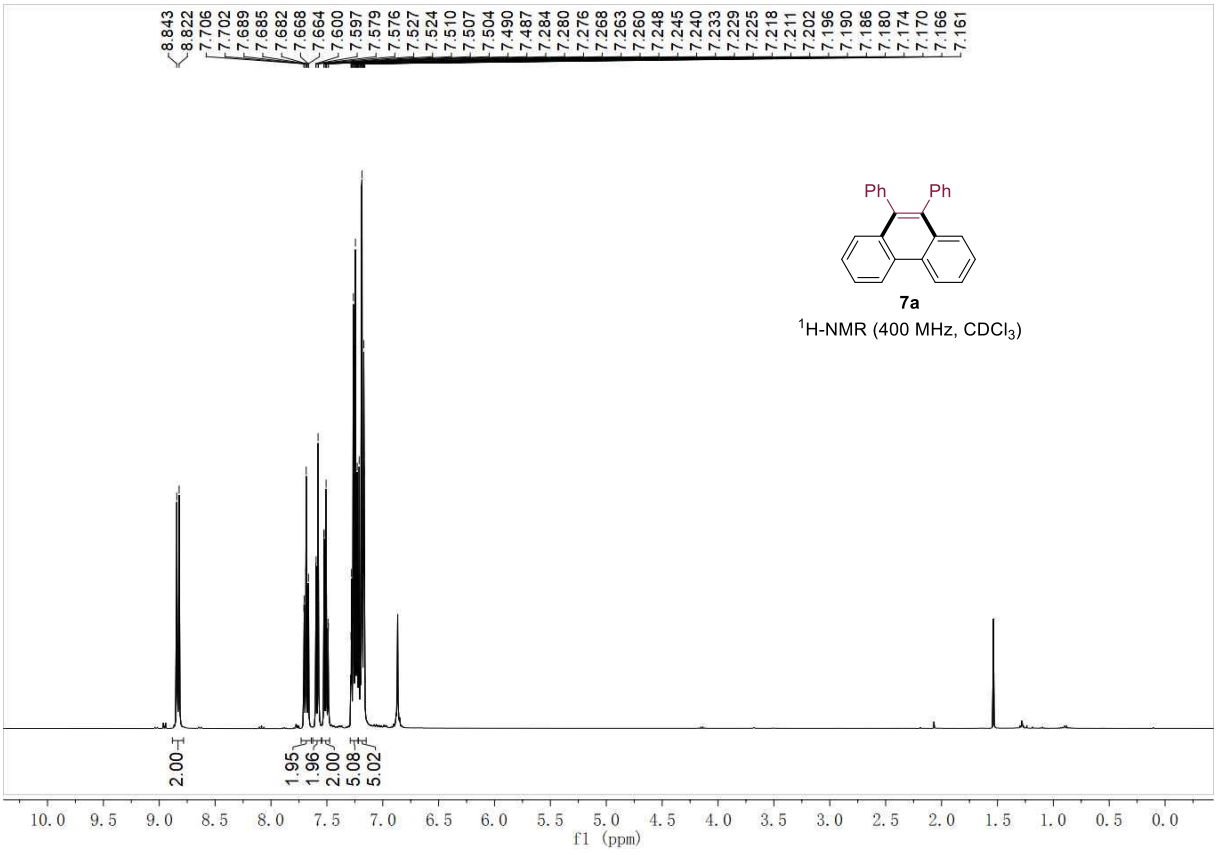


6e

^{13}C-NMR (100 MHz, $CDCl_3$)

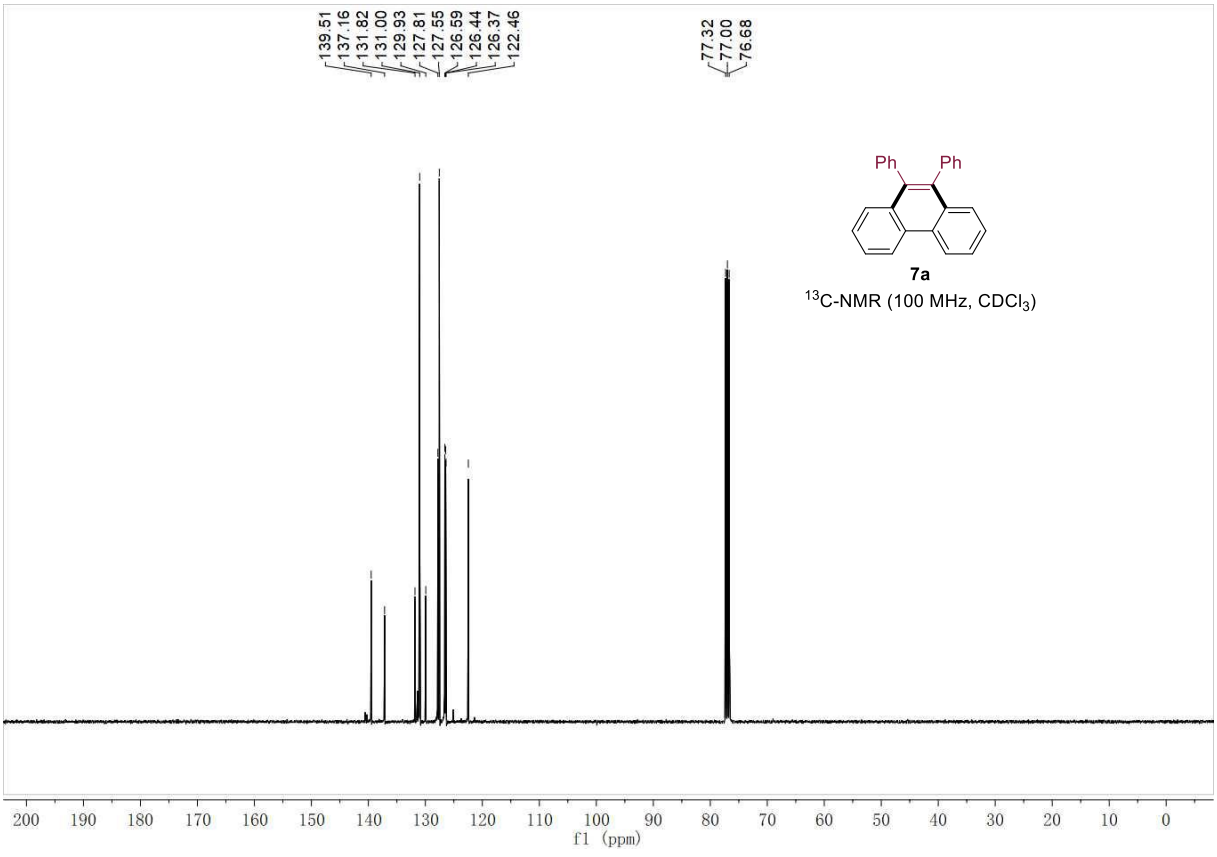

8.122
8.121
8.104
8.102
7.783
7.762
7.474
7.456
7.442
7.439
7.424
7.422
7.404
7.401
7.366
7.363
7.346
7.345
7.328
7.325
7.310
7.308
7.305
7.290
7.287
7.249
7.247
7.229
7.212
7.209
7.183
7.165
1.00
1.00
1.00
1.10
2.16
1.07
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O
S
6f
1H-NMR (400 MHz, CDCl3)


187.20
162.16
143.90
138.57
136.78
134.71
133.54
132.36
129.48
126.50
125.20
123.42
123.09
122.87
120.13
77.32
77.00
76.68
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
S
6f
13C-NMR (100 MHz, CDCl3)



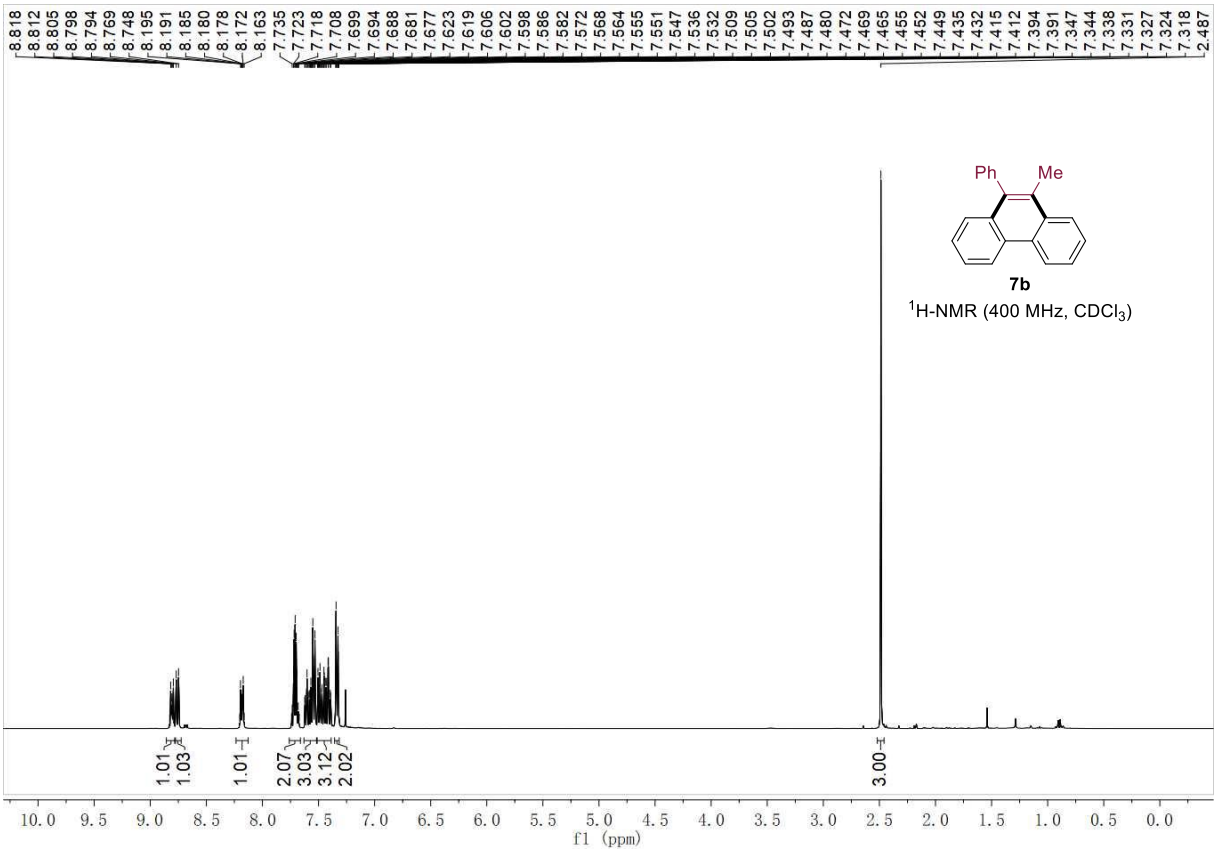
7a

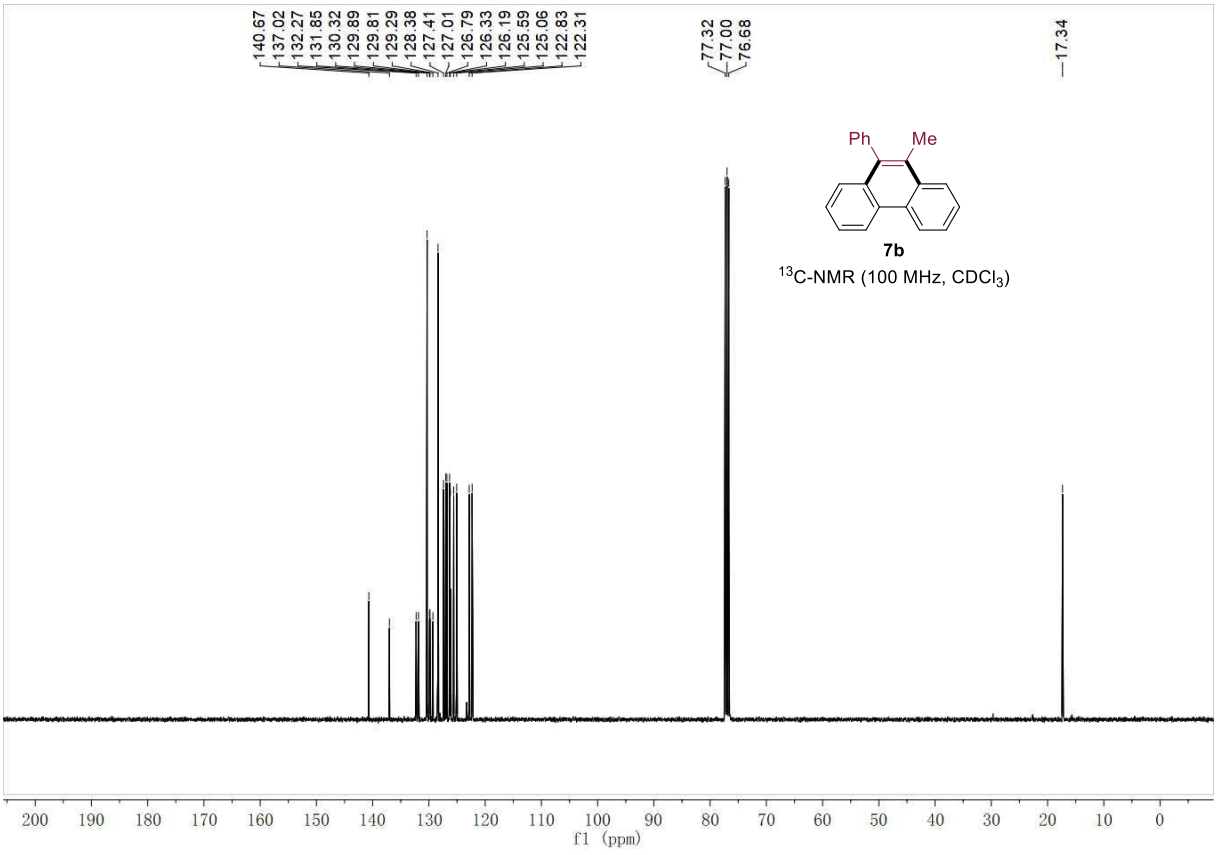
^{1}H-NMR (400 MHz, $CDCl_3$)

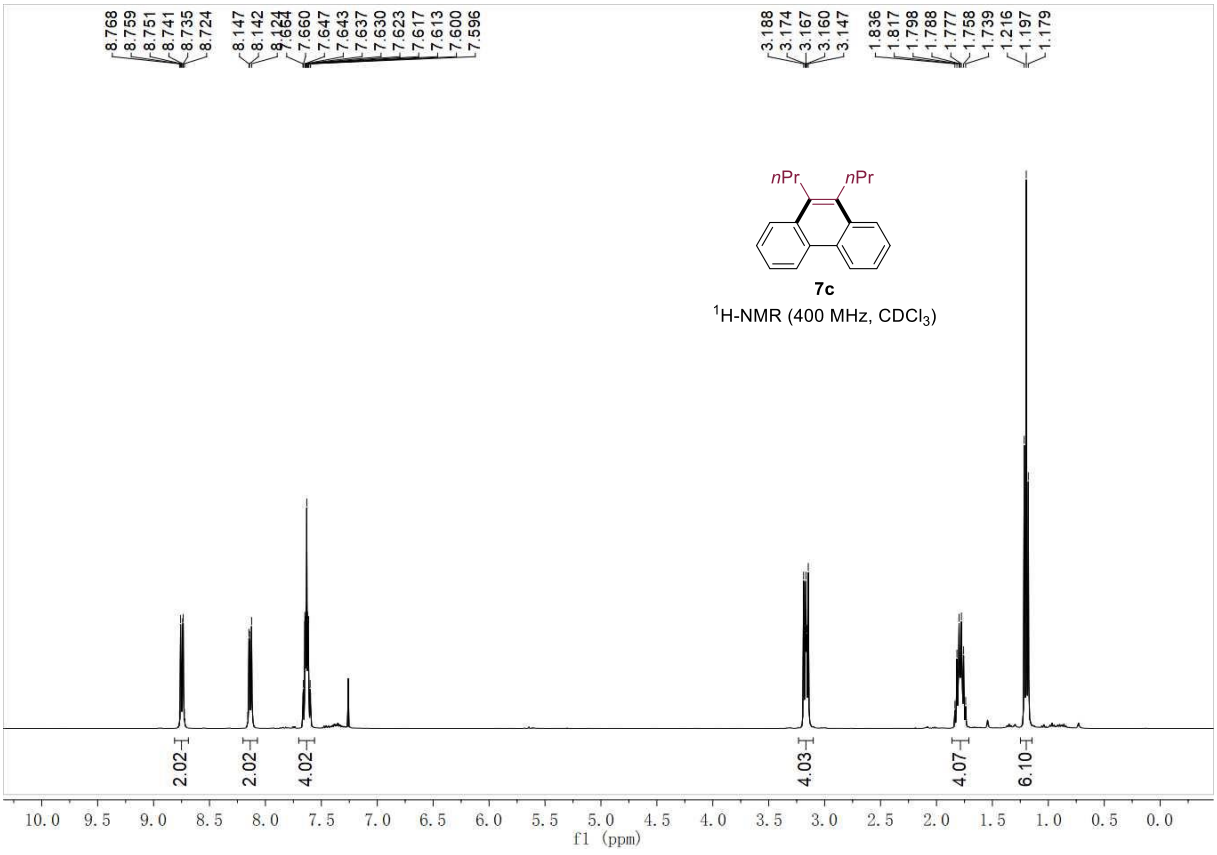


7a

^{13}C-NMR (100 MHz, $CDCl_3$)

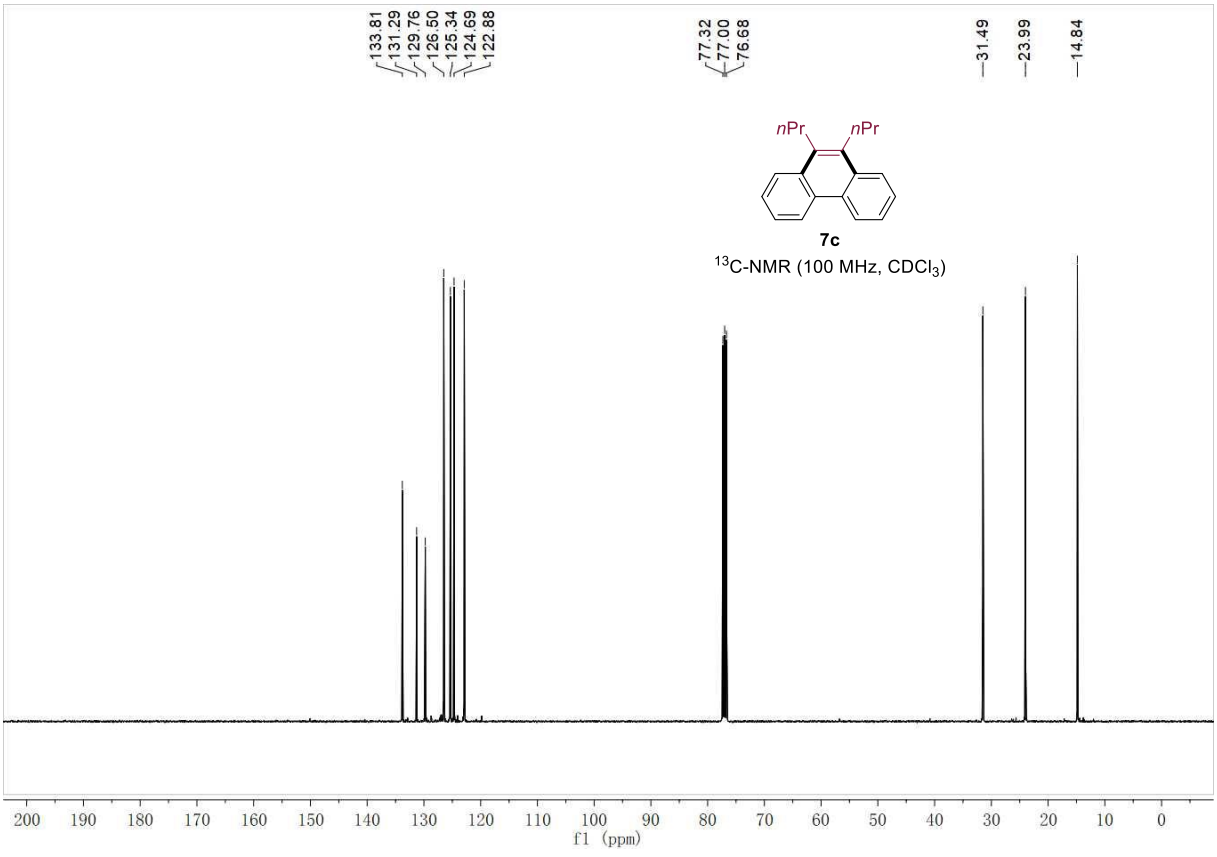

8.818
8.812
8.805
8.798
8.794
8.769
8.748
8.195
8.191
8.185
8.180
8.178
8.172
8.163
7.735
7.723
7.718
7.708
7.699
7.694
7.688
7.681
7.677
7.623
7.619
7.606
7.602
7.598
7.586
7.582
7.572
7.568
7.564
7.555
7.551
7.547
7.536
7.532
7.509
7.505
7.502
7.493
7.487
7.480
7.472
7.469
7.465
7.455
7.452
7.449
7.435
7.432
7.415
7.412
7.394
7.391
7.347
7.344
7.338
7.331
7.327
7.324
7.318
2.487
Ph
Me
7b
1H-NMR (400 MHz, CDCl3)
1.01
1.03
1.01
2.07
3.03
3.12
2.02
3.00
10.0 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 0.0
f1 (ppm)


140.67
137.02
132.27
131.85
130.32
129.89
129.81
129.29
128.38
127.41
127.01
126.79
126.33
126.19
125.59
125.06
122.83
122.31
77.32
77.00
76.68
17.34
Ph
Me
7b
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



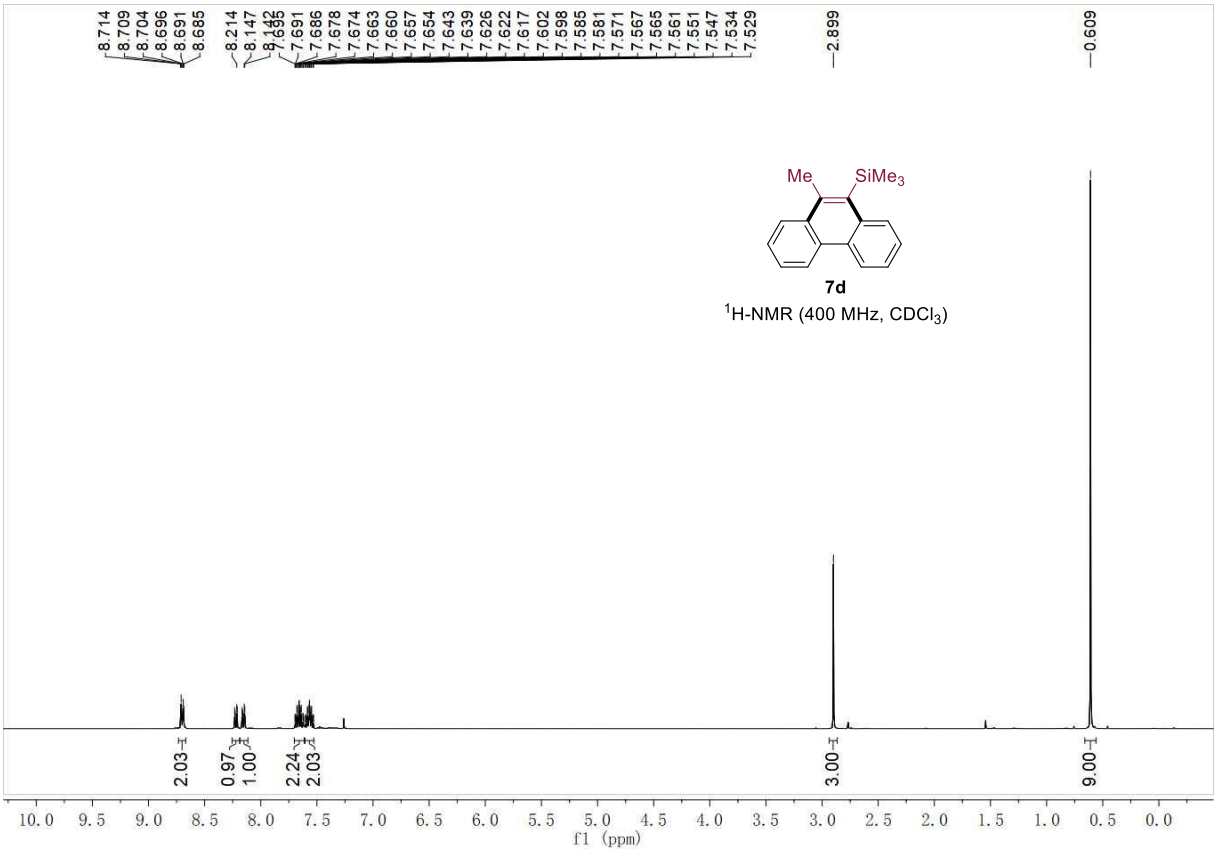
7c

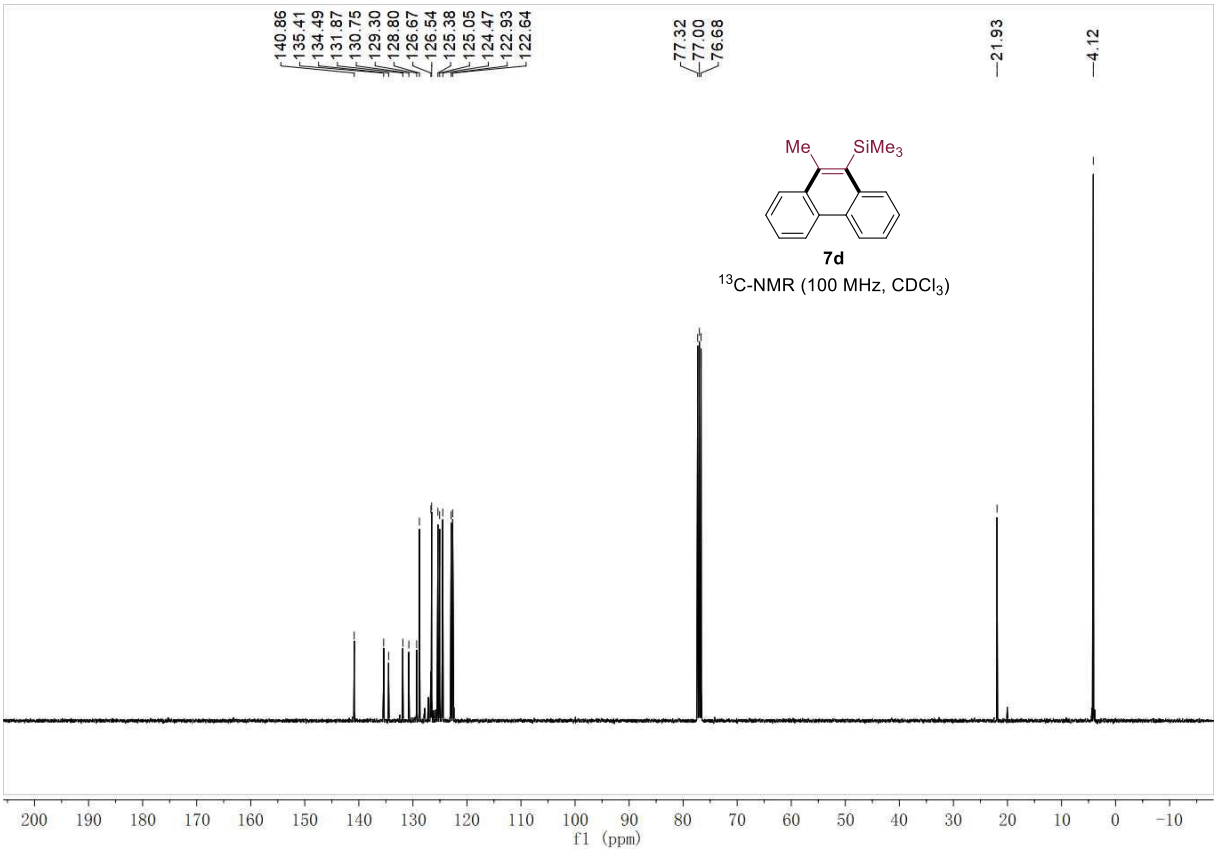
^{1}H-NMR (400 MHz, $CDCl_3$)

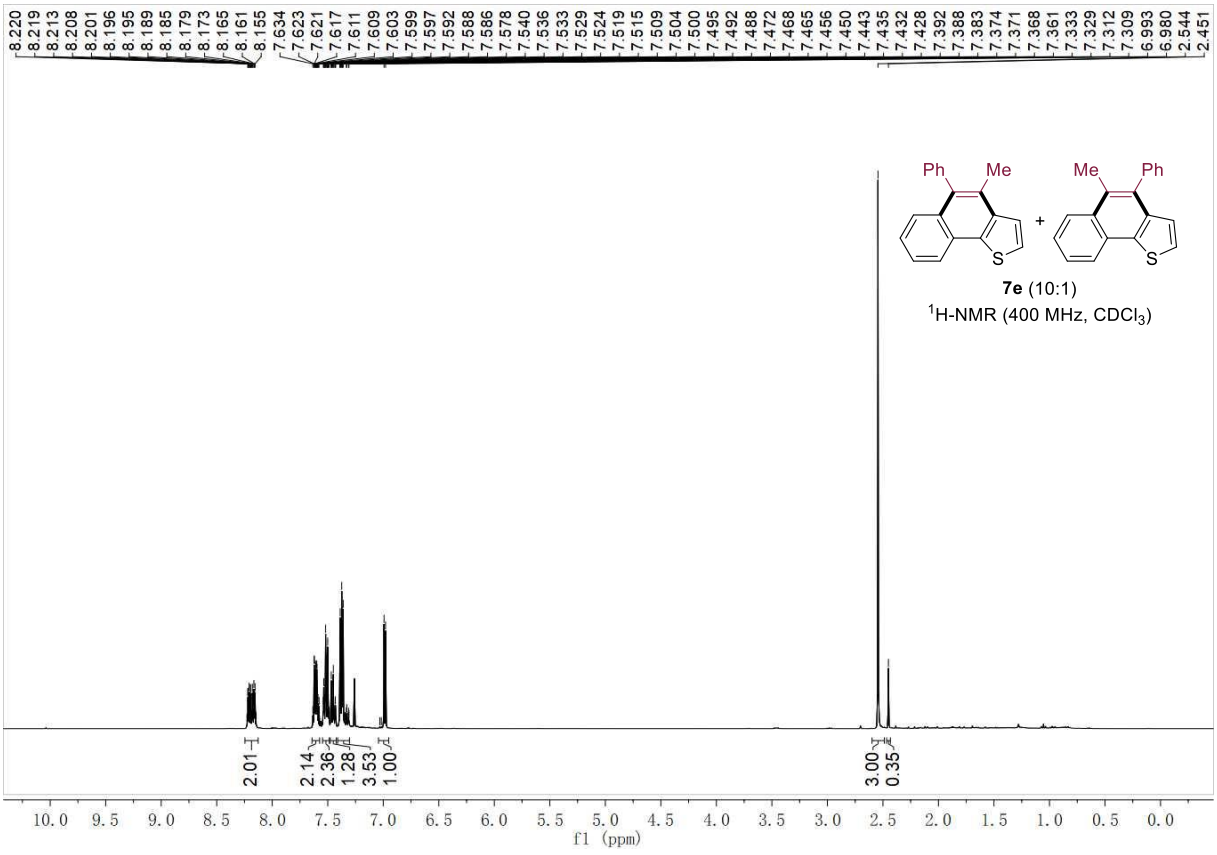


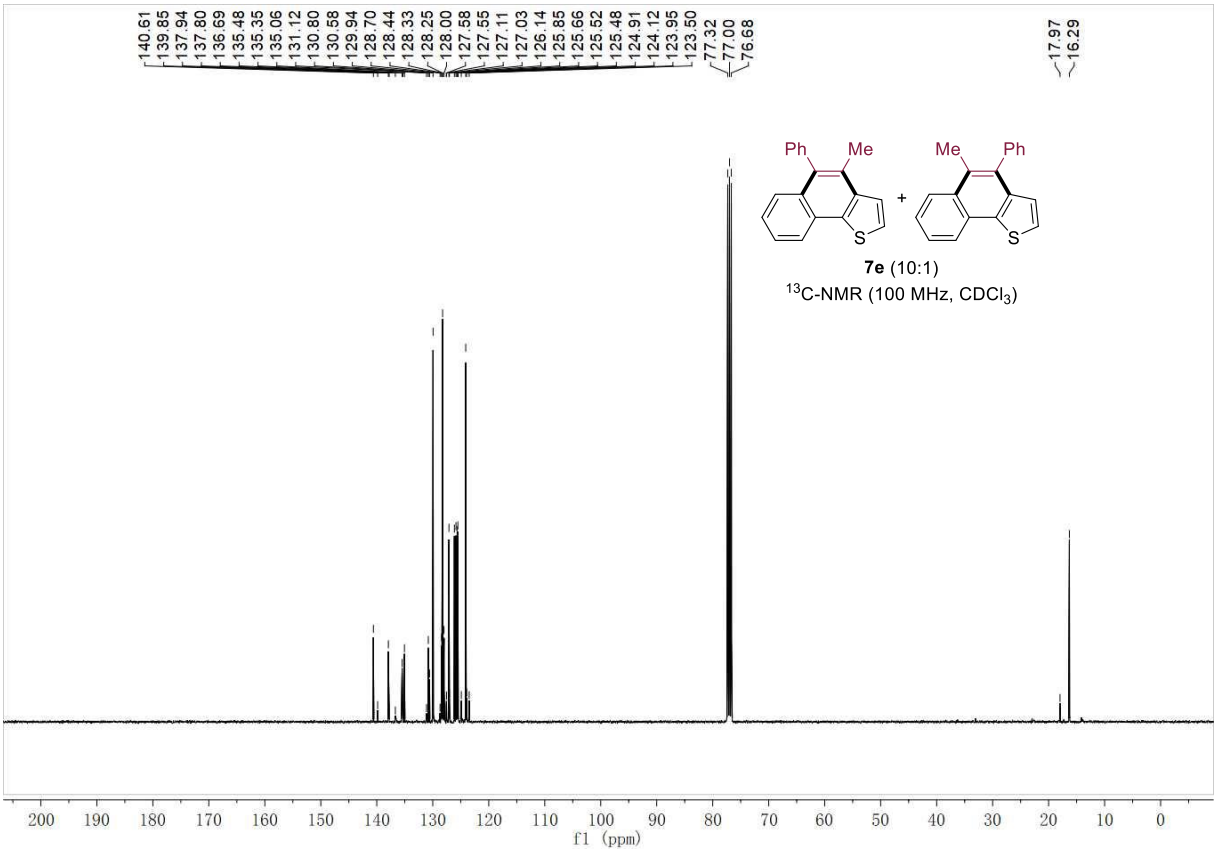
7c

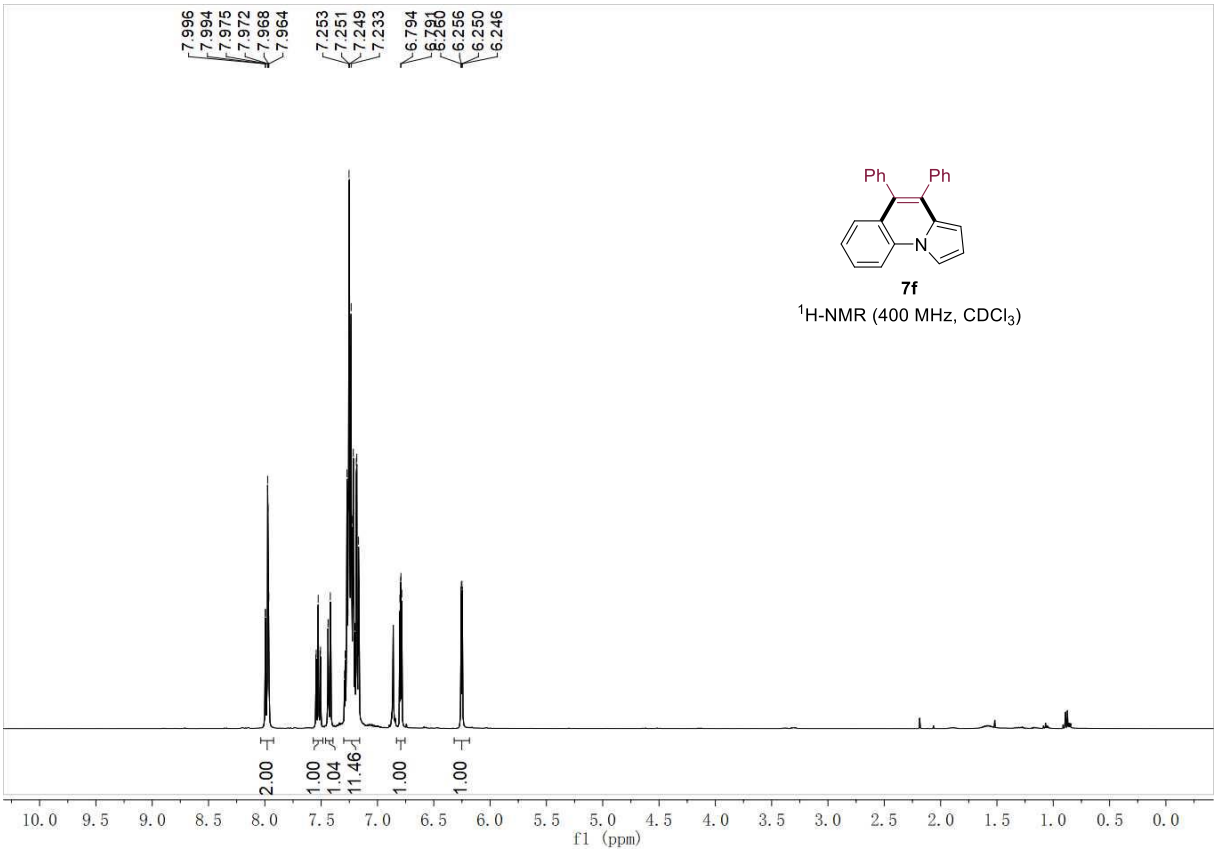
^{13}C-NMR (100 MHz, $CDCl_3$)


8.714
8.709
8.704
8.696
8.691
8.685
8.214
8.147
7.695
7.691
7.686
7.678
7.674
7.663
7.660
7.657
7.654
7.643
7.639
7.626
7.622
7.617
7.602
7.598
7.585
7.581
7.571
7.567
7.565
7.561
7.551
7.547
7.534
7.529
2.899
0.609
Me
SiMe3
7d
1H-NMR (400 MHz, CDCl3)
2.03
0.97
1.00
2.24
2.03
3.00
9.00
f1 (ppm)


140.86
135.41
134.49
131.87
130.75
129.30
128.80
126.67
126.54
125.38
125.05
124.47
122.93
122.64
77.32
77.00
76.68
21.93
4.12
Me
SiMe3
7d
13C-NMR (100 MHz, CDCl3)
f1 (ppm)

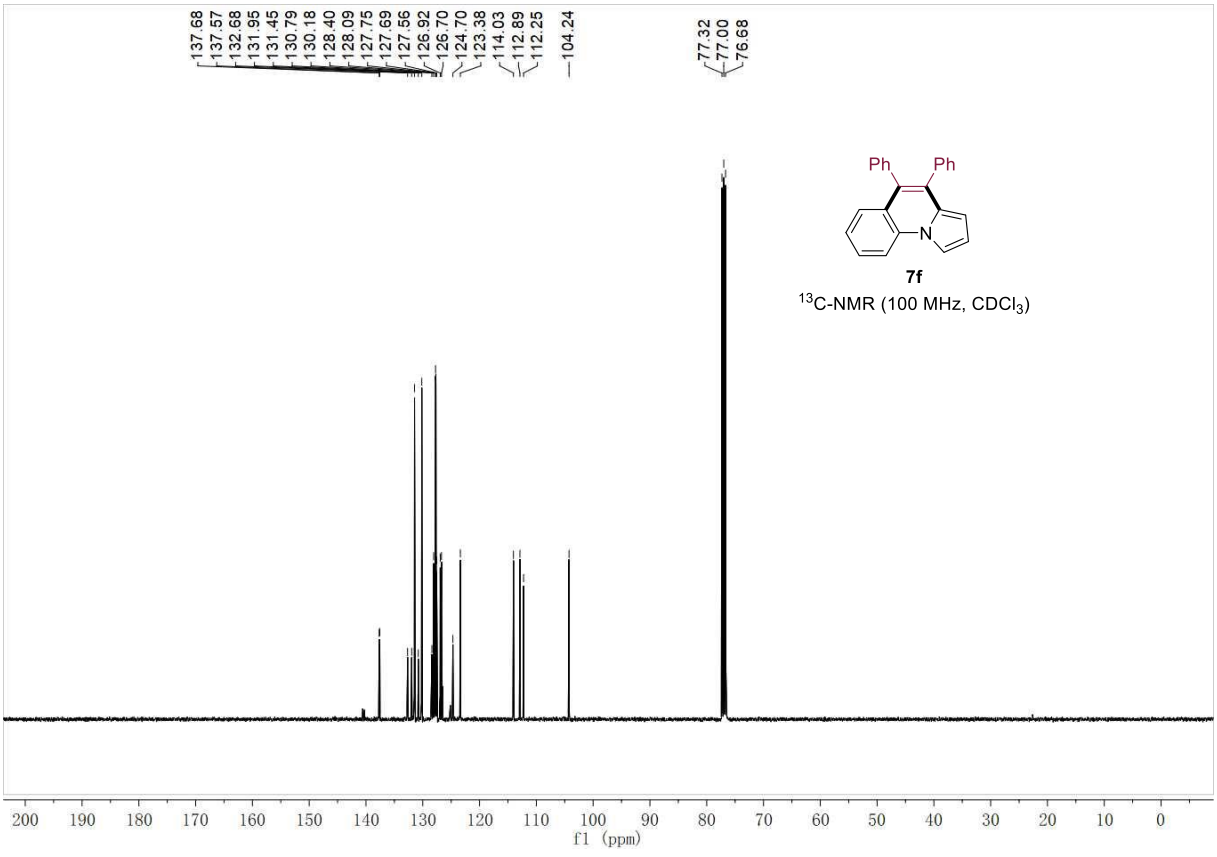

8.220
8.219
8.213
8.208
8.201
8.196
8.195
8.189
8.185
8.179
8.173
8.165
8.161
8.155
7.634
7.623
7.621
7.617
7.611
7.609
7.603
7.599
7.597
7.592
7.588
7.586
7.578
7.540
7.536
7.533
7.529
7.524
7.519
7.515
7.509
7.504
7.500
7.495
7.492
7.488
7.472
7.468
7.465
7.456
7.450
7.443
7.435
7.432
7.428
7.392
7.388
7.383
7.374
7.371
7.368
7.361
7.333
7.329
7.312
7.309
6.993
6.980
2.544
2.451
Ph
Me
Me
Ph
S
S
7e (10:1)
1H-NMR (400 MHz, CDCl3)
2.01
2.14
2.36
1.28
3.53
1.00
3.00
0.35
10.0 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 0.0
f1 (ppm)


140.61
139.85
137.94
137.80
136.69
135.48
135.35
135.06
131.12
130.80
130.58
129.94
128.70
128.44
128.33
128.25
128.00
127.58
127.55
127.11
127.03
126.14
125.85
125.66
125.52
125.48
124.91
124.12
123.95
123.50
77.32
77.00
76.68
17.97
16.29
Ph
Me
Me
Ph
S
S
7e (10:1)
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



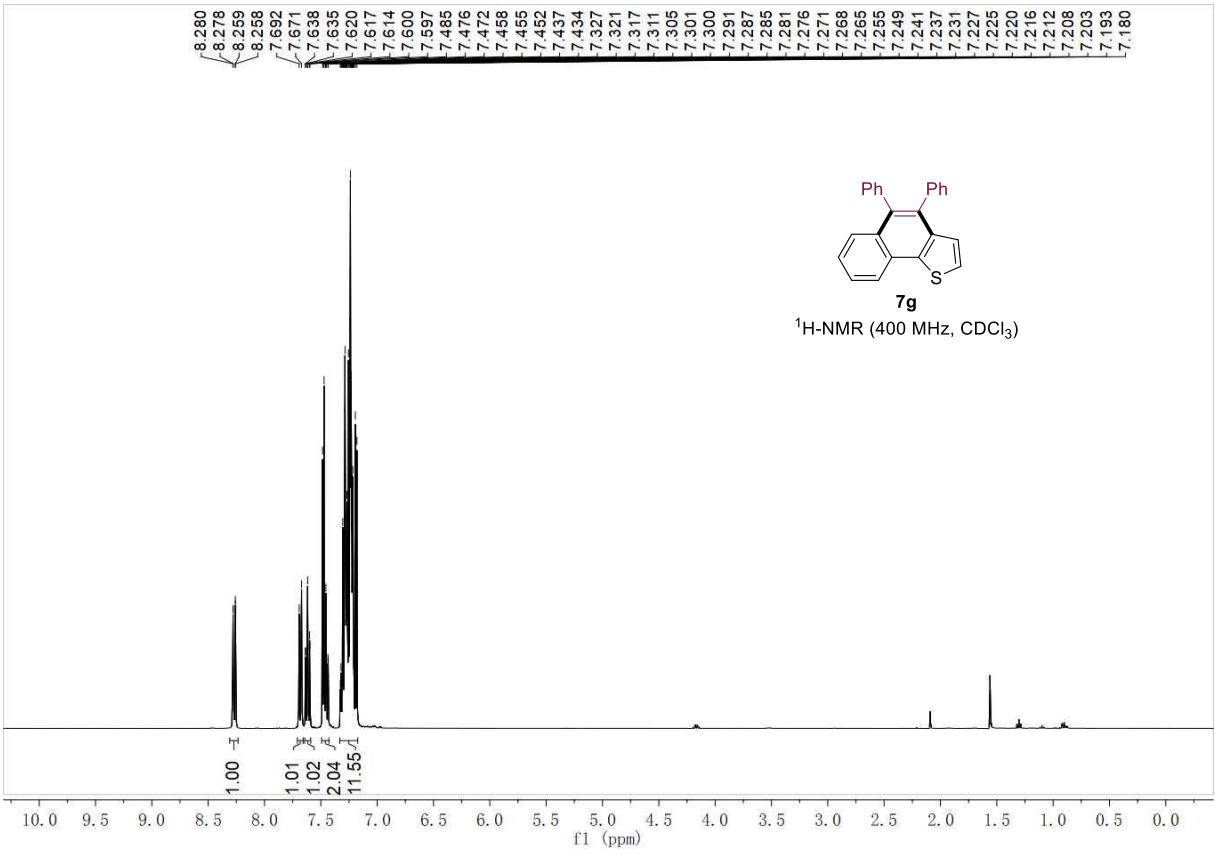
7f

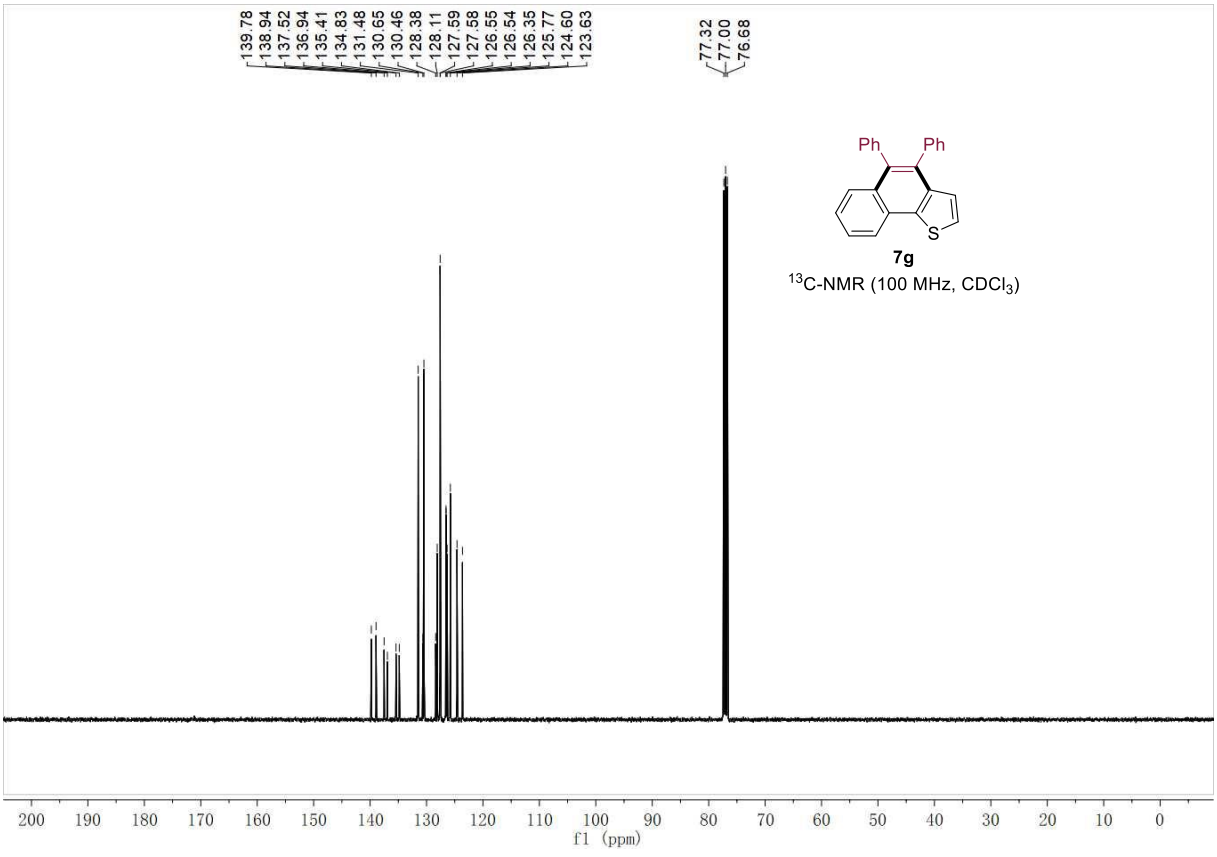
^{1}H-NMR (400 MHz, $CDCl_3$)

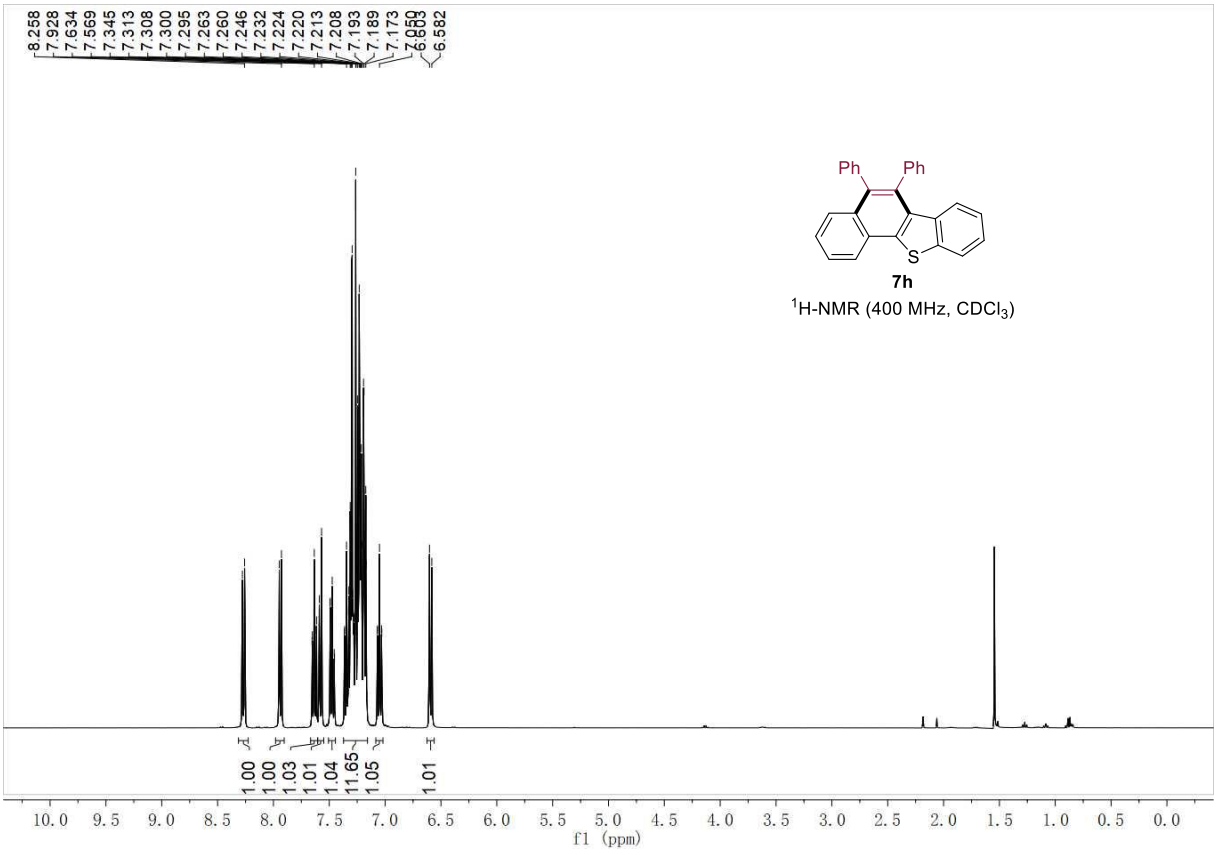


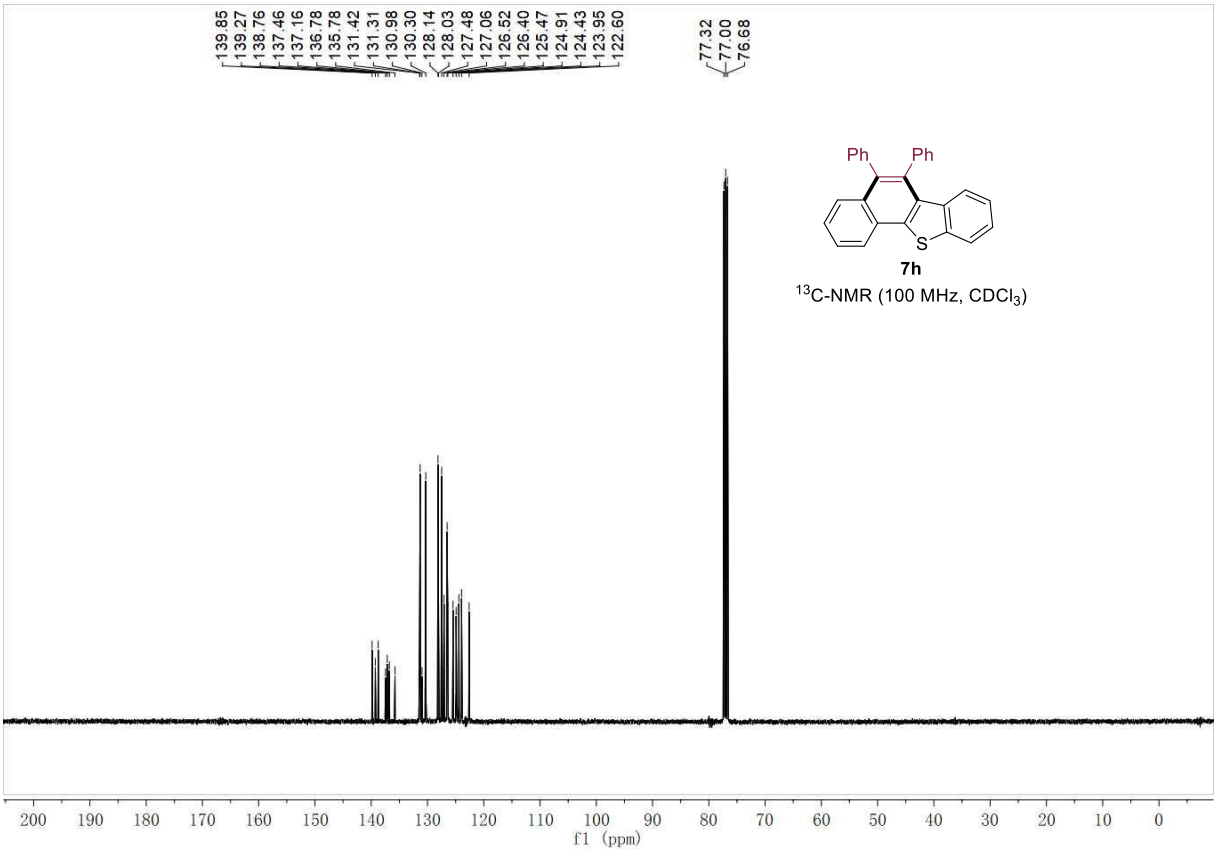
7f

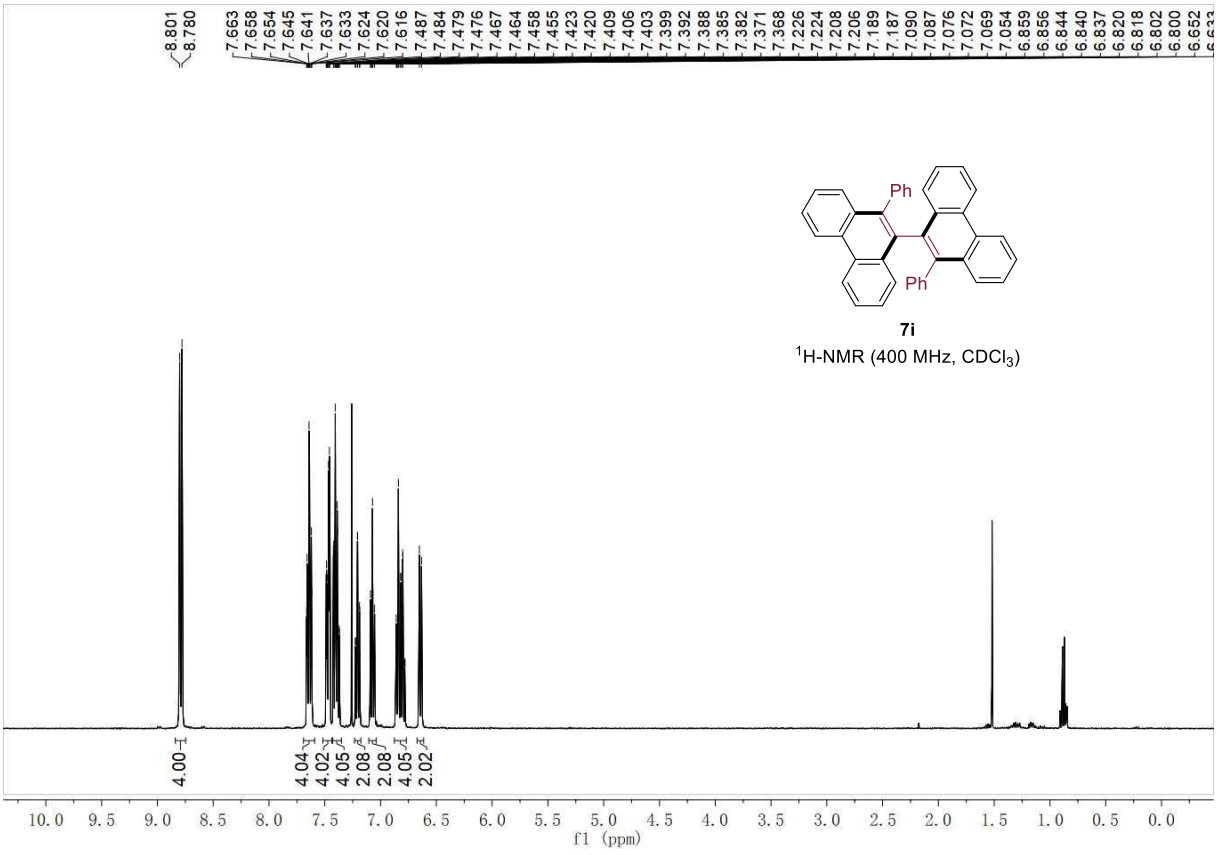
^{13}C-NMR (100 MHz, $CDCl_3$)


8.280
8.278
8.259
8.258
7.692
7.671
7.638
7.635
7.620
7.617
7.614
7.600
7.597
7.485
7.476
7.472
7.458
7.455
7.452
7.437
7.434
7.327
7.321
7.317
7.311
7.305
7.301
7.300
7.291
7.287
7.285
7.281
7.276
7.271
7.268
7.265
7.255
7.249
7.241
7.237
7.231
7.227
7.225
7.220
7.216
7.212
7.208
7.203
7.193
7.180
Ph
Ph
S
7g
1H-NMR (400 MHz, CDCl3)
1.00
1.01
1.02
2.04
11.55
10.0 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 0.0
f1 (ppm)


139.78
138.94
137.52
136.94
135.41
134.83
131.48
130.65
130.46
128.38
128.11
127.59
127.58
126.55
126.54
126.35
125.77
124.60
123.63
77.32
77.00
76.68
Ph
Ph
S
7g
13C-NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

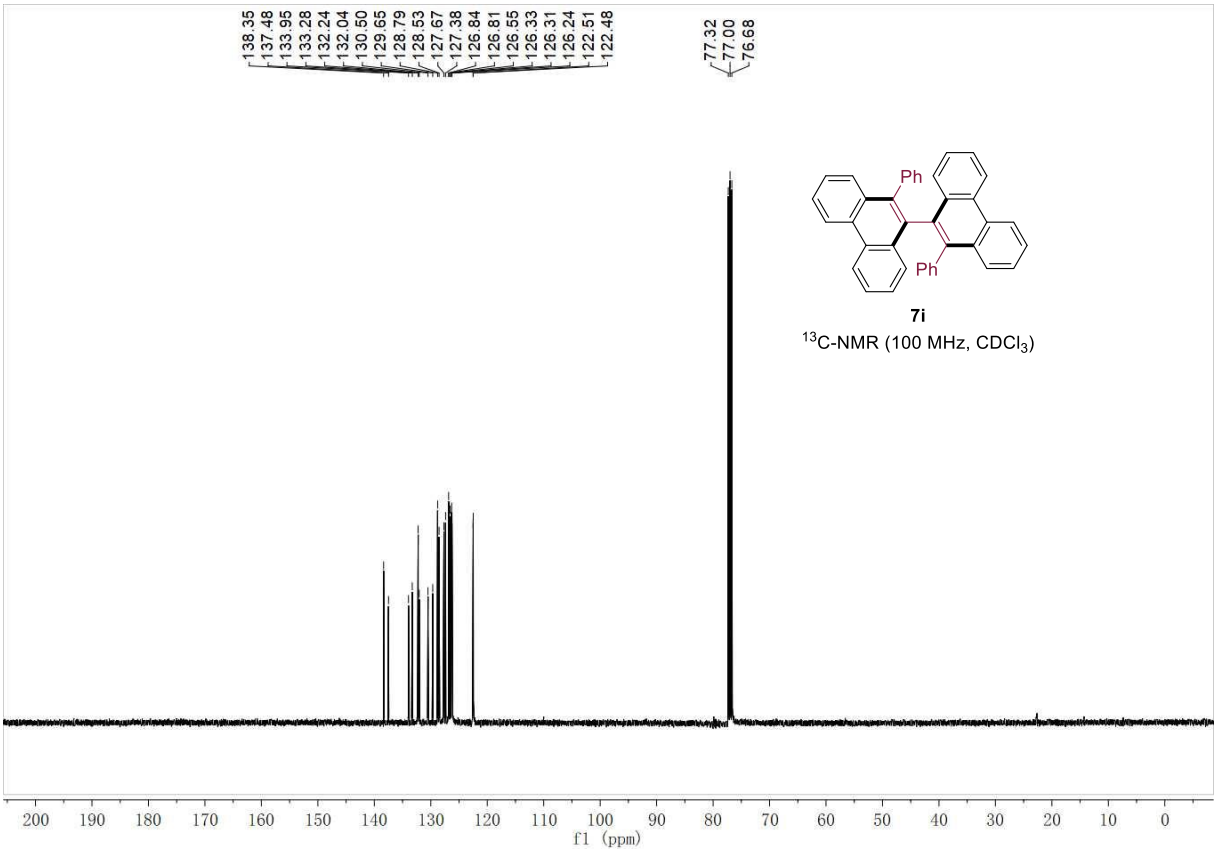

8.258
7.928
7.634
7.569
7.345
7.313
7.308
7.300
7.295
7.263
7.260
7.246
7.232
7.224
7.220
7.213
7.208
7.193
7.189
7.173
7.050
6.803
6.582
1.00
1.00
1.03
1.01
1.04
11.65
1.05
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
Ph
Ph
S
7h
^{1}H-NMR (400 MHz, $CDCl_3$)


139.85
139.27
138.76
137.46
137.16
136.78
135.78
131.42
131.31
130.98
130.30
128.14
128.03
127.48
127.06
126.52
126.40
125.47
124.91
124.43
123.95
122.60
77.32
77.00
76.68
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
Ph
Ph
S
7h
^{13}C-NMR (100 MHz, $CDCl_3$)



7i

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



7i

^{13}C-NMR (100 MHz, $CDCl_3$)

8. References

[1] a) D. Leifert, A. Studer, *Org. Lett*. **2015**, *17*, 386−389; b) L. Omann, M. Oestreich, *Angew. Chem. Int. Ed*. **2015**, *54*, 10276−10279; *Angew. Chem*. **2015**, *127*, 10414−10418.

[2] A. Krasovskiy, V. Krasovskaya, P. Knochel, *Angew. Chem. Int. Ed*. **2006**, *45*, 2958−2961; *Angew. Chem*. **2006**, *118*, 3024−3027.

[3] H.-J. Deng, Y.-J. Fang, G.-W. Chen, M.-C. Liu, H.-Y. Wu, J.-X. Chen, *Appl. Organometal. Chem*. **2012**, *26*, 164−167.

[4] K. Mitsudo, S. Tanaka, R. Isobuchi, T. Inada, H. Mandai, T. Korenaga, A. Wakamiya, Y. Murata, S. Suga, *Org. Lett*. **2017**, *19*, 2564−2567.